Supporting Information

Electrocatalytic Isomerization of Allylic Alcohols: Straightforward Preparation of β-Aryl-Ketones

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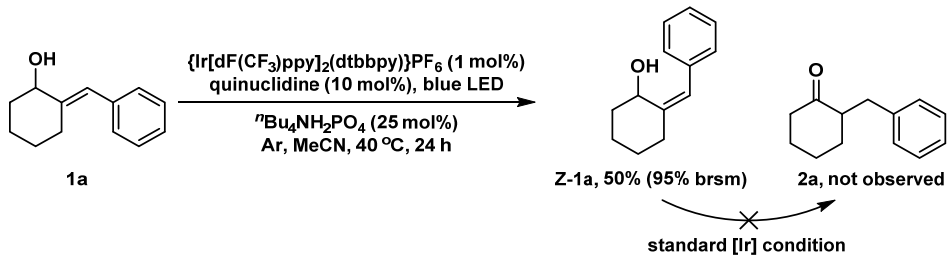
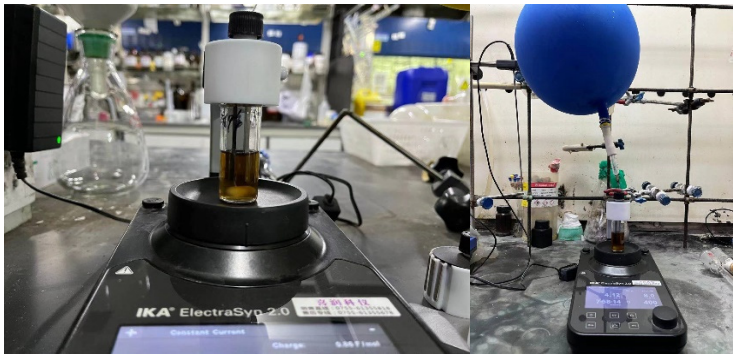
1 Supporting Scheme



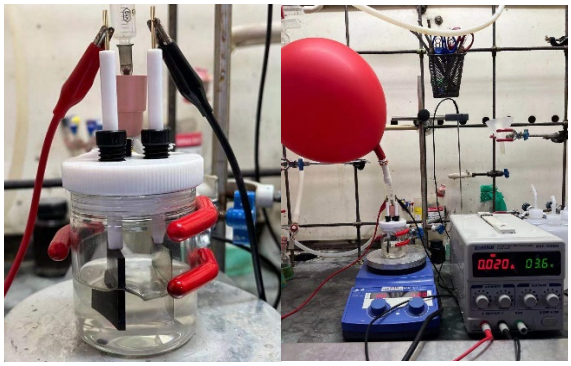
Scheme S1. Initial attempts of photoredox-catalyzed isomerization of **1a**. Only olefin isomerization product **Z-1a** was obtained. Both **1a** and **Z-1a** cannot be converted to ketone **2a** under standard photoredox conditions.

2 Reaction Setup for Electrolysis

For small-scale experiments, the electrochemical reactions were carried out in a galvanostatic mode using IKA ElectraSyn 2.0 system (https://www.ika.com/zh/Products-Lab-Eq/Electrochemistry-Kit-csp-516/ElectraSyn-20-Package-cpdt-20008980/). Glassy carbon electrode (C, 2 mm × 8 mm × 52 mm) and Platinum plate electrode (Pt, 2 mm × 8 mm × 52 mm) were both commercially available. The EletraSyn 2.0 cap equipped with anode and cathode were inserted into the mixture in the ElectraSyn vial. The cell was then plugged into ElectraSyn 2.0 system for reaction. The cell assembly process is depicted below:

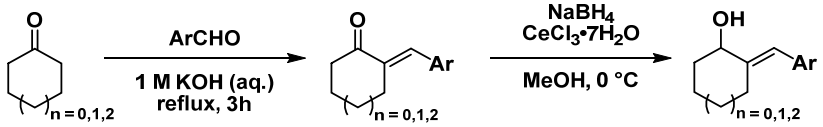


For large-scale experiments, the via cap equipped with graphite electrode (30 mm ×30 mm × 3 mm) and platinum plate electrode (30 mm × 30 mm × 0.1 mm) were inserted into the mixture in the reaction vial. Electrodes were connected with KRP-305DH power supply (Zhaoxin) commercially available from www.taobao.com. The cell assembly process is depicted below:



3 Preparation of the Substrates

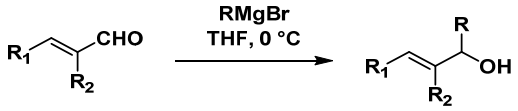
3.1 General Procedure A. (Substrates 1a-1i and *d*-1a)



Aryl aldehyde (10 mmol, 1.0 equiv.) and corresponding cyclic ketone (15 mmol, 1.5 equiv.) were mixed round bottom flask followed by slow addition of aqueous potassium hydroxide solution (1 M, 15 mL). Then the reaction mixture was refluxed for 3h. After full consumption of Aryl aldehyde, the mixture was cooled to rt and extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (2 x 15 mL), dried over Na_2SO_4, and concentrated in vacuo to afford the crude enone. Without further purification, the crude enone was used for Luche reduction.

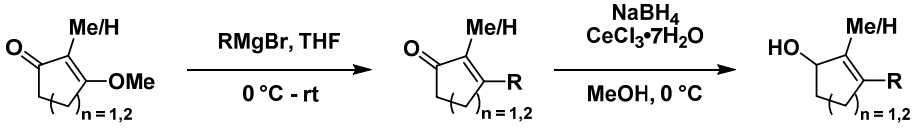
To the solution of crude enone in MeOH (30 mL) was added at 0 ℃ in sequence $CeCl_3 \cdot 7H_2O$ (4.5 g, 12 mmol, 1.2 equiv.) and $NaBH_4$ (454 mg, 12 mmol, 1.2 equiv.). The reaction mixture was allowed to be stirred for 0.5 h at 0 ℃ and quenched by carefully adding saturated aq. NH_4Cl solution (30 mL). After removing the MeOH in reduced pressure, the mixture was extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine (2 x 15 mL) and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel to generate the corresponding allylic alcohol.

3.2 General Procedure B. (Substrates 1k-1j)



To a solution of corresponding aldehyde (1.0 equiv.) in anhydrous THF (10 mL) was slowly added Grignard reagent (1.39 mmol, 1.1 equiv.) via syringe at 0 ºC, and the reaction mixture was stirred for 30 min. Upon completion, the reaction mixture was quenched by adding aq. saturated NH_4Cl solution (15 mL) and was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine (2 x 15 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the product.

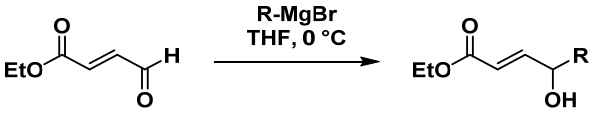
3.3 General Procedure C. (Substrates 1l-1u)



To the solution of corresponding 3-methoxy-enone (3.96 mmol, 1.0 equiv.) in anhydrous THF (20 mL) was slowly added Grignard reagent (7.92 mmol, 2.0 equiv.) via syringe at 0 ℃, and the reaction mixture was stirred for 24 h at room temperature. The reaction mixture was quenched by 2 M HCl (20 mL) and then stirred for another 30 min. The reaction mixture was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with brine (2 x 15 mL), dried over Na_2SO_4, and concentrated in vacuo to afford the crude enone. Without further purification, the crude enone was used for Luche reduction.

o the solution of crude enone in MeOH (30 mL) was added at 0 ℃ in sequence $CeCl_3 \cdot 7H_2O$ (4.5 g, 12 mmol, 1.2 equiv.) and $NaBH_4$ (454 mg, 12 mmol, 1.2 equiv.). The reaction mixture was allowed to be stirred for 0.5 h at 0 ℃ and quenched by carefully adding saturated aq. NH_4Cl solution (30 mL). After removing the MeOH in reduced pressure, the mixture was extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine (2 x 15 mL) and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel to generate the corresponding allylic alcohol.

3.4 General Procedure D. (Substrates 1u-1w)

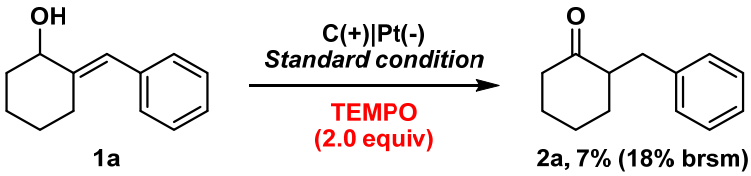


To a solution of Ethyl *trans*-4-oxo-2-butenoate (commercially available, 300 mg, 2.34 mmol, 1.0 equiv.) in anhydrous THF (12 mL) was slowly added the corresponding Grignard reagent (R-MgBr, 2.46 mmol, 1.05 equiv.) via syringe at 0 °C, and the reaction mixture was monitored by TLC (reaction completed within 15-30 minutes). Upon completion, the reaction mixture was quenched with saturated aq. NH_4Cl solution (10 mL) and then the mixture was extracted with EtOAc (2 x 15 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel to yield the desired allylic alcohol.

4 Mechanistic Studies

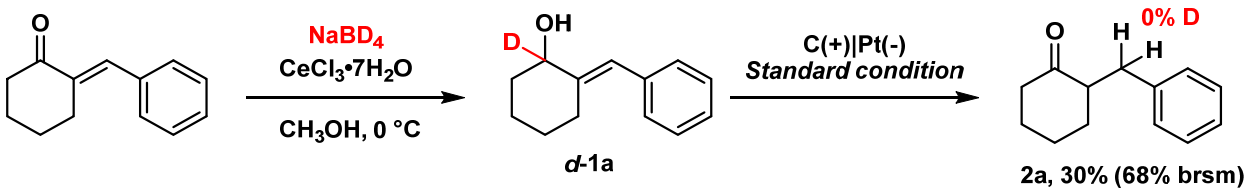
4.1 Cyclic voltammetry analysis. Cyclic voltammetry was recorded on the CHI 660D instrument. A glassy carbon disc electrode was used as the working electrode, a platinum wire electrode was used as the counter electrode, SCE was used as reference electrode. Each sample, **1a** (5 mM) or quinuclidine (5 mM), was performed in mixed solution of MeCN/toluene (5 mL + 1 mL) containing $^{n}Bu_4NH_2PO_4$ (5 mM) under argon. The spectra were recorded with the scan rate of 100 mV/s.

4.2 Radical inhibition experiment.



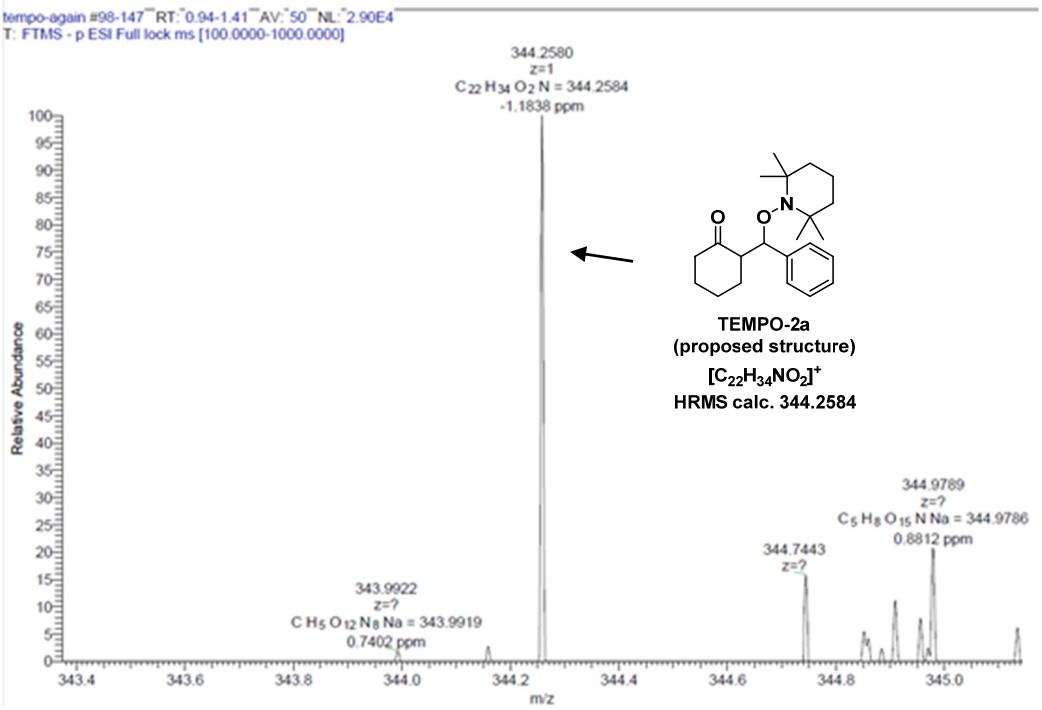
To a flame-dried and argon charged ElectraSyn 2.0 vial (10 mL) with a stir bar was added quinuclidine (20 mol%, 12 mg), TEMPO (156 mg, 2 equiv.) and $^{n}Bu_4NH_2PO_4$ (0.5 mmol, 170 mg). MeCN (5 mL), toluene (1 mL) and **1a** (0.5 mmol, 1.0 equiv) was added into the vial. The vial cap equipped with anode (glassy carbon) and cathode (platinum) were inserted into the mixture. The reaction system was strictly deoxygenated several under argon. The reaction mixture was electrolyzed under a constant current of 8 mA for 12 h under Ar. When reaction completed, the cap was removed and electrodes were rinsed with ethyl acetate. The mixture was filtered through a plug of celite with ethyl acetate. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel to provide 1b (6 mg, 7% yield) with 60 mg **1a** recovered.

4.3 Deuterium-label experiment.

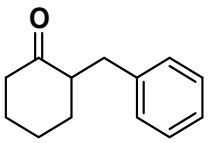


Deuterium-labeled substrate ***d*-1a** was synthesized following substrate synthesis general procedure A with the use of $NaBD_4$ instead of $NaBH_4$ in the second step Luche reduction reaction. The electrolysis was carried following General experimental procedure for electrocatalytic isomerization "standard conditions".

4.4 Detection of TEMPO-2a via HRMS

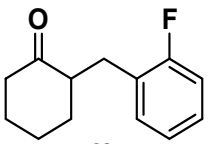


5 Characterization Data of Compounds



2a

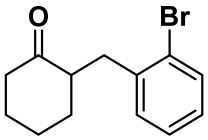
Compound **2a** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 20:1) as a colorless oil (67 mg, 72% yield). Rf = 0.58 (silica gel, hexane/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 - 7.24 (m, 2H), 7.22 - 6.92 (m, 3H), 3.24 (dd, *J* = 13.7, 4.6 Hz, 1H), 2.66 - 2.49 (m, 1H), 2.51 - 2.21 (m, 3H), 2.04 (tdd, *J* = 12.0, 6.3, 3.0 Hz, 2H), 1.90 - 1.78 (m, 1H), 1.76 - 1.51 (m, 2H), 1.35 (ddd, *J* = 11.8, 3.7, 1.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.73, 140.47, 129.24, 128.40, 126.06, 52.59, 42.28, 35.56, 33.51, 28.17, 25.17 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO^+$ $[M+Na]^+$: 211.1093; found: 211.1095.



2b

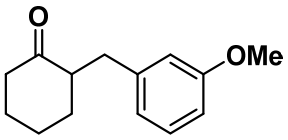
Compound **2b** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 15:1) as a colorless oil (70 mg, 68% yield). Rf = 0.59 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (dddd, *J* = 13.0, 7.3, 6.3, 1.9 Hz, 2H), 7.10 - 6.77 (m, 2H), 3.20 (ddd, *J* = 13.7, 5.0, 1.5 Hz, 1H), 2.67 - 2.57 (m, 1H), 2.52 (ddd, *J* = 13.9, 8.8, 1.1 Hz, 1H), 2.45 - 2.40 (m, 1H), 2.32 (tdd, *J* = 13.4, 6.0, 1.3 Hz, 1H), 2.12 - 1.98 (m, 2H), 1.92 - 1.79 (m, 1H), 1.75 - 1.52 (m, 2H), 1.40 (td, *J* = 12.5, 3.7 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$)

δ 212.18, 162.44, 160.49, 131.87, 131.83, 127.90, 127.83, 127.38, 127.26, 123.99, 123.96, 115.36, 115.19, 51.21, 42.24, 33.59, 29.07, 28.16, 25.21 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{15}FNaO^+$ $[M+Na]^+$: 229.0999; found: 229.0999.



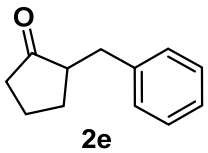
2c

Compound **2c** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 15:1) as a colorless oil (103 mg, 70% yield). Rf = 0.70 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.34 - 7.10 (m, 2H), 7.05 (td, *J* = 7.6, 2.0 Hz, 1H), 3.35 (dd, *J* = 13.9, 5.4 Hz, 1H), 2.91 - 2.61 (m, 1H), 2.56 (dd, *J* = 13.9, 8.1 Hz, 1H), 2.50 - 2.39 (m, 1H), 2.38 - 2.17 (m, 1H), 2.05 (dddd, *J* = 21.6, 12.6, 5.9, 2.9 Hz, 2H), 1.93 - 1.79 (m, 1H), 1.86 - 1.53 (m, 2H), 1.50 - 1.29 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.05, 140.00, 132.96, 131.97, 127.90, 127.33, 124.90, 50.82, 42.39, 35.88, 33.89, 28.26, 25.42 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{15}BrNaO^+$ $[M+Na]^+$: 289.0198; found: 289.0198.



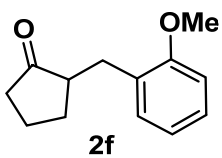
2d

Compound **2d** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (68 mg, 62% yield). Rf = 0.43 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.8 Hz, 1H), 7.03 - 6.38 (m, 3H), 3.79 (s, 3H), 3.21 (dd, *J* = 13.9, 4.8 Hz, 1H), 2.55 (dddd, *J* = 13.4, 10.0, 5.7, 1.2 Hz, 1H), 2.51 - 2.10 (m, 3H), 2.19 - 1.93 (m, 2H), 1.95 - 1.80 (m, 1H), 1.76 - 1.46 (m, 2H), 1.43 - 1.27 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.53, 159.70, 142.13, 129.32, 121.63, 115.07, 111.27, 55.22, 52.47, 42.23, 35.61, 33.53, 28.12, 25.16 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{18}NaO_2^+$ $[M+Na]^+$: 241.1199; found: 241.1199.



2e

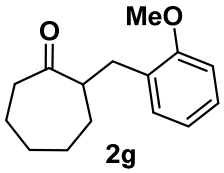
Compound **2e** was synthetized following **General electrolysis procedure** and purified by a flash chromatography on silica gel (PE: EtOAc = 20:1) as a colorless oil (46 mg, 53% yield). Rf = 0.58 (silica gel, hexane/EtOAc = 8:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.22 - 6.96 (m, 3H), 3.15 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.55 (dd, *J* = 13.9, 9.5 Hz, 1H), 2.49 - 2.27 (m, 2H), 2.25 - 2.03 (m, 2H), 2.06 - 1.89 (m, 1H), 1.84 - 1.66 (m, 1H), 1.68 - 1.39 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.21, 140.08, 128.96, 128.49, 126.22, 51.07, 38.26, 35.67, 29.21, 20.61 ppm. **HRMS** (ESI): m/z calcd for: $C_{12}H_{14}NaO^+$ $[M+Na]^+$: 197.0936; found: 197.0937.



2f

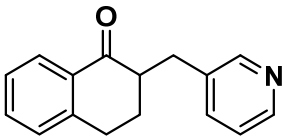
Compound **2f** was synthetized following **General electrolysis procedure** and purified by flash chromatography on

silica gel (PE: EtOAc = 20:1) as a colorless oil (64 mg, 62% yield). Rf = 0.65 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (td, *J* = 7.8, 1.8 Hz, 1H), 7.11 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.92 - 6.59 (m, 2H), 3.80 (s, 3H), 3.22 (d, *J* = 9.2 Hz, 1H), 2.61 - 2.36 (m, 2H), 2.32 (dddt, *J* = 18.7, 8.5, 3.0, 1.5 Hz, 1H), 2.13 (ddd, *J* = 18.7, 10.1, 8.6 Hz, 1H), 2.05 - 1.88 (m, 2H), 1.83 - 1.63 (m, 1H), 1.62 - 1.40 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.79, 157.64, 130.55, 128.54, 127.51, 120.43, 110.30, 55.22, 49.63, 38.18, 30.24, 29.38, 20.61 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO_2^+$ $[M+Na]^+$: 227.1042; found: 227.1042.



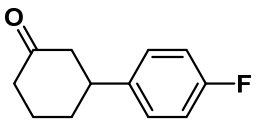
2g

Compound **2g** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (95 mg, 82% yield). Rf = 0.45 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.18 (td, *J* = 7.6, 1.8 Hz, 1H), 7.09 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.95 - 6.59 (m, 2H), 3.80 (s, 3H), 3.03 (dd, *J* = 13.4, 6.0 Hz, 1H), 2.86 (dt, *J* = 8.2, 2.8 Hz, 1H), 2.60 (dd, *J* = 13.4, 8.1 Hz, 1H), 2.55 - 2.34 (m, 2H), 1.96 - 1.72 (m, 4H), 1.70 - 1.53 (m, 1H), 1.36 - 1.17 (m, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 216.00, 157.72, 131.10, 128.35, 127.46, 120.33, 110.32, 55.23, 52.13, 42.86, 32.61, 30.46, 29.58, 28.49, 24.61 ppm. **HRMS** (ESI): m/z calcd for: $C_{15}H_{20}NaO_2^+$ $[M+Na]^+$: 255.1356; found: 255.1355.



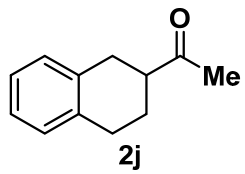
2h

Compound 2h was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 1:1) as a colorless oil (42 mg, 40% yield). Rf = 0.43 (silica gel, hexane/EtOAc = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 - 8.32 (m, 2H), 8.05 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.58 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.39 - 6.93 (m, 3H), 3.43 (d, *J* = 9.6 Hz, 1H), 2.95 (dd, *J* = 8.1, 4.3 Hz, 2H), 2.83 - 2.63 (m, 2H), 2.39 - 2.00 (m, 1H), 1.87 - 1.64 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.84, 150.64, 147.73, 143.96, 137.02, 135.60, 133.58, 132.43, 128.86, 127.67, 126.85, 123.53, 49.19, 33.02, 28.87, 27.99 ppm. **HRMS** (ESI): m/z calcd for: $C_{16}H_{16}NO^+$ $[M+Na]^+$: 238.1226; found: 238.1227.



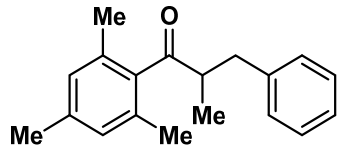
2i

Compound **2i** was synthetized following **General electrolysis procedure** from 3-methoxycyclohex-2-en-1-one and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (59 mg, 61% yield). Rf = 0.31 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 - 7.05 (m, 2H), 7.09 - 6.85 (m, 2H), 2.99 (ddd, *J* = 15.8, 8.0, 4.1 Hz, 1H), 2.57 (ddt, *J* = 13.9, 4.2, 1.9 Hz, 1H), 2.53 - 2.42 (m, 2H), 2.43 - 2.29 (m, 1H), 2.14 (dddd, *J* = 12.6, 6.4, 3.8, 2.3 Hz, 1H), 2.10 - 2.00 (m, 1H), 1.94 - 1.72 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.84, 162.90, 160.47, 140.19, 140.16, 128.15, 128.07, 115.68, 115.47, 49.21, 44.13, 41.24, 33.03, 25.53 ppm. **HRMS** (ESI): m/z calcd for: $C_{12}H_{13}FNaO^+$ $[M+Na]^+$: 215.0842; found: 215.0844.



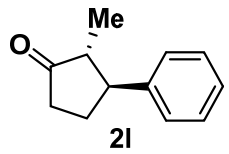
2j

Compound **2j** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (64 mg, 74% yield). Rf = 0.30 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (q, *J* = 3.5 Hz, 4H), 2.94 (d, *J* = 8.0 Hz, 2H), 2.91 - 2.84 (m, 2H), 2.82 - 2.73 (m, 1H), 2.25 (s, 3H), 2.22 - 2.13 (m, 1H), 1.75 (dddd, *J* = 13.2, 11.2, 10.4, 6.6 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.14, 135.89, 135.17, 129.24, 128.93, 126.04, 125.99, 48.06, 31.07, 28.90, 28.26, 25.51 ppm. **HRMS** (ESI): m/z calcd for: $C_{12}H_{14}NaO^+$ $[M+Na]^+$: 197.0936; found: 197.0938.



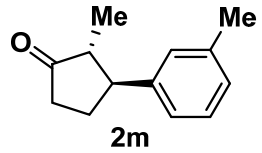
2k

Compound **2k** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 15:1) as a colorless oil (20 mg, 15% yield). Rf = 0.62 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 - 7.23 (m, 2H), 7.24 - 7.09 (m, 3H), 6.83 (s, 2H), 3.23 (dd, *J* = 13.3, 4.8 Hz, 1H), 3.14 (ddd, *J* = 9.5, 7.0, 4.8 Hz, 1H), 2.56 (dd, *J* = 13.3, 9.4 Hz, 1H), 2.27 (s, 3H), 2.16 (s, 6H), 1.08 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.10, 140.03, 138.73, 138.66, 133.64, 129.41, 128.88, 128.49, 126.33, 49.88, 38.09, 21.17, 19.80, 15.62 ppm. **HRMS** (ESI): m/z calcd for: $C_{19}H_{22}NaO^+$ $[M+Na]^+$: 289.1563; found: 289.1562.



2l

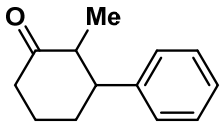
Compound 2l was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (52 mg, 60% yield). Rf = 0.57 (silica gel, hexane/EtOAc = 4:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45 - 7.30 (m, 2H), 7.29 - 7.09 (m, 3H), 2.80 (td, *J* = 12.0, 5.5 Hz, 1H), 2.67 - 2.40 (m, 1H), 2.40 - 2.11 (m, 3H), 2.16 - 1.67 (m, 1H), 1.03 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 219.61, 142.37, 128.75, 127.14, 126.90, 51.42, 50.99, 37.73, 29.59, 12.22 ppm. **HRMS** (ESI): m/z calcd for: $C_{12}H_{15}O^+$ $[M+H]^+$: 175.1117; found: 175.1119.



2m

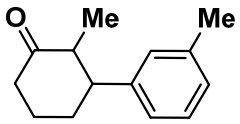
Compound **2m** was synthetized following **General electrolysis procedure** and purified by a flash chromatography on silica gel (PE: EtOAc = 20:1) as a colorless oil (70 mg, 75% yield). Rf = 0.60 (silica gel, hexane/EtOAc = 10:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 - 7.17 (m, 1H), 7.14 - 6.91 (m, 3H), 2.78 (td, *J* = 12.0, 5.5 Hz, 1H), 2.64 - 2.46 (m, 1H), 2.37 (s, 3H), 2.32 - 2.17 (m, 3H), 2.06 - 1.85 (m, 1H), 1.04 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 219.86, 142.41, 138.40, 128.70, 127.97, 127.72, 124.21, 51.45, 51.03, 37.82, 29.71, 21.59, 12.32 ppm. **HRMS** (ESI): m/z calcd

for: $C_{13}H_{17}O^+$ $[M+H]^+$: 189.1274; found: 189.1274.



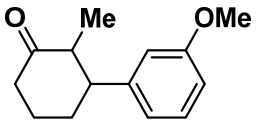
2n

Compound **2n** (trans/cis = 1:1.3) was synthetized following **General electrolysis procedure** and purified by a flash chromatography on silica gel (PE: EtOAc = 20:1) as a colorless oil (75 mg, 80% yield). Rf = 0.55 (silica gel, hexane/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 - 7.15 (m, 7H), 7.17 - 6.93 (m, 2H), 3.34 (dq, *J* = 8.6, 4.8, 4.4 Hz, 1H), 2.74 (ddd, *J* = 7.0, 5.4, 1.5 Hz, 1H), 2.71 - 2.42 (m, 4H), 2.36 (ddd, *J* = 13.2, 6.7, 5.1 Hz, 1H), 2.24 - 1.89 (m, 5.1H), 1.85 - 1.70 (m, 1.98H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.81 (d, *J* = 6.3 Hz, 2.27H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.86, 212.53, 143.99, 141.98, 128.75, 128.44, 128.09, 127.29, 126.75, 126.51, 77.48, 77.16, 76.84, 53.33, 50.64, 49.81, 47.86, 41.95, 39.03, 34.64, 27.55, 26.63, 23.88, 12.38, 12.24 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO^+$ $[M+Na]^+$: 211.1093; found: 211.1094.



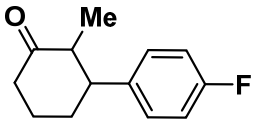
2o

Compound **2o** (trans/cis = 1.6:1) was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 30:1) as a colorless oil (77 mg, 76% yield). Rf = 0.59 (silica gel, hexane/EtOAc = 15:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 - 7.14 (m, 1.6H), 7.08 - 6.97 (m, 3.6H), 6.95 - 6.85 (m, 1.2H), 3.30 (dt, *J* = 8.7, 4.7 Hz, 0.6H), 2.76 - 2.43 (m, 5.4H), 2.38 - 2.25 (m, 5.5H), 2.20 - 1.86 (m, 5H), 1.84 - 1.69 (m, 1.8H), 0.93 (d, *J* = 7.1 Hz, 1.9H), 0.81 (d, *J* = 6.4 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.92, 212.64, 143.98, 141.96, 138.29, 138.01, 128.95, 128.61, 128.29, 128.07, 127.49, 127.26, 125.05, 124.31, 53.31, 50.62, 49.86, 47.80, 41.98, 39.00, 34.70, 27.51, 26.66, 23.96, 21.61, 21.59, 12.41, 12.27 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{18}NaO^+$ $[M+Na]^+$: 225.1250; found: 225.1251.



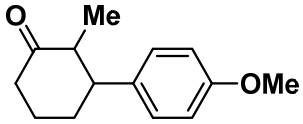
2p

Compound **2p** (trans/cis = 1:1.2) was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (60 mg, 55% yield). Rf = 0.41 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 - 7.09 (m, 2H), 6.84 - 6.53 (m, 5.4H), 3.80 (d, *J* = 8.9 Hz, 5.5H), 3.30 (dt, *J* = 8.8, 4.6 Hz, 1H), 2.73 (ddd, *J* = 6.9, 5.3, 1.5 Hz, 1H), 2.65 - 2.42 (m, 4.4H), 2.41 - 2.31 (m, 1H), 2.22 - 1.90 (m, 5.6H), 1.84 - 1.73 (m, 1.8H), 0.93 (d, *J* = 7.1 Hz, 3H), 0.82 (d, *J* = 6.3 Hz, 2.5H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.86, 212.48, 159.92, 159.72, 145.69, 143.68, 129.74, 129.38, 120.40, 119.69, 114.16, 113.43, 111.59, 111.57, 55.29, 55.26, 53.35, 50.62, 49.90, 47.79, 41.95, 38.91, 34.57, 27.28, 26.61, 24.05, 12.38, 12.25 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{18}NaO_2^+$ $[M+Na]^+$: 241.1199; found: 241.1199.



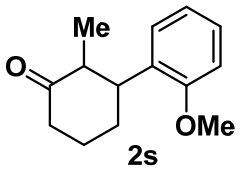
2q

Compound **2q** (trans/cis = 1.6:1) was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 15:1) as a colorless oil (71 mg, 69% yield). Rf = 0.48 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.19 - 7.10 (m, 2H), 7.10 - 6.81 (m, 4.6H), 3.38 - 3.22 (m, 0.6H), 2.77 - 2.65 (m, 0.6H), 2.61 - 2.41 (m, 4.6H), 2.40 - 2.26 (m, 0.8H), 2.12 (ddd, *J* = 12.7, 5.3, 3.1 Hz, 1H), 2.05 - 1.84 (m, 4H), 1.84 - 1.63 (m, 1.9H), 0.88 (d, J = 7.1 Hz, 1.9H), 0.77 (d, J = 6.0 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 214.62, 212.14, 163.17, 163.11, 159.93, 159.86, 139.68, 139.64, 137.63, 137.58, 129.46, 129.35, 128.65, 128.55, 115.60, 115.32, 115.03, 52.46, 50.71, 49.70, 47.09, 41.81, 38.93, 34.66, 27.65, 26.42, 23.71, 12.26, 12.09 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{15}FNaO^+$ $[M+Na]^+$: 229.0999; found: 229.0999.



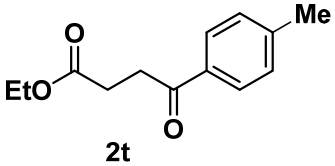
2r

Compound **2r** (trans/cis = 1:1.9) was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (49 mg, 45% yield). Rf = 0.45 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 - 7.06 (m, 1H), 7.05 - 6.97 (m, 2H), 6.89 - 6.69 (m, 3H), 3.77 (s, 4.7H), 3.32 - 3.22 (m, 1H), 2.69 (ddd, *J* = 7.1, 5.4, 1.5 Hz, 1H), 2.61 - 2.40 (m, 3.2H), 2.39 - 2.27 (m, 1H), 2.16 - 1.84 (m, 5.1H), 1.79 - 1.69 (m, 1.6H), 0.90 (d, *J* = 7.1 Hz, 3.1H), 0.79 (d, *J* = 6.4 Hz, 1.6H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 214.96, 212.56, 158.29, 158.14, 136.15, 133.98, 128.97, 128.12, 114.02, 113.76, 55.28, 55.25, 52.49, 50.89, 49.88, 47.11, 41.90, 39.03, 34.75, 27.85, 26.50, 23.81, 12.31, 12.18 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{18}NaO_2^+$ $[M+Na]^+$: 241.1199; found: 241.1200.



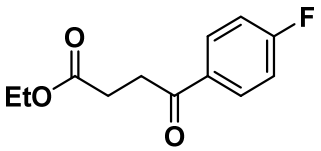
2s

Compound **2s** (trans/cis = 1:1.7) was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 15:1) as a colorless oil (84 mg, 77% yield). **trans-2s**: Rf = 0.27 (silica gel, hexane/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 - 7.13 (m, 2H), 6.95 (td, *J* = 7.4, 1.2 Hz, 1H), 6.90 - 6.78 (m, 1H), 3.80 (s, 3H), 3.10 (td, *J* = 11.8, 4.0 Hz, 1H), 2.78 (dd, *J* = 12.2, 6.3 Hz, 1H), 2.54 - 2.40 (m, 2H), 2.11 (ddt, *J* = 12.2, 5.2, 3.3 Hz, 1H), 2.02 - 1.87 (m, 2H), 1.84 - 1.71 (m, 1H), 0.81 (d, *J* = 6.5 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.24, 157.27, 132.12, 127.63, 127.46, 120.90, 110.96, 55.50, 49.70, 42.08, 32.91, 26.66, 12.17 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{18}NaO_2^+$ $[M+Na]^+$: 241.1199; found: 241.1199. **cis-2s**: Rf = 0.23 (silica gel, hexane/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 7.05 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.96 - 6.75 (m, 2H), 3.79 (s, 3H), 3.75 - 3.59 (m, 1H), 2.82 (ddd, *J* = 7.0, 5.4, 1.5 Hz, 1H), 2.54 (ddd, *J* = 14.9, 9.3, 5.7 Hz, 1H), 2.41 - 2.28 (m, 1H), 2.17 - 1.91 (m, 2H), 1.92 - 1.71 (m, 2H), 0.90 (d, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.28, 156.98, 130.10, 128.72, 127.49, 120.18, 110.45, 55.15, 47.63, 41.05, 39.05, 26.75, 24.17, 12.54 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{18}NaO_2^+$ $[M+Na]^+$: 241.1199; found: 241.1195.



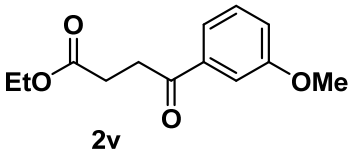
2t

Compound **2t** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (85 mg, 77% yield). Rf = 0.41 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.30 (t, *J* = 6.7 Hz, 2H), 2.76 (t, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.89, 173.12, 144.10, 134.21, 129.38, 128.25, 60.73, 33.36, 28.42, 21.76, 14.30 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO_3^+$ $[M+Na]^+$: 243.0991; found: 243.0092.



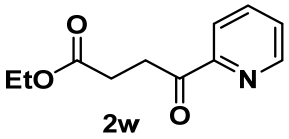
2u

Compound **2u** was synthetized following **General electrolysis procedure** and purified byflash chromatography on silica gel (PE: EtOAc = 8:1) as a white solid (88 mg, 78% yield). Rf = 0.42 (silica gel, hexane/EtOAc = 4:1). m.p.: 39-41 ^{o}C. **^{1}H NMR** (400 MHz, CDCl3) δ 8.12 - 7.89 (m, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.27 (t, *J* = 6.6 Hz, 2H), 2.75 (t, *J* = 6.6 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.71, 172.98, 167.21, 164.68, 133.18, 133.15, 130.85, 130.75, 115.95, 115.74, 60.84, 33.40, 28.38, 14.32 ppm. **HRMS** (ESI): m/z calcd for: $C_{12}H_{13}FNaO_3^+$ $[M+Na]^+$: 247.0740; found: 247.0740.



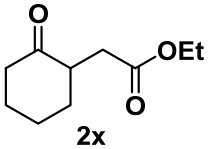
2v

Compound **2v** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 8:1) as a colorless oil (86 mg, 73% yield). Rf = 0.38 (silica gel, hexane/EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.50 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.10 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.29 (t, *J* = 6.7 Hz, 2H), 2.74 (t, *J* = 6.7 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.10, 173.01, 159.93, 138.04, 129.72, 120.80, 119.85, 112.32, 60.77, 55.55, 33.63, 28.44, 14.31 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO_4^+$ $[M+Na]^+$: 259.0940; found: 259.0944.



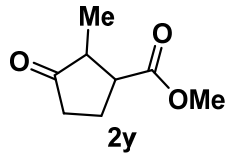
2w

Compound **2w** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 1:1) as a colorless oil (42 mg, 40% yield). Rf = 0.43 (silica gel, hexane/EtOAc = 1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 1H), 7.99 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.79 (td, *J* = 7.7, 1.7 Hz, 1H), 7.43 (ddd, *J* = 7.6, 4.7, 1.3 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.51 (t, *J* = 6.7 Hz, 2H), 2.71 (t, *J* = 6.7 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.06, 172.95, 153.09, 149.04, 136.91, 127.29, 121.79, 60.59, 32.87, 28.36, 14.24 ppm. **HRMS** (ESI): m/z calcd for: $C_{11}H_{14}NO_3^+$ $[M+H]^+$: 208.0968; found: 208.0966.



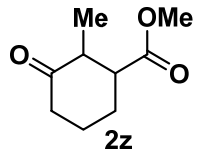
2x

Compound **2x** was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (64 mg, 69% yield). Rf = 0.65 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.12 (qd, *J* = 7.2, 1.9 Hz, 2H), 2.94 - 2.80 (m, 1H), 2.75 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.53 - 2.25 (m, 2H), 2.27 - 2.00 (m, 3H), 1.98 - 1.79 (m, 1H), 1.83 - 1.55 (m, 2H), 1.53 - 1.33 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.16, 172.74, 60.56, 47.25, 41.96, 34.59, 34.01, 27.91, 25.34, 14.32 ppm. **HRMS** (ESI): m/z calcd for: $C_{10}H_{16}NaO_3^+$ $[M+Na]^+$: 207.0092; found: 207.0091.



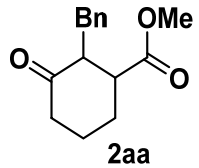
2y

Compound **2y** (trans/cis = 5.1:1) was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 15:1) as a colorless oil (57 mg, 73% yield). **trans-2z**: Rf = 0.51 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 2.63 (td, *J* = 11.1, 6.6 Hz, 1H), 2.54 - 2.36 (m, 2H), 2.37 - 2.25 (m, 1H), 2.19 (ddd, *J* = 18.8, 10.7, 8.9 Hz, 1H), 2.08 - 1.89 (m, 1H), 1.14 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 217.87, 174.63, 52.22, 49.04, 47.73, 36.93, 24.57, 13.29 ppm. **HRMS** (ESI): m/z calcd for: $C_8H_{12}NaO_3^+$ $[M+Na]^+$: 179.0679; found: 179.0683. **cis-2z**: Rf = 0.43 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.22 (ddd, *J* = 8.2, 6.8, 3.4 Hz, 1H), 2.70 - 2.36 (m, 2H), 2.33 - 2.15 (m, 2H), 2.17 - 2.00 (m, 1H), 1.04 (d, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 218.09, 174.30, 51.76, 46.47, 45.79, 35.27, 23.67, 10.71 ppm. **HRMS** (ESI): m/z calcd for: $C_8H_{12}NaO_3^+$ $[M+Na]^+$: 179.0679; found: 179.0680.



2z

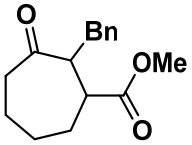
Compound **2z** (trans/cis = 1.2:1) was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (66 mg, 78% yield). **trans-2aa**: Rf = 0.26 (silica gel, hexane/EtOAc = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.72 (s, 3H), 2.68 (ddd, *J* = 11.7, 6.5, 1.2 Hz, 1H), 2.51 - 2.23 (m, 3H), 2.21 - 2.08 (m, 1H), 2.05 (ddd, *J* = 13.4, 3.6, 1.7 Hz, 1H), 2.00 - 1.82 (m, 1H), 1.81- 1.66 (m, 1H), 1.00 (d, *J* = 6.5 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 210.90, 174.51, 52.06, 51.78, 46.64, 41.30, 29.15, 25.96, 12.76 ppm. **HRMS** (ESI): m/z calcd for: $C_9H_{14}NaO_3^+$ $[M+Na]^+$: 193.0835; found: 193.0835. **cis-2aa**: Rf = 0.20 (silica gel, hexane/EtOAc = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.12 - 2.92 (m, 1H), 2.54 (ddd, *J* = 6.7, 5.2, 1.4 Hz, 1H), 2.49 - 2.38 (m, 1H), 2.33 - 2.17 (m, 1H), 2.11 - 1.91 (m, 3H), 1.86 (ddd, *J* = 4.9, 2.6, 1.4 Hz, 1H), 1.05 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 210.40, 173.67, 51.77, 48.60, 45.84, 39.83, 26.59, 23.17, 12.69 ppm. **HRMS** (ESI): m/z calcd for: $C_9H_{14}NaO_3^+$ $[M+Na]^+$: 193.0835; found: 193.0835.



2aa

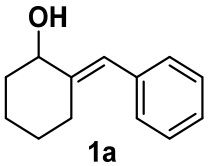
The compound **2aa** (trans/cis = 1.4:1) was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (88 mg, 72% yield). **trans-2aa**: Rf = 0.53 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 - 6.98 (m, 5H), 3.62 (s, 3H), 3.11 (dd, *J* = 13.7, 7.6 Hz, 1H),

3.02 (dddd, *J* = 10.8, 7.6, 4.2, 1.1 Hz, 1H), 2.76 - 2.49 (m, 2H), 2.50 - 2.24 (m, 2H), 2.17 - 1.99 (m, 2H), 1.94 - 1.79 (m, 1H), 1.77 - 1.63 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.92, 174.33, 139.90, 129.52, 128.31, 126.23, 53.59, 52.06, 49.82, 41.52, 33.97, 28.98, 25.76 ppm. **HRMS** (ESI): m/z calcd for: $C_{15}H_{18}NaO_3^+$ $[M+Na]^+$: 269.1148; found: 269.1150. **cis-2aa**: Rf = 0.48 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, CDCl3) δ 7.39 - 7.23 (m, 2H), 7.22 - 7.16 (m, 1H), 7.18 - 6.97 (m, 2H), 3.71 (s, 3H), 3.33 (dd, *J* = 14.0, 4.8 Hz, 1H), 3.05 - 2.95 (m, 1H), 2.75 - 2.42 (m, 3H), 2.39 - 2.20 (m, 1H), 2.13 - 1.99 (m, 1H), 1.91 (dddd, *J* = 9.0, 5.8, 3.5, 1.4 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.66, 173.73, 139.79, 129.10, 128.64, 126.39, 53.31, 51.93, 46.12, 40.67, 33.17, 27.80, 23.02 ppm. **HRMS** (ESI): m/z calcd for: $C_{15}H_{18}NaO_3^+$ $[M+Na]^+$: 269.1148; found: 269.1152.



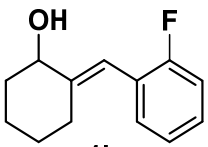
2ab

Compound **2ab** (trans/cis = 1.5:1) was synthetized following **General electrolysis procedure** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (97 mg, 75% yield). **trans-2ab**: Rf = 0.63 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 - 7.18 (m, 2H), 7.19 - 6.97 (m, 3H), 3.63 (s, 3H), 3.36 (ddd, *J* = 9.4, 8.0, 5.8 Hz, 1H), 2.98 (dd, J = 13.7, 7.9 Hz, 1H), 2.67 (dd, *J* = 13.7, 5.7 Hz, 1H), 2.62 - 2.49 (m, 1H), 2.34 - 2.20 (m, 2H), 1.91 - 1.59 (m, 5H), 1.53 - 1.40 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.96, 212.94, 175.18, 138.54, 129.25, 128.36, 126.40, 54.68, 51.99, 46.20, 43.04, 37.18, 30.98, 26.56, 24.29 ppm. **HRMS** (ESI): m/z calcd for: $C_{16}H_{20}NaO_3^+$ $[M+Na]^+$: 283.1305; found: 283.1305. **cis-2ab**: Rf = 0.60 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.23 - 7.02 (m, 3H), 3.65 (s, 3H), 3.33 (dd, *J* = 14.5, 4.7 Hz, 1H), 3.04 - 2.76 (m, 2H), 2.73 - 2.37 (m, 3H), 2.27 - 2.10 (m, 1H), 1.84 (ddt, *J* = 11.7, 4.7, 2.2 Hz, 2H), 1.69 - 1.45 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.11, 173.74, 140.22, 129.21, 128.55, 126.27, 54.94, 51.82, 44.01, 43.91, 35.40, 32.98, 26.69, 23.61 ppm. **HRMS** (ESI): m/z calcd for: $C_{16}H_{20}NaO_3^+$ $[M+Na]^+$: 283.1305; found: 283.1304.



1a

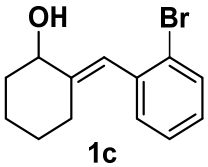
Compound **1a** was prepared according to **General Procedure A** and purified by flash chromatography on silica gel (PE: EtOAc = 30:1) as a white solid (756 mg, 40% yield in 2 steps). Rf = 0.50 (silica gel, hexane/EtOAc = 10:1). m.p.: 56-57 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 - 7.30 (m, 2H), 7.30 - 6.84 (m, 3H), 6.57 (s, 1H), 4.26 (ddd, *J* = 8.2, 4.0, 1.4 Hz, 1H), 2.83 - 2.67 (m, 1H), 2.38 (s, 1H), 2.22 - 1.96 (m, 2H), 1.96 - 1.82 (m, 1H), 1.73 - 1.40 (m, 4H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.40, 137.74, 128.97, 128.12, 126.23, 120.77, 73.68, 36.56, 27.40, 27.05, 23.30 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO^+$ $[M+Na]^+$: 211.1093; found: 211.1090.



1b

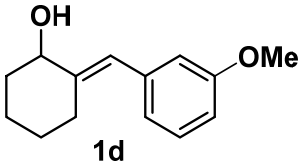
Compound **1b** was prepared according to **General Procedure A** and purified by flash chromatography on silica gel

(PE: EtOAc = 15:1) as a white solid (1.27 g, 62% yield in 2 steps). Rf = 0.48 (silica gel, hexane/EtOAc = 5:1). m.p.: 42-44 °C. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.26 - 7.15 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.05 (dd, *J* = 10.1, 8.3 Hz, 1H), 6.45 (s, 1H), 4.23 (dd, *J* = 8.7, 4.0 Hz, 1H), 2.60 (dt, *J* = 13.7, 5.0 Hz, 1H), 2.01 (ddt, *J* = 17.8, 9.9, 4.1 Hz, 3H), 1.94 - 1.76 (m, 1H), 1.71 - 1.47 (m, 3H), 1.50 - 1.36 (m, 1H) ppm. **^{13}C NMR** (125 MHz, CD_2Cl_2) δ 161.64, 159.69, 147.55, 131.42, 131.39, 128.55, 128.49, 125.84, 125.72, 124.03, 124.00, 115.68, 115.50, 113.42, 113.41, 73.73, 37.24, 28.11, 27.69, 23.86 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{15}FNaO^+$ $[M+Na]^+$: 229.0999; found: 229.1000.



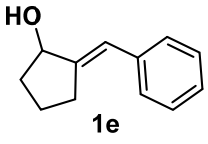
1c

Compound **1c** was prepared according to **General Procedure A** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (2.01 g, 76% yield in 2 steps). Rf = 0.38 (silica gel, hexane/EtOAc = 5:1). ^{1}H NMR (500 MHz, CD_3OD) δ 7.56 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.28 (td, *J* = 7.5, 1.2 Hz, 1H), 7.24 - 7.11 (m, 1H), 7.10 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.49 (s, 1H), 2.07 - 1.97 (m, 1H), 1.99 - 1.89 (m, 1H), 1.89 - 1.79 (m, 1H), 1.67 - 1.47 (m, 3H), 1.48 - 1.33 (m, 1H) ppm. **^{13}C NMR** (126 MHz, CD3OD) δ 146.84, 139.51, 133.49, 131.99, 129.14, 128.04, 125.20, 121.21, 73.88, 37.74, 28.56, 28.47, 24.69 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}BrO^+$ $[M+H]^+$: 267.0379; found: 267.0379.



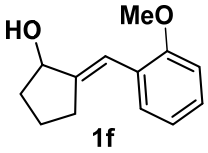
1d

Compound **1d** was prepared according to **General Procedure A** and purified by flash chromatography on silica gel (PE: EtOAc = 8:1) as a colorless oil (1.2 g, 55% yield in 2 steps). Rf = 0.24 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 - 7.08 (m, 1H), 6.93 - 6.79 (m, 1H), 6.80 - 6.68 (m, 2H), 6.50 (s, 1H), 4.23 (ddd, *J* = 8.3, 4.0, 1.5 Hz, 1H), 3.80 (s, 3H), 2.95 - 2.51 (m, 1H), 2.25 - 2.04 (m, 1H), 2.07 - 1.93 (m, 1H), 1.95 - 1.72 (m, 2H), 1.69 - 1.42 (m, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.52, 144.77, 139.26, 129.15, 121.58, 120.78, 114.70, 111.86, 73.81, 55.27, 36.71, 27.48, 27.25, 23.34 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{19}O_2^+$ $[M+H]^+$: 219.1379; found: 219.1380.



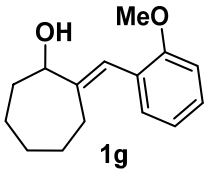
1e

Compound **1e** was prepared according to **General Procedure A** and purified by flash chromatography on silica gel (PE: EtOAc = 20:1) as a white solid (530 mg, 31% yield in 2 steps). Rf = 0.29 (silica gel, hexane/EtOAc = 8:1). m.p.: 76-78 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 - 7.28 (m, 4H), 7.22 (ddd, *J* = 6.1, 4.7, 2.5 Hz, 1H), 6.58 (td, *J* = 2.7, 1.6 Hz, 1H), 4.60 (tt, *J* = 5.6, 1.7 Hz, 1H), 2.78 - 2.67 (m, 1H), 2.59 (dddd, *J* = 17.4, 11.5, 5.3, 2.5 Hz, 1H), 2.15 - 1.85 (m, 2H), 1.82 - 1.62 (m, 2H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.95, 137.87, 128.54, 128.45, 126.74, 123.81, 77.52, 35.00, 29.50, 22.69 ppm. **HRMS** (ESI): m/z calcd for: $C_{12}H_{14}NaO^+$ $[M+Na]^+$: 197.0936; found: 197.0938.



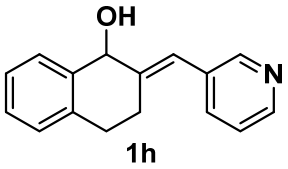
1f

Compound **1f** was prepared according to **General Procedure A** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (918 mg, 45% yield in 2 steps). Rf = 0.25 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.26 - 7.08 (m, 1H), 6.94 (td, *J* = 7.5, 1.1 Hz, 1H), 6.93 - 6.75 (m, 2H), 4.63 (dd, *J* = 5.6, 3.7 Hz, 1H), 3.84 (s, 3H), 2.68 (dtt, *J* = 15.0, 4.7, 2.7 Hz, 1H), 2.60 - 2.41 (m, 1H), 2.18 - 1.87 (m, 2H), 1.76 (s, 1H), 1.69 (dddd, *J* = 13.2, 7.1, 5.0, 1.2 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.00, 148.09, 128.91, 128.05, 126.87, 120.32, 118.10, 110.61, 77.28, 55.57, 34.92, 29.22, 22.72 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO_2^+$ $[M+Na]^+$: 227.1042; found: 227.1042.



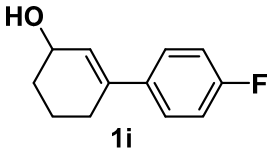
1g

Compound **1g** was prepared according to **General Procedure A** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a white solid (1.86 g, 80% yield in 2 steps). Rf = 0.25 (silica gel, hexane/EtOAc = 5:1). m.p.: 38-39 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.29 - 7.10 (m, 2H), 6.99 - 6.74 (m, 2H), 6.60 (s, 1H), 4.33 (ddd, *J* = 8.1, 5.1, 1.1 Hz, 1H), 3.79 (s, 3H), 2.34 (t, *J* = 5.9 Hz, 2H), 2.03 (dd, *J* = 8.1, 5.5 Hz, 1H), 1.80 - 1.57 (m, 4H), 1.54 - 1.31 (m, 3H) ppm. **^{13}C NMR** (100 MHz, CD_3OD) δ 158.56, 146.57, 130.69, 129.01, 128.05, 123.76, 121.06, 111.63, 77.54, 55.82, 37.95, 30.09, 29.19, 27.42, 25.03 ppm. **HRMS** (ESI): m/z calcd for: $C_{15}H_{20}NaO_2^+$ $[M+Na]^+$: 255.1356; found: 255.1355.



