Supporting Information

Visible light-mediated enantioselective photoreactions of 3-alkylquinolones with 4-*O*-tethered alkenes and allenes

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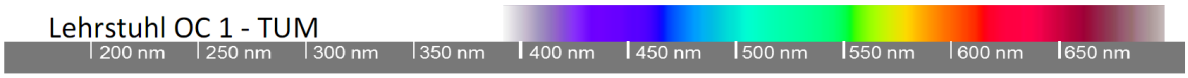
1. General Information

All reactions sensitive to air or moisture were carried out in flame-dried glassware under argon pressure using standard Schlenk techniques. Dry tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were obtained from an *MBraun* MB-SPS 800 solvent purification system. Other dry solvents were obtained from *Merck* and *Acros* in the highest purity available and used without further purification. Technical solvents used for aqueous workup and for column chromatography [dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), *n*-hexane (Hex), methanol (MeOH), *n*-pentane (Pn)] were distilled prior to use. Photochemical experiments were performed in Duran phototubes (ø = 1.0 cm for racemic and enantioselective reactions and ø = 1.8 cm for 0.5 mmol scale reactions) under argon atmosphere in a positive geometry setup [cylindrical array of 16 fluorescent light tubes, λ = 420 nm (Luzchem LZC-420, 8 W)]. Reactions at -25 °C were performed inside a Duran cool finger which was attached to a cryostat (Huber CC410). Solvents used in the photochemical reactions were degassed under a continuous argon flow in an ultrasonication bath for 15 minutes. Flash chromatography was performed on silica 60 (Merck, 230-400 mesh) with the indicated eluent mixtures. Thin layer chromatography (TLC) was performed on silica coated glass plates (silica 60 F254) with detection by UV (λ = 254 and 366 nm) and/or by staining with a potassiumpermanganate solution ($KMnO_4$) followed by heat treatment. High performance liquid chromatography (HPLC) analyses were performed using a chiral stationary phase [ChiralPak AD-H (250 x 4.6 mm), Chiralpak OD-H (250 x 4.6 mm), Chiralpak AS-H (250 x 4.6 mm), *Daicel Chemical Industries*] with UVD 340 Photodiode Array Detector, P580 Pump and an ASI-100 Automated Sample Injector at 20 °C. Preparative HPLC was conducted on a apparatus consiting of a HPG 3200BX pump (*Thermo Fisher*) and a MWD 3000-RS UV-detector (*Dionex*). For normal-phase HPLC a *Daicel* ChiralPak AD-H, ChiralPak OD-H, and a ChiralPak AS-H was used as stationary phase and a mixture of *n*-heptane/*i*-propanol was used as mobile phase. Analytical gaschromatography was performed at a HP 6890 Series GC (*Agilent*, achiral stationary phase: HP-5 column, poly-dimethyl/diphenyl-siloxane, 95/5) with a flame ionisation detector. IR spectra were recorded on a *JASCO* IR-4100 (ATR). ^{1}H, ^{13}C, and ^{19}F-NMR spectra were recorded at 303 K either on a Bruker AVHD300, AVHD400, or AVHD500 spectrometer. NMR spectra were calibrated to the respective residual solvent signals of $CDCl_3$ [δ (^{1}H) = 7.26 ppm, δ (^{13}C) = 77.16 ppm]. Apparent multiplets which occur as a result of coupling constant equality between magnetically non-equivalent protons are marked as virtual (*virt.*). The following abbreviations for single multiplicities were used: *br*-broad, s-singlet, d-doublet, t-triplet, q-quartet, quint-quintet, sext-sextet. High resolution mass spectroscopy (HR-MS) was performed on a *Thermo Scientific* LTQ-FT Ultra (ESI) or a *Thermo Scientific* DFS-HRMS spectrometer (EI). Melting points were measured on a *Büchi* M-565 instrument and are not corrected. Specific rotations were determined with a ADP440+ polarimeter. Optical rotation was measured using a Perkin-Elmer 241 MC polarimeter in a 1.00 dm cuvette at 589 nm (Na D-Line) at room temperature. The specific rotation was calculated with the Drude equation. $[\alpha]_D^T$ and is given in 10^1 grad cm^2 g^{-1}.

2. Emission Spectrum of the Light Source

Lehrstuhl OC 1 - TUM



Datasheet FLT022 LZC-420

Basic Information

Type	Fluorescent light tube
Description	Luzchem LZC-420
Manufacturer / Supplier	n/a / Luzchem
Order number / Date of purch.	n/a / 07/2017
Internal lot / serial number	2017-07 / FLT022

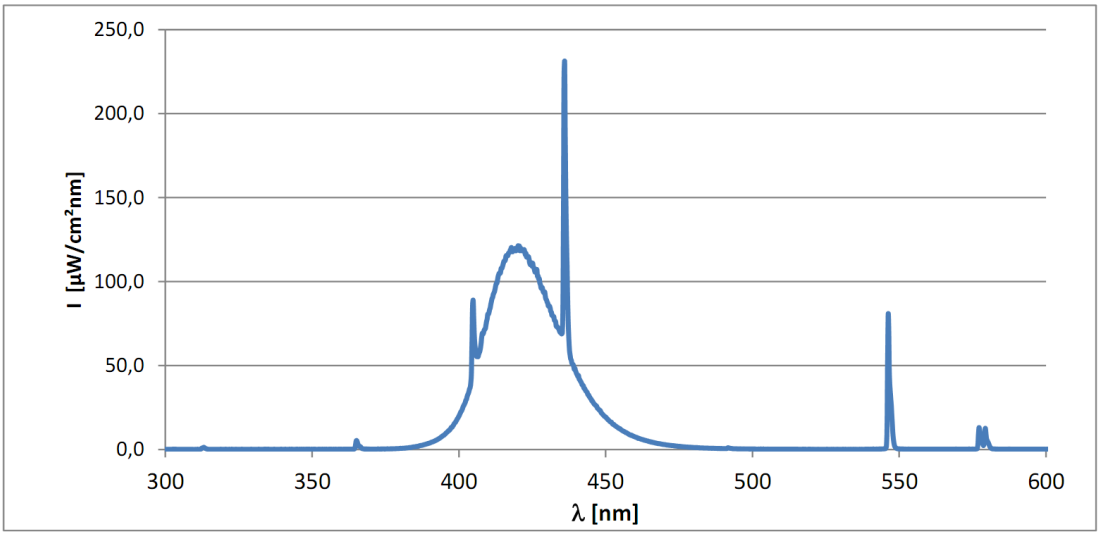
Specification Manufacturer

Type / size	T5 tube, G5 socket
Mechanical specification	16 mm diameter, 288 mm length
Electrical specification	8 W
Wavelength (range, typ.)	400 - 440 nm
Spectral width (FWHM)	~ 30 nm
Datasheet	LES-420-016

Characterization

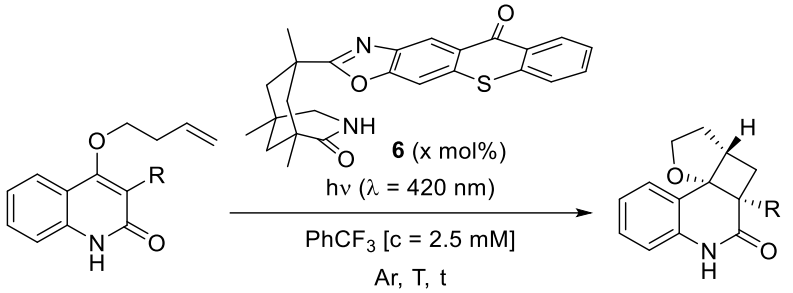
Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The cosine corrector was placed at 20 mm distance from a single fluorescent tube at half height.	
Measured dominant wavelength / Int.	421 nm	121 µW/mm²nm
Measured spectral width (FWHM)	30 nm	
Integral Reference intensity / range	4142 µW/cm²	350-500 nm

Spectrum



3. Optimization of Irradiation Conditions

Table S1. Optimization of the enantioselective [2 + 2] photocycloaddition of 4-alkenyloxyquinolones



5a, R = H
5b, R = Me

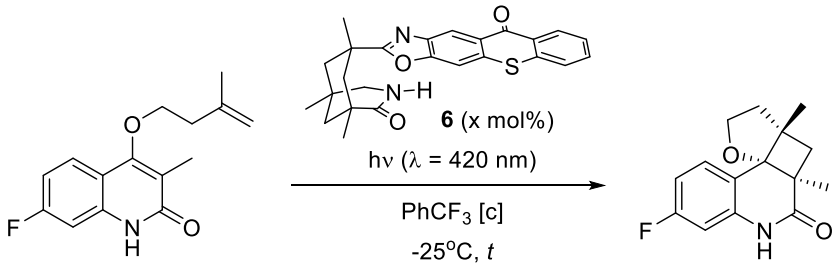
7a
7b

Entry	Sub.	**6** (x mol%)	T [°C]	*t* [h]	Yield [%]	ee [%]
1	**5a**	10	25	1	0	--
2	**5b**	10	25	1	98	72
3	**5b**	10	-25	1	97	88
4	**5b**	5	-25	1.5	97	86
5	**5b**	2.5	-25	2.5	97	86
6[a]	**5b**	1	-25	4	91	83
7[b]	**5b**	10	-25	1	98	55

[a] The reaction was performed at a concentration of c = 5 mM. [b] The reaction was performed in MeCN.

4. Screening of Catalyst Loadings

Table S2. [2+2] photocycloaddition of substrate **5n** to cyclobutane **7n**: Efficiency of sensitizer **6** at low catalyst loadings.



5n
0.5 mmol (130.6 mg)

7n

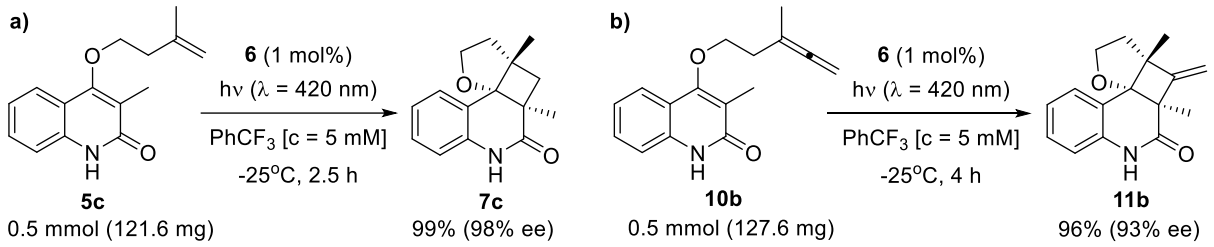
Entry	**6** (x mol%)	c [mM]	*t* [h]	Yield [%]	ee [%]
1	10	2.5	1	>99	99
2	1	5	2.5	>99	95
3	0.5	5	7	99	93

(***Entry 1***): **5n** (130.6 mg, 0.5 mmol) and **6** (21.6 mg, 0.05 mmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (200 mL, *c* = 2.5 mmol/L), cooled to -25 °C and irradiated at λ = 420 nm for 1 h. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), compound **7n** was obtained as a colorless solid (130.5 mg, >99%, 99% *ee*).

(***Entry 2***): **5n** (130.6 mg, 0.5 mmol) and **6** (2.2 mg, 5 µmol, 1 mol%) were dissolved in α,α,α-trifluorotoluene (100 mL, *c* = 5 mmol/L) and reacted for 2.5 h at -25 °C. Following flash column chromatography, compound **7n** was obtained as a colorless solid (130.3 mg, >99%, 95% *ee*).

(***Entry 3***): **5n** (130.6 mg, 0.5 mmol) and **6** (1.1 mg, 2.5 µmol, 0.5 mol%) were dissolved in α,α,α-trifluorotoluene (100 mL, *c* = 5 mmol/L) and reacted for 7 h at -25 °C. Following flash column chromatography, compound **7n** was obtained as a colorless solid (129.5 mg, 99%, 93% *ee*).

Scheme S1. [2+2] photocycloaddition of substrate **5c** and **10b** to cyclobutane **7c** and **11b**: Efficiency of sensitizer **6** at low catalyst loadings.



(**Scheme S1a**): **5c** (121.6 mg, 0.5 mmol) and **6** (2.2 mg, 5 µmol, 1 mol%) were dissolved in α,α,α-trifluorotoluene (100 mL, *c* = 5 mmol/L), cooled to -25 °C and irradiated at λ = 420 nm for 2.5 h. Following flash column chromatography, compound **7c** was obtained as a colorless solid (120.5 mg, 99%, 98% *ee*).

(**Scheme S1b**): **10b** (127.6 mg, 0.5 mmol) and **6** (2.2 mg, 5 µmol, 1 mol%) were dissolved in α,α,α-trifluorotoluene (100 mL, *c* = 5 mmol/L), cooled to -25 °C and irradiated at λ = 420 nm for 4 h. Following flash column chromatography, compound **11b** was obtained as a colorless solid (122.0 mg, 96%, 93% *ee*).

5. Emission Spectra and Triplet Energy of Quinolones

General information

UV/Vis absorption spectra were measured on a Perkin Elmer Lambda 35 UV/Vis Spectrometer in quartz cuvettes. Emission spectra where recorded on a Horiba Scientific FlouroMax-4P Spectrofluorometer equipped with a continuous Xe source for steady state spectra and a Xe flashlight source for the observation of phosphorescence spectra. Spectra were recorded in quartz tubes (4 mm internal diameter) in a small quartz Dewar vessel which was filled with liquid nitrogen for recording spectra at cryogenic temperatures (77 K). Ethanol was filtered over silica and neutral aluminium oxide and subsequently distilled over a 20 cm vacuum insulated Vigreux column and was degassed prior to use. All solutions have been handled under dry nitrogen to exclude oxygen as triplet quencher.

Quinolone characterization

Quinolone **5a** was dissolved in ethanol to give a 100 µM solution. The absorption spectrum (d = 4 mm) is shown in Figure S1a, normalized to the long-wavelength absorption maximum at λ = 315 nm (ε = 6625 $Lmol^{-1}cm^{-1}$). Luminescence of a 100 µM solution in ethanol after excitation at λ = 315 nm was recorded in a quartz tube (4 mm internal diameter) and is shown normalized to the emission-maximum at λ = 360 nm in Figure S1a. The emission is attributed to fluorescence and the crossing of the normalized spectra at λ = 336 nm assigned to a S_1 energy of 356 kJ/mol.

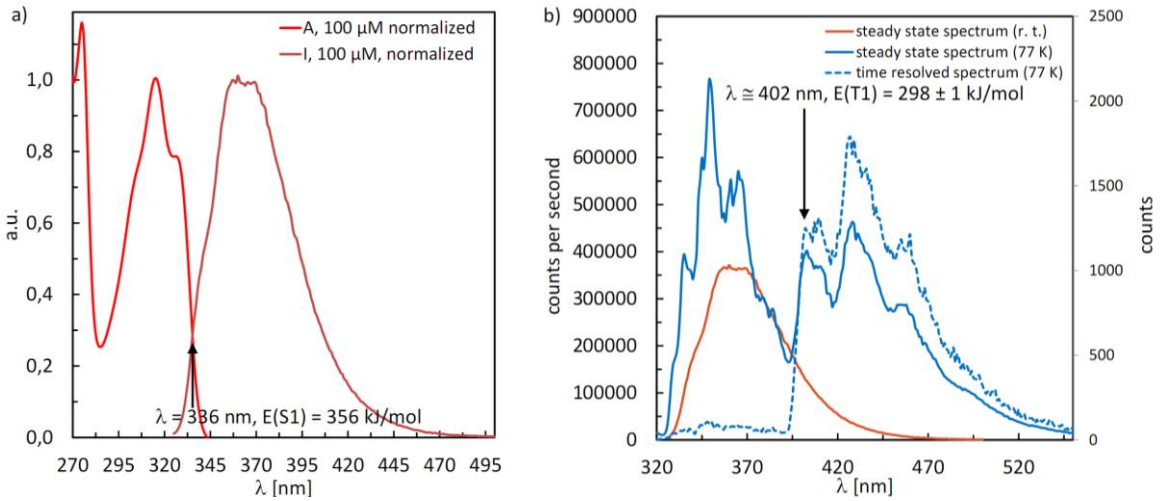


Figure S1. a) Recorded UV/Vis of **5a** in ethanol (c = 100 µM) normalized to $A_{315\ nm}$, recorded luminescence of **5a** in ethanol (c = 100 µM) at ambient conditions, normalized to $I_{360\ nm}$. b) Steady state spectra of **5a** in ethanol (c = 100 µM) at ambient conditions and at 77 K given in counts per second (solid lines), time resolved spectrum of **5a** in ethanol (c = 100 µM) after 250 µs delay (counts, dashed line).

The solution of **5a** in ethanol was cooled to 77 K in a quartz tube to give an amorphous or microcrystalline solid ("snowy"). Excitation at λ = 312 nm gave a spectrum, in which contributions from the previously recorded fluorescence spectrum can be qualitatively assigned together with a very broad and unstructured signature with a maximum at approx. λ = 430 nm (Figure S1b). Introducing a delay between excitation and detection led to a complete bleach of signatures assigned to fluorescence and the resulting spectrum (Figure S1b, dashed line) was attributed to phosphorescence. Tentatively assigning the most blueshifted shoulder (λ_{max} ≅ 402 nm) to the 0→0 transition of the phosphorescence allows to give an estimate for the triplet energy of 298 ± 1 kJ/mol for **5a** in ethanol.

Excitation spectra were recorded under steady state at 77 K. The spectra match qualitatively the room temperature solution spectrum. The two major differences are a red shift of about 5 nm and an additional shoulder/feature at ~340 nm. Figure S2 shows the excitation spectrum under steady state at 77 K and the room temperature solution spectra of **5a** in ethanol normalized to the respective local maxima.

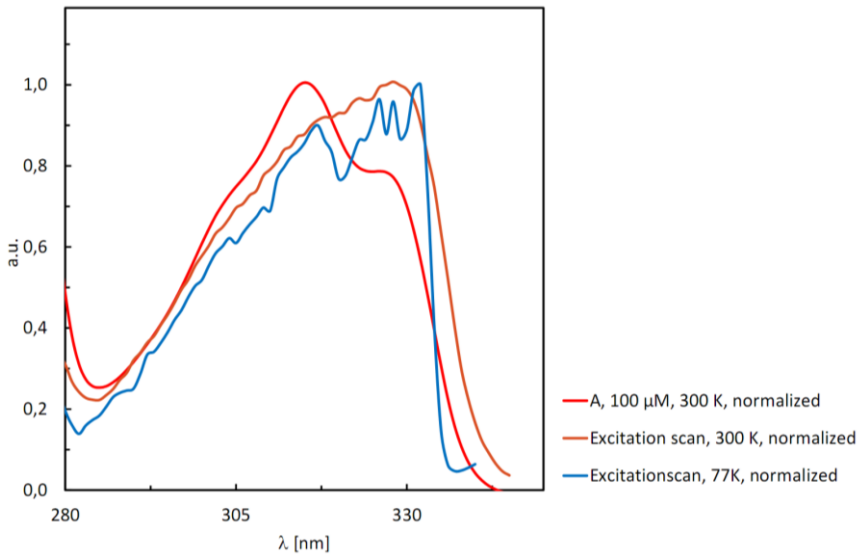


Figure S2. Recorded UV/Vis of **5a** in ethanol (c = 100 µM) normalized to $A_{315\,nm}$, recorded steady state spectrum of **5a** in ethanol (c = 100 µM) at 300 K and 77 K, normalized to the respective local maxima.

Quinolone **5b** was dissolved in ethanol to give a 100 µM solution. The absorption spectrum (d = 4 mm) is shown in Figure S3a, normalized to the long-wavelength absorption maximum at λ = 322 nm (ε = 8847 $Lmol^{-1}cm^{-1}$). Luminescence of a 100 µM solution in ethanol after excitation at λ = 322 nm was recorded in a quartz tube (4 mm internal diameter) and is shown normalized to the emission-maximum at λ = 363 nm in Figure S3a. The emission is attributed to fluorescence and the crossing of the normalized spectra at λ = 342 nm assigned to a S1 energy of 350 kJ/mol.

The solution of **5b** in ethanol was cooled to 77 K in a quartz tube to give an amorphous or microcrystalline solid ("snowy"). Excitation at λ = 330 nm gave a spectrum, in which contributions from the previously recorded fluorescence spectrum can be qualitatively assigned together with a very broad and unstructured signature with a maximum at approx. λ = 470 nm (Figure S3b). Introducing a delay between excitation and detection led to a complete bleach of signatures assigned to fluorescence and the resulting spectrum (Figure S3b, dashed line) was attributed to phosphorescence. Tentatively assigning the most blueshifted shoulder ($\lambda_{max} \cong$ 435-440 nm) to the 0→0 transition of the phosphorescence allows to give an estimate for the triplet energy of 273 ± 2 kJ/mol for **5b** in ethanol.

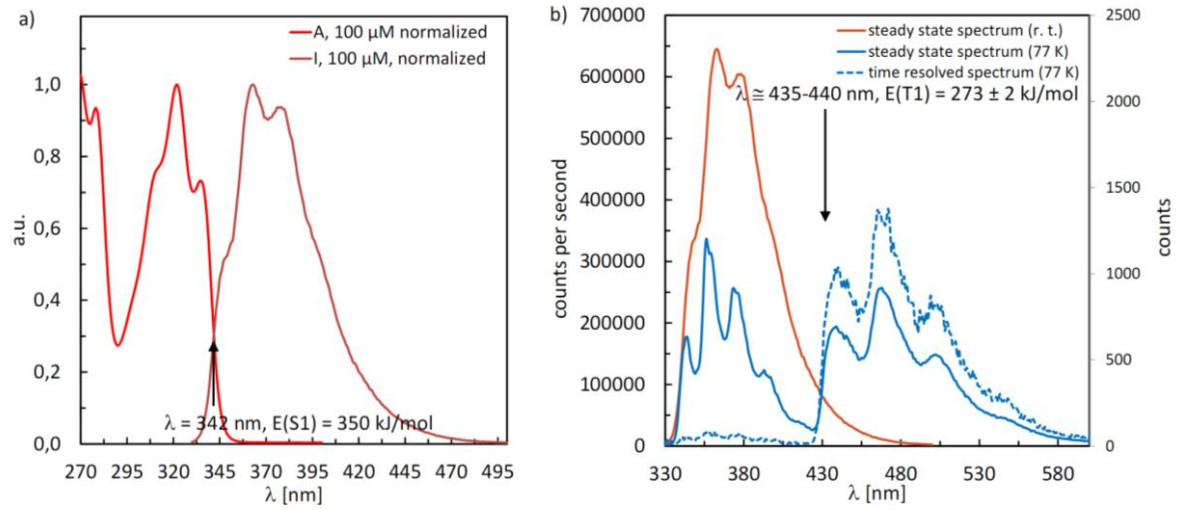


Figure S3. a) Recorded UV/Vis of **5b** in ethanol (c = 100 µM) normalized to $A_{322\ nm}$, recorded luminescence of **5b** in ethanol (c = 100 µM) at ambient conditions, normalized to $I_{363\ nm}$. b) Steady state spectra of **5b** in ethanol (c = 100 µM) at ambient conditions and at 77 K given in counts per second (solid lines), time resolved spectrum of **5b** in ethanol (c = 100 µM) after 250 µs delay (counts, dashed line).

Excitation spectra were recorded under steady state at 77 K. The spectra match qualitatively the room temperature solution spectrum. The two major differences are a red shift of about 5 nm and an additional shoulder/feature at ~340 nm. Figure S4 shows the excitation spectrum under steady state at 77 K and the room temperature solution spectra of **5b** in ethanol normalized to the respective local maxima.

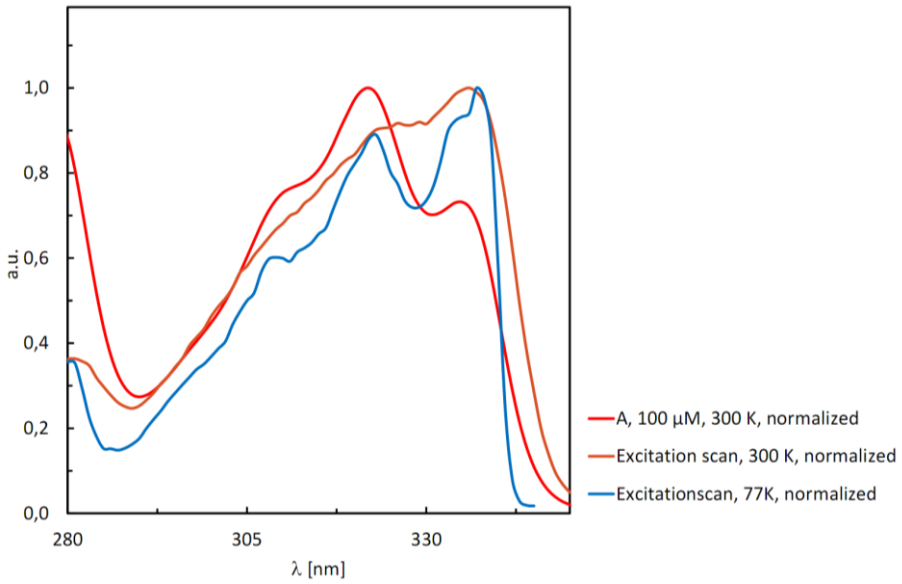
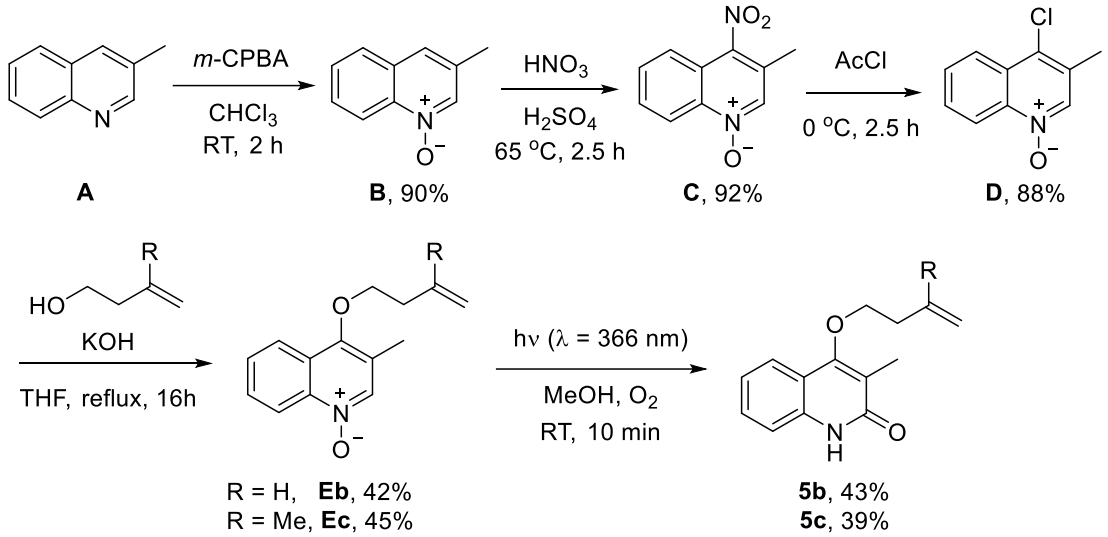


Figure S4. Recorded UV/Vis of **5b** in ethanol (c = 100 µM) normalized to $A_{322\ nm}$, recorded steady state spectrum of **5b** in ethanol (c = 100 µM) at 300 K and 77 K, normalized to the respective local maxima.

6. Synthetic Procedures and Analytical Data

The ether substrate **5a** was obtained following a literature procedure[1] starting from 4-chloroquinoline-*N*-oxide[2] and the commercially available alcohol. The substrates **5b** and **5c** for the photocycloaddition reaction was prepared as previously described[1] starting from 3-methylquinoline.

General Procedure 1: Synthesis of ether substrates **5b** and **5c** *by photochemical rearrangement of N-oxides*[3]

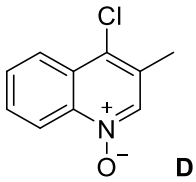


A solution of 3-methylquinoline (**A**) (2.86 g, 20 mmol) in 50 mL of chloroform was treated with *meta*-chloroperbenzoic acid (5.18 g, 30 mmol). The mixture was stirred for 2 h at room temperature. Subsequently, saturated $NaHCO_3$ (100 mL) and 2M NaOH (100 mL) were added and the mixture was extracted with dichloromethane. The combined organic layers were dried with Na_2SO_4 and the solvent was removed at reduced pressure yielding the quinoline *N*-oxide **B** (2.87 g, 18 mmol, 90 %) as a bright yellow solid which was used in the following step without further purification.

To a solution of quinoline *N*-oxide **B** (2.87 g, 18 mmol) in 6.6 mL of concentrated sulfuric acid at 65 °C in an oil bath, 1.5 mL of 65% nitric acid solution was added dropwise over an hour. The reaction solution was stirred for another 2.5 hours at 65 °C and after cooling, carefully poured into 60 mL ice water. The solid precipitates were filtered off, washed with water until neutral and dried in a desiccator. The desired 4-nitroquinoline-*N*-oxide **C** (3.38 g, 16.6 mmol, 92%) was obtained as a yellow solid, which was used in the following step without further purification.

16.0 mL acetyl chloride (17.6 g, 224 mmol) was cooled to 0 °C and *N*-oxide **C** (2.37 g, 11.6 mmol) was added in portions over an hour, and the temperature must not rise above 10 °C. Then the solution stirred for another 2.5 hours in an ice bath and then added dropwise with ice water, until the highly exothermic hydrolysis of the excess acetyl chloride has ended. The reaction solution was mixed with potassium carbonate with vigorous stirring until the solution is basic and then extracted with dichloromethane (3 x 50 mL). The combined organic phases were washed with 50 mL saturated sodium chloride solution, dried over sodium sulfate, filtered and the solvent removed in vacuo. The crude product 4-chloro-3-methylquinoline 1-oxide (**D**) (1.97 g, 10.2 mmol, 88%) was obtained as a yellow solid, which can be further purified by recrystallization from acetone.

4-chloro-3-methylquinoline 1-oxide (D):



D

Chemical Formula: $C_{10}H_8ClNO$
Exact Mass: 193.0294

TLC: R_f = 0.51 (EtOAc:MeOH, 95:5) [UV].

M.p.:164-166 °C.

IR (film) υ_{max}/cm^{-1} 3098, 3071, 1656, 1561, 1534, 1345, 1332, 1201, 1088, 1035, 919, 853, 770, 744, 658.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.63 (s, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 2.55 (s, 3H).

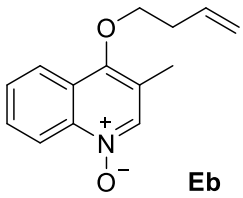
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 137.4, 131.1, 130.6, 130.0, 129.6, 128.2, 124.9, 120.2, 18.0.

GC-MS; EI (70 eV): t_R = 14.42 Min. [STDHT]; m/z (%) = 195 (34) [M+2+], 193 (100) [M+], 179 (17), 177 (52), 164 (14), 151 (34), 142 (37), 130 (29), 115 (34).

HRMS (**ESI**) m/*z*: $[C_{10}H_8ClNO+H]^+$ calcd.: 194.0367; found: 194.0367.

4-Chloroquinolin-*N*-oxide **D** (968 mg, 5 mmol) and powdered potassium hydroxide (560 mg, 10 mmol) were dissolved under argon in dry tetrahydrofuran (0.3 M). The appropriate alcohol (20 mmol) was added and the solution was heated to reflux in an oil bath until the reaction was complete. After cooling to room temperature the solvent was removed *in vacuo* and the residue was dissolved in dichloromethane (20 mL/mmol). The solution was washed with water (10 mL/mmol) and brine (10 mL/mmol), dried over Na_2SO_4, filtered and evaporated *in vacuo*. The crude product was purified by column chromatography.

4-(but-3-en-1-yloxy)-3-methylquinoline 1-oxide (Eb):



Eb

Chemical Formula: $C_{14}H_{15}NO_2$
Exact Mass: 229.1103

Following the general procedure, compound **Eb** was obtained as a light yellow oil (480 mg, 42%) by column chromatography (silica, DCM/MeOH 96:4).

TLC: R_f = 0.37 (DCM:MeOH, 95:5) [UV].

IR (film) υ_{max}/cm^{-1} 3385, 3075, 2928, 1640, 1573, 1400, 1353, 1329, 1201, 1085, 968, 916, 872, 765, 733.

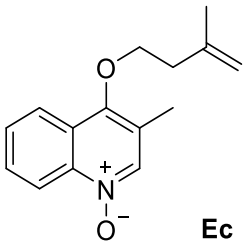
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.7 Hz, 1H), 8.42 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 5.96 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.23 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 4.07 (t, *J* = 6.6 Hz, 2H), 2.65 (*virt.* q, *J* ≈ *J* = 6.6 Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 140.8, 138.6, 133.9, 129.9, 128.6, 125.6, 122.6, 120.2, 118.0, 74.1, 34.7, 13.9.

GC-MS; EI (70 eV): t_R = 16.52 Min. [STDHT]; m/z (%) = 229 (21) [M+], 213 (74), 175 (37), 172 (38), 159 (93), 158 (39), 130 (57), 115 (24), 104 (22), 77 (32), 55 (100).

HRMS (**EI**) m/*z*: $[C_{14}H_{15}NO_2+H]^+$ calcd.: 230.1176; found: 230.1176.

3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinoline 1-oxide (Ec):



Ec

Chemical Formula: $C_{15}H_{17}NO_2$
Exact Mass: 243.1259

Following the general procedure, compound **Ec** was obtained as a light-yellow oil (545 mg, 45%) by column chromatography (silica, DCM/MeOH 96:4).

TLC: R_f = 0.39 (DCM:MeOH, 95:5) [UV].

IR (film) υ_{max}/cm^{-1} 3385, 3075, 2933, 1650, 1573, 1450, 1400, 1353, 1329, 1262, 1200, 1085, 975, 890, 866, 765, 731.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.7 Hz, 1H), 8.45 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.72 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.63 (ddd, *J* = 8.2, 7.6, 1.2 Hz, 1H), 4.92 (s, 1H), 4.87 (s, 1H), 4.16 (t, *J* = 6.8 Hz, 2H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.39 (s, 3H), 1.84 (s, 3H).

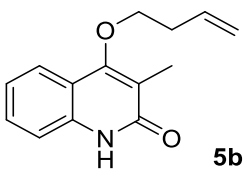
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 141.5, 140.8, 138.9, 130.1, 128.7, 125.7, 122.7, 122.6, 120.2, 113.0, 73.4, 38.4, 22.9, 14.0.

GC-MS; EI (70 eV): t_R = 17.02 Min. [STDHT]; m/z (%) = 243 (1) [M+], 227 (23), 159 (100), 130 (22), 115 (10), 77 (10), 69 (28).

HRMS (**EI**) m/*z*: $[C_{15}H_{17}NO_2+H]^+$ calcd.: 244.1332; found: 244.1333.

The 4-alkenyloxyquinolin-*N*-oxide **E** was dissolved in methanol (200 mL/mmol), saturated with oxygen and run through a double coiled tubular flow reactor (Duran tube 7 mm, coil outer diameter: 75 mm, height: 200 mm, internal volume: 150 mL) placed in the middle of a Rayonet (RPR-100) photoreactor equipped with 16 lamps of the given wavelength. After passing the reactor, the product solution was collected in a septum stoppered flask which was filled with inert gas and equipped with a balloon for pressure equalization. Reaction progress was monitored by UV/VIS-spectrometry (flow-cuvette, detection of the *N*-oxide absorption band at λ > 360 nm). The collected product solution was evaporated *in vacuo*. The crude product was purified by flash column chromatography and recrystallisation.

4-(but-3-en-1-yloxy)-3-methylquinolin-2(1*H*)-one (5b):



5b

Chemical Formula: $C_{14}H_{15}NO_2$
Exact Mass: 229.1103

Following the general procedure, compound **5b** was obtained as a colorless solid (148 mg, 43%) by column chromatography (silica, pentane/ethyl acetate 1.5:1).

TLC: R_f = 0.44 (Pentane:EtOAc, 1:1) [UV].

M.p.: 152-153 °C.

IR (film) υ_{max}/cm^{-1} 3065, 2944, 2876, 2852, 1638, 1613, 1569, 1497, 1433, 1373, 1353, 1271, 1157, 1144, 1107, 1015, 975, 915, 871, 755, 741, 697, 667.

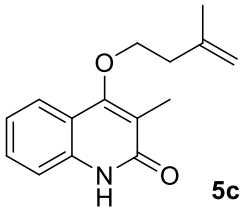
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.86 (*br* s, 1H), 7.79 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.48 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.41 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.22 (ddd, *J* = 8.2, 7.1, 1.3 Hz, 1H), 5.98 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.24 (*virt.* dq, *J* = 17.2 Hz, *J* ≈ *J* = 1.6 Hz, 1H), 5.18 (*virt.* dq, *J* = 10.3 Hz, *J* ≈ *J* = 1.6 Hz, 1H), 4.09 (t, *J* = 6.7 Hz, 2H), 2.66 (*virt.* qt, *J* ≈ *J* = 6.7 Hz, *J* = 1.4 Hz, 2H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 161.5, 137.3, 134.2, 130.1, 122.9, 122.4, 118.8, 117.8, 117.7, 116.0, 73.2, 34.9, 10.4.

GC-MS; EI (70 eV): t_R = 15.90 Min. [STDHT]; m/*z* (%) = 229 (18) [M+], 214 (35), 175 (100), 146 (17), 130 (13), 120 (20), 55 (48).

HRMS (**ESI**) m/*z*: $[C_{14}H_{15}NO_2+H]^+$ calcd.: 230.1176; found: 230.1177.

3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5c):



5c

Chemical Formula: $C_{15}H_{17}NO_2$
Exact Mass: 243.1259

Following the general procedure, compound **5c** was obtained as a colorless solid (142 mg, 39%) by column chromatography (silica, pentane/ethyl acetate 1.5:1).

TLC: R_f = 0.36 (Pentane:EtOAc, 1:1) [UV].

M.p.: 114-115 °C.

IR (film) υ_{max}/cm^{-1} 3067, 2948, 2917, 2870, 1646, 1611, 1572, 1434, 1348, 1266, 1144, 1103, 1031, 979, 896, 837, 746, 698, 689.

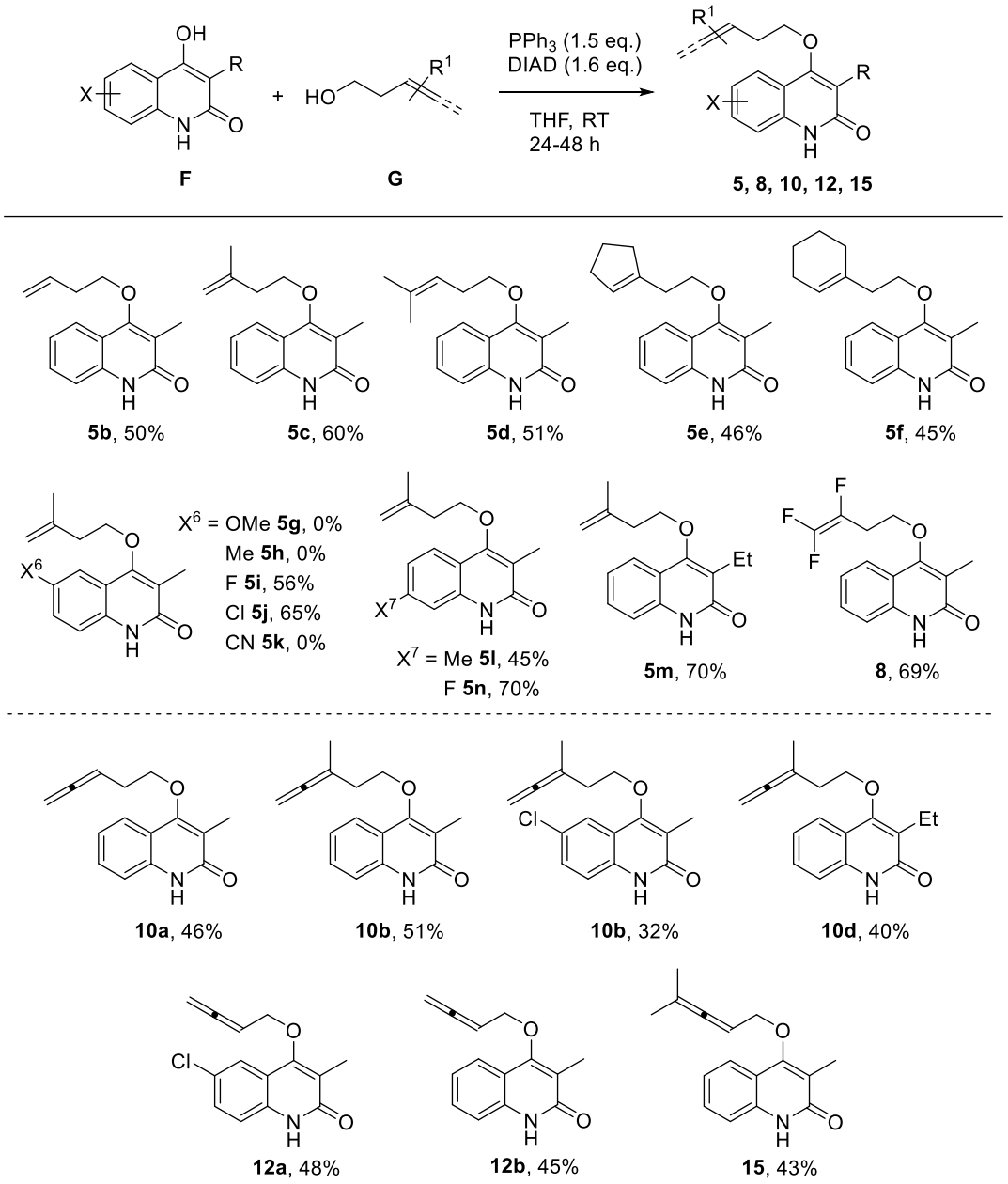
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.16 (*br* s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 4.91 (s, 1H), 4.87 (s, 1H), 4.15 (t, *J* = 6.9 Hz, 2H), 2.62 (t, *J* = 6.9 Hz, 1H), 2.26 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 161.6, 141.8, 137.3, 130.0, 122.8, 122.4, 118.7, 117.7, 116.1, 112.8, 72.3, 38.5, 22.9, 10.4.

GC-MS; EI (70 eV): t_R = 16.45 Min. [STDHT]; m/*z* (%) = 243 (20) [M+], 175 (100), 146 (10), 120 (12), 69 (25).

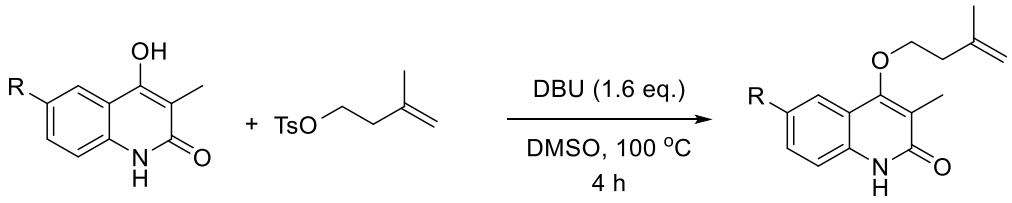
HRMS (**ESI**) m/*z*: $[C_{15}H_{17}NO_2+H]^+$ calcd.: 244.1332; found: 244.1334.

*General Procedure 2: Synthesis of ether substrates **5**, **8**, **10**, **12**, and **15** by Mitsunobu reactions* [4]



A flask was charged with 4-hydroxy-2-quinolone[5] **F** (2.0 mmol) and triphenylphoshine (3.0 mmol, 786 mg) under an inert atmosphere. After solvation in dry THF (4 mL) alcohol **G** (3.0 mmol) was added and the stirred solution was cooled by an external ice/water bath. Diisopropyl azodicarboxylate (3.2 mmol, 647 mg) was added dropwise and the solution was allowed to come to room temperature and stirred for additional 24-48 h. After evaporation of the solvent under reduced pressure, the residue was purified by silica gel flash chromatography.

*General Procedure 3: Synthesis of ether substrates **5g**, **5h**, and **5k** by nucleophilic substitution*[6]

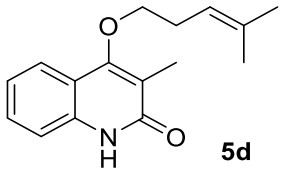


F **H**

5g: R = MeO, 51%
5h: R = Me, 55%
5k: R = CN, 20%

3-Methylbut-3-en-1-yl 4-methylbenzenesulfonate **H** (1.25 eq) was added dropwise to a solution of 4-hydroxy-2-quinolone[5] **F** (1 eq) and DBU (1.56 eq) in DMSO (0.25 mol/L) and the mixture was stirred at 100 °C in an oil bath for 4 h. The solvent was dissolved in dichloromethane, washed successively with 0.5 N NaOH, 0.1 N HCl and water, and dried over sodium sulfate. After removal of the solvent, the crude product was purified by flash column chromatography.

3-methyl-4-((4-methylpent-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5d):



5d

Chemical Formula: $C_{16}H_{19}NO_2$
Exact Mass: 257.1416

Following the *general procedure 2*, compound **5d** was obtained as a colorless solid (260 mg, 51%) by column chromatography (silica, pentane/diethyl ether 1:1.5).

TLC: R_f = 0.54 (Pentane:EtOAc, 1:2) [UV].

M.p.: 109-110 °C.

IR (film) υ_{max}/cm^{-1} 3071, 2961, 2868, 1658, 1614, 1574, 1500, 1436, 1354, 1265, 1144, 1100, 1012, 975, 883, 836, 748, 737, 692, 666.

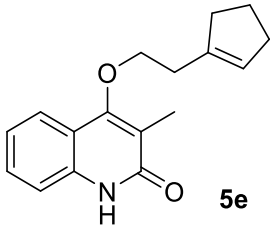
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.10 (*br* s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 5.27 (t, *J* = 7.0 Hz, 1H), 4.01 (t, *J* = 7.0 Hz, 2H), 2.59 (*virt.* q, *J* ≈ *J* = 7.0 Hz, 2H), 2.25 (s, 3H), 1.76 (s, 3H), 1.69 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7, 137.3, 135.1, 130.0, 122.9, 122.3, 119.5, 117.8, 116.1, 73.7, 29.4, 25.9, 18.1, 10.3.

GC-MS; EI (70 eV): t_R = 17.08 Min. [STDHT]; m/z (%) = 257 (2) [M+], 242 (98), 175 (60), 83 (77), 55 (100).

HRMS (**ESI**) m/z: $[C_{16}H_{19}NO_2+H]^+$ calcd.: 258.1489; found: 258.1490.

4-(2-(cyclopent-1-en-1-yl)ethoxy)-3-methylquinolin-2(1*H*)-one (5e):



5e

Chemical Formula: $C_{17}H_{19}NO_2$
Exact Mass: 269.1416

Following the *general procedure 2*, compound **5e** was obtained as a colorless solid (247 mg, 46%) by column chromatography (silica, pentane/diethyl ether 1:2).

TLC: R_f = 0.34 (Pentane:EtOAc, 1:1) [UV].

M.p.: 141-142 °C.

IR (film) υ_{max}/cm^{-1} 3158, 3065, 2946, 2890, 2846, 1644, 1610, 1571, 1498, 1432, 1373, 1356, 1316, 1270, 1262, 1181, 1155, 1143, 1032, 970, 946, 898, 858, 751, 689, 659.

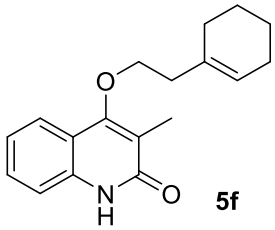
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.25 (*br* s, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.47 (ddd, *J* = 8.2, 6.6, 1.5 Hz, 1H), 7.45 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.20 (ddd, *J* = 8.2, 6.6, 1.5 Hz, 1H), 5.58-5.49 (m, 1H), 4.16 (t, *J* = 6.9 Hz, 2H), 2.68 (t, *J* = 6.9 Hz, 2H), 2.41-2.29 (m, 4H), 2.26 (s, 3H), 1.90 (*virt.* quint, *J* ≈ *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 161.6, 140.3, 137.3, 130.0, 126.3, 122.8, 122.3, 118.6, 117.7, 116.1, 72.5, 35.5, 32.7, 32.2, 23.5, 10.4.

GC-MS; EI (70 eV): t_R = 18.19 Min. [STDHT]; m/*z* (%) = 269 (11) [M+], 176 (100), 175 (47), 146 (8), 130 (9), 95 (57), 79 (16), 67 (24).

HRMS (**ESI**) m/*z*: $[C_{17}H_{19}NO_2+H]^+$ calcd.: 270.1489; found: 270.1490.

4-(2-(cyclohex-1-en-1-yl)ethoxy)-3-methylquinolin-2(1*H*)-one (5f):



5f

Chemical Formula: $C_{18}H_{21}NO_2$
Exact Mass: 283.1572

Following the *general procedure 2*, compound **5f** was obtained as a colorless solid (254 mg, 45%) by column chromatography (silica, pentane/diethyl ether 1:2).

TLC: R_f = 0.39 (Pentane:EtOAc, 1:1) [UV].

M.p.: 137-138 °C.

IR (film) υ_{max}/cm^{-1} 3002, 2912, 2833, 1648, 1615, 1574, 1501, 1436, 1382, 1356, 1319, 1270, 1156, 1142, 1103, 1014, 986, 945, 910, 861, 748, 700, 655.

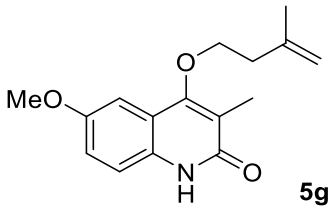
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.64 (*br* s, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 5.60 (s, 1H), 4.10 (t, *J* = 6.9 Hz, 2H), 2.53 (t, *J* = 6.8 Hz, 2H), 2.25 (s, 3H), 2.03-2.02 (m, 4H), 1.69-1.62 (m, 2H), 1.62-1.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 161.7, 137.2, 133.8, 130.0, 124.3, 123.0, 122.3, 118.6, 117.8, 115.9, 72.6, 38.9, 28.7, 25.5, 23.1, 22.5, 10.4.

GC-MS; EI (70 eV): t_R = 17.03 Min. [STDHT]; m/*z* (%) = 283 (21) [M+], 176 (100), 175 (64), 109 (48), 67 (41).

HRMS (**ESI**) m/*z*: $[C_{18}H_{21}NO_2+H]^+$ calcd.: 284.1645; found: 284.1646.

6-methoxy-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5g):



5g

Chemical Formula: $C_{16}H_{19}NO_3$
Exact Mass: 273.1365

Following the *general procedure 3*, compound **5g** was obtained as a colorless solid (254 mg, 51%) by column chromatography (silica, pentane/ethyl acetate 1:1).

TLC: R_f = 0.43 (Pentane:EtOAc, 1:1.5) [UV].

M.p.: 145-146 °C.

IR (film) υ_{max}/cm^{-1} 2999, 2916, 2868, 2826, 1643, 1621, 1579, 1499, 1418, 1370, 1352, 1272, 1218, 1172, 1143, 1105, 1036, 902, 891, 841, 708.

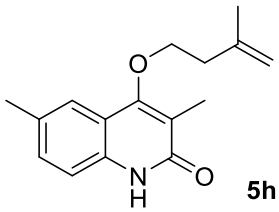
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.45 (*br* s, 1H), 7.30 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 2.7 Hz, 1H), 7.11 (dd, *J* = 8.9, 2.7 Hz, 1H), 4.93 (s, 1H), 4.90 (s, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 2.61 (t, *J* = 6.7 Hz, 2H), 2.25 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 161.1, 155.3, 142.0, 131.8, 119.5, 119.0, 118.4, 117.3, 112.9, 104.3, 72.0, 55.8, 38.5, 22.9, 10.5.

GC-MS; EI (70 eV): t_R = 16.11 Min. [STDHT]; m/*z* (%) = 273 (69) [M+], 258 (4), 228 (8), 205 (100), 190 (25), 176 (8), 69 (19).

HRMS (**ESI**) m/*z*: $[C_{16}H_{19}NO_3+H]^+$ calcd.: 274.1438; found: 274.1439.

3,6-dimethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5h):



5h

Chemical Formula: $C_{16}H_{19}NO_2$
Exact Mass: 257.1416

Following the *general procedure 3*, compound **5h** was obtained as a colorless solid (282 mg, 55%) by column chromatography (silica, pentane/ethyl acetate 1:1).

TLC: R_f = 0.48 (Pentane:EtOAc, 1:2) [UV].

M.p.: 155-156 °C.

IR (film) υ_{max}/cm^{-1} 2965, 2853, 1656, 1579, 1505, 1480, 1421, 1378, 1356, 1310, 1270, 1257, 1172, 1111, 1004, 917, 880, 810, 774, 711, 653.

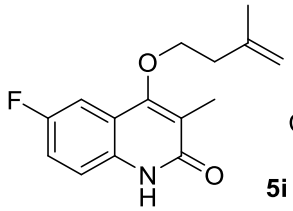
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.24 (*br* s, 1H), 7.56 (s, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 8.3, 1.6 Hz, 1H), 4.92 (s, 1H), 4.89 (s, 1H), 4.13 (t, *J* = 6.9 Hz, 2H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 2.25 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 161.4, 141.9, 135.4, 131.8, 131.4, 122.3, 118.6, 117.6, 116.1, 112.9, 72.1, 38.5, 22.9, 21.3, 10.4.

GC-MS; EI (70 eV): t_R = 16.88 Min. [STDHT]; m/*z* (%) = 257 (26) [M+], 212 (6), 189 (100), 160 (11), 134 (9), 69 (18).

HRMS (**ESI**) m/*z*: $[C_{16}H_{19}NO_2+H]^+$ calcd.: 258.1489; found: 258.1489.

6-fluoro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5i):



5i

Chemical Formula: $C_{15}H_{16}FNO_2$
Exact Mass: 261.1165

Following the *general procedure 2*, compound **5i** was obtained as a colorless solid (292 mg, 56%) by column chromatography (silica, pentane/diethyl ether 1:2).

TLC: R_f = 0.28 (Pentane:EtOAc, 1:1) [UV].

M.p.: 148-149 °C.

IR (film) υ_{max}/cm^{-1} 2929, 2881, 2828, 1651, 1631, 1502, 1428, 1353, 1308, 1251, 1188, 1168, 1135, 1097, 1031, 940, 908, 893, 876, 843, 813, 790, 712.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.82 (*br* s, 1H), 7.52-7.35 (m, 2H), 7.21 (td, *J* = 8.5, 2.8 Hz, 1H), 4.93 (s, 1H), 4.88 (s, 1H), 4.13 (t, *J* = 6.8 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 2.24 (s, 3H), 1.85 (s, 3H).

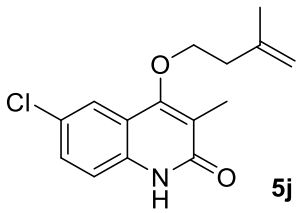
^{19}F NMR (376 MHz, $CDCl_3$) δ -119.8.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 160.9 (d, *J* = 3.3 Hz), 158.4 (d, *J* = 240.9 Hz), 141.6, 133.8, 119.6, 118.6 (d, *J* = 8.4 Hz), 118.3 (d, *J* = 24.8 Hz), 117.9 (d, *J* = 8.1 Hz), 113.0, 108.0 (d, *J* = 24.2 Hz), 72.3, 38.4, 22.8, 10.5.

GC-MS; EI (70 eV): t_R = 16.36 Min. [STDHT]; m/*z* (%) = 261 (28) [M+], 246 (4), 216 (5), 193 (100), 164 (12), 138 (9), 69 (40).

HRMS (**ESI**) m/*z*: $[C_{15}H_{16}FNO_2+H]^+$ calcd.: 262.1238; found: 262.1238.

6-chloro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5j):



5j

Chemical Formula: $C_{15}H_{16}ClNO_2$
Exact Mass: 277.0870

Following the *general procedure 2*, compound **5j** was obtained as a colorless solid (360 mg, 65%) by column chromatography (silica, pentane/diethyl ether 1:2).

TLC: R_f = 0.35 (Pentane:EtOAc, 1:1) [UV].

M.p.: 172-174 °C.

IR (film) υ_{max}/cm^{-1} 2985, 2966, 2922, 2884, 2852, 2737, 1656, 1608, 1573, 1479, 1445, 1416, 1375, 1351, 1307, 1263, 1235, 1179, 1146, 1116, 1077, 978, 967, 881, 810, 701.

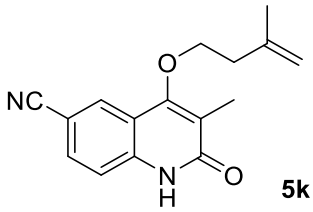
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.45 (*br* s, 1H), 7.76 (d, *J* = 2.0 Hz, 1H), 7.42 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 4.94 (s, 1H), 4.89 (s, 1H), 4.14 (t, *J* = 6.8 Hz, 2H), 2.61 (t, *J* = 6.7 Hz, 2H), 2.24 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 160.6, 141.6, 135.7, 130.3, 128.0, 122.3, 119.6, 118.9, 117.6, 113.2, 72.4, 38.5, 22.8, 10.5.

GC-MS; EI (70 eV): t_R = 17.34 Min. [STDHT]; m/z (%) = 279 (8) [M+2+], 277 (26) [M+], 211 (33), 209 (100), 180 (9), 154 (9), 69 (60).

HRMS (**ESI**) m/*z*: $[C_{15}H_{16}ClNO_2+H]^+$ calcd.: 278.0942; found: 278.0944.

3-methyl-4-((3-methylbut-3-en-1-yl)oxy)-2-oxo-1,2-dihydroquinoline-6-carbonitrile (5k):



5k

Chemical Formula: $C_{16}H_{16}N_2O_2$
Exact Mass: 268.1212

Following the *general procedure 3*, compound **5k** was obtained as a colorless solid (108 mg, 20%) by column chromatography (silica, pentane/ethyl acetate 1:1).

TLC: R_f = 0.27 (Pentane:EtOAc, 1:1) [UV].

M.p.: 232-235 °C.

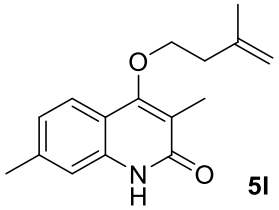
IR (film) υ_{max}/cm^{-1} 3152, 2977, 2920, 2851, 2228, 1652, 1624, 1578, 1478, 1423, 1377, 1351, 1319, 1274, 1261, 1168, 1111, 972, 890, 821, 763, 715, 652.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.25 (*br* s, 1H), 8.15 (d, *J* = 1.5 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 4.96 (s, 1H), 4.89 (s, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 2.62 (t, *J* = 6.7 Hz, 2H), 2.26 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 160.6, 141.4, 139.5, 132.5, 128.5, 120.2, 119.0, 118.1, 116.9, 113.4, 106.0, 72.7, 38.4, 22.8, 10.1.

HRMS (**ESI**) m/*z*: $[C_{16}H_{16}N_2O_2+H]^+$ calcd.: 269.1285; found: 269.1287.

3,7-dimethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5l):



5l

Chemical Formula: $C_{16}H_{19}NO_2$
Exact Mass: 257.1416

Following the *general procedure 2*, compound **5l** was obtained as a colorless solid (231 mg, 45%) by column chromatography (silica, pentane/diethyl ether 1:1.5).

TLC: R_f = 0.47 (Pentane:EtOAc, 1:1) [UV].

M.p.: 168-170 °C.

IR (film) υ_{max}/cm^{-1} 2944, 2892, 2853, 1641, 1611, 1566, 1513, 1480, 1439, 1394, 1375, 1358, 1316, 1256, 1190, 1176, 1148, 1111, 1080, 1038, 999, 981, 901, 849, 815, 786, 767, 741, 702, 669.

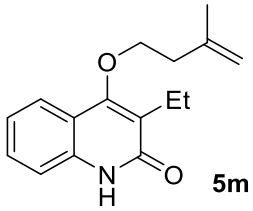
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (*br* s, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.23 (s, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 4.90 (s, 1H), 4.86 (s, 1H), 4.14 (t, *J* = 6.9 Hz, 2H), 2.61 (t, *J* = 6.9 Hz, 2H), 2.46 (s, 3H), 2.25 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 162.1, 141.8, 140.9, 137.3, 124.2, 122.7, 117.2, 116.1, 115.6, 112.8, 72.3, 38.5, 22.9, 21.8, 10.3.

GC-MS; EI (70 eV): t_R = 17.04 Min. [STDHT]; m/z (%) = 257 (14) [M+], 207 (12), 189 (100), 160 (11), 134 (13), 69 (20).

HRMS (**ESI**) m/z: $[C_{16}H_{19}NO_2+H]^+$ calcd.: 258.1489; found: 258.1489.

3-ethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5m):



5m

Chemical Formula: $C_{16}H_{19}NO_2$
Exact Mass: 257.1416

Following the *general procedure 2*, compound **5m** was obtained as a colorless solid (360 mg, 70%) by column chromatography (silica, pentane/diethyl ether 1:1.5).

TLC: R_f = 0.60 (Pentane:EtOAc, 1:1) [UV].

M.p.: 130-131 °C.

IR (film) υ_{max}/cm^{-1} 2957, 2930, 2868, 1651, 1612, 1571, 1499, 1433, 1396, 1374, 1355, 1321, 1259, 1144, 1106, 1065, 1049, 1031, 983, 959, 891, 864, 758, 687, 665.

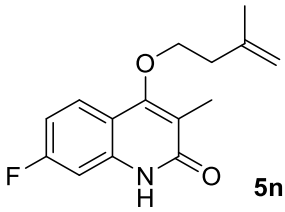
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.67 (*br* s, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.47 (td, *J* = 7.5, 1.0 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 4.92 (s, 1H), 4.88 (s, 1H), 4.15 (t, *J* = 6.9 Hz, 2H), 2.76 (q, *J* = 7.4 Hz, 2H), 2.64 (t, *J* = 6.9 Hz, 2H), 1.86 (s, 3H), 1.27 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 161.2, 141.8, 137.5, 130.0, 125.0, 123.0, 122.3, 117.7, 116.0, 112.8, 73.2, 38.5, 22.9, 18.2, 13.6.

GC-MS; EI (70 eV): t_R = 16.57 Min. [STDHT]; m/z (%) = 257 (27) [M+], 212 (24), 189 (94), 188 (78), 174 (100), 161 (21), 69 (41).

HRMS (**ESI**) m/z: $[C_{16}H_{19}NO_2+H]^+$ calcd.: 258.1489; found: 258.1489.

7-fluoro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5n):



5n

Chemical Formula: $C_{15}H_{16}FNO_2$
Exact Mass: 261.1165

Following the *general procedure 2*, compound **5n** was obtained as a colorless solid (365 mg, 70%) by column chromatography (silica, pentane/diethyl ether 1:1.5).

TLC: R_f = 0.67 (Pentane:EtOAc, 1:1.5) [UV].

M.p.: 138-139 °C.

IR (film) υ_{max}/cm^{-1} 3066, 2919, 2863, 1645, 1612, 1577, 1511, 1396, 1373, 1355, 1312, 1249, 1194, 1139, 1104, 1027, 895, 847, 811, 795, 761, 667.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.47 (*br* s, 1H), 7.77 (dd, *J* = 8.9, 5.9 Hz, 1H), 7.15 (dd, *J* = 9.4, 2.1 Hz, 1H), 6.94 (td, *J* = 8.7, 2.3 Hz, 1H), 4.92 (s, 1H), 4.87 (s, 1H), 4.15 (t, *J* = 6.9 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 2.23 (s, 3H), 1.84 (s, 3H).

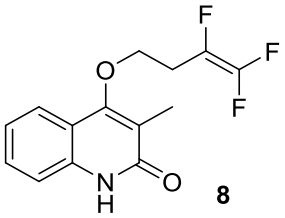
^{19}F NMR (376 MHz, $CDCl_3$) δ -109.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 163.8 (d, *J* = 249.5 Hz), 161.5, 141.7, 138.7 (d, *J* = 12.0 Hz), 125.1 (d, *J* = 10.1 Hz), 117.4, 114.5, 112.9, 110.9 (d, *J* = 23.3 Hz), 102.3 (d, *J* = 25.3 Hz), 72.4, 38.5, 22.9, 10.3.

GC-MS; EI (70 eV): t_R = 16.17 Min. [STDHT]; m/z (%) = 261 (19) [M+], 246 (4), 216 (5), 193 (100), 164 (11), 138 (14), 69 (39).

HRMS (**ESI**) m/*z*: $[C_{15}H_{16}FNO_2+H]^+$ calcd.: 262.1238; found: 262.1239.

3-methyl-4-((3,4,4-trifluorobut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (8):



8

Chemical Formula: $C_{14}H_{12}F_3NO_2$
Exact Mass: 283.0820

Following the *general procedure 2*, compound **8** was obtained as a colorless solid (390 mg, 69%) by column chromatography (silica, pentane/diethyl ether 1:2).

TLC: R_f = 0.44 (Pentane:EtOAc, 1:1.5) [UV].

M.p.: 125-126 °C.

