Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Switch to Vinylogous Reactivity of Vinyl Diazo Esters for the C–H Allylation of Benzamides by Merging Cobalt and Photoredox Catalysis

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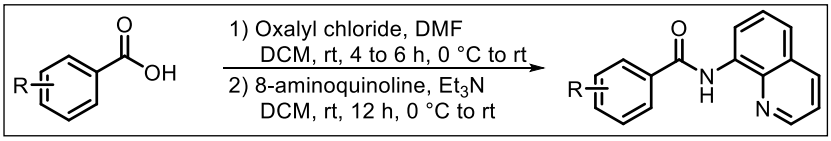
Experimental:

(1) General Methods:

All commercially available compounds were used without purification. Unless otherwise noted, all reactions were performed in oven-dried glassware. 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 was distilled from CaH_2.[1] Petroleum ether with a boiling range of 40−60 °C were used. Melting points are uncorrected. ^{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; 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 7.26; ^{13}C δ 77.0). HRMS: Bruker Daltonics MicroTOF Q-II with electron spray ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI). 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.

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

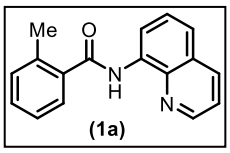
1. Synthesis of *N*-(quinolin-8-yl) benzamides:



Procedure: To an oven-dried round bottom flask charged with a magnetic stir bar, were added the 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.

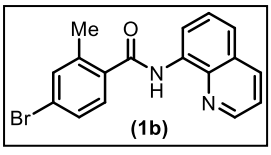
To another oven-dried round bottom flask charged with a magnetic stir bar was added 8-aminoquinoline (1 equiv.), Et_3N (1.5 equiv.) and DCM (15 mL) under N_2 atmosphere. To this, was added dropwise, the solution of acid chloride (1.5 equiv.) in DCM (5 mL) under ice-cold conditions and the mixture was stirred overnight at room temperature. Then the reaction mixture was 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):[1a]



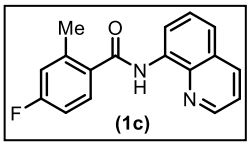
Prepared by following the general procedure and the title compound was isolated in 78% (306 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1a]

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



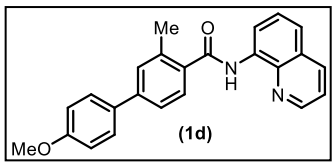
Prepared by following the general procedure and the title compound was isolated in 72% (368 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1a]

4-fluoro-2-methyl-*N*-(quinolin-8-yl)benzamide (1c):[1b]



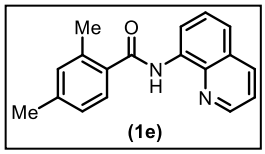
Prepared by following the general procedure and the title compound was isolated in 80% (336 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1b]

4'-methoxy-3-methyl-*N*-(quinolin-8-yl)-[1,1'-biphenyl]-4-carboxamide (1d):[1c]



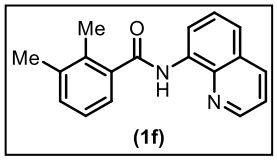
Prepared by following the general procedure and the title compound was isolated in 71% (390 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1c]

2,4-dimethyl-*N*-(quinolin-8-yl)benzamide (1e):[1b]



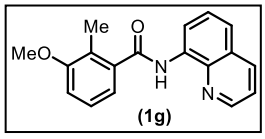
Prepared by following the general procedure and the title compound was isolated in 81% (336 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1c]

2,3-dimethyl-*N*-(quinolin-8-yl)benzamide (1f):[1b]



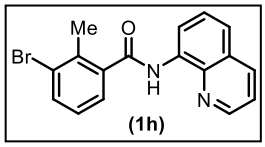
Prepared by following the general procedure and the title compound was isolated in 81% (336 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1c]

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



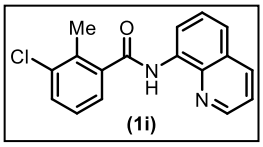
Prepared by following the general procedure and the title compound was isolated in 73% (321 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1b]

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



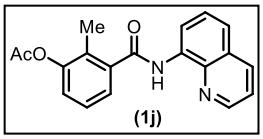
Prepared by following the general procedure and the title compound was isolated in 75% (383 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1d]

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



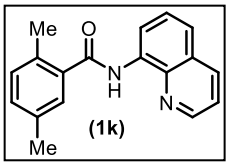
Prepared by following the general procedure and the title compound was isolated in 82% (365 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1e]

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



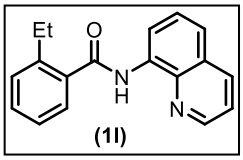
Prepared by following the general procedure and the title compound was isolated in 70% (335 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1a]

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



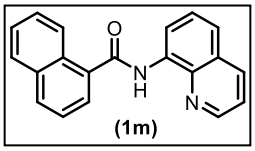
Prepared by following the general procedure and the title compound was isolated in 88% (364 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1b]

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



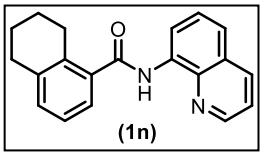
Prepared by following the general procedure and the title compound was isolated in 82% (340 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1a]

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



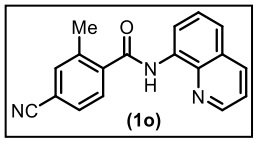
Prepared by following the general procedure and the title compound was isolated in 75% (334 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1a]

***N*-(quinolin-8-yl)-5,6,7,8-tetrahydronaphthalene-1-carboxamide (1n):**[1d]



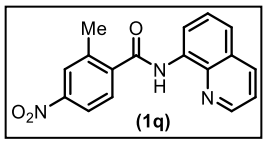
Prepared by following the general procedure and the title compound was isolated in 82% (381 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1d]

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



Prepared by following the general procedure and the title compound was isolated in 78% (224 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1d]

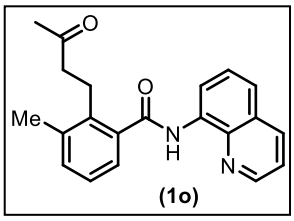
2-Methyl-4-nitro-*N*-(quinoline-8-yl)benzamide (1p):[1g]



Prepared by following the general procedure and the title compound was isolated in 64% (196 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.[1d]

Synthesis of 3-methyl-2-(3-oxobutyl)-*N*-(quinolin-8-yl)benzamide (1q):[1f]

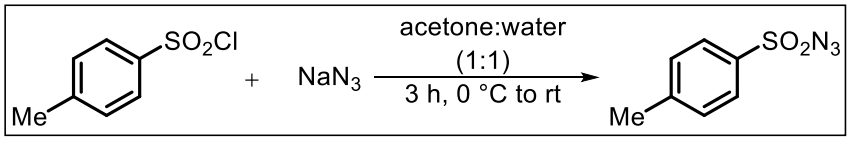
To an oven-dried sealed tube charged with a magnetic stir-bar, 3-methyl-*N*-(quinolin-8-yl)benzamide (0.50 mmol, 130 mg), methyl vinyl ketone (MVK) (1.00 mmol, 110 μL), $RuCl_2(PPh_3)_2$ (0.05 mmol, 63.5 mg), sodium pivalate (13.5 mg, 0.12 mmol) and toluene (1 mL) were added under N_2 atmosphere. The tube was capped and introduced into an oil bath preheated to 105 °C. After stirring for 4h at that temperature, the mixture was cooled and filtered through a Celite pad and concentrated under reduced pressure. The resulting residue was purified by silica gel flash column chromatography (eluent: Petroleum ether/EtOAc = 19/1) to obtain the desired alkylated product (83 mg, 50% yield). Spectral data obtained were in good agreement with those reported in the literature.[1f]



2. Preparation of vinyl diazoesters:

(A) General Procedure:

(i) Synthesis of *p*-toluenesulfonylazide:

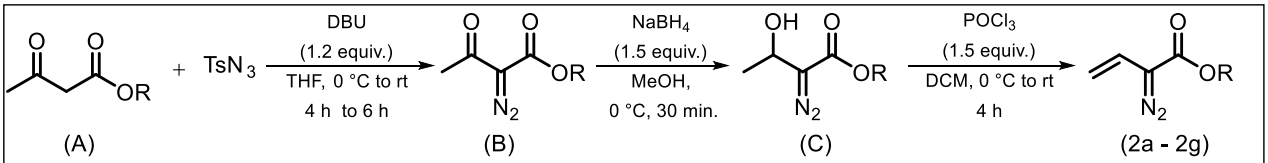


To a solution of *p*-toluenesulfonylchloride (10 g, 52.45 mmol, 1 equiv.) in a mixture of acetone (158 mL) and H_2O (158 mL), was added sodium azide (3.41 g, 52.45 mmol, 1 equiv.) portion-wise

over 15 min at 0 °C. After stirring for 3h at room temperature, the reaction mixture was concentrated under reduced pressure until all the acetone was evaporated. The concentrated reaction mixture was extracted thrice with diethyl ether which is dried over Na_2SO_4 and the solvent was evaporated under reduced pressure maintaining the bath temperature at 30 °C, resulting in *p*-toluenesulfonylazide (10.25 g, 99% crude yield) as a colorless oil.

(II) **Synthesis of vinyl diazo esters:**

To a solution of the alkyl acetoacetate (**A**) (1 equiv., 20 mmol) in anhydrous THF (30 mL) was added DBU (1.2 equiv., 24.0 mmol) at 0 °C. The resulting solution was stirred for 5 minutes, and to this, a solution of tosyl azide (1.1 equiv., 22 mmol) in THF (10 mL) was added over 5 minutes. The resulting solution was warmed to room temperature and stirred for 4 h. The solvent was evaporated, and the resulting residue was diluted with water (100 mL) and extracted with ethyl acetate (100 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (hexane/ethyl acetate = 6/1) to give alkyl diazo acetoacetate (**B)** as a yellow oil.



R = ^{t}Bu	R = ^{t}Bu, 82%	R = ^{t}Bu, 88%	2a, R = ^{t}Bu, 80%
R = Me	R = Me, 85%	R = Me, 86%	2b, R = Me, 78%
R = Et	R = Et, 86%	R = Et, 89%	2c, R = Et, 78%
R = ^{i}Pr	R = ^{i}Pr, 88%	R = ^{i}Pr, 82%	2d, R = ^{i}Pr, 79%
R = Bn	R = Bn, 84%	R = Bn, 86%	2e, R = Bn, 82%
R = Isoamyl	R = Isoamyl, 81%	R = Isoamyl, 89%	2f, R = Isoamyl, 70%
R = *n*-Octane	R = *n*-Octane, 80%	R = *n*-Octane, 88%	2g, R = *n*-Octane, 74%

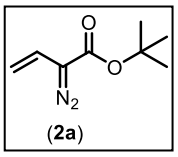
To a solution of (**B**) (1 equiv., 16.1 mmol) in MeOH (20 mL) cooled to 0 °C, was slowly added $NaBH_4$ (1.5 equiv., 24 mmol). The resulting solution was warmed to room temperature and stirred for 30 minutes following which the solvent was removed under reduced pressure and the residue was diluted with water (50 mL) and extracted with ethyl acetate (50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 4/1) to give **C** as a yellow oil.

To a solution of **C** (1 equiv., 10 mmol) and Et_3N (4.0 equiv., 40 mmol) in DCM (100 mL) at 0 °C was slowly added a solution of $POCl_3$ (1.5 equiv.) in DCM (10 mL) over 25 minutes. The resulting

solution was warmed to room temperature and stirred for 4 h. The solution was quenched with water (20 mL) and transferred to a separatory funnel and the layers were separated. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 50/1) to give the vinyl diazo esters (**2a–2g**) as red oils.

***tert*-butyl 2-diazobut-3-enoate (2a)**: [2a]

Reaction performed by following the general procedure (II), using ethyl *tert*-butyl acetoacetate

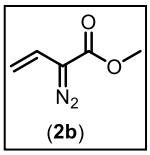


(**2a**)

(3.16 g, 20 mmol); Yield: 80%, (2.36 g); Physical appearance: red oil; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.15 (dd, J = 17.4, 11.0 Hz, 1H), 5.10 (d, J = 11.0 Hz, 1H), 4.84 (d, J = 17.4 Hz, 1H), 1.52 (s, 9H). Spectral data obtained were in good agreement with those reported in the literature.[2a]

Methyl 2-diazobut-3-enoate (2b): [2b]

Reaction performed by following the general procedure (II), using ethyl methyl acetoacetate (2.32

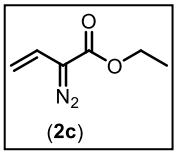


(**2b**)

g, 20 mmol); Yield: 78%, (1.69 g); Physical appearance: red oil; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.18 (dd, J = 17.4, 11.0 Hz, 1H), 5.15 (d, J = 11.9 Hz, 1H), 4.89 (d, J = 17.4 Hz, 1H), 3.83 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.[2b]

Ethyl 2-diazobut-3-enoate (2c): [2a]

Reaction performed by following the general procedure (II), using ethyl acetoacetate (1.30 g, 10

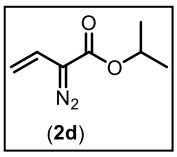


(**2c**)

mmol); Yield: 78%, (1.09 g); Physical appearance: red oil; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.19 (dd, J = 17.4, 11.0 Hz, 1H), 5.13 (d, J = 11.0 Hz, 1H), 4.88 (d, J = 17.4 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). Spectral data obtained were in good agreement with those reported in the literature.[2a]

Isopropyl 2-diazobut-3-enoate (2d): [2b]

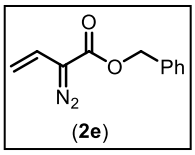
Reaction performed by following the general procedure (II), using ethyl acetoacetate (2.88 g, 20 mmol); Yield: 79%, (2.00 g); Physical appearance: red oil; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.19 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.20 – 5.14 (m, 1H), 5.12 (d, *J* = 11.0 Hz, 1H), 4.86 (d, *J* = 17.4 Hz, 1H), 1.31 (s, 3H), 1.29 (s, 4H). Spectral data obtained were in good agreement with those reported in the literature.[2b]



(**2d**)

Benzyl 2-diazobut-3-enoate (2e): [2a]

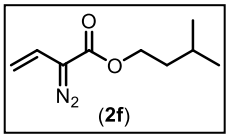
Reaction performed by following the general procedure (II), using benzyl acetoacetate (3.84 g, 20 mmol); Yield: 82%, (2.85 g); Physical appearance: red oil; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 5H), 6.22 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.29 (s, 2H), 5.15 (d, *J* = 11.0 Hz, 1H), 4.90 (d, *J* = 17.4 Hz, 1H). Spectral data obtained were in good agreement with those reported in the literature.[2a]



(**2e**)

Isopentyl 2-diazobut-3-enoate (2f): [2a]

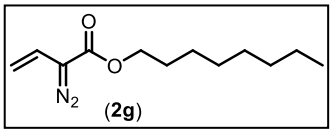
Reaction performed by following the general procedure (II), using isoamyl acetoacetate (3.44 g, 20 mmol); Yield: 90%, (2.27 g); Physical appearance: red oil; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.19 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.13 (d, *J* = 11.0 Hz, 1H), 4.88 (d, *J* = 17.4 Hz, 1H), 4.27 (t, *J* = 6.8 Hz, 2H), 1.78 – 1.67 (m, 1H), 1.63 – 1.53 (m, 3H), 0.96 (s, 3H), 0.95 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.[2a]



(**2f**)

Octyl 2-diazobut-3-enoate (2g):

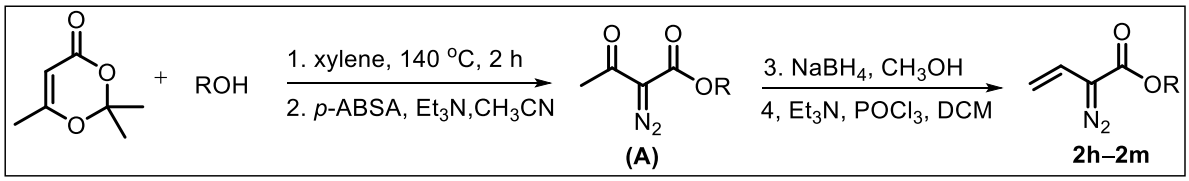
Reaction performed by following the general procedure (II), using octyl acetoacetate (4.28 g, 20 mmol); Yield: 74%, (2.92 g); Physical appearance: red oil; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.24 – 6.03 (m, 1H), 5.11 (d, *J* = 11.0 Hz, 1H), 4.85 (d, *J* = 17.4Hz, 1H), 4.25 – 4.16 (m, 2H), 1.71 – 1.58 (m, 2H), 1.41 – 1.17 (m, 10H), 0.95 – 0.81 (m, 3H); **^{13}C NMR** (126



(**2g**)

MHz, CDCl3) δ 164.86, 120.51, 107.24, 65.26, 31.74, 29.15, 29.13, 28.75, 25.80, 22.60, 14.02; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{20}N_2O_2$ 247.1417; Found 247.1394.

(i) General Procedure for the synthesis of vinyl diazo esters:



In an oven-dried round bottom flask equipped with a magnetic stir bar, the alcohol (10 mmol, 1 equiv.) and 2,2,6-trimethyl-1,3-dioxene-4-one (12 mmol, 1.2 equiv.) were dissolved in xylene (6 mL) and the resulting mixture was refluxed at 140 °C for 2 h under argon. The solvent was then evaporated by vacuum distillation, leaving behind a black oil. The crude mixture was purified by silica gel flash column chromatography (PE/EA = 10:1) to give the acetoacetate.

To a solution of the acetoacetate synthesized above (1 equiv., 12 mmol,) in MeCN (25 mL), cooled to 0 °C, was added *p*-acetamidobenzenesulfonyl azide (1.1 equiv., 13.2 mmol,), followed by triethylamine (1.5 equiv., 18 mmol,) and the resulting reaction was allowed to warm to rt for 2 h. The resulting pale-yellow precipitate was filtered, and the residue was concentrated, which is dissolved in DCM, and washed with brine, after which the DCM layer was concentrated and then purified by silica gel flash column chromatography (PE/EA = 10:1) to give 2-diazo-3-oxobutanoate **A**.

To a solution of 2-diazo-3-oxobutanoate **A** (1 equiv., 10 mmol,) in MeOH (30 mL) cooled to 0 °C, was added $NaBH_4$ (1.5 equiv., 15 mmol), slowly, in portions. The resulting solution was warmed to room temperature and stirred for 1 h. Thereafter, the MeOH was evaporated under reduced pressure and the residue was diluted with water and the mixture was extracted with ethyl acetate. The resulting residue was dried over anhydrous Na_2SO_4 and filtered. After the solvent was removed under reduced pressure, the crude product was purified by silica gel flash column chromatography (PE/EA = 5:1) to give 2-diazo-3-hydroxybutanoate as a yellow oil.

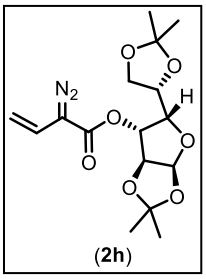
To a solution of 2-diazo-3-hydroxybutanoate (8 mmol, 1 equiv.) and Et_3N (4.0 equiv., 32 mmol) in DCM (40 mL) cooled to 0 °C, was slowly added a solution of $POCl_3$ (1.5 equiv., 12.0 mmol) in

DCM (10 mL) over 20 minutes. The resulting solution was warmed to room temperature and stirred for 2 h. The solution was washed with water and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel flash chromatography (PE/EA = 50:1) to afford the vinyl diazoesters (**2h–2l**).

Notes: *(a) We have never observed any explosion during the preparation and manipulation of vinyl diazo compounds at the scales indicated here. (b) All the vinyl diazo ester were stored in the freezer at –20 °C.*

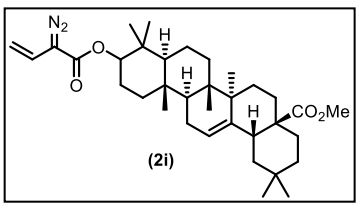
(3a*S*,5*S*,6*R*,6a*S*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*] [1,3]dioxol-6-yl 2-diazobut-3-enoate (2h):[2c]

Reaction performed by following above general procedure (II), using (3a*S*,5*S*,6*R*,6a*S*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 3-oxobutanoate (3.4 g, 10 mmol); Yield: 80%, (2.52 g); Physical appearance: red oil; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.15 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.91 (d, *J* = 3.6 Hz, 1H), 5.36 (d, *J* = 2.6 Hz, 1H), 5.18 (d, *J* = 11.0 Hz, 1H), 4.93 (d, *J* = 17.4 Hz, 1H), 4.61 (d, *J* = 3.6 Hz, 1H), 4.26 (dd, *J* = 8.0, 2.9 Hz, 1H), 4.22 – 4.16 (m, 1H), 4.16 – 4.07 (m, 1H), 4.03 (dd, *J* = 8.5, 4.9 Hz, 1H), 1.55 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.[2c]



(4a*R*,6a*R*,6b*S*,8a*S*,12a*S*,12b*S*,14b*R*)-methyl 10-((2-diazobut-3-enoyl)oxy)-2,2,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-4a-carboxylate (2i): [2c]

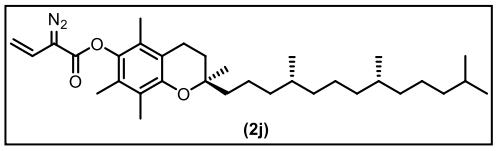
Reaction performed by following above general procedure (II), using methyl (4a*R*,6a*R*,6b*S*,8a*S*,12a*S*,12b*S*,14b*R*)-2,2,6a,6b,9,9,12a-heptamethyl-10-((3-oxobutanoyl)oxy)-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(*2H*)-carboxylate (2.77 g, 5 mmol); Yield: 71%, (1.20 g); Physical appearance: red solid; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.19 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.31 (t, *J* = 3.5 Hz, 1H), 5.13 (d, *J* = 11.0 Hz, 1H), 4.88 (d, *J* = 17.4 Hz, 1H), 4.63 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.65 (s, 3H), 2.89 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.04 – 1.95 (m, 1H), 1.95 –



1.87 (m, 2H), 1.77 – 1.59 (m, 10H), 1.51 – 1.24 (m, 5H), 1.24 – 1.02 (m, 7H), 0.96 (d, *J* = 4.9 Hz, 6H), 0.94 – 0.90 (m, 6H), 0.86 (d, *J* = 8.8 Hz, 3H), 0.75 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.[2c]

(*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 2-diazobut-3-enoate (2j): [2c]

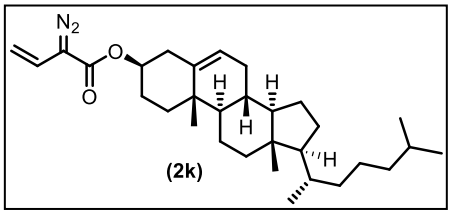
Reaction performed by following above general procedure (II), using (*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 3-oxobutanoate (2.57 g, 5 mmol); Yield: 70%,



(1.52 g); Physical appearance: red oil; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.33 (dd, *J* = 17.2, 11.1 Hz, 1H), 5.22 (d, *J* = 11.0 Hz, 1H), 5.00 (d, *J* = 17.4 Hz, 1H), 2.63 (t, *J* = 6.7 Hz, 2H), 2.14 (d, *J* = 10.7 Hz, 3H), 2.08 (s, 3H), 2.05 (d, *J* = 8.4 Hz, 3H), 1.94 – 1.96 (m, 2H), 1.61 – 1.52 (m, 3H), 1.39 – 1.21 (m, 15H), 1.18 – 1.07 (m, 6H), 0.92 – 0.88 (m, 12H). Spectral data obtained were in good agreement with those reported in the literature.[2]

(3*R*,8*R*,9*R*,10*S*,13*S*,14*R*)-3-((1-diazoallyl)oxy)-10,13-dimethyl-17-((*S*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene (2k): [2c]

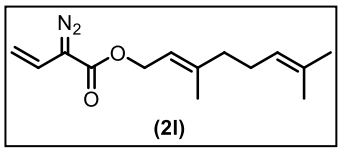
Reaction performed by following above general procedure (II), using (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-oxobutanoate (2.35 g, 5 mmol); Yield: 66%,



(9.52 g); Physical appearance: red solid; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.20 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.41 (d, *J* = 4.9 Hz, 1H), 5.13 (d, *J* = 11.0 Hz, 1H), 4.87 (d, *J* = 17.4 Hz, 1H), 4.75 (dt, *J* = 10.6, 5.5 Hz, 1H), 2.44 – 2.31 (m, 2H), 2.13 – 1.77 (m, 6H), 1.69 – 1.39 (m, 10H), 1.29 – 0.95 (m, 16H), 0.89 (dd, *J* = 6.6, 2.2 Hz, 6H), 0.70 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.[2c]

(*E*)-3,7-dimethylocta-2,6-dien-1-yl 2-diazobut-3-enoate (2l):

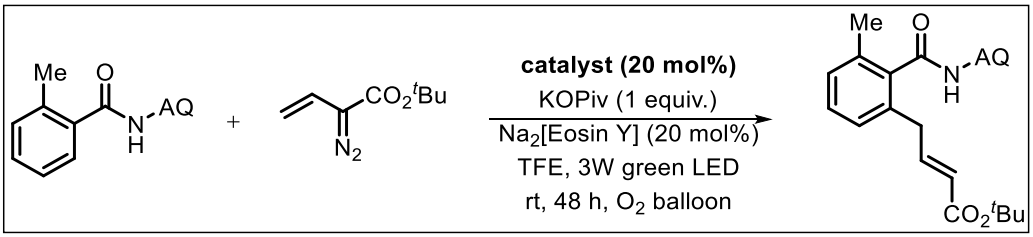
Reaction performed by following above general procedure (II), using 3,7-dimethyloct-6-en-1-yl 3-oxobutanoate (2.38 g, 10 mmol); Yield: 60%, (1.48 g); Physical appearance: red oil; TLC R_f 0.3 (50:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.19 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.39 (t, *J* = 7.1 Hz, 1H), 5.16 – 5.07 (m, 2H), 4.86 (d, *J* = 17.3 Hz, 1H), 4.72 (d, *J* = 7.3 Hz, 2H), 2.21 – 2.05 (m, 4H), 1.79 (s, 3H), 1.70 (s, 3H), 1.62 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.69, 137.75, 127.01, 118.29, 115.36, 113.85, 102.04, 56.47, 48.21, 26.96, 21.43, 20.45, 18.30, 12.44; **ESI-HRMS**: Calcd. for $C_{14}H_{20}N_2O_2$ $[M+Na]^+$ 271.1417; Found 271.1411.



(2l)

(2) Optimization details for C–H bond allylation of benzamides:

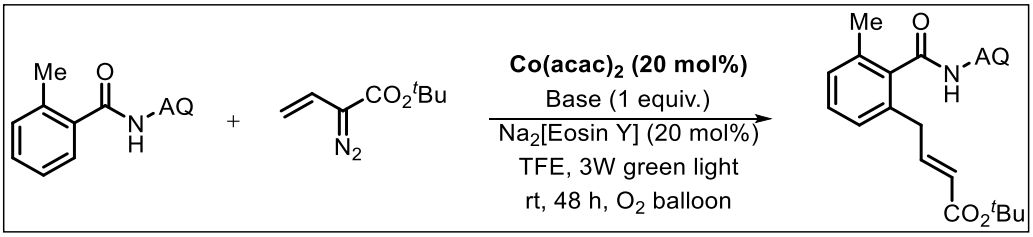
Table S1: Optimization of catalyst:



Sr. No.	Catalyst	Yield (%)[a]
1.	$Co(OAc)_2$	28%
2.	$Co(OAc)_2.4H_2O$	26%
3.	**$Co(acac)_2$**	**45%**
4.	$Co(acac)_3$	NR
5.	$CoCl_2$	NR
6.	$Ni(acac)_2$	NR
7.	$Ni(OAc)_2$	NR

[a] *Isolated yield; NR = No reaction*

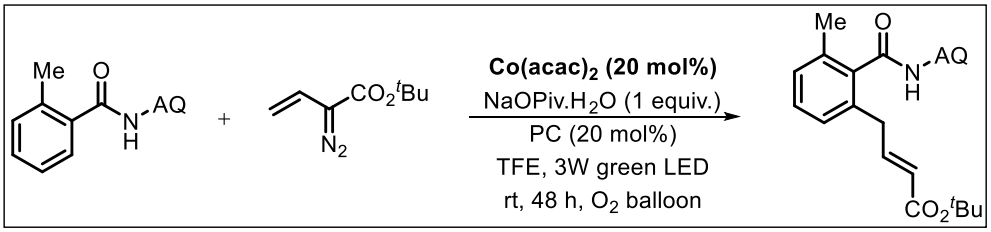
Table S2. Optimization of base:



Sr. No.	Base	Yield (%)[a]
1.	KOPiv	45%
2.	KOAc	26%
3.	CsOPiv	NR
4.	**$NaOPiv.H_2O$**	**65%**
5.	NaOAc	21%
6.	$NaOPiv.H_2O$ (2 equiv.)	61%
7.	NaOPiv. H_2O (50 mol%)	56%

[a] *Isolated yield; NR = No reaction*

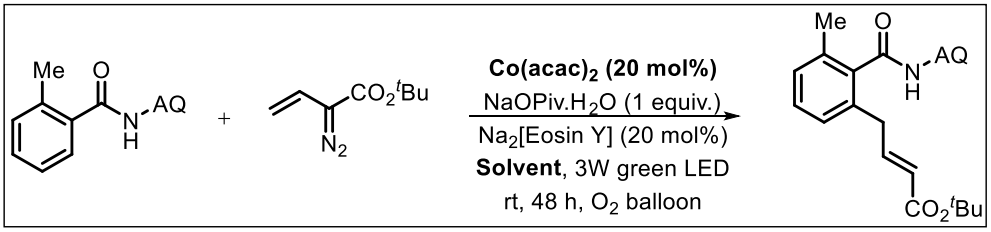
Table S3. Optimization of photocatalyst:



Sr. No.	Photocatalyst (PC)	Yield (%)[a]
1.	Eosin blue	45%
2.	$Ru(bpy)_3Cl_2$	41%
3.	**Na_2[Eosin Y]**	**65%**
4.	Rose Bengal	NR
5.	Na_2[Eosin Y] (10 mol%)	40%
6.	Na_2[Eosin Y] (30 mol%)	63%
7.[b]	Na_2[Eosin Y]	21%

[a] Isolated yield; [b] N_2 balloon were used; N.R. = No reaction

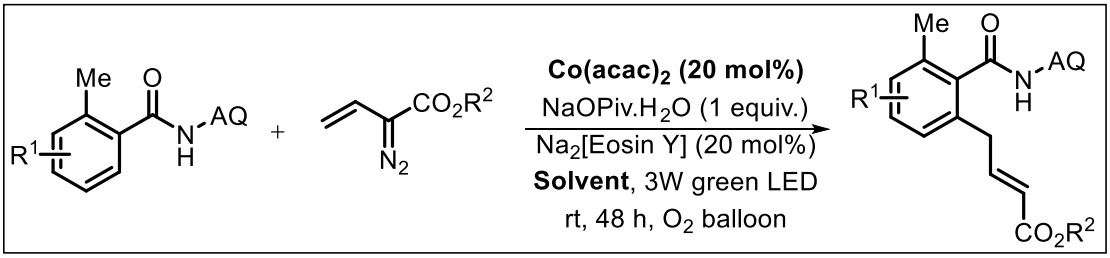
Table S4. Optimization of solvent:



Sr. No.	Solvent	Yield (%)[a]
1.	DCE	NR
2.	MeOH	29%
3.	**TFE**	**65%**
4.	HFIP	34%
5.	MeCN	39%
6.	EtOH	21%
7.	DMF	NR
8.[b]	TFE	41%

[a] Isolated yield; NR = No reaction; [b]10 mol% of $Co(acac)_2$ was used.

(3) General procedure for the cobalt-catalyzed C–H allylation of benzamides:



In an oven-dried pressure tube equipped with a stir bar, the *N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and vinyl diazo ester (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol), and Na_2[Eosin Y] (20 mol%, 0.02 mmol) were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a green LED (3W × 20) environment under an O_2 atmosphere using oxygen balloon. After 24 hours, the second portion of vinyl diazo ester (1.5 equiv., 0.15 mmol) was added and the reaction progress was further 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 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.

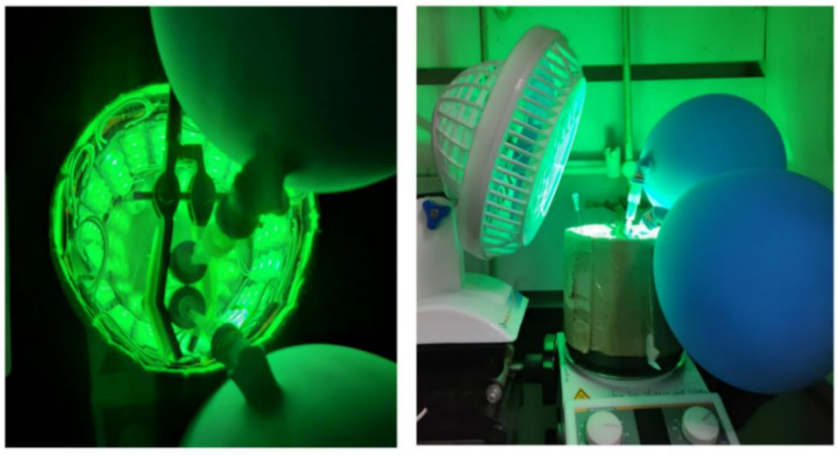
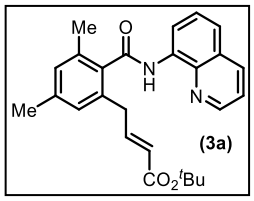


Figure 1: Reaction Setup (0.1 mmol scale)

Analytical data of C–H allylated products:

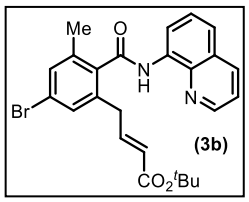
***tert*-butyl (*E*)-4-(3,5-dimethyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3a):**

Reaction performed on 0.1 mmol scale (28 mg); Yield: 61% (26 mg); Physical appearance: brown gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.99 (dd, *J* = 7.5, 1.4 Hz, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.03 (s, 1H), 7.02 – 6.96 (m, 1H), 6.95 (s, 1H), 5.71 (d, *J* = 15.9 Hz, 1H), 3.60 (d, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 2.38 (s, 3H), 1.37 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.43, 165.67, 148.34, 145.50, 139.25, 138.51, 136.27, 135.26, 134.96, 134.78, 134.29, 129.60, 128.03, 128.00, 127.40, 124.37, 121.97, 121.64, 116.73, 79.95, 35.88, 28.03, 21.22, 19.53; **IR** (KBr cm^{-1}): 2976, 2927, 1709, 1674, 1596, 1482, 1145, 982, 885, 851, 826; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{26}H_{29}N_2O_3$ $[M+H]^+$ 417.2173; found 417.2198.



