Supporting Information

Room Temperature C–O Bond Cleavage of Vinyl Cyclic Synthons *via* Metallaphotoredox Approach

Santosh Kumar Keshri[a] and Manmohan Kapur[a,*]

[a]Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhauri, Bhopal, 462066, MP, India.

E-mail: mk@iiserb.ac.in

Table of contents

General methods S2

General procedures and analytical data of starting materials S3

Optimization table for allylated arene synthesis S8

General procedures and analytical data of linear allyl alcohols S10

General procedures and analytical data of branched selective allyl alcohols S18

General procedures and analytical data of linear allyl alcohols from vinyl epoxide S20

General procedure for the hydrogenation reaction S22

General procedure for the removal of the DG of linear allylated arene S23

General procedure for 1 mmol scale reaction S24

Mechanistic studies S25

Control experiments S28

Mass spectrometry studies of intermediates S45

References S48

Copies of ^{1}H, ^{13}C, ^{19}F, and HRMS spectra of all new compounds S49

X-ray diffraction data of (*E*)-5b S118

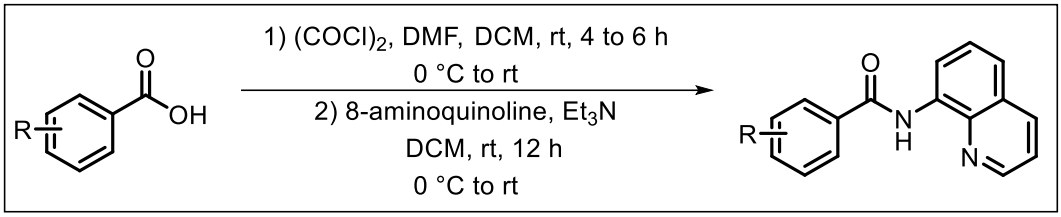
Experimental Section:

(1) General Methods:

All commercially available compounds were used without purification. Unless otherwise noted, all reactions were performed in oven-dried glassware. Unless otherwise specified, all reactions were run under an argon or nitrogen atmosphere. All solvents used in the reactions were purified before use. Dry tetrahydrofuran and toluene were distilled from sodium and benzophenone, whereas dichloroethane, dichloromethane, dimethylsulfoxide and *N*, *N*-dimethylformamide were distilled from CaH_2.[1] TFE was distilled and stored over 3Å molecular sieves prior to use. Petroleum ether with a boiling range of 40 – 60 °C was used. Melting points are uncorrected. ^{1}H, ^{13}C and ^{19}F NMR: Recorded on 400, 500 and 700 MHz NMR Spectrometers; spectra were recorded at 295 K in $CDCl_3$; chemical shifts are calibrated to the residual proton and carbon resonance of the solvent: $CDCl_3$ (^{1}H δ 7.28; ^{13}C δ 77.0). ^{1}H, ^{13}C, and ^{19}F NMR: Recorded on Bruker Avance III 400 MHz NMR Spectrometer, Bruker Avance III 500 MHz NMR Spectrometer, and Bruker Avance III 700 MHz NMR Spectrometer; 'br s' in the analytical data corresponds to 'broad singlet'. HRMS: Bruker Daltonics MicroTOF Q-II with electron spray ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI). IR were recorded on: Perkin Elmer Spectrum BX FTIR, Shimadzu IRAffinity-1 FTIR, PerkinElmer Spectrum Two FTIR and are reported in the frequency of absorption (cm^{-1}). Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at different low temperatures for each crystal.

(2) General procedures and analytical data of starting materials:

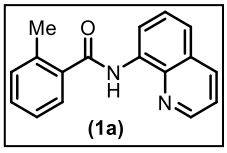
Scheme S1: Synthesis of *N*-(quinolin-8-yl) benzamides:



Procedure: To an oven-dried round bottom flask equipped with a magnetic stir bar, were added the substituted benzoic acid (1.5 equiv.), DMF (3 drops) and DCM (15 mL) under an N_2 atmosphere. Oxalyl chloride (3 equiv.) was added dropwise under ice-cold conditions. The ice bath was removed, and the reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure under an atmosphere of nitrogen. The residue was used immediately for the next step.

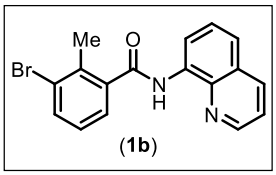
To another oven-dried round bottom flask equipped with a magnetic stir bar was added 8-aminoquinoline (1 equiv.), Et_3N (1.5 equiv.) and DCM (15 mL) under N_2 atmosphere. To this, was added dropwise, the solution of the acid chloride (1.5 equiv.) in DCM (5 mL) under ice-cold conditions and the mixture was stirred overnight at room temperature. The reaction mixture was then quenched with water and extracted with DCM (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (1:20 EtOAc: Petroleum ether) to afford the product in good yield.

2-methyl-*N*-(quinolin-8-yl)benzamide (1a):[2a]



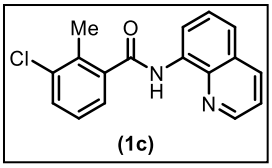
Prepared by following the general procedure and the title compound was isolated in 80% (315 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

3-bromo-2-methyl-*N*-(quinolin-8-yl)benzamide (1b):[2d]



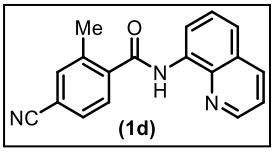
Prepared by following the general procedure and the title compound was isolated in 65% (320 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2d]

3-chloro-2-methyl-*N*-(quinolin-8-yl)benzamide (1c):[2e]



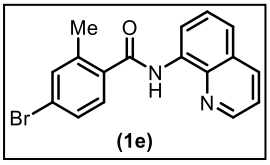
Prepared by following the general procedure and the title compound was isolated in 70% (312 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2e]

4-cyano-2-methyl-*N*-(quinolin-8-yl)benzamide (1d):[2d]



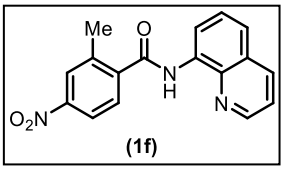
Prepared by following the general procedure and the title compound was isolated in 70% (324 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2d]

4-bromo-2-methyl-*N*-(quinolin-8-yl)benzamide (1e):[2a]



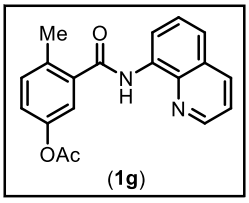
Prepared by following the general procedure and the title compound was isolated in 77% (394 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

2-methyl-4-nitro-*N*-(quinolin-8-yl)benzamide (1f):[2g]



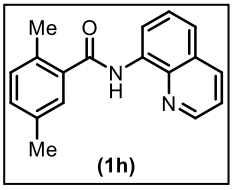
Prepared by following the general procedure and the title compound was isolated in 45% (208 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2g]

4-methyl-3-(quinolin-8-ylcarbamoyl)phenyl acetate (1g):[2a]



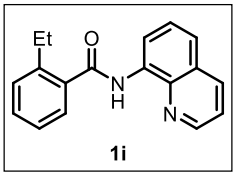
Prepared by following the general procedure and the title compound was isolated in 68% (308 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

2,5-dimethyl-*N*-(quinolin-8-yl)benzamide (1h):[2b]



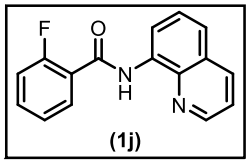
Prepared by following the general procedure and the title compound was isolated in 80% (336 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2b]

2-ethyl-*N*-(quinolin-8-yl)benzamide (1i):[2a]



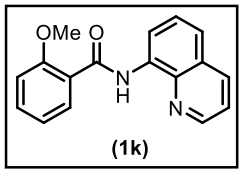
Prepared by following the general procedure and the title compound was isolated in 71% (390 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

2-fluoro-*N*-(quinolin-8-yl)benzamide (1j):[2a]



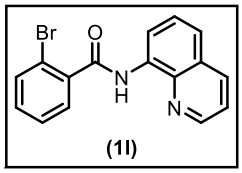
Prepared by following the general procedure and the title compound was isolated in 70% (294 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

2-methoxy-*N*-(quinolin-8-yl)benzamide (1k):[2a]



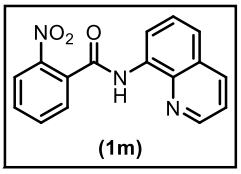
Prepared by following the general procedure and the title compound was isolated in 60% (240 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

2-bromo-*N*-(quinolin-8-yl)benzamide (1l):[2a]



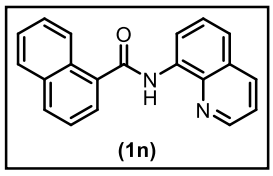
Prepared by following the general procedure and the title compound was isolated in 65% (320 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

2-nitro-*N*-(quinolin-8-yl)benzamide (1m):[2a]



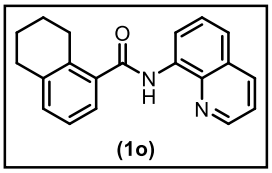
Prepared by following the general procedure and the title compound was isolated in 42% (200 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

***N*-(quinolin-8-yl)-1-naphthamide (1n):**[2a]



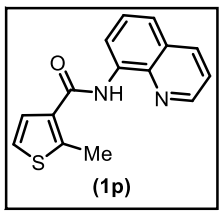
Prepared by following the general procedure and the title compound was isolated in 70% (329 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

***N*-(quinolin-8-yl)-5,6,7,8-tetrahydronaphthalene-1-carboxamide (1o):**[2a]



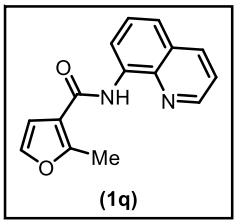
Prepared by following the general procedure and the title compound was isolated in 66% (308 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

2-methyl-*N*-(quinoline-8-yl)thiopene-3-carboxamide (1p): [2a]



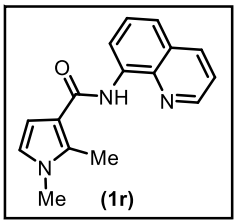
Prepared by following the general procedure and the title compound was isolated in 55% (280 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[2a]

2-methyl-*N*-(quinoline-8-yl)furan-3-carboxamide (1q):



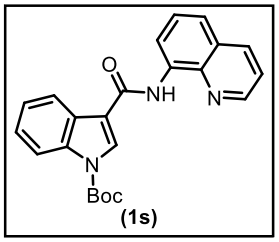
Prepared by following the general procedure and the title compound was isolated in 60% (300 mg) yield. Physical appearance: yellow solid; TLC R_f 0.30 (2:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.88 (dd, *J* = 7.5, 1.4 Hz, 1H), 8.85 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.54 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.37 (d, *J* = 2.1 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 2.76 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.18, 157.56, 148.23, 140.51, 138.57, 136.44, 134.65, 128.02, 127.50, 121.64, 121.38, 116.75, 116.33, 108.94, 13.82; **ESI-HRMS:** Calculated for $C_{15}H_{12}N_2O_2$ $[M+H]^+$ 253.0972; found mass 253.0966.

2-methyl-*N*-(quinoline-8-yl)furan-3-carboxamide (1r):



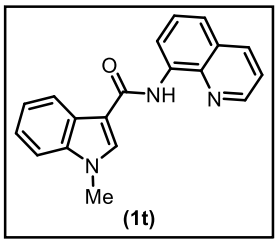
Prepared by following the general procedure and the title compound was isolated in 40% (337 mg) yield. Physical appearance: yellow solid; TLC R_f 0.35 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.92 (dd, *J* = 7.8, 1.3 Hz, 1H), 8.83 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.49 – 7.40 (m, 2H), 6.66 (d, *J* = 3.0 Hz, 1H), 6.59 (d, *J* = 3.0 Hz, 1H), 3.57 (s, 3H), 2.66 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.32, 148.01, 138.71, 136.25, 135.48, 134.76, 128.04, 127.52, 121.46, 120.89, 120.50, 115.88, 115.76, 106.30, 33.74, 10.97; **ESI-HRMS:** Calculated for $C_{16}H_{15}N_3O$ $[M+H]^+$ 266.1288; found mass 266.1295.

***tert*-butyl-3-(quinoline-8-ylcarbamoyl)-1*H*-indol-1-carboxylate (1s):**[2h]



Prepared by following the general procedure and the title compound was isolated in 50% (345 mg) yield. Physical appearance: yellow solid; TLC R_f 0.40 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.96 (d, *J* = 7.6 Hz, 1H), 8.92 – 8.87 (m, 1H), 8.48 – 8.40 (m, 2H), 8.31 – 8.24 (m, 1H), 8.23 – 8.17 (m, 1H), 7.65 – 7.59 (m, 1H), 7.58 – 7.53 (m, 1H), 7.53 – 7.48 (m, 1H), 7.47 – 7.43 (m, 2H), 1.75 (s, 9H). Spectral data obtained were in good agreement with those reported in the literature.[2h]

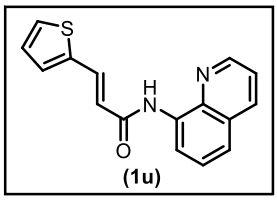
1-methyl-*N*-(quinoline-8-yl)-1*H*-indole-3-carboxamide (1t):



(1t)

Prepared by following the general procedure and the title compound was isolated in 50% (345 mg) yield. Physical appearance: yellow solid; TLC R_f 0.40 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.58 (s, 1H), 8.99 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.92 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.57 – 8.45 (m, 1H), 8.22 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.97 (s, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.47 – 7.35 (m, 3H), 3.92 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.32, 148.08, 138.56, 137.47, 136.56, 135.31, 133.15, 128.12, 127.69, 125.56, 122.71, 121.87, 121.53, 120.86, 120.78, 116.49, 111.79, 110.10, 33.47; **ESI-HRMS:** Calculated for $C_{19}H_{15}N_3O$ $[M+H]^+$ 302.1288; found mass 302.1316.

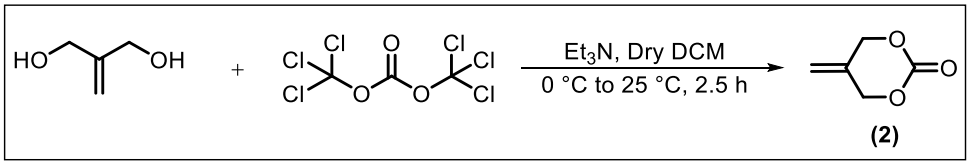
(*E*)-*N*-(quinoline-8-yl)-3-(thiopen-2-yl)acrylamide (1u):[2i]



(1u)

Prepared by following the general procedure and the title compound was isolated in 30% (250 mg) yield. Physical appearance: white solid; TLC R_f 0.35 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.92 (d, *J* = 7.5 Hz, 1H), 8.87 – 8.83 (m, 1H), 8.23 – 8.14 (m, 1H), 7.95 (dd, *J* = 15.3, 1.7 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.54 – 7.51 (m, 1H), 7.50 – 7.45 (m, 1H), 7.38 (d, *J* = 4.7 Hz, 1H), 7.31 (d, *J* = 3.7 Hz, 1H), 7.14 – 7.05 (m, 1H), 6.63 (d, *J* = 15.4 Hz, 1H). Spectral data obtained were in good agreement with those reported in the literature.[2i]

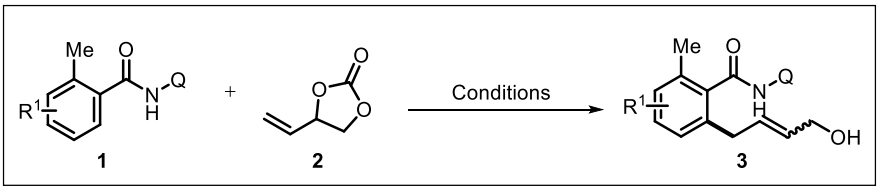
Scheme S2: Synthesis of 5-methylene-1,3-dioxan-2-one:[3]



(2)

A solution of triphosgene (1.5 g, 5.0 mmol) in dry CH_2Cl_2 (20.0 mL) was slowly added to a solution of 2-methylenepropane-1,3-diol (220 mg, 2.5 mmol) and triethylamine (3.5 mL, 25 mmol) in CH_2Cl_2 (25 mL) at 0 °C (ice bath) over 30 min. The resulting mixture was stirred for 2 h while gradually raising the temperature to 25 °C. The reaction was quenched with aq. NH_4Cl and this was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel flash column chromatography (3:7 EtOAc: Petroleum ether) and the solid thus obtained was washed with hexane to afford the desired product **2** as a white gel (228 mg, 80% yield).[3]

Table S1. Optimization of reaction conditions:



Entry	Conditions	(*E*)/(*Z*)	Yield (%)[a] (3)
1	$Co(acac)_2$ (10 mol%), Na_2[Eosin Y] (10 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, green LED strip (3W × 20), O_2 balloon, 24 h	1/1	44
2	$Co(acac)_2$ (10 mol%), Na_2[Eosin Y] (10 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), HFIP (0.1 M), 25 ℃, green LED strip (3W × 20), O_2 balloon, 24 h	2/1	39
3	$Co(acac)_2$ (10 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, green LED strip (3W × 20), O_2 balloon, 24 h	1/1	47
4	$Co(acac)_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, green LED strip (3W × 20), O_2 balloon, 24 h	1/1	51
5	$Co(OAc)_2.4H_2O$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, green LED strip (3W × 20), O_2 balloon, 24 h	1/1	40
6	$Co(OAc)_2.4H_2O$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	2/1	58
7	$CoCl_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
8	$Ni(acac)_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
9	$Co(acac)_3$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
10	**$Co(acac)_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), 2 (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h**	**4/1**	**83**
11	$Co(acac)_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), HFIP (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	1/1	50

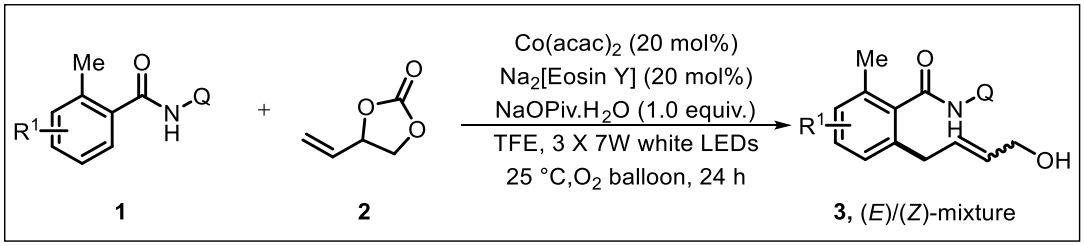
12	$Co(acac)_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), MeOH (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
13	$Co(acac)_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), DCE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
14	$Co(acac)_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), 1,4-Dioxane (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
15	$Co(acac)_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), THF (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
16	$Co(acac)_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), Toluene (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	CM
17	$Co(acac)_2$ (20 mol%), Na_2[Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), DCM (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
18	$Co(acac)_2$ (20 mol%), Fluorescein (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	2/1	68
19	$Co(acac)_2$ (20 mol%), Eosin Y (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	2/1	70
20	$Co(acac)_2$ (20 mol%), $[Ru(bpy)_3]Cl_2$ (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
21	$Co(acac)_2$ (20 mol%), Rhodamine-6G (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
22	$Co(acac)_2$ (20 mol%), Methyl Orange (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	CM
23	$Co(acac)_2$ (20 mol%), Rose Bengal (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
24	$Co(acac)_2$ (20 mol%), Na_2 [Eosin Y] (20 mol%), NaOAc (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	1/1	52
25	$Co(acac)_2$ (20 mol%), Na_2 [Eosin Y] (20 mol%), KOAc (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	1/1	58
26	$Co(acac)_2$ (20 mol%), Na_2 [Eosin Y] (20 mol%), KOPiv (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	2/1	60
27	$Co(acac)_2$ (20 mol%), Na_2 [Eosin Y] (20 mol%), Na(OPiv).H_2O (2.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 ℃, 3 × 7W white LEDs, O_2 balloon, 24 h	4/1	75

28	$Co(acac)_2$ (20 mol%), Na_2 [Eosin Y] (20 mol%), Na(OPiv).H_2O (50 mol%), **2** (2.0 equiv.), TFE (0.1 M), 25 °C, 3 × 7W white LEDs, O_2 balloon, 24 h	4/1	70
29	$Co(acac)_2$ (20 mol%), Na_2 [Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 °C, 15W CFL Bulbs, O_2 balloon, 24 h	1/1	40
30	$Co(acac)_2$ (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 °C, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
31	Na_2 [Eosin Y] (20 mol%), Na(OPiv).H_2O (1 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 °C, 3 × 7W white LEDs, O_2 balloon, 24 h	-	NR
32	$Co(acac)_2$ (20 mol%), Na_2 [Eosin Y] (20 mol%), **2** (2.0 equiv.), TFE (0.1 M), 25 °C, 3 × 7W white LEDs, O_2 balloon, 24 h	-	trace
33	$Co(acac)_2$ (20 mol%), Na_2 [Eosin Y] (20 mol%), Na(OPiv).H_2O (1.0 equiv.), **2** (2.0 equiv.), TFE (0.1 M), 25 °C, 3 × 7W white LEDs, O_2 balloon, 48 h	4/1	81

[a]*Isolated yield; N.R. = No reaction; CM = Complex Mixture.*

3. General procedure for the synthesis of allyl alcohol derivatives

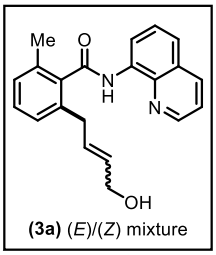
Scheme S3: General procedure for the synthesis of linear allyl alcohols:



In an oven-dried pressure tube equipped with a stir bar, 2-methyl-*N*-(quinolin-8-yl) benzamide **1** (1.0 equiv., 0.1 mmol) and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol) were dissolved in TFE (1.0 mL). The solution was degassed with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), Na_2[Eosin Y] (20 mol%, 0.02 mmol) and NaOPiv.H_2O (1.0 equiv., 0.1 mmol) were added one after another. O_2 was then bubbled into the pressure tube after which it was sealed tightly with a septum cap. This reaction mixture was then placed under white LEDs (3 × 7W) and stirred at room temperature (25 °C) for 24 h and the reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was then diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography to yield the desired product **3**.

Figure S1. Reaction Setup (0.1 mmol scale).

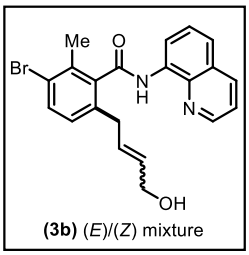
2-(4-hydroxybut-2-en-1-yl)-6-methyl-*N*-(quinolin-8yl)benzamide (3a):



(3a) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (27 mg); Yield 83% (28.5 mg); (*E*)/(*Z*) = 4:1; Physical appearance: Colorless oil; TLC R_f 0.35 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 9.05 – 8.99 (m, 1H), 8.81 – 8.73 (m, 1H), 8.26 – 8.18 (m, 1H), 7.68 – 7.58 (m, 2H), 7.51 – 7.45 (m, 1H), 7.38 – 7.30 (m, 1H), 7.22 – 7.14 (m, 2H), 5.97 – 5.81 (m, 1H), 5.65 – 5.52 (m, 1H), 3.95 (d, *J* = 5.8 Hz, 2H), 3.52 (d, *J* = 6.5 Hz, 2H), 2.46 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.60, 148.42, 138.45, 137.79, 136.55, 136.44, 135.02, 134.24, 131.55, 130.71, 129.25, 128.47, 128.11, 127.49, 127.38, 122.14, 121.76, 116.96, 63.48, 36.39, 19.47; **ESI-HRMS:** Calculated for $C_{21}H_{20}N_2O_2$ $[M+Na]^+$ 355.1417; found mass 355.1440; **IR** (thin film, neat, cm^{-1}): 3344, 2924, 1717, 1672, 1522, 1483, 1424, 1386, 1326, 1264, 827, 792, 763.

3-bromo-6-(4-hydroxybut-2-en-1-yl)-2-methyl-*N*-(quinolin-8yl)benzamide (3b):

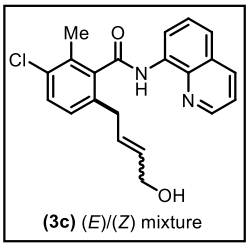


(3b) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (35 mg); Yield 71% (30 mg); (*E*)/(*Z*) = 1.5:1; Physical appearance: red oil; TLC R_f 0.40 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 9.00 (dd, *J* = 7.0 Hz, 2.0 Hz, 1H), 8.81 – 8.75 (m, 1H), 8.23 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.70 – 7.58 (m, 3H), 7.53 – 7.47 (m, 1H), 7.13 – 7.00 (m, 1H), 5.91 –

5.82 (m, 1H), 5.70 – 5.62 (m, 1H), 3.94 (d, *J* = 5.8 Hz, 2H), 3.46 (d, *J* = 6.2 Hz, 2H), 2.50 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.53, 148.51, 139.28, 138.44, 136.60, 134.66, 133.30, 131.10, 129.70, 128.93, 128.10, 127.45, 123.78, 122.58, 122.43, 121.85, 117.05, 116.95, 58.07, 36.03, 20.28; **ESI-HRMS:** Calculated for $C_{21}H_{19}BrN_2O_2$ $[M+Na]^+$ 433.0522, 435.0503; found mass 433.0518, 435.0502; **IR** (thin film, neat, cm^{-1}): 3332, 1720, 1672, 1522, 1487, 1425, 1325, 1266, 1120, 826, 791, 763.

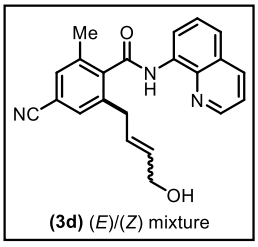
3-chloro-6-(4-hydroxybut-2-en-1-yl)-2-methyl-*N*-(quinolin-8yl)benzamide (3c):



(3c) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (30 mg); Yield 62% (23 mg); (*E*)/(*Z*) = 1.6:1; Physical appearance: Colorless oil; TLC R_f 0.40 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 9.00 (dd, *J* = 6.9, 2.1 Hz, 1H), 8.83 – 8.74 (m, 1H), 8.23 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.72 – 7.58 (m, 2H), 7.55 – 7.46 (m, 1H), 7.42 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.20 – 7.08 (m, 1H), 5.95 – 5.79 (m, 1H), 5.72 – 5.59 (m, 1H), 3.94 (dd, *J* = 5.8, 1.4 Hz, 2H), 3.47 (d, *J* = 6.4 Hz, 2H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.53, 148.50, 139.30, 138.37, 136.61, 135.09, 133.96, 133.24, 131.07, 130.87, 129.97, 129.66, 128.64, 128.24, 127.45, 122.43, 121.85, 117.06, 63.35, 36.00, 17.30; **ESI-HRMS:** Calculated for $C_{21}H_{19}ClN_2O_2$ $[M+H]^+$ 367.1208; found mass 367.1226; **IR** (thin film, neat, cm^{-1}): 3333, 2923, 1725, 1672, 1574, 1519, 1424, 1384, 1325, 1263, 1018, 826, 791, 763.

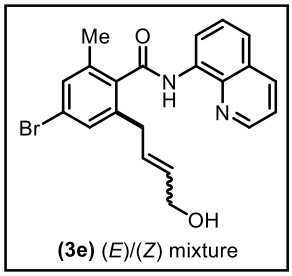
4-cyano-2-(4-hydroxybut-2-en-1-yl)-6-methyl-*N*-(quinolin-8yl)benzamide (3d):



(3d) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (30 mg); Yield 51% (19 mg); (*E*)/(*Z*) = 3:1; Physical appearance: Colorless oil; TLC R_f 0.35 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 9.02 – 8.93 (m, 1H), 8.83 – 8.75 (m, 1H), 8.24 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.55 – 7.45 (m, 3H), 5.93 – 5.81 (m, 1H), 5.74 – 5.56 (m, 1H), 3.99 (d, *J* = 5.4 Hz, 2H), 3.54 (d, *J* = 6.3 Hz, 2H), 2.49 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.51, 148.60, 141.64, 138.34, 138.14, 136.66, 133.66, 132.06, 131.89, 131.00, 129.52, 128.11, 127.42, 122.71, 121.95, 118.37, 117.19, 113.17, 63.17, 35.93, 19.33; **ESI-HRMS:** Calculated for $C_{22}H_{19}N_3O_2$ $[M+Na]^+$ 380.1369; found mass 380.1372; **IR** (thin film, neat, cm^{-1}): 3331, 2918, 2229, 1722, 1672, 1523, 1484, 1424, 1386, 1326, 1264, 1110, 827, 792.

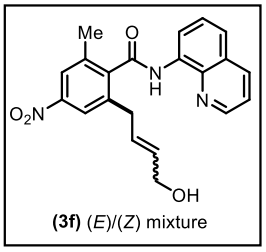
4-bromo-2-(4-hydroxybut-2-en-1-yl)-6-methyl-*N*-(quinolin-8yl)benzamide (3e):



(3e) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (35 mg); Yield 55% (21 mg); (*E*)/(*Z*) = 6:1; Physical appearance: brown oil; TLC R_f 0.40 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.97 (dt, *J* = 6.8, 2.0 Hz, 1H), 8.80 – 8.74 (m, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.69 – 7.57 (m, 2H), 7.52 – 7.45 (m, 1H), 7.36 – 7.29 (m, 2H), 5.92 – 5.76 (m, 1H), 5.69 – 5.56 (m, 1H), 3.95 (d, *J* = 5.7 Hz, 2H), 3.47 (d, *J* = 6.6 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.65, 148.53, 139.32, 138.76, 138.39, 137.26, 136.60, 133.99, 131.52, 131.29, 130.18, 129.49, 128.10, 127.44, 123.21, 122.41, 121.86, 117.02, 63.23, 36.10, 19.31; **ESI-HRMS:** Calculated for $C_{21}H_{19}BrN_2O_2$ $[M+Na]^+$ 433.0522, 435.0503; found mass 433.0522, 435.0506. **IR** (thin film, neat, cm^{-1}): 3340, 2922, 1672, 1575, 1483, 1420, 1325, 1326, 1261, 1022, 827, 783.

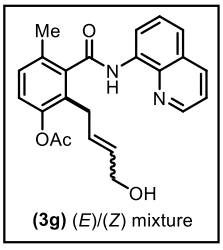
2-(4-hydroxybut-2-en-1-yl)-6-methyl-4-nitro-*N*-(quinolin-8yl)benzamide (3f):



(3f) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (30 mg); Yield 46% (17 mg); (*E*)/(*Z*) = 2:1; Physical appearance: colorless oil; TLC R_f 0.30 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 9.07 – 8.93 (m, 1H), 8.80 (d, *J* = 4.5 Hz, 1H), 8.38 – 8.27 (m, 1H), 8.05 (d, *J* = 9.9 Hz, 2H), 7.74 – 7.66 (m, 2H), 7.60 – 7.52 (m, 1H), 6.01 – 5.80 (m, 1H), 5.78 – 5.60 (m, 1H), 3.99 (d, *J* = 5.8 Hz, 2H), 3.61 (d, *J* = 6.8 Hz, 2H), 2.21 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.19, 156.14, 148.33, 143.04, 142.85, 138.83, 137.36, 133.35, 132.22, 129.46, 128.78, 127.65, 123.34, 123.02, 122.91, 122.36, 121.98, 121.95, 63.18, 36.25, 29.71; **ESI-HRMS:** Calculated for $C_{21}H_{19}N_3O_4$ $[M+Na]^+$ 400.1268; found mass 400.1218. **IR** (thin film, neat, cm^{-1}): 3121, 2920, 2900, 1784, 1581, 1420, 1384, 1326, 1080, 749.

2-(4-hydroxybut-2-en-1-yl)-4-methyl-3-(quinolin-8ylcarbamoyl)phenyl acetate (3g):

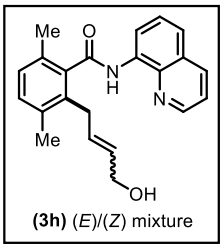


(3g) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (33 mg); Yield 63% (24 mg); (*E*)/(*Z*) = 7:1; Physical appearance: yellow oil; TLC R_f 0.40 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.94 (dd, *J* = 7.0, 1.8 Hz, 1H), 8.78 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.22 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.49 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 5.66 – 5.59 (m, 1H), 5.58 – 5.46 (m, 1H), 4.08 (d, *J* = 6.7 Hz, 2H), 3.49 (d, *J* = 6.7 Hz, 2H), 2.44 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ

169.71, 167.76, 148.49, 147.17, 138.97, 138.47, 136.40, 133.95, 132.76, 129.62, 129.19, 129.08, 128.04, 127.43, 123.50, 122.50, 121.86, 116.85, 57.87, 26.61, 20.96, 19.20; **ESI-HRMS:** Calculated for $C_{23}H_{22}N_2O_4$ $[M+H]^+$ 391.1652; found mass 391.1646. **IR** (thin film, neat, cm^{-1}): 3338, 2925, 1761, 1674, 1523, 1484, 1425, 1386, 1320, 1263, 1013, 827, 749.

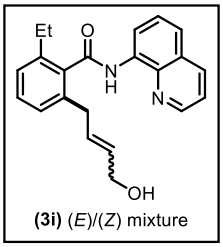
2-(4-hydroxybut-2-en-1-yl)-3,6-dimethyl-*N*-(quinolin-8yl)benzamide (3h):



(3h) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (33 mg); Yield 53% (22 mg); (*E*)/(*Z*) = 5:1; Physical appearance: Colorless oil; TLC R_f 0.35 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.97 (d, *J* = 7.4 Hz, 1H), 8.80 – 8.72 (m, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.53 – 7.43 (m, 1H), 7.24 – 7.15 (m, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 5.67 – 5.57 (m, 1H), 5.56 – 5.44 (m, 1H), 4.08 (d, *J* = 5.2 Hz, 2H), 3.56 (d, *J* = 4.7 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H), **^{13}C NMR** (126 MHz, $CDCl_3$) 169.47, 148.38, 138.50, 136.45, 134.83, 134.32, 134.14, 132.34, 131.28, 130.75, 130.16, 129.65, 128.92, 128.46, 127.54, 122.30, 121.78, 116.83, 57.98, 29.36, 19.41, 19.21; **ESI-HRMS:** Calculated for $C_{22}H_{22}N_2O_2$ $[M+H]^+$ 347.1754; found mass 347.1766. **IR** (thin film, neat, cm^{-1}): 3340, 2922, 1720, 1642, 1522, 1480, 1424, 1385, 1326, 1264, 763.

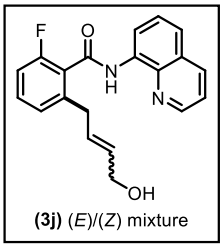
2-ethyl-6-(4-hydroxybut-2-en-1-yl)-*N*-(quinolin-8yl)benzamide (3i):



(3i) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (33 mg); Yield 66% (22 mg); (*E*)/(*Z*) = 5:1; Physical appearance: brown oil; TLC R_f 0.40 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 9.03 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.79 – 8.73 (m, 1H), 8.22 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.51 – 7.45 (m, 1H), 7.42 – 7.34 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.15 (m, 1H), 5.96 – 5.83 (m, 1H), 5.66 – 5.54 (m, 1H), 3.93 (d, *J* = 6.0 Hz, 2H), 3.52 (d, *J* = 6.5 Hz, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.59, 148.39, 141.20, 138.38, 137.28, 136.93, 136.56, 134.22, 131.50, 130.67, 129.42, 128.10, 127.50, 127.38, 126.84, 122.12, 121.75, 116.96, 63.45, 36.42, 26.48, 15.89; **ESI-HRMS:** Calculated for $C_{22}H_{22}N_2O_2$ $[M+H]^+$ 347.1754; found mass 347.1744. **IR** (thin film, neat, cm^{-1}): 3340, 2928, 1672, 1595, 1521, 1483, 1420, 1224, 827, 791, 750.

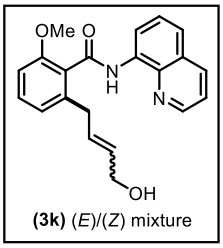
2-fluoro-6-(4-hydroxybut-2-en-1-yl)-*N*-(quinolin-8yl)benzamide (3j):



(3j) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (28 mg); Yield 57% (20 mg); (*E*)/(*Z*) = 4:1; Physical appearance: Colorless oil; TLC R_f 0.35 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.98 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.70 – 7.58 (m, 2H), 7.49 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.45 – 7.35 (m, 1H), 7.18 – 7.05 (m, 2H), 5.95 – 5.83 (m, 1H), 5.72 – 5.59 (m, 1H), 3.96 (d, *J* = 5.9 Hz, 2H), 3.61 (d, *J* = 6.4 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.41, 160.46, 158.49, 148.49, 140.45, 138.42, 136.54, 134.16, 131.28, 130.52, 128.07, 127.45, 125.87, 125.40 (*J* = 17.6 Hz), 125.33, 122.36, 121.80, 117.09, 114.12, 63.37, 35.99; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.97; **ESI-HRMS:** Calculated for $C_{20}H_{17}FN_2O_2$ $[M+Na]^+$ 359.1166; found mass 359.1162. **IR** (thin film, neat, cm^{-1}): 3324, 2914, 1715, 1672, 1522, 1483, 1424, 1320, 1264, 792, 749.

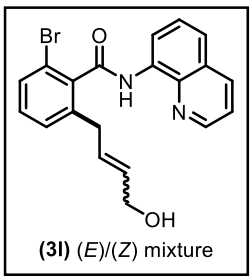
2-(4-hydroxybut-2-en-1-yl)-6-methoxy-*N*-(quinolin-8yl)benzamide (3k):



(3k) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (30 mg); Yield 53% (20 mg); (*E*)/(*Z*) = 10:1; Physical appearance: Colorless oil; TLC R_f 0.35 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 9.02 (dd, *J* = 7.6, 1.4 Hz, 1H), 8.77 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.62 (t, *J* = 8.1 Hz, 1H), 7.57 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 6.91 (dd, *J* = 12.1, 8.0 Hz, 2H), 5.94 – 5.81 (m, 1H), 5.67 – 5.56 (m, 1H), 3.94 (d, *J* = 5.9 Hz, 2H), 3.86 (s, 3H), 3.53 (dd, *J* = 6.5, 1.4 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.29, 156.62, 148.31, 139.05, 138.49, 136.49, 134.59, 131.25, 130.77, 130.42, 128.09, 127.54, 126.95, 122.30, 121.89, 121.66, 116.96, 109.25, 63.46, 55.90, 36.18; **ESI-HRMS:** Calculated for $C_{21}H_{20}N_2O_3$ $[M+Na]^+$ 371.1366; found mass 371.1368. **IR** (thin film, neat, cm^{-1}): 3321, 2920, 1715, 1672, 1522, 1425, 1380, 1326, 1264, 849, 749.

2-bromo-6-(4-hydroxybut-2-en-1-yl)-*N*-(quinolin-8yl)benzamide (3l):

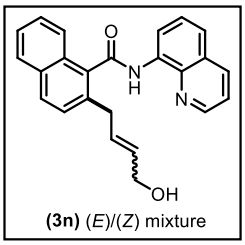


(3l) (*E*)/(*Z*) mixture

Reaction performed on 0.1 mmol scale (35 mg); Yield 47% (20 mg); (*E*)/(*Z*) = 10:1; Physical appearance: yellow oil; TLC R_f 0.40 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.95 (d, *J* = 7.1 Hz, 1H), 8.80 (d, *J* = 4.2 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.50 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.33 – 7.28 (m, 2H), 5.73 – 5.59 (m, 2H), 4.13 (d, *J* = 5.7 Hz,

2H), 3.61 (d, *J* = 6.2 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.44, 148.49, 139.86, 138.63, 138.52, 136.48, 133.92, 130.88, 130.82, 129.99, 129.63, 128.62, 128.10, 127.48, 122.58, 121.84, 120.03, 117.07, 58.07, 31.97; **ESI-HRMS:** Calculated for $C_{20}H_{17}BrN_2O_2$ $[M+H]^+$ 397.0546, 399.0527; found mass 397.0552, 399.0537. **IR** (thin film, neat, cm^{-1}): 3320, 2920, 1672, 1522, 1483, 1420, 1386, 827, 792, 761.

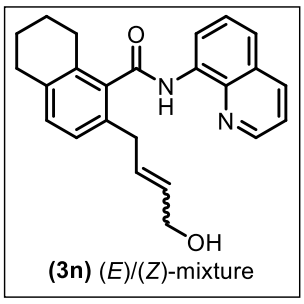
2-(4-hydroxybut-2-en-1-yl)-*N*-(quinolin-8yl)-1-napthamide (3n):



(3n) (*E*)/(*Z*) mixture

Reaction performed on 0.06 mmol scale (20 mg); Yield 61% (15 mg); (*E*)/(*Z*) = 8:1; Physical appearance: brown oil; TLC R_f 0.35 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.10 (s, 1H), 9.16 (dd, *J* = 7.4, 1.0 Hz, 1H), 8.70 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.07 – 7.86 (m, 3H), 7.73 – 7.67 (m, 1H), 7.66 – 7.62 (m, 1H), 7.53 – 7.44 (m, 4H), 6.06 – 5.90 (m, 1H), 5.73 – 5.60 (m, 1H), 3.99 (dd, *J* = 5.9, 1.3 Hz, 2H), 3.70 (d, *J* = 6.4 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.18, 148.26, 136.80, 134.77, 134.27, 134.05, 132.18, 131.16, 130.99, 130.23, 129.83, 129.61, 128.18, 128.04, 127.82, 127.61, 127.16, 125.96, 124.96, 122.35, 121.75, 117.36, 63.46, 36.69; **ESI-HRMS:** Calculated for $C_{24}H_{20}N_2O_2$ $[M+H]^+$ 369.1598; found mass 369.1592. **IR** (thin film, neat, cm^{-1}): 3335, 2923, 1670, 1595, 1482, 1424, 1382, 1324, 1275, 825, 792, 749.

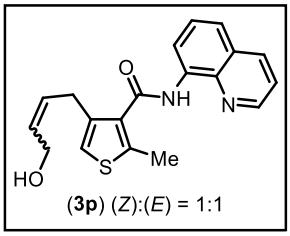
2-(4-hydroxybut-2-en-1-yl)-*N*-(quinolin-8yl)-1-napthamide (3o):



(3n) (*E*)/(*Z*)-mixture

Reaction performed on 0.07 mmol scale (23 mg); Yield 60% (17 mg); (*E*)/(*Z*) = 2:1; Physical appearance: red oil; TLC R_f 0.40 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.98 (d, *J* = 7.3 Hz, 1H), 8.79 – 8.75 (m, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.57 (m, 3H), 7.50 – 7.45 (m, 1H), 7.18 – 7.04 (m, 1H), 5.95 – 5.81 (m, 1H), 5.75 – 5.65 (m, 1H), 3.93 (d, *J* = 6.0 Hz, 2H), 3.53 (d, *J* = 7.2 Hz, 2H), 2.83 (t, *J* = 6.0 Hz, 4H), 1.83 – 1.78 (m, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.90, 148.32, 137.61, 136.65, 135.93, 133.92, 133.40, 131.86, 130.46, 130.27, 129.02, 128.12, 127.53, 127.05, 126.66, 122.09, 121.73, 117.03, 63.51, 58.06, 36.14, 29.54, 26.67, 22.92; **ESI-HRMS:** Calculated for $C_{24}H_{24}N_2O_2$ $[M+Na]^+$ 395.1730; found mass 395.1723. **IR** (thin film, neat, cm^{-1}): 3335, 2923, 1670, 1595, 1482, 1424, 1324, 1264, 827, 792.

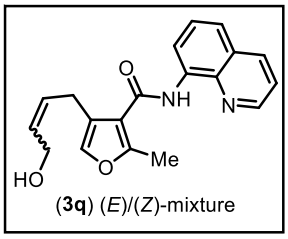
4-(4-hydroxybut-2-en-1-yl)-2-methyl-*N*-(quinolin-8yl)thiopene-3-carboxamide (3p):



(**3p**) (*Z*):(*E*) = 1:1

Reaction performed on 0.09 mmol scale (25 mg); Yield 51% (16 mg); (*E*)/(*Z*) = 1:1, Physical appearance: red oil; TLC R_f 0.25 (2:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.92 (d, *J* = 7.3 Hz, 1H), 8.85 – 8.81 (m, 1H), 8.31 – 8.21 (m, 1H), 7.68 – 7.58 (m, 2H), 7.56 – 7.49 (m, 1H), 6.83 (d, *J* = 6.7 Hz, 1H), 5.96 – 5.83 (m, 1H), 5.72 – 5.64 (m, 1H), 4.20 (d, *J* = 6.0 Hz, 2H), 3.65 (d, *J* = 5.7 Hz, 2H), 2.73 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.54, 147.70, 141.91, 140.19, 139.30, 134.45, 130.97, 130.68, 130.07, 129.61, 128.30, 128.06, 127.89, 122.29, 121.70, 119.11, 63.55, 32.58, 15.22; **ESI-HRMS:** Calculated for $C_{19}H_{18}N_2O_2S$ $[M+Na]^+$ 361.0981; found mass 361.0976. **IR** (thin film, neat, cm^{-1}): 3338, 2929, 2858, 1807, 1714, 1672, 1518, 1424, 1384, 1324, 1264, 827, 792.

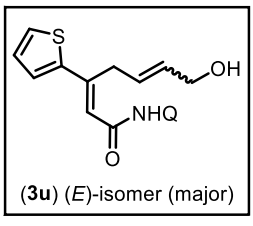
4-(4-hydroxybut-2-en-1-yl)-2-methyl-*N*-(quinolin-8yl)furan-3-carboxamide (3q):



(**3q**) (*E*)/(*Z*)-mixture

Reaction performed on 0.1 mmol scale (25 mg); Yield 55% (17.5 mg); (*E*)/(*Z*) = 2:1, Physical appearance: brown oil; TLC R_f 0.30 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.90 – 8.80 (m, 3H), 8.22 (dt, *J* = 8.3, 1.7 Hz, 2H), 7.63 – 7.53 (m, 3H), 7.50 (dd, *J* = 8.3, 4.2 Hz, 2H), 7.17 (d, *J* = 5.5 Hz, 2H), 6.05 – 5.94 (m, 1H), 5.83 – 5.72 (m, 1H), 4.11 (d, *J* = 5.7 Hz, 2H), 3.56 (d, *J* = 6.0 Hz, 2H), 2.70 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.02, 156.74, 155.26, 148.18, 138.26, 138.12, 131.06, 130.30, 130.05, 129.73, 127.58, 123.94, 122.43, 121.70, 121.65, 117.58, 63.51, 27.23, 14.17; **ESI-HRMS:** Calculated for $C_{19}H_{18}N_2O_3$ $[M+H]^+$ 323.1390; found mass 323.1393. **IR** (thin film, neat, cm^{-1}): 3340, 2920, 2800, 1805, 1721, 1660, 1384, 1320, 1264, 821, 790.

(2*E*,5*E*)-7-hydroxy-*N*-(quinolin-8yl)-3-(thiopen-2-yl)hepta-2,5-dienamide (3u):

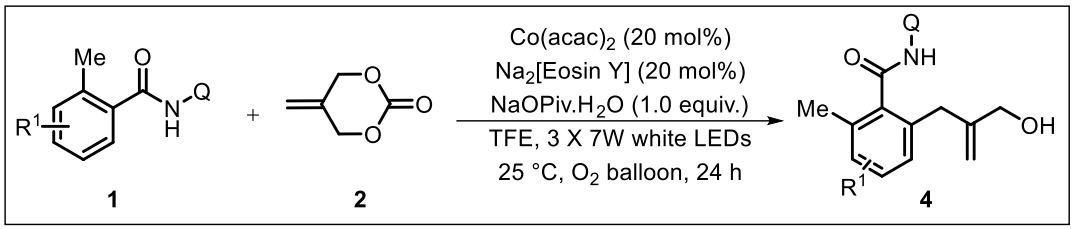


(**3u**) (*E*)-isomer (major)

Reaction performed on 0.1 mmol scale (28 mg); Yield 67% (23.5 mg); (*E*)/(*Z*) > 16:1, Physical appearance: green oil; TLC R_f 0.25 (2:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.90 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.86 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.51 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.40 (d, *J* = 3.7 Hz, 1H), 7.37 (d, *J* = 5.1 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.61 (s, 1H), 6.04 – 5.84 (m, 2H), 4.12 (d, *J* = 5.5 Hz, 2H), 4.04 (d, *J* = 5.9 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 189.51, 164.30, 148.10, 146.97, 144.74, 136.57, 134.71, 131.05, 129.75, 128.07, 127.49, 126.84, 126.79, 121.67, 121.63, 118.20, 116.72, 63.66, 33.60, 26.10; **IR** (thin film, neat, cm^{-}

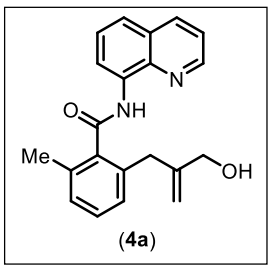
^{1}): 3440, 2900, 2735, 1805, 1741, 1600, 1425, 1367, 1320, 1234, 1189, 1085, 825, 721; **ESI-HRMS:** Calculated for $C_{20}H_{18}N_2O_2S$ $[M+H]^+$ 351.1162; found mass 351.1197.

Scheme S4: General procedure for the synthesis of branched-selective allyl alcohols:



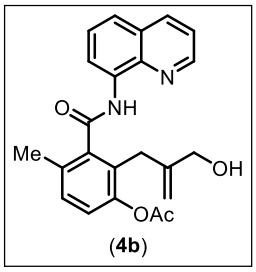
In an oven-dried pressure tube equipped with a stir bar, 2-methyl *N*-(quinolin-8-yl) benzamide **1** (1.0 equiv., 0.1 mmol) and 5-methylene-1,3-dioxan-2-one **2** (2.0 equiv., 0.2 mmol) were dissolved in TFE (1.0 mL). The solution was degassed with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), Na_2[Eosin Y] (20 mol%, 0.02 mmol) and $NaOPiv.H_2O$ (1.0 equiv., 0.1 mmol) were added one after another. O_2 was then bubbled into the pressure tube after which it was sealed tightly with a septum cap. This reaction mixture was then placed under 3 x 7W white LEDs and stirred at room temperature (25 °C) for 24 h. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was diluted with EtOAc, filtered through a short pad of Celite, and concentrated under reduced pressure. The residue was dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography to yield the desired product **4**.

2-(2-hydroxymethyl)allyl)-6-methyl-*N*-(quinolin-8yl)benzamide (4a):



Reaction performed on 0.1 mmol scale (26 mg); Yield 66% (20 mg); Physical appearance: green oil; TLC R_f 0.30 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.99 (d, *J* = 7.1 Hz, 1H), 8.82 – 8.71 (m, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.59 (m, 2H), 7.54 – 7.42 (m, 1H), 7.38 – 7.29 (m, 1H), 7.25 – 7.13 (m, 2H), 5.06 (s, 1H), 4.94 (s, 1H), 3.99 (s, 2H), 3.57 (s, 2H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.21, 148.42, 148.14, 141.47, 138.56, 137.86, 136.55, 136.06, 134.71, 134.08, 129.25, 128.55, 128.10, 127.48, 122.35, 121.75, 117.34, 113.05, 65.22, 31.78, 19.69; **ESI-HRMS:** Calculated for $C_{21}H_{20}N_2O_2$ $[M+H]^+$ 333.1598; found mass 333.1593. **IR** (thin film, neat, cm^{-1}): 3337, 2922, 1712, 1671, 1595, 1482, 1424, 1385, 1326, 1264, 827, 791, 763.

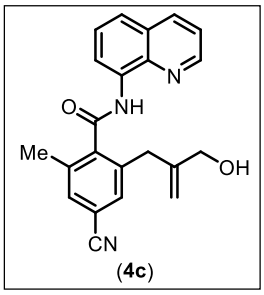
2-(2-hydroxymethyl)allyl)-4-methyl-3-(quinolin-8ylcarbamoyl)phenyl acetate (4b):



(**4b**)

Reaction performed on 0.1 mmol scale (30 mg); Yield 51% (18.5 mg); Physical appearance: Red oil; TLC R_f 0.30 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.96 (dd, *J* = 6.3, 2.7 Hz, 1H), 8.78 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.25 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.54 – 7.48 (m, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 5.04 (d, *J* = 5.2 Hz, 1H), 4.88 (d, *J* = 1.6 Hz, 1H), 3.96 (s, 2H), 3.55 (s, 2H), 2.46 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.55, 168.27, 153.16, 147.86, 146.71, 139.31, 138.88, 133.53, 132.60, 131.39, 130.02, 129.78, 128.25, 127.97, 127.77, 123.70, 122.70, 121.70, 113.20, 65.17, 32.67, 20.97, 19.37; **ESI-HRMS:** Calculated for $C_{23}H_{22}N_2O_4$ $[M+H]^+$ 391.1652; found mass 391.1663. **IR** (thin film, neat, cm^{-1}): 3337, 2924, 1760, 1673, 1521, 1484, 1425, 1324, 1262, 896, 827, 792, 764, 702.

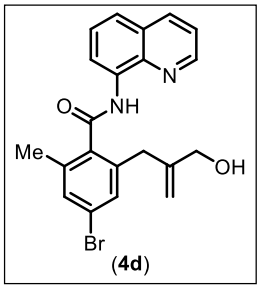
4-cyano-2-(2-hydroxymethyl)allyl)-6-methyl-*N*-(quinolin-8yl)benzamide (4c):



(**4c**)

Reaction performed on 0.1 mmol scale (30 mg); Yield 62% (23.5 mg); Physical appearance: colorless oil; TLC R_f 0.30 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.97 – 8.92 (m, 1H), 8.78 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.25 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.65 (d, *J* = 4.3 Hz, 2H), 7.54 – 7.48 (m, 3H), 5.13 (s, 1H), 4.95 (s, 1H), 4.02 (s, 2H), 3.59 (s, 2H), 2.50 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 189.48, 167.49, 147.01, 146.59, 141.47, 137.58, 136.47, 131.85, 130.98, 128.68, 128.58, 128.48, 128.43, 128.31, 123.43, 121.80, 114.50, 113.21, 97.09, 65.04, 36.96, 19.77; **ESI-HRMS:** Calculated for $C_{22}H_{19}N_3O_2$ $[M+H]^+$ 358.1550; found mass 358.1549. **IR** (thin film, neat, cm^{-1}): 3331, 2923, 2228, 1750, 1673, 1518, 1483, 1424, 1386, 1326, 1264, 827, 750.

4-bromo-2-(2-hydroxymethyl)allyl)-6-methyl-*N*-(quinolin-8yl)benzamide (4d):

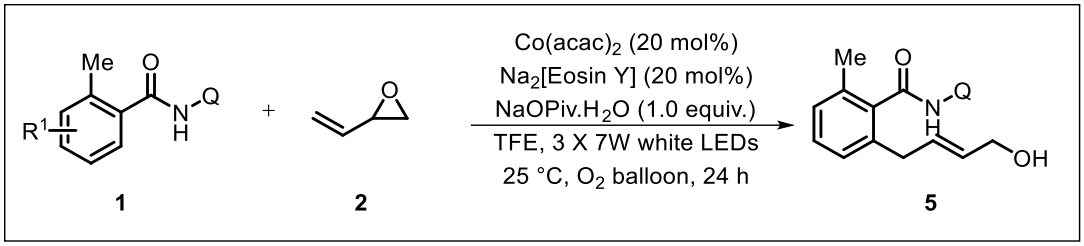


(**4d**)

Reaction performed on 0.08 mmol scale (30 mg); Yield 60% (22 mg); Physical appearance: Brown oil; TLC R_f 0.35 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.94 (dd, *J* = 6.4, 2.6 Hz, 1H), 8.77 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.23 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.50 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.35 (s, 2H), 5.09 (s, 1H), 4.96 (s, 1H), 4.00 (s, 2H), 3.53 (s, 2H), 2.45 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.18, 148.48, 147.34, 138.47, 138.38, 136.99, 136.73, 136.66, 133.84, 131.45, 130.28, 128.12, 127.46, 123.33, 122.57, 121.82, 117.43, 113.77, 65.20, 36.98, 19.51; **ESI-HRMS:** Calculated for $C_{21}H_{19}BrN_2O_2$ $[M+Na]^+$ 433.0522; found mass 433.0489.

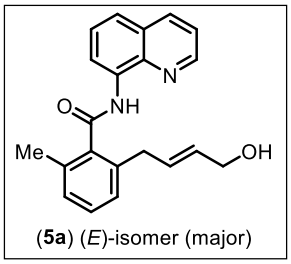
IR (thin film, neat, cm^{-1}): 3311, 2922, 1768, 1630, 1525, 1463, 1407, 1386, 1326, 1264, 827, 764.

Scheme S5: General procedure for the synthesis of (*E*)-selective allyl alcohols:



In an oven-dried pressure tube equipped with a stir bar, 2-methyl *N*-(quinolin-8-yl) benzamide **1** (1.0 equiv., 0.1 mmol) and 2-vinyloxirane **2** (2.0 equiv., 0.2 mmol) were dissolved in TFE (1.0 mL). The solution was degassed with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), Na_2[Eosin Y] (20 mol%, 0.02 mmol) and $NaOPiv.H_2O$ (1.0 equiv., 0.1 mmol) were added sequentially after which the tube was sealed tightly with a septum cap. This reaction mixture was then placed under 3 x 7W white LEDs and continued for stirring at room temperature (25 °C) for 24 h. The reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography to yield the desired product **5**.

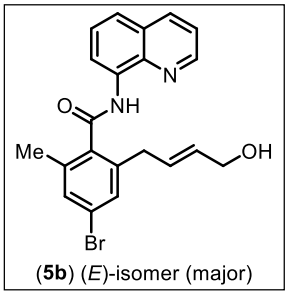
(*E*)-2-(4-hydroxybut-2-en-1-yl)-6-methyl-*N*-(quinolin-8yl)benzamide (5a):



(**5a**) (*E*)-isomer (major)

Reaction performed on 0.1 mmol scale (28 mg); Yield 70% (25 mg); (*E*)/(*Z*) > 16:1, Physical appearance: brown oil; TLC R_f 0.35 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 9.03 (dd, *J* = 7.4, 1.6 Hz, 1H), 8.78 (dd, *J* = 4.4, 1.7 Hz, 1H), 8.25 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.70 – 7.59 (m, 2H), 7.50 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.21 – 7.13 (m, 2H), 5.95 – 5.84 (m, 1H), 5.64 – 5.53 (m, 1H), 3.94 (d, *J* = 5.8 Hz, 2H), 3.52 (d, *J* = 6.4 Hz, 2H), 2.21 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.89, 168.50, 147.57, 137.58, 136.39, 134.98, 133.68, 131.63, 130.66, 129.32, 128.46, 128.39, 128.03, 127.77, 127.38, 122.42, 121.64, 63.48, 36.39, 19.55; **ESI-HRMS:** Calculated for $C_{21}H_{20}N_2O_2$ $[M+Na]^+$ 355.1417; found mass 355.1421. **IR** (thin film, neat, cm^{-1}): 3340, 2925, 1717, 1672, 1522, 1483, 1424, 1386, 1326, 1264, 825, 792, 763.

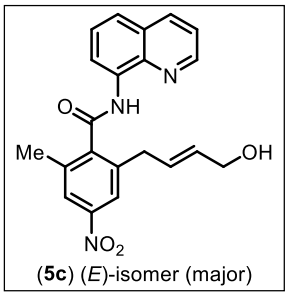
(*E*)-4-bromo-2-(4-hydroxybut-2-en-1-yl)-6-methyl-*N*-(quinolin-8yl)benzamide (5b):



(**5b**) (*E*)-isomer (major)

Reaction performed on 0.12 mmol scale (40 mg); Yield 52% (30 mg); (*E*)/(*Z*) = 6:1, Physical appearance: red oil; TLC R_f 0.30 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.99 (dd, *J* = 7.0, 2.2 Hz, 1H), 8.81 – 8.75 (m, 1H), 8.24 (dt, *J* = 8.3, 1.7 Hz, 1H), 7.69 – 7.59 (m, 3H), 7.50 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 5.93 – 5.78 (m, 1H), 5.72 – 5.55 (m, 1H), 3.96 (dd, *J* = 5.8, 1.3 Hz, 2H), 3.48 (dd, *J* = 6.6, 1.5 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.71, 148.20, 139.28, 138.70, 137.26, 136.57, 136.38, 133.78, 131.29, 130.35, 130.19, 129.91, 129.59, 128.19, 127.63, 123.20, 122.46, 121.79, 63.30, 36.09, 19.32; **ESI-HRMS:** Calculated for $C_{21}H_{19}BrN_2O_2$ $[M+Na]^+$ 433.0522 and 435.0503; found mass 433.0530 and 435.0521. **IR** (thin film, neat, cm^{-1}): 3333, 2924, 1720, 1670, 1576, 1520, 1482, 1424, 1384, 1326, 1264, 896, 763.

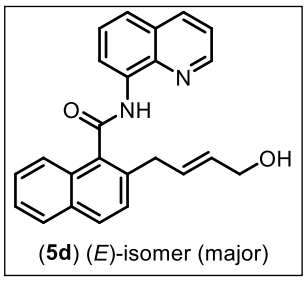
(*E*)-2-(4-hydroxybut-2-en-1-yl)-6-methyl-4-nitro-*N*-(quinolin-8yl)benzamide (5c):



(**5c**) (*E*)-isomer (major)

Reaction performed on 0.1 mmol scale (28 mg); Yield 38% (22 mg); (*E*)/(*Z*) = 10:1, Physical appearance: Yellow oil; TLC R_f 0.35 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 9.02 – 8.94 (m, 1H), 8.78 (d, *J* = 4.1 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 13.8 Hz, 2H), 7.69 – 7.63 (m, 2H), 7.51 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.95 – 5.84 (m, 1H), 5.68 – 5.59 (m, 1H), 3.99 (d, *J* = 5.6 Hz, 2H), 3.61 (d, *J* = 6.5 Hz, 2H), 2.56 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$ δ 166.44, 148.65, 148.09, 143.12, 138.86, 137.38, 136.69, 133.63, 132.21, 129.40, 128.13, 127.44, 123.35, 122.79, 122.38, 121.99, 117.22, 63.18, 36.20, 19.62; **ESI-HRMS:** Calculated for $C_{21}H_{19}N_3O_4$ $[M+Na]^+$ 400.1268; found mass 400.1259. **IR** (thin film, neat, cm^{-1}): 3341, 2924, 1717, 1675, 1522, 1483, 1420, 1386, 1326, 1260, 827, 792, 763.

(*E*)-2-(4-hydroxybut-2-en-1-yl)-*N*-(quinolin-8yl)1-napthamide (5d):

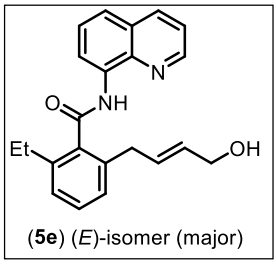


(**5d**) (*E*)-isomer (major)

Reaction performed on 0.1 mmol scale (30 mg); Yield 62% (23 mg); (*E*)/(*Z*) = 7:1, Physical appearance: colorless oil; TLC R_f 0.35 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 9.18 (d, *J* = 7.7 Hz, 1H), 8.70 (d, *J* = 4.2 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.08 – 7.98 (m, 1H), 7.96 – 7.88 (m, 2H), 7.75 – 7.61 (m, 2H), 7.56 – 7.48 (m, 3H), 6.08 – 5.89 (m, 1H), 5.73 – 5.59 (m, 1H), 3.99 (d, *J* = 5.8 Hz, 2H), 3.69 (d, *J* = 6.3 Hz, 2H), **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.35,

147.78, 134.08, 133.93, 132.16, 131.16, 130.98, 130.41, 130.23, 129.86, 129.66, 129.54, 128.33, 128.07, 127.81, 127.39, 127.23, 127.15, 125.94, 124.91, 122.50, 121.70, 63.45, 36.73; **ESI-HRMS:** Calculated for $C_{24}H_{20}N_2O_2$ $[M+Na]^+$ 391.1417; found mass 391.1412. **IR** (thin film, neat, cm^{-1}): 3336, 2920, 1717, 1670, 1573, 1483, 1424, 1382, 1326, 1264, 827, 792, 763.

(*E*)-2-ethyl-6-(4-hydroxybut-2-en-1-yl)-*N*-(quinolin-8yl)benzamide (5e):

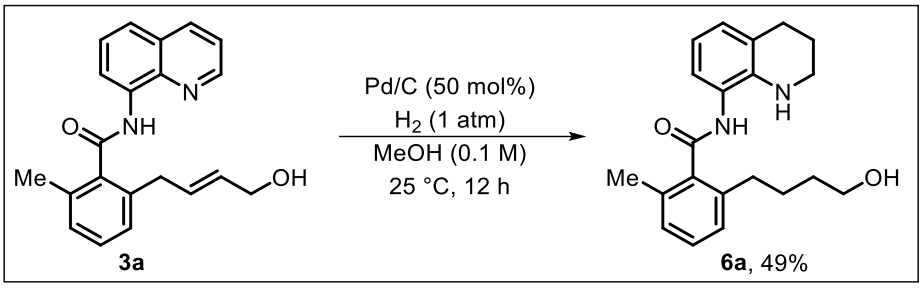


(**5e**) (*E*)-isomer (major)

Reaction performed on 0.1 mmol scale (30 mg); Yield 65% (24.5 mg); (*E*)/(*Z*) = 2:1, Physical appearance: brown oil; TLC R_f 0.30 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 9.03 (dd, *J* = 7.5, 1.4 Hz, 1H), 8.79 – 8.74 (m, 1H), 8.27 – 8.20 (m, 1H), 7.70 – 7.58 (m, 2H), 7.49 (dd, *J* = 8.2, 4.3 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.15 (m, 1H), 5.96 – 5.83 (m, 1H), 5.66 – 5.54 (m, 1H), 3.93 (dd, *J* = 5.9, 1.3 Hz, 2H), 3.52 (d, *J* = 6.5 Hz, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.71, 148.04, 141.18, 137.19, 136.91, 136.34, 133.98, 131.56, 130.62, 129.63, 129.46, 128.23, 127.74, 127.38, 127.01, 126.83, 122.24, 121.70, 63.46, 36.42, 26.48, 15.87; **ESI-HRMS:** Calculated for $C_{22}H_{22}N_2O_2$ $[M+Na]^+$ 369.1573; found mass 369.1567. **IR** (thin film, neat, cm^{-1}): 3339, 2965, 2872, 1716, 1672, 1522, 1483, 1424, 1385, 1325, 1264, 1009, 827, 792, 763.

4. Synthetic Applications:

Scheme S6: General procedure for the hydrogenation reaction of linear allylated arene:

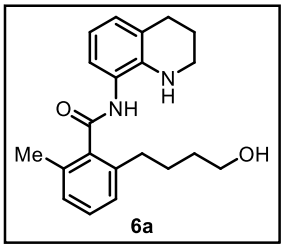


3a **6a**, 49%

Procedure: In an oven-dried RB-flask equipped with a magnetic stir bar, was dissolved 2-(4-hydroxybut-2-en-1-yl)-6-methyl-*N*-(quinoline-8-yl)benzamide **3a** (20 mg, 1.0 equiv.) in MeOH (0.6 mL) following which was added Pd/C (4 mg, 10 wt.%). The vessel was evacuated and backfilled with H_2. The reaction was stirred at room temperature for 12 h under an H_2 balloon. Upon completion of the reaction (as indicated by TLC), the crude reaction mixture was degassed with N_2 and passed through a pad of Celite, eluted with EtOAc (5 mL) and the filtrate was concentrated under reduced pressure. The crude product obtained was purified by

silica gel flash column chromatography (eluent: Petroleum ether: EtOAc = 4:1) to afford the corresponding product **6a** in 49% yield.

