Electronic supplementary information

Rh(III)-Catalyzed C-H Activation/Regiospecific Annulation Cascade of Benzoic acids with Propargyl Acetates to Unusual 3-Alkylidene-Isochromanones

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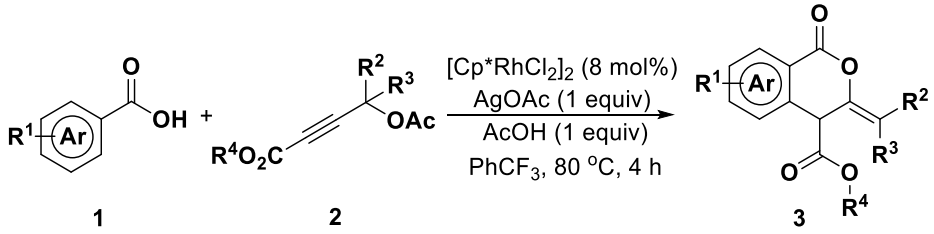
1. General information

The reagents (chemicals) were purchased from commercial sources, and used without further purification. Analytical thin layer chromatography (TLC) was HSGF 254 (0.15-0.2 mm thickness). Column chromatography was performed using silica gel FCP 300-400. All products were characterized by their NMR and MS spectra. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz, 500 MHz or 600 MHz instrument. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane (TMS). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd). High-resolution mass spectra (HRMS) were measured on Micromass Ultra Q-TOF spectrometer or Thermo DFS double-focusing spectrometer.

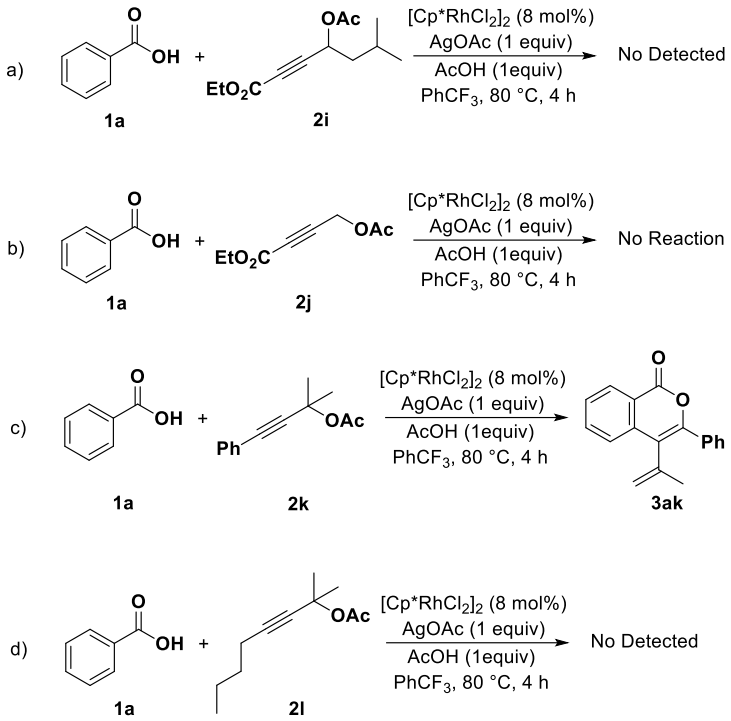
2. General procedures



1 2 3

To a 25 mL of Schlenk tube were sequentially added benzoic acid **1** (0.2 mmol), 4-acetoxy-2-alkynoates **2** (0.3 mmol), $[Cp^*RhCl_2]_2$ (8.0 mol%), AgOAc (1.0 equiv), AcOH (1.0 equiv) and 2 mL triflorotoluene ($PhCF_3$). The mixture was sealed under argon and stirred at 80 ℃ for 4 h. After the reaction was completed, dichloromethane (DCM) 10 mL was added and the mixture was filtered through a pad of Celite which was subsequently washed with DCM. The combined organic phase was concentrated under reduced pressure, and the residue was purified by a silica gel column chromatography (PE/EA = 5:1) to afford the desired product **3**.

3. Substrate scope of propargyl acetates



Scheme S1. Substrate scope of propargyl acetates.

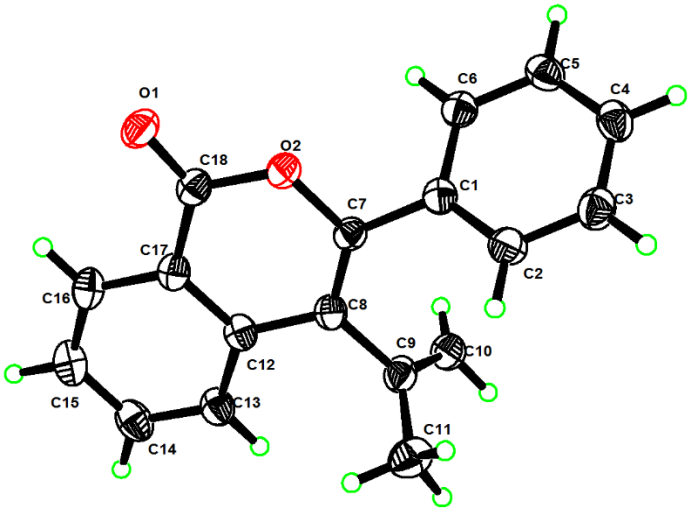


Figure S1. X-ray crystallography of compound **3ak**.

To a 25 mL of Schlenk tube were sequentially added benzoic acid **1** (0.2 mmol), ethyl 4-acetoxy-6-methylhept-2-ynoate **2i** (0.3 mmol), $[Cp^*RhCl_2]_2$ (8.0 mol%), AgOAc (1.0 equiv), AcOH (1.0 equiv) and 2 mL triflorotoluene ($PhCF_3$). The mixture was sealed under argon and stirred at 80 °C for 4 h. After the reaction was completed, there was no obvious major product could be detected by TLC and LC-MS analysis (Scheme S1a).

To a 25 mL of Schlenk tube were sequentially added benzoic acid **1** (0.2 mmol), ethyl

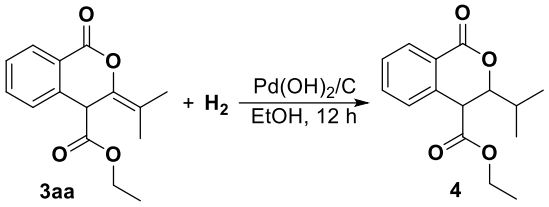
4-acetoxybut-2-ynoate **2j** (0.3 mmol), $[Cp^*RhCl_2]_2$ (8.0 mol%), AgOAc (1.0 equiv), AcOH (1.0 equiv) and 2 mL triflorotoluene ($PhCF_3$). The mixture was sealed under argon and stirred at 80 ℃ for 4 h. After the reaction was completed, no reaction took place and the substrates remained intact (Scheme S1b).

To a 25 mL of Schlenk tube were sequentially added benzoic acid **1** (0.2 mmol), 2-methyl-4-phenylbut-3-yn-2-yl acetate **2k** (0.3 mmol), $[Cp^*RhCl_2]_2$ (8.0 mol%), AgOAc (1.0 equiv), AcOH (1.0 equiv) and 2 mL triflorotoluene ($PhCF_3$). The mixture was sealed under argon and stirred at 80 ℃ for 4 h. After the reaction was completed, 10 mL DCM was added and the mixture was filtered through a pad of Celite which was subsequently washed with DCM. The combined organic phase was concentrated under reduced pressure, and the residue was purified by a silica gel column chromatography (PE/EA = 10:1) to afford the **3ak** with 19% yield (10.3 mg, Scheme S1c). The structure was confirmed by X-ray crystallography (Figure S1).

To a 25 mL of Schlenk tube were sequentially added benzoic acid **1** (0.2 mmol), 2-methyl-4-phenylbut-3-yn-2-yl acetate **2k** (0.3 mmol), $[Cp^*RhCl_2]_2$ (8.0 mol%), AgOAc (1.0 equiv), AcOH (1.0 equiv) and 2 mL triflorotoluene ($PhCF_3$). The mixture was sealed under argon and stirred at 80 ℃ for 4 h. After the reaction was completed, we did not detected a major product and the substrates were remained (Figure S1).

4. Synthetic transformation

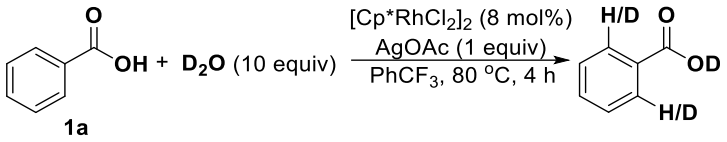
Ethyl 3-isopropyl-1-oxoisochromane-4-carboxylate (4)



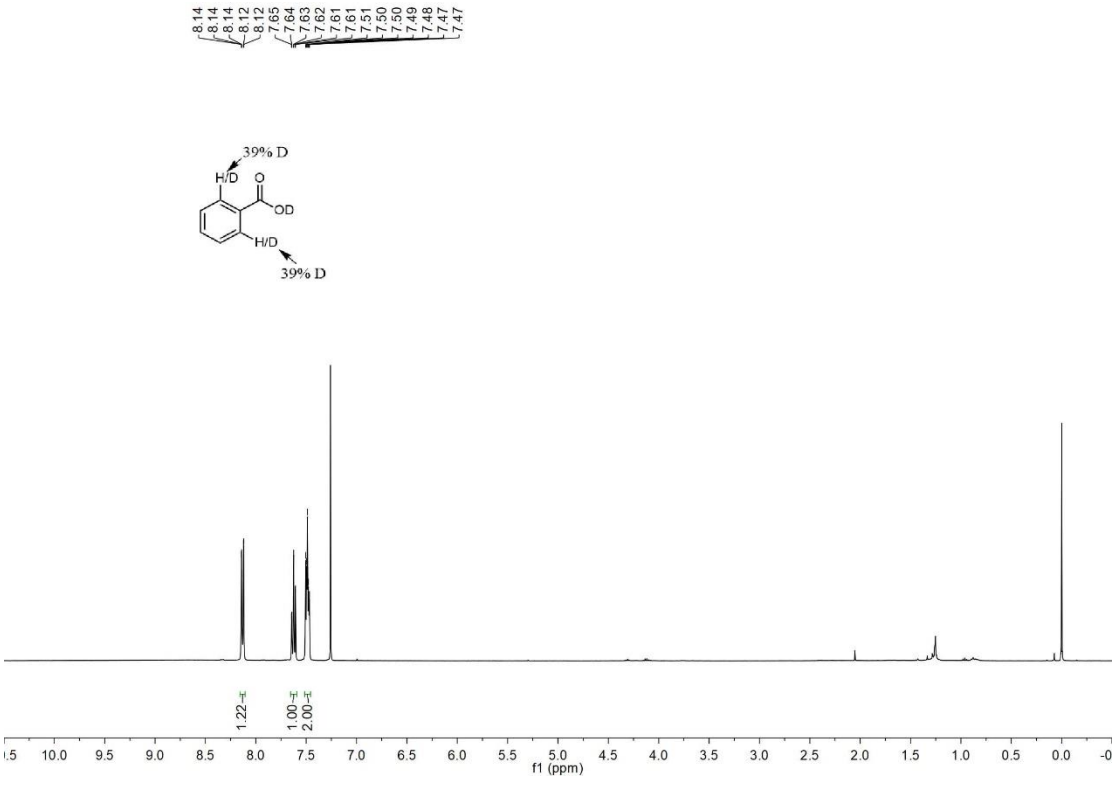
To a solution of **3aa** (100.0 mg, 0.38 mmol) in methanol (10 mL) was added Palladium hydroxide (20% on carbon). This system was evacuated and refilled with hydrogen then stirred at room temperature overnight. After the reaction was completed, dichloromethane (DCM) 10 mL was added and the mixture was filtered through a pad of Celite which was subsequently washed with DCM. The solvent was removed under vacuum and the resulting residue was purified by a silica gel column chromatography with 20% EtOAc in PE as the solvent to afford **4** in 93% yield (92.7 mg).

5. Mechanistic investigations

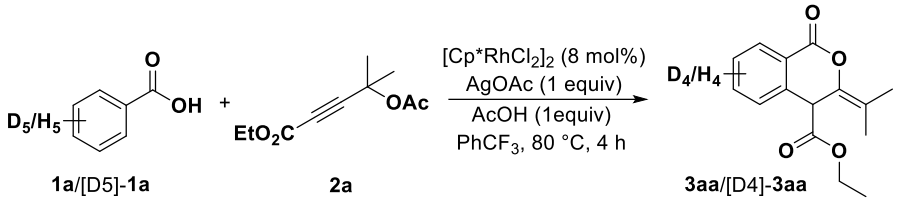
5.1 H/D Exchange Experiment



A mixture of **1a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (8 mol%), AgOAc (1.0 equiv), AcOH (1.0 equiv) and D_2O (10.0 equiv) was added into a 25 mL of Schlenk tube. The mixture was sealed under argon and stirred at 80 °C for 4 h. Afterward, the mixture was diluted with DCM and filtered through a pad of Celite, which was washed with DCM. The combined organic phase was concentrated in vacuo to yield the crude product which was further purified by silica gel column chromatography eluting with PE/EA = 50:1 to afford the deuterium product as a colorless oil. H/D exchange occurred at the C2-position of benzoic acid (39% D).

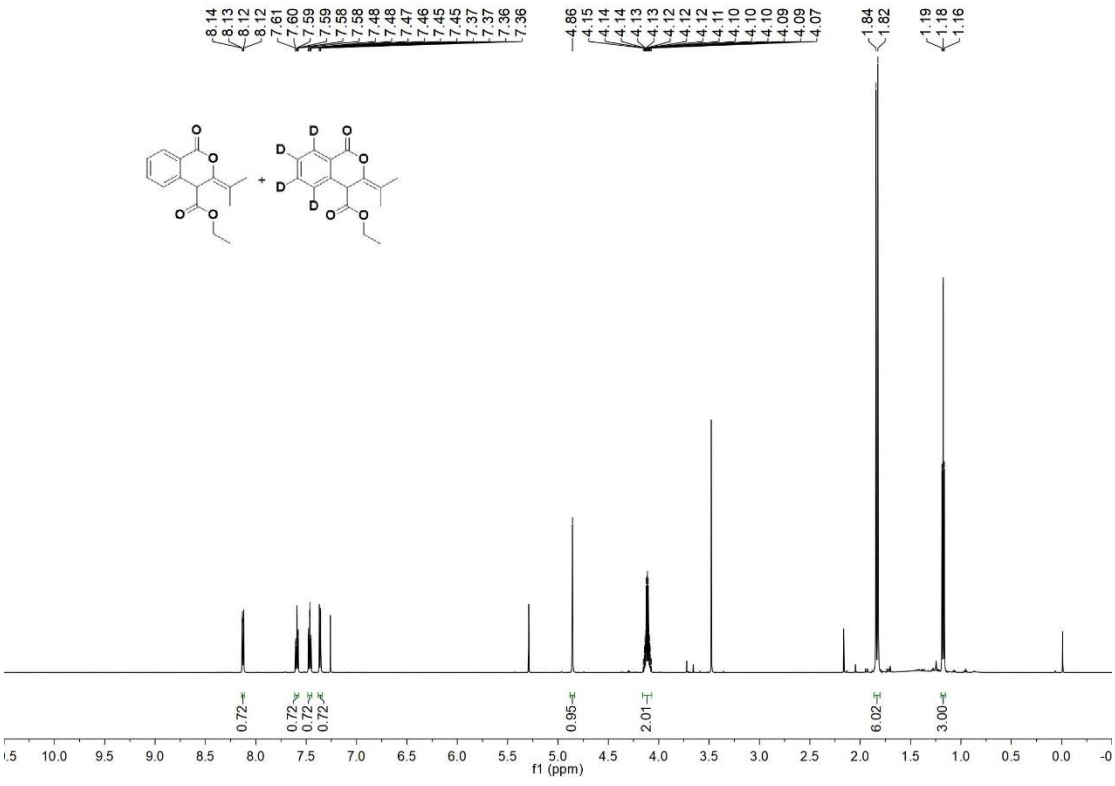


5.2 KIE Experiment



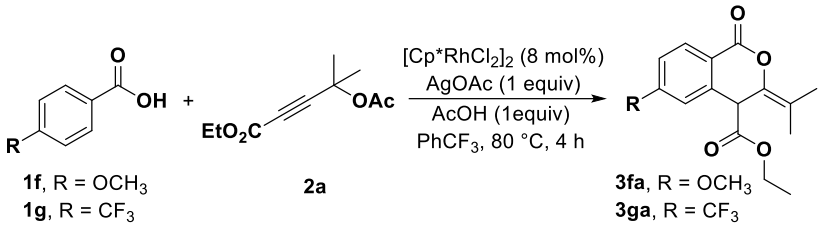
1a/[D5]-**1a** **2a** **3aa**/[D4]-**3aa**

Compounds **1a** (0.2 mmol) and [D_5]-**1a** (0.2 mmol) were added to a mixture of [Cp*$RhCl_2$]$_2$ (8 mol%), AgOAc (1.0 equiv), AcOH (1 equiv) and **2a** (0.2 mmol) in $PhCF_3$ (4.0 mL). The resulting mixture was stirred at 80 ^oC for 1 h. Then the reaction was stopped and filtered through a pad of Celite which was subsequently washed with DCM and the combined organic phase was concentrated under reduced pressure. The mixture of **3aa** and [D_4]-**3aa** was isolated by silica gel column chromatography eluting with PE/EA from 30:1 to 20:1. The KIE value was determined by ^1H NMR.



K_H/K_D = 2.57

5.3 Competition Experiment



To a 25 mL of Schlenk tube were added **1f** (0.2 mmol), **1g** (0.2 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (8.0 mol%), AgOAc (1.0 equiv), AcOH (1.0 equiv) and 4.0 mL triflorotoluene ($PhCF_3$). The mixture was sealed under argon and stirred at 80 ℃ for 1 h. After the reaction was completed, dichloromethane (DCM) 10 mL was added and the mixture was filtered through a pad of Celite which was subsequently washed with DCM. The combined organic phase was concentrated under reduced pressure, and the residue was purified by a silica gel column chromatography (PE/EA = 5:1) to afford the desired product **3fa** (32.3 mg, 56%) and **3ga** (25.5 mg, 39%), **1fa**/**1ga** = 1.44.

6. Characterization of compounds

Ethyl 1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3aa)

Light yellow oil (91% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.60 (td, *J* = 7.6, 1.4 Hz, 1H), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H), 7.38 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.87 (s, 1H), 4.17 – 4.07 (m, 2H), 1.84 (d, *J* = 8.1 Hz, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.9, 162.4, 136.8, 135.8, 134.1, 130.3, 128.7, 127.4, 124.4, 117.5, 62.0, 45.0, 18.4, 17.2, 13.9; HRMS (ESI) m/z: calcd. for $C_{15}H_{17}O_4^+$ [M + H] $^+$: 261.1121, found: 261.1118

Ethyl 6-fluoro-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3ba)

Light yellow oil (93% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 8.7, 5.6 Hz, 1H), 7.16 (td, *J* = 8.5, 2.5 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.84 (s, 1H), 4.14 (qd, *J* = 7.2, 1.9 Hz, 2H), 1.84 (d, *J* = 9.9 Hz, 6H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.4, 165.9 (d, *J* = 257.1 Hz), 161.4, 138.6 (d, *J* = 9.2 Hz), 136.4, 133.3 (d, *J* = 9.7 Hz), 120.8 (d, *J* = 3.0 Hz), 118.2, 116.4 (d, *J* = 22.0 Hz), 114.4 (d, *J* = 22.8 Hz), 62.3, 45.0, 18.4, 17.2, 13.9; HRMS (ESI) m/z: calcd. for $C_{15}H_{14}FO_4^-$ [M − H] $^-$: 277.0882, found: 277.0882

Ethyl 6-chloro-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3ca)

White solid (86% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.45 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 4.82 (s, 1H), 4.14 (qq, *J* = 7.0, 3.7 Hz, 2H), 1.84 (d, *J* = 8.6 Hz, 6H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.9, 161.1, 140.0, 136.9, 135.9, 131.3, 128.8, 127.1, 122.5, 117.9, 61.8, 44.3, 18.0, 16.8, 13.5; HRMS (ESI) m/z: calcd. for $C_{15}H_{16}ClO_4^+$ [M + H] $^+$, 295.0732; found, 295.0725.

Ethyl 6-bromo-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3da)

White solid (87% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.61 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 4.81 (s, 1H), 4.19 – 4.09 (m,

2H), 1.83 (d, *J* = 8.5 Hz, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.9, 161.3, 137.0, 135.9, 131.8, 131.3, 130.0, 128.6, 122.9, 117.9, 61.8, 44.2, 18.0, 16.8, 13.5; HRMS (ESI) m/z: calcd. for $C_{15}H_{16}BrO_4^+$ [M + H] $^+$, 339.0226; found, 339.0217.

Ethyl 6-methyl-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3ea)

Light yellow oil (78% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.17 (s, 1H), 4.81 (s, 1H), 4.17 – 4.07 (m, 2H), 2.43 (s, 3H), 1.83 (d, *J* = 8.4 Hz, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.0, 162.5, 145.2, 137.0, 135.7, 130.3, 129.7, 127.9, 121.8, 117.3, 62.0, 45.0, 21.8, 18.4, 17.2, 14.0; HRMS (EI) m/z: calcd. for $C_{16}H_{18}O_4^+$ $[M]^+$, 274.1200; found, 274.1197.

Ethyl 6-methoxy-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3fa)

Light yellow oil (84% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.7 Hz, 1H), 6.96 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.83 (d, *J* = 2.5 Hz, 1H), 4.81 (s, 1H), 4.17 – 4.08 (m, 2H), 3.88 (s, 3H), 1.83 (d, *J* = 9.4 Hz, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.4, 163.6, 161.8, 137.4, 136.4, 132.1, 116.9, 116.4, 114.3, 111.6, 61.5, 55.2, 44.9, 17.9, 16.8, 13.5; HRMS (ESI) m/z: calcd. for $C_{16}H_{19}O_5^+$ [M + H] $^+$, 291.1227; found, 291.1222.

Ethyl 1-oxo-3-(propan-2-ylidene)-6-(trifluoromethyl)isochromane-4-carboxylate (3ga)

White solid (76% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.74 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.65 (d, *J* = 1.8 Hz, 1H), 4.94 (s, 1H), 4.25 – 4.07 (m, 2H), 1.86 (d, *J* = 3.9 Hz, 6H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.2, 161.1, 136.6, 136.1, 135.5 (q, *J* = 33.1 Hz), 131.0, 127.6, 125.6 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 273.1 Hz), 118.8, 62.4, 44.9, 18.4, 17.2, 13.9; HRMS (ESI) m/z: calcd. for $C_{16}H_{16}F_3O_4^+$ [M + H] $^+$, 329.0995; found, 329.0987.

Ethyl 6-nitro-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3ha)

Light yellow solid (53% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.35 – 8.28 (m, 2H), 8.24 (d, *J* = 2.0 Hz, 1H), 4.98 (s, 1H), 4.21 – 4.13 (m, 2H), 1.87 (d, *J* = 3.2 Hz, 6H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.4, 160.0, 150.3, 137.1, 135.3, 131.4, 129.2, 123.0, 122.2, 119.0, 62.2, 44.4, 18.1, 16.9, 13.5; HRMS (ESI) m/z: calcd. for $C_{15}H_{14}NO_6^-$ [M − H] $^-$, 304.0827; found, 304.0824.

Ethyl 8-fluoro-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3ia)

White solid (61% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.53 (m, 1H), 7.21 – 7.14 (m, 2H), 4.86 (s, 1H), 4.21 – 4.07 (m, 2H), 1.84 (d, *J* = 2.5 Hz, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.4, 162.7 (d, *J* = 266.3 Hz), 158.0 (d, *J* = 4.4 Hz), 138.2, 136.2, 135.3 (d, *J* = 9.8 Hz), 123.1 (d, *J* = 4.2 Hz), 117.7, 117.1 (d, *J* = 21.6 Hz), 113.4 (d, *J* = 7.9 Hz), 62.3, 45.2, 18.4, 17.2, 13.9; HRMS (ESI) m/z: calcd. for $C_{15}H_{15}FNaO_4^+$ [M + Na] $^+$, 301.0847; found, 301.0846.

Ethyl 8-methyl-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3ja)

White solid (59% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 4.81 (s, 1H), 4.20 – 4.06 (m, 2H), 2.71 (s, 3H), 1.82 (d, *J* = 1.6 Hz, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.1, 161.9, 143.0, 136.7, 136.7, 132.9, 132.1, 125.2, 123.2, 116.0, 62.0, 45.9, 22.1, 18.4, 17.1, 14.0; HRMS (ESI) m/z: calcd. for $C_{16}H_{19}O_4^+$ [M + H] $^+$, 275.1278; found, 275.1271.

Ethyl 7-fluoro-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3ka)

Light yellow oil (35% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 8.4, 2.7 Hz, 1H), 7.40 – 7.28 (m, 2H), 4.85 (s, 1H), 4.20 – 4.08 (m, 2H), 1.84 (d, *J* = 7.3 Hz, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.7, 162.4 (d, *J* = 249.3 Hz), 161.3 (d, *J* = 2.7 Hz), 136.6, 131.7 (d, *J* = 3.3 Hz), 129.4 (d, *J* = 7.6 Hz), 126.3 (d, *J* = 7.8 Hz), 121.5 (d, *J* = 22.2 Hz), 118.1, 116.7 (d, *J* = 23.5 Hz), 62.1, 44.3, 18.4, 17.2, 13.9; HRMS (ESI) m/z: calcd. for $C_{15}H_{15}FO_4^+$ [M + H] $^+$, 279.1035; found,

279.1039.

Ethyl 7-methoxy-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3la)

Yellow oil (70% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 2.7 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.15 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.82 (s, 1H), 4.17 – 4.07 (m, 2H), 3.86 (d, *J* = 1.0 Hz, 3H), 1.84 (d, *J* = 8.0 Hz, 6H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.2, 162.4, 159.7, 137.1, 128.6, 128.1, 125.3, 121.9, 117.3, 112.9, 61.9, 55.7, 44.2, 18.4, 17.2, 14.0; HRMS (ESI) m/z: calcd. for $C_{16}H_{19}O_5^+$ $[M + H]^+$, 291.1227; found, 291.1225.

Ethyl 7-methyl-6-nitro-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3ma)

White solid (59% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.93 (s, 1H), 4.91 (s, 1H), 4.21 – 4.09 (m, 2H), 2.64 (s, 3H), 1.85 (d, *J* = 4.9 Hz, 6H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.1, 160.6, 152.1, 136.0, 134.8, 134.7, 133.8, 127.8, 123.5, 119.2, 62.5, 44.3, 19.8, 18.5, 17.3, 14.0; HRMS (ESI) m/z: calcd. for $C_{16}H_{16}NO_6^-$ $[M - H]^-$, 318.0983; found, 318.0979.

Ethyl 5-methyl-1-oxo-3-(propan-2-ylidene)-1,3,4,5-tetrahydropyrano[4,3-b]indole-4-carboxylate (3na)

Yellow oil (28% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.18 – 8.14 (m, 1H), 7.41 – 7.38 (m, 1H), 7.38 – 7.31 (m, 2H), 5.00 (s, 1H), 4.22 – 4.15 (m, 2H), 3.83 (s, 3H), 1.93 (s, 3H), 1.87 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.3, 160.1, 141., 138.0, 136.7, 125.0, 123.8, 122.8, 121.2, 118.7, 109.8, 101.9, 62.5, 40.5, 30.5, 18.6, 17.7, 14.0; HRMS (ESI) m/z: calcd. for $C_{18}H_{20}NO_4^+$ $[M + H]^+$, 314.1387; found, 314.1386.

Ethyl 7-oxo-5-(propan-2-ylidene)-4,7-dihydro-5H-furo[2,3-c]pyran-4-carboxylate (3oa)

Light yellow oil (41% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 1.8 Hz, 1H), 6.58 (d, *J* = 1.8 Hz, 1H), 4.85 (s, 1H), 4.23 – 4.13 (m, 2H), 1.88 (s, 3H), 1.79 (s, 3H), 1.23 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.1, 153.6, 148.7, 139.1, 137.5, 130.6, 120.0, 110.4, 62.2, 41.2, 18.5, 17.6, 14.0; HRMS (ESI) m/z: calcd. for $C_{13}H_{15}O_5^+$ [M + H] $^+$, 251.0914; found, 251.0907.

Ethyl 1-oxo-3-(propan-2-ylidene)-3,4-dihydro-1H-benzo[g]isochromene-4-carboxylate (3pa)

White solid (77% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.93 – 7.86 (m, 1H), 7.83 (s, 1H), 7.66 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.59 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 5.07 (s, 1H), 4.20 – 4.09 (m, 2H), 1.90 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.2, 162.8, 137.2, 135.7, 132.6, 132.4, 130.7, 129.6, 129.2, 127.6, 127.1, 126.2, 122.0, 117.5, 62.0, 45.3, 18.5, 17.3, 14.0; HRMS (ESI) m/z: calcd. for $C_{19}H_{19}O_4^+$ [M + H] $^+$, 311.1278; found, 311.1280.

Ethyl 7-oxo-9-(propan-2-ylidene)-9,10-dihydro-7H-phenaleno[1,9-fg] isochromene-10-carboxylate (3qa)

Yellow solid (84% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.59 (d, *J* = 9.4 Hz, 1H), 8.35 – 8.31 (m, 4H), 8.28 (d, *J* = 7.5 Hz, 1H), 8.23 (d, *J* = 8.9 Hz, 1H), 8.11 – 8.04 (m, 3H), 5.26 (s, 1H), 4.22 – 4.10 (m, 2H), 1.92 (d, *J* = 5.6 Hz, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.7, 162.2, 136.1, 134.6, 133.9, 132.0, 130.6, 130.3, 129.8, 126.6, 126.6, 126.2, 126.2, 124.7, 124.3, 123.3, 122.5, 116.1, 115.8, 61.7, 46.5, 18.1, 16.8, 13.5; HRMS (ESI) m/z: calcd. for $C_{25}H_{21}O_4^+$ [M + H] $^+$, 385.1434; found, 385.1431.

Ethyl 1-oxo-3-(pentan-3-ylidene)isochromane-4-carboxylate (3ab)

Colorless oil (87% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.11 (m, 1H), 7.61 (td, *J* = 7.6, 1.5 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.38 (ddt, *J* = 7.6, 1.2, 0.6 Hz, 1H), 4.83 (s, 1H), 4.21 – 4.04 (m, 2H), 2.37 – 2.24 (m, 2H), 2.24 – 2.13 (m, 2H),

1.19 (t, *J* = 7.1 Hz, 3H), 1.04 (dt, *J* = 15.9, 7.5 Hz, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.6, 162.0, 136.4, 135.5, 133.6, 129.9, 128.5, 128.3, 126.8, 124.0, 61.6, 44.5, 22.7, 21.1, 13.4, 12.6, 12.2; HRMS (ESI) m/z: calcd. for $C_{17}H_{21}O_4^+$ [M + H] $^+$, 289.1434; found, 289.1433.

