Visible light-induced dehydrohalogenative coupling for intramolecular α-alkenylation: A way to build seven- and eight-membered rings.

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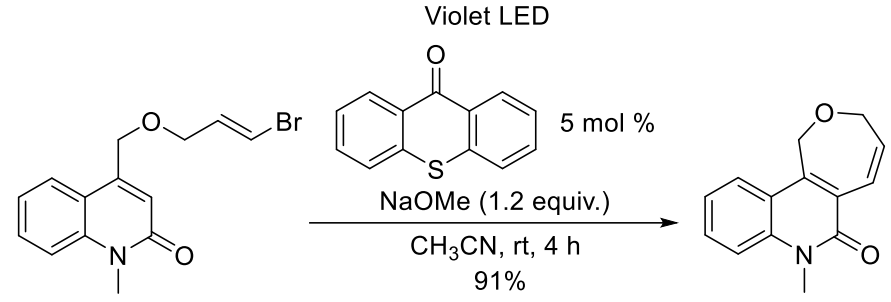
Supporting Information



1a
1.002 g, 3.25 mmol

2a
0.672 g

Scheme S1. Gram scale experiment of 1a under standard condition

Supplementary Experimental Procedures

General information

^{1}H (400 MHz), ^{1}H (500 MHz), ^{13}C (100 MHz), ^{13}C (126 MHz) NMR and ^{19}F (376 MHz) NMR spectra are acquired on a Bruker Avance Ultrashield 400 MHz, 500 MHZ and a Bruker DPX 400 MHz, 500 MHZ spectrometer. Mass Spectroscopy (MS) and High Resolution Mass Spectroscopy (HR-MS) are performed on a Thermo Scientific LTQ-FT Ultra (ESI), The LTQ FT Ultra (Thermo) is a linear ion trap with a Fourier Transform Ion Cyclotron Resonance (FT-ICR) MS detector. The ICR analyzer is based on a 7 Tesla superconducting magnet. The instrument is coupled online to an analytical HPLC (UltiMate 3000 HPLC system, Dionex). The elemental analysis data are acquired on a Fast Sequential Atomic Absorption Spectrometer, VARIAN, AA280FS. IR spectra are recorded on a Varian FTIR-670 spectrometer using a GladiATR accessory with a diamond ATR element. Melting points are determined on a MPM-H2 apparatus. Anhydrous CH_2Cl_2, THF and CH_3CN are obtained from a M. Braun SPS purification system. Anhydrous MeOH is prepared using CaH_2 as drying agent. Anhydrous acetone is prepared using $CaCl_2$ as drying agent.

Light sources

The violet LED strips 12v-5050-60 are purchased from GreeThink®. Please refer to the homepage of GreeThink (http://www.greethink.com.cn/English/). The wavelength and intensity of the led strips are given as below.

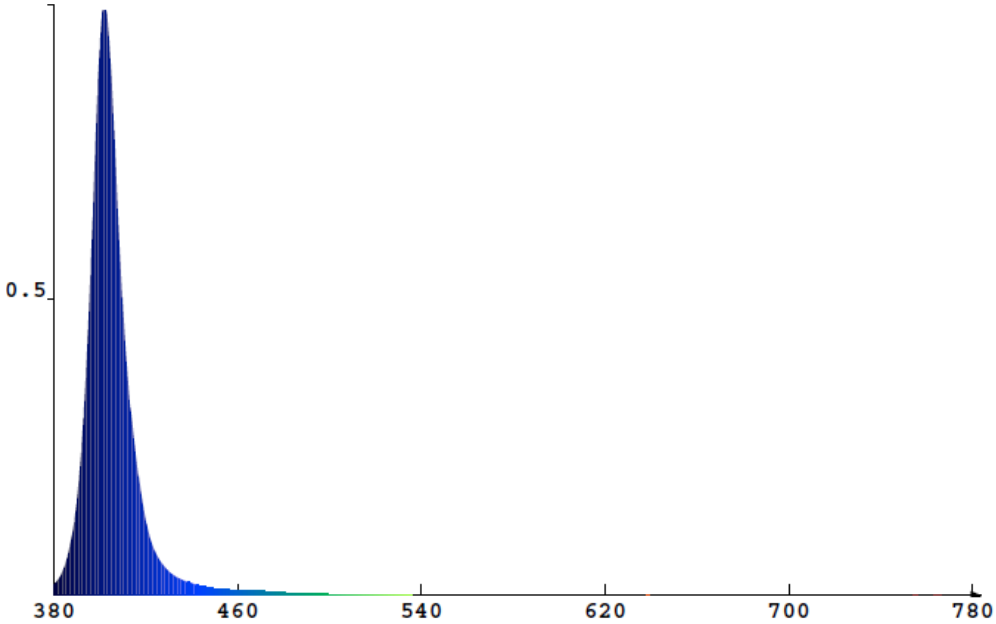


Figure S1. Spectral distribution of irradiance density for the violet LED strip

Reaction setup

The photoreaction is conducted in a borosilicate glass vessel made by Synthware®. For technical information on this glass, the reader is directed to the homepage of the manufacturer: http://www.xinweier.com/

The distance from the irradiation source to the irradiation vessel is about 5-7 cm. A typical reaction setup is shown as below.

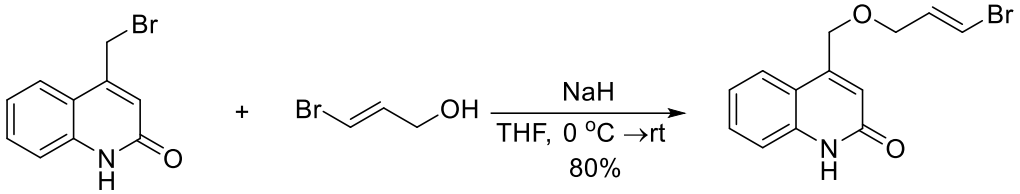
Figure S2. Typical reaction setup for general photoreaction

X-ray Crystallographic Details

The crystal samples were prepared by dissolving the respective compounds in ethyl acetate/*n*-hexane solvent system. The solvent was placed in the refrigerator, the crystals were grown by slow cooling.

Data were collected on a single crystal x-ray diffractometer equipped with a CMOS detector (Bruker APEX III, κ-CMOS), an IMS microsource with MoK_α radiation (λ = 0.71073 Å) and a Helios optic using the APEX3 software package.[1] 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.[2] Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS.[3] Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structures were solved using SHELXS or SHELXT with the aid of successive difference Fourier maps, and were refined against all data using SHELXL in conjunction with SHELXLE.[4,5,6] Hydrogen atoms 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, and 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.[4] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[7] A split layer refinement was used for disordered groups and additional SIMU, DELU, RIGU, ISOR and SAME restraints were used, if necessary. The unit cell of **2r** contains 1.5 (not fully occupied sites) disordered molecules of hexane which was treated as a diffuse contribution to the overall scattering without specific atom positions using the PLATON/SQUEEZE procedure.[8] Images of the crystal structures were generated with PLATON.[9] Crystallographic data are provided free of charge by The Cambridge Crystallographic Data Centre.

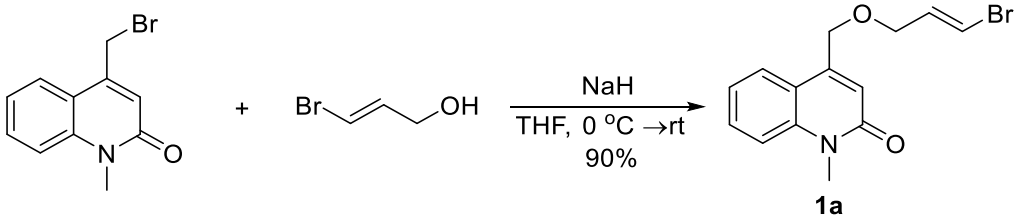
Synthesis of *E*-4-(((3-bromoallyl)oxy)methyl)quinolin-2(1*H*)-one



To a Schlenk flask are added *E*-3-bromoprop-2-en-1-ol[10] (164 mg, 1.2 mmol) and anhydrous THF (10 mL). The mixture is stirred under 0 °C for 10 min and then NaH (48 mg, 2 mmol) is added. The mixture is stirred under 0 °C for 2 h and 4-(bromomethyl)quinolin-2(1*H*)-one (238 mg, 1 mmol) is added subsequently. The mixture is stirred at room temperature overnight, and then cooled to 0 °C, treated with 1 N HCl (10 mL). The solvent is evaporated and the residue is filtered, washed with water (10 mL × 3), dried under vacuum to afford *E*-4-(((3-bromoallyl)oxy)methyl)quinolin-2(1*H*)-one without further purification (234 mg, 80%). Mp: 217.3-218.1 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.71 (s, 1H, N-H), 7.66 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.50 (t, *J* = 8.2 Hz, 1H, Ar-H), 7.32 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.18 (t, *J* = 7.6 Hz, 1H, Ar-H), 6.67 (d, *J* = 13.6 Hz, 1H, Alkene-H), 6.54-6.36 (m, 2H, Alkene-H), 4.75 (s, 2H, Alkane-H), 4.09 (dd, *J* = 6.1, 1.3 Hz, 2H, Alkane-H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.0, 147.6, 139.3, 134.8, 130.8, 124.6, 122.2, 119.5, 117.8, 116.0, 109.7, 70.1, 68.4. IR (neat) 3062, 1646, 1613, 1556, 1513, 1439 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{13}BrNO_2^+$ [M+H]$^+$: 294.0124, found: 294.0124.

General Procedure I for the synthesis of substrates

Synthesis of *E*-4-(((3-bromoallyl)oxy)methyl)-1-methylquinolin-2(1*H*)-one (1a)



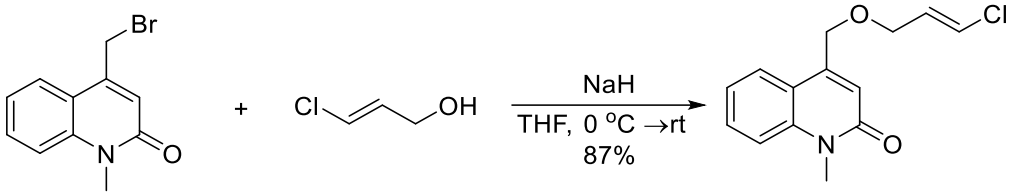
1a

To a Schlenk flask are added *E*-3-bromoprop-2-en-1-ol (329 mg, 2.4 mmol) and anhydrous THF (20 mL). The mixture is stirred under 0 °C for 10 min and then NaH (96 mg, 4 mmol) is added. The mixture is stirred under 0 °C for 1 h and 4-(bromomethyl)-1-methylquinolin-2(1*H*)-one[11] (504 mg, 2 mmol) is added

subsequently. The mixture is stirred at room temperature overnight, and then cooled to 0 °C, treated with 1 N HCl (10 mL). The solvent is evaporated and the residue is extracted with ethyl acetate (30 mL × 3). The combined organic layers are washed with brine (15 mL), dried over $MgSO_4$, filtered, and evaporated. The crude product is purified by column chromatography (*n*-hexane/ethyl acetate = 3:1) to give the product **1a** as a solid (553 mg, 90%). Mp: 100.8-101.1 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.33-7.21 (m, 1H), 6.80 (s, 1H), 6.46-6.21 (m, 2H), 4.74 (s, 2H), 4.08 (d, *J* = 5.7 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9, 144.9, 140.0, 133.4, 130.6, 124.5, 122.1, 119.9, 119.1, 114.6, 109.1, 70.2, 68.7, 29.3. IR (neat) 1656, 1553, 1435, 1405 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{15}BrNO_2^+$ $[M+H]^+$: 308.0281, found: 308.0281.

The following compounds were synthesized according to general procedure I.

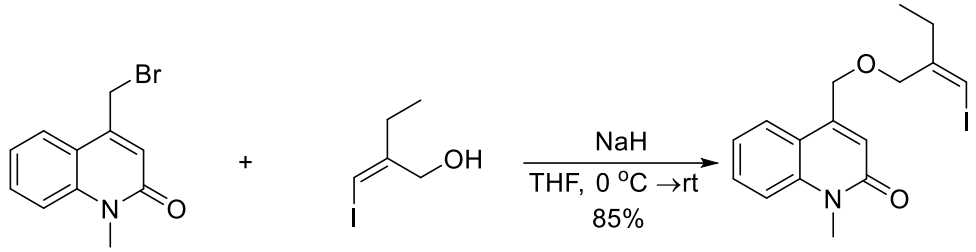
(1) *E*-4-(((3-chloroallyl)oxy)methyl)-1-methylquinolin-2(1*H*)-one (1p)



1p

The reaction of 4-(bromomethyl)-1-methylquinolin-2(1*H*)-one (252 mg, 1 mmol), *E*-3-chloroprop-2-en-1-ol[12] (112 mg, 1.2 mmol), NaH (48 mg, 2 mmol), and THF (10 mL) affords **1p** as a solid (229 mg, 87%). Mp: 96.5-97.1 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.29-7.22 (m, 1H), 6.80 (s, 1H), 6.30 (d, *J* = 13.4 Hz, 1H), 6.06 (dt, *J* = 12.5, 6.1 Hz, 1H), 4.72 (s, 2H), 4.10 (dd, *J* = 6.1, 1.5 Hz, 2H), 3.72 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9, 144.9, 140.0, 130.6, 129.2, 124.6, 122.1, 121.8, 120.0, 119.1, 114.6, 68.7, 29.4. IR (neat) 1646, 1614, 1588, 1557, 1462, 1438, 1413 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{15}ClNO_2^+$ $[M+H]^+$: 264.0786, found: 264.0786.

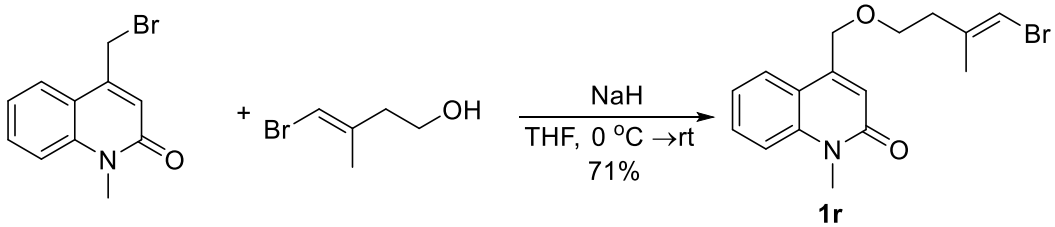
(2) *Z*-4-((2-(iodomethylene)butoxy)methyl)-1-methylquinolin-2(1*H*)-one (1q)



1q

The reaction of 4-(bromomethyl)-1-methylquinolin-2(1*H*)-one (180 mg, 0.7 mmol), *Z*-2-(iodomethylene)butan-1-ol[13] (148 mg, 0.7 mmol), NaH (34 mg, 1.4 mmol), and THF (10 mL) affords **1q** as an oil (228 mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.30-7.20 (m, 1H), 6.85 (s, 1H), 6.15 (s, 1H), 4.71 (s, 2H), 4.28 (s, 2H), 3.72 (s, 3H), 2.32 (q, *J* = 7.4 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 149.0, 145.3, 140.0, 130.5, 124.6, 122.0, 119.8, 119.1, 114.5, 74.4, 68.6, 29.3, 28.8, 12.3. IR (neat) 1654, 1590, 1455, 1415 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{19}INO_2^+$ $[M+H]^+$: 384.0455, found: 384.0455.

(3) *E*-4-(((4-bromo-3-methylbut-3-en-1-yl)oxy)methyl)-1-methylquinolin-2(1*H*)-one (1r)

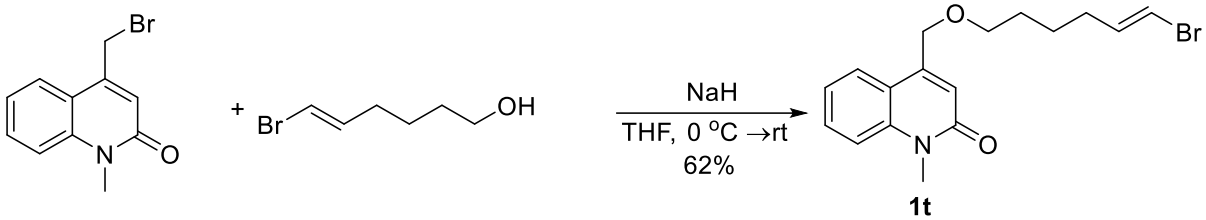


1r

The reaction of 4-(bromomethyl)-1-methylquinolin-2(1*H*)-one (252 mg, 1 mmol), *E*-4-bromo-3-methylbut-3-en-1-ol[14] (198 mg, 1.2 mmol), NaH (48 mg, 2 mmol), and THF (10 mL) affords **1r** as a solid (238 mg, 71%). Mp: 85.2-86.7 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.62-7.53 (m, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.31-7.21 (m, 1H), 6.78 (s, 1H), 5.98 (s, 1H), 4.71 (s, 2H), 3.72 (s, 3H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.44 (t, *J* = 6.3 Hz, 2H), 1.79 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 145.3, 140.0, 138.5, 130.6, 124.8, 122.1, 120.0, 119.2, 114.5, 103.1, 69.8, 68.7, 38.2, 29.3, 19.3. IR (neat) 1649, 1590, 1456, 1407 cm^{-1}. HRMS (ESI):

calcd for $C_{16}H_{19}BrNO_2^+$ [M+H]$^+$: 336.0594, found: 336.0595.

(4) *E*-4-(((6-bromohex-5-en-1-yl)oxy)methyl)-1-methylquinolin-2(1*H*)-one (1t)

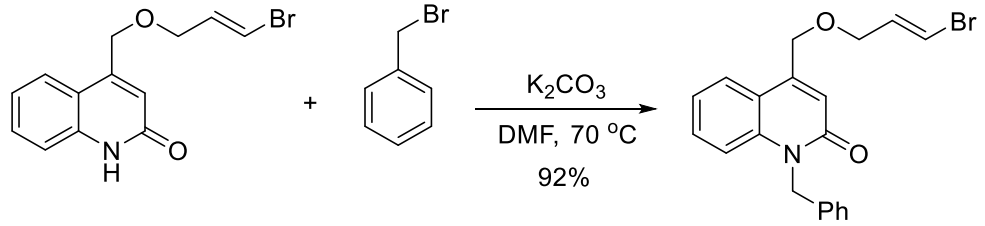


1t

The reaction of 4-(bromomethyl)-1-methylquinolin-2(1*H*)-one (252 mg, 1 mmol), *E*-6-bromohex-5-en-1-ol[15] (214 mg, 1.2 mmol), NaH (48 mg, 2 mmol), and THF (10 mL) affords **1t** as a solid (217 mg, 62%). Mp: 56.1-57.1 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62-7.54 (m, 1H), 7.39 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.28-7.22 (m, 1H), 6.81 (s, 1H), 6.14 (dt, *J* = 11.4, 6.0 Hz, 1H), 6.01 (dt, *J* = 11.4, 1.2 Hz, 1H), 4.71 (d, *J* = 1.2 Hz, 2H), 3.73 (s, 3H), 3.55 (t, *J* = 6.3 Hz, 2H), 2.11-2.01 (m, 2H), 1.68-1.62 (m, 2H), 1.54-1.45 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.0, 144.6, 138.9, 136.6, 129.5, 123.5, 120.9, 118.7, 118.2, 113.5, 103.4, 69.6, 68.5, 31.6, 28.3, 27.9, 24.1. IR (neat) 1655, 1617, 1592, 1564, 1456 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{21}BrNO_2^+$ [M+H]$^+$: 350.0750, found: 350.0748.

General Procedure II for the synthesis of substrates

Synthesis of *E*-1-benzyl-4-(((3-bromoallyl)oxy)methyl)quinolin-2(1*H*)-one (1b)

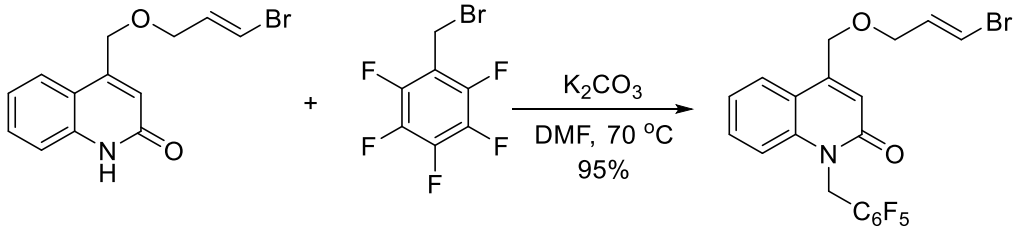


1b

To a Schlenk flask are added *E*-4-(((3-bromoallyl)oxy)methyl)quinolin-2(1*H*)-one (294 mg, 1 mmol), benzyl bromide (342 mg, 2 mmol), K_2CO_3 (414 mg, 3 mmol), and DMF (15 mL). The mixture is stirred under 70 °C with an oil bath for 4 h as monitored by TLC (eluent: *n*-hexane/ethyl acetate = 3:1). The solvent is evaporated and the residue is purified by column chromatography (eluent: *n*-hexane/ethyl acetate = 3:1) to afford **1b** as a solid (352 mg, 92%). Mp: 96.8-97.9 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.33-7.27 (m, 3H), 7.25-7.17 (m, 4H), 6.91 (s, 1H), 6.45 (d, *J* = 13.6 Hz, 1 H), 6.36 (dt, *J* = 13.6, 5.6 Hz, 1 H), 5.56 (s, 2H), 4.76 (s, 2H), 4.11 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.1, 145.5, 139.4, 136.3, 133.4, 130.6, 128.8, 127.2, 126.5, 124.5, 122.2, 119.8, 119.3, 115.5, 109.2, 70.3, 68.8, 45.8. IR (neat) 1649, 1592, 1452 cm^{-1}. HRMS (ESI): calcd for $C_{20}H_{19}BrNO_2^+$ [M+H]$^+$: 384.0594, found: 384.0595.

The following compounds were synthesized according to general procedure II.

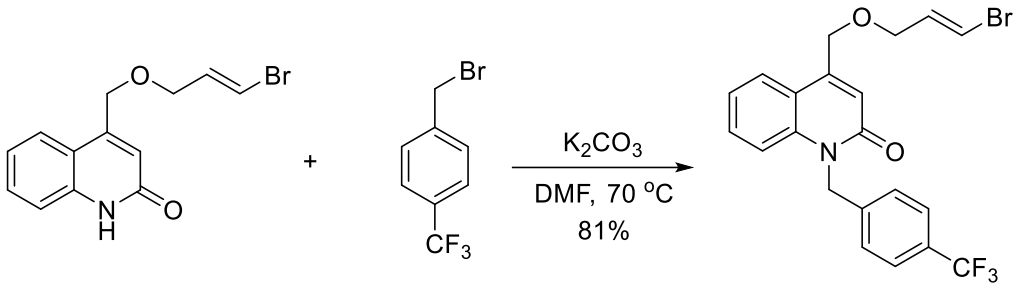
(1) *E*-4-(((3-bromoallyl)oxy)methyl)-1-((perfluorophenyl)methyl)quinolin-2(1*H*)-one (1c)



1c

The reaction of *E*-4-(((3-bromoallyl)oxy)methyl)quinolin-2(1*H*)-one (294 mg, 1 mmol), 2,3,4,5,6-pentafluorobenzyl bromide (521 mg, 2 mmol), K_2CO_3 (414 mg, 3 mmol), and DMF (15 mL) affords **1c** as a solid (449 mg, 95%). Mp: 110.7-111.3 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.26-7.20 (m, 2H), 6.84 (s, 1H), 6.44 (d, *J* = 13.6 Hz, 1H), 6.35 (dt, *J* = 13.6, 6.0 Hz, 1H), 5.69 (s, 2H), 4.74 (s, 2H), 4.09 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.7, 146.0, 138.7, 133.3, 130.9, 125.0, 122.6, 119.47, 119.35, 113.9, 109.3, 70.4, 68.6, 35.0. IR (neat) 1661, 1597, 1523, 1500, 1478, 1456, 1419 cm^{-1}. HRMS (ESI): calcd for $C_{20}H_{14}BrF_5NO_2^+$ [M+H]$^+$: 474.0123, found: 474.0125.

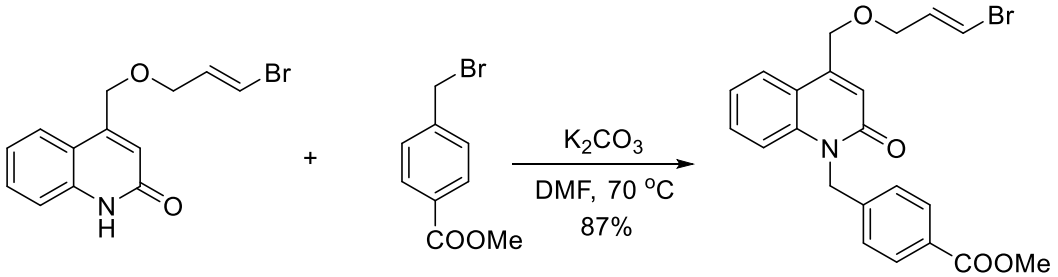
(2) *E*-4-(((3-bromoallyl)oxy)methyl)-1-(4-(trifluoromethyl)benzyl)quinolin-2(1*H*)-one (1d)



1d

The reaction of *E*-4-(((3-bromoallyl)oxy)methyl)quinolin-2(1*H*)-one (441 mg, 1.5 mmol), 1-(bromomethyl)-4-(trifluoromethyl)benzene (718 mg, 3 mmol), K_2CO_3 (621 mg, 4.5 mmol), and DMF (15 mL) affords **1d** as a solid (547 mg, 81%). Mp: 91.1-92.2 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25-7.16 (m, 2H), 6.91 (s, 1H), 6.46 (d, *J* = 13.6 Hz, 1H), 6.36 (dt, *J* = 13.6, 6.0 Hz, 1H), 5.61 (s, 2H), 4.78 (s, 2H), 4.12 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 146.0, 140.5, 139.2, 133.3, 130.8, 129.5, 126.9, 125.9, 125.87, 125.83, 125.80, 124.8, 122.5, 119.7, 119.4, 115.2, 109.3, 70.5, 68.8, 45.5. IR (neat) 1729, 1649, 1593, 1454, 1419 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{18}BrF_3NO_2^+$ [M+H]$^+$: 452.0468, found: 452.0467.

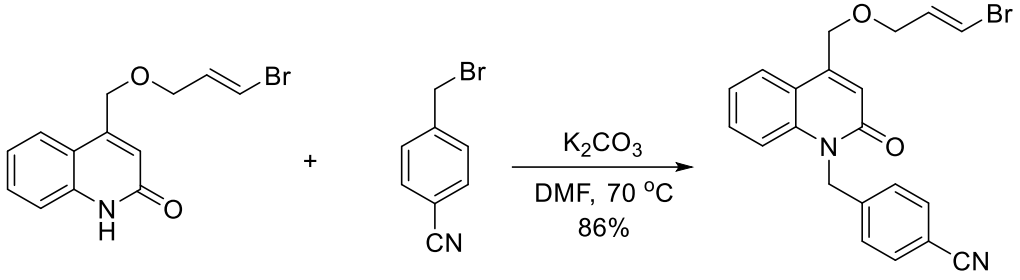
(3) *E*-4-(((3-bromoallyl)oxy)methyl)-1-(4-methoxycarbonylbenzyl)quinolin-2(1*H*)-one (1e)



1e

The reaction of *E*-4-(((3-bromoallyl)oxy)methyl)quinolin-2(1*H*)-one (450 mg, 1.5 mmol), methyl 4-(bromomethyl)benzoate (687 mg, 3 mmol), K_2CO_3 (621 mg, 4.5 mmol), and DMF (15 mL) affords **1e** as a solid (576 mg, 87%). Mp: 137.5-138.9 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.28-7.16 (m, 2H), 7.24-7.15 (m, 2H), 6.92 (s, 1H), 6.46 (d, *J* = 13.6 Hz, 1H), 6.36 (dt, *J* = 13.6, 5.6 Hz, 1H), 5.61 (s, 2H), 4.77 (s, 2H), 4.12 (d, *J* = 5.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 162.1, 145.9, 141.6, 139.2, 133.4, 130.8, 130.2, 129.3, 126.5, 124.7, 122.4, 119.7, 119.4, 115.3, 109.3, 70.5, 68.8, 52.1, 45.7. IR (neat) 1707, 1651, 1593, 1457, 1434, 1425 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{21}BrNO_4^+$ [M+H]$^+$: 442.0648, found: 442.0648.

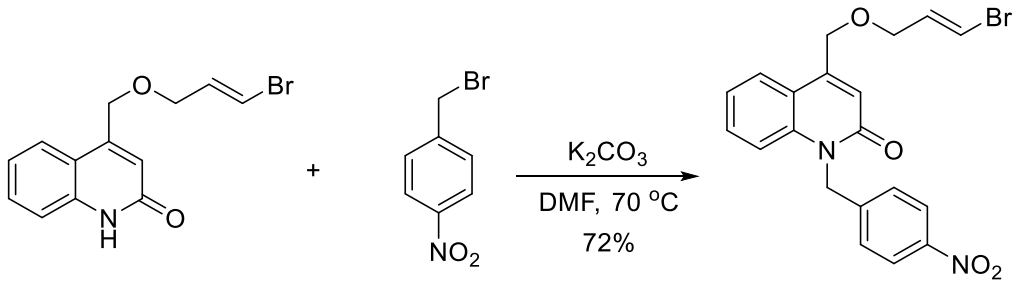
(4) *E*-4-(((3-bromoallyl)oxy)methyl)-1-(4-cyanobenzyl)quinolin-2(1*H*)-one (1f)



1f

The reaction of *E*-4-(((3-bromoallyl)oxy)methyl)quinolin-2(1*H*)-one (445 mg, 1.5 mmol), 4-(bromomethyl)benzonitrile (580 mg, 3 mmol), K_2CO_3 (621 mg, 4.5 mmol), and DMF (15 mL) affords **1f** as a solid (526 mg, 86%). Mp: 130.9-132.0 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.26-7.21 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 6.91 (s, 1H), 6.45 (d, *J* = 13.6 Hz, 1H), 6.36 (dt, *J* = 13.6, 6.0 Hz, 1H), 5.60 (s, 2H), 4.77 (s, 2H), 4.12 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9, 146.1, 141.9, 139.0, 133.3, 132.6, 130.9, 127.3, 124.9, 122.6, 119.5, 119.4, 118.5, 114.9, 111.4, 109.3, 70.5, 68.7, 45.5. IR (neat) 2226, 1651, 1591, 1458, 1432, 1413 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{18}BrN_2O_2^+$ [M+H]$^+$: 409.0546, found: 409.0546.

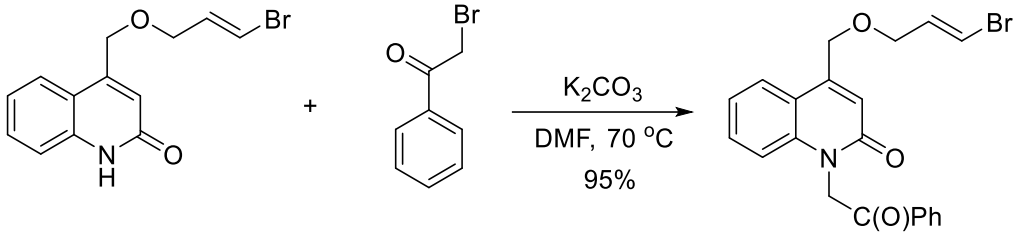
(5) *E*-4-(((3-bromoallyl)oxy)methyl)-1-(4-nitrobenzyl)quinolin-2(1*H*)-one (1g)



1g

The reaction of *E*-4-(((3-bromoallyl)oxy)methyl)quinolin-2(1*H*)-one (294 mg, 1 mmol), 1-(bromomethyl)-4-nitrobenzene (259 mg, 1.2 mmol), K_2CO_3 (621 mg, 4.5 mmol), and DMF (15 mL) affords **1g** as a solid (309 mg, 72%). Mp: 165.9-166.7 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.26-7.21 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.92 (s, 1H), 6.46 (d, *J* = 13.6 Hz, 1H), 6.36 (dt, *J* = 13.6, 6.0 Hz, 1H), 5.65 (s, 2H), 4.78 (s, 2H), 4.13 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9, 147.3, 146.2, 143.9, 139.0, 133.3, 130.9, 127.4, 124.9, 124.1, 122.6, 119.5, 119.4, 114.9, 109.3, 70.5, 68.7, 45.4. IR (neat) 1648, 1590, 1515, 1458, 1440, 1417 cm^{-1}. HRMS (ESI): calcd for $C_{20}H_{18}BrN_2O_4^+$ $[M+H]^+$: 429.0444, found: 429.0444.

(6) *E*-4-(((3-bromoallyl)oxy)methyl)-1-(2-oxo-2-phenylethyl)quinolin-2(1*H*)-one (1h)

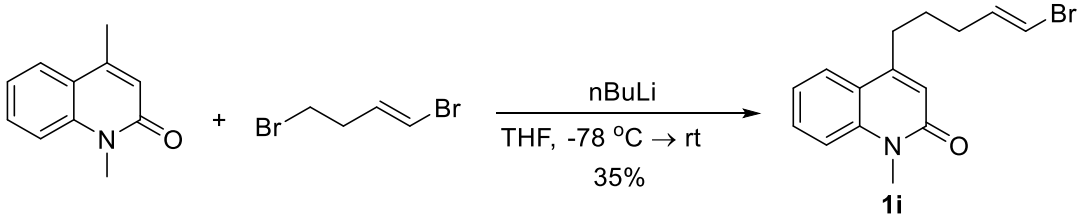


1h

The reaction of *E*-4-(((3-bromoallyl)oxy)methyl)quinolin-2(1*H*)-one (294 mg, 1 mmol), 2-bromo-1-phenylethan-1-one (256 mg, 1.2 mmol), K_2CO_3 (276 mg, 2 mmol), and DMF (10 mL) affords **1h** as a solid (390 mg, 95%). Mp: 173.5-174.6 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.1 Hz, 2H), 7.71 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.1 Hz, 1H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 6.44 (dt, *J* = 13.6, 1.2 Hz, 1H), 6.34 (dt, *J* = 13.6, 5.6 Hz, 1H), 5.82 (s, 2H), 4.77 (s, 2H), 4.10 (dd, *J* = 5.7, 1.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.3, 146.0, 139.4, 134.8, 134.0, 133.4, 130.7, 128.9, 128.1, 124.6, 122.3, 119.1, 114.5, 109.1, 70.3, 68.7, 48.6. IR (neat) 1690, 1653, 1595, 1449, 1424 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{19}BrNO_3^+$ $[M+H]^+$: 412.0543, found: 412.0543.

General procedure III for the synthesis of substrates

Synthesis of *E*-4-(5-bromopent-4-en-1-yl)-1-methylquinolin-2(1*H*)-one (1i)



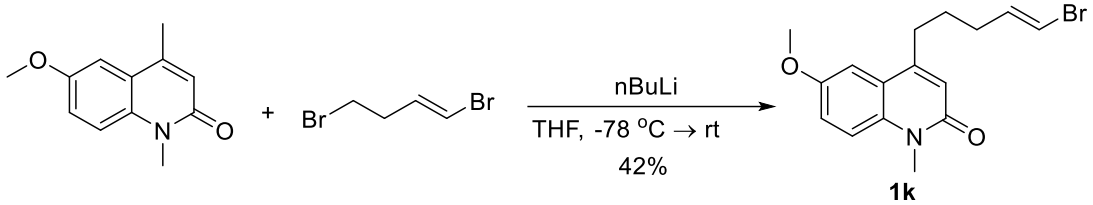
1i

To a flame dried flask are added 1,4-dimethylquinolin-2(1*H*)-one (1.731g, 10 mmol) and THF (50 mL). The mixture is cooled to -78 °C under argon atmosphere and treated dropwise with *n*-butyl lithium (2.5 M in *n*-hexane, 8.0 mL, 20 mmol). The solution is stirred at room temperature for 3 h, cooled to -78 °C and treated with *E*-1,4-dibromobut-1-ene (4.240 g, 20 mmol). The solution is stirred at room temperature overnight and then cooled to 0 °C, treated with 1 N HCl (20 mL). The solvent is evaporated and the residue is extracted with ethyl acetate (40 mL × 3). The combined organic layers are washed with brine (50 mL), dried over $MgSO_4$, filtered, and evaporated. The crude product is purified by column chromatography (*n*-hexane/ethyl acetate = 10:1 to 1:1) to give the product **1i** as a solid (1.067 g, 35%). Mp: 80.9-81.2 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.58 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.39 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.31-7.23 (m, 1H, Ar-H), 6.59 (s, 1H, Alkene-H), 6.20 (dt, *J* = 13.2, 7.2 Hz, 1H, Alkene-H), 6.09 (d, *J* = 13.2 Hz, 1H, Alkene-H), 3.72 (s, 3H, N-Me), 2.83 (t, *J* = 7.7 Hz, 2H, Alkane-H), 2.19 (q, *J* = 7.2 Hz, 2H, Alkane-H), 1.91-1.77 (m, 2H, Alkane-H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.1, 149.9, 140.0, 136.9, 130.6, 124.8, 122.2, 120.6, 119.9,

114.8, 105.4, 32.5, 31.2, 29.5, 27.6. IR (neat) 1636, 1597, 1459 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{17}BrNO^+$ $[M+H]^+$: 306.0488, found: 306.0490.

The following compound was synthesized according to general procedure III.

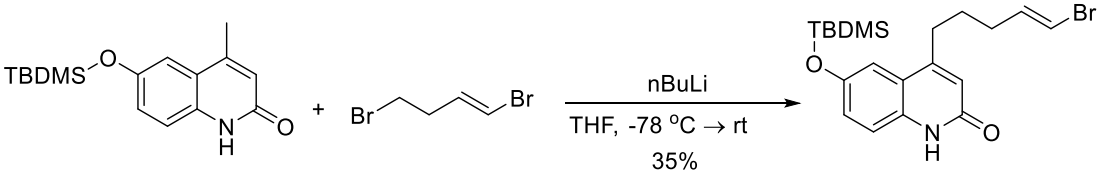
(1) *E*-4-(5-bromopent-4-en-1-yl)-6-methoxy-1-methylquinolin-2(1*H*)-one (1k)



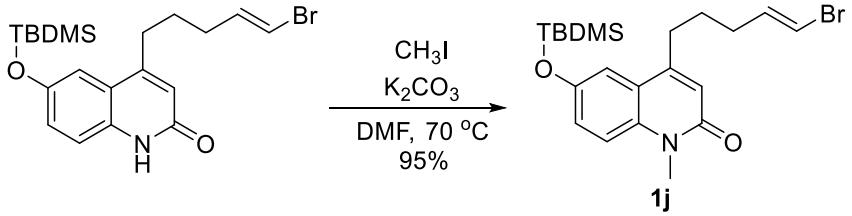
1k

The reaction of 6-methoxy-1,4-dimethylquinolin-2(1*H*)-one (406 mg, 2 mmol), *E*-1,4-dibromobut-1-ene (857 mg, 4 mmol), nBuLi (2.5 M in hexane, 1.6 mL, 4 mmol), and THF (20 mL) affords **1k** as a solid (281 mg, 42%). Mp: 142.0-143.9 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 9.2 Hz, 1H), 7.18 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.13 (d, *J* = 2.8 Hz, 1H), 6.58 (s, 1H), 6.21 (dt, *J* = 13.6, 7.2 Hz, 1H), 6.09 (d, *J* = 13.6 Hz, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 2.78 (t, *J* = 8.4 Hz, 2H), 2.18 (q, *J* = 7.2 Hz, 2H), 1.88-1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.6, 154.6, 148.6, 136.9, 134.6, 121.2, 120.9, 118.0, 115.8, 107.8, 105.4, 55.7, 32.4, 31.1, 29.4, 27.3. IR (neat) 1646, 1618, 1588, 1568, 1506, 1460, 1426, 1413 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{19}BrNO_2^+$ $[M+H]^+$: 336.0594, found: 336.0595.

Synthesis of *E*-4-(5-bromopent-4-en-1-yl)-6-((*tert*-butyldimethylsilyl)oxy)-1-methylquinolin-2(1*H*)-one (1j)



To a flame dried flask are added 6-((*tert*-butyldimethylsilyl)oxy)-4-methylquinolin-2(1*H*)-one (920 mg, 3.18 mmol), and THF (20 mL). The mixture is cooled to -78 °C under argon atmosphere and treated dropwise with *n*-butyl lithium (2.5 M in *n*-hexane, 2.5 mL, 6.25 mmol). The solution is stirred at 0 °C for 3 h, cooled to -78 °C and treated with *E*-1,4-dibromobut-1-ene (1.360 g, 6.38 mmol). The solution is stirred at room temperature overnight and then cooled to 0 °C, treated with 1 N HCl (20 mL). The solvent is evaporated and the residue is extracted with ethyl acetate (40 mL × 3). The combined organic layers are washed with brine (50 mL), dried over $MgSO_4$, filtered, and evaporated. The crude product is purified by column chromatography (*n*-hexane/ethyl acetate = 1:1) to give the product *E*-4-(5-bromopent-4-en-1-yl)-6-((*tert*-butyldimethylsilyl)oxy)-quinolin-2(1*H*)-one as a solid (469 mg, 35%). Mp: 174.5-175.6 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.58 (s, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.13-6.99 (m, 2H), 6.56 (s, 1H), 6.21 (dt, *J* = 13.6, 5.6 Hz, 1H), 6.11 (d, *J* = 13.6 Hz, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.20 (q, *J* = 7.2 Hz, 2H), 1.95-1.77 (m, 2H), 1.01 (s, 9H), 0.22 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 151.6, 150.9, 136.9, 133.5, 124.2, 120.4, 119.9, 117.8, 113.4, 105.4, 32.5, 31.4, 27.5, 25.7, 18.3, -4.4. IR (neat) 1662, 1619, 1499, 1470, 1462, 1425 cm^{-1}. Anal. Calc. for $C_{20}H_{28}BrNO_2Si$ (421.11), C, 56.87; H, 6.68; N, 3.32. found: C, 56.93; H, 6.72; N, 3.41.

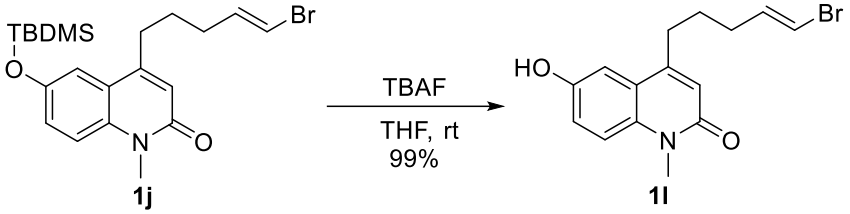


1j

To a sealed tube are added *E*-4-(5-bromopent-4-en-1-yl)-6-((*tert*-butyldimethylsilyl)oxy)quinolin-2(1*H*)-one (422 mg, 1 mmol), CH_3I (427 mg, 3 mmol), K_2CO_3 (827 mg, 6 mmol), and anhydrous DMF (10 mL). The mixture is stirred at 70 °C with an oil bath for 4 h as monitored by TLC (eluent: *n*-hexane/ethyl acetate = 5:1). The reaction is quenched with 1 N HCl (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layers are washed with brine (30 mL x 3), dried over Na_2SO_4, filtered, and evaporated. The residue is purified by flash chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 5:1) to afford product **1j** as an oil (402 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 9.5 Hz, 1H), 7.13-7.02 (m, 2H), 6.53 (s, 1H), 6.17 (dt, *J* = 13.6, 7.2 Hz, 1H), 6.06 (d, *J* = 13.6 Hz, 1H), 3.65 (s, 3H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.15 (q, *J* = 7.2 Hz, 2H), 1.89-1.67 (m, 2H), 0.98 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 150.3, 148.5, 136.8, 134.9, 123.3, 121.2, 120.6, 115.6, 114.4, 105.2, 32.4, 31.1, 29.2, 27.4, 25.6, 18.2, -4.4. IR (neat) 1638, 1593, 1499, 1450, 1415 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{17}BrNO_2^+$ $[M-TBDMS]^+$: 322.0437, found: 322.0437. Anal. Calc. for

$C_{20}H_{28}BrNO_2Si$ (435.12), C, 57.79; H, 6.93; N, 3.21. found: C, 57.88; H, 7.07; N, 3.36.

Synthesis of *E*-4-(5-bromopent-4-en-1-yl)-6-hydroxy-1-methylquinolin-2(1*H*)-one (1l)

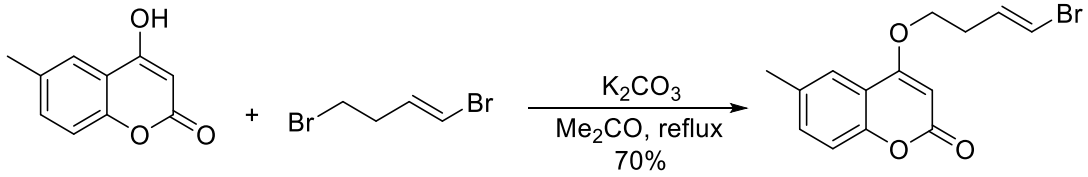


1j **1l**

To a flask are added **1j** (436 mg, 1 mmol), *tetra*-*n*-butylammonium fluoride (TBAF) (522 mg, 2 mmol), and anhydrous THF (10 mL). The mixture is stirred at room temperature for 1 h as monitored by TLC (eluent: *n*-hexane/ethyl acetate = 1:1). The crude product is washed with water and extracted with ethyl acetate (20 mL x 3). The combined organic layers are washed with brine (30 mL x 3), dried over Na_2SO_4, filtered, and evaporated. The residue is purified by flash chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 1:1) to afford product **1l** as a solid (321 mg, 99%)**.** Mp: 135.9-137.0 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.51 (s, 1H), 7.38 (d, *J* = 8.9 Hz, 1H), 7.15-7.05 (m, 2H), 6.45 (s, 1H), 6.36 (d, *J* = 13.6 Hz, 1H), 6.29 (dt, *J* = 13.6, 6.8 Hz, 1H), 3.55 (s, 3H), 2.77-2.69 (m, 2H), 2.15 (q, *J* = 7.1 Hz, 2H), 1.72 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.1, 160.7, 152.6, 149.2, 138.1, 121.1, 120.3, 119.7, 116.7, 109.7, 105.9, 32.4, 31.1, 29.3, 27.5. IR (neat) 3389, 1655 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{17}BrNO_2^+$ $[M+H]^+$: 322.0437, found: 322.0437.

General procedure IV for the synthesis of substrates

Synthesis of *E*-4-((4-bromobut-3-en-1-yl)oxy)-6-methyl-2*H*-chromen-2-one (1m)

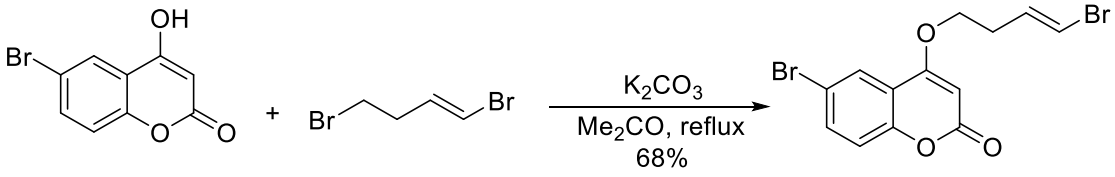


1m

To a flask are added 4-hydroxy-6-methyl-2*H*-chromen-2-one (880 mg, 5 mmol), *E*-1,4-dibromobut-1-ene (1.065 g, 5 mmol), K_2CO_3 (1.656 g, 12 mmol), and anhydrous acetone (15 mL). The mixture is refluxed with an oil bath for 24 h as monitored by TLC (*n*-hexane/ethyl acetate = 1:1). The solvent is evaporated and the residue is purified by flash chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 5:1) to afford product **1m** as a solid (1.078 g, 70%). Mp: 127.9-129.1 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 0.4 Hz, 1H, Ar-H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H, Ar-H), 7.19 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.40-6.22 (m, 2H, Alkene-H), 5.62 (s, 1H, Alkene-H), 4.14 (t, *J* = 6.3 Hz, 2H, O-Alkane-H), 2.70-2.63 (m, 2H, Alkane-H), 2.41 (s, 3H, Me). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.2, 162.9, 151.4, 133.6, 133.4, 132.6, 122.5, 116.5, 115.1, 107.8, 90.5, 67.3, 32.1, 20.9. IR (neat) 1695, 1625, 1572, 1462, 1440 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{14}BrO_3^+$ $[M+H]^+$: 309.0121, found: 309.0121.

The following compounds were synthesized according to general procedure IV.

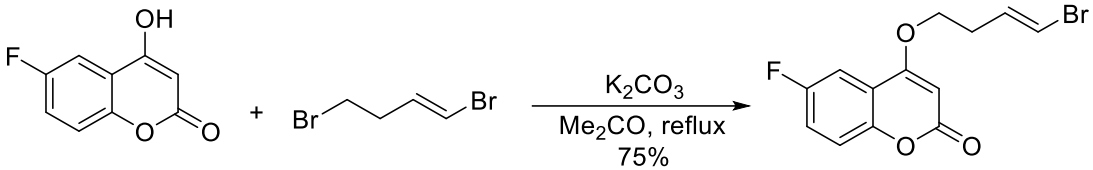
(1) *E*-6-bromo-4-((4-bromobut-3-en-1-yl)oxy)-2*H*-chromen-2-one (1n)



1n

The reaction of 6-bromo-4-hydroxy-2*H*-chromen-2-one (964 mg, 4 mmol), *E*-1,4-dibromobut-1-ene (1.026 g, 4.8 mmol), K_2CO_3 (1.656 g, 12 mmol), and anhydrous acetone (15 mL) affords **1n** as a solid (967 mg, 68%). Mp: 151.5-152.0 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 2.3 Hz, 1H), 7.64 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 6.36-6.22 (m, 2H), 5.67 (s, 1H), 4.16 (t, *J* = 6.3 Hz, 2H), 2.68 (q, *J* = 6.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.0, 161.9, 152.1, 135.3, 132.2, 125.6, 118.6, 117.1, 116.8, 108.2, 91.4, 67.7, 32.1. IR (neat) 1725, 1622, 1558, 1478, 1459, 1431, 1421 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{11}Br_2O_3^+$ $[M+H]^+$: 372.9069, found: 372.9069.

