
Supporting Information

Intramolecular difunctionalization of methylenecyclopropanes tethered with carboxylic acid by visible-light photoredox catalysis

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Content

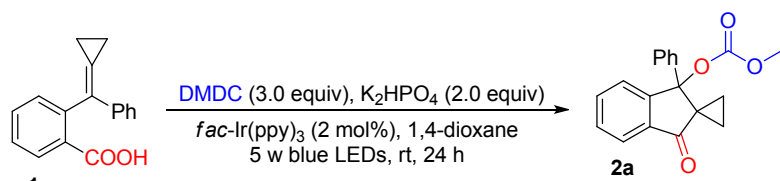
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1. General remarks

¹H NMR spectra were recorded on Agilent-400, Varian Mercury-400 and Bruker-400 spectrometer for solution in CDCl₃ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ¹³C NMR spectra were recorded on Agilent-400, Varian Mercury-400 and Bruker-400 spectrophotometers with complete proton decoupling spectrophotometers (CDCl₃: 77.0 ppm). The reference of ¹⁹F NMR (376 MHz) spectra is trichlorofluoromethane (δ ppm 0). Mass and HRMS spectra were recorded by ESI, EI or FI method. Organic solvents used were dried by standard methods when necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm⁻¹. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

2. Optimization of reaction conditions

Table S1 Optimization of reaction conditions



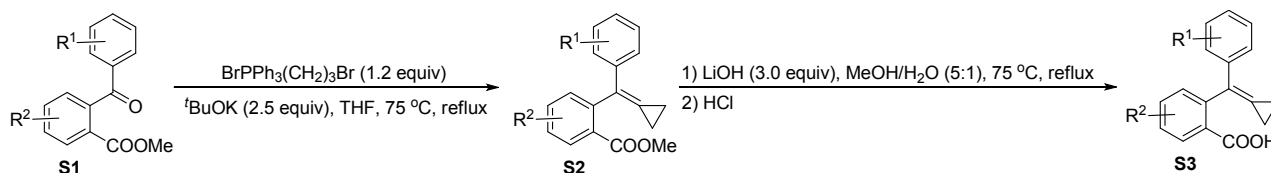
1a $\xrightarrow[\text{5 w blue LEDs, rt, 24 h}]{\text{DMDC (3.0 equiv), K}_2\text{HPO}_4 \text{ (2.0 equiv), } \text{fac-Ir(ppy)}_3 \text{ (2 mol\%)}, \text{1,4-dioxane}}$ **2a**

entry	variations	yield/ 2a ^a
1	none	> 99%
2	DMF instead of 1,4-dioxane	Trace
3	MeCN instead of 1,4-dioxane	23%
4	DCE instead of 1,4-dioxane	88%
5	K ₂ CO ₃ instead of K ₂ HPO ₄	> 99%
6	Cs ₂ CO ₃ instead of K ₂ HPO ₄	> 99%
7	no light	0%
8	no <i>fac-Ir(ppy)</i> ₃	0%
9	no K₂HPO₄	> 99%
10	no K ₂ HPO ₄	97% ^b

^a ¹H NMR yield using methyl benzoate as an internal standard. ^b isolated yield.

3. Procedures for preparation of reactants and transformations

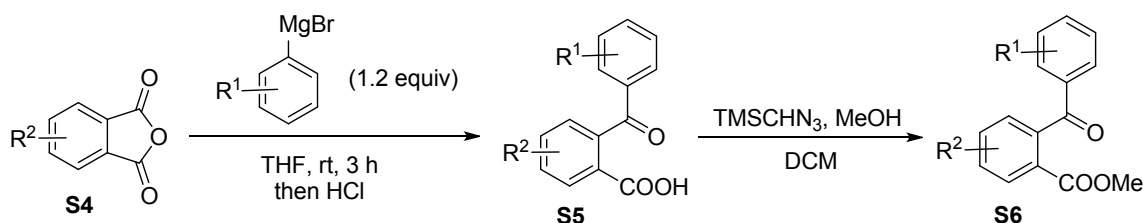
General procedure for preparation of carboxylic acids tethered MCP groups:



A solution of 3-bromopropyltriphenylphosphonium bromide (2.4 mmol, 1.2 equiv) and $t\text{BuOK}$ (5.0 mmol, 2.5 equiv) in 5 mL THF was stirred at 75 °C in oil bath under Ar for 30 min. Afterward, a solution of compound **S1** (2.0 mmol, 1.0 equiv) in 3 mL THF was added, and the reaction solution was stirred at 75 °C in oil bath for 8 h. Upon completion, the reaction was cooled to room temperature, and the mixture was filtered through a Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by a silica gel chromatography (EtOAc/hexane) to afford the corresponding products (**S2**) in 40% to 80% yields.

A mixture of **S2** (1.0 mmol) and LiOH (3.0 mmol, 3.0 equiv) in $\text{MeOH}/\text{H}_2\text{O}$ (5:1, 10 mL) was heated at 75 °C for 8 h, followed by concentrating under reduced pressure. 10 mL EtOAc was added to the residue, and the mixture was extracted with water (3 x 8 mL). The water layers were combined, of which pH value was adjusted to 2 with 2 M HCl , and then extracted with DCM, dried over anhydrous Na_2SO_4 , which afforded the products (**S3**) in high yields after removing the solvent.

General procedure A for preparation of methyl benzoate:



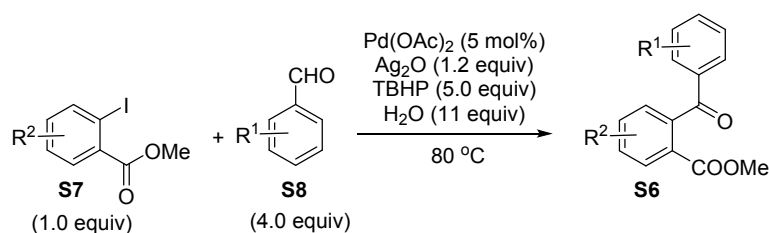
To a solution of phthalic anhydride (**S4**) (10 mmol, 1.0 equiv) in THF (20 mL) was added Grignard reagent (12 mmol, 1.2 equiv) at 0 °C. The reaction solution was stirred at room temperature for 3 h,

quenched with 2 M HCl (10 mL), extracted with EtOAc (3 x 8 mL), dried over Na₂SO₄ and concentrated. Purification by chromatography on silica gel (EtOAc/hexane) afforded **S5**.

To a solution of **S5** (5 mmol, 1.0 equiv) in 20 mL DCM was added 1 mL MeOH, then azidotrimethylsilane was added into the reaction solution dropwise until no obvious bubbles could be observed. Purification by chromatography on silica gel (EtOAc/hexane) afforded **S6**.

This method was applied for substrates **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1j**, **1k**, **1m**, **1u**, **1v**, **1w**, and **1x**.

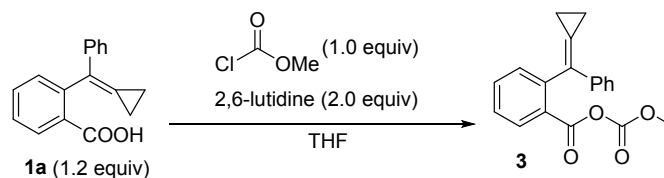
General procedure B for preparation of methyl benzoylbenzoate:



S6 was prepared with the similar procedures according to the previous protocol.¹

This method was applied for substrates **1h**, **1i**, **1l**, **1n**, **1o**, **1p**, **1q**, **1r**, **1s**, and **1t**.

Procedure for preparation of **3**:

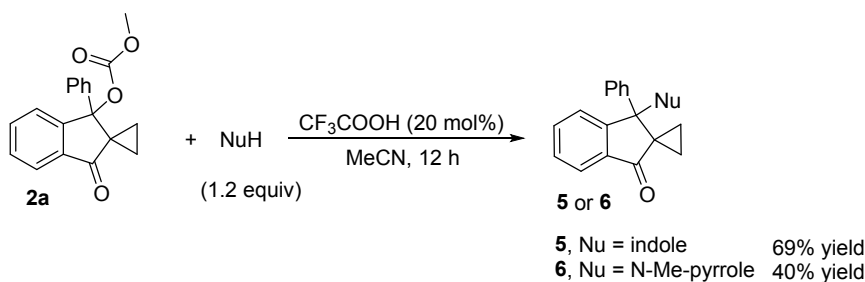


To a solution of **1a** (2 mmol, 1.2 equiv) in THF, methylchloroformate was added slowly (1.0 equiv). Afterward, 2,6-lutidine (2.0 equiv) was added slowly. After 10 min, Purification by chromatography on silica gel (EtOAc/hexane = 1:10) afforded **3**.

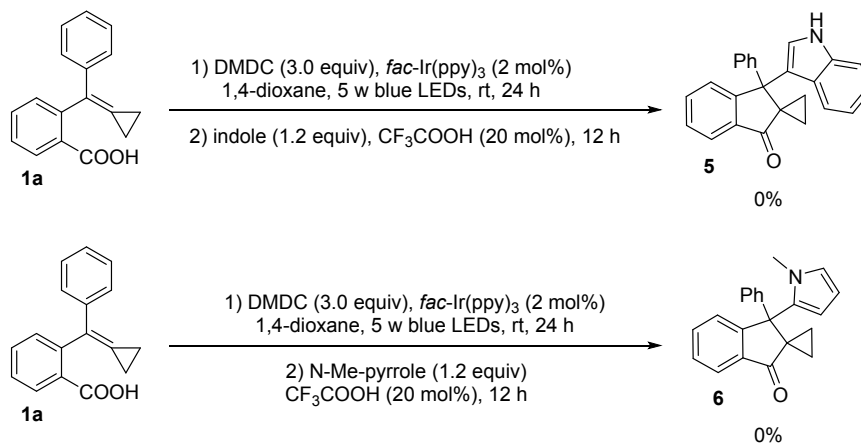
The preparation of **4** was according to the previous literature.²

The preparation of **10** was similar to the preparation of **1a**, in which BrPh₃(CH₂)₃Br was changed to BrPh₃(CH₂)₄Br.

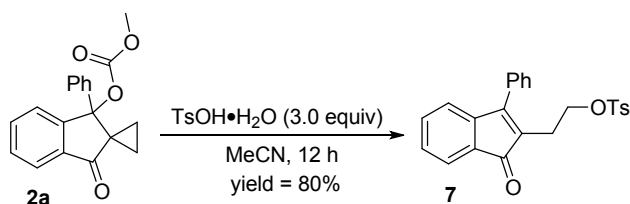
Procedures for the transformations of **2a**:



CF₃COOH (0.04 mmol) was added into the stirred solution of **2a** (0.2 mmol) and NuH (0.24 mmol) in 2 mL MeCN. After 12 h, purification by a chromatography on silica gel (EtOAc/hexane = 1:4) afforded **5** and **6** in 69% and 40% yields, respectively.

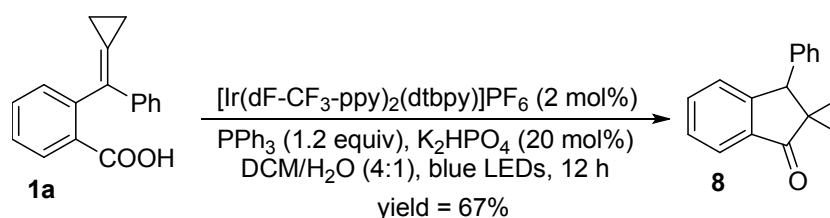


To a solution of **1** (0.2 mmol, 1.0 equiv) and dimethyl dicarbonate (0.6 mmol, 3.0 equiv) in dry 1,4-dioxane, *fac*-Ir(ppy)₃ (0.004 mmol, 2 mol%) was added. Afterward, the solution was sparged with argon for 10 min, and stirred at room temperature for 24 h under the radiation of 5 w blue LEDs. Indole or N-Me-pyrrole (1.2 equiv) and CF₃COOH (20 mol%) were added to the reaction solution respectively, and the mixture solution was stirred for 12 h. **5** and **6** could not be detected.



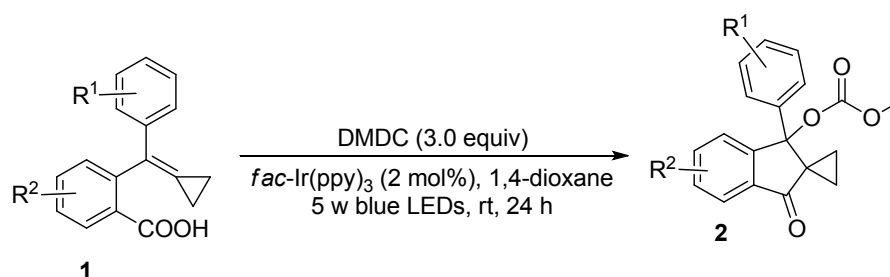
Toluenesulfonic acid monohydrate (0.6 mmol) and **2a** (0.2 mmol) were dissolved in 2 mL MeCN, and the reaction solution was stirred at room temperature for 12 h. Afterward, purification by a chromatography on silica gel (EtOAc/hexane = 1:4) afforded **7** in 80% yield.

Procedure for photocatalyzed oxidized triphenylphosphine's deoxygenation:

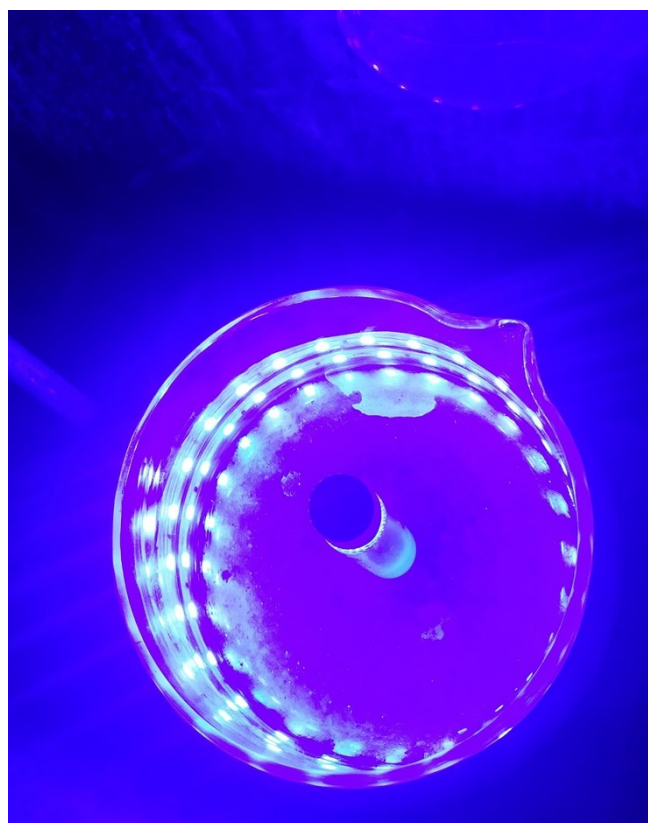


1a (0.2 mmol, 1.0 equiv), Ir catalyst (2 mol%), PPh₃ (0.24 mmol, 1.2 equiv), K₂HPO₄ (0.04 mmol, 20 mol%) and DCM/H₂O (4:1, 2 mL) was added into a Schlenk tube and degassed with argon for 5 minutes. The reaction solution was stirred for 12 h under 5 w blue LEDs. Afterward, purification by a chromatography on silica gel (EtOAc/hexane = 1:10) afforded **8** in 67% yield.

4. General procedure of cyclization reactions



To a solution of **1** (0.2 mmol, 1.0 equiv) and dimethyl dicarbonate (0.6 mmol, 3.0 equiv) in dry 1,4-dioxane, *fac*-Ir(ppy)₃ (0.004 mmol, 2 mol%) was added. Afterward, the solution was sparged with argon for 10 min, and stirred at room temperature for 24 h under the radiation of 5 w blue LEDs. The reaction solution was mixed with silica gel for 10 min. Purification by chromatography on silica gel (EtOAc:hexane = 1:10) afforded the cyclized products.



5. Emission quenching experiments

Emission intensities were recorded using an Agilent Cary Eclipse fluorescence spectrophotometer. Solutions 0.001 M of *fac*-Ir(ppy)₃ and different concentrations of quencher in anhydrous 1,4-dioxane were degassed by sparging with argon for 10 minutes in 10 mm path length quartz cuvette, irradiated at 375 nm and emission intensity collected at 513 nm.

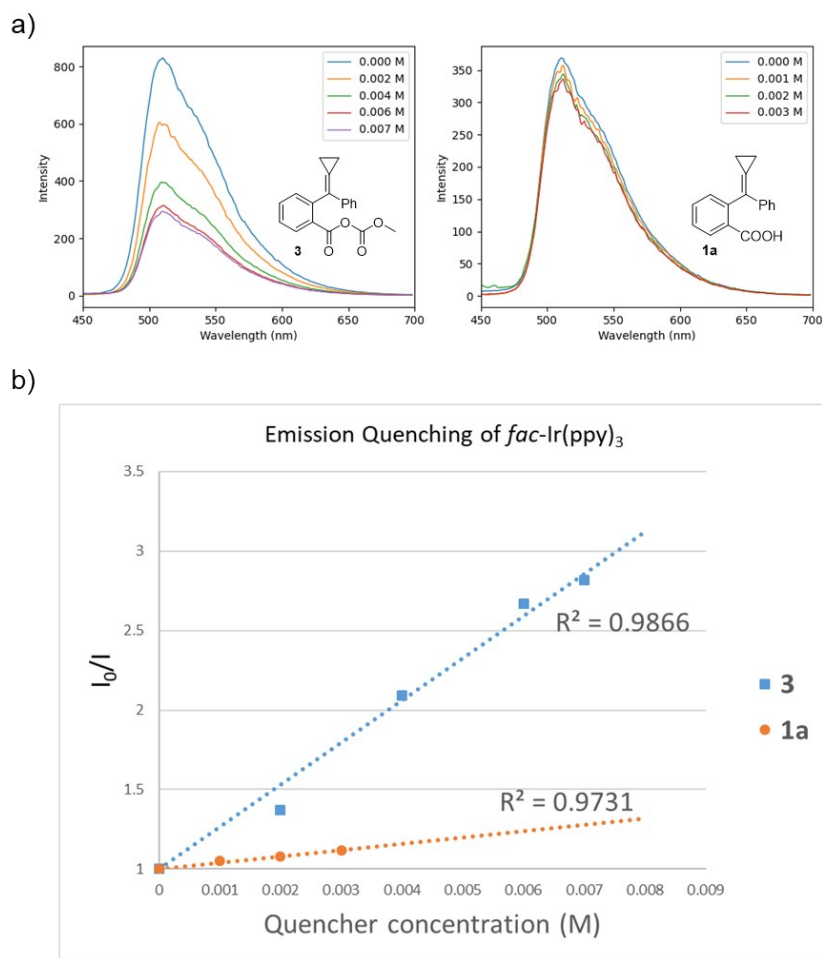


Figure S1. *fac*-Ir(ppy)₃ emission quenching with **1a** and **3**.

6. Reduction potential measurement

Determination of the reduction potential of **3** was performed by cyclic voltammetry which was studied with a CHI 660C electrochemical workstation using a glassy carbon working electrode, a platinum wire counter electrode and an $\text{Ag}^+/\text{AgNO}_3$ reference electrode. Measurements were performed on 25 mL samples prepared with a substrate concentration of 0.01 M in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in an acetonitrile electrolyte solution with a sweep rate of 100 mV/s. Before each measurement, the samples were sparged with argon for 20 min. Measured reduction potentials were converted to reference the saturated calomel electrode (SCE) by adding 0.327 mV. The reduction potential of **3** was calculated considering an irreversible process and gives and $E_{1/2}^{\text{red}} = -1.775 \text{ V vs SCE}$.

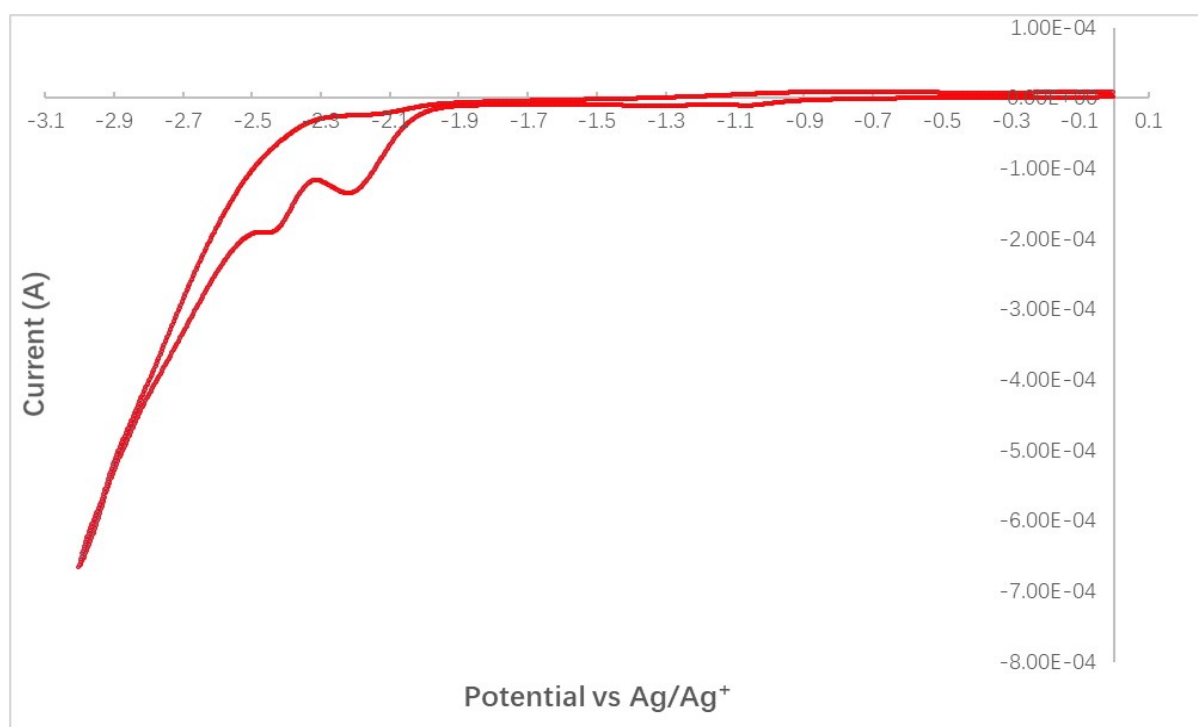
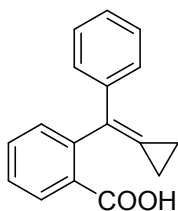
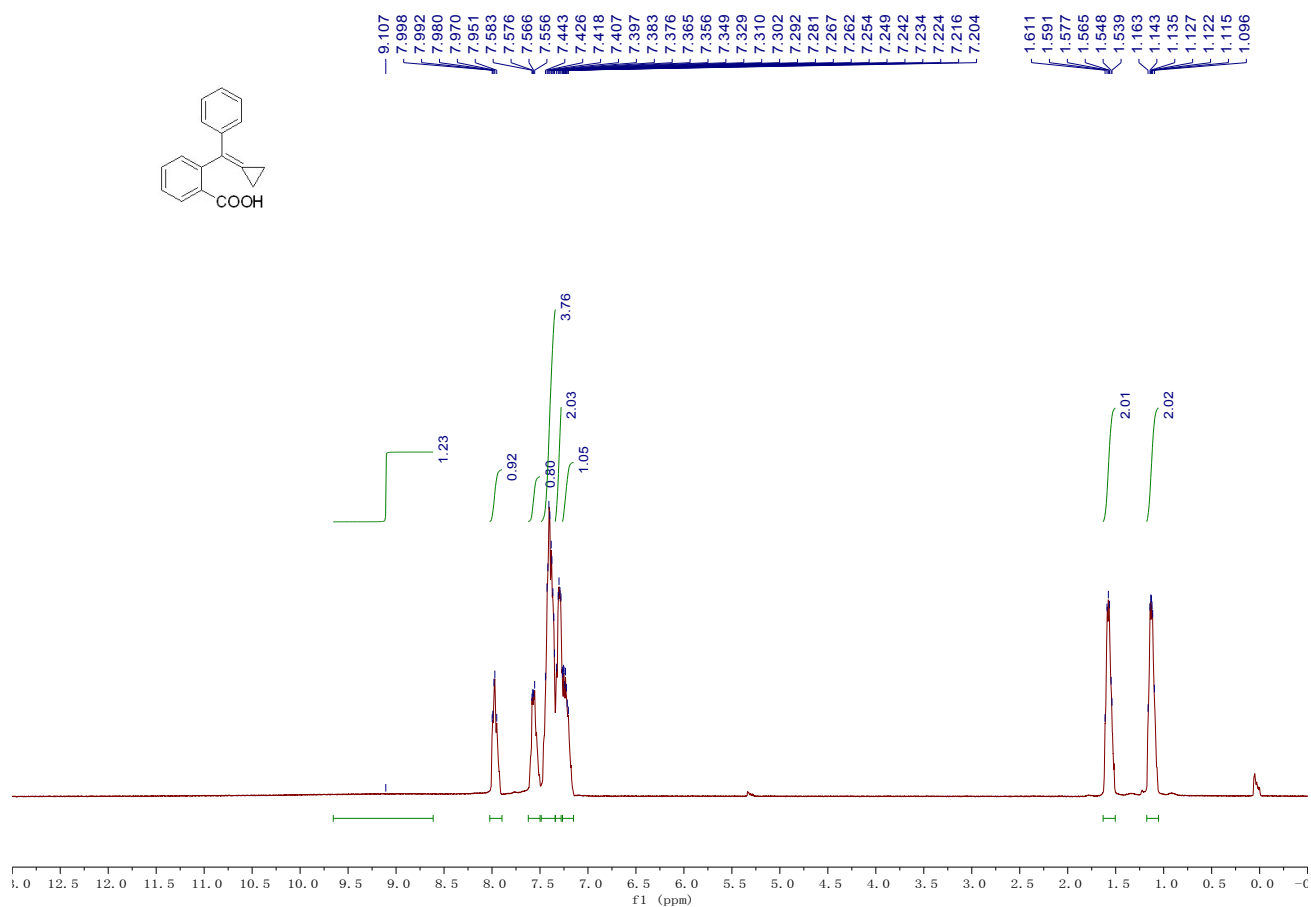


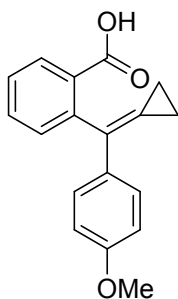
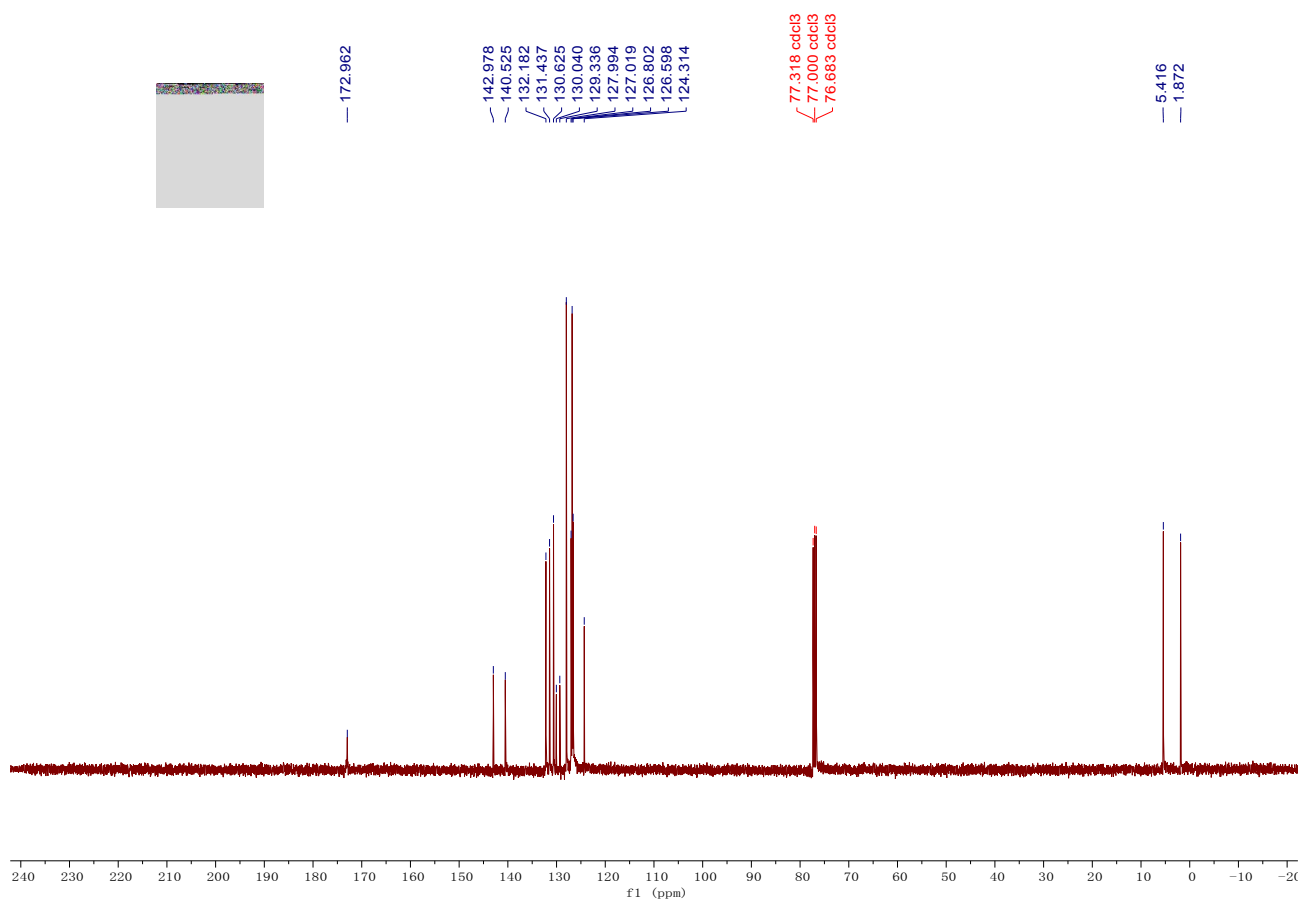
Figure S2. cyclic voltammetry curve of **3**.

7. Characterization and spectra charts

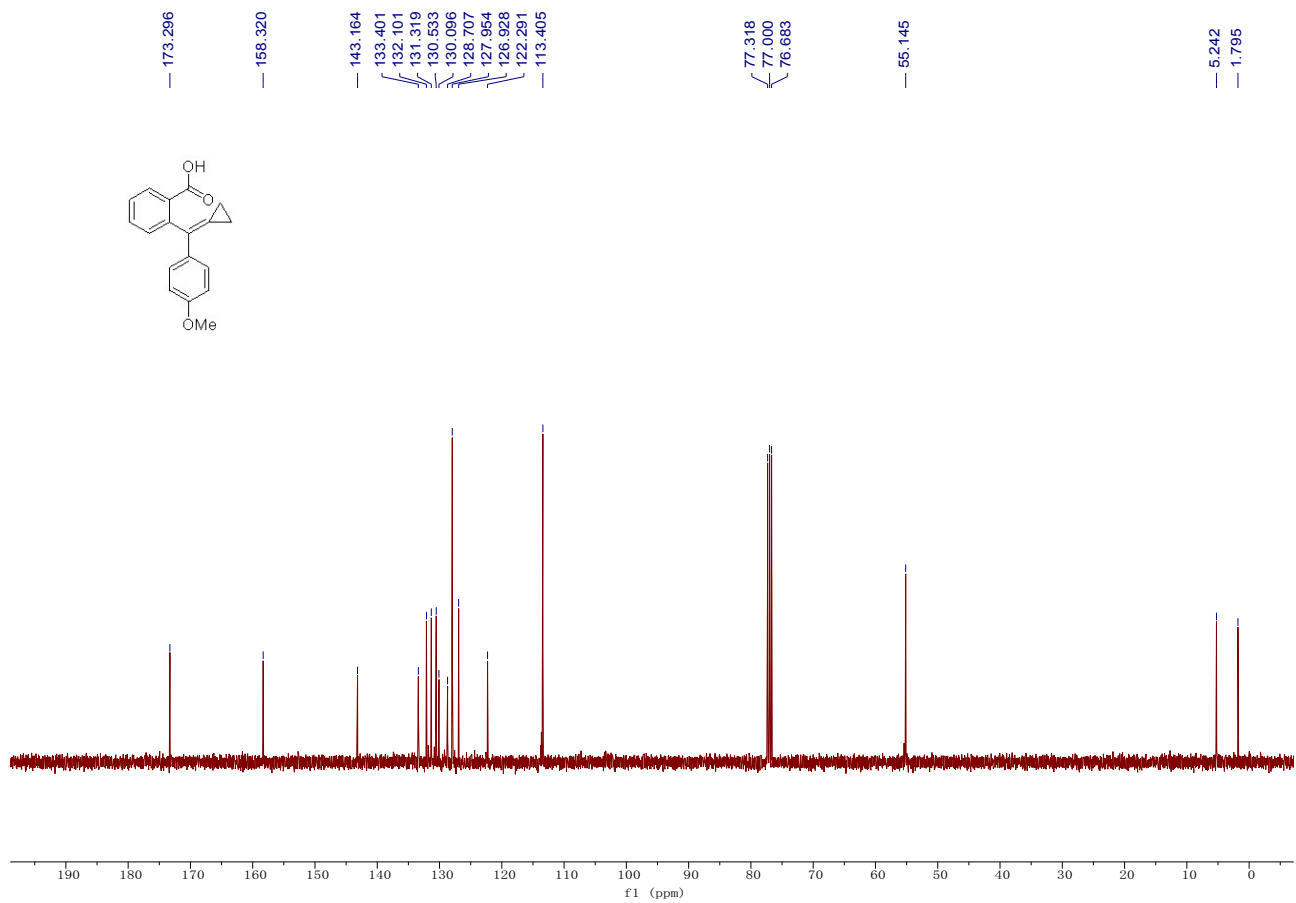
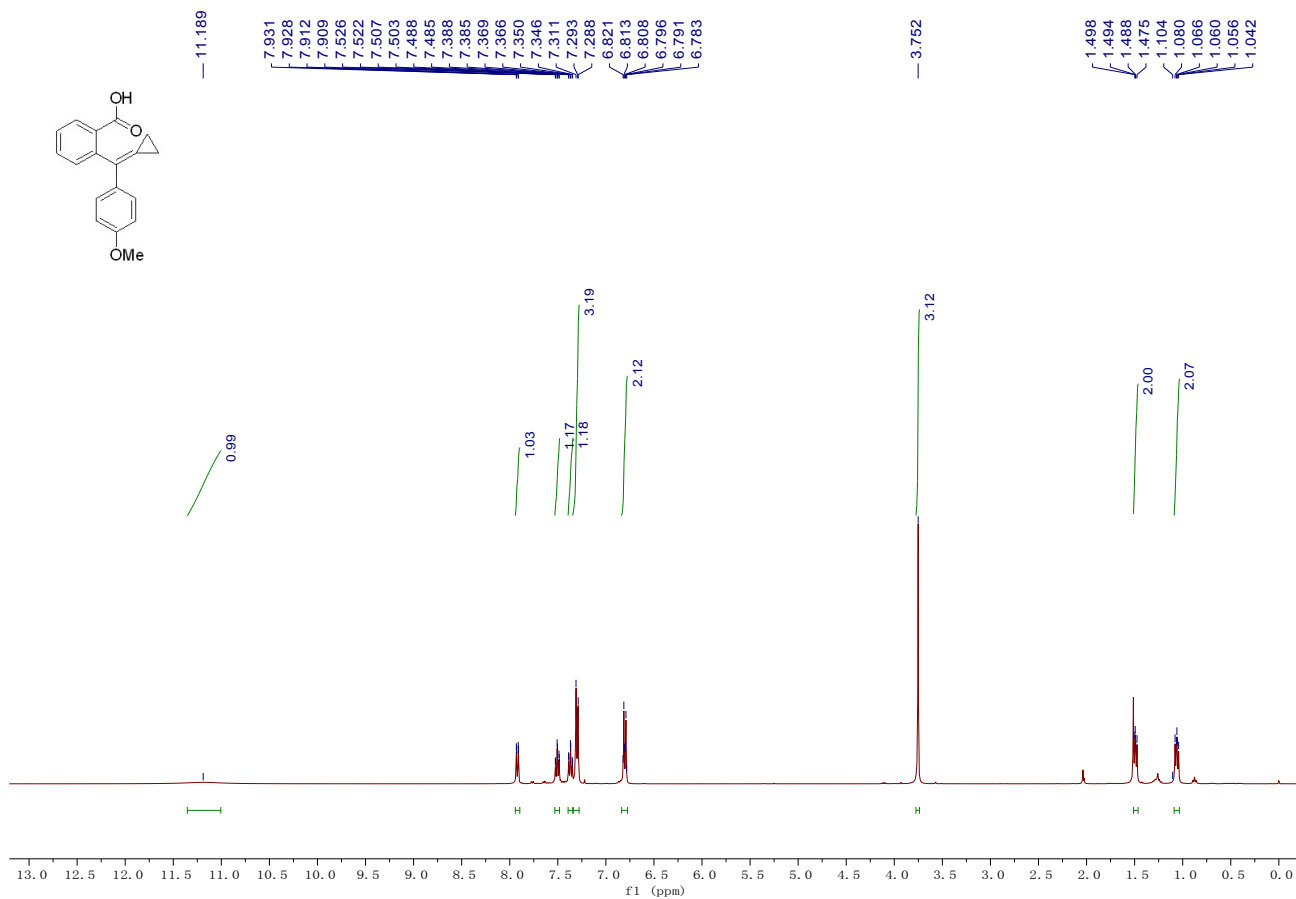


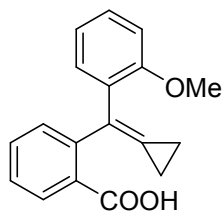
Compound 1a: Yield: 0.9 g, 84%; A white solid; Mp: 141 - 143 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.10 (br, 1H), 8.02 – 7.90 (m, 1H), 7.62 – 7.50 (m, 1H), 7.49 – 7.34 (m, 4H), 7.34 – 7.28 (m, 2H), 7.27 – 7.15 (m, 1H), 1.63 – 1.50 (m, 2H), 1.18 – 1.05 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.0, 143.0, 140.5, 132.2, 131.4, 130.6, 130.0, 129.3, 128.0, 127.0, 126.8, 126.6, 124.3, 5.4, 1.9; IR (neat): ν 2979, 1694, 1677, 1299, 1263 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_2$ $[\text{M}]^+$: 250.0988, found: 250.0987.



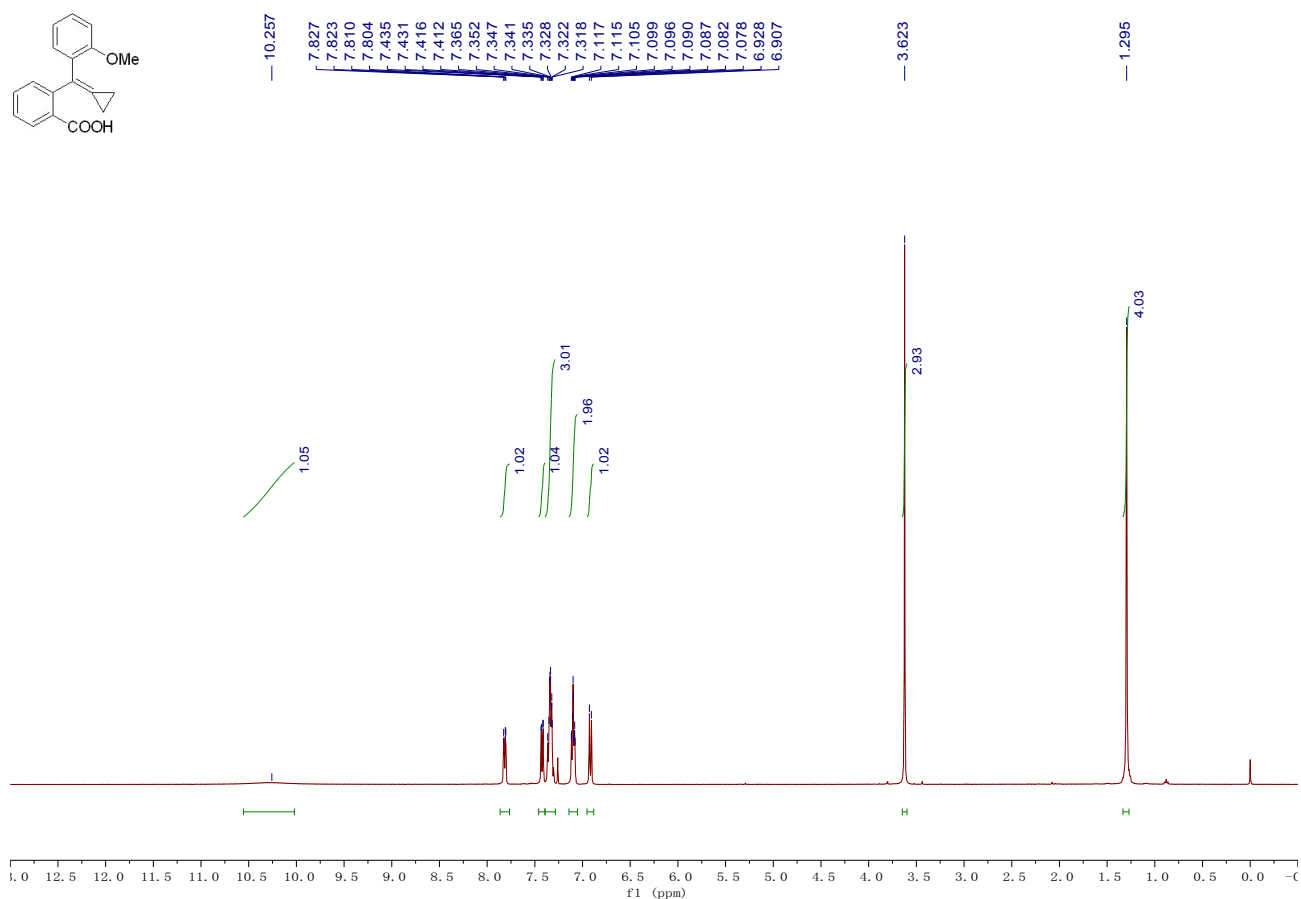


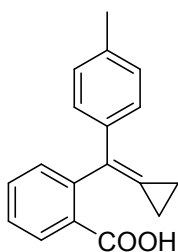
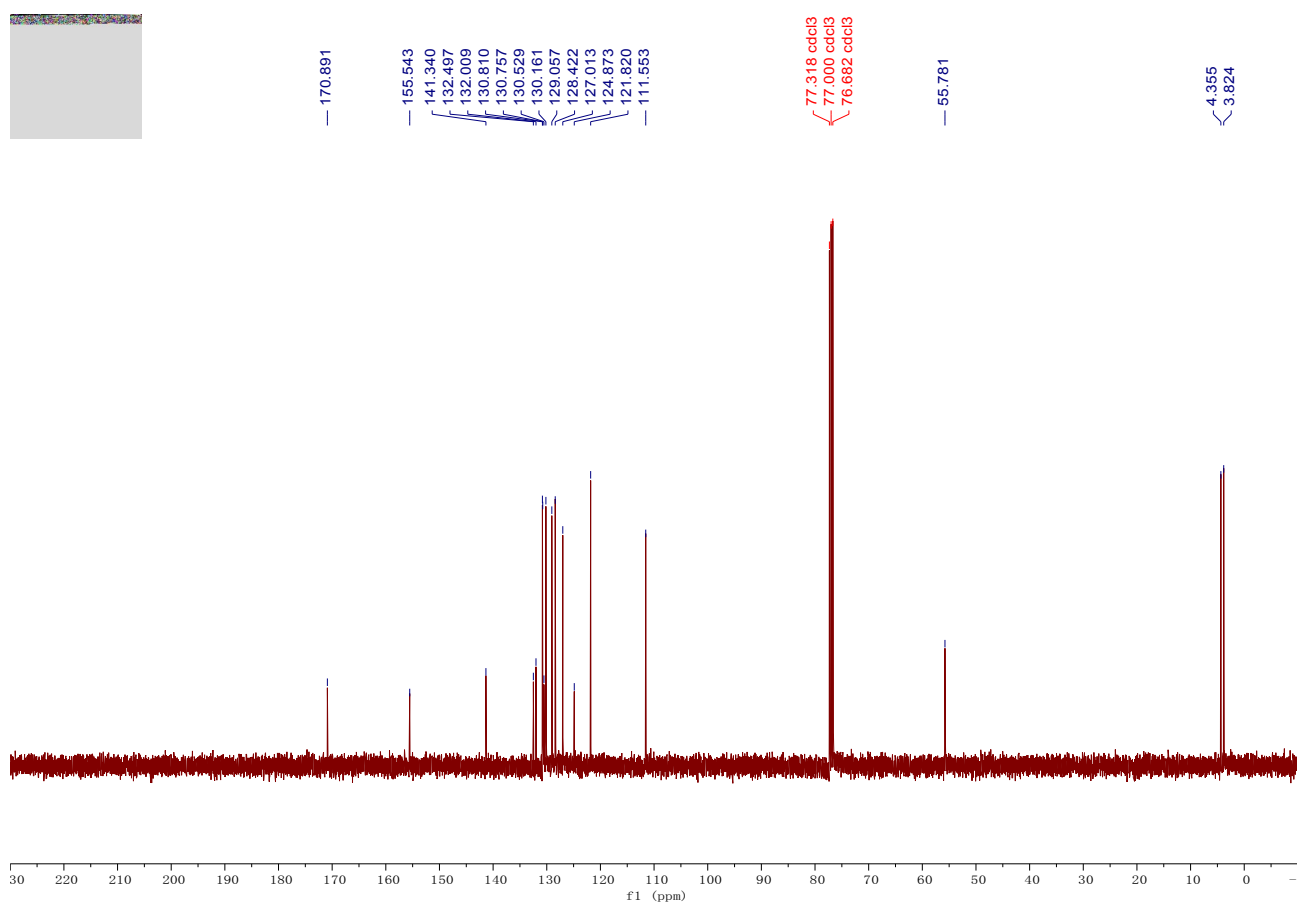
Compound 1b: Yield: 1.87 g, 87%; A white solid; Mp: 170 - 172 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 11.19 (br, 1H), 7.92 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.51 (td, $J = 7.5, 1.3$ Hz, 1H), 7.37 (td, $J = 7.6, 1.3$ Hz, 1H), 7.34 – 7.28 (m, 3H), 6.84 – 6.78 (m, 2H), 3.75 (s, 3H), 1.51 – 1.46 (m, 2H), 1.09 – 1.03 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.3, 158.3, 143.2, 133.4, 132.1, 131.3, 130.5, 130.1, 128.7, 128.0, 126.9, 122.3, 113.4, 55.1, 5.2, 1.8; IR (neat): ν 2989, 1612, 1240, 989, 750 cm^{-1} ; HRMS (EI) Calcd. For $\text{C}_{18}\text{H}_{16}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 303.0992, found: 303.0994.



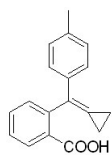


Compound 1c: Yield: 1.07 g, 75%; A white solid; Mp: 158 - 160 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.26 (br, 1H), 7.86 – 7.77 (m, 1H), 7.42 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.39 – 7.28 (m, 3H), 7.14 – 7.05 (m, 2H), 6.92 (d, $J = 8.3$ Hz, 1H), 3.62 (s, 3H), 1.33 – 1.27 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9, 155.5, 141.3, 132.5, 132.0, 130.81, 130.76, 130.5, 130.2, 129.1, 128.4, 127.0, 124.9, 121.8, 111.6, 55.8, 4.4, 3.8; IR (neat): ν 2980, 1690, 1601, 1293, 750 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_3$ $[\text{M}]^+$: 280.1094, found: 280.1101.

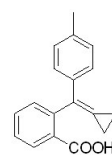
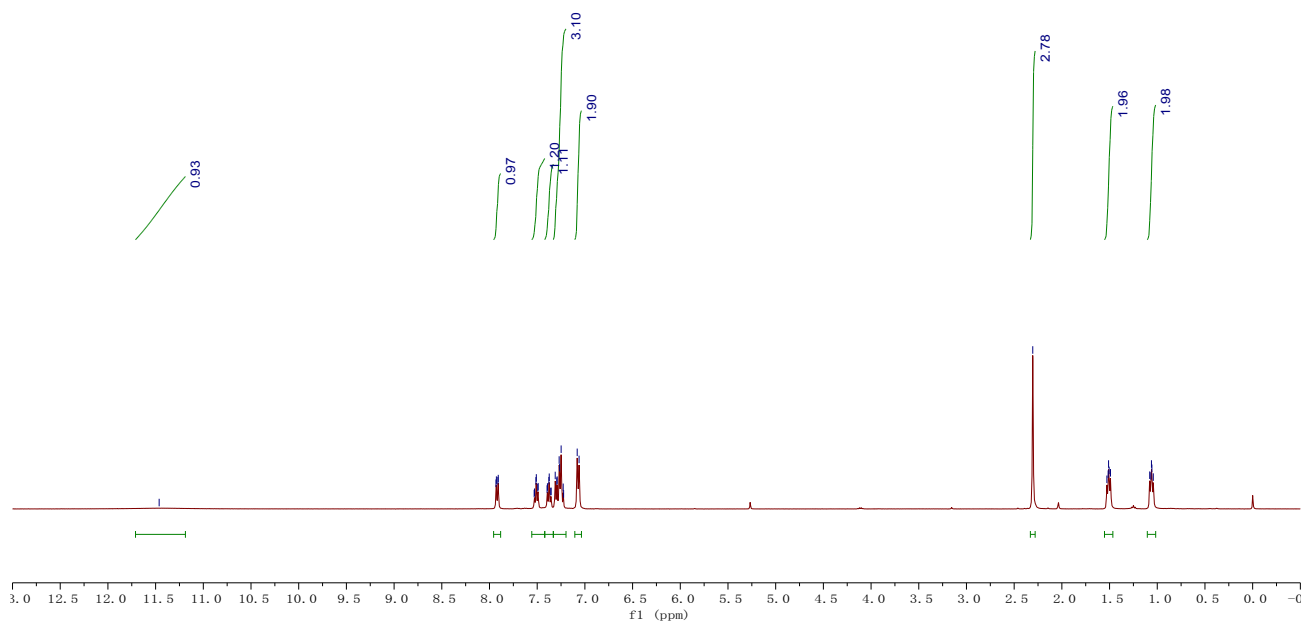




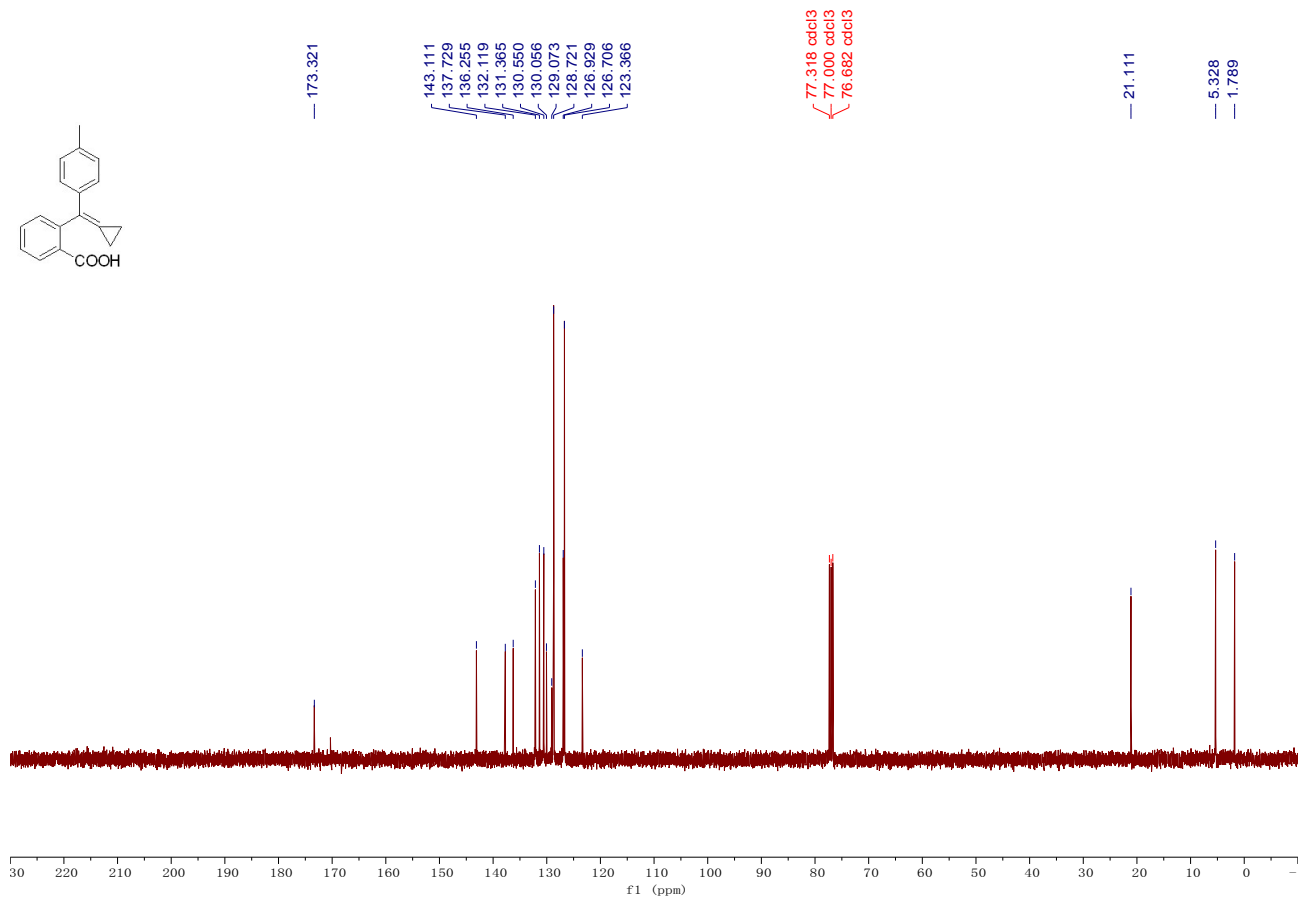
Compound 1d: Yield: 0.87 g, 73%; A white solid; Mp: 168 - 170 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 11.46 (br, 1H), 7.92 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.51 (td, $J = 7.5, 1.6$ Hz, 1H), 7.42 – 7.33 (m, 1H), 7.33 – 7.20 (m, 3H), 7.07 (d, $J = 7.8$ Hz, 2H), 2.31 (s, 3H), 1.55 – 1.47 (m, 2H), 1.10 – 1.02 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.3, 143.1, 137.7, 136.3, 132.1, 131.4, 130.5, 130.1, 129.1, 128.7, 126.9, 126.7, 123.4, 21.1, 5.3, 1.8; IR (neat): ν 2974, 2531, 1690, 1510, 1294 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 287.1043, found: 287.1040.