1h

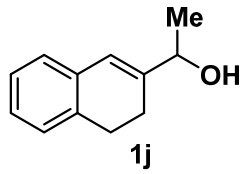
Compound **1h** was prepared according to **General Procedure A** and purified by flash chromatography on silica gel (DCM:MeOH = 50:1) as a foamy solid (1.95 g, 60% yield in 2 steps). Rf = 0.41 (silica gel, DCM:MeOH = 10:1). m.p.: 90-92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 2.2 Hz, 1H), 8.32 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.55 (ddd, *J* = 9.1, 5.5, 2.0 Hz, 2H), 7.39 - 7.14 (m, 3H), 7.11 (dd, *J* = 7.2, 1.7 Hz, 1H), 6.67 (d, *J* = 1.8 Hz, 1H), 5.21 (s, 1H), 3.12 - 2.86 (m, 1H), 2.84 - 2.73 (m, 2H), 2.72 - 2.57 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.47, 147.04, 144.30, 139.13, 136.95, 136.10, 133.51, 128.00, 127.63, 127.26, 126.61, 123.31, 120.43, 72.93, 29.60, 24.71 ppm. **HRMS** (ESI): m/z calcd for: $C_{16}H_{16}NO^+$ $[M+H]^+$: 238.1226; found: 238.1227.



1i

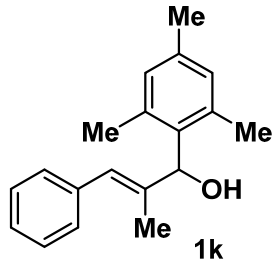
Compound **1i** was prepared according to **General Procedure C** and was purified by flash chromatography on silica gel (PE:EtOAc = 5:1) as a white solid (1.78 g, 78% yield in 2 steps). Rf = 0.35 (silica gel, hexane/EtOAc = 2:1). m.p.: 43-45 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 - 7.21 (m, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 6.07 (dt, *J* = 3.8, 1.9 Hz, 1H), 4.38 (d,

J = 5.3 Hz, 1H), 2.57 - 2.37 (m, 1H), 2.32 (dt, *J* = 17.5, 5.9 Hz, 1H), 1.92 (tq, *J* = 13.7, 5.7, 4.3 Hz, 2H), 1.82 - 1.45 (m, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.31, 161.35, 139.00, 137.52, 127.01, 126.95, 126.66, 115.21, 115.04, 66.29, 31.64, 27.65, 19.52 ppm. **HRMS** (ESI): m/z calcd for: $C_{12}H_{13}FNaO^+$ $[M+Na]^+$: 215.0843; found: 215.0840.



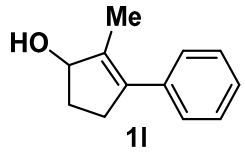
1j

Compound **1j** was prepared according to **General Procedure B** from a known starting material[1], and was purified by flash chromatography on silica gel (PE:EtOAc = 8:1) as a colorless oil (190 mg, 86% yield). Rf = 0.27 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, CDCl3) δ 7.23 - 7.09 (m, 3H), 7.04 (dd, *J* = 6.4, 1.7 Hz, 1H), 6.45 (q, *J* = 1.4 Hz, 1H), 4.44 (q, *J* = 6.5 Hz, 1H), 3.42 - 2.49 (m, 2H), 2.64 - 2.05 (m, 2H), 1.74 (s, 1H), 1.36 (d, *J* = 6.5 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, CDCl3) δ 144.63, 135.25, 134.20, 127.37, 126.93, 126.63, 126.23, 121.58, 71.20, 28.22, 23.25, 21.64 ppm. **HRMS** (ESI): m/z calcd for: $C_{12}H_{14}NaO^+$ $[M+Na]^+$: 197.0936; found: 197.0938.



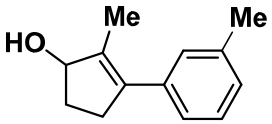
1k

Compound **1k** was prepared according to **General Procedure B** from α-methylcinnamaldehyde, and was purified by flash chromatography on silica gel (PE:EtOAc = 20:1) to give the allylic alcohol as a white solid (1.27 g, 70% yield). Rf = 0.52 (silica gel, hexane/EtOAc = 8:1). m.p.: 81-83 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 - 7.35 (m, 2H), 7.33 - 7.29 (m, 2H), 7.25 (ddt, *J* = 8.7, 6.5, 1.5 Hz, 1H), 6.89 (s, 2H), 6.74 (t, *J* = 1.8 Hz, 1H), 5.70 (s, 1H), 2.45 (s, 6H), 2.32 (s, 3H), 2.15 (s, 1H), 1.79 (t, *J* = 1.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.44, 138.24, 137.35, 137.22, 134.94, 130.21, 129.01, 128.17, 126.23, 124.02, 77.48, 77.16, 76.84, 73.91, 20.93, 20.68, 15.67 ppm. **HRMS** (ESI): m/z calcd for: $C_{19}H_{22}NaO^+$ $[M+Na]^+$: 289.1563; found: 289.1563.



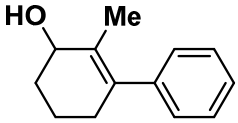
1l

Compound **1l** was prepared according to **General Procedure C** from a known starting material 3-methoxy-2-methylcyclopent-2-en-1-one,[2] and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a white solid (380 mg, 55% yield in 2 steps). Rf = 0.32 (silica gel, hexane/EtOAc = 5:1). m.p.: 58-60 °C. **^{1}H NMR** (500 MHz, CD_3OD) δ 7.40 - 7.25 (m, 4H), 7.23 (d, *J* = 7.2 Hz, 1H), 4.67 (t, *J* = 6.3 Hz, 1H), 2.76 (ddt, *J* = 13.2, 6.5, 2.1 Hz, 1H), 2.62 (ddd, *J* = 15.1, 6.9, 4.1 Hz, 1H), 2.33 (dtd, *J* = 12.6, 8.1, 4.1 Hz, 1H), 1.86 (d, *J* = 2.3 Hz, 3H), 1.73 (ddt, *J* = 13.8, 9.0, 5.4 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, CD_3OD) δ 139.43, 139.04, 137.41, 129.12, 128.74, 127.82, 82.38, 34.88, 33.20, 12.92 ppm. **HRMS** (ESI): m/z calcd for: $C_{12}H_{14}NaO^+$ $[M+Na]^+$: 197.0937; found: 197.0938.



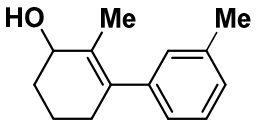
1m

Compound **1m** was prepared according to **General Procedure C** and was purified by flash chromatography on silica gel (PE: EtOAc = 20:1) as a colorless oil (290 mg, 39% yield in 2 steps). Rf = 0.41 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, CD_3OD) δ 7.21 (t, *J* = 7.6 Hz, 1H), 7.17 - 6.87 (m, 3H), 4.66 (t, *J* = 6.3 Hz, 1H), 2.75 (d, *J* = 2.2 Hz, 1H), 2.60 (ddd, *J* = 8.9, 6.9, 4.7 Hz, 1H), 2.33 (s, 4H), 1.85 (d, *J* = 2.2 Hz, 3H), 1.79 - 1.68 (m, 1H) ppm. **^{13}C NMR** (126 MHz, CD3OD) δ 139.39, 139.18, 138.72, 137.17, 129.31, 129.02, 128.49, 125.89, 82.39, 34.95, 33.20, 21.52, 12.95 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO^+$ $[M+Na]^+$: 211.1093; found: 211.1095.



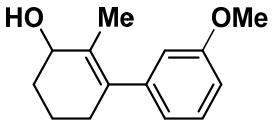
1n

Compound **1n** was prepared according to **General Procedure C** from a known starting material 3-methoxy-2-methylcyclohex-2-en-1-one,[3] and purified by flash chromatography on silica gel (PE: EtOAc = 20:1) as a white solid (667 mg, 62% yield in 2 steps). Rf = 0.36 (silica gel, hexane/EtOAc = 5:1). m.p.: 45-47 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 - 7.29 (m, 2H), 7.28 - 7.21 (m, 1H), 7.22 - 6.89 (m, 2H), 4.46 - 3.89 (m, 1H), 2.64 - 2.07 (m, 2H), 1.84 (dtd, *J* = 15.3, 6.9, 5.2 Hz, 4H), 1.76 - 1.44 (m, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.44, 136.86, 130.48, 128.19, 128.18, 126.48, 69.56, 32.40, 32.13, 18.76, 17.77 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO^+$ $[M+Na]^+$: 211.1093; found: 211.1095.



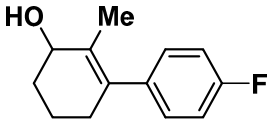
1o

Compound **1o** was prepared according to **General Procedure C** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (427 mg, 59% yield in 2 steps). Rf = 0.54 (silica gel, hexane/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.6 Hz, 1H), 7.09 - 7.01 (m, 1H), 7.00 - 6.83 (m, 2H), 4.12 (s, 1H), 2.35 (s, 3H), 2.24 (dt, *J* = 6.2, 2.2 Hz, 2H), 1.85 (tt, *J* = 3.9, 3.0, 1.4 Hz, 3H), 1.74 - 1.60 (m, 5H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.43, 137.73, 137.00, 130.30, 128.89, 128.10, 127.23, 125.25, 69.62, 32.46, 32.17, 21.56, 18.79, 17.81 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{18}NaO^+$ $[M+Na]^+$: 225.1250; found: 225.1251.



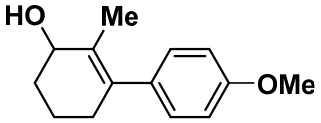
1p

Compound **1p** was prepared according to **General Procedure C** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (747 mg, 60% yield in 2 steps). Rf = 0.21(silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (400 MHz, CD_3OD) δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.77 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.72 - 6.55 (m, 2H), 4.04 (s, 1H), 3.75 (s, 3H), 2.20 (dq, *J* = 6.2, 2.0 Hz, 2H), 1.90 - 1.73 (m, 3H), 1.64 (t, *J* = 2.1 Hz, 4H) ppm. **^{13}C NMR** (100 MHz, CD_3OD) δ 160.91, 146.34, 137.56, 131.53, 130.15, 121.43, 114.78, 112.70, 69.84, 55.55, 33.35, 33.12, 19.76, 18.01 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{18}NaO_2^+$ $[M+Na]^+$: 241.1199; found: 241.1200.



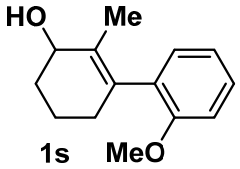
1q

Compound **1q** was prepared according to **General Procedure C** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (400 mg, 34% yield in 2 steps). Rf = 0.34(silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 - 7.04 (m, 2H), 7.03 - 6.83 (m, 2H), 4.11 (t, *J* = 3.9 Hz, 1H), 2.30 - 2.11 (m, 2H), 1.86 - 1.76 (m, 4H), 1.71 - 1.63 (m, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.53, 160.59, 139.28, 139.25, 135.84, 131.04, 129.78, 129.71, 115.10, 114.94, 69.47, 32.50, 32.11, 18.74, 17.73, 17.71 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{15}FNaO^+$ $[M+Na]^+$: 229.0999; found: 229.1001.

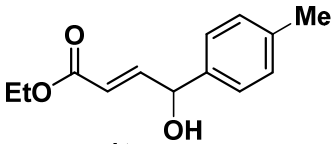


1r

Compound **1r** was prepared according to **General Procedure C** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a white solid (800 mg, 65% yield in 2 steps). Rf = 0.25(silica gel, hexane/EtOAc = 5:1). m.p.: 46-47 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.13 - 6.97 (m, 2H), 6.92 - 6.70 (m, 2H), 4.04 (t, *J* = 4.4 Hz, 1H), 3.76 (s, 3H), 2.19 (dddt, *J* = 7.9, 5.9, 3.9, 1.9 Hz, 2H), 1.92 - 1.71 (m, 3H), 1.68 - 1.55 (m, 4H) ppm. **^{13}C NMR** (100 MHz, CD_3OD) δ 159.60, 137.14, 137.08, 131.37, 130.19, 114.46, 70.01, 55.62, 33.50, 33.17, 19.83, 18.08 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{18}NaO_2^+$ $[M+Na]^+$: 241.1199; found: 241.1200.



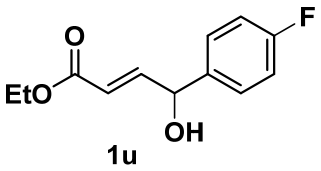
Compound **1s** was prepared according to **General Procedure C** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a white solid (870 mg, 70% yield in 2 steps). Rf = 0.27(silica gel, hexane/EtOAc = 5:1). m.p.: 52-54 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.20 (ddd, *J* = 9.0, 7.3, 2.0 Hz, 1H), 7.04 - 6.67 (m, 3H), 4.06 (d, *J* = 8.1 Hz, 1H), 2.28 (d, *J* = 18.1 Hz, 1H), 2.04 (t, *J* = 9.9 Hz, 1H), 1.90 - 1.71 (m, 3H), 1.69 - 1.57 (m, 1H), 1.51 (s, 3H) ppm. **^{13}C NMR** (100 MHz, CD_3OD) δ 157.92, 157.60, 135.19, 134.83, 133.43, 132.09, 130.93, 130.56, 128.96, 121.53, 112.14, 70.03, 69.78, 55.84, 33.35, 32.33, 20.10, 19.60, 17.76 ppm. **HRMS** (ESI): m/z calcd for: $C_{14}H_{18}NaO_2^+$ $[M+Na]^+$: 241.1199; found: 241.1199.



1t

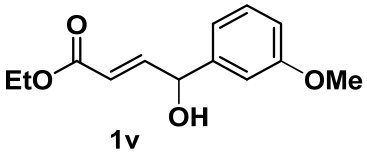
Compound **1t** was prepared according to **General Procedure C** from Ethyl trans-4-oxo-2-butenoate and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (302 mg, 60% yield). Rf = 0.3 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.04 (dd, *J* = 15.6, 4.8 Hz, 1H), 6.14 (dd, *J* = 15.6, 1.7 Hz, 1H), 5.32 (dd, *J* = 4.9, 1.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 2.18 (s,

1H), 1.28 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.62, 148.75, 138.39, 138.17, 129.67, 126.70, 120.32, 73.56, 60.62, 21.28, 14.35 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO_3^+$ [M+Na]$^+$: 243.0991; found: 243.0092.



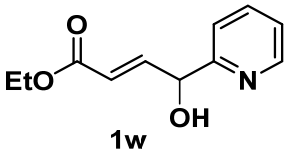
1u

Compound **1u** was prepared according to **General Procedure C** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (370 mg, 70% yield). Rf = 0.25 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 - 7.28 (m, 2H), 7.08 - 7.01 (m, 2H), 6.99 (dd, J = 15.6, 5.0 Hz, 1H), 5.32 (dd, J = 4.9, 1.8 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.61 (s, 1H), 1.27 (t, J = 7.2 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.58, 163.69, 161.73, 148.44, 136.88, 136.86, 128.52, 128.45, 120.57, 115.90, 115.73, 72.91, 60.76, 14.30 ppm. HRMS (ESI): m/z calcd for: $C_{12}H_{13}FNaO_3^+$ [M+Na]$^+$: 247.0740; found: 247.0741.



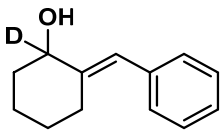
1v

Compound **1v** was prepared according to **General Procedure C** and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a colorless oil (350 mg, 64% yield). Rf = 0.26 (silica gel, hexane/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 - 7.16 (m, 1H), 7.01 (dd, J = 15.6, 4.9 Hz, 1H), 6.97 - 6.87 (m, 2H), 6.84 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 6.13 (dd, J = 15.6, 1.7 Hz, 1H), 5.31 (d, J = 4.8 Hz, 1H), 4.17 (d, J = 7.1 Hz, 2H), 3.80 (s, 3H), 2.48 (d, J = 3.1 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.61, 160.08, 148.53, 142.71, 130.00, 120.42, 118.91, 113.95, 112.11, 73.54, 60.67, 55.40, 14.32 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{16}NaO_4^+$ [M+Na]$^+$: 259.0940; found: 259.0941.



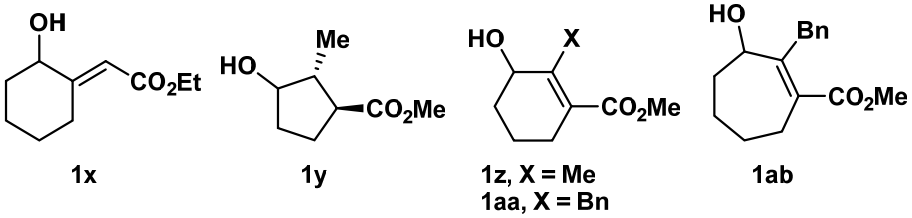
1w

To the solution of 2-bromopyridine (1.00 g, 6.33 mmol, 1.0 equiv.) in anhydrous Et_2O (20 mL) was slowly added the nBuLi (6.69 mmol, 1.1 equiv.) via syringe at -78 °C, and the reaction mixture was stirred for 1 hour. Ethyl trans-4-oxo-2-butenoate (0.84 mL, 6.69 mmol, 1.1 equiv.) in Et_2O (5 mL) was added to the reaction. After 30 min, the reaction mixture was quenched by addition of a cold saturated aq. NH_4Cl solution (10 mL) and then the mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by a flash chromatography on silica gel (PE: EtOAc = 1:1) to yield the desired allylic alcohol **1w** (390 mg, 30% yield) as a yellowish oil. Rf = 0.26 (silica gel, hexane/EtOAc = 1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (dt, J = 4.9, 1.5 Hz, 1H), 7.71 (td, J = 7.7, 1.7 Hz, 1H), 7.30 (dq, J = 8.0, 0.8 Hz, 1H), 7.24 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H), 7.03 (dd, J = 15.5, 5.3 Hz, 1H), 6.23 (dd, J = 15.5, 1.6 Hz, 1H), 5.36 (dd, J = 5.4, 1.7 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.44, 158.19, 148.56, 148.03, 137.32, 123.16, 121.52, 121.12, 72.26, 60.63, 14.33 ppm. **HRMS** (ESI): m/z calcd for: $C_{11}H_{13}NNaO_3^+$ [M+Na]$^+$: 230.0787; found: 230.0786.



***d*-1a**

Compound ***d*-1a** was prepared according to **General Procedure A** using $NaBD_4$ instead of $NaBH_4$ and purified by flash chromatography on silica gel (PE: EtOAc = 10:1) as a as a white solid (756 mg, 40% yield in 2 steps). Rf = 0.50 (silica gel, hexane/EtOAc = 10:1). m.p.: 56-57 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.27 - 6.95 (m, 3H), 6.53 (s, 1H), 2.78 - 2.57 (m, 1H), 2.21 - 2.07 (m, 1H), 2.06 - 1.96 (m, 1H), 1.87 (ddd, *J* = 8.7, 6.8, 4.3 Hz, 1H), 1.80 (s, 1H), 1.71 - 1.42 (m, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.42, 137.78, 129.04, 128.21, 126.34, 120.97, 73.58, 73.41, 73.23, 36.53, 27.47, 27.06, 23.26 ppm. **HRMS** (ESI): m/z calcd for: $C_{13}H_{15}DNaO^+$ $[M+Na]^+$: 212.1156; found: 212.1159.

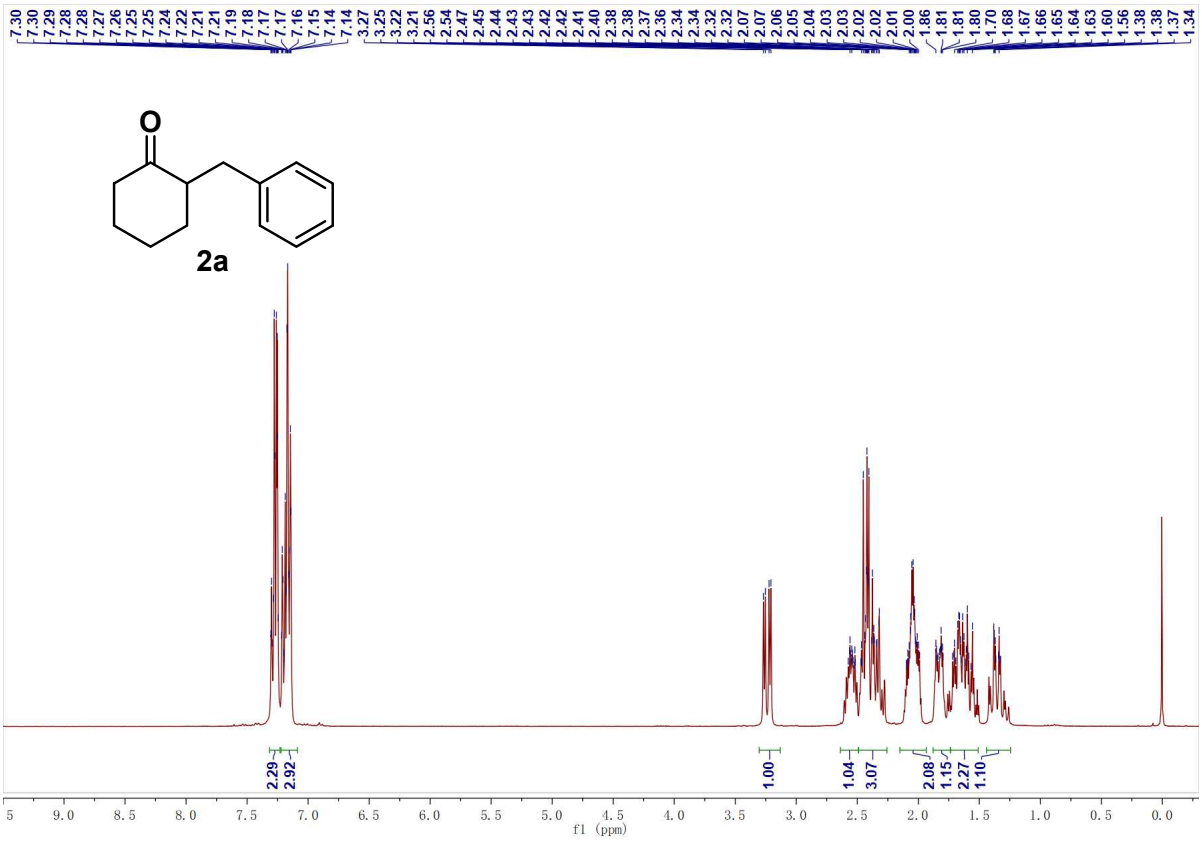


1x **1y** **1z, X = Me** **1aa, X = Bn** **1ab**

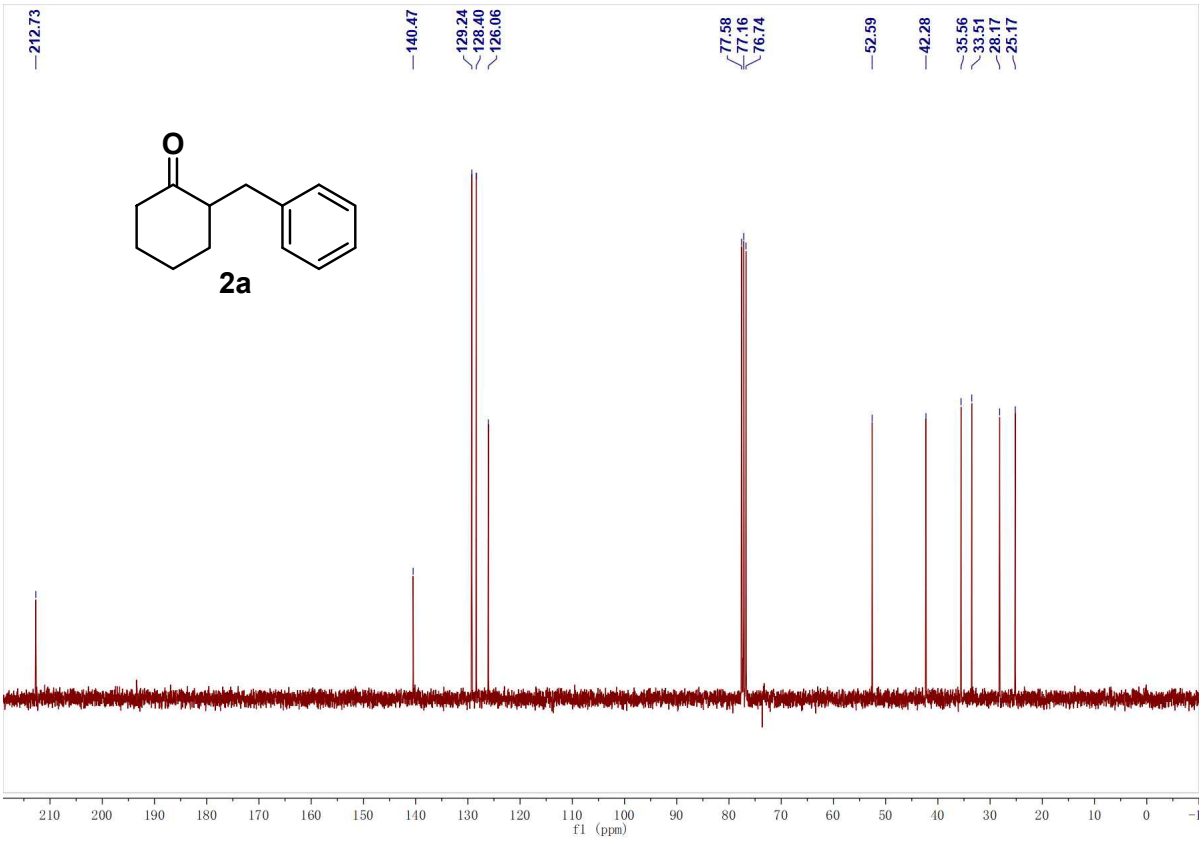
Compounds **1x, 1y**, **1z**, **1aa**, **1ab** were prepared according to our previously reported methods.[4]