IR (film) υ_{max}/cm^{-1} 3151, 3103, 3013, 2955, 2895, 1803, 1642, 1611, 1573, 1498, 1481, 1429, 1373, 1359, 1303, 1259, 1246, 1211, 1145, 1118, 1104, 1034, 1010, 991, 870, 850, 829, 783, 760, 694.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.24 (*br* s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.55-7.43 (m, 2H), 7.24 (ddd, *J* = 8.2, 6.6, 1.6 Hz, 1H), 4.20 (t, *J* = 6.3 Hz, 2H), 2.90 (tdd, *J* = 6.4, 4.0, 2.7 Hz, 1H), 2.85 (tdd, *J* = 6.3, 4.0, 2.7 Hz, 1H), 2.25 (s, 3H).

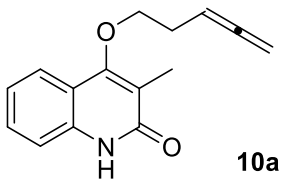
^{19}F NMR (376 MHz, $CDCl_3$) δ -102.7 (dd, *J* = 84.4, 32.9 Hz), -122.9 (dd, *J* = 114.4, 84.4 Hz), -175.7 (dd, *J* = 114.4, 32.9 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 161.1, 154.0 (ddd, *J* = 287.0, 274.2, 46.1 Hz), 137.2, 130.4, 126.1 (ddd, *J* = 234.5, 53.5, 17.0 Hz), 122.8, 122.4, 118.7, 117.4, 116.4, 68.4, 27.4 (dd, *J* = 21.9, 2.4 Hz), 10.1.

GC-MS; EI (70 eV): t_R = 15.54 Min. [STDHT]; m/z (%) = 283 (7) [M+], 269 (15), 268 (100), 175 (23), 174 (29), 146 (11), 130 (18), 120 (15), 109 (7), 89 (16).

HRMS (**ESI**) m/*z*: $[C_{14}H_{12}F_3NO_2+H]^+$ calcd.: 284.0893; found: 284.0894.

4-((4λ^5-penta-3,4-dien-1-yl)oxy)-3-methylquinolin-2(1*H*)-one (10a):



10a

Chemical Formula: $C_{15}H_{15}NO_2$
Exact Mass: 241.1103

Following the *general procedure 2*, compound **10a** was obtained as a colorless solid (222 mg, 46%) by column chromatography (silica, pentane/diethyl ether 1:2).

TLC: R_f = 0.22 (Pentane:EtOAc, 1:1) [UV].

M.p.: 104-105 °C.

IR (film) υ_{max}/cm^{-1} 3162, 3110, 2955, 2886, 2859, 2751, 1952, 1730, 1655, 1615, 1572, 1499, 1434, 1376, 1361, 1318, 1269, 1145, 1104, 1012, 979, 862, 750, 695.

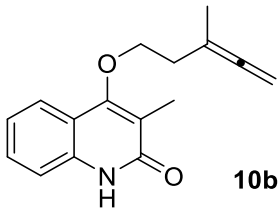
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (*br* s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.22 (td, *J* = 7.6, 1.2 Hz, 1H), 5.28 (*virt.* quint, *J* ≈ *J* = 6.8 Hz, 1H), 4.75 (dt, *J* = 6.4, 3.2 Hz, 2H), 4.12 (t, *J* = 6.6 Hz, 2H), 2.60 (dtt, *J* = 6.8, 6.6, 3.2 Hz, 2H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 166.4, 161.5, 137.3, 130.0, 122.8, 122.4, 118.7, 117.7, 116.1, 86.2, 75.8, 73.1, 29.5, 10.4.

GC-MS; EI (70 eV): t_R = 16.83 Min. [STDHT]; m/z (%) = 241 (15) [M+], 240 (22), 226 (100), 175 (95), 146 (23), 120 (27), 92 (16), 77 (12), 67 (30), 65 (25).

HRMS (**ESI**) m/*z*: $[C_{15}H_{15}NO_2+H]^+$ calcd.: 242.1176; found: 242.1179.

3-methyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (10b):



10b

Chemical Formula: $C_{16}H_{17}NO_2$
Exact Mass: 255.1259

Following the *general procedure 2*, compound **10b** was obtained as a colorless solid (260 mg, 51%) by column chromatography (silica, pentane/diethyl ether 1:2).

TLC: R_f = 0.16 (Pentane:EtOAc, 2:1) [UV].

M.p.: 134-135 °C.

IR (film) υ_{max}/cm^{-1} 3150, 3107, 3073, 3051, 2993, 2936, 2916, 2899, 2848, 1960, 1655, 1640, 1615, 1600, 1572, 1497, 1479, 1426, 1374, 1356, 1269, 1253, 1142, 1104, 1009, 975, 891, 874, 749, 694.

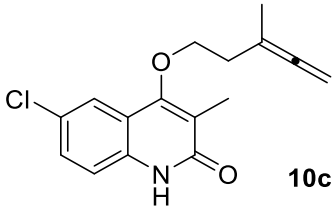
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.90 (*br* s, 1H), 7.81 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.48 (td, *J* = 7.5, 1.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.21 (td, *J* = 7.5, 1.0 Hz, 1H), 4.66 (*virt.* sext, *J* ≈ *J* = 3.1 Hz, 2H), 4.15 (t, *J* = 6.5 Hz, 2H), 2.53 (tt, *J* = 6.5, 3.1 Hz, 2H), 2.26 (s, 3H), 1.80 (t, *J* = 3.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 166.5, 161.6, 137.3, 130.0, 122.9, 122.3, 118.6, 117.8, 116.1, 94.9, 75.3, 72.1, 34.1, 19.3, 10.4.

GC-MS; EI (70 eV): t_R = 17.15 Min. [STDHT]; m/z (%) = 255 (1) [M+], 241 (17), 240 (100), 175 (42), 146 (9), 120 (10), 79 (26).

HRMS (**ESI**) m/*z*: $[C_{16}H_{17}NO_2+H]^+$ calcd.: 256.1332; found: 256.1333.

6-chloro-3-methyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (10c):



10c

Chemical Formula: $C_{16}H_{16}ClNO_2$
Exact Mass: 289.0870

Following the *general procedure 2*, compound **10c** was obtained as a colorless solid (186 mg, 32%) by column chromatography (silica, pentane/diethyl ether 1:2).

TLC: R_f = 0.38 (Pentane:EtOAc, 1:1) [UV].

M.p.: 126-127 °C.

IR (film) υ_{max}/cm^{-1} 3147, 3050, 2984, 2939, 2913, 2890, 2852, 1960, 1661, 1608, 1486, 1414, 1373, 1351, 1305, 1255, 1148, 1119, 973, 881, 816, 699.

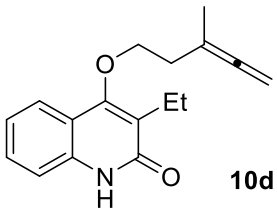
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.28 (*br* s, 1H), 7.80 (d, *J* = 2.2 Hz, 1H), 7.42 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 4.70 (*virt.* sext, *J* ≈ *J* = 3.2 Hz, 2H), 4.16 (t, *J* = 6.7 Hz, 2H), 2.52 (tt, *J* = 6.5, 3.1 Hz, 2H), 2.25 (s, 3H), 1.81 (t, *J* = 3.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 166.3, 160.7, 135.7, 130.3, 127.9, 122.5, 119.5, 119.0, 117.5, 94.9, 75.5, 72.1, 34.2, 19.3, 10.6.

GC-MS; EI (70 eV): t_R = 16.18 Min. [STDHT]; m/z (%) = 289 (1) [M+], 276 (33), 275 (16), 274 (100), 209 (14), 79 (11).

HRMS (**ESI**) m/z: $[C_{16}H_{16}ClNO_2+H]^+$ calcd.: 290.0942; found: 290.0944.

3-ethyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (10d):



10d

Chemical Formula: $C_{17}H_{19}NO_2$
Exact Mass: 269.1416

Following the *general procedure 2*, compound **10d** was obtained as a colorless solid (215 mg, 40%) by column chromatography (silica, pentane/diethyl ether 1:1.5).

TLC: R_f = 0.48 (Pentane:EtOAc, 1:1) [UV].

M.p.: 113-114 °C.

IR (film) υ_{max}/cm^{-1} 3110, 3009, 2979, 2963, 2930, 2887, 2851, 1960, 1655, 1613, 1571, 1499, 1428, 1358, 1266, 1141, 1104, 1043, 993, 873, 854, 747, 680.

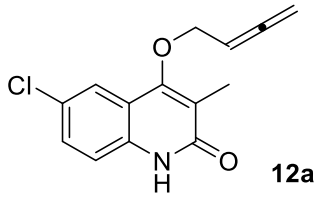
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.85 (*br* s, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.46 (td, *J* = 7.6, 1.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 4.67 (*virt.* sext, *J* ≈ *J* = 3.1 Hz, 2H), 4.14 (t, *J* = 7.0 Hz, 2H), 2.75 (q, *J* = 7.4 Hz, 2H), 2.55 (tt, *J* = 7.0, 3.1 Hz, 2H), 1.81 (t, *J* = 3.1 Hz, 3H), 1.25 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 166.0, 161.2, 137.5, 130.0, 124.9, 123.0, 122.2, 117.8, 116.0, 95.0, 75.3, 72.9, 34.2, 19.3, 18.2, 13.6.

GC-MS; EI (70 eV): t_R = 17.22 Min. [STDHT]; m/z (%) = 269 (1) [M+], 241 (17), 240 (100), 189 (19), 188 (22), 174 (39), 79 (22).

HRMS (**ESI**) m/z: $[C_{17}H_{19}NO_2+H]^+$ calcd.: 270.1489; found: 270.1489.

4-((3λ^5-buta-2,3-dien-1-yl)oxy)-6-chloro-3-methylquinolin-2(1*H*)-one (12a):



12a

Chemical Formula: $C_{14}H_{12}ClNO_2$
Exact Mass: 261.0557

Following the *general procedure 2*, compound **12a** was obtained as a colorless solid (251 mg, 48%) by column chromatography (silica, pentane/diethyl ether 1:2).

TLC: R_f = 0.14 (Pentane:EtOAc, 2:1) [UV].

M.p.: 174-176 °C.

IR (film) υ_{max}/cm^{-1} 3156, 2995, 2882, 2828, 2744, 1955, 1665, 1609, 1486, 1412, 1351, 1305, 1263, 1143, 1114, 954, 940, 880, 843, 814, 769, 702.

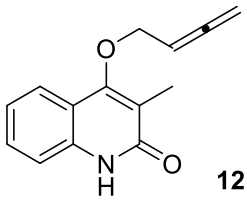
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.35 (*br* s, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.43 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 5.48 (*virt.* quint, *J* ≈ *J* = 7.0 Hz, 1H), 4.90 (dt, *J* = 7.0, 2.0 Hz, 2H), 4.60 (dt, *J* = 7.0, 2.0 Hz, 2H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.1, 166.2, 160.1, 135.7, 130.3, 128.0, 122.5, 120.2, 118.9, 117.6, 87.0, 77.0, 71.8, 10.7.

GC-MS; EI (70 eV): t_R = 15.77 Min. [STDHT]; m/*z* (%) = 263 (2) [M+2+], 261 (6) [M+], 248 (34), 246 (100), 232 (20), 218 (10), 204 (6), 180 (7), 153 (11), 126 (10), 79 (20).

HRMS (**ESI**) m/*z*: $[C_{14}H_{12}ClNO_2+H]^+$ calcd.: 262.0629; found: 262.0630.

4-((3λ^5-buta-2,3-dien-1-yl)oxy)-3-methylquinolin-2(1*H*)-one (12b):



12b

Chemical Formula: $C_{14}H_{13}NO_2$
Exact Mass: 227.0946

Following the *general procedure 2*, compound **12b** was obtained as a colorless solid (205 mg, 45%) by column chromatography (silica, pentane/diethyl ether 1:2).

TLC: R_f = 0.40 (Pentane:EtOAc, 1:1) [UV].

M.p.: 145-146 °C.

IR (film) υ_{max}/cm^{-1} 3162, 3107, 3057, 3006, 2980, 2953, 2923, 2880, 2856, 1961, 1659, 1615, 1573, 1499, 1434, 1351, 1311, 1267, 1137, 1098, 1007, 969, 941, 876, 864, 856, 845, 748, 737, 697, 687, 666.

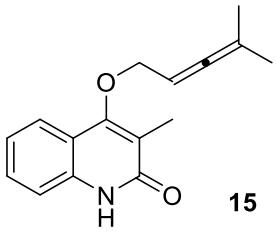
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.84 (*br* s, 1H), 7.81 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.48 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.22 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 5.49 (*virt.* quint, *J* ≈ *J* = 6.9 Hz, 1H), 4.87 (dt, *J* = 6.6, 2.3 Hz, 2H), 4.61 (dt, *J* = 7.1, 2.3 Hz, 2H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.0, 166.2, 161.0, 137.2, 130.1, 123.0, 122.4, 119.2, 117.7, 116.0, 87.1, 76.8, 71.7, 10.6.

GC-MS; EI (70 eV): t_R = 14.60 Min. [STDHT]; m/*z* (%) = 227 (5) [M+], 226 (13), 212 (100), 198 (24), 184 (12), 170 (10), 119 (11), 92 (16), 79 (14).

HRMS (**ESI**) m/*z*: $[C_{14}H_{13}NO_2+H]^+$ calcd.: 228.1019; found: 228.1020.

3-methyl-4-((4-methyl-3λ^5-penta-2,3-dien-1-yl)oxy)quinolin-2(1*H*)-one (15):



15

Chemical Formula: $C_{16}H_{17}NO_2$
Exact Mass: 255.1259

Following the *general procedure 2*, compound **15** was obtained as a colorless solid (220 mg, 43%) by column chromatography (silica, pentane/diethyl ether 1:1.5).

TLC: R_f = 0.47 (Pentane:EtOAc, 1:1) [UV].

M.p.: 110-111 °C.

IR (film) υ_{max}/cm^{-1} 3109, 3073, 2946, 2855, 1971, 1653, 1614, 1573, 1436, 1360, 1269, 1185, 1138, 1098, 986, 967, 881, 750, 736, 690, 666.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.07 (*br* s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.21 (td, *J* = 7.6, 1.2 Hz, 1H), 5.35-5.26 (m, 1H), 4.56 (d, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 1.64 (s, 3H), 1.64 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 166.4, 161.3, 137.2, 130.0, 123.3, 122.3, 119.1, 118.0, 116.0, 97.2, 85.5, 73.0, 20.3, 10.6.

GC-MS; EI (70 eV): t_R = 15.56 Min. [STDHT]; m/*z* (%) = 255 (1) [M+], 240 (100), 227 (10), 212 (11), 198 (7), 120 (15), 93 (14), 91 (14), 77 (9).

HRMS (**ESI**) m/*z*: $[C_{16}H_{17}NO_2+H]^+$ calcd.: 256.1332; found: 256.1333.

General Procedure 4: Non-catalyzed [2+2] Photocycloaddition

The corresponding quinolone (*c* = 10.0 mmol/L) was dissolved in 10 mL of acetonitrile and irradiated at λ = 300 nm at room temperature until full conversion was achieved. The solvent was removed under reduced presure. The crude product was purified by flash column chromatography.

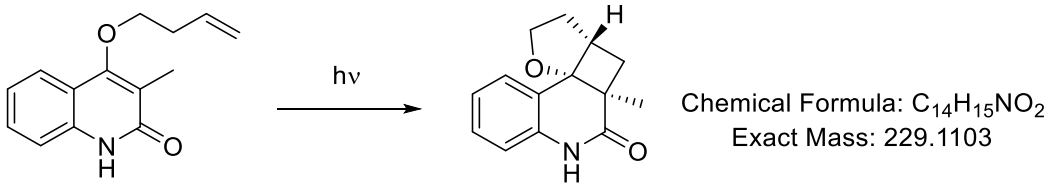
General Procedure 5: TXT-Catalyzed [2+2] Photocycloaddition

The corresponding quinolone (*c* = 10.0 mmol/L, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in 10 mL of acetonitrile and irradiated at λ = 420 nm at room temperature until full conversion. The solvent was evaporated in vacuo. The crude product was purified by flash column chromatography.

General Procedure 6: (+)-TXT-Catalyzed [2+2] Photocycloaddition

The corresponding quinolone (*c* = 2.50 mmol/L, 1.0 eq.) and enantiomerically *(+)-TXT* **6** (1.1 mg, 10 mol%) were dissolved in 10 mL of α,α,α-trifluorotoluene, cooled to -25 °C and irradiated at λ = 420 nm until full conversion. The solvent was evaporated *in vacuo*. The crude product was purified by flash column chromatography.

(3a*S*,4a*R*,10b*S*)-4a-methyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7b):



Non-catalyzed [2+2] Photocycloaddition

4-(but-3-en-1-yloxy)-3-methylquinolin-2(1*H*)-one (**5b**) (22.9 mg, 0.1 mmol) was dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *General Procedure 4*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the racemic compound *rac*-**7b** was obtained as a colorless solid (22.7 mg, 99 µmol, 99%).

TXT-Catalyzed [2+2] Photocycloaddition

4-(but-3-en-1-yloxy)-3-methylquinolin-2(1*H*)-one (**5b**) (22.9 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *General Procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the racemic compound *rac*-**7b** was obtained as a colorless solid (22.7 mg, 99 µmol, 99%).

Enantioselective [2+2] Photocycloaddition

4-(but-3-en-1-yloxy)-3-methylquinolin-2(1*H*)-one (**5b**) (5.8 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *General Procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the title compound **7b** was obtained as a colorless solid (5.6 mg, 24.4 µmol, 97%, 88% *ee*).

TLC: R_f = 0.60 (Pentane:EtOAc, 1:1) [UV].

M.p.: 221-224 °C.

IR (film) υ_{max}/cm^{-1} 3187, 3057, 2978, 2926, 1666, 1594, 1491, 1484, 1376, 1362, 1254, 1063, 1026, 936, 881, 859, 764, 684.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (*br* s, 1H), 7.28 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.18 (td, *J* = 7.6, 1.5 Hz, 1H), 7.01 (td, *J* = 7.5, 1.2 Hz, 1H), 6.81 (dd, *J* = 7.9, 1.2 Hz, 1H), 4.54 (t, *J* = 8.1 Hz, 1H), 4.22 (ddd, *J* = 11.1, 8.7, 5.6 Hz, 1H), 2.99 (*virt.* q, *J* ≈ *J* = 7.6 Hz, 1H), 2.73 (dd, *J* = 12.8, 9.1 Hz, 1H), 1.96 (dddd, *J* = 12.6, 11.2, 8.2, 6.6 Hz, 1H), 1.85 (dd, *J* = 12.8, 7.9 Hz, 1H), 1.76 (dd, *J* = 12.6, 5.5 Hz, 1H), 1.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 135.5, 129.0, 125.7, 124.9, 123.7, 115.3, 86.8, 70.5, 46.7, 43.8, 35.9, 30.5, 18.0.

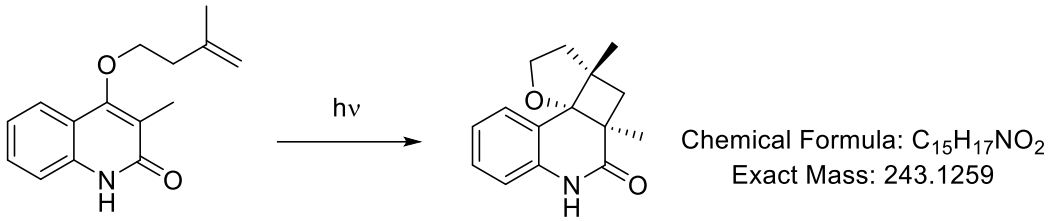
GC-MS; EI (70 eV): t_R = 14.85 Min. [STDHT]; m/*z* (%) = 229 (26) [M+], 214 (45), 175 (100), 146 (17), 130 (11), 120 (13), 55 (25).

HRMS (**ESI**) m/*z*: $[C_{14}H_{15}NO_2+H]^+$ calcd.: 230.1176; found: 230.1177.

Optical Rotation: $[\alpha]_D^{26}$: −60.0 (c = 2.0, $CHCl_3$) [88% *ee*].

Chiral HPLC: 88% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 12.77 min (minor), 13.60 min (major)].

(3a*S*,4a*R*,10b*S*)-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7c):



Non-catalyzed [2+2] Photocycloaddition

3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5c**) (24.3 mg, 0.1 mmol) was dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 4*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the racemic compound *rac*-**7c** was obtained as a colorless solid (23.5 mg, 97 µmol, 97%).

TXT-Catalyzed [2+2] Photocycloaddition

3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5c**) (24.3 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the racemic compound *rac*-**7c** was obtained as a colorless solid (24.3 mg, 100 µmol, >99%).

Enantioselective [2+2] Photocycloaddition

3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5c**) (6.1 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the title compound **7c** was obtained as a colorless solid (6.1 mg, 25 µmol, >99%, 99% *ee*).

TLC: R_f = 0.60 (Pentane:EtOAc, 1:1) [UV].

M.p.: 164-165 °C.

IR (film) υ_{max}/cm^{-1} 3179, 3059, 2953, 2923, 2871, 1662, 1596, 1490, 1440, 1377, 1254, 1060, 1017, 893, 873, 859, 757, 733, 685, 660.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (*br* s, 1H), 7.24 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.18 (td, *J* = 7.6, 1.5 Hz, 1H), 7.02 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (dd, *J* = 7.9, 0.7 Hz, 1H), 4.43 (ddd, *J* = 9.0, 8.0, 1.1 Hz, 1H), 4.13 (ddd, *J* = 11.2, 9.0, 5.6 Hz, 1H), 2.41 (d, *J* = 12.8 Hz, 1H), 2.06 (d, *J* = 12.8 Hz, 1H), 1.77 (dd, *J* = 12.3, 5.1 Hz, 1H), 1.69 (td, *J* = 11.8, 8.0 Hz, 1H), 1.40 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 136.1, 129.1, 126.8, 123.7, 122.4, 115.2, 88.0, 69.3, 48.7, 44.6, 42.5, 38.6, 21.6, 18.2.

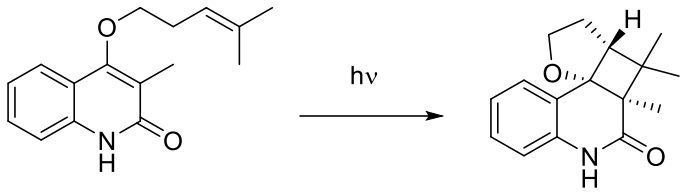
GC-MS; EI (70 eV): t_R = 14.74 Min. [STDHT]; m/z (%) = 243 (33) [M+], 228 (7), 198 (10), 175 (100), 146 (13), 120 (10), 69 (22).

HRMS (**ESI**) m/*z*: $[C_{15}H_{17}NO_2+H]^+$calcd.: 244.1332; found: 244.1333.

Optical Rotation: $[\alpha]_D^{26}$: −57.0 (c = 2.0, $CHCl_3$) [99% *ee*].

Chiral HPLC: 99% *ee* [Daicel Chiralpak OD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 12.13 min (major), 14.74 min (minor)].

(3a*R*,4a*R*,10b*S*)-4,4,4a-trimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7d):



Chemical Formula: $C_{16}H_{19}NO_2$
Exact Mass: 257.1416

Non-catalyzed [2+2] Photocycloaddition

3-methyl-4-((4-methylpent-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5d**) (25.7 mg, 0.1 mmol, 1.0 eq.) was dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 4*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the racemic compound *rac*-**7d** was obtained as a colorless solid (23.9 mg, 93 µmol, 93%).

TXT-Catalyzed [2+2] Photocycloaddition

3-methyl-4-((4-methylpent-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5d**) (25.7 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the racemic compound *rac*-**7d** was obtained as a colorless solid (24.1 mg, 94 µmol, 94%).

Enantioselective [2+2] Photocycloaddition

3-methyl-4-((4-methylpent-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5d**) (6.4 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the title compound **7d** was obtained as a colorless solid (6.3 mg, 24.5 µmol, 98%, 96% *ee*).

TLC: R_f = 0.72 (Pentane:EtOAc, 1:2) [UV].

M.p.: 176-178 °C.

IR (film) υ_{max}/cm^{-1} 3188, 3058, 2967, 2932, 2880, 1663, 1596, 1490, 1372, 1253, 1057, 991, 856, 758.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (*br* s, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 4.46 (td, *J* = 8.3, 5.3 Hz, 1H), 4.26 (*virt.* q, *J* ≈ *J* = 8.4 Hz, 1H), 2.58 (dd, *J* = 7.2, 4.0 Hz, 1H), 2.10 (q, *J* = 7.9 Hz, 2H), 1.34 (s, 3H), 1.21 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 135.2, 128.8, 126.3, 126.0, 123.7, 115.2, 84.1, 73.0, 58.5, 51.9, 38.7, 29.2, 27.4, 19.4, 14.6.

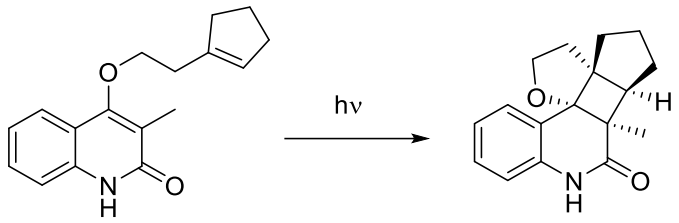
GC-MS; EI (70 eV): t_R = 15.79 Min. [STDHT]; m/z (%) = 257 (5) [M+], 242 (100), 175 (45), 97 (35), 83 (46), 55 (40).

HRMS (**ESI**) m/*z*: $[C_{16}H_{19}NO_2+H]$+calcd.: 258.1489; found: 258.1489.

Optical Rotation: $[\alpha]_D^{26}$: +102.0 (c = 2.0, $CHCl_3$) [96% *ee*].

Chiral HPLC: 96% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 9.50 min (minor), 11.63 min (major)].

(6a*R*,6b*R*,9a*R*,12a*S*)-6a-methyl-6b,7,8,9,10,11-hexahydro-5*H*-cyclopenta[3,4]furo[2',3':2,3]cyclobuta-[1,2-*c*]quinolin-6(6a*H*)-one (7e):



Chemical Formula: $C_{17}H_{19}NO_2$
Exact Mass: 269.1416

TXT-Catalyzed [2+2] Photocycloaddition

4-(2-(cyclopent-1-en-1-yl)ethoxy)-3-methylquinolin-2(1*H*)-one (**5e**) (26.9 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), the racemic compound *rac*-**7e** was obtained as a colorless solid (26.9 mg, 100 µmol, >99%).

Enantioselective [2+2] Photocycloaddition

4-(2-(cyclopent-1-en-1-yl)ethoxy)-3-methylquinolin-2(1*H*)-one (**5e**) (6.7 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), the title compound **7e** was obtained as a colorless solid (6.7 mg, 25 µmol, >99%, 98% *ee*).

TLC: R_f = 0.40 (Pentane:EtOAc, 2:1) [UV].

M.p.: 193-195 °C.

IR (film) υ_{max}/cm^{-1} 3186, 3052, 2982, 2922, 2862, 1666, 1597, 1494, 1433, 1375, 1249, 1164, 1046, 999, 908, 873, 856, 752, 730, 692, 669.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (*br* s, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.16 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.02 (td, *J* = 7.5, 0.8 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 4.41 (t, *J* = 8.5 Hz, 1H), 4.12 (ddd, *J* = 11.5, 9.0, 5.6 Hz, 1H), 2.36 (d, *J* = 7.2 Hz, 1H), 2.12 (dd, *J* = 12.9, 4.7 Hz, 1H), 2.03 (td, *J* = 12.1, 8.4 Hz, 1H), 1.87 (dd, *J* = 12.7, 5.4 Hz, 1H), 1.59 (ddd, *J* = 15.8, 11.1, 6.0 Hz, 2H), 1.51-1.42 (m, 5H), 1.30-1.23 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 136.1, 129.1, 128.0, 123.5, 121.7, 115.2, 86.0, 69.6, 61.8, 53.2, 47.3, 36.5, 32.3, 29.6, 26.4, 20.0.

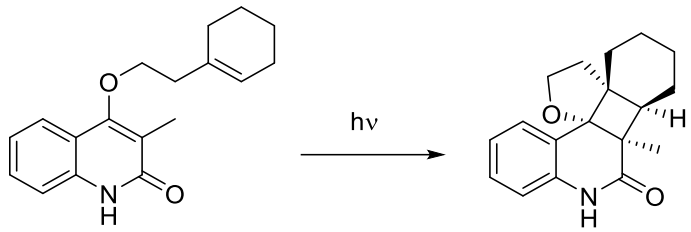
GC-MS; EI (70 eV): t_R = 16.34 Min. [STDHT]; m/*z* (%) = 269 (17) [M+], 177 (12), 176 (100), 175 (41), 146 (7), 130 (7), 120 (7), 95 (36), 79 (10), 67 (14).

HRMS (**ESI**) m/*z*: $[C_{17}H_{19}NO_2+H]^+$ calcd.: 270.1489; found: 270.1490.

Optical Rotation: $[\alpha]_D^{26}$: −15.0 (c = 2.0, $CHCl_3$) [98% *ee*].

Chiral HPLC: 98% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 9.64 min (major), 10.60 min (minor)].

(6a*R*,6b*R*,10a*R*,13a*S*)-6a-methyl-6a,6b,7,8,9,10,11,12-octahydrobenzo[3,4]furo[2',3':2,3]cyclobuta-[1,2-*c*]quinolin-6(5*H*)-one (7f):



Chemical Formula: $C_{18}H_{21}NO_2$
Exact Mass: 283.1572

TXT-Catalyzed [2+2] Photocycloaddition

4-(2-(cyclohex-1-en-1-yl)ethoxy)-3-methylquinolin-2(1*H*)-one (**5f**) (28.3 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), the racemic compound *rac*-**7f** was obtained as a colorless solid (25.5 mg, 90 µmol, 90%).

Enantioselective [2+2] Photocycloaddition

4-(2-(cyclohex-1-en-1-yl)ethoxy)-3-methylquinolin-2(1*H*)-one (**5f**) (7.1 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), the title compound **7f** was obtained as a colorless solid (6.6 mg, 23.3 µmol, 93%, 96% *ee*).

TLC: R_f = 0.68 (Pentane:EtOAc, 1:1) [UV].

M.p.: 164-165 °C.

IR (film) υ_{max}/cm^{-1} 3186, 3060, 2940, 2866, 1660, 1595, 1489, 1436, 1348, 1222, 1119, 1064, 1046, 993, 940, 871, 852, 785, 758, 735, 694, 678, 664.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (*br* s, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 4.50 (t, *J* = 8.6 Hz, 1H), 4.20 (ddd, *J* = 11.1, 9.1, 5.8 Hz, 1H), 2.20 (dd, *J* = 7.6, 5.8 Hz, 1H), 2.01 (dd, *J* = 12.4, 5.6 Hz, 1H), 1.91 (dt, *J* = 19.7, 5.6 Hz, 1H), 1.63-1.50 (m, 3H), 1.41-1.34 (m, 6H), 1.15 (ddd, *J* = 18.0, 10.6, 4.3 Hz, 1H), 1.03 (dt, *J* = 13.8, 2.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 136.2, 128.9, 126.7, 123.4, 122.8, 115.0, 87.7, 70.0, 51.9, 48.4, 45.7, 38.2, 27.8, 21.9, 20.9, 20.7, 19.4.

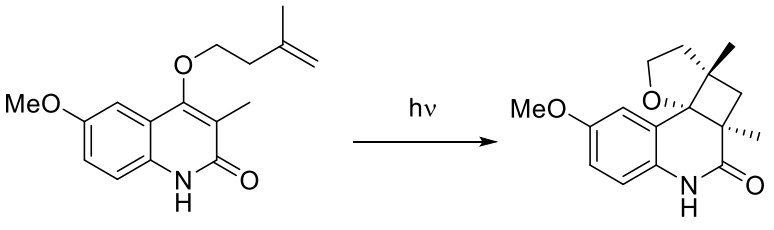
GC-MS; EI (70 eV): t_R = 17.03 Min. [STDHT]; m/z (%) = 283 (21) [M+], 176 (100), 175 (64), 109 (48), 67 (41).

HRMS (**ESI**) m/*z*: $[C_{18}H_{21}NO_2+H]^+$ calcd.: 284.1645; found: 284.1645.

Optical Rotation: $[\alpha]_D^{26}$: −87.0 (c = 2.0, $CHCl_3$) [96% *ee*].

Chiral HPLC: 96% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 8.28 min (major), 9.81 min (minor)].

(3a*S*,4a*R*,10b*S*)-9-methoxy-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7g):



Chemical Formula: $C_{16}H_{19}NO_3$
Exact Mass: 273.1365

TXT-Catalyzed [2+2] Photocycloaddition

6-methoxy-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5g**) (27.3 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the racemic compound *rac*-**7g** was obtained as a colorless solid (27.3 mg, 100 µmol, >99%).

Enantioselective [2+2] Photocycloaddition

6-methoxy-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5g**) (6.8 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the title compound **7g** was obtained as a colorless solid (6.8 mg, 25 µmol, >99%, 93% *ee*).

TLC: R_f = 0.66 (Pentane:EtOAc, 1:1.5) [UV].

M.p.: 172-174 °C.

IR (film) υ_{max}/cm^{-1} 3185, 3046, 2968, 2926, 2872, 1660, 1505, 1458, 1444, 1415, 1388, 1378, 1284, 1226, 1195, 1174, 1151, 1109, 1056, 1041, 995, 930, 869, 853, 811, 798, 696, 666.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (*br* s, 1H), 6.80 (s, 1H), 6.73 (d, *J* = 1.4 Hz, 2H), 4.43 (t, *J* = 8.3 Hz, 1H), 4.12 (ddd, *J* = 11.4, 9.0, 5.6 Hz, 1H), 3.77 (s, 3H), 2.40 (d, *J* = 12.8 Hz, 1H), 2.04 (d, *J* = 12.8 Hz, 1H), 1.77 (dd, *J* = 12.3, 5.2 Hz, 1H), 1.68 (td, *J* = 11.8, 8.0 Hz, 1H), 1.38 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 156.2, 129.8, 123.7, 116.2, 114.5, 111.9, 88.1, 69.4, 55.8, 48.7, 44.3, 42.4, 38.6, 21.5, 18.1.

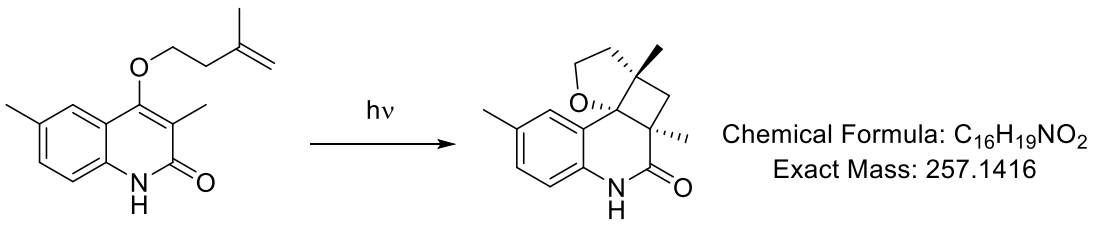
GC-MS; EI (70 eV): t_R = 16.21 Min. [STDHT]; m/z (%) = 273 (86) [M+], 228 (11), 205 (100), 204 (31), 190 (33), 176 (12), 69 (20).

HRMS (**ESI**) m/*z*: $[C_{16}H_{19}NO_3+H]^+$ calcd.: 274.1438; found: 274.1439.

Optical Rotation: $[\alpha]_D^{26}$: −37.0 (c = 2.0, $CHCl_3$) [93% *ee*].

Chiral HPLC: 93% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 12.44 min (minor), 14.92 min (major)].

(3a*S*,4a*R*,10b*S*)-3a,4a,9-trimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7h):



TXT-Catalyzed [2+2] Photocycloaddition

3,6-dimethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5h**) (25.7 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted

for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the racemic compound *rac*-**7h** was obtained as a colorless solid (25.4 mg, 99 µmol, 99%).

Enantioselective [2+2] Photocycloaddition

3,6-dimethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5h**) (6.4 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the title compound **7h** was obtained as a colorless solid (6.0 mg, 23.3 µmol, 94%, 98% *ee*).

TLC: R_f = 0.68 (Pentane:EtOAc, 1:1.5) [UV].

M.p.: 176-178 °C.

IR (film) υ_{max}/cm^{-1} 3177, 3043, 2960, 2924, 2863, 1655, 1602, 1504, 1442, 1387, 1375, 1246, 1151, 1054, 885, 870, 807, 725, 696, 667.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (*br* s, 1H), 7.04 (s, 1H), 6.98 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.44 (t, *J* = 8.1 Hz, 1H), 4.12 (ddd, *J* = 11.1, 9.0, 5.7 Hz, 1H), 2.40 (d, *J* = 12.8 Hz, 1H), 2.28 (s, 3H), 2.05 (d, *J* = 12.8 Hz, 1H), 1.77 (dd, *J* = 12.2, 5.4 Hz, 1H), 1.69 (td, *J* = 12.0, 8.0 Hz, 1H), 1.39 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 133.6, 133.0, 129.5, 126.9, 122.1, 115.0, 88.0, 69.2, 48.5, 44.4, 42.3, 38.5, 21.4, 20.9, 18.0.

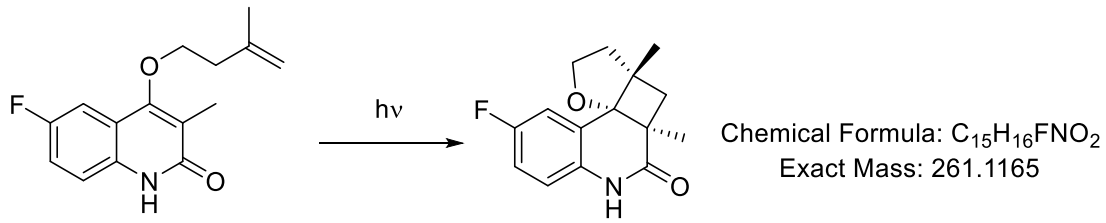
GC-MS; EI (70 eV): t_R = 15.31 Min. [STDHT]; m/z (%) = 257 (50) [M+], 242 (8), 212 (13), 189 (100), 160 (15), 69 (19).

HRMS (**ESI**) m/*z*: $[C_{16}H_{19}NO_2+H]^+$ calcd.: 258.1489; found: 258.1490.

Optical Rotation: $[\alpha]_D^{26}$: −49.0 (c = 2.0, $CHCl_3$) [98% *ee*].

Chiral HPLC: 98% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 8.74 min (minor), 10.31 min (major)].

(3a*S*,4a*R*,10b*S*)-9-fluoro-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7i):



TXT-Catalyzed [2+2] Photocycloaddition

6-fluoro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5i**) (26.1 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the racemic compound *rac*-**7i** was obtained as a colorless solid (25.8 mg, 99 µmol, 99%).

Enantioselective [2+2] Photocycloaddition

6-fluoro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5i**) (6.5 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the title compound **7i** was obtained as a colorless solid (6.4 mg, 24.5 µmol, 98%, 94% *ee*).

TLC: R_f = 0.60 (Pentane:EtOAc, 1:1) [UV].

M.p.: 163-164 °C.

IR (film) υ_{max}/cm^{-1} 3193, 3104, 3066, 2963, 2929, 2896, 1659, 1491, 1446, 1416, 1376, 1364, 1251, 1199, 1168, 1148, 1053, 1034, 928, 885, 870, 851, 805, 750, 698, 669.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (*br* s, 1H), 6.96 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.88 (td, *J* = 8.3, 2.9 Hz, 1H), 6.80 (dd, *J* = 8.6, 4.7 Hz, 1H), 4.43 (t, *J* = 8.3 Hz, 1H), 4.13 (ddd, *J* = 11.4, 9.0, 5.5 Hz, 1H), 2.40 (d, *J* = 12.9 Hz, 1H), 2.06 (d, *J* = 12.9 Hz, 1H), 1.78 (dd, *J* = 12.4, 5.3 Hz, 1H), 1.68 (td, *J* = 11.8, 7.9 Hz, 1H), 1.39 (s, 3H), 1.01 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.3.

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 159.3 (d, *J* = 241.9 Hz), 132.3 (d, *J* = 2.4 Hz), 124.4 (d, *J* = 6.7 Hz), 116.6 (d, *J* = 7.9 Hz), 115.7 (d, *J* = 23.2 Hz), 113.4 (d, *J* = 23.8 Hz), 87.8, 69.5, 48.9, 44.1, 42.4, 38.5, 21.5, 18.1.

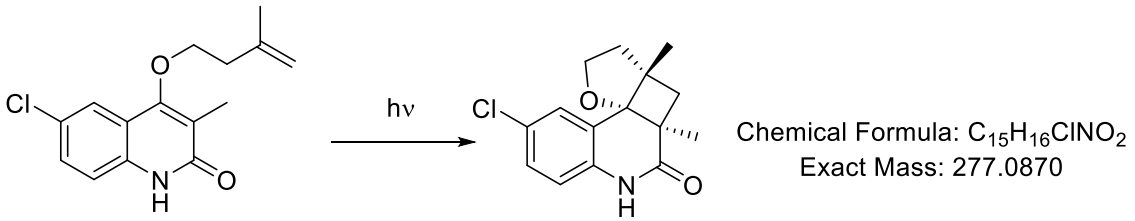
GC-MS; EI (70 eV): t_R = 14.81 Min. [STDHT]; m/z (%) = 261 (42) [M+], 246 (8), 216 (9), 193 (100), 164 (14), 69 (38).

HRMS (**ESI**) m/z: $[C_{15}H_{16}FNO_2+H]^+$ calcd.: 262.1238; found: 262.1238.

Optical Rotation: $[\alpha]_D^{26}$: −103.0 (c = 2.0, $CHCl_3$) [94% *ee*].

Chiral HPLC: 94% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 10.3 min ((major), 11.7 min (minor)].

(3a*S*,4a*R*,10b*S*)-9-chloro-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7j):



TXT-Catalyzed [2+2] Photocycloaddition

6-chloro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5j**) (27.8 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the racemic compound *rac*-**7j** was obtained as a colorless solid (26.4 mg, 95 µmol, 95%).

Enantioselective [2+2] Photocycloaddition

6-chloro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5j**) (6.9 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted

for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the title compound **7j** was obtained as a colorless solid (6.9 mg, 25 µmol, >99%, 93% *ee*).

TLC: R_f = 0.57 (Pentane:EtOAc, 1:1) [UV].

M.p.: 183-185 °C.

IR (film) υ_{max}/cm^{-1} 3183, 3051, 2961, 2925, 2889, 1662, 1588, 1487, 1445, 1405, 1374, 1363, 1252, 1192, 1091, 1054, 1029, 990, 877, 810, 720, 686, 668.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (*br* s, 1H), 7.23 (d, *J* = 2.3 Hz, 1H), 7.15 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.44 (t, *J* = 8.4 Hz, 1H), 4.13 (ddd, *J* = 11.4, 9.1, 5.5 Hz, 1H), 2.40 (d, *J* = 12.9 Hz, 1H), 2.06 (d, *J* = 12.9 Hz, 1H), 1.78 (dd, *J* = 12.4, 5.4 Hz, 1H), 1.70 (td, *J* = 12.0, 8.0 Hz, 1H), 1.38 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 134.8, 129.0, 128.7, 126.7, 124.2, 116.7, 87.7, 69.5, 49.0, 44.3, 42.4, 38.5, 21.5, 18.1.

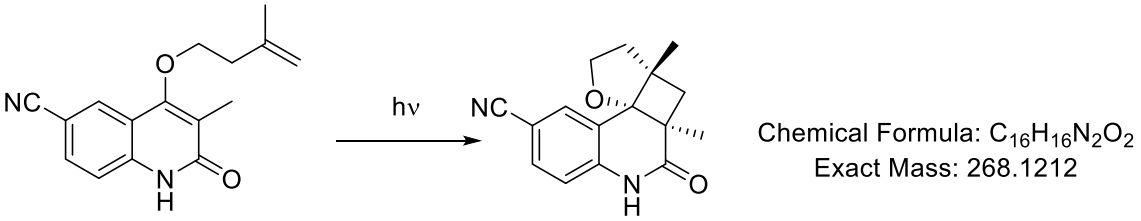
GC-MS; EI (70 eV): t_R = 16.02 Min. [STDHT]; m/z (%) = 279 (13) [M+2+], 277 (37) [M+], 211 (38), 209 (100), 180 (11), 69 (44).

HRMS (**ESI**) m/*z*: $[C_{15}H_{16}ClNO_2+H]^+$ calcd.: 278.0942; found: 278.0942.

Optical Rotation: $[\alpha]_D^{26}$: −25.0 (c = 2.0, $CHCl_3$) [93% *ee*].

Chiral HPLC: 93% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 9.89 min (major), 10.98 min (minor)].

(3a*S*,4a*R*,10b*S*)-3a,4a-dimethyl-5-oxo-3,3a,4,4a,5,6-hexahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinoline-9-carbonitrile (7k):



TXT-Catalyzed [2+2] Photocycloaddition

3-methyl-4-((3-methylbut-3-en-1-yl)oxy)-2-oxo-1,2-dihydroquinoline-6-carbonitrile (**5k**) (26.8 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the racemic compound *rac*-**7k** was obtained as a colorless solid (26.5 mg, 99 µmol, 99%).

Enantioselective [2+2] Photocycloaddition

3-methyl-4-((3-methylbut-3-en-1-yl)oxy)-2-oxo-1,2-dihydroquinoline-6-carbonitrile (**5k**) (6.7 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (17 mL, *c* = 1.5 mmol/L) and reacted for 1.5 h at -25 °C, as modified in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 2:1), the title compound **7k** was obtained as a colorless solid (6.3 mg, 23.5 µmol, 94%, 96% *ee*).

TLC: R_f = 0.54 (Pentane:EtOAc, 1:1) [UV].

M.p.: 210-213 °C.

IR (film) υ_{max}/cm^{-1} 3185, 3054, 2955, 2888, 2227, 1665, 1606, 1596, 1499, 1443, 1353, 1307, 1255, 1195, 1140, 1056, 1039, 902, 887, 822, 731, 700.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (*br* s, 1H), 7.57 (d, *J* = 1.7 Hz, 1H), 7.49 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 4.48 (t, *J* = 8.4 Hz, 1H), 4.14 (ddd, *J* = 11.4, 9.2, 5.6 Hz, 1H), 2.42 (d, *J* = 13.0 Hz, 1H), 2.10 (d, *J* = 13.0 Hz, 1H), 1.82 (dd, *J* = 12.6, 5.3 Hz, 1H), 1.71 (td, *J* = 11.9, 8.0 Hz, 1H), 1.40 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 139.9, 133.2, 131.3, 123.9, 119.0, 115.9, 107.0, 87.2, 69.7, 49.3, 44.6, 42.4, 38.5, 21.5, 18.2.

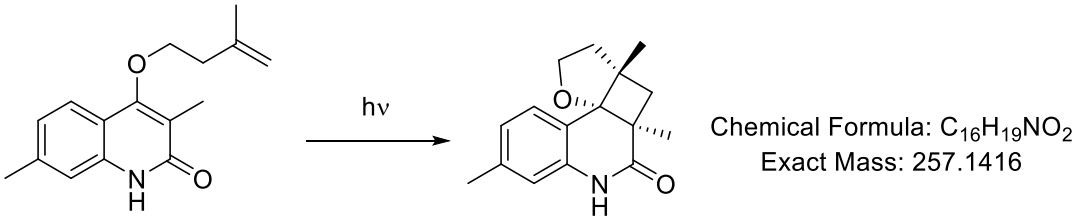
GC-MS; EI (70 eV): t_R = 15.42 Min. [STDHT]; m/z (%) = 268 (58) [M+], 253 (10), 223 (9), 200 (100), 171 (18), 145 (13), 69 (97).

HRMS (**ESI**) m/*z*: $[C_{16}H_{16}N_2O_2+H]^+$ calcd.: 269.1285; found: 269.1285.

Optical Rotation: $[\alpha]_D^{26}$: +30.5 (c = 1.0, $CHCl_3$) [96% *ee*].

Chiral HPLC: 96% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 15.02 min (major), 16.73 min (minor)].

(3a*S*,4a*R*,10b*S*)-3a,4a,8-trimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7l):



TXT-Catalyzed [2+2] Photocycloaddition

3,7-dimethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5l**) (25.7 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the racemic compound *rac*-**7l** was obtained as a colorless solid (25.5 mg, 99 µmol, 99%).

Enantioselective [2+2] Photocycloaddition

3,7-dimethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5l**) (6.4 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the title compound **7l** was obtained as a colorless solid (6.4 mg, 25 µmol, >99%, 98% *ee*).

TLC: R_f = 0.61 (Pentane:EtOAc, 1:1) [UV].

M.p.: 178-180 °C.

IR (film) υ_{max}/cm^{-1} 3194, 3083, 3043, 2996, 2963, 2920, 2878,1659, 1630, 1588, 1487, 1441, 1396, 1372, 1363, 1265, 1194, 1056, 1020, 903, 873, 853, 831, 801, 667, 654.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (*br* s, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.53 (s, 1H), 4.42 (t, *J* = 8.4 Hz, 1H), 4.11 (ddd, *J* = 11.4, 9.0, 5.6 Hz, 1H), 2.38 (d, *J* = 12.8 Hz, 1H), 2.29 (s, 3H), 2.04 (d, *J* = 12.8 Hz, 1H), 1.76 (dd, *J* = 11.0, 6.3 Hz, 1H), 1.67 (td, *J* = 11.8, 8.0 Hz, 1H), 1.38 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 139.1, 136.0, 126.7, 124.5, 119.5, 115.8, 88.0, 69.2, 48.5, 44.6, 42.4, 38.6, 21.6, 21.3, 18.2.

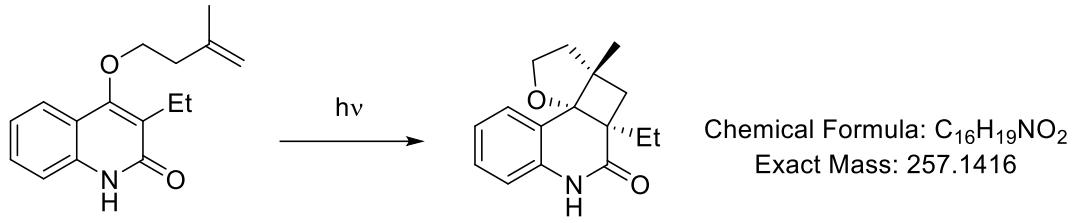
GC-MS; EI (70 eV): t_R = 15.42 Min. [STDHT]; m/*z* (%) = 257 (46) [M+], 242 (9), 212 (14), 189 (100), 160 (18), 134 (15), 69 (19).

HRMS (**ESI**) m/*z*: $[C_{16}H_{19}NO_2+H]^+$ calcd.: 258.1489; found: 258.1490.

Optical Rotation: $[\alpha]_D^{26}$: −66.0 (c = 2.0, $CHCl_3$) [98% *ee*].

Chiral HPLC: 98% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 11.74 min ((major), 13.05 min (minor)].

(3a*S*,4a*R*,10b*S*)-4a-ethyl-3a-methyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7m):



TXT-Catalyzed [2+2] Photocycloaddition

3-ethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5m**) (25.7 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the racemic compound *rac*-**7m** was obtained as a colorless solid (25.5 mg, 99 µmol, 99%).

Enantioselective [2+2] Photocycloaddition

3-ethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5m**) (6.4 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the title compound **7m** was obtained as a colorless solid (6.2 mg, 24.5 µmol, 97%, 93% *ee*).

TLC: R_f = 0.72 (Pentane:EtOAc, 1:1) [UV].

M.p.: 157-158 °C.

IR (film) υ_{max}/cm^{-1} 3216, 3064, 2964, 2928, 2864, 1657, 1613, 1594, 1486, 1440, 1372, 1249, 1061, 1046, 1019, 949, 905, 895, 769, 744, 729, 672.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (*br* s, 1H), 7.23 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.17 (td, *J* = 7.7, 1.5 Hz, 1H), 7.01 (td, *J* = 7.5, 1.1 Hz, 1H), 6.78 (dd, *J* = 7.8, 0.9 Hz, 1H), 4.45 (t, *J* = 8.0 Hz, 1H), 4.14 (ddd, *J* = 11.2, 8.9, 5.7 Hz, 1H), 2.34 (d, *J* = 12.8 Hz, 1H), 2.03 (d, *J* = 12.8 Hz, 1H), 1.89 (q, *J* = 7.4 Hz, 2H), 1.75 (dd, *J* = 12.3, 5.3 Hz, 1H), 1.68 (td, *J* = 12.0, 8.0 Hz, 1H), 0.97 (s, 3H), 0.81 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 136.0, 128.9, 126.1, 123.6, 115.2, 87.6, 69.7, 49.3, 48.3, 41.4, 38.5, 26.9, 21.6, 9.8.

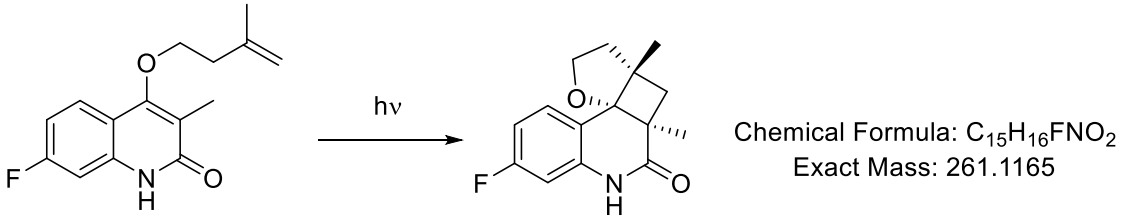
GC-MS; EI (70 eV): t_R = 15.04 Min. [STDHT]; m/*z* (%) = 257 (47) [M+], 212 (36), 189 (100), 174 (89), 161 (25), 146 (14), 69 (27).

HRMS (**ESI**) m/*z*: $[C_{16}H_{19}NO_2+H]^+$ calcd.: 258.1489; found: 258.1489.

Optical Rotation: $[\alpha]_D^{26}$: −101.0 (c = 2.0, $CHCl_3$) [93% *ee*].

Chiral HPLC: 93% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 8.7 min (minor), 9.8 min (major)].

(3a*S*,4a*R*,10b*S*)-8-fluoro-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7n):



TXT-Catalyzed [2+2] Photocycloaddition

7-fluoro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5n**) (26.1 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), the racemic compound *rac*-**7n** was obtained as a colorless solid (25.9 mg, 99 µmol, 99%).

Enantioselective [2+2] Photocycloaddition

7-fluoro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**5n**) (6.5 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), the title compound **7n** was obtained as a colorless solid (6.5 mg, 25 µmol, >99%, 99% *ee*).

TLC: R_f = 0.69 (Pentane:EtOAc, 1:1) [UV].

M.p.: 167-168 °C.

IR (film) υ_{max}/cm^{-1} 3196, 3095, 3051, 2962, 2925, 2887, 1663, 1607, 1490, 1443, 1404, 1375, 1366, 1271, 1194, 1152, 1108, 1054, 1019, 987, 904, 846, 810, 755, 685, 667.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (*br* s, 1H), 7.21 (dd, *J* = 8.5, 6.2 Hz, 1H), 6.71 (td, *J* = 8.5, 2.4 Hz, 1H), 6.55 (dd, *J* = 9.4, 2.4 Hz, 1H), 4.42 (t, *J* = 8.4 Hz, 1H), 4.12 (ddd, *J* = 11.3, 9.1, 5.5 Hz, 1H), 2.39 (d, *J* = 12.9 Hz, 1H), 2.06 (d, *J* = 12.9 Hz, 1H), 1.78 (dd, *J* = 12.4, 5.4 Hz, 1H), 1.68 (td, *J* = 12.0, 8.0 Hz, 1H), 1.39 (s, 3H), 0.99 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.7.

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 163.1 (d, *J* = 246.1 Hz), 137.5 (d, *J* = 10.7 Hz), 128.6 (d, *J* = 9.4 Hz), 118.2 (d, *J* = 3.0 Hz), 110.3 (d, *J* = 21.3 Hz), 102.6 (d, *J* = 25.7 Hz), 87.7, 69.3, 48.6, 44.6, 42.4, 38.5, 21.6, 18.2.

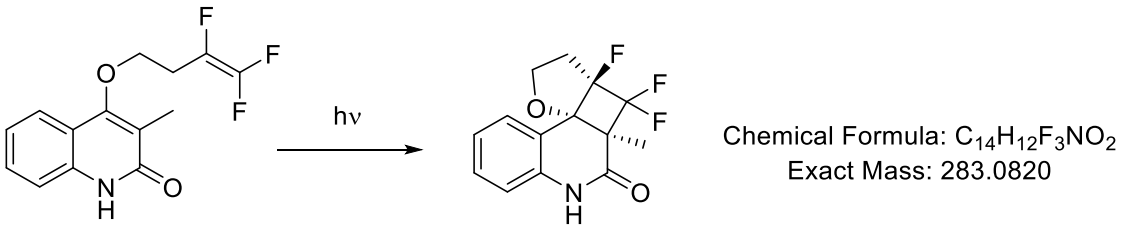
GC-MS; EI (70 eV): t_R = 14.66 Min. [STDHT]; m/z (%) = 261 (5) [M+], 246 (7), 216 (9), 193 (100), 164 (15), 138 (14), 69 (36).

HRMS (**ESI**) m/*z*: $[C_{15}H_{16}FNO_2+H]^+$ calcd.: 262.1238; found: 262.1238.

Optical Rotation: $[\alpha]_D^{26}$: −57.0 (c = 2.0, $CHCl_3$) [99% *ee*].

Chiral HPLC: 99% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 10.65 min (minor), 11.95 min (major)].

(3a*R*,4a*R*,10b*S*)-3a,4,4-trifluoro-4a-methyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (9):



TXT-Catalyzed [2+2] Photocycloaddition

3-methyl-4-((3,4,4-trifluorobut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**8**) (28.3 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the racemic compound *rac*-**9** was obtained as a colorless solid (27.4 mg, 97 µmol, 97%).

Enantioselective [2+2] Photocycloaddition

3-methyl-4-((3,4,4-trifluorobut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (**8**) (7.1 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 2 h at -65 °C, as modified in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 3:1), the title compound **9** was obtained as a colorless solid (5.1 mg, 18.0 µmol, 72%, 81% *ee*).

TLC: R_f = 0.32 (Pentane:EtOAc, 4:1) [UV].

M.p.: 162-163 °C.

IR (film) υ_{max}/cm^{-1} 3195, 3120, 3064, 2988, 2954, 2921, 2888, 1669, 1595, 1495, 1449, 1438, 1389, 1381, 1324, 1301, 1250, 1234, 1213, 1155, 1145, 1127, 1106, 1083, 1049, 989, 871, 848, 815, 804, 752, 691.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (*br* s, 1H), 7.34-7.30 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 4.56 (*virt.* td, *J* ≈ *J* = 8.5 Hz, *J* = 7.5 Hz, 1H), 4.32 (*virt.* td, *J* ≈ *J* = 8.5 Hz, *J* = 7.5 Hz, 1H), 2.80 (*virt.* tt, *J* ≈ *J* = 14.5 Hz, *J* ≈ *J* = 7.5 Hz, 1H), 2.54 (*virt.* ttd, *J* ≈ *J* = 14.5 Hz, *J* ≈ *J* = 7.5 Hz, *J* = 7.0 Hz, 1H), 1.55 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.8 (dd, *J* = 208.8, 9.1 Hz), -119.5 (dd, *J* = 208.8, 9.2 Hz), -168.4 (t, *J* = 9.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 135.6, 130.7, 129.0, 124.0, 116.3, 116.2 (d, *J* = 2.5 Hz), 116.1 (ddd, *J* = 298.0, 284.8, 24.4 Hz), 106.6 (ddd, *J* = 245.9, 29.3, 20.4 Hz), 83.8 (ddd, *J* = 21.4, 14.0, 4.5 Hz), 70.3 (d, *J* = 4.2 Hz), 55.2 (ddd, *J* = 23.5, 20.5, 6.8 Hz), 32.1 (d, *J* = 21.7 Hz), 12.4 (d, *J* = 4.6 Hz).

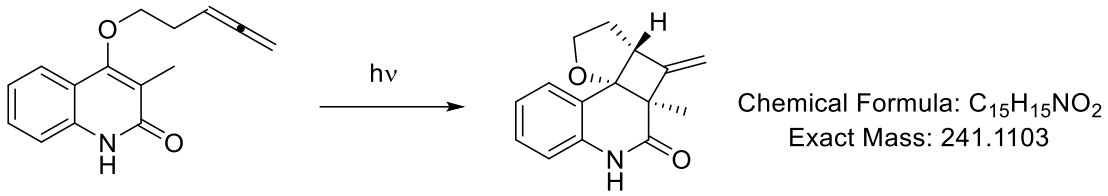
GC-MS; EI (70 eV): t_R = 14.82 Min. [STDHT]; m/z (%) = 283 (22) [M+], 269 (16), 268 (100), 175 (24), 174 (25), 159 (9), 146 (10), 130 (11), 120 (8), 105 (10).

HRMS (**ESI**) m/z: $[C_{14}H_{12}F_3NO_2+H]^+$ calcd.: 284.0893; found: 284.0893.

Optical Rotation: $[\alpha]_D^{26}$: −50.0 (c = 2.0, $CHCl_3$) [81% *ee*].

Chiral HPLC: 81% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 22.59 min (major), 25.65 min (minor)].

(3a*R*,4a*R*,10b*S*)-4a-methyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (11a):



TXT-Catalyzed [2+2] Photocycloaddition

4-((4λ^5-penta-3,4-dien-1-yl)oxy)-3-methylquinolin-2(1*H*)-one (**10a**) (24.1 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1.5 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), the racemic compound *rac*-**11a** was obtained as a colorless solid (21.7 mg, 90 µmol, 90%).

Enantioselective [2+2] Photocycloaddition

4-((4λ^5-penta-3,4-dien-1-yl)oxy)-3-methylquinolin-2(1*H*)-one (**10a**) (6.0 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1.5 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), the title compound **11a** was obtained as a colorless solid (5.1 mg, 21.1 µmol, 85%, 91% *ee*).

TLC: R_f = 0.41 (Pentane:EtOAc, 2:1) [UV].

M.p.: 181-183 °C.

IR (film) υ_{max}/cm^{-1} 3189, 3061, 2975, 2929, 2892, 1667, 1594, 1492, 1478, 1441, 1368, 1353, 1253, 1212, 1104, 1053, 995, 967, 939, 906, 872, 854, 769, 747, 681.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (*br* s, 1H), 7.37 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.21 (td, *J* = 7.7, 1.5 Hz, 1H), 7.04 (td, *J* = 7.6, 1.1 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 5.44 (dd, *J* = 2.6, 0.9 Hz, 1H), 5.09 (dd, *J* = 2.2, 1.0 Hz, 1H), 4.46 (td, *J* = 8.0, 0.5 Hz, 1H), 4.13 (ddd, *J* = 11.0, 8.6, 5.9 Hz, 1H), 3.65-3.47 (m, 1H), 2.07-1.95 (m, 2H), 1.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 152.2, 135.4, 129.0, 125.9, 124.3, 123.6, 115.4, 109.7, 85.4, 70.7, 56.3, 55.3, 31.0, 16.5.

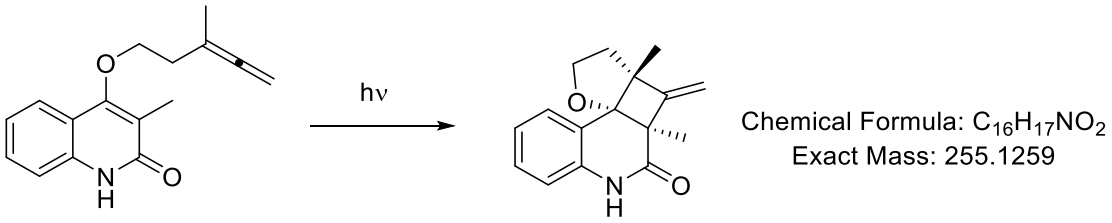
GC-MS; EI (70 eV): t_R = 16.16 Min. [STDHT]; m/z (%) = 241 (27) [M+], 240 (39), 226 (100), 212 (20), 198 (15), 186(26), 175 (11), 120 (8), 77 (9).

HRMS (**ESI**) m/z: $[C_{15}H_{15}NO_2+H]^+$ calcd.: 242.1176; found: 242.1177.

Optical Rotation: $[\alpha]_D^{26}$: +105.0 (c = 2.0, $CHCl_3$) [91% *ee*].

Chiral HPLC: 91% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 11.57 min (major), 20.73 min (minor)].

(3a*R*,4a*R*,10b*S*)-3a,4a-dimethyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (11b):



TXT-Catalyzed [2+2] Photocycloaddition

3-methyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (**10b**) (25.5 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1.5 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), the racemic compound *rac*-**11b** was obtained as a colorless solid (23.7 mg, 93 µmol, 93%).

Enantioselective [2+2] Photocycloaddition

3-methyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (**10b**) (6.4 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1.5 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 4:1), the title compound **11b** was obtained as a colorless solid (6.3 mg, 24.8 µmol, 98%, 96% *ee*).

TLC: R_f = 0.54 (Pentane:EtOAc, 2:1) [UV].

M.p.: 174-175 °C.