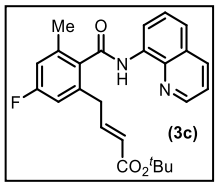
***tert*-butyl (*E*)-4-(5-bromo-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3b):**

Reaction performed on 0.1 mmol scale (34 mg); Yield: 62% (30 mg); Physical appearance: colorless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.94 (dd, *J* = 6.9, 2.0 Hz, 1H), 8.77 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.38 (s, 1H), 7.30 (s, 1H), 6.95 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.72 (d, *J* = 15.5 Hz, 1H), 3.60 (d, *J* = 6.7 Hz, 2H), 2.45 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.17, 165.37, 148.48, 144.24, 138.43, 137.31, 137.00, 136.80, 136.35, 133.94, 131.77, 130.28, 128.00, 127.35, 125.05, 123.32, 122.32, 121.76, 116.86, 80.19, 35.61, 28.02, 19.42; **IR** (KBr cm^{-1}): 2976, 2954, 2131, 1708, 1672, 1481, 1143, 982, 896, 847, 791; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{25}H_{26}BrN_2O_3$ 481.1121 and 483.1102; Found 481.1095 and 483.1074.

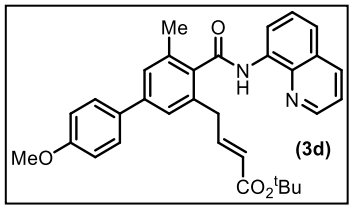


***tert*-butyl (*E*)-4-(5-fluoro-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3c):**

Reaction performed on 0.1 mmol scale (28 mg); Yield: 58% (24 mg); Physical appearance: yellowish gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.97 (dd, *J* = 7.3, 1.6 Hz, 1H), 8.78 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.01 – 6.89 (m, 2H), 6.86 (dd, *J* = 9.3, 2.4 Hz, 1H), 5.73 (d, *J* = 15.5 Hz, 1H), 3.62 (d, *J* = 6.1 Hz, 2H), 2.47 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.52, 165.41, 162.75 (d, *J* = 249.4 Hz), 148.13, 144.31, 137.99 (d, *J* = 8.4 Hz), 137.60 (d, *J* = 7.1 Hz), 136.96, 133.95 (d, *J* = 2.4 Hz), 128.13, 127.58, 125.01, 122.35, 121.69, 117.41, 115.76, 115.59, 114.23, 114.05, 80.18, 35.80, 28.02, 19.75; **^{19}F NMR** (471 MHz, CDCl3) δ –111.94; **IR** (KBr cm^{-1}): 2954, 2925, 1714, 1608, 1483, 1286, 1199, 1049, 826, 791; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{25}H_{26}FN_2O_3$ 421.1922; Found 421.1924.

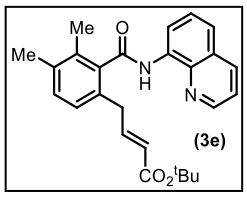


***tert*-butyl (*E*)-4-(4'-methoxy-5-methyl-4-(quinolin-8-ylcarbamoyl)-[1,1'-biphenyl]-3-yl)but 2-enoate (3d):** Reaction performed on 0.1 mmol scale (37 mg); Yield: 61% (31 mg); Physical appearance: yellow solid; M.p. 126–128 °C; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 9.01 (dd, *J* = 7.2, 1.7 Hz, 1H), 8.77 (dd, *J* = 4.6, 1.4 Hz, 1H), 8.20 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.59 – 7.55 (m, 2H), 7.46 (dd, *J* = 8.5, 4.6 Hz, 1H), 7.39 (s, 1H), 7.32 (s, 1H), 7.07 – 7.01 (m, 1H), 5.75 (d, *J* = 15.7 Hz, 1H), 3.90 (s, 3H), 3.70 (d, *J* = 6.2 Hz, 1H), 2.54 (s, 3H), 1.36 (s, 9H).; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.18, 165.58, 159.51, 148.39, 145.34, 141.94, 138.50, 136.30, 136.24, 135.54, 135.36, 134.22, 132.86, 128.28, 128.01, 127.39, 127.28, 125.83, 124.51, 122.08, 121.68, 116.80, 114.31, 80.00, 55.40, 36.14, 28.02, 19.80; **IR** (KBr cm^{-1}): 2976, 2925, 1709, 1674, 1488, 1178, 1034, 955, 906, 827, 791; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{32}H_{33}N_2O_4$ 509.2435; Found 509.2432.



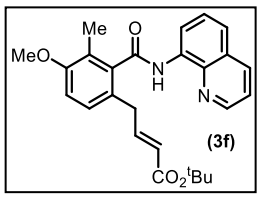
***tert*-butyl (*E*)-4-(3,4-dimethyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3e):**

Reaction performed on 0.1 mmol scale (28 mg); Yield: 65% (27 mg); Physical appearance: colourless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.99 (dd, *J* = 7.2, 1.5 Hz, 1H), 8.74 (dd, *J* = 4.2 Hz, 1.5 Hz, 1H), 8.19 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.67 – 7.54 (m, 2H), 7.44 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.96 (dt, *J* = 15.6, 6.2 Hz, 1H), 5.59 (dt, *J* = 15.6, 1.7 Hz, 1H), 3.62 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.80, 165.70, 148.26, 144.76, 138.69, 138.33, 136.43, 134.84, 134.18, 132.43, 132.31, 131.20, 128.91, 128.03, 127.43, 123.91, 122.06, 121.60, 116.92, 79.92, 33.44, 28.05, 19.40, 19.27; **IR** (KBr cm^{-1}): 2975, 2923, 1708, 1674, 1456, 1273, 1144, 973, 907, 826, 791; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. For $C_{26}H_{29}N_2O_3$ 417.2173; Found 417.2189.



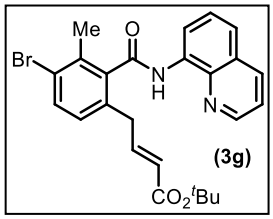
***tert*-butyl (*E*)-4-(4-methoxy-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3f):**

Reaction performed on 0.1 mmol scale (29 mg); Yield: 62% (26 mg); Physical appearance: yellowish gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.99 (dd, *J* = 7.4, 1.6 Hz, 1H), 8.75 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz,, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.98 (dt, *J* = 15.6, 6.3 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 5.69 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.89 (s, 3H), 3.57 (dd, *J* = 6.7, 1.2 Hz, 2H), 2.32 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.02, 165.68, 156.64, 148.26, 145.87, 139.04, 138.35, 136.45, 134.13, 128.21, 128.04, 127.44, 126.30, 124.11, 123.74, 122.09, 121.65, 116.95, 111.06, 79.88, 55.69, 35.33, 28.01, 13.09; **IR** (KBr cm^{-1}): 2975, 927, 1707, 675, 1325, 1145, 1095, 985, 847, 826 ; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{26}H_{29}N_2O_4$ 433.2122; Found 433.2143.



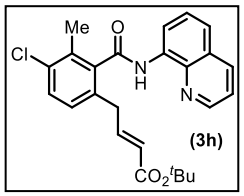
***tert*-butyl (*E*)-4-(4-bromo-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3g):**

Reaction performed on 0.1 mmol scale (34 mg); Yield: 61% (29 mg); Physical appearance: colourless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.96 (d, *J* = 6.8 Hz, 1H), 8.77 (d, *J* = 4.2 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.58 (m, 3H), 7.47 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.95 (dt, *J* = 15.6, 6.4 Hz, 1H), 5.69 (d, *J* = 15.5 Hz, 1H), 3.57 (d, *J* = 6.5 Hz, 2H), 2.52 (s, 3H), 1.37 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.13, 165.39, 148.48, 144.54, 139.42, 138.42, 136.34, 134.75, 134.11, 133.89, 133.44, 128.92, 128.00, 127.33, 124.81, 124.25, 122.40, 121.77, 116.92, 80.12, 35.57, 28.02, 20.40; **IR** (KBr cm^{-1}): 2977, 2926, 1709, 1675, 1482, 1325, 1146, 983, 901, 826, 791; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{25}H_{26}BrN_2O_3$ 481.1121 and 483.1102; Found 481.1140 and 483.1127.



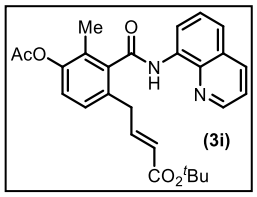
***tert*-butyl (*E*)-4-(4-chloro-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3h):**

Reaction performed on 0.1 mmol scale (30 mg); Yield: 64% (28 mg); Physical appearance: yellowish gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.96 (d, *J* = 6.9 Hz, 1H), 8.77 (d, *J* = 4.4 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.55 (m, 2H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.95 (dt, *J* = 15.5, 6.5 Hz, 1H), 5.69 (d, *J* = 15.5 Hz, 1H), 3.59 (d, *J* = 6.6 Hz, 2H), 2.49 (s, 3H), 1.37 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.11, 165.42, 148.47, 144.65, 139.46, 138.43, 136.34, 133.89, 133.69, 133.39, 133.10, 130.12, 128.64, 128.00, 127.34, 124.77, 122.38, 121.76, 116.92, 80.12, 35.53, 28.01, 17.40; **IR** (KBr cm^{-1}): 2979, 2929, 1710, 1675, 1483, 1147, 1120, 984, 904, 826, 791; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{25}H_{26}ClN_2O_3$ 437.1626; Found 437.1655.



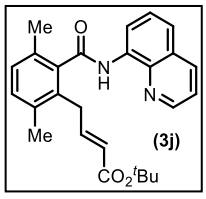
***tert*-butyl (*E*)-4-(4-acetoxy-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3i):**

Reaction performed on 0.1 mmol scale (32 mg); Yield: 57% (26 mg); Physical appearance: Off-white solid; M.p. 112–114 °C TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.97 (d, *J* = 7.9 Hz, 1H), 8.76 (d, *J* = 2.0 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.67 – 7.55 (m, 2H), 7.46 (dd, *J* = 7.9, 4.1 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.15 – 7.07 (m, 2H), 6.90 (dt, *J* = 15.4, 6.4 Hz, 1H), 5.67 (d, *J* = 15.5 Hz, 1H), 3.55 (d, *J* = 6.4 Hz, 2H), 2.46 (s, 3H), 2.33 (s, 3H), 1.33 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.31, 167.05, 165.44, 148.44, 147.38, 143.72, 139.34, 138.45, 136.27, 134.02, 132.74, 130.02, 127.98, 127.32, 126.81, 124.39, 123.49, 122.26, 121.72, 116.84, 79.96, 30.96, 27.98, 21.00, 19.24; **IR** (KBr cm^{-1}): 2978, 2930, 1763, 1708, 1674, 1483, 1179, 983, 895, 848, 827; **HRMS** (ESI-ToF) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{29}N_2O_5$ 461.2071; Found 461.2086.



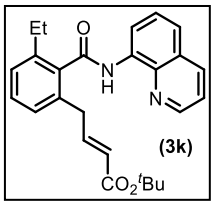
***tert*-butyl (*E*)-4-(3,6-dimethyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3j):**

Reaction performed on 0.1 mmol scale (28 mg); Yield: 64% (27 mg); Physical appearance: Off-white solid; M.p. 110–112 °C; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 9.01 (dd, *J* = 7.4, 1.4 Hz, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.69 – 7.56 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.98 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.69 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.59 (d, *J* = 6.7 Hz, 2H), 2.36 (s, 3H), 2.34 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.85, 165.64, 148.23, 145.61, 138.32, 138.16, 136.52, 135.91, 134.16, 133.27, 132.13, 130.78, 128.06, 127.47, 127.24, 124.28, 122.11, 121.64, 117.01, 79.92, 35.79, 28.03, 19.98, 16.72; **IR** (KBr cm^{-1}): 276, 2927, 1708, 1674, 1482, 1151, 1083, 982, 898, 849, 826; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{26}H_{28}N_2O_3Na$ 439.1992; Found 439.2022.



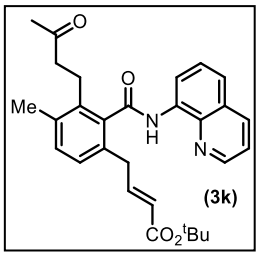
***tert*-butyl (*E*)-4-(3-ethyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3k):**

Reaction performed on 0.1 mmol scale (28 mg); Yield: 66% (28 mg); Physical appearance: colorless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.99 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.69 – 7.57 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.00 (dt, *J* = 15.5, 6.9 Hz, 1H), 5.71 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.63 (dd, *J* = 6.7, 1.2 Hz, 2H), 2.80 (q, *J* = 7.6 Hz, 2H), 1.36 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.18, 165.58, 148.37, 145.29, 141.22, 138.46, 137.43, 136.27, 134.69, 134.19, 129.54, 128.00, 127.40, 127.39, 127.24, 124.46, 122.08, 121.67, 116.79, 79.97, 35.92, 28.01, 26.55, 15.89; **IR** (KBr cm^{-1}): 2976, 2930, 1708, 1673, 1488, 1180, 1034, 955, 906, 827, 791, 764; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{26}H_{29}N_2O_3$ 417.2173; Found 417.2191.



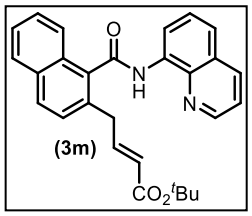
***tert*-butyl (E)-4-(4-methyl-3-(3-oxobutyl)-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3l):**

Reaction performed on 0.1 mmol scale (33 mg); Yield: 50% (23 mg); Physical appearance: colourless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.95 (dd, *J* = 7.1, 1.6 Hz, 1H), 8.73 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.45 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.95 (dt, *J* = 15.6, 6.0 Hz, 1H), 5.57 (d, *J* = 15.6 Hz, 1H), 3.61 (d, *J* = 5.8 Hz, 2H), 3.00 – 2.91 (m, 2H), 2.90 – 2.85 (m, 2H), 2.33 (s, 3H), 2.07 (s, 3H), 1.35 (m, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.86, 168.45, 165.63, 148.39, 144.52, 138.53, 138.43, 136.28, 135.76, 135.58, 134.06, 132.44, 131.49, 128.20, 128.00, 127.33, 123.98, 122.20, 121.65, 116.81, 79.98, 45.63, 33.47, 28.22, 28.04, 27.47, 19.44; **IR** (KBr cm^{-1}): 2977, 1711, 1678, 1520, 1482, 1150, 828, 764; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{29}H_{32}N_2O_4Na$ 495.2254; Found 495.2276.



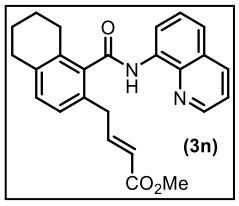
***tert*-butyl (*E*)-4-(1-(quinolin-8-ylcarbamoyl)naphthalen-2-yl)but-2-enoate (3m):**

Reaction performed on 0.1 mmol scale (30 mg); Yield: 41% (18 mg); Physical appearance: brown



gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 9.12 (d, *J* = 7.5 Hz, 1H), 8.69 (d, *J* = 3.8 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 8.09 – 8.02 (m, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.90 (m, 1H), 7.69 (t, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.46 – 7.40 (m, 2H), 7.09 (dt, *J* = 15.4, 6.6 Hz, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 3.81 (d, *J* = 6.2 Hz, 2H), 1.39 (s, 9H).; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.69, 165.55, 148.39, 145.01, 138.47, 136.26, 134.67, 134.29, 132.34, 132.32, 130.33, 129.78, 128.08, 128.02, 127.57, 127.39, 127.30, 126.20, 125.10, 124.77, 122.26, 121.70, 116.93, 80.10, 36.25, 28.05; **IR** (KBr cm^{-1}): 2976, 2923, 1710, 1674, 1481, 1090, 907, 830, 791; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{28}H_{27}N_2O_3$ 439.2016; Found 439.2042.

methyl (*E*)-4-(1-(quinolin-8-ylcarbamoyl)-5,6,7,8-tetrahydronaphthalen-2-yl)but-2-enoate (3n): Reaction performed on 0.1 mmol scale (30 mg); Yield: 61% (24 mg); Physical appearance:



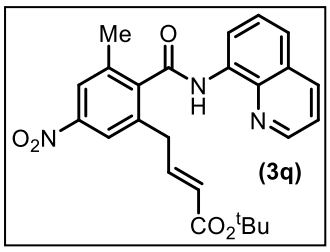
Off-white solid; M.p. 118–120 °C; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.99 (dd, *J* = 7.3, 1.4 Hz, 1H), 8.73 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.59 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.46 (dd, *J* = 8.2, 4.0 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 5.76 (d, *J* = 15.7 Hz, 1H), 3.61 – 3.60 (m, 2H), 3.59 (s, 3H), 2.95 – 2.87 (m, 2H), 2.84 (t, *J* = 5.8 Hz, 2H), 1.88 – 1.73 (m, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.43, 166.66, 148.27, 147.34, 138.45, 137.86, 136.53, 136.30, 134.18, 134.08, 131.28, 130.44, 128.01, 127.38, 127.01, 122.11, 122.08, 121.64, 116.79, 51.25, 35.92, 29.55, 26.74, 22.88, 22.67; **IR** (KBr cm^{-1}):2927, 2856, 1718, 1671, 1481, 1146, 984, 826, 791, 757; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{25}H_{25}N_2O_3$ 401.1860; Found 401.1869.

***tert*-butyl (*E*)-4-(1-(quinolin-8-ylcarbamoyl)-5,6,7,8-tetrahydronaphthalen-2-yl)but-2-enoate (3o):** Reaction performed on 0.1 mmol scale (30 mg); Yield: 59% (26 mg); Physical appearance: colorless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.99 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.76 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.99 (dt, *J* = 15.4, 6.8 Hz, 1H), 5.70 (d, *J* = 15.5 Hz, 1H), 3.58 (d, *J* = 6.6 Hz, 2H), 2.94 – 2.87 (m, 2H), 2.84 (t, *J* = 5.7 Hz, 2H), 1.87 – 1.75 (m, 4H), 1.37 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.46, 165.62, 148.35, 145.61, 138.48, 137.80, 136.37, 136.28, 134.23, 133.97, 131.68, 130.39, 128.00, 127.38, 127.05, 124.28, 122.03, 121.65, 116.77, 79.92, 35.67, 29.55, 28.04, 26.78, 22.89, 22.68; **IR** (KBr cm^{-1}): 2976, 2931, 1708, 1672, 1481, 1143, 982, 908, 826, 791;**HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{28}H_{31}N_2O_3$ 443.2329; Found 443.2348.

***tert*-butyl (*E*)-4-(5-cyano-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3p):** Reaction performed on 0.1 mmol scale (29 mg); Yield: 56% (24 mg); Physical appearance: brown gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (700 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.93 (t, *J* = 4.5 Hz, 1H), 8.77 (d, *J* = 4.1 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 4.1 Hz, 2H), 7.52 (s, 1H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.46 (s, 1H), 6.97 – 6.90 (m, 1H), 5.71 (dd, *J* = 15.6, 1.6 Hz, 1H), 3.65 (d, *J* = 6.7 Hz, 2H), 2.51 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 166.09, 165.13, 148.60, 143.42, 141.75, 138.36, 136.79, 136.74, 136.44, 133.57, 132.32, 131.05, 128.01, 127.32, 125.55, 122.70, 121.89, 118.23, 117.06, 113.35, 80.42, 35.45, 28.01, 22.36; **IR** (KBr cm^{-1}): 2978, 2925, 1709, 1676, 1523, 1484, 1258, 1148, 828, 759; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{26}H_{26}N_3O_3Na$ 428.1969; Found 428.1979.

***tert*-butyl (*E*)-4-(3-methyl-5-nitro-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3q):**

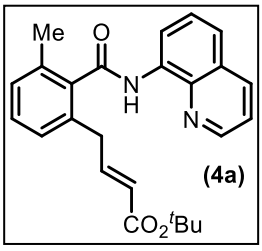
Reaction performed on 0.1 mmol scale (30 mg); Yield: 51% (23 mg); Physical appearance:



yellowish gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (700 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.93 (dd, *J* = 4.9, 3.9 Hz, 1H), 8.76 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.09 (d, *J* = 2.2 Hz, 1H), 8.02 (d, *J* = 2.2 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.99 – 6.93 (m, 1H), 5.72 (d, *J* = 15.6 Hz, 1H), 3.71 (d, *J* = 6.8 Hz, 2H), 2.58 (s, 3H), 1.37 (s, 9H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 166.00, 165.11, 160.98, 148.62, 148.10, 143.32, 143.21, 139.03, 138.35, 137.46, 137.07, 136.45, 133.52, 128.01, 127.32, 125.58, 123.78, 122.77, 122.51, 121.91, 117.09, 80.42, 35.76, 28.00, 25.58; **IR** (KBr cm^{-1}): 2977, 1711, 1677, 1522, 1483, 1367, 1325, 1147, 827, 745; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{25}H_{25}N_3O_5Na$ 470.1686; Found 470.1703.

***tert*-butyl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4a):**

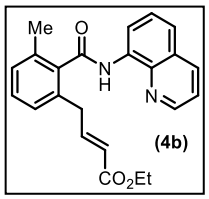
Reaction performed on 0.1 mmol scale (26 mg); Yield: 65% (26 mg) and 1 mmol scale (260 mg)



Yield: 46% (185 mg); Physical appearance: colorless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.98 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.76 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.00 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.71 (d, *J* = 15.5 Hz, 1H), 3.64 (d, *J* = 6.7 Hz, 2H), 2.48 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.19, 165.60, 148.40, 145.33, 138.50, 137.92, 136.31, 135.04, 134.80, 134.18, 129.38, 128.87, 128.01, 127.43, 127.39, 124.49, 122.11, 121.69, 116.82, 79.99, 35.90, 28.02, 19.59; **IR** (KBr cm^{-1}): 2980, 2923, 1715, 1670, 1479, 1150, 982, 908, 820, 795; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{25}H_{26}N_2O_3Na$ 425.1836; Found 425.1813.

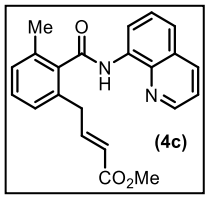
Ethyl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4b):

Reaction performed on 0.1 mmol scale (26 mg); Yield: 66% (25 mg); Physical appearance: brown gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.98 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.74 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.11 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.77 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.65 (dd, *J* = 6.7, 1.6 Hz, 2H), 2.48 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.15, 166.23, 148.32, 146.66, 138.48, 136.30, 135.14, 134.50, 134.15, 129.42, 128.96, 128.01, 127.42, 127.39, 122.75, 122.14, 121.68, 116.85, 60.09, 36.11, 19.55, 14.14; **IR** (KBr cm^{-1}): 2980, 2921, 1720, 1689, 1510, 1120, 990, 885, 820, 751; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{23}H_{23}N_2O_3$ 375.1703; Found 375.1723.



***tert*-butyl (*E*)-4-(4-chloro-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4c):**

Reaction performed on 0.1 mmol scale (26 mg); Yield: 61% (29 mg); Physical appearance: yellowish gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.99 (dd, *J* = 7.3, 1.6 Hz, 1H), 8.74 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.21 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.48 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.16 – 7.14 (m, 1H), 7.13 – 7.08 (m, 1H), 5.77 (dt, *J* = 15.6, 1.4 Hz, 1H), 3.66 (dd, *J* = 6.7, 1.5 Hz, 2H), 3.59 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.19, 166.62, 148.13, 147.02, 138.20, 137.92, 136.63, 135.14, 134.39, 134.01, 129.44, 128.97, 128.07, 127.49, 127.37, 122.30, 122.20, 121.64, 117.15, 51.28, 36.17, 29.71, 19.55; **IR** (KBr cm^{-1}): 2923, 2852, 1718, 1672, 1481, 1153, 983, 896, 826, 791; **HRMS** (APCI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{22}H_{20}N_2O_3Na$ 383.1366; Found 383.1394.



Isopropyl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4d):

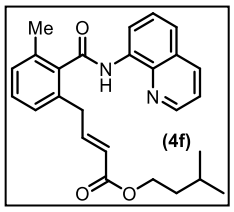
Reaction performed on 0.1 mmol scale (26 mg); Yield: 64% (25 mg); Physical appearance: colorless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.99 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.09 (dt, *J* = 15.5, 1.6 Hz, 1H), 5.76 (dt, *J* = 15.5, 1.6 Hz, 1H), 4.94 (sep, *J* = 6.3 Hz, 1H), 3.65 (dd, *J* = 6.7, 1.4 Hz, 2H), 2.48 (s, 3H), 1.15 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.22, 165.80, 148.33, 146.32, 138.42, 137.90, 136.43, 135.11, 134.59, 134.10, 129.42, 128.94, 128.04, 127.44, 127.42, 123.24, 122.19, 121.69, 117.00, 67.41, 36.04, 21.78, 19.57; **IR** (KBr cm^{-1}): 3054, 2924, 1720, 1667, 1457, 1131, 982, 898, 824, 790, 735; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{24}H_{24}N_2O_3Na$ 411.1679; Found 411.1682.

Benzyl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4e):

Reaction performed on 0.1 mmol scale (26 mg); Yield: 61% (27 mg); Physical appearance: yellowish gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.99 (d, *J* = 7.3 Hz, 1H), 8.64 (d, *J* = 4.1 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.41 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.39 – 7.29 (m, 4H), 7.29 – 7.26 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.20 – 7.12 (m, 2H), 5.83 (d, *J* = 15.6 Hz, 1H), 5.05 (s, 2H), 3.67 (d, *J* = 6.5 Hz, 2H), 2.48 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.14, 165.99, 148.24, 147.40, 138.30, 137.95, 136.43, 135.98, 135.18, 134.32, 134.05, 129.43, 128.99, 128.48, 128.15, 128.11, 128.02, 127.44, 127.42, 122.42, 122.18, 121.66, 117.02, 65.97, 36.15, 19.56; **IR** (KBr cm^{-1}): 3032, 2952, 1715, 1672, 1482, 1151, 1071, 982, 896, 791, 751; **HRMS** (APCI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{28}H_{24}N_2O_3Na$ 459.1679; Found 459.1708.

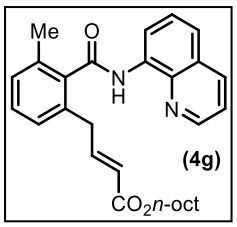
Isopentyl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4f):

Reaction performed on 0.1 mmol scale (26 mg); Yield: 63% (26 mg); Physical appearance: colorless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.98 (dd, *J* = 7.3, 1.5 Hz, 1H), 8.74 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.34 (t, *J* = 7.1 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.09 (dt, *J* = 15.6, 1.5 Hz, 1H), 5.78 (d, *J* = 15.6 Hz, 1H), 4.01 (t, *J* = 7.1 Hz, 2H), 3.66 (dd, *J* = 6.7, 1.2 Hz, 2H), 2.48 (s, 3H), 1.67 – 1.55 (m, 1H), 1.43 (q, *J* = 6.9 Hz, 2H), 0.88 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.15, 166.32, 148.34, 146.59, 138.49, 137.97, 136.31, 135.13, 134.52, 134.15, 129.42, 128.96, 128.01, 127.41, 127.38, 122.80, 122.15, 121.69, 116.85, 62.85, 37.26, 36.09, 24.99, 22.44, 19.56; **IR** (KBr cm^{-1}): 2955, 1714, 1674, 1423, 1126, 1089, 982, 895, 826, 790; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{26}H_{29}N_2O_3$ 417.2173; Found 417.2164.

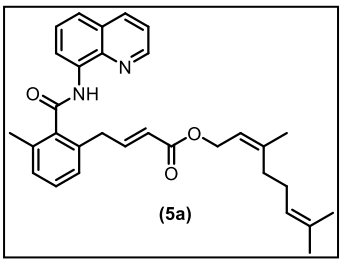


Octyl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4g):

Reaction performed on 0.1 mmol scale (26 mg); Yield: 62% (28 mg); Physical appearance: colorless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.99 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.74 (d, *J* = 4.2, 1.6 Hz 1H), 8.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.09 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.78 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.97 (t, *J* = 6.8 Hz, 2H), 3.66 (dd, *J* = 6.7, 1.2 Hz, 2H), 2.48 (s, 3H), 1.58 – 1.47 (m, 2H), 1.30 – 1.25 (m, 10H), 0.90 (t, *J* = 6.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.15, 166.33, 148.34, 146.59, 138.49, 137.97, 136.30, 135.14, 134.51, 134.15, 129.41, 128.95, 128.01, 127.41, 127.38, 122.81, 122.14, 121.68, 116.85, 64.38, 36.09, 31.79, 29.21, 29.15, 28.55, 25.88, 22.64, 19.56, 14.10; **IR** (KBr cm^{-1}): 2975, 29726, 1711, 1676, 1484, 1157, 899, 826, 791; **HRMS** (APCI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{29}H_{35}N_2O_3$ 459.2642; Found 459.2665.



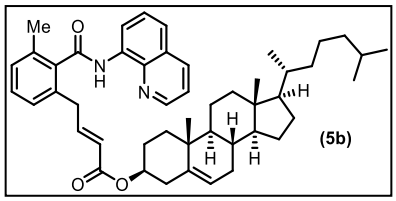
(*Z*)-3,7-dimethylocta-2,6-dien-1-yl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (5a):



Reaction performed on 0.1 mmol scale (26 mg); Yield: 45% (21 mg); Physical appearance: colorless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.98 (dd, *J* = 7.3, 1.6 Hz, 1H), 8.74 (dd, *J* = 4.3, 1.5 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.08 (m, 2H), 5.78 (dt, *J* = 15.5, 1.7 Hz, 1H), 5.28 (t, *J* = 7.2 Hz, 1H), 5.15 – 5.02 (m, 1H), 4.51 (d, *J* = 7.2 Hz, 2H), 3.65 (dd, *J* = 6.7, 1.6 Hz, 2H), 2.47 (s, 3H), 2.13 – 2.03 (m, 4H), 1.76 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.13, 166.23, 148.34, 146.81, 142.24, 138.48, 137.94, 136.27, 135.14, 134.42, 134.14, 132.14, 129.39, 128.93, 128.00, 127.41, 127.37, 124.43, 123.82, 123.56, 122.73, 122.13, 121.66, 119.24, 116.85, 60.84, 59.01, 36.06, 32.16, 26.62, 25.69, 23.49, 19.55, 17.66; **IR** (KBr cm^{-1}): 2980, 2929, 1720, 1675, 1522, 1483, 11120, 94, 904, 829, 791, 764; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{31}H_{34}N_2O_3$ 483.2642; Found 483.2666.

(3*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (5b):

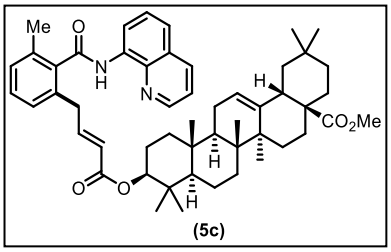
Reaction performed on 0.1 mmol scale (26 mg); Yield: 58% (41 mg); Physical appearance:



colorless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.99 (dd, *J* = 7.4, 1.4 Hz, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.09 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.76 (d, *J* = 15.6 Hz, 1H), 5.34 (d, *J* = 4.8 Hz, 1H), 4.69 – 4.39 (m, 1H), 3.67 (d, *J* = 6.7 Hz, 2H), 2.49 (s, 3H), 2.23 – 2.14 (m, 2H), 2.08 – 1.93 (m, 2H), 1.88 – 1.79 (m, 2H), 1.77 – 1.68 (m, 1H), 1.59 – 1.43 (m, 7H), 1.39 – 1.32 (m, 3H), 1.30 – 1.26 (m, 2H), 1.23 – 1.04 (m, 9H), 1.00 (s, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 2.2 Hz, 3H), 0.88 (d, *J* = 3.6 Hz, 3H), 0.70 (s, 3H); **^{13}C NMR** (126

MHz, $CDCl_3$) δ 168.15, 165.63, 148.37, 146.42, 139.71, 138.49, 137.95, 136.30, 135.11, 134.60, 134.16, 129.42, 128.95, 128.01, 127.48, 127.40, 123.16, 122.54, 122.13, 121.69, 116.84, 73.70, 56.69, 56.14, 50.01, 42.32, 39.73, 39.53, 38.03, 36.96, 36.57, 36.19, 36.09, 35.80, 31.90, 31.86, 28.24, 28.02, 27.67, 24.29, 23.83, 22.83, 22.57, 21.02, 19.58, 19.31, 18.72, 11.86; **IR** (KBr cm^{-1}): 2926, 2851, 1714, 1676, 1520, 1482, 1325, 1195, 1012, 790, 755; **HRMS** (ESI-ToF) *m/z*: $[\alpha]_D^{25}$ = -52.400 (c = 0.0025, $CHCl_3$); $[M+H]^+$ Calcd. for $C_{48}H_{63}N_2O_3$ 715.4833; Found 715.4855.

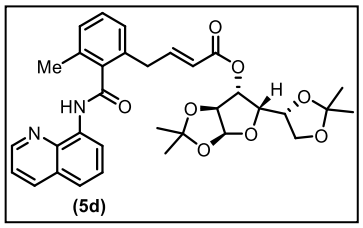
Methyl (4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*R*,12b*R*,14b*S*)-2,2,6a,6b,9,9,12a-heptamethyl-10-(((*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoyl)oxy) 1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2*H*)-carboxylate (5c):



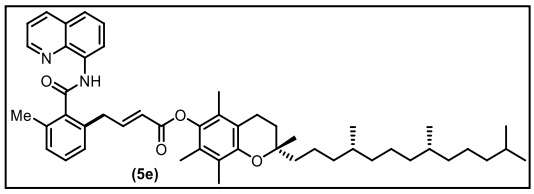
Reaction performed on 0.1 mmol scale (26 mg); Yield: 60% (48 mg); Physical appearance: Pale yellow gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.98 (d, *J* = 7.1 Hz, 1H), 8.75 (d, *J* = 2.9 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.13 – 7.04 (m, 1H), 5.80 (d, *J* = 15.6 Hz, 1H), 5.30 (s, 1H), 4.44 (dd, *J* = 11.1, 5.1 Hz, 1H), 3.70 – 3.66 (m, 2H), 3.65 (s, 3H), 2.88 (d, *J* = 12.0 Hz, 1H), 2.48 (s, 3H), 2.03 – 1.95 (m, 1H), 1.91 – 1.86 (m, 2H), 1.74 – 1.64 (m, 2H), 1.58 – 1.54 (m, 3H), 1.49 – 1.43 (m, 3H), 1.38 – 1.32 (m, 3H), 1.31 – 1.27 (m, 2H), 1.24 – 1.18 (m, 2H), 1.14 (s, 3H), 1.10 – 1.01 (m, 3H), 0.95 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H), 0.74 – 0.72 (m, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.29, 168.11, 166.02, 148.42, 146.12, 143.79, 138.49, 137.91, 136.27, 135.07, 134.68, 134.14, 129.41, 128.94, 128.01, 127.39, 127.37, 123.27, 122.27, 122.10, 121.68, 116.80, 80.59, 55.25, 51.52, 47.51, 46.73, 45.85, 41.63, 41.30, 39.27, 38.05, 37.72, 36.88, 36.04, 33.86, 33.11, 32.58, 32.39, 30.70, 27.93, 27.68, 25.89, 23.65, 23.40, 23.07, 19.60, 18.17, 16.83, 16.66, 15.32; $[\alpha]_D^{25}$ = -52.400 (c = 0.0025, $CHCl_3$); **IR** (KBr cm^{-1}): 2925, 2853, 1715, 1676, 1596, 1199, 11161, 987, 825, 791, 752, 701, 667; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{52}H_{67}N_2O_5$ 799.5044; Found 799.5028.