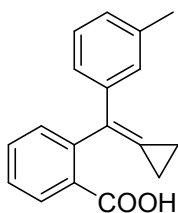


— 11.463

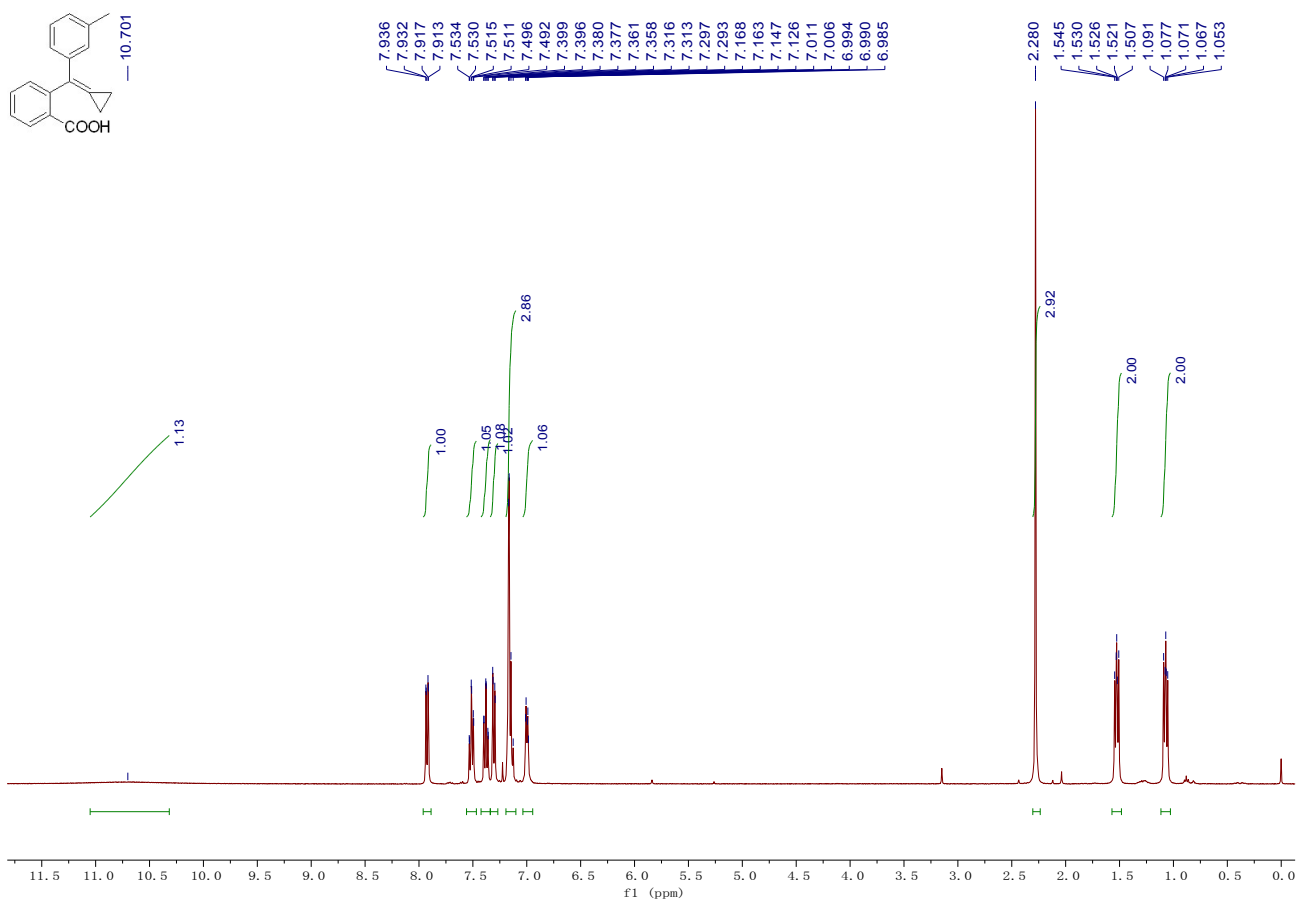


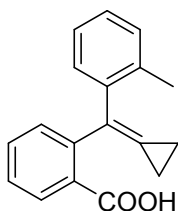
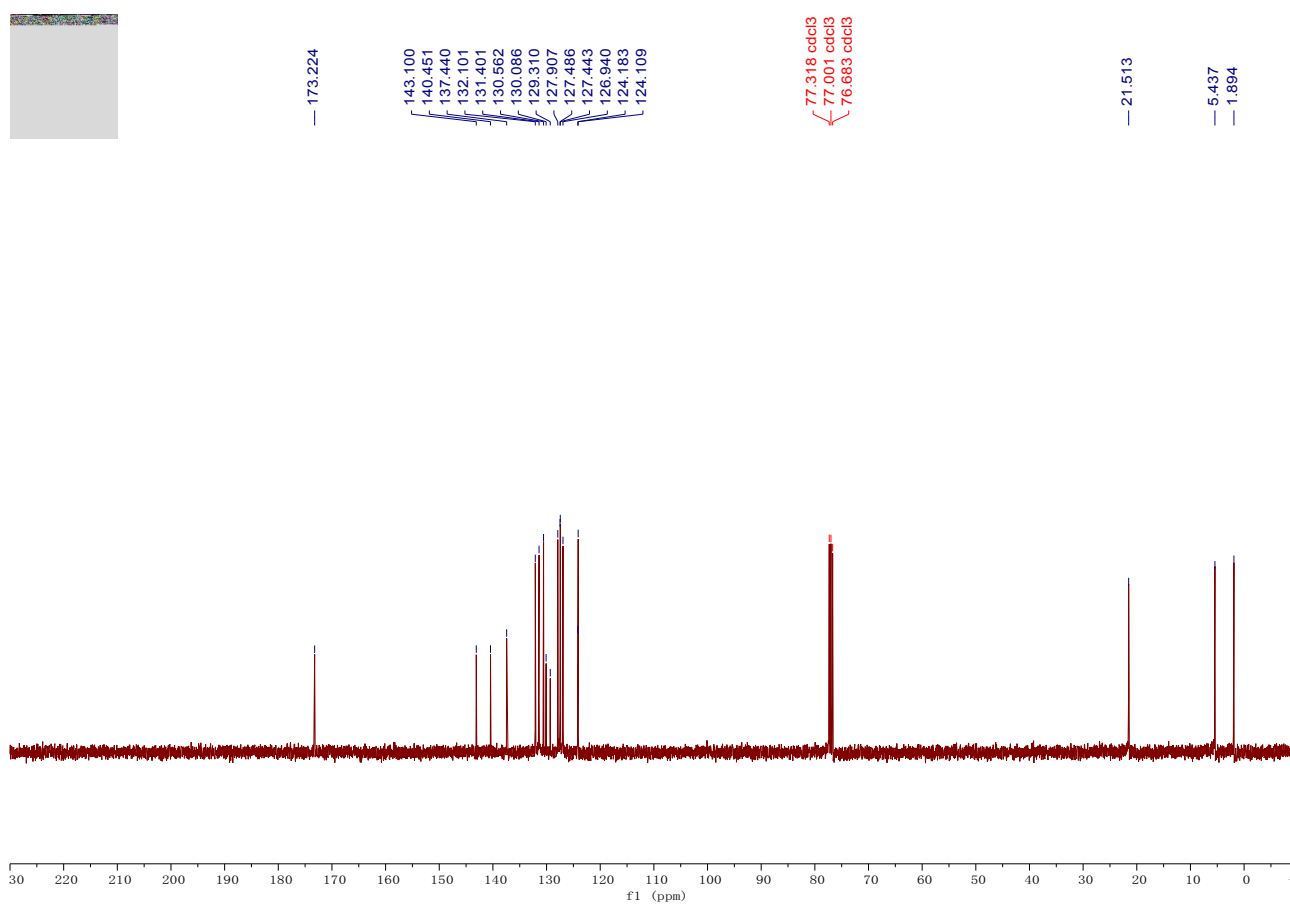
— 173.321



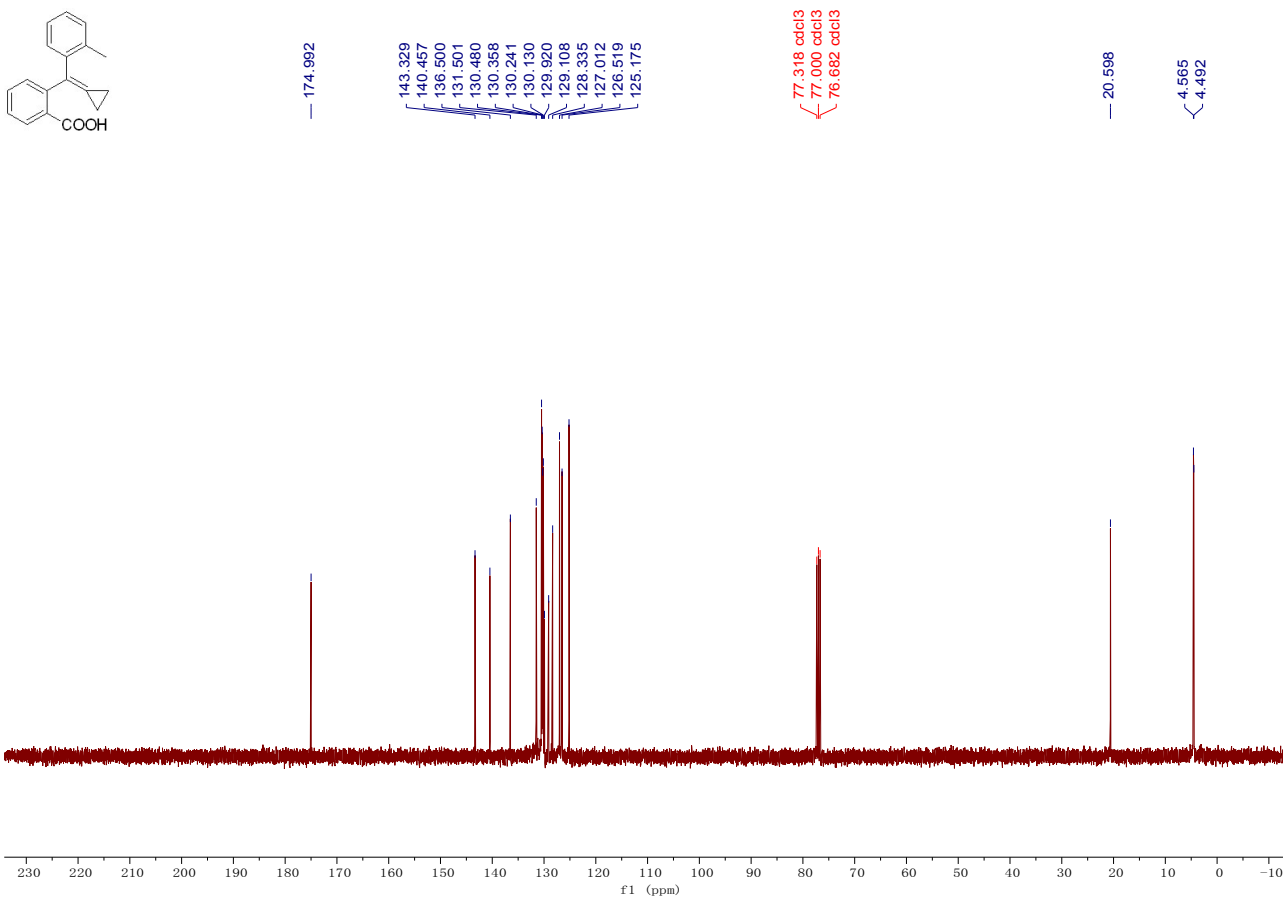
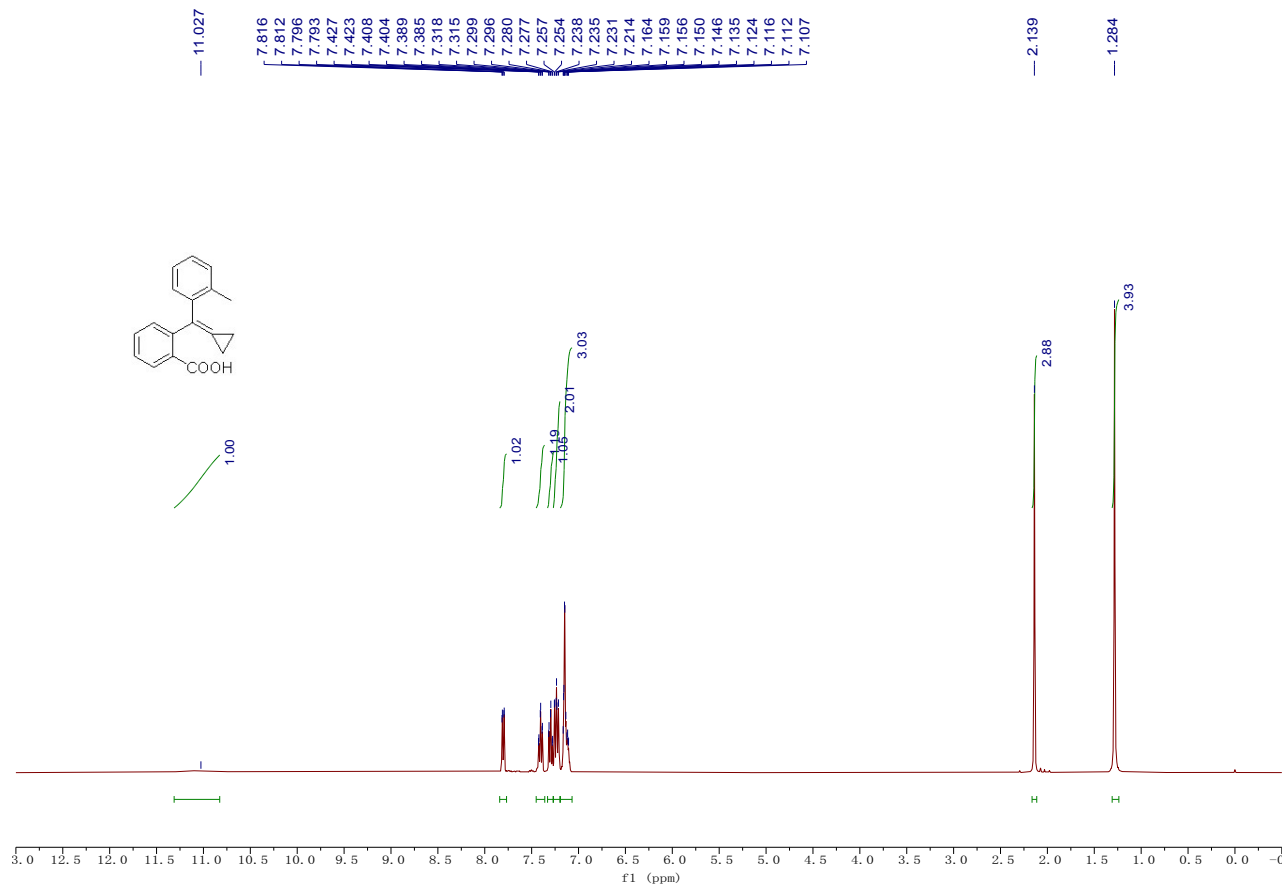


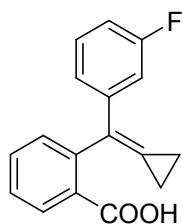
Compound 1e: Yield: 1.32 g, 72%; A white solid; Mp: 159 - 161 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.70 (br, 1H), 7.92 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.51 (td, $J = 7.6, 1.5$ Hz, 1H), 7.38 (td, $J = 7.6, 1.3$ Hz, 1H), 7.30 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.19 – 7.10 (m, 3H), 7.04 – 6.94 (m, 1H), 2.28 (s, 3H), 1.57 – 1.48 (m, 2H), 1.12 – 1.03 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.2, 143.1, 140.5, 137.4, 132.1, 131.4, 130.6, 130.1, 129.3, 127.9, 127.5, 127.4, 126.9, 124.2, 124.1, 21.5, 5.4, 1.9; IR (neat): ν 2966, 1962, 1600, 1295, 1263 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 287.1043, found: 287.1044.



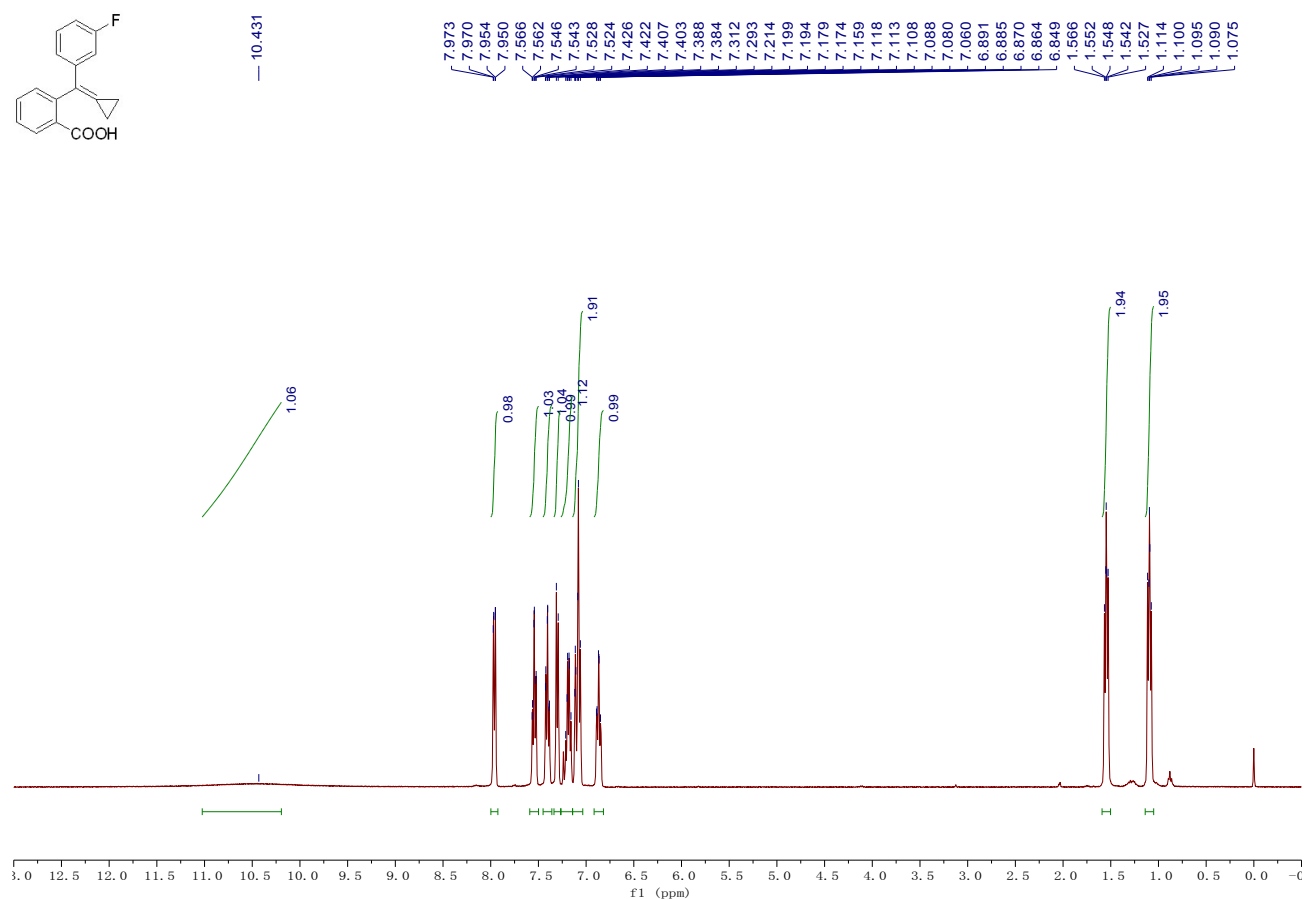


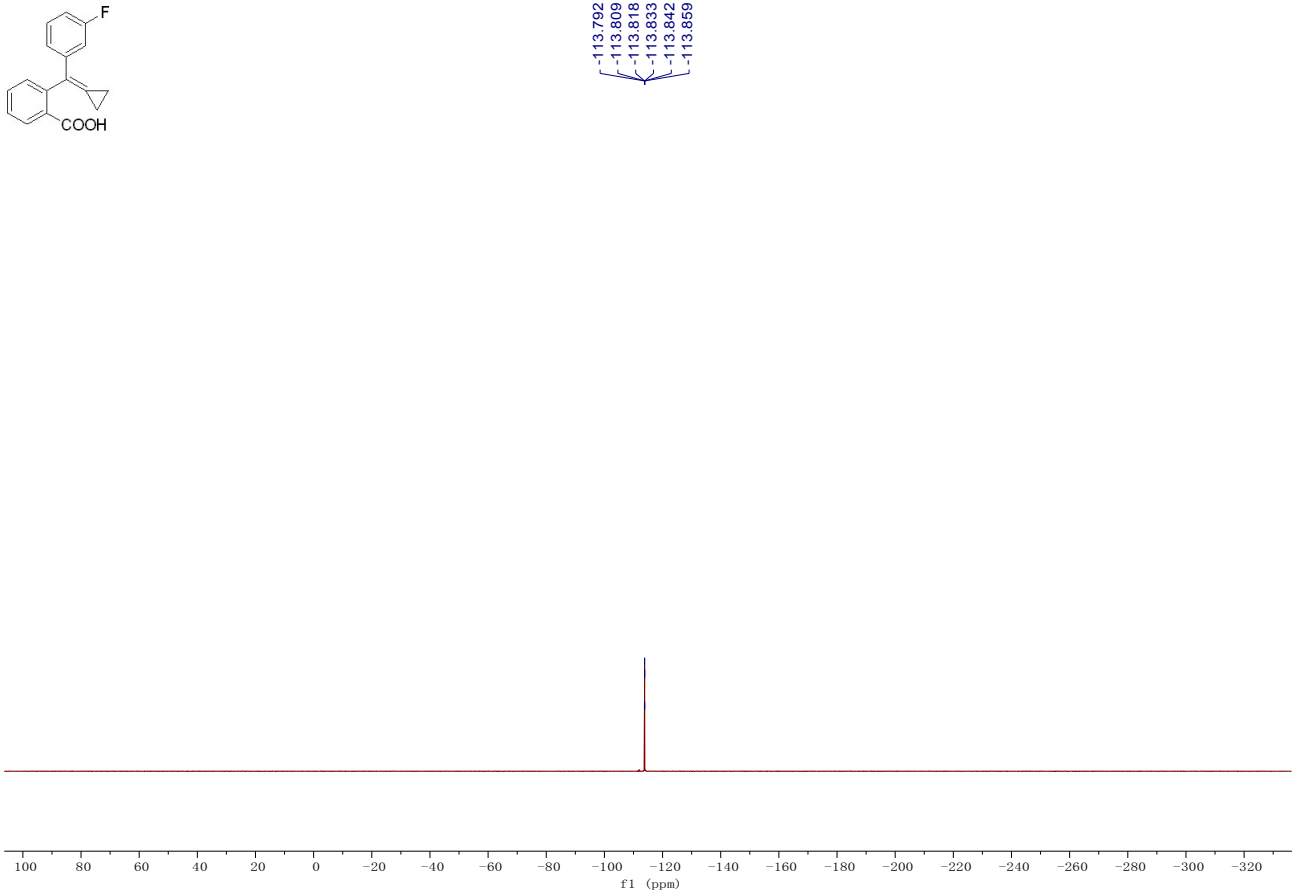
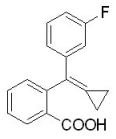
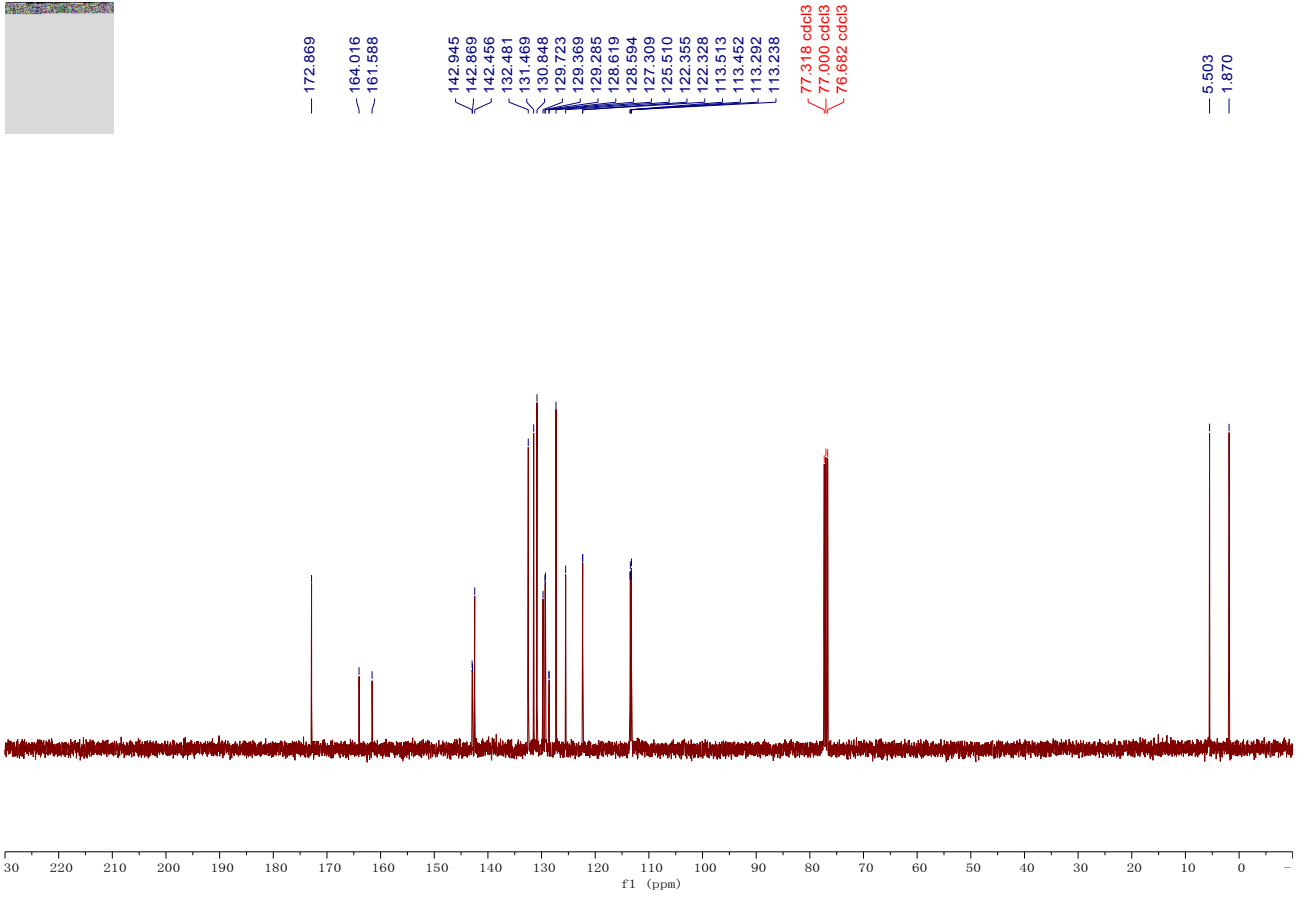
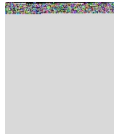
Compound 1f: Yield: 0.7 g, 74%; A white solid; Mp: 163 - 165 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 11.03 (br, 1H), 7.80 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.41 (td, $J = 7.5, 1.5$ Hz, 1H), 7.33 – 7.27 (m, 1H), 7.27 – 7.20 (m, 2H), 7.19 – 7.07 (m, 3H), 2.14 (s, 3H), 1.31 – 1.24 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.0, 143.3, 140.5, 136.5, 131.5, 130.5, 130.4, 130.2, 130.1, 129.9, 129.1, 128.3, 127.0, 126.5, 125.2, 20.6, 4.6, 4.5; IR (neat): ν 3079, 2374, 2084, 1717, 746 cm^{-1} ; HRMS (FI) Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$: 264.1145, found: 264.1147.

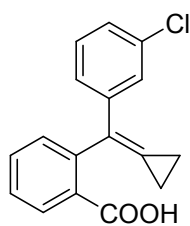




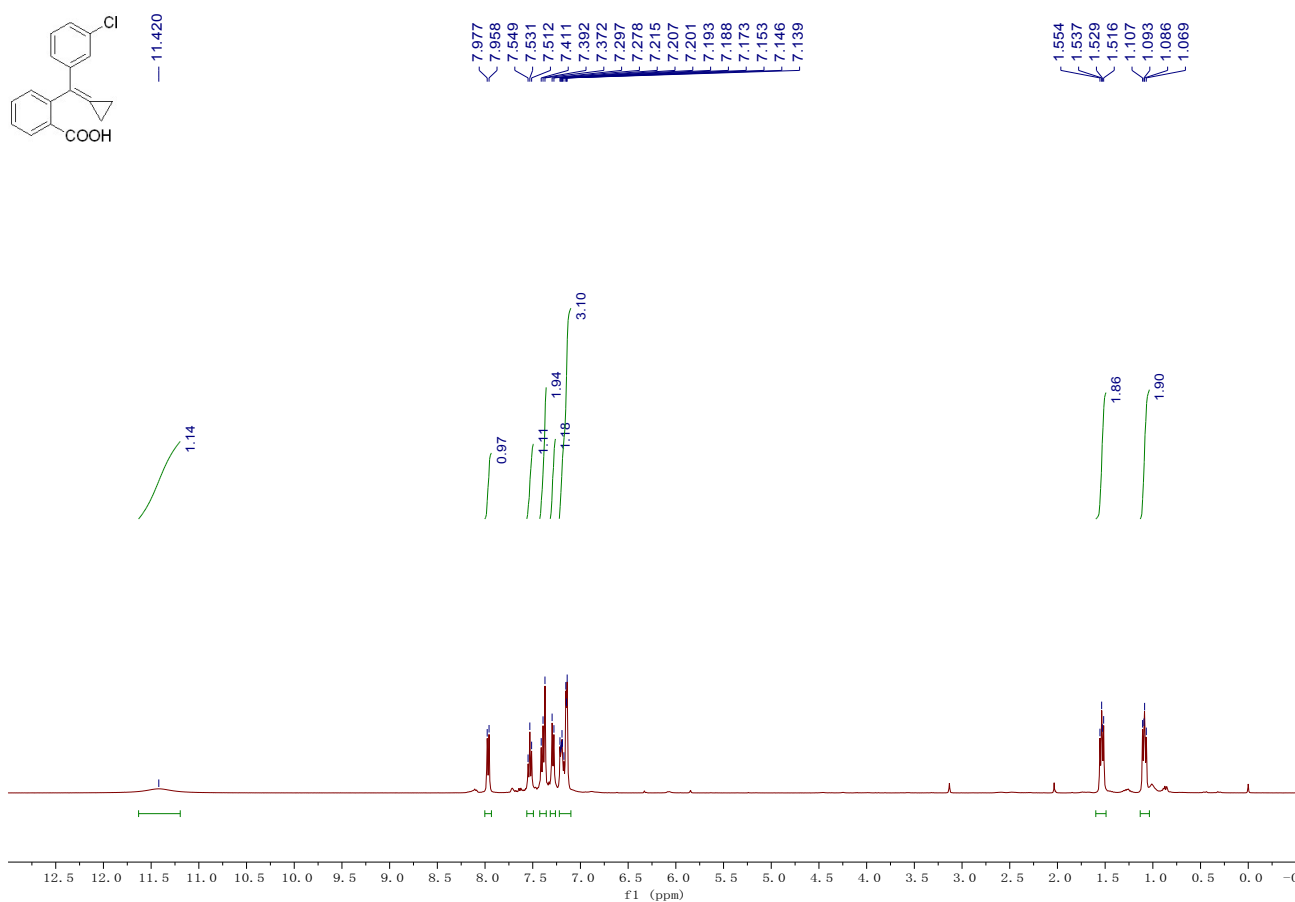
Compound 1g: Yield: 1.22 g, 95%; A white solid; Mp: 119 - 121 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.43 (br, 1H), 8.00 – 7.92 (m, 1H), 7.59 – 7.50 (m, 1H), 7.45 – 7.36 (m, 1H), 7.30 (d, $J = 7.7$ Hz, 1H), 7.26 – 7.14 (m, 1H), 7.14 – 7.04 (m, 2H), 6.92 – 6.82 (m, 1H), 1.59 – 1.50 (m, 2H), 1.14 – 1.05 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.9, 162.8 (d, $J = 244.2$ Hz), 142.9 (d, $J = 7.6$ Hz), 142.5, 132.5, 131.5, 130.8, 129.7, 129.3 (d, $J = 8.4$ Hz), 128.6 (d, $J = 2.6$ Hz), 127.3, 125.5, 122.3 (d, $J = 2.7$ Hz), 113.4 (d, $J = 22.2$ Hz), 113.3 (d, $J = 21.4$ Hz), 5.5, 1.9; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.76 – -113.90 (m); IR (neat): ν 3044, 2858, 1678, 1232, 787 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{17}\text{H}_{13}\text{O}_2\text{F}$ $[\text{M}]^+$: 268.0894, found: 268.0901.

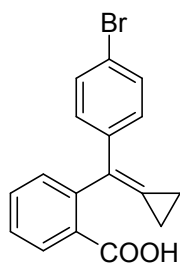
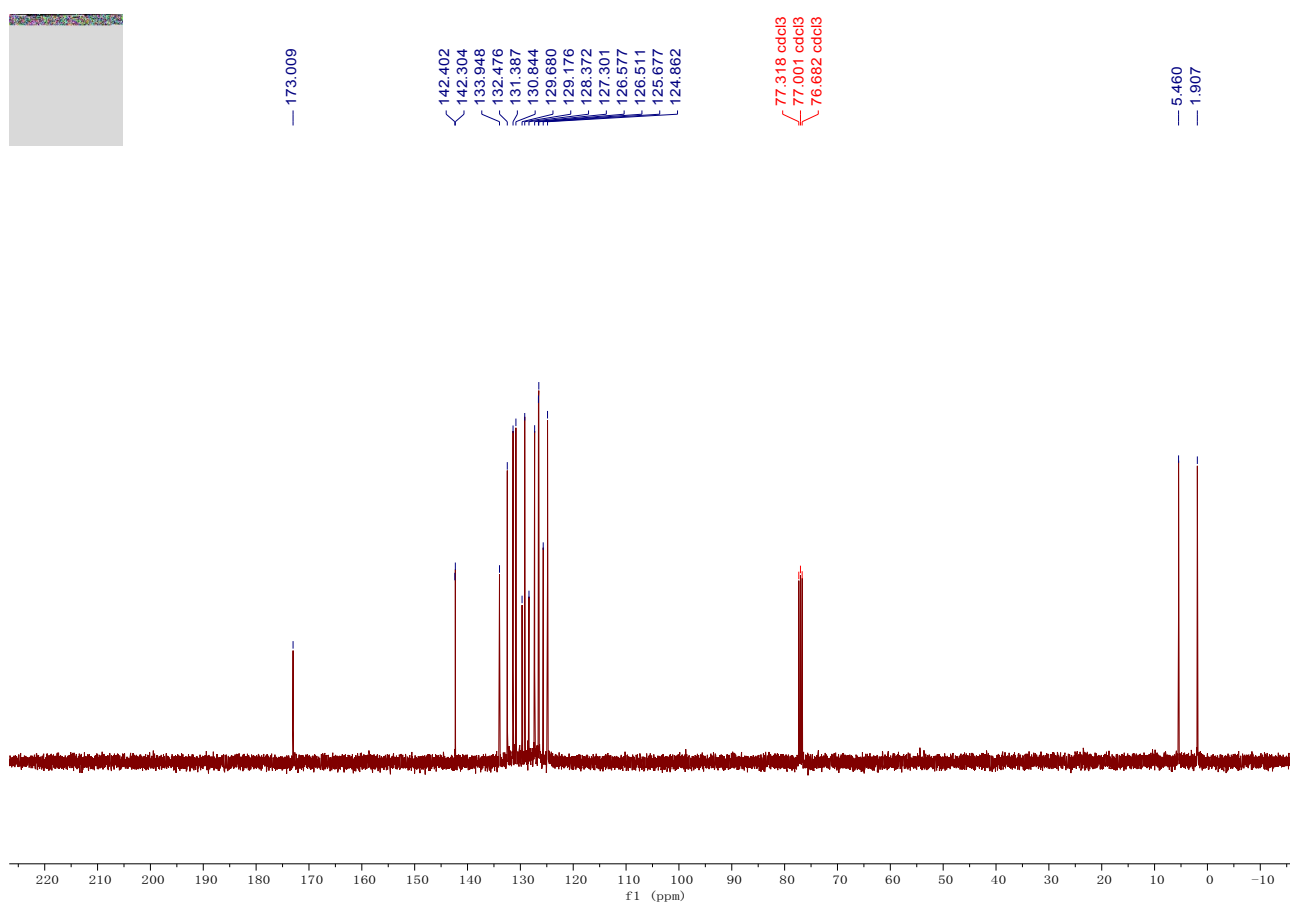




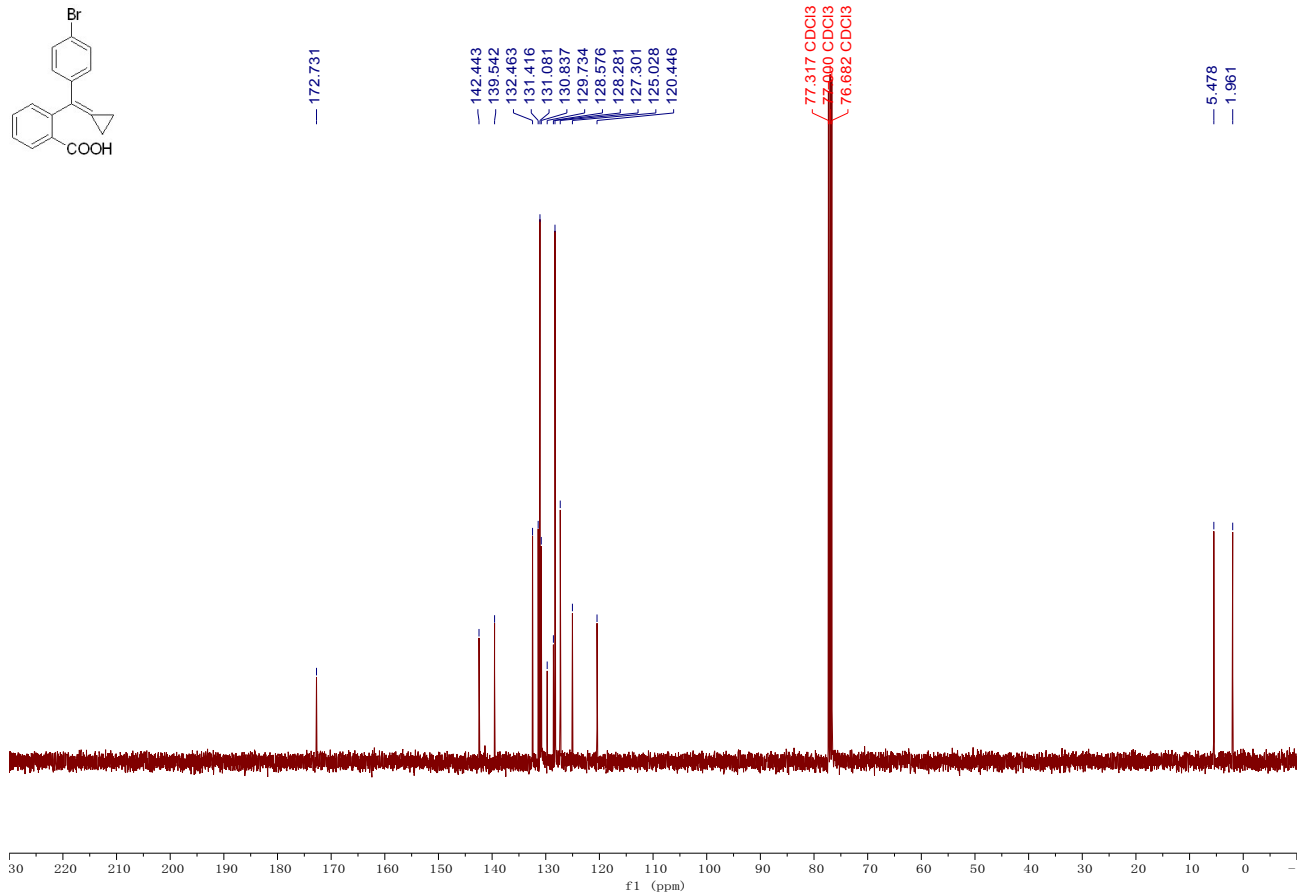
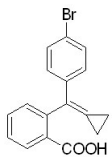
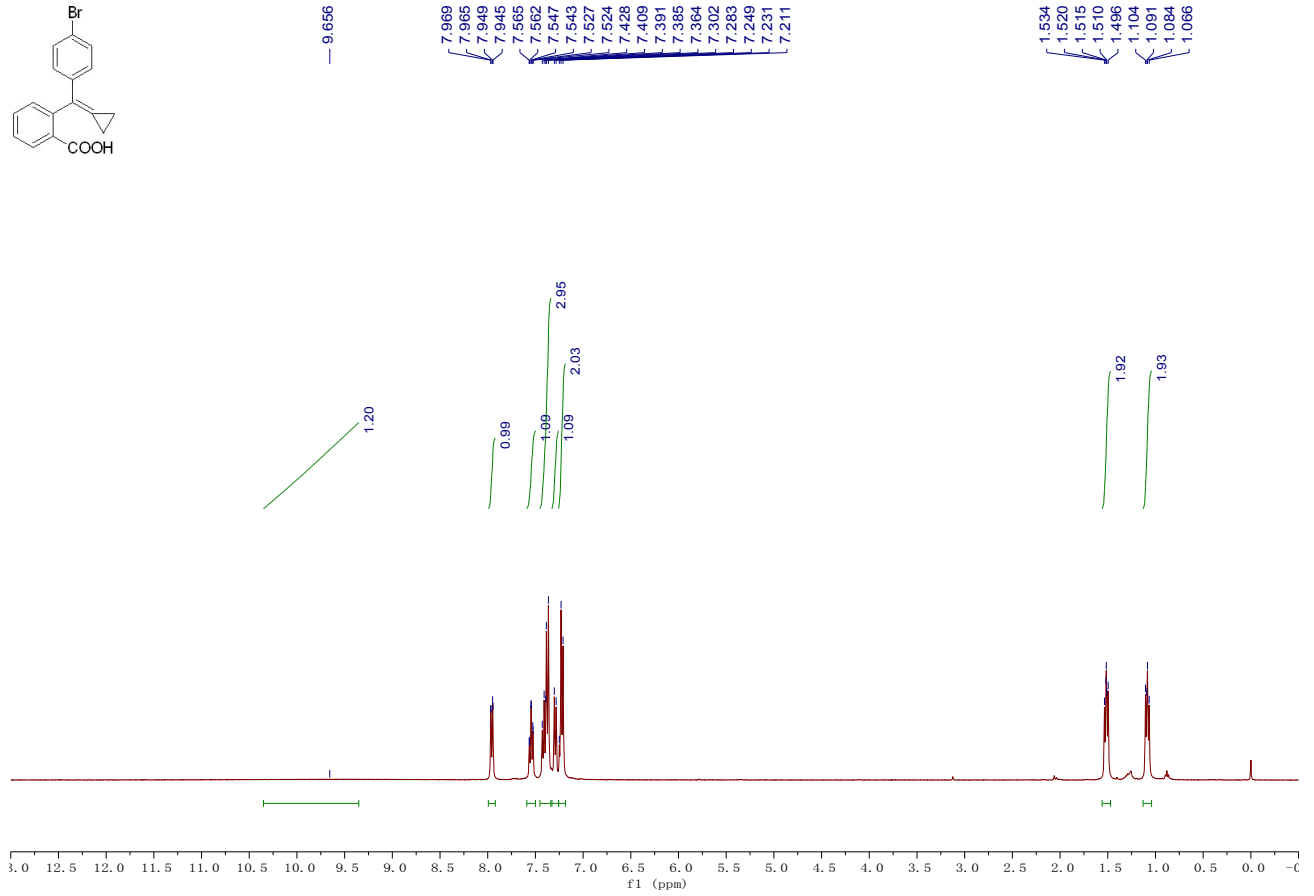
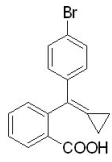


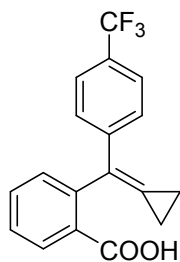
Compound 1h: Yield: 1.18 g, 75%; A white solid; Mp: 102 - 104 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 11.42 (br, 1H), 7.97 (d, $J = 7.7$ Hz, 1H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.43 – 7.36 (m, 2H), 7.32 – 7.26 (m, 1H), 7.22 – 7.10 (m, 3H), 1.60 – 1.49 (m, 2H), 1.13 – 1.04 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.0, 142.4, 142.3, 133.9, 132.5, 131.4, 130.8, 129.7, 129.2, 128.4, 127.3, 126.6, 126.5, 125.7, 124.9, 5.5, 1.9; IR (neat): ν 3005, 1748, 1716, 1285, 986 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{17}\text{H}_{13}\text{ClO}_2$ $[\text{M}]^+$: 284.0599, found: 284.0597.



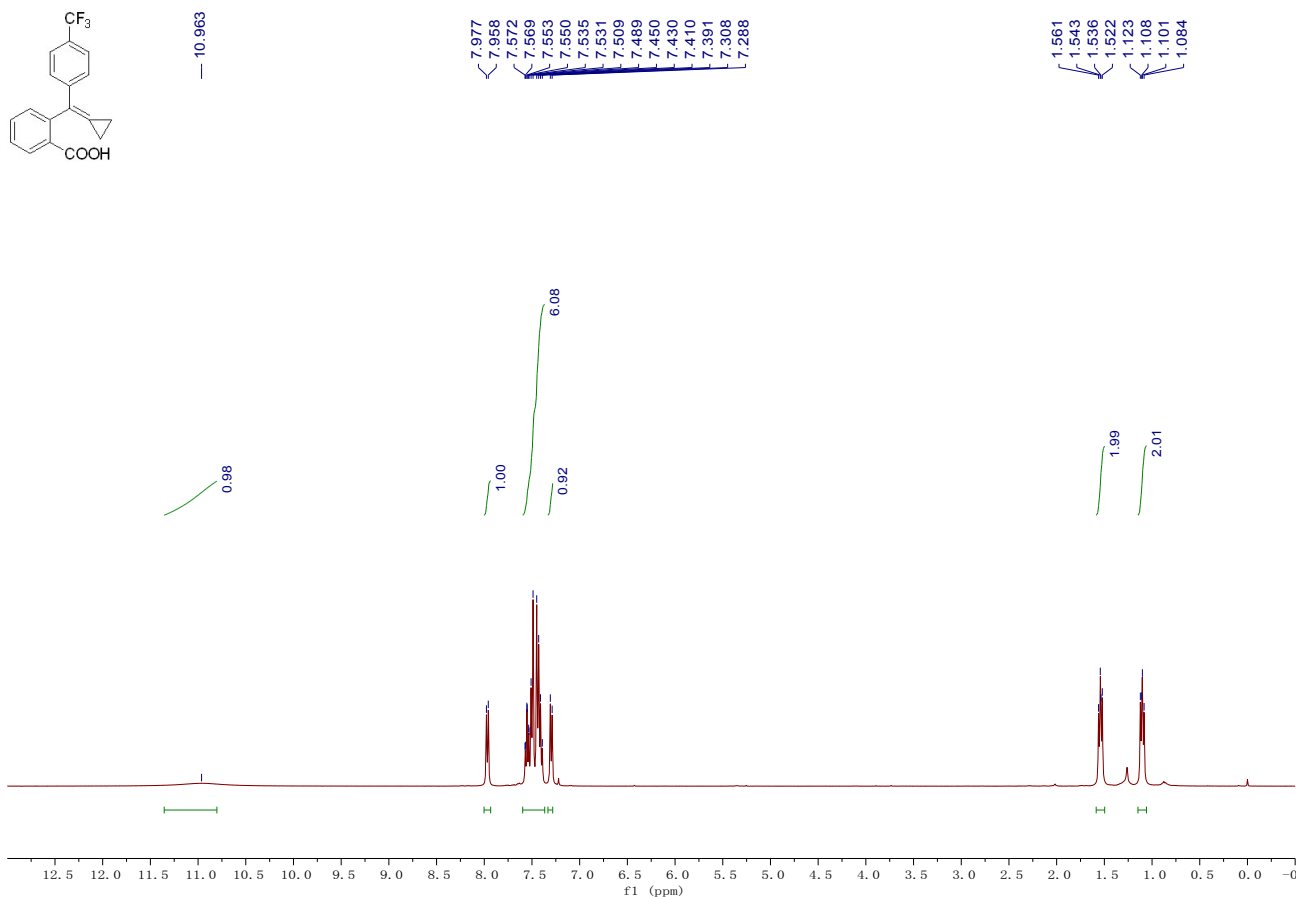


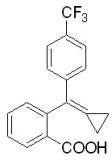
Compound 1i: Yield: 1.35 g, 82%; A white solid; Mp: 108 - 110 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.66 (br, 1H), 7.96 (d, $J = 7.8$ Hz, 1H), 7.59 – 7.50 (m, 1H), 7.45 – 7.34 (m, 3H), 7.29 (d, $J = 7.6$ Hz, 1H), 7.26 – 7.19 (m, 2H), 1.56 – 1.47 (m, 2H), 1.13 – 1.04 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.7, 142.4, 139.5, 132.5, 131.4, 131.1, 130.8, 129.7, 128.6, 128.3, 127.3, 125.0, 120.4, 5.5, 2.0; IR (neat): ν 3372, 1717, 1652, 1338, 1145 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{17}\text{H}_{13}\text{O}_2\text{Br}$ $[\text{M}]^+$: 328.0093, found: 328.0097.





Compound 1j: Yield: 1.36 g, 87%; A white solid; Mp: > 200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.96 (br, 1H), 7.97 (d, $J = 7.7$ Hz, 1H), 7.60 – 7.37 (m, 6H), 7.33 – 7.28 (m, 1H), 1.59 – 1.50 (m, 2H), 1.15 – 1.06 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.0, 144.1, 142.3, 132.6, 131.5, 131.0, 129.6, 128.7, 128.3 (q, $J = 32.4$ Hz), 127.5, 126.9, 126.8, 124.9 (q, $J = 3.4$ Hz), 124.4 (q, $J = 272.3$ Hz), 5.5, 1.9; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.34; IR (neat): ν 1758, 1326, 1270, 1125, 993 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{18}\text{H}_{13}\text{O}_2\text{F}_3$ $[\text{M}]^+$: 318.0862, found: 318.0861.

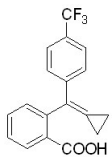
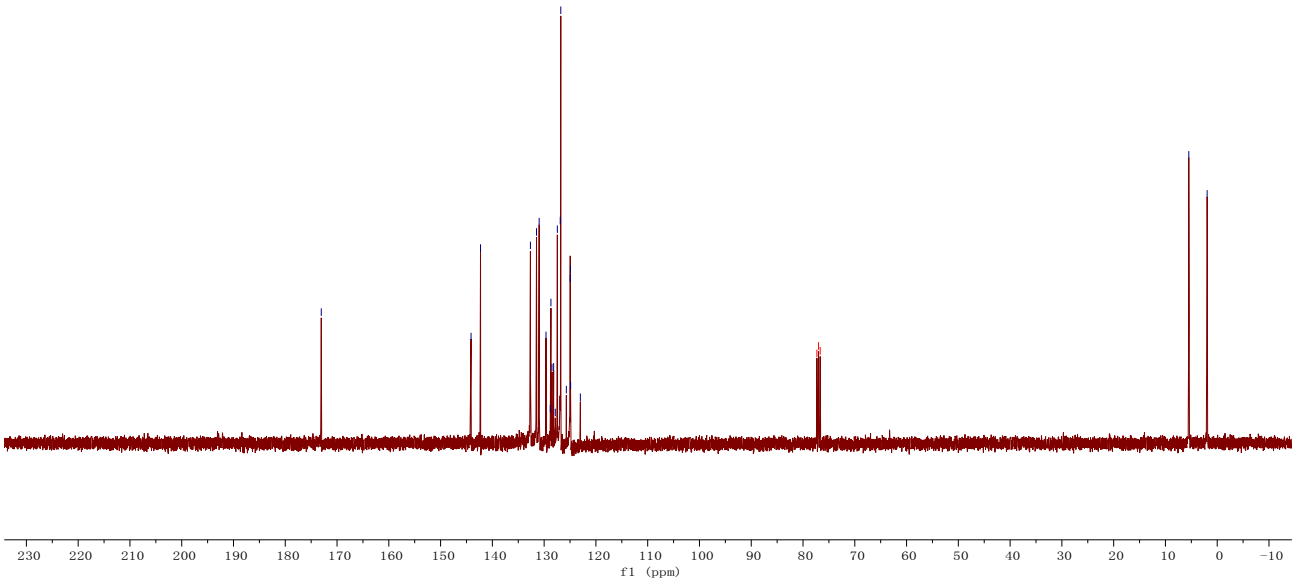




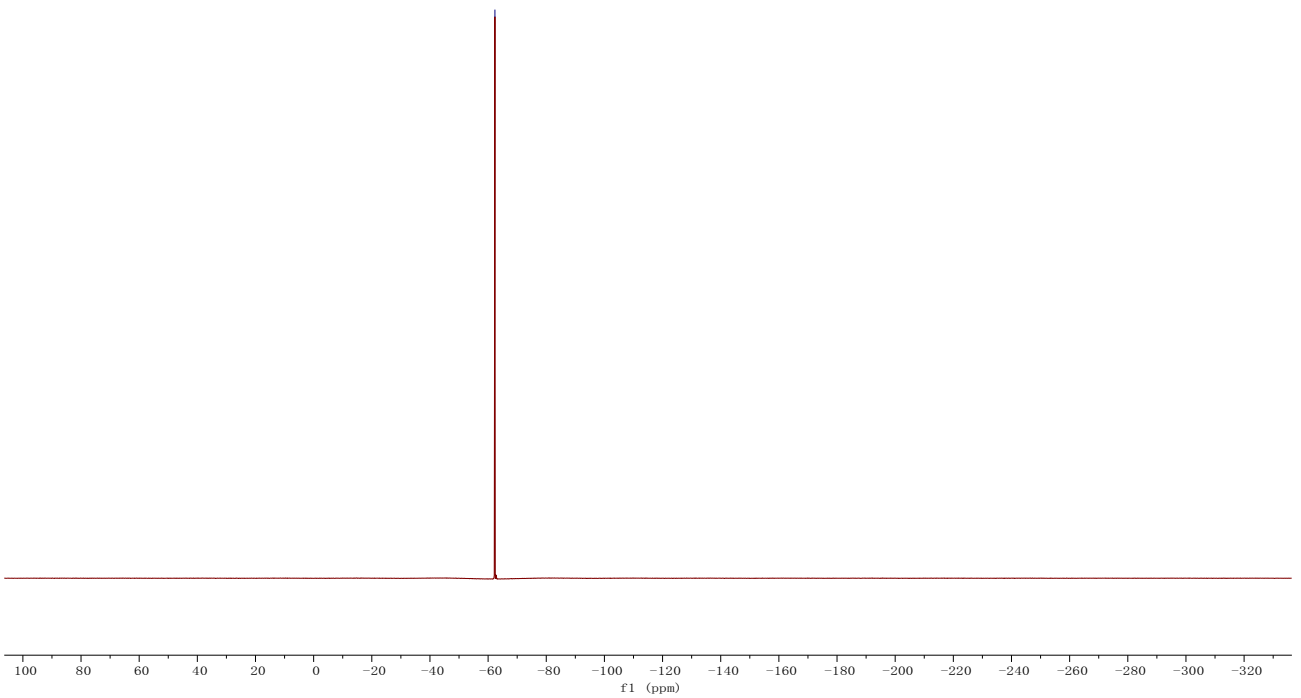
— 173.046

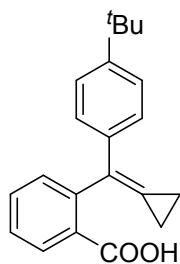
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 142.289
 132.649
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 130.963
 129.641
 128.687
 128.486
 128.165
 127.844
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 126.786
 125.708
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 124.886
 123.004
 77.318 cdc13
 77.000 cdc13
 76.682 cdc13

— 5.489
 — 1.945

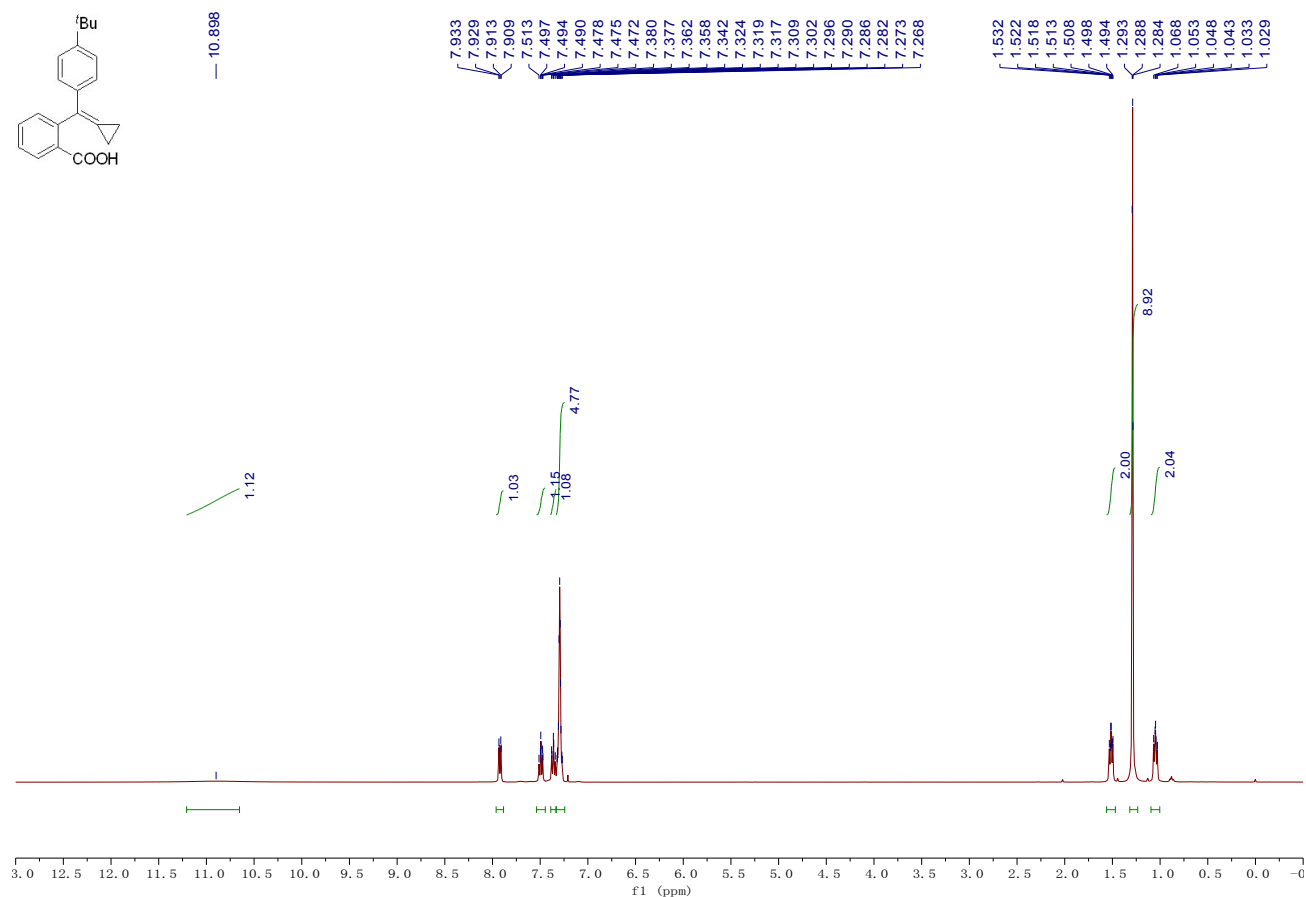


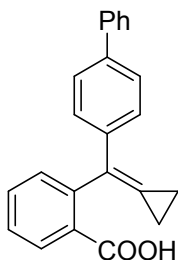
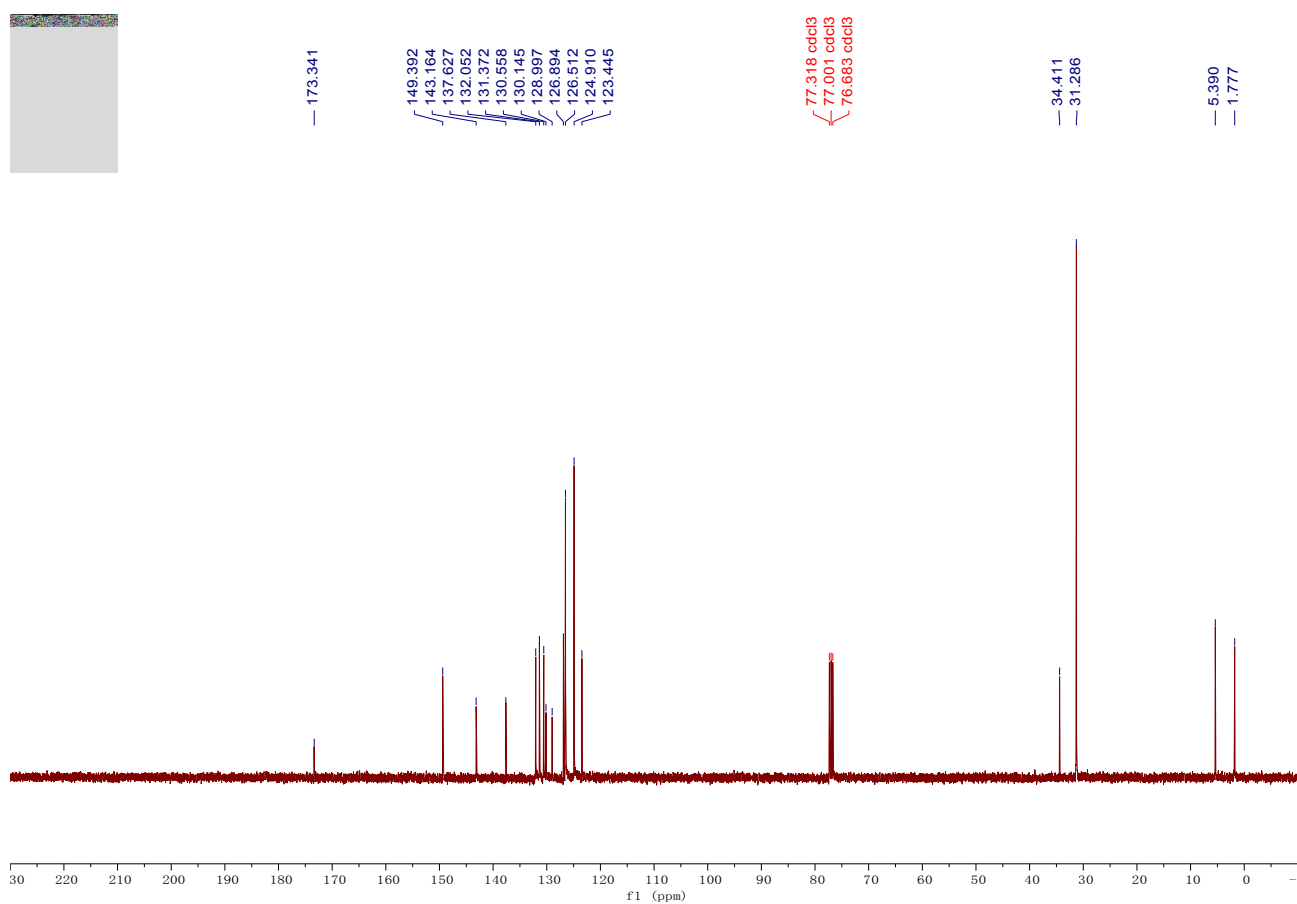
— -62.344



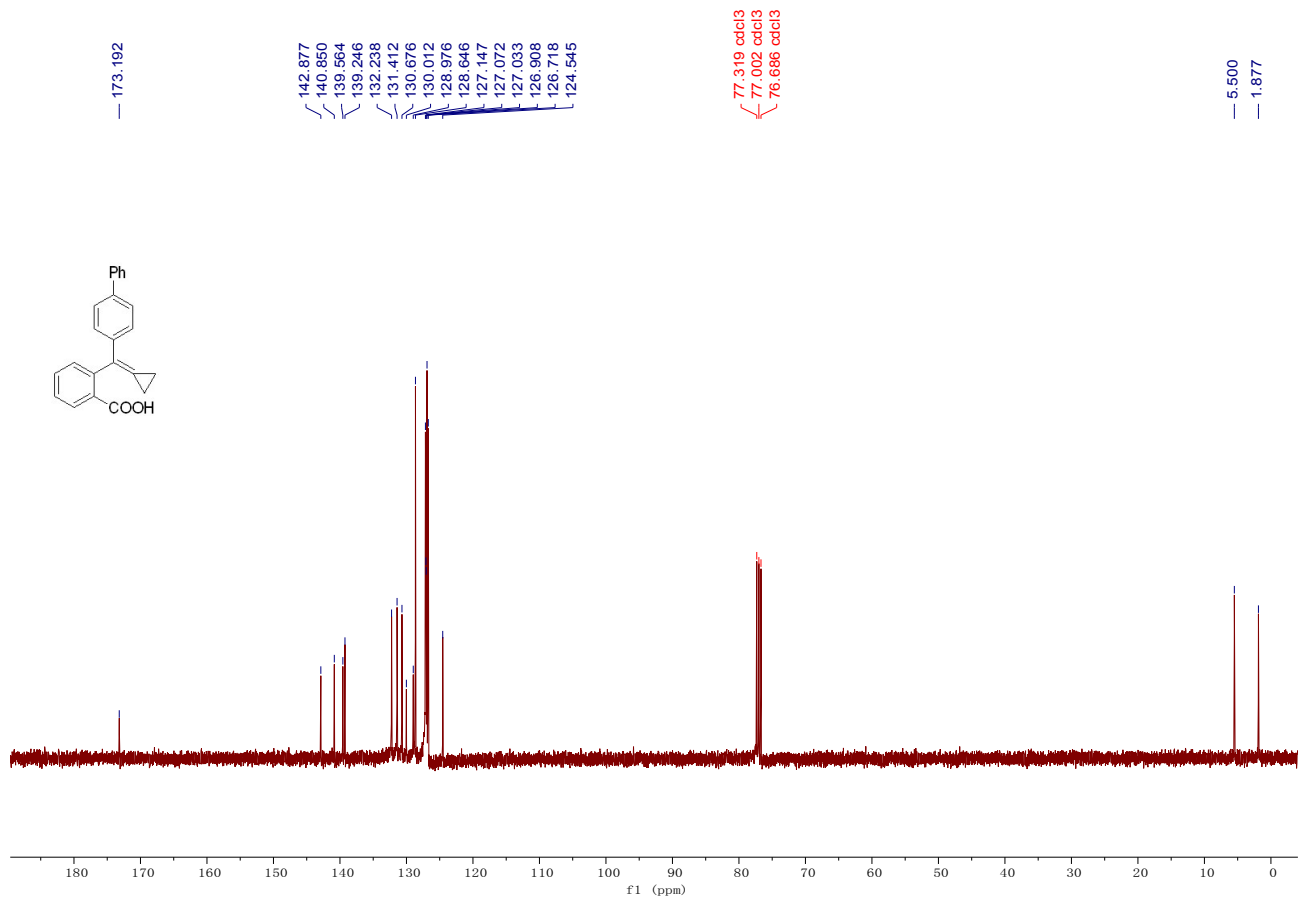
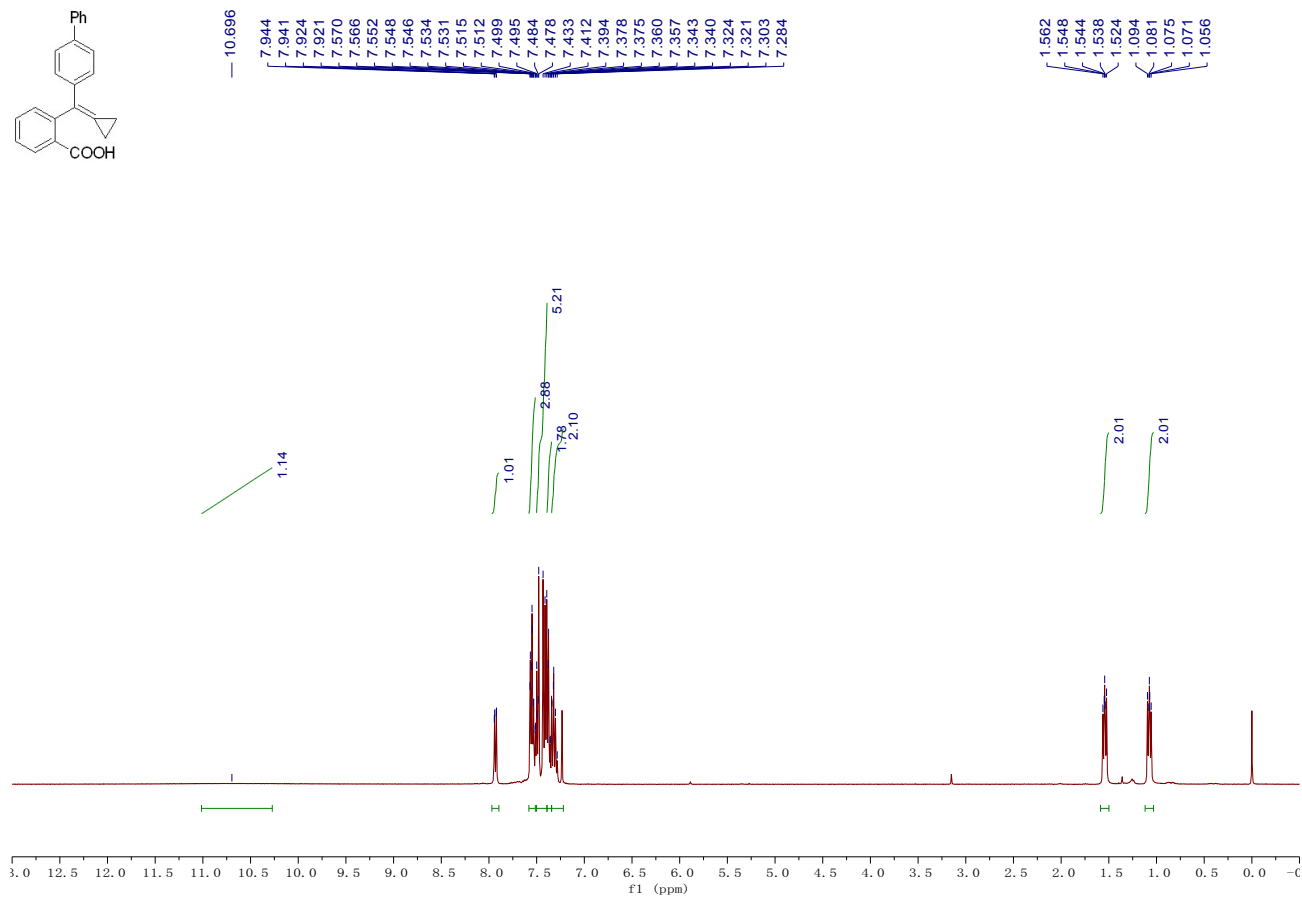
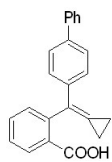


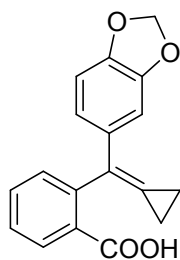
Compound 1k: Yield: 1.34 g, 83%; A white solid; Mp: 171 - 173 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.90 (br, 1H), 7.96 – 7.88 (m, 1H), 7.54 – 7.45 (m, 1H), 7.39 – 7.33 (m, 1H), 7.33 – 7.24 (m, 5H), 1.56 – 1.47 (m, 2H), 1.32 – 1.23 (m, 9H), 1.10 – 1.00 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.3, 149.4, 143.2, 137.6, 132.1, 131.4, 130.6, 130.1, 129.0, 126.9, 126.5, 124.9, 123.4, 34.4, 31.3, 5.4, 1.8; IR (neat): ν 2962, 1765, 1716, 1465, 1286, 1258, 760 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 329.1512, found: 329.1516.



