Supplementary Information

Electrochemistry-Enabled Rh-Catalyzed Regioselective [4+1] and [4+2] Cycloaddition Reactions of Benzoic Acid with Alkynyl Esters/Amides

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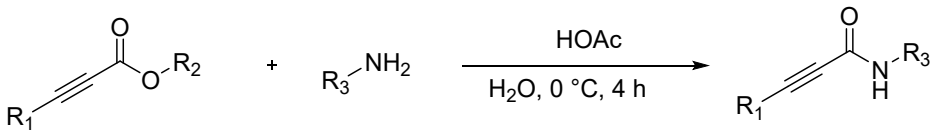
1. General Information

All the electrochemical oxidations were performed in an undivided cell equipped with a platinum electrode (1.0 ×1.5 cm^2) unless otherwise noted. All reactions were carried out in oven-dried round bottoms. All other chemicals were purchased from Sigma-Aldrich and TCI and used as received. All the solvents were distilled before use.

2. Analytical Methods

Analytical thin-layer chromatography (TLC) was performed using 0.25mm silica gel coated plates. Flash chromatography was performed using the indicated solvent and silica gel 60 (230-400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on 400 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) on the δ scale from an internal standard (TMS). Chemical shifts were expressed in parts per million (δ) downfield from d (doublet), t (triplet), dd (doublets of doublet), dt (doublets of triplet), and m (multiplet). Components were visualized by observation under UV light (254 and 365 nm). High resolution mass spectra (HRMS) were recorded in ESI mode using TOF mass spectrometer. The benzoic acids were purchased from commercial sources.

3. General procedure for synthesis of 2



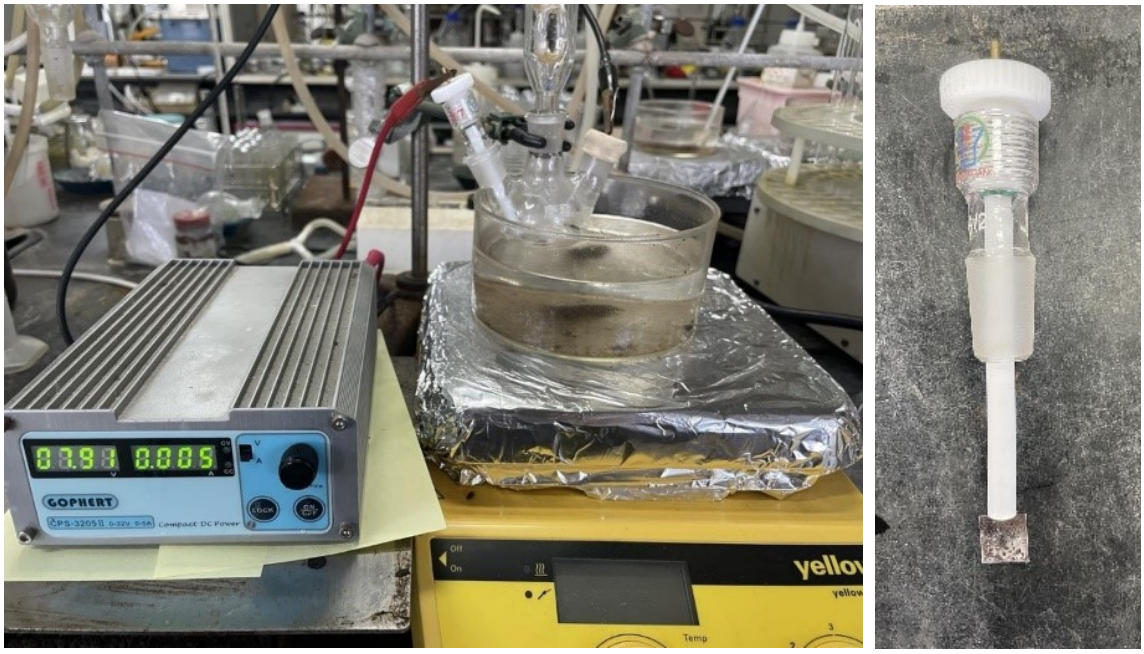
S3 **S4** **2**

To a solution of alkyl amine **S4** (1.2 equiv.) in 5 mL, alkynyl ester **S3** (1 equiv.) was added dropwise at 0 ◦C for 30 min. The mixture was stirred for 2 h at 0 ◦C, and then a few drops of acetic acid were added. The mixture was stirred for another 2h and saturated with NaCl, followed by extraction with ethyl acetate (3 × 10 mL), dried over $MgSO_4$, then the residue was separated by silica gel chromatography with hexane/ethyl acetate (1:1) to obtain the desired alkynyl amide **2** in 66-78% yield.

4. Graphical Guide for the electrochemical setup

For electrolysis, use a three-neck flask with a capacity of 25 mL. Insert the platinum electrode (1.0 × 1.5 cm², from LEDONLAB) and platinum wire into the three-neck flask. Install a condenser and a magnetic stirring rod on the reaction flask containing the reaction mixture. Use a Gopher cps-3205 DC power supply as the power source.

Figure S1. Reaction setup.



5. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded on a Biologic VSP-3e instrument using a Pt electrode (1.0 × 1.5 cm², from LEDONLAB) and a Pt wire, with an SCE reference electrode, at a scan rate of 100 mV/s.

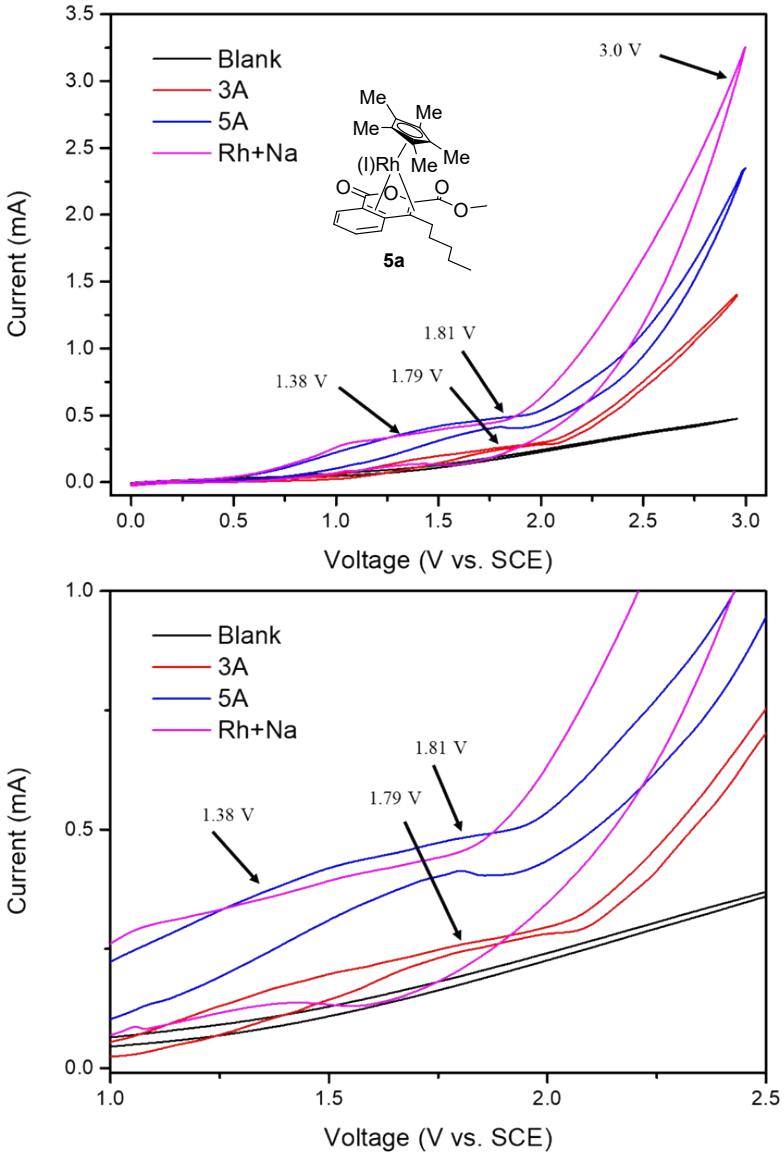
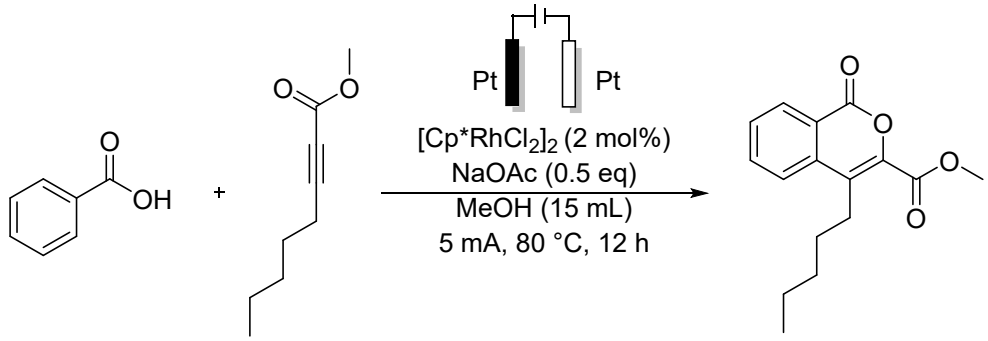


Figure S2. Cyclic voltammograms measured in MeOH, containing 0.1 M $^{n}Bu_4NPF_6$ as the supporting electrolyte. NaOAc was used as the additive. SCE was used as the reference electrode. a) background. b) **3a** (3 mM). c) **5a** (3 mM) d) $[Cp^*RhCl_2]_2$ (3 mM).

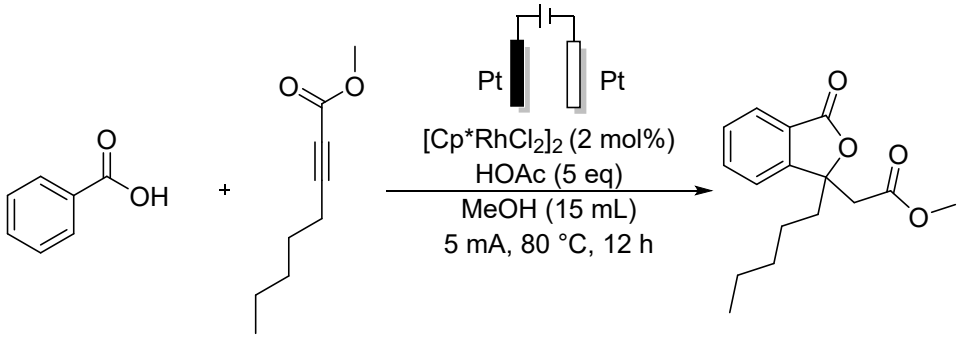
6. General procedure for synthesis of 3a



1a **2a** **3a**

To an oven-dried 25 mL round bottom equipped with magnetic stir bar, **1a** (200 mg, 1.64 mmol), methyl oct-2-ynoate **2a** (303 mg, 1.97 mmol), $[Cp^*RhCl_2]_2$ (20 mg, 2.0 mol%) and NaOAc (67.0 mg, 0.82 mmol) were dissolved in MeOH (15.0 mL). The resulting solution was stirred at 80 °C for 12 h in an undivided cell with a Pt electrodes (1.0 × 1.5 cm^2) and a Pt wire by applying 5.0 mA constant current. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with hexane/ethyl acetate (10:1) as eluent to afford corresponding products.

7. General procedure for synthesis of 4a



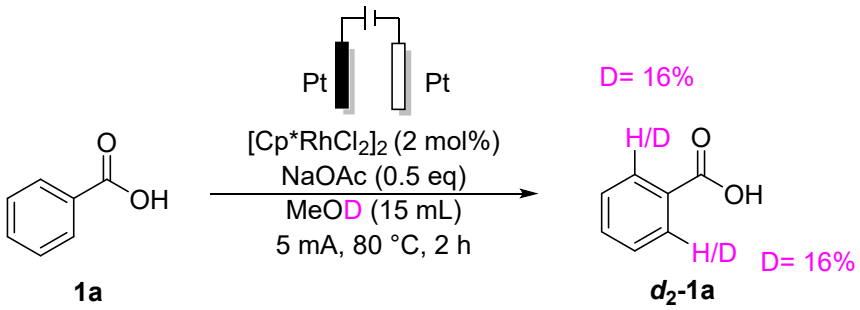
1a **2a** **4a**

To an oven-dried 25 mL round bottom equipped with magnetic stir bar, **1a** (200 mg, 1.64 mmol), methyl oct-2-ynoate **2a** (303 mg, 1.97 mmol), $[Cp^*RhCl_2]_2$ (20 mg, 2.0 mol%) and HOAc (492 mg, 8.2 mmol) were dissolved in MeOH (15.0 mL). The

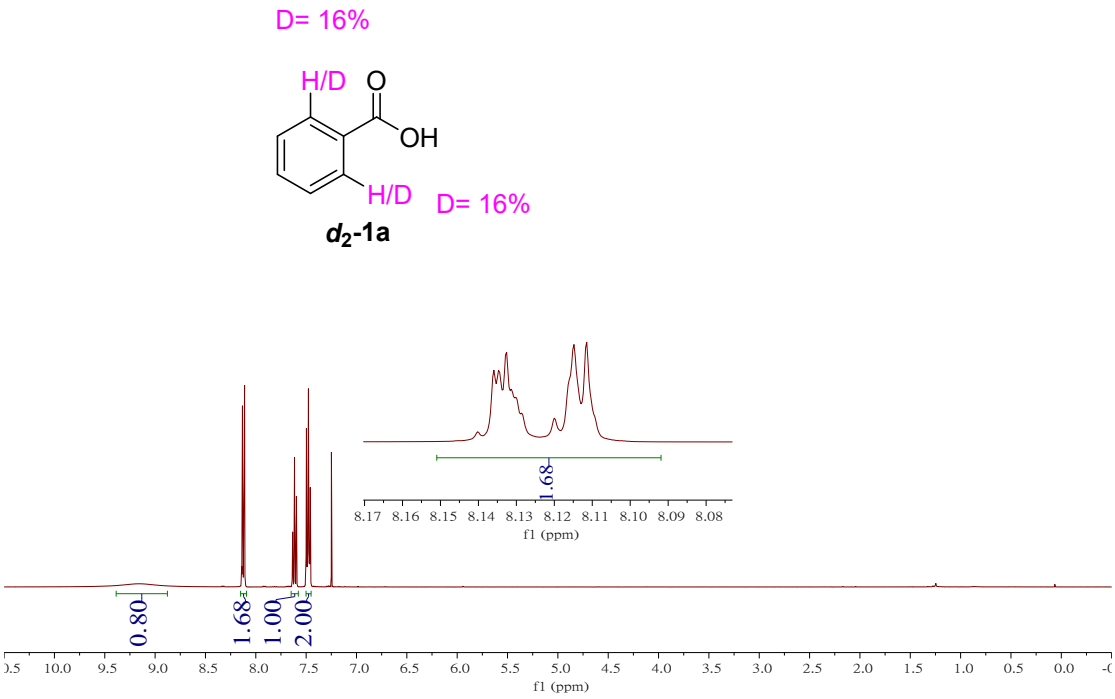
resulting solution was stirred at 80 °C for 12 h in an undivided cell with a Pt electrode (1.0 × 1.5 cm^2) and a Pt wire by applying 5.0 mA constant current. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with hexane/ethyl acetate (6:1) as eluent to afford corresponding products.

8. Mechanistic Study

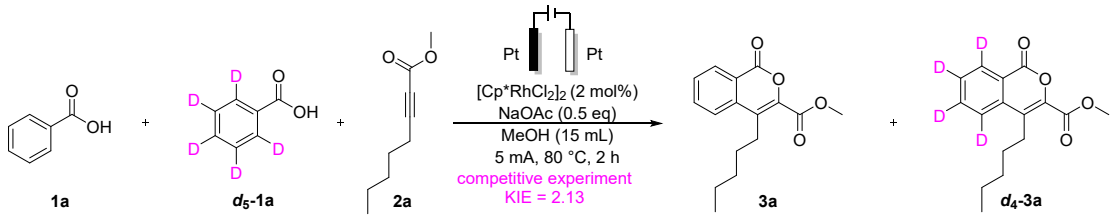
Deuterium exchange



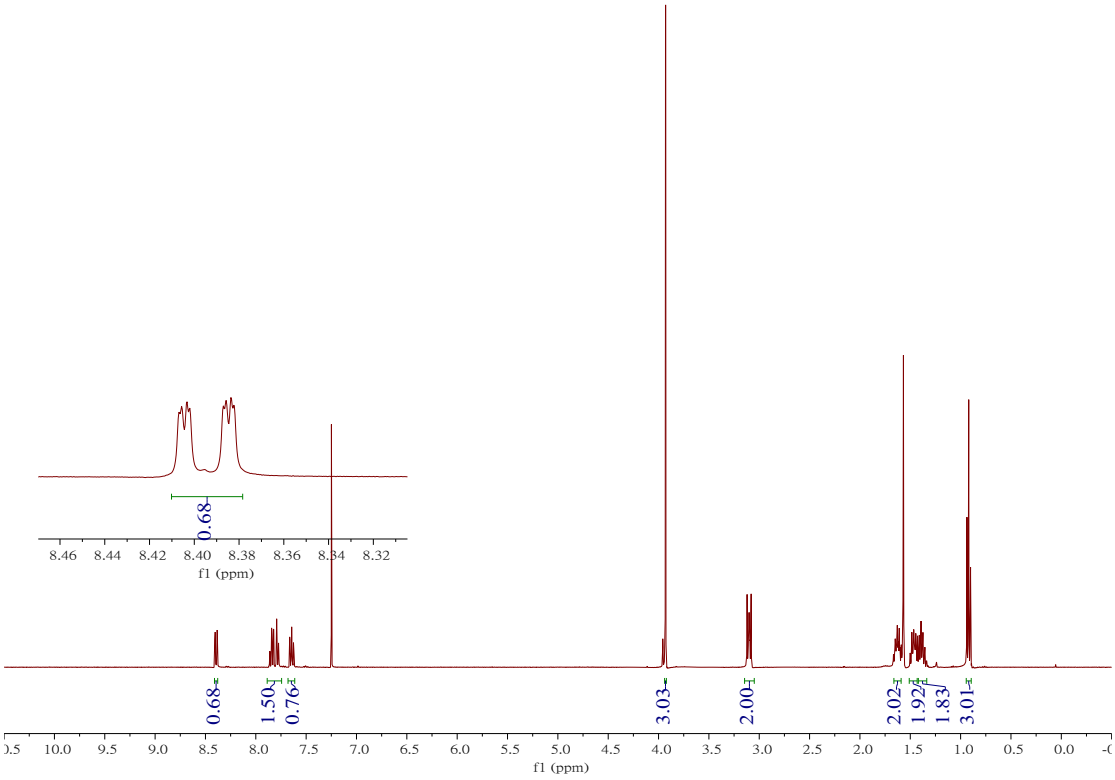
To an oven-dried 25 mL round bottom equipped with magnetic stir bar, **1a** (200 mg, 1.64 mmol), $[Cp^*RhCl_2]_2$ (20 mg, 2.0 mol%) and NaOAc (67.0 mg, 0.82 mmol) were dissolved in MeOD (15.0 mL). The resulting solution was stirred at 80 °C for 2 h in an undivided cell with a Pt electrode (1.0 × 1.5 cm^2) and a Pt wire by applying 5.0 mA constant current. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with hexane/ethyl acetate (6:1) as eluent to afford corresponding products. The H/D exchange was found to be 16 % at the protons attached to C-2′ and C-6′ in the recovered ***d_2*-1a.**



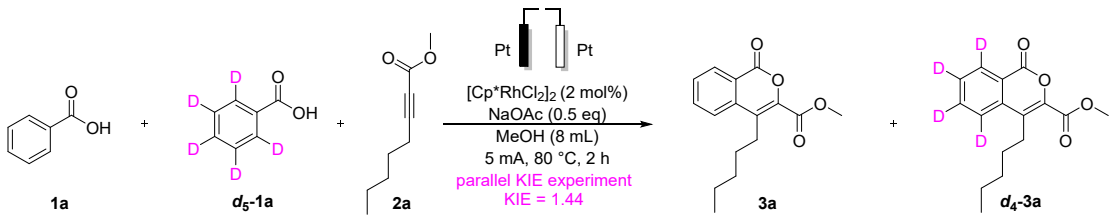
(2) Competition KIE study



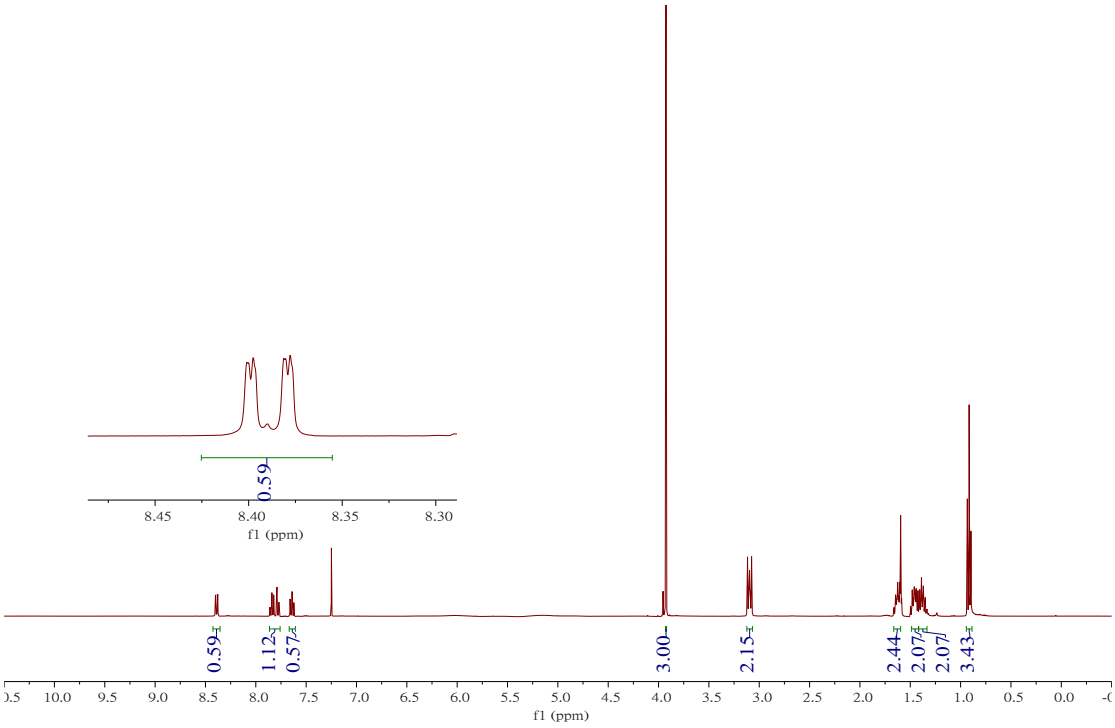
To an oven-dried 25 mL round bottom equipped with magnetic stir bar, **1a** (100 mg, 0.82 mmol) and **1a-*d*$_5$** (101mg, 0.82 mmol), methyl oct-2-ynoate **2a** (303 mg, 1.97 mmol), $[Cp^*RhCl_2]_2$ (20 mg, 2.0 mol%) and NaOAc (67.0 mg, 0.82 mmol) were dissolved in MeOH (15.0 mL). The resulting solution was stirred at 80 °C for 2 h in an undivided cell with a Pt electrode (1.0 × 1.5 cm^2) and a Pt wire by applying 5.0 mA constant current. by applying 5.0 mA constant current. The solvent was then removed under reduced pressure and purification was performed by flash column chromatography on silica gel with hexane/ethyl acetate (10:1) as eluent to afford corresponding products. The KIE value was determined using ^1H NMR.



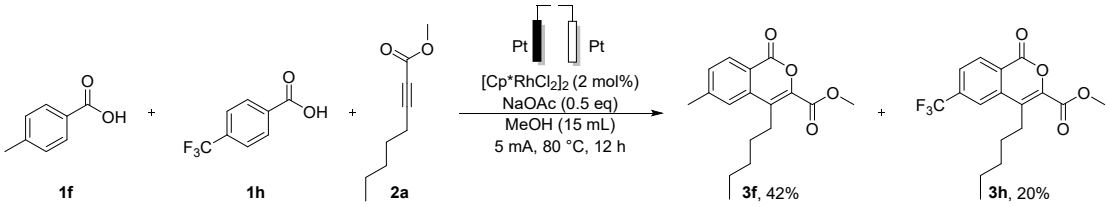
(3) Parallel KIE study



Two separated oven-dried 25 mL round bottom containing **1a** (100 mg, 0.82 mmol) or **1a-*d*$_5$** (101 mg, 0.82 mmol), methyl oct-2-ynoate **2a** (151 mg, 0.98 mmol), $[Cp^*RhCl_2]_2$ (10 mg, 2.0 mol%) and NaOAc (33.6 mg, 0.41 mmol) were dissolved in MeOH (8.0 mL). The resulting solution was stirred at 80 °C for 2 h in an undivided cell with a Pt electrode (1.0 × 1.5 cm^2) and a Pt wire by applying 5.0 mA constant current. Then the two separated reaction mixture was transferred to 25-mL round bottom flask. The solvent was then removed under reduced pressure and purification was performed by flash column chromatography on silica gel with hexane/ethyl acetate (10:1) as eluent to afford corresponding products. The KIE value was determined using ^1H NMR.

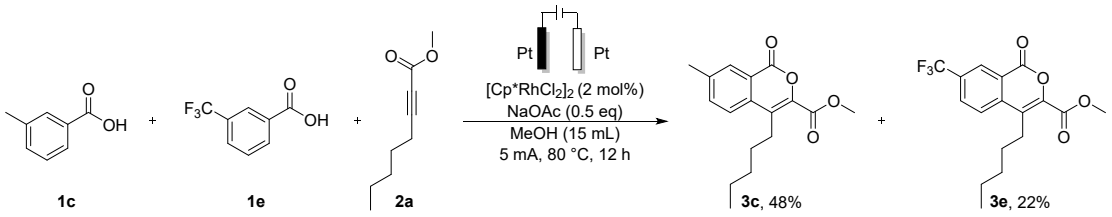


(4) Intermolecular competition experiments



To an oven-dried 25 mL round bottom equipped with magnetic stir bar, **1f** (112 mg, 0.82 mmol) and **1h** (155 mg, 0.82 mmol), methyl oct-2-ynoate **2a** (303 mg, 1.97 mmol), $[Cp^*RhCl_2]_2$ (20 mg, 2.0 mol%) and NaOAc (67.0 mg, 0.82 mmol) were dissolved in MeOH (15.0 mL). The resulting solution was stirred at 80 °C for 12 h in an undivided cell with a Pt electrode (1.0 × 1.5 cm^2) and a Pt wire by applying 5.0 mA constant current. The solvent was then removed under reduced pressure and purification was performed by flash column chromatography on silica gel with hexane/ethyl acetate (10:1) as eluent to afford the **3f** and **3h** in 42% and 20% yields respectively.

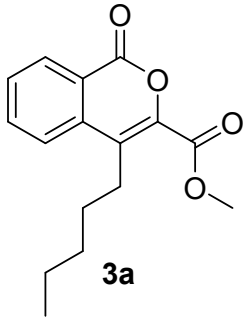
(5) Intermolecular competition experiments



To an oven-dried 25 mL round bottom equipped with magnetic stir bar, **1c** (112 mg, 0.82 mmol) and **1e** (155 mg, 0.82 mmol), methyl oct-2-ynoate **2a** (303 mg, 1.97 mmol), $[Cp^*RhCl_2]_2$ (20 mg, 2.0 mol%) and NaOAc (67.0 mg, 0.82 mmol) were dissolved in MeOH (15.0 mL). The resulting solution was stirred at 80 °C for 12 h in an undivided cell with a Pt electrode (1.0 × 1.5 cm^2) and a Pt wire by applying 5.0 mA constant current. The solvent was then removed under reduced pressure and purification was performed by flash column chromatography on silica gel with hexane/ethyl acetate (10:1) as eluent to afford the **3c** and **3e** in 48% and 22% yields respectively.

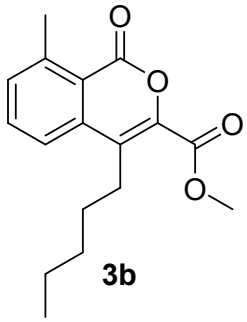
9. Characterization Data of 3a-4j

methyl 1-oxo-4-pentyl-1H-isochromene-3-carboxylate (3a)



Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 373 mg (83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 - 8.34 (m, 1H), 7.88 - 7.75 (m, 2H), 7.69 - 7.58 (m, 1H), 3.92 (s, 3H), 3.08 (d, J = 8.2 Hz, 2H), 1.67 - 1.57 (m, 2H), 1.51 - 1.33 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 161.7, 160.6, 139.6, 136.6, 135.1, 130.3, 130.3, 125.3, 124.9, 123.1, 52.8, 32.2, 29.8, 25.9, 22.6, 14.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}O_4$ 275.1278, found 275.1280.

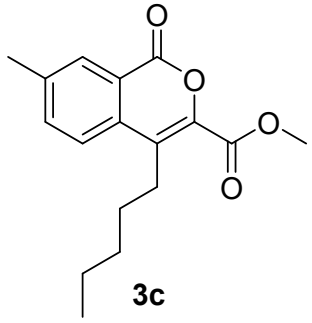
methyl 8-methyl-1-oxo-4-pentyl-1H-isochromene-3-carboxylate (3b)



Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 85 mg (18%); ^{1}H NMR (400 MHz,

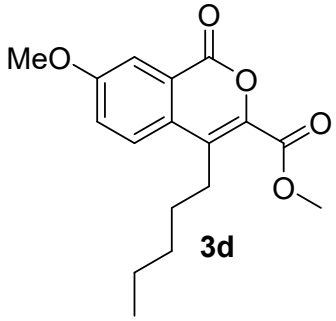
$CDCl_3$) δ 8.21 - 8.18 (m, 1H), 7.70 - 7.61 (m, 2H), 3.92 (s, 3H), 3.13 - 3.05 (m, 2H), 2.49 (s, 3H), 1.64 - 1.56 (m, 2H), 1.49 - 1.42 (m, 2H), 1.40 - 1.34 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 167.1, 160.8, 159.9, 143.9, 136.2, 134.4, 131.3, 122.1, 118.2, 110.6, 52.6, 32.6, 31.5, 27.4, 23.7, 22.5, 14.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}O_4$ 389.1434, found 389.1436.

methyl 7-methyl-1-oxo-4-pentyl-1H-isochromene-3-carboxylate (3c)



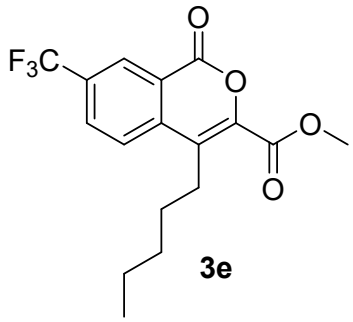
Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 345 mg (73%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 3.94 (s, 3H), 2.80 (s, 3H), 2.63 - 2.56 (m, 2H), 1.78 - 1.67 (m, 2H), 1.34 (dt, *J* = 7.2, 3.7 Hz, 4H), 0.89 (t, *J* = 5.8 Hz, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 161.6, 160.7, 140.9, 138.7, 136.2, 134.0, 130.0, 125.6, 124.7, 122.8, 52.6, 32.0, 29.7, 25.8, 22.5, 21.4, 14.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}O_4$ 389.1434, found 389.1434.

methyl 7-methoxy-1-oxo-4-pentyl-1H-isochromene-3-carboxylate (3d)



Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 394 mg (79%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 2.8 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.39 (dd, *J* = 8.9, 2.8 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.14 - 3.05 (m, 2H), 1.64 - 1.61 (m, 2H), 1.50 - 1.34 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 161.7, 161.1, 160.8, 137.8, 130.0, 126.7, 126.0, 124.7, 124.5, 110.9, 56.1, 52.7, 32.2, 29.9, 26.0, 22.6, 14.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}O_5$ 305.1384, found 305.1387.

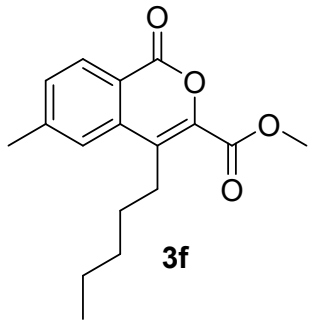
methyl 1-oxo-4-pentyl-7-(trifluoromethyl)-1H-isochromene-3-carboxylate (3e)



3e

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 370 mg (66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 1.9 Hz, 1H), 8.07 - 8.02 (m, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 3.95 (s, 3H), 3.15 - 3.07 (m, 2H), 1.66 - 1.58 (m, 2H), 1.51 - 1.43 (m, 2H), 1.42 - 1.34 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 161.2, 159.5, 141.1, 139.5, 132.7, 132.3, 132.0, 131.4, 131.3, 131.3, 131.3, 127.8, 127.7, 127.7, 127.6, 125.8, 124.5, 123.9, 123.3, 121.8, 53.0, 32.0, 29.6, 25.9, 22.5, 14.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}F_3O_4$ 343.1156, found 343.1152.