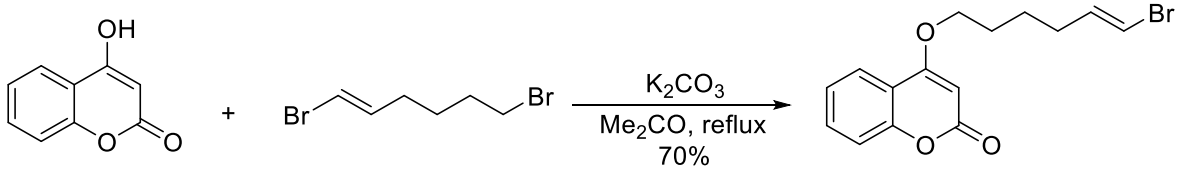
(2) *E*-4-((4-bromobut-3-en-1-yl)oxy)-6-fluoro-2*H*-chromen-2-one (1o)



1o

The reaction of 6-fluoro-4-hydroxy-2*H*-chromen-2-one (180 mg, 1 mmol), *E*-1,4-dibromobut-1-ene (257 mg, 1.2 mmol), K_2CO_3 (414 mg, 3 mmol), and anhydrous acetone (10 mL) affords **1o** as a solid (235 mg, 75%). Mp: 159.8-160.0 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 8.3, 2.7 Hz, 1H), 7.33-7.24 (m, 2H), 6.35-6.22 (m, 2H), 5.69 (s, 1H), 4.17 (t, *J* = 6.3 Hz, 2H), 2.67 (q, *J* = 6.1 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.40, 164.37, 162.3, 159.9, 157.4, 149.45, 149.43, 132.3, 120.1, 119.9, 118.5, 118.4, 116.5, 116.4, 108.9, 108.6, 108.1, 91.4, 67.6, 32.1. IR (neat) 1646, 1587, 1567, 1460, 1426, 1413 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{11}BrFO_3^+$ [M+H]$^+$: 312.9870, found: 312.9870.

(3) *E*-4-((6-bromohex-5-en-1-yl)oxy)-2*H*-chromen-2-one (1s)

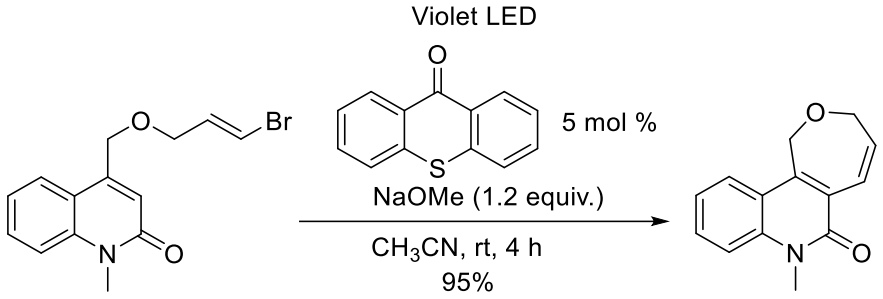


1s

The reaction of 4-hydroxy-2*H*-chromen-2-one (160 mg, 1 mmol), *E*-1,6-dibromohex-1-ene (290 mg, 1.2 mmol), K_2CO_3 (417 mg, 3 mmol), and anhydrous acetone (10 mL) affords **1s** as a solid (226 mg, 70%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.30-7.26 (m, 1H), 6.20 (dt, *J* = 10.8, 5.6 Hz, 1H), 6.10 (dt, *J* = 10.8 Hz, 1.2 Hz, 1H), 5.66 (s, 1H), 4.13 (t, *J* = 6.2 Hz, 2H), 2.17 (qd, *J* = 7.3, 1.3 Hz, 2H), 1.99-1.89 (m, 2H), 1.71-1.60 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.5, 161.9, 152.3, 136.1, 131.3, 122.8, 121.9, 115.7, 114.7, 104.1, 89.4, 67.9, 31.4, 26.8, 24.0. IR (neat) 1708, 1620, 1607, 1565, 1495, 1475, 1454, 1417 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{16}BrO_3^+$ [M+H]$^+$: 323.0277, found: 323.0275.

General procedure V for the photoreaction

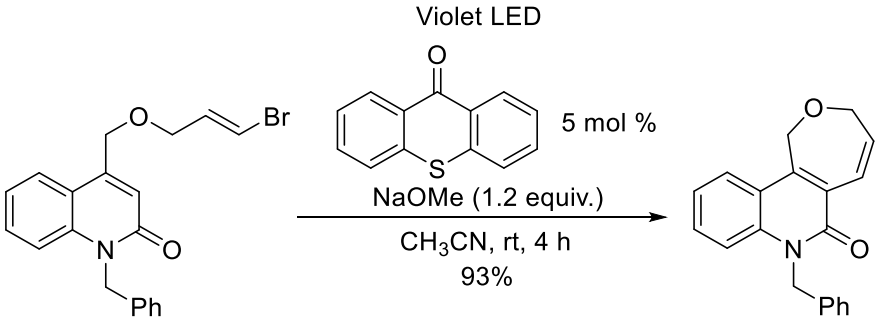
(1) 7-Methyl-3,7-dihydrooxepino[4,3-*c*]quinolin-6(1*H*)-one (2a)



1a **2a**

To a flame dried Schlenk tube are added **1a** (31 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and anhydrous CH_3CN (10 mL). The reaction is irradiated by a violet LED strips under argon atmosphere at room temperature. The reaction is completed after 4 h as monitored by TLC (eluent: *n*-hexane/ethyl acetate = 3:1). The solvent is removed and the residue is purified by flash chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 5:1) to afford **2a** as an oil (22 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.54 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.37 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.28-7.22 (m, 1H, Ar-H), 7.13 (dt, *J* = 12.6, 2.2 Hz, 1H, Alkene-H), 6.20 (dt, *J* = 12.5, 3.2 Hz, 1H, Alkene-H), 4.93 (s, 2H, H-Alkane-O), 4.59 (t, *J* = 2.7 Hz, 2H, O-Alkane-H), 3.76 (s, 3H, N-Me). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.3, 144.5, 138.9, 135.9, 130.2, 127.3, 124.24, 124.15, 122.3, 119.2, 114.6, 73.3, 65.6, 30.1. IR (neat) 1629, 1586, 1457, 1417 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{14}NO_2^+$ [M+H]$^+$: 228.1019, found: 228.1019.

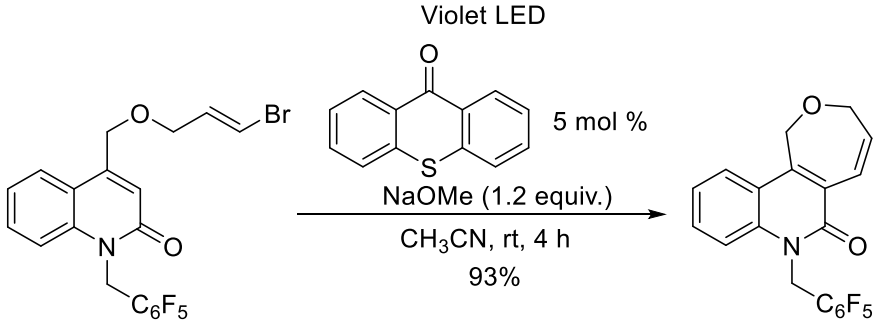
(2) 7-Benzyl-3,7-dihydrooxepino[4,3-*c*]quinolin-6(1*H*)-one (2b)



1b **2b**

The reaction of **1b** (38 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2b** as an oil (28 mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.32-7.17 (m, 8H), 6.23 (dt, *J* = 12.5, 3.1 Hz, 1H), 5.61 (s, 2H), 4.98 (s, 2H), 4.63 (t, *J* = 2.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 145.1, 138.4, 136.3, 136.1, 130.2, 128.8, 127.3, 127.2, 126.5, 124.21, 124.19, 122.4, 119.4, 115.5, 73.5, 65.7, 46.7. IR (neat) 1630, 1585, 1452 cm^{-1}. HRMS (ESI): calcd for $C_{20}H_{18}NO_2^+$ [M+H]$^+$: 304.1332, found: 304.1332.

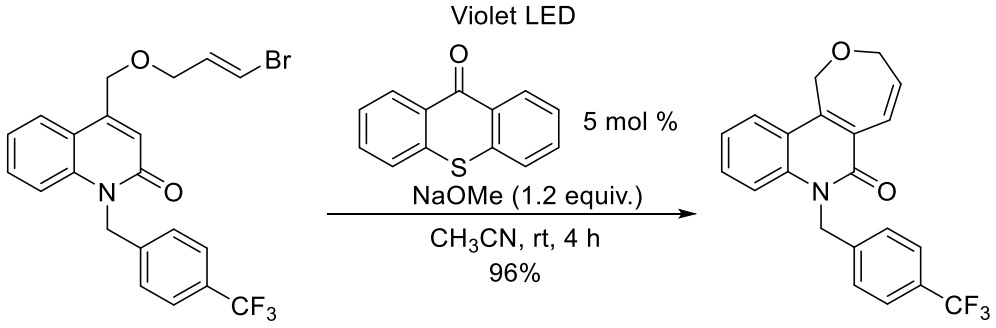
(3) 7-((Perfluorophenyl)methyl)-3,7-dihydrooxepino[4,3-*c*]quinolin-6(1*H*)-one (2c)



1c **2c**

The reaction of **1c** (48 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2c** as an oil (37 mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.29-7.22 (m, 2H), 7.12 (dt, *J* = 12.5, 2.0 Hz, 1H), 6.23 (dt, *J* = 12.5, 3.1 Hz, 1H), 5.72 (s, 2H), 4.95 (s, 2H), 4.61 (t, *J* = 2.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.3, 145.3, 137.6, 136.6, 130.4, 127.0, 124.8, 123.8, 122.8, 119.7, 113.9, 73.5, 65.7, 35.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -141.9--142.8 (m), -154.5 (t, *J* = 22.4 Hz), -161.4--163.7 (m), IR (neat) 1656, 1502, 1456, 1421 cm^{-1}. HRMS (ESI): calcd for $C_{20}H_{13}F_5NO_2^+$ [M+H]$^+$: 394.0861, found: 394.0860.

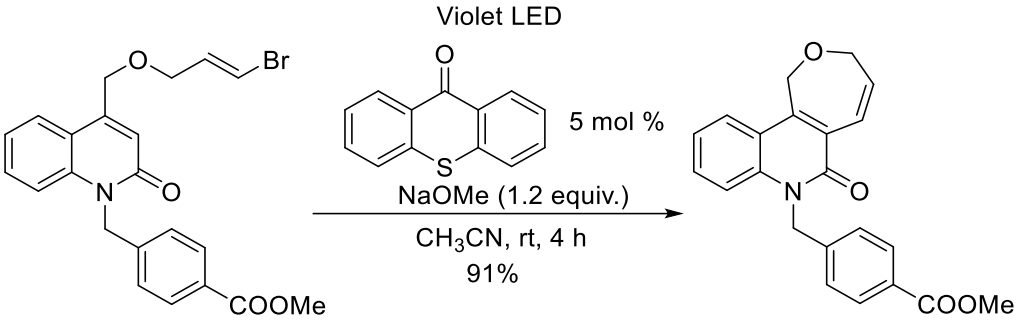
(4) 7-(4-(Trifluoromethyl)benzyl)-3,7-dihydrooxepino[4,3-c]quinolin-6(1*H*)-one (2d)



1d **2d**

The reaction of **1d** (45 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2d** as a solid (36 mg, 96%). Mp: 89.1-90.1 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26-7.20 (m, 1H), 7.19-7.14 (m, 2H), 6.25 (dt, *J* = 12.5, 3.0 Hz, 1H), 5.65 (s, 2H), 4.99 (s, 2H), 4.64 (t, *J* = 2.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 145.3, 140.4, 138.1, 136.5, 130.4, 129.8, 129.5, 127.2, 126.9, 125.9, 125.82, 125.78, 125.7, 125.4, 124.4, 123.9, 122.73, 122.66, 119.5, 115.1, 73.6, 65.8, 46.3. IR (neat) 1635, 1598, 1458 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{17}F_3NO_2^+$ [M+H]$^+$: 372.1206, found: 372.1206.

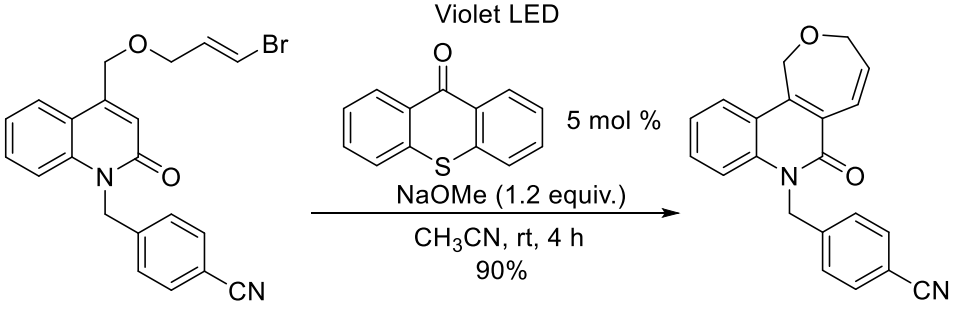
(5) 7-(4-Methoxycarbonylbenzyl)-3,7-dihydrooxepino[4,3-c]quinolin-6(1*H*)-one (2e)



1e **2e**

The reaction of **1e** (44 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2e** as an oil (33 mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.28-7.12 (m, 5H), 6.24 (dt, *J* = 12.5, 3.0 Hz, 1H), 5.65 (s, 2H), 4.98 (s, 2H), 4.64 (t, *J* = 2.5 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 161.5, 145.3, 141.6, 138.1, 136.4, 130.3, 130.1, 129.2, 127.2, 126.5, 124.4, 124.0, 122.6, 119.5, 115.2, 73.6, 65.7, 52.1, 46.5. IR (neat) 1719, 1641, 1457, 1436, 1416 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{20}NO_4^+$ [M+H]$^+$: 362.1387, found: 362.1386.

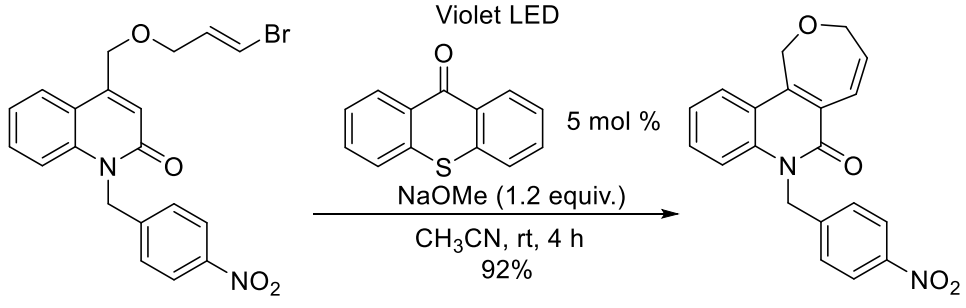
(6) 7-(4-Cyanobenzyl)-3,7-dihydrooxepino[4,3-c]quinolin-6(1*H*)-one (2f)



1f **2f**

The reaction of **1f** (41 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2f** as a solid (30 mg, 90%). Mp: 110.1-110.7 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26-7.21 (m, 1H), 7.13 (t, *J* = 11.0 Hz, 2H), 6.25 (dt, *J* = 12.4, 2.9 Hz, 1H), 5.65 (s, 2H), 4.99 (s, 2H), 4.65 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4, 145.4, 141.9, 137.9, 136.6, 132.7, 130.4, 127.3, 127.2, 124.6, 123.8, 122.9, 119.5, 118.6, 114.9, 111.3, 73.6, 65.7, 46.4. IR (neat) 2250, 1718, 1642, 1456, 1436 cm^{-1}. Anal. Calc. for $C_{21}H_{16}N_2O_2$ (328.12), C, 76.81; H, 4.91; N, 8.53. found: C, 77.01; H, 5.20; N, 8.61.

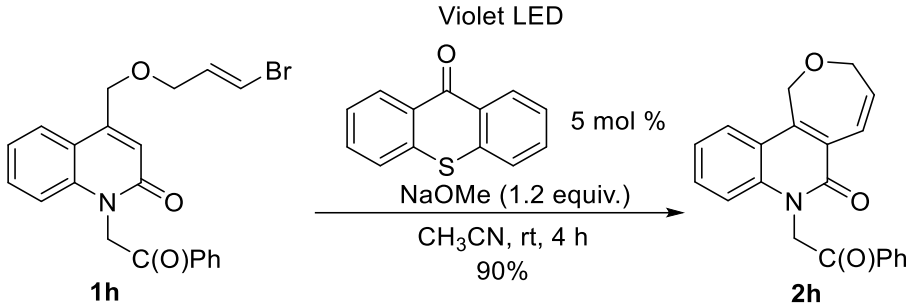
(7) 7-(4-Nitrobenzyl)-3,7-dihydrooxepino[4,3-c]quinolin-6(1*H*)-one (2g)



1g **2g**

The reaction of **1g** (43 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2g** as a solid (32 mg, 92%). Mp: 120.5-121.7 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.48-7.34 (m, 3H), 7.25-7.22 (m, 1H), 7.20-7.08 (m, 2H), 6.26 (dt, *J* = 13.2, 3.1 Hz, 1H), 5.69 (s, 2H), 5.00 (s, 2H), 4.66 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4, 145.5, 143.9, 137.9, 136.7, 130.4, 127.4, 127.2, 124.6, 124.1, 123.8, 122.9, 119.6, 114.9, 73.6, 65.8, 46.2. IR (neat) 1624, 1586, 1512, 1455, 1435 cm^{-1}. HRMS (ESI): calcd for $C_{20}H_{17}N_2O_4^+$ [M+H]$^+$: 349.1183, found: 349.1182.

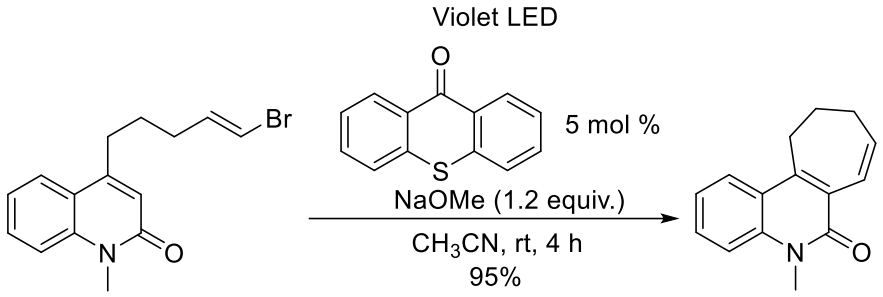
(8) 7-(2-Oxo-2-phenylethyl)-3,7-dihydrooxepino[4,3-c]quinolin-6(1*H*)-one (2h)



1h **2h**

The reaction of **1h** (41 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2h** as an oil (30 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 12.7 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.21 (dt, *J* = 12.7, 3.3 Hz, 1H), 5.86 (s, 2H), 4.98 (s, 2H), 4.62 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.4, 161.3, 145.4, 138.5, 136.1, 133.9, 130.3, 129.0, 128.2, 127.1, 124.5, 124.1, 122.6, 119.5, 114.5, 73.3, 65.9, 49.4. IR (neat) 1690, 1653, 1595, 1469, 1450, 1424 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{18}NO_3^+$ $[M+H]^+$: 332.1281, found: 332.1281.

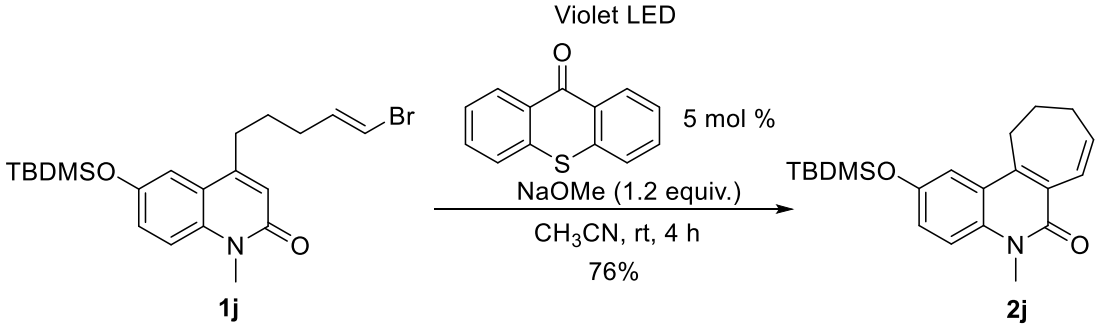
(9) 5-Methyl-5,9,10,11-tetrahydro-6*H*-cyclohepta[*c*]quinolin-6-one (2i)



1i **2i**

The reaction of **1i** (31 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2i** as an oil (21 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 9.3 Hz, 1H, Ar-H), 7.53 (t, *J* = 8.5 Hz, 1H, Ar-H), 7.37 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.28-7.23 (m, 1H, Ar-H), 6.95 (d, *J* = 11.8 Hz, 1H, Alkene-H), 6.38-6.24 (m, 1H, Alkene-H), 3.76 (s, 3H, N-Me), 3.04-2.94 (m, 2H, Alkane-H), 2.32 (q, *J* = 5.9 Hz, 2H, Alkane-H), 2.26-2.12 (m, 2H, Alkane-H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 138.9, 135.4, 129.6, 127.4, 125.9, 124.9, 122.0, 121.6, 120.7, 114.4, 31.6, 30.0, 29.8, 27.5. IR (neat) 1639, 1588, 1452 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{16}NO^+$ $[M+H]^+$: 226.1226, found: 226.1227.

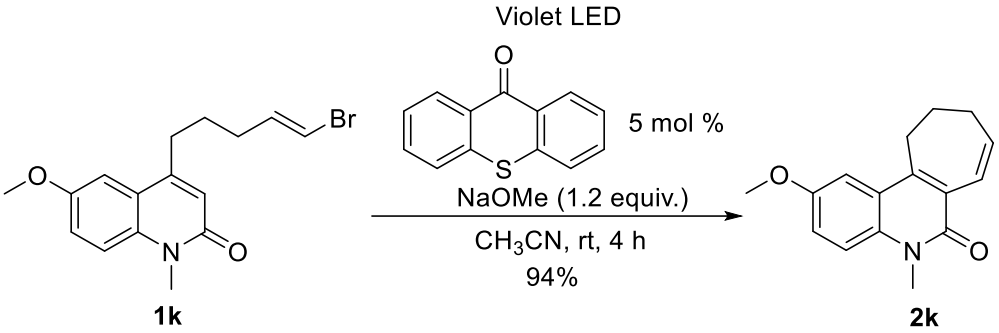
(10) 2-((*tert*-Butyldimethylsilyl)oxy)-5-methyl-5,9,10,11-tetrahydro-6*H*-cyclohepta [*c*] quinolin-6-one (2j)



1j **2j**

The reaction of **1j** (44 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2j** as a solid (27 mg, 76%). Mp: 143.2-145.0 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 2.6 Hz, 1H), 7.23 (d, *J* = 9.0 Hz, 1H), 7.05 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.94 (d, *J* = 11.7 Hz, 1H), 6.37-6.25 (m, 1H), 3.72 (s, 3H), 2.94-2.86 (m, 2H), 2.31 (q, *J* = 6.0 Hz, 2H), 2.25-2.13 (m, 2H), 1.02 (s, 9H), 0.23 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.1, 150.6, 146.7, 135.4, 133.9, 127.7, 126.1, 122.4, 121.6, 115.4, 114.8, 31.6, 29.93, 29.85, 27.7, 25.7, 18.3, -4.4. IR (neat) 1632, 1564, 1506, 1461, 1428 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{16}NO_2^+$ $[M-TBDMS]^+$: 242.1176, found: 242.1176.

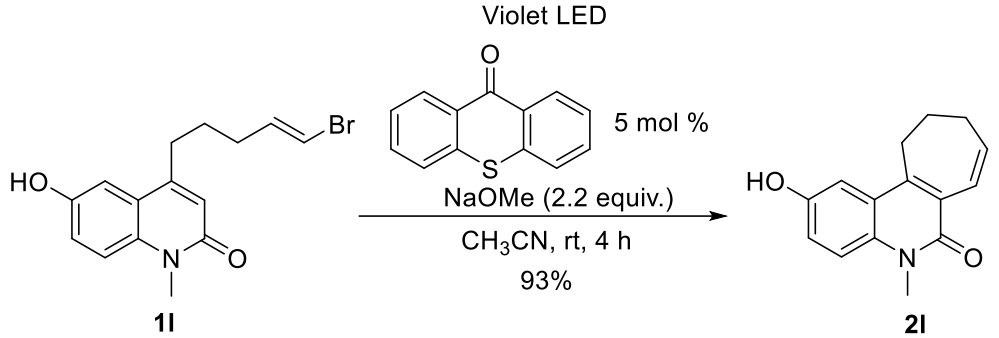
(11) 2-Methoxy-5-methyl-5,9,10,11-tetrahydro-6*H*-cyclohepta[*c*]quinolin-6-one (2k)



1k **2k**

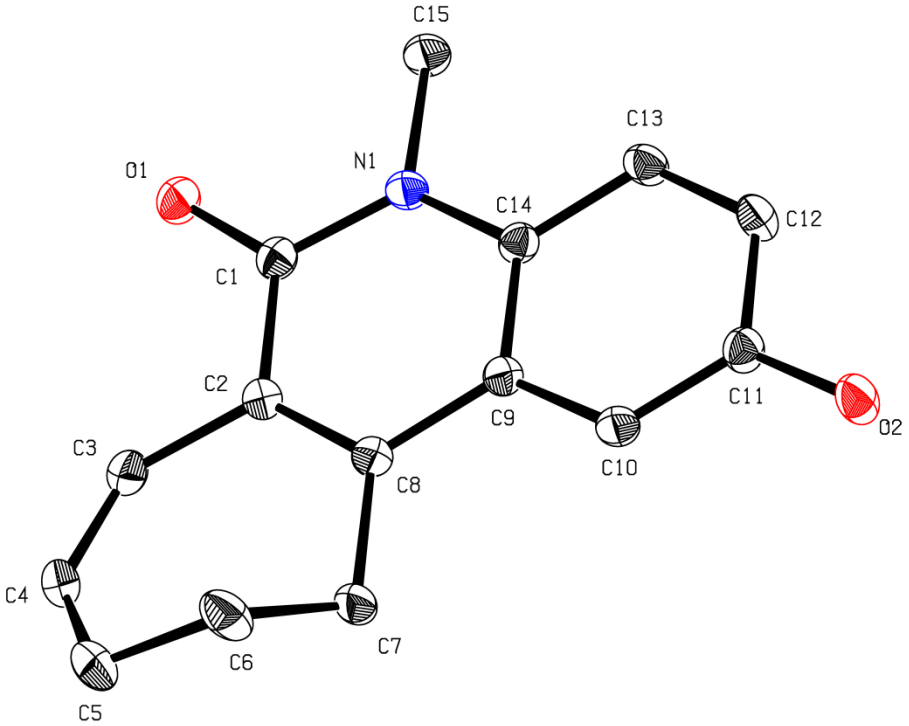
The reaction of **1k** (34 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2k** as an oil (24 mg, 94%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36-7.28 (m, 2H), 7.15 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.95 (d, *J* = 11.8 Hz, 1H), 6.36-6.26 (m, 1H), 3.90 (s, 3H), 3.74 (s, 3H), 2.99-2.90 (m, 2H), 2.32 (q, *J* = 6.2 Hz, 2H), 2.25-2.13 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.0, 154.7, 146.8, 135.4, 133.6, 128.0, 126.1, 121.5, 117.2, 115.6, 108.1, 55.8, 31.6, 30.0, 29.9, 27.7. IR (neat) 1615, 1568, 1508, 1458, 1428 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{18}NO_2^+$ $[M+H]^+$: 256.1332, found: 256.1332.

(12) 2-Hydroxy-5-methyl-5,9,10,11-tetrahydro-6*H*-cyclohepta[*c*]quinolin-6-one (2l)



1l **2l**

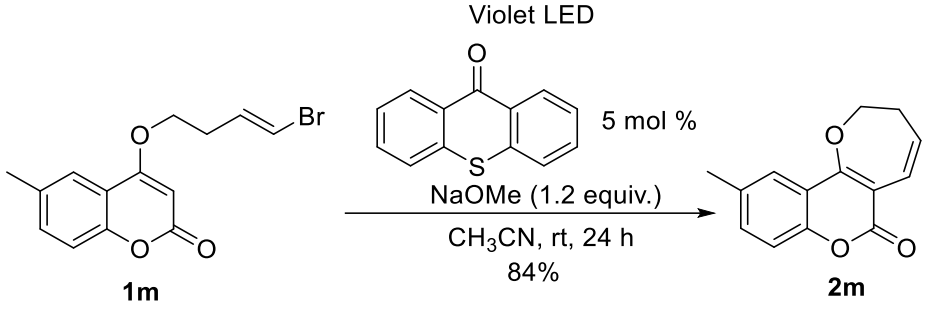
The reaction of **1l** (32 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (12 mg, 0.22 mmol), and CH_3CN (10 mL) affords **2l** as a solid (22 mg, 93%). Mp: 136.1-136.7 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.43 (d, *J* = 9.1 Hz, 1H), 7.34 (d, *J* = 2.7 Hz, 1H), 7.13 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.82 (dd, *J* = 11.7, 1.7 Hz, 1H), 6.37-6.26 (m, 1H), 3.73 (s, 3H), 2.99-2.91 (m, 2H), 2.36-2.15 (m, 4H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 162.5, 154.4, 149.6, 136.4, 133.5, 128.0, 126.9, 123.0, 120.3, 117.4, 110.4, 33.0, 30.6, 30.5, 28.6. IR (neat) 2920, 1602, 1570, 1511, 1455, 1434 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{16}NO_2^+$ $[M+H]^+$: 242.1176, found: 242.1176. Supplementary crystallographic data for **2l** have been deposited at the Cambridge Crystallographic Data Center. CCDC: 1990197.



Ortep drawing with 50% ellipsoids for **2l**

Compound	**2l**
formula	$C_{15}H_{15}NO_2$
CCDC number	1990197
fw	241.28
color/habit	clear yellow fragment
Cryst. Dimens. [mm^3]	0.110 x 0.249 x 0.479
Cryst. Syst.	monoclinic
space group	*P* 1 2_1/c 1
a [Å]	8.4227(3)
b [Å]	16.6533(6)
c [Å]	8.2953(3)
α [deg]	90
β [deg]	95.7590(10)
γ [deg]	90
V [Å^3]	1157.67(7)
Z	4
T [K]	100(2)
D_{calcd} [g/cm^{-3}]	1.384
μ [mm^{-1}]	0.092
ϑ range [deg]	2.43 to 26.39
index range (h, k, l)	–10 ≤ h ≤ 10 –20 ≤ k ≤ 20 –10 ≤ l ≤ 10
Reflections collected	18989
no. of indep refIns/R_{int}	2375/0.0289
no. of data/ restraints/params	2375/0/166
R1/wR2 (*I*>2σ(I))	0.0400/0.1072
R1/wR2 (*all data*)	0.0432/0.1094
GOF (on F^2)	1.100
Largest diff peak and hole [e Å^{-3}]	0.286/-0.219

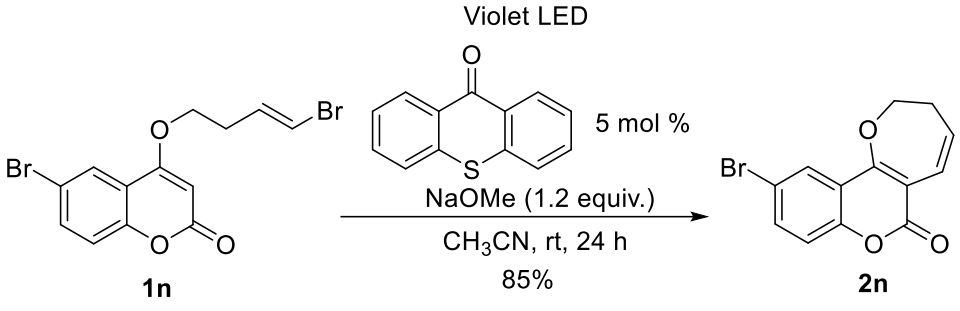
(13) 10-Methyl-2,3-dihydro-6*H*-oxepino[3,2-*c*]chromen-6-one (2m)



1m **2m**

The reaction of **1m** (31 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2m** as an oil (19 mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (s, 1H, Ar-H), 7.32-7.25 (m, 1H, Ar-H), 7.16 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.81 (d, *J* = 11.8 Hz, 1H, Alkene-H), 6.18-6.08 (m, 1H, Alkene-H), 4.54 (t, *J* = 4.4 Hz, 2H, Alkane-H), 2.77 (q, *J* = 4.6 Hz, 2H, Alkane-H), 2.40 (s, 3H, N-Me). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8, 162.9, 149.6, 133.7, 132.6, 131.6, 123.4, 122.3, 116.8, 116.0, 105.3, 71.4, 33.7, 20.9. IR (neat) 1694, 1621, 1576, 1495, 1426 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{13}O_3^+$ $[M+H]^+$: 229.0859, found: 229.0860.

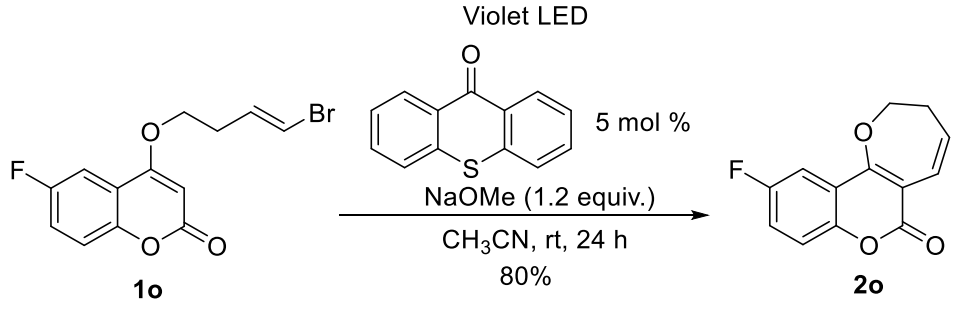
(14) 10-Bromo-2,3-dihydro-6*H*-oxepino[3,2-*c*]chromen-6-one (2n)



1n **2n**

The reaction of **1n** (37 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2n** as a solid (26 mg, 85%). Mp: 118.1-119.2 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 2.4 Hz, 1H), 7.56 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 6.79 (d, *J* = 11.8 Hz, 1H), 6.24-6.14 (m, 1H), 4.54 (t, *J* = 4.4 Hz, 2H), 2.83-2.74 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.0, 161.3, 150.2, 134.3, 132.8, 126.3, 122.0, 118.7, 117.9, 116.8, 106.0, 71.6, 33.6. IR (neat) 1704, 1600, 1556, 1474, 1416 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{10}BrO_3^+$ $[M+H]^+$: 292.9808, found: 292.9808.

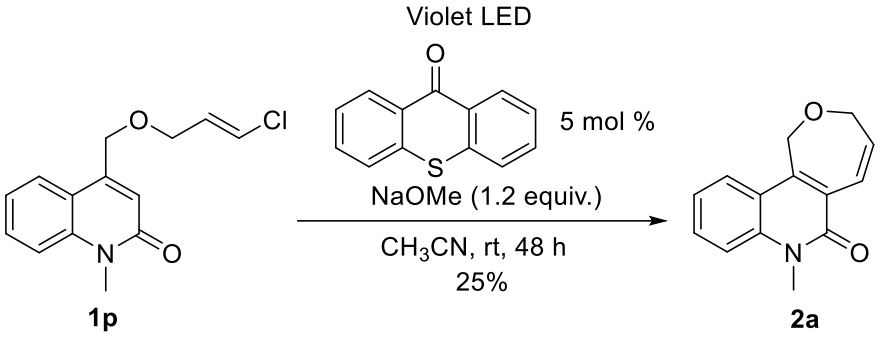
(15) 10-Fluoro-2,3-dihydro-6*H*-oxepino[3,2-*c*]chromen-6-one (2o)



1o **2o**

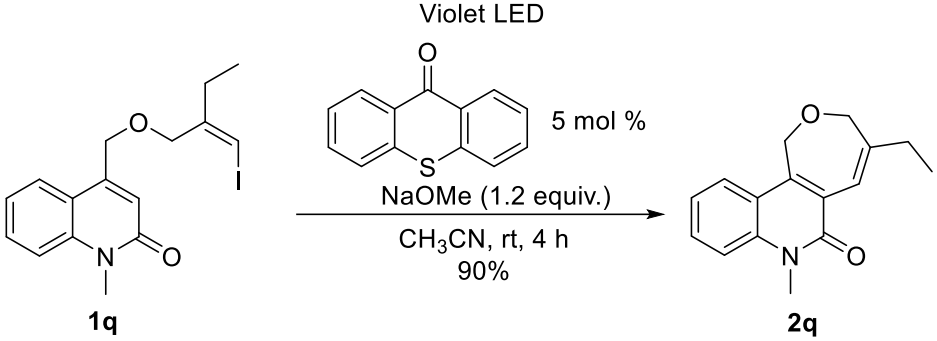
The reaction of **1o** (31 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2o** as a solid (19 mg, 80%). Mp: 110.4-111.3 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 8.8, 2.9 Hz, 1H), 7.27-7.17 (m, 2H), 6.81 (d, *J* = 11.8 Hz, 1H), 6.26-6.15 (m, 1H), 4.55 (t, *J* = 4.4 Hz, 2H), 2.84-2.73 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3, 161.73, 161.70, 160.0, 157.6, 147.5, 132.7, 122.0, 119.1, 118.9, 118.2, 118.1, 117.8, 117.7, 109.5, 109.3, 106.0, 71.5, 33.6. IR (neat) 1741, 1460 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{10}FO_3^+$ $[M+H]^+$: 233.0608, found: 233.0609.

(16) 7-Methyl-3,7-dihydrooxepino[4,3-*c*]quinolin-6(1*H*)-one (2a)



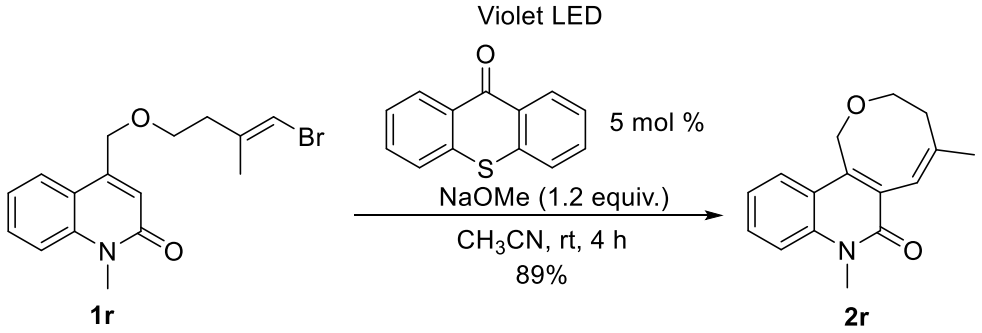
The reaction of **1p** (26 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2a** as an oil (7 mg, 25%).

(17) 4-Ethyl-7-methyl-3,7-dihydrooxepino[4,3-*c*]quinolin-6(1*H*)-one (2q)

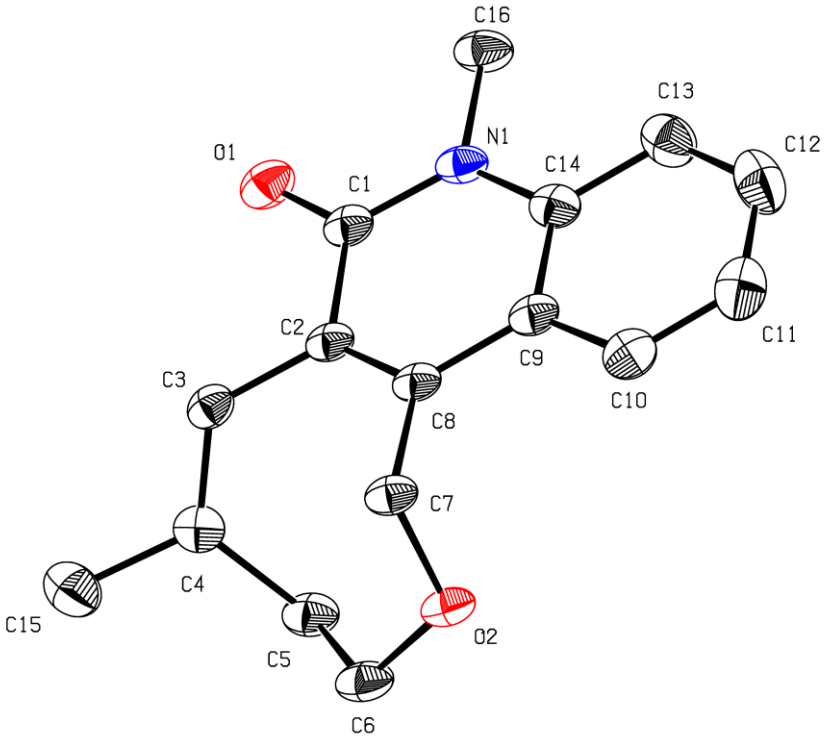


The reaction of **1q** (38 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2q** as an oil (23 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.26-7.19 (m, 1H), 6.98 (s, 1H), 4.88 (s, 2H), 4.45 (s, 2H), 3.76 (s, 3H), 2.25 (q, *J* = 7.5 Hz, 2H), 1.20 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4, 150.2, 143.0, 138.6, 129.7, 127.6, 123.9, 122.2, 120.0, 119.3, 114.5, 74.7, 65.5, 30.1, 28.8, 13.5. IR (neat) 1637, 1590, 1459 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{18}NO_2^+$ [M+H]$^+$: 256.1332, found: 256.1332.

(18) 5,8-Dimethyl-4,8-dihydro-1*H*-oxocino[4,3-c]quinolin-7(3*H*)-one (2r)



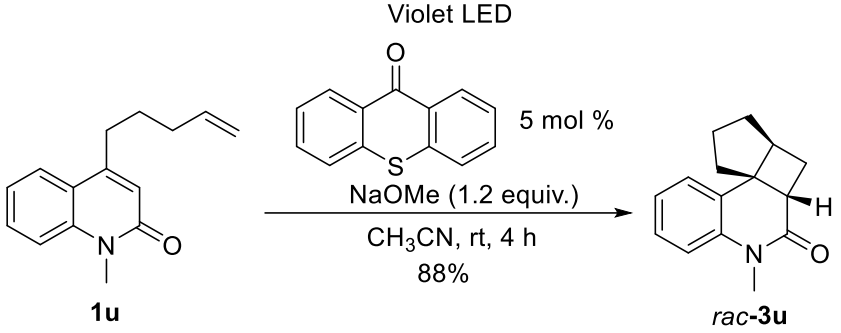
The reaction of **1r** (34 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords **2r** as a solid (23 mg, 89%). Mp: 107.4-109.0 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 4.64 (brs, 2H), 3.76 (s, 3H), 3.65 (brs, 2H), 2.23-2.10 (m, 2H), 2.06 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 142.7, 139.2, 139.0, 129.7, 129.6, 125.8, 122.5, 122.0, 120.9, 114.2, 66.6, 63.8, 36.9, 29.7, 25.6. IR (neat) 1646, 1588, 1459, 1411 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{18}NO_2^+$ [M+H]$^+$: 256.1332, found: 256.1332. Supplementary crystallographic data for **2r** have been deposited at the Cambridge Crystallographic Data Center. CCDC: 1990198.



Ortep drawing with 50% ellipsoids for **2r**

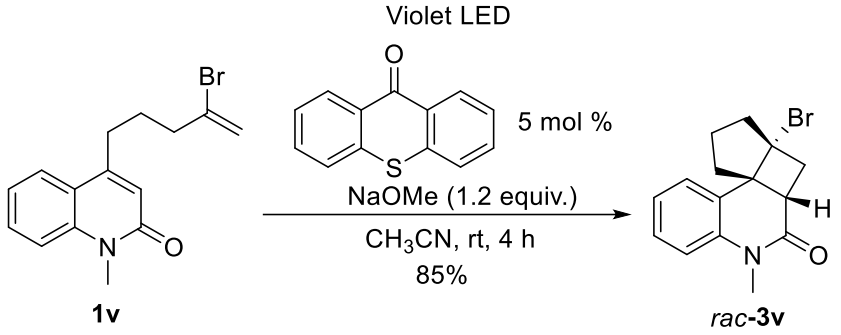
Compound	**2r**
formula	$C_{16}H_{17}NO_2$
CCDC number	1990198
fw	255.30
color/habit	clear colourless fragment
Cryst. Dimens. [mm^3]	0.122 x 0.292 x 0.377
Cryst. Syst.	trigonal
space group	*R* -1
a [Å]	27.772(12)
b [Å]	27.772(12)
c [Å]	9.413(4)
α [deg]	90
β [deg]	90
γ [deg]	120
V [$Å^3$]	6287.(6)
Z	6
T [K]	100(2)
D_{calcd} [g/cm^{-3}]	1.214
μ [mm^{-1}]	0.080
ϑ range [deg]	2.32 to 25.34
index range (h, k, l)	-33 ≤ h ≤ 33 -33 ≤ k ≤ 33 -11 ≤ l ≤ 11
Reflections collected	61427
no. of indep reflns/R_{int}	2568/0.0574
no. of data/ restraints/params	2568/0/174
R1/wR2 (*I*>2σ(I))	0.0494/0.0984
R1/wR2 (*all data*)	0.0540/0.1003
GOF (on F^2)	1.162
Largest diff peak and hole [e $Å^{-3}$]	0.202/-0.208

(19) 6-Methyl-1,2,3,3a,4,4a-hexahydrocyclopenta[2,3]cyclobuta[1,2-c]quinolin-5(6*H*)-one (*rac*-3u)



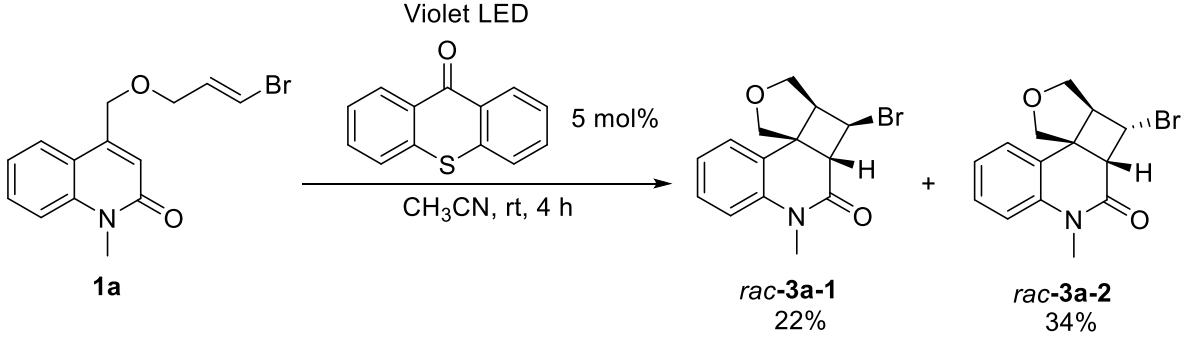
The reaction of **1u**[16] (23 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords *rac*-**3u** as a solid (20 mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 3.37 (s, 3H), 3.11-2.99 (m, 1H), 2.68-2.43 (m, 2H), 2.17-2.02 (m, 3H), 1.99-1.83 (m, 3H), 1.71-1.64 (m, 1H).

(20) 3a-Bromo-6-methyl-1,2,3,3a,4,4a-hexahydrocyclopenta[2,3]cyclobuta[1,2-c]quinolin-5(6*H*)-one (*rac*-3v)

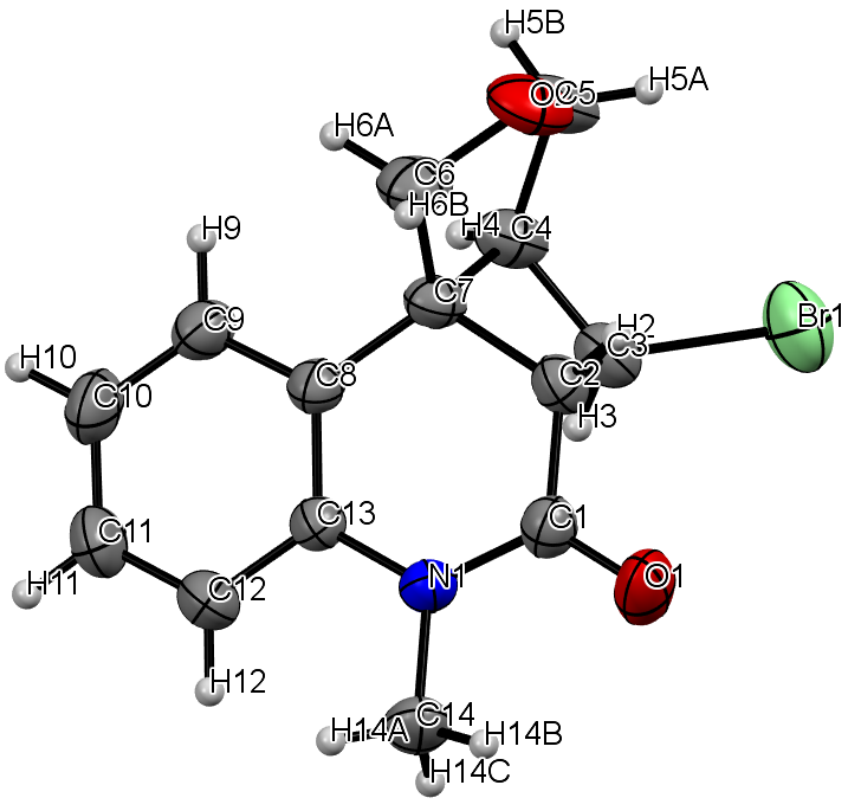


The reaction of **1v** (31 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), NaOMe (6.5 mg, 0.12 mmol), and CH_3CN (10 mL) affords *rac*-**3v** as an oil (26 mg, 85%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.32 (t, *J* = 7.7 Hz, 1H), 7.24-7.09 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 3.35 (s, 3H), 3.12-2.91 (m, 2H), 2.89-2.78 (m, 1H), 2.50-2.31 (m, 2H), 2.25-1.96 (m, 4H). ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 168.6, 140.3, 129.1, 128.8, 125.3, 122.8, 115.0, 71.3, 56.5, 46.1, 43.9, 41.5, 39.0, 29.3, 25.0. IR (neat) 1625, 1592, 1570, 1453 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{17}BrNO^+$ $[M+H]^+$: 306.0488, found: 306.0489.