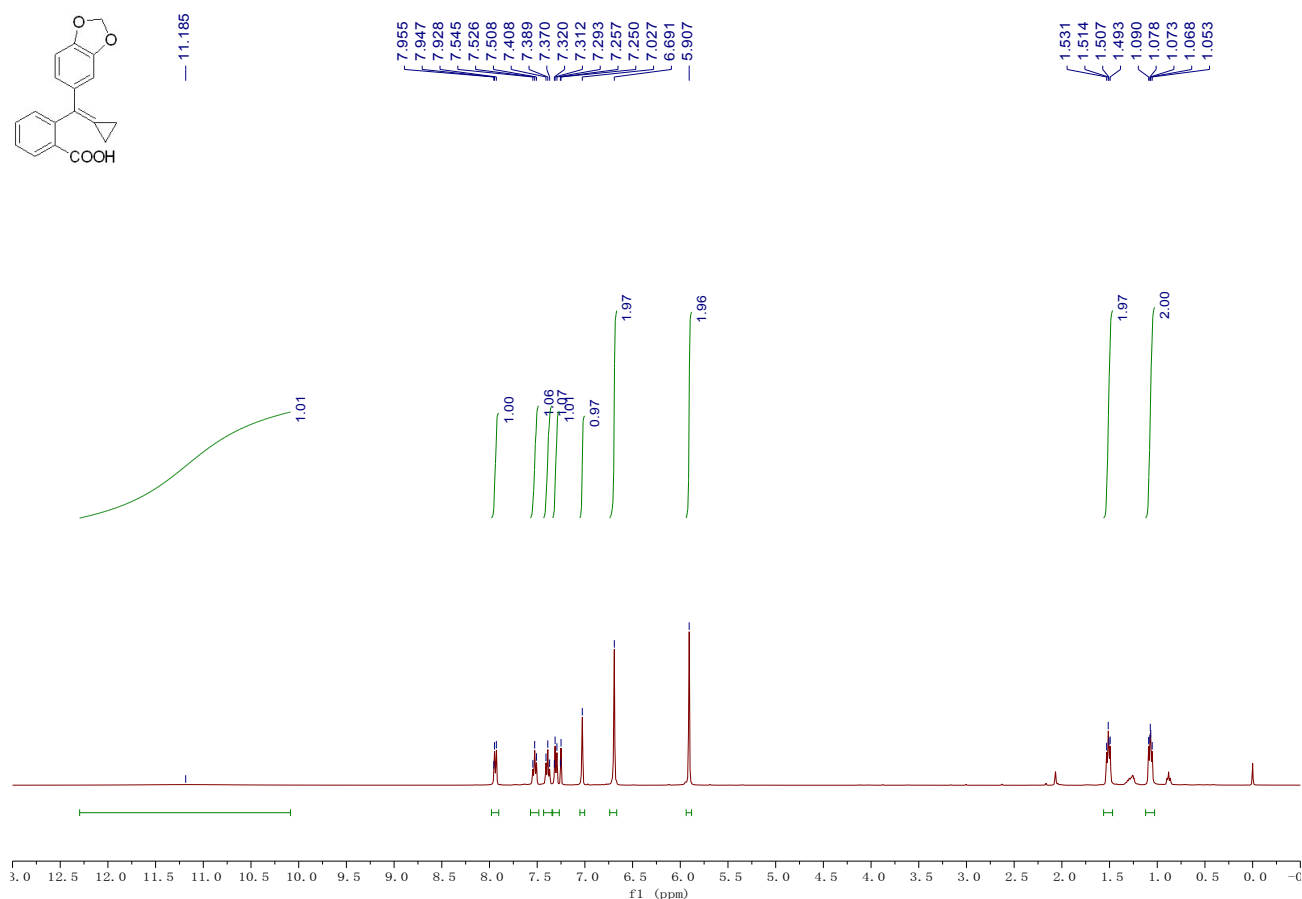


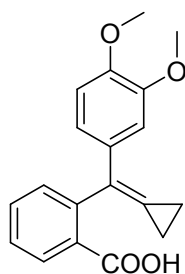
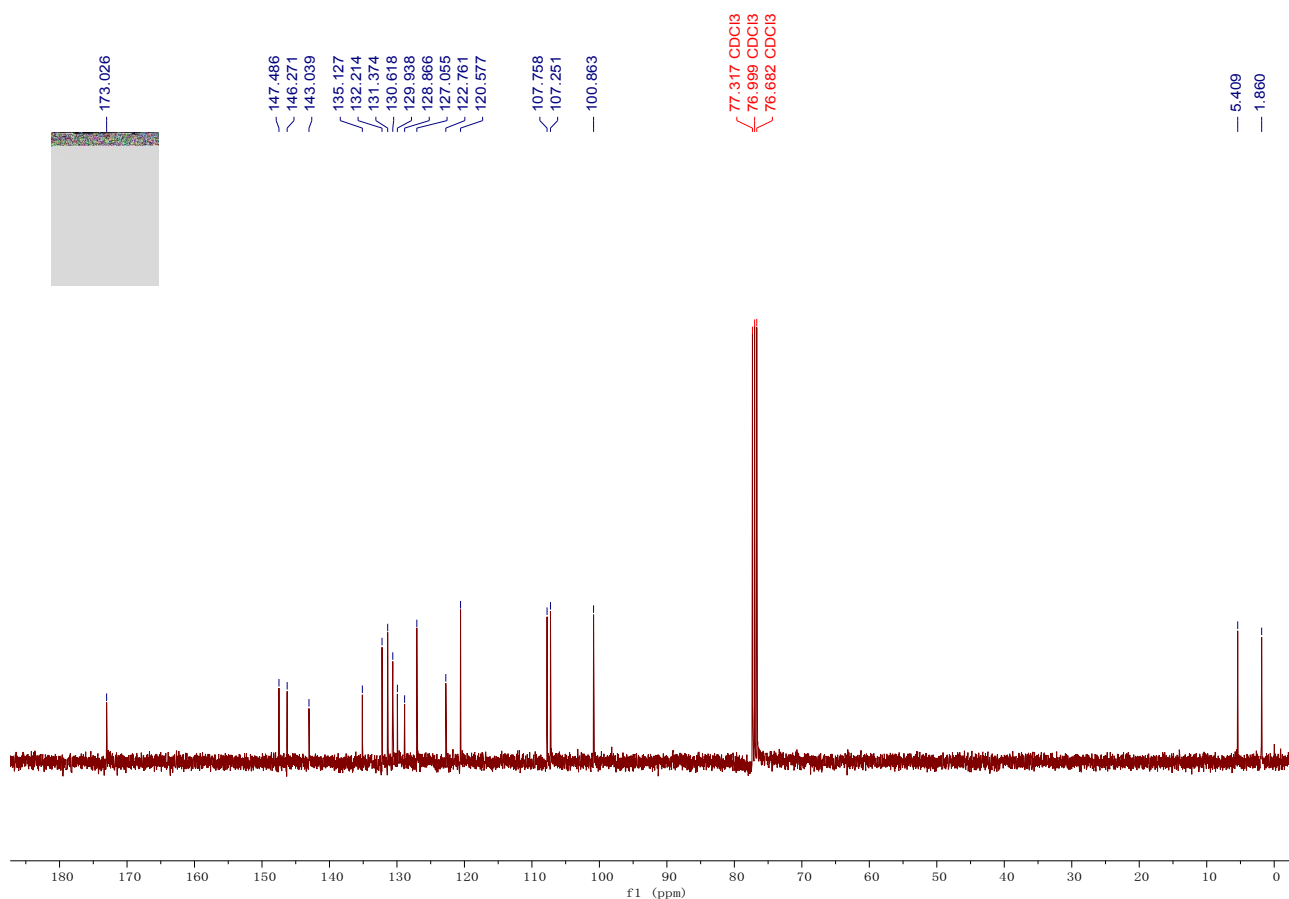
Compound 11: Yield: 1.01 g, 95%; A white solid; Mp: 189 - 191 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 10.70 (br, 1H), 7.93 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.50 – 7.39 (m, 5H), 7.39 – 7.34 (m, 2H), 7.34 – 7.22 (m, 2H), 1.59 – 1.50 (m, 2H), 1.12 – 1.03 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 173.2, 142.9, 140.9, 139.6, 139.2, 132.2, 131.4, 130.7, 130.0, 129.0, 128.6, 127.15, 127.07, 127.0, 126.9, 126.7, 124.5, 5.5, 1.9; IR (neat): ν 2965, 1765, 1465, 1289, 1250 cm⁻¹; HRMS (EI) Calcd. for C₂₃H₁₈O₂ [M]⁺: 326.1301, found: 326.1303.



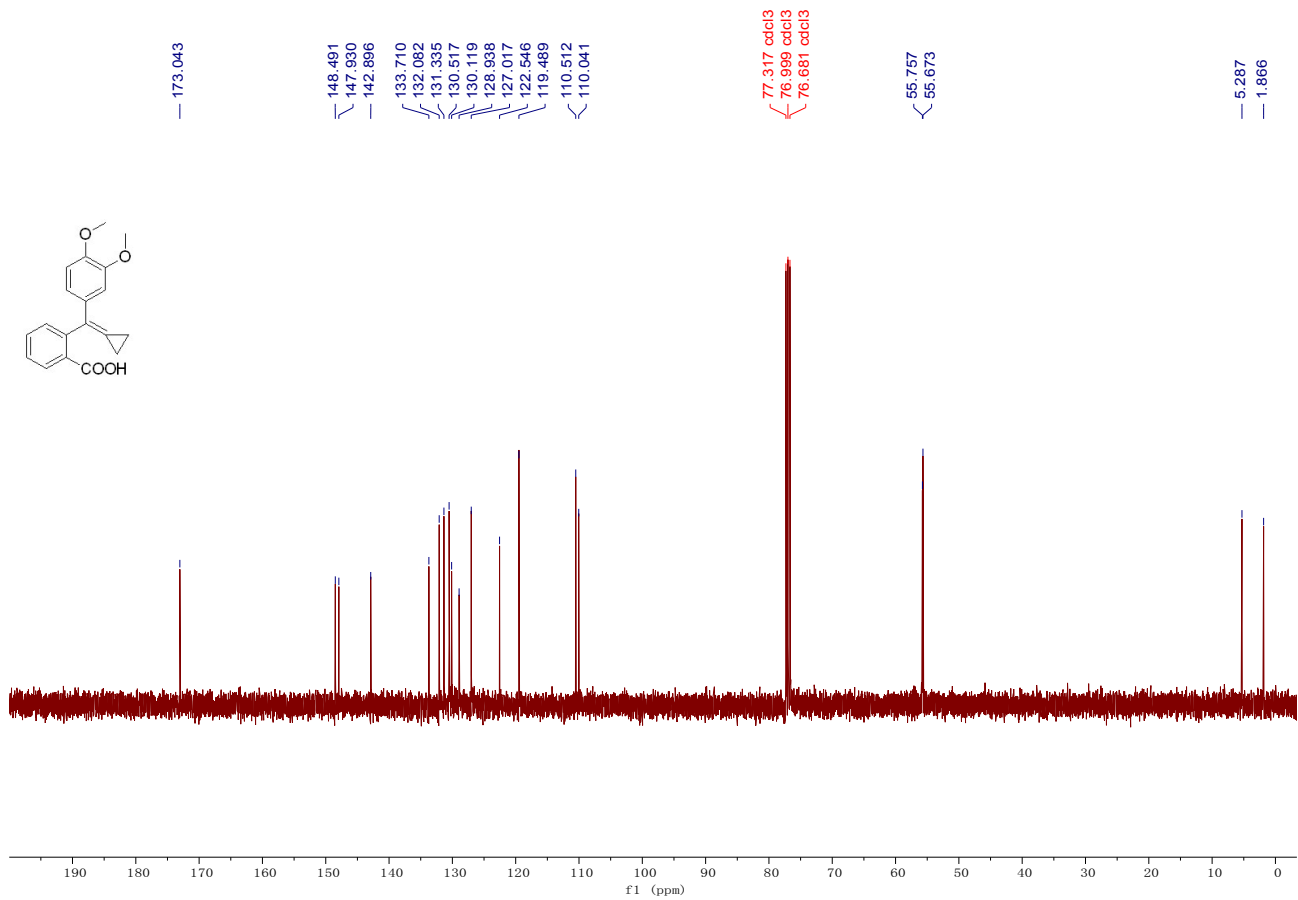
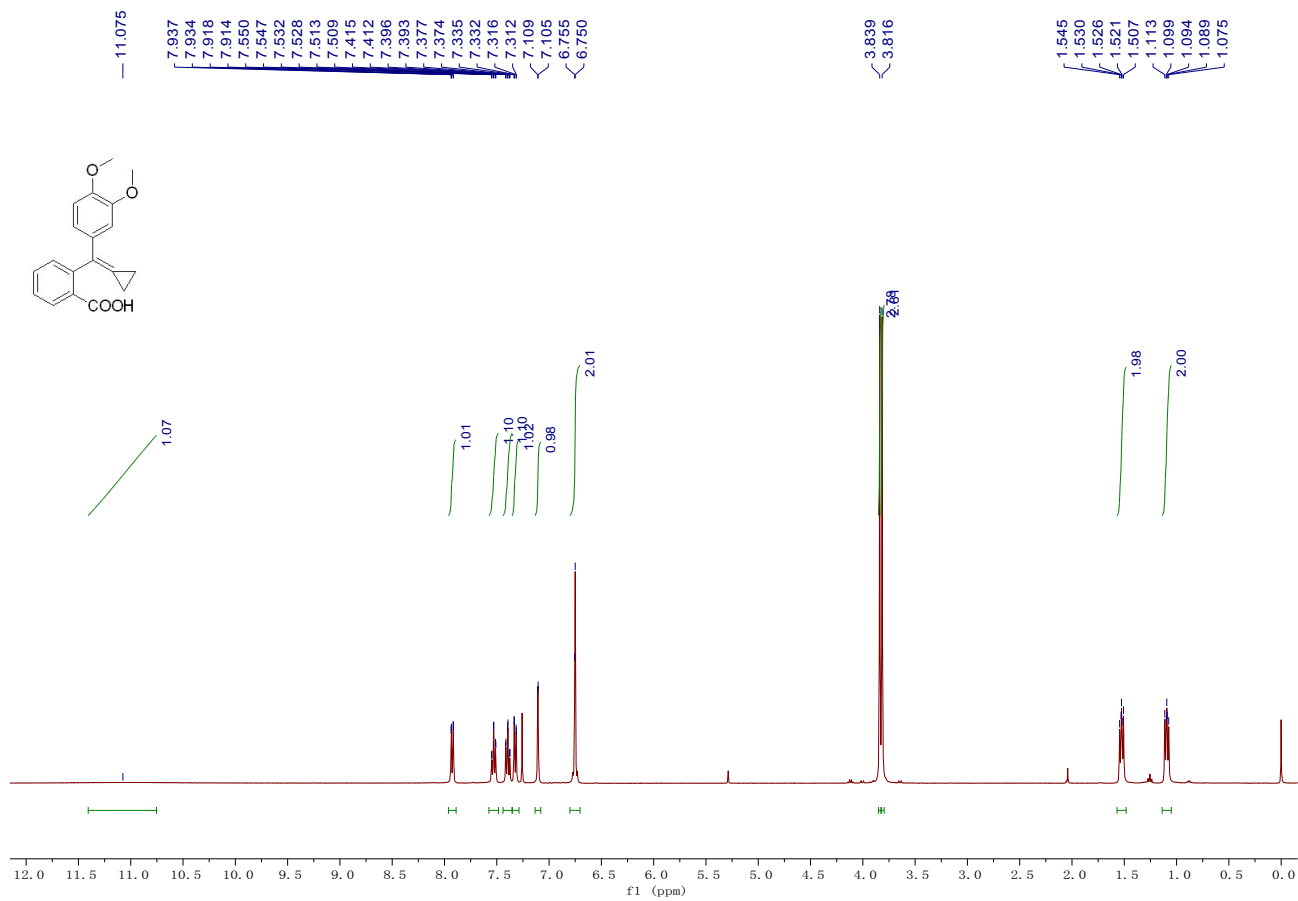


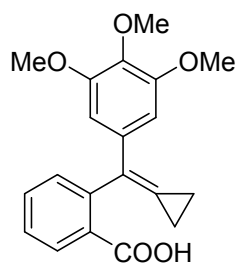
Compound 1m: Yield: 1.29 g, 94%; A white solid; Mp: 190 - 192 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 11.18 (br, 1H), 7.94 (d, $J = 7.7$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.03 (s, 1H), 6.74 – 6.67 (m, 2H), 5.94 – 5.88 (m, 2H), 1.56 – 1.47 (m, 2H), 1.12 – 1.03 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.0, 147.5, 146.3, 143.0, 135.1, 132.2, 131.4, 130.6, 129.9, 128.9, 127.1, 122.8, 120.6, 107.8, 107.3, 100.9, 5.4, 1.9; IR (neat): ν 2910, 2840, 1750, 1265, 990 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_4$ $[\text{M}]^+$: 294.0887, found: 294.0889.



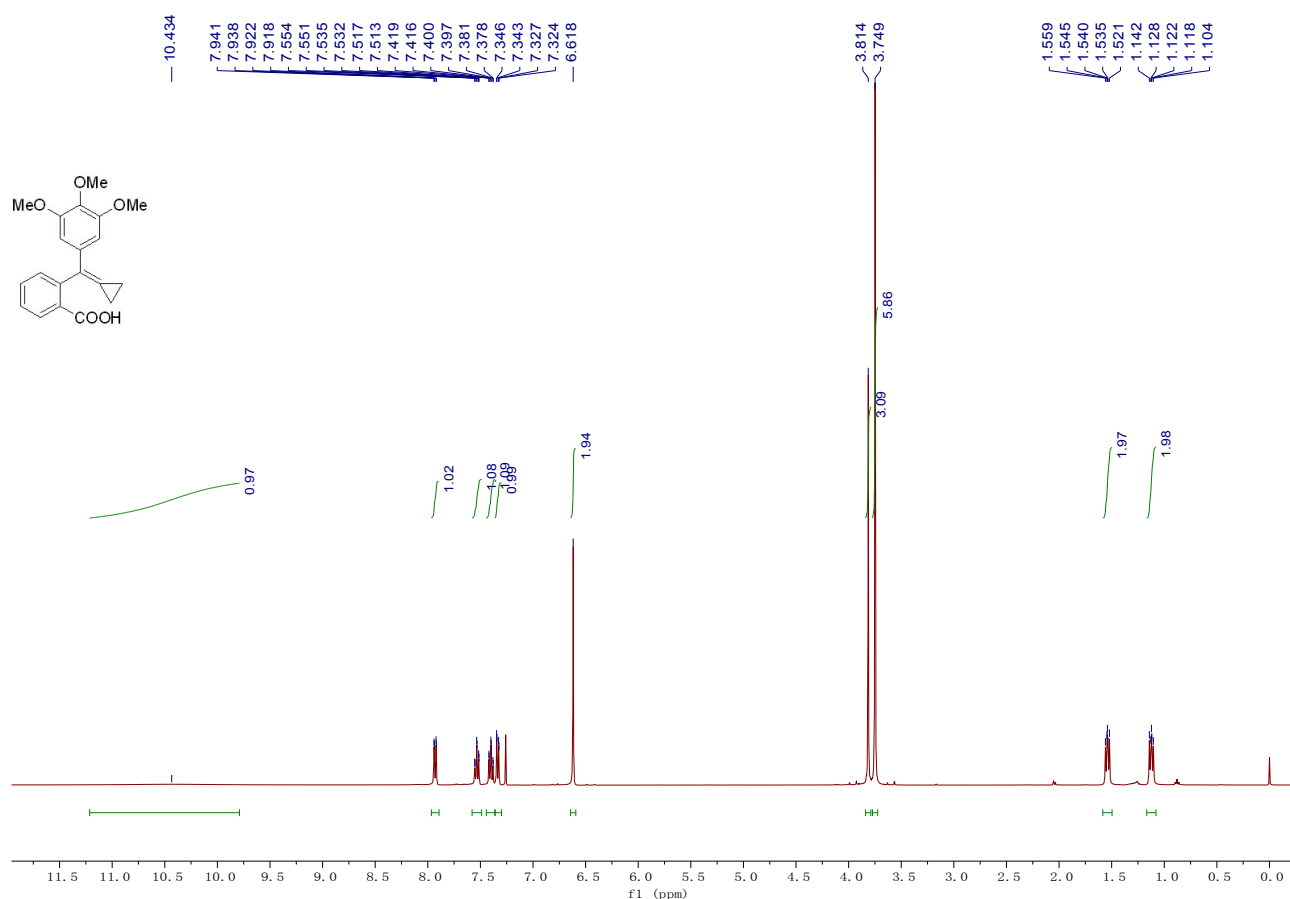


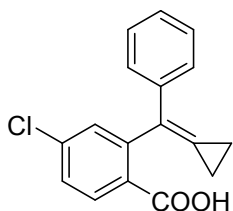
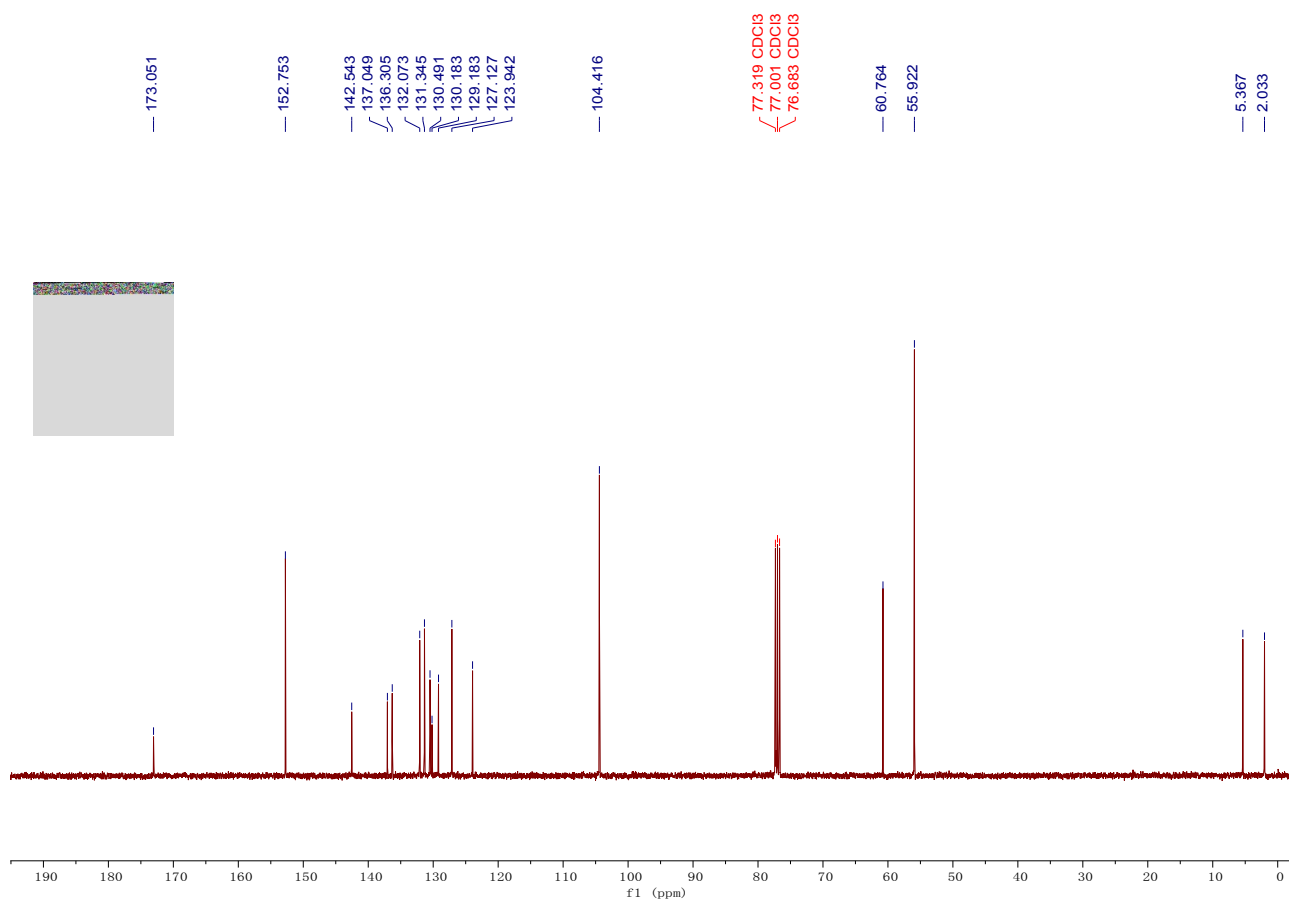
Compound 1n: Yield: 0.53 g, 80%; A white solid; Mp: 172 - 174 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 11.08 (br, 1H), 7.93 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.53 (td, $J = 7.5, 1.4$ Hz, 1H), 7.39 (td, $J = 7.6, 1.3$ Hz, 1H), 7.35 – 7.29 (m, 1H), 7.11 (s, 1H), 6.80 – 6.70 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 1.57 – 1.48 (m, 2H), 1.14 – 1.05 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.0, 148.5, 147.9, 142.9, 133.7, 132.1, 131.3, 130.5, 130.1, 128.9, 127.0, 122.5, 119.5, 110.5, 110.0, 55.8, 55.7, 5.3, 1.9; IR (neat): ν 2911, 2845, 1753, 1265, 764 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 333.1097, found: 333.1098.



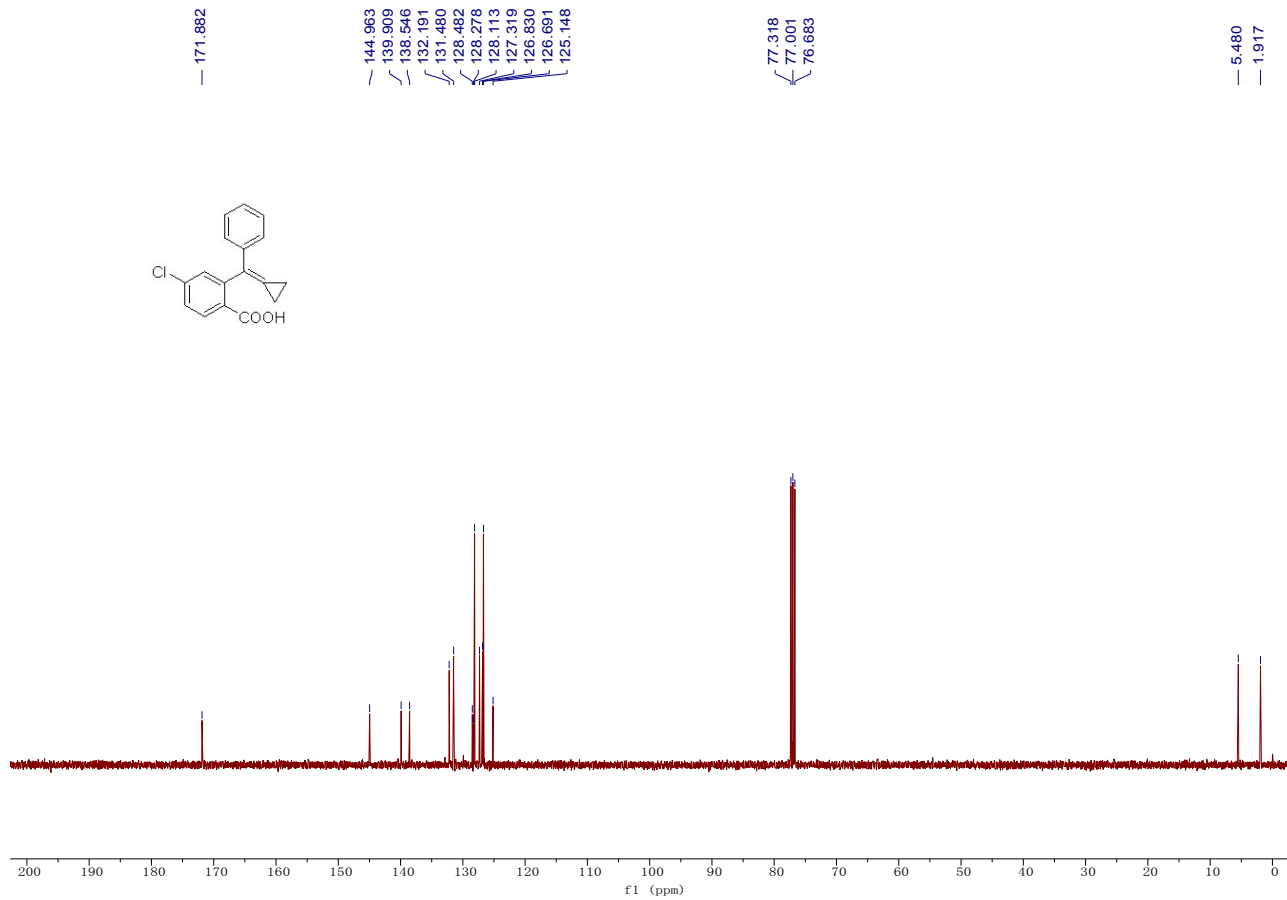
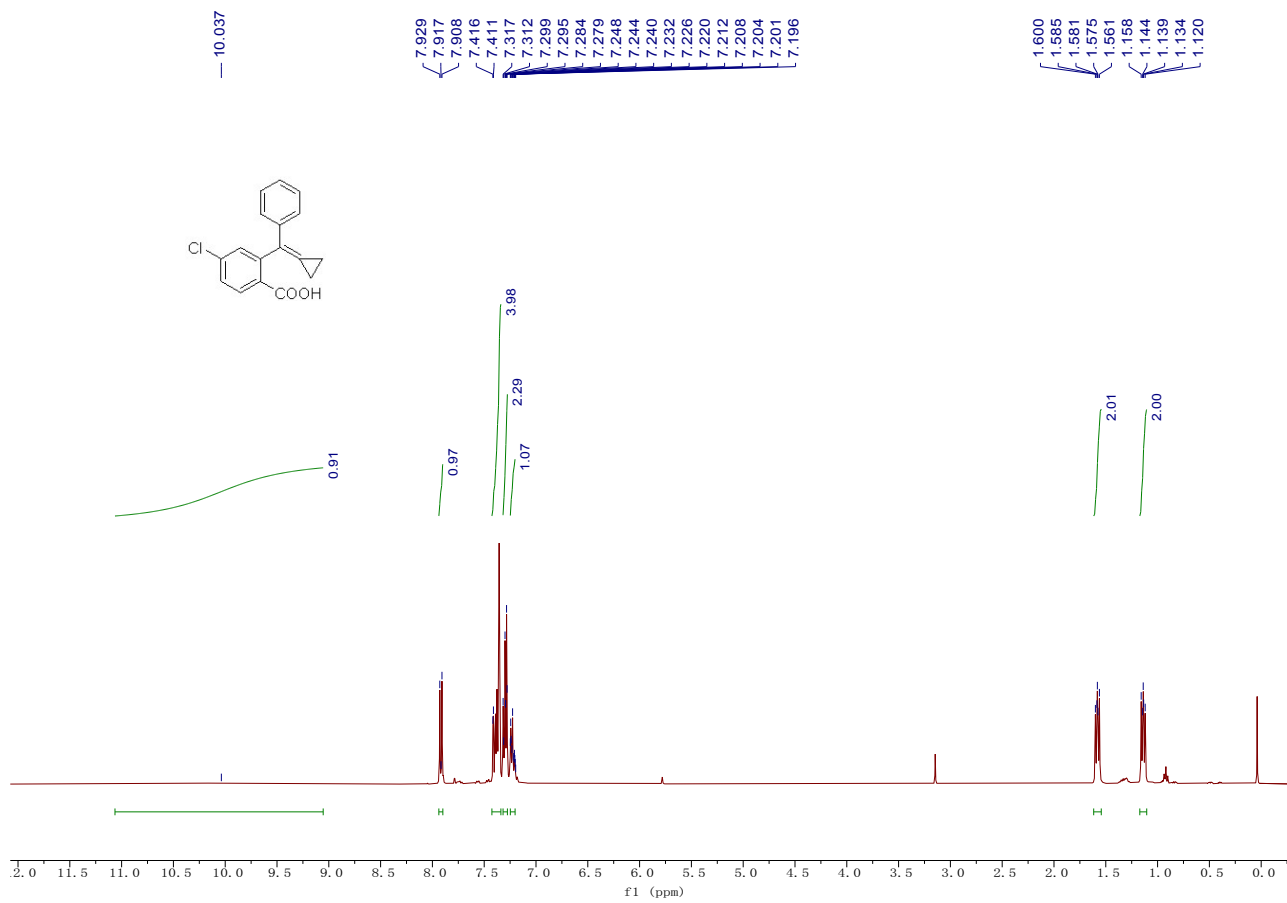


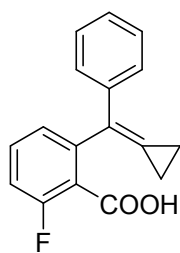
Compound 10: Yield: 1.4 g, 71%; A white solid; Mp: 189 - 191 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.43 (br, 1H), 7.93 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.53 (td, $J = 7.5, 1.4$ Hz, 1H), 7.40 (td, $J = 7.6, 1.2$ Hz, 1H), 7.33 (dd, $J = 7.7, 1.2$ Hz, 1H), 6.62 (s, 2H), 3.81 (s, 3H), 3.75 (s, 6H), 1.58 – 1.50 (m, 2H), 1.17 – 1.08 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.1, 152.8, 142.5, 137.0, 136.3, 132.1, 131.3, 130.5, 130.2, 129.2, 127.1, 123.9, 104.4, 60.8, 55.9, 5.4, 2.0; IR (neat): ν 3316, 1760, 1617, 1594, 1488 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 363.1203, found: 363.1202.



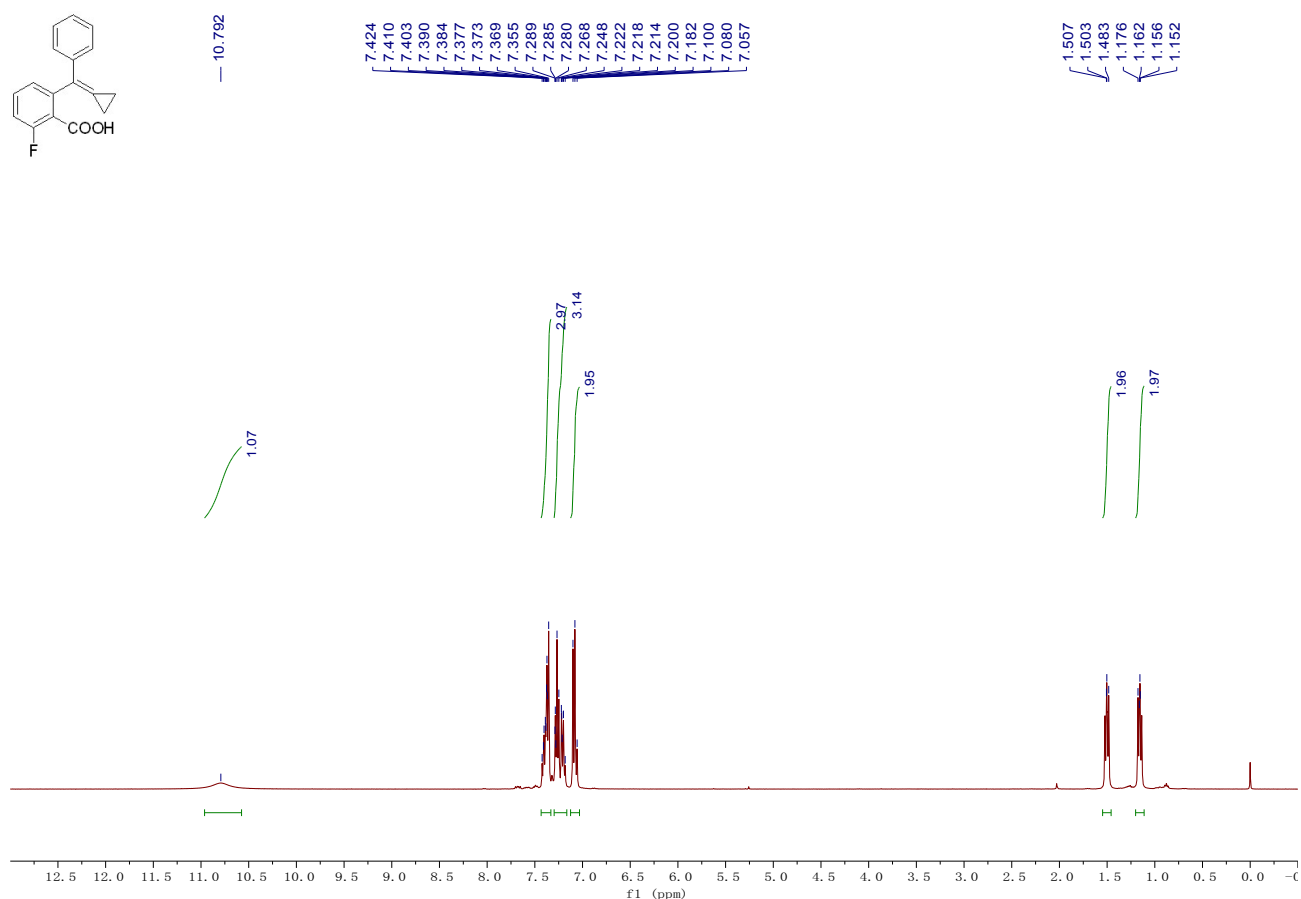


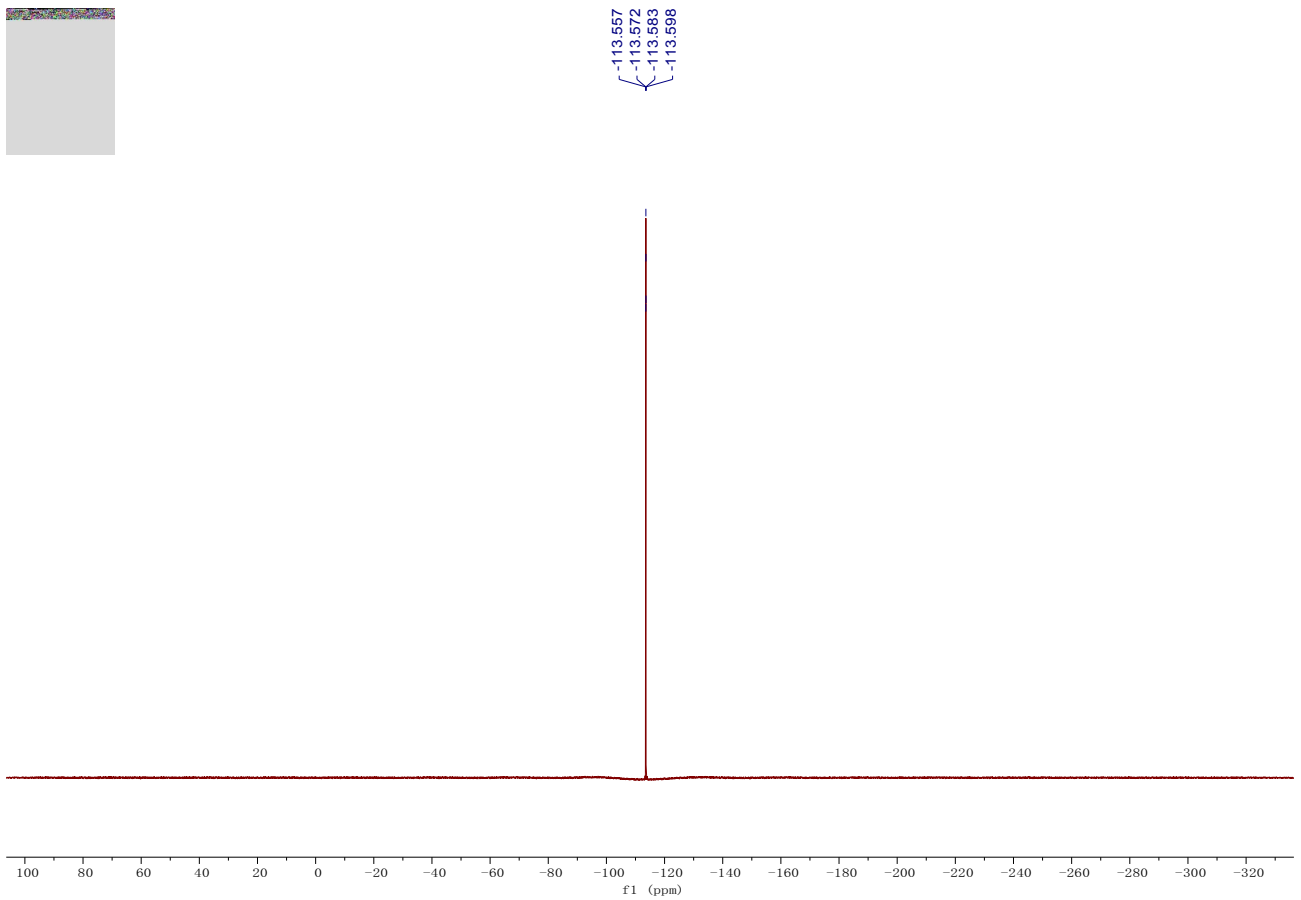
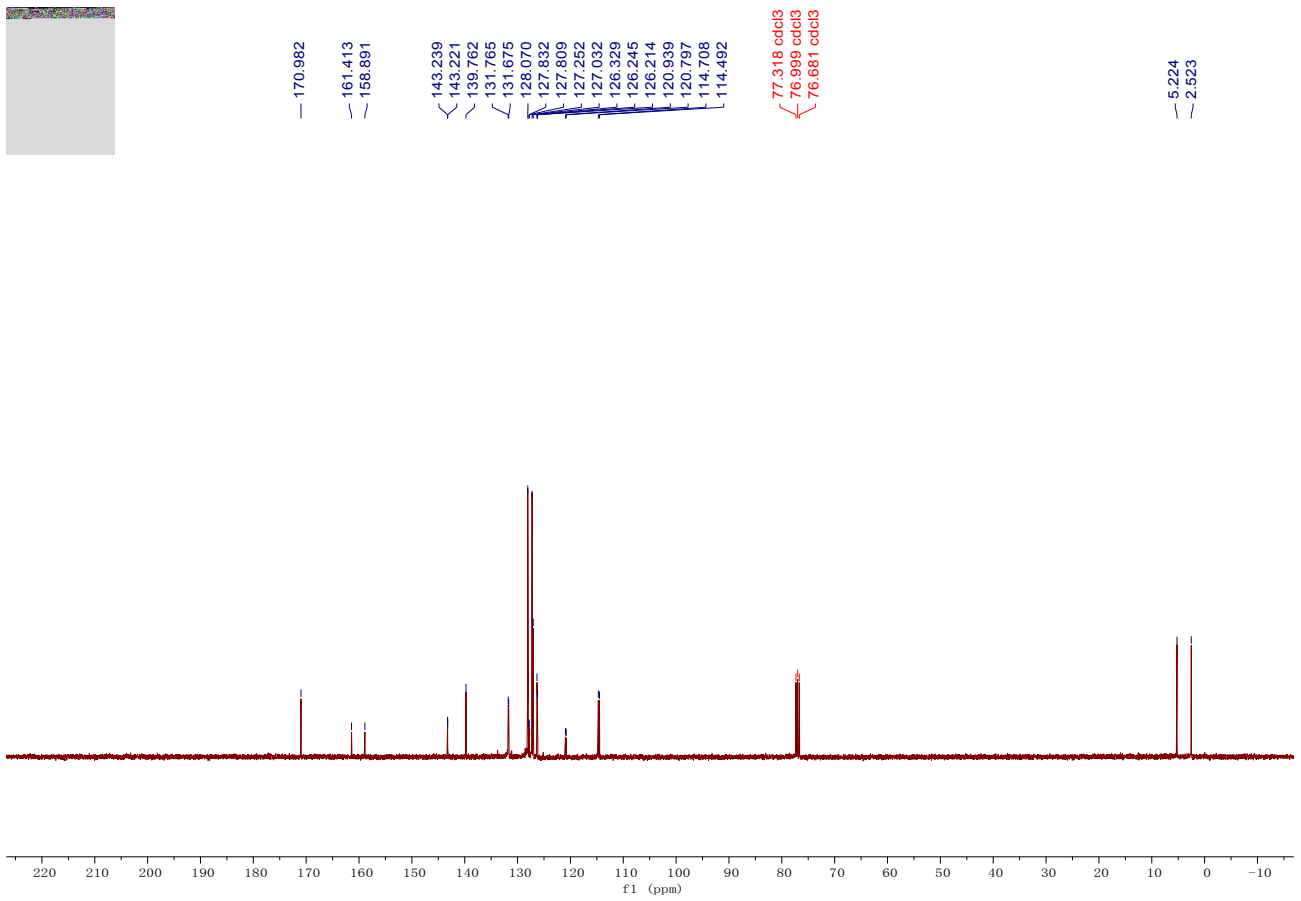
Compound 1p: Yield: 0.72 g, 83%; A white solid; Mp: 101 - 103 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.04 (br, 1H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.43 – 7.34 (m, 4H), 7.32 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 1.62 – 1.54 (m, 2H), 1.17 – 1.10 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.9, 145.0, 139.9, 138.5, 132.2, 131.5, 128.5, 128.3, 128.1, 127.3, 126.8, 126.7, 125.1, 5.5, 1.9; IR (neat): ν 3052, 2974, 1706, 1588, 1278 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{17}\text{H}_{13}\text{O}_2\text{Cl}$ $[\text{M}]^+$: 284.0599, found: 284.0596.

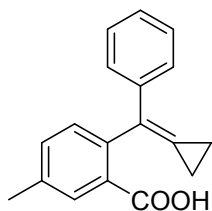




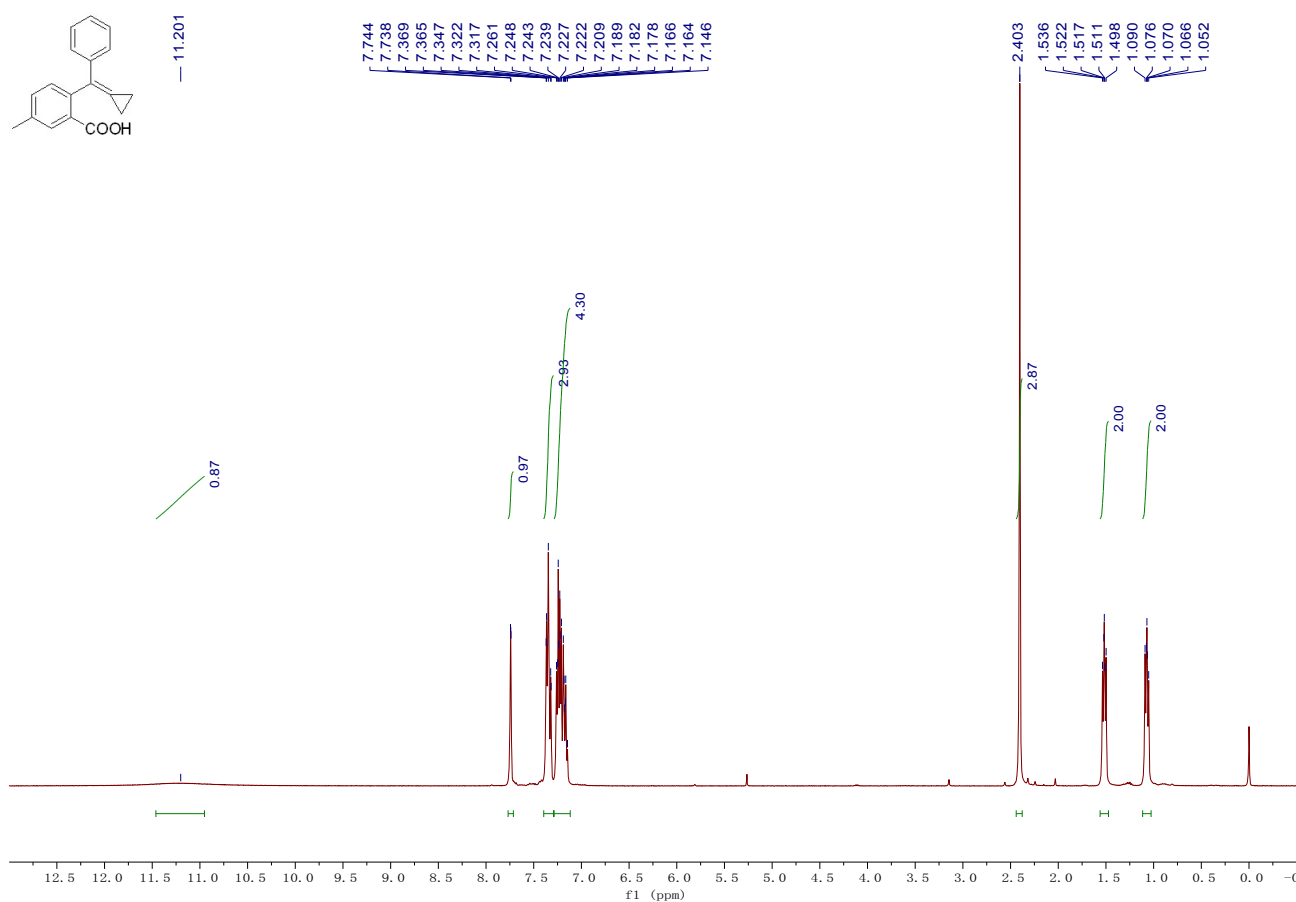
Compound 1q: Yield: 1.45 g, 90%; A white solid; Mp: 137 - 139 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.79 (br, 1H), 7.43 – 7.33 (m, 3H), 7.30 – 7.16 (m, 3H), 7.13 – 7.03 (m, 2H), 1.55 – 1.46 (m, 2H), 1.20 – 1.11 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.0, 160.2 (d, $J = 253.7$ Hz), 143.2 (d, $J = 1.9$ Hz), 139.8, 131.7 (d, $J = 9.1$ Hz), 128.1, 127.8 (d, $J = 2.3$ Hz), 127.3, 127.0, 126.3, 126.2 (d, $J = 3.2$ Hz), 120.9 (d, $J = 14.3$ Hz), 114.6 (d, $J = 21.7$ Hz), 5.2, 2.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.56 – -113.59 (m); IR (neat): ν 2980, 1290, 1675, 1263, 768 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{17}\text{H}_{13}\text{O}_2\text{F}$ $[\text{M}]^+$: 268.0894, found: 268.0897.