6 NMR Spectra of Compounds

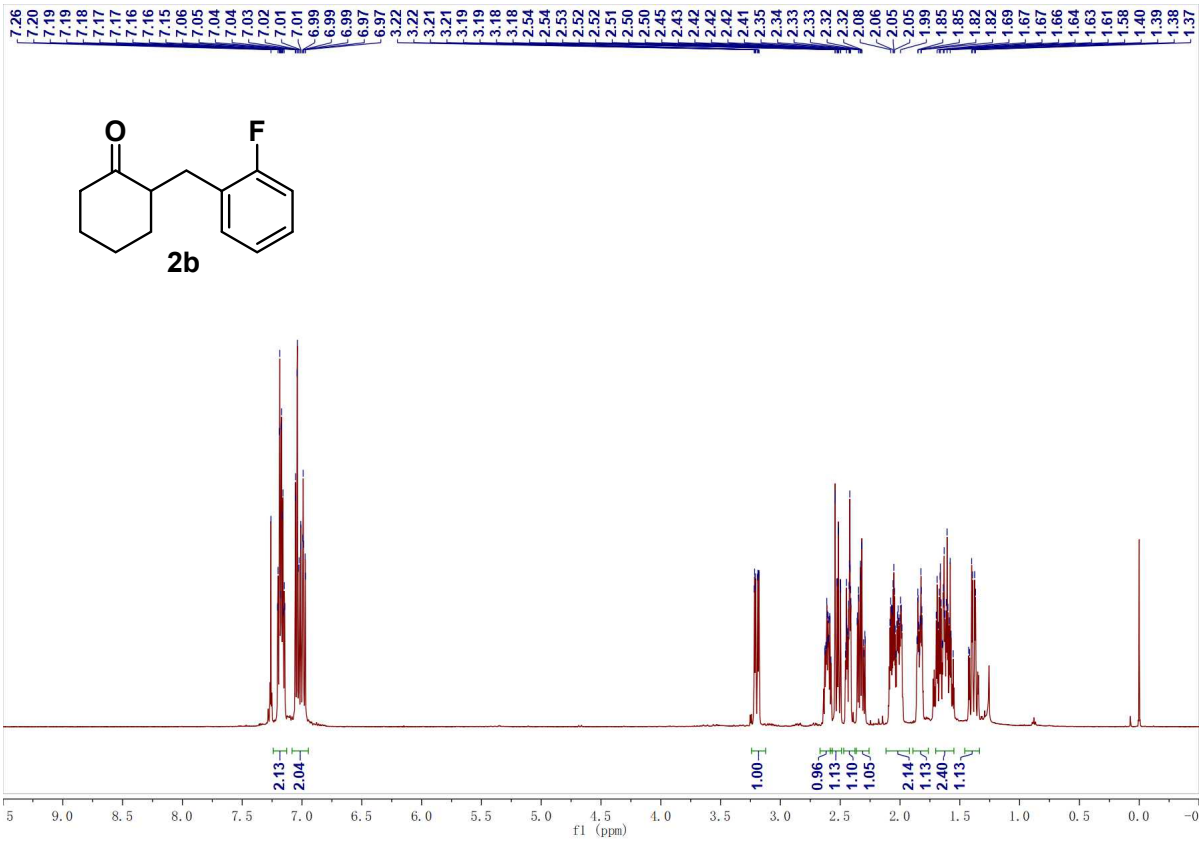
Compound **2a,** ^{1}H NMR



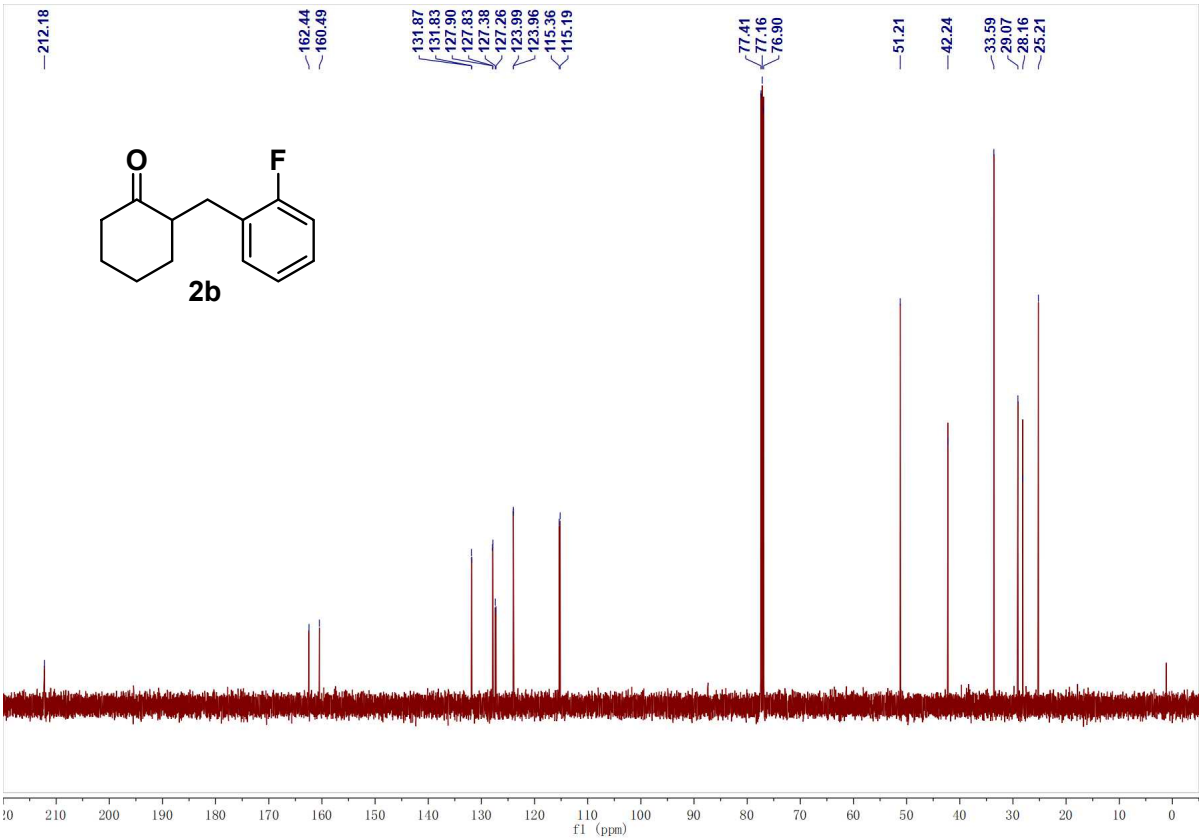
Compound **2a,** ^{13}C NMR



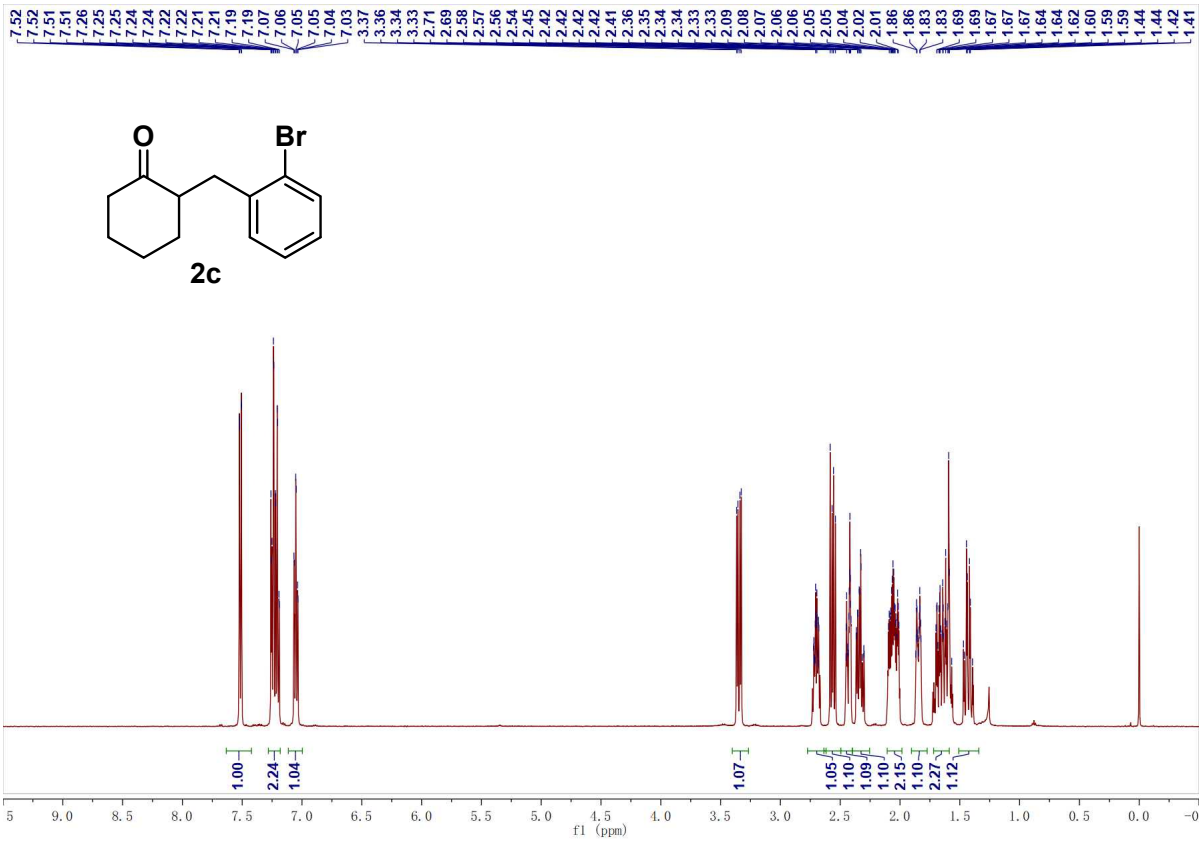
Compound **2b,** ^{1}H NMR



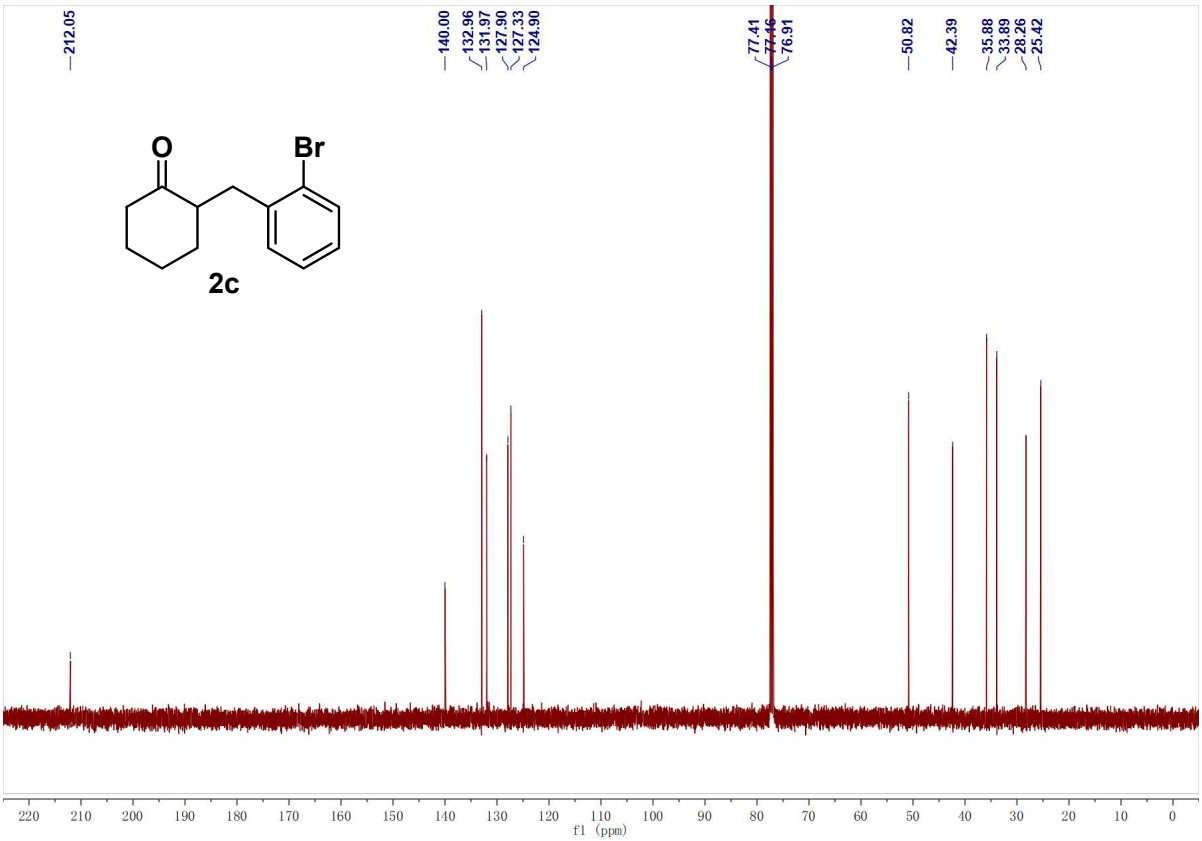
Compound **2b,** ^{13}C NMR



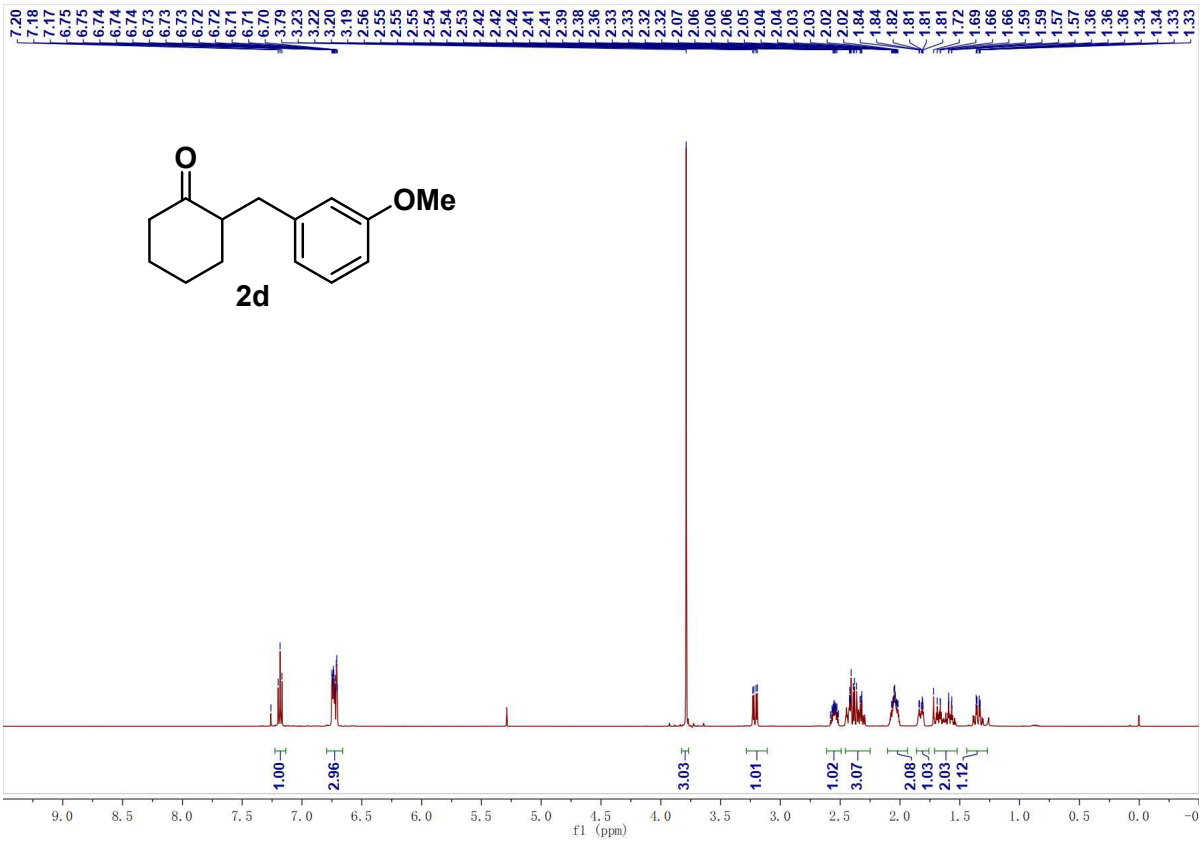
Compound **2c,** ^{1}H NMR



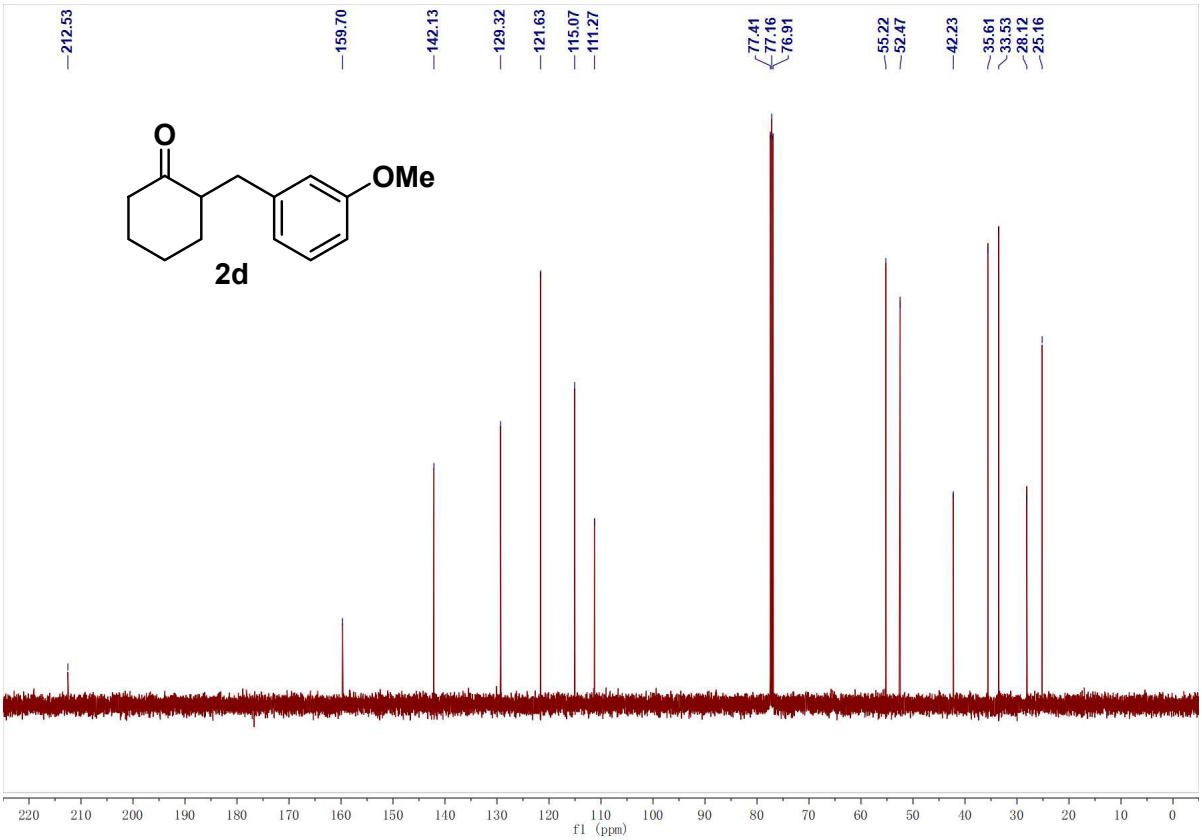
Compound **2c,** ^{13}C NMR



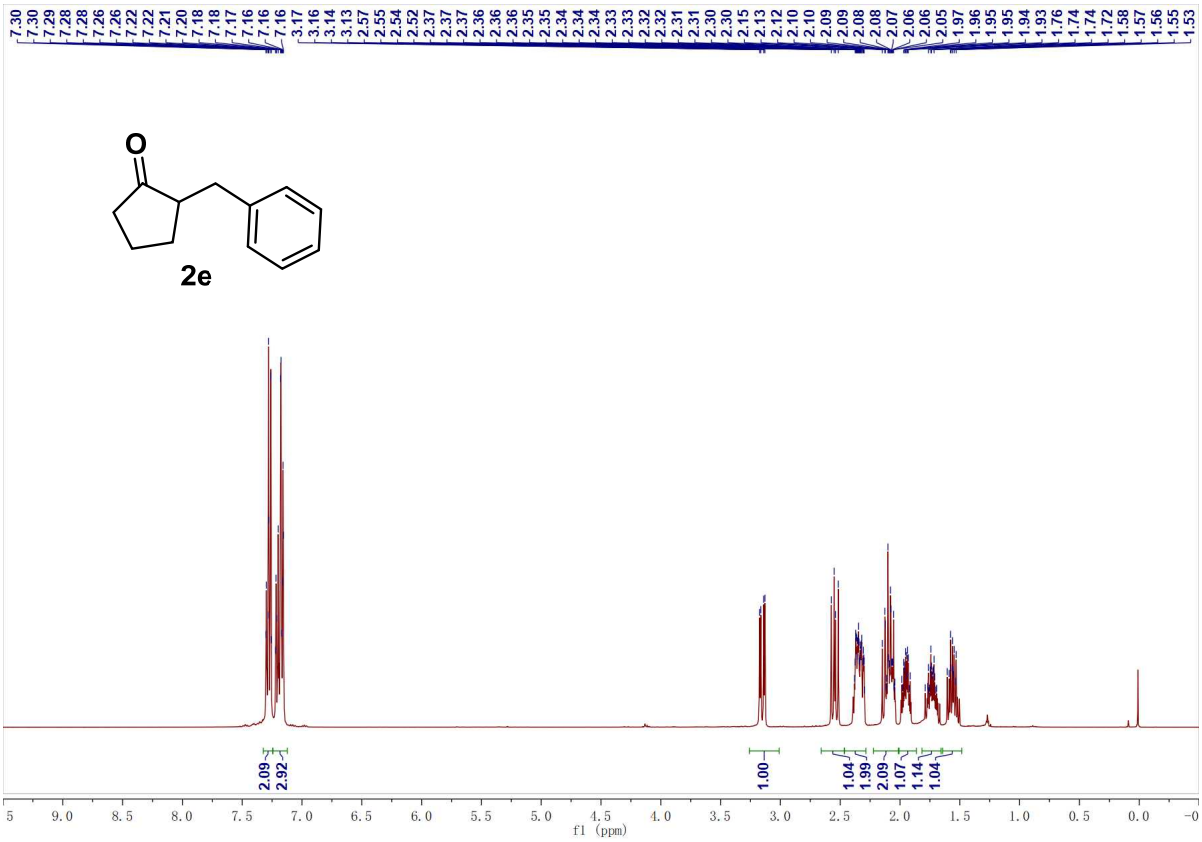
Compound **2d,** ^{1}H NMR



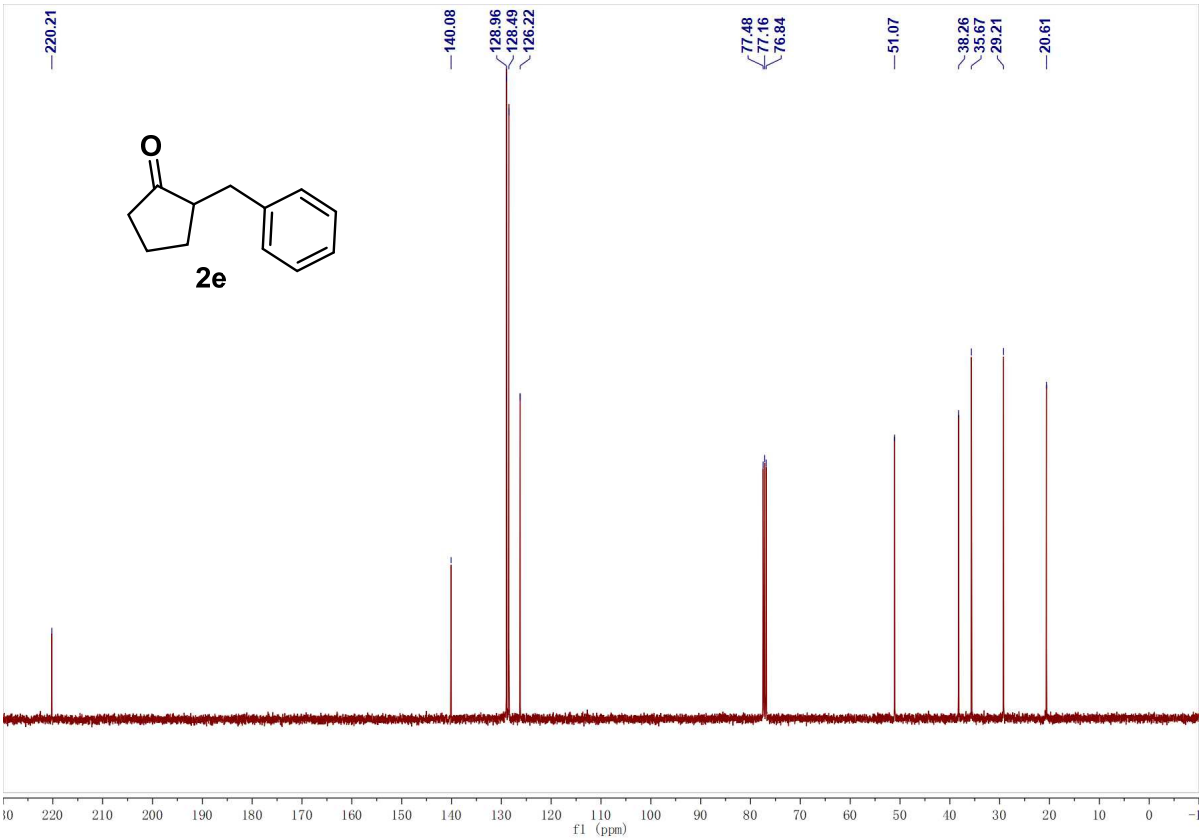
Compound **2d,** ^{13}C NMR



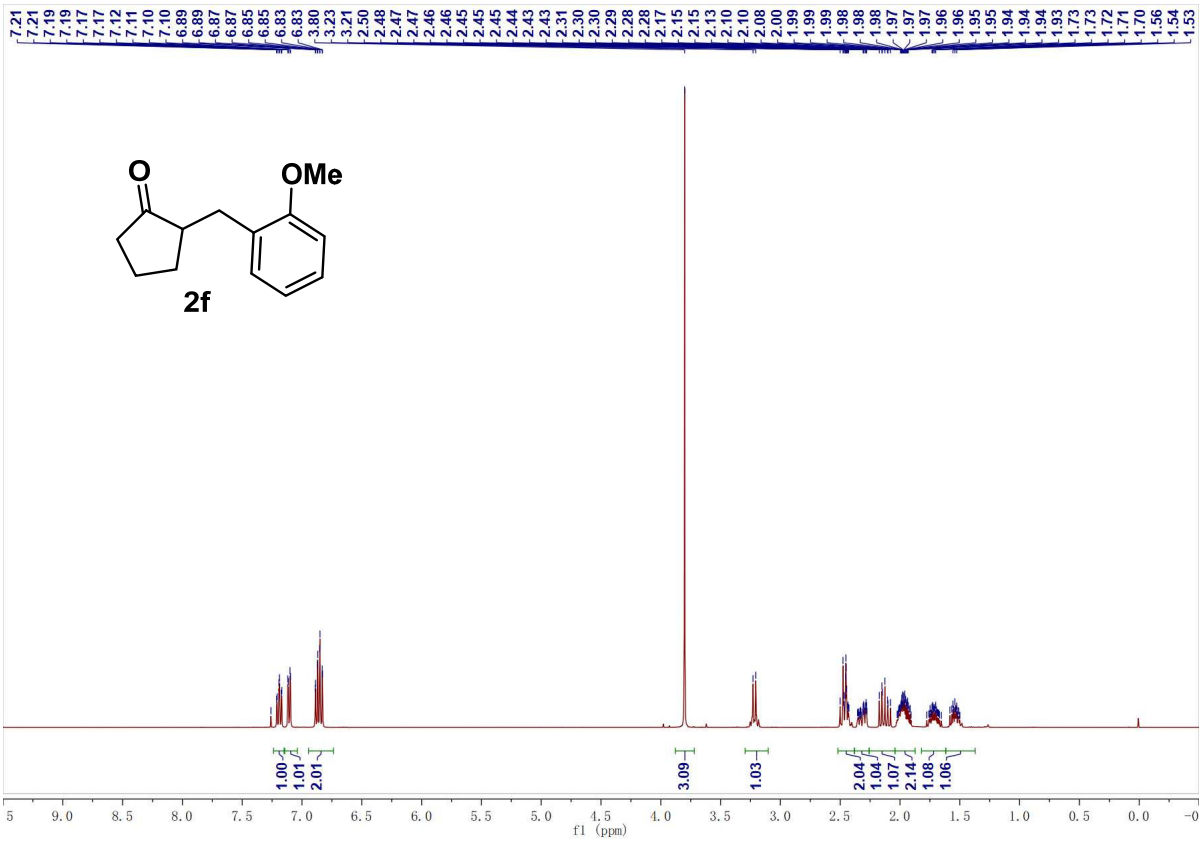
Compound **2e,** ^{1}H NMR



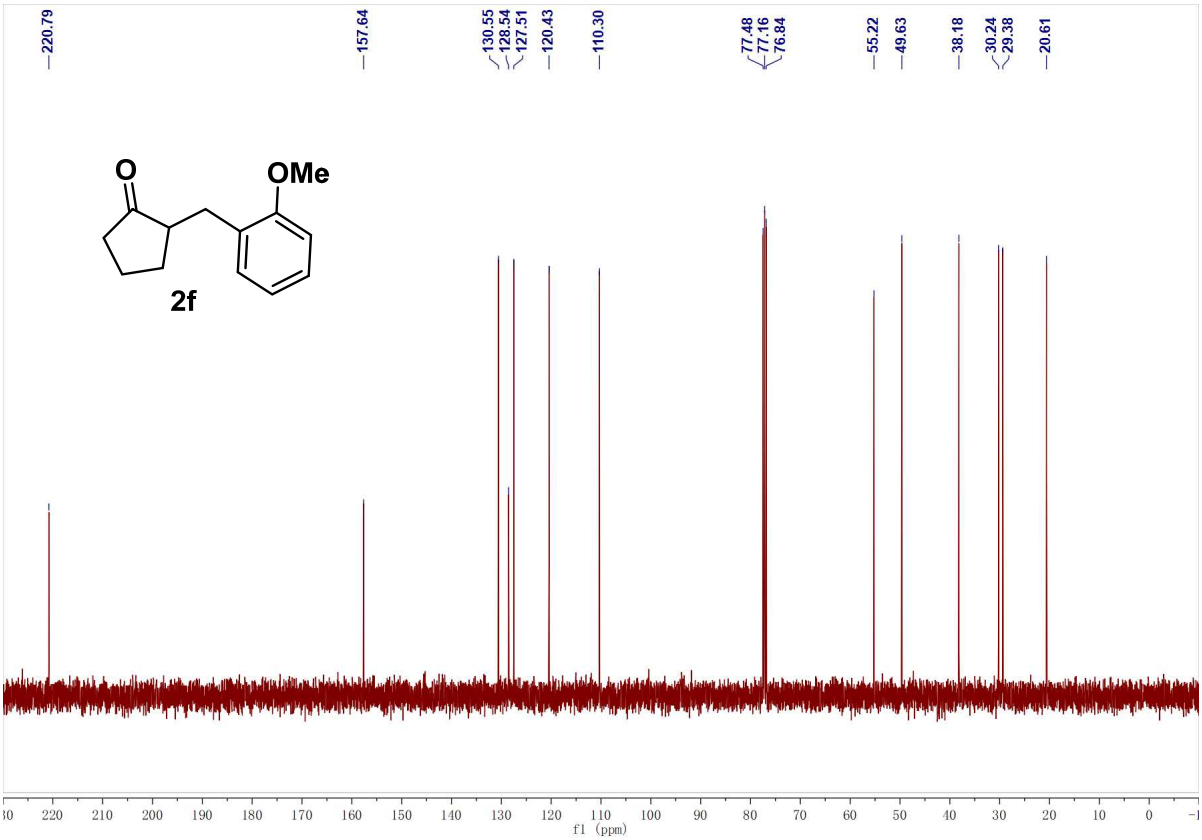
Compound **2e,** ^{13}C NMR



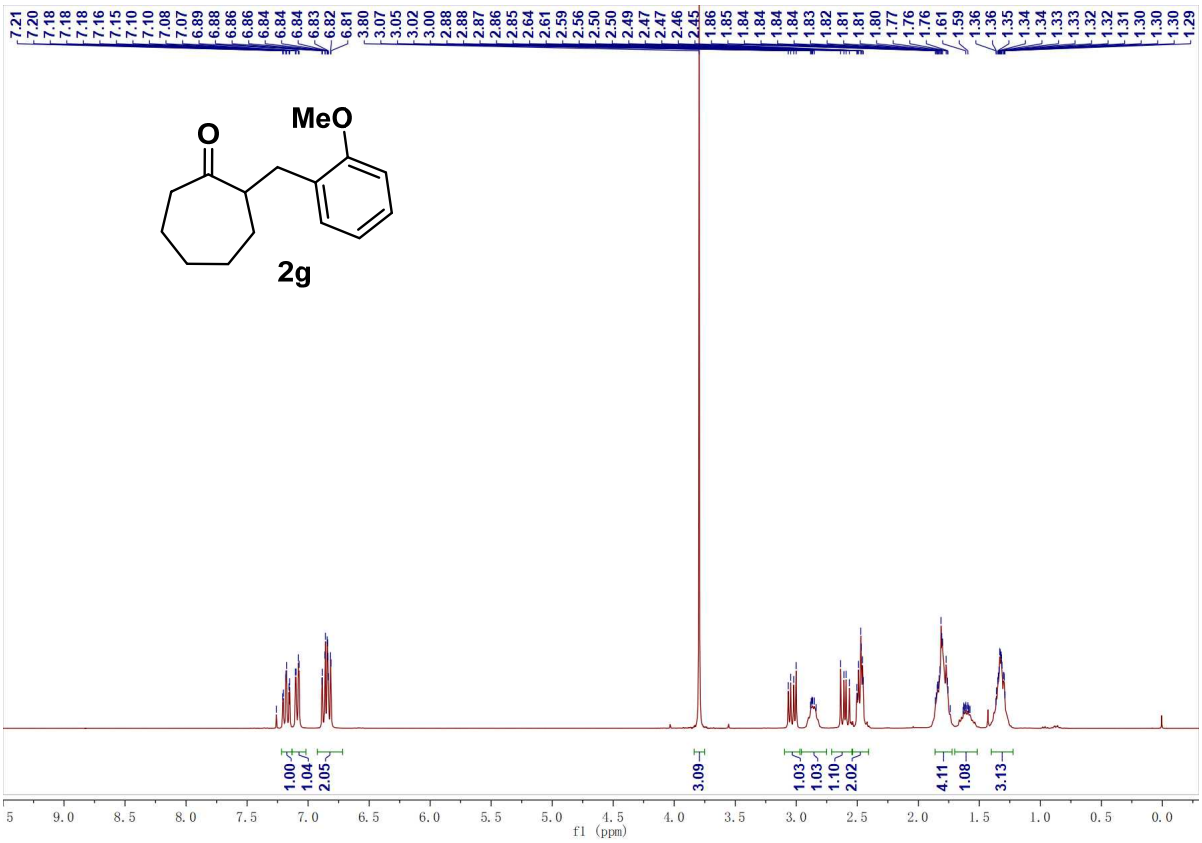
Compound **2f,** ^{1}H NMR



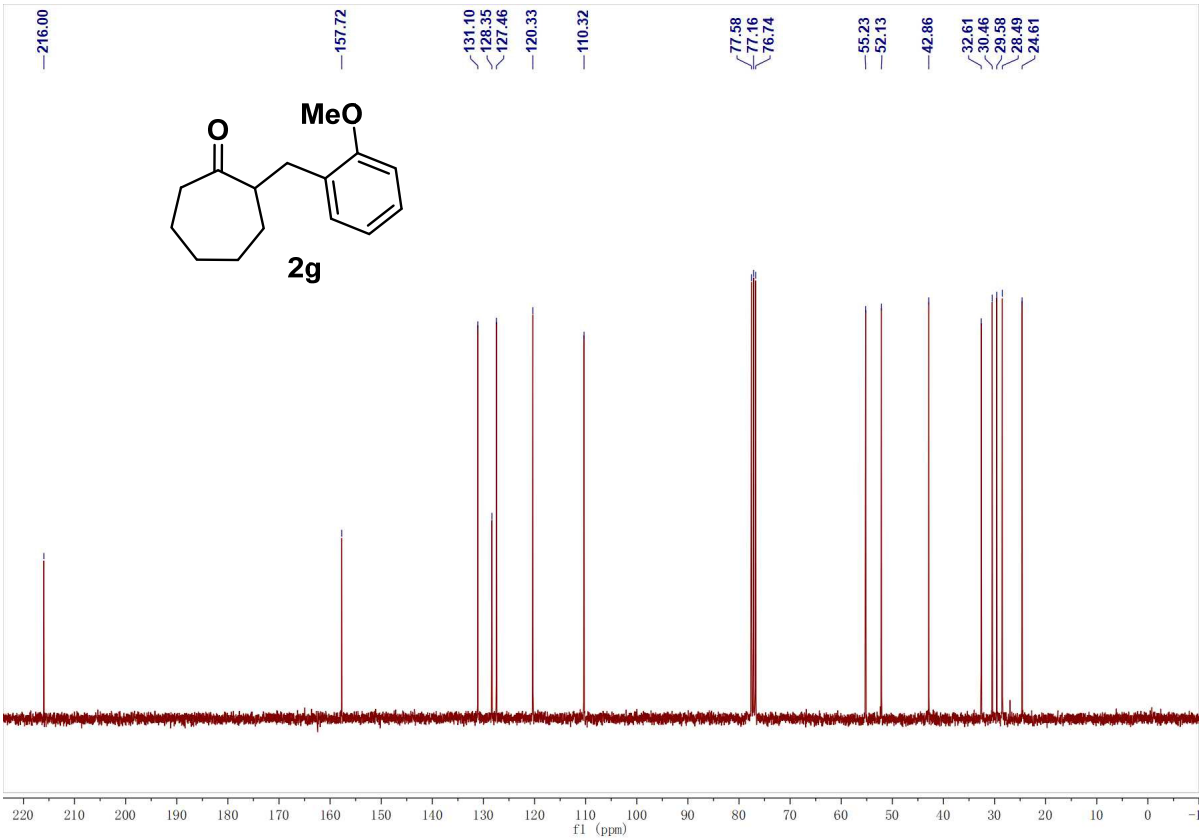
Compound **2f,** ^{13}C NMR



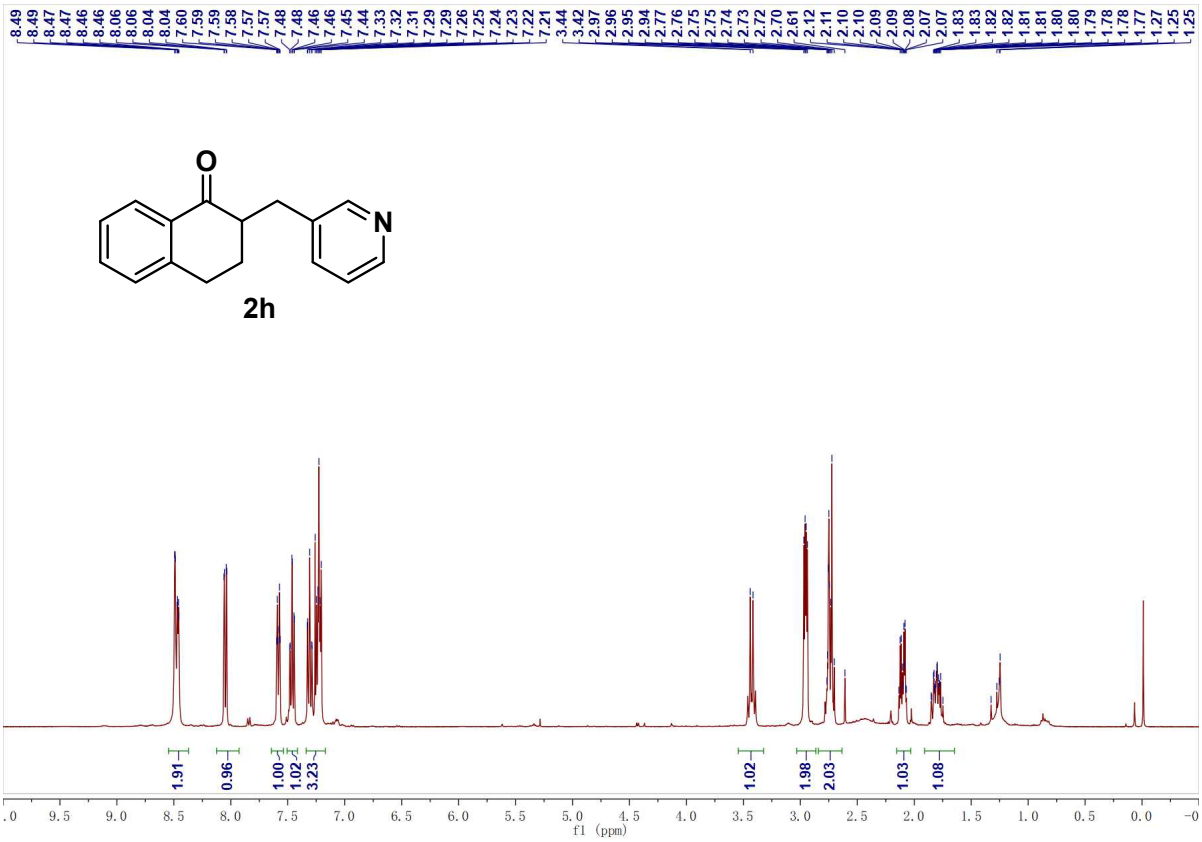
Compound **2g,** ^{1}H NMR



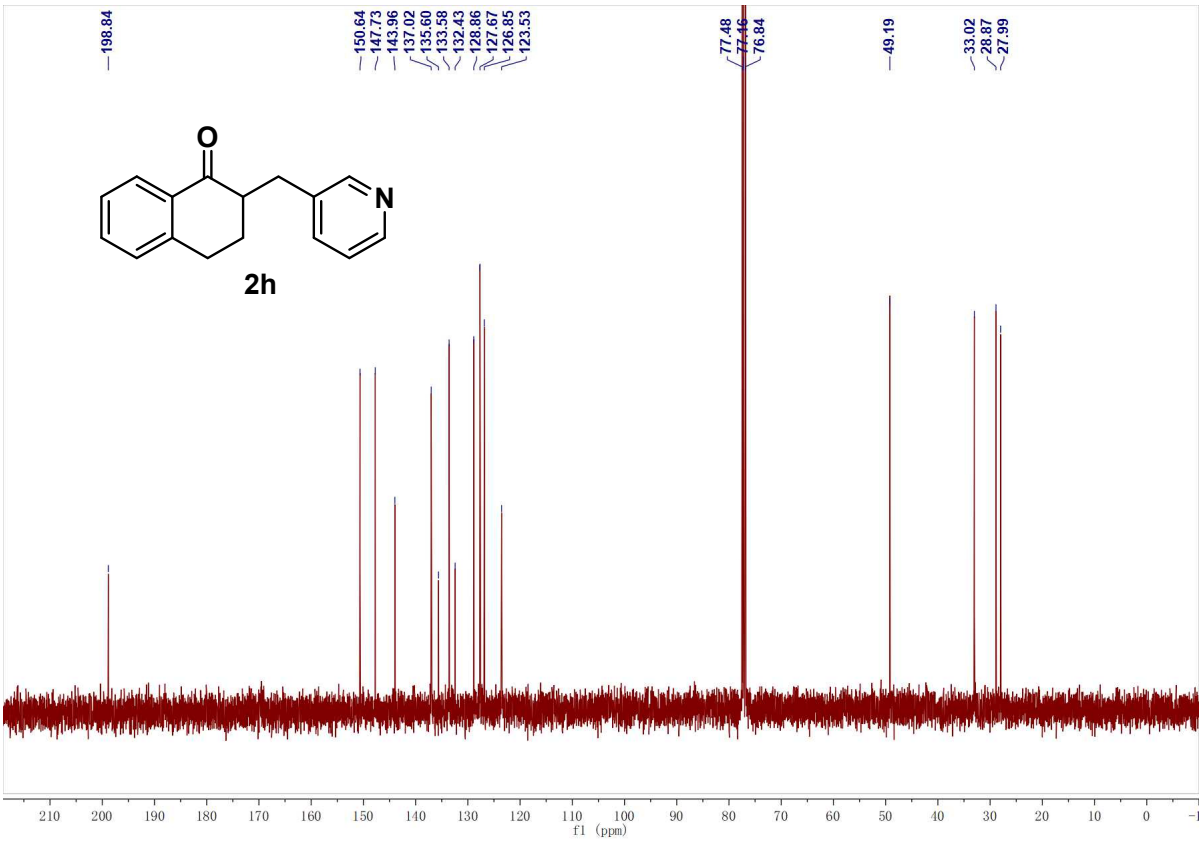
Compound **2g,** ^{13}C NMR



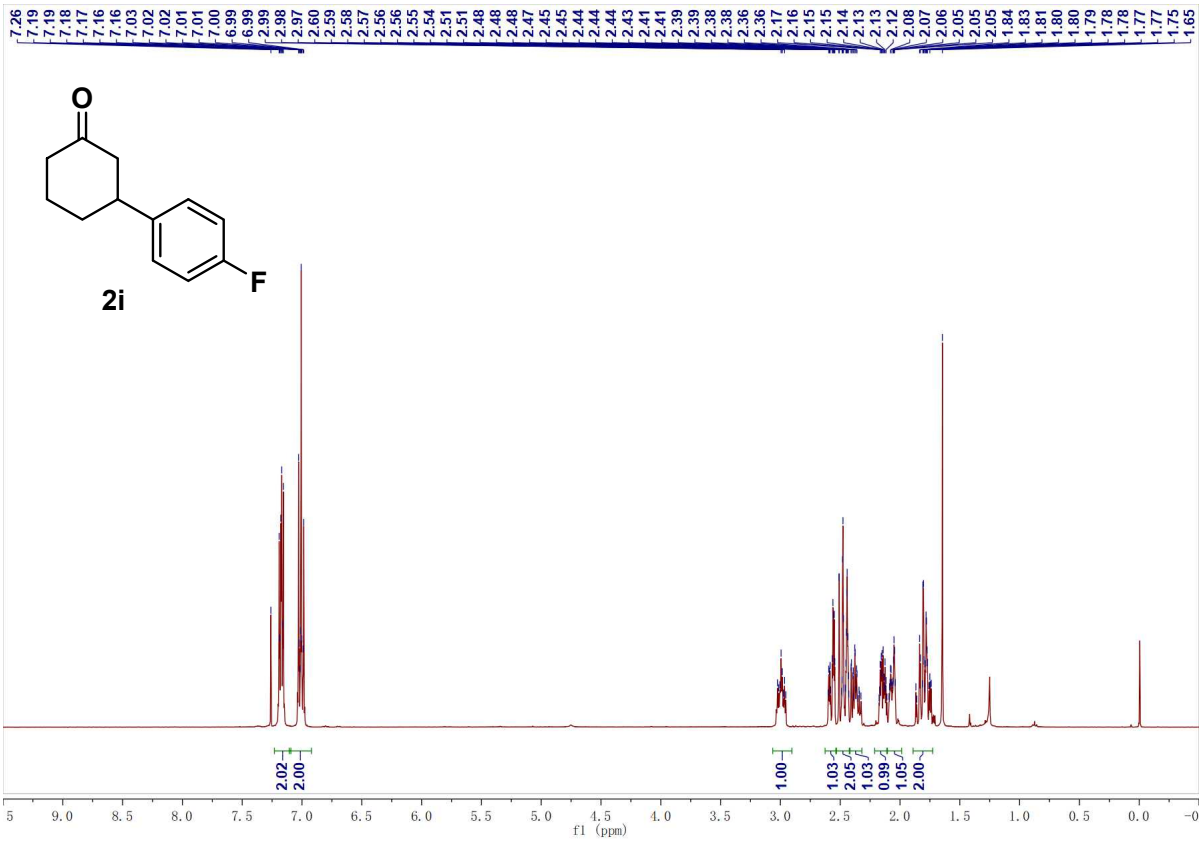
Compound **2h,** ^{1}H NMR



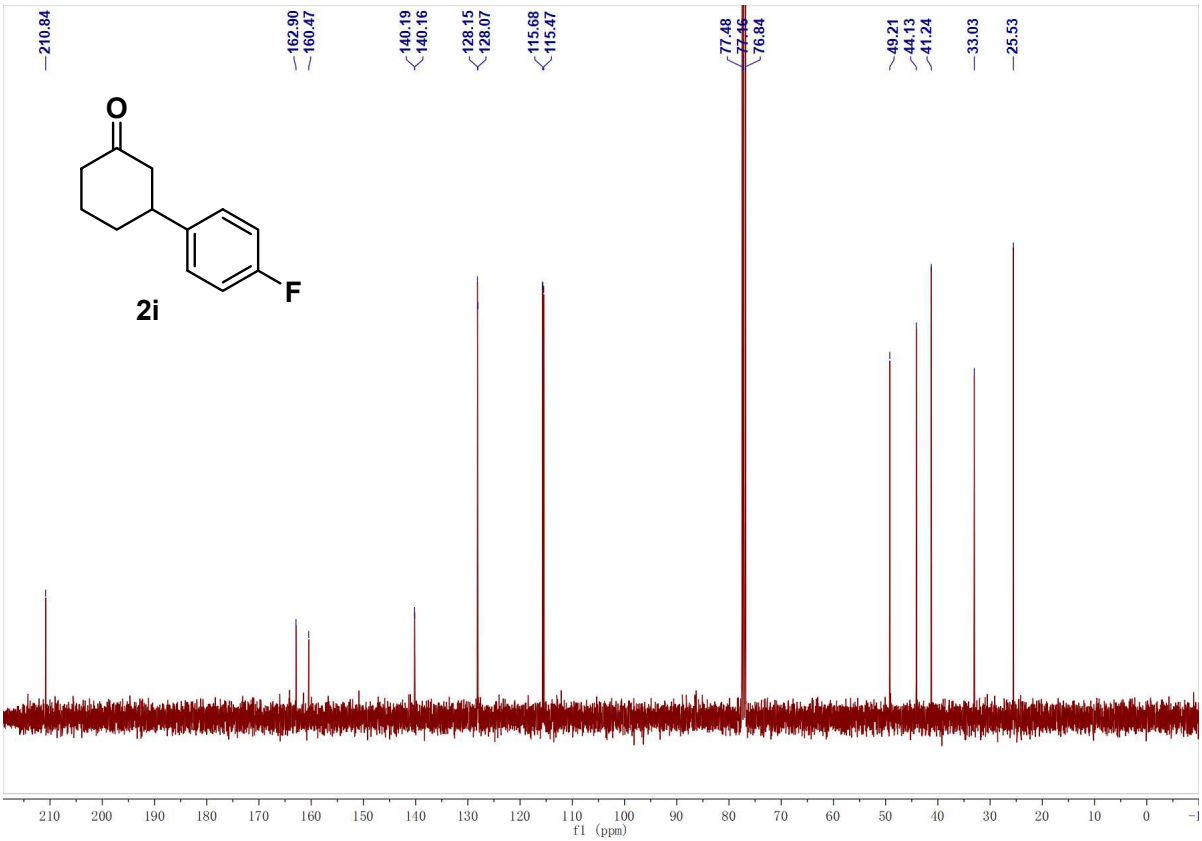
Compound **2h,** ^{13}C NMR



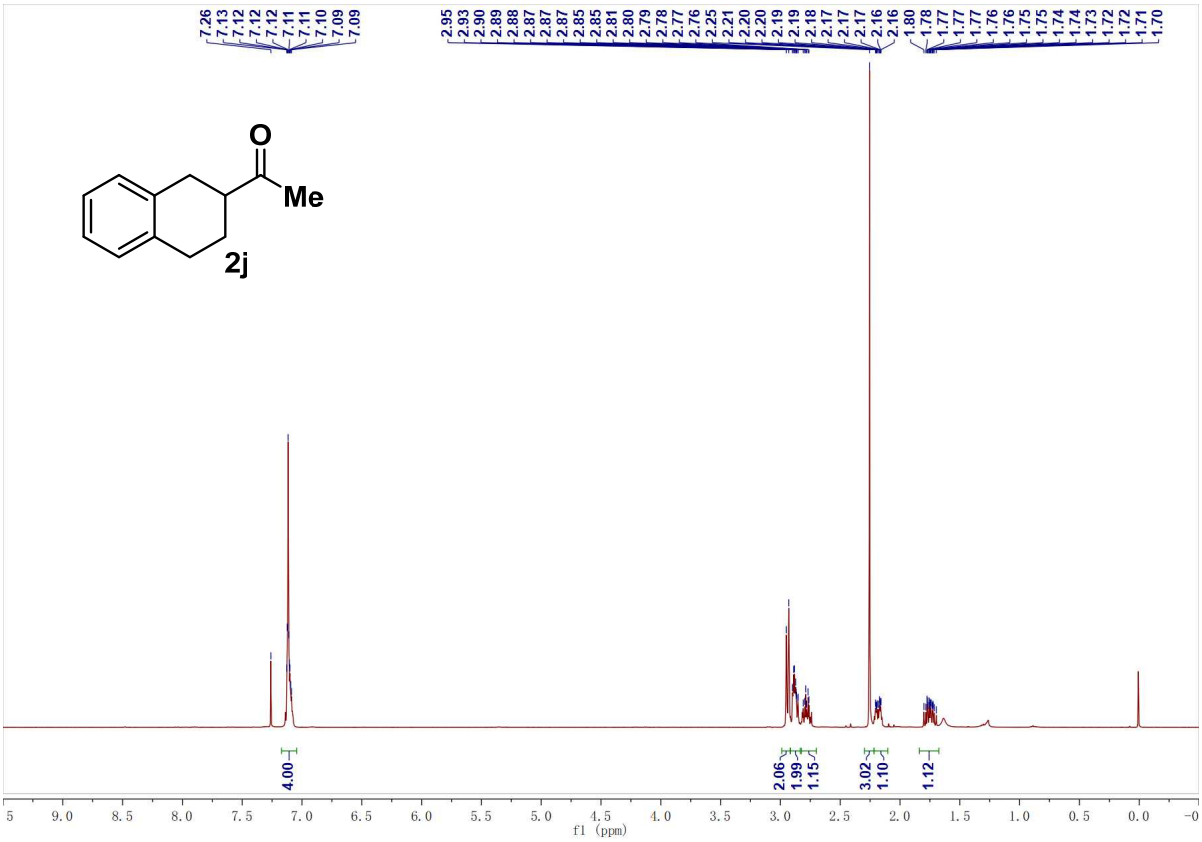
Compound **2i,** ^{1}H NMR



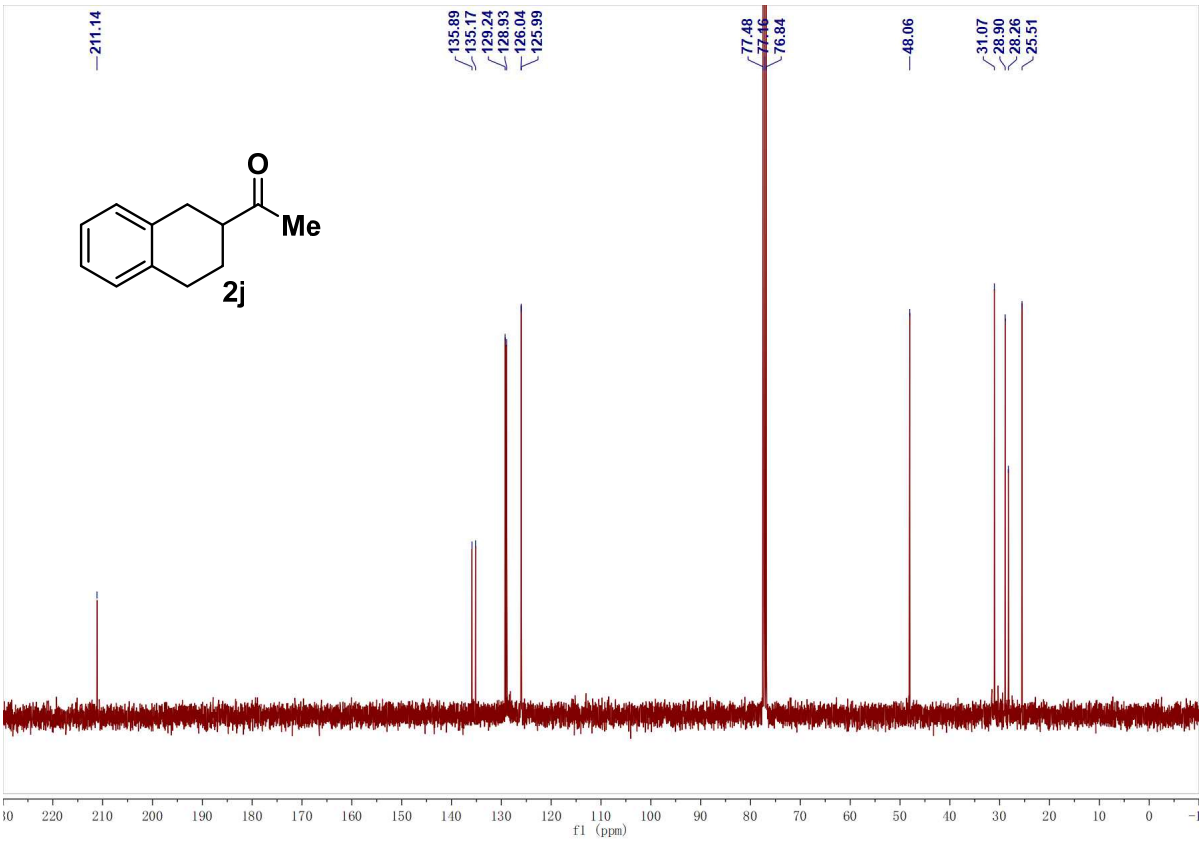