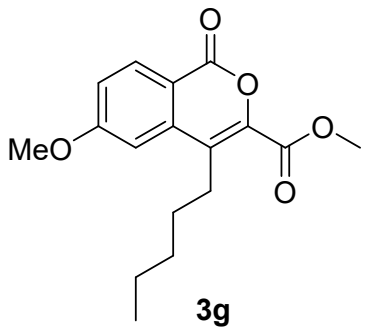
methyl 6-methyl-1-oxo-4-pentyl-1H-isochromene-3-carboxylate (3f)



3f

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 350 mg (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.53 (s, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 3.92 (s, 3H), 3.12 - 3.04 (m, 2H), 2.54 (s, 3H), 1.66 - 1.56 (m, 2H), 1.51 - 1.34 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 161.7, 160.7, 146.2, 139.6, 136.6, 131.5, 130.3, 125.2, 124.8, 120.6, 52.7, 32.1, 29.7, 25.7, 22.5, 22.5, 14.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}O_4$ 289.1434., found 289.1436.

methyl 6-methoxy-1-oxo-4-pentyl-1H-isochromene-3-carboxylate (3g)

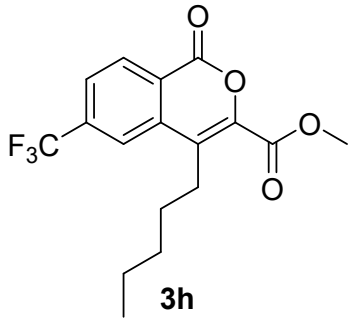


3g

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 384 mg (77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.5 Hz, 1H), 7.18 - 7.13 (m, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 3.08 - 3.00 (m, 2H), 1.67 - 1.59 (m, 2H), 1.49 - 1.42 (m, 2H), 1.41 - 1.35 (m, 2H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 165.0, 161.8,

140.2, 138.9, 132.7, 124.9, 117.0, 116.1, 116.1, 108.6, 55.9, 52.8, 32.2, 29.5, 26.0, 22.6, 14.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}O_5$ 305.1384, found 305.1382.

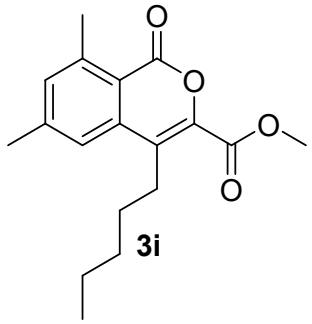
methyl 1-oxo-4-pentyl-6-(trifluoromethyl)-1H-isochromene-3-carboxylate (3h)



3h

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 393 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.2 Hz, 1H), 8.00 (s, 1H), 7.89 - 7.85 (m, 1H), 3.95 (s, 3H), 3.15 - 3.07 (m, 2H), 1.68 - 1.58 (m, 2H), 1.51 - 1.35 (m, 4H), 0.93 (t, J = 7.1 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 161.3, 159.5, 140.8, 137.3, 136.9, 136.6, 131.4, 126.6, 126.5, 125.5, 124.7, 124.3, 122.1, 122.0, 122.0, 122.0, 53.0, 32.0, 29.6, 25.8, 22.4, 14.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}F_3O_4$ 343.1156, found 343.1157.

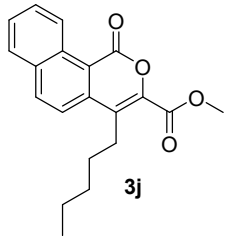
methyl 6,8-dimethyl-1-oxo-4-pentyl-1H-isochromene-3-carboxylate (3i)



3i

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 59 mg (12%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.10 (s, 1H), 3.94 (s, 3H), 2.75 (s, 3H), 2.59 - 2.54 (m, 2H), 2.39 (s, 3H), 1.77 - 1.67 (m, 2H), 1.32 (m, 4H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 161.8, 159.9, 145.0, 144.2, 139.5, 138.1, 134.5, 125.0, 123.1, 119.0, 52.7, 32.1, 29.6, 26.0, 23.6, 22.6, 22.2, 14.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}O_4$ 303.1591, found 303.1583.

methyl 1-oxo-4-pentyl-1H-benzo[h]isochromene-3-carboxylate (3j)

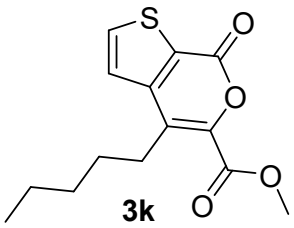


3j

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 393 mg (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (d, J = 8.6 Hz, 1H), 8.25 (d, J = 8.9 Hz, 1H), 7.95 (d, J = 8.0

Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.79 (ddd, *J* = 8.6, 6.9, 1.4 Hz, 1H), 7.72 - 7.67 (m, 1H), 3.97 (s, 3H), 3.24 - 3.17 (m, 2H), 1.72 - 1.62 (m, 2H), 1.53 - 1.45 (m, 2H), 1.44 - 1.36 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 161.6, 159.7, 140.6, 138.9, 136.6, 133.6, 131.7, 129.8, 128.6, 128.2, 127.5, 125.0, 121.0, 117.8, 52.9, 32.1, 29.9, 26.2, 22.6, 14.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}O_4$ 325.1434, found 325.1439.

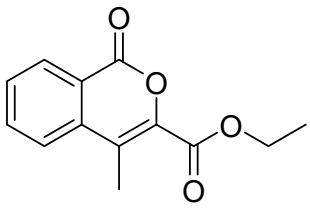
methyl 7-oxo-4-pentyl-7H-thieno[2,3-c]pyran-5-carboxylate (3k)



3k

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 326 mg (71%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 5.2 Hz, 1H), 7.38 (d, *J* = 5.2 Hz, 1H), 3.92 (s, 3H), 3.10 - 3.02 (m, 2H), 1.63 (d, *J* = 3.9 Hz, 2H), 1.45 - 1.32 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 161.2, 156.3, 147.9, 141.0, 136.8, 127.6, 124.7, 124.3, 52.6, 31.9, 29.7, 27.9, 22.4, 14.0.; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}O_4S$ 281.0842, found 281.0847.

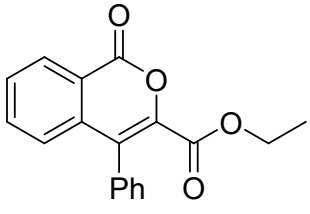
ethyl 4-methyl-1-oxo-1H-isochromene-3-carboxylate (3m)



3m

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 289 mg (76%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.87 - 7.76 (m, 2H), 7.67 - 7.61 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 161.4, 160.6, 140.0, 137.3, 135.0, 130.1, 129.9, 124.7, 122.5, 119.9, 62.0, 14.2, 12.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}O_4$ 233.0808, found 233.0807.

ethyl 1-oxo-4-phenyl-1H-isochromene-3-carboxylate (3n)

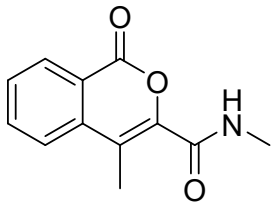


3n

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 381 mg (79%); ^1H NMR (400

MHz, $CDCl_3$) δ 8.37 (ddd, *J* = 7.9, 1.3, 0.6 Hz, 1H), 7.83 - 7.73 (m, 2H), 7.67 - 7.62 (m, 2H), 7.58 (ddd, *J* = 8.1, 7.0, 1.4 Hz, 1H), 7.49 - 7.44 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 166.4, 161.2, 155.5, 135.4, 134.8, 132.7, 130.6, 130.0, 128.9, 128.6, 128.3, 124.2, 119.9, 111.0, 62.0, 13.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}O_4$ 295.0965, found 295.0972.

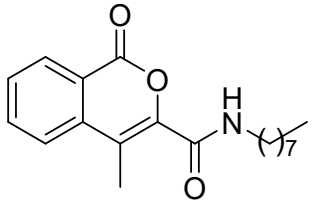
N,4-dimethyl-1-oxo-1H-isochromene-3-carboxamide (3o)



3o

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 310 mg (87%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.0 Hz, 1H), 7.90 - 7.78 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.11 (s, 1H), 2.98 (d, *J* = 4.9 Hz, 3H), 2.78 (s, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 160.5, 138.2, 135.3, 129.9, 129.8, 124.8, 122.1, 122.0, 118.2, 26.3, 11.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}NO_3$ 218.0812, found 218.0811.

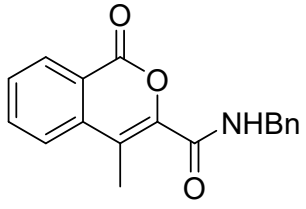
4-methyl-N-octyl-1-oxo-1H-isochromene-3-carboxamide (3p)



3p

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 434 mg (84%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 6.6 Hz, 1H), 7.88 - 7.79 (m, 2H), 7.66 - 7.59 (m, 1H), 7.08 (s, 1H), 3.44 - 3.36 (m, 2H), 2.78 (s, 3H), 1.40 - 1.22 (m, 12H), 0.94 - 0.84 (t, *J* = 7.2 Hz, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 161.0, 160.6, 141.2, 138.3, 135.3, 129.9, 129.7, 124.8, 122.0, 118.2, 39.7, 31.9, 29.5, 29.3, 29.3, 27.1, 22.7, 14.2, 11.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}NO_3$ 316.1907, found 316.1906.

N-benzyl-4-methyl-1-oxo-1H-isochromene-3-carboxamide (3q)

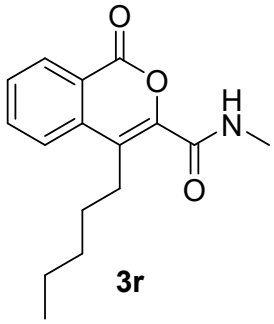


3q

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 413 mg (86%); ^1H NMR (400

MHz, $CDCl_3$) δ 8.35 (d, *J* = 9.7 Hz, 1H), 7.90 - 7.78 (m, 2H), 7.67 - 7.60 (m, 1H), 7.41 (s, 1H), 7.37 - 7.33 (m, 4H), 7.31 - 7.27 (m, 1H), 4.60 (d, *J* = 5.9 Hz, 2H), 2.81 (s, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 160.9, 160.3, 140.9, 138.0, 137.5, 135.2, 129.9, 129.8, 128.8, 128.0, 127.7, 124.7, 122.0, 118.7, 43.6, 11.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}NO_3$ 294.1125, found 294.1119.

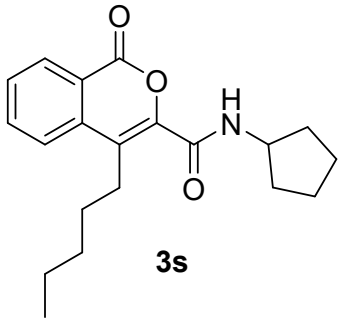
N-methyl-1-oxo-4-pentyl-1H-isochromene-3-carboxamide (3r)



3r

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 323 mg (72%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.0 Hz, 1H), 7.88 - 7.77 (m, 2H), 7.65 - 7.57 (m, 1H), 3.31 - 3.24 (m, 2H), 2.96 (d, *J* = 5.0 Hz, 3H), 1.62 (q, *J* = 8.1, 7.6 Hz, 2H), 1.53 - 1.43 (m, 2H), 1.42 - 1.33 (m, 2H), 0.96 - 0.88 (m, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 161.4, 160.5, 141.0, 137.4, 135.2, 130.1, 129.7, 124.8, 123.0, 122.4, 32.3, 29.9, 26.2, 25.2, 22.7, 14.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}NO_3$ 274.1438, found 274.1438.

N-cyclopentyl-1-oxo-4-pentyl-1H-isochromene-3-carboxamide (3s)

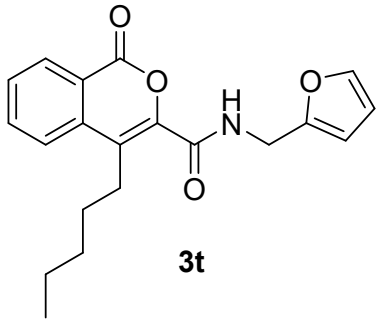


3s

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 424 mg (79%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 9.1 Hz, 1H), 7.84 - 7.72 (m, 2H), 7.58 (t, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 4.38 - 4.24 (m, 1H), 3.27 - 3.18 (m, 2H), 2.11 - 1.99 (m, 2H), 1.79 - 1.68 (m, 2H), 1.67 - 1.55 (m, 4H), 1.55 - 1.40 (m, 4H), 1.40 - 1.31 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 160.6, 160.3, 141.2, 137.5, 135.2, 130.1, 129.6, 124.8, 122.8, 122.4, 51.4, 33.1, 32.3, 29.9, 25.3, 24.0, 22.7, 14.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for

$C_{20}H_{26}O_3$ 328.1907, found 328.1906.

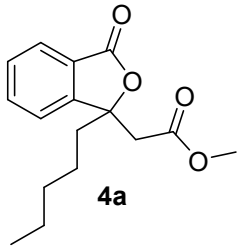
N-(furan-2-ylmethyl)-1-oxo-4-pentyl-1H-isochromene-3-carboxamide (3t)



3t

Flash chromatography for purification: hexane/ethyl acetate = 10:1. Yellow solid; Yield = 423 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 9.1 Hz, 1H), 7.87 - 7.76 (m, 2H), 7.61 (t, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 0.7 Hz, 1H), 7.35 (s, 1H), 6.35 - 6.23 (m, 2H), 4.58 (d, *J* = 5.6 Hz, 2H), 3.33 - 3.23 (m, 2H), 1.70 - 1.59 (m, 2H), 1.53 - 1.43 (m, 2H), 1.41 - 1.34 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 165.2, 161.8, 156.7, 150.5, 142.6, 135.3, 135.1, 129.8, 128.4, 123.6, 119.8, 113.6, 110.7, 108.2, 36.9, 32.0, 31.4, 27.4, 22.4, 14.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}NO_3$ 340.1543, found 340.1544.

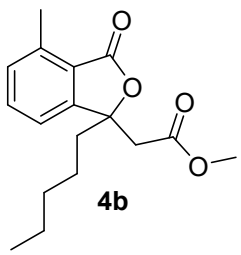
methyl 2-(3-oxo-1-pentyl-1,3-dihydroisobenzofuran-1-yl)acetate (4a)



4a

Flash chromatography for purification: hexane/ethyl acetate = 8:1. Yellow solid; Yield = 317 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 3.52 (s, 3H), 2.98 (s, 2H), 2.20 - 2.07 (m, 1H), 2.00 - 1.89 (m, 1H), 1.28 - 1.23 (m, 1H), 1.22 - 1.12 (m, 4H), 0.96 - 0.85 (m, 1H), 0.78 (t, *J* = 6.8 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 169.8, 169.0, 151.8, 139.4, 133.7, 130.9, 124.0, 118.8, 85.2, 51.6, 42.8, 38.5, 31.5, 22.6, 22.2, 17.3, 13.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}O_4$ 277.1434; Found 277.1435.

methyl 2-(4-methyl-3-oxo-1-pentyl-1,3-dihydroisobenzofuran-1-yl)acetate (4b)

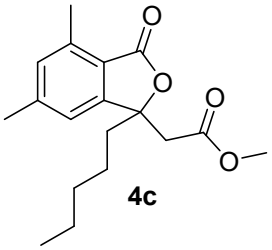


4b

Flash chromatography for purification: hexane/ethyl acetate = 8:1. Yellow solid; Yield = 362 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 2H), 3.50 (s,

3H), 2.92 (s, 2H), 2.64 (s, 3H), 2.17 - 2.03 (m, 1H), 1.95 - 1.84 (m, 1H), 1.28 - 1.11 (m, 5H), 0.97 - 0.84 (m, 1H), 0.79 - 0.70 (m, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 169.6, 169.0, 151.2, 134.0, 129.2, 126.6, 125.5, 121.5, 86.5, 51.7, 42.7, 38.4, 31.4, 22.6, 22.2, 13.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}O_4$ 291.1591; Found 291.1592.

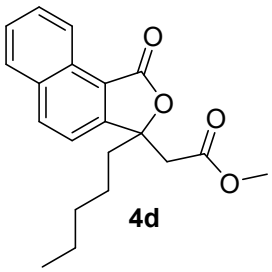
methyl 2-(4,6-dimethyl-3-oxo-1-pentyl-1,3-dihydroisobenzofuran-1-yl)acetate (4c)



4c

Flash chromatography for purification: hexane/ethyl acetate = 8:1. Yellow solid; Yield = 369 mg (74%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.98 (s, 1H), 3.54 (s, 3H), 2.91 (s, 2H), 2.61 (s, 3H), 2.40 (s, 3H), 2.17 - 2.02 (m, 1H), 1.86 (d, *J* = 18.6 Hz, 1H), 1.30 - 1.14 (m, 3H), 0.99 - 0.86 (m, 1H), 0.79 (t, *J* = 6.6 Hz, 3H).; $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 170.1, 169.3, 152.5, 145.0, 139.3, 132.2, 121.8, 119.4, 85.1, 52.0, 43.3, 38.7, 31.7, 22.8, 22.5, 22.1, 17.5, 14.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}O_4$ 305.1747; Found 305.1747.

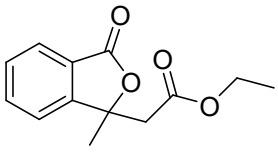
methyl 2-(1-oxo-3-pentyl-1,3-dihydronaphtho[1,2-c]furan-3-yl)acetate (4d)



4d

Flash chromatography for purification: hexane/ethyl acetate = 8:1. Yellow solid; Yield = 423 mg (79%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 3.54 (s, 3H), 3.05 (s, 2H), 2.32 - 2.16 (m, 1H), 2.09 - 1.98 (m, 1H), 1.36 - 1.13 (m, 5H), 0.98 - 0.85 (m, 1H), 0.79 (t, *J* = 7.0 Hz, 3H); $^{13}C\{1\ H\}$ NMR (101 MHz, $CDCl_3$) δ 170.1, 169.2, 152.9, 135.7, 133.5, 129.2, 129.2, 128.5, 127.4, 123.8, 120.8, 118.4, 85.7, 52.0, 42.9, 38.1, 31.6, 22.8, 22.4, 14.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}O_4$ 327.1591; Found 327.1588.

ethyl 2-(1-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (4e)

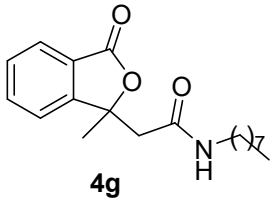


4e

Flash chromatography for purification: hexane/ethyl acetate =

8:1. Yellow solid; Yield = 284 mg (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 - 7.46 (m, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.97 (s, 2H), 1.75 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 169.5, 168.6, 152.6, 134.2, 129.4, 126.1, 125.7, 121.5, 84.3, 60.9, 44.2, 26.4, 14.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}O_4$ 235.0965; Found 235.0963.

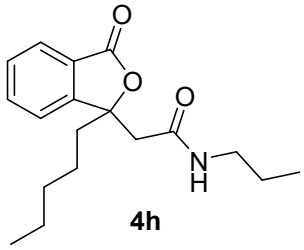
2-(1-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)-N-octylacetamide (4g)



4g

Flash chromatography for purification: hexane/ethyl acetate = 6:1. Yellow solid; Yield = 369 mg (71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 - 8.17 (m, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.49 - 7.40 (m, 2H), 6.03 (s, 1H), 3.49 (q, *J* = 7.0 Hz, 2H), 2.33 (s, 3H), 1.68 - 1.61 (m, 2H), 1.45 - 1.19 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 165.4, 161.7, 152.7, 135.3, 129.8, 128.3, 123.5, 119.7, 114.3, 40.2, 31.8, 29.6, 29.3, 29.3, 27.1, 22.7, 18.2, 14.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{28}NO_3$ 318.2064; Found 318.2063.

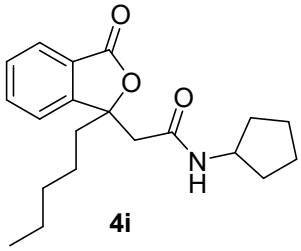
N-benzyl-2-(1-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetamide (4h)



4h

Flash chromatography for purification: hexane/ethyl acetate = 6:1. Yellow solid; Yield = 378 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.52 - 7.42 (m, 2H), 5.91 (s, 1H), 3.46 (q, *J* = 6.7 Hz, 2H), 2.64 - 2.52 (m, 2H), 1.78 - 1.69 (m, 2H), 1.39 - 1.27 (m, 6H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 165.4, 156.3, 135.3, 135.2, 129.9, 128.3, 123.6, 114.1, 100.0, 41.9, 32.1, 31.5, 27.4, 23.0, 22.4, 14.0, 11.6; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{17}NNaO_3$ 318.1101; Found 318.1100.

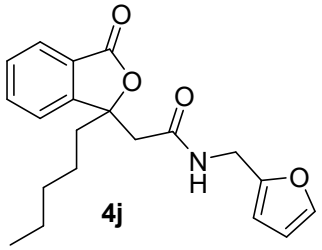
N-cyclopentyl-2-(3-oxo-1-pentyl-1,3-dihydroisobenzofuran-1-yl)acetamide (4i)



4i

Flash chromatography for purification: hexane/ethyl acetate = 6:1. Yellow solid; Yield = 443 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.4 Hz, 1H), 7.68 (t, *J* = 8.3 Hz, 1H), 7.47 - 7.38 (m, 2H), 6.02 (d, *J* = 7.5 Hz, 1H), 4.46 (q, *J* = 6.6 Hz, 1H), 2.62 - 2.54 (m, 2H), 2.17 - 2.06 (m, 2H), 1.82 - 1.60 (m, 8H), 1.59 - 1.45 (m, 2H), 1.39 - 1.27 (m, 4H), 0.90 - 0.87 (m, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 165.0, 162.0, 156.3, 135.3, 129.9, 128.4, 123.6, 119.9, 114.2, 52.0, 33.3, 33.3, 32.1, 31.6, 27.5, 23.9, 22.5, 14.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}NO_3$ 330.2064; Found 330.2062.

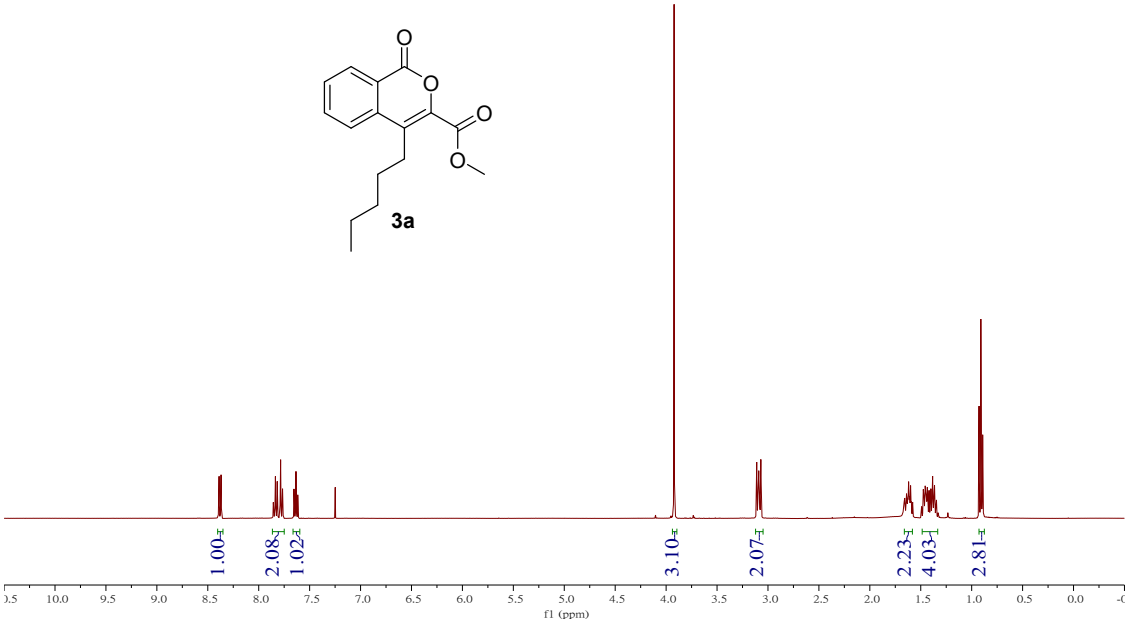
N-(furan-2-ylmethyl)-2-(3-oxo-1-pentyl-1,3-dihydroisobenzofuran-1-yl)acetamide (4j)



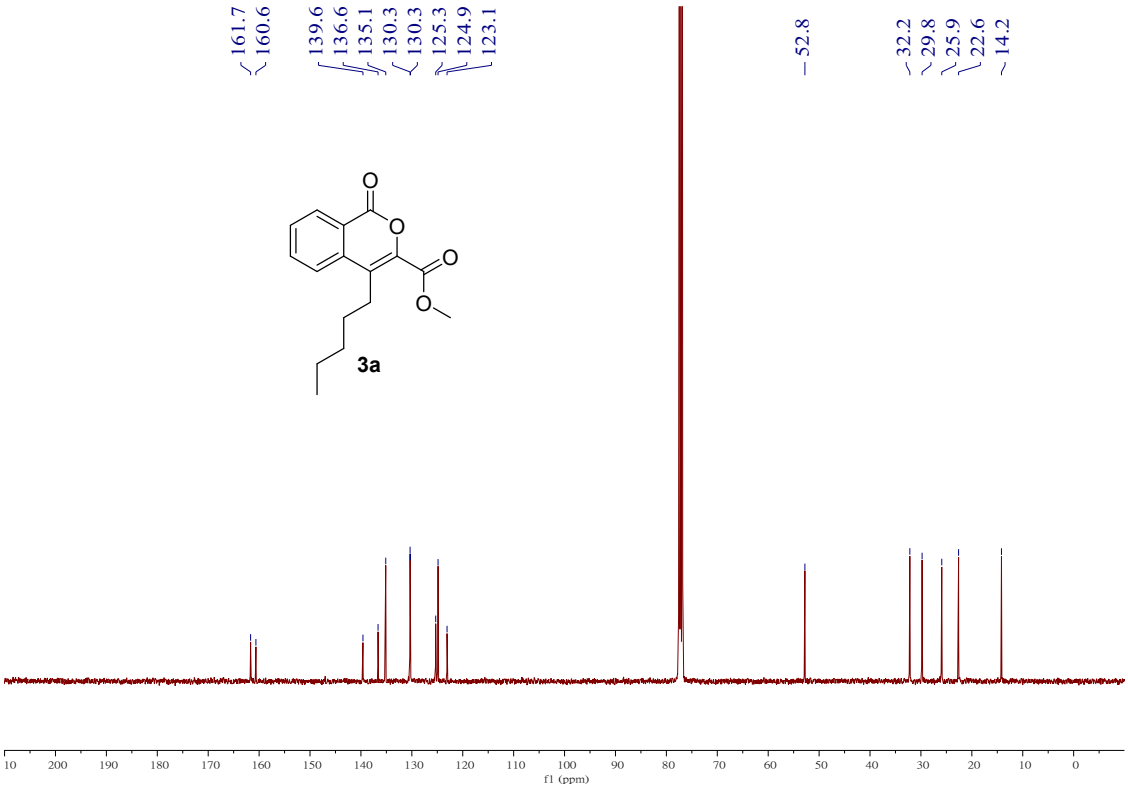
4j

Flash chromatography for purification: hexane/ethyl acetate = 6:1. Yellow solid; Yield = 425 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 1H), 7.69 (t, *J* = 8.4 Hz, 1H), 7.46 (dd, *J* = 17.2, 9.1 Hz, 2H), 7.38 (d, *J* = 2.5 Hz, 1H), 6.39 - 6.31 (m, 1H), 6.19 (s, 1H), 4.67 (d, *J* = 5.7 Hz, 2H), 2.59 - 2.50 (m, 2H), 1.75 - 1.64 (m, 2H), 1.32 - 1.26 (m, 4H), 0.91 - 0.81 (m, 3H); ^{13}C{1 H} NMR (101 MHz, $CDCl_3$) δ 165.2, 161.8, 156.7, 150.5, 142.6, 135.3, 135.1, 129.8, 123.6, 119.8, 113.6, 110.7, 108.2, 36.9, 36.9, 32.0, 31.4, 27.4, 22.4, 14.0; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}NNaO_4$ 364.1519; Found 364.1521.

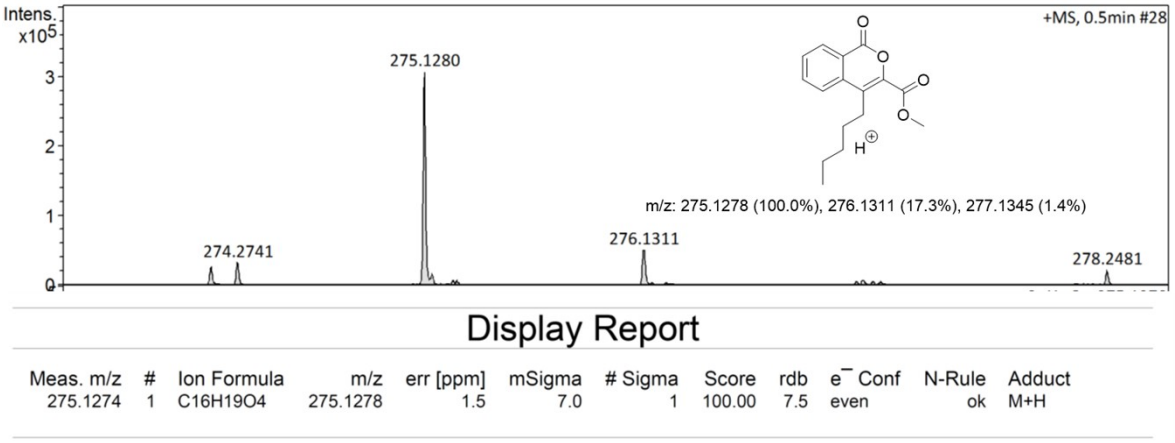
10. Spectral Data of 3a-4j



^{1}H spectrum (400 MHz) of compound **3a** in $CDCl_3$



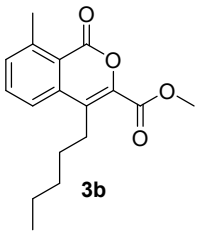
$^{13}C\{1H\}$ spectrum (101 MHz) of compound **3a** in $CDCl_3$



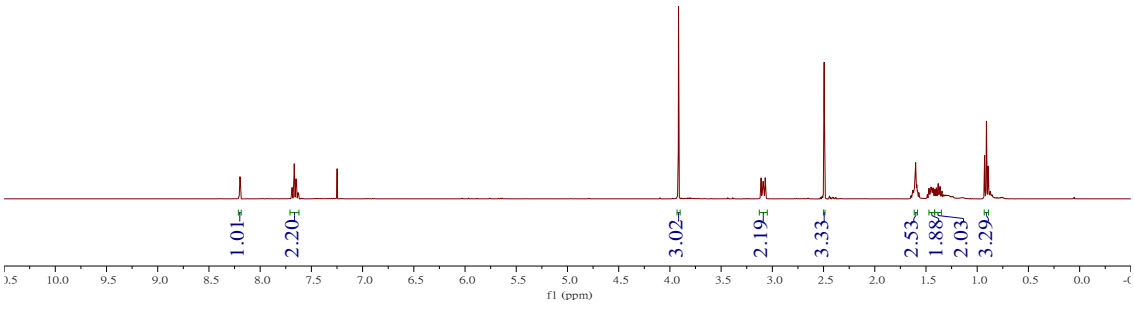
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
275.1274	1	C16H19O4	275.1278	1.5	7.0	1	100.00	7.5	even	ok	M+H

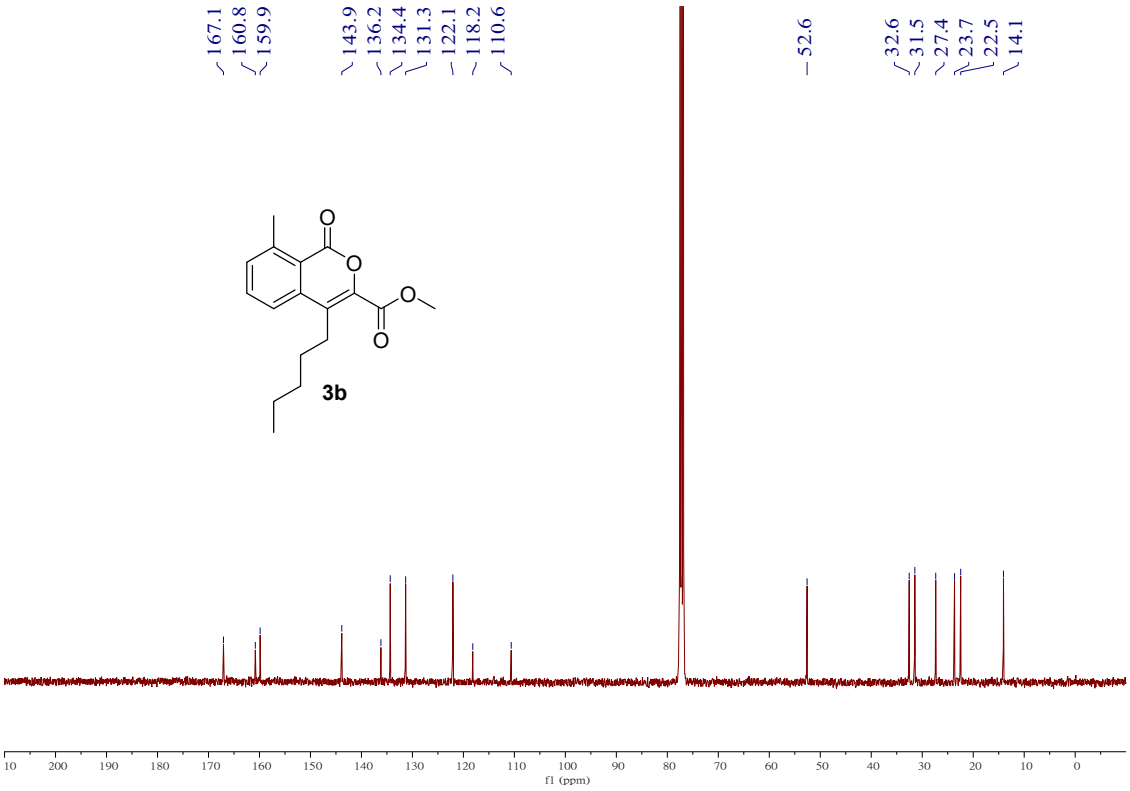
HRMS Mass (ESI) spectrum of compound **3a**