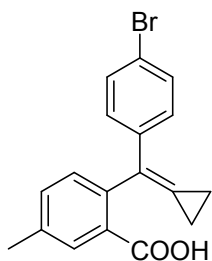
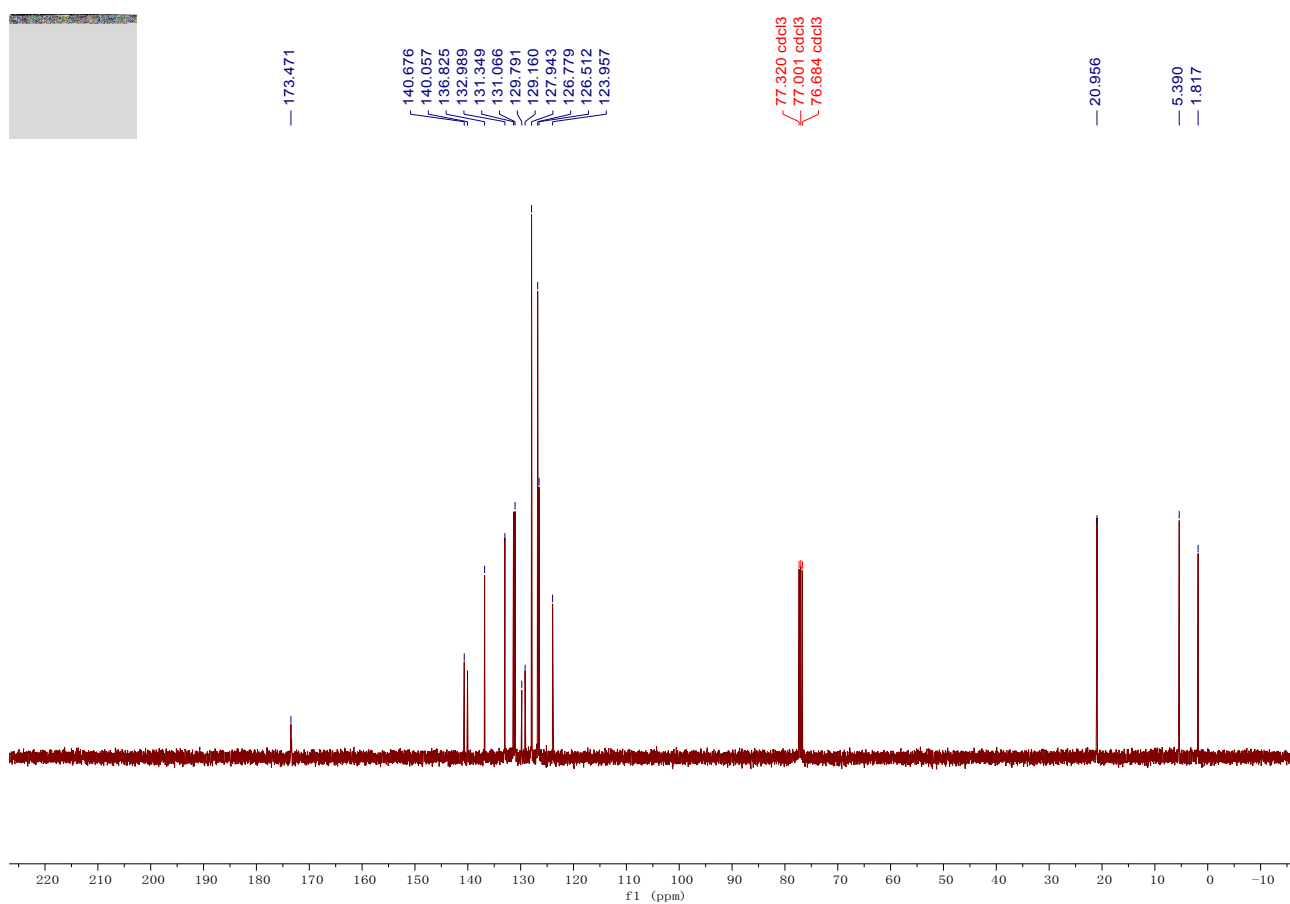




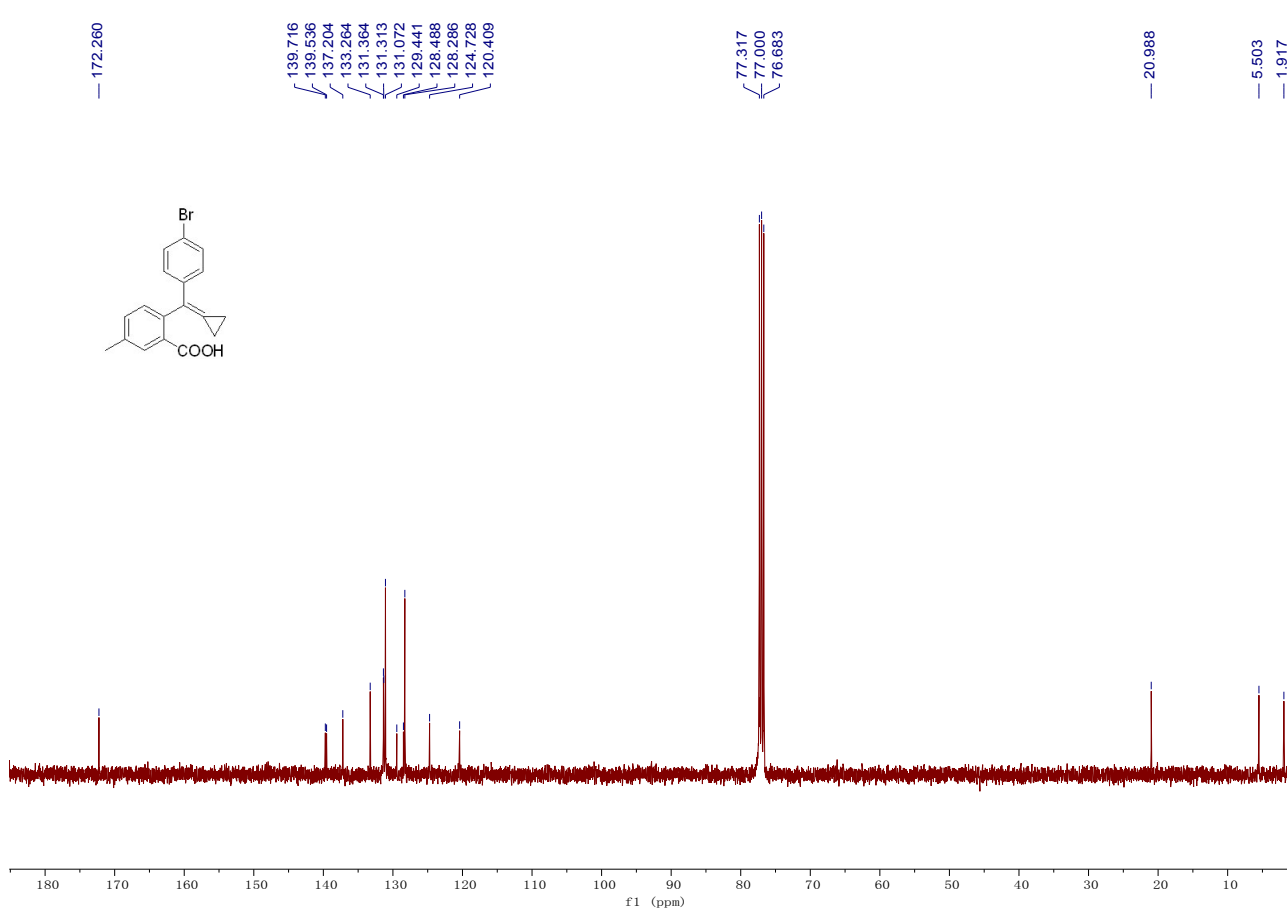
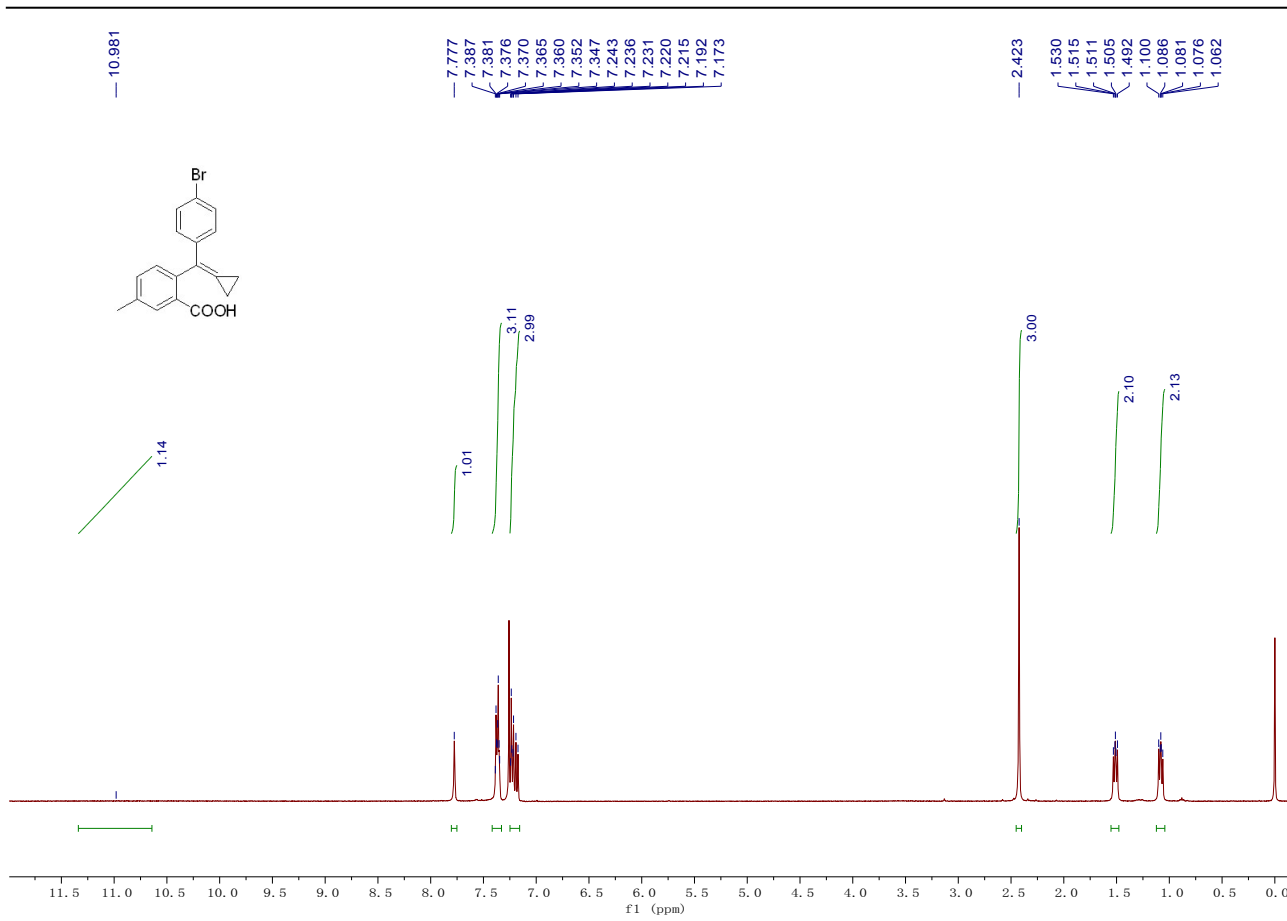


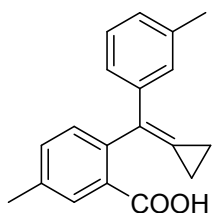
Compound 1r: Yield: 1.26 g, 92%; A white solid; Mp: 170 - 172 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 11.20 (br, 1H), 7.74 (s, 1H), 7.39 – 7.29 (m, 3H), 7.29 – 7.12 (m, 4H), 2.40 (s, 3H), 1.56 – 1.47 (m, 2H), 1.11 – 1.03 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.5, 140.7, 140.1, 136.8, 133.0, 131.3, 131.1, 129.8, 129.2, 127.9, 126.8, 126.5, 124.0, 21.0, 5.4, 1.8; IR (neat): ν 1689, 1494, 1298, 1255, 765 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 287.1043, found: 287.1047.



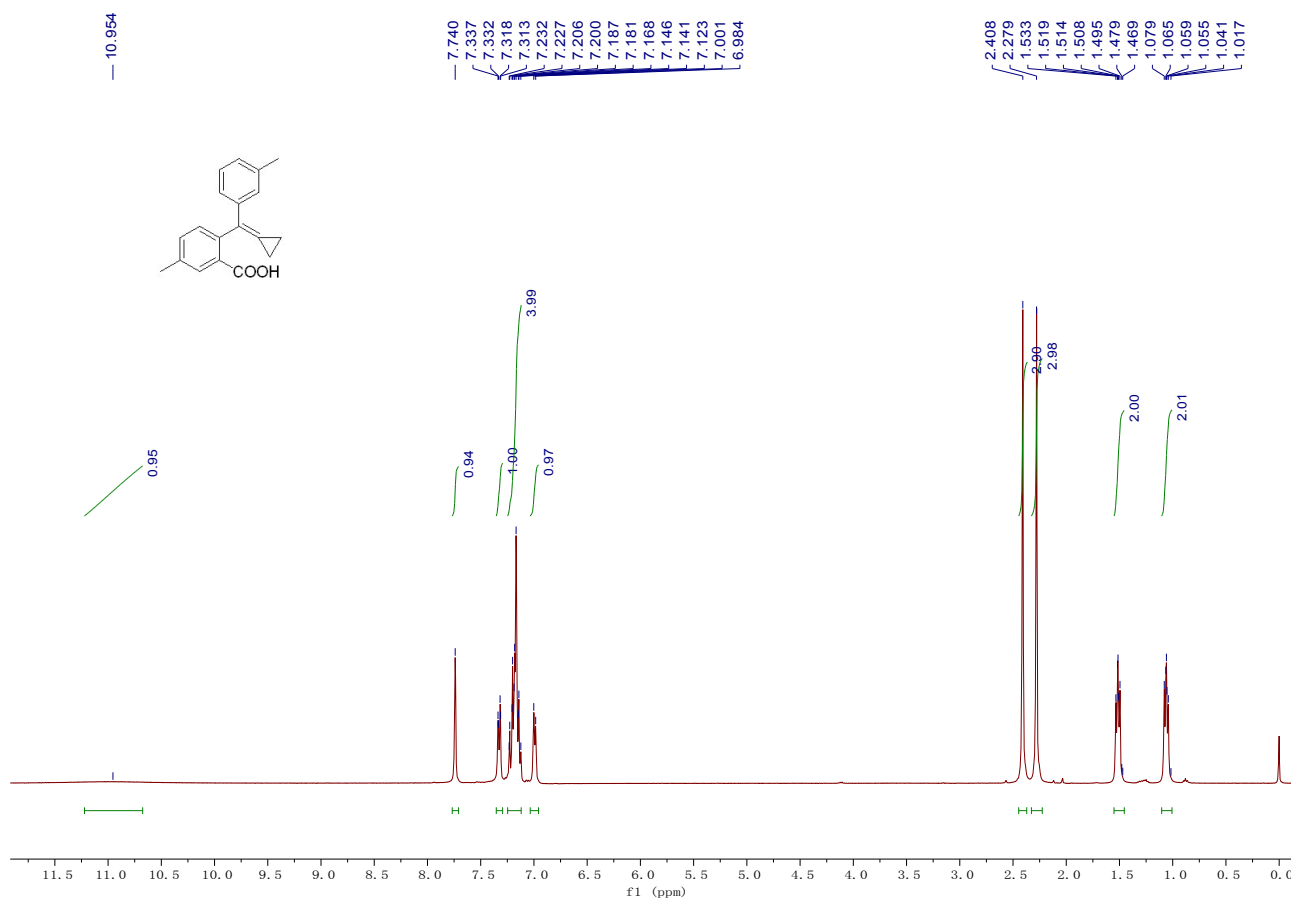


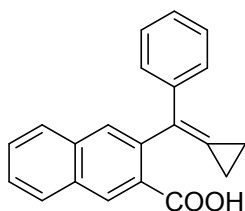
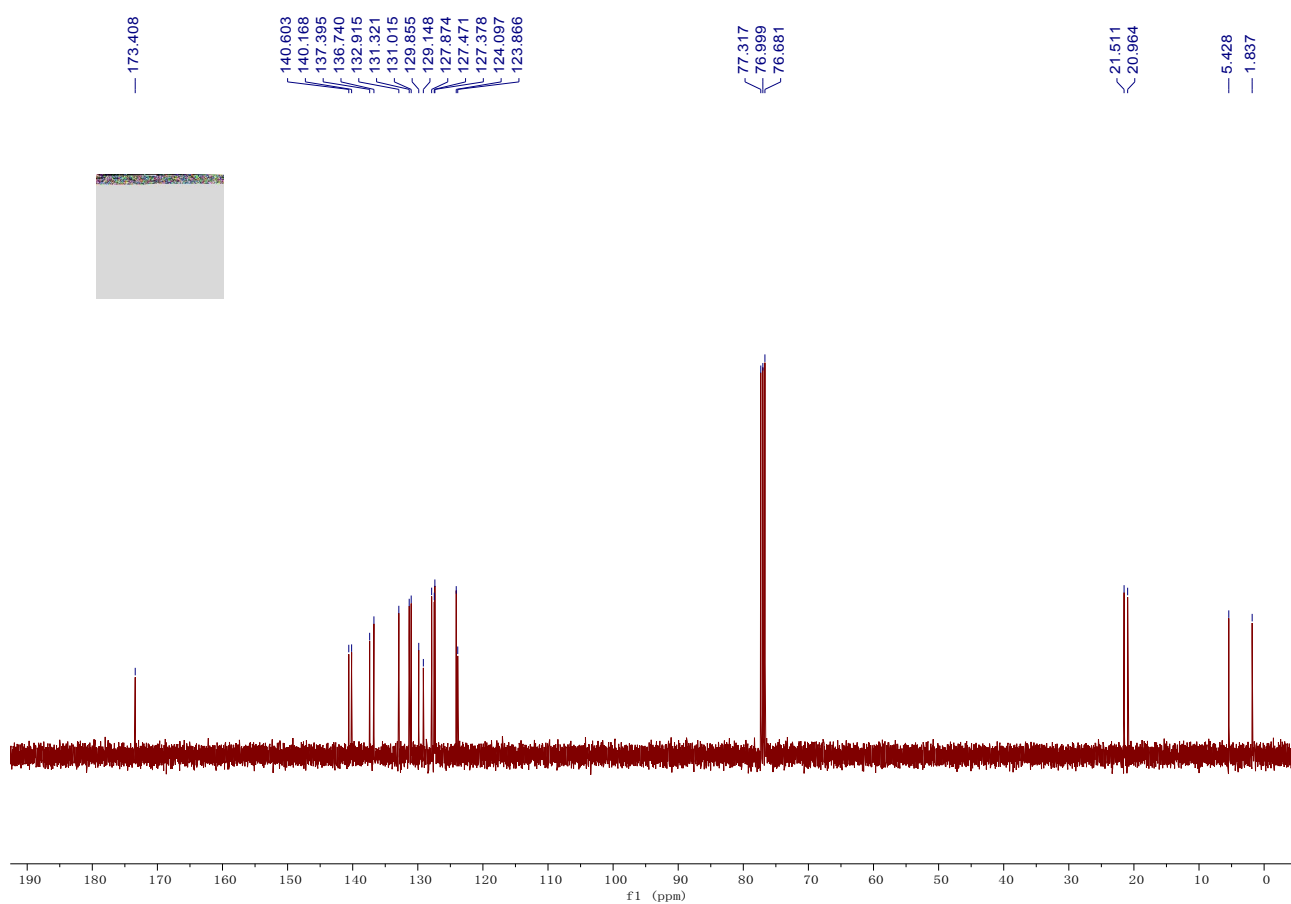
Compound 1s: Yield: 1.49 g, 74%; A white solid; Mp: > 200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.98 (br, 1H), 7.78 (s, 1H), 7.42 – 7.33 (m, 3H), 7.25 – 7.16 (m, 3H), 2.42 (s, 3H), 1.55 – 1.48 (m, 2H), 1.12 – 1.04 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.2, 139.7, 139.5, 137.2, 133.2, 131.36, 131.31, 131.0, 129.4, 128.4, 128.2, 124.7, 120.4, 20.9, 5.5, 1.9; IR (neat): ν 3371, 1717, 1652, 1338, 1144 cm^{-1} ; HRMS (FI) Calcd. for $\text{C}_{18}\text{H}_{15}\text{O}_2\text{Br}$ $[\text{M}]^+$: 342.0250, Found: 342.0245.



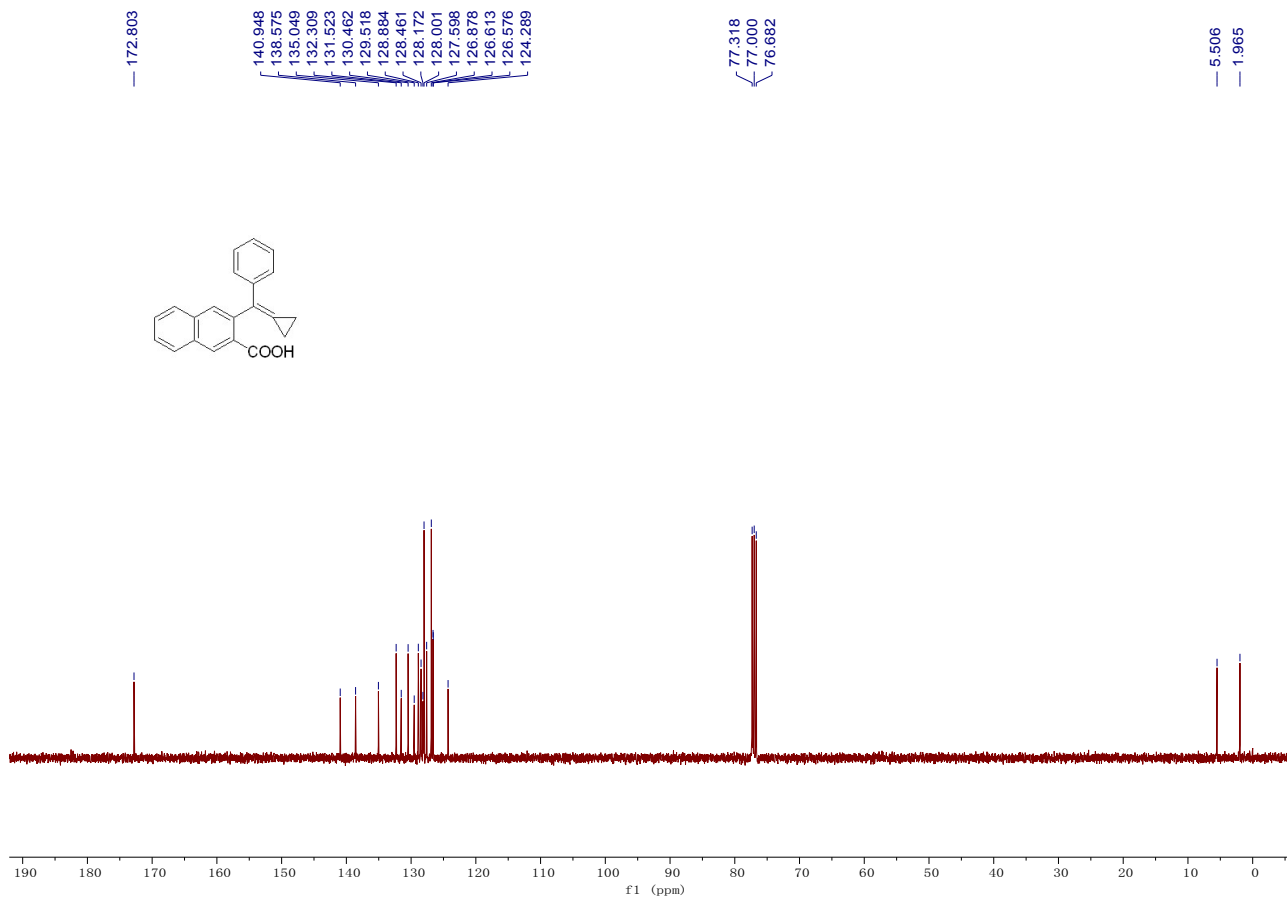
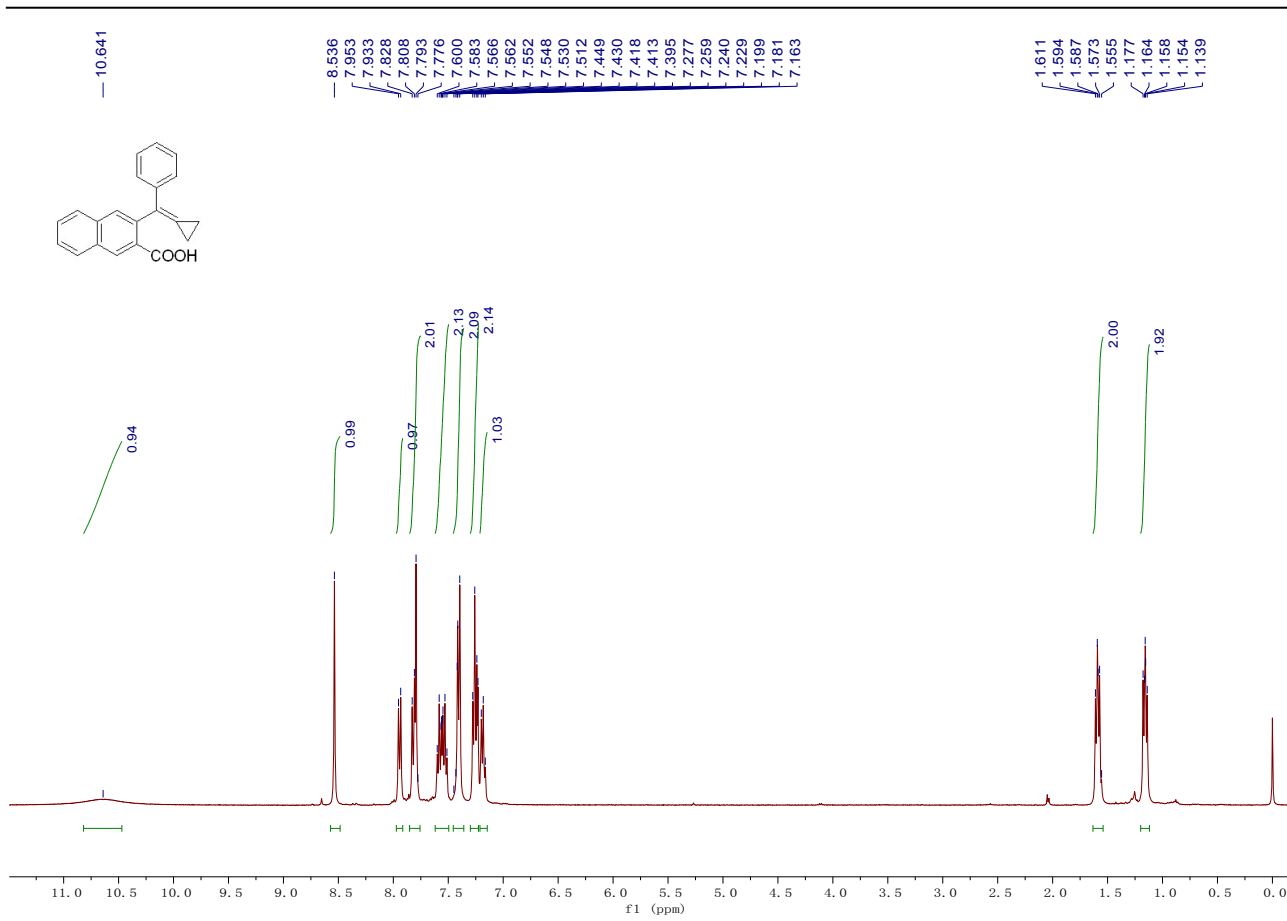


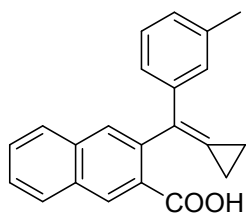
Compound 1t: Yield: 1.83 g, 81%; A white solid; Mp: 160 - 162 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.95 (br, 1H), 7.74 (s, 1H), 7.35 – 7.29 (m, 1H), 7.25 – 7.12 (m, 4H), 6.99 (d, J = 7.2 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 1.55 – 1.45 (m, 2H), 1.10 – 1.01 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.4, 140.6, 140.1, 137.3, 136.7, 132.9, 131.3, 131.0, 129.8, 129.1, 127.8, 127.4, 127.3, 124.1, 123.8, 21.5, 20.9, 5.4, 1.8; IR (neat): ν 2967, 1690, 1600, 1293, 750 cm^{-1} ; HRMS (FI) Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$: 278.1301, Found: 278.1303.



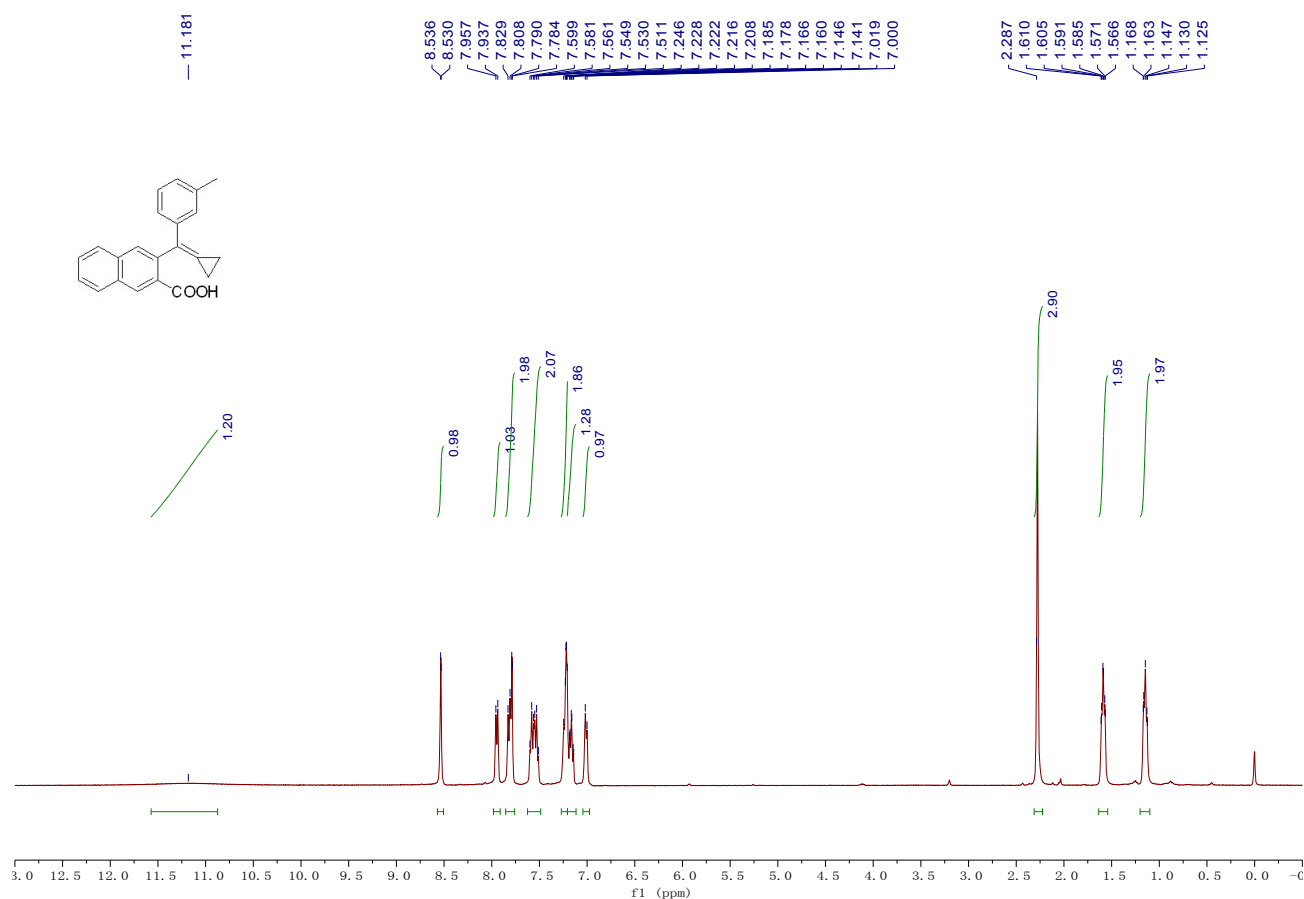


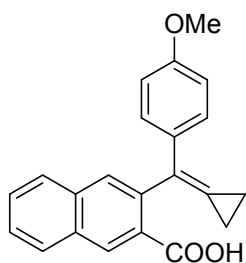
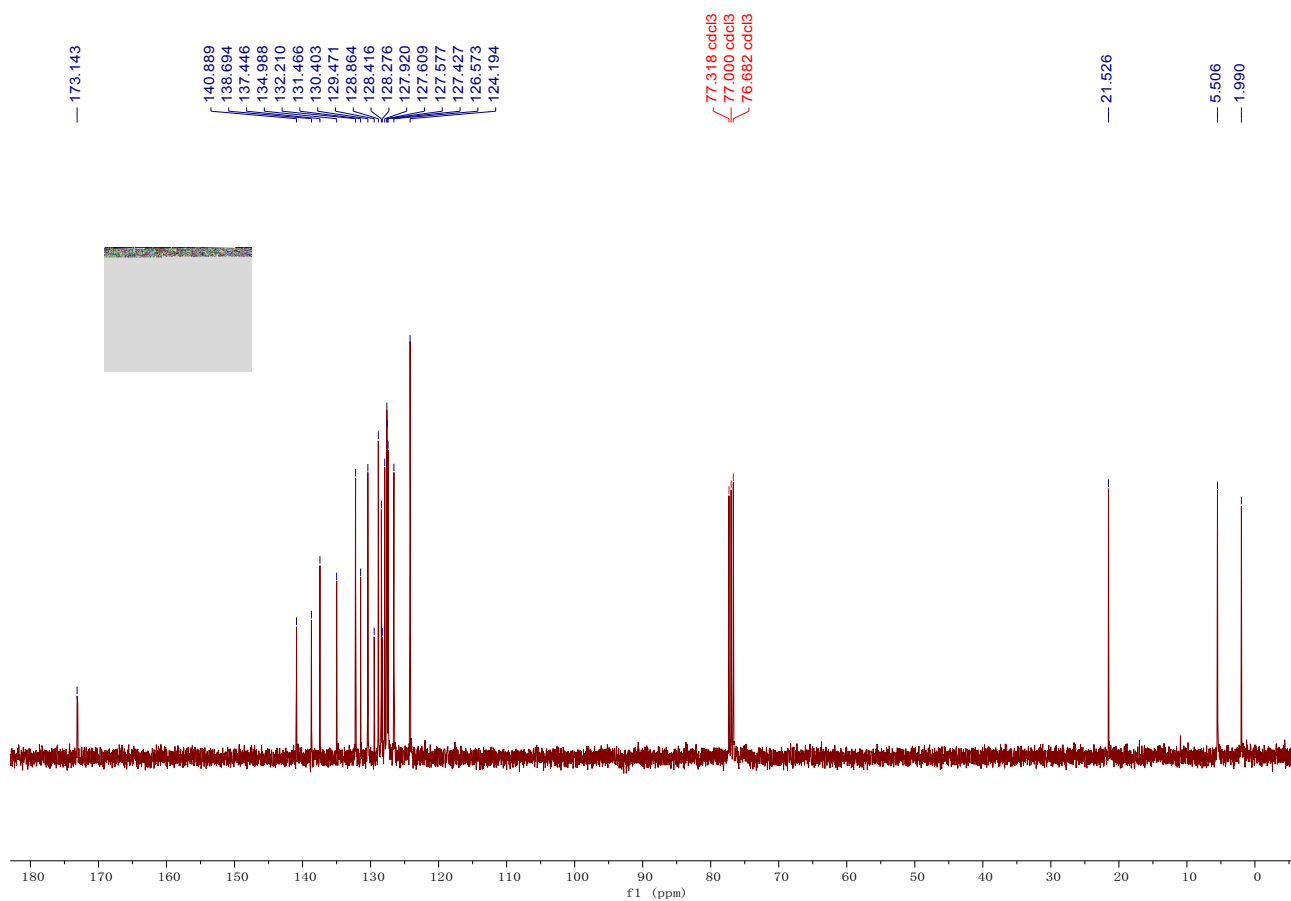
Compound 1u: Yield: 1.8 g, 81%; A white solid; Mp: > 200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.64 (br, 1H), 8.54 (s, 1H), 7.97 – 7.91 (m, 1H), 7.85 – 7.76 (m, 2H), 7.62 – 7.50 (m, 2H), 7.45 – 7.36 (m, 2H), 7.30 – 7.23 (m, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 1.63 – 1.54 (m, 2H), 1.20 – 1.12 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.8, 140.9, 138.5, 135.0, 132.3, 131.5, 130.4, 129.5, 128.8, 128.4, 128.1, 128.0, 127.6, 126.8, 126.6, 126.5, 124.2, 5.5, 1.9; IR (neat): ν 2963, 1672, 1282, 919, 745 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{21}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$: 300.1145, Found: 300.1150.



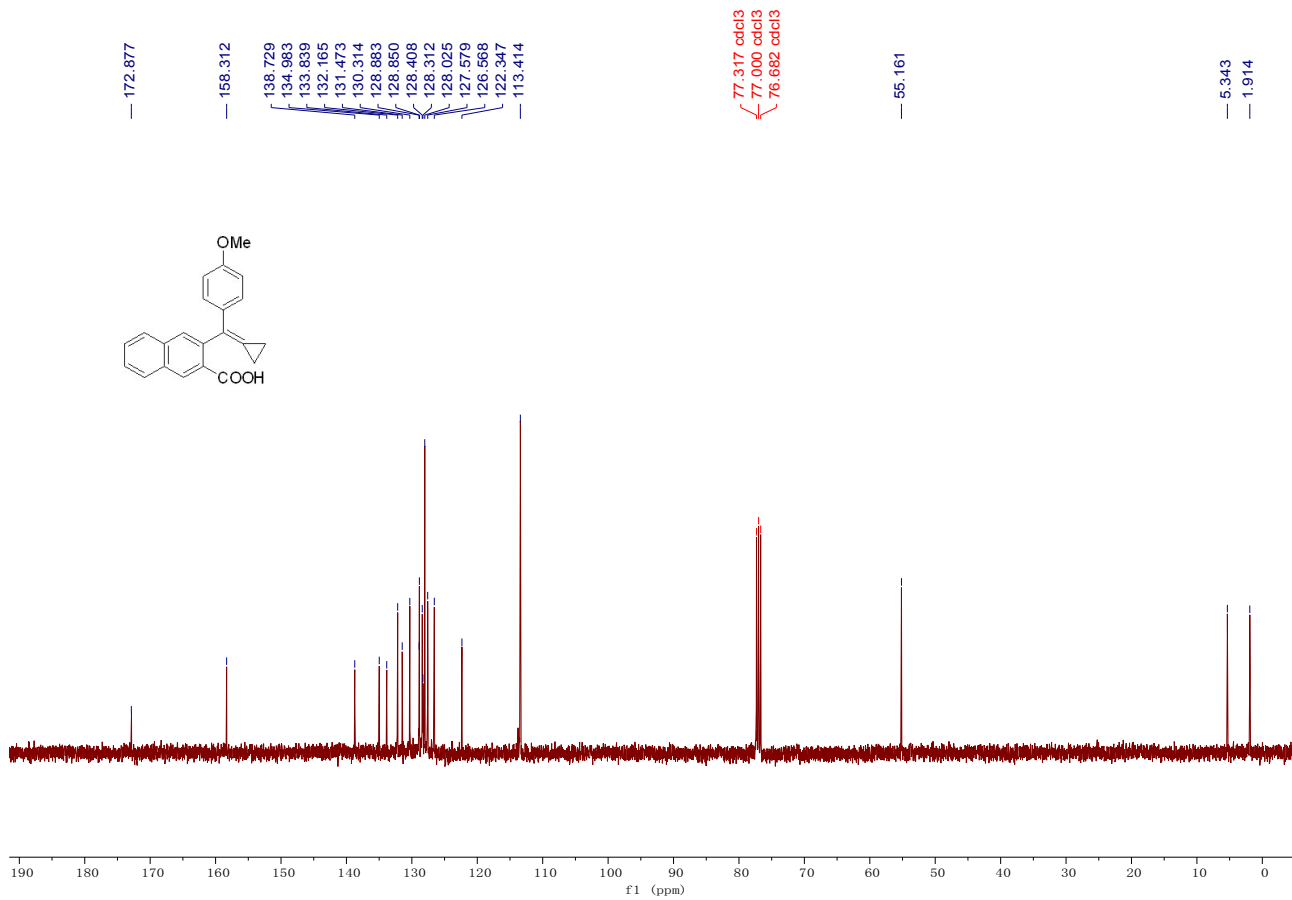
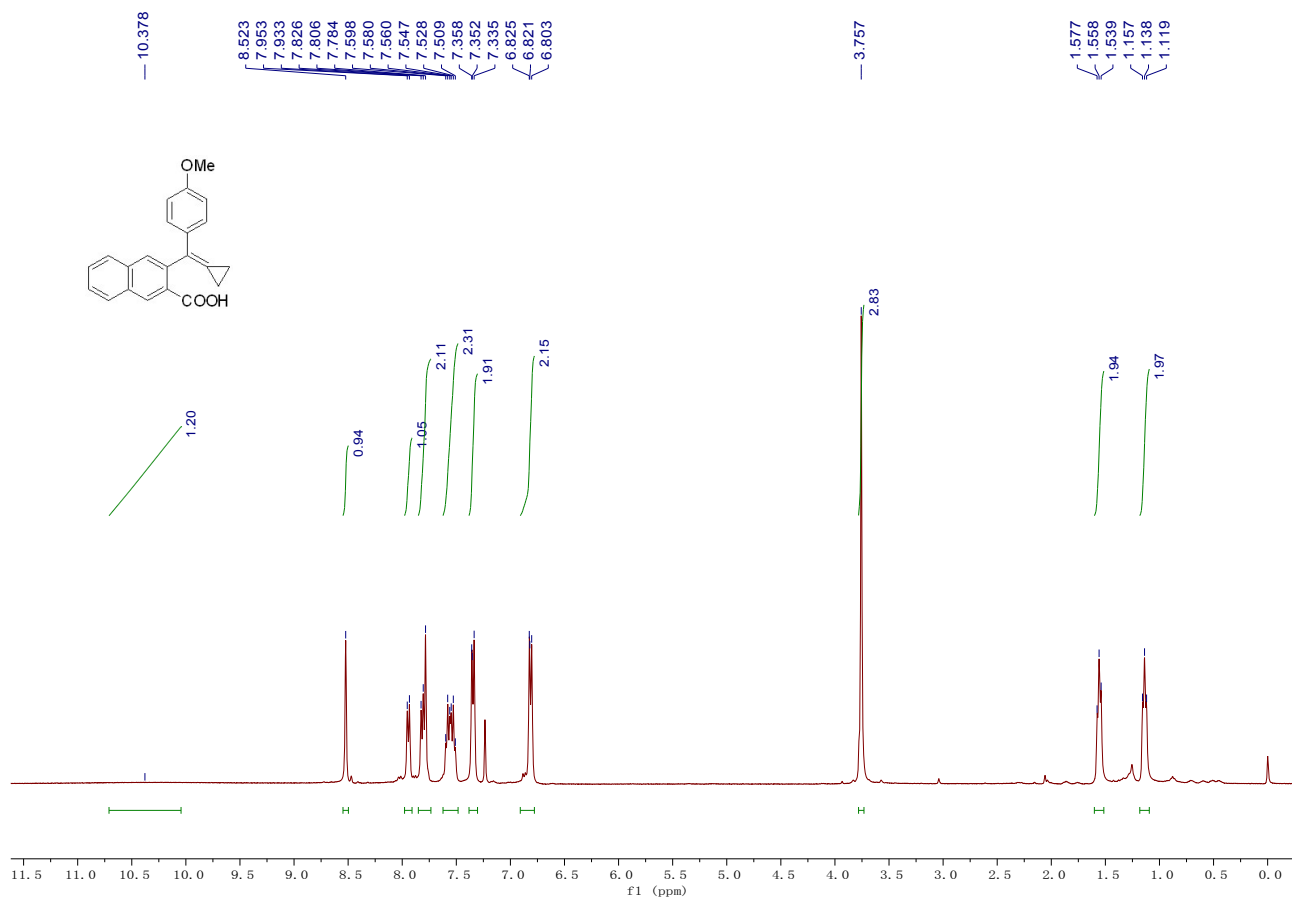


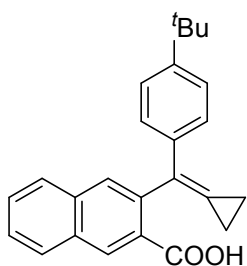
Compound 1v: Yield: 1.3 g, 88%; A white solid; Mp: > 200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 11.18 (br, 1H), 8.57 – 8.51 (m, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.85 – 7.76 (m, 2H), 7.62 – 7.49 (m, 2H), 7.27 – 7.21 (m, 2H), 7.16 (td, $J = 7.6, 2.3$ Hz, 1H), 7.01 (d, $J = 7.4$ Hz, 1H), 2.28 (s, 3H), 1.64 – 1.54 (m, 2H), 1.20 – 1.10 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.1, 140.8, 138.6, 137.4, 134.9, 132.2, 131.4, 130.4, 129.4, 128.8, 128.4, 128.2, 127.9, 127.6, 127.5, 127.4, 126.5, 124.1, 21.5, 5.5, 1.9; IR (neat): ν 2972, 1695, 1279, 1208, 747 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 337.1199, found: 337.1197.



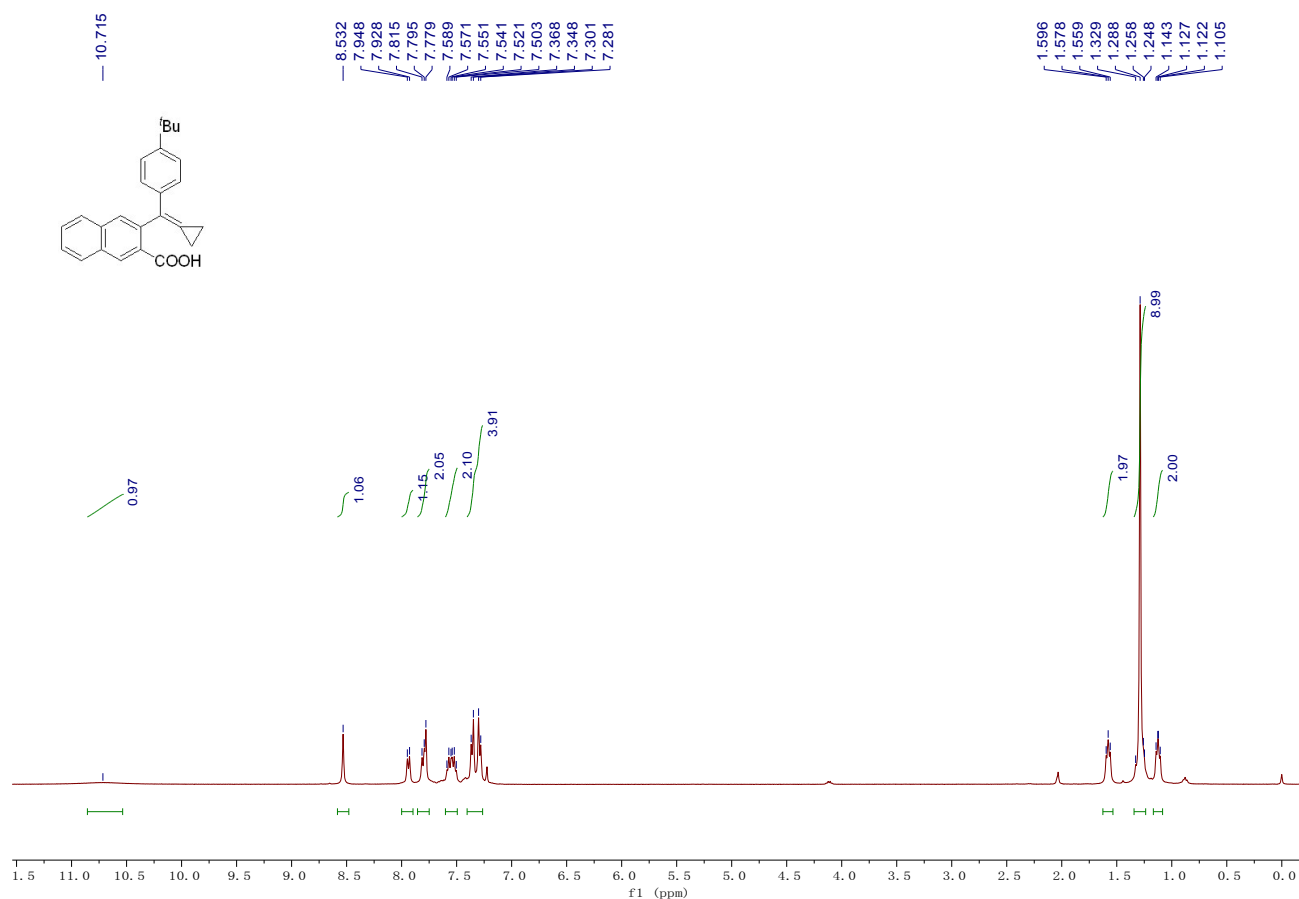


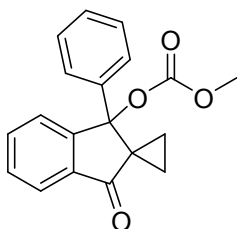
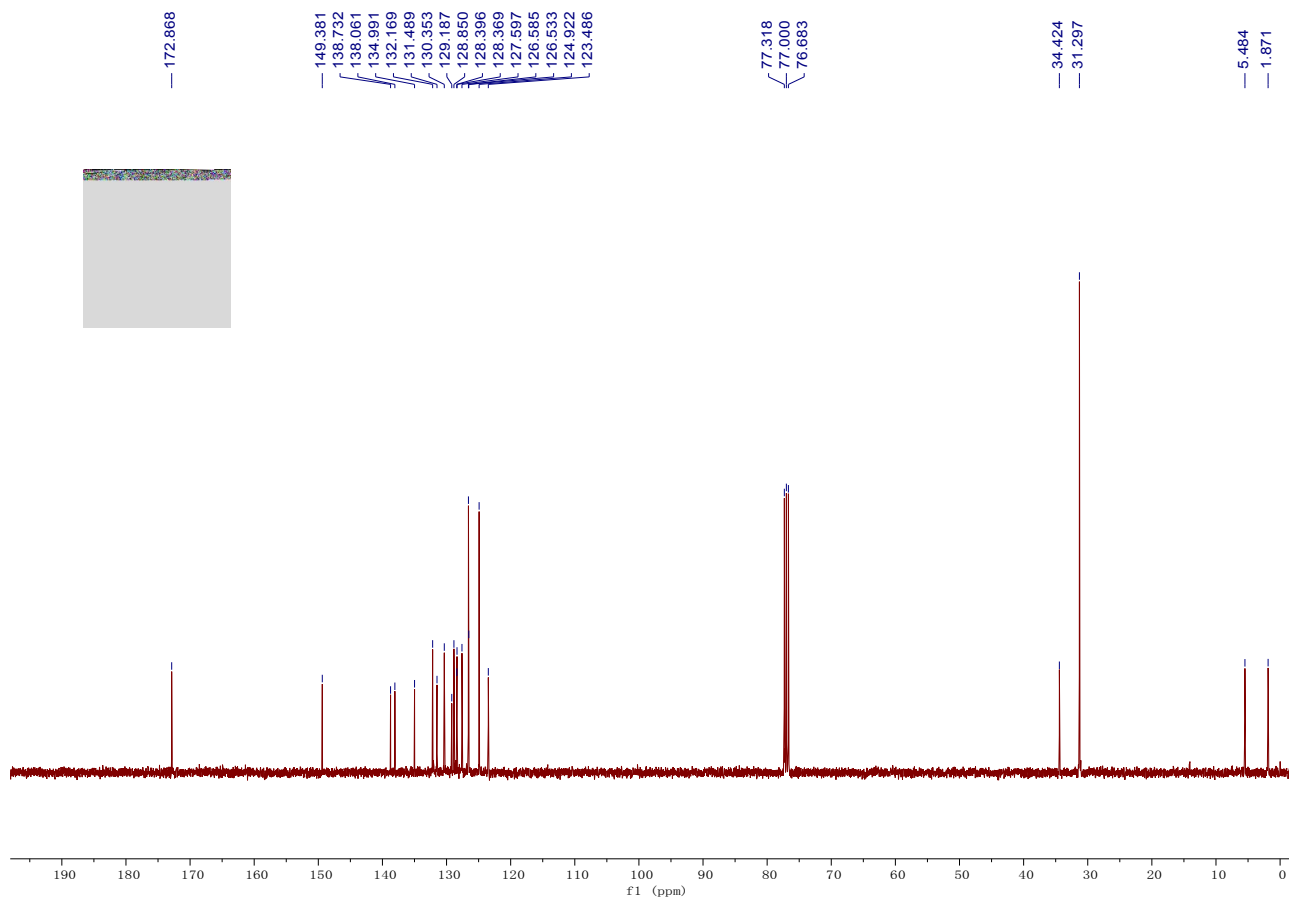
Compound 1w: Yield: 1.23 g, 88%; A white solid; Mp: > 200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.38 (br, 1H), 8.52 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.62 – 7.48 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.91 – 6.78 (m, 2H), 3.78 – 3.73 (m, 3H), 1.60 – 1.51 (m, 2H), 1.18 – 1.09 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.8, 158.3, 138.7, 134.9, 133.8, 132.1, 131.4, 130.3, 128.88, 128.85, 128.4, 128.3, 128.0, 127.5, 126.5, 122.3, 113.4, 55.1, 5.3, 1.9; IR (neat): ν 2960, 1759, 1630, 1220, 989 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 353.1148, found: 353.1148.



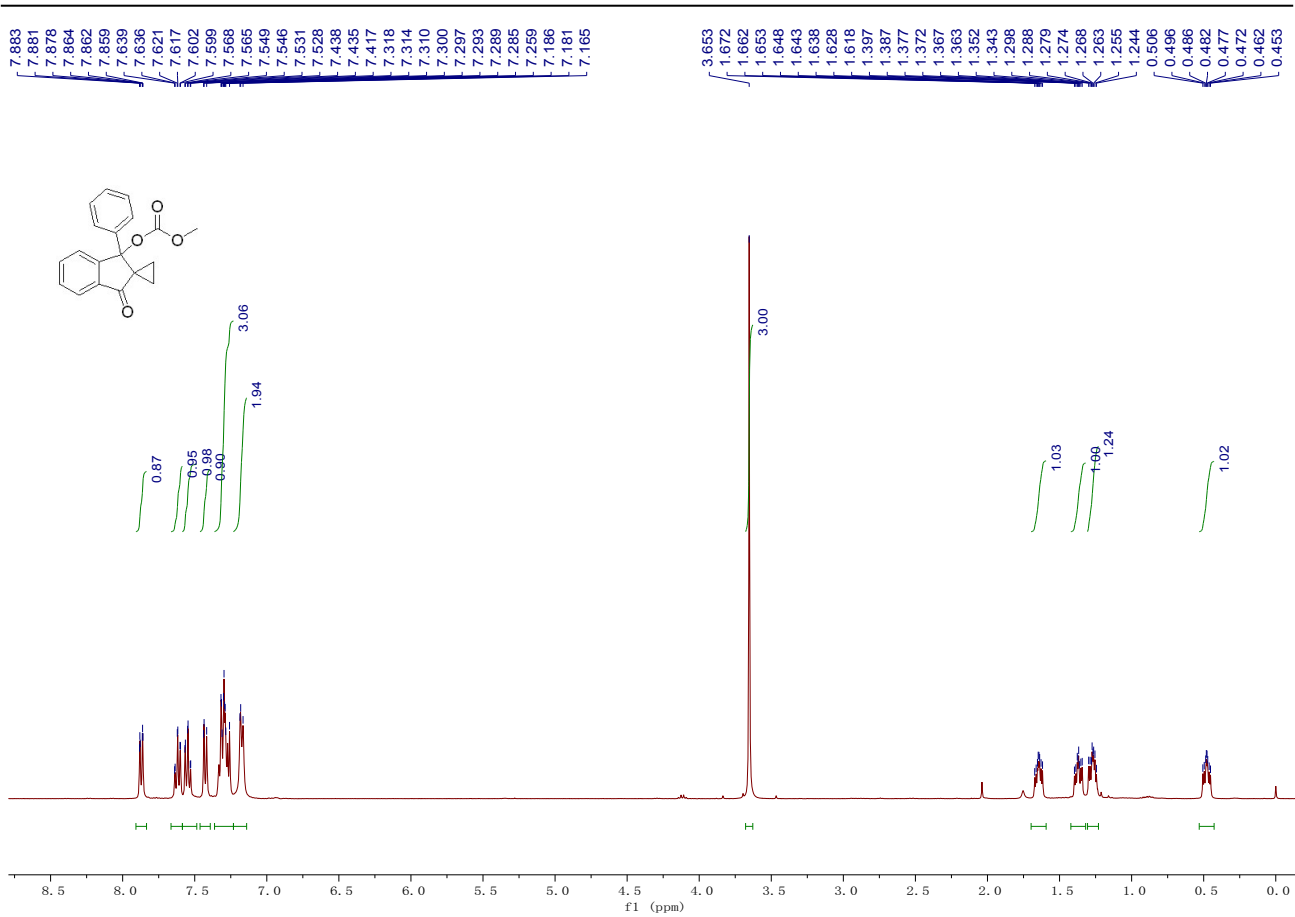


Compound 1x: Yield: 0.78 g, 70%; A white solid; Mp: > 200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 10.72 (br, 1H), 8.53 (s, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.86 – 7.75 (m, 2H), 7.60 – 7.49 (m, 2H), 7.40 – 7.26 (m, 4H), 1.63 – 1.53 (m, 2H), 1.29 (s, 9H), 1.17 – 1.08 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.8, 149.3, 138.7, 138.0, 134.9, 132.1, 131.4, 130.3, 129.1, 128.8, 128.4, 128.3, 127.6, 126.59, 126.53, 124.9, 123.4, 34.4, 31.3, 5.4, 1.8; IR (neat): ν 2958, 1758, 1713, 1628, 1258 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{25}\text{H}_{24}\text{O}_2$ $[\text{M}]^+$: 356.1771, found: 356.1781.





Compound 2a: Yield: 1.47 g, 83%; A white solid; Mp: 112 - 114 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.83 (m, 1H), 7.62 (td, $J = 7.5, 1.4$ Hz, 1H), 7.55 (td, $J = 7.4, 1.2$ Hz, 1H), 7.46 – 7.39 (m, 1H), 7.36 – 7.23 (m, 3H), 7.23 – 7.14 (m, 2H), 3.65 (s, 3H), 1.70 – 1.59 (m, 1H), 1.42 – 1.32 (m, 1H), 1.31 – 1.23 (m, 1H), 0.53 – 0.43 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.7, 153.01, 152.96, 140.3, 137.8, 134.5, 129.8, 128.3, 127.7, 125.6, 125.5, 122.3, 88.3, 54.5, 41.0, 21.3, 16.0; IR (neat): ν 2979, 2660, 1694, 1677, 1299, 1263 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 331.0941, found: 331.0939.