Ethyl 3-(diphenylmethylene)-1-oxoisochromane-4-carboxylate (3ac)

White solid (46% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.59 (td, *J* = 7.5, 1.5 Hz, 1H), 7.50 (td, *J* = 7.6, 1.3 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.32 – 7.28 (m, 4H), 7.27 – 7.24 (m, 4H), 4.67 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.8, 161.9, 140.0, 138.5, 137.2, 135.7, 134.4, 130.4, 130.2, 130.1, 130.0, 128.9, 128.7, 128.5, 128.0, 128.0, 127.9, 127.7, 127.6, 127.5, 124.0, 122.4, 62.3, 47.1, 14.0; HRMS (ESI) m/z: calcd. for $C_{25}H_{21}O_4^+$ [M + H] $^+$, 385.1434; found, 385.1434.

Ethyl 3-cyclopentylidene-1-oxoisochromane-4-carboxylate (3ad)

Colorless oil (49% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.60 (td, *J* = 7.6, 1.4 Hz, 1H), 7.47 (td, *J* = 7.7, 1.2 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 4.67 (s, 1H), 4.16 – 4.10 (m, 2H), 2.60 – 2.52 (m, 1H), 2.50 – 2.41 (m, 2H), 2.38 – 2.30 (m, 1H), 1.78 – 1.70 (m, 3H), 1.69 – 1.65 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.5, 161.9, 135.2, 133.7, 133.6, 130.0, 128.3, 128.3, 126.8, 124.1, 61.6, 46.1, 28.7, 28.5, 26.2, 25.9, 13.5; HRMS (ESI) m/z: calcd. for $C_{17}H_{19}O_4^+$ [M + H] $^+$, 287.1278; found, 287.1275.

Ethyl 3-cyclohexylidene-1-oxoisochromane-4-carboxylate (3ae)

Colorless oil (86% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.61 (td, *J* = 7.6, 1.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 4.90 (s, 1H), 4.13 (qd, *J* = 7.1, 1.4 Hz, 2H), 2.61 – 2.53 (m, 1H), 2.38 – 2.24 (m, 1H), 2.24 – 2.16 (m, 1H), 1.65 – 1.52 (m, 7H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.5, 164.0, 137.4, 135.7, 135.5, 131.7, 130.2, 128.9, 126.9, 126.0, 63.4, 45.9, 30.5, 29.0, 28.4, 28.3, 27.8, 15.4; HRMS (ESI) m/z: calcd. for

$C_{18}H_{21}O_4^+$ [M + H] $^+$, 301.1434; found, 301.1433.

Ethyl 3-cycloheptylidene-1-oxoisochromane-4-carboxylate (3af)

Colorless oil (30% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.60 (td, *J* = 7.6, 1.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.38 (dd, *J* = 7.7, 1.1 Hz, 1H), 4.88 (s, 1H), 4.18 – 4.08 (m, 2H), 2.66 – 2.58 (m, 1H), 2.45 – 2.30 (m, 3H), 1.72 – 1.59 (m, 4H), 1.57 – 1.43 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.6, 162.0, 136.4, 135.4, 133.6, 129.8, 128.3, 126.9, 126.5, 124.0, 61.6, 44.4, 29.3, 28.6, 28.5, 27.9, 27.1, 26.6, 13.5; HRMS (ESI) m/z: calcd. for $C_{19}H_{23}O_4^+$ [M + H] $^+$, 315.1591; found, 315.1586.

Ethyl 3-(butan-2-ylidene)-1-oxoisochromane-4-carboxylate (3ag)

Colorless oil (71% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (dt, *J* = 7.8, 1.7 Hz, 2H), 7.60 (tt, *J* = 7.5, 1.6 Hz, 2H), 7.47 (td, *J* = 7.6, 1.2 Hz, 2H), 7.37 (ddd, *J* = 7.7, 3.6, 1.2 Hz, 2H), 4.87 (s, 1H), 4.84 (s, 1H), 4.16 – 4.09 (m, 4H), 2.35 – 2.27 (m, 2H), 2.19 (q, *J* = 7.5 Hz, 2H), 1.83 (d, *J* = 10.9 Hz, 6H), 1.19 (td, *J* = 7.1, 1.5 Hz, 6H), 1.06 (t, *J* = 7.6 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.5, 168.5, 162.0, 161.9, 136.3, 136.0, 135.4, 135.4, 133.6, 129.9, 129.8, 128.3, 128.3, 127.0, 126.8, 124.1, 123.9, 122.7, 122.6, 61.6, 61.5, 44.6, 44.4, 25.1, 23.4, 15.4, 14.2, 13.5, 13.5, 12.2, 11.7; HRMS (ESI) m/z: calcd. for $C_{16}H_{19}O_4^+$ [M + H] $^+$, 275.1278; found, 275.1278.

Ethyl 6-fluoro-1-oxo-3-(pentan-3-ylidene)isochromane-4-carboxylate (3bb)

Colorless oil (63% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 8.7, 5.6 Hz, 1H), 7.15 (td, *J* = 8.5, 2.5 Hz, 1H), 7.07 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.79 (s, 1H), 4.19 – 4.08 (m, 2H), 2.36 – 2.23 (m, 2H), 2.23 – 2.12 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.6 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.5, 165.9 (d, *J* = 257.1 Hz), 161.6, 138.8 (d, *J* = 9.2 Hz), 136.4, 133.3 (d, *J* = 9.8 Hz), 129.6, 120.9 (d, *J* = 2.9 Hz), 116.4 (d, *J* = 22.2 Hz), 114.4 (d, *J* = 22.7 Hz), 62.2, 45.0, 23.1, 21.6, 13.9, 13.0, 12.6; HRMS (ESI) m/z: calcd. for $C_{17}H_{20}FO_4^+$ [M + H]$^+$,

307.1340; found, 307.1348.

Ethyl 3-cyclopentylidene-6-fluoro-1-oxoisochromane-4-carboxylate (3bd)

Colorless oil (50% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 8.7, 5.6 Hz, 1H), 7.15 (td, *J* = 8.5, 2.5 Hz, 1H), 7.06 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.63 (s, 1H), 4.18 – 4.10 (m, 2H), 2.59 – 2.52 (m, 1H), 2.48 – 2.40 (m, 2H), 2.35 – 2.29 (m, 1H), 1.78 – 1.64 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.4, 165.9 (d, *J* = 257.5 Hz), 161.4, 138.5 (d, *J* = 9.2 Hz), 133.7, 133.4 (d, *J* = 9.7 Hz), 129.4, 120.9 (d, *J* = 3.0 Hz), 116.4 (d, *J* = 22.0 Hz), 114.3 (d, *J* = 22.9 Hz), 62.2, 46.6, 29.2, 29.0, 26.7, 26.3, 14.0; HRMS (ESI) m/z: calcd. for $C_{17}H_{18}FO_4^+$ [M + H] $^+$, 305.1184; found, 305.1180.

Ethyl 3-cyclohexylidene-6-fluoro-1-oxoisochromane-4-carboxylate (3be)

Colorless oil (63% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 8.7, 5.6 Hz, 1H), 7.16 (td, *J* = 8.5, 2.5 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.88 (s, 1H), 4.19 – 4.10 (m, 2H), 2.61 – 2.54 (m, 1H), 2.36 – 2.24 (m, 2H), 2.23 – 2.16 (m, 1H), 1.66 – 1.53 (m, 6H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.0, 165.4 (d, *J* = 257.1 Hz), 161.2, 138.3 (d, *J* = 9.2 Hz), 133.3, 132.7 (d, *J* = 9.8 Hz), 125.6, 120.4 (d, *J* = 2.9 Hz), 115.9 (d, *J* = 22.1 Hz), 114.1 (d, *J* = 22.7 Hz), 61.8, 44.0, 28.6, 27.1, 26.5, 26.4, 25.9, 13.5; HRMS (ESI) m/z: calcd. for $C_{18}H_{20}FO_4^+$ [M + H] $^+$, 319.1340; found, 319.1338.

Ethyl 3-(butan-2-ylidene)-6-fluoro-1-oxoisochromane-4-carboxylate (3bg)

Colorless oil (67% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 (ddd, *J* = 8.6, 5.6, 2.0 Hz, 2H), 7.15 (td, *J* = 8.5, 2.5 Hz, 2H), 7.06 (ddd, *J* = 8.3, 4.5, 2.5 Hz, 2H), 4.83 (s, 1H), 4.79 (s, 1H), 4.17 – 4.10 (m, 4H), 2.35 – 2.24 (m, 2H), 2.17 (q, *J* = 7.6 Hz, 2H), 1.83 (s, 3H), 1.80 (s, 3H), 1.19 (td, *J* = 7.1, 1.7 Hz, 6H), 1.05 (t, *J* = 7.5 Hz, 3H), 1.00 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.4, 168.4, 165.9 (dd, *J* = 257.2, 2.1 Hz), 161.5, 161.4, 138.7 (dd, *J* = 9.3, 6.7 Hz), 136.4, 136.0, 133.3 (dd, *J* = 9.7, 3.6 Hz), 123.8, 123.7, 121.0 (d, *J* = 2.9 Hz), 120.8 (d, *J* = 2.9 Hz), 116.4 (d, *J* =

22.2 Hz), 114.4 (dd, *J* = 22.8, 19.8 Hz), 62.3, 62.2, 45.1, 44.9, 25.6, 23.9, 15.9, 14.6, 13.9, 13.9, 12.6, 12.1; HRMS (ESI) m/z: calcd. for $C_{16}H_{18}FO_4^+$ [M + H] $^+$, 293.1184; found, 293.1188.

Ethyl 10-oxo-8-(pentan-3-ylidene)-5,7,8,10-tetrahydro-1H-phenaleno[1,9-gh] isochromene-7-carboxylate (3qb)

Yellow solid (64% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.60 (d, *J* = 9.4 Hz, 1H), 8.32 (dd, *J* = 8.5, 4.5 Hz, 2H), 8.28 (d, *J* = 7.5 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.12 – 8.03 (m, 3H), 5.23 (s, 1H), 4.24 – 4.09 (m, 2H), 2.44 – 2.33 (m, 2H), 2.33 – 2.24 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.5 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.3, 162.7, 136.7, 135.1, 134.6, 132.5, 131.0, 130.8, 130.3, 127.6, 127.0, 127.0, 126.7, 125.1, 124.8, 123.8, 122.9, 116.6, 62.1, 46.9, 23.2, 21.5, 14.0, 13.4, 12.7; HRMS (ESI) m/z: calcd. for $C_{27}H_{25}O_4^+$ [M + H] $^+$, 413.1747; found, 413.1741.

Ethyl 8-cyclopentylidene-10-oxo-7,10-dihydro-8H-phenaleno[1,9-gh] isochromene-7-carboxylate (3qd)

Yellow solid (45% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.60 (d, *J* = 9.5 Hz, 1H), 8.35 – 8.29 (m, 2H), 8.28 (d, *J* = 7.6 Hz, 1H), 8.22 (d, *J* = 8.9 Hz, 1H), 8.12 – 8.02 (m, 3H), 5.06 (s, 1H), 4.23 – 4.08 (m, 2H), 2.69 – 2.56 (m, 2H), 2.53 – 2.40 (m, 2H), 1.83 – 1.65 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.2, 162.5, 135.1, 134.3, 134.0, 132.5, 131.0, 130.8, 130.7, 130.3, 127.3, 127.0, 127.0, 126.7, 125.2, 124.8, 123.8, 122.9, 116.6, 62.1, 48.6, 29.2, 29.0, 26.8, 26.5, 14.0; HRMS (ESI) m/z: calcd. for $C_{27}H_{23}O_4^+$ [M + H] $^+$, 411.1591; found, 411.1587.

Ethyl 8-cyclohexylidene-10-oxo-7,10-dihydro-8H-phenaleno[1,9-gh]isochromene-7-carboxylate (3qe)

Yellow solid (53% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.59 (d, *J* = 9.4 Hz, 1H), 8.35 – 8.30 (m, 2H), 8.28 (d, *J* = 7.5 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.12 – 8.03 (m, 3H), 5.29 (s, 1H), 4.23 – 4.10 (m, 2H), 2.69 – 2.62 (m, 1H), 2.49 – 2.43 (m, 1H),

2.36 – 2.27 (m, 2H), 1.67 – 1.53 (m, 6H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.3, 162.8, 135.1, 134.6, 134.1, 132.4, 131.0, 130.8, 130.7, 130.3, 127.0, 127.0, 126.7, 125.2, 124.8, 124.2, 123.8, 123.1, 116.6, 62.1, 46.4, 29.2, 27.7, 27.0, 26.9, 26.4, 14.0; HRMS (ESI) m/z: calcd. for $C_{28}H_{25}O_4^+$ [M + H] $^+$, 425.1747; found, 425.1758.

Ethyl 8-(butan-2-ylidene)-10-oxo-7,10-dihydro-8H-phenaleno[1,9-gh] isochromene-7-carboxylate (3qg)

Yellow solid (43% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.59 (dd, *J* = 9.5, 6.0 Hz, 2H), 8.34 – 8.30 (m, 4H), 8.27 (d, *J* = 7.5 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 8.11 – 8.03 (m, 6H), 5.26 (s, 1H), 5.23 (s, 1H), 4.22 – 4.10 (m, 4H), 2.45 – 2.33 (m, 2H), 2.32 – 2.25 (m, 2H), 1.91 (s, 3H), 1.91 (s, 3H), 1.20 (td, *J* = 7.1, 1.8 Hz, 6H), 1.11 (t, *J* = 7.5 Hz, 3H), 1.05 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.2, 169.2, 162.7, 136.6, 135.1, 134.4, 132.4, 131.0, 131.0, 130.8, 130.3, 127.1, 127.0, 126.7, 125.1, 125.1, 124.8, 123.8, 123.0, 122.8, 121.8, 121.7, 116.6, 62.2, 62.1, 47.0, 46.8, 25.7, 23.8, 15.9, 14.7, 14.0, 14.0, 12.9, 12.2; HRMS (ESI) m/z: calcd. for $C_{26}H_{23}O_4^+$ [M + H] $^+$, 399.1591; found, 399.1594.

Methyl 1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3ah)

Colorless oil (86% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.61 (td, *J* = 7.6, 1.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 4.89 (s, 1H), 3.68 (s, 3H), 1.84 (d, *J* = 7.4 Hz, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.9, 161.9, 136.2, 135.2, 133.7, 129.9, 128.4, 127.0, 124.0, 117.3, 52.6, 44.3, 18.0, 16.8; HRMS (EI) m/z: calcd. for $C_{14}H_{14}O_4^+$ [M] $^+$, 246.0887; found, 246.0896.

Methyl 6-fluoro-1-oxo-3-(propan-2-ylidene)isochromane-4-carboxylate (3bh)

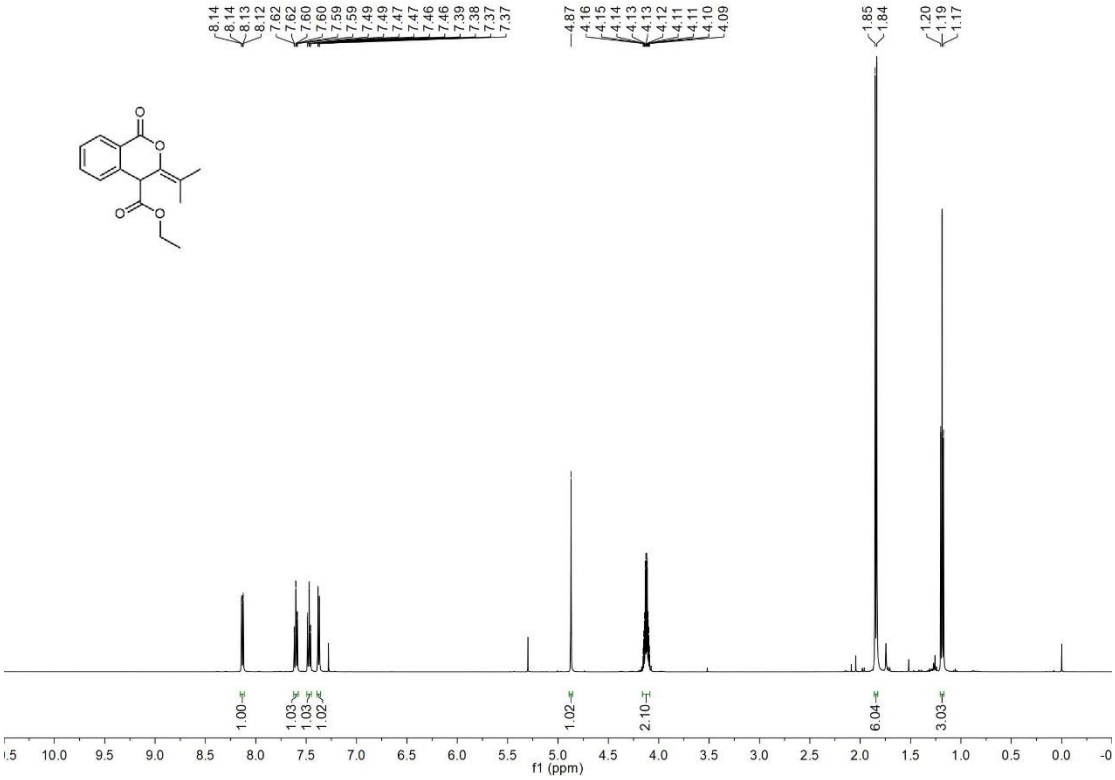
Colorless oil (73% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 8.7, 5.6 Hz, 1H), 7.16 (td, *J* = 8.5, 2.5 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.86 (s, 1H), 3.70 (s, 3H), 1.85 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.3, 167.3

(d, *J* = 257.4 Hz), 162.8, 139.9 (d, *J* = 9.2 Hz), 137.7, 134.7 (d, *J* = 9.7 Hz), 122.2 (d, *J* = 2.9 Hz), 119.9, 117.9 (d, *J* = 22.0 Hz), 116.0 (d, *J* = 22.8 Hz), 54.6, 46.2, 19.8, 18.7; HRMS (ESI) m/z: calcd. for $C_{14}H_{14}FO_4^+$ [M + H] $^+$, 265.0871; found, 265.0872.

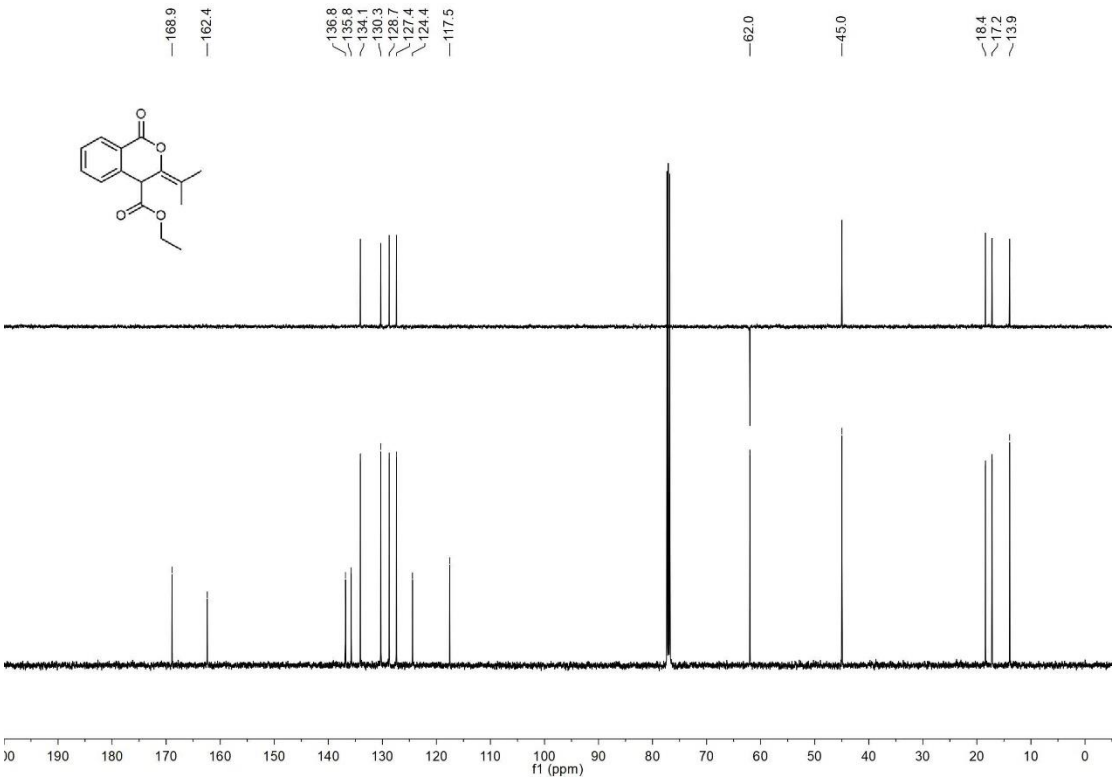
Methyl 10-oxo-8-(propan-2-ylidene)-7,10-dihydro-8H-phenaleno[1,9-gh] isochromene-7-carboxylate (3qh)

Yellow solid (65% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.59 (d, *J* = 9.4 Hz, 1H), 8.35 – 8.29 (m, 2H), 8.28 (d, *J* = 7.5 Hz, 1H), 8.22 (d, *J* = 8.9 Hz, 1H), 8.12 – 8.02 (m, 3H), 5.28 (s, 1H), 3.71 (s, 3H), 1.92 (d, *J* = 2.6 Hz, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.7, 162.5, 136.5, 135.1, 134.2, 132.5, 131.0, 130.8, 130.8, 130.3, 127.1, 127.1, 126.7, 126.7, 125.1, 124.8, 123.8, 123.0, 116.4, 116.4, 53.1, 46.7, 18.5, 17.2; HRMS (ESI) m/z: calcd. for $C_{24}H_{19}O_4^+$ [M + H] $^+$, 371.1278; found, 371.1281.