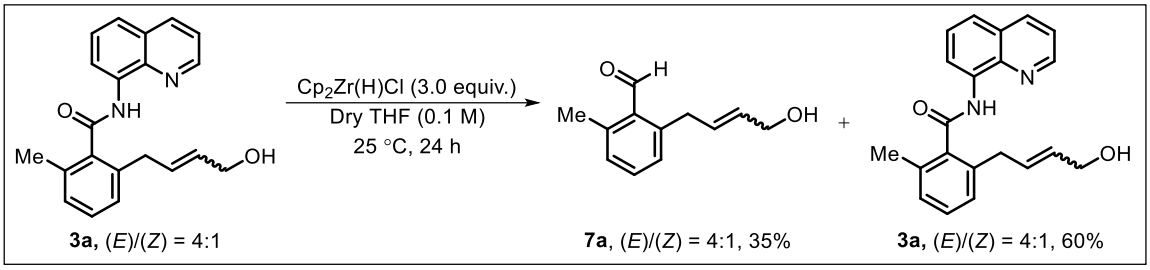
2-(4-hydroxybutyl)-6-methyl-*N*-(1,2,3,4-tetraquinolin-8-yl)benzamide (6a):



6a

Reaction performed on 0.1 mmol scale (20 mg); Yield 49% (10 mg), Physical appearance: white oil; TLC R_f 0.20 (1:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.18 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 2H), 6.94 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.72 (t, *J* = 7.7 Hz, 1H), 3.62 (t, *J* = 6.3 Hz, 2H), 3.36 (t, *J* = 5.4 Hz, 2H), 2.84 (t, *J* = 6.4 Hz, 2H), 2.79 – 2.70 (m, 2H), 2.45 (s, 3H), 1.94 (p, *J* = 6.3 Hz, 3H), 1.81 – 1.70 (m, 2H), 1.61 (p, *J* = 6.5 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.22, 139.05, 138.82, 137.07, 134.32, 129.16, 127.88, 127.83, 126.87, 125.01, 123.61, 122.35, 117.84, 61.96, 42.39, 33.14, 32.29, 27.97, 27.42, 21.84, 19.55; **ESI-HRMS:** Calculated for $C_{21}H_{26}N_2O_2$ $[M+H]^+$ 339.2067; found mass 339.2062. **IR** (thin film, neat, cm^{-1}): 3340, 2920, 1710, 1672, 1522, 1485, 1424, 1386, 1326, 1264, 827, 791, 749.

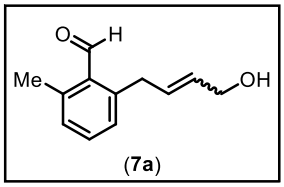
Scheme S7: General procedure for removal of the DG from linear allylated arene:



3a, (*E*)/(*Z*) = 4:1 **7a**, (*E*)/(*Z*) = 4:1, 35% **3a,** (*E*)/(*Z*) = 4:1, 60%

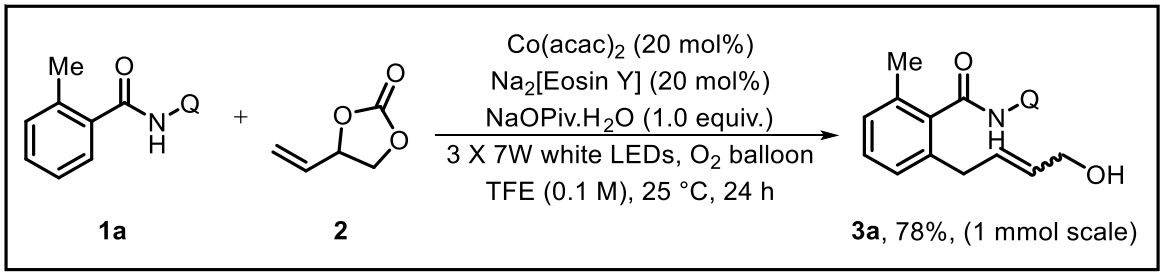
Procedure: In an oven-dried pressure tube equipped with a stir-bar, was dissolved 2-(4-hydroxybut-2-en-1-yl)-6-methyl-*N*-(quinoline-8-yl)benzamide **3a** (20 mg, 1.0 equiv.) in dry THF (0.5 mL, 0.1 M). This is followed by the addition of $Cp_2Zr(H)Cl$ (47 mg, 3.0 equiv.) under a N_2 atmosphere and the mixture was degassed with N_2 for about 10 min following which it was sealed tightly with a septum cap. The reaction was then stirred at room temperature for 24 h. Upon completion of the reaction (as indicated by TLC), the crude reaction mixture was passed through a pad of Celite, eluted with EtOAc (5 mL) and the filtrate was concentrated under reduced pressure. The crude product obtained was purified by silica gel flash column chromatography (eluent: Petroleum ether: EtOAc = 10:1) to afford the corresponding product **7a** in 35% (5 mg) yield (*i.e.* 65% (brsm)) and 60% yield (45 mg) of the starting material was recovered back.

2-(4-hydroxybut-2-en-1-yl)-6-methylbenzaldehyde (7a):



Reaction performed on 0.23 mmol scale (75 mg); Yield 35% (15 mg); (*E*)/(*Z*) = 4:1, Physical appearance: colorless oil; TLC R_f 0.30 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.10 (m, 2H), 5.99 – 5.86 (m, 1H), 5.66 – 5.57 (m, 1H), 4.12 (dd, *J* = 5.8, 1.3 Hz, 2H), 3.75 (d, *J* = 6.2 Hz, 2H), 2.64 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.51, 142.68, 141.29, 133.19, 132.22, 131.25, 130.70, 130.36, 129.13, 63.44, 35.94, 20.66; **ESI-HRMS:** Calculated for $C_{12}H_{14}O_2$ $[M+Na]^+$ 213.0886; found mass 213.0892. **IR** (thin film, neat, cm^{-1}): 3385, 2923, 1688, 1592, 1465, 1386, 1275, 1191, 974, 764, 749.

Scheme S7: 1 mmol scale synthesis of linear allylated arenes (3a):



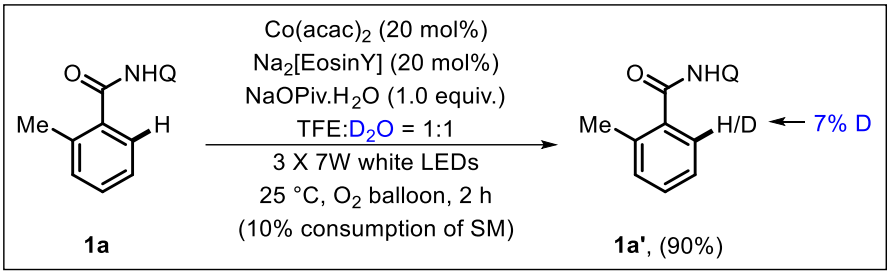
Procedure:

In a pressure tube equipped with a stir bar, 2-methyl-*N*-(quinolin-8-yl)benzamide **1a** (265 mg, 1.0 equiv., 1 mmol), 4-vinyl-1,3-dioxolan-2-one **2** (231 mg, 2.0 equiv., 2 mmol) were dissolved in TFE (HPLC grade, 5 mL) and degassed with oxygen for about 10 min. This was followed by the sequential addition of $Co(acac)_2$ (52.0 mg, 20 mol%), Na_2[Eosin Y] (140 mg, 20 mol%) and $NaOPiv.H_2O$ (144 mg, 1.0 equiv.) under an oxygen atmosphere. The reaction tube was then sealed with a Teflon screw cap and placed under white LEDs (3 x 7W) and stirred at room temperature (25 °C) for 24 hours. Upon completion of the reaction (as monitored by TLC), the reaction mixture was filtered through a pad of Celite and eluted with EtOAc. The solvent was removed under reduced pressure and the residue was re-dissolved in EtOAc (10 mL) and washed with sat. $NaHCO_3$ for several times and then with brine. The organic extract was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (eluting with 4:1, Petroleum ether:EtOAc) to yield the desired product **3a** in 78% (262 mg) yield.

5. Mechanistic Studies:

Scheme S8: Reversibility studies for C–H metalation of 2-methyl-*N*-(quinoline-8-yl)benzamide (1a) in the synthesis of linear allylated arenes

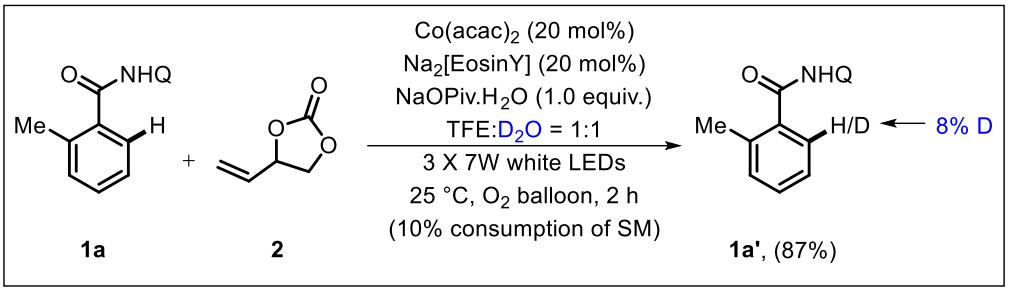
(A) (i) Reversibility study of 2-methyl-*N*-(quinoline-8-yl)benzamide (1a) in absence of the coupling partner:



Procedure:

In an oven-dried pressure tube equipped with a stir bar, the 2-methyl-*N*-(quinolin-8-yl)benzamide **1a** (1.0 equiv., 0.1 mmol, 15 mg) was dissolved in TFE (0.02 mL) and D_2O (10 equiv., 1 mmol, 0.02 mL) was added to this solution. The solution was degassed with oxygen for about 5 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol, 3 mg), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol, 8.1 mg), and Na_2[Eosin Y] (20 mol%, 0.02 mmol, 8.0 mg) were added. The pressure tube was sealed with a septum cap and placed under white LEDs (3 x 7W) and stirred at room temperature (25 °C) for 2 hours. After that, the reaction mixture was diluted with EtOAc, washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (eluting with 9:1, Petroleum ether: EtOAc). The isolated starting material was analyzed by ^1H NMR, indicating ~7% deuteration at the *ortho*-position of the recovered starting material. This indicated that the C–H metallation step for Co-catalysis was reversible in absence of coupling partner.

(ii) Reversibility study of 2-methyl-*N*-(quinoline-8-yl)benzamide (1a) in presence of coupling partner:

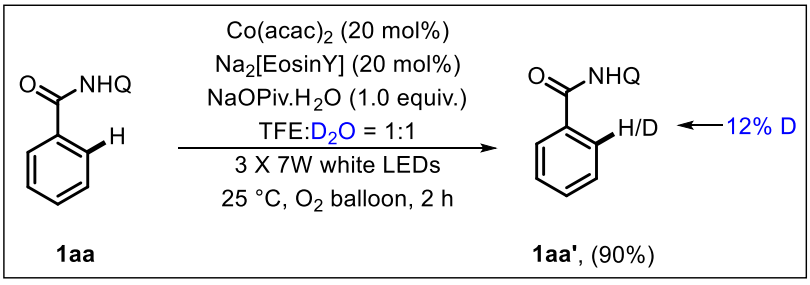


Procedure:

In an oven-dried pressure tube equipped with a stir bar, the 2-methyl-*N*-(quinolin-8-yl)benzamide **1a** (1.0 equiv., 0.1 mmol, 15 mg) and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 13 mg) were dissolved in TFE (0.02 mL) and D_2O (10 equiv., 1 mmol, 0.02 mL) was added to this solution. The solution was degassed with oxygen for about 5 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol, 3 mg), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol, 8.1 mg), and Na_2[Eosin Y] (20 mol%, 0.02 mmol, 8.0 mg) were added. The pressure tube was sealed with a septum cap and placed under white LEDs (3 x 7W) and stirred at room temperature (25 °C) for 2 hours. After that, the reaction mixture was diluted with EtOAc, washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (eluting with 9:1, Petroleum ether: EtOAc). The isolated starting material was analyzed by ^{1}H NMR, indicating ~8% deuteration at the *ortho*-position of the recovered starting material. This indicated that the C–H metallation step for Co catalysis in presence of coupling partner was reversible.

(iii) Experiment to check for the reason of *ortho*-constraint in the starting material: Reversibility of C–H metallation of *N*-(quinoline-8-yl)benzamide under the reaction conditions:

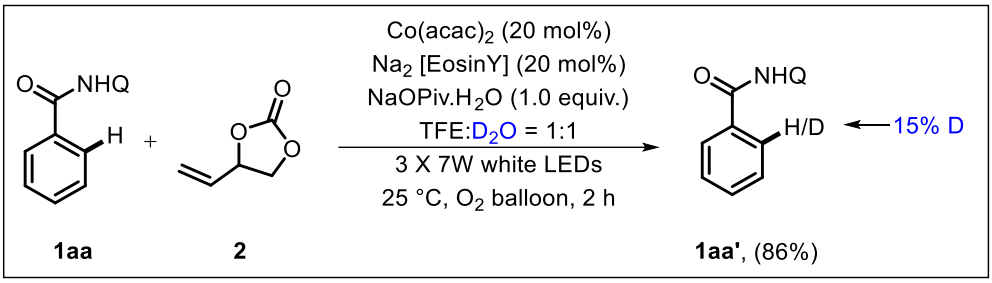
(a) Reversibility study in absence of coupling partner



Procedure:

The same procedure as previous was followed with *N*-(quinolin-8-yl)benzamide **1aa** (1.0 equiv., 0.1 mmol, 15 mg). After 2 h, the reaction was worked-up and the isolated starting material was analyzed by ^{1}H NMR, indicating ~12% deuteration at the *ortho*-position of the recovered starting material **(1aa')**.

(b) Reversibility study in presence of coupling partner:



Procedure:

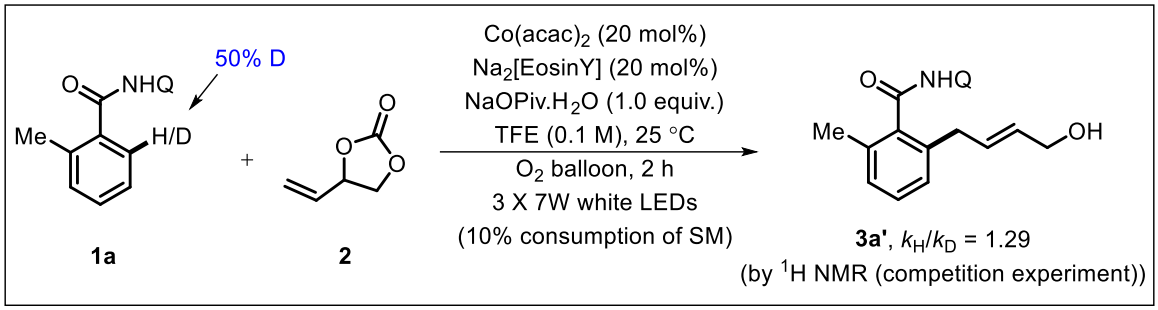
The same procedure as previous was followed with *N*-(quinolin-8-yl)benzamide **1aa** (1.0 equiv., 0.1 mmol, 15 mg) and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 13 mg). After 2 h, the reaction was worked-up and the isolated starting material was analyzed by ^{1}H NMR, indicating ~15% deuteration at the *ortho*-position of the recovered starting material **(1aa')**.

The comparatively higher deuterium extent in the recovered starting material observed in these experiments suggested that the absence of the *ortho*-methyl group may contribute to the thermodynamic instability of the corresponding cobaltacycle (Co assumes +III oxidation state), which may fail to deliver the allylated product under the optimized reaction conditions.

Scheme S9: Studies to check for a Kinetic Isotope Effect (KIE) under the Co-catalysis:

To further investigate whether the C−H metalation step is rate-limiting, we carried out studies to check for a kinetic isotope effect.

(i) Competition Experiment (by NMR):

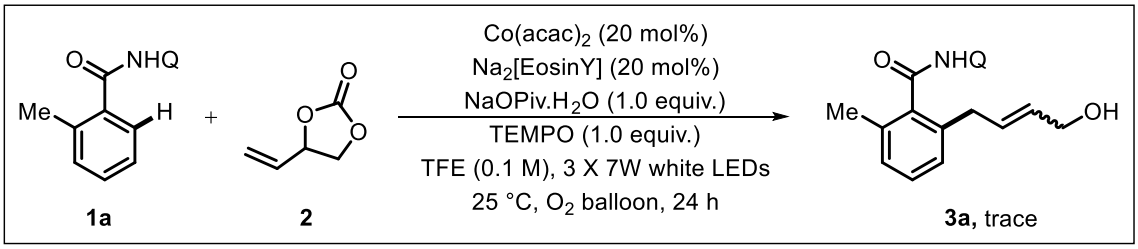


Procedure:

In an oven-dried pressure tube equipped with a stir bar, 2-methyl-*N*-(quinolin-8-yl)benzamide **1a-D** (50% D) (1.0 equiv., 0.05 mmol, 12 mg) and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 17 mg) were dissolved in TFE (1 mL, 0.1 M) and the solution was degassed with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol, 3.9 mg), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol, 11 mg), and Na_2[Eosin Y] (20 mol%, 0.02 mmol, 11 mg) were added sequentially. The pressure tube was then sealed with a septum cap and the reaction mixture was then placed under white LEDs (3 × 7W) under an O_2 atmosphere by using an oxygen balloon. The reaction was stirred for 2 hours (10% consumption of starting material), after which the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude material was purified by silica gel flash column chromatography. The recovered starting material was analyzed by ^{1}H NMR. Relative integration of the peaks of the recovered starting materials indicated a value of 1.29 for k_H/k_D. This study suggested that the C–H activation may be the rate-limiting step of the overall catalytic cycle.

6. Control Experiments:

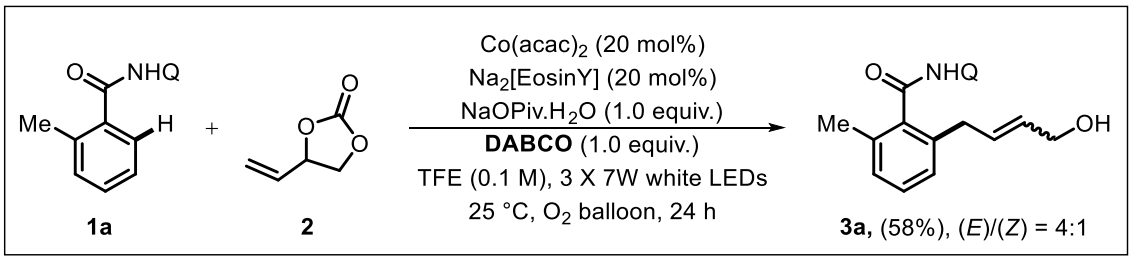
Scheme S10: Radical Quenching Experiments:



Procedure:

In an oven-dried pressure tube equipped with a stir bar, *N*-(quinolin-8-yl)benzamide **1a** (1.0 equiv., 0.038 mmol, 10 mg) and 4-vinyl-1,3-dioxolan-2-one **2** (2 equiv., 0.076 mmol, 8.7 mg) were dissolved in TFE (0.5 mL, 0.05 M). The solution was degassed with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.008 mmol, 2.0 mg), Na_2[Eosin Y] (20 mol%, 0.008 mmol, 5.3 mg) and $NaOPiv.H_2O$ (1.0 equiv., 0.038 mmol, 5.4 mg) followed by the radical scavenger TEMPO (1.0 equiv., 0.076 mmol, 12 mg) were added and the pressure tube was then sealed with a septum cap and put under white LEDs (7W × 3) and then stirred for 24 h. The reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the starting materials were purified by silica gel flash column chromatography (eluted with Petroleum ether : EA = 9 : 1) and only a trace amount of product was obtained and 70% yield (6.5 mg) of the starting material was observed. This suggested that the reaction involved the formation of a C-centered radical species in one of the intermediate steps.

Scheme S11: Experiment to check for the involvement of singlet oxygen:



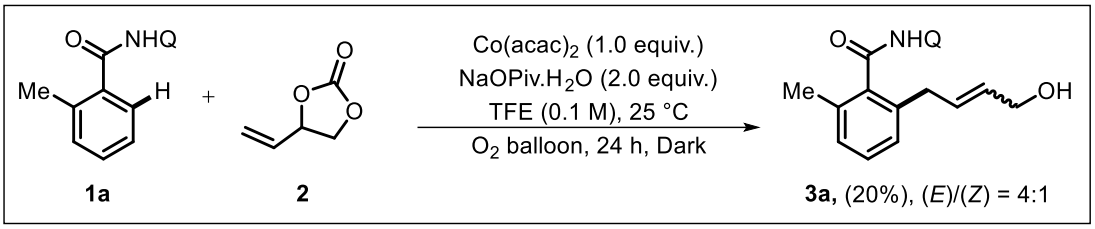
Procedure:

In an oven-dried pressure tube equipped with a stir bar, 2-methyl-*N*-(quinolin-8-yl)benzamide **1a** (1.0 equiv., 0.1 mmol, 30 mg) and 4-vinyl-1,3-dioxolan-2-one **2** (2 equiv., 0.23 mmol, 26 mg) were dissolved in TFE (0.5 mL, 0.1 M). The solution was degassed with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.023 mmol, 5.9 mg), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol, 16 mg), and Na_2[Eosin Y] (20 mol%, 0.023 mmol, 5.3 mg) along with DABCO (1 equiv., 0.1 mmol, 13 mg) were added. The pressure tube was sealed with a septum cap and the reaction mixture was then placed under white LEDs (7W × 3) environment under an oxygen

balloon. The reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. It was observed that in the presence of DABCO there was no significant effect on the reaction and 58% yield of the desired coupling product **3a** (22 mg) was obtained after purification by a silica gel flash column chromatography (eluted with Petroleum Ether : EA = 4:1) and 38% yield (11.5 mg) of the starting material was observed. From this experiment, the possibility of involvement of singlet oxygen was ruled out.

Scheme S12: Role of Oxygen (O_2) as an oxidant:

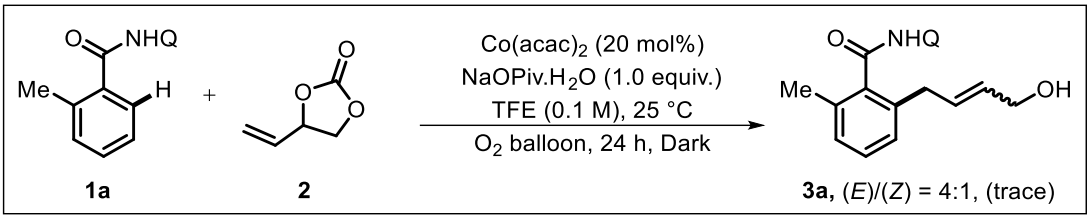
(i) Reaction in presence of O_2 balloon by using Co-catalyst in stoichiometric amount:



Procedure:

In an oven-dried pressure tube equipped with a stir bar, *N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol, 27 mg) **1a** and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 23 mg) were dissolved in TFE (1.0 mL, 0.1 M). The solution was degassed with oxygen for about 15 min, following which $Co(acac)_2$ (1.0 equiv., 0.1 mmol, 26 mg), $NaOPiv.H_2O$ (2.0 equiv., 0.2 mmol, 29 mg), were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under an oxygen balloon. The progress of the reaction was monitored by TLC. After 24 hours, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was re-dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (eluted with Pet Ether:EA = 4:1) giving the allylated product **3a** (8 mg) in 20% yield and 70% yield (11 mg) of the starting material **1a** was observed.

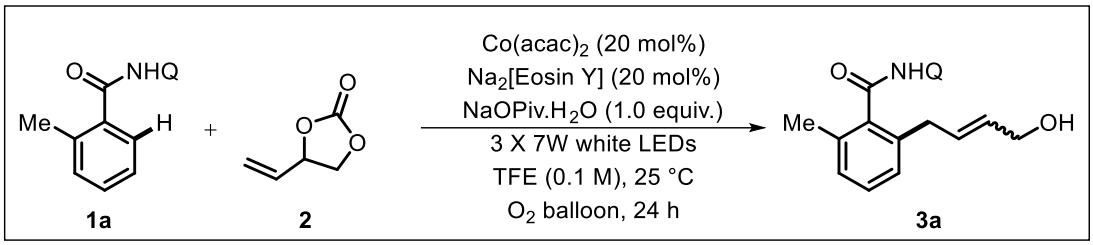
(ii) Reaction in presence of O_2 balloon by using Co-catalyst in catalytic amount:



Procedure:

In an oven-dried pressure tube equipped with a stir bar, *N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol, 27 mg) **1a** and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 23 mg) were dissolved in TFE (1.0 mL). The solution was degassed with oxygen for about 15 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol, 5.2 mg), $NaOPiv.H_2O$ (2.0 equiv., 0.2 mmol, 15 mg) were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under an oxygen balloon. The progress of the reaction was monitored by TLC. After 24 hours, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (eluted with Pet Ether:EA (4:1)) giving the allylated product only in trace amount and 80% yield (23 mg) of the starting material **1a** was observed.

(iii) Experiment to check for the formation of H_2O_2 in the reaction:[4]



Procedure: In an oven-dried pressure tube equipped with a stir bar, 2-methyl-*N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol, 40 mg) **1a** and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 35 mg) were dissolved in TFE (1.0 mL, 0.1 M). The solution was saturated with oxygen for about 15 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol, 4 mg), Na_2[Eosin Y] (20 mol%, 0.02 mmol, 5.4 mg), $NaOPiv.H_2O$ (1.0 equiv., 0.1 mmol, 44 mg), were added and the pressure tube was sealed with a septum cap. The reaction mixture was irradiated with 3 X 7W white LEDs at 25 °C for 24 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with EtOAc (2 mL) and

filtered through a short pad of Celite. Deionized water (2 mL) was then added to the filtrate, and this was transferred to a separatory funnel. The solution was shaken vigorously several times. All the aqueous part (pink color) was then collected in a 100 mL conical flask. The process was repeated thrice. To the combined aqueous extract, a spatula-full amount of activated charcoal was added, and the solution was stirred for several minutes until the color of Na_2[Eosin Y] disappeared. This was then passed through activated charcoal again and filtered and collected in an Erlenmeyer flask. H_2SO_4 (0.2 mL 1N) was added to this solution. In another Erlenmeyer flask, starch solution (3 mL, (3wt.%)) and KI (1 mmol, 10 mg) were added to deionized water (5 mL). The liquids of these two flasks were mixed and stirred well. Within 5-10 minutes, a pale purple color started appearing which darkened in the next 1–2 h (Figure S1). This study suggested that the generation of H_2O_2 took place in the reaction.

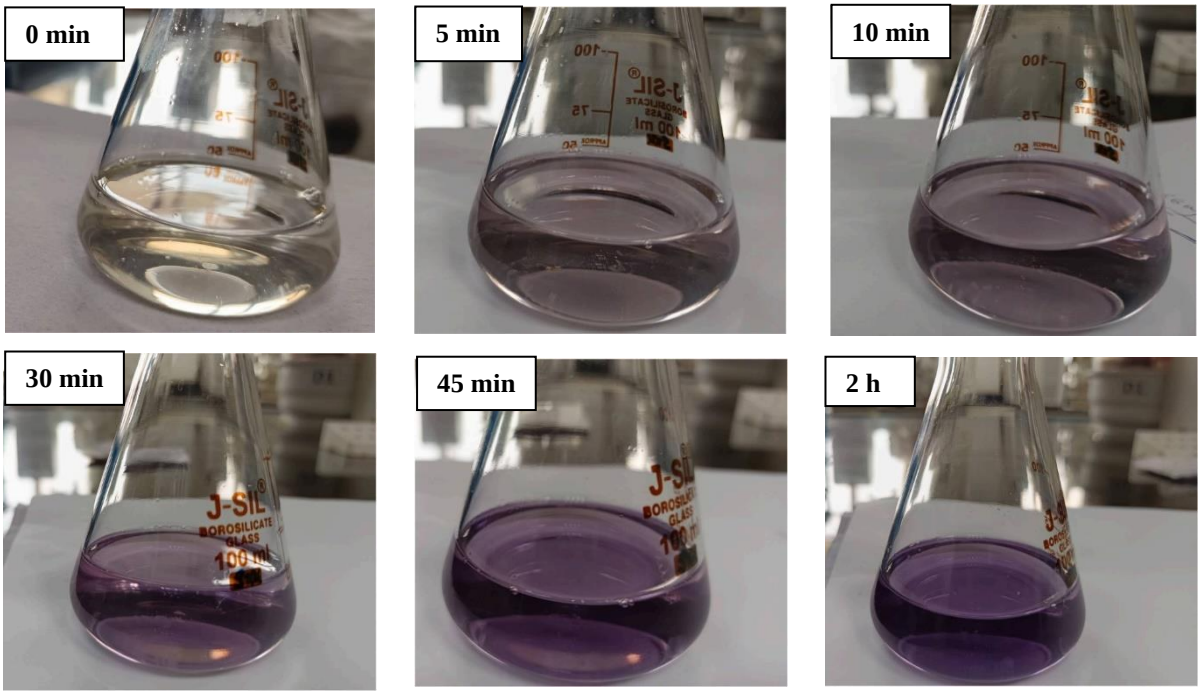
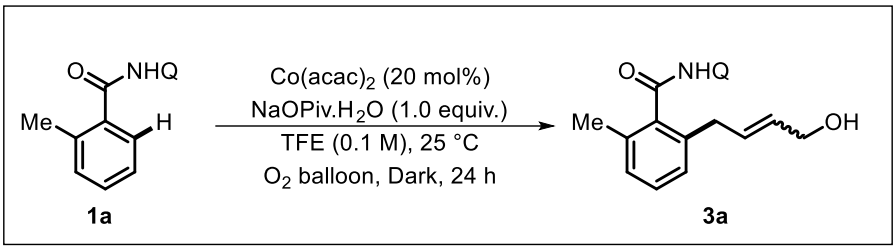


Fig S2: Aqueous extract of the reaction mixture with KI-starch solution.[4]

(iv) Confirmation for the formation of H_2O_2 in the first step of the catalytic cycle:[4]



1a 3a

Procedure: In an oven-dried pressure tube equipped with a stir bar, 2-methyl-*N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol, 40 mg) **1a** was dissolved in TFE (1.0 mL). The solution was saturated with oxygen for about 15 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol, 4 mg), $NaOPiv.H_2O$ (1.0 equiv., 0.1 mmol, 44 mg), were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under an oxygen balloon. After 24 h, the reaction mixture was diluted with EtOAc (2 mL) and filtered through a short pad of Celite. Deionized water (2 mL) was then added to the filtrate, and this was transferred to a separatory funnel. The solution was shaken vigorously several times. All the aqueous part (pink color) was then collected in a 100 mL conical flask. The process was repeated thrice. To the combined aqueous extract, a spatula-full amount of activated charcoal was added, and the solution was stirred for several minutes until the color of Na_2[Eosin Y] disappeared. This was then passed through activated charcoal again and filtered and collected in an Erlenmeyer flask. H_2SO_4 (0.2 mL 1N) was added to this solution. In another Erlenmeyer flask, starch solution (3 mL, (3wt.%)) and KI (1 mmol, 10 mg) were added to deionized water (5 mL). The liquids of these two flasks were mixed and stirred well. Within 15–45 minutes, the pale purple color started appearing which became dark in the next 4–6 h (Figure S2). This study suggested that the slow generation of H_2O_2 was observed in the first step of the catalytic cycle and O_2 played a crucial role in the oxidation of Co(II) to Co(III) and reduced itself to O_2 radical anion.

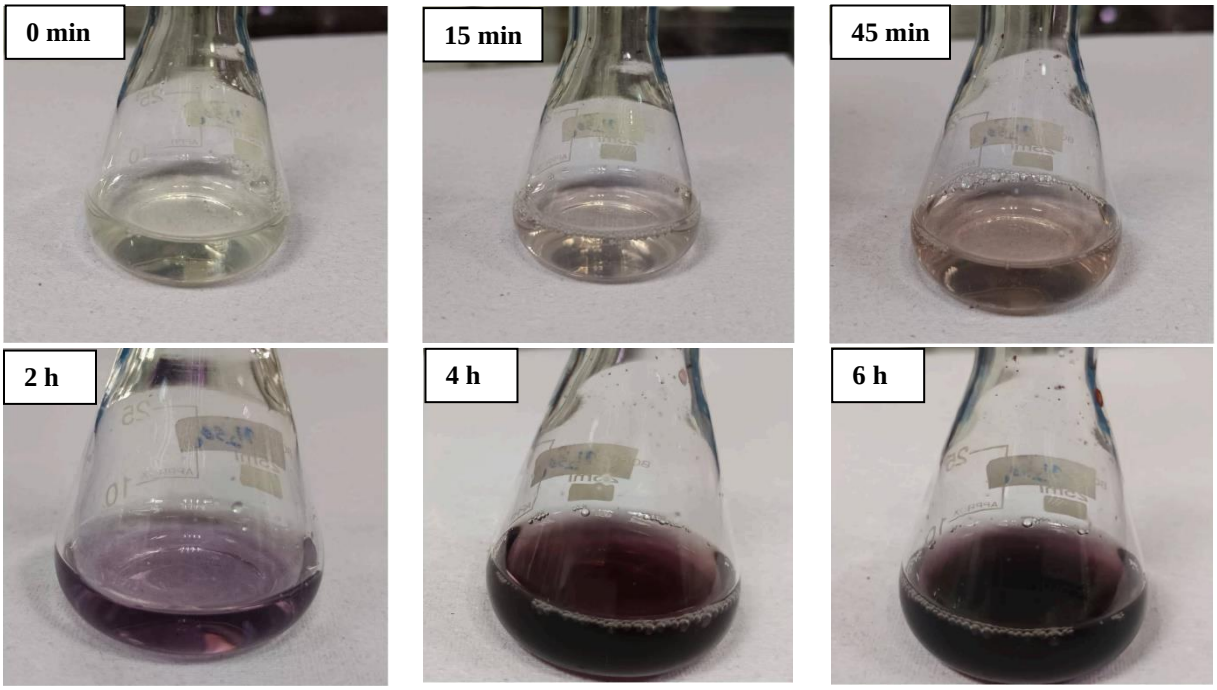
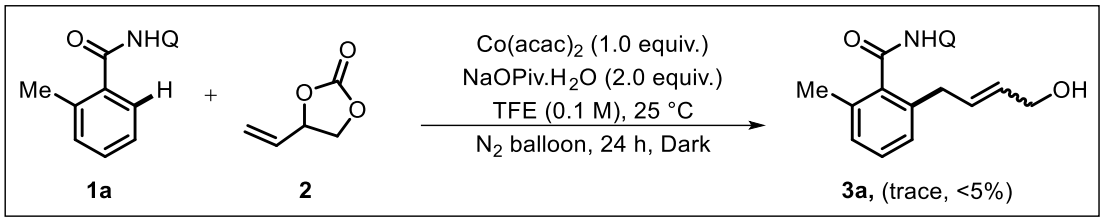


Fig S3: Aqueous extract of the reaction mixture with KI-starch solution.[4]

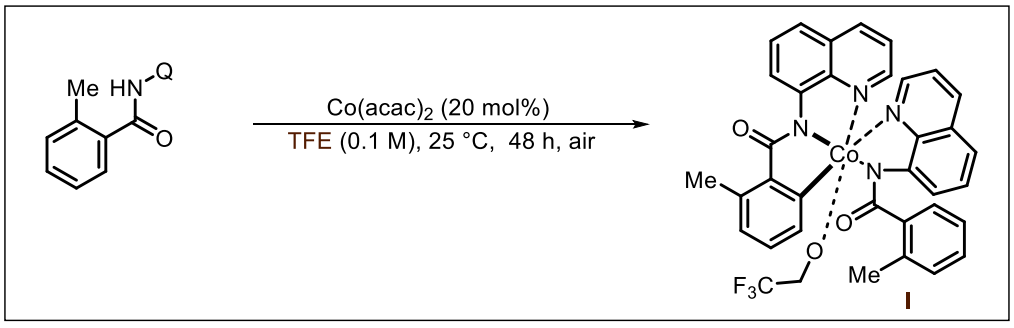
(v) Reaction in presence of N_2 balloon:



Procedure:

In an oven-dried pressure tube equipped with a stir bar, *N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol, 27 mg) **1a** and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 23 mg) were dissolved in TFE (1.0 mL, 0.1 M). The solution was degassed with nitrogen for about 15 min, following which $Co(acac)_2$ (1.0 equiv., 0.1 mmol, 26 mg), $NaOPiv.H_2O$ (2.0 equiv., 0.2 mmol, 29 mg) were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under an N_2 atmosphere. The progress of the reaction was monitored by TLC. After 24 hours, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (eluted with Pet Ether:EA (4:1)) affording the allylated product in trace amount (< 5% yield) and 89% yield (24 mg) of the starting material **1a** was observed. This indicated that oxygen is necessary for the overall transformation and the reaction was hampered under inert atmosphere in absence of light.

Scheme S13: Synthesis of cobaltacycle intermediate (I):[5]



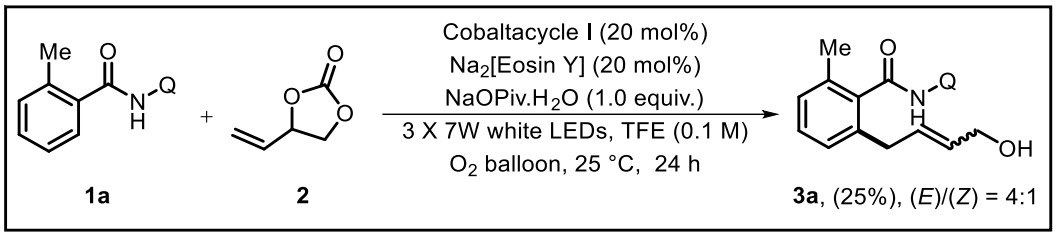
Procedure:

To an oven-dried round bottom flask charged with a magnetic stir bar was dissolved $Co(acac)_2$ (258 mg, 1.0 mmol, 1.0 equiv.) in TFE (8 mL), and to this solution was added **1a** (263 mg, 1.0

mmol, 1.0 equiv.) under air, and the reaction mixture was stirred at room temperature for 48 h. After completion of the reaction, the solvent was concentrated under reduced pressure to give a residue which was purified by silica gel column chromatography (PET ether: EA = 1:1) to give the desired cobalt complex **I in** 25% yield (190 mg), as reported in the literature.[5]

ESI-HRMS: Calculated for $C_{34}H_{25}CoN_4O_2$ $[M+H]^+$ 581.1377; found mass 581.1388.

Scheme S14: Allylation experiment using pre-formed cobaltacycle (I) as the catalyst:

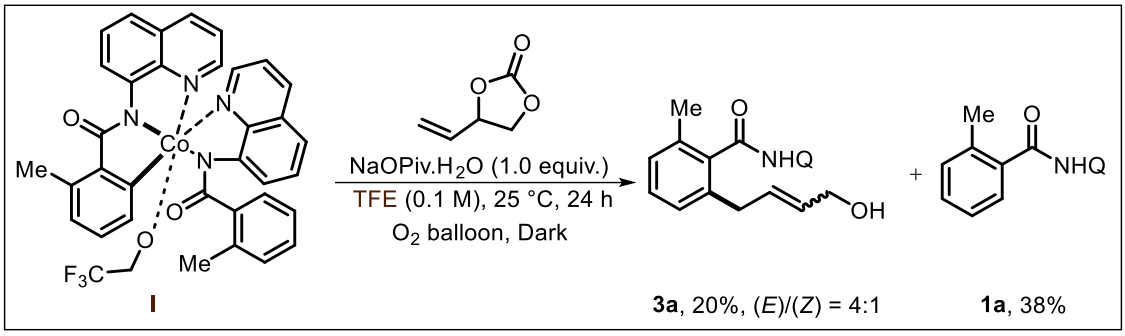


Procedure:

In an oven-dried pressure tube equipped with a stir bar, *N*-(quinolin-8-yl)benzamide **1a** (1.0 equiv., 0.1 mmol, 27 mg) and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 23 mg) were dissolved in TFE (1.0 mL, 0.1 M). The solution was saturated with oxygen for about 10 min, following which cobaltacycle **I** (20 mol%, 0.02 mmol, 14 mg), NaOPiv.H_2O (1.0 equiv., 0.1 mmol, 15 mg) and Na_2[Eosin Y] (20 mol%, 0.02 mmol, 14 mg) were added sequentially, following which the pressure tube was sealed with a septum cap. This reaction mixture was then placed under white LEDs (3 X 7W) environment under an oxygen balloon. The progress of the reaction was monitored by TLC. After 24 hours, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (eluted with Pet Ether:EA (4:1)) giving the allylated product **3a** (8.5 mg) with 25% yield and 56% yield (15 mg) of the starting material **1a** was observed. This experiment indicates that cobaltacycle intermediate **I** may be involved in the reaction.

Scheme S15: Role of additive:

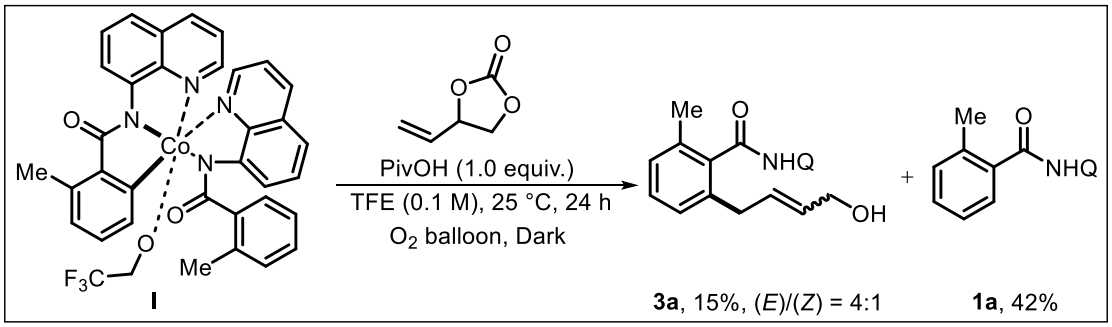
(i) Reaction in presence of NaOPiv.H_2O as an additive:-



Procedure:

In an oven-dried pressure tube equipped with a stir bar, cobaltacycle **I** (1.0 equiv., 0.1 mmol, 10 mg) and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 3.4 mg) were dissolved in TFE (0.5 mL, 0.1 M). The solution was saturated with oxygen for about 10 min, following which NaOPiv.H_2O (1.0 equiv., 0.1 mmol, 2.1 mg) was added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under an O_2 balloon. The progress of the reaction was monitored by TLC. After 24 hours, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (eluted with Pet Ether:EA = 4:1) giving the allylated product **3a** (1 mg) with 20% yield ((*E*)/(*Z*) ~ 4:1) and 38% of **1a** (1.5 mg) was obtained.

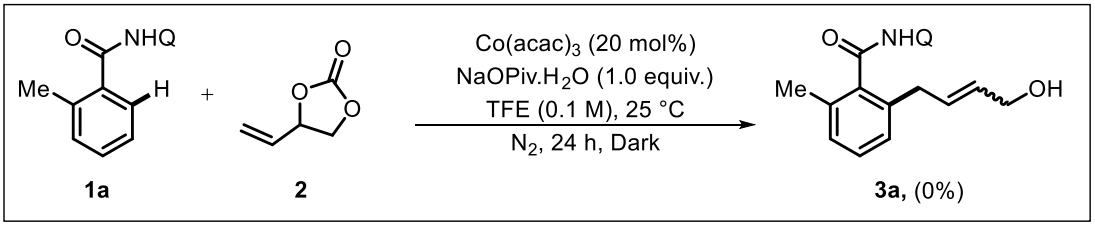
(ii) Reaction in presence of PivOH as an additive:-



Procedure:

In an oven-dried pressure tube equipped with a stir bar, cobaltacycle **I** (1.0 equiv., 0.1 mmol, 10 mg) and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 3.4 mg) were dissolved in TFE (0.5 mL, 0.1 M). The solution was saturated with oxygen for about 10 min, following which PivOH (1.0 equiv., 0.1 mmol, 2.3 mg) was added and the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under an O_2 balloon. The progress of the reaction was monitored by TLC. After 24 hours, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (eluted with Pet Ether:EA (4:1)) giving the allylated product **3a** (0.8 mg) with 15% yield ((*E*)/(*Z*) ~ 4:1) and 42% of **1a** (1.7 mg) was obtained.

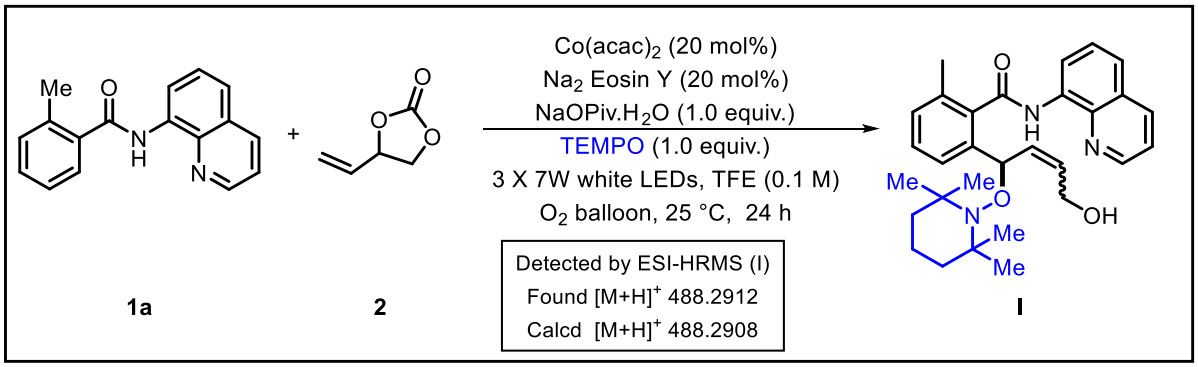
Scheme S16: Reaction in presence of $Co(acac)_3$ catalyst in dark:



Procedure:

In an oven-dried pressure tube equipped with a stir bar, *N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol, 27 mg) **1a** and 4-vinyl-1,3-dioxolan-2-one **2** (2.0 equiv., 0.2 mmol, 23 mg) were dissolved in TFE (1.0 mL, 0.1 M). The solution was degassed with nitrogen for about 10 min, following which $Co(acac)_3$ (20 mol%, 0.02 mmol, 7.3 mg), $NaOPiv.H_2O$ (1.0 equiv., 0.1 mmol, 15 mg), were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under an N_2 balloon. The progress of the reaction was monitored by TLC. After 24 hours, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated $NaHCO_3$ solution and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the starting materials **1a** (24 mg) and **2** (10 mg) were recovered back (purified by silica gel flash column chromatography, eluted with Pet Ether:EA (9:1)) in 89% & 85% yields respectively. This indicates that $Co(acac)_3$ is not the active catalyst in this transformation.

Scheme S17: Detection of the TEMPO adduct:



Procedure:

In an oven-dried pressure tube equipped with a stir bar, *N*-(quinolin-8-yl)benzamide **1a** (1.0 equiv., 0.1 mmol, 60 mg) and 4-vinyl-1,3-dioxolan-2-one **2** (2 equiv., 0.20 mmol, 52 mg) were dissolved in TFE (1.0 mL). The solution was saturated with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol, 12 mg), Na_2[Eosin Y] (20 mol%, 0.02 mmol, 32 mg) and $NaOPiv.H_2O$ (1.0 equiv., 33 mg) and the radical scavenger TEMPO (1.0 equiv., 36 mg) were added sequentially in the reaction mixture. The pressure tube was then sealed with a septum cap and stirred under white LEDs (3 × 7W) for 24 h. Upon completion of the reaction, an aliquot was drawn, passed through a frit, and subjected immediately to mass analysis. The key radical adduct **I** was detected by ESI-HRMS and indicates that the corresponding benzylic radical has been formed as one of the key intermediates.

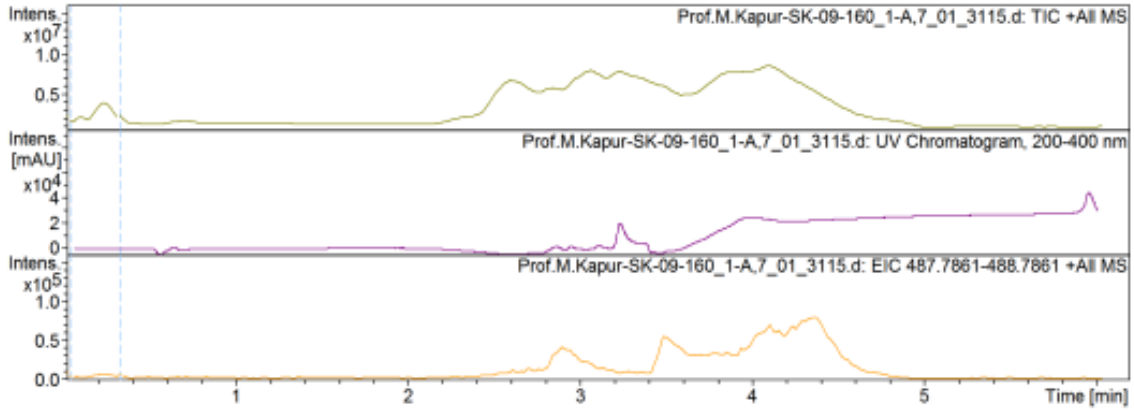
Display Report

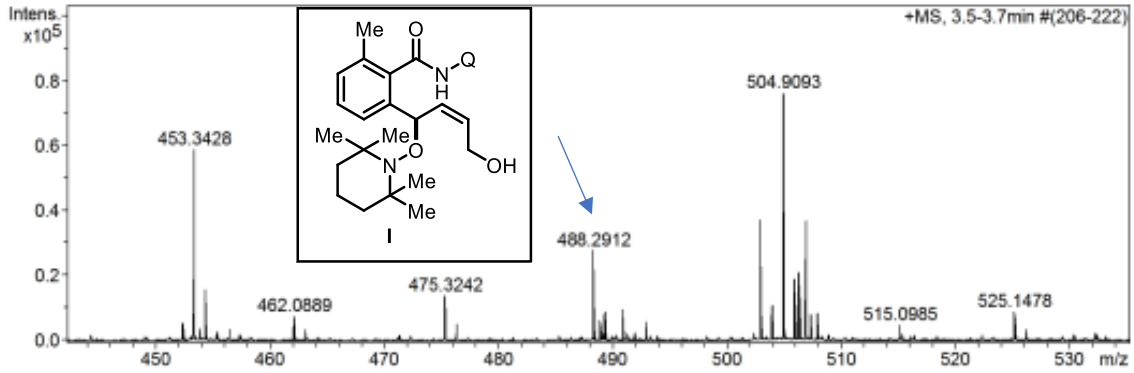
Analysis Info

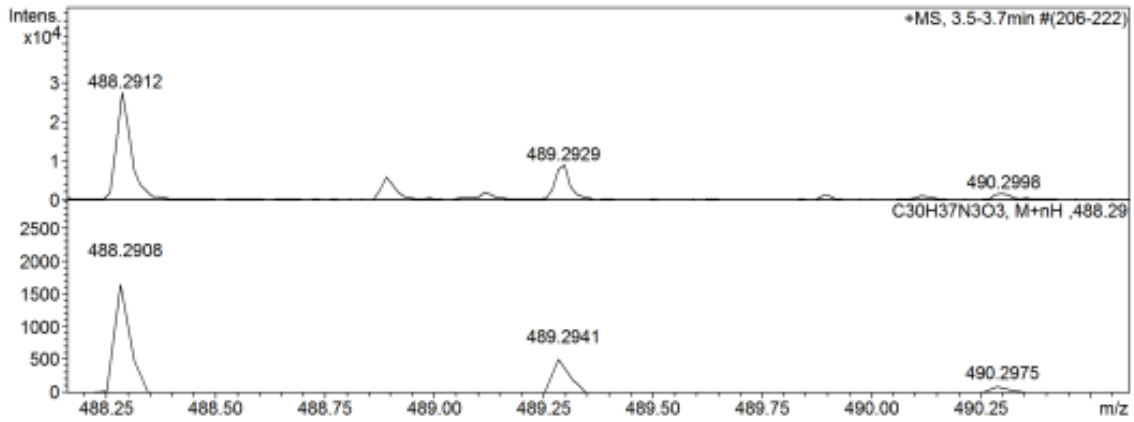
Analysis Name	D:\Data\USER DATA 2023\sep 23\26-sep\Prof.M.Kapur-SK-09-160_1-A,7_01_3115.d	Acquisition Date	26-09-2023 12:34:43
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-160	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

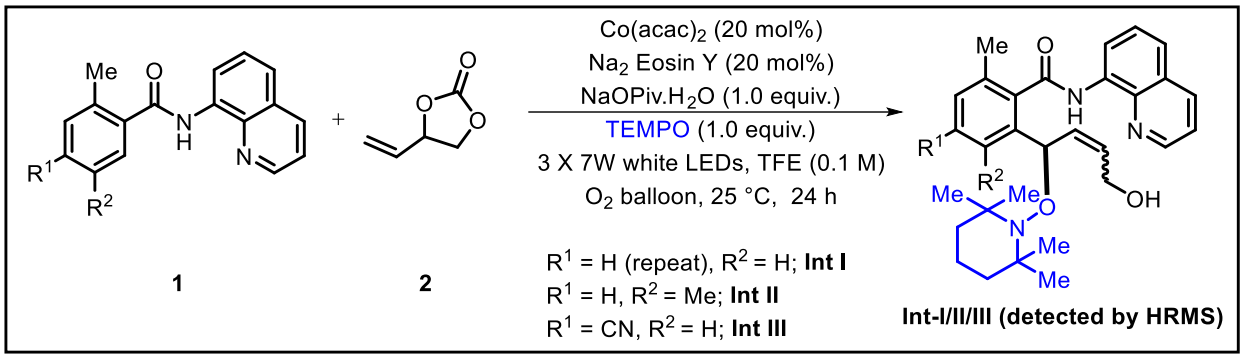






Bruker Compass DataAnalysis 4.0 printed: 26-09-2023 15:22:37 Page 1 of 1

Scheme S18: Attempts towards isolation of the TEMPO adduct:



Procedure:

In an oven-dried pressure tube equipped with a stir bar, *N*-(quinolin-8-yl)benzamides **1** (1.0 equiv., 0.1 mmol) and 4-vinyl-1,3-dioxolan-2-one **2** (2 equiv., 0.20 mmol) were dissolved in TFE (1.0 mL). The solution was saturated with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), Na_2[Eosin Y] (20 mol%, 0.02 mmol) and $NaOPiv.H_2O$ (1.0 equiv.) and the radical scavenger TEMPO (1.0 equiv.) were added sequentially to the reaction mixture. The pressure tube was then sealed with a septum cap and stirred under white LEDs (3 × 7W) for 24 h. The reaction progress was monitored by TLC. After 24 h, no definite spots were observed in the TLC other than the starting materials. We tried our best to isolate the corresponding adduct by repeating the reaction on higher scales, but we were only able to detect the corresponding adduct *via* ESI-HRMS analysis for compounds **1a**, **1h** and **1d**. The key radical adducts **I**, **II**, **III** were only detected by ESI-HRMS.

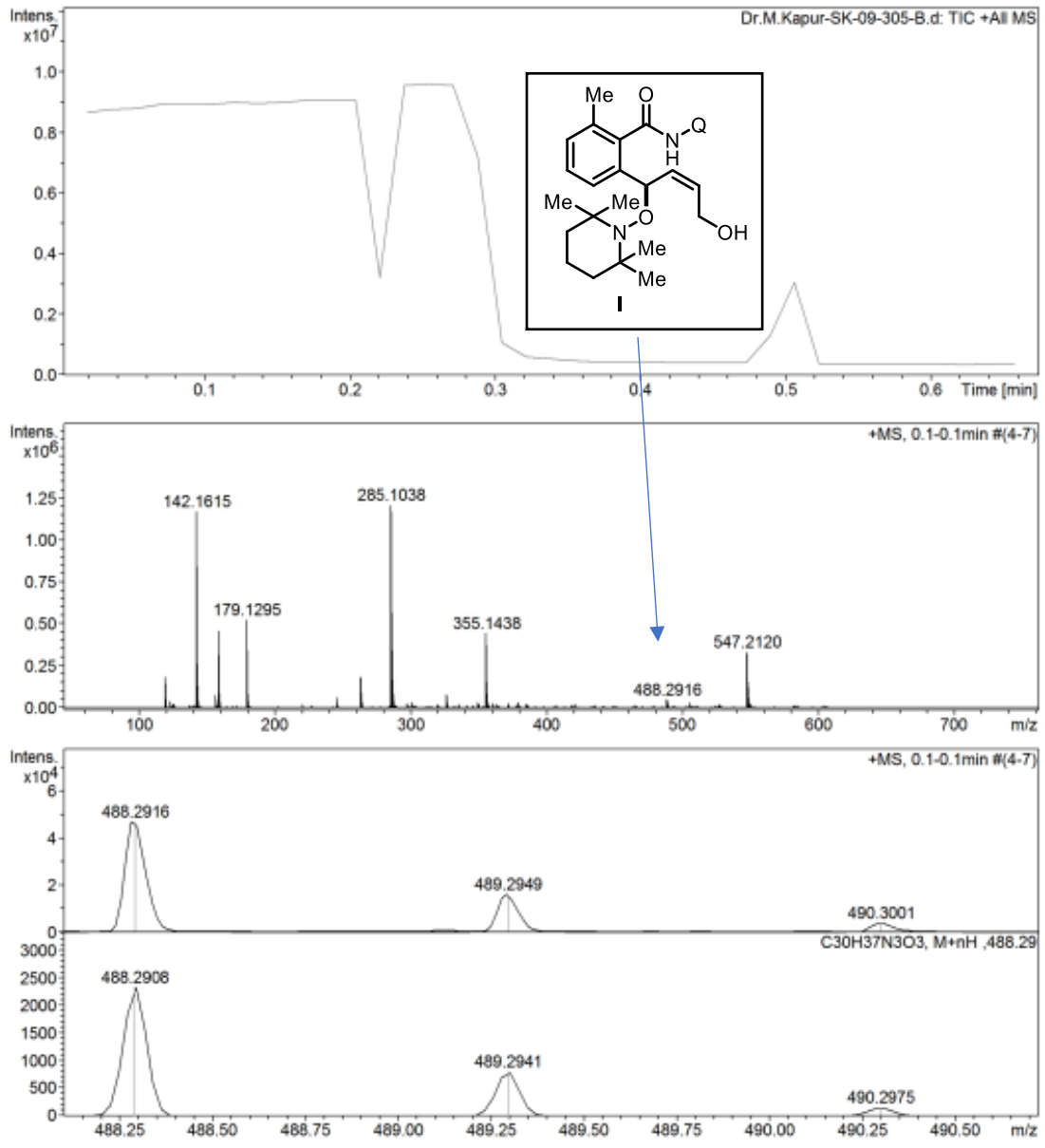
Display Report

Analysis Info

Analysis Name	D:\Data\USER DATA 2024\Aug-2024\22-aug\Dr.M.Kapur-SK-09-305-B.d	Acquisition Date	22-08-2024 12:29:21
Method	tune_low_8Aug2024.m	Operator	Bruker
Sample Name	SK-09-305-B	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	7.3 psi
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



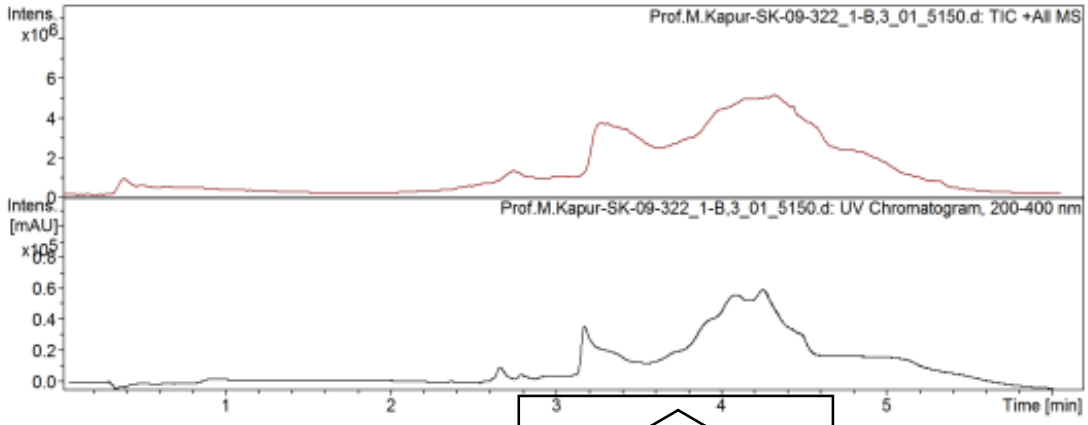
Display Report

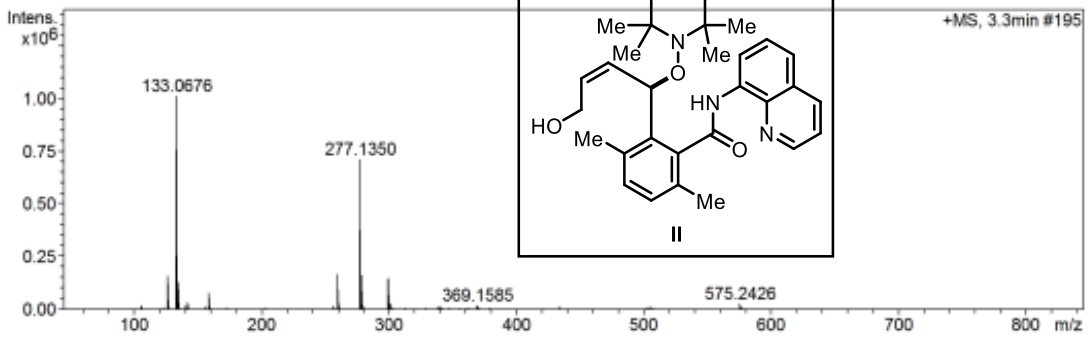
Analysis Info

Analysis Name	D:\Data\USER DATA 2024\Aug-2024\27-Aug\Prof.M.Kapur-SK-09-322_1-B,3_01_5150.d	Acquisition Date	27-08-2024 15:33:30
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-322	Instrument	micrOTOF-Q 10330
Comment			

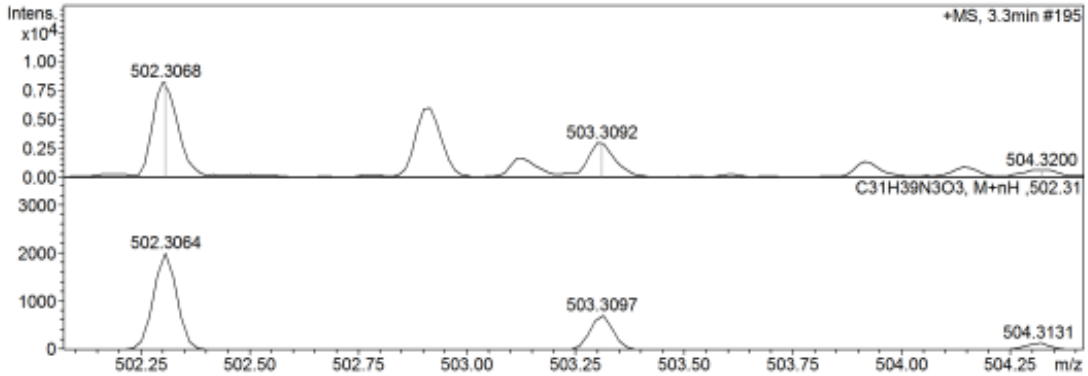
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	40.6 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	10.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste





II



Bruker Compass DataAnalysis 4.0 printed: 27-08-2024 15:48:51 Page 1 of 1

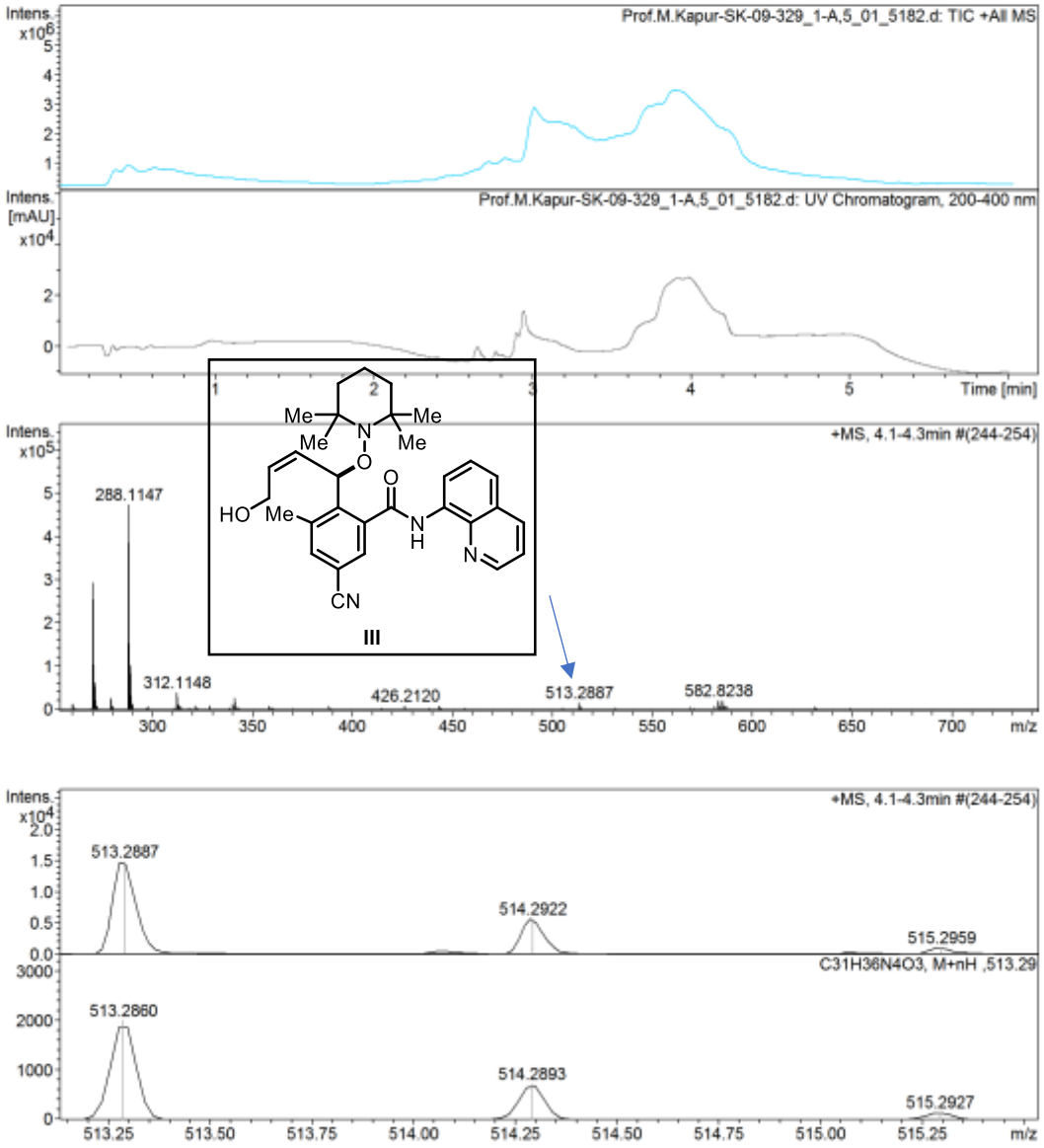
Display Report

Analysis Info

Acquisition Date	30-08-2024 11:44:54		
Analysis Name	D:\Data\USER DATA 2024\Aug-2024\30-aug\Prof.M.Kapur-SK-09-329_1-A,5_01_5182.d		
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-329	Instrument	micrOTOF-Q 10330
Comment			

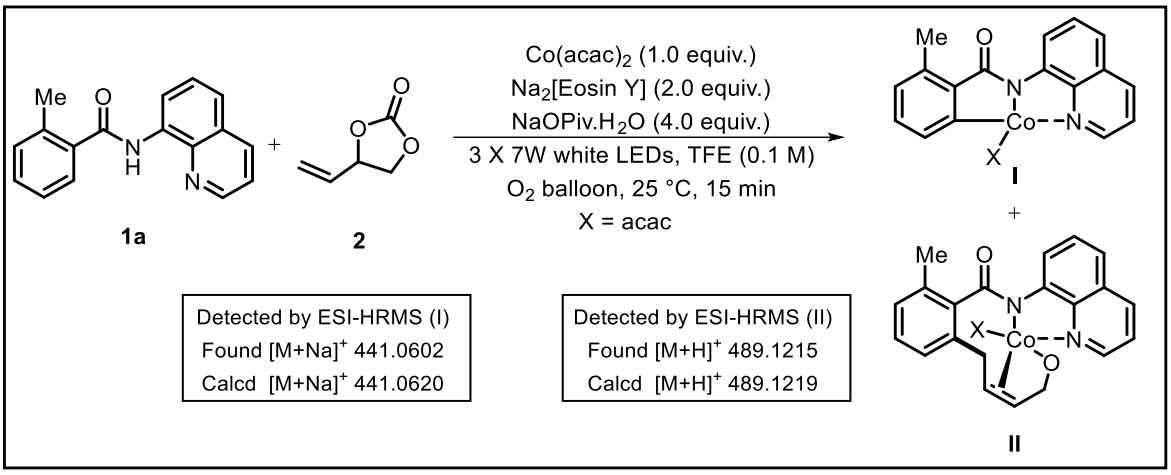
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	40.6 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	10.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 30-08-2024 14:03:20 Page 1 of 1