Compound **2i,** ^{13}C NMR



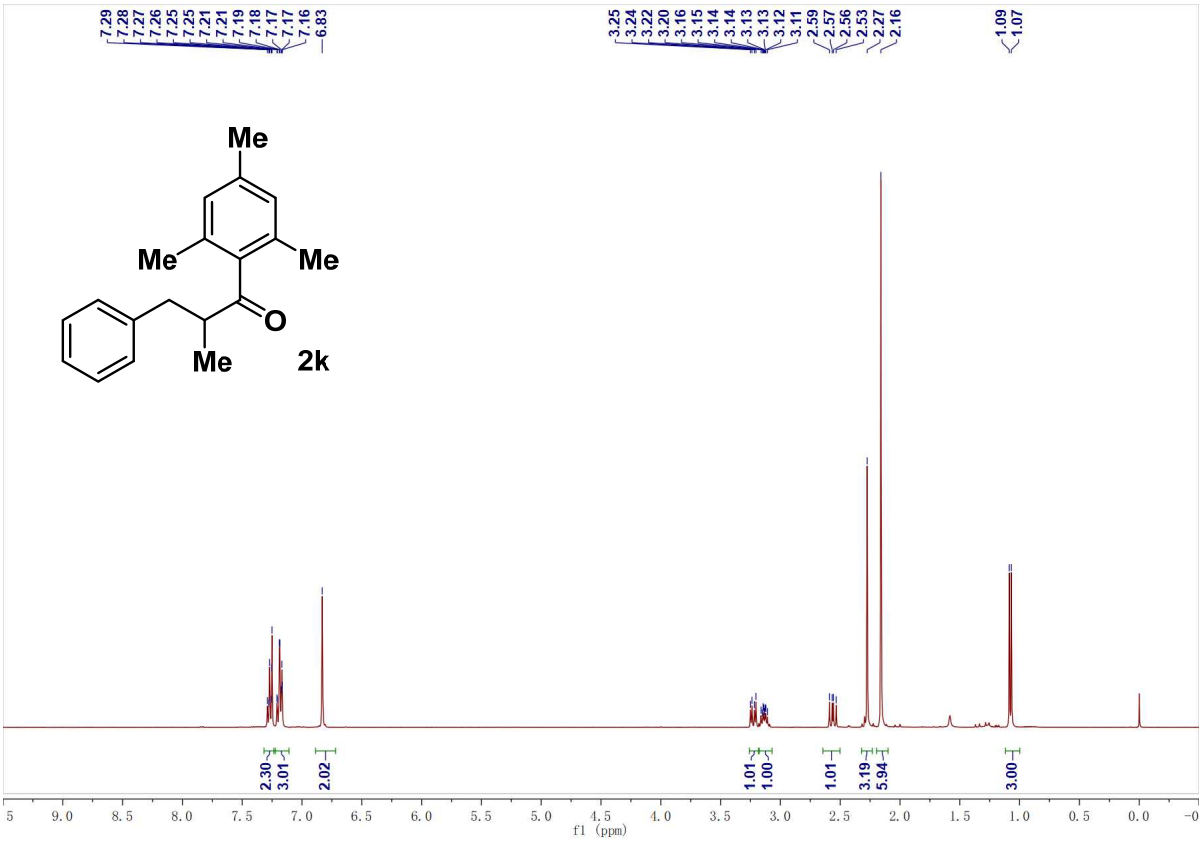
Compound **2j,** ^{1}H NMR



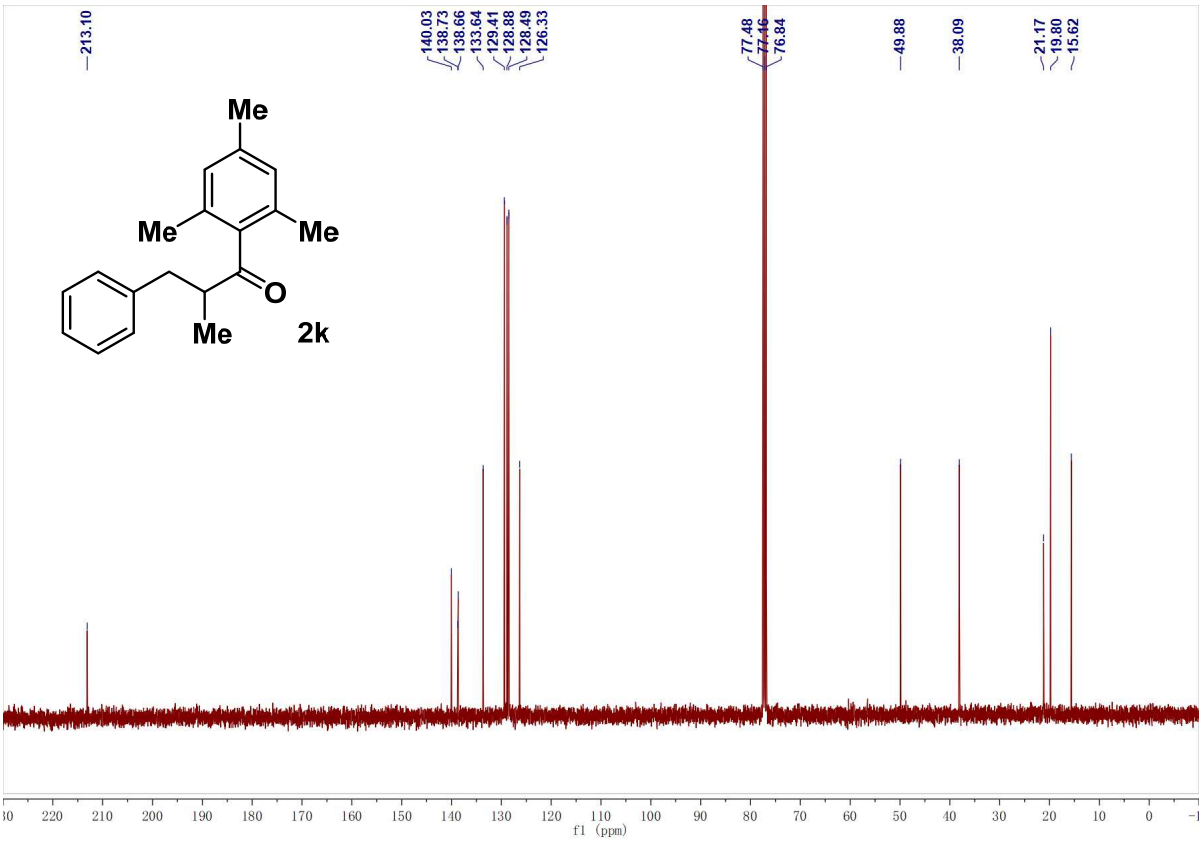
Compound **2j,** ^{13}C NMR



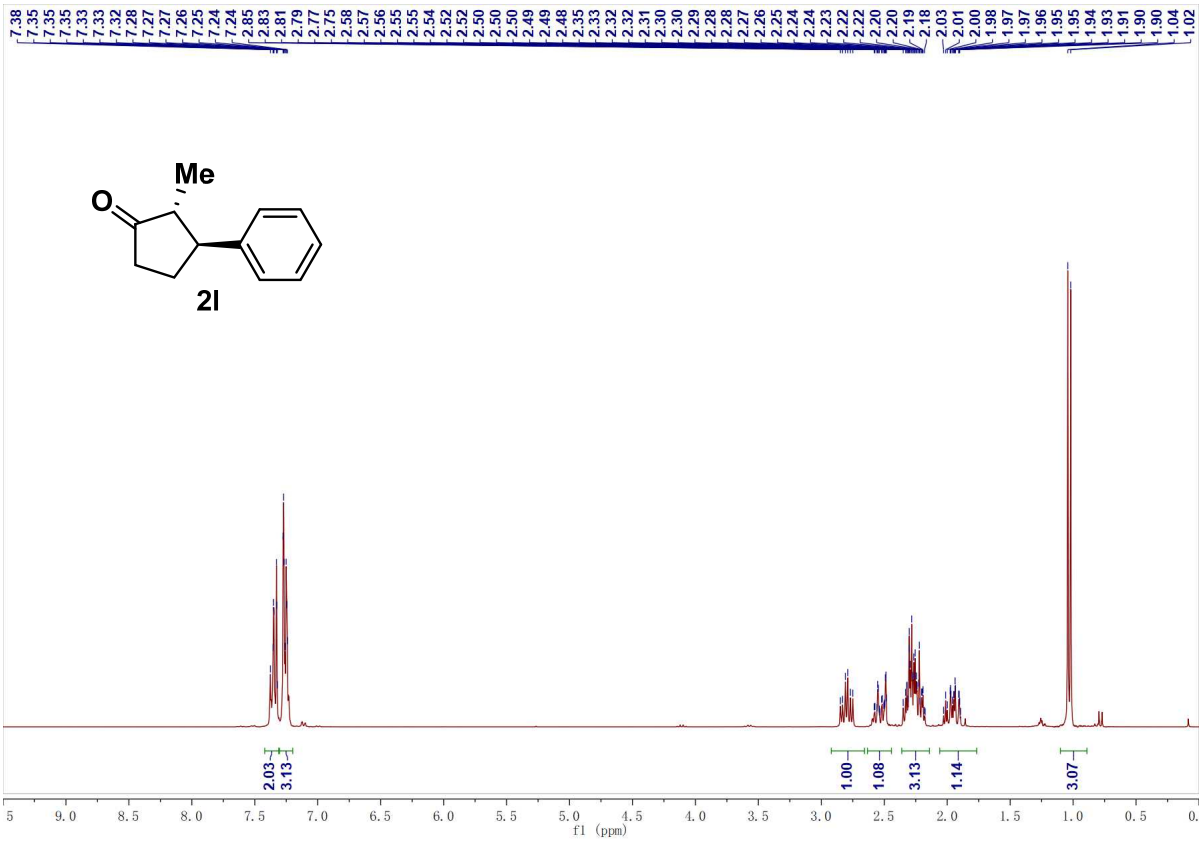
Compound **2k,** ^{1}H NMR



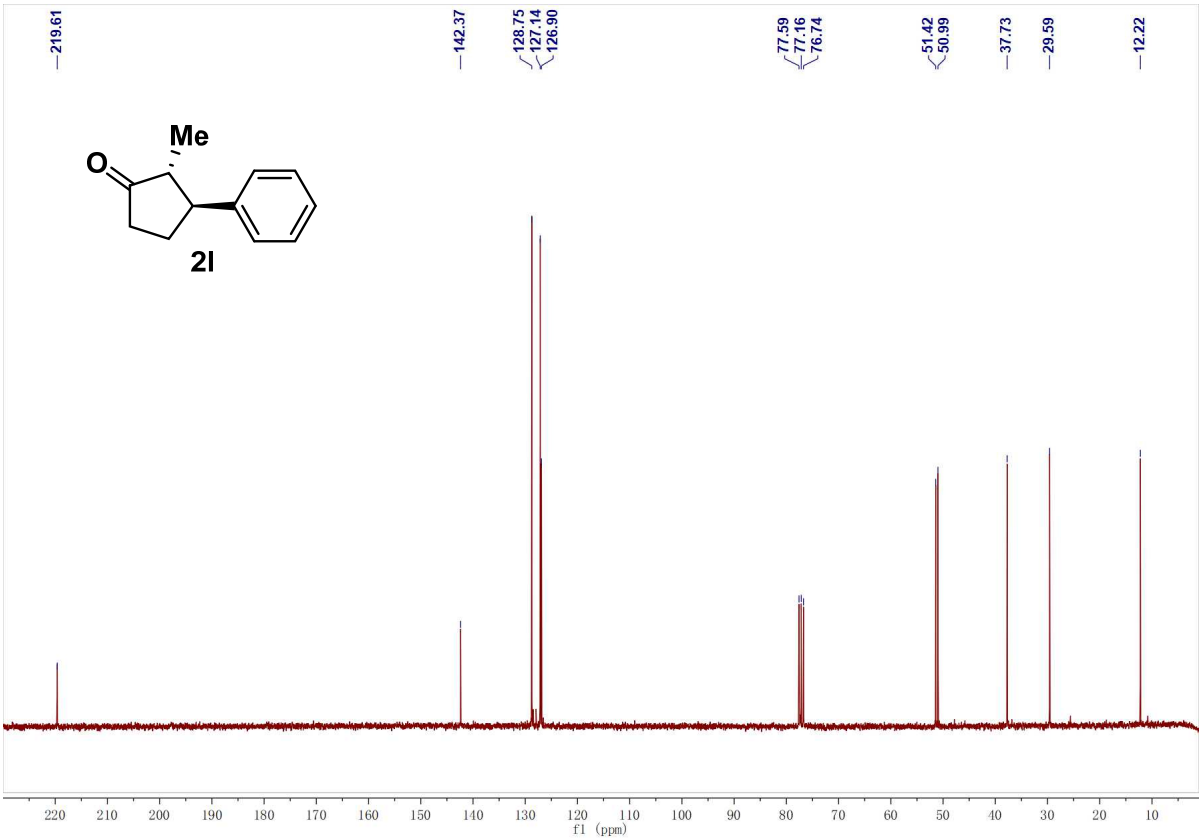
Compound **2k,** ^{13}C NMR



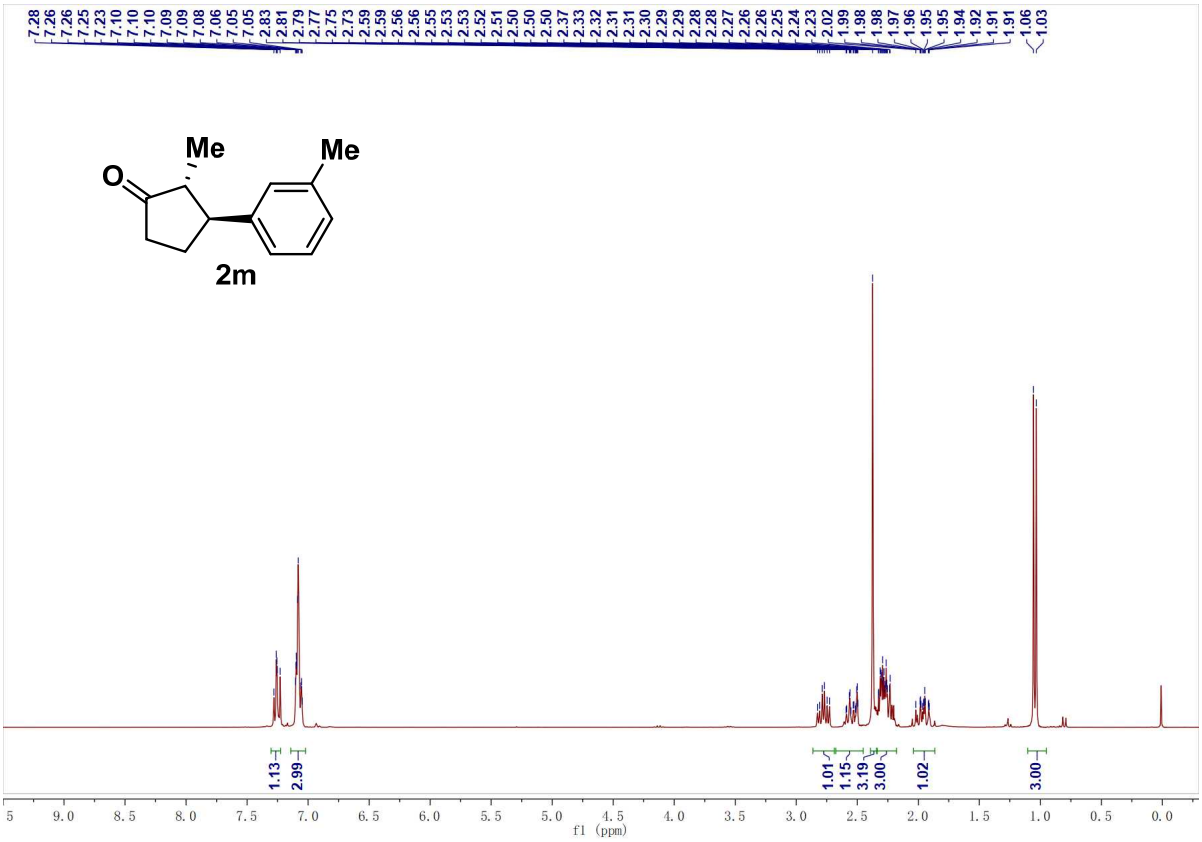
Compound **2l,** ^{1}H NMR



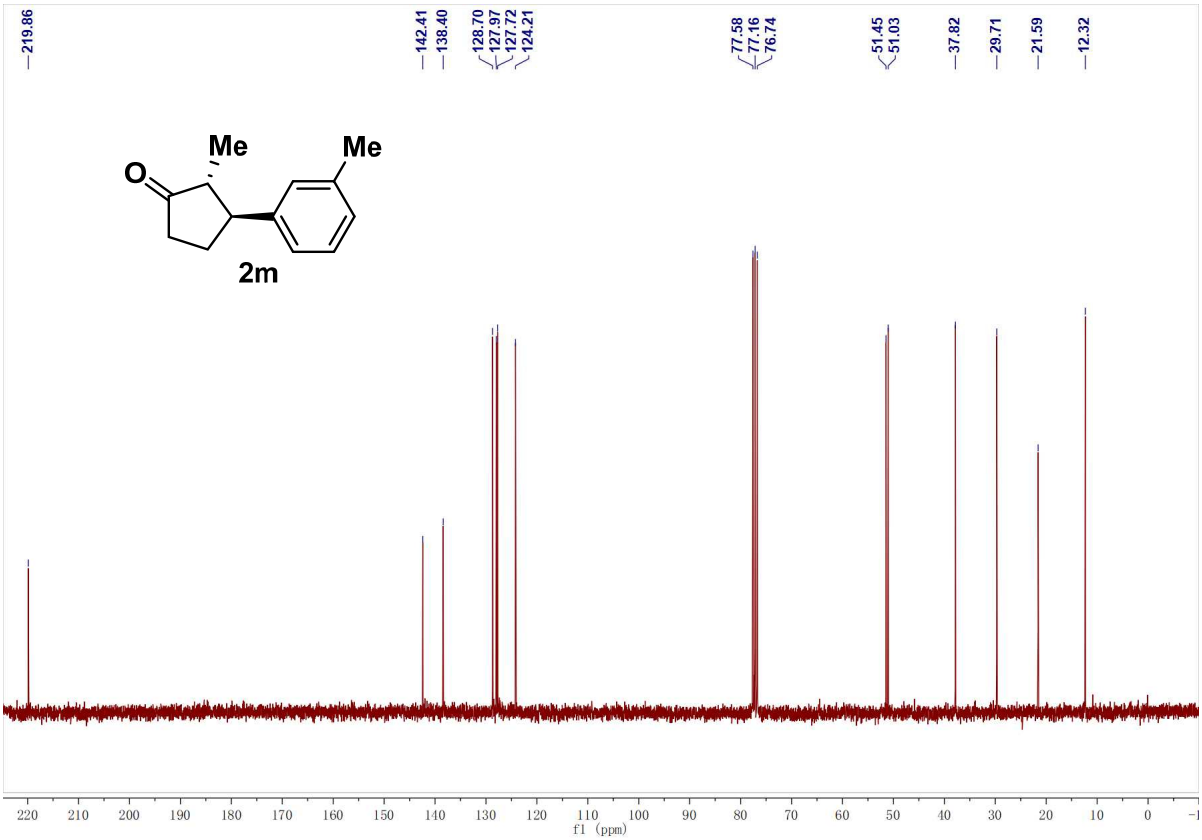
Compound **2l,** ^{13}C NMR



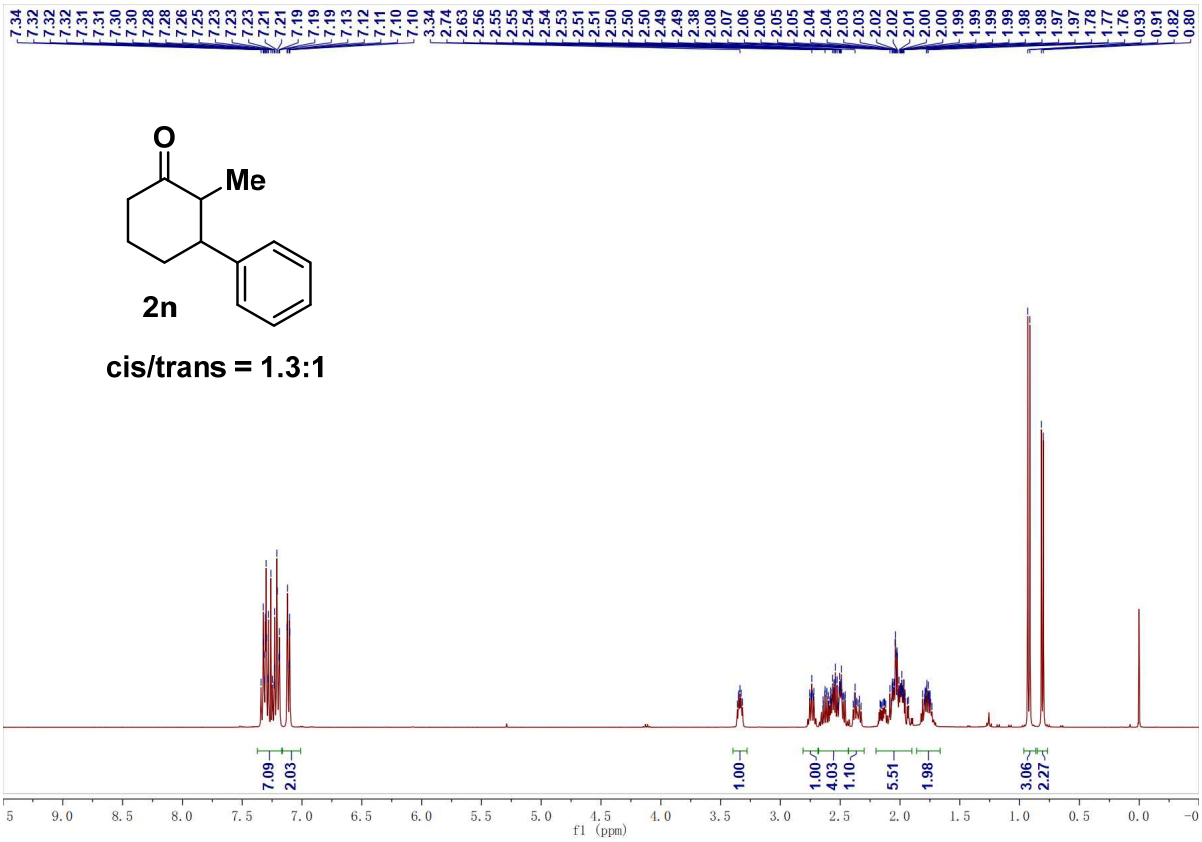
Compound **2m,** ^{1}H NMR



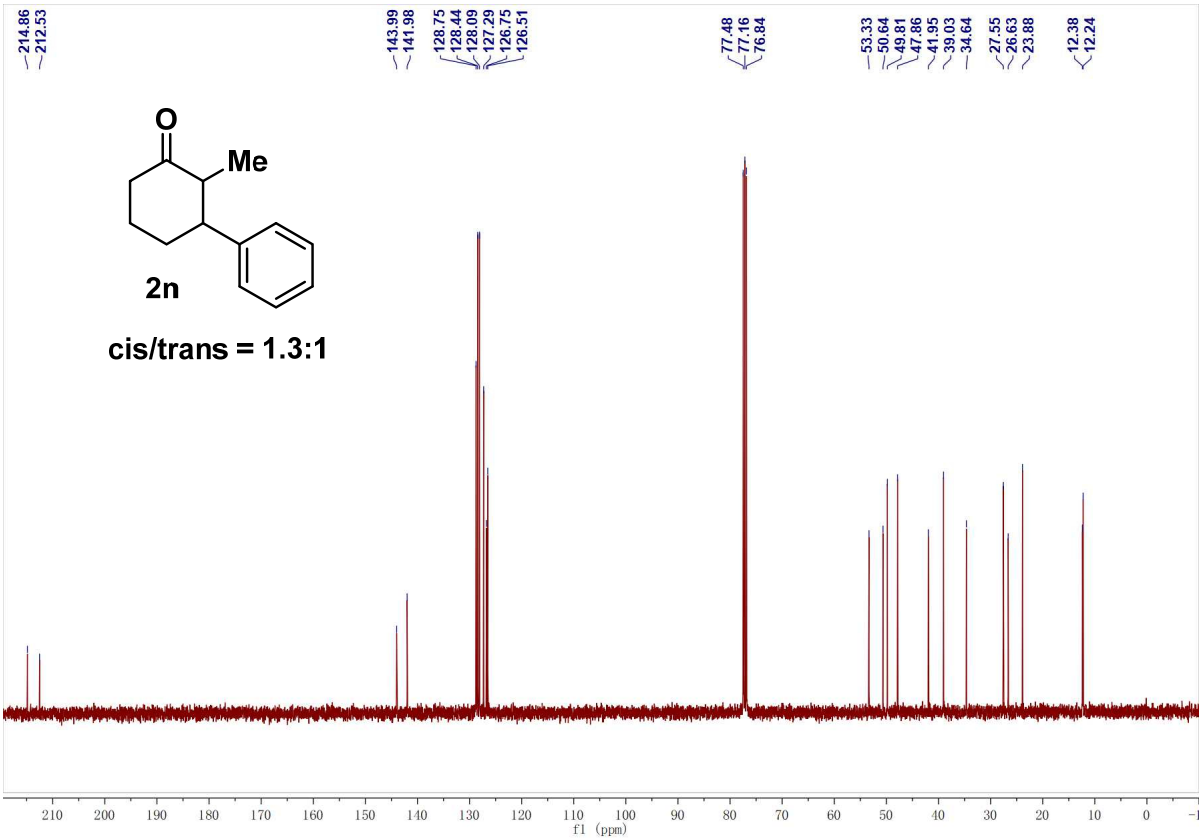
Compound **2m,** ^{13}C NMR



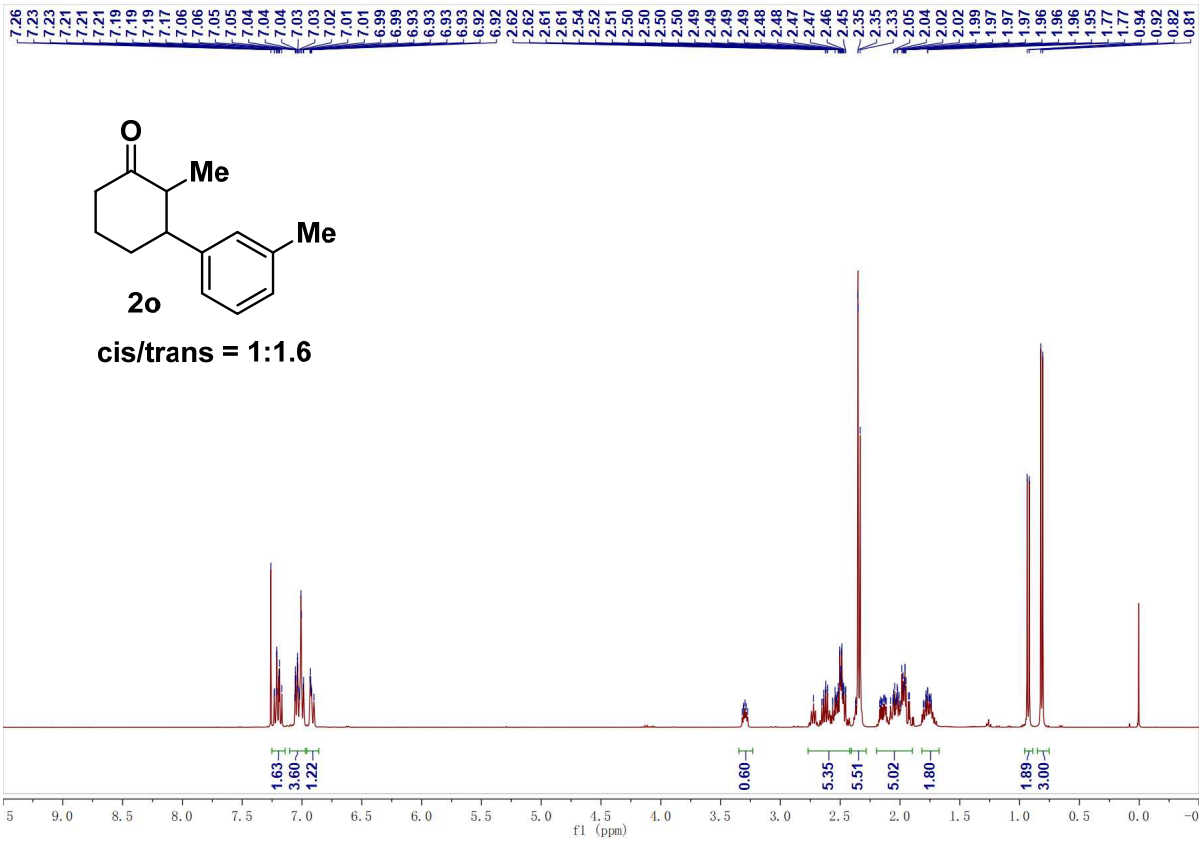
Compound **2n,** ^{1}H NMR



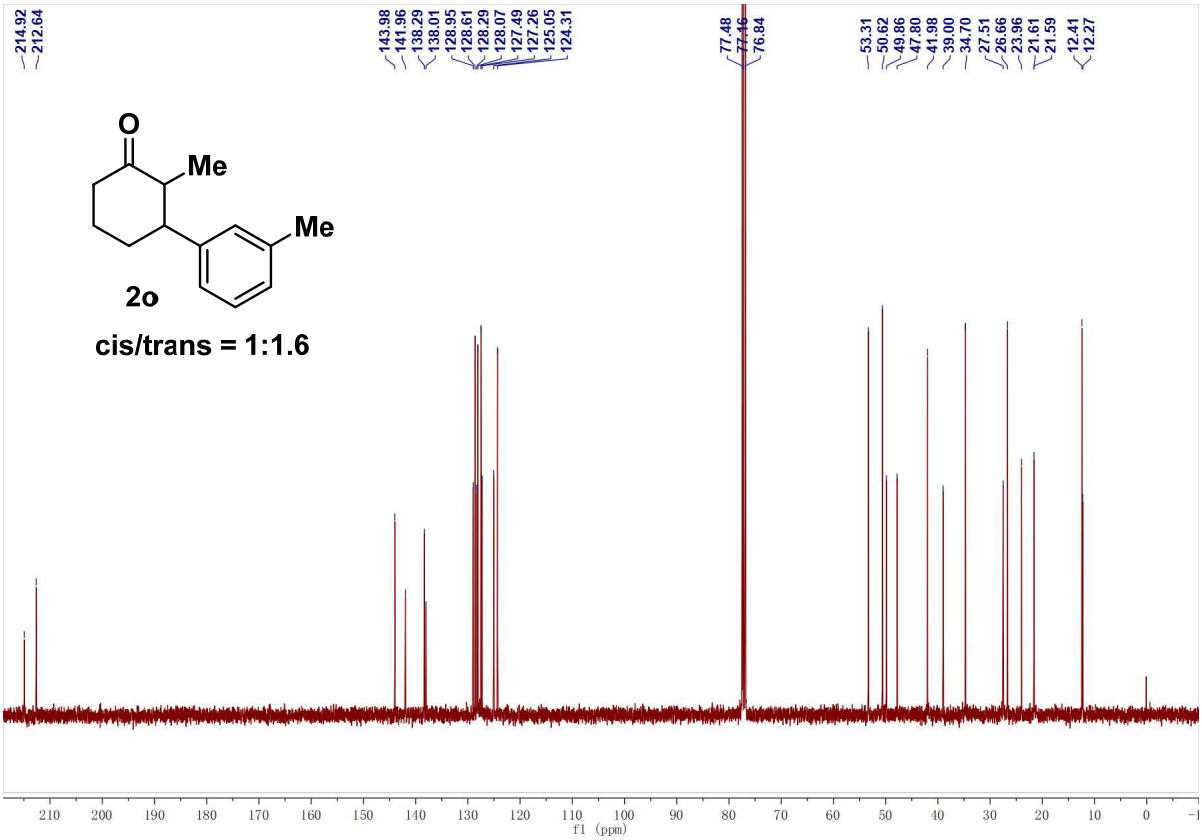
Compound **2n,** ^{13}C NMR



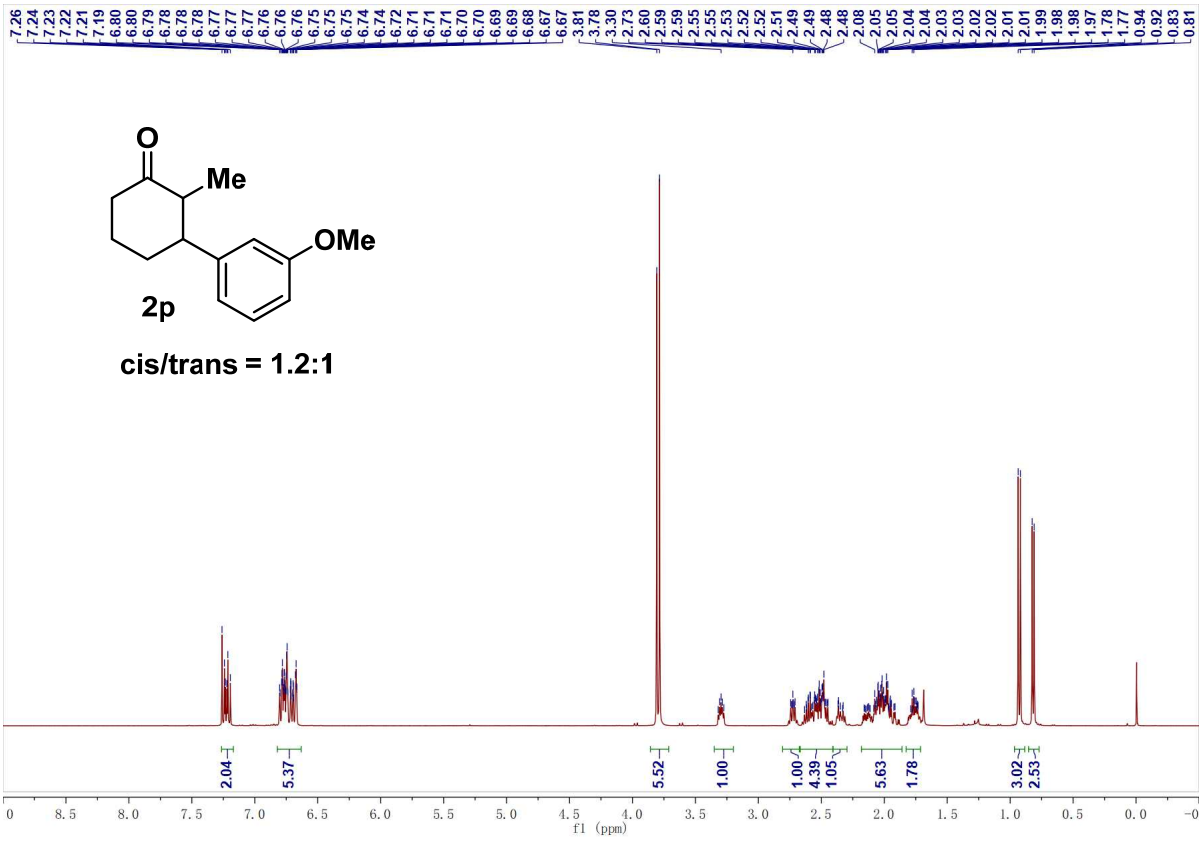
Compound **2o,** ^{1}H NMR



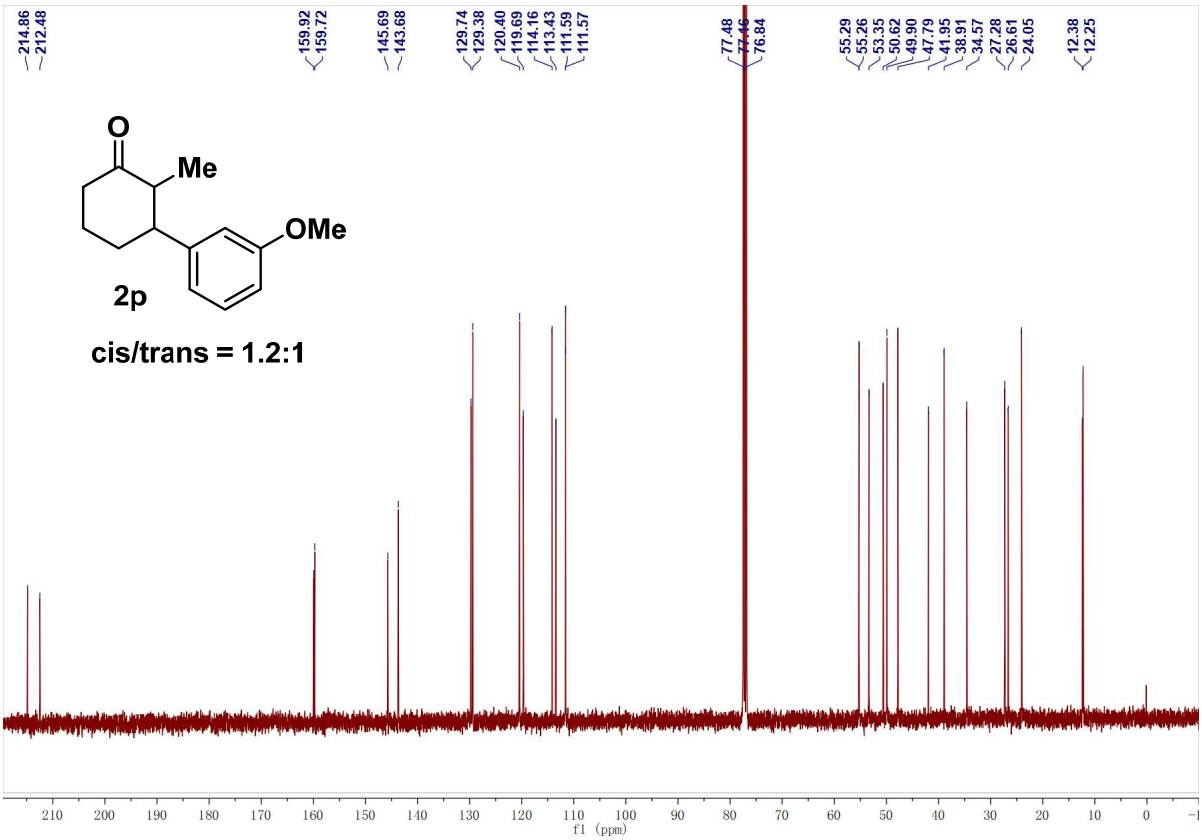
Compound **2o,** ^{13}C NMR



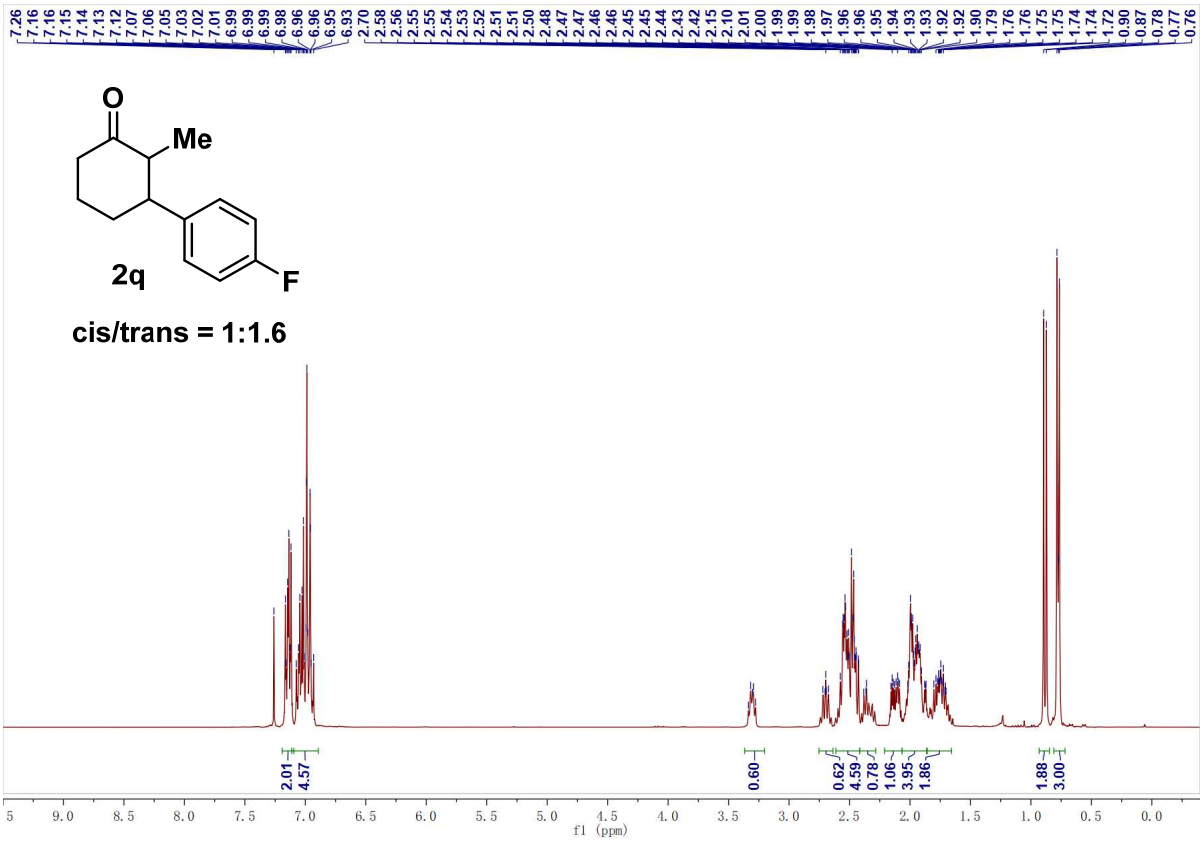
Compound **2p,** ^{1}H NMR



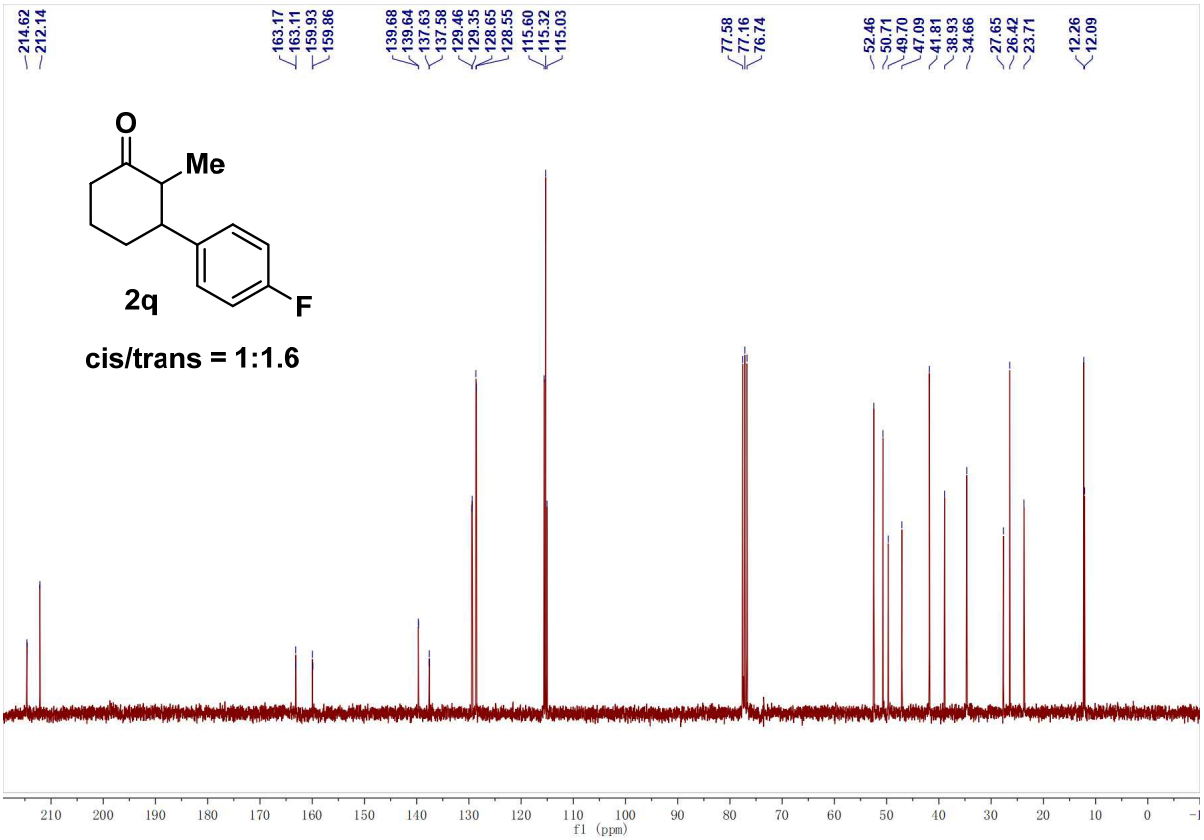
Compound **2p,** ^{13}C NMR



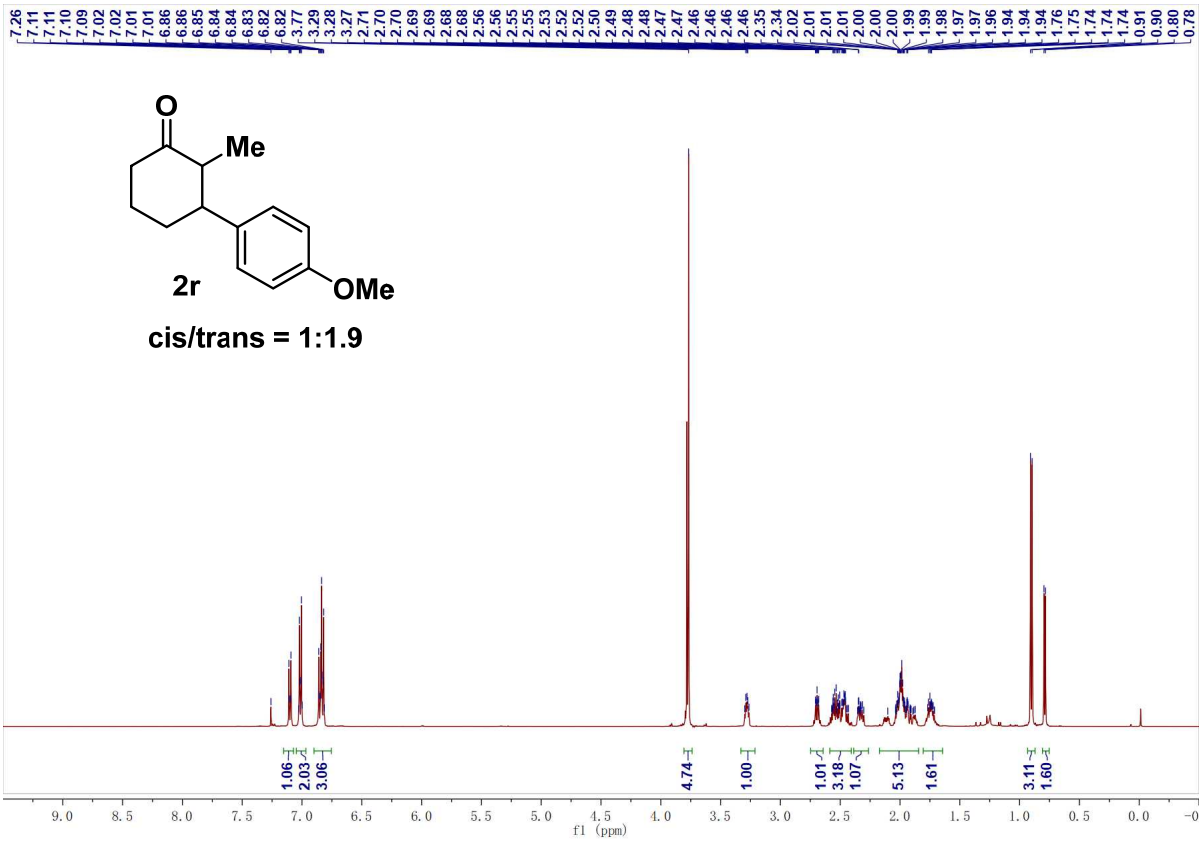
Compound **2q,** ^{1}H NMR



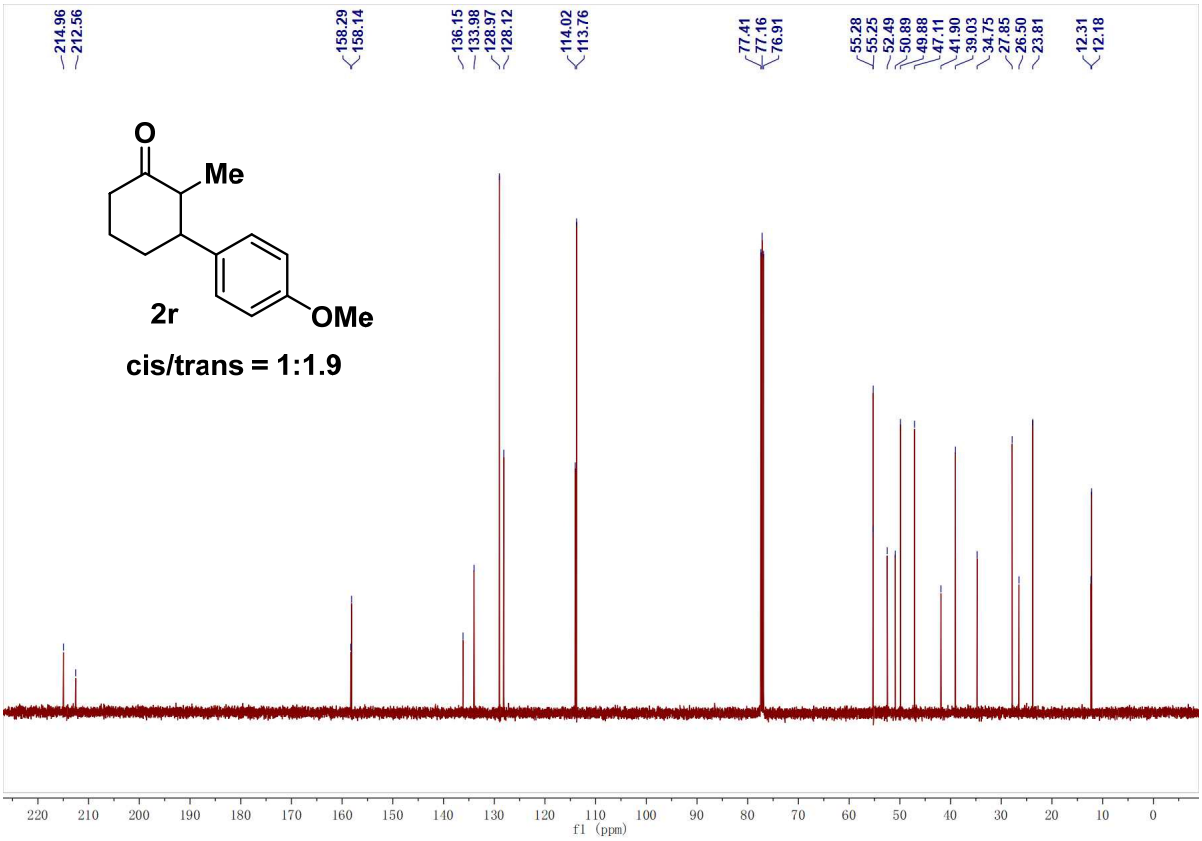
Compound **2q,** ^{13}C NMR



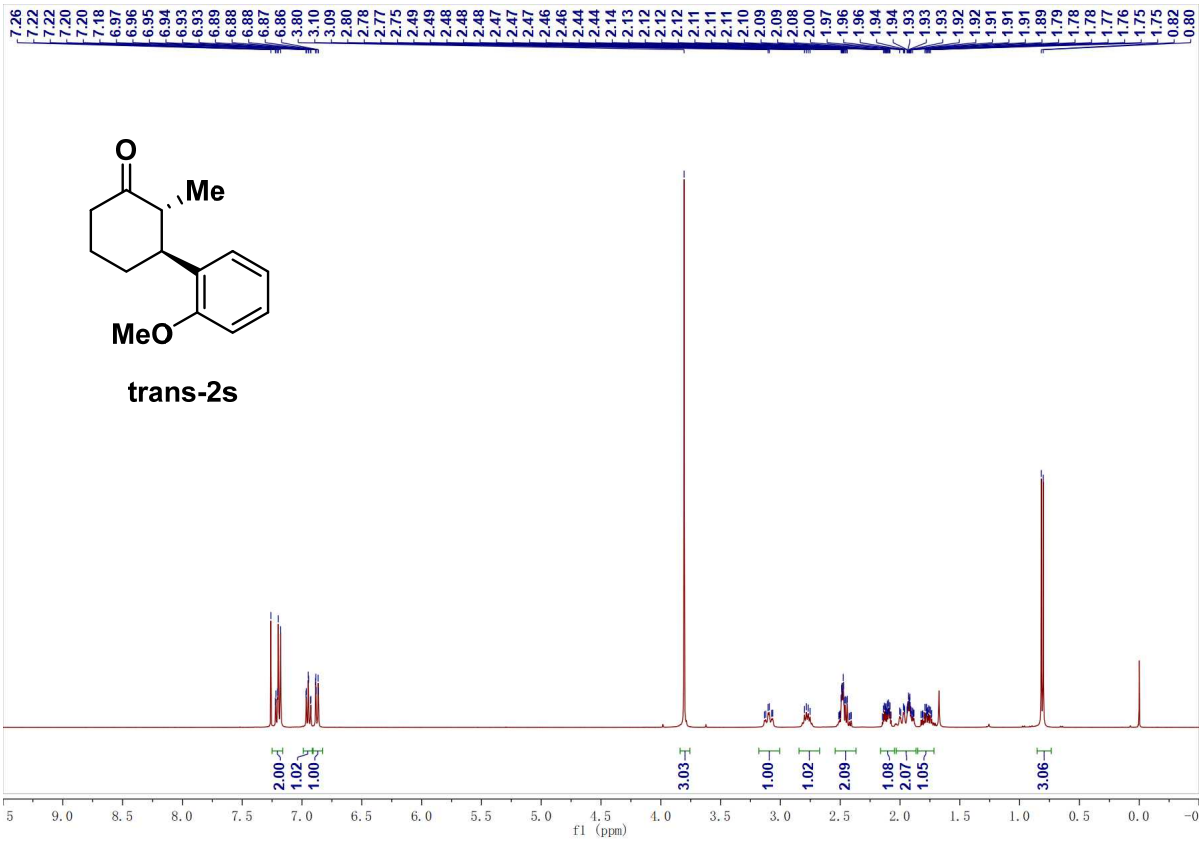
Compound **2r,** ^{1}H NMR



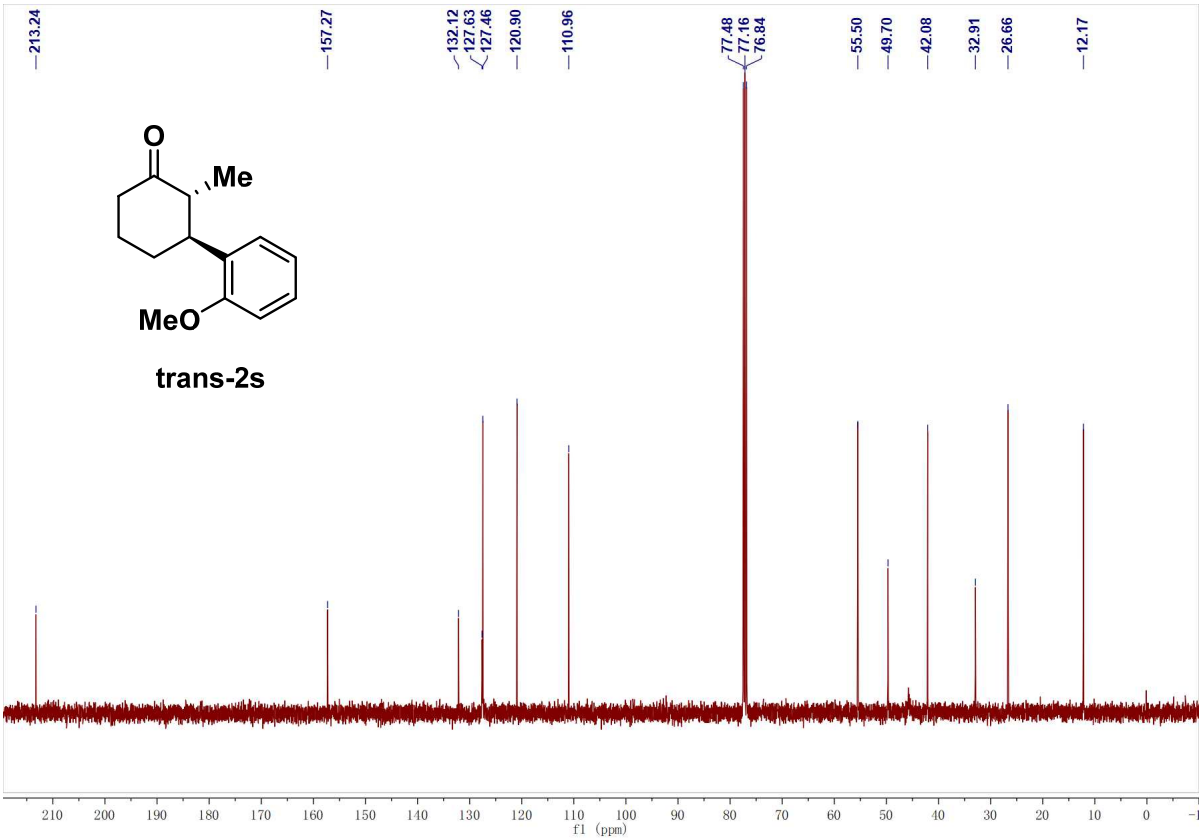
Compound **2r,** ^{13}C NMR