Synthesis of 4-bromo-6-methyl-3,3a,4,4a-tetrahydro-1*H*-furo[3',4':2,3]cyclobuta[1,2-c]quinolin-5(6*H*)-one (*rac*-3a-1 and *rac*-3a-2)



To a flame dried Schlenk tube are added **1a** (31 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), and CH_3CN (10 mL). The reaction is irradiated by a violet LED strips under argon atmosphere at room temperature. The reaction is completed after 4 h as monitored by TLC (eluent: *n*-hexane/ethyl acetate = 3:1). The solvent is removed and the residue is purified by flash chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 5:1) to afford *rac*-**3a-1** and *rac*-**3a-2** as a solid. *rac*-**3a-1** (7 mg, 22%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 7.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 4.77 (t, *J* = 8.3 Hz, 1H), 4.57 (d, *J* = 10.4 Hz, 1H), 4.16-4.07 (m, 1H), 4.03 (d, *J* = 9.4 Hz, 1H), 3.68 (d, *J* = 9.4 Hz, 1H), 3.59 (d, *J* = 8.6 Hz, 1H), 3.39 (s, 3H), 3.17 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 139.4, 128.9, 127.1, 123.5, 121.7, 115.4, 78.6, 71.8, 57.0, 50.4, 49.2, 44.3, 29.1. IR (neat) 1664, 1600, 1468, 1419, 1366 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{15}BrNO^+$ $[M+H]^+$: 308.0281, found: 308.0281. Supplementary crystallographic data for *rac*-**3a-1** have been deposited at the Cambridge Crystallographic Data Center. CCDC: 1986917.

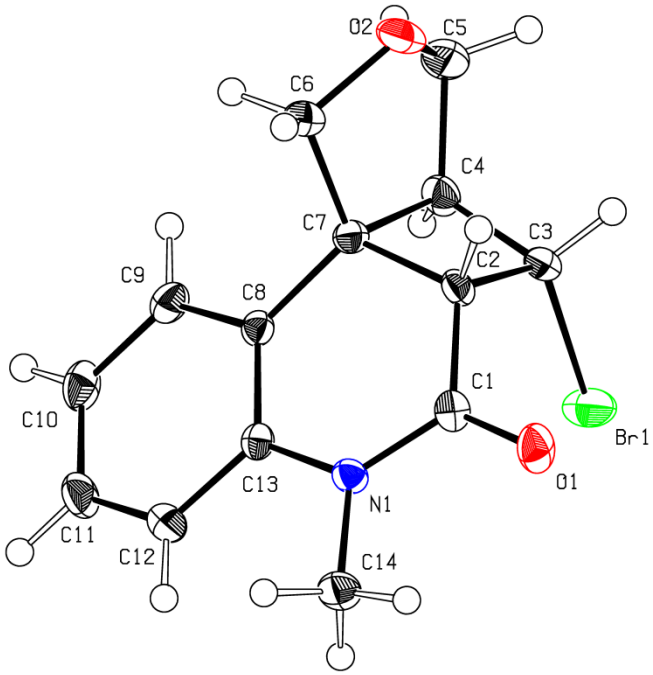


Ortep drawing with 50% ellipsoids for *rac*-**3a-1**

Compound	*rac*-**3a-1**
formula	$C_{14}H_{14}BrNO_2$
CCDC number	1986917
fw	308.17
color/habit	clear colourless fragment
Cryst. Dimens. [mm³]	0.05 x 0.05 x 0.05
Cryst. Syst.	monoclinic
space group	*P2₁/n*
a [Å]	9.1885(6)
b [Å]	14.2679(9)
c [Å]	10.1298(6)
α [deg]	90
β [deg]	107.630(2)
γ [deg]	90
V [Å³]	1265.65(14)
Z	4
T [K]	298(2)
D_{calcd} [g/cm^{-3}]	1.617
μ [mm^{-1}]	2.890
ϑ range [deg]	5.2 to 59.3
index range (h, k, l)	-11<=h<=11, -18<=k<=18, -12<=l<=12
Reflections collected	18648
no. of indep reflns/R_{int}	2725 / 0.042
no. of data/ restraints/params	2465 / 0 / 164
R1/wR2 (*I*>2σ(I))	0.0531/0.1576
R1/wR2 (*all data*)	0.0565/0.1621
GOF (on F^2)	1.068

Largest diff peak and hole [e Å^{-3}]	1.432/-1.100

rac-**3a-2** (11 mg, 34%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.32 (td, *J* = 8.4, 2.0 Hz, 1H), 7.23 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 4.44 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.15 (d, *J* = 10.4 Hz, 1H), 4.02 (d, *J* = 9.6 Hz, 1H), 3.92 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.76 (dd, *J* = 8.5, 1.7 Hz, 1H), 3.65 (d, *J* = 9.6 Hz, 1H), 3.39 (s, 3H), 3.20 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 165.1, 140.2, 128.9, 126.7, 123.7, 123.5, 115.6, 79.0, 74.1, 62.2, 49.4, 47.5, 46.8, 29.3. IR (neat) 1662, 1599, 1467, 1367 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{15}BrNO^{+}$ [M+H]$^{+}$: 308.0281, found: 308.0281. Supplementary crystallographic data for *rac*-**3a-2** have been deposited at the Cambridge Crystallographic Data Center. CCDC: 1990199.

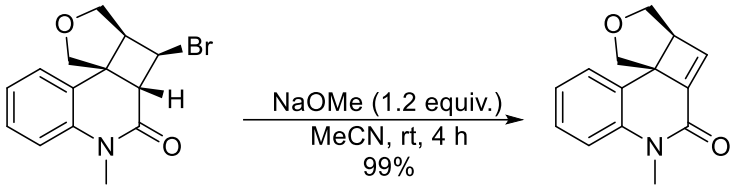


Ortep drawing with 50% ellipsoids for *rac*-**3a-2**

Compound	*rac*-**3a-2**
formula	$C_{14}H_{14}BrNO_2$
CCDC number	1990199
fw	308.17
color/habit	clear colourless fragment
Cryst. Dimens. [mm^3]	0.084 x 0.211 x 0.243
Cryst. Syst.	monoclinic
space group	*P* 1 2$_1$/n 1
a [Å]	7.5317(15)
b [Å]	10.0907(19)
c [Å]	16.552(3)
α [deg]	90
β [deg]	96.368(8)
γ [deg]	90
V [Å^3]	1250.2(4)
Z	4
T [K]	100(2)
D_{calcd} [g/cm^{-3}]	1.637
μ [mm^{-1}]	3.281
ϑ range [deg]	2.37 to 25.35

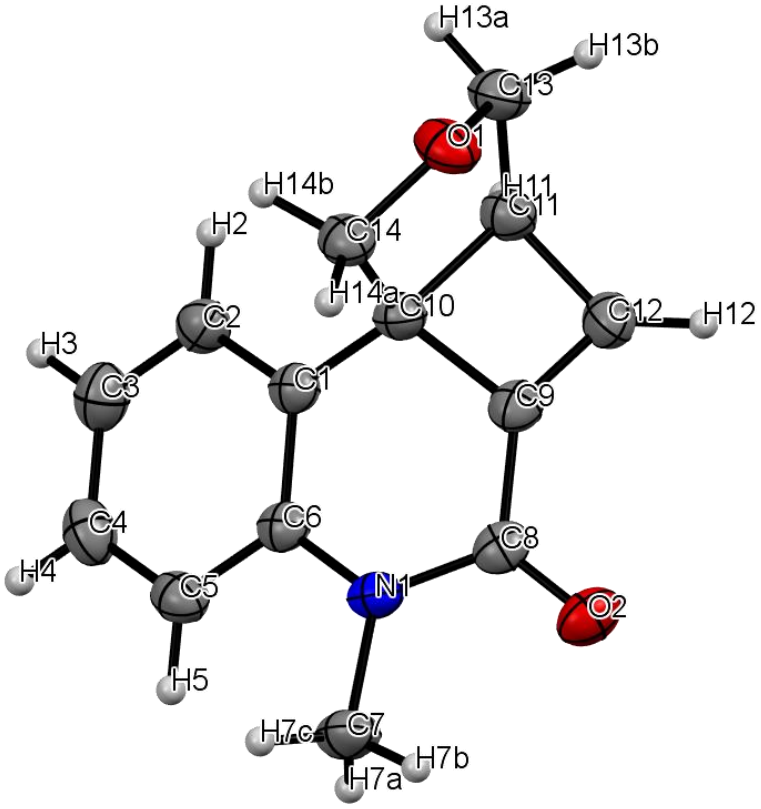
index range (h, k, l)	-9 ≤ h ≤ 9 -12 ≤ k ≤ 12 -19 ≤ l ≤ 19
Reflections collected	16733
no. of indep reflns/R_{int}	2283/0.0651
no. of data/ restraints/params	2283/0/164
R1/wR2 (*I*>2σ(I))	0.0296/0.0753
R1/wR2 (*all data*)	0.0314/0.0766
GOF (on F^2)	1.061
Largest diff peak and hole [e $Å^{-3}$]	0.470/-0.555

Synthesis of 6-methyl-3,3a-dihydro-1*H*-furo[3',4':2,3]cyclobuta[1,2-c]quinolin-5(6*H*)-one (*rac*-4a)



rac-**3a-1** *rac*-**4a**

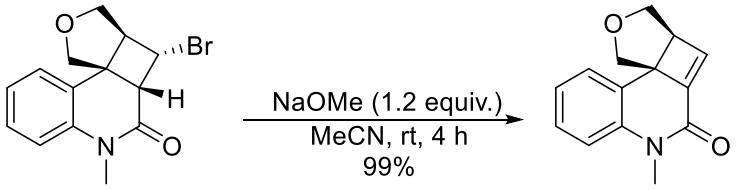
rac-**3a-1** (31 mg, 0.1 mmol), NaOMe (6.5 mg, 0.12 mmol), and anhydrous MeCN (10 mL) are added into a 25 mL of dry Schlenk flask. The reaction mixture is degassed with argon. The reaction mixture is stirred at room temperature under argon atmosphere. The reaction is completed after 4 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 3:1). The solvent is removed and the residue is purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford *rac*-**4a** as a solid (22 mg, 99%). Mp 83.1-84.1 °C (petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.27 (m, 2H), 7.10 (t, *J* = 6.8 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.66 (s, 1H), 4.00 (d, *J* = 9.8 Hz, 2H), 3.64-3.54 (m, 1H), 3.49-3.41 (m, 1H), 3.36 (s, 3H), 3.26 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.8, 142.3, 140.6, 140.2, 128.6, 127.0, 126.5, 123.4, 116.0, 71.8, 67.9, 55.8, 54.6, 29.3; IR (neat) 1676, 1627, 1598, 1456 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{14}NO_2^+$ [M+H]$^+$: 228.1019, found: 228.1018. Supplementary crystallographic data for *rac*-**4a** have been deposited at the Cambridge Crystallographic Data Center. CCDC: 1986918.



Ortep drawing with 50% ellipsoids for *rac*-**4a**

Compound	*rac*-**4a**
formula	$C_{14}H_{13}NO_2$
CCDC number	1986918
fw	227.27
color/habit	clear colourless fragment
Cryst. Dimens. [mm^3]	0.09 x 0.08 x 0.07
Cryst. Syst.	monoclinic
space group	$P\ 2_1/c$
a [Å]	9.0750(2)
b [Å]	9.0233(2)
c [Å]	13.9880(3)
α [deg]	90
β [deg]	107.620(1)
γ [deg]	90
V [$Å^3$]	1091.69(4)
Z	4
T [K]	180(2)
D_{calcd} [g/cm^{-3}]	1.383
μ [mm^{-1}]	0.750
ϑ range [deg]	3.560 to 26.37
index range (h, k, l)	-10<=h<=10, -10<=k<=10, -16<=l<=16
Reflections collected	1936
no. of indep reflns/R_{int}	1936/ 0.039
no. of data/ restraints/params	13949 / 0 / 155
R1/wR2 (*I*>2σ(I))	0.0387/0.0990
R1/wR2 (*all data*)	0.0344/0.0924
GOF (on F^2)	1.072
Largest diff peak and hole [e $Å^{-3}$]	0.36/-0.16

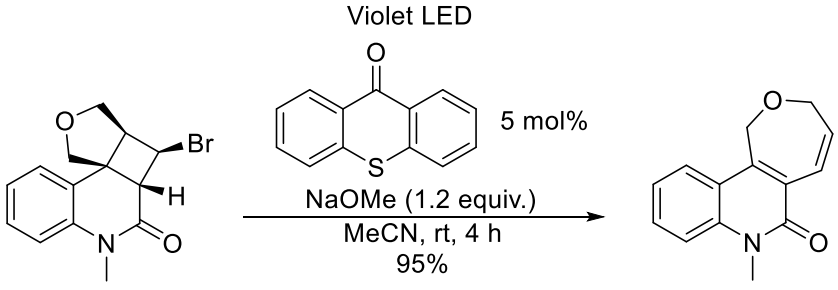
Procedure for the transformation of *rac*-3a-2 into *rac*-4a



rac-**3a-2** *rac*-**4a**

rac-**3a-2** (31 mg, 0.1 mmol), NaOMe (6.5 mg, 0.12 mmol), and anhydrous MeCN (10 mL) are added into a 25 mL of dry Schlenk flask. The reaction mixture is degassed with argon. The reaction mixture is stirred at room temperature under argon atmosphere. The reaction is completed after 4 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 3:1). The solvent is removed and the residue is purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford *rac*-**4a** as a solid (22 mg, 99%).

Procedure for the transformation of *rac*-3a-1 into 2a

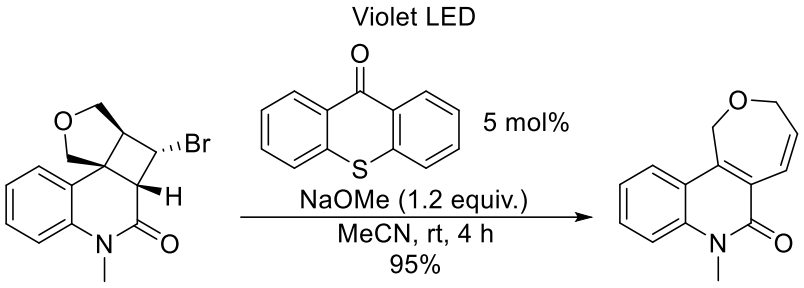


rac-**3a-1** **2a**

rac-**3a-1** (16 mg, 0.05 mmol), NaOMe (3.3 mg, 0.06 mmol), thioxanthone (0.6 mg, 0.0028 mmol), and anhydrous MeCN (10 mL) are added into a 25 mL of dry Schlenk flask. The reaction mixture is degassed with argon. The reaction mixture is irradiated at room temperature under argon atmosphere. The reaction is completed after 4 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 3:1). The

solvent is removed and the residue is purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford **2a** as an oil (10.5 mg, 95%).

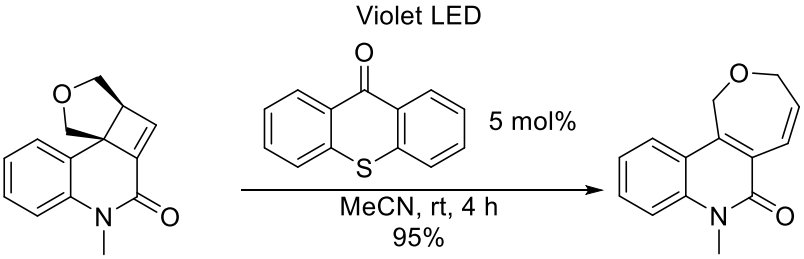
Procedure for the transformation of *rac*-3a-2 into 2a



rac-**3a-2** **2a**

rac-**3a-2** (31 mg, 0.1 mmol), NaOMe (6.5 mg, 0.12 mmol), thioxanthone (1.1 mg, 0.005 mmol), and anhydrous MeCN (10 mL) are added into a 25 mL of dry Schlenk flask. The reaction mixture is degassed with argon. The reaction mixture is irradiated at room temperature under argon atmosphere. The reaction is completed after 4 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 3:1). The solvent is removed and the residue is purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford **2a** as an oil (22 mg, 95%).

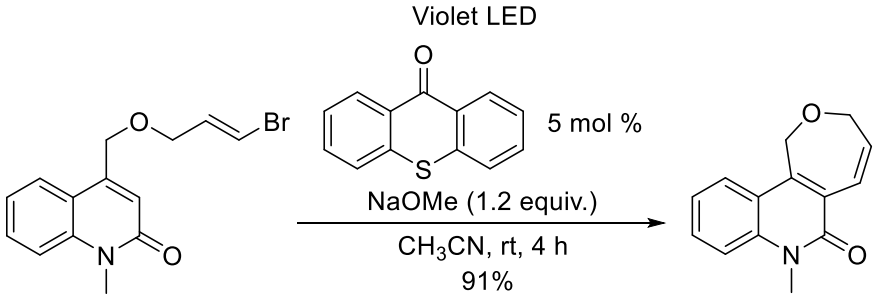
Procedure for the transformation of *rac*-4a into 2a



rac-**4a** **2a**

rac-**4a** (23 mg, 0.1 mmol), thioxanthone (1.1 mg, 0.005 mmol), and anhydrous MeCN (10 mL) are added into a 25 mL of dry Schlenk flask. The reaction mixture is degassed with argon. The reaction mixture is irradiated at room temperature under argon atmosphere. The reaction is completed after 4 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 3:1). The solvent is removed and the residue is purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford **2a** as an oil (21 mg, 95%).

Procedure for gram scale experiment of 1a to 2a



1a **2a**

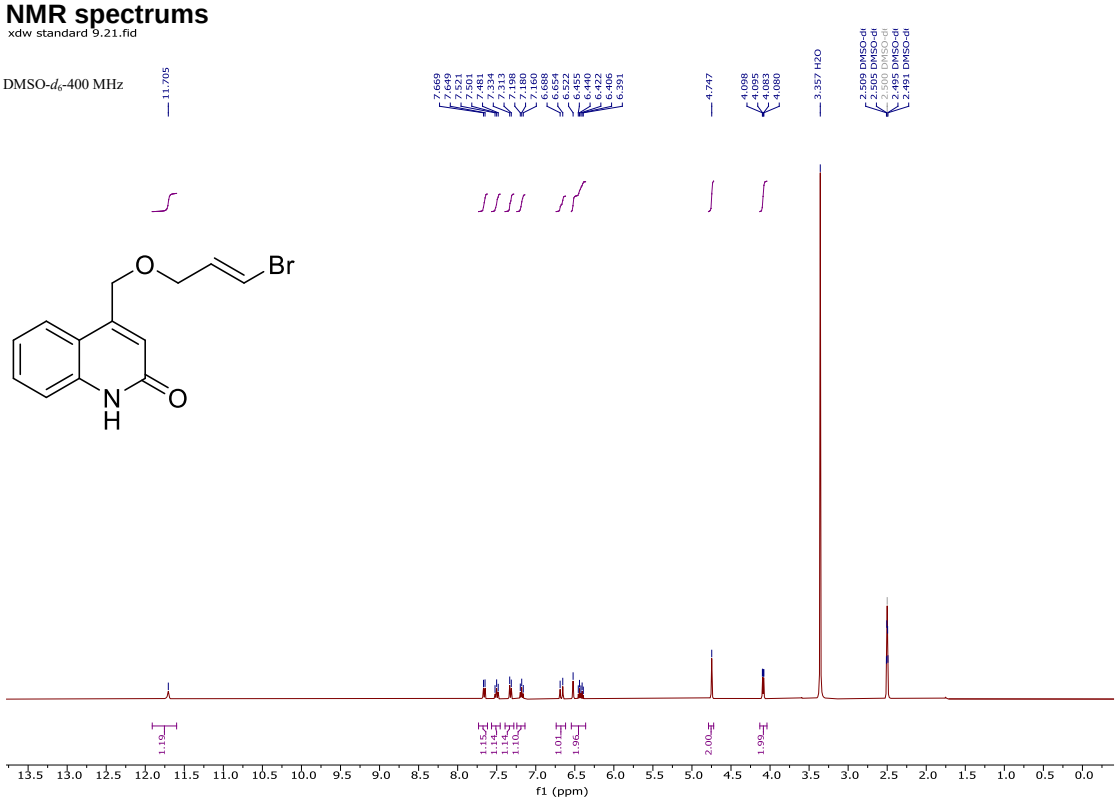
1.002 g, 3.25 mmol 0.672 g

To a flame dried three-necked bottle (500 mL) are added **1a** (1002 mg, 3.25 mmol), thioxanthone (34.5 mg, 0.1625 mmol), NaOMe (210.9 mg, 3.9 mmol), and anhydrous CH_3CN (325 mL). The reaction mixture is degassed with argon and irradiated by a violet LED strips under argon atmosphere at room temperature. The reaction is completed after 4 h as monitored by TLC (eluent: *n*-hexane/ethyl acetate = 3:1). The solvent is removed and the residue is purified by flash chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 3:1) to afford **2a** as an oil (672 mg, 91%).

NMR spectrums

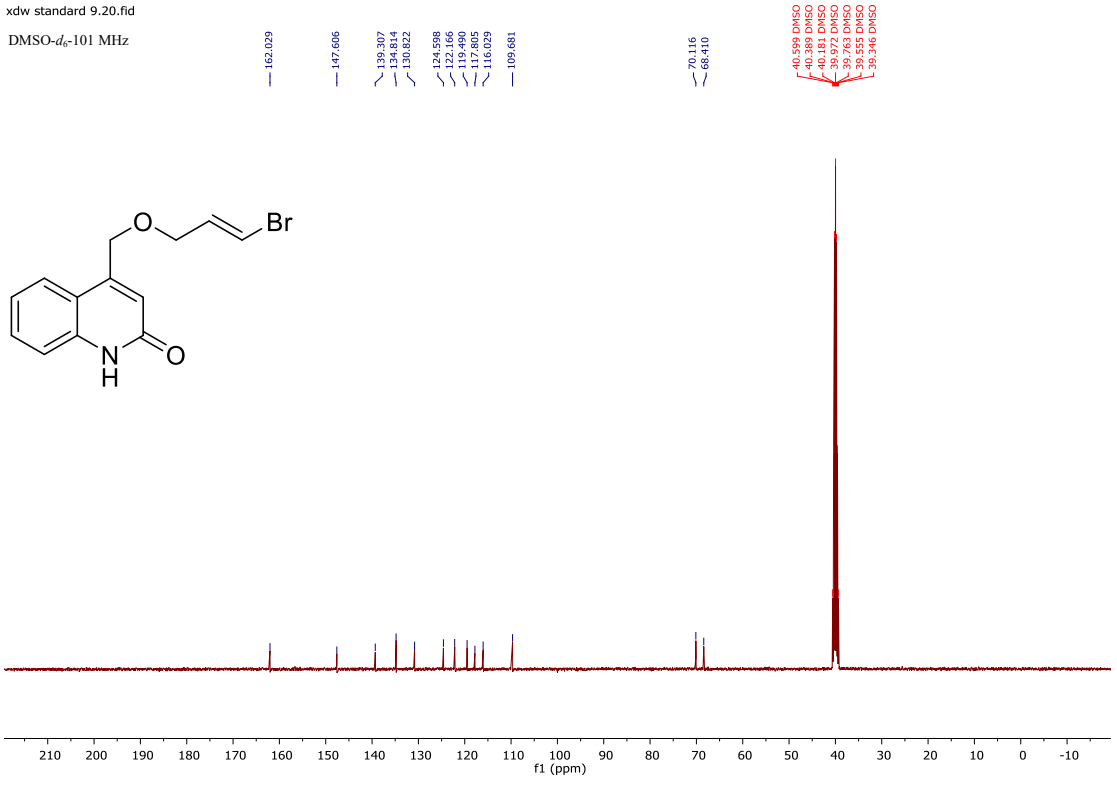
xdw standard 9.21.fid

DMSO-d_6-400 MHz



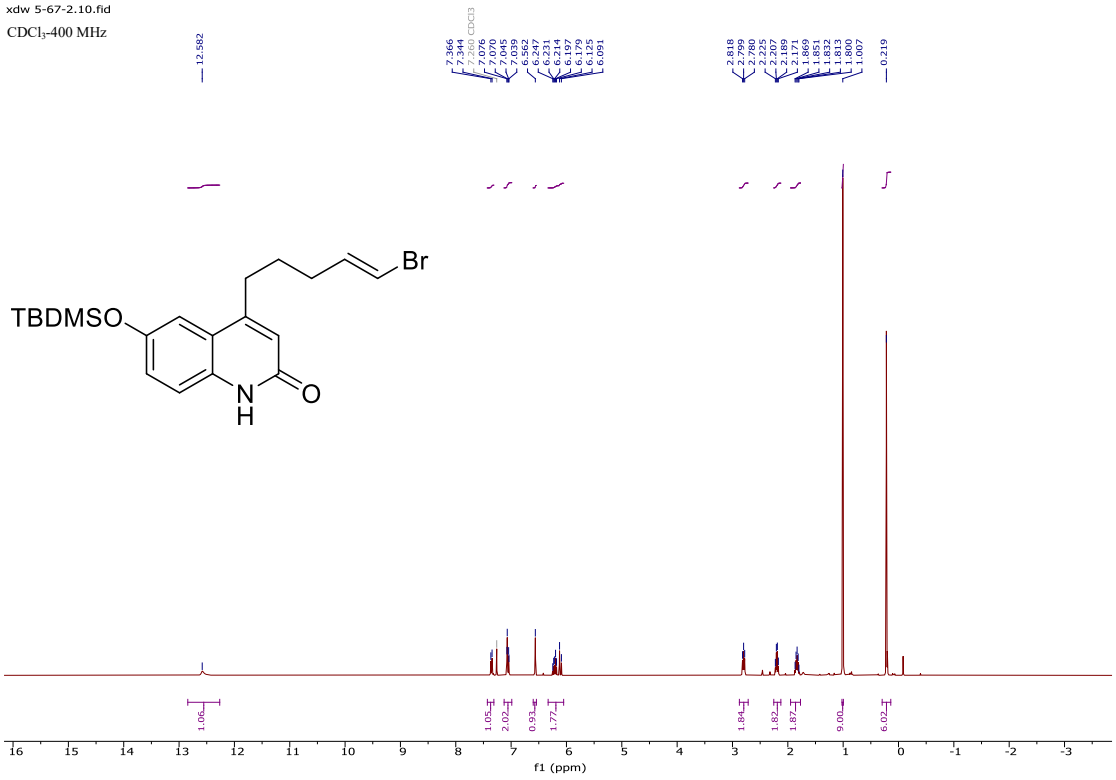
xdw standard 9.20.fid

DMSO-d_6-101 MHz



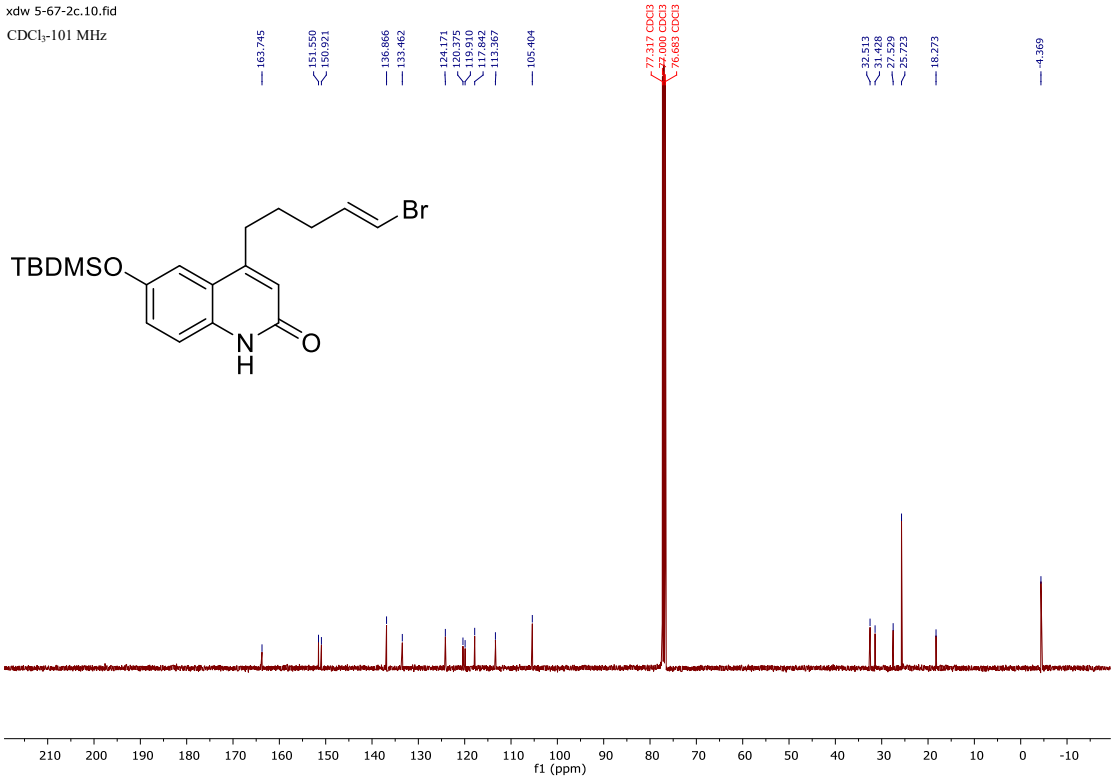
xdw 5-67-2.10.fid

$CDCl_3$-400 MHz



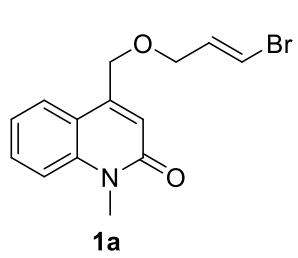
xdw 5-67-2c.10.fid

$CDCl_3$-101 MHz

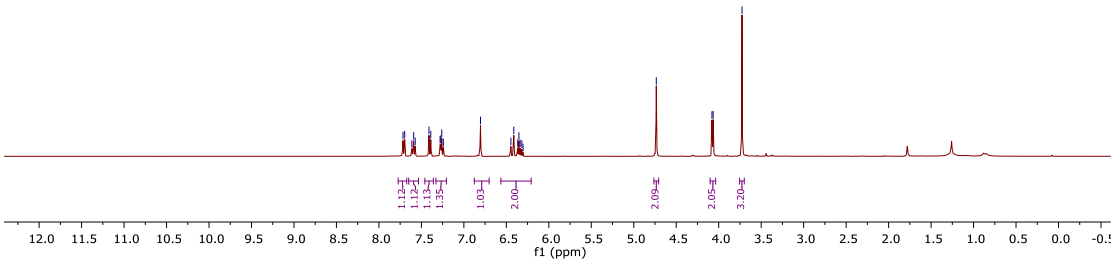


xdw 5-9-2.10.fid

$CDCl_3$-400 MHz

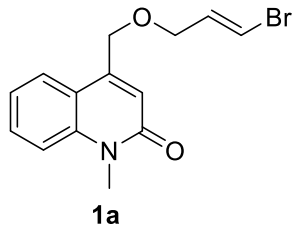


1a

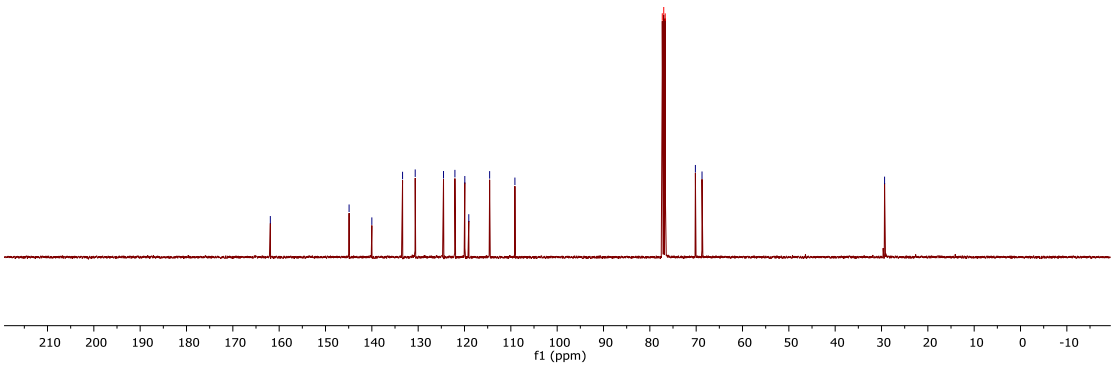


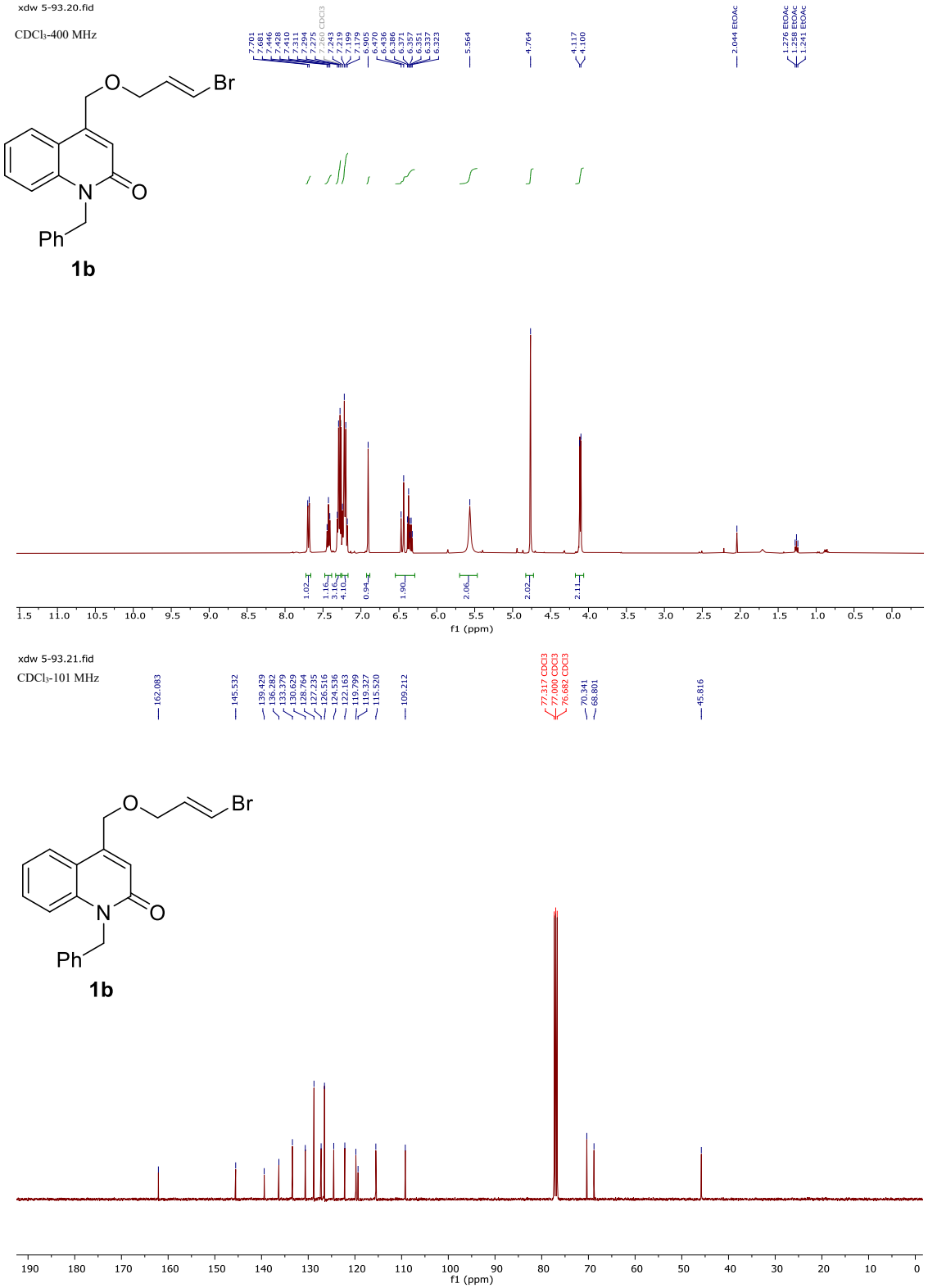
xdw 5-9-2.21.fid

$CDCl_3$-101 MHz



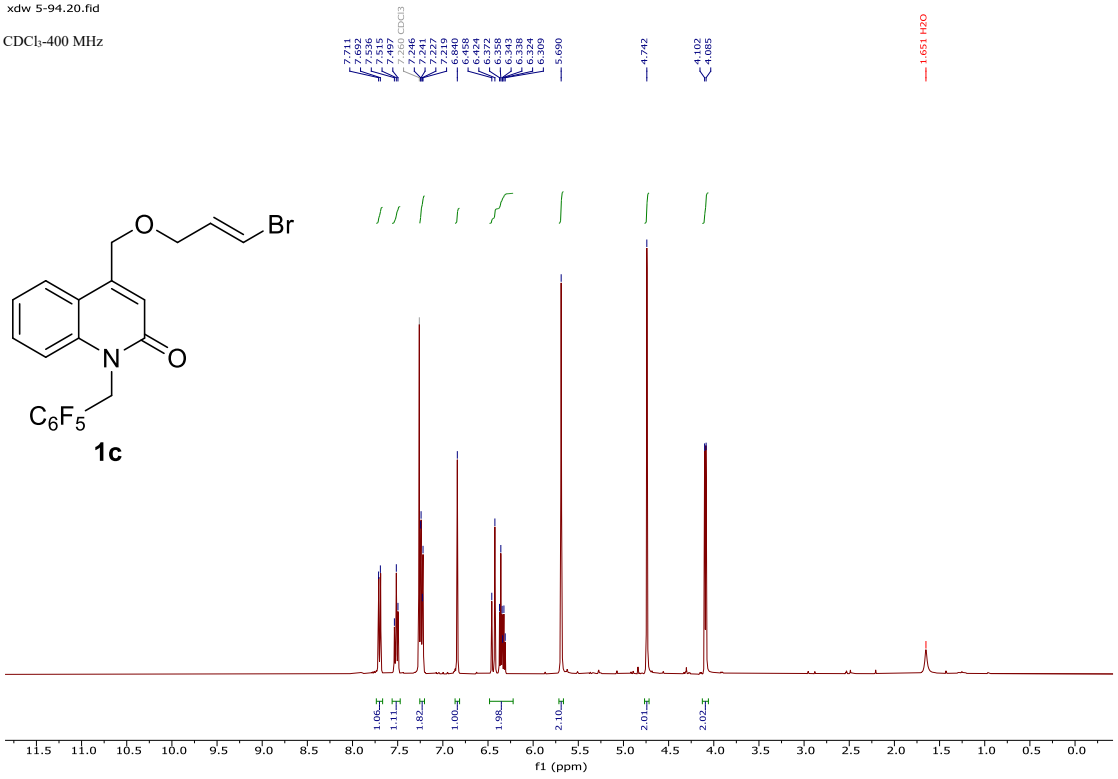
1a




xdw 5-93.20.fid
CDCl3-400 MHz
Br
O
N
O
Ph
1b
f1 (ppm)
xdw 5-93.21.fid
CDCl3-101 MHz
Br
O
N
O
Ph
1b
f1 (ppm)