IR (film) υ_{max}/cm^{-1} 3196, 3061, 2976, 2925, 2873, 1659, 1594, 1489, 1435, 1366, 1354, 1309, 1245, 1054, 898, 851, 759, 675.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (*br* s, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.21 (td, *J* = 7.7, 1.5 Hz, 1H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 6.81 (dd, *J* = 7.6, 0.4 Hz, 1H), 5.42 (d, *J* = 1.0 Hz, 1H), 5.10 (d, *J* = 1.0 Hz, 1H), 4.35 (t, *J* = 8.2 Hz, 1H), 4.07 (ddd, *J* = 11.6, 8.8, 5.3 Hz, 1H), 2.02 (dd, *J* = 12.2, 5.1 Hz, 1H), 1.78 (td, *J* = 11.9, 7.9 Hz, 1H), 1.48 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 157.7, 135.9, 129.1, 126.9, 123.6, 121.8, 115.4, 108.1, 87.5, 69.4, 60.8, 53.6, 38.9, 20.5, 16.8.

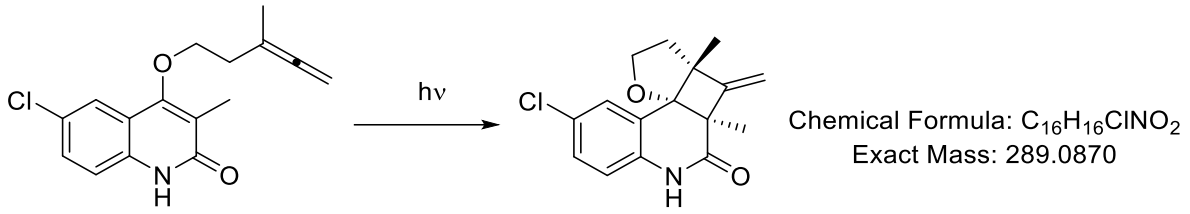
GC-MS; EI (70 eV): t_R = 15.03 Min. [STDHT]; m/z (%) = 255 (1) [M+], 241 (23), 240 (100), 175 (23), 146 (6), 120 (6), 79 (10).

HRMS (**ESI**) m/*z*: $[C_{16}H_{17}NO_2+H]^+$ calcd.: 256.1332; found: 256.1334.

Optical Rotation: $[\alpha]_D^{26}$: +95.0 (c = 2.0, $CHCl_3$) [96% *ee*].

Chiral HPLC: 96% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 9.13 min (major), 12.56 min (minor)].

(3a*R*,4a*R*,10b*S*)-9-chloro-3a,4a-dimethyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]-cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (11c):



TXT-Catalyzed [2+2] Photocycloaddition

6-chloro-3-methyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (**10c**) (29.0 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (20 mL, *c* = 5 mmol/L) and reacted for 1.5 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 5:1), the racemic compound *rac*-**11c** was obtained as a colorless solid (28.0 mg, 97 µmol, 97%).

Enantioselective [2+2] Photocycloaddition

6-chloro-3-methyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (**10c**) (7.2 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (16.7 mL, *c* = 1.5 mmol/L) and reacted for 2.5 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 5:1), the title compound **11c** was obtained as a colorless solid (7.0 mg, 24.2 µmol, 97%, 91% *ee*).

TLC: R_f = 0.70 (Pentane:EtOAc, 2:1) [UV].

M.p.: 172-173 °C.

IR (film) υ_{max}/cm^{-1} 3193, 3068, 2970, 2881, 1675, 1592, 1491, 1410, 1367, 1356, 1250, 1094, 1056, 898, 846, 688.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (*br* s, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.17 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.42 (d, *J* = 1.2 Hz, 1H), 5.11 (d, *J* = 1.2 Hz, 1H), 4.36 (t, *J* = 8.2 Hz, 1H), 4.06 (ddd, *J* = 11.6, 8.8, 5.3 Hz, 1H), 2.02 (dd, *J* = 12.3, 5.1 Hz, 1H), 1.78 (dt, *J* = 12.0, 7.8 Hz, 1H), 1.46 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 157.2, 134.6, 129.1, 128.8, 126.8, 123.6, 116.8, 108.5, 87.2, 69.6, 61.1, 53.3, 38.8, 20.4, 16.7.

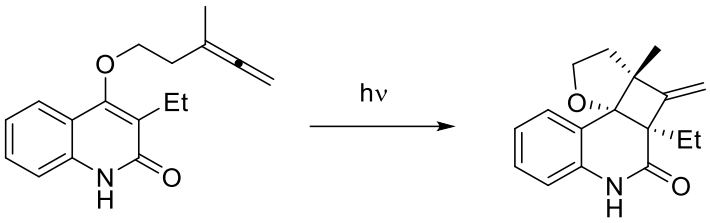
GC-MS; EI (70 eV): t_R = 16.32 Min. [STDHT]; m/z (%) = 289 (2) [M+], 277 (8), 276 (45), 275 (23), 274 (100), 209 (19), 79 (13).

HRMS (**ESI**) m/*z*: $[C_{16}H_{16}ClNO_2+H]^+$ calcd.: 290.0942; found: 290.0943.

Optical Rotation: $[\alpha]_D^{24}$: +134.5 (c = 1.0, $CHCl_3$) [91% *ee*].

Chiral HPLC: 91% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 8.64 min (major), 11.15 min (minor)].

(3a*R*,4a*R*,10b*S*)-4a-ethyl-3a-methyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta [1,2-*c*]quinolin-5(6*H*)-one (11d):



Chemical Formula: $C_{17}H_{19}NO_2$
Exact Mass: 269.1416

TXT-Catalyzed [2+2] Photocycloaddition

3-ethyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (**10d**) (26.9 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1.5 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 6:1), the racemic compound *rac*-**11d** was obtained as a colorless solid (25.0 mg, 93 µmol, 93%).

Enantioselective [2+2] Photocycloaddition

3-ethyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (**10d**) (6.7 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 2 h at -25 °C, as described in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 6:1), the title compound **11d** was obtained as a colorless solid (6.0 mg, 22.3 µmol, 90%, 92% *ee*).

TLC: R_f = 0.59 (Pentane:EtOAc, 2:1) [UV].

M.p.: 166-167 °C.

IR (film) υ_{max}/cm^{-1} 3190, 3066, 2974, 2934, 2877, 1659, 1595, 1490, 1435, 1352, 1310, 1193, 1057, 1046, 1013, 893, 871, 845, 757, 671.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (*br* s, 1H), 7.32 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.20 (td, *J* = 7.7, 1.5 Hz, 1H), 7.04 (td, *J* = 7.6, 1.0 Hz, 1H), 6.80 (dd, *J* = 7.9, 0.7 Hz, 1H), 5.38 (d, *J* = 0.9 Hz, 1H), 5.08 (d, *J* = 0.9 Hz, 1H), 4.37 (t, *J* = 8.2 Hz, 1H), 4.09 (ddd, *J* = 11.6, 8.7, 5.3 Hz, 1H), 2.12 (dq, *J* = 14.8, 7.4 Hz, 1H), 2.00 (dd, *J* = 12.2, 5.2 Hz, 1H), 1.90 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.77 (td, *J* = 11.8, 7.9 Hz, 1H), 0.99 (s, 3H), 0.82 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 157.0, 135.7, 128.9, 126.3, 123.6, 123.0, 115.4, 108.1, 87.3, 69.9, 60.4, 58.4, 38.6, 25.5, 20.6, 9.7.

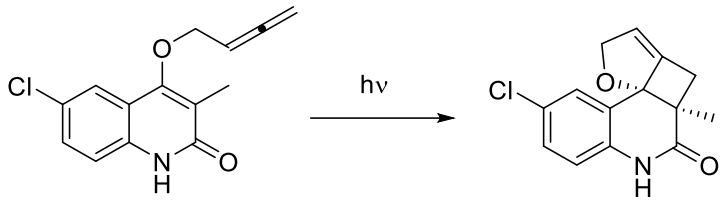
GC-MS; EI (70 eV): t_R = 15.23 Min. [STDHT]; m/z (%) = 269 (1) [M+], 241 (24), 240 (100), 189 (7), 174 (18), 146 (5), 79 (6).

HRMS (**ESI**) m/*z*: $[C_{17}H_{20}NO_2+H]^+$ calcd.: 270.1489; found: 270.1489.

Optical Rotation: $[\alpha]_D^{24}$: +88.5 (c = 1.0, $CHCl_3$) [92% *ee*].

Chiral HPLC: 92% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 7.57 min (major), 10.34 min (minor)].

(4a*R*,10b*S*)-9-chloro-4a-methyl-4,4a-dihydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (13a):



Chemical Formula: $C_{14}H_{12}ClNO_2$
Exact Mass: 261.0557

TXT-Catalyzed [2+2] Photocycloaddition

4-((3λ^5-buta-2,3-dien-1-yl)oxy)-6-chloro-3-methylquinolin-2(1*H*)-one (**12a**) (26.2 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (20 mL, *c* = 5 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/ethyl acetate 3.5:1), the racemic compound *rac*-**13a** was obtained as a colorless solid (22.0 mg, 84 µmol, 84%).

Enantioselective [2+2] Photocycloaddition

4-((3λ^5-buta-2,3-dien-1-yl)oxy)-6-chloro-3-methylquinolin-2(1*H*)-one (**12a**) (6.5 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (16.7 mL, *c* = 1.5 mmol/L) and reacted for 1.5 h at -25 °C, as modified in *general procedure 6*. Following flash column chromatography (silica, pentane/ethyl acetate 3.5:1), the title compound **13a** was obtained as a colorless solid (5.5 mg, 21.0 µmol, 85%, 88% *ee*).

TLC: R_f = 0.36 (Pentane:EtOAc, 2:1) [UV].

M.p.: 210-212 °C.

IR (film) υ_{max}/cm^{-1} 3204, 3086, 2990, 2940, 2863, 1670, 1589, 1488, 1390, 1368, 1248, 1140, 1071, 1029, 1005, 959, 834, 779, 757, 679.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (*br* s, 1H), 7.36 (d, *J* = 2.3 Hz, 1H), 7.22 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 5.74 (tt, *J* = 2.5, 1.2 Hz, 1H), 5.33 (ddt, *J* = 13.0, 3.0, 1.5 Hz, 1H), 4.84 (ddd, *J* = 12.5, 2.8, 1.1 Hz, 1H), 2.93 (ddt, *J* = 12.5, 2.5, 1.2 Hz, 1H), 2.53 (d, *J* = 12.3 Hz, 1H), 1.44 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d6) δ 168.7, 142.3, 135.3, 129.4, 128.5, 126.1, 124.2, 117.6, 117.3, 92.4, 80.4, 48.5, 40.0, 13.3.

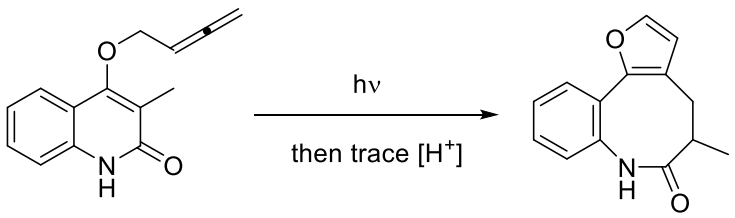
GC-MS; EI (70 eV): t_R = 15.79 Min. [STDHT]; m/z (%) = 263 (2) [M+2+], 262 (4) [M+1+], 261 (6) [M+], 260 (11), 248 (34), 246 (100), 234 (8), 232 (21), 218 (10), 126 (11), 79 (21).

HRMS (**ESI**) m/z: $[C_{14}H_{12}ClNO_2+H]^+$ calcd.: 262.0629; found: 262.0630.

Optical Rotation: $[\alpha]_D^{24}$: −142.0 (c = 1.0, $CHCl_3$) [88% *ee*].

Chiral HPLC: 88% *ee* [Daicel Chiralpak AS-H, 250×4.6, *i*-PrOH/*n*-heptane = 30/70, 1 mL/min, 210 nm, t_R = 9.03 min (minor), 12.59 min (major)].

5-methyl-4,7-dihydrobenzo[*b*]furo[2,3-*d*]azocin-6(5*H*)-one (*rac*-14b):



Chemical Formula: $C_{14}H_{13}NO_2$
Exact Mass: 227.0946

4-((3λ^5-buta-2,3-dien-1-yl)oxy)-3-methylquinolin-2(1*H*)-one (**12b**) (22.7 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted at 0 °C for 1 h, as described in *general procedure 5*, then with traces of acid such as H_2SO_4 (0.5 mol%) for 0.5 h. Following flash column chromatography (silica, pentane/ethyl acetate 3.5:1), the racemic compound *rac*-**14b** was obtained as a colorless solid (21.7 mg, 96 µmol, 96%).

TLC: R_f = 0.35 (Pentane:EtOAc, 2:1) [UV].

M.p.: 175-176 °C.

IR (film) υ_{max}/cm^{-1} 3184, 3058, 2939, 2903, 1659, 1576, 1491, 1419, 1400, 1290, 1156, 1056, 1047, 892, 809, 757, 714, 675.

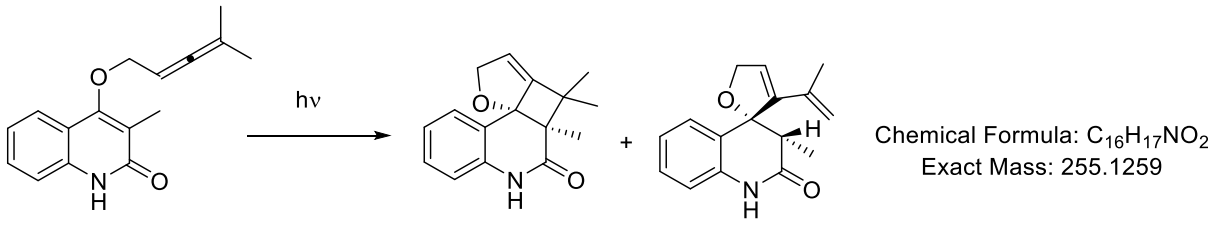
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (*br* s, 1H), 7.62-7.56 (m, 1H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.38-7.31 (m, 2H), 7.21-7.14 (m, 1H), 6.27 (d, *J* = 1.8 Hz, 1H), 3.04 (dqd, *J* = 12.0, 6.4, 4.8 Hz, 1H), 2.86 (dd, *J* = 16.6, 12.0 Hz, 1H), 2.79 (dd, *J* = 16.6, 4.8 Hz, 1H), 1.15 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 145.4, 142.7, 134.1, 130.5, 129.4, 129.0, 126.9, 125.6, 121.0, 113.3, 33.0, 32.4, 17.4.

GC-MS; EI (70 eV): t_R = 15.05 Min. [STDHT]; m/*z* (%) = 228 (16) [M+1+], 227 (100) [M+], 210 (20), 199 (55), 198 (39), 184 (86), 170 (90), 115 (30).

HRMS (**ESI**) m/*z*: $[C_{14}H_{13}NO_2+H]^+$ calcd.: 228.1019; found: 228.1020.

(4a*R*,10b*S*)-4,4,4a-trimethyl-4,4a-dihydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (16) and (2*S*,3'*S*)-3'-methyl-3-(prop-1-en-2-yl)-1'*H*,5*H*-spiro[furan-2,4'-quinolin]-2'(3'*H*)-one (18):

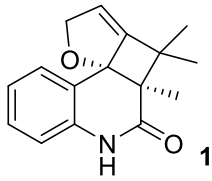


TXT-Catalyzed [2+2] Photocycloaddition

3-methyl-4-((4-methyl-3λ^5-penta-2,3-dien-1-yl)oxy)quinolin-2(1*H*)-one (**15**) (25.5 mg, 0.1 mmol, 1.0 eq.) and thioxanthenone (TXT) (4.2 mg, 20 mol%) were dissolved in acetonitrile (10 mL, *c* = 10 mmol/L) and reacted for 1 h, as described in *general procedure 5*. Following flash column chromatography (silica, pentane/diethylether 1:1), the racemic compound *rac*-**16** was obtained as a colorless solid (11.2 mg, 44 µmol, 44%), along with *rac*-**18** as a colorless solid (14.0 mg, 55 µmol, 55%).

Enantioselective [2+2] Photocycloaddition

3-methyl-4-((4-methyl-3λ^5-penta-2,3-dien-1-yl)oxy)quinolin-2(1*H*)-one (**15**) (6.4 mg, 25 µmol, 1.0 eq.) and **6** (1.1 mg, 2.5 µmol, 10 mol%) were dissolved in α,α,α-trifluorotoluene (10 mL, *c* = 2.5 mmol/L) and reacted for 1 h at -25 °C, as modified in *general procedure 6*. Following flash column chromatography (silica, pentane/diethylether 1:1), the title compound **16** was obtained as a colorless solid (3.2 mg, 12.5 µmol, 50%, 98% *ee*), along with title compound **18** as a colorless solid (3.0 mg, 11.8 µmol, 47%, 92% *ee*).



16

TLC: R_f = 0.48 (Pentane:Et_2O, 1:3) [UV].

M.p.: 175-176 °C.

IR (film) υ_{max}/cm^{-1} 3209, 3063, 2925, 2855, 1665, 1597, 1491, 1375, 1237, 1028, 1008, 754.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (*br* s, 1H), 7.39 (d, *J* = 7.1 Hz, 1H), 7.22 (td, *J* = 7.9, 1.4 Hz, 1H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 6.71 (dd, *J* = 8.0, 0.7 Hz, 1H), 5.73 (dd, *J* = 3.3, 1.5 Hz, 1H), 5.27 (dd, *J* = 12.5, 1.5 Hz, 1H), 4.72 (dd, *J* = 12.5, 3.3 Hz, 1H), 1.29 (s, 3H), 1.22 (s, 3H), 1.14 (s, 3H).

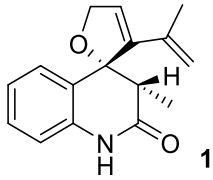
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 152.0, 136.1, 129.6, 124.9, 123.8, 117.3, 115.5, 91.9, 79.5, 54.7, 52.6, 23.5, 21.4, 12.3.

GC-MS; EI (70 eV): t_R = 15.56 Min. [STDHT]; m/*z* (%) = 255 (1) [M+], 241 (17), 240 (100), 212 (11), 120 (13), 79 (8).

HRMS (**ESI**) m/*z*: $[C_{16}H_{17}NO_2+H]^+$ calcd.: 256.1332; found: 256.1333.

Optical Rotation: $[\alpha]_D^{24}$: −153.5 (c = 1.0, $CHCl_3$) [98% *ee*].

Chiral HPLC: 98% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 10/90, 1 mL/min, 210 nm, t_R = 8.87 min (major), 15.18 min (minor)].



18

TLC: R_f = 0.40 (Pentane:Et_2O, 1:3) [UV].

M.p.: 160-161 °C.

IR (film) υ_{max}/cm^{-1} 3237, 2924, 2852, 1665, 1595, 1488, 1458, 1366, 1260, 1241, 1059, 1015, 923, 890, 757, 732, 654.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (*br* s, 1H), 7.24 (td, *J* = 7.6, 1.2 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.96 (td, *J* = 7.6, 0.9 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.29 (s, 1H), 5.03 (s, 1H), 4.693 (d, *J* = 13.6 Hz, 1H), 4.686 (s, 1H), 4.61 (d, *J* = 14.4 Hz, 1H), 3.29 (q, *J* = 6.8 Hz, 1H), 2.06 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 139.7, 136.6, 135.4, 129.6, 128.9, 127.6, 125.9, 122.9, 116.7, 116.0, 91.7, 74.3, 43.0, 22.6, 8.1.

GC-MS; EI (70 eV): t_R = 16.05 Min. [STDHT]; m/*z* (%) = 255 (32) [M+], 240 (30), 212 (24), 198 (16), 185 (93), 184 (100), 130 (13), 79 (26).

HRMS (**ESI**) m/*z*: $[C_{16}H_{17}NO_2+H]^+$ calcd.: 256.1332; found: 256.1334.

Optical Rotation: $[\alpha]_D^{24}$: +139.5 (c = 1.0, $CHCl_3$) [92% *ee*].

Chiral HPLC: 92% *ee* [Daicel Chiralpak AD-H, 250×4.6, *i*-PrOH/*n*-heptane = 30/70, 1 mL/min, 210 nm, t_R = 10.51 min (minor), 23.82 min (major)].

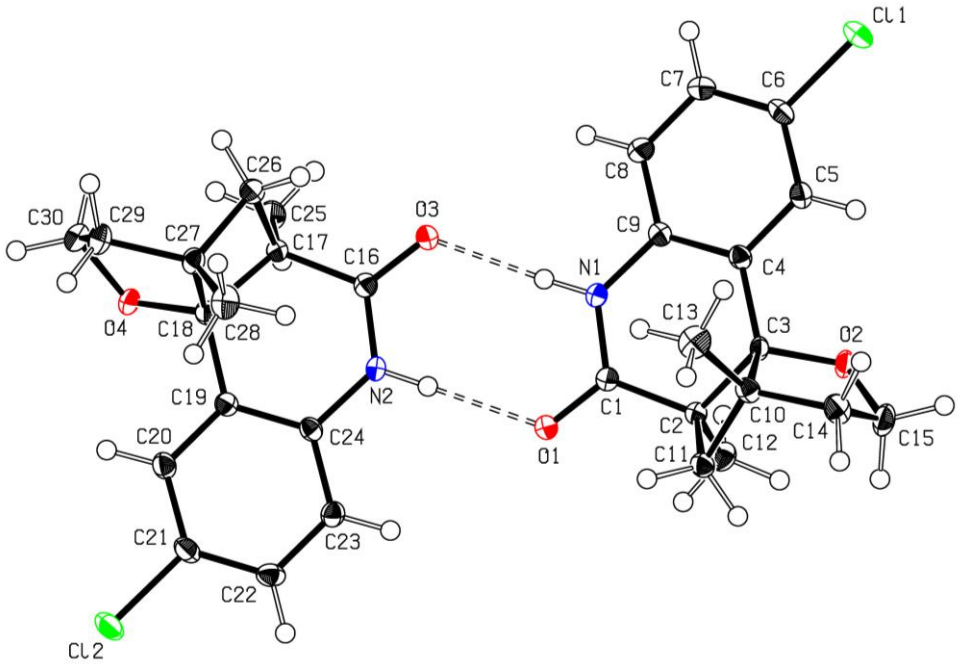
7. X-ray Crystallographic Detail

Data were collected on a single crystal x-ray diffractometer equipped with a CMOS detector (Bruker APEX III, κ-CMOS), an IMS micro source with MoK_α radiation (λ = 0.71073 Å) and a Helios optic using the APEX3 software package.[7] Measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[8] Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS.[8] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. The structures were solved using SHELXT with the aid of successive difference Fourier maps, and were refined against all data using SHELXL in conjunction with SHELXLE.[9-11] Hydrogen atoms (except on heteroatoms) were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å, all with $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL weighting scheme.[9] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[12] Images of the crystal structures were generated with Mercury (main article)[13] and PLATON (SI).[14]

Stereochemistry determination **7j** via X-ray crystallographic analysis

Product **7j** was crystallized as a colorless crystal via slow vaporization of EtOH solution at room temperature, and its absolute configuration was determined by x-ray structure analysis. The CCDC number was 1988524. The supplementary crystallographic data that could be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif

Compound 7j (CCDC 1988524)



Diffractometer operator C. Jandl
scanspeed 2-10 s per frame
dx 37 mm
3405 frames measured in 13 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

$C_{15}H_{16}ClNO_2 \cdot H_2O$

M_r = 295.75	D_x = 1.323 Mg m^{-3}
Monoclinic, $P2_1$	Melting point: 458 K
Hall symbol: P 2yb	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 10.1162 (9) Å	Cell parameters from 9992 reflections
b = 13.1872 (13) Å	θ = 2.5–27.1°
c = 11.1569 (12) Å	μ = 0.26 mm^{-1}
β = 94.081 (4)°	T = 100 K
V = 1484.6 (3) Å^3	Fragment, colourless
Z = 4	0.46 × 0.23 × 0.17 mm
F(000) = 624	

Data collection

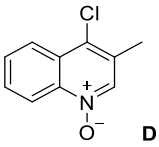
Bruker Photon CMOS diffractometer	6269 independent reflections
Radiation source: IMS microsource	6217 reflections with $I > 2\sigma(I)$
Helios optic monochromator	R_{int} = 0.030
Detector resolution: 16 pixels mm^{-1}	θ_{max} = 26.7°, θ_{min} = 2.0°
phi– and ω–rotation scans	h = −12 12
Absorption correction: multi-scan *SADABS* 2016/2, Bruker	k = −16 16
T_{min} = 0.730, T_{max} = 0.746	l = −14 14
90432 measured reflections	

Refinement

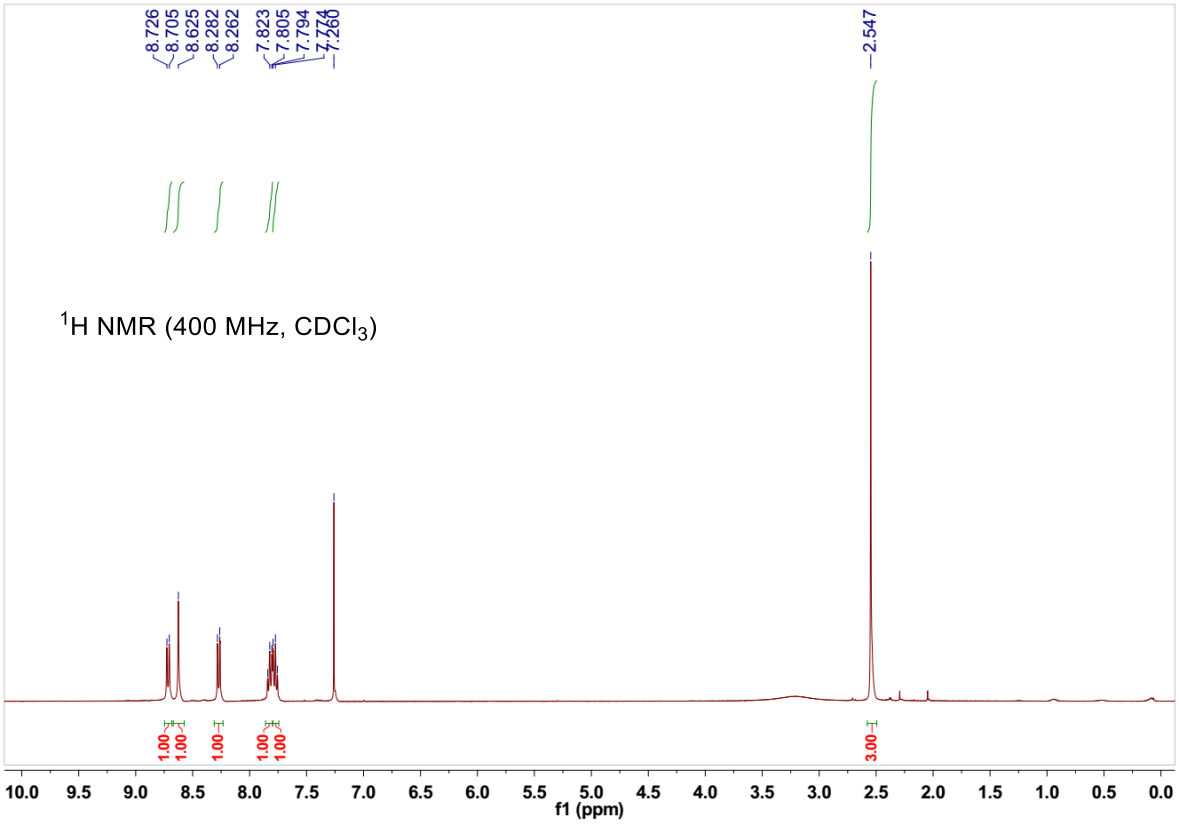
Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.022	$W = 1/[\Sigma^2(FO^2) + (0.0321P)^2 + 0.3053P]$ WHERE $P = (FO^2 + 2FC^2)/3$
$wR(F^2)$ = 0.058	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.06	$\Delta\rho_{max}$ = 0.24 e $Å^{-3}$
6269 reflections	$\Delta\rho_{min}$ = −0.26 e $Å^{-3}$
389 parameters	Extinction correction: none
1 restraint	Extinction coefficient: -
0 constraints	Absolute structure: Flack[9,10]
Primary atom site location: intrinsic phasing	Absolute structure parameter: 0.004 (6)
Secondary atom site location: difference Fourier map	

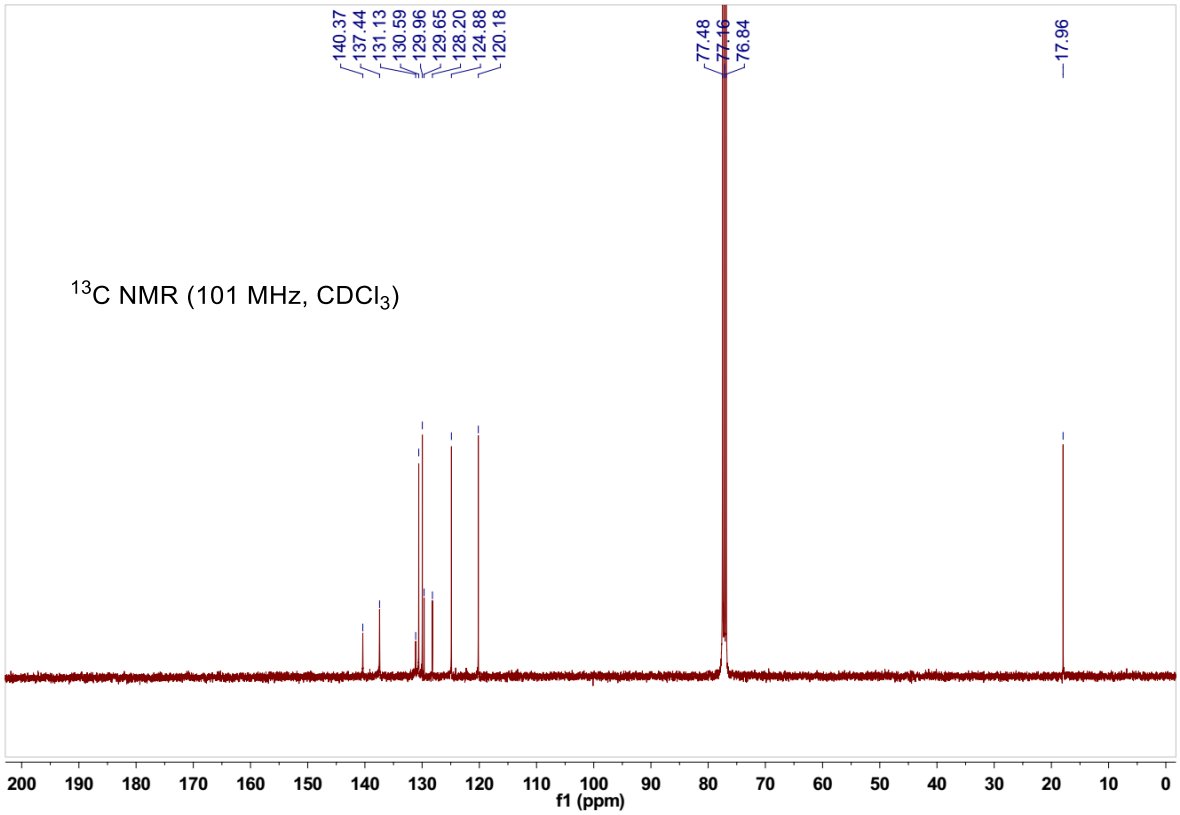
8. NMR-Spectra of New Compounds

4-chloro-3-methylquinoline 1-oxide (D):

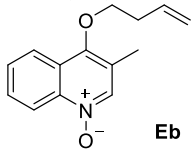


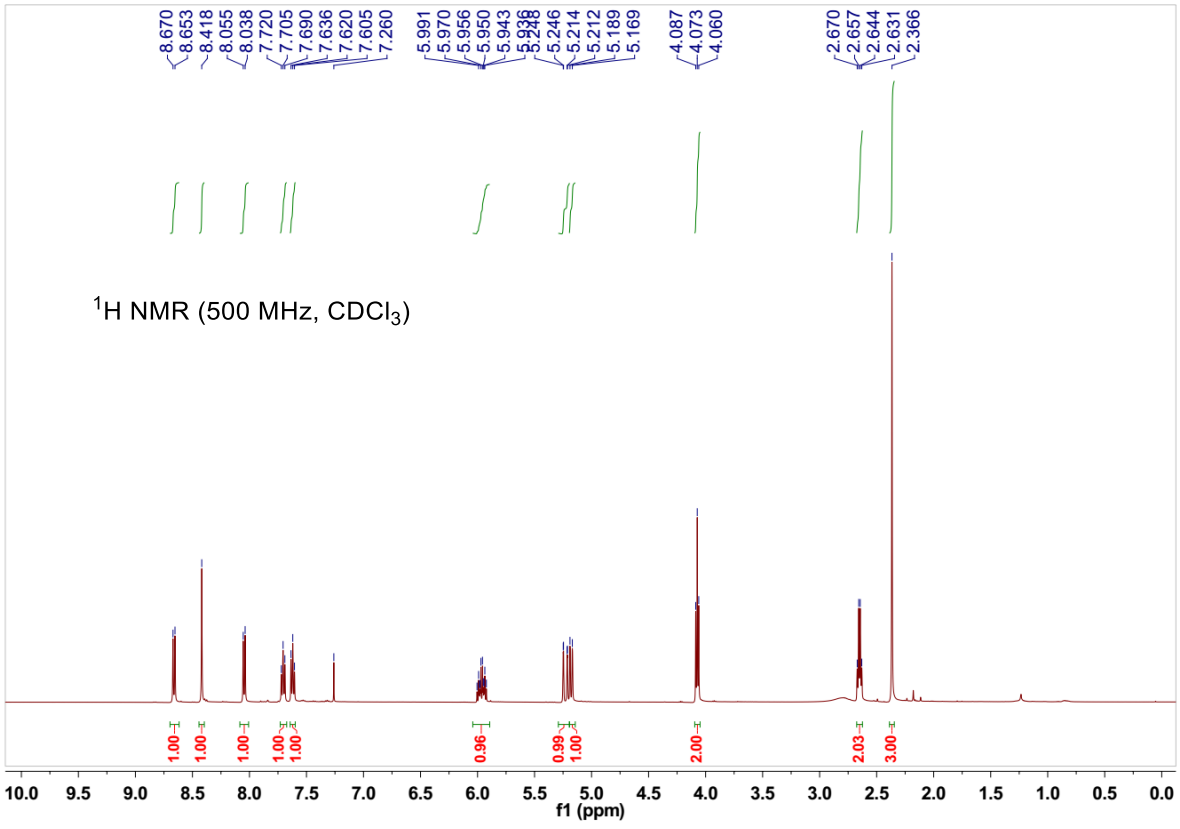
D

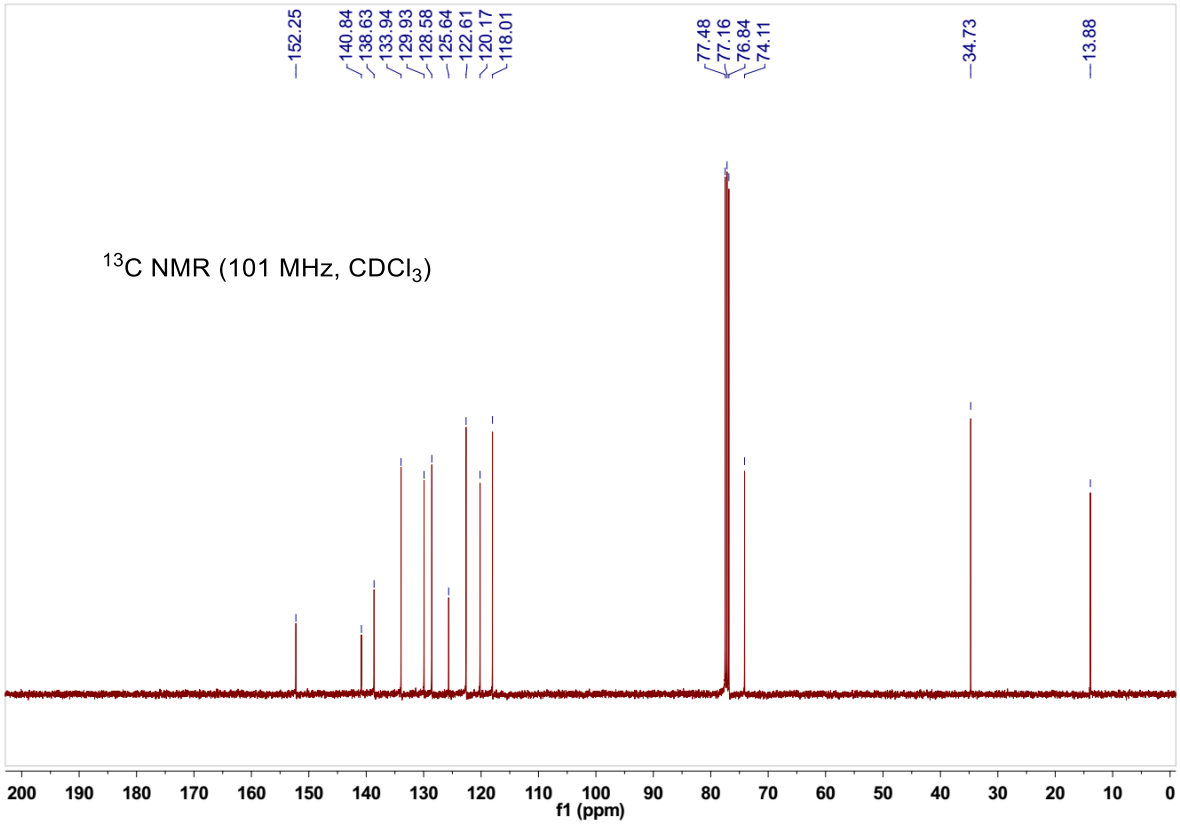




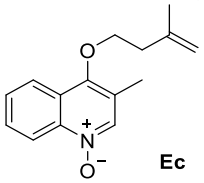
4-(but-3-en-1-yloxy)-3-methylquinoline 1-oxide (Eb):



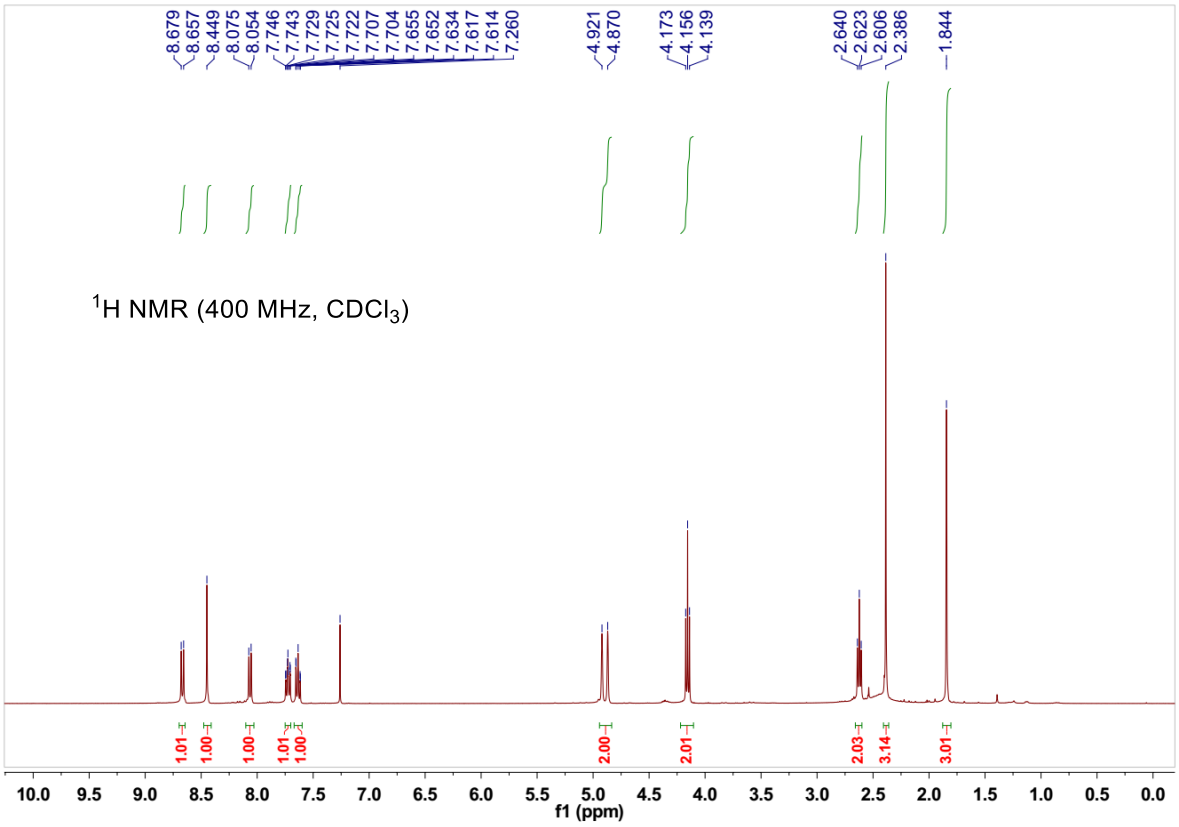


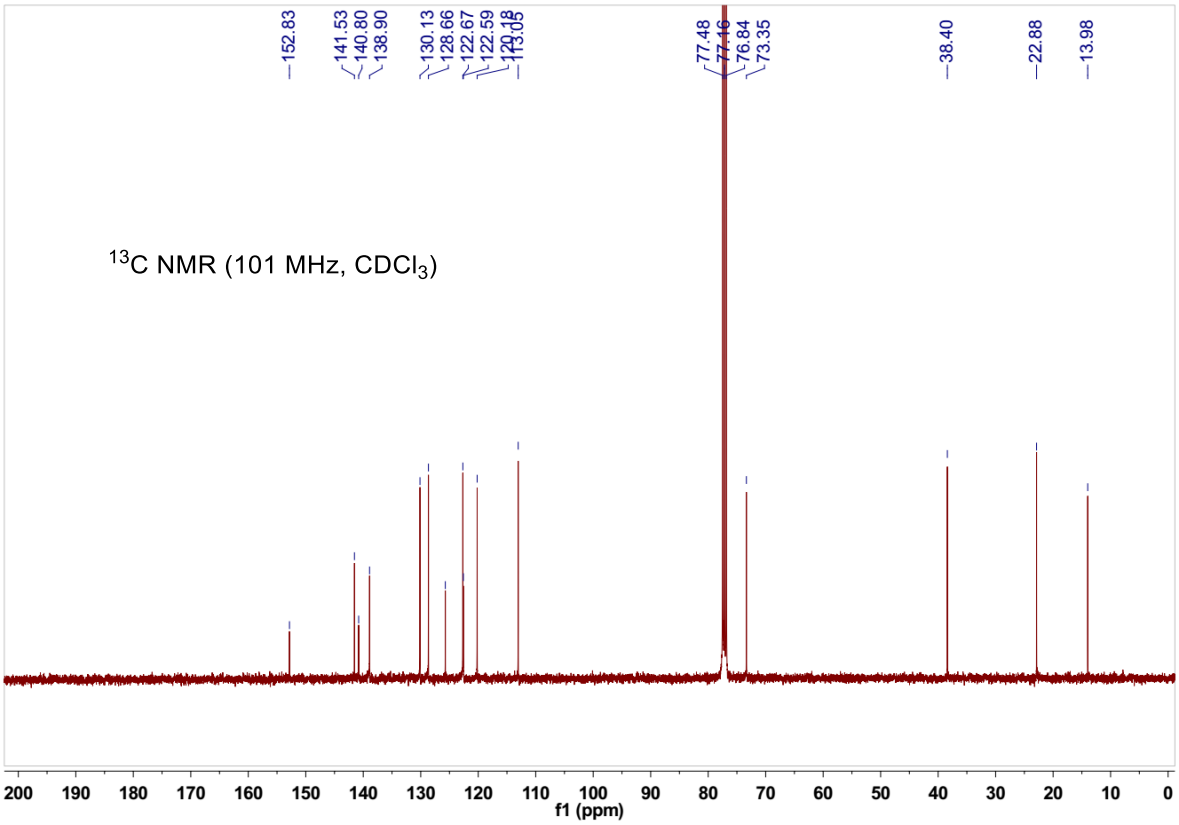


3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinoline 1-oxide (Ec):

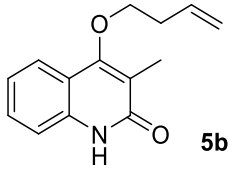


Ec

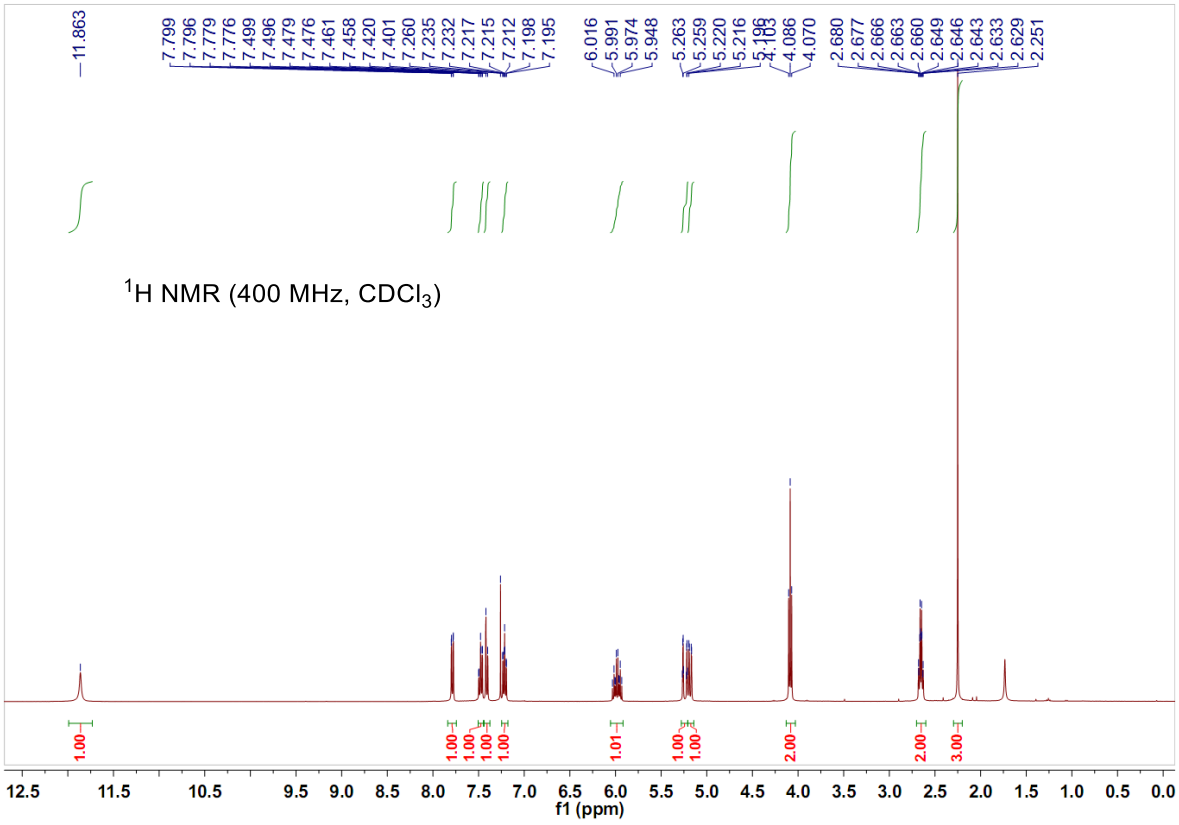


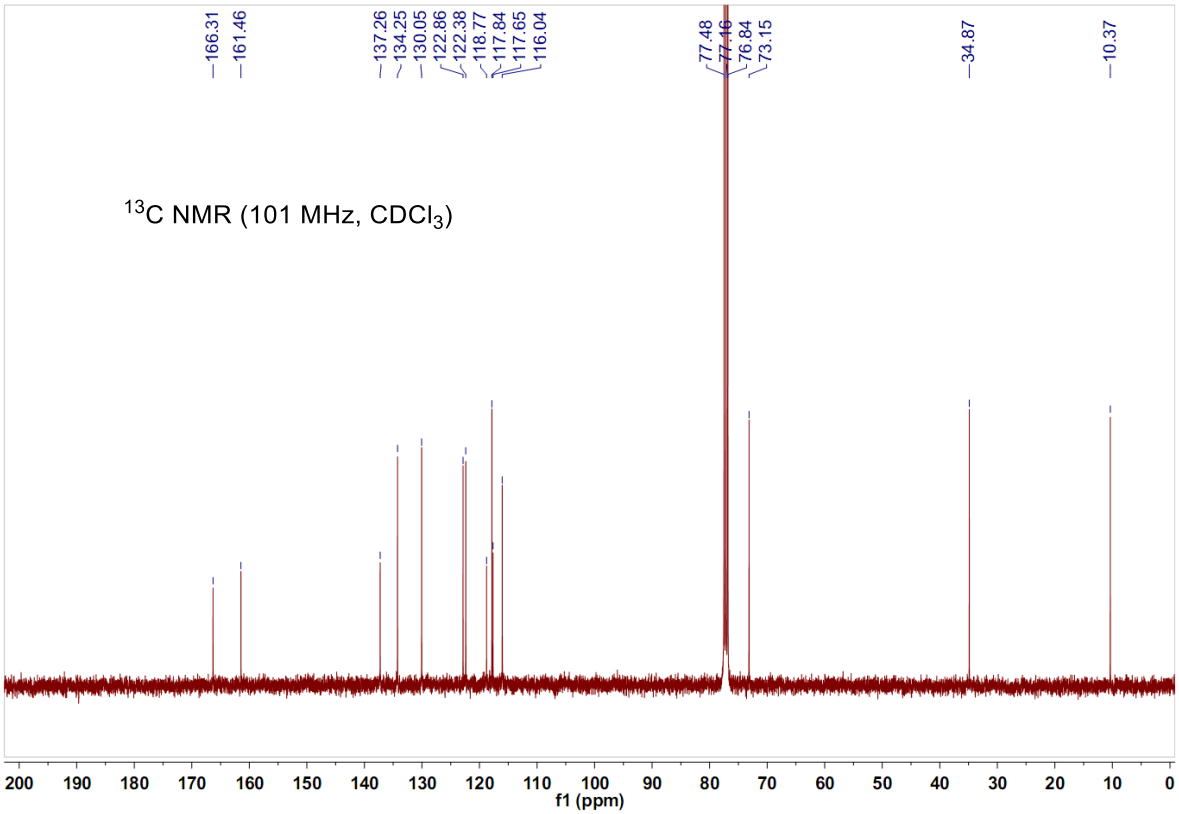


4-(but-3-en-1-yloxy)-3-methylquinolin-2(1*H*)-one (5b):

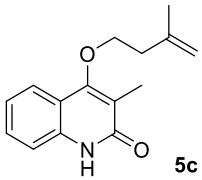


5b

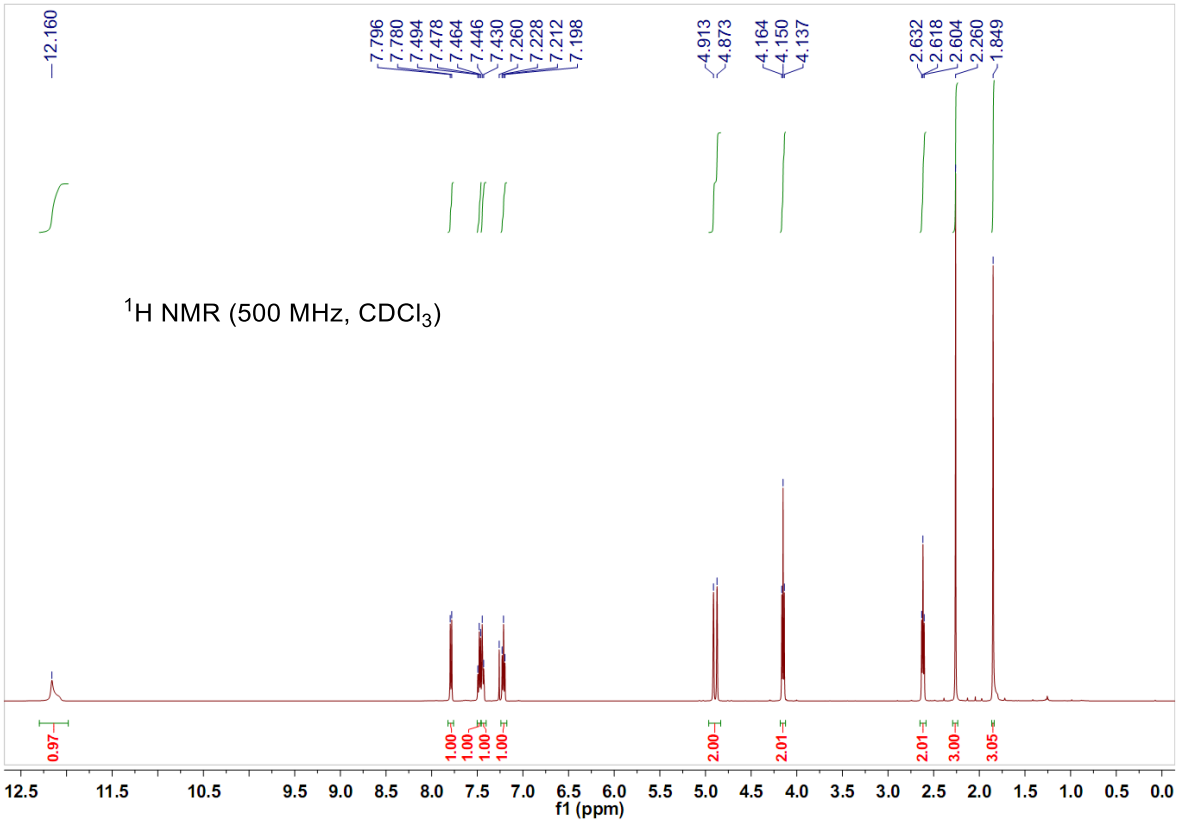


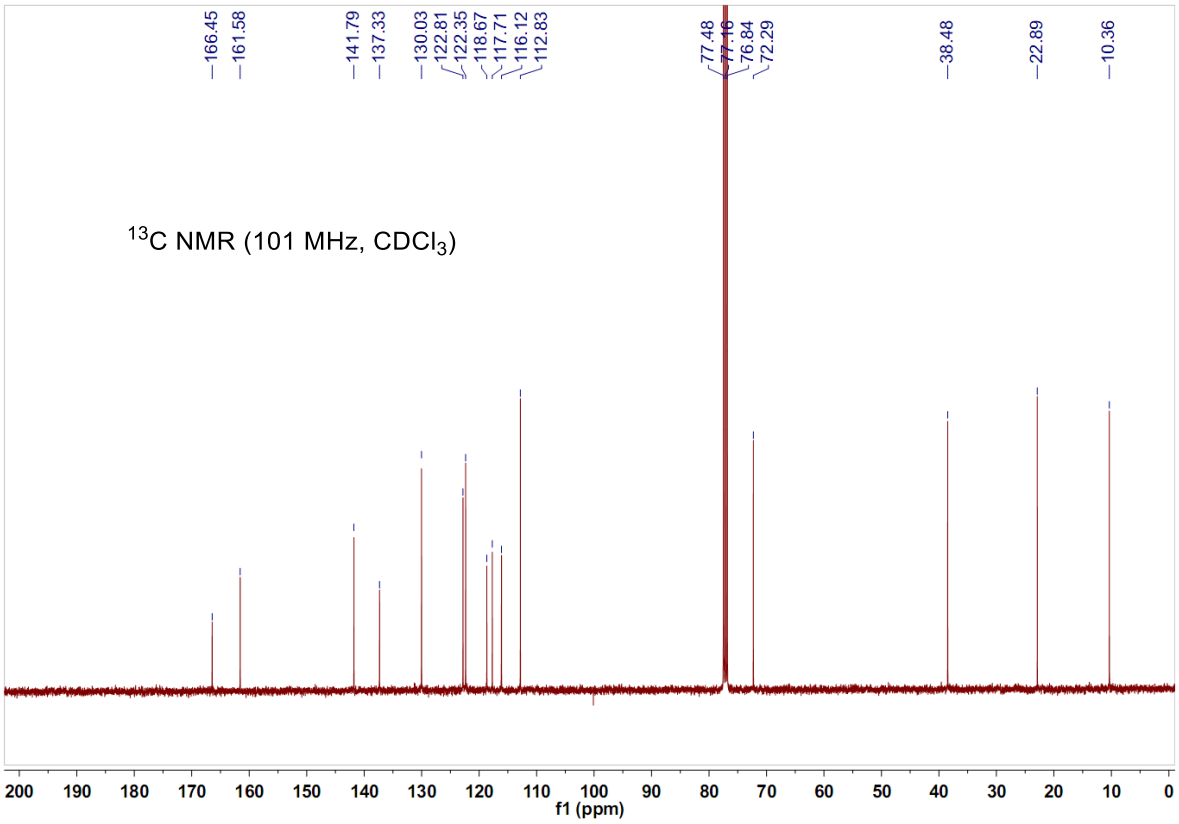


3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5c):

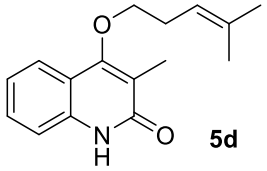

O
N
H
O

5c

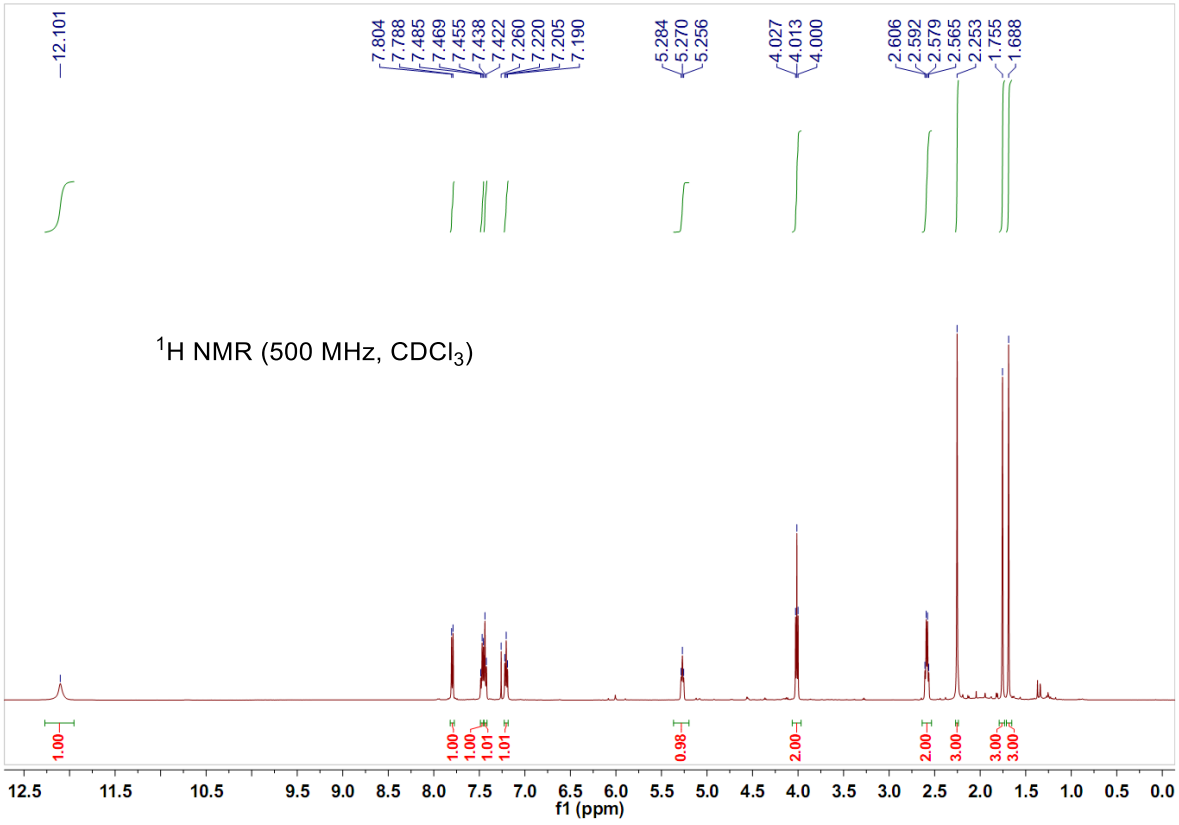

12.160
7.796
7.780
7.494
7.478
7.464
7.446
7.430
7.260
7.228
7.212
7.198
4.913
4.873
4.164
4.150
4.137
2.632
2.618
2.604
2.260
1.849
^{1}H NMR (500 MHz, CDCl$_3$)
0.97
1.00
1.00
1.00
1.00
2.00
2.01
2.01
3.00
3.05
f1 (ppm)

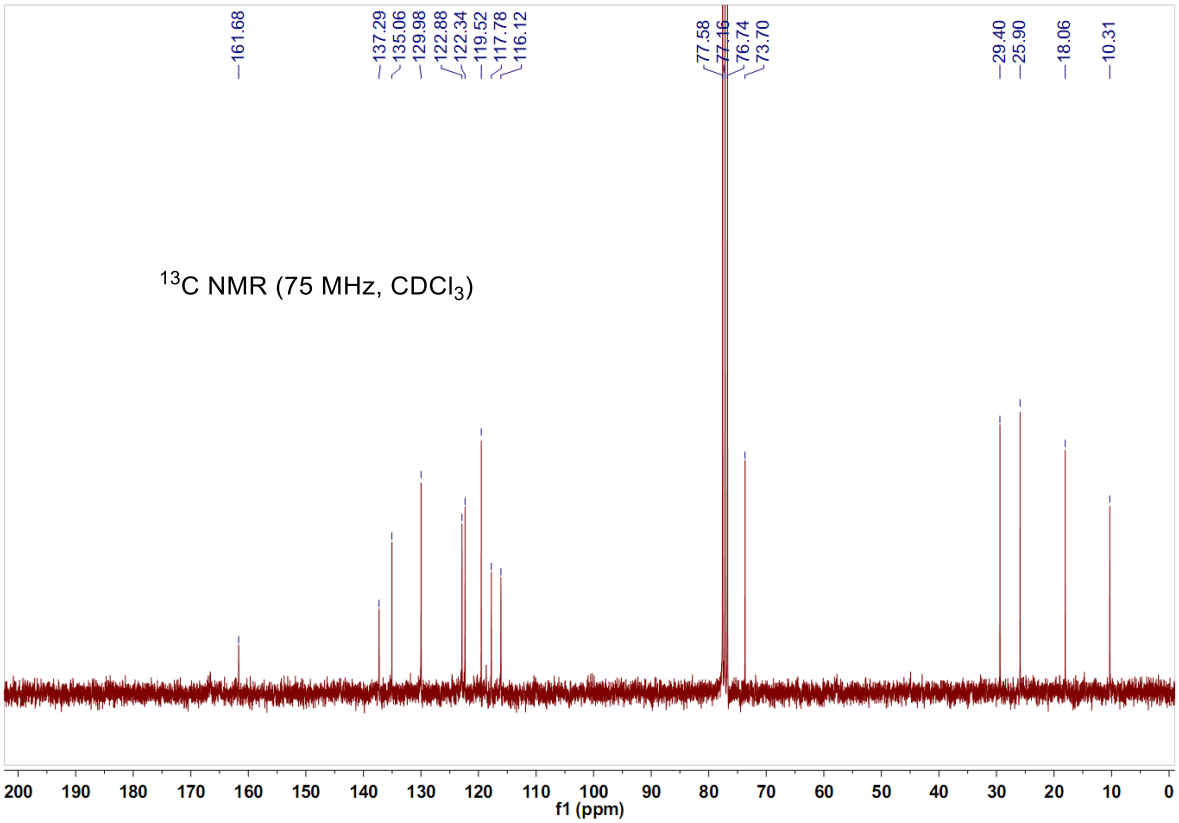

166.45
161.58
141.79
137.33
130.03
122.81
122.35
118.67
117.71
116.12
112.83
77.48
77.16
76.84
72.29
38.48
22.89
10.36
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

3-methyl-4-((4-methylpent-3-en-1-yl)oxy)quinolin-2(1H)-one (5d):