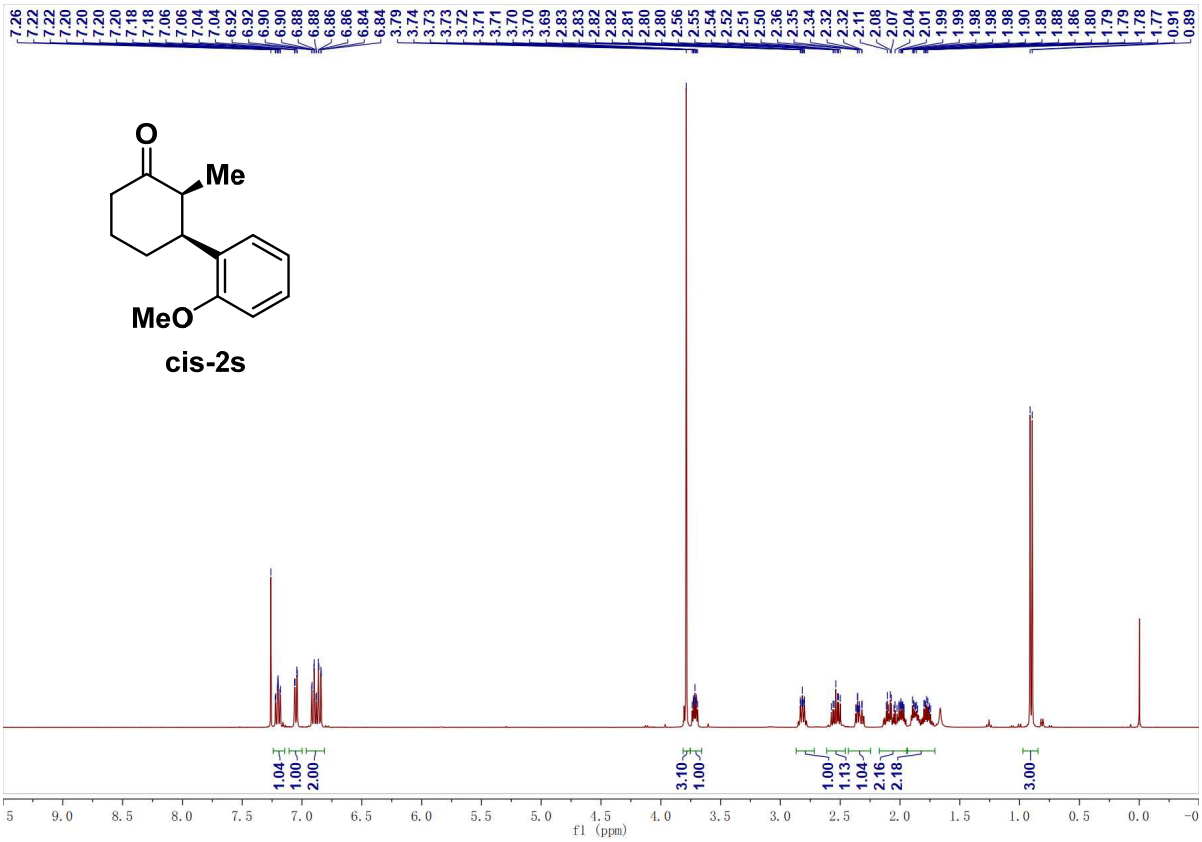
Compound **trans-2s,** ^{1}H NMR



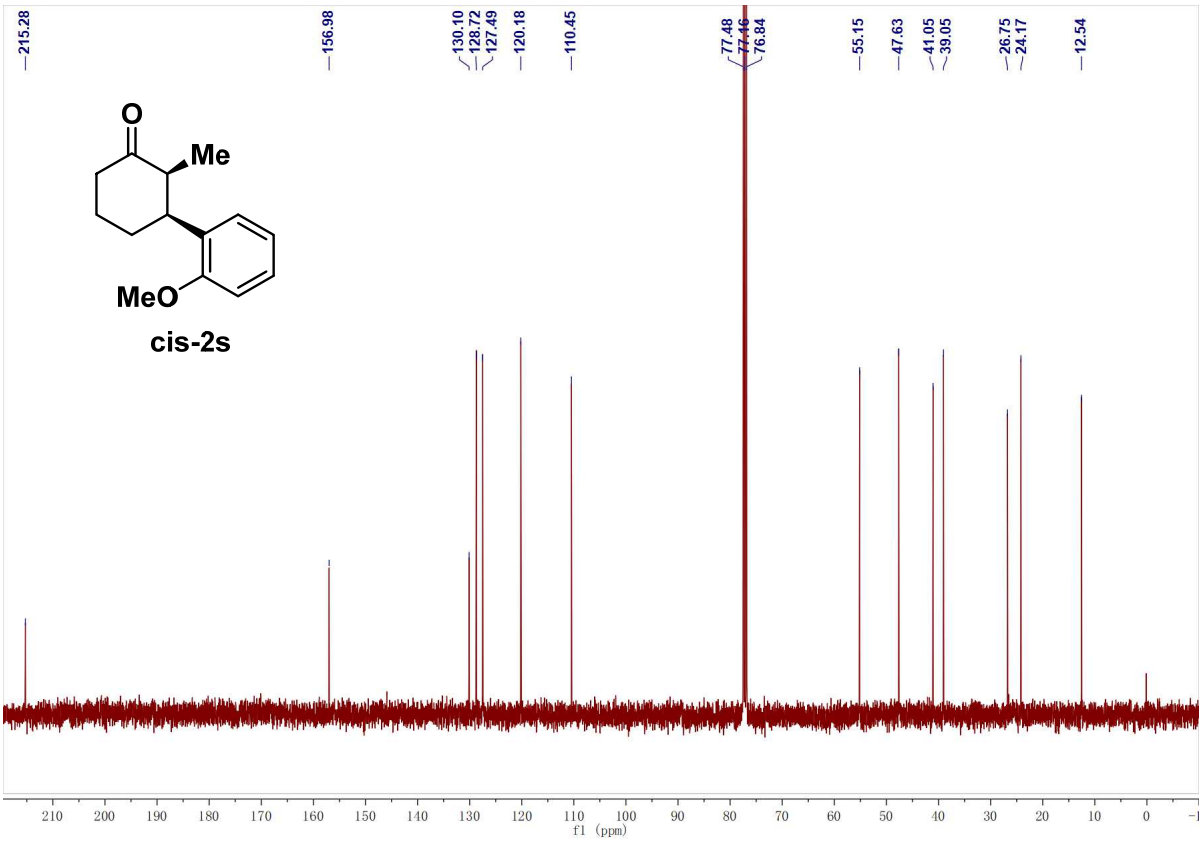
Compound **trans-2s,** ^{13}C NMR



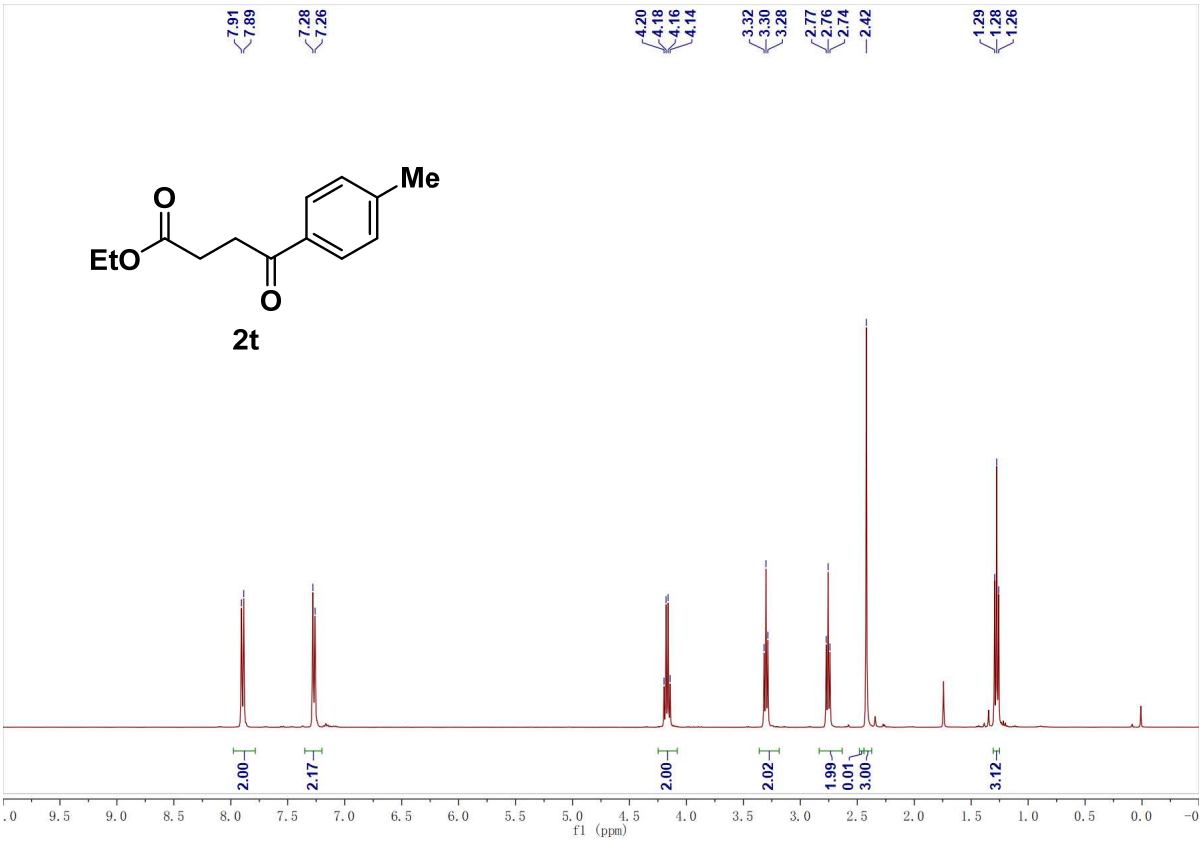
Compound **cis-2s,** ^{1}H NMR



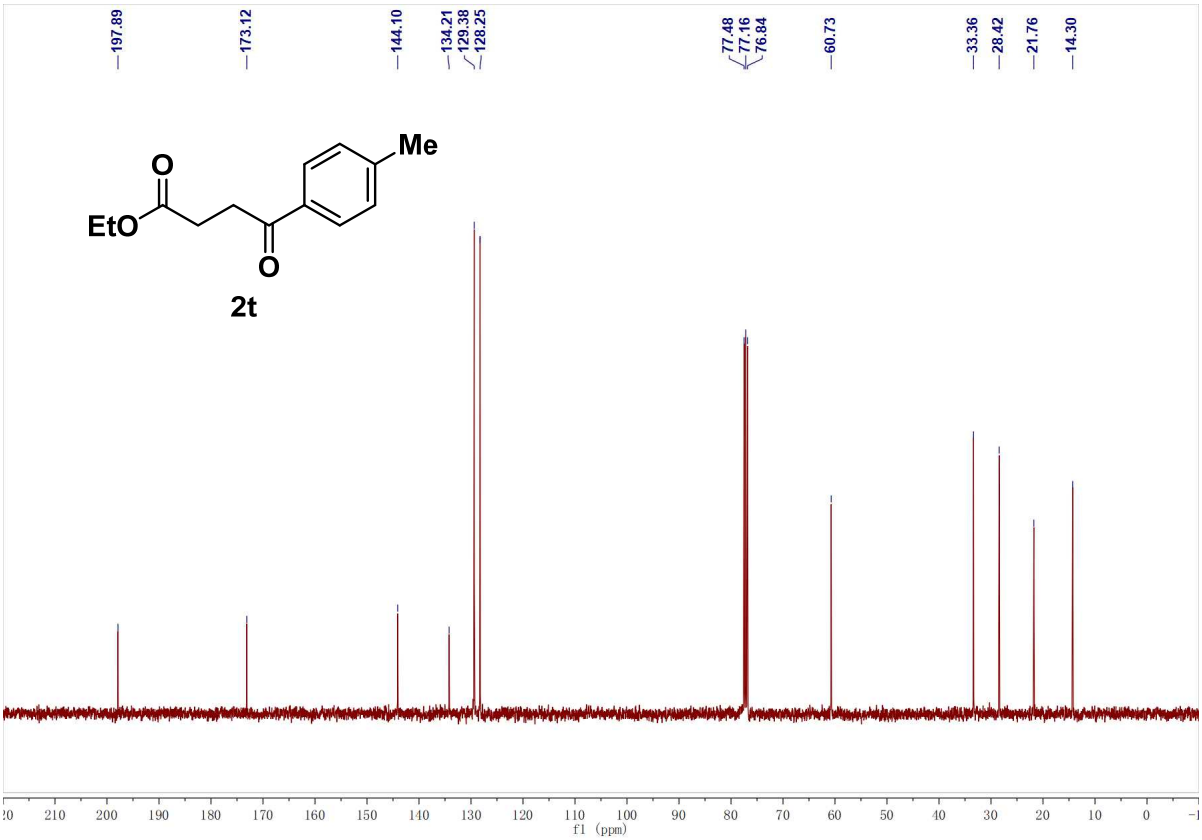
Compound **cis-2s,** ^{13}C NMR



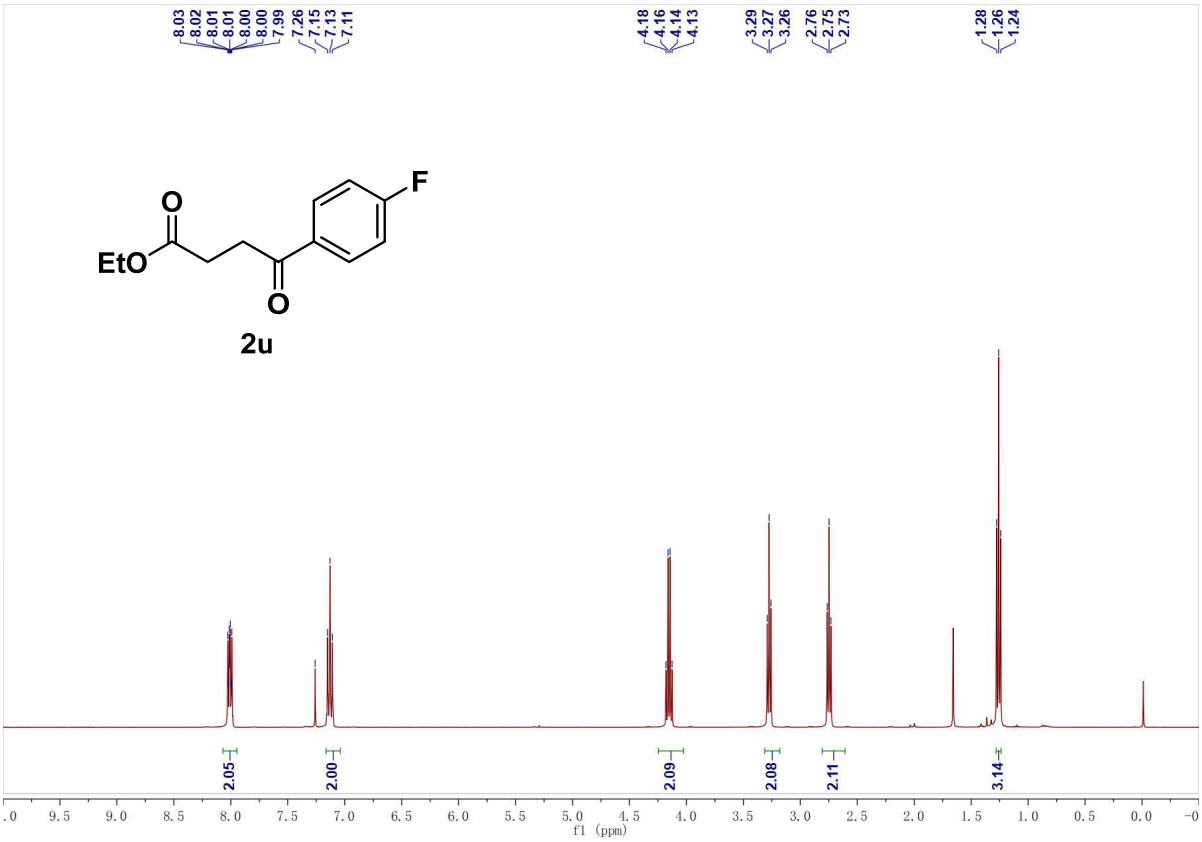
Compound **2t,** ^{1}H NMR



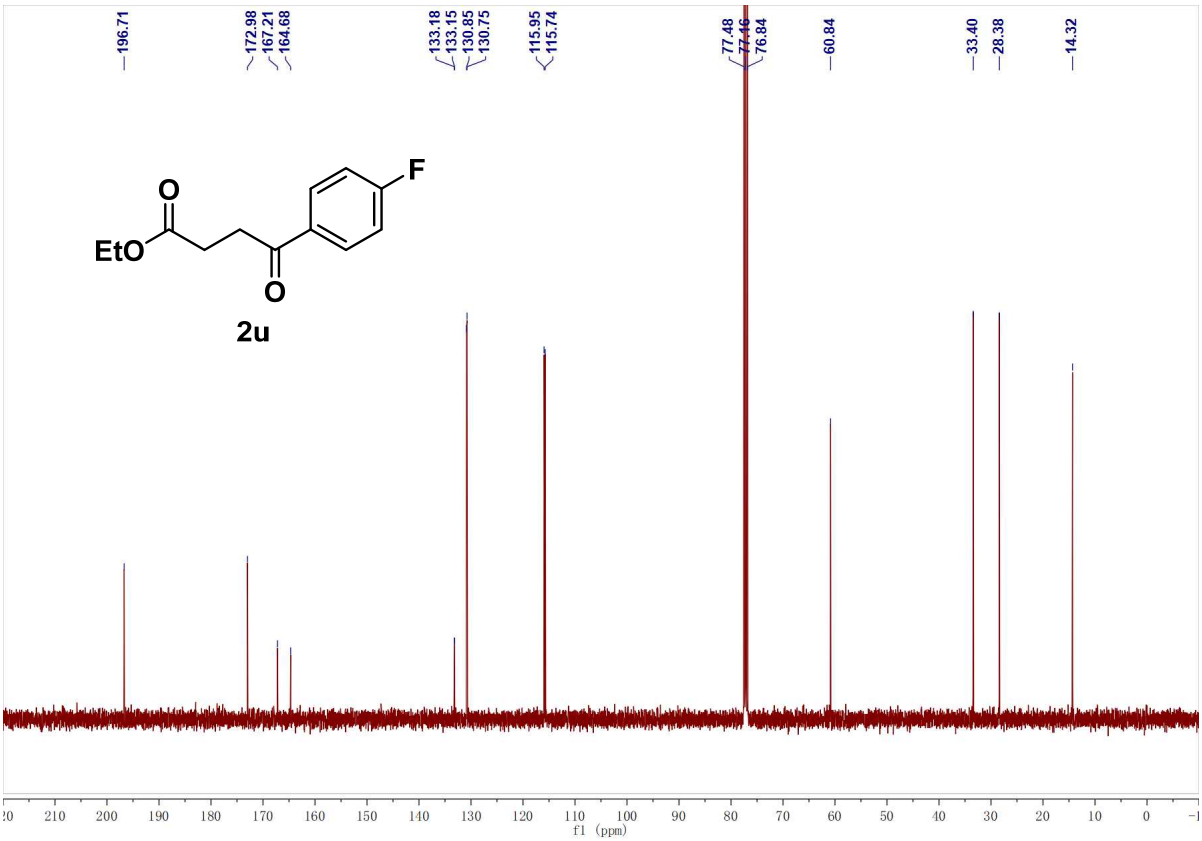
Compound **2t,** ^{13}C NMR



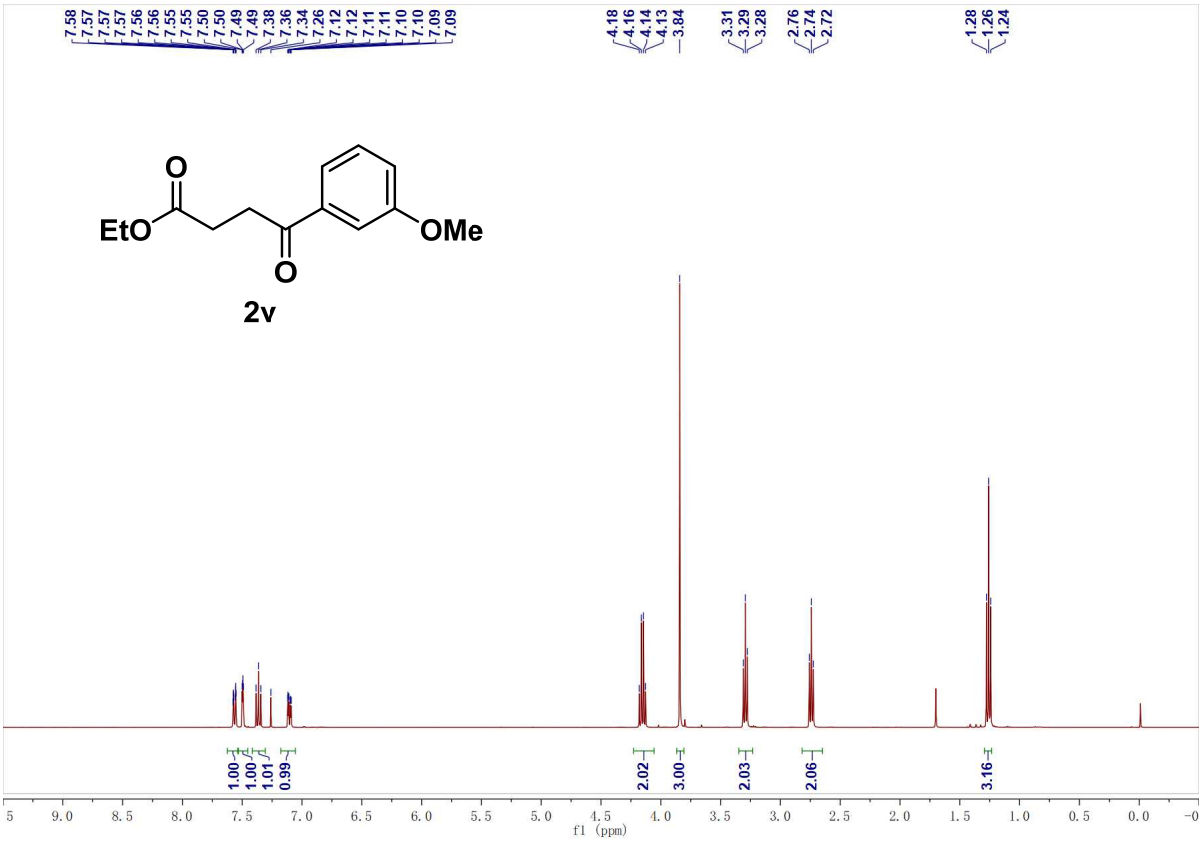
Compound **2u,** ^{1}H NMR



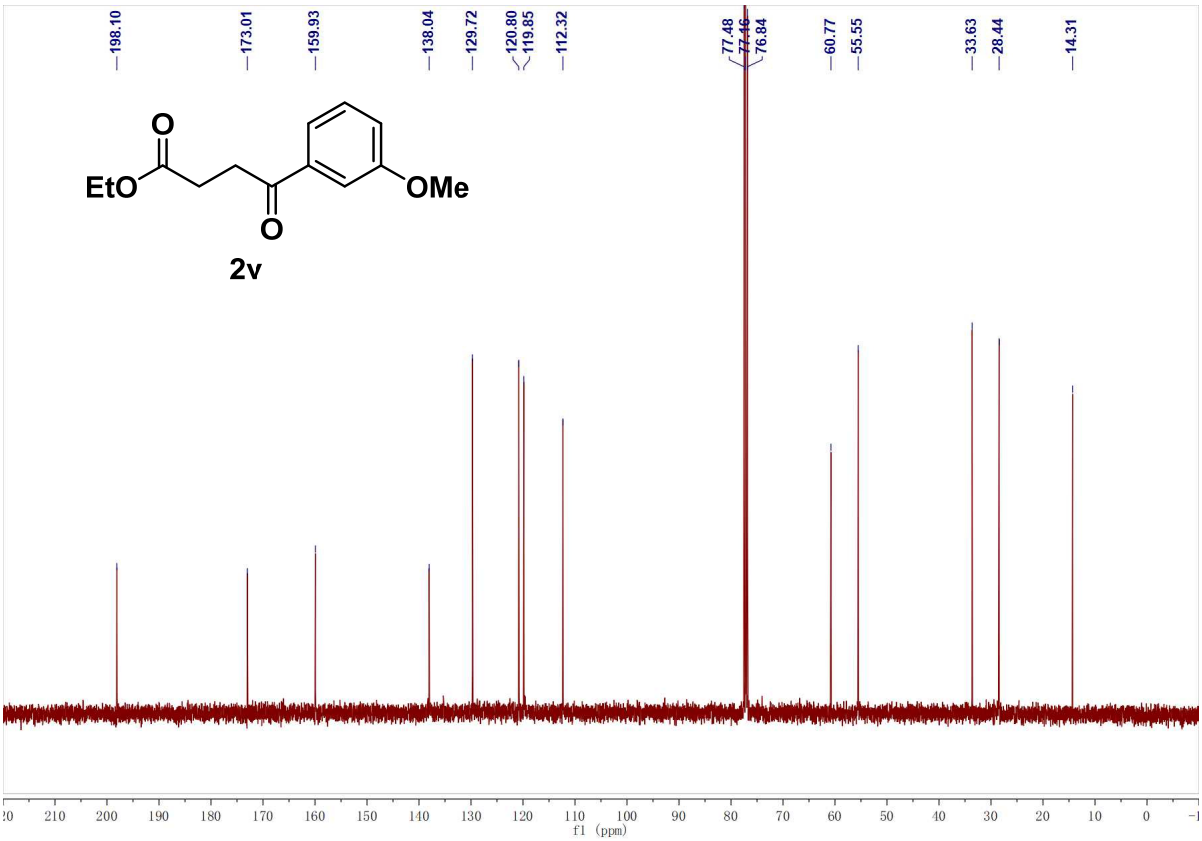
Compound **2u,** ^{13}C NMR



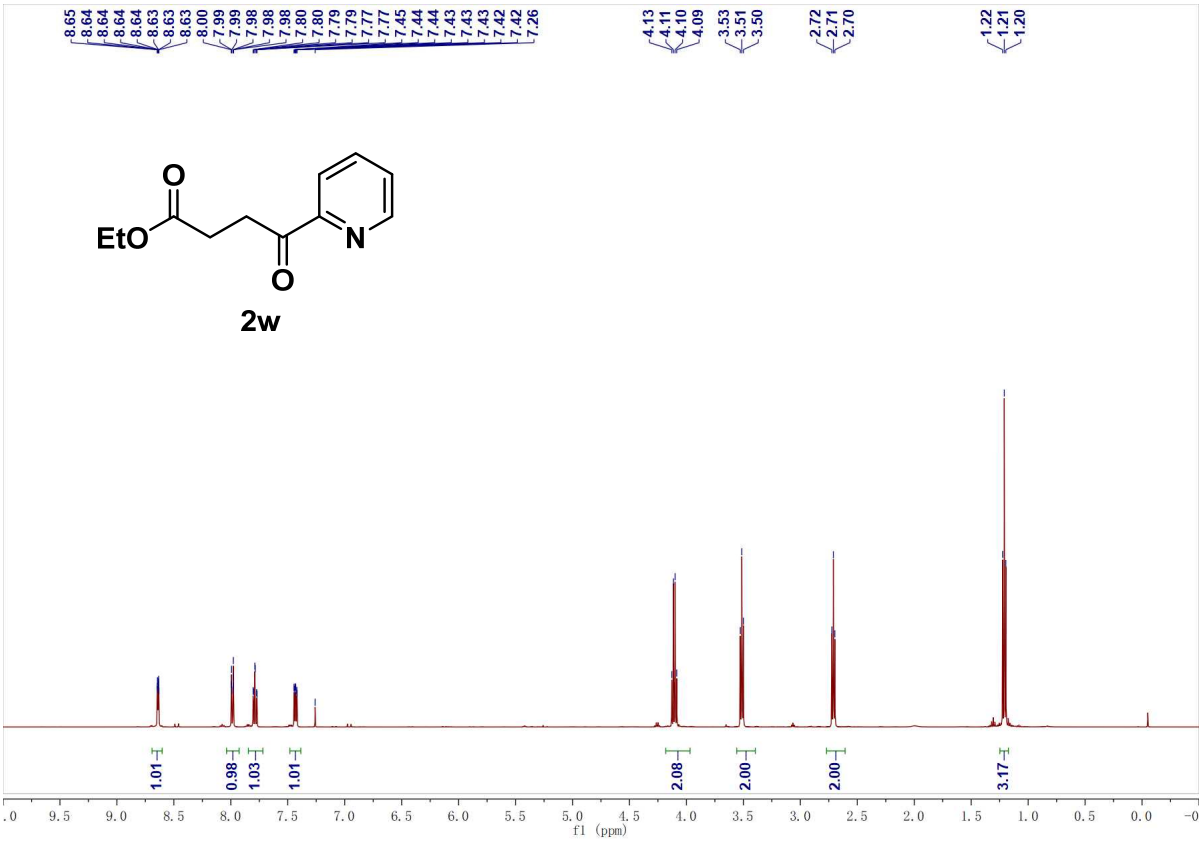
Compound **2v,** ^{1}H NMR



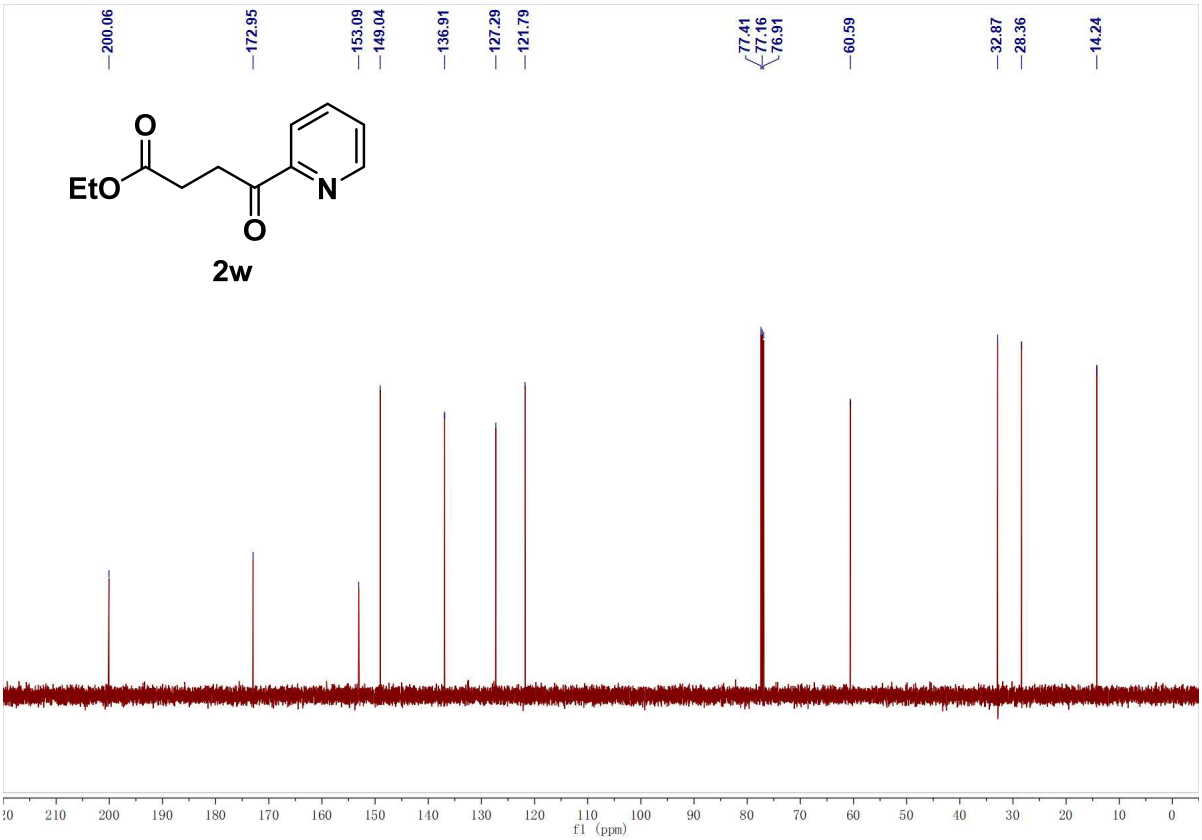
Compound **2v,** ^{13}C NMR



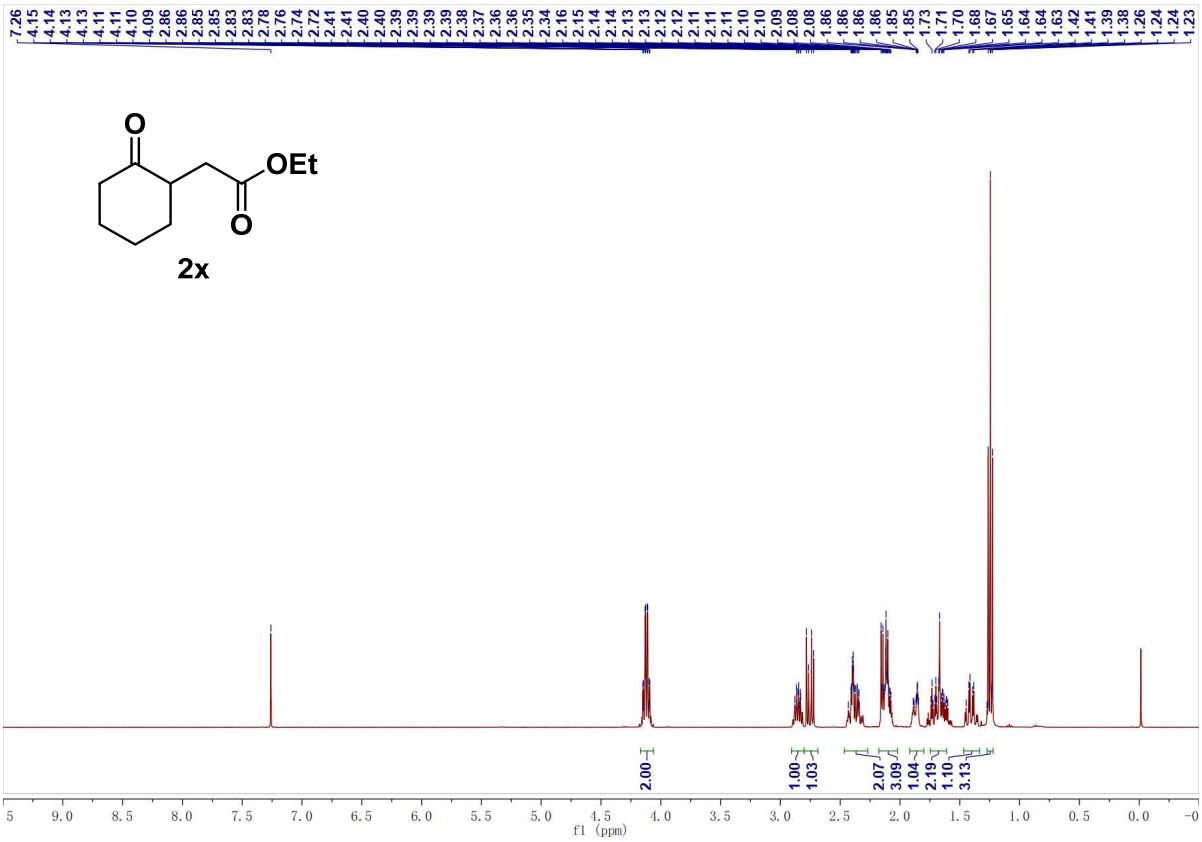
Compound **2w,** ^{1}H NMR



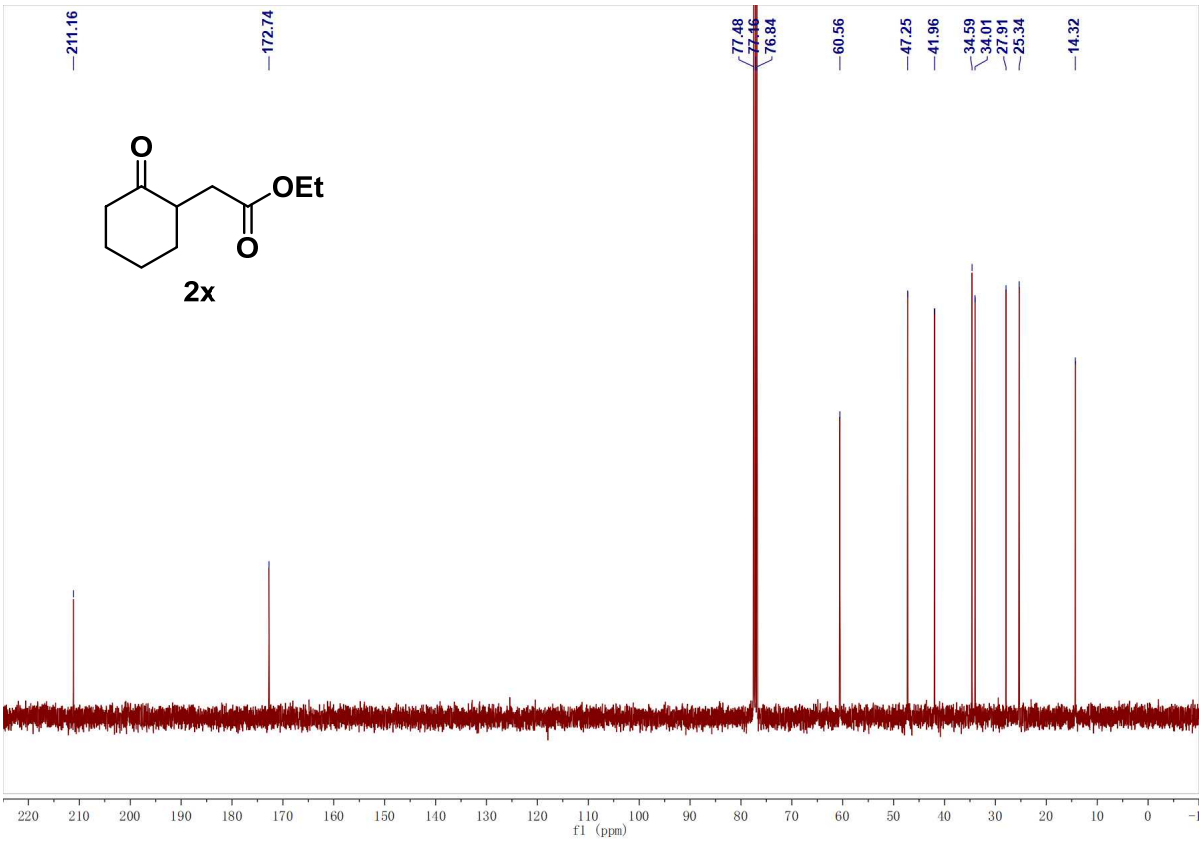
Compound **2w,** ^{13}C NMR



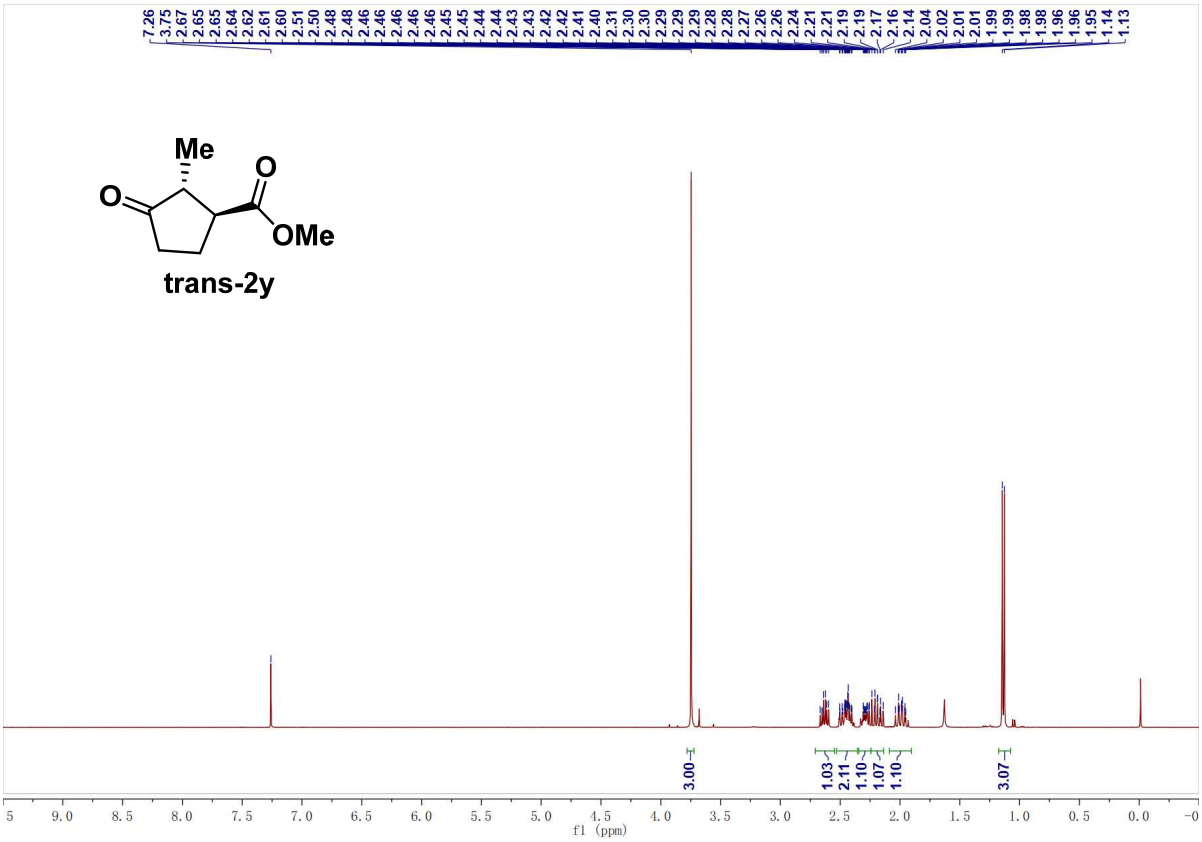
Compound **2x,** ^{1}H NMR



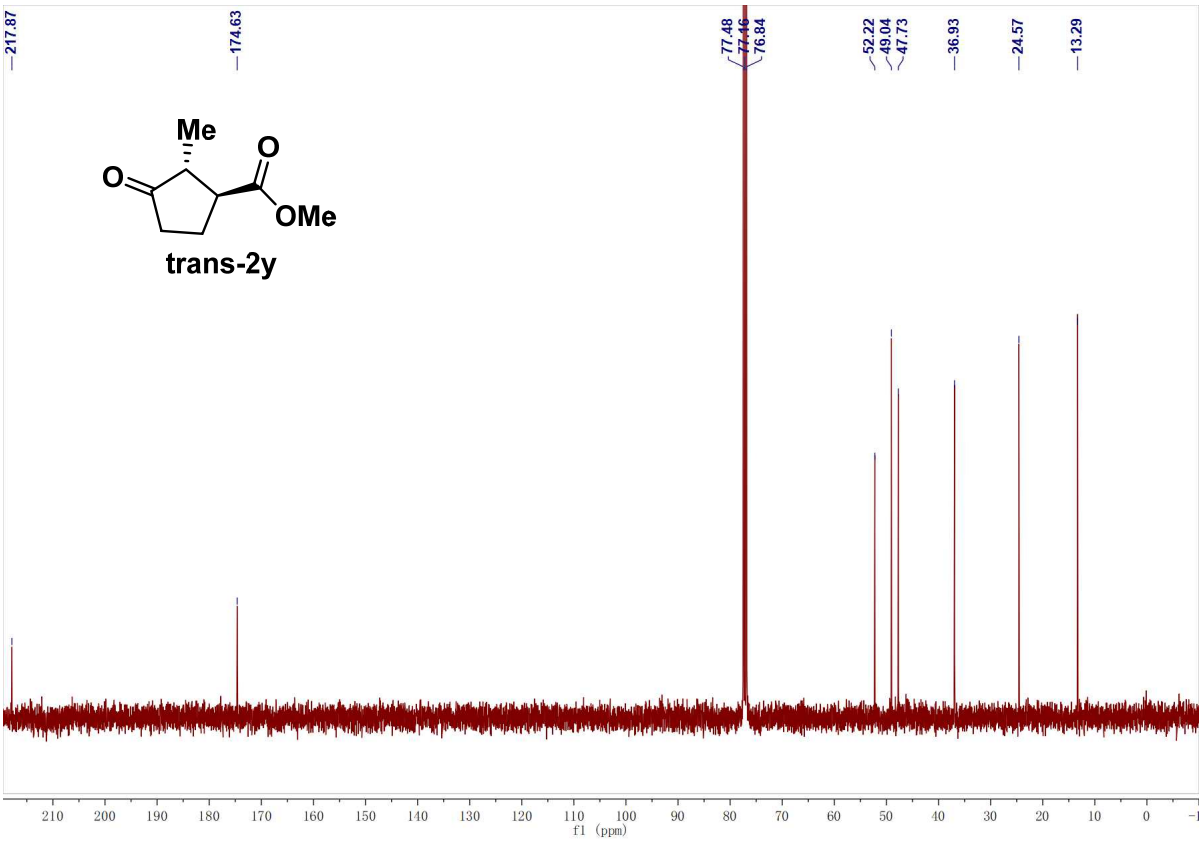
Compound **2x,** ^{13}C NMR



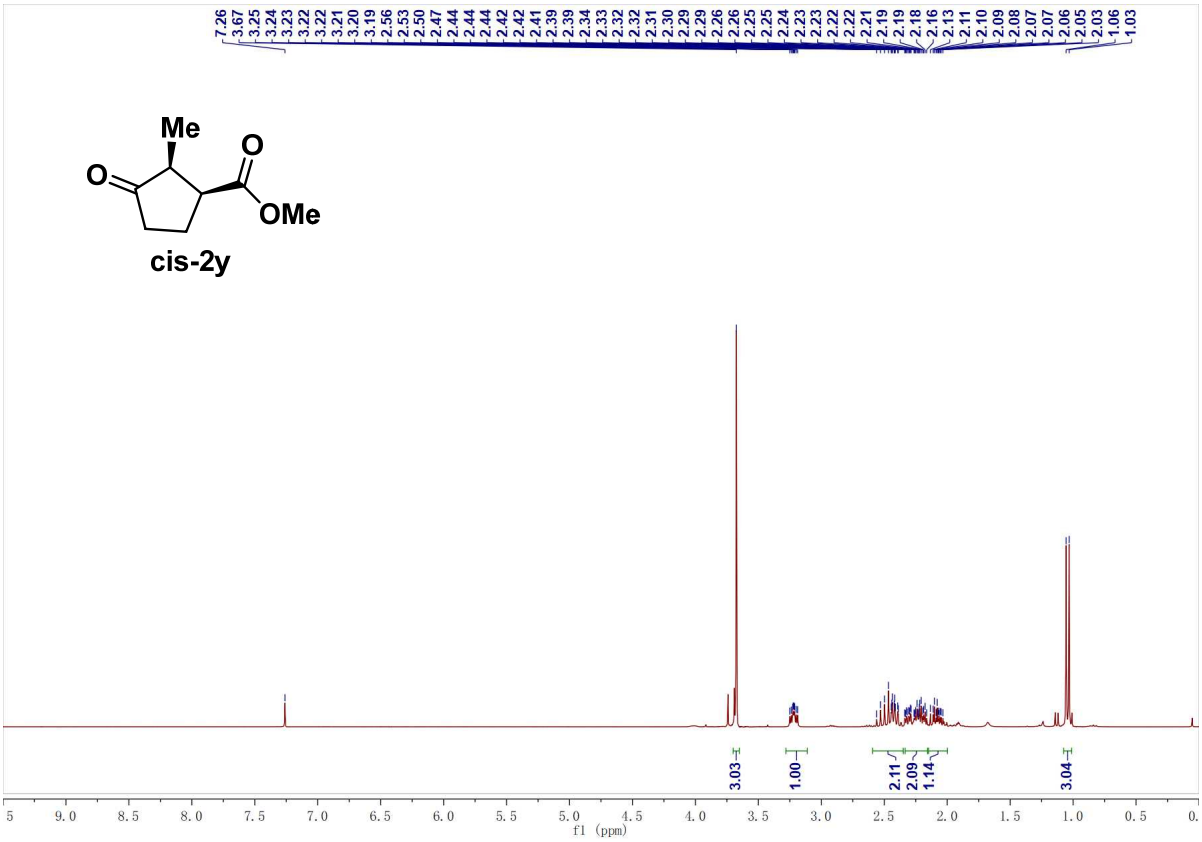
Compound **trans-2y,** ^{1}H NMR



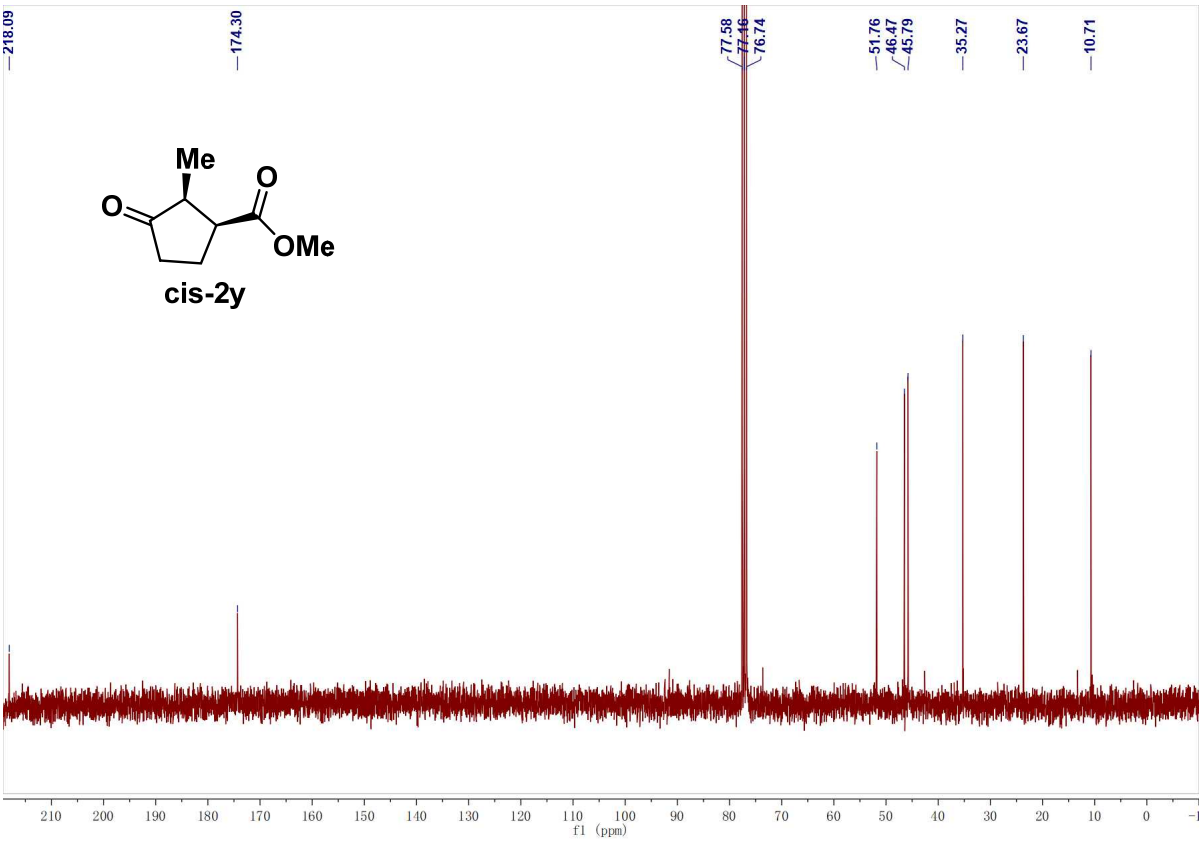
Compound **trans-2y,** ^{13}C NMR



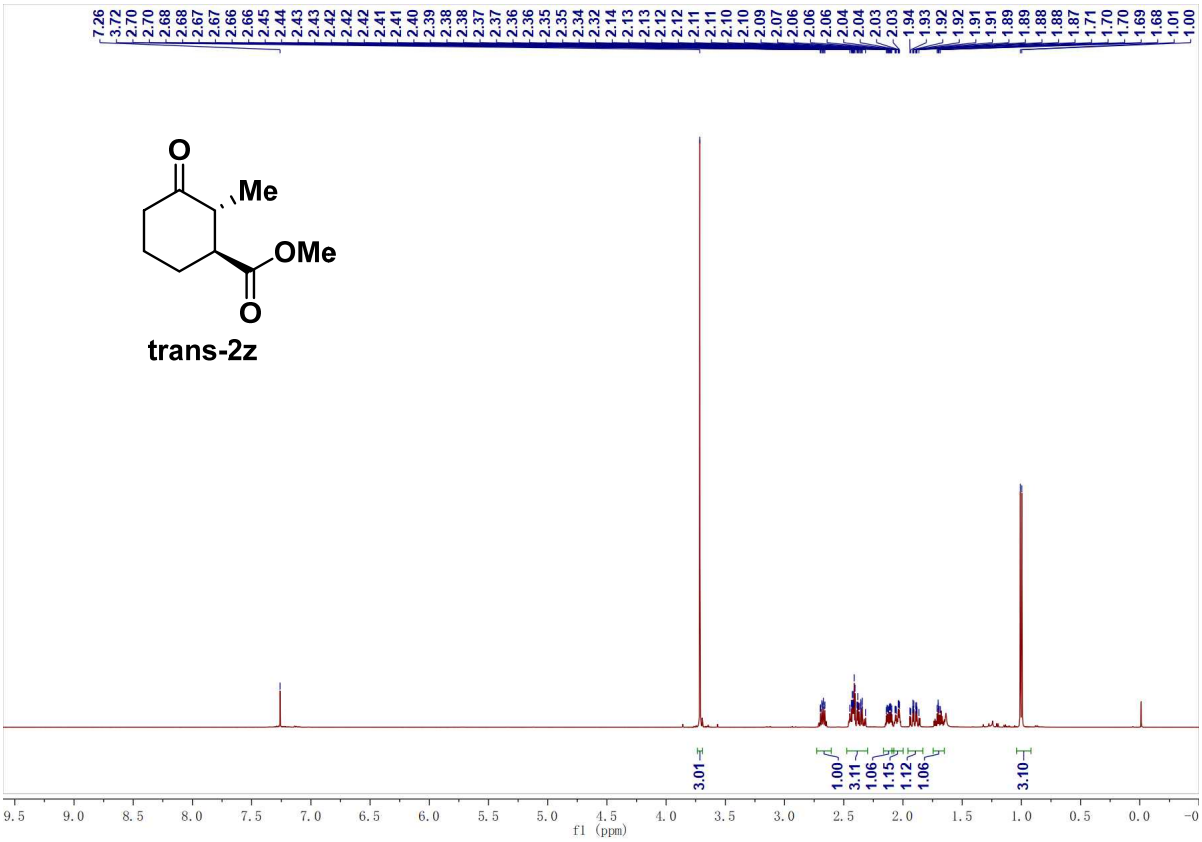
Compound **cis-2y,** ^{1}H NMR



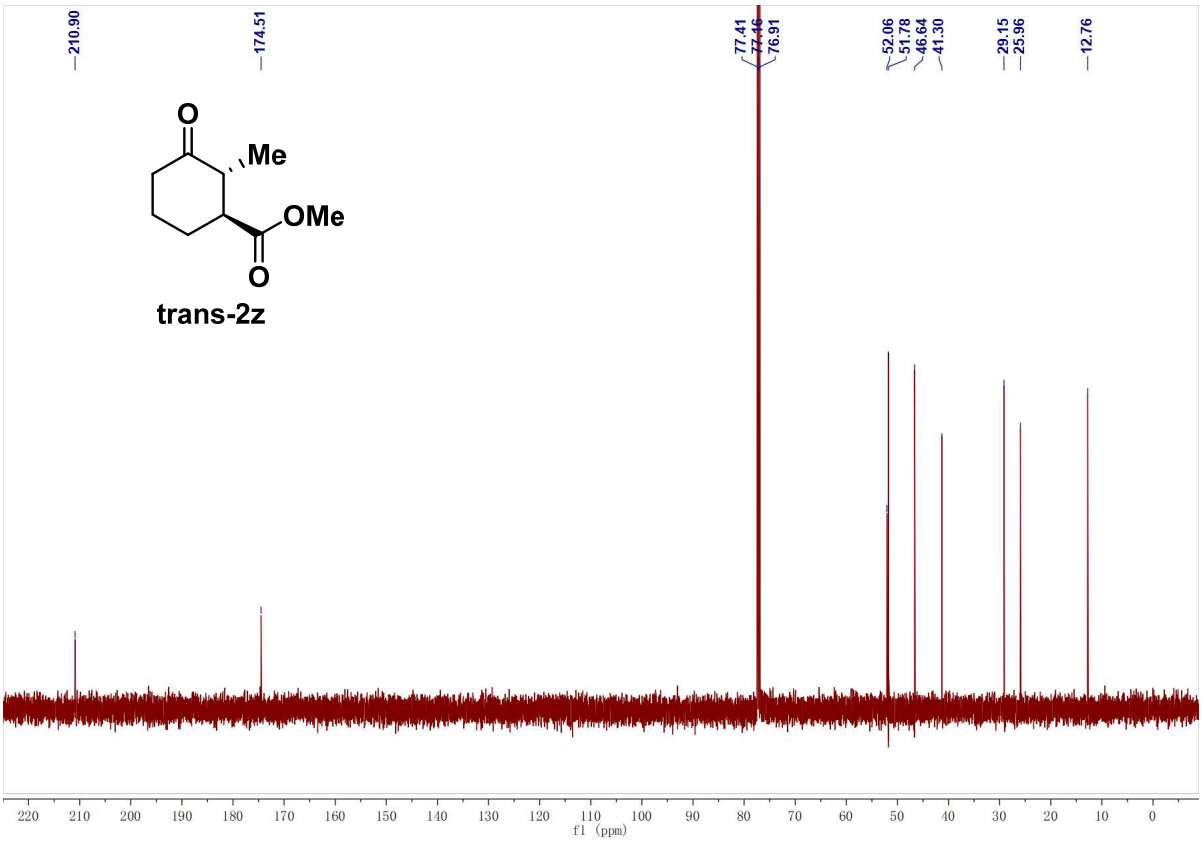