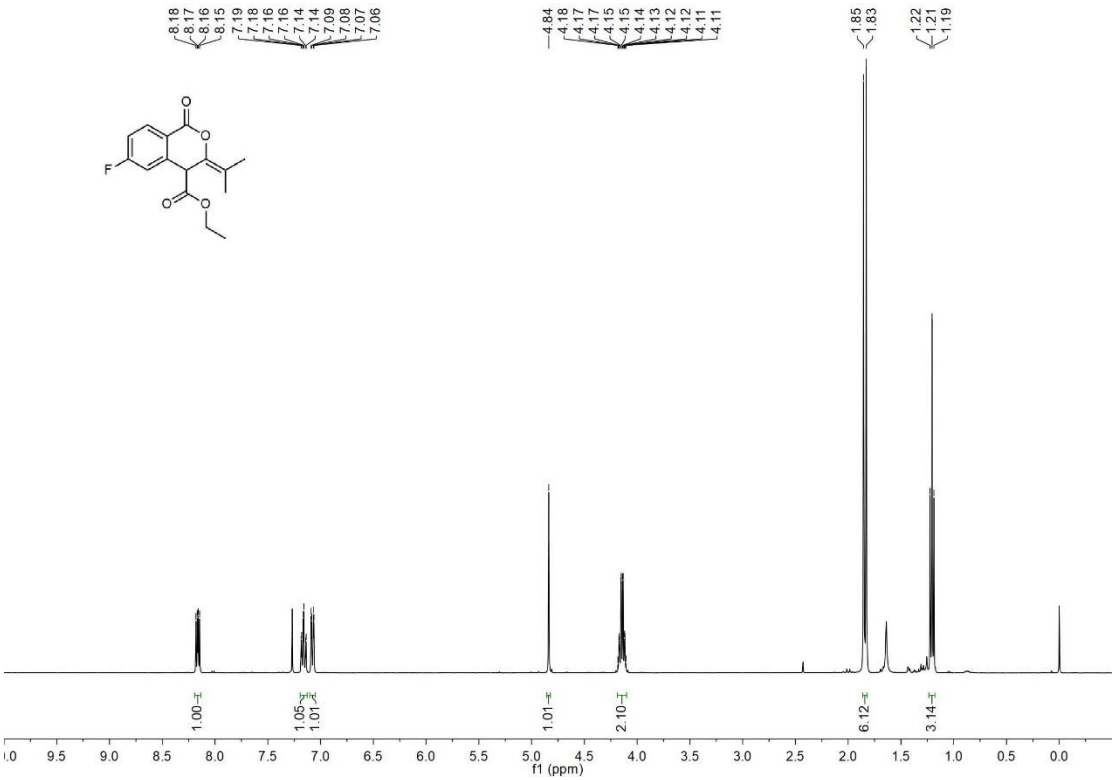
7. NMR spectra of the products



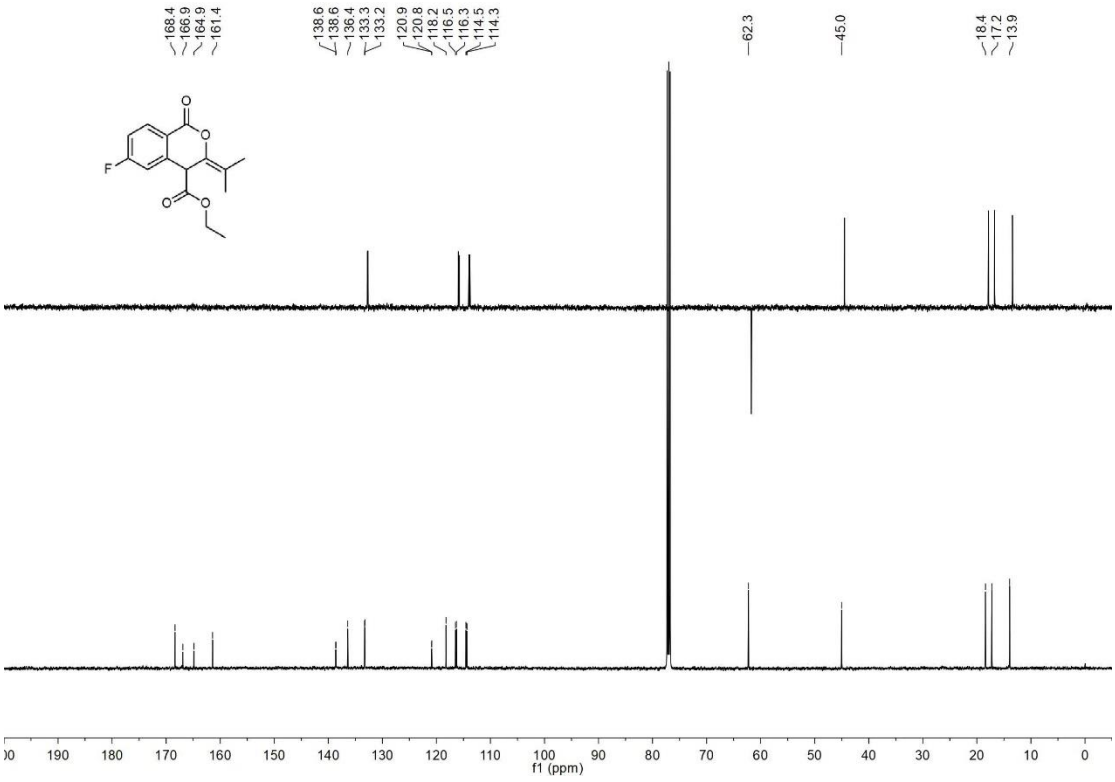
^{1}H NMR spectrum of compound **3aa**



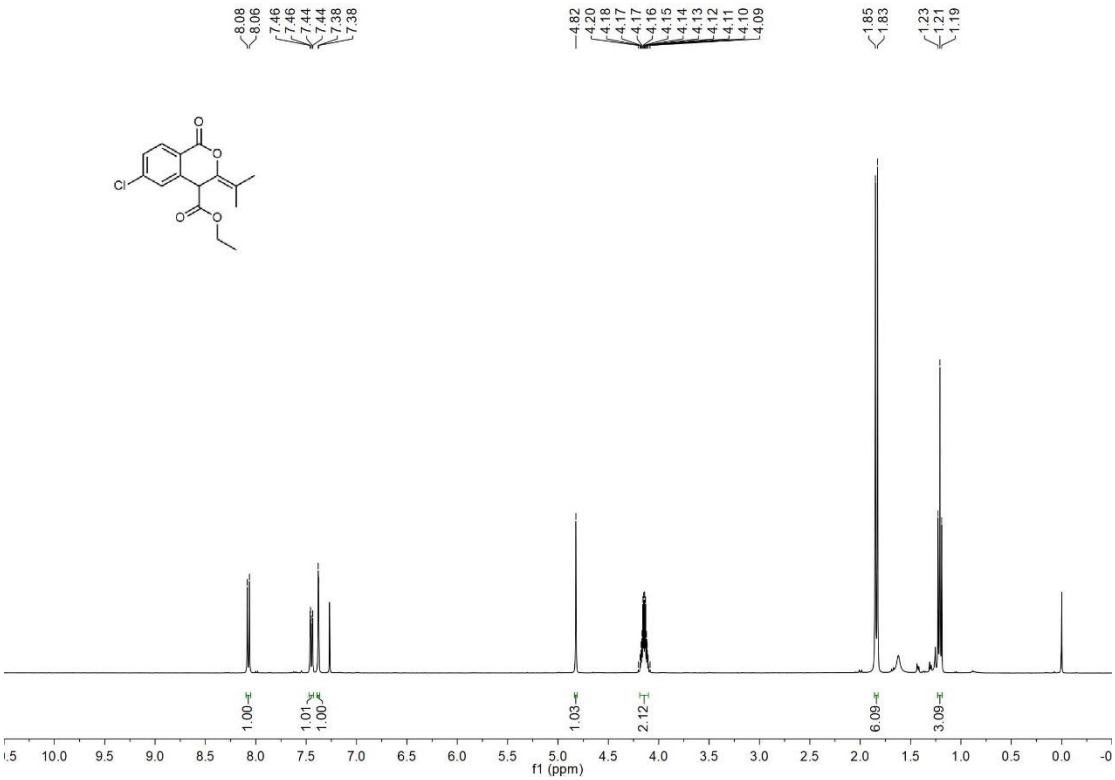
^{13}C NMR spectrum of compound **3aa**



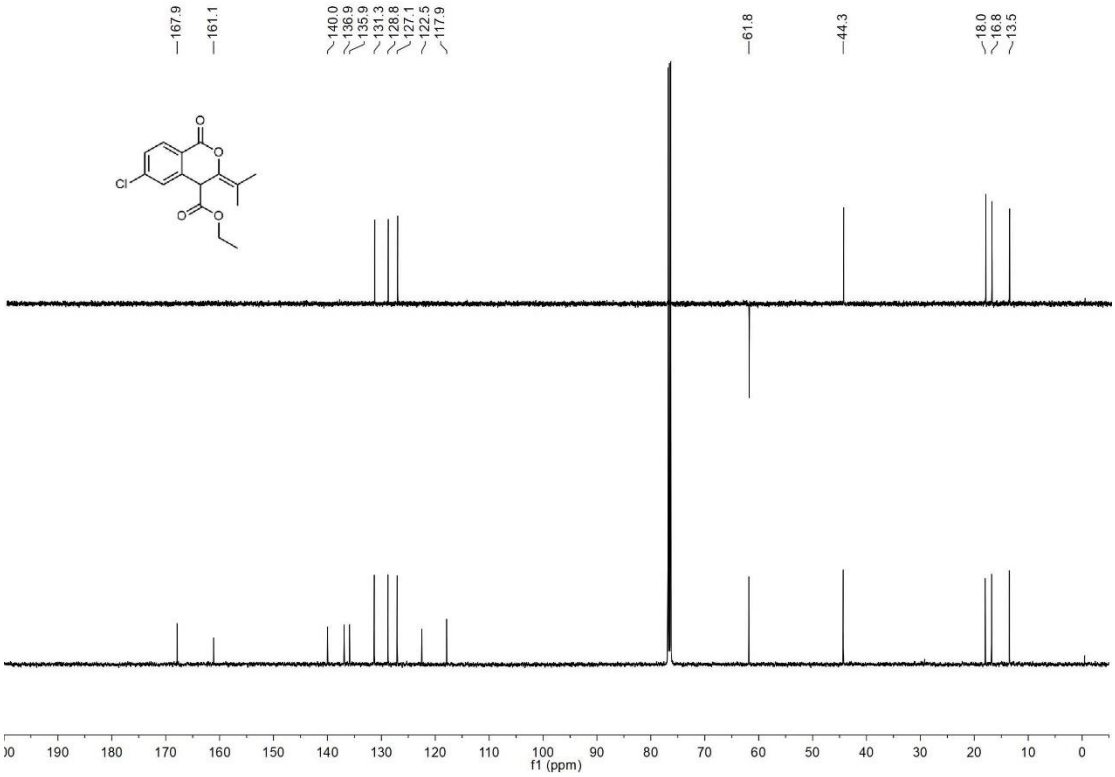
^{1}H NMR spectrum of compound **3ba**



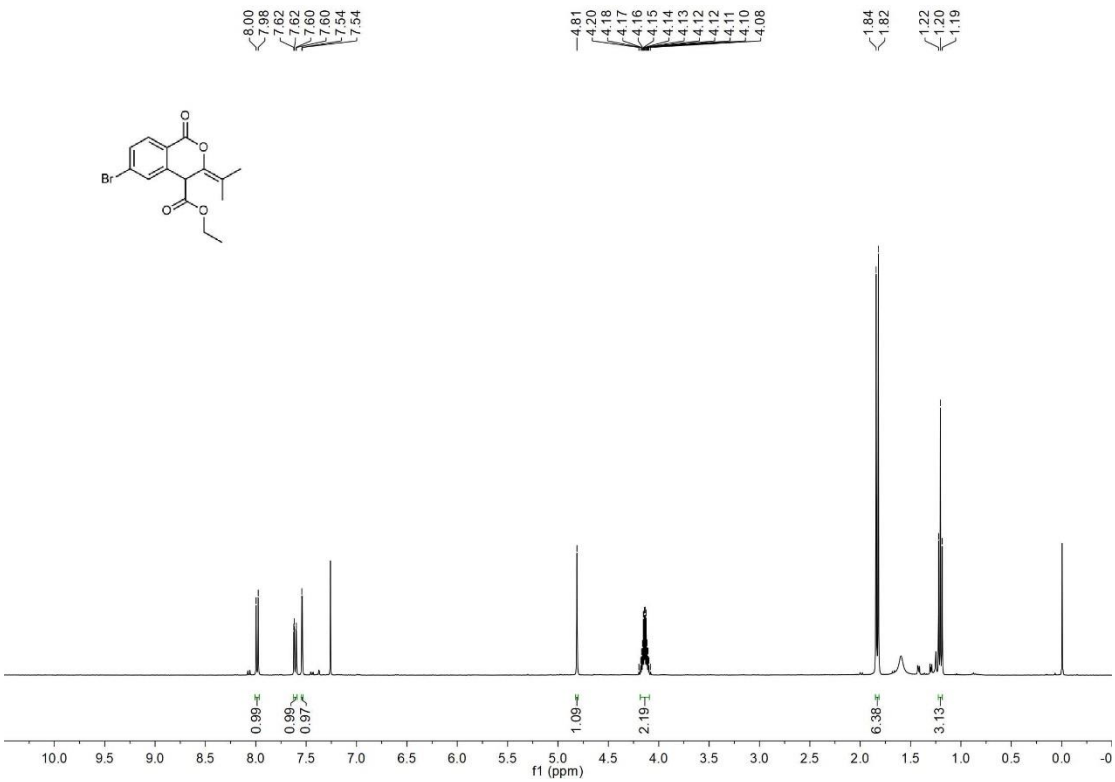
^{13}C NMR spectrum of compound **3ba**



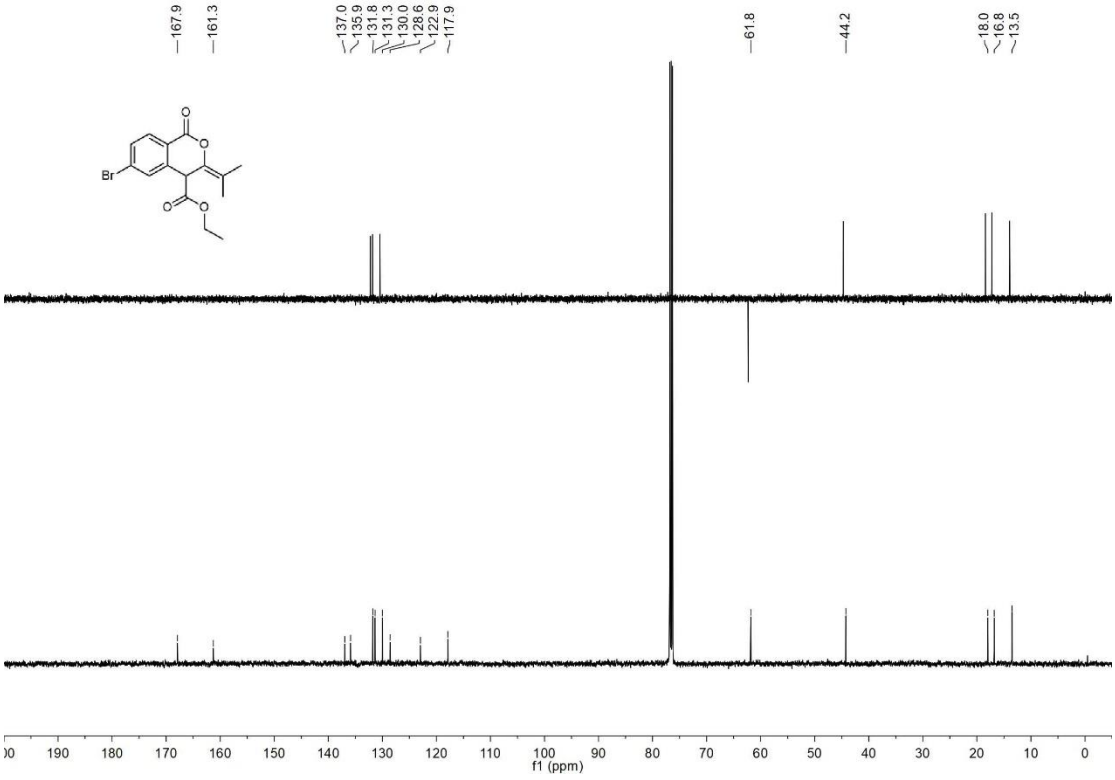
^{1}H NMR spectrum of compound **3ca**



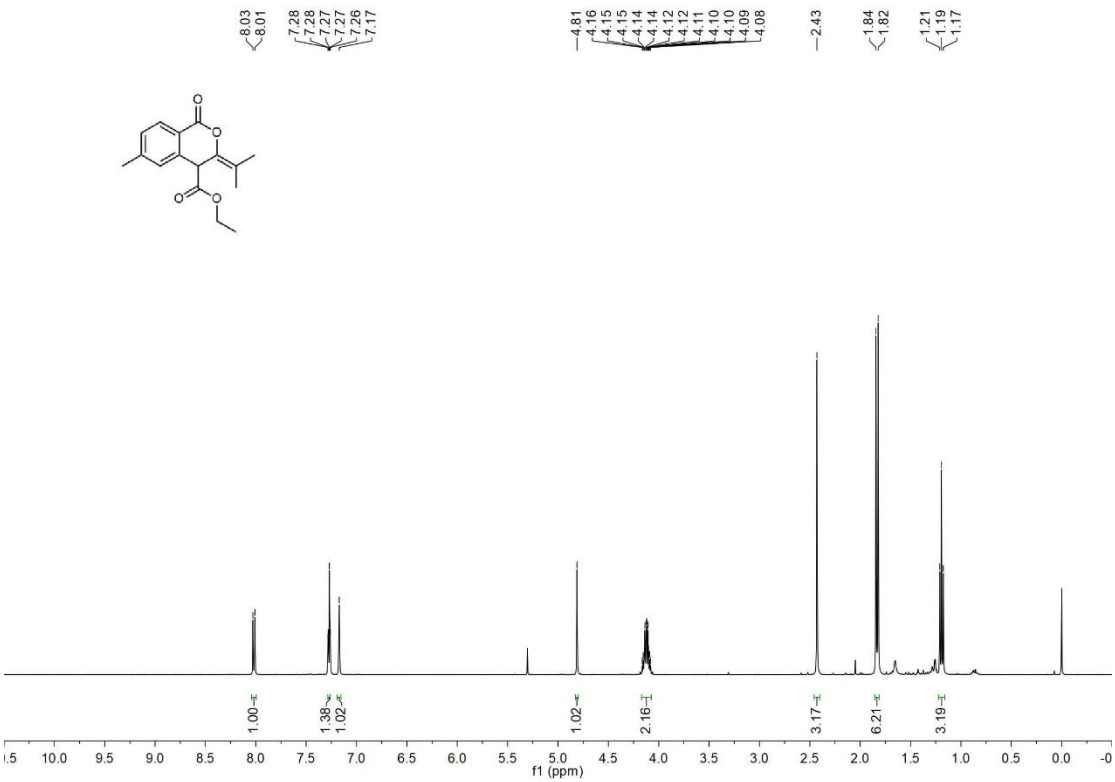
^{13}C NMR spectrum of compound **3ca**



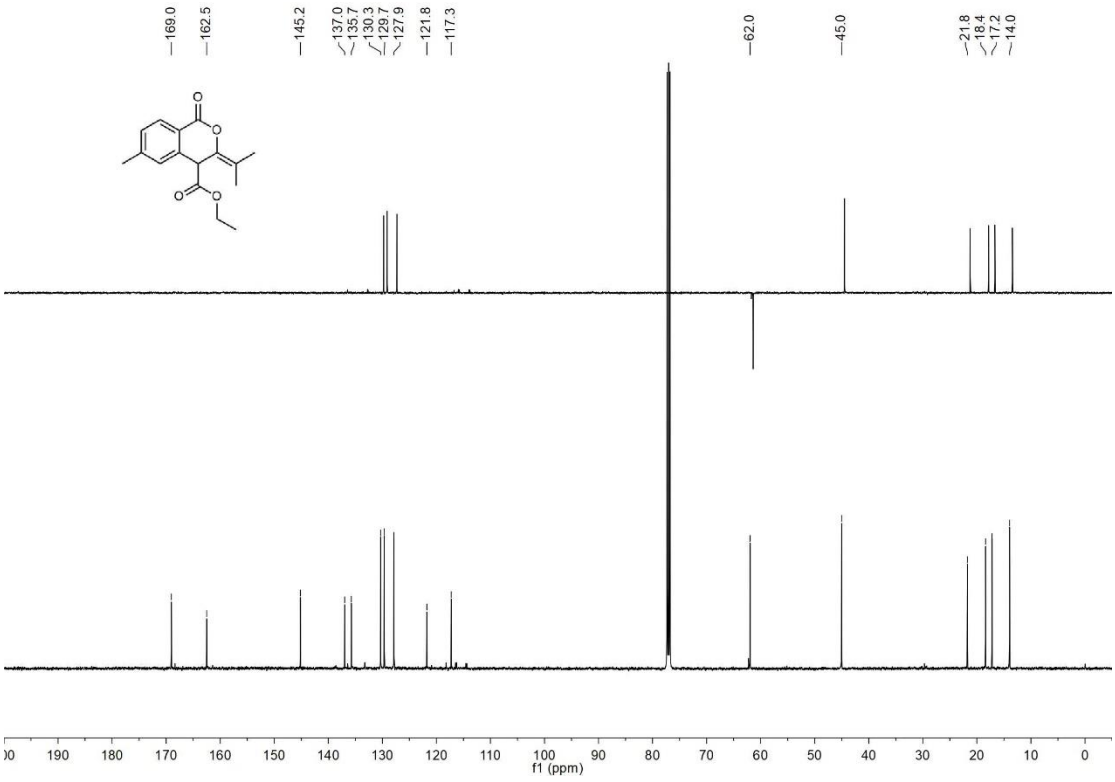
^{1}H NMR spectrum of compound **3da**



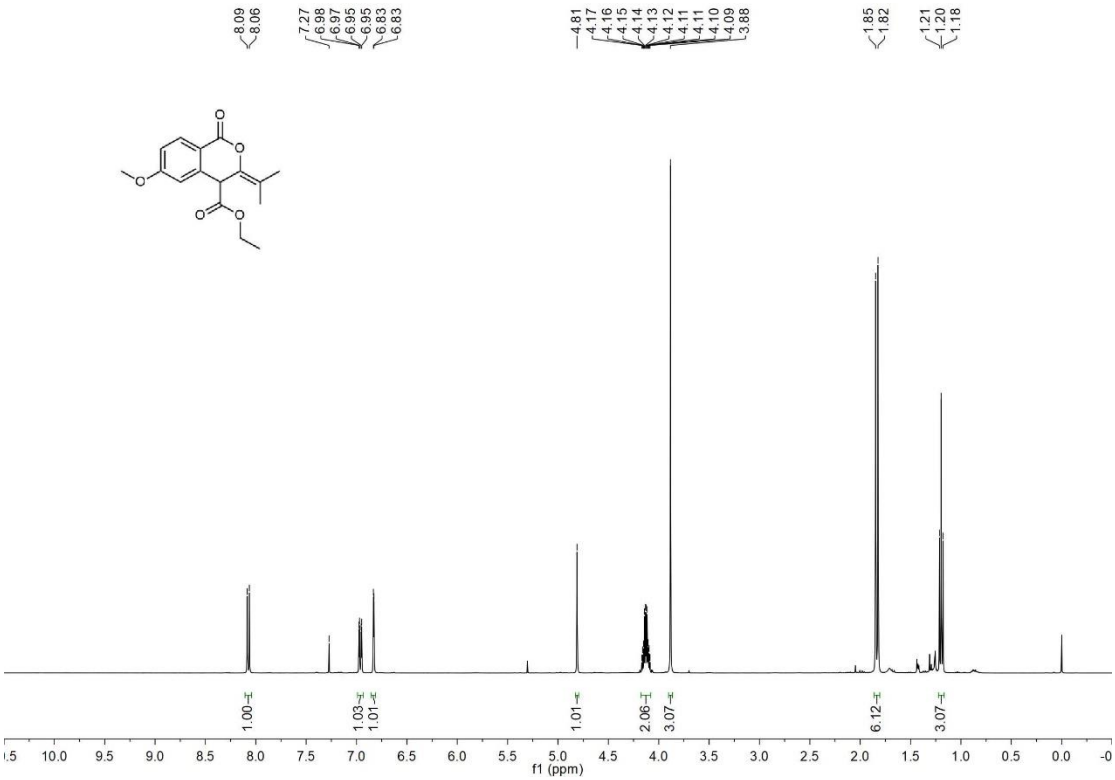
^{13}C NMR spectrum of compound **3da**



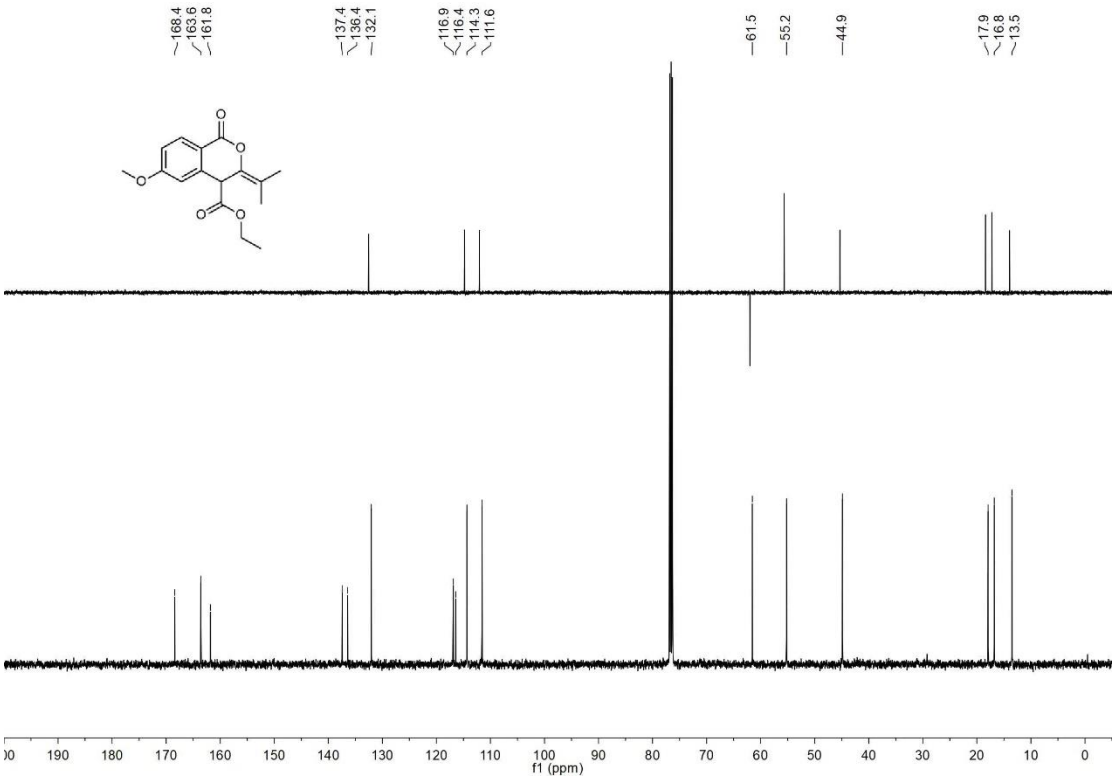
^{1}H NMR spectrum of compound **3ea**



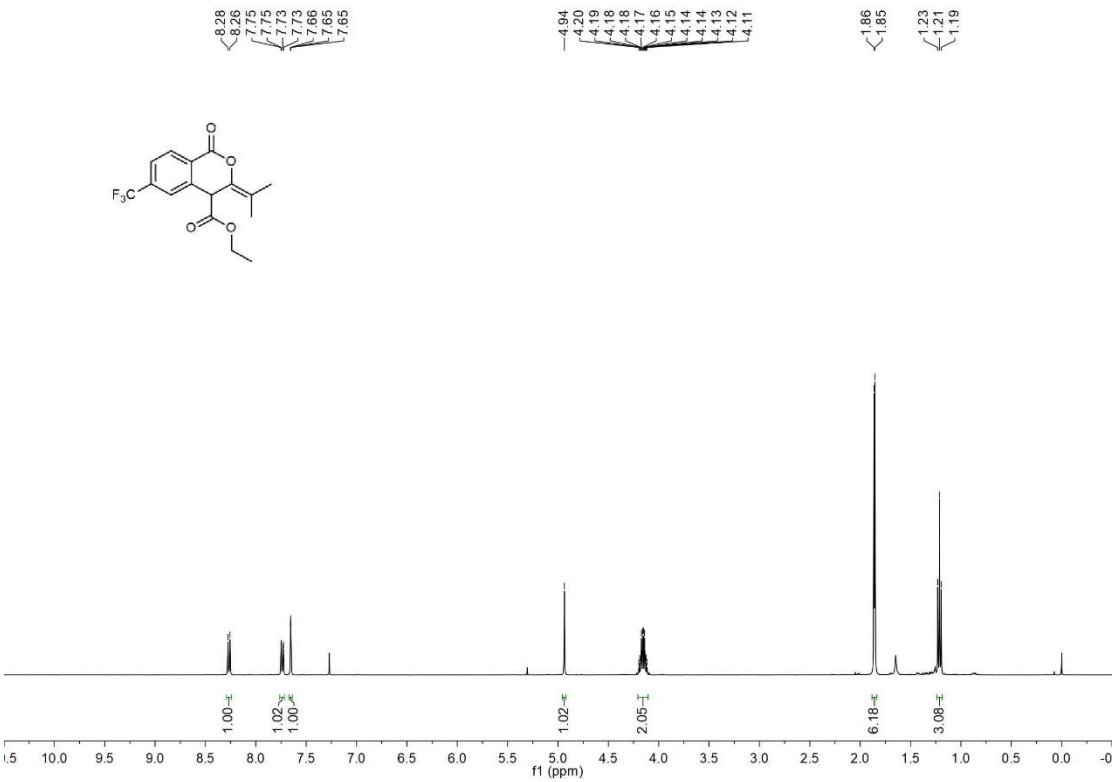
^{13}C NMR spectrum of compound **3ea**



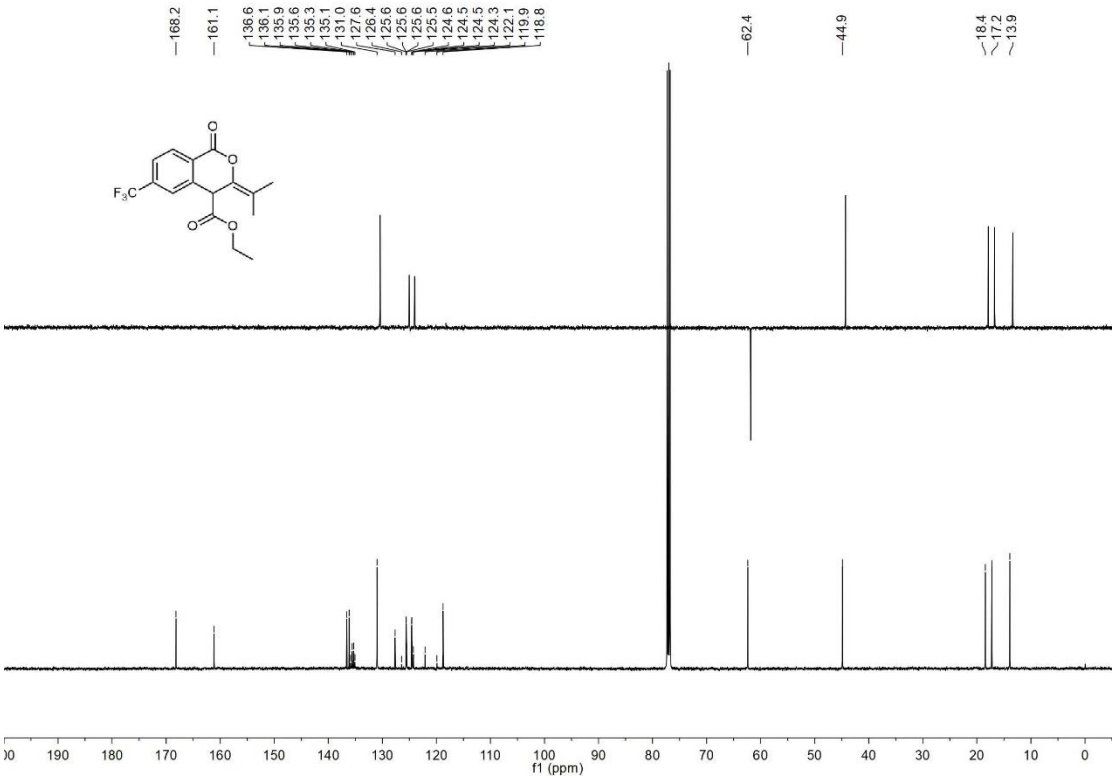
^{1}H NMR spectrum of compound **3fa**



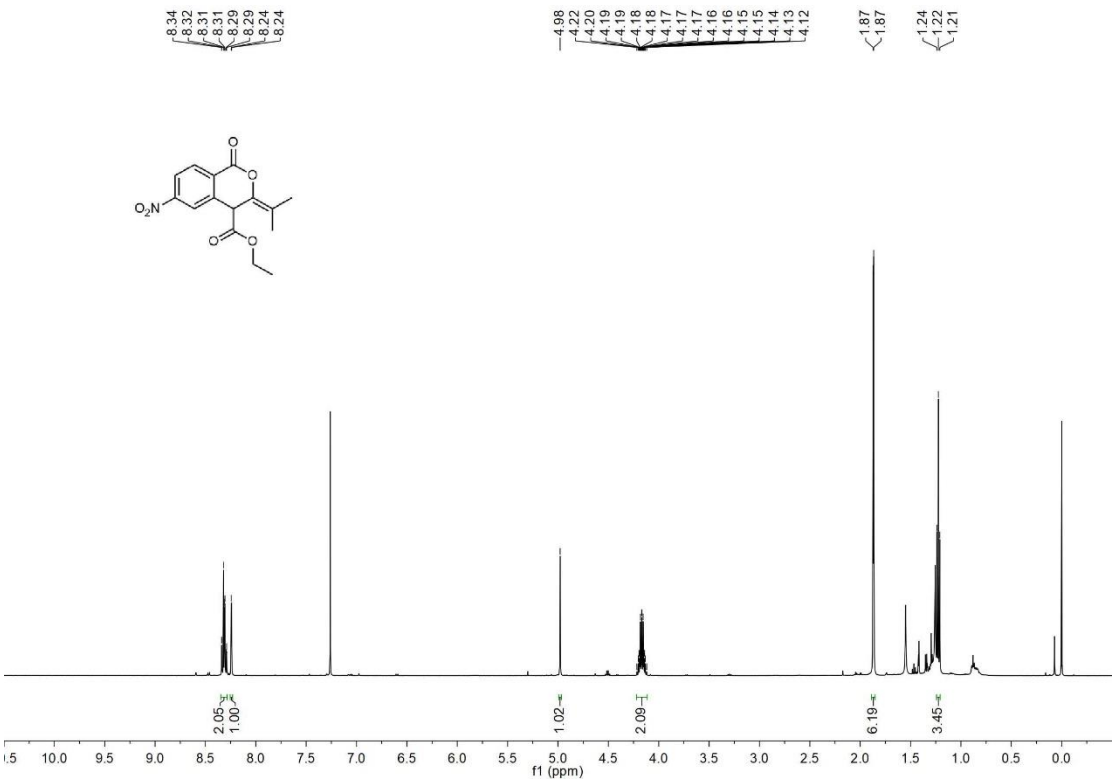
^{13}C NMR spectrum of compound **3fa**



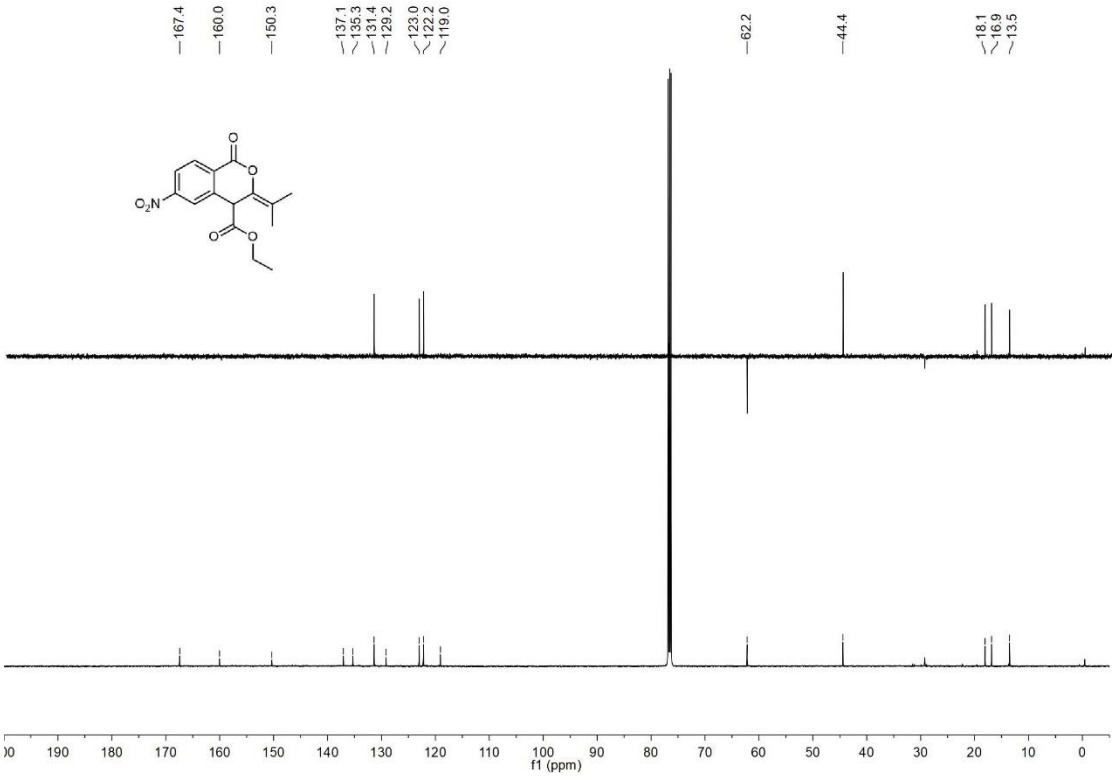
^{1}H NMR spectrum of compound **3ga**



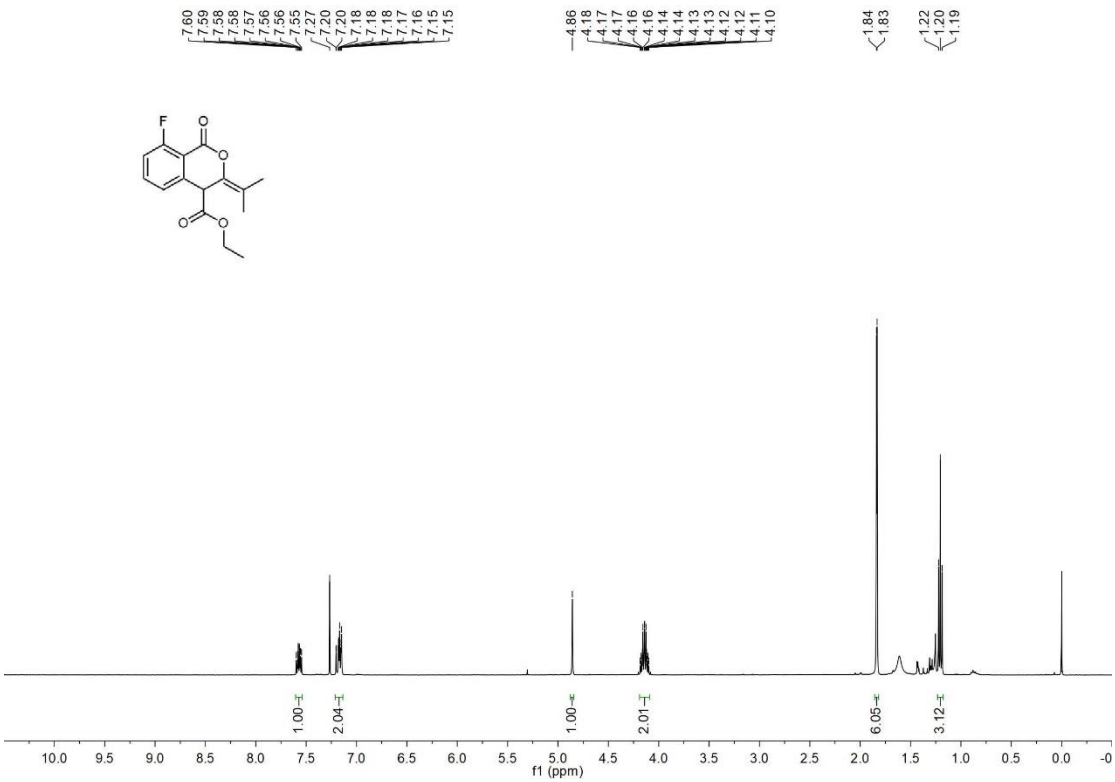