(3a*S*,5*S*,6*R*,6a*S*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (5d):

Reaction performed on 0.1 mmol scale (26 mg); Yield: 59% (35 mg); Physical appearance: brown gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.97 (dd, *J* = 7.1, 1.3 Hz, 1H), 8.78 (dd, *J* = 4.1, 1.2 Hz, 1H), 8.21 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.21 – 7.10 (m, 2H), 5.82 (d, *J* = 15.6 Hz, 1H), 5.74 (d, *J* = 3.6 Hz, 1H), 5.22 (d, *J* = 2.7 Hz, 1H), 4.31 (d, *J* = 3.6 Hz, 1H), 4.22 (dd, *J* = 7.6, 2.8 Hz, 1H), 4.18 – 4.11 (m, 1H), 3.99 (d, *J* = 5.5 Hz, 2H), 3.77 – 3.62 (m, 2H), 2.48 (s, 3H), 1.52 (s, 3H), 1.40 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.00, 164.70, 148.48, 148.34, 138.46, 137.91, 136.35, 135.22, 134.20, 134.10, 129.47, 129.12, 127.99, 127.40, 127.37, 122.18, 121.81, 121.75, 116.86, 112.16, 109.21, 104.94, 83.23, 79.69, 75.90, 72.38, 66.96, 36.16, 26.80, 26.71, 26.21, 25.22, 19.61; $[\alpha]_D^{25}$ = 111.600 (c = 0.0025, $CHCl_3$); **IR** (KBr cm^{-1}2986, 2923, 1725, 1675, 1596, 1152, 1036, 1021, 894, 844, 763; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{33}H_{37}N_2O_8$ 589.2544; Found 589.2562.



(*R*)-2,5,8-trimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (5e):

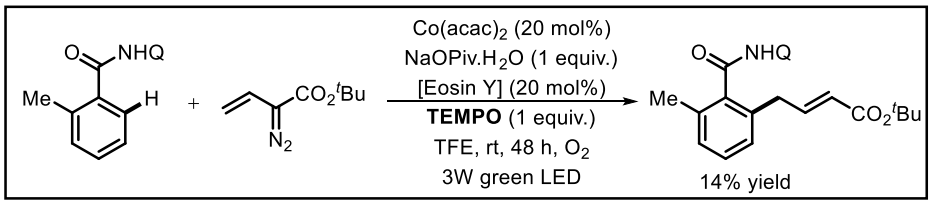


Reaction performed on 0.1 mmol scale (26 mg); Yield: 41% (31 mg); Physical appearance: colorless gel; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 9.00 (d, *J* = 7.3 Hz, 1H), 8.73 (d, *J* = 4.1 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.43 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 6.07 (d, *J* = 15.5 Hz, 1H), 3.78 (d, *J* = 6.6 Hz, 2H), 2.55 (t, *J* = 7.7 Hz, 2H), 2.50 (s, 3H), 2.06 (s, 3H), 1.83 (s, 3H), 1.80 (s, 3H), 1.57 – 1.50 (m, 3H), 1.49 – 1.39 (m, 4H), 1.30 – 1.27 (m, 7H), 1.24 (s, 3H), 1.19 – 1.14 (m, 3H), 1.11 – 1.08 (m, 2H), 0.90 – 0.85 (m, 16H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.09, 164.74, 149.25, 148.53, 148.45, 140.26, 138.50, 137.97, 136.25, 135.20, 134.41, 134.13, 129.49, 129.08, 128.90, 128.00, 127.47, 127.36, 126.77, 124.99, 122.86, 122.17, 121.89, 121.71, 117.22,

116.85, 75.00, 39.38, 37.56, 37.46, 37.40, 37.30, 36.25, 32.79, 32.72, 29.71, 27.99, 24.82, 24.46, 22.73, 22.64, 21.05, 20.56, 19.76, 19.69, 19.64, 12.83, 11.99, 11.79; $[a]_D^{23}$ = -170.000 (c = 0.0025, $CHCl_3$); **IR** (KBr cm^{-1}): 2989, 2930, 1730, 1675, 1482, 1030, 901, 849, 763, 697, ; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. For $C_{50}H_{67}N_2O_4$ 759.5095; Found 759.5083.

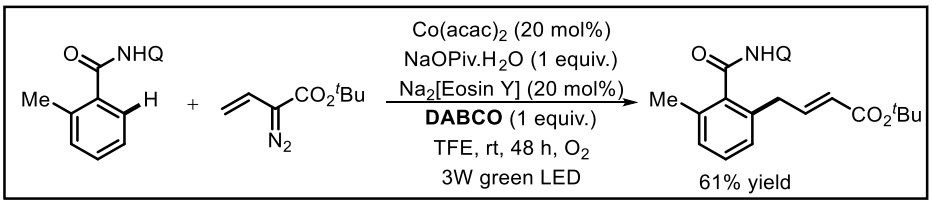
(4) Control Experiments and Mechanistic Studies:

(A) Radical quenching experiment:



In an oven-dried pressure tube equipped with a stir bar, 2-methyl-*N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol), and Na_2[Eosin Y] (20 mol%, 0.02 mmol) along with TEMPO (1 equiv., 0.1 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O_2 atmosphere using oxygen balloon. After 24 hours, a second portion of the *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and the reaction progress was monitored by TLC. It was observed that in the presence of TEMPO, the yield of the reaction was reduced to 14%. This result suggests that the reaction may proceed through a single electron transfer mechanism.

(B) DABCO experiment:

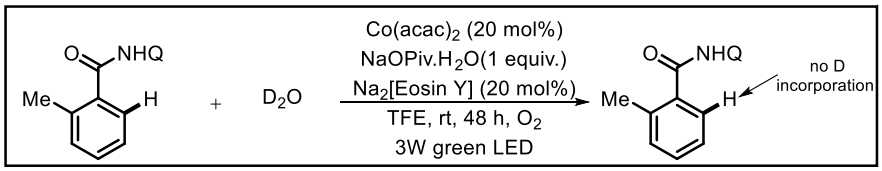


In an oven-dried pressure tube equipped with a stir bar, the 2-methyl-*N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved

in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol), and Na_2[Eosin Y] (20 mol%, 0.02 mmol) along with DABCO (1 equiv., 0.1 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O_2 atmosphere using oxygen balloon. After 24 hours, a second portion of the *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and the reaction progress was monitored by TLC. It was observed that in the presence of DABCO there is no effect on the reaction and a yield 61% was obtained after purification by a silica gel flash column chromatography. From this observation, we can eliminate the possibility of singlet oxygen being involved in the reaction.

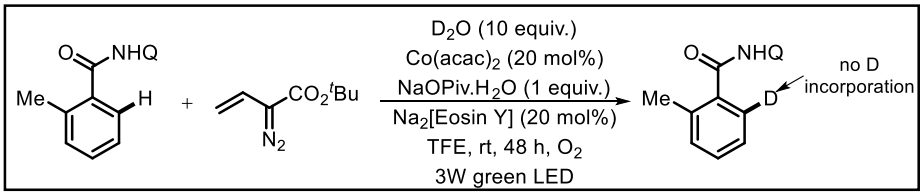
(C) Reversibility experiment: To investigate the reversibility of the formation of the cobaltacycle, we performed D-quenching studies, both in the presence and absence of the coupling partner.

(I) Reversibility experiment in absence of vinyl diazo ester:



In an oven-dried pressure tube equipped with a stir bar, the 2-methyl-*N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and D_2O (10 equiv., 1 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol), and Na_2[Eosin Y] (20 mol%, 0.02 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O_2 atmosphere using oxygen balloon. After 24 hours the reaction mixture was diluted with 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. ^{1}H NMR analysis of the isolated compound shows no deuterium incorporation in the starting material

(II) Reversibility experiment in the presence of vinyl diazo ester:

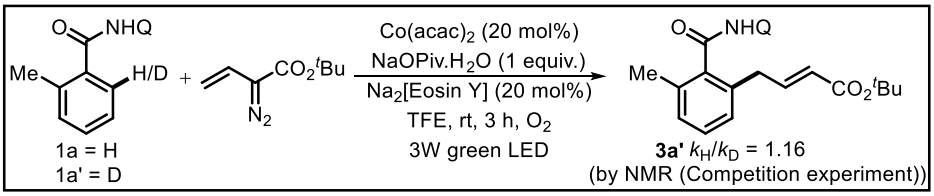


In an oven-dried pressure tube equipped with a stir bar, the 2-methyl-*N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol), *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) and D_2O (10 equiv., 1 mmol) was dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol), and Na_2 [Eosin Y] (20 mol%, 0.02 mmol), were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O_2 atmosphere using oxygen balloon. After 24 hours, the reaction mixture was diluted with 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. ^1H NMR of the isolated compound shows no deuterium incorporation in the starting material as well as in the product.

No D-incorporation into the starting material at the *ortho* position of benzamide, both, in the absence of the coupling partner as well as in the presence of the coupling partner suggests that the C–H activation is irreversible in nature.

(D) Studies to check for a Kinetic Isotopic Effect: 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):

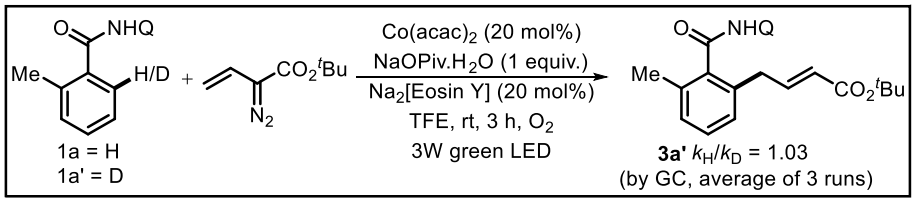


In an oven-dried pressure tube equipped with a stir bar, 2-methyl-*N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.05 mmol) and 2-methyl-*N*-(quinolin-8-yl)benzamide-6-*d* (1 equiv., 0.05 mmol) and *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution

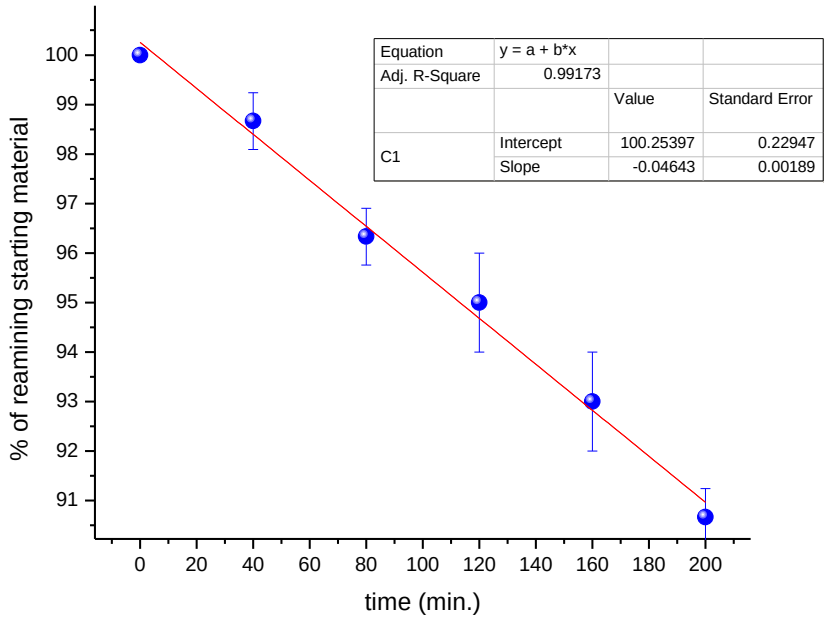
was bubbled with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol), and Na_2[Eosin Y] (20 mol%, 0.02 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O_2 atmosphere using oxygen balloon. The reaction was continued for 3 hours, after which, the reaction mixture was diluted with 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 ^1H NMR. Relative integration of the peaks of the recovered starting materials indicated a value of 1.16 for k_H/k_D.

(II) Parallel Experiment (*via* GC):

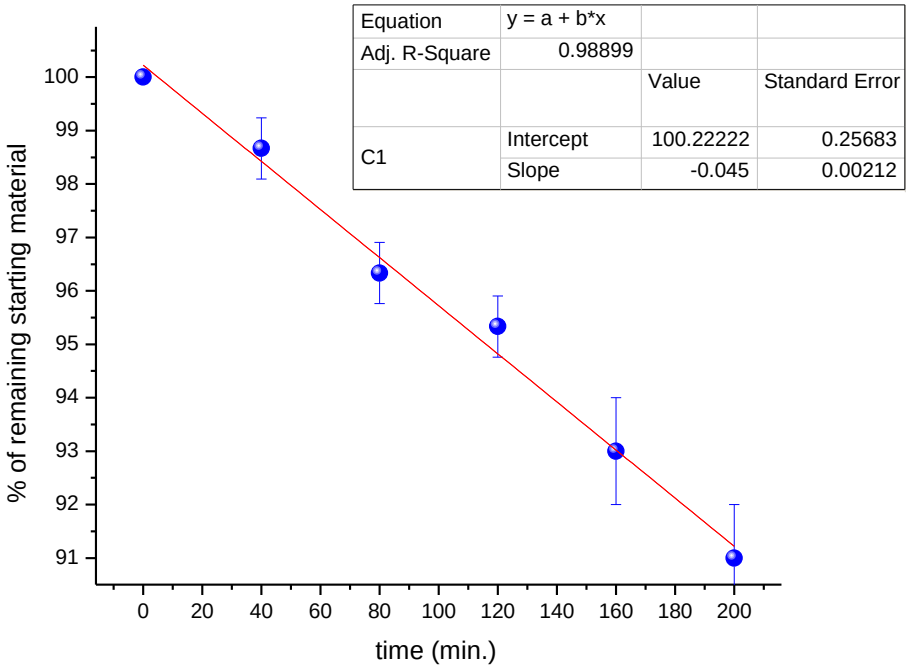
Two parallel reactions for 2-methyl-*N*-(quinolin-8-yl)benzamide (1 equiv., 0.1 mmol) and 2-methyl-*N*-(quinolin-8-yl)benzamide-6-*d* (1 equiv., 0.1 mmol) with *tert*-butyl 2-diazobut-3-enoate (2 equiv., 0.4 mmol) were performed according to the general procedure A, using dodecane (0.5 equiv., 0.1) as the internal standard. Aliquots were drawn at 40 minutes intervals and conversions were checked by GC-MS. The consumption starting material was plotted with time and k_H/k_D was found to be 1.03 (average of 3 runs).



Plot A (Rate of reaction of 2-methyl-*N*-(quinolin-8-yl)benzamide):

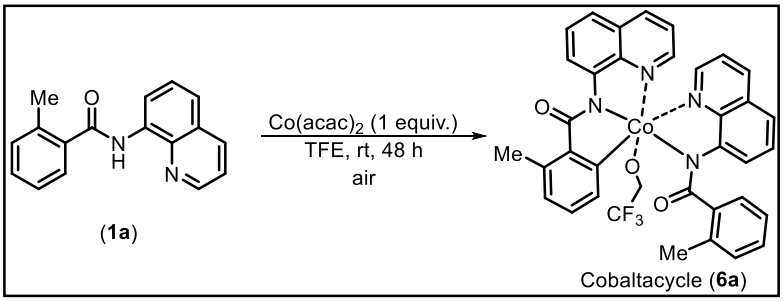


Plot B (Rate of reaction of 2-methyl-*N*-(quinolin-8-yl)benzamide-6-*d*):



A moderately low value of 1.16 and 1.03 obtained with competition and parallel experiments respectively, indicated that the C–H cleavage step is unlikely to be the rate-determining step. It is quite possible the allyl carbene migratory insertion step may be the rate-limiting step.

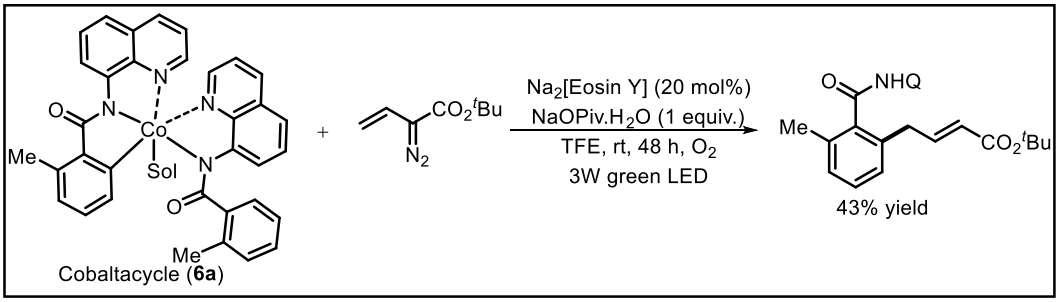
(E) Synthesis of the cobaltacycle intermediate (6a):[3]



To an oven-dried round bottom flask charged with a magnetic stir bar was added $Co(acac)_2$ (488.3 mg, 1.90 mmol, 1.0 equiv.) which is dissolved in 8 mL of 2,2,2- trifluoroethanol, to this solution **1a** (497.8 mg, 1.90 mmol, 1.0 equiv.) was added under air, and the reaction mixture was kept 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 (10:90 PET ether: Ethyl acetate) to give the desired cobalt complex **6a** as reported.

HRMS (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{34}H_{26}CoN_2O_4$ 581.1382; Found 581.1411.

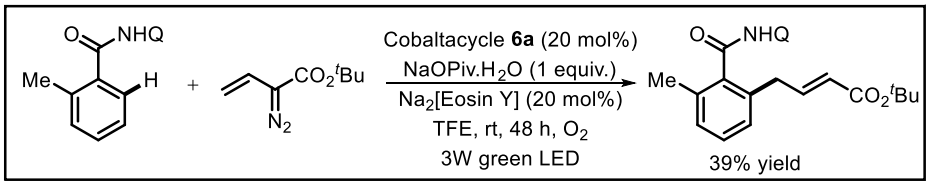
(F) Stoichiometric experiment:



In an oven-dried pressure tube equipped with a stir bar, the cobaltacycle (**6a**) (1.0 equiv., 0.1 mmol) and *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which $NaOPiv.H_2O$ (1 equiv., 0.1 mmol), and Na_2[Eosin Y] (20 mol%, 0.02 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment

under an O_2 atmosphere using oxygen balloon. After 24 hours, the second portion of the *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and 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 the solution was 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, giving the product in 43% yield.

(G) Cobaltacycle intermediate as a catalyst:



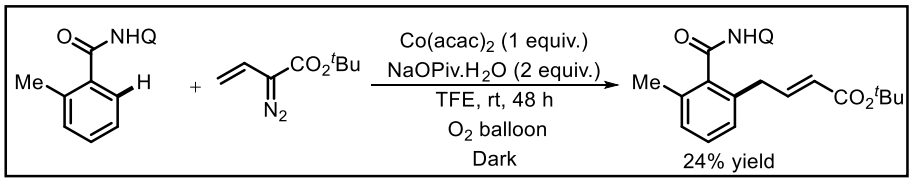
In an oven-dried pressure tube equipped with a stir bar, the cobaltacycle (**6a**) (1.0 equiv., 0.1 mmol) and *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which $NaOPiv.H_2O$ (1 equiv., 0.1 mmol), and Na_2[Eosin Y] (20 mol%, 0.02 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O_2 atmosphere using oxygen balloon. After 24 hours, the second portion of *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and 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 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 giving the product in 39% yield.

(H) Role of oxygen oxidant:

(I) reaction in presence of oxygen balloon:

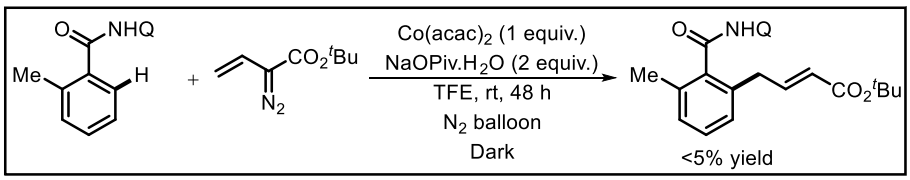
In an oven-dried pressure tube equipped with a stir bar, the *N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which $Co(acac)_2$

(1 equiv. 0.1 mmol), NaOPiv.H_2O (2 equiv., 0.2 mmol), were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under an O_2 atmosphere using oxygen balloon. After 24 hours, the second portion of vinyl diazo ester (1.5 equiv., 0.15 mmol) was added and the reaction progress was further monitored by TLC. 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 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 giving the allylated product in 24% yield.



(II) reaction in presence of nitrogen balloon:

In an oven-dried pressure tube equipped with a stir bar, the *N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with nitrogen for about 10 min, following which $Co(acac)_2$ (1 equiv. 0.1 mmol), NaOPiv.H_2O (2 equiv., 0.2 mmol), were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under inert conditions. After 24 hours, the second portion of vinyl diazo ester (1.5 equiv., 0.15 mmol) was added, and the reaction progress was further monitored by TLC. 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 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 giving the trace amount of allylated product.

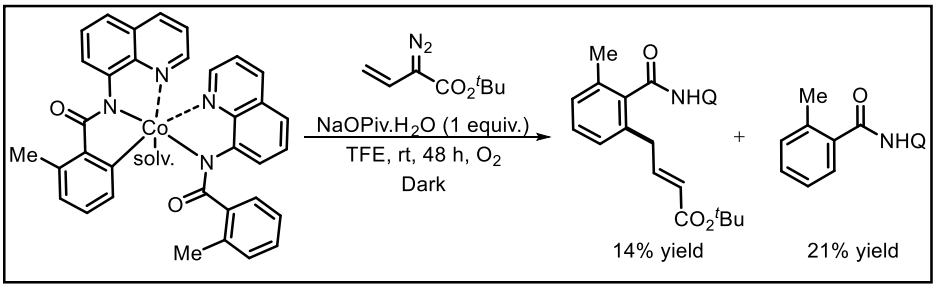


A moderately low yield *i.e.* 24% was obtained in the presence of oxygen balloon, however, only trace amount of product was obtained under the inert conditions, indicating that oxygen is necessary for this transformation.

(I) Role of additive:

(I) reaction in presence of NaOPiv.H_2O

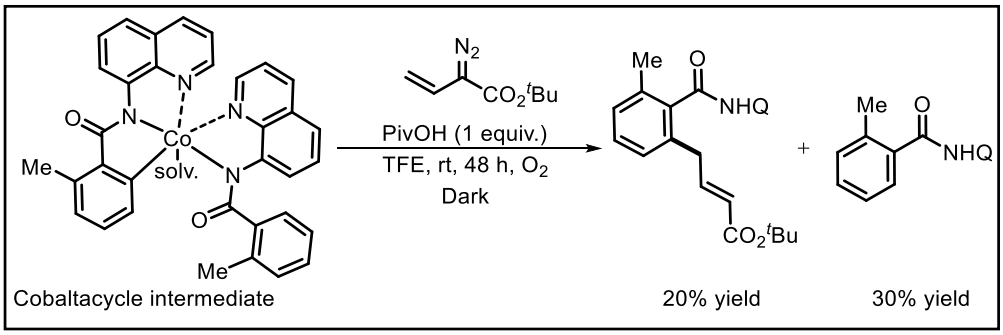
In an oven-dried pressure tube equipped with a stir bar, the cobaltacycle (**6a**) (1.0 equiv., 0.1 mmol) and *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which NaOPiv.H_2O (1 equiv., 0.1 mmol) was added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in dark environment under an O_2 atmosphere using oxygen balloon. After 24 hours, the second portion of *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and 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 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 giving the allylated product in 14% yield, however recovered starting material in 21% yield.



(II) reaction in presence of PivOH

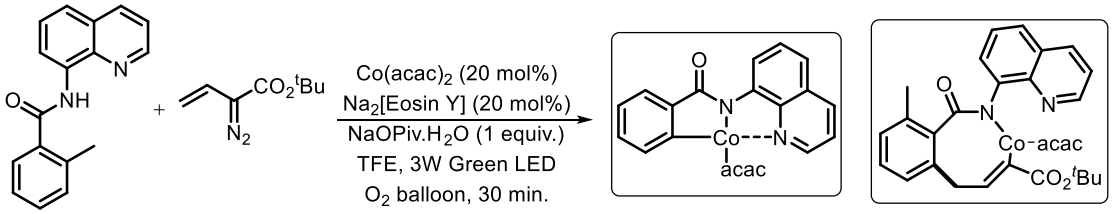
In an oven-dried pressure tube equipped with a stir bar, the cobaltacycle (**6a**) (1.0 equiv., 0.1 mmol) and *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which PivOH (1 equiv., 0.1 mmol) was added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in dark environment under an O_2 atmosphere using oxygen balloon. After 24 hours, the second portion of *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and 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 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 giving the allylated product in 20% yield, however recovered starting material in 30% yield.



These results indicating that role of additive may be for the facilitation of protodemetalation step in this transformation.

(X) Mass Spectrometry Experiment:



ESI-HRMS for C'
calcd. [M+H] 419.0800
found [M+H] 419.0785

ESI-HRMS for F
calcd. [M+H] 559.1638
found [M+H] 559.1645

Procedure: In an oven-dried pressure tube equipped with a stir bar, the 2-methyl-*N*-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and *tert*-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which $Co(acac)_2$ (20 mol%, 0.02 mmol), $NaOPiv.H_2O$ (1 equiv., 0.1 mmol), and Na_2[Eosin Y] (20 mol%, 0.02 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O_2 atmosphere using

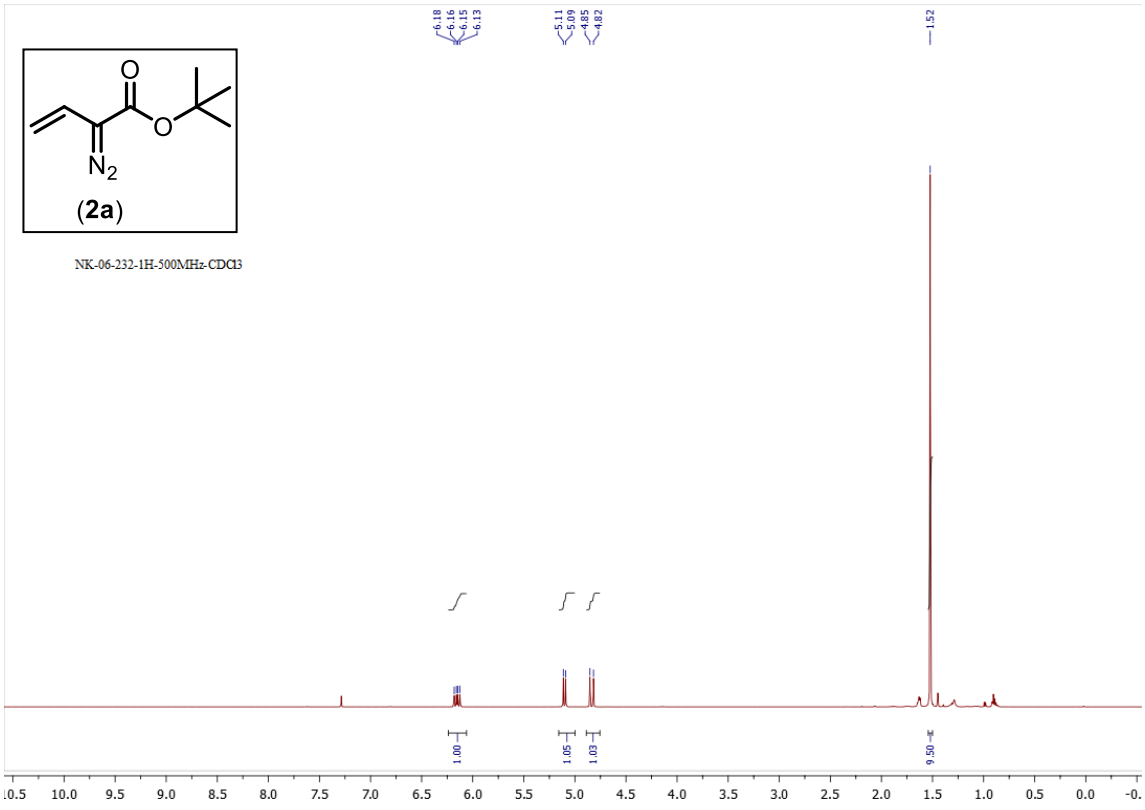
oxygen balloon for 30 minutes. An aliquot was drawn, passed through a frit, and subjected immediately to mass analysis

(5) References:

1. (a) B. He, X. Liu, H. Li, X, Zhang, Y. Ren and W. Su, *Org. Lett.* 2021, **23**, 4191–4196. (b) J. Tang, P. Liu and X. Zeng, *Chem. Commun.* 2018, **54**, 9325–9328. (c) W. Sarkar, A. Mishra, A. Bhowmik and I. Deb, *Org. Lett.* 2021, **23**, 4521–4526. (d) S. Liu, B. He, H. Li, X. Zhang, Y. Shang and W. Su, *Chem. – A Eur. J.* 2021, **27**, 15628–15633. (e) A. P. Honeycutt and J. M. Hoover, *Org. Lett.* 2018, **20**, 7216–7219. (f) G. Rouquet and N. Chatani, *Chem. Sci.* 2013, **4**, 2201–2208. (g) X. Luo, X. Song, W. Xiong, J. Li, M. Li, Z. Zhu, S. Wei, A. S. C. Chan and Y. Zhou *Org. Lett.* 2019, **21**, 2013–2018.

2. (a) J.-Q. Wu, Z. Yang, S.-S. Zhang, C.-Y. Jiang, Q. Li, Z.-S. Huang and H. Wang, *ACS Catal.* 2015, **5**, 6453–6457. (b) L. De Angelis, H. Zheng, M. T. Perz, H. Arman and M. P. Doyle, *Org. Lett.* 2021, **23**, 6542–6546. (c) W. Li, X. Zhou, T. Xiao, Z. Ke and L. Zhou, *CCS Chem.* 2022, **4**, 638–649.