Compound **cis-2y,** ^{13}C NMR



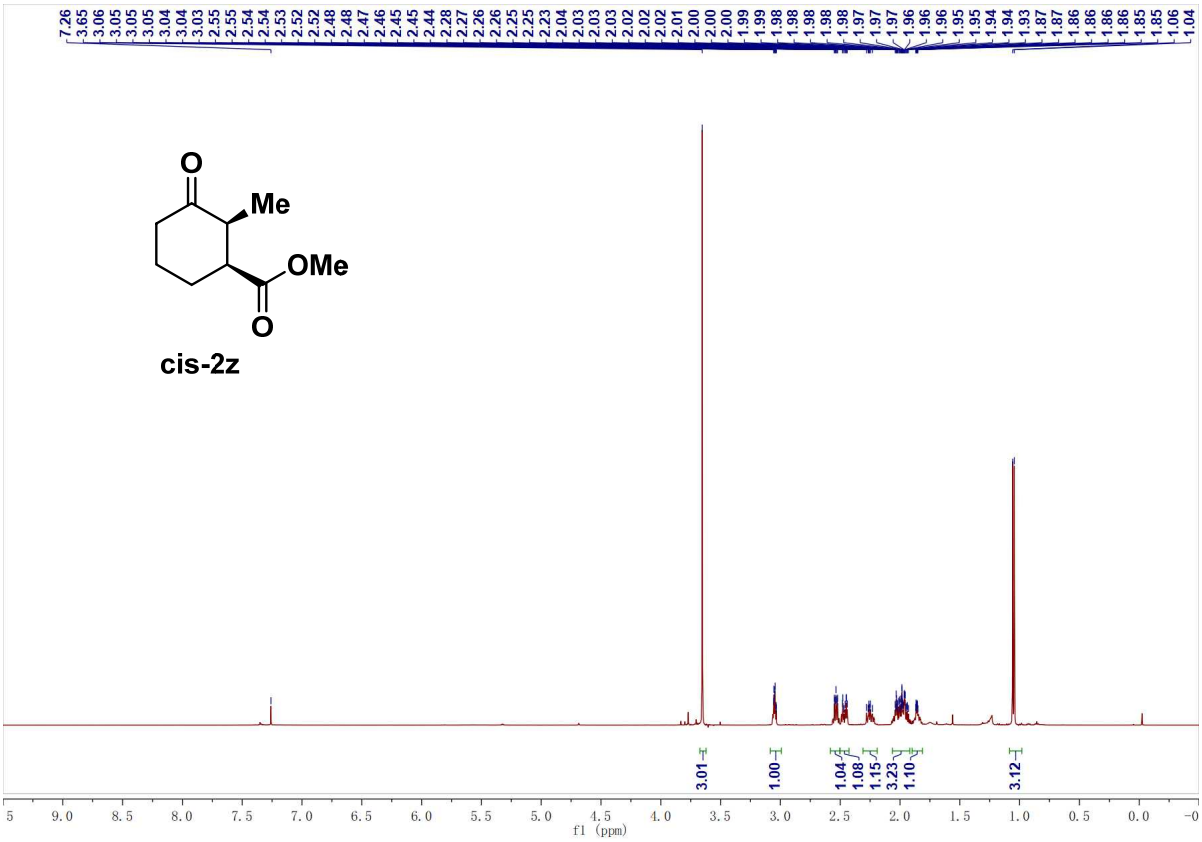
Compound **trans-2z,** ^{1}H NMR



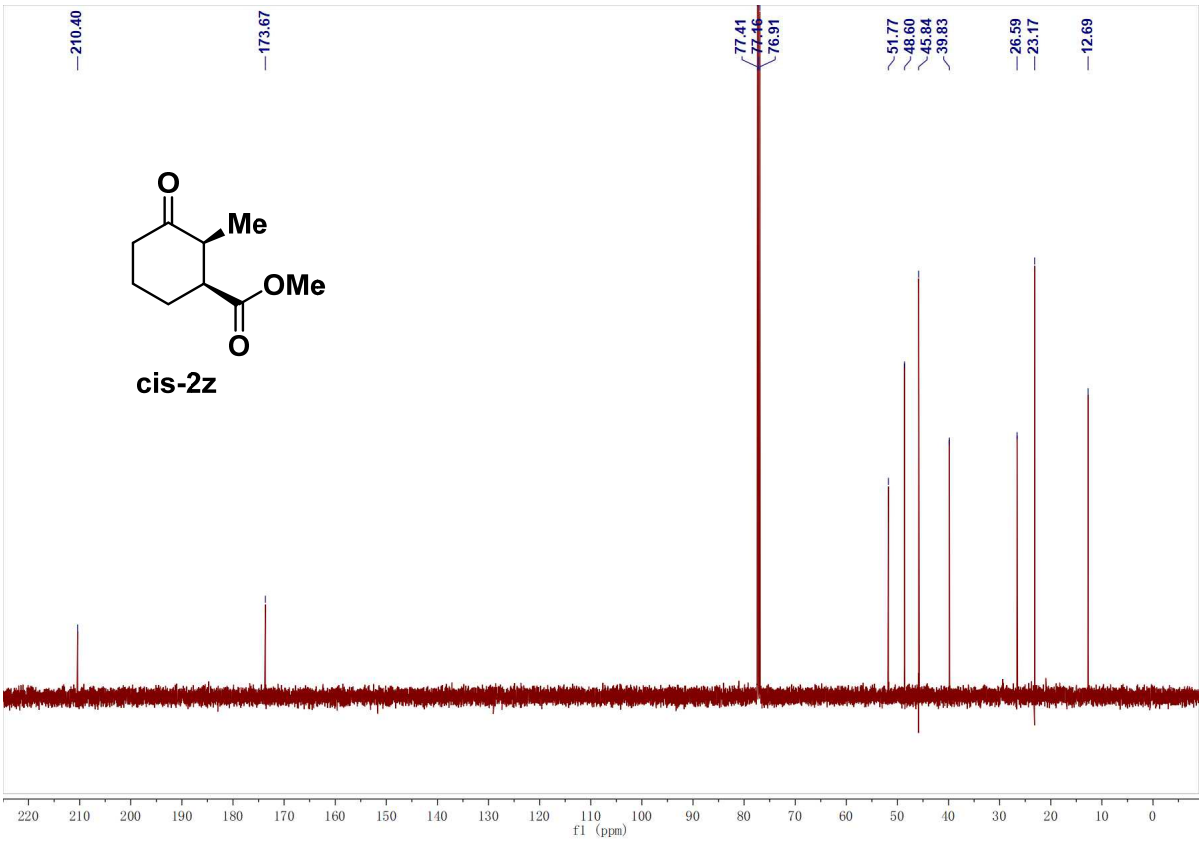
Compound **trans-2z,** ^{13}C NMR



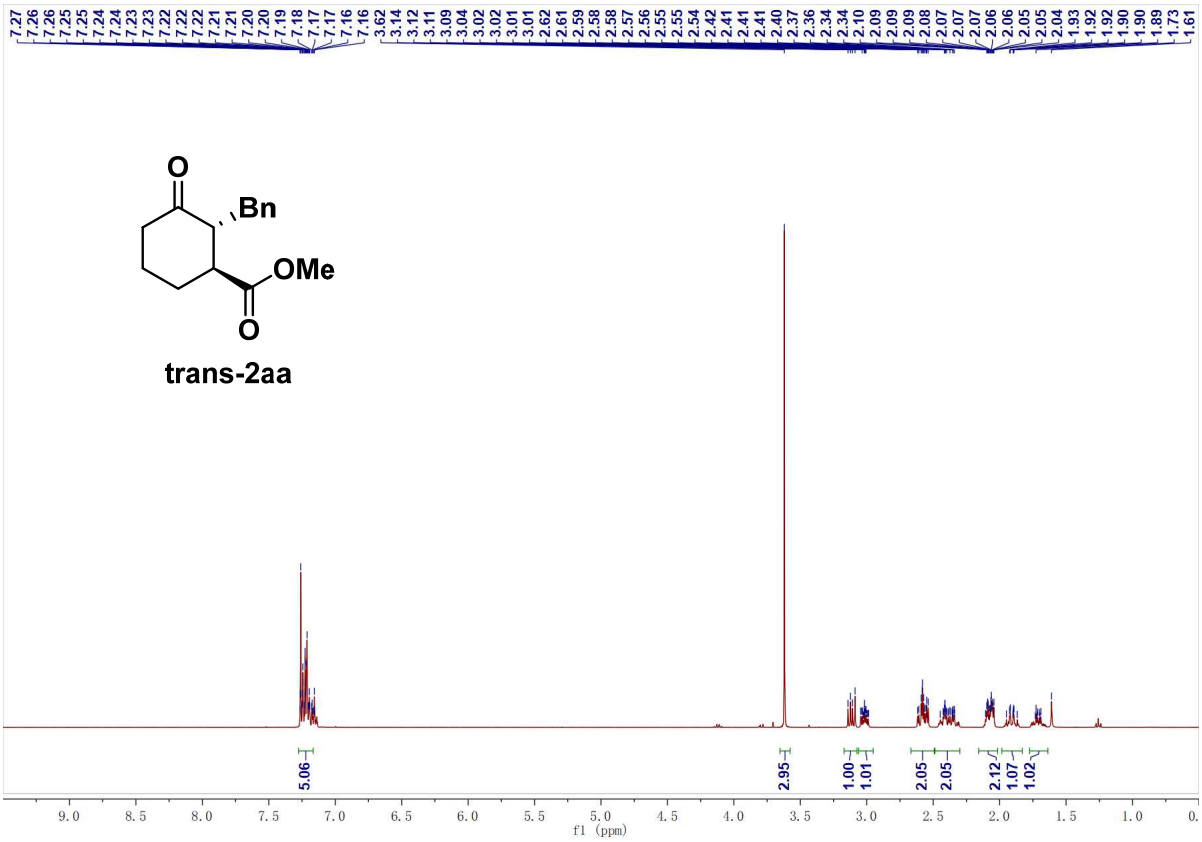
Compound **cis-2z,** ^{1}H NMR



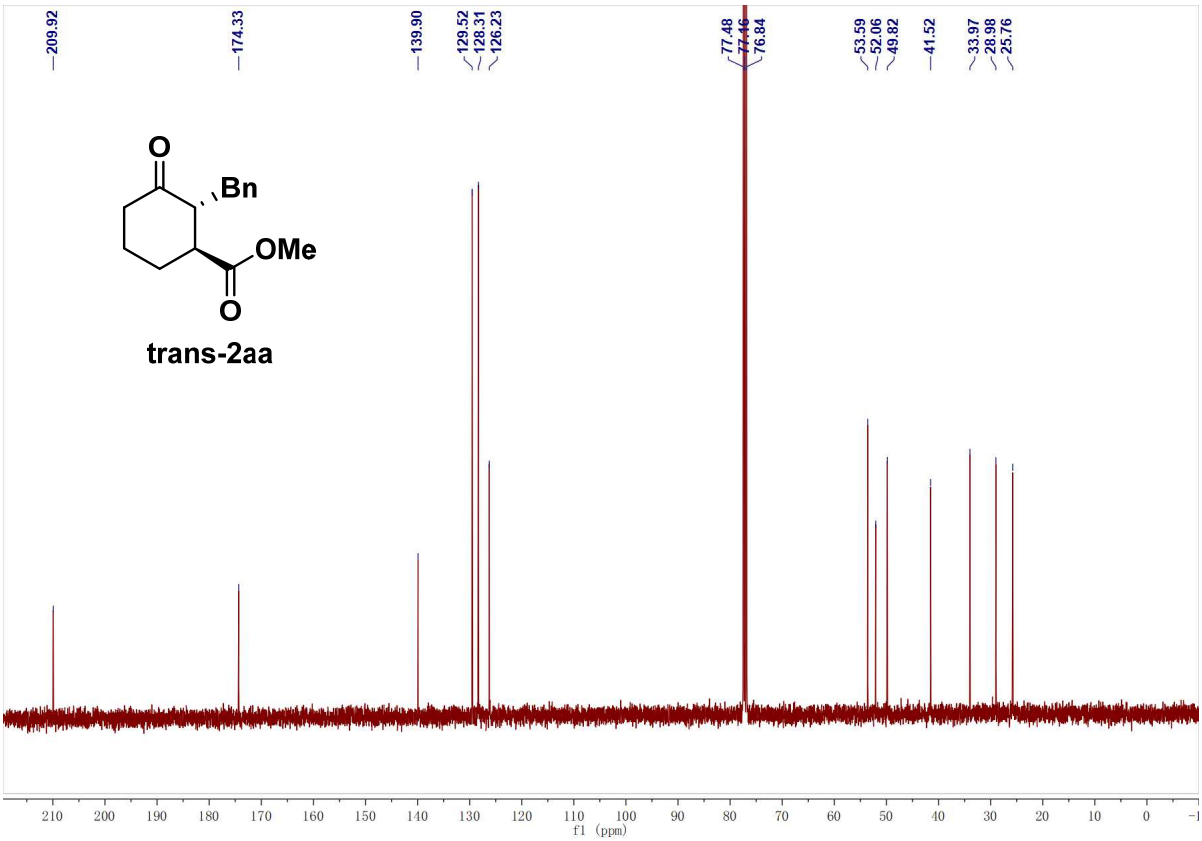
Compound **cis-2z,** ^{13}C NMR



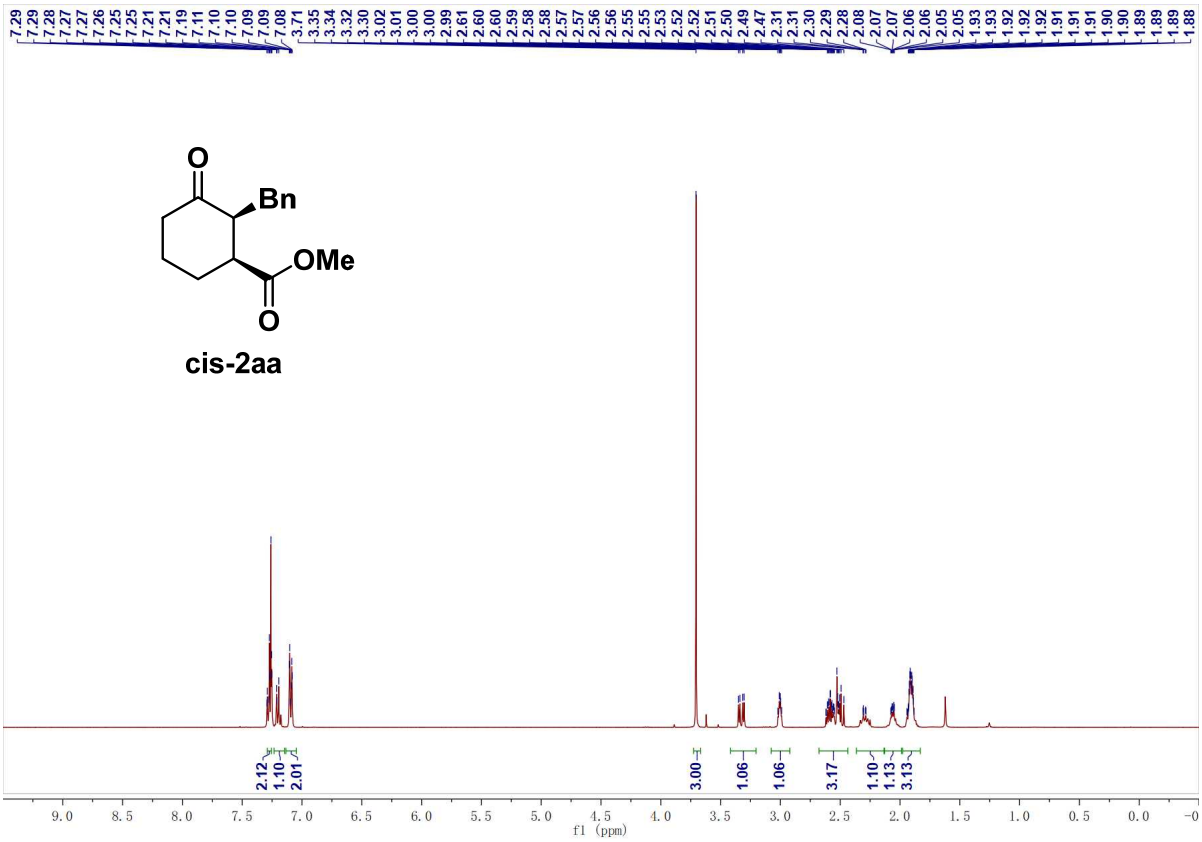
Compound **trans-2aa,** ^{1}H NMR



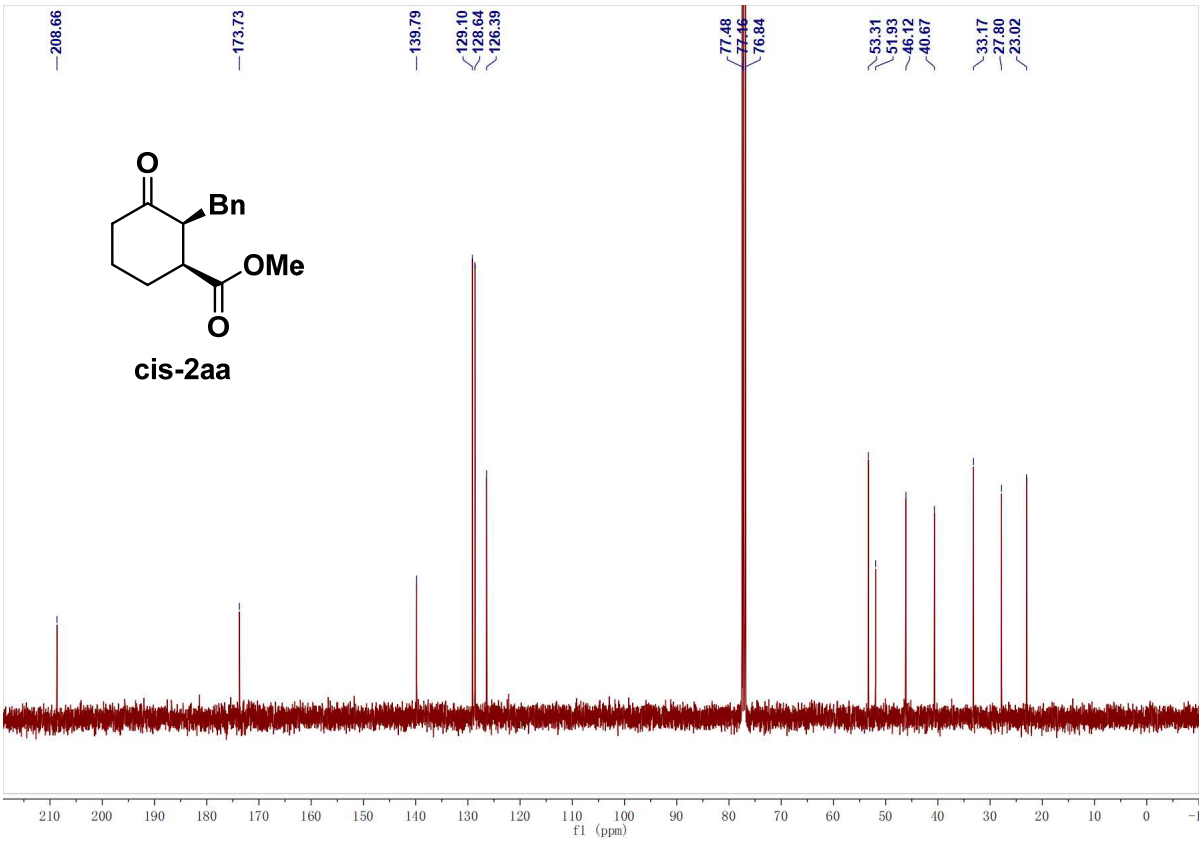
Compound **trans-2aa,** ^{13}C NMR



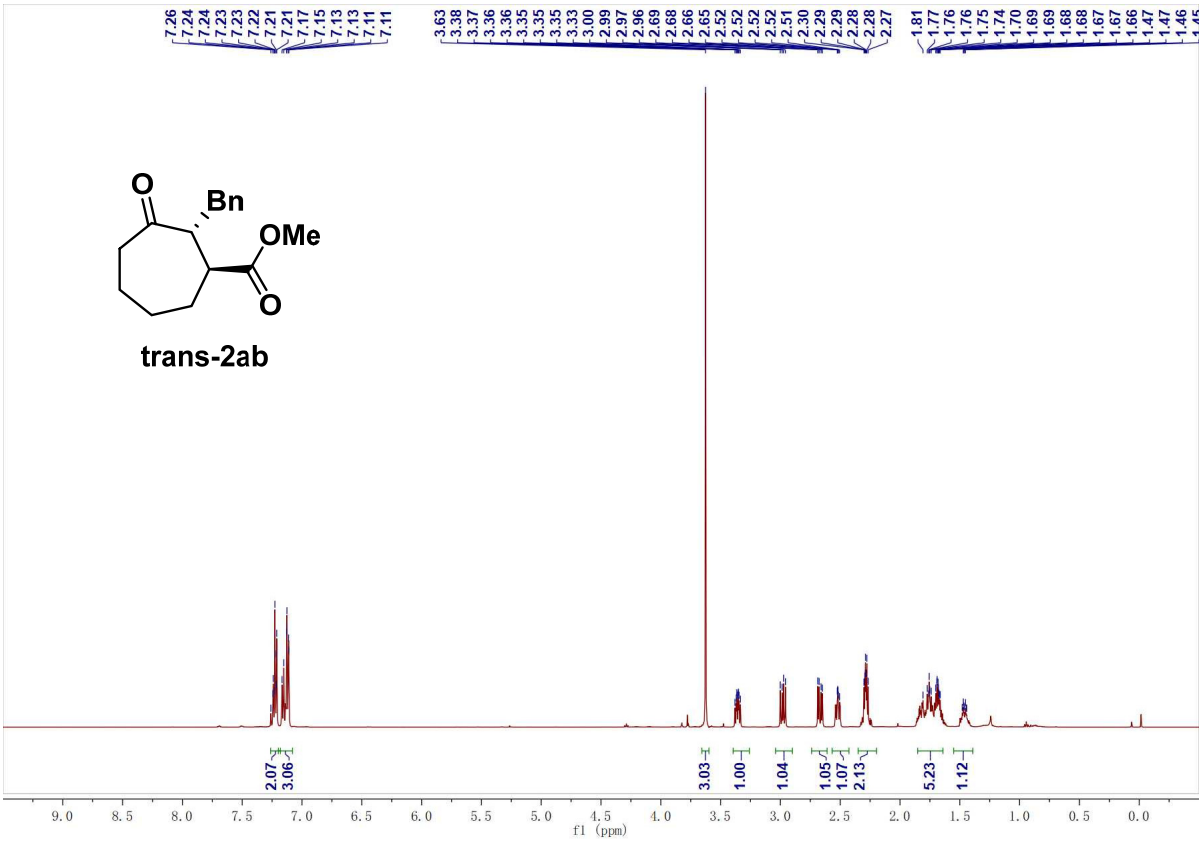
Compound **cis-2aa,** ^{1}H NMR



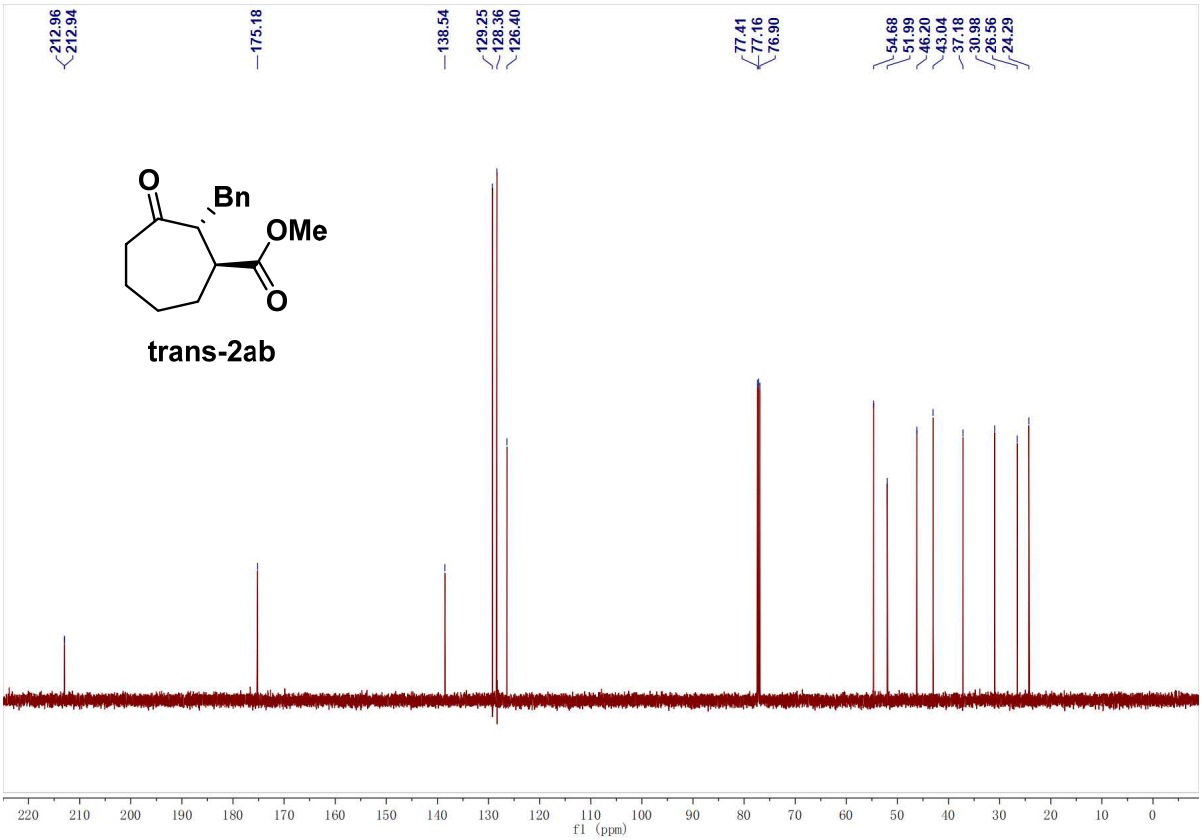
Compound **cis-2aa,** ^{13}C NMR



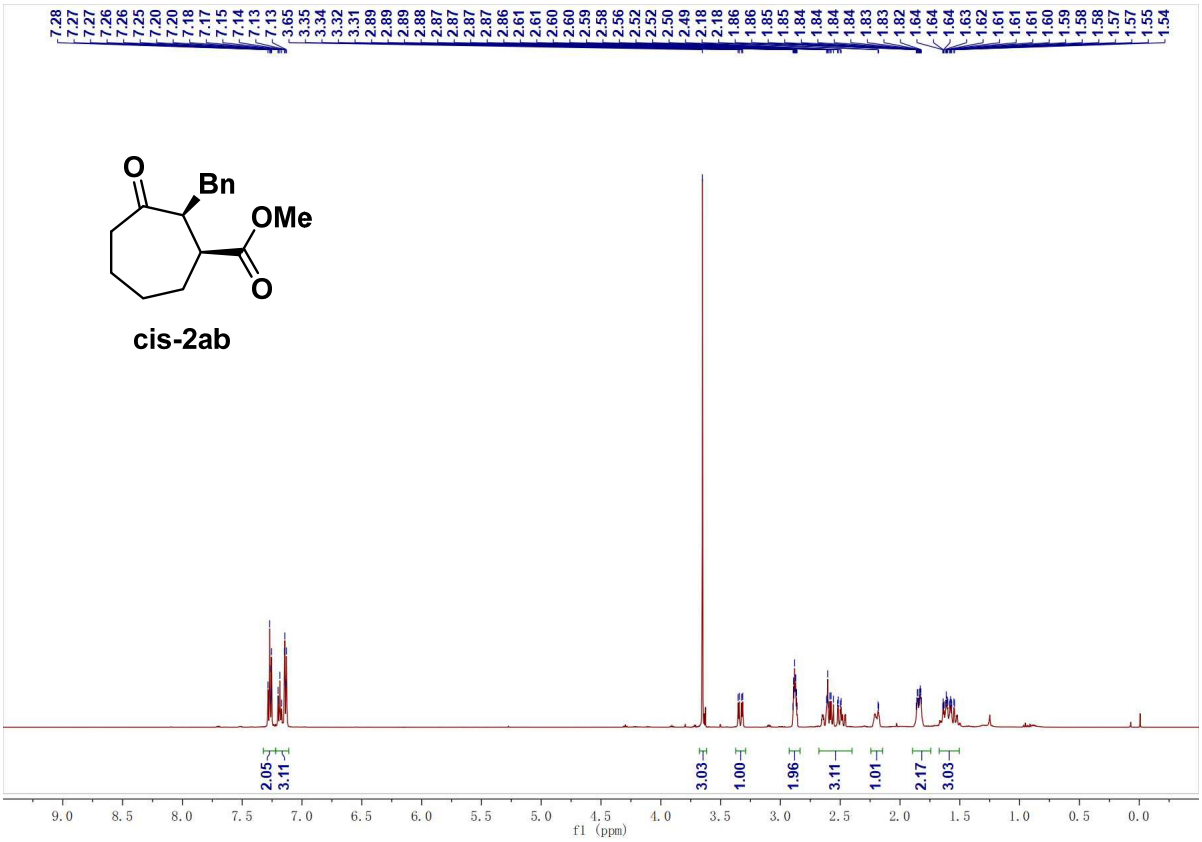
Compound **trans-2ab,** ^{1}H NMR



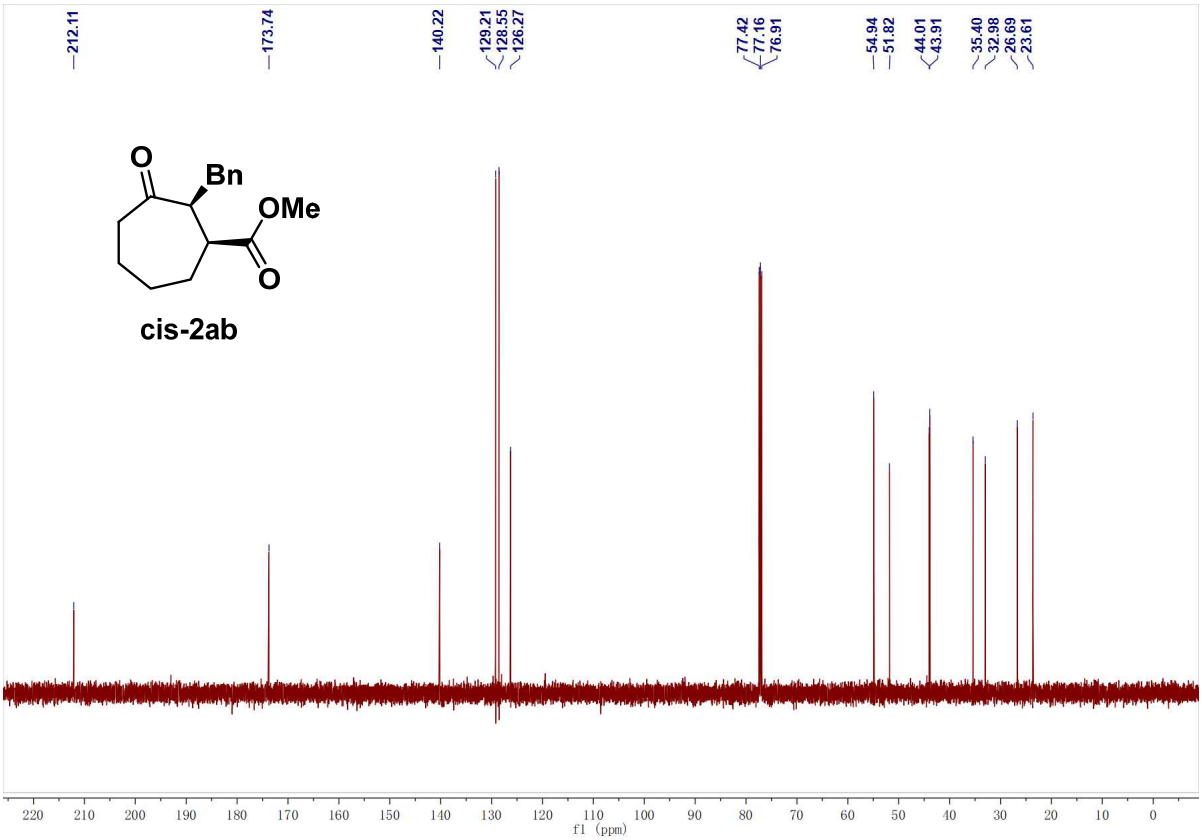
Compound **trans-2ab,** ^{13}C NMR



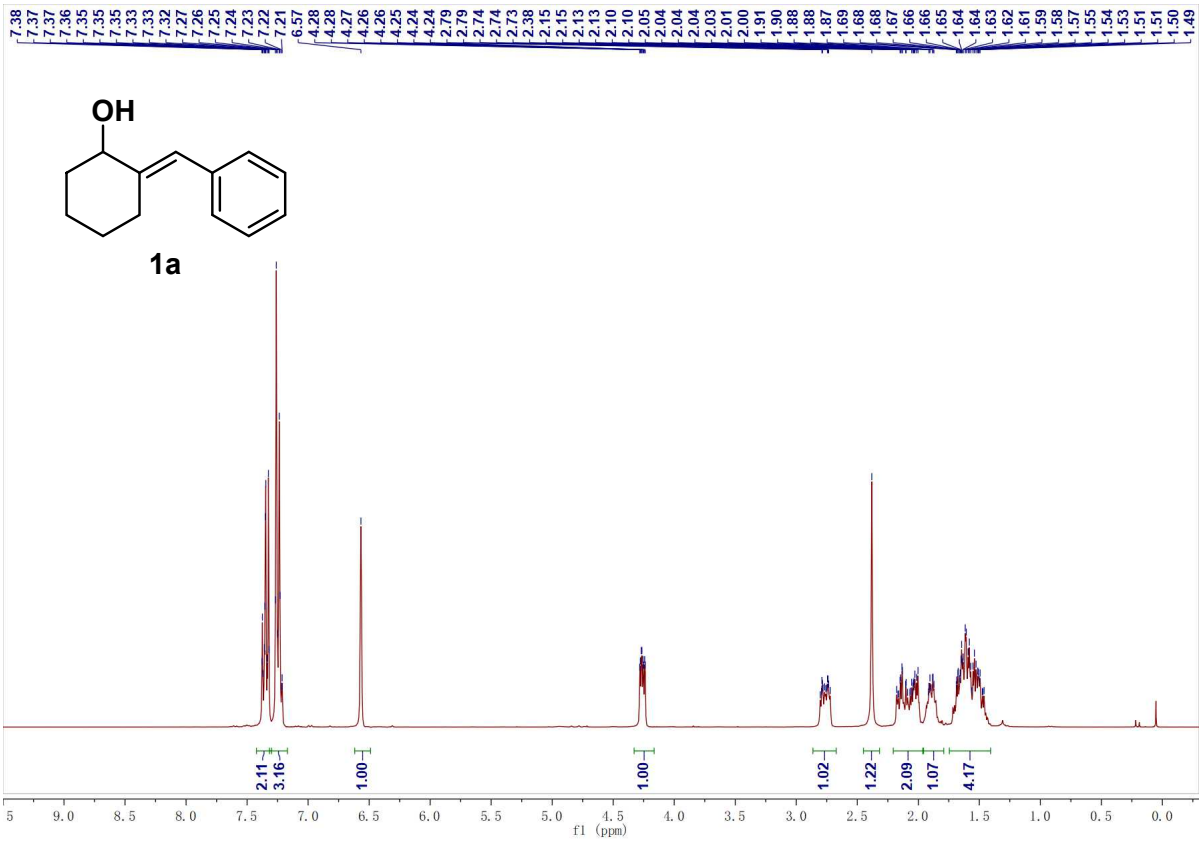
Compound **cis-2ab,** ^{1}H NMR



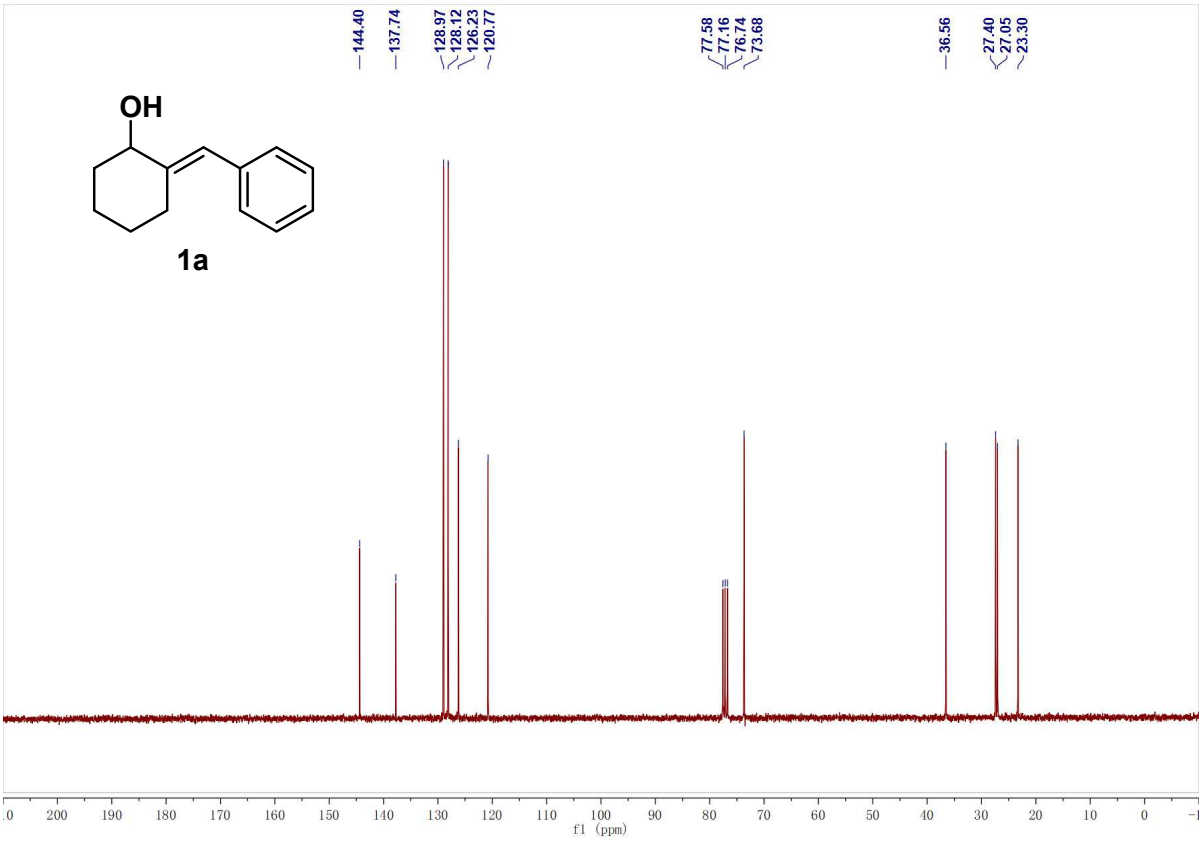
Compound **cis-2ab,** ^{13}C NMR



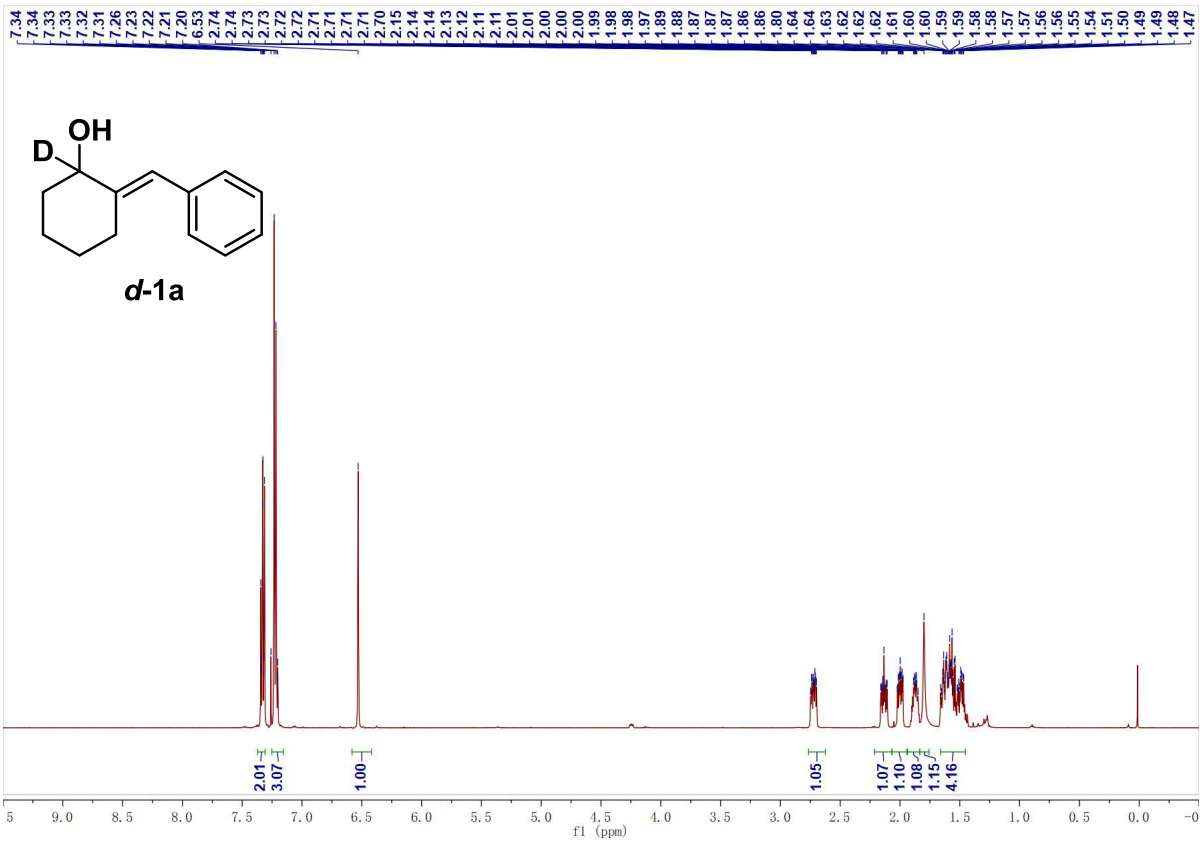
Compound **1a,** ^{1}H NMR



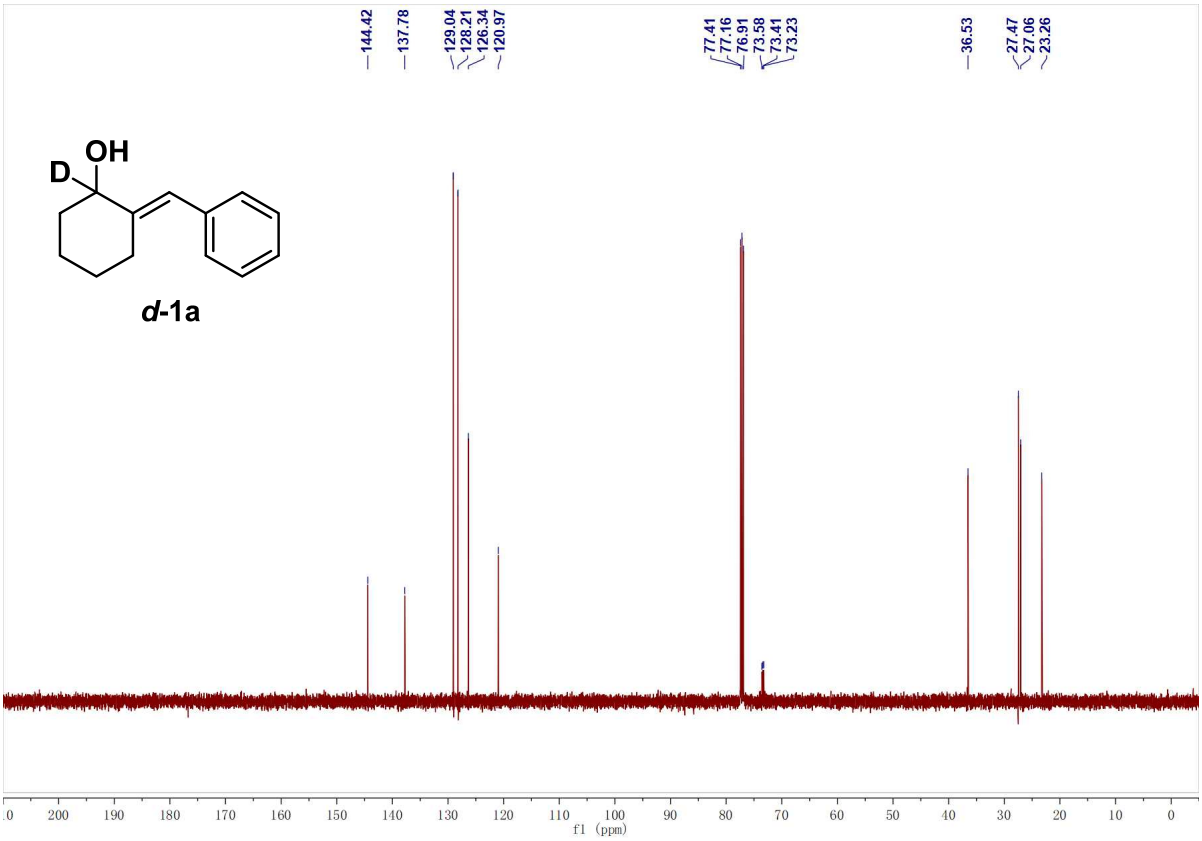
Compound **1a,** ^{13}C NMR



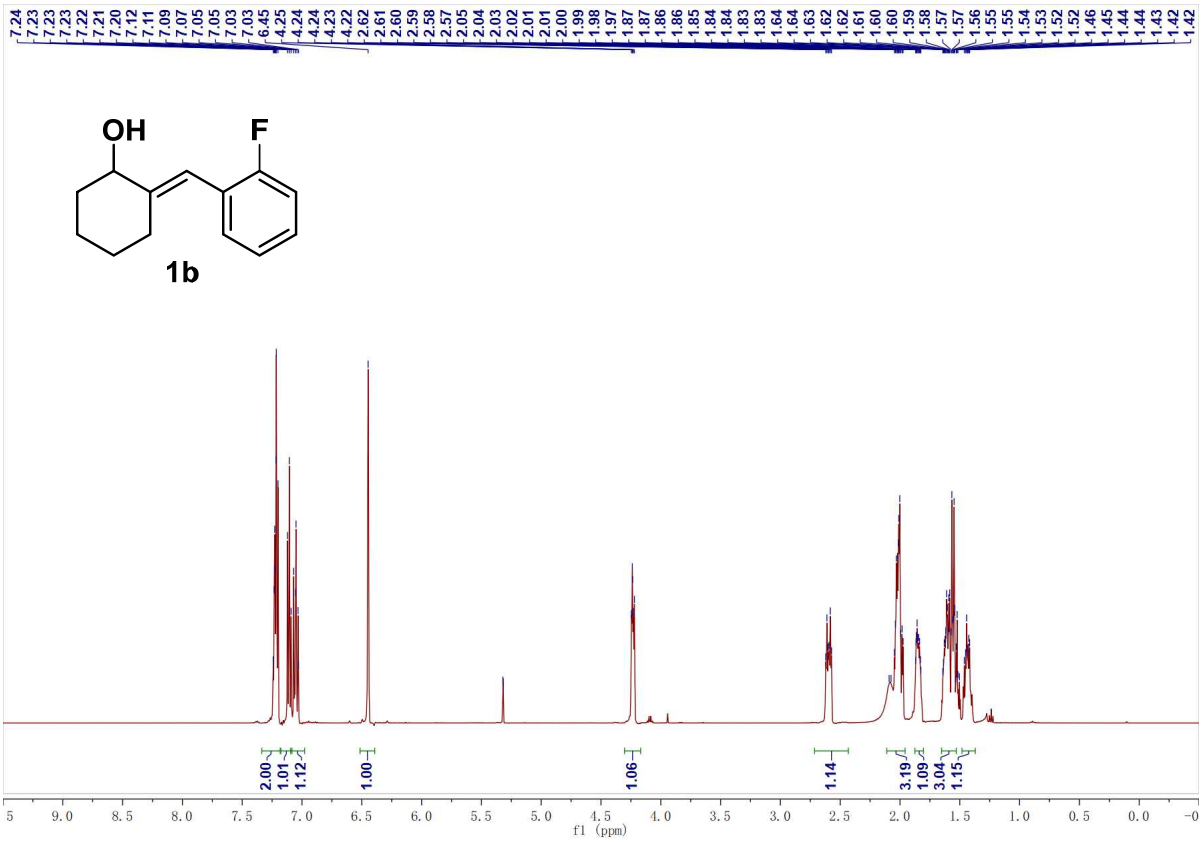
Compound ***d*-1a,** ^{1}H NMR



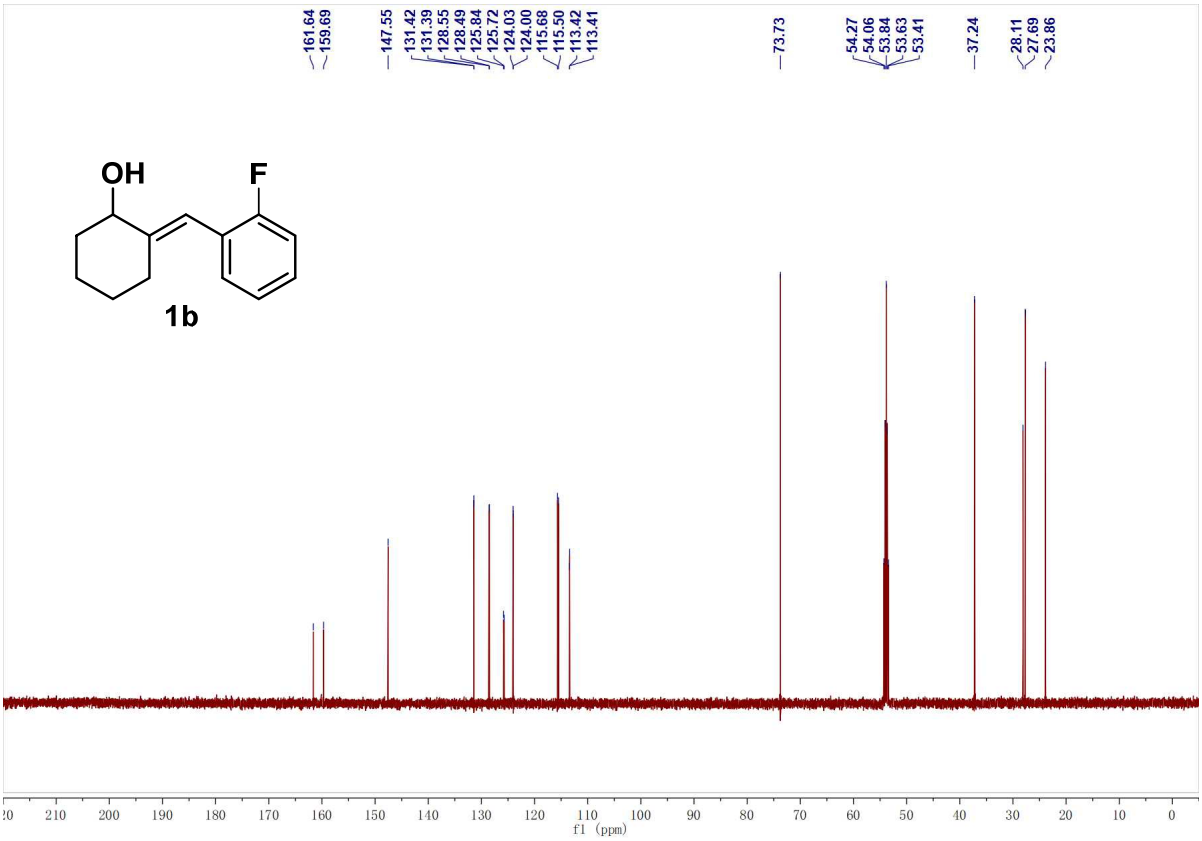
Compound ***d*-1a,** ^{13}C NMR



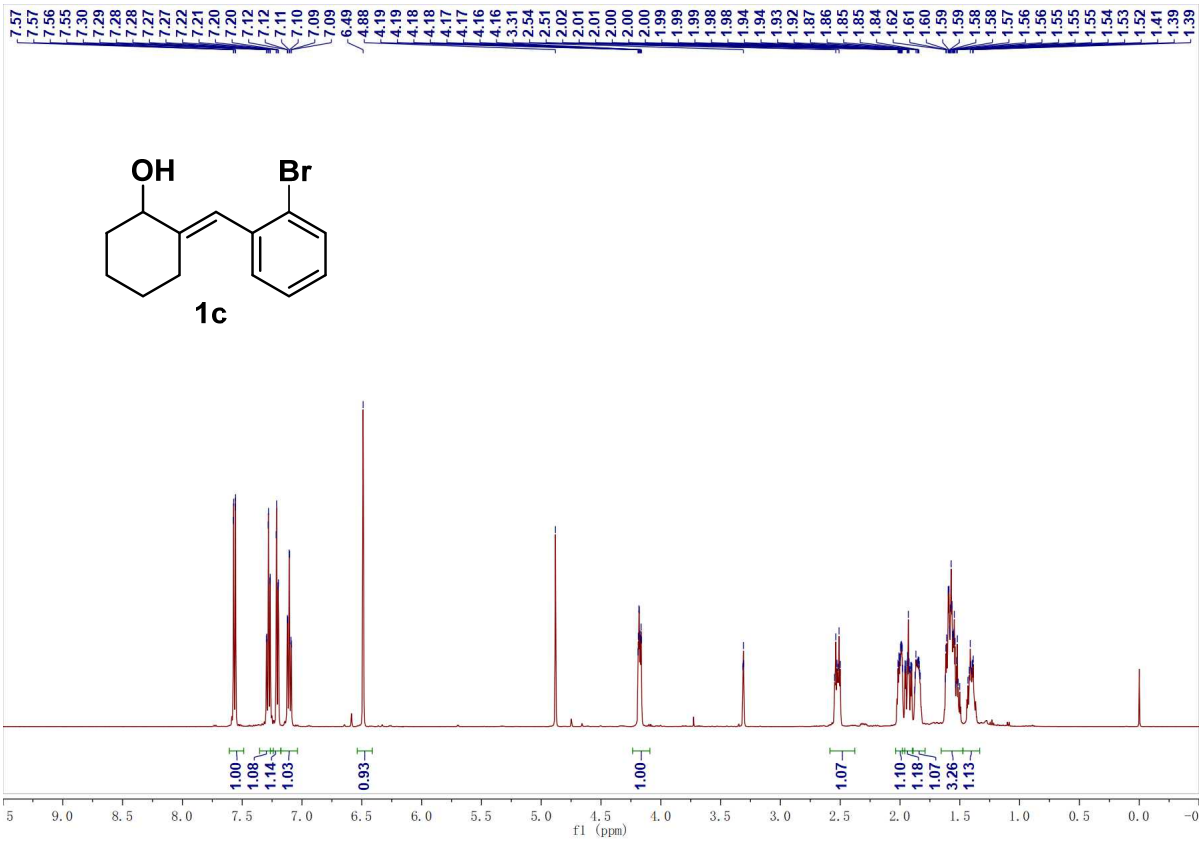