^{13}C NMR spectrum of compound **3ga**



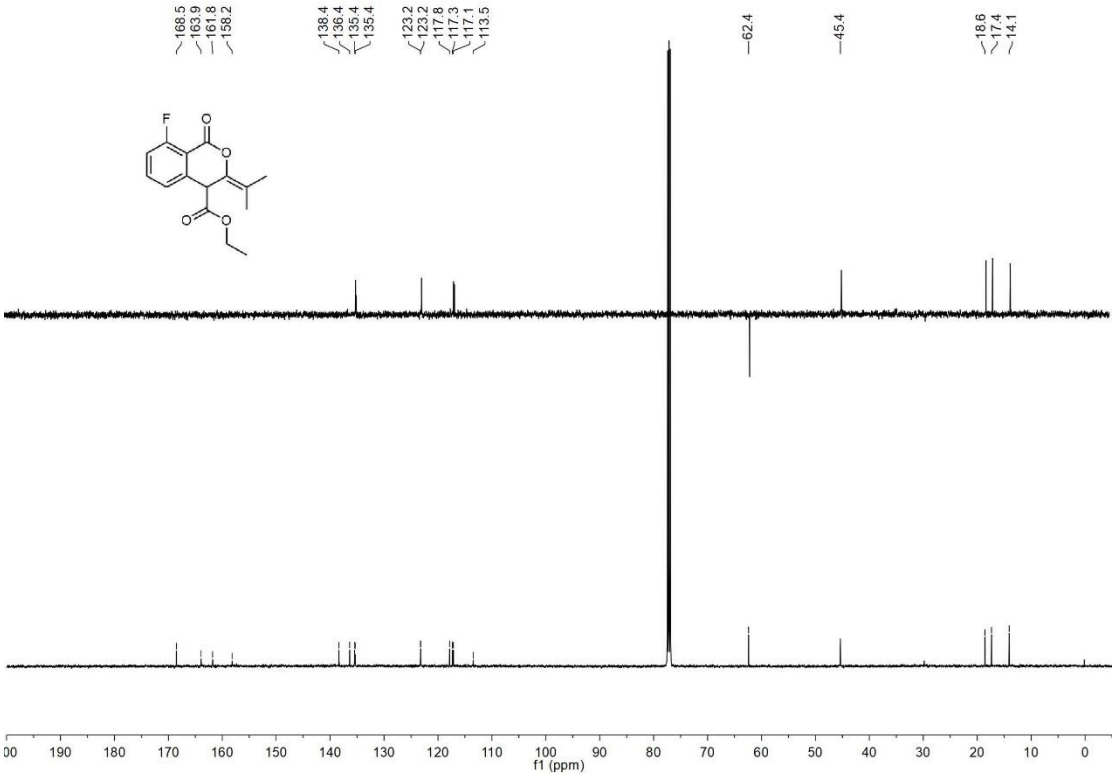
^{1}H NMR spectrum of compound **3ha**



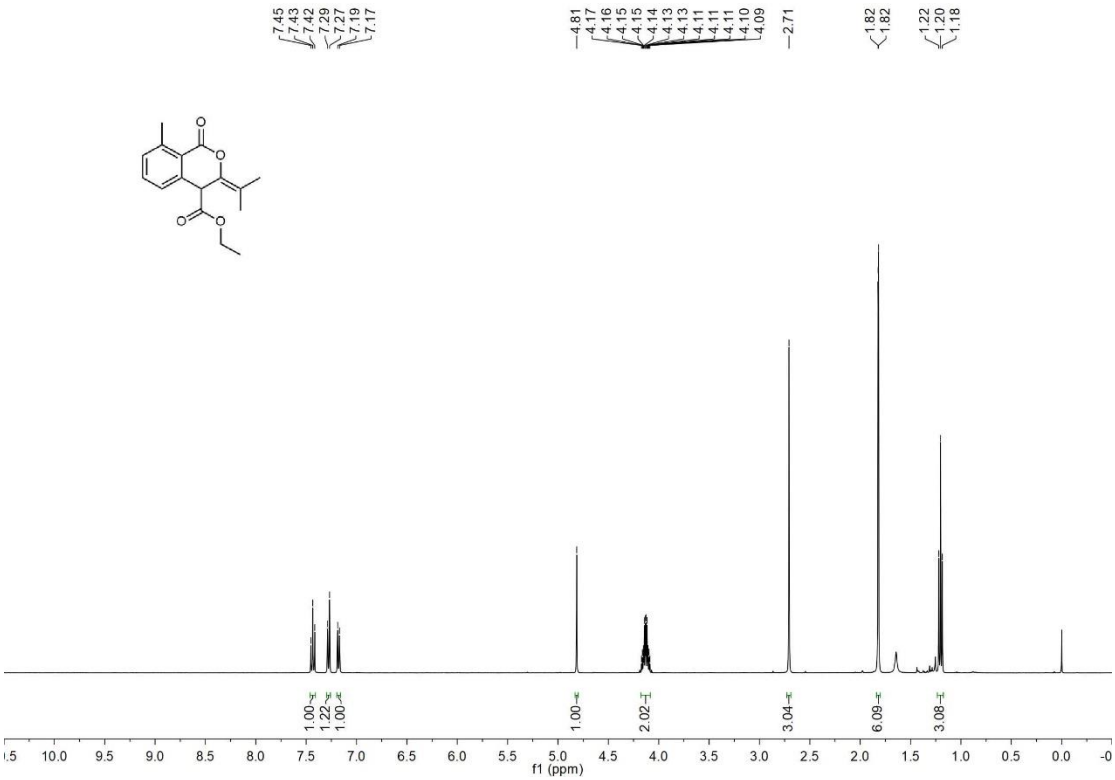
^{13}C NMR spectrum of compound **3ha**



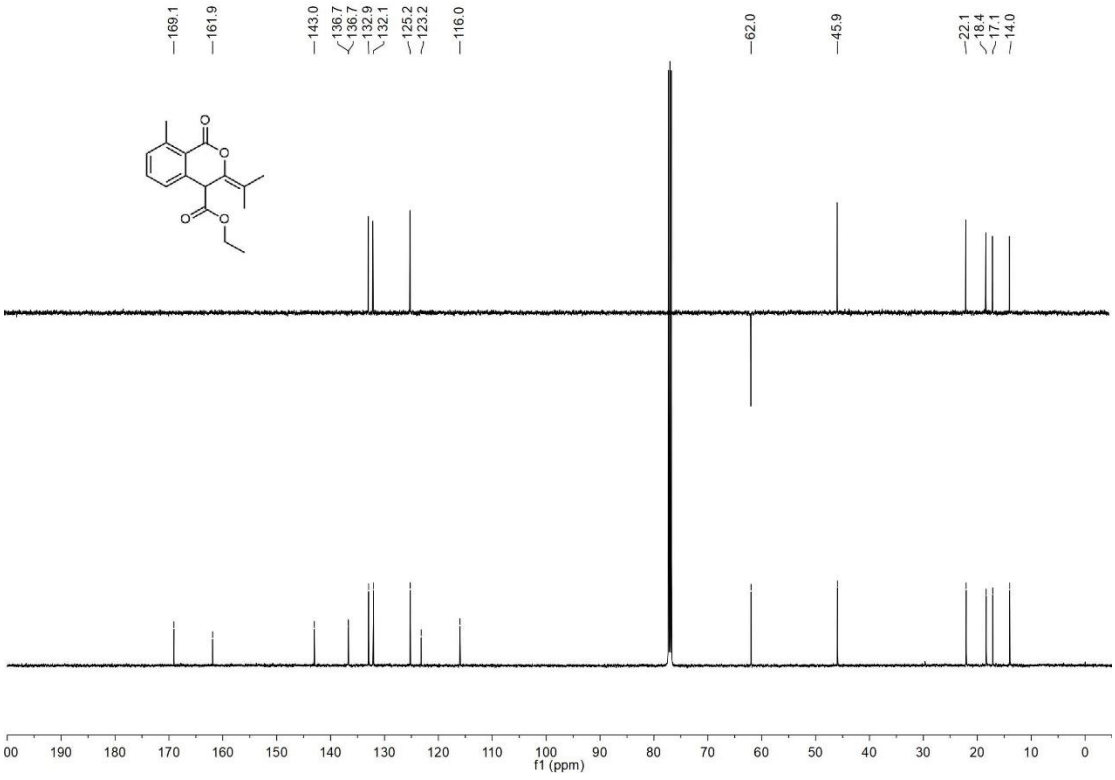
^{1}H NMR spectrum of compound **3ia**



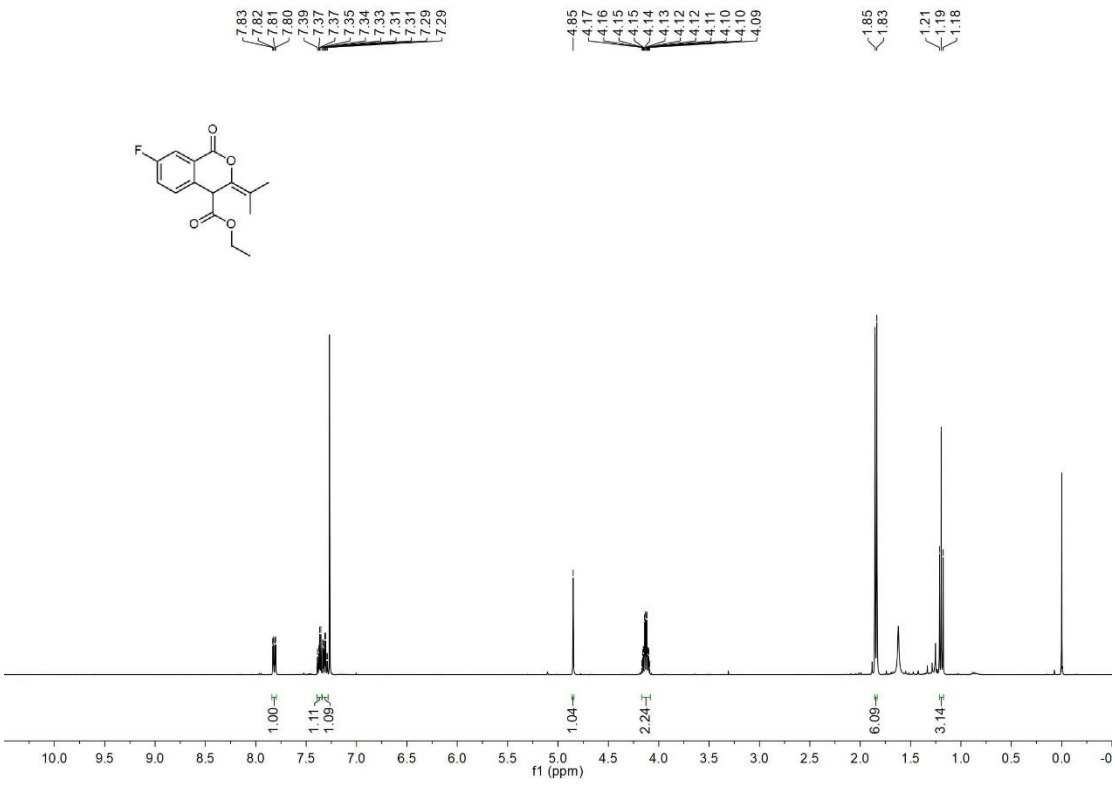
^{13}C NMR spectrum of compound **3ia**



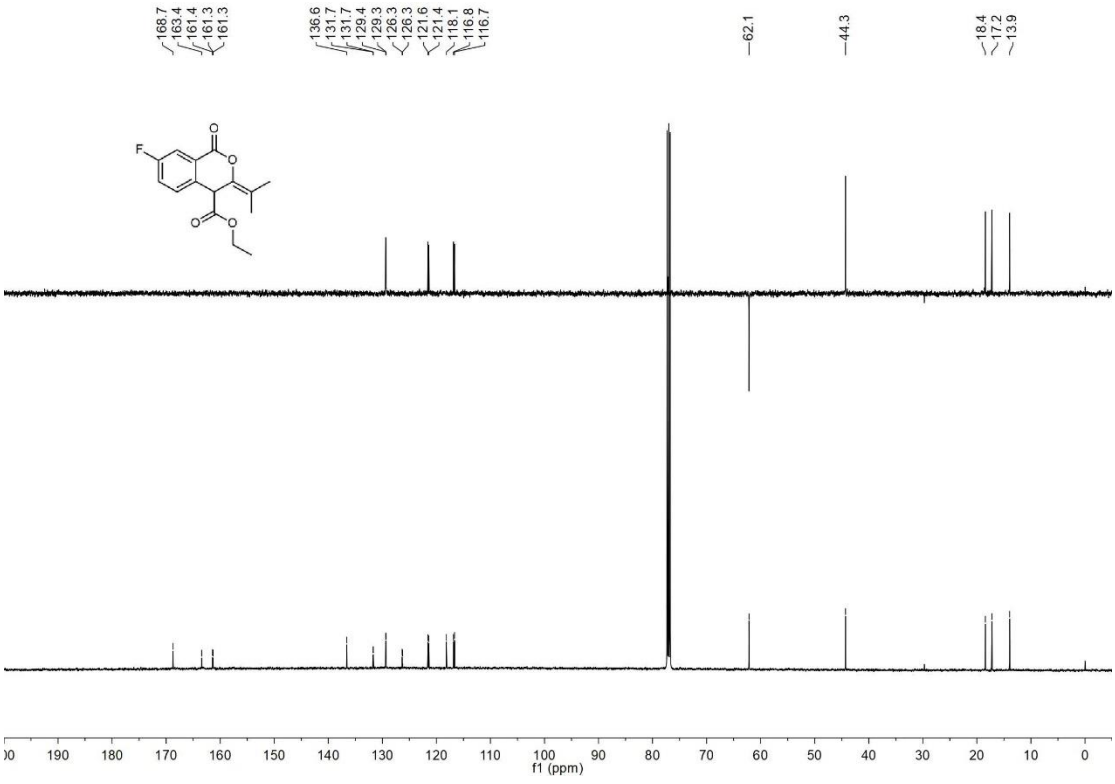
^{1}H NMR spectrum of compound **3ja**



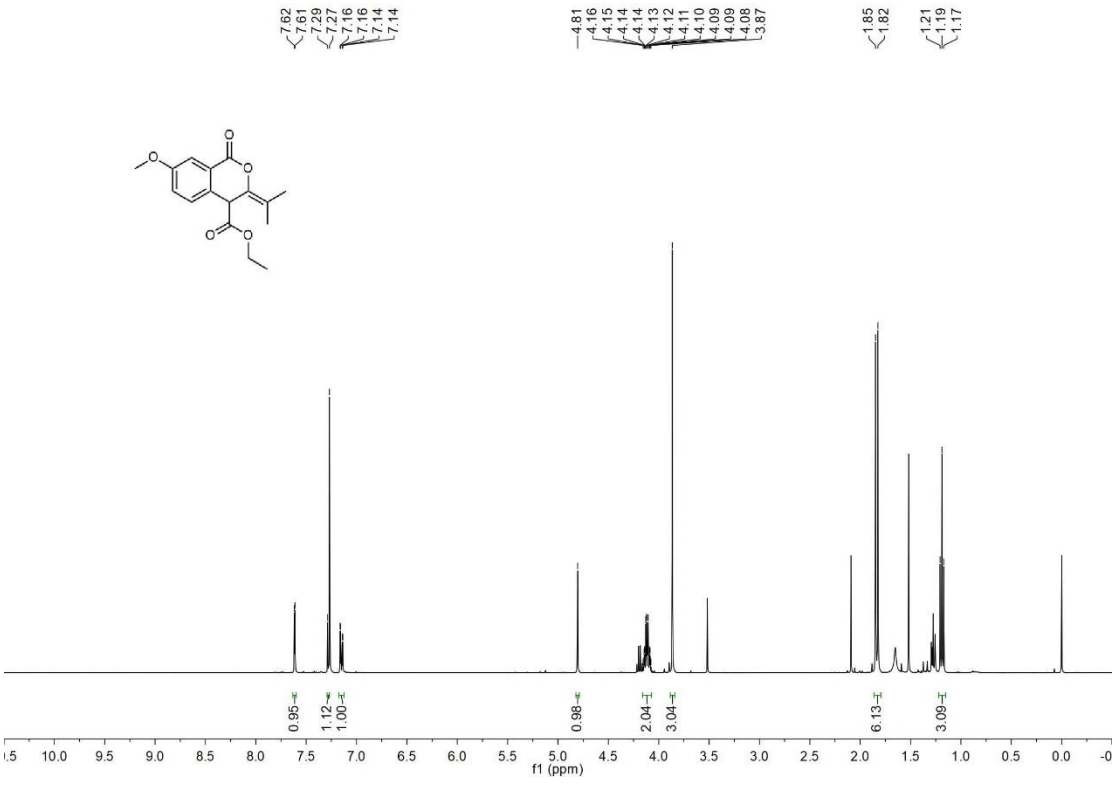
^{13}C NMR spectrum of compound **3ja**



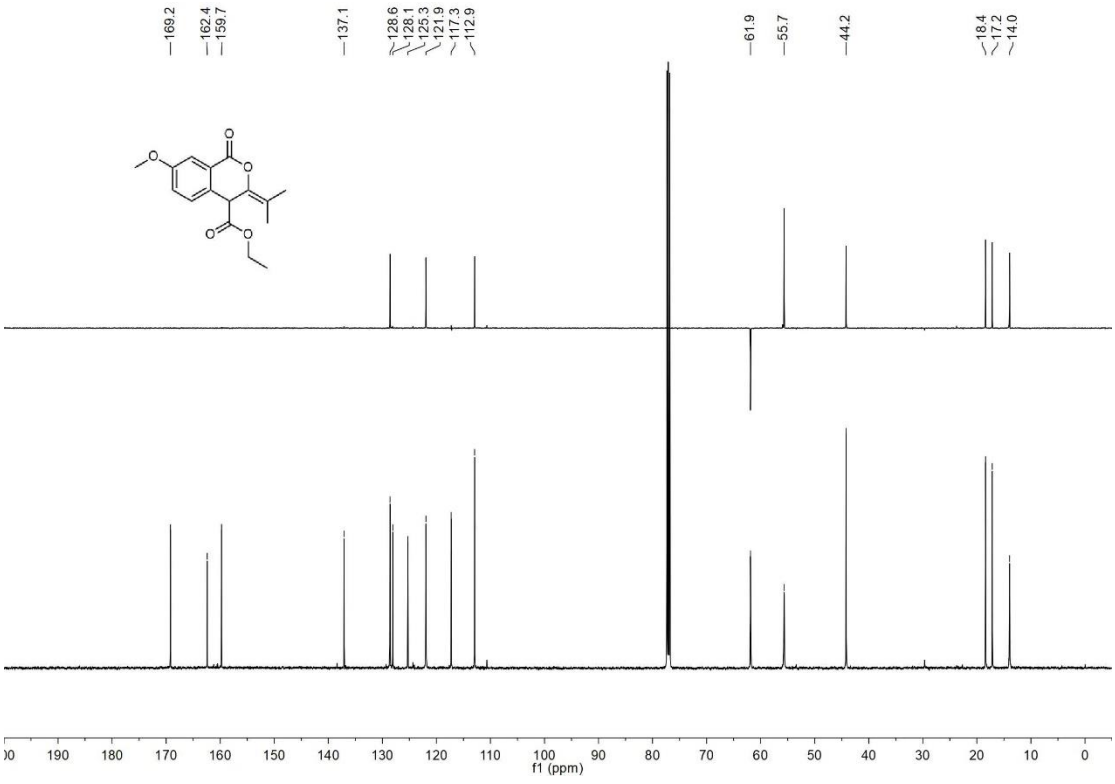
^{1}H NMR spectrum of compound **3ka**



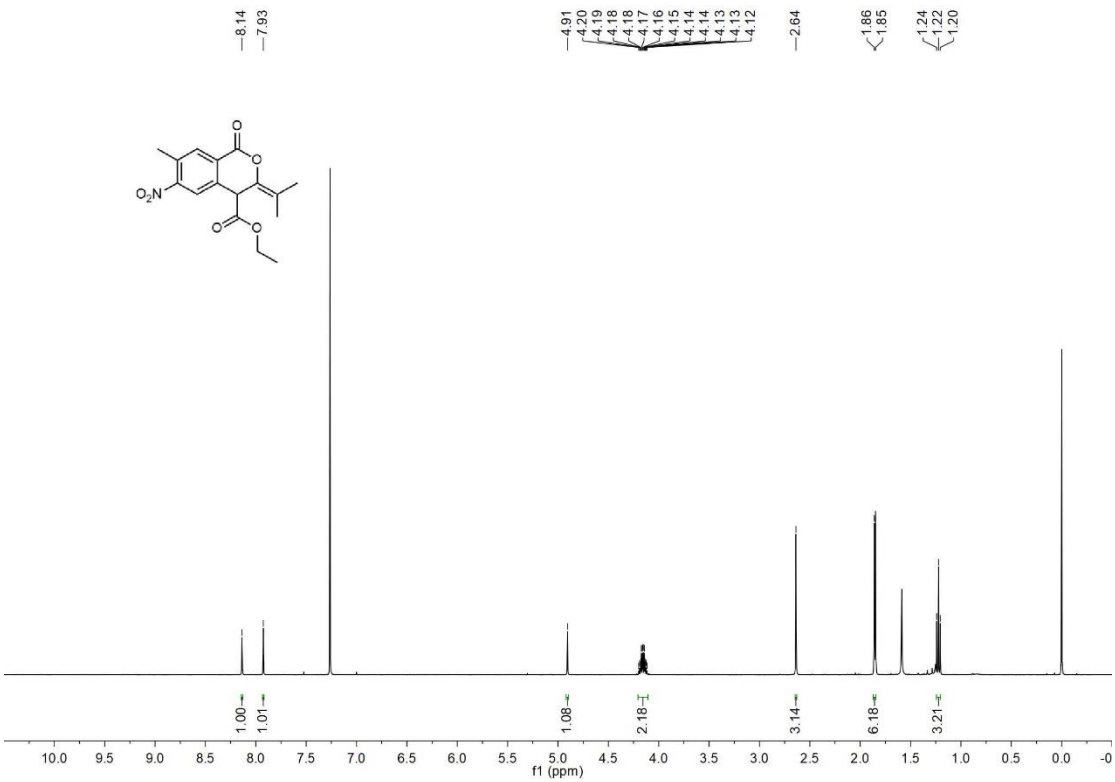
^{13}C NMR spectrum of compound **3ka**



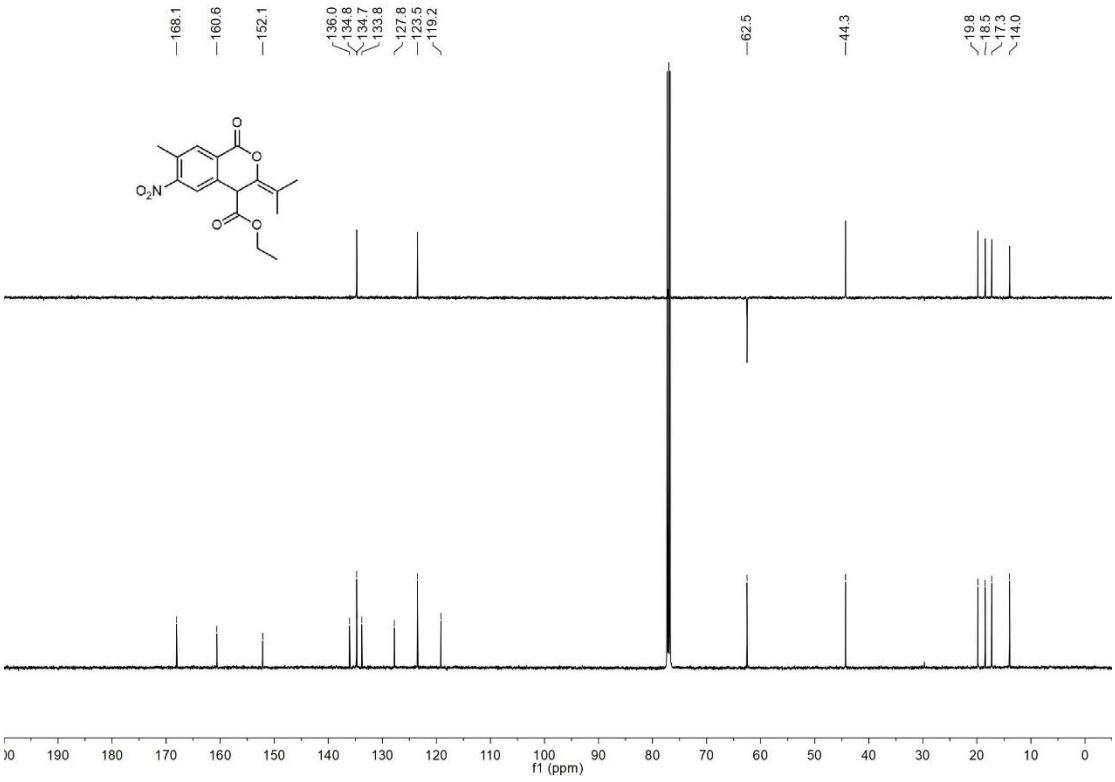
^{1}H NMR spectrum of compound **3la**



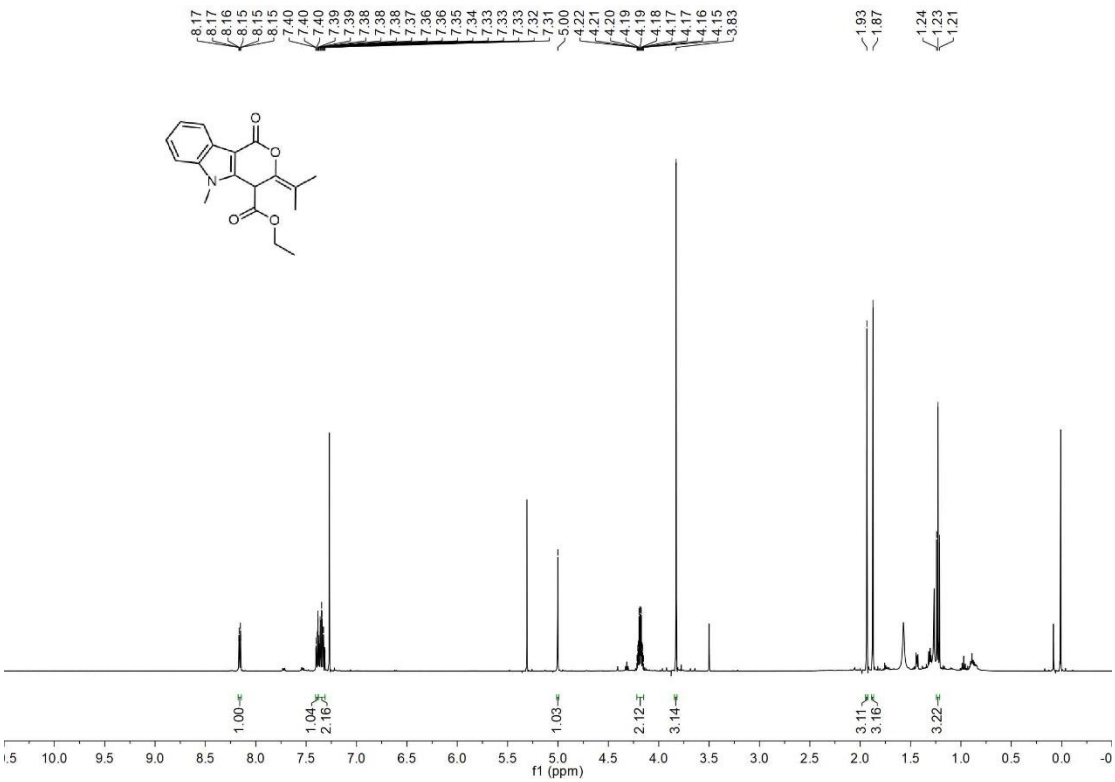
^{13}C NMR spectrum of compound **3la**



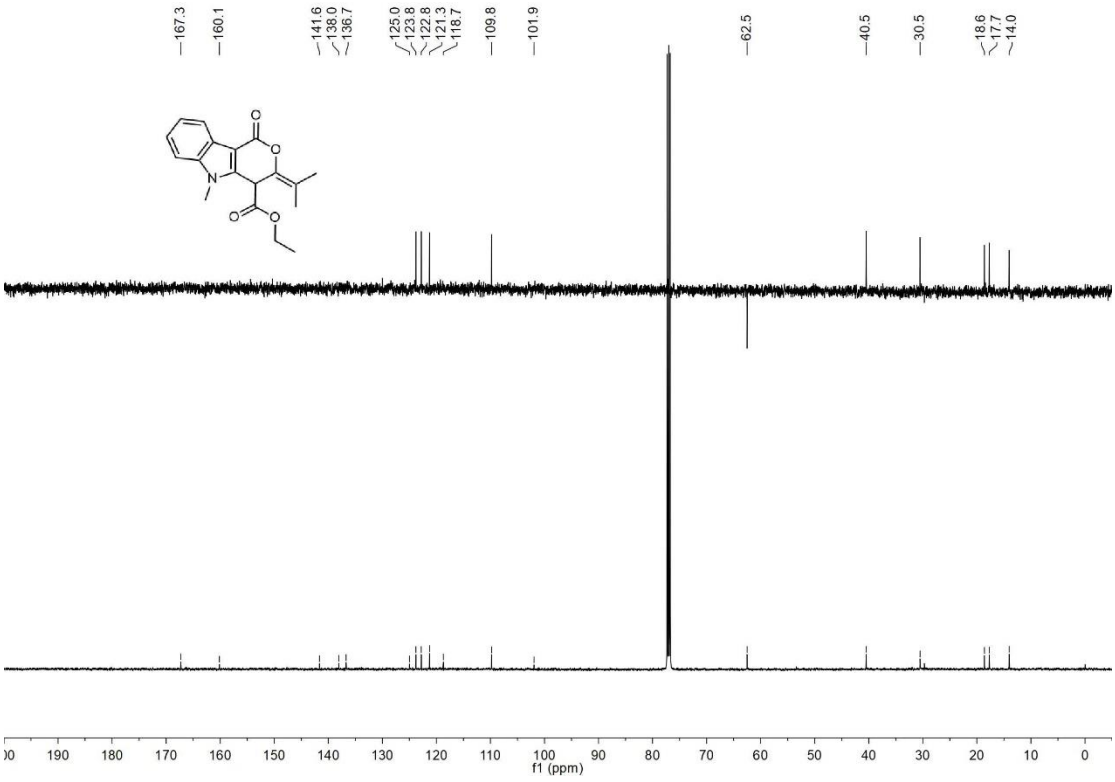
^{1}H NMR spectrum of compound **3ma**



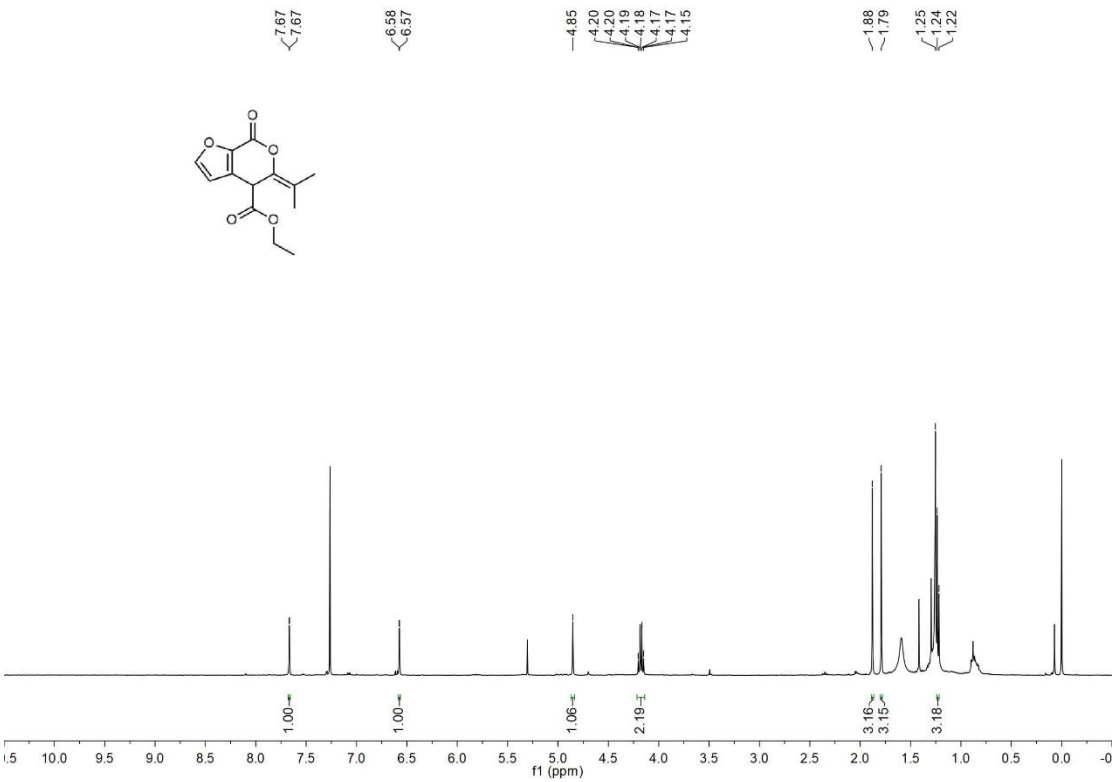
^{13}C NMR spectrum of compound **3ma**



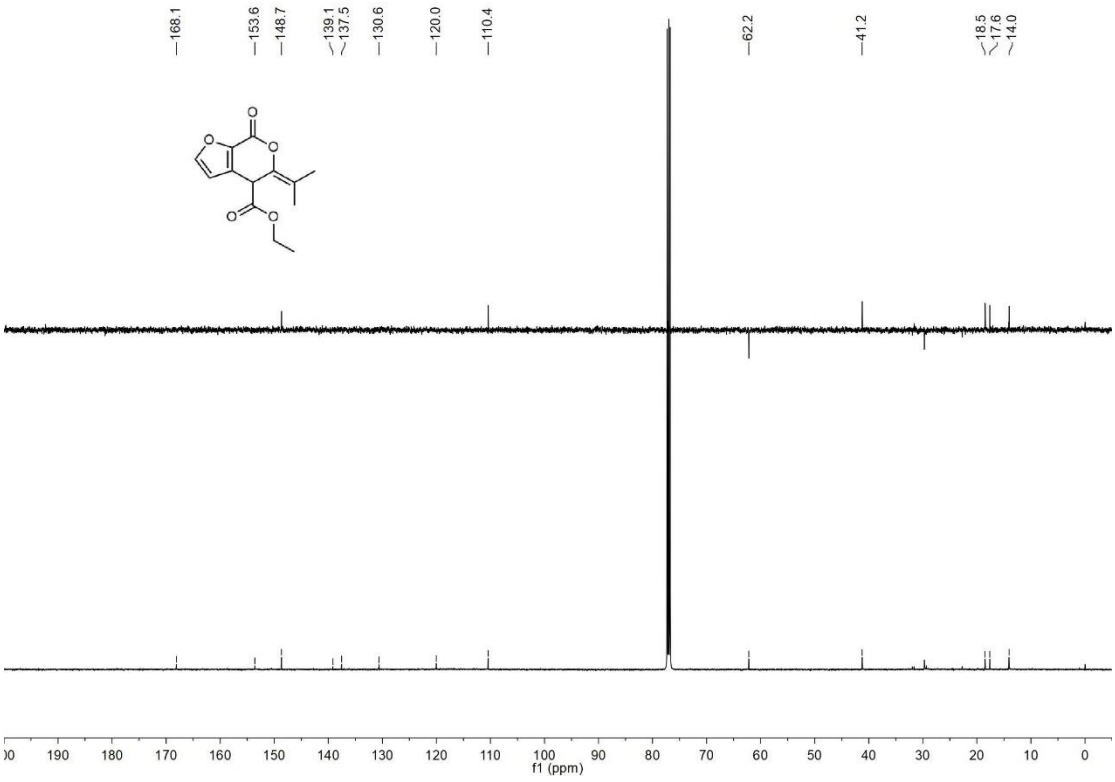
^{1}H NMR spectrum of compound **3na**



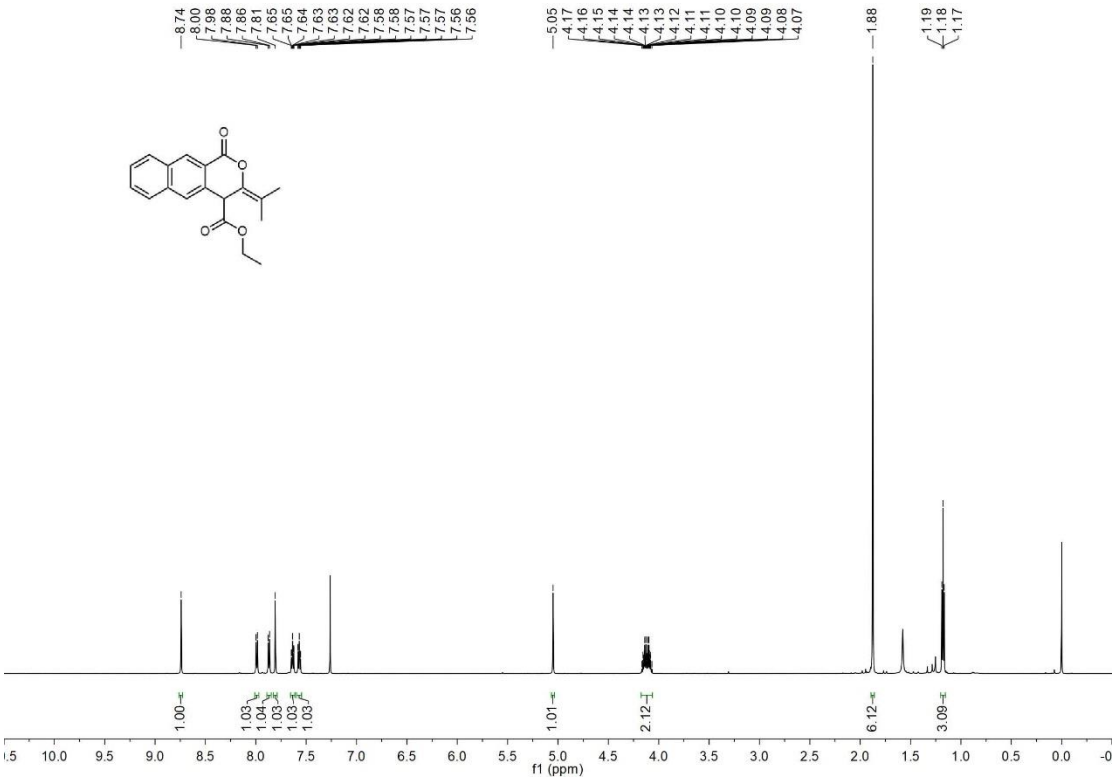
^{13}C NMR spectrum of compound **3na**



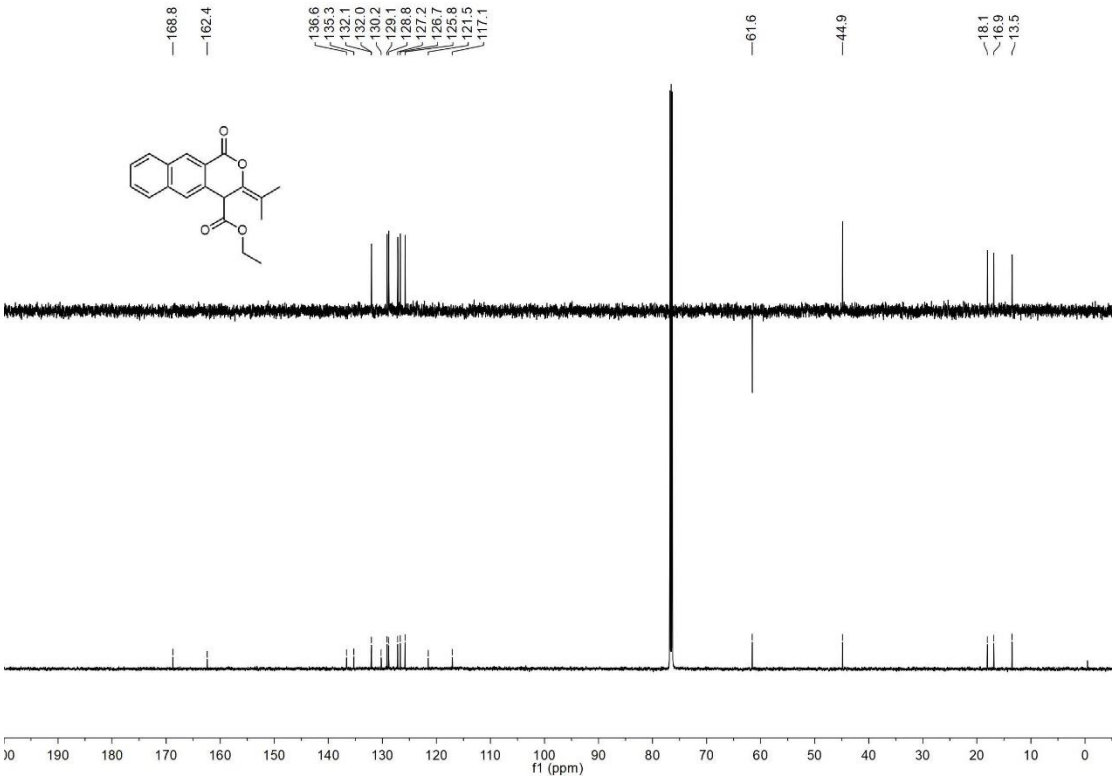