xdw 5-94.20.fid

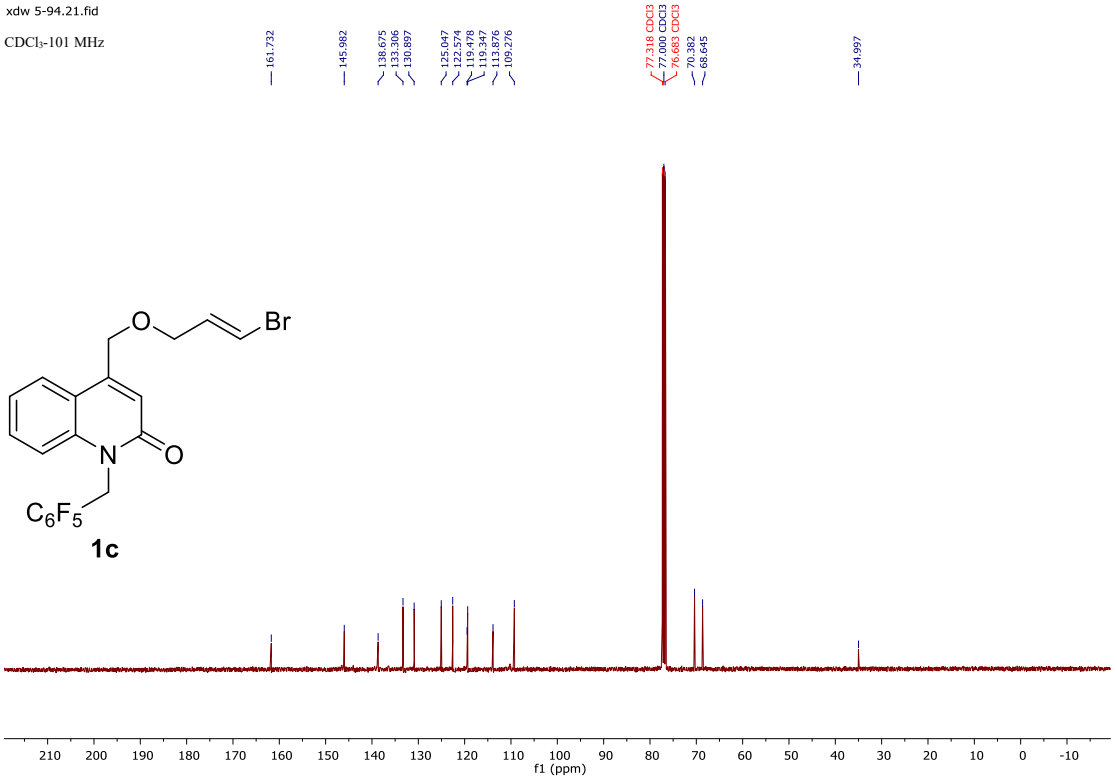
$CDCl_3$-400 MHz



1c

xdw 5-94.21.fid

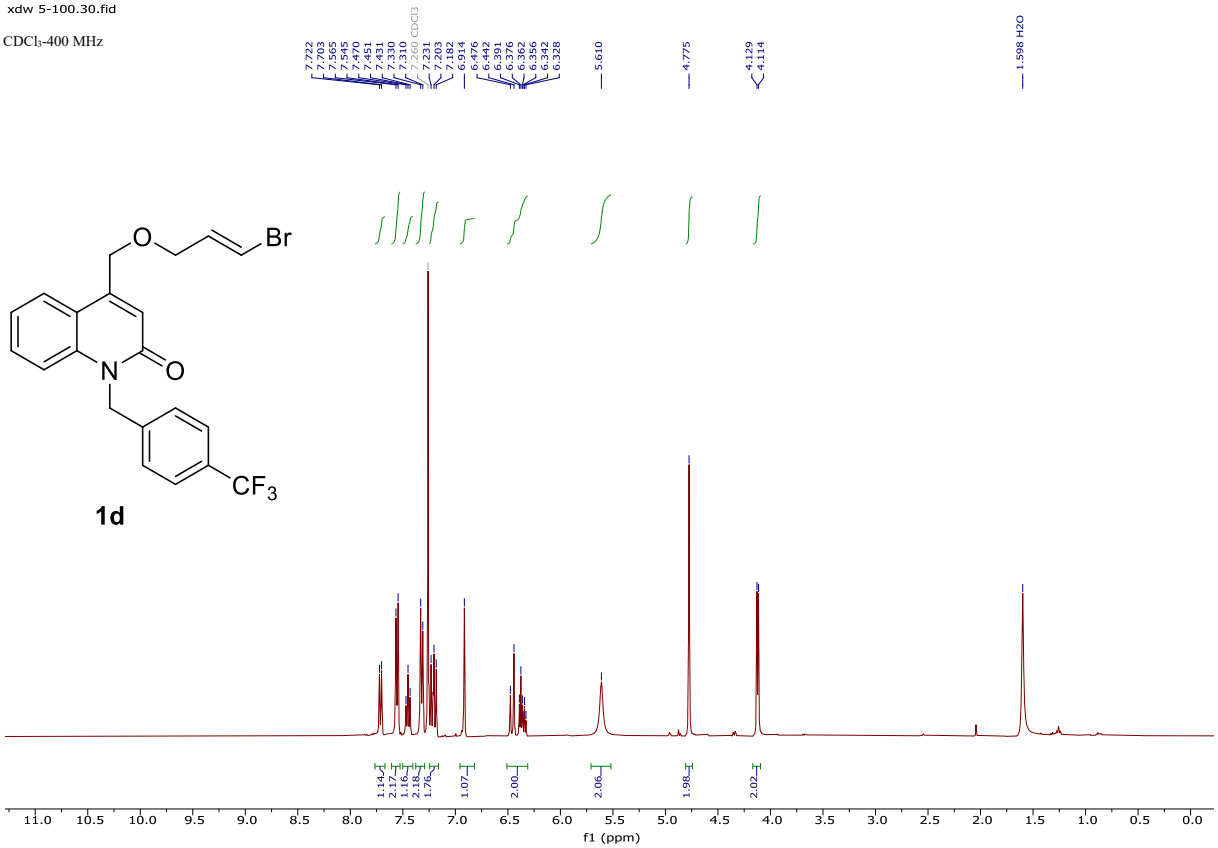
$CDCl_3$-101 MHz



1c

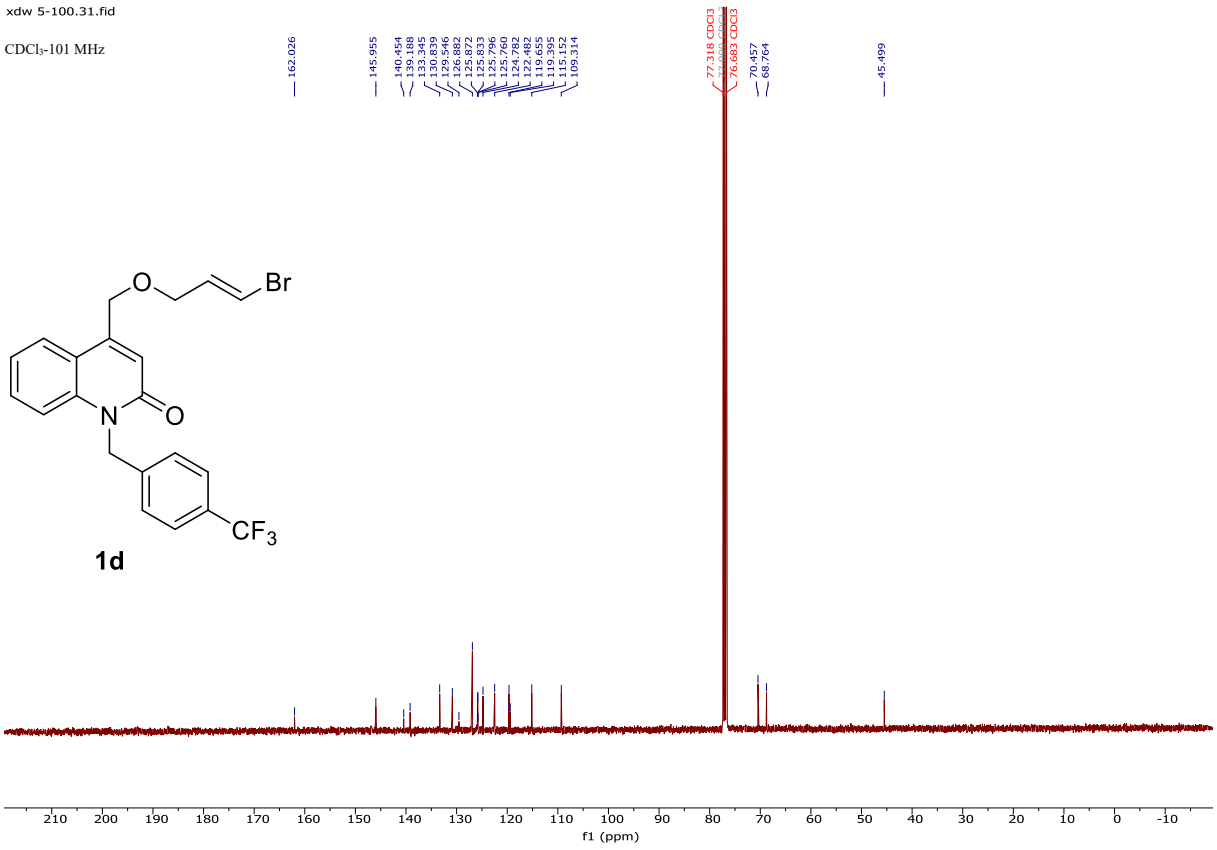
xdw 5-100.30.fid

$CDCl_3$-400 MHz



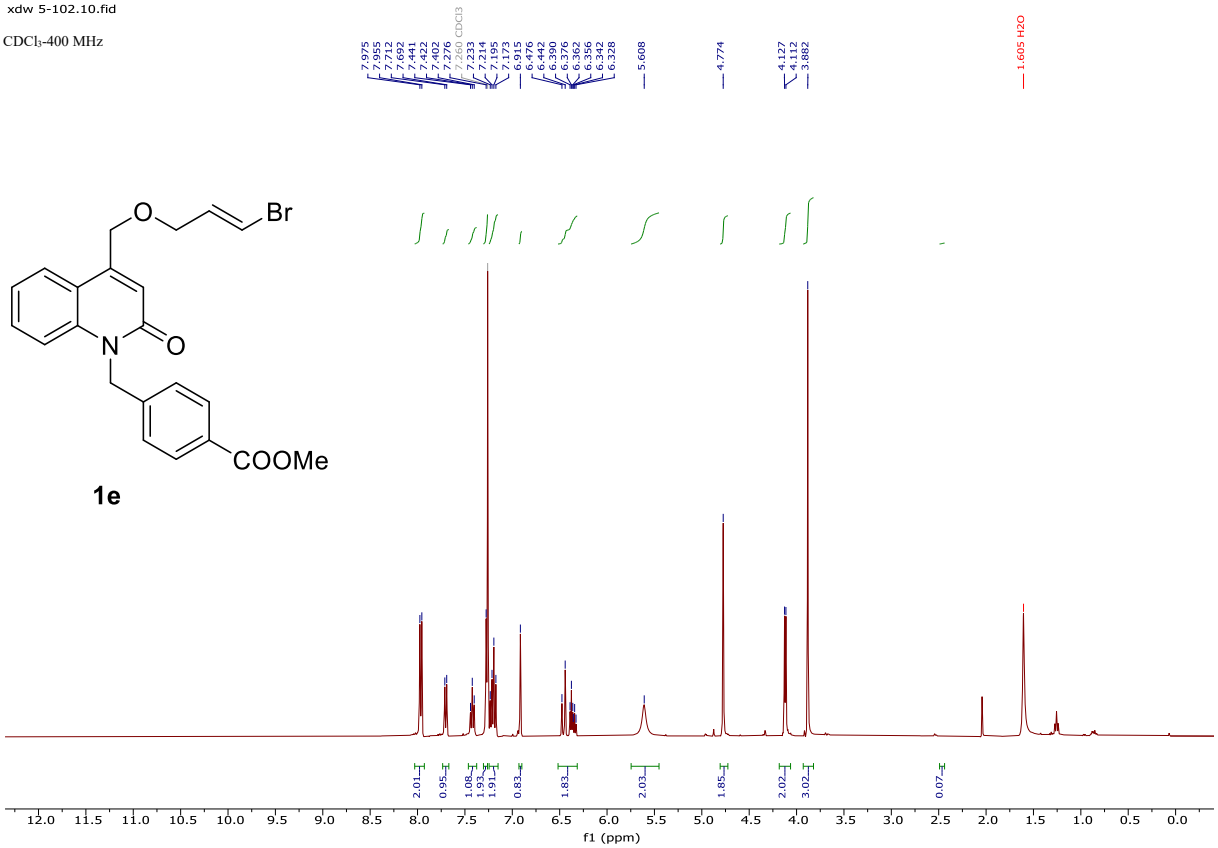
xdw 5-100.31.fid

$CDCl_3$-101 MHz



xdw 5-102.10.fid

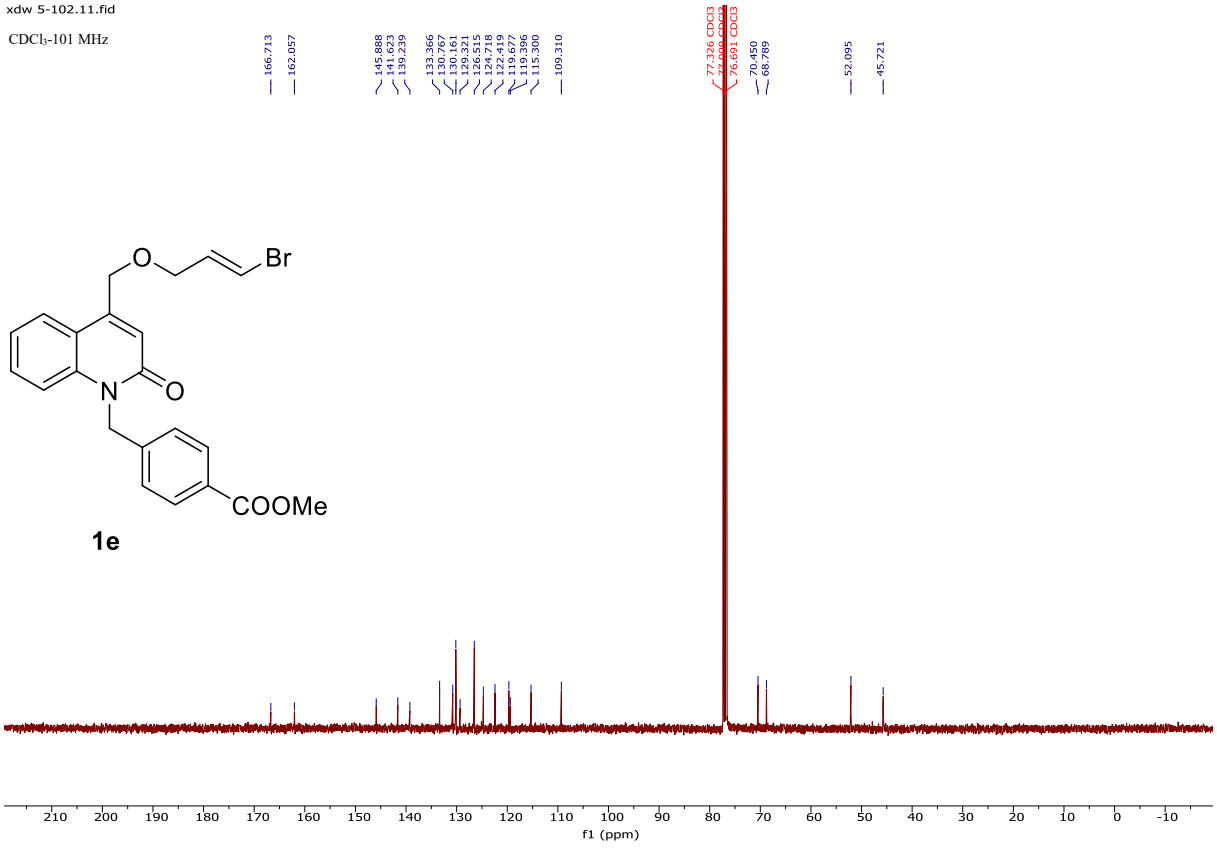
$CDCl_3$-400 MHz



1e

xdw 5-102.11.fid

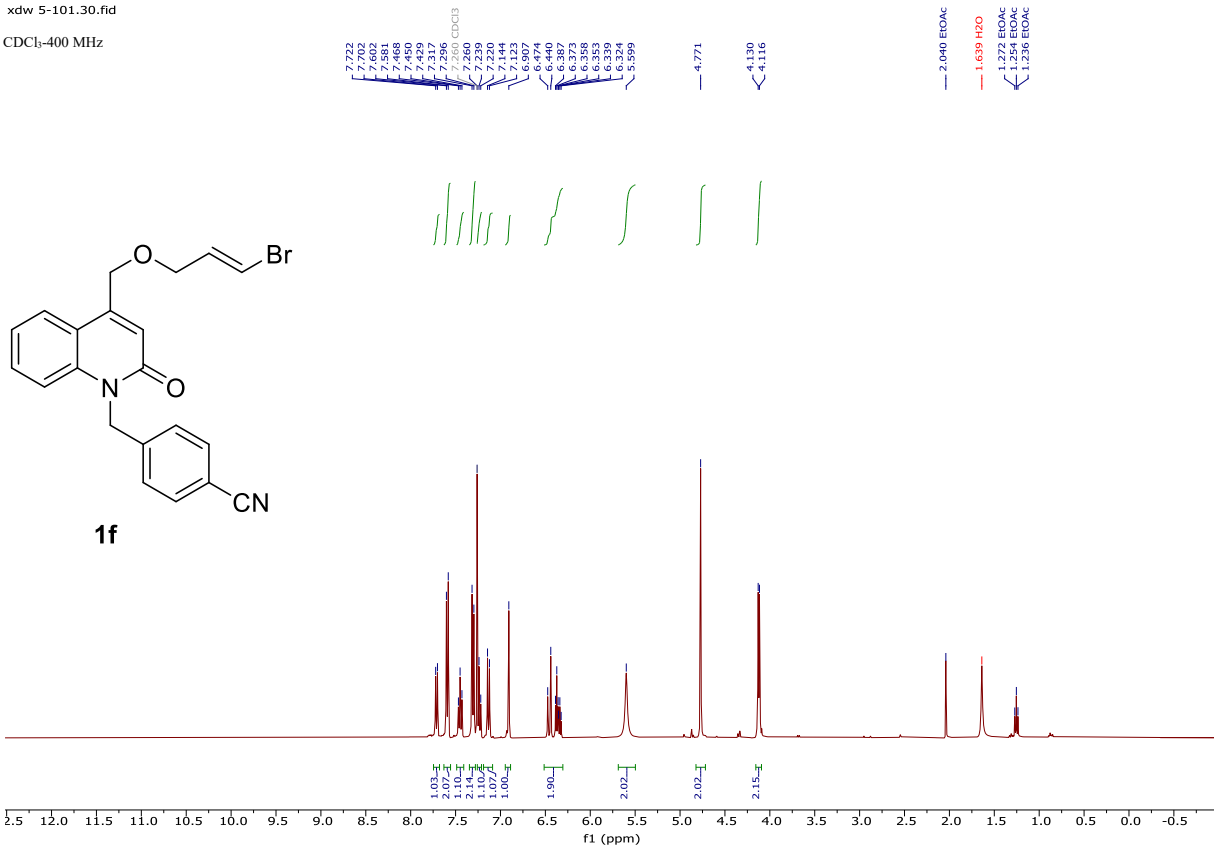
$CDCl_3$-101 MHz



1e

xdw 5-101.30.fid

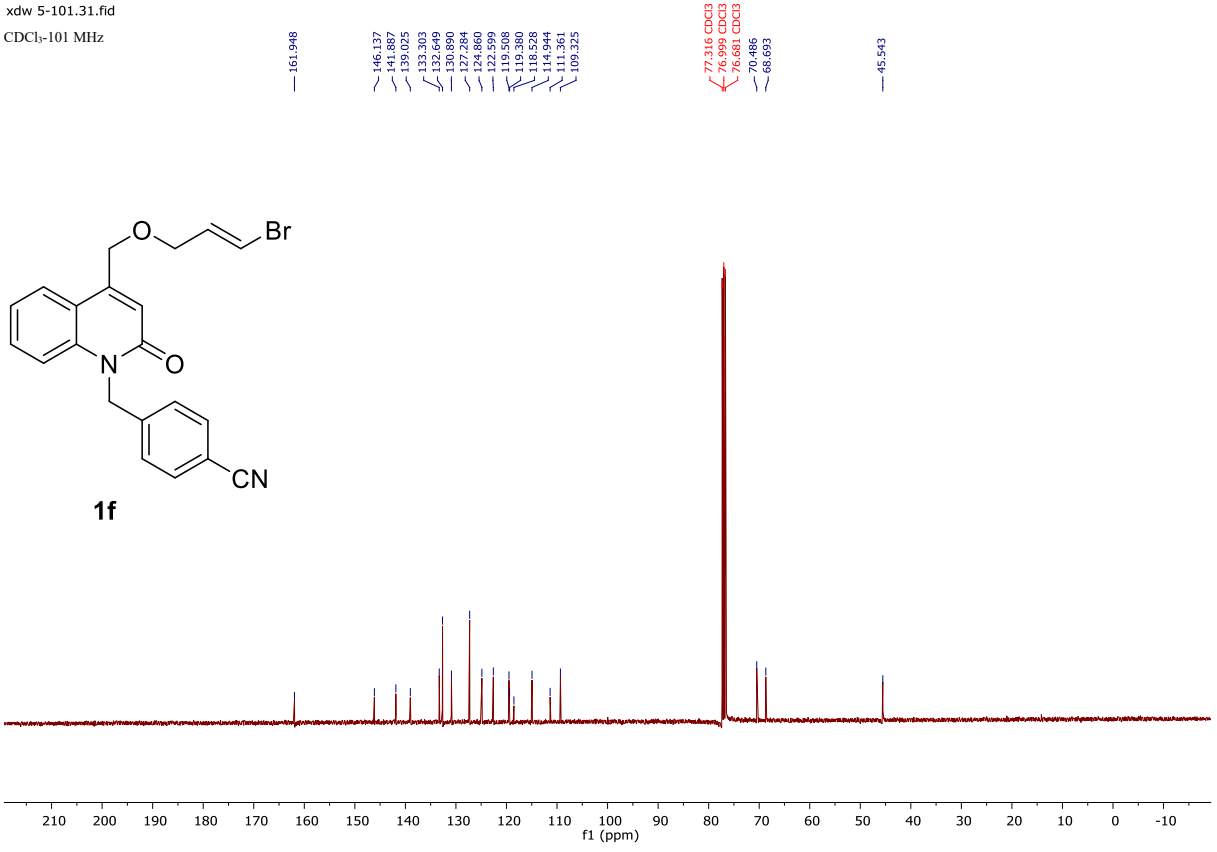
$CDCl_3$-400 MHz



1f

xdw 5-101.31.fid

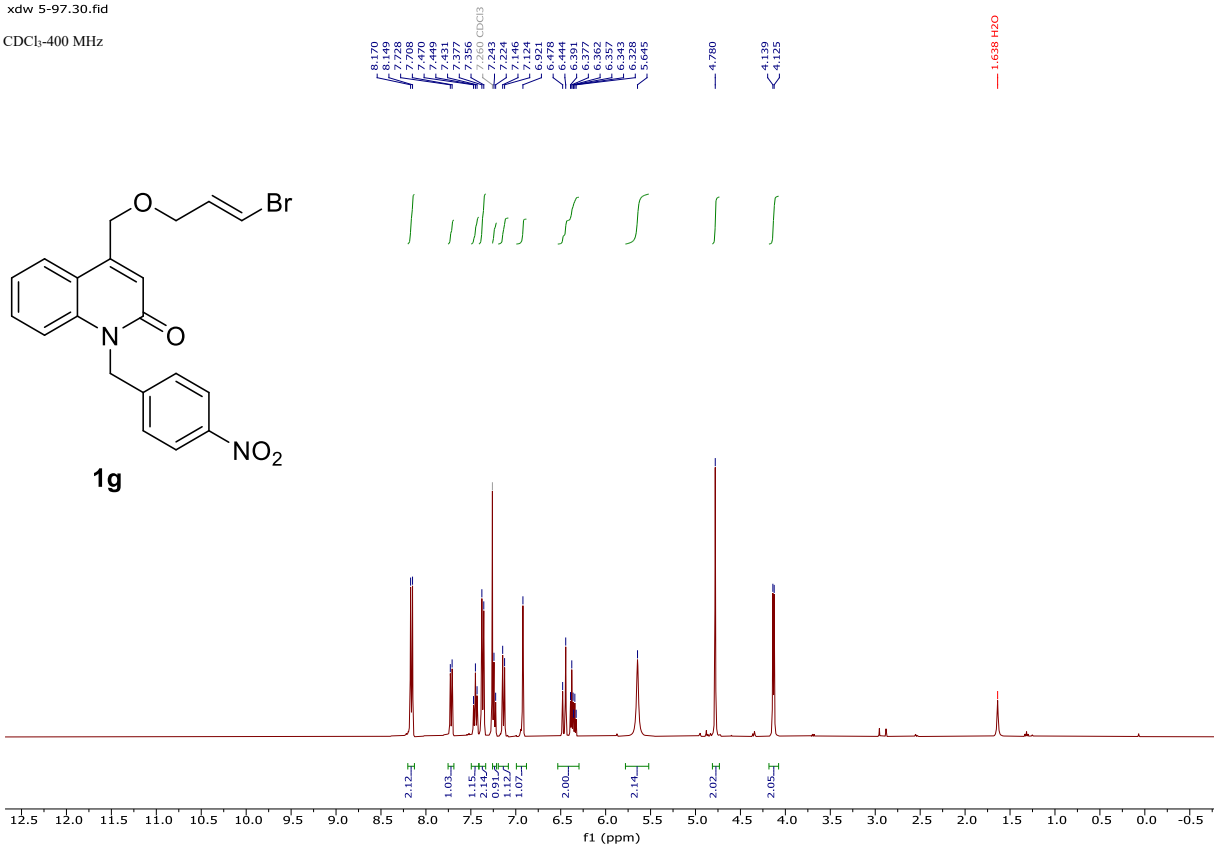
$CDCl_3$-101 MHz



1f

xdw 5-97.30.fid

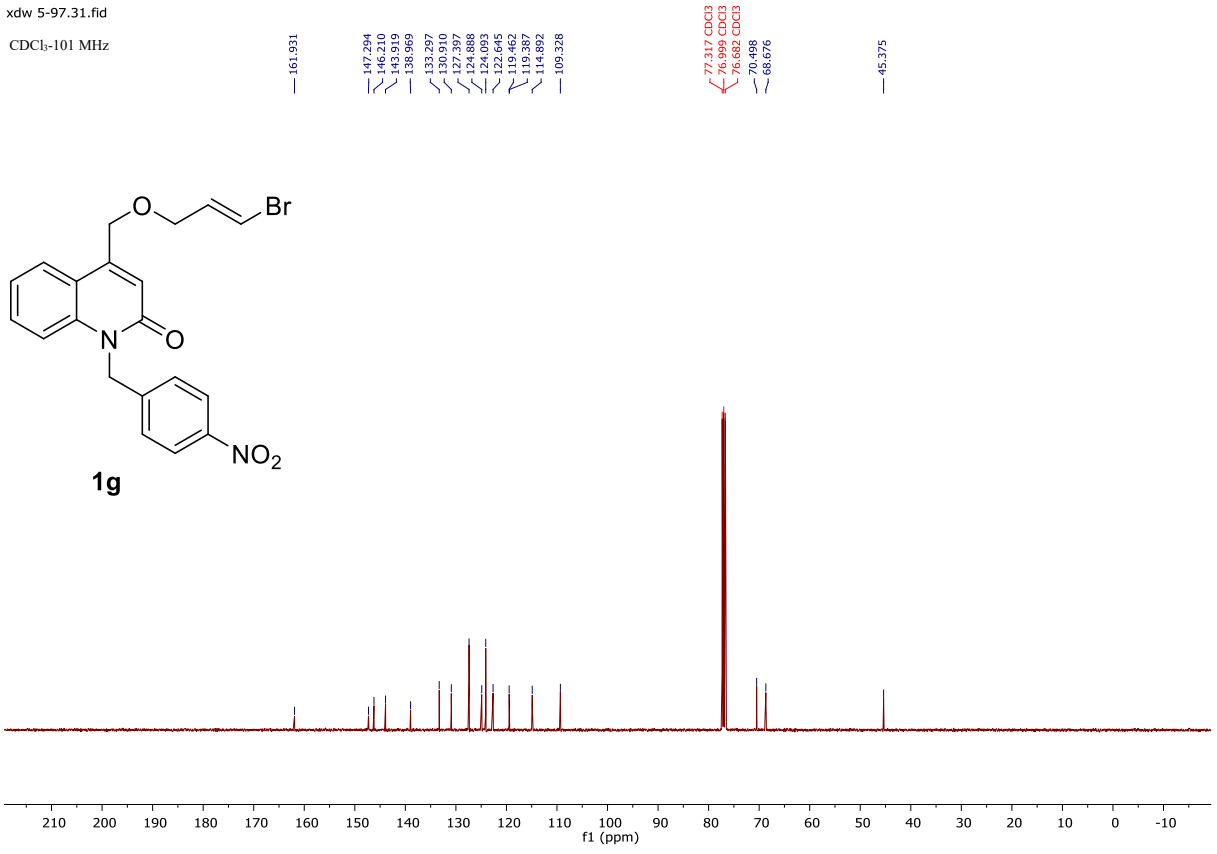
$CDCl_3$-400 MHz



1g

xdw 5-97.31.fid

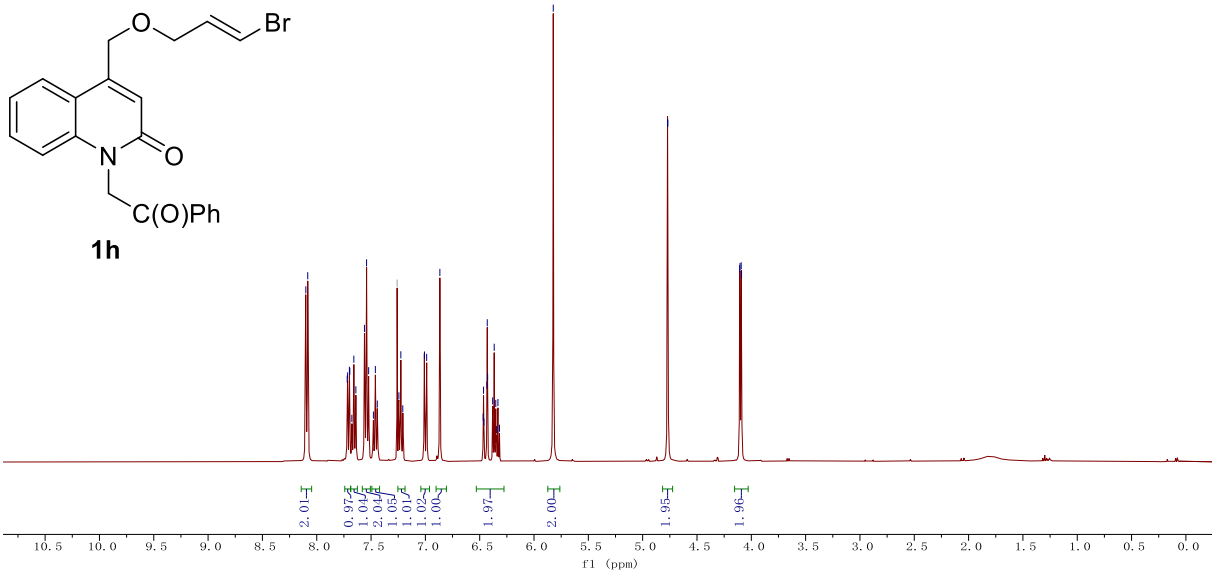
$CDCl_3$-101 MHz



1g

lh-dw-5-89.10.fid

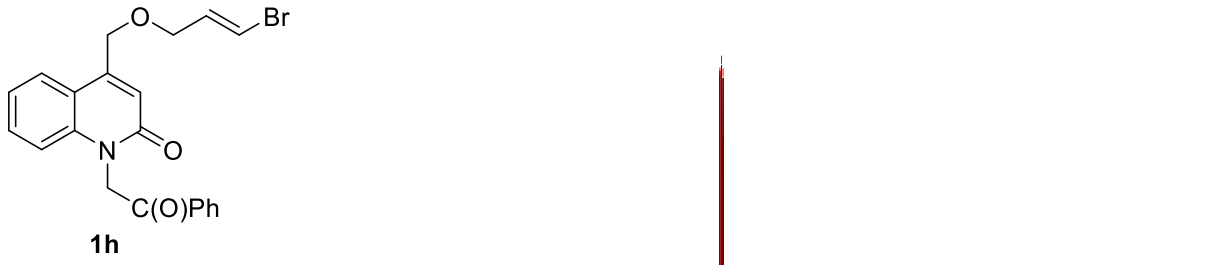
$CDCl_3$-400 MHz



1h

xdw 5-98.21.fid

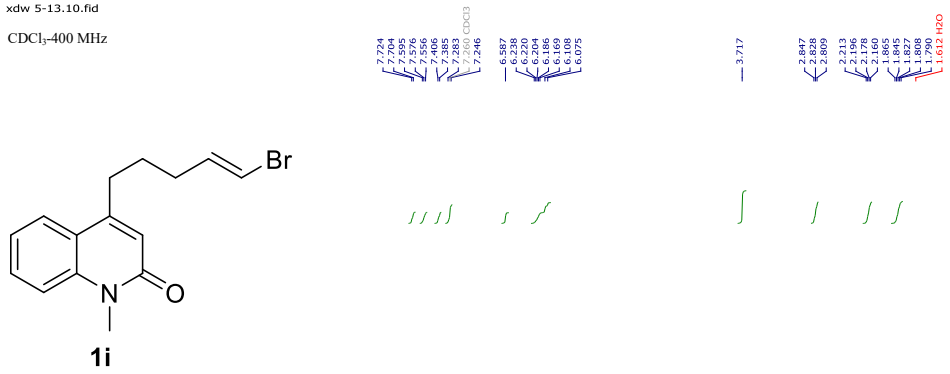
$CDCl_3$-101 MHz



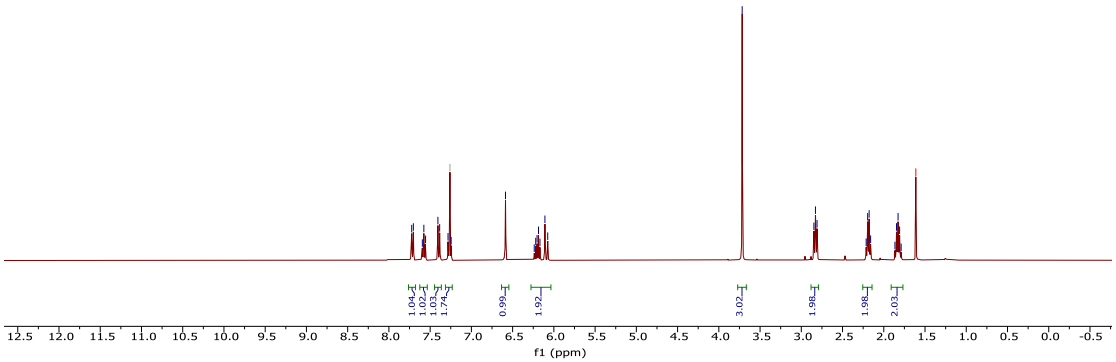
1h

xdw 5-13.10.fid

$CDCl_3$-400 MHz

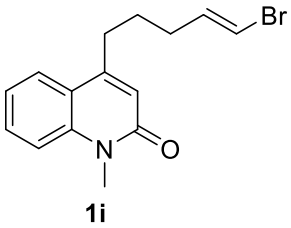


1i

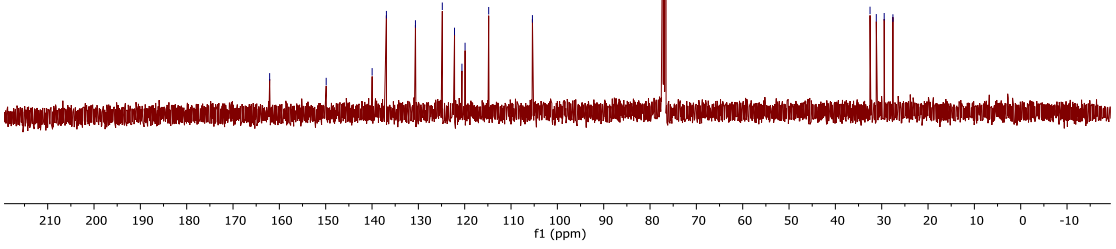


xdw 5-13.21.fid

$CDCl_3$-101 MHz

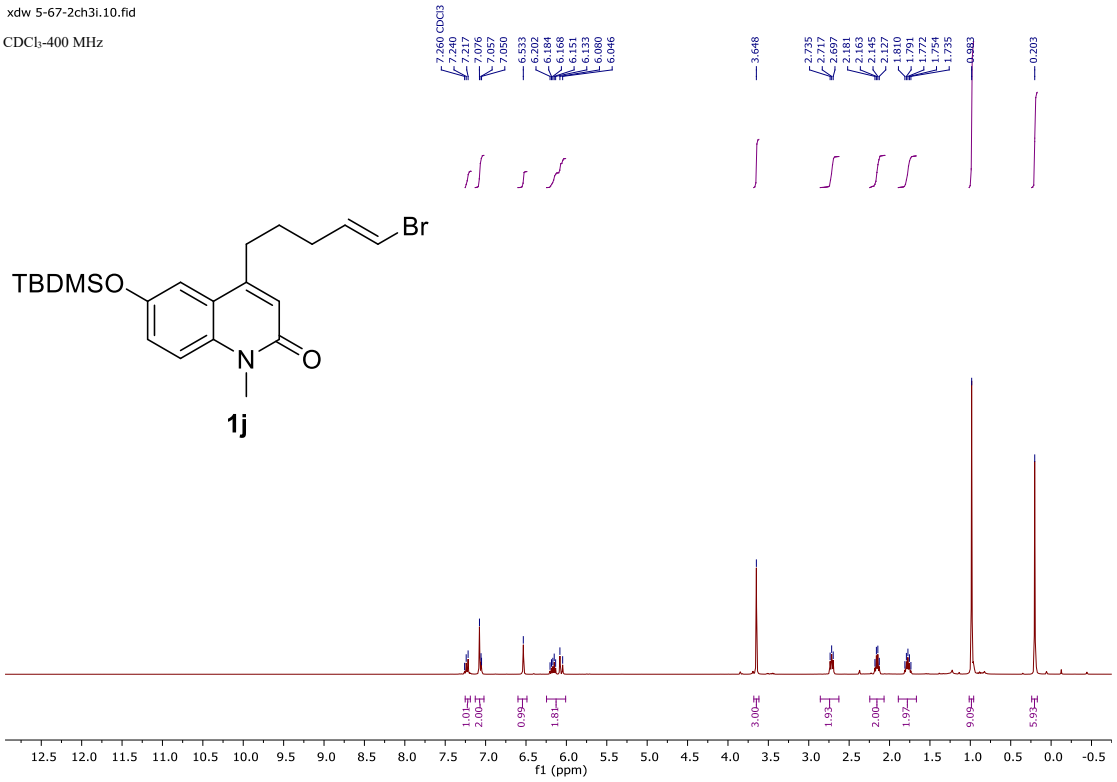


1i



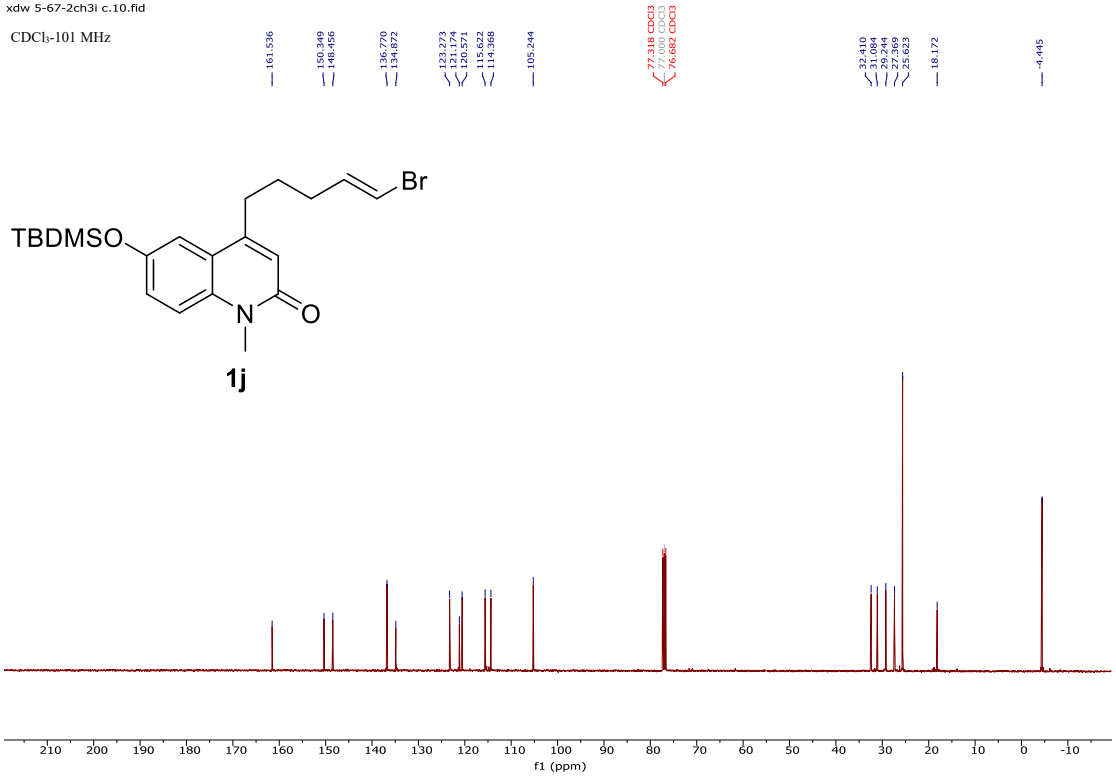
xdw 5-67-2ch3i.10.fid

$CDCl_3$-400 MHz



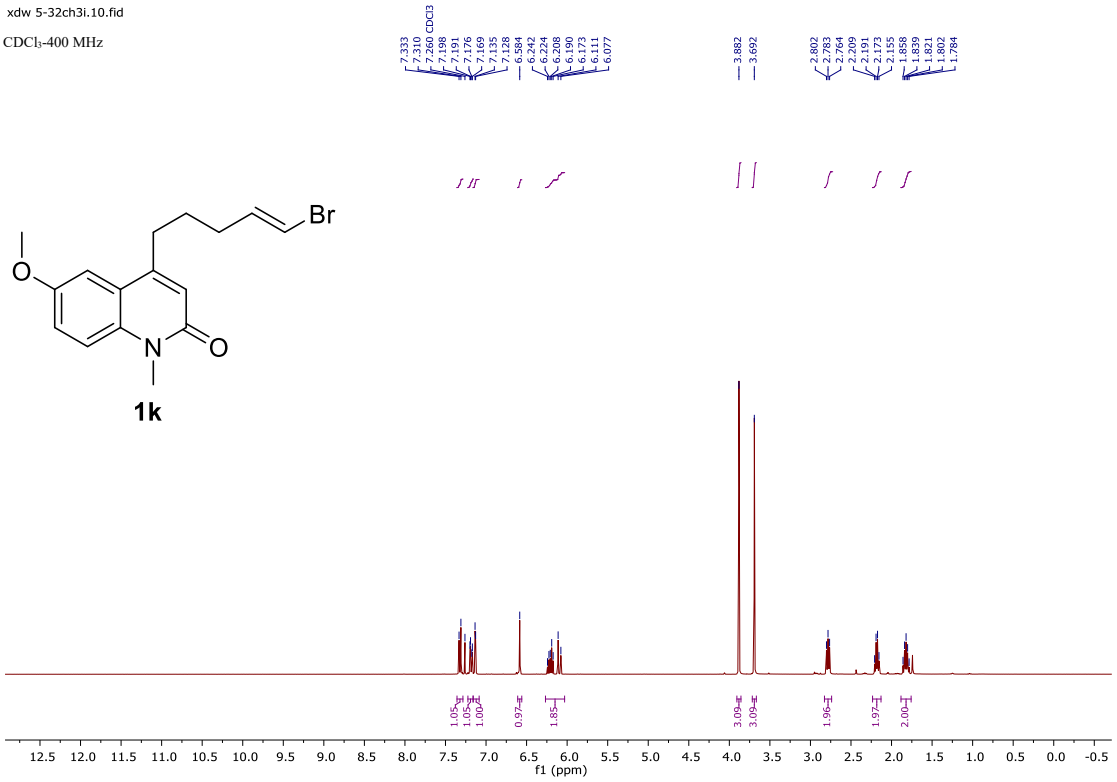
xdw 5-67-2ch3i c.10.fid

$CDCl_3$-101 MHz



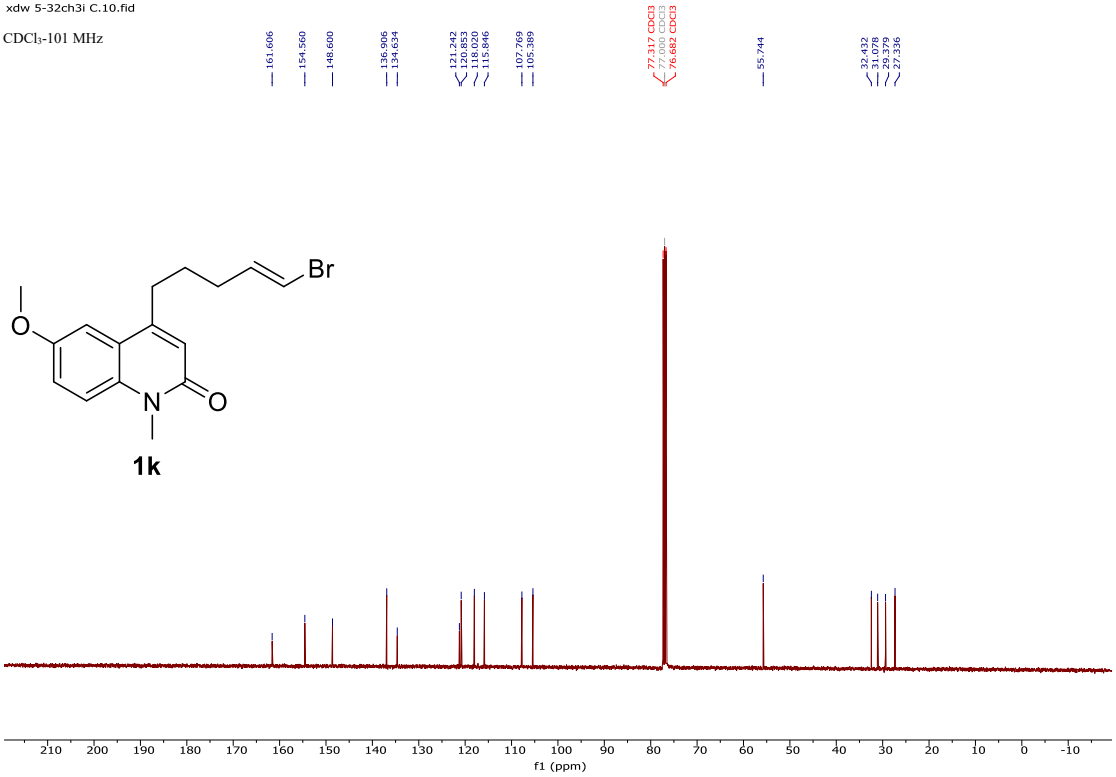
xdw 5-32ch3i.10.fid

$CDCl_3$-400 MHz



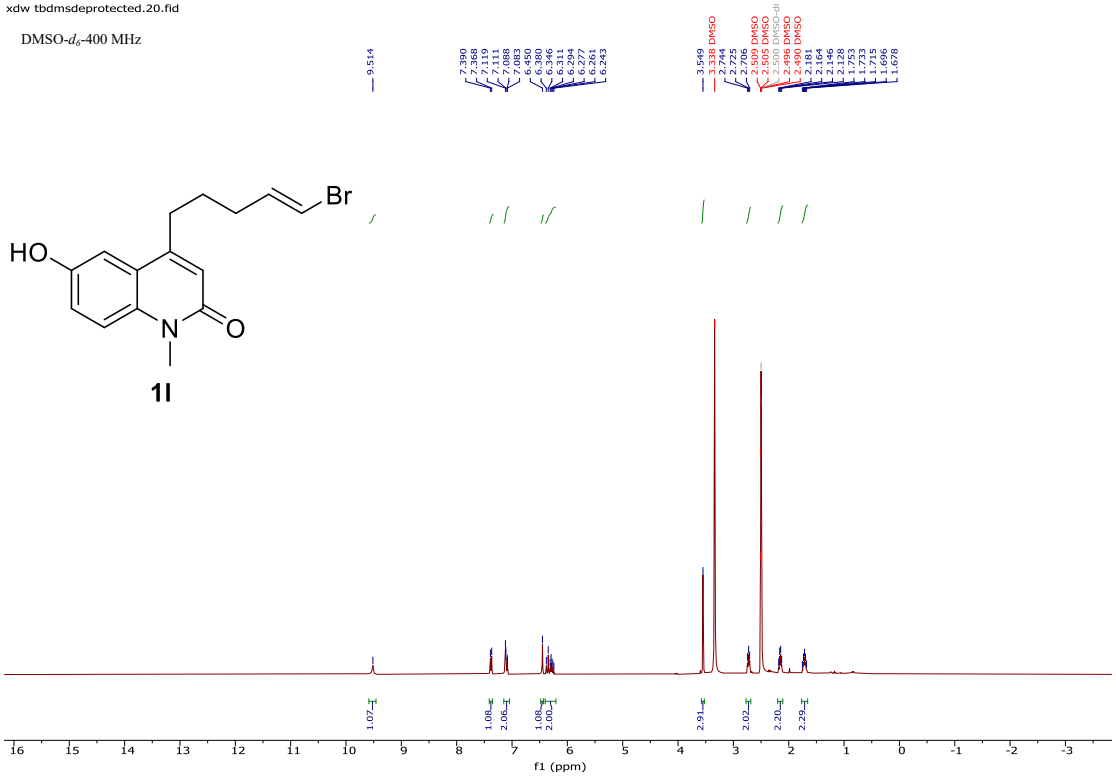
xdw 5-32ch3i C.10.fid

$CDCl_3$-101 MHz



xdw tbdmsdeprotected.20.fid

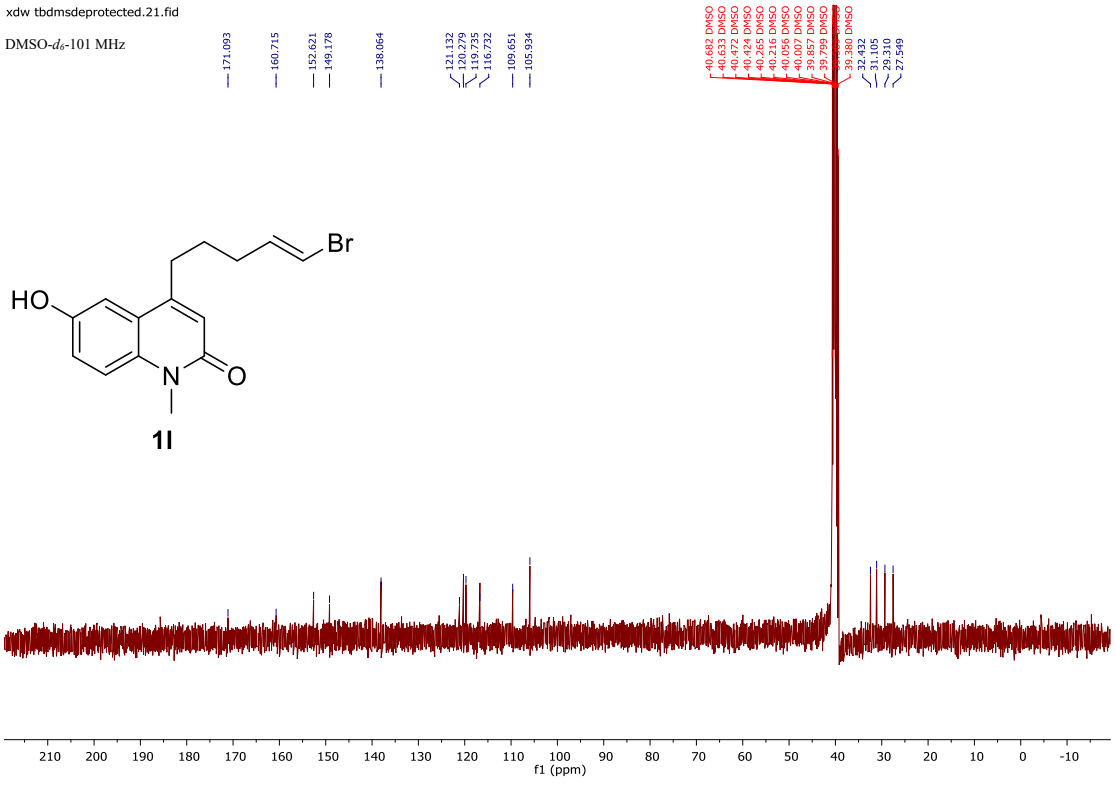
DMSO-d_6-400 MHz



1l

xdw tbdmsdeprotected.21.fid

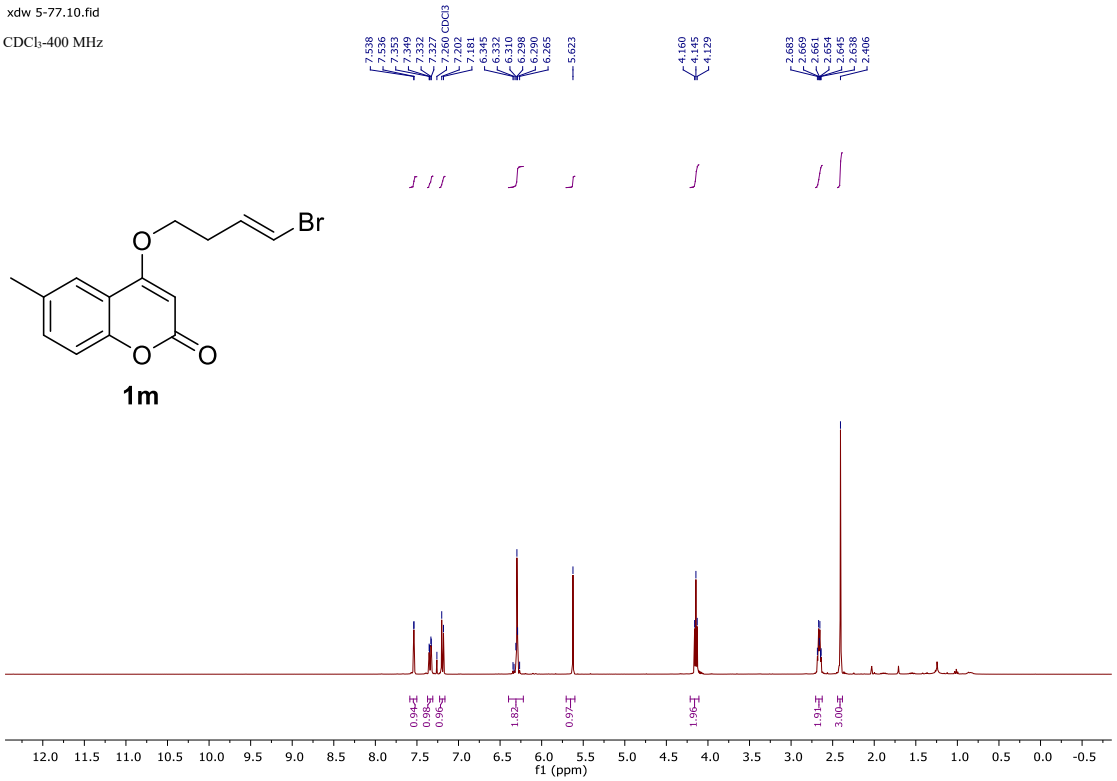
DMSO-d_6-101 MHz



1l

xdw 5-77.10.fid

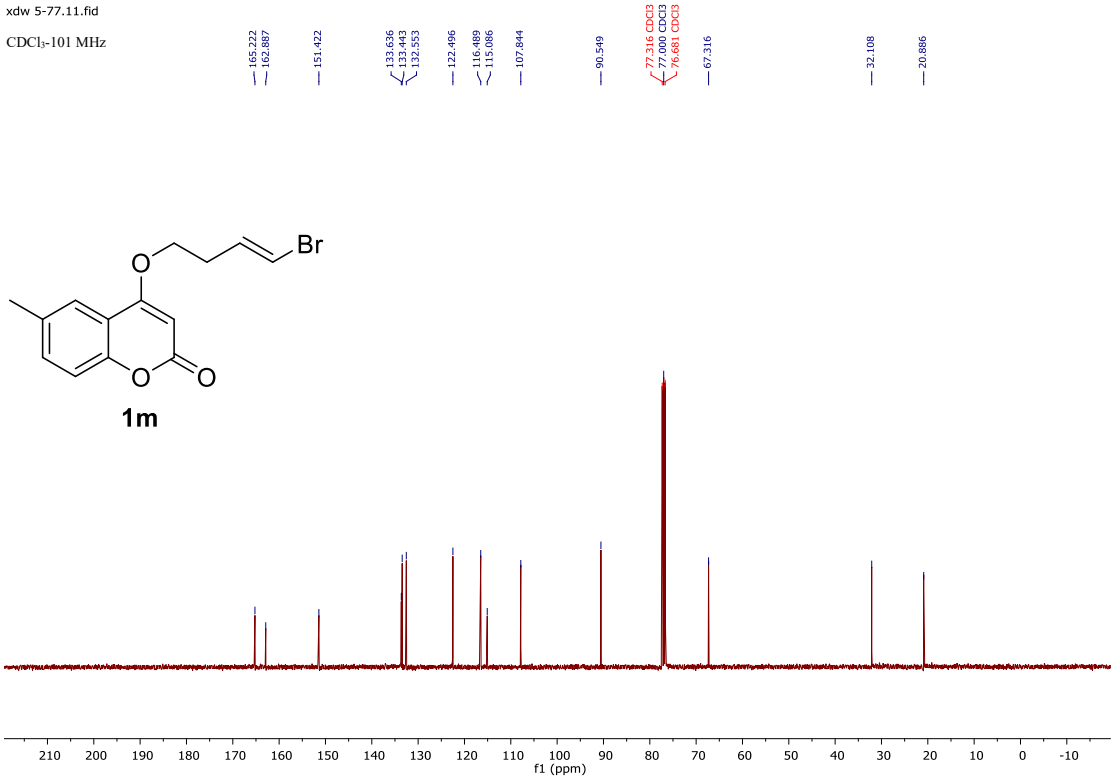
$CDCl_3$-400 MHz



1m

xdw 5-77.11.fid

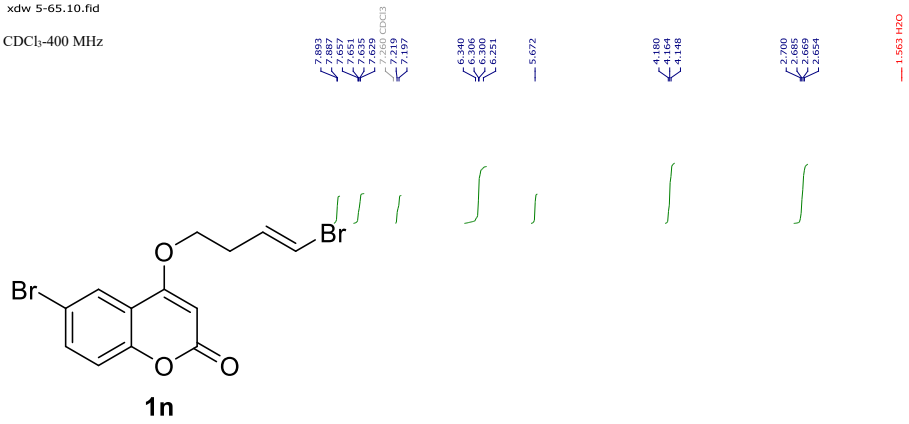
$CDCl_3$-101 MHz



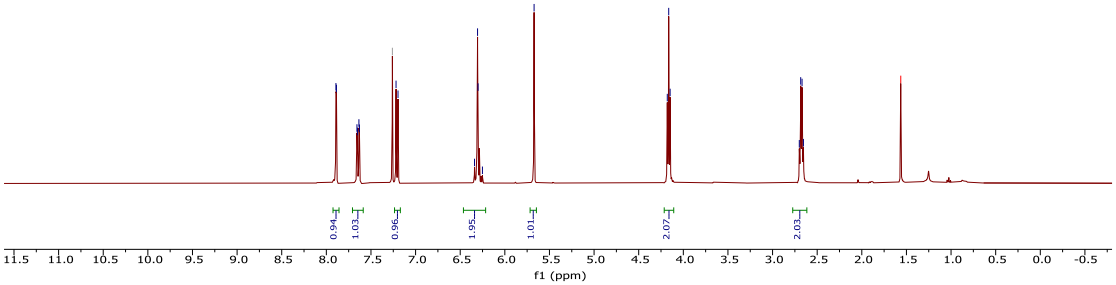
1m

xdw 5-65.10.fid

$CDCl_3$-400 MHz

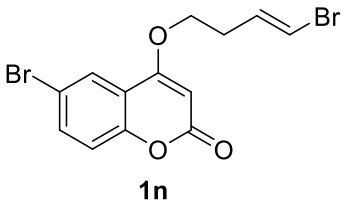


1n

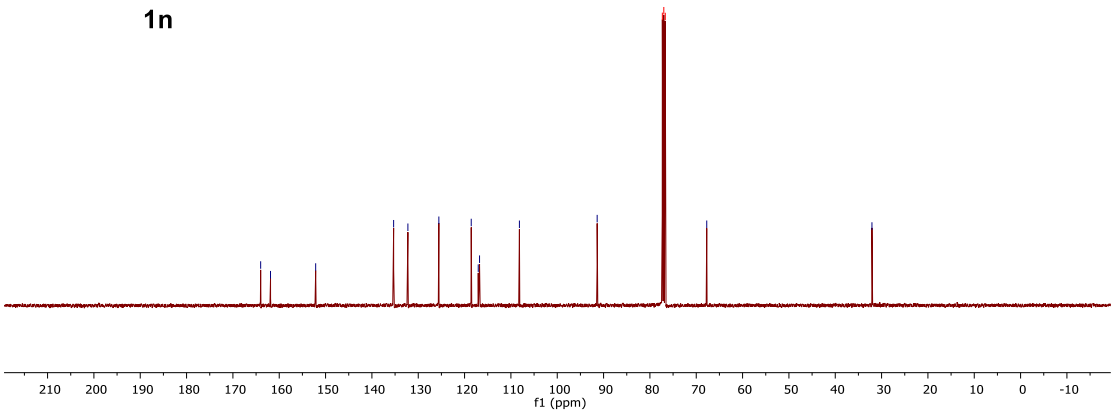


xdw 5-65c.10.fid

$CDCl_3$-101 MHz

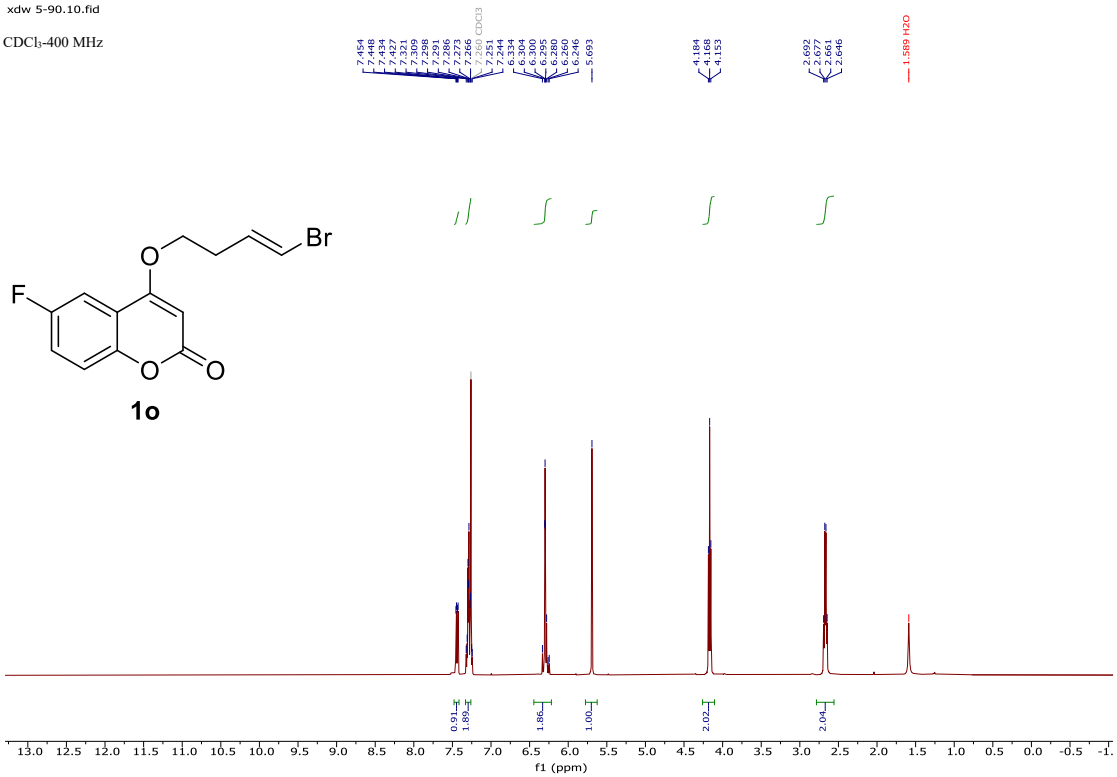