3. S. Maity, R. Kancherla, U. Dhawa, E. Hoque, S. Pimparkar and D. Maiti, *ACS Catal.* 2016, **6**, 5493–5499.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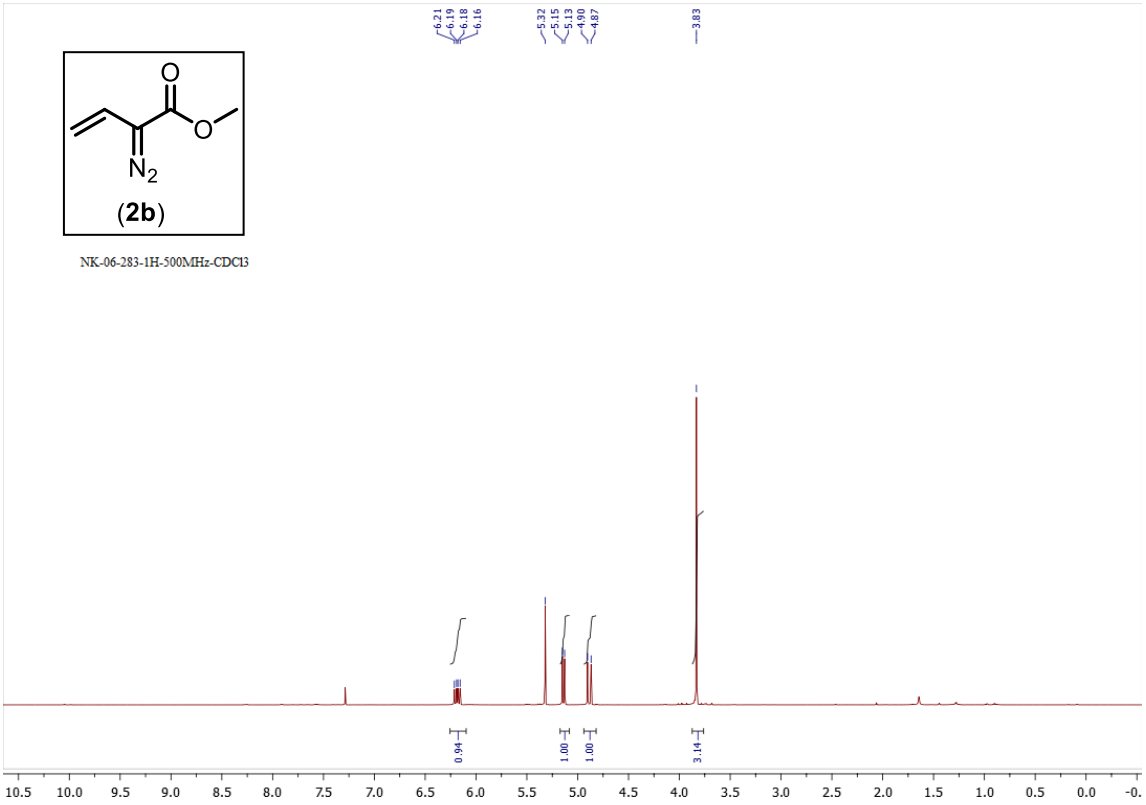
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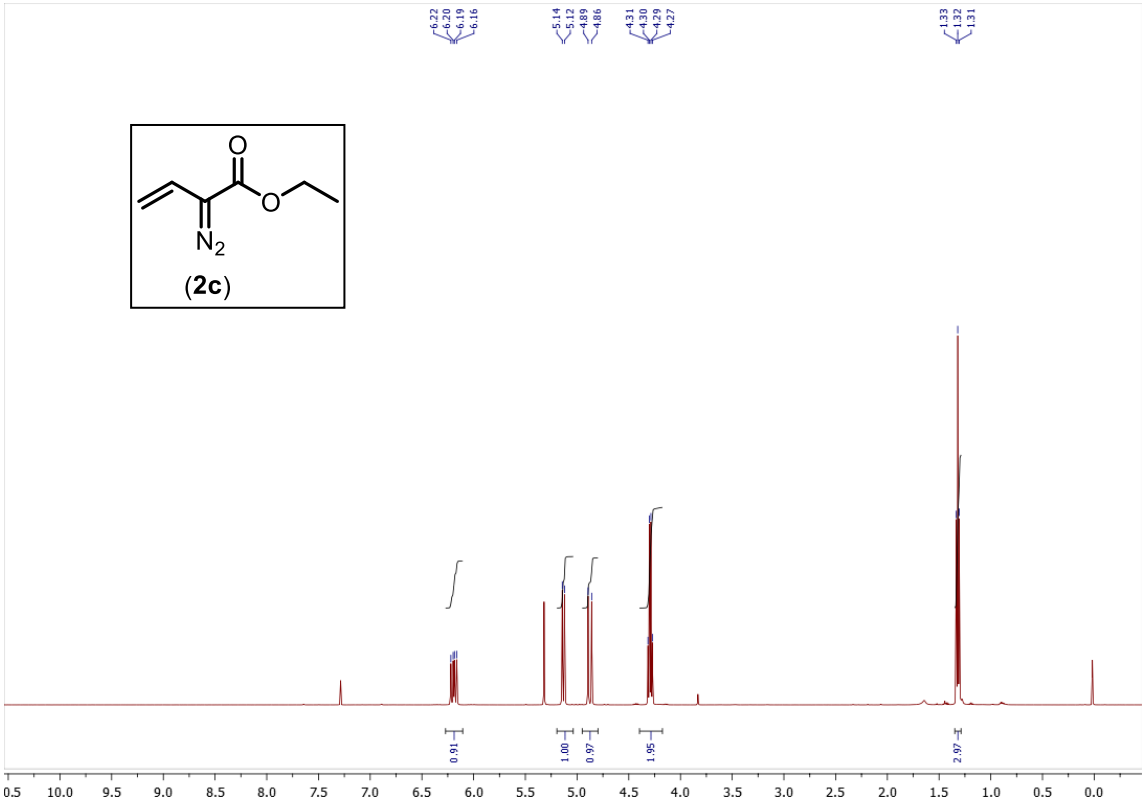
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5.12
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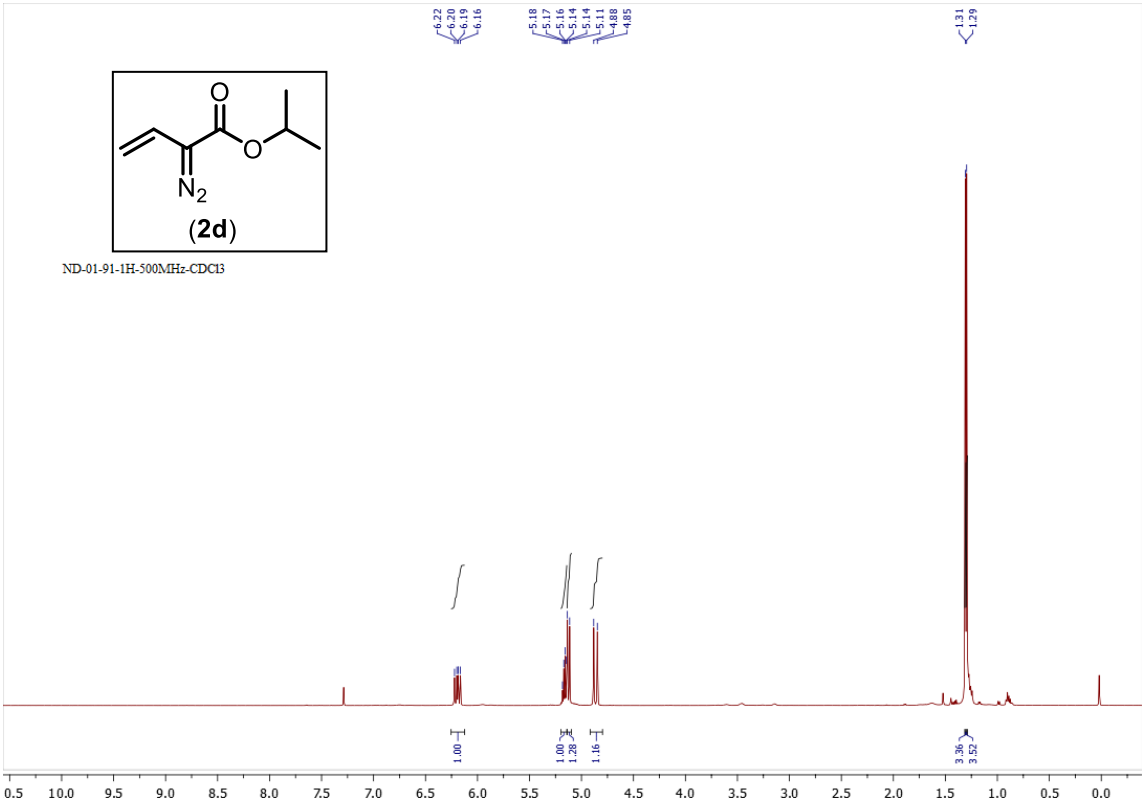
4.30
4.29
4.27
1.33
1.32
1.31
O
O
N2
(2c)
0.91
1.00
0.97
1.95
2.97
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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4.85
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1.29
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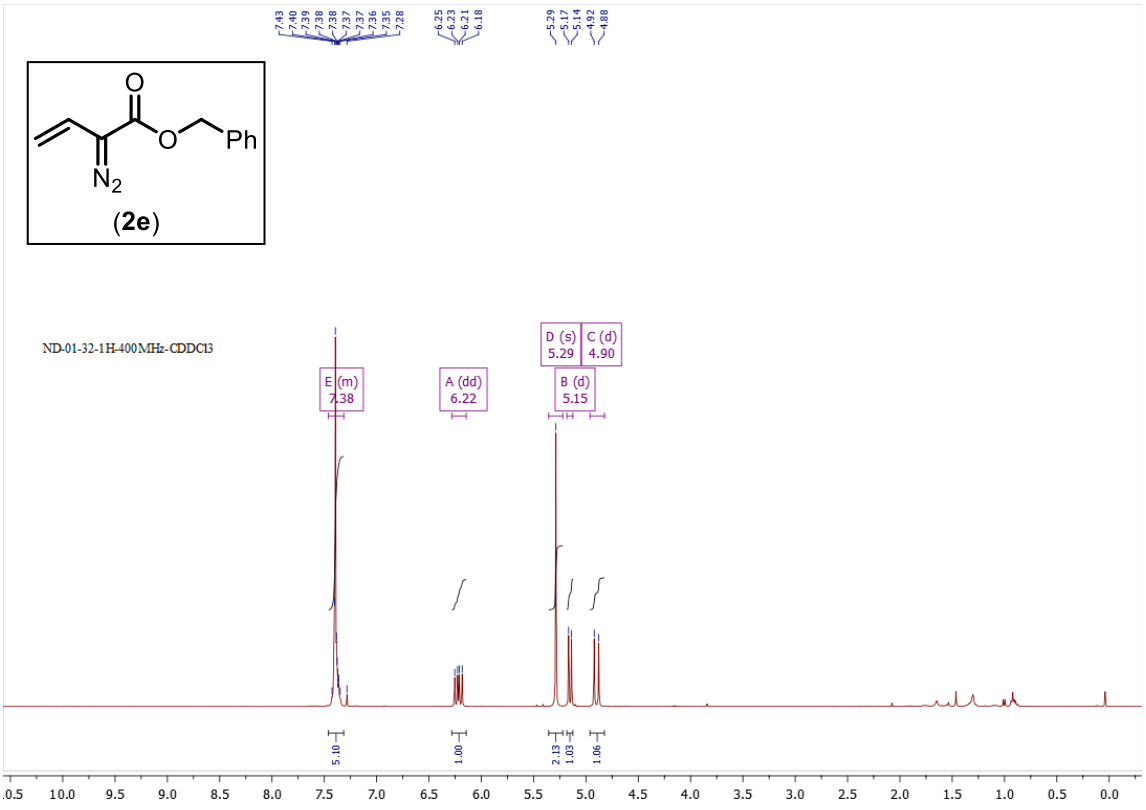
O
N2
(2d)
ND-01-91-1H-500MHz-CDCl3
1.00
1.00
1.28
1.16
3.36
3.52
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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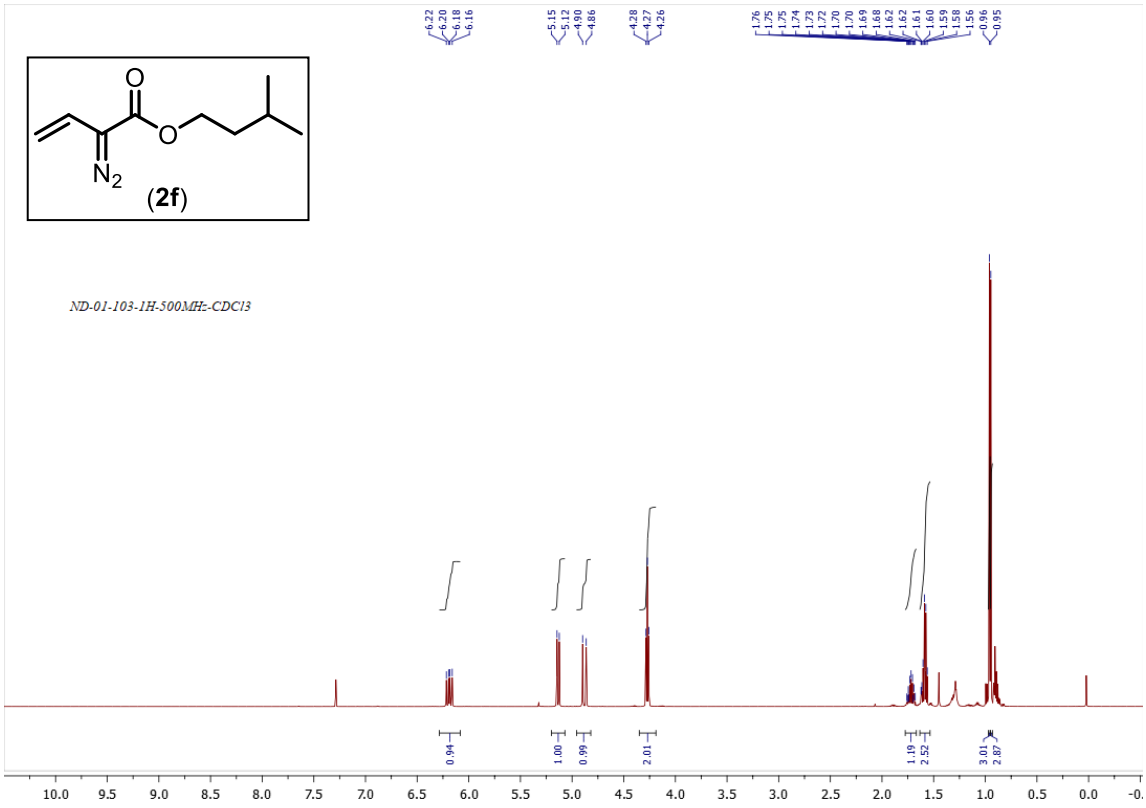
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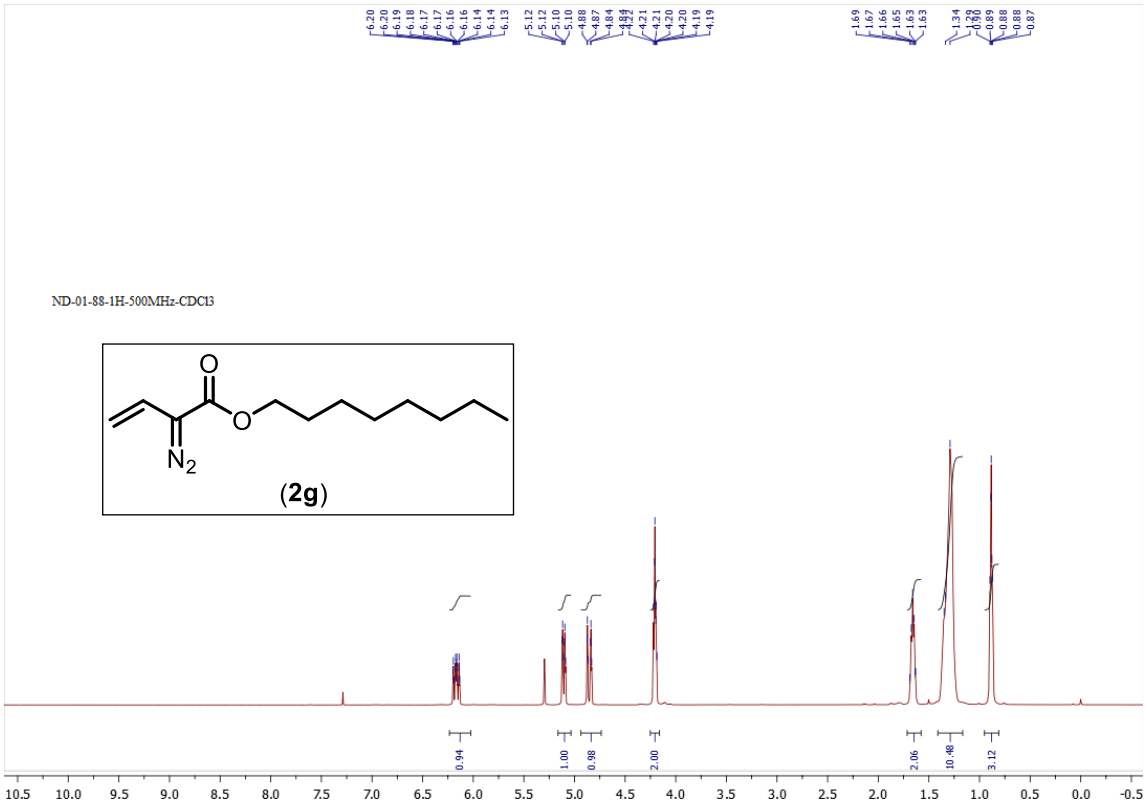
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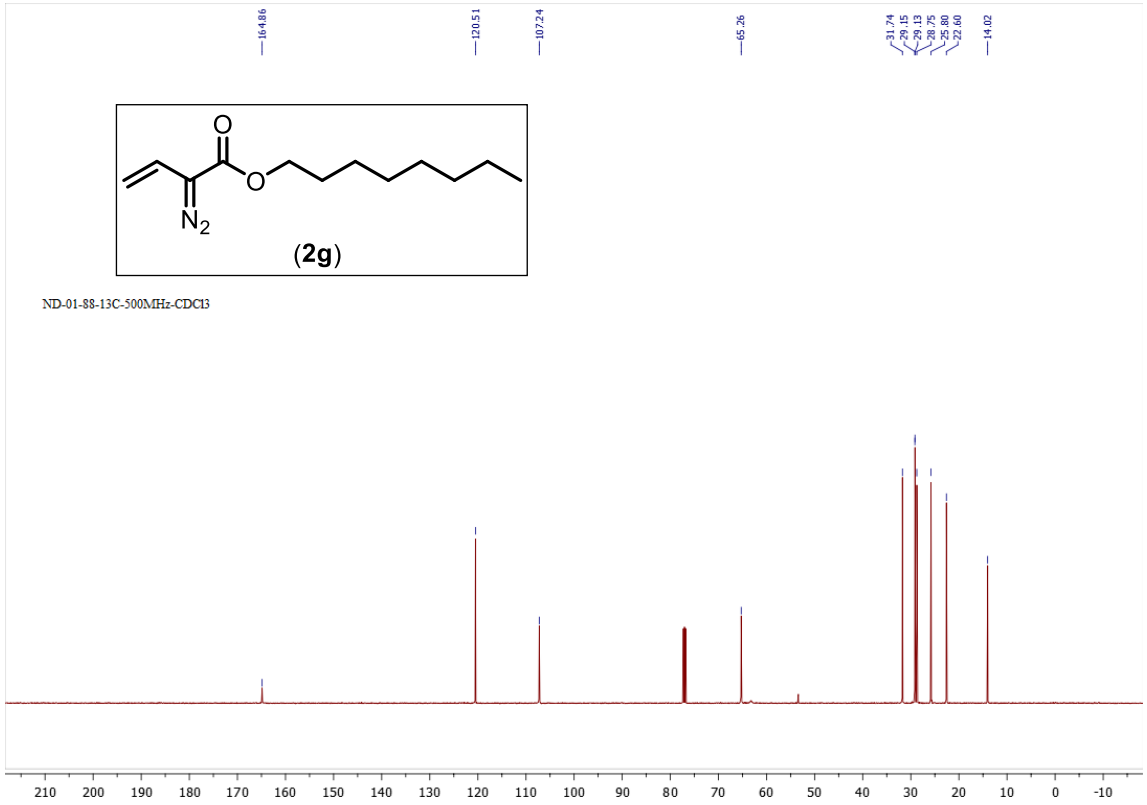
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Comment			

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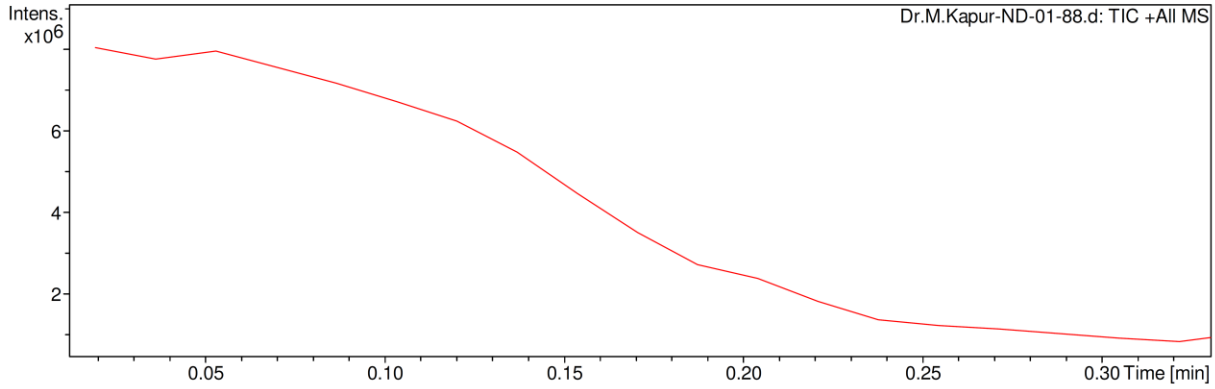

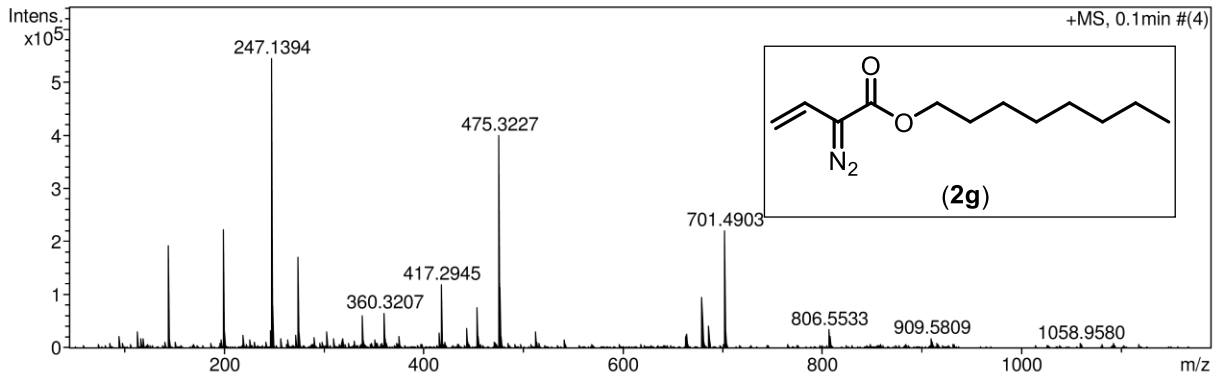

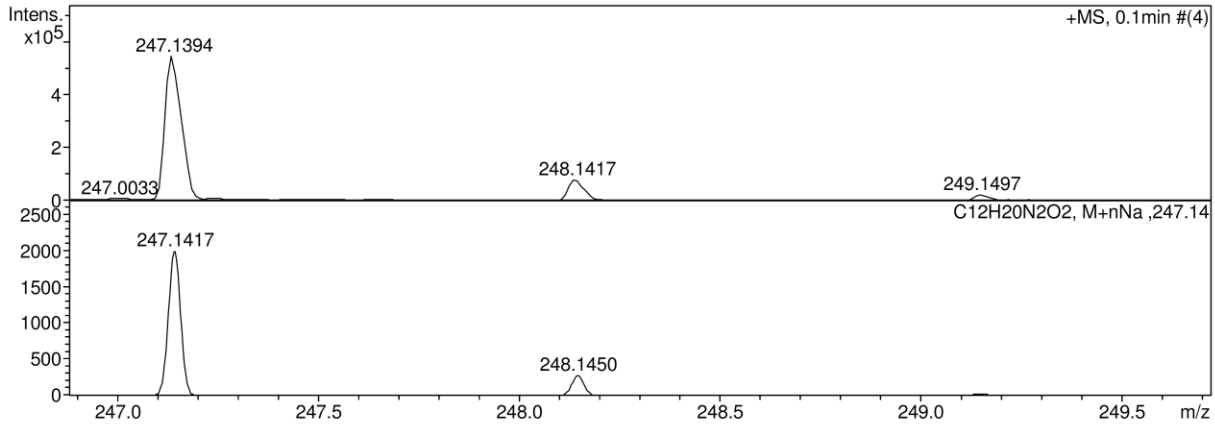

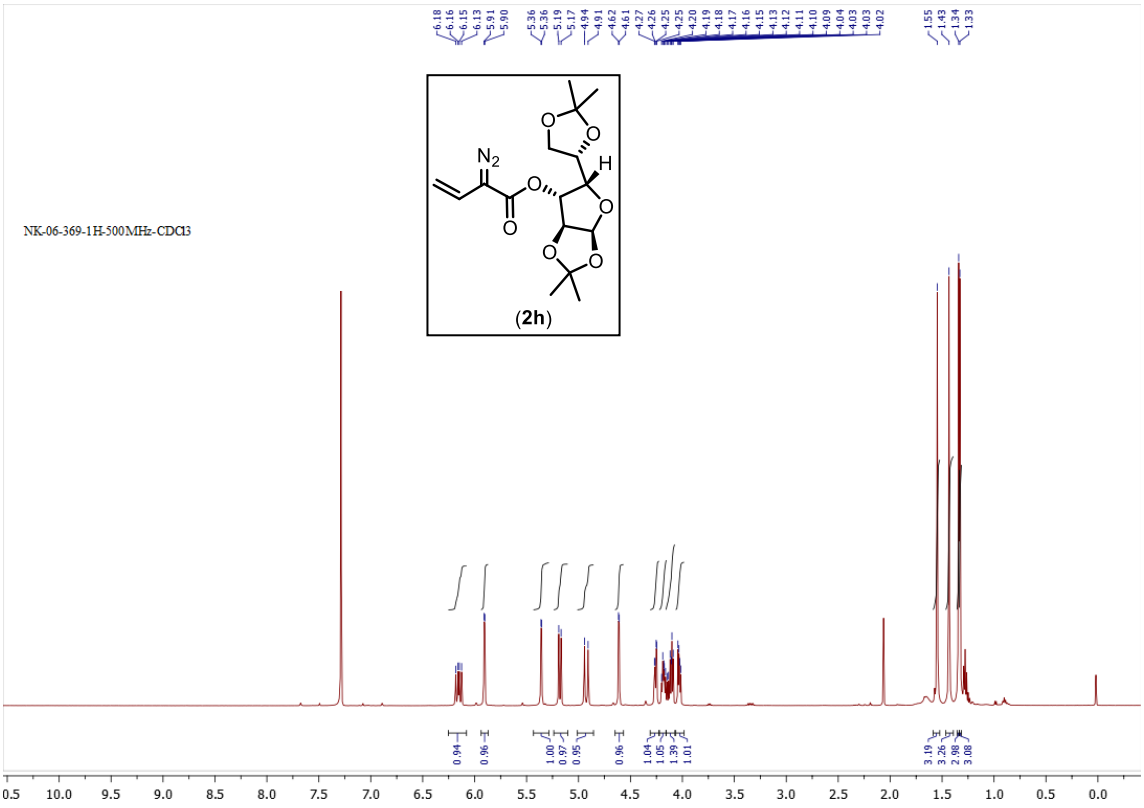
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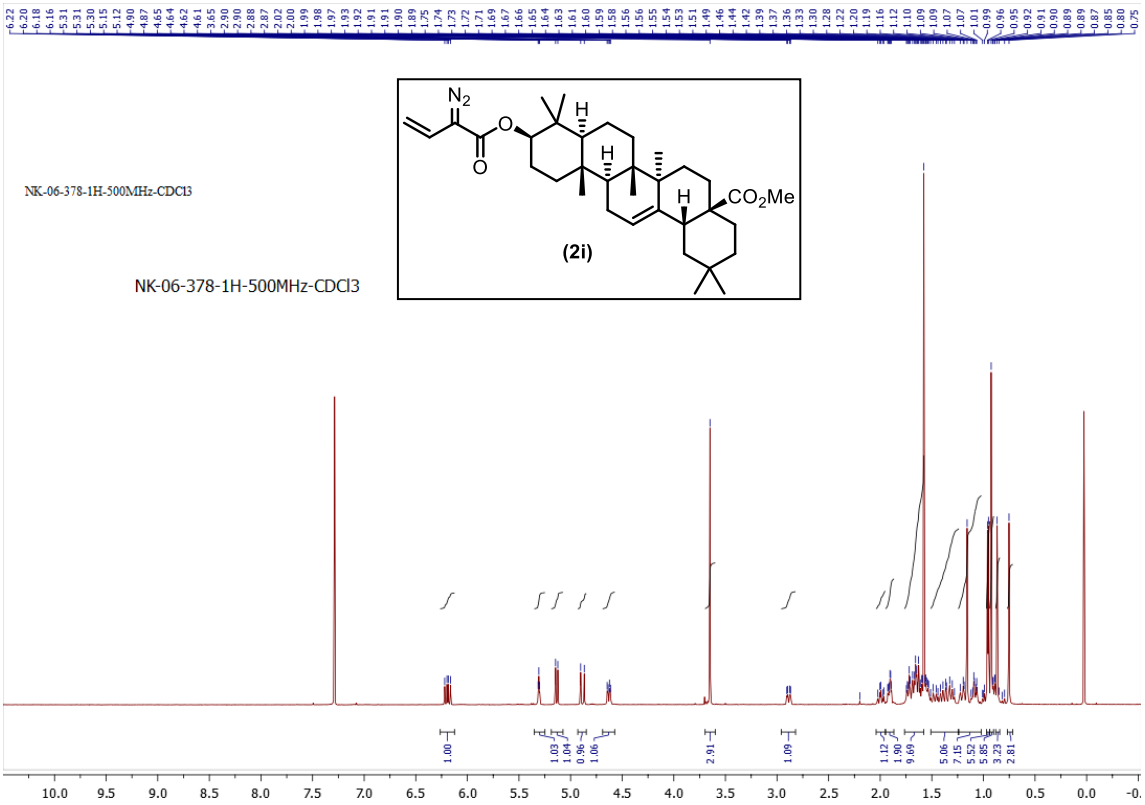
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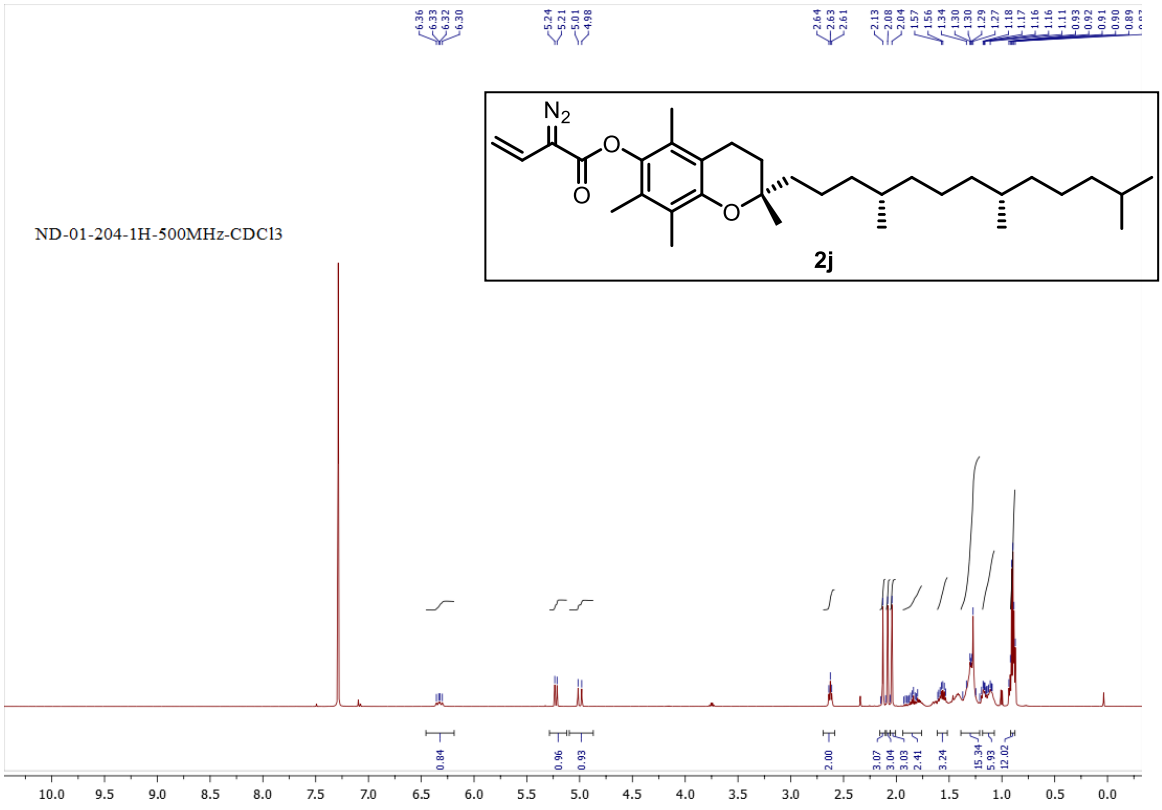
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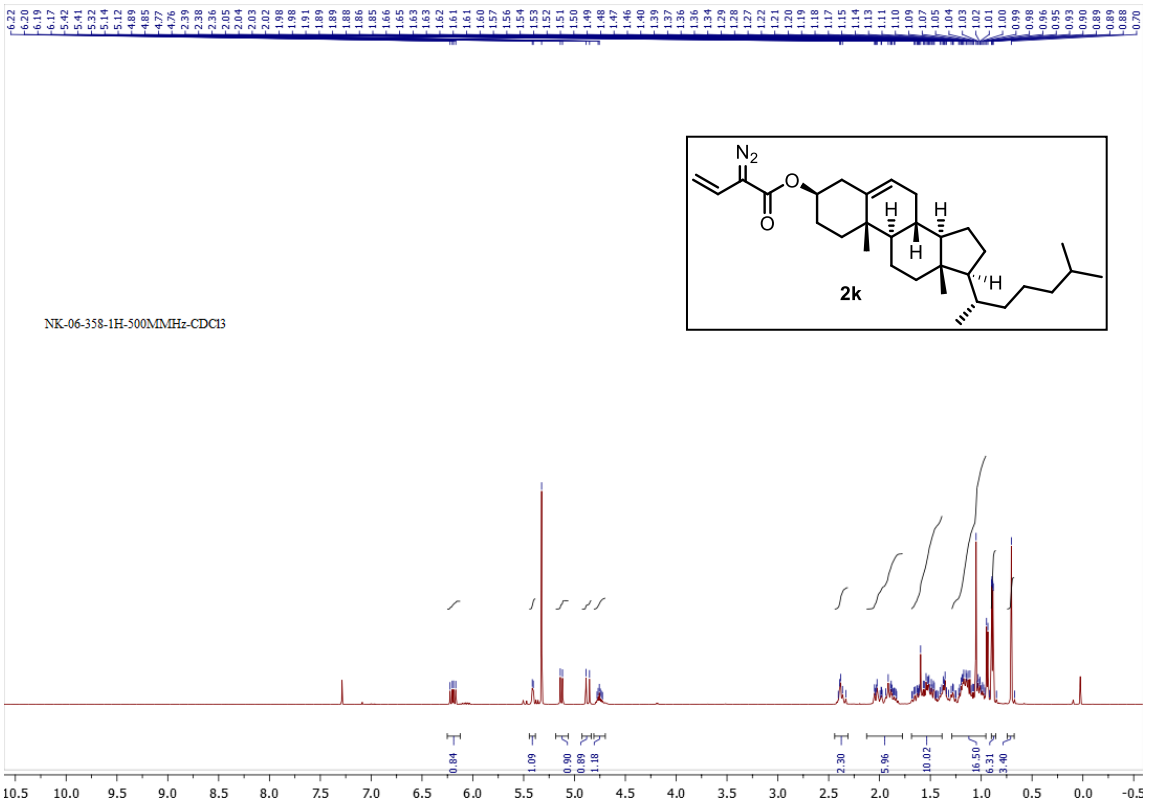
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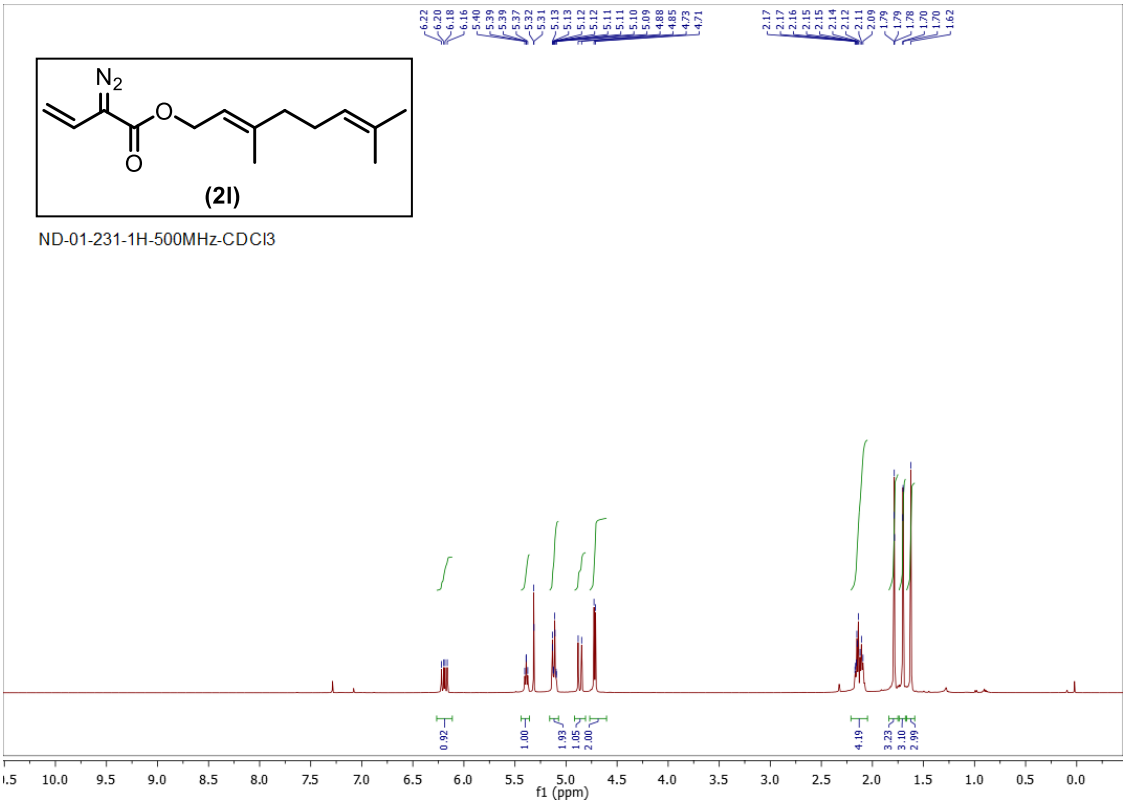
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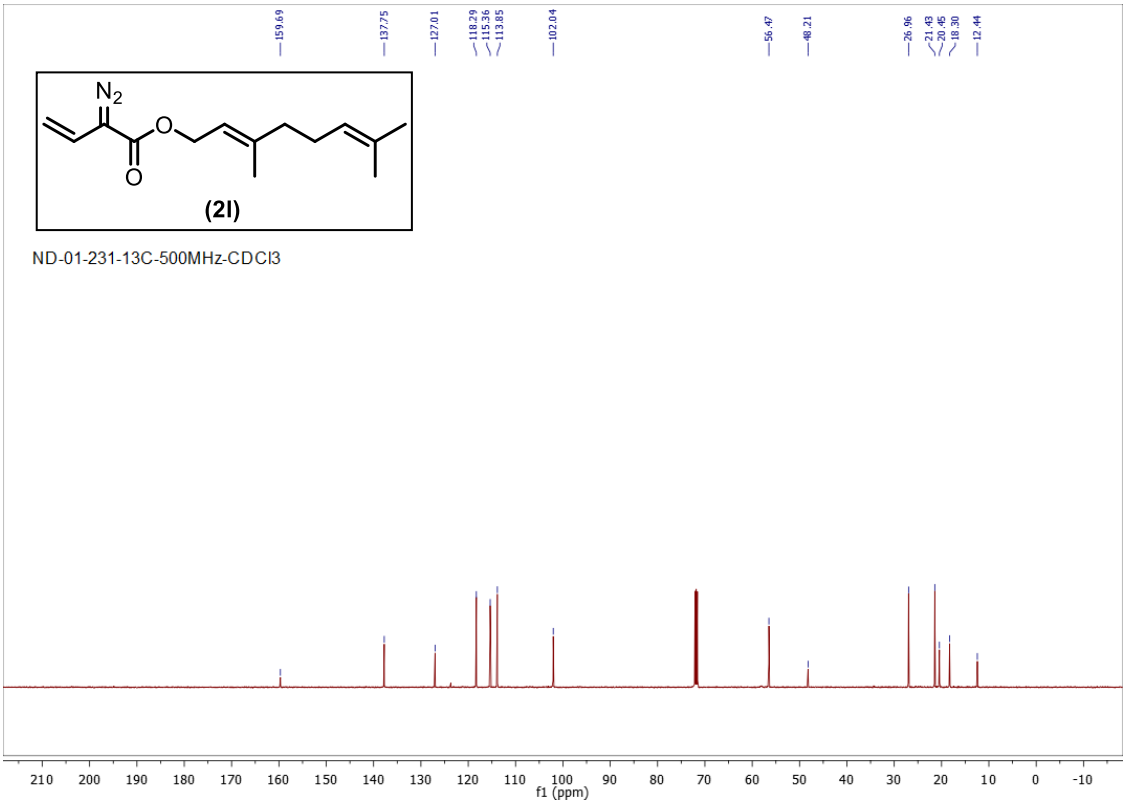
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Display Report