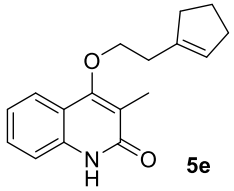


5d

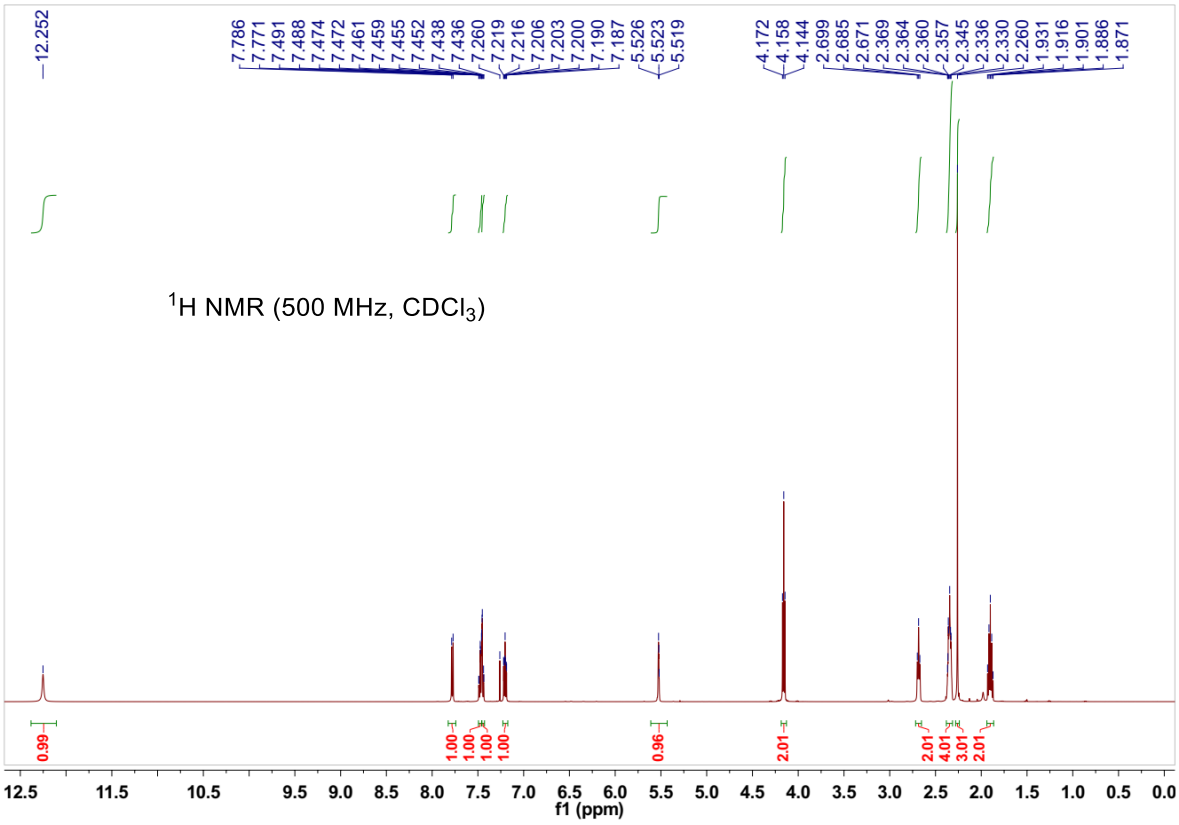




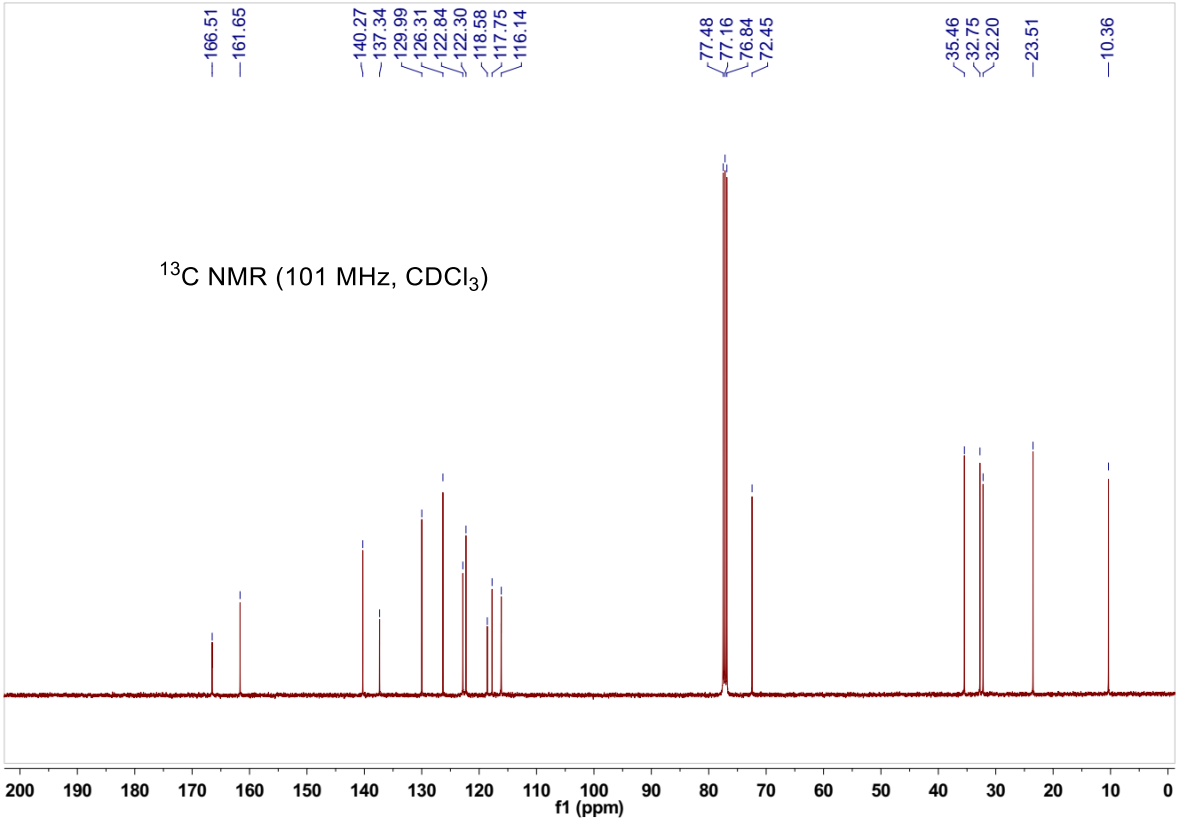
4-(2-(cyclopent-1-en-1-yl)ethoxy)-3-methylquinolin-2(1*H*)-one (5e):



5e

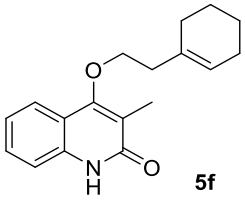


^{1}H NMR (500 MHz, $CDCl_3$)

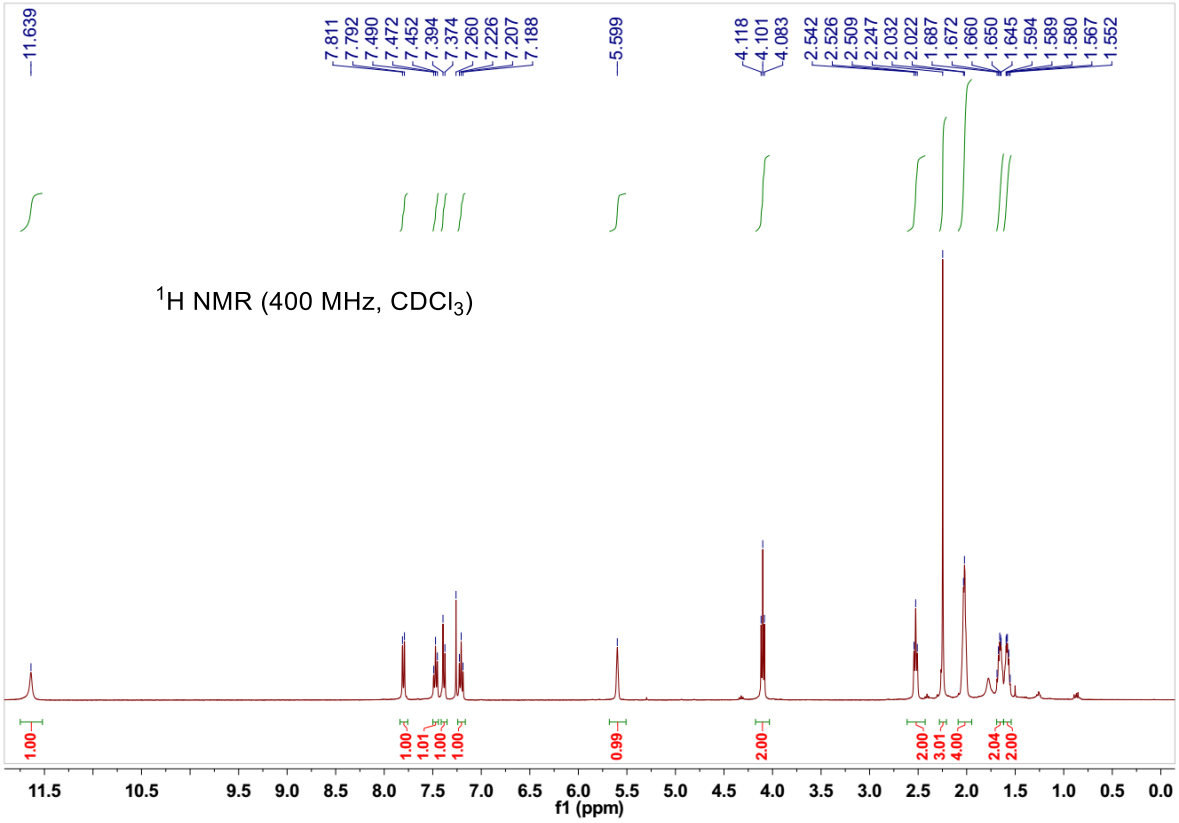


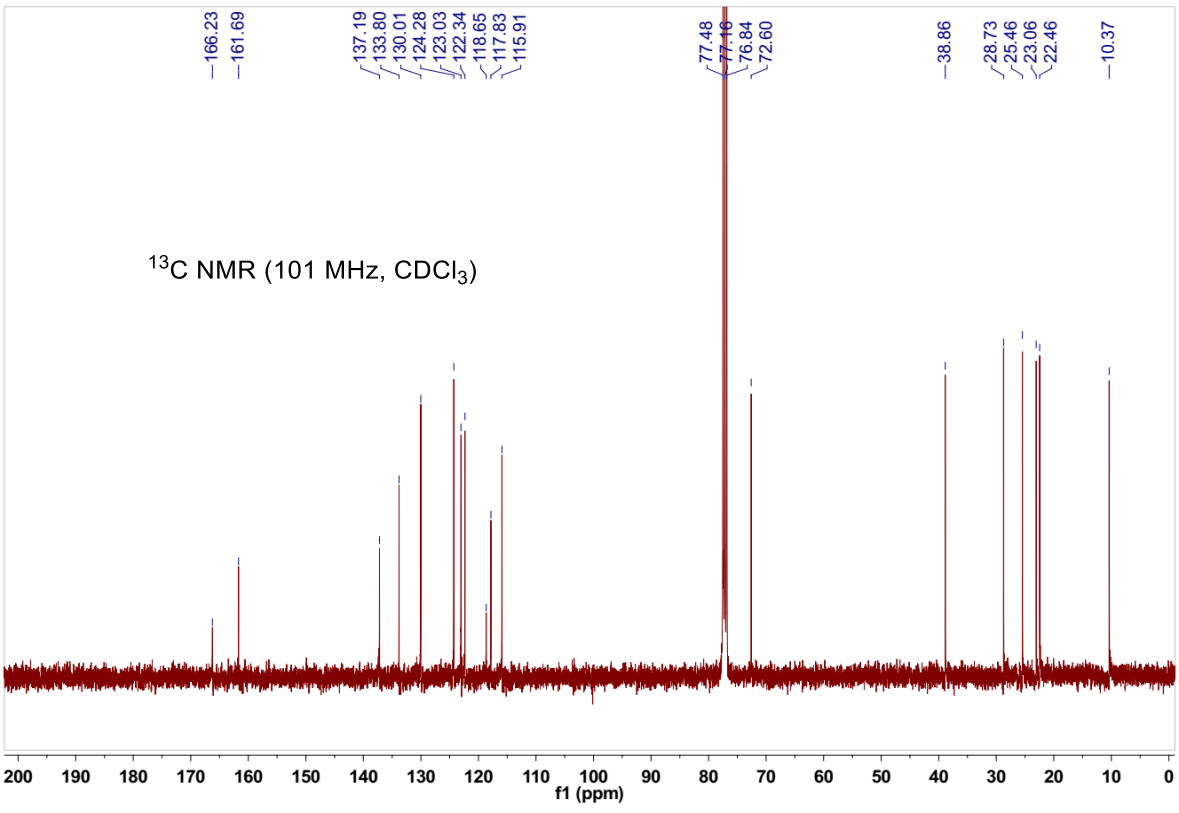
^{13}C NMR (101 MHz, $CDCl_3$)

4-(2-(cyclohex-1-en-1-yl)ethoxy)-3-methylquinolin-2(1*H*)-one (5f):

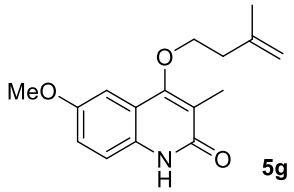


5f

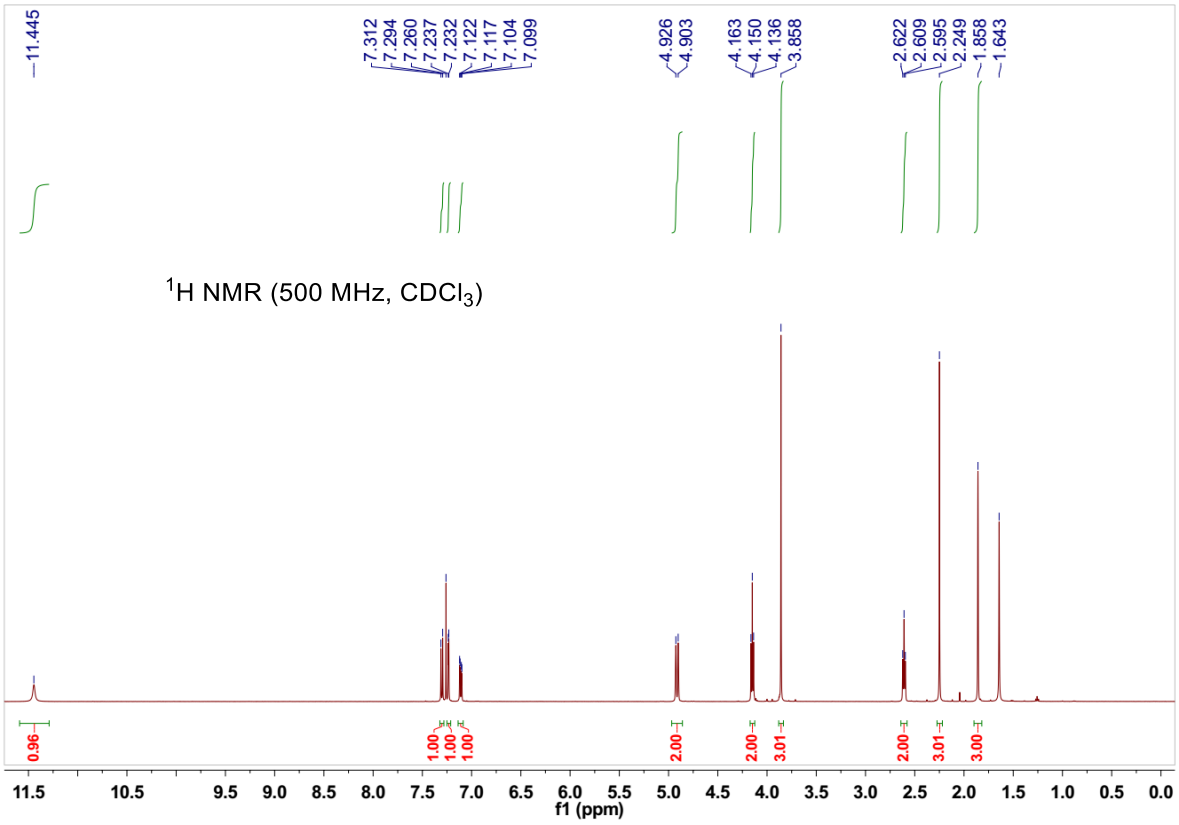


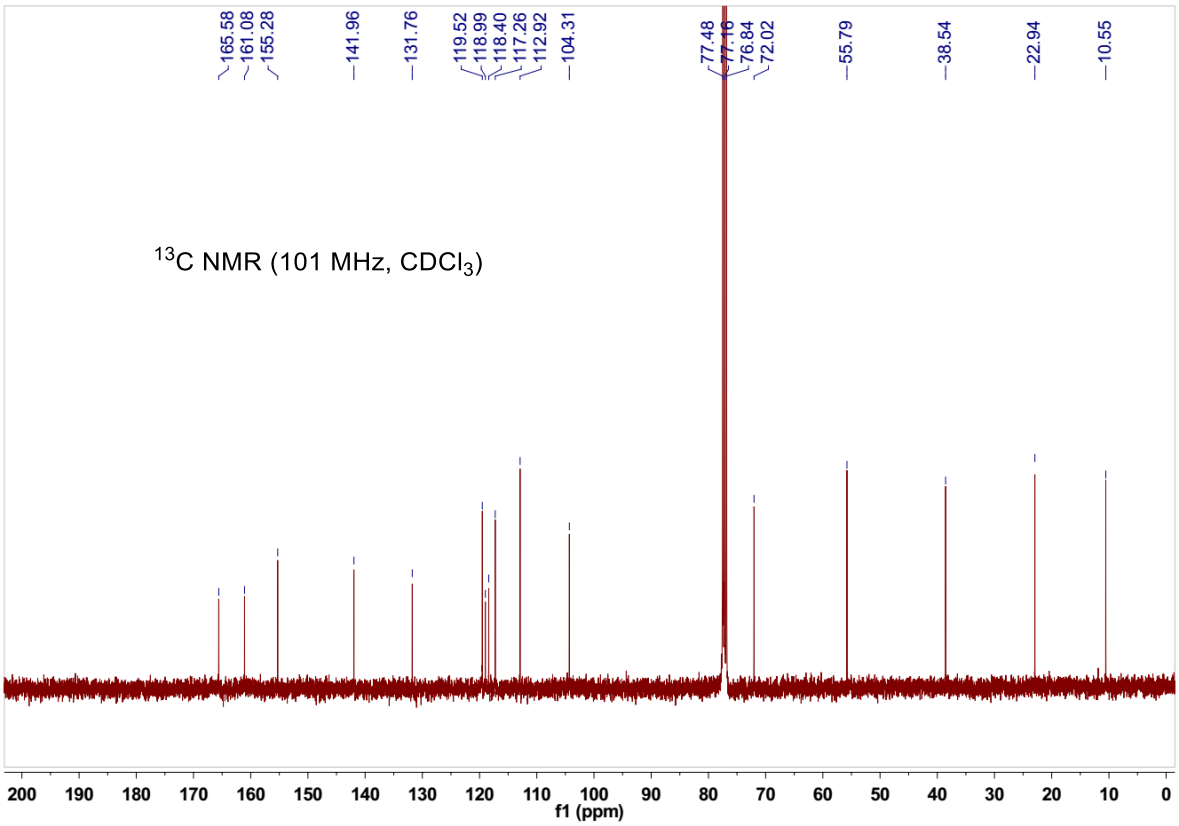


6-methoxy-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5g):

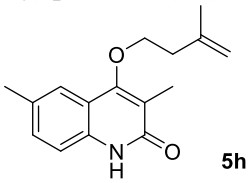


5g

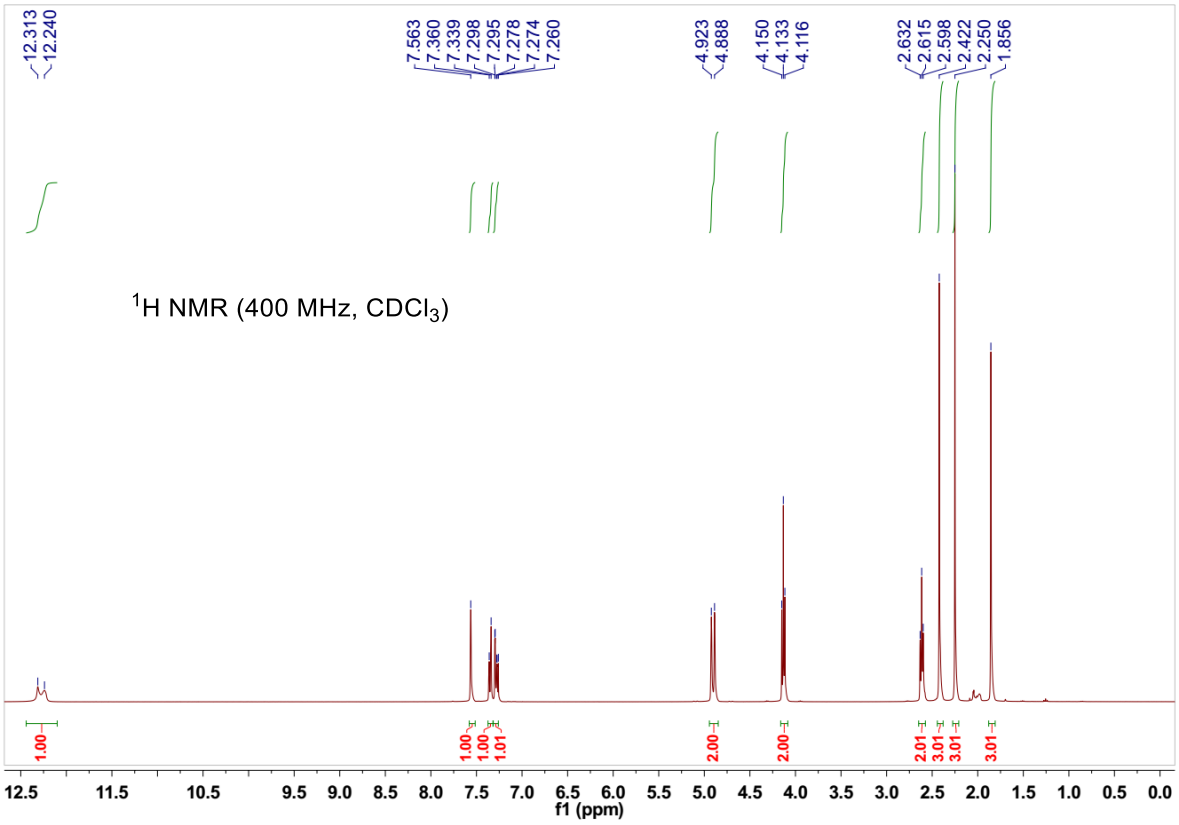


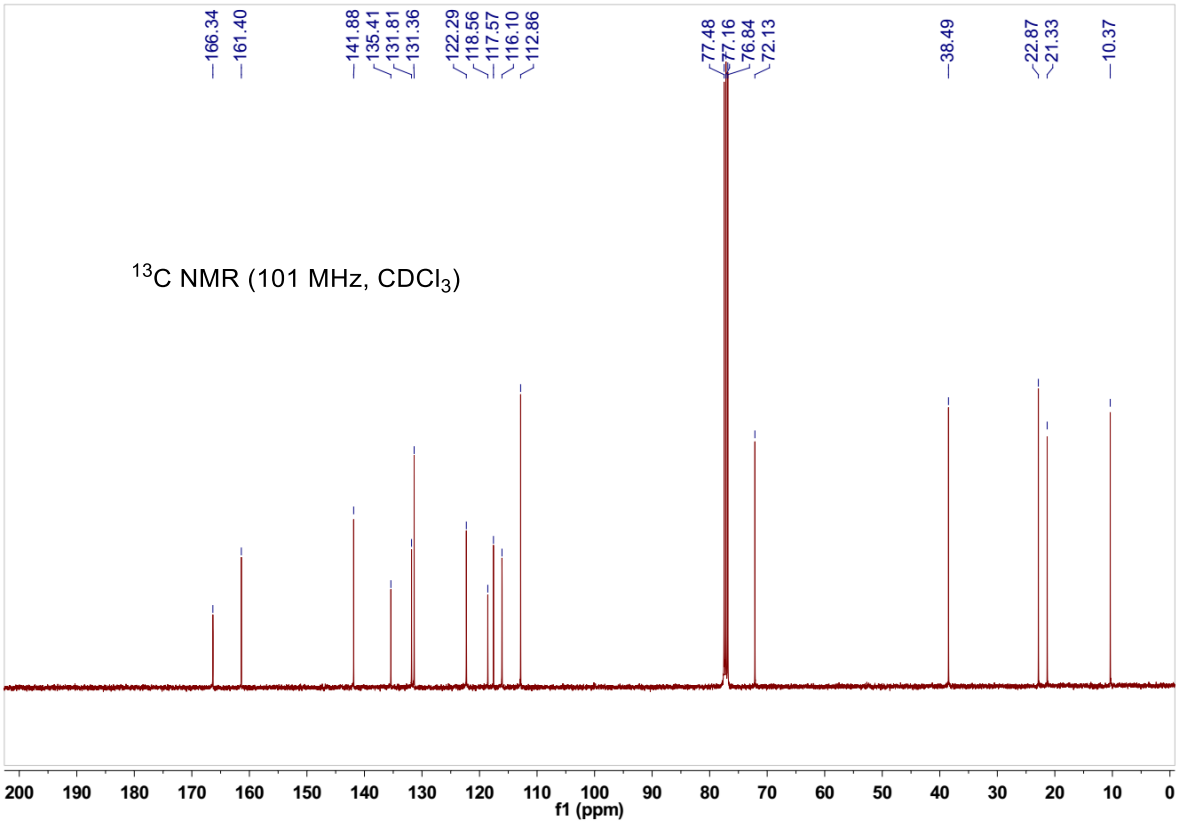


3,6-dimethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5h):

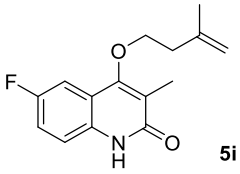


5h

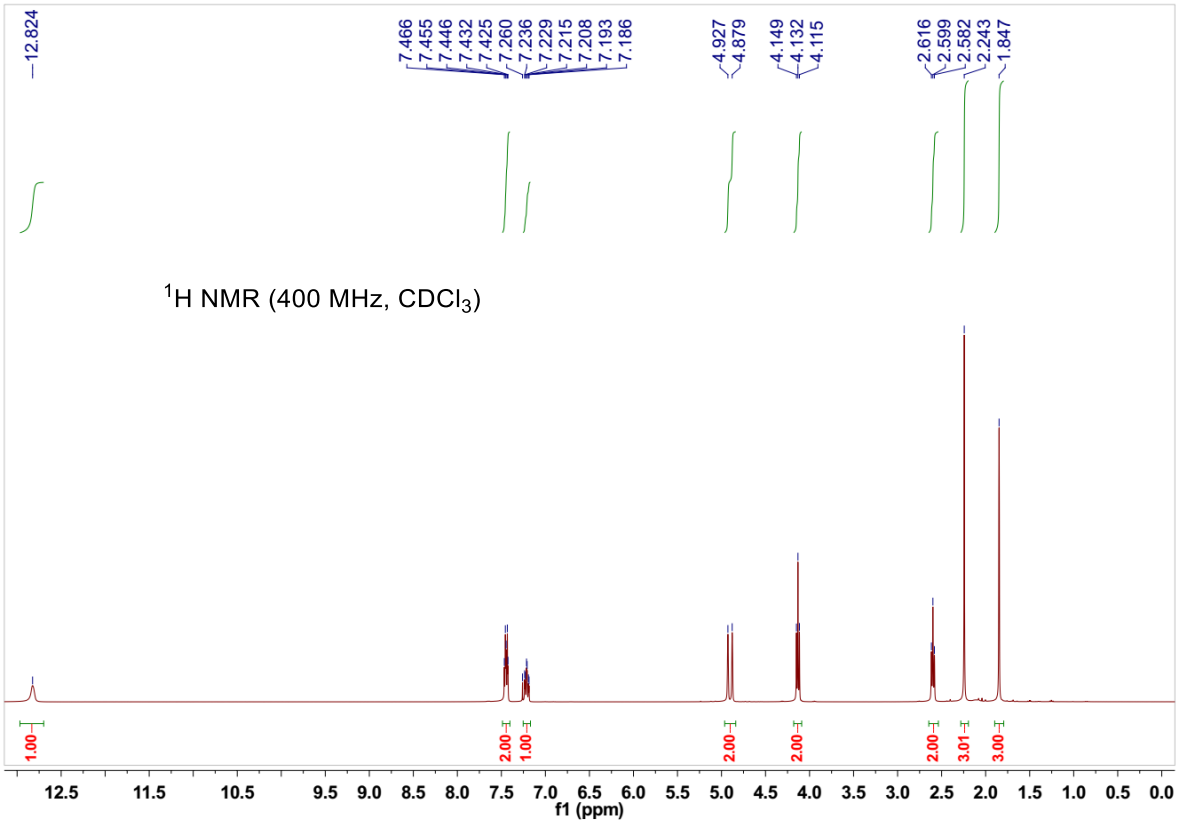


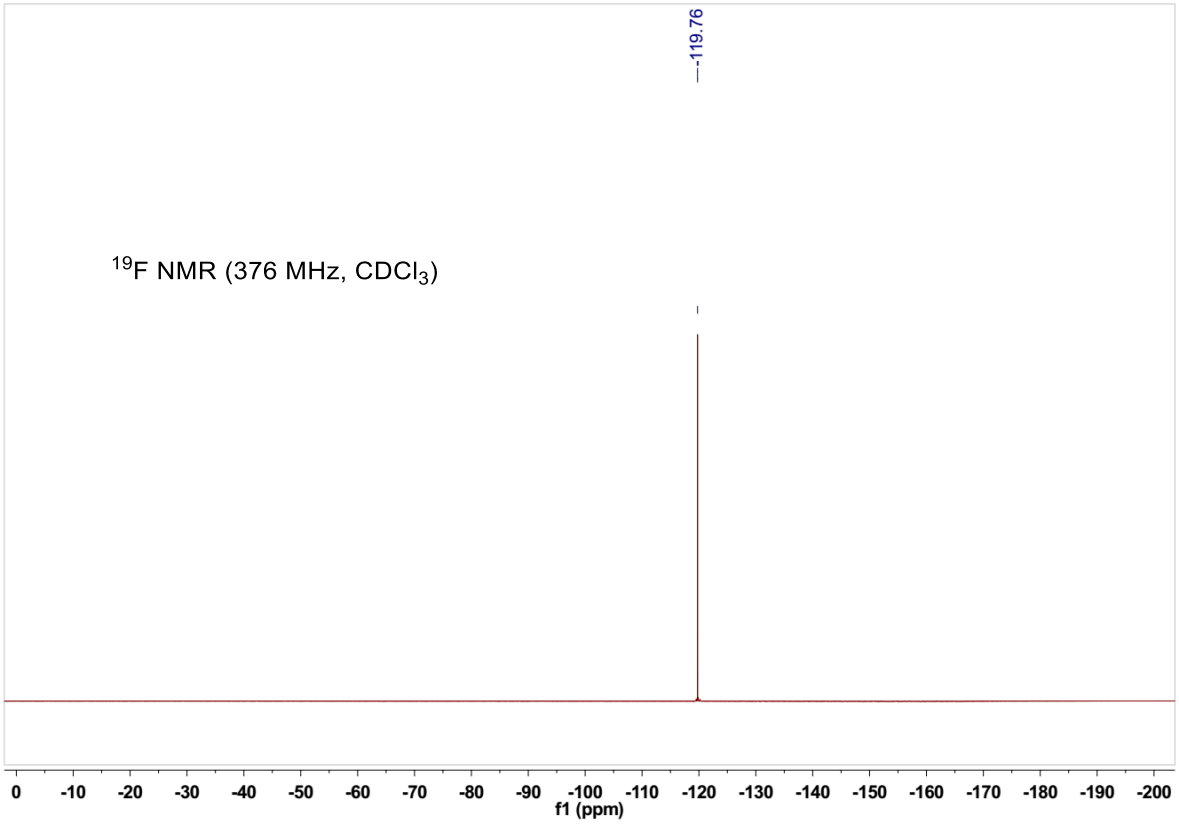


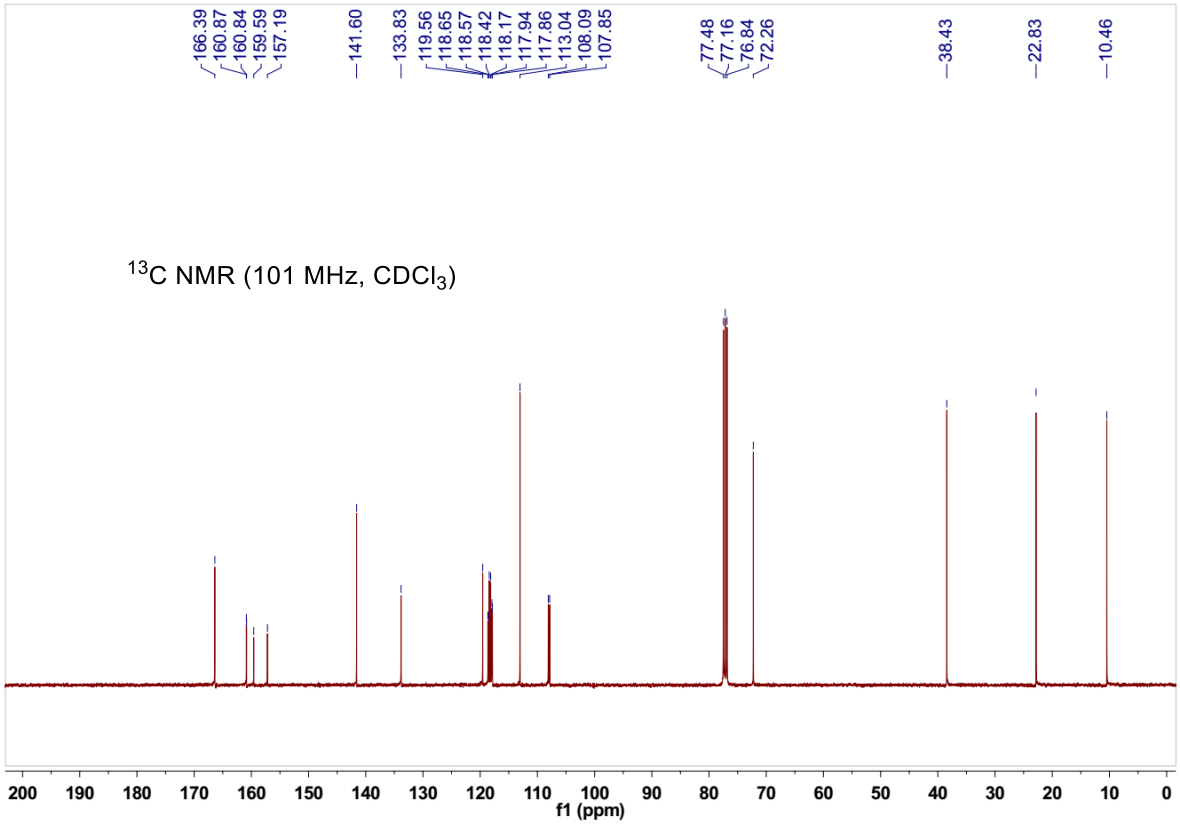
6-fluoro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5i):



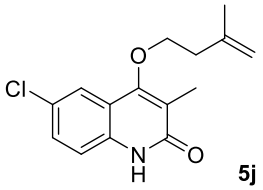
5i



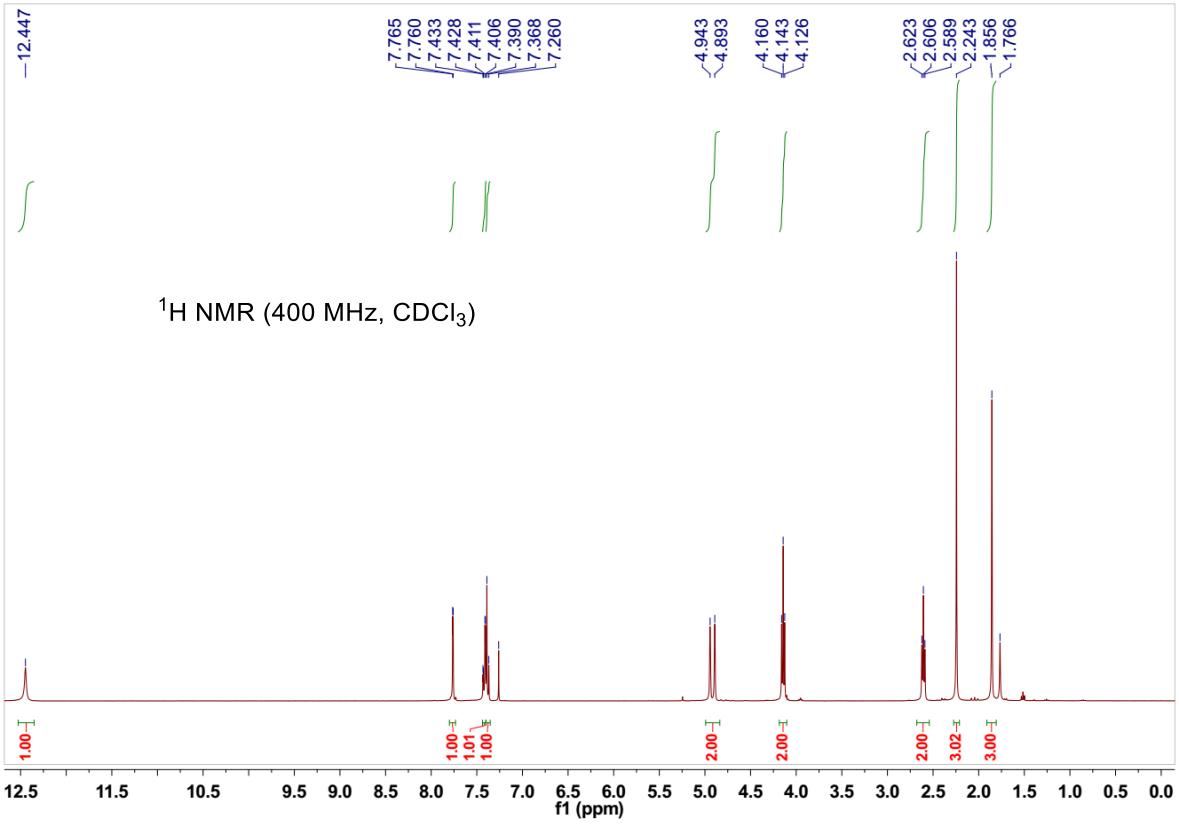


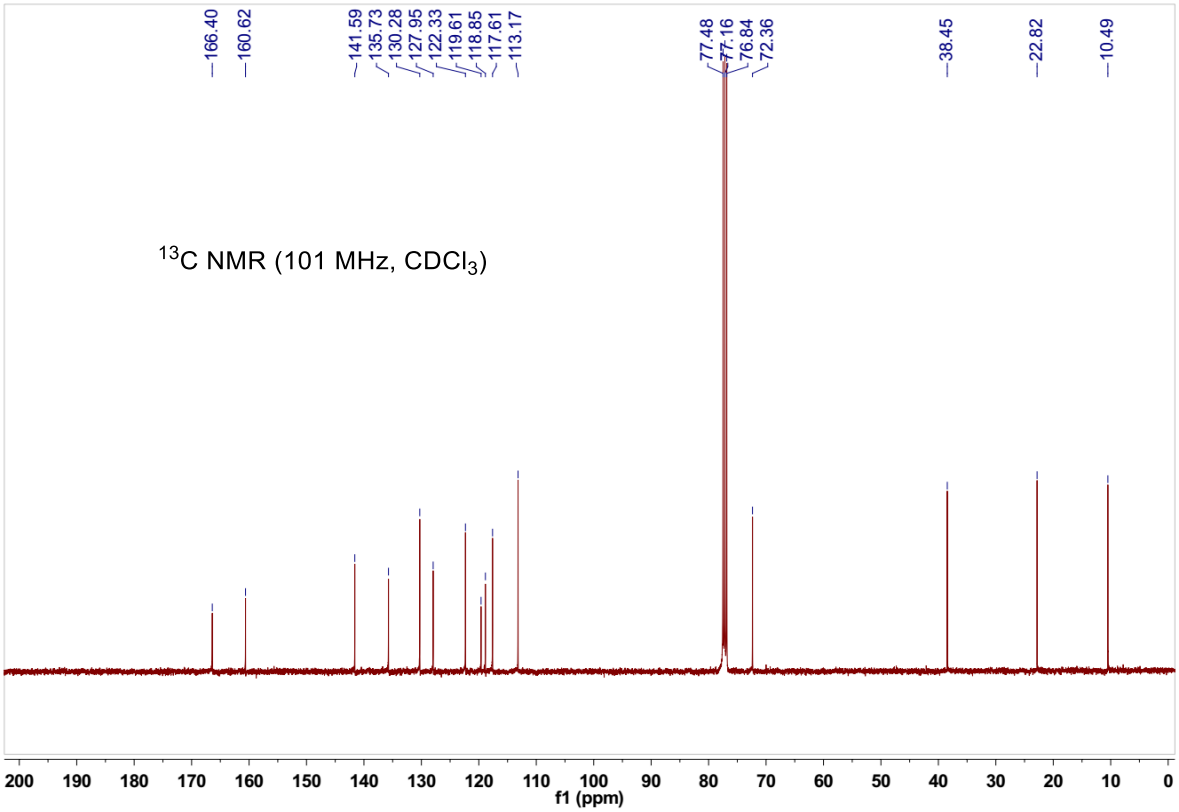

166.39
160.87
160.84
159.59
157.19
141.60
133.83
119.56
118.65
118.57
118.42
118.17
117.94
117.86
113.04
108.09
107.85
77.48
77.16
76.84
72.26
38.43
22.83
10.46
^{13}C NMR (101 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

6-chloro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5j):

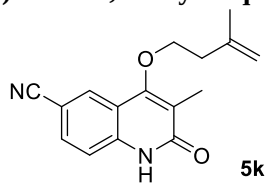


5j

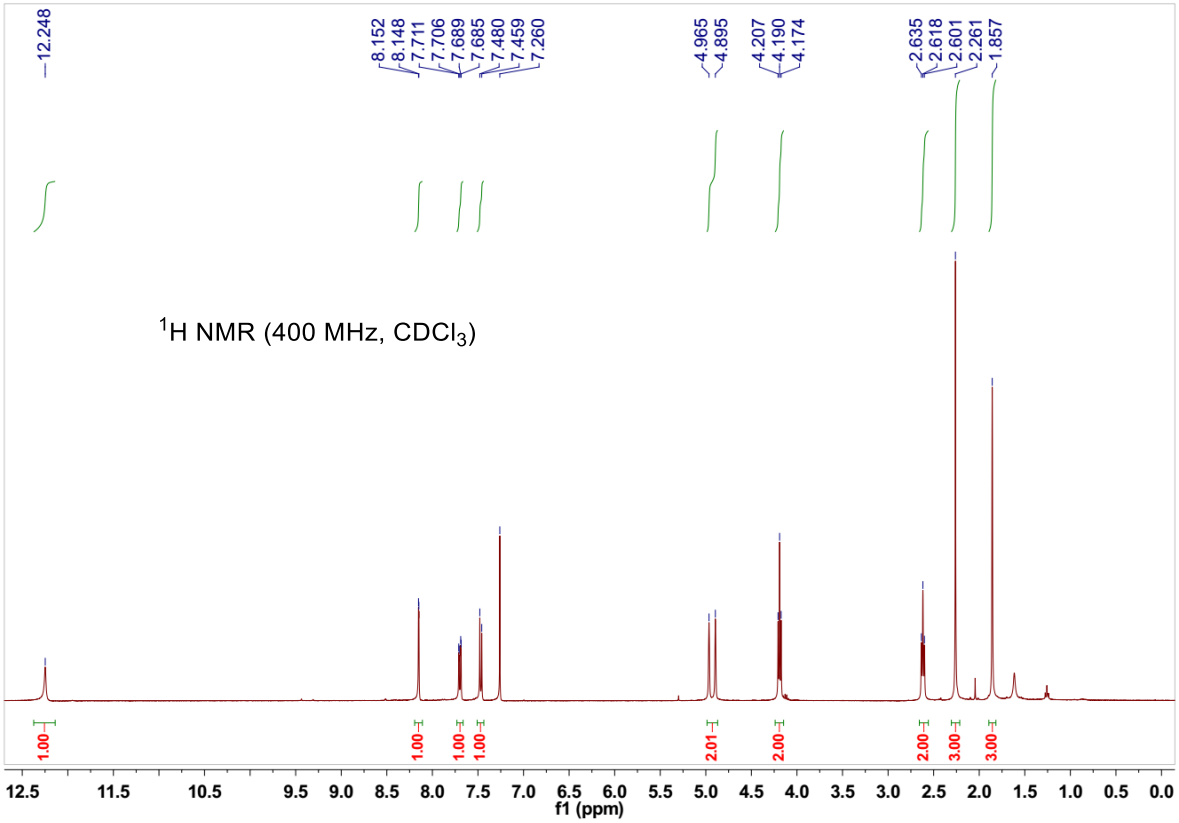


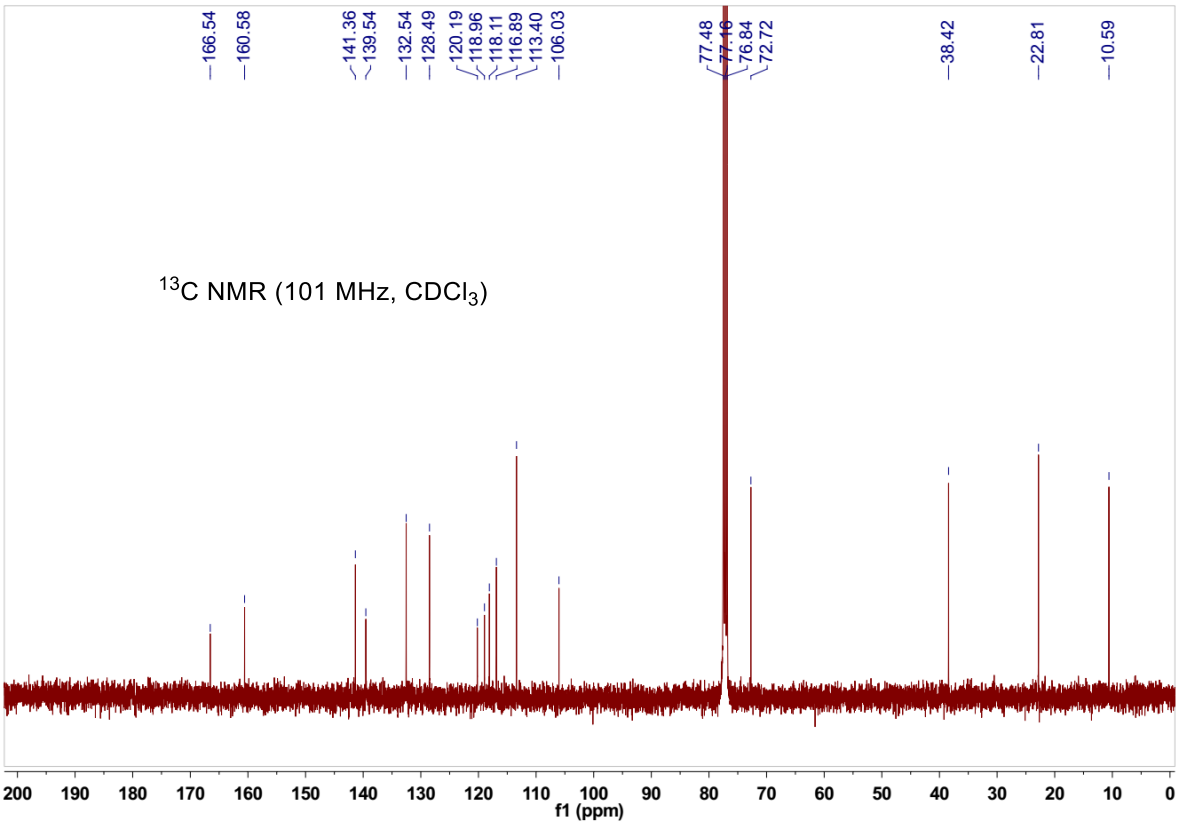


3-methyl-4-((3-methylbut-3-en-1-yl)oxy)-2-oxo-1,2-dihydroquinoline-6-carbonitrile (5k):

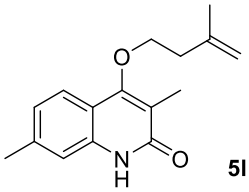


5k

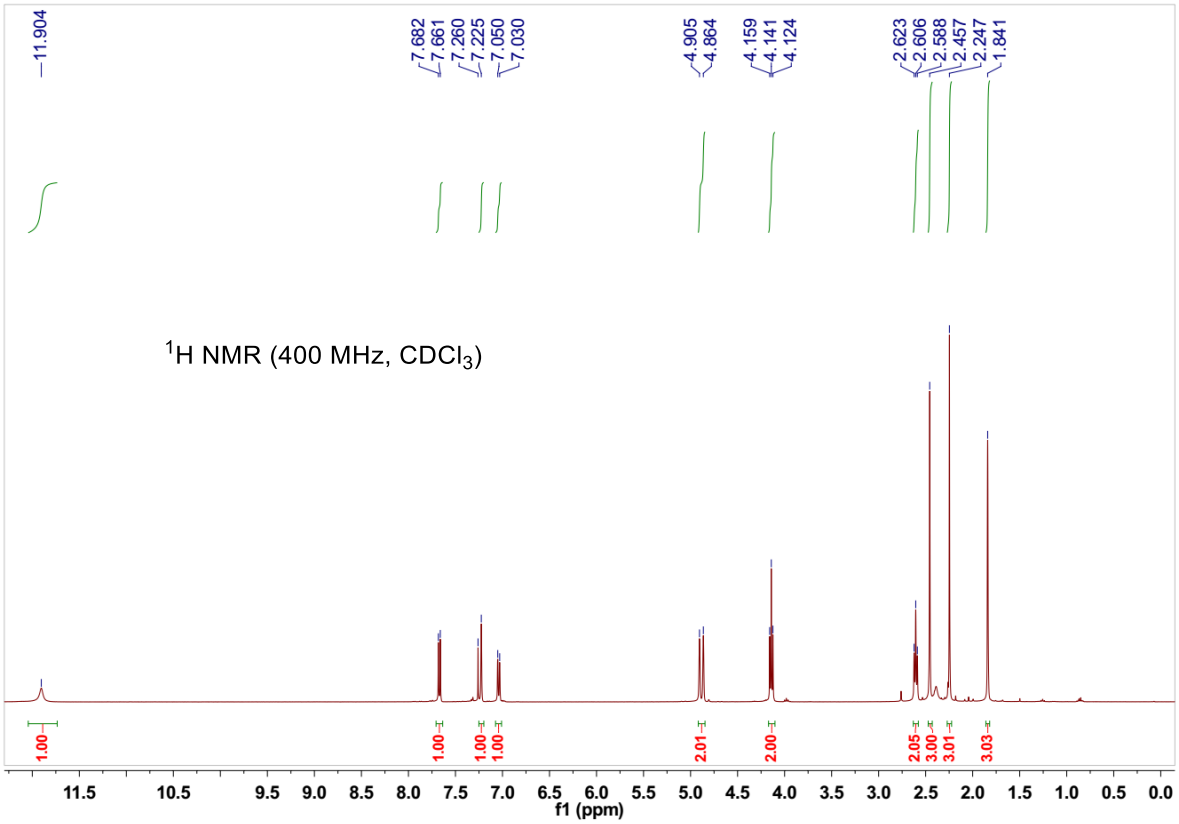


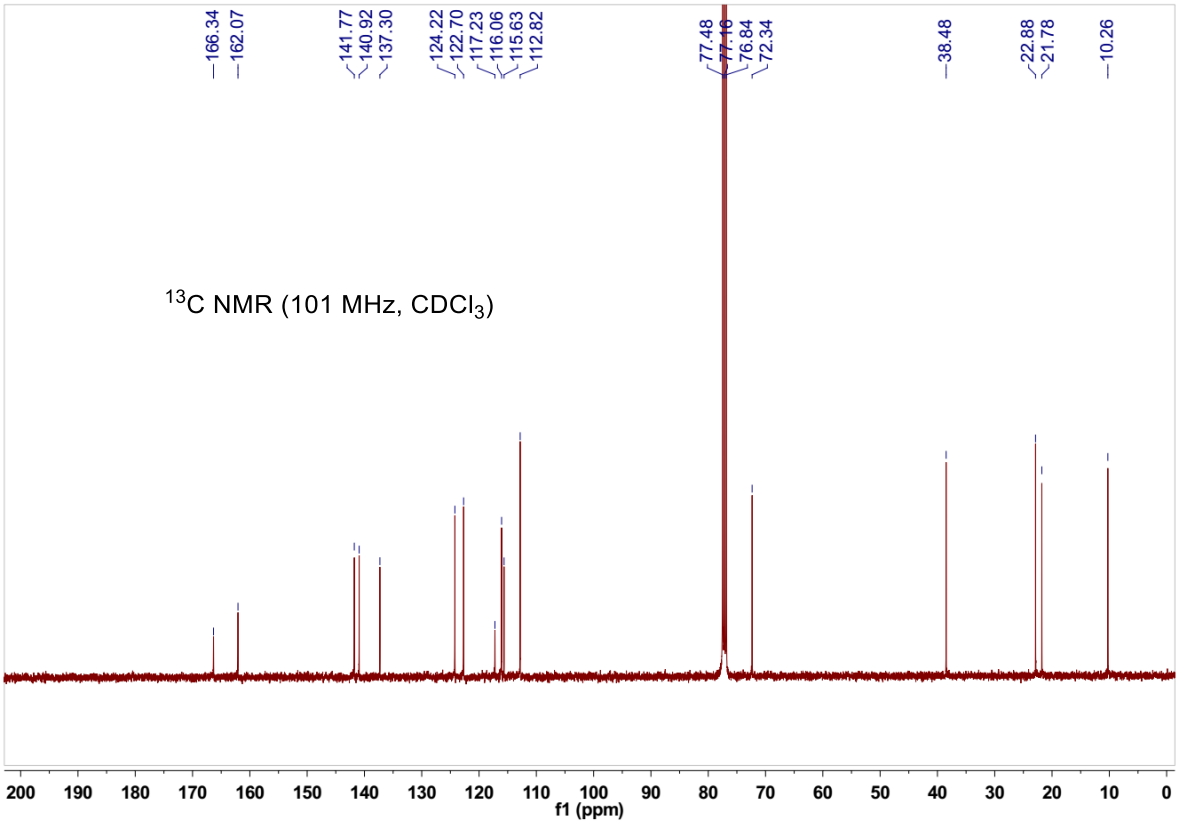


3,7-dimethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5l):

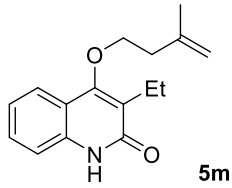


5l

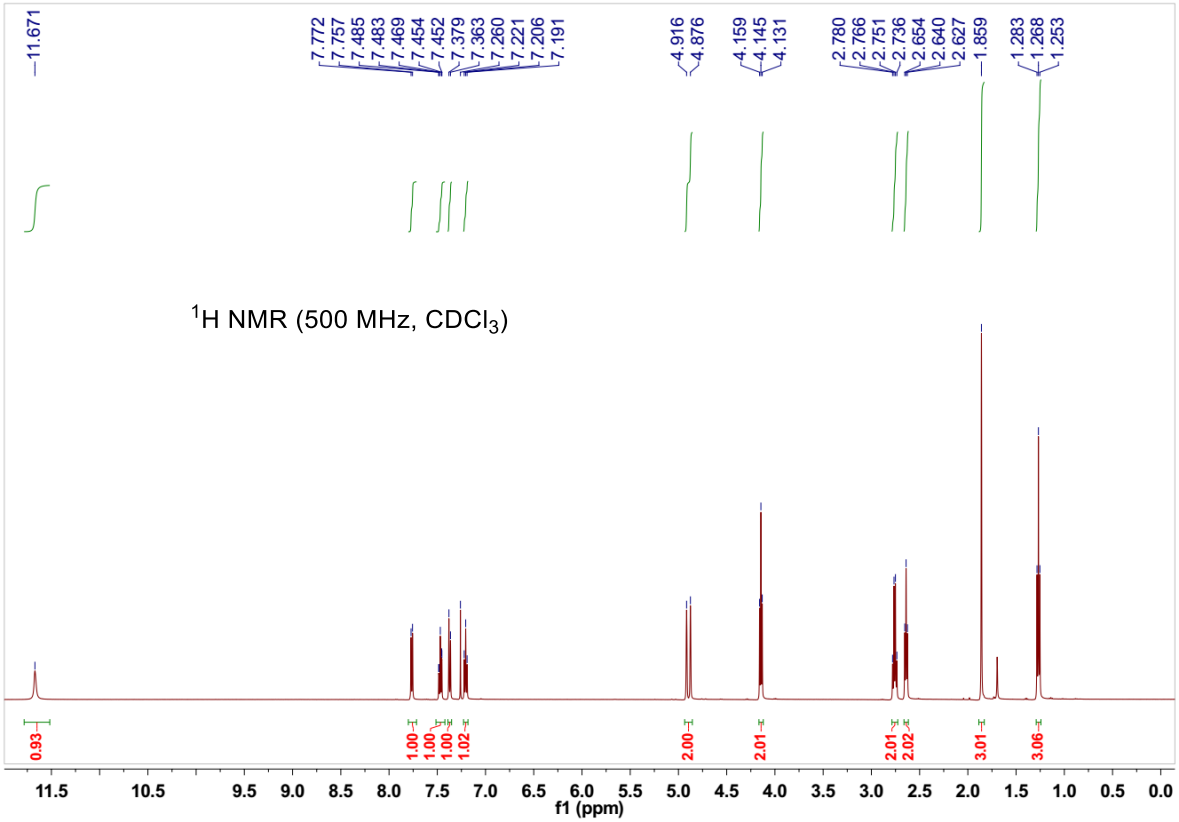


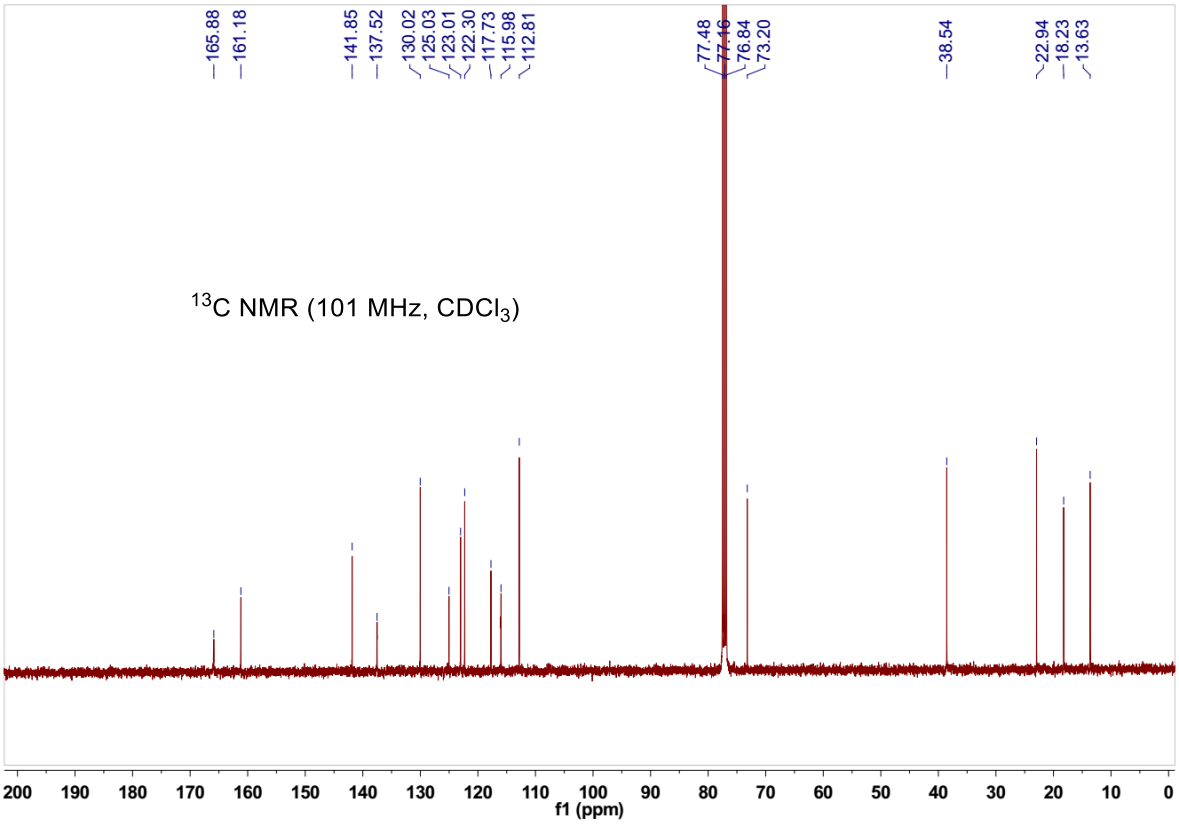


3-ethyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5m):