1n



xdw 5-90.10.fid

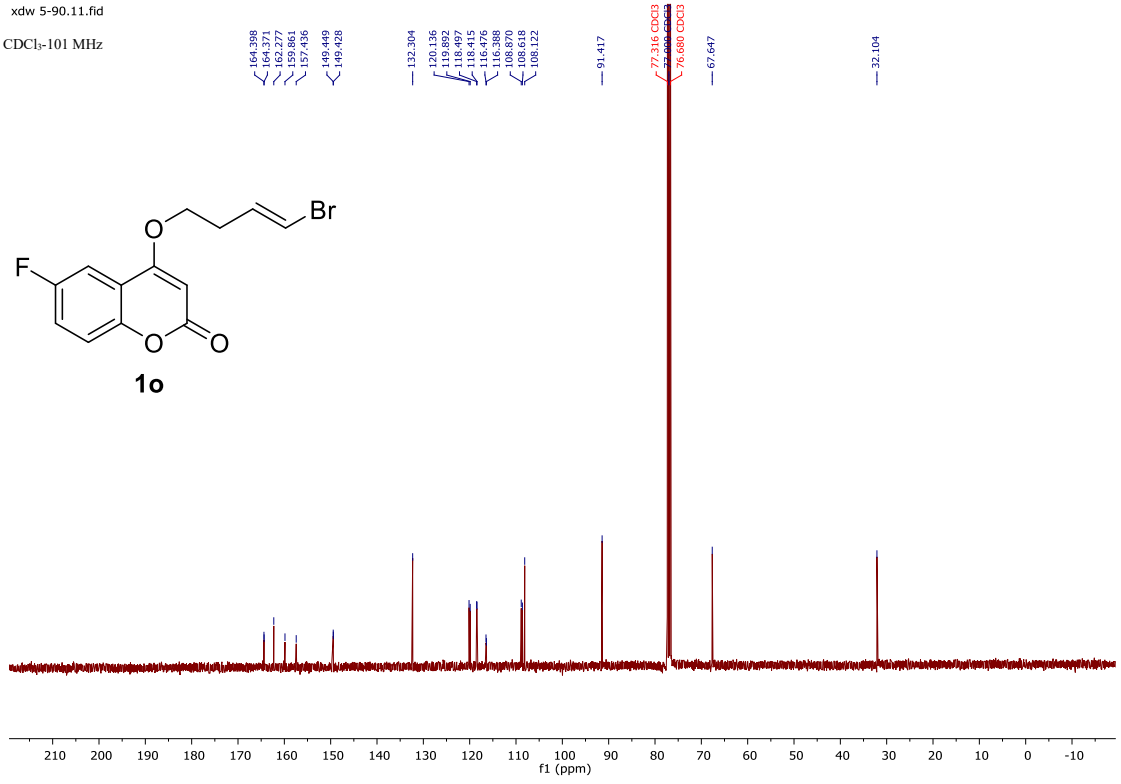
$CDCl_3$-400 MHz



1o

xdw 5-90.11.fid

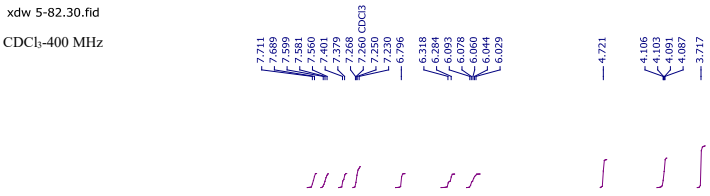
$CDCl_3$-101 MHz

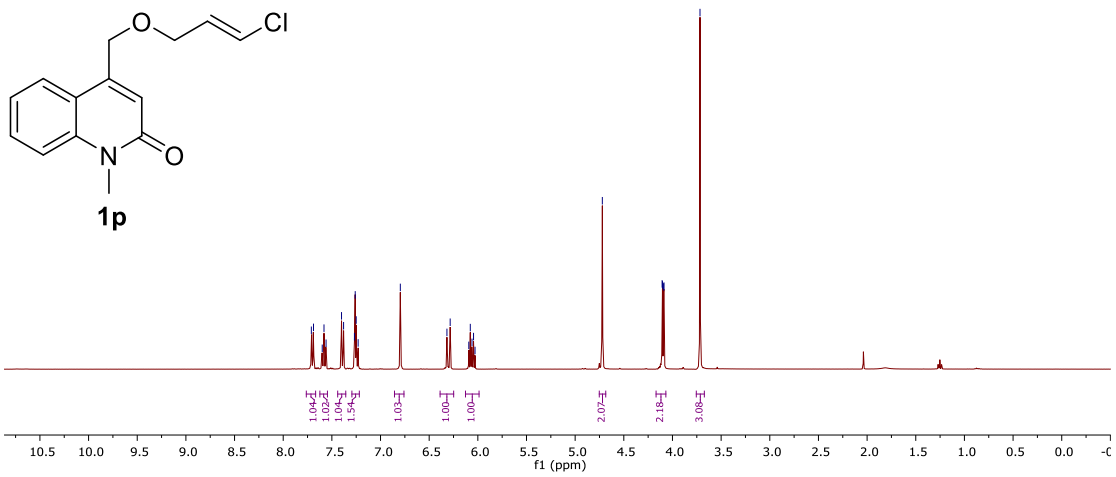


1o

xdw 5-82.30.fid

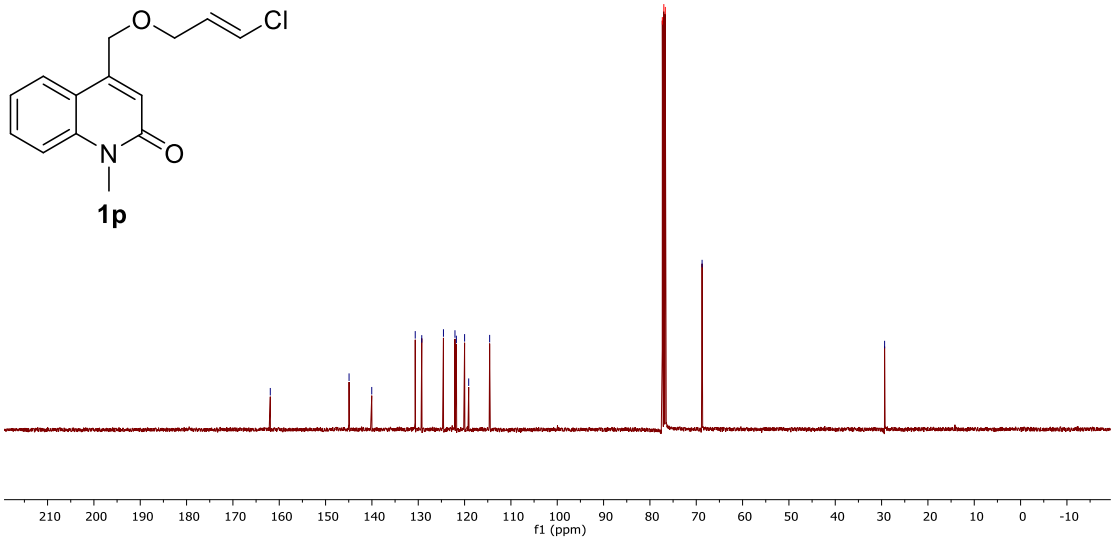
$CDCl_3$-400 MHz

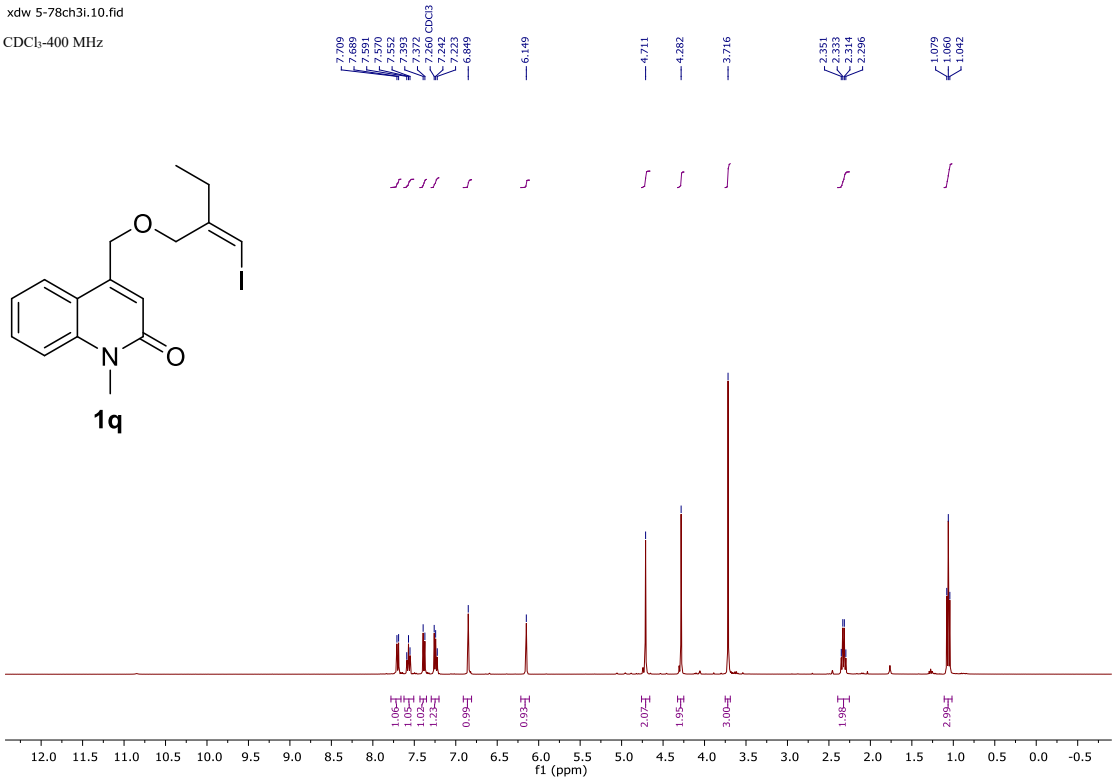


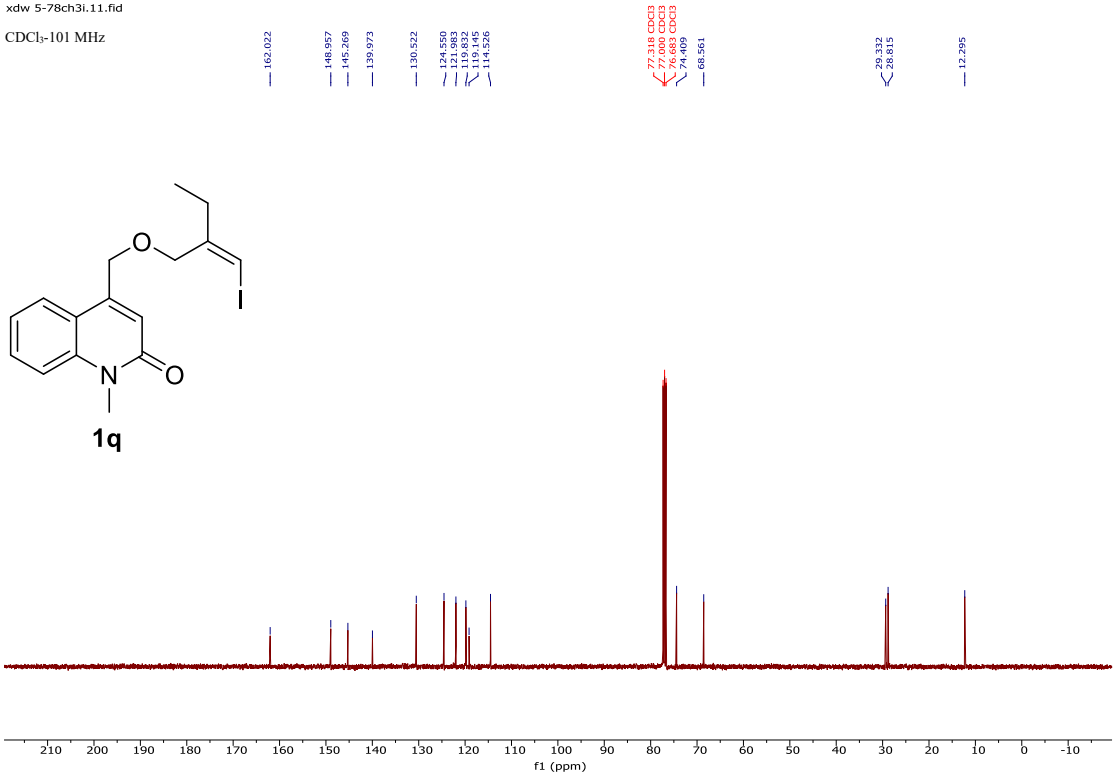


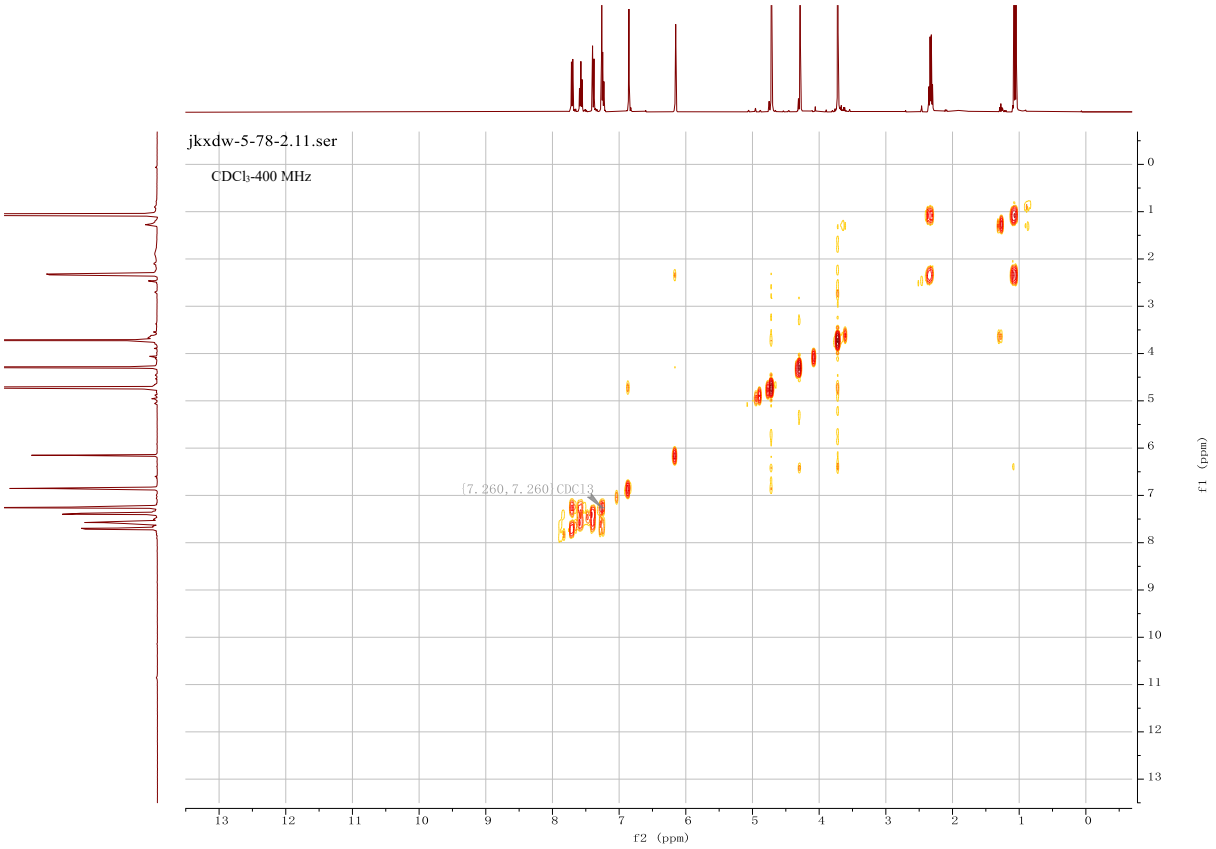
xdw 5-82.31.fid

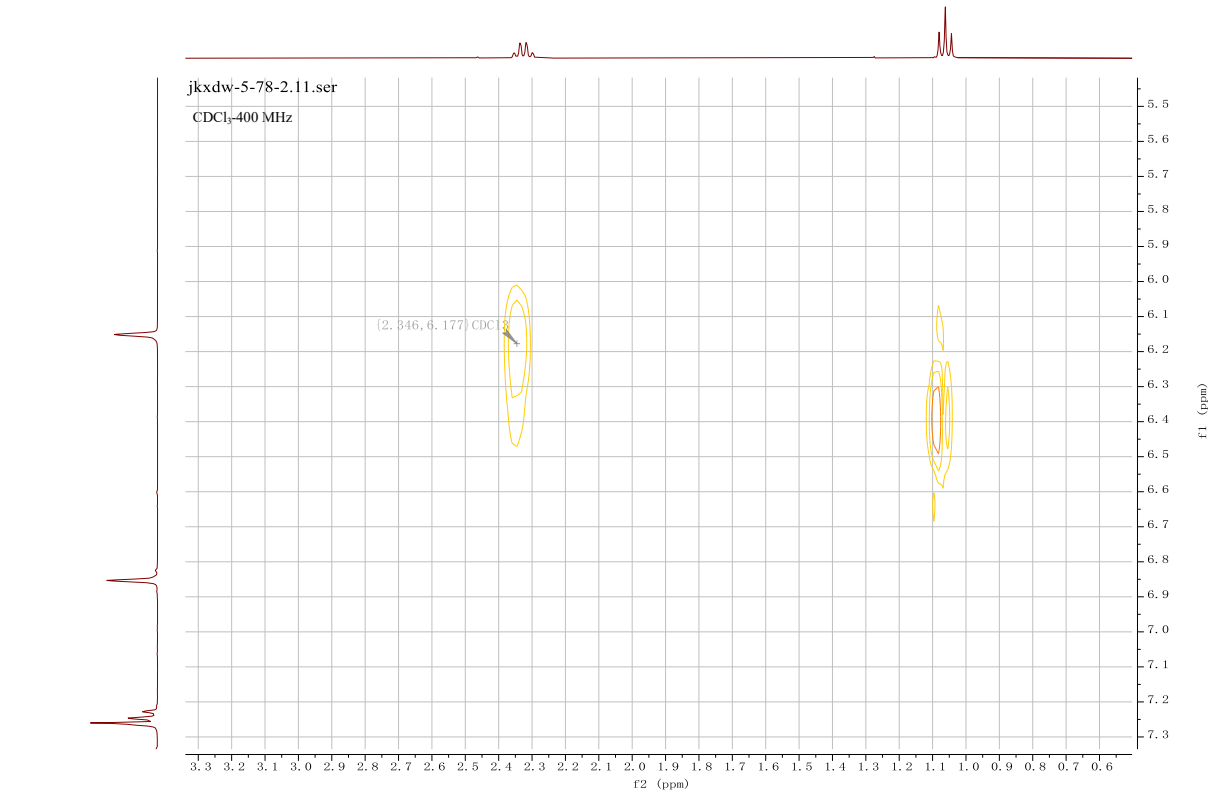
$CDCl_3$-101 MHz

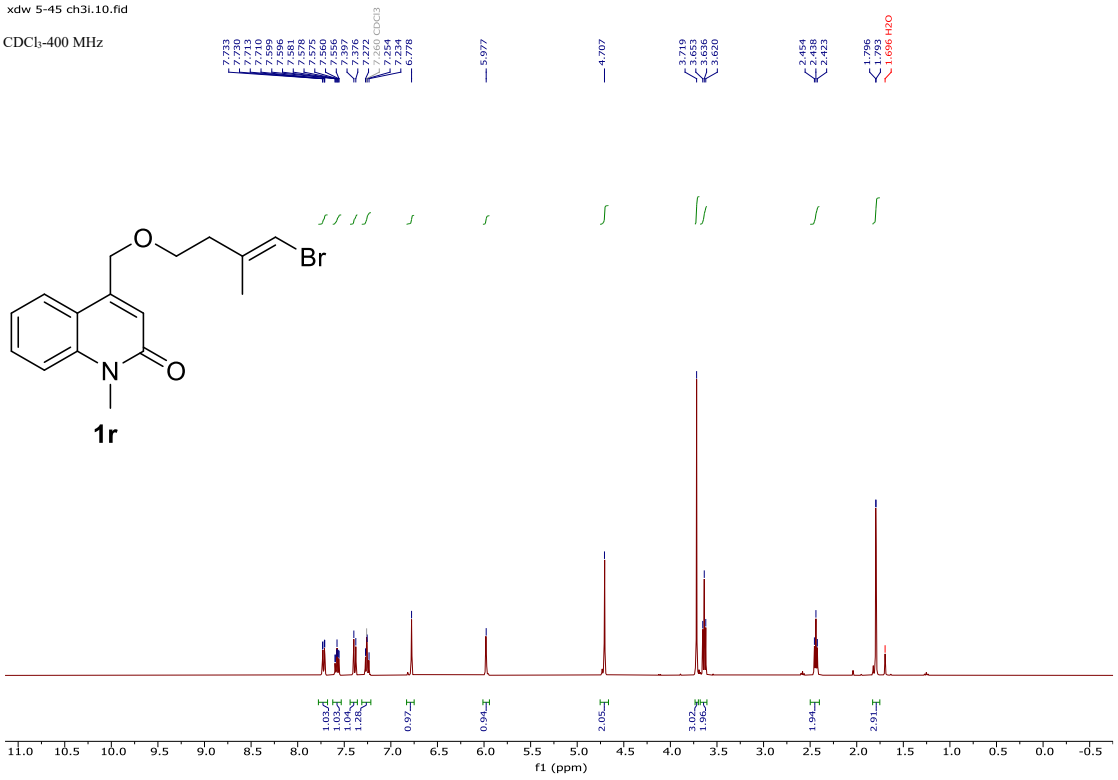


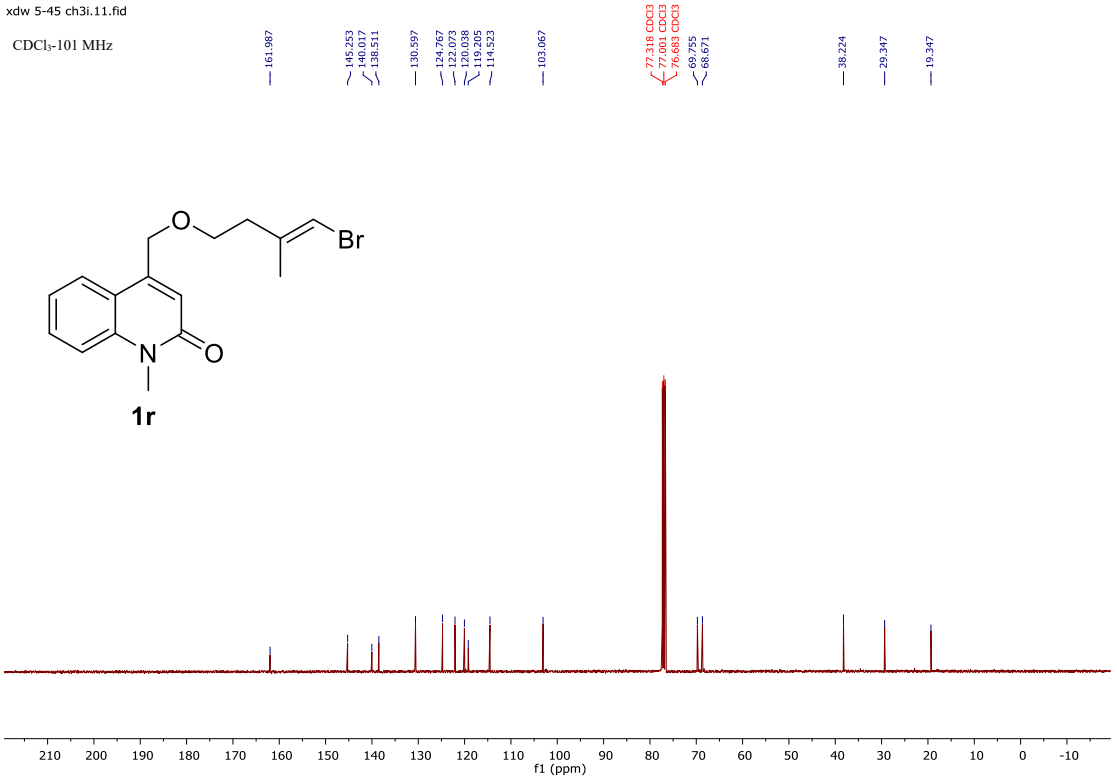

xdw 5-78ch3i.10.fid
CDCl3-400 MHz
7.709
7.689
7.591
7.570
7.552
7.393
7.372
7.260 CDCl3
7.242
7.223
6.849
6.149
4.711
4.282
3.716
2.351
2.333
2.314
2.296
1.079
1.060
1.042
O
I
N
O
1q
1.06
1.05
1.02
1.23
0.99
0.93
2.07
1.95
3.00
1.98
2.99
f1 (ppm)


xdw 5-78ch3i.11.fid
CDCl3-101 MHz
162.022
148.957
145.269
139.973
130.522
124.550
121.983
119.832
119.145
114.526
77.318 CDCl3
77.000 CDCl3
76.683 CDCl3
74.409
68.561
29.332
28.815
12.295
O
I
N
O
1q
f1 (ppm)


jkxdw-5-78-2.11.ser
CDCl3-400 MHz
{7.260,7.260}CDCl3
f2 (ppm)
f1 (ppm)

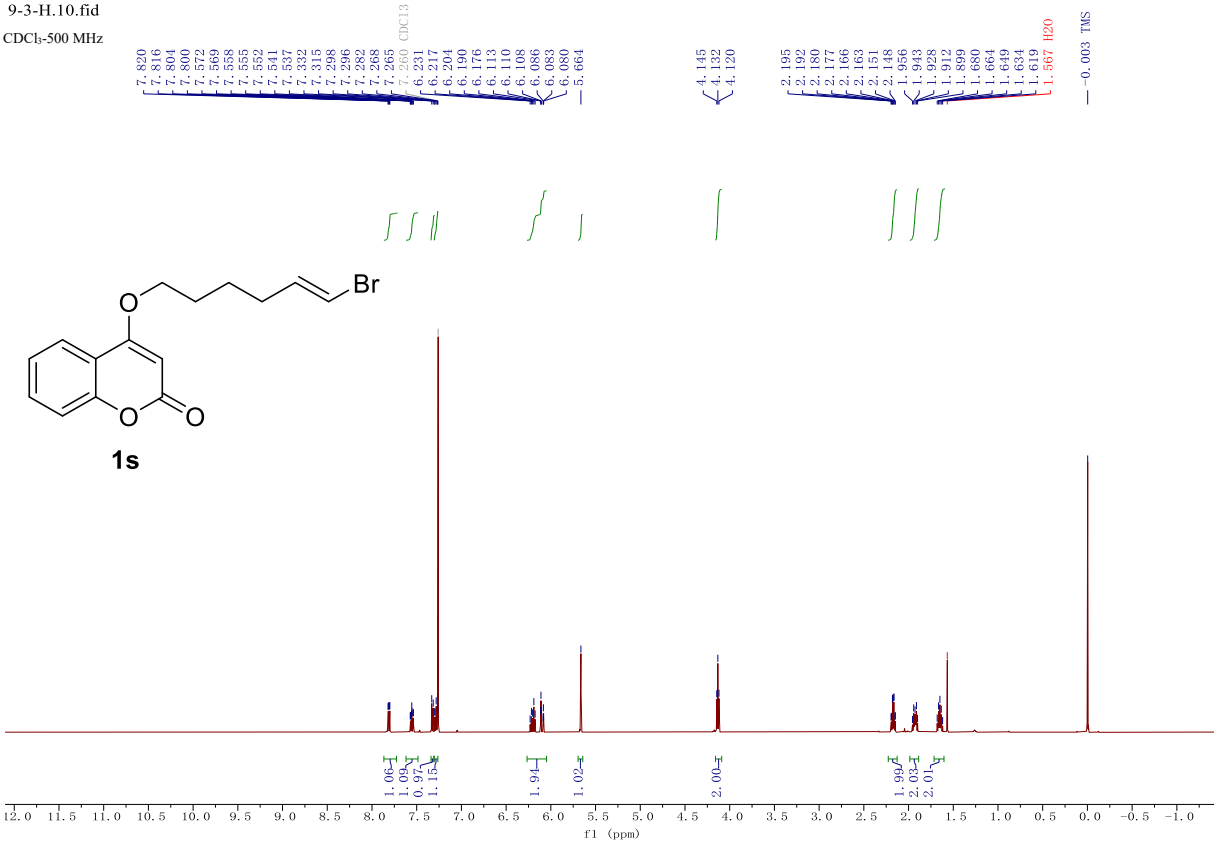

jkxdw-5-78-2.11.ser
CDCl3-400 MHz
{2.346,6.177}CDCl3
f2 (ppm)
f1 (ppm)


xdw 5-45 ch3i.10.fid
CDCl3-400 MHz
7.733
7.730
7.713
7.710
7.599
7.596
7.581
7.578
7.575
7.560
7.555
7.397
7.376
7.272
7.260 CDCl3
7.254
7.234
6.778
5.977
4.707
3.719
3.653
3.636
3.620
2.454
2.438
2.423
1.796
1.793
1.696 H2O
O
Br
N
O
1r
1.03
1.03
1.00
1.28
0.97
0.94
2.05
3.02
1.96
1.94
2.91
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


xdw 5-45 ch3i.11.fid
CDCl3-101 MHz
161.987
145.253
140.017
138.511
130.597
124.767
122.073
120.038
119.205
114.523
103.067
77.318 CDCl3
77.001 CDCl3
76.683 CDCl3
69.755
68.671
38.224
29.347
19.347
O
Br
N
O
1r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

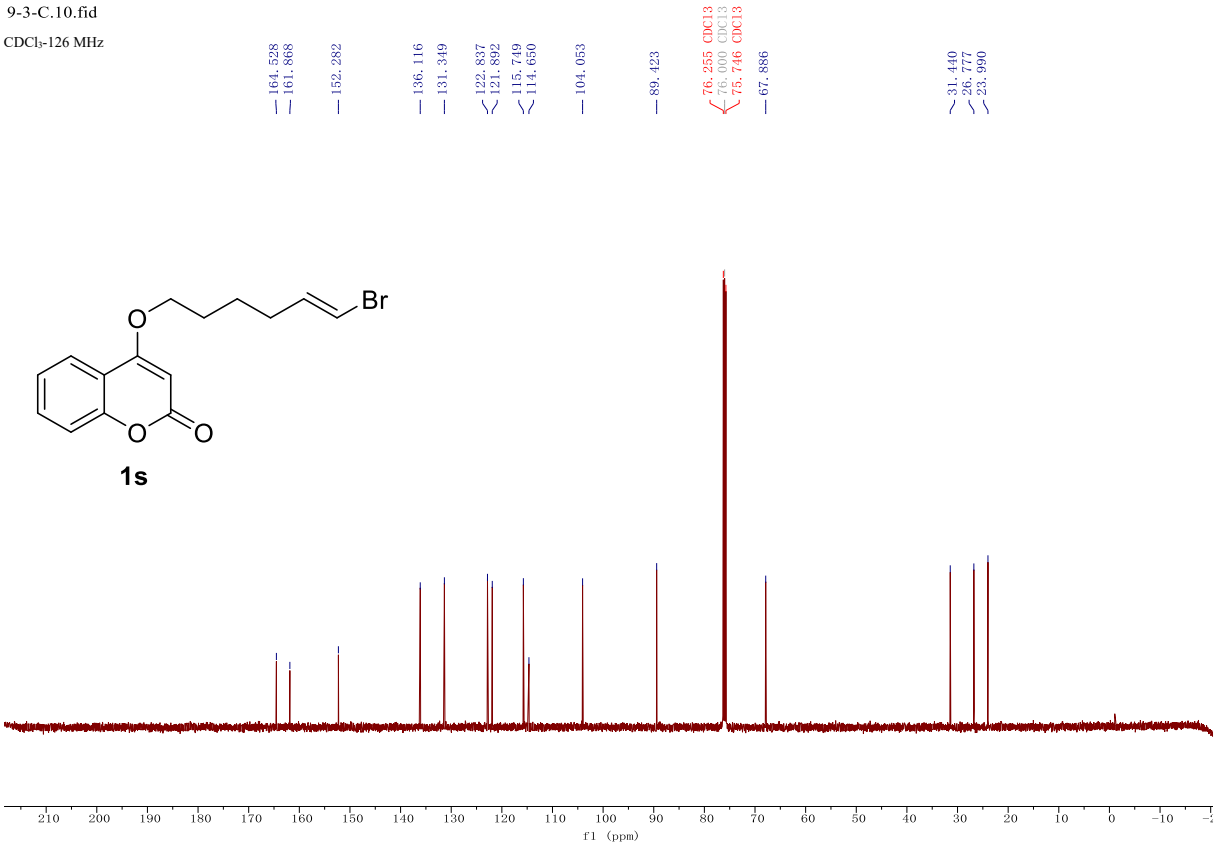
9-3-H.10.fid

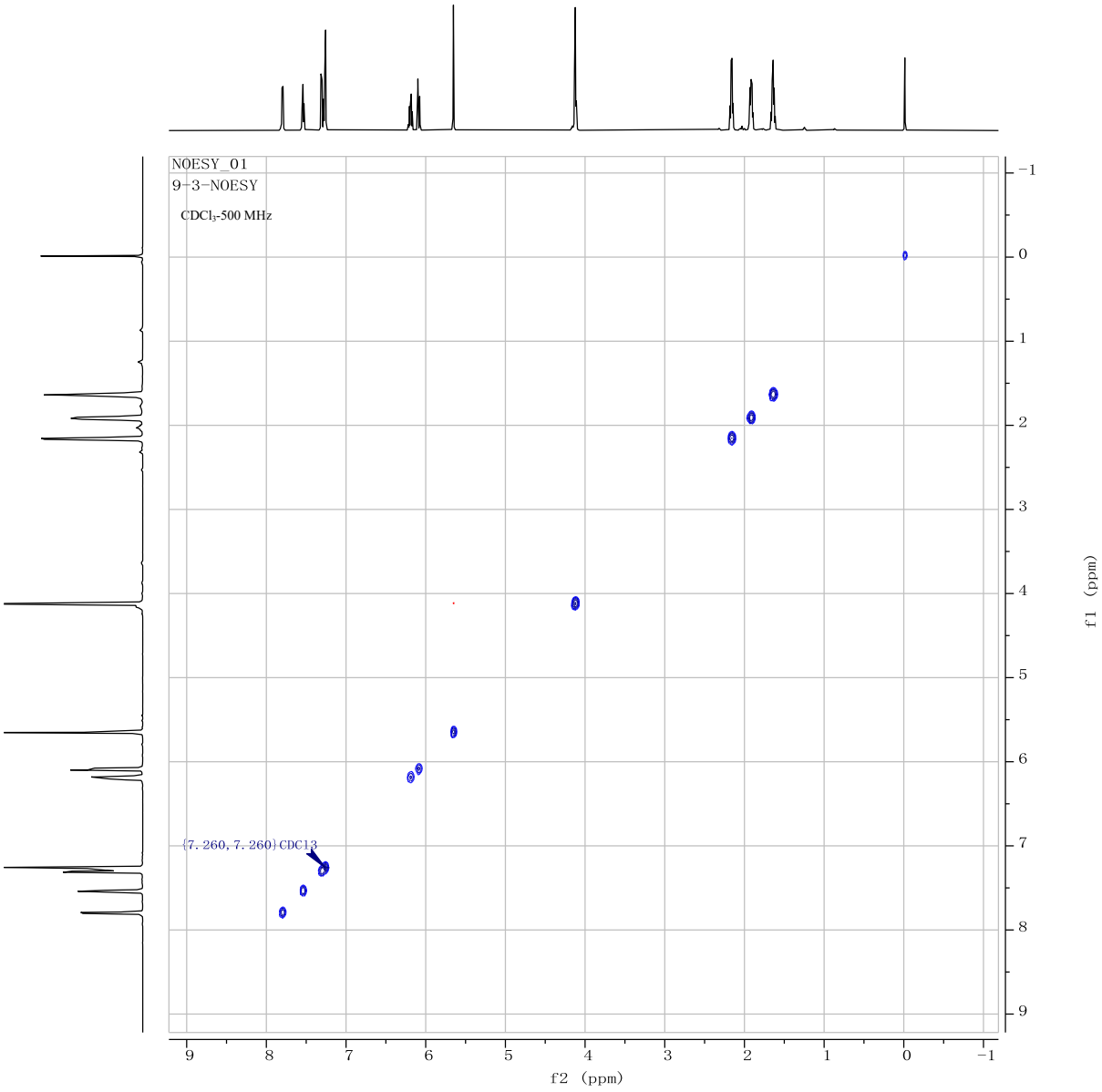
$CDCl_3$-500 MHz

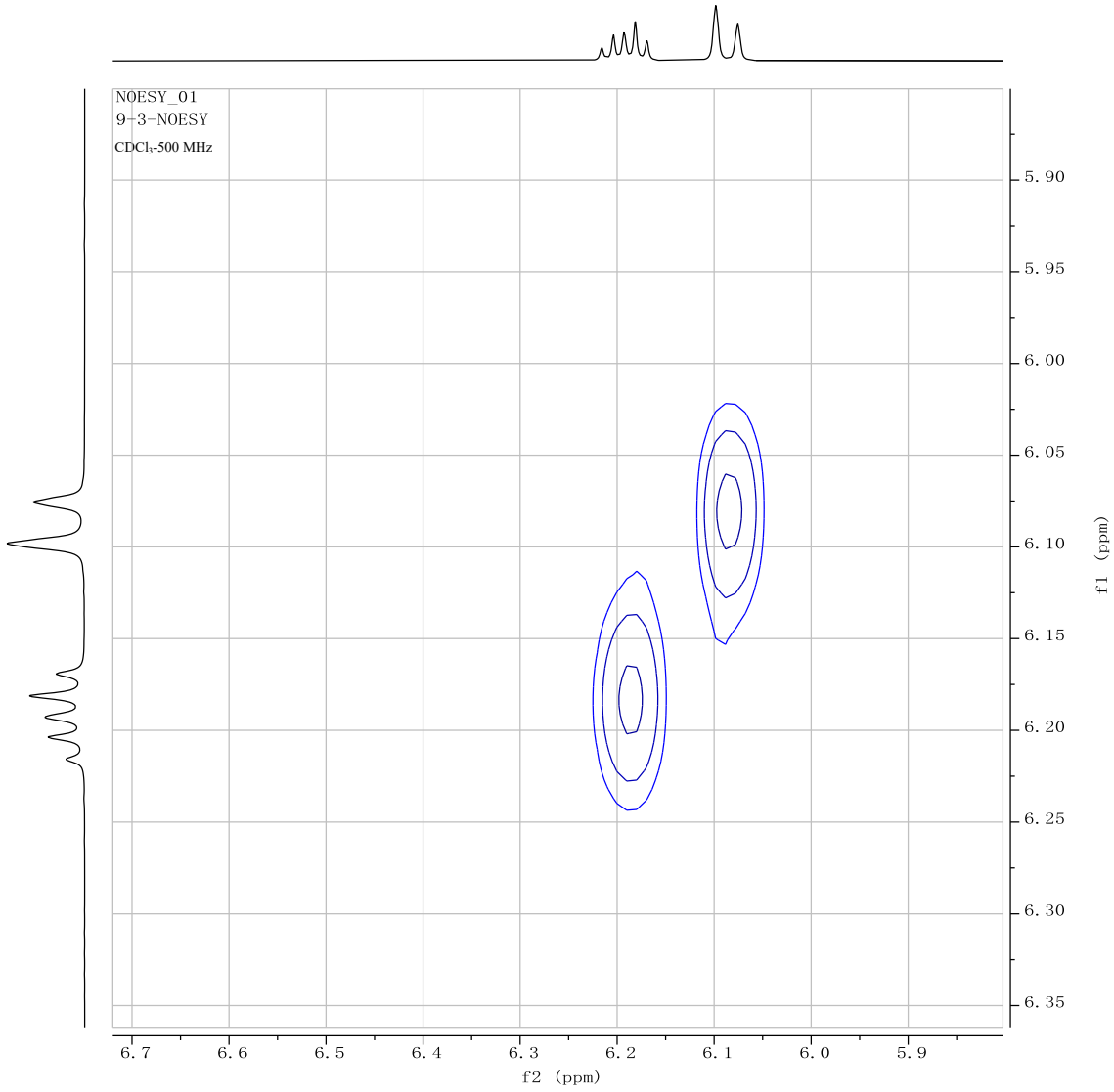


9-3-C.10.fid

$CDCl_3$-126 MHz

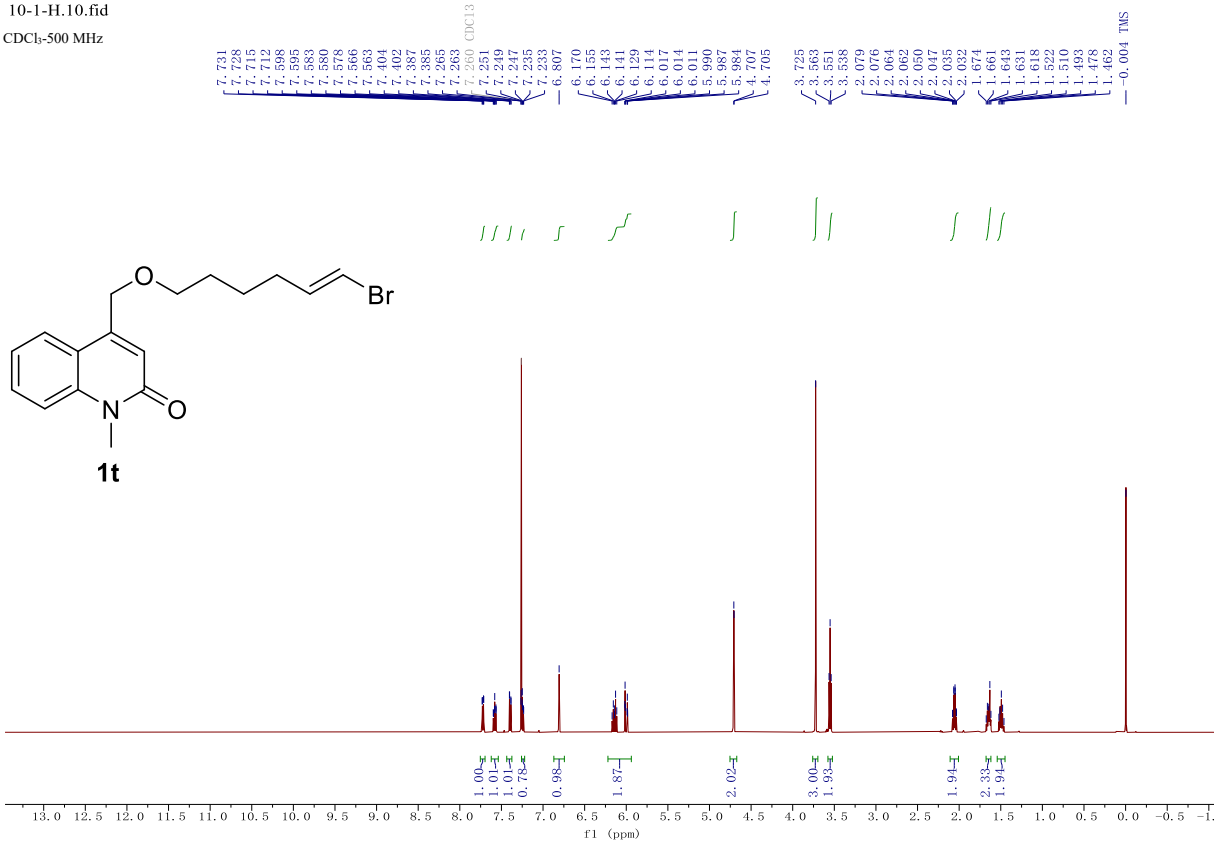



NOESY_01
9-3-NOESY
CDCl3-500 MHz
{7.260, 7.260}CDCl3
f2 (ppm)
f1 (ppm)