^{1}H NMR spectrum of compound **3oa**



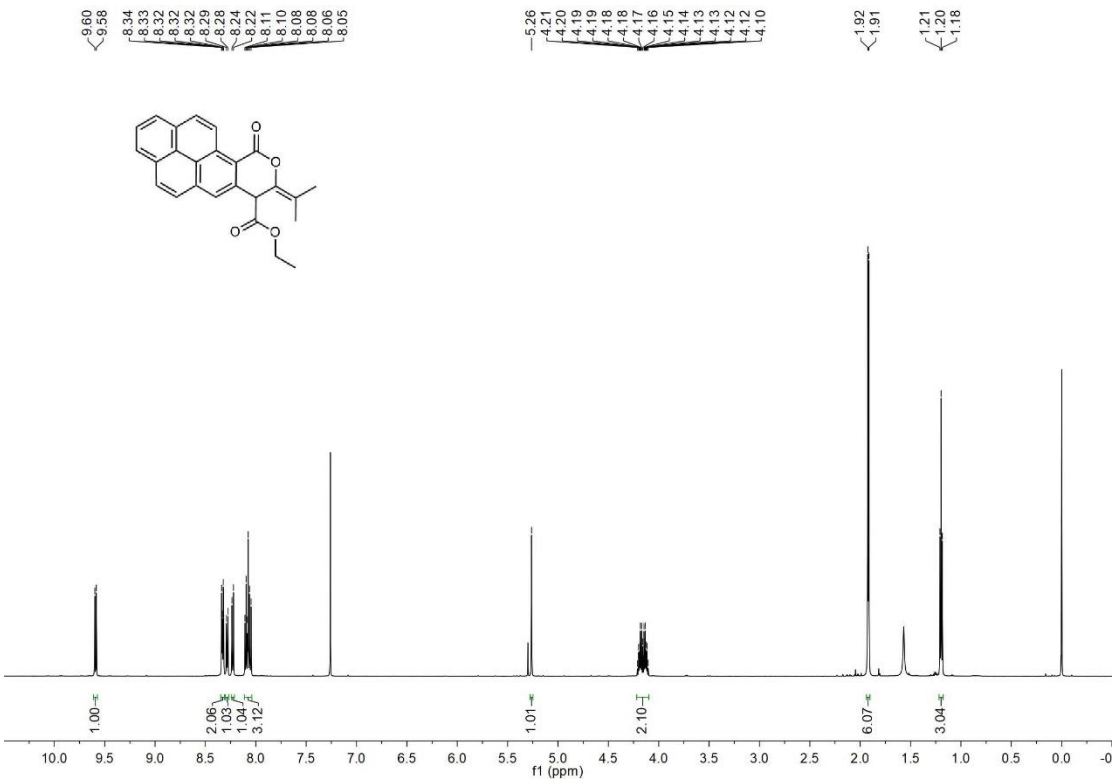
^{13}C NMR spectrum of compound **3oa**



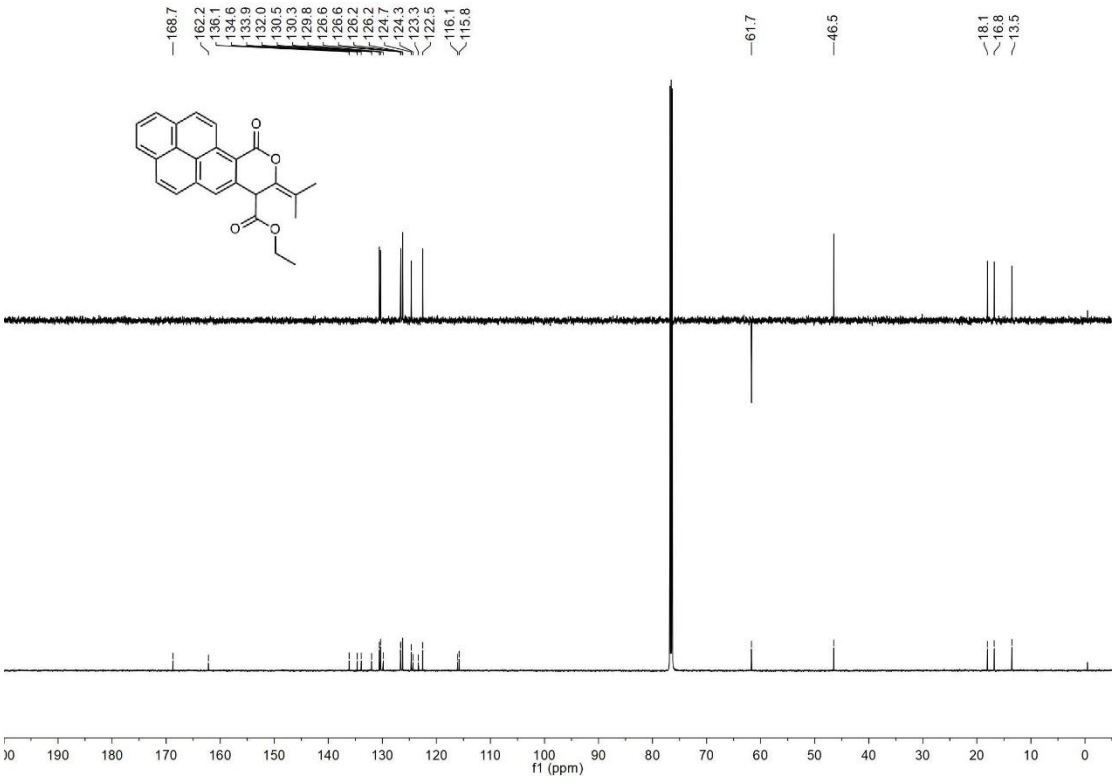
^{1}H NMR spectrum of compound **3pa**



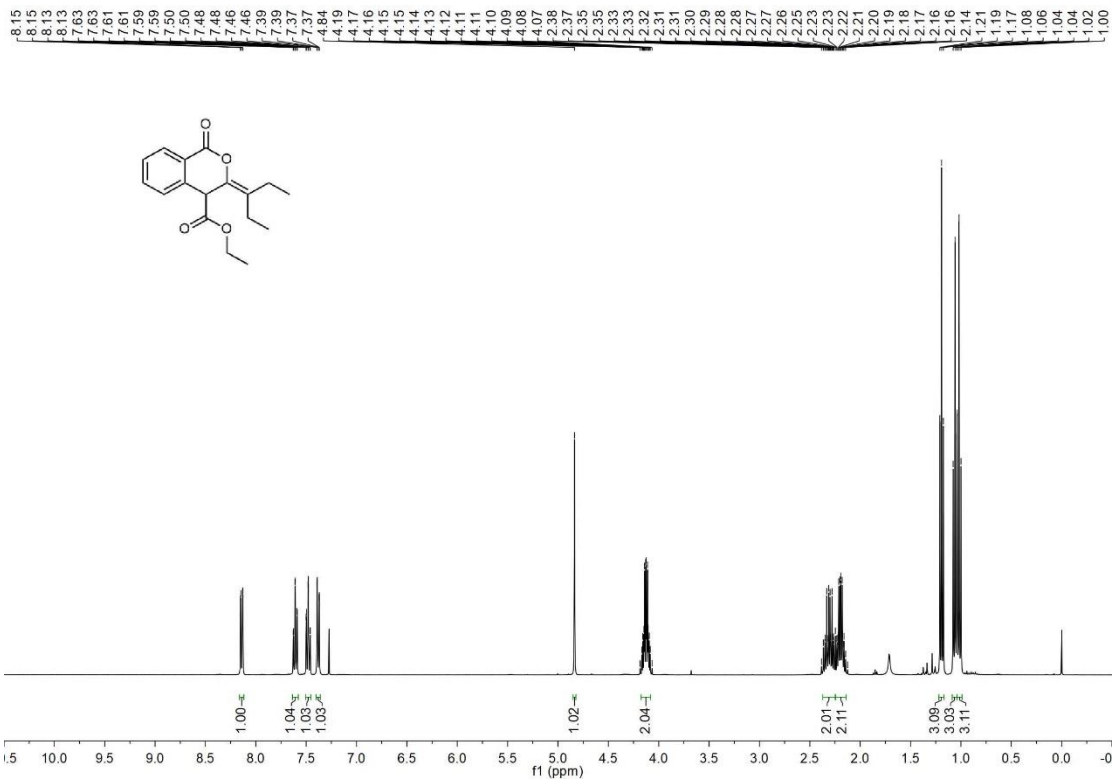
^{13}C NMR spectrum of compound **3pa**



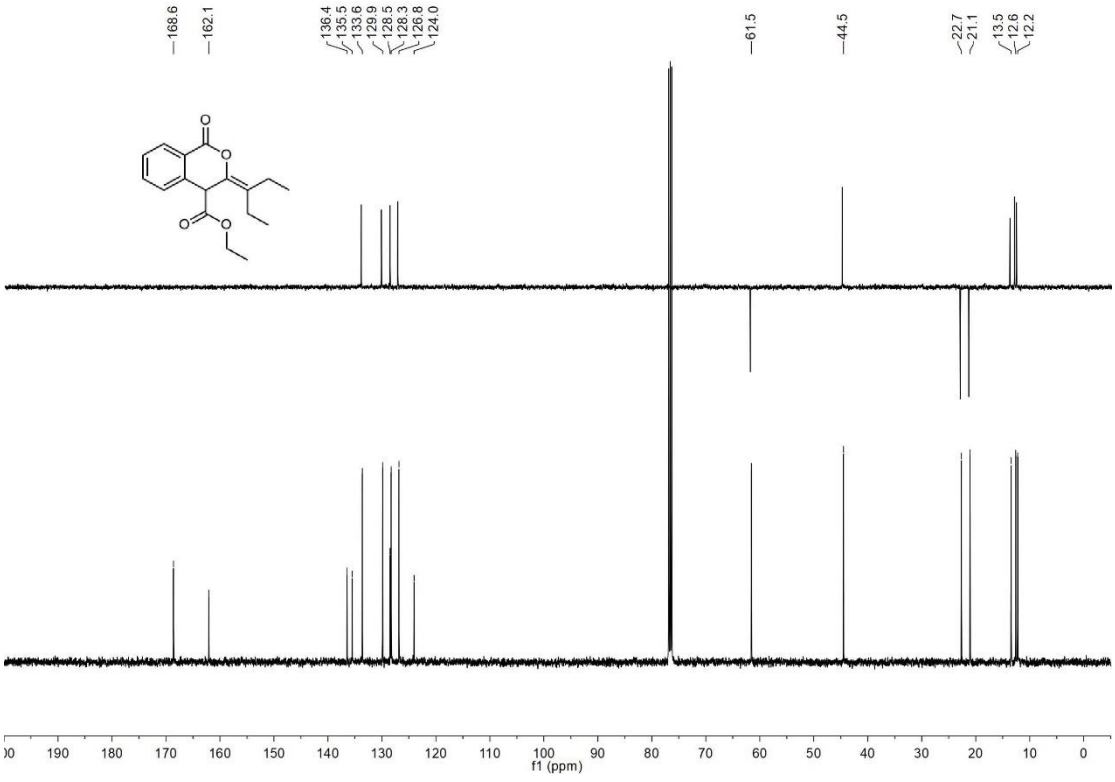
^{1}H NMR spectrum of compound **3qa**



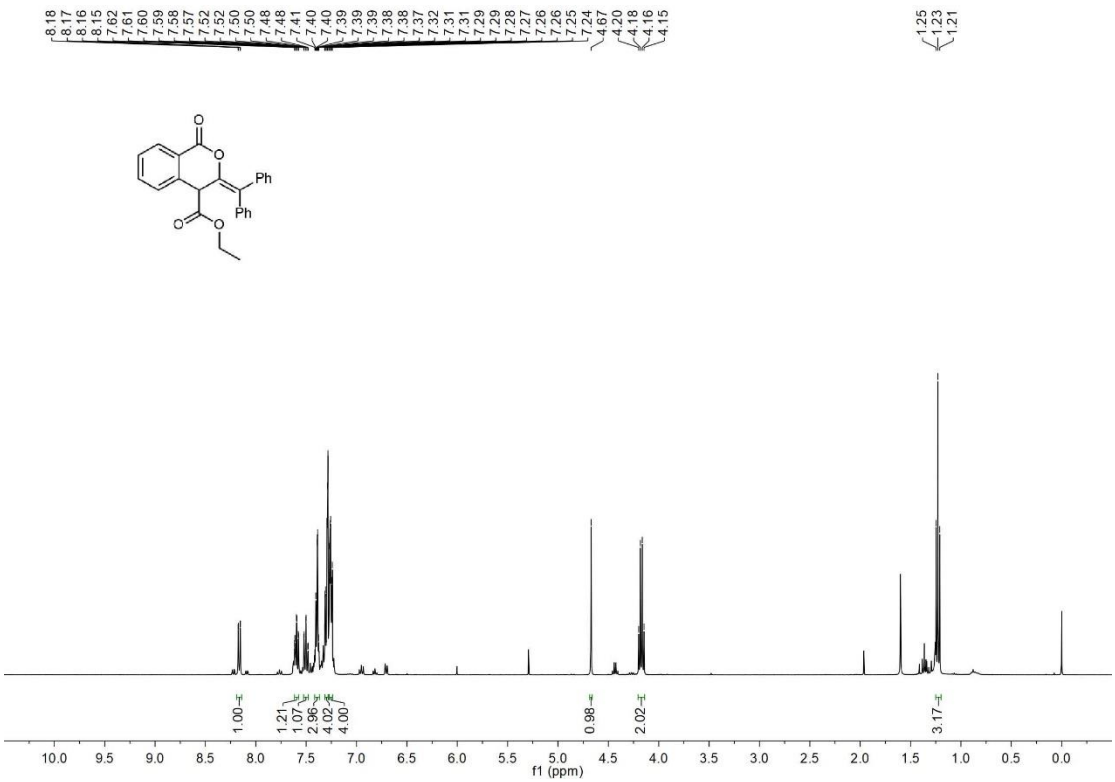
^{13}C NMR spectrum of compound **3qa**



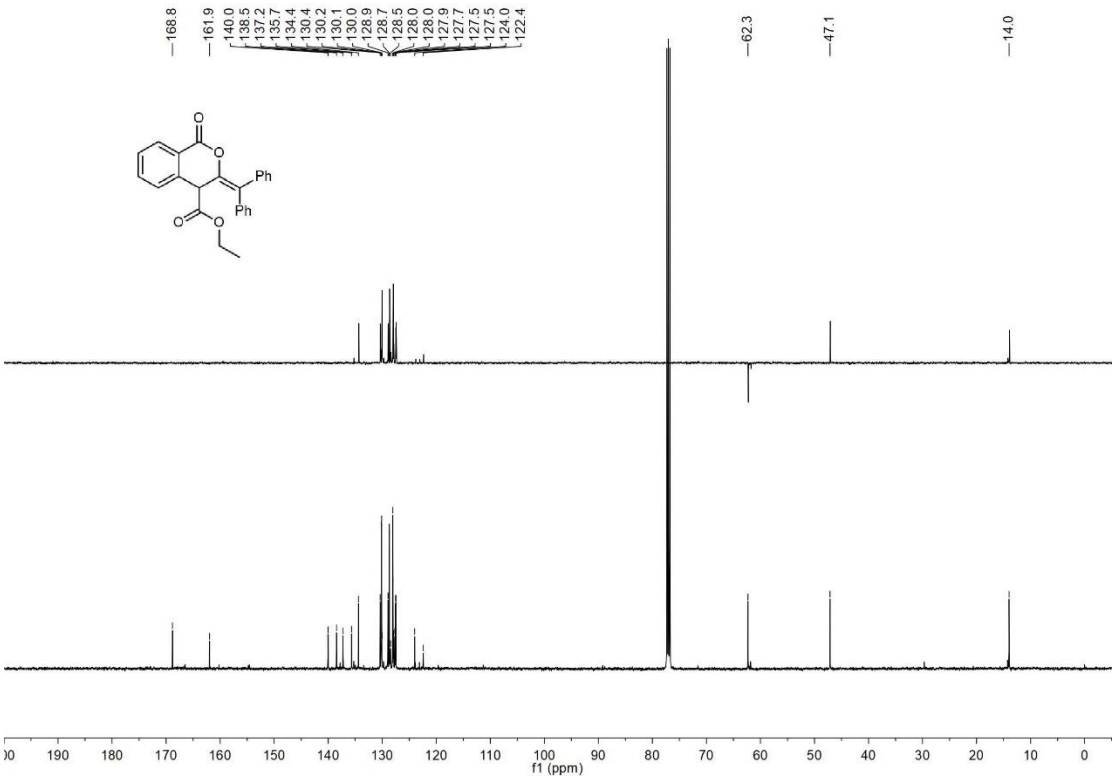
^{1}H NMR spectrum of compound **3ab**



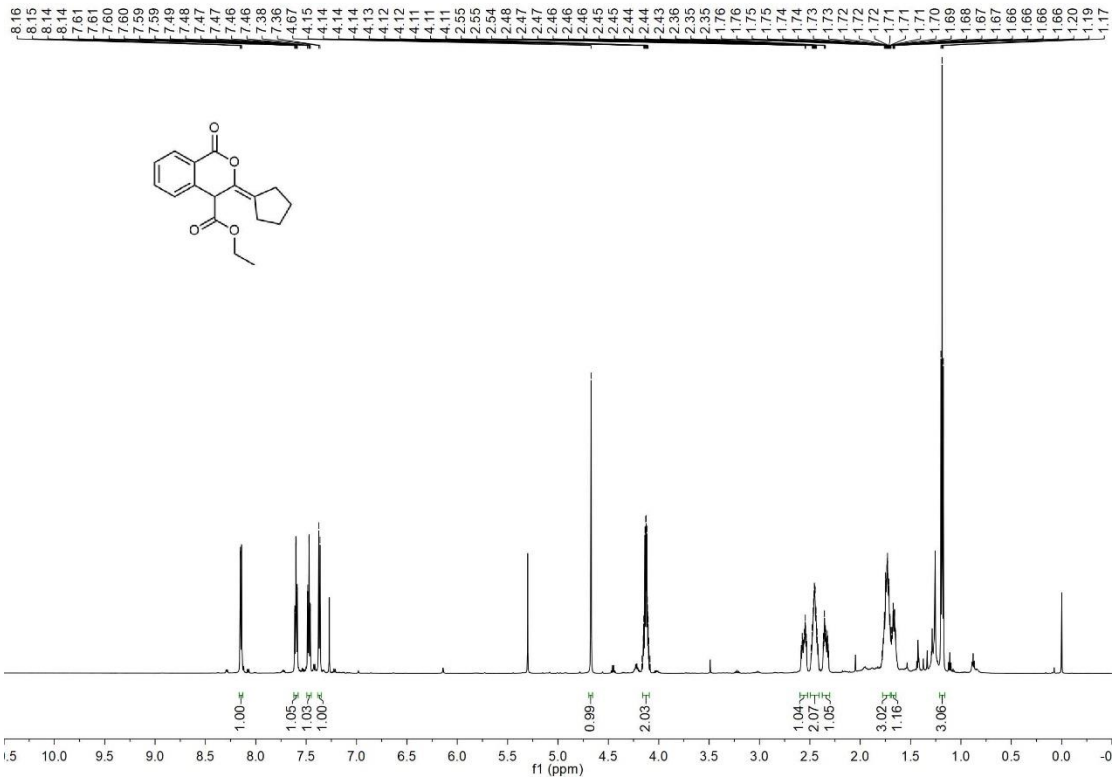
^{13}C NMR spectrum of compound **3ab**



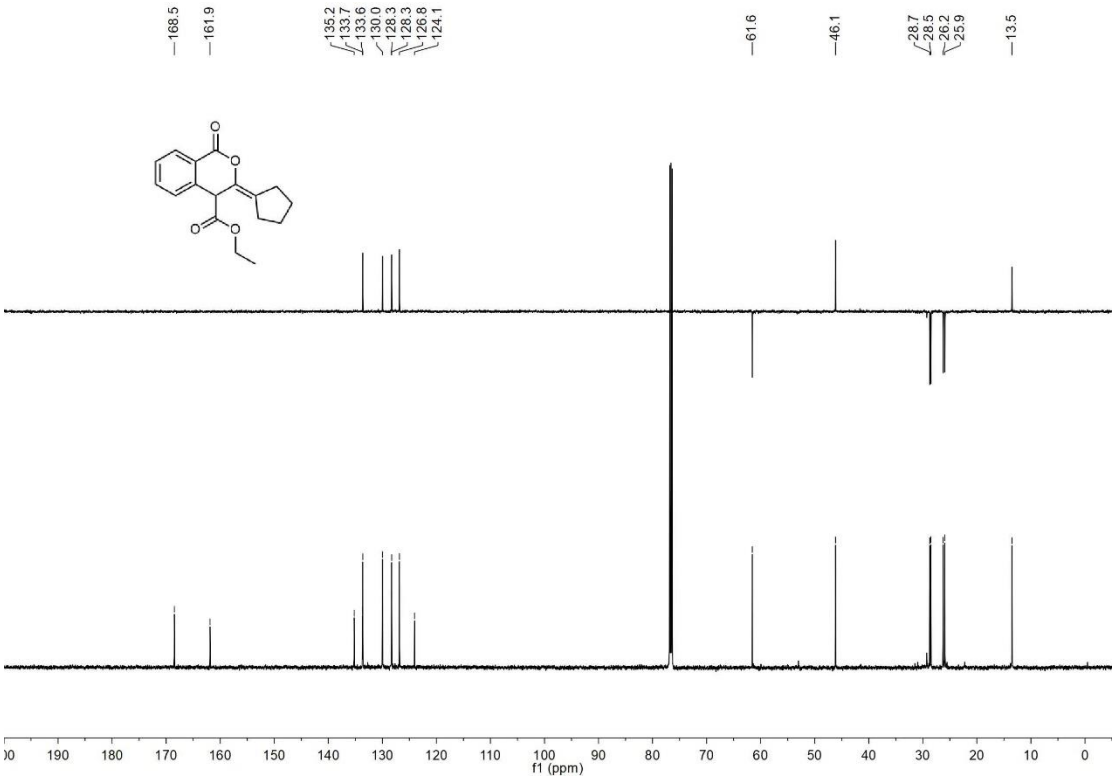
^{1}H NMR spectrum of compound **3ac**



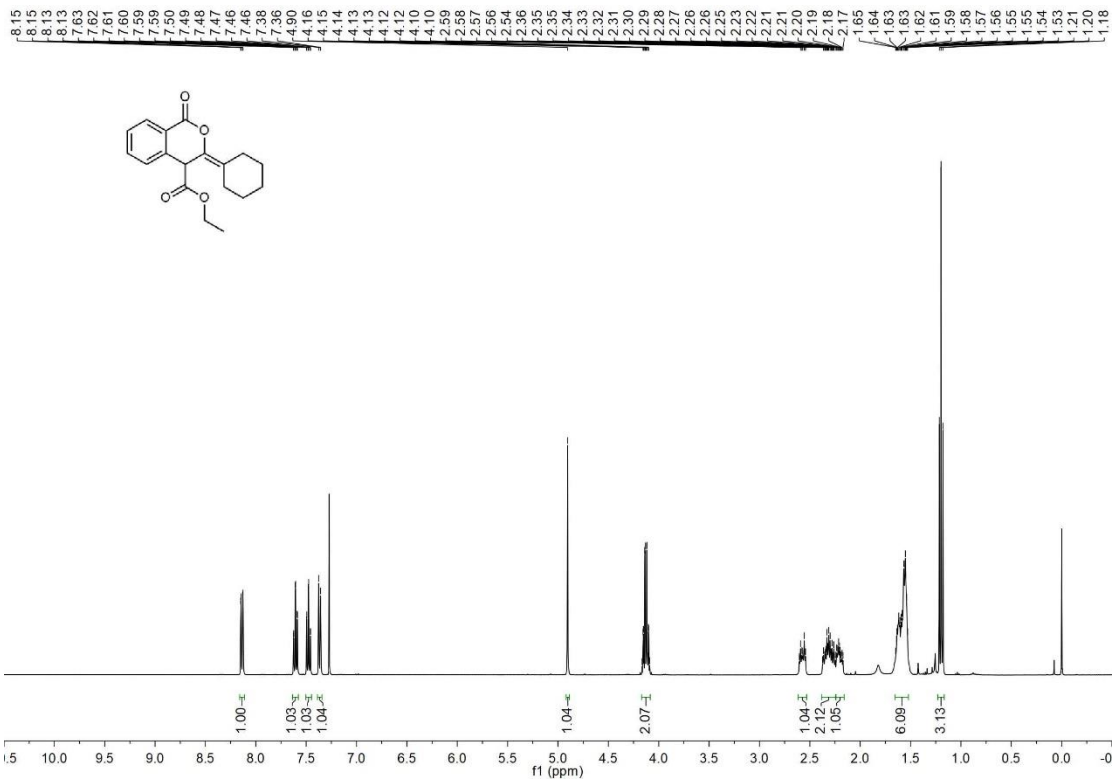
^{13}C NMR spectrum of compound **3ac**



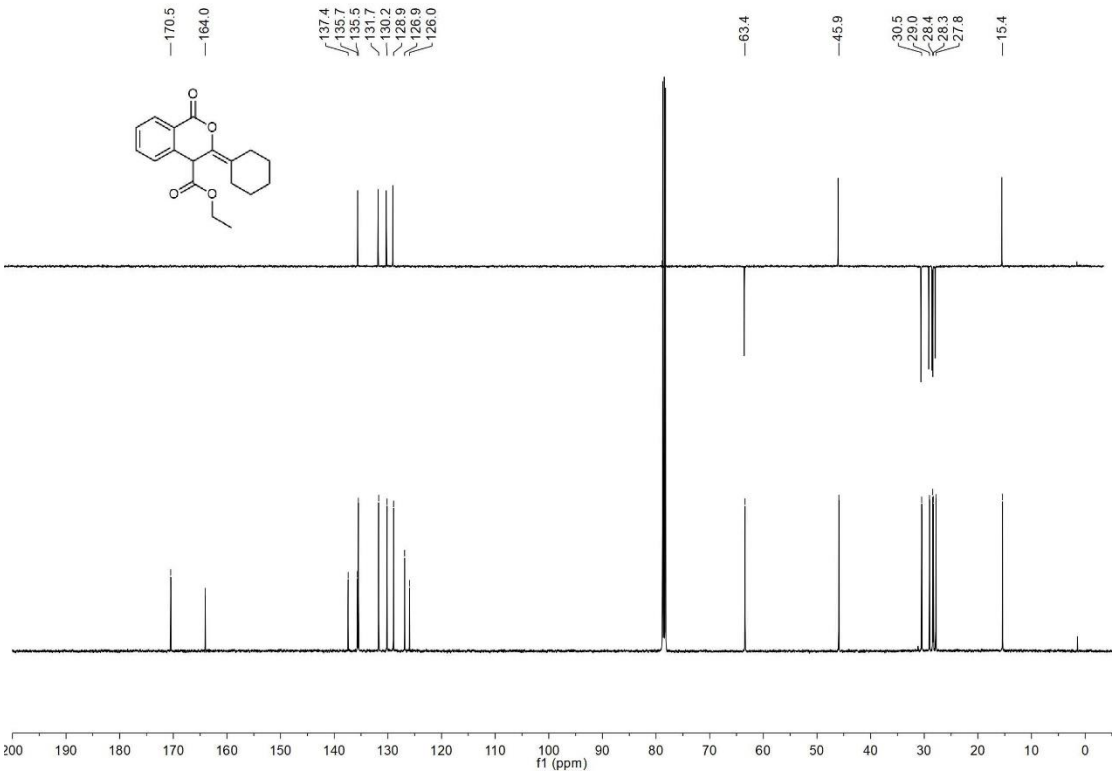
^{1}H NMR spectrum of compound **3ad**



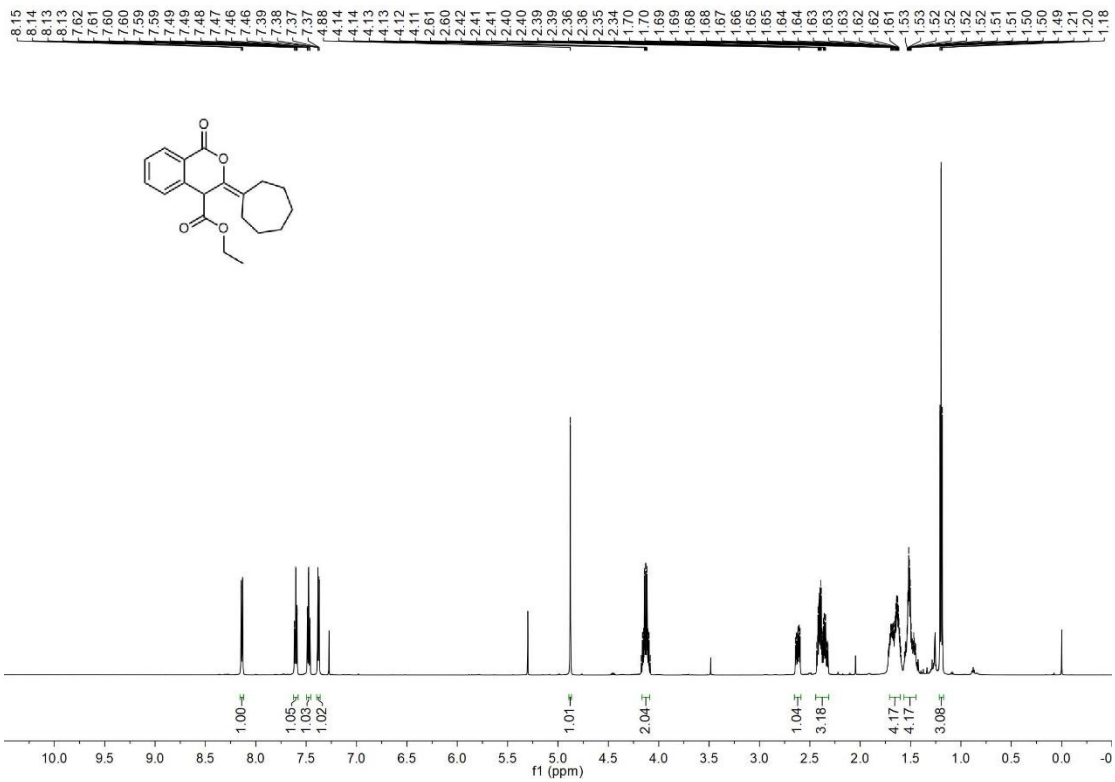
^{13}C NMR spectrum of compound **3ad**



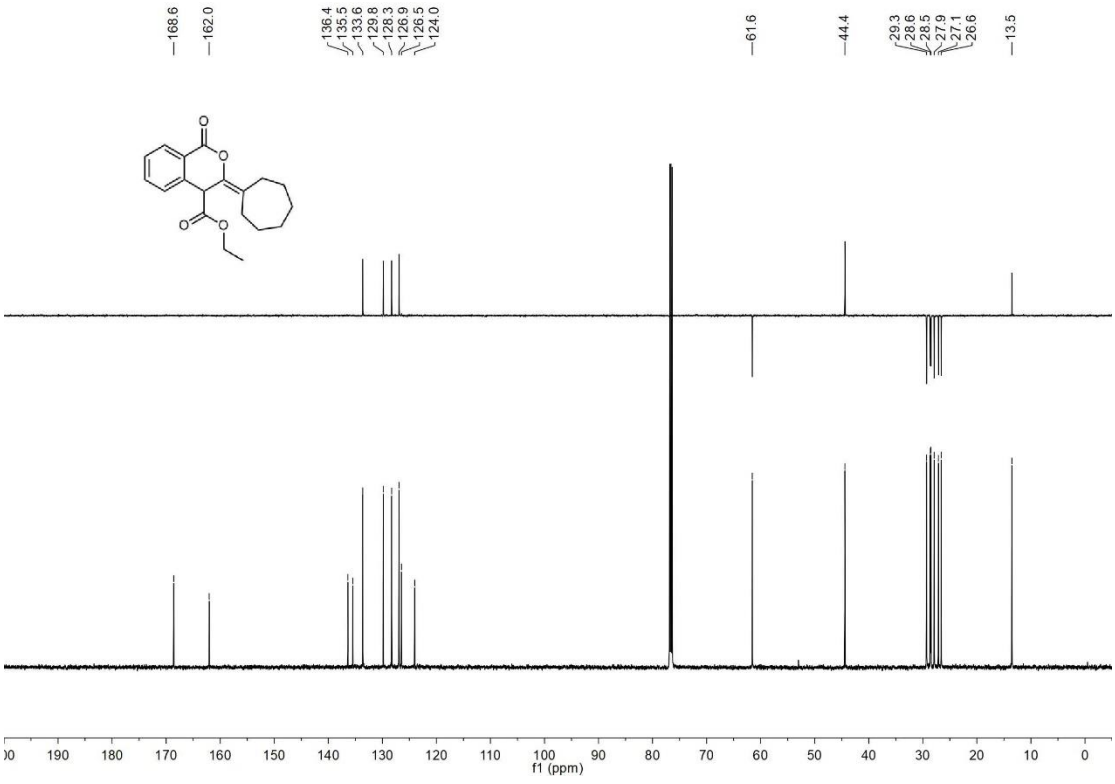
^{1}H NMR spectrum of compound **3ae**



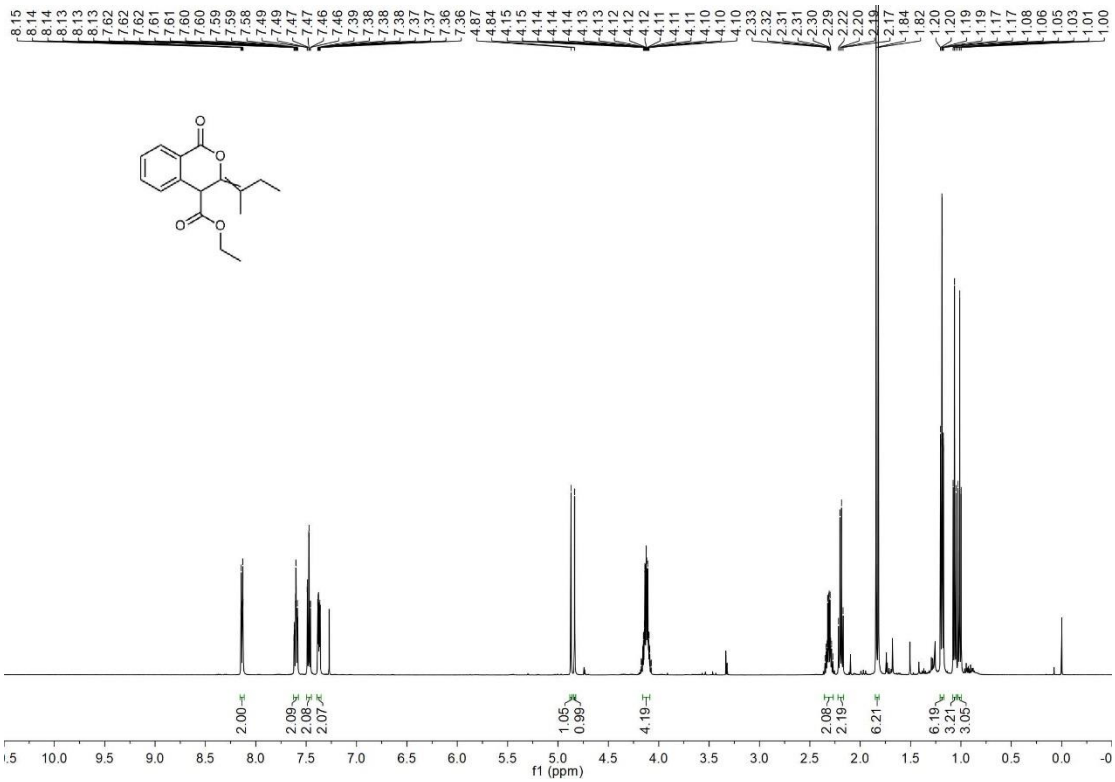
^{13}C NMR spectrum of compound **3ae**



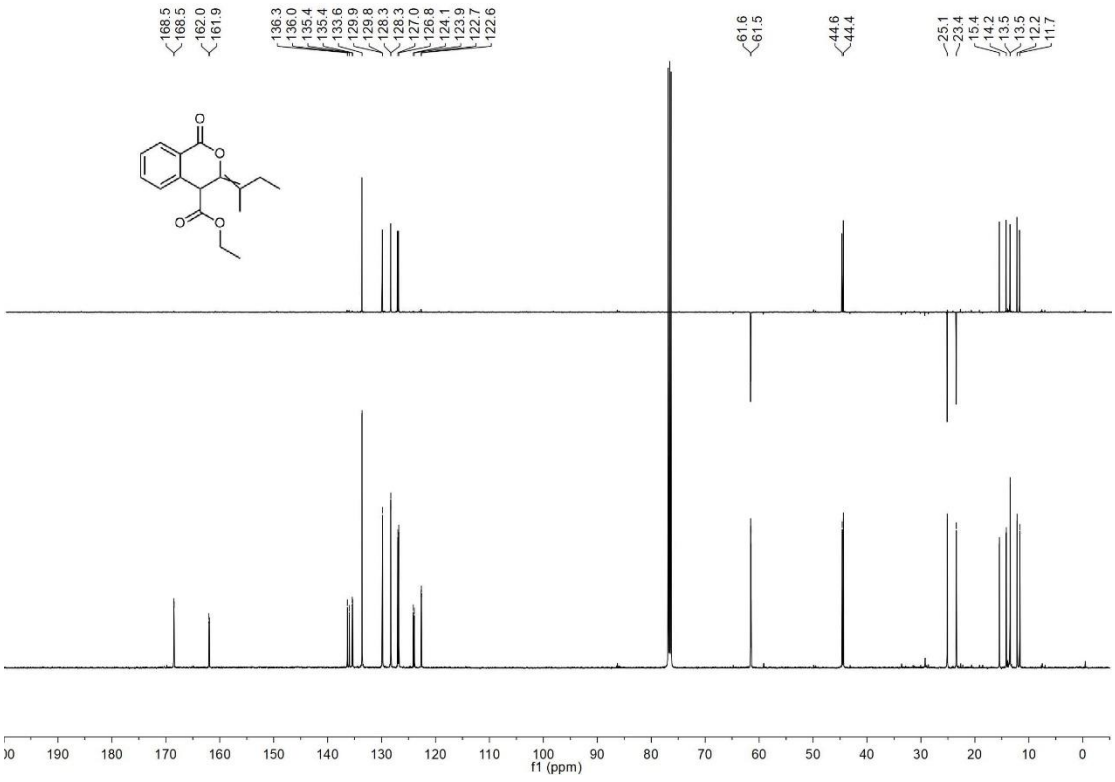
^{1}H NMR spectrum of compound **3af**