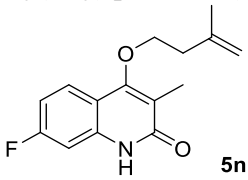


5m

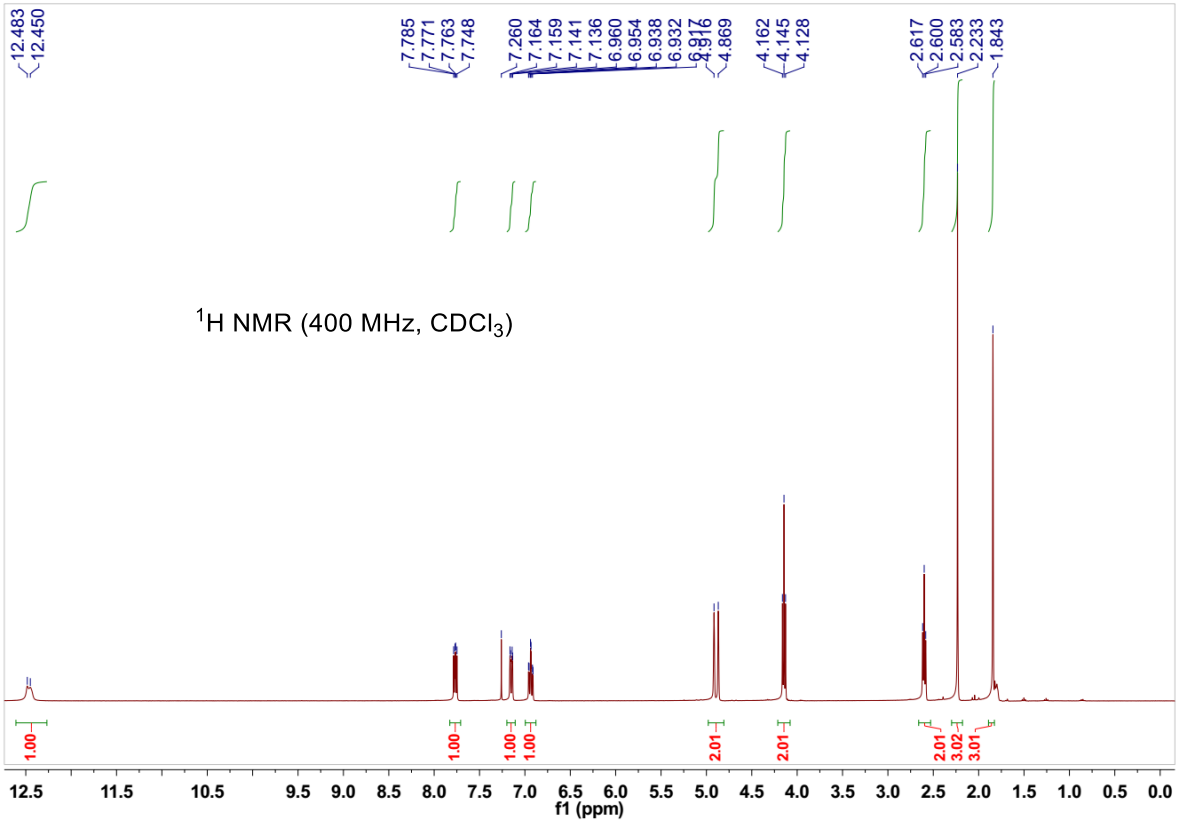


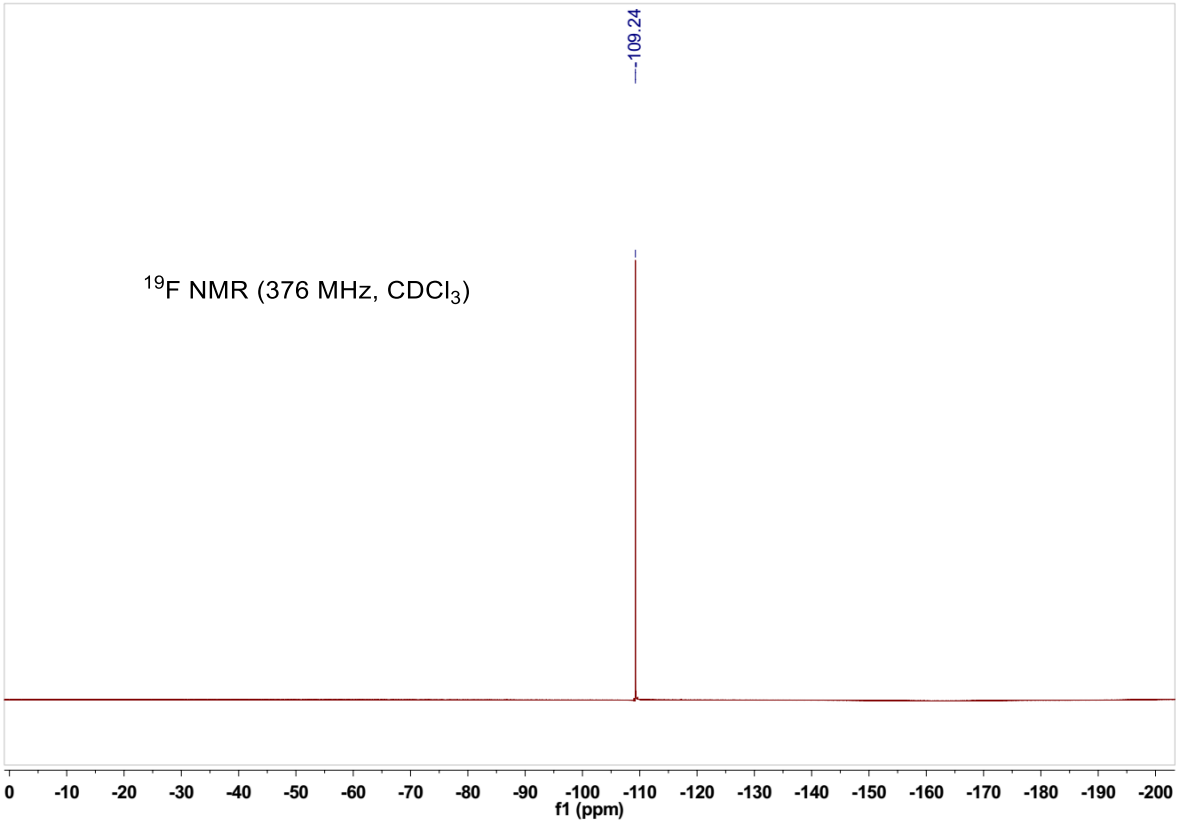


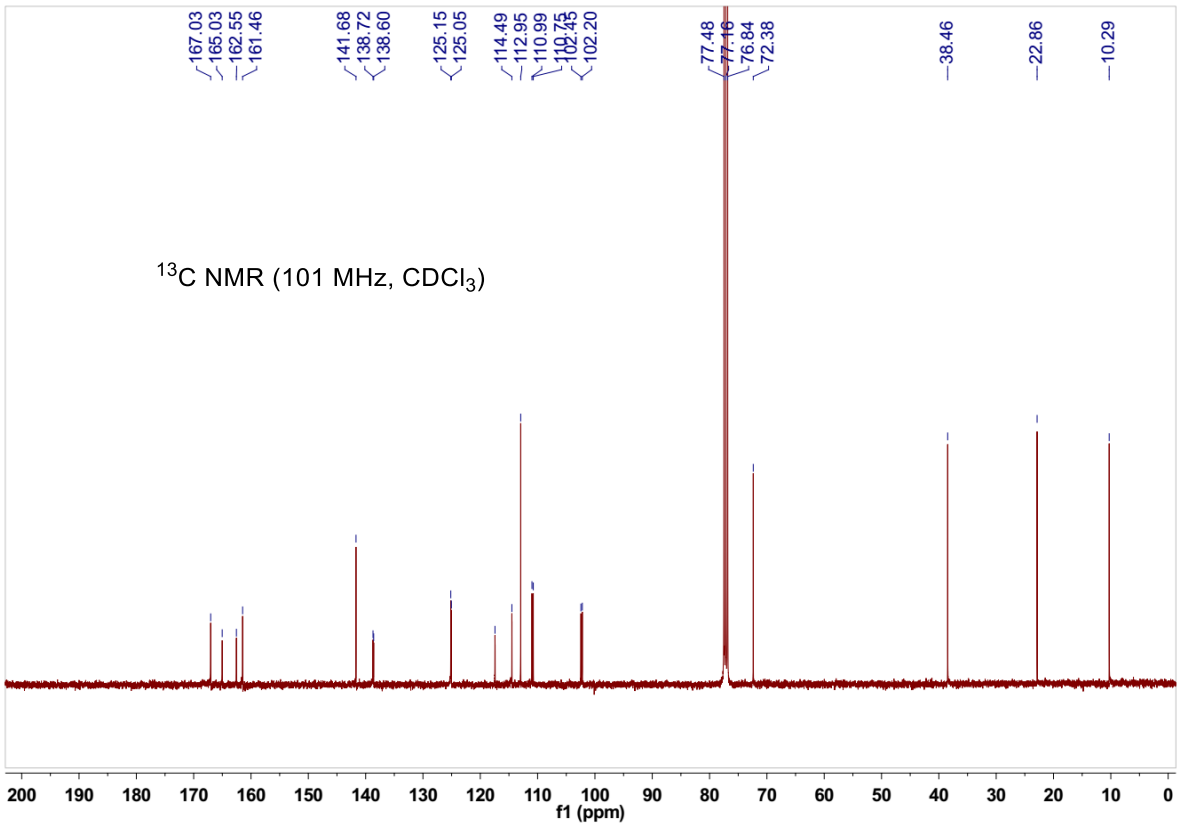
7-fluoro-3-methyl-4-((3-methylbut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (5n):



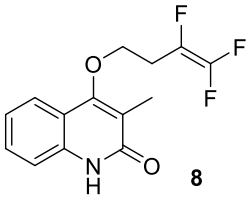
5n



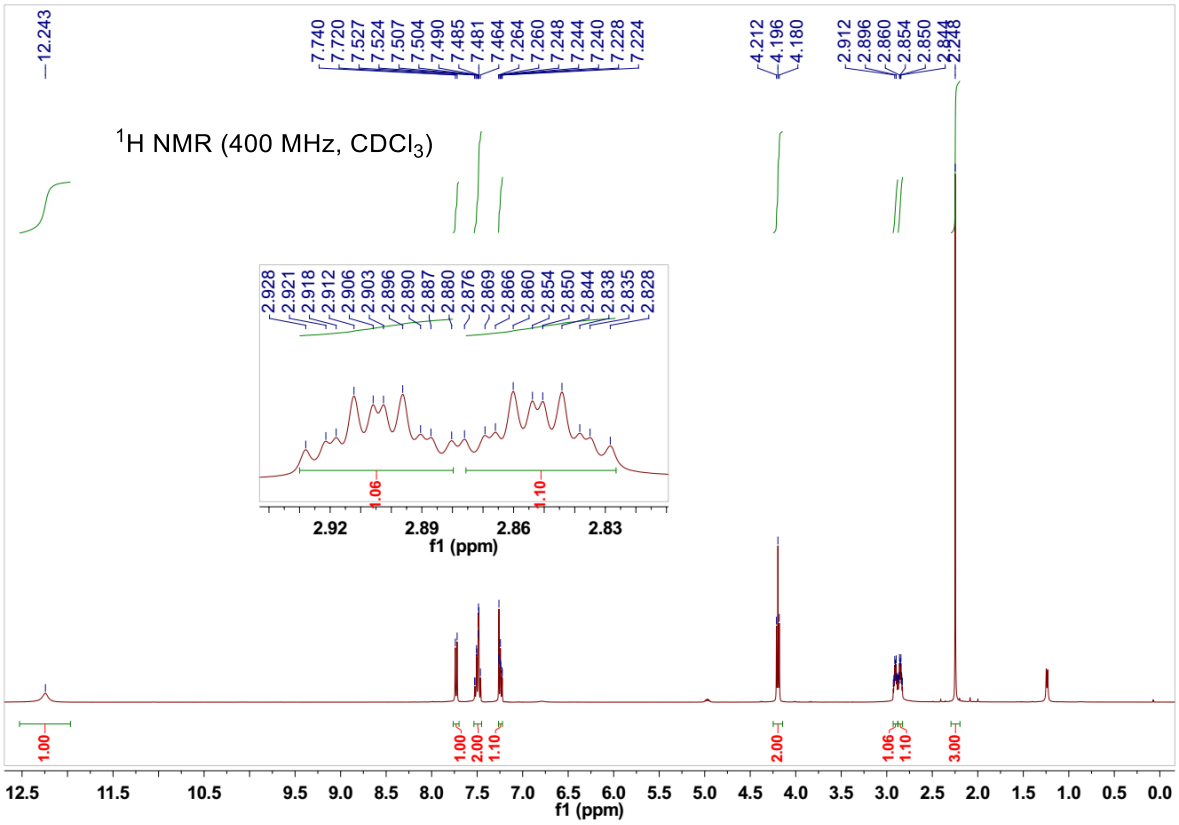


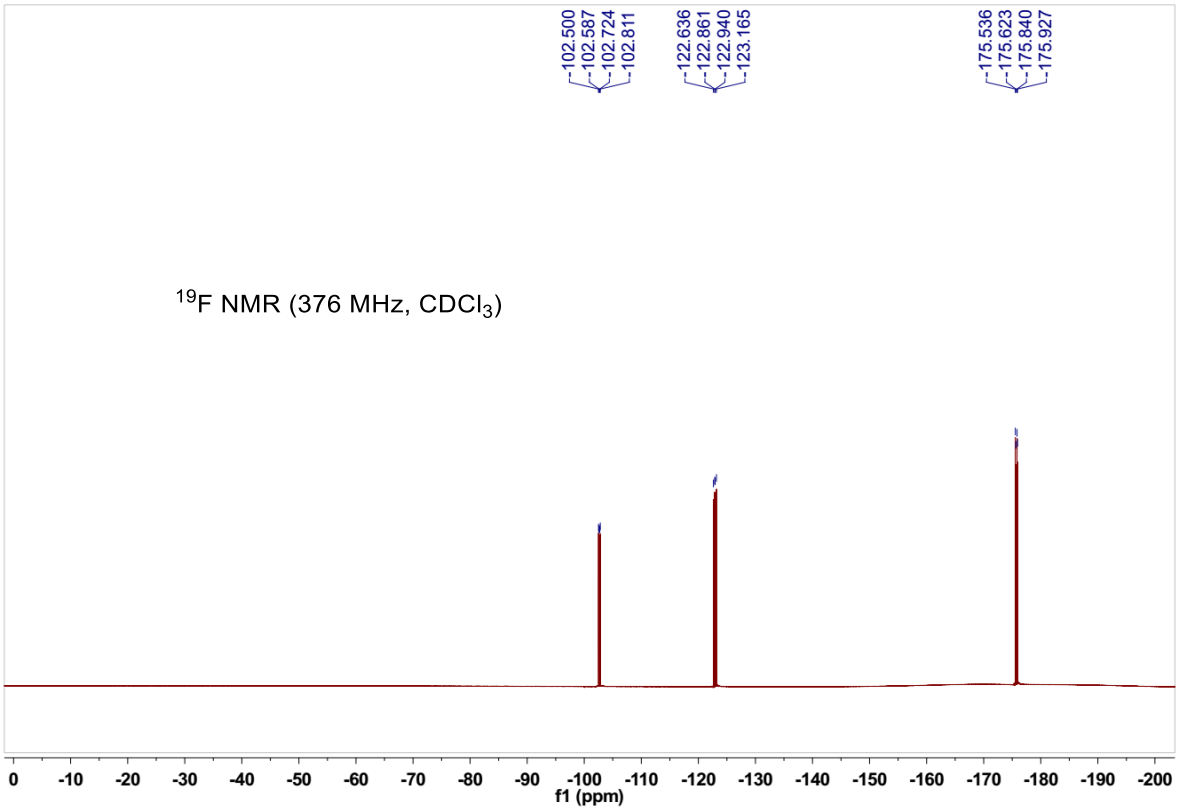

167.03
165.03
162.55
161.46
141.68
138.72
138.60
125.15
125.05
114.49
112.95
110.99
77.48
77.16
76.84
72.38
38.46
22.86
10.29
^{13}C NMR (101 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

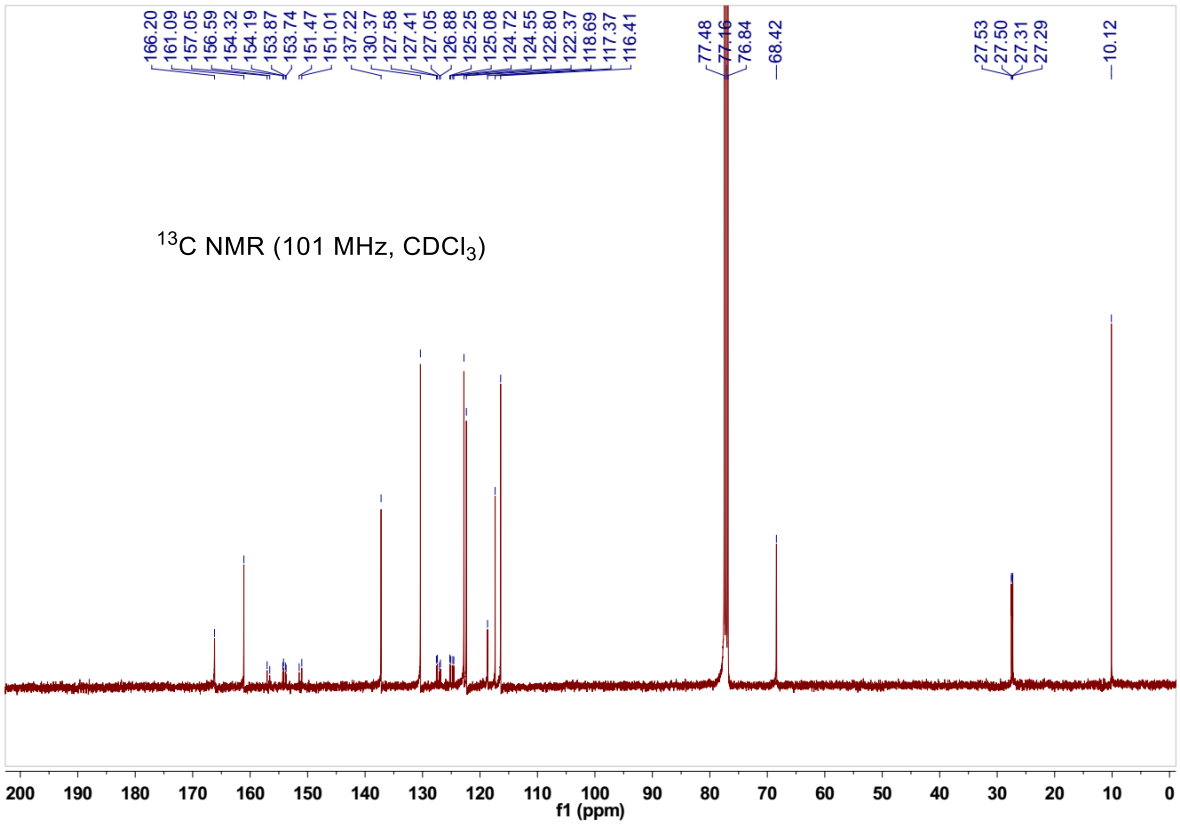
3-methyl-4-((3,4,4-trifluorobut-3-en-1-yl)oxy)quinolin-2(1*H*)-one (8):



8






166.20
161.09
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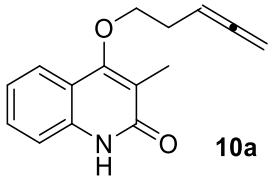
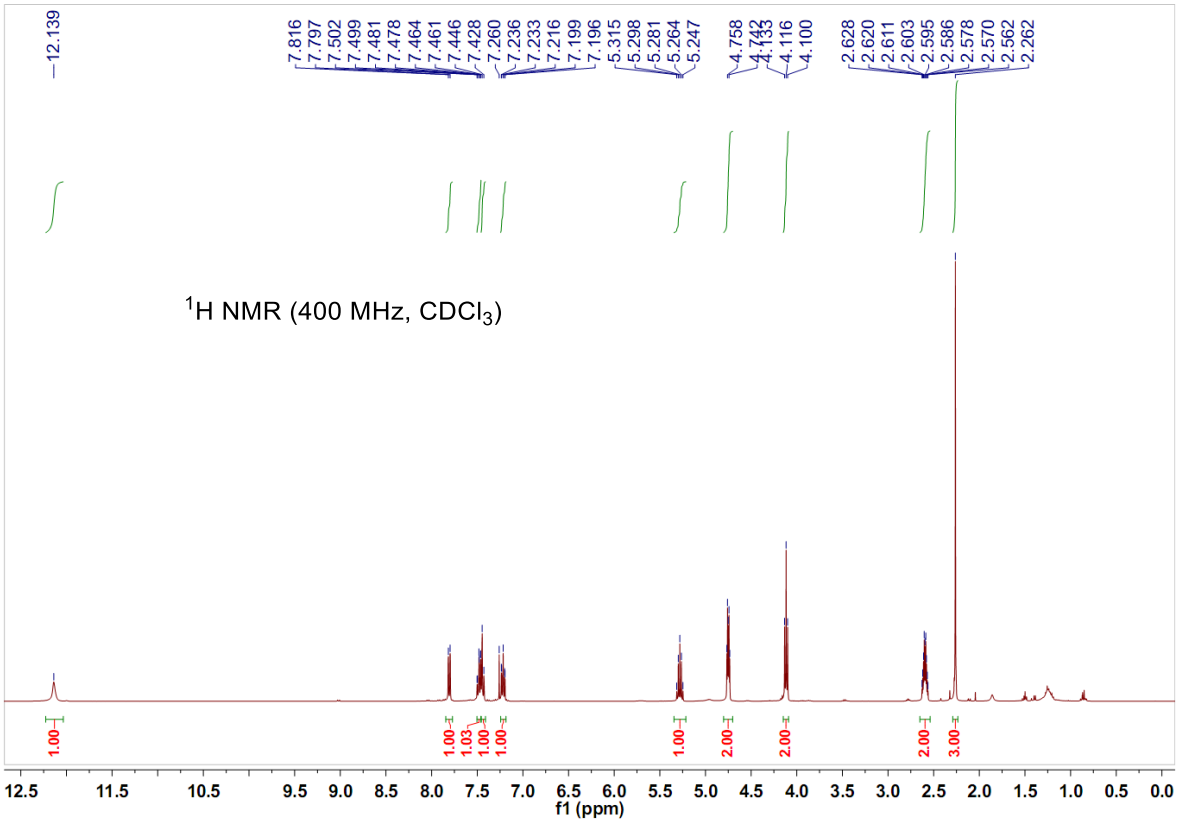
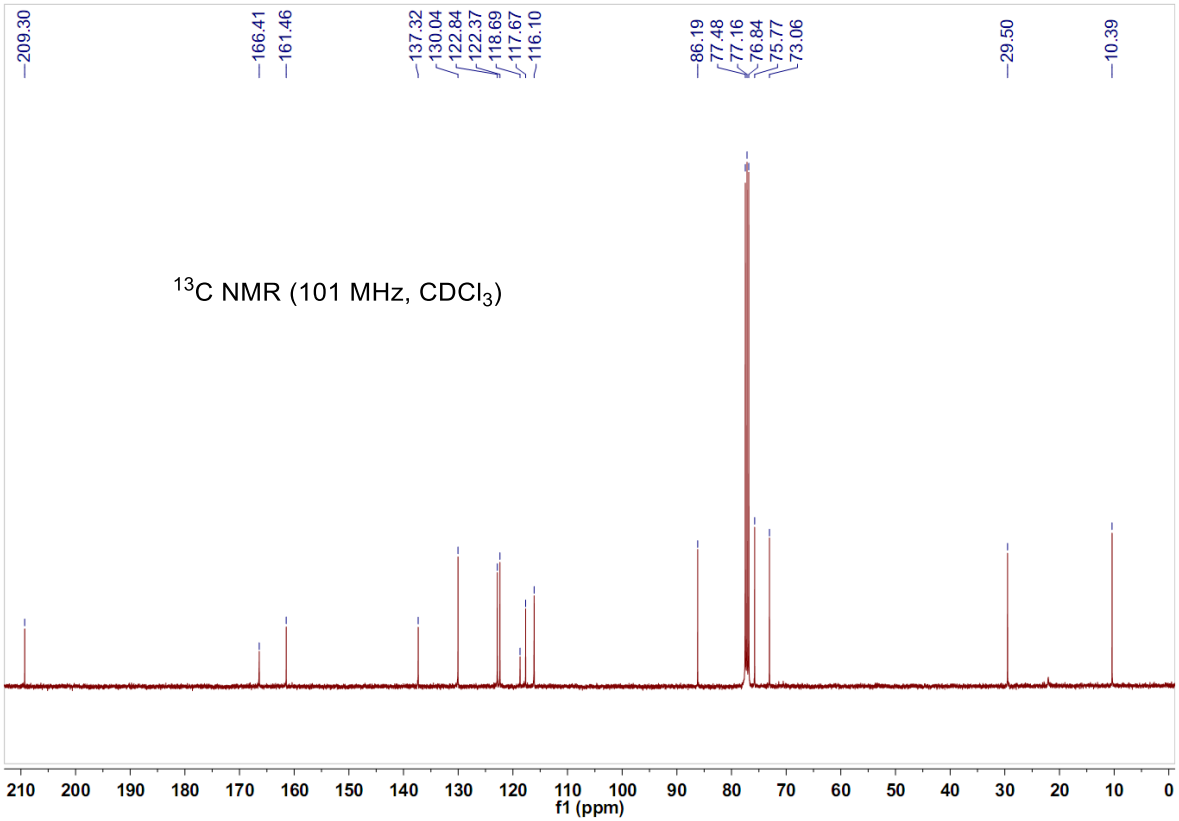
156.59
154.32
154.19
153.87
153.74
151.47
151.01
137.22
130.37
127.58
127.41
127.05
126.88
125.25
125.08
124.72
124.55
122.80
122.37
118.69
117.37
116.41
77.48
77.16
76.84
68.42
27.53
27.50
27.31
27.29
10.12
^{13}C NMR (101 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4-((4λ^5-penta-3,4-dien-1-yl)oxy)-3-methylquinolin-2(1*H*)-one (10a):

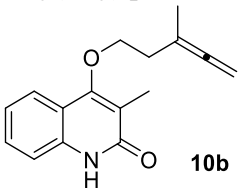


10a

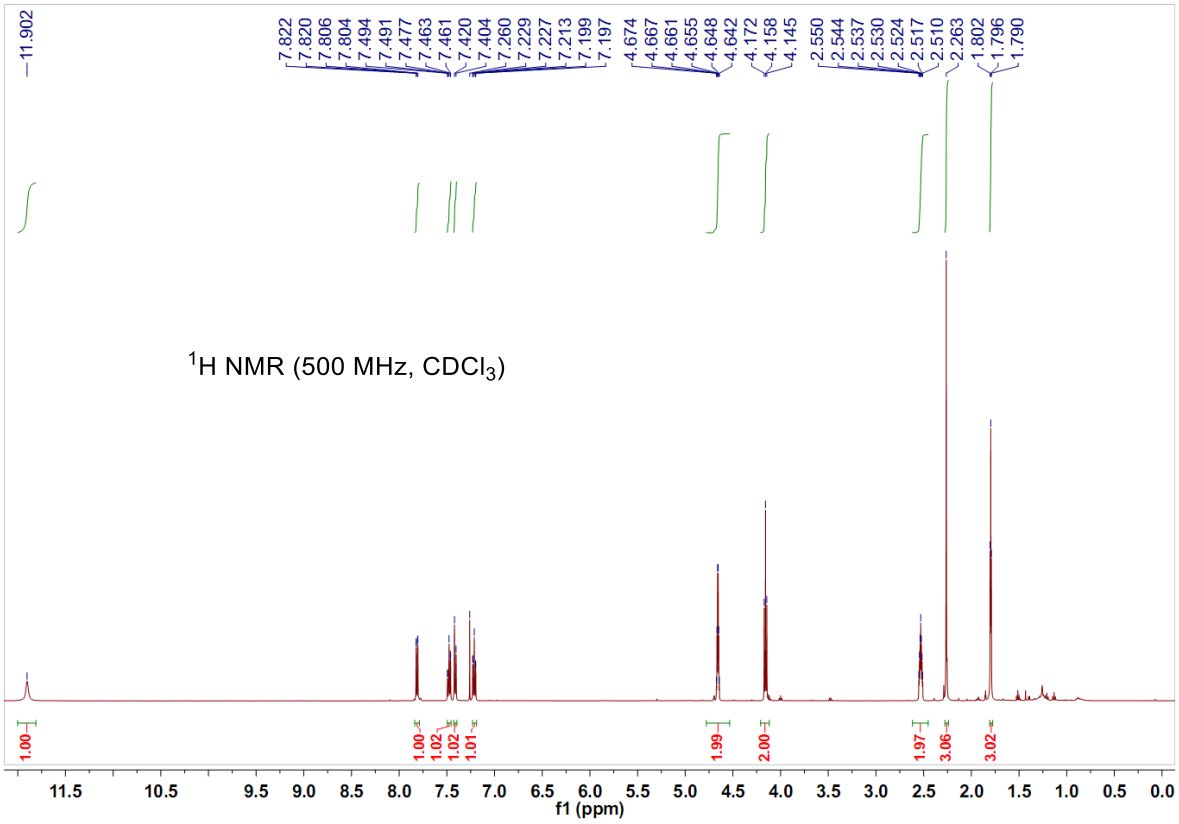


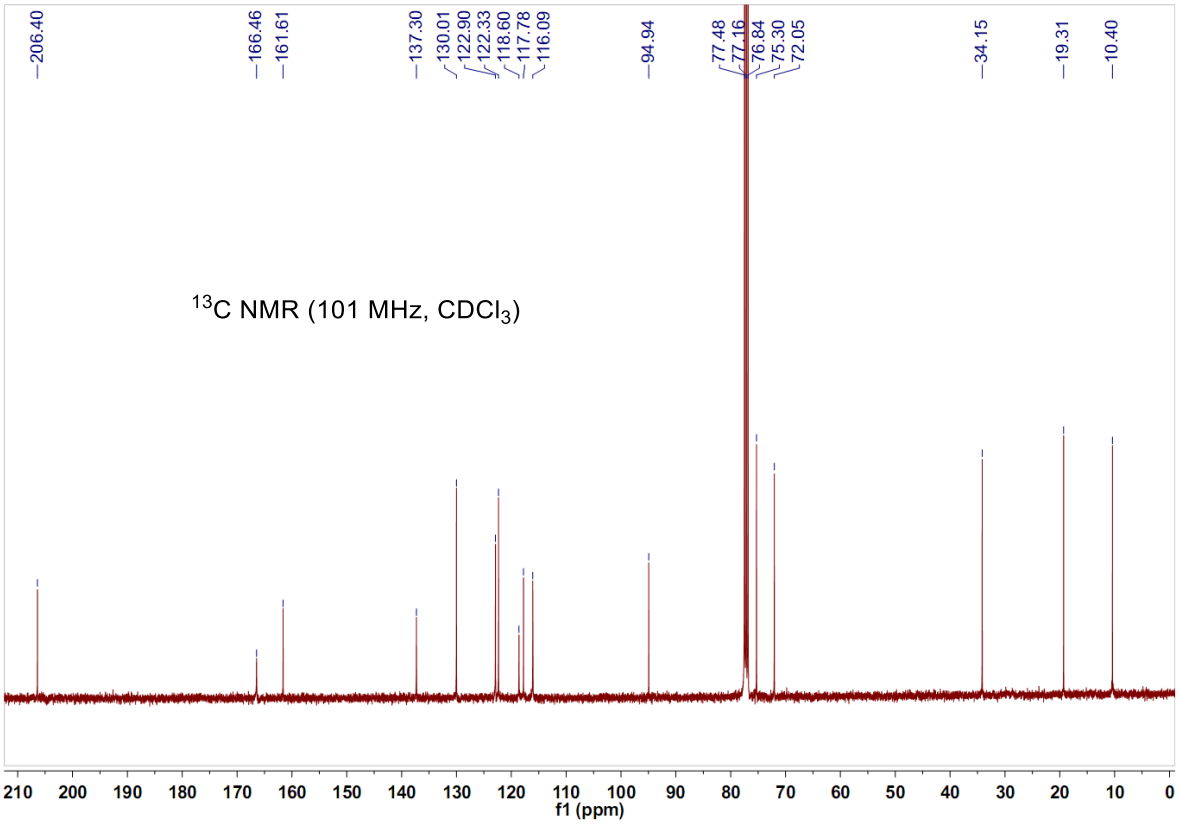


3-methyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (10b):

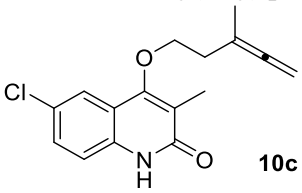


10b

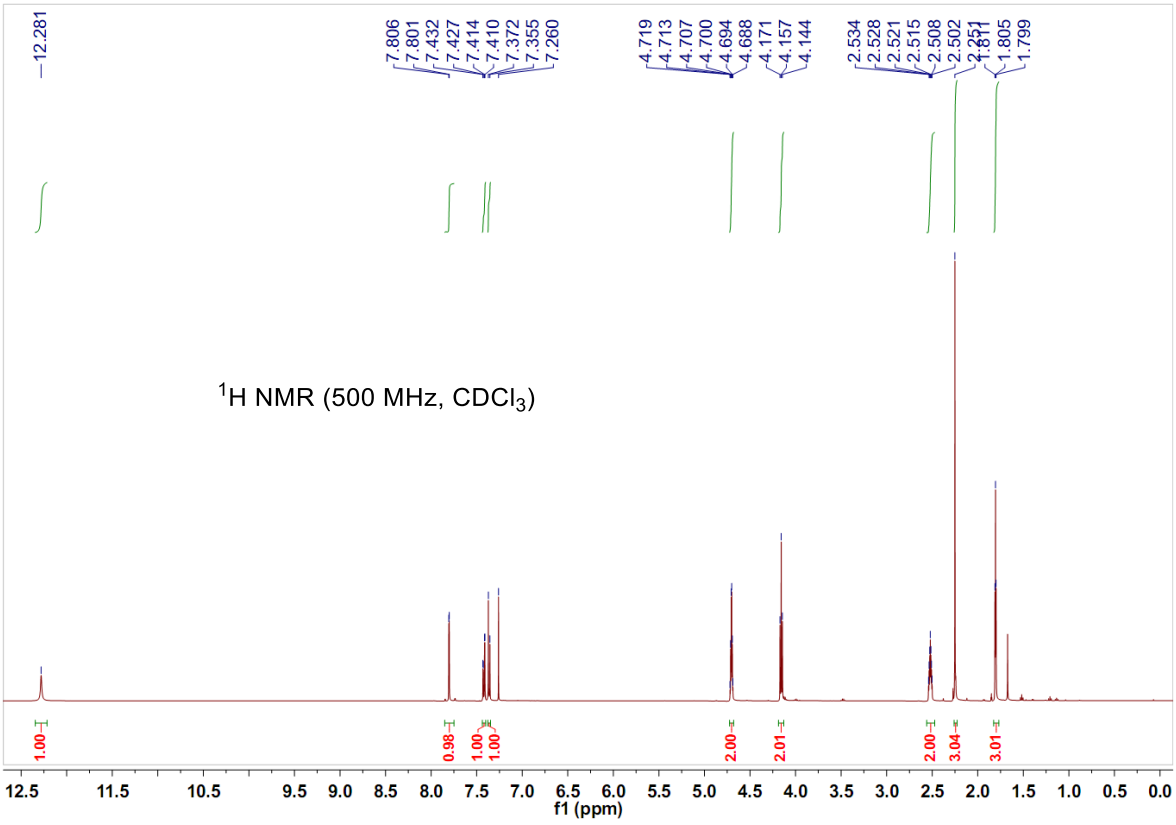


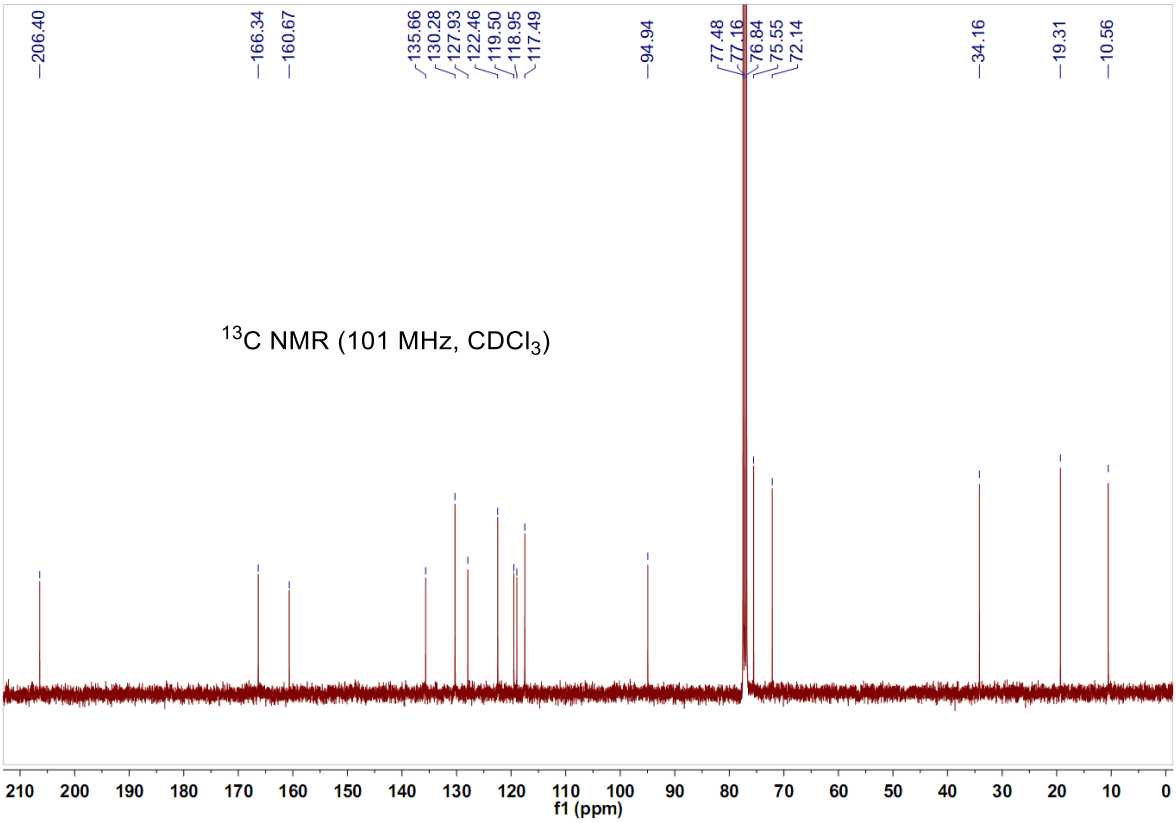


6-chloro-3-methyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (10c):

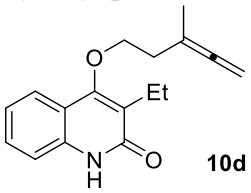


10c

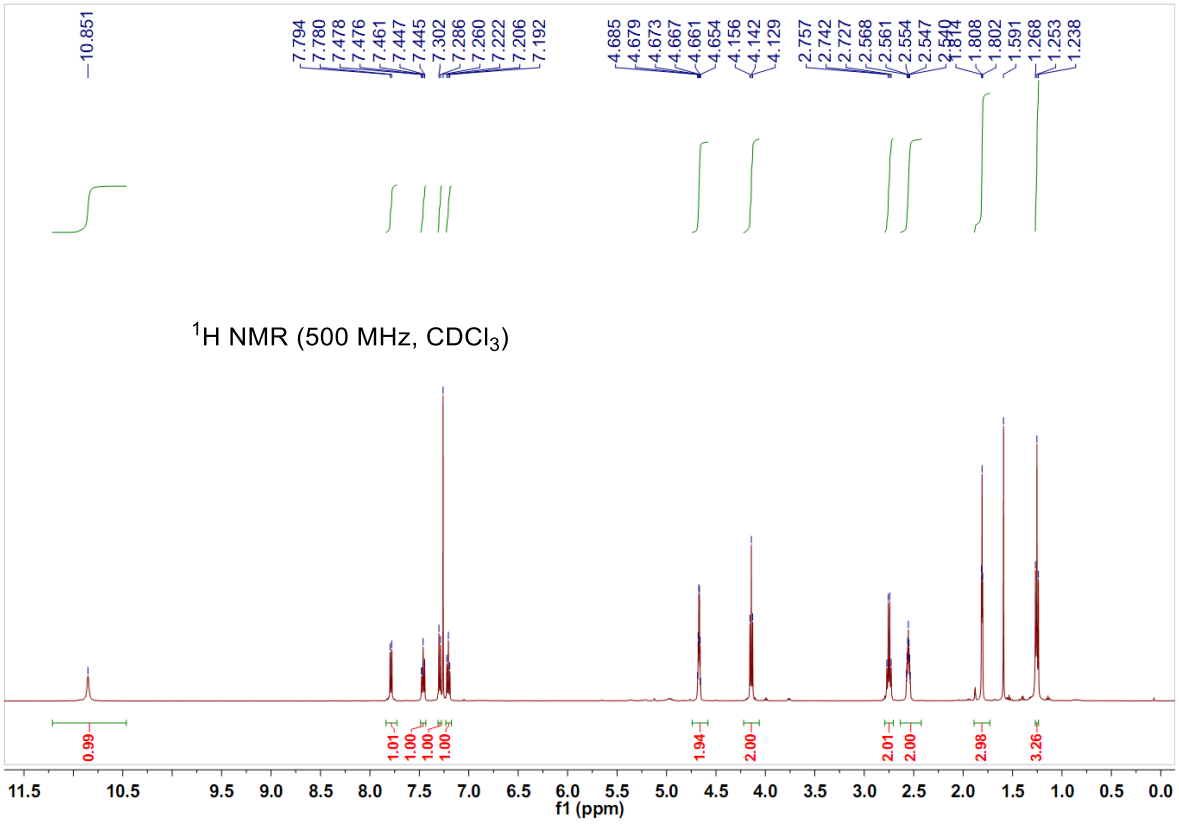


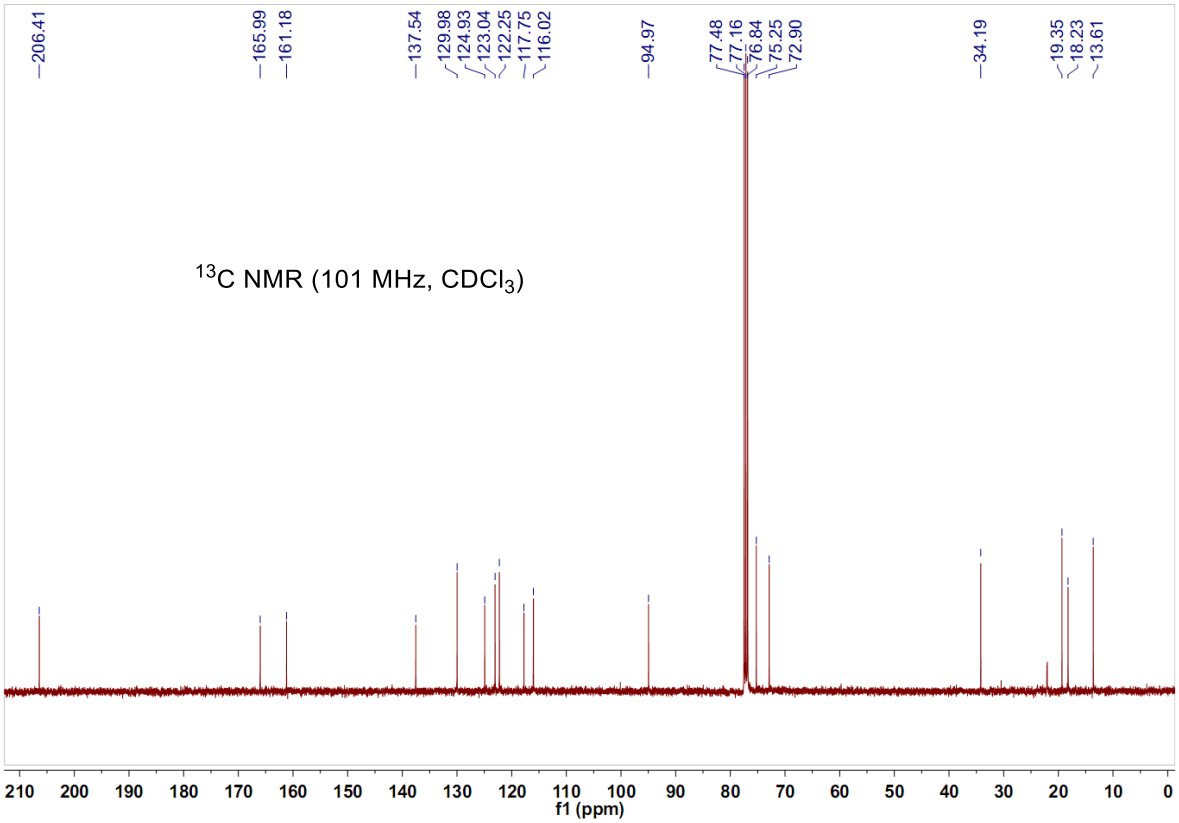


3-ethyl-4-((3-methyl-4λ^5-penta-3,4-dien-1-yl)oxy)quinolin-2(1*H*)-one (10d):

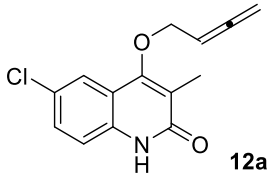


10d

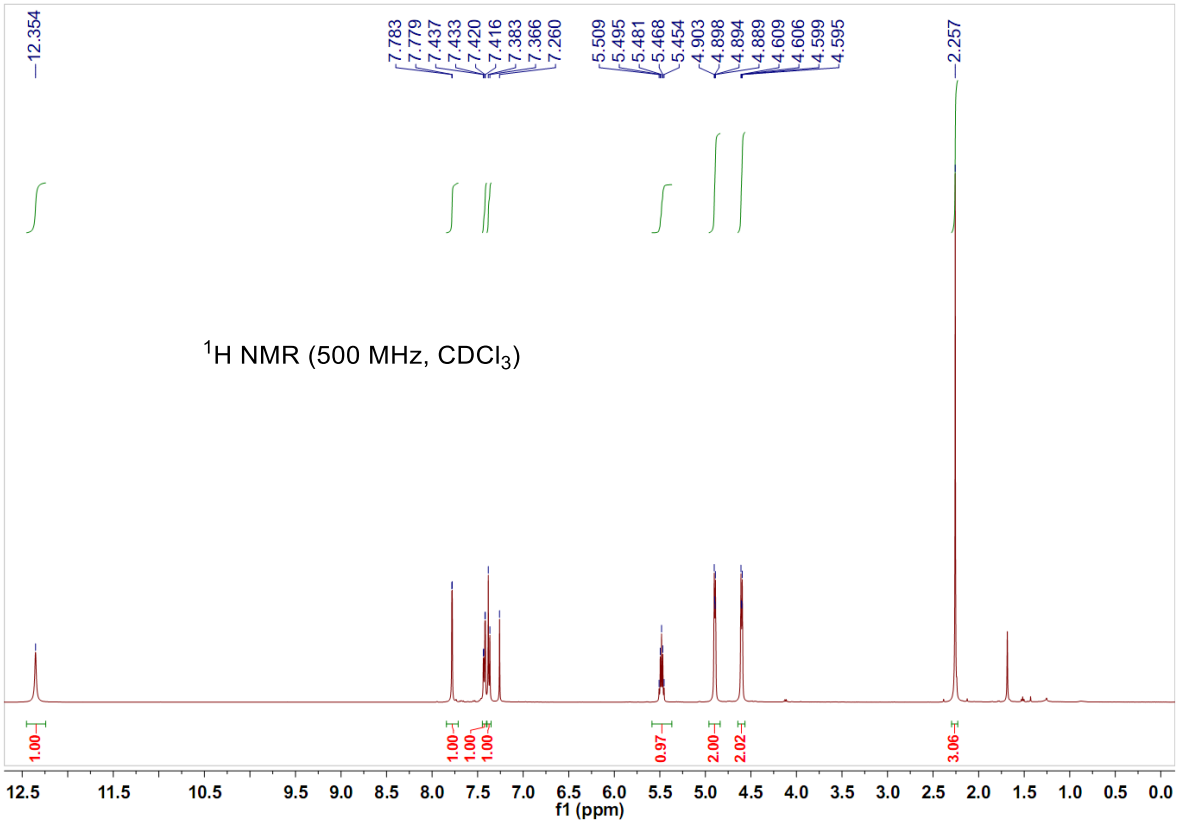


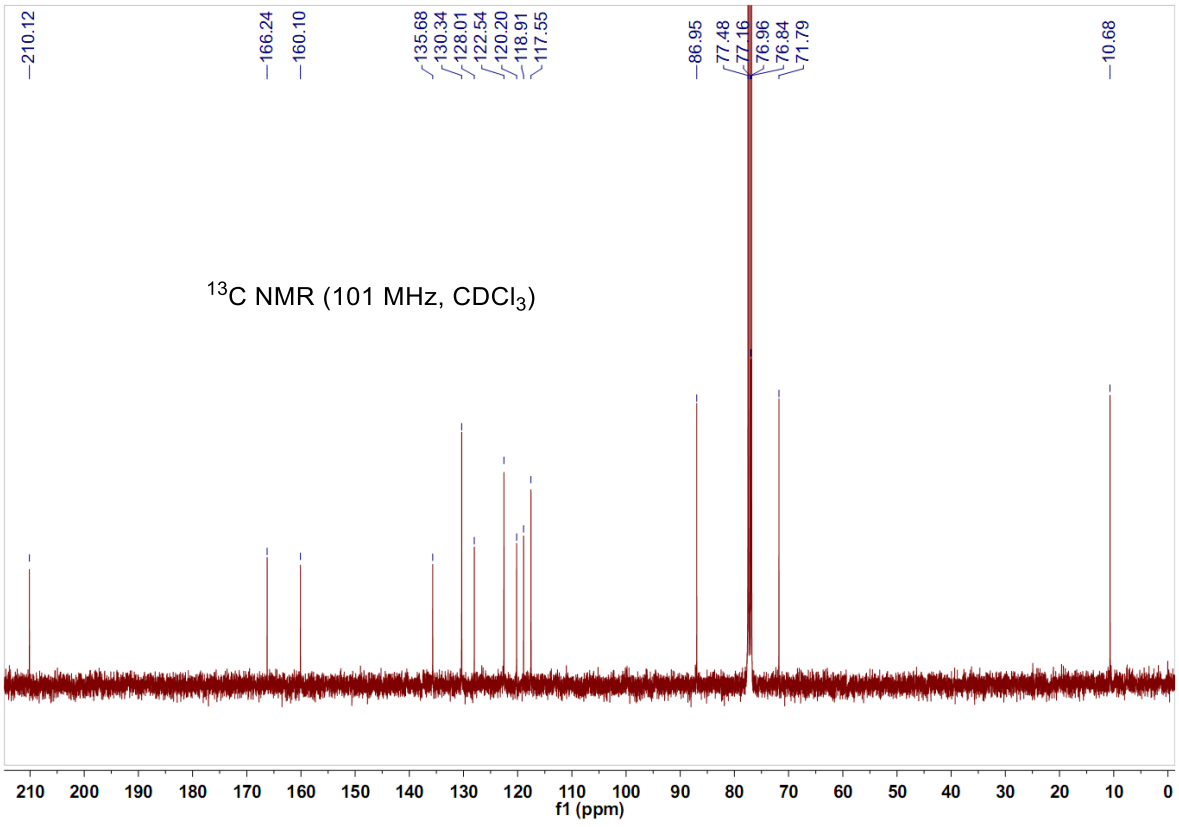


4-((3λ^5-buta-2,3-dien-1-yl)oxy)-6-chloro-3-methylquinolin-2(1*H*)-one (12a):

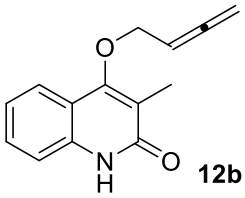


12a

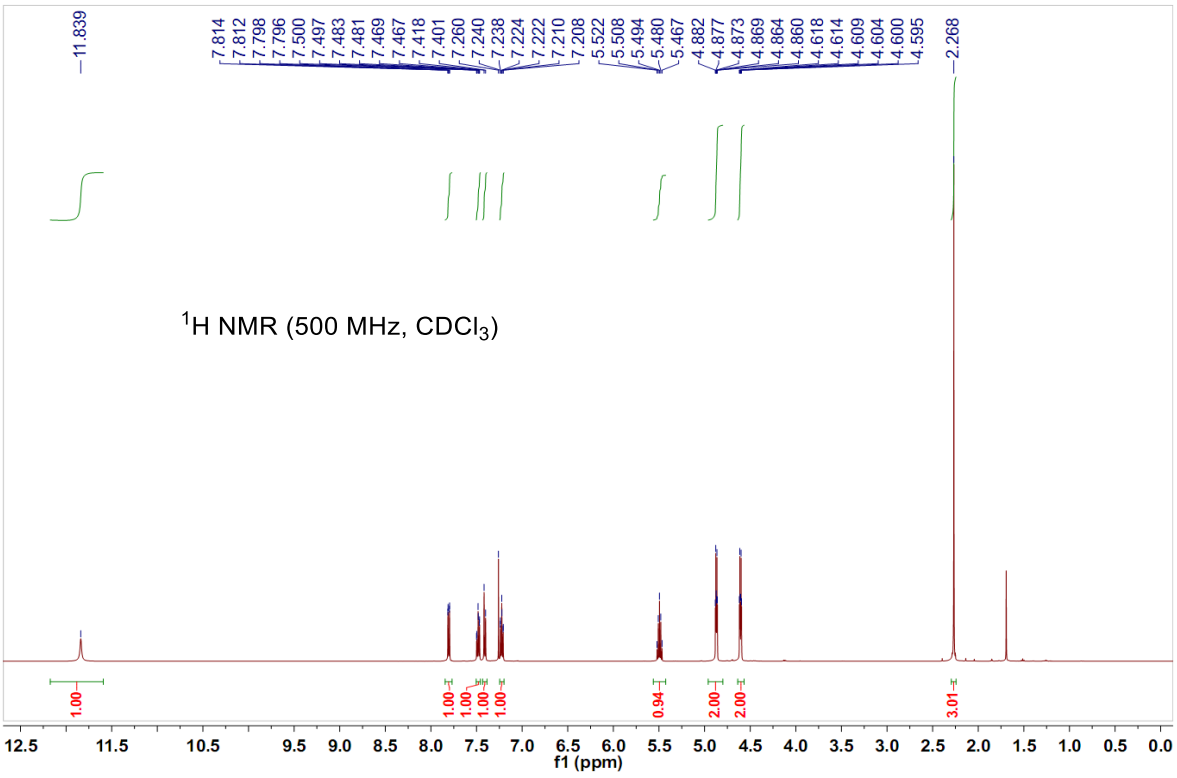


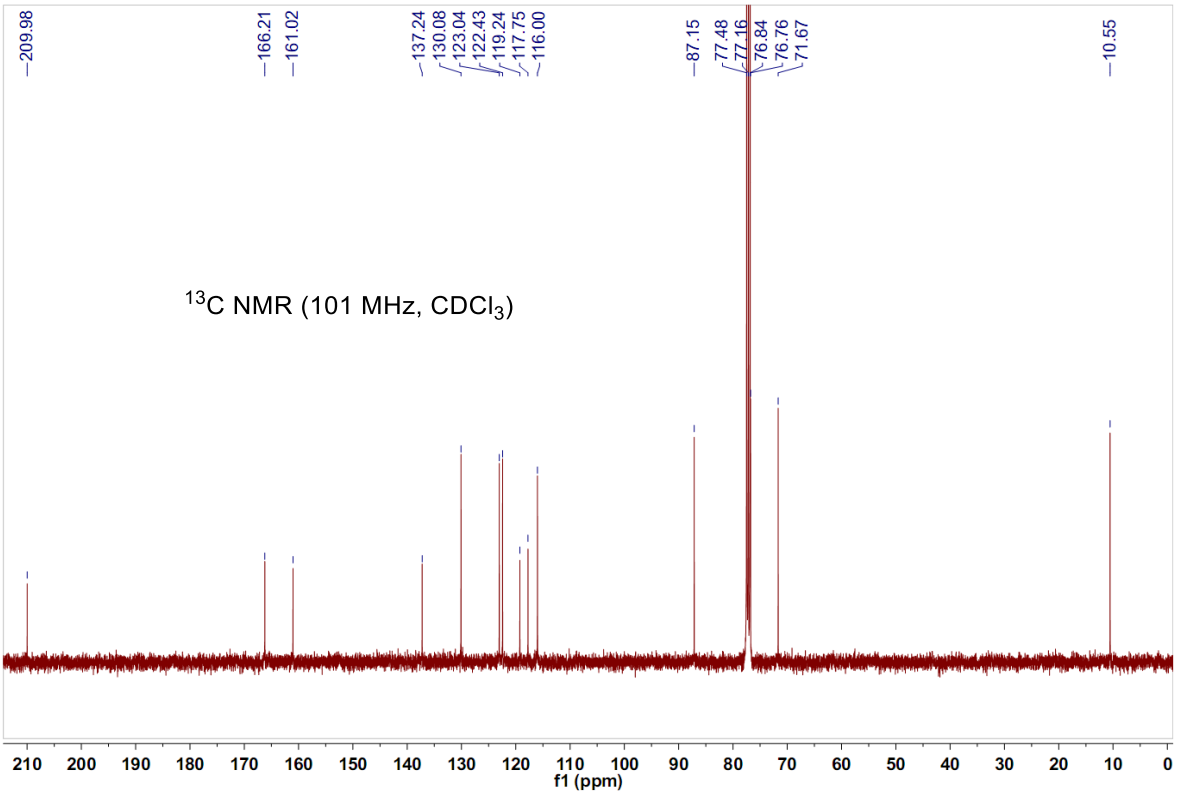


4-((3λ^5-buta-2,3-dien-1-yl)oxy)-3-methylquinolin-2(1*H*)-one (12b):

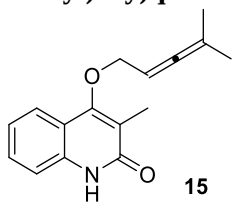


12b

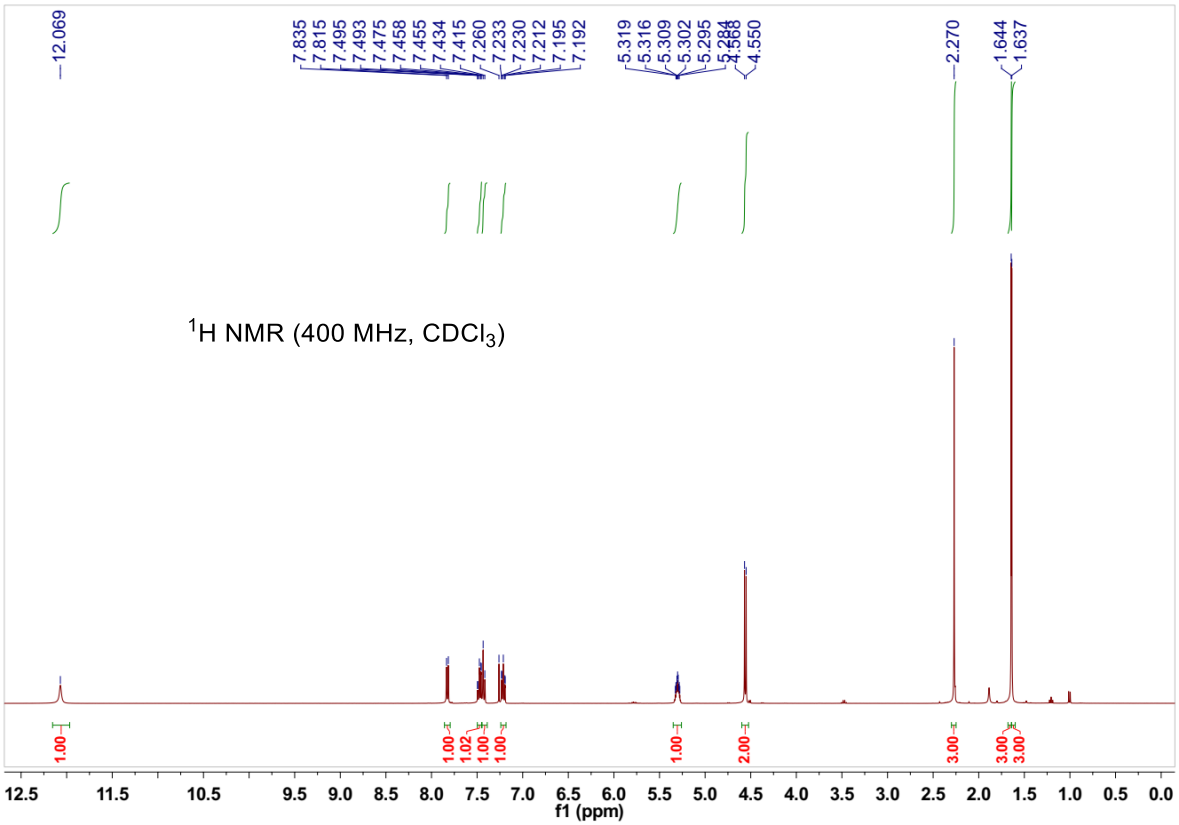


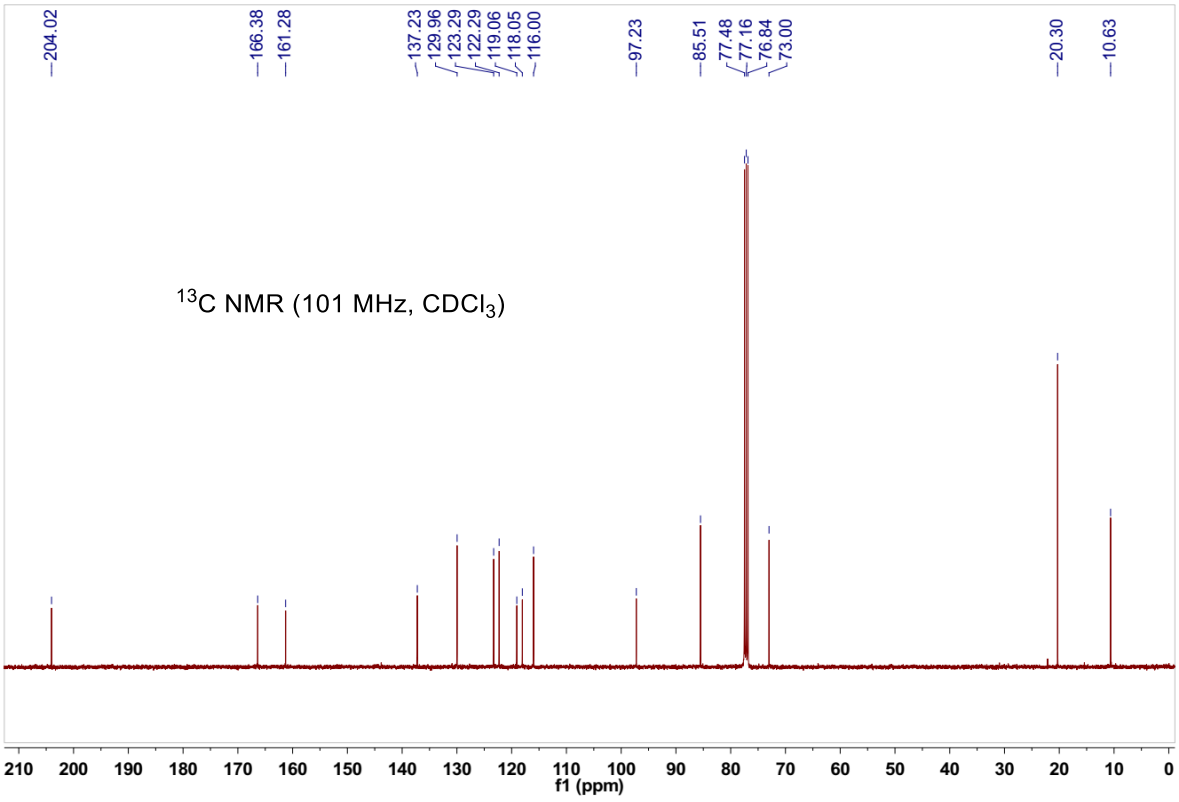


3-methyl-4-((4-methyl-3λ^5-penta-2,3-dien-1-yl)oxy)quinolin-2(1*H*)-one (15):

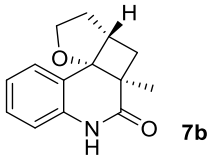


15

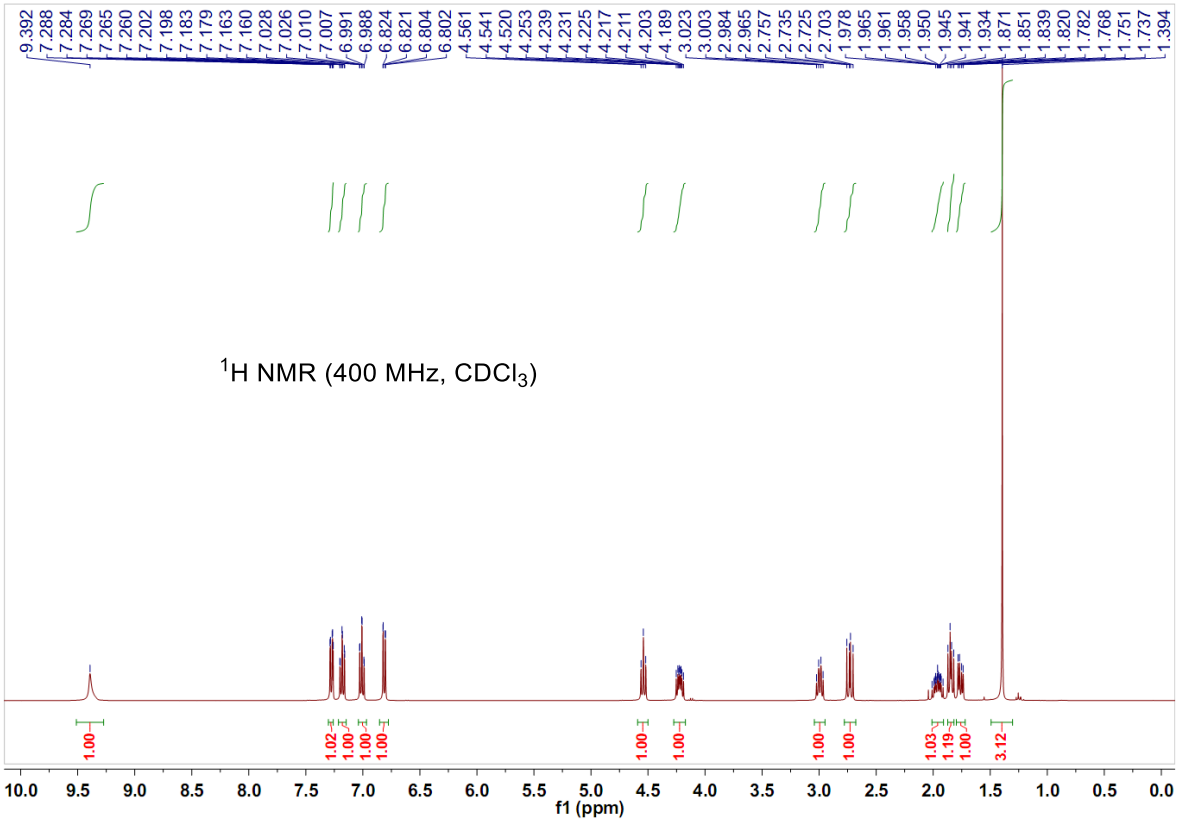


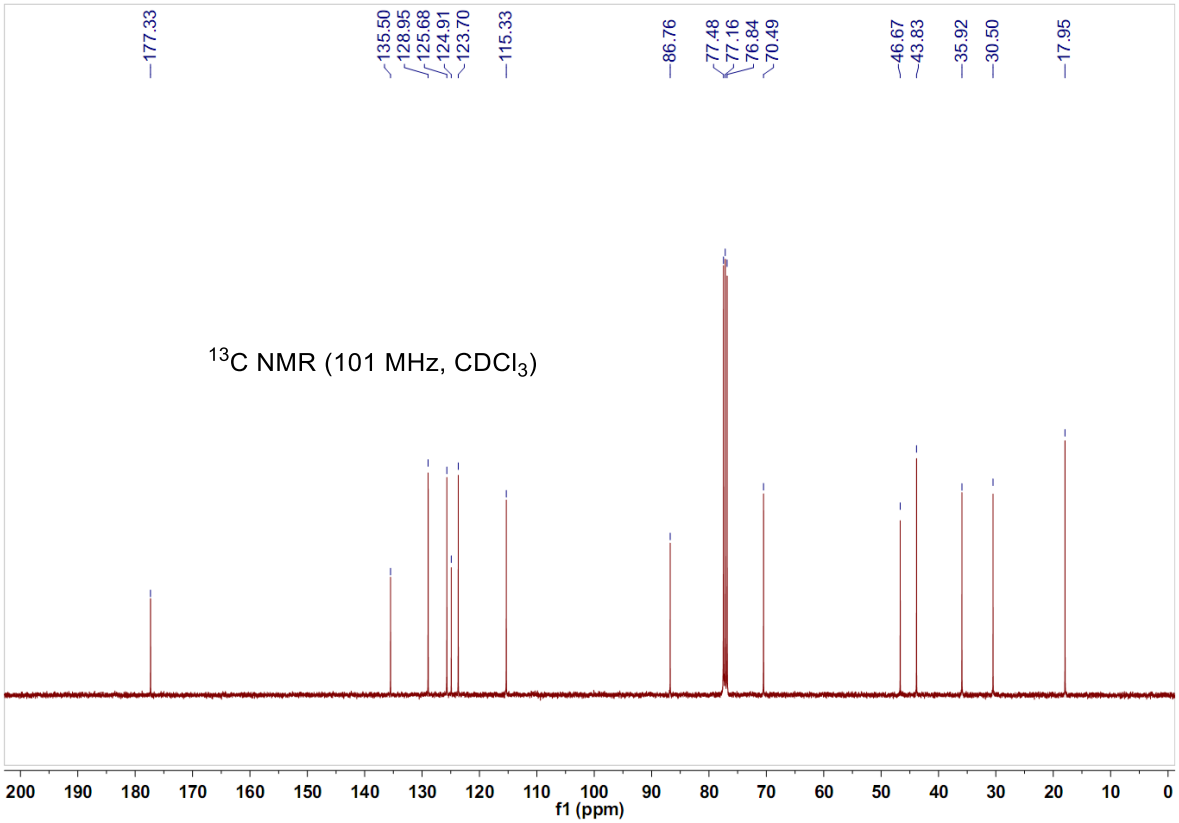


(3a*S*,4a*R*,10b*S*)-4a-methyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7b):