Scheme S19: Mass Spectrometry Experiments:



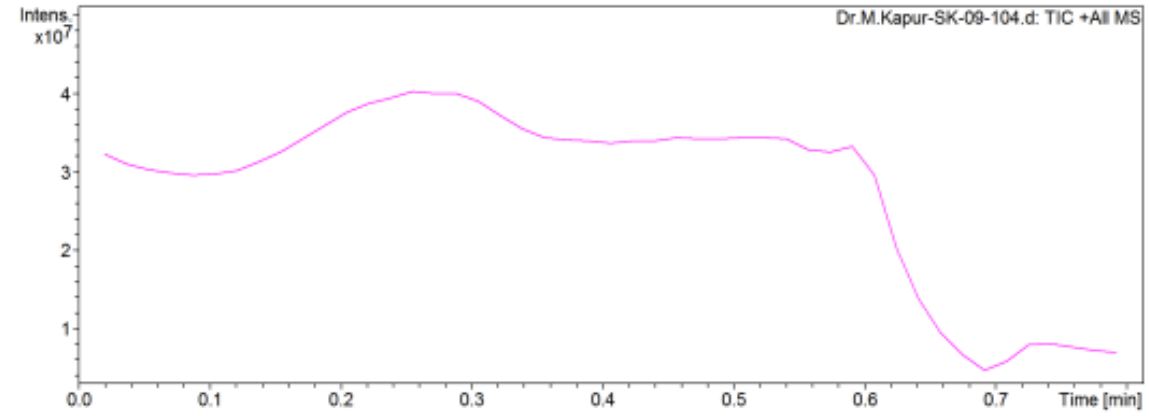
Display Report

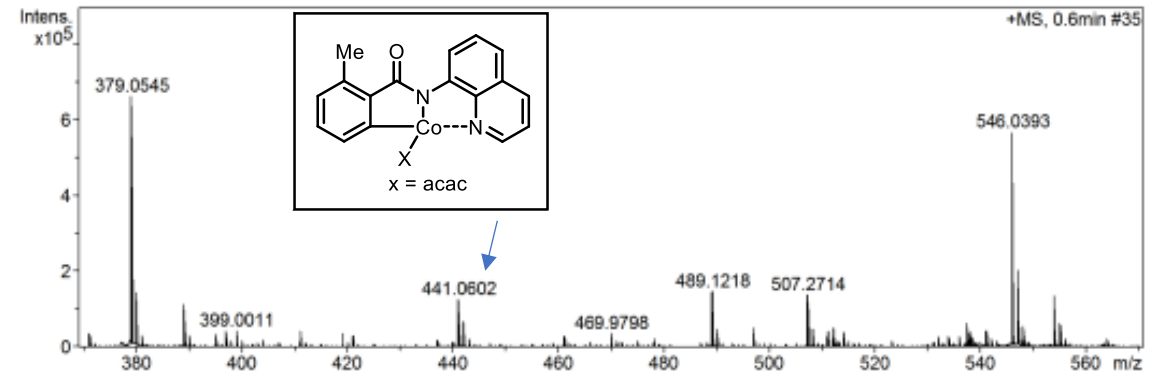
Analysis Info

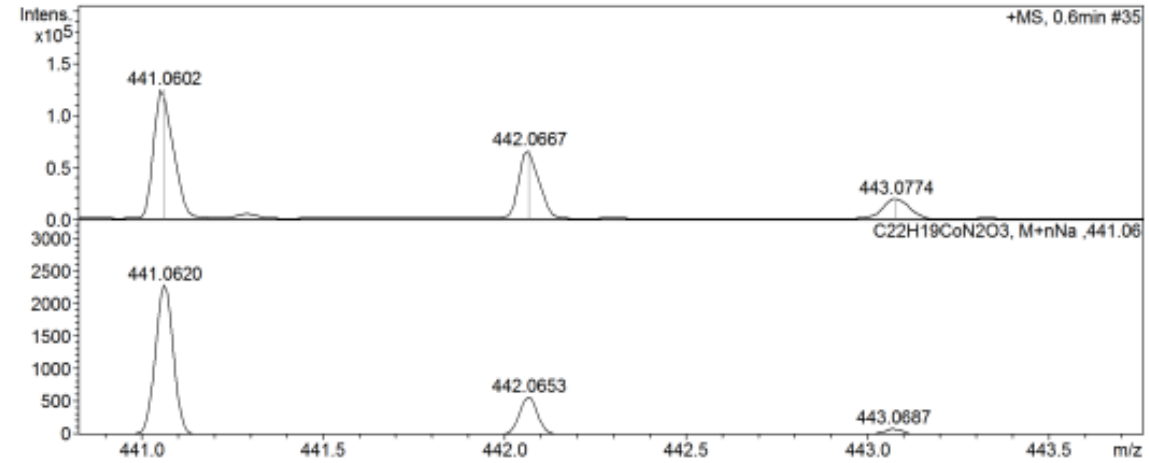
Analysis Name	D:\Data\USER DATA 2023\Aug-23\02-aug\Dr.M.Kapur-SK-09-104.d	Acquisition Date	02-08-2023 16:35:16
Method	tune_wide_Jan_2019.m	Operator	Bruker
Sample Name	SK-09-104	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste







Bruker Compass DataAnalysis 4.0 printed: 02-08-2023 16:38:57 Page 1 of 1

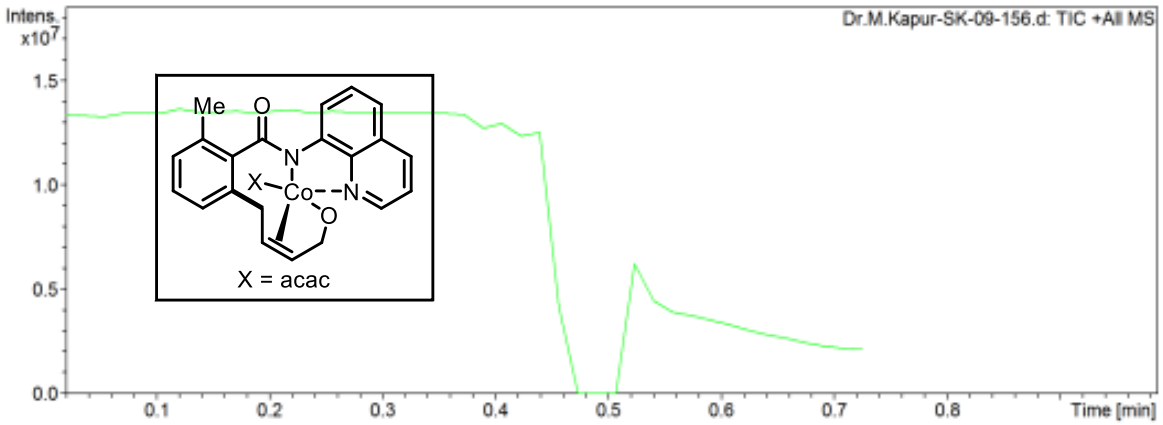
Display Report

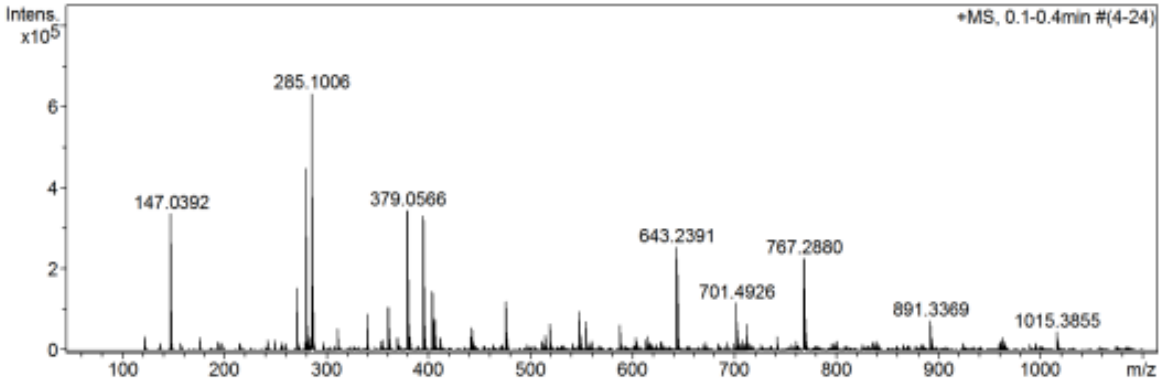
Analysis Info

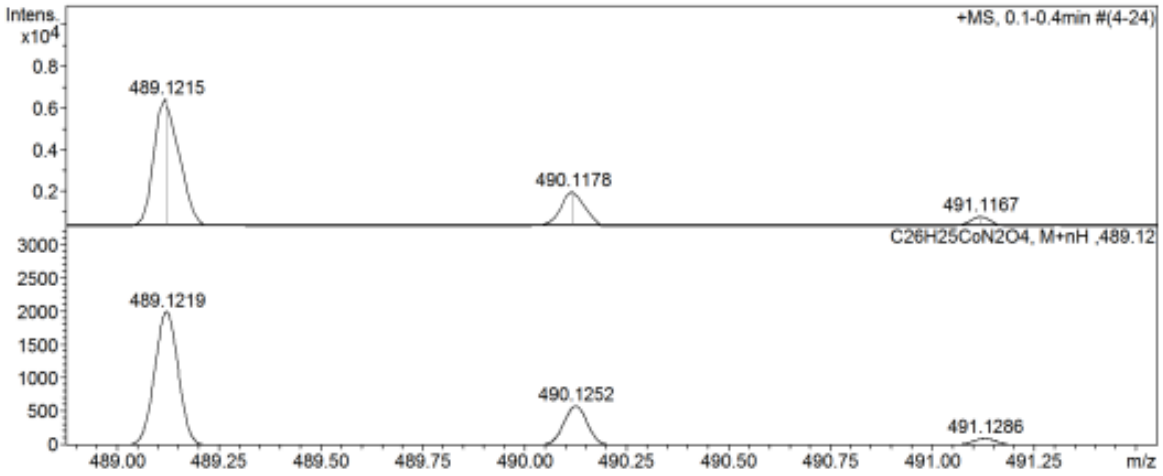
Analysis Name	D:\Data\USER DATA 2023\sep 23\20-sep\Dr.M.Kapur-SK-09-156.d	Acquisition Date	20-09-2023 10:06:43
Method	tune_low_APR23.m	Operator	Bruker
Sample Name	SK-09-156	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

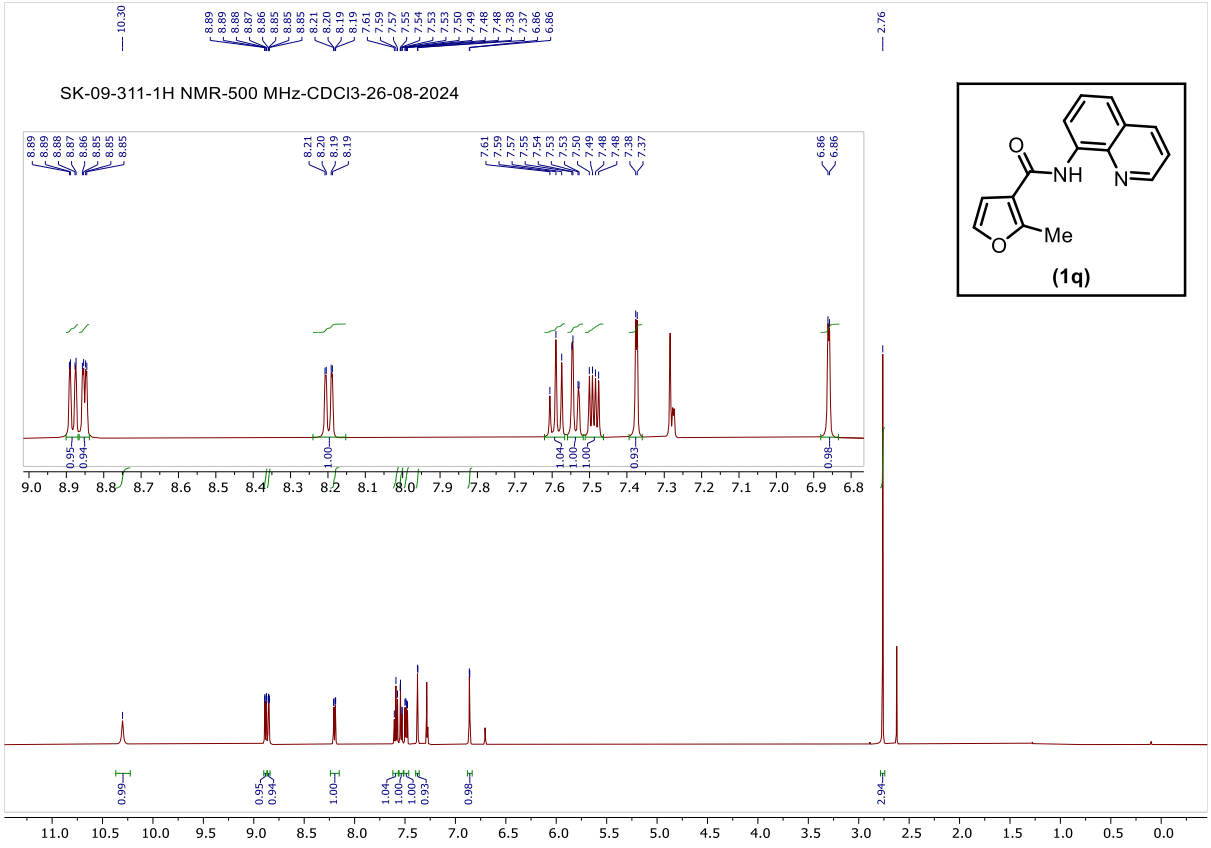


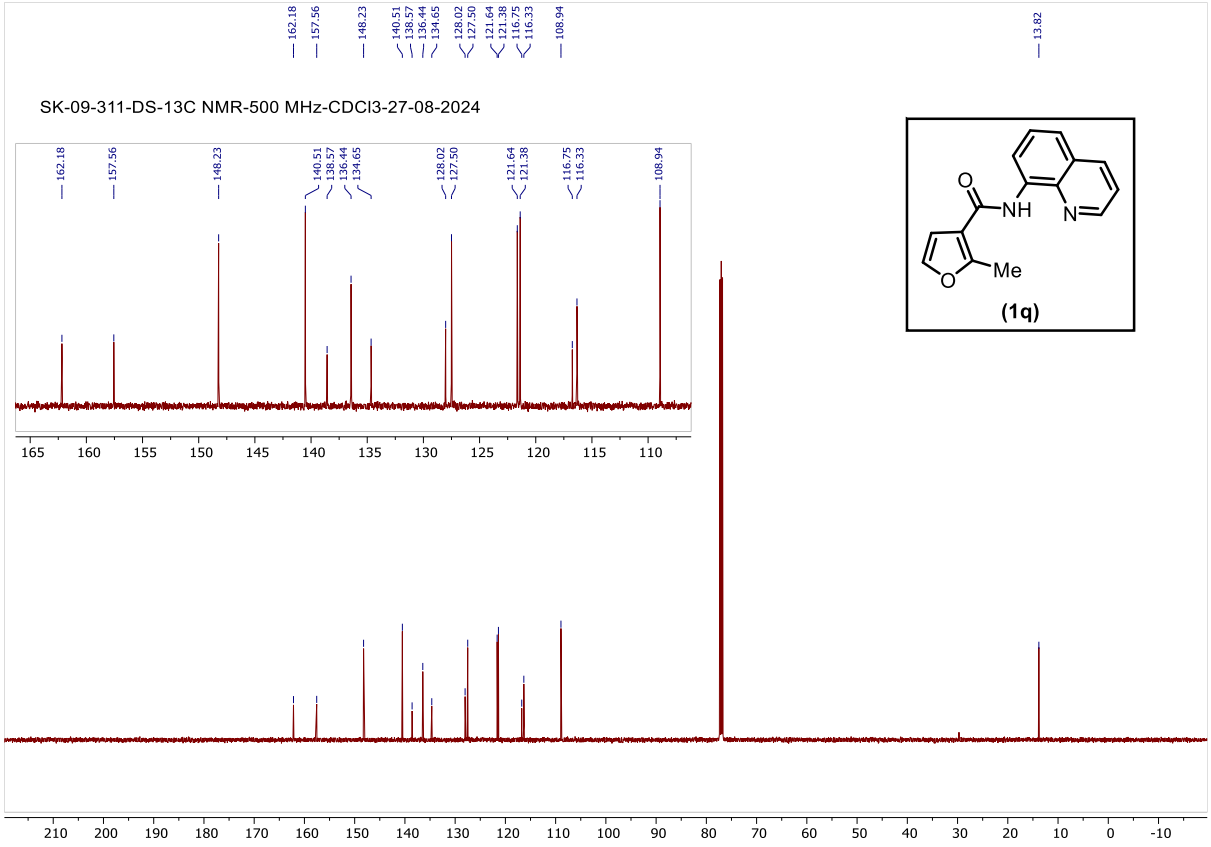




7. References

1. Armarego, W. L. F.; *Purification of Laboratory Chemicals*; 8th Ed.; Butterworth-Heinemann, **2017**.
2. (a) He, B.; Liu, X.; Li, H.; Zhang, X.; Ren Y.; Su, W. *Org. Lett.* **2021**, *23*, 4191–4196; (b) Tang, J.; Liu P.; Zeng, X. *Chem. Commun.* **2018**, *54*, 9325–9328; (c) Sarkar, W.; Mishra, A.; Bhowmik A.; Deb, I. *Org. Lett.* **2021**, *23*, 4521–4526; (d) Liu, S.; He, B.; Li, H.; Zhang, X.; Shang Y.; Su, W. *Chem. – A Eur. J.* **2021**, *27*, 15628–15633; (e) Honeycutt, A. P.; Hoover, J. M. *Org. Lett.* **2018**, *20*, 7216–7219; (f) Rouquet G.; Chatani, N. *Chem. Sci.* **2013**, *4*, 2201–2208; (g) Luo, X.; Song, X.; Xiong, W.; Li, J.; Li, M.; Zhu, Z.; Wei, S.; Chan, A. S. C.; Zhou, Y. *Org. Lett.* **2019**, *21*, 2013−2018; (h) Zhang, T.-Y.; Liu, C.; Chen, C.; Liu, J.-X.; Xiang, H.-Y.; Jiang, W.; Ding, T.-M.; Zhang, S.-Y. *Org. Lett.* **2018**, *20*, 220−223; (i) Wang, J.; Hong, H.; Hu, D.; Liu, J.; Liu, W.; Shi, Y. *Org. Chem. Front.* **2024**, *11*, 484.
3. Zhang, S.-S.; Zheng, Y.-C.; Zhang, Z.-W.; Chen, S.-Y.; Xie, H.; Shu, B.; Song, J.-L.; Liu, Y.-Z.; Zeng Y.-F.; Zhang. L. *Org. Lett.* **2021**, *23*, 5719–5723.
4. Das, A.; Thomas, K. R. J. *Green Chem.* **2022**, *24*, 4952-4957.
5. Maity, S.; Kancherla, R.; Dhawa, U.; Hoque, E.; Pimparkar S.; Maiti, D. *ACS Catal.* **2016**, *6*, 5493–5499.


SK-09-311-1H NMR-500 MHz-CDCl3-26-08-2024
(1q)


SK-09-311-DS-13C NMR-500 MHz-CDCl3-27-08-2024
(1q)

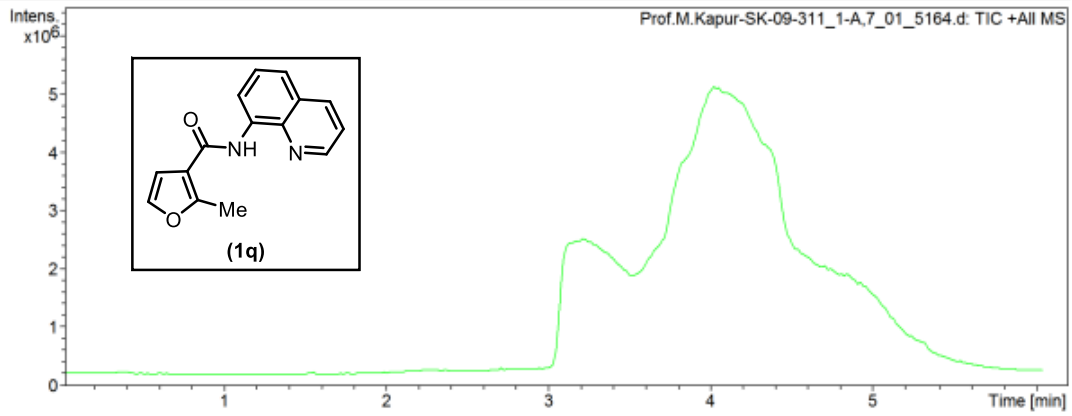
Display Report

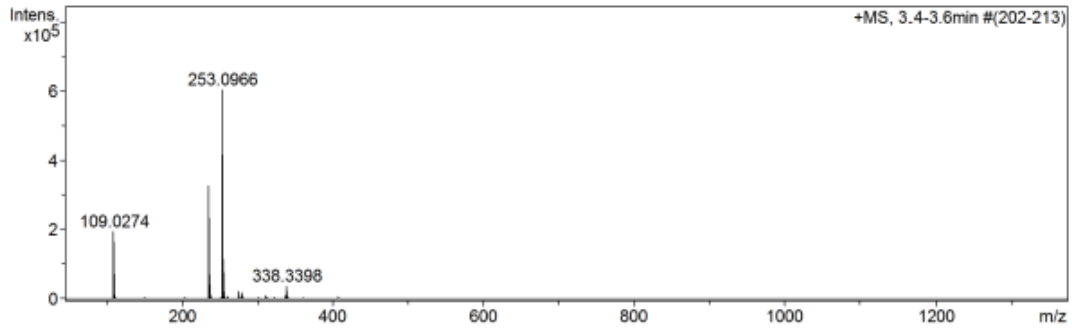
Analysis Info

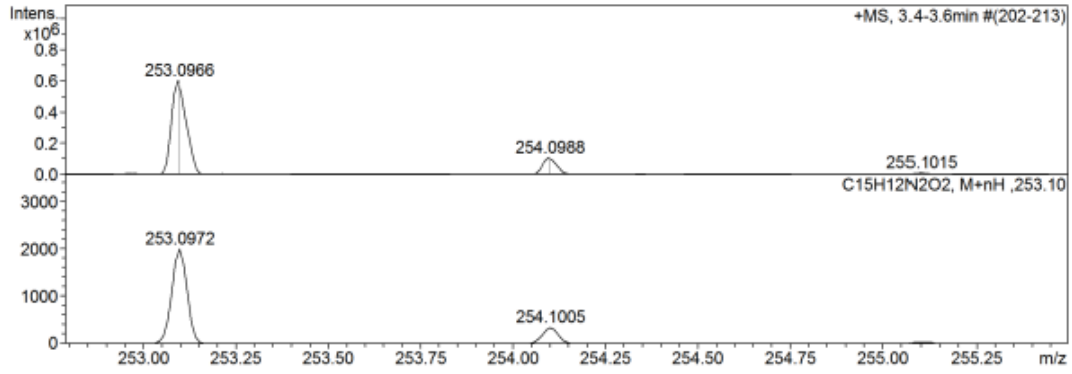
Acquisition Date	28-08-2024 12:49:27		
Analysis Name	D:\Data\USER DATA 2024\Aug-2024\28-aug\Prof.M.Kapur-SK-09-311_1-A,7_01_5164.d		
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-311	Instrument	micrOTOF-Q 10330
Comment			

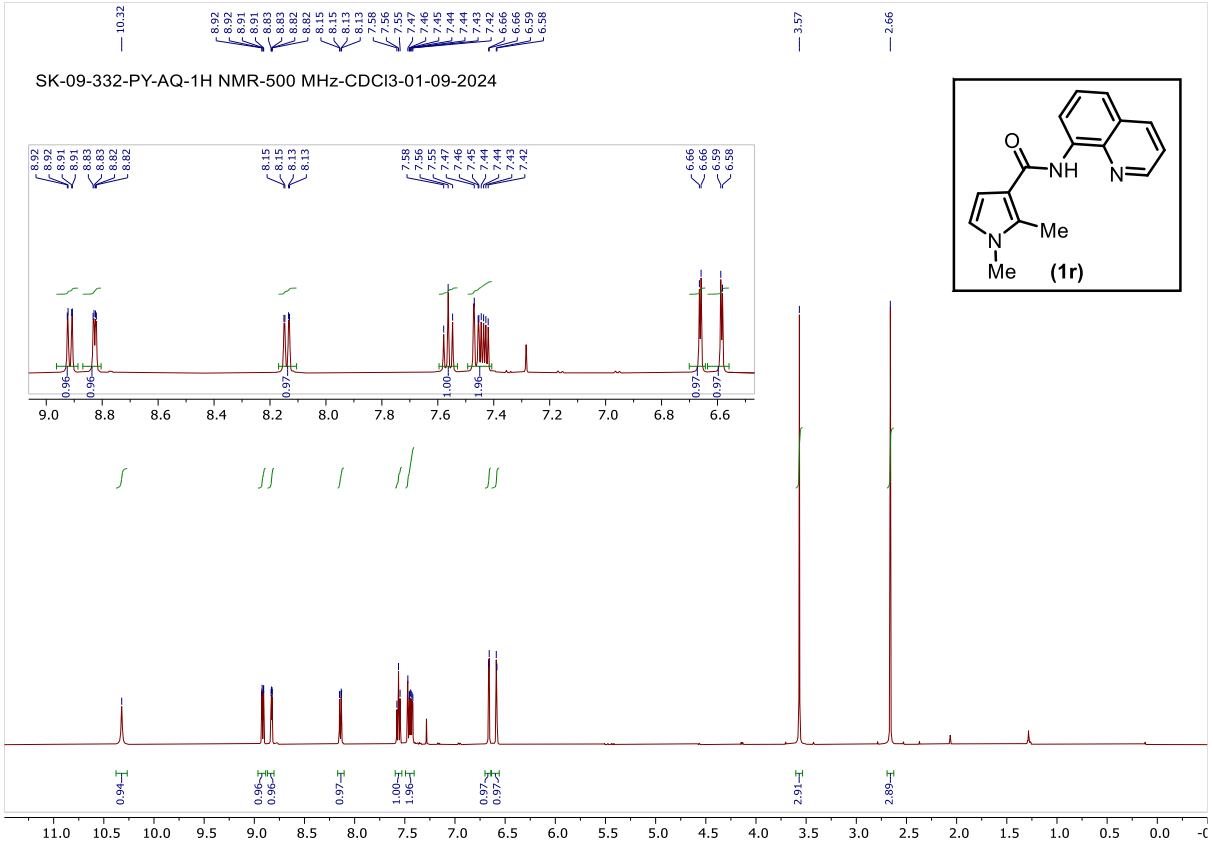
Acquisition Parameter

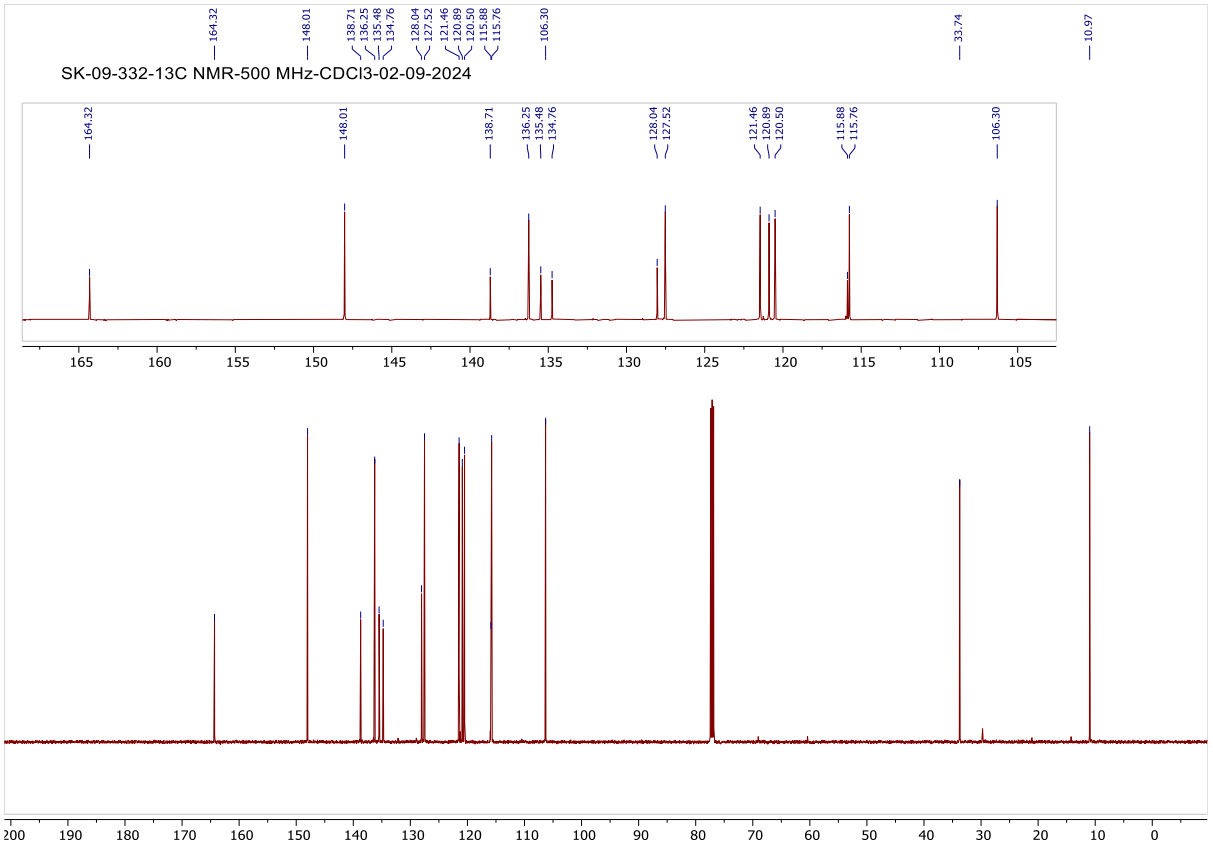
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	40.6 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	10.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste








SK-09-332-PY-AQ-1H NMR-500 MHz-CDCl3-01-09-2024
O
NH
N
Me
N
Me
(1r)


SK-09-332-13C NMR-500 MHz-CDCl3-02-09-2024

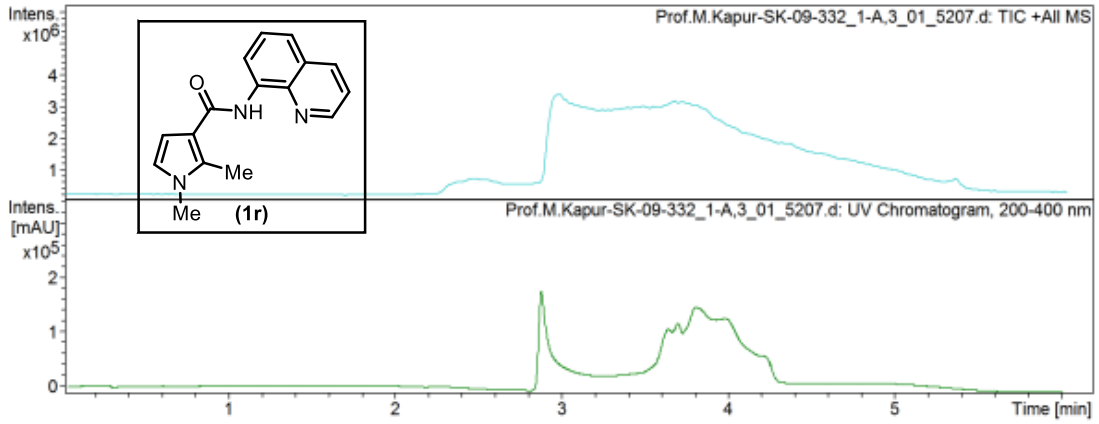
Display Report

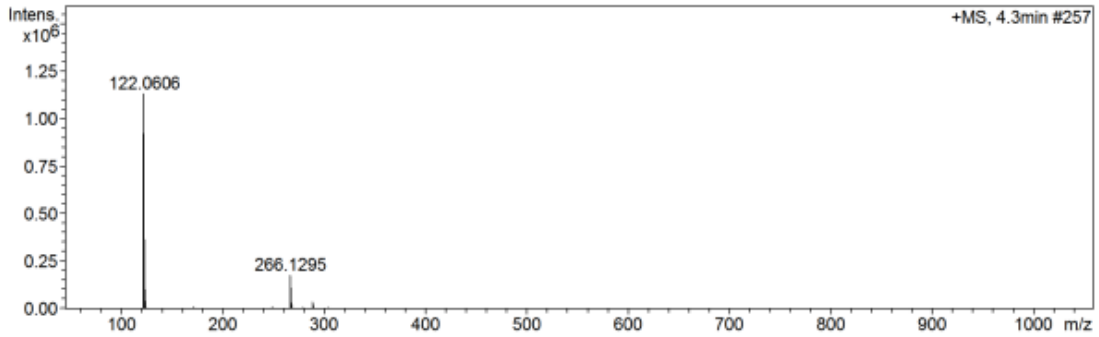
Analysis Info

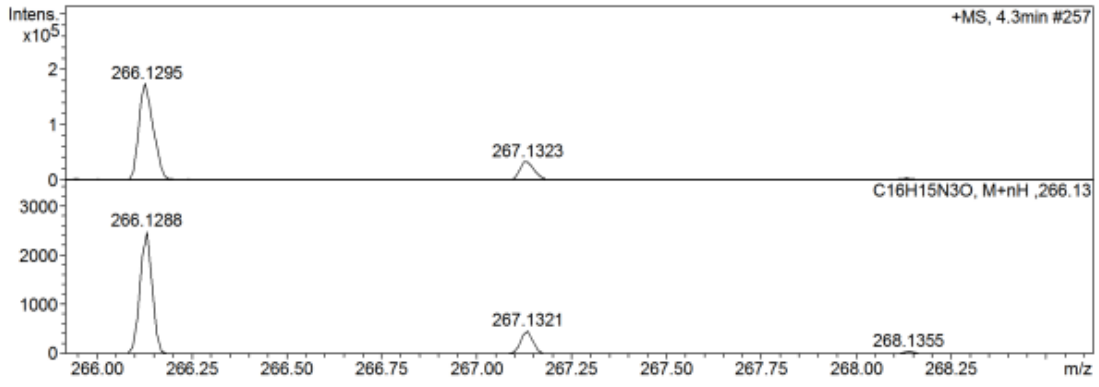
Analysis Name	D:\Data\USER DATA 2024\Sept-2024\03-sept-24\Prof.M.Kapur-SK-09-332_1-A,3_01_5207.d	Acquisition Date	03-09-2024 15:53:59
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-332	Instrument	micrOTOF-Q 10330
Comment			

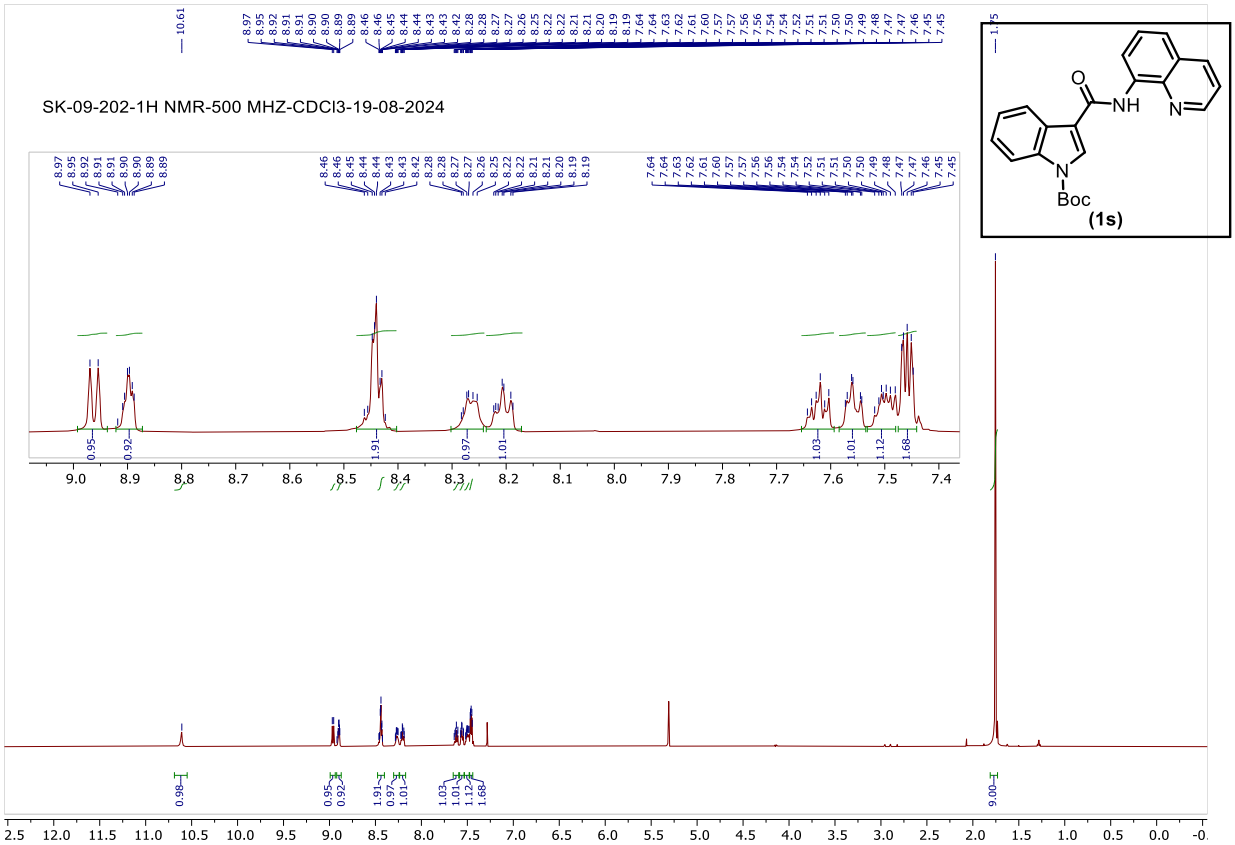
Acquisition Parameter

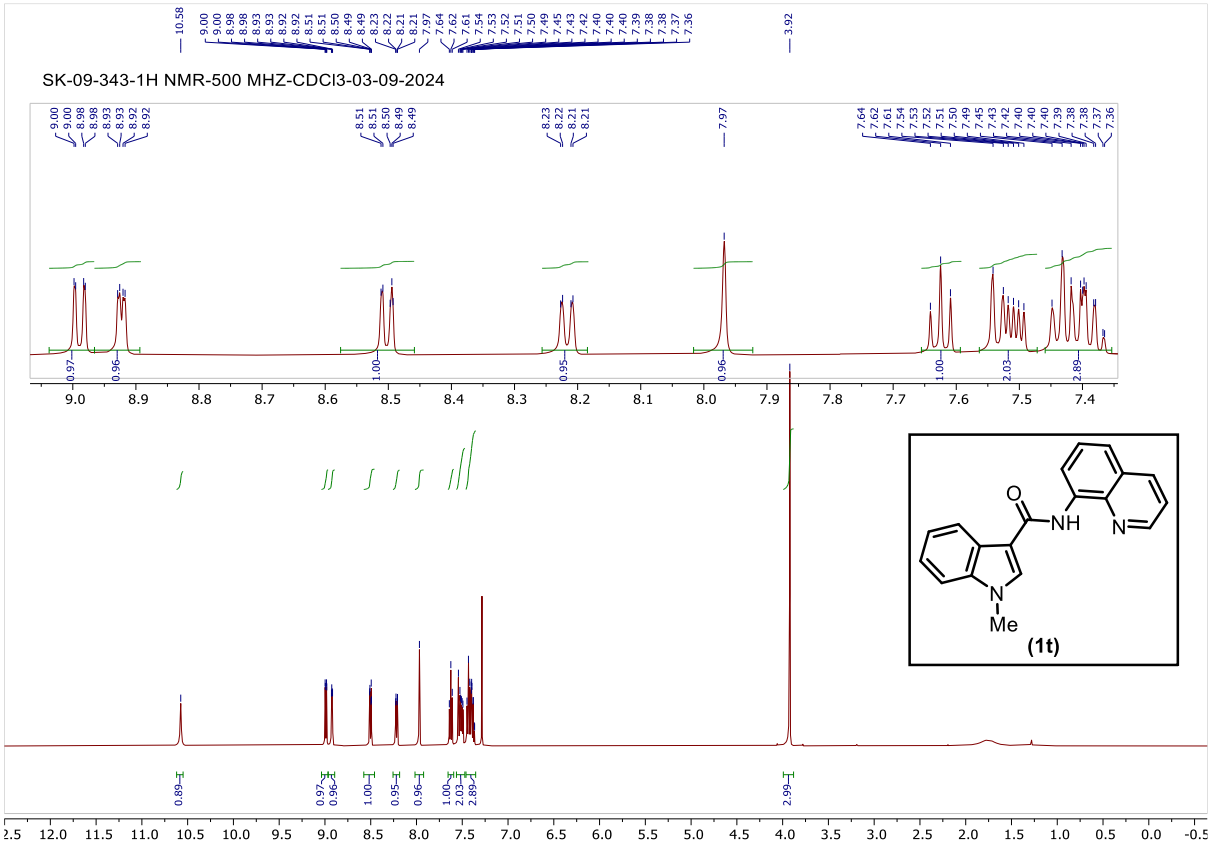
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	40.6 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	10.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

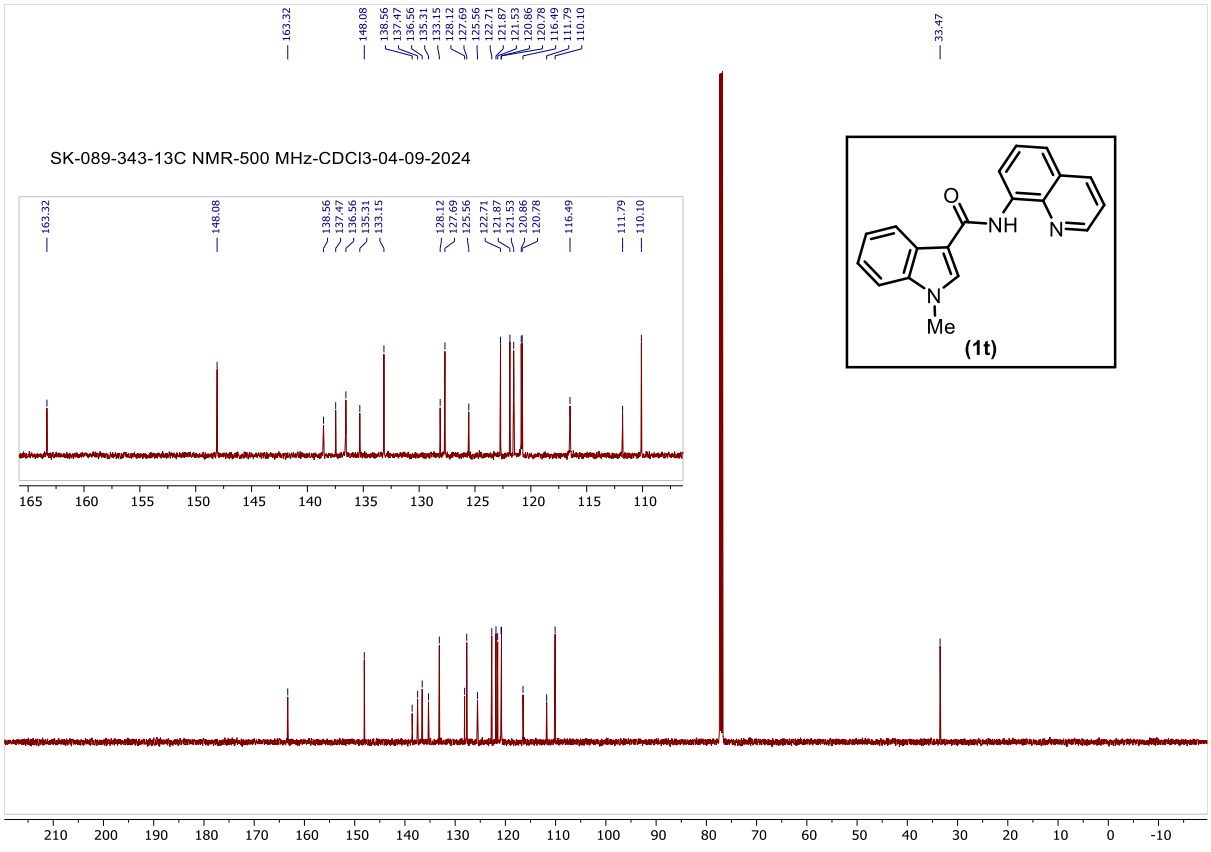







SK-09-202-1H NMR-500 MHZ-CDCl3-19-08-2024
O
NH
N
N
Boc
(1s)


SK-09-343-1H NMR-500 MHZ-CDCl3-03-09-2024
O
NH
N
N
Me
(1t)


SK-089-343-13C NMR-500 MHz-CDCl3-04-09-2024
163.32
148.08
138.56
137.47
136.56
135.31
133.15
128.12
127.69
125.56
122.71
121.87
121.53
120.86
120.78
116.49
111.79
110.10
33.47
O
NH
N
N
Me
(1t)

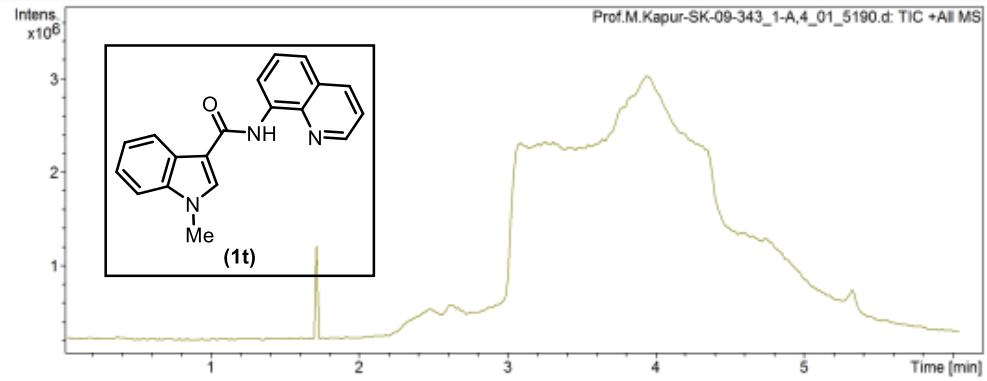
Display Report

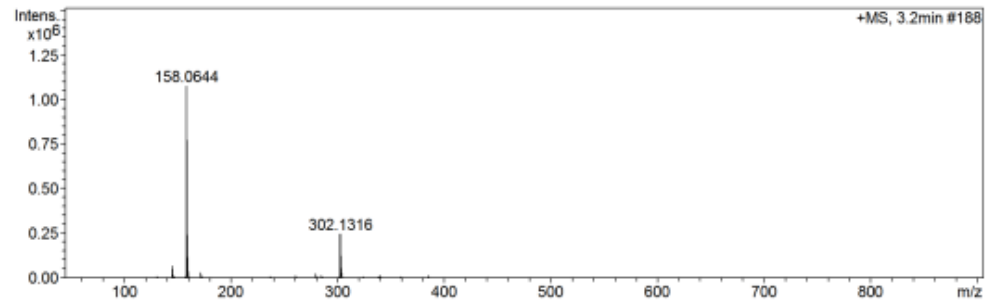
Analysis Info

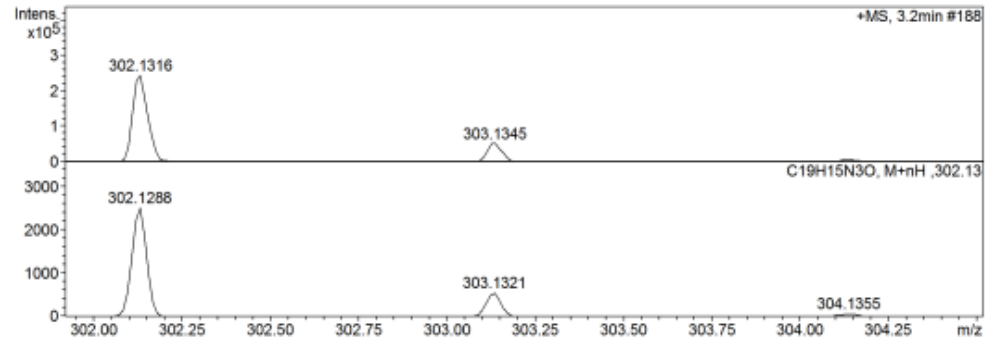
Acquisition Date	02-09-2024 12:46:53		
Analysis Name	D:\Data\USER DATA 2024\Sept-2024\02-Sept-24\Prof.M.Kapur-SK-09-343_1-A,4_01_5190.d		
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-343	Instrument	micrOTOF-Q 10330
Comment			

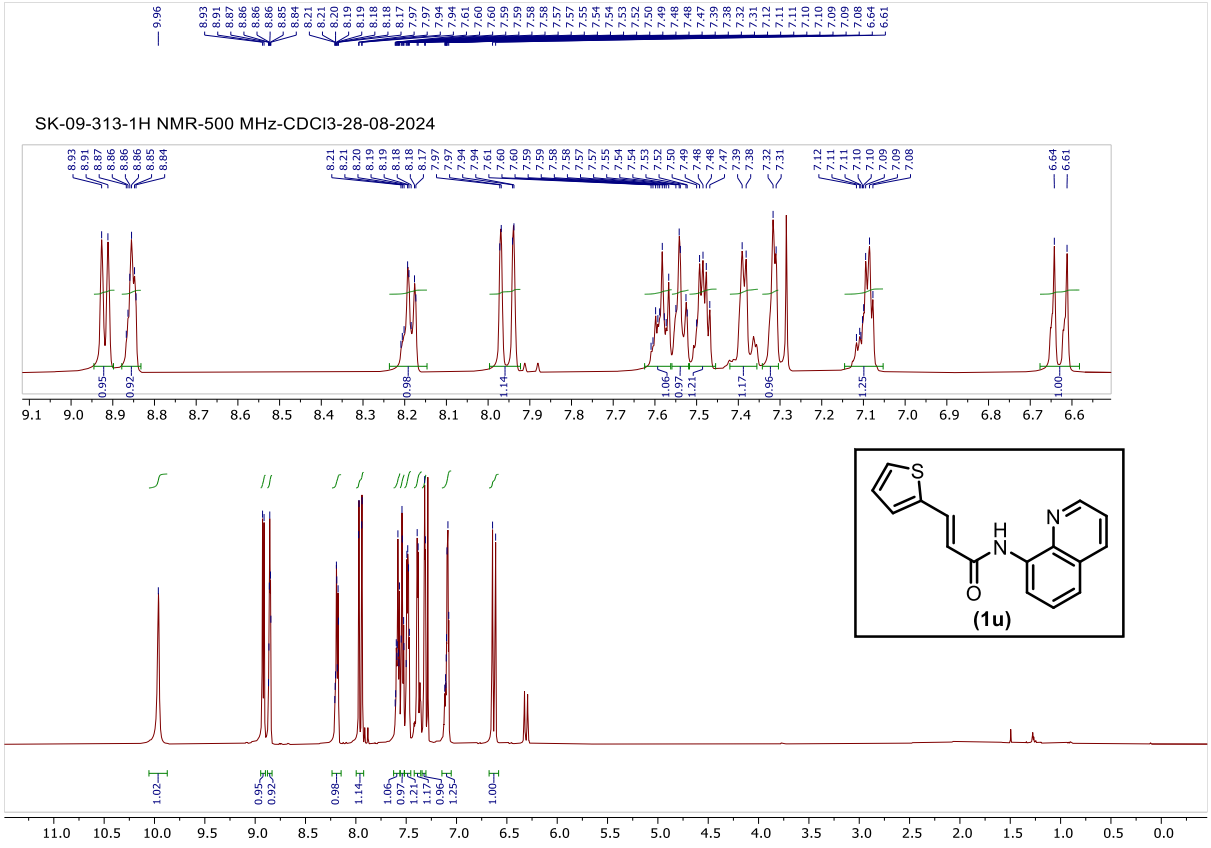
Acquisition Parameter

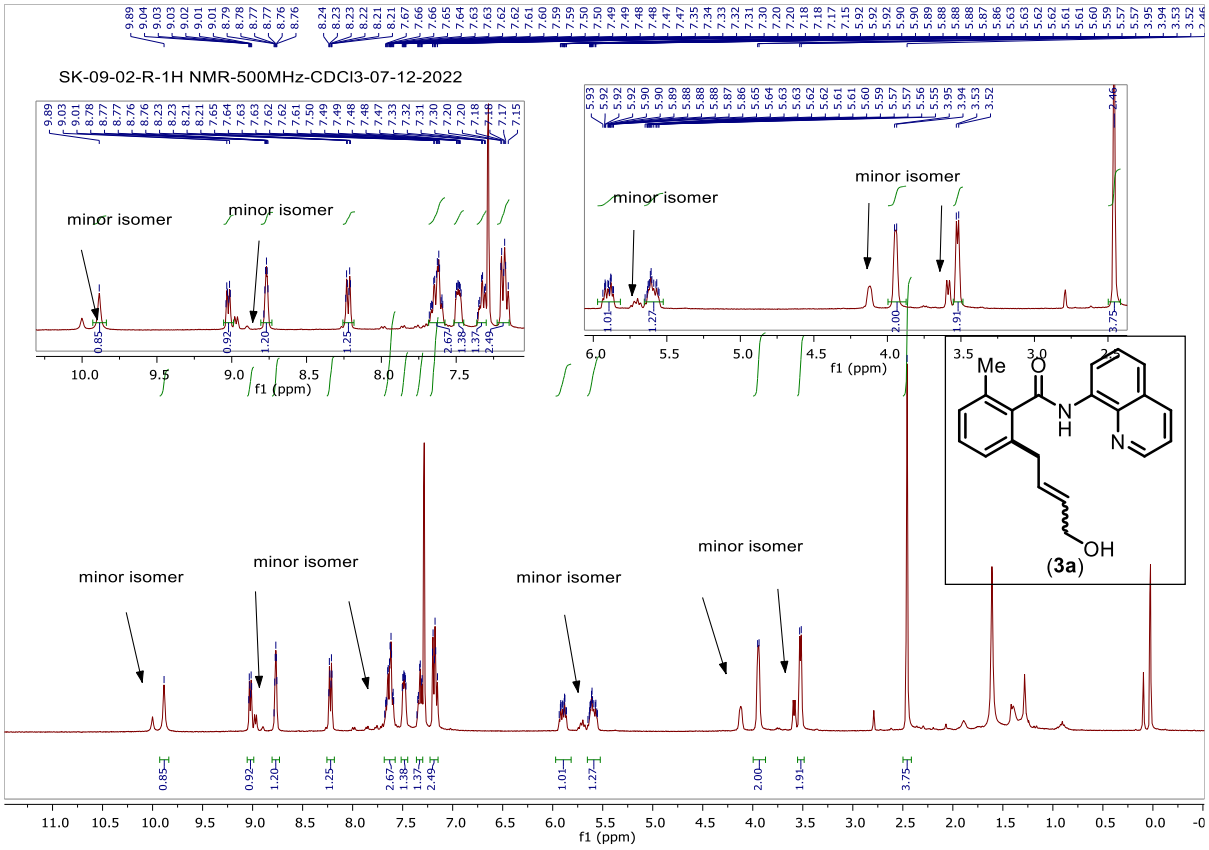
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	40.6 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	10.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

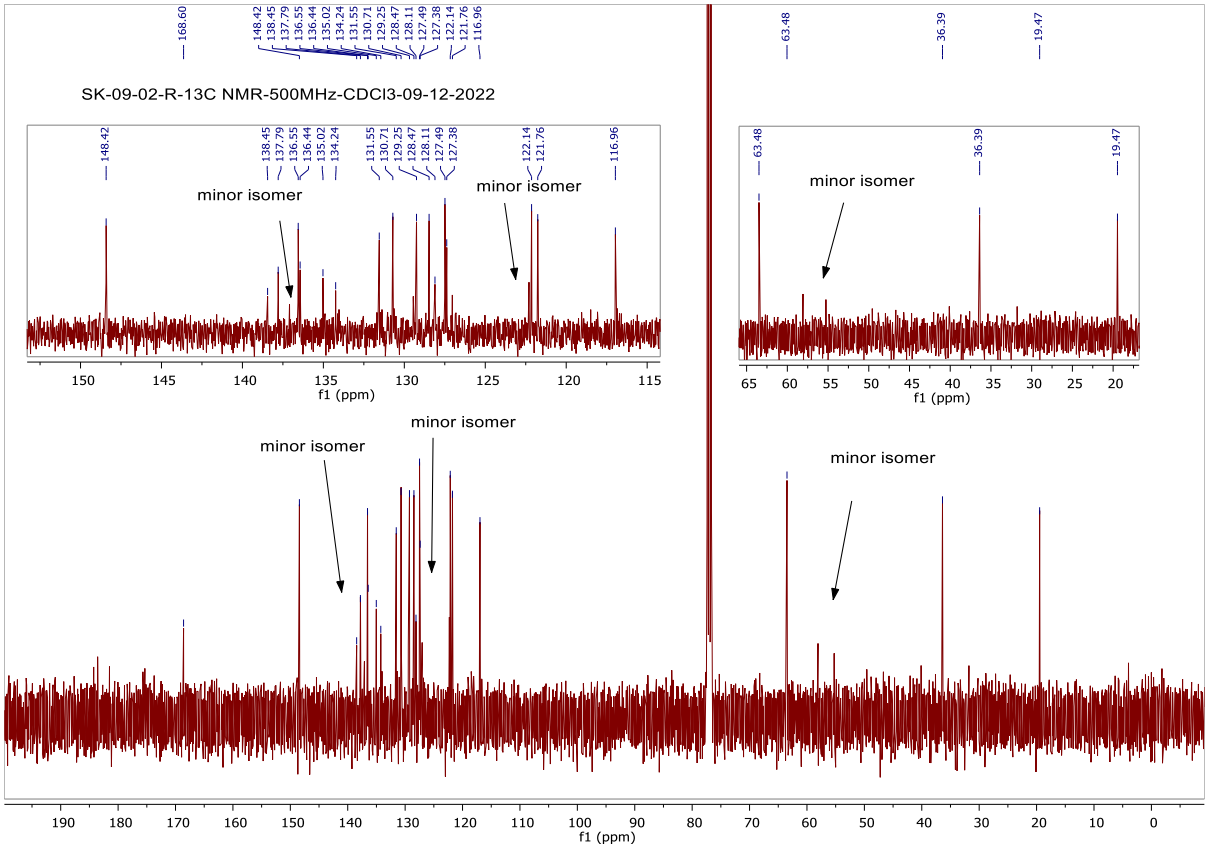







SK-09-313-1H NMR-500 MHz-CDCl3-28-08-2024
(1u)


SK-09-02-R-1H NMR-500MHz-CDCl3-07-12-2022
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
Me
O
N
H
N
OH
(3a)
f1 (ppm)


SK-09-02-R-13C NMR-500MHz-CDCl3-09-12-2022
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)

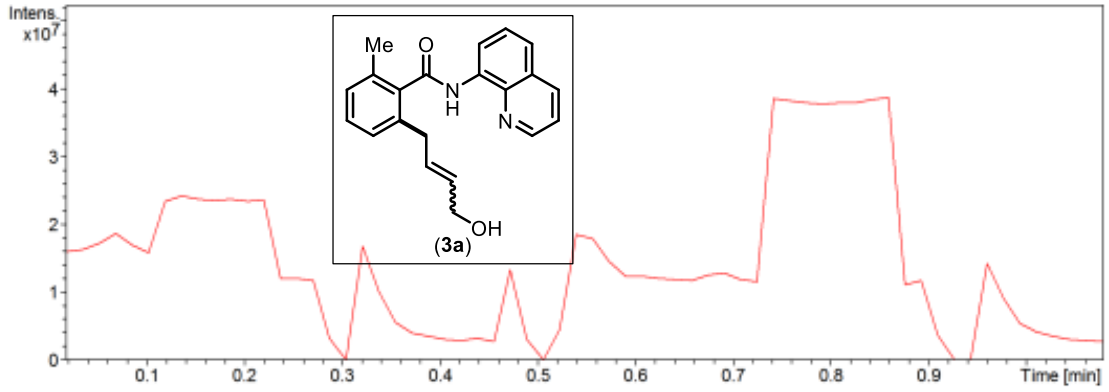
Display Report

Analysis Info

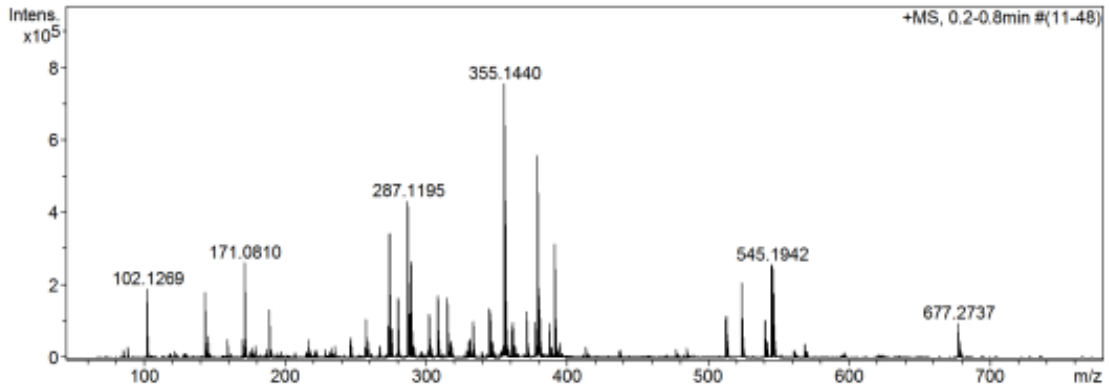
Analysis Name	D:\Data\USER DATA 2023\Feb\20-02-2023\Prog M Kapur-SK-09-17.d	Acquisition Date	20-02-2023 13:00:18
Method	tune_low_Jan23.m	Operator	Bruker
Sample Name	SK-09-17	Instrument	micrOTOF-Q 10330
Comment			

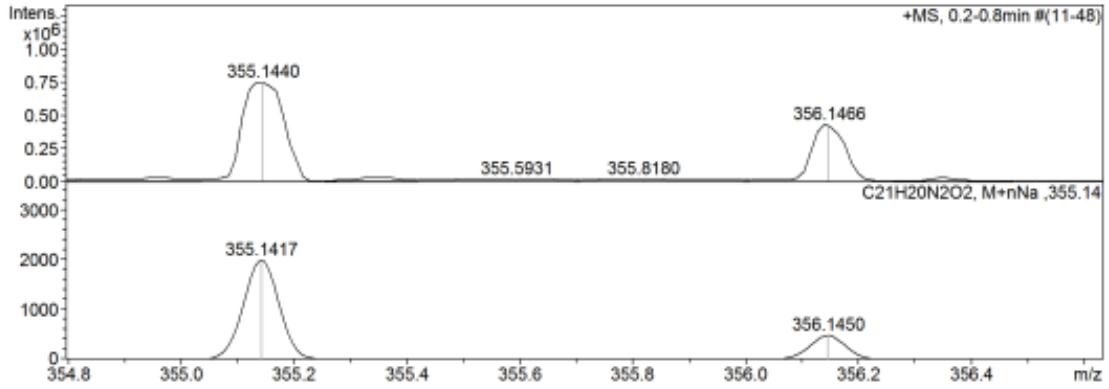
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.5 l/min
Scan End	3000 m/z	Set Collision Cell RF	70.0 Vpp	Set Divert Valve	Waste

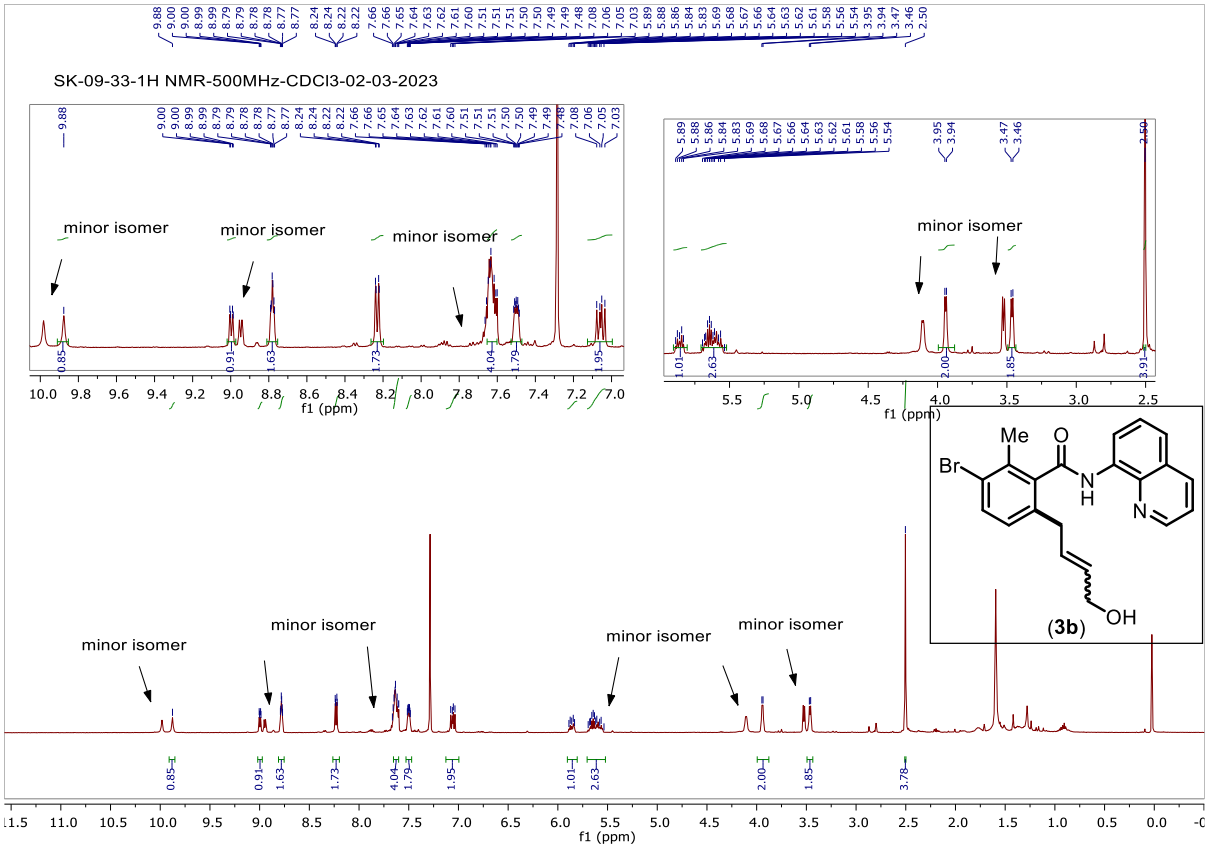


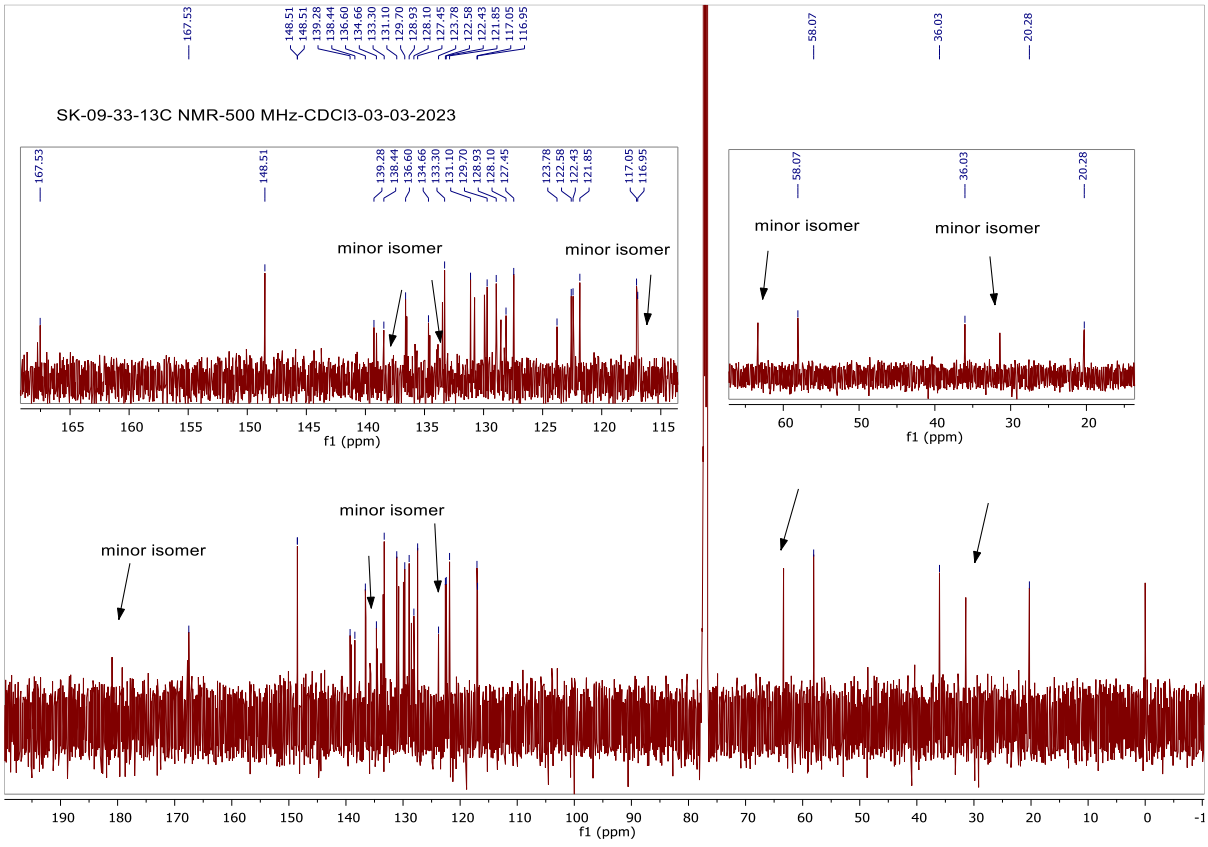
TIC +All MS





Bruker Compass DataAnalysis 4.0 printed: 20-02-2023 13:02:17 Page 1 of 1


SK-09-33-1H NMR-500MHz-CDCl3-02-03-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
Me
O
Br
N
H
N
OH
(3b)
f1 (ppm)