— 202.682

— 153.013
— 152.961

— 140.347
— 137.819
— 134.512
— 129.829
— 128.277
— 127.723
— 125.626
— 125.500
— 122.272

— 88.304

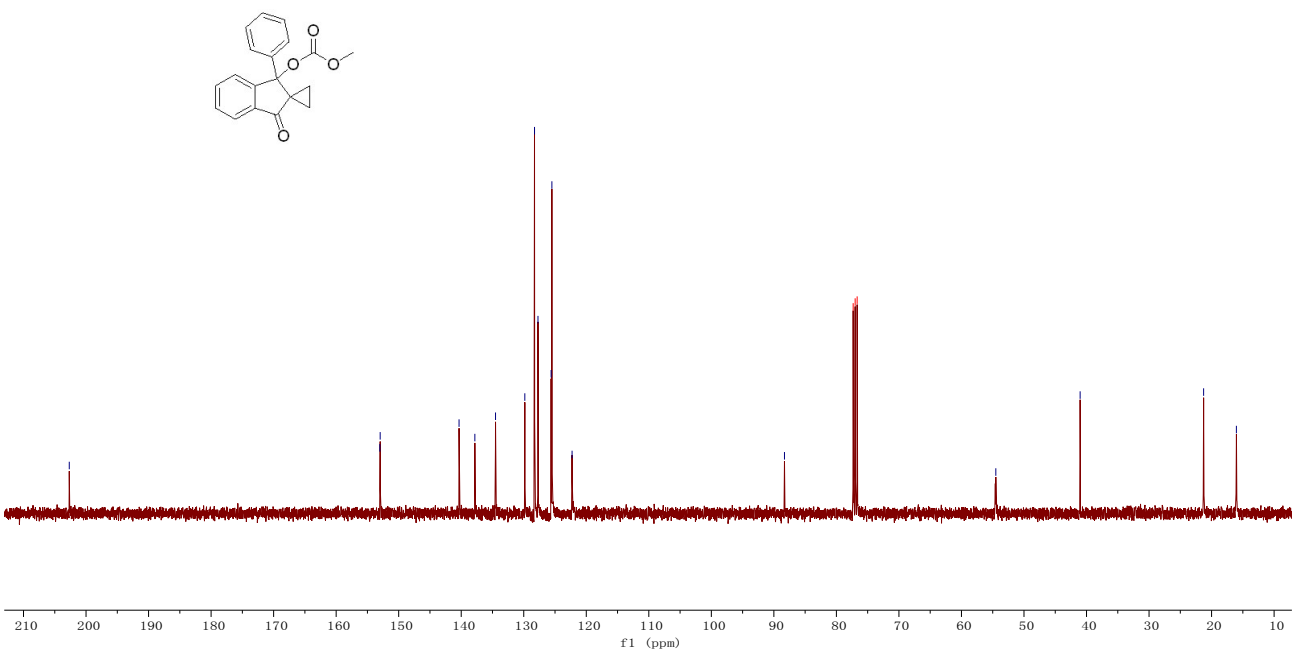
— 77.319 cdcl3
— 77.000 cdcl3
— 76.682 cdcl3

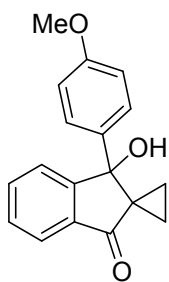
— 54.504

— 41.021

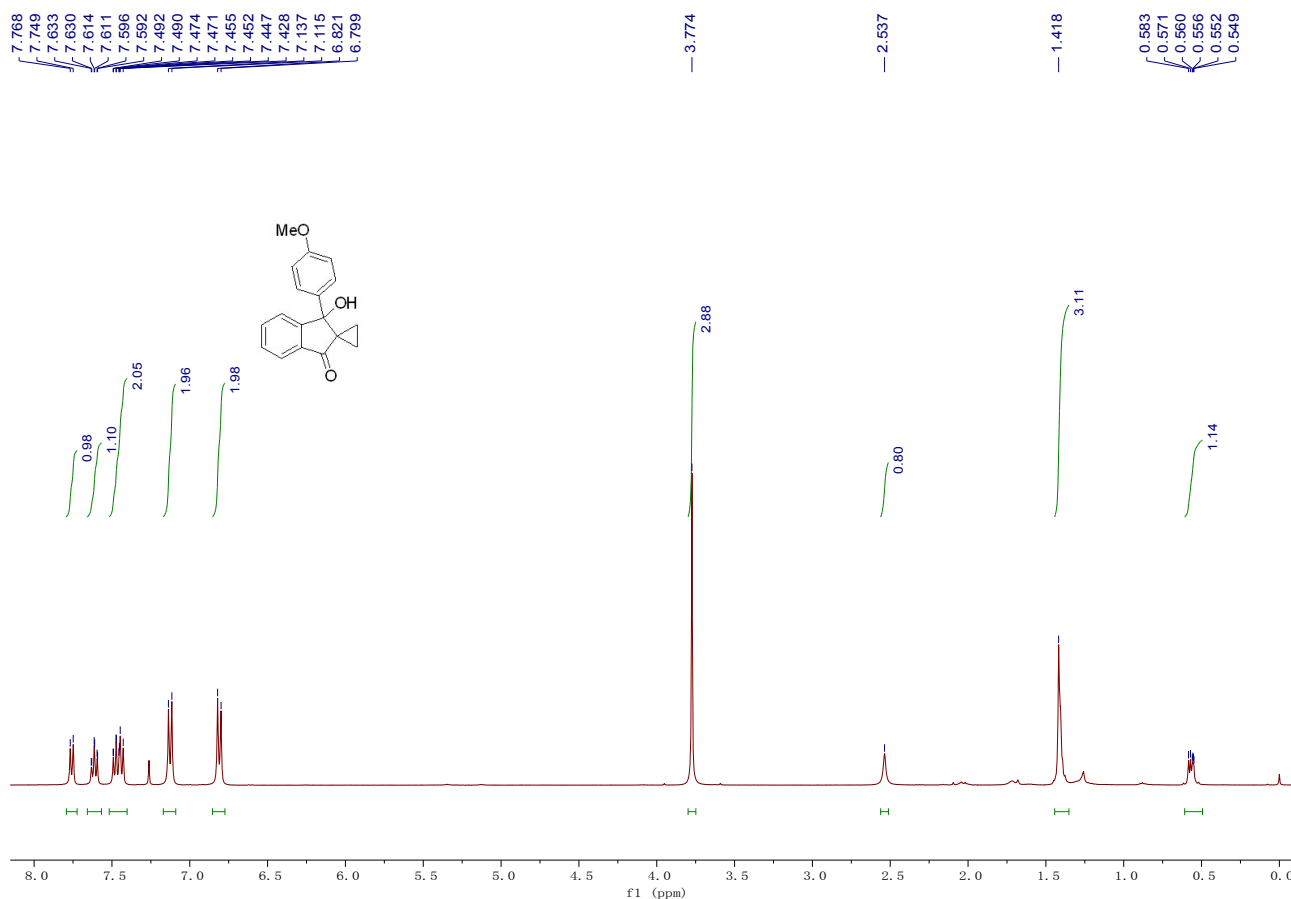
— 21.273

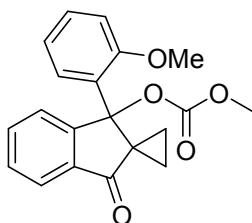
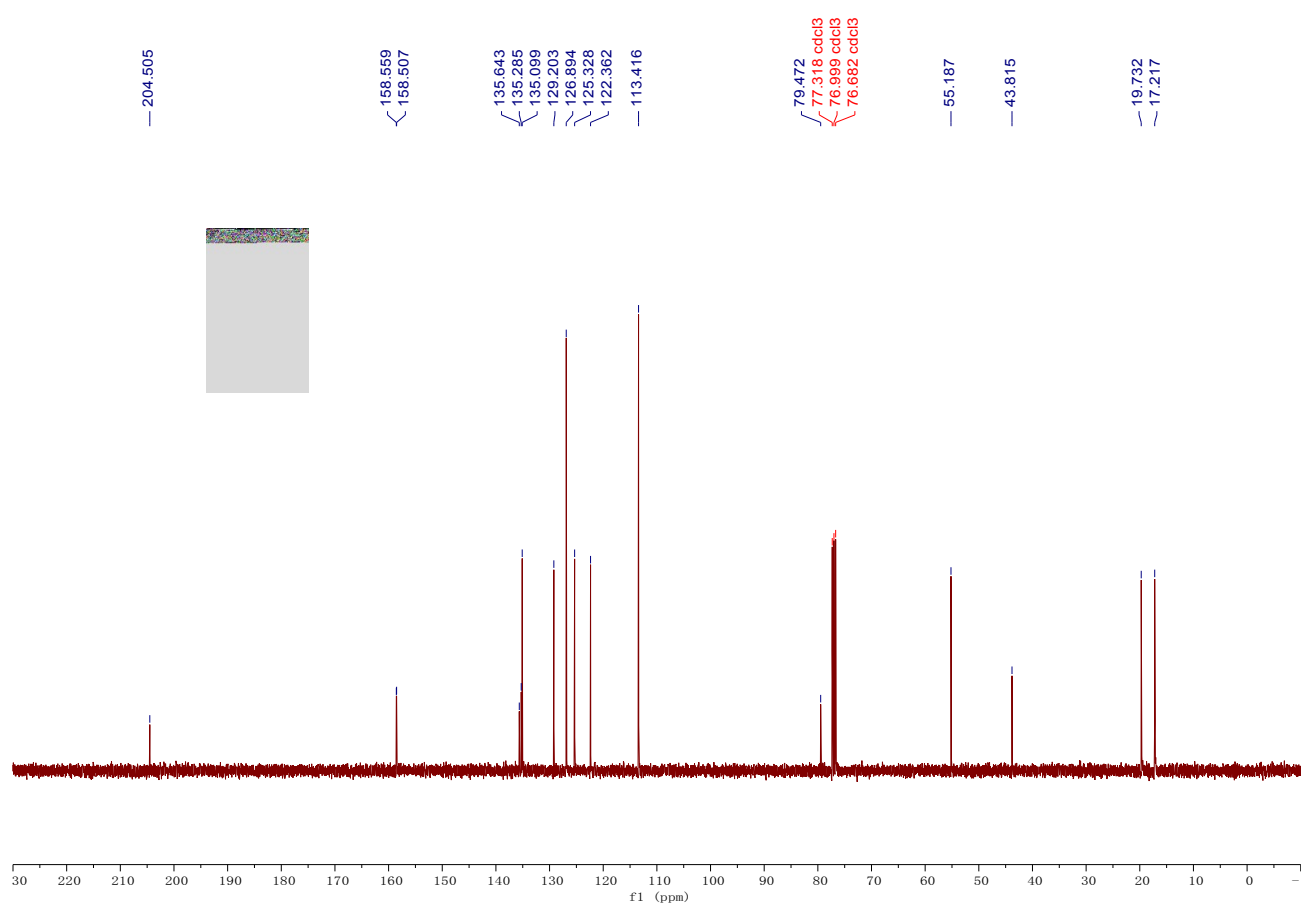
— 16.032



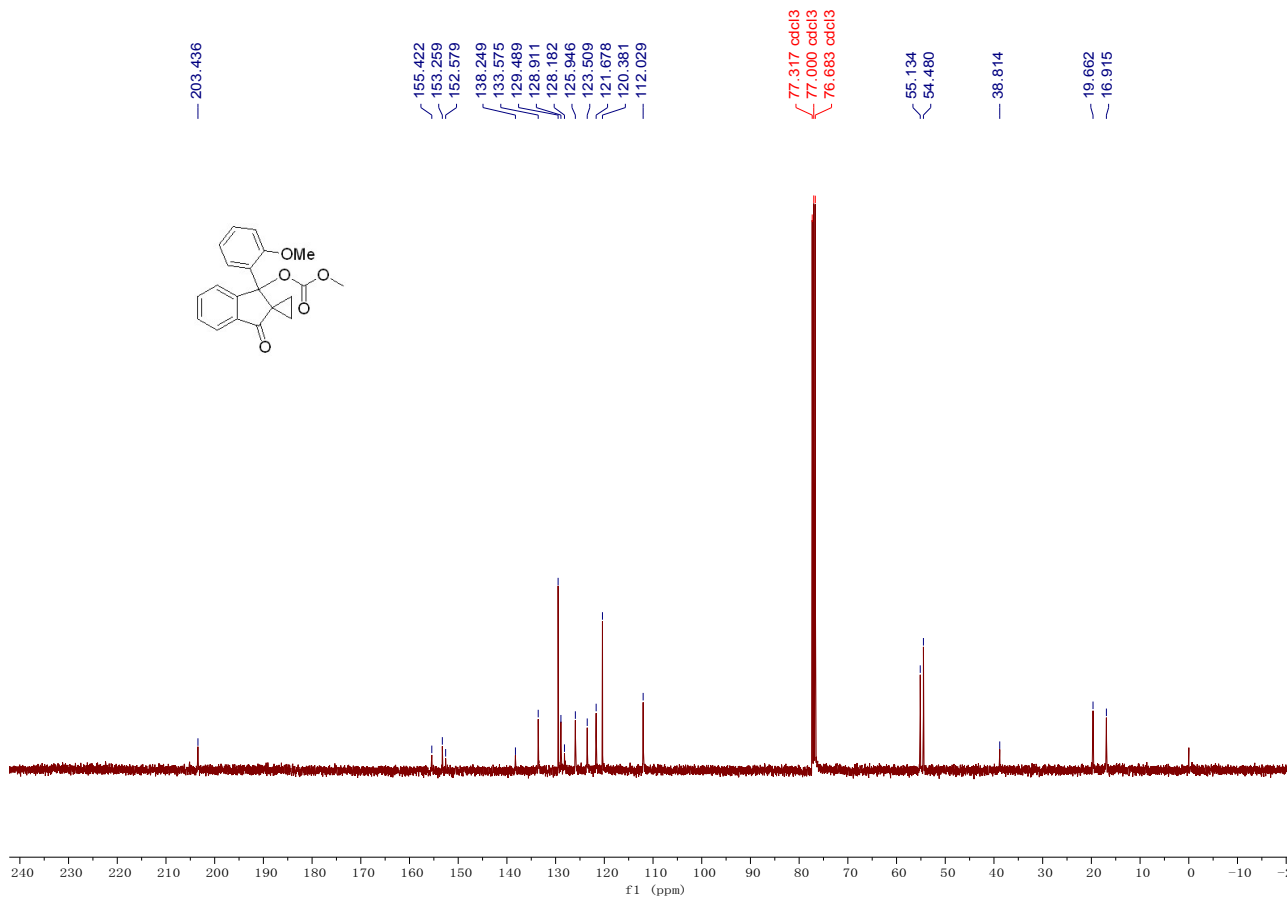
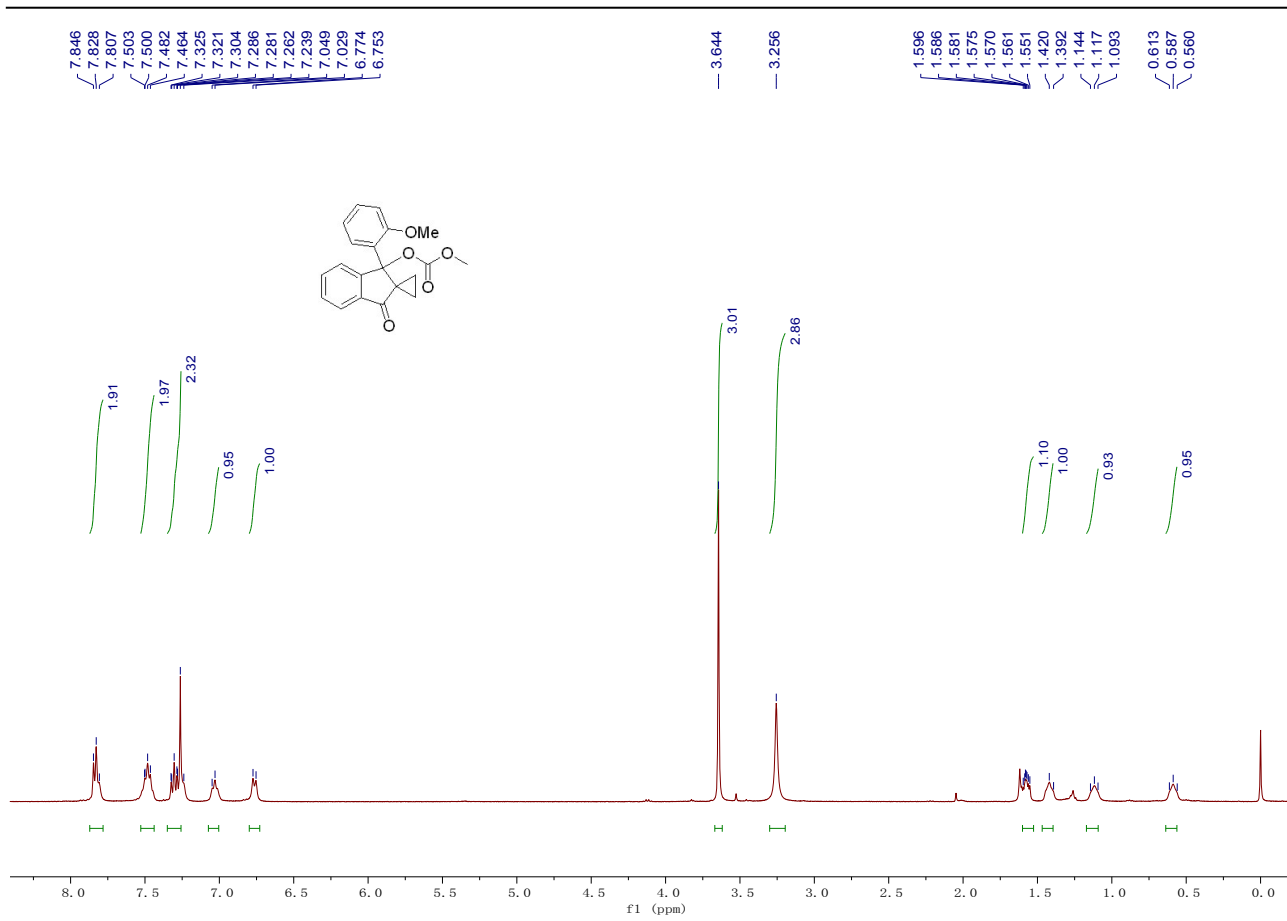


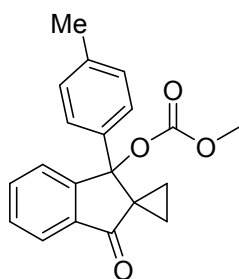
Compound 2b': Yield: 50.4 mg, 90%; A colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.61 (td, $J = 7.5, 1.3$ Hz, 1H), 7.52 – 7.40 (m, 2H), 7.17 – 7.09 (m, 2H), 6.85 – 6.77 (m, 2H), 3.77 (s, 3H), 2.54 (br, 1H), 1.44 – 1.35 (m, 3H), 0.61 – 0.49 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.5, 158.6, 158.5, 135.6, 135.3, 135.1, 129.2, 126.9, 125.3, 122.4, 113.4, 79.5, 55.2, 43.8, 19.7, 17.2; IR (neat): ν 2983, 1680, 1659, 1287, 1265 cm^{-1} ; HRMS (FI) Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_3$ $[\text{M}]^+$: 280.1094, found: 280.1096.



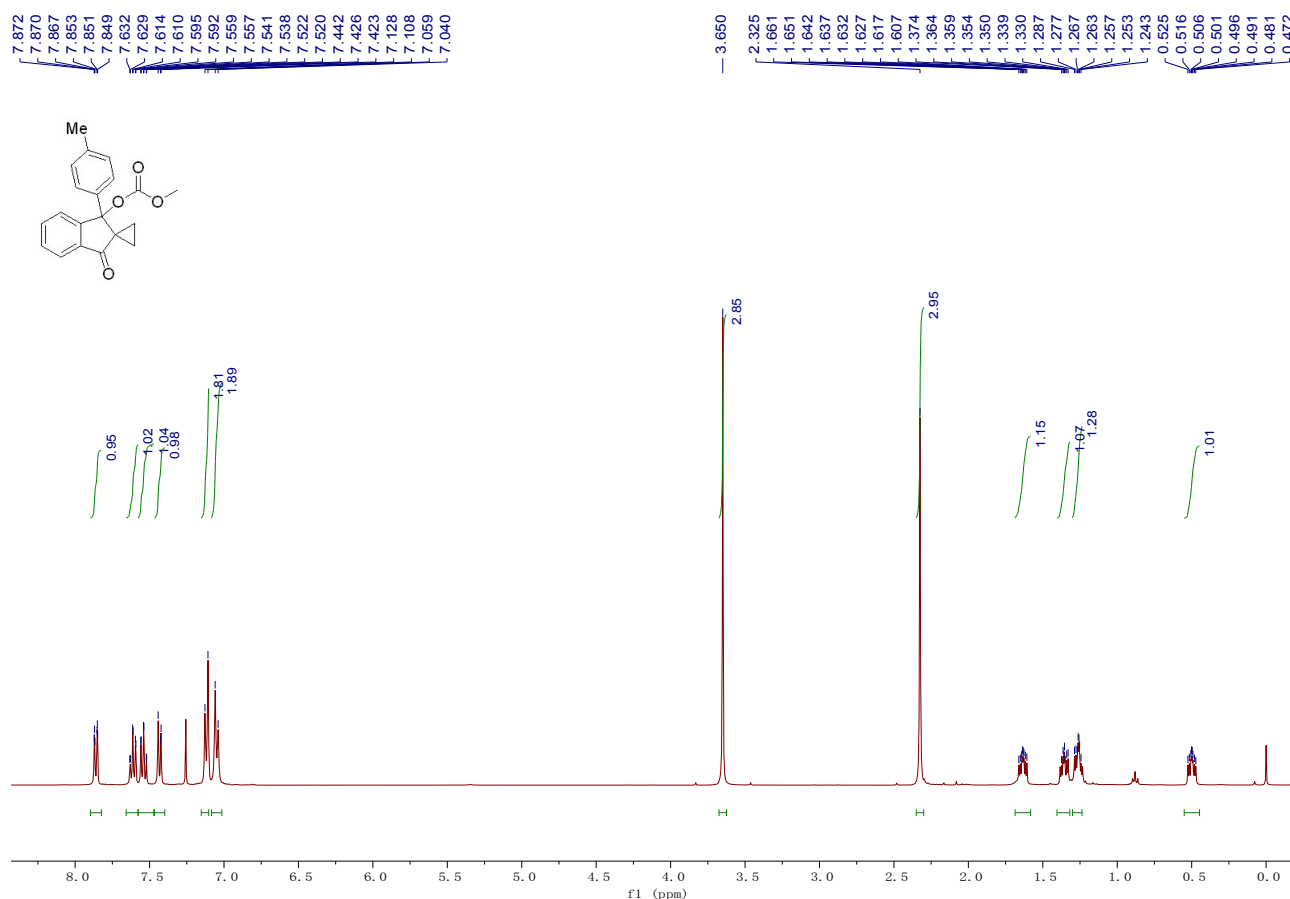


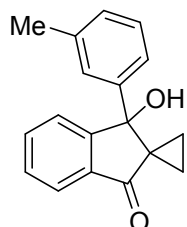
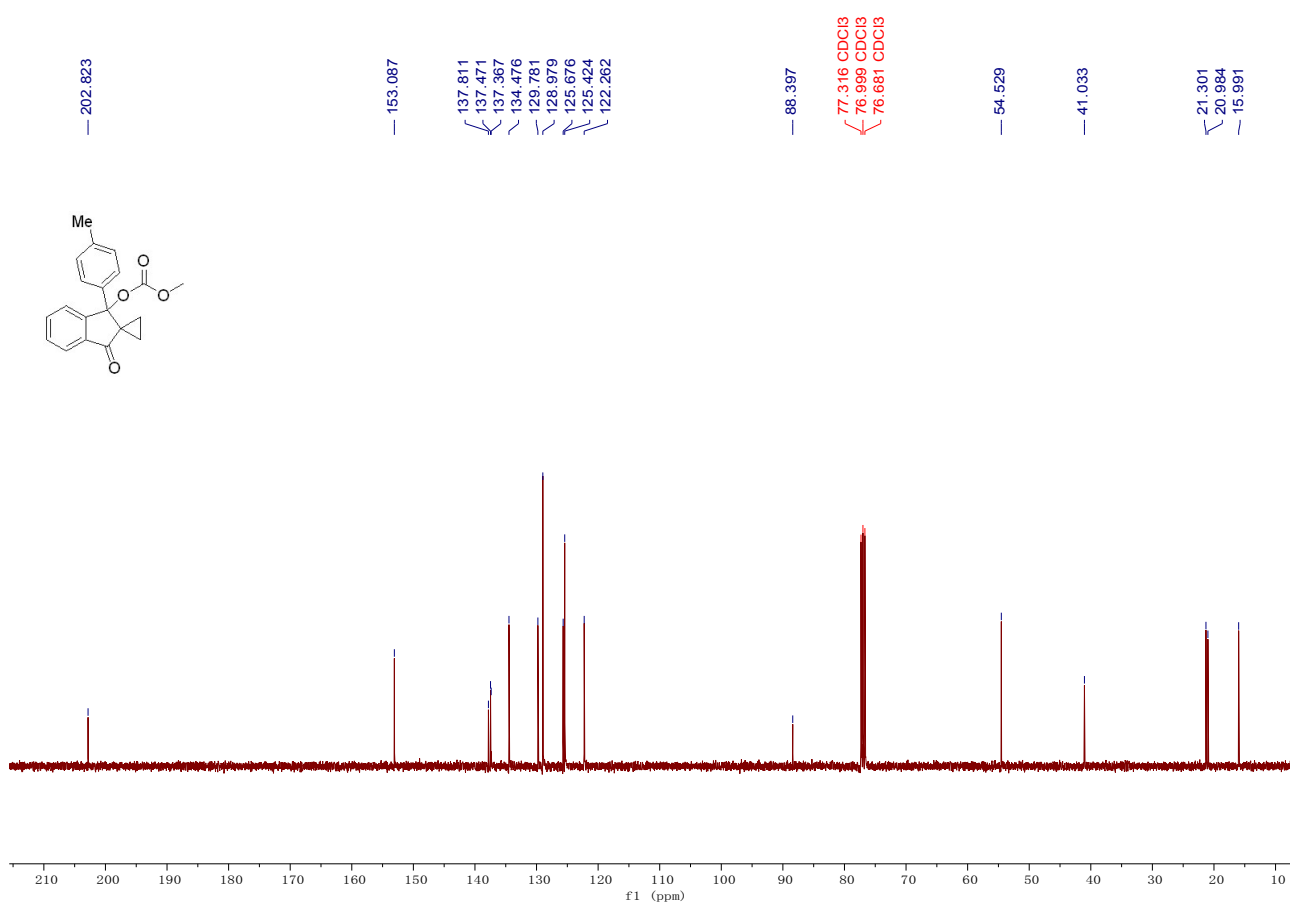
Compound 2c: Yield: 64.2 mg, 95%; A white solid; Mp: 149 - 151 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.78 (m, 2H), 7.53 – 7.44 (m, 2H), 7.35 – 7.26 (m, 2H), 7.07 – 7.00 (m, 1H), 6.76 (d, J = 8.2 Hz, 1H), 3.64 (s, 3H), 3.26 (s, 3H), 1.60 – 1.53 (m, 1H), 1.47 – 1.40 (m, 1H), 1.17 – 1.09 (m, 1H), 0.64 – 0.56 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.4, 155.4, 153.3, 152.6, 138.2, 133.6, 129.5, 128.9, 128.2, 125.9, 123.5, 121.7, 120.4, 112.0, 55.1, 54.5, 38.8, 19.7, 16.9; IR (neat): ν 1690, 1626, 1245, 1161, 835 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 361.1046, found: 361.1042.



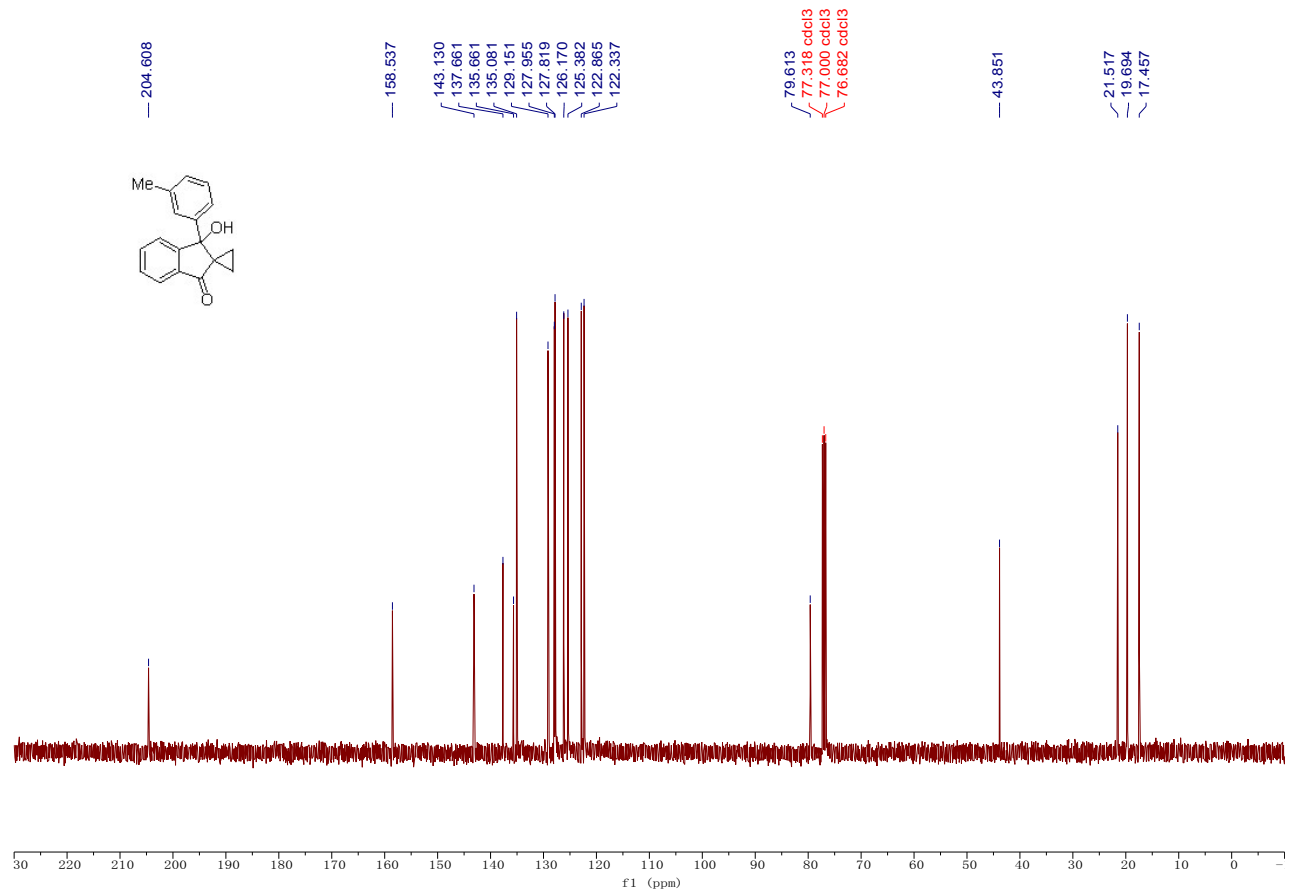
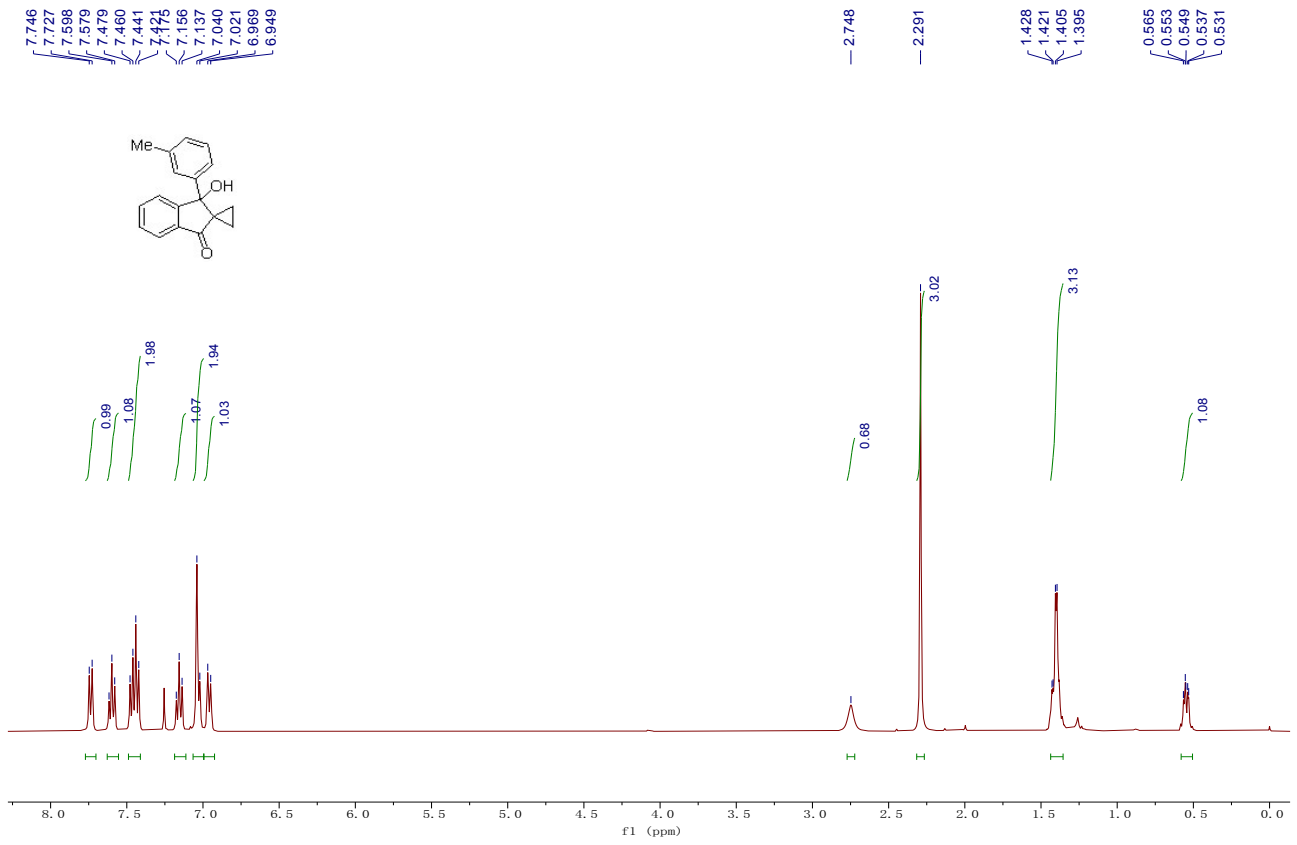


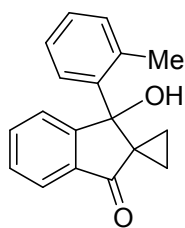
Compound 2d: Yield: 56.0 mg, 87%; A white solid; Mp: 148 - 150 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.82 (m, 1H), 7.61 (td, $J = 7.5, 1.3$ Hz, 1H), 7.54 (td, $J = 7.4, 1.1$ Hz, 1H), 7.43 (d, $J = 7.8$ Hz, 1H), 7.13 (d, $J = 8.2$ Hz, 2H), 7.05 (d, $J = 8.0$ Hz, 2H), 3.65 (s, 3H), 2.32 (s, 3H), 1.69 – 1.58 (m, 1H), 1.40 – 1.32 (m, 1H), 1.30 – 1.24 (m, 1H), 0.55 – 0.45 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.8, 153.1, 137.8, 137.5, 137.4, 134.5, 129.8, 129.0, 125.7, 125.4, 122.3, 88.4, 54.5, 41.0, 21.3, 21.0, 16.0; IR (neat): ν 2919, 2856, 1755, 1718, 1254 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 345.1097, found: 345.1091.



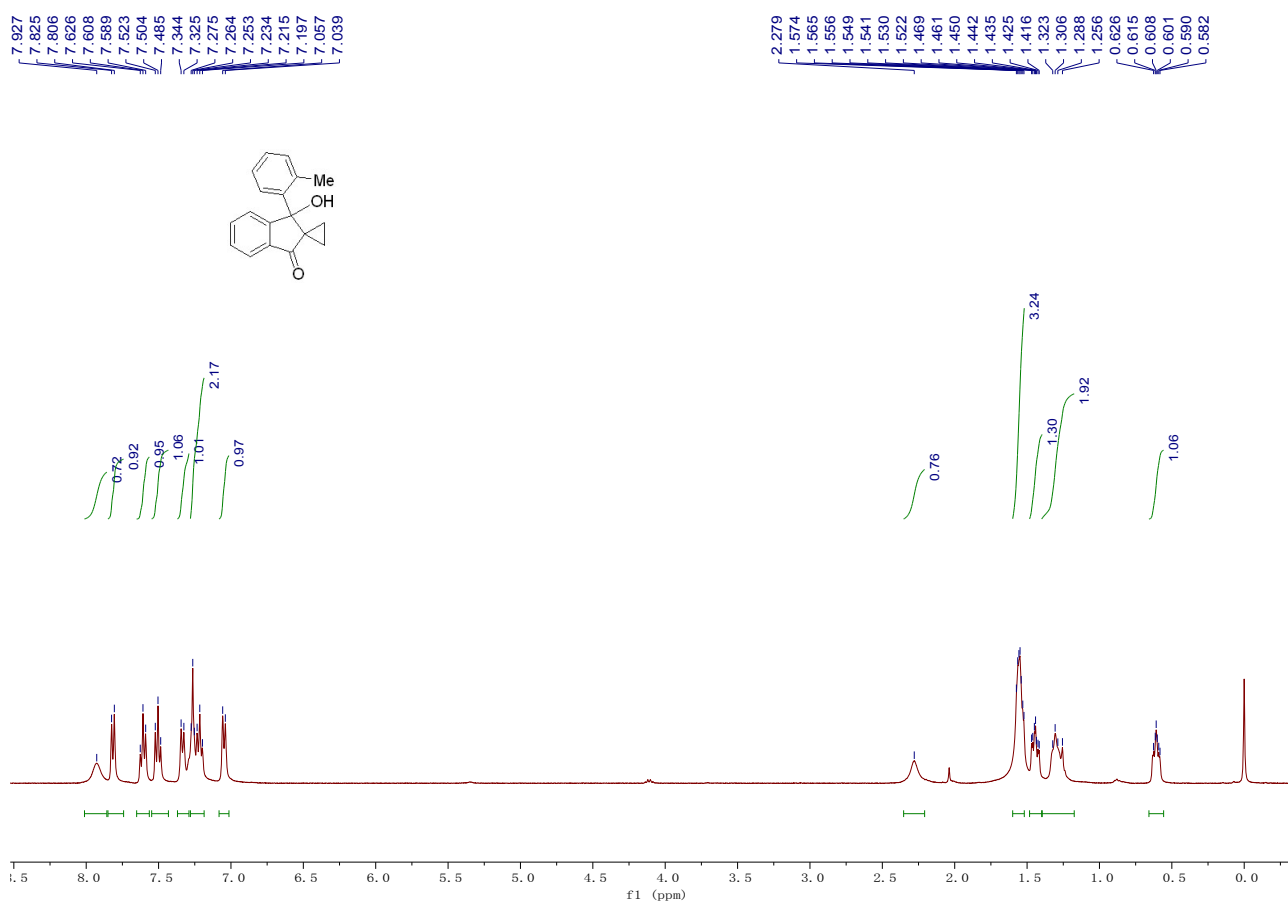


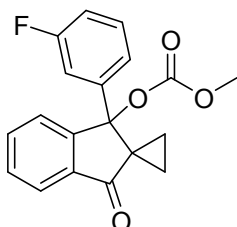
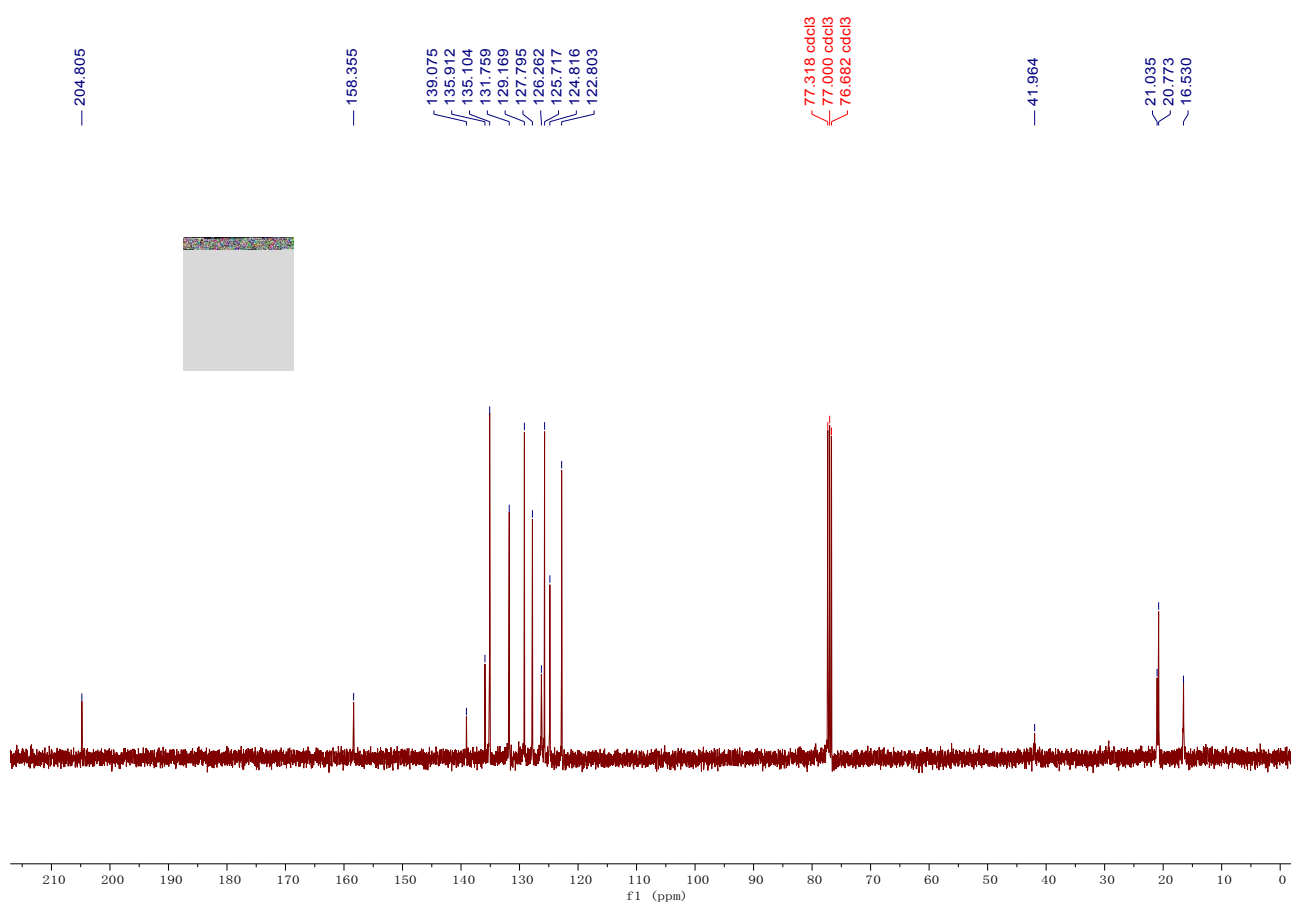
Compound 2e': Yield: 47.5 mg, 90%; A colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, $J = 7.6$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.49 – 7.41 (m, 2H), 7.16 (t, $J = 7.6$ Hz, 1H), 7.06 – 7.00 (m, 2H), 6.96 (d, $J = 7.7$ Hz, 1H), 2.75 (br, 1H), 2.29 (s, 3H), 1.44 – 1.36 (m, 3H), 0.58 – 0.51 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.6, 158.5, 143.1, 137.7, 135.7, 135.1, 129.2, 128.0, 127.8, 126.2, 125.4, 122.9, 122.3, 79.6, 43.9, 21.5, 19.7, 17.5; IR (neat): ν 3432, 1697, 1603, 1328, 1041 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$: 264.1145, found: 264.1151.



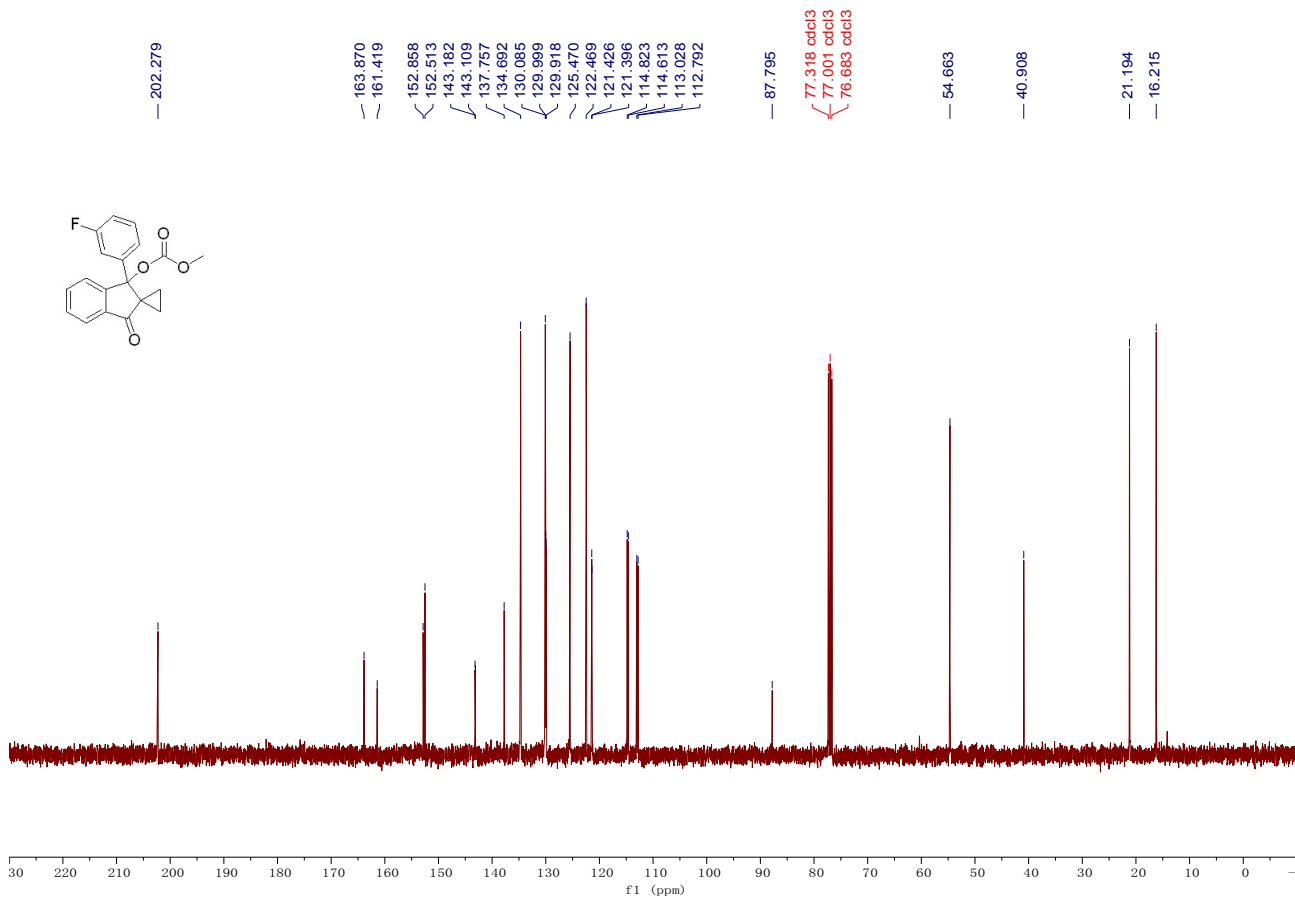
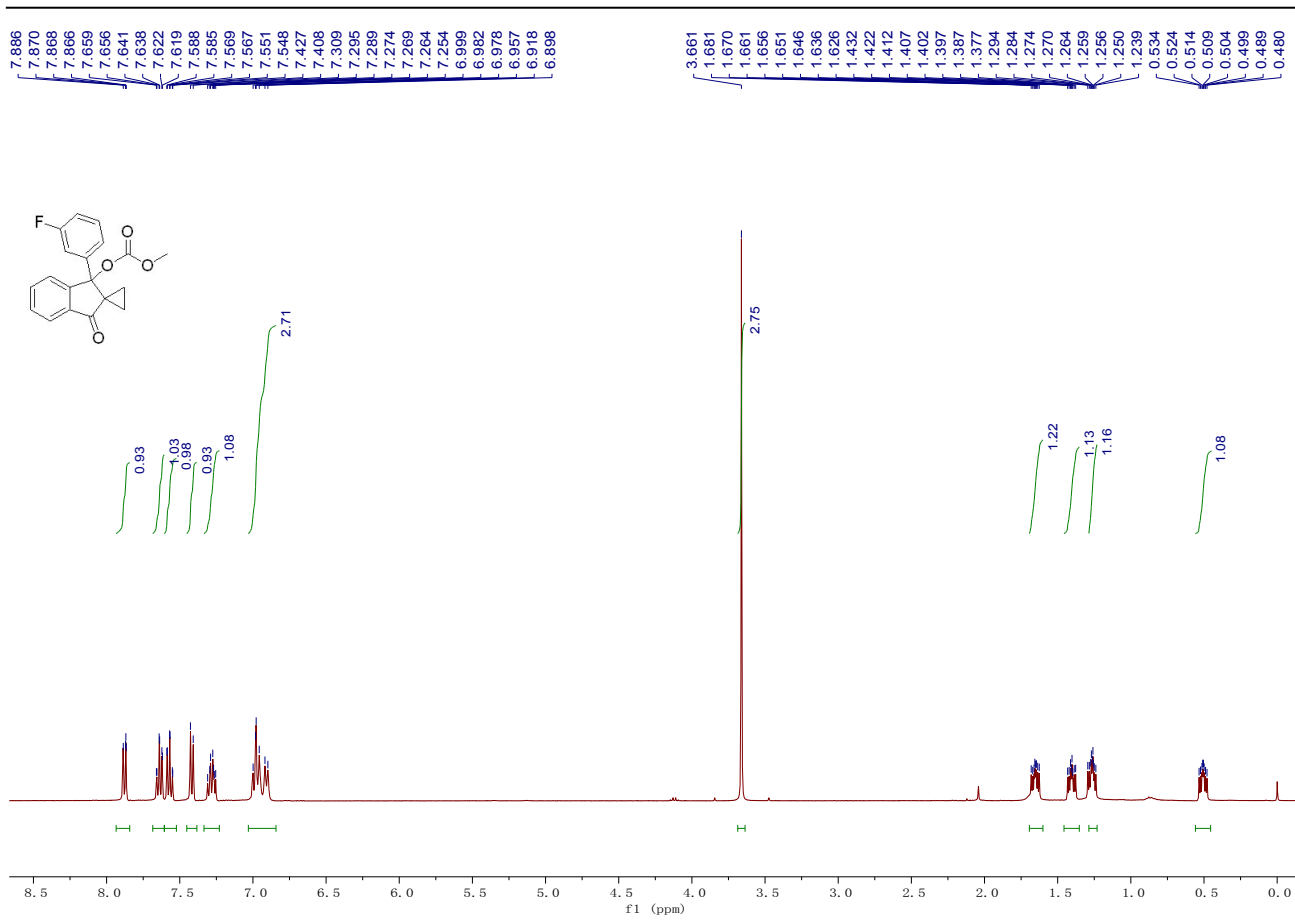


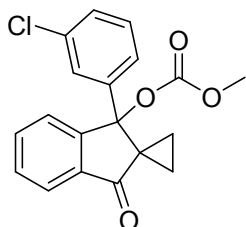
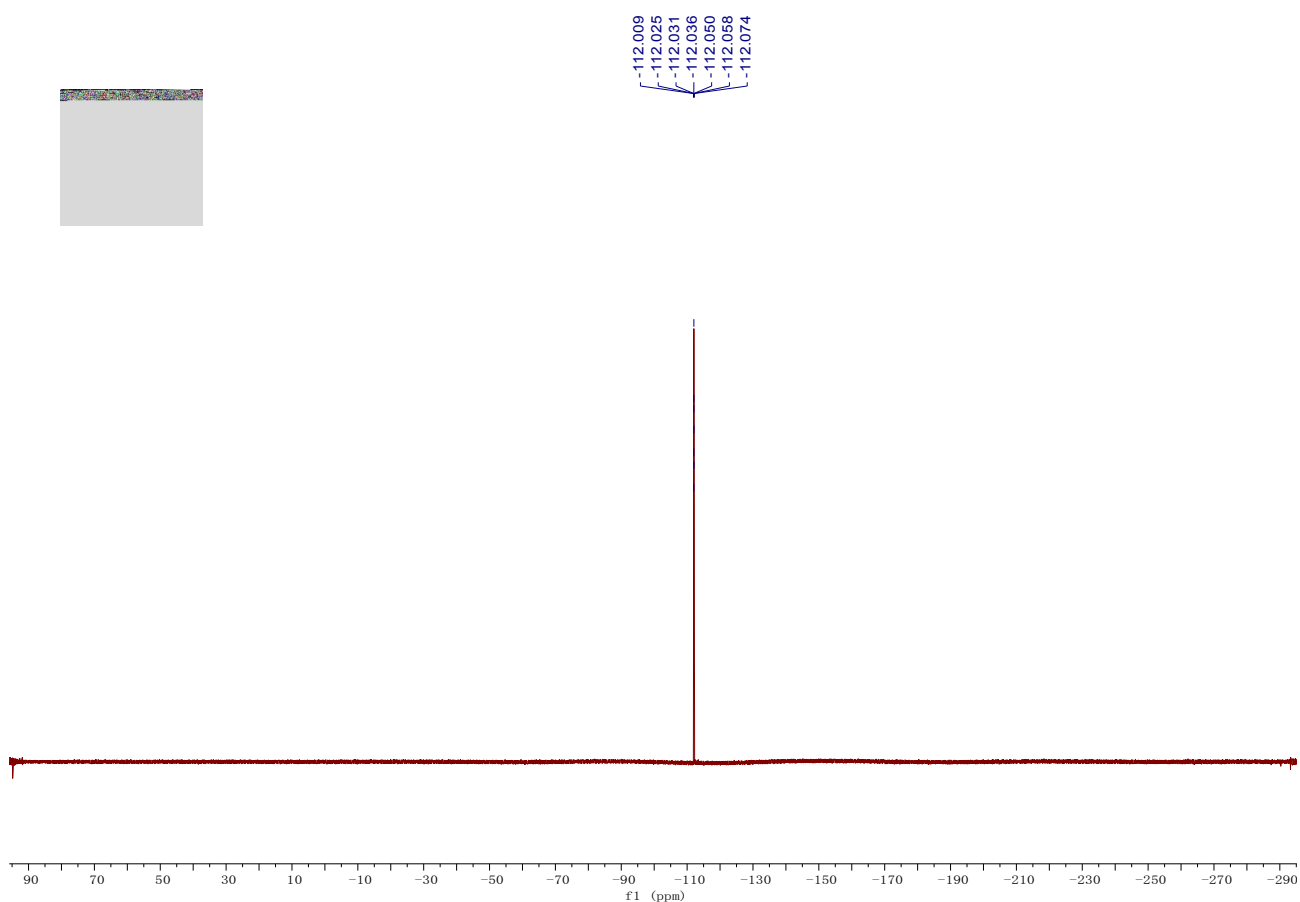
Compound 2f: Yield: 37.0 mg, 70%; A colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.82 (d, $J = 7.7$ Hz, 1H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.28 – 7.19 (m, 2H), 7.05 (d, $J = 7.4$ Hz, 1H), 2.28 (br, 1H), 1.60 – 1.52 (m, 3H), 1.48 – 1.40 (m, 1H), 1.40 – 1.17 (m, 2H), 0.66 – 0.56 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.8, 158.4, 139.1, 135.9, 135.1, 131.8, 129.2, 127.8, 126.3, 125.7, 124.8, 122.8, 42.0, 21.0, 20.8, 16.5; IR (neat): ν 3430, 1710, 1600, 1329, 1040 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$: 264.1145, found: 264.1149.