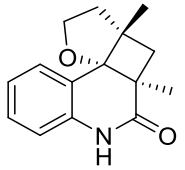


7b

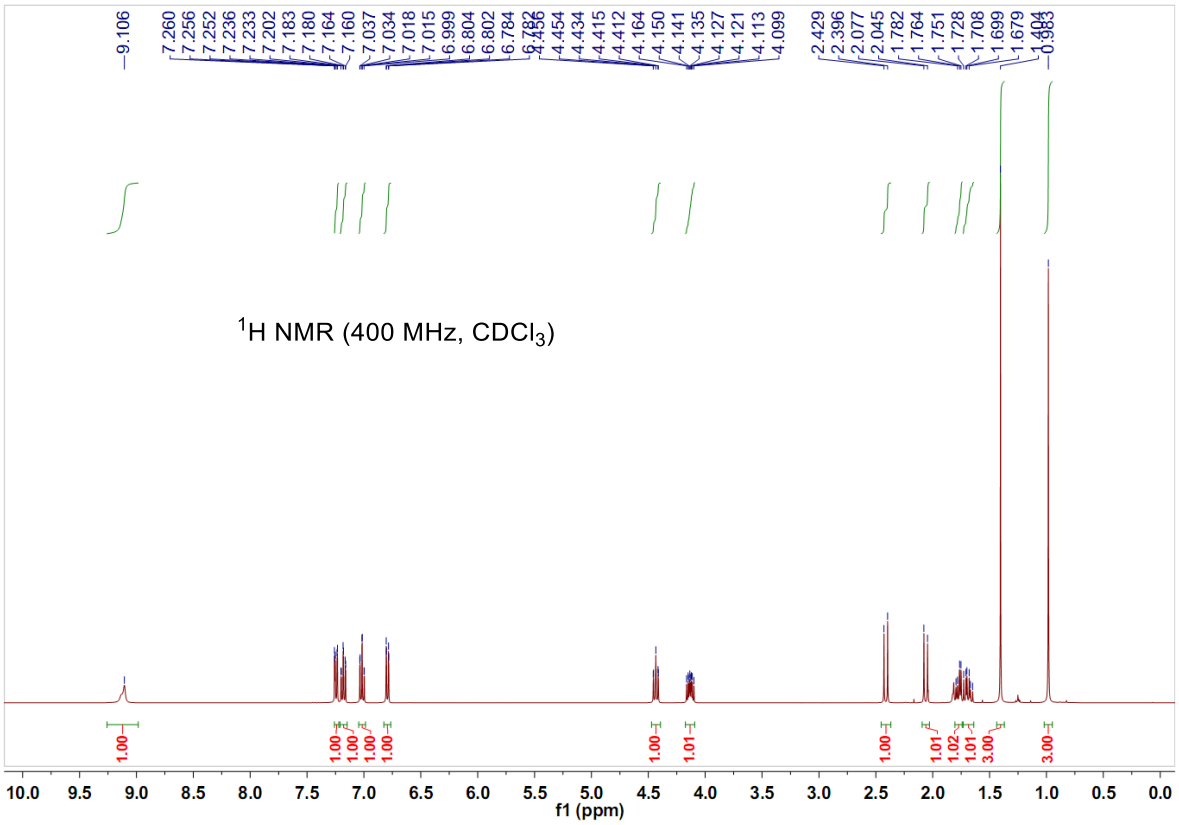


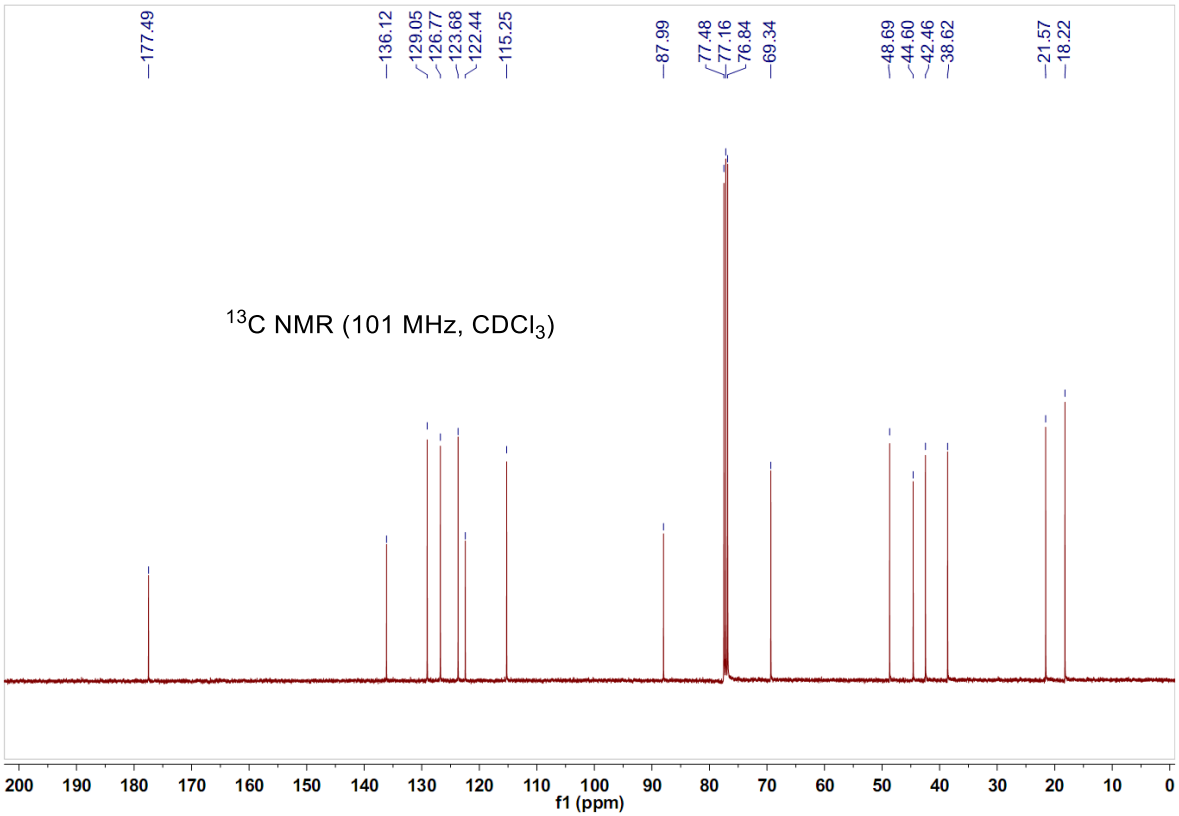


(3a*S*,4a*R*,10b*S*)-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7c):

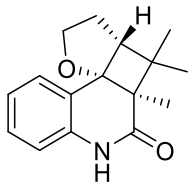


7c

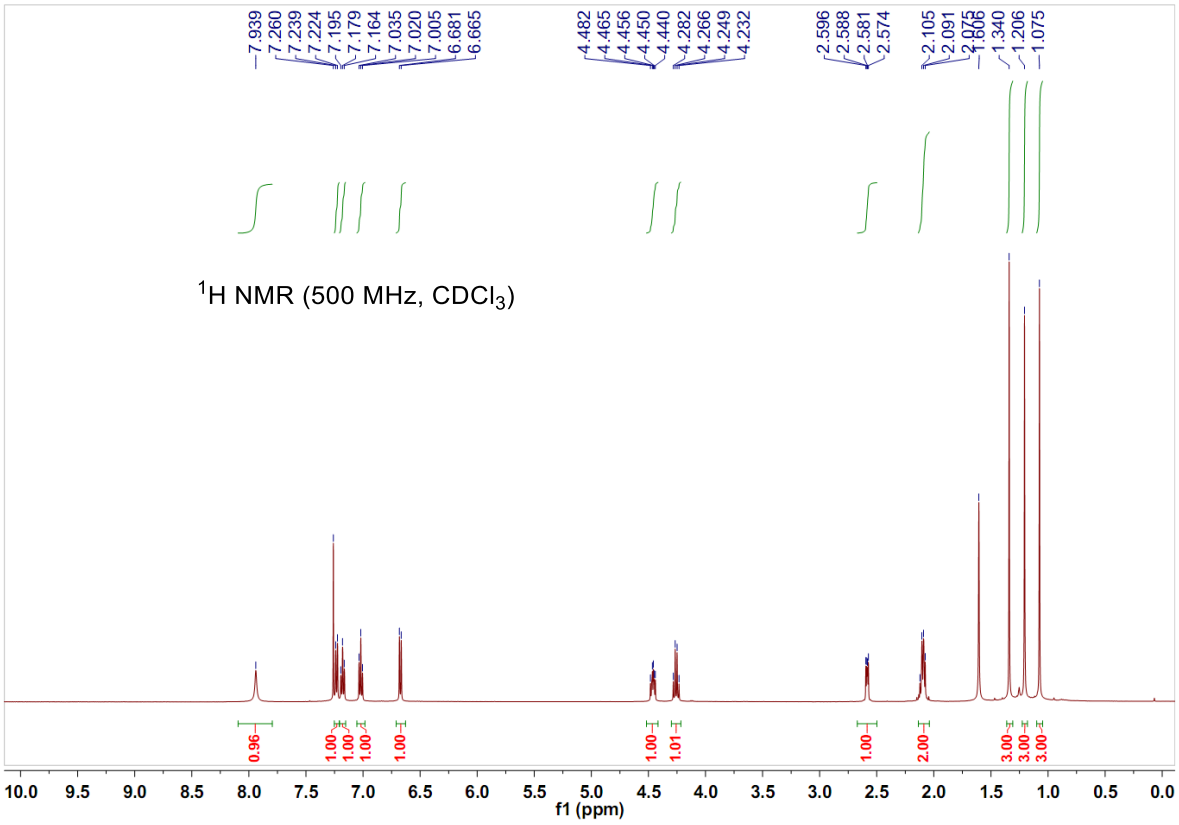


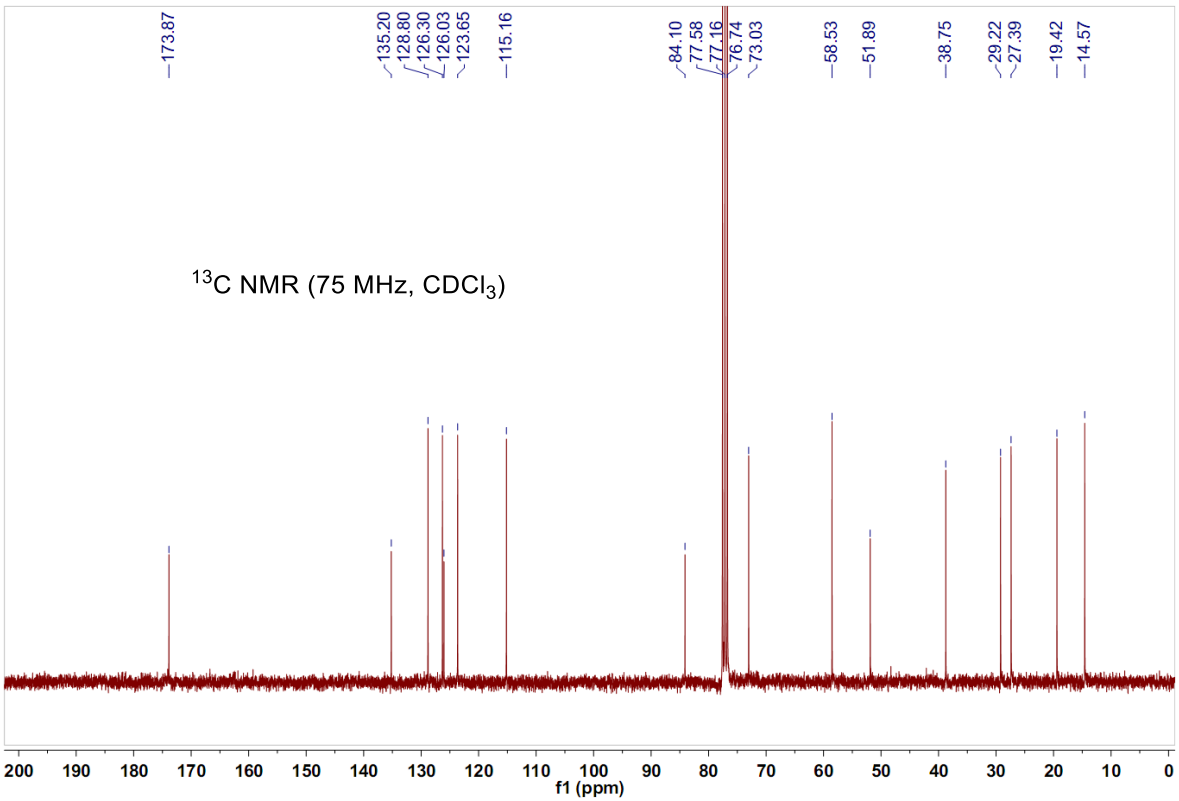


(3a*R*,4a*R*,10b*S*)-4,4,4a-trimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7d):

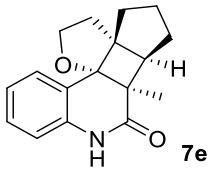


7d

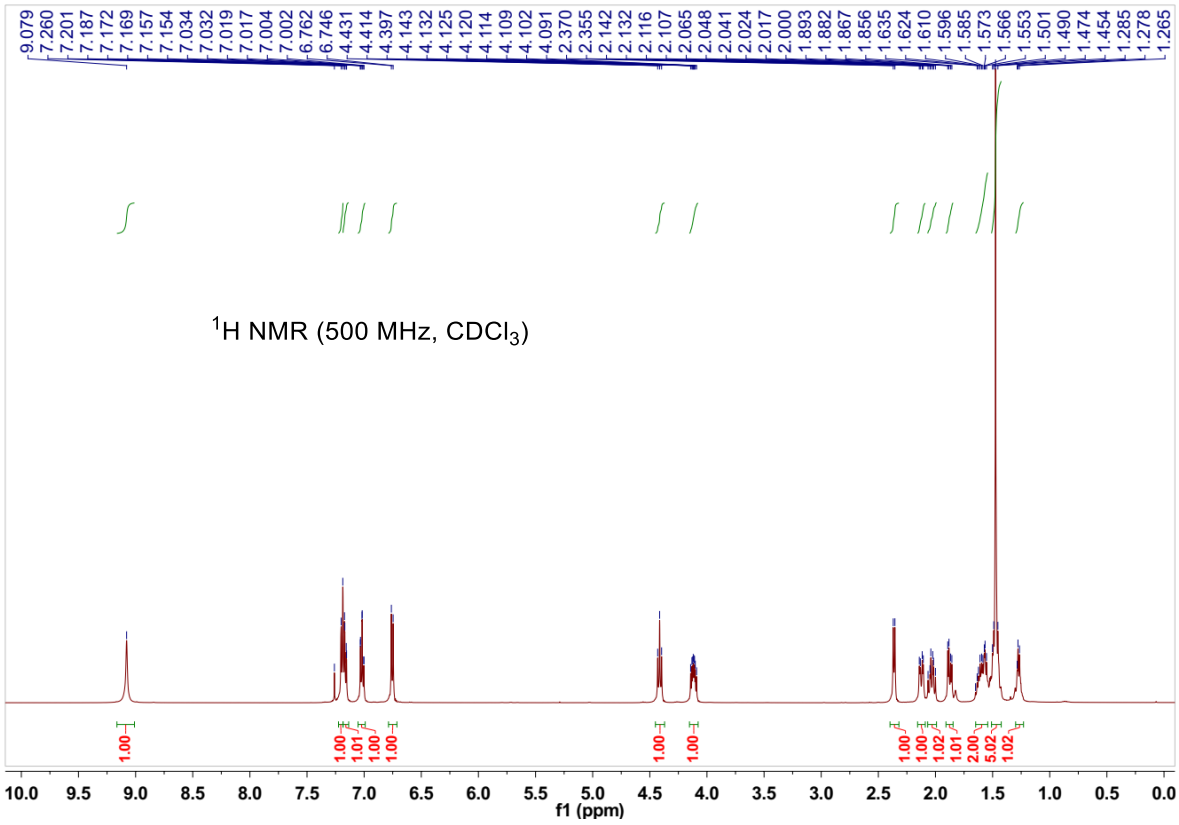


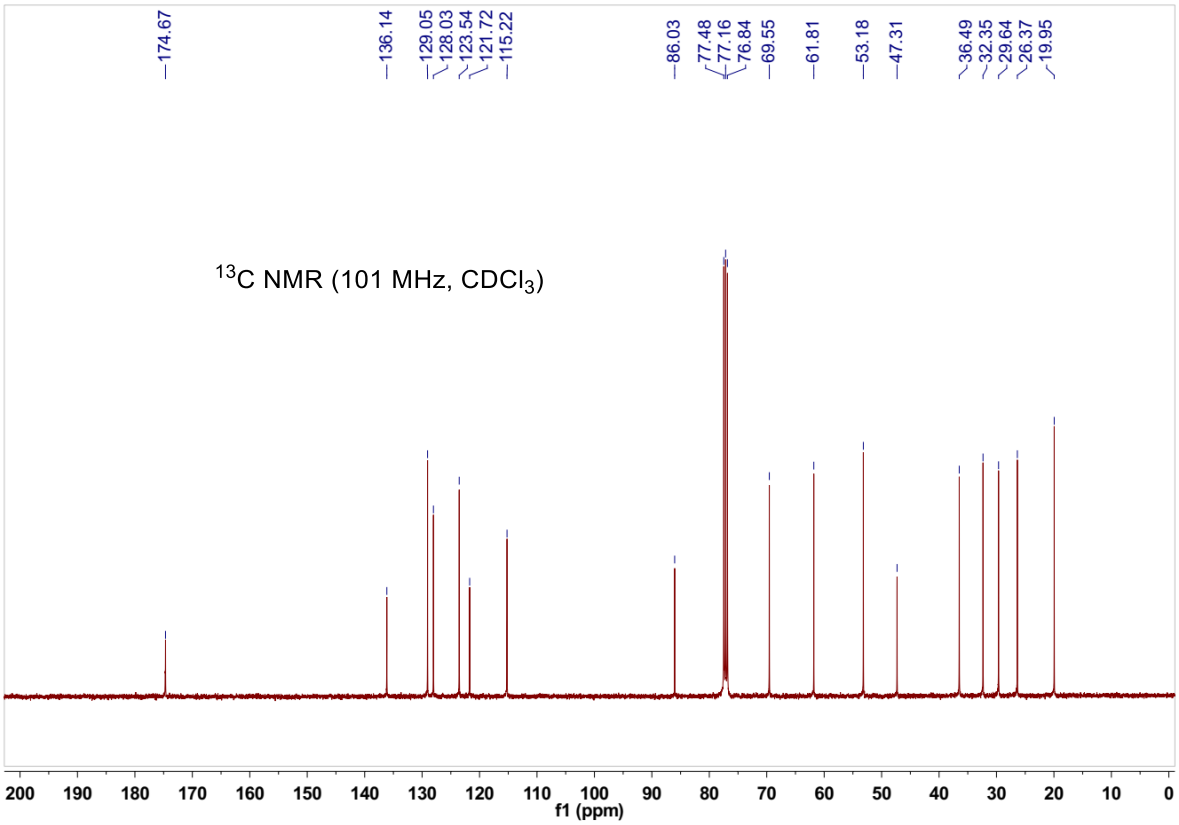


(6a*R*,6b*R*,9a*R*,12a*S*)-6a-methyl-6b,7,8,9,10,11-hexahydro-5*H*-cyclopenta[3,4]furo[2',3':2,3]cyclobuta-[1,2-*c*]quinolin-6(6a*H*)-one (7e):

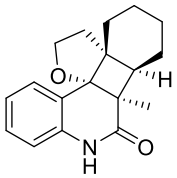


7e

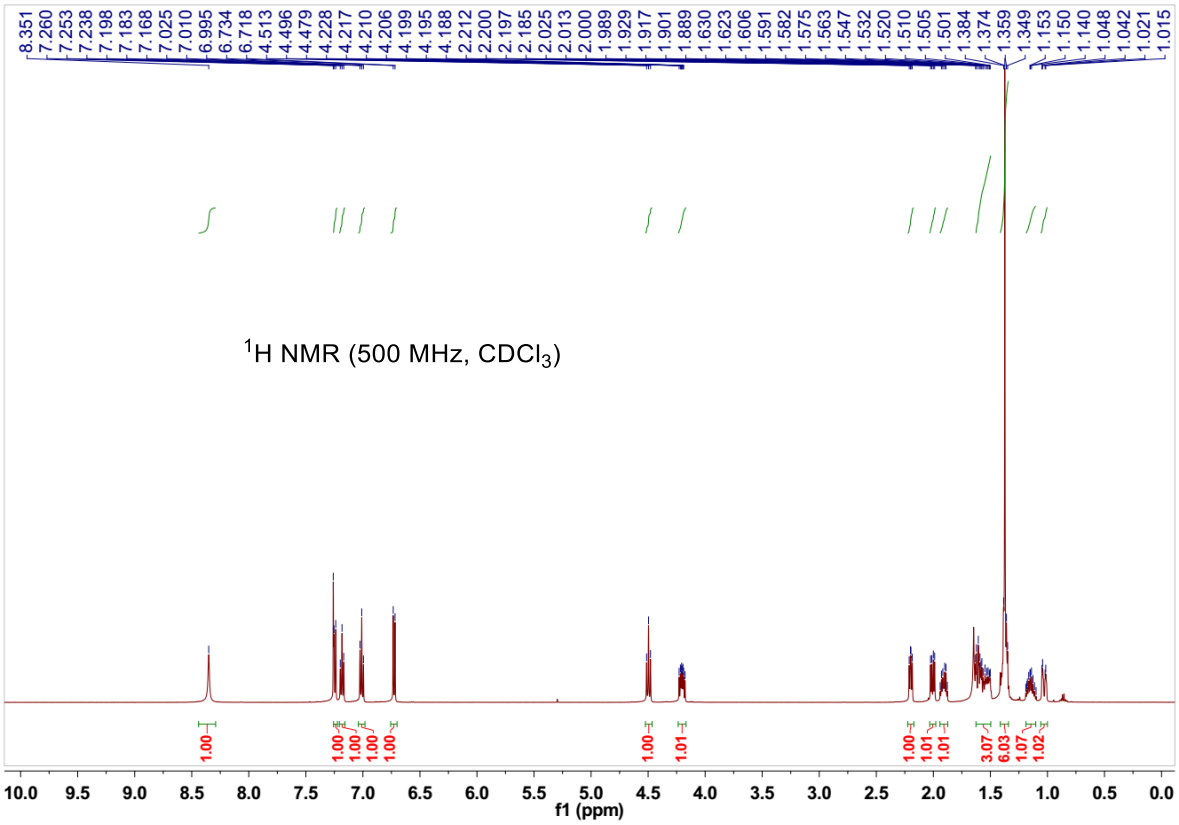


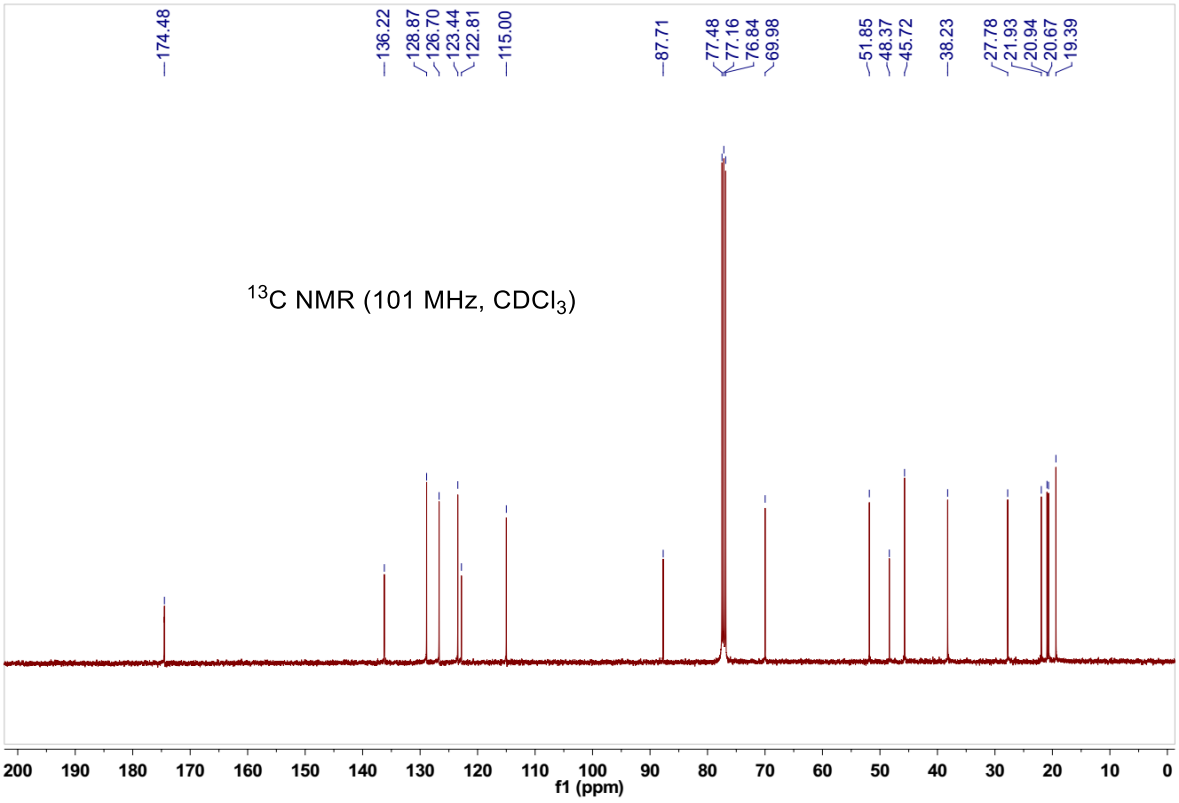


(6a*R*,6b*R*,10a*R*,13a*S*)-6a-methyl-6a,6b,7,8,9,10,11,12-octahydrobenzo[3,4]furo[2',3':2,3]cyclobuta-[1,2-*c*]quinolin-6(5*H*)-one (7f):

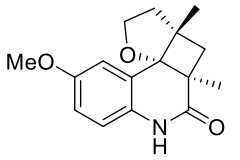


7f

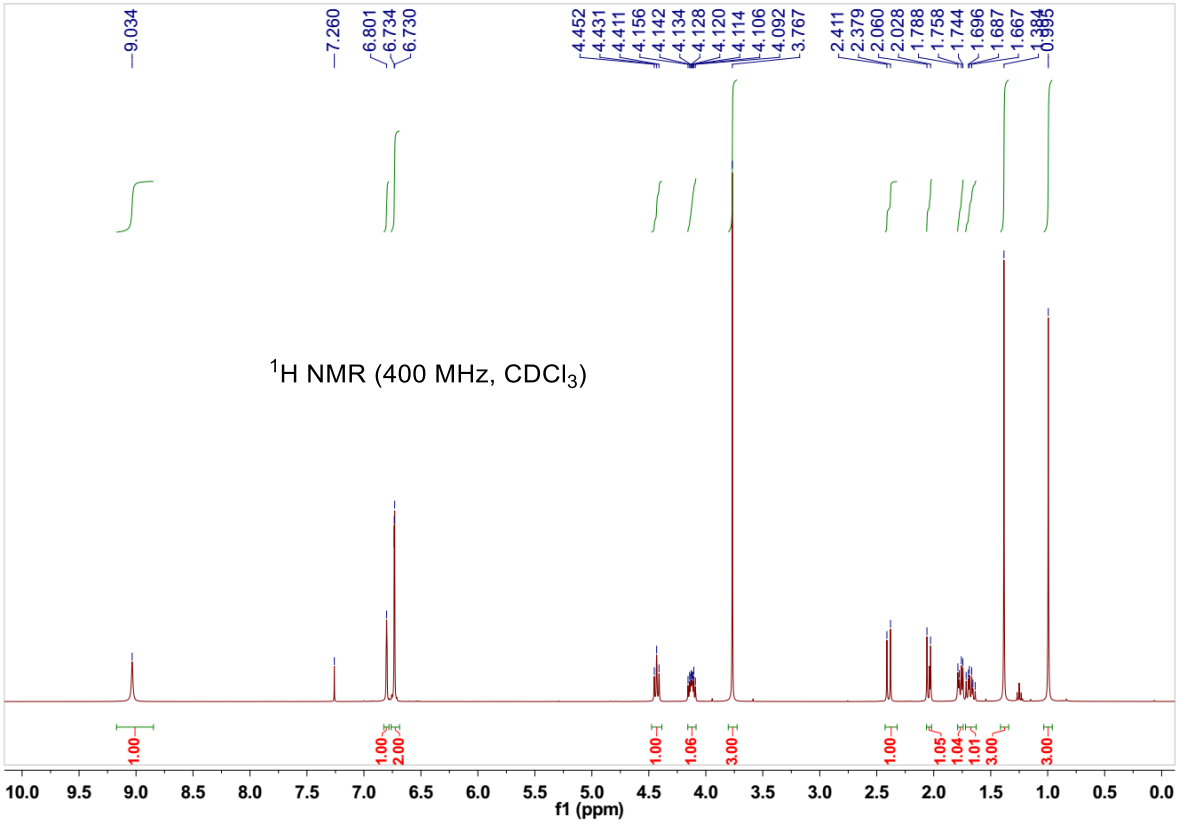




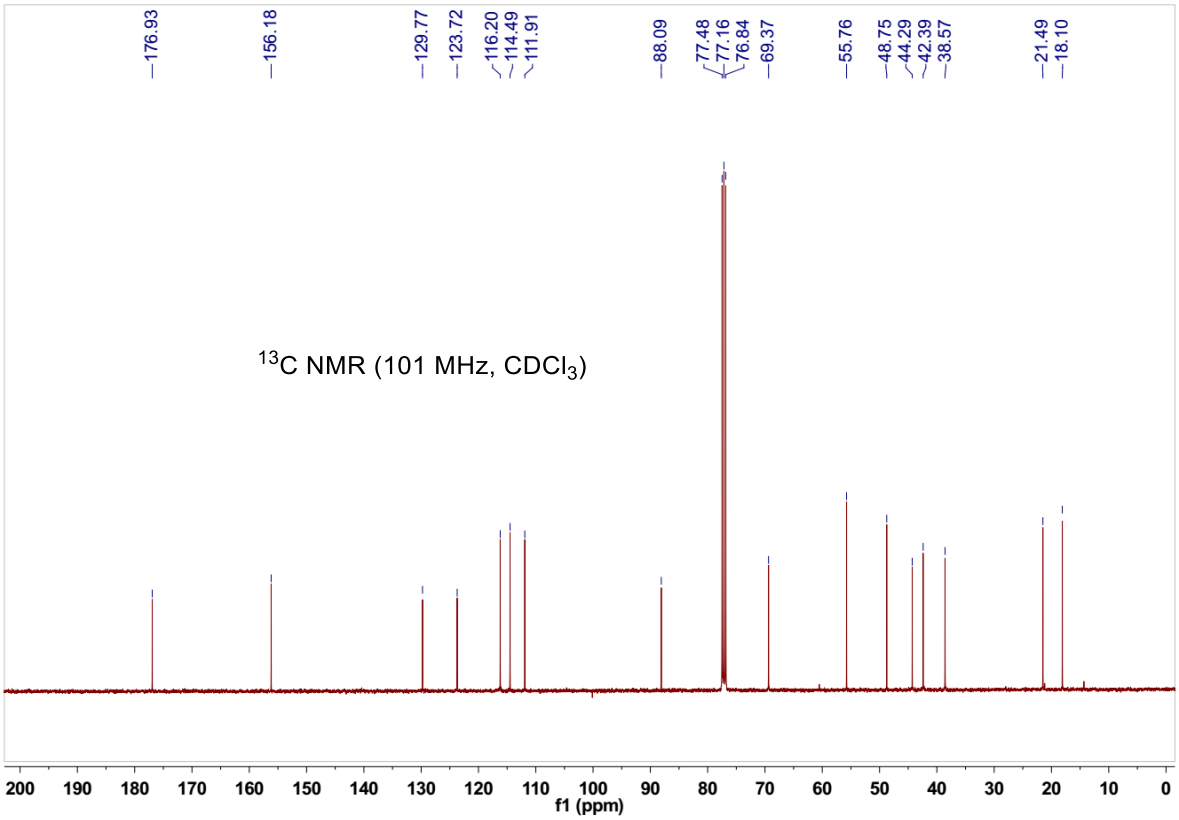
(3a*S*,4a*R*,10b*S*)-9-methoxy-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7g):



7g

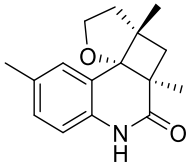


^{1}H NMR (400 MHz, $CDCl_3$)

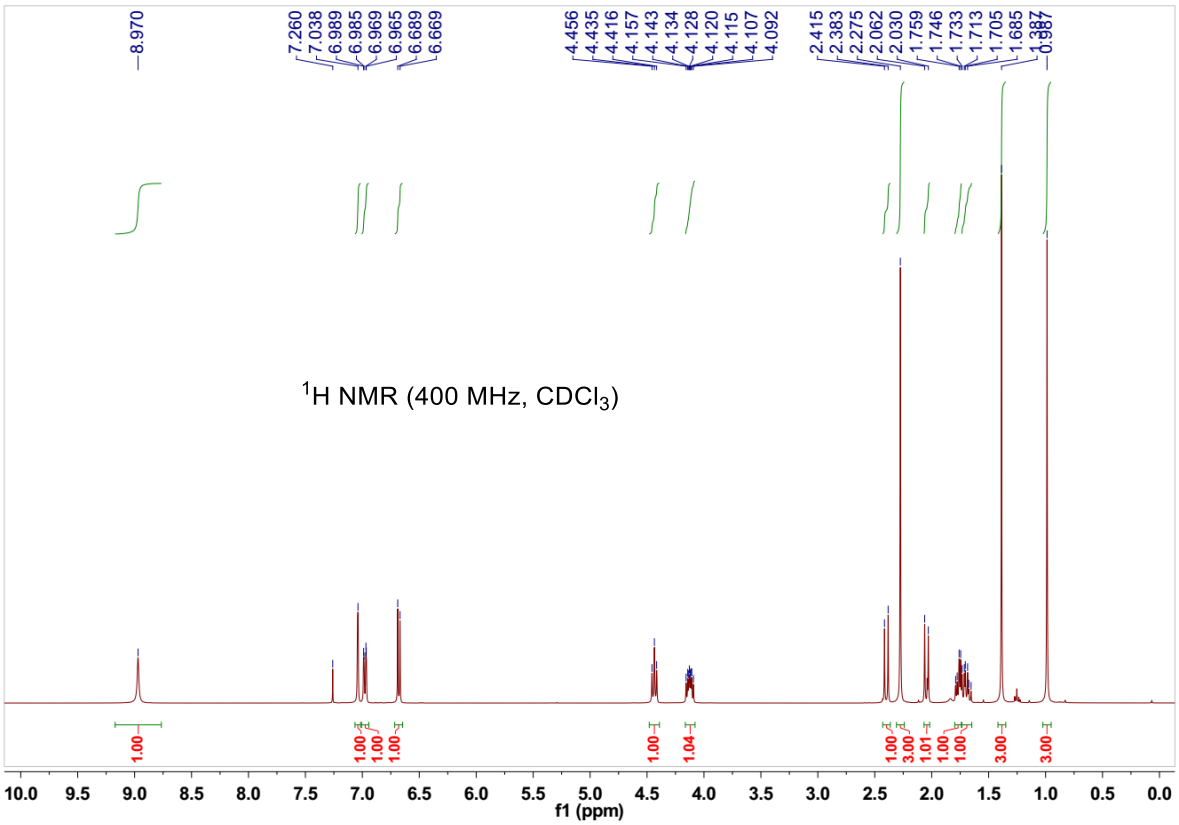


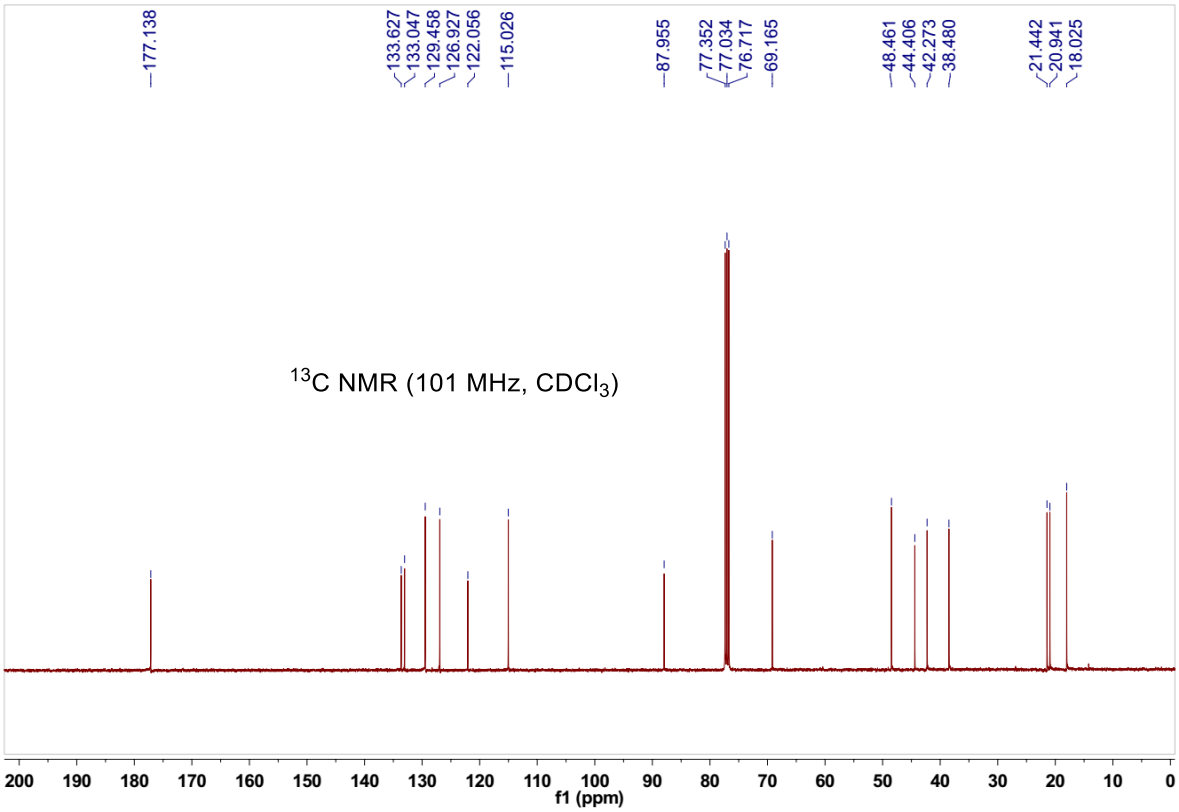
^{13}C NMR (101 MHz, $CDCl_3$)

(3a*S*,4a*R*,10b*S*)-3a,4a,9-trimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7h):

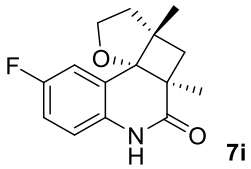


7h

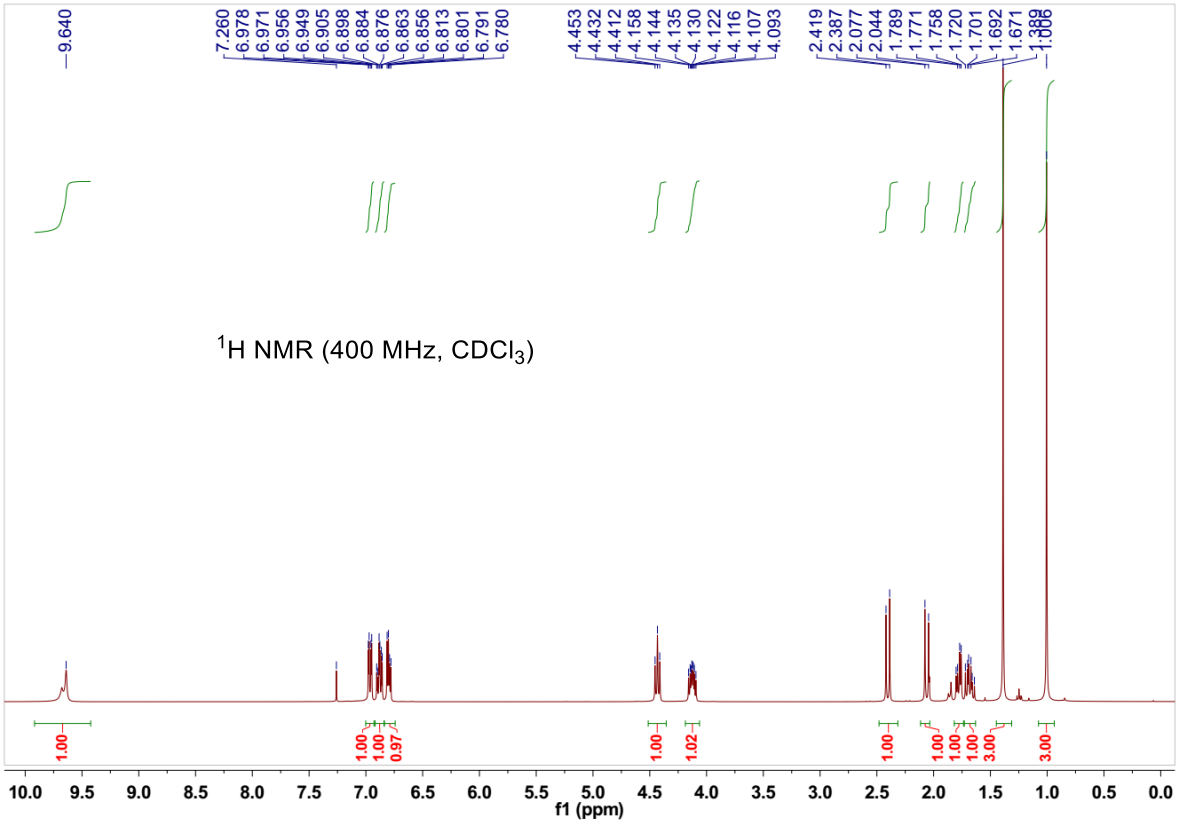


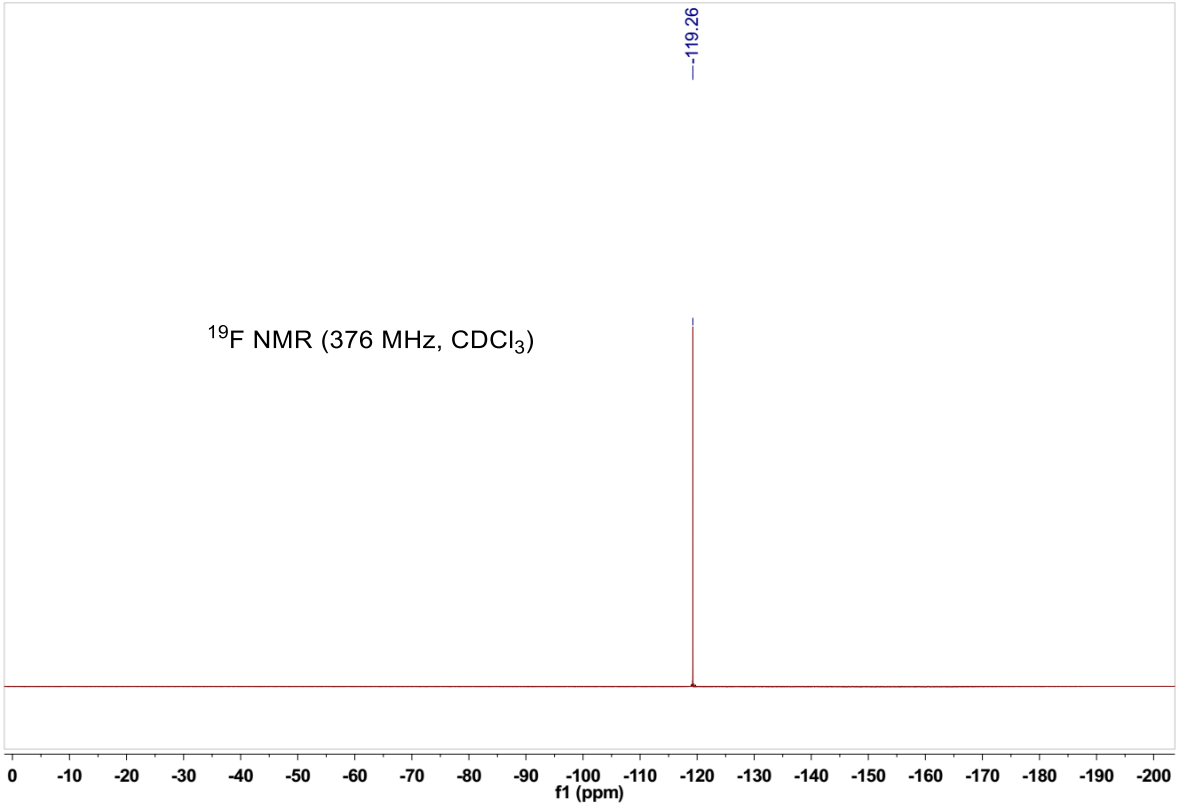


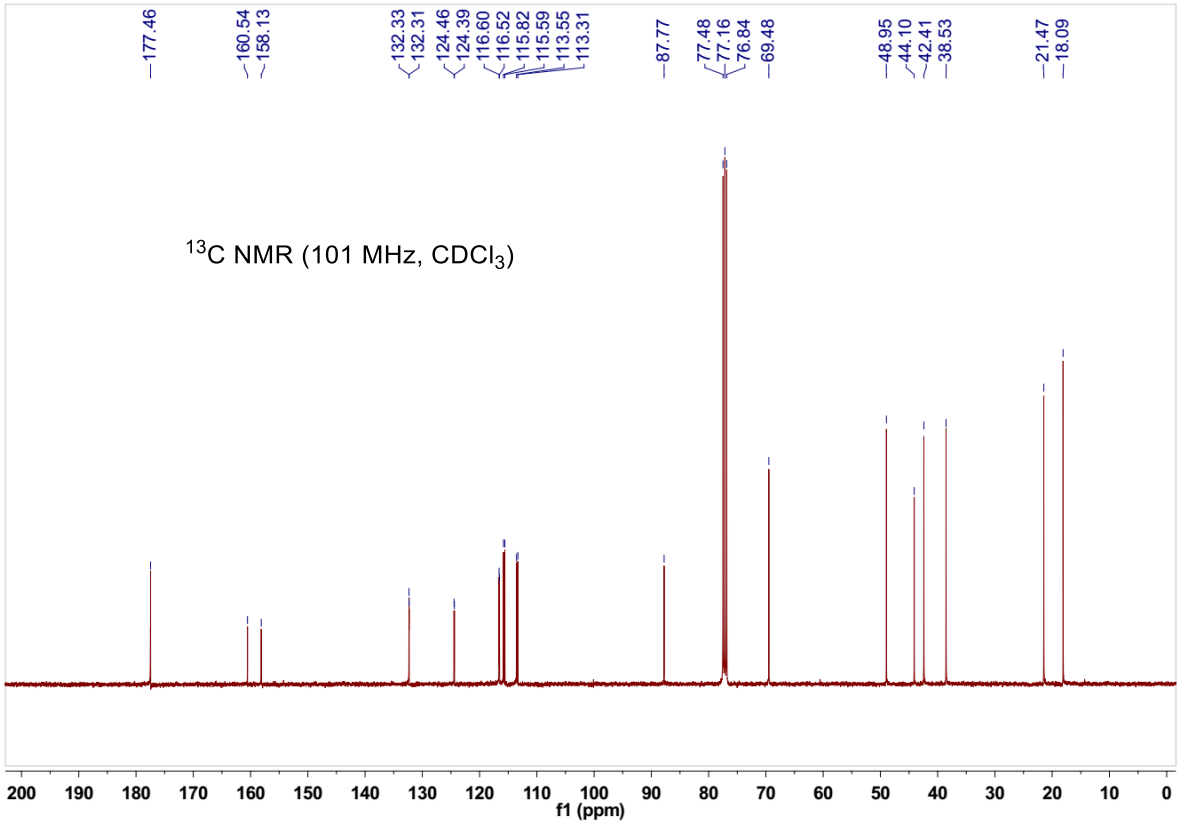
(3a*S*,4a*R*,10b*S*)-9-fluoro-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7i):



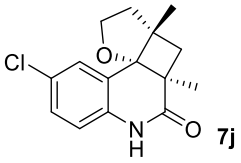
7i

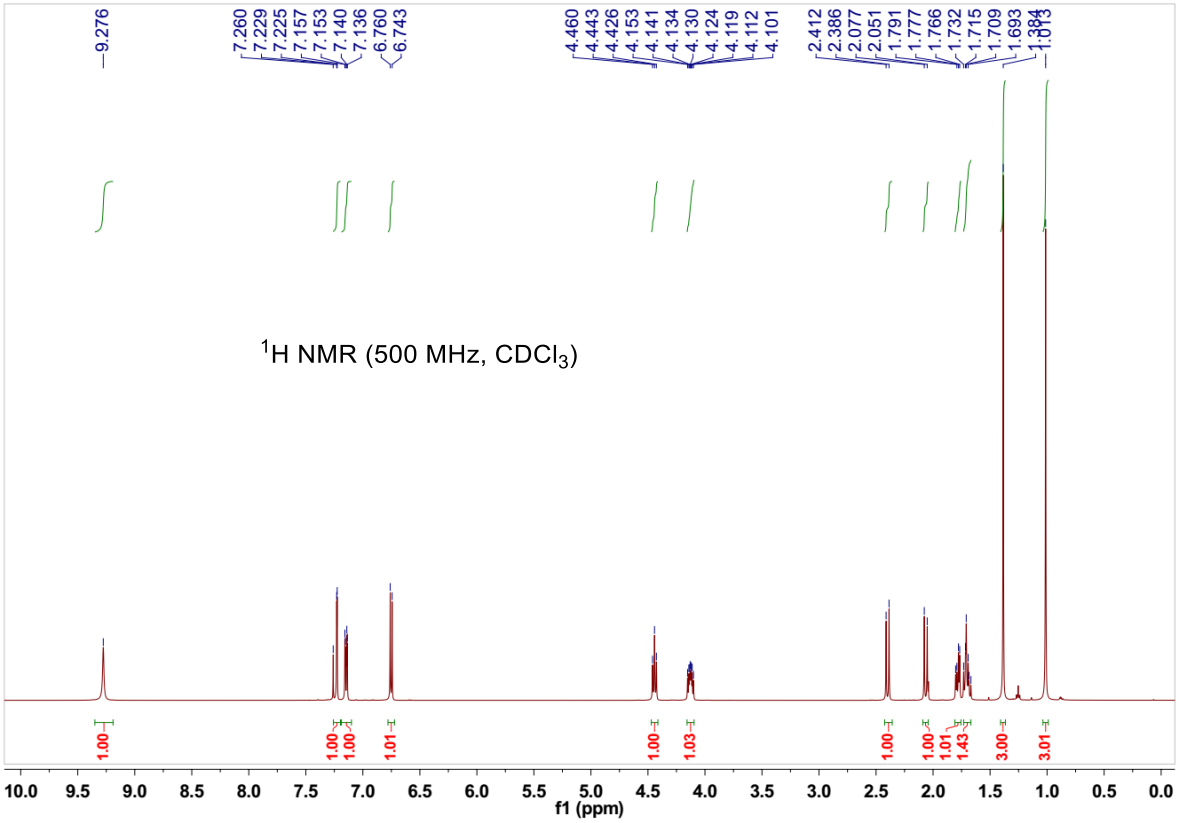


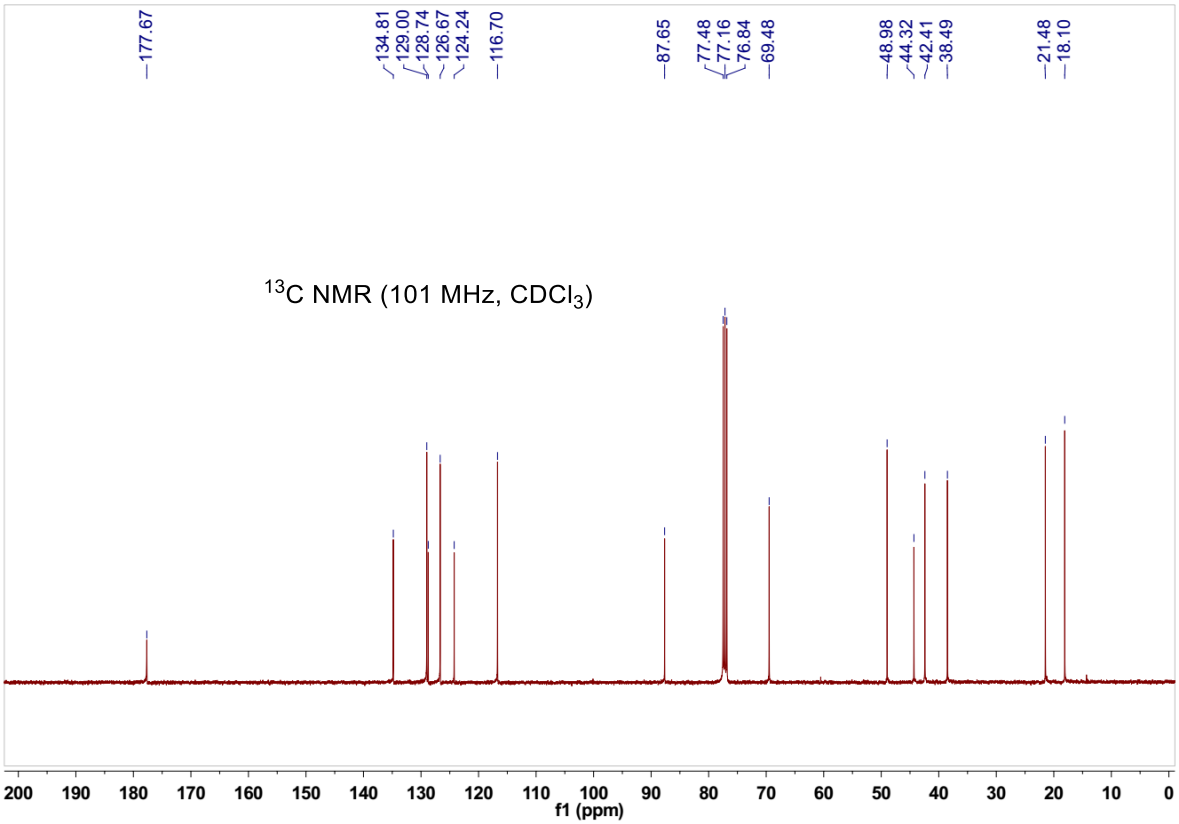



177.46
160.54
158.13
132.33
132.31
124.46
124.39
116.60
116.52
115.82
115.59
113.55
113.31
87.77
77.48
77.16
76.84
69.48
48.95
44.10
42.41
38.53
21.47
18.09
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

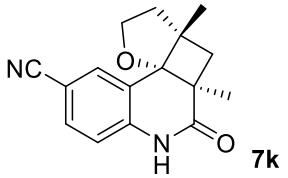
(3a*S*,4a*R*,10b*S*)-9-chloro-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7j):



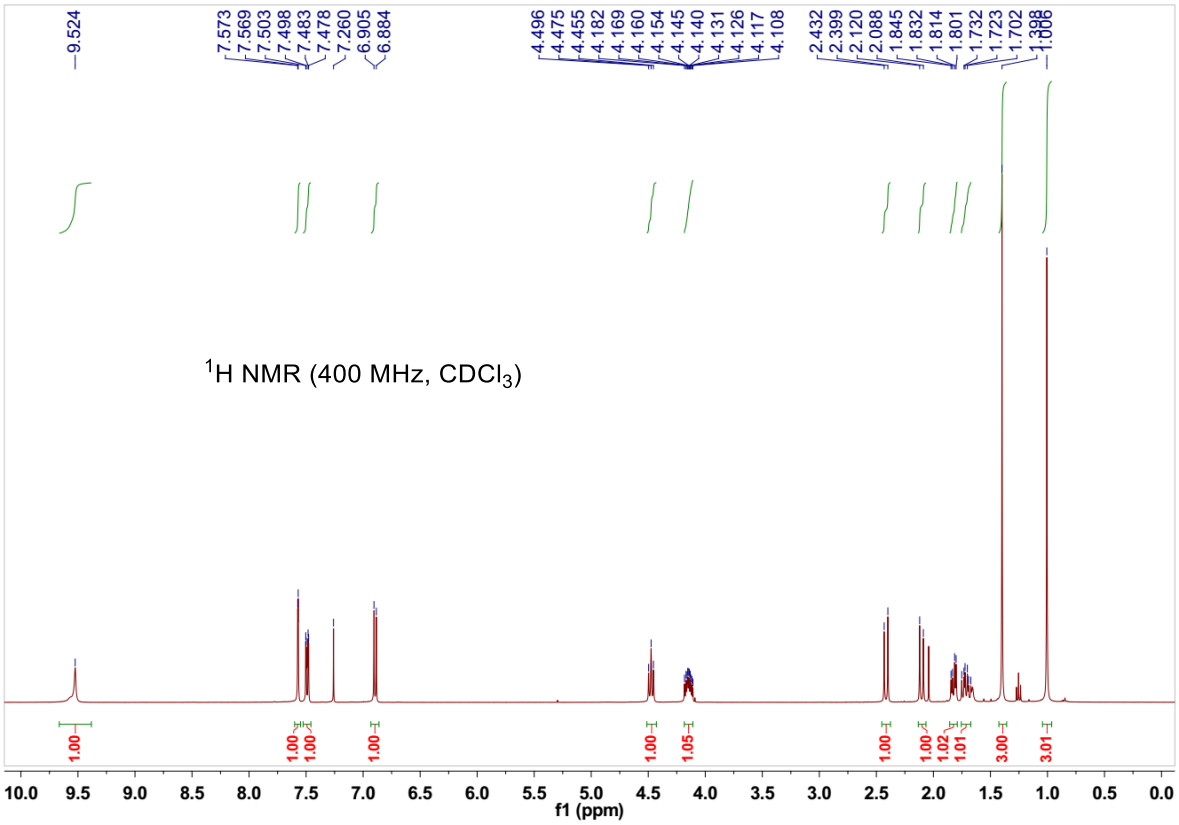


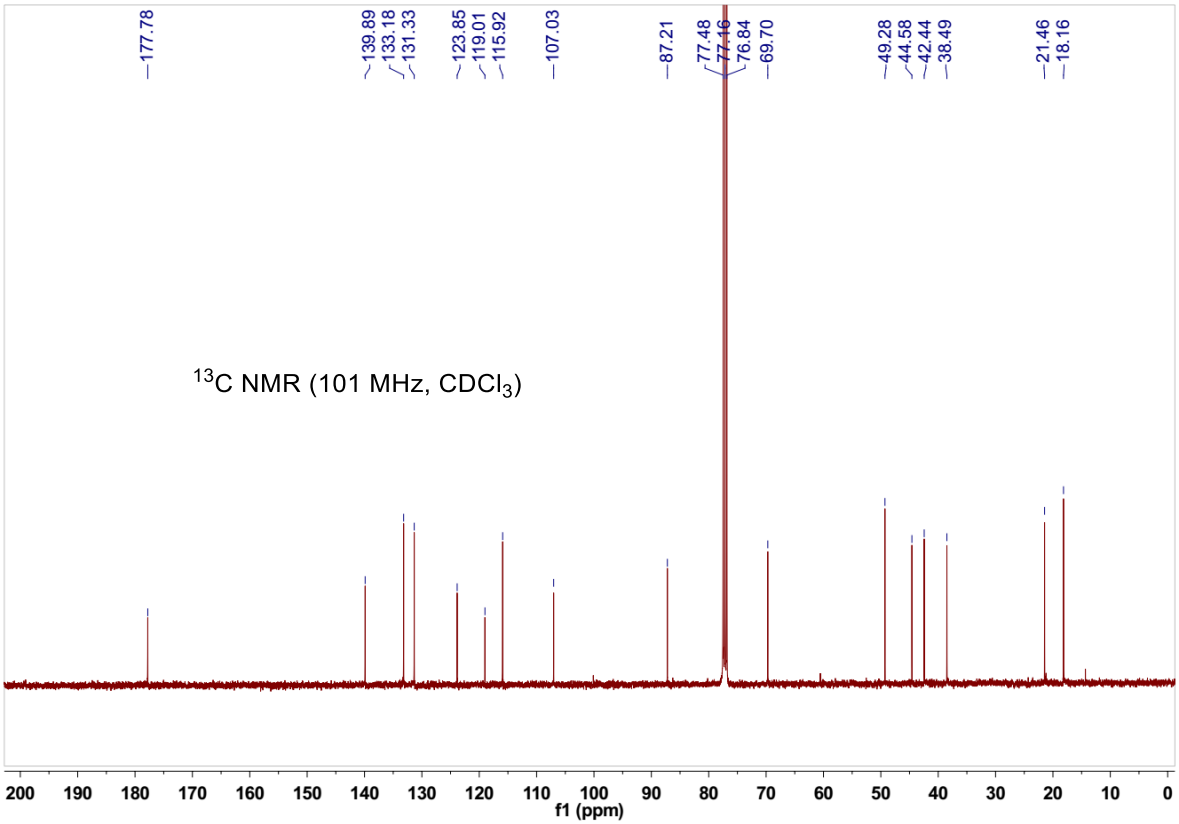


(3a*S*,4a*R*,10b*S*)-3a,4a-dimethyl-5-oxo-3,3a,4,4a,5,6-hexahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinoline-9-carbonitrile (7k):