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Comment			

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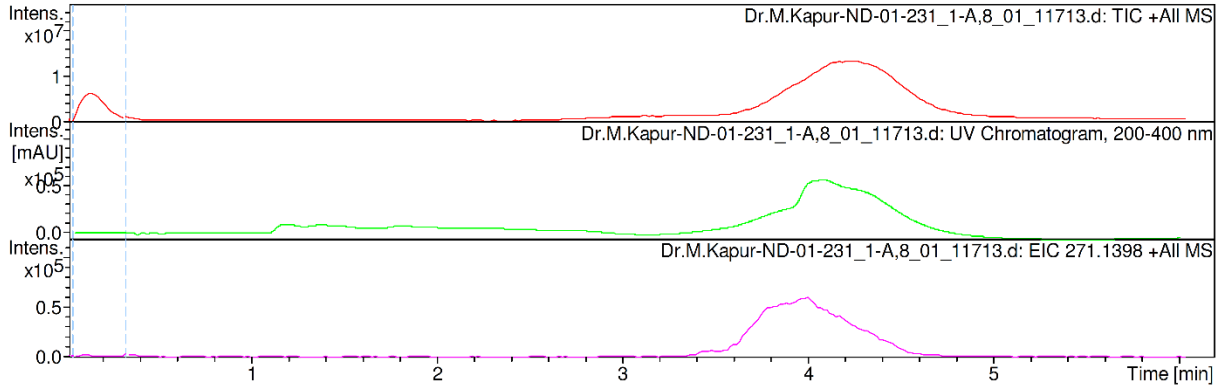

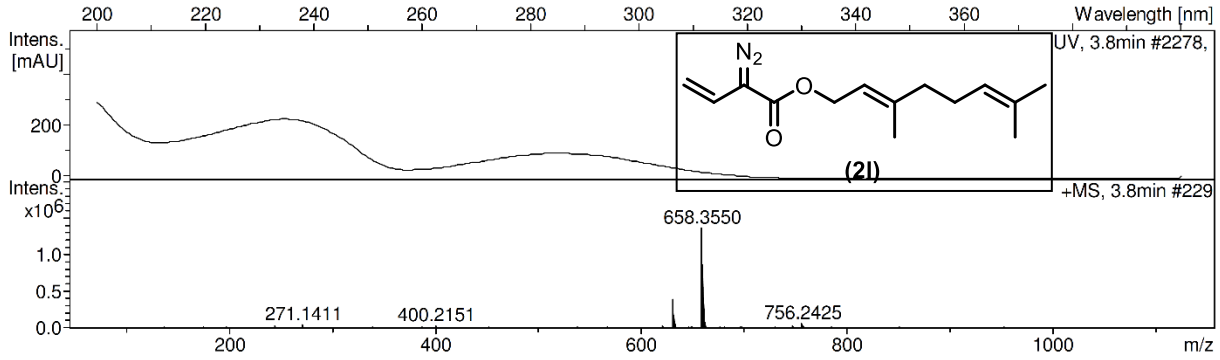

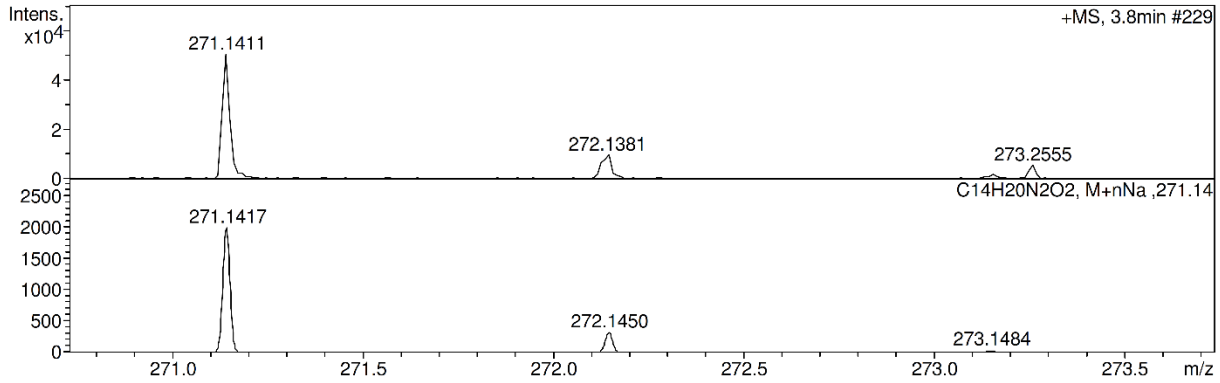

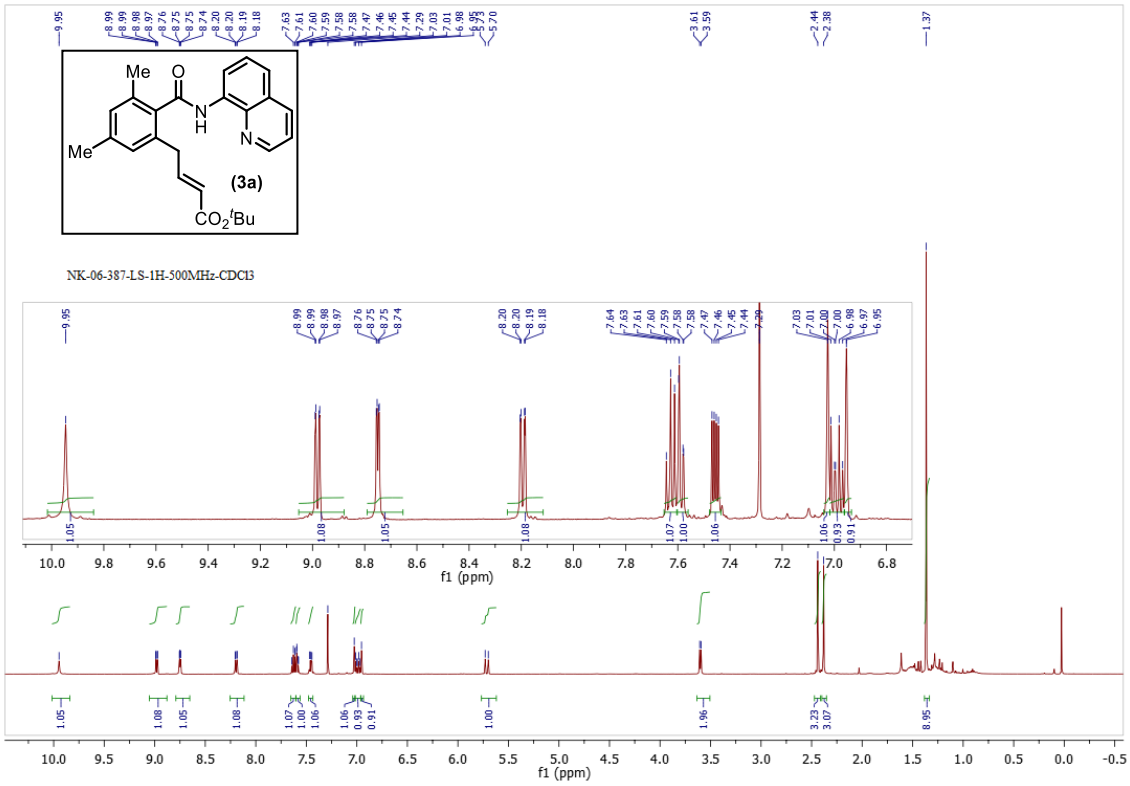
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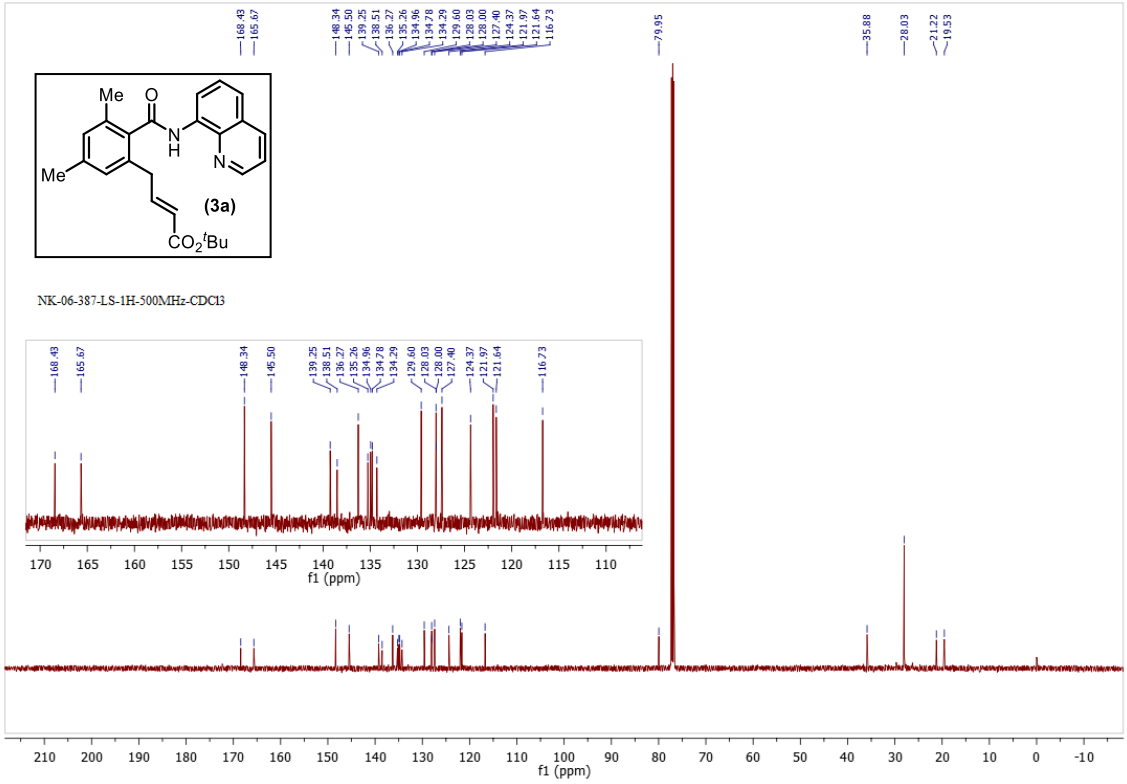
NK-06-387-LS-1H-500MHz-CDCl3
f1 (ppm)


Me
O
N
H
N
Me
(3a)
CO2tBu
NK-06-387-LS-1H-500MHz-CDCl3
f1 (ppm)

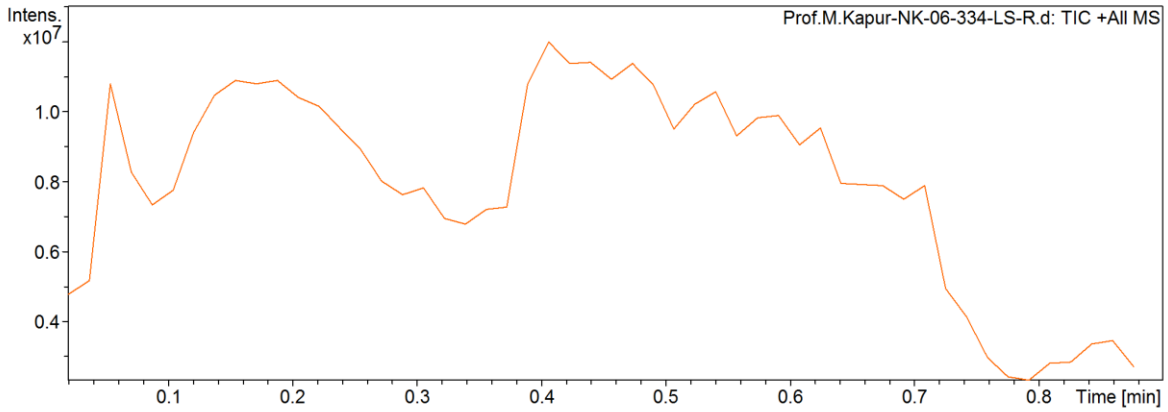
Display Report

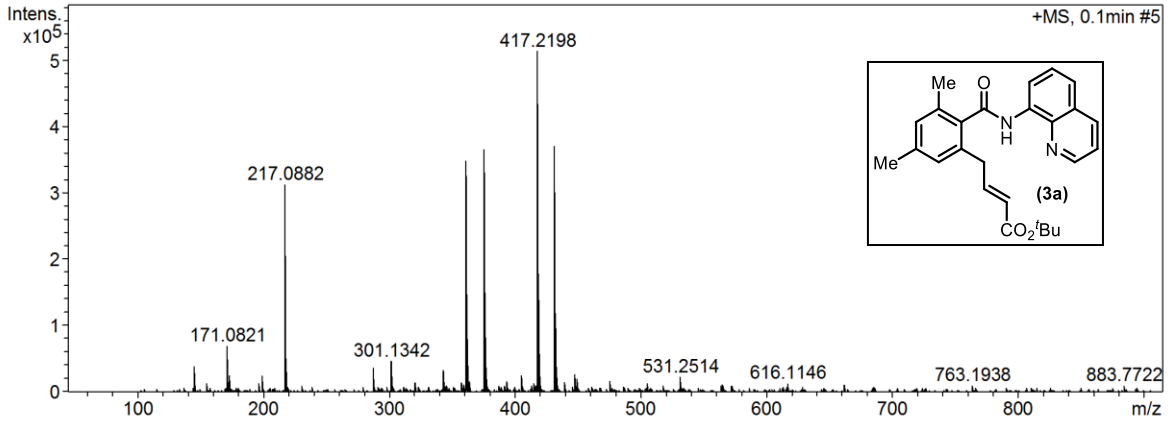
Analysis Info

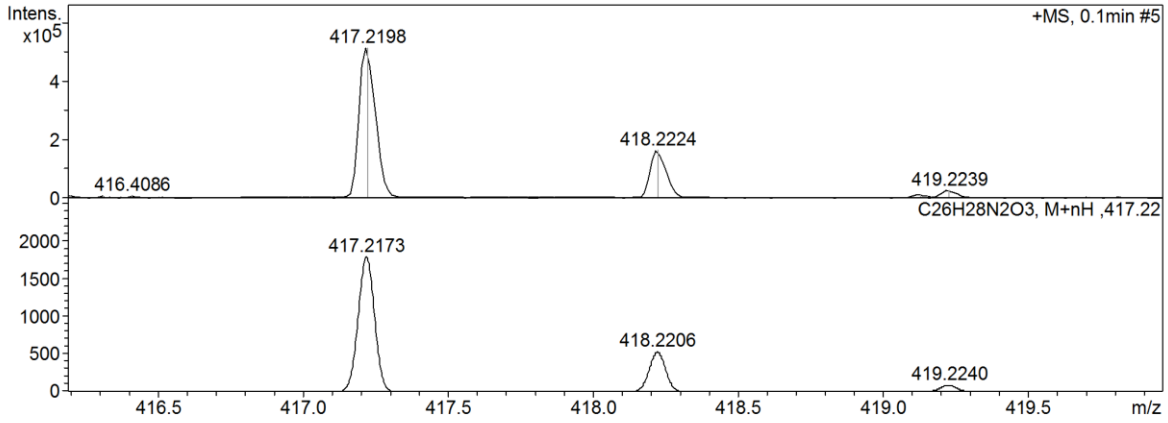
Analysis Name	C:\Users\HP\Desktop\31-jan-2022\Prof.M.Kapur-NK-06-334-LS-R.d	Acquisition Date	31-01-2022 10:49:27
Method	tune mix_low.New.021117.m	Operator	RUCHI
Sample Name	NK-06-334-LS-R	Instrument	micrOTOF-Q II 10330
Comment			

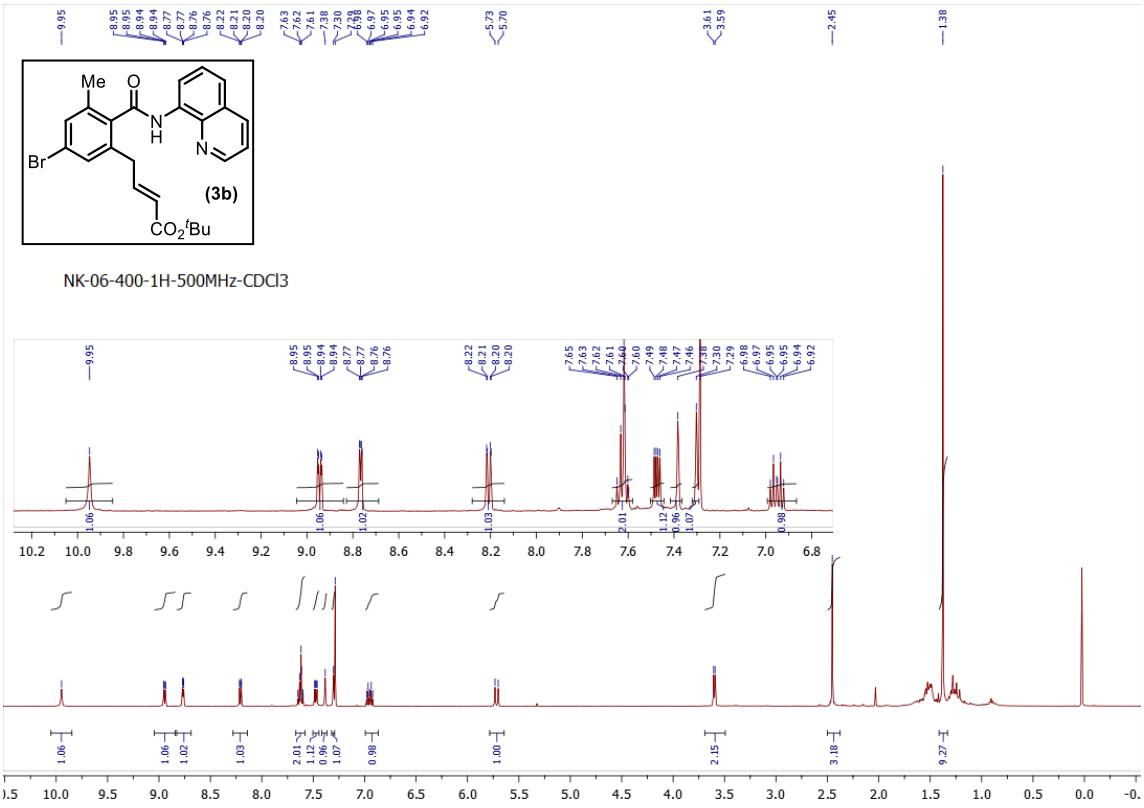
Acquisition Parameter

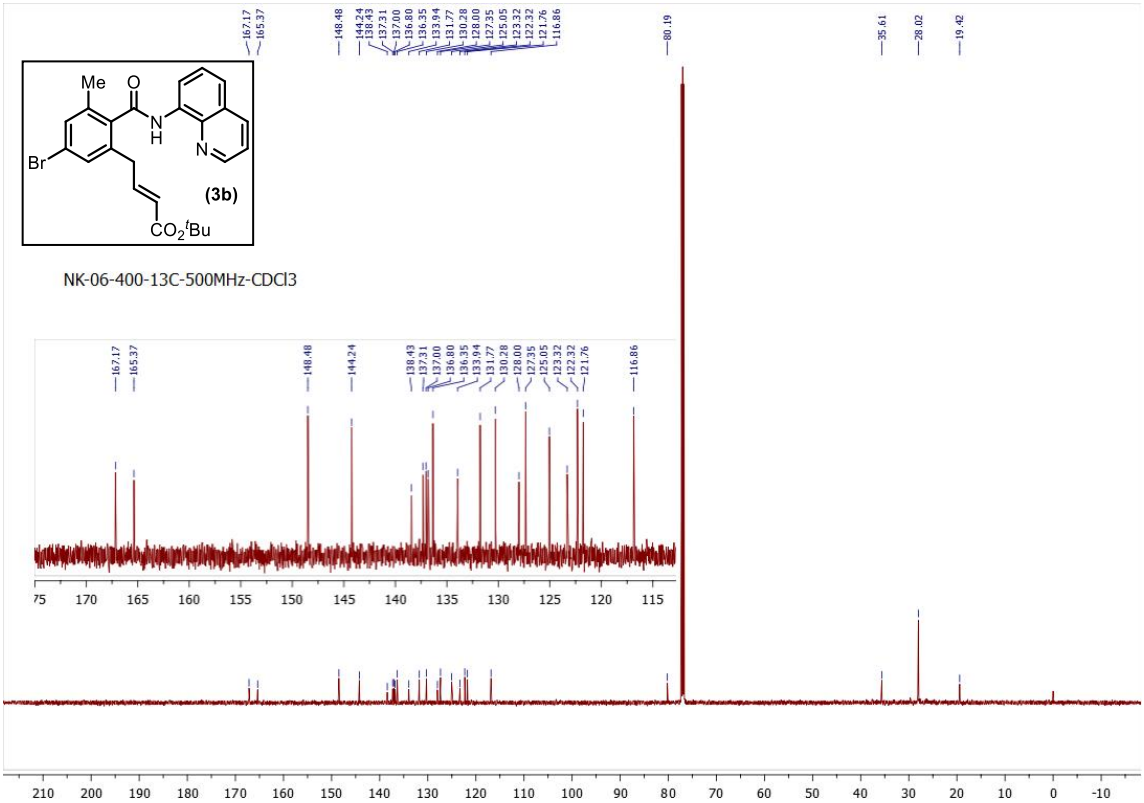
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source








Me
O
N
H
Br
N
(3b)
CO2tBu
NK-06-400-1H-500MHz-CDCl3


Me
O
N
H
Br
N
(3b)
CO2tBu
NK-06-400-13C-500MHz-CDCl3

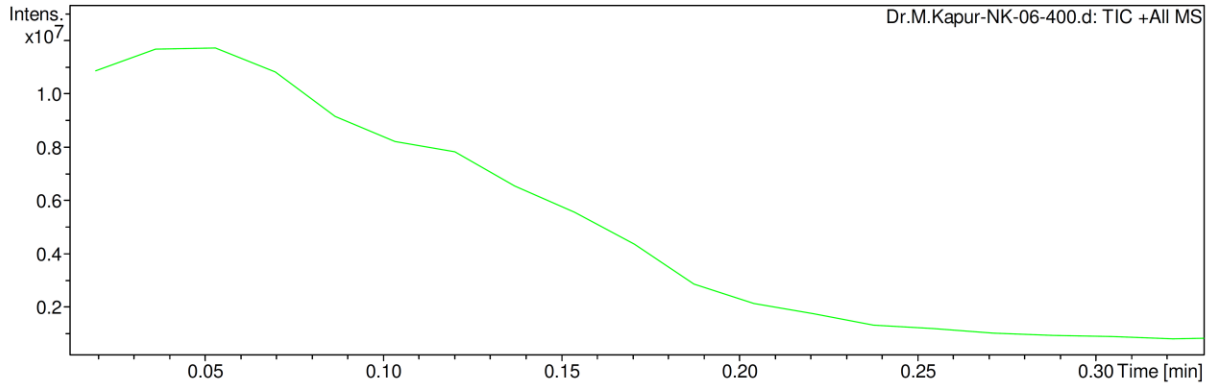
Display Report

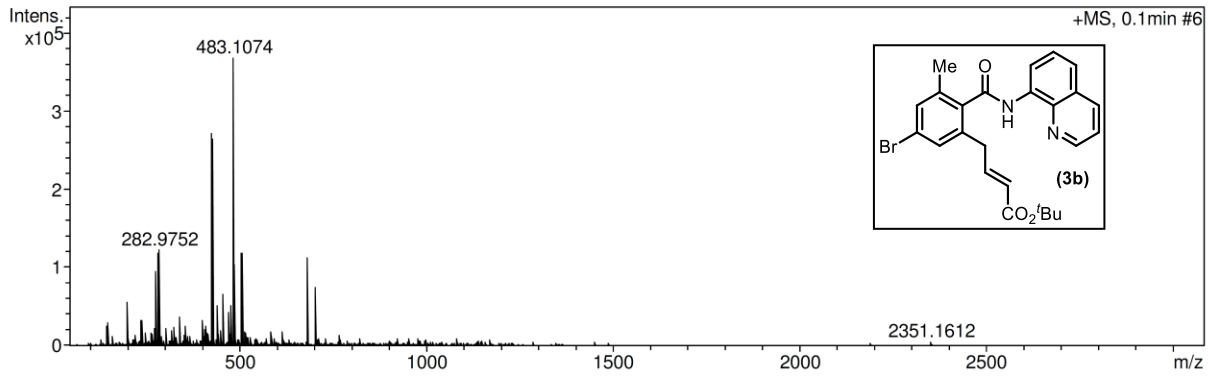
Analysis Info

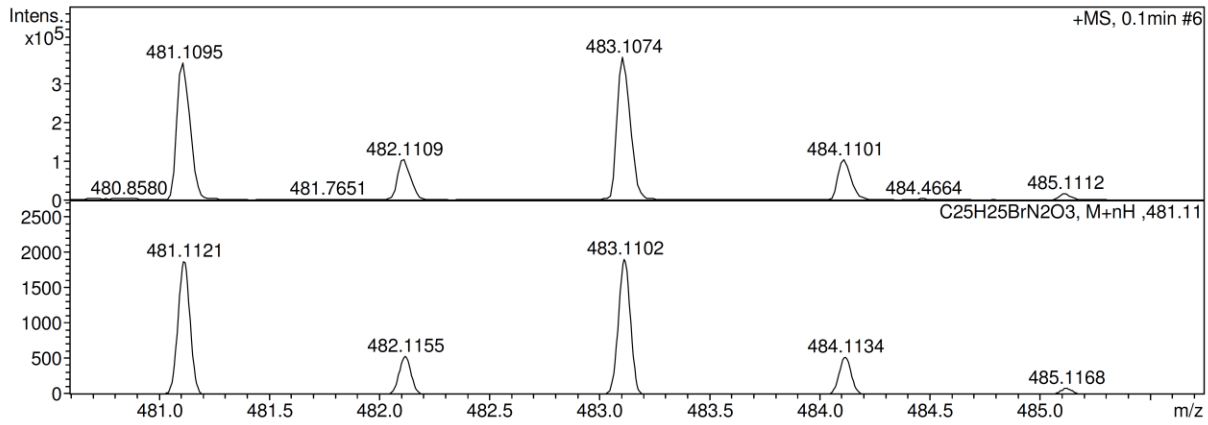
Analysis Name	D:\Data\NEW USER DATA 2022\April-2022\01-April\Dr.M.Kapur-NK-06-400.d	Acquisition Date	4/1/2022 3:54:31 PM
Method	tune mix_low.New.021117.m	Operator	RUCHI
Sample Name	NK-06-400	Instrument	micrOTOF-Q II 10330
Comment			

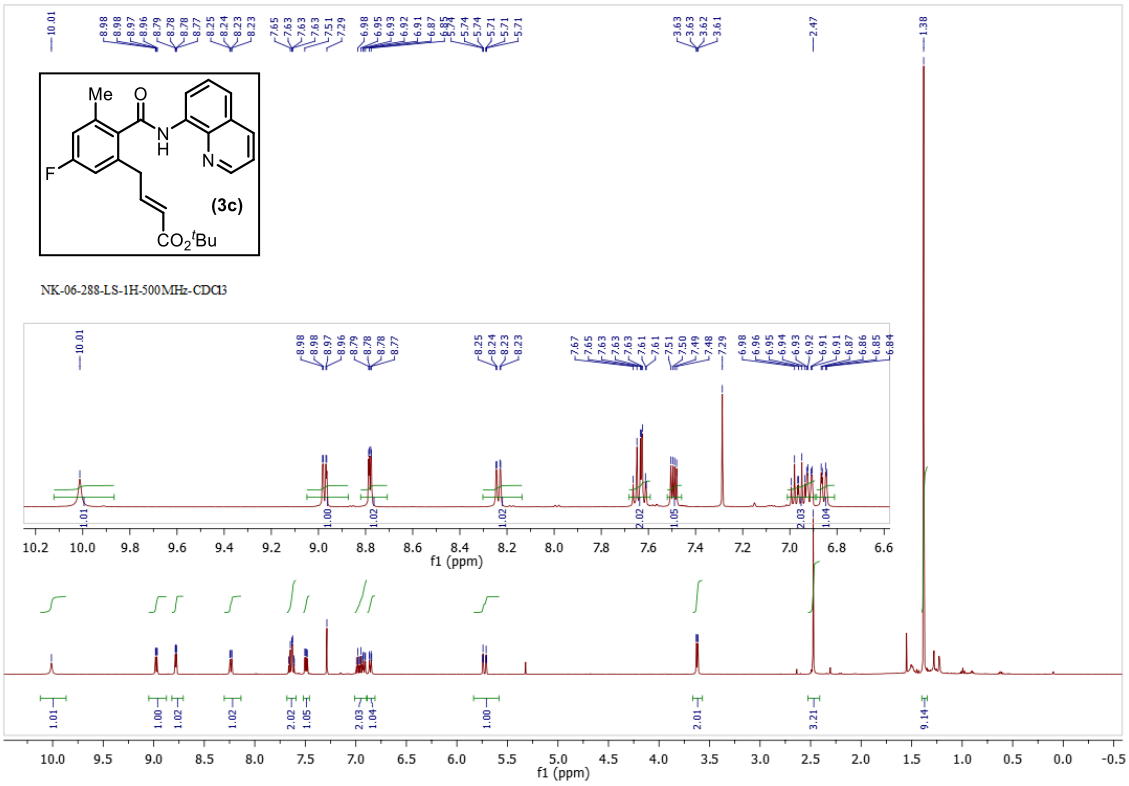
Acquisition Parameter

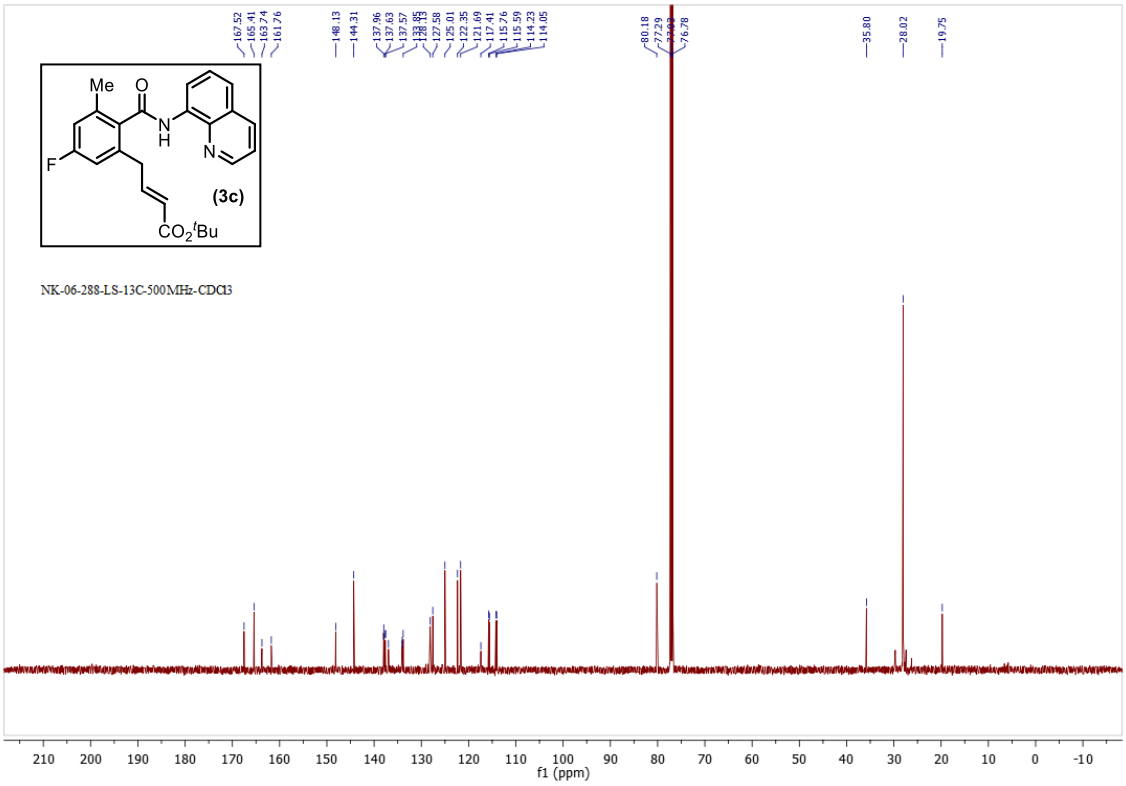
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source