NOESY_01
9-3-NOESY
CDCl3-500 MHz
5.90
5.95
6.00
6.05
6.10
6.15
6.20
6.25
6.30
6.35
f1 (ppm)
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
f2 (ppm)

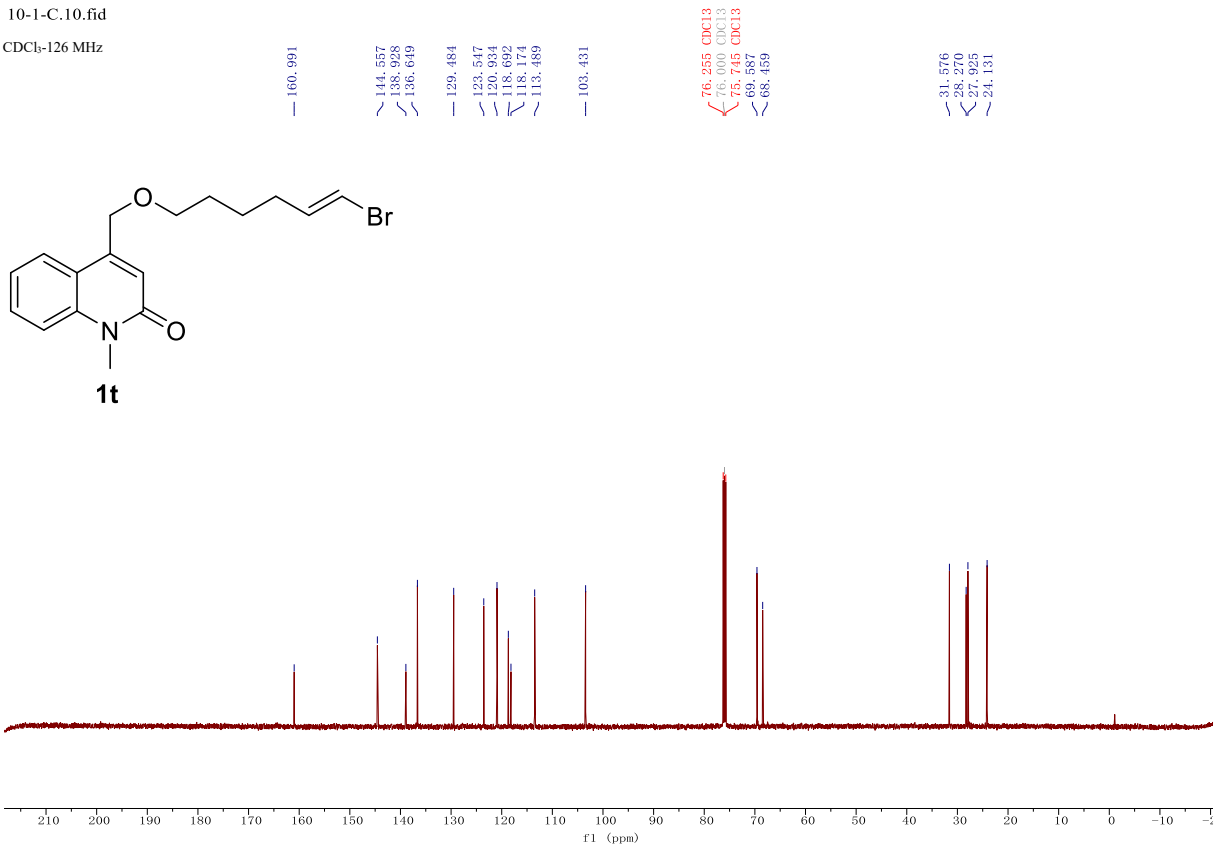
10-1-H.10.fid

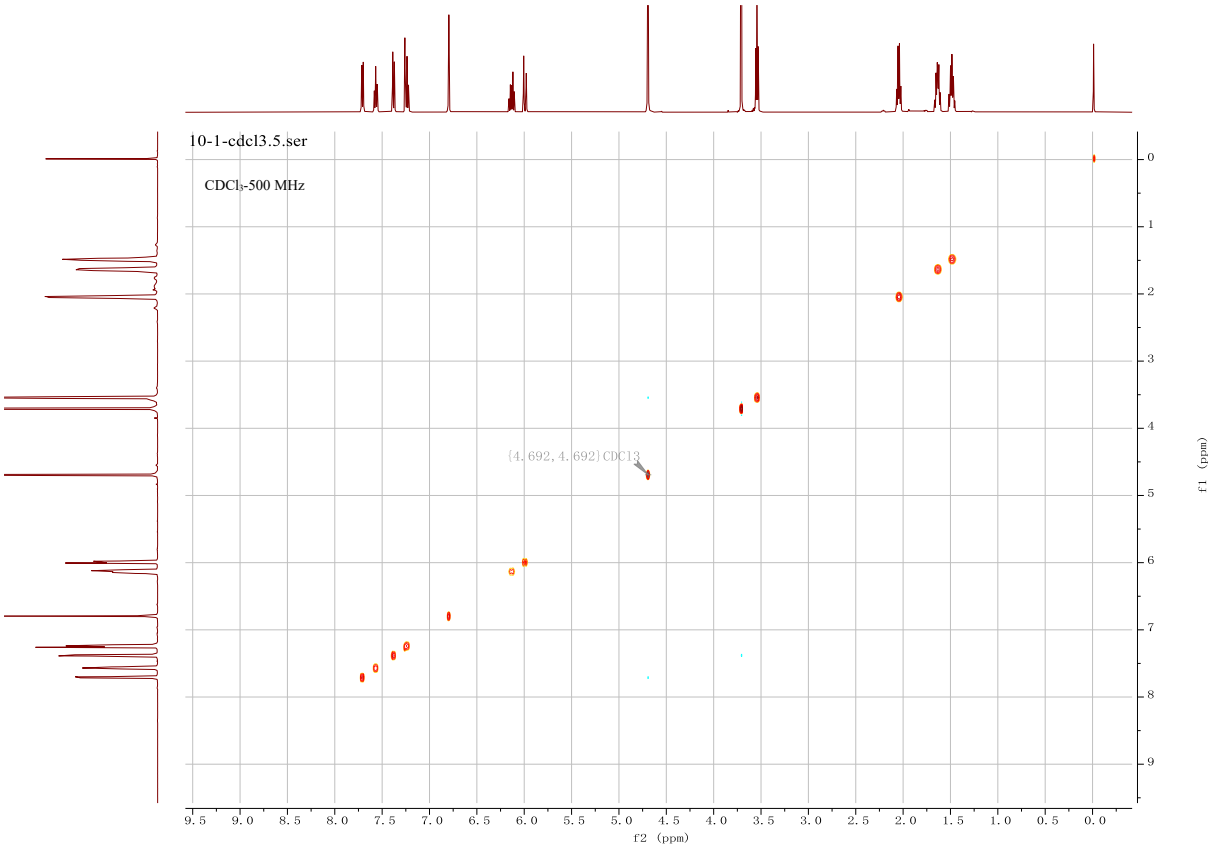
$CDCl_3$-500 MHz



10-1-C.10.fid

$CDCl_3$-126 MHz

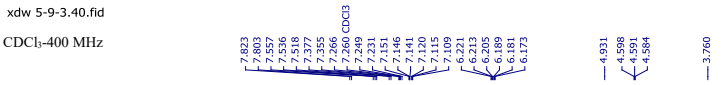


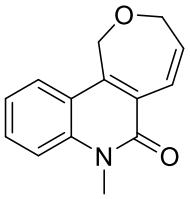

10-1-cdcl3.5.ser
CDCl3-500 MHz
{4.692,4.692}CDCl3
f2 (ppm)
f1 (ppm)


10-1-cdcl3.5.ser
CDCl3-500 MHz
f2 (ppm)
f1 (ppm)

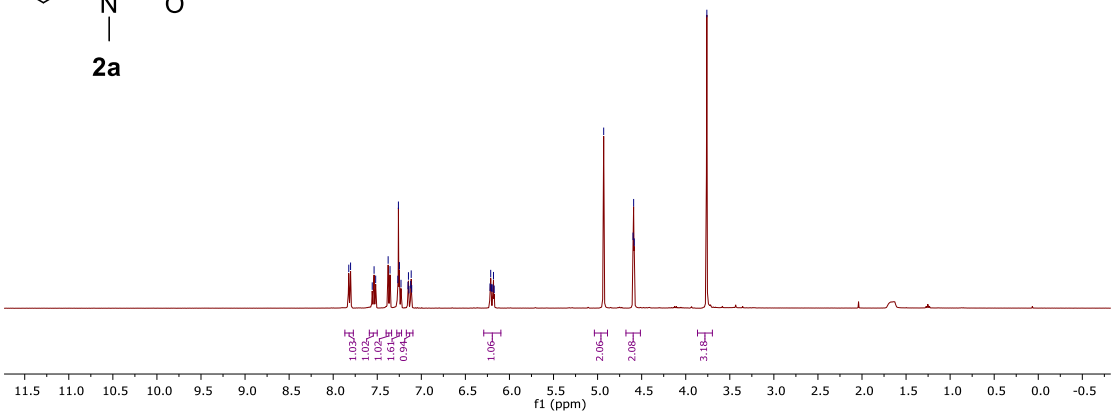
xdw 5-9-3.40.fid

$CDCl_3$-400 MHz



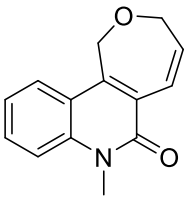


2a



xdw 5-9-3.41.fid

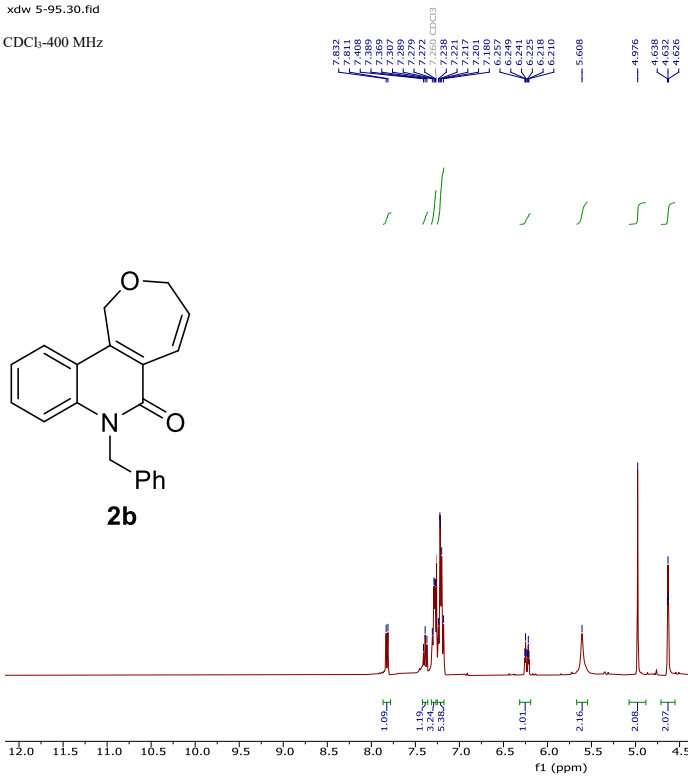
$CDCl_3$-101 MHz



2a

xdw 5-95.30.fid

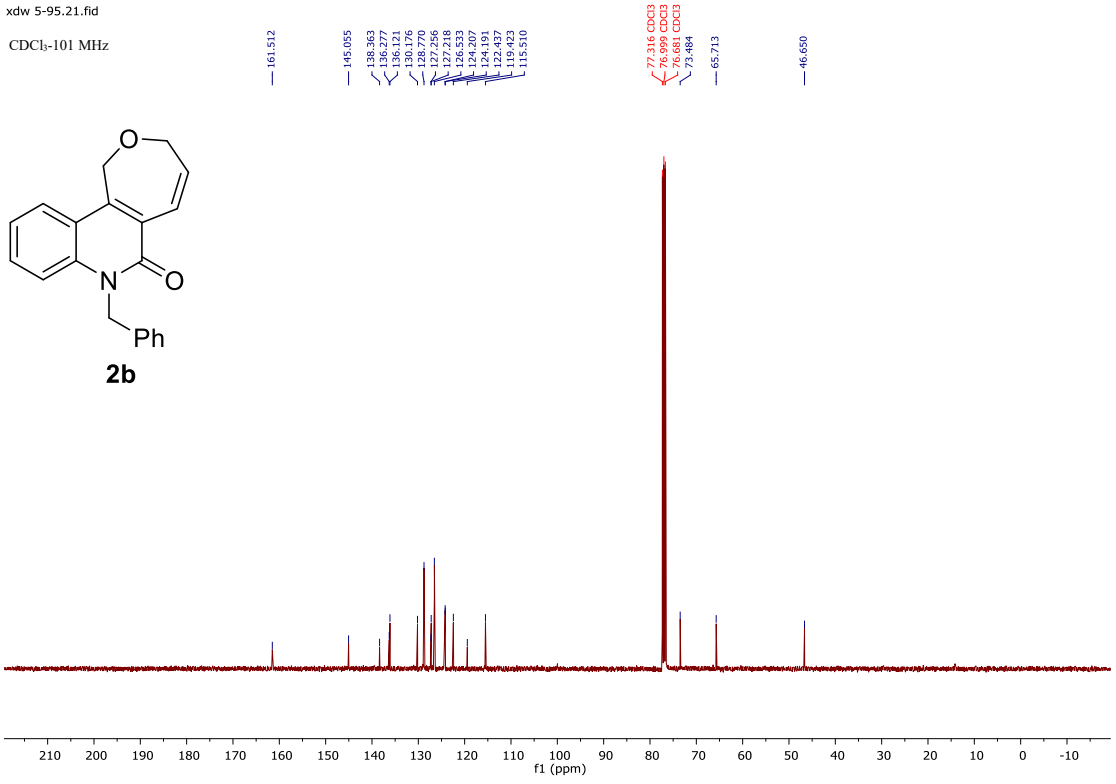
$CDCl_3$-400 MHz



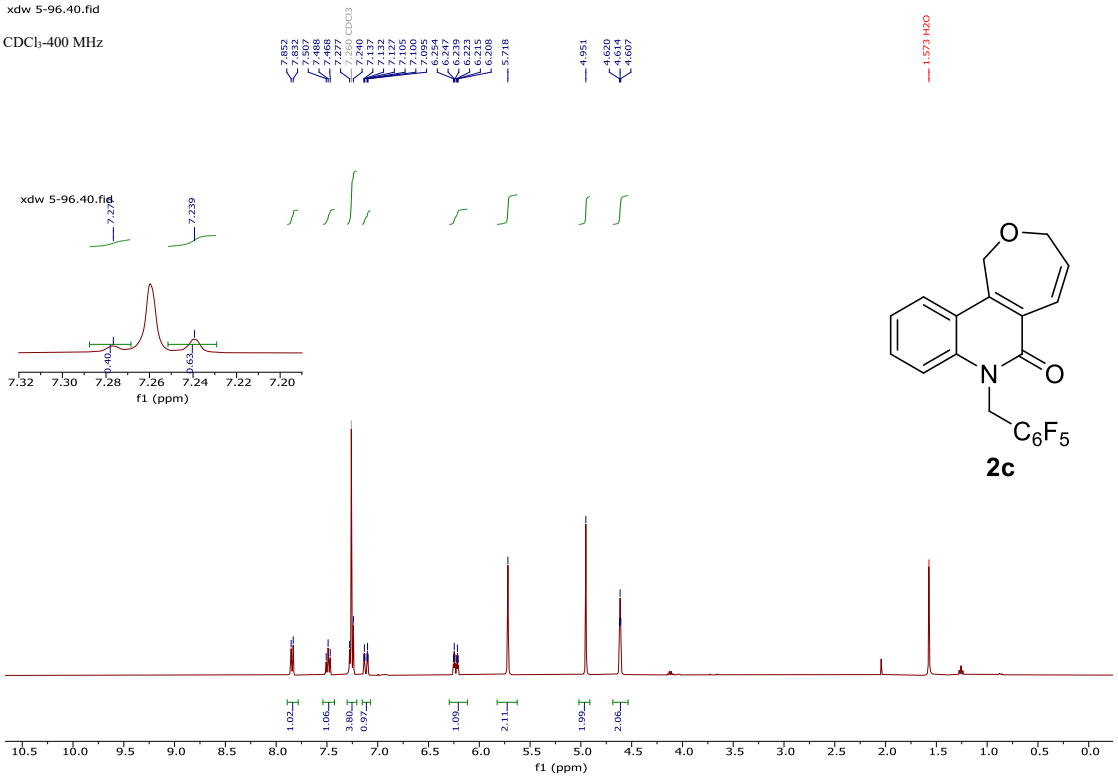
2b

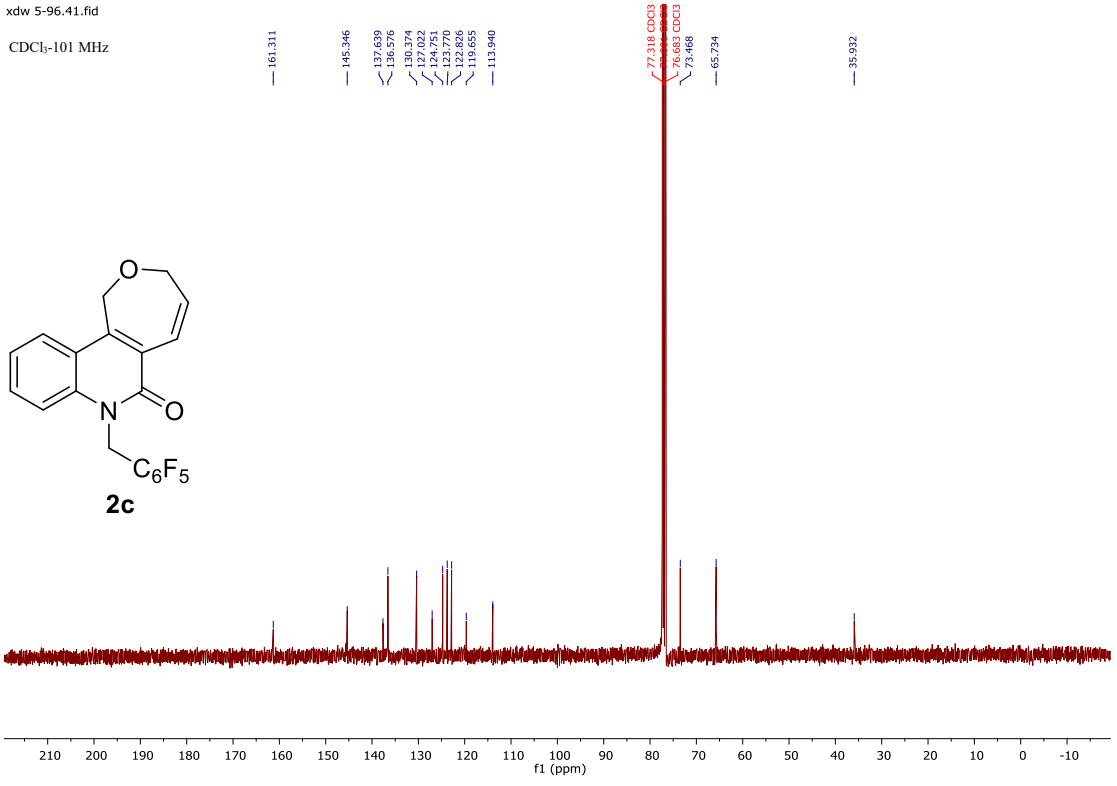
xdw 5-95.21.fid

$CDCl_3$-101 MHz



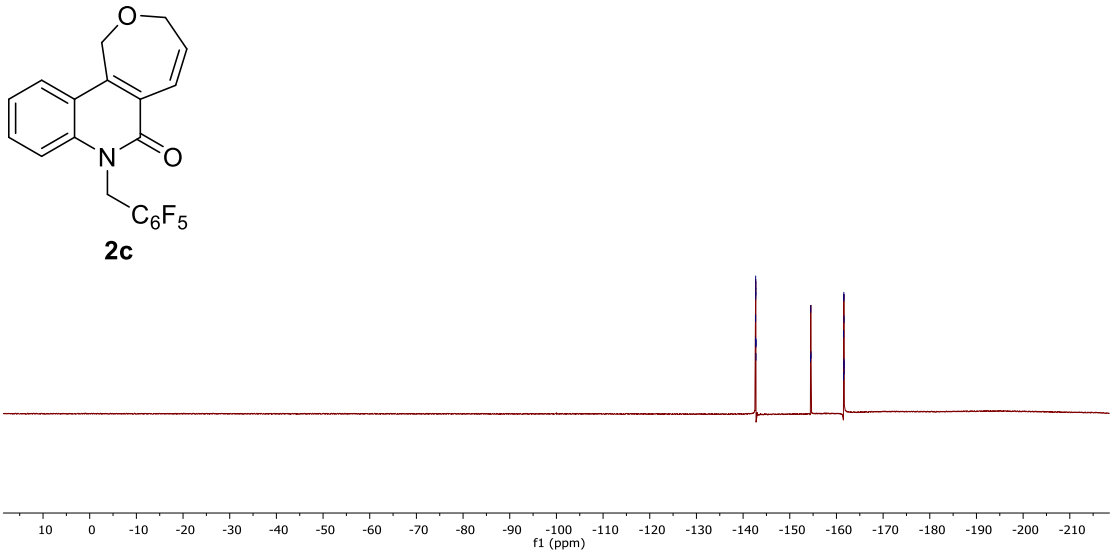
2b


xdw 5-96.40.fid
CDCl3-400 MHz
7.852
7.832
7.507
7.488
7.468
7.277
CDCl3
7.240
7.137
7.132
7.127
7.105
7.100
7.095
6.254
6.247
6.239
6.223
6.215
6.208
5.718
4.951
4.620
4.614
4.607
1.573 H2O
7.274
7.239
3.40
3.63
7.32 7.30 7.28 7.26 7.24 7.22 7.20
f1 (ppm)
O
N
O
C6F5
2c
1.02
1.06
3.80
0.97
1.09
2.11
1.99
2.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


xdw 5-96.41.fid
CDCl3-101 MHz
161.311
145.346
137.639
136.576
130.374
127.022
124.751
123.770
122.826
119.655
113.940
77.318 CDCl3
76.683 CDCl3
73.468
65.734
35.932
O
N
O
C6F5
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