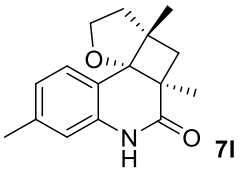


7k

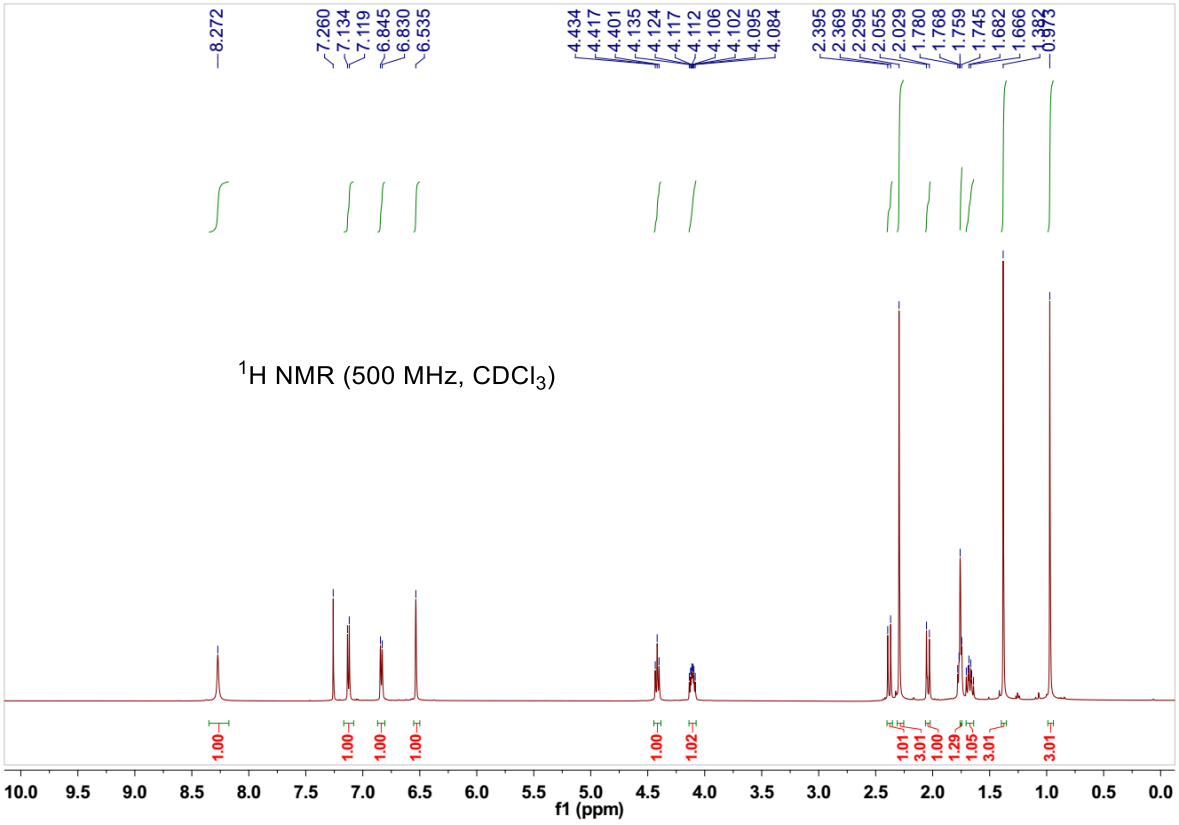


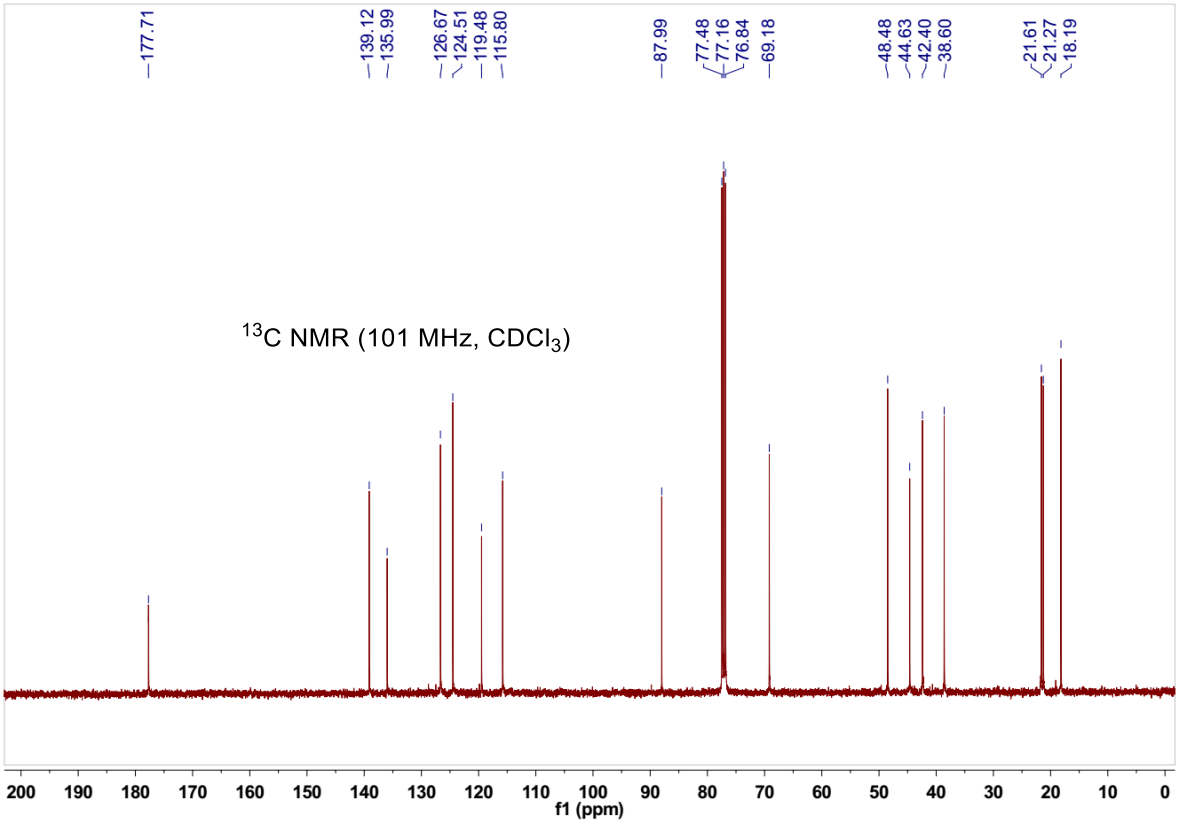


(3a*S*,4a*R*,10b*S*)-3a,4a,8-trimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7l):

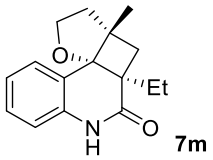


7l

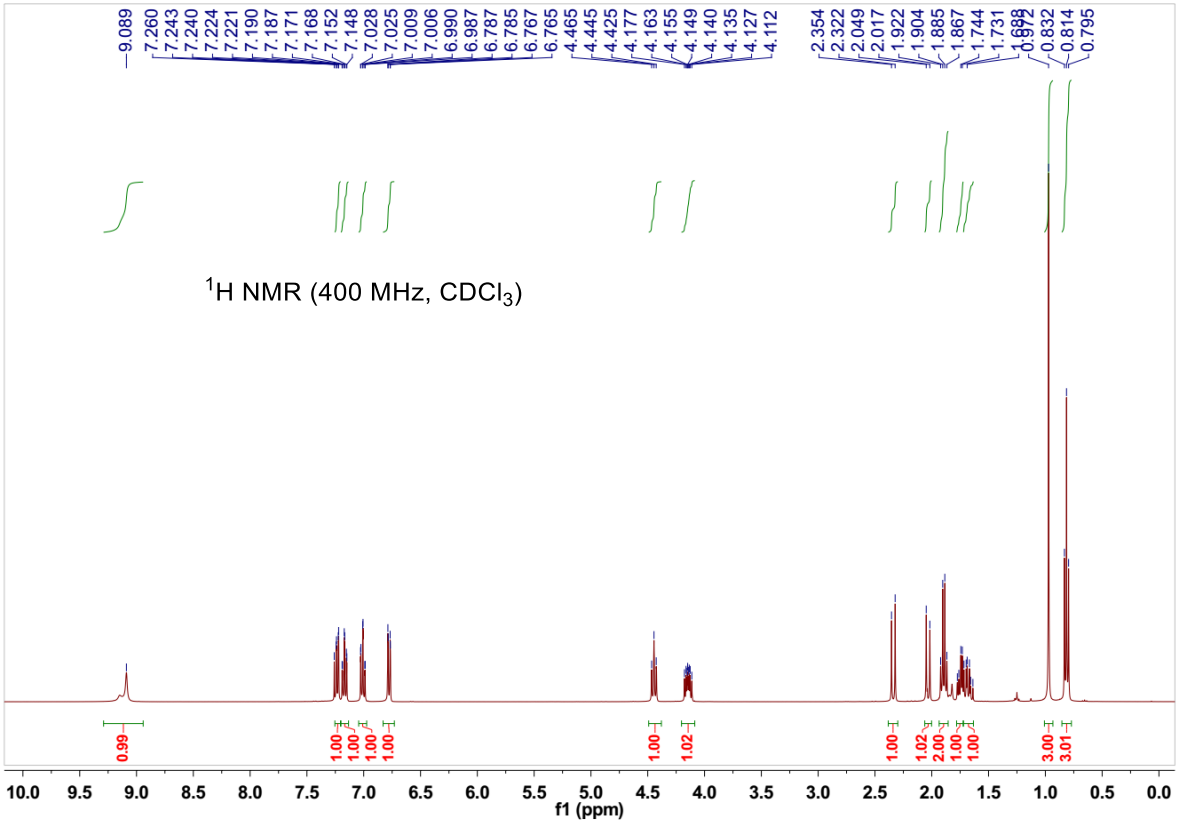


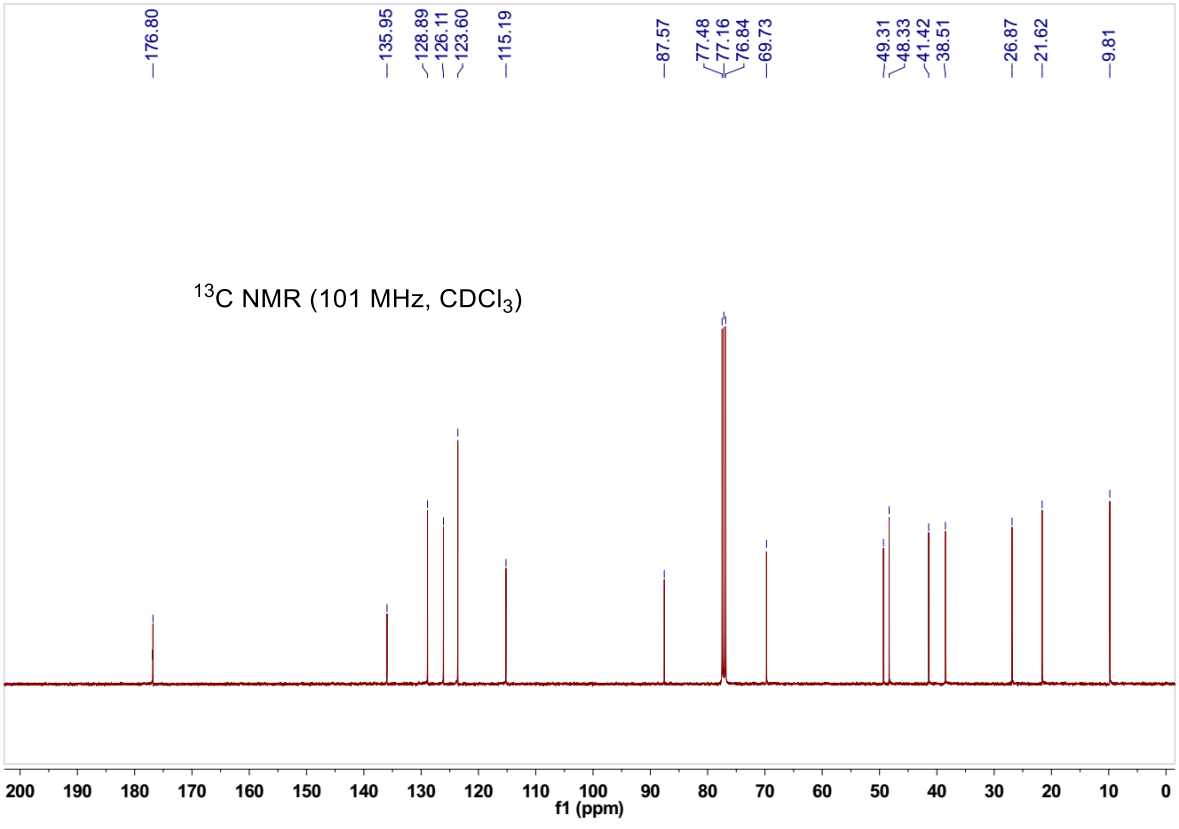


(3a*S*,4a*R*,10b*S*)-4a-ethyl-3a-methyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7m):

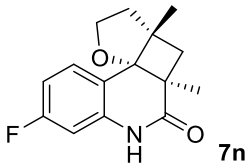


7m

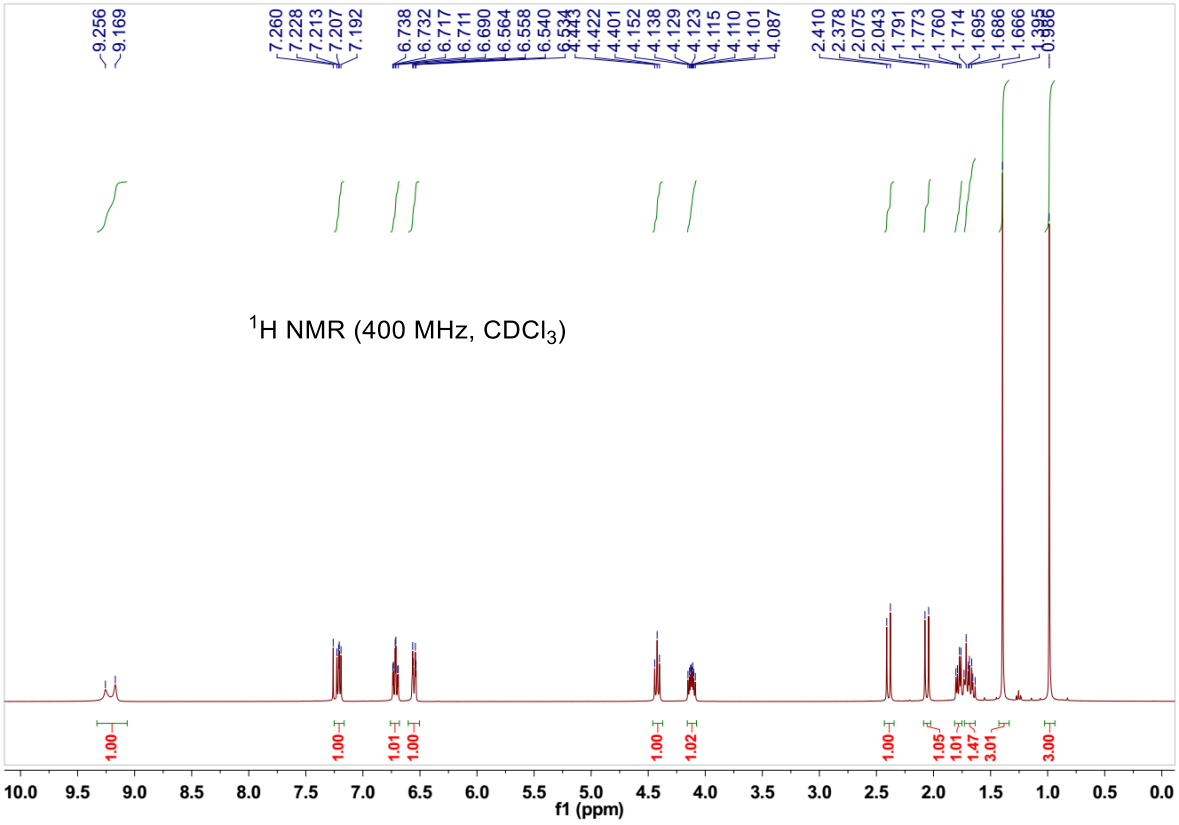


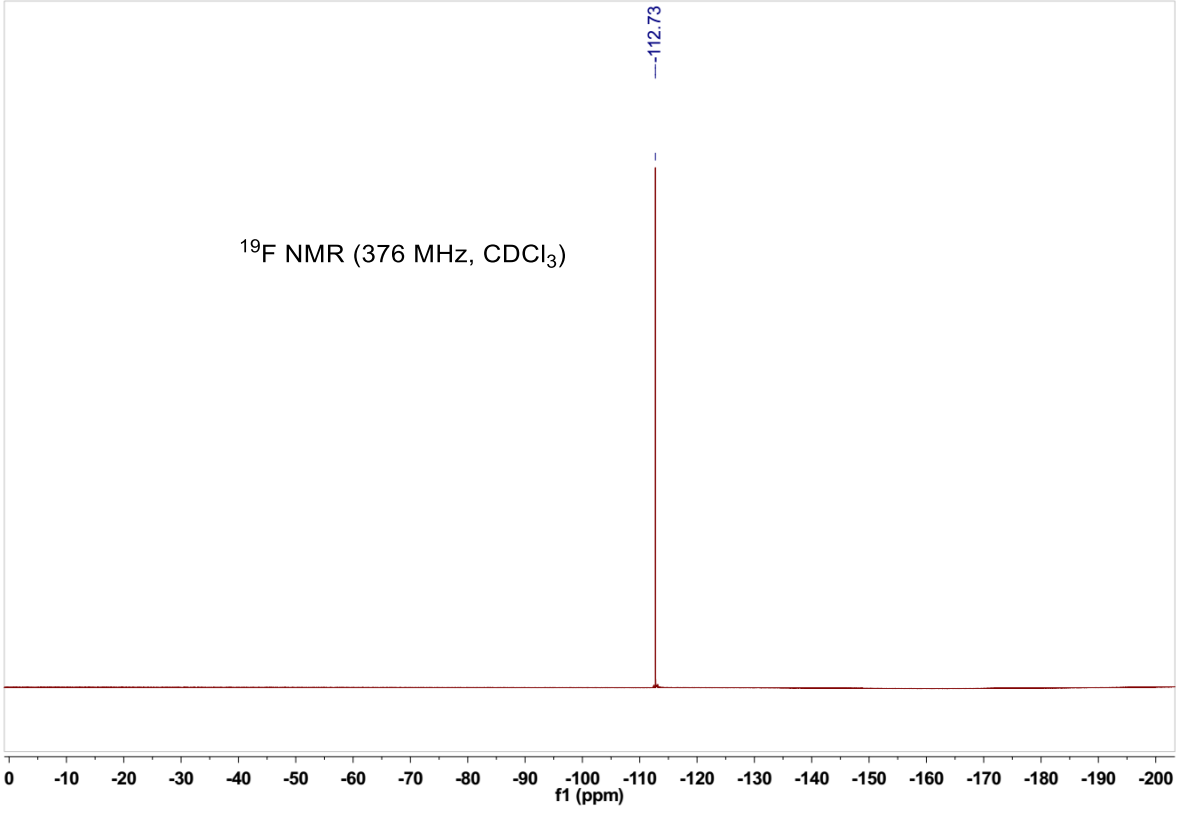


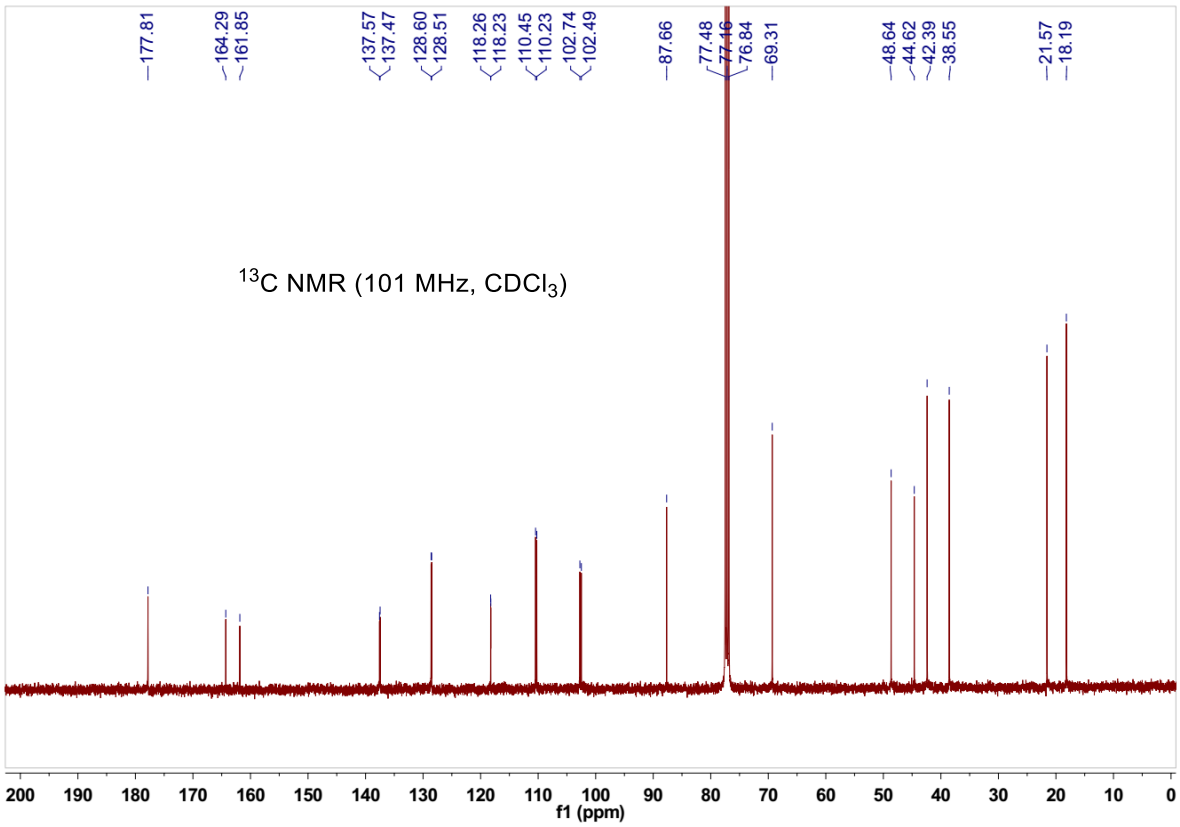
(3a*S*,4a*R*,10b*S*)-8-fluoro-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7n):



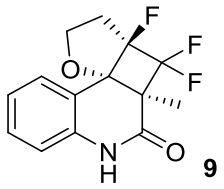
7n



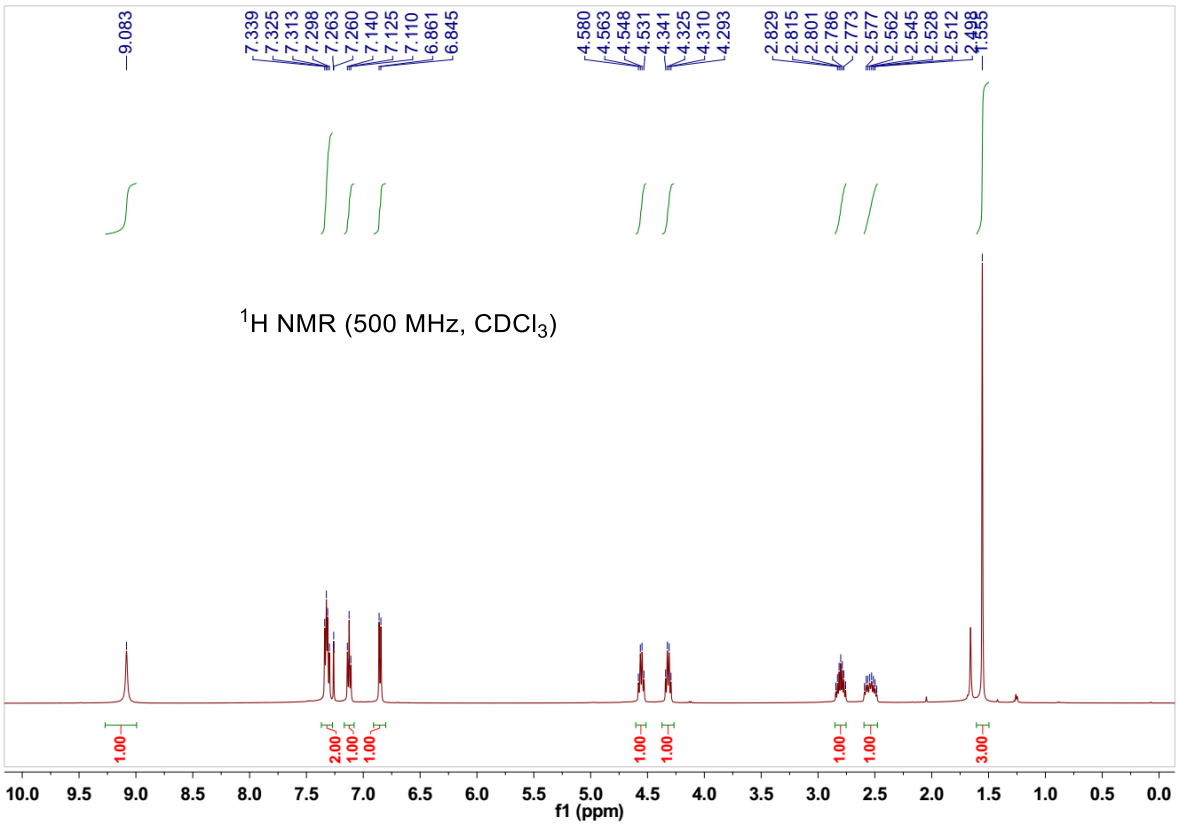


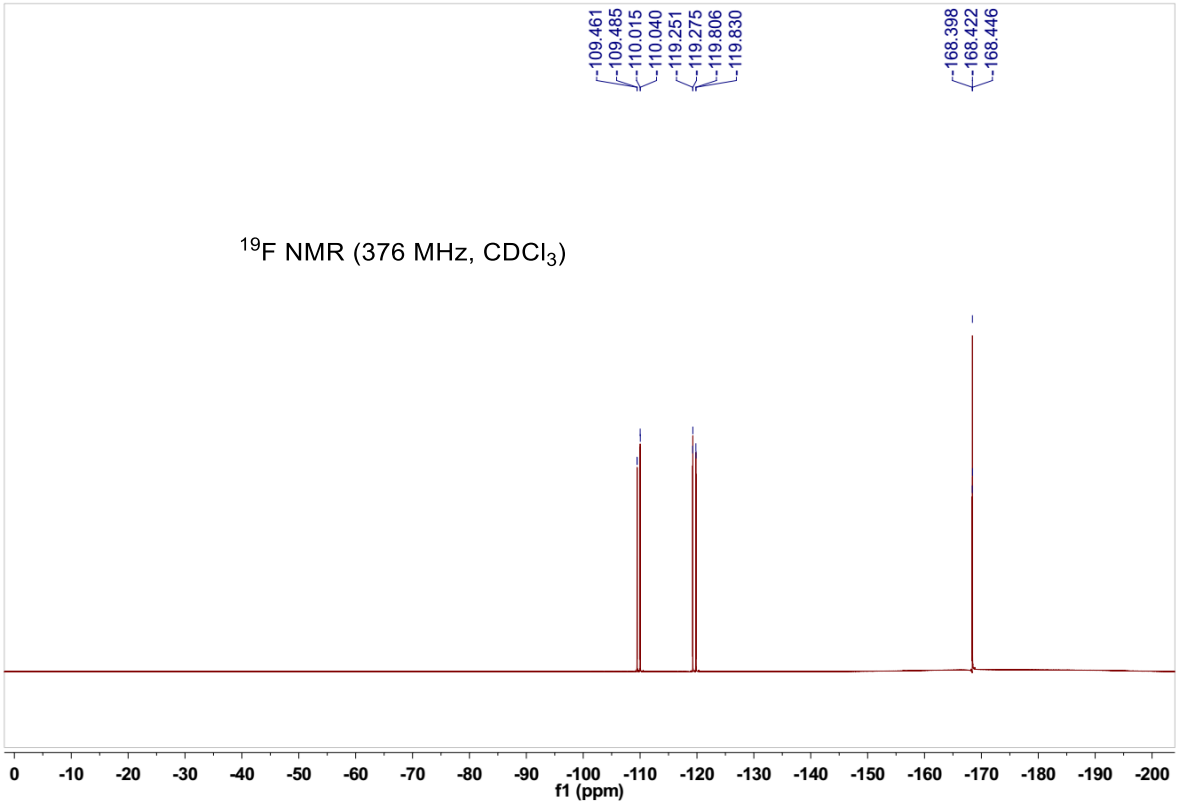

177.81
164.29
161.85
137.57
137.47
128.60
128.51
118.26
118.23
110.45
110.23
102.74
102.49
87.66
77.48
77.16
76.84
69.31
48.64
44.62
42.39
38.55
21.57
18.19
^{13}C NMR (101 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

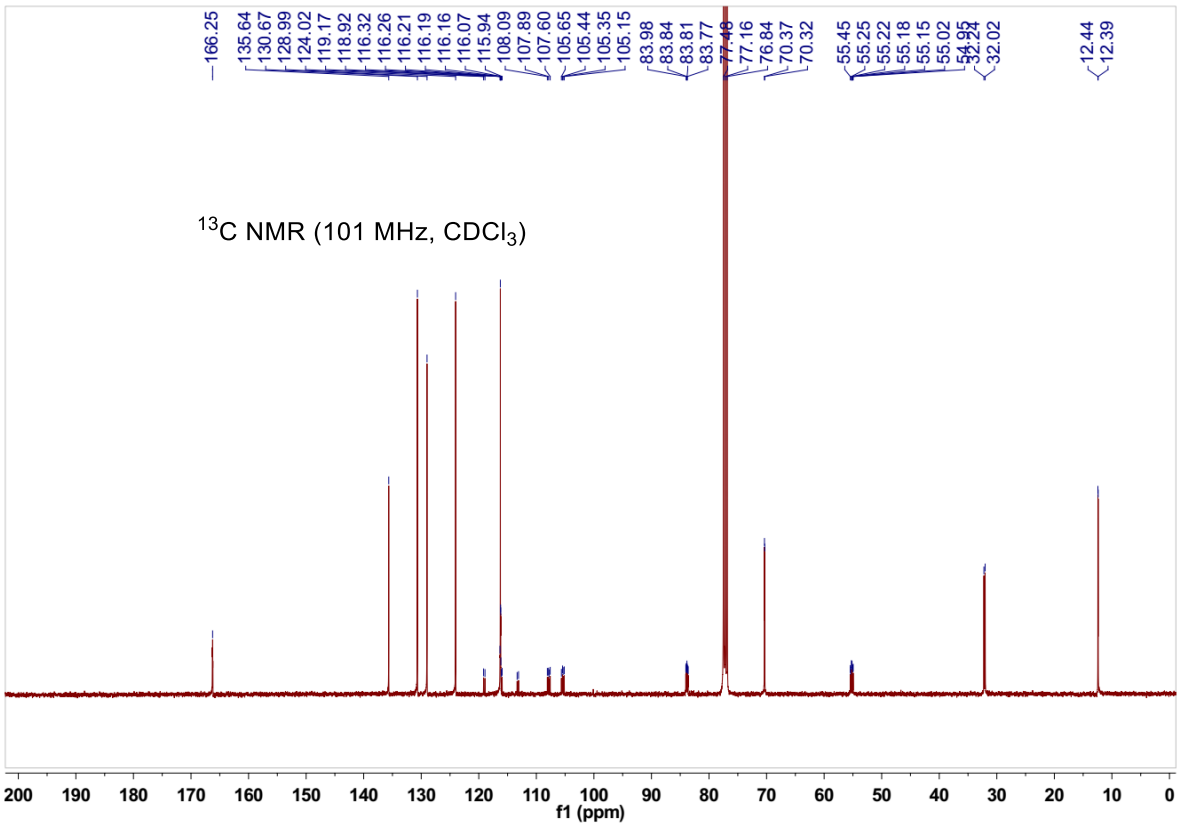
(3a*R*,4a*R*,10b*S*)-3a,4,4-trifluoro-4a-methyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (9):



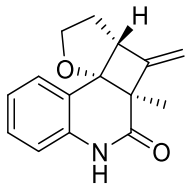
9



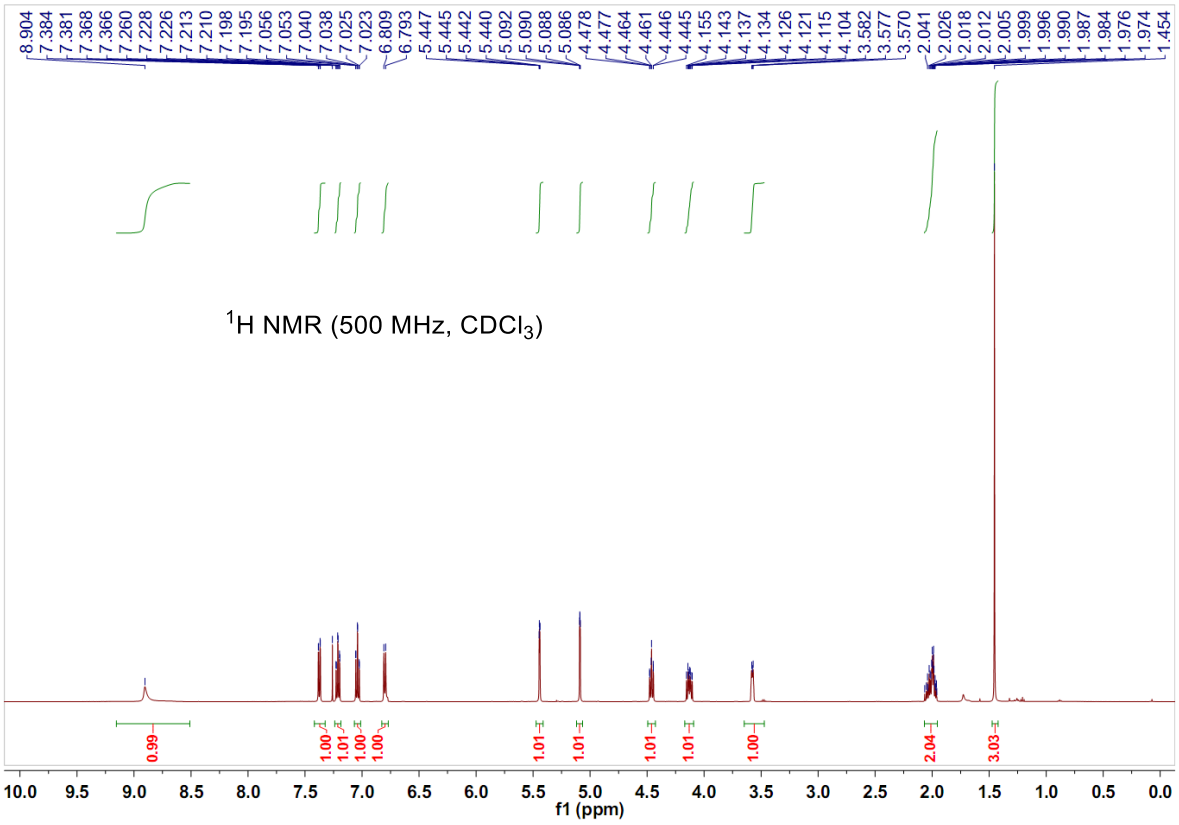


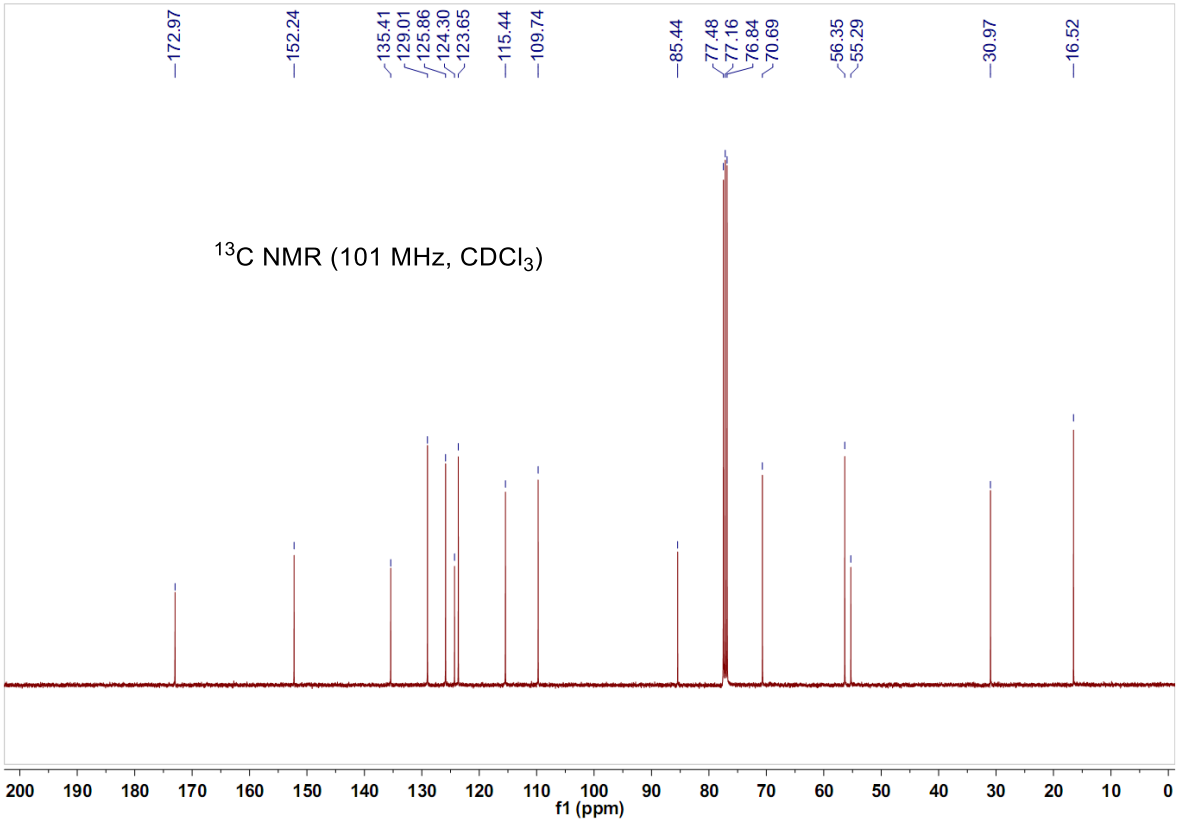

166.25
135.64
130.67
128.99
124.02
119.17
118.92
116.32
116.26
116.21
116.19
116.16
116.07
115.94
108.09
107.89
107.60
105.65
105.44
105.35
105.15
83.98
83.84
83.81
83.77
77.48
77.16
76.84
70.37
70.32
55.45
55.25
55.22
55.18
55.15
55.02
32.24
32.02
12.44
12.39
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(3a*R*,4a*R*,10b*S*)-4a-methyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*] quinolin-5(6*H*)-one (11a):

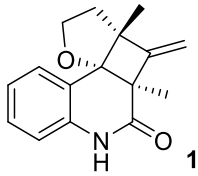


11a

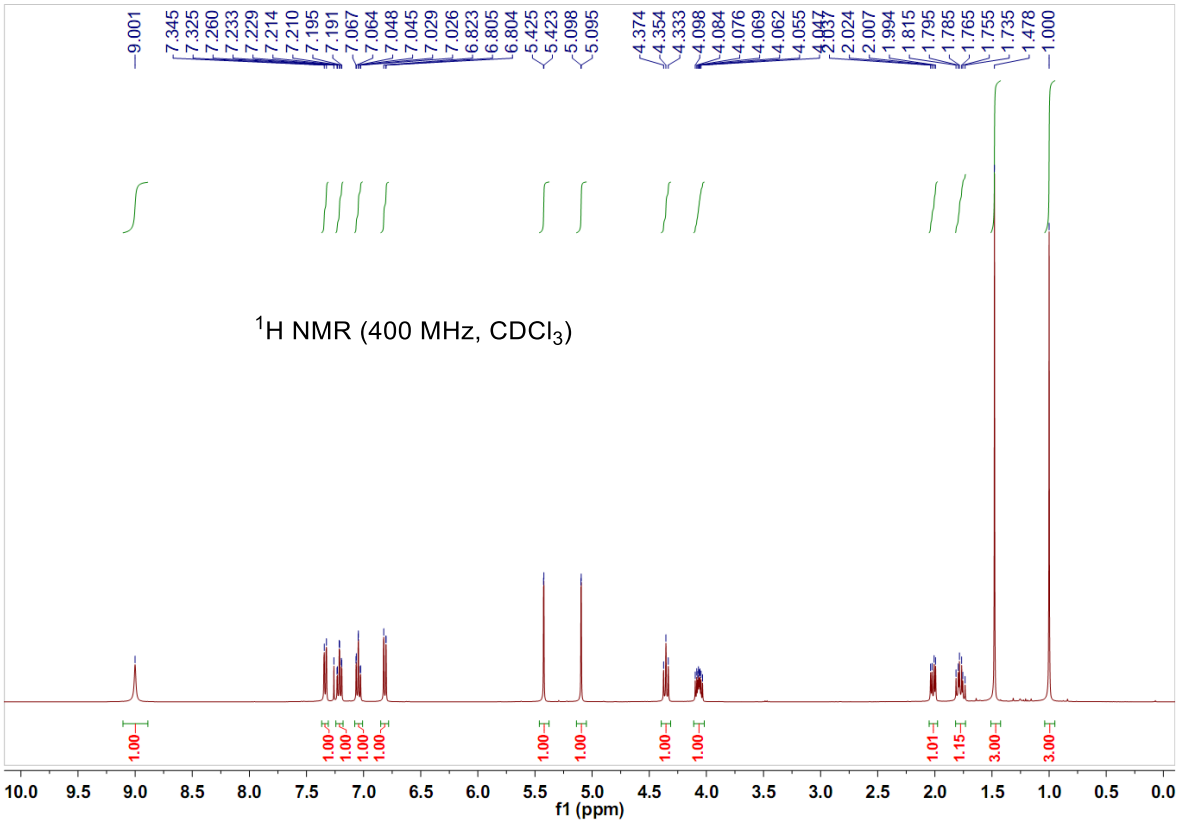


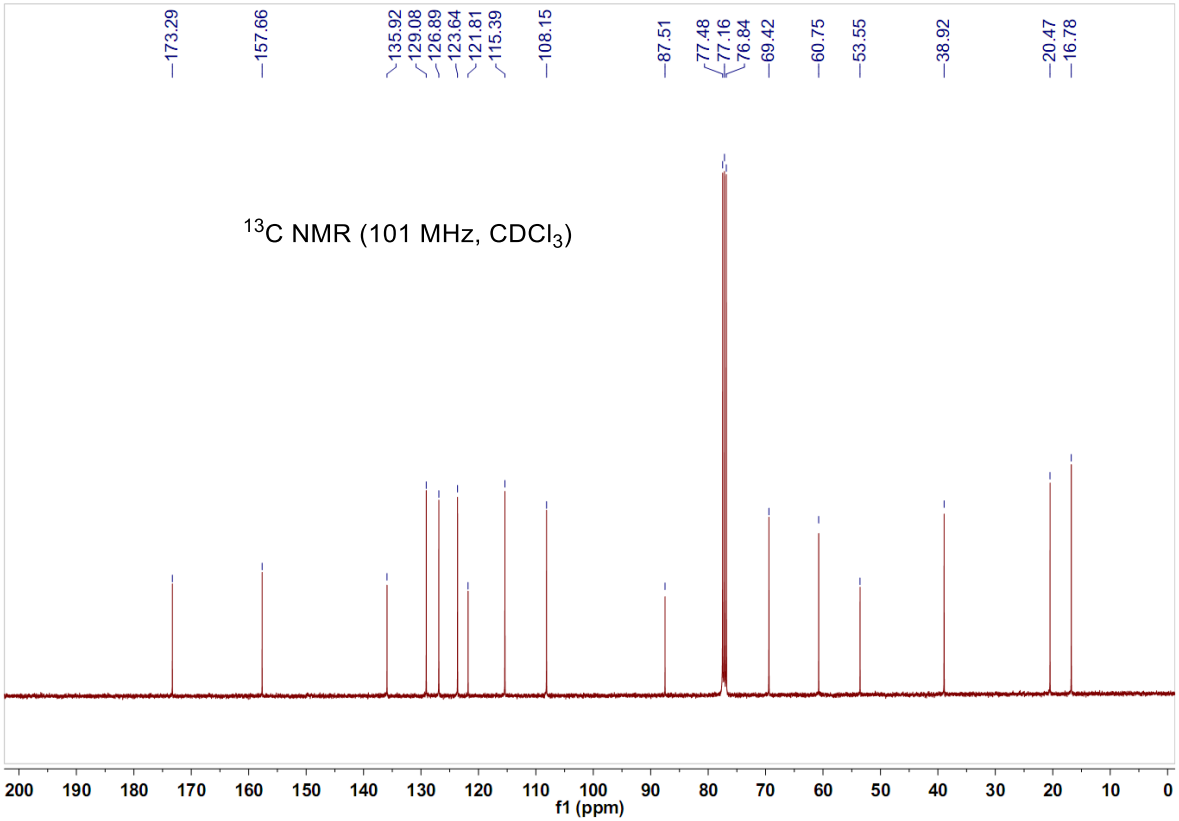


(3a*R*,4a*R*,10b*S*)-3a,4a-dimethyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (11b):

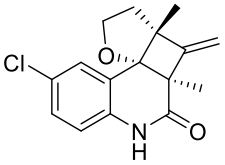


11b

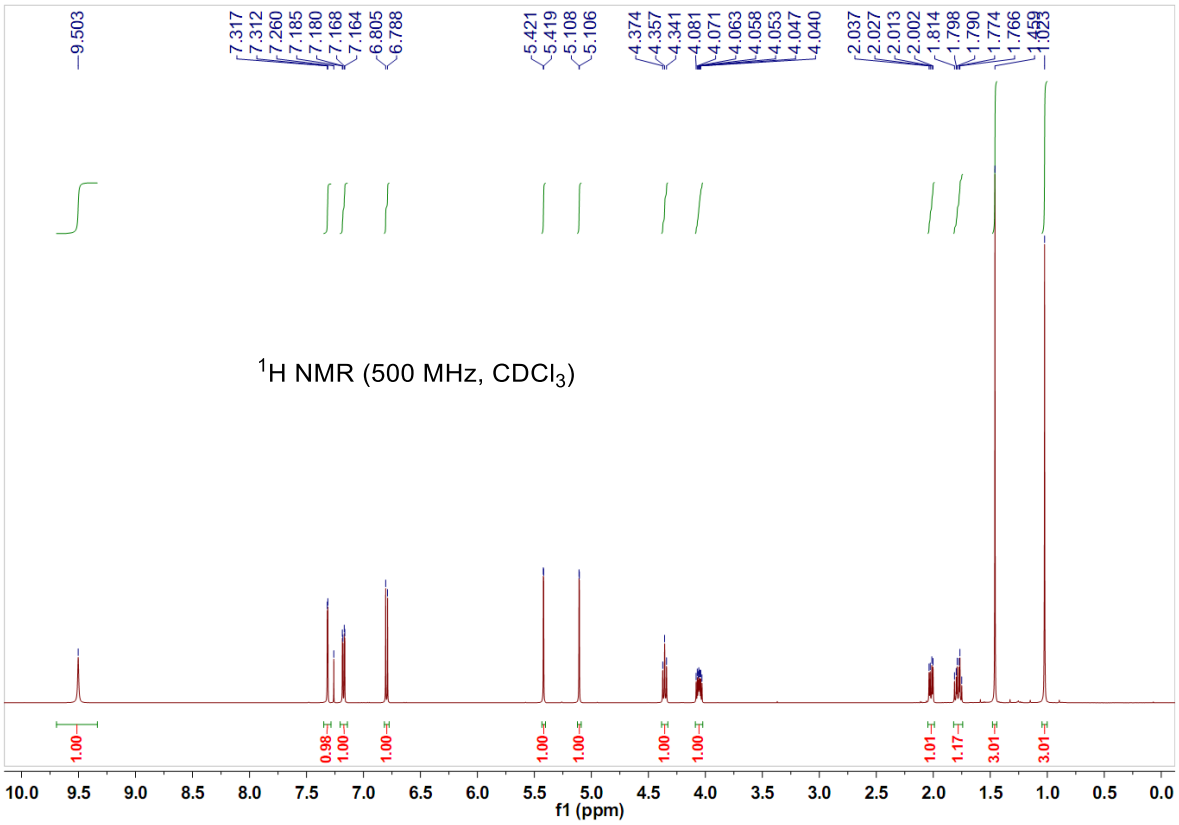


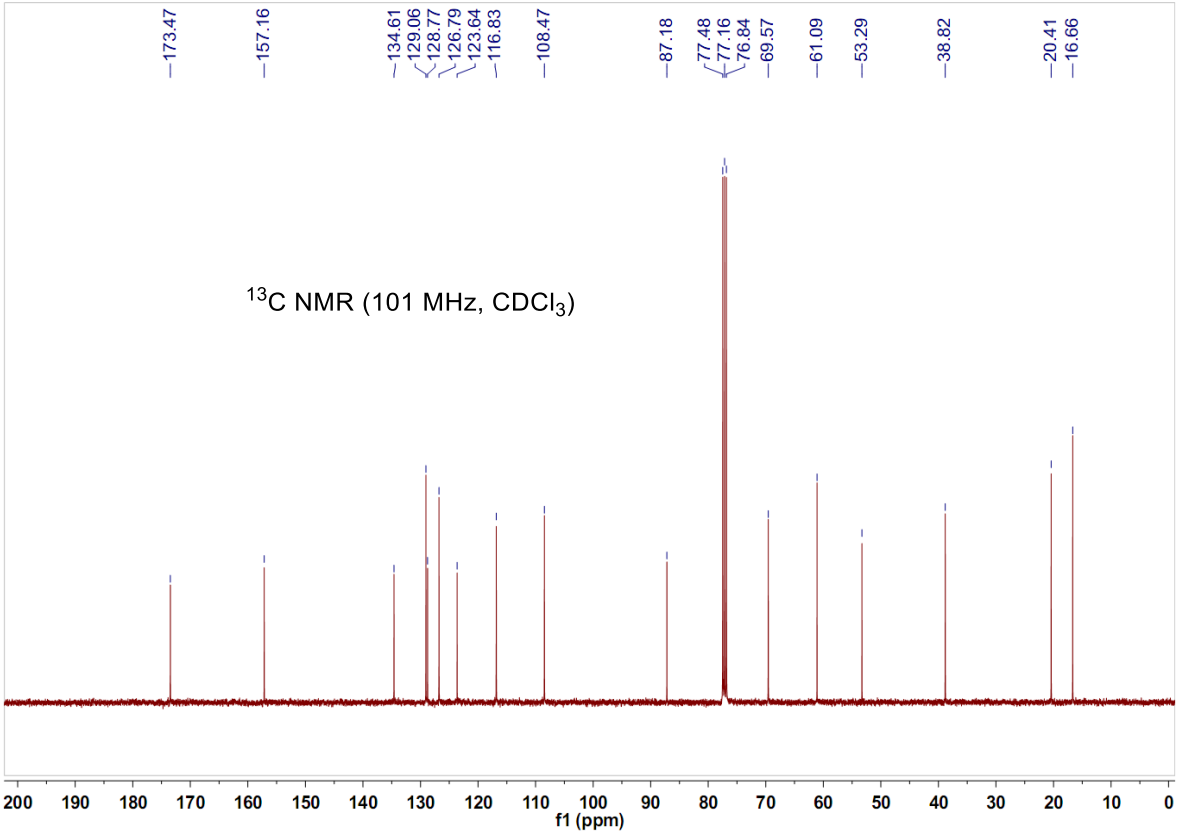


(3a*R*,4a*R*,10b*S*)-9-chloro-3a,4a-dimethyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]-cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (11c):

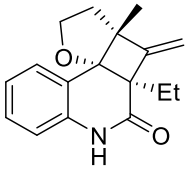


11c

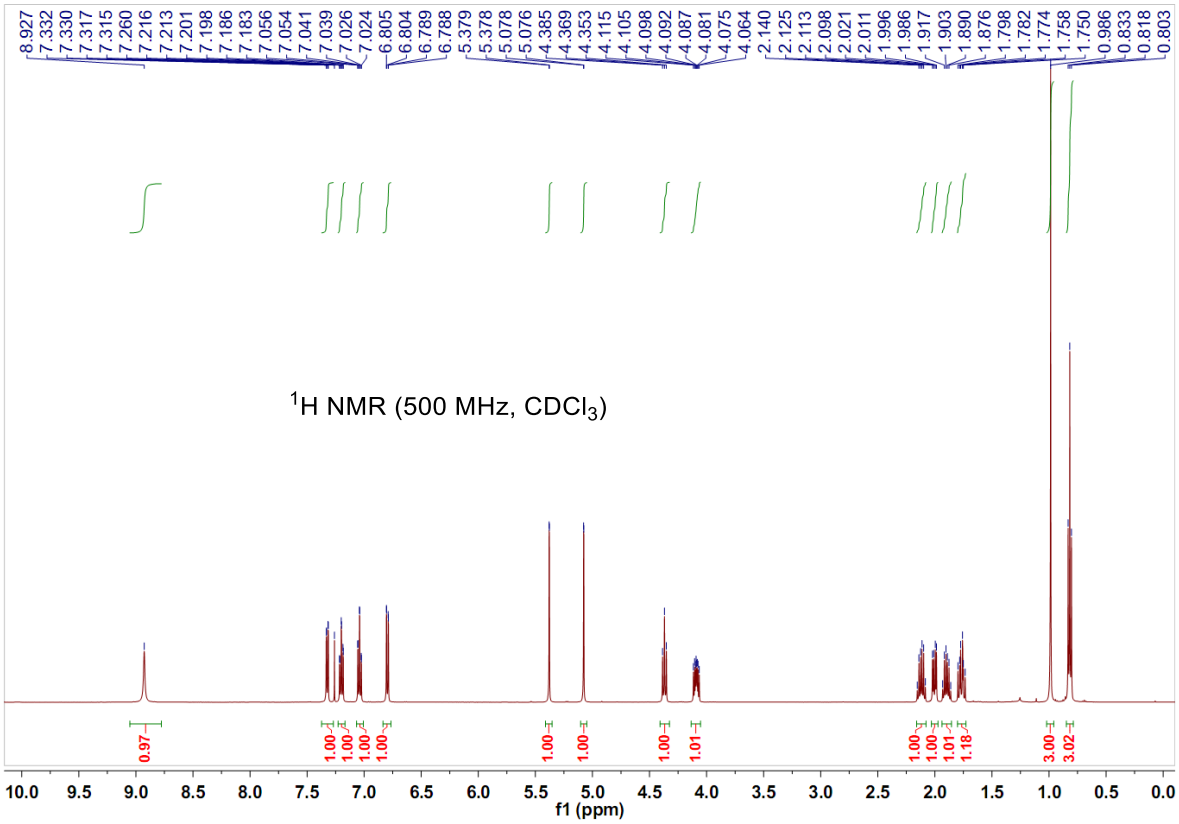


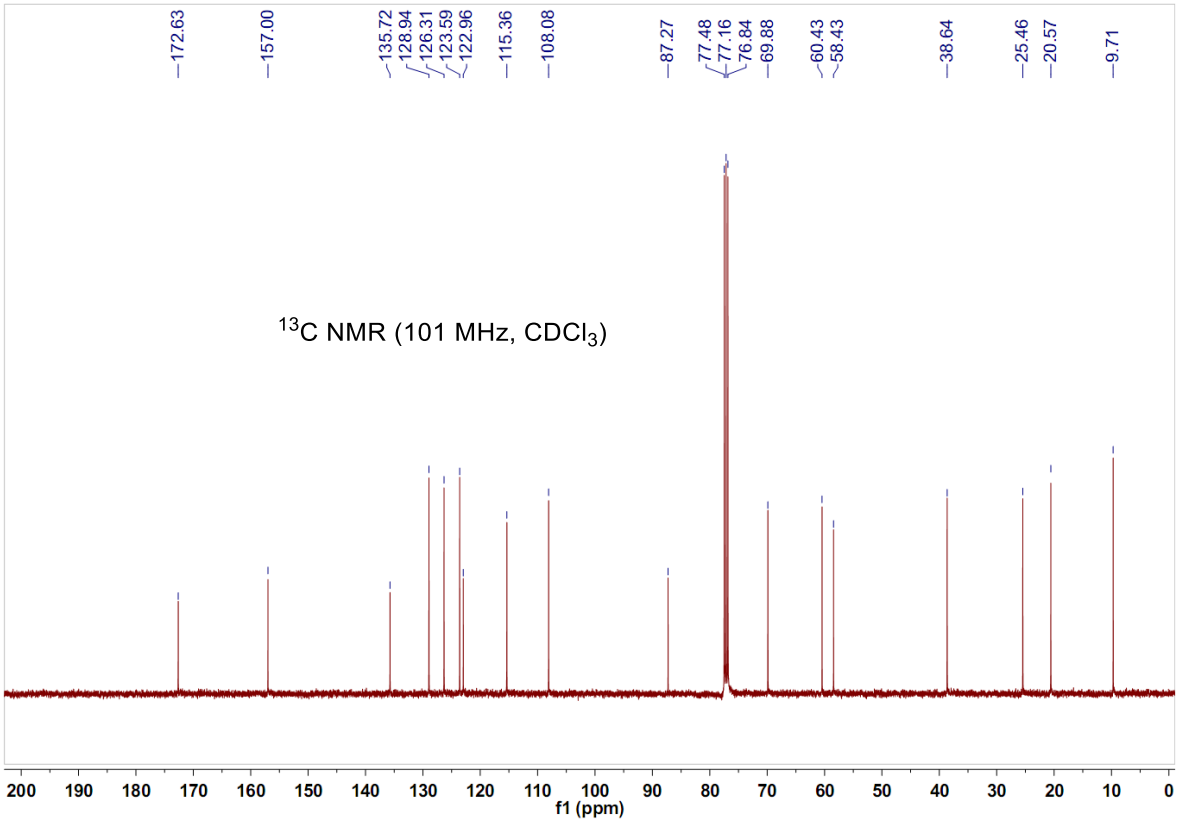


(3a*R*,4a*R*,10b*S*)-4a-ethyl-3a-methyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (11d):

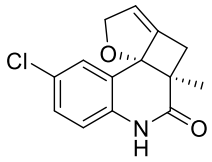


11d

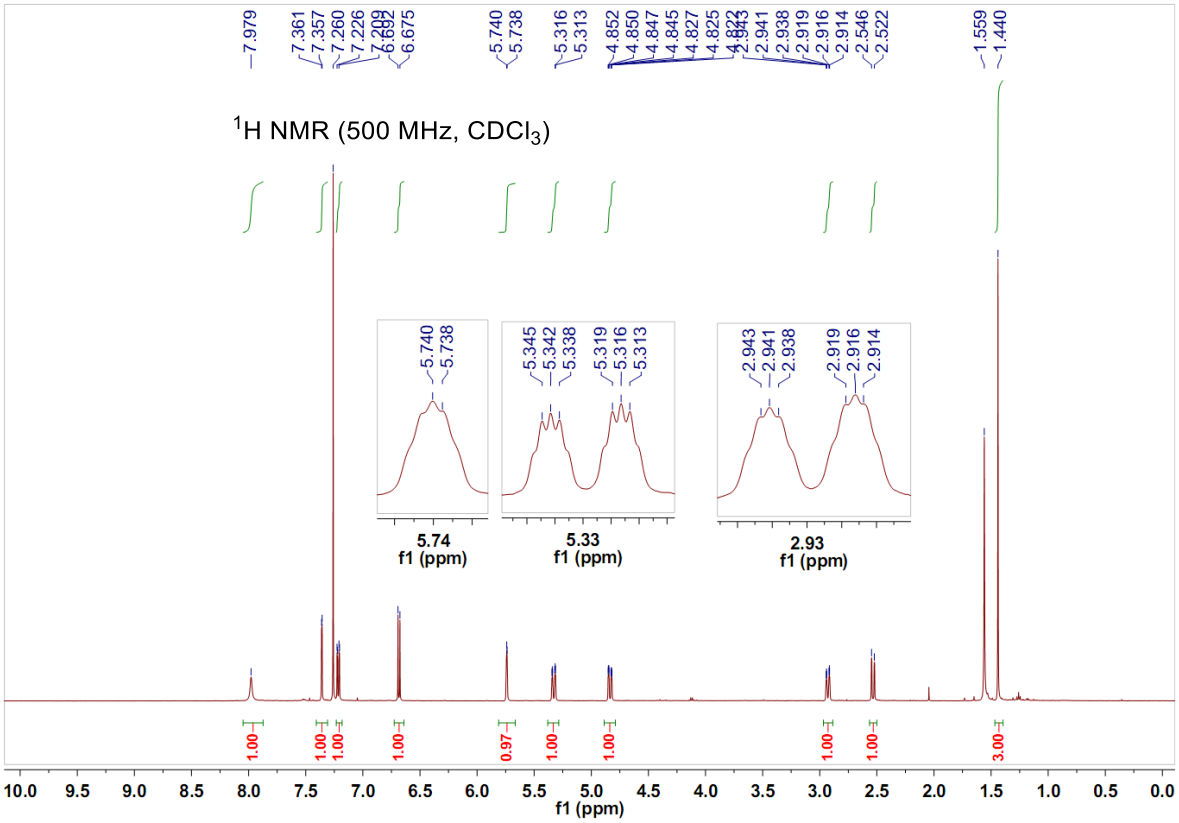


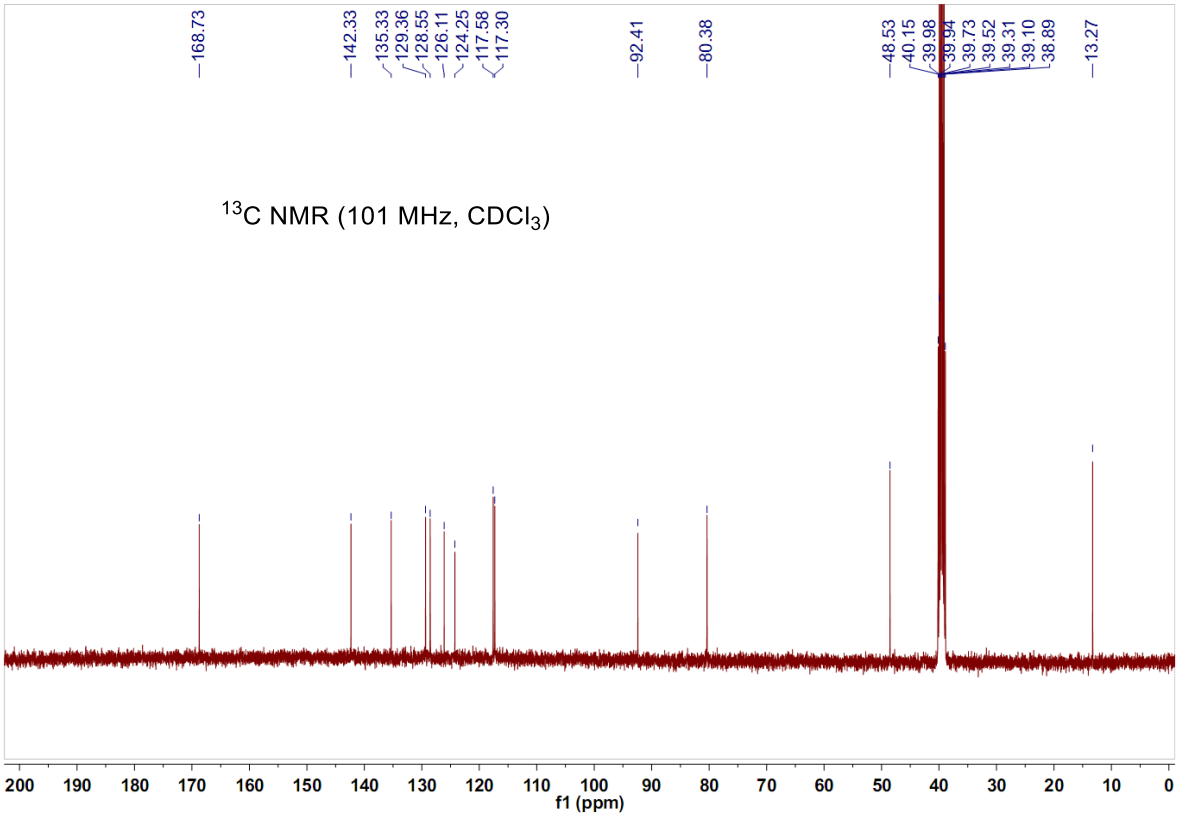


(4a*R*,10b*S*)-9-chloro-4a-methyl-4,4a-dihydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (13a):