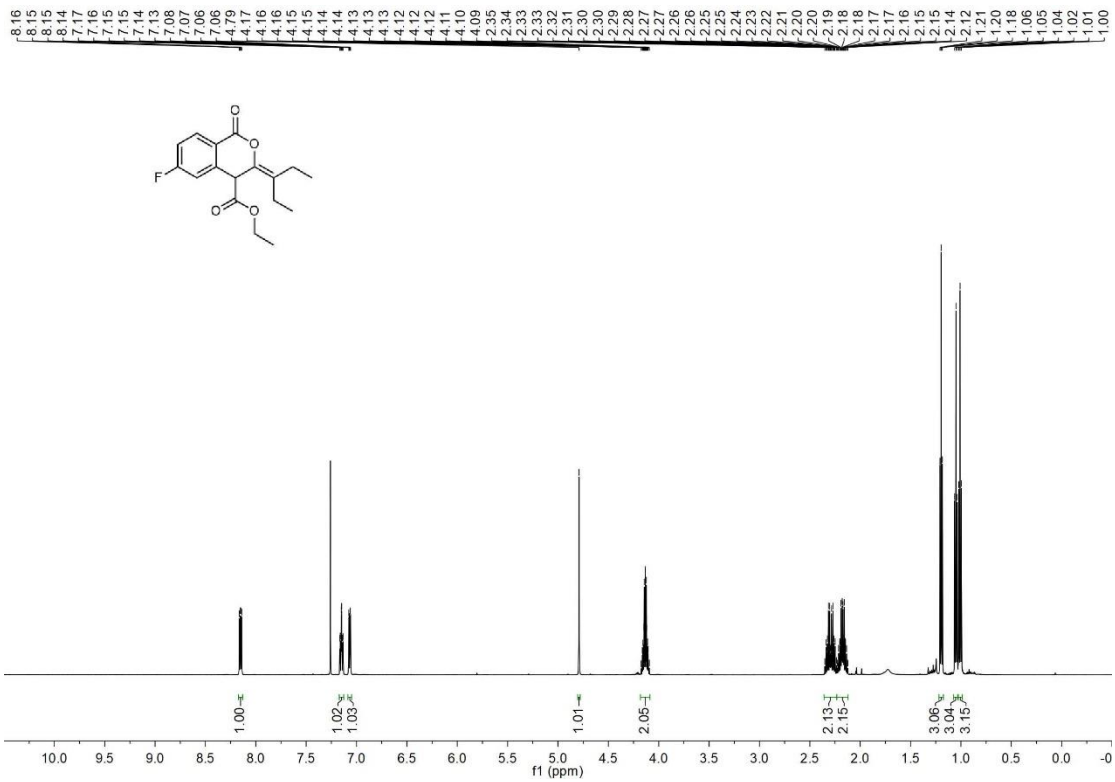
^{13}C NMR spectrum of compound **3af**



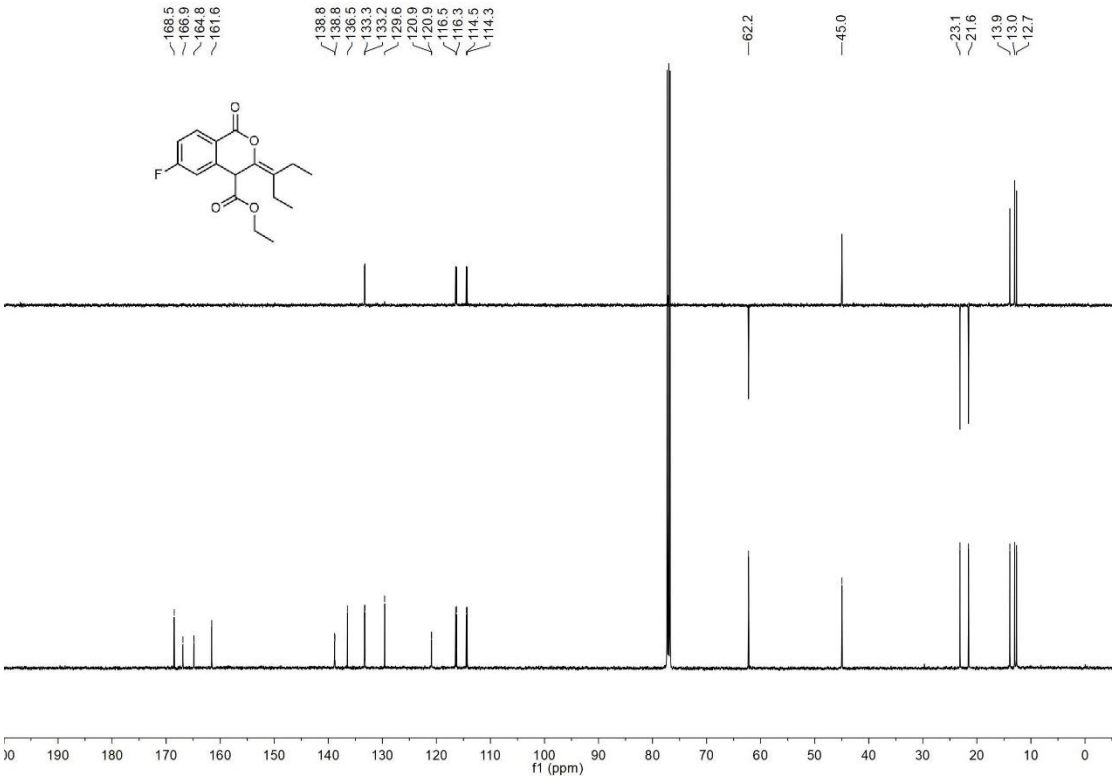
^{1}H NMR spectrum of compound **3ag**



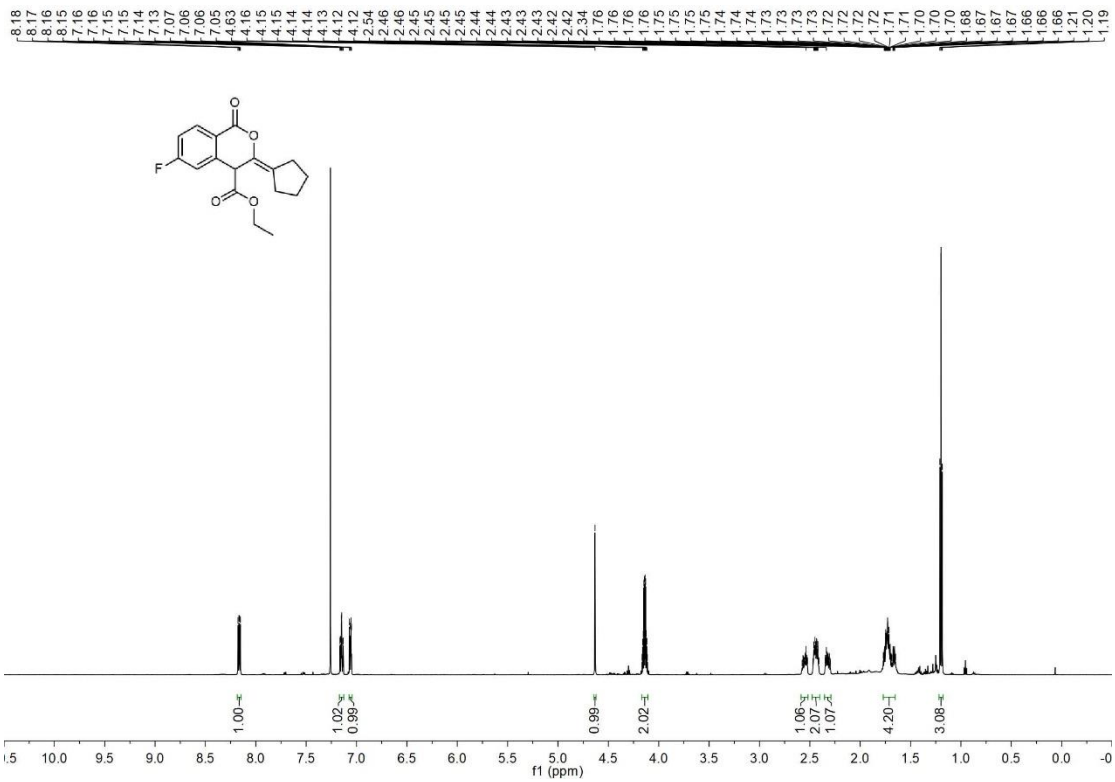
^{13}C NMR spectrum of compound **3ag**



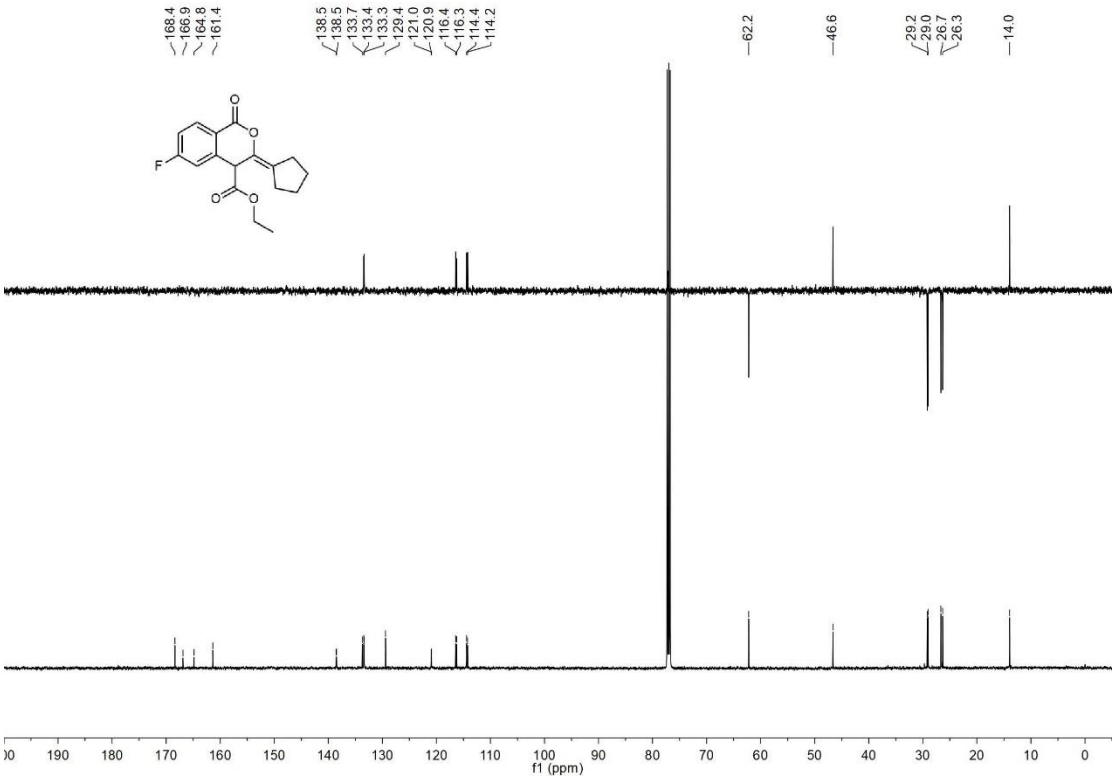
^{1}H NMR spectrum of compound **3bb**



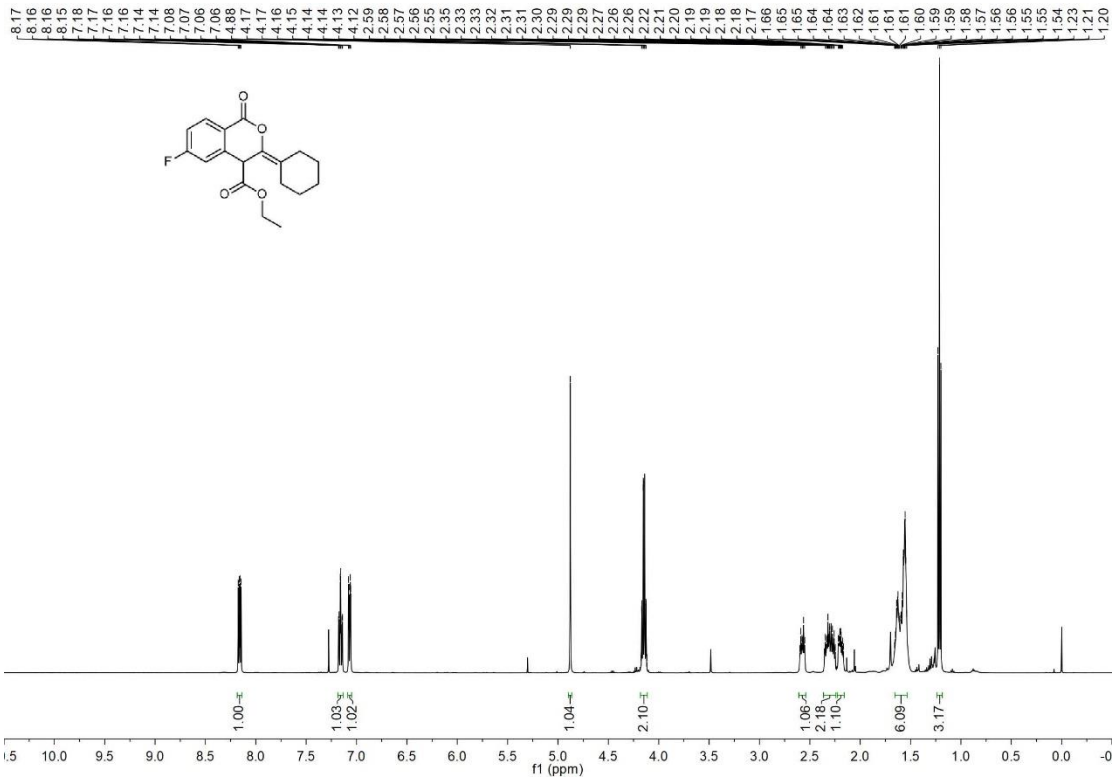
^{13}C NMR spectrum of compound **3bb**



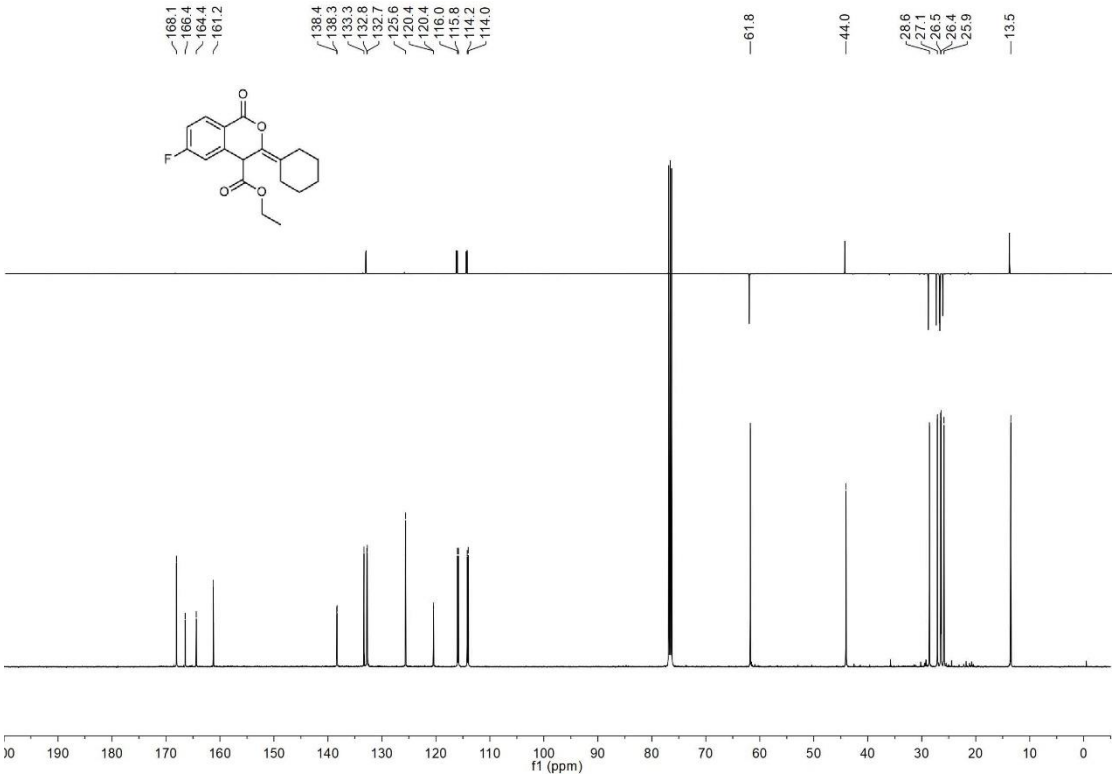
^{1}H NMR spectrum of compound **3bd**



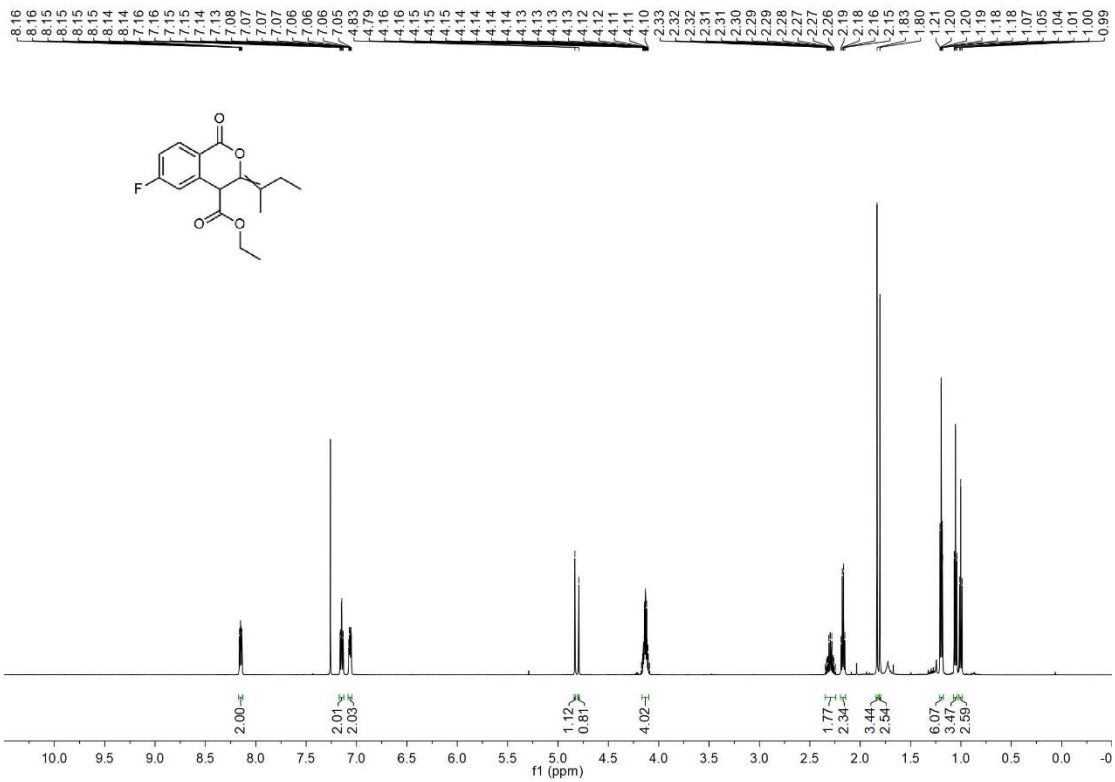
^{13}C NMR spectrum of compound **3bd**



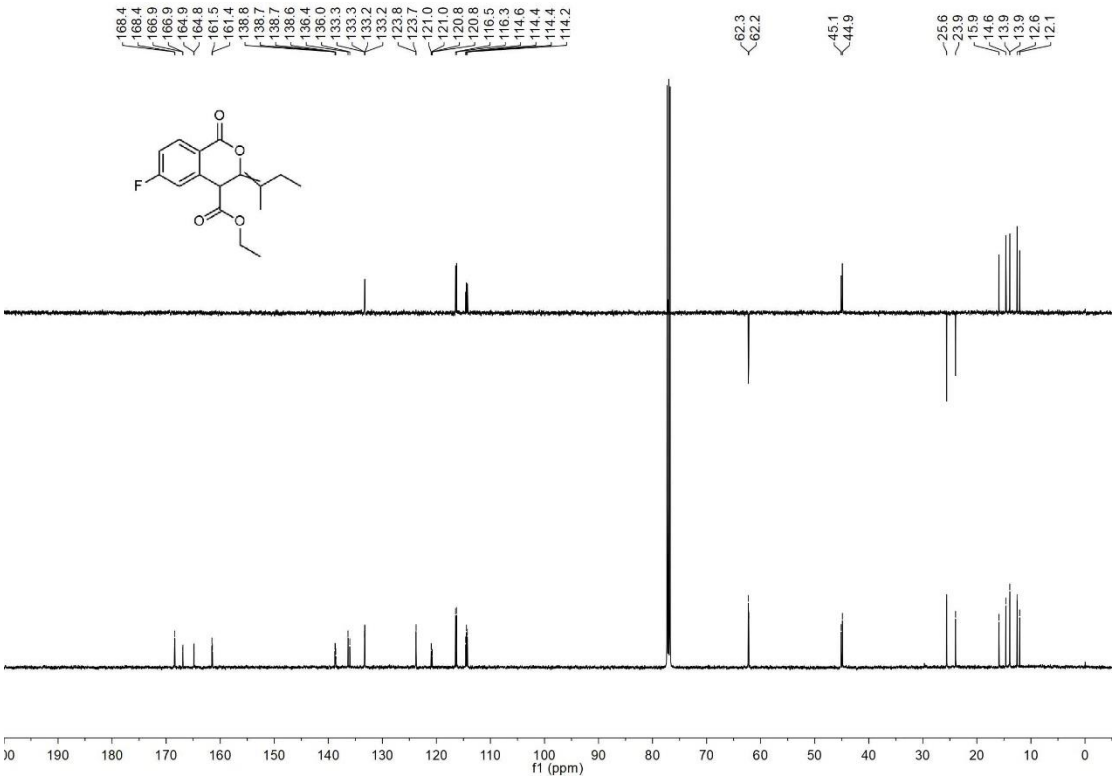
^{1}H NMR spectrum of compound **3be**



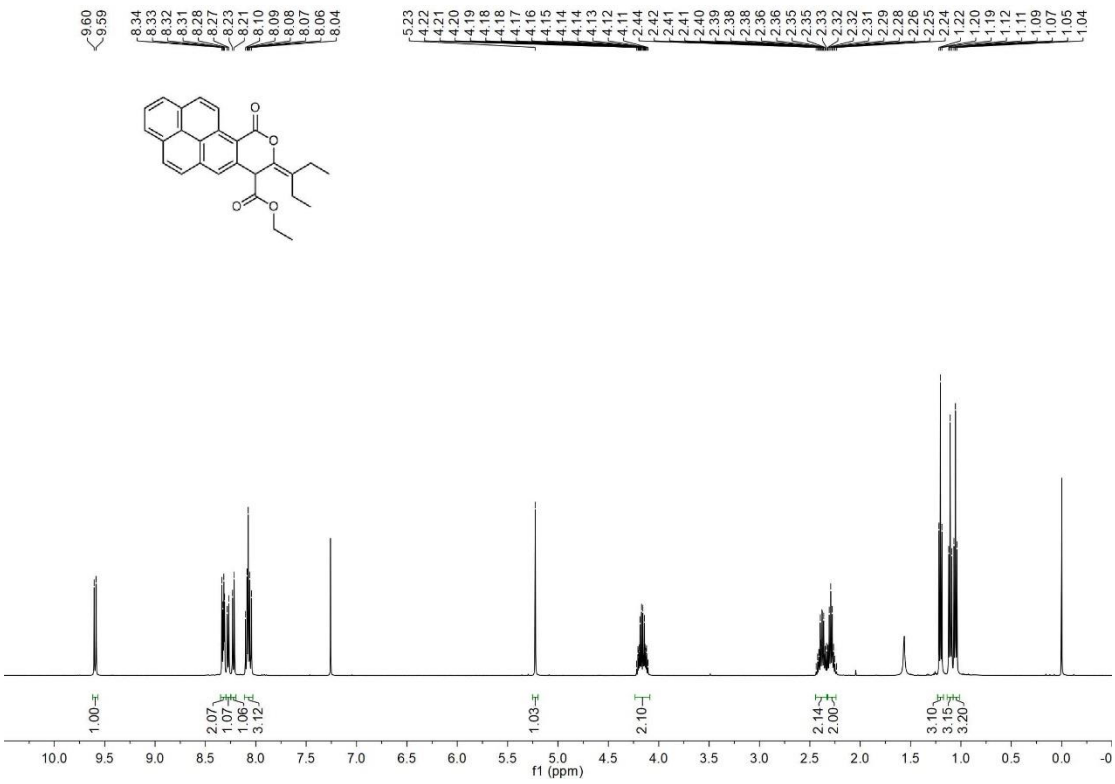
^{13}C NMR spectrum of compound **3be**



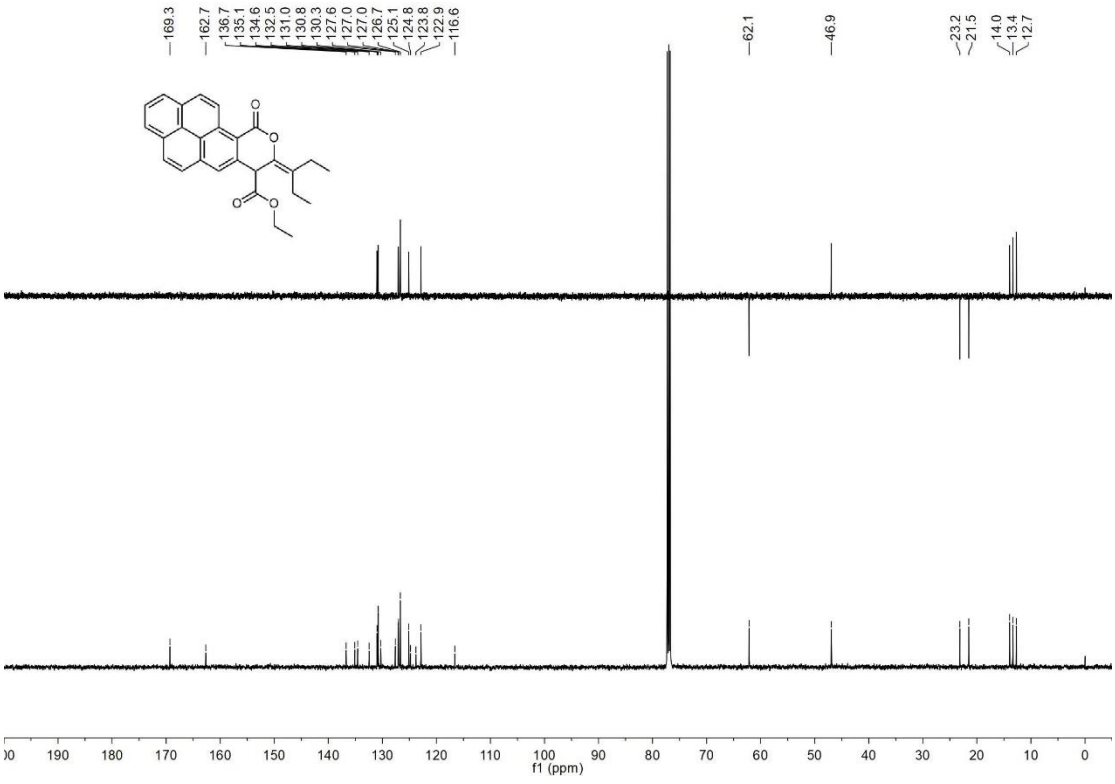
^{1}H NMR spectrum of compound **3bg**



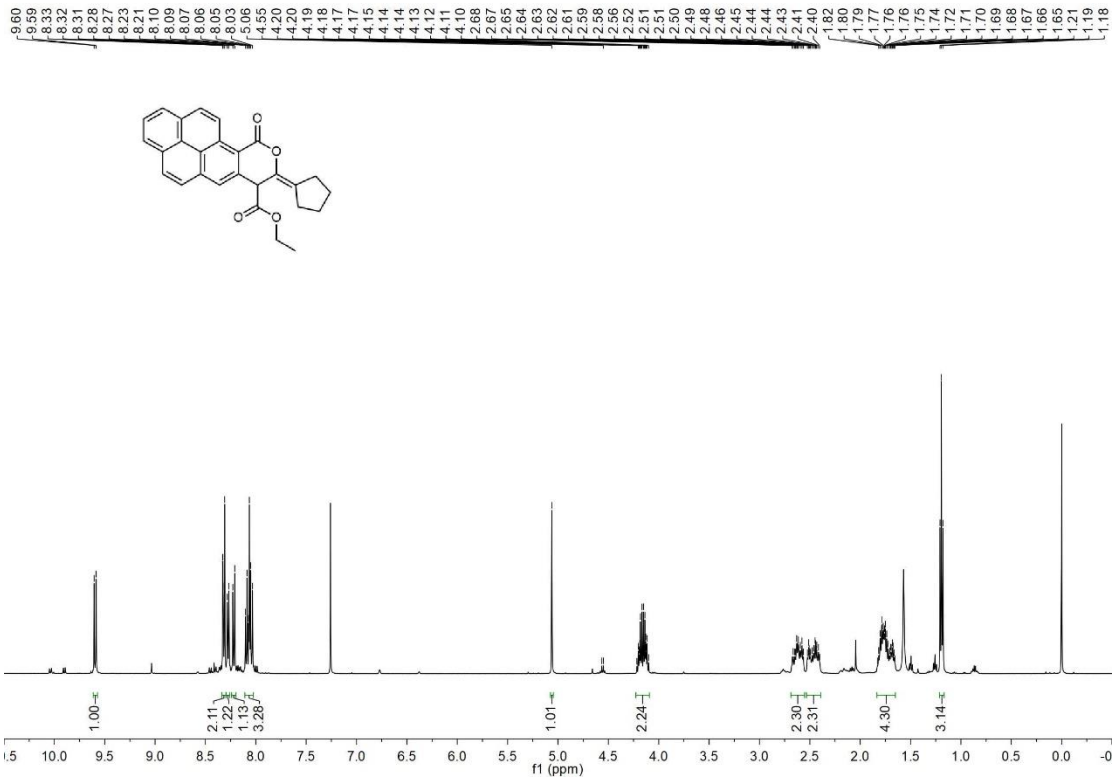
^{13}C NMR spectrum of compound **3bg**



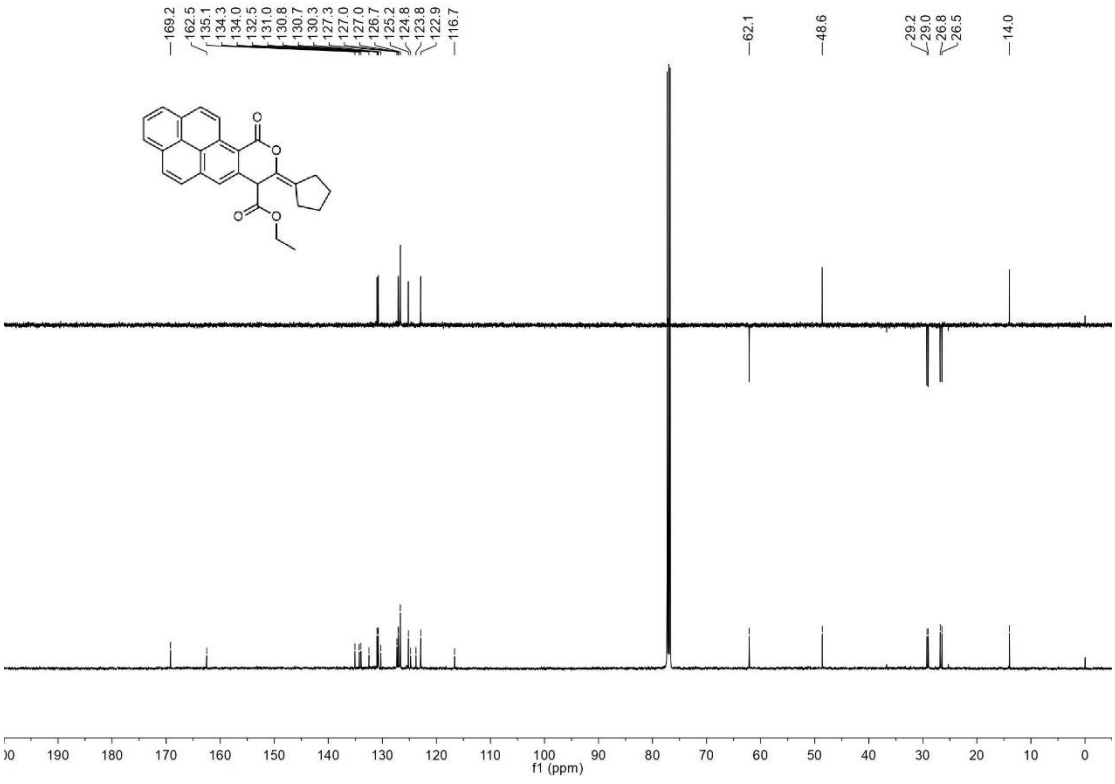
^{1}H NMR spectrum of compound **3qb**



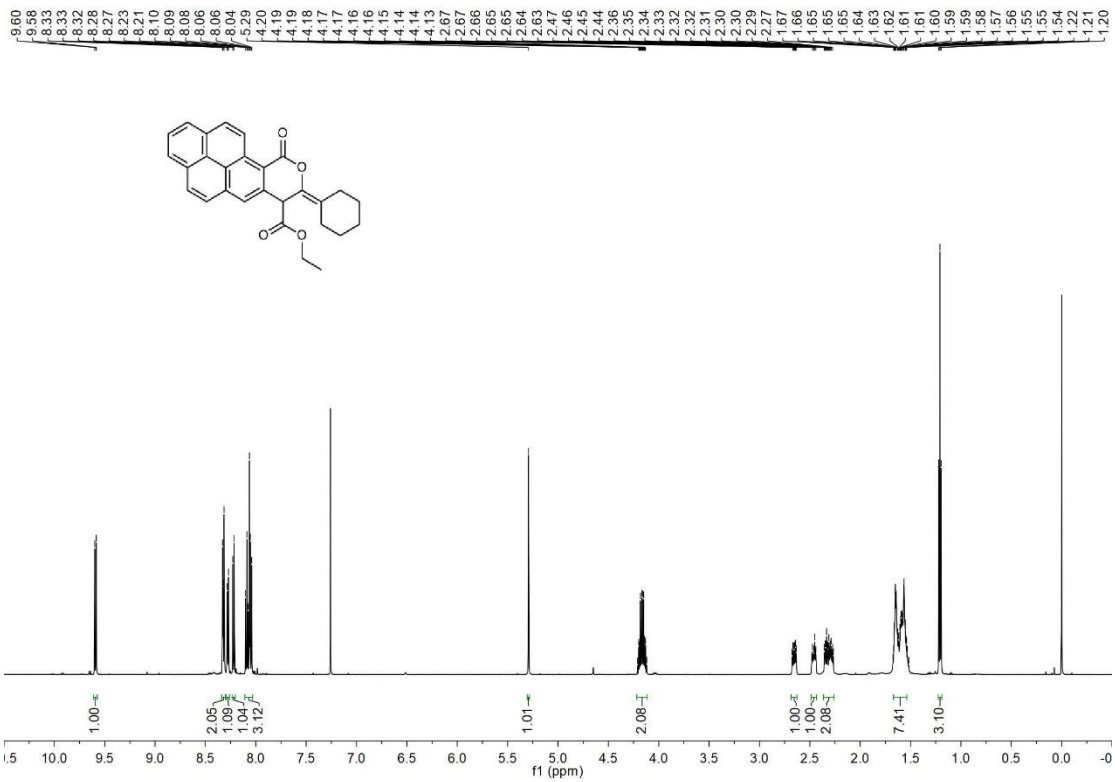
^{13}C NMR spectrum of compound **3qb**



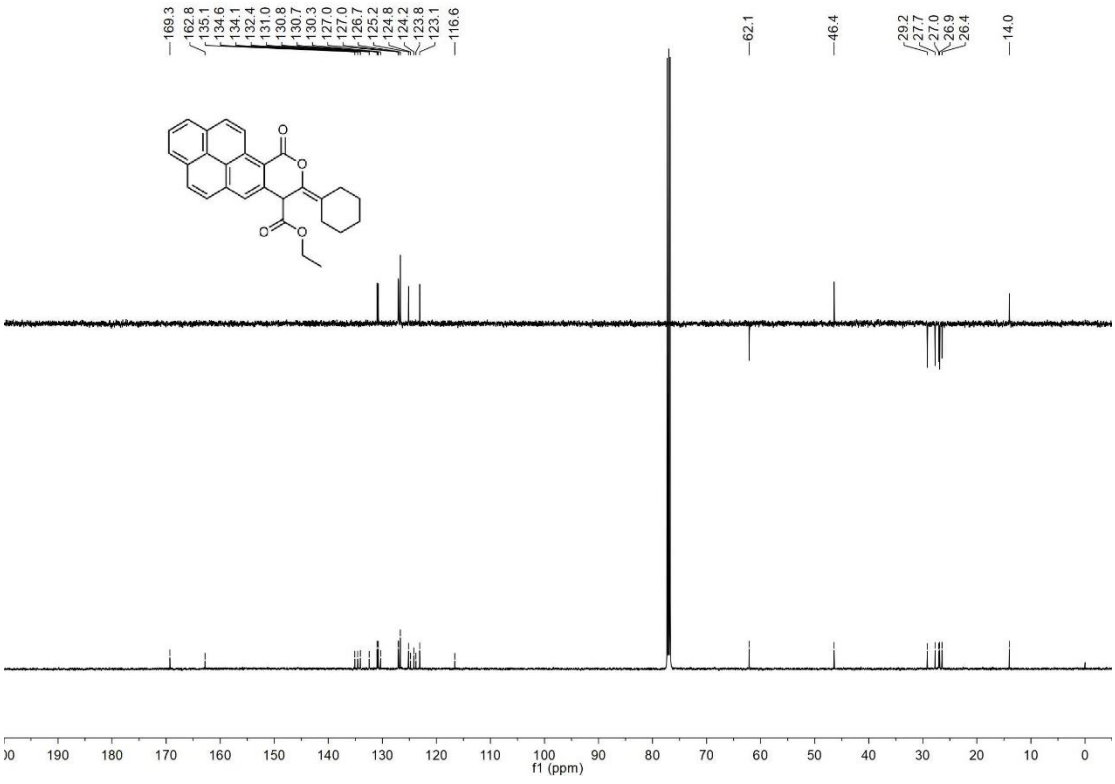
^{1}H NMR spectrum of compound **3qd**



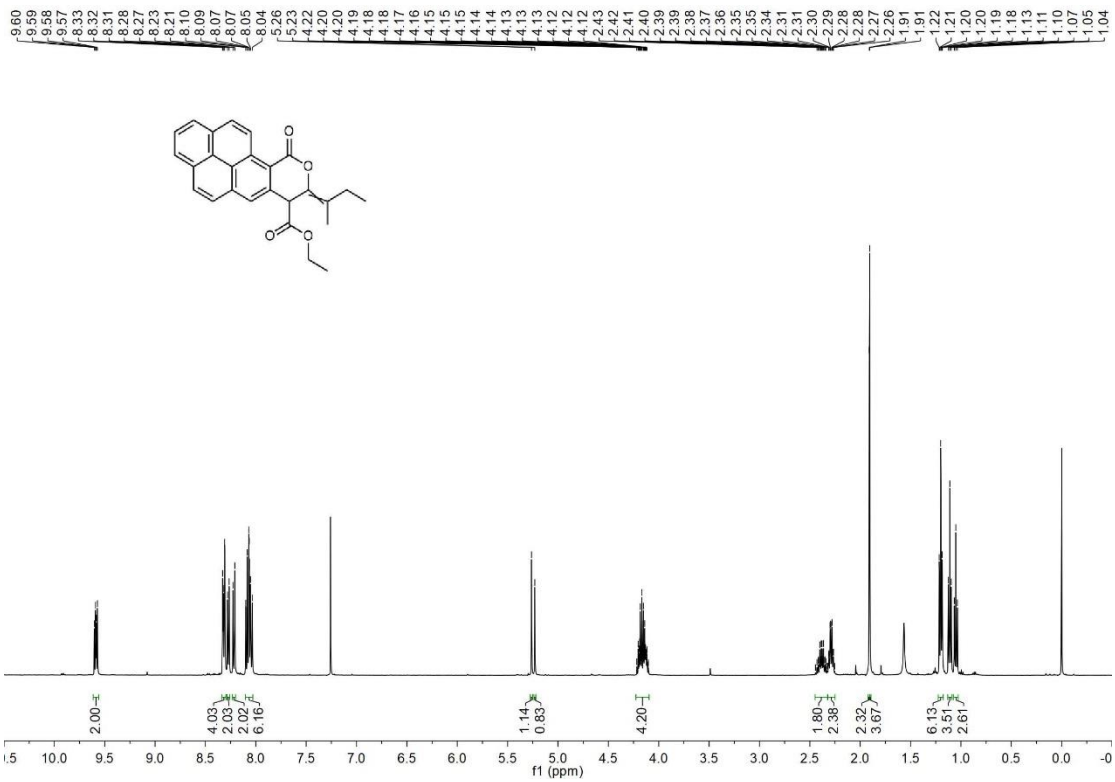