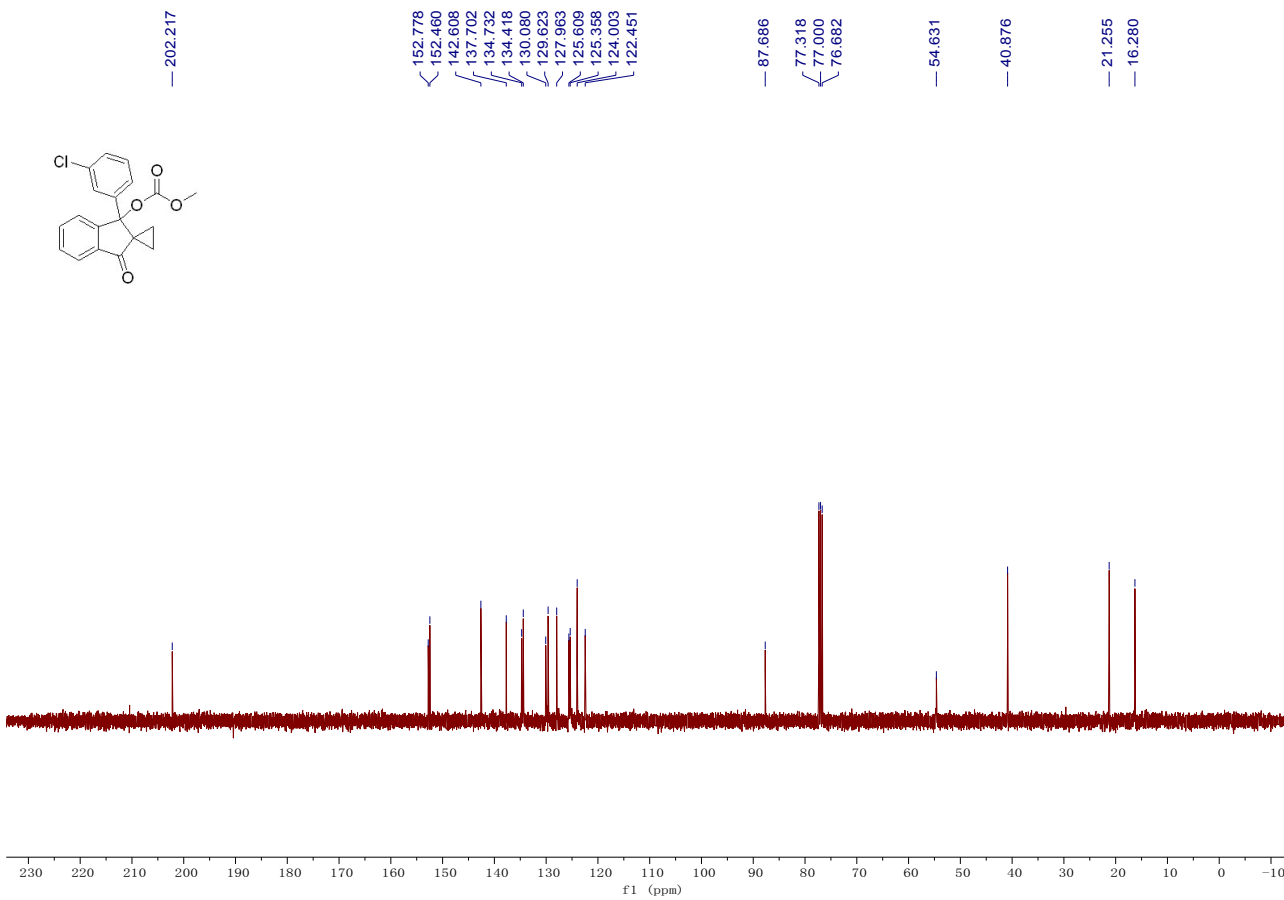
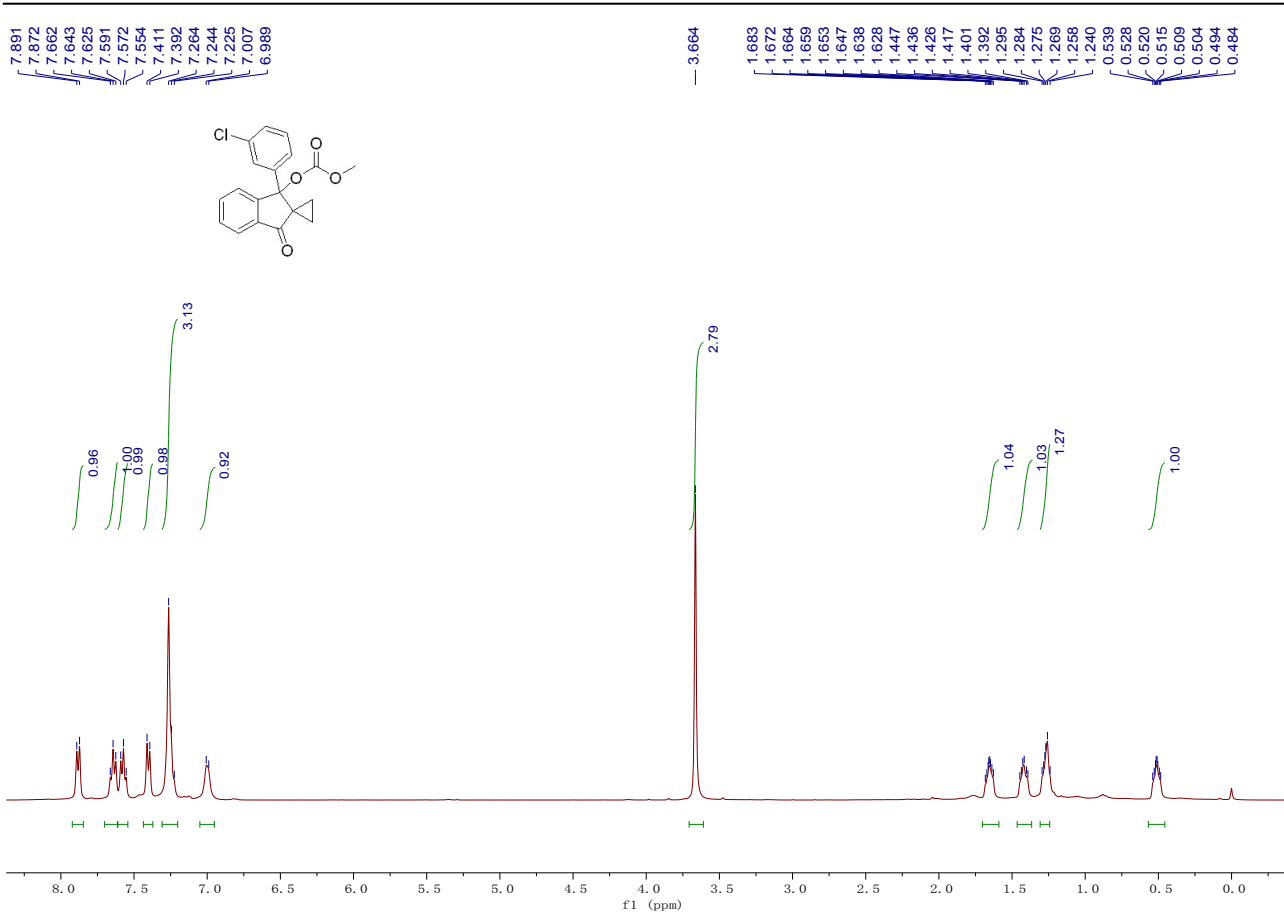


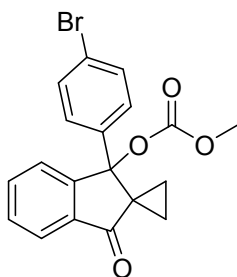
Compound 2g: Yield: 60.0 mg, 92%; A white solid; Mp: 101 - 102 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.84 (m, 1H), 7.68 – 7.61 (m, 1H), 7.61 – 7.52 (m, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.33 – 7.23 (m, 1H), 7.03 – 6.84 (m, 3H), 3.66 (s, 3H), 1.69 – 1.60 (m, 1H), 1.46 – 1.35 (m, 1H), 1.29 – 1.23 (m, 1H), 0.56 – 0.45 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.3, 162.6 (d, $J = 246.6$ Hz), 152.9, 152.5, 143.1 (d, $J = 7.3$ Hz), 137.8, 134.7, 130.1, 130.0 (d, $J = 8.2$ Hz), 125.5, 122.5, 121.4 (d, $J = 3.0$ Hz), 114.7 (d, $J = 21.1$ Hz), 112.9 (d, $J = 23.8$ Hz), 87.8, 54.7, 40.9, 21.2, 16.2; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.94 – -112.16 (m); IR (neat): ν 3005, 2848, 1748, 1715, 1280, 986 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{19}\text{H}_{15}\text{O}_4\text{FNa}$ $[\text{M}+\text{Na}]^+$: 349.0847, found: 349.0841.



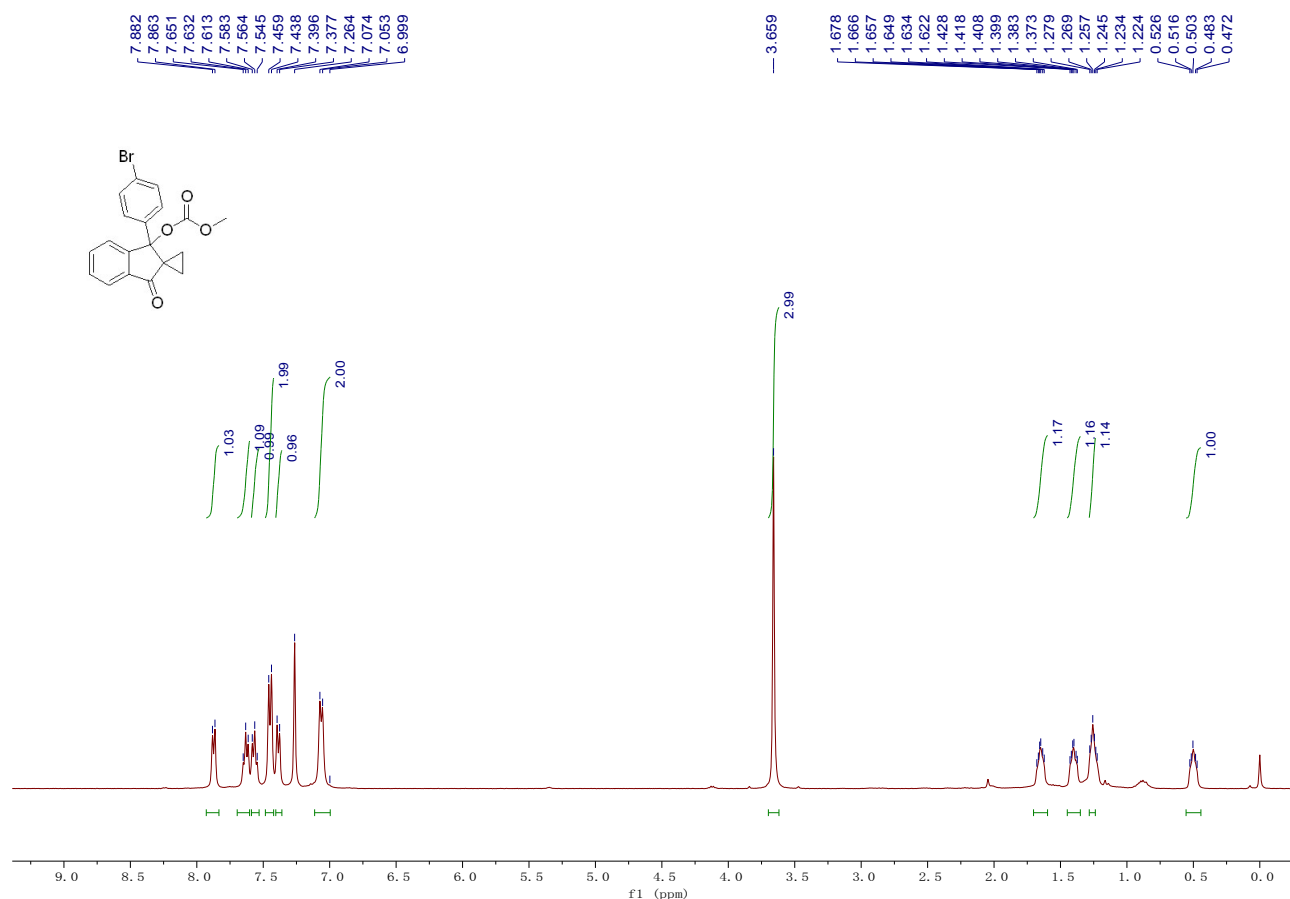


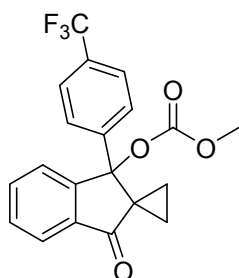
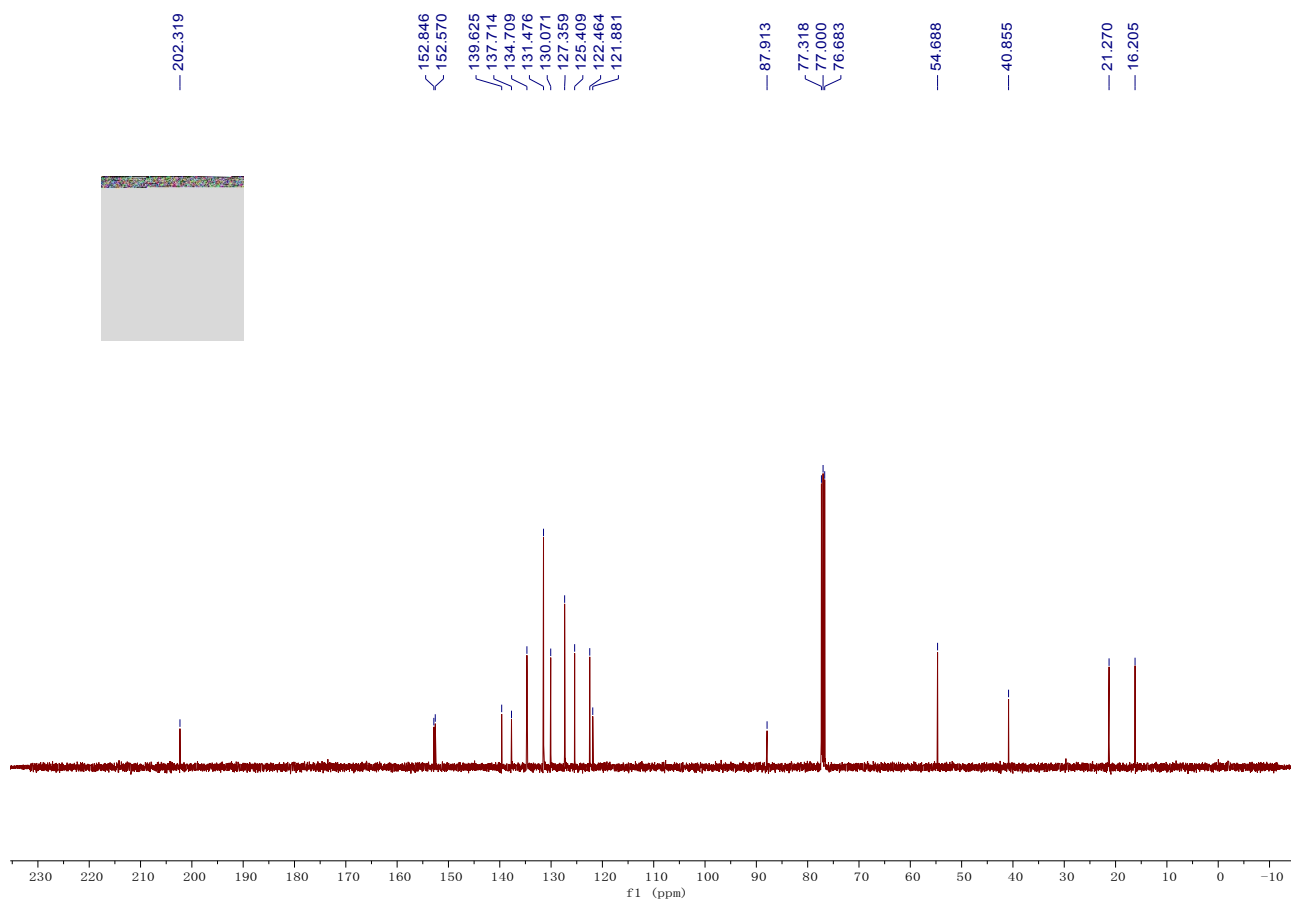
Compound 2h: Yield: 54.0 mg, 79%; A white solid; Mp: 73 - 75 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, $J = 7.5$ Hz, 1H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.40 (d, $J = 7.6$ Hz, 1H), 7.31 – 7.20 (m, 3H), 7.05 – 6.95 (m, 1H), 3.66 (s, 3H), 1.70 – 1.59 (m, 1H), 1.46 – 1.37 (m, 1H), 1.31 – 1.24 (m, 1H), 0.57 – 0.46 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.2, 152.8, 152.5, 142.6, 137.7, 134.7, 134.4, 130.1, 129.6, 128.0, 125.6, 125.4, 124.0, 122.5, 87.7, 54.6, 40.9, 21.3, 16.3; IR (neat): ν 1725, 1258, 1159, 980, 888 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{19}\text{H}_{15}\text{O}_4\text{Cl}$ $[\text{M}]^+$: 342.0653, found: 342.0647.



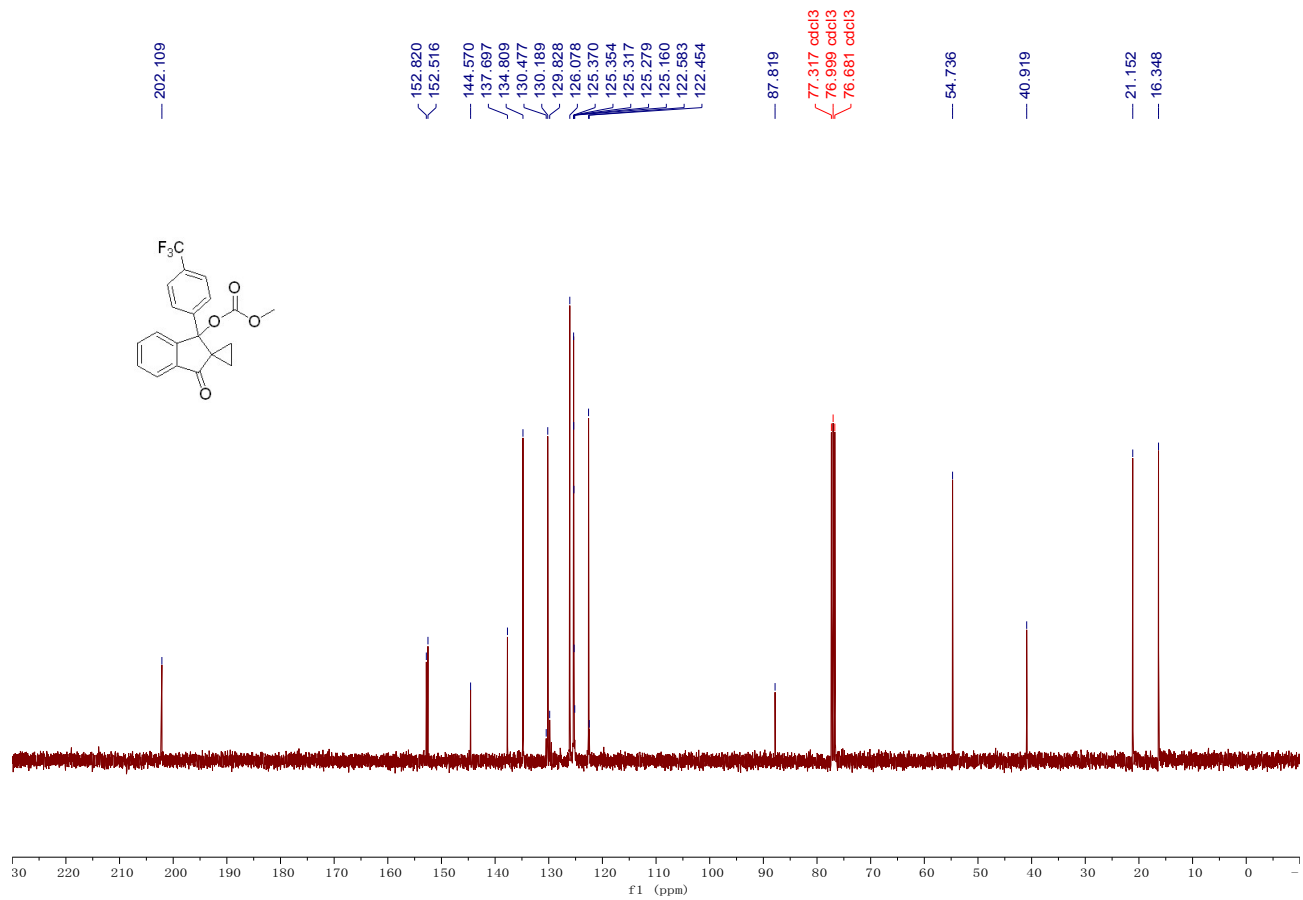
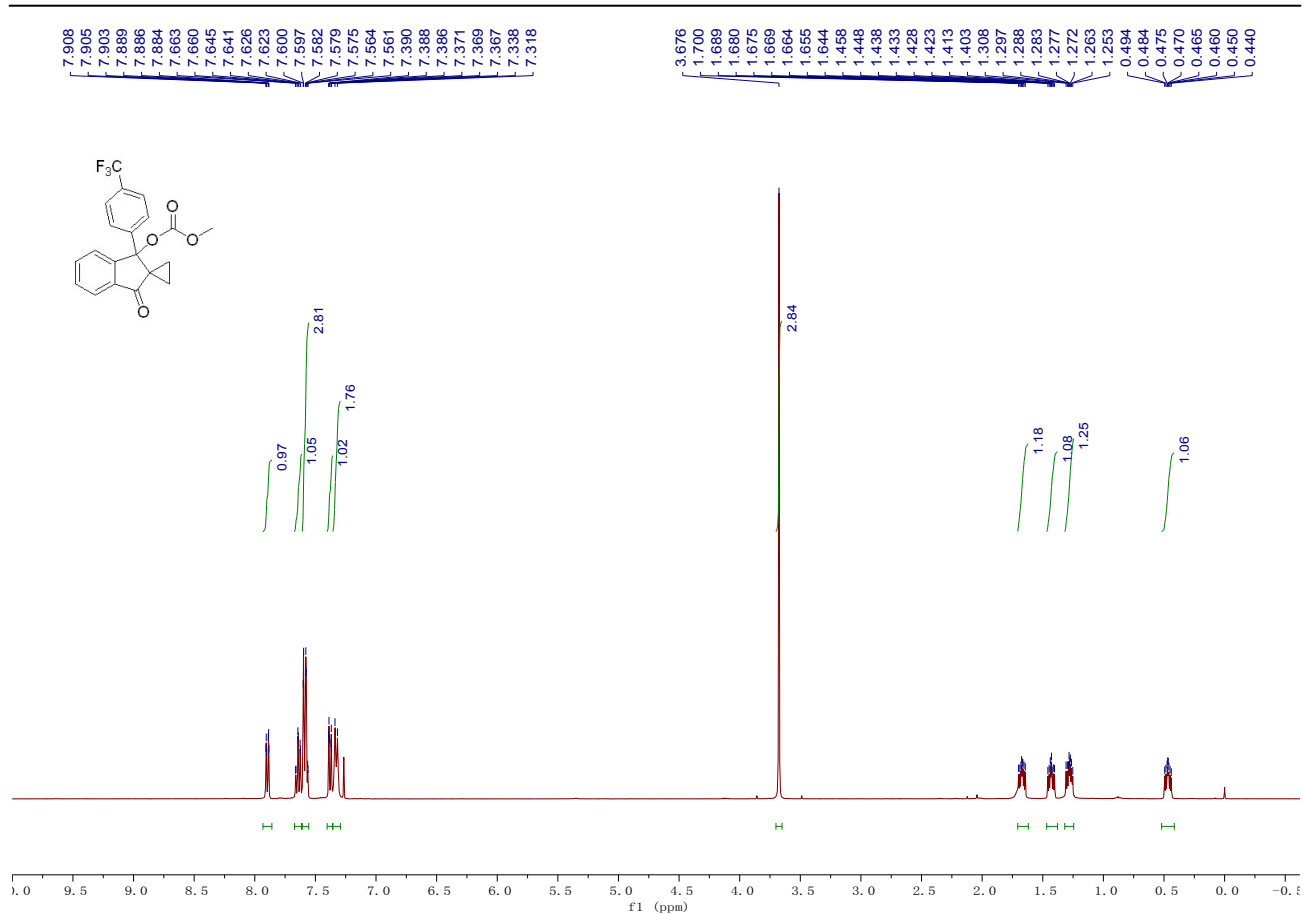


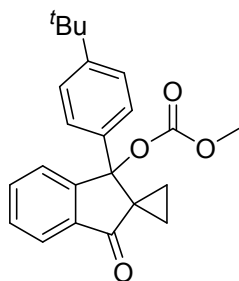
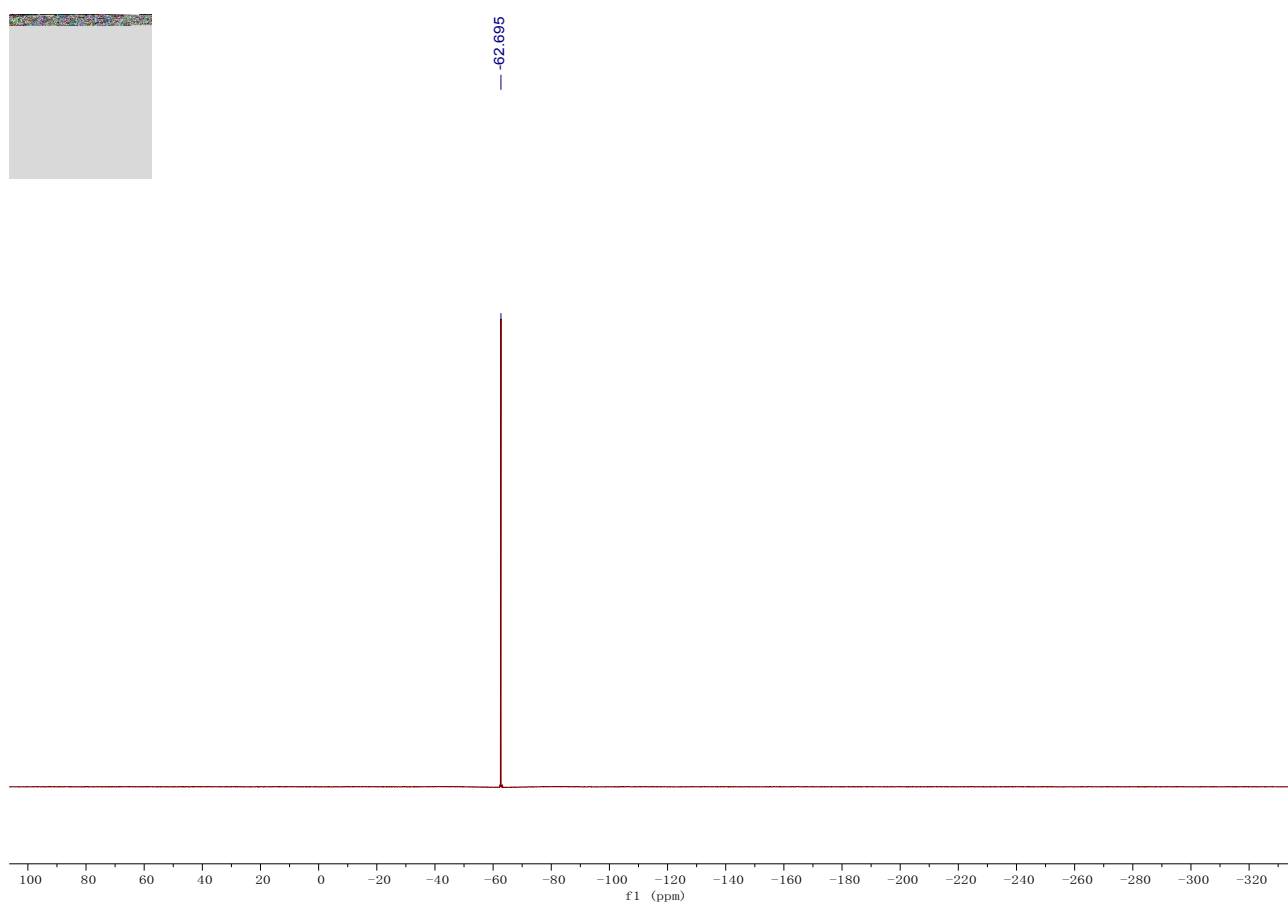
Compound 2i: Yield: 69.5 mg, 90%; A white solid; Mp: 77 - 79 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, $J = 7.5$ Hz, 1H), 7.63 (t, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.45 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 8.2$ Hz, 2H), 3.66 (s, 3H), 1.70 – 1.60 (m, 1H), 1.45 – 1.35 (m, 1H), 1.28 – 1.24 (m, 1H), 0.55 – 0.44 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.3, 152.8, 152.5, 139.6, 137.7, 134.7, 131.4, 130.0, 127.3, 125.4, 122.4, 121.8, 87.9, 54.6, 40.8, 21.2, 16.2; IR (neat): ν 1754, 1720, 1271, 1250, 819 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{19}\text{H}_{15}\text{O}_4\text{BrNa}$ $[\text{M}+\text{Na}]^+$: 409.0046, found: 409.0044.



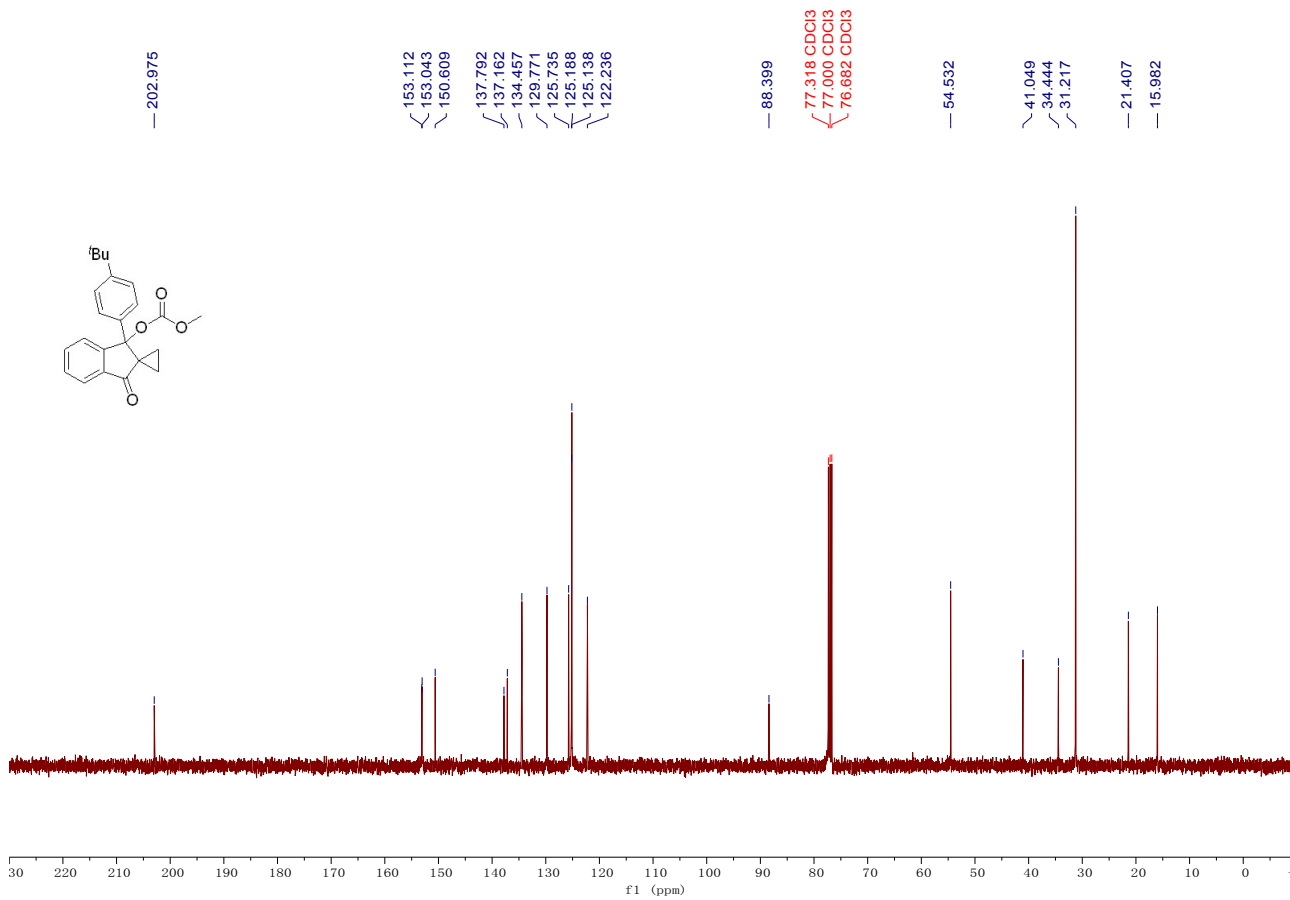
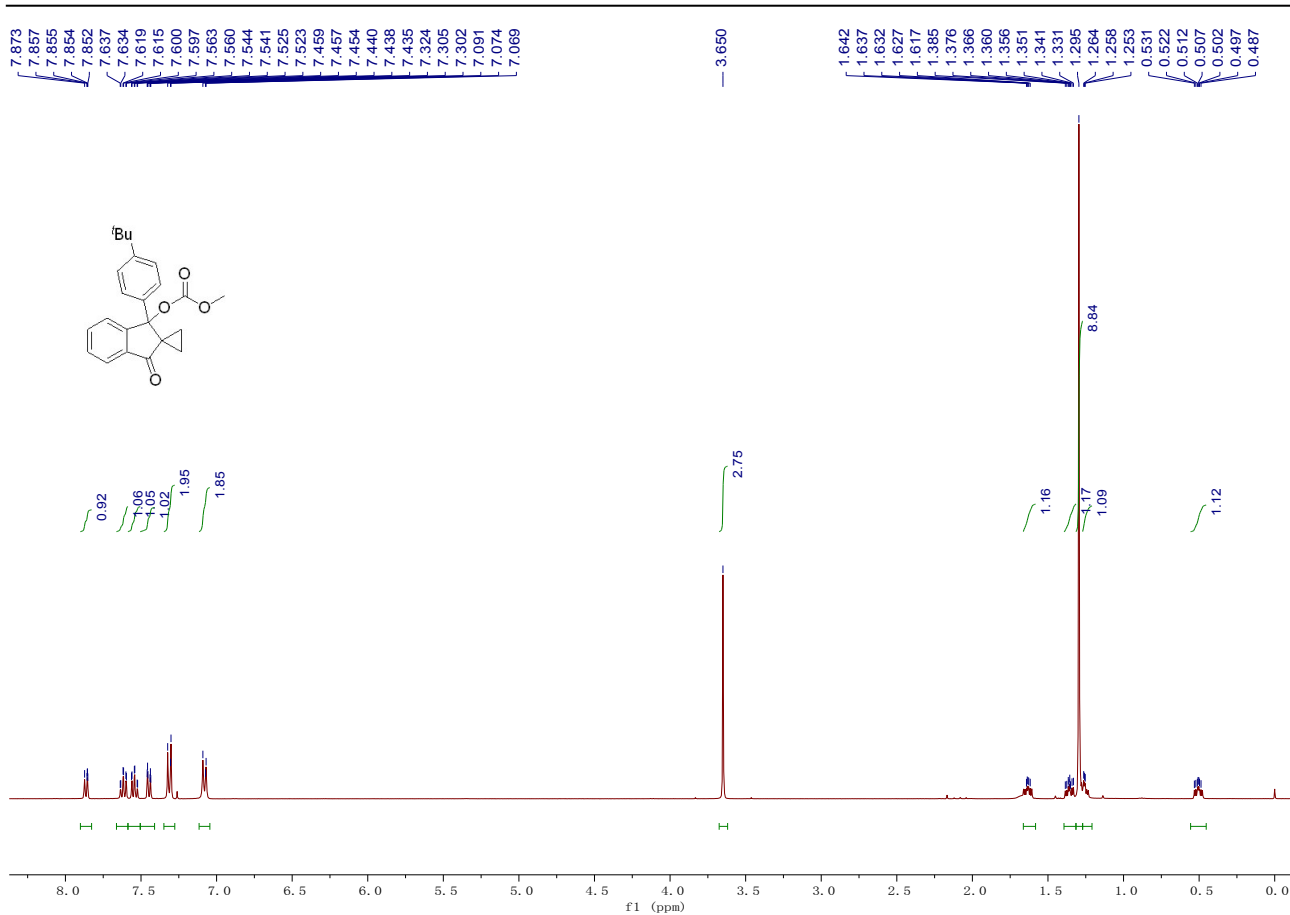


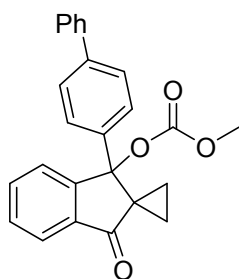
Compound 2j: Yield: 58.7 mg, 78%; A white solid; Mp: 159 - 161 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dt, $J = 7.5, 0.9$ Hz, 1H), 7.64 (td, $J = 7.5, 1.4$ Hz, 1H), 7.61 – 7.55 (m, 3H), 7.38 (dt, $J = 7.7, 1.0$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 3.68 (s, 3H), 1.71 – 1.62 (m, 1H), 1.47 – 1.38 (m, 1H), 1.32 – 1.24 (m, 1H), 0.52 – 0.42 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.1, 152.8, 152.5, 144.6, 137.7, 134.8, 130.2, 130.0 (q, $J = 32.6$ Hz), 126.1, 125.4, 125.3 (q, $J = 3.8$ Hz), 123.8 (q, $J = 272.2$ Hz), 122.6, 87.8, 54.7, 40.9, 21.2, 16.3; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.69; IR (neat): ν 2849, 1750, 1720, 1231, 755 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{15}\text{O}_4\text{F}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 399.0815, found: 399.0818.



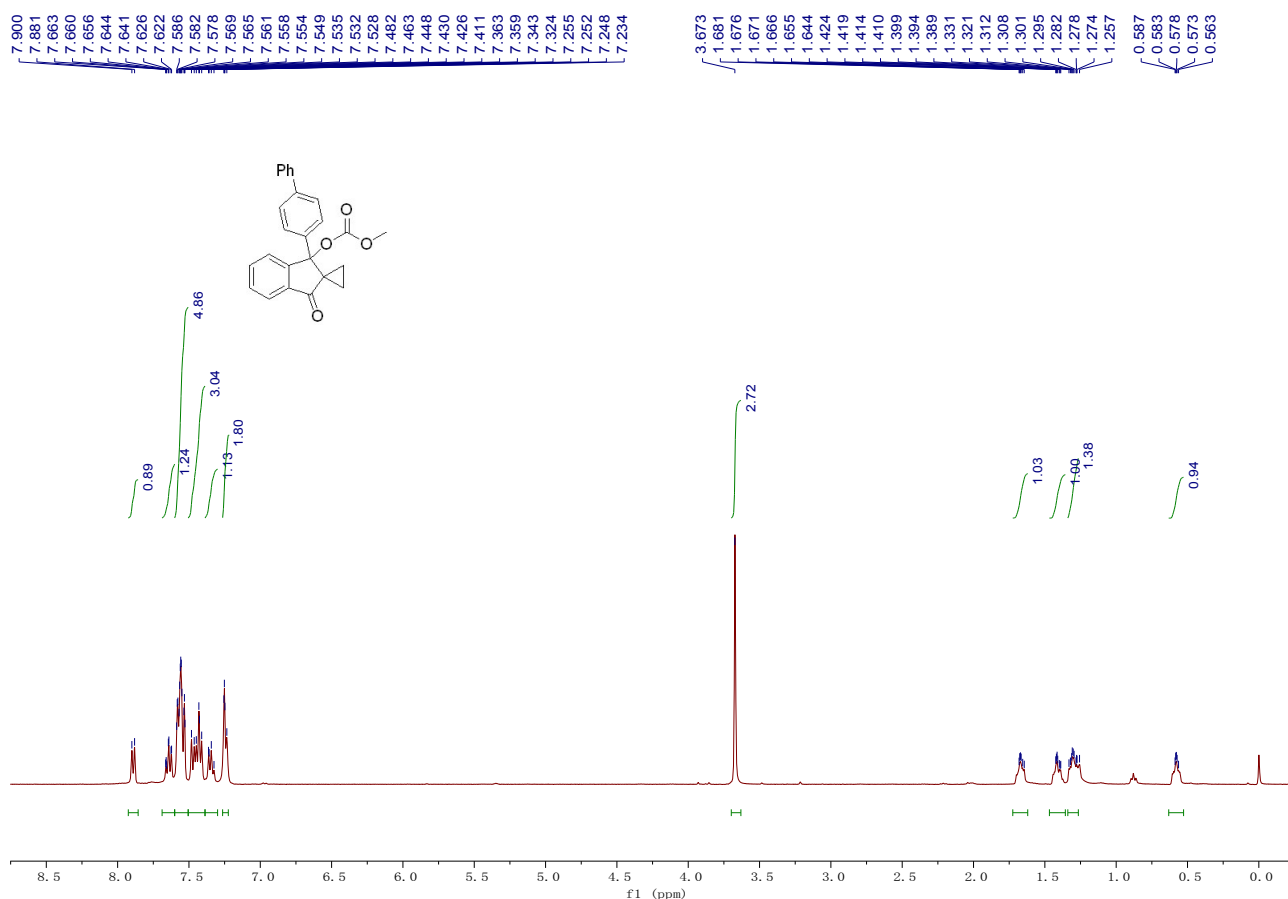


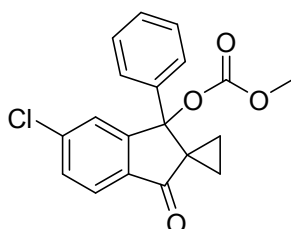
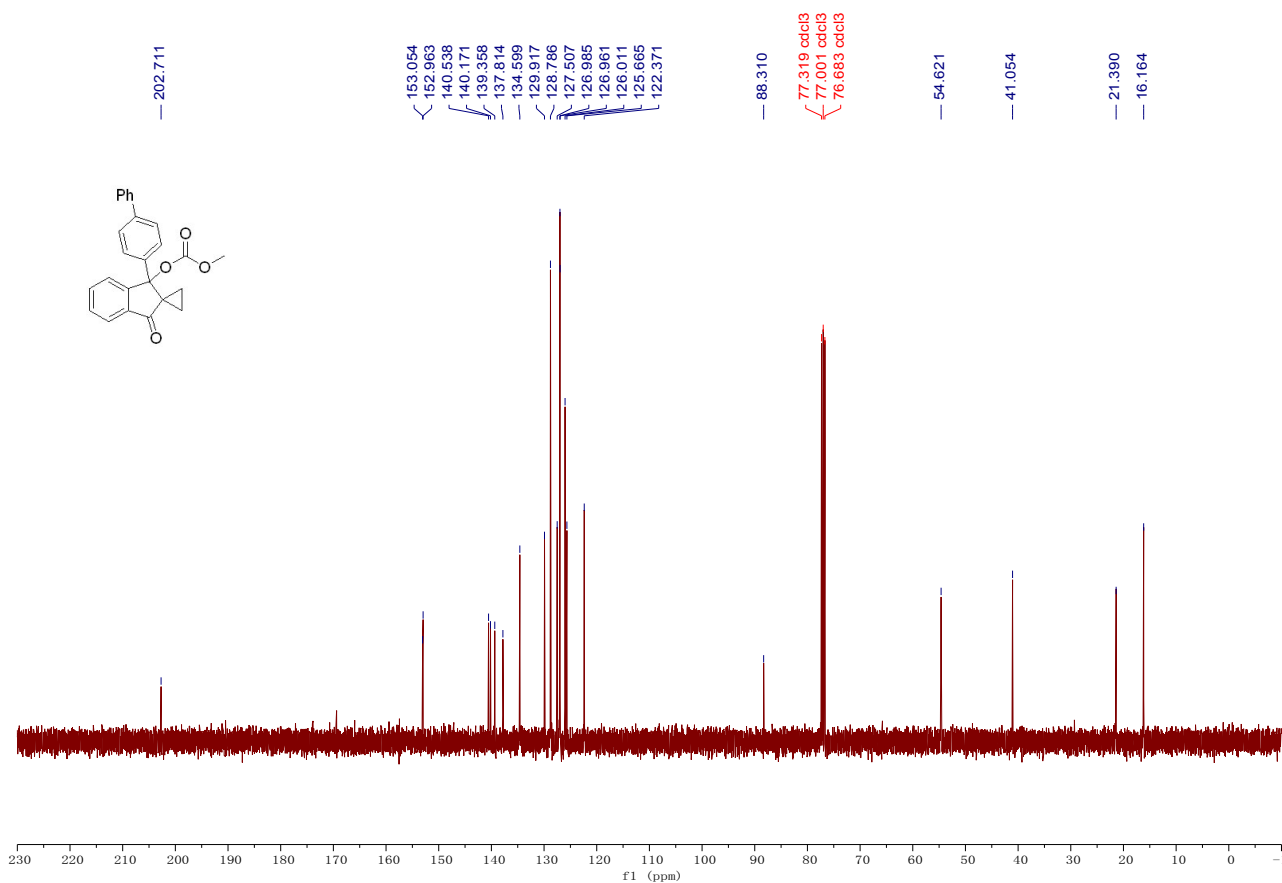
Compound 2k: Yield: 72.1 mg, 99%; A white solid; Mp: 65 - 67 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.83 (m, 1H), 7.62 (td, $J = 7.5, 1.3$ Hz, 1H), 7.54 (td, $J = 7.4, 1.2$ Hz, 1H), 7.50 – 7.41 (m, 1H), 7.35 – 7.28 (m, 2H), 7.12 – 7.04 (m, 2H), 3.65 (s, 3H), 1.66 – 1.58 (m, 1H), 1.39 – 1.31 (m, 1H), 1.30 (s, 9H), 1.27 – 1.21 (m, 1H), 0.56 – 0.45 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.0, 153.1, 153.0, 150.6, 137.8, 137.2, 134.5, 129.8, 125.7, 125.2, 125.1, 122.2, 88.4, 54.5, 41.0, 34.4, 31.2, 21.4, 16.0; IR (neat): ν 2960, 1756, 1719, 1269, 992 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{23}\text{H}_{24}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 387.1567, found: 387.1568.



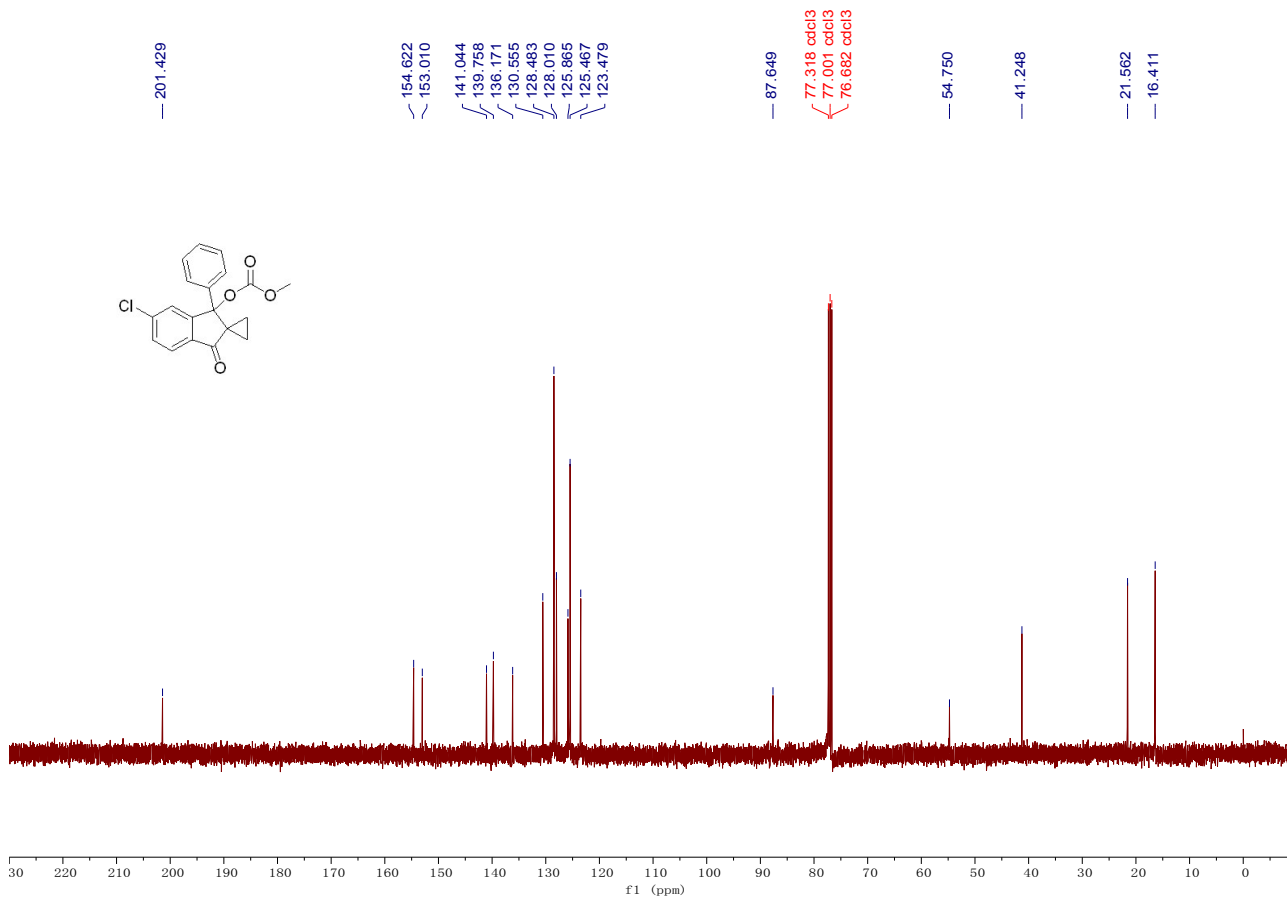
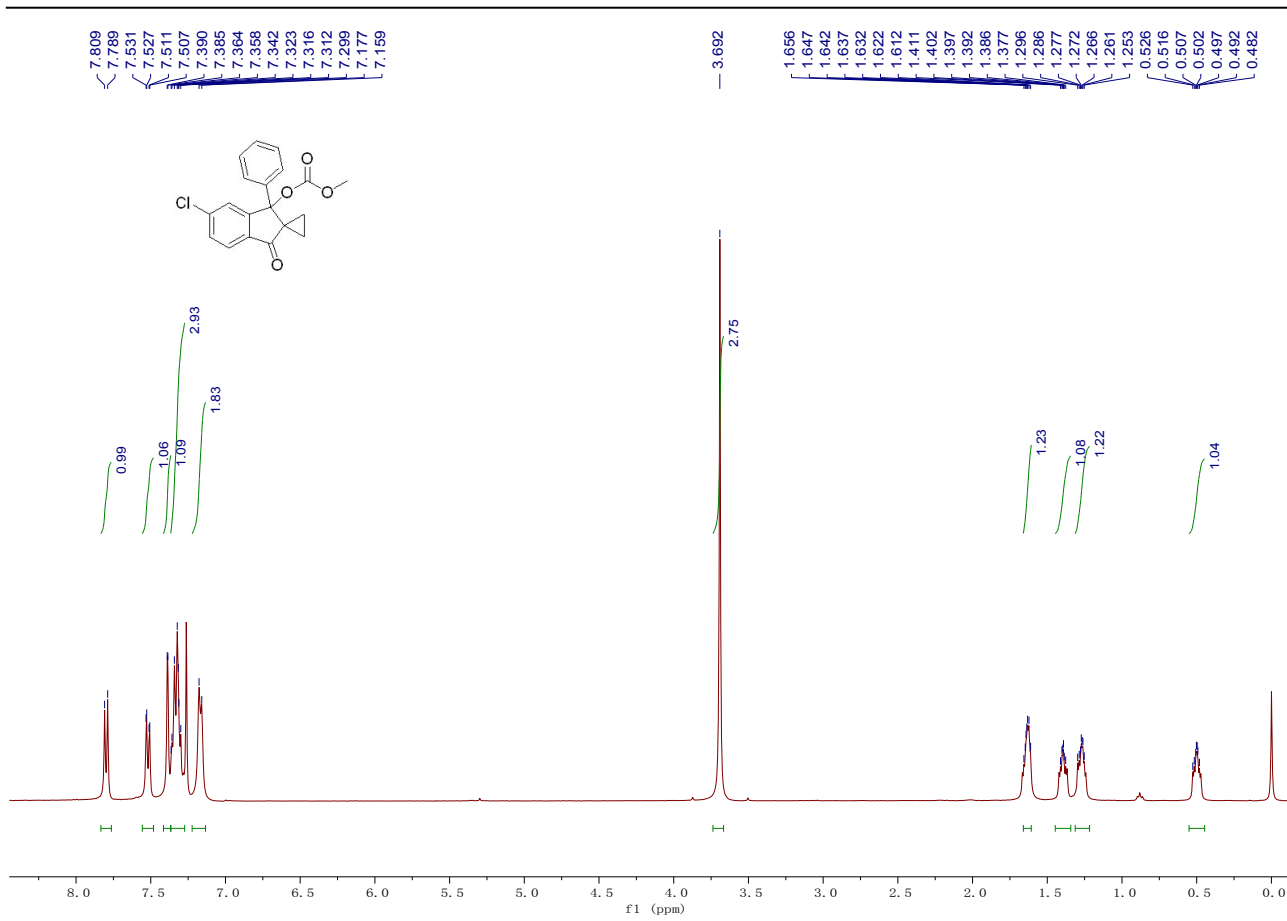


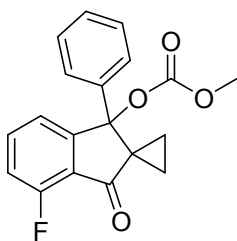
Compound 2l: Yield: 69.1 mg, 90%; A white solid; Mp: 70 - 72 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, $J = 7.6$ Hz, 1H), 7.64 (td, $J = 7.5, 1.5$ Hz, 1H), 7.60 – 7.51 (m, 5H), 7.51 – 7.39 (m, 3H), 7.34 (t, $J = 7.7$ Hz, 1H), 7.26 – 7.22 (m, 2H), 3.67 (s, 3H), 1.72 – 1.62 (m, 1H), 1.47 – 1.36 (m, 1H), 1.34 – 1.27 (m, 1H), 0.63 – 0.53 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.7, 153.1, 153.0, 140.5, 140.2, 139.4, 137.8, 134.6, 129.9, 128.8, 127.5, 126.99, 126.96, 126.0, 125.7, 122.4, 88.3, 54.6, 41.1, 21.4, 16.2; IR (neat): ν 1738, 1718, 1260, 1159, 889 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{25}\text{H}_{20}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 407.1254, found: 407.1251.



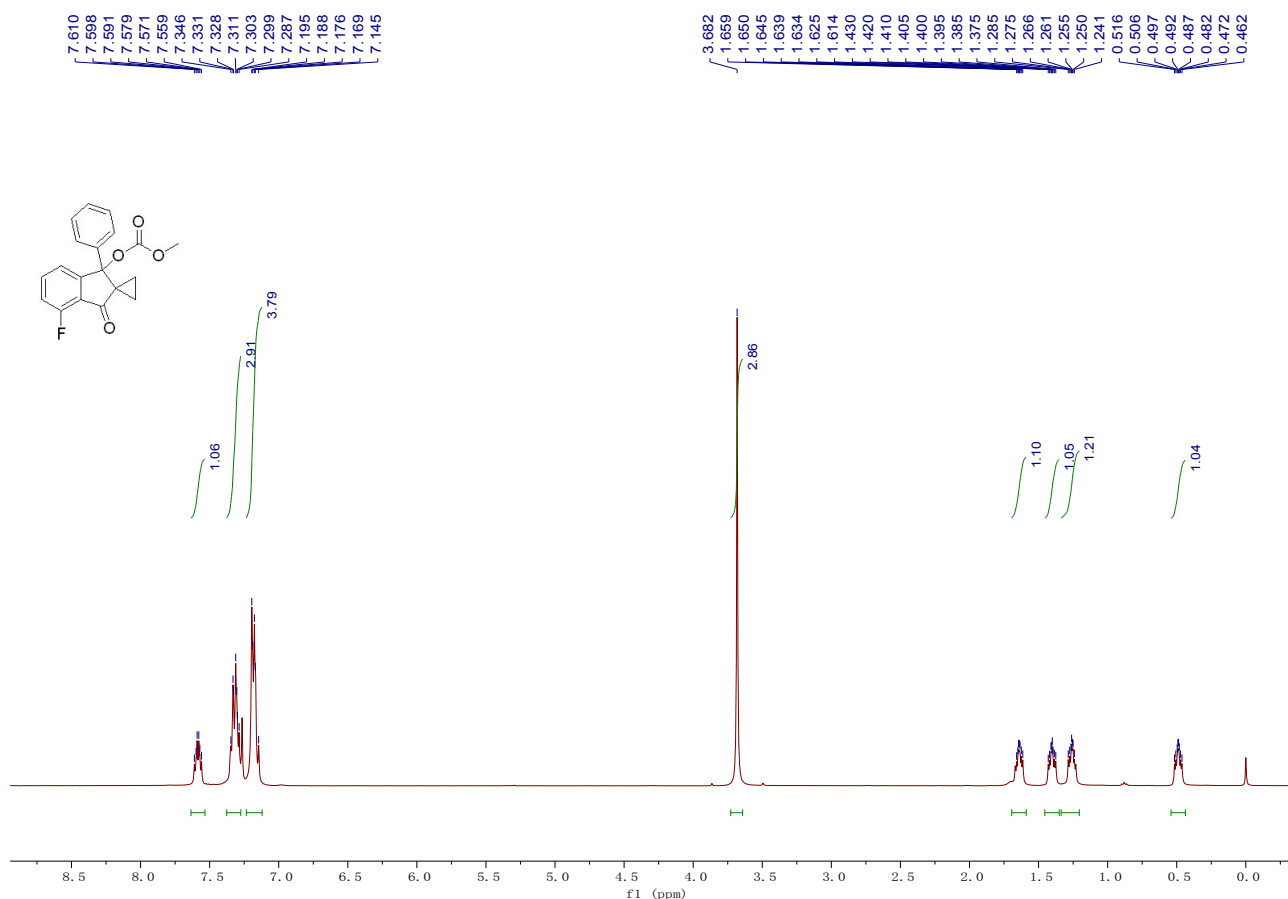


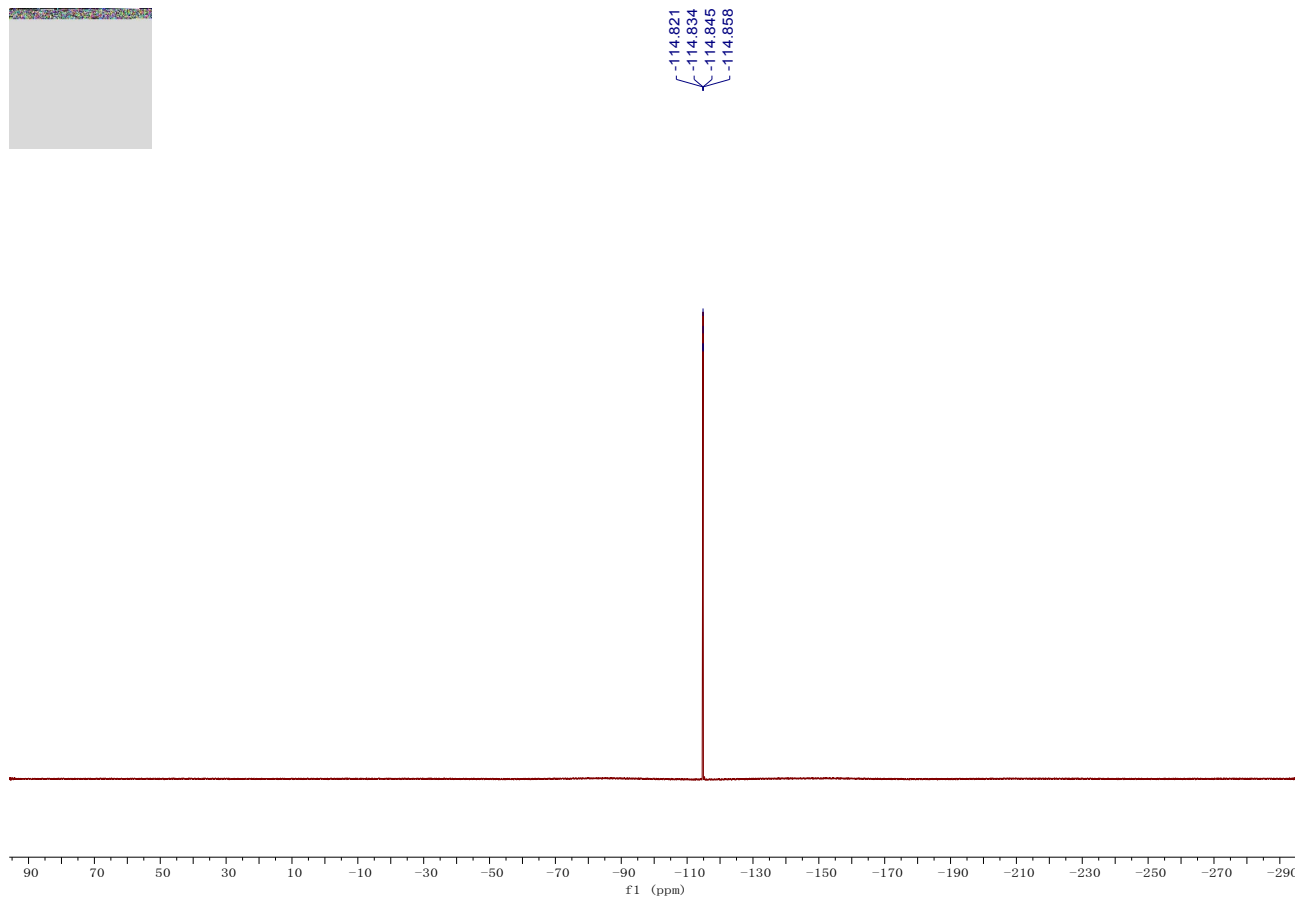
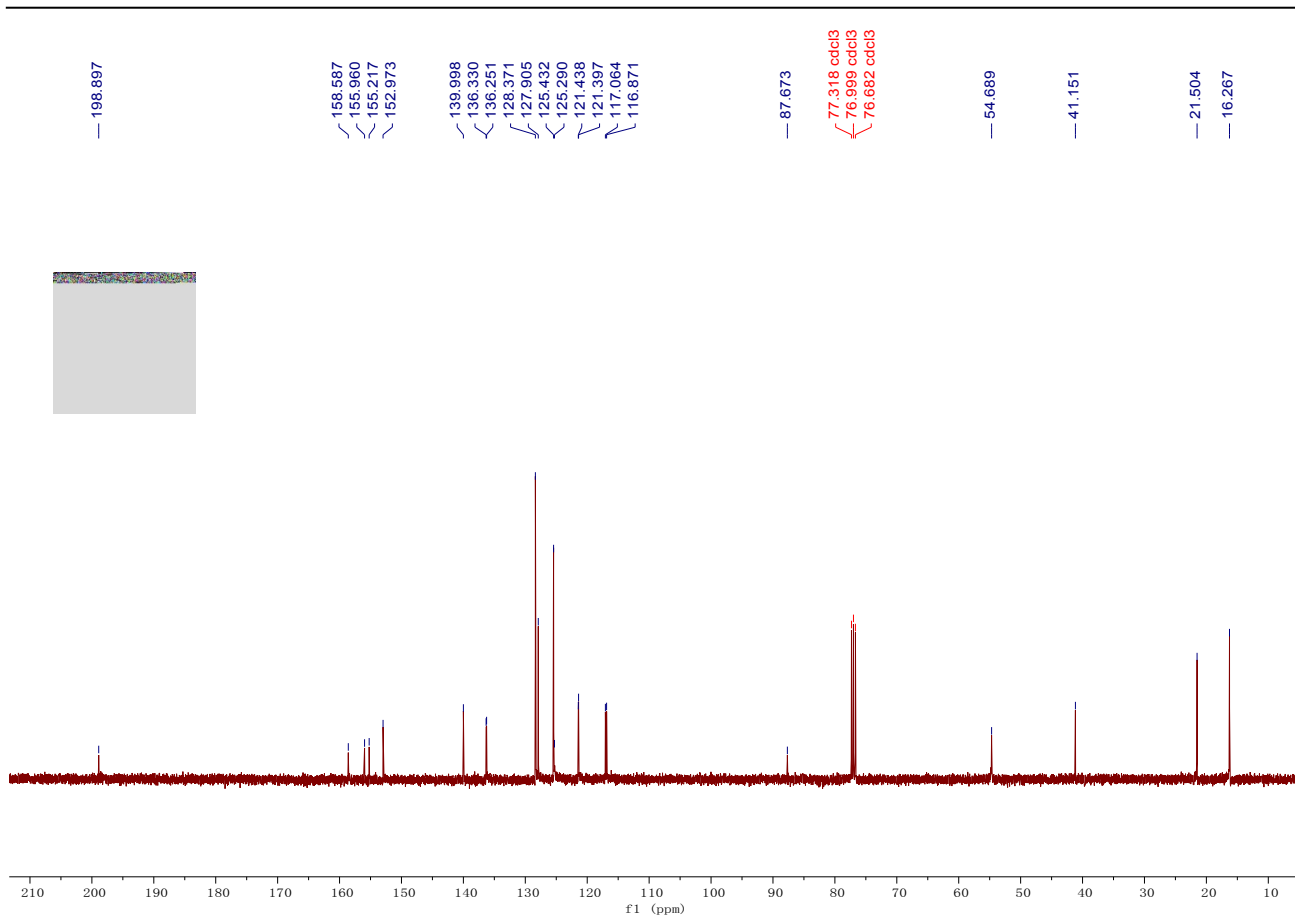
Compound 2p: Yield: 52.7 mg, 77%; A white solid; Mp: 78 - 80 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, $J = 8.1$ Hz, 1H), 7.52 (dd, $J = 8.1, 1.9$ Hz, 1H), 7.39 (s, 1H), 7.37 – 7.27 (m, 3H), 7.17 (d, $J = 7.4$ Hz, 2H), 3.69 (s, 3H), 1.66 – 1.61 (m, 1H), 1.45 – 1.34 (m, 1H), 1.31 – 1.22 (m, 1H), 0.55 – 0.45 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.4, 154.6, 153.0, 141.0, 139.8, 136.2, 130.6, 128.5, 128.0, 125.9, 125.5, 123.5, 87.6, 54.7, 41.2, 21.6, 16.4; IR (neat): ν 2960, 1752, 1721, 1280, 986 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{19}\text{H}_{15}\text{O}_4\text{NaCl}$ $[\text{M}+\text{Na}]^+$: 365.0551, found: 365.0547.