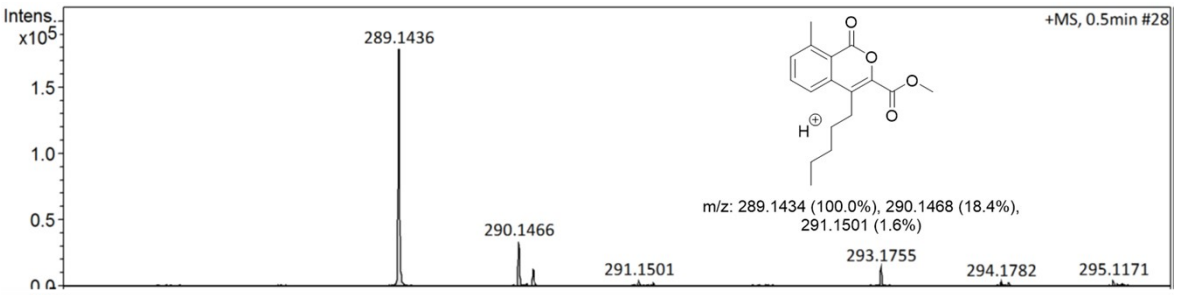
3b



^{1}H spectrum (400 MHz) of compound **3b** in $CDCl_3$



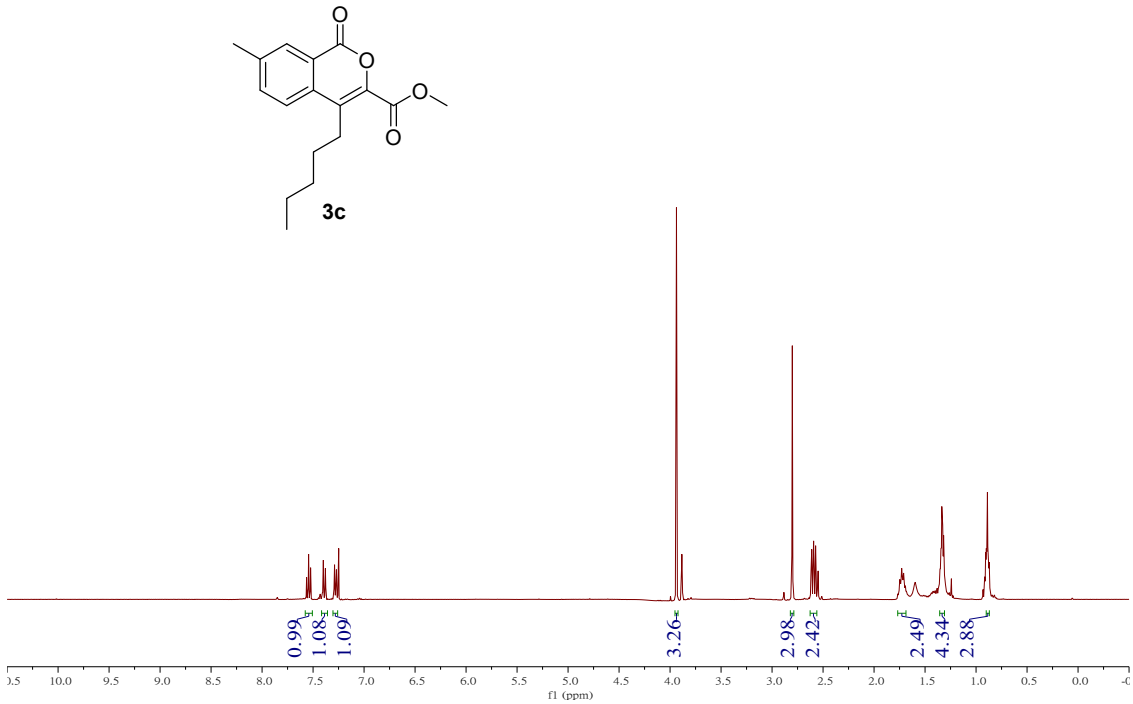
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3b** in $CDCl_3$



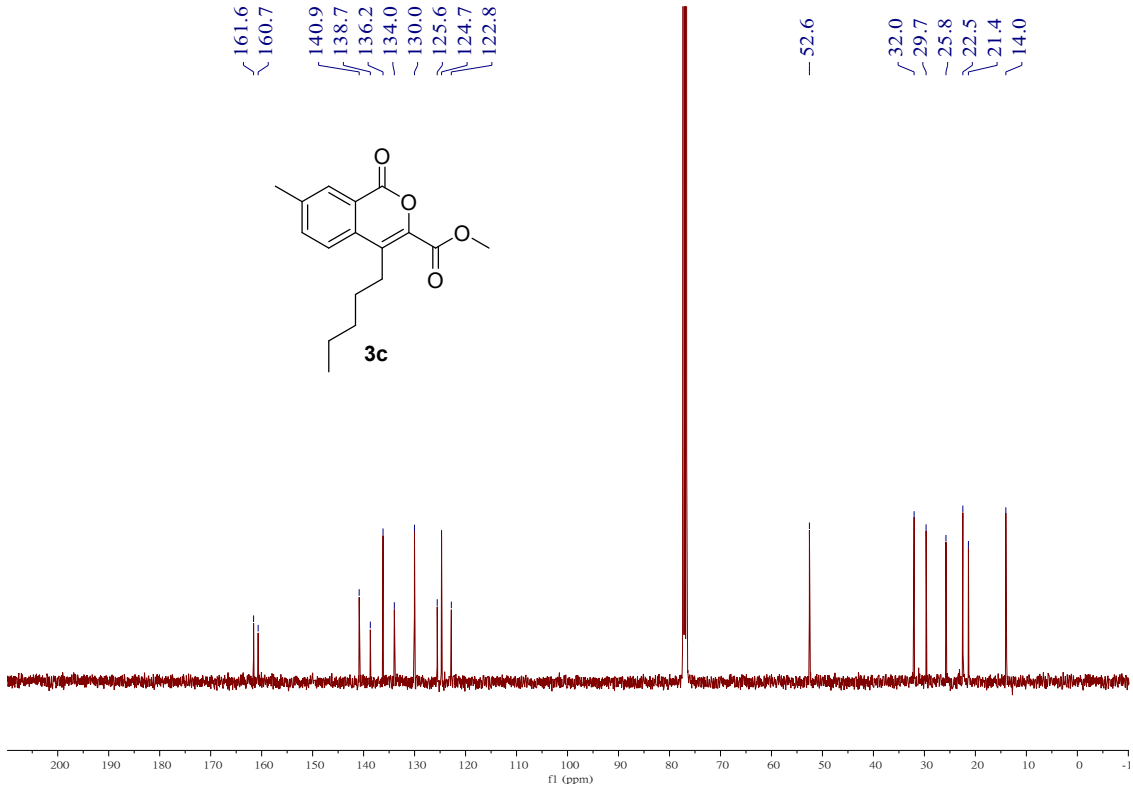
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule	Adduct
289.1436	1	C17H21O4	289.1434	0.7	1.8	1	100.00	7.5	even	ok	M+H

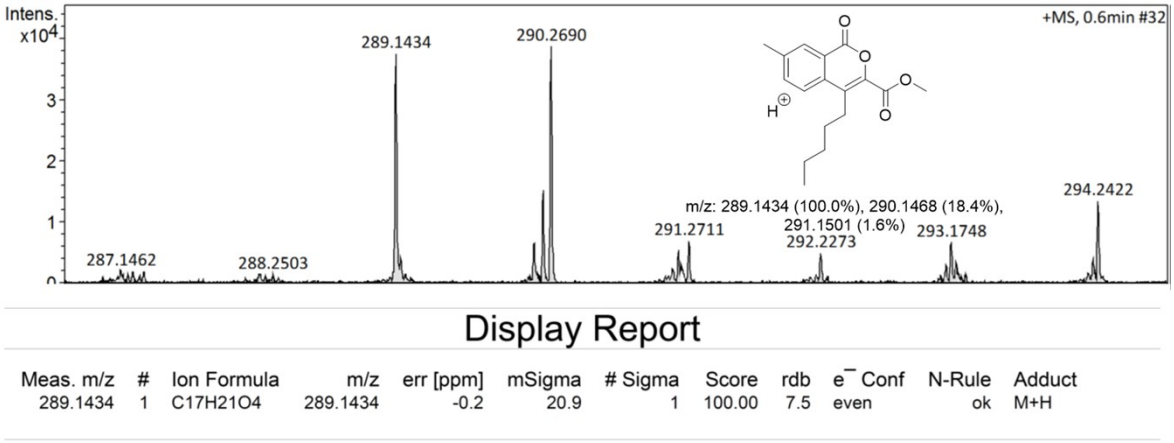
HRMS Mass (ESI) spectrum of compound **3b**



^{1}H spectrum (400 MHz) of compound **3c** in $CDCl_3$



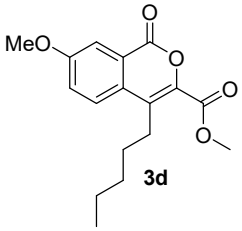
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3c** in $CDCl_3$

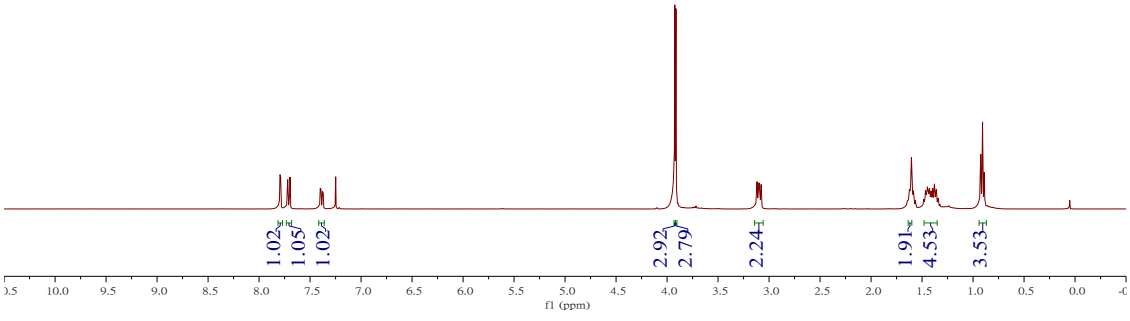


Display Report

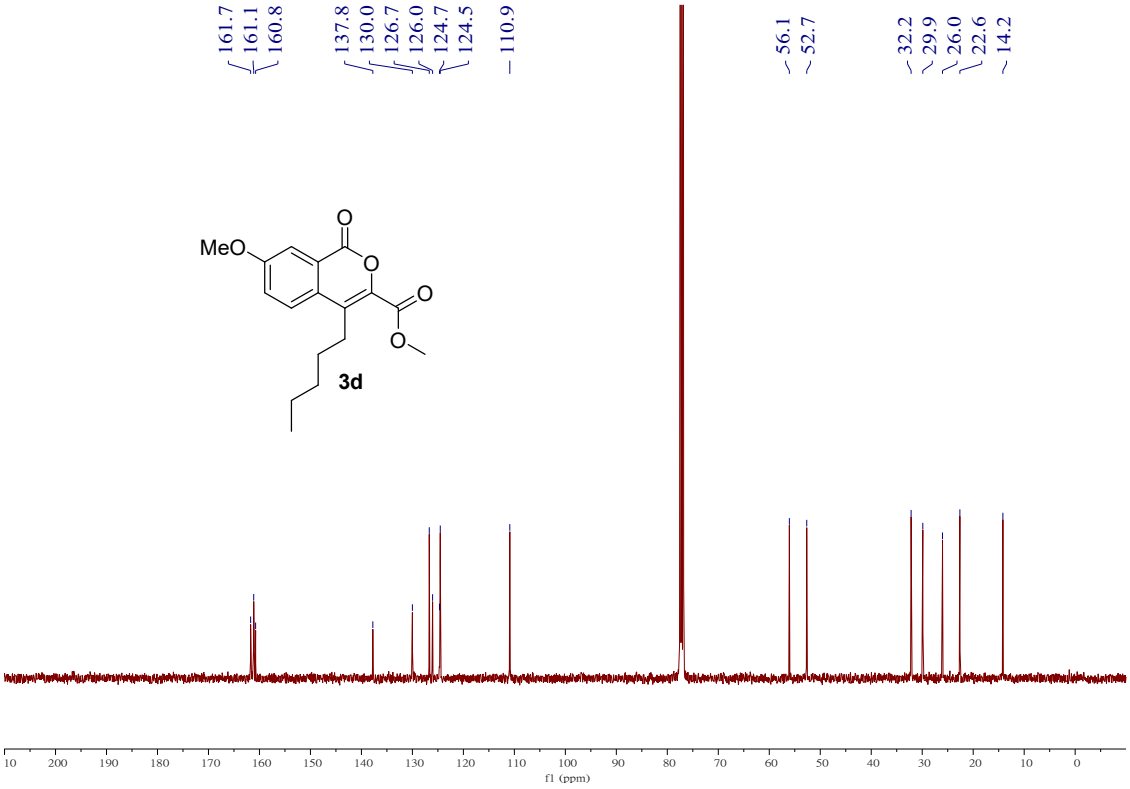
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
289.1434	1	C17H21O4	289.1434	-0.2	20.9	1	100.00	7.5	even	ok	M+H

HRMS Mass (ESI) spectrum of compound **3c**

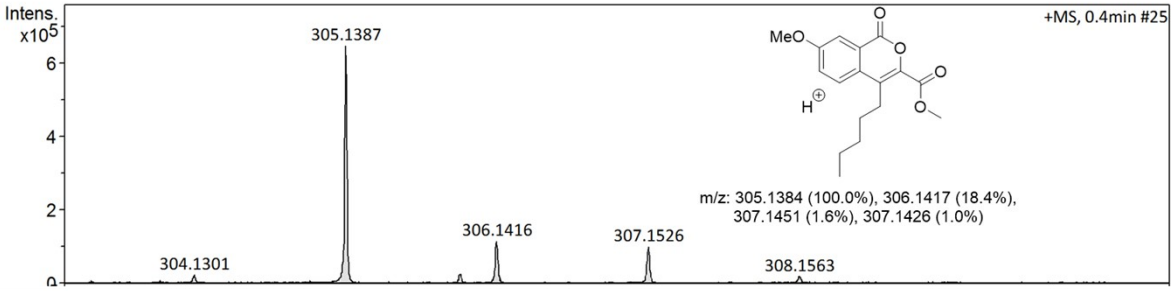




^{1}H spectrum (400 MHz) of compound **3d** in $CDCl_3$



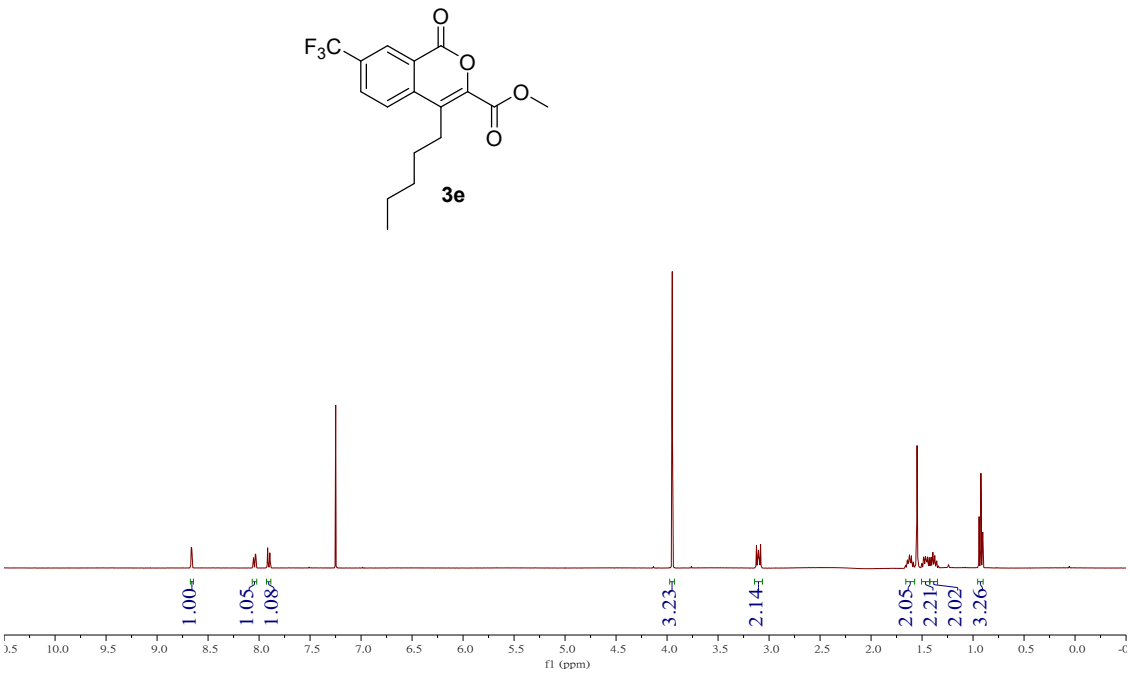
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3d** in $CDCl_3$



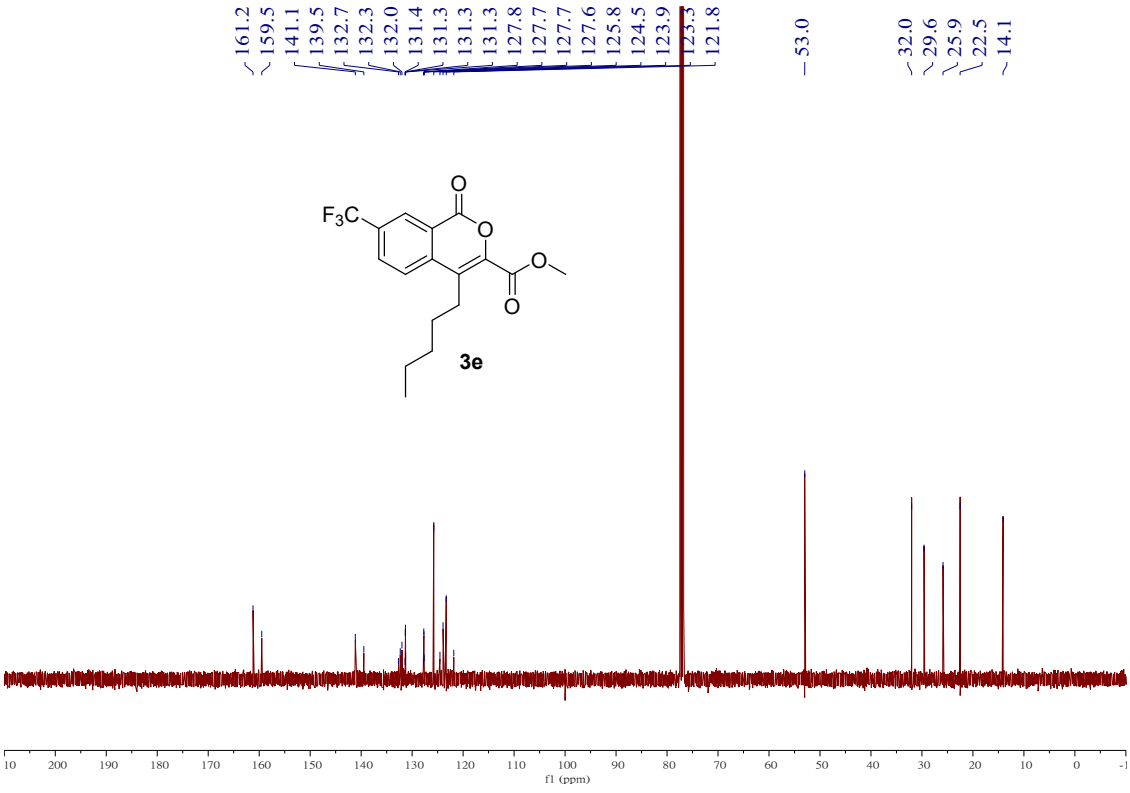
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
305.1387	1	C17H21O5	305.1384	1.1	74.0	1	100.00	7.5	even	ok	M+H

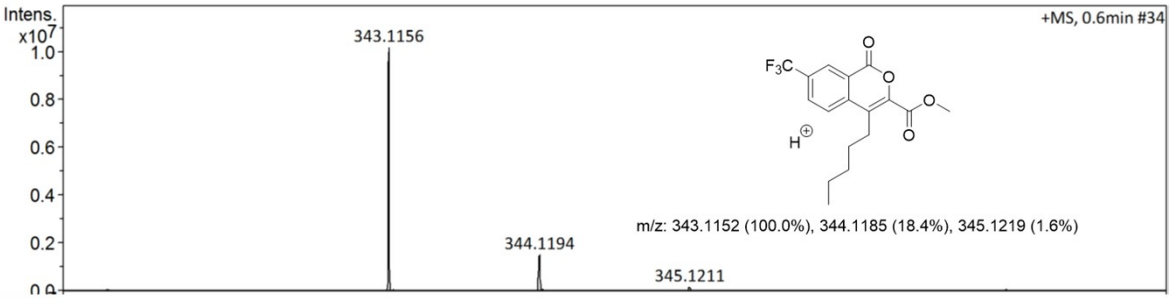
HRMS Mass (ESI) spectrum of compound **3d**



^{1}H spectrum (400 MHz) of compound **3e** in $CDCl_3$



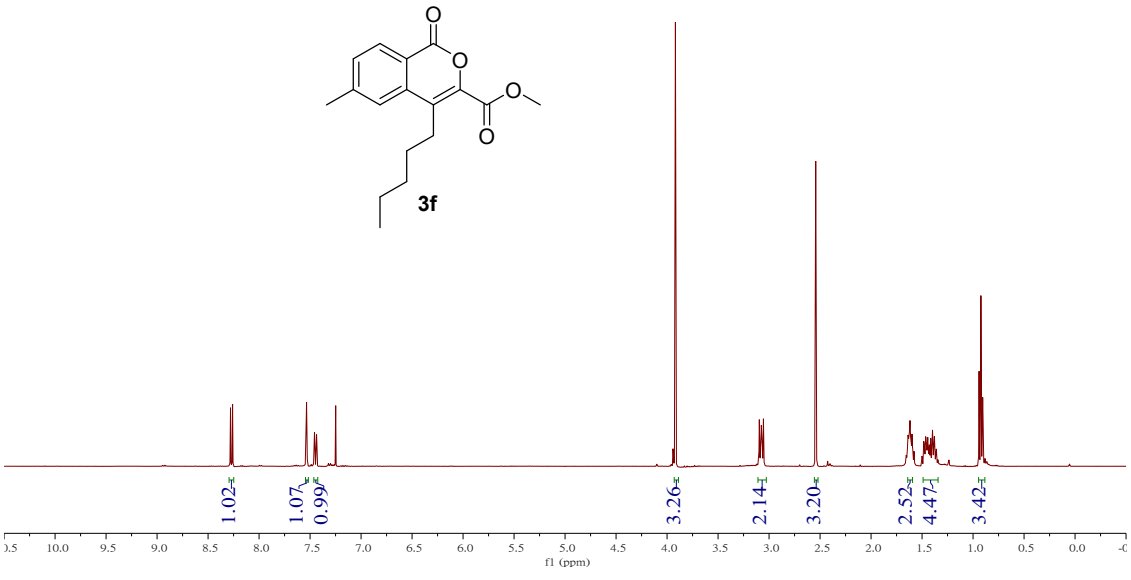
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3e** in $CDCl_3$



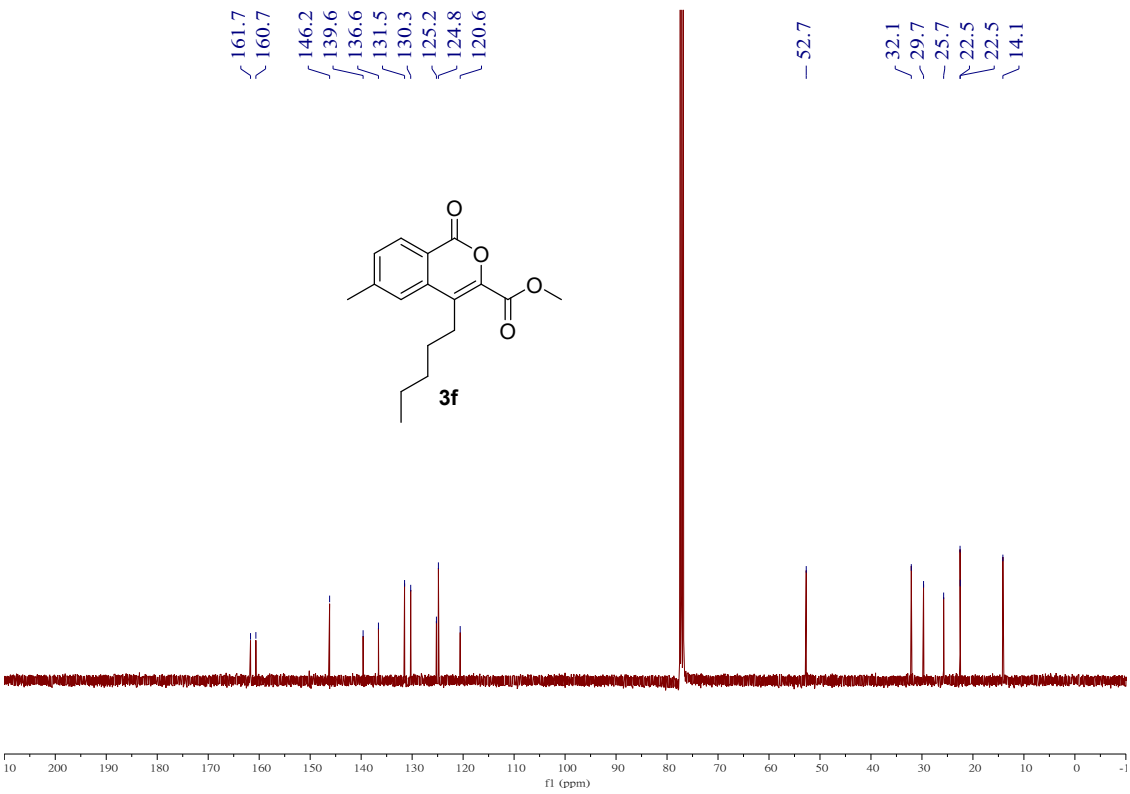
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
343.1156	1	C17H18F3O4	343.1152	-1.4	23.2	2	100.00	7.5	even	ok	M+H

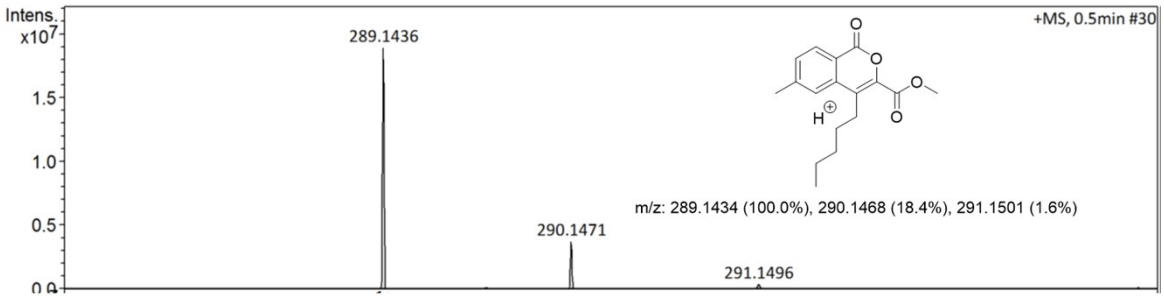
HRMS Mass (ESI) spectrum of compound **3e**



^{1}H spectrum (400 MHz) of compound **3f** in $CDCl_3$



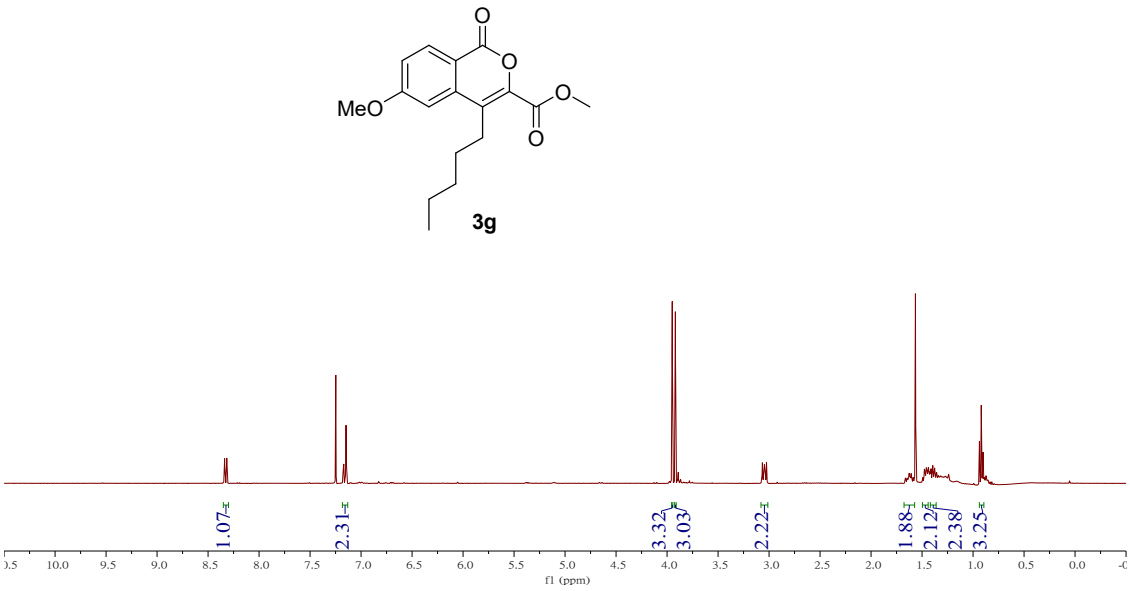
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3f** in $CDCl_3$



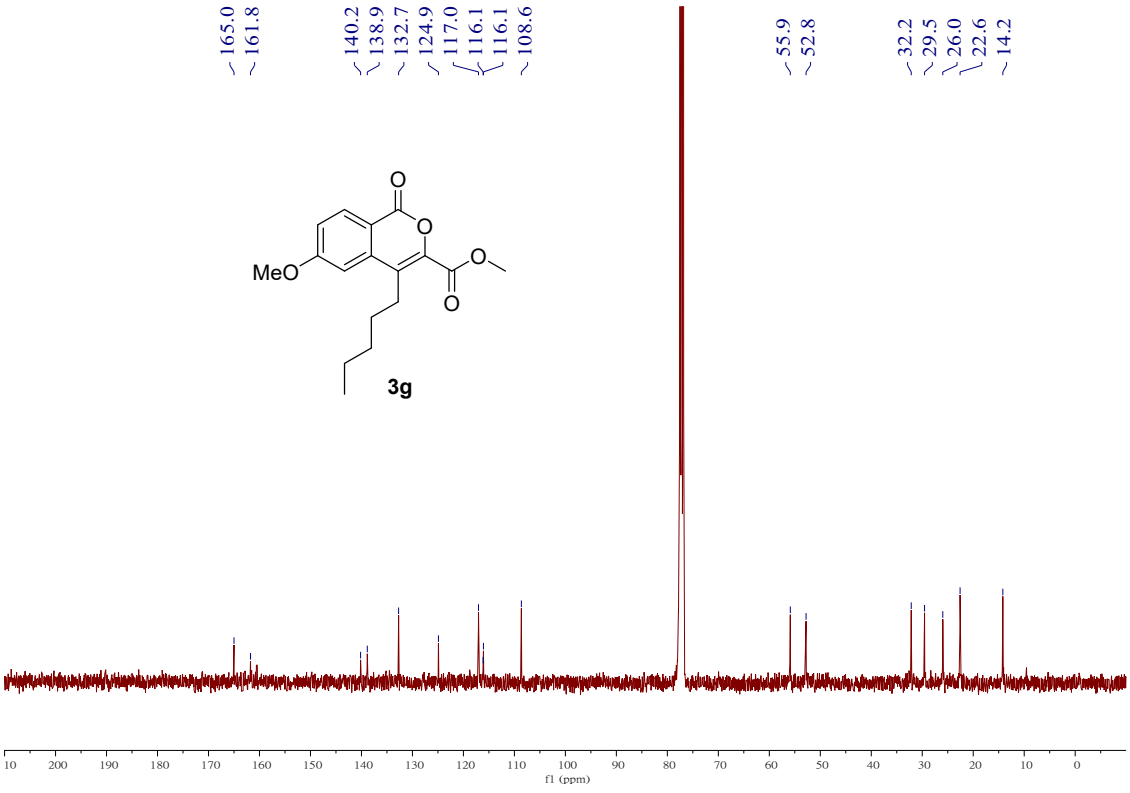
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
289.1436	1	C17H21O4	289.1434	-0.6	6.4	1	100.00	7.5	even	ok	M+H