lxy-5-96.33.fid

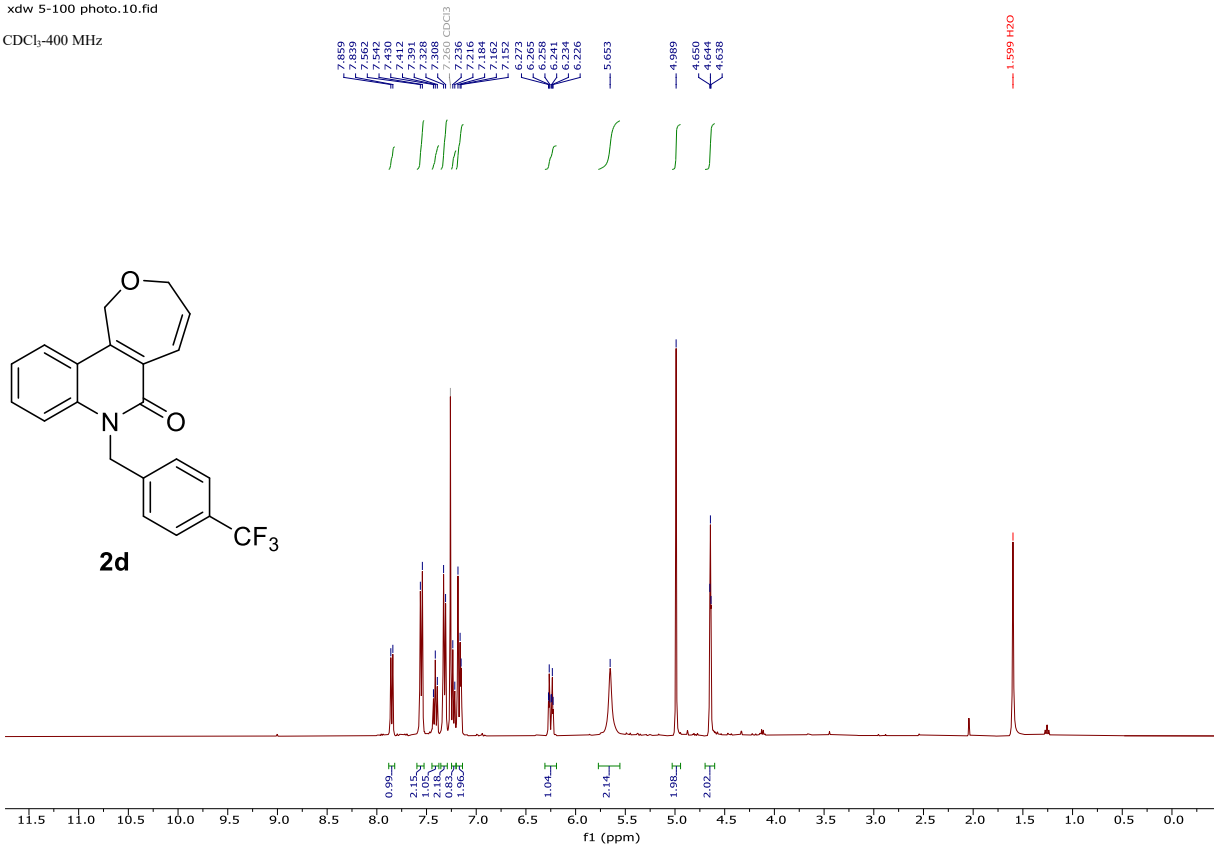
$CDCl_3$-376 MHz



2c

xdw 5-100 photo.10.fid

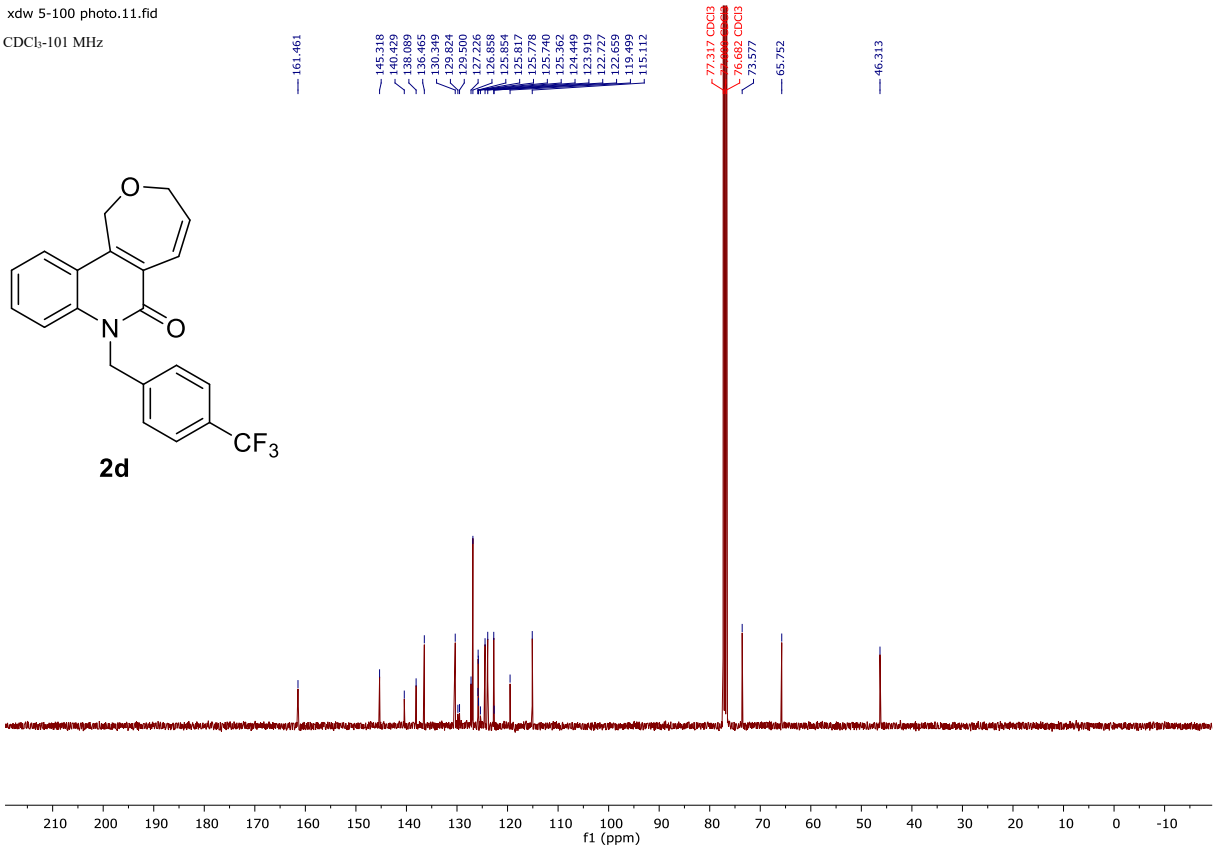
$CDCl_3$-400 MHz



2d

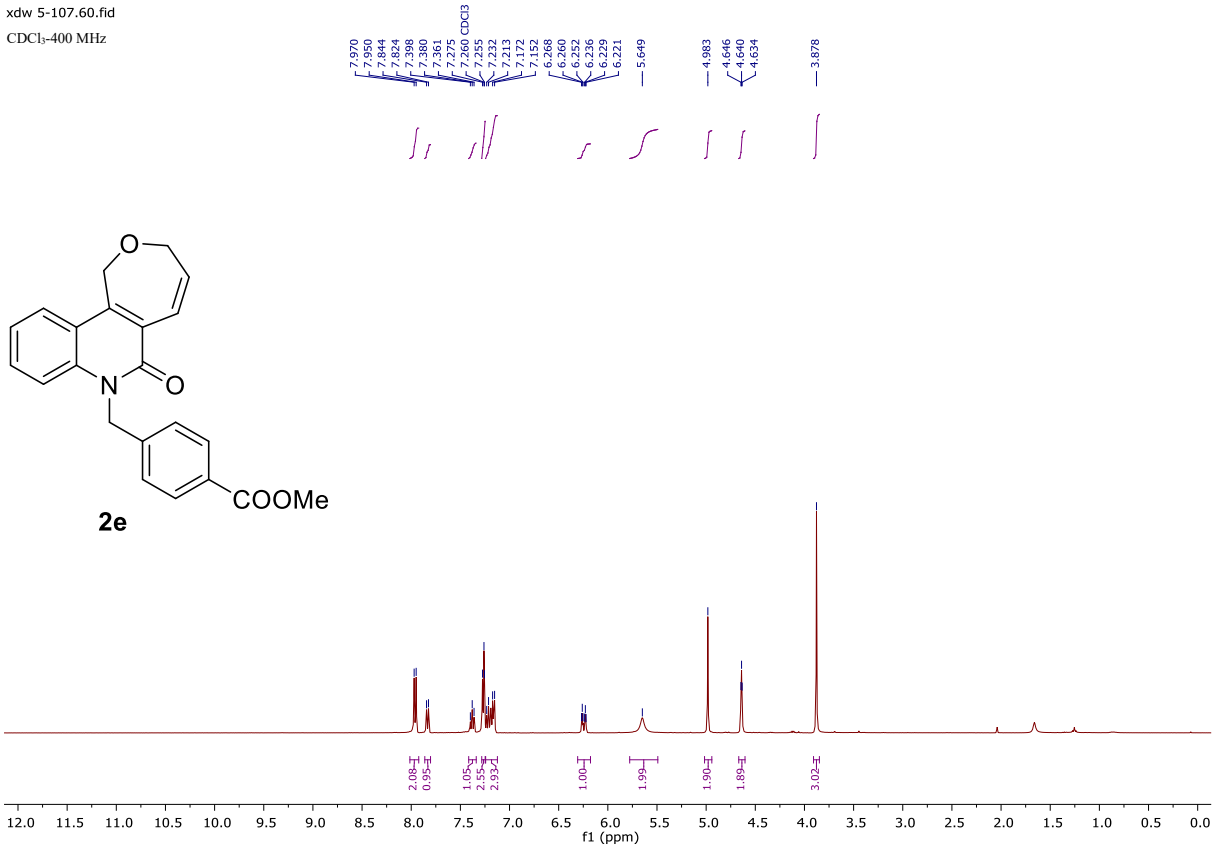
xdw 5-100 photo.11.fid

$CDCl_3$-101 MHz



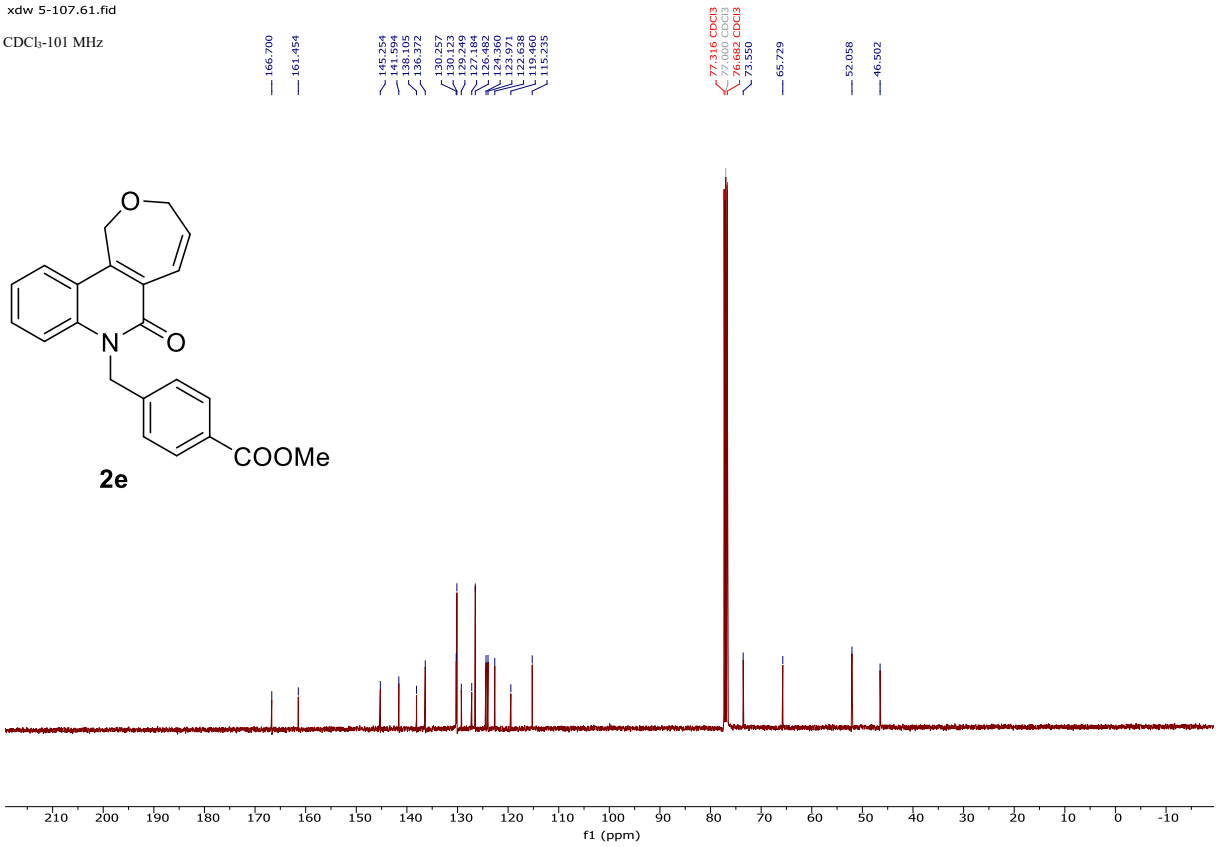
xdw 5-107.60.fid

$CDCl_3$-400 MHz



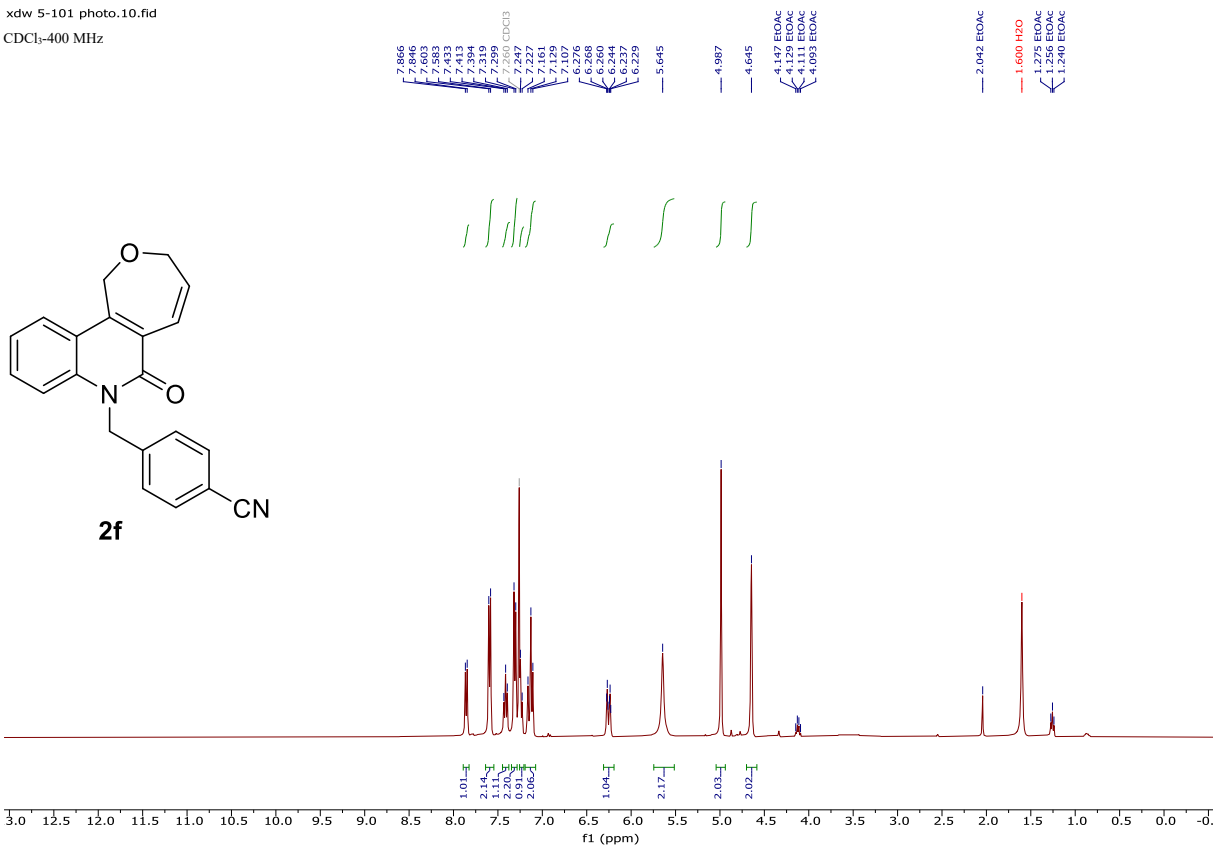
xdw 5-107.61.fid

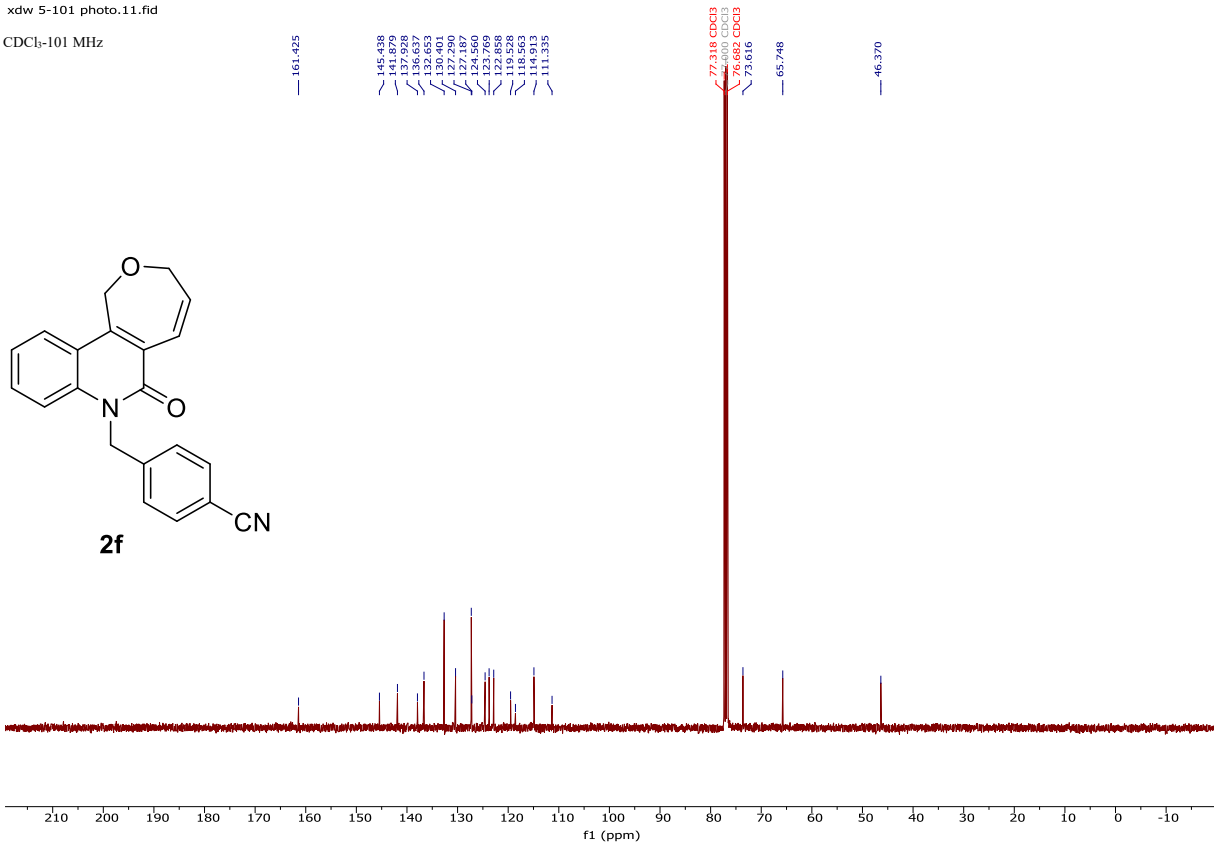
$CDCl_3$-101 MHz

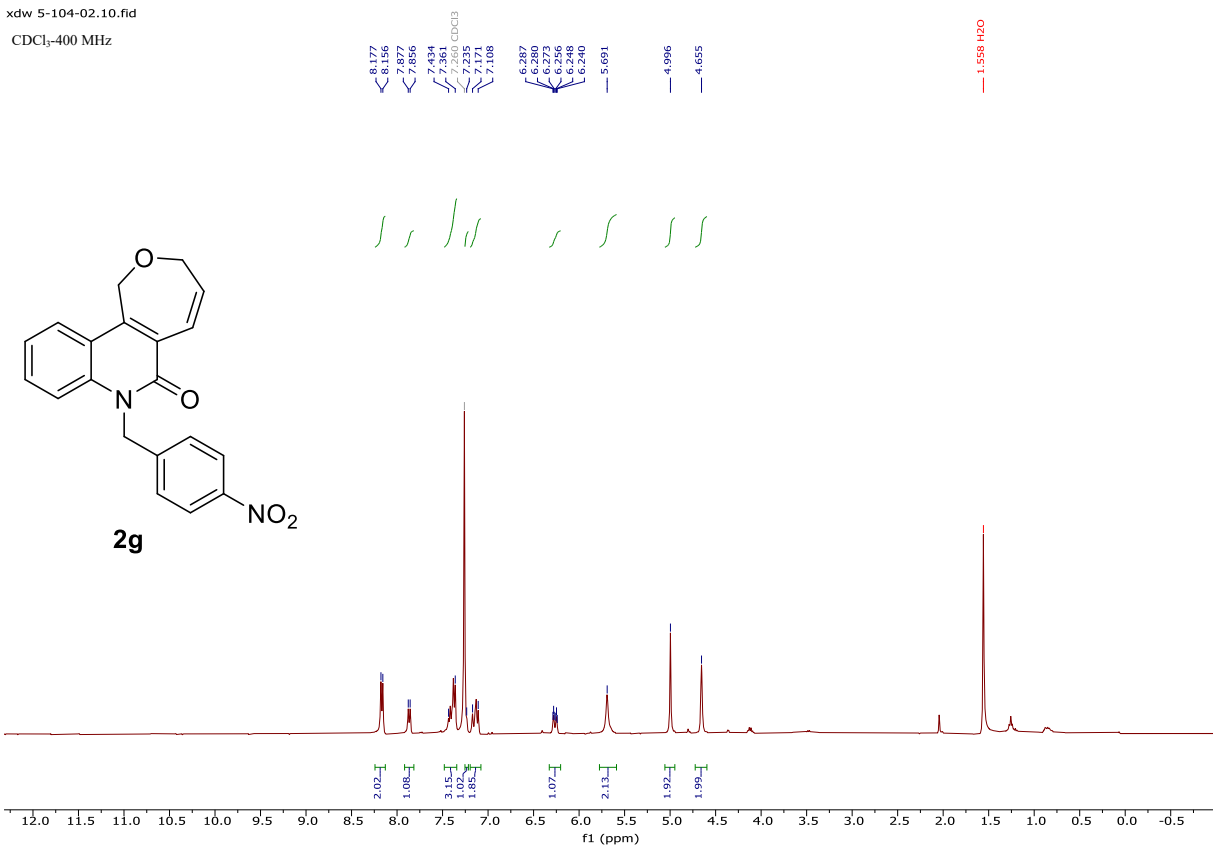


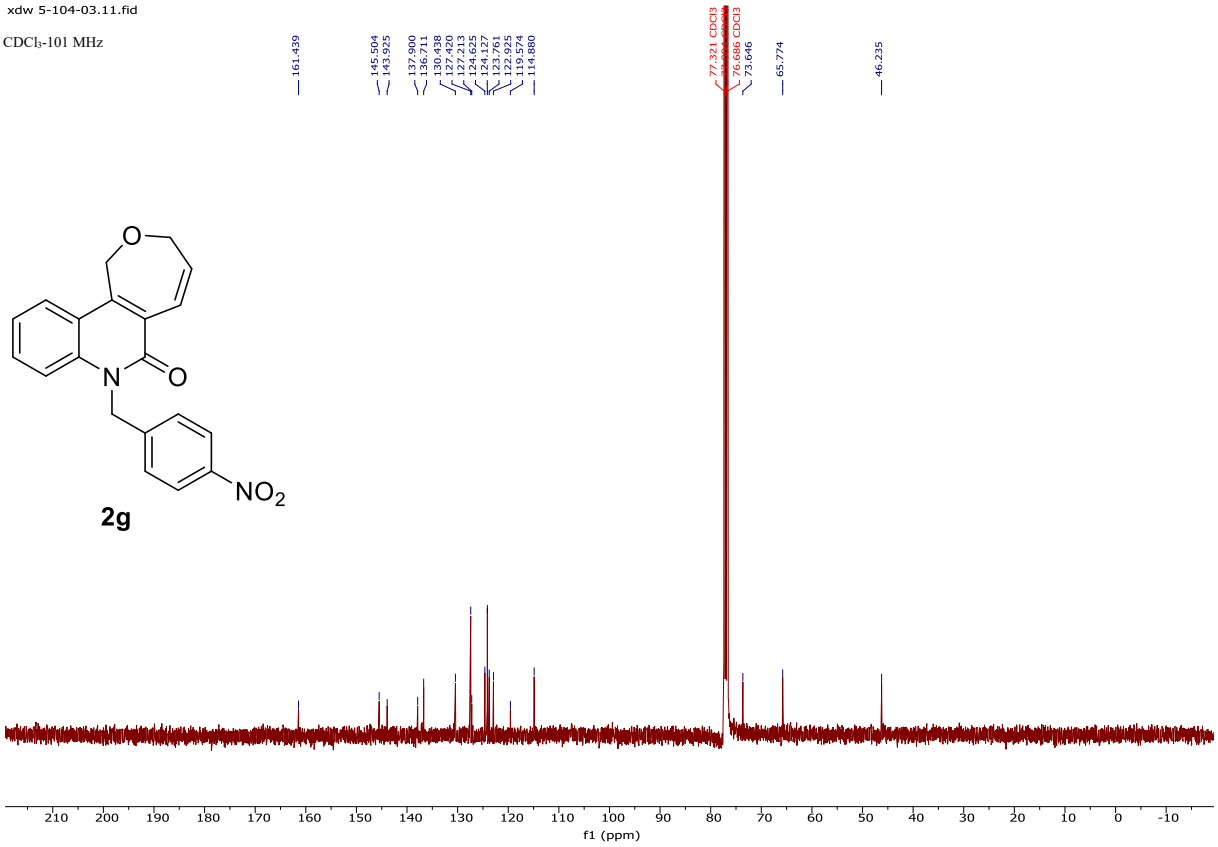
xdw 5-101 photo.10.fid

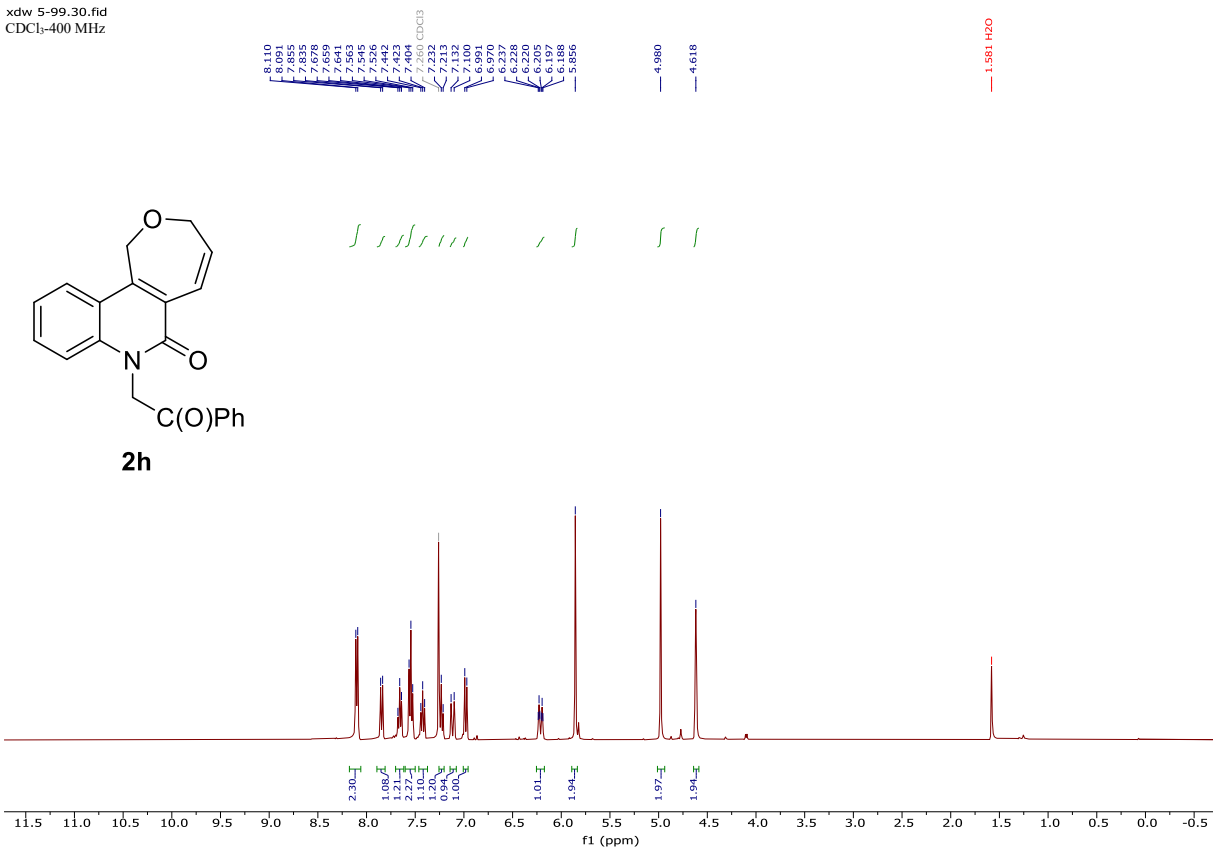
$CDCl_3$-400 MHz

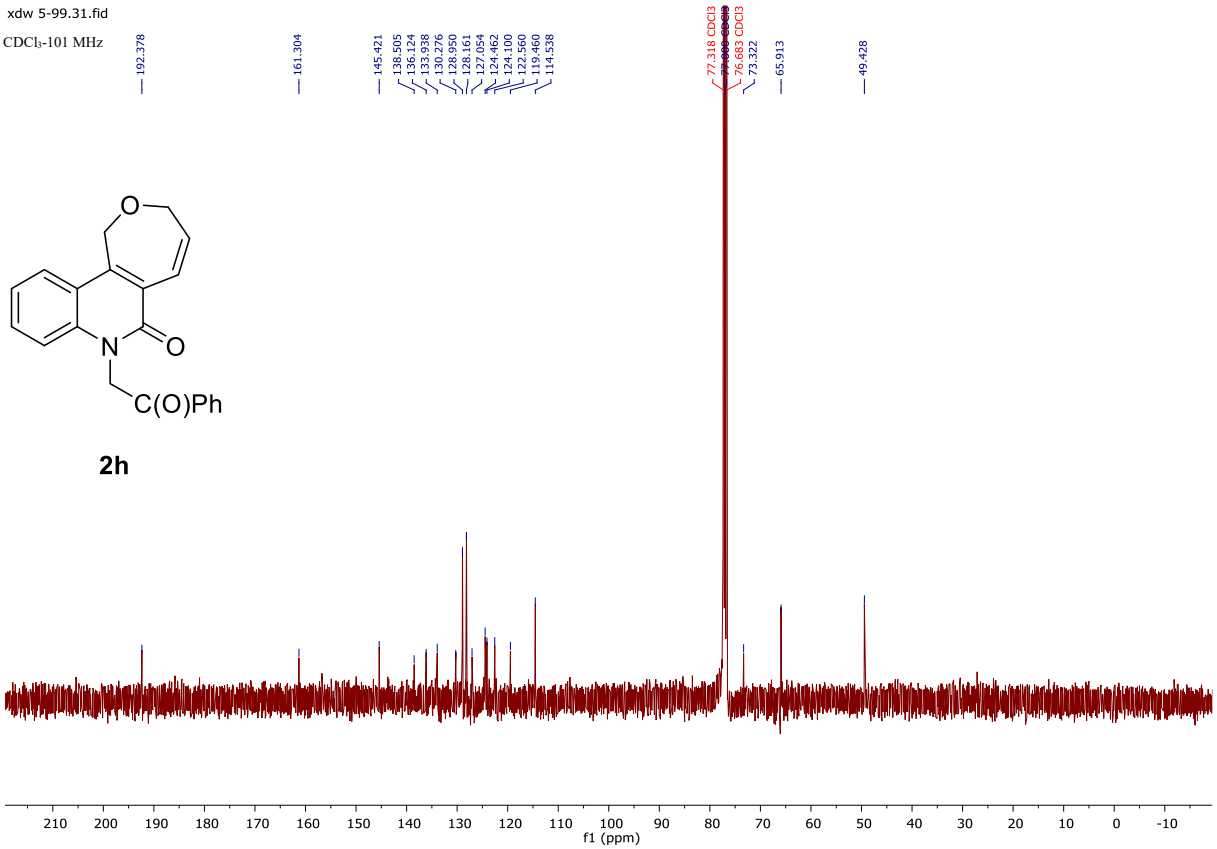


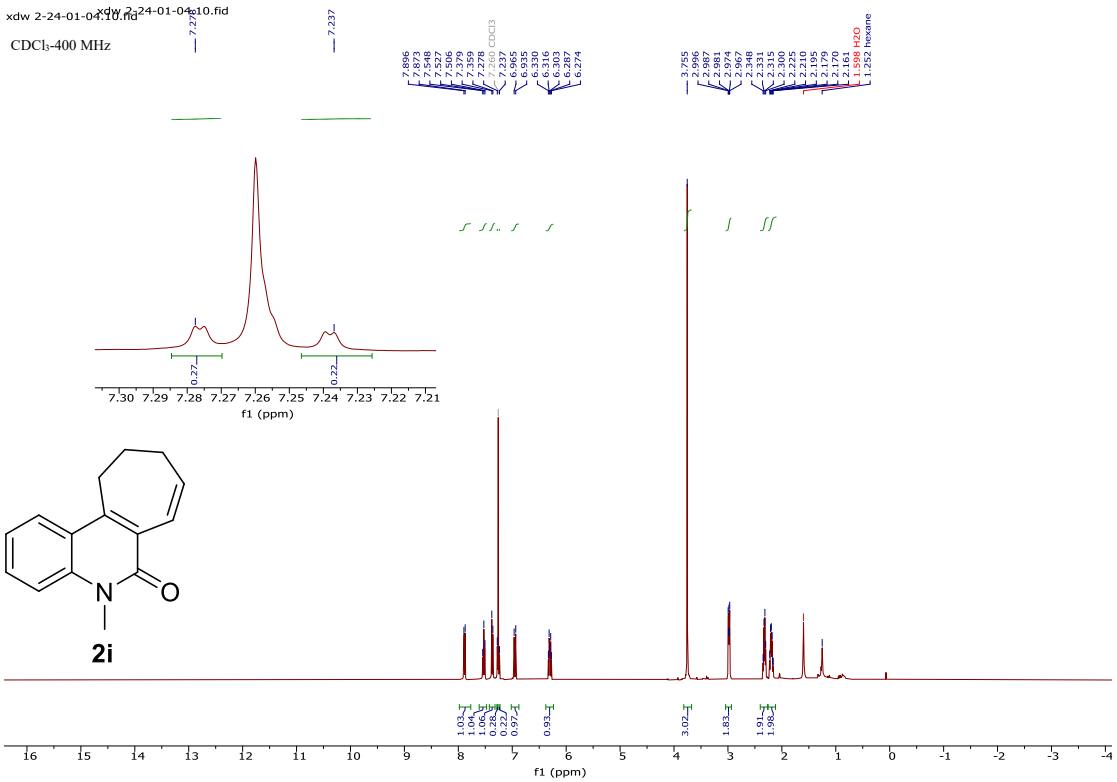

xdw 5-101 photo.11.fid
CDCl3-101 MHz
161.425
145.438
141.879
137.298
136.637
132.653
130.401
127.290
127.187
124.560
123.769
122.858
119.528
118.563
114.913
111.335
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
73.616
65.748
46.370
O
N
O
CN
2f
f1 (ppm)


xdw 5-104-02.10.fid
CDCl3-400 MHz
8.177
8.156
7.877
7.856
7.434
7.361
7.260 CDCl3
7.235
7.171
7.108
6.287
6.280
6.273
6.256
6.248
6.240
5.691
4.996
4.655
1.558 H2O
2.02
1.08
3.15
1.02
1.85
1.07
2.13
1.92
1.99
O
N
O
NO2
2g
f1 (ppm)


xdw 5-104-03.11.fid
CDCl3-101 MHz
161.439
145.504
143.925
137.900
136.711
130.438
127.420
127.213
124.435
124.127
123.761
122.925
119.574
114.880
77.321 CDCl3
77.000 CDCl3
76.686 CDCl3
73.646
65.774
46.235
O
N
O
NO2
2g
f1 (ppm)

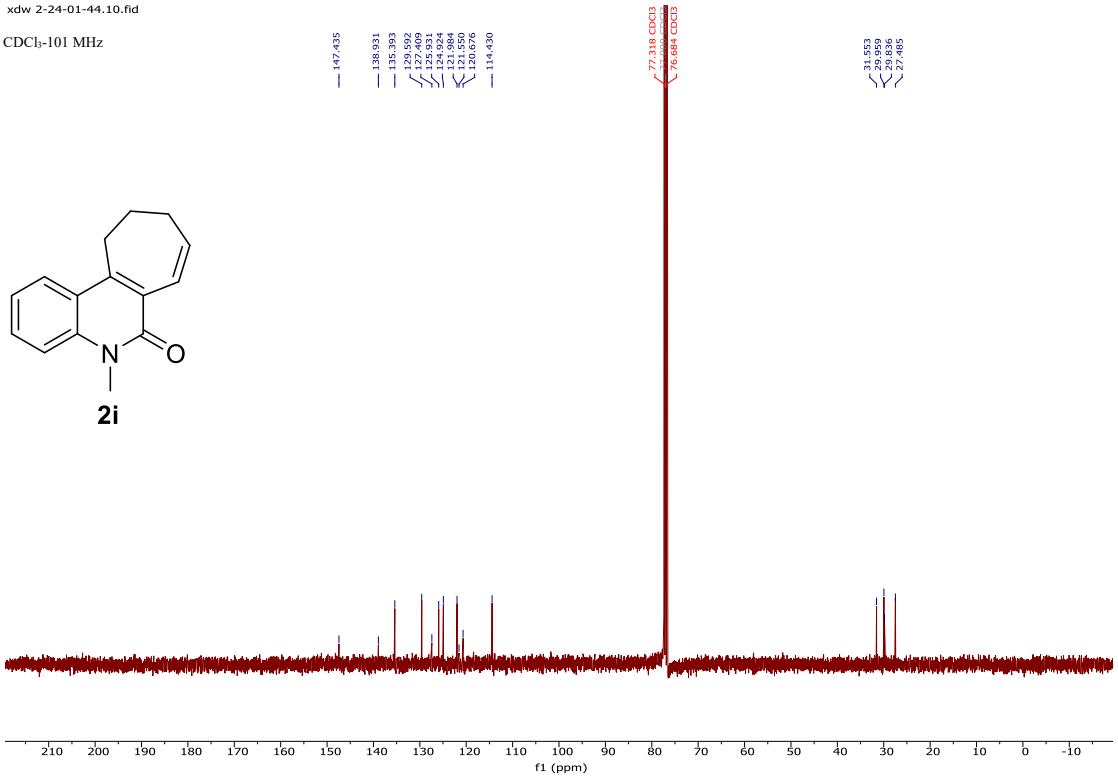

xdw 5-99.30.fid
CDCl3-400 MHz
8.110
8.091
7.865
7.835
7.678
7.659
7.641
7.563
7.545
7.526
7.442
7.423
7.404
7.260 CDCl3
7.232
7.213
7.132
7.100
6.991
6.970
6.237
6.228
6.220
6.205
6.197
6.188
5.856
4.980
4.618
1.581 H2O
O
N
O
C(O)Ph
2h
2.30
1.08
1.21
2.27
1.10
1.20
0.84
1.00
1.01
1.94
1.97
1.94
f1 (ppm)


xdw 5-99.31.fid
CDCl3-101 MHz
192.378
161.304
145.421
138.505
136.124
133.938
130.276
128.950
128.161
127.054
124.462
124.100
122.560
119.460
114.538
77.318 CDCl3
76.683 CDCl3
73.322
65.913
49.428
O
N
O
C(O)Ph
2h
f1 (ppm)


xdw 2-24-01-04-10.fid
CDCl3-400 MHz
7.237
7.260 CDCl3
1.598 H2O
1.252 hexane
0.27
0.22
f1 (ppm)
N
O
2i
f1 (ppm)

xdw 2-24-01-44.10.fid

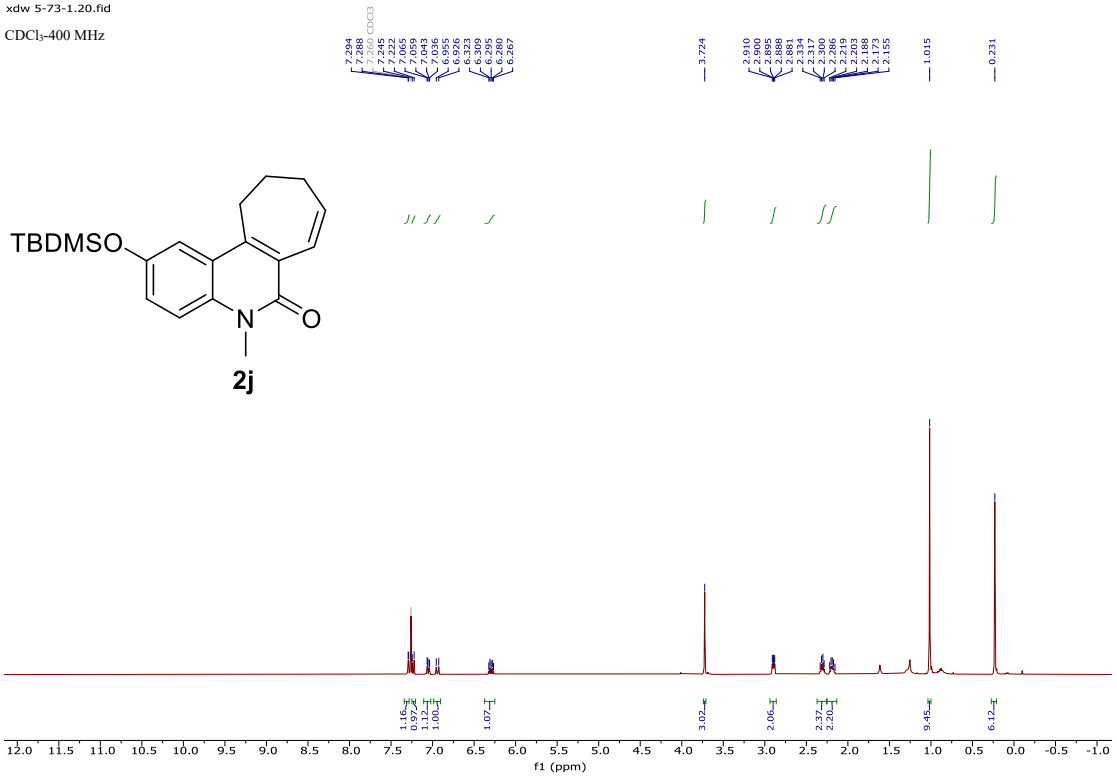
$CDCl_3$-101 MHz



2i

xdw 5-73-1.20.fid

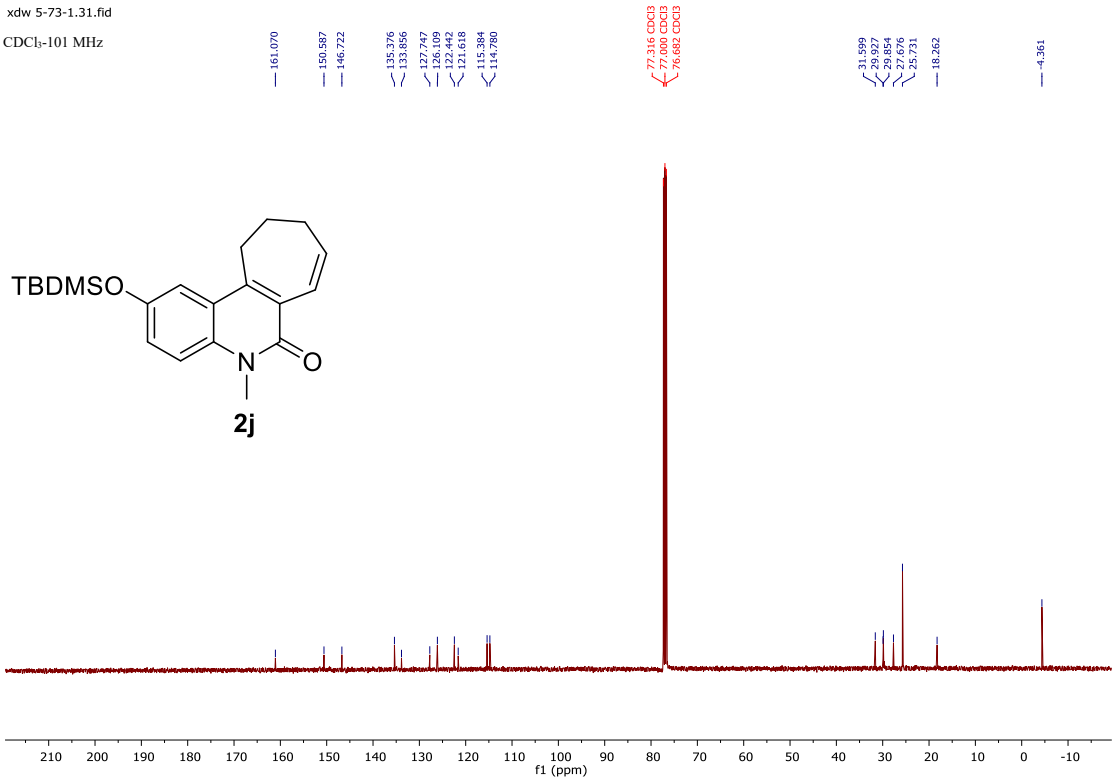
$CDCl_3$-400 MHz



2j

xdw 5-73-1.31.fid

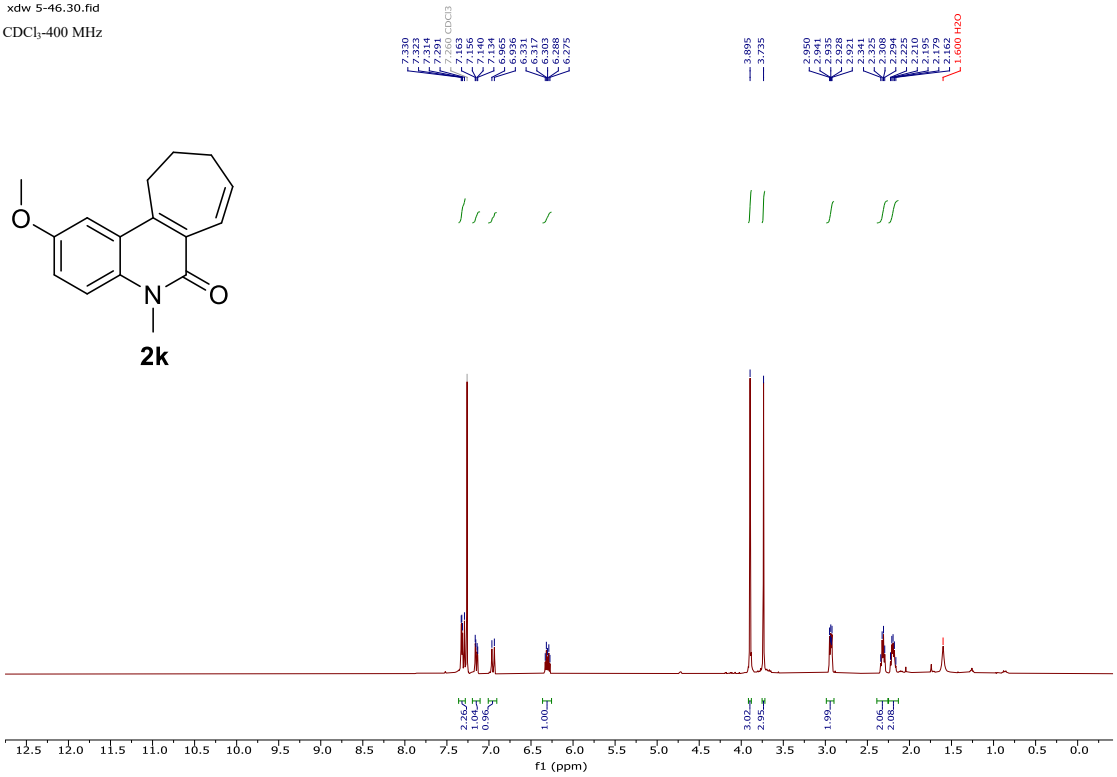
$CDCl_3$-101 MHz



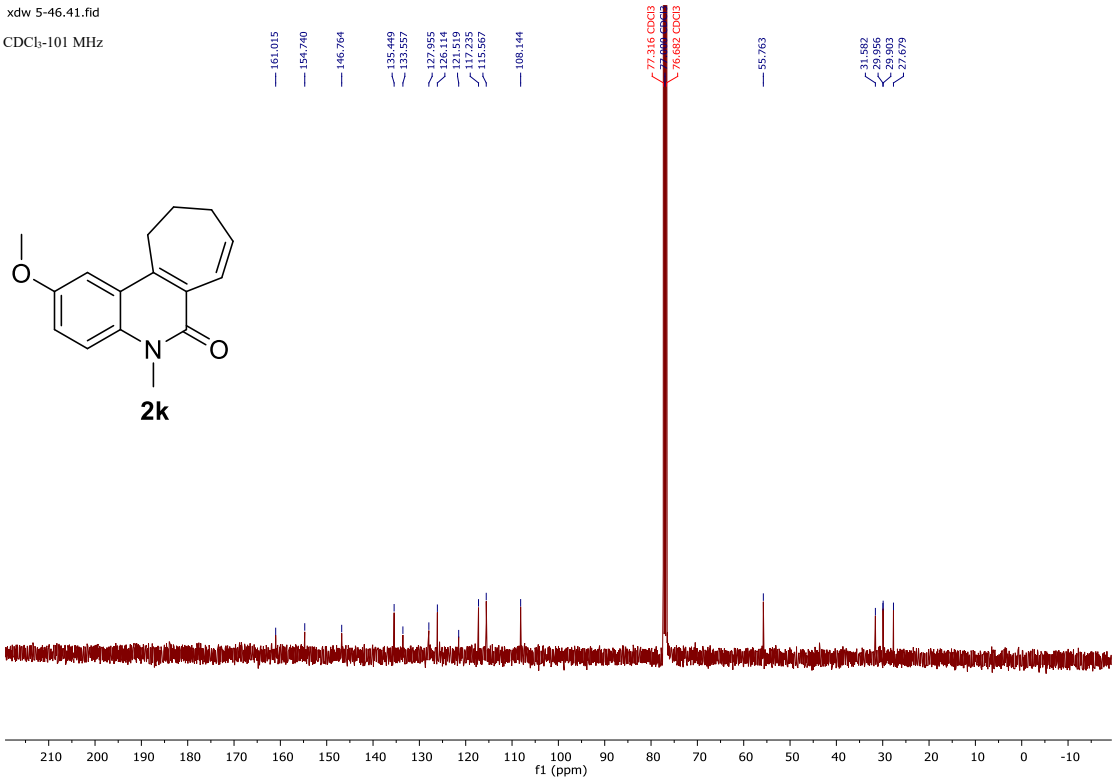
2j

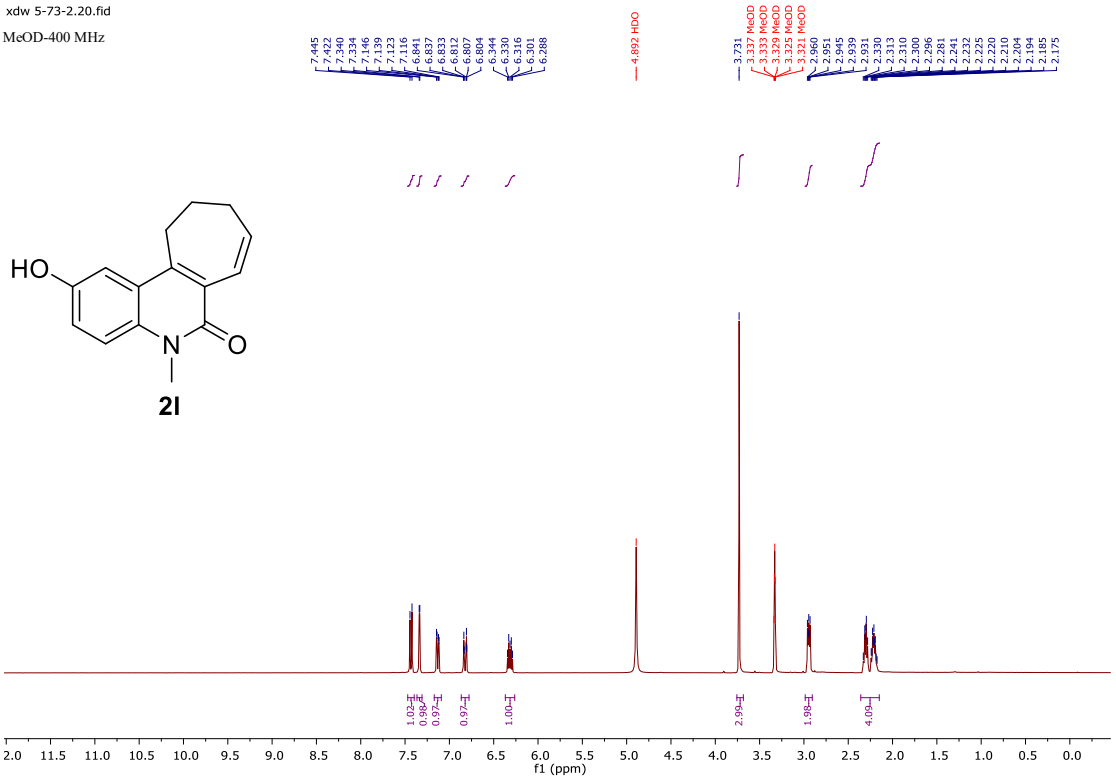
xdw 5-46.30.fid

$CDCl_3$-400 MHz



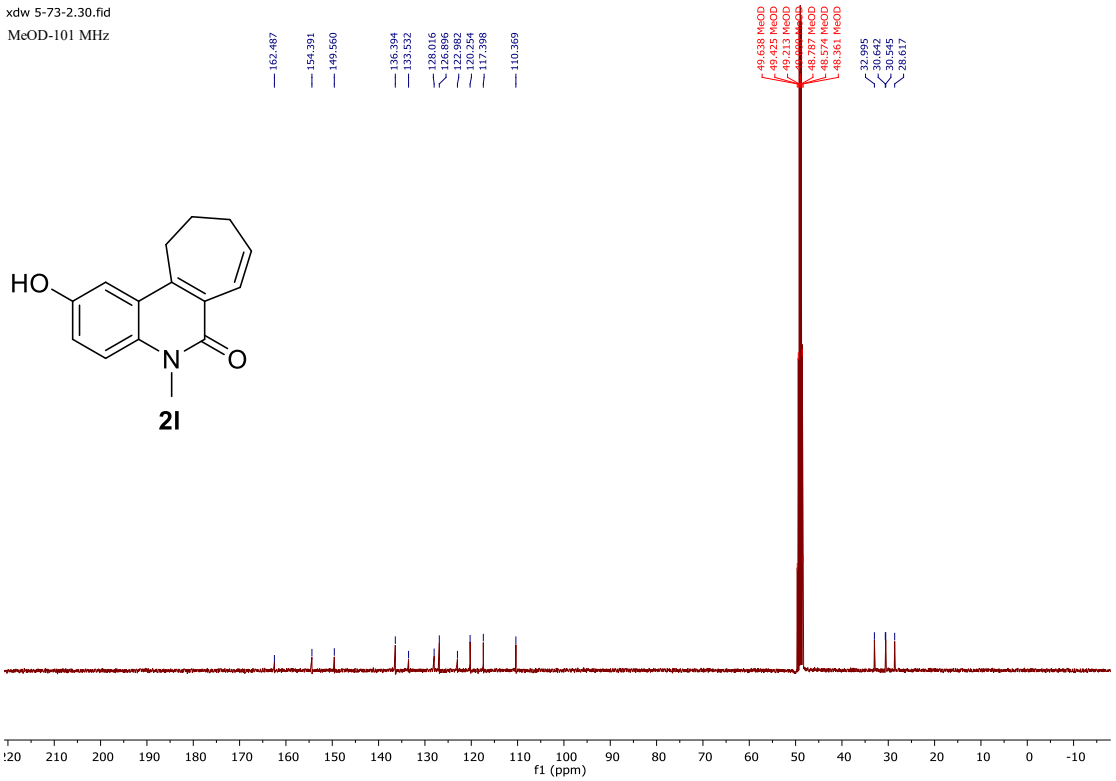
2k


xdw 5-46.41.fid
CDCl3-101 MHz
161.015
154.740
146.764
135.449
133.557
127.955
126.114
121.519
117.235
115.567
108.144
77.316 CDCl3
76.682 CDCl3
55.763
31.582
29.956
29.903
27.679
O
N
O
2k
f1 (ppm)


xdw 5-73-2.20.fid
MeOD-400 MHz
7.445
7.422
7.340
7.334
7.146
7.139
7.123
7.116
7.041
6.837
6.833
6.812
6.807
6.804
6.344
6.330
6.316
6.301
6.288
4.892 HDO
3.731
3.337 MeOD
3.333 MeOD
3.329 MeOD
3.325 MeOD
3.321 MeOD
2.960
2.951
2.945
2.939
2.931
2.330
2.313
2.310
2.300
2.296
2.281
2.241
2.232
2.225
2.220
2.210
2.204
2.194
2.185
2.175
1.02
0.98
0.97
0.97
1.00
2.99
1.98
4.09
HO
N
O
2l
f1 (ppm)

xdw 5-73-2.30.fid

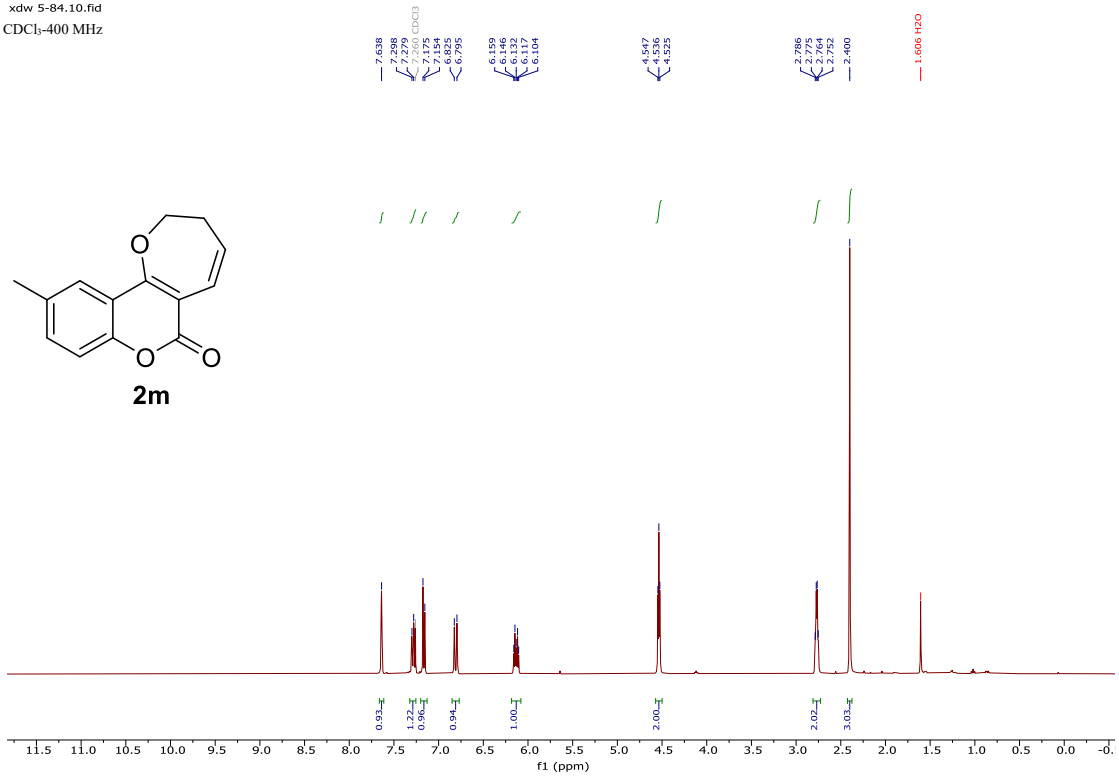
MeOD-101 MHz



2l

xdw 5-84.10.fid

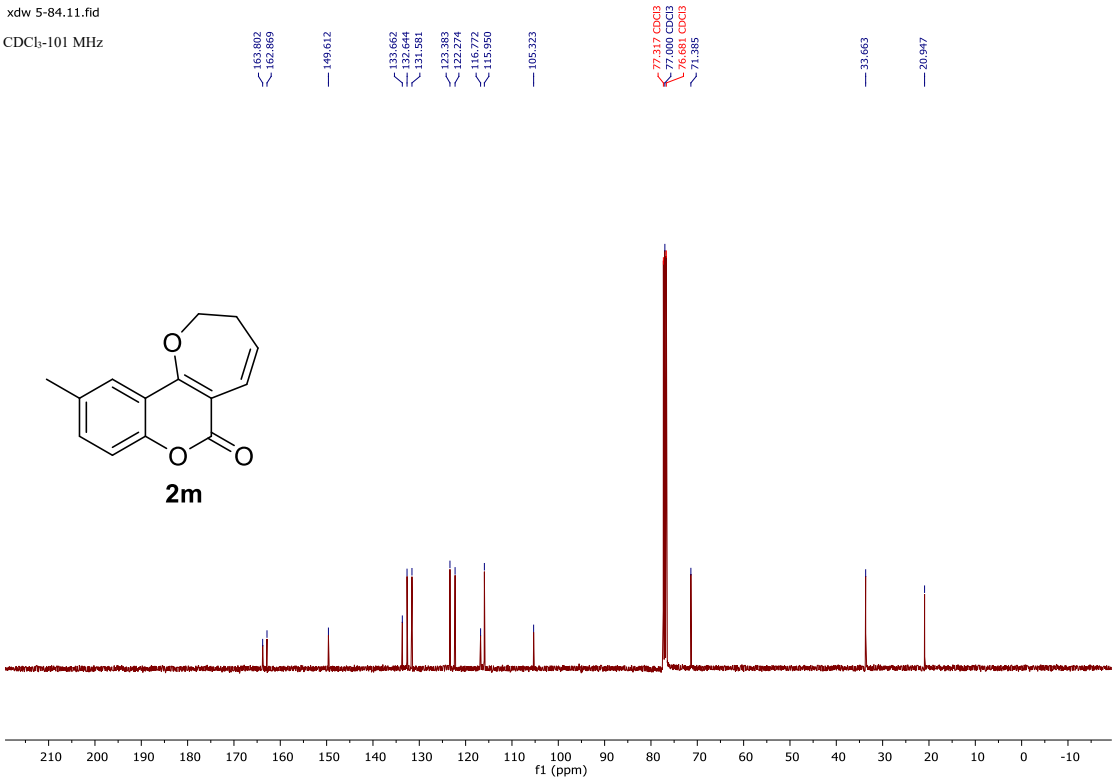
$CDCl_3$-400 MHz



2m

xdw 5-84.11.fid

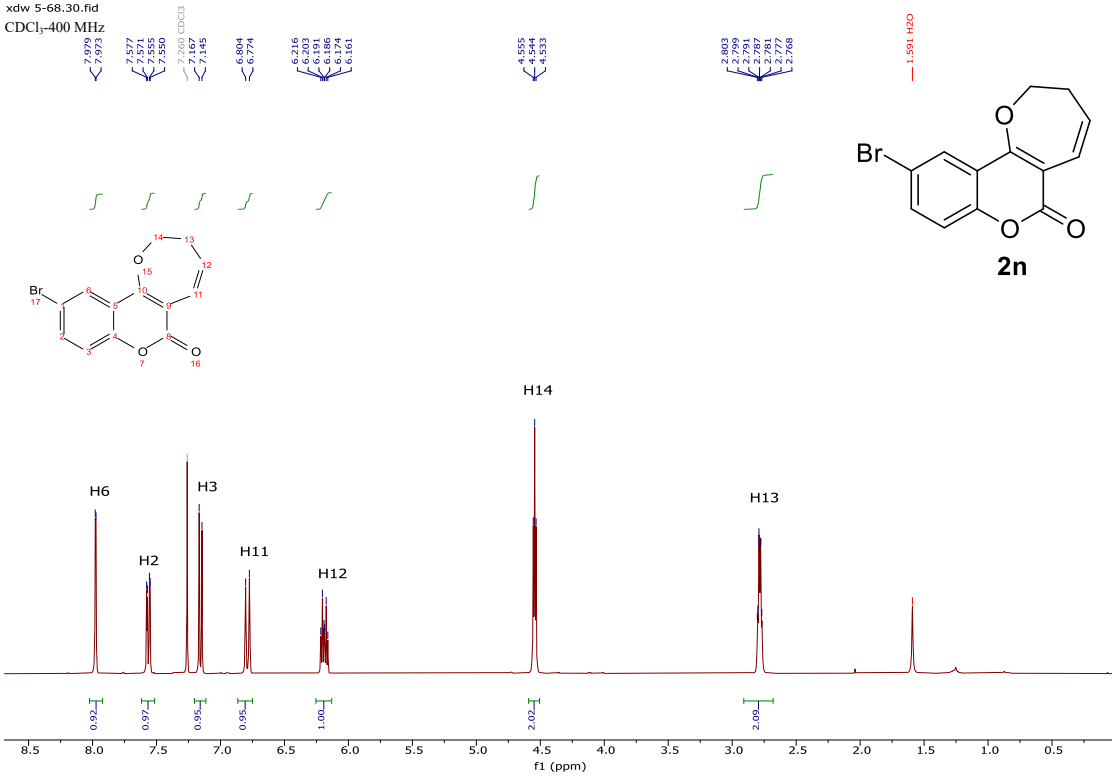
$CDCl_3$-101 MHz



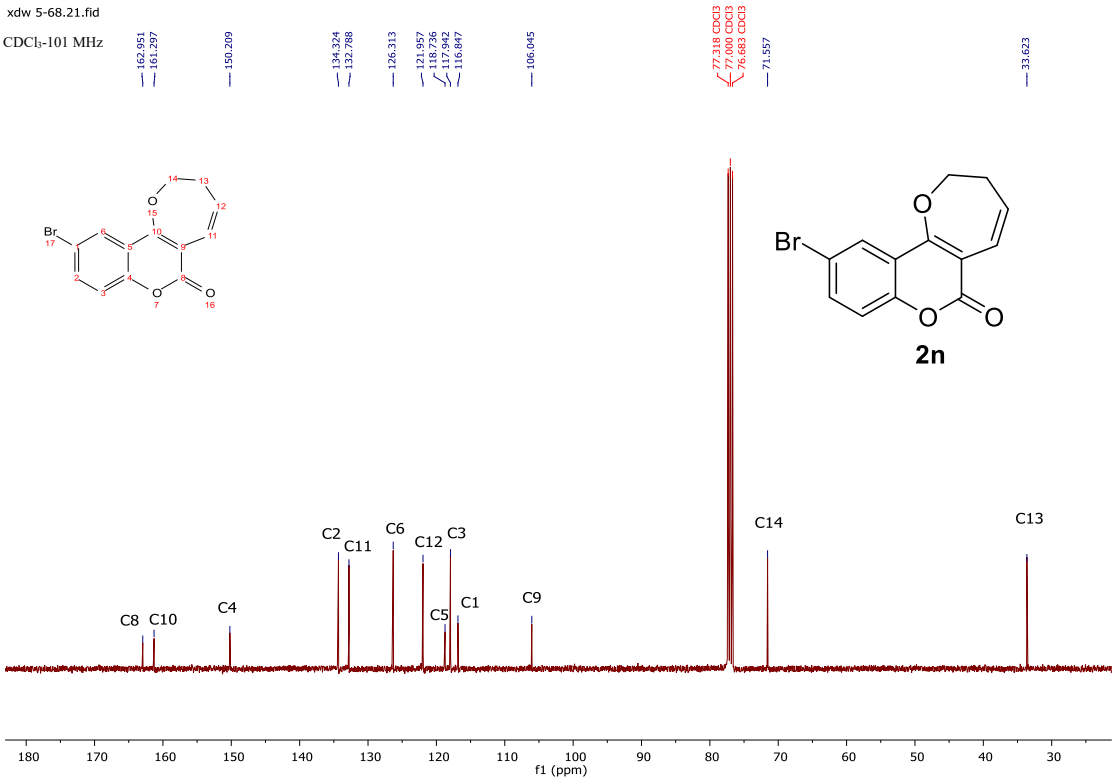
2m

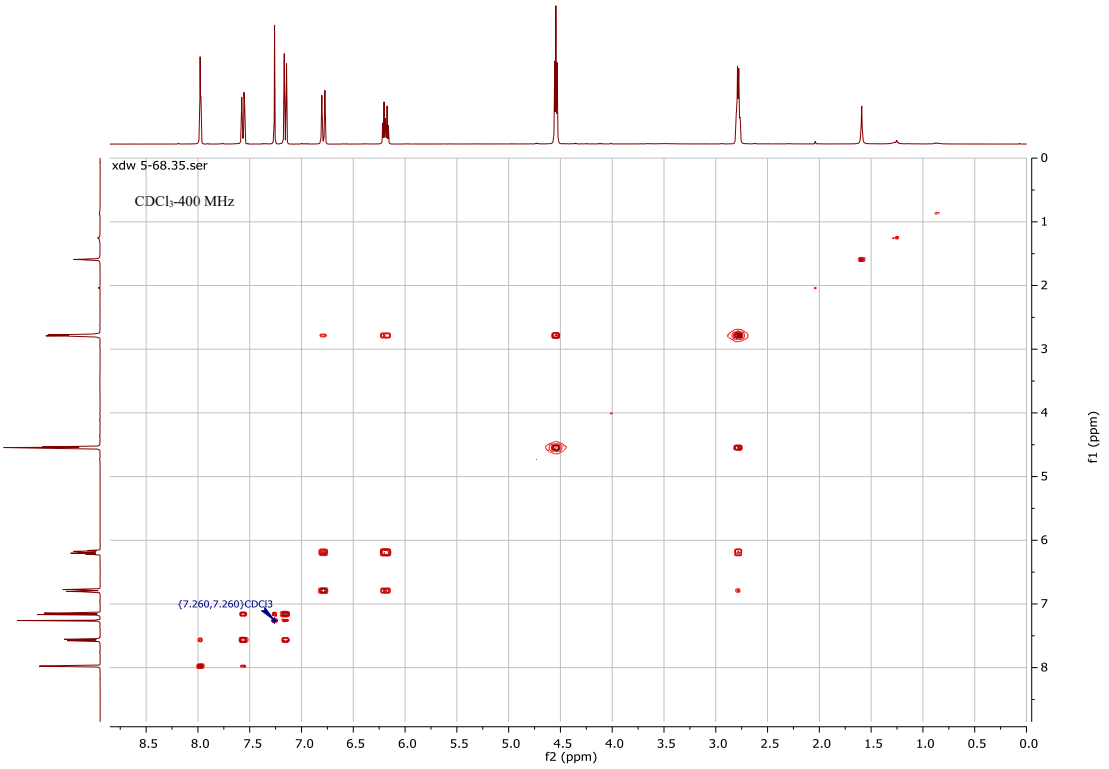
xdw 5-68.30.fid

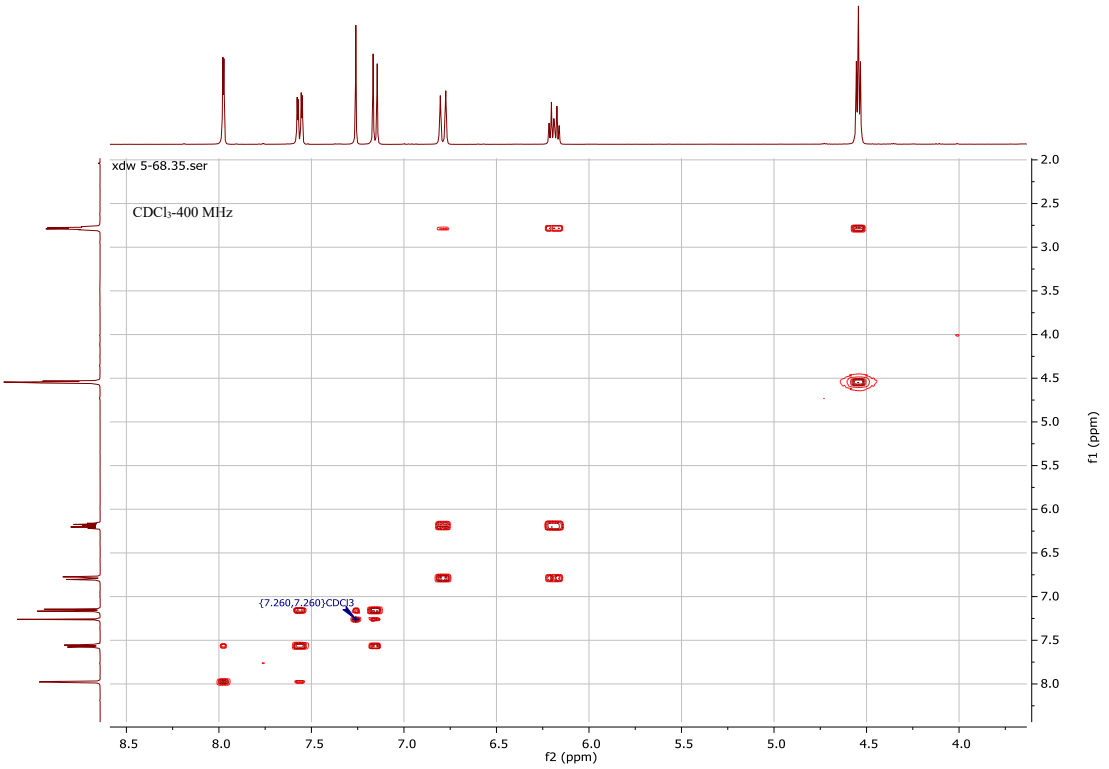
$CDCl_3$-400 MHz



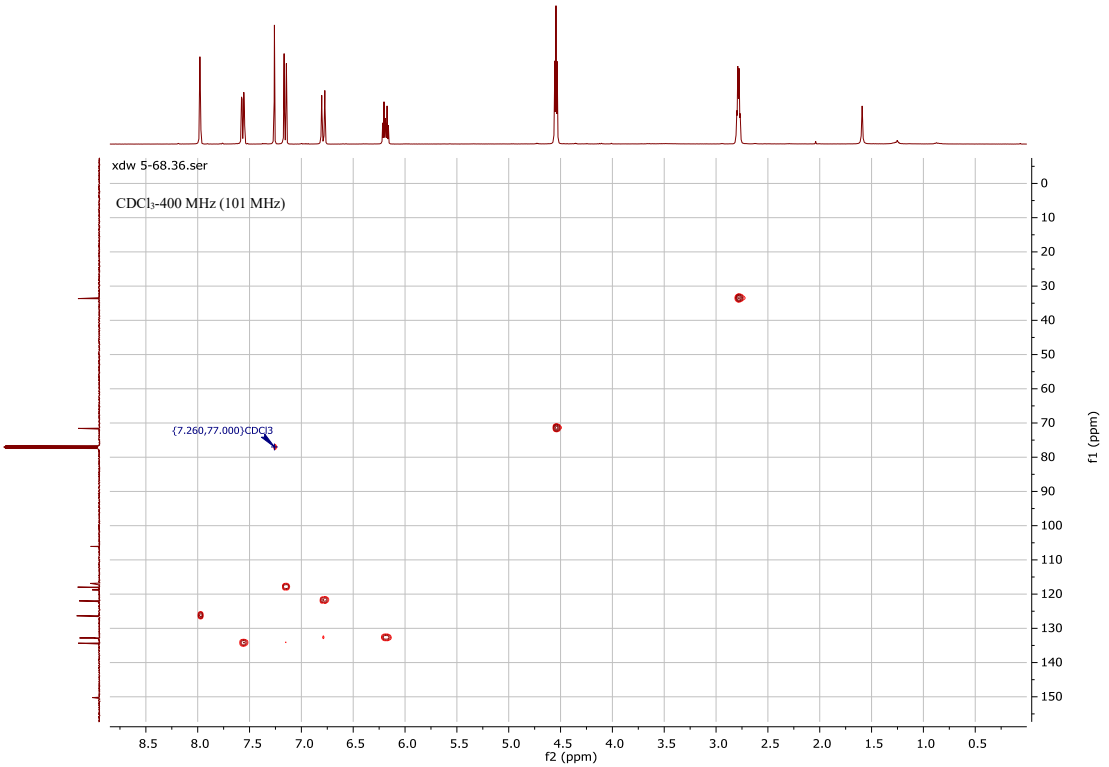
2n

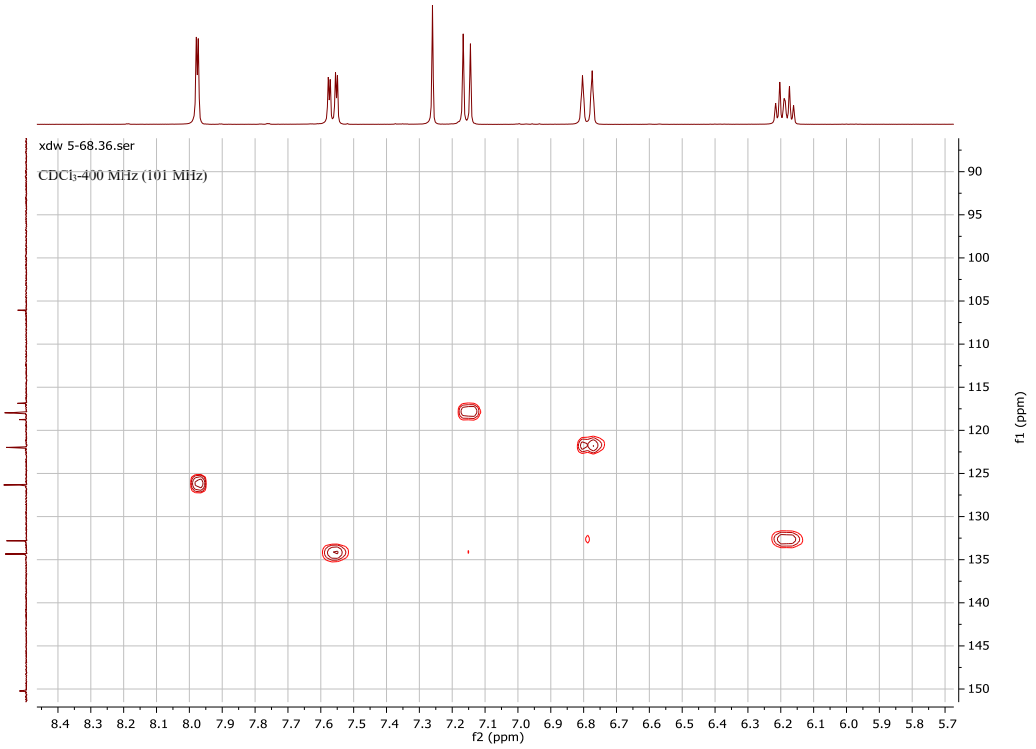

xdw 5-68.21.fid
CDCl3-101 MHz
162.951
161.297
150.209
134.324
132.788
126.313
121.957
118.736
117.943
116.847
106.045
77.318 CDCl3
77.000 CDCl3
76.683 CDCl3
71.557
33.623
Br
O
O
O
2n
C8
C10
C4
C2
C11
C6
C12
C3
C5
C1
C9
C14
C13
f1 (ppm)


xdw 5-68.35.ser
CDCl3-400 MHz
{7.260,7.260}CDCl3
f2 (ppm)
f1 (ppm)