SK-09-33-13C NMR-500 MHz-CDCl3-03-03-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)

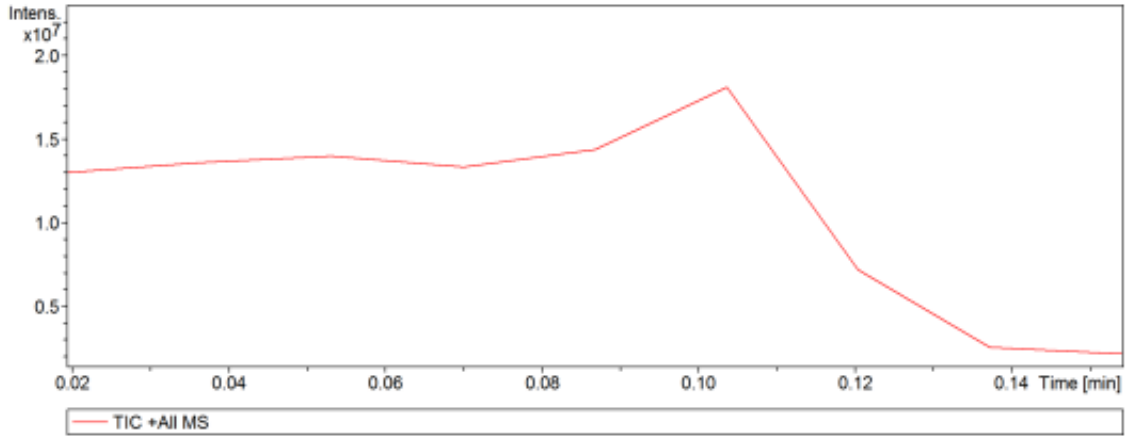
Display Report

Analysis Info

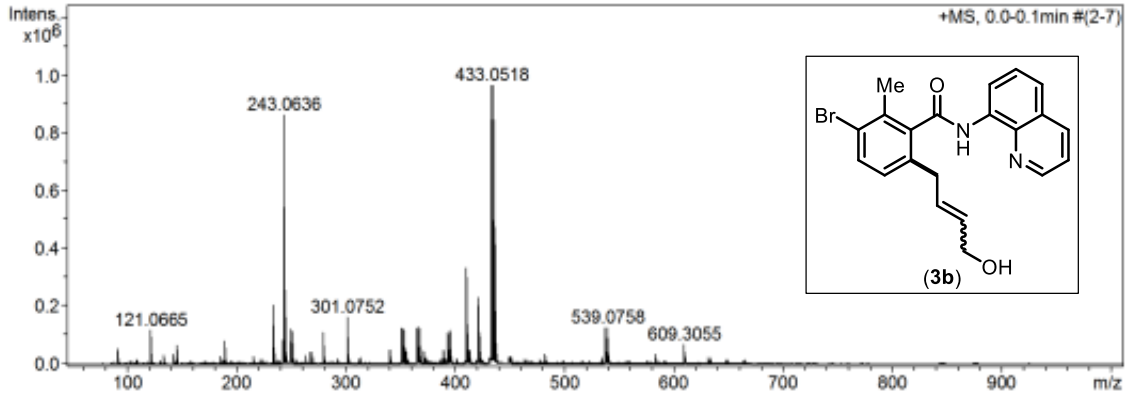
Analysis Name	D:\Data\Data-USER DATA 2023-Mar-03-03-23\Prof M Kapur-SK-09-33.d	Acquisition Date	03-03-2023 12:45:11
Method	tune_low_Jan23.m	Operator	Bruker
Sample Name	SK-09-33	Instrument	micrOTOF-Q 10330
Comment			

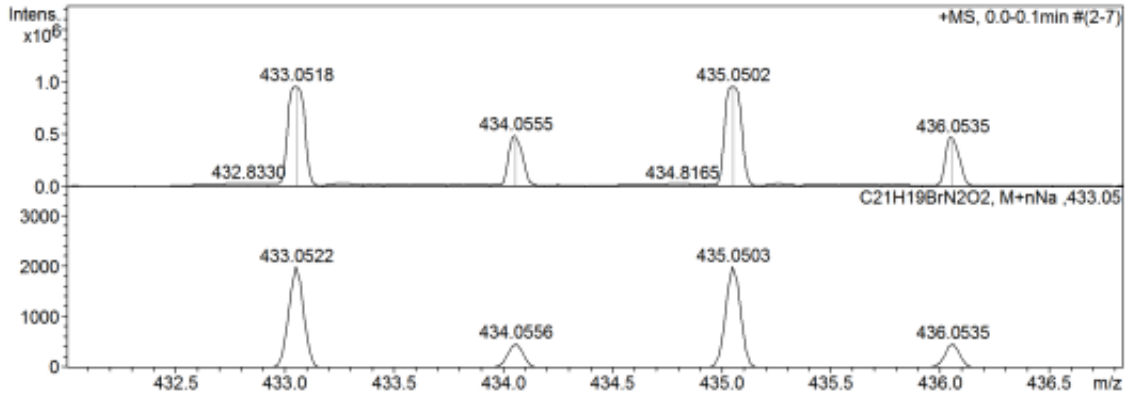
Acquisition Parameter

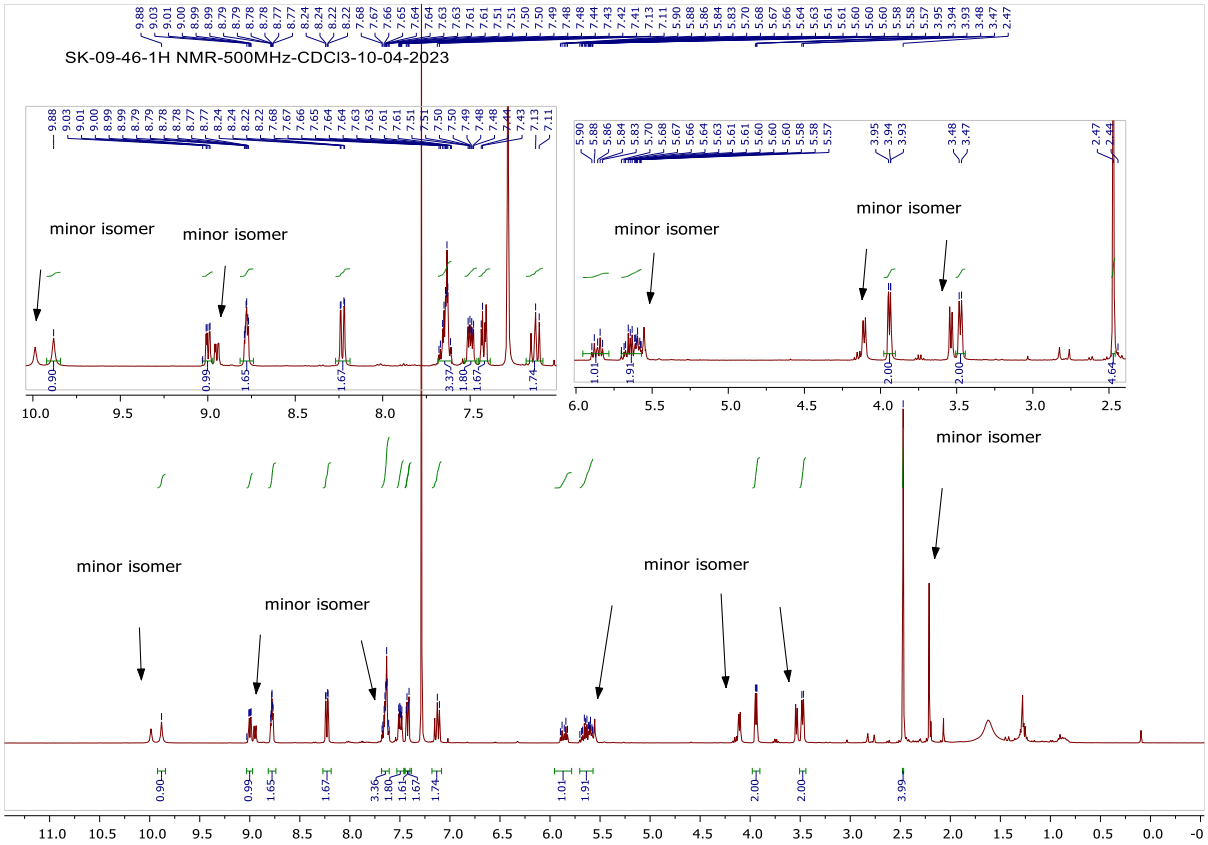
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

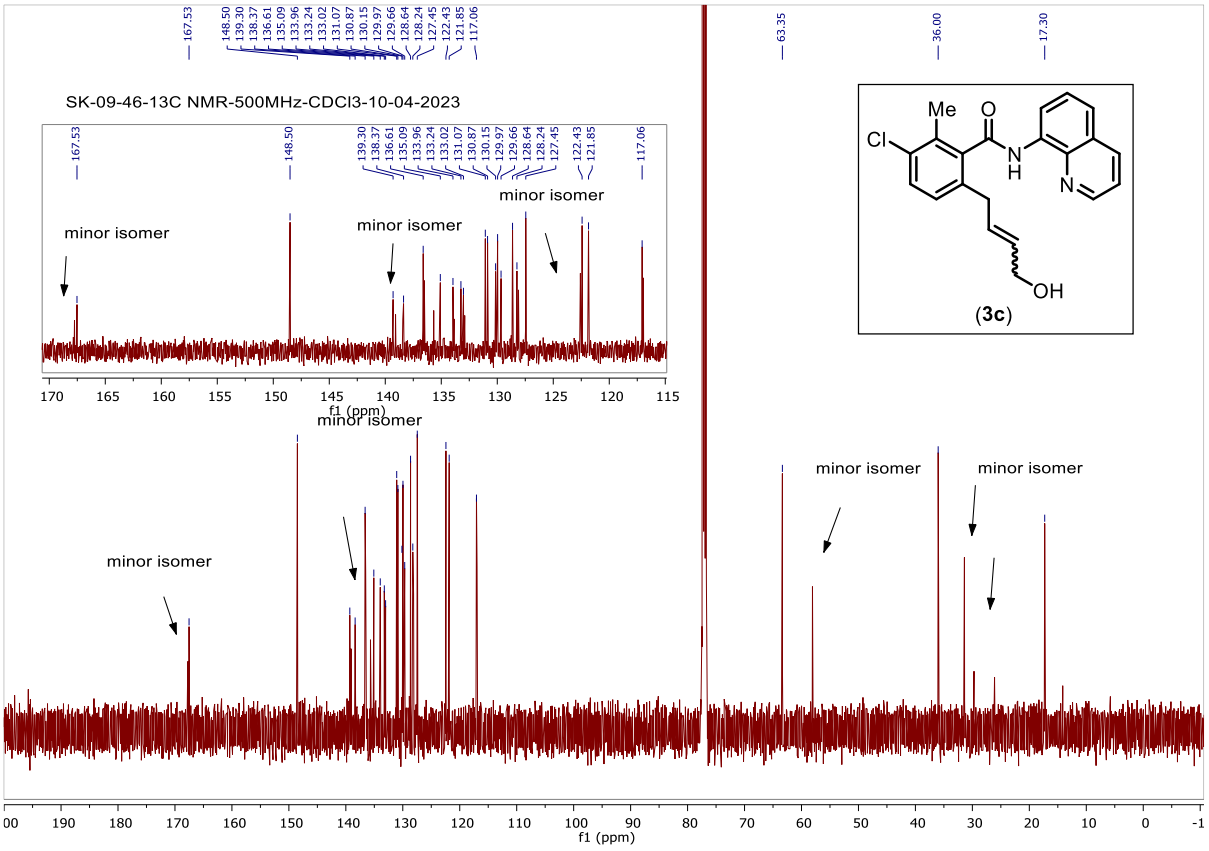


TIC +All MS






SK-09-46-1H NMR-500MHz-CDCl3-10-04-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer


SK-09-46-13C NMR-500MHz-CDCl3-10-04-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
Me
O
Cl
N
H
N
OH
(3c)
f1 (ppm)
f1 (ppm)

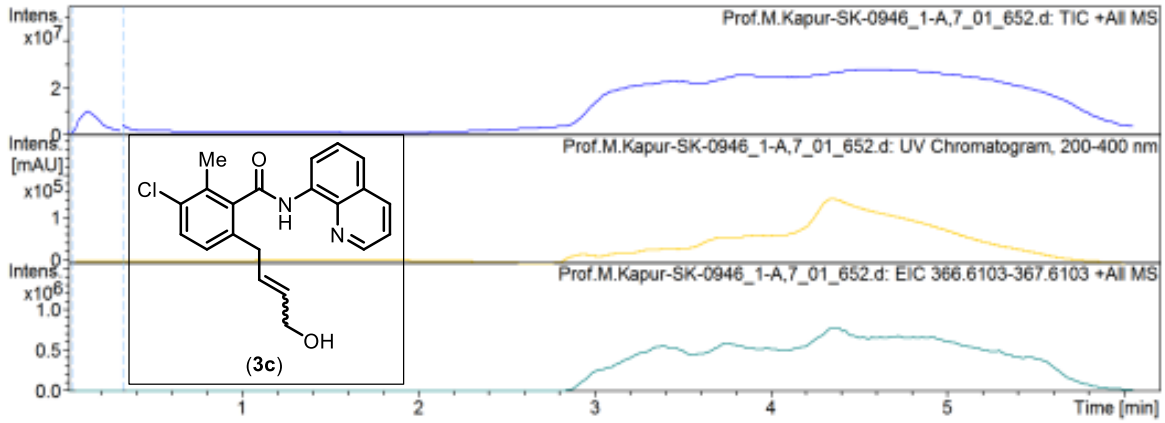
Display Report

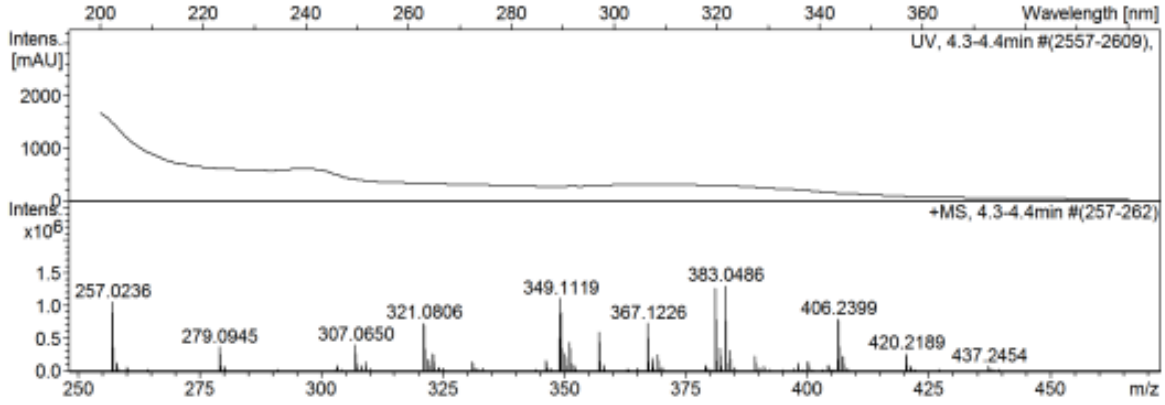
Analysis Info

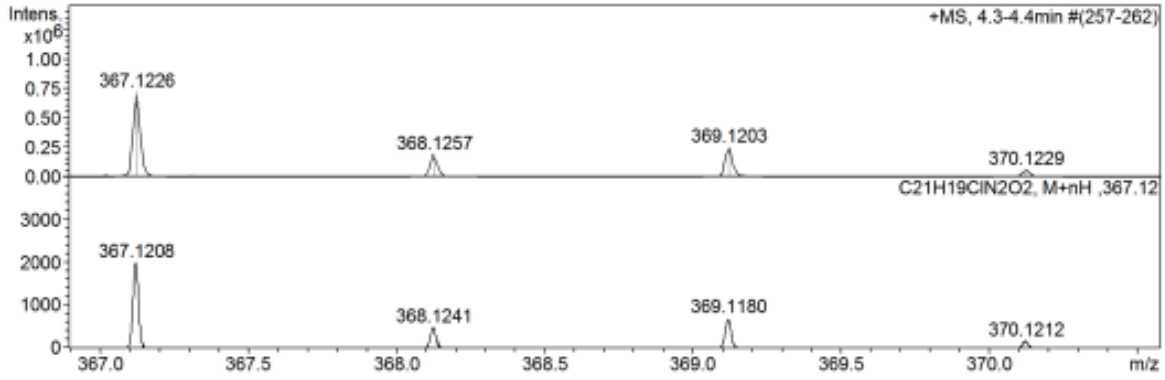
Acquisition Date	11-04-2023 12:49:34		
Analysis Name	D:\Data\USER DATA 2023\April\11-april\Prof.M.Kapur-SK-0946_1-A,7_01_652.d		
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-0946	Instrument	micrOTOF-Q 10330
Comment			

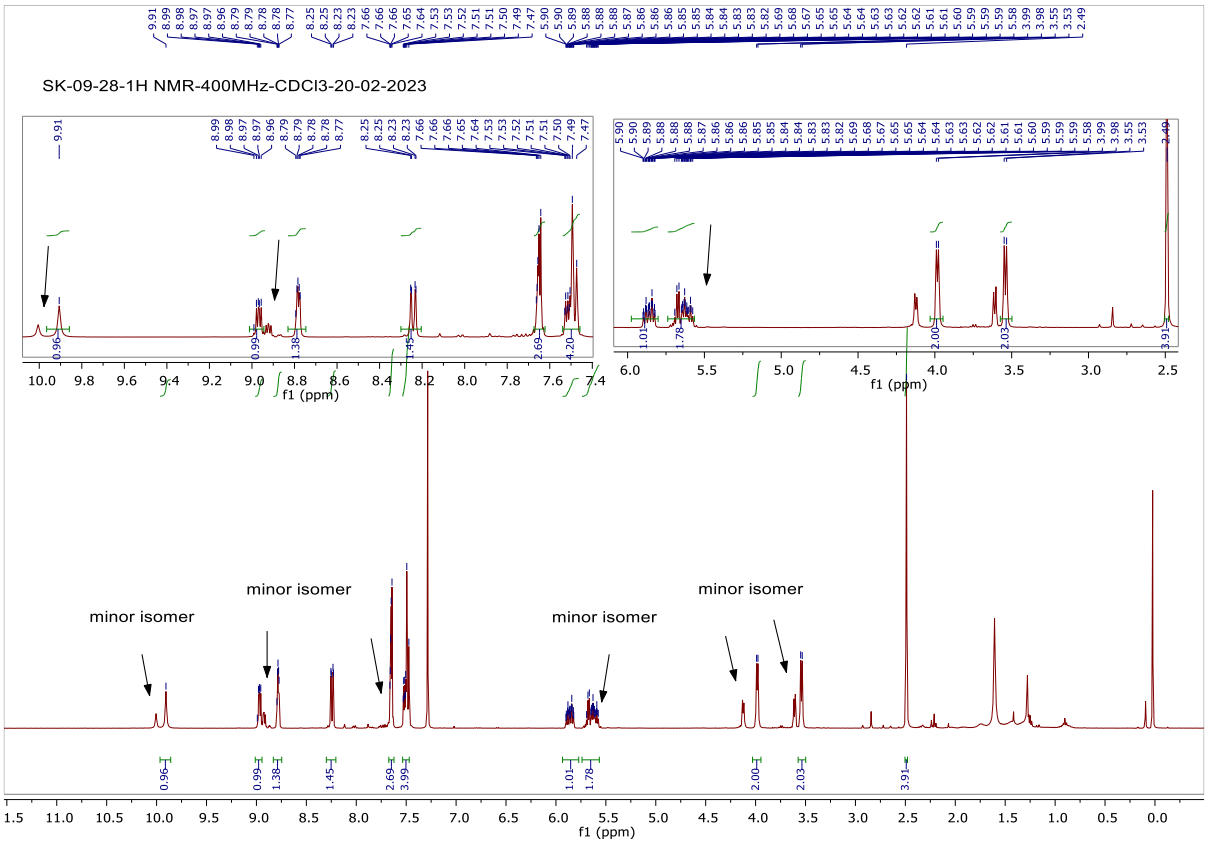
Acquisition Parameter

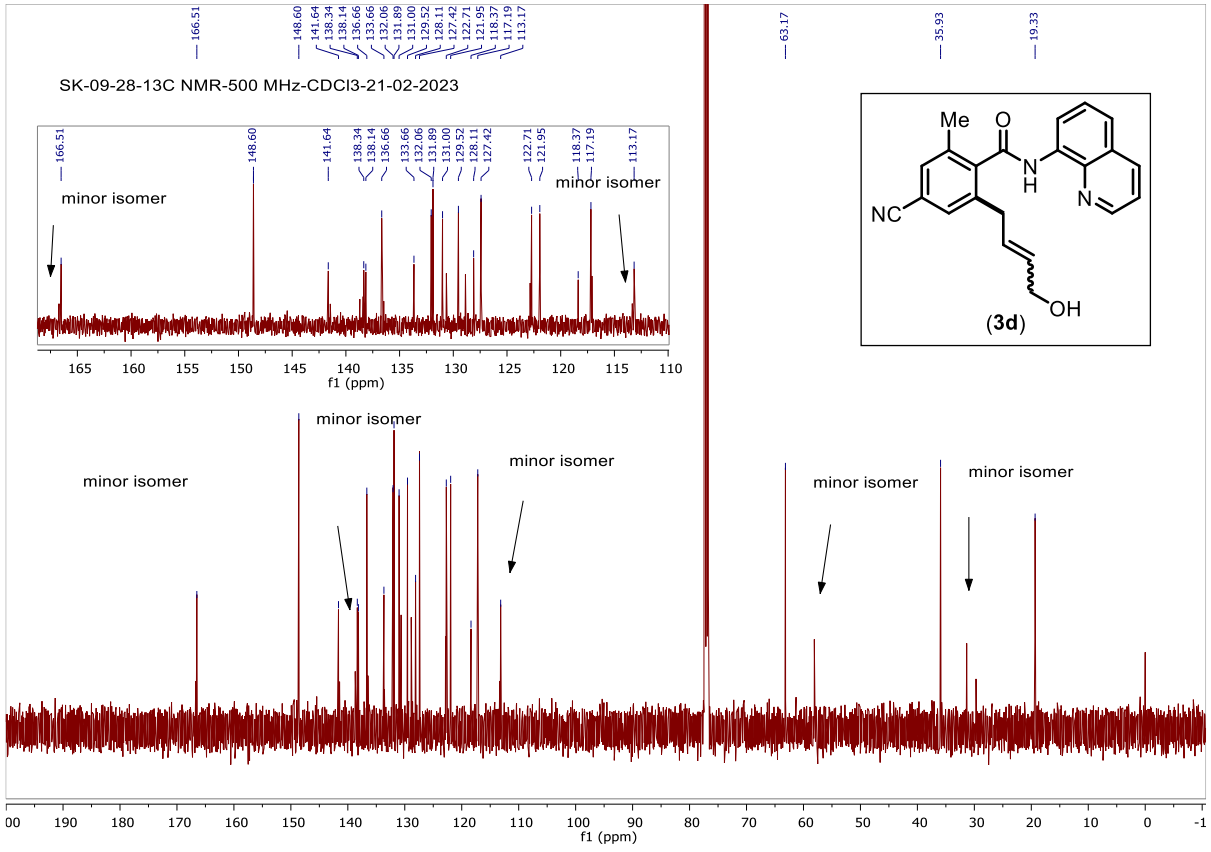
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








SK-09-28-1H NMR-400MHz-CDCl3-20-02-2023
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)


SK-09-28-13C NMR-500 MHz-CDCl3-21-02-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
Me
O
N
H
N
NC
OH
(3d)
f1 (ppm)

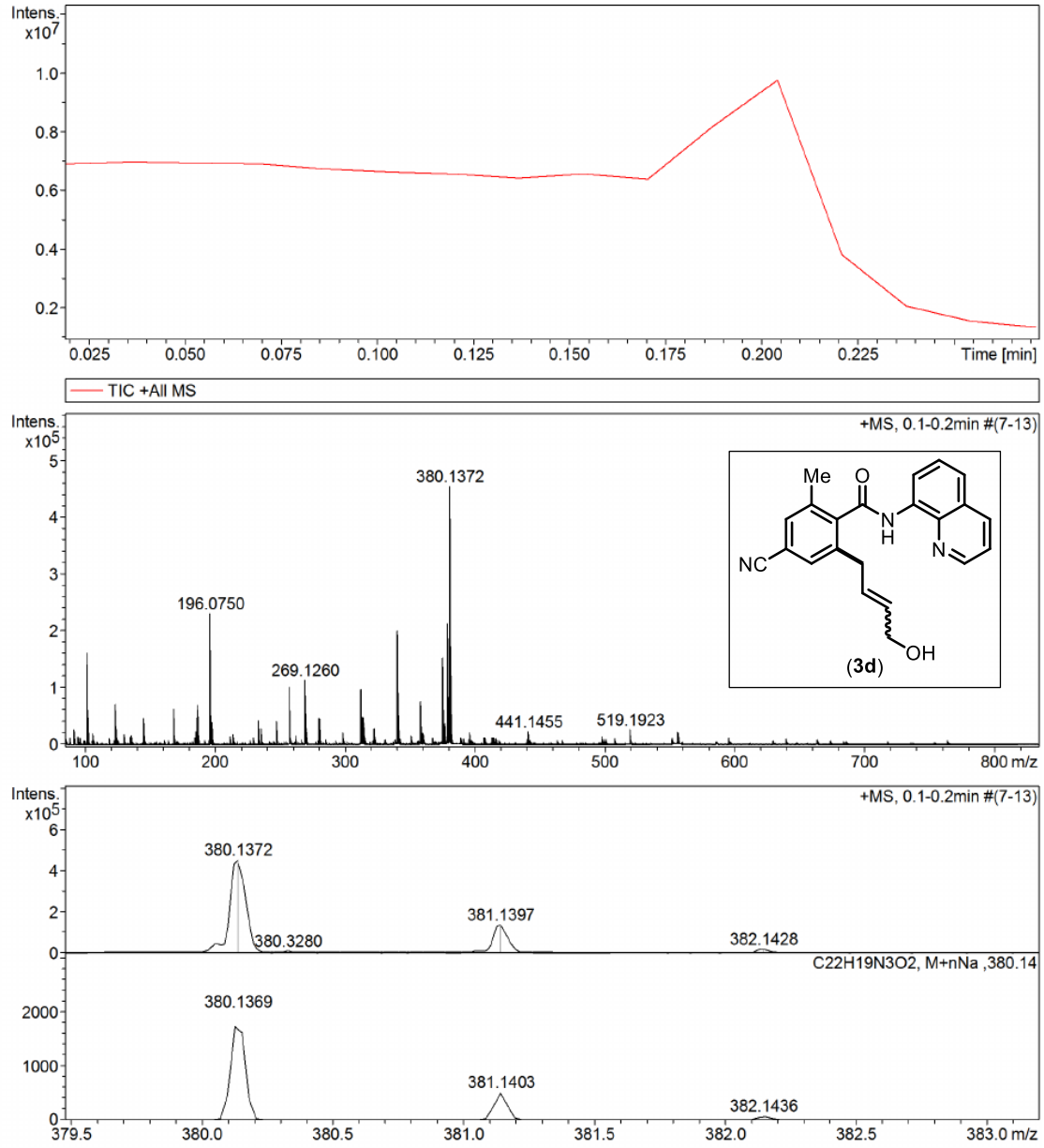
Display Report

Analysis Info

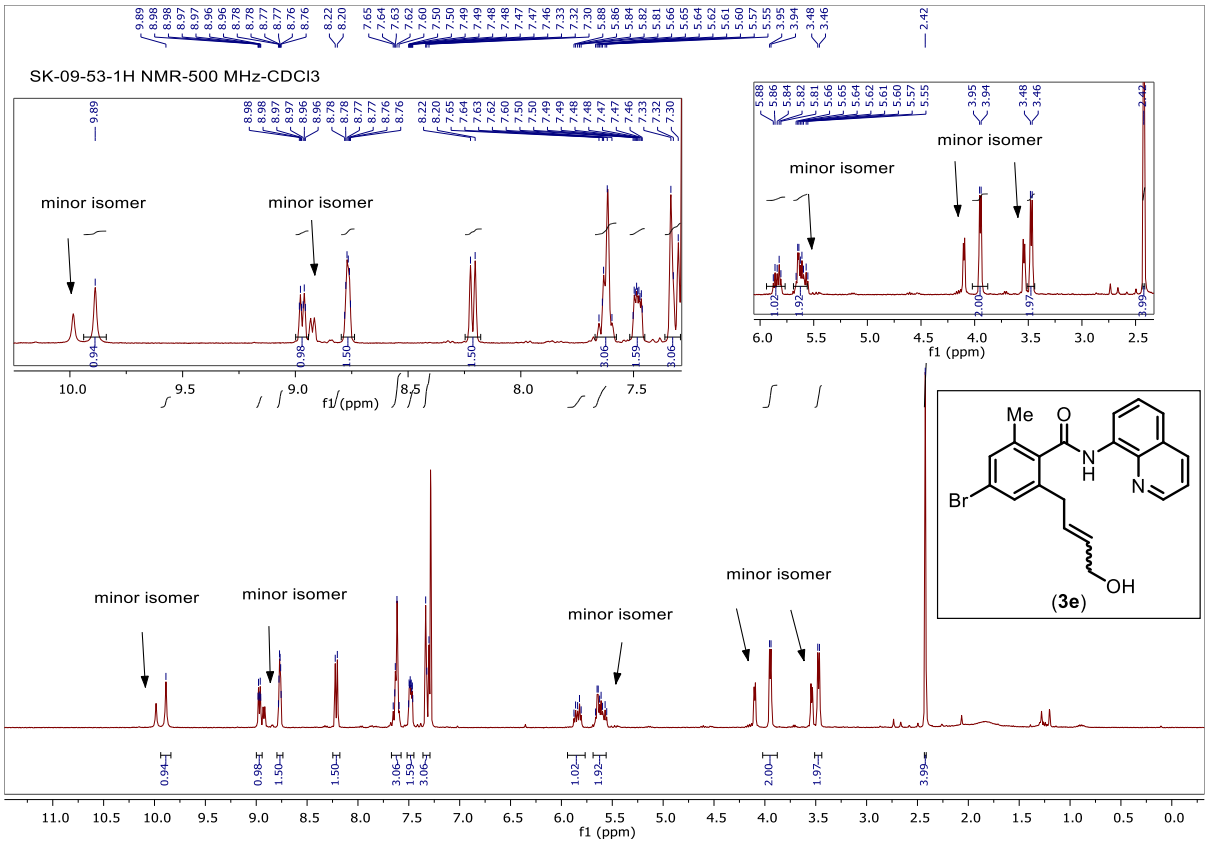
Analysis Name	D:\Data\USER DATA 2023\Feb\27-02-2023\Prof M Kapur-SK-09-28-S-I.d	Acquisition Date	27-02-2023 13:00:41
Method	tune_low_Jan23.m	Operator	Bruker
Sample Name	SK-09-28-S-I	Instrument	micrOTOF-Q 10330
Comment			

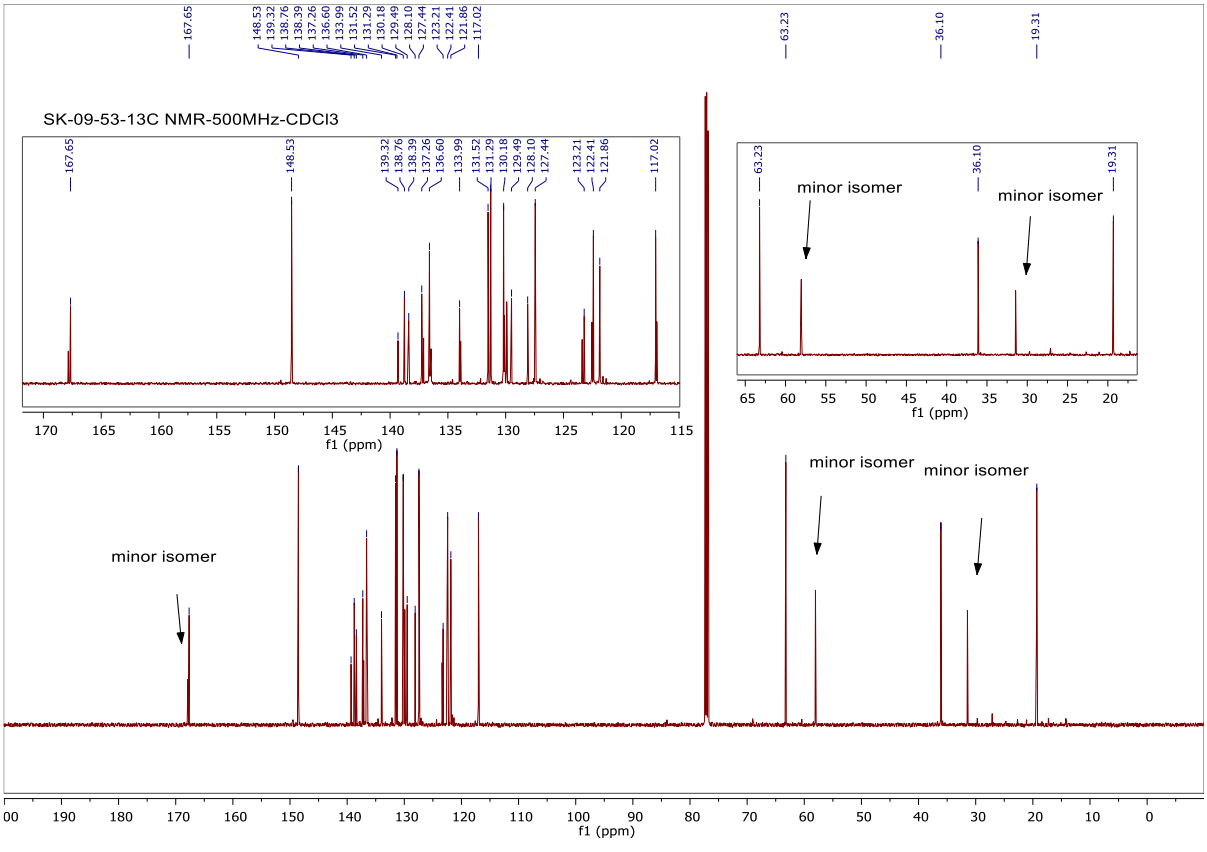
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	70.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 27-02-2023 13:01:45 Page 1 of 1


SK-09-53-1H NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
Me
O
N
H
Br
N
OH
(3e)
f1 (ppm)


SK-09-53-13C NMR-500MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)

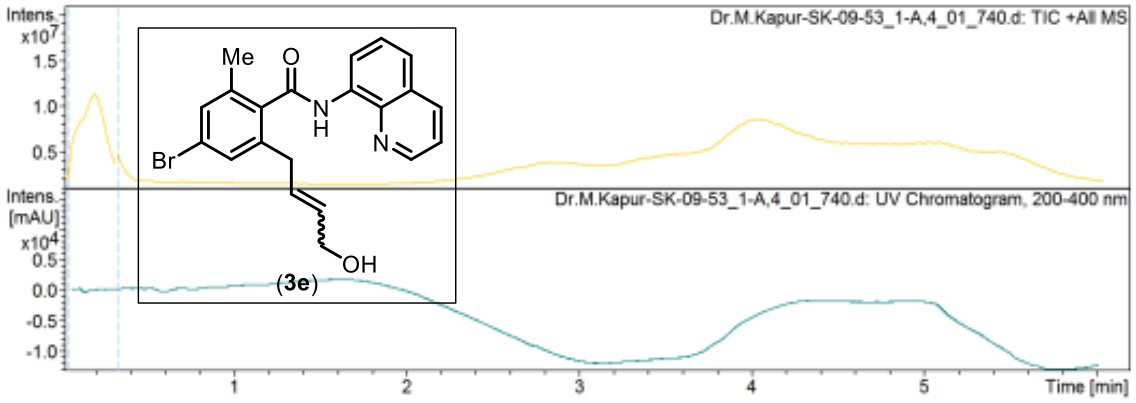
Display Report

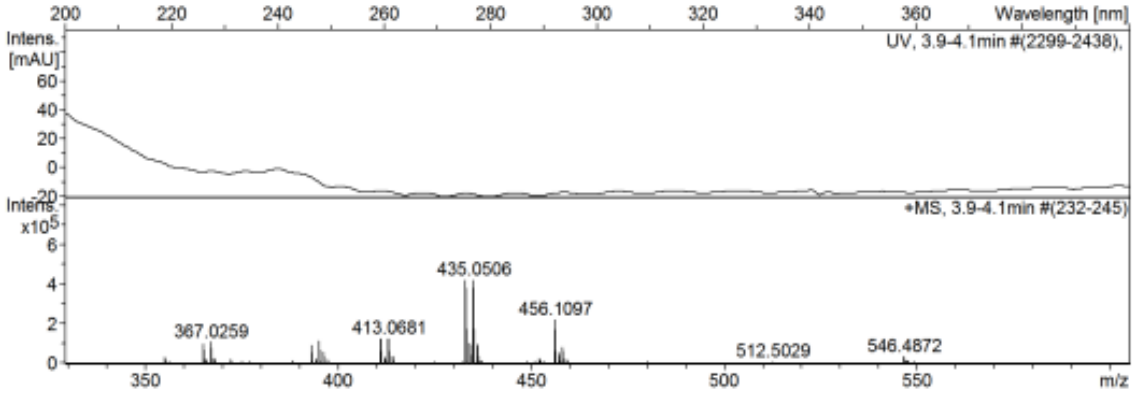
Analysis Info

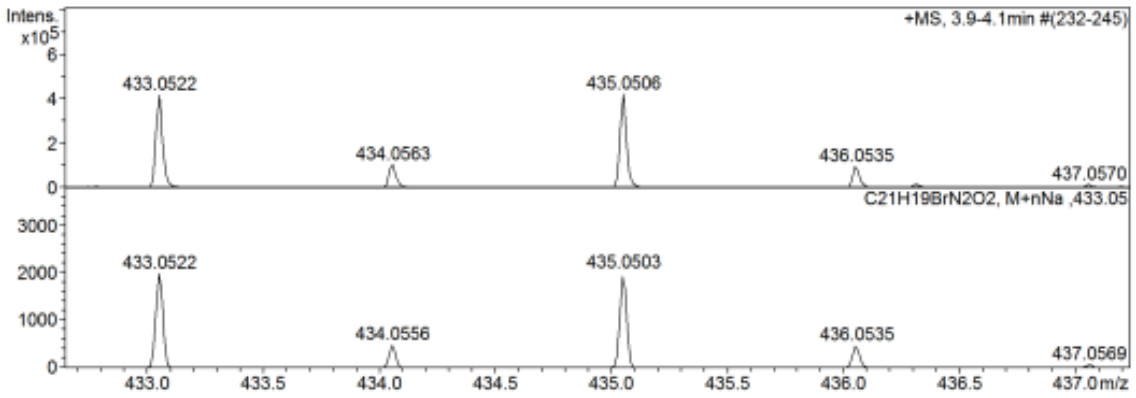
Analysis Name	D:\Data\USER DATA 2023\April\17-april\Dr.M.Kapur-SK-09-53_1-A,4_01_740.d	Acquisition Date	17-04-2023 11:15:43
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Dr.M.Kapur-SK-09-53	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

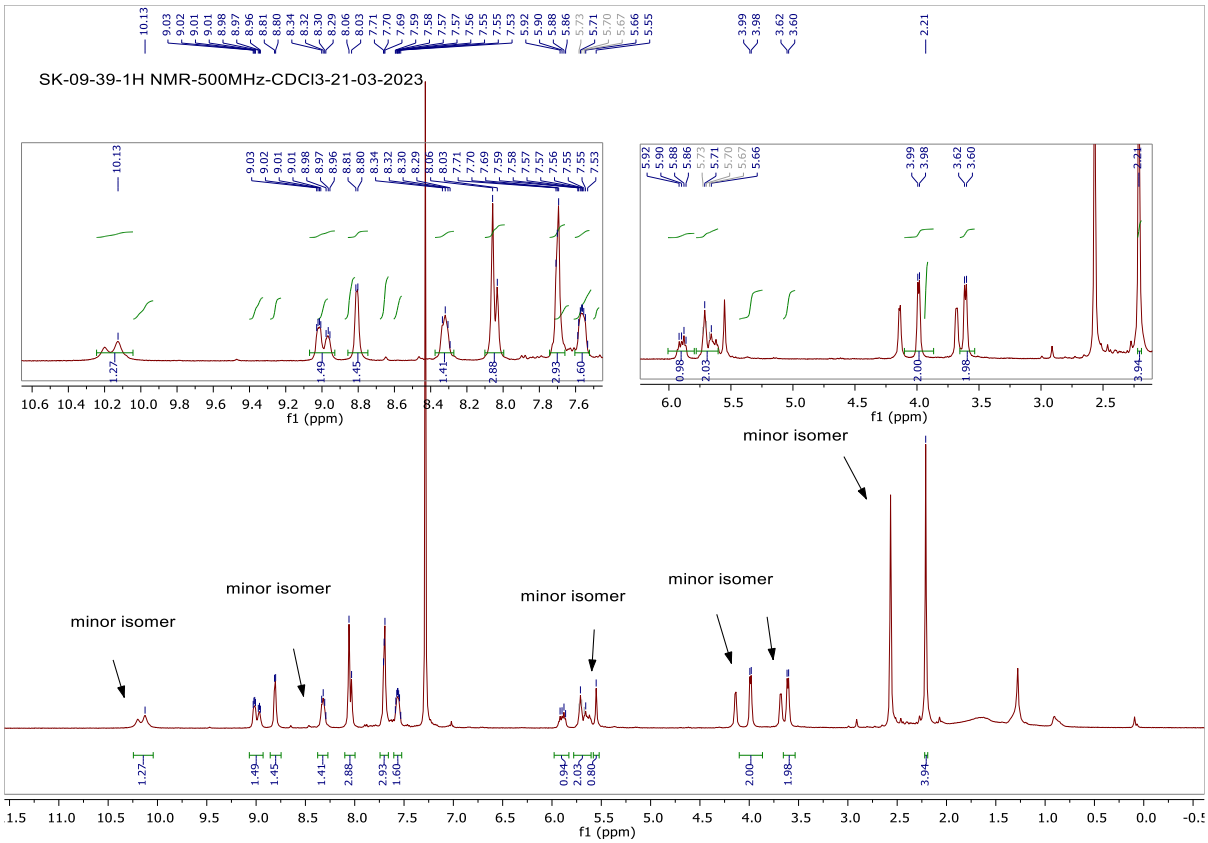
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

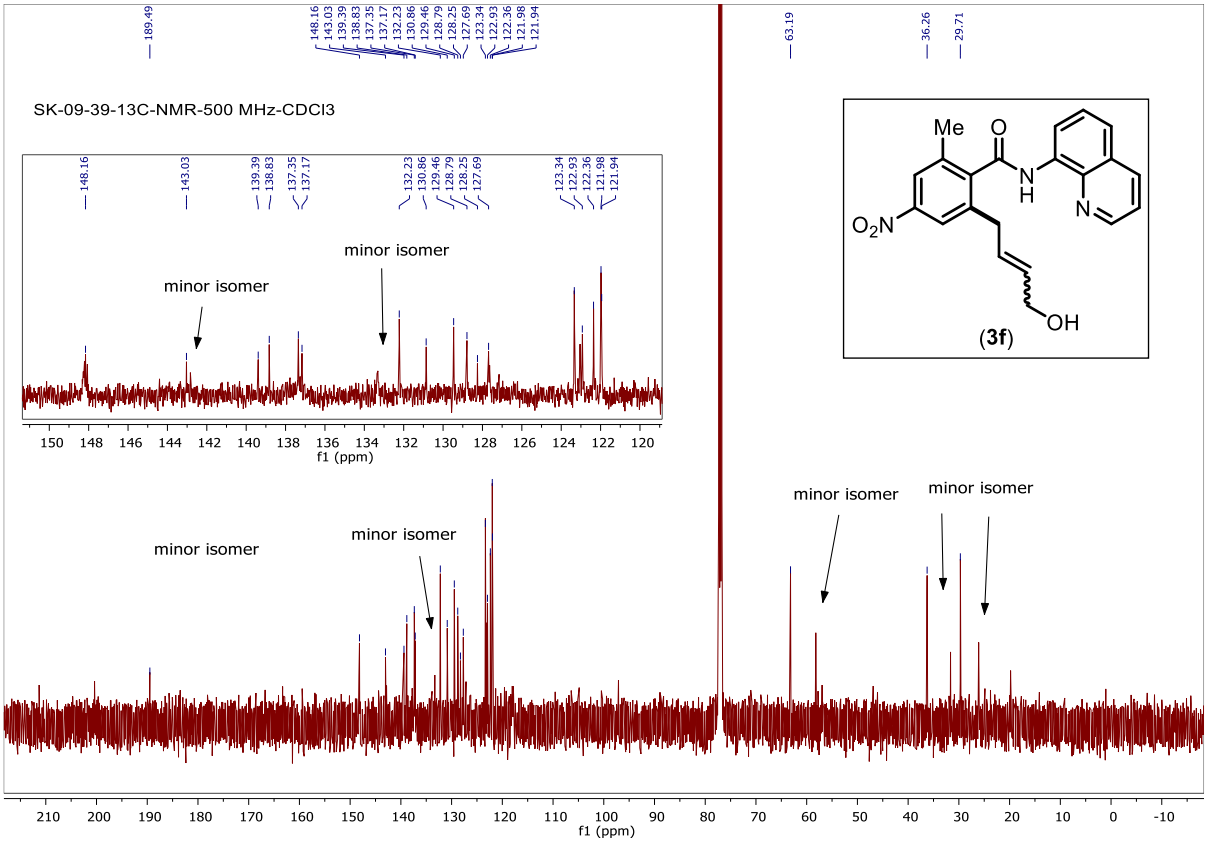






Bruker Compass DataAnalysis 4.0 printed: 17-04-2023 12:16:55 Page 1 of 1


SK-09-39-1H NMR-500MHz-CDCl3-21-03-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)


SK-09-39-13C-NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)
Me
O
N
H
N
O_2N
OH
(3f)

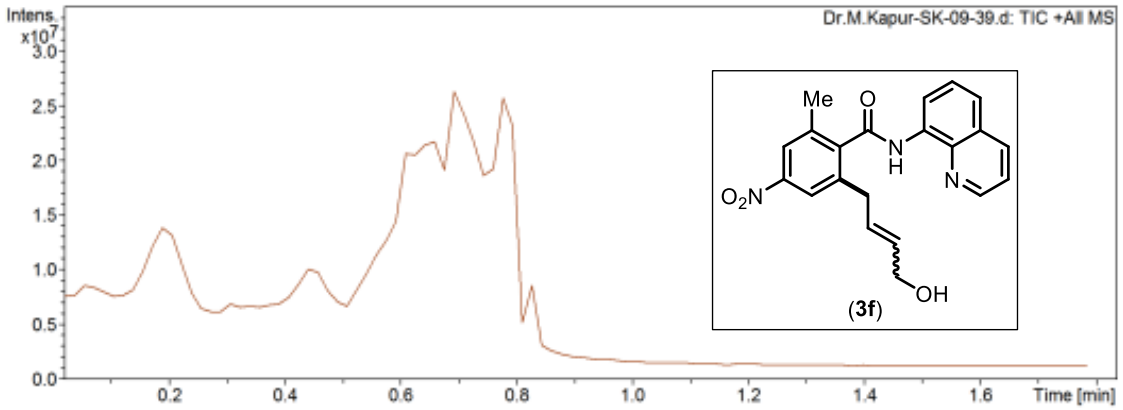
Display Report

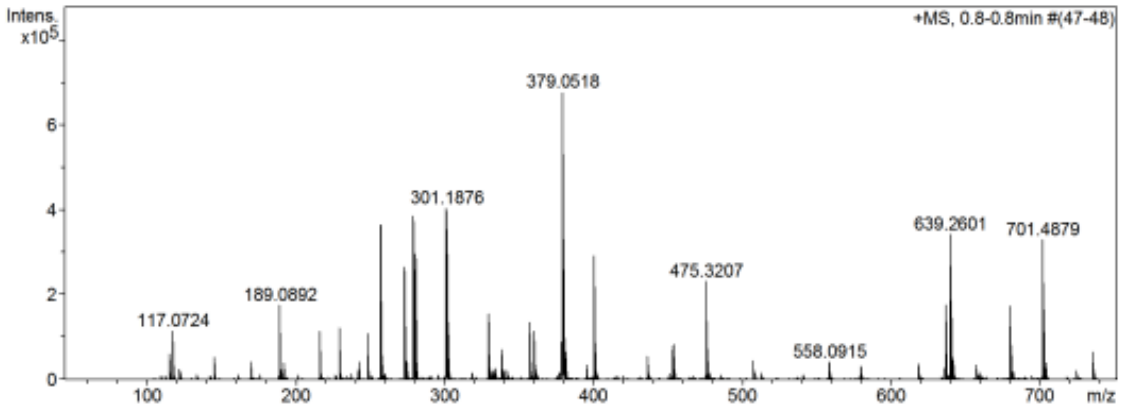
Analysis Info

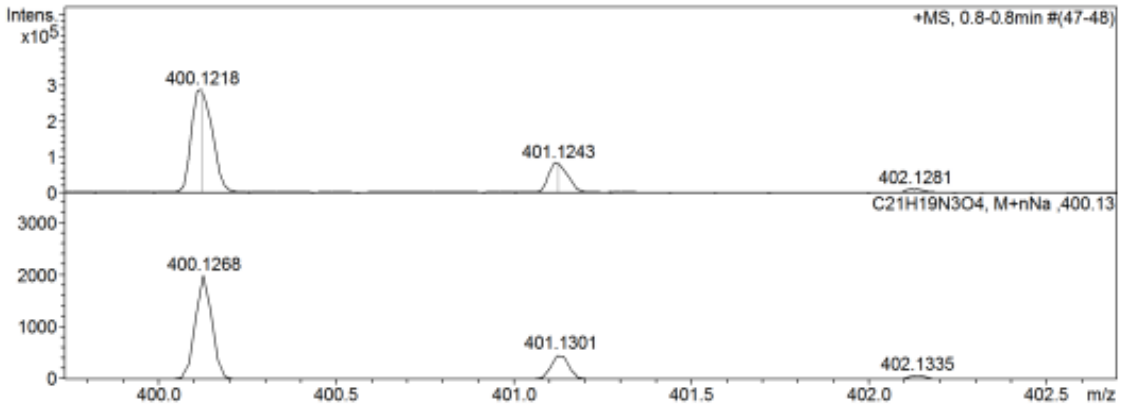
Analysis Name	D:\Data\USER DATA 2023\March\21-march\Dr.M.Kapur-SK-09-39.d	Acquisition Date	21-03-2023 16:42:06
Method	tune_low_Jan23.m	Operator	Bruker
Sample Name	SK-09-39	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

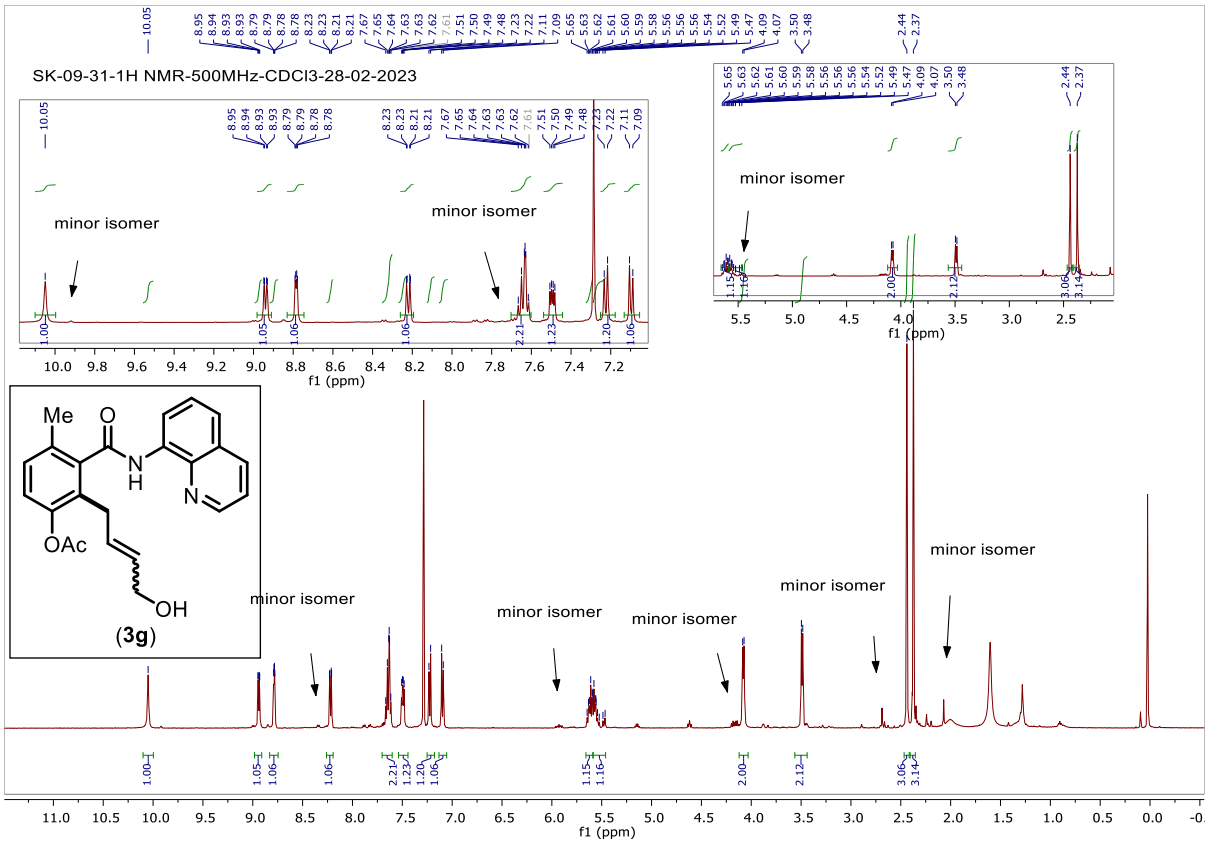
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

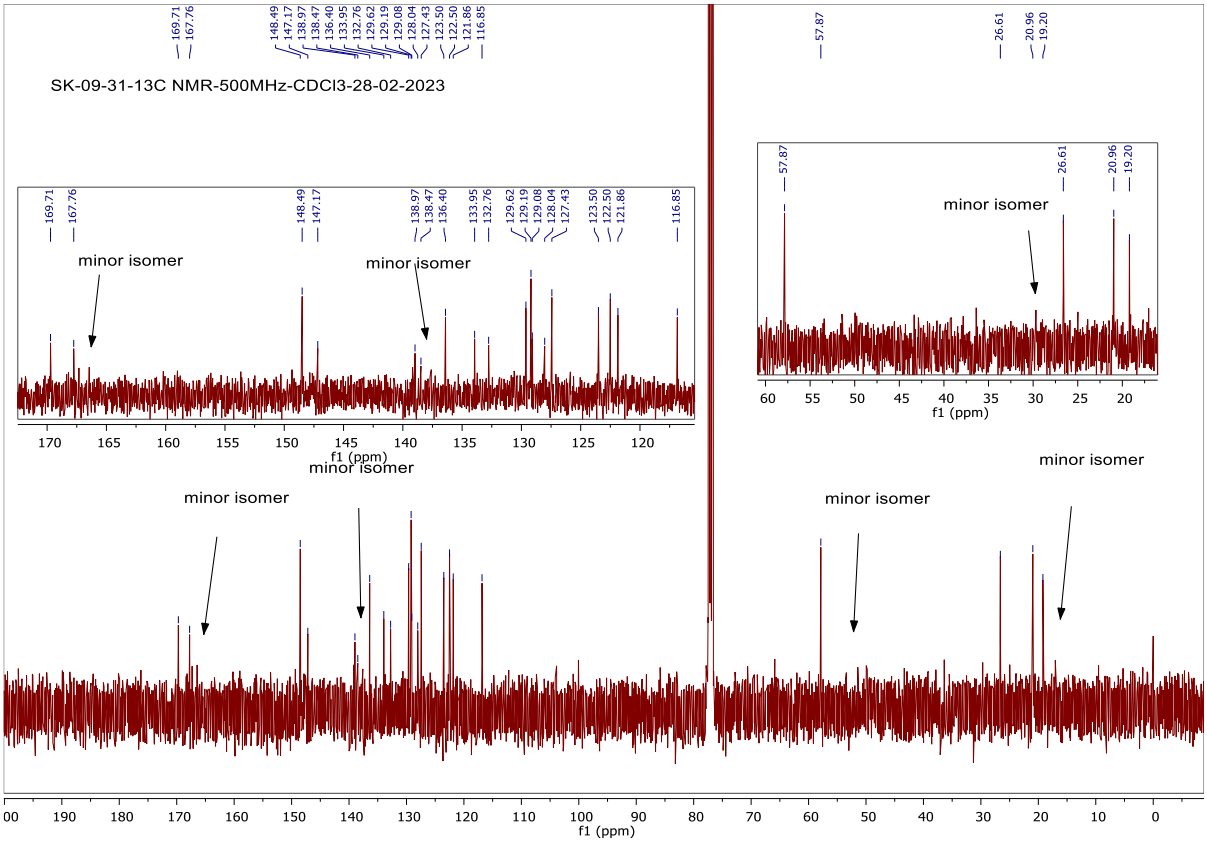






Bruker Compass DataAnalysis 4.0 printed: 21-03-2023 16:44:59 Page 1 of 1


SK-09-31-1H NMR-500MHz-CDCl3-28-02-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
Me
O
N
H
N
OAc
OH
(3g)
f1 (ppm)


SK-09-31-13C NMR-500MHz-CDCl3-28-02-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)

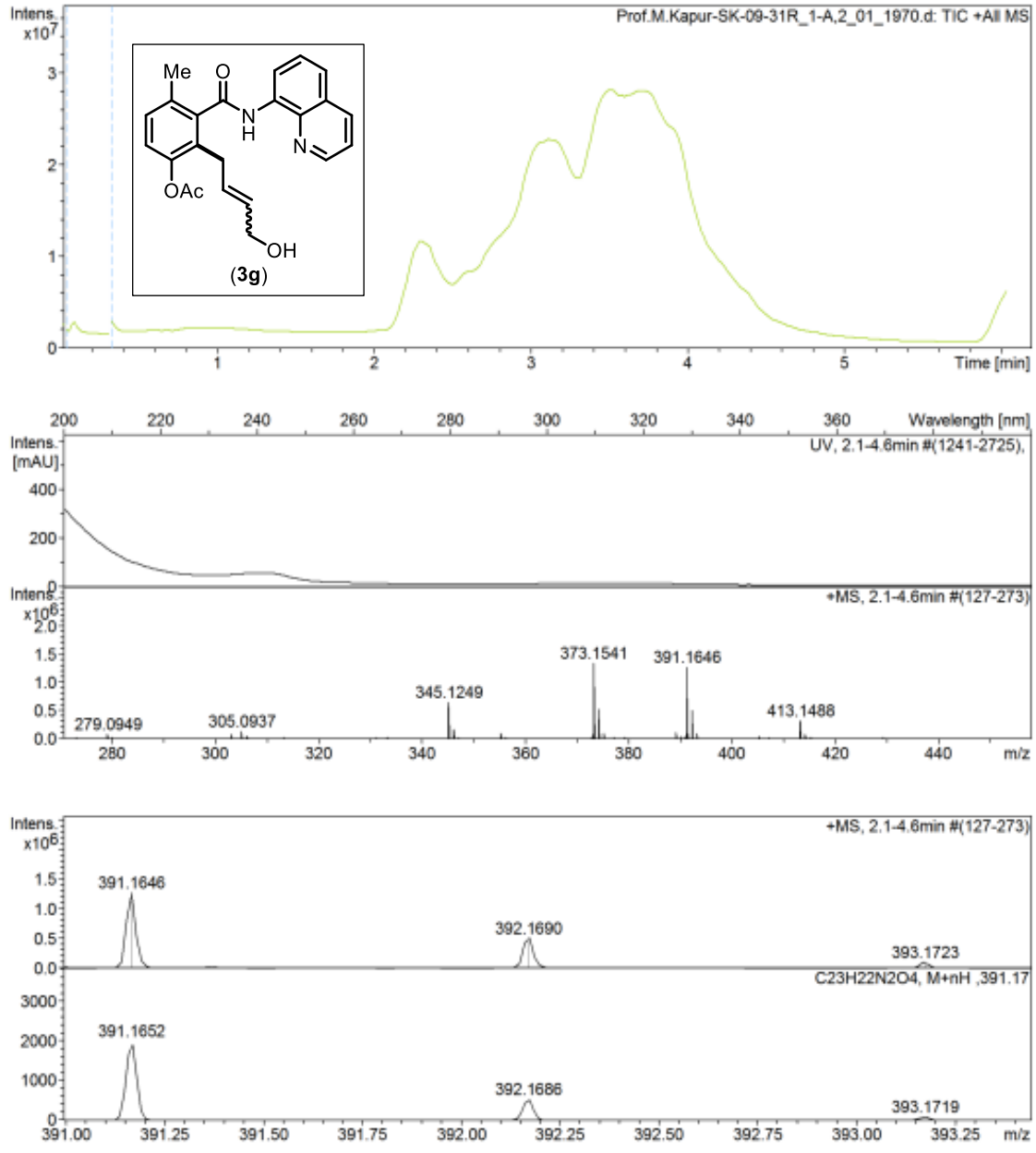
Display Report

Analysis Info

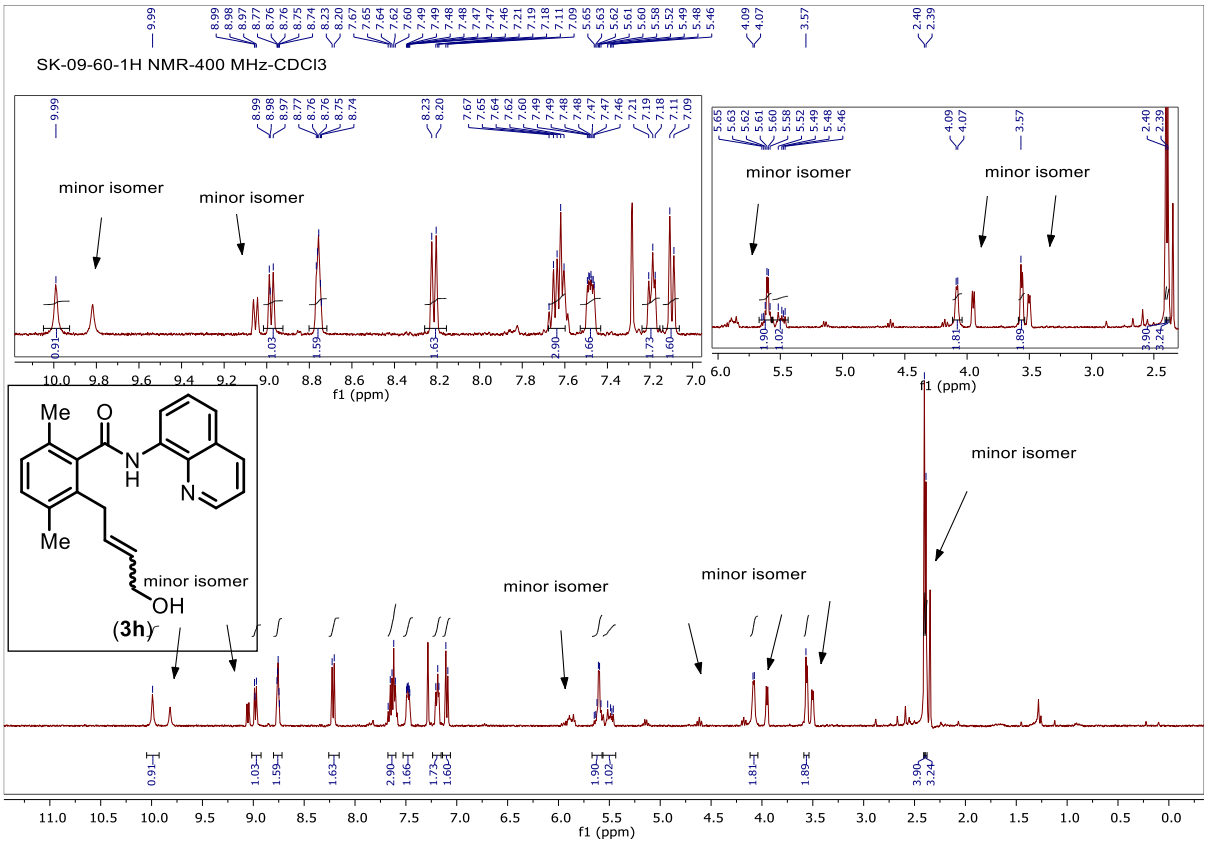
Acquisition Date	20-06-2023 11:42:40		
Analysis Name	D:\Data\USER DATA 2023\June\20-june\Prof.M.Kapur-SK-09-31R_1-A,2_01_1970.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-31R	Instrument	micrOTOF-Q 10330
Comment			