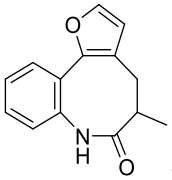


13a

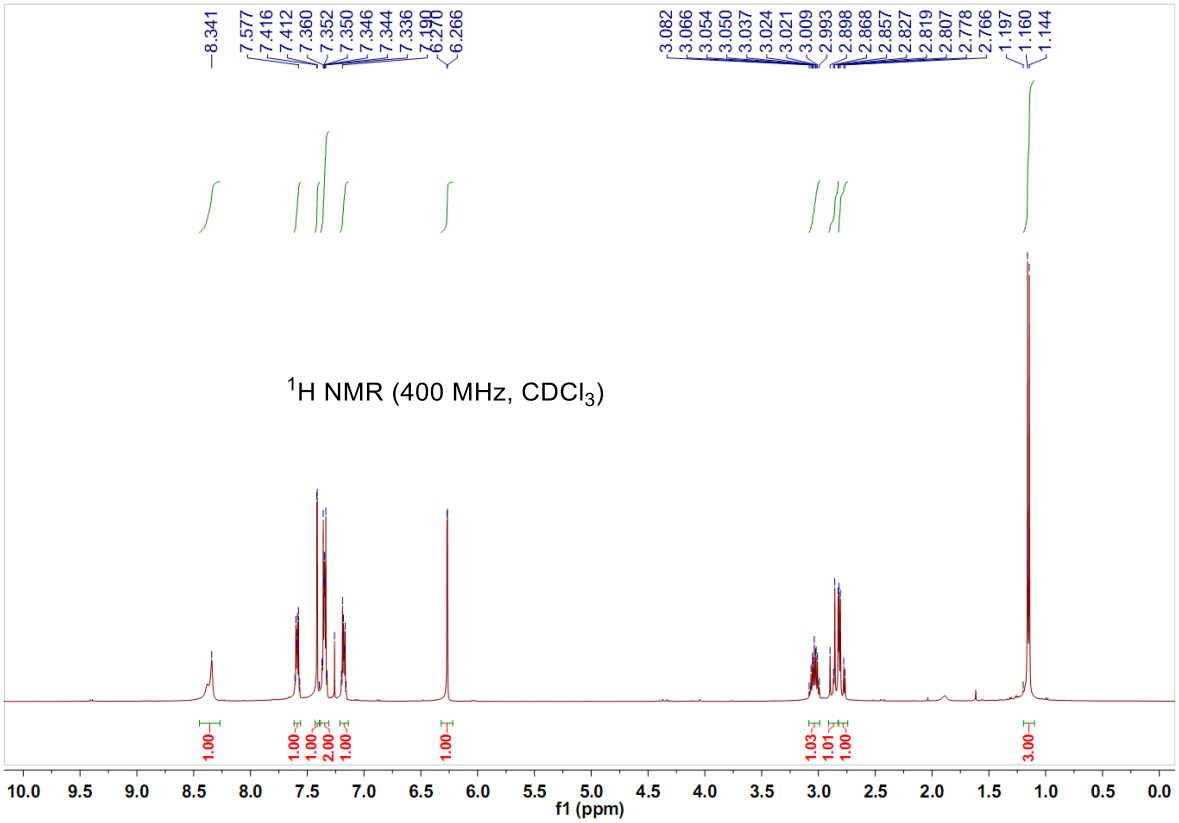


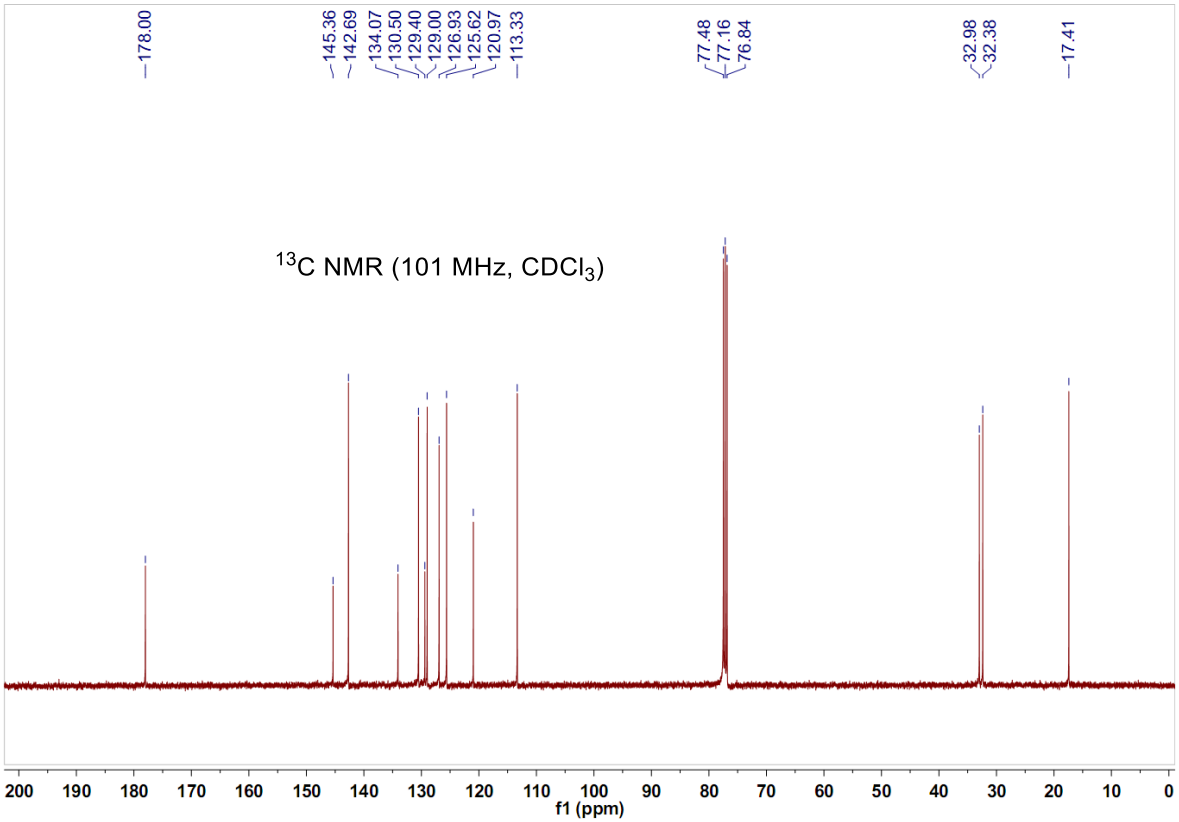


5-methyl-4,7-dihydrobenzo[*b*]furo[2,3-*d*]azocin-6(5*H*)-one (*rac*-14b):

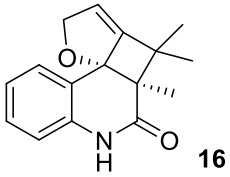


rac-**14b**

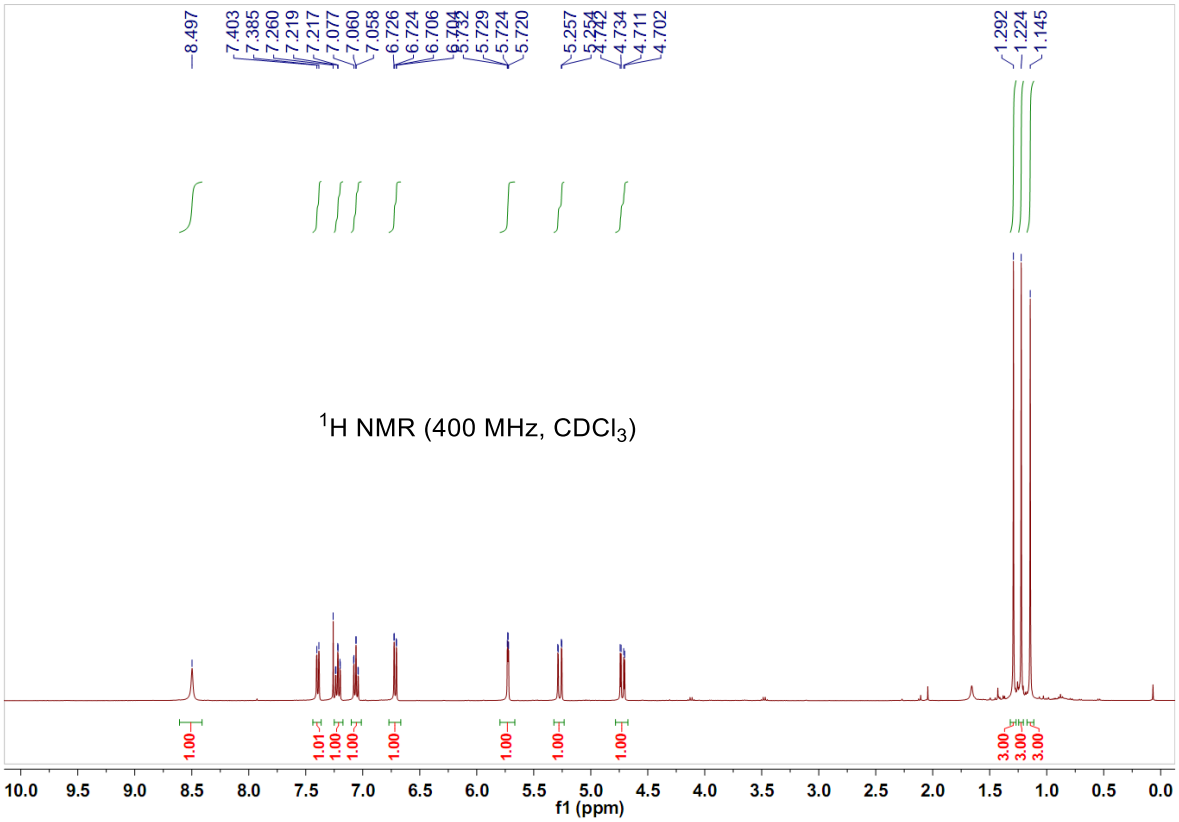


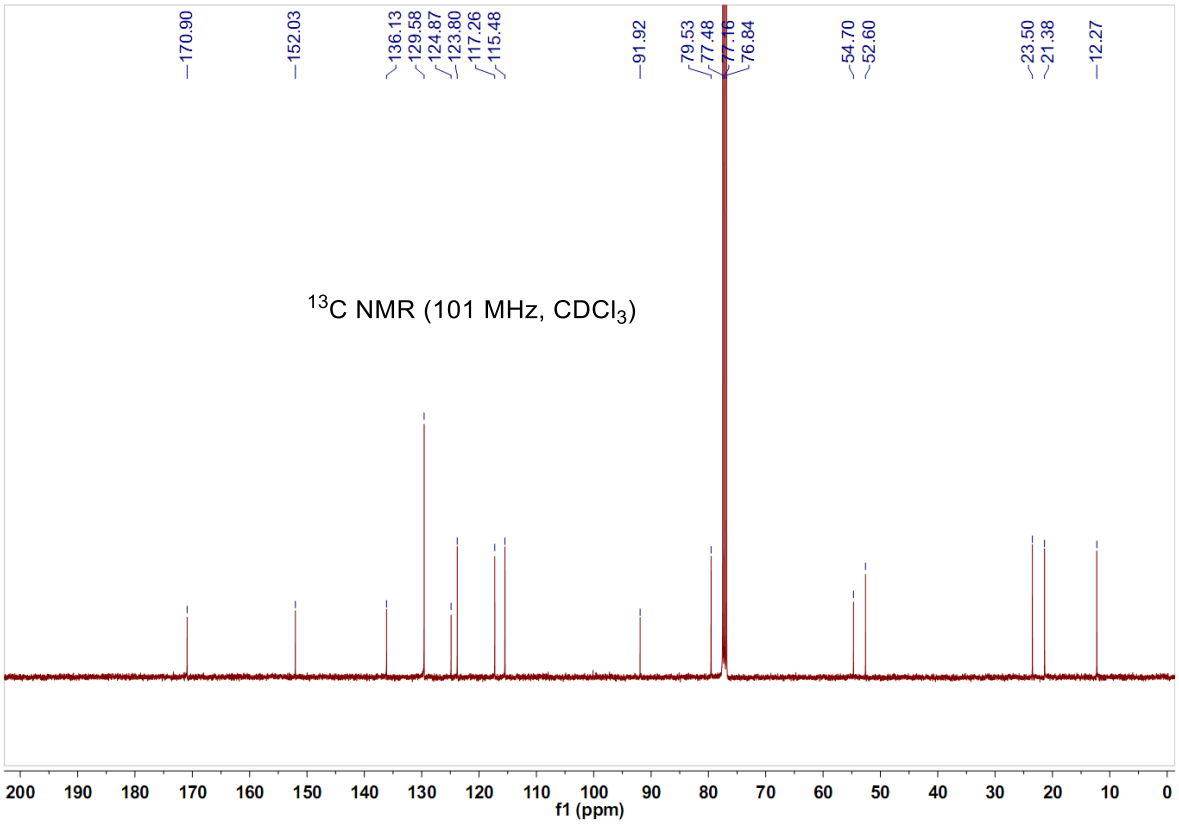


(4a*R*,10b*S*)-4,4,4a-trimethyl-4,4a-dihydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (16):

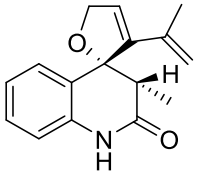


16

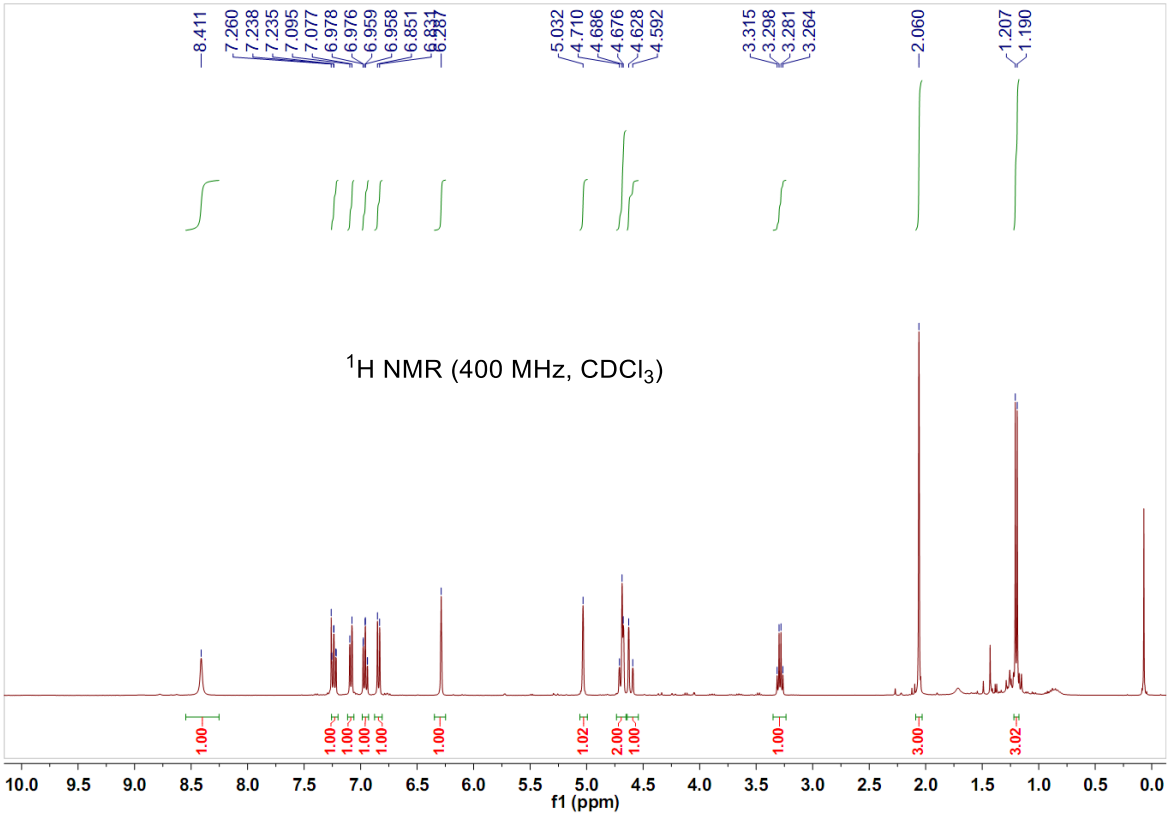


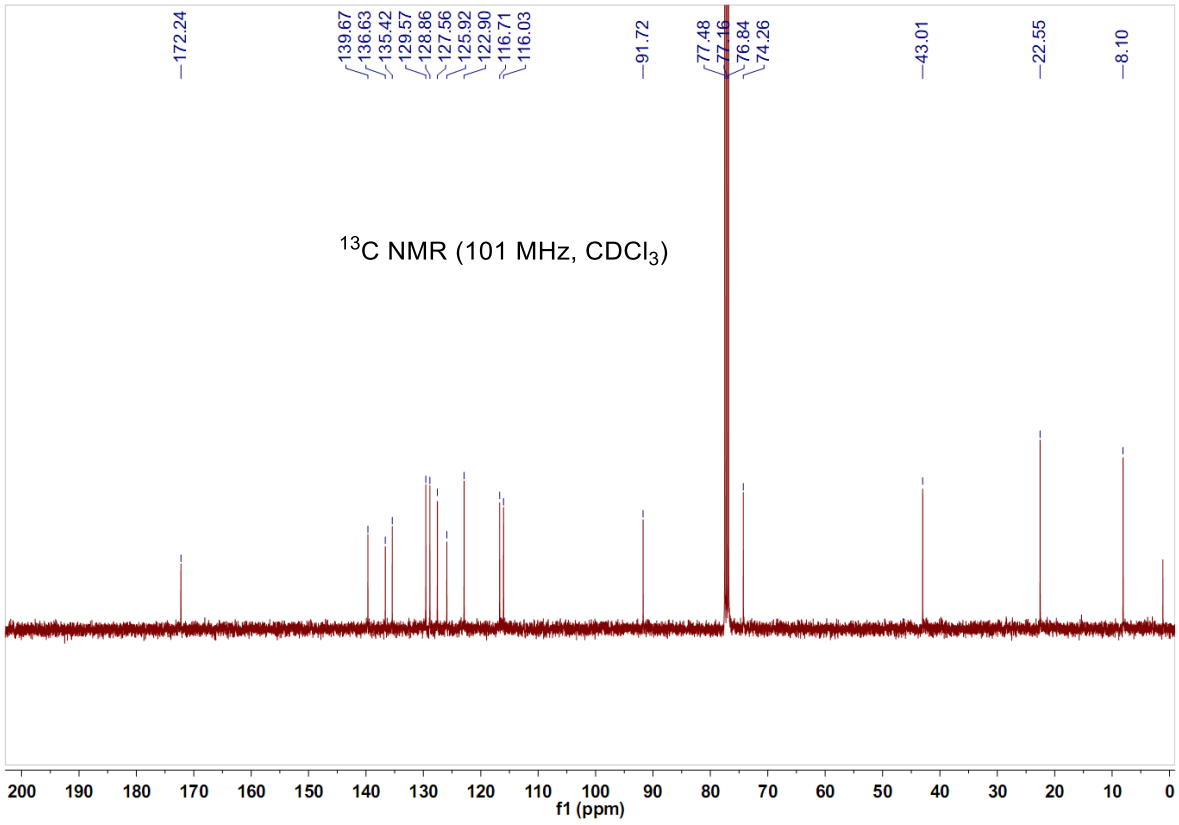


(2*S*,3'*S*)-3'-methyl-3-(prop-1-en-2-yl)-1'*H*,5*H*-spiro[furan-2,4'-quinolin]-2'(3'*H*)-one (18):



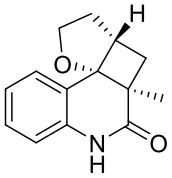
18



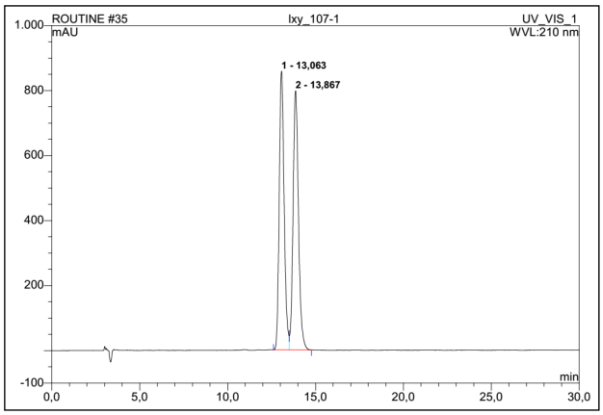


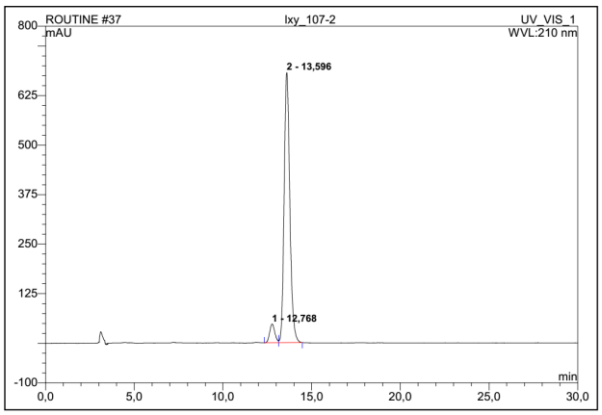
9. HPLC Traces

(3a*S*,4a*R*,10b*S*)-4a-methyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7a):



7b, 88% ee

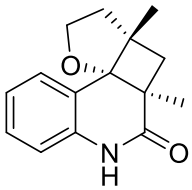




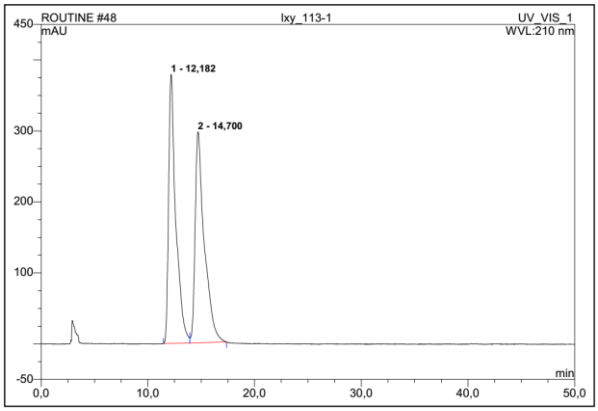
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13,06	n.a.	857,914	279,032	49,51	n.a.	BM
2	13,87	n.a.	797,443	284,579	50,49	n.a.	MB
Total:			1655,357	563,612	100,00	0,000	

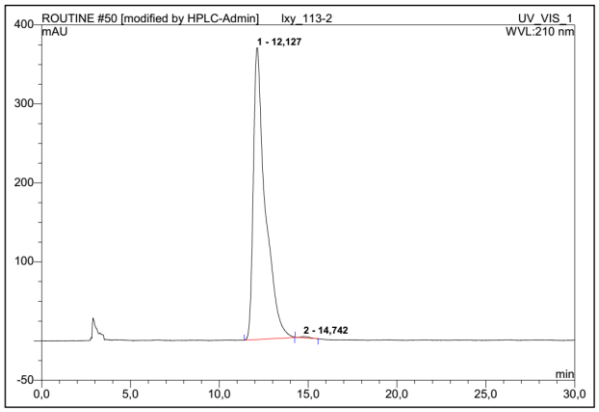
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,77	n.a.	47,218	16,021	5,96	n.a.	BM
2	13,60	n.a.	681,534	252,580	94,04	n.a.	MB
Total:			728,752	268,600	100,00	0,000	

(3a*S*,4a*R*,10b*S*)-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7c):



7c, 99% ee

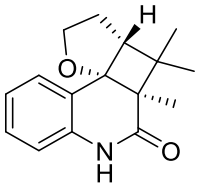




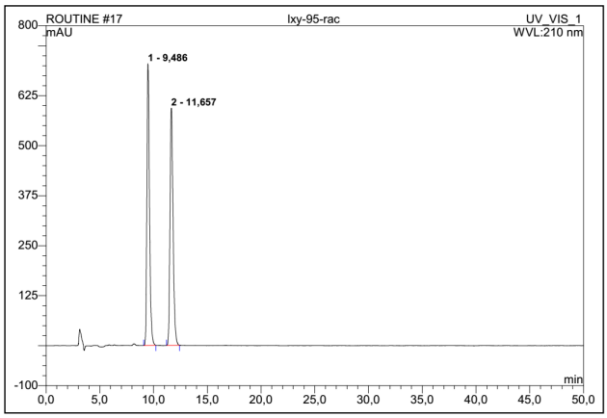
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,18	n.a.	379,101	296,487	49,92	n.a.	BM
2	14,70	n.a.	297,002	297,393	50,08	n.a.	MB
Total:			676,102	593,880	100,00	0,000	

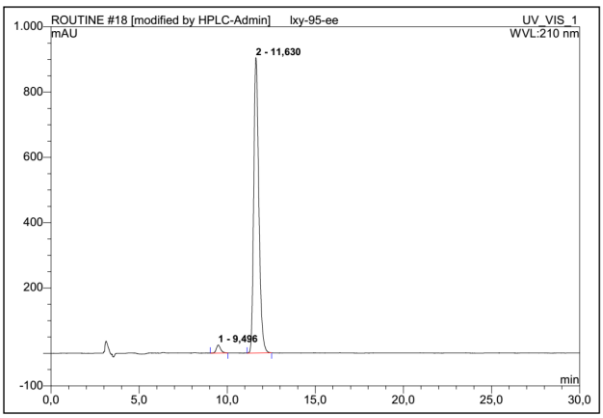
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,13	n.a.	369,697	287,231	99,69	n.a.	BMB
2	14,74	n.a.	1,700	0,898	0,31	n.a.	BMB*
Total:			371,397	288,129	100,00	0,000	

(3a*R*,4a*R*,10b*S*)-4,4,4a-trimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7d):



7d, 96% ee

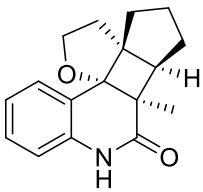




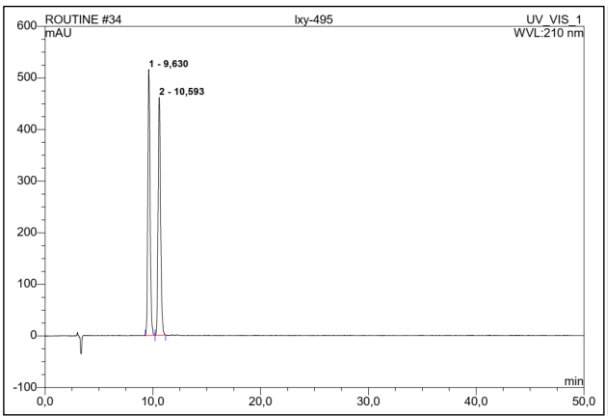
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,49	n.a.	704,277	197,682	50,08	n.a.	BMB
2	11,66	n.a.	592,764	197,050	49,92	n.a.	BMB
Total:			1297,041	394,731	100,00	0,000	

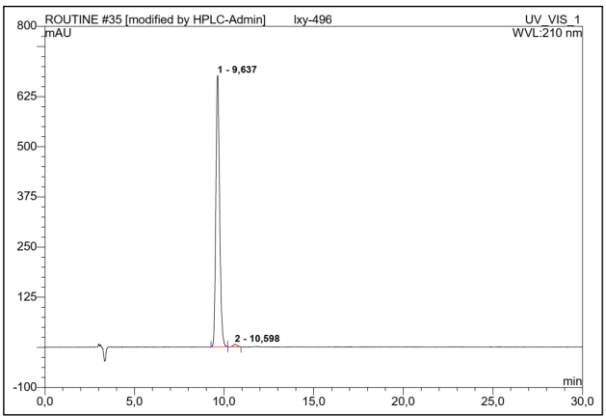
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,50	n.a.	24,325	6,757	2,18	n.a.	BMB*
2	11,63	n.a.	904,775	303,849	97,82	n.a.	BMB
Total:			929,099	310,606	100,00	0,000	

(6a*R*,6b*R*,9a*R*,12a*S*)-6a-methyl-6b,7,8,9,10,11-hexahydro-5*H*-cyclopenta[3,4]furo[2',3':2,3]cyclobuta-[1,2-*c*]quinolin-6(6a*H*)-one (7e):



7e, 98% ee

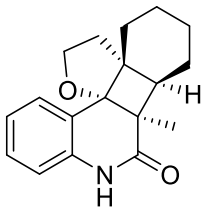




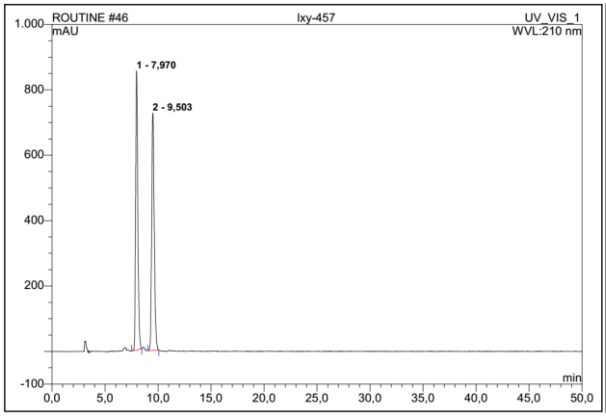
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,63	n.a.	515,351	125,073	50,05	n.a.	BM
2	10,59	n.a.	460,831	124,800	49,95	n.a.	MB
Total:			976,182	249,873	100,00	0,000	

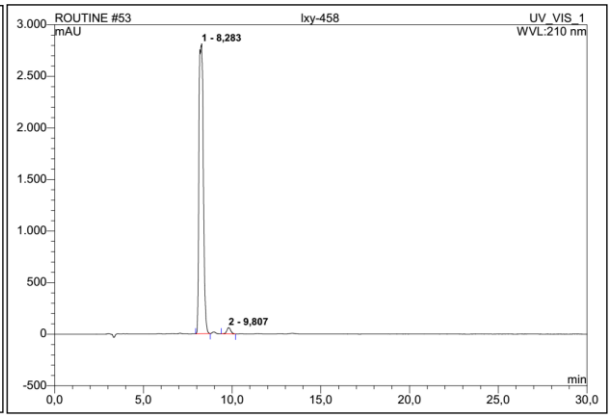
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,64	n.a.	675,887	163,676	99,14	n.a.	BMb*
2	10,60	n.a.	5,858	1,427	0,86	n.a.	bMB*
Total:			681,745	165,103	100,00	0,000	

(6a*R*,6b*R*,10a*R*,13a*S*)-6a-methyl-6a,6b,7,8,9,10,11,12-octahydrobenzo[3,4]furo[2',3':2,3]cyclobuta-[1,2-*c*]quinolin-6(5*H*)-one (7f):



7f, 96% ee

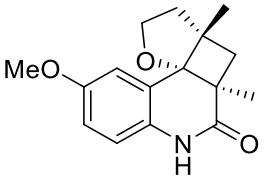




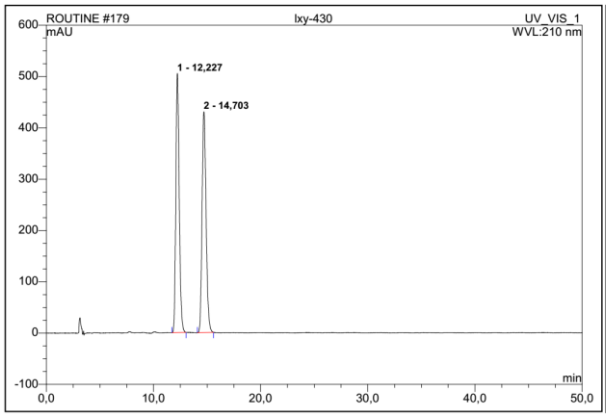
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,97	n.a.	853,670	204,047	49,72	n.a.	BMB
2	9,50	n.a.	726,601	206,312	50,28	n.a.	BMB
Total:			1580,271	410,359	100,00	0,000	

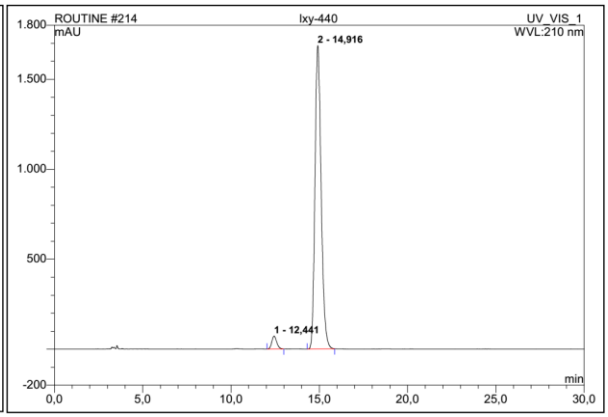
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,28	n.a.	2812,448	804,110	98,03	n.a.	BMB
2	9,81	n.a.	62,555	16,179	1,97	n.a.	BMB
Total:			2875,003	820,288	100,00	0,000	

(3a*S*,4a*R*,10b*S*)-9-methoxy-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7g):



7g, 93% ee

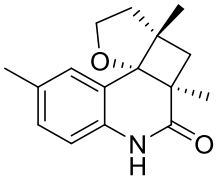




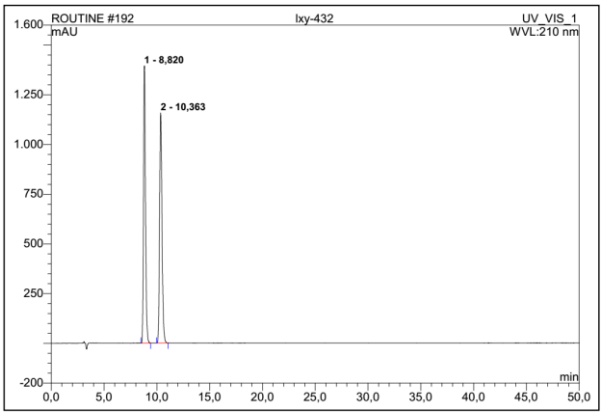
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,23	n.a.	505,707	186,629	49,95	n.a.	BMB
2	14,70	n.a.	430,813	186,998	50,05	n.a.	BMB
Total:			936,519	373,627	100,00	0,000	

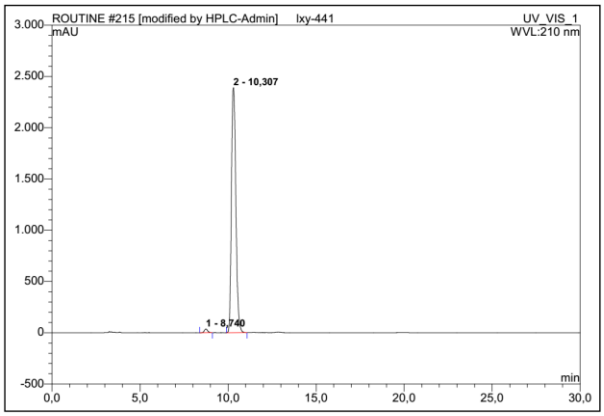
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,44	n.a.	71,949	23,474	3,30	n.a.	BMB
2	14,92	n.a.	1686,329	686,825	96,70	n.a.	BMB
Total:			1758,278	710,299	100,00	0,000	

(3a*S*,4a*R*,10b*S*)-3a,4a,9-trimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7h):



7h, 98% ee

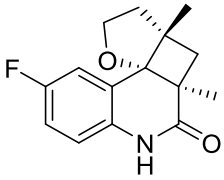




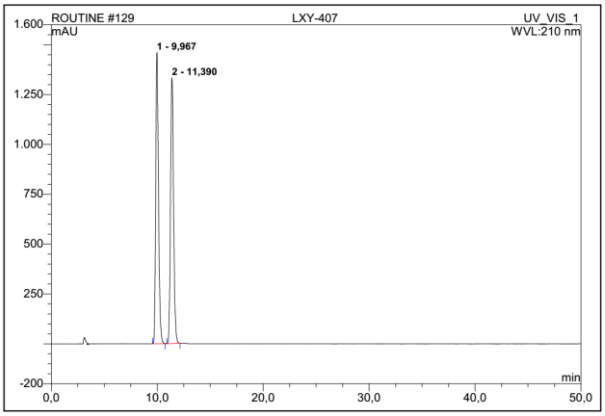
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,82	n.a.	1394,538	309,128	49,91	n.a.	BMB
2	10,36	n.a.	1157,457	310,279	50,09	n.a.	BMB
Total:			2551,995	619,407	100,00	0,000	

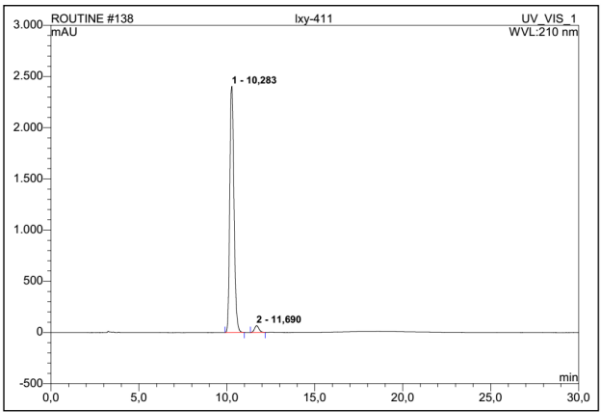
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,74	n.a.	36,618	7,875	1,12	n.a.	BMB*
2	10,31	n.a.	2389,092	694,958	98,88	n.a.	BMB
Total:			2425,709	702,834	100,00	0,000	

(3a*S*,4a*R*,10b*S*)-9-fluoro-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7i):



7i, 94% ee

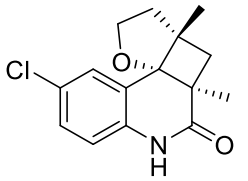




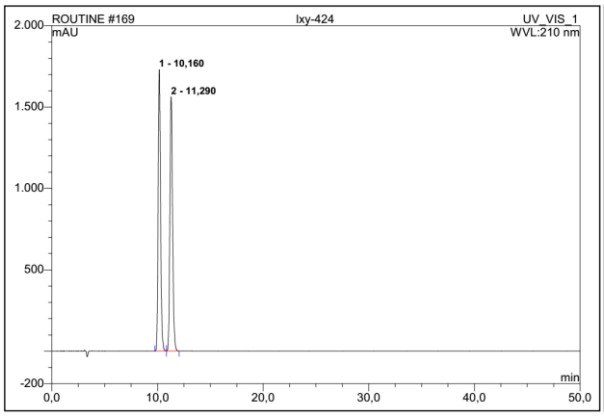
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,97	n.a.	1459,626	443,167	50,03	n.a.	BMB
2	11,39	n.a.	1331,903	442,621	49,97	n.a.	BMB
Total:			2791,530	885,788	100,00	0,000	

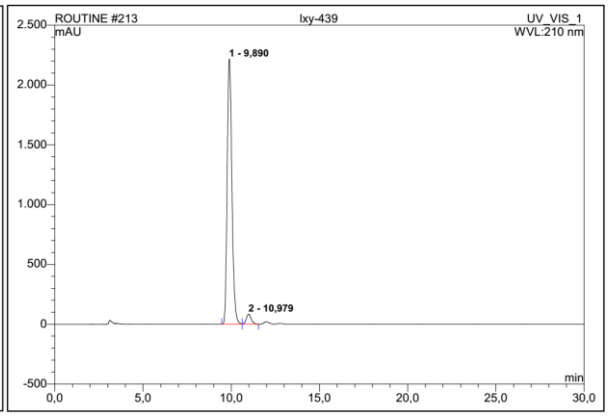
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,28	n.a.	2405,703	667,202	97,20	n.a.	BMB
2	11,69	n.a.	65,589	19,191	2,80	n.a.	BMB
Total:			2471,292	686,393	100,00	0,000	

(3a*S*,4a*R*,10b*S*)-9-chloro-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7j):



7j, 93% ee

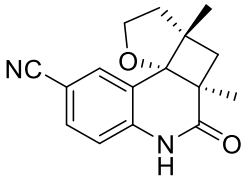




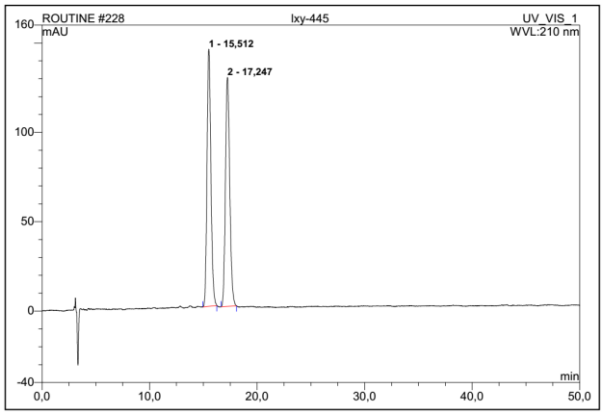
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,16	n.a.	1730,241	462,054	49,92	n.a.	BM
2	11,29	n.a.	1561,727	463,550	50,08	n.a.	MB
Total:			3291,968	925,604	100,00	0,000	

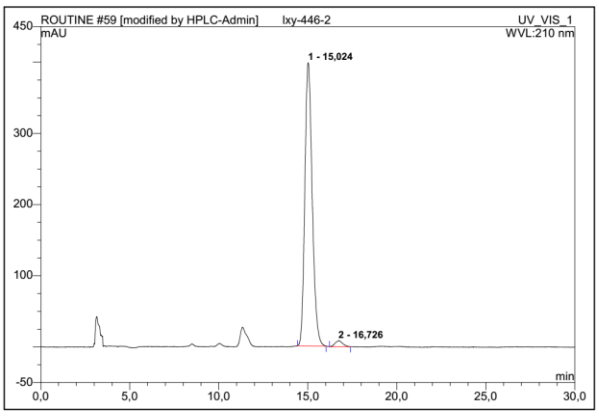
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,89	n.a.	2216,791	686,647	96,27	n.a.	BM
2	10,98	n.a.	82,593	26,622	3,73	n.a.	MB
Total:			2299,385	713,269	100,00	0,000	

(3a*S*,4a*R*,10b*S*)-3a,4a-dimethyl-5-oxo-3,3a,4,4a,5,6-hexahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinoline-9-carbonitrile (7k):



7k, 96% ee

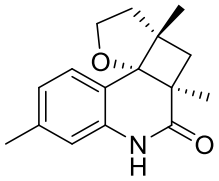




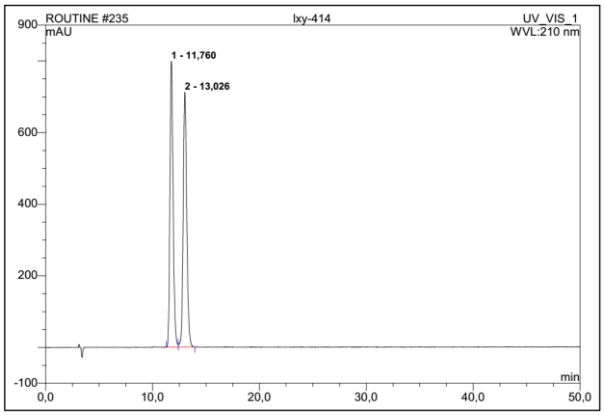
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15,51	n.a.	143,837	60,442	50,32	n.a.	BMB
2	17,25	n.a.	128,156	59,669	49,68	n.a.	BMB
Total:			271,993	120,110	100,00	0,000	

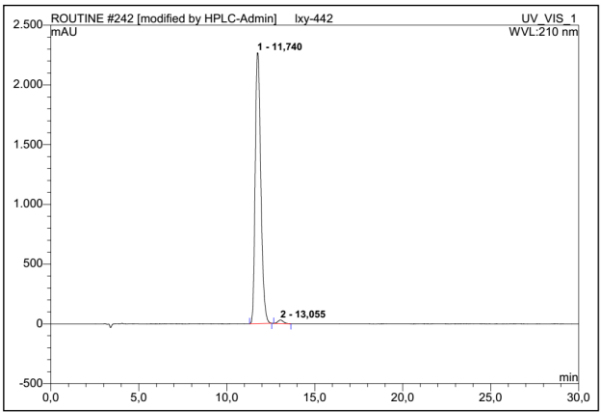
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15,02	n.a.	398,107	191,206	97,86	n.a.	BMB
2	16,73	n.a.	8,445	4,185	2,14	n.a.	BMB*
Total:			406,552	195,391	100,00	0,000	

(3a*S*,4a*R*,10b*S*)-3a,4a,8-trimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7l):



7l, 98% ee

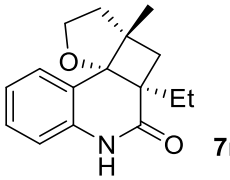




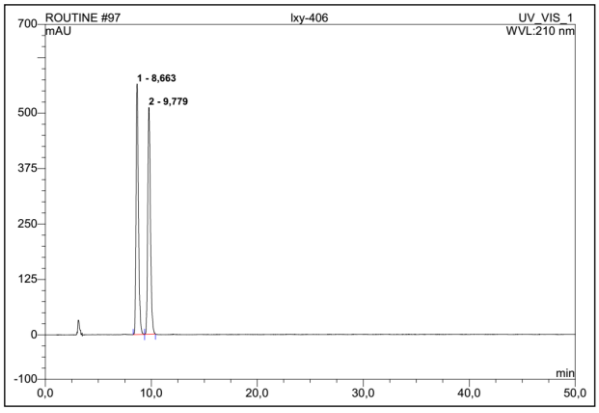
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,76	n.a.	797,720	276,272	49,91	n.a.	BM
2	13,03	n.a.	711,795	277,305	50,09	n.a.	MB
Total:			1509,514	553,577	100,00	0,000	

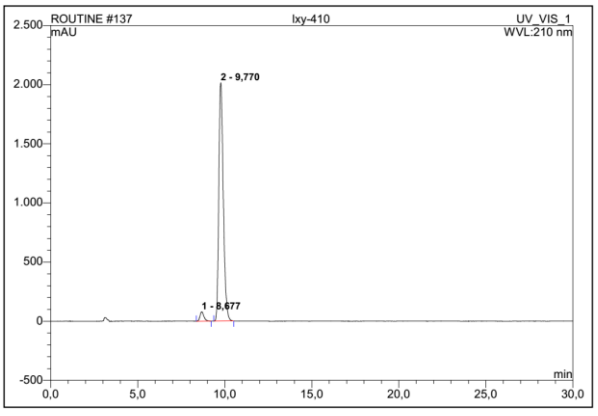
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,74	n.a.	2265,833	840,007	98,76	n.a.	BMB*
2	13,06	n.a.	28,964	10,526	1,24	n.a.	BMB*
Total:			2294,797	850,533	100,00	0,000	

(3a*S*,4a*R*,10b*S*)-4a-ethyl-3a-methyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7m):



7m, 93% ee

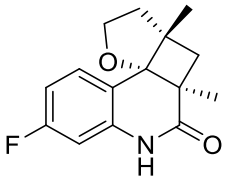




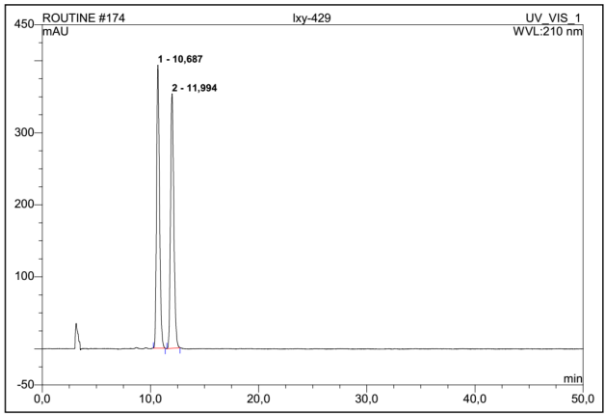
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,66	n.a.	565,043	148,149	49,98	n.a.	BM
2	9,78	n.a.	510,858	148,244	50,02	n.a.	MB
Total:			1075,900	296,393	100,00	0,000	

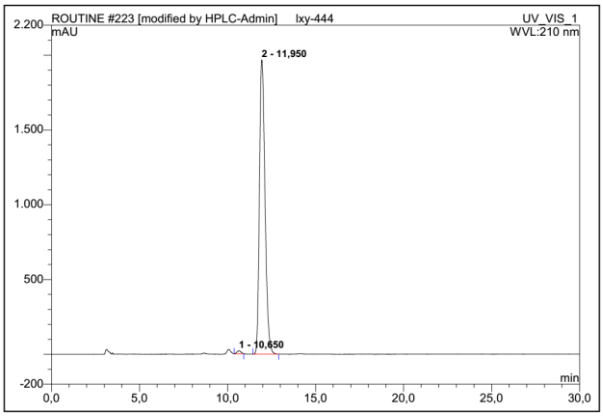
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,68	n.a.	79,911	20,587	3,29	n.a.	BMB
2	9,77	n.a.	2014,748	604,313	96,71	n.a.	BMB
Total:			2094,659	624,900	100,00	0,000	

(3a*S*,4a*R*,10b*S*)-8-fluoro-3a,4a-dimethyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (7n):



7n, 99% ee

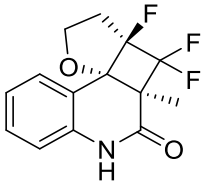




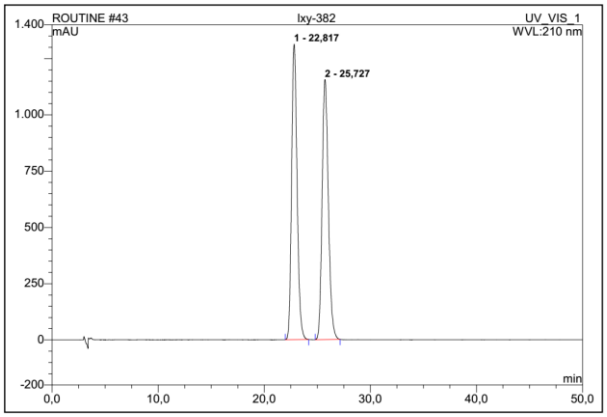
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,69	n.a.	393,094	125,404	50,08	n.a.	BMB
2	11,99	n.a.	353,353	125,024	49,92	n.a.	BMB
Total:			746,447	250,429	100,00	0,000	

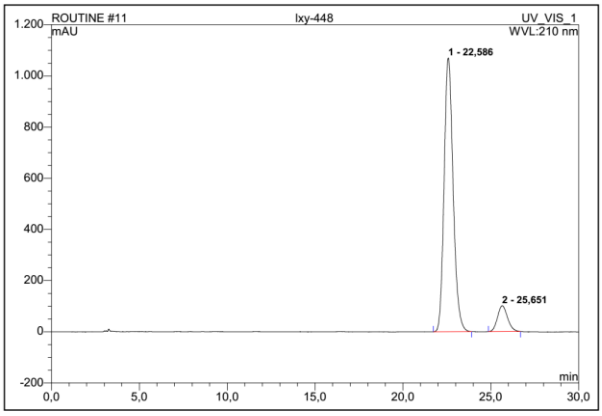
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,65	n.a.	19,733	5,414	0,74	n.a.	MB*
2	11,95	n.a.	1968,163	725,502	99,26	n.a.	BMB
Total:			1987,896	730,916	100,00	0,000	

(3a*R*,4a*R*,10b*S*)-3a,4,4-trifluoro-4a-methyl-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (9):



9, 81% ee

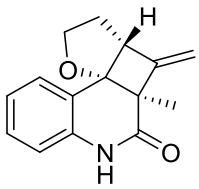




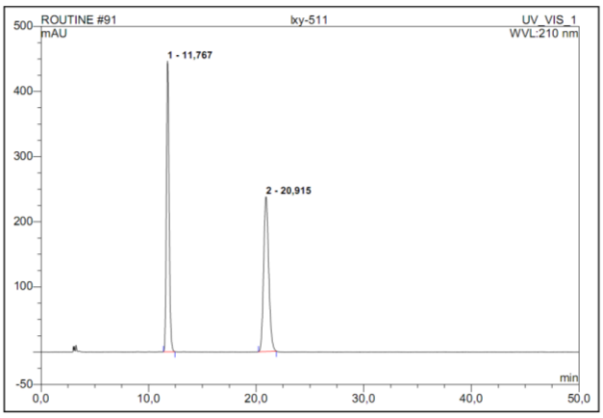
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22,82	n.a.	1312,814	787,461	49,92	n.a.	BMB
2	25,73	n.a.	1155,386	790,094	50,08	n.a.	BMB
Total:			2468,200	1577,555	100,00	0,000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22,59	n.a.	1069,746	638,689	90,48	n.a.	BMB
2	25,65	n.a.	101,004	67,208	9,52	n.a.	BMB
Total:			1170,751	705,897	100,00	0,000	

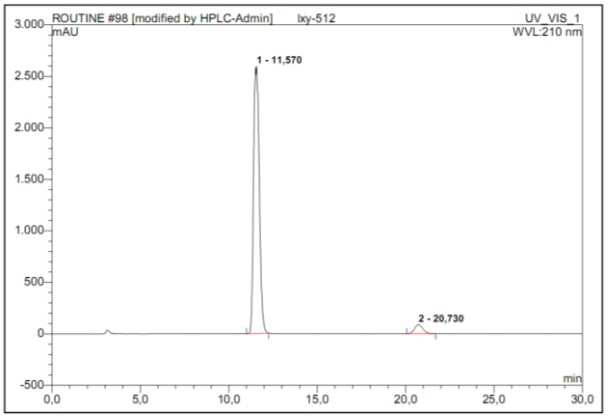
(3a*R*,4a*R*,10b*S*)-4a-methyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (11a):



11a, 91% ee

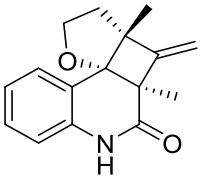


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,77	n.a.	446,346	131,378	50,17	n.a.	BMB
2	20,91	n.a.	237,860	130,471	49,83	n.a.	BMB
Total:			684,206	261,849	100,00	0,000	

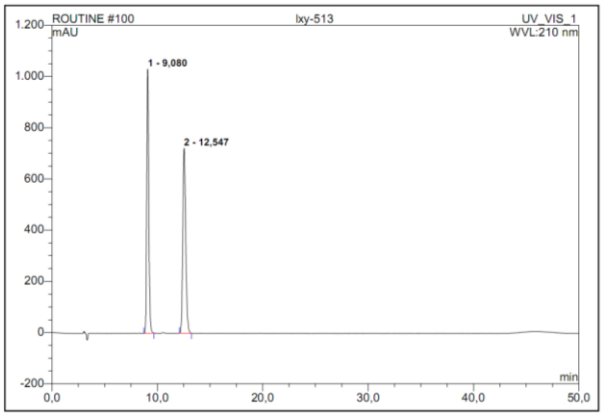


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,57	n.a.	2595,406	979,901	95,28	n.a.	BMB*
2	20,73	n.a.	87,844	48,566	4,72	n.a.	BMB
Total:			2683,250	1028,467	100,00	0,000	

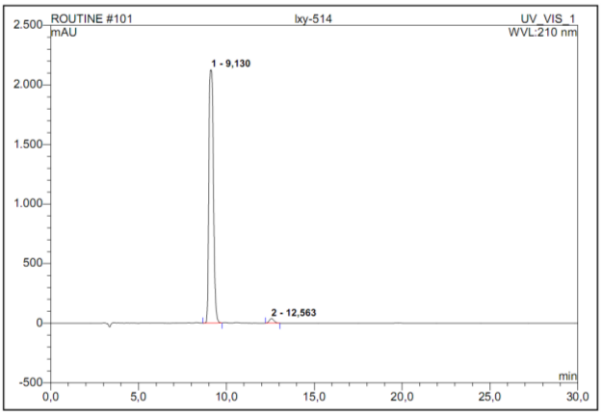
(3a*R*,4a*R*,10b*S*)-3a,4a-dimethyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (11b):



11b, 96% ee

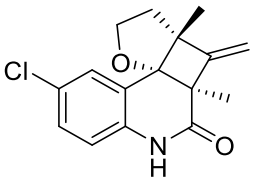


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,08	n.a.	1032,433	232,317	49,96	n.a.	BMB
2	12,55	n.a.	722,311	232,703	50,04	n.a.	BMB
Total:			1754,745	465,019	100,00	0,000	

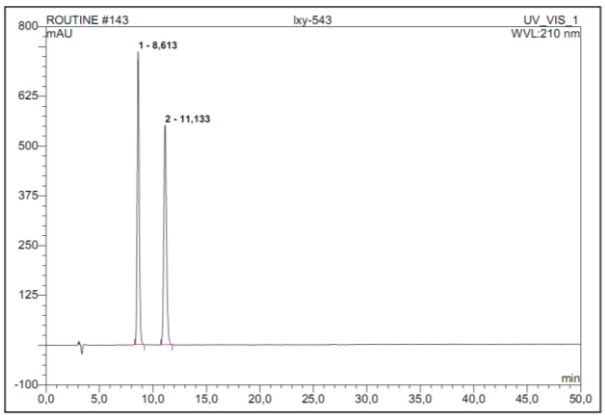


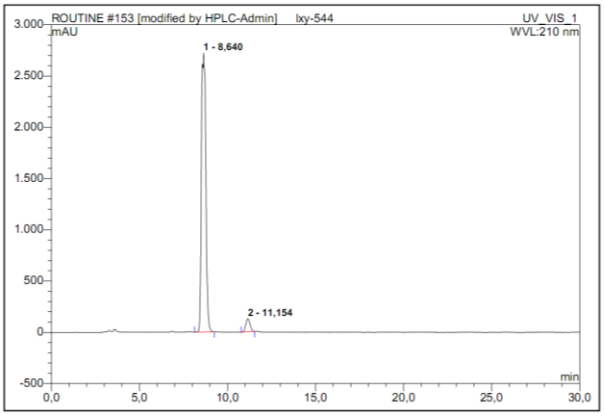
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,13	n.a.	2125,964	638,501	98,13	n.a.	BMB
2	12,56	n.a.	38,764	12,196	1,87	n.a.	BMB
Total:			2164,728	650,697	100,00	0,000	

(3a*R*,4a*R*,10b*S*)-9-chloro-3a,4a-dimethyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]-cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (11c):



11c, 91% ee

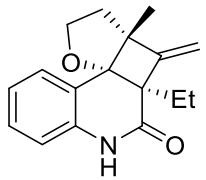




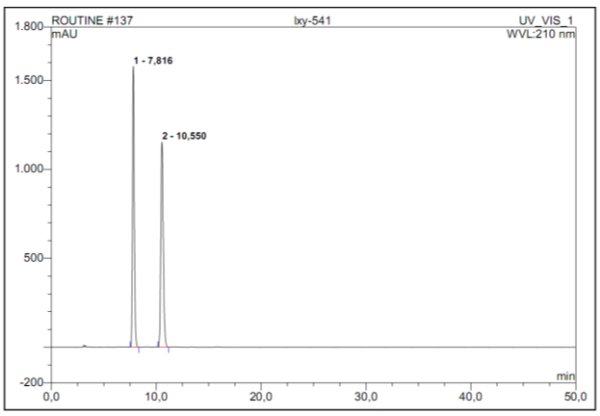
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,61	n.a.	736,294	160,481	50,00	n.a.	BMB
2	11,13	n.a.	551,727	160,504	50,00	n.a.	BMB
Total:			1288,021	320,985	100,00	0,000	

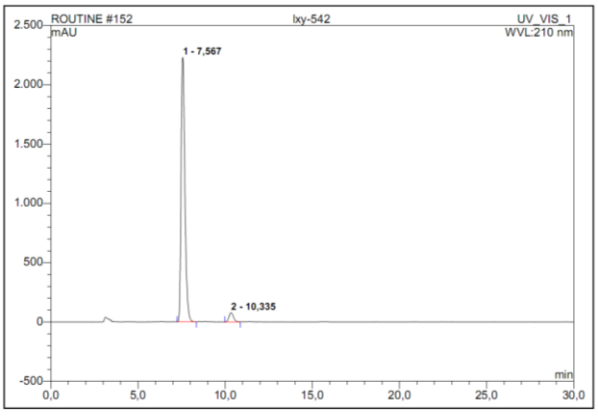
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,64	n.a.	2722,928	793,278	95,68	n.a.	BMB*
2	11,15	n.a.	129,425	35,790	4,32	n.a.	BMB
Total:			2852,353	829,068	100,00	0,000	

(3a*R*,4a*R*,10b*S*)-4a-ethyl-3a-methyl-4-methylene-3,3a,4,4a-tetrahydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (11d):



11d, 92% ee

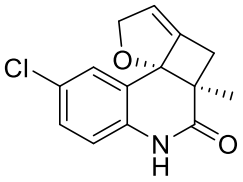




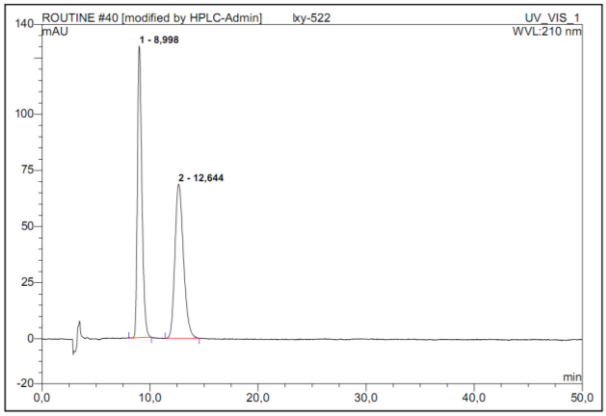
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,82	n.a.	1578,476	311,970	49,85	n.a.	BMB
2	10,55	n.a.	1152,602	313,906	50,15	n.a.	BMB
Total:			2731,079	625,876	100,00	0,000	

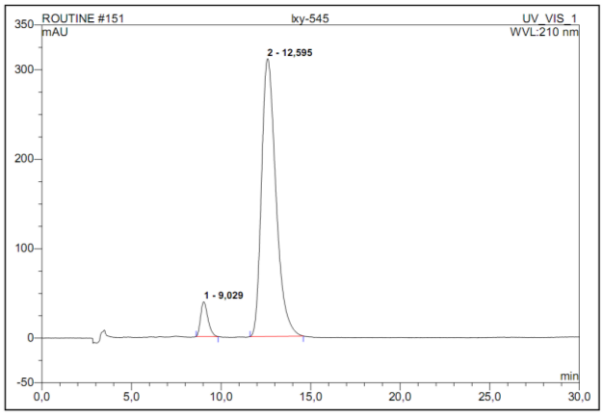
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,57	n.a.	2230,949	564,263	96,01	n.a.	BMB
2	10,34	n.a.	78,936	23,421	3,99	n.a.	BMB
Total:			2309,886	587,684	100,00	0,000	

(4a*R*,10b*S*)-9-chloro-4a-methyl-4,4a-dihydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (13a):



13a, 88% ee

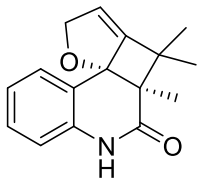




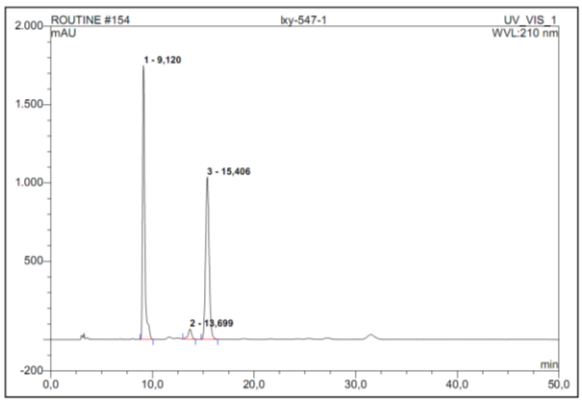
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,00	n.a.	129,866	62,513	49,76	n.a.	BMB*
2	12,64	n.a.	68,670	63,122	50,24	n.a.	BMB*
Total:			198,536	125,634	100,00	0,000	

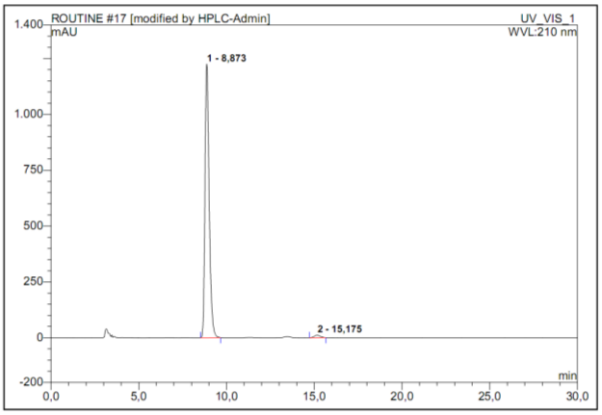
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,03	n.a.	39,045	18,325	5,96	n.a.	BMB
2	12,59	n.a.	310,707	289,026	94,04	n.a.	BMB
Total:			349,752	307,351	100,00	0,000	

(4a*R*,10b*S*)-4,4,4a-trimethyl-4,4a-dihydro-2*H*-furo[2',3':2,3]cyclobuta[1,2-*c*]quinolin-5(6*H*)-one (16):



16, 98% ee

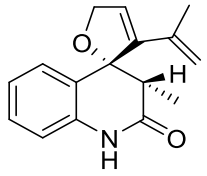




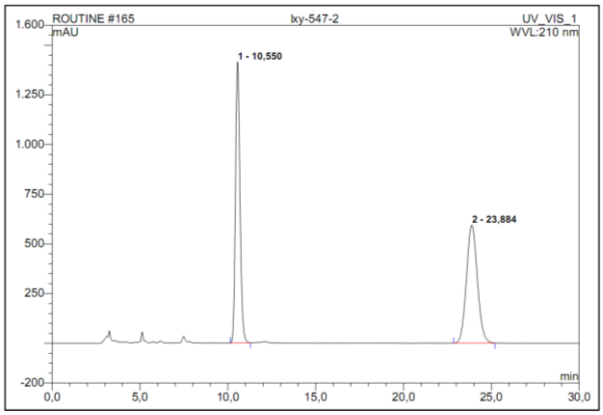
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,12	n.a.	1747,858	442,914	49,83	n.a.	BMB
2	13,70	n.a.	64,335	25,670	2,89	n.a.	BMB
3	15,41	n.a.	1036,661	420,262	47,28	n.a.	BMB
Total:			2848,854	888,847	100,00	0,000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,87	n.a.	1224,475	338,023	98,76	n.a.	BMB
2	15,17	n.a.	10,733	4,247	1,24	n.a.	BMB*
Total:			1235,208	342,270	100,00	0,000	

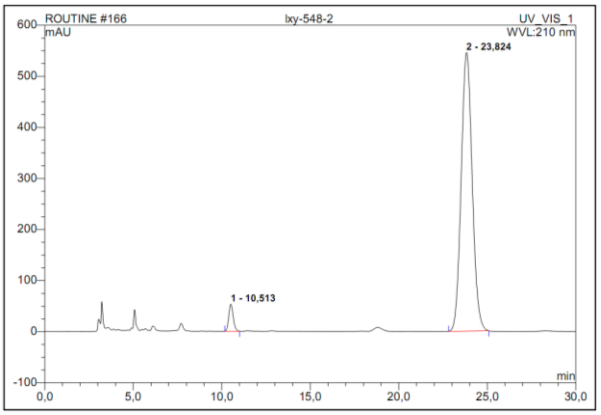
(2*S*,3'*S*)-3'-methyl-3-(prop-1-en-2-yl)-1'*H*,5*H*-spiro[furan-2,4'-quinolin]-2'(3'*H*)-one (18):



18, 92% ee



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,55	n.a.	1413,753	421,051	49,58	n.a.	BMB
2	23,88	n.a.	593,330	428,252	50,42	n.a.	BMB
Total:			2007,083	849,302	100,00	0,000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,51	n.a.	53,000	15,484	3,79	n.a.	BMB
2	23,82	n.a.	545,588	392,956	96,21	n.a.	BMB
Total:			598,588	408,440	100,00	0,000	

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