Compound **1b,** ^{1}H NMR



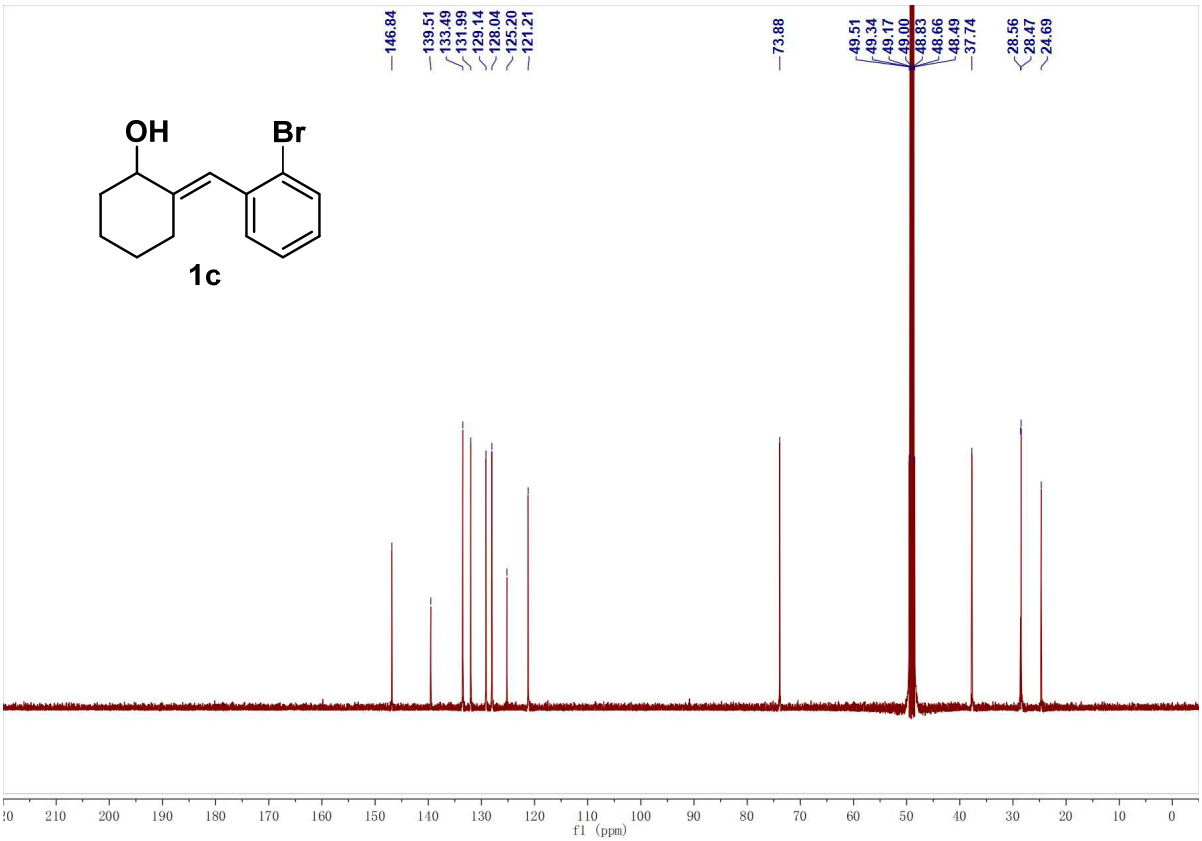
Compound **1b,** ^{13}C NMR



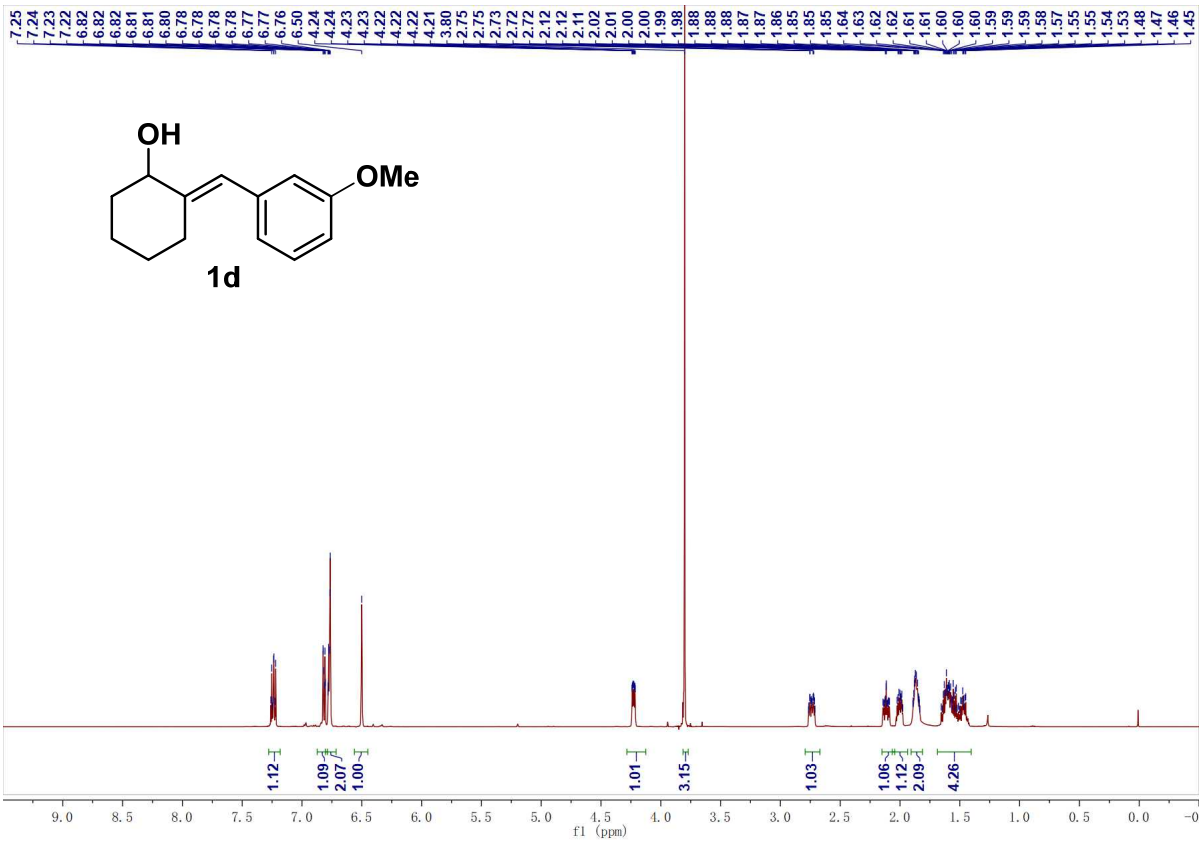
Compound **1c,** ^{1}H NMR



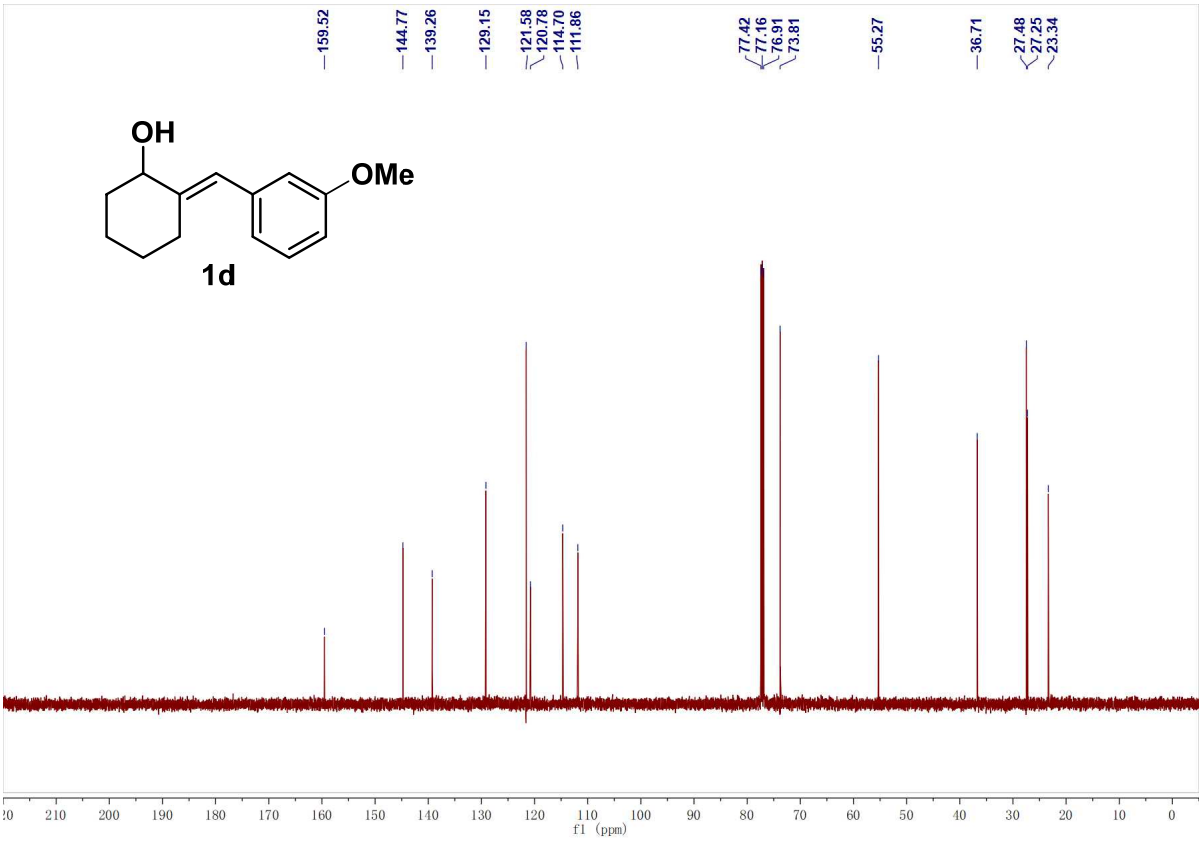
Compound **1c,** ^{13}C NMR



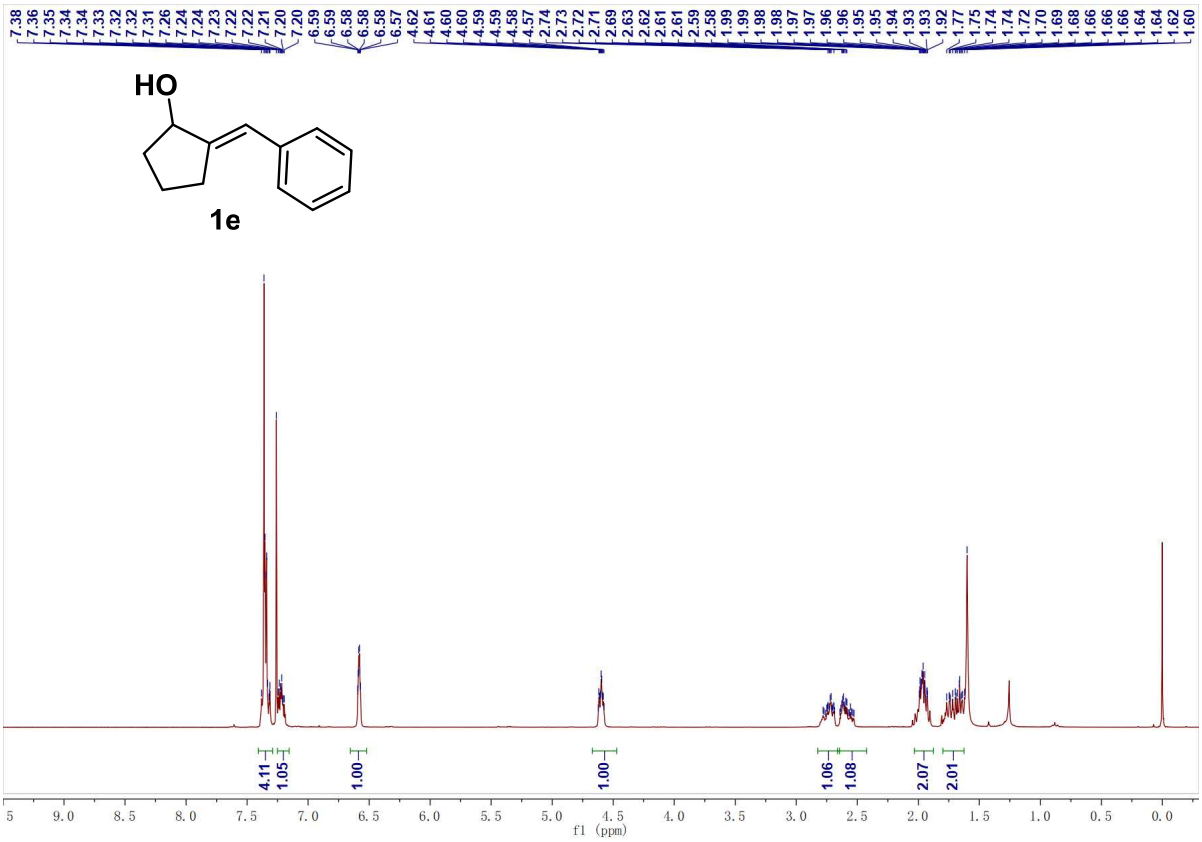
Compound **1d,** ^{1}H NMR



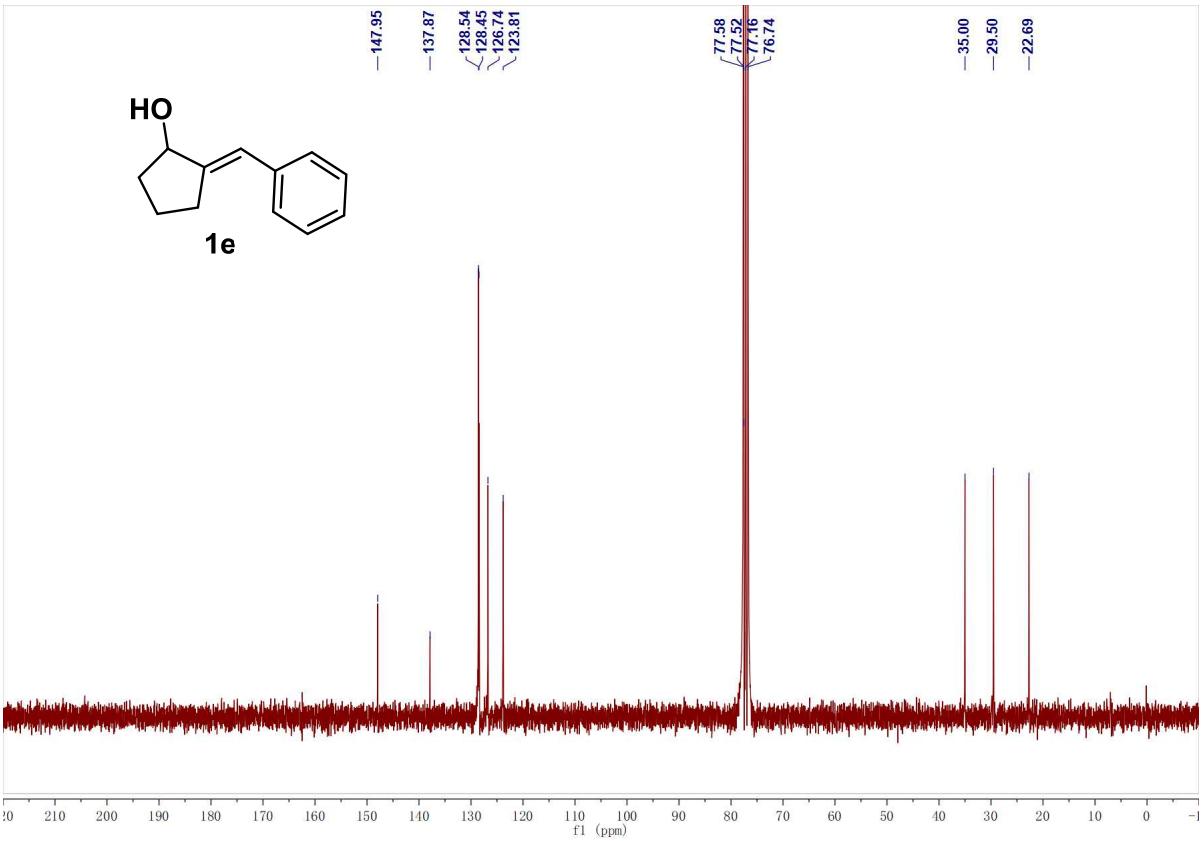
Compound **1d,** ^{13}C NMR



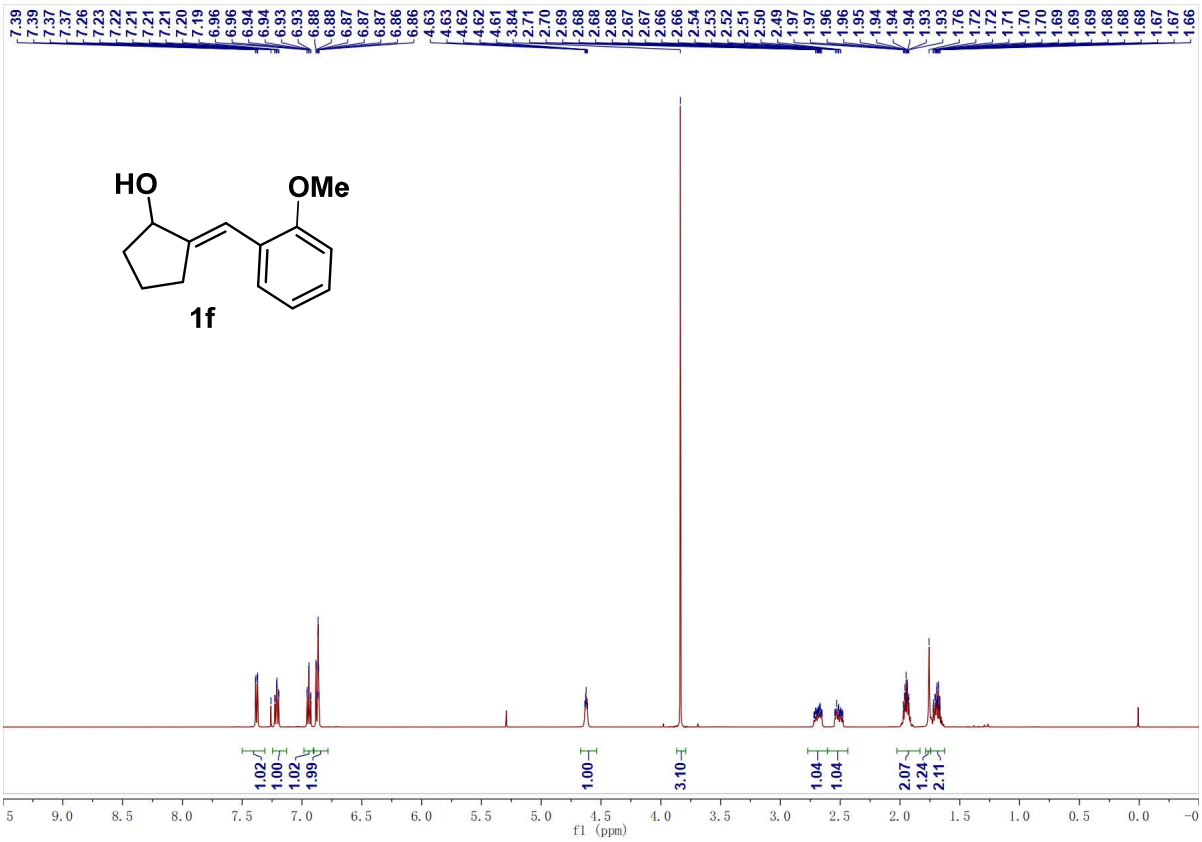
Compound **1e,** ^{1}H NMR



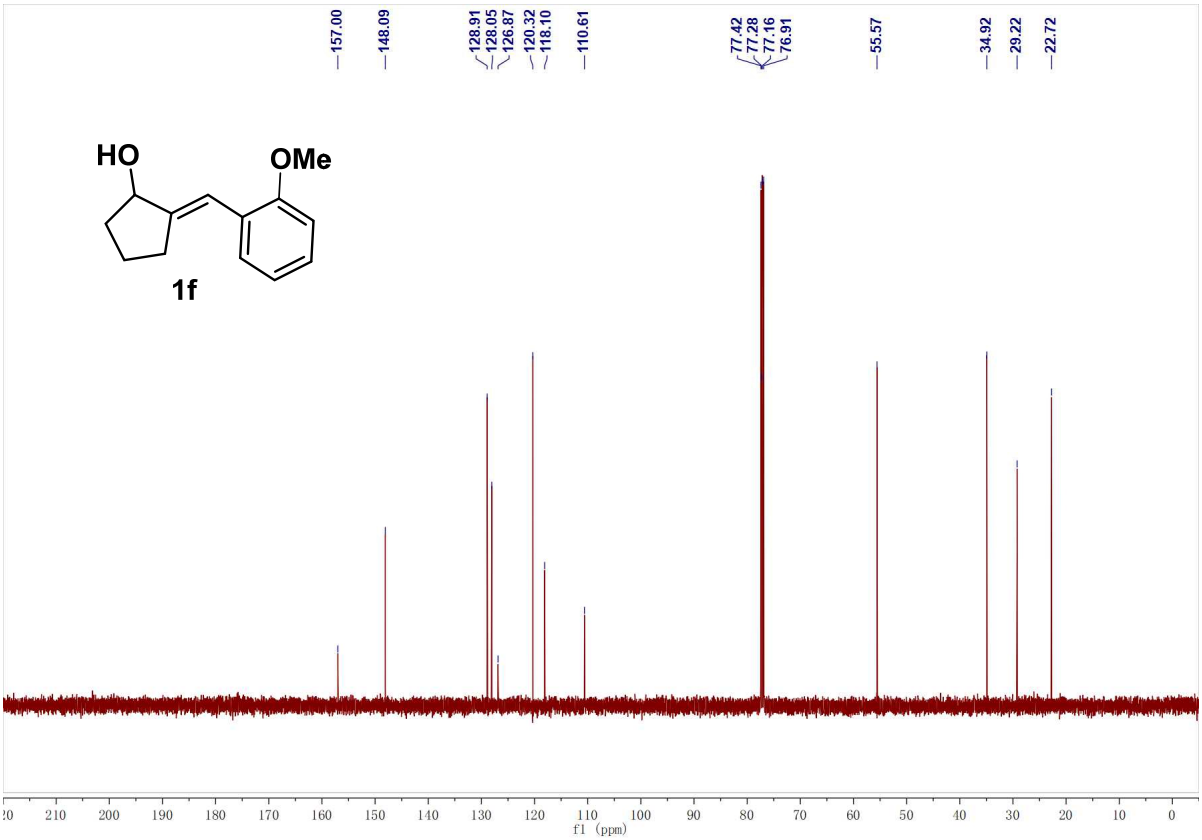
Compound **1e,** ^{13}C NMR



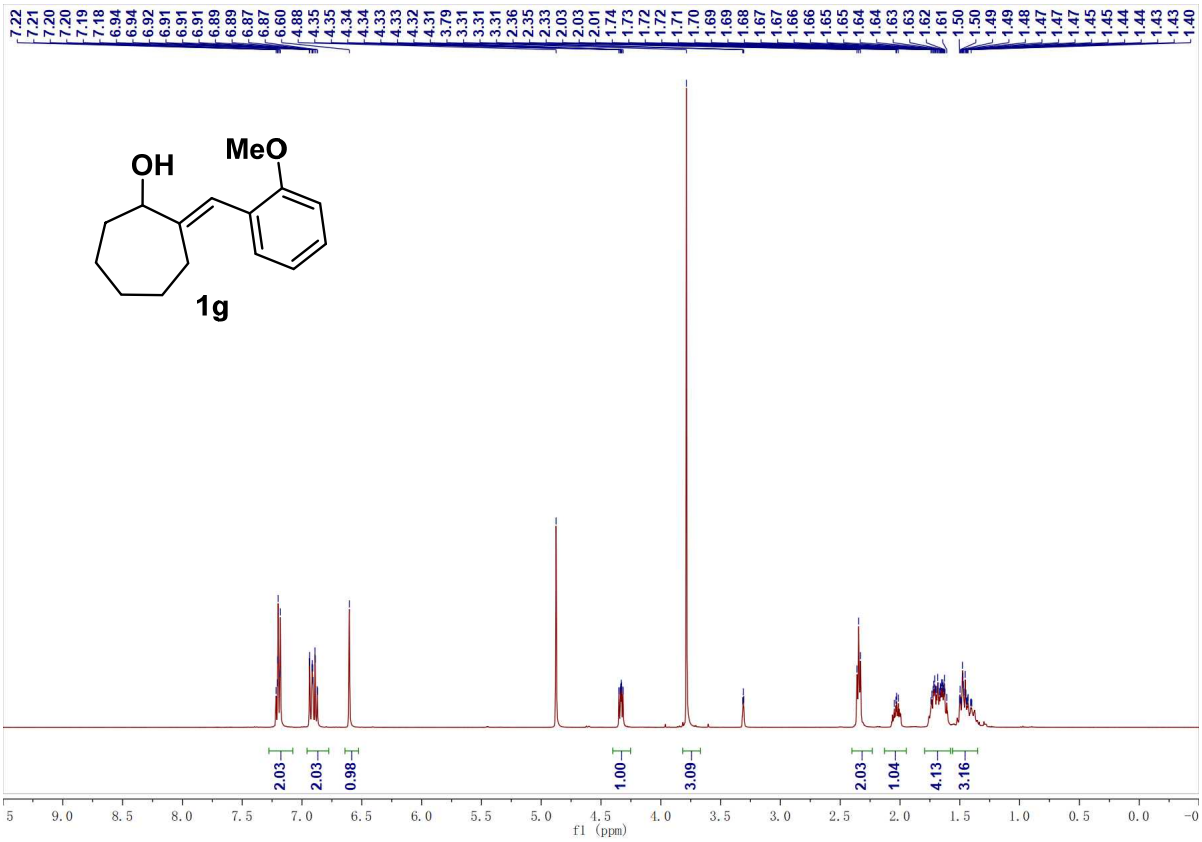
Compound **1g,** ^{1}H NMR



Compound **1g,** ^{13}C NMR



Compound **1g,** ^{1}H NMR



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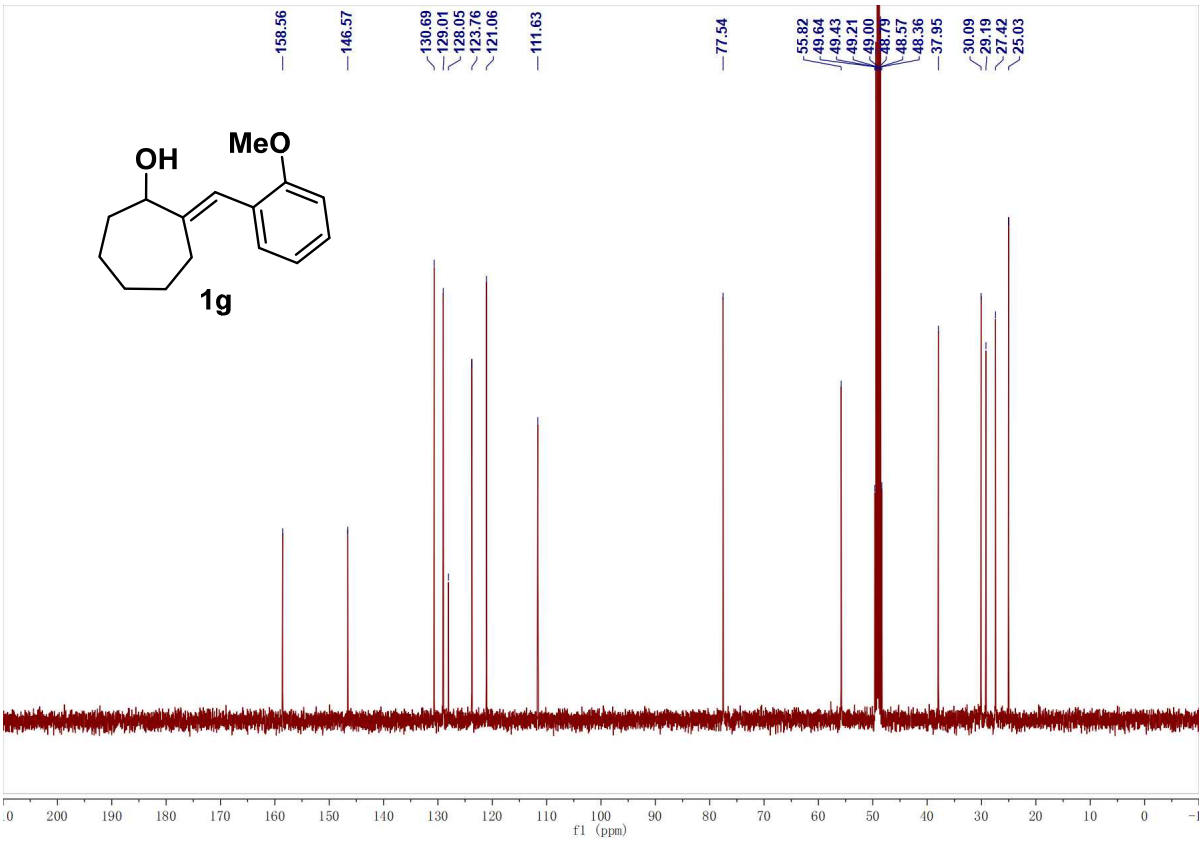
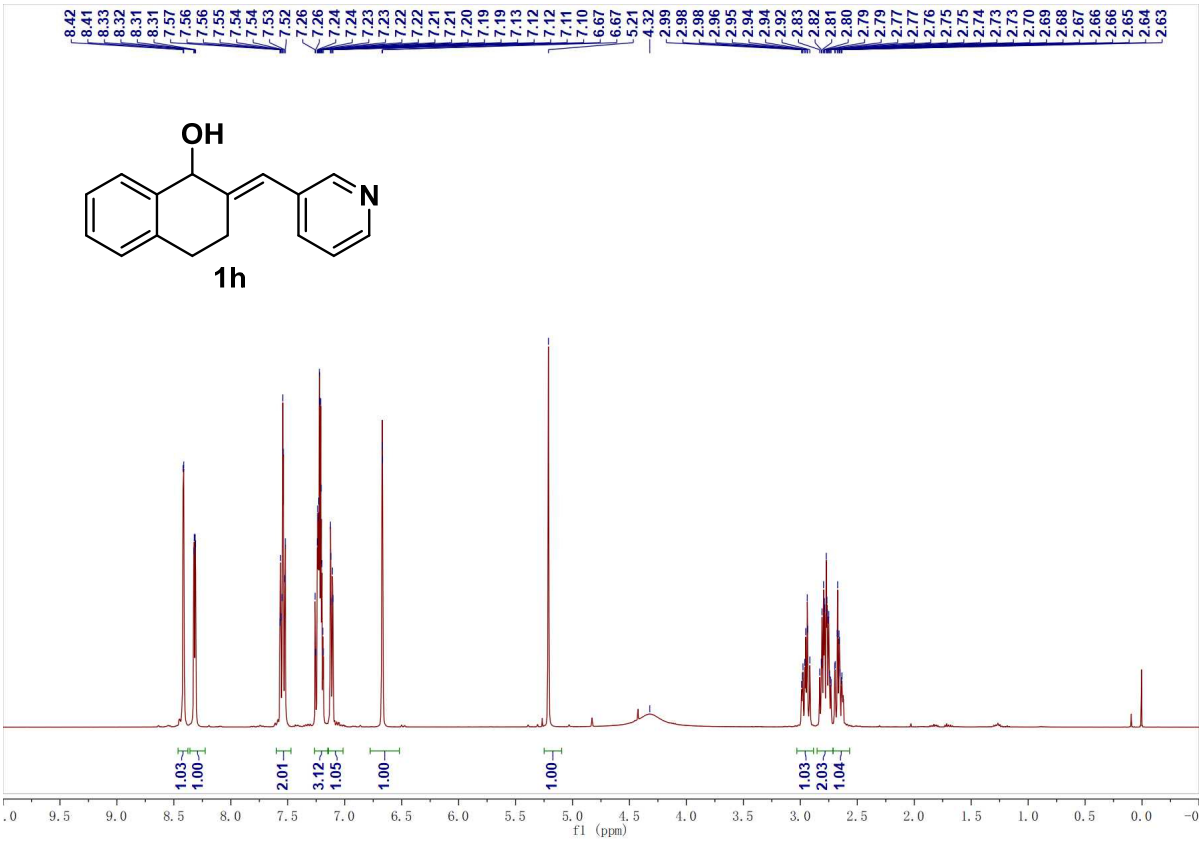
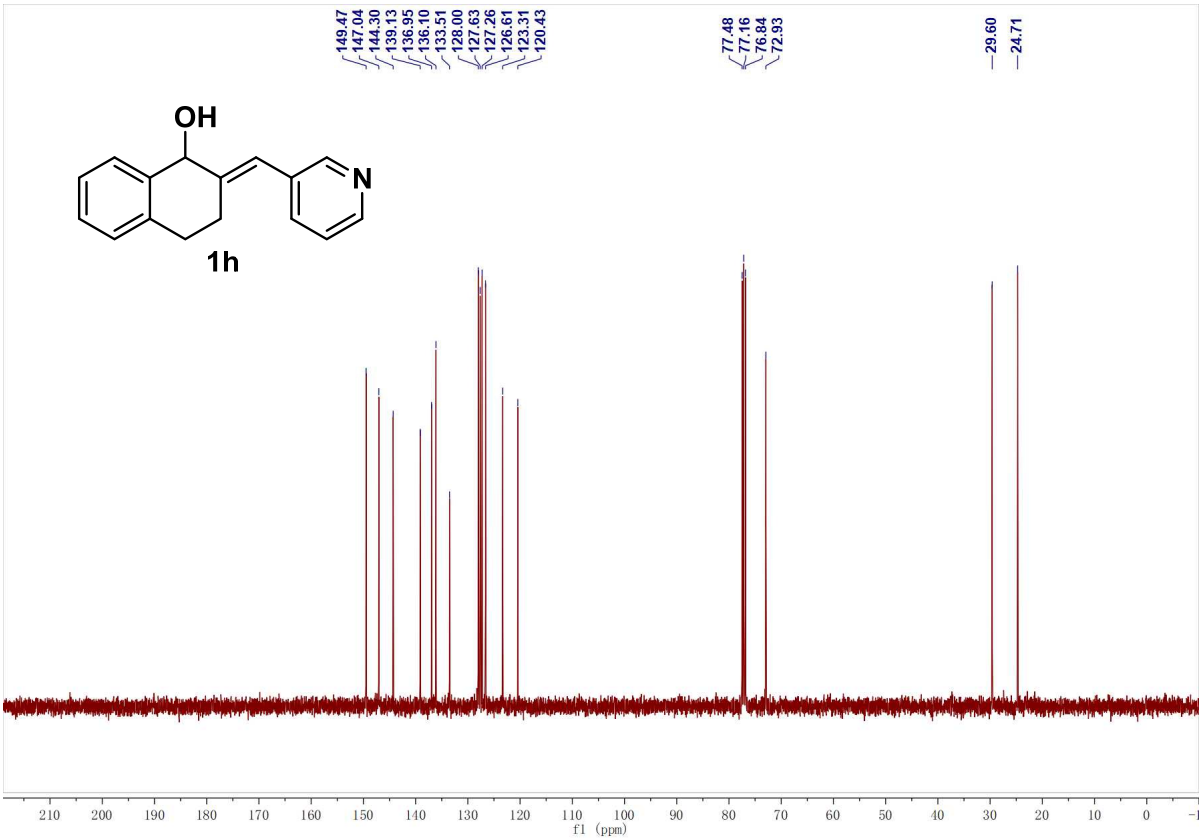


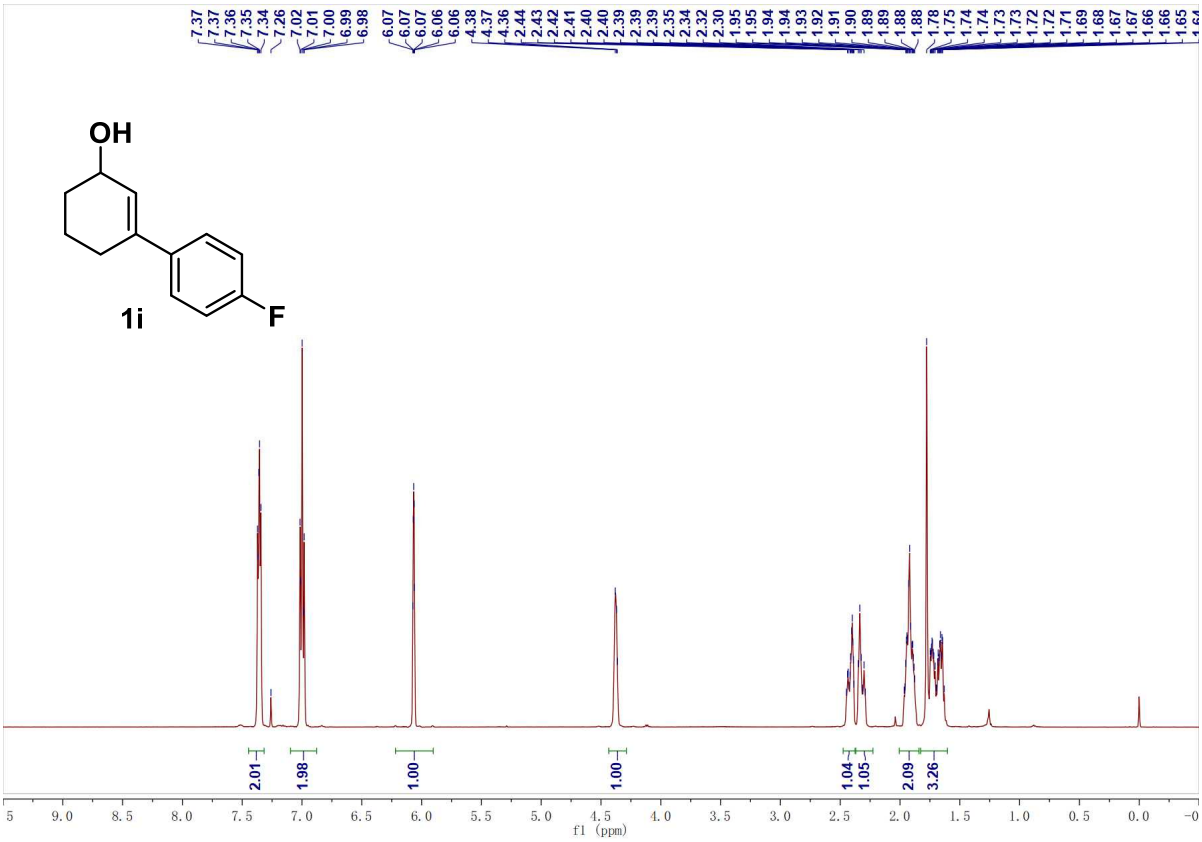
Compound **1h,** ^{1}H NMR



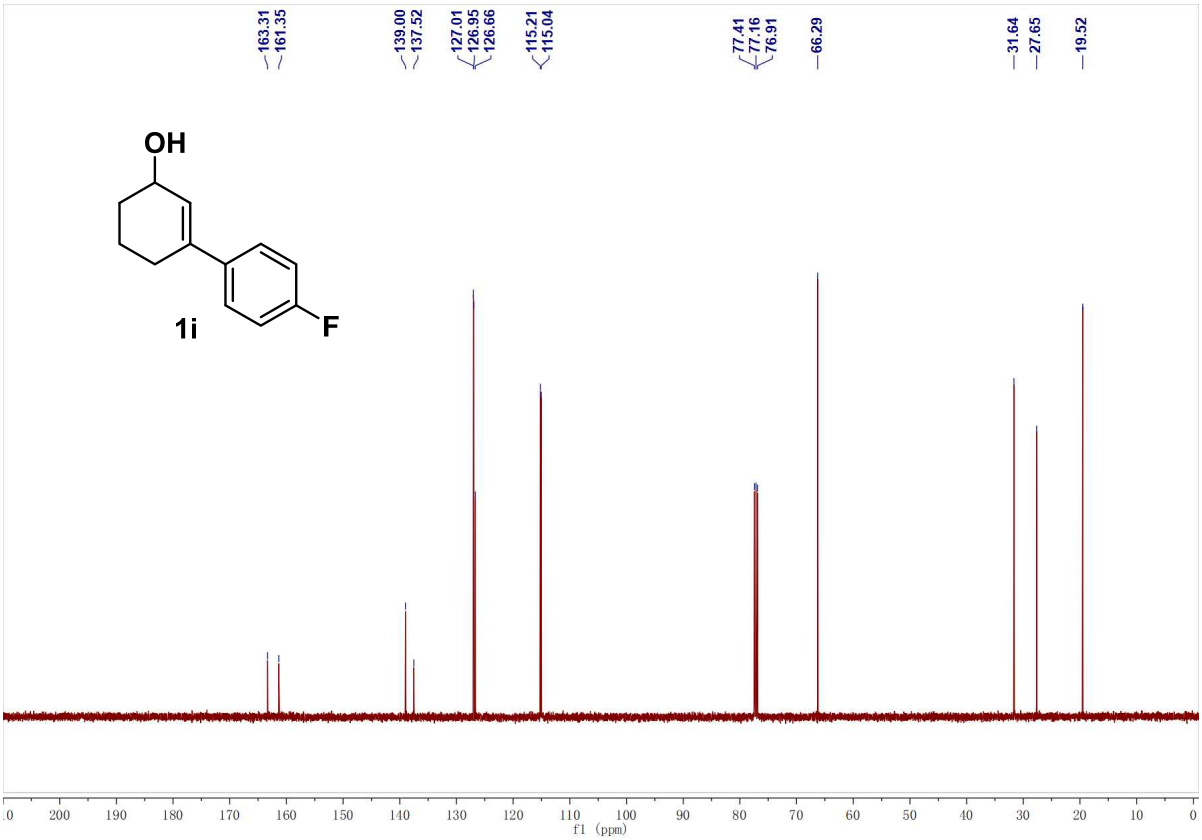
Compound **1h,** ^{13}C NMR



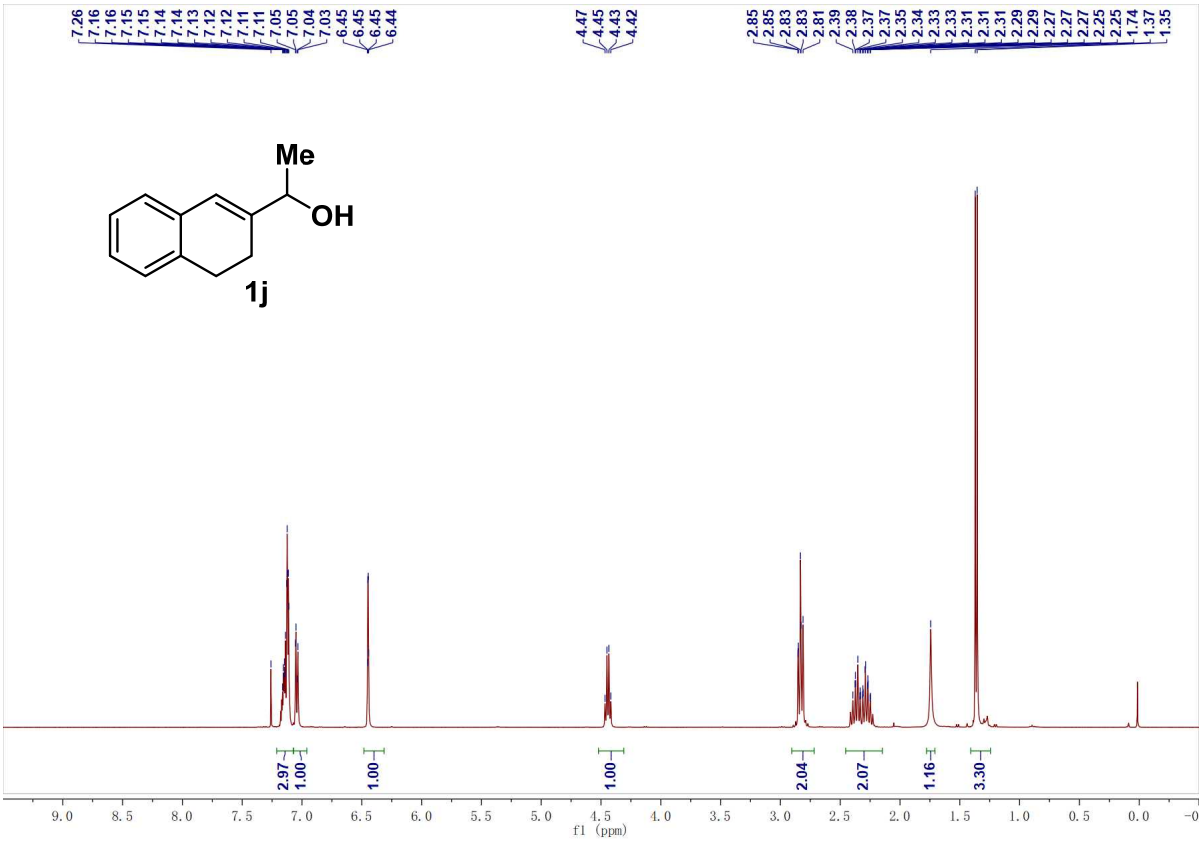
Compound **1i,** ^{1}H NMR



Compound **1i,** ^{13}C NMR



Compound **1j,** ^{1}H NMR



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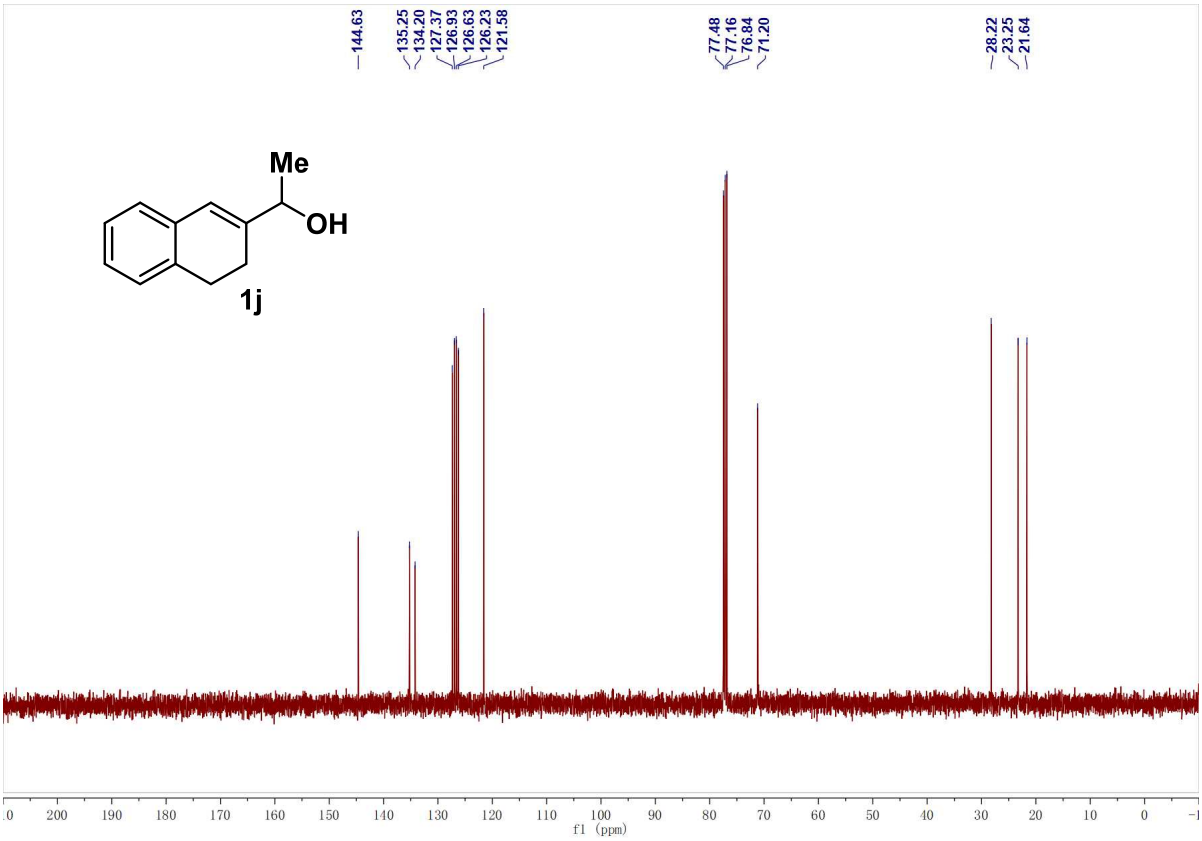
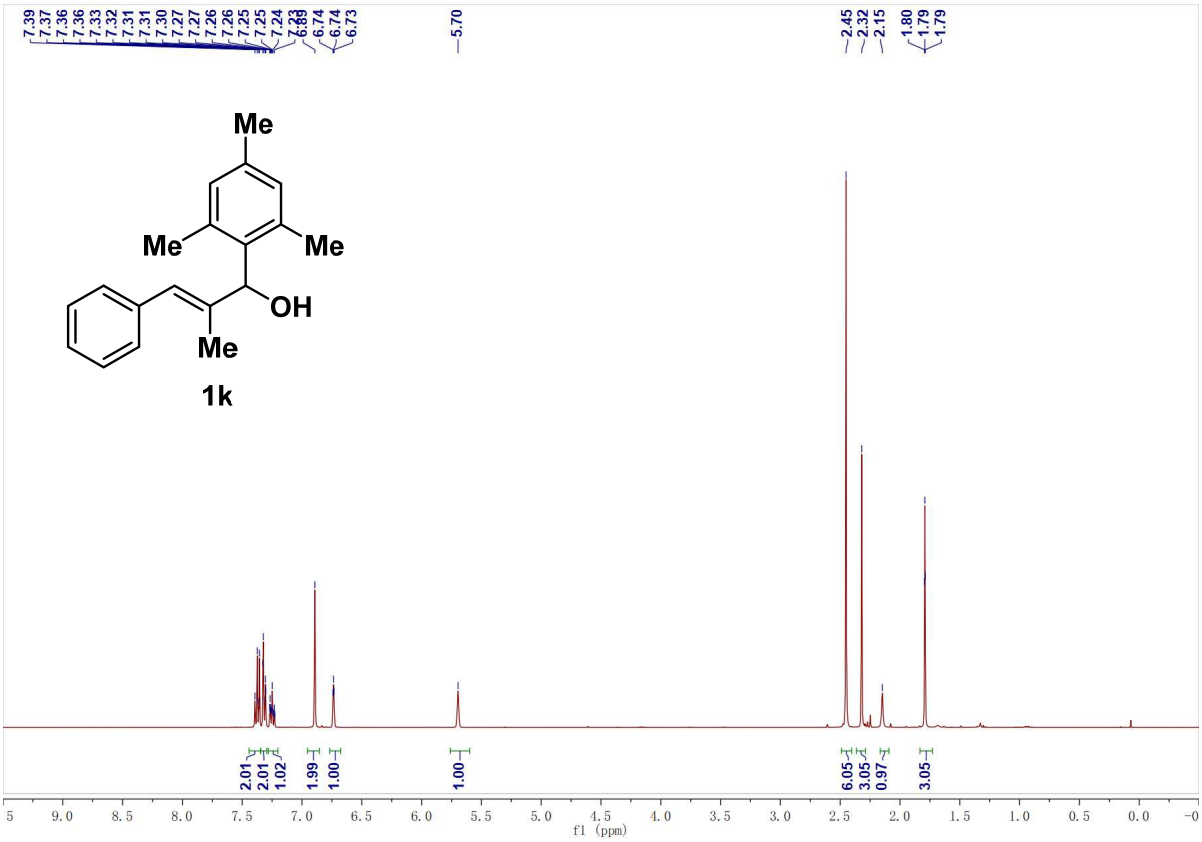
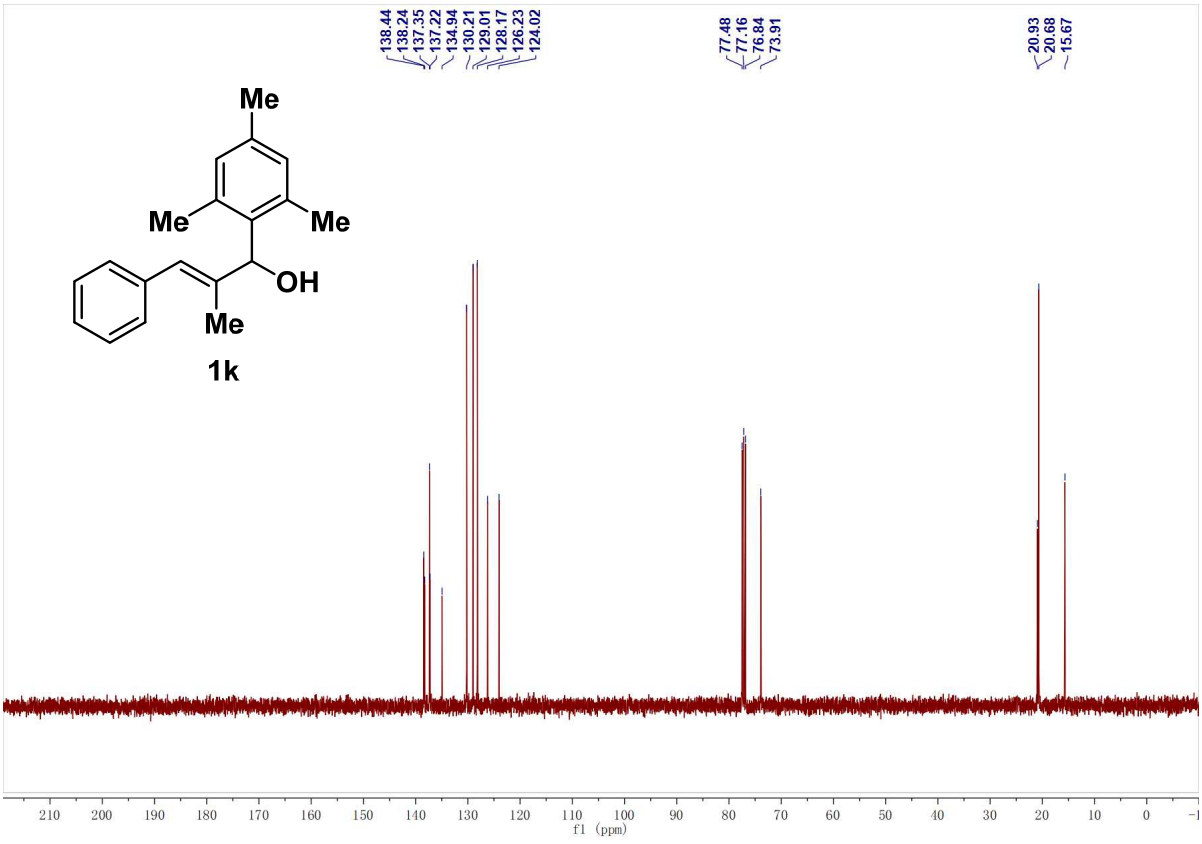