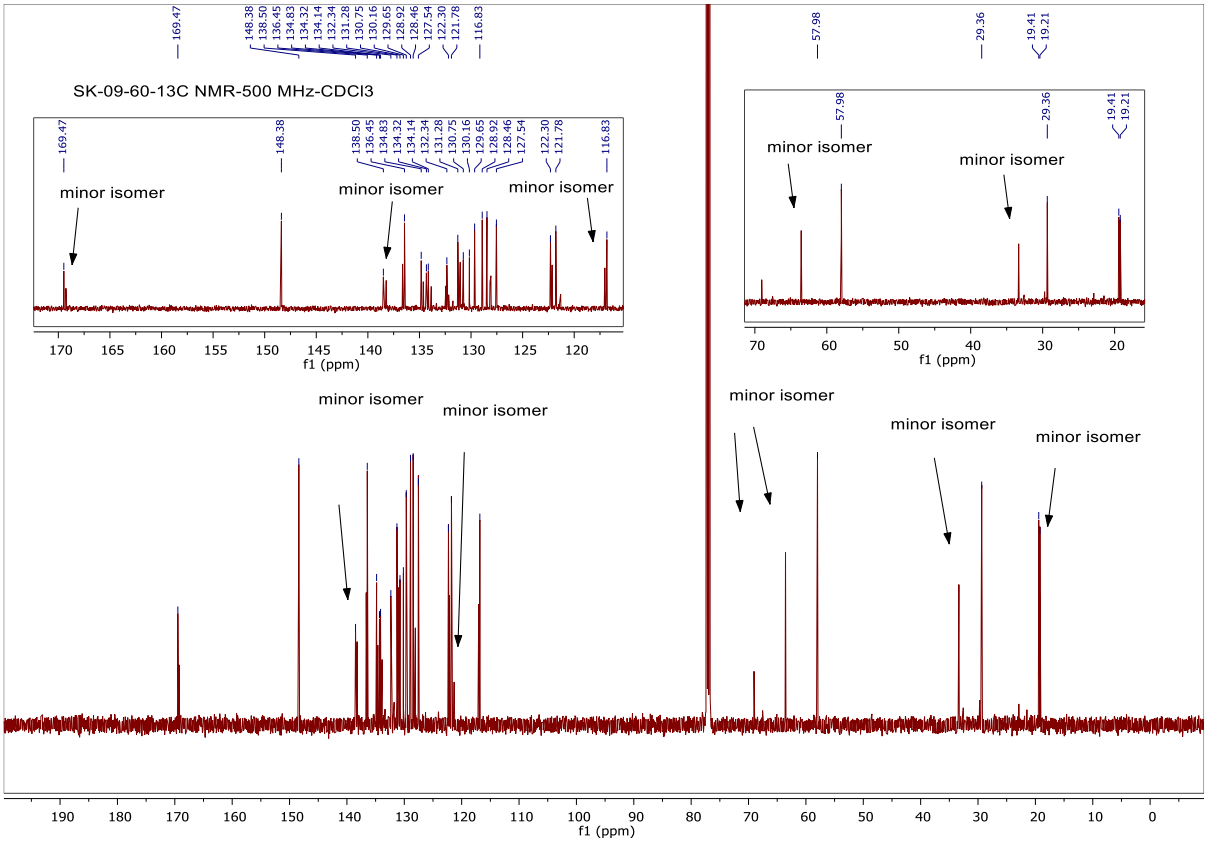
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 20-06-2023 12:40:43 Page 1 of 1


SK-09-60-1H NMR-400 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
Me
O
N
H
N
Me
OH
(3h)
f1 (ppm)


SK-09-60-13C NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)

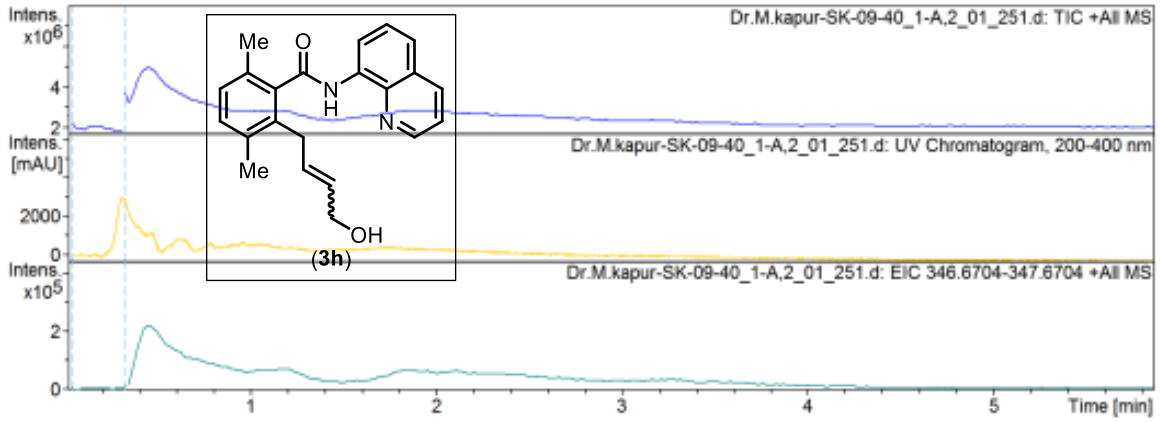
Display Report

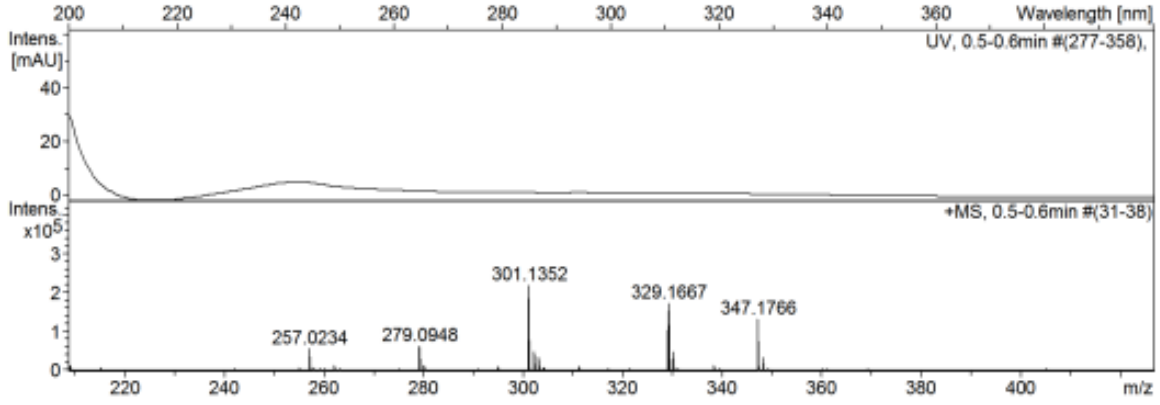
Analysis Info

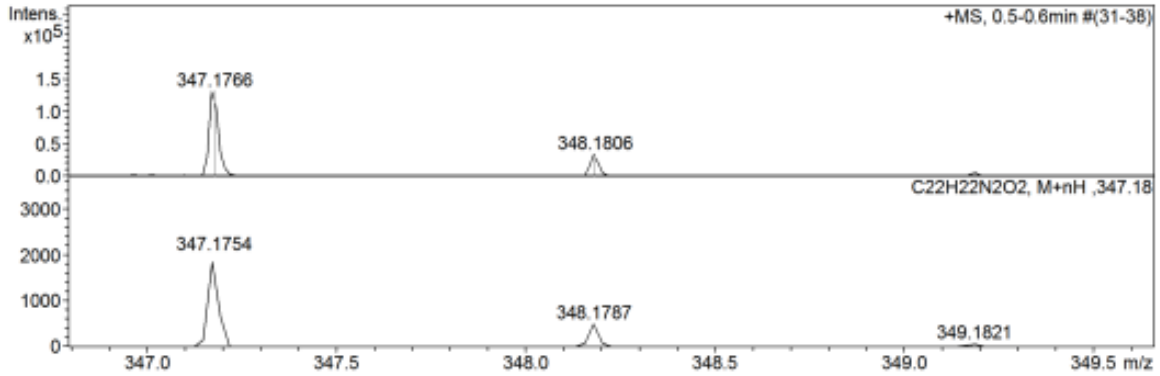
Analysis Name	D:\Data\USER DATA 2023\March\20-march\Dr.M.kapur-SK-09-40_1-A,2_01_251.d	Acquisition Date	20-03-2023 11:38:08
Method	HRLCMS-20 Sept-PUMP E.m	Operator	Bruker
Sample Name	Dr.M.kapur-SK-09-40	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

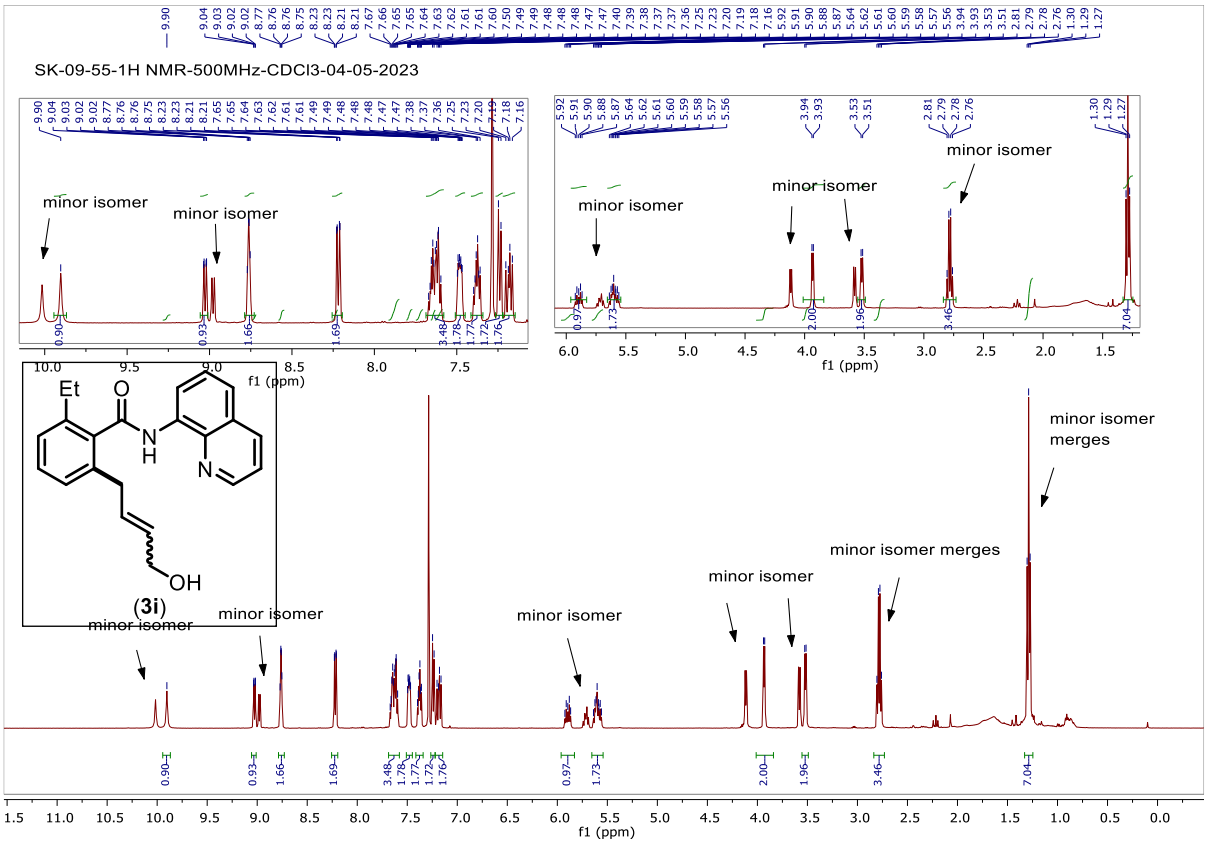
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

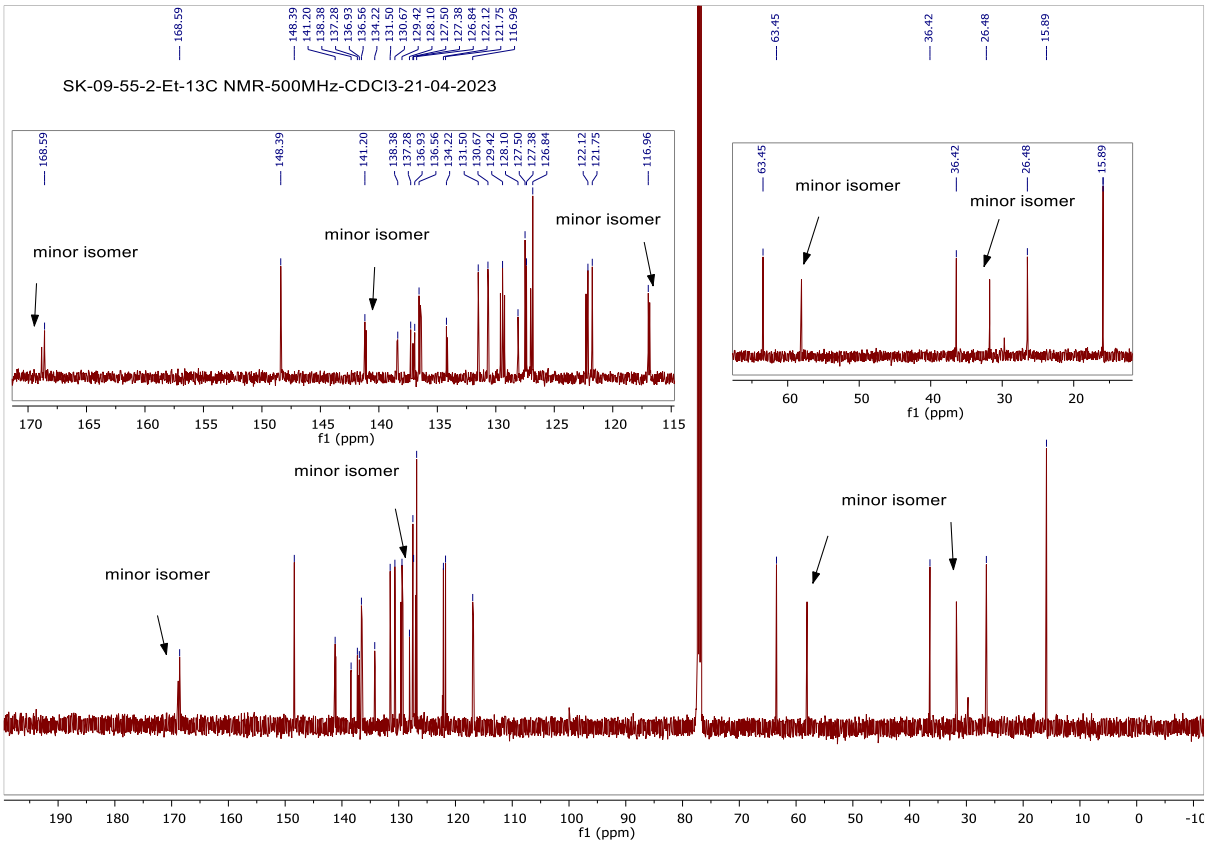






Bruker Compass DataAnalysis 4.0 printed: 20-03-2023 12:03:09 Page 1 of 1


SK-09-55-1H NMR-500MHz-CDCl3-04-05-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer merges
minor isomer merges
minor isomer
minor isomer
minor isomer
Et
O
N
H
N
OH
(3i)
f1 (ppm)


SK-09-55-2-Et-13C NMR-500MHz-CDCl3-21-04-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)

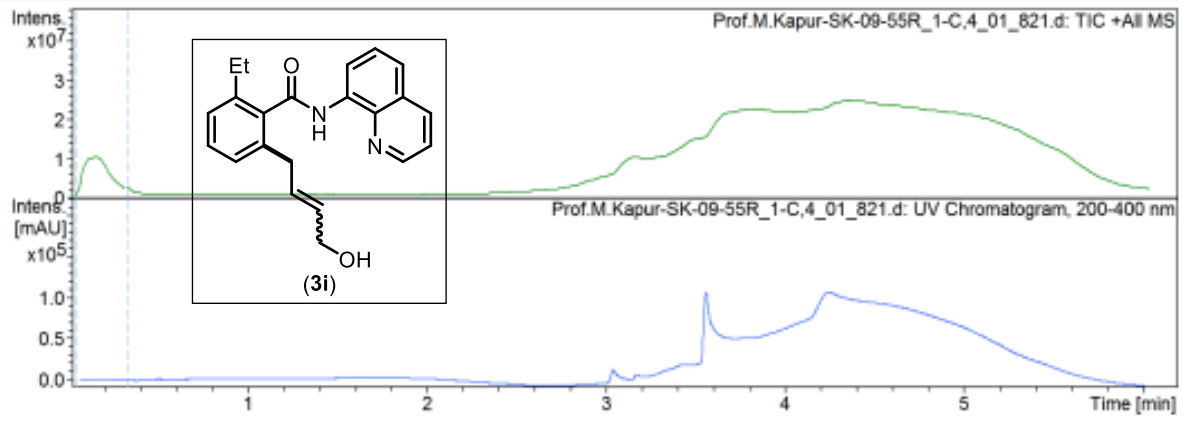
Display Report

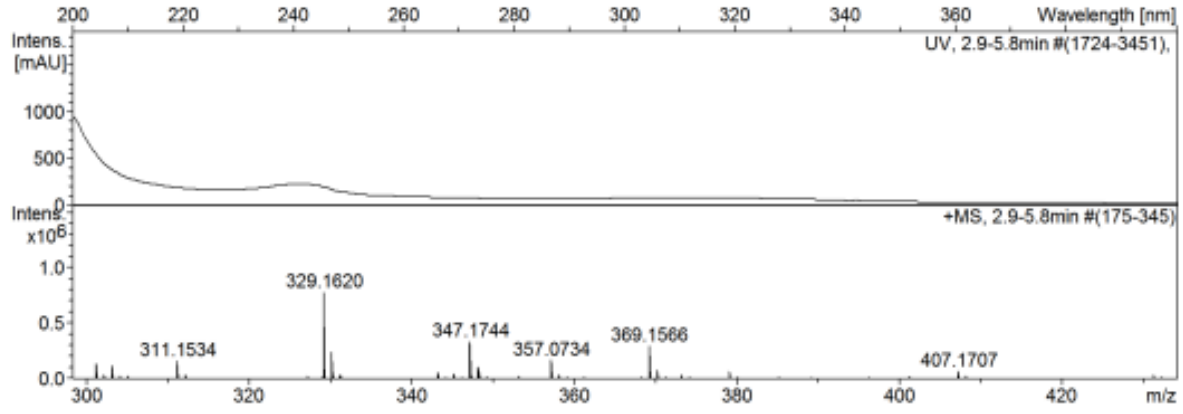
Analysis Info

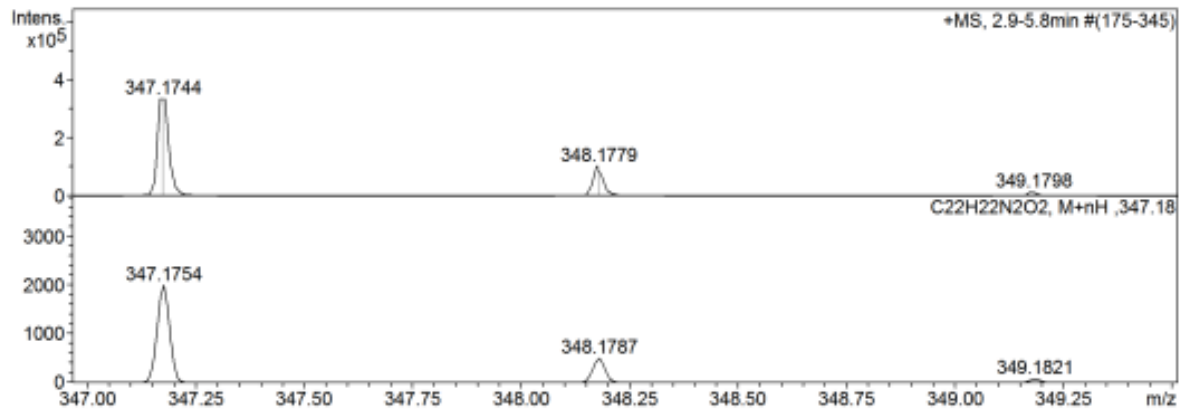
		Acquisition Date	19-04-2023 14:07:54
Analysis Name	D:\Data\USER DATA 2023\April\19-april\Prof.M.Kapur-SK-09-55R_1-C,4_01_821.d		
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-55R	Instrument	micrOTOF-Q 10330
Comment			

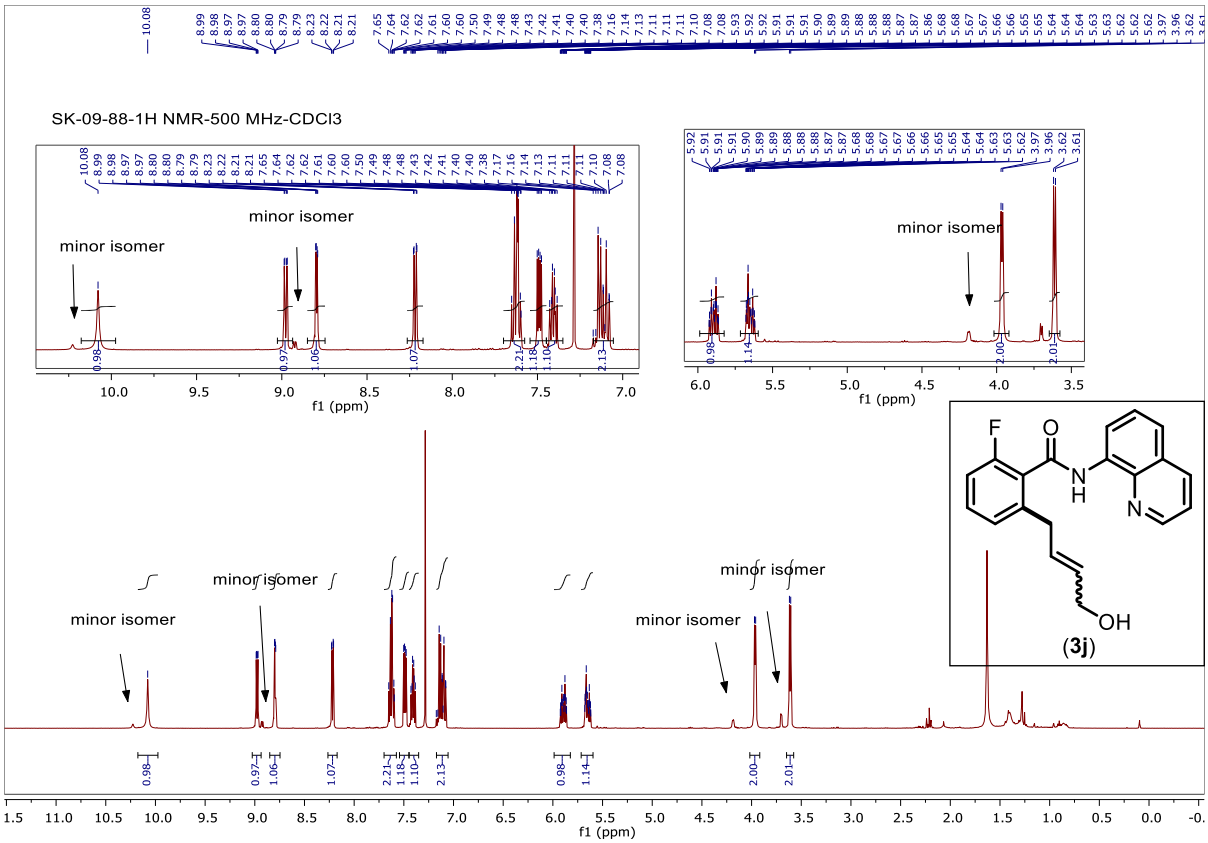
Acquisition Parameter

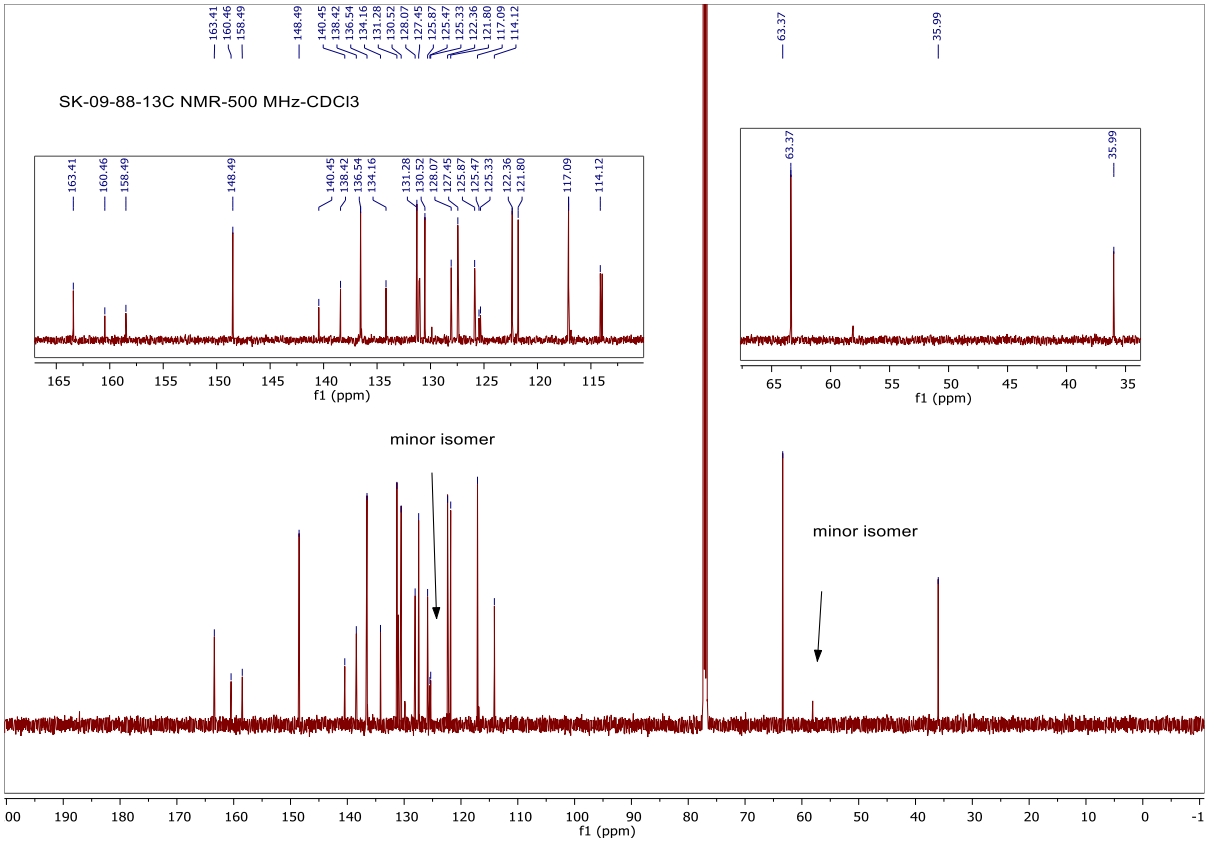
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

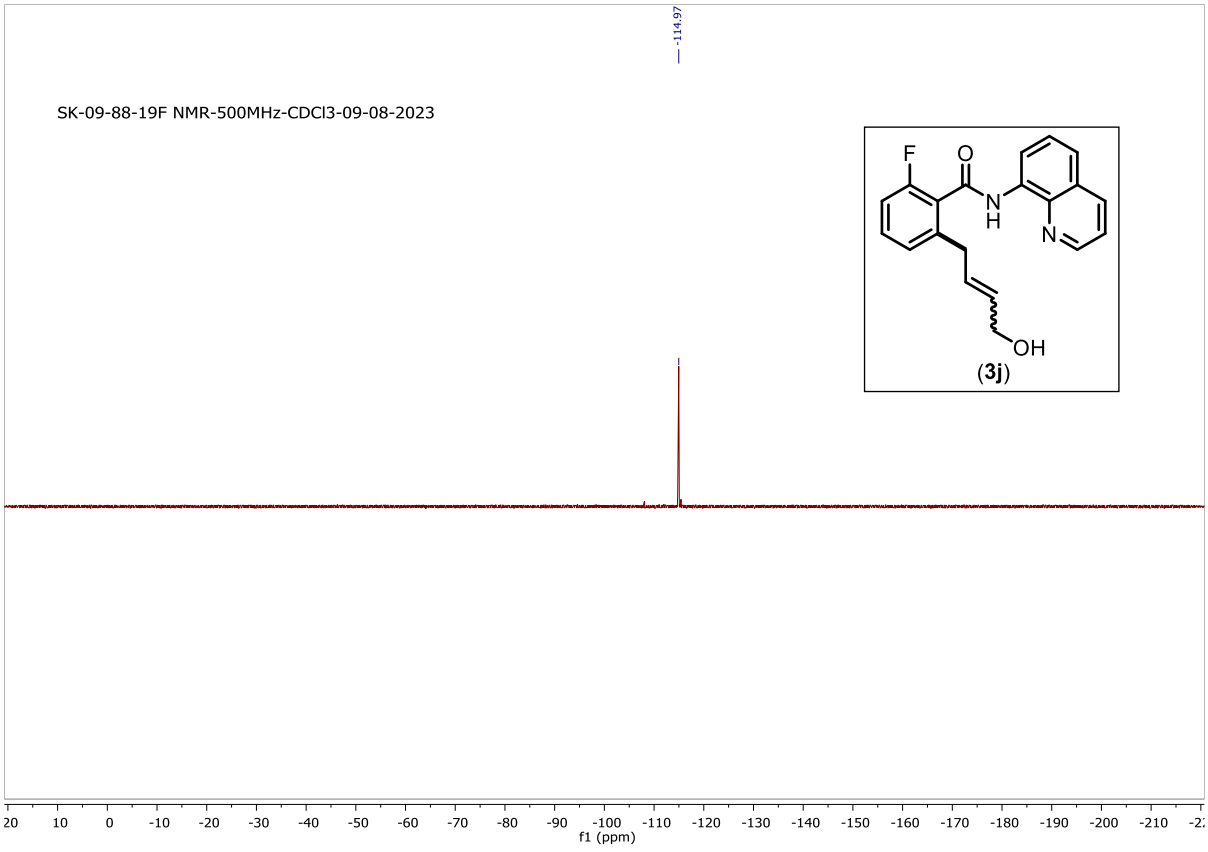







SK-09-88-1H NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
F
O
N
H
N
OH
(3j)
f1 (ppm)


SK-09-88-13C NMR-500 MHz-CDCl3
minor isomer
minor isomer
f1 (ppm)


-114.97
SK-09-88-19F NMR-500MHz-CDCl3-09-08-2023
F
O
N
H
N
OH
(3j)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

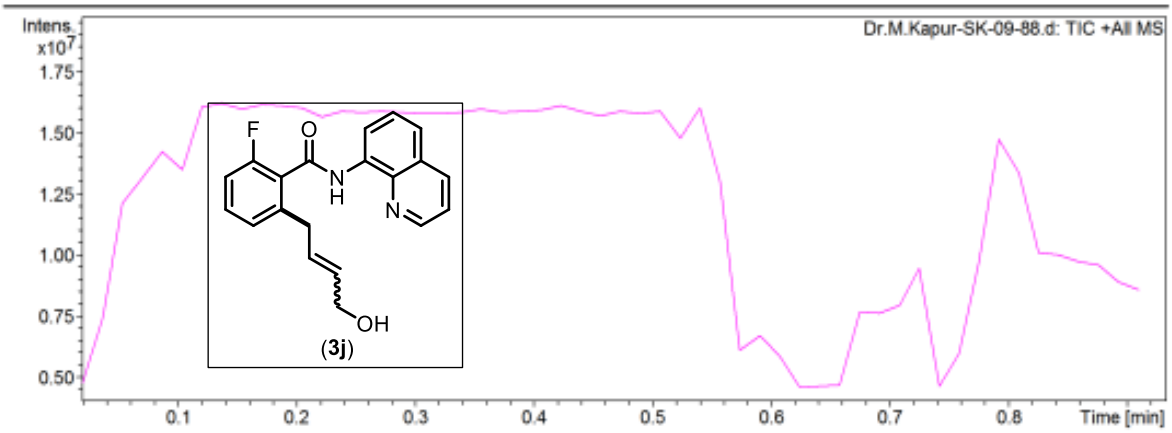
Display Report

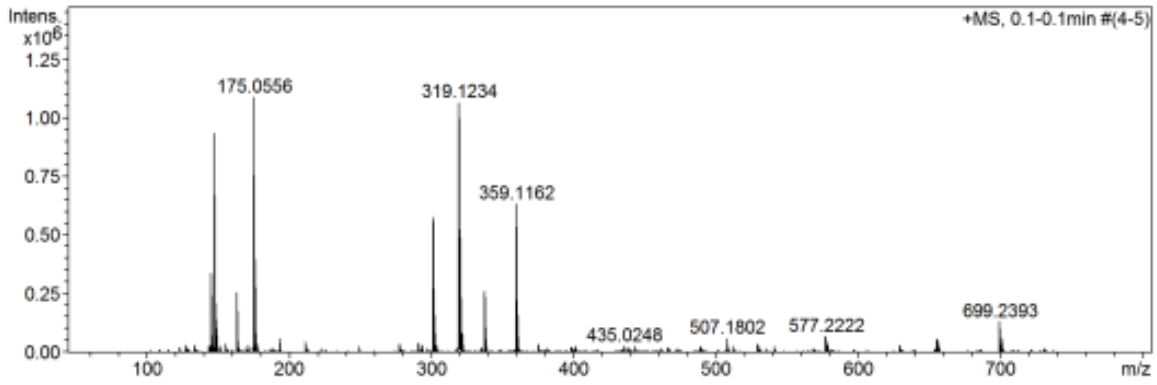
Analysis Info

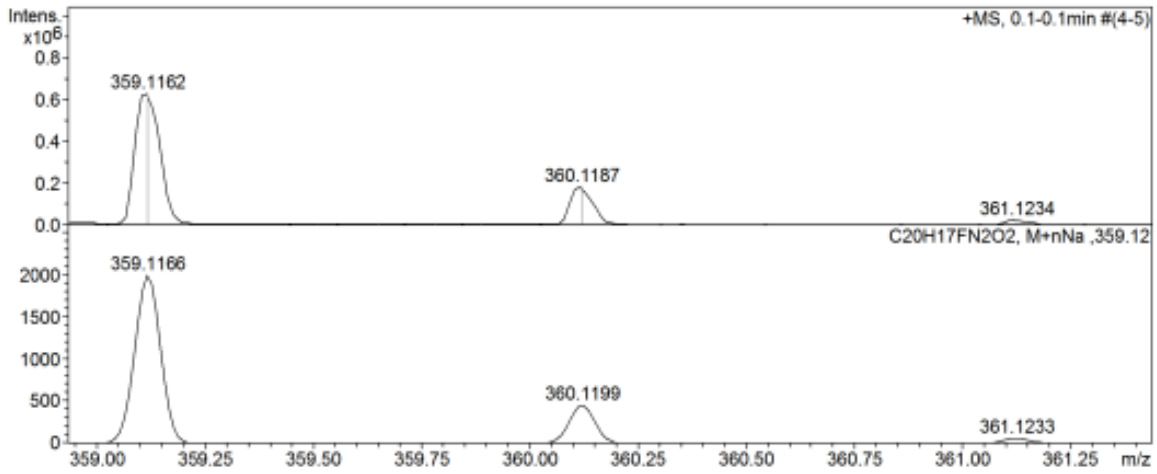
Analysis Name	D:\Data\USER DATA 2023\Dec23\13-dec\Dr.M.Kapur-SK-09-88.d	Acquisition Date	13-12-2023 16:11:18
Method	tune_low_APR23.m	Operator	Bruker
Sample Name	SK-09-88	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

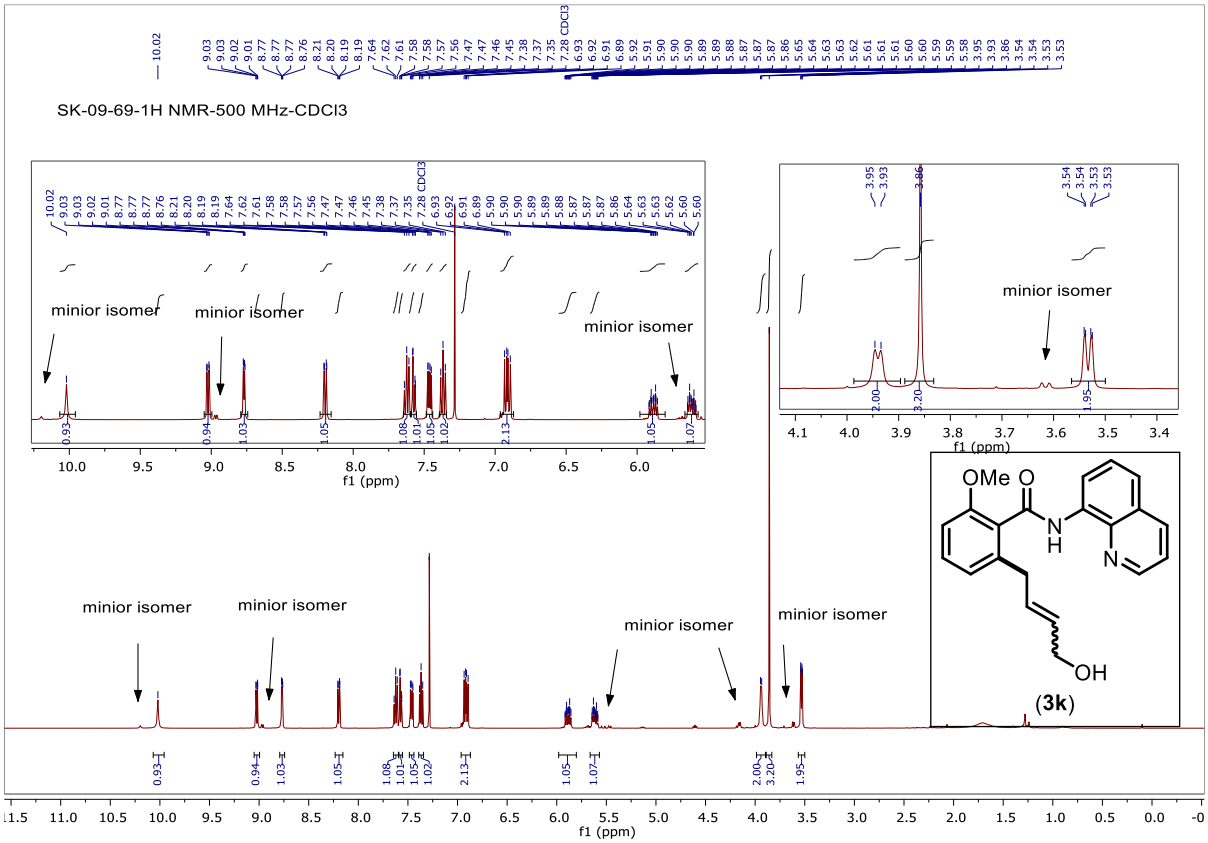
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

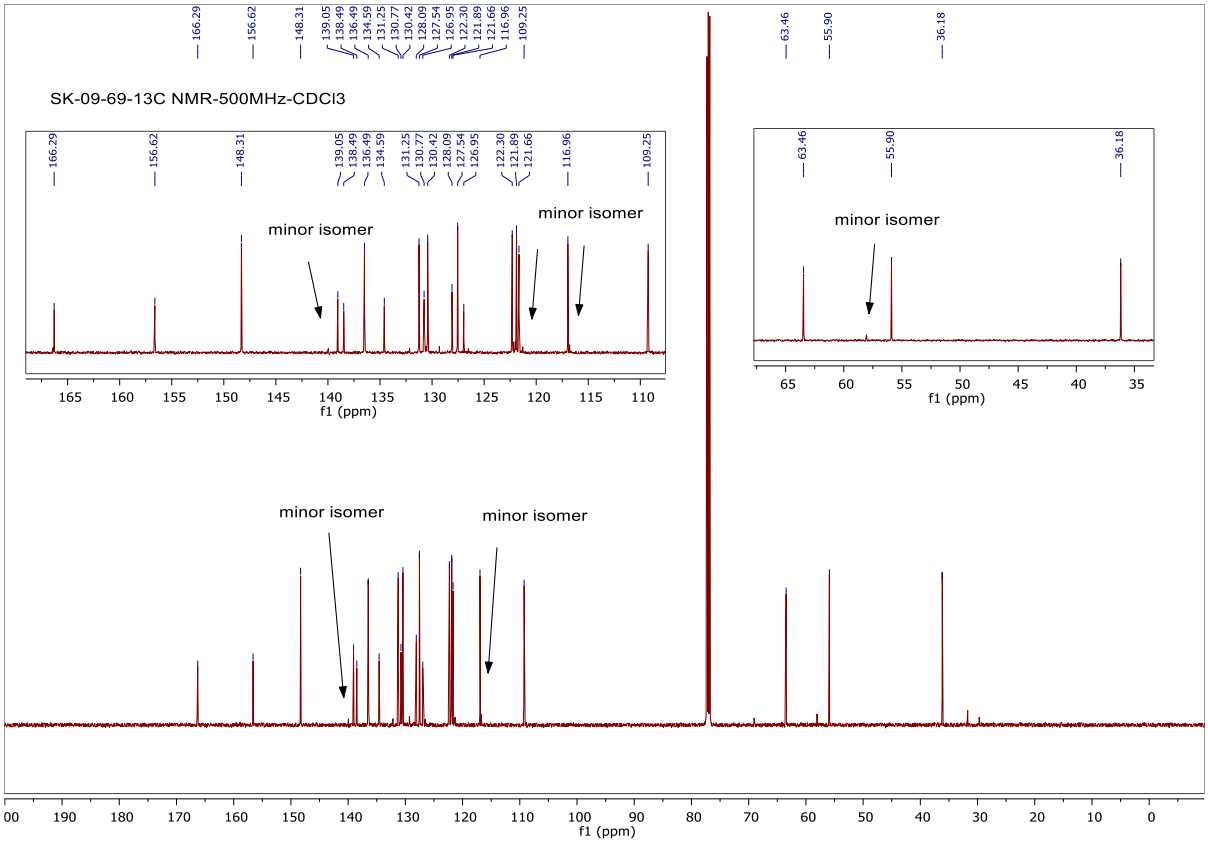






Bruker Compass DataAnalysis 4.0 printed: 13-12-2023 16:12:59 Page 1 of 1


SK-09-69-1H NMR-500 MHz-CDCl3
minior isomer
minior isomer
minior isomer
minior isomer
minior isomer
minior isomer
minior isomer
OMe O
N
H
N
OH
(3k)
f1 (ppm)


SK-09-69-13C NMR-500MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)

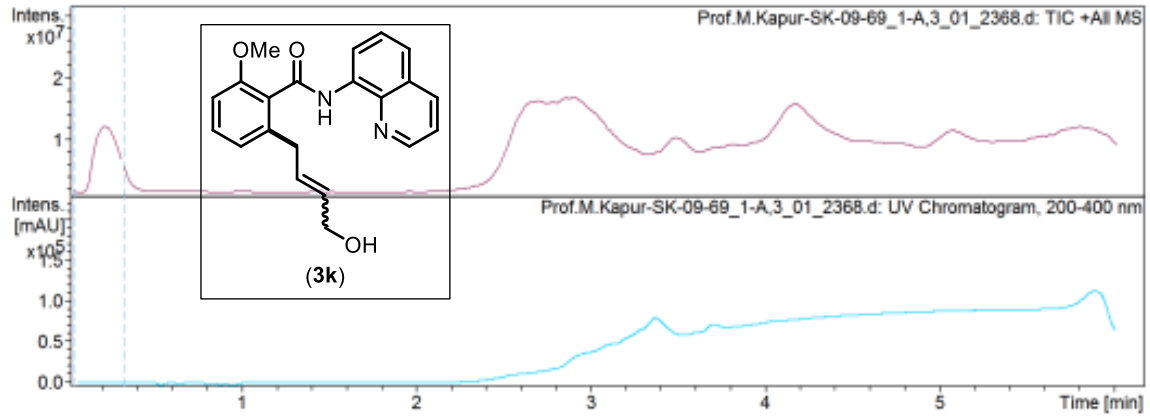
Display Report

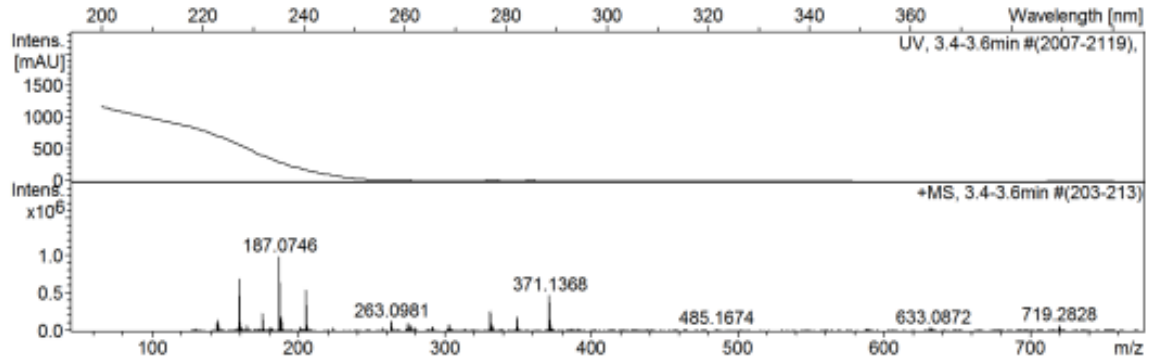
Analysis Info

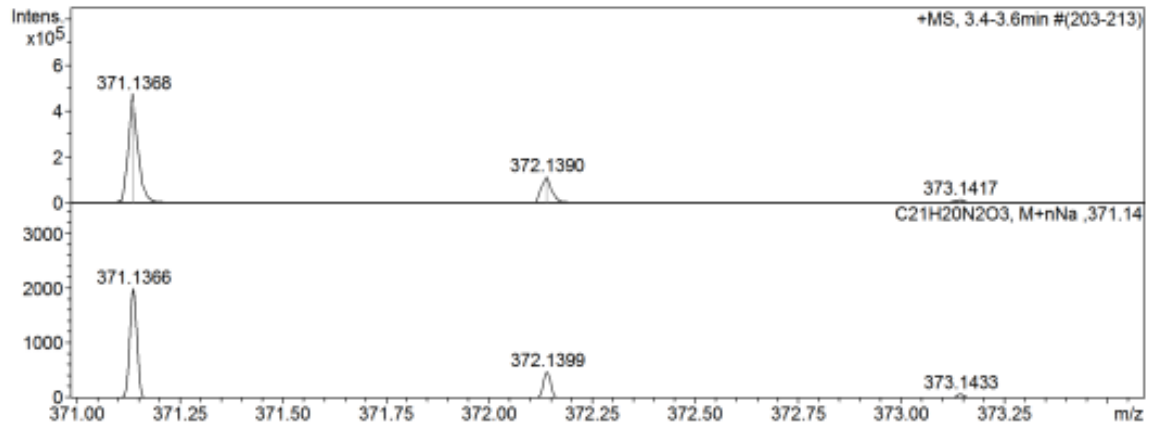
Acquisition Date	14-07-2023 11:57:52		
Analysis Name	D:\Data\USER DATA 2023\July\14-July\Prof.M.Kapur-SK-09-69_1-A,3_01_2368.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-69	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

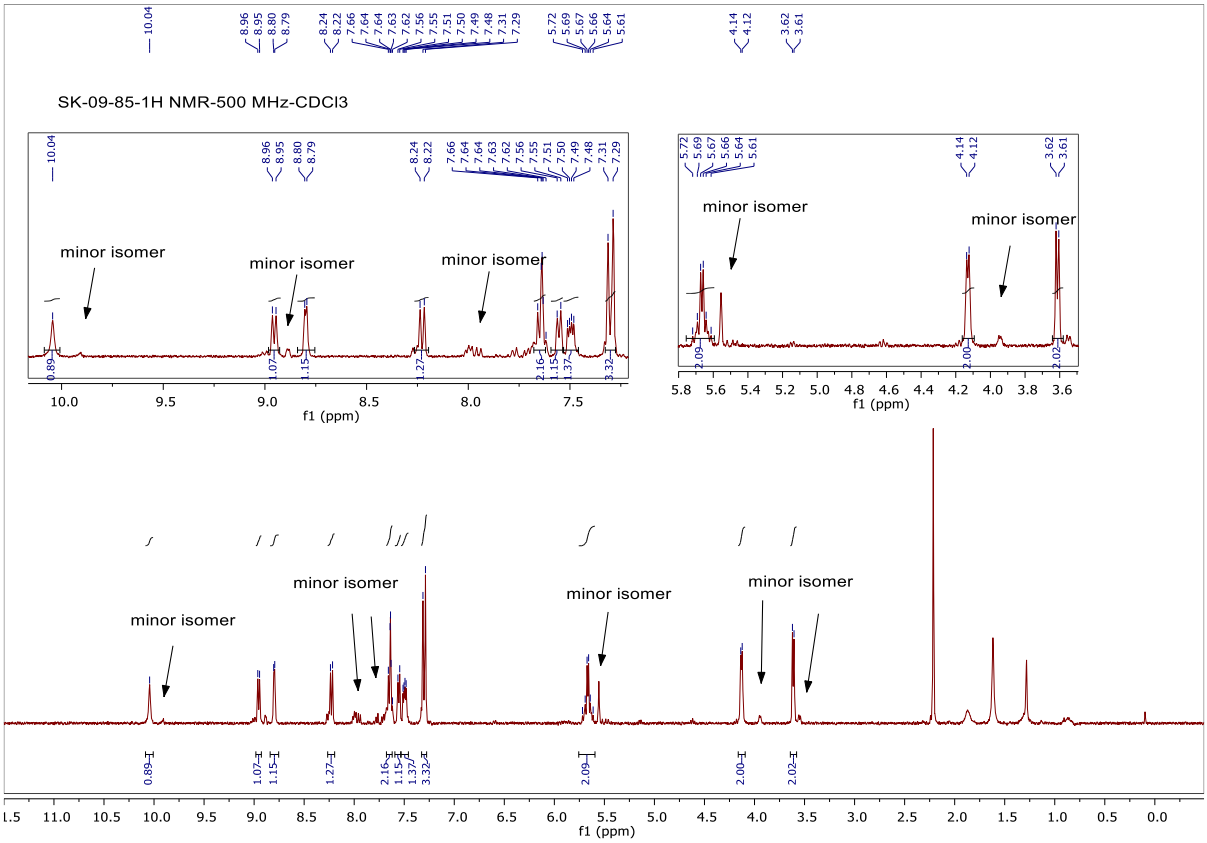
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

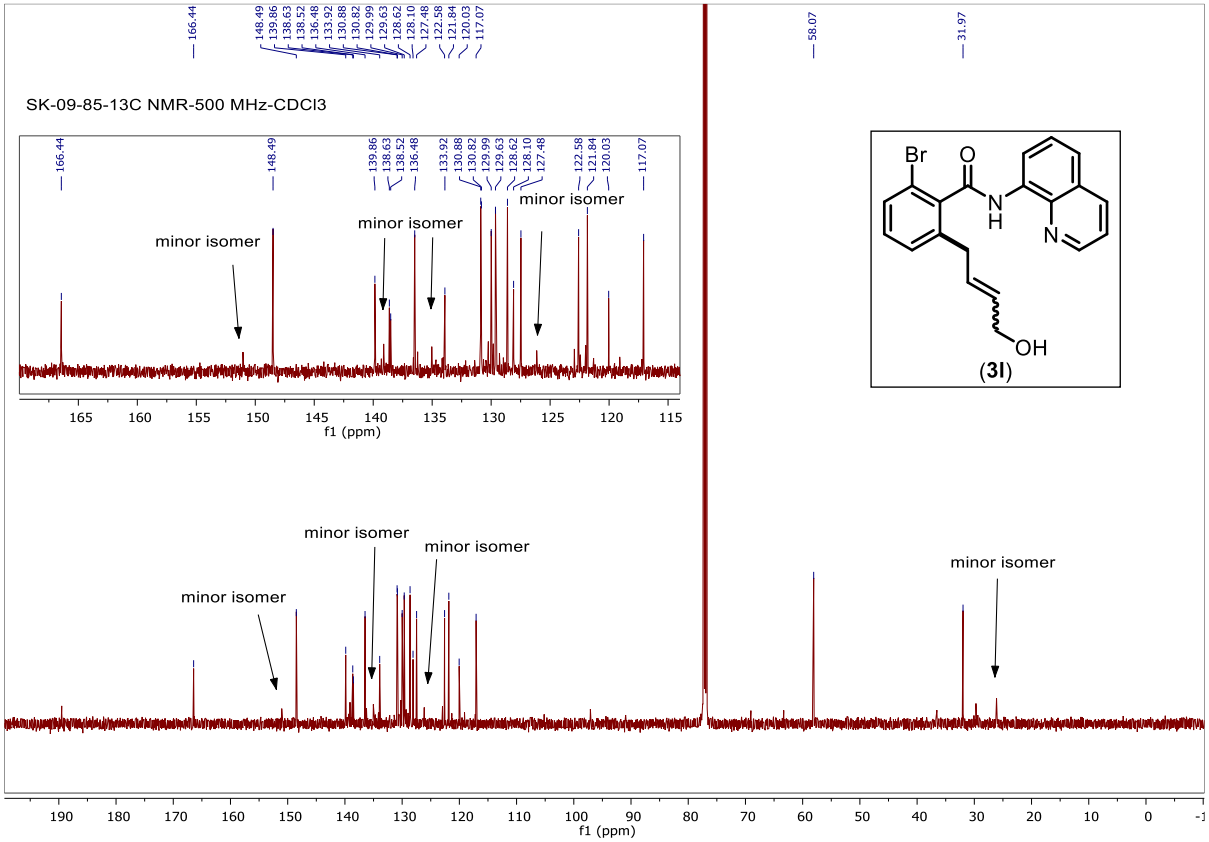






Bruker Compass DataAnalysis 4.0 printed: 14-07-2023 12:20:00 Page 1 of 1


SK-09-85-1H NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)


SK-09-85-13C NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)
Br
O
N
H
N
OH
(3l)

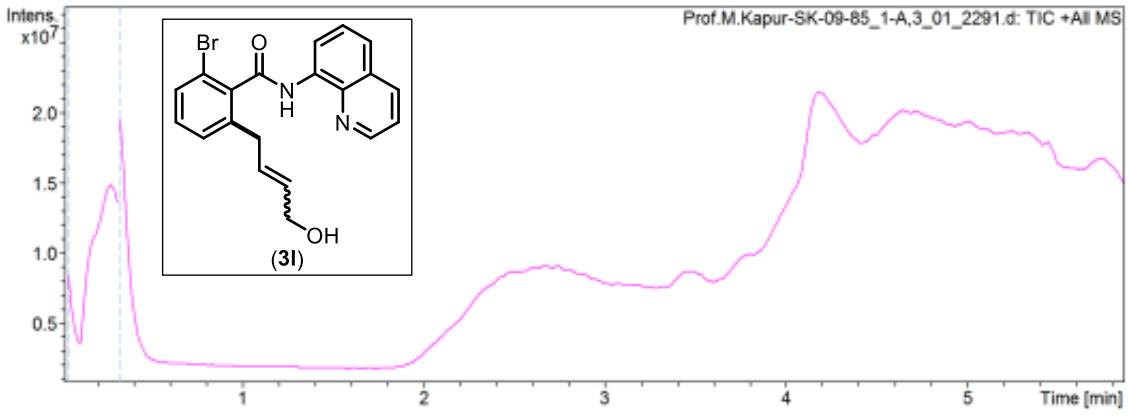
Display Report

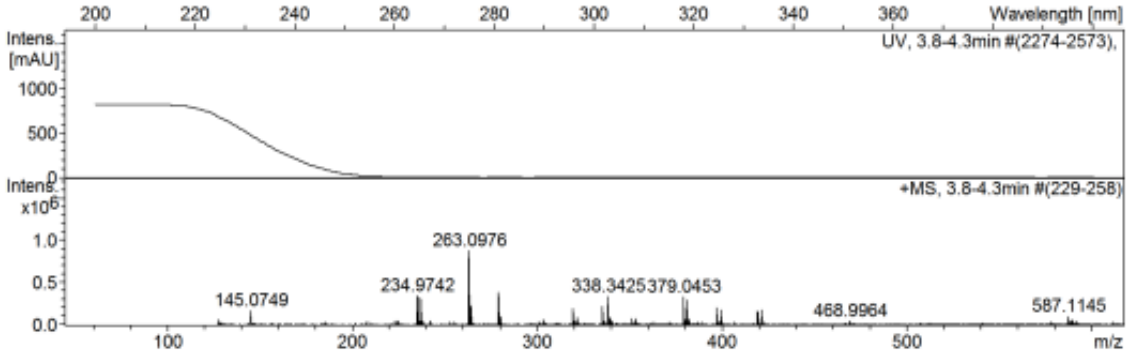
Analysis Info

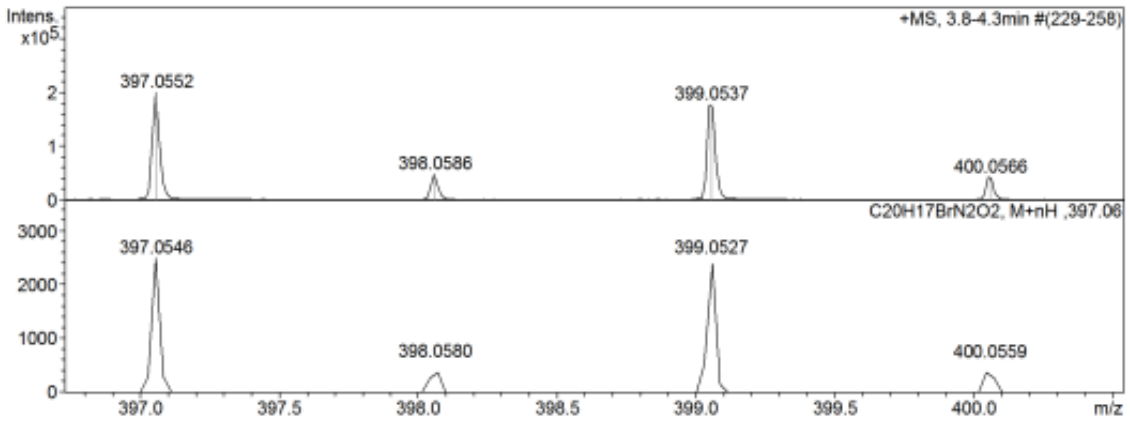
Acquisition Date	10-07-2023 10:23:58		
Analysis Name	D:\Data\USER DATA 2023\July\10-july\Prof.M.Kapur-SK-09-85_1-A,3_01_2291.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-85	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

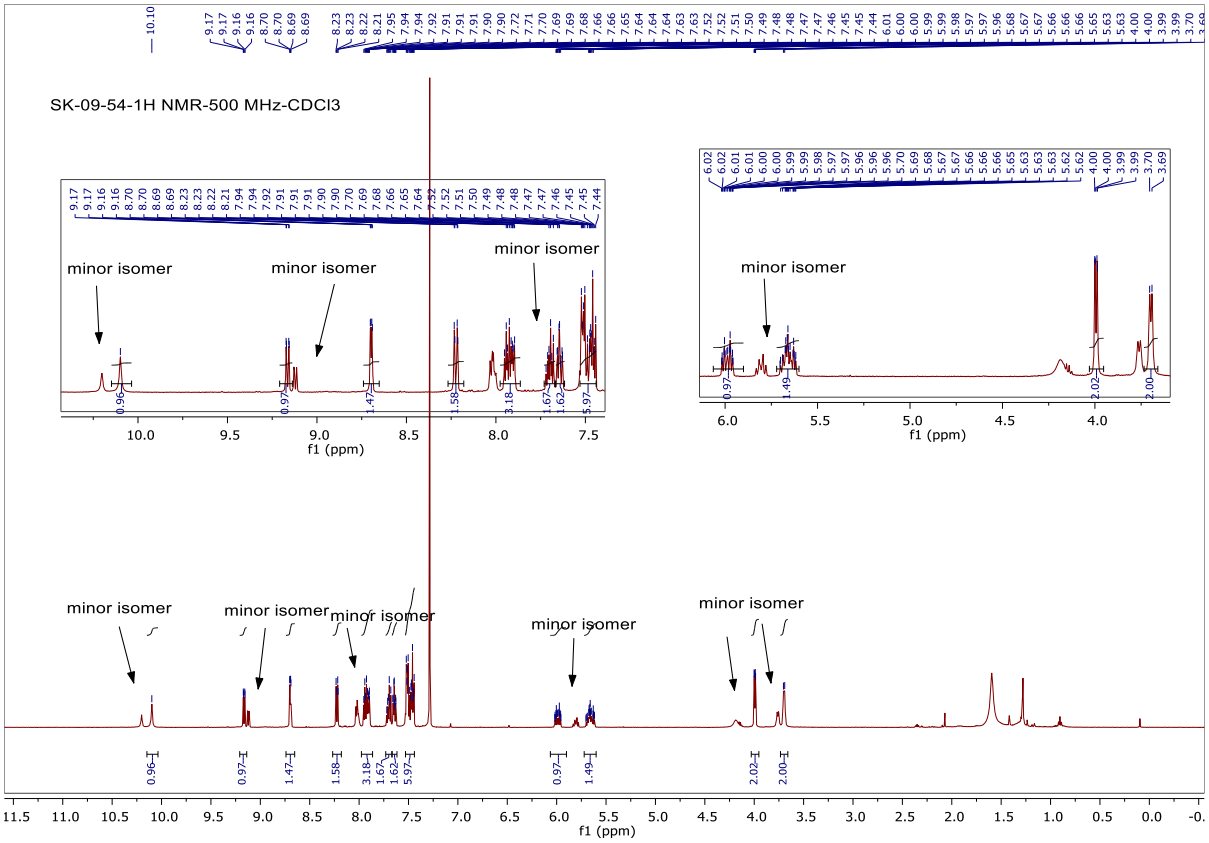
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

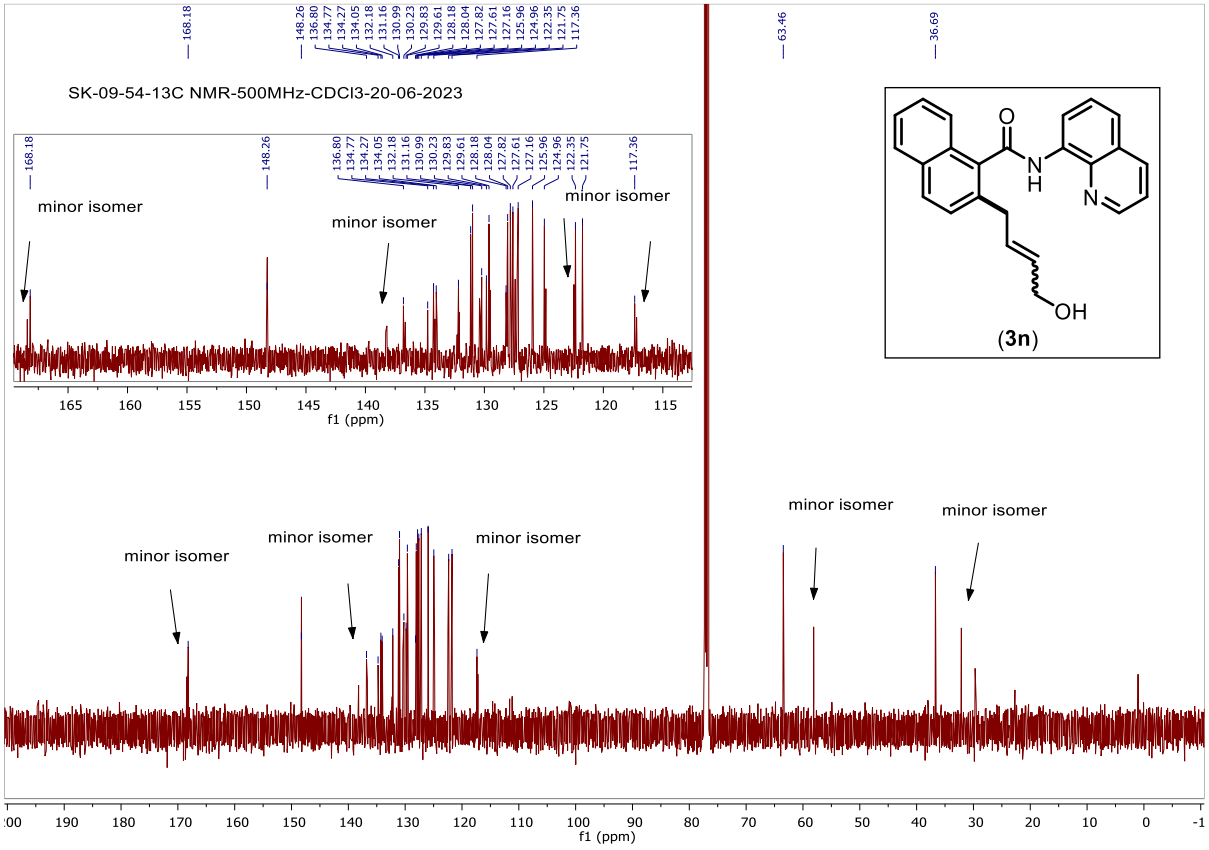






Bruker Compass DataAnalysis 4.0 printed: 10-07-2023 10:47:36 Page 1 of 1


SK-09-54-1H NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)


SK-09-54-13C NMR-500MHz-CDCl3-20-06-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)
O
N
H
N
OH
(3n)

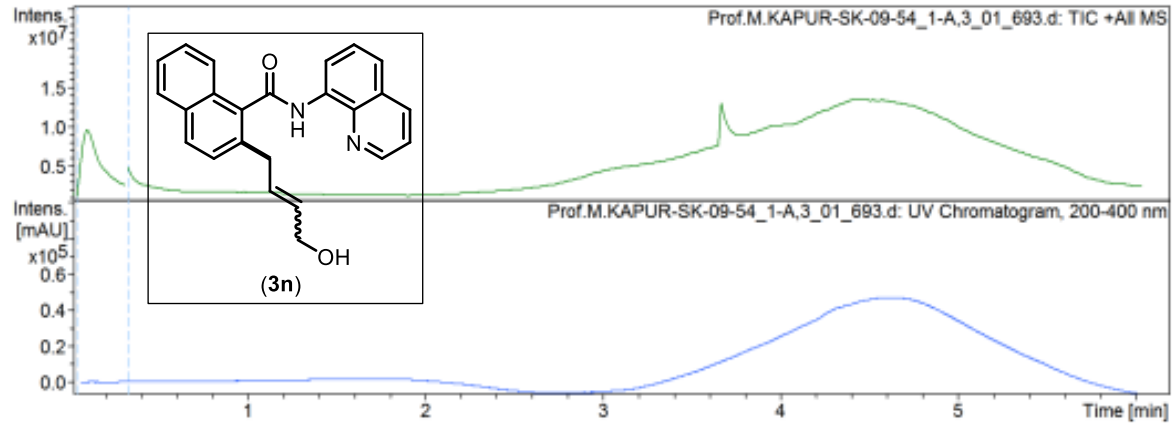
Display Report

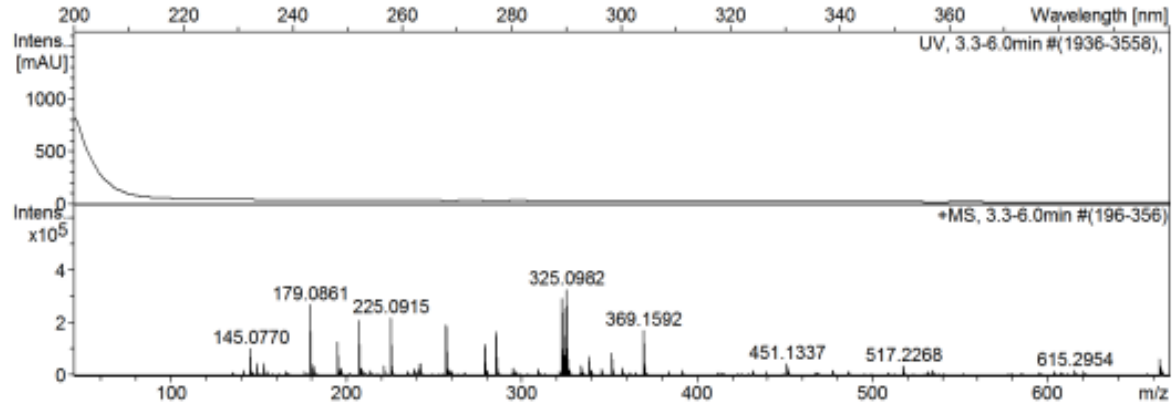
Analysis Info

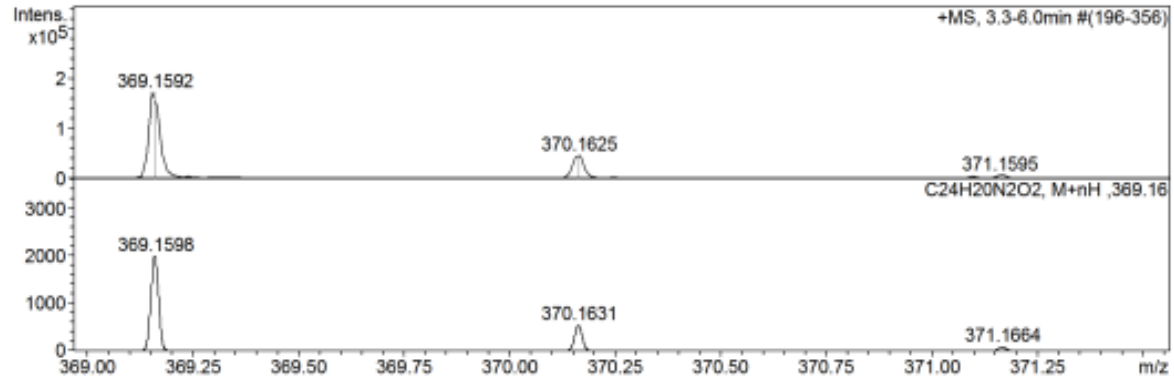
Acquisition Date	12-04-2023 12:15:26		
Analysis Name	D:\Data\USER DATA 2023\April\12-apri\Prof.M.KAPUR-SK-09-54_1-A,3_01_693.d		
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Prof.M.KAPUR-SK-09-54	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