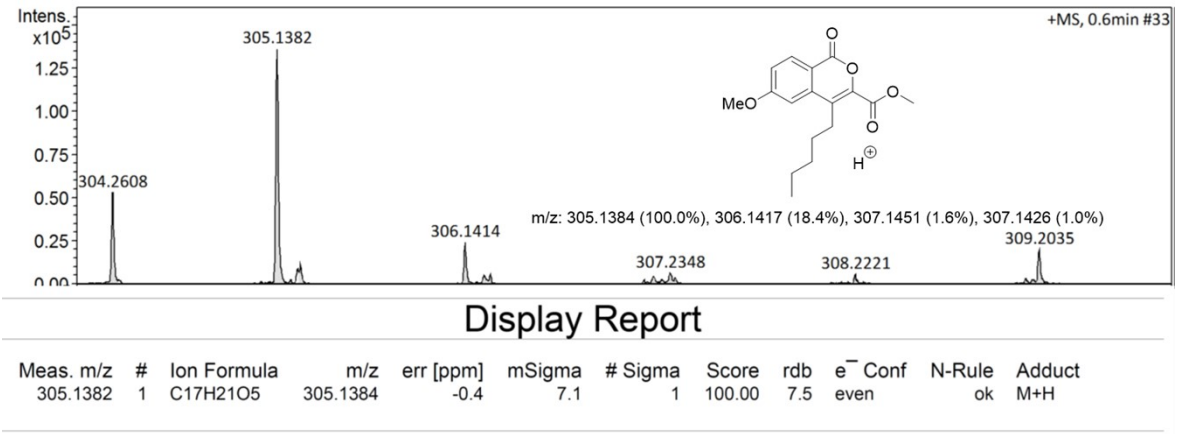
HRMS Mass (ESI) spectrum of compound **3f**



^{1}H spectrum (400 MHz) of compound **3g** in $CDCl_3$



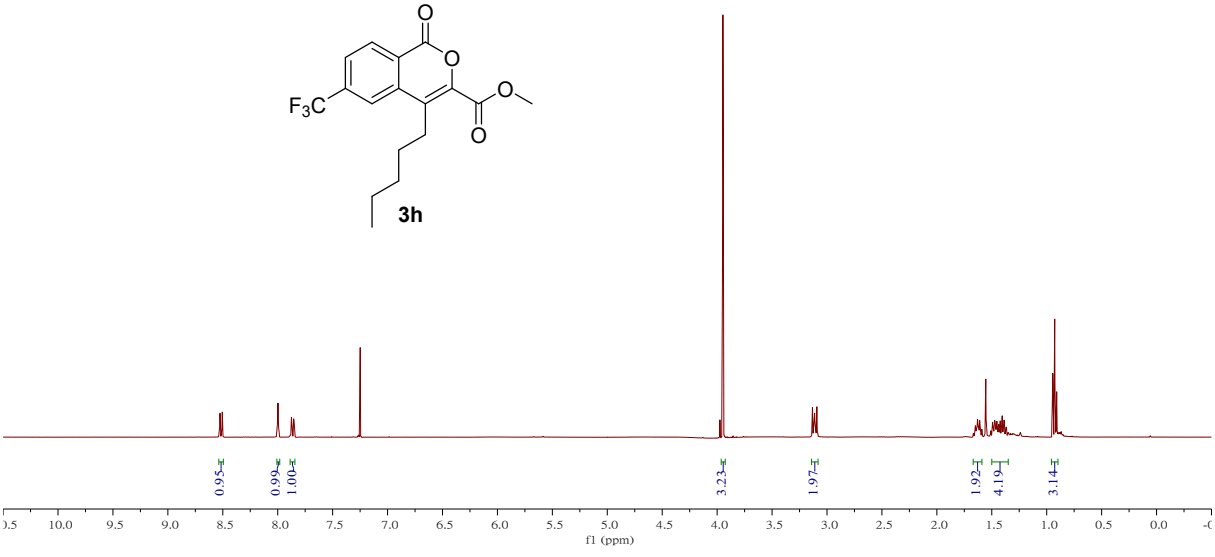
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3g** in $CDCl_3$



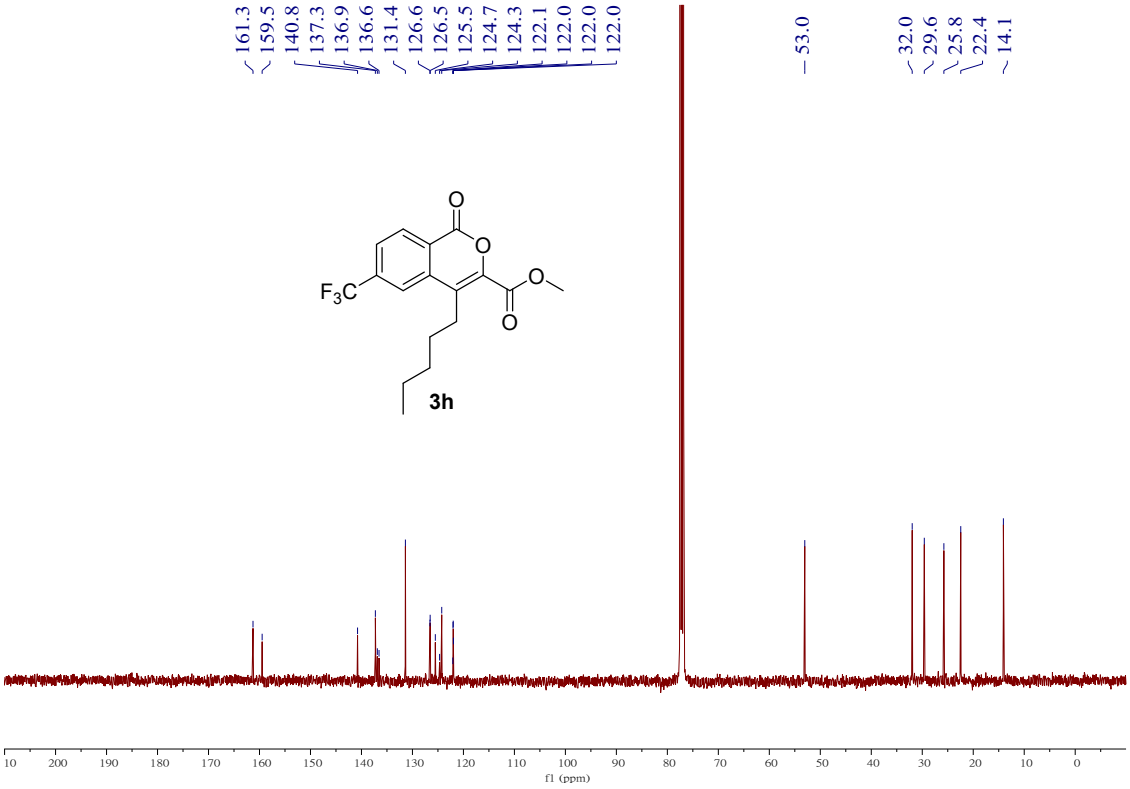
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
305.1382	1	C17H21O5	305.1384	-0.4	7.1	1	100.00	7.5	even	ok	M+H

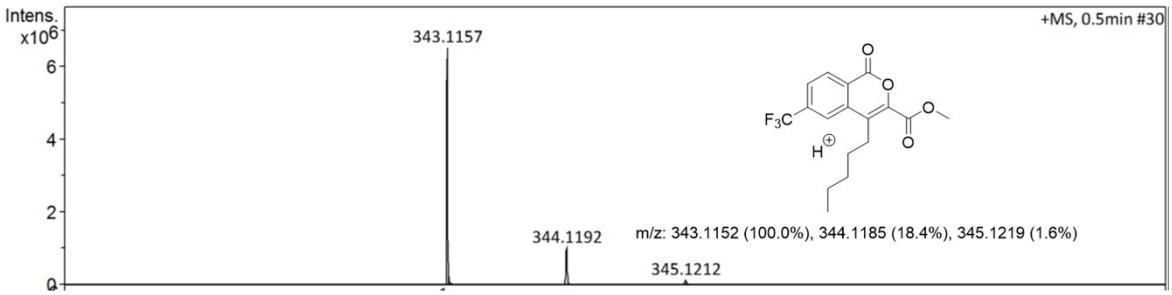
HRMS Mass (ESI) spectrum of compound **3g**



^{1}H spectrum (400 MHz) of compound **3h** in $CDCl_3$



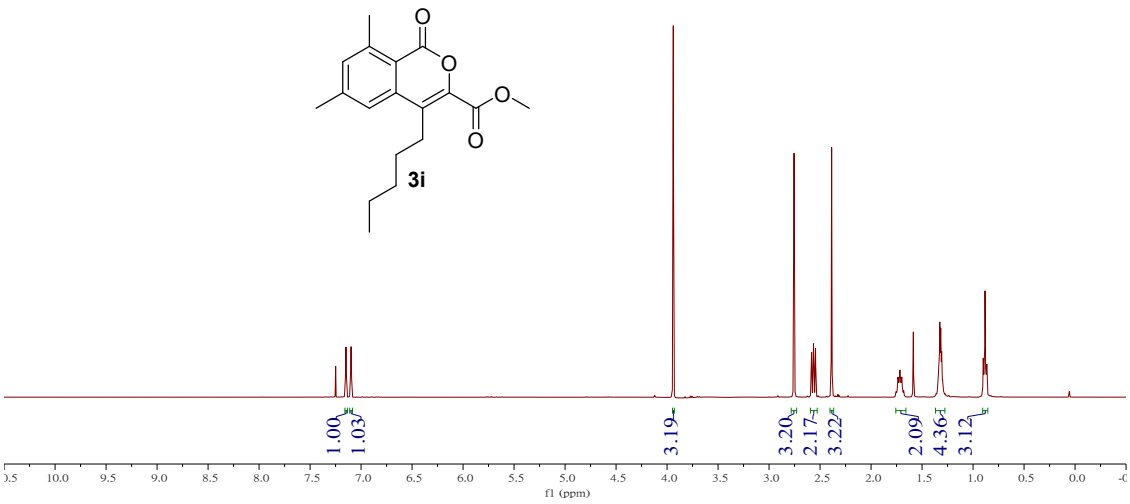
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3h** in $CDCl_3$



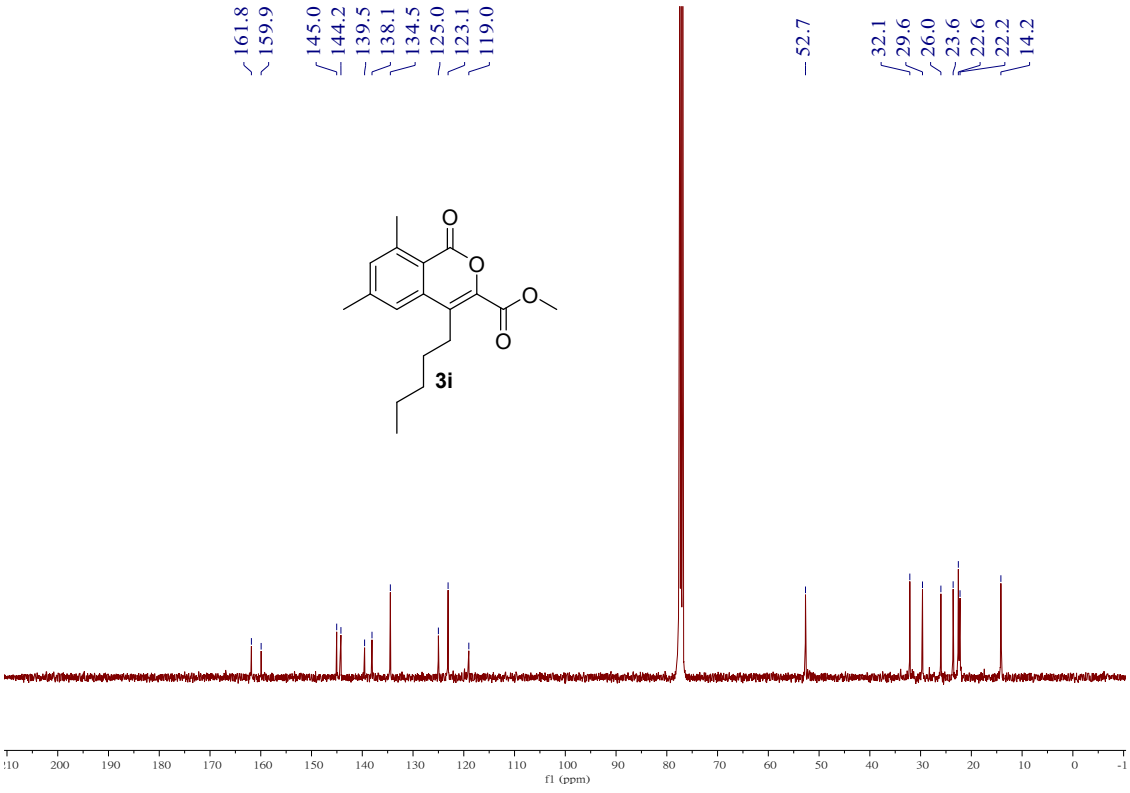
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
343.1157	1	C17H18F3O4	343.1152	1.4	19.3	2	100.00	7.5	even	ok	M+H

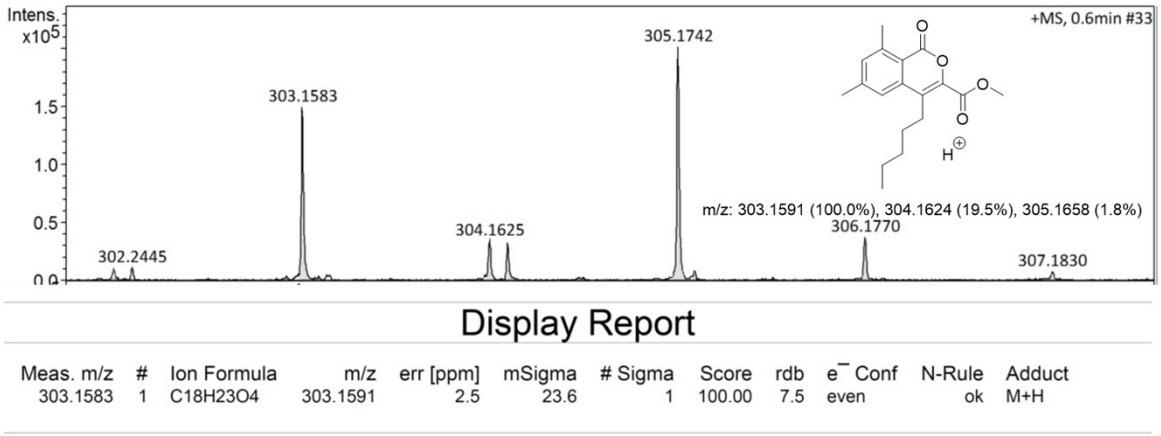
HRMS Mass (ESI) spectrum of compound **3h**



^{1}H spectrum (400 MHz) of compound **3i** in $CDCl_3$



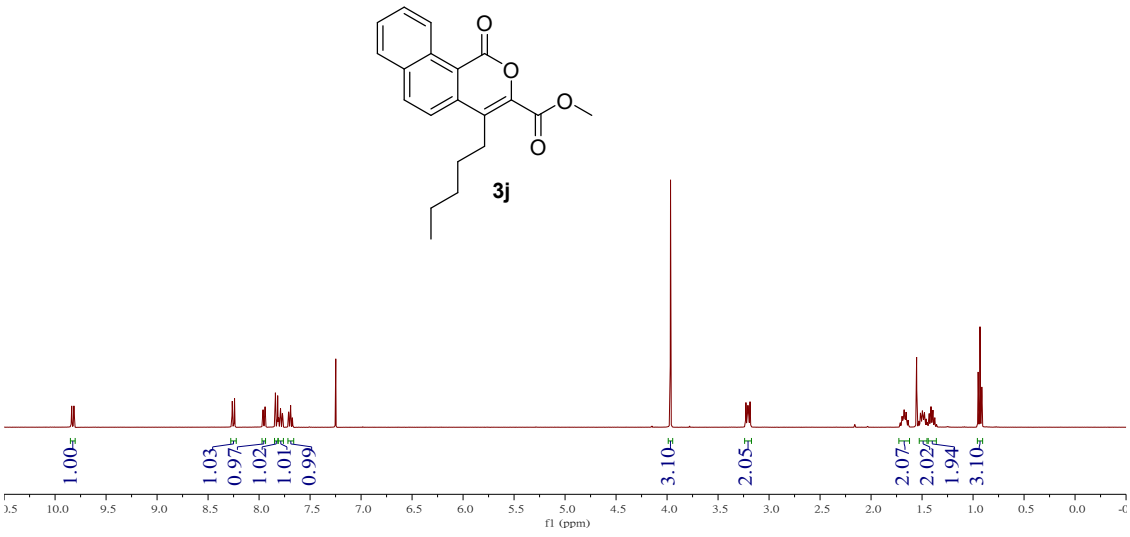
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3i** in $CDCl_3$



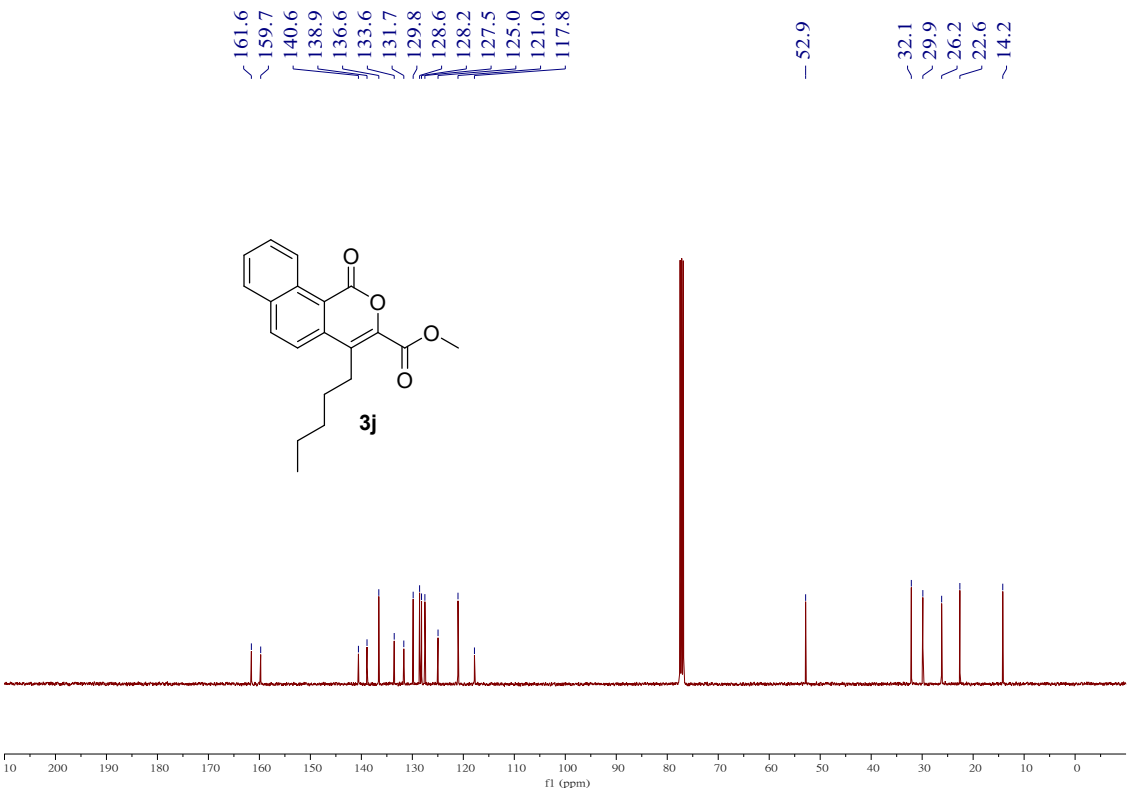
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
303.1583	1	C18H23O4	303.1591	2.5	23.6	1	100.00	7.5	even	ok	M+H

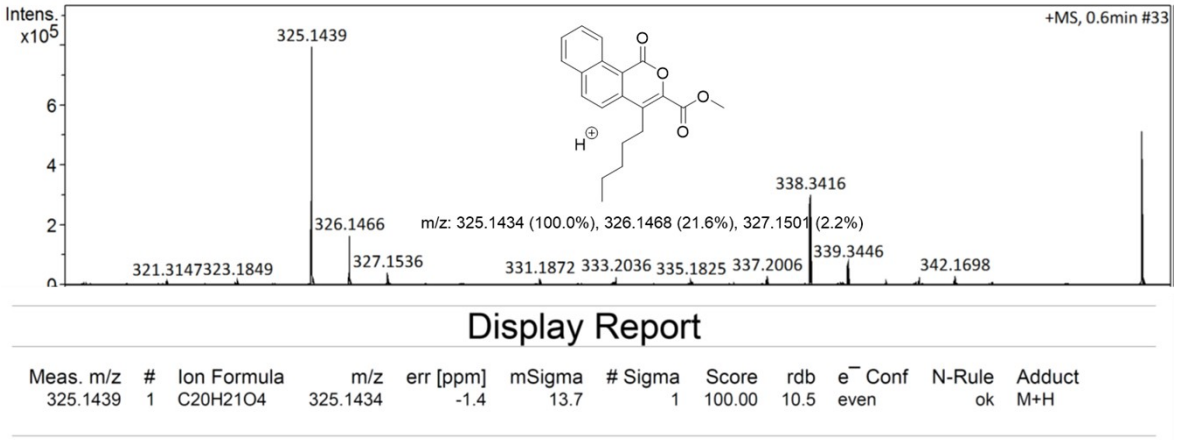
HRMS Mass (ESI) spectrum of compound **3i**



^{1}H spectrum (400 MHz) of compound **3j** in $CDCl_3$



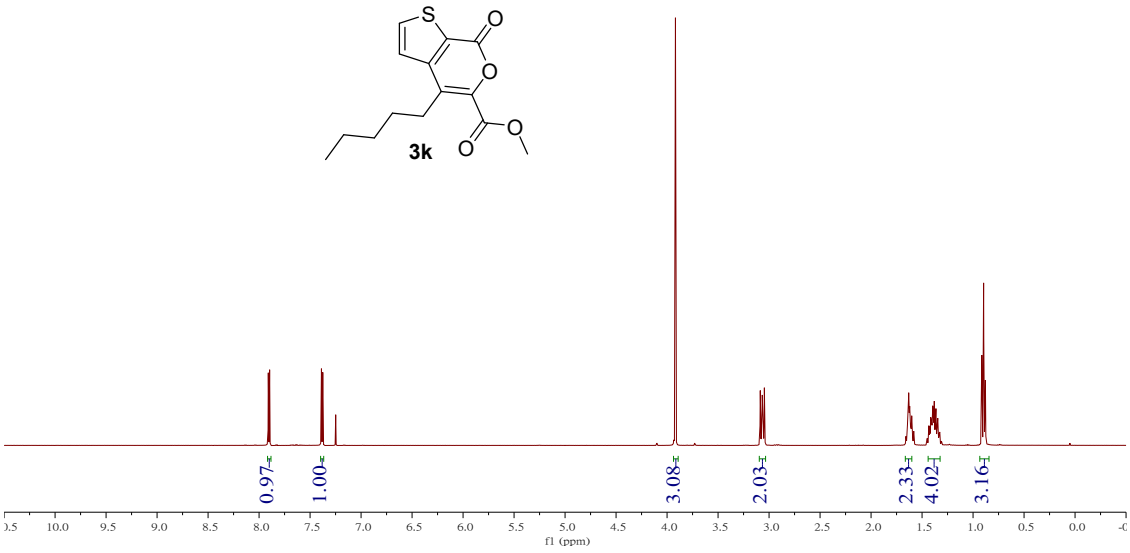
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3j** in $CDCl_3$



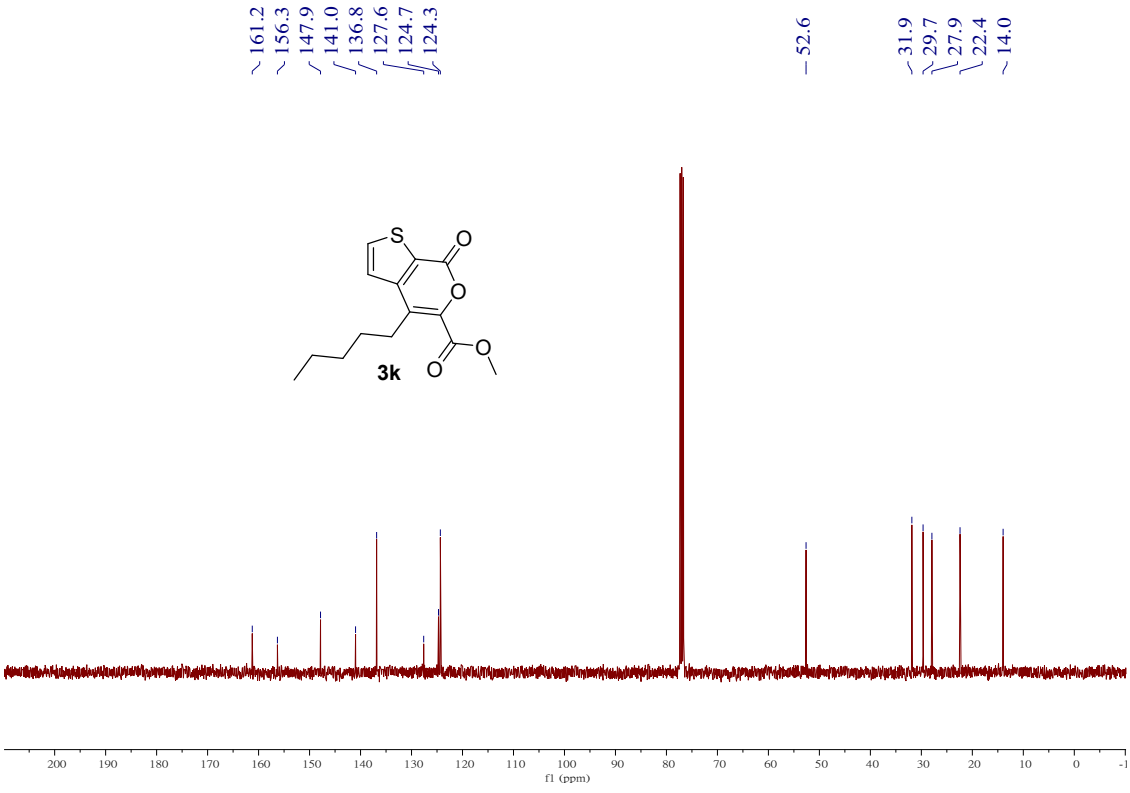
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
325.1439	1	C20H21O4	325.1434	-1.4	13.7	1	100.00	10.5	even	ok	M+H

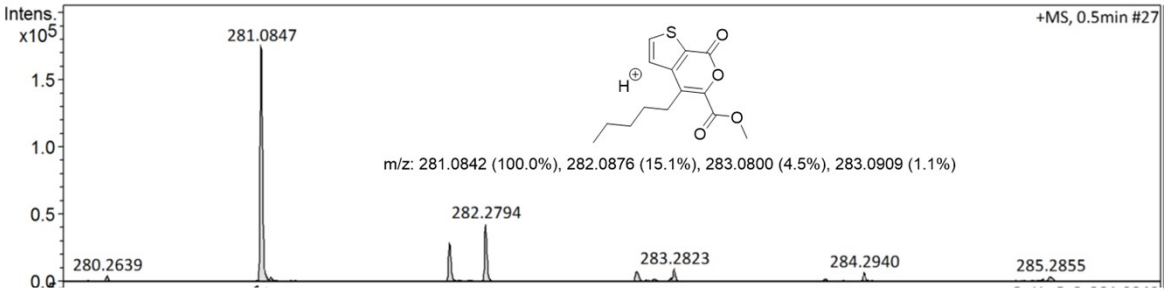
HRMS Mass (ESI) spectrum of compound **3j**



^{1}H spectrum (400 MHz) of compound **3k** in $CDCl_3$



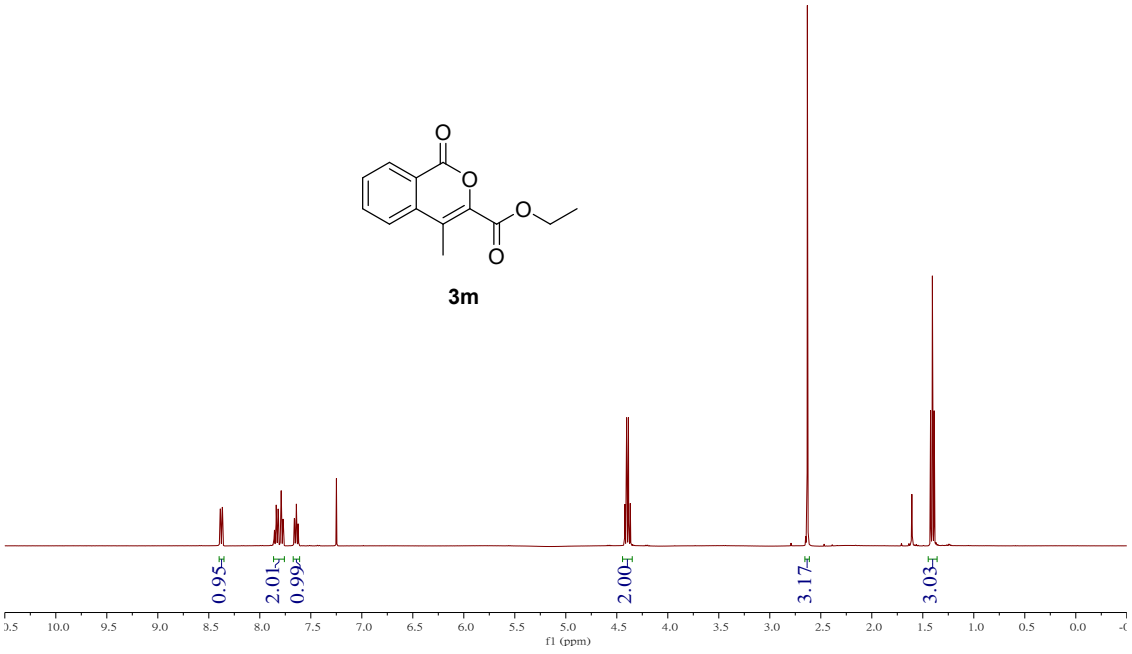
$^{13}C\{1H\}$ spectrum (101 MHz) of compound **3k** in $CDCl_3$



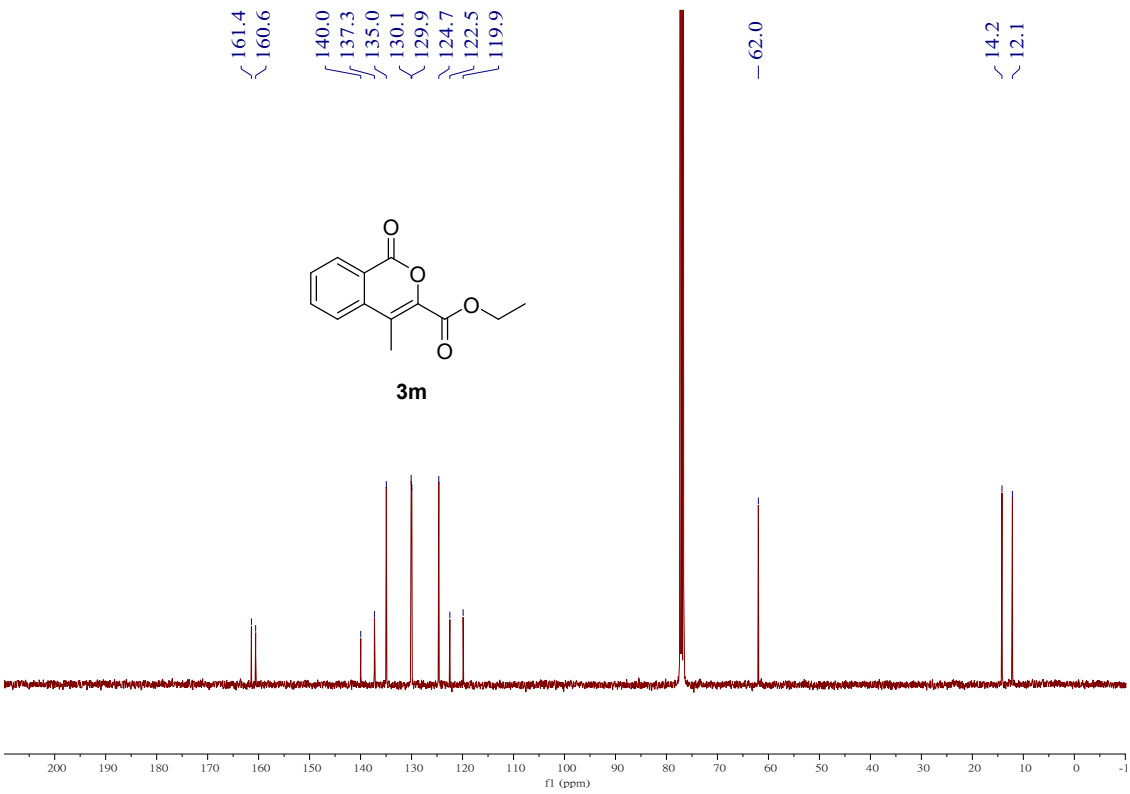
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
281.0847	1	C14H17O4S	281.0842	1.6	10.7	1	100.00	6.5	even	ok	M+H