^{13}C NMR spectrum of compound **3qd**



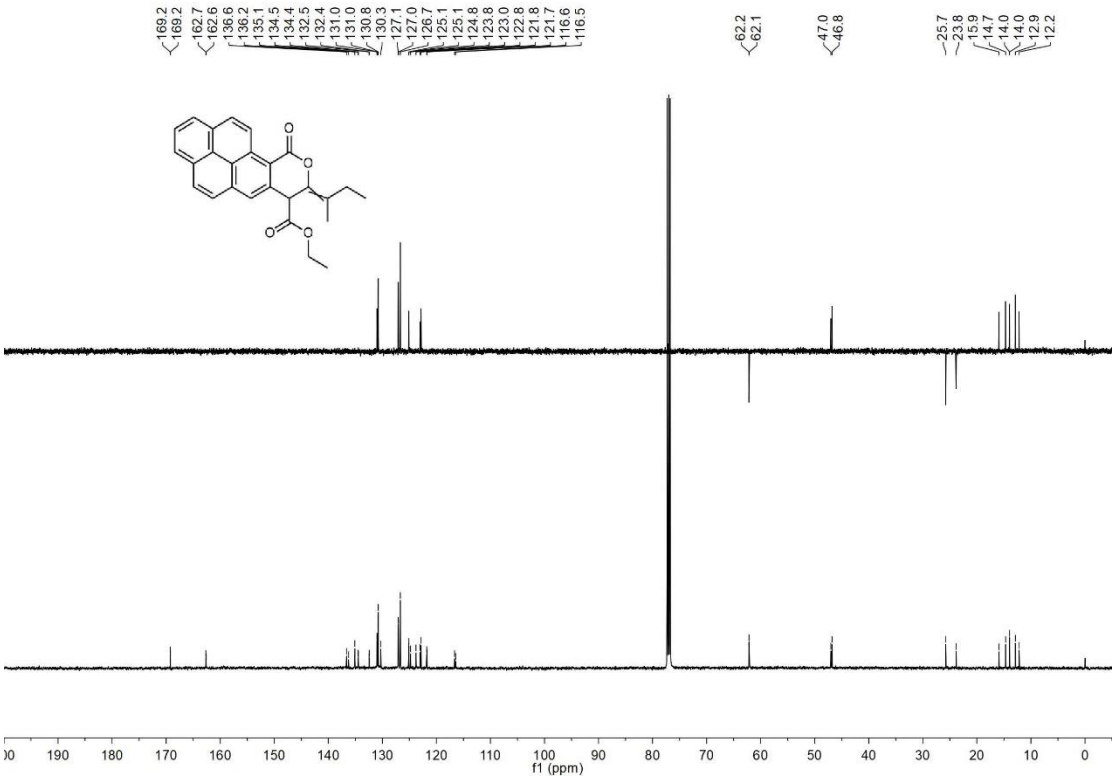
^{1}H NMR spectrum of compound **3qe**



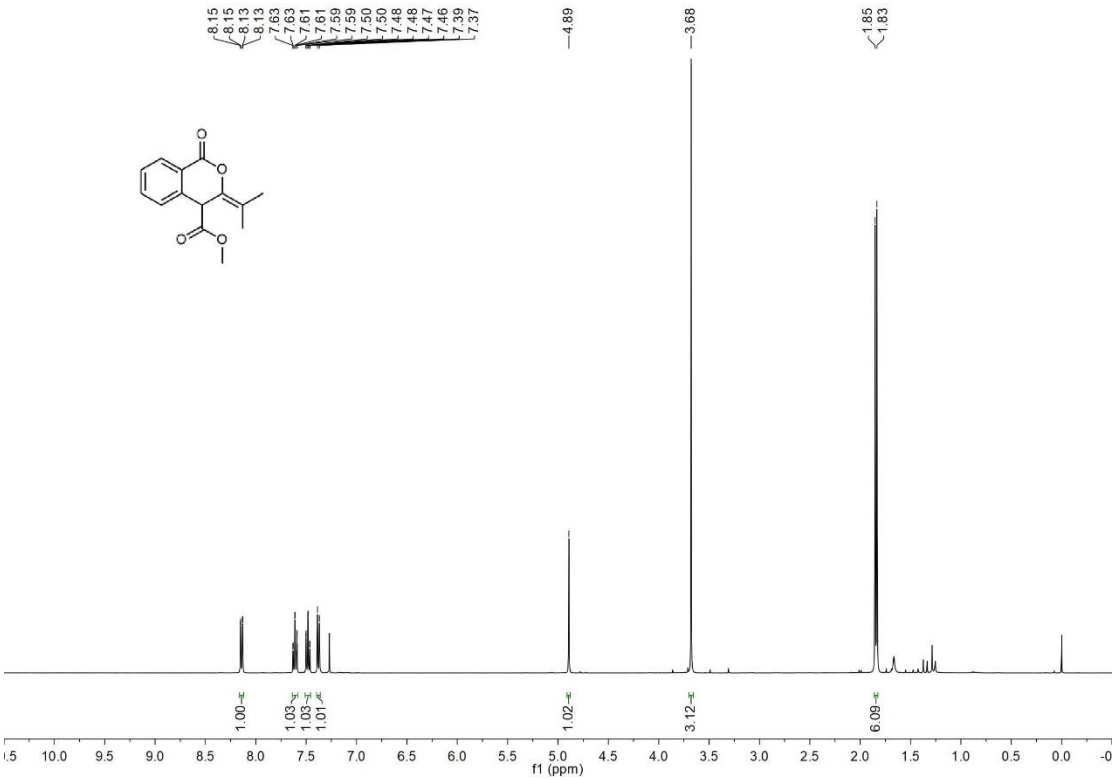
^{13}C NMR spectrum of compound **3qe**



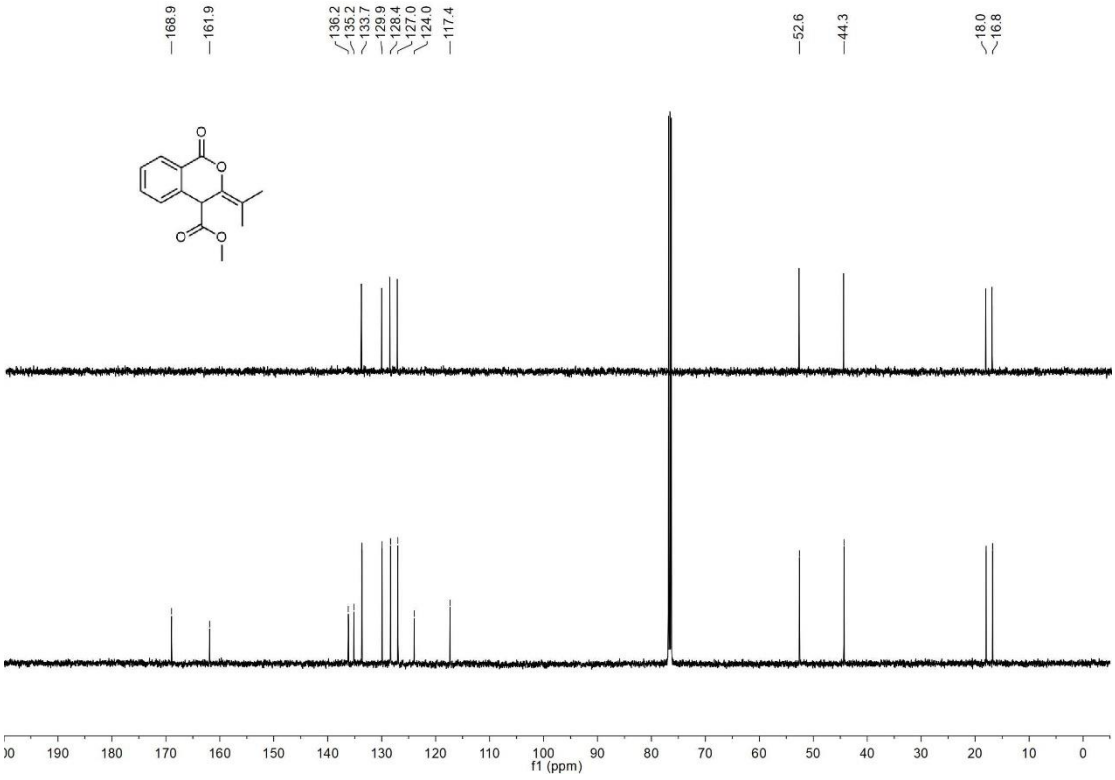
^{1}H NMR spectrum of compound **3qg**



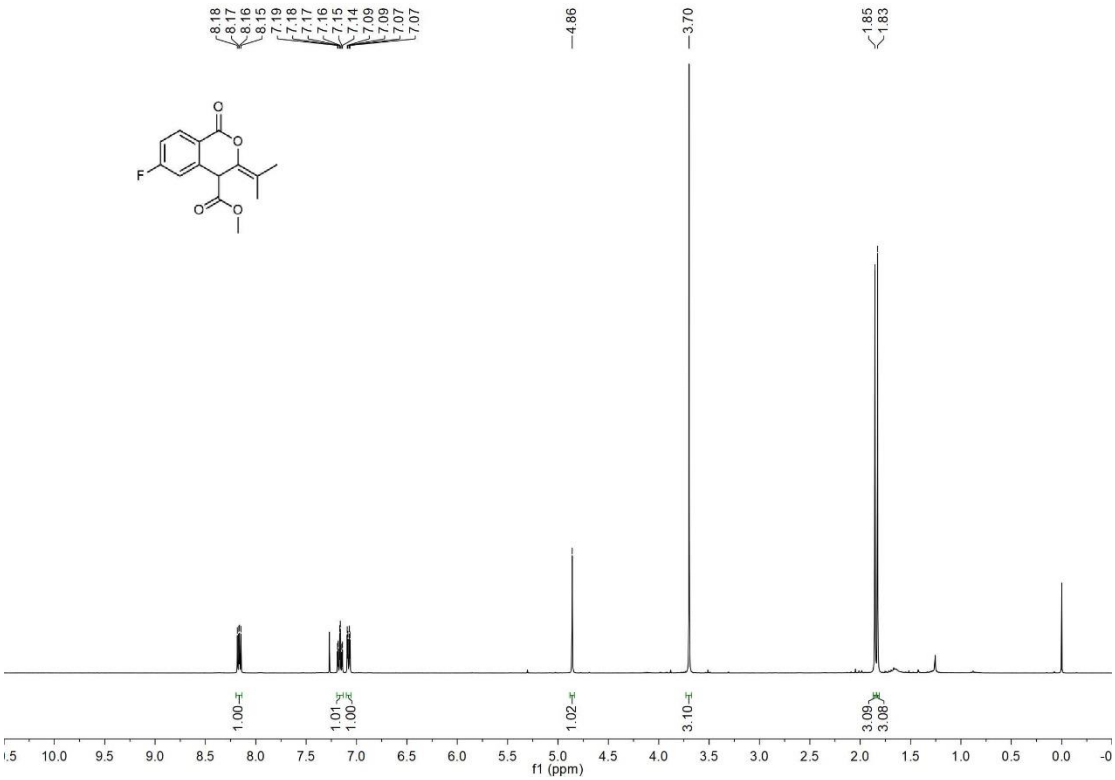
^{13}C NMR spectrum of compound **3qg**



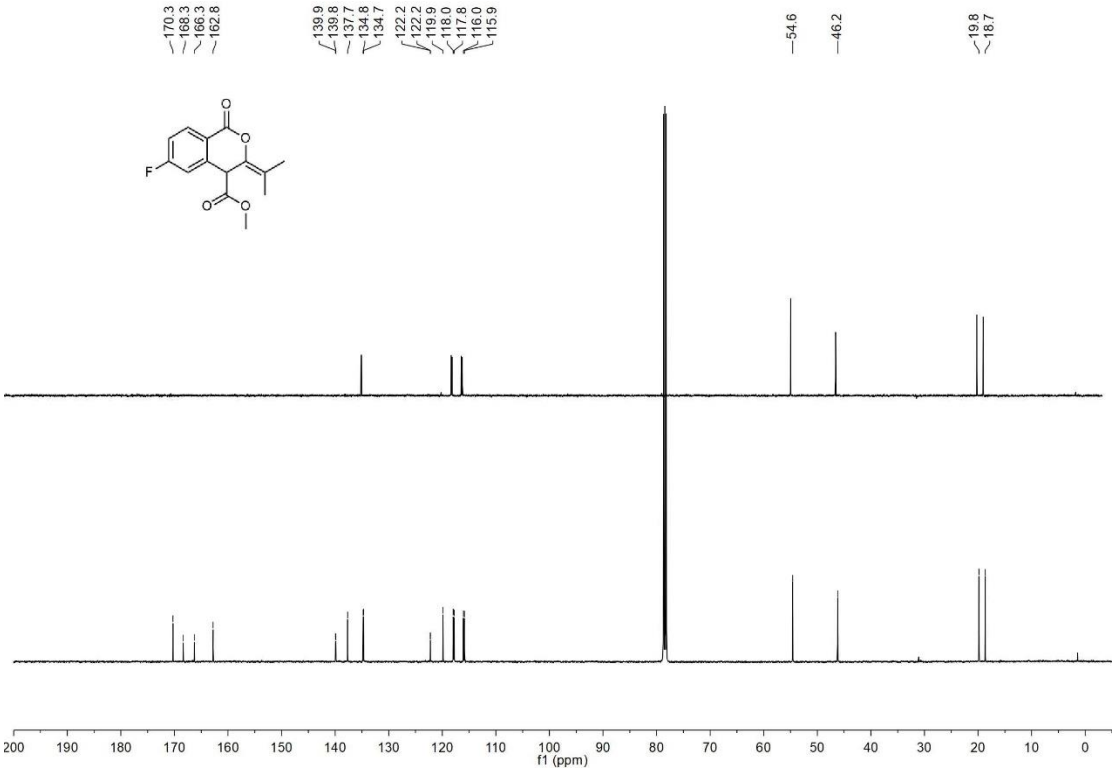
^{1}H NMR spectrum of compound **3ah**



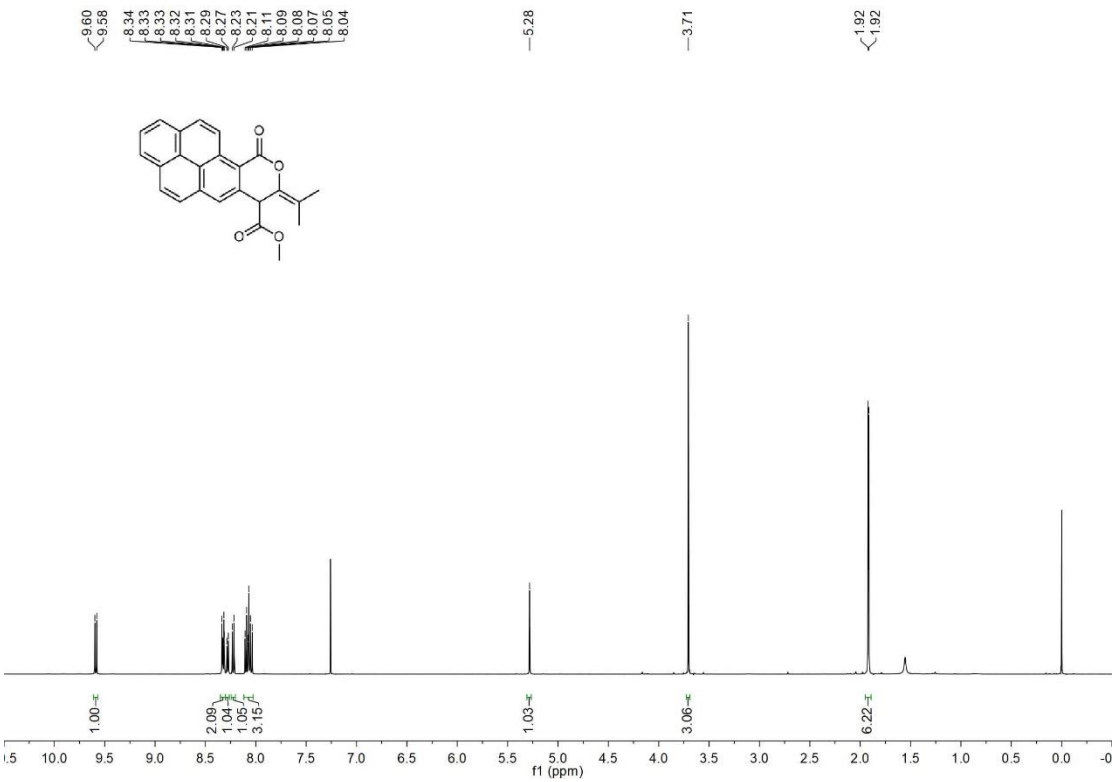
^{13}C NMR spectrum of compound **3ah**



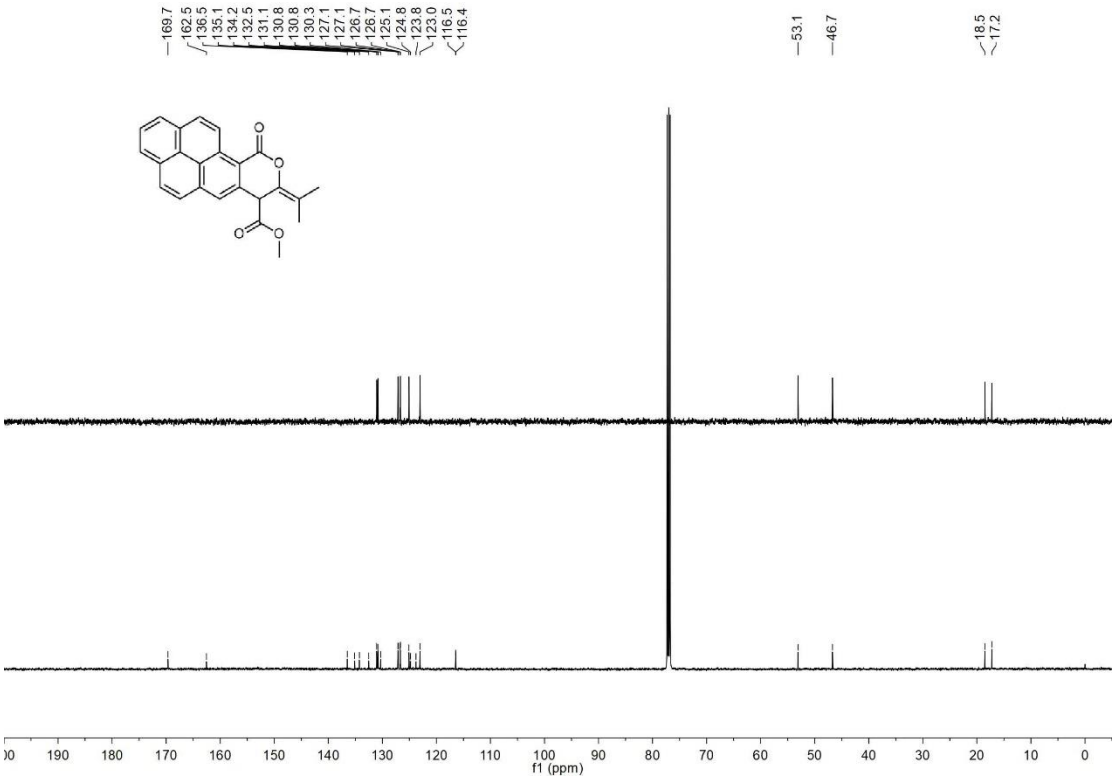
^{1}H NMR spectrum of compound **3bh**



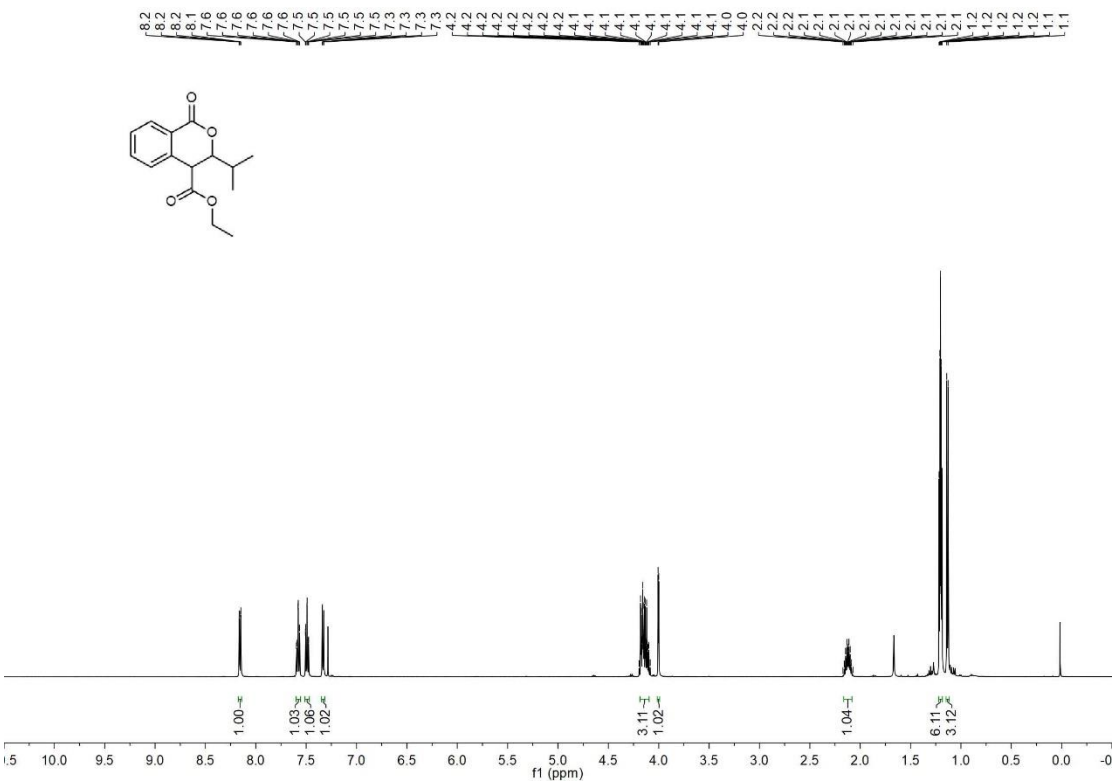
^{13}C NMR spectrum of compound **3bh**



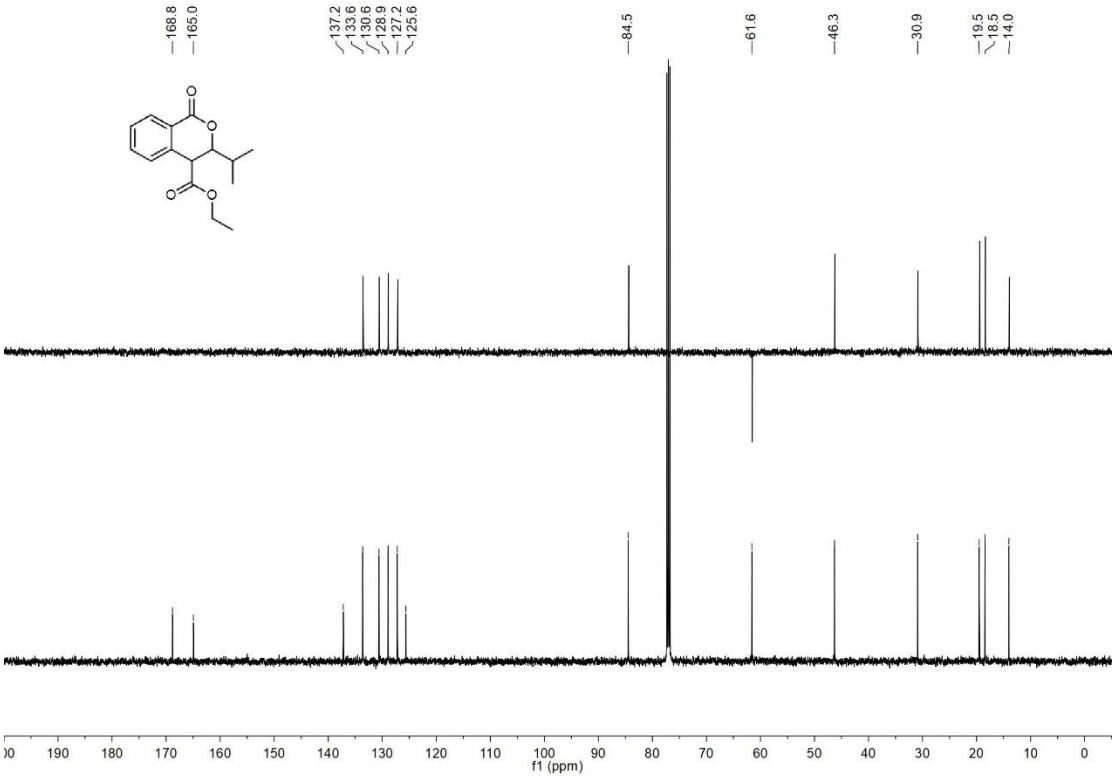
^{1}H NMR spectrum of compound **3qh**



^{13}C NMR spectrum of compound **3qh**

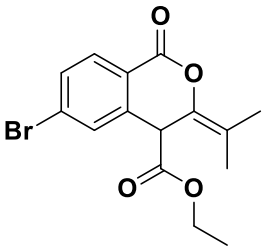


^{1}H NMR spectrum of compound **4**



^{13}C NMR spectrum of compound **4**

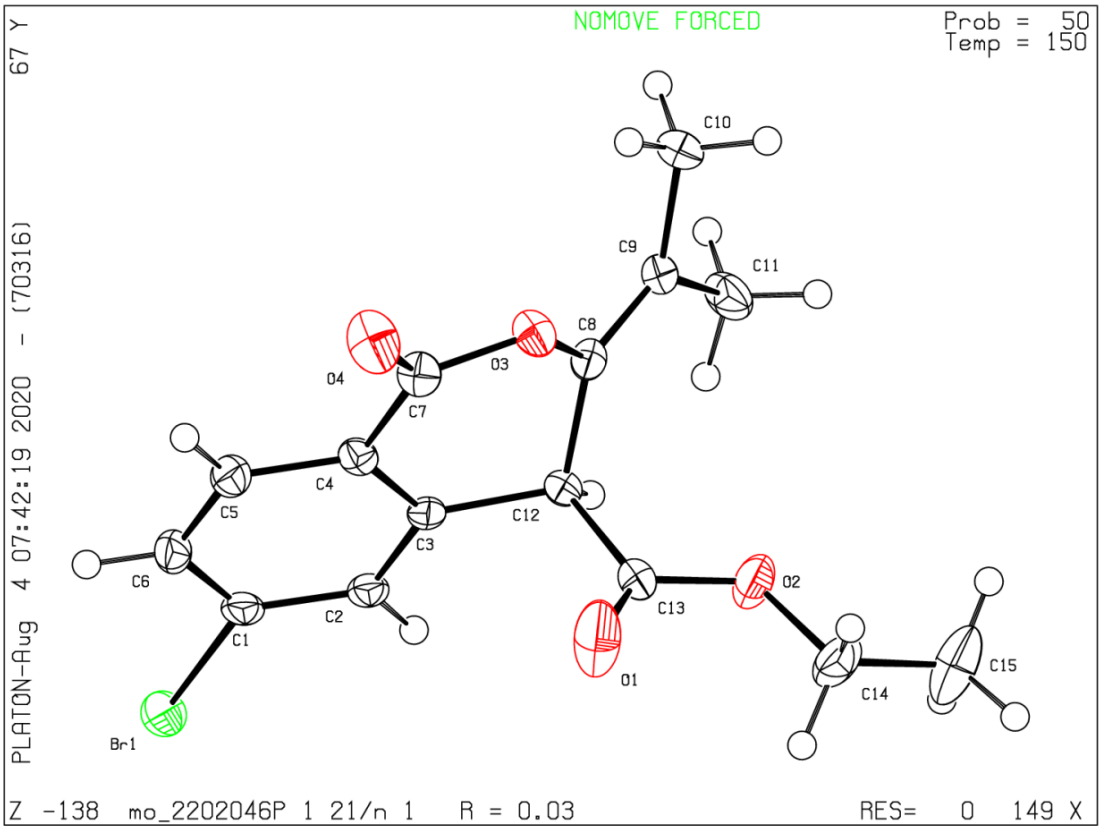
8. X-ray single crystal diffraction data of compound 3da



3da