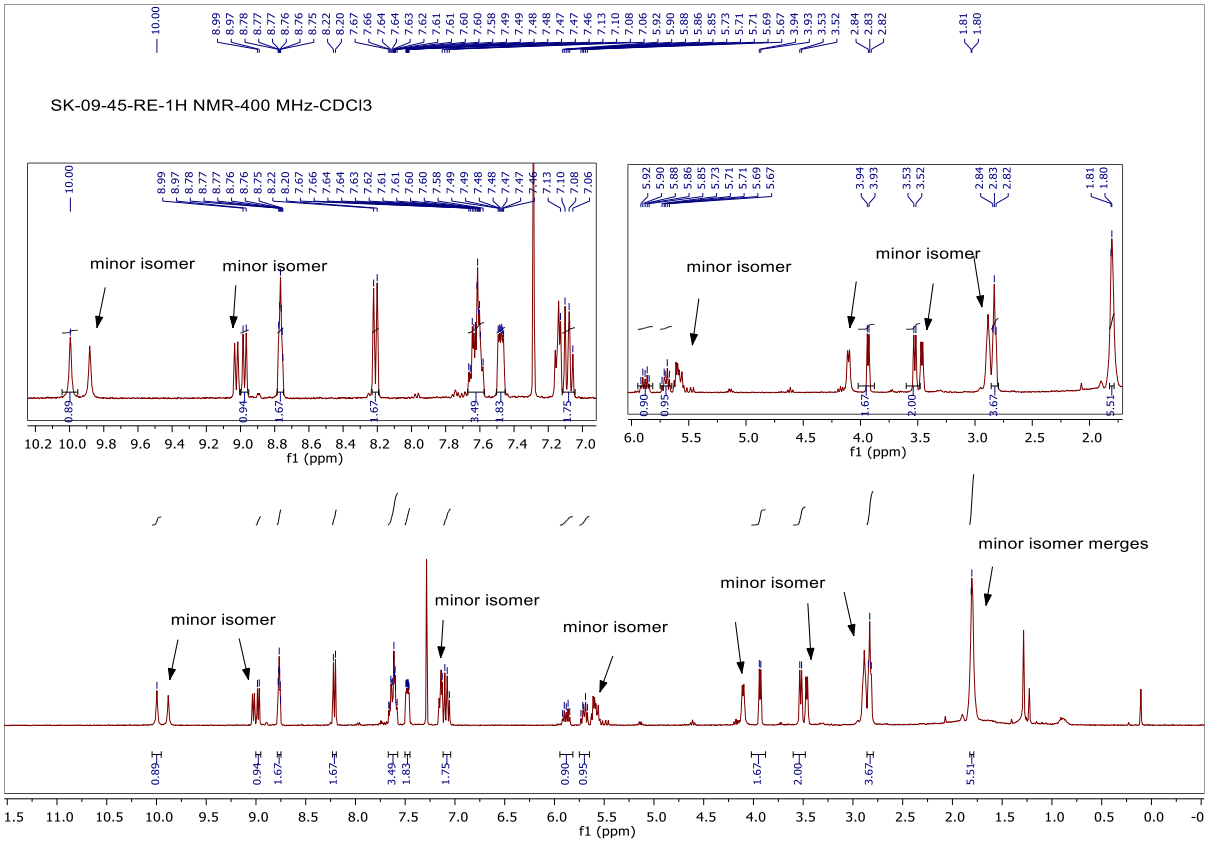
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

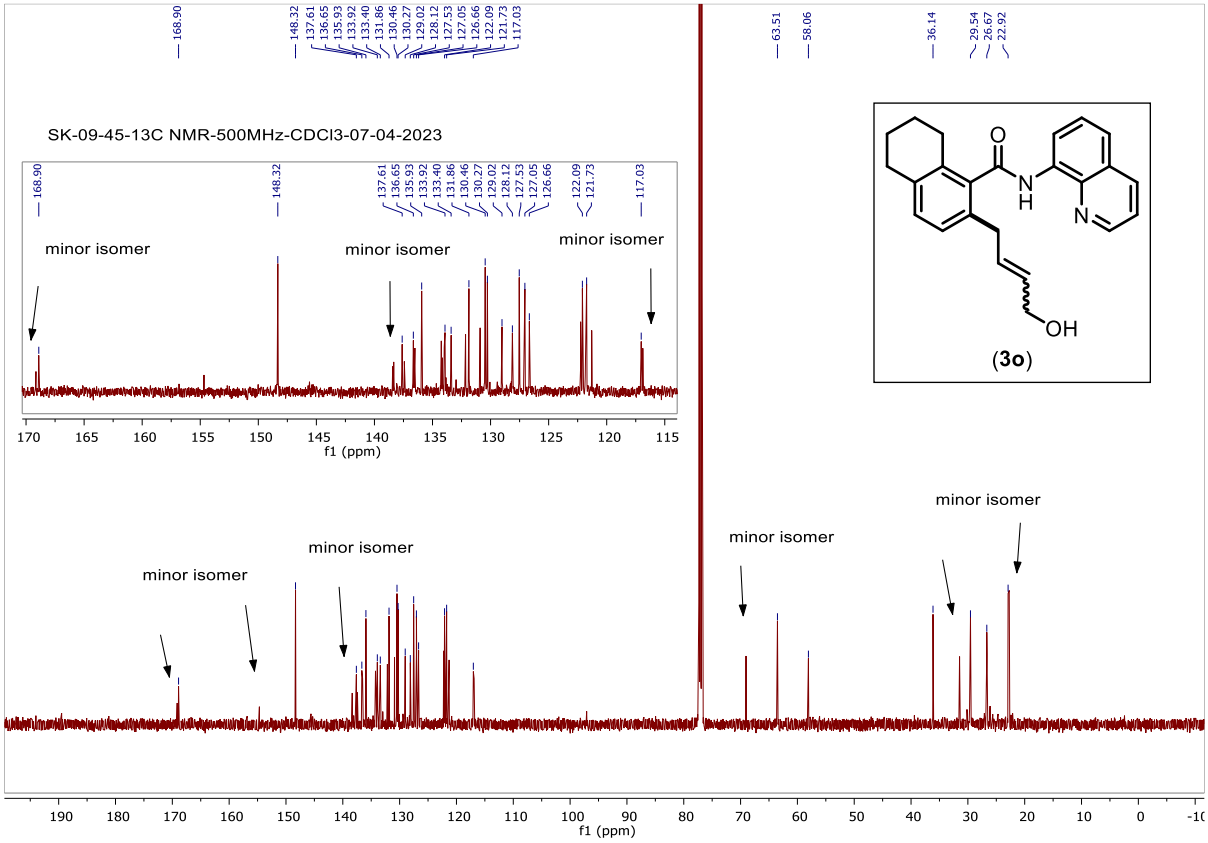






Bruker Compass DataAnalysis 4.0 printed: 12-04-2023 13:00:20 Page 1 of 1


SK-09-45-RE-1H NMR-400 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer merges
f1 (ppm)


SK-09-45-13C NMR-500MHz-CDCl3-07-04-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
O
N
H
N
OH
(3o)
f1 (ppm)

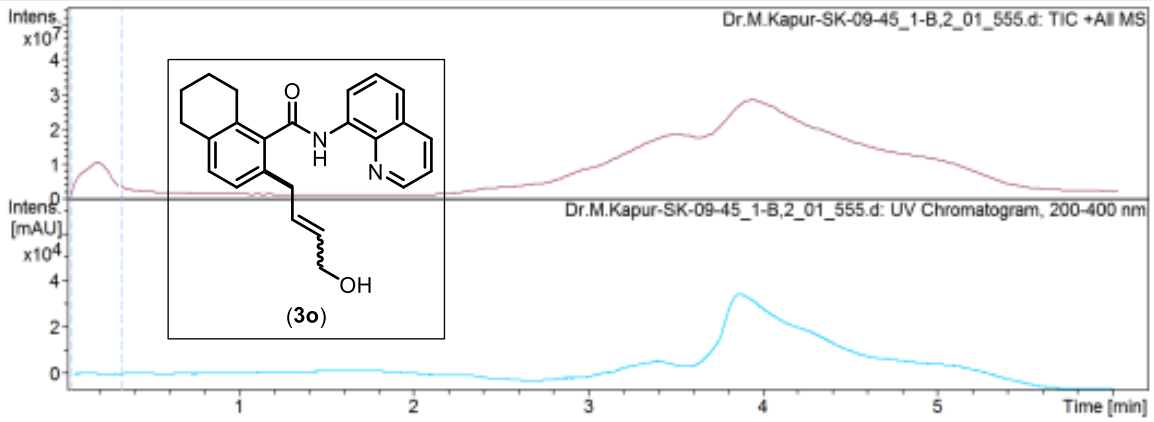
Display Report

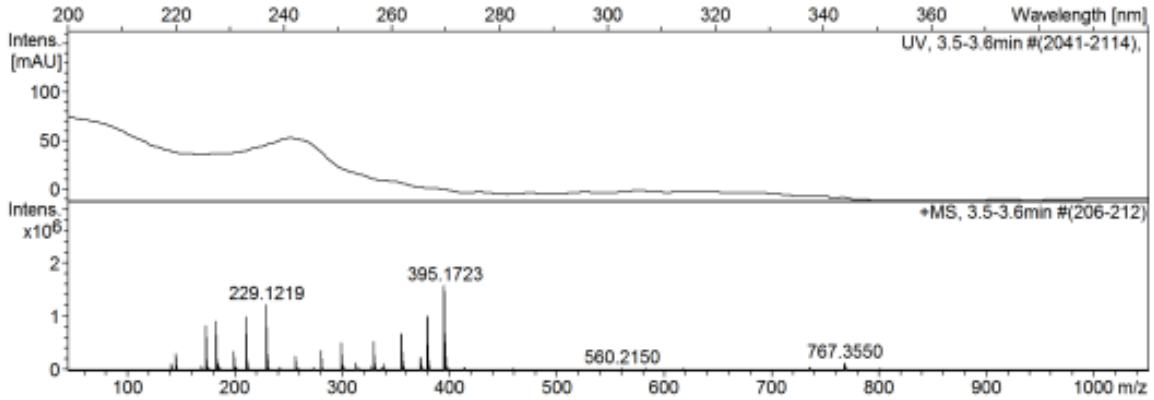
Analysis Info

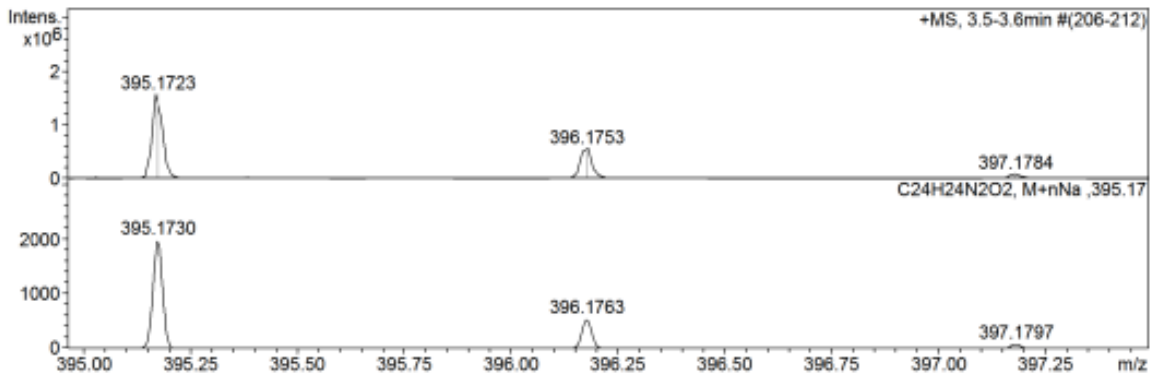
Acquisition Date	05-04-2023 12:57:39		
Analysis Name	D:\Data\USER DATA 2023\April\05-april\Dr.M.Kapur-SK-09-45_1-B,2_01_555.d		
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Dr.M.Kapur-SK-09-45	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

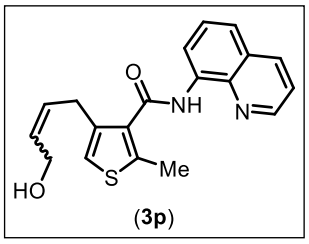
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



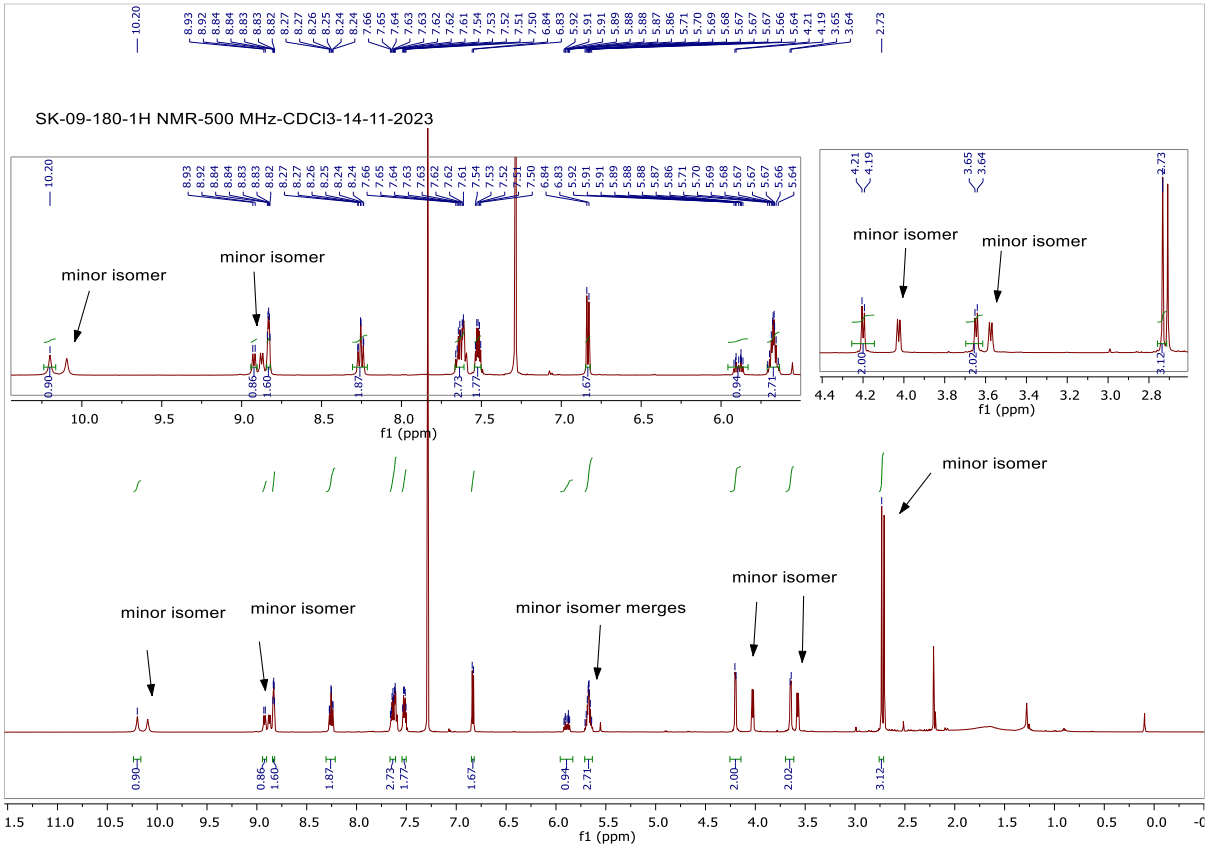


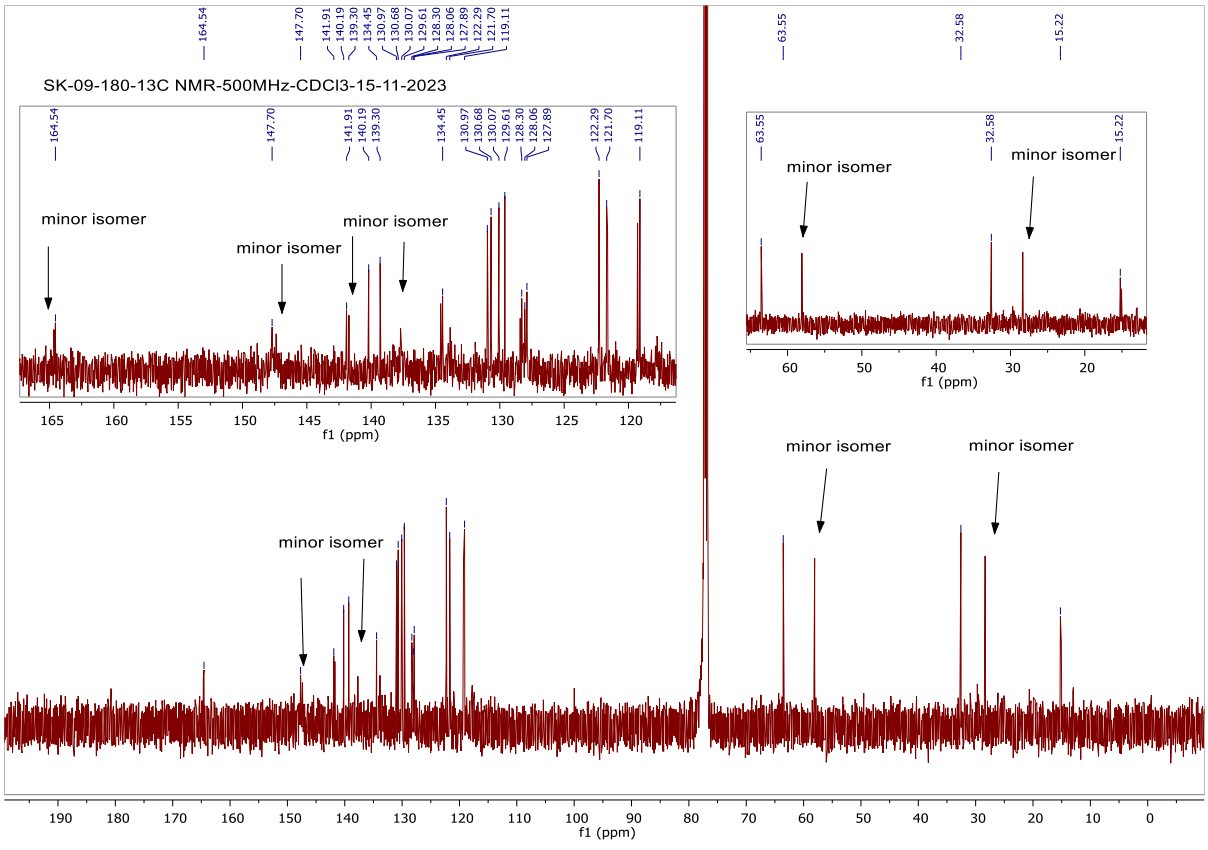


Bruker Compass DataAnalysis 4.0 printed: 05-04-2023 13:05:01 Page 1 of 1


O
NH
N
Me
S
HO

(**3p**)


SK-09-180-1H NMR-500 MHz-CDCl3-14-11-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer merges
minor isomer
minor isomer
f1 (ppm)


SK-09-180-13C NMR-500MHz-CDCl3-15-11-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)

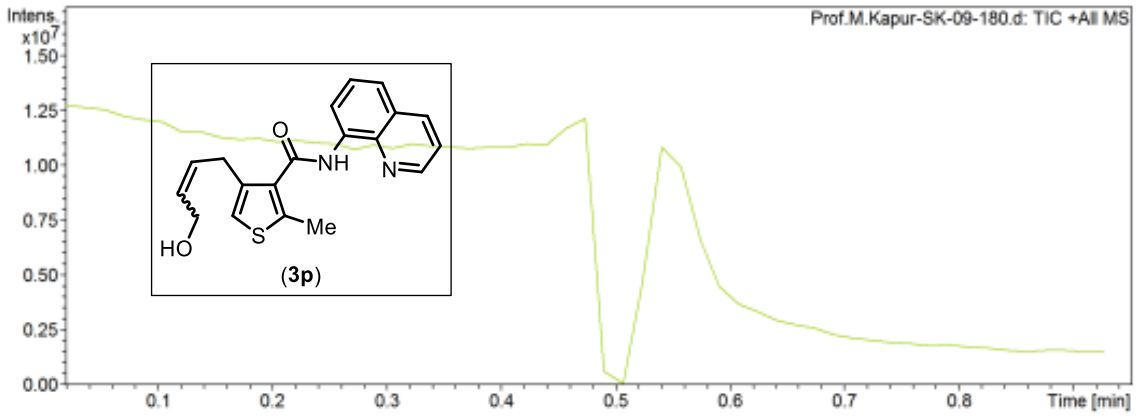
Display Report

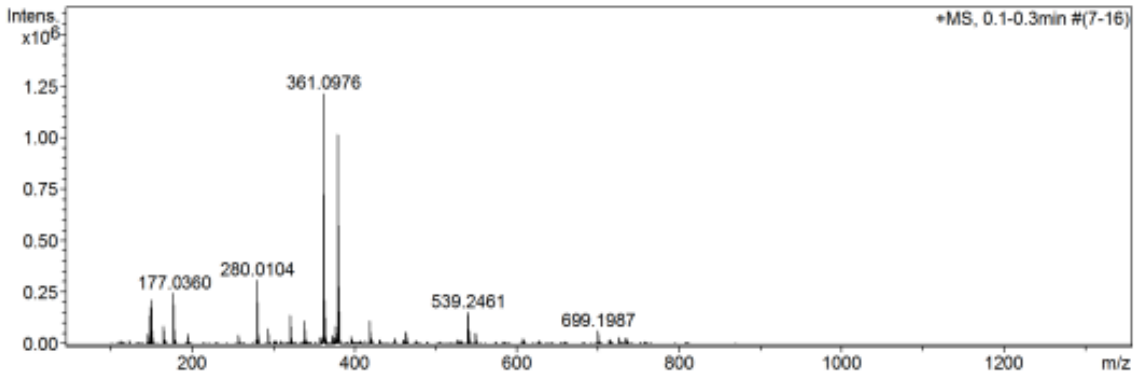
Analysis Info

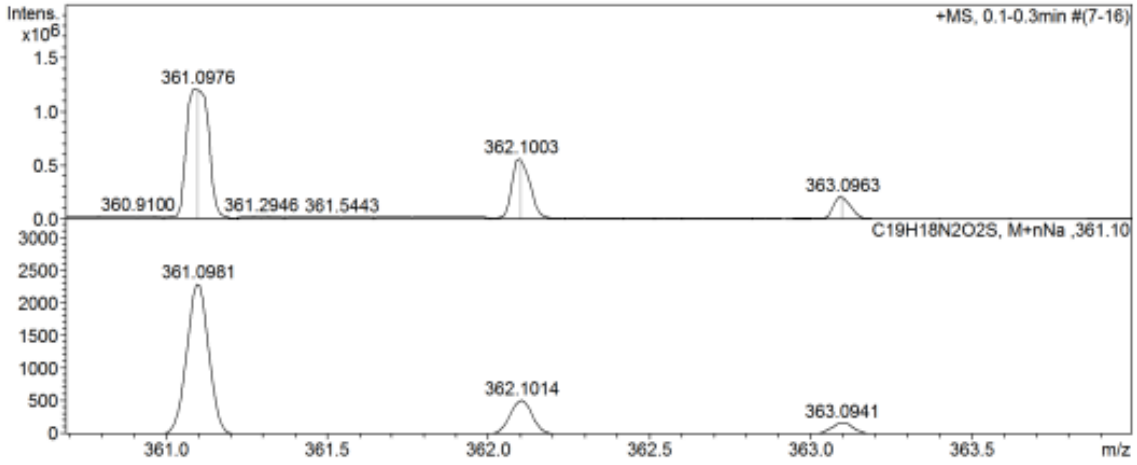
Analysis Name	D:\Data\USER DATA 2023\Nov23\03-nov\Prof.M.Kapur-SK-09-180.d	Acquisition Date	03-11-2023 16:55:14
Method	tune_low_APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-180	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

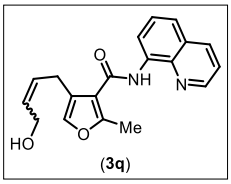
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste





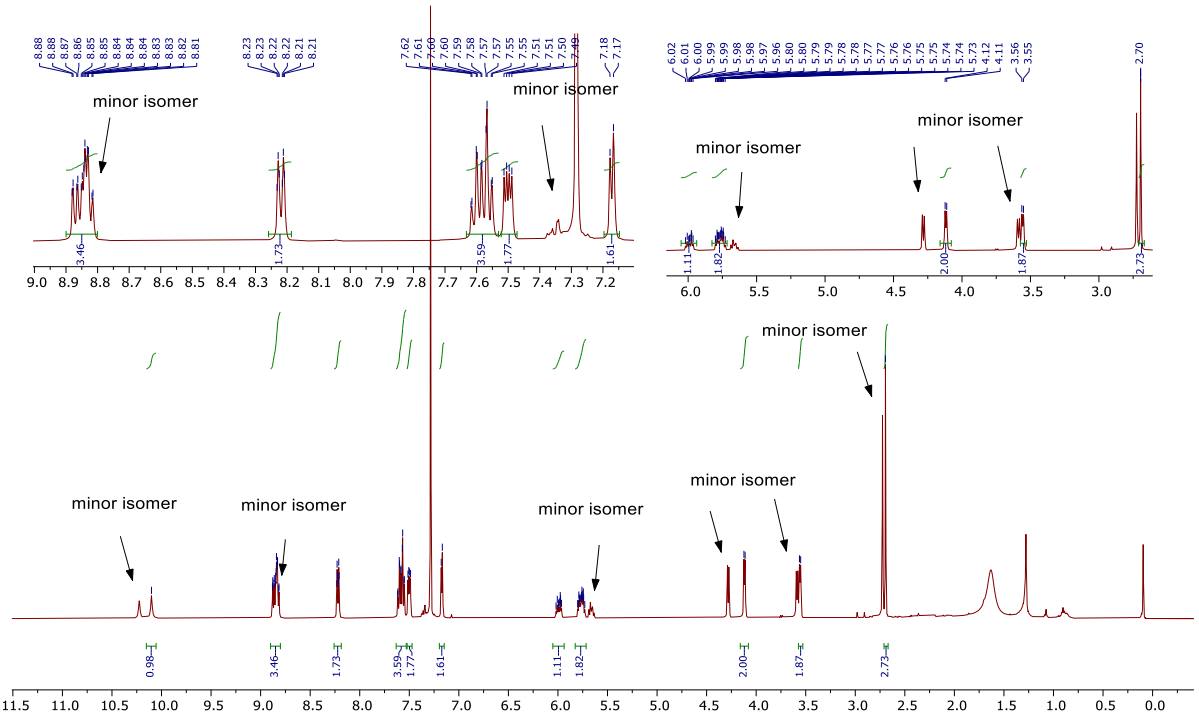


Bruker Compass DataAnalysis 4.0 printed: 03-11-2023 16:59:36 Page 1 of 1

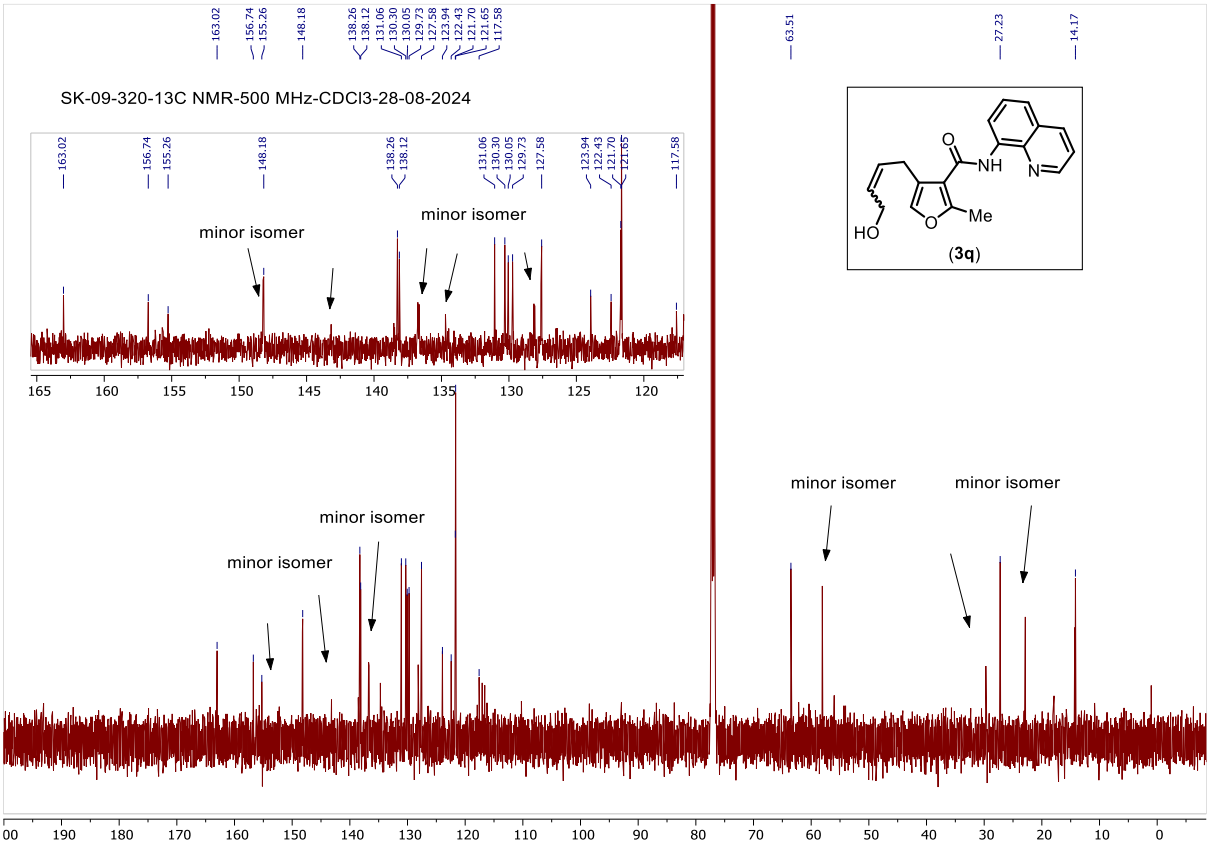


(**3q**)

SK-09-320-1H NMR-500 MHz-CDCl3-28-08-2024



SK-09-320-13C NMR-500 MHz-CDCl3-28-08-2024



(**3q**)

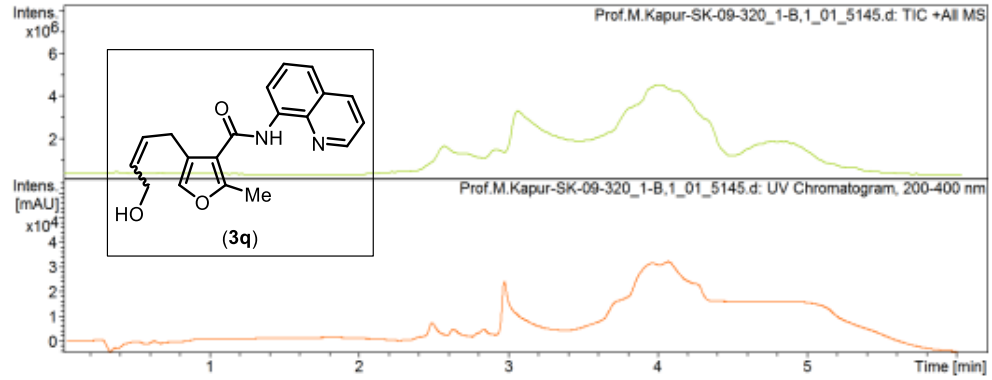
Display Report

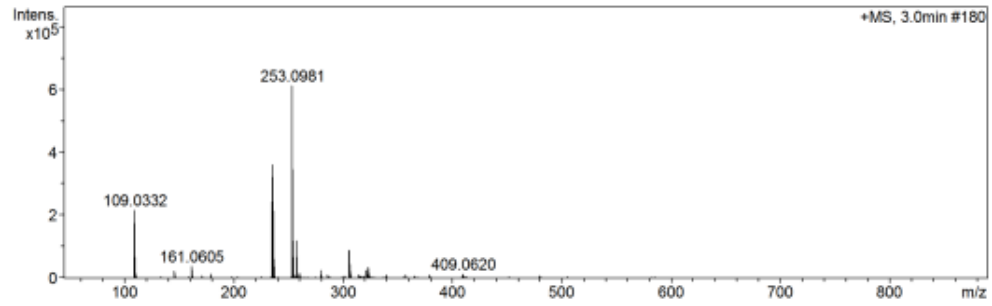
Analysis Info

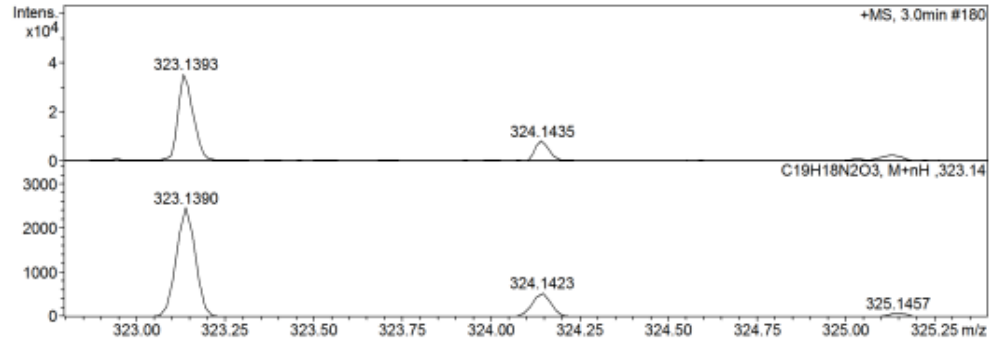
Analysis Name	D:\Data\USER DATA 2024\Aug-2024\27-Aug\Prof.M.Kapur-SK-09-320_1-B,1_01_5145.d	Acquisition Date	27-08-2024 13:29:16
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-320	Instrument	micrOTOF-Q 10330
Comment			

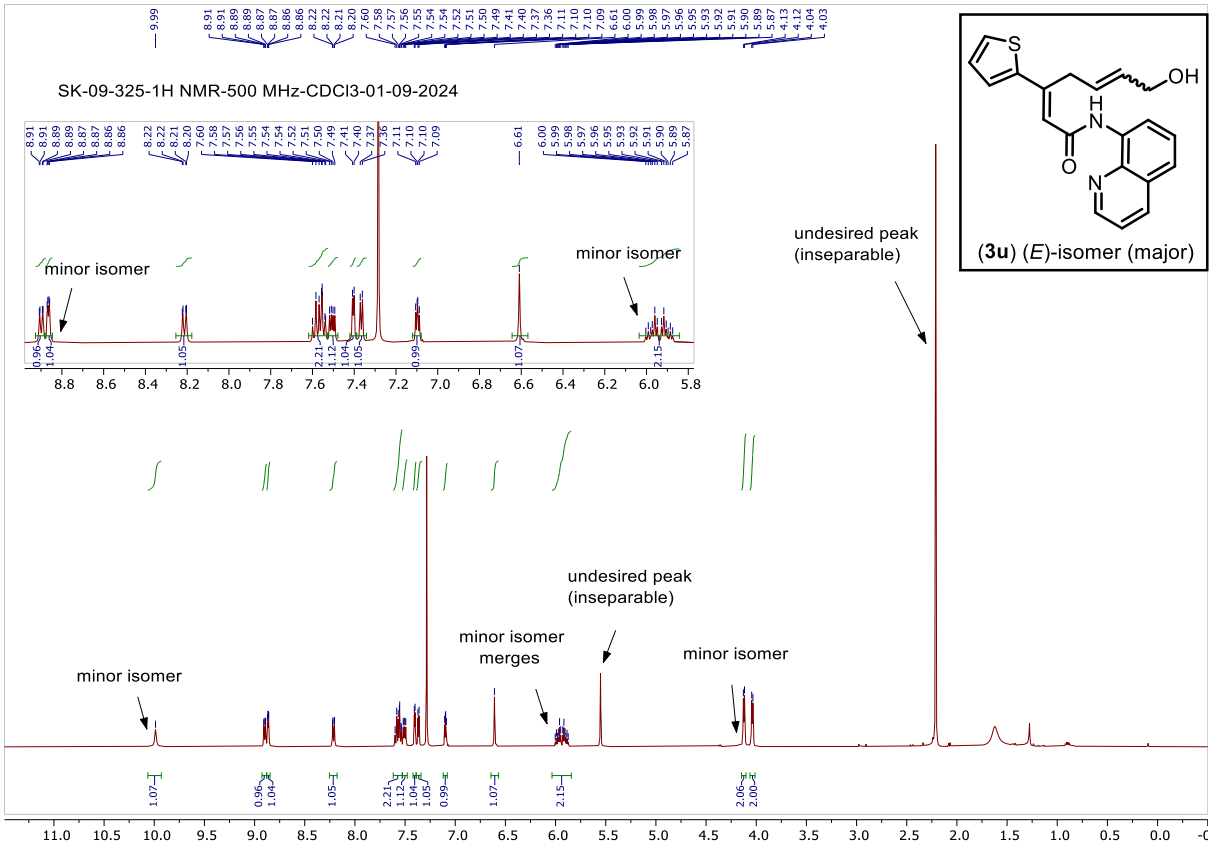
Acquisition Parameter

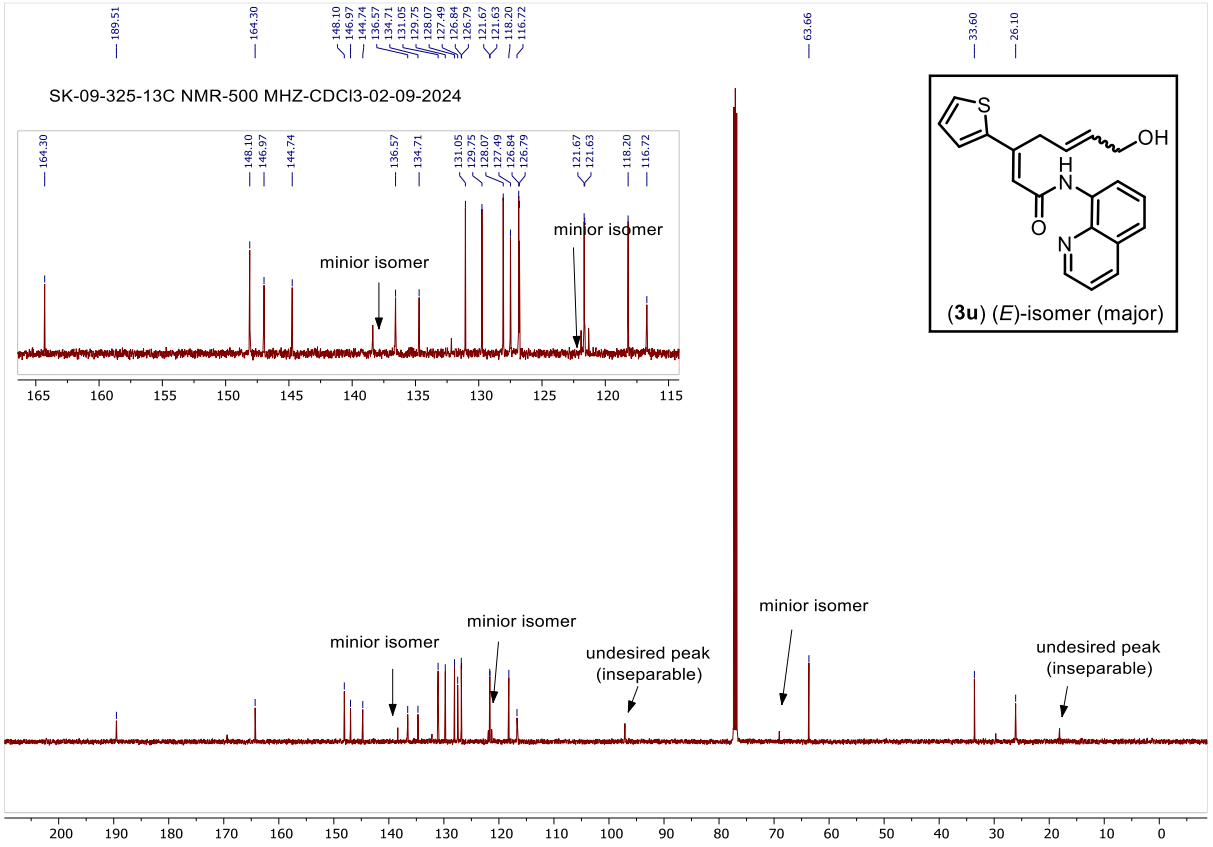
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	40.6 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	10.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste








SK-09-325-1H NMR-500 MHz-CDCl3-01-09-2024
minor isomer
minor isomer
undesired peak
(inseparable)
undesired peak
(inseparable)
minor isomer
merges
minor isomer
minor isomer
(3u) (E)-isomer (major)


SK-09-325-13C NMR-500 MHZ-CDCl3-02-09-2024
minior isomer
minior isomer
minior isomer
minior isomer
minior isomer
undesired peak
(inseparable)
undesired peak
(inseparable)
(3u) (E)-isomer (major)

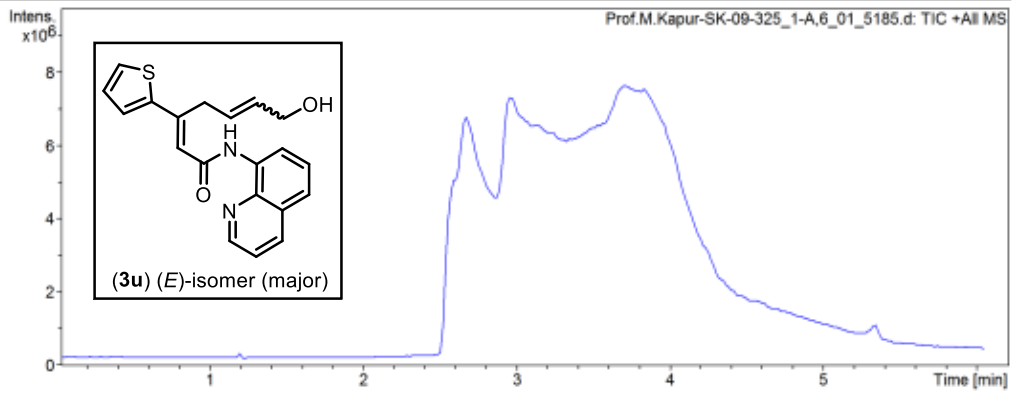
Display Report

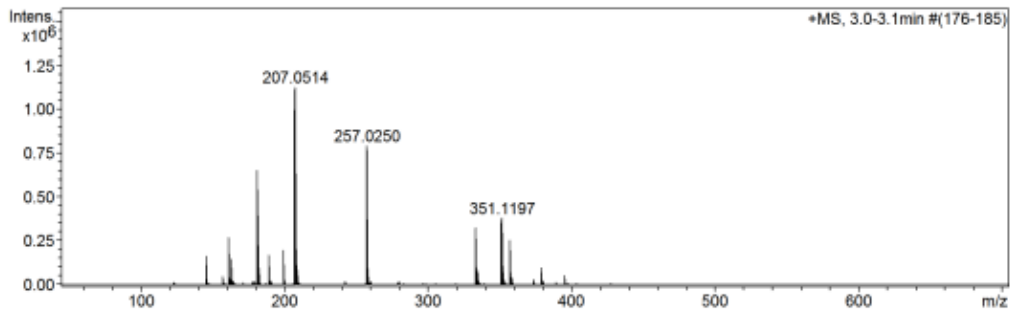
Analysis Info

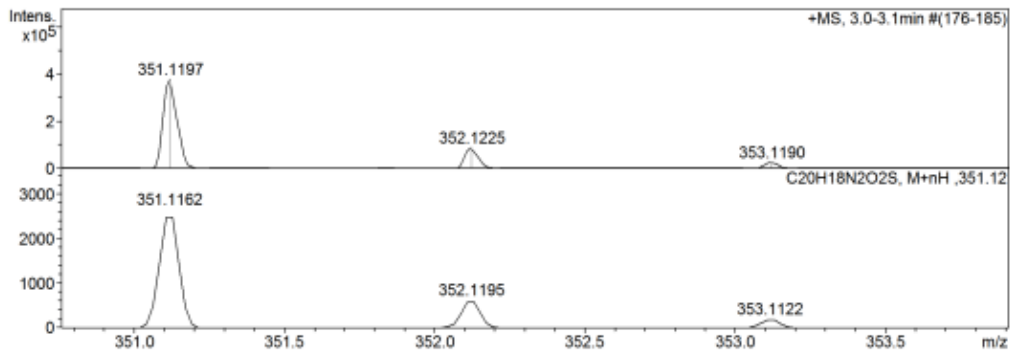
Acquisition Date	30-08-2024 12:06:46		
Analysis Name	D:\Data\USER DATA 2024\Aug-2024\30-aug\Prof.M.Kapur-SK-09-325_1-A,6_01_5185.d		
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-325	Instrument	micrOTOF-Q 10330
Comment			

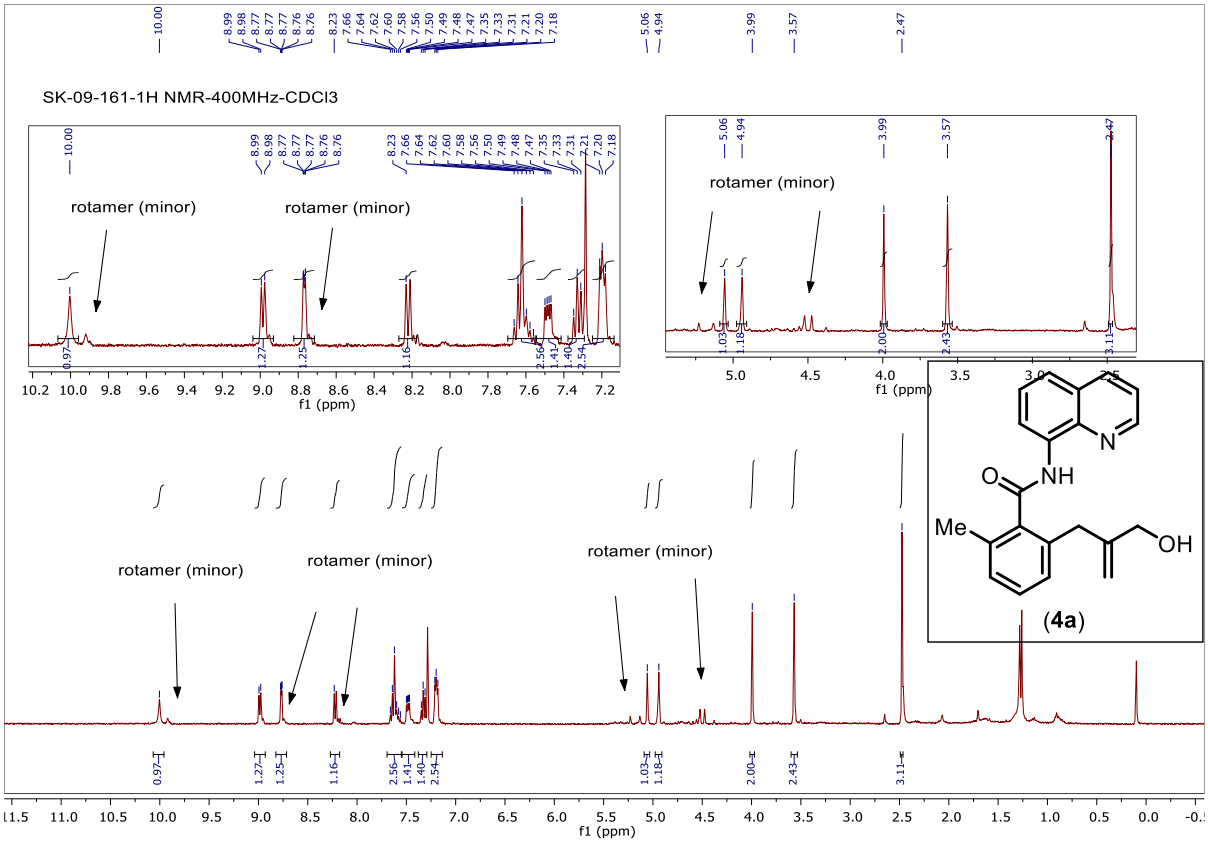
Acquisition Parameter

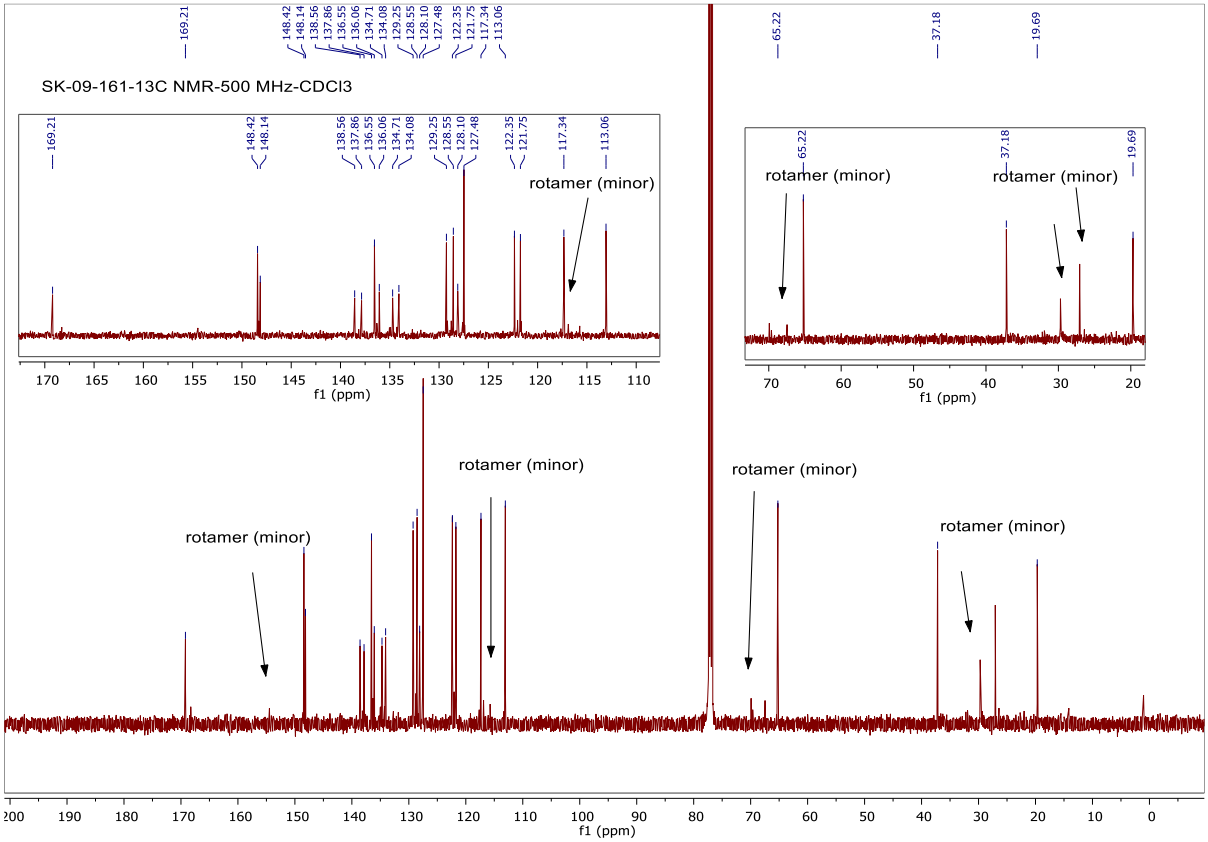
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	40.6 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	10.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste








SK-09-161-1H NMR-400MHz-CDCl3
rotamer (minor)
rotamer (minor)
rotamer (minor)
rotamer (minor)
rotamer (minor)
NH
O
N
Me
OH
(4a)
f1 (ppm)


SK-09-161-13C NMR-500 MHz-CDCl3
rotamer (minor)
rotamer (minor)
rotamer (minor)
rotamer (minor)
rotamer (minor)
rotamer (minor)
f1 (ppm)

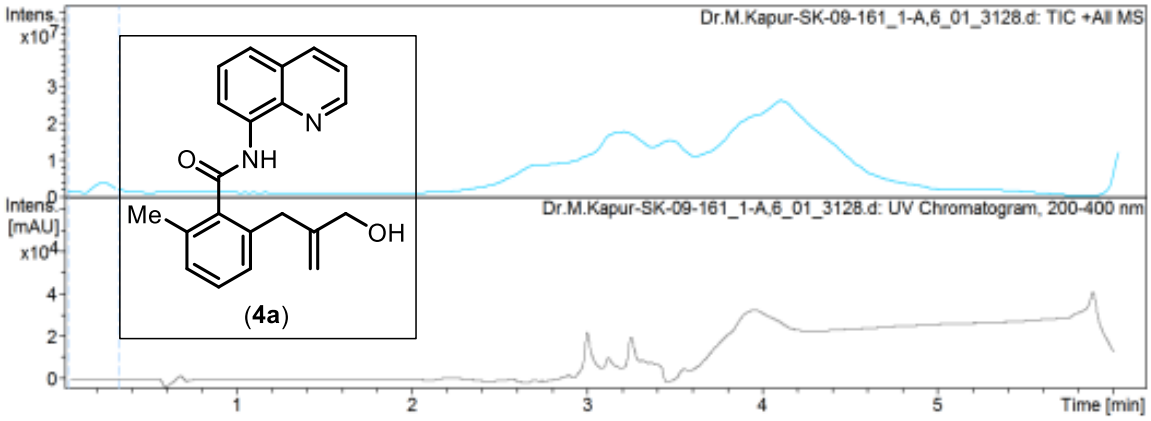
Display Report

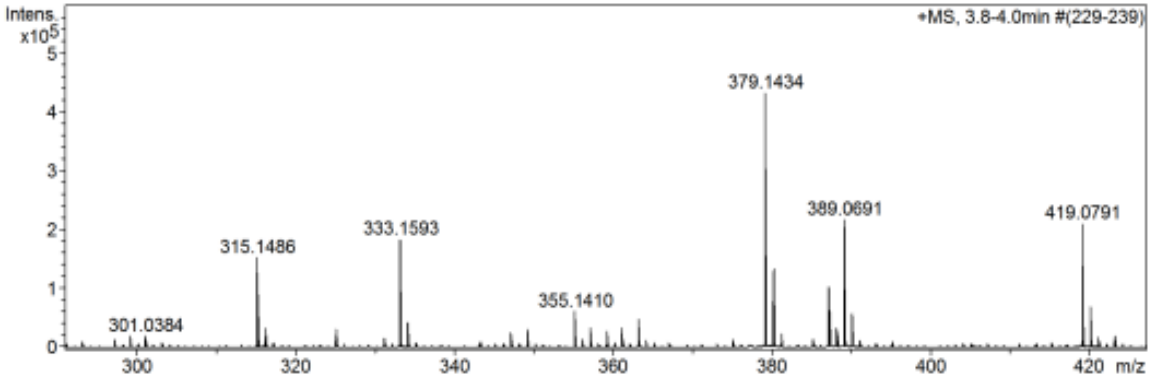
Analysis Info

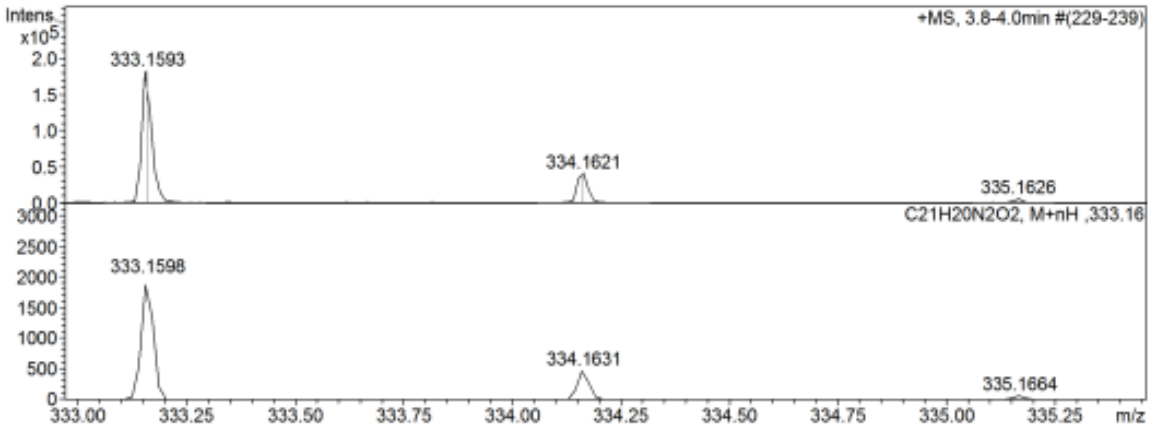
Acquisition Date	27-09-2023 11:00:29		
Analysis Name	D:\Data\USER DATA 2023\sep 23\27-sep\Dr.M.Kapur-SK-09-161_1-A,6_01_3128.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Dr.M.Kapur-SK-09-161	Instrument	micrOTOF-Q 10330
Comment			

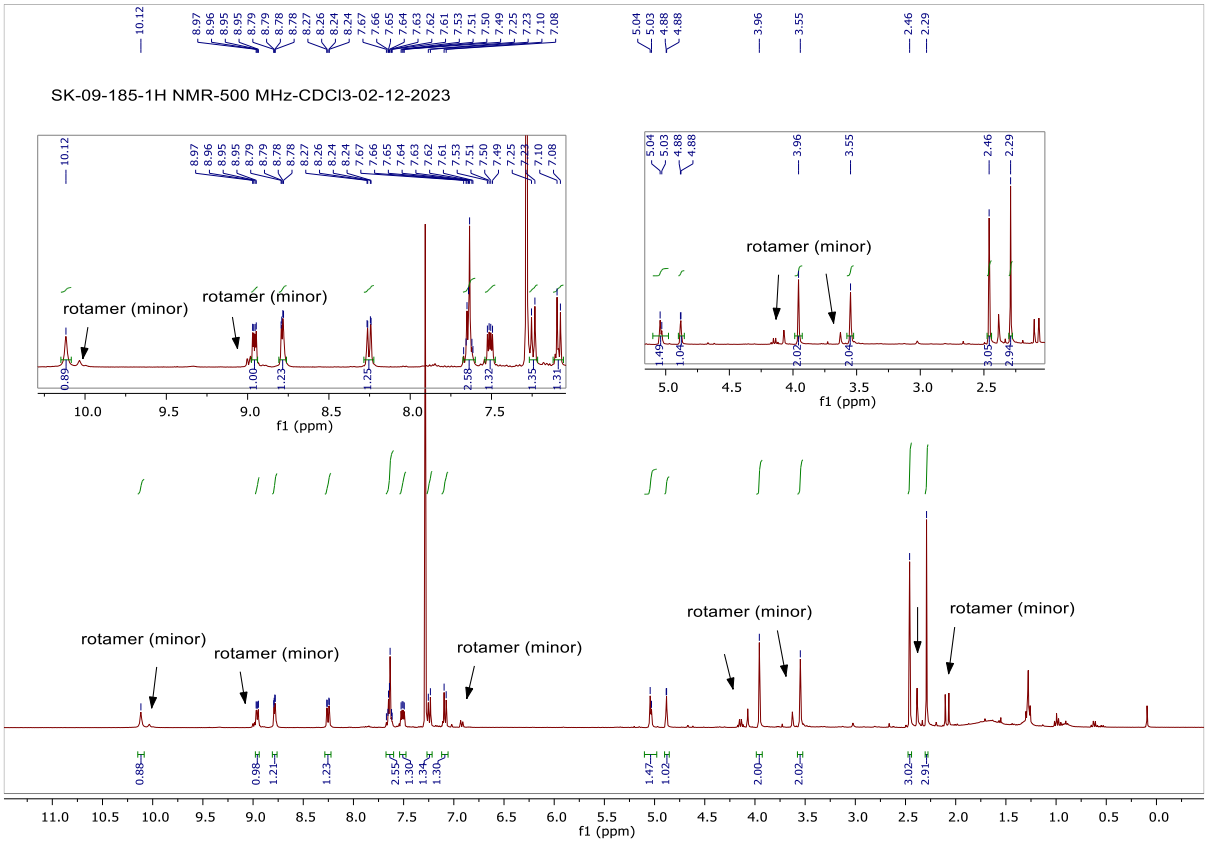
Acquisition Parameter

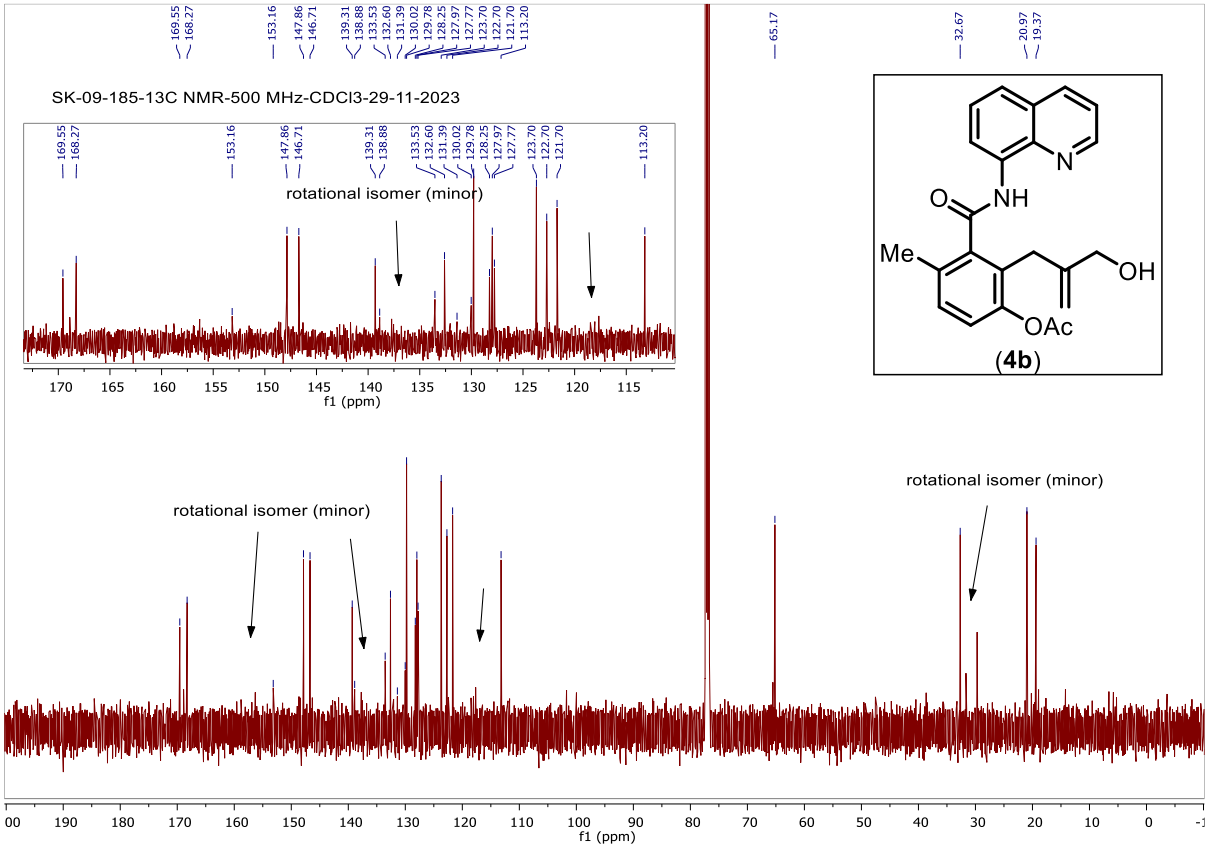
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








SK-09-185-1H NMR-500 MHz-CDCl3-02-12-2023
rotamer (minor)
rotamer (minor)
rotamer (minor)
rotamer (minor)
rotamer (minor)
rotamer (minor)
rotamer (minor)
f1 (ppm)


SK-09-185-13C NMR-500 MHz-CDCl3-29-11-2023
rotational isomer (minor)
rotational isomer (minor)
rotational isomer (minor)
N
O
NH
Me
OH
OAc
(4b)
f1 (ppm)

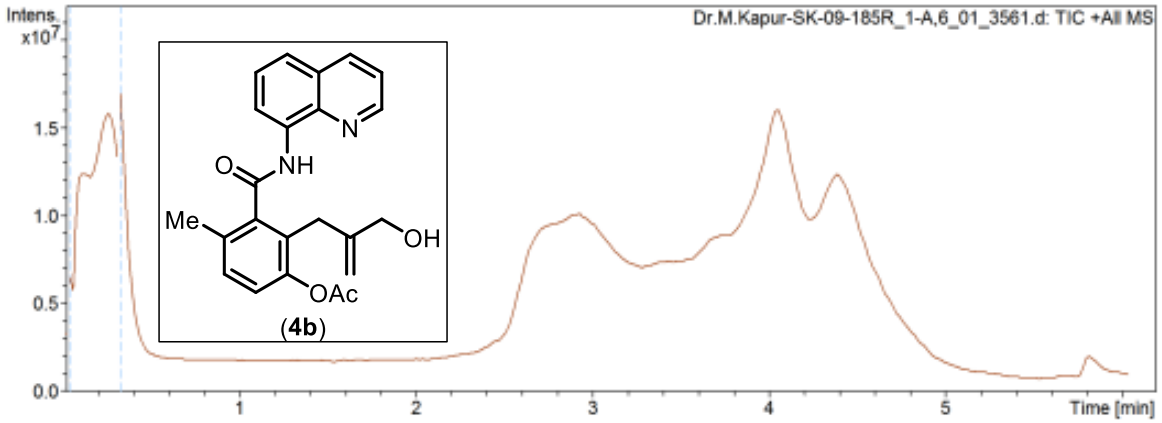
Display Report

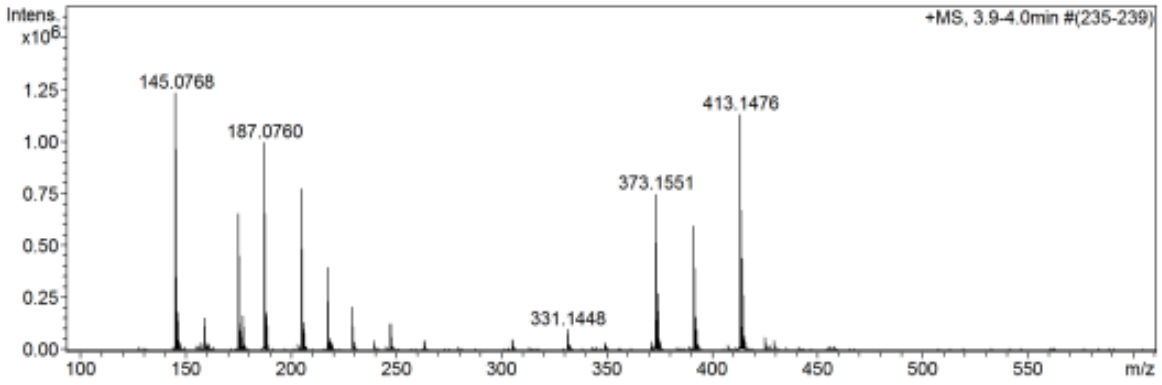
Analysis Info

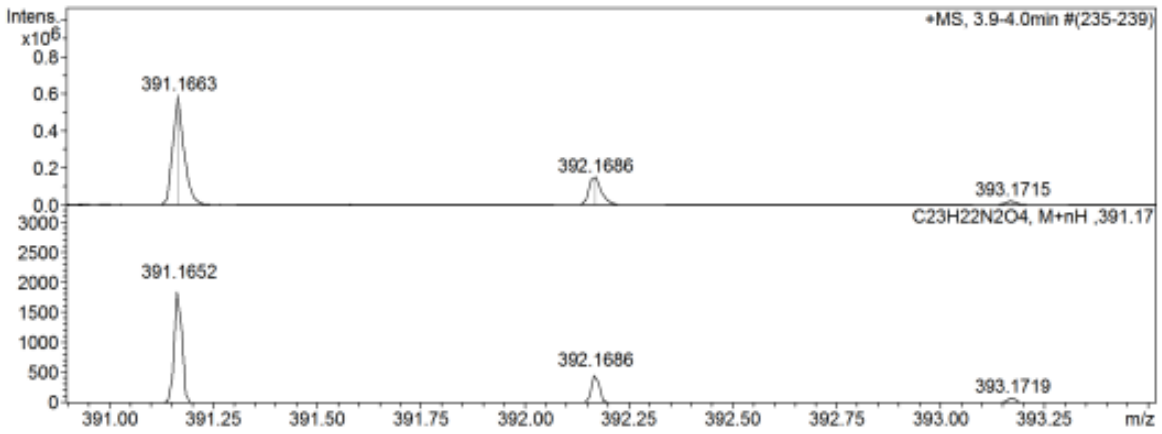
Analysis Name	D:\Data\USER DATA 2023\Dec23\01-Dec\Dr.M.Kapur-SK-09-185R_1-A,6_01_3561.d	Acquisition Date	01-12-2023 11:55:27
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Dr.M.Kapur-SK-09-185R	Instrument	micrOTOF-Q 10330
Comment			