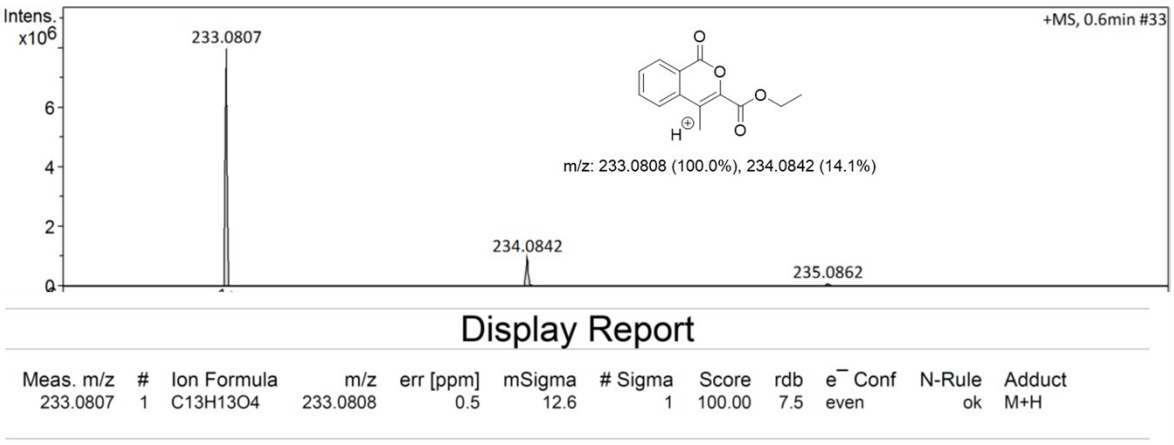
HRMS Mass (ESI) spectrum of compound **3k**



^{1}H spectrum (400 MHz) of compound **3m** in $CDCl_3$



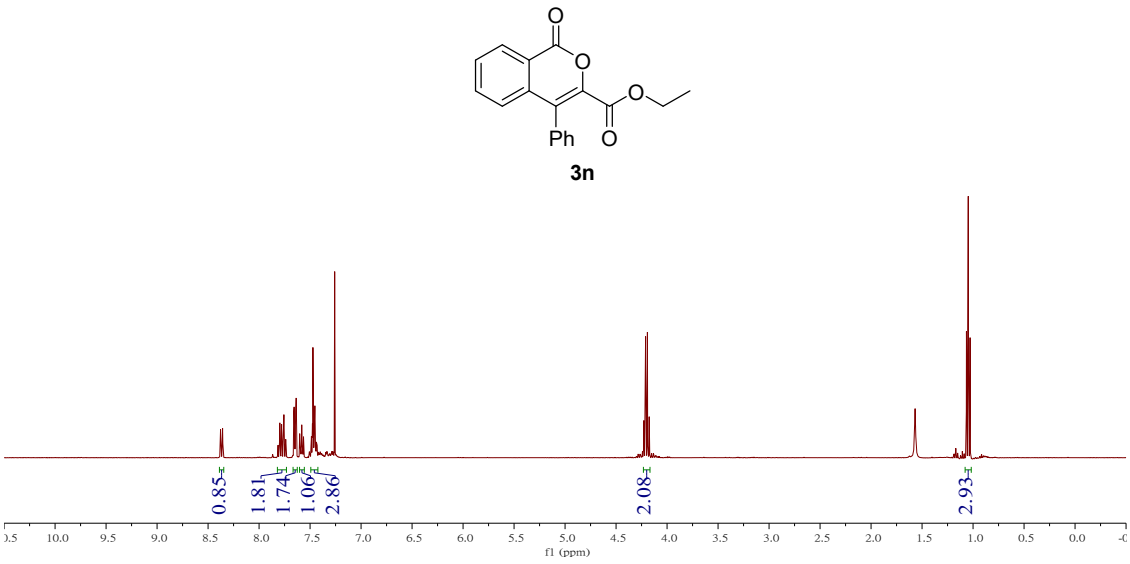
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3m** in $CDCl_3$



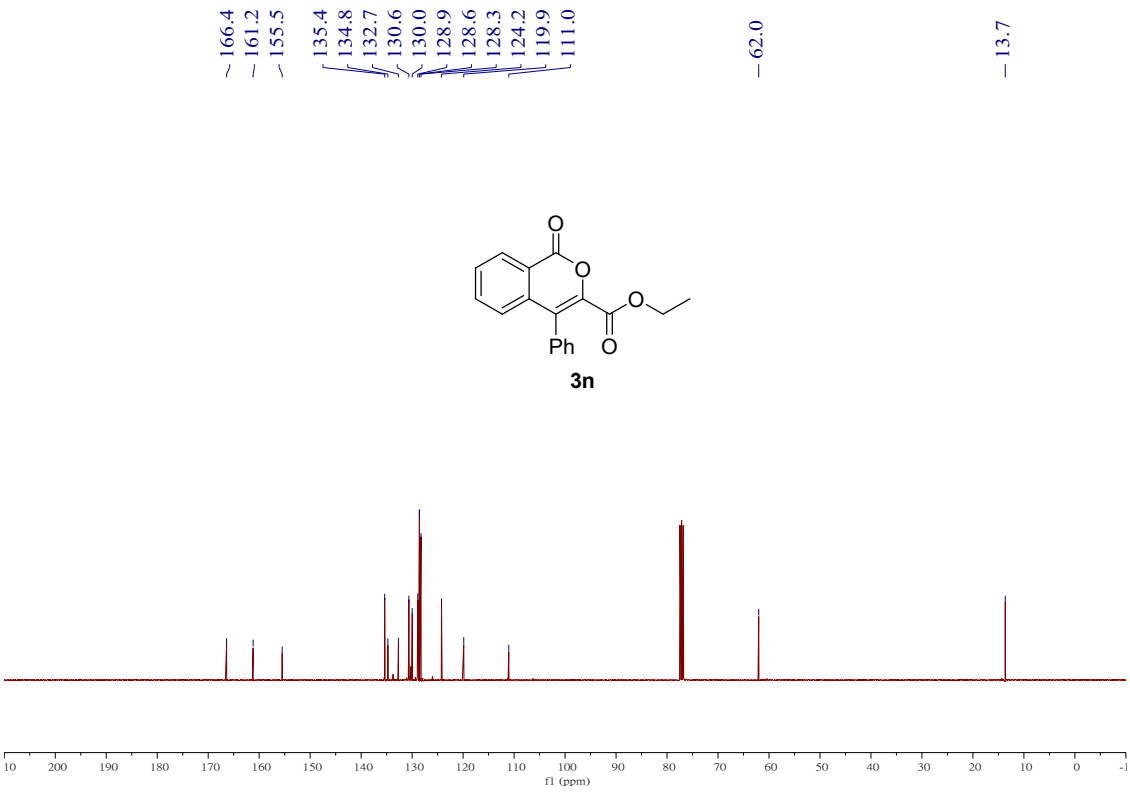
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
233.0807	1	C13H13O4	233.0808	0.5	12.6	1	100.00	7.5	even	ok	M+H

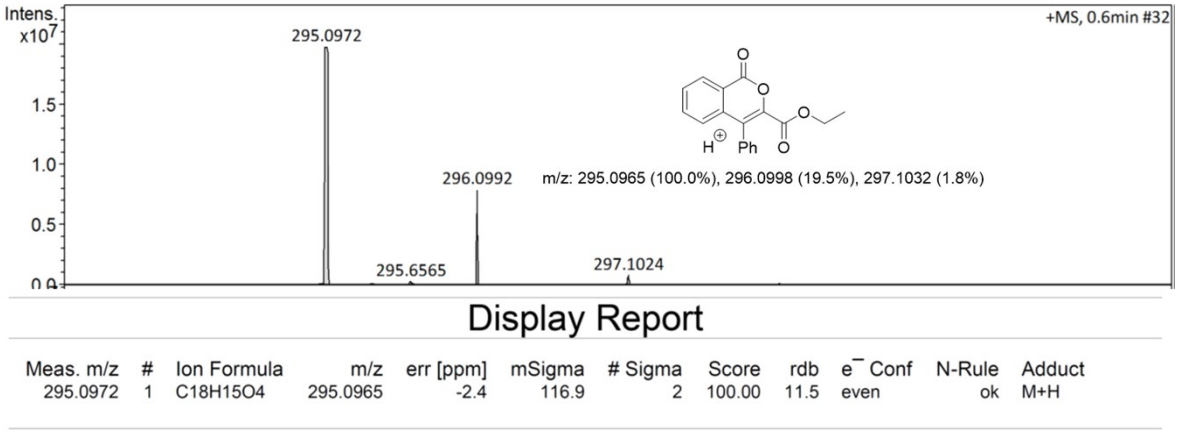
HRMS Mass (ESI) spectrum of compound **3m**



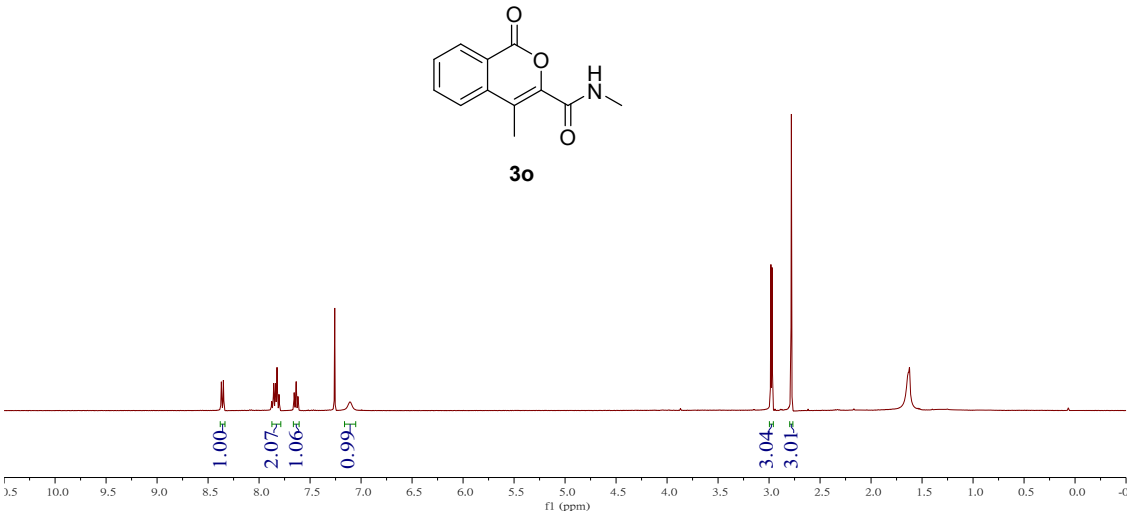
^{1}H spectrum (400 MHz) of compound **3n** in $CDCl_3$



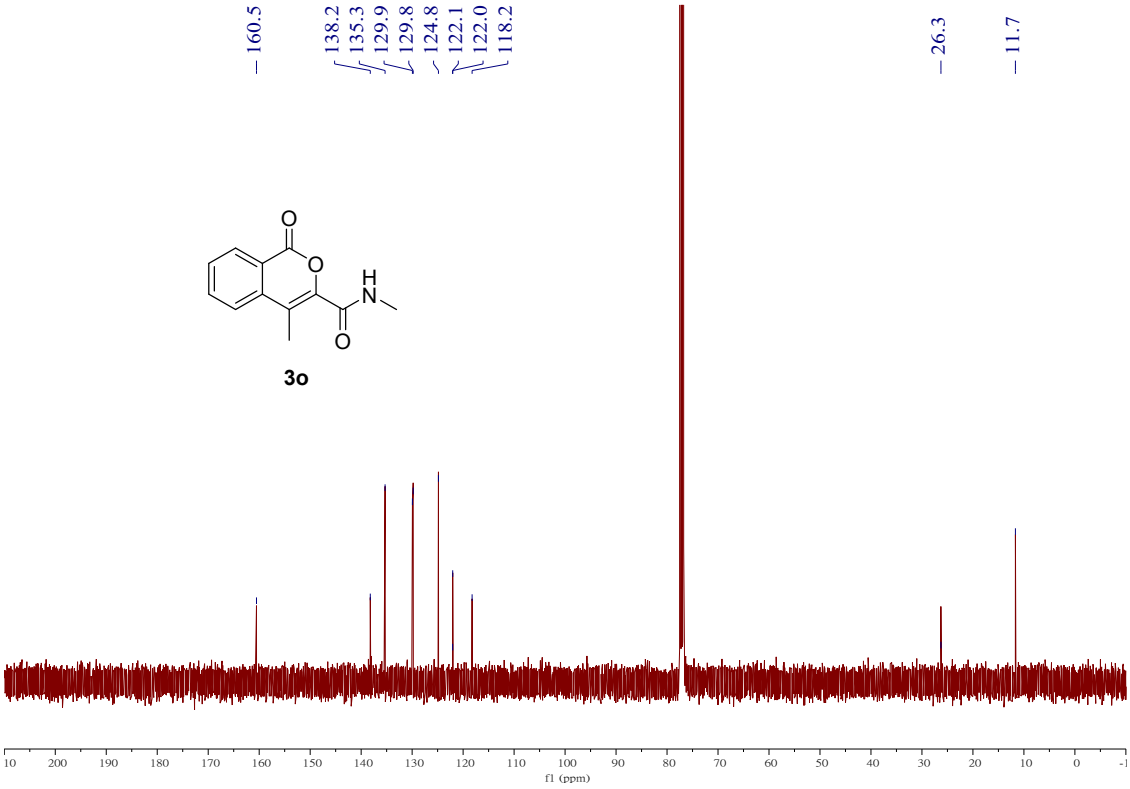
$^{13}C\{^{1}H\}$ spectrum (101 MHz) of compound **3n** in $CDCl_3$



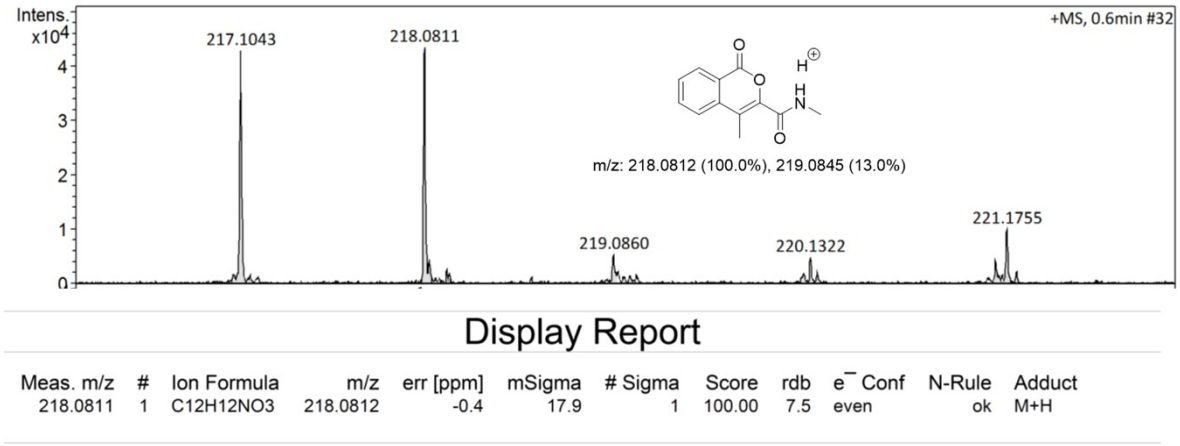
HRMS Mass (ESI) spectrum of compound **3n**



^{1}H spectrum (400 MHz) of compound **3o** in $CDCl_3$



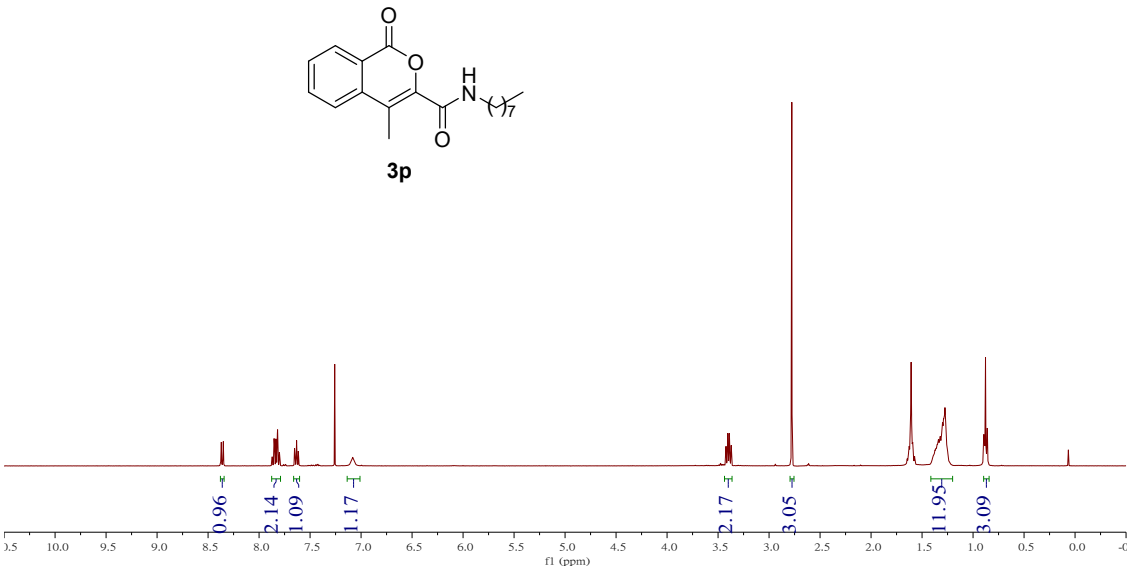
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3o** in $CDCl_3$



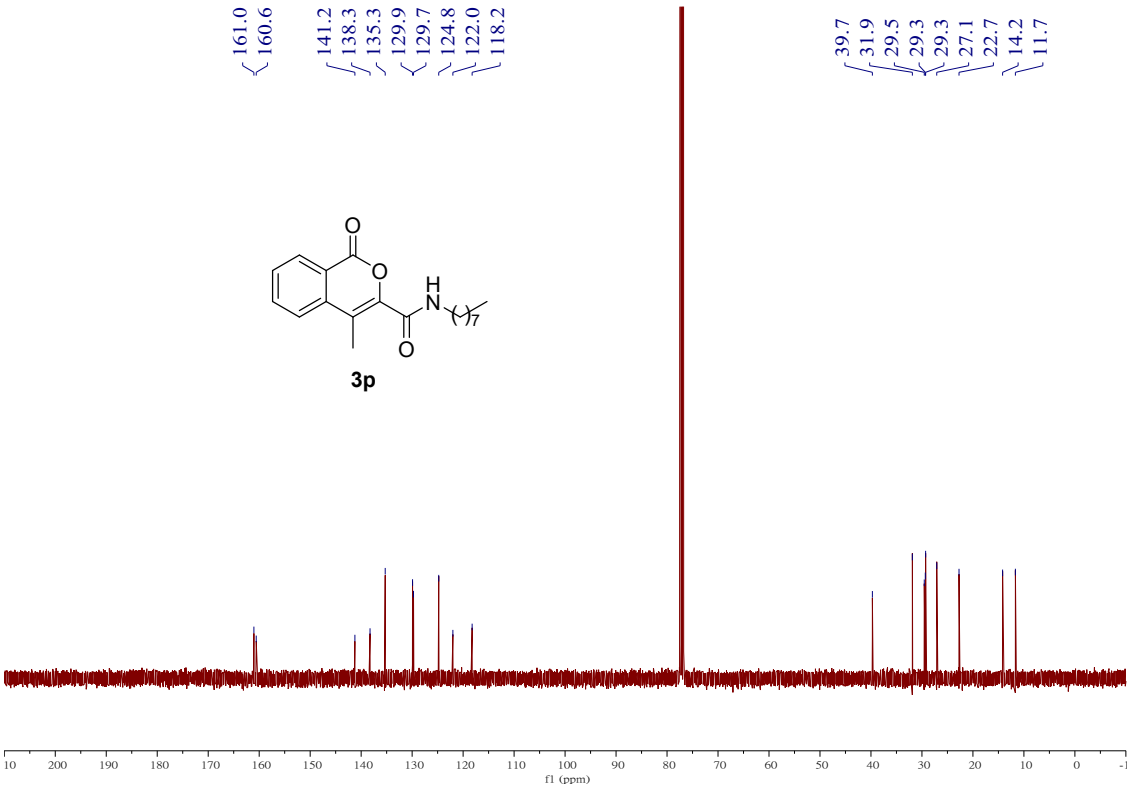
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
218.0811	1	C12H12NO3	218.0812	-0.4	17.9	1	100.00	7.5	even	ok	M+H

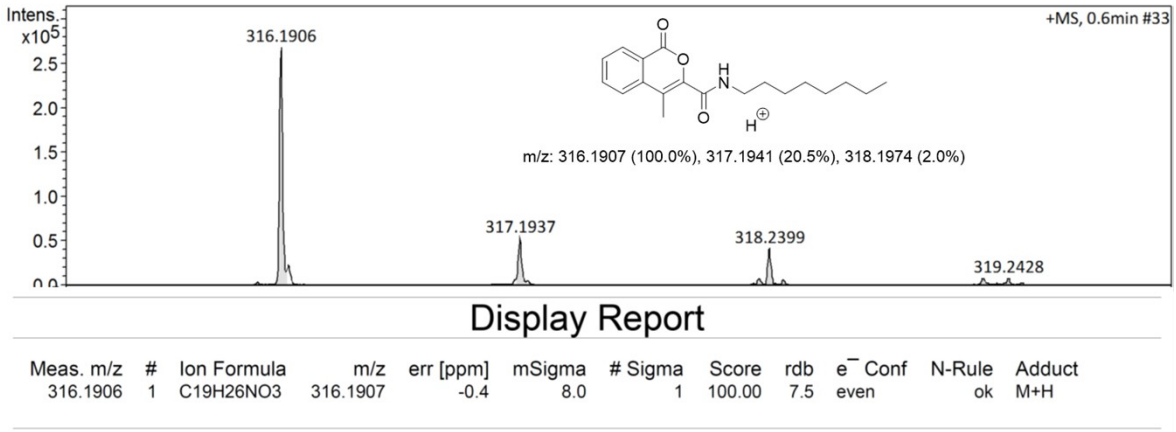
HRMS Mass (ESI) spectrum of compound **3o**



^{1}H spectrum (400 MHz) of compound **3p** in $CDCl_3$



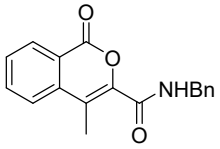
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3p** in $CDCl_3$



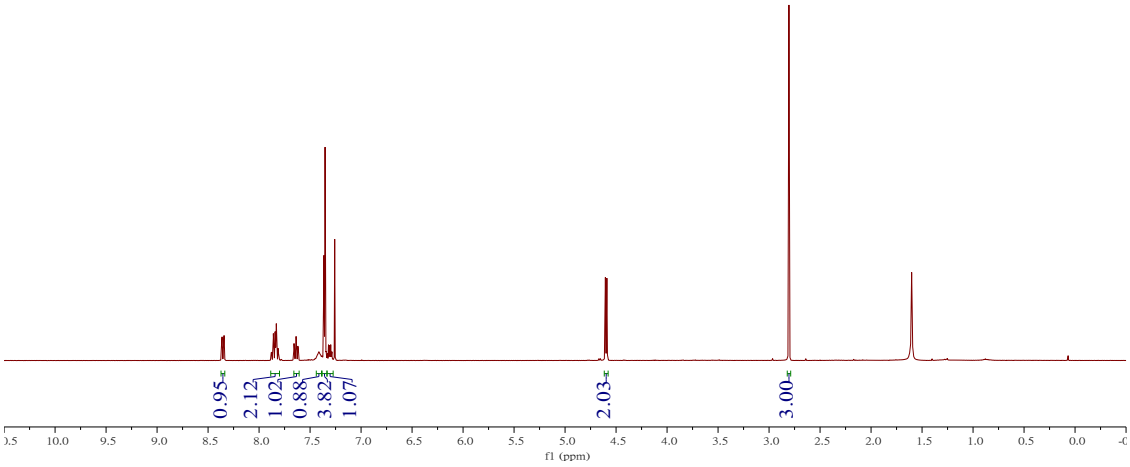
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule	Adduct
316.1906	1	C19H26NO3	316.1907	-0.4	8.0	1	100.00	7.5	even	ok	M+H

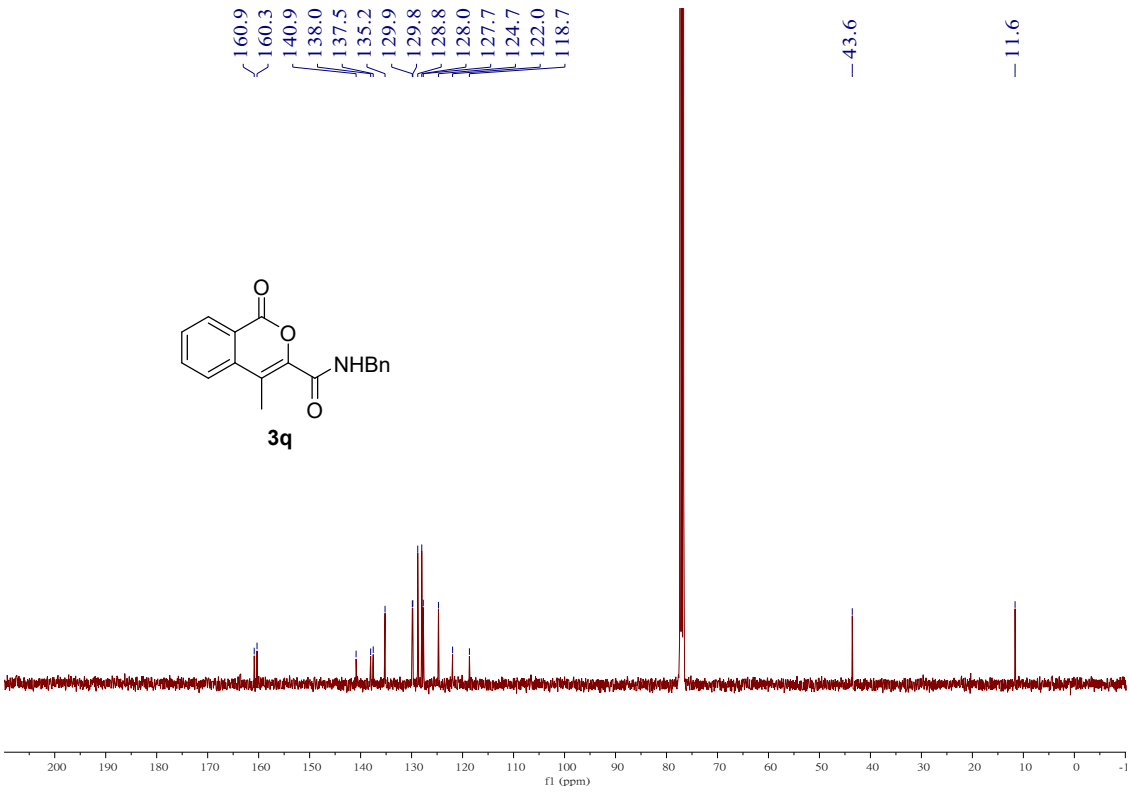
HRMS Mass (ESI) spectrum of compound **3p**



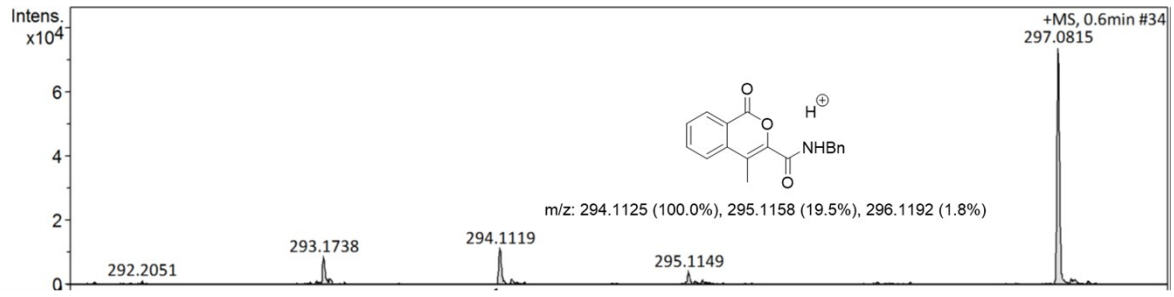
3q



^{1}H spectrum (400 MHz) of compound **3q** in $CDCl_3$



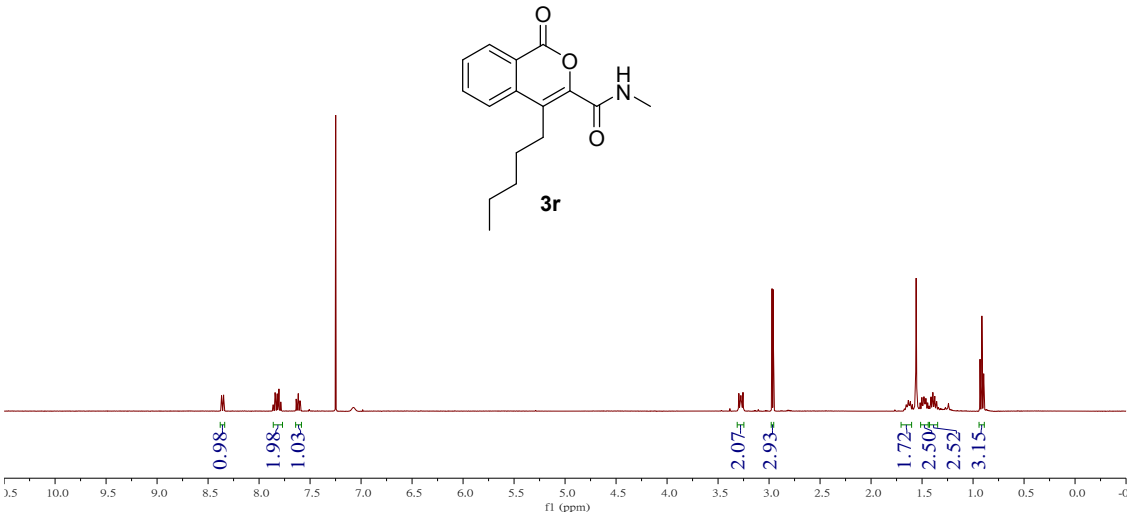
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3q** in $CDCl_3$



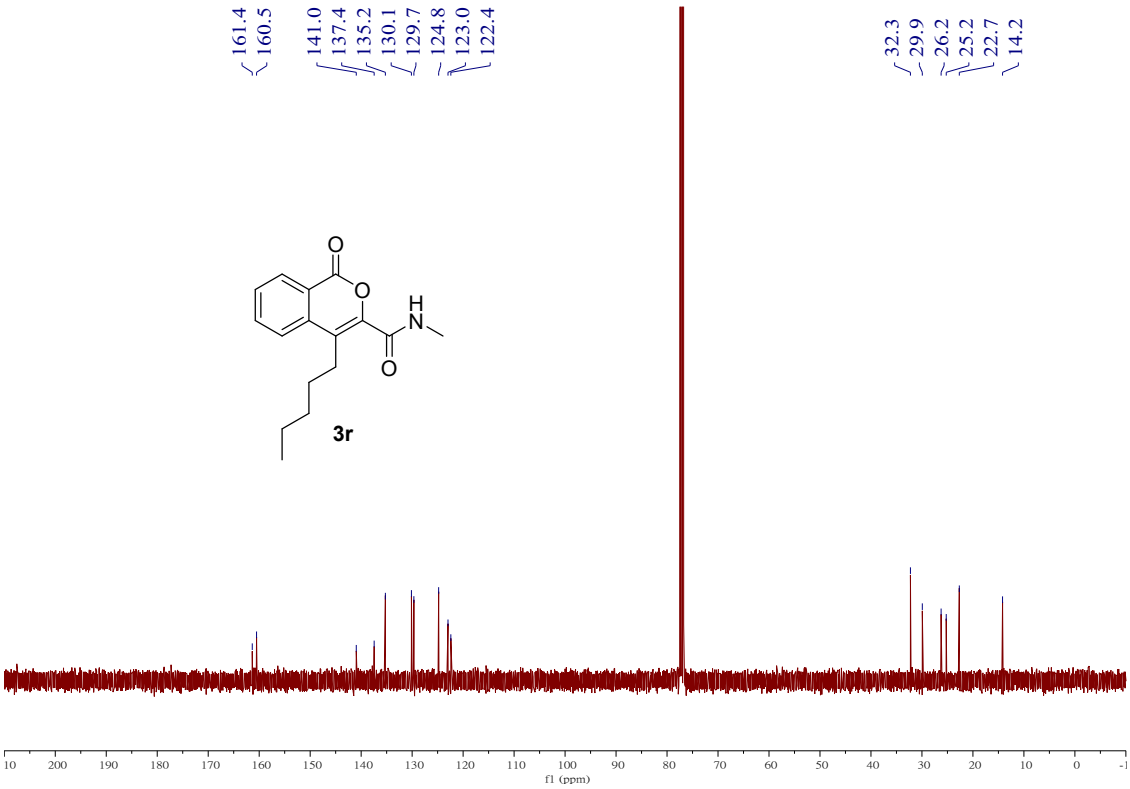
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
294.1119	1	C18H16NO3	294.1125	1.9	82.5	1	100.00	11.5	even	ok	M+H