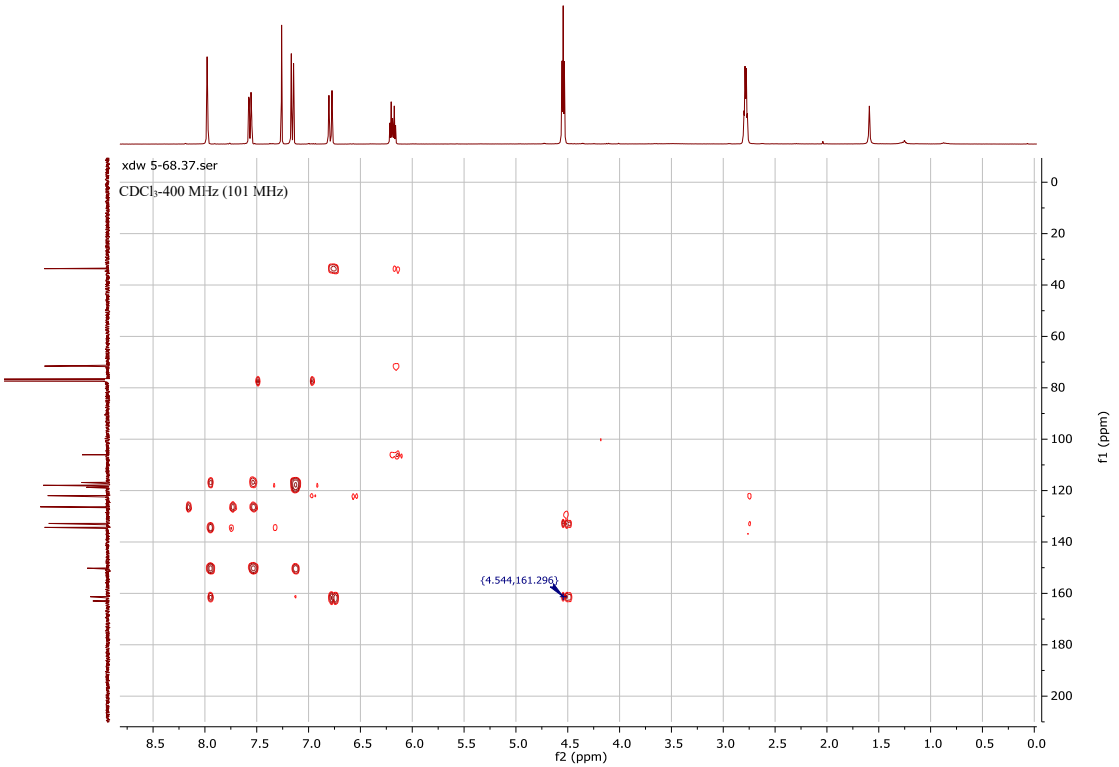


COSY spectrum of **2n**

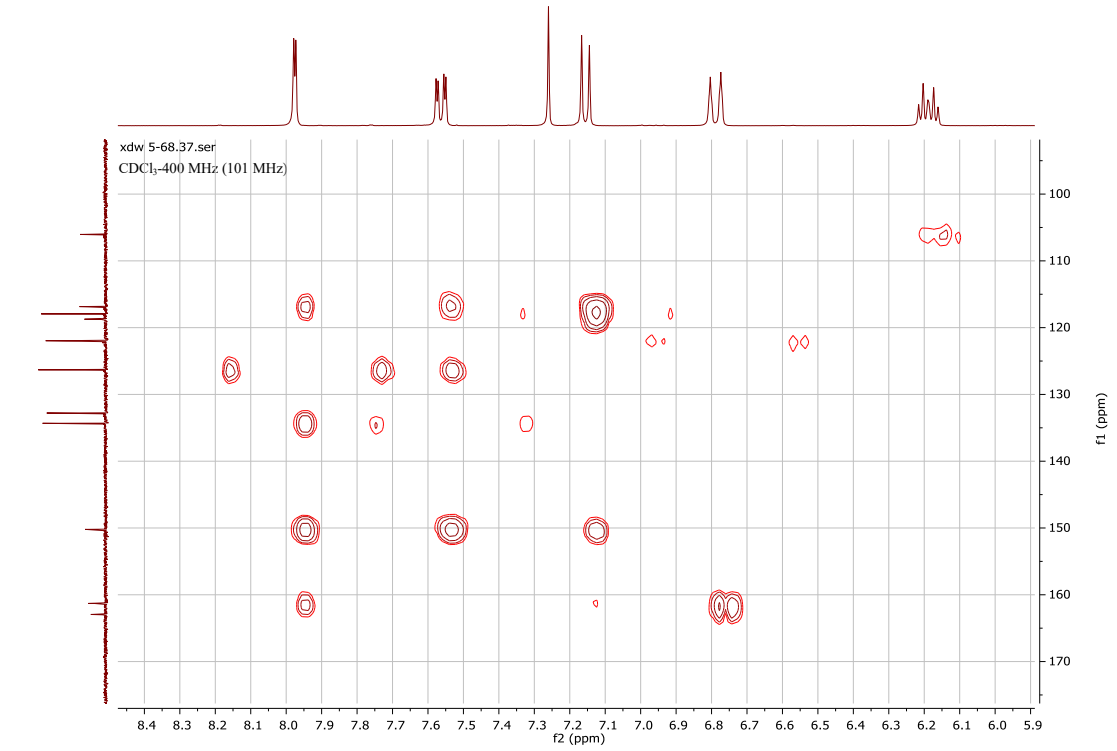


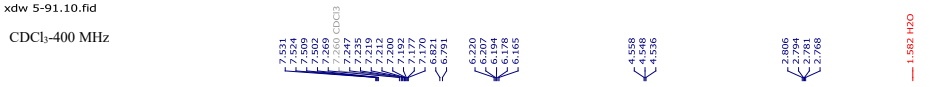


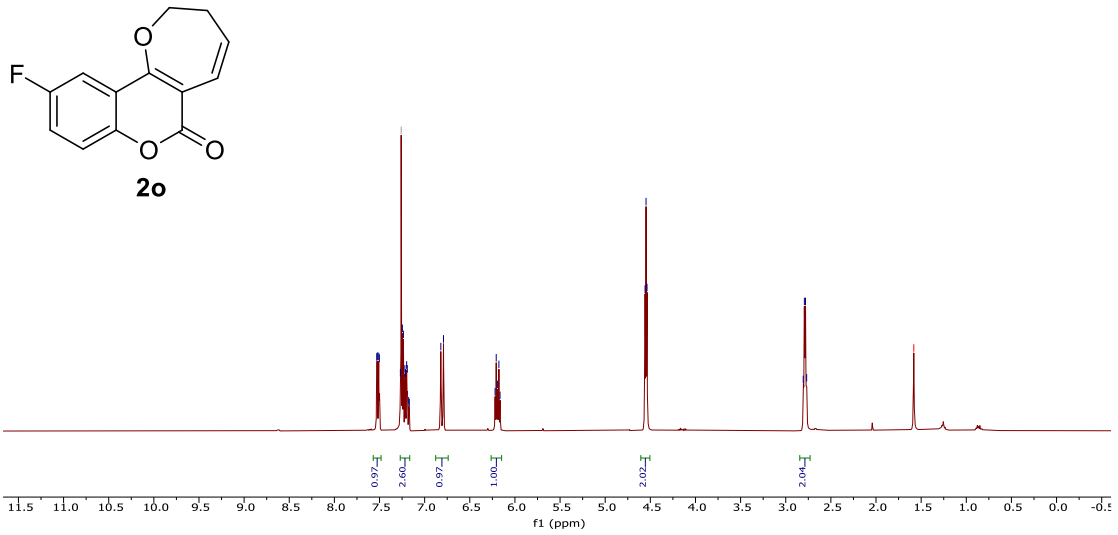
HSQC spectrum of **2n**

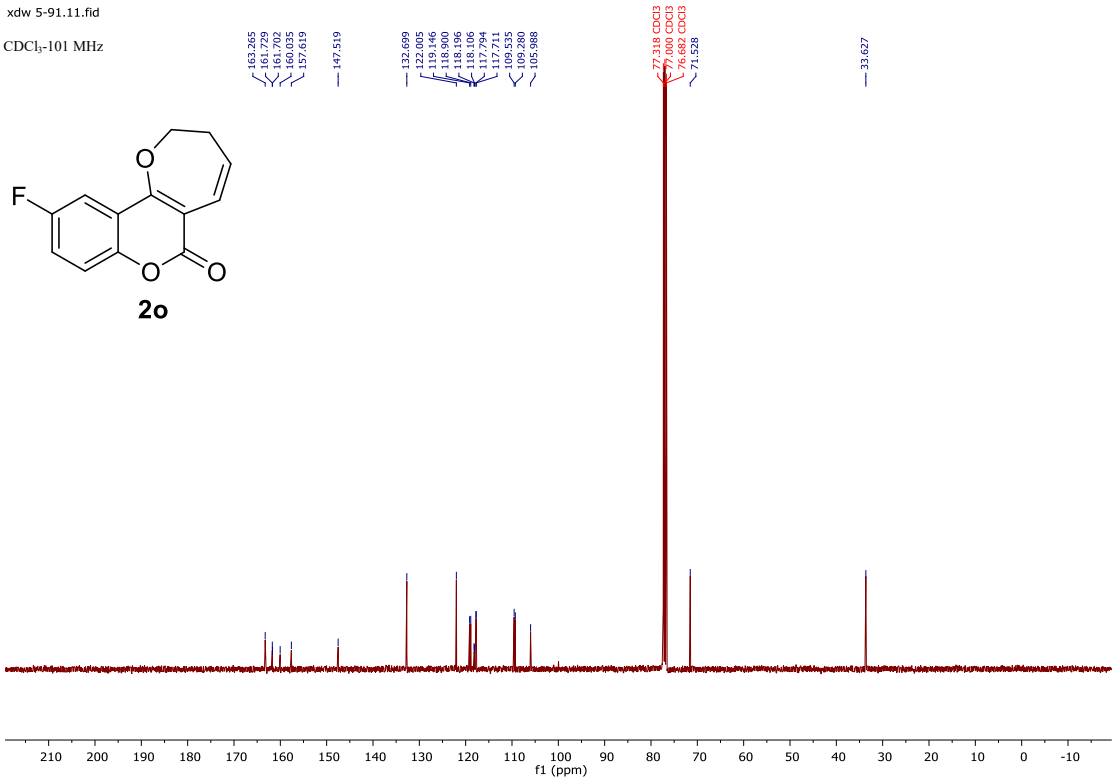


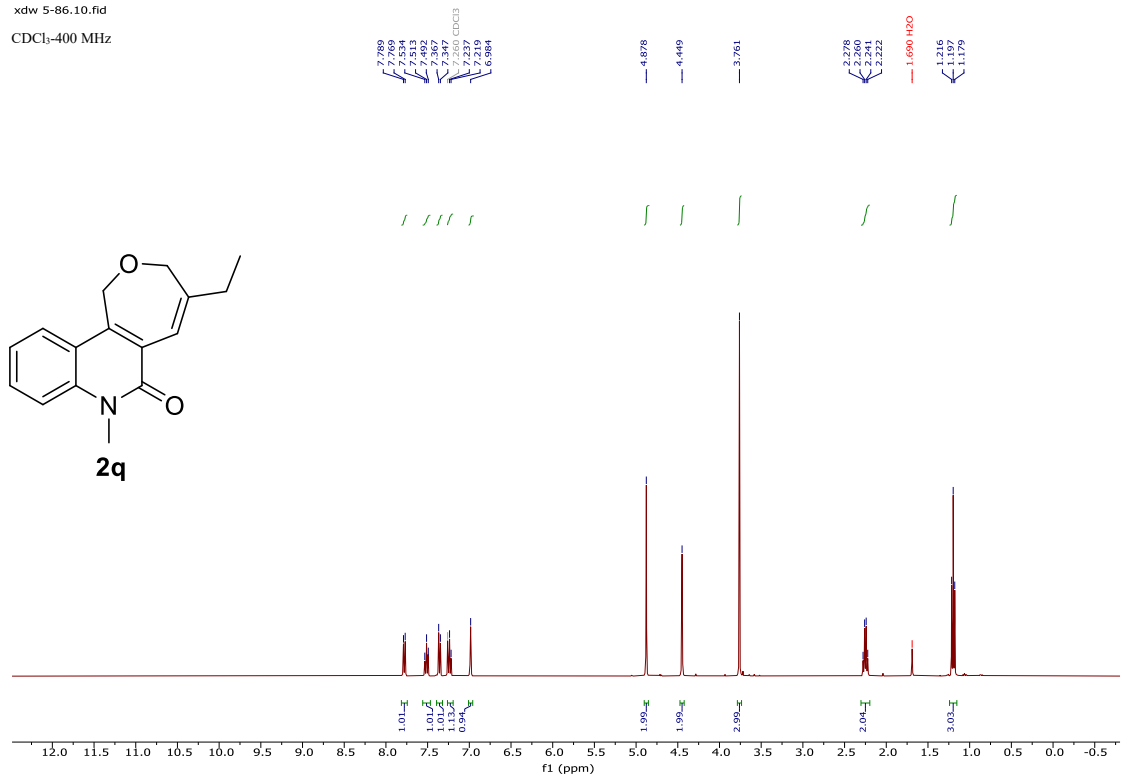
HMBC spectrum of **2n**





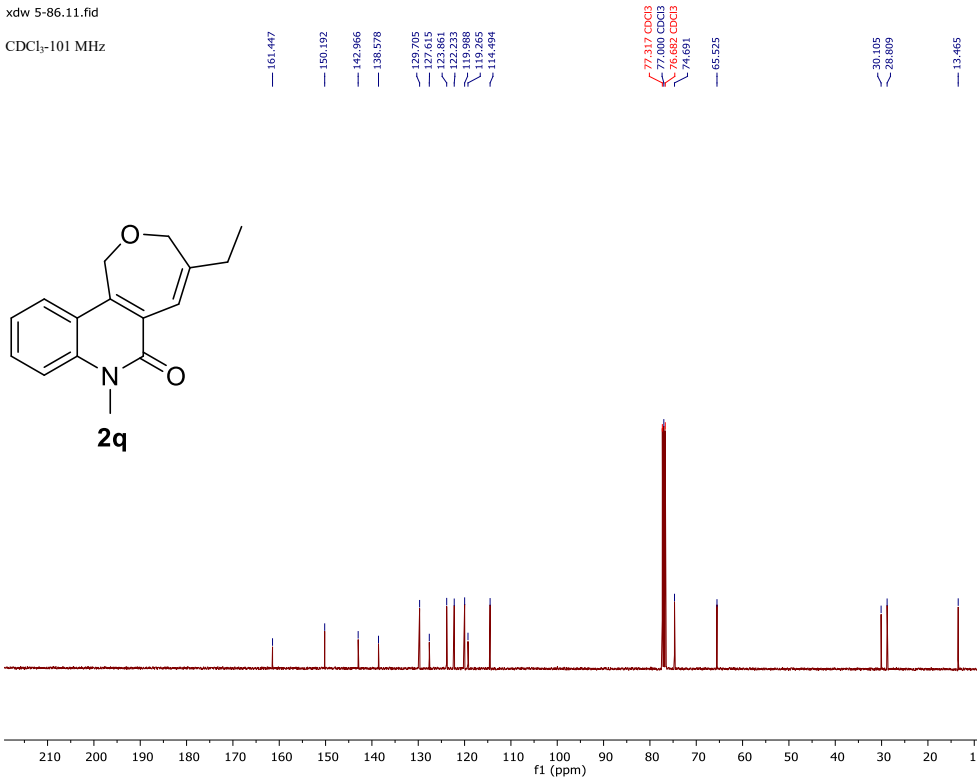



xdw 5-91.11.fid
CDCl3-101 MHz
163.265
161.729
161.702
160.035
157.619
147.519
132.699
122.005
119.146
118.900
118.196
118.106
117.794
117.711
109.535
109.280
105.988
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
71.528
33.627
F
O
O
O
2o
f1 (ppm)


xdw 5-86.10.fid
CDCl3-400 MHz
7.789
7.769
7.534
7.513
7.492
7.367
7.347
7.260 CDCl3
7.237
7.219
6.984
4.878
4.449
3.761
2.278
2.260
2.241
2.222
1.690 H2O
1.216
1.197
1.179
1.01
1.01
1.01
1.13
0.94
1.99
1.99
2.99
2.04
3.03
O
N
O
2q
f1 (ppm)

xdw 5-86.11.fid

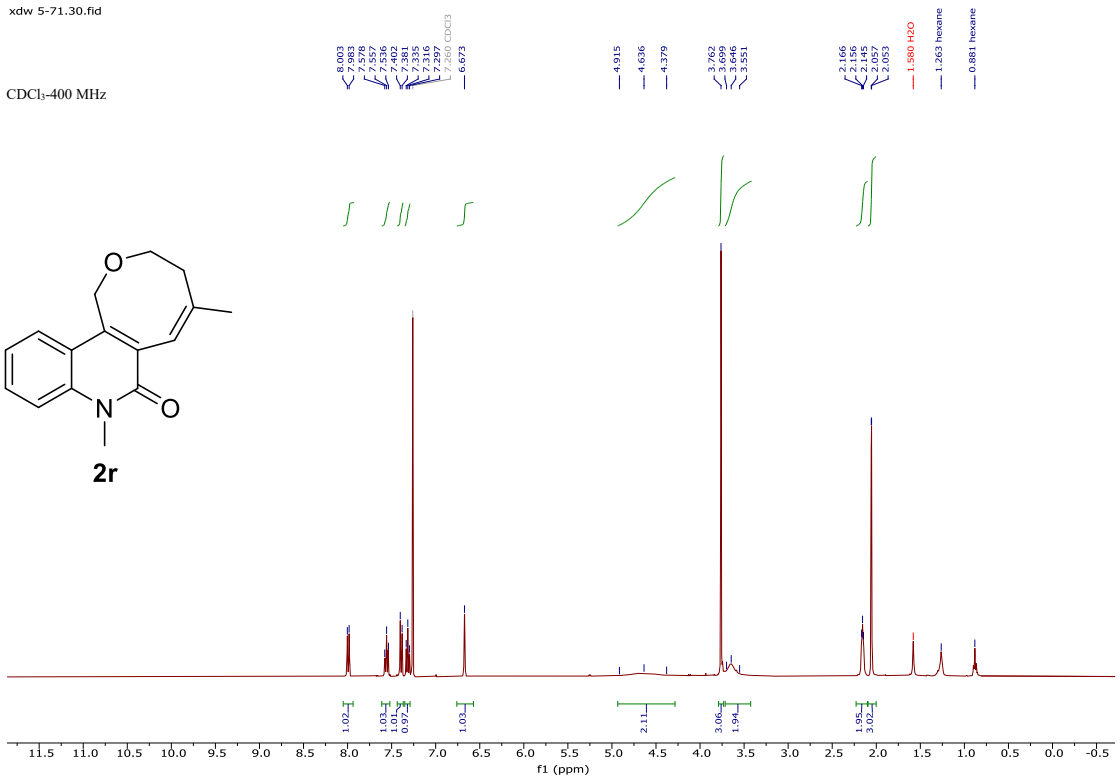
$CDCl_3$-101 MHz



2q

xdw 5-71.30.fid

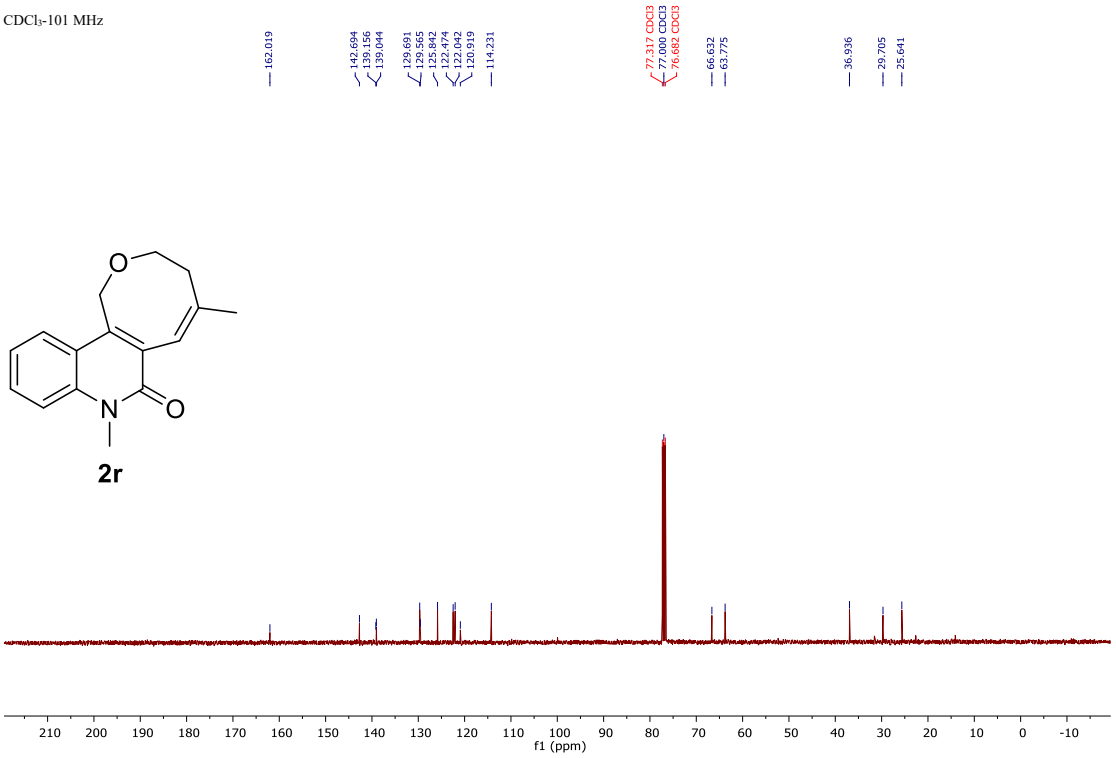
$CDCl_3$-400 MHz



2r

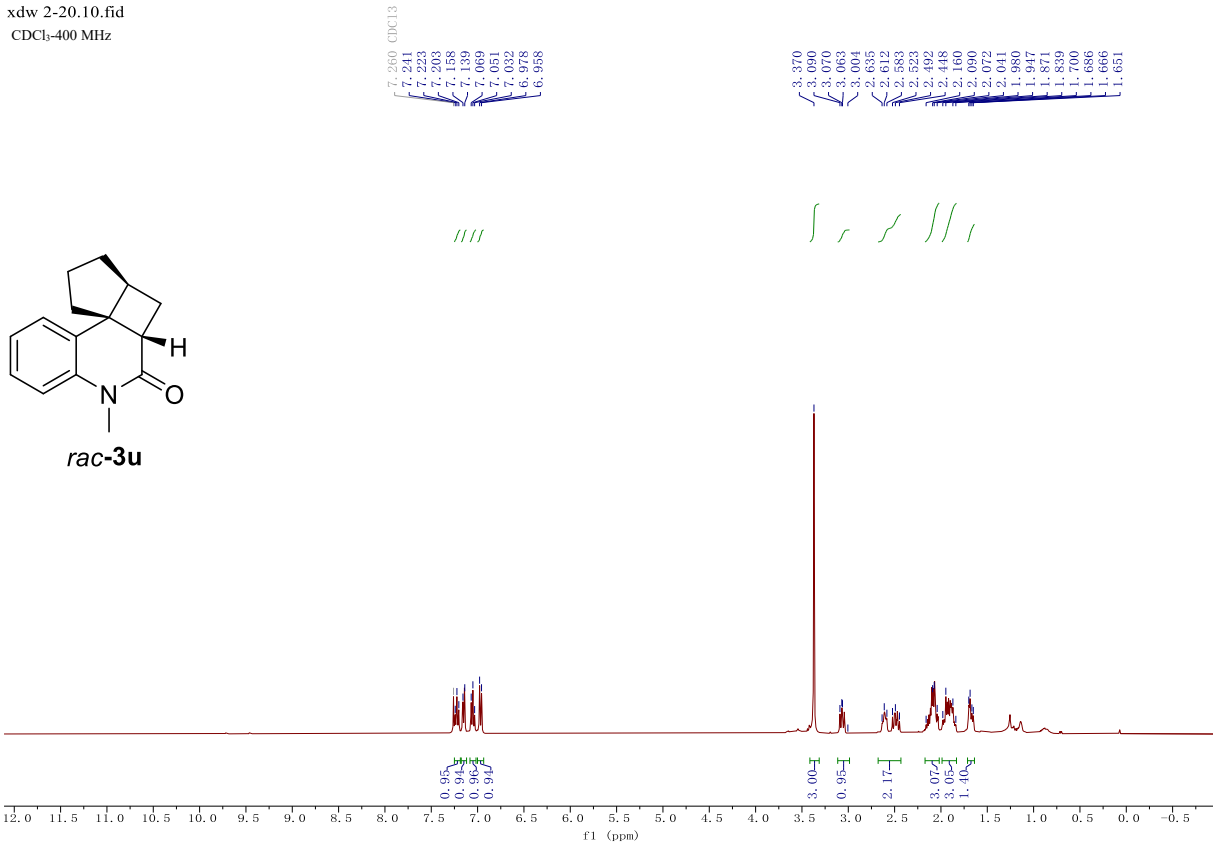
xdw 5-71.21.fid

$CDCl_3$-101 MHz



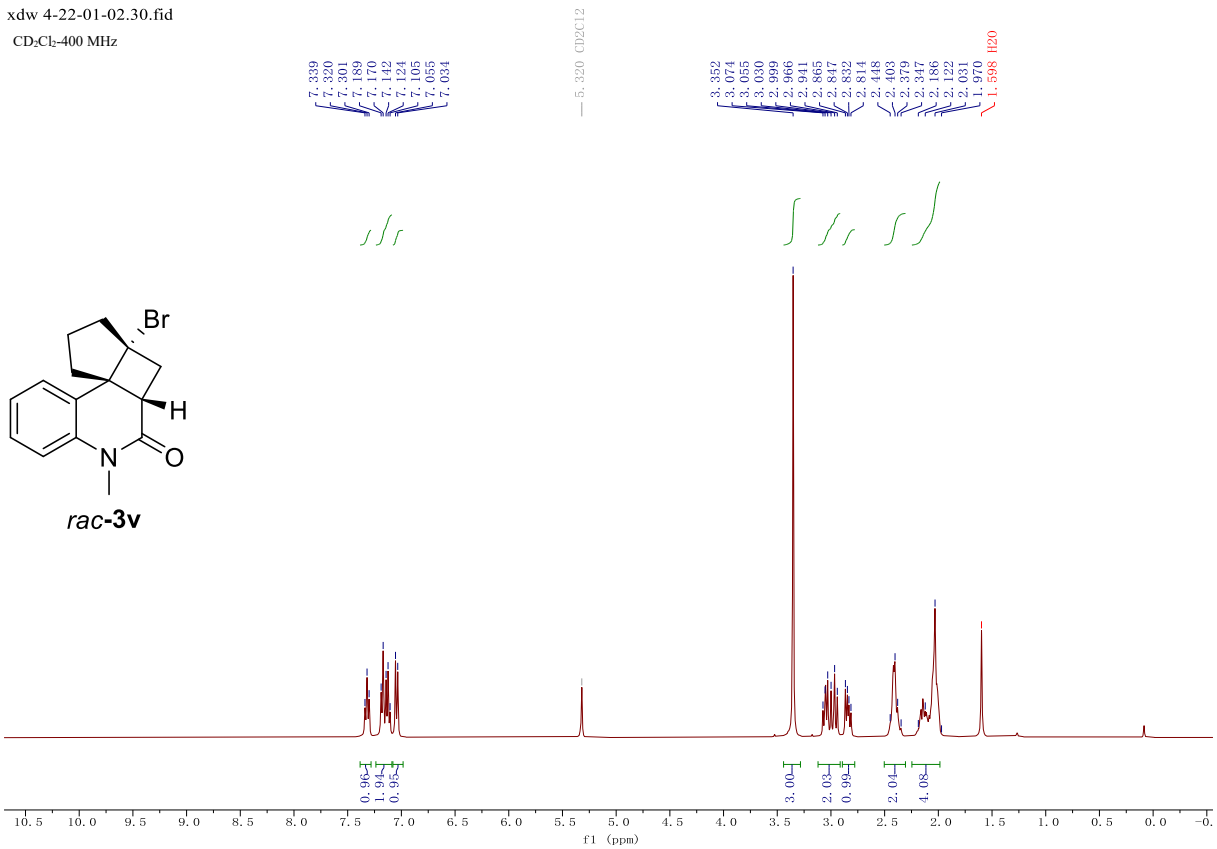
xdw 2-20.10.fid

$CDCl_3$-400 MHz



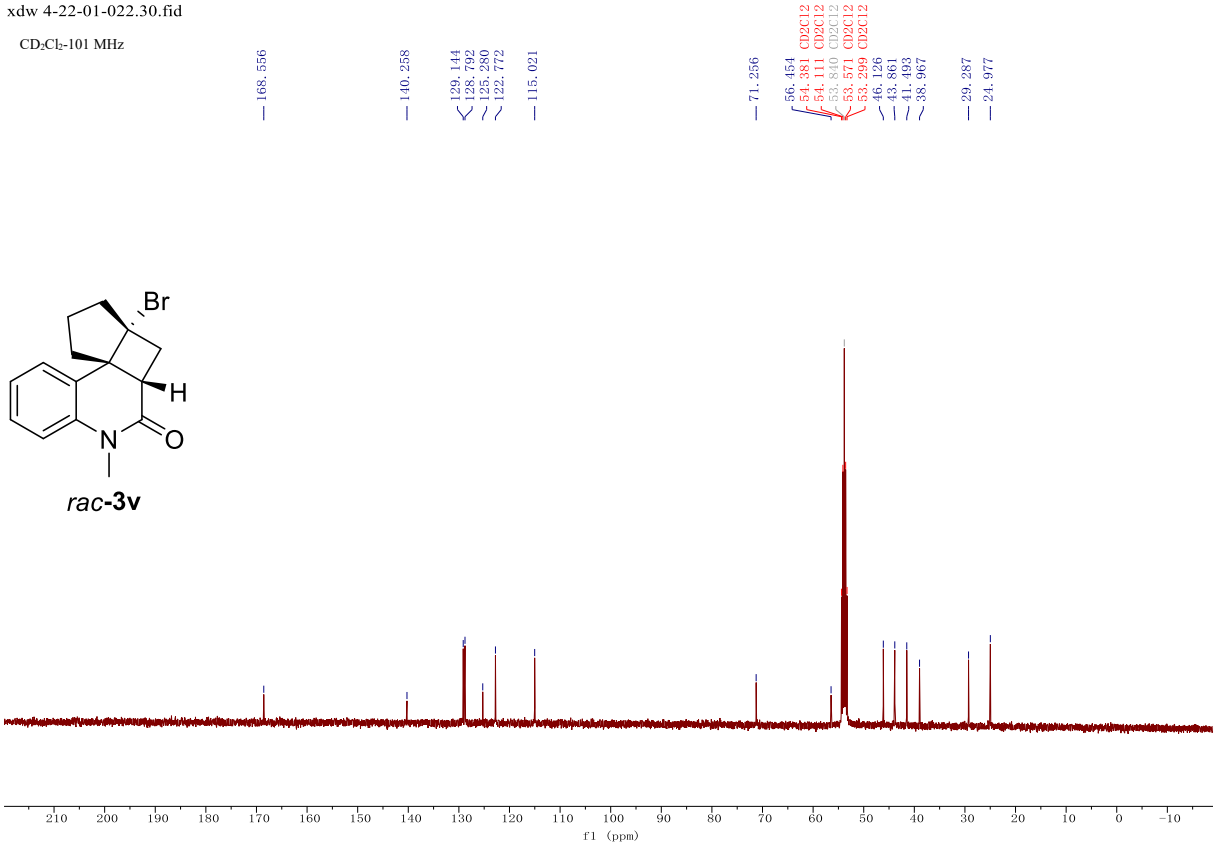
xdw 4-22-01-02.30.fid

CD_2Cl_2-400 MHz



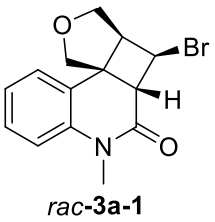
xdw 4-22-01-022.30.fid

CD_2Cl_2-101 MHz



xdw-p1.30.fid

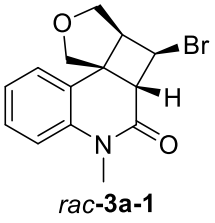
$CDCl_3$-400 MHz



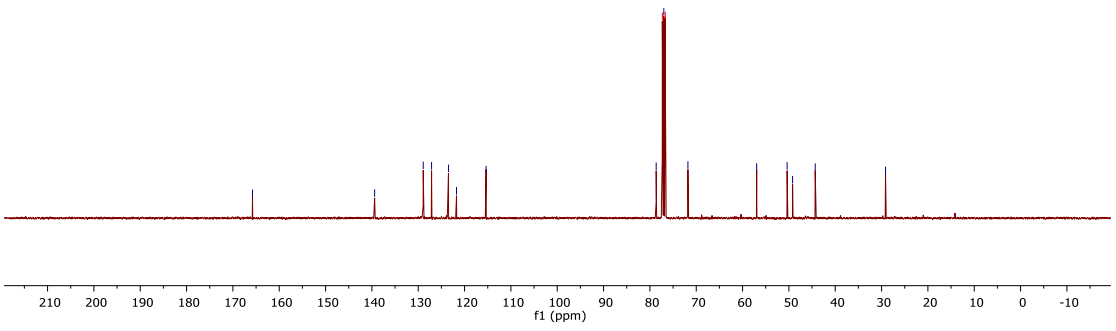
rac-**3a-1**

xdw-p1.31.fid

$CDCl_3$-101 MHz

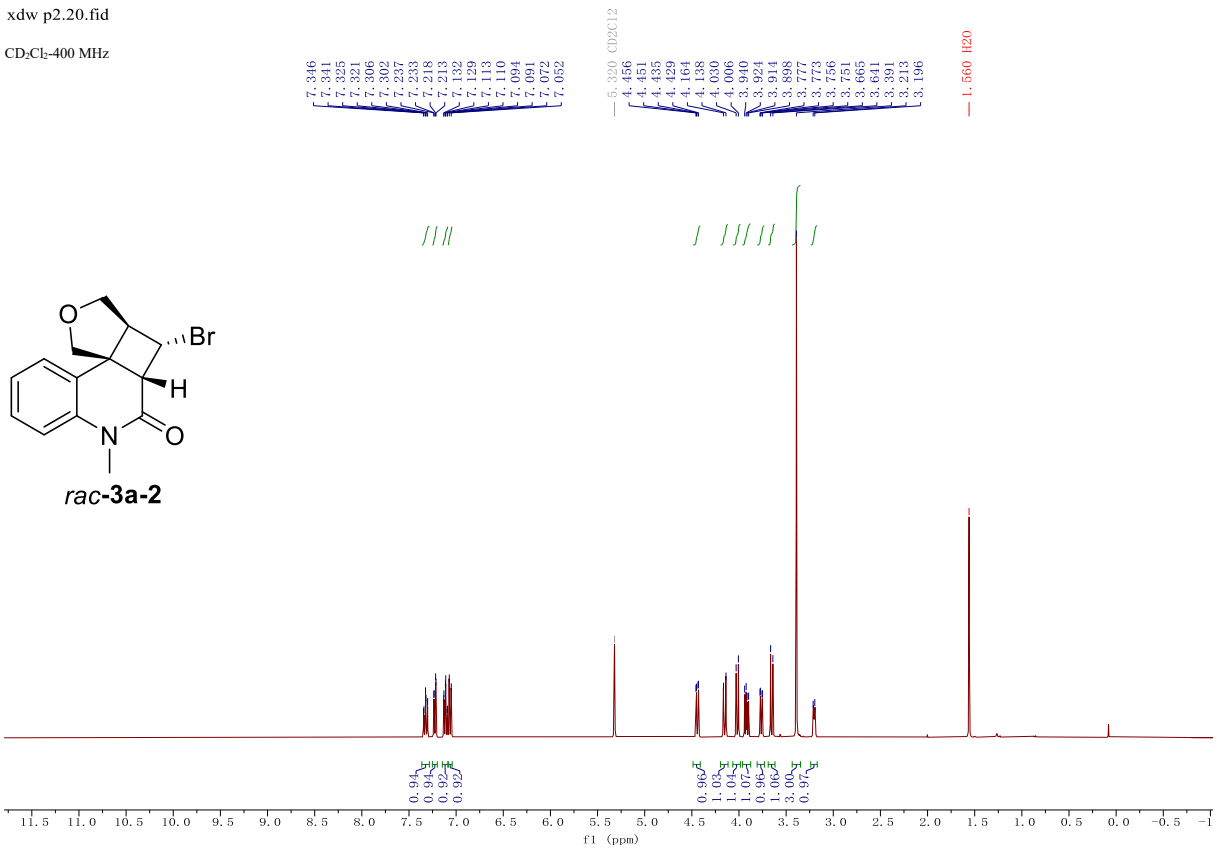


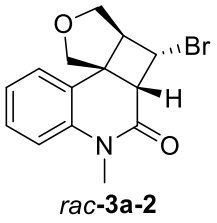
rac-**3a-1**



xdw p2.20.fid

CD_2Cl_2-400 MHz





rac-**3a-2**

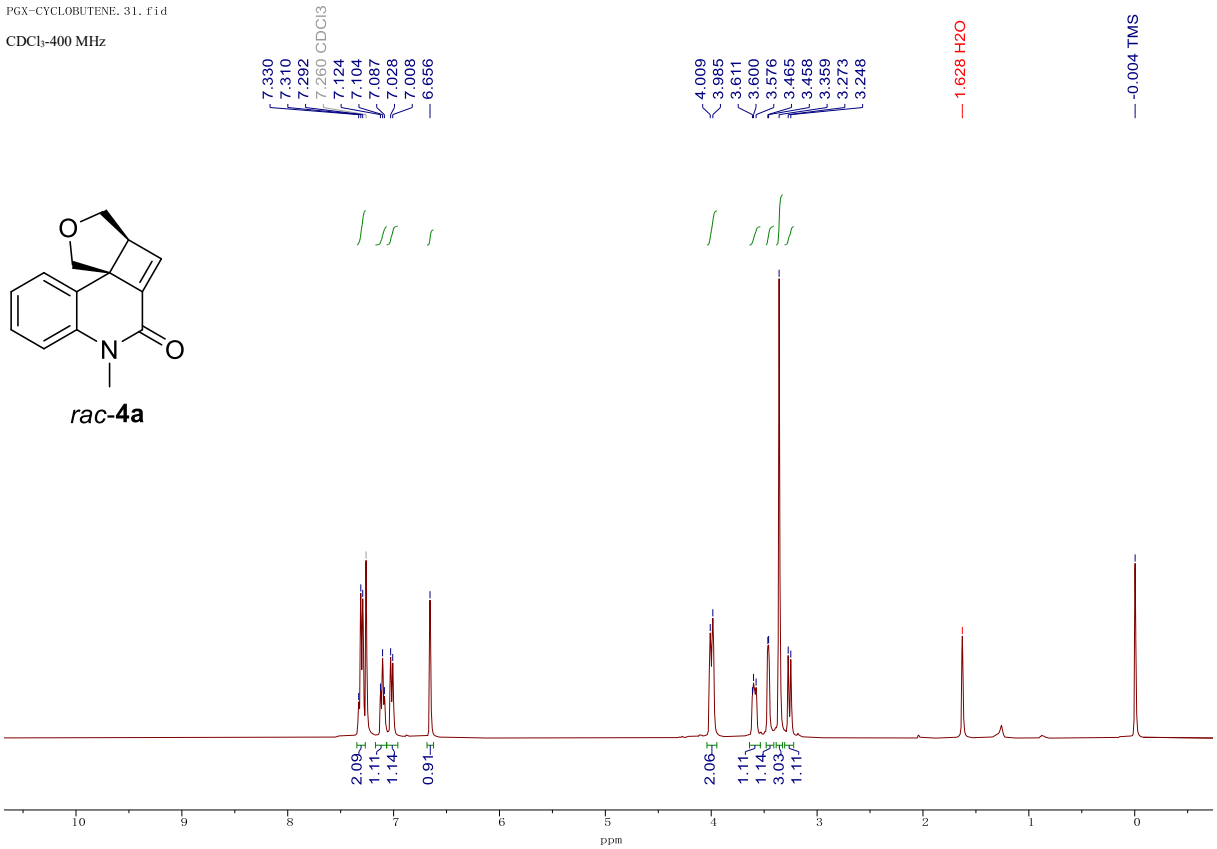
xdw p2.21.fid

CD_2Cl_2-101 MHz

rac-**3a-2**

PGX-CYCLOBUTENE. 31. fid

$CDCl_3$-400 MHz

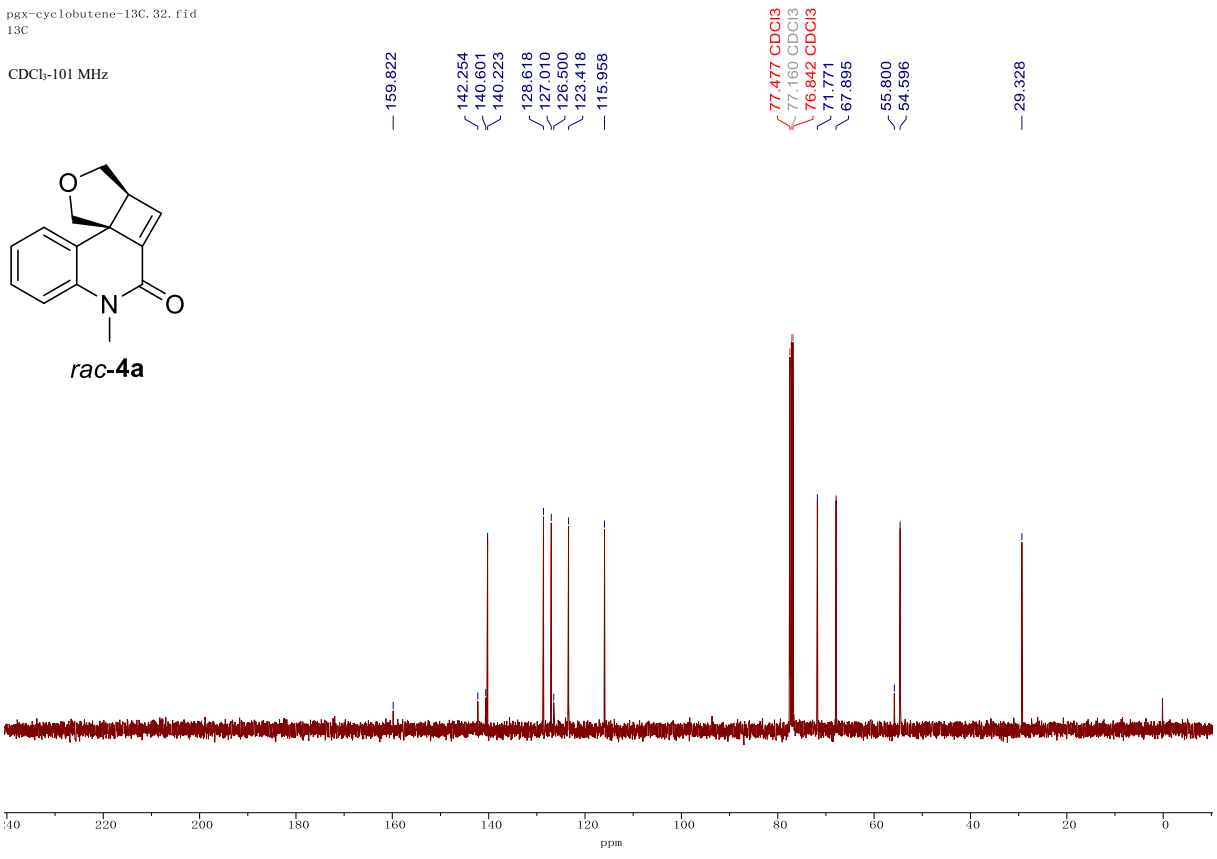


rac-**4a**

pgx-cyclobutene-13C. 32. fid

13C

$CDCl_3$-101 MHz



rac-**4a**

Supplementary References:

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