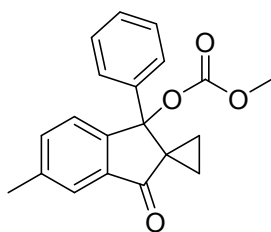




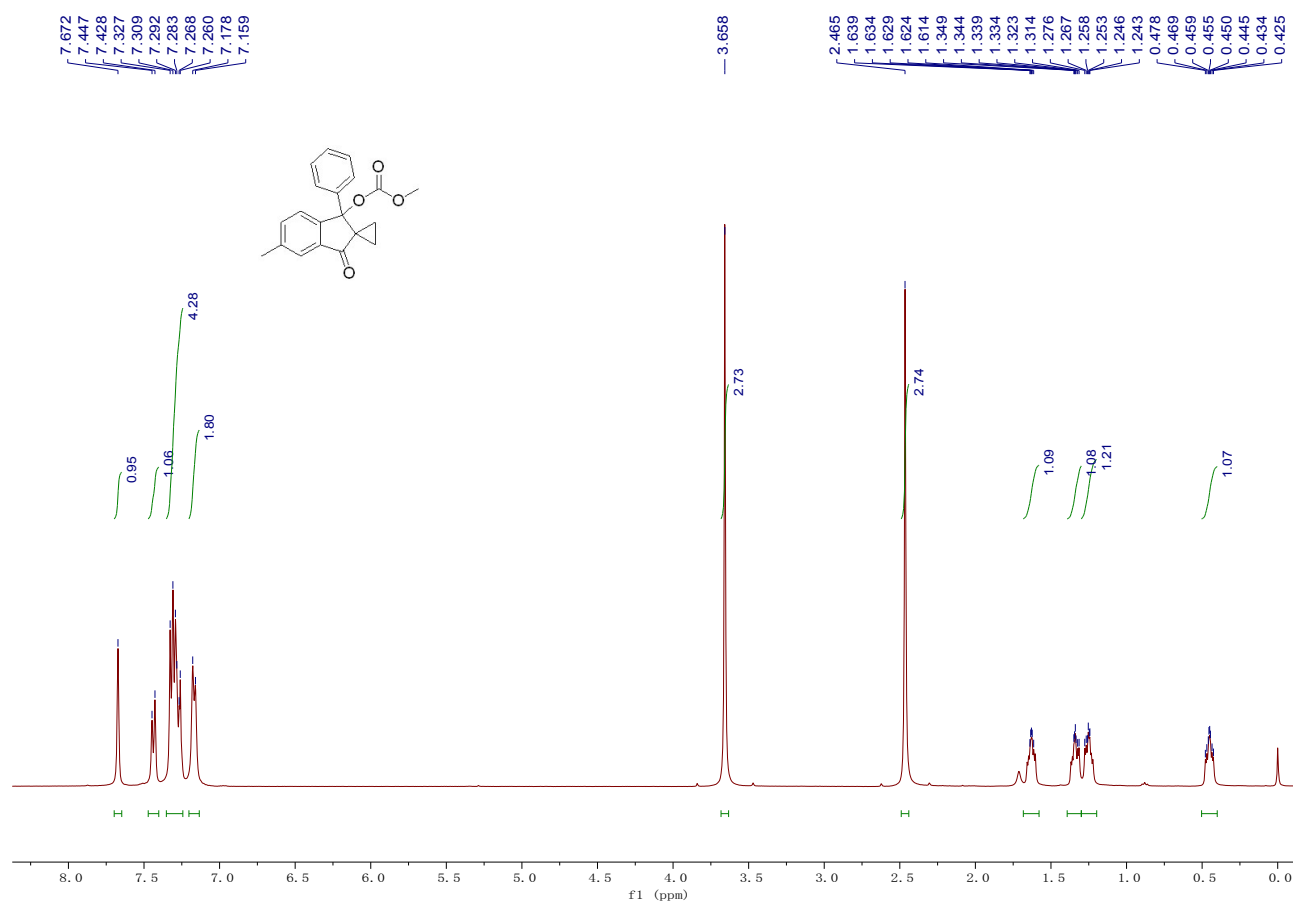
Compound 2q: Yield: 61.3 mg, 94%; A white solid; Mp: 134 - 136 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.58 (td, $J = 7.9, 4.8$ Hz, 1H), 7.38 – 7.27 (m, 3H), 7.23 – 7.12 (m, 4H), 3.68 (s, 3H), 1.69 – 1.59 (m, 1H), 1.46 – 1.35 (m, 1H), 1.34 – 1.21 (m, 1H), 0.54 – 0.44 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.9, 157.3 (d, $J = 264.0$ Hz), 155.2, 153.0, 140.0, 136.3 (d, $J = 8.0$ Hz), 128.4, 127.9, 125.4, 125.3, 121.4 (d, $J = 4.1$ Hz), 117.0 (d, $J = 19.3$ Hz), 87.7, 54.7, 41.2, 21.5, 16.3; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.75 – -114.94 (m); IR (neat): ν 2998, 1756, 1723, 1280, 757 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{19}\text{H}_{15}\text{O}_4\text{FNa}$ $[\text{M}+\text{Na}]^+$: 349.0847, found: 349.0845.

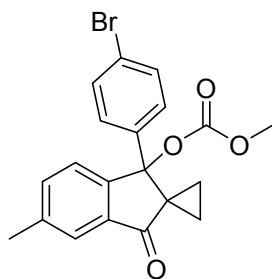
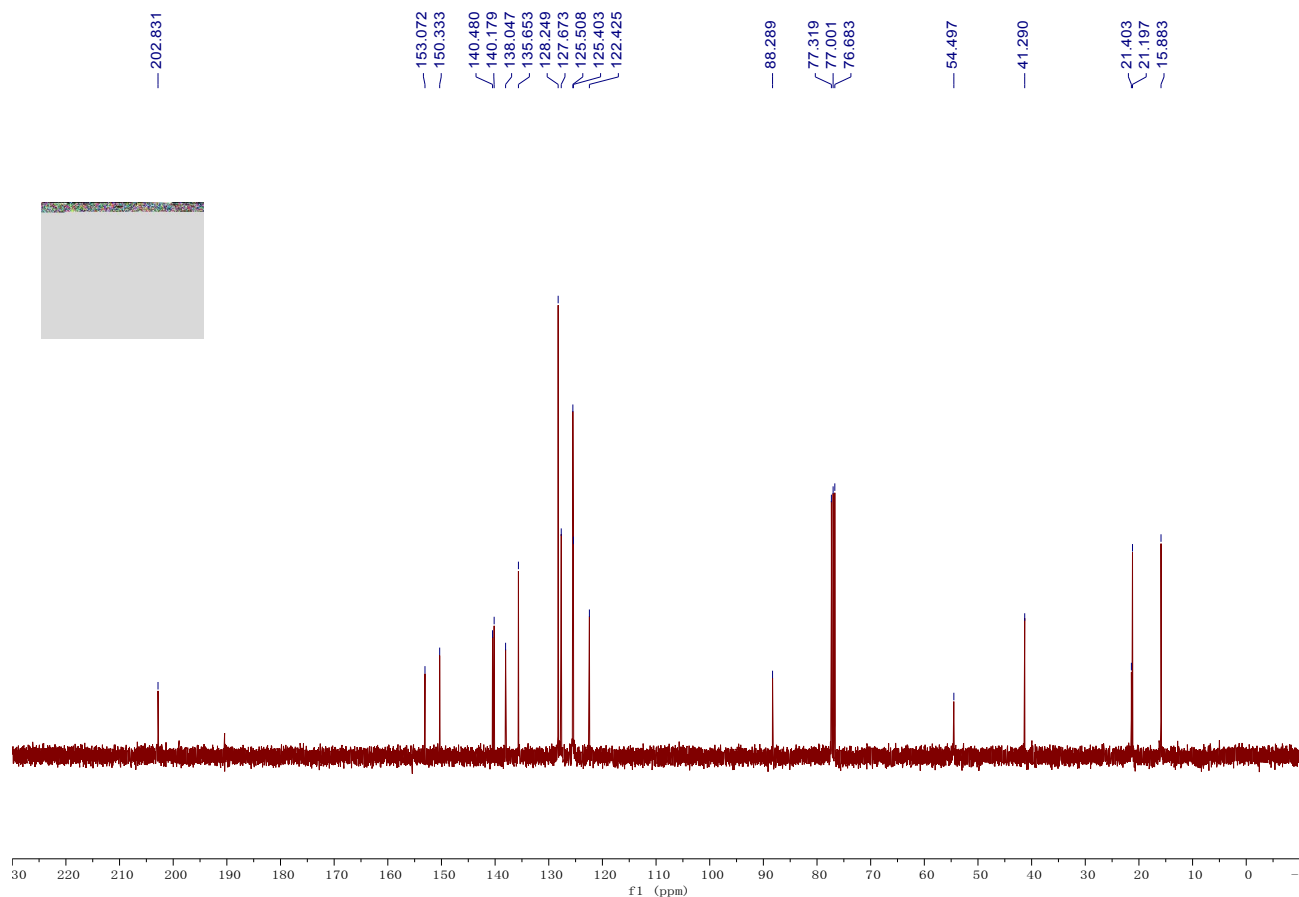




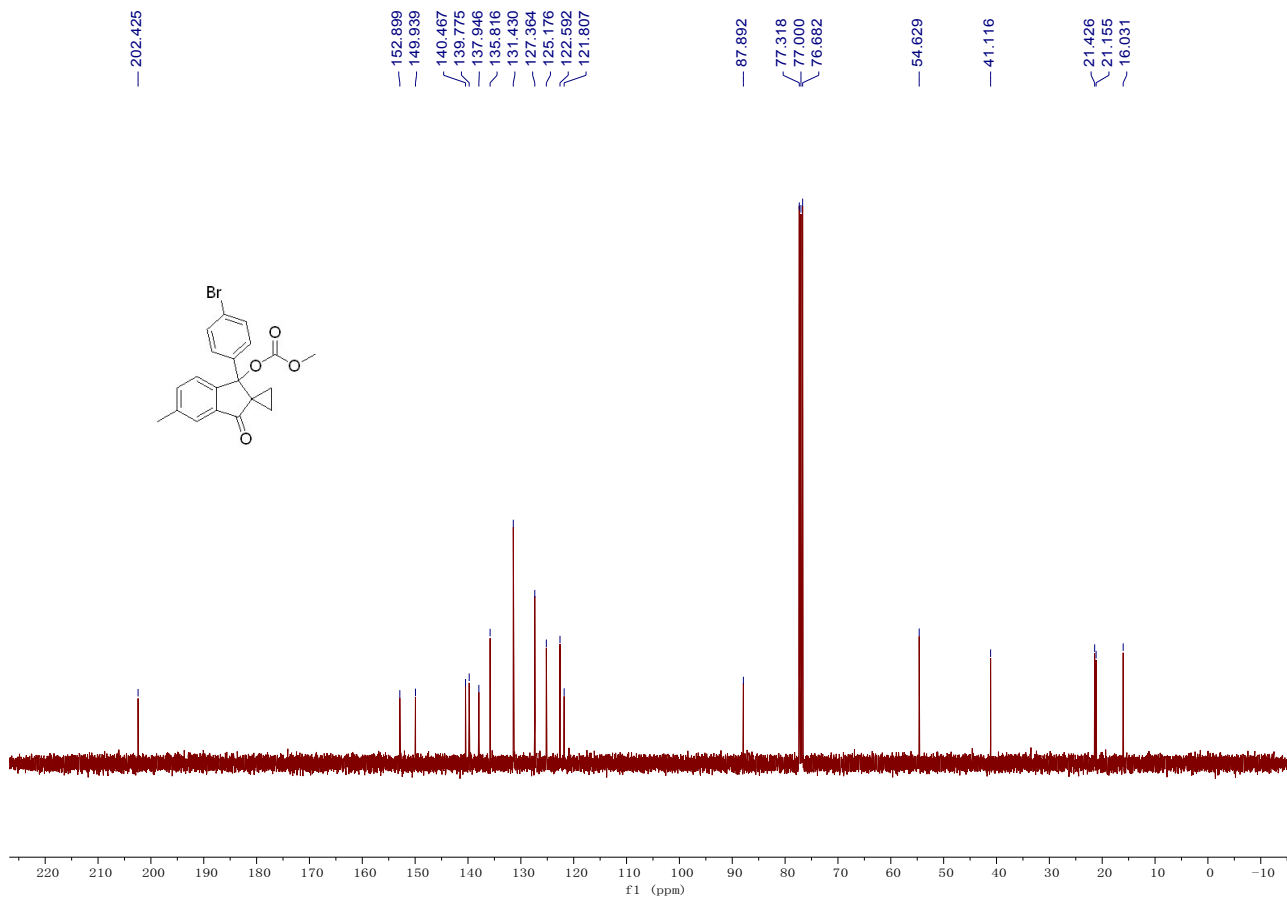
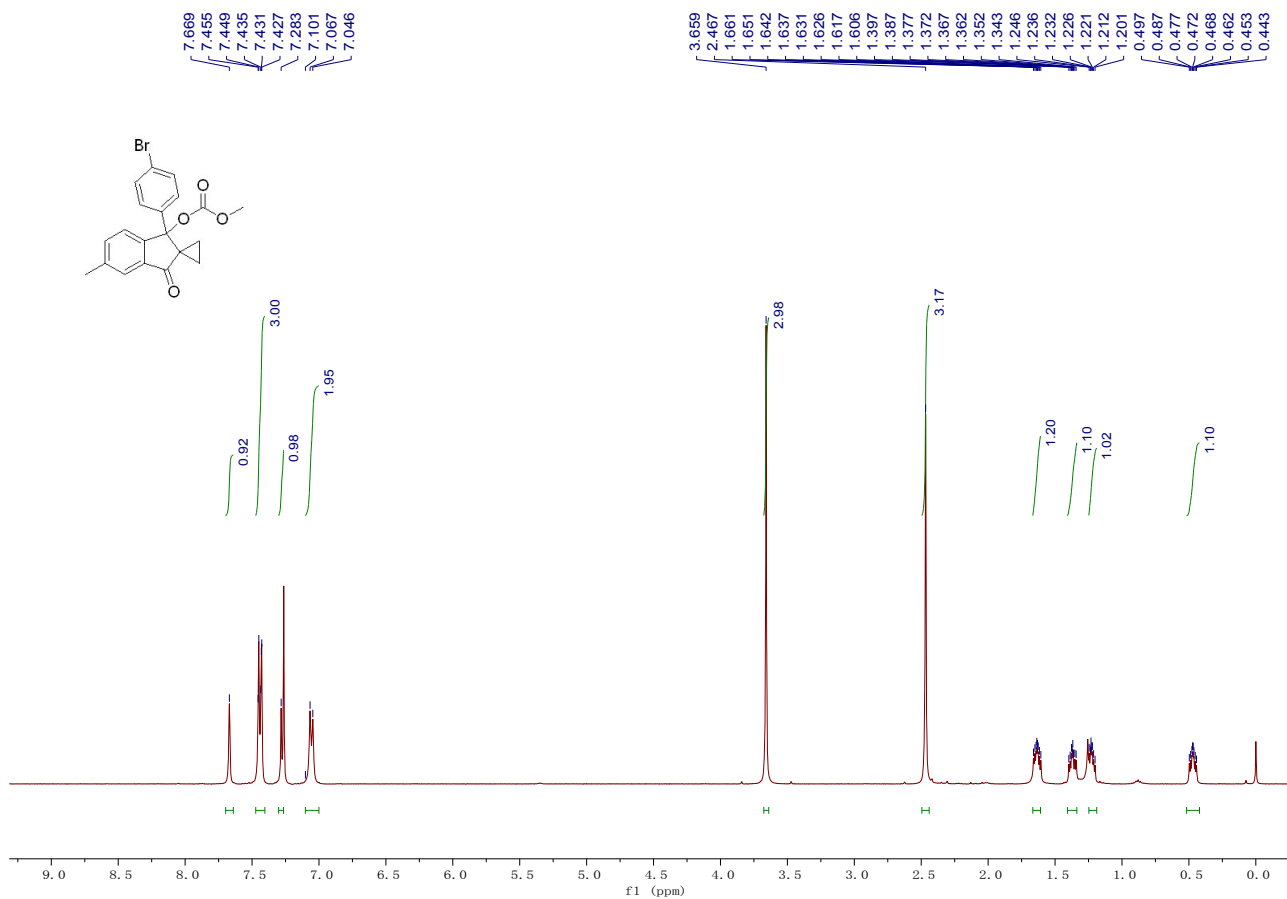


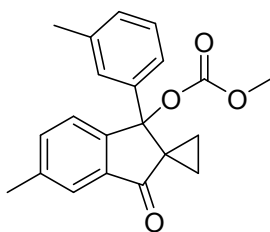
Compound 2r: Yield: 59.2 mg, 92%; A white solid; Mp: 160 - 162 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.35 – 7.24 (m, 4H), 7.17 (d, $J = 7.3$ Hz, 2H), 3.66 (s, 3H), 2.47 (s, 3H), 1.68 – 1.58 (m, 1H), 1.39 – 1.30 (m, 1H), 1.30 – 1.20 (m, 1H), 0.50 – 0.40 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.8, 153.1, 150.3, 140.5, 140.2, 138.0, 135.7, 128.2, 127.7, 125.5, 125.4, 122.4, 88.3, 54.5, 41.3, 21.4, 21.2, 15.9; IR (neat): ν 1755, 1719, 1326, 1209, 987 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 345.1097, found: 345.1092.



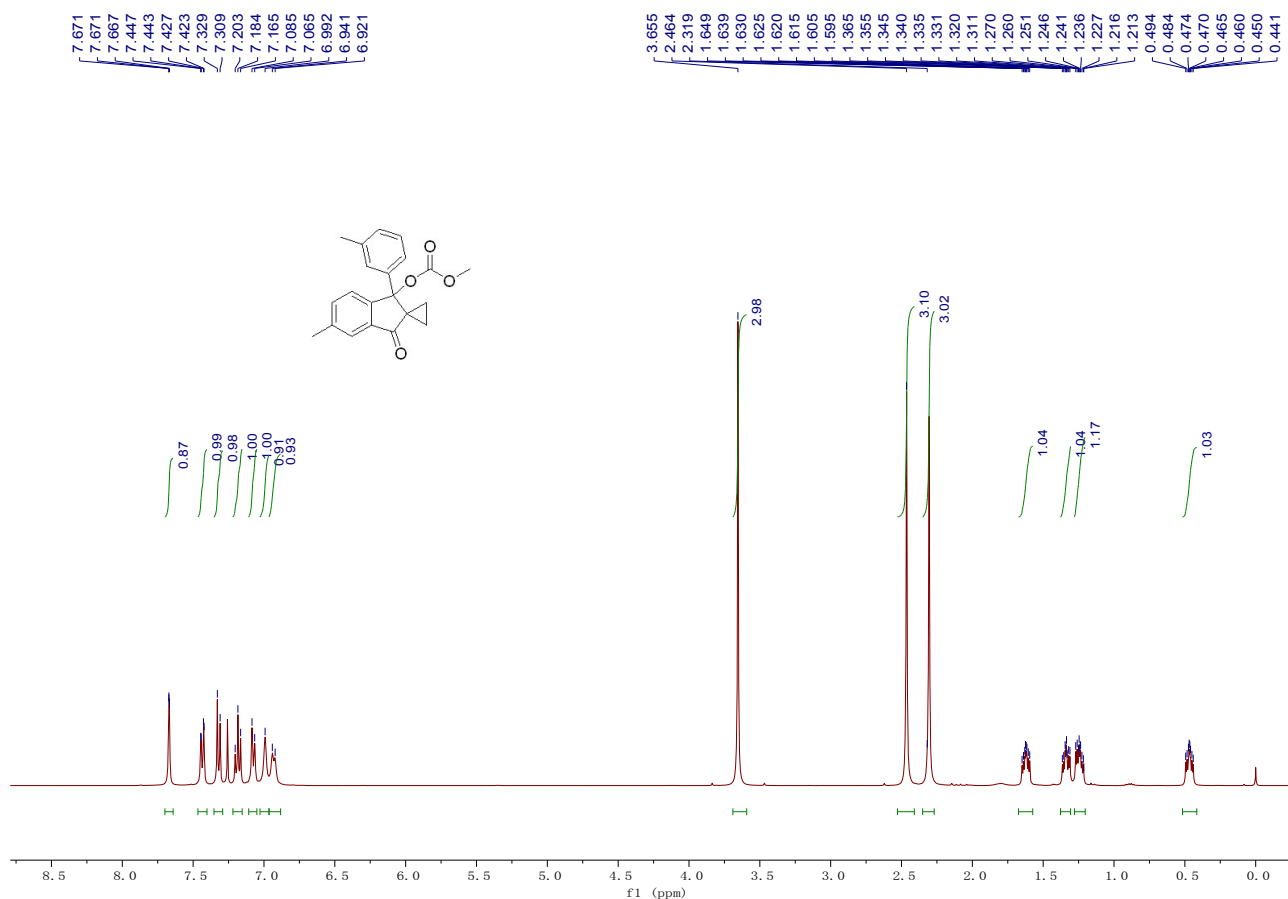


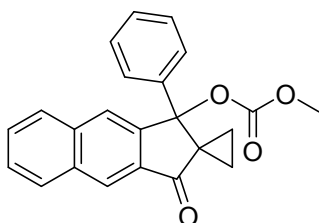
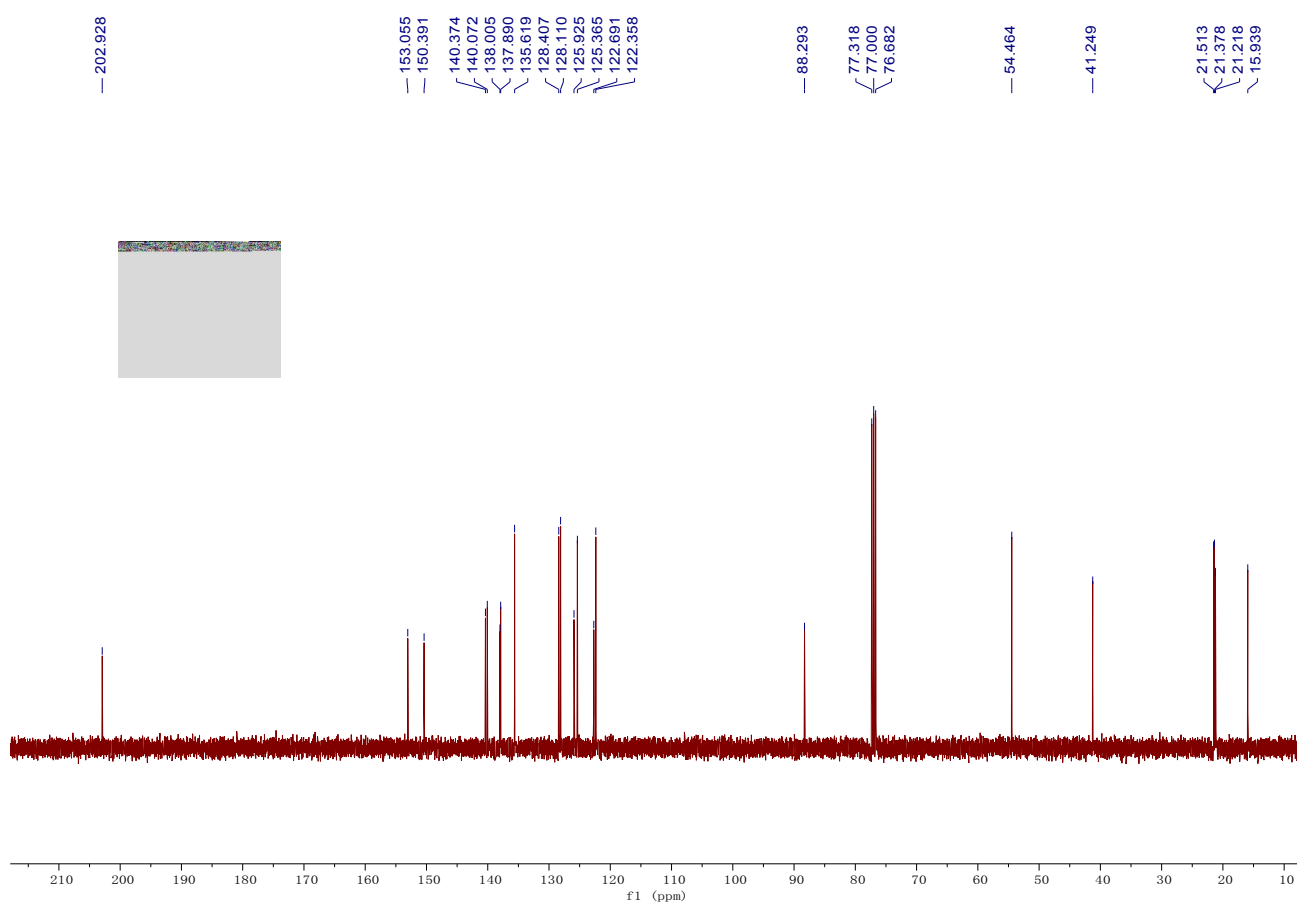
Compound 2s: Yield: 66.4 mg, 83%; A white solid; Mp: 79 - 81 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.47 – 7.40 (m, 3H), 7.30 – 7.26 (m, 1H), 7.06 (d, $J = 8.2$ Hz, 2H), 3.66 (s, 3H), 2.47 (s, 3H), 1.67 – 1.61 (m, 1H), 1.41 – 1.34 (m, 1H), 1.25 – 1.19 (m, 1H), 0.52 – 0.42 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.4, 152.9, 149.9, 140.5, 139.8, 137.9, 135.8, 131.4, 127.4, 125.2, 122.6, 121.8, 87.9, 54.6, 41.1, 21.4, 21.2, 16.0; IR (neat): ν 1754, 1718, 1668, 1269, 816 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{17}\text{O}_4\text{BrNa}$ $[\text{M}+\text{Na}]^+$: 423.0202, found: 423.0206.



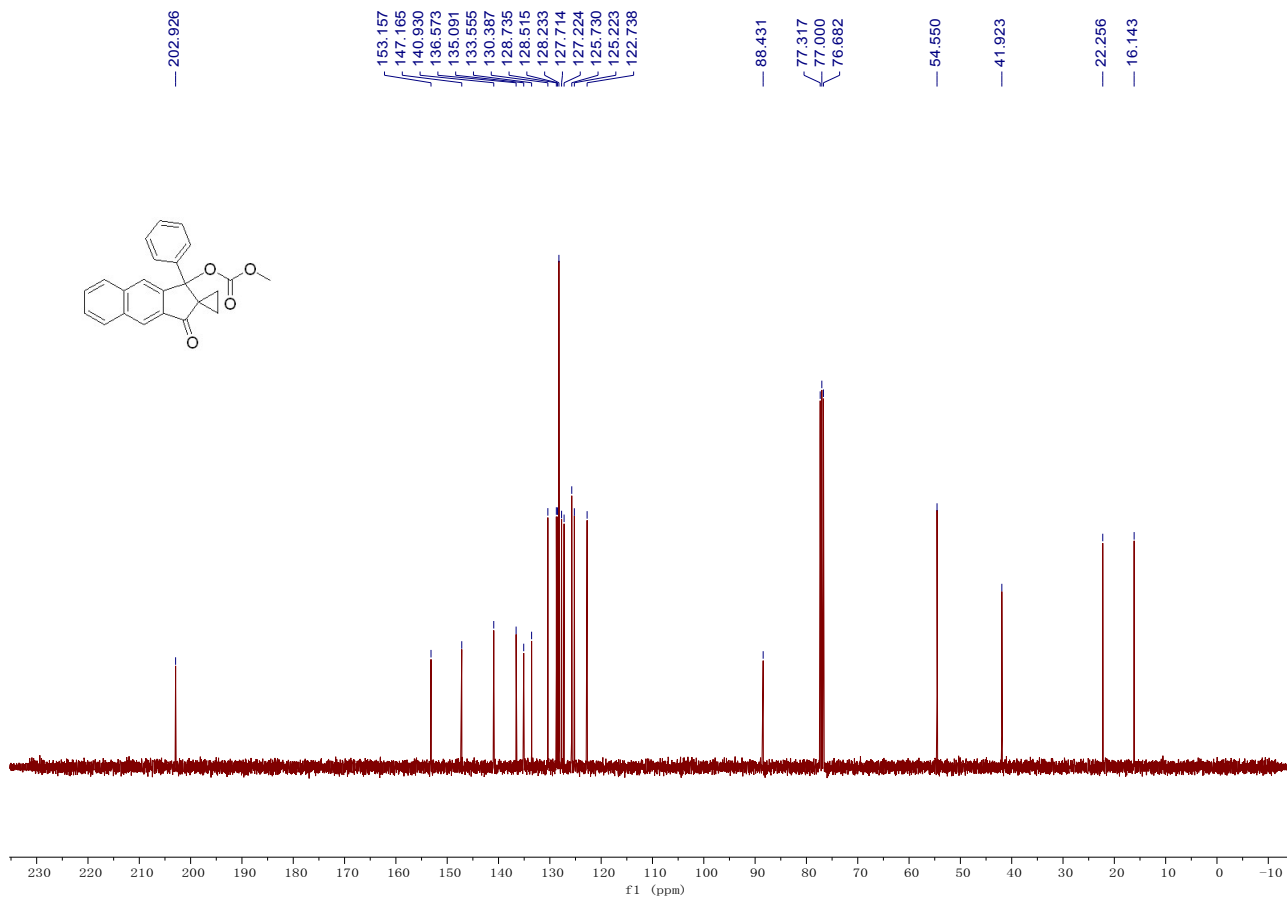
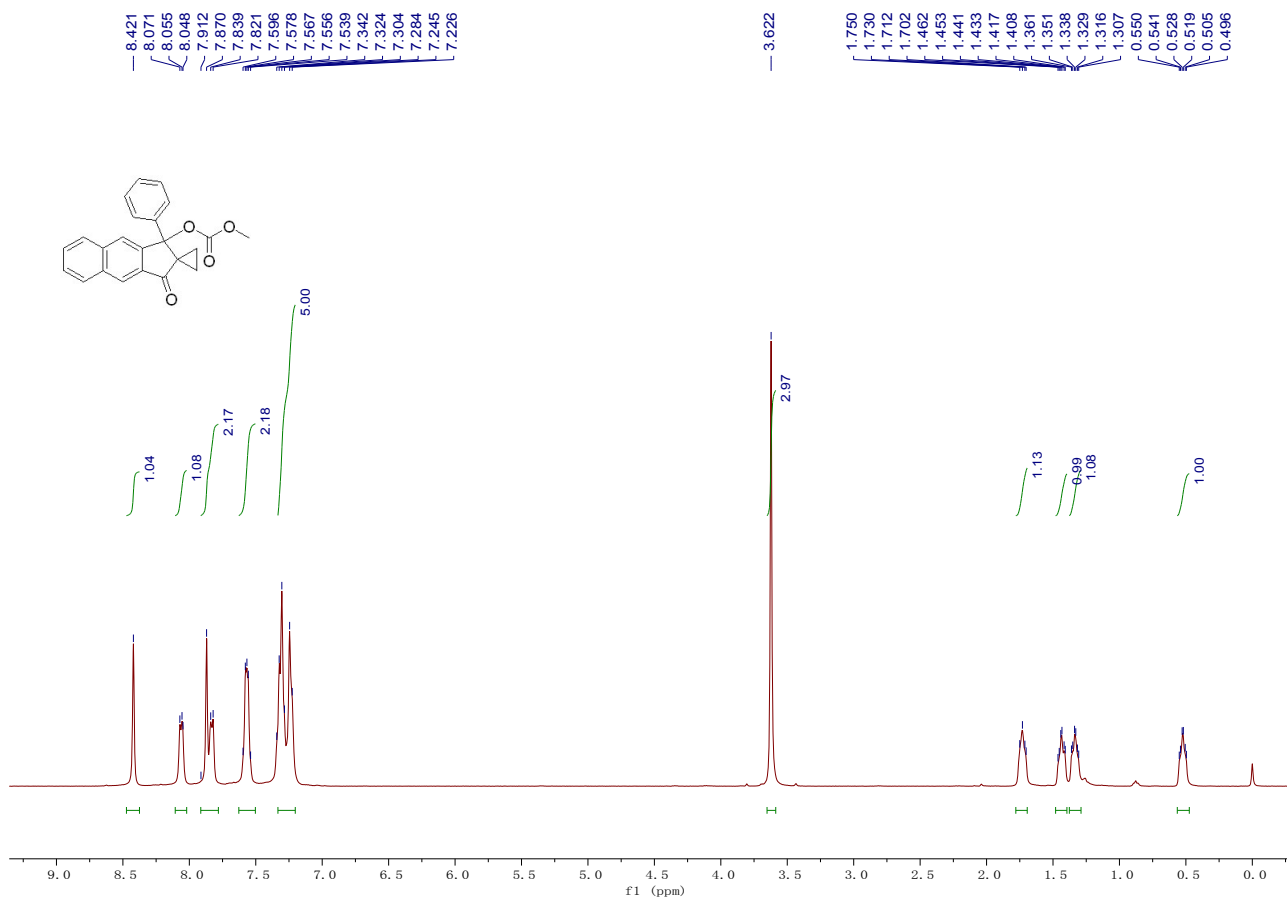


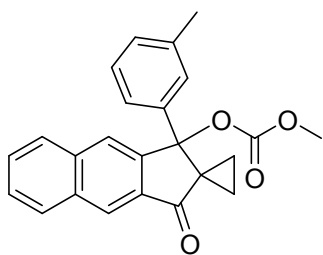
Compound 2t: Yield: 53.1 mg, 79%; A white solid; Mp: 126 - 128 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.43 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.99 (s, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 3.65 (s, 3H), 2.46 (s, 3H), 2.32 (s, 3H), 1.67 – 1.57 (m, 1H), 1.38 – 1.31 (m, 1H), 1.28 – 1.20 (m, 1H), 0.52 – 0.42 (m, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 202.9, 153.1, 150.4, 140.4, 140.1, 138.0, 137.9, 135.6, 128.4, 128.1, 125.9, 125.4, 122.7, 122.4, 88.3, 54.5, 41.2, 21.5, 21.4, 21.2, 15.9; IR (neat): ν 1759, 1754, 1258, 1157, 869 cm⁻¹; HRMS (ESI) Calcd. for C₂₁H₂₀O₄Na [M+Na]⁺: 359.1254, found: 359.1260.



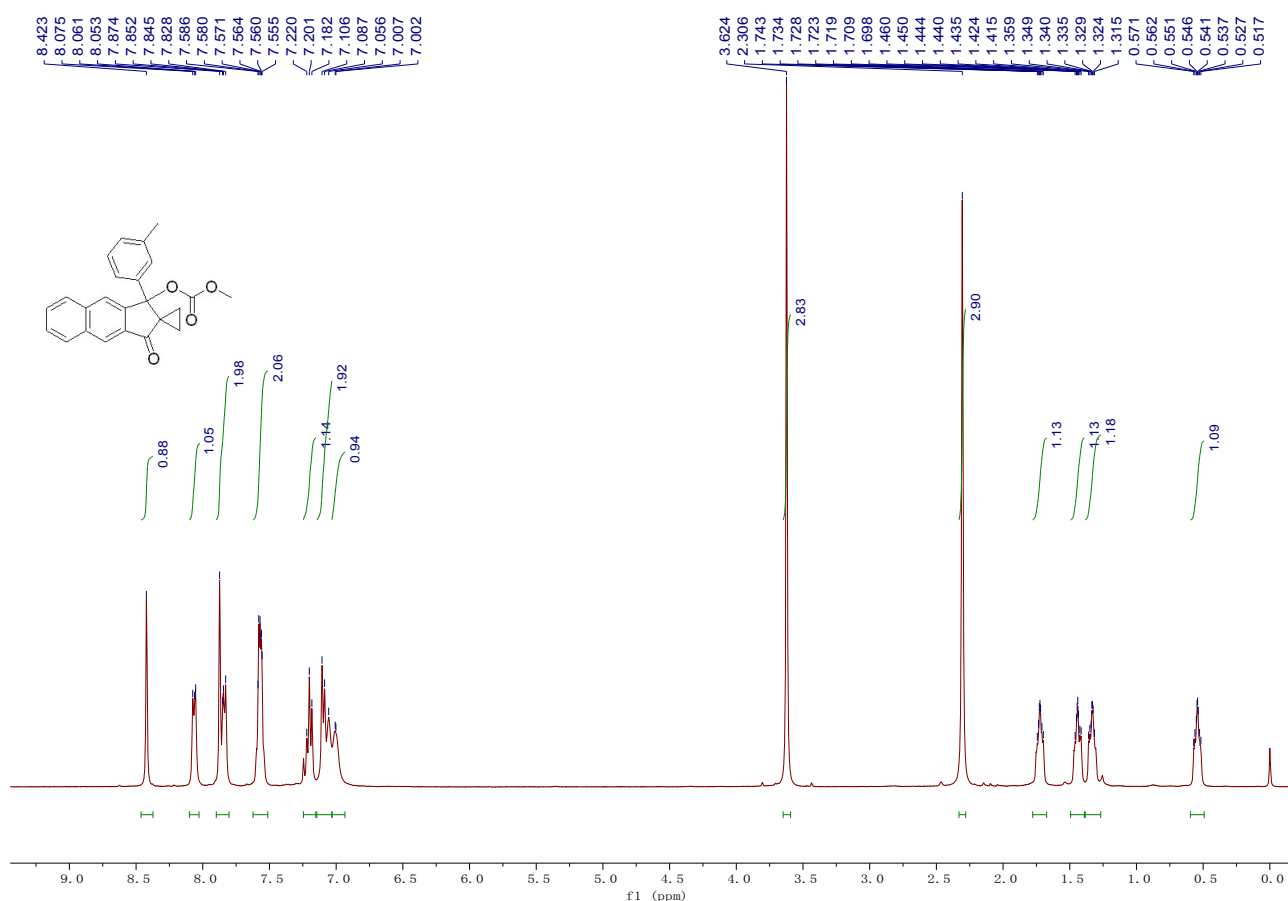


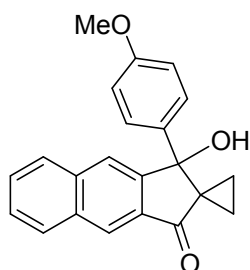
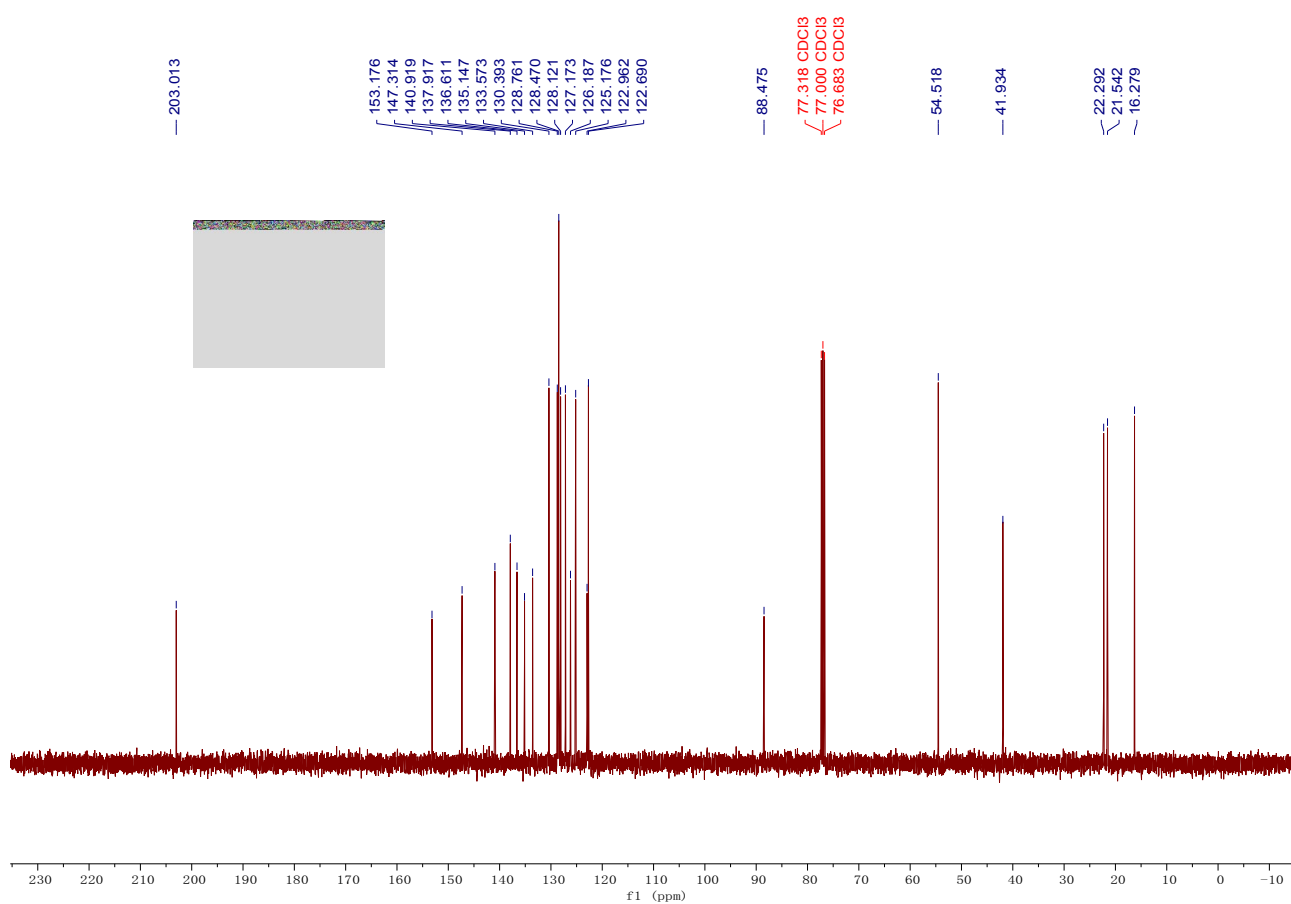
Compound 2u: Yield: 65.9 mg, 92%; A white solid; Mp: 169 - 171 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 8.11 – 8.02 (m, 1H), 7.91 – 7.78 (m, 2H), 7.63 – 7.50 (m, 2H), 7.33 – 7.20 (m, 5H), 3.62 (s, 3H), 1.78 – 1.69 (m, 1H), 1.48 – 1.40 (m, 1H), 1.38 – 1.29 (m, 1H), 0.56 – 0.47 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.9, 153.2, 147.2, 140.9, 136.6, 135.1, 133.6, 130.4, 128.7, 128.5, 128.2, 127.7, 127.2, 125.7, 125.2, 122.7, 88.4, 54.5, 41.9, 22.3, 16.1; IR (neat): ν 1757, 1718, 1259, 1207, 984 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{23}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 381.1097, found: 381.1102.



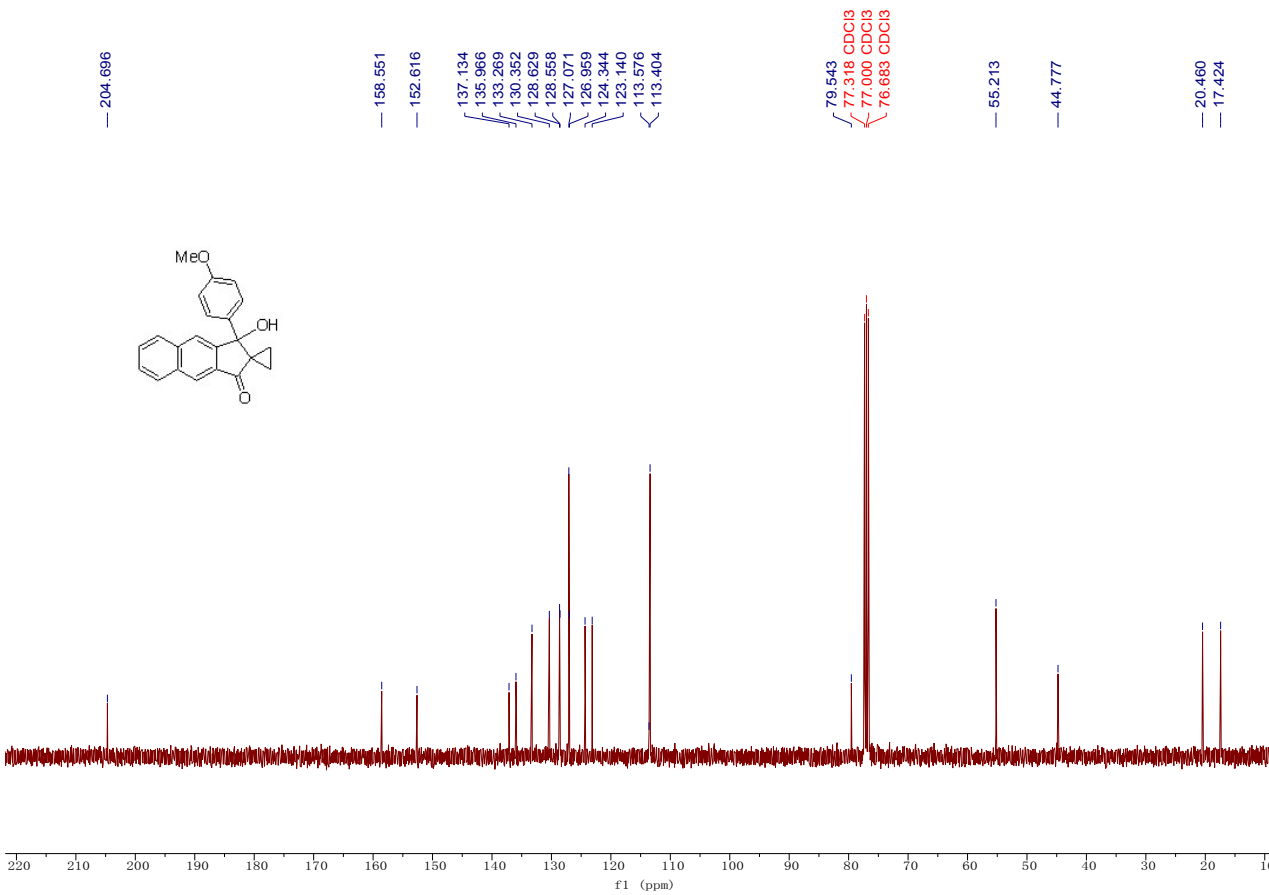
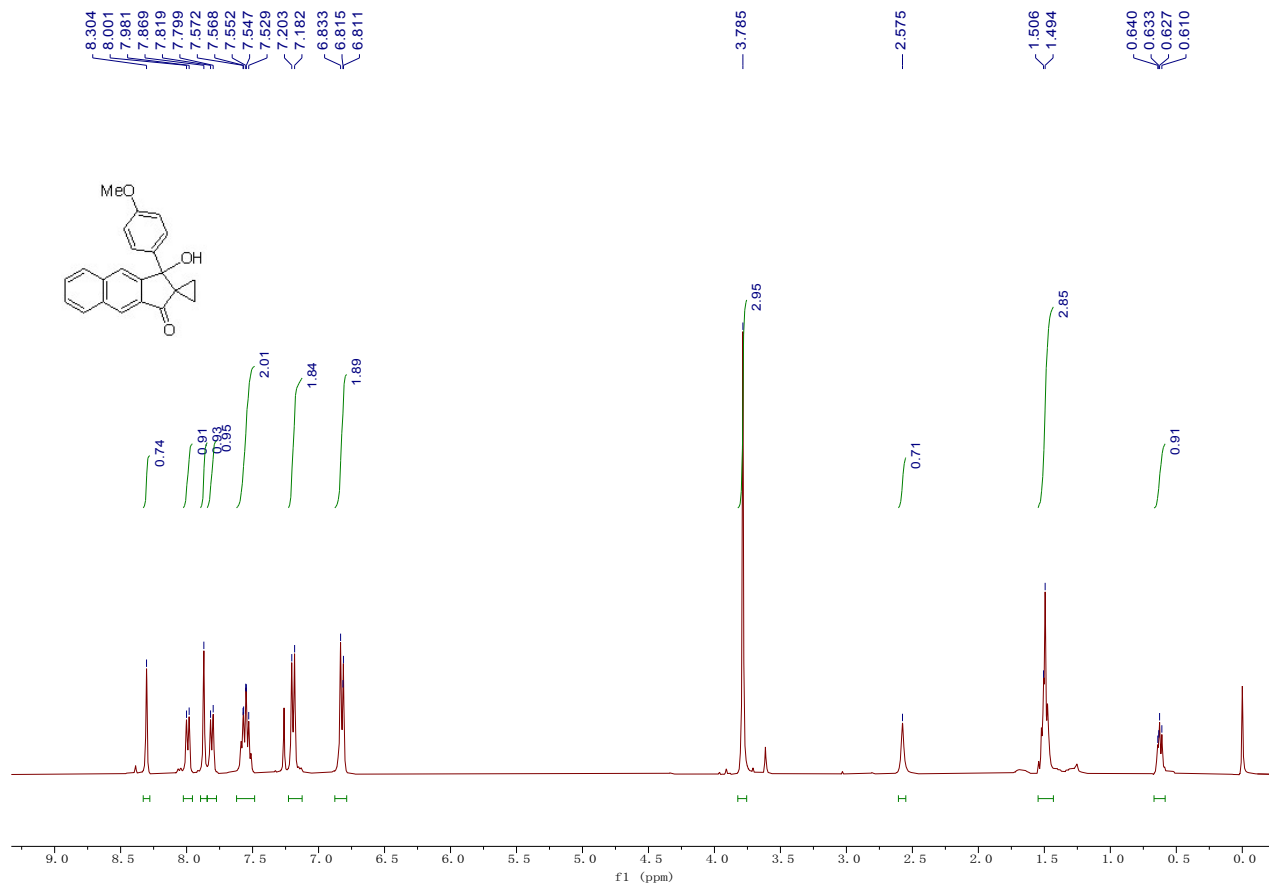


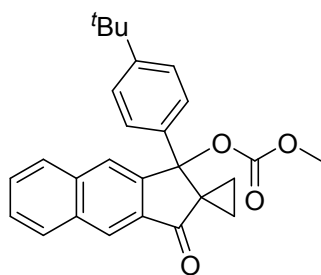
Compound 2v: Yield: 73.7 mg, 99%; A white solid; Mp: 170 - 172 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 8.10 – 8.03 (m, 1H), 7.90 – 7.80 (m, 2H), 7.62 – 7.51 (m, 2H), 7.25 – 7.15 (m, 1H), 7.15 – 7.03 (m, 2H), 7.03 – 6.93 (m, 1H), 3.62 (s, 3H), 2.31 (s, 3H), 1.78 – 1.67 (m, 1H), 1.49 – 1.39 (m, 1H), 1.38 – 1.27 (m, 1H), 0.60 – 0.49 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.0, 153.2, 147.3, 140.9, 137.9, 136.6, 135.1, 133.6, 130.4, 128.8, 128.5, 128.1, 127.2, 126.2, 125.2, 123.0, 122.7, 88.5, 54.5, 41.9, 22.3, 21.5, 16.3; IR (neat): ν 1752, 1718, 1278, 1261, 763 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 395.1254, found: 395.1258.



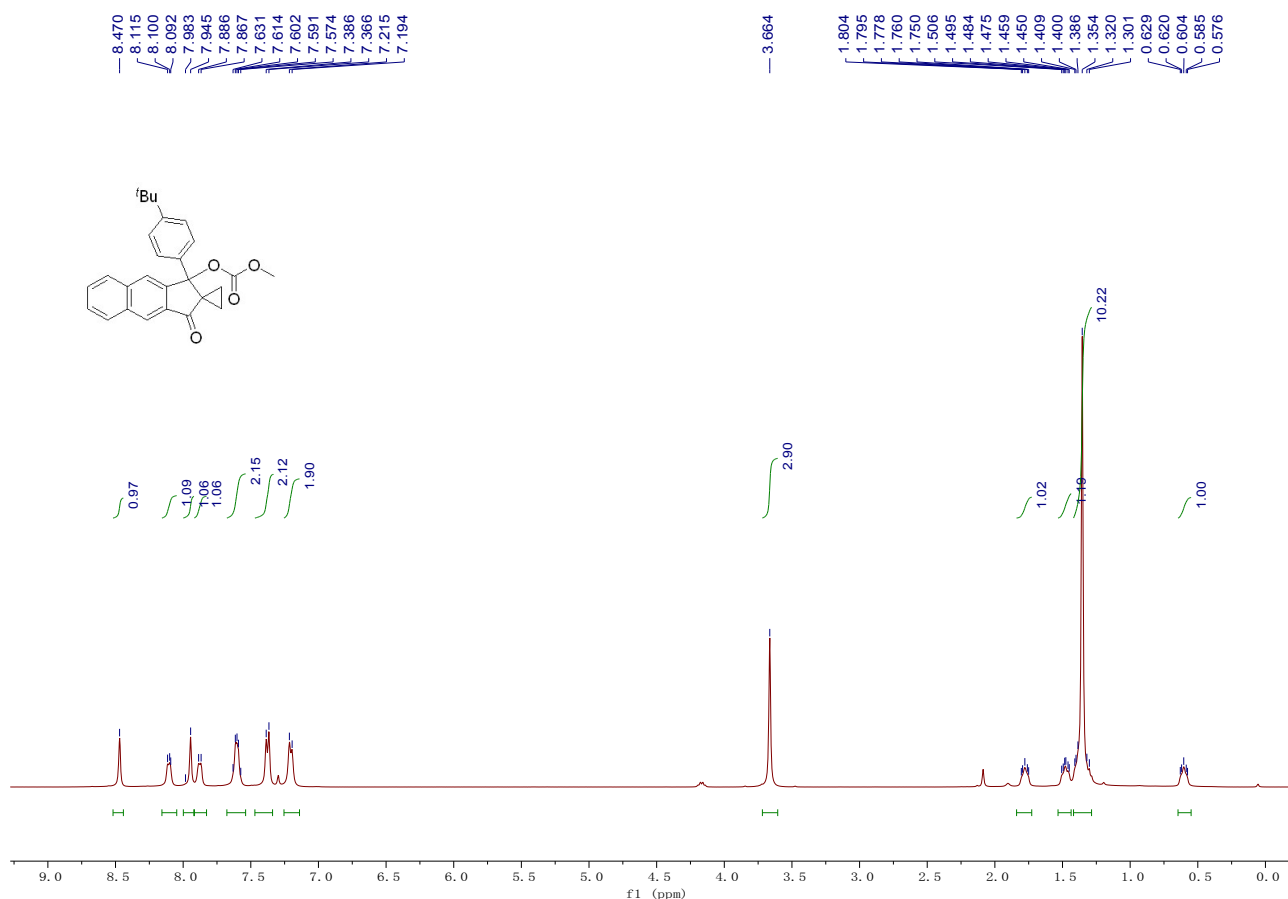


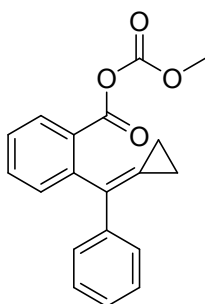
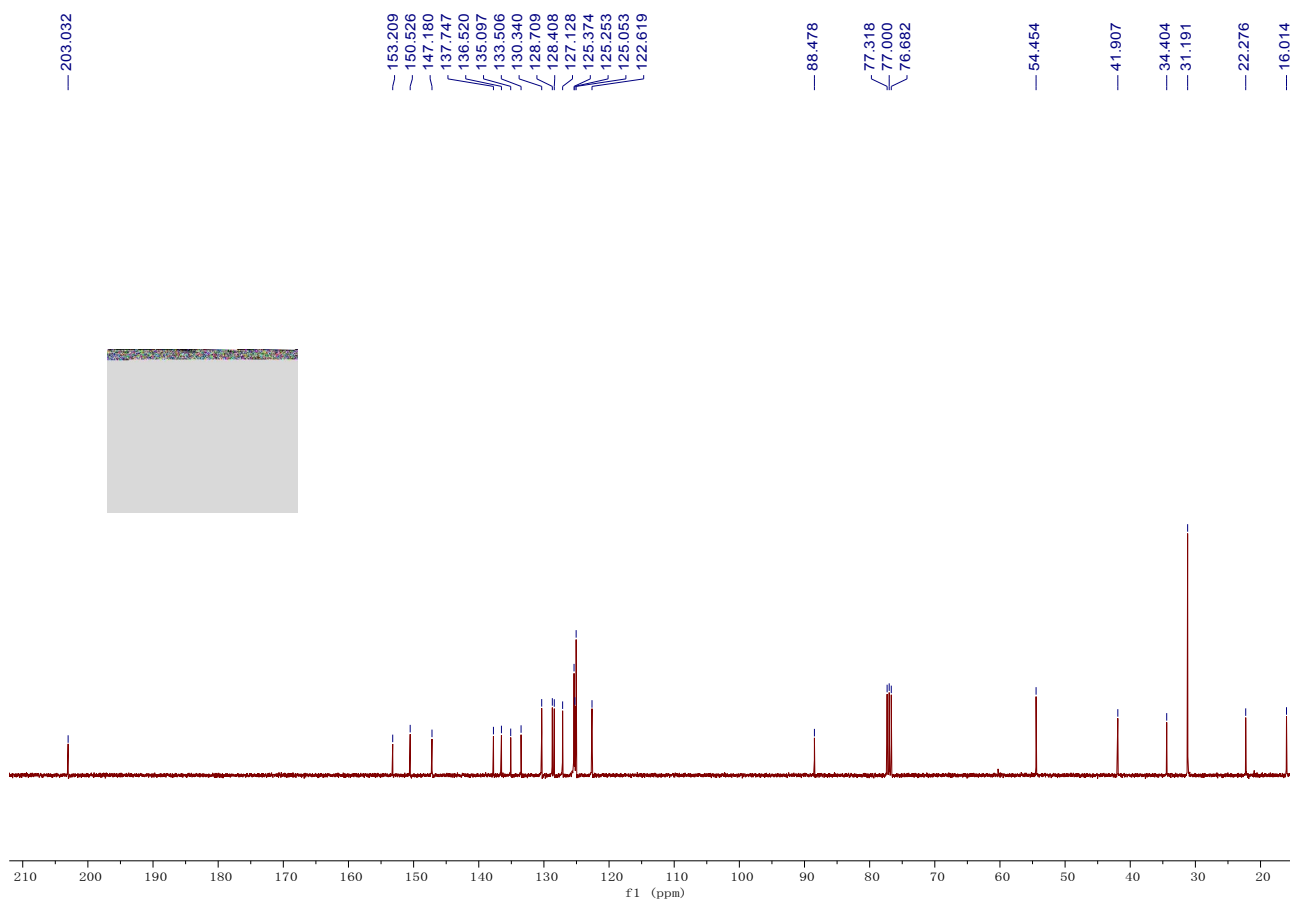
Compound 2w': Yield: 59.4 mg, 90%; A white solid; Mp: 147 - 149 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 7.99 (d, $J = 7.9$ Hz, 1H), 7.87 (s, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.62 – 7.48 (m, 2H), 7.23 – 7.12 (m, 2H), 6.88 – 6.79 (m, 2H), 3.78 (s, 3H), 2.58 (br, s, 1H), 1.55 – 1.43 (m, 3H), 0.67 – 0.58 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.7, 158.6, 152.6, 137.1, 136.0, 133.3, 130.4, 128.63, 128.56, 127.1, 127.0, 124.3, 123.1, 113.6, 113.4, 79.5, 55.2, 44.8, 20.5, 17.4; IR (neat): ν 3327, 1682, 1626, 1244, 1161 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 353.1148, found: 353.1144.