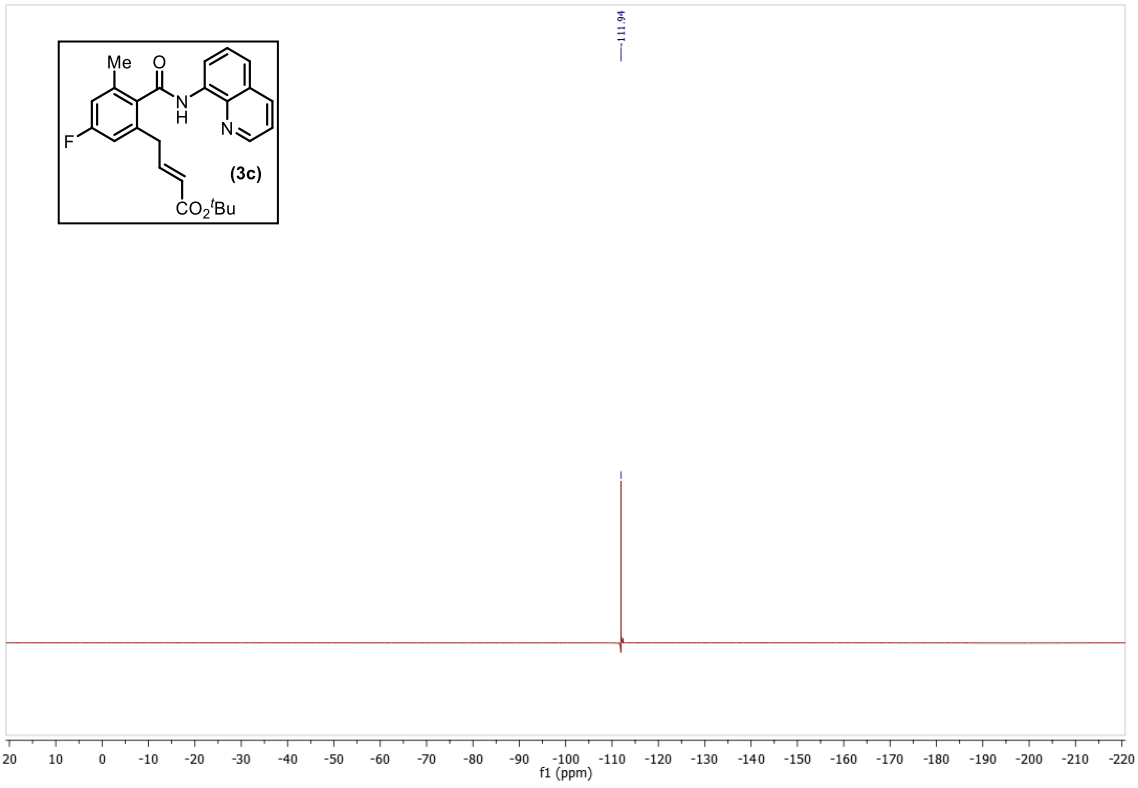







Me
O
N
H
F
N
(3c)
CO2tBu
NK-06-288-LS-1H-500MHz-CDCl3
f1 (ppm)


Me
O
N
H
F
N
(3c)
CO2tBu
NK-06-288-LS-13C-500MHz-CDCl3
f1 (ppm)


Me
O
N
H
N
F
(3c)
CO2tBu
-111.94
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

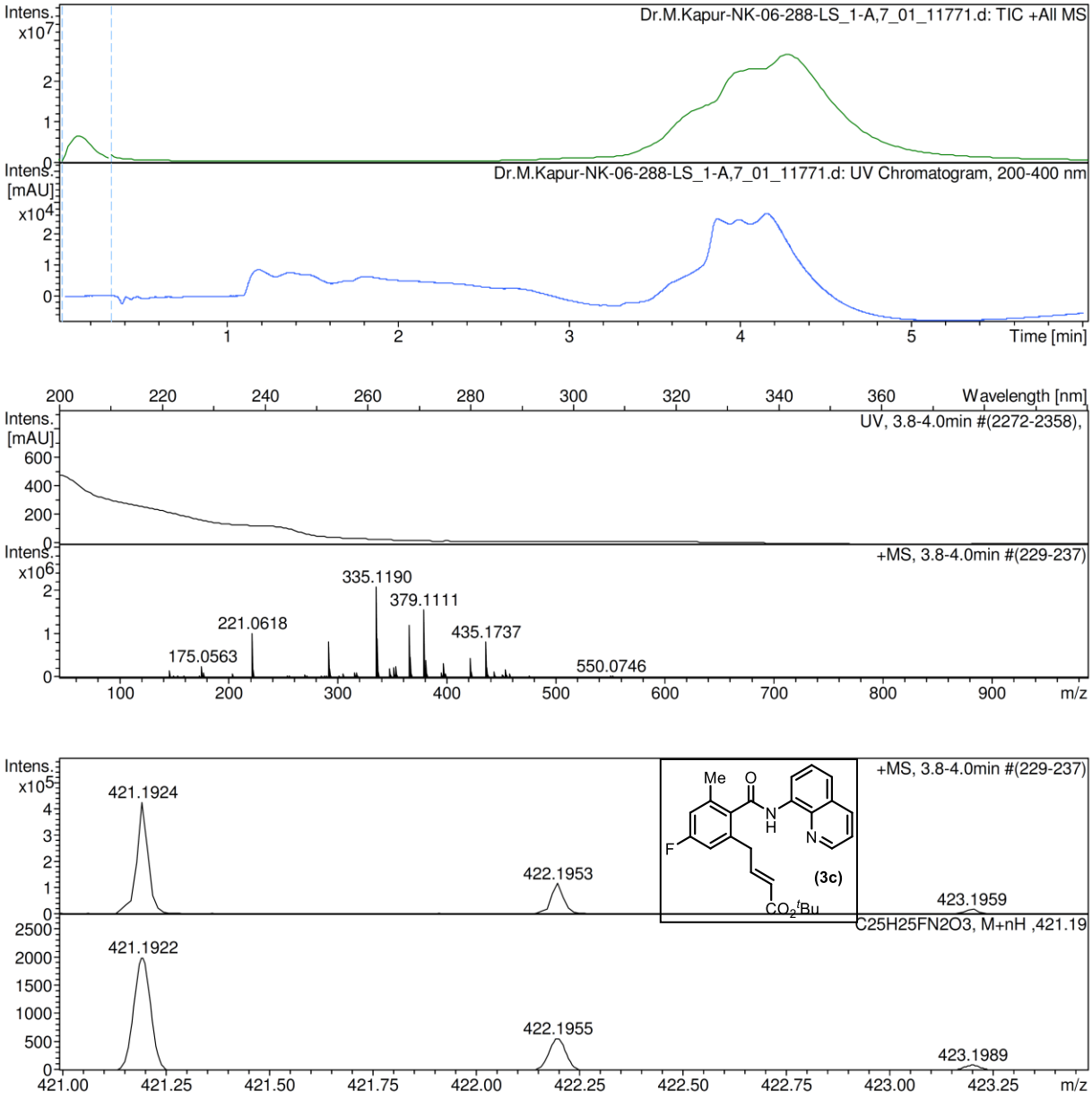
Display Report

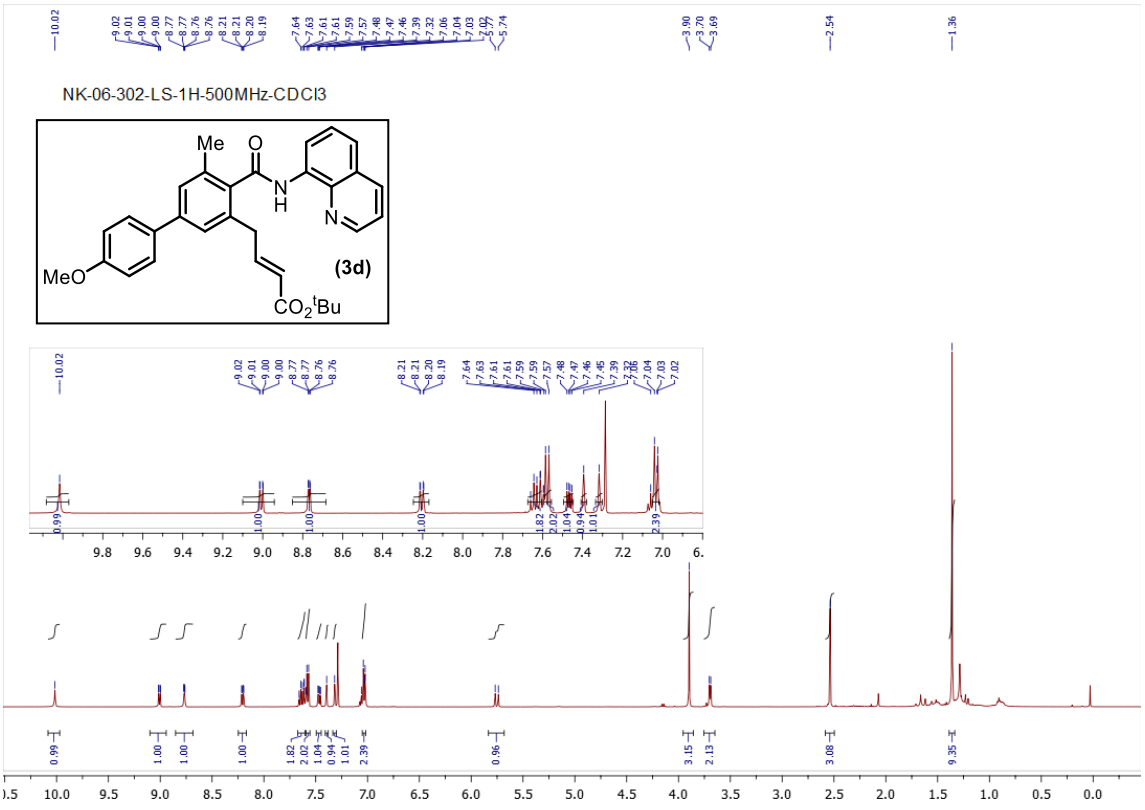
Analysis Info

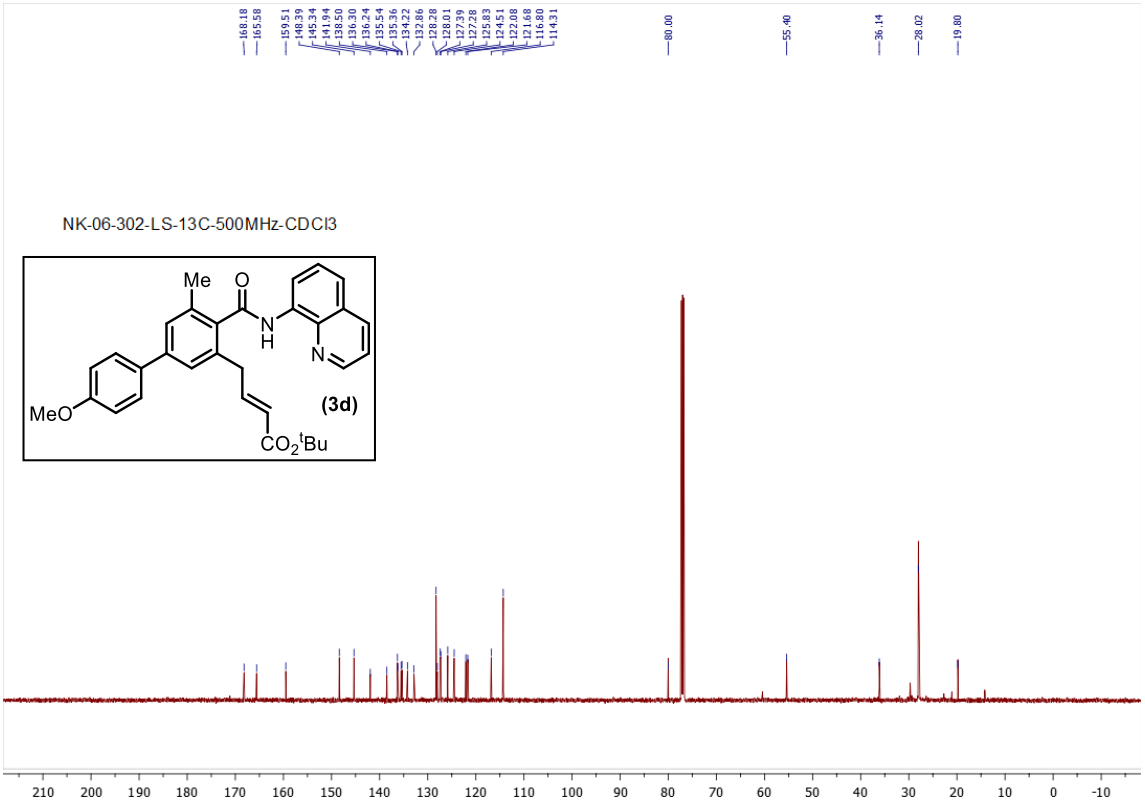
Acquisition Date	4/18/2022 1:04:26 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\April-2022\18-april\Dr.M.Kapur-NK-06-288-LS_1-A,7_01_11771.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr.M.Kapur-NK-06-288-LS	Instrument	micrOTOF-Q II 10330
Comment			

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




NK-06-302-LS-1H-500MHz-CDCl3
Me
O
N
H
N
MeO
(3d)
CO2tBu


NK-06-302-LS-13C-500MHz-CDCl3
Me
O
N
H
N
MeO
(3d)
CO2tBu

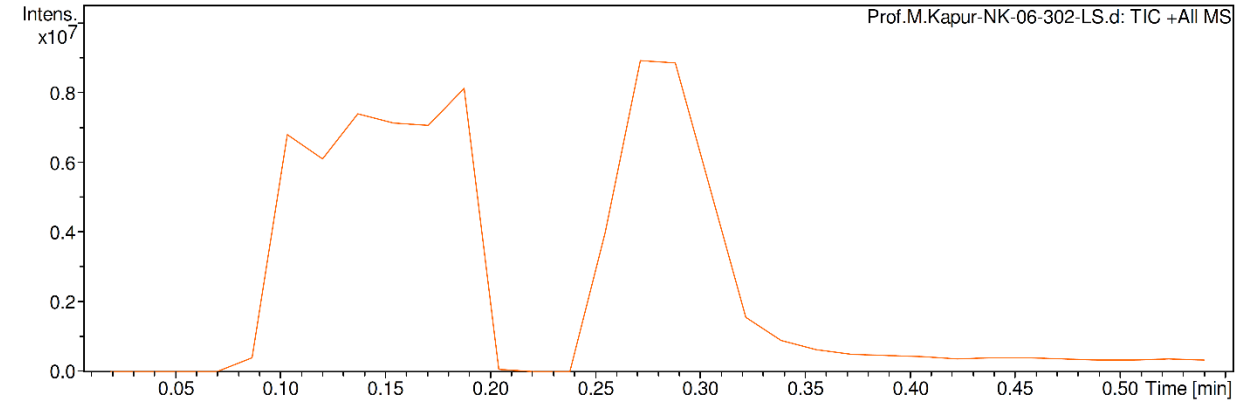
Display Report

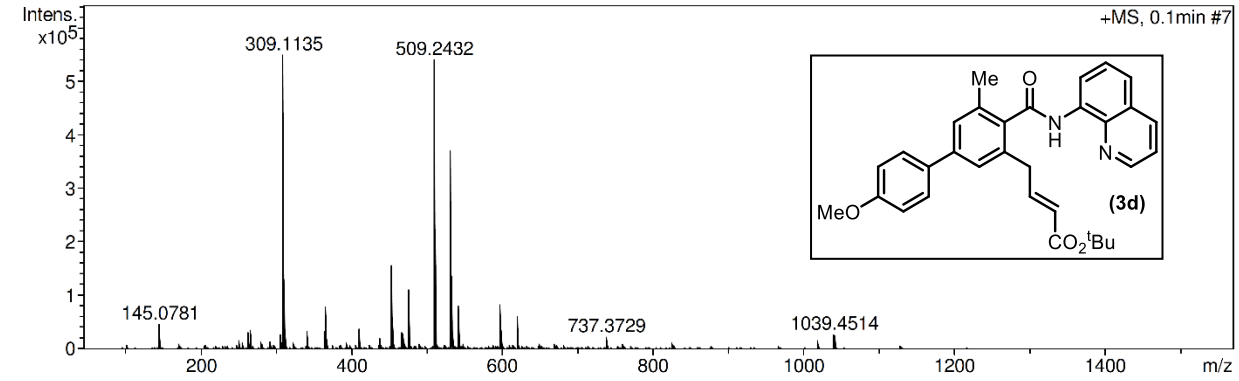
Analysis Info

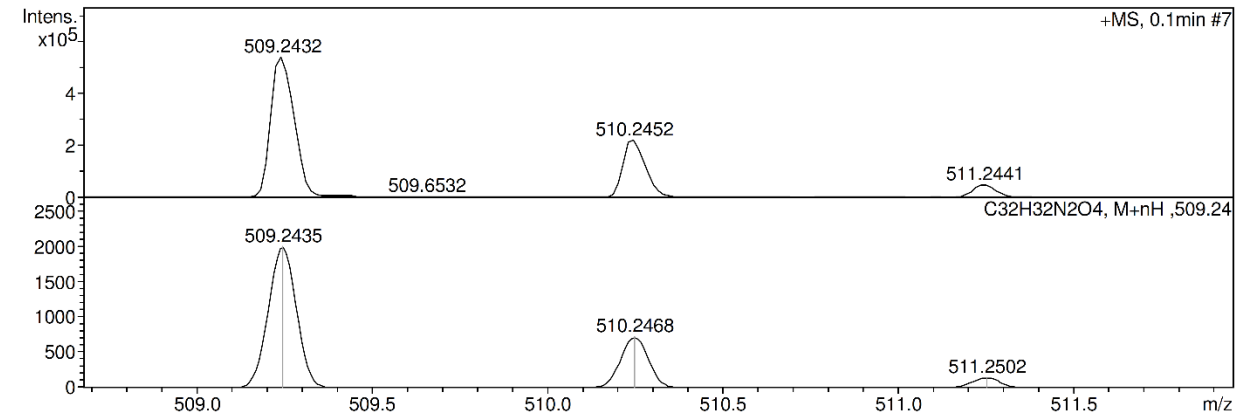
Analysis Name	D:\Data\new user data 2021\Oct-2021\29-oct\Prof.M.Kapur-NK-06-302-LS.d	Acquisition Date	10/29/2021 3:38:39 PM
Method	tune mix_low.New.021117.m	Operator	RUCHI
Sample Name	NK-06-302-LS	Instrument	micrOTOF-Q II 10330
Comment			

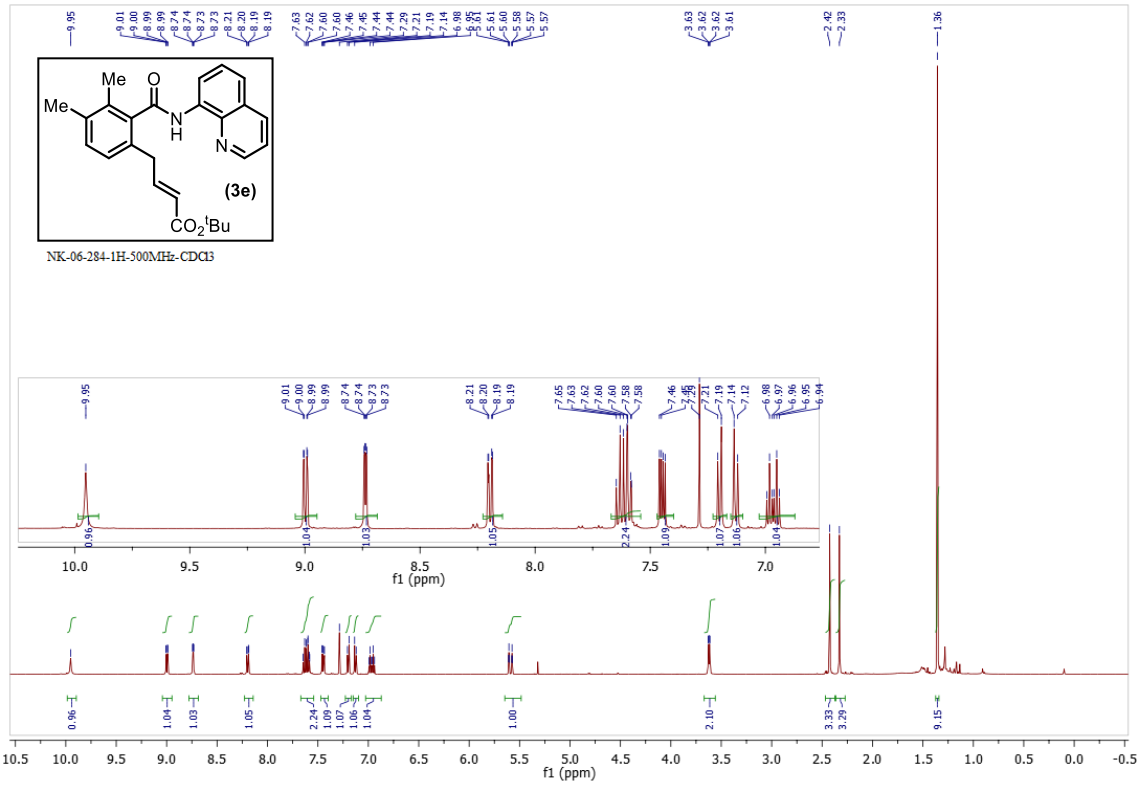
Acquisition Parameter

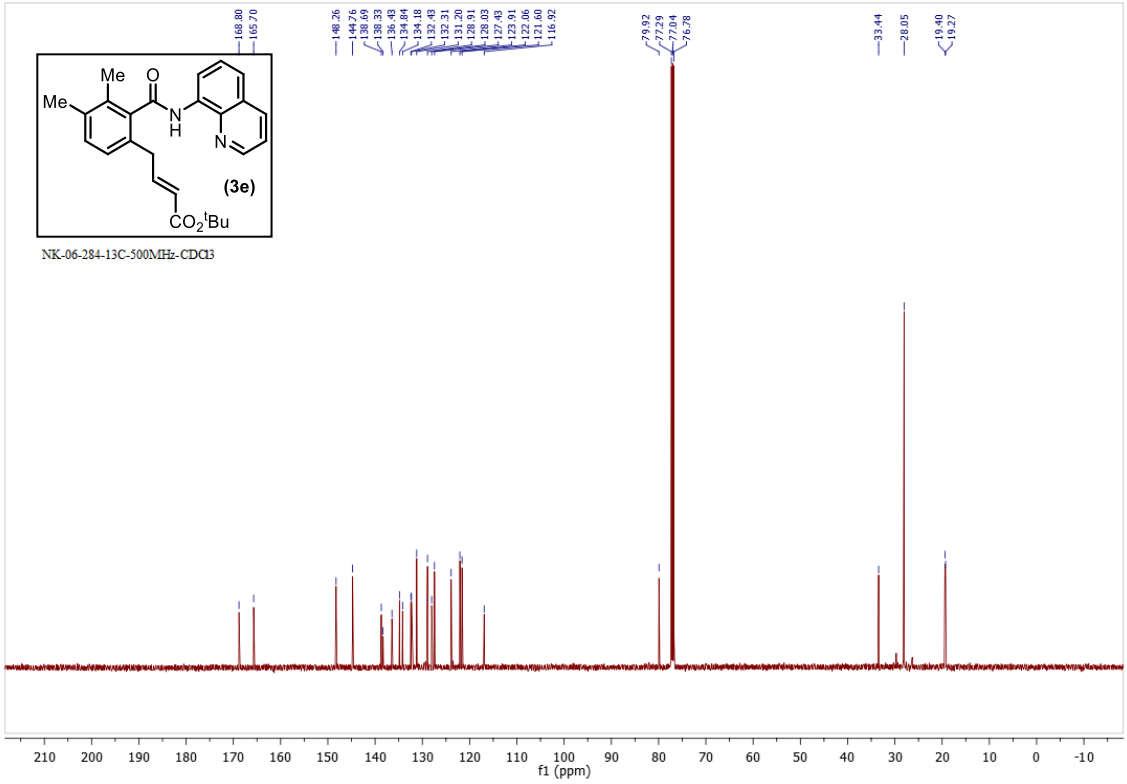
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste








Me
Me
O
N
H
N
(3e)
CO2tBu
NK-06-284-1H-500MHz-CDCl3
f1 (ppm)


Me
Me
O
N
H
N
(3e)
CO2tBu
NK-06-284-13C-500MHz-CDCl3
f1 (ppm)

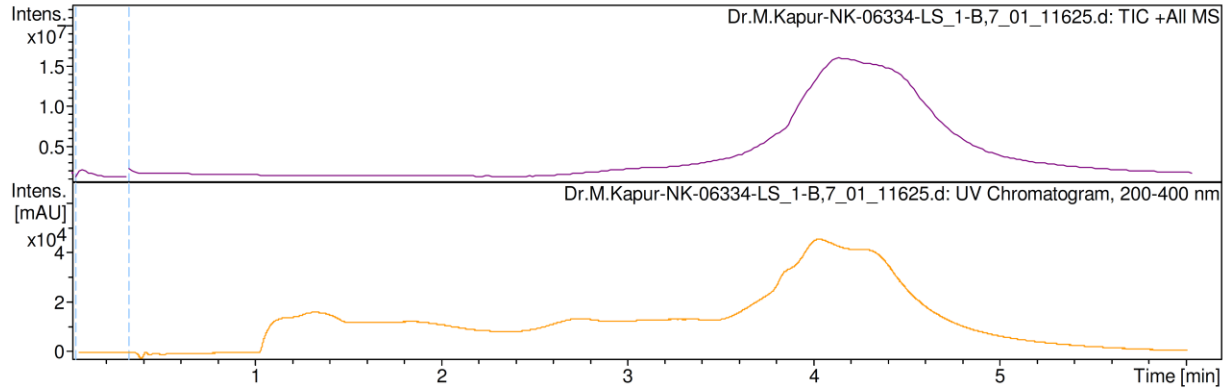
Display Report

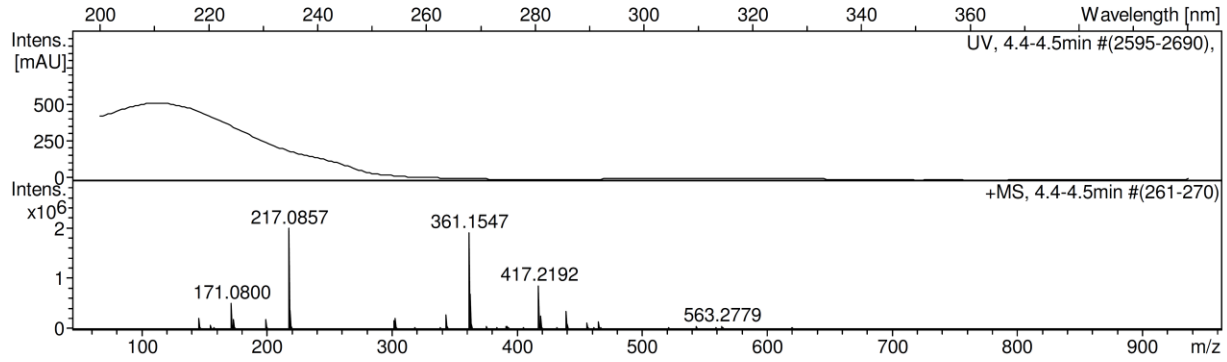
Analysis Info

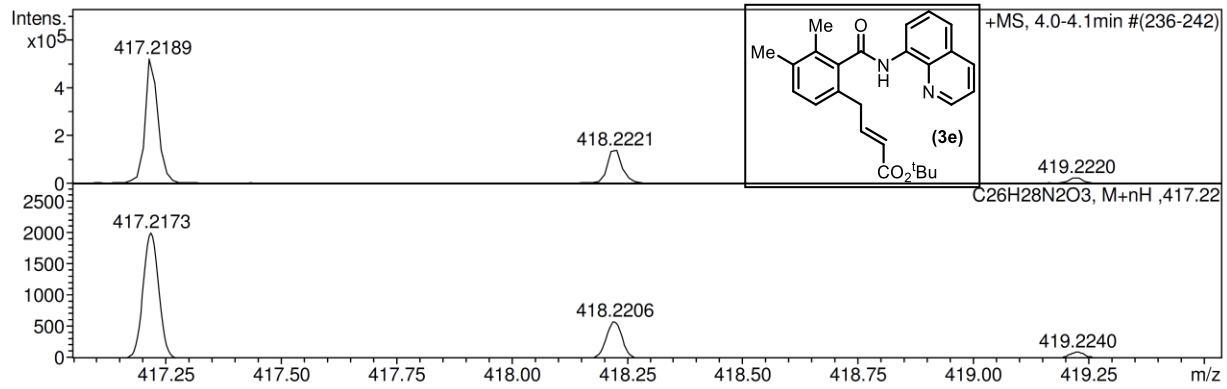
		Acquisition Date	4/1/2022 3:02:03 PM
Analysis Name	D:\Data\NEW USER DATA 2022\April-2022\01-April\Dr.M.Kapur-NK-06334-LS_1-B,7_01_11625.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr.M.Kapur-NK-06334-LS	Instrument	micrOTOF-Q II 10330
Comment			

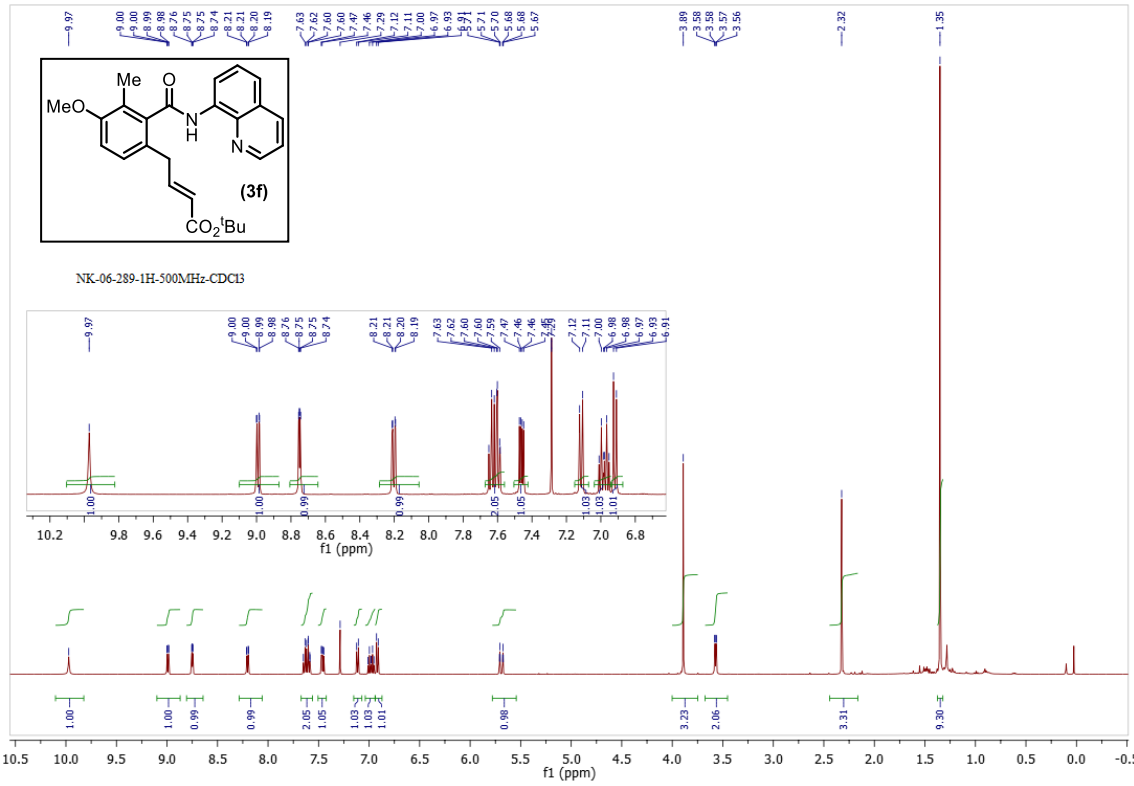
Acquisition Parameter

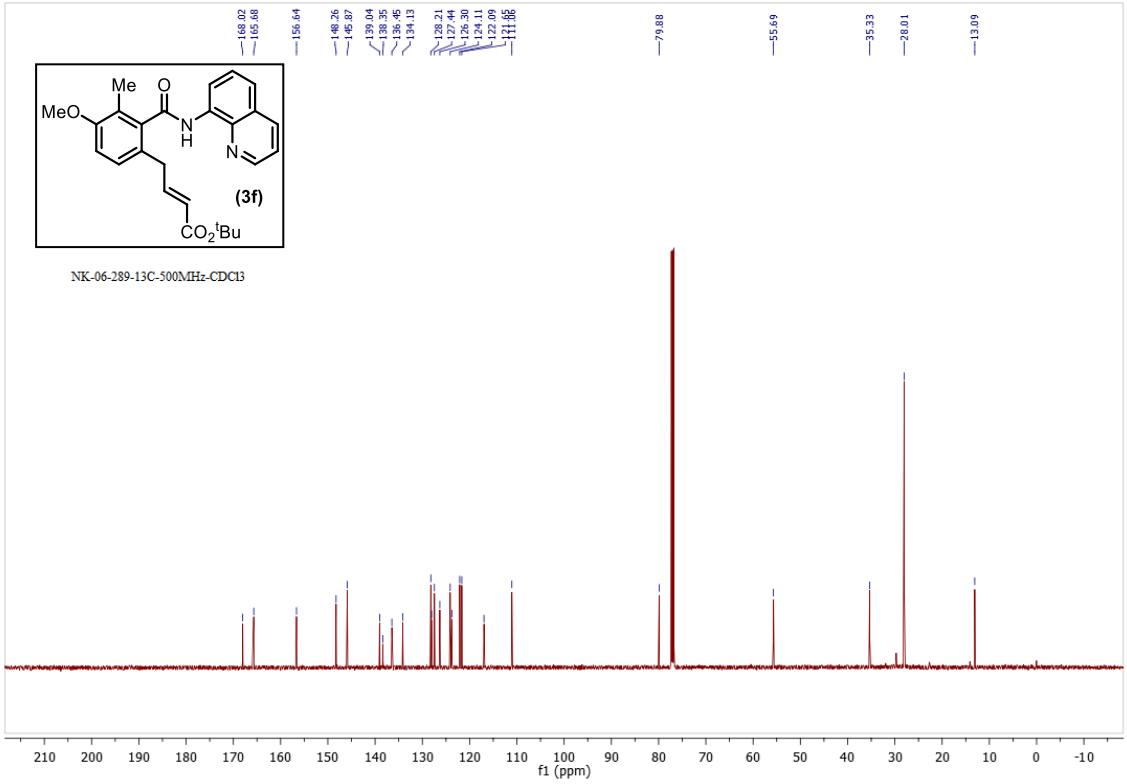
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








Me
O
MeO
N
H
N
(3f)
CO2tBu
NK-06-289-1H-500MHz-CDCl3
f1 (ppm)


Me
O
MeO
N
H
N
(3f)
CO2tBu
NK-06-289-13C-500MHz-CDCl3
f1 (ppm)