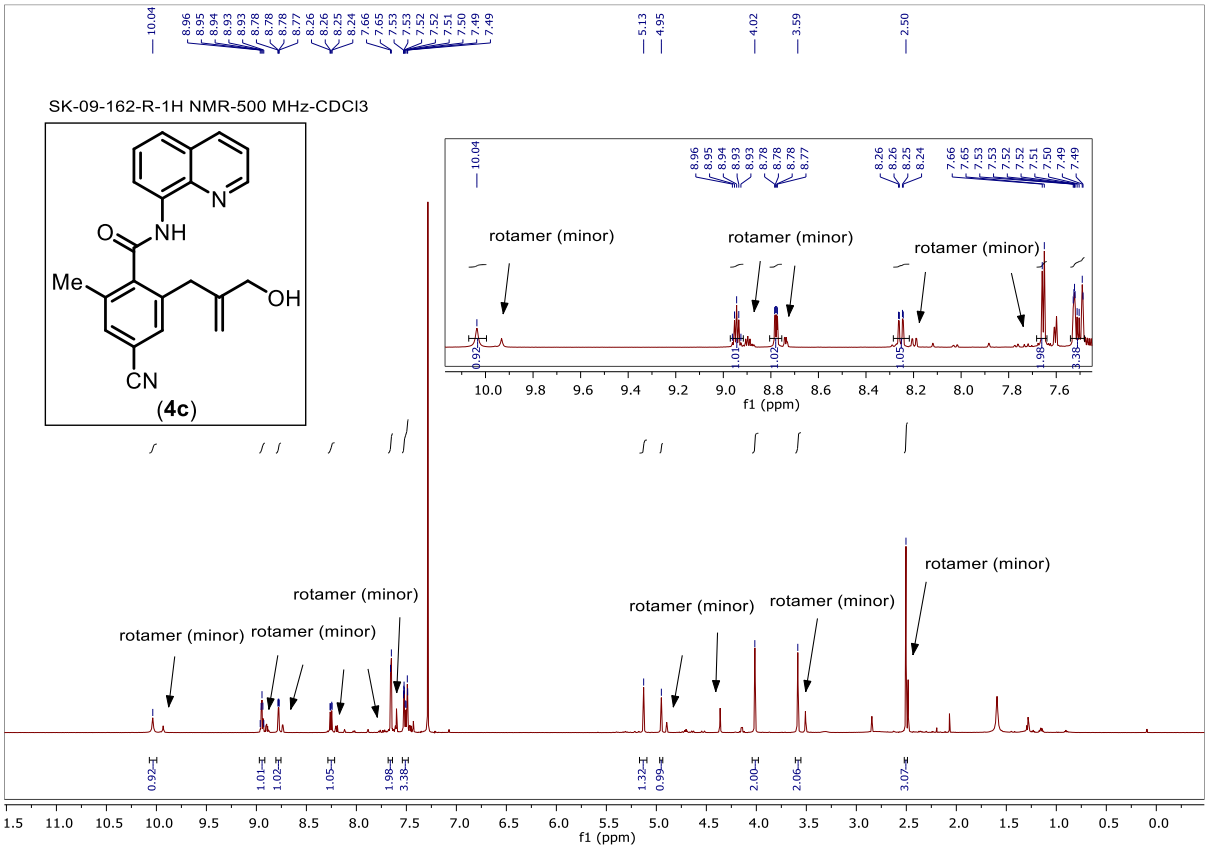
Acquisition Parameter

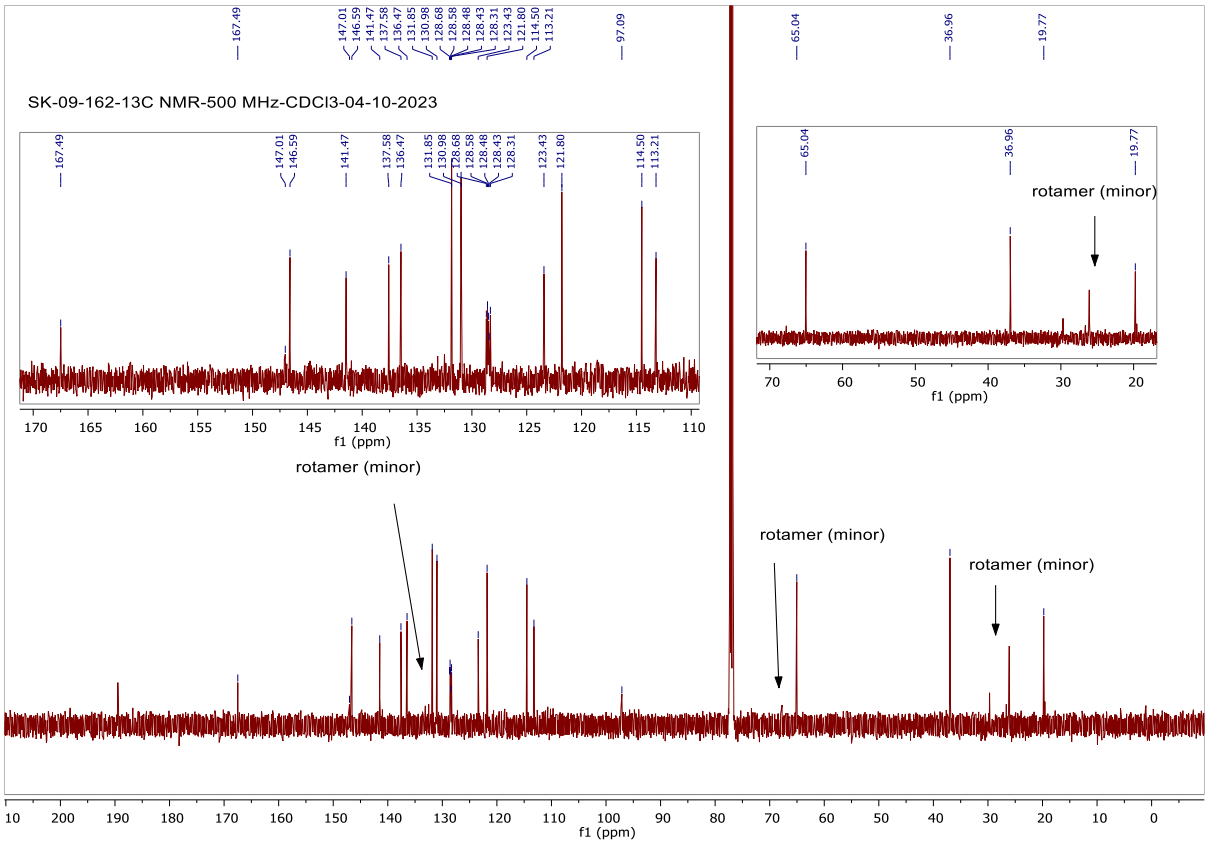
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








SK-09-162-R-1H NMR-500 MHz-CDCl3
(4c)
rotamer (minor)
f1 (ppm)


SK-09-162-13C NMR-500 MHz-CDCl3-04-10-2023
rotamer (minor)
f1 (ppm)

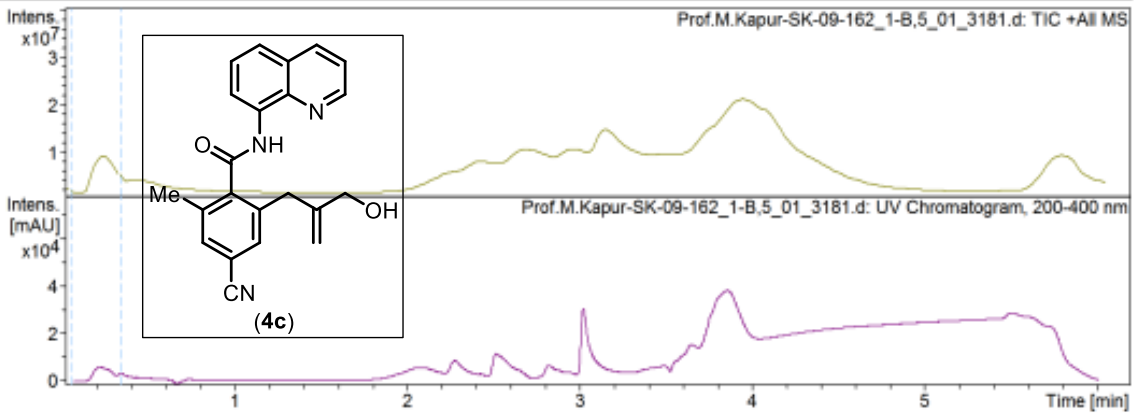
Display Report

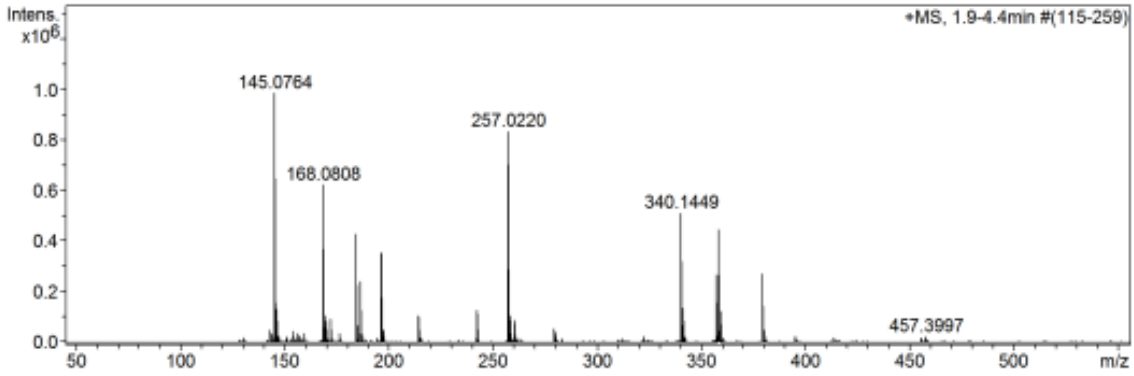
Analysis Info

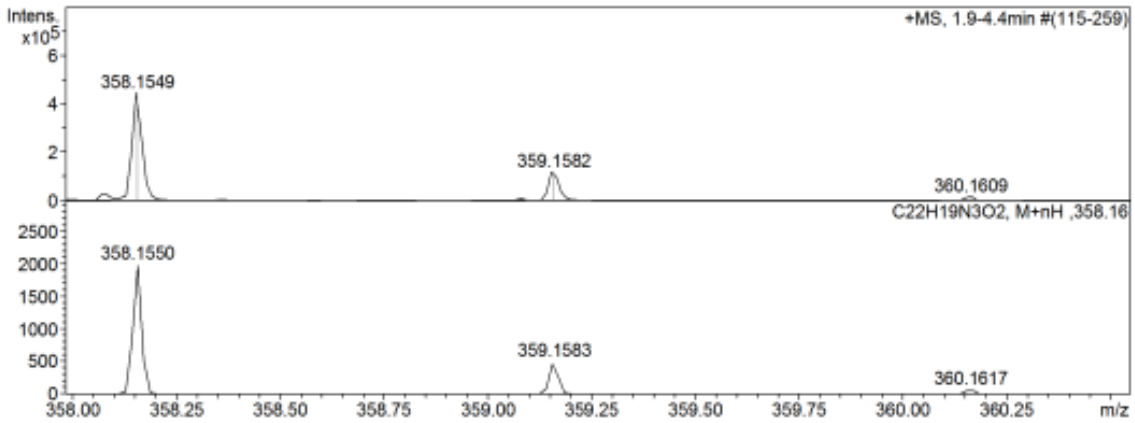
Analysis Name	D:\Data\USER DATA 2023\Oct 23\03-Oct\Prof.M.Kapur-SK-09-162_1-B,5_01_3181.d	Acquisition Date	03-10-2023 15:27:54
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-162	Instrument	micrOTOF-Q 10330
Comment			

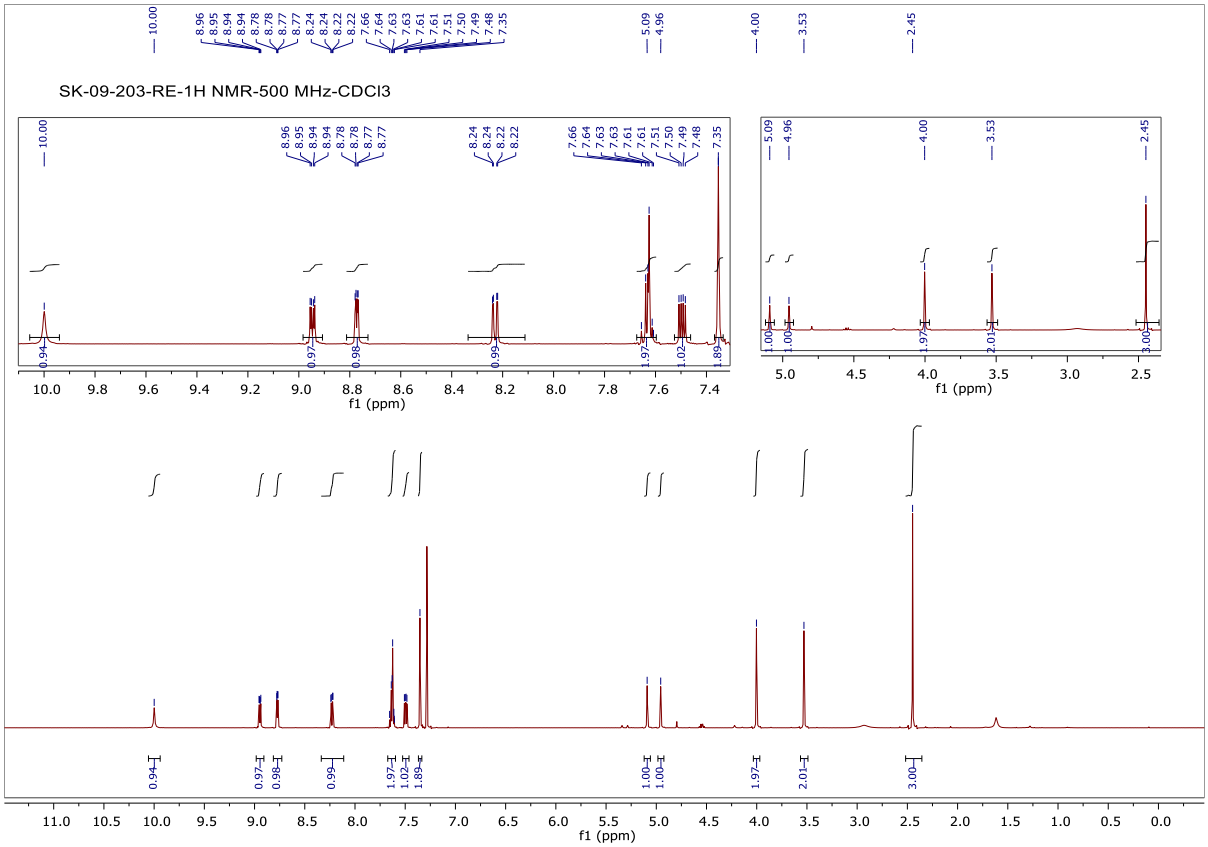
Acquisition Parameter

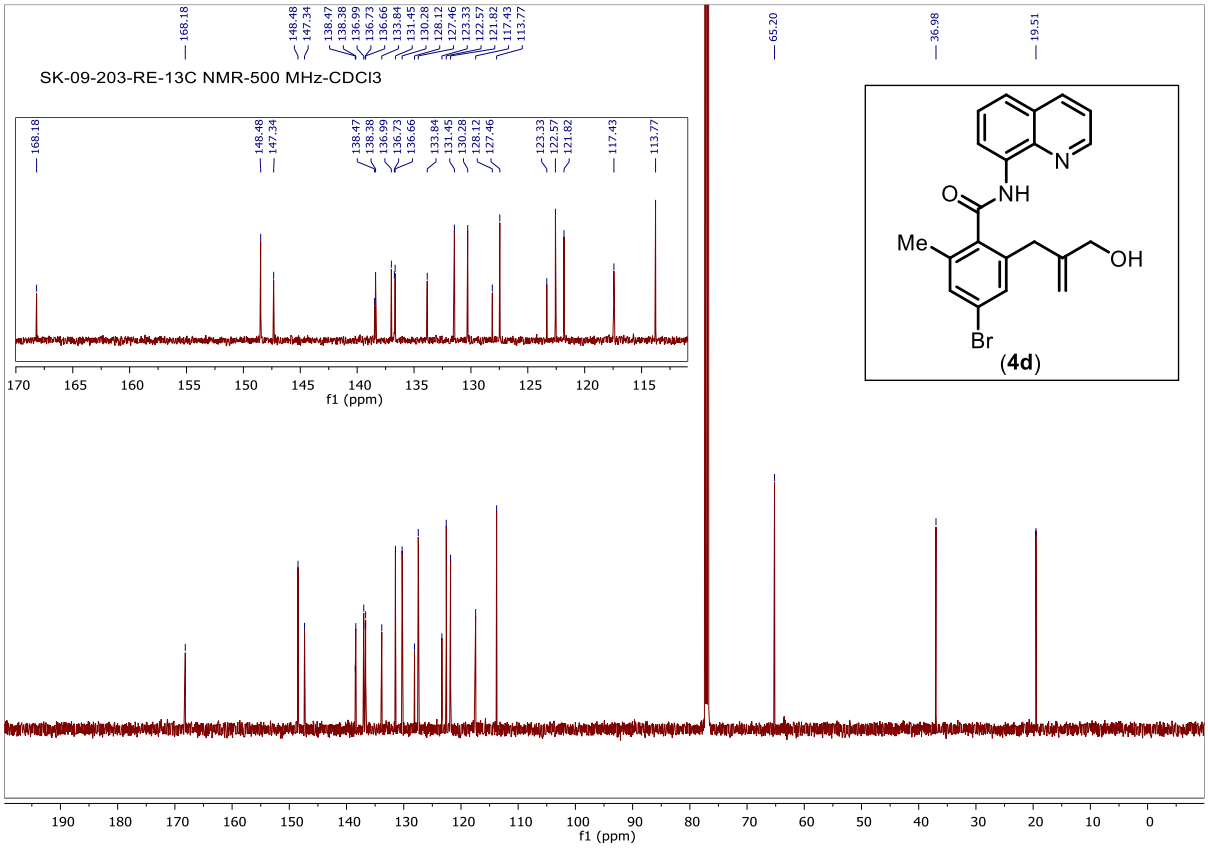
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








SK-09-203-RE-1H NMR-500 MHz-CDCl3
f1 (ppm)


SK-09-203-RE-13C NMR-500 MHz-CDCl3
f1 (ppm)
N
O
NH
Me
OH
Br
(4d)

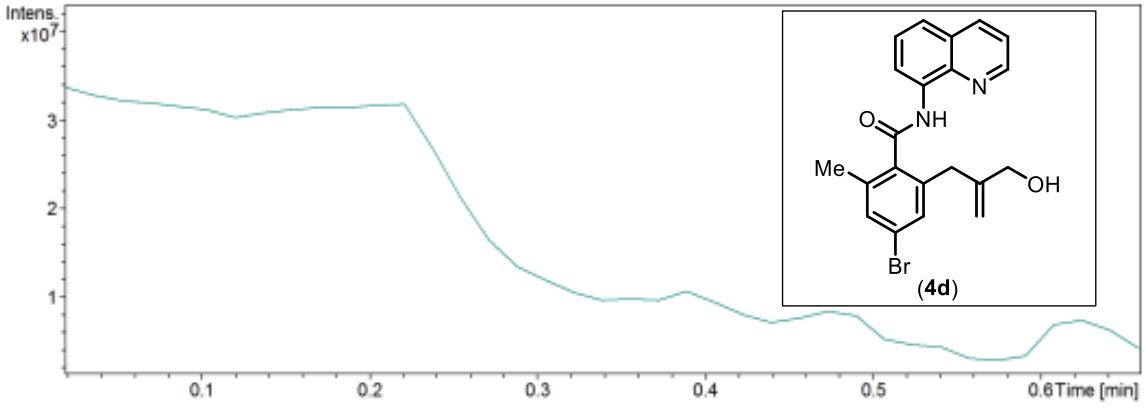
Display Report

Analysis Info

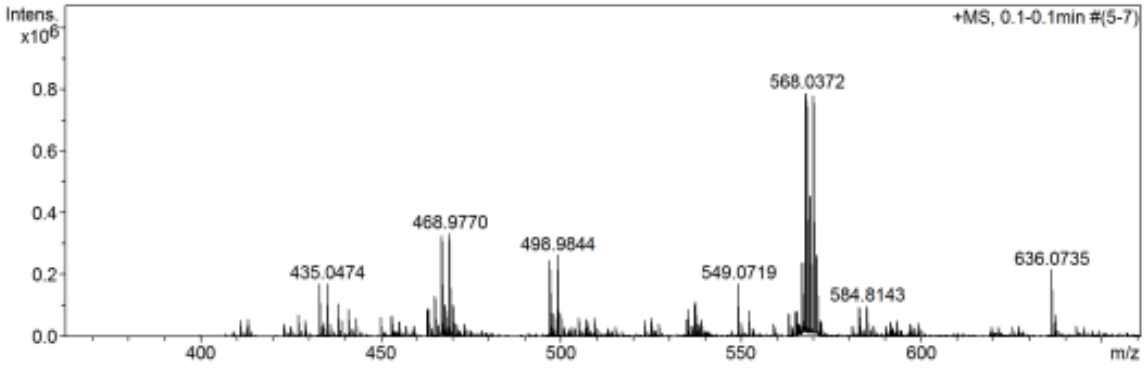
Analysis Name	D:\Data\USER DATA 2023\Dec23\15-dec\Dr.M.Kapur-SK-09-203.d	Acquisition Date	15-12-2023 12:28:43
Method	tune_wide.m	Operator	Bruker
Sample Name	SK-09-203	Instrument	micrOTOF-Q 10330
Comment			

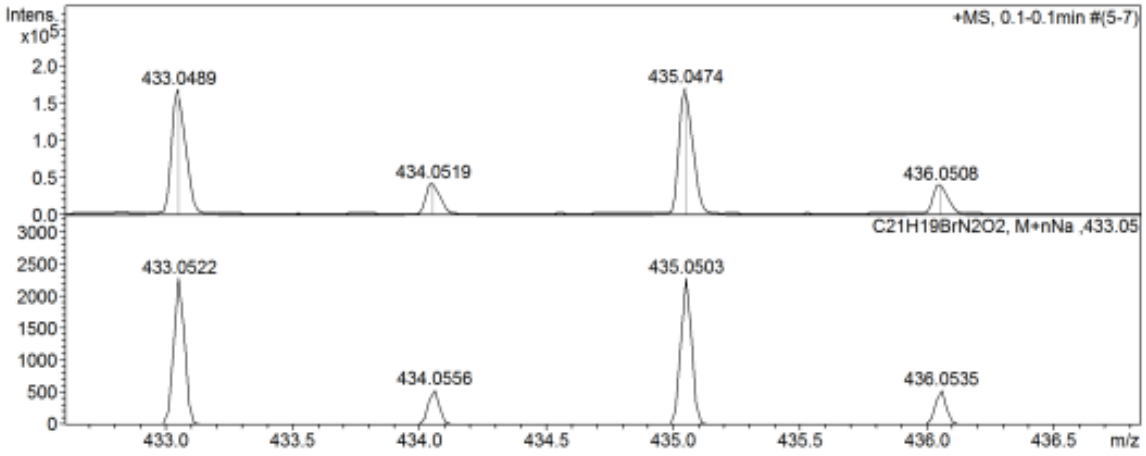
Acquisition Parameter

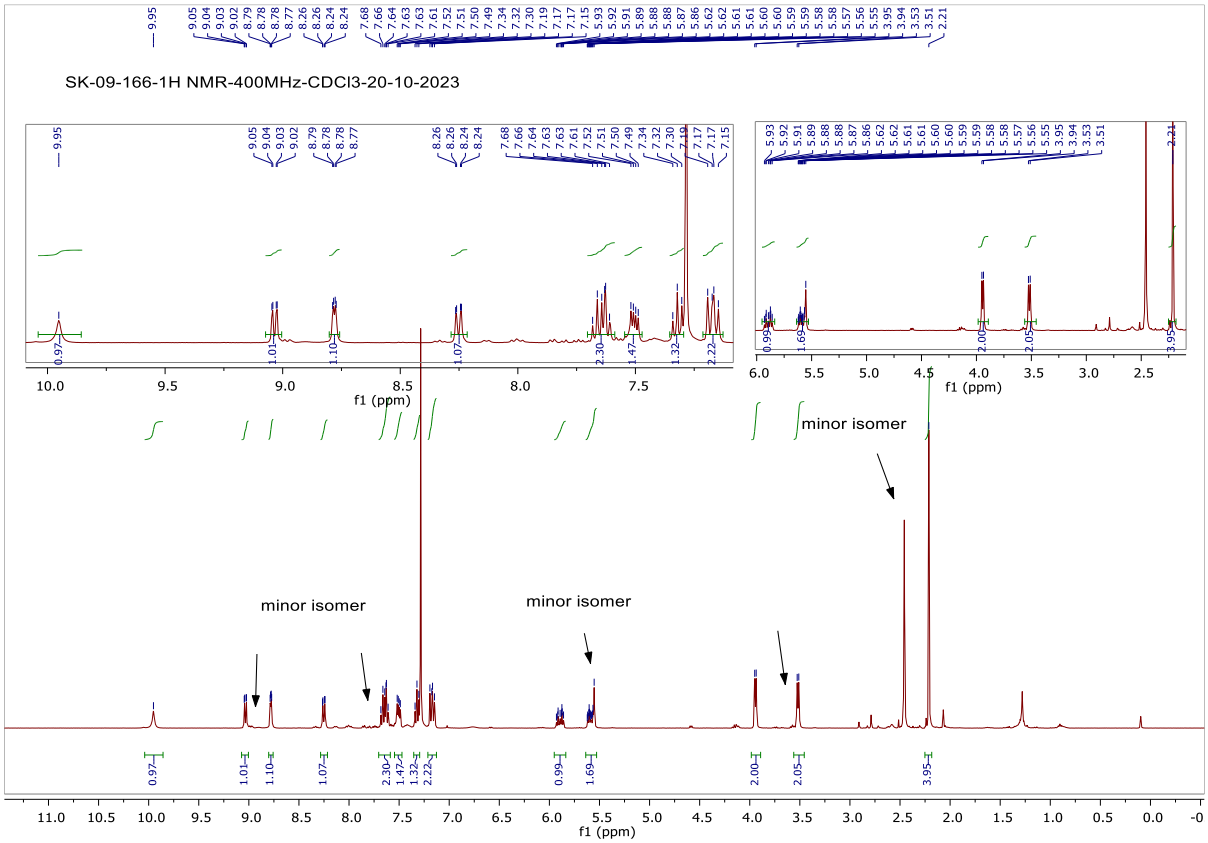
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	800.0 Vpp	Set Divert Valve	Waste

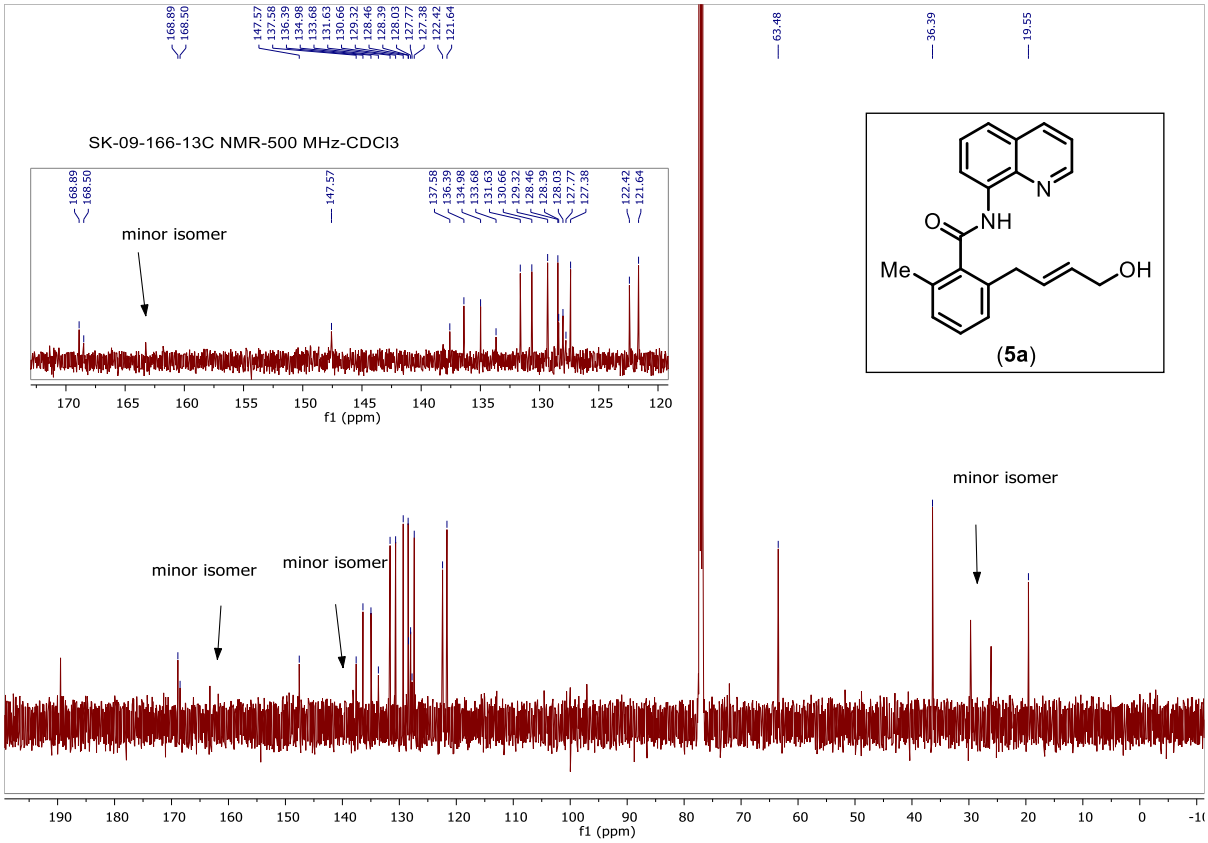


TIC +All MS






SK-09-166-1H NMR-400MHz-CDCl3-20-10-2023
minor isomer
minor isomer
minor isomer
f1 (ppm)


SK-09-166-13C NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
N
NH
O
Me
OH
(5a)
f1 (ppm)

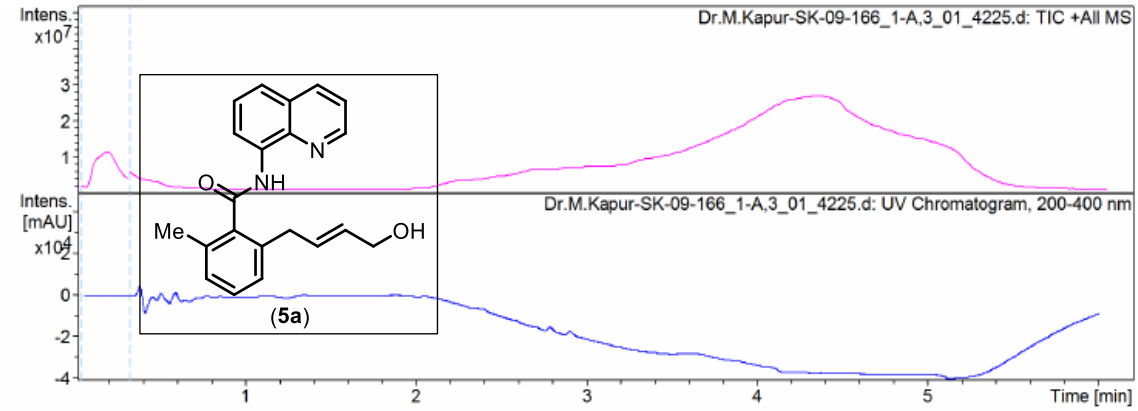
Display Report

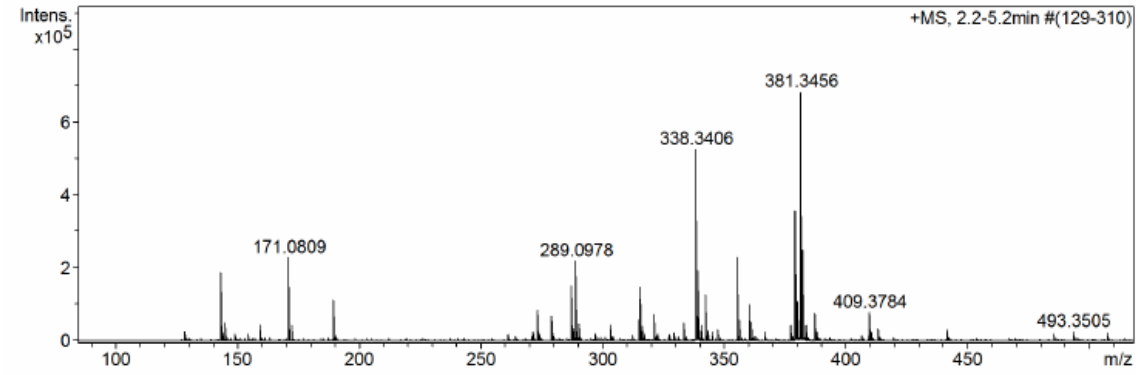
Analysis Info

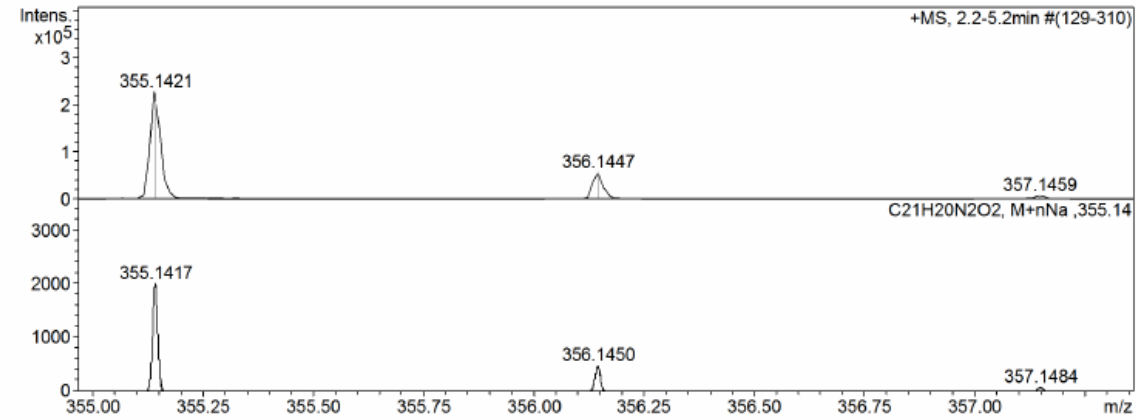
Acquisition Date	20-02-2024 12:25:20		
Analysis Name	D:\Data\USER DATA 2024\Feb2024\20-FEB\Dr.M.Kapur-SK-09-166_1-A,3_01_4225.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Dr.M.Kapur-SK-09-166	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

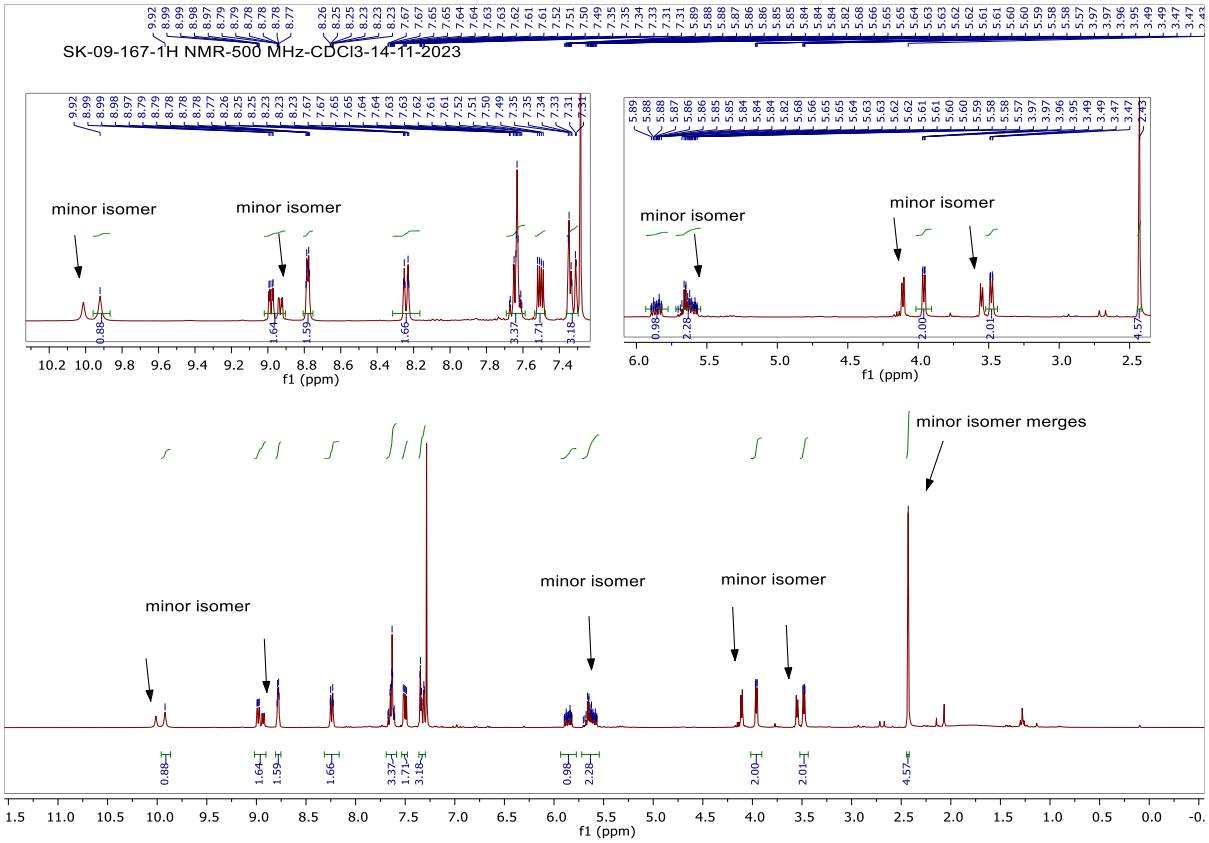
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

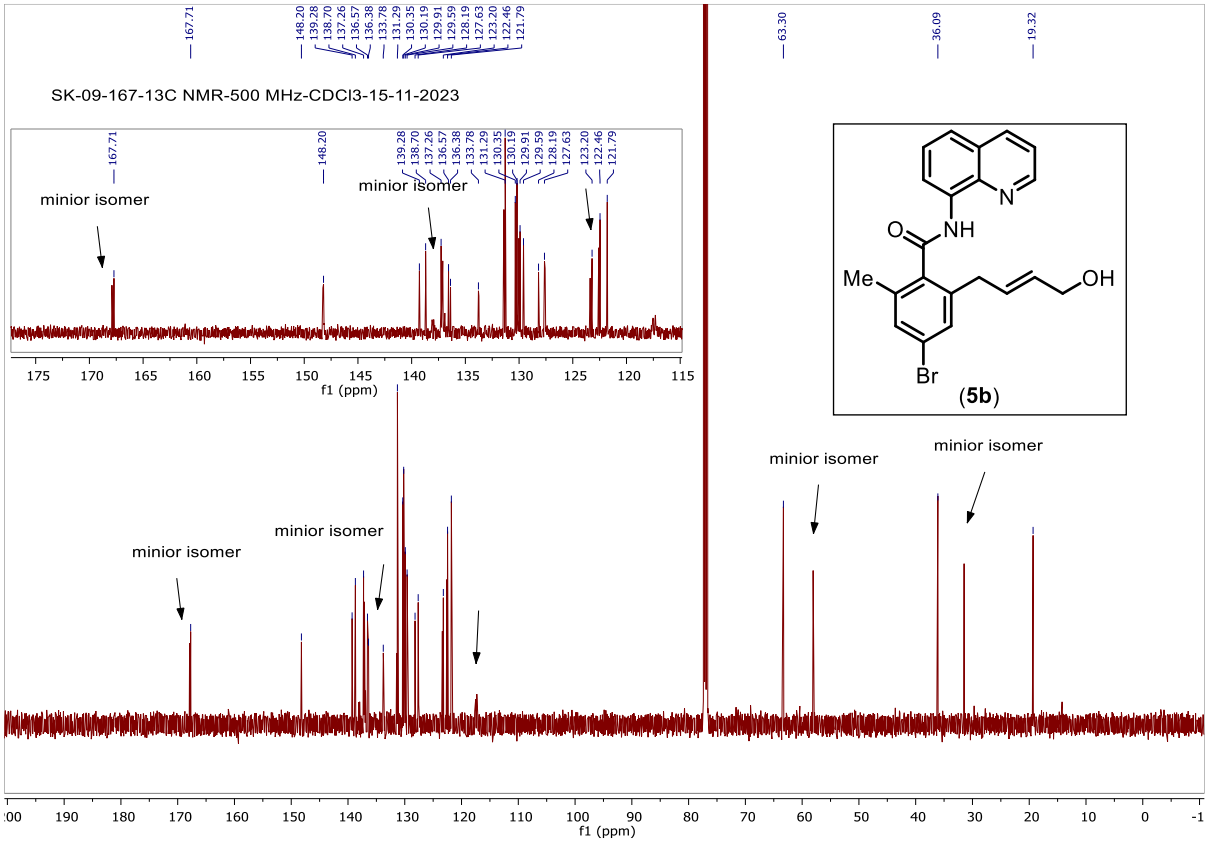






Bruker Compass DataAnalysis 4.0 printed: 20-02-2024 16:46:04 Page 1 of 1


SK-09-167-1H NMR-500 MHz-CDCl3-14-11-2023
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer merges
minor isomer
minor isomer
f1 (ppm)


SK-09-167-13C NMR-500 MHz-CDCl3-15-11-2023
minior isomer
minior isomer
minior isomer
minior isomer
minior isomer
minior isomer
f1 (ppm)
N
NH
O
Me
OH
Br
(5b)

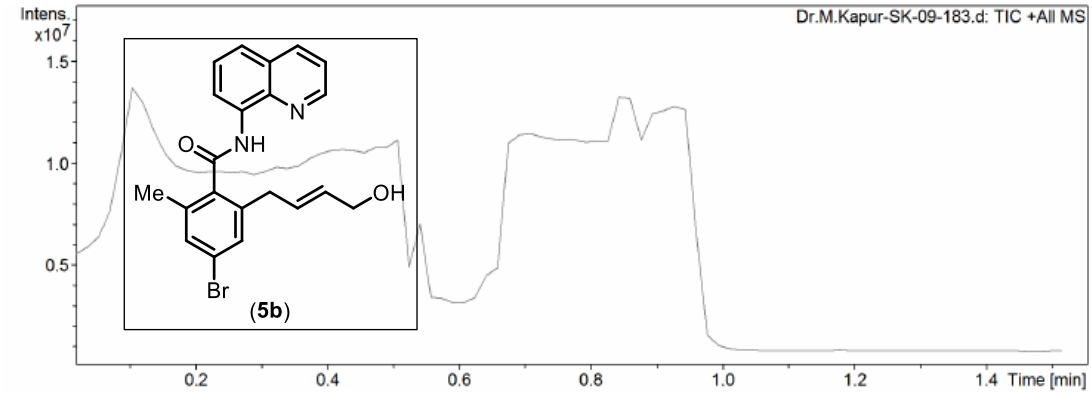
Display Report

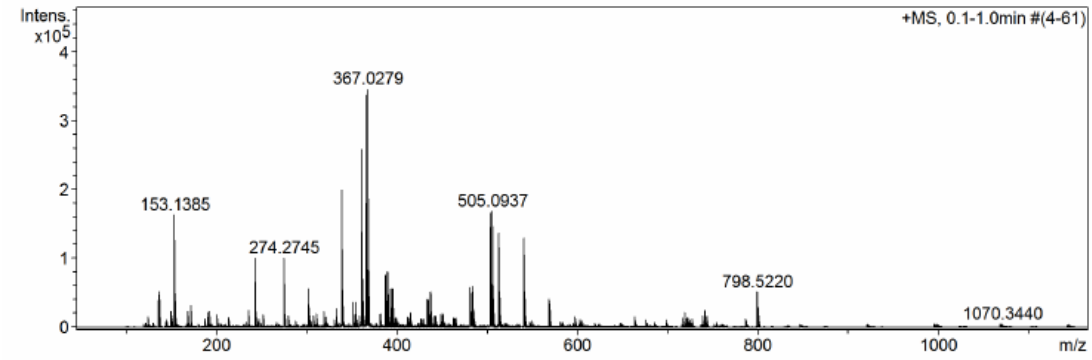
Analysis Info

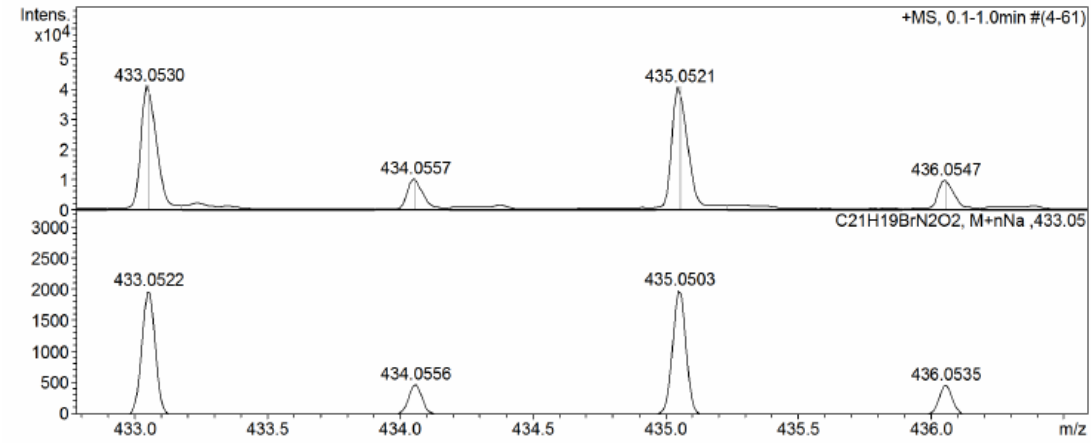
Analysis Name	D:\Data\USER DATA 2024\April2024\26-april\Dr.M.Kapur-SK-09-183.d	Acquisition Date	26-04-2024 17:00:24
Method	tune_low.m	Operator	Bruker
Sample Name	SK-09-183	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

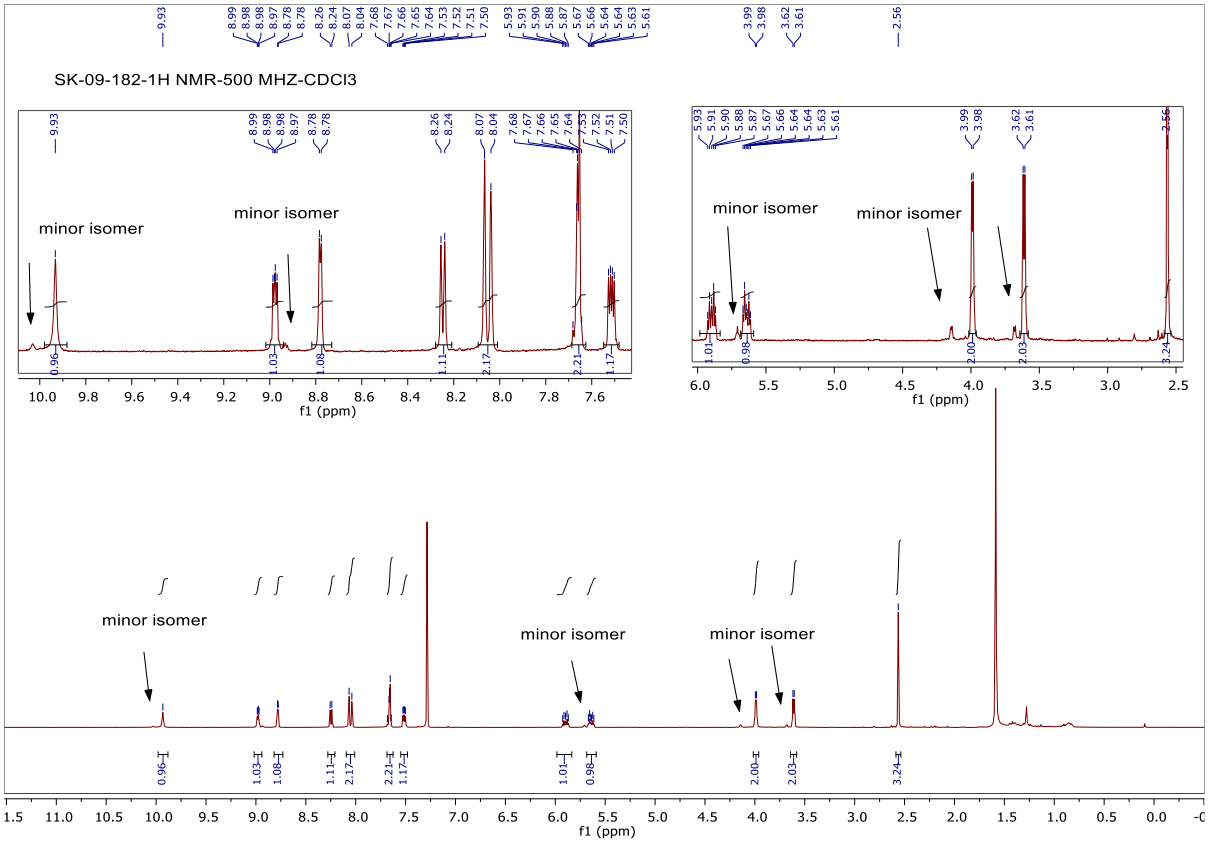
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	5.8 psi
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

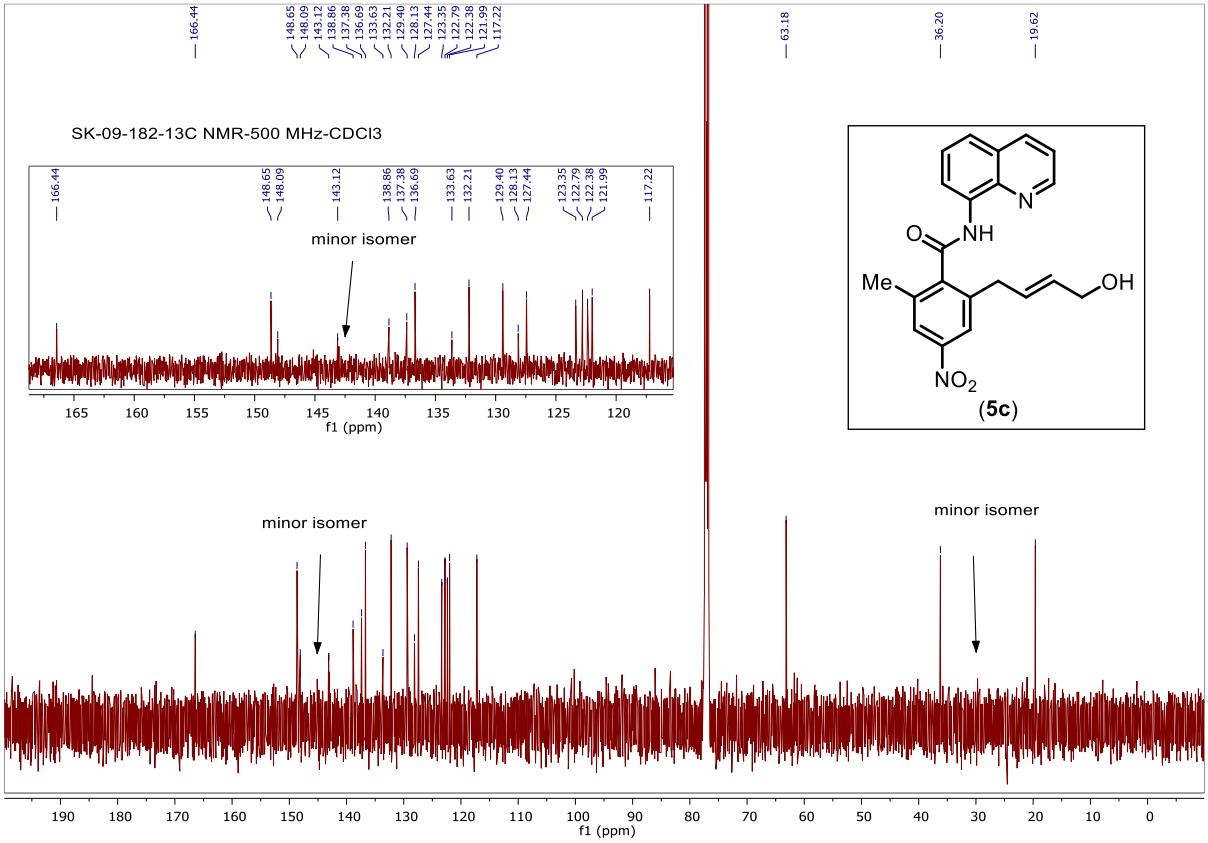






Bruker Compass DataAnalysis 4.0 printed: 26-04-2024 17:03:59 Page 1 of 1


SK-09-182-1H NMR-500 MHZ-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)


SK-09-182-13C NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
f1 (ppm)
N
O
NH
Me
OH
NO2
(5c)

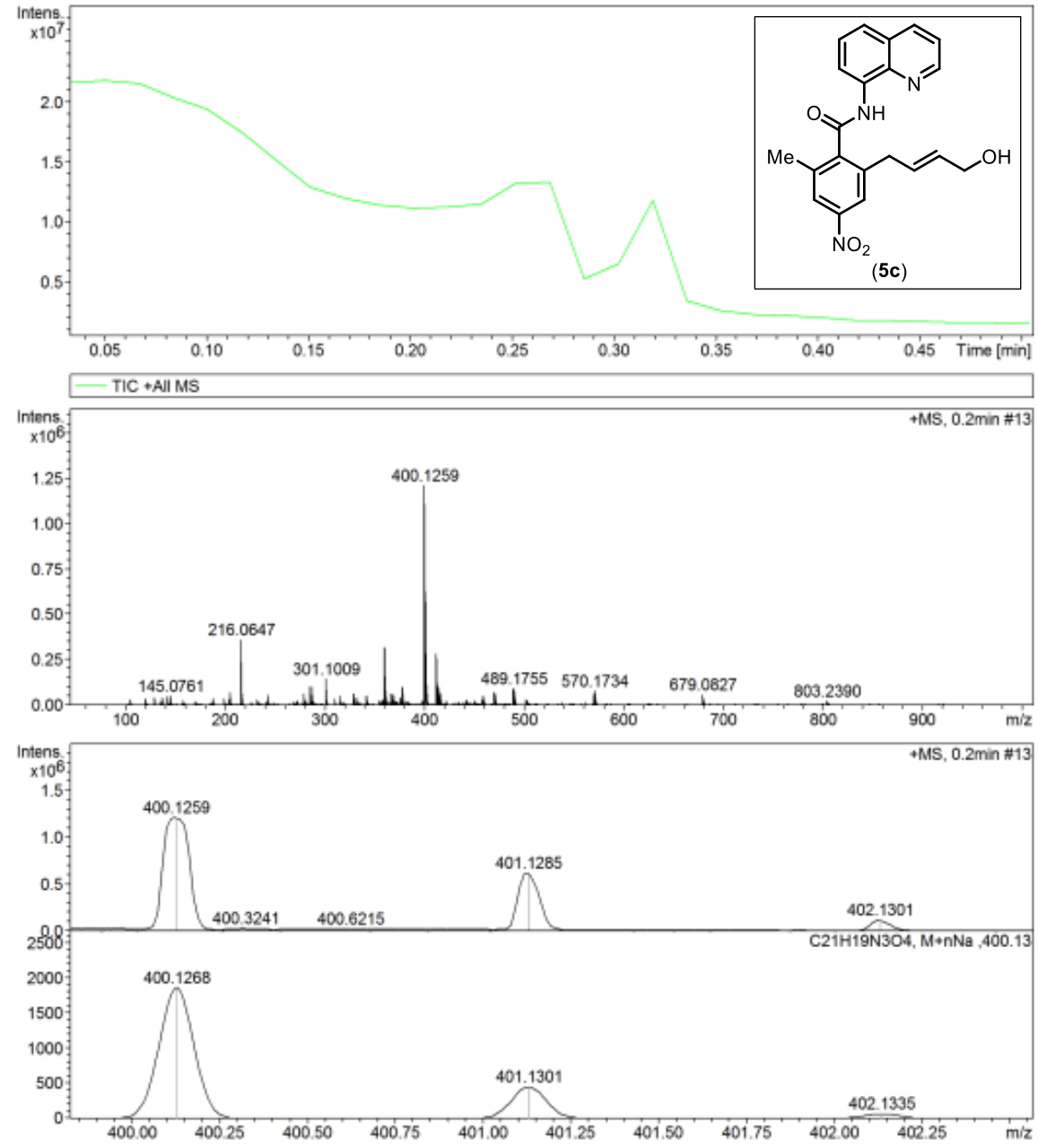
Display Report

Analysis Info

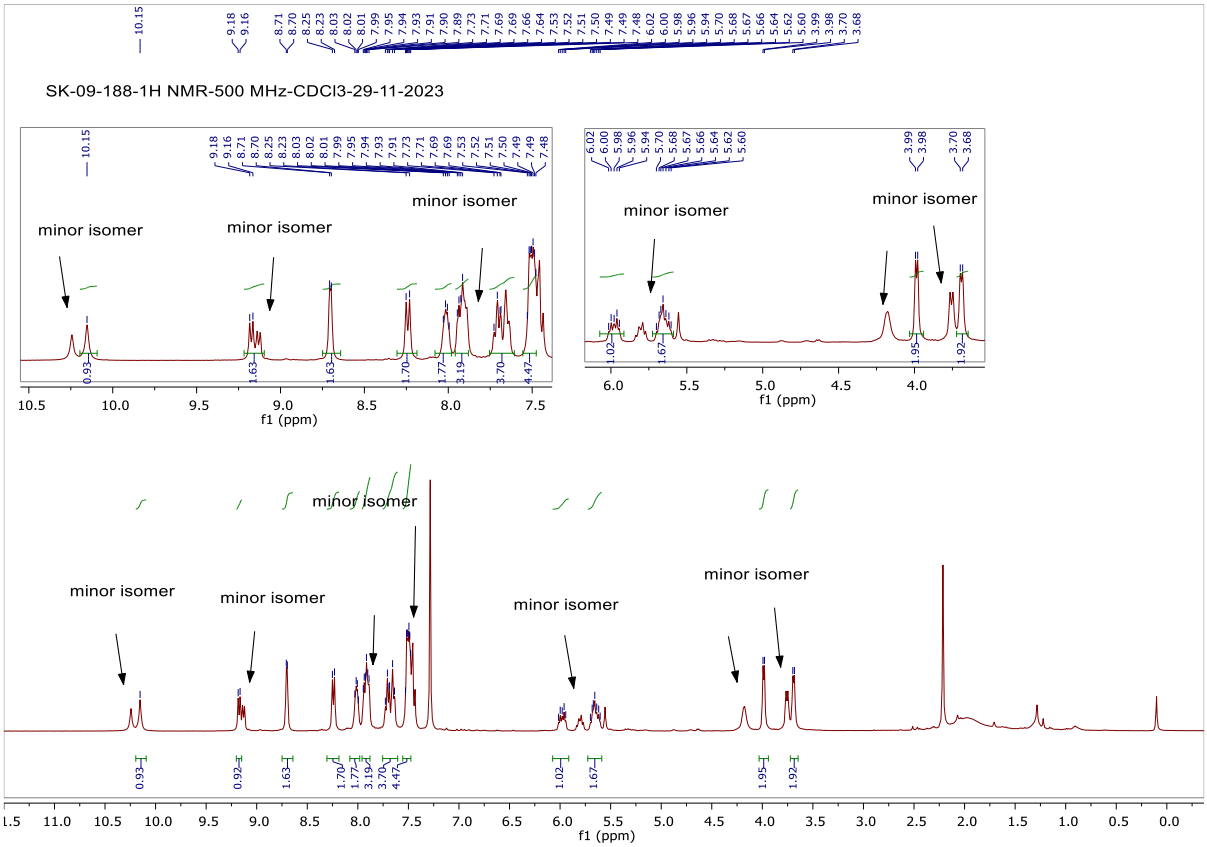
Analysis Name	D:\Data\USER DATA 2023\Nov23\20-nov\Dr M.Kapur-SK-09-182-1.d	Acquisition Date	20-11-2023 12:01:51
Method	tune_low_APR23.m	Operator	Bruker
Sample Name	SK-09-182-1	Instrument	micrOTOF-Q 10330
Comment			

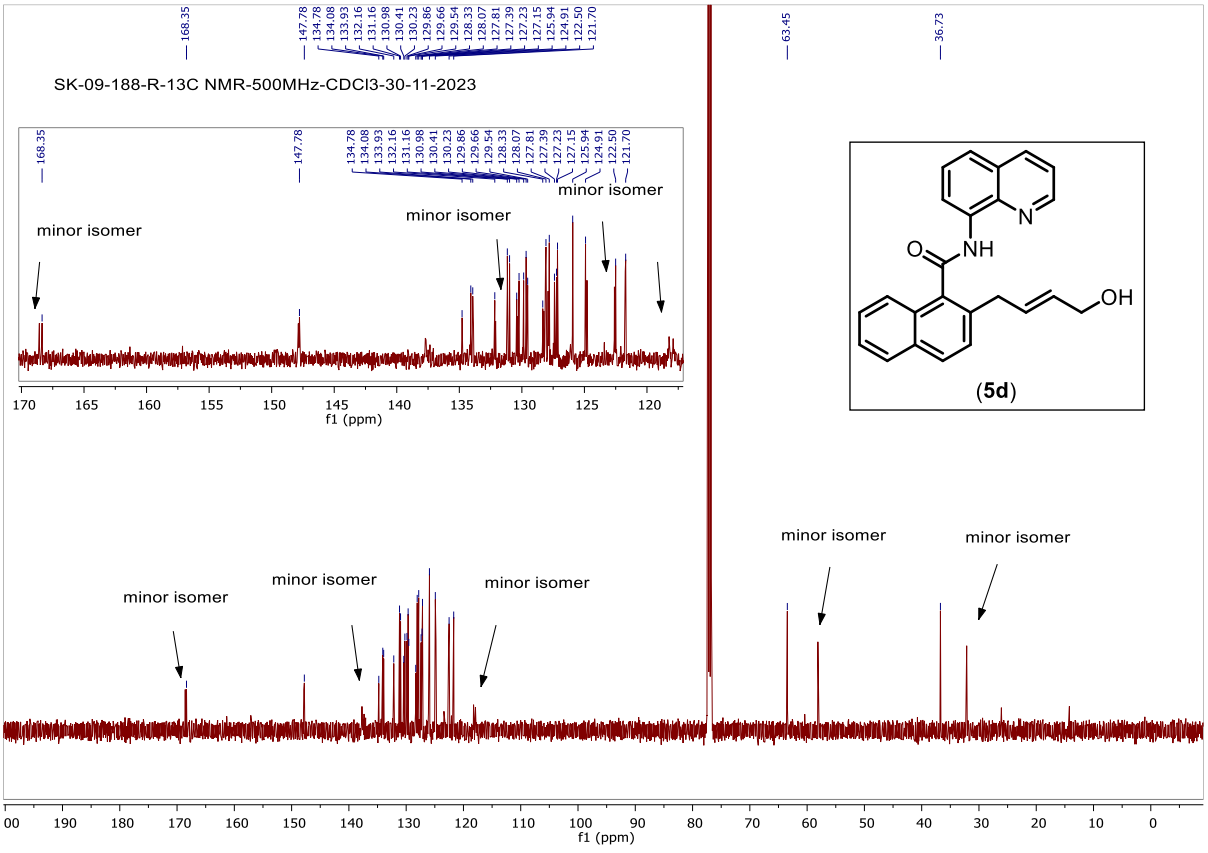
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 20-11-2023 12:04:07 Page 1 of 1


SK-09-188-1H NMR-500 MHz-CDCl3-29-11-2023
minor isomer
f1 (ppm)


SK-09-188-R-13C NMR-500MHz-CDCl3-30-11-2023
minor isomer
f1 (ppm)
N
O
NH
OH
(5d)