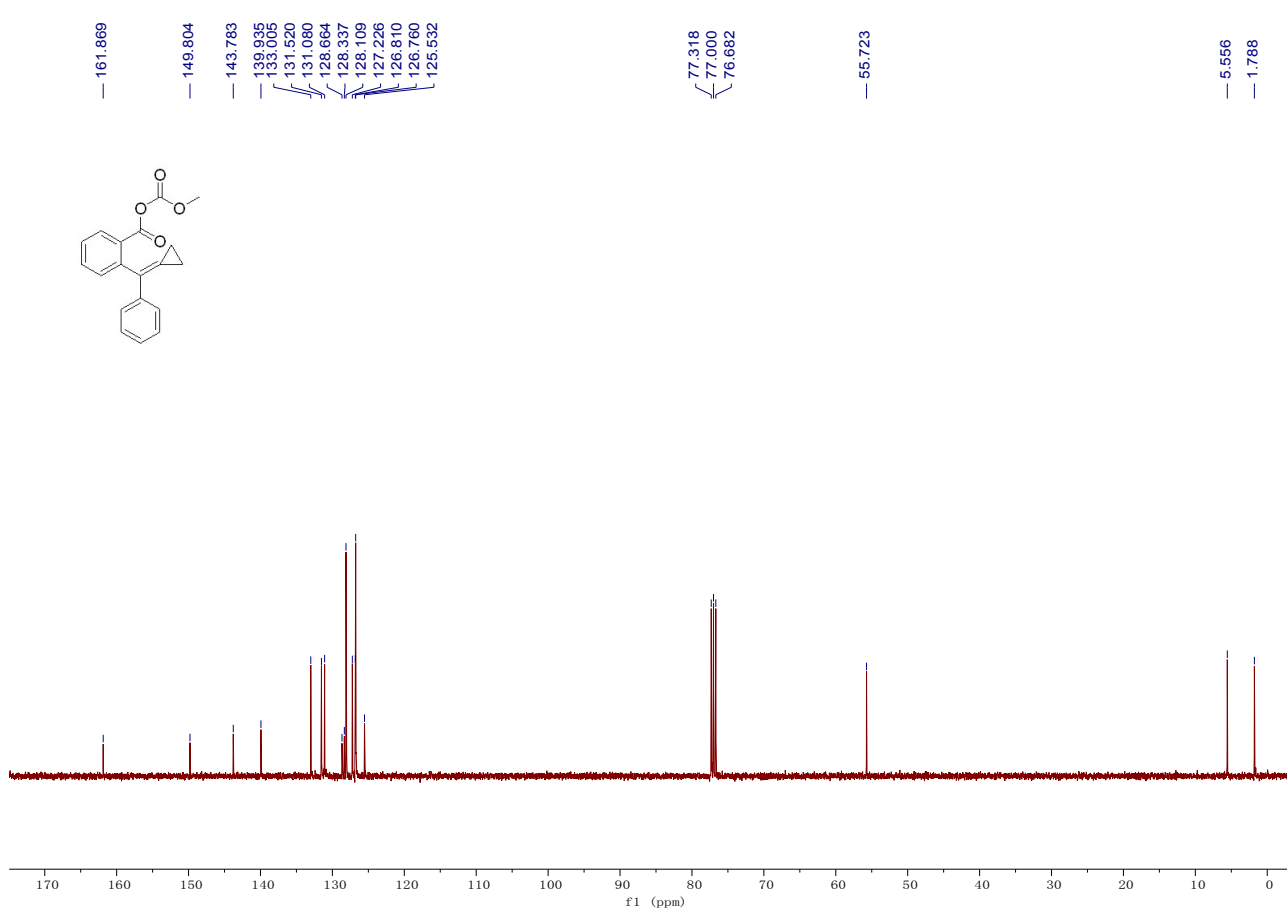
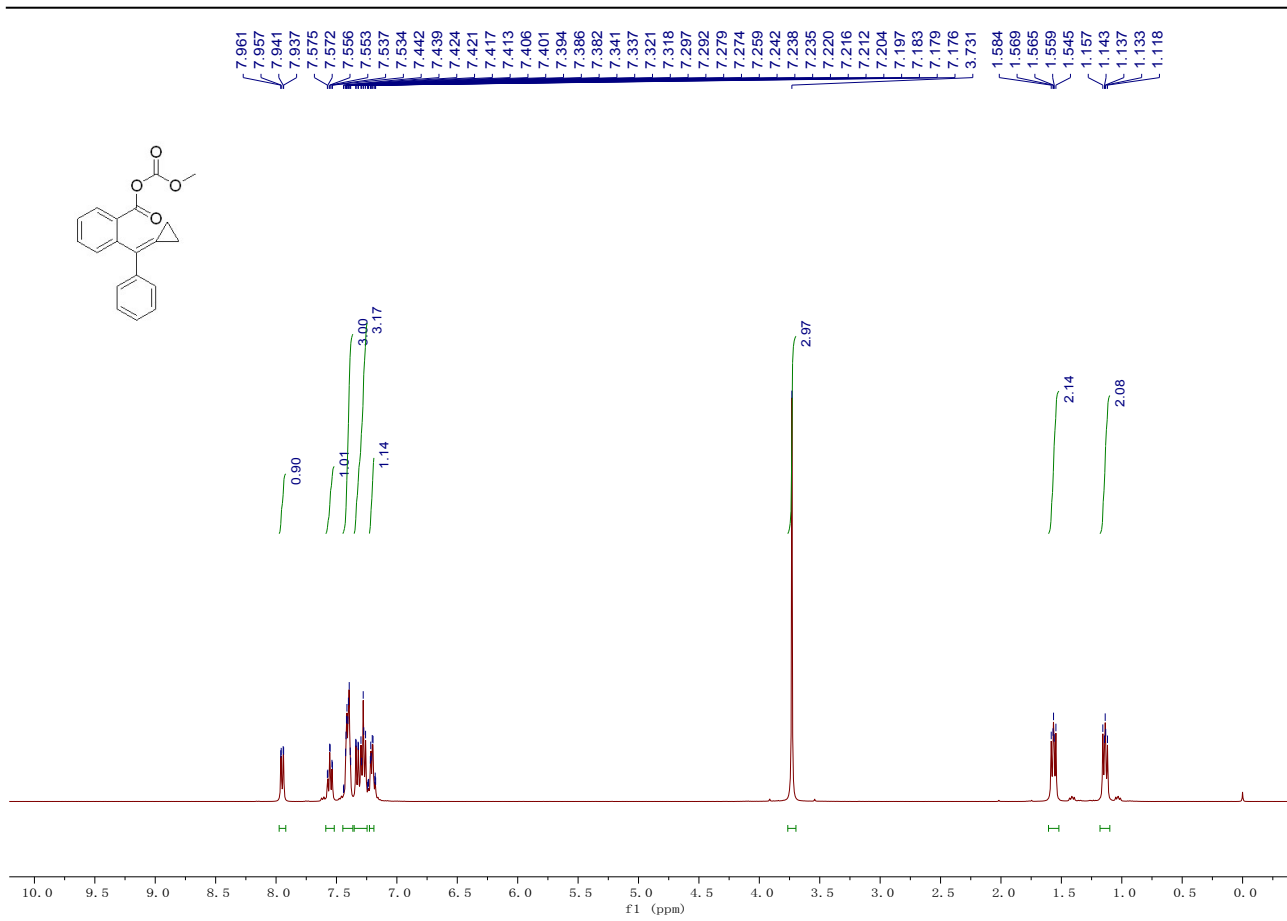


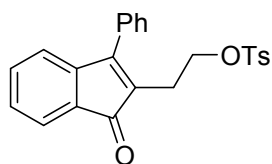
Compound 2x: Yield: 78.7 mg, 95%; A white solid; Mp: > 200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.16 – 8.05 (m, 1H), 7.94 (s, 1H), 7.92 – 7.83 (m, 1H), 7.68 – 7.54 (m, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 3.66 (s, 3H), 1.84 – 1.73 (m, 1H), 1.53 – 1.44 (m, 1H), 1.42 – 1.29 (m, 10H), 0.65 – 0.55 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.0, 153.2, 150.5, 147.2, 137.7, 136.5, 135.1, 133.5, 130.3, 128.7, 128.4, 127.1, 125.4, 125.3, 125.1, 122.6, 88.5, 54.5, 41.9, 34.4, 31.2, 22.3, 16.0; IR (neat): ν 1759, 1719, 1263, 1208, 889 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{27}\text{H}_{26}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 437.1723, found: 437.1722.



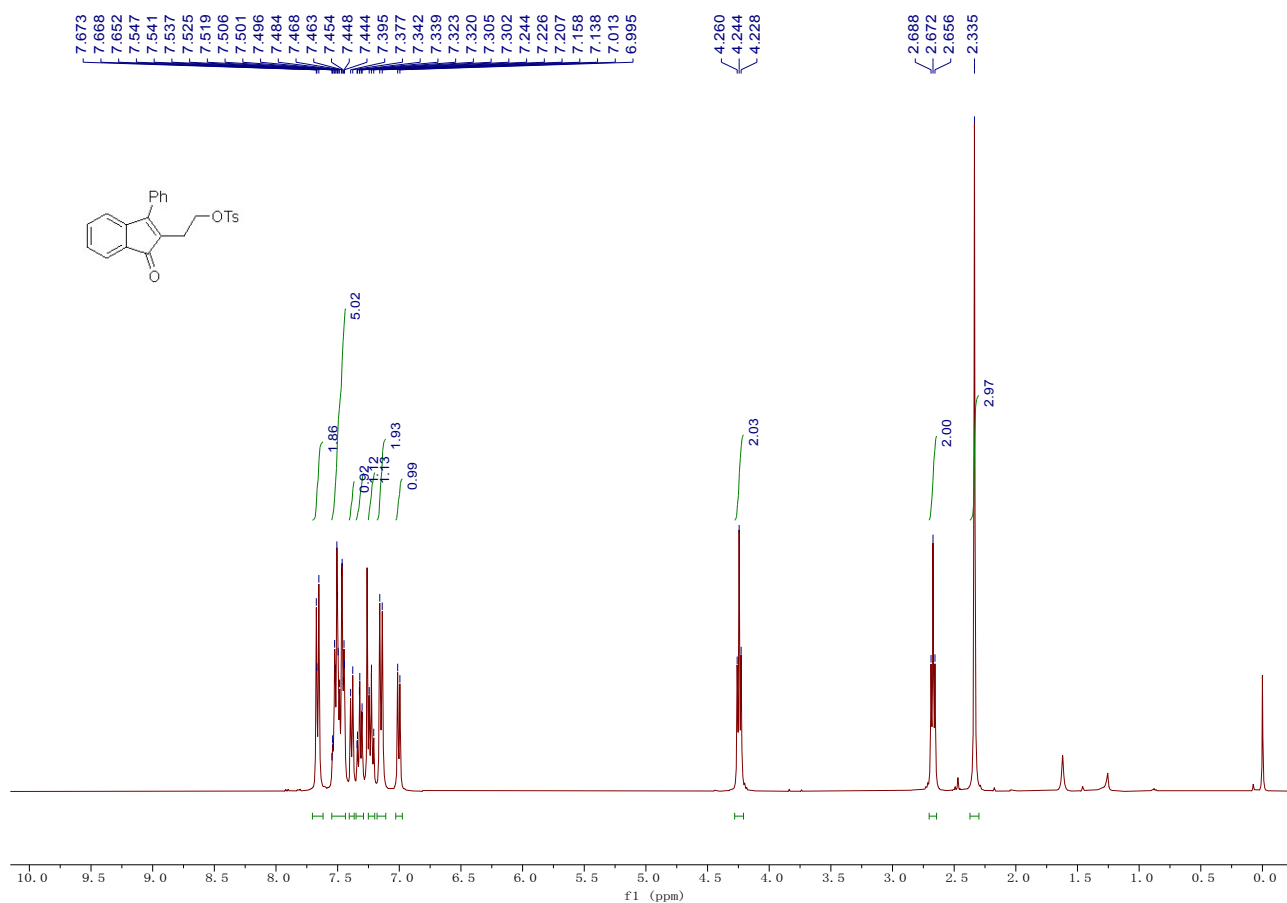


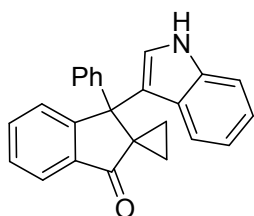
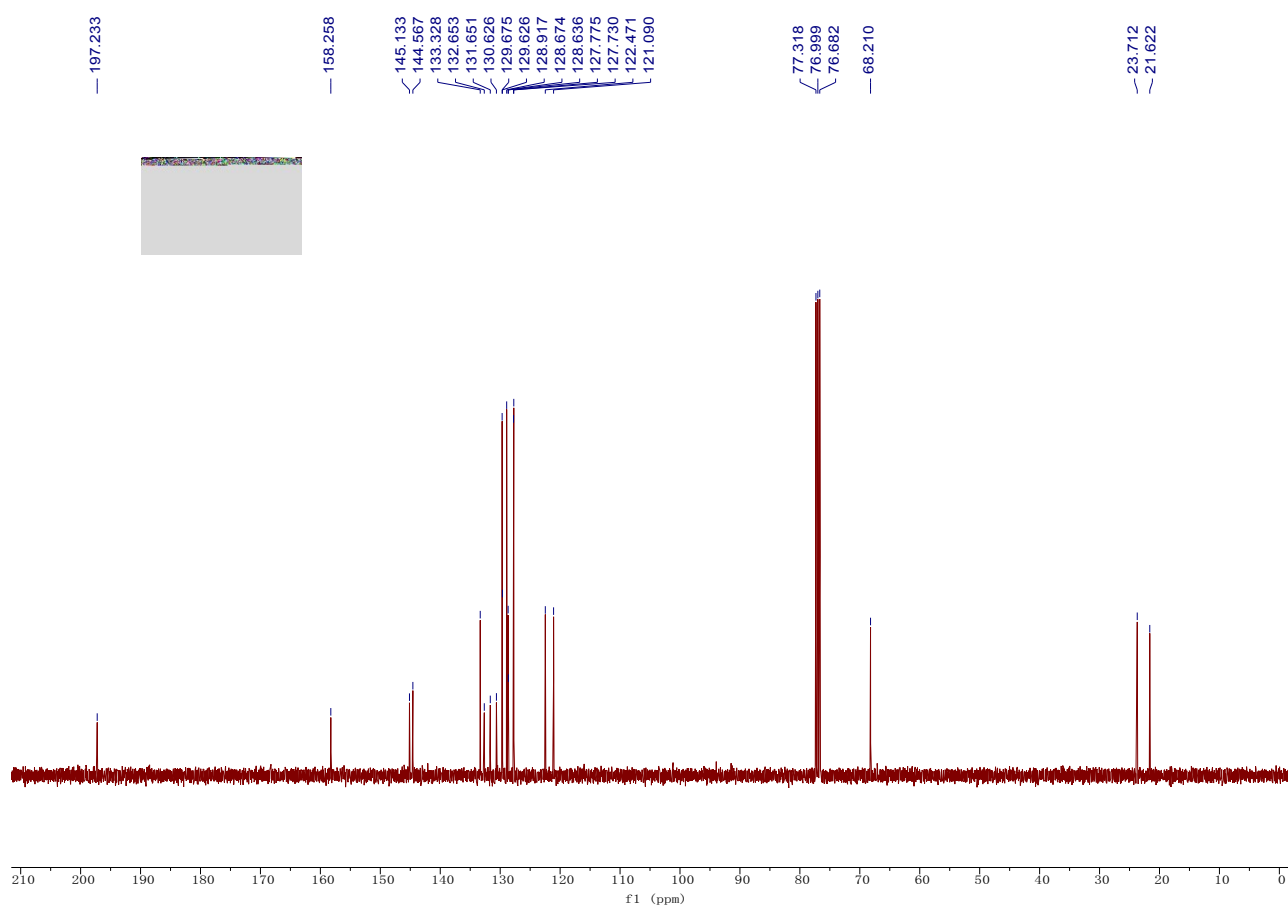
Compound 3: Yield: 0.54 g, 90%; A white solid; Mp: 84 - 86 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.95 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.55 (td, $J = 7.6, 1.4$ Hz, 1H), 7.45 – 7.36 (m, 3H), 7.35 – 7.25 (m, 3H), 7.23 – 7.19 (m, 1H), 3.73 (s, 3H), 1.61 – 1.52 (m, 2H), 1.18 – 1.10 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.9, 149.8, 143.8, 139.9, 133.0, 131.5, 131.1, 128.7, 128.3, 128.1, 127.2, 126.81, 126.76, 125.5, 55.7, 5.6, 1.8; IR (neat): ν 2980, 1756, 1727, 1616, 759 cm^{-1} ; HRMS (FI) Calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_4$ $[\text{M}]^+$: 308.1043, found: 308.1048.



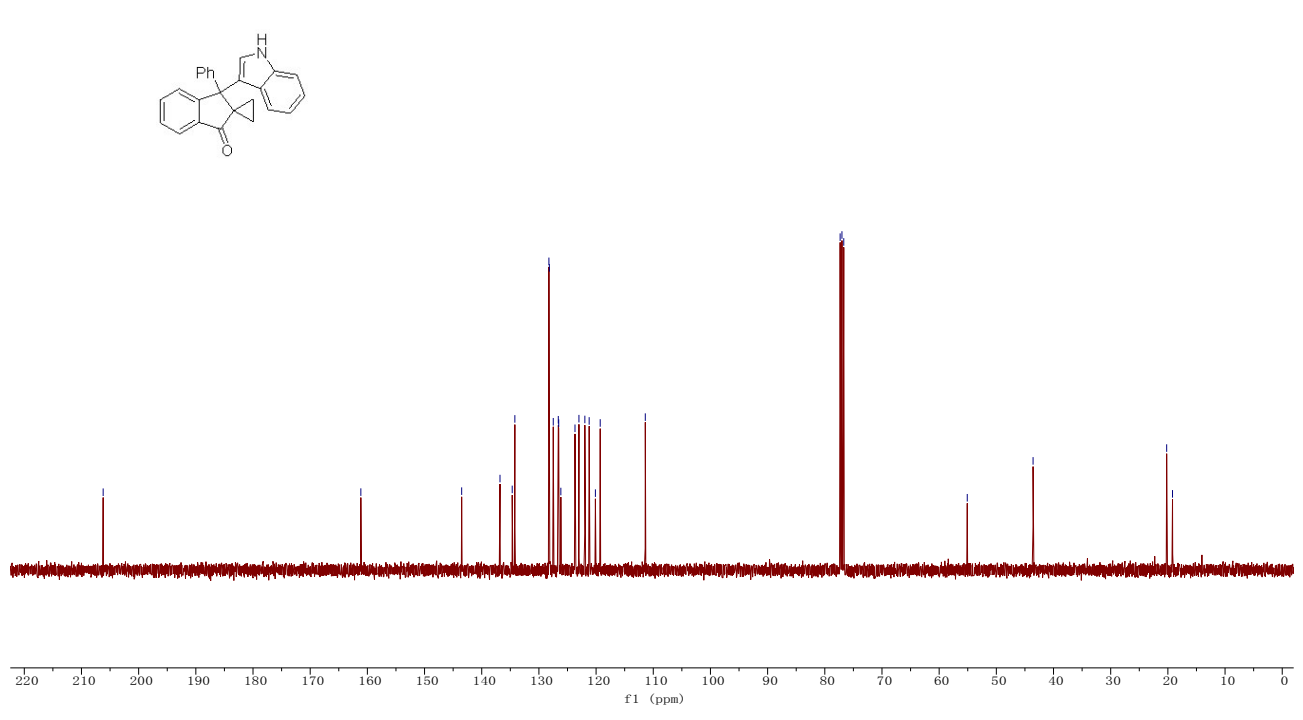
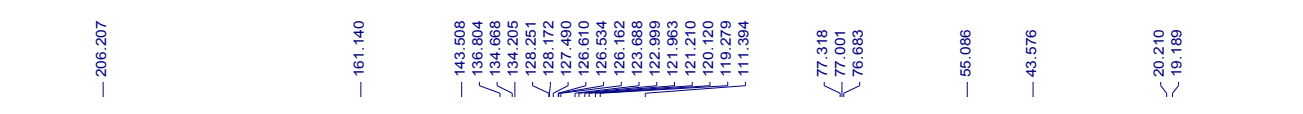
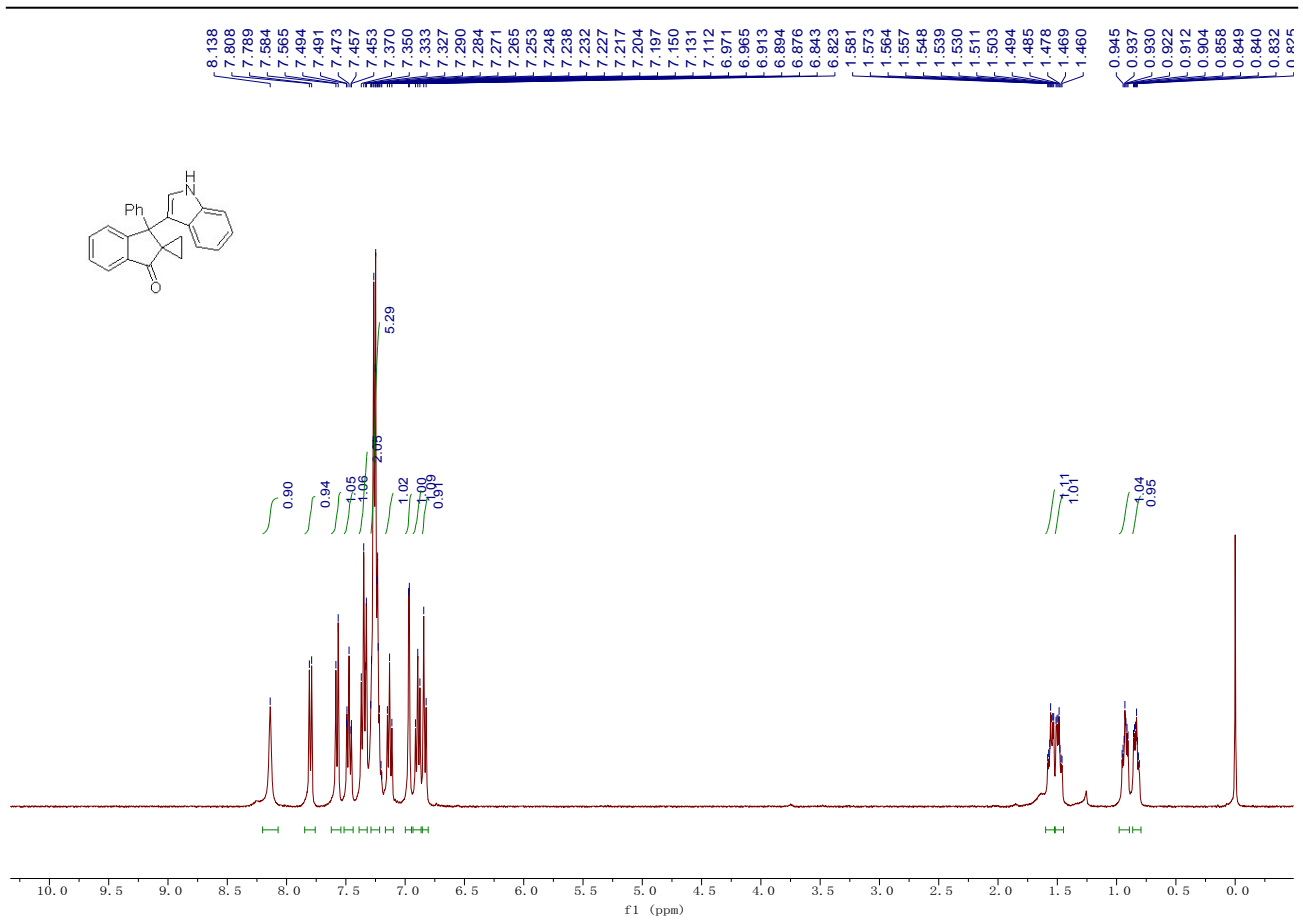


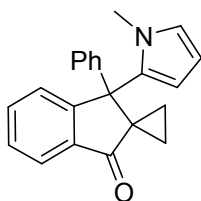
Compound 7: Yield: 64.6 mg, 80%; A white solid; Mp: 171 - 173 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, J = 8.3 Hz, 2H), 7.55 – 7.44 (m, 5H), 7.39 (d, J = 7.0 Hz, 1H), 7.32 (td, J = 7.5, 1.3 Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 7.2 Hz, 1H), 4.24 (t, J = 6.4 Hz, 2H), 2.67 (t, J = 6.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.2, 158.3, 145.1, 144.6, 133.3, 132.7, 131.7, 130.6, 129.7, 129.6, 128.9, 128.7, 128.6, 127.8, 127.7, 122.5, 121.1, 68.2, 23.7, 21.6; IR (neat): ν 2997, 2848, 1752, 1619, 750 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{24}\text{H}_{21}\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 405.1155, found: 405.1153.



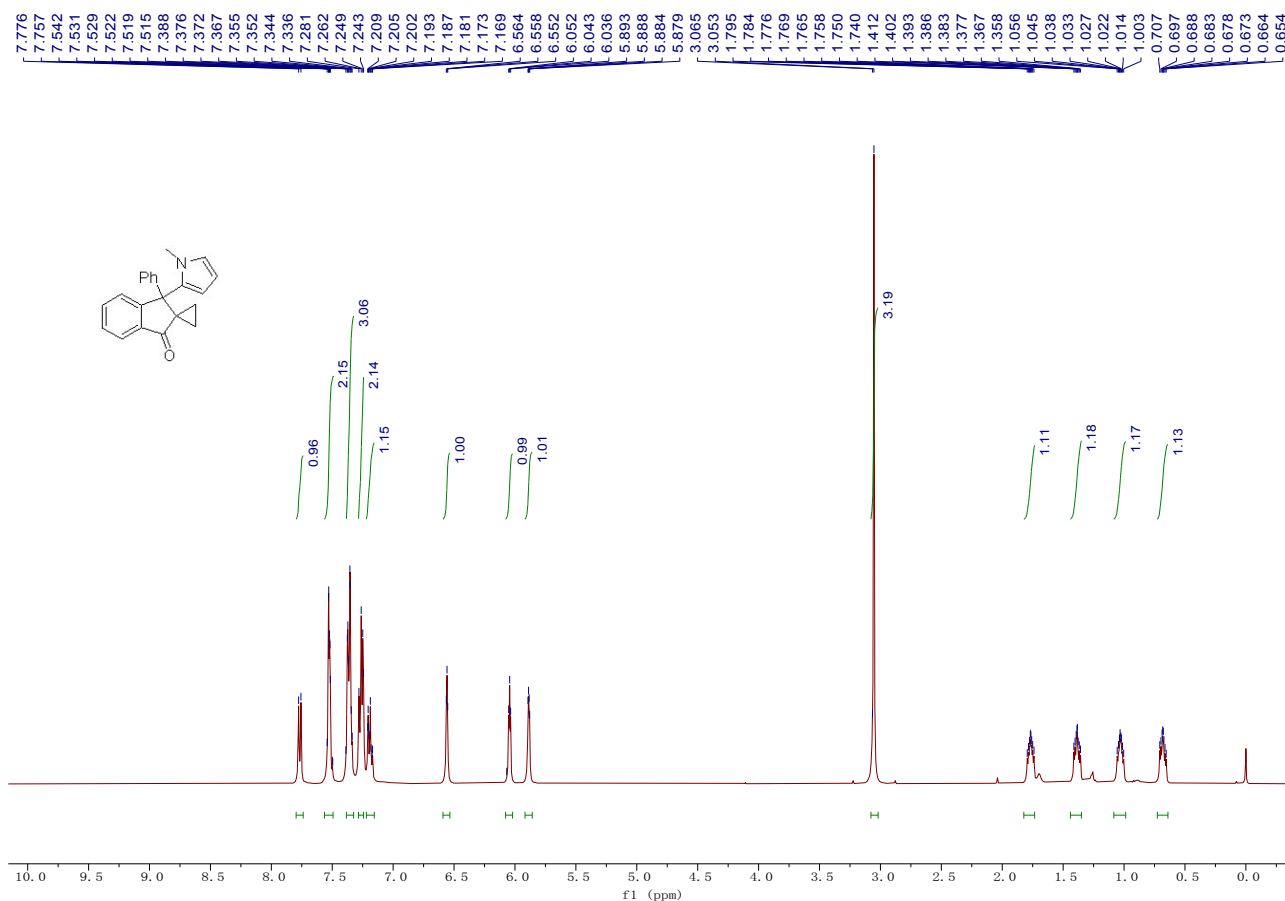


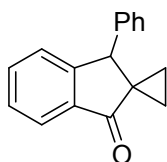
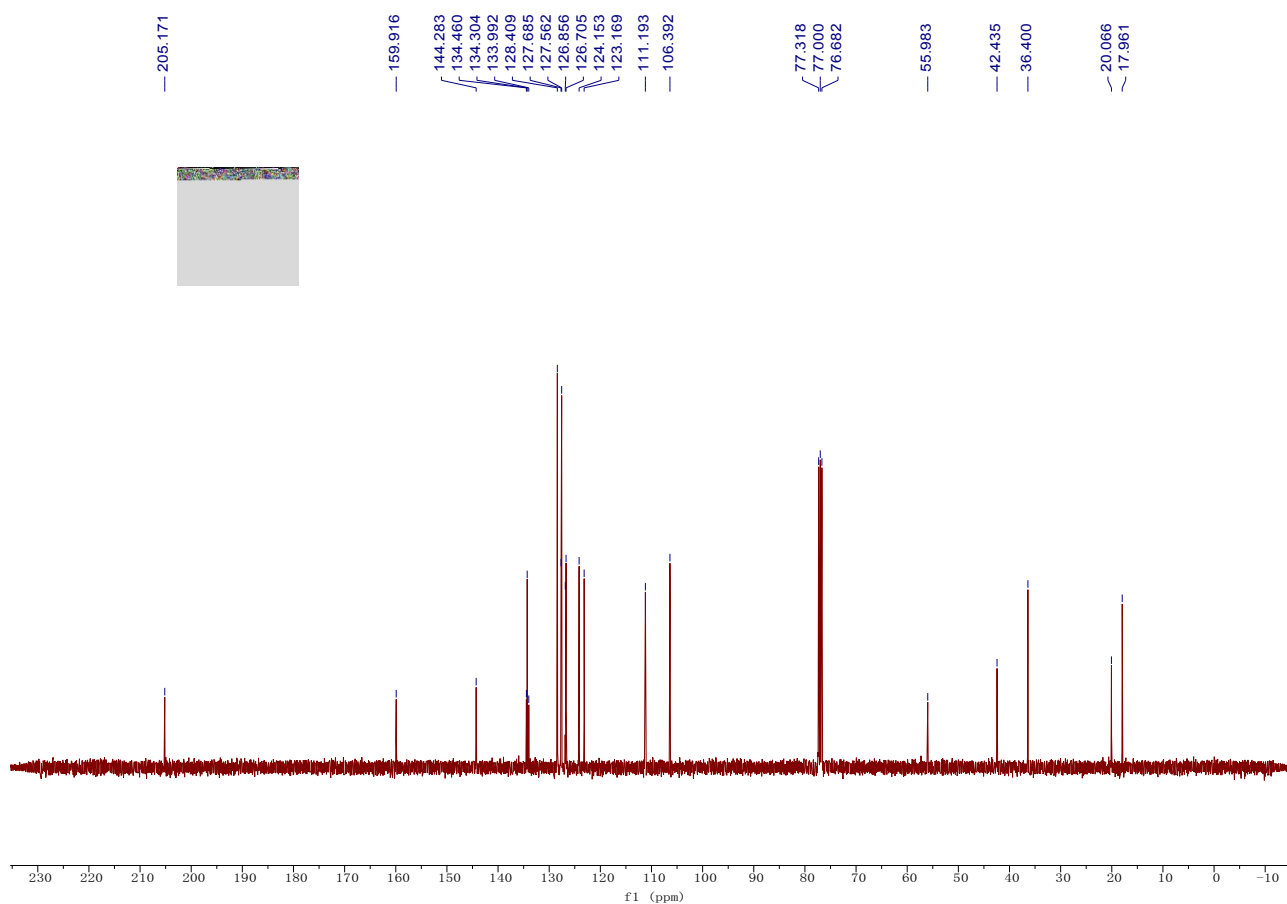
Compound 5: Yield: 48.2 mg, 69%; A white solid; Mp: > 200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.80 (d, $J = 7.6$ Hz, 1H), 7.57 (d, $J = 7.8$ Hz, 1H), 7.52 – 7.44 (m, 1H), 7.39 – 7.32 (m, 2H), 7.29 – 7.22 (m, 5H), 7.17 – 7.10 (m, 1H), 7.00 – 6.95 (m, 1H), 6.89 (t, $J = 7.5$ Hz, 1H), 6.83 (d, $J = 8.1$ Hz, 1H), 1.60 – 1.52 (m, 1H), 1.52 – 1.45 (m, 1H), 0.98 – 0.89 (m, 1H), 0.86 – 0.79 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.2, 161.1, 143.5, 136.8, 134.7, 134.2, 128.3, 128.2, 127.5, 126.6, 126.5, 126.2, 123.7, 123.0, 122.0, 121.2, 120.1, 119.3, 111.4, 55.1, 43.6, 20.2, 19.2; IR (neat): ν 2980, 2872, 1735, 1620, 755 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{25}\text{H}_{20}\text{ON}$ $[\text{M}+\text{H}]^+$: 350.1539, found: 350.1538.



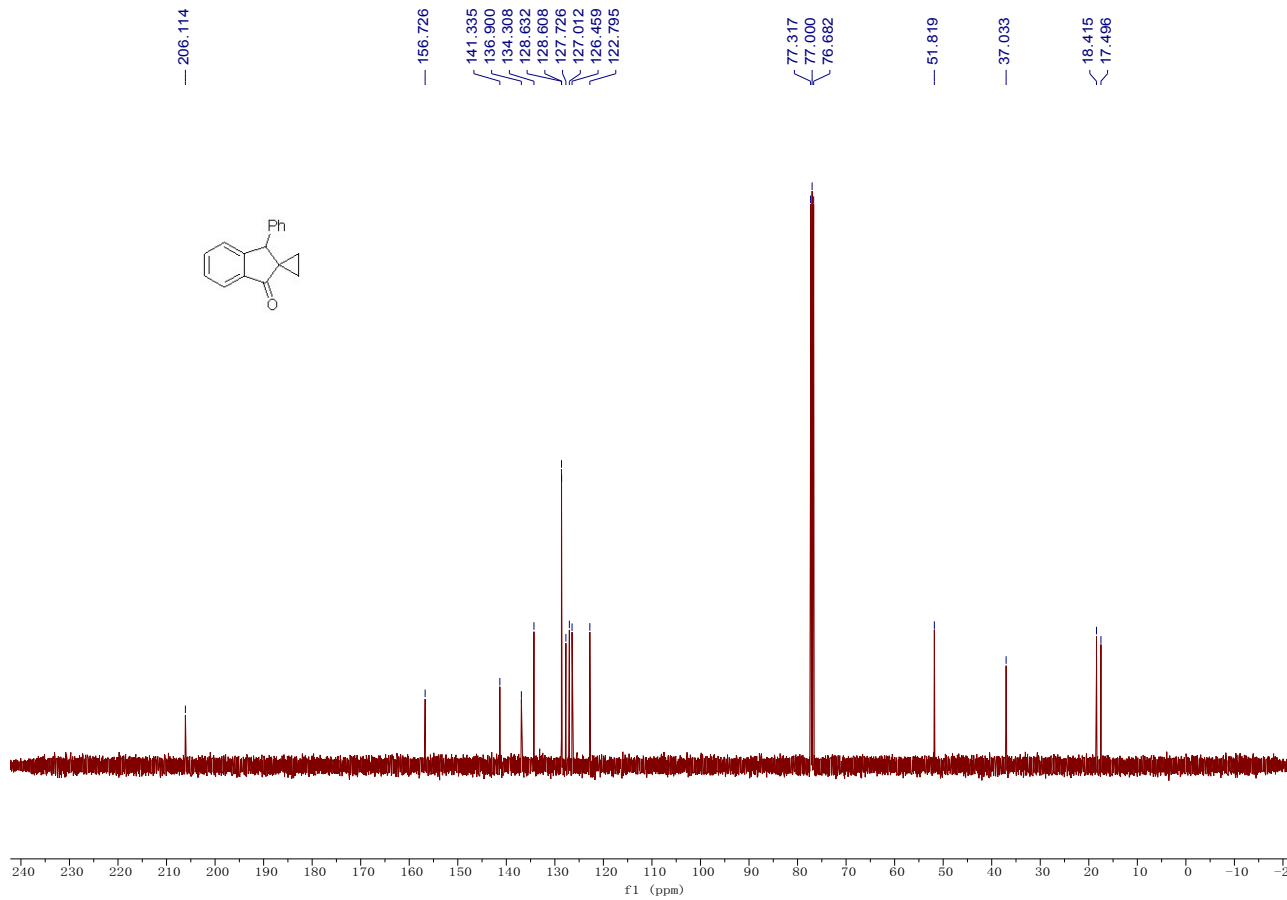
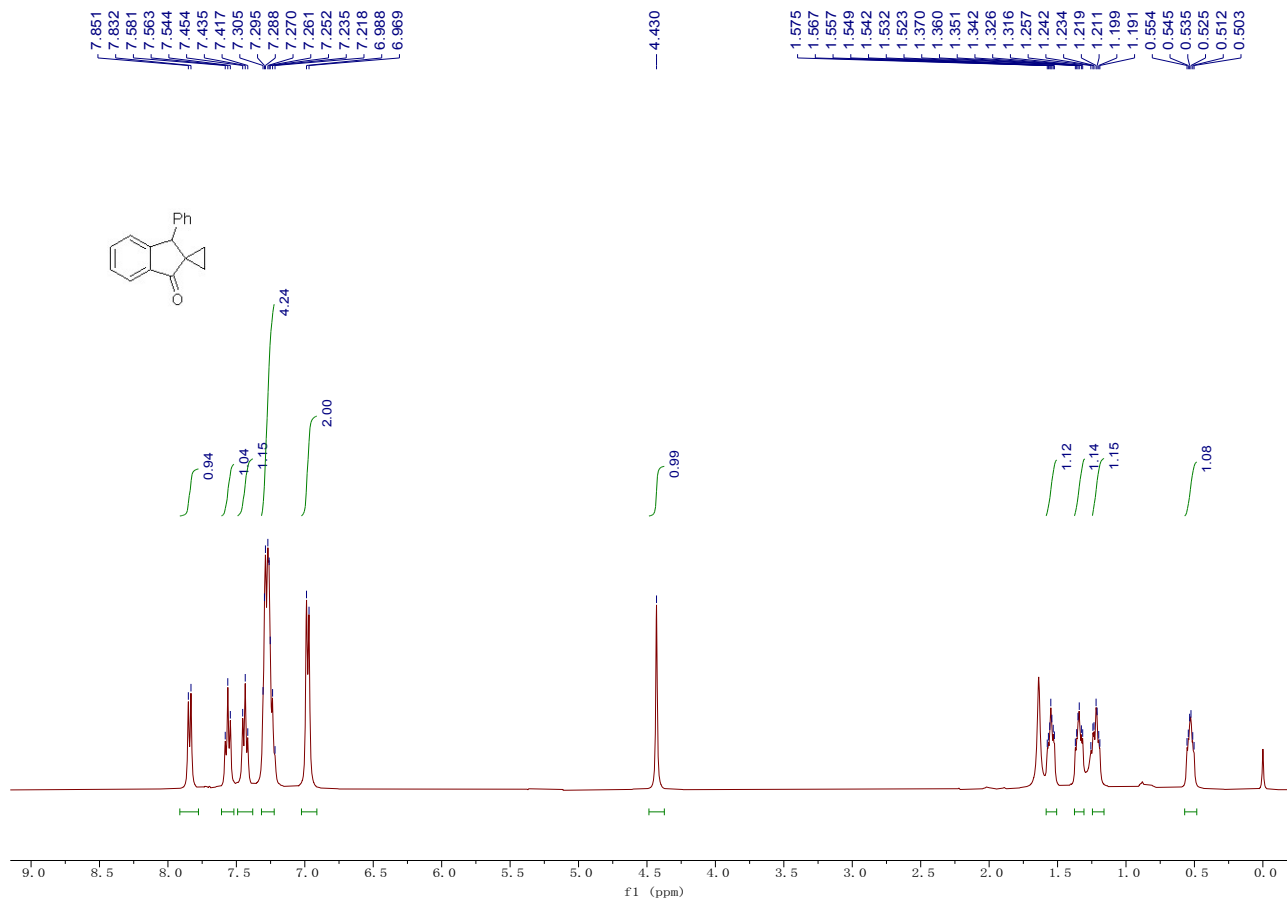


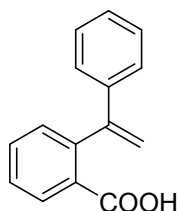
Compound 6: Yield: 25.0 mg, 40%; A white solid; Mp: > 200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, $J = 7.6$ Hz, 1H), 7.56 – 7.49 (m, 2H), 7.38 – 7.32 (m, 3H), 7.28 – 7.24 (m, 2H), 7.22 – 7.15 (m, 1H), 6.59 – 6.53 (m, 1H), 6.08 – 6.02 (m, 1H), 5.92 – 5.86 (m, 1H), 3.05 (s, 3H), 1.82 – 1.73 (m, 1H), 1.44 – 1.35 (m, 1H), 1.08 – 0.99 (m, 1H), 0.73 – 0.64 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.1, 159.9, 144.2, 134.4, 134.3, 133.9, 128.4, 127.6, 127.5, 126.8, 126.7, 124.1, 123.1, 111.1, 106.3, 55.9, 42.4, 36.4, 20.0, 17.9; IR (neat): ν 2989, 2875, 1753, 1625, 755 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{20}\text{ON}$ $[\text{M}+\text{H}]^+$: 314.1539, found: 314.1539.



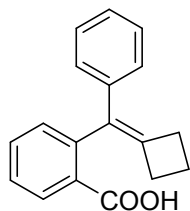
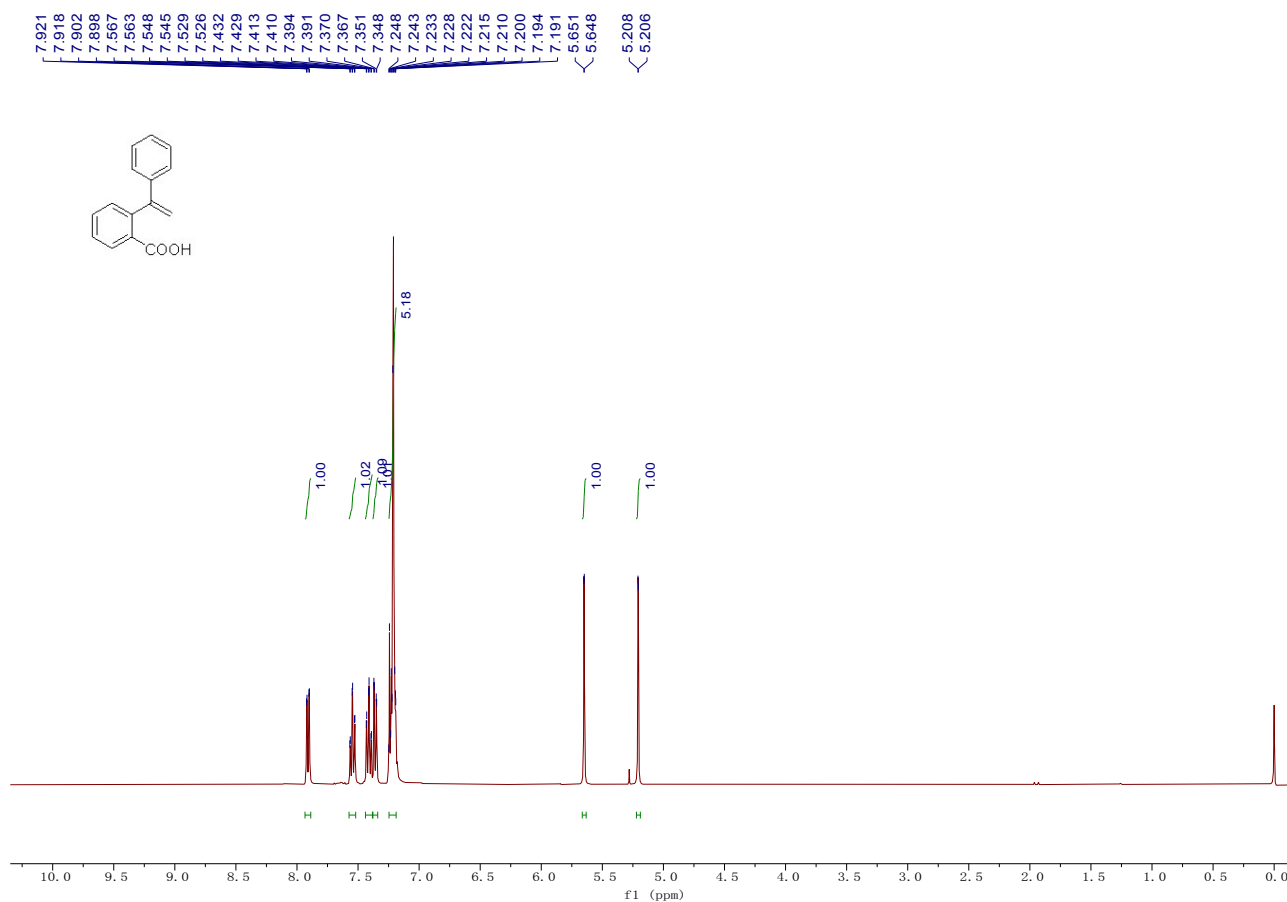


Compound 8: Yield: 31.4 mg, 67%; A white solid; Mp: 67 - 69 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 7.4$ Hz, 1H), 7.31 – 7.23 (m, 4H), 7.03 – 6.92 (m, 2H), 4.43 (s, 1H), 1.58 – 1.51 (m, 1H), 1.38 – 1.31 (m, 1H), 1.24 – 1.18 (m, 1H), 0.56 – 0.49 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.1, 156.7, 141.3, 136.9, 134.3, 128.63, 128.61, 127.7, 127.0, 126.5, 122.8, 51.8, 37.0, 18.4, 17.5; IR (neat): ν 1756, 1616, 1449, 1280, 888 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}$ $[\text{M}]^+$: 234.1039, found: 234.1040.



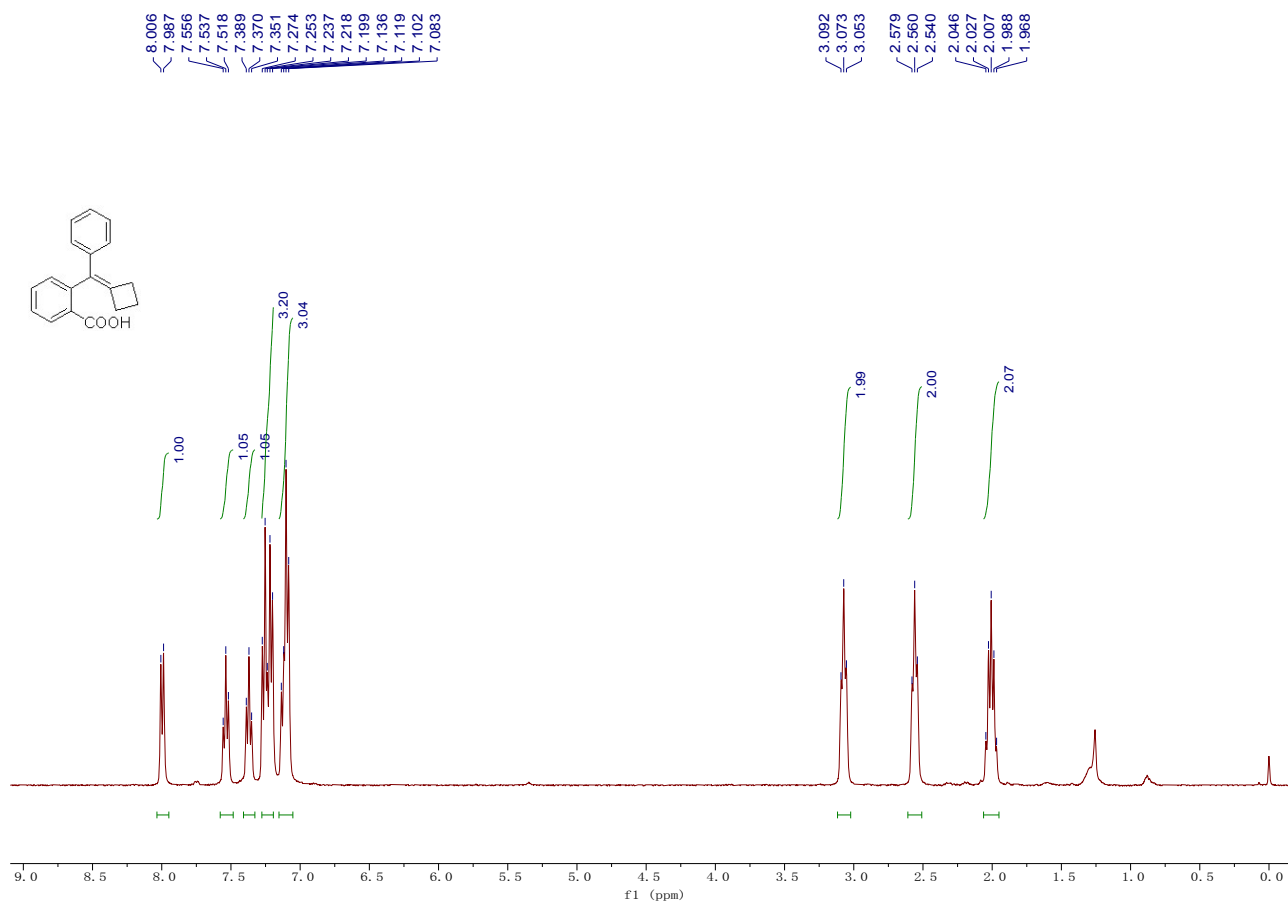


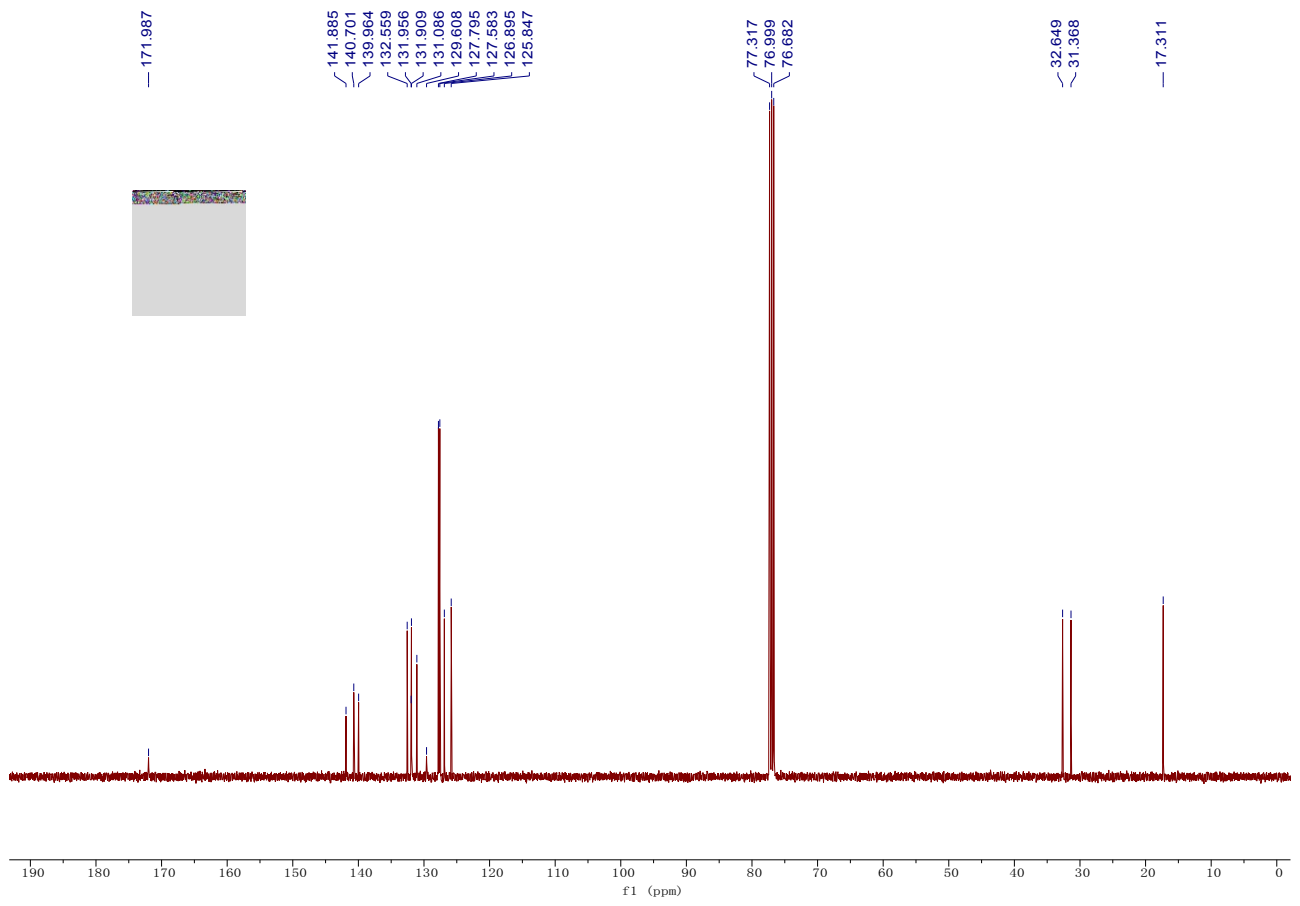
Compound 4:³ yield: 2.0 g, 80%; A white solid; Mp: 130 - 131 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.55 (td, $J = 7.5, 1.4$ Hz, 1H), 7.41 (td, $J = 7.6, 1.3$ Hz, 1H), 7.36 (dd, $J = 7.6, 1.3$ Hz, 1H), 7.25 – 7.19 (m, 5H), 5.65 (d, $J = 1.1$ Hz, 1H), 5.21 (d, $J = 1.1$ Hz, 1H).



Compound 9: Yield: 0.2 g, 89%; A white solid; Mp: 160 - 162 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, $J = 7.8$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.7$ Hz, 1H), 7.28 – 7.19 (m, 3H), 7.15 – 7.05 (m, 3H), 3.07 (t, $J = 7.9$ Hz, 2H), 2.56 (t, $J = 7.8$ Hz, 2H), 2.01 (p, $J = 7.7$

Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.0, 141.9, 140.7, 140.0, 132.6, 132.0, 131.9, 131.1, 129.6, 127.8, 127.6, 126.9, 125.8, 32.6, 31.4, 17.3; IR (neat): ν 2919, 1671, 1595, 1289, 1258, 706, 694 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{15}\text{O}_2$ $[\text{M}-\text{H}]^-$: 263.1067, found: 263.1066.





8. References

1. B. Suchand and G. Satyanarayana, *J. Org. Chem.*, 2016, **81**, 6409-6423.
2. D. Chen, I. A. Berhane and S. R. Chemler, *Org. Lett.*, 2020, **22**, 7409-7414.
3. S. Song, S. Zhu, Y. Yu and Q. Zhou, *Angew. Chem. Int. Ed.*, 2012, **52**, 1556-1559.