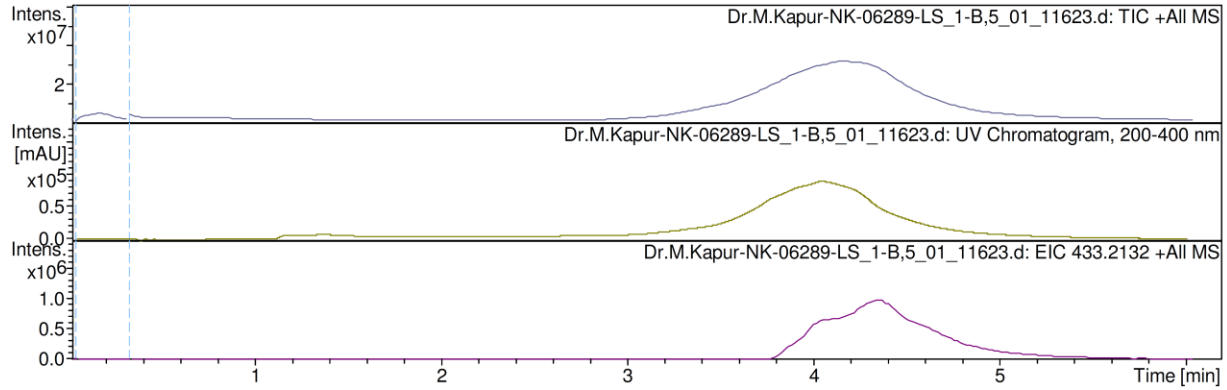
Display Report

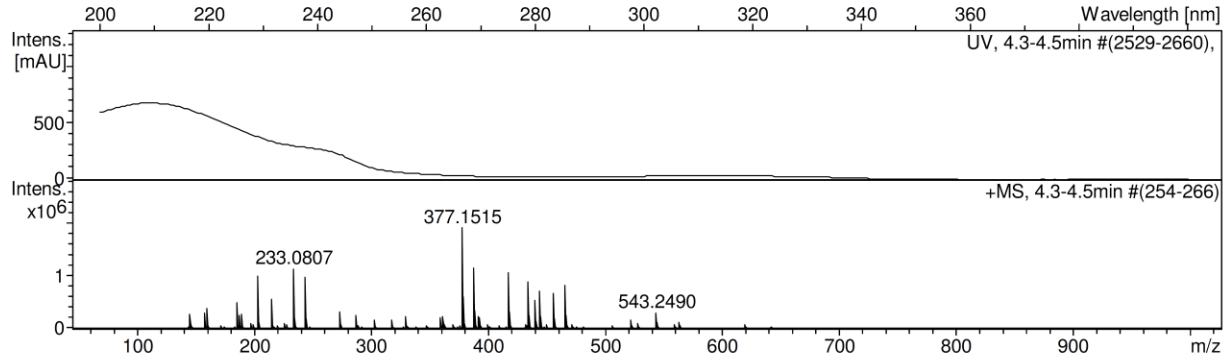
Analysis Info

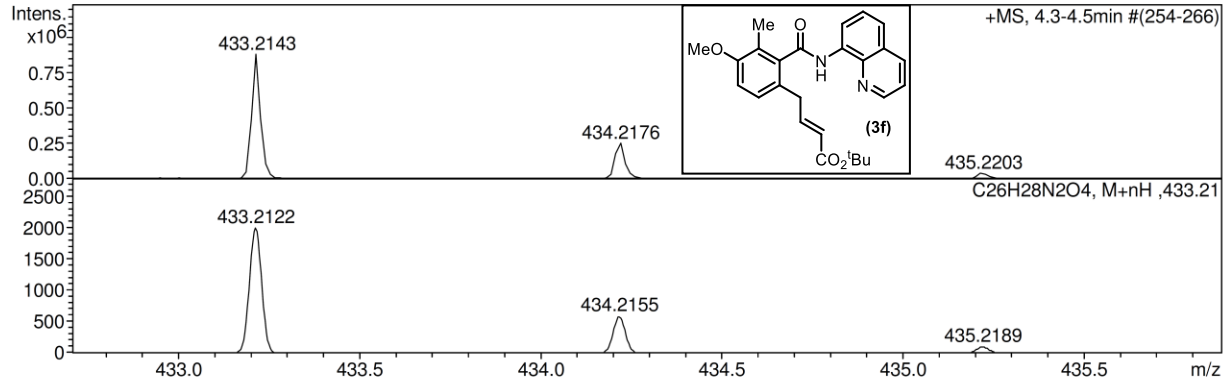
Acquisition Date	4/1/2022 2:47:38 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\April-2022\01-April\Dr.M.Kapur-NK-06289-LS_1-B,5_01_11623.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr.M.Kapur-NK-06289-LS	Instrument	micrOTOF-Q II 10330
Comment			

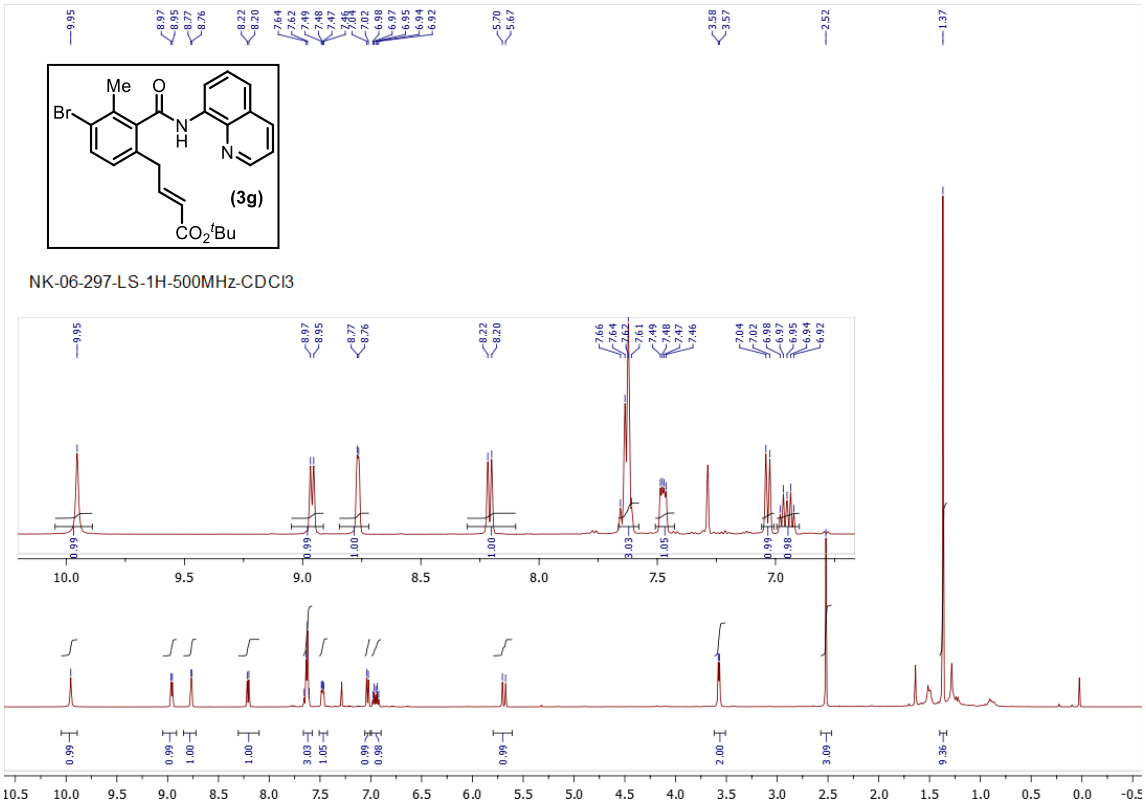
Acquisition Parameter

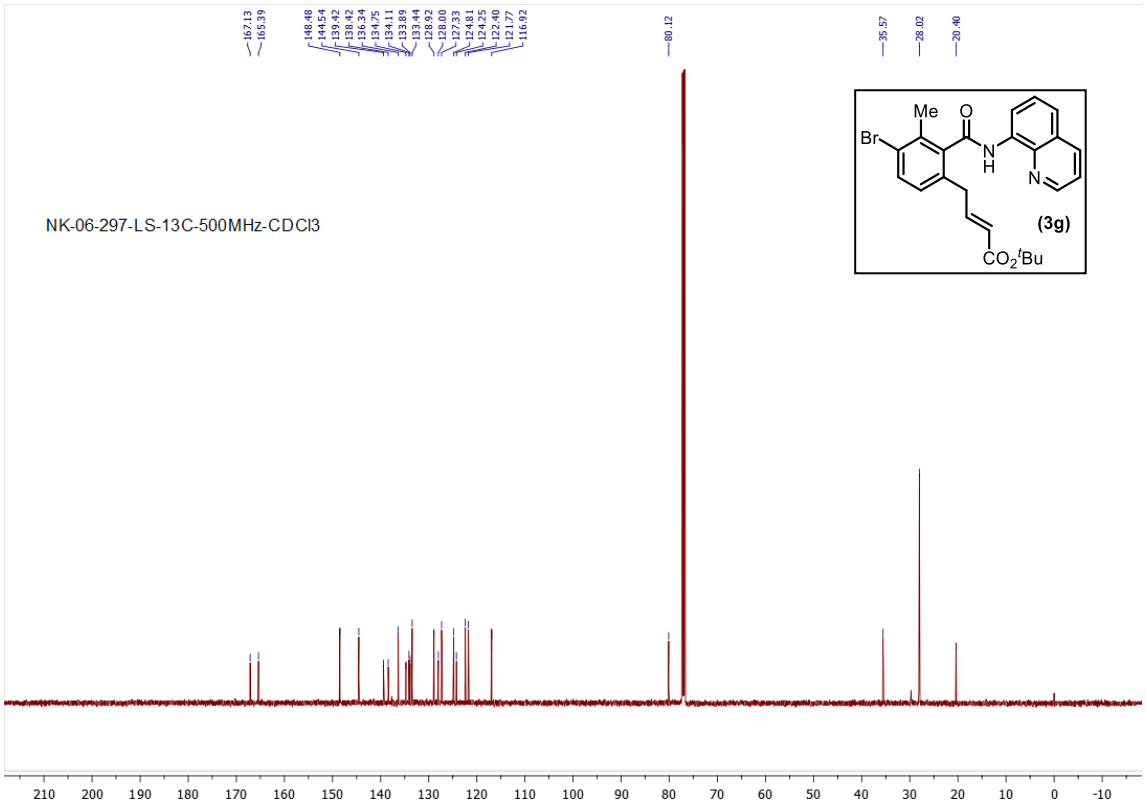
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








Me
O
Br
N
H
N
(3g)
CO2tBu
NK-06-297-LS-1H-500MHz-CDCl3


NK-06-297-LS-13C-500MHz-CDCl3
Me
O
Br
N
H
N
(3g)
CO2tBu

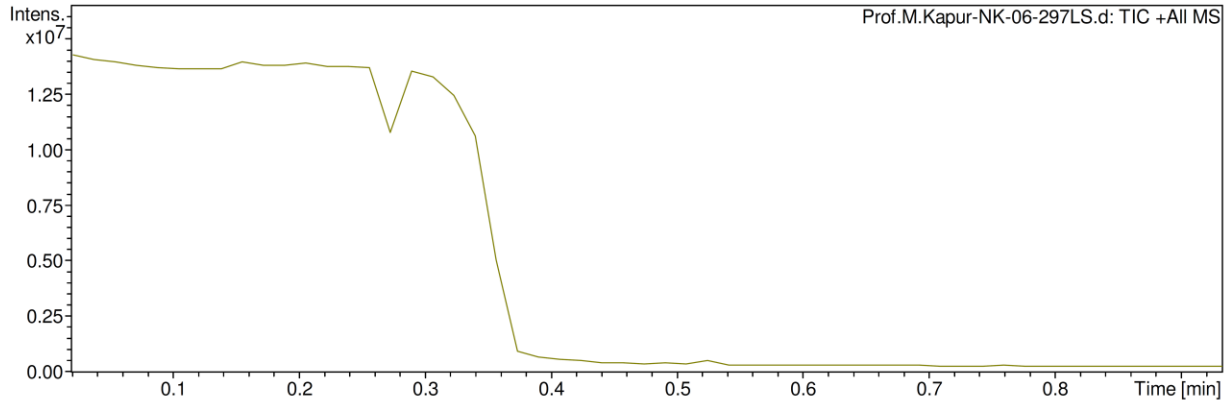
Display Report

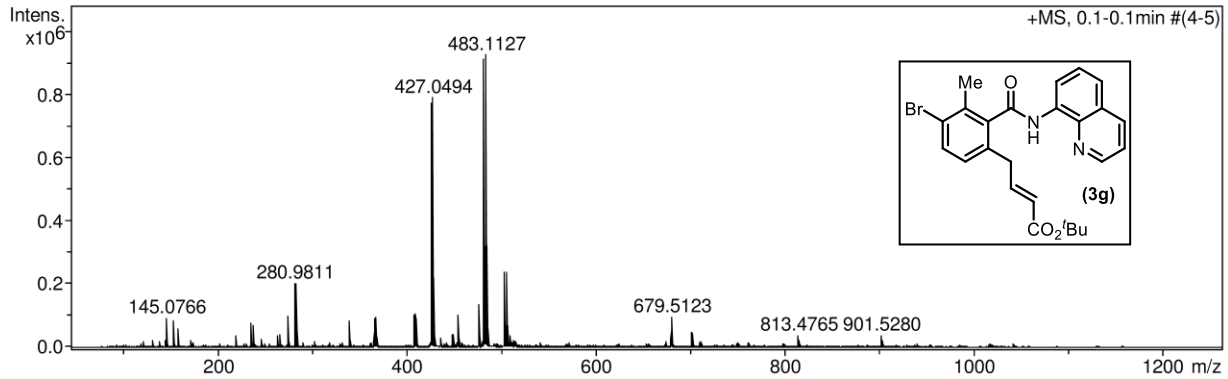
Analysis Info

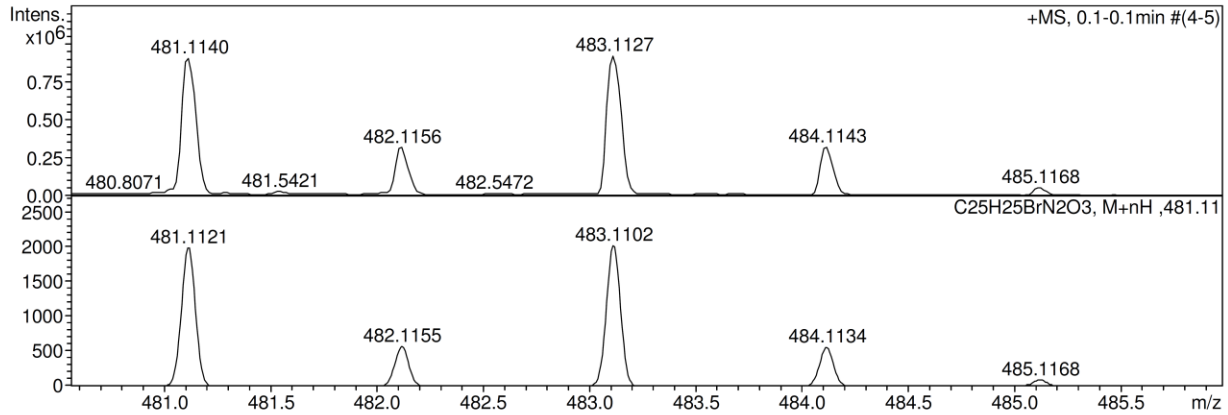
Analysis Name	D:\Data\new user data 2021\Oct-2021\22-oct\Prof.M.Kapur-NK-06-297LS.d	Acquisition Date	10/22/2021 10:43:07 AM
Method	tune mix_low.New.021117.m	Operator	RUCHI
Sample Name	NK-06-297LS	Instrument	micrOTOF-Q II 10330
Comment			

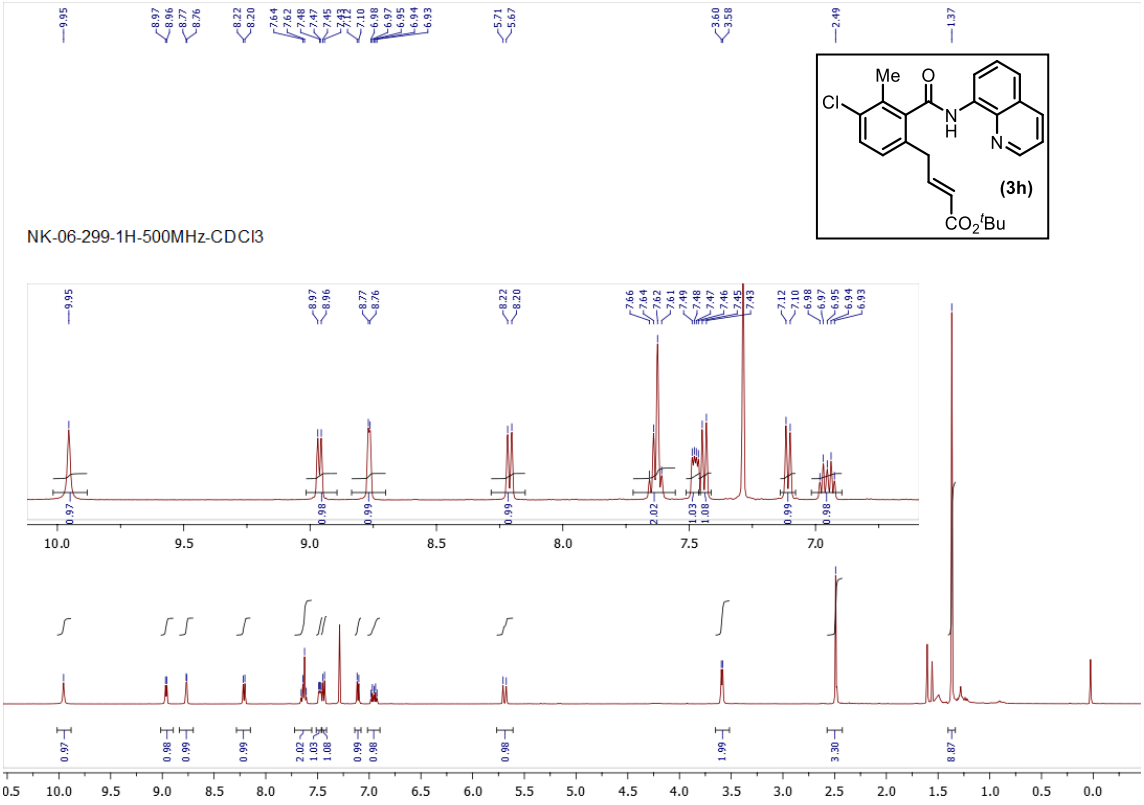
Acquisition Parameter

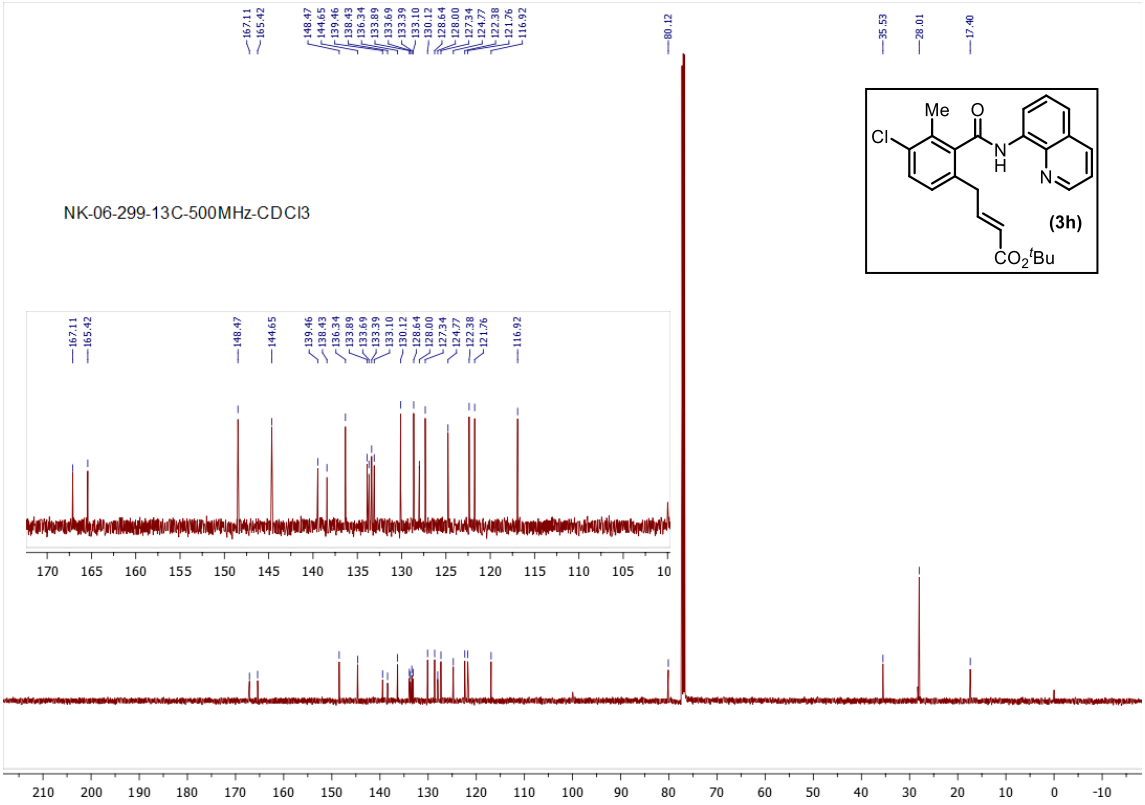
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste








NK-06-299-1H-500MHz-CDCl3
(3h)


NK-06-299-13C-500MHz-CDCl3
(3h)

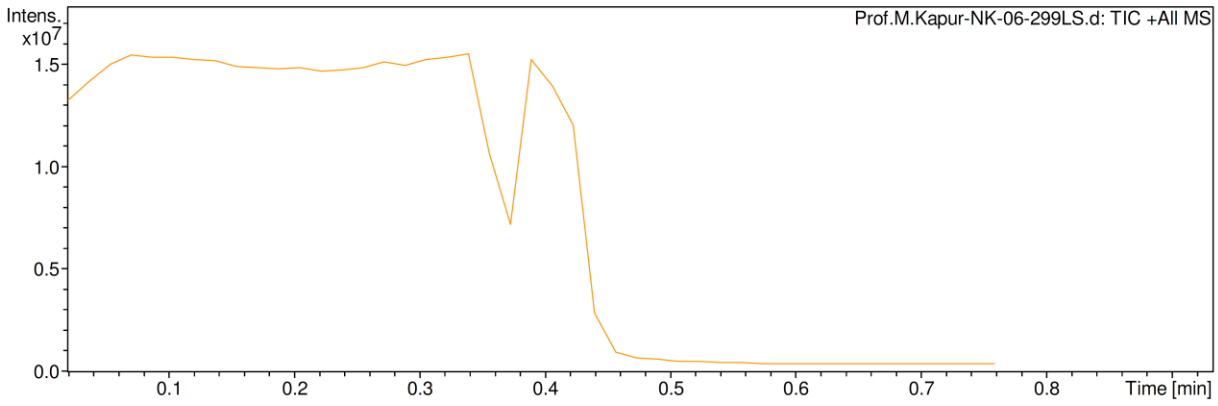
Display Report

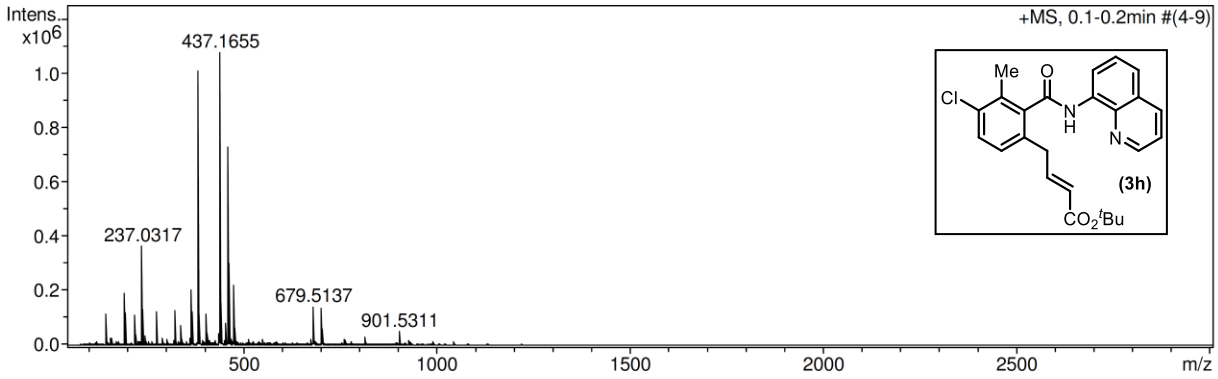
Analysis Info

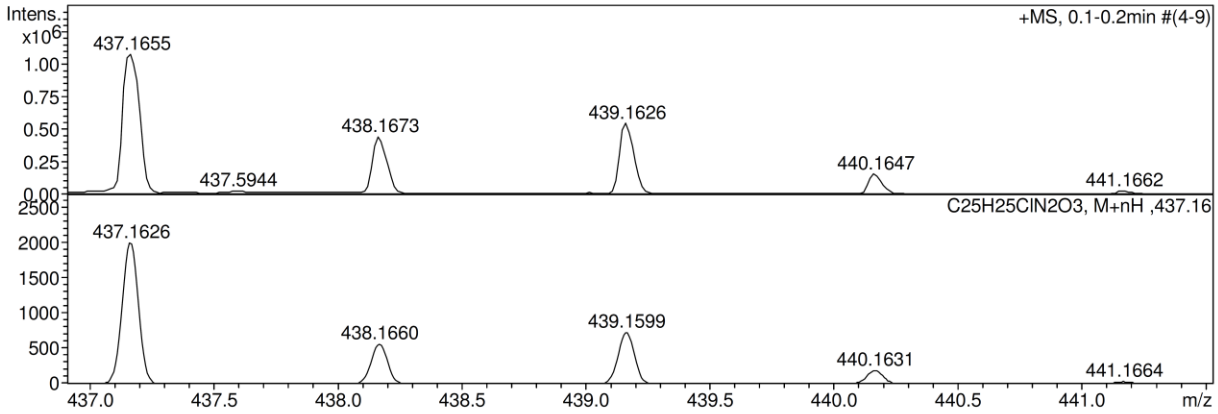
		Acquisition Date	10/22/2021 10:52:43 AM
Analysis Name	D:\Data\new user data 2021\Oct-2021\22-oct\Prof.M.Kapur-NK-06-299LS.d		
Method	tune mix_low.New.021117.m	Operator	RUCHI
Sample Name	NK-06-299LS	Instrument	micrOTOF-Q II 10330
Comment			

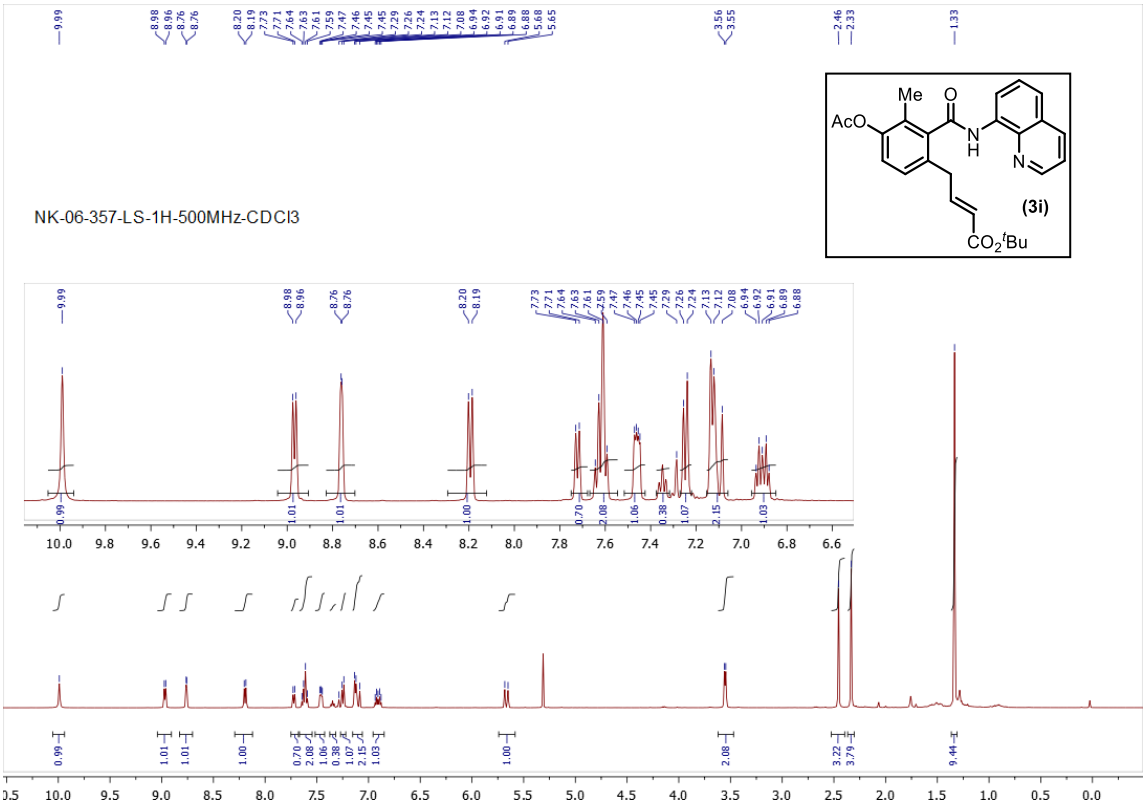
Acquisition Parameter

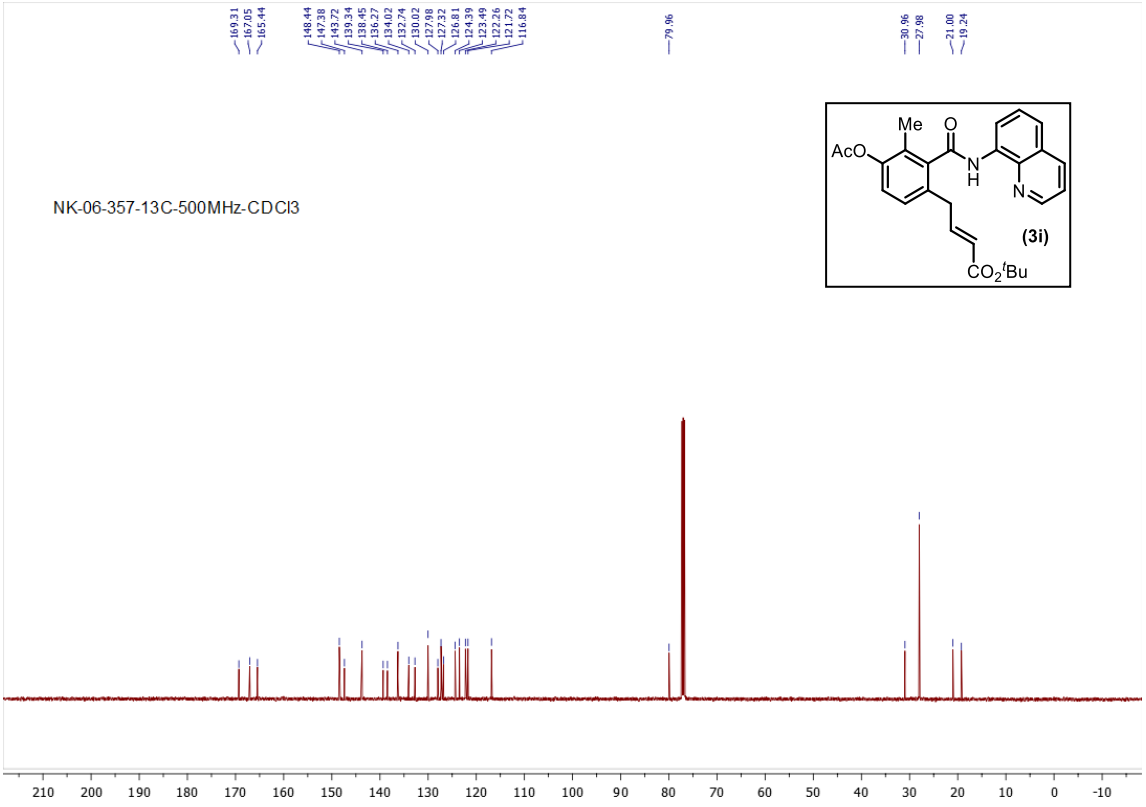
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste