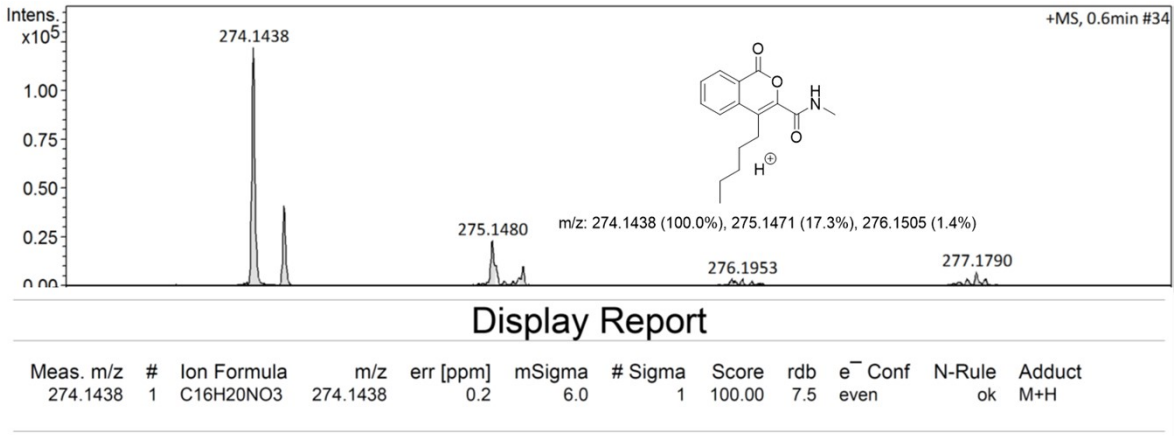
HRMS Mass (ESI) spectrum of compound **3q**



^{1}H spectrum (400 MHz) of compound **3r** in $CDCl_3$



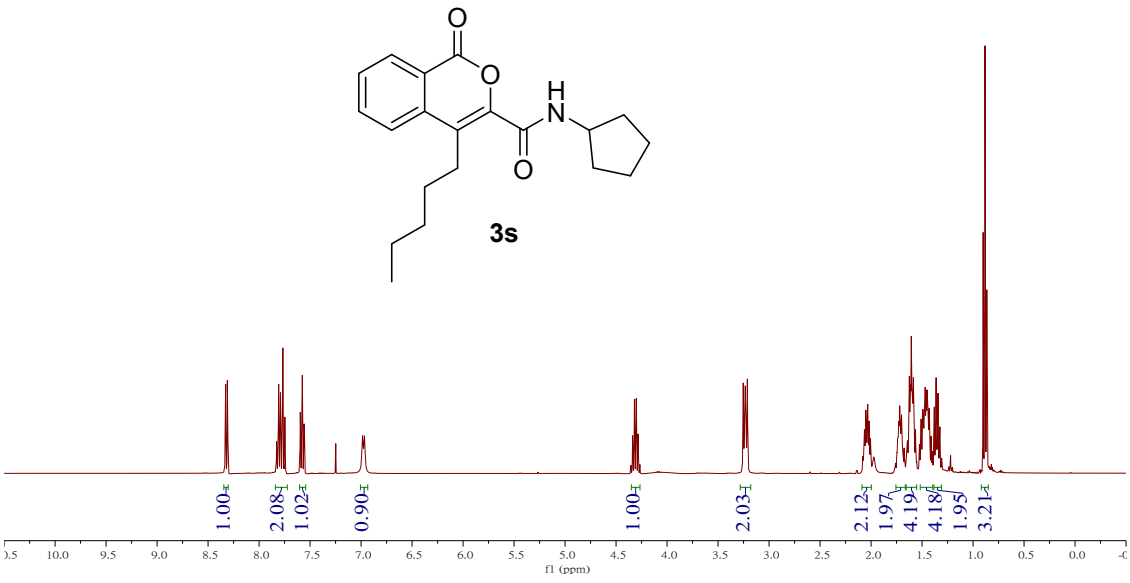
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3r** in $CDCl_3$



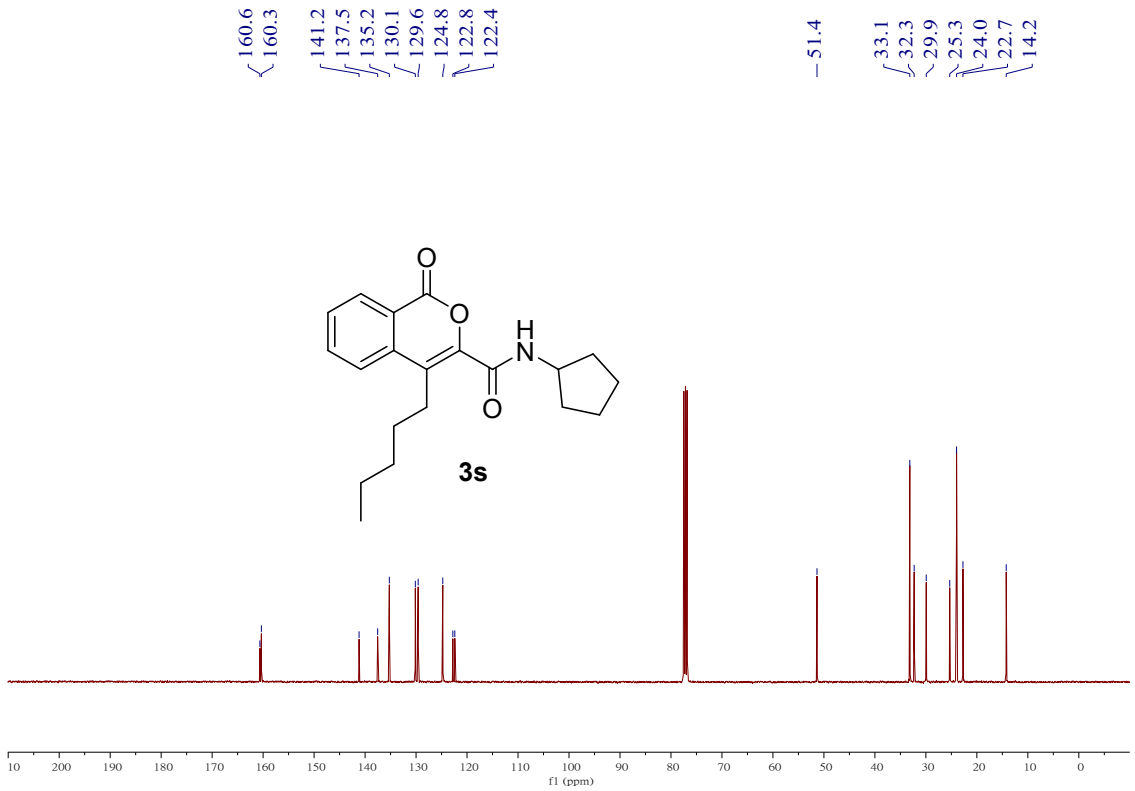
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
274.1438	1	C16H20NO3	274.1438	0.2	6.0	1	100.00	7.5	even	ok	M+H

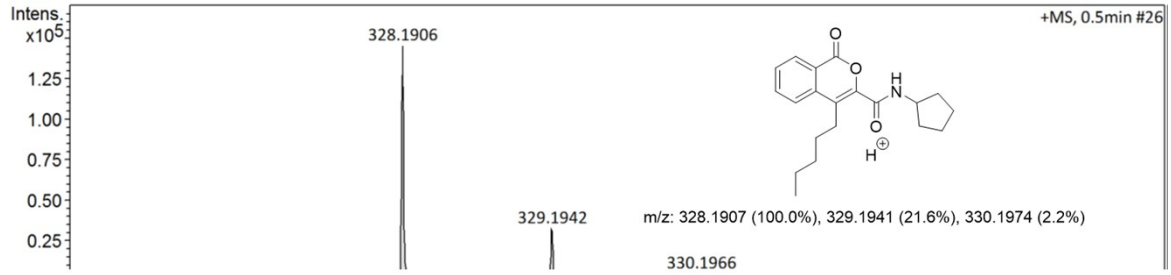
HRMS Mass (ESI) spectrum of compound **3r**



^{1}H spectrum (400 MHz) of compound **3s** in $CDCl_3$



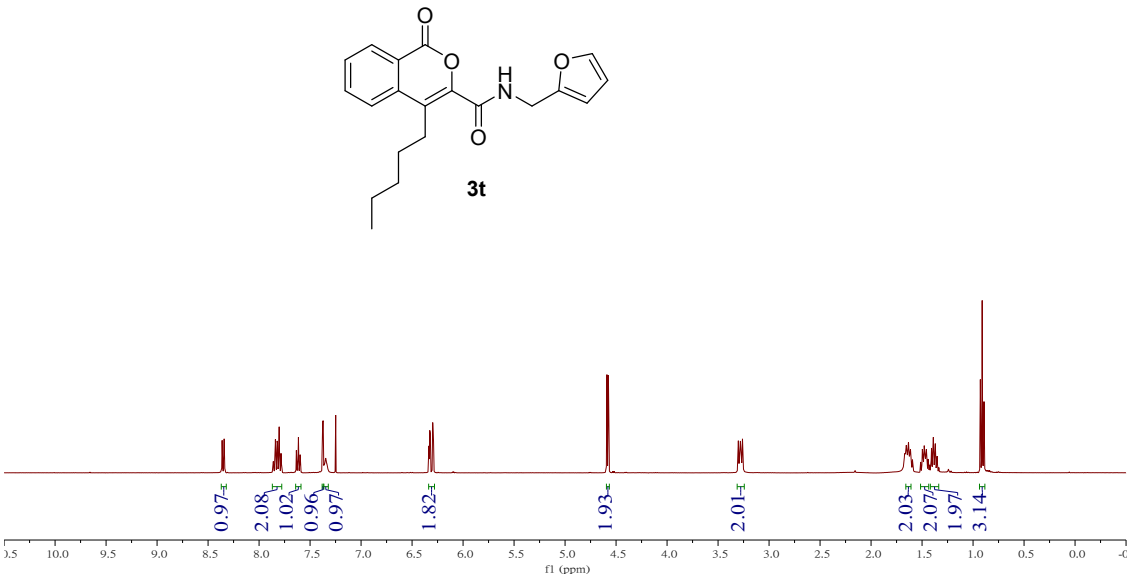
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **3s** in $CDCl_3$



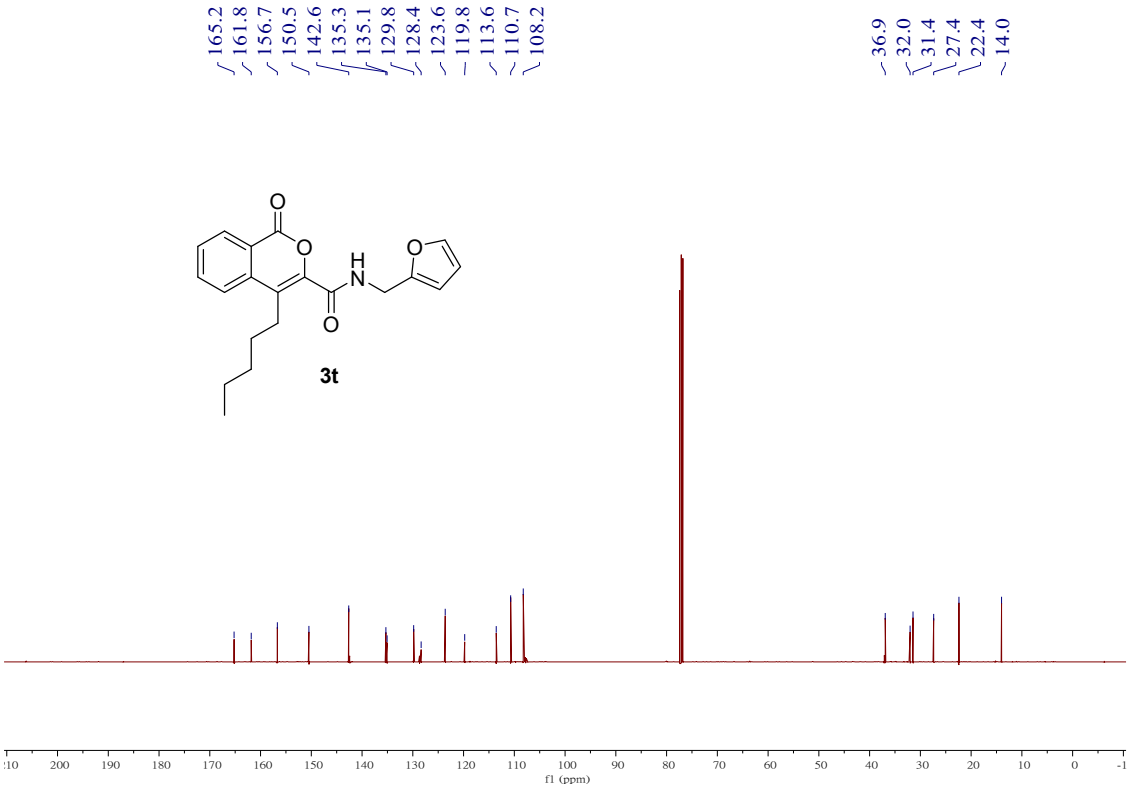
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule	Adduct
328.1906	1	C20H26NO3	328.1907	0.3	2.1	1	100.00	8.5	even	ok	M+H

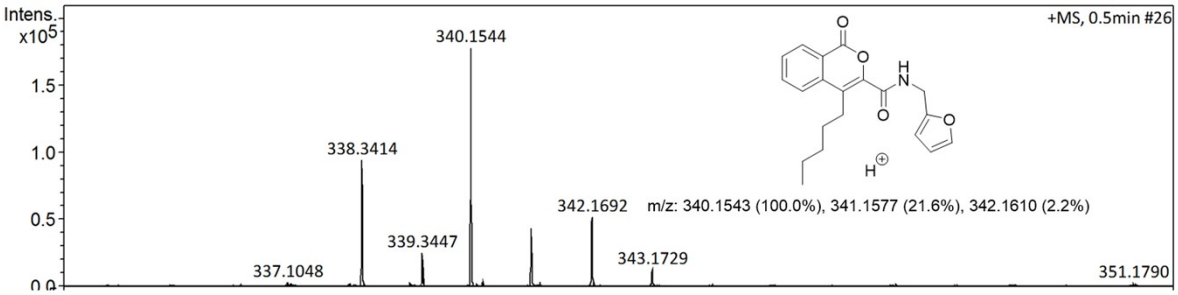
HRMS Mass (ESI) spectrum of compound **3s**



^{1}H spectrum (400 MHz) of compound **3t** in $CDCl_3$



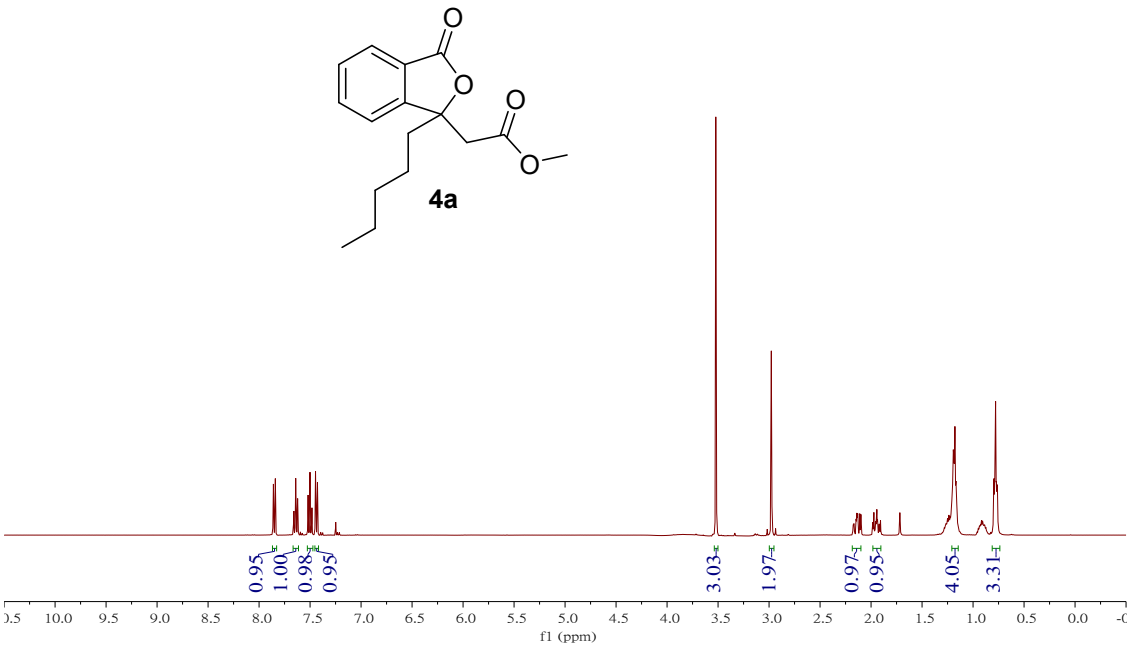
$^{13}C\{1H\}$ spectrum (101 MHz) of compound **3t** in $CDCl_3$



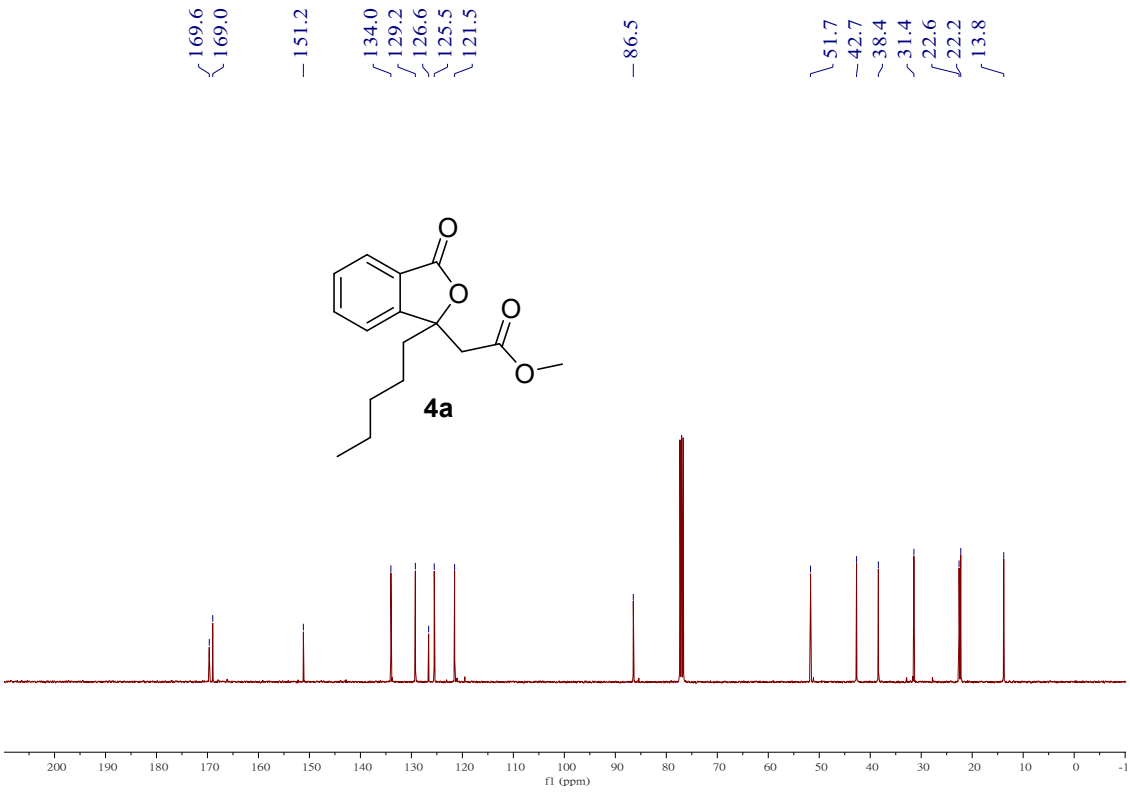
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
340.1544	1	C20H22NO4	340.1543	0.3	21.8	1	100.00	10.5	even	ok	M+H

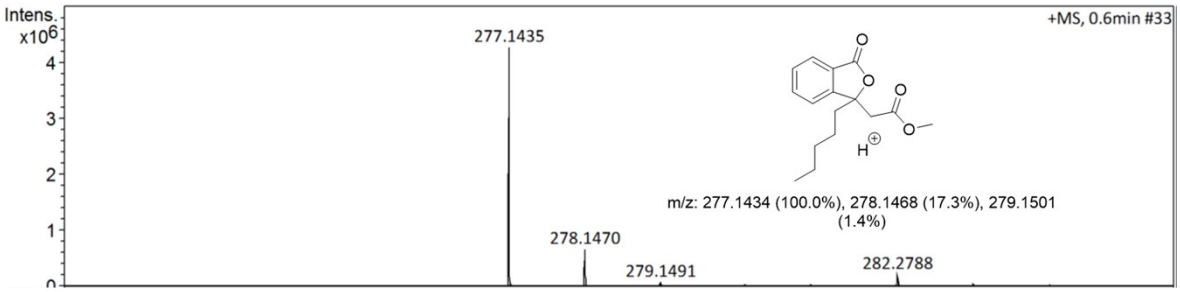
HRMS Mass (ESI) spectrum of compound **3t**



^{1}H spectrum (400 MHz) of compound **4a** in $CDCl_3$



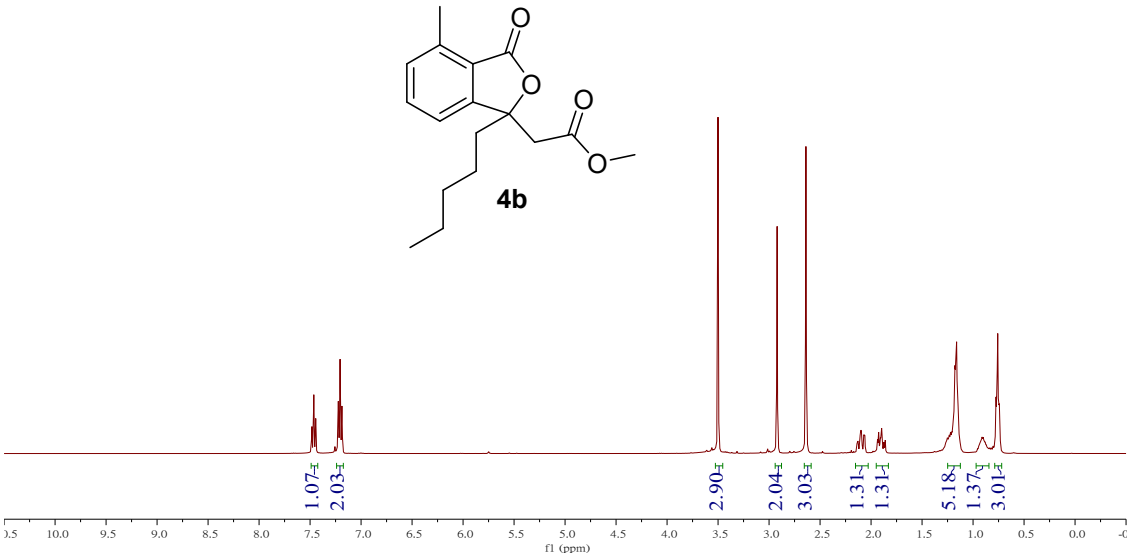
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **4a** in $CDCl_3$



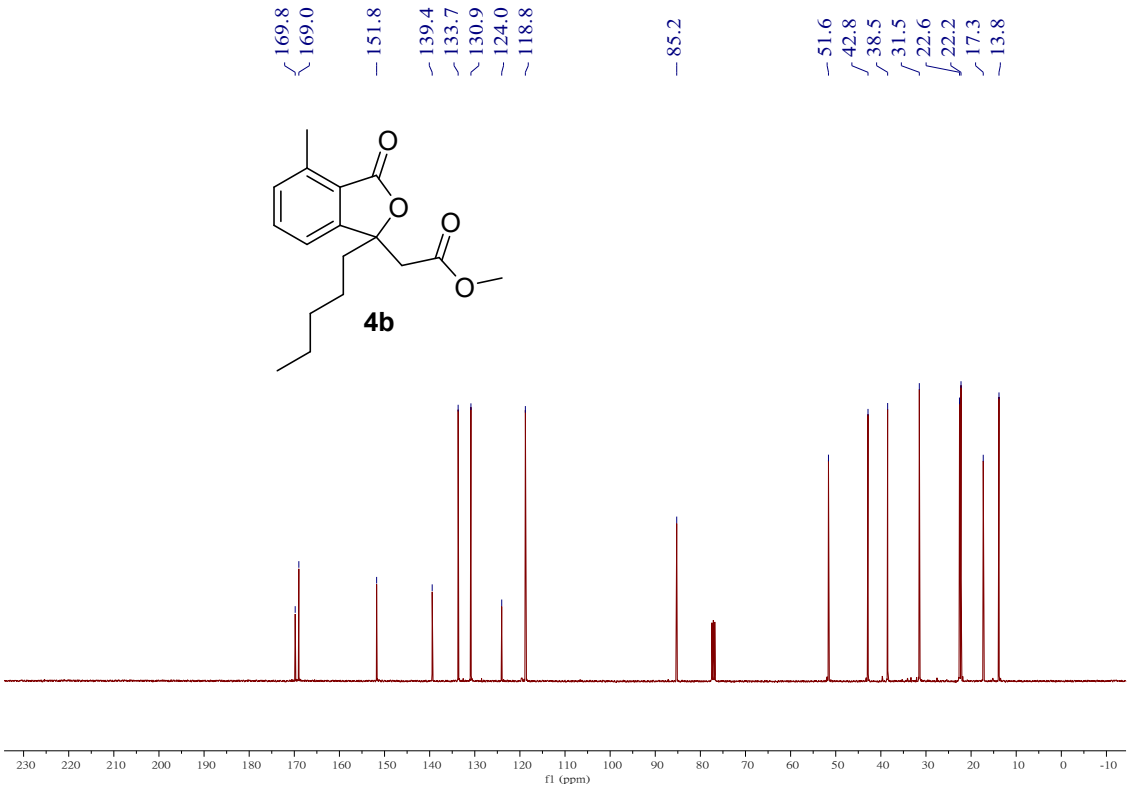
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
277.1435	1	C16H21O4	277.1434	-0.2	14.1	1	100.00	6.5	even	ok	M+H

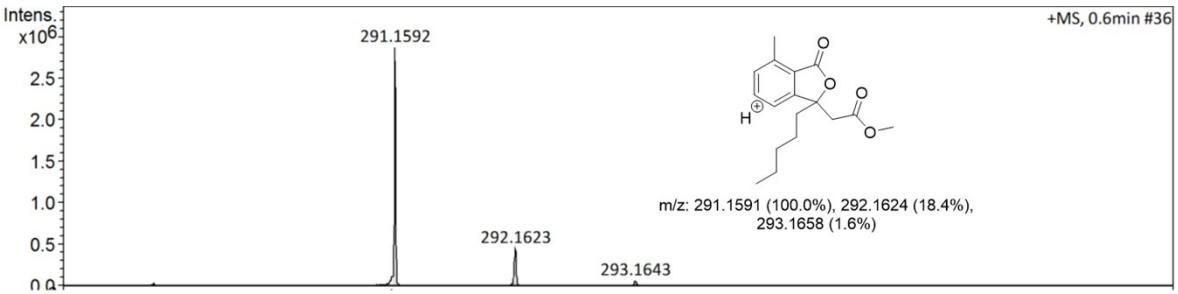
HRMS Mass (ESI) spectrum of compound **4a**



^{1}H spectrum (400 MHz) of compound **4b** in $CDCl_3$



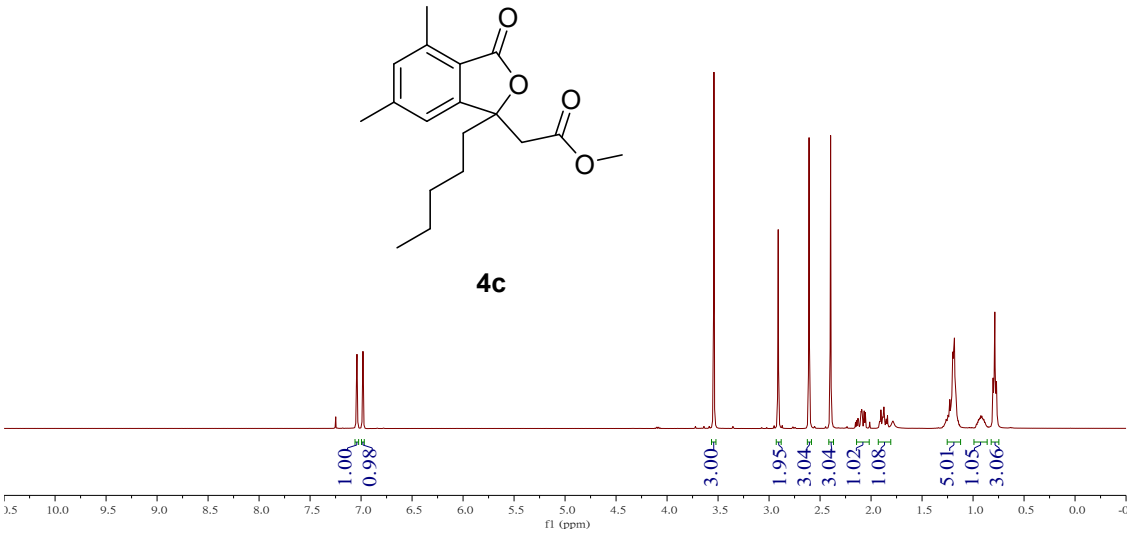
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **4b** in $CDCl_3$



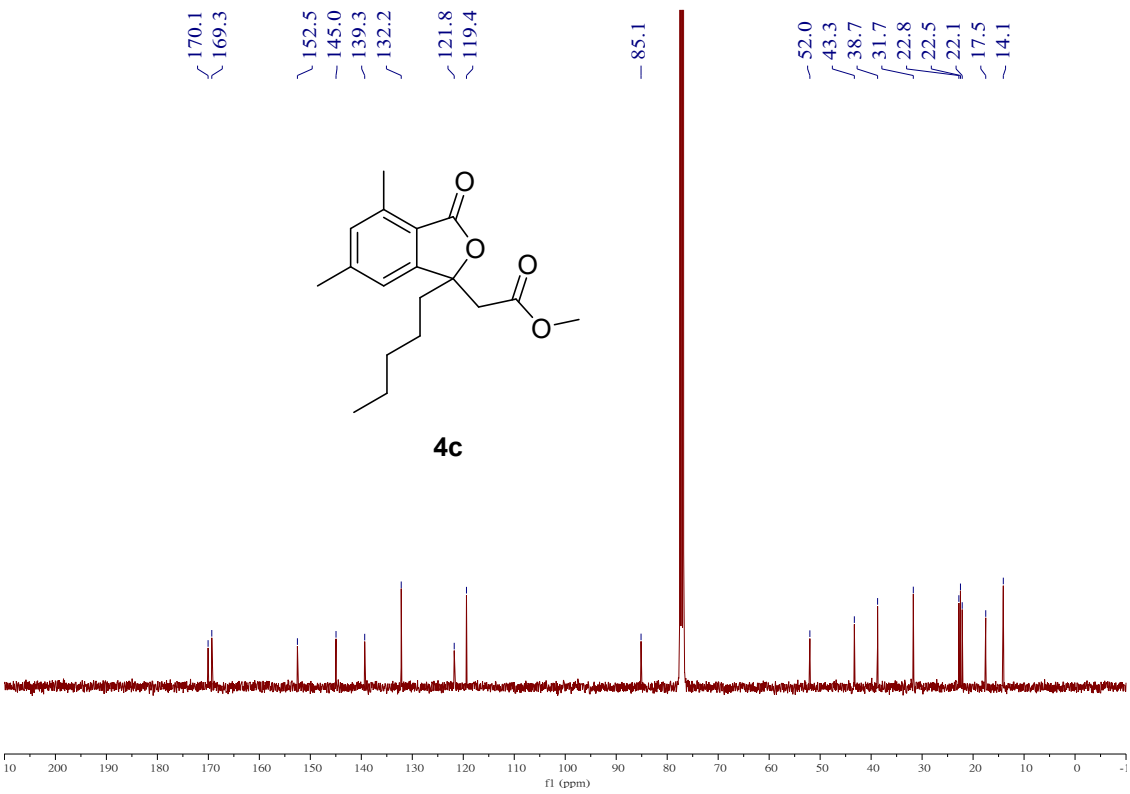
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
291.1592	1	C17H23O4	291.1591	-0.5	18.7	2	100.00	6.5	even	ok	M+H