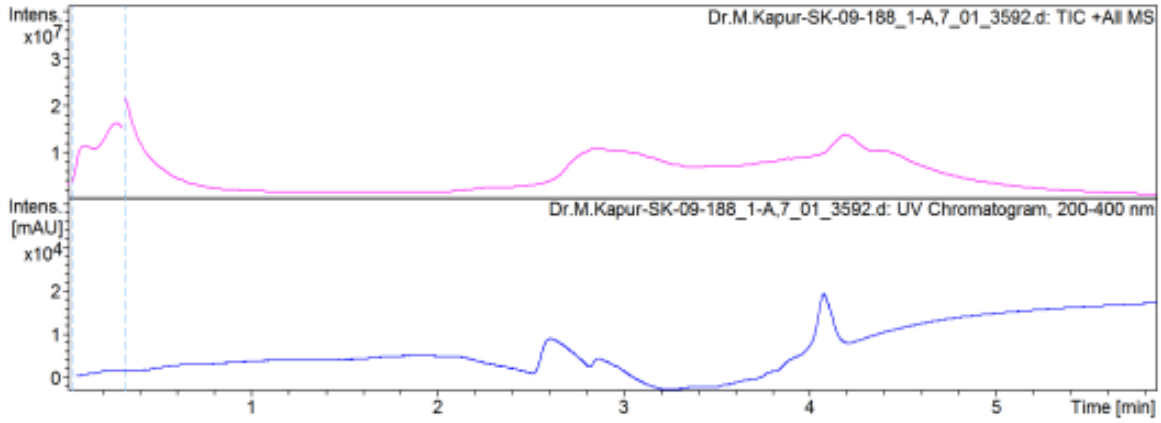
Display Report

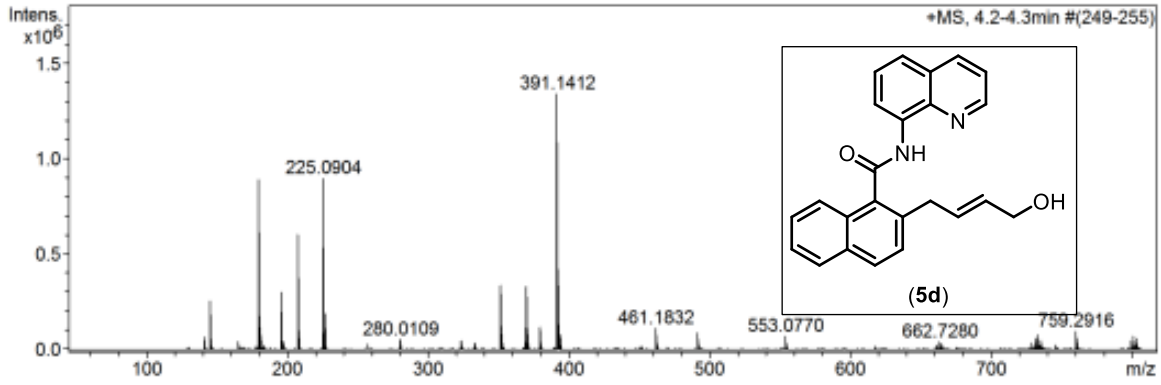
Analysis Info

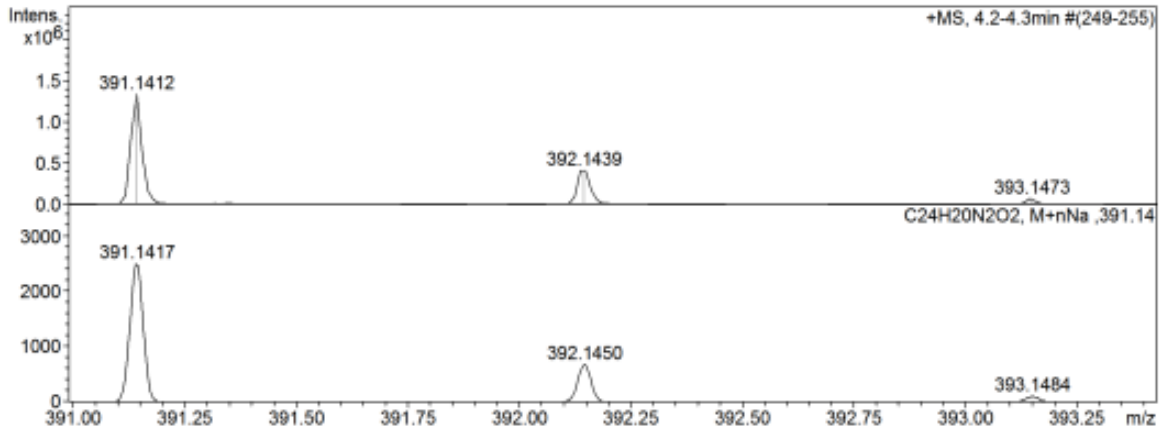
Acquisition Date	04-12-2023 12:55:46		
Analysis Name	D:\Data\USER DATA 2023\Dec23\04-dec\Dr.M.Kapur-SK-09-188_1-A,7_01_3592.d		
Method	HRLCMS-20 Sept.m	Operator	Bruker
Sample Name	Dr.M.Kapur-SK-09-188	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

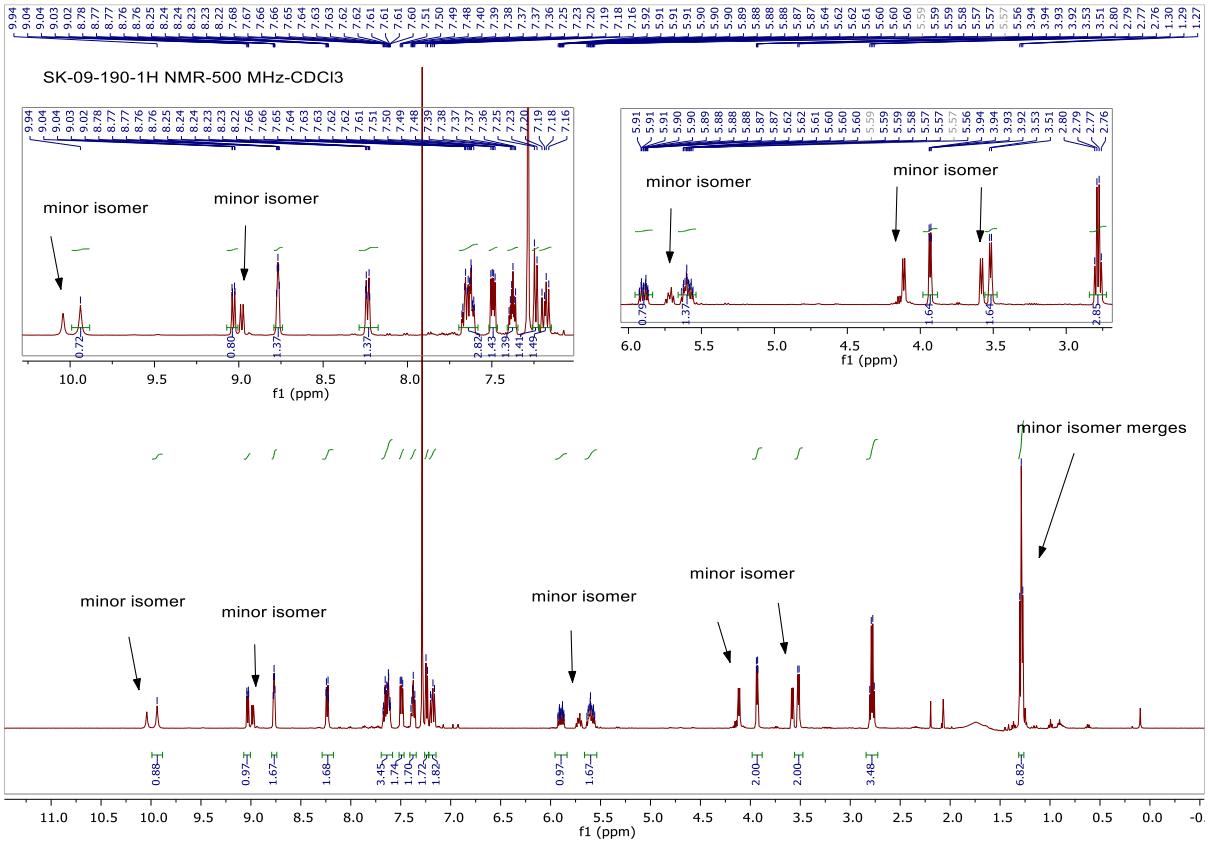
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

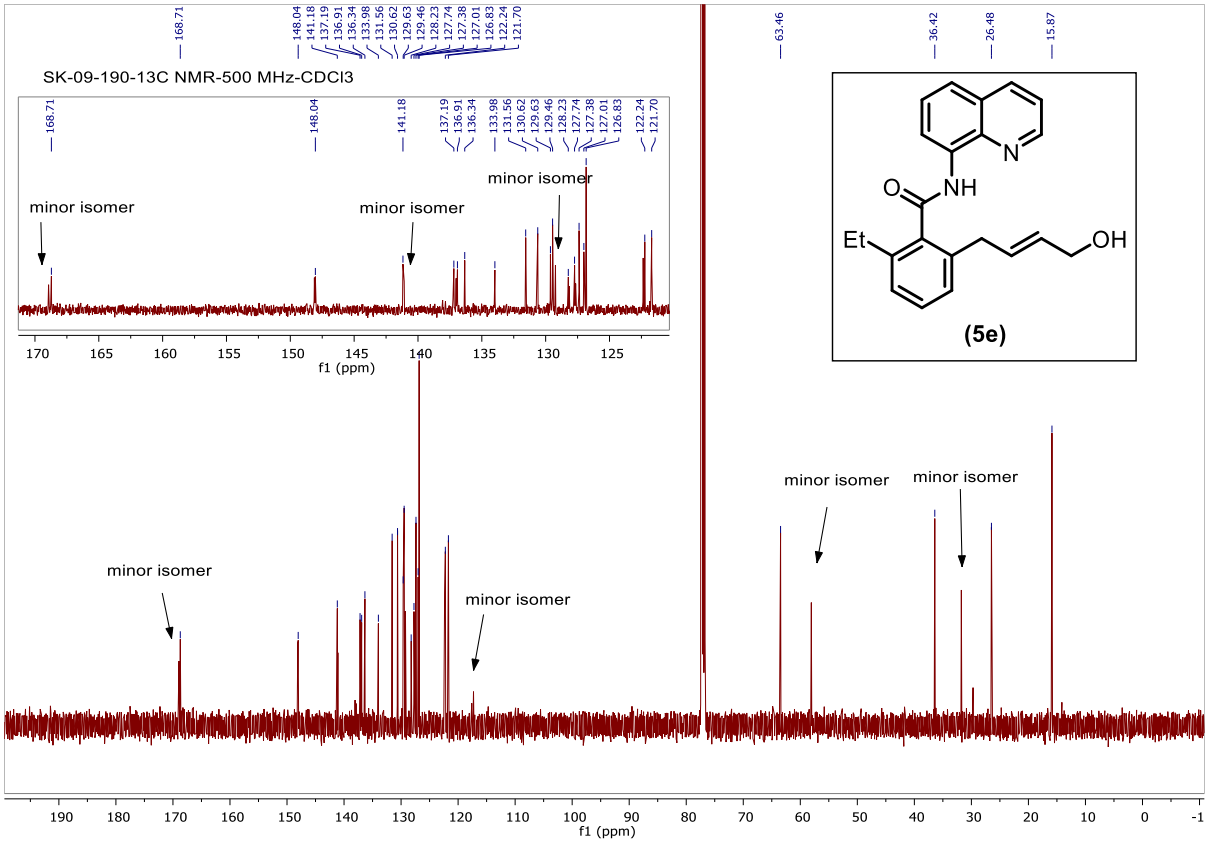






Bruker Compass DataAnalysis 4.0 printed: 04-12-2023 14:44:25 Page 1 of 1


SK-09-190-1H NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer merges
f1 (ppm)


SK-09-190-13C NMR-500 MHz-CDCl3
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
minor isomer
f1 (ppm)

N
O
NH
Et
OH
(5e)

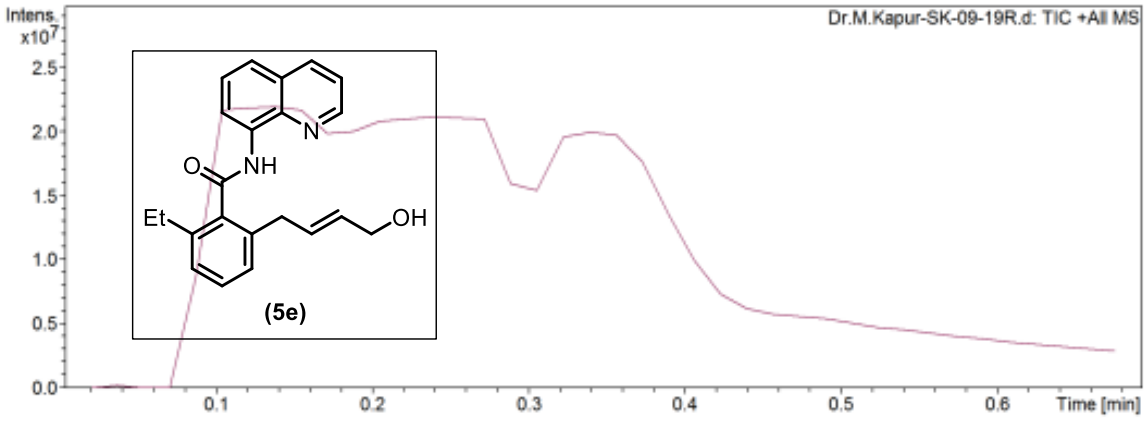
Display Report

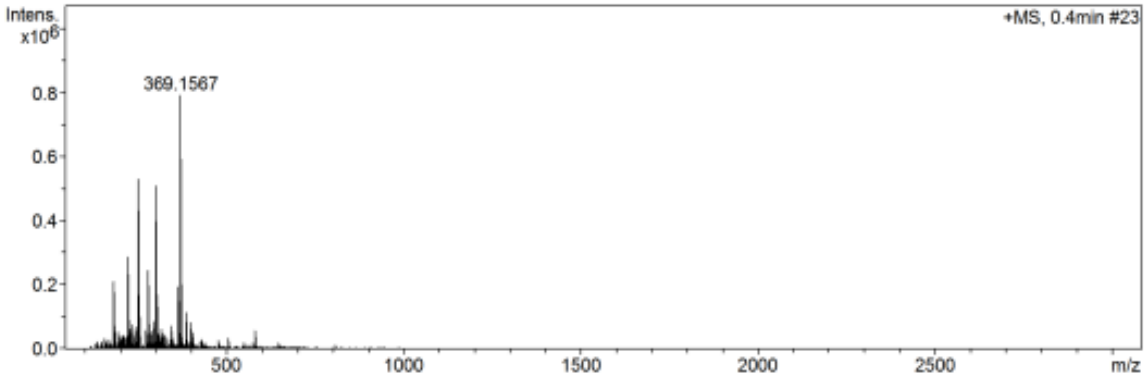
Analysis Info

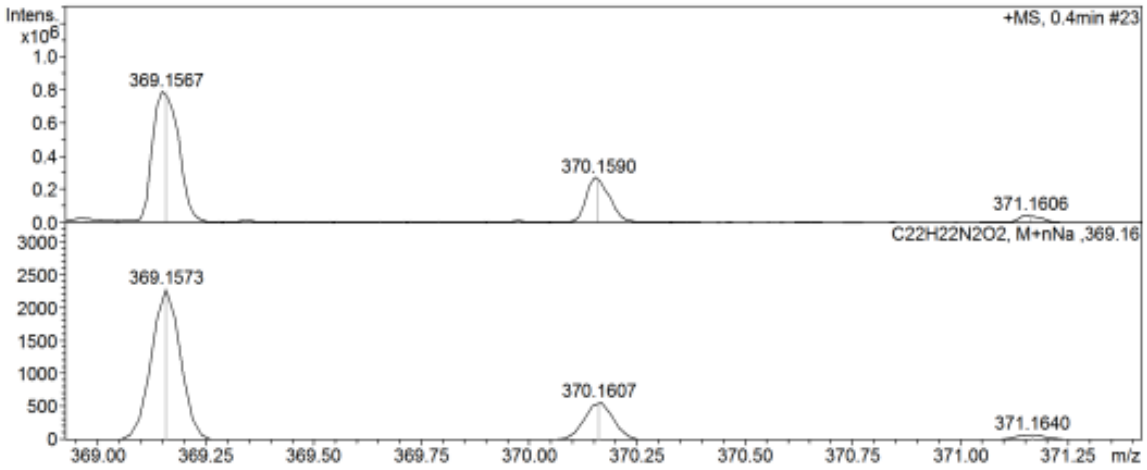
Analysis Name	D:\Data\USER DATA 2023\Dec23\08-dec\Dr.M.Kapur-SK-09-19R.d	Acquisition Date	08-12-2023 11:59:10
Method	tune_low_APR23.m	Operator	Bruker
Sample Name	SK-09-19R	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

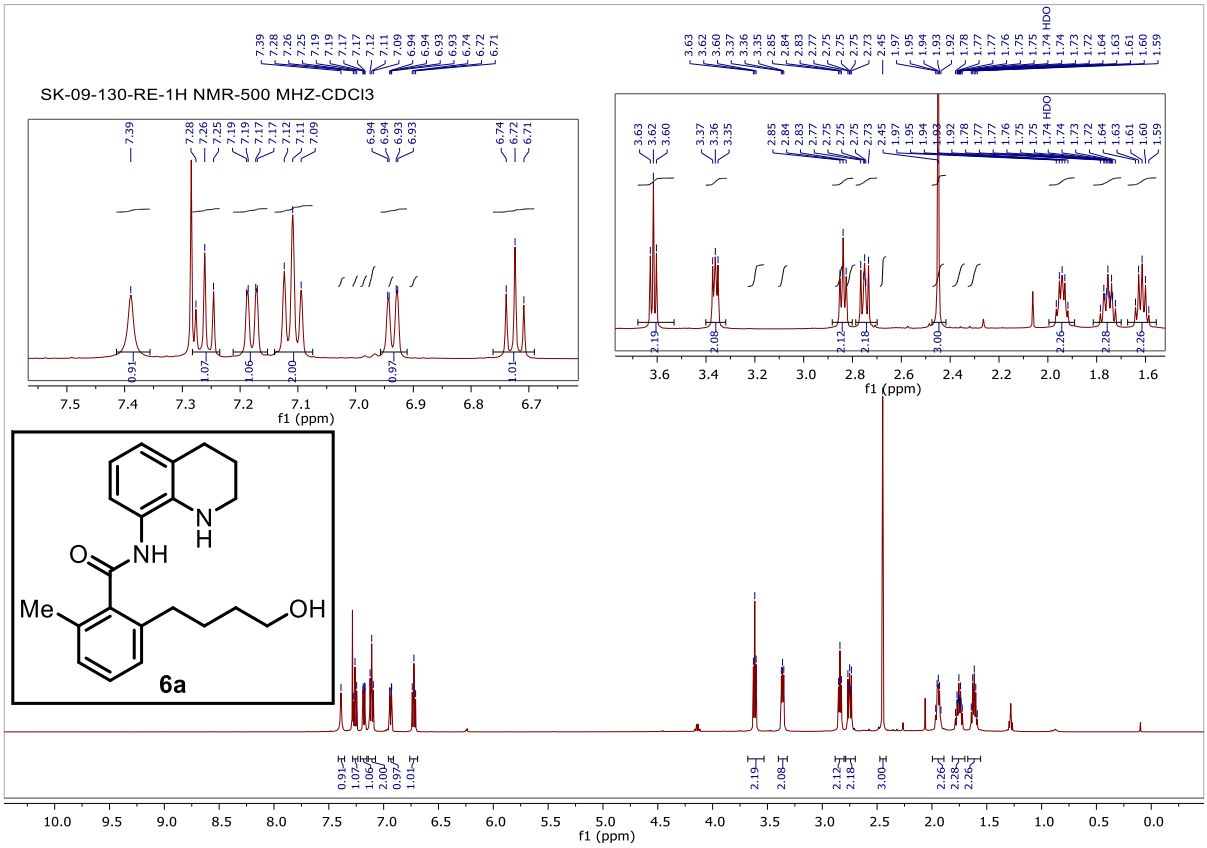


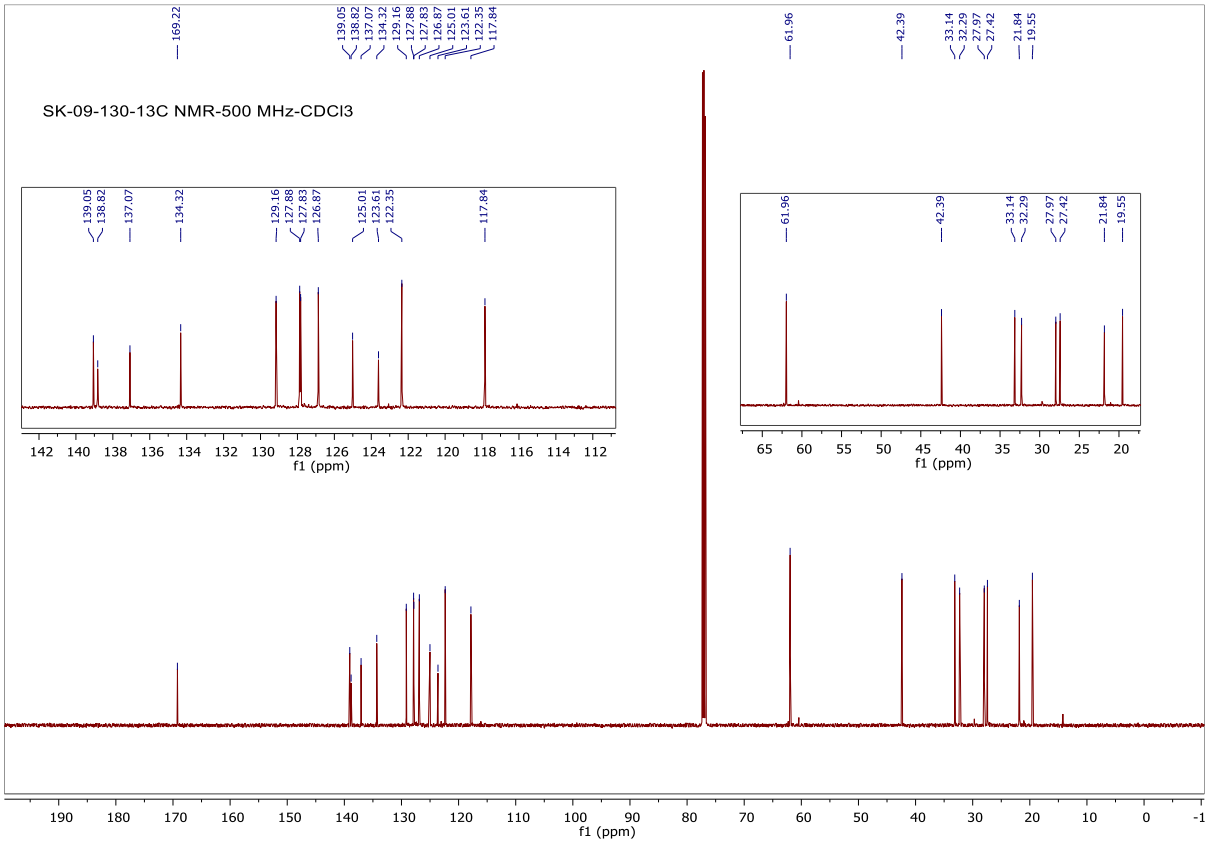




Bruker Compass DataAnalysis 4.0 printed: 08-12-2023 12:01:15 Page 1 of 1

Copies of NMR spectra of 6a:





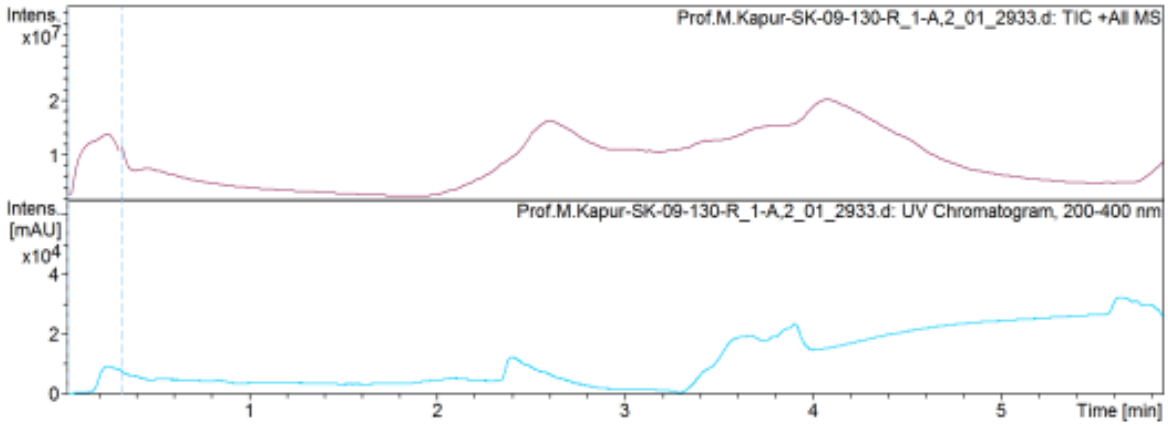
Display Report

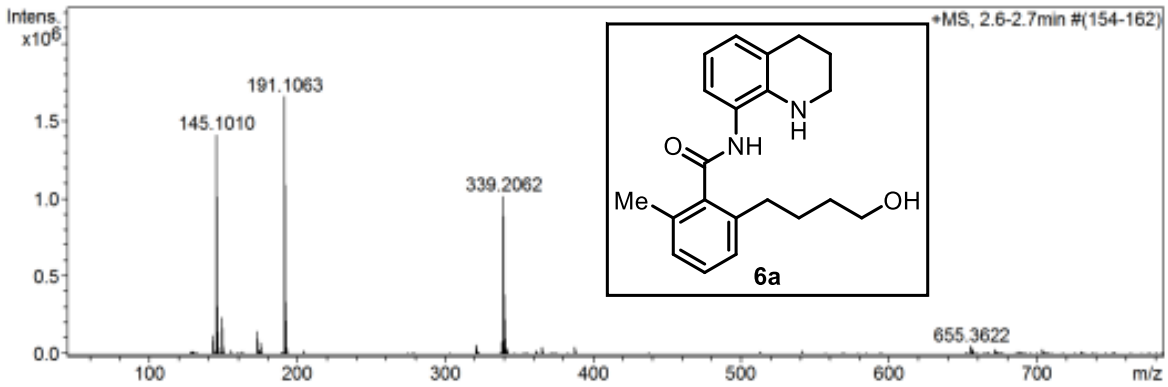
Analysis Info

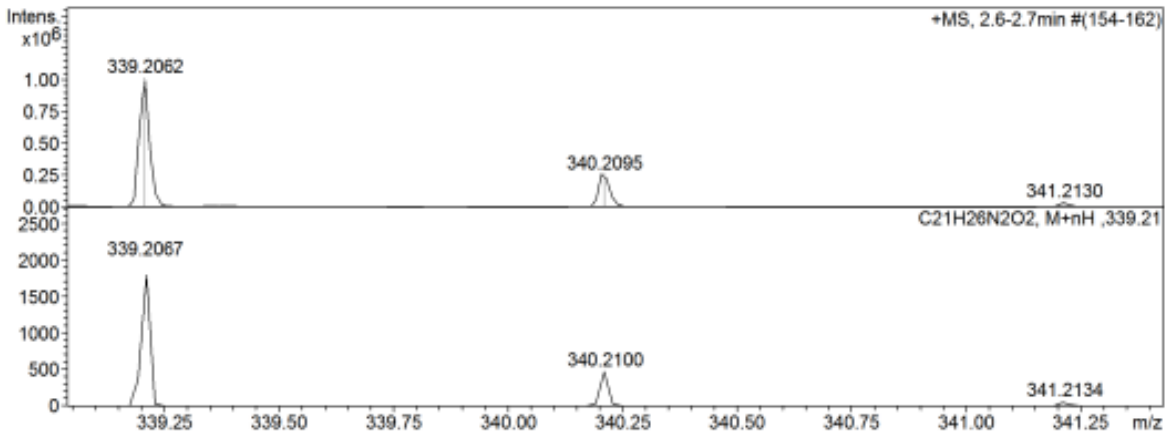
Analysis Name	D:\Data\USER DATA 2023\sep 23\06 sep\Prof.M.Kapur-SK-09-130-R_1-A,2_01_2933.d	Acquisition Date	06-09-2023 11:51:42
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-SK-09-130-R	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

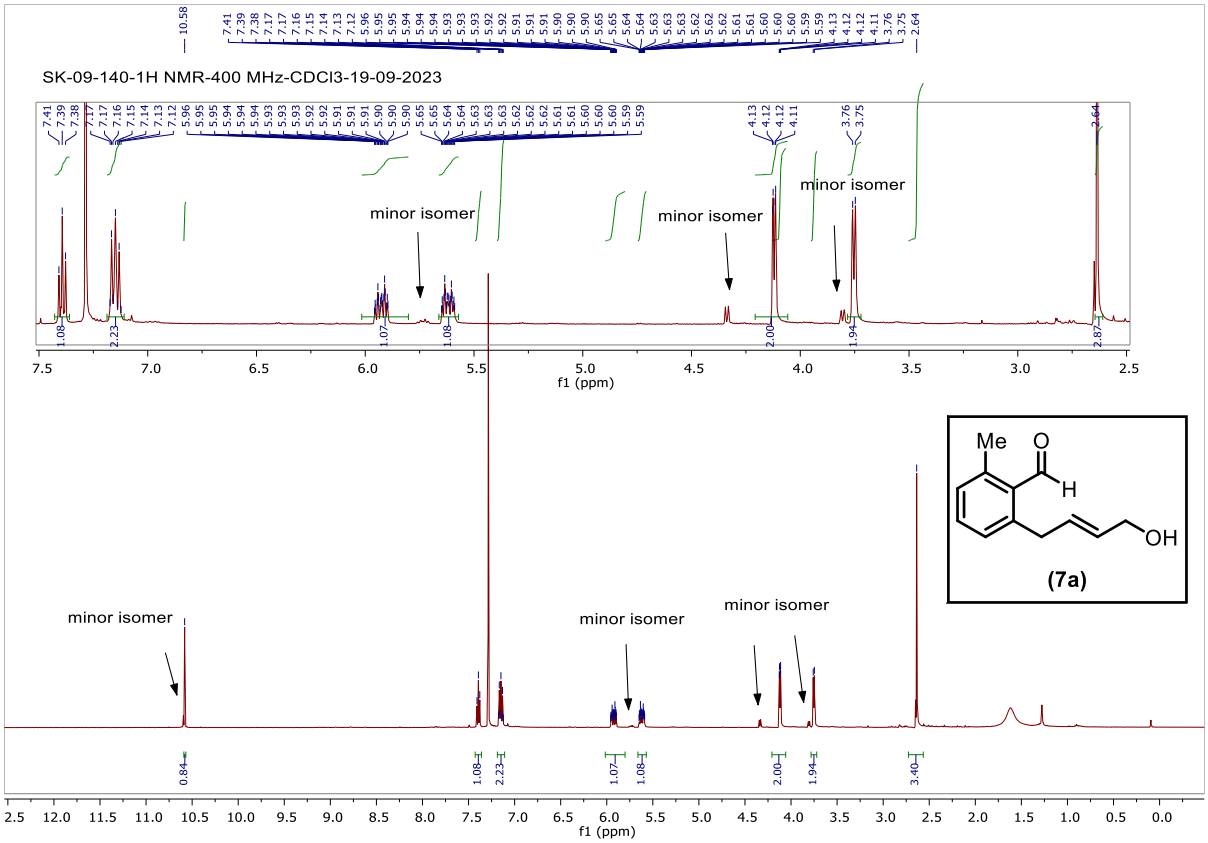


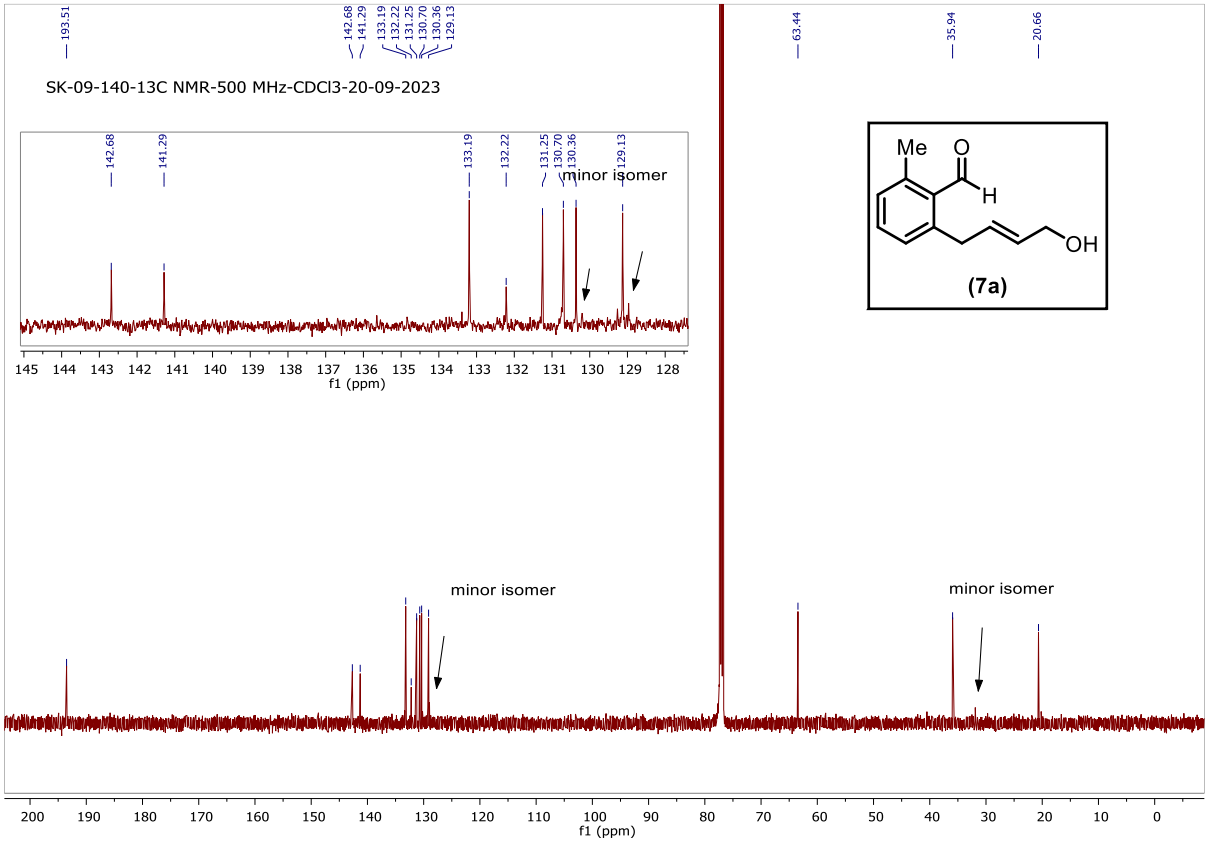




Bruker Compass DataAnalysis 4.0 printed: 06-09-2023 12:51:34 Page 1 of 1

Copies of NMR spectra of 7a:





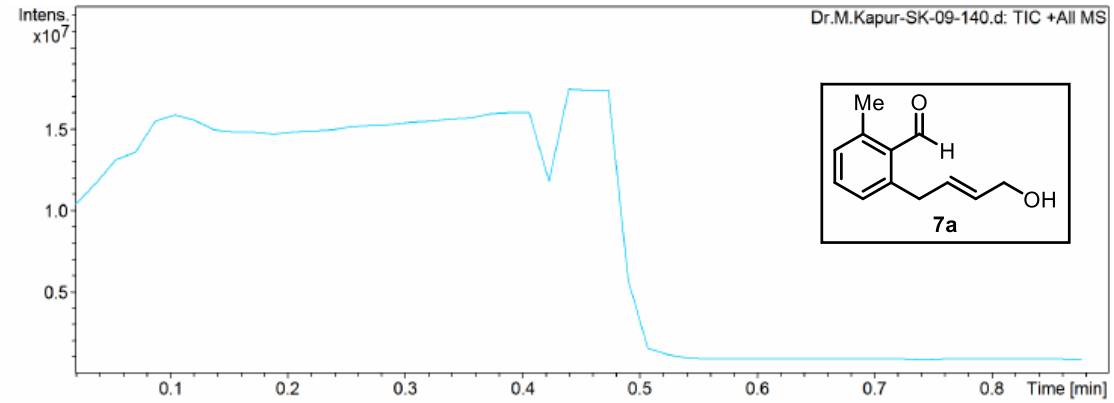
Display Report

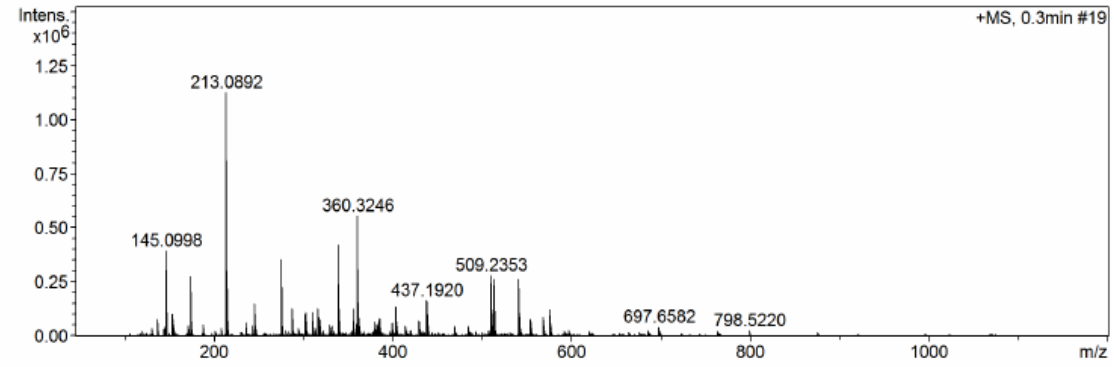
Analysis Info

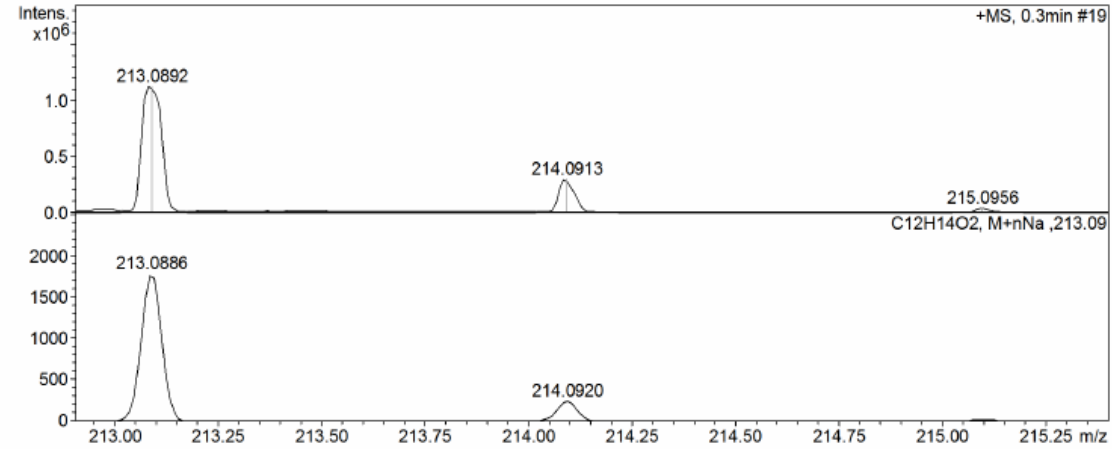
Analysis Name	D:\Data\USER DATA 2024\April2024\26-april\Dr.M.Kapur-SK-09-140.d	Acquisition Date	26-04-2024 16:57:41
Method	tune_low.m	Operator	Bruker
Sample Name	SK-09-140	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	5.8 psi
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

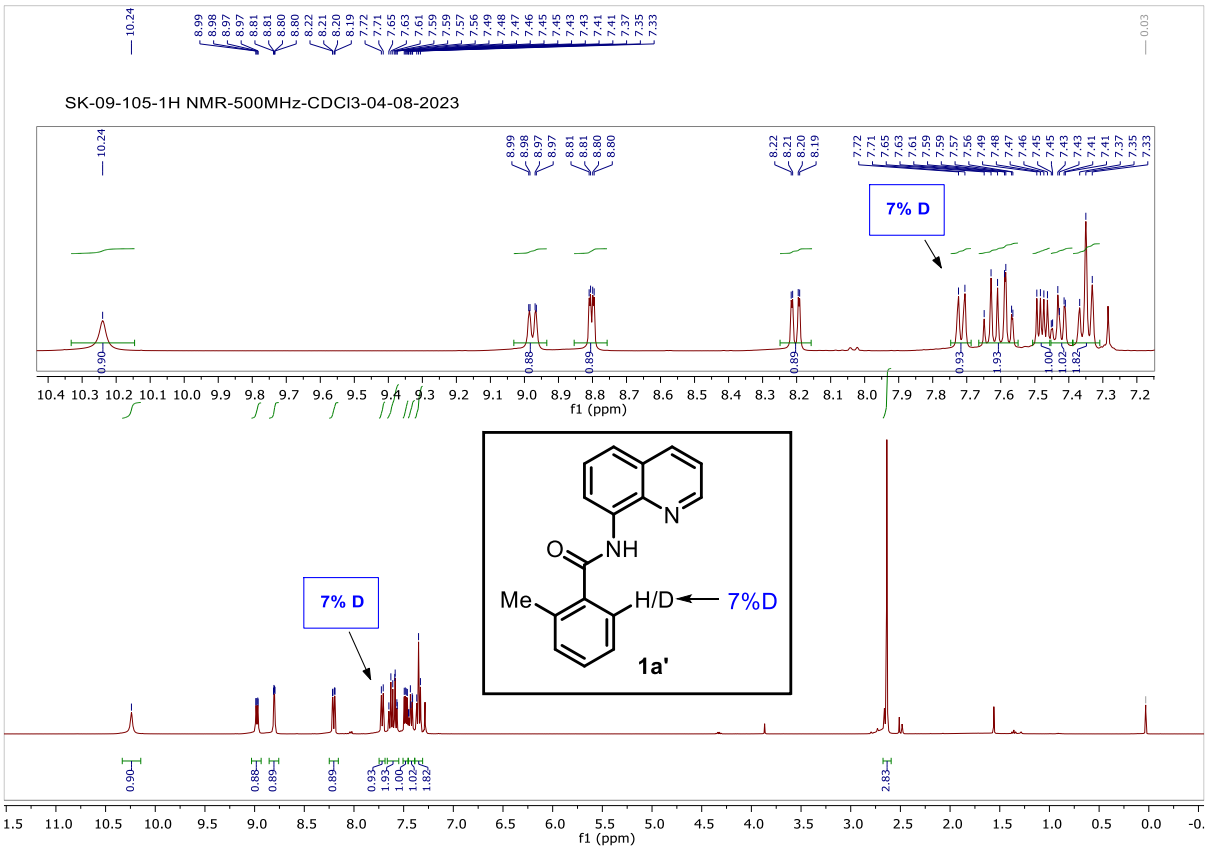


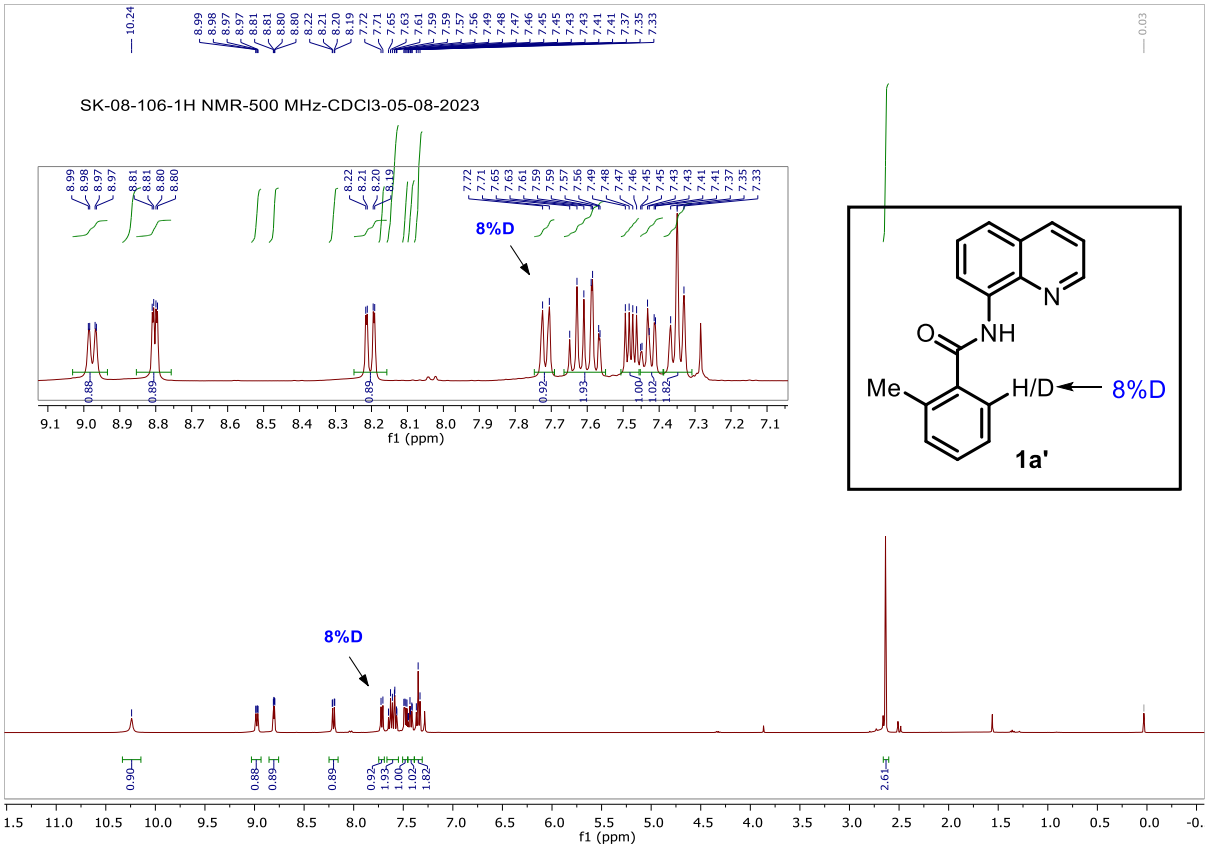




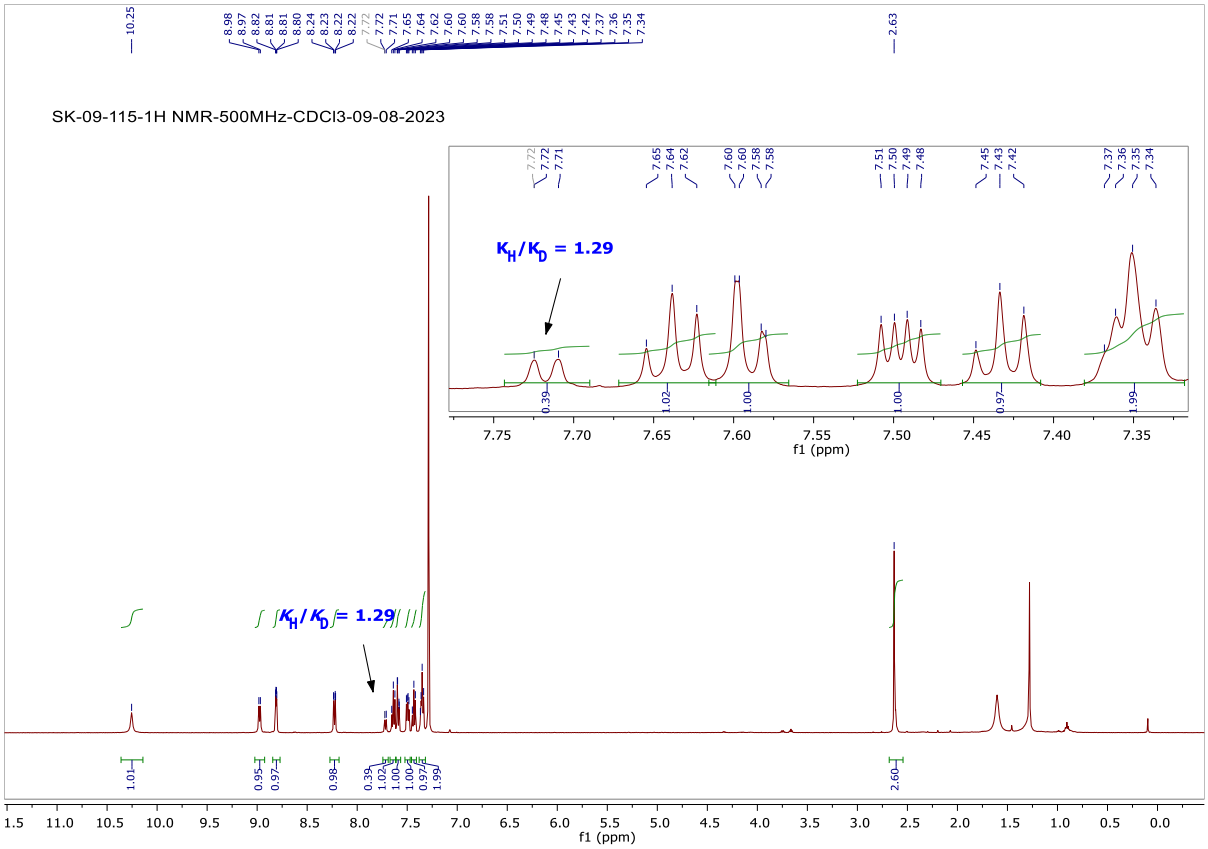
Copies of NMR spectra of Mechanistic Studies and Control Experiments:

Reversibility Studies:

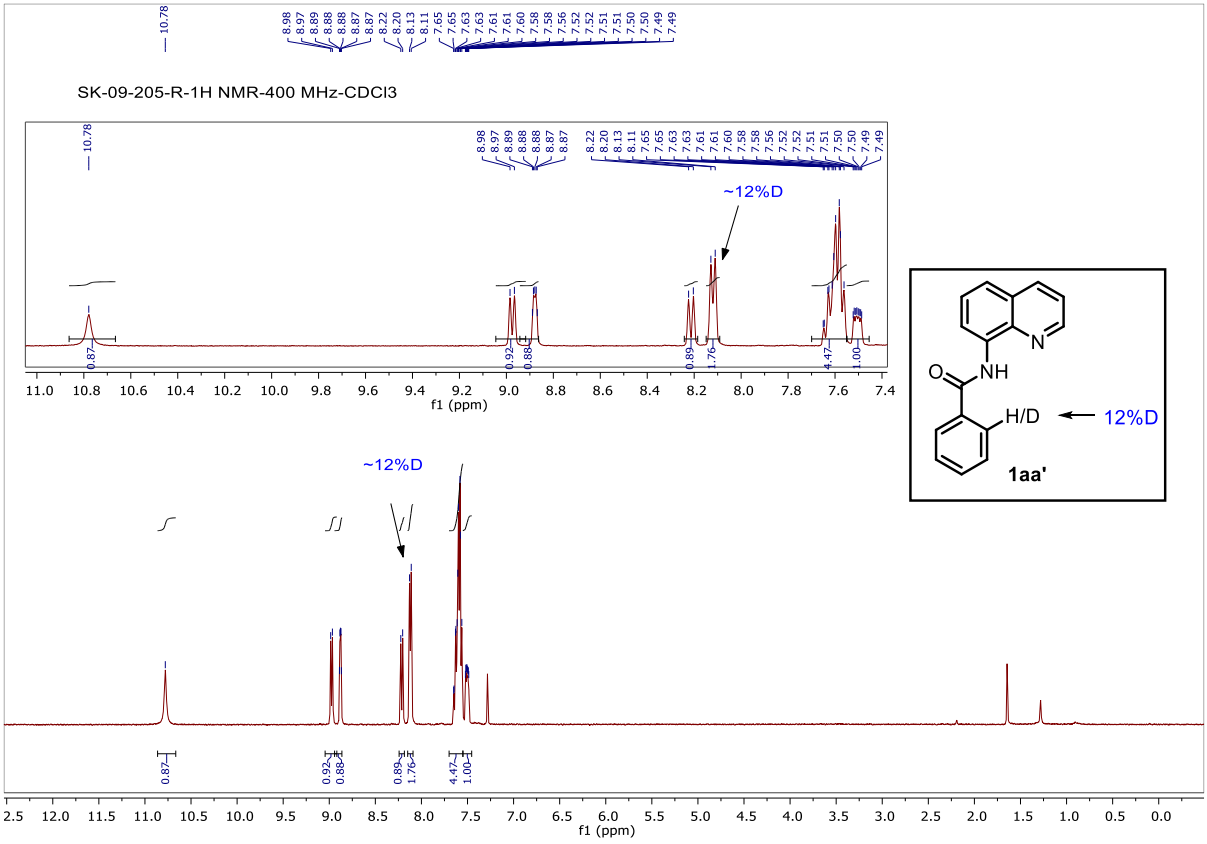


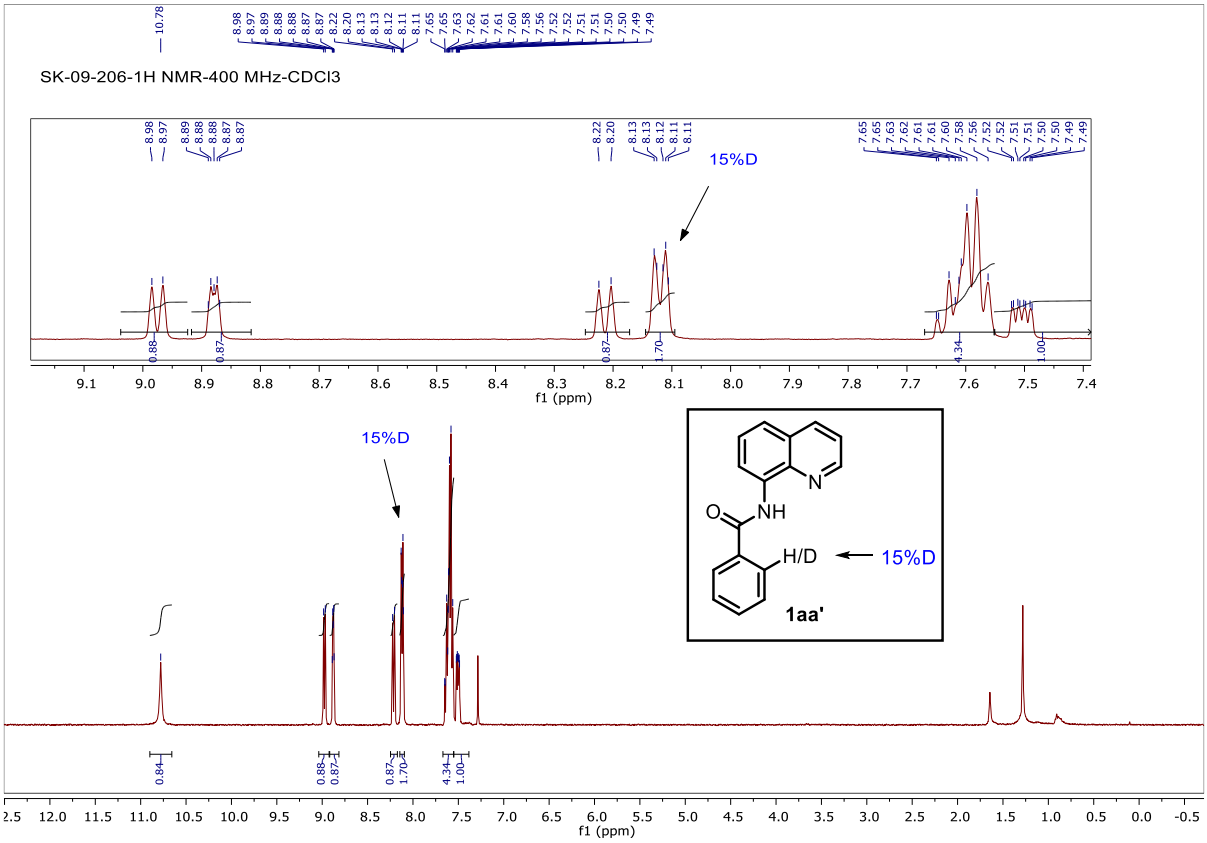


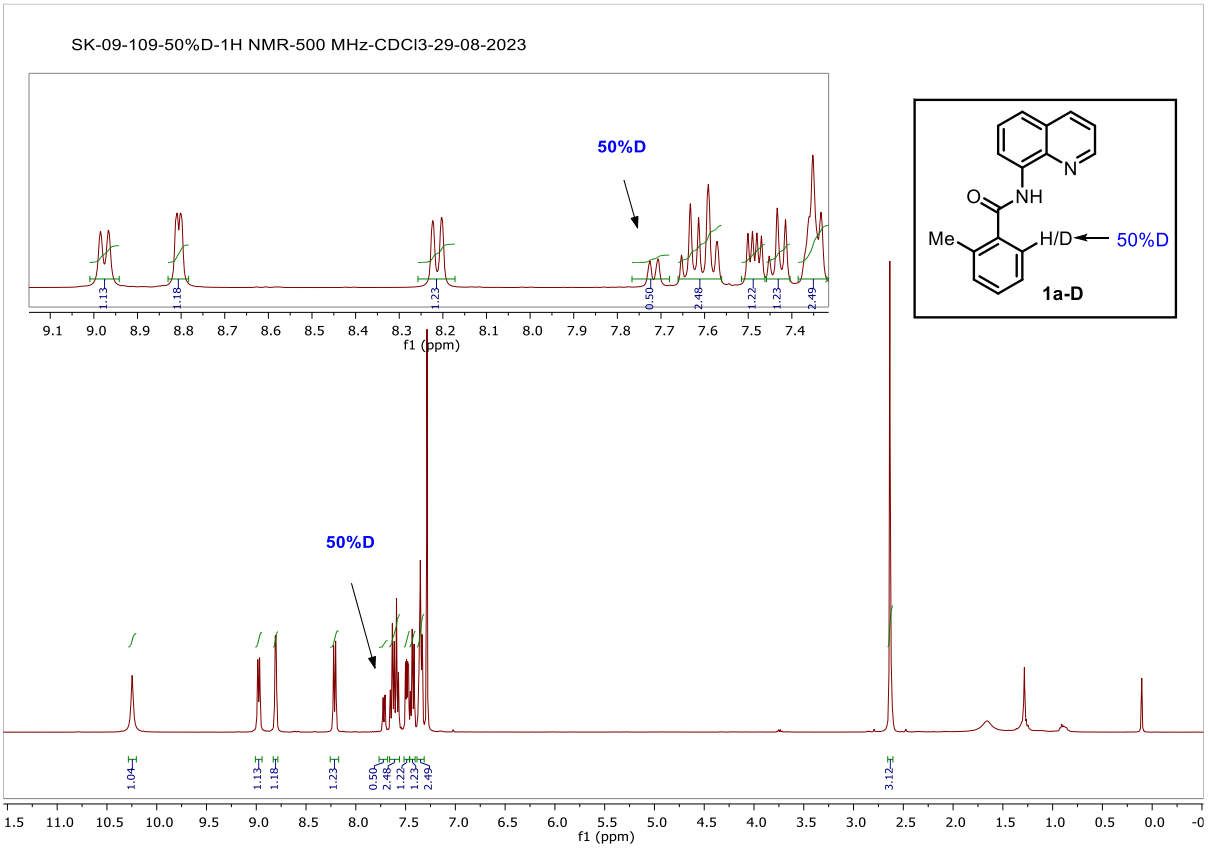
Studies to check for a KIE:

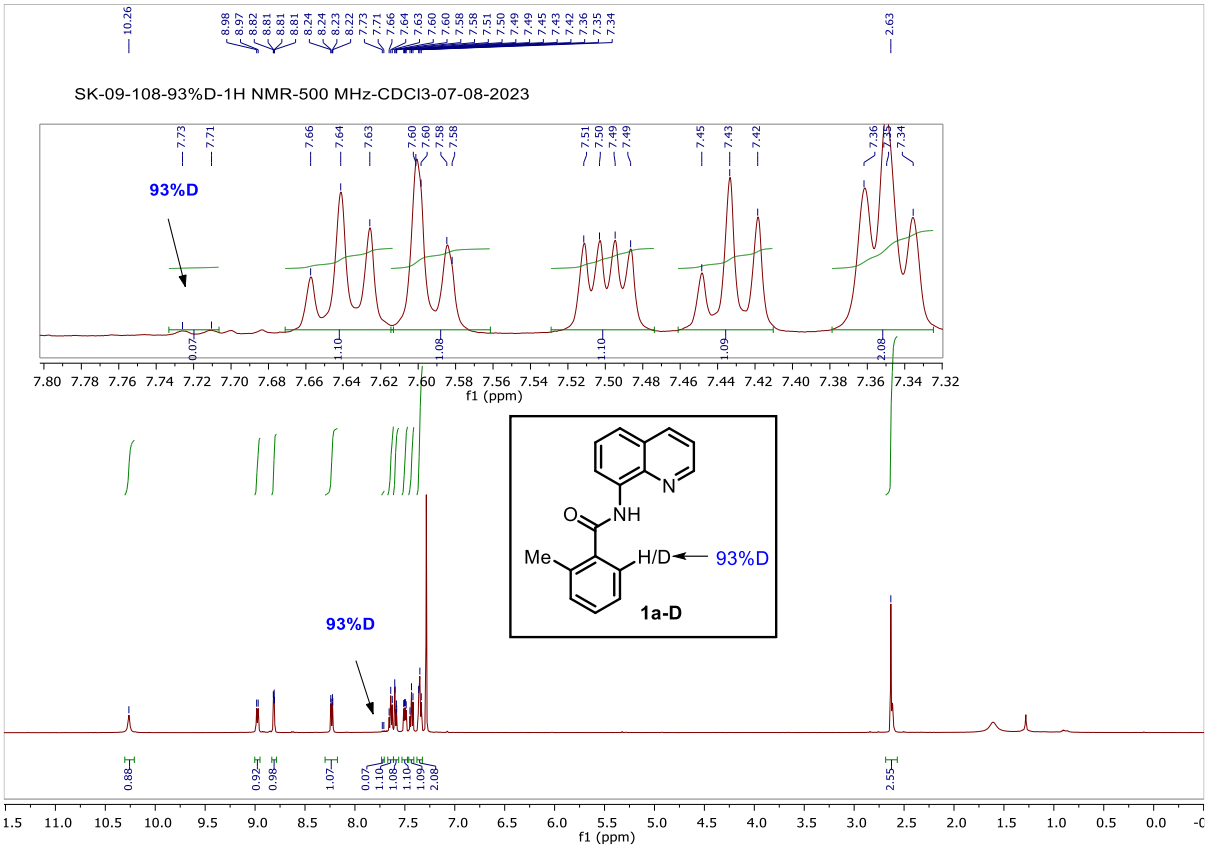


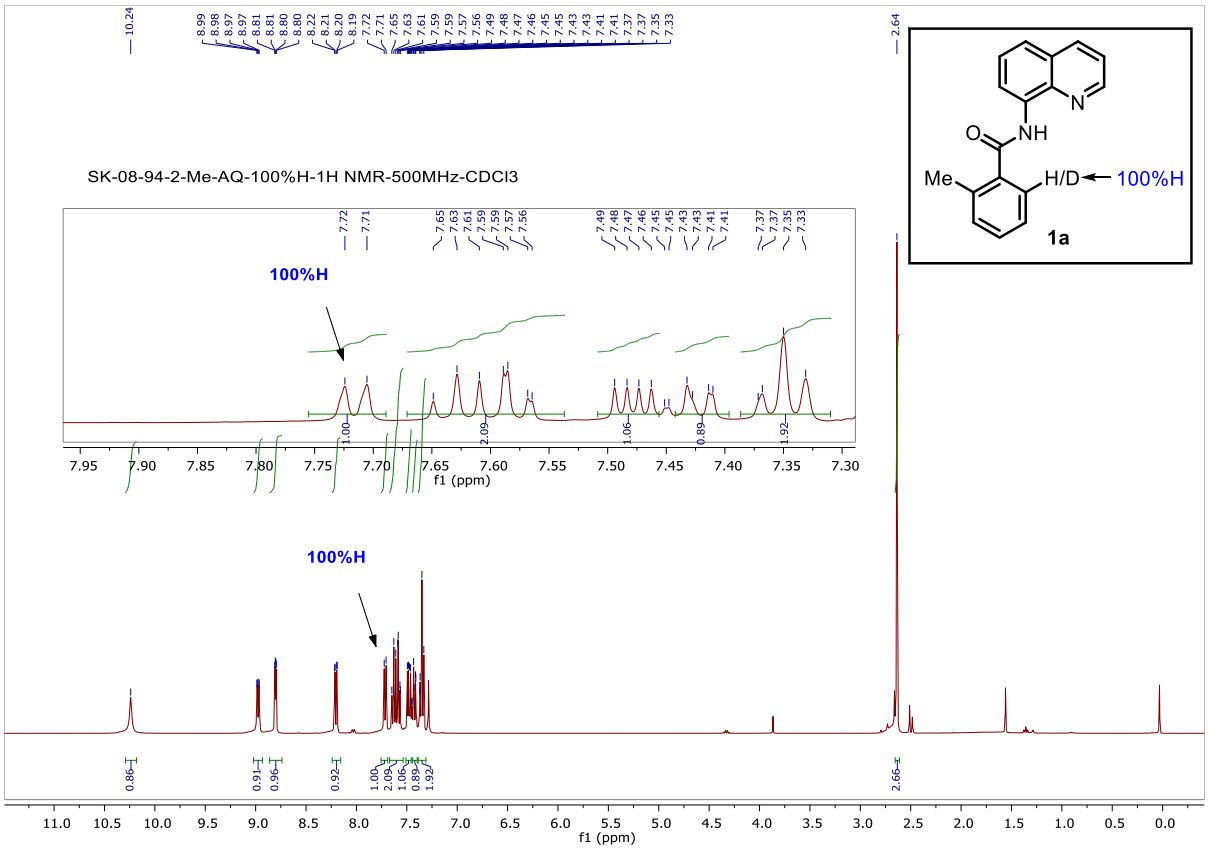
Reversibility studies to check for reason of *ortho*-constraint in the starting materials:




SK-09-206-1H NMR-400 MHz-CDCl3
15%D
15%D
O
NH
N
H/D
15%D
1aa'
f1 (ppm)


SK-09-109-50%D-1H NMR-500 MHz-CDCl3-29-08-2023
50%D
50%D
O
NH
N
Me
H/D
50%D
1a-D
f1 (ppm)


SK-09-108-93%D-1H NMR-500 MHz-CDCl3-07-08-2023
93%D
93%D
93%D
1a-D
f1 (ppm)


SK-08-94-2-Me-AQ-100%H-1H NMR-500MHz-CDCl3
100%H
100%H
100%H
1a
f1 (ppm)

Crystal Data:

X-ray diffraction structural analysis data of (*E*)-5b:

Sample preparation: 5 mg of **5** (colorless gel) was taken in a 10 mL beaker and dissolved in a minimal amount of dichloromethane. Hexane (5 mL) was added to the beaker along the wall. The beaker was capped loosely and kept at 4 ℃ for slow evaporation. After 10 days, a single crystal was obtained which was subjected to X-ray diffraction.

Table 1 Crystal data and structure refinement for (*E*)-5b.

Identification code	5b
Empirical formula	$C_{21}H_{19}BrN_2O_2$
Formula weight	411.28
Temperature/K	140.00
Crystal system	monoclinic
Space group	C2/c
a/Å	29.287(7)
b/Å	8.8974(18)
c/Å	14.848(3)
α/°	90
β/°	110.050(12)
γ/°	90
Volume/Å^3	3634.4(14)
Z	8
ρ_{calc}g/cm^3	1.500
μ/mm^{-1}	2.280
F(000)	1672.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.812 to 55.972
Index ranges	-38 ≤ h ≤ 38, -11 ≤ k ≤ 11, -19 ≤ l ≤ 19
Reflections collected	39175
Independent reflections	4360 [R_{int} = 0.1291, R_{sigma} = 0.0732]

Data/restraints/parameters	4360/2/246
Goodness-of-fit on F^2	1.112
Final R indexes [I>=2σ (I)]	R_1 = 0.0961, wR_2 = 0.2067
Final R indexes [all data]	R_1 = 0.1572, wR_2 = 0.2342
Largest diff. peak/hole / e $Å^{-3}$	1.54/-0.69

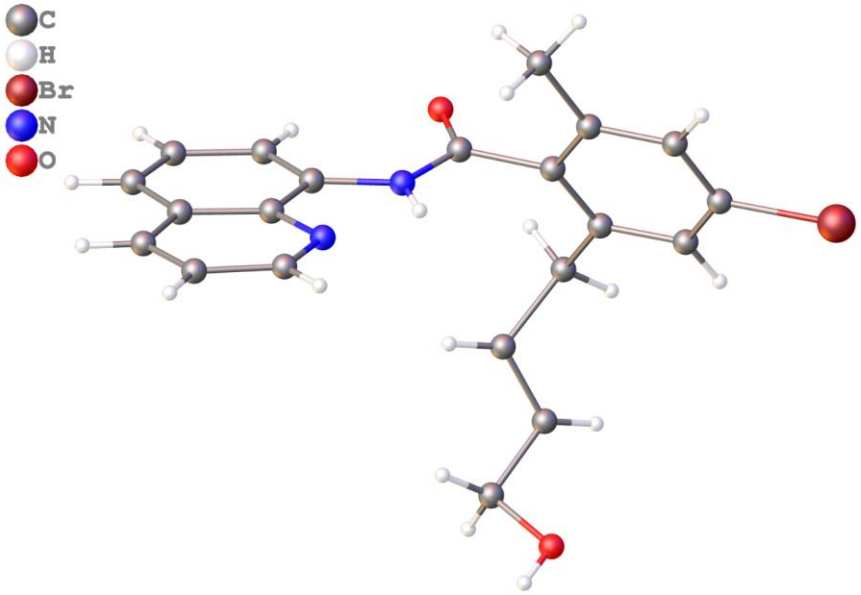


Figure 1: Thermal ellipsoidal plot (50% probability) for compound **(*E*)-5b.**

CCDC−2349339 contains the supplementary crystallographic data for (*E*)-**5b**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.