Sample preparation: Compound **3da** was dissolved in ethyl ether and the mixture was sonicated until the solid was completely dissolved. The solution was transferred into a clean 2 mL vial and sealed with a thin layer of parafilm on the top of one hole was made with a capillary (0.3 mm) to allow the solvent slowly violated at room temperature to afford the single crystal **3da**.

Single crystal structure of 3da: X-ray crystal structure of **3da** was determined at 150K with the ellipsoid contour at 50% probability level



Crystal data and structure refinement for mo_22020468_0m.

Identification code	mo_22020468_0m

Empirical formula	$C_{15}H_{15}BrO_4$
Formula weight	339.18
Temperature/K	150.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.8766 (2)
b/Å	14.3950 (5)
c/Å	14.8086 (5)
α/°	90
β/°	94.0020 (10)
γ/°	90
Volume/Å^3	1462.31 (8)
Z	4
ρ_{calc}g/cm^3	1.541
μ/mm^{-1}	2.821
F(000)	688.0
Crystal size/mm^3	0.15 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.95 to 52.764
Index ranges	$-7 \leq h \leq 8$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$
Reflections collected	16150
Independent reflections	2984 [R_{int} = 0.0477, R_{sigma} = 0.0352]
Data/restraints/parameters	2984/0/184
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0300, wR_2 = 0.0628
Final R indexes [all data]	R_1 = 0.0428, wR_2 = 0.0696
Largest diff. peak/hole / e Å^{-3}	0.34/-0.50