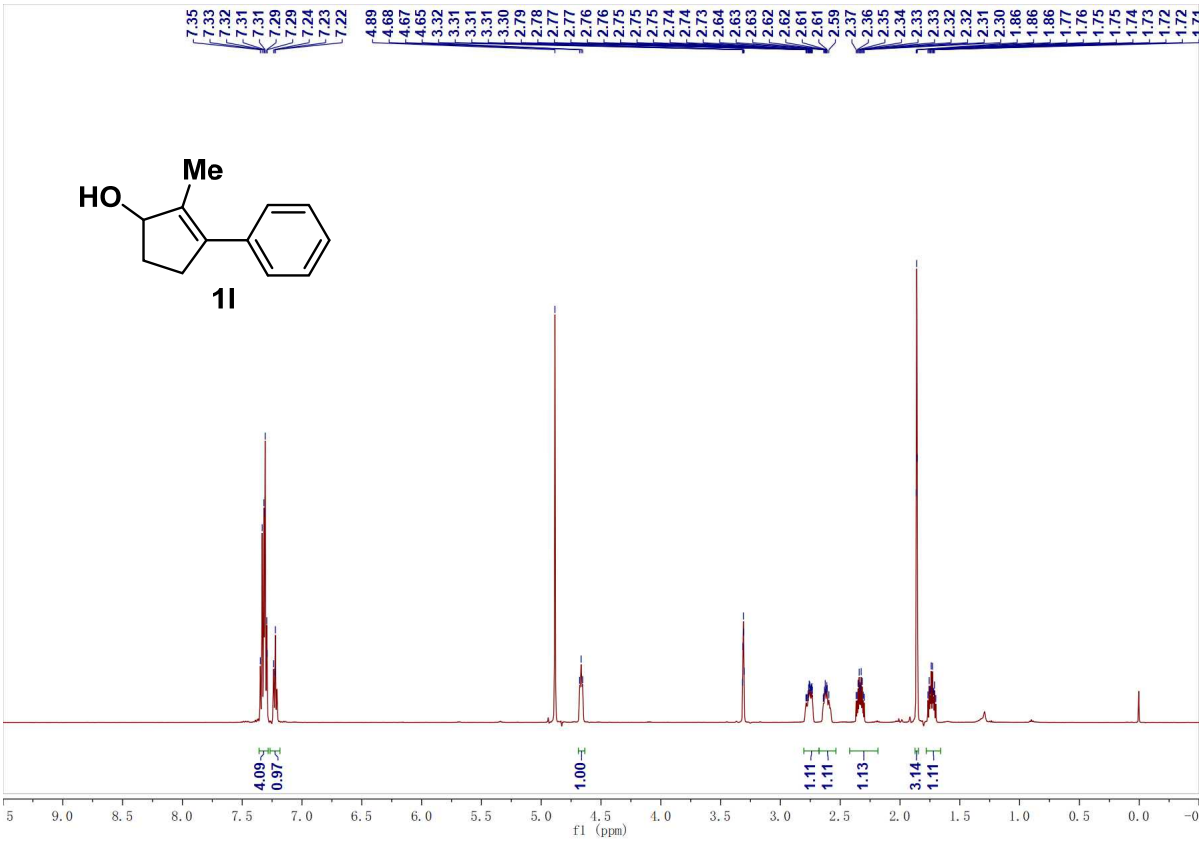
Compound **1k,** ^{1}H NMR



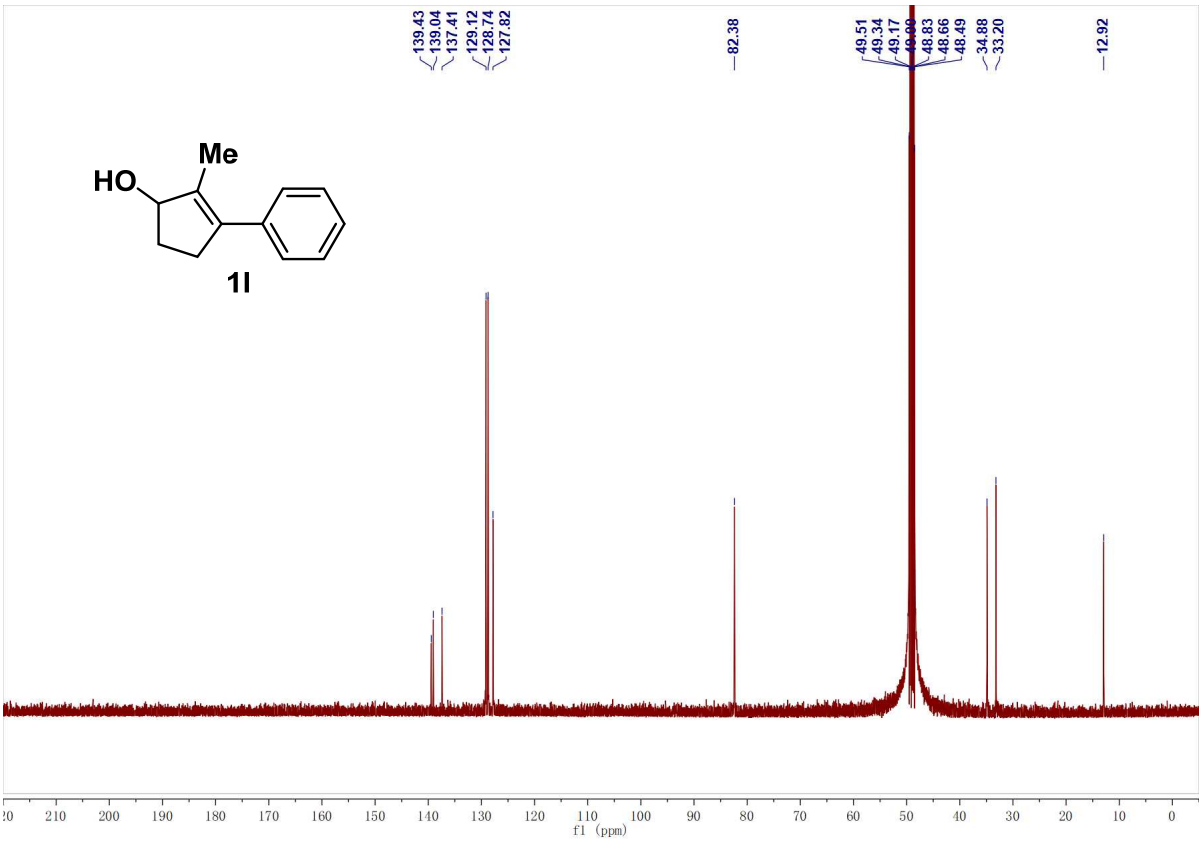
Compound **1k,** ^{13}C NMR



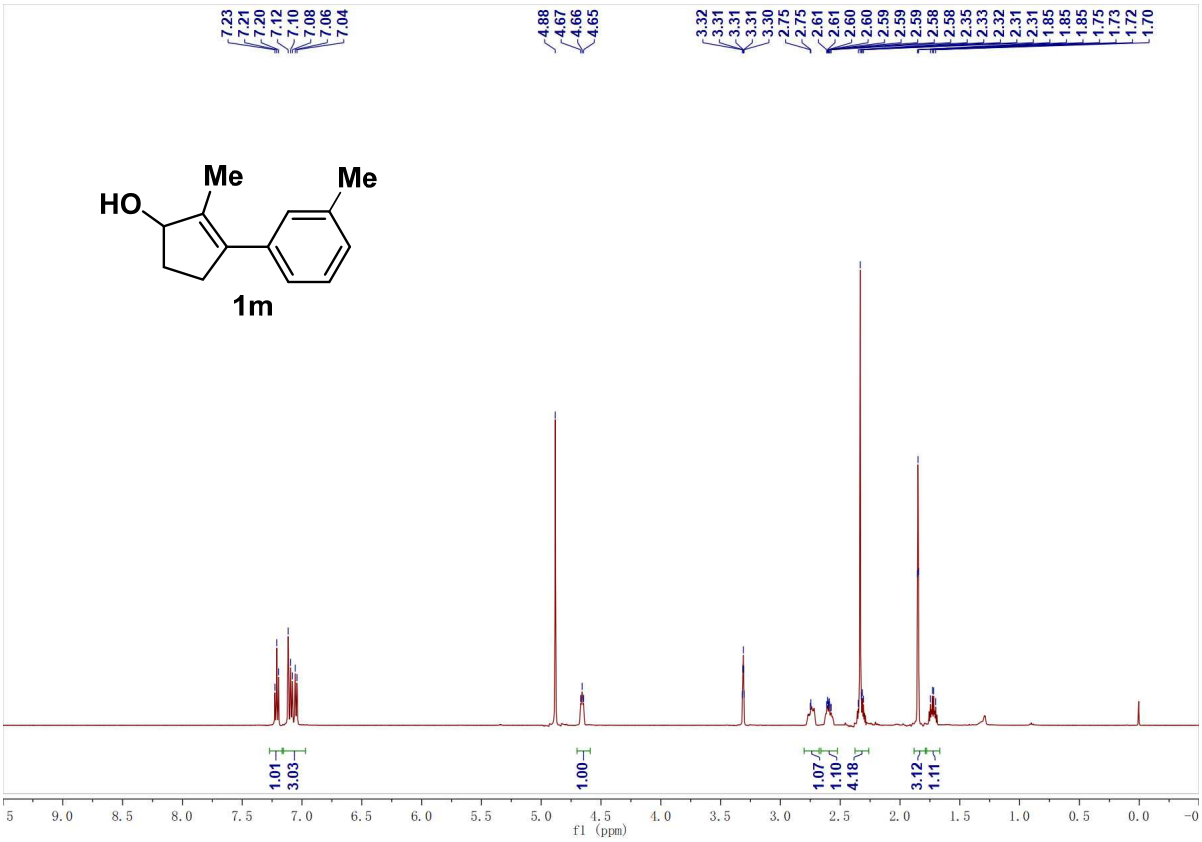
Compound **1l,** ^{1}H NMR



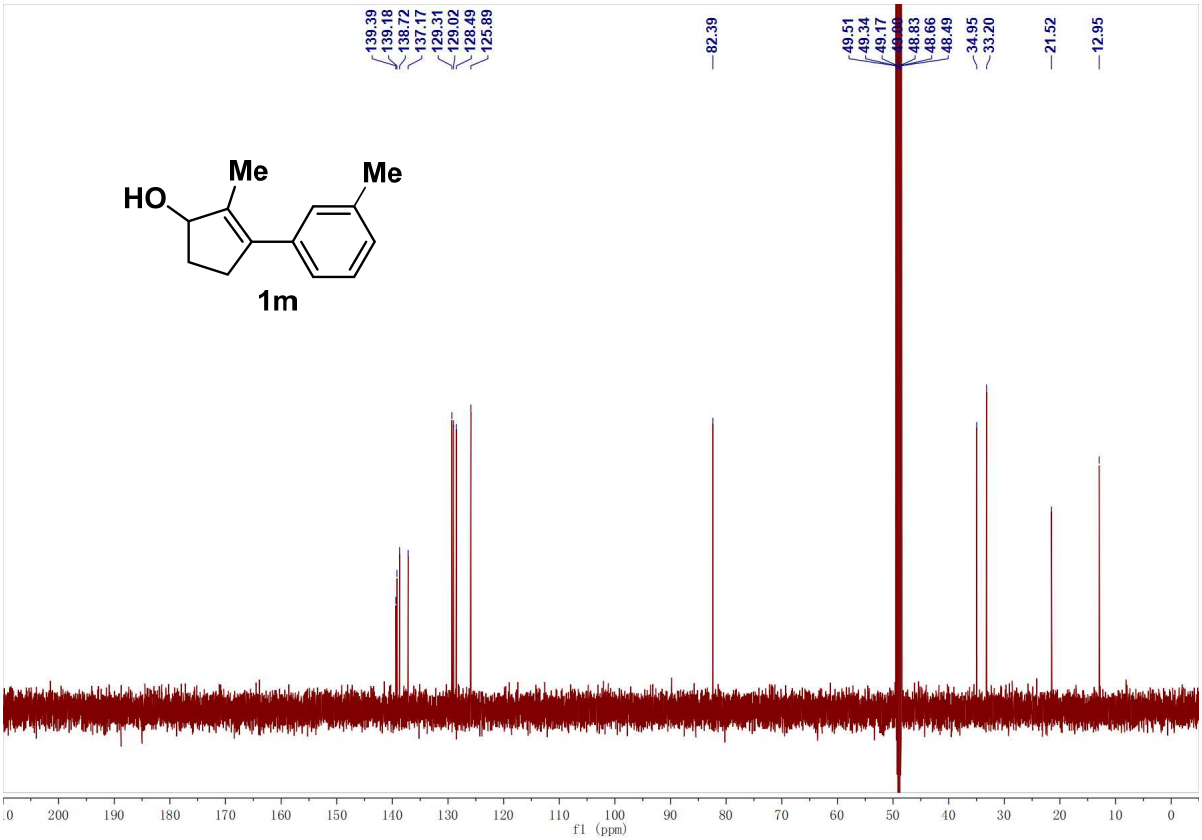
Compound **1l,** ^{13}C NMR



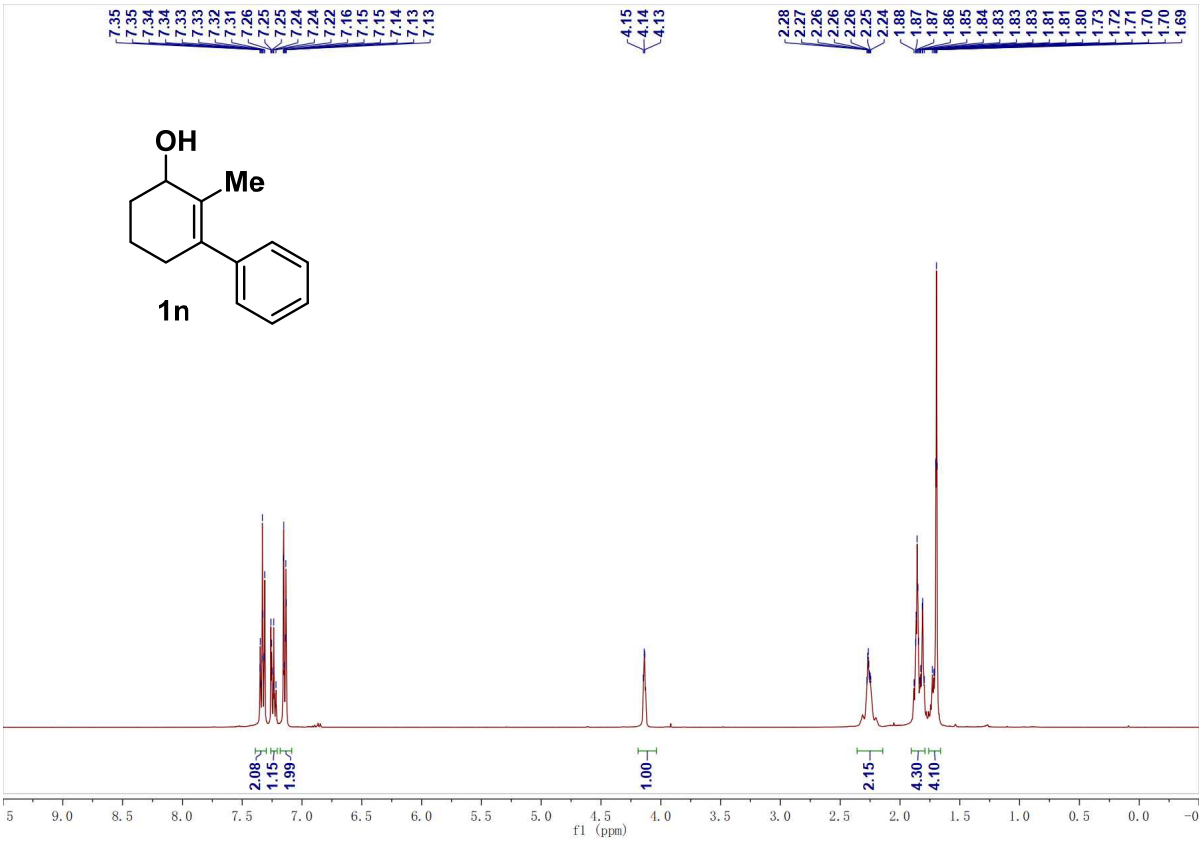
Compound **1m,** ^{1}H NMR



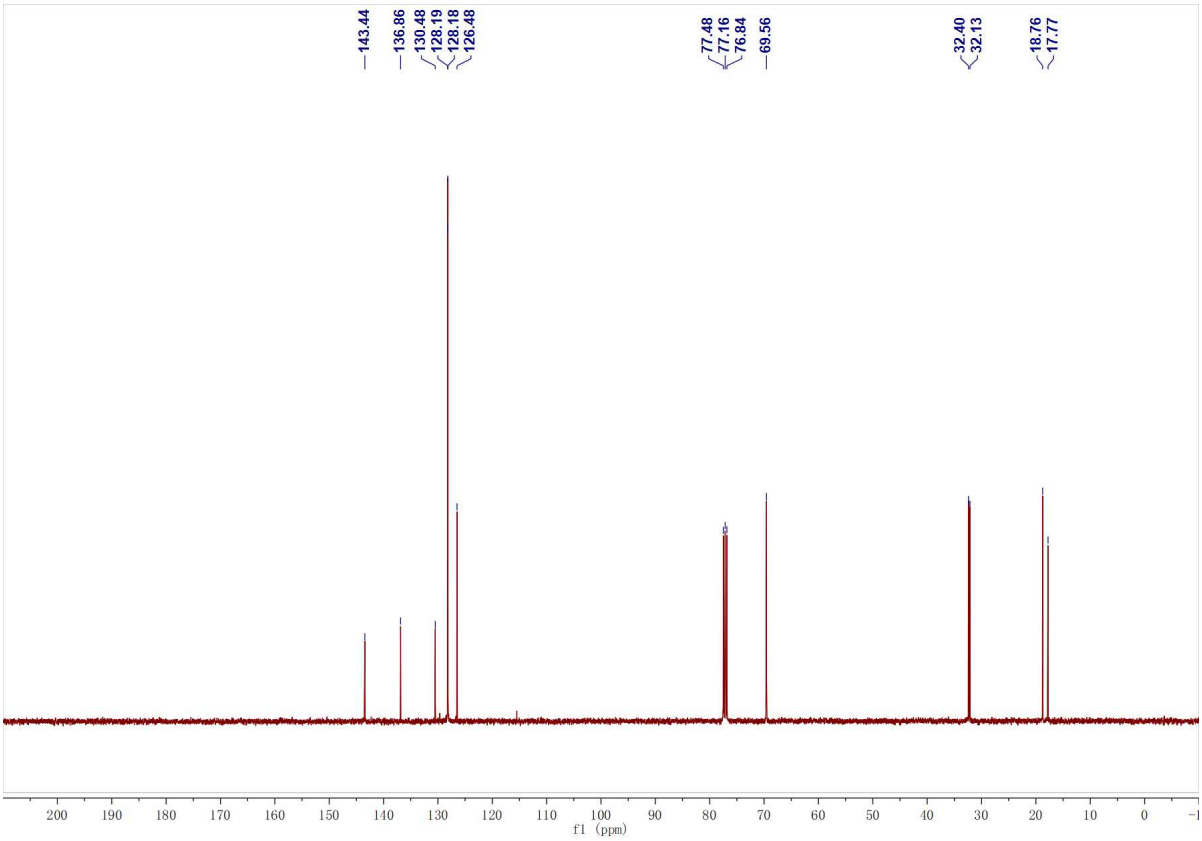
Compound **1m,** ^{13}C NMR



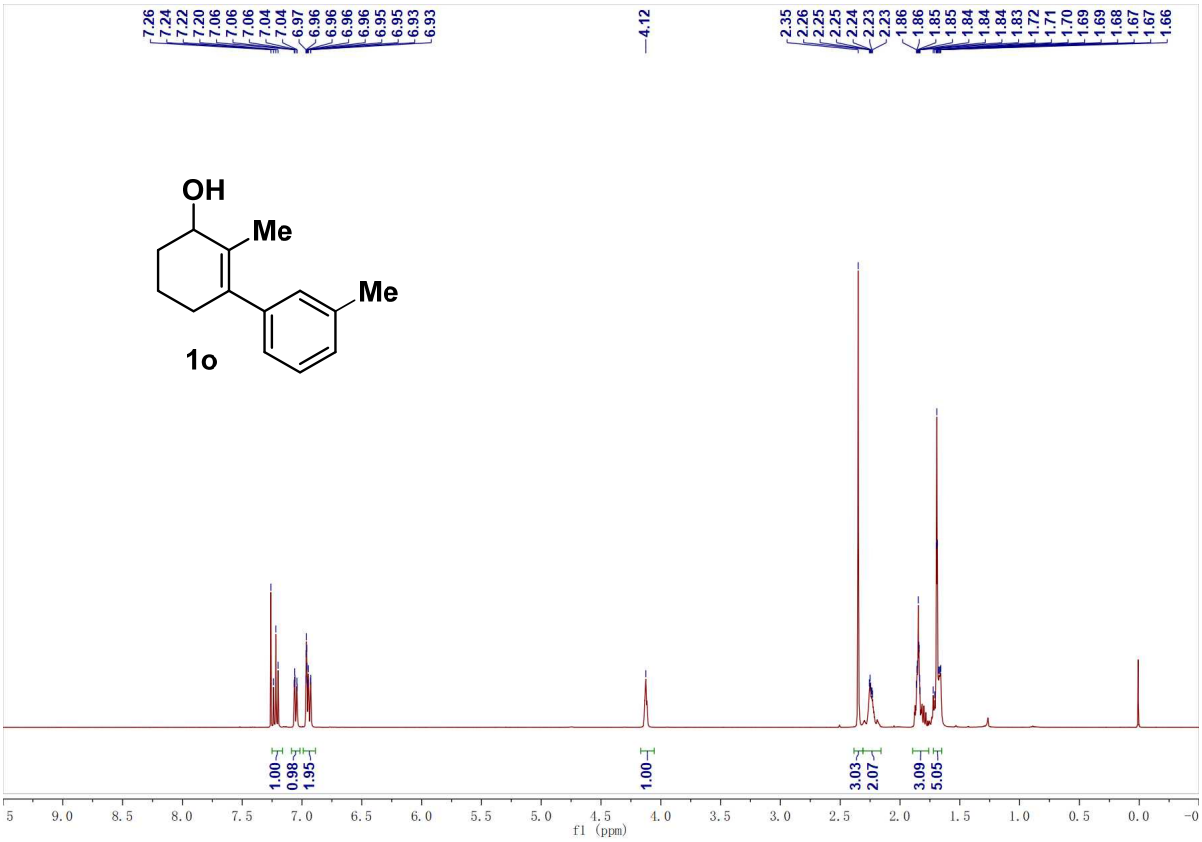
Compound **1n,** ^{1}H NMR



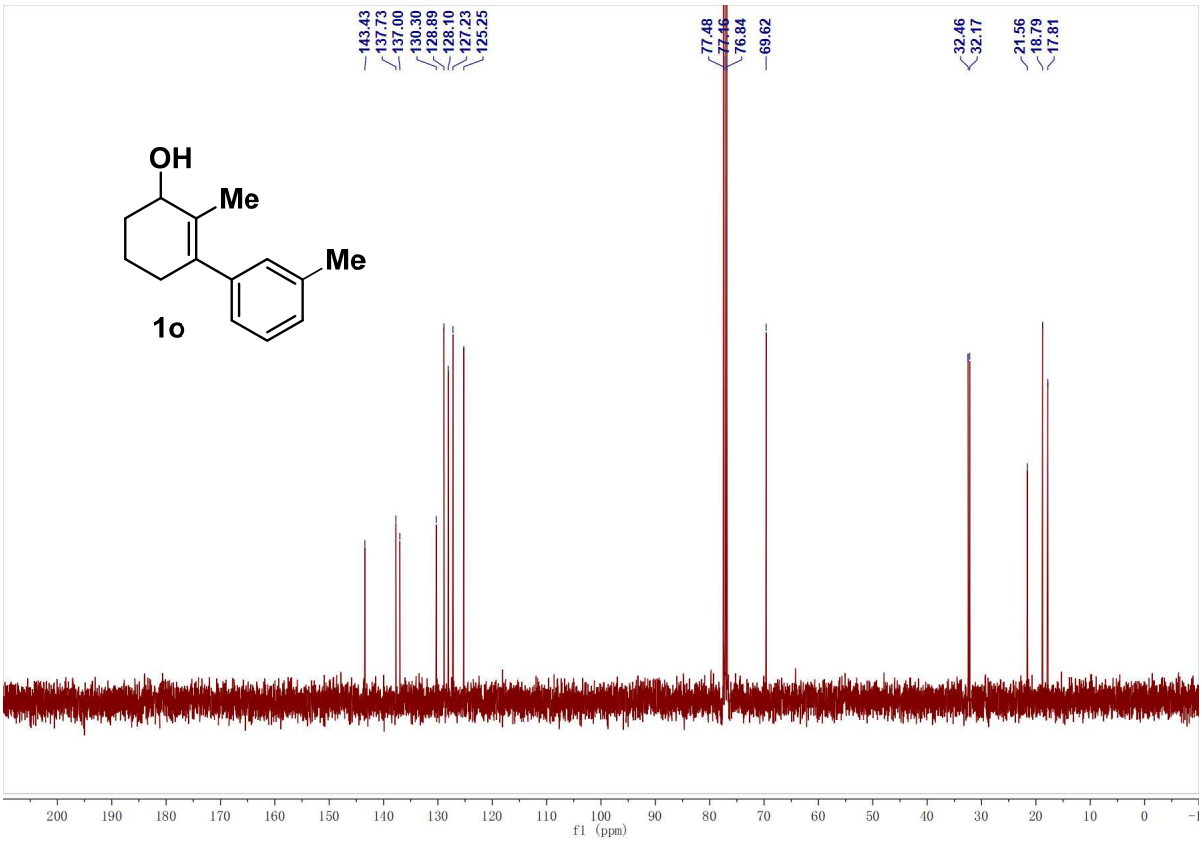
Compound **1n,** ^{13}C NMR



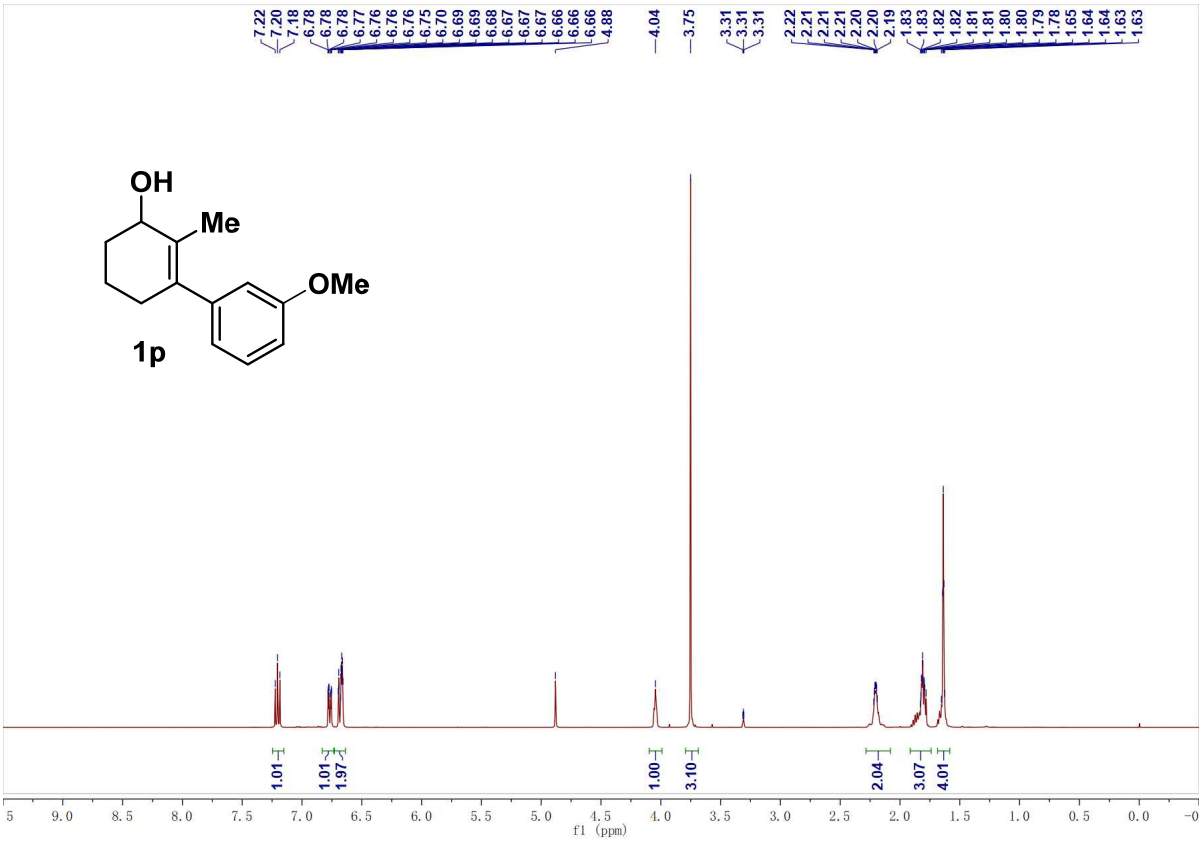
Compound **1o,** ^{1}H NMR



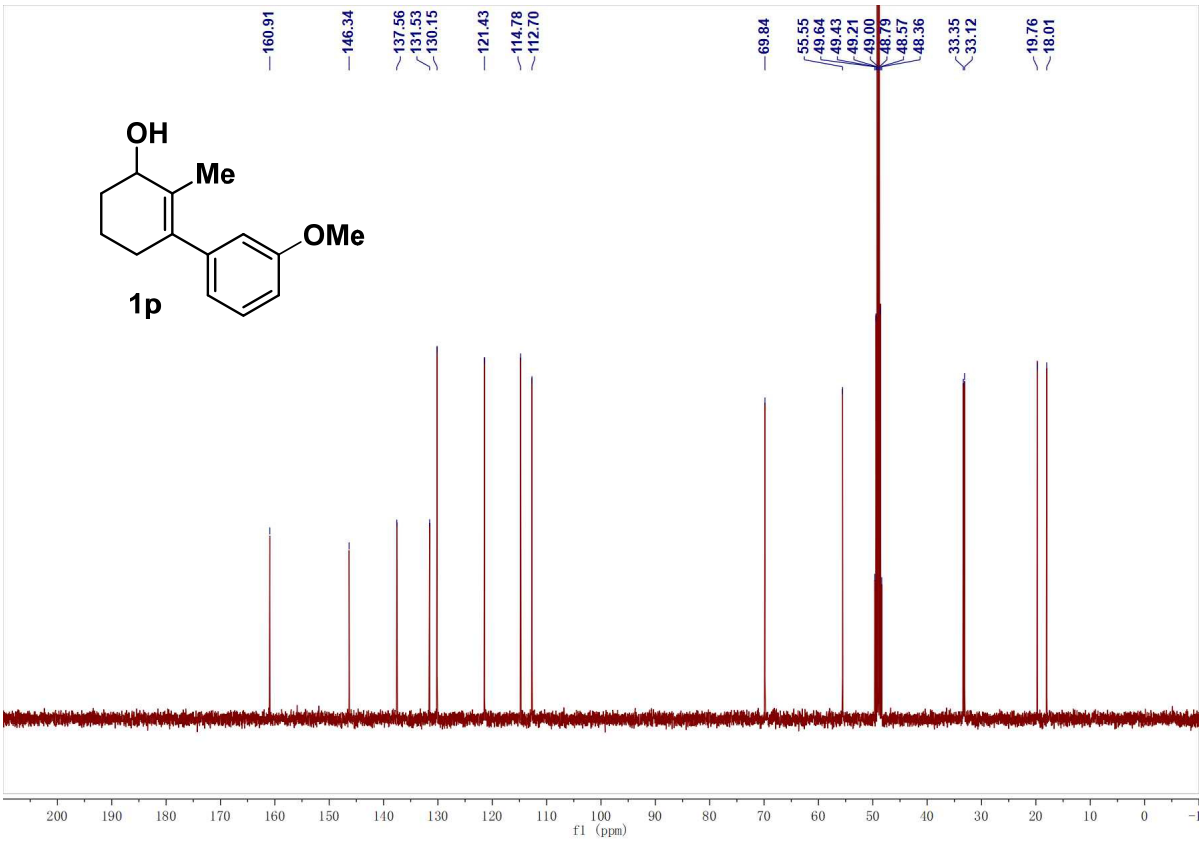
Compound **1o,** ^{13}C NMR



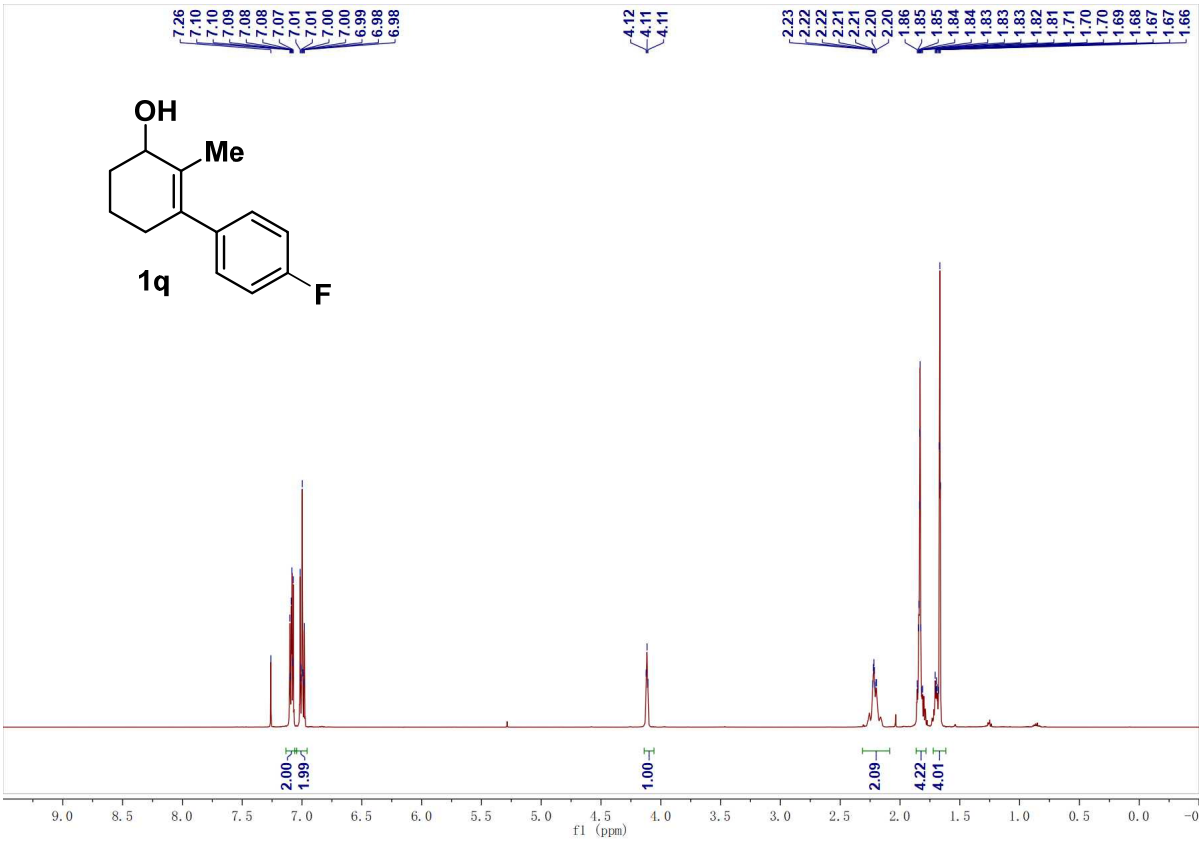
Compound **1p,** ^{1}H NMR



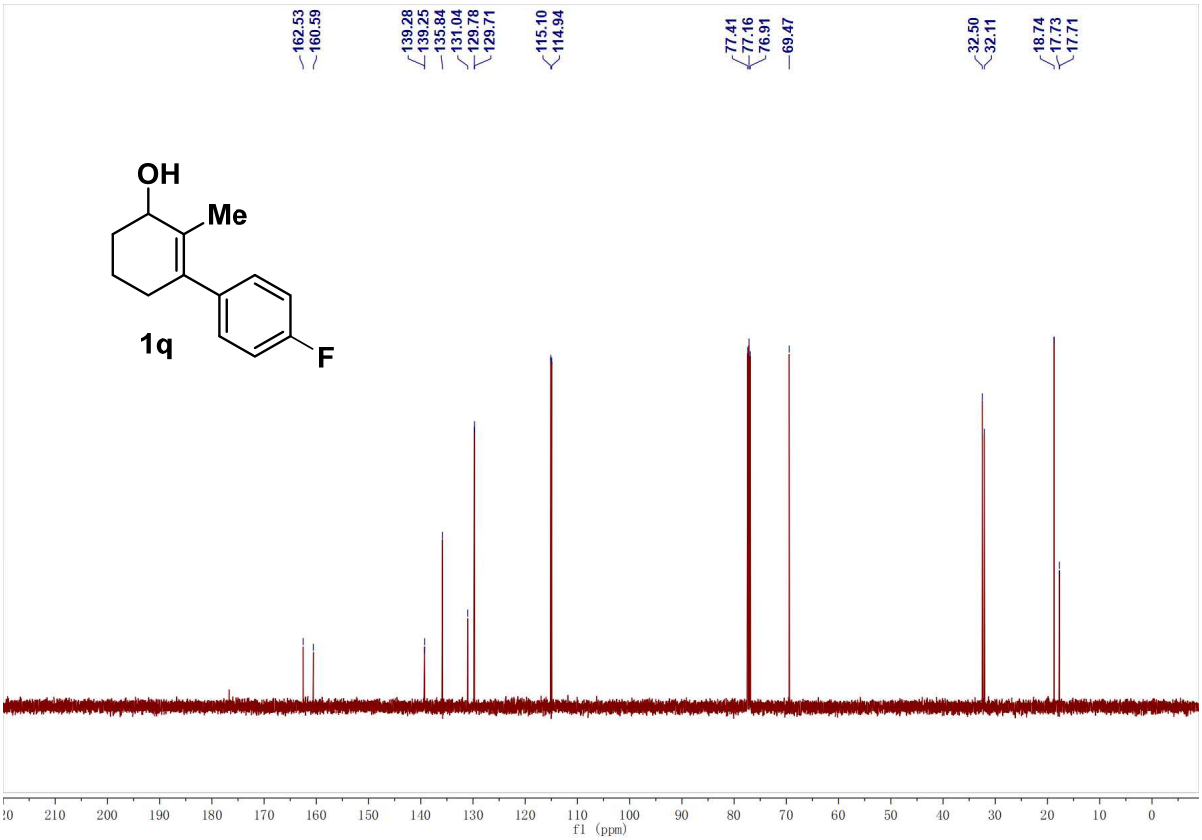
Compound **1p,** ^{13}C NMR



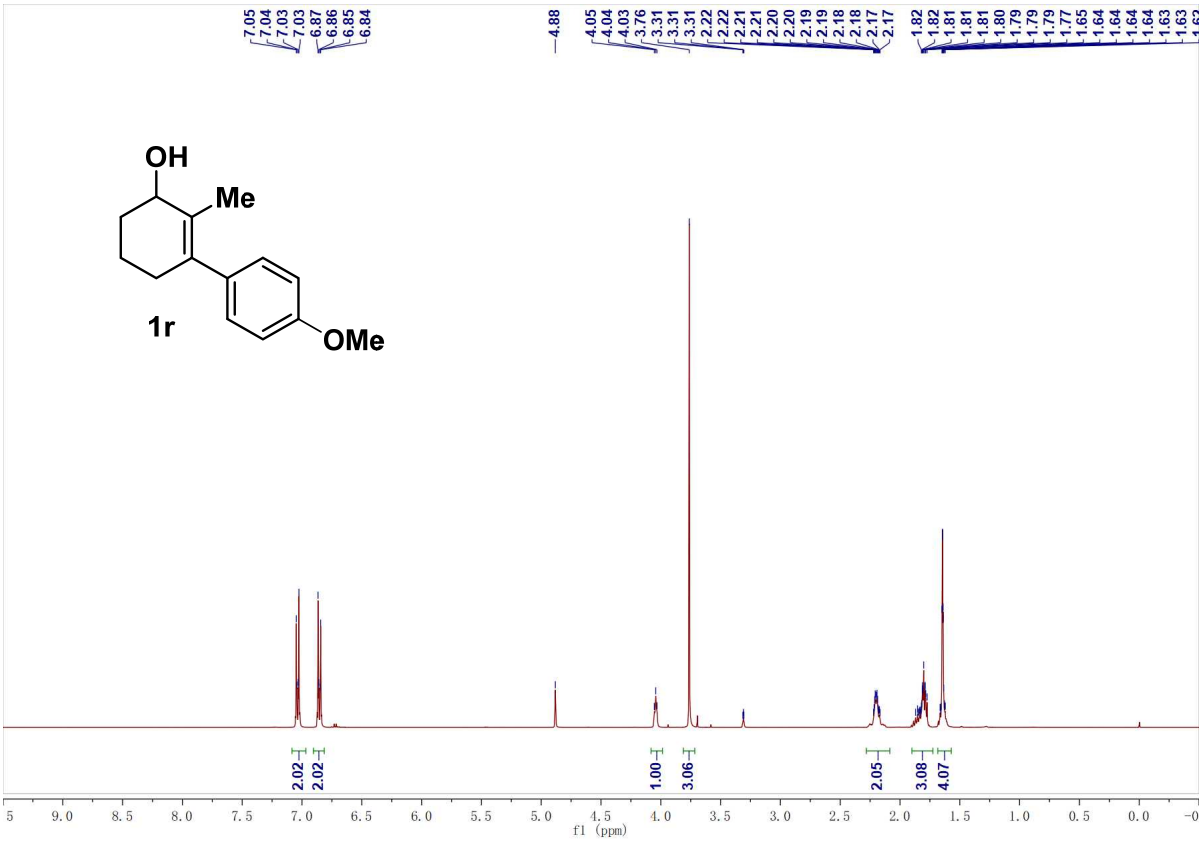
Compound **1q,** ^{1}H NMR



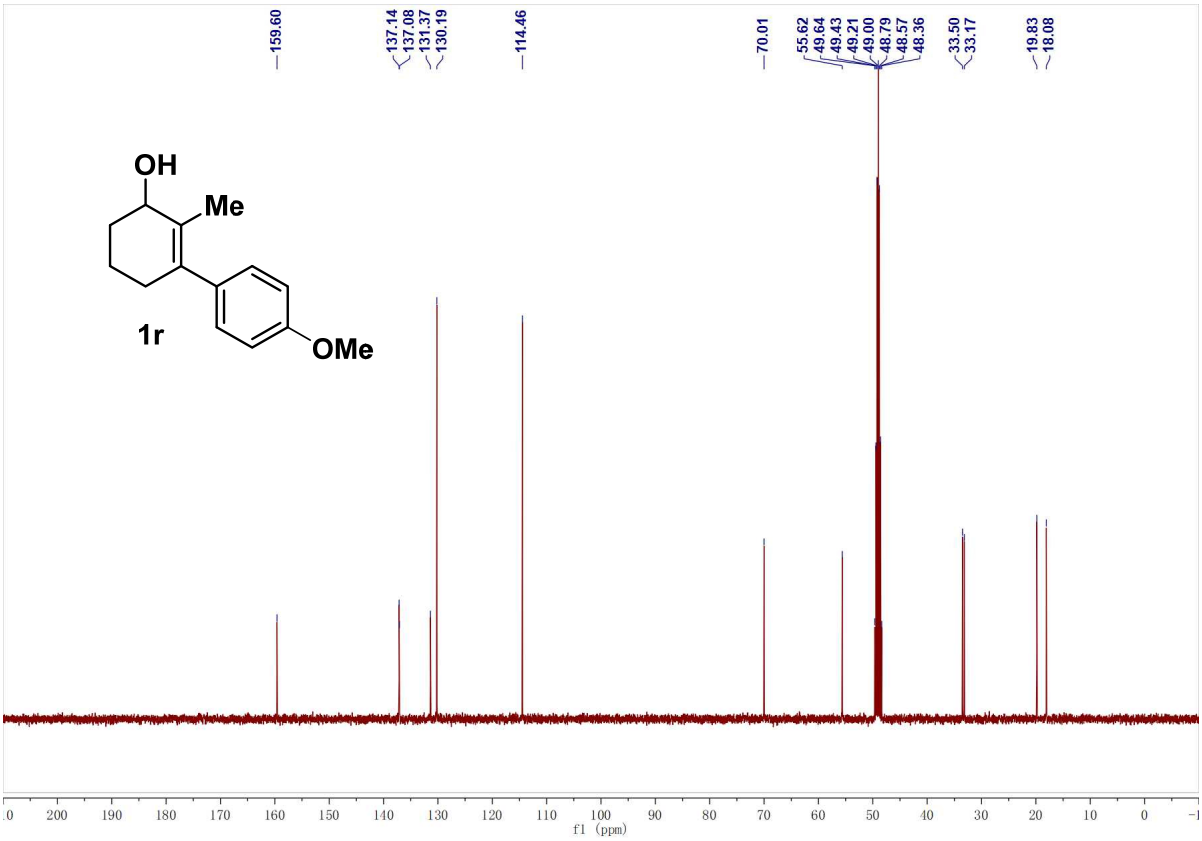
Compound **1q,** ^{13}C NMR



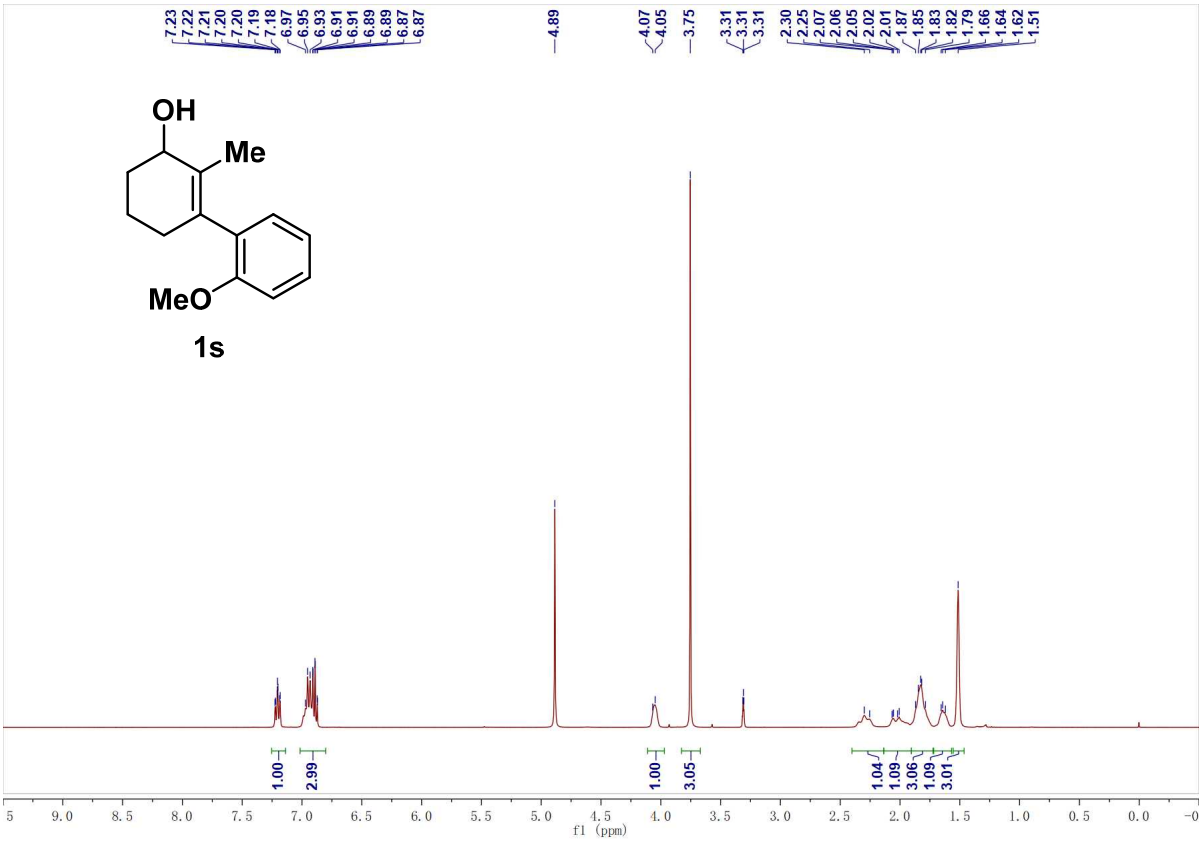
Compound **1r,** ^{1}H NMR



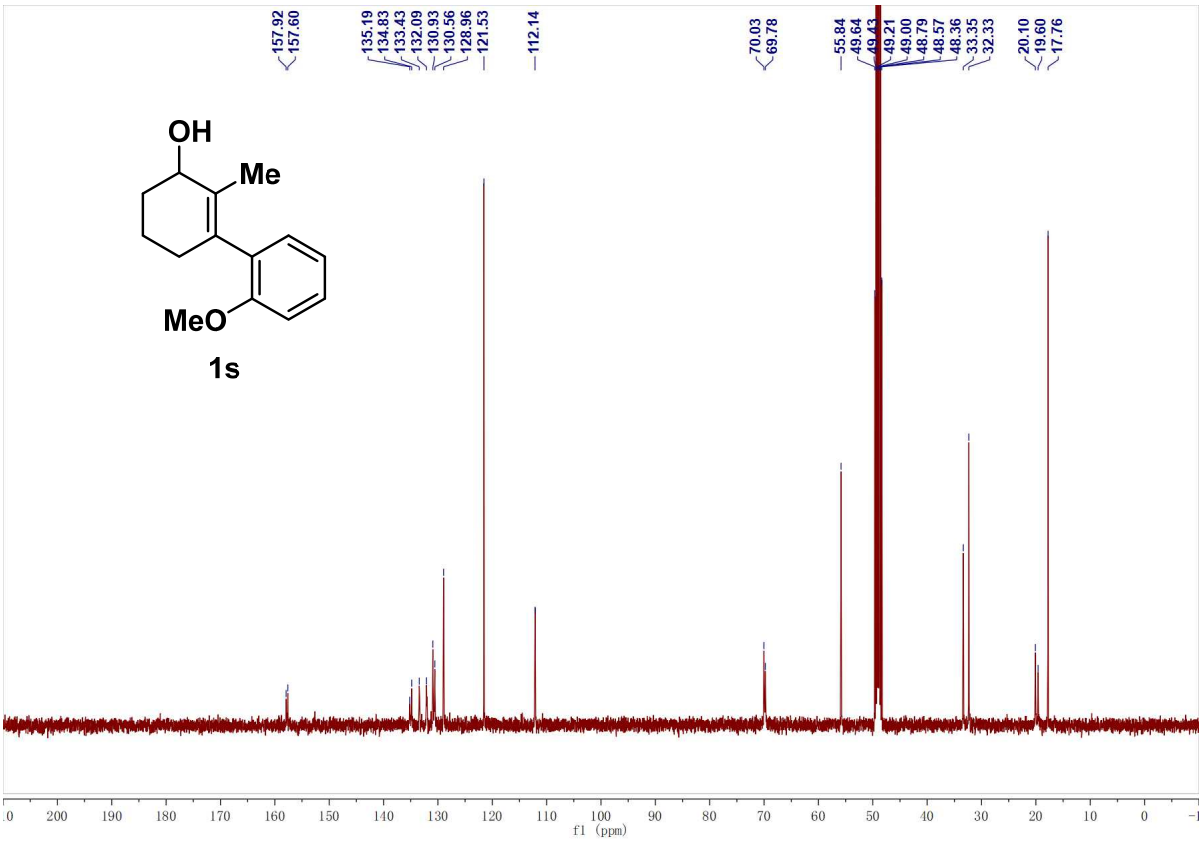
Compound **1r,** ^{13}C NMR



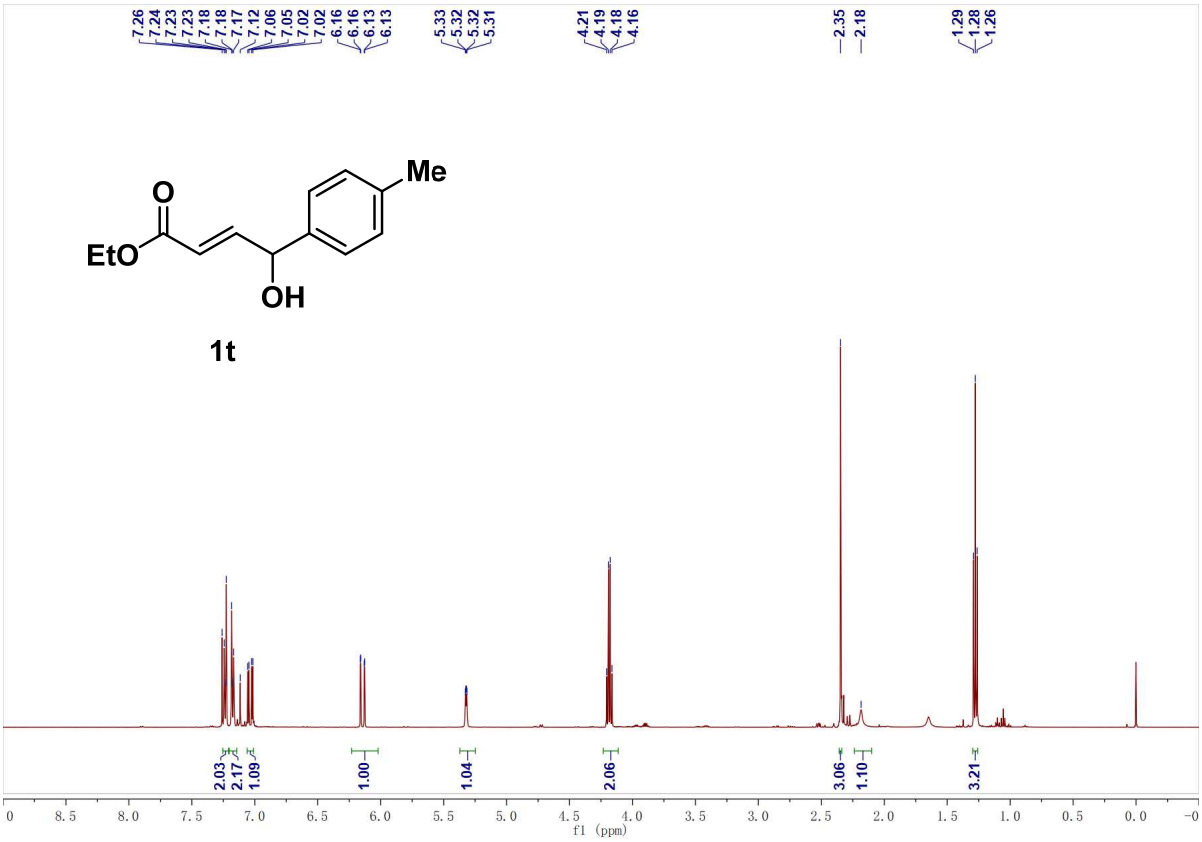
Compound **1s,** ^{1}H NMR



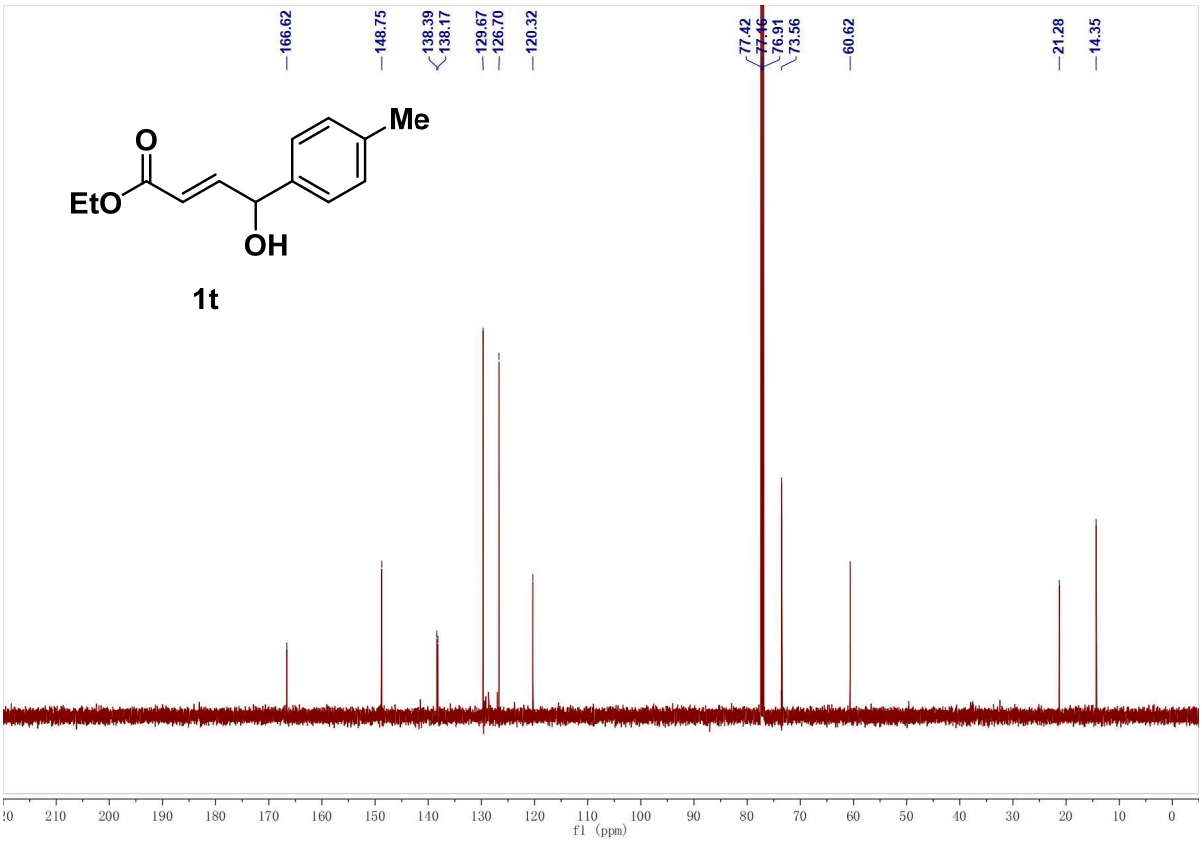
Compound **1s,** ^{13}C NMR[5]



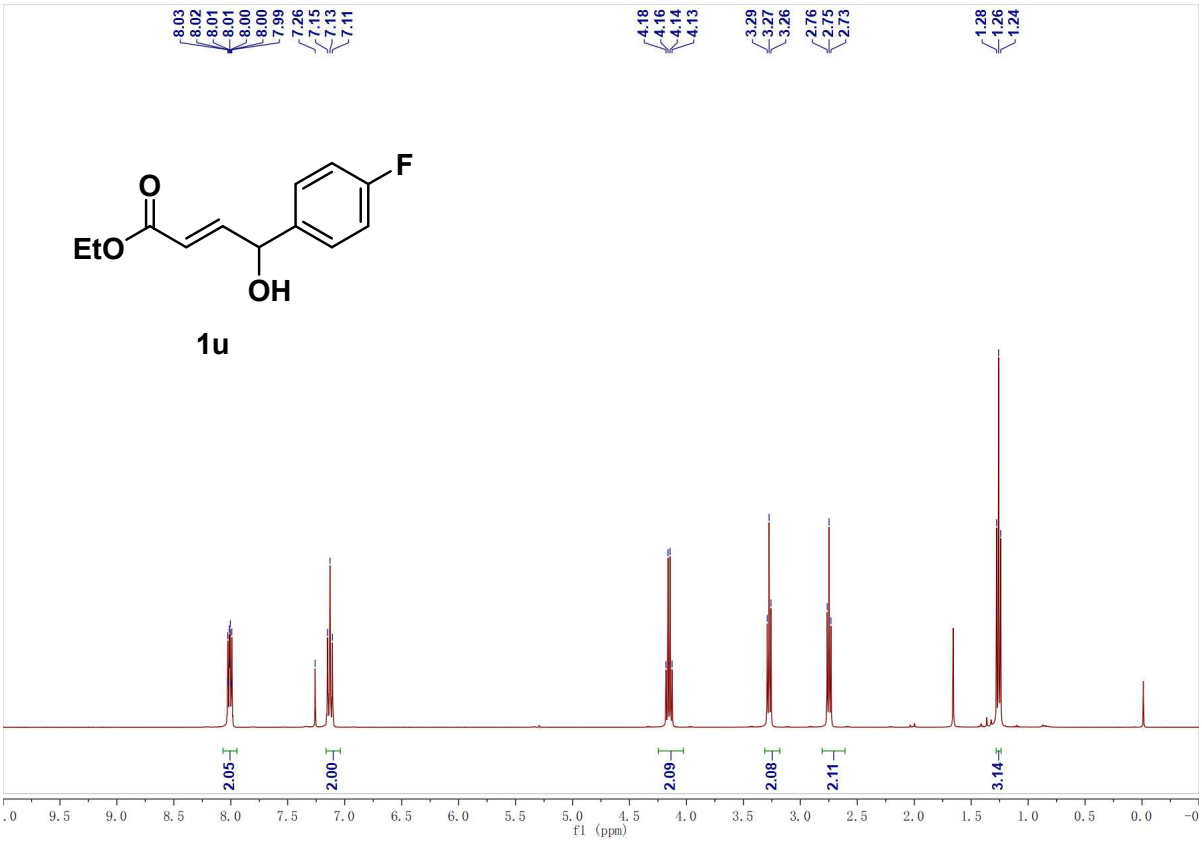
Compound **1t,** ^{1}H NMR



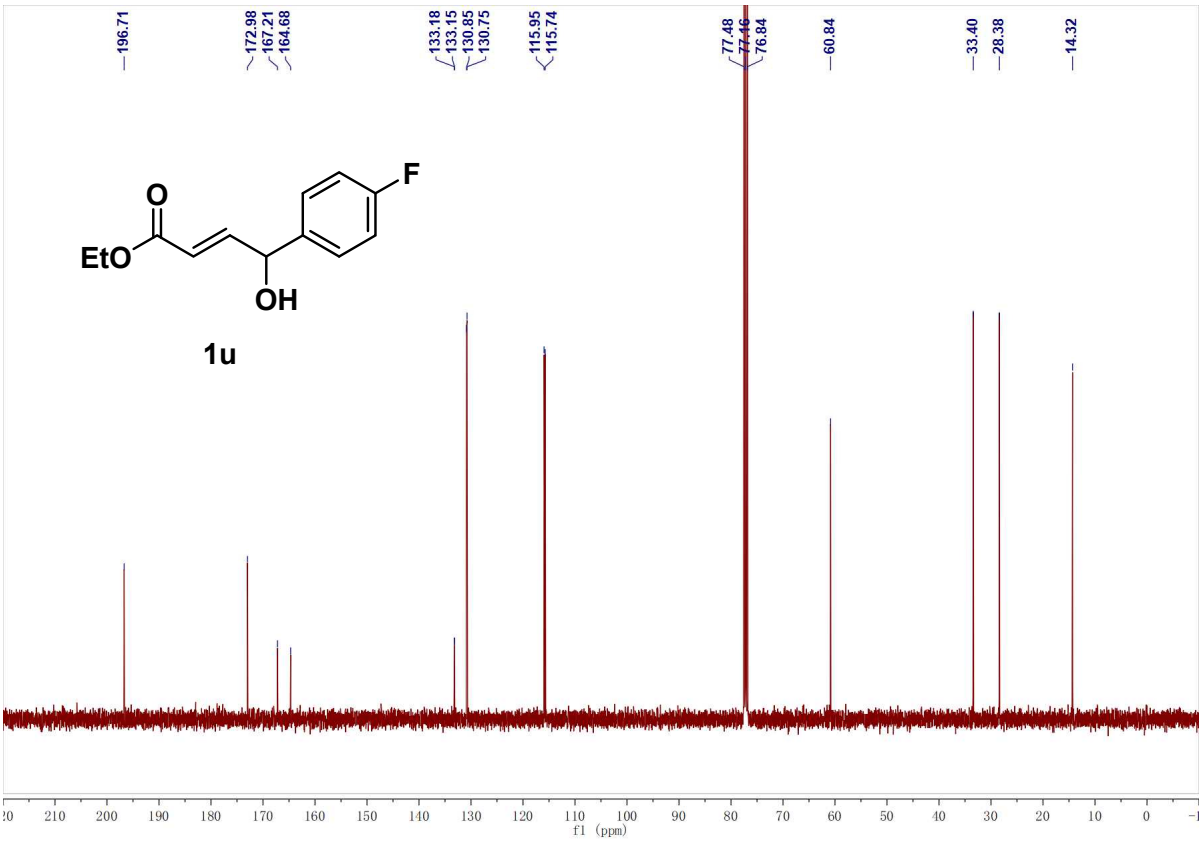
Compound **1t,** ^{13}C NMR



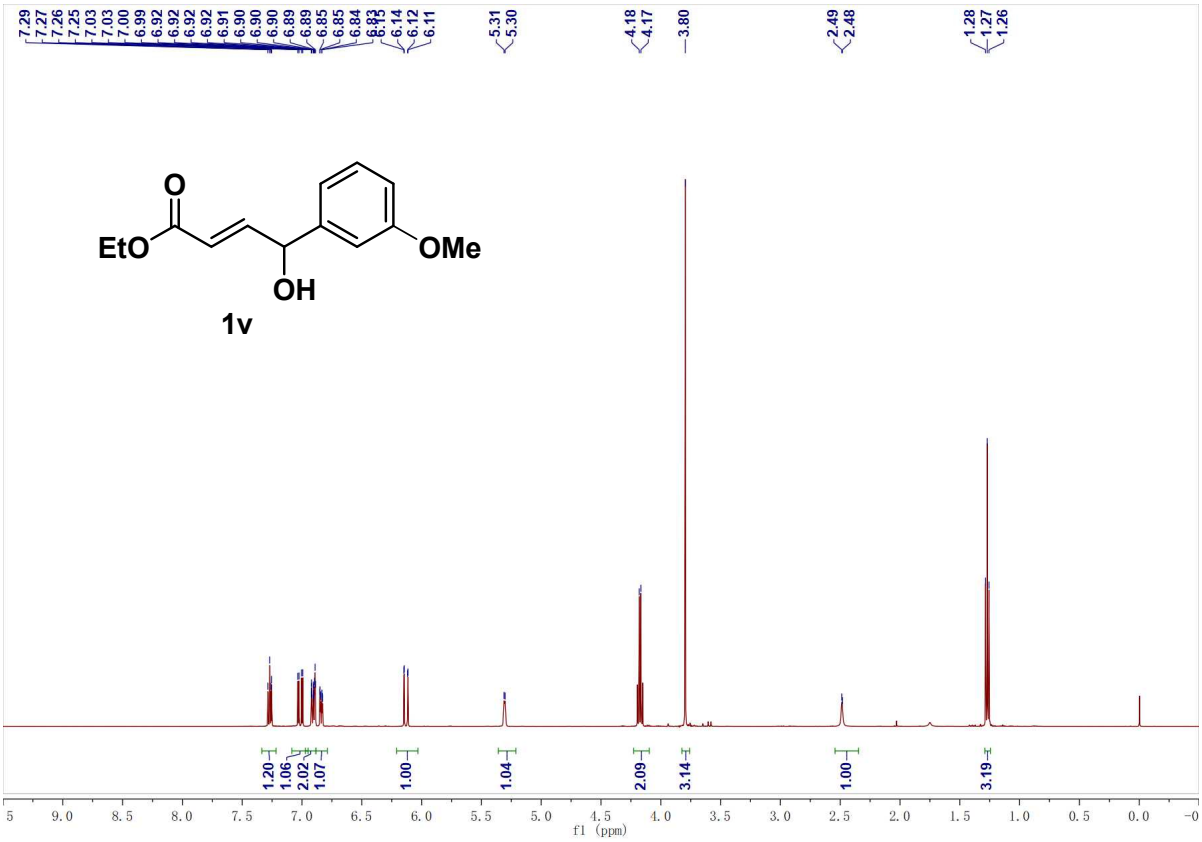
Compound **1u,** ^{1}H NMR



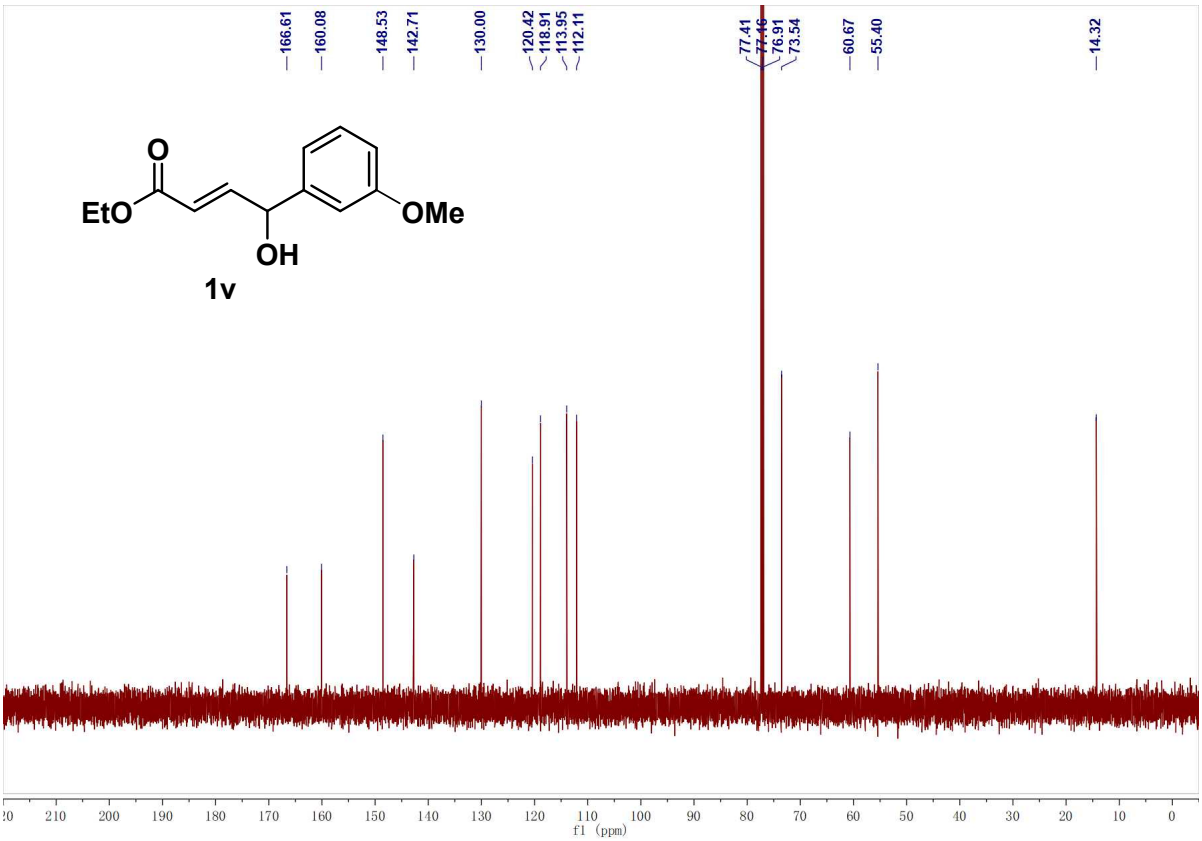
Compound **1u,** ^{13}C NMR



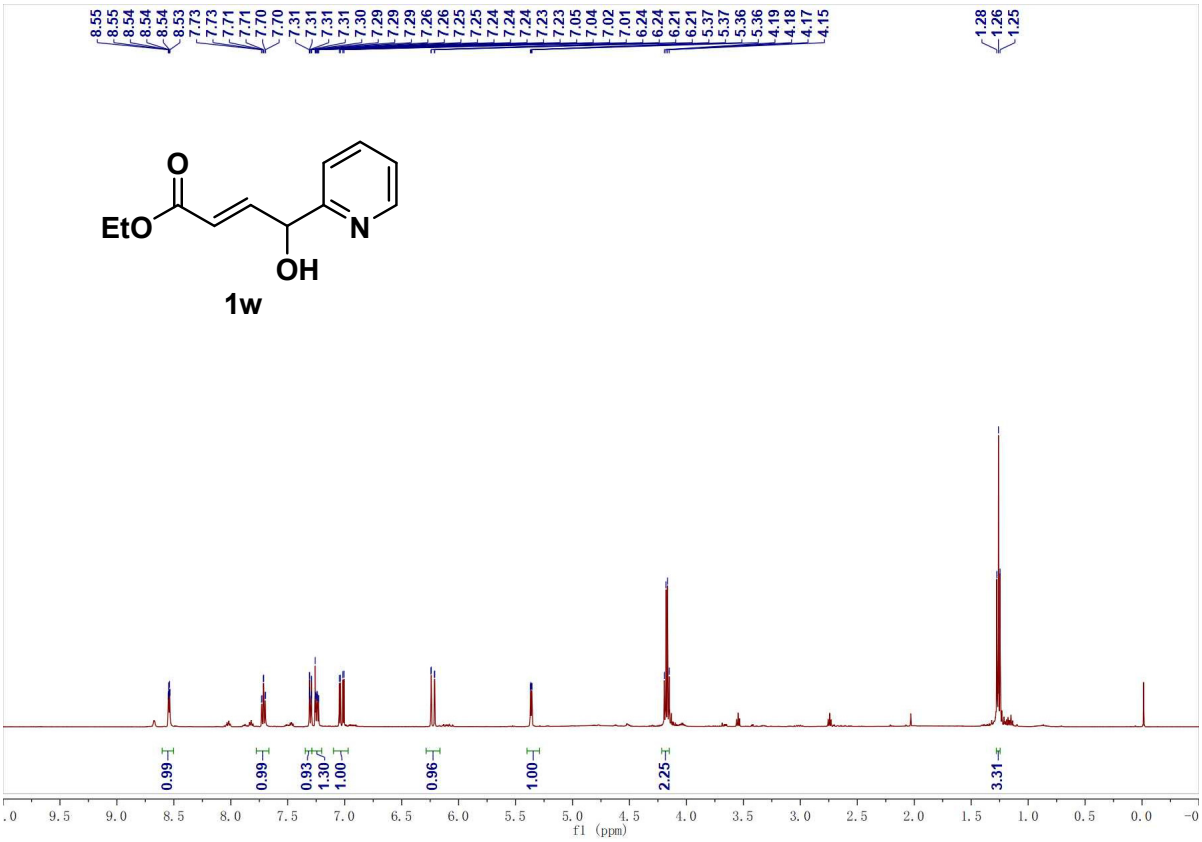
Compound **1v,** ^{1}H NMR



Compound **1v,** ^{13}C NMR



Compound **1w,** ^{1}H NMR



Compound **1w,** ^{13}C NMR