NK-06-357-LS-1H-500MHz-CDCl3
Me
O
AcO
N
H
N
(3i)
CO2tBu


NK-06-357-13C-500MHz-CDCl3
Me
O
AcO
N
H
N
(3i)
CO2tBu

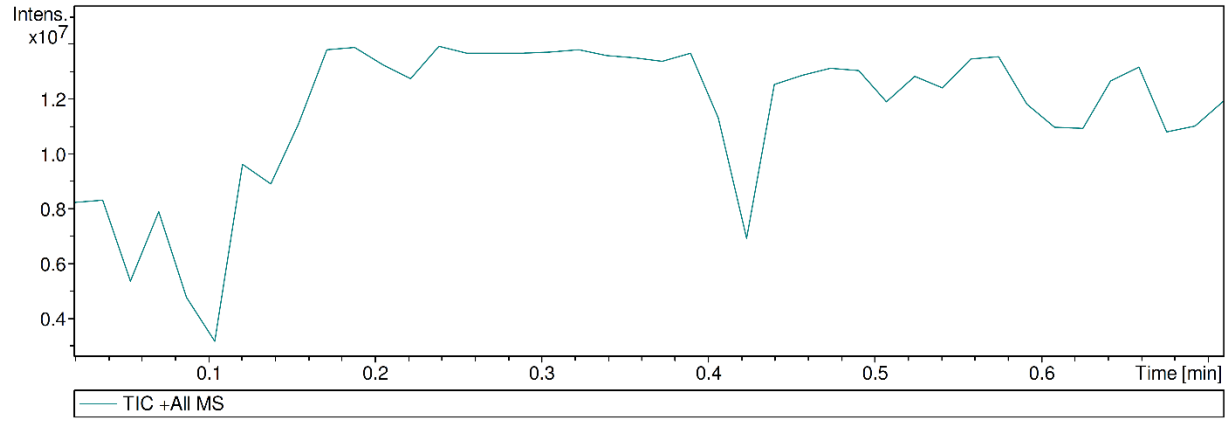
Display Report

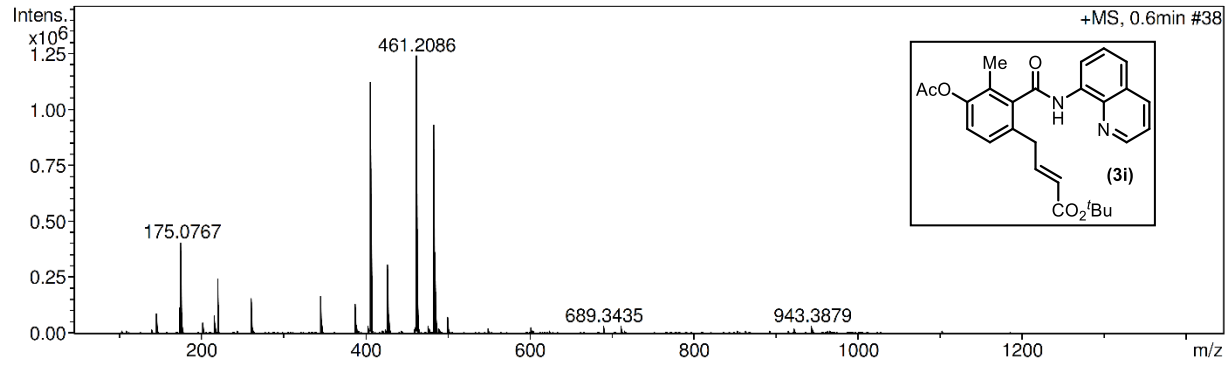
Analysis Info

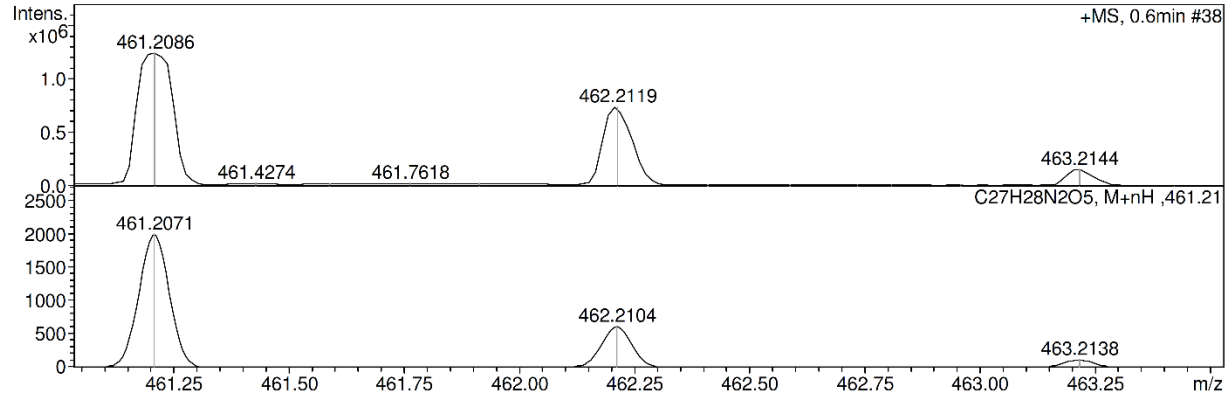
Acquisition Date	1/31/2022 10:55:12 AM		
Analysis Name	D:\Data\NEW USER DATA 2022\Jan-2022\31-jan-2022\Prof.M.Kapur-NK-06-357-LS-R.d		
Method	tune mix_low.New.021117.m	Operator	RUCHI
Sample Name	NK-06-357-LS-R	Instrument	micrOTOF-Q II 10330
Comment			

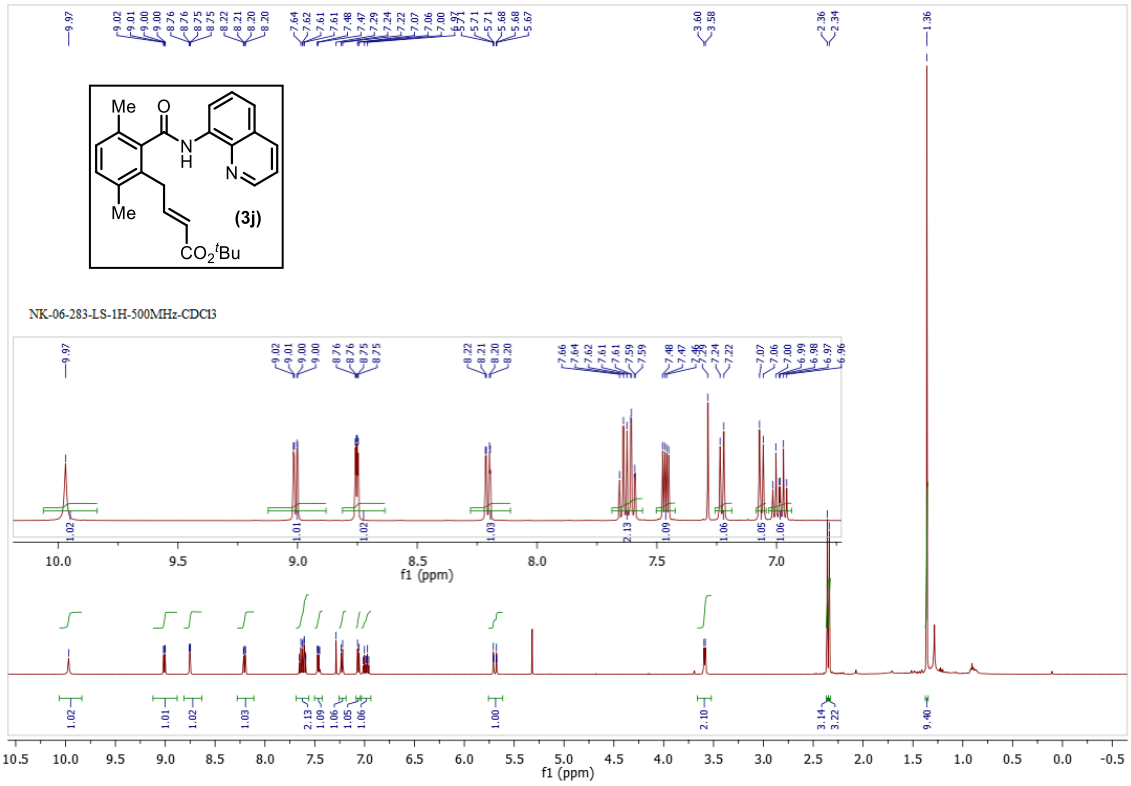
Acquisition Parameter

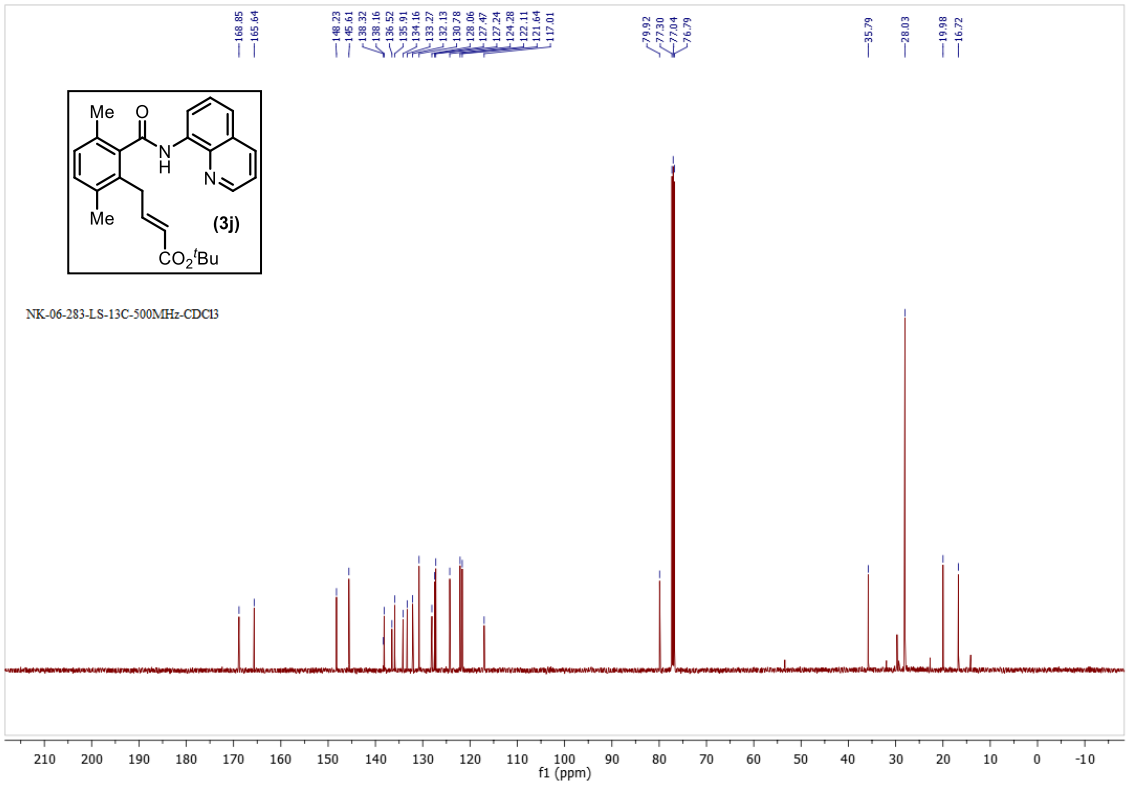
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source








Me
O
N
H
N
Me
(3j)
CO2tBu
NK-06-283-LS-1H-500MHz-CDCl3
f1 (ppm)


Me
O
N
H
N
Me
(3j)
CO2tBu
NK-06-283-LS-13C-500MHz-CDCl3
f1 (ppm)

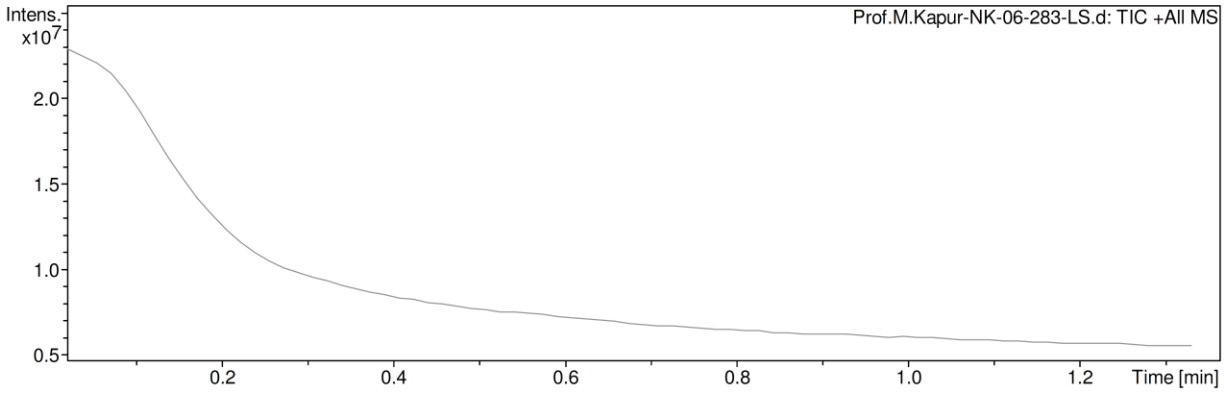
Display Report

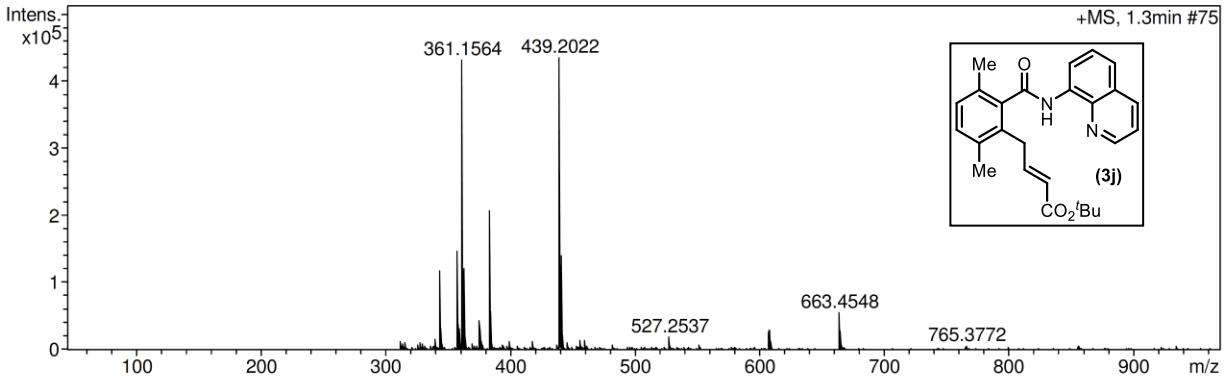
Analysis Info

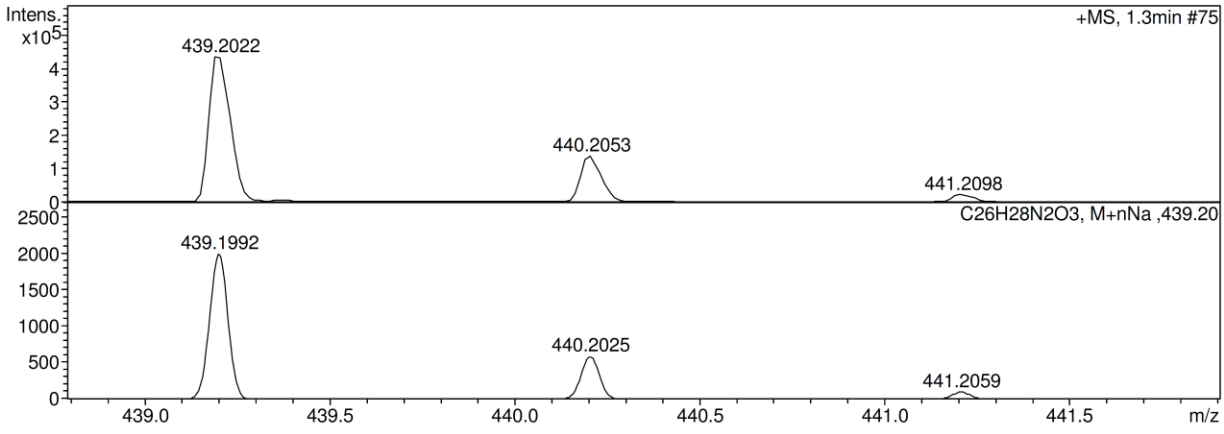
Acquisition Date	3/31/2022 2:47:33 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\March-2022\31march\Prof.M.Kapur-NK-06-283-LS.d		
Method	tune_wide _APCI_23.06.m	Operator	RUCHI
Sample Name	NK-06-283-LS	Instrument	micrOTOF-Q II 10330
Comment			

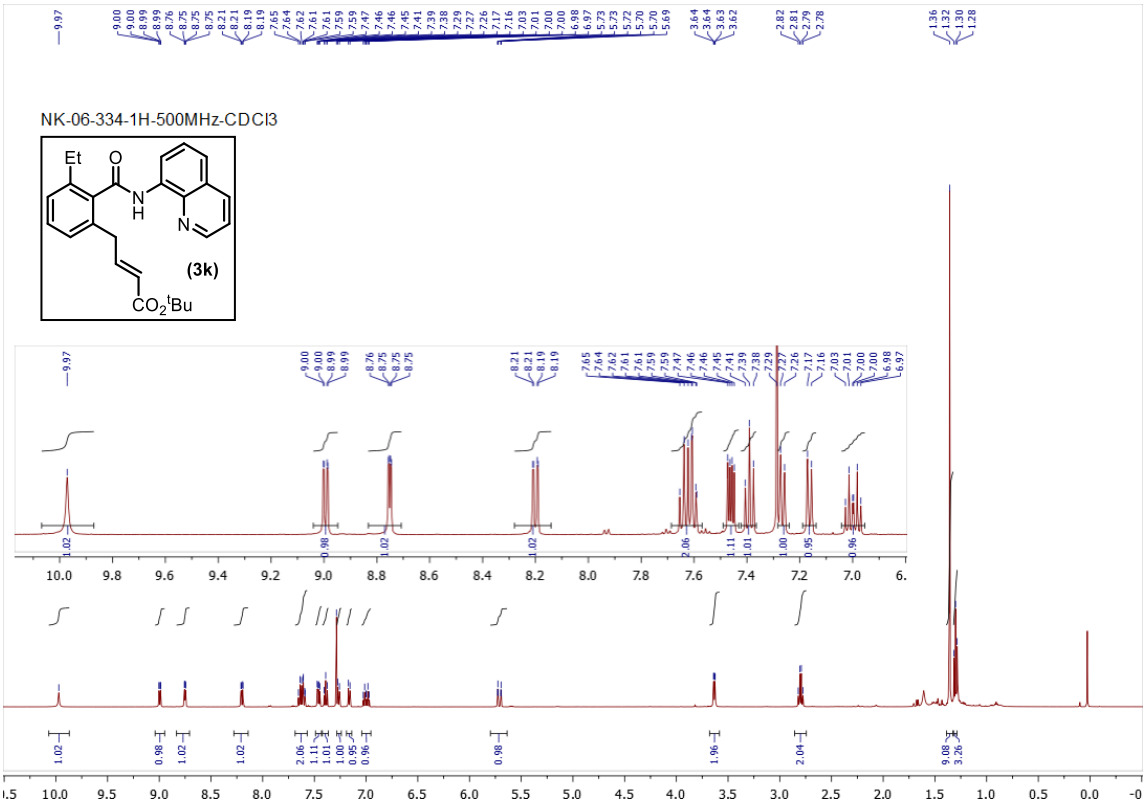
Acquisition Parameter

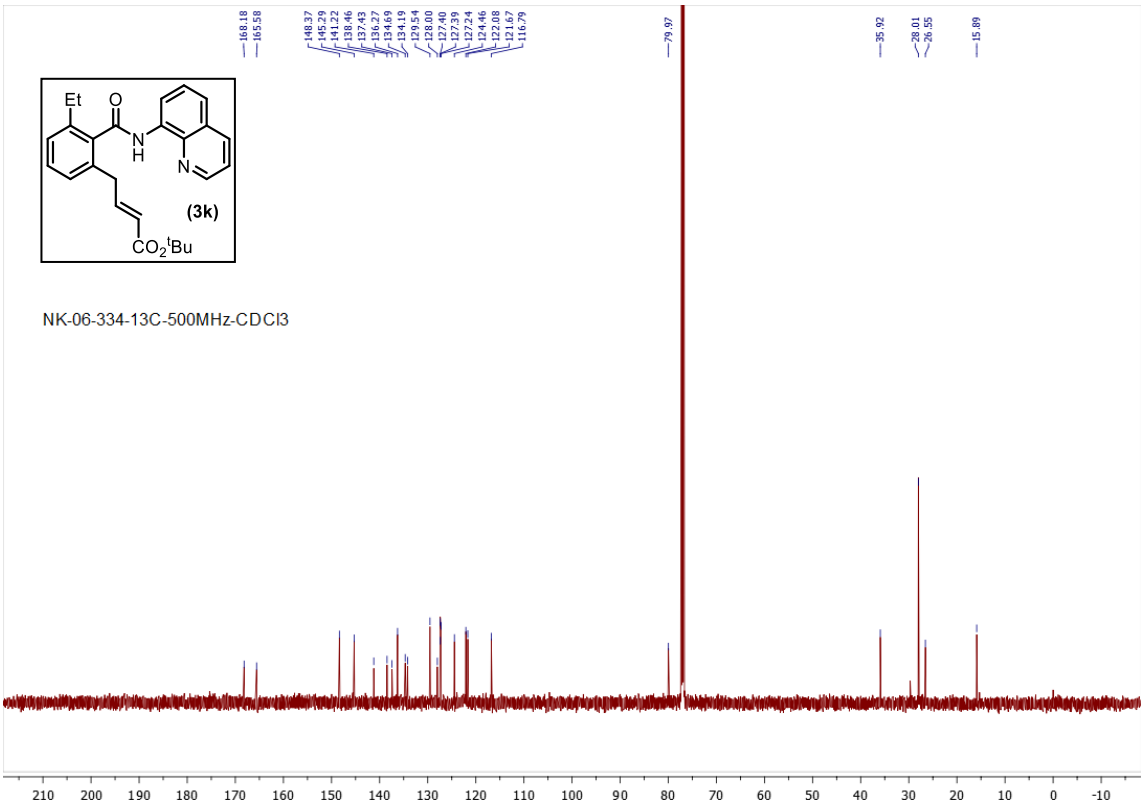
Source Type	Multi Mode	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	2500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source








NK-06-334-1H-500MHz-CDCl3
Et
O
N
H
N
(3k)
CO2tBu


Et
O
N
H
N
(3k)
CO2tBu
NK-06-334-13C-500MHz-CDCl3

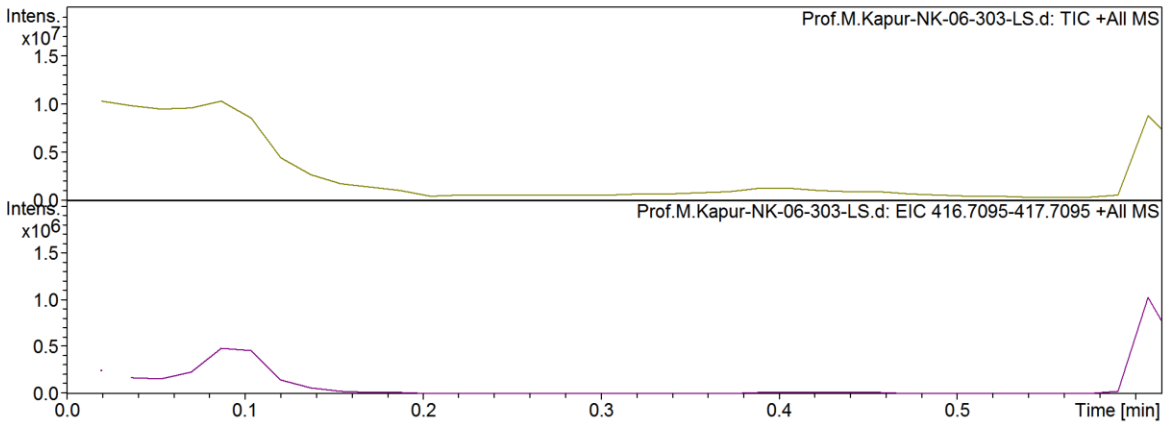
Display Report

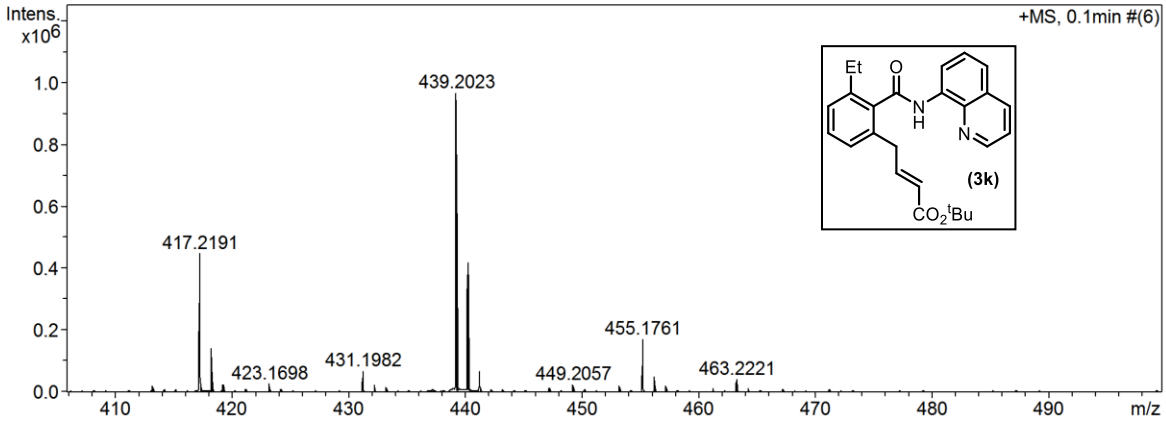
Analysis Info

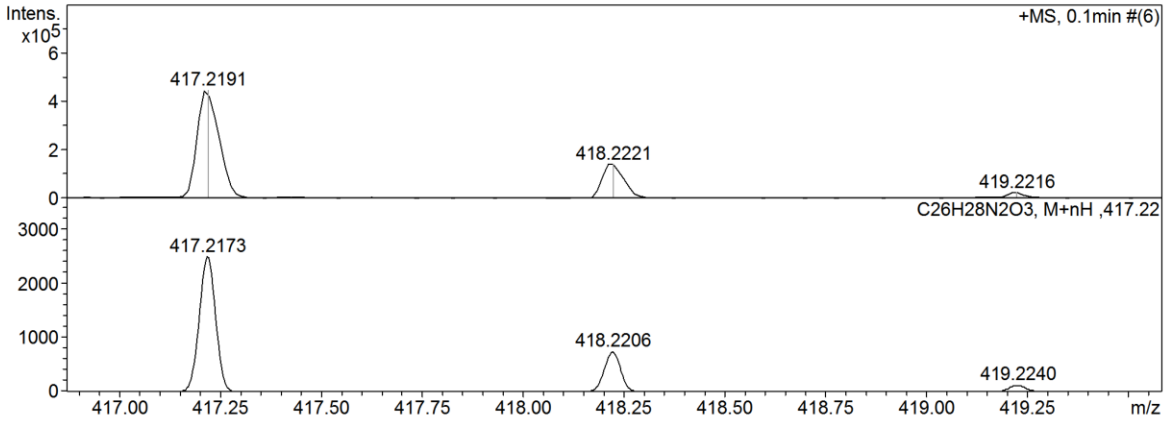
Acquisition Date	20-06-2022 15:49:19		
Analysis Name	D:\Data\USER DATA 2022\JUNE2022\20-06-22\Prof.M.Kapur-NK-06-303-LS.d		
Method	tune mix_low.New.021117_1.m	Operator	Bruker
Sample Name	NK-06-303-LS	Instrument	micrOTOF-Q 10330
Comment			

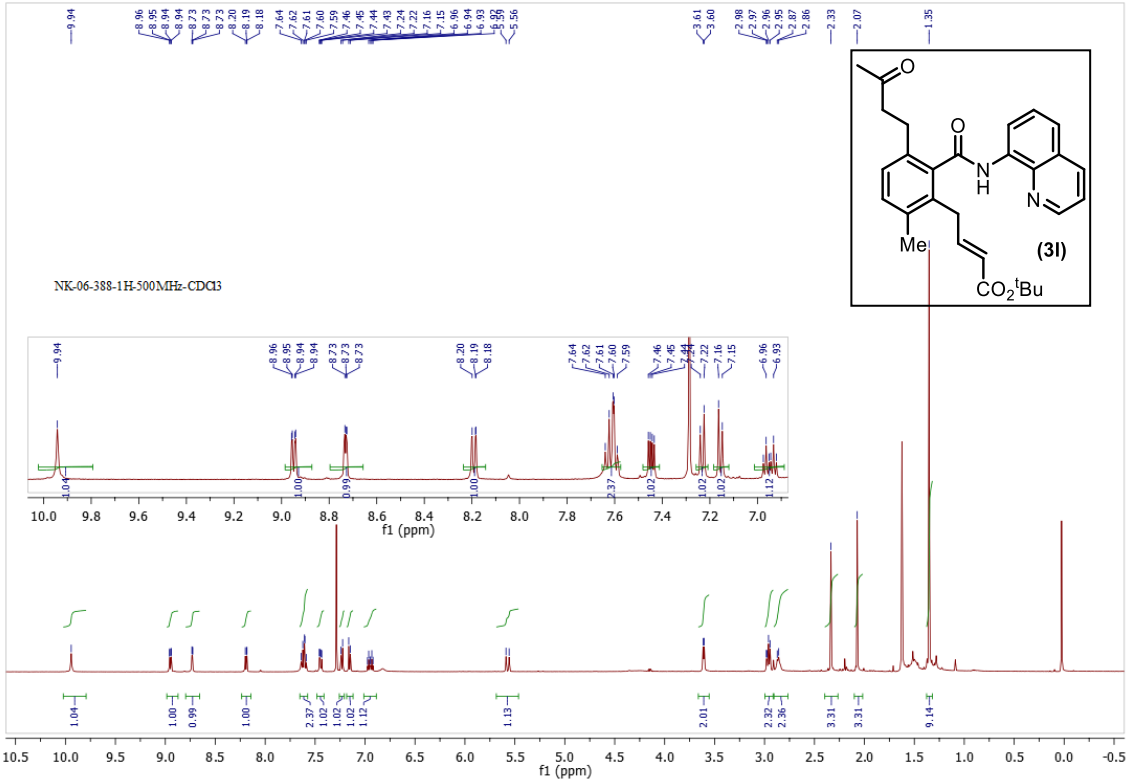
Acquisition Parameter

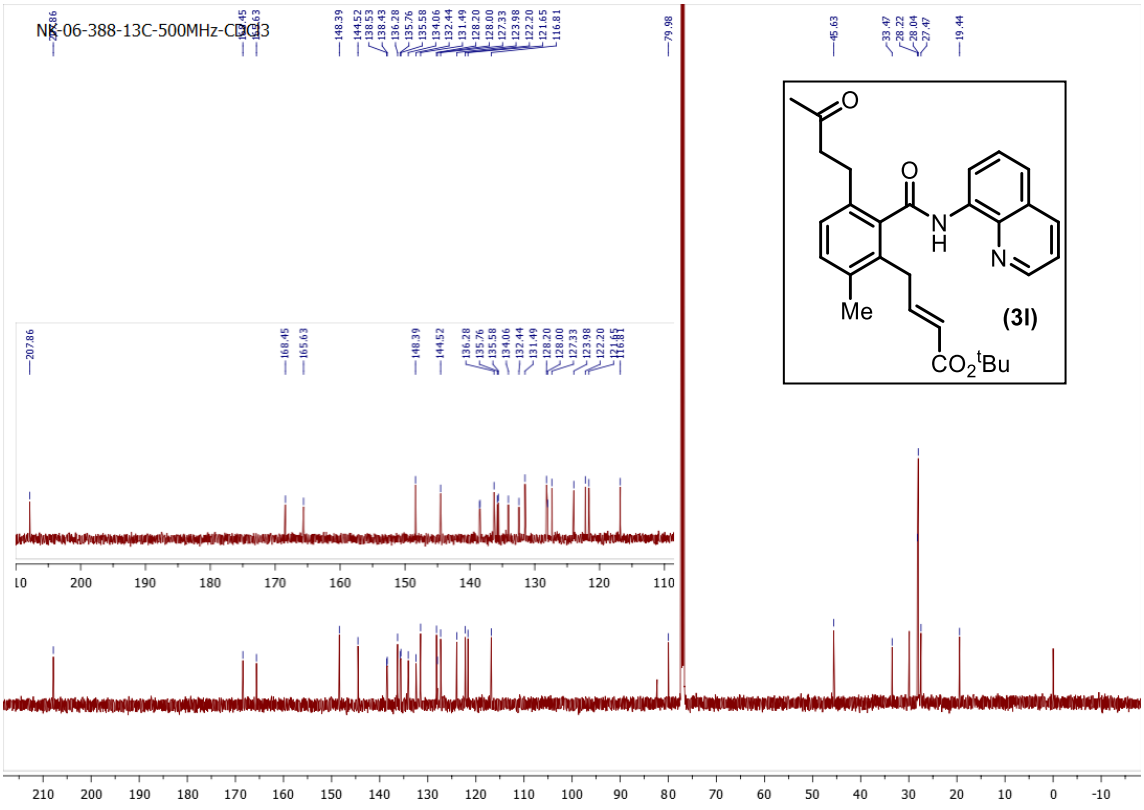
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source








NK-06-388-1H-500MHz-CDCl3
f1 (ppm)
(3l)


NK-06-388-13C-500MHz-CDCl3
(3l)

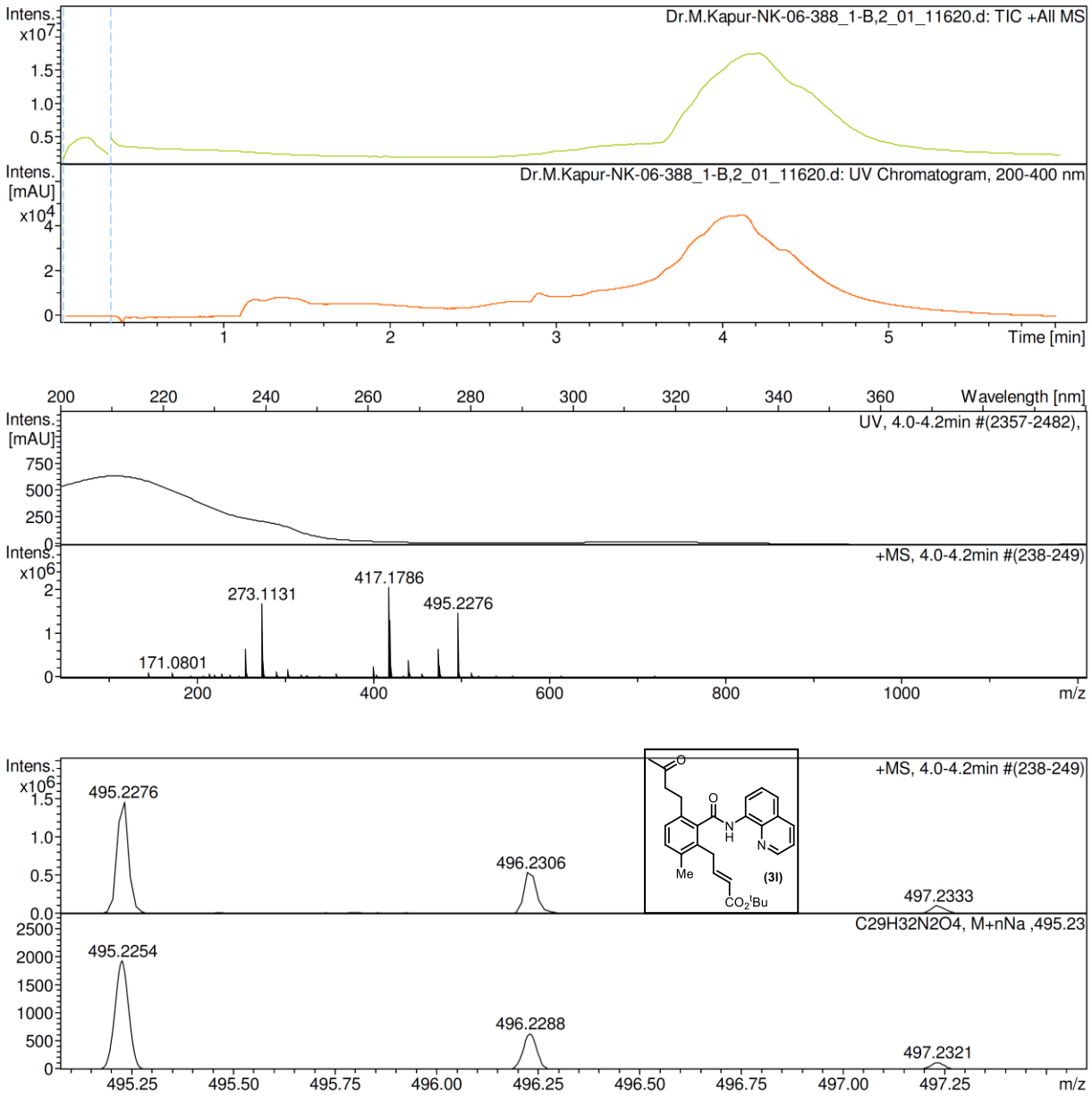
Display Report