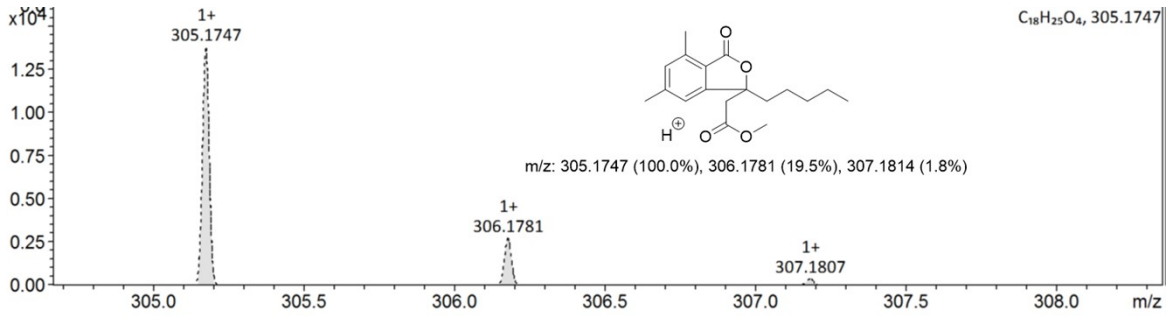
HRMS Mass (ESI) spectrum of compound **4b**



^{1}H spectrum (400 MHz) of compound **4c** in $CDCl_3$



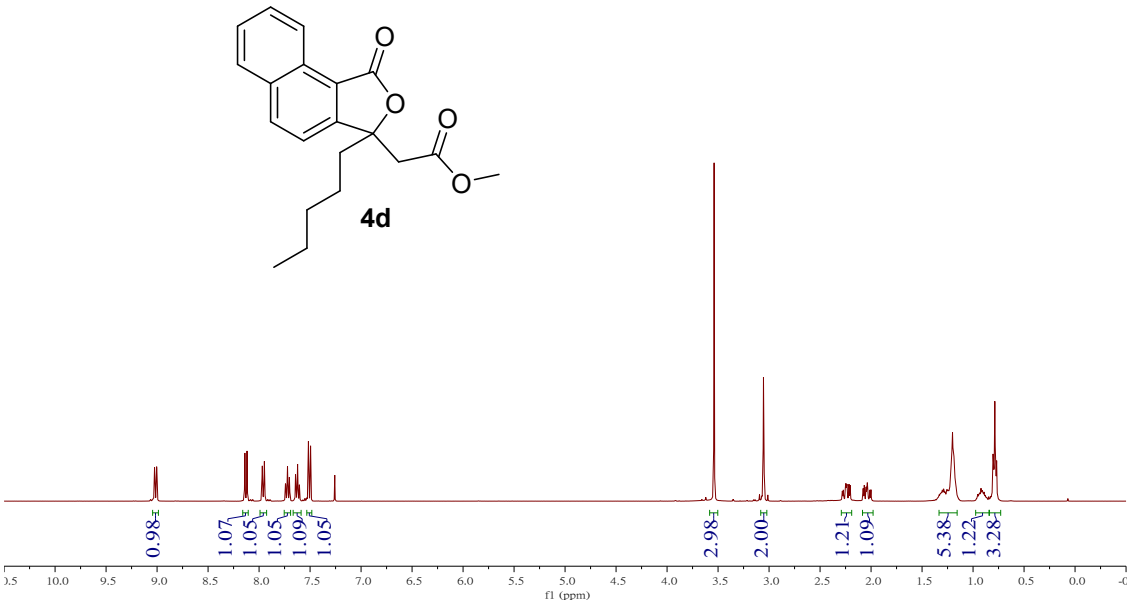
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **4c** in $CDCl_3$



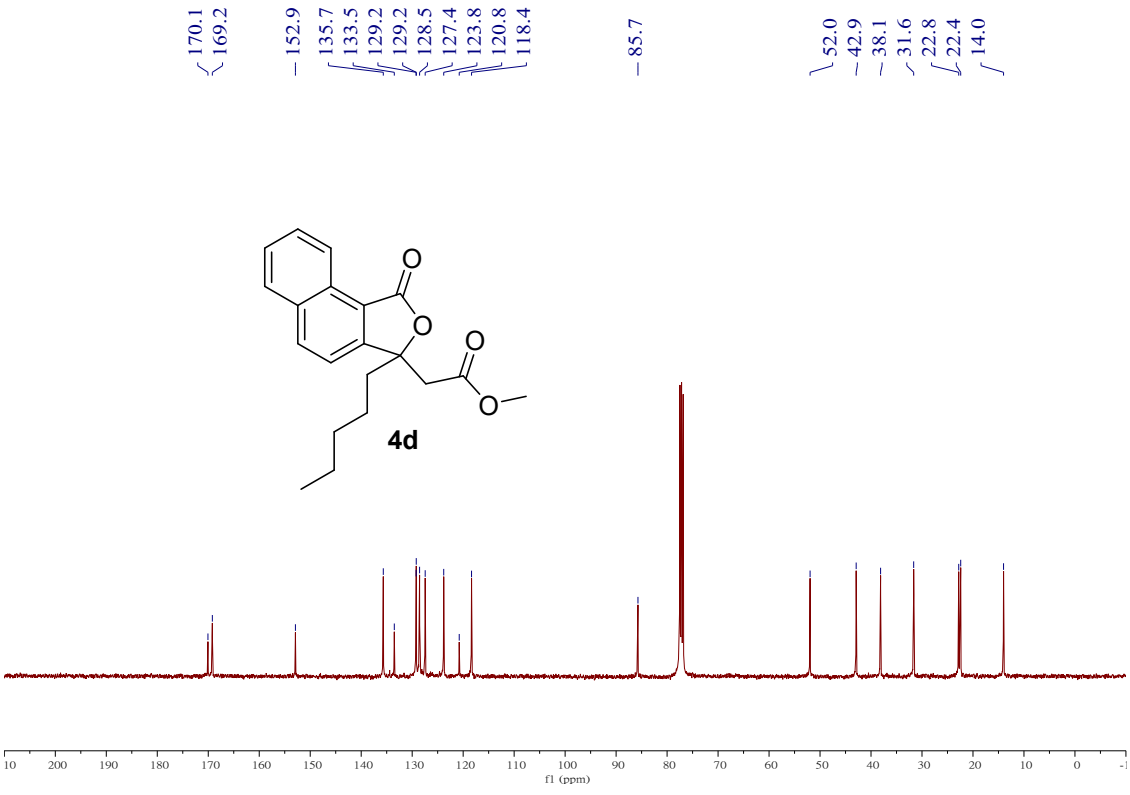
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule	Adduct
305.1731	1	C18H25O4	305.1747	-5.3	n.a.	1	-1.#J	6.5	even	ok	M+H

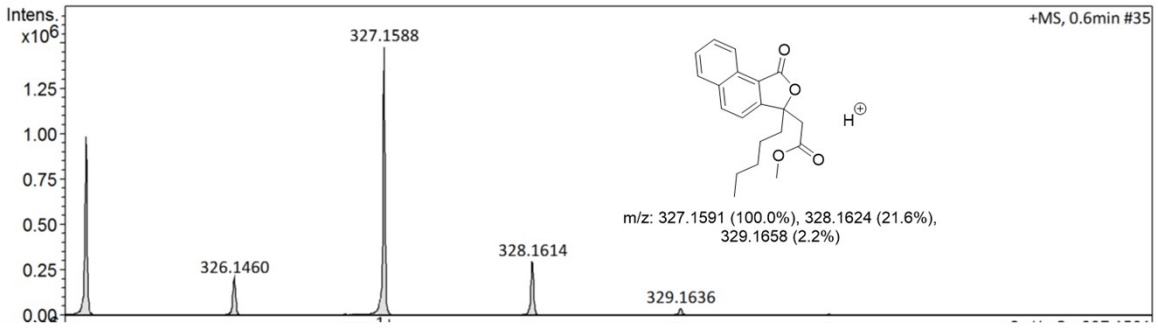
HRMS Mass (ESI) spectrum of compound **4c**



^{1}H spectrum (400 MHz) of compound **4d** in $CDCl_3$



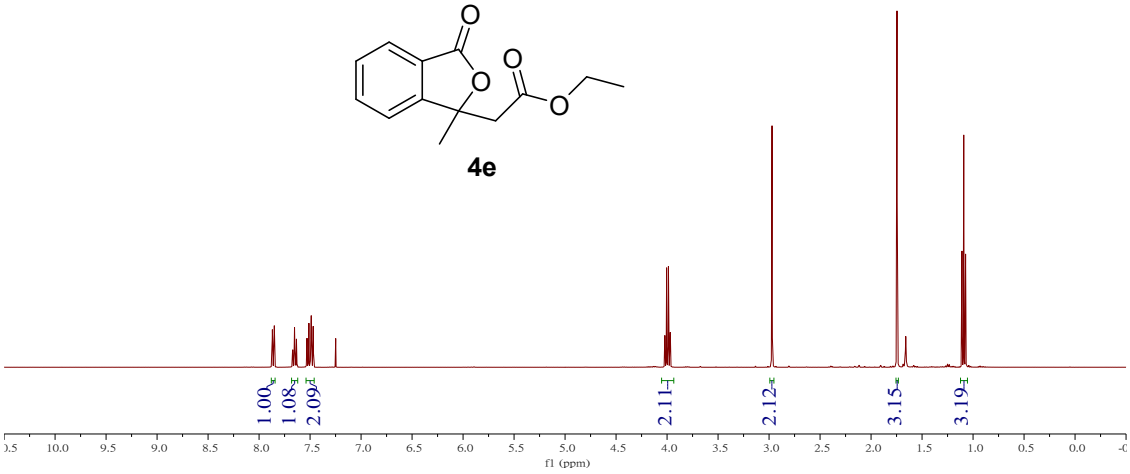
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **4d** in $CDCl_3$



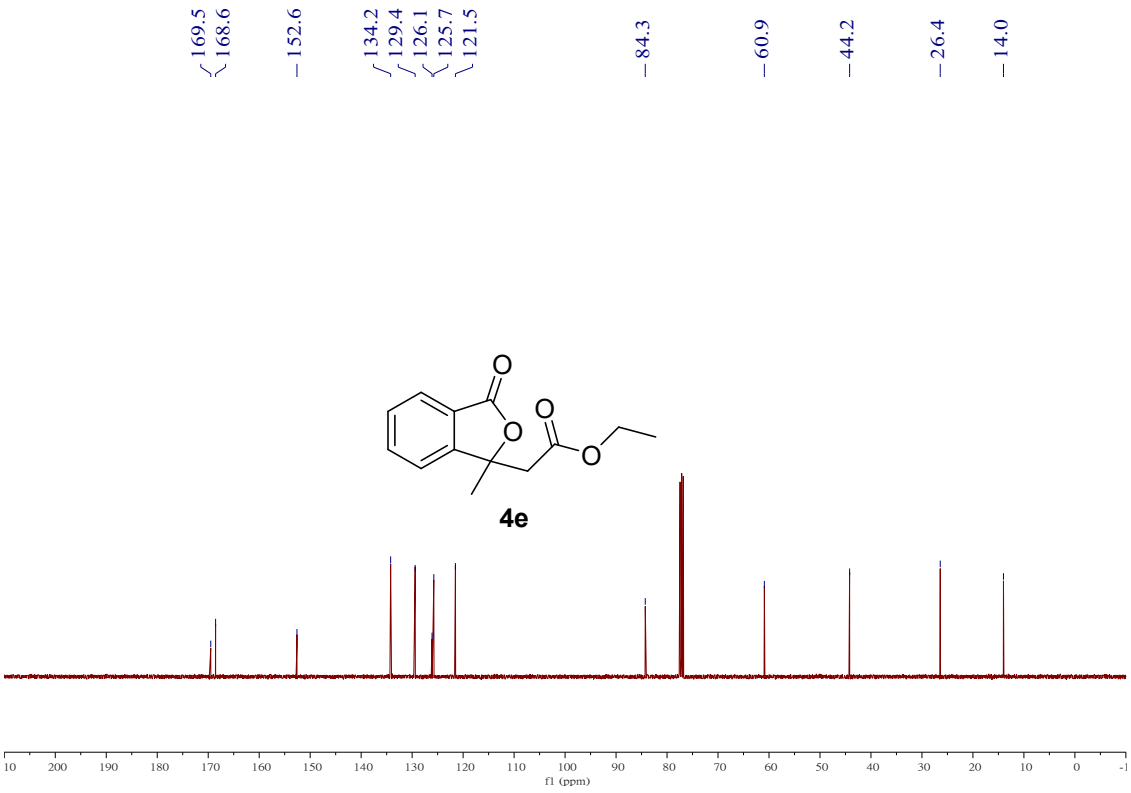
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule	Adduct
327.1588	1	C20H23O4	327.1591	0.9	11.7	1	100.00	9.5	even	ok	M+H

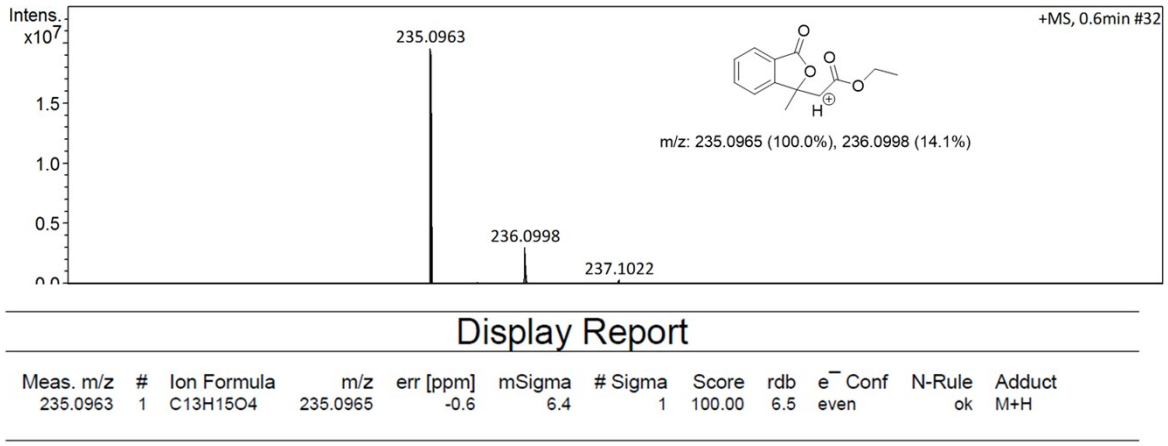
HRMS Mass (ESI) spectrum of compound **4d**



^{1}H spectrum (400 MHz) of compound **4e** in $CDCl_3$



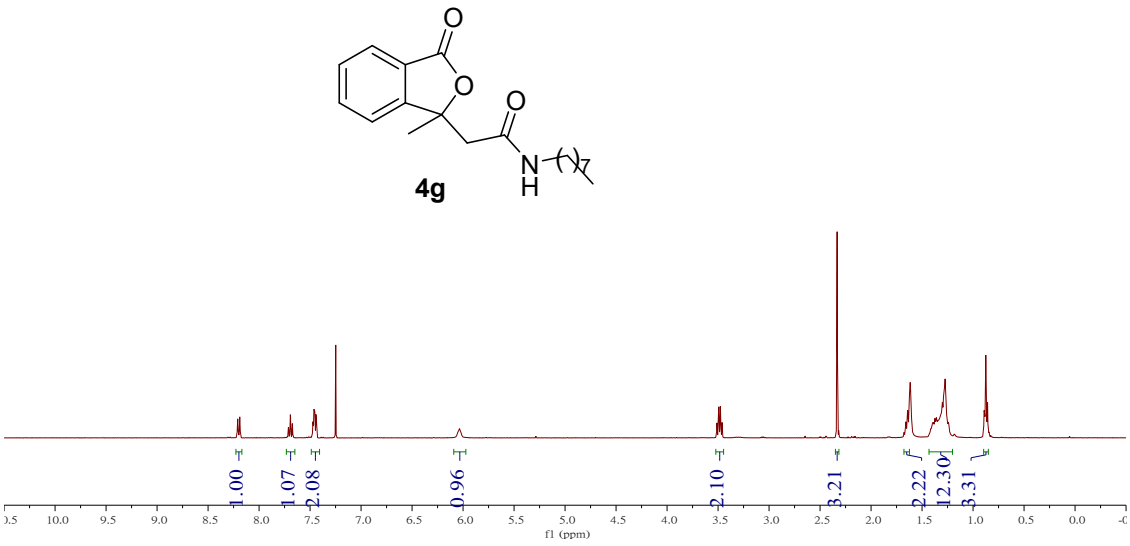
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **4e** in $CDCl_3$



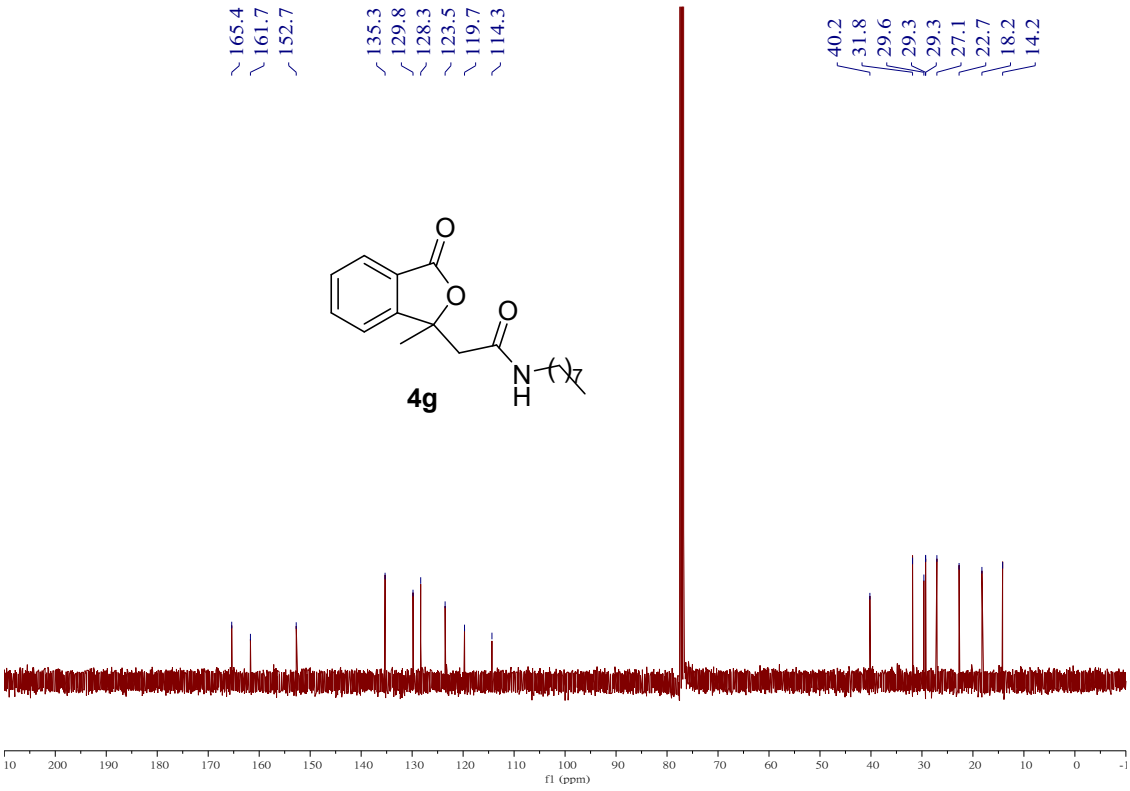
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
235.0963	1	C13H15O4	235.0965	-0.6	6.4	1	100.00	6.5	even	ok	M+H

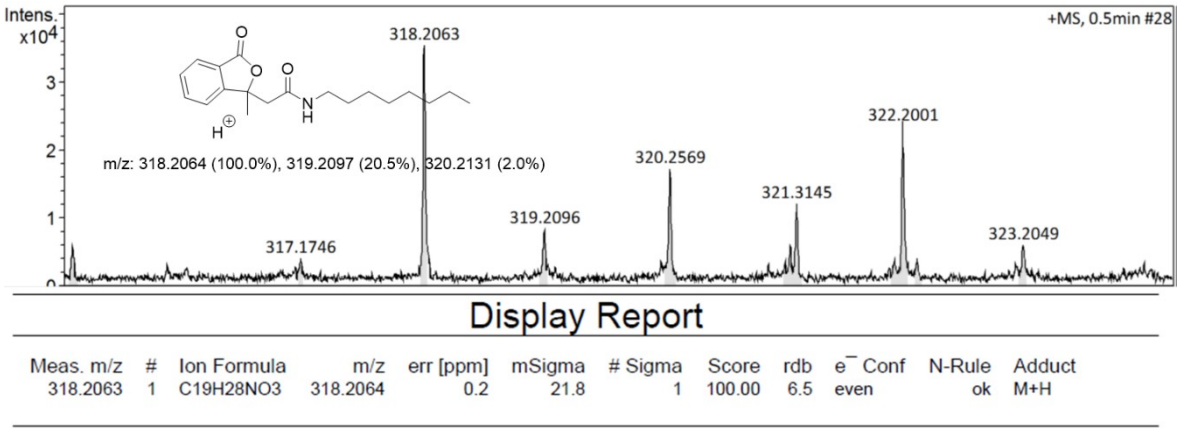
HRMS Mass (ESI) spectrum of compound **4e**



^{1}H spectrum (400 MHz) of compound **4g** in $CDCl_3$



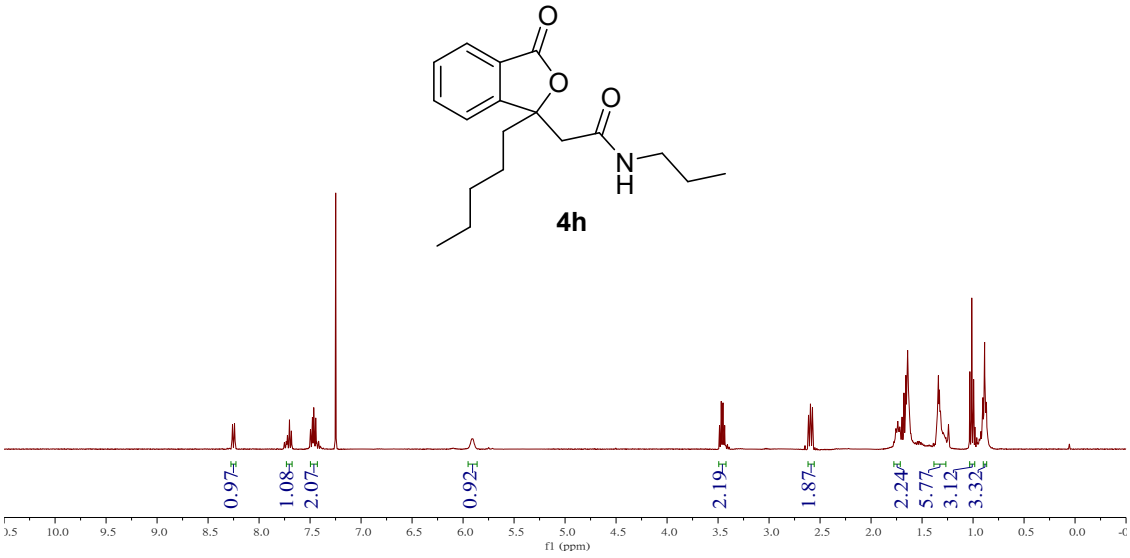
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **4g** in $CDCl_3$



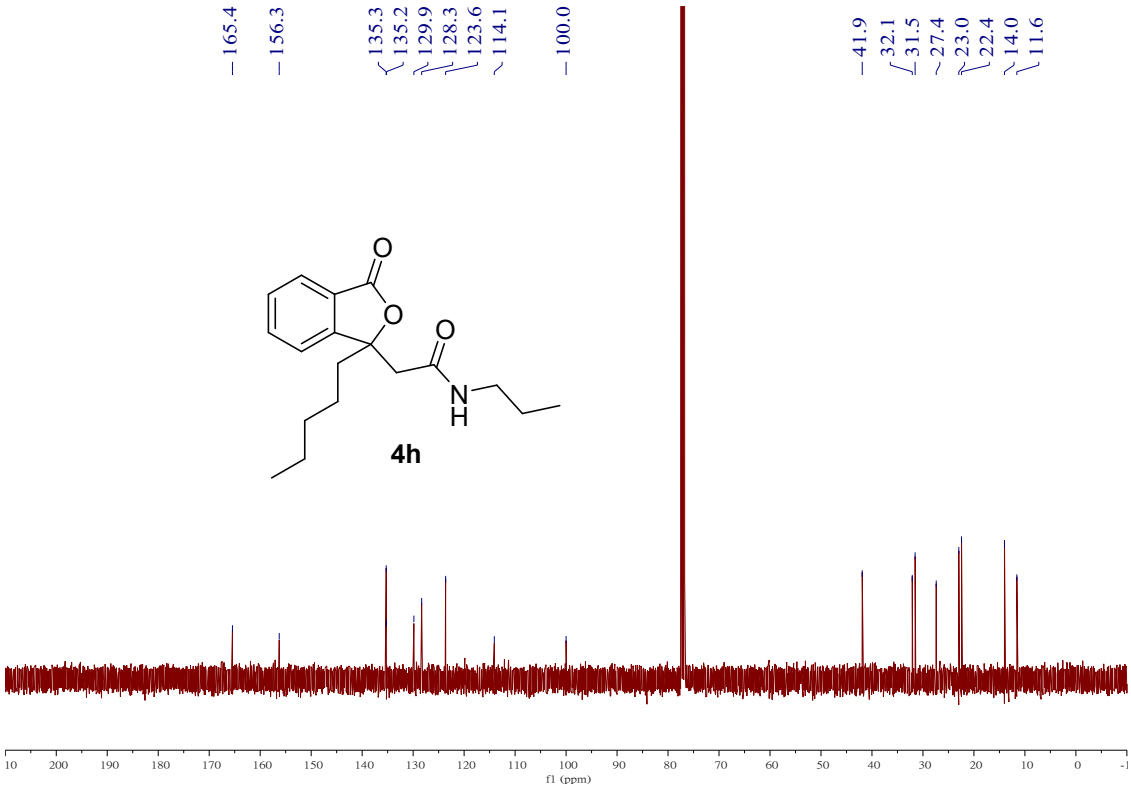
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
318.2063	1	C19H28NO3	318.2064	0.2	21.8	1	100.00	6.5	even	ok	M+H

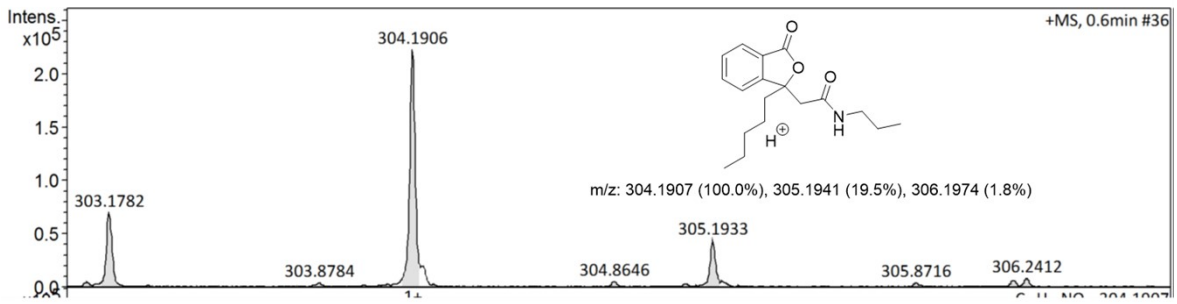
HRMS Mass (ESI) spectrum of compound **4g**



^{1}H spectrum (400 MHz) of compound **4h** in $CDCl_3$



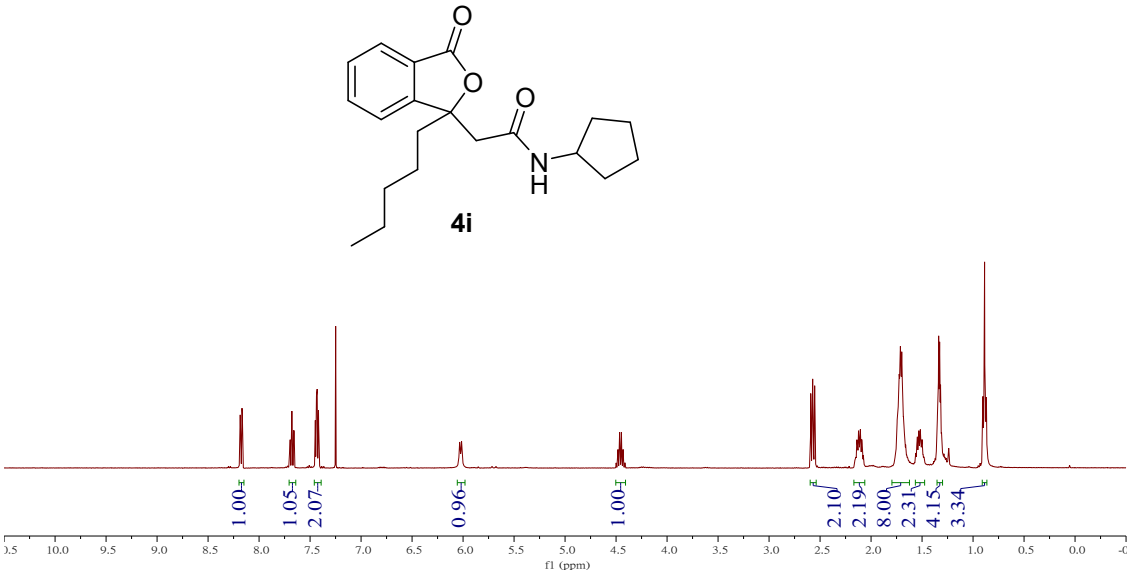
$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **4h** in $CDCl_3$



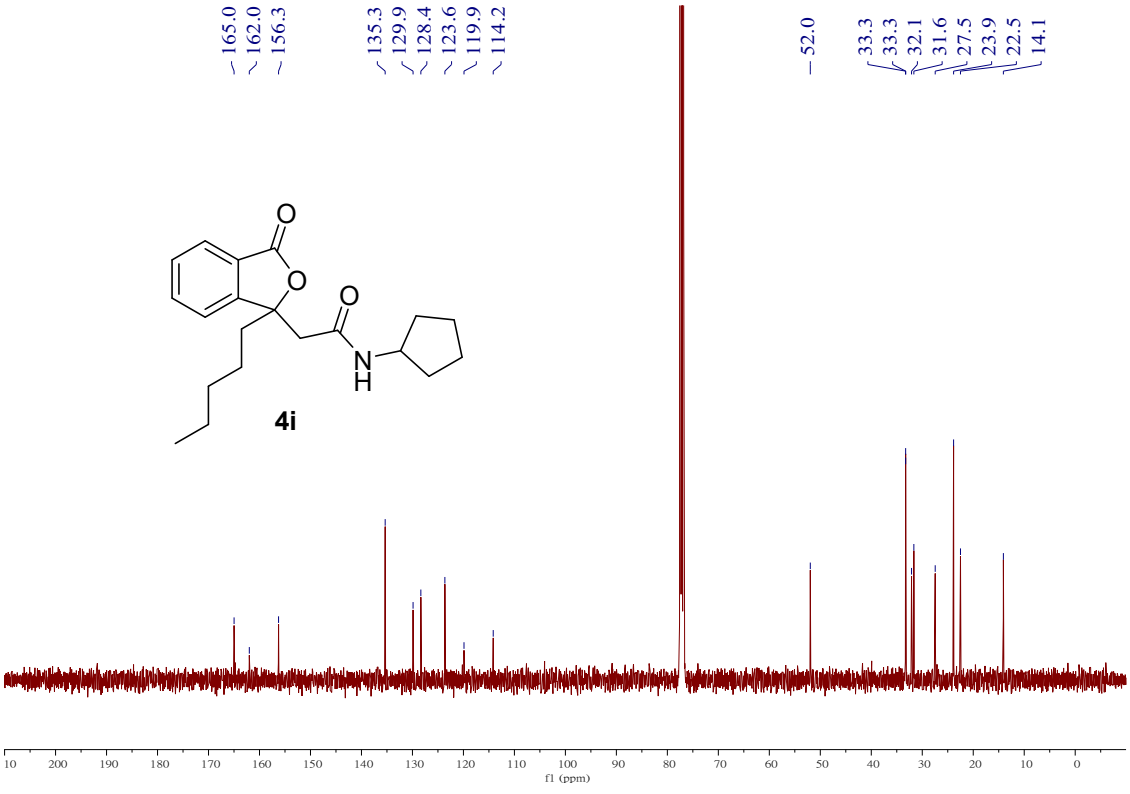
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
304.1906	1	C18H26NO3	304.1907	-0.3	3.9	1	100.00	6.5	even	ok	M+H

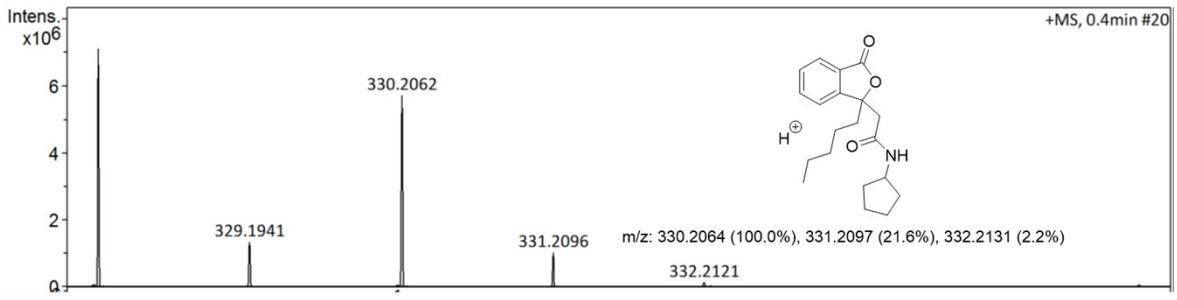
HRMS Mass (ESI) spectrum of compound **4h**



^{1}H spectrum (400 MHz) of compound **4i** in $CDCl_3$



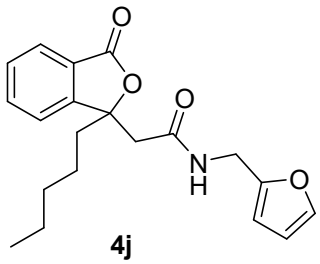
$^{13}C\{^{1}H\}$ spectrum (101 MHz) of compound **4i** in $CDCl_3$



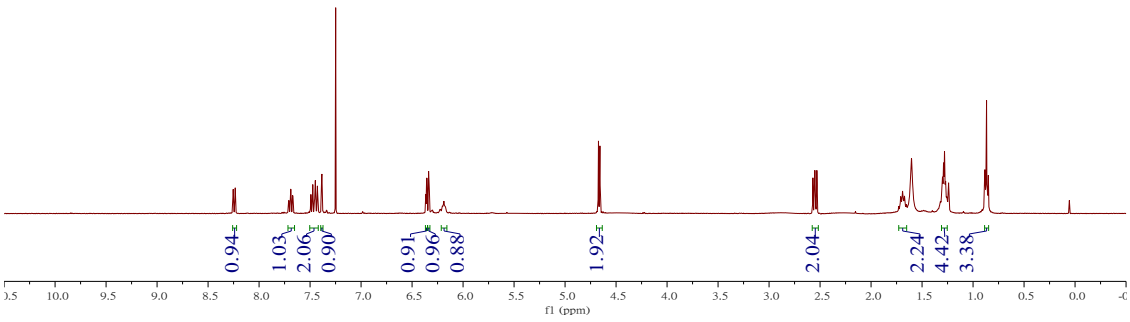
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
330.2062	1	C20H28NO3	330.2064	-0.5	25.6	1	100.00	7.5	even	ok	M+H

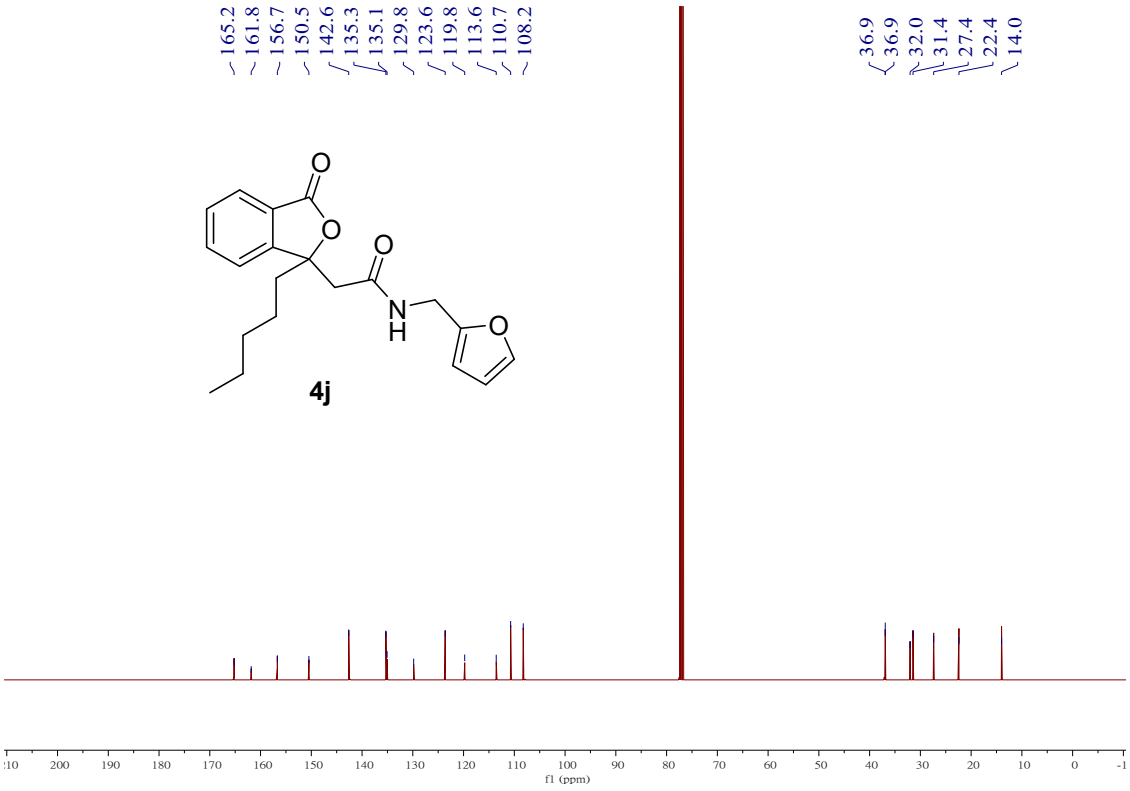
HRMS Mass (ESI) spectrum of compound **4i**



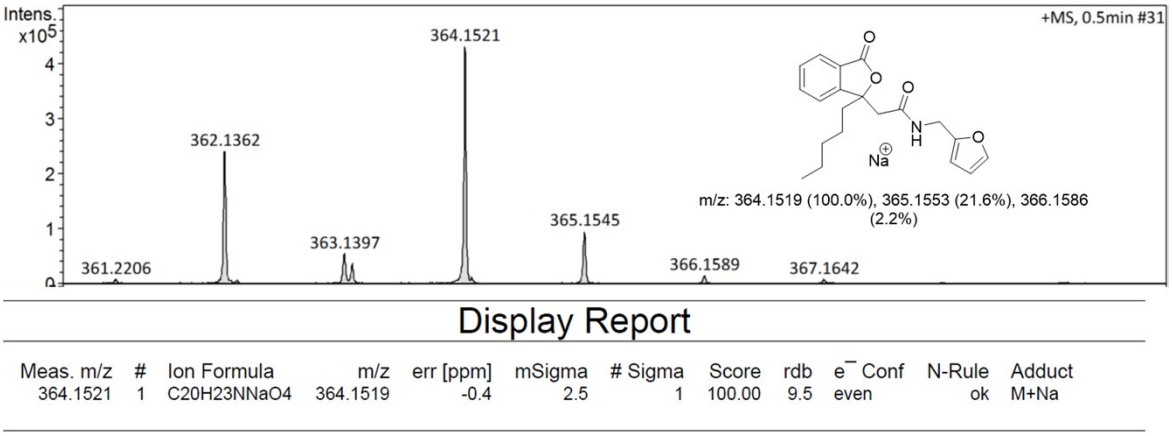
4j



^{1}H spectrum (400 MHz) of compound **4j** in $CDCl_3$



$^{13}C\{1\ H\}$ spectrum (101 MHz) of compound **4j** in $CDCl_3$

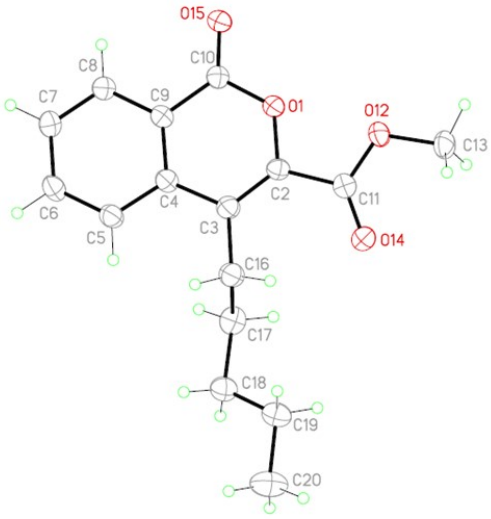


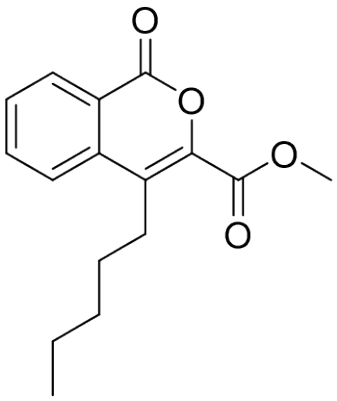
Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
364.1521	1	C20H23NNaO4	364.1519	-0.4	2.5	1	100.00	9.5	even	ok	M+Na

HRMS Mass (ESI) spectrum of compound **4j**

11. X-Ray Crystallographic Data





CCDC 2323184

X-ray single crystallographic data of the compounds 3a

Table S1 Crystal data and structure refinement for 230653lt_auto.

Identification code	230653lt_auto
Empirical formula	$C_{16}H_{18}O_4$
Formula weight	274.30
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.7049(3)
b/Å	14.6860(3)
c/Å	8.72913(18)
α/°	90
β/°	110.758(2)
γ/°	90
Volume/Å^3	1403.13(5)
Z	4
ρ_{calc}g/cm^3	1.299
μ/mm^{-1}	0.760
F(000)	584.0
Crystal size/mm^3	0.18 × 0.18 × 0.03
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/°	8.078 to 149.82
Index ranges	$-14 \le h \le 13$, $-17 \le k \le 18$, $-8 \le l \le 10$
Reflections collected	9347
Independent reflections	2744 [R_{int} = 0.0224, R_{sigma} = 0.0244]
Data/restraints/parameters	2744/0/184
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1332
Final R indexes [all data]	R_1 = 0.0590, wR_2 = 0.1386
Largest diff. peak/hole / e Å^{-3}	0.80/-0.31

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 230653lt_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C2	2298.5(17)	685.6(12)	5997(2)	23.1(4)
C3	1965.6(18)	-117.2(13)	6447(2)	26.7(4)
C4	1253.8(17)	-737.2(12)	5144(2)	24.4(4)
C5	868.3(19)	-1600.0(13)	5458(2)	28.9(4)
C6	145.9(18)	-2143.6(13)	4191(2)	28.9(4)
C7	-231.4(17)	-1842.9(13)	2580(2)	25.6(4)
C8	149.2(17)	-1005.7(12)	2232(2)	24.2(4)
C9	892.4(16)	-457.8(12)	3508(2)	21.9(4)
C10	1253.0(16)	434.1(12)	3103(2)	23.1(4)
C11	2997.9(17)	1428.4(13)	7108(2)	25.1(4)
C13	3554.3(19)	2979.2(13)	7246(3)	31.4(5)
C16	2223.4(18)	-381.3(14)	8209(2)	29.9(4)
C17	3322.8(19)	-1015.2(15)	8871(3)	33.5(5)
C18	3438(2)	-1426.3(15)	10541(3)	34.9(5)
C19	3690(2)	-731.5(15)	11934(2)	33.5(5)
C20	3927(2)	-1181.4(18)	13589(3)	45.8(6)
O1	1974.8(12)	951.3(8)	4381.2(15)	24.9(3)
O12	2923.2(13)	2204.1(9)	6281.9(16)	28.7(3)
O14	3548.4(13)	1332.9(9)	8551.3(16)	31.5(4)
O15	986.2(13)	757.1(9)	1745.9(16)	30.6(3)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 230653lt_auto. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	24.9(9)	23.6(9)	21.9(9)	0.6(7)	9.7(7)	2.0(7)
C3	31.7(10)	25.0(9)	23.6(9)	-0.6(7)	10.0(8)	-0.6(8)
C4	29.0(10)	22.3(9)	24.5(9)	-0.8(7)	12.8(8)	0.5(7)
C5	36.5(11)	25.4(10)	26.5(10)	1.6(8)	13.2(8)	-2.0(8)
C6	37.3(11)	21.4(9)	32.4(10)	-1.1(7)	18.0(9)	-2.7(8)
C7	27.8(10)	22.1(9)	30.1(10)	-5.2(7)	14.2(8)	0.3(7)
C8	27.1(9)	22.3(9)	24.5(9)	-1.5(7)	10.7(7)	3.3(7)
C9	22.7(9)	20.1(9)	25.1(9)	0.7(7)	11.2(7)	3.4(7)
C10	23.0(9)	21.7(9)	25.1(9)	-0.5(7)	9.0(7)	2.1(7)
C11	24.0(9)	24.6(9)	28.5(10)	-0.9(7)	11.7(8)	0.8(7)
C13	35.5(11)	22.2(9)	35.3(11)	-6.7(8)	10.9(9)	-3.5(8)
C16	32.7(10)	28.2(10)	28.9(10)	1.3(8)	11.2(8)	0.4(8)
C17	32.1(11)	34.4(11)	34.8(11)	-3.5(9)	12.9(9)	0.2(9)
C18	34.1(11)	31.5(11)	34.9(11)	6.2(9)	7.0(9)	2.4(9)
C19	34.5(11)	34.0(11)	33.9(11)	7.0(9)	14.5(9)	6.4(9)
C20	56.7(15)	49.6(14)	35.1(12)	9.9(10)	21.2(11)	17.2(12)
O1	29.3(7)	21.1(6)	22.6(7)	1.4(5)	7.3(5)	-1.4(5)
O12	36.5(8)	20.1(7)	28.3(7)	-1.8(5)	10.2(6)	-4.2(5)
O14	32.8(7)	29.3(7)	27.4(7)	0.0(6)	4.7(6)	-2.3(6)
O15	37.8(8)	24.8(7)	25.6(7)	4.2(5)	6.9(6)	-1.6(6)

Table S4 Bond Lengths for 230653lt_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C2	C3	1.343(3)	C9	C10	1.458(2)
C2	C11	1.496(3)	C10	O1	1.367(2)
C2	O1	1.381(2)	C10	O15	1.210(2)
C3	C4	1.465(3)	C11	O12	1.335(2)

Table S4 Bond Lengths for 230653lt_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C3	C16	1.509(3)	C11	O14	1.202(2)
C4	C5	1.404(3)	C13	O12	1.452(2)
C4	C9	1.399(3)	C16	C17	1.526(3)
C5	C6	1.383(3)	C17	C18	1.539(3)
C6	C7	1.388(3)	C18	C19	1.534(3)
C7	C8	1.378(3)	C19	C20	1.522(3)
C8	C9	1.399(3)			

Table S5 Bond Angles for 230653lt_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C2	C11	126.81(17)	C4	C9	C10	120.16(16)
C3	C2	O1	122.93(17)	C8	C9	C10	118.37(16)
O1	C2	C11	110.20(15)	O1	C10	C9	116.71(15)
C2	C3	C4	117.56(17)	O15	C10	C9	126.41(17)
C2	C3	C16	123.34(17)	O15	C10	O1	116.87(16)
C4	C3	C16	119.00(17)	O12	C11	C2	110.84(15)
C5	C4	C3	122.88(17)	O14	C11	C2	124.12(17)
C9	C4	C3	119.55(17)	O14	C11	O12	125.04(17)
C9	C4	C5	117.52(17)	C3	C16	C17	112.32(17)
C6	C5	C4	120.81(18)	C16	C17	C18	112.15(17)
C5	C6	C7	120.76(18)	C19	C18	C17	114.70(18)
C8	C7	C6	119.71(18)	C20	C19	C18	112.53(19)
C7	C8	C9	119.73(17)	C10	O1	C2	122.92(14)
C4	C9	C8	121.43(17)	C11	O12	C13	115.68(15)

Table S6 Torsion Angles for 230653lt_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C3	C4	C5	179.02(18)	C7	C8	C9	C4	-0.5(3)
C2	C3	C4	C9	-3.5(3)	C7	C8	C9	C10	-

							178.42(16)
C2	C3	C16	C17	-100.8(2)	C8	C9	C10	O1	179.76(15)
C2	C11	O12	C13	179.05(15)	C8	C9	C10	O15	-1.0(3)
C3	C2	C11	O12	-165.30(18)	C9	C4	C5	C6	-0.8(3)
C3	C2	C11	O14	14.6(3)	C9	C10	O1	C2	-4.0(2)
C3	C2	O1	C10	2.3(3)	C11	C2	C3	C4	178.50(17)
C3	C4	C5	C6	176.77(18)	C11	C2	C3	C16	2.2(3)
C3	C4	C9	C8	-176.05(17)	C11	C2	O1	C10	-175.07(15)
C3	C4	C9	C10	1.8(3)	C16	C3	C4	C5	-4.6(3)
C3	C16	C17	C18	-169.21(17)	C16	C3	C4	C9	172.92(17)
C4	C3	C16	C17	83.0(2)	C16	C17	C18	C19	-64.4(2)
C4	C5	C6	C7	-1.1(3)	C17	C18	C19	C20	-174.06(19)
C4	C9	C10	O1	1.9(2)	O1	C2	C3	C4	1.6(3)
C4	C9	C10	O15	-178.94(18)	O1	C2	C3	C16	-174.69(17)
C5	C4	C9	C8	1.6(3)	O1	C2	C11	O12	12.0(2)
C5	C4	C9	C10	179.40(17)	O1	C2	C11	O14	-168.17(17)
C5	C6	C7	C8	2.1(3)	O14	C11	O12	C13	-0.8(3)
C6	C7	C8	C9	-1.3(3)	O15	C10	O1	C2	176.74(16)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230653lt_auto.

Atom	*x*	*y*	*z*	U(eq)
H5	1106.43	-1812.86	6554.7	35
H6	-94.53	-2729.59	4425	35
H7	-749.97	-2212.59	1721.81	31
H8	-91.87	-801.21	1130.47	29
H13A	3361.26	3528.63	6564.97	47

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230653lt_auto.

Atom	*x*	*y*	*z*	U(eq)
H13B	4437.67	2871.4	7639.41	47
H13C	3289.84	3060.49	8184.12	47
H16A	1494.91	-687.08	8295.31	36
H16B	2376.65	176.01	8889.99	36
H17A	4076.15	-671.35	8985.01	40
H17B	3243.19	-1513.68	8075.87	40
H18A	2671.89	-1753.54	10421.56	42
H18B	4107.46	-1879.73	10851.64	42
H19A	4409.81	-359.93	11990.25	40
H19B	2980.58	-317.44	11690.42	40
H20A	3215.01	-1546.87	13543.99	69
H20B	4070.89	-711.39	14434.1	69
H20C	4646.78	-1575.56	13855.8	69

Experimental

Single crystals of $C_{16}H_{18}O_4$ **[230653lt_auto]** were **[]**. A suitable crystal was selected and **[]** on a **XtaLAB Synergy R, DW system, HyPix-Arc 150** diffractometer. The crystal was kept at 99.99(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [230653lt_auto]

Crystal Data for $C_{16}H_{18}O_4$ (M =274.30 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 11.7049(3) Å, b = 14.6860(3) Å, c = 8.72913(18) Å, β = 110.758(2)°, V = 1403.13(5) Å^3, Z = 4, T = 99.99(10) K, μ(Cu Kα) = 0.760 mm^{-1}, *Dcalc* = 1.299 g/cm^3, 9347 reflections measured (8.078° ≤ 2Θ ≤ 149.82°), 2744 unique (R_{int} = 0.0224, R_{sigma} = 0.0244) which were used in all calculations. The final R_1 was 0.0517 (I > 2σ(I)) and wR_2 was 0.1386 (all data).

Refinement model description

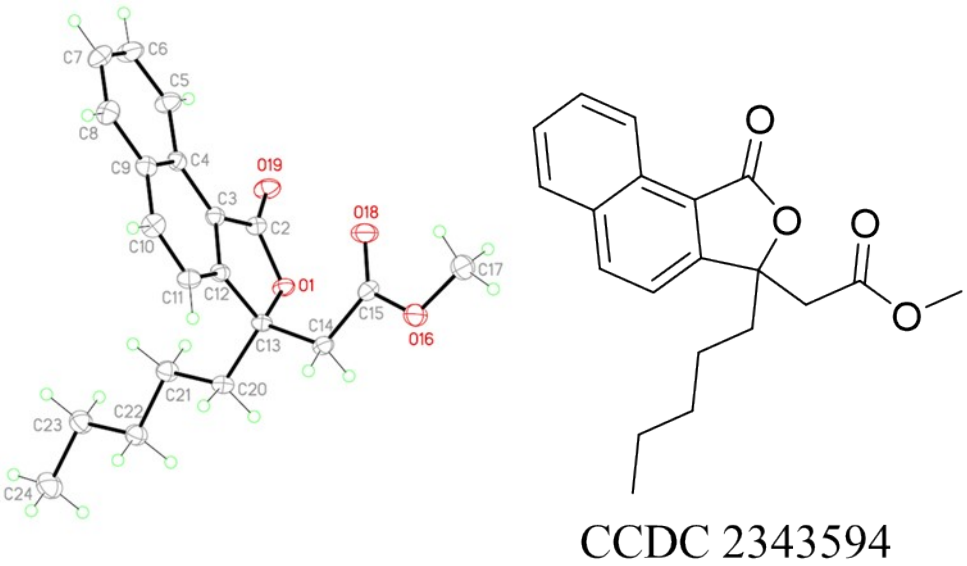
Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C16(H16A,H16B), C17(H17A,H17B), C18(H18A,H18B), C19(H19A,H19B)
2.b Aromatic/amide H refined with riding coordinates:
 C5(H5), C6(H6), C7(H7), C8(H8)
2.c Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C), C20(H20A,H20B,H20C)
```

This report has been created with Olex2, compiled on 2023.03.06 svn.rbb2c1857 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

X-ray single crystallographic data of the compounds 4d



CCDC 2343594

X-ray single crystallographic data of the compounds 4d

Table S8 Crystal data and structure refinement for 240370lt_auto.

Identification code	240370lt_auto

Empirical formula	$C_{20}H_{22}O_4$
Formula weight	326.37
Temperature/K	99.98(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.4776(2)
b/Å	9.1826(2)
c/Å	12.9115(3)
α/°	83.847(2)
β/°	78.595(2)
γ/°	81.772(2)
Volume/Å^3	857.25(4)
Z	2
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	0.707
F(000)	348.0
Crystal size/mm^3	0.21 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.008 to 134.136
Index ranges	-7 ≤ h ≤ 8, -10 ≤ k ≤ 10, -15 ≤ l ≤ 15
Reflections collected	10200
Independent reflections	3011 [R_{int} = 0.0318, R_{sigma} = 0.0226]
Data/restraints/parameters	3011/0/219
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0352, wR_2 = 0.0892
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.0943
Largest diff. peak/hole / e Å^{-3}	0.28/-0.24

Table S9 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 240370lt_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	4486.7(11)	4785.7(9)	6262.5(6)	17.2(2)

O16	1535.7(13)	1112.0(10)	7189.1(7)	25.0(2)
O18	3446.3(15)	2342.6(11)	7789.1(8)	31.3(3)
O19	6760.2(11)	5215.6(10)	7043.6(7)	22.8(2)
C2	5126.3(16)	5267.8(13)	7066.9(9)	16.6(3)
C3	3536.7(16)	5801.9(13)	7865.9(9)	15.5(3)
C4	3472.8(16)	6394.7(13)	8846.9(9)	16.3(3)
C5	5024.8(17)	6684.0(15)	9224.0(10)	23.1(3)
C6	4818.3(19)	7265.3(16)	10181.8(11)	27.3(3)
C7	3066.0(19)	7567.4(15)	10813.7(10)	25.3(3)
C8	1545.6(18)	7300.0(15)	10466.2(10)	22.9(3)
C9	1693.6(17)	6721.8(13)	9474.2(9)	18.1(3)
C10	110.1(17)	6470.3(14)	9096.7(10)	21.3(3)
C11	219.3(17)	5934.0(14)	8132.4(10)	19.2(3)
C12	1979.6(16)	5597.1(13)	7523.9(9)	15.6(3)
C13	2481.8(16)	4994.9(13)	6452.4(9)	16.3(3)
C14	1810.1(17)	3508.3(13)	6411.9(10)	19.1(3)
C15	2384.0(17)	2296.4(14)	7210.9(9)	19.3(3)
C17	2012(2)	-145.6(15)	7906.7(11)	29.5(3)
C20	1845.6(16)	6082.5(14)	5565.5(9)	18.1(3)
C21	2685.5(17)	7524.5(14)	5378.9(10)	20.8(3)
C22	2176.6(17)	8464.5(14)	4408.6(10)	20.7(3)
C23	3035.6(19)	9904.9(14)	4201.7(10)	23.7(3)
C24	2514(2)	10856.2(16)	3239.3(12)	31.4(3)

Table S10 Anisotropic Displacement Parameters ($Å^2×10^3$) for 240370lt_auto. The Anisotropic displacement factor exponent takes the form: -$2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	14.8(4)	22.6(4)	15.3(4)	-4.5(3)	-4.2(3)	-1.7(3)
O16	33.3(5)	18.7(5)	26.8(5)	3.4(4)	-13.4(4)	-8.4(4)
O18	45.1(6)	24.7(5)	31.6(5)	3.0(4)	-24.6(5)	-8.8(4)
O19	14.7(5)	33.5(5)	21.7(5)	-8.7(4)	-4.2(3)	-1.7(4)
C2	17.4(6)	18.2(6)	15.1(6)	-1.9(4)	-4.9(5)	-2.4(5)

C3	16.4(6)	14.9(6)	15.4(6)	0.4(4)	-3.4(5)	-2.7(4)
C4	18.8(6)	14.9(6)	15.1(6)	0.3(4)	-3.6(5)	-2.3(5)
C5	16.8(6)	32.2(7)	21.6(7)	-7.4(5)	-4.6(5)	-2.0(5)
C6	24.2(7)	37.1(8)	24.2(7)	-9.3(6)	-9.4(5)	-4.0(6)
C7	31.0(7)	28.8(7)	17.5(6)	-7.5(5)	-4.5(5)	-4.5(6)
C8	23.6(7)	25.8(7)	17.8(6)	-3.8(5)	1.2(5)	-3.5(5)
C9	19.8(6)	17.2(6)	16.8(6)	0.5(5)	-2.0(5)	-4.0(5)
C10	15.9(6)	26.1(7)	20.7(6)	-2.2(5)	1.3(5)	-4.6(5)
C11	15.1(6)	23.6(6)	19.9(6)	-0.9(5)	-4.2(5)	-5.3(5)
C12	17.9(6)	13.8(6)	15.4(6)	1.6(4)	-4.3(5)	-3.7(4)
C13	13.7(6)	19.8(6)	16.4(6)	-1.1(5)	-4.9(4)	-2.7(5)
C14	22.0(6)	20.1(6)	17.6(6)	-1.8(5)	-7.8(5)	-4.2(5)
C15	22.6(6)	19.2(6)	17.1(6)	-3.7(5)	-4.7(5)	-3.1(5)
C17	43.0(8)	19.3(7)	28.1(7)	4.6(5)	-12.5(6)	-6.8(6)
C20	16.5(6)	21.9(6)	16.7(6)	-0.6(5)	-5.3(5)	-2.6(5)
C21	21.3(6)	22.1(6)	19.4(6)	0.4(5)	-5.5(5)	-3.4(5)
C22	22.6(6)	21.1(6)	18.8(6)	-0.3(5)	-5.8(5)	-2.6(5)
C23	24.9(7)	22.0(7)	24.5(7)	0.1(5)	-6.2(5)	-3.7(5)
C24	37.4(8)	25.1(7)	32.8(8)	6.7(6)	-11.2(6)	-7.4(6)

Table S11 Bond Lengths for 240370lt_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C2	1.3635(14)	C7	C8	1.3636(19)
O1	C13	1.4583(14)	C8	C9	1.4168(17)
O16	C15	1.3406(15)	C9	C10	1.4226(18)
O16	C17	1.4500(15)	C10	C11	1.3708(18)
O18	C15	1.2005(16)	C11	C12	1.4044(17)
O19	C2	1.2103(15)	C12	C13	1.5033(16)
C2	C3	1.4746(16)	C13	C14	1.5298(17)
C3	C4	1.4211(16)	C13	C20	1.5394(16)
C3	C12	1.3674(17)	C14	C15	1.5097(17)
C4	C5	1.4120(17)	C20	C21	1.5217(17)
C4	C9	1.4240(17)	C21	C22	1.5238(17)

Table S11 Bond Lengths for 240370lt_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C5	C6	1.3714(18)	C22	C23	1.5274(18)
C6	C7	1.4075(19)	C23	C24	1.5233(18)

Table S12 Bond Angles for 240370lt_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	O1	C13	110.95(9)	C10	C11	C12	117.46(11)
C15	O16	C17	115.29(10)	C3	C12	C11	121.90(11)
O1	C2	C3	108.42(10)	C3	C12	C13	109.89(10)
O19	C2	O1	120.89(11)	C11	C12	C13	128.20(11)
O19	C2	C3	130.69(11)	O1	C13	C12	103.03(9)
C4	C3	C2	130.25(11)	O1	C13	C14	108.59(10)
C12	C3	C2	107.57(10)	O1	C13	C20	108.60(9)
C12	C3	C4	122.16(11)	C12	C13	C14	114.24(10)
C3	C4	C9	116.23(11)	C12	C13	C20	113.15(10)
C5	C4	C3	124.79(11)	C14	C13	C20	108.90(9)
C5	C4	C9	118.97(11)	C15	C14	C13	115.50(10)
C6	C5	C4	120.39(12)	O16	C15	C14	110.08(10)
C5	C6	C7	120.89(12)	O18	C15	O16	123.31(12)
C8	C7	C6	119.83(12)	O18	C15	C14	126.62(12)
C7	C8	C9	121.14(12)	C21	C20	C13	115.04(10)
C8	C9	C4	118.76(11)	C20	C21	C22	112.13(10)
C8	C9	C10	121.43(11)	C21	C22	C23	112.69(10)
C10	C9	C4	119.81(11)	C24	C23	C22	112.89(11)
C11	C10	C9	122.40(11)				

Table S13 Torsion Angles for 240370lt_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C2	C3	C4	179.31(11)	C6	C7	C8	C9	-0.1(2)
O1	C2	C3	C12	1.13(13)	C7	C8	C9	C4	1.15(19)

O1 C13 C14 C15	59.76(13)	C7 C8 C9 C10	-178.62(12)
O1 C13 C20 C21	-51.71(13)	C8 C9 C10 C11	178.94(12)
O19 C2 C3 C4	-0.8(2)	C9 C4 C5 C6	0.26(19)
O19 C2 C3 C12	-179.02(13)	C9 C10 C11 C12	1.57(19)
C2 O1 C13 C12	-3.13(12)	C10 C11 C12 C3	-0.54(18)
C2 O1 C13 C14	-124.62(10)	C10 C11 C12 C13	179.73(12)
C2 O1 C13 C20	117.10(10)	C11 C12 C13 O1	-176.41(11)
C2 C3 C4 C5	4.6(2)	C11 C12 C13 C14	-58.83(16)
C2 C3 C4 C9	-176.01(11)	C11 C12 C13 C20	66.53(15)
C2 C3 C12 C11	177.10(11)	C12 C3 C4 C5	-177.48(12)
C2 C3 C12 C13	-3.13(13)	C12 C3 C4 C9	1.95(17)
C3 C4 C5 C6	179.68(12)	C12 C13 C14 C15	-54.59(14)
C3 C4 C9 C8	179.31(11)	C12 C13 C20 C21	62.03(13)
C3 C4 C9 C10	-0.92(17)	C13 O1 C2 O19	-178.46(11)
C3 C12 C13 O1	3.84(12)	C13 O1 C2 C3	1.42(13)
C3 C12 C13 C14	121.42(11)	C13 C14 C15 O16	172.40(10)
C3 C12 C13 C20	-113.22(11)	C13 C14 C15 O18	-8.00(19)
C4 C3 C12 C11	-1.27(18)	C13 C20 C21 C22	173.15(10)
C4 C3 C12 C13	178.50(10)	C14 C13 C20 C21	-169.79(10)
C4 C5 C6 C7	0.8(2)	C17 O16 C15 O18	-1.09(18)
C4 C9 C10 C11	-0.83(19)	C17 O16 C15 C14	178.52(11)
C5 C4 C9 C8	-1.23(17)	C20 C13 C14 C15	177.84(10)
C5 C4 C9 C10	178.55(11)	C20 C21 C22 C23	-179.10(10)
C5 C6 C7 C8	-0.9(2)	C21 C22 C23 C24	-179.38(11)

Table S14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 240370lt_auto.

Atom	*x*	*y*	*z*	U(eq)
H5	6218.98	6474.62	8811.79	28
H6	5872.32	7466.97	10422.16	33
H7	2942.82	7956.47	11480.45	30
H8	366.76	7504.98	10896.62	27
H10	-1066.01	6681.61	9528.66	26
H11	-854.87	5795.62	7885.16	23
H14A	450.39	3659.13	6520.83	23
H14B	2270.84	3172.01	5693.01	23
H17A	3322.07	-505.39	7707.34	44
H17B	1279.24	-933.3	7864.56	44
H17C	1758.08	151.84	8633.34	44
H20A	2148.01	5587.78	4896.92	22
H20B	491.21	6314.56	5739.71	22
H21A	4040.54	7303.28	5283.09	25
H21B	2255.29	8091	6011.29	25
H22A	822.08	8696.2	4510.36	25
H22B	2587.81	7889.46	3779.39	25
H23A	2635.47	10473.94	4834.44	28
H23B	4390.52	9672.1	4092.71	28
H24A	2957.4	10317.16	2603.98	47
H24B	3075.86	11773.13	3153.62	47
H24C	1173.73	11090.46	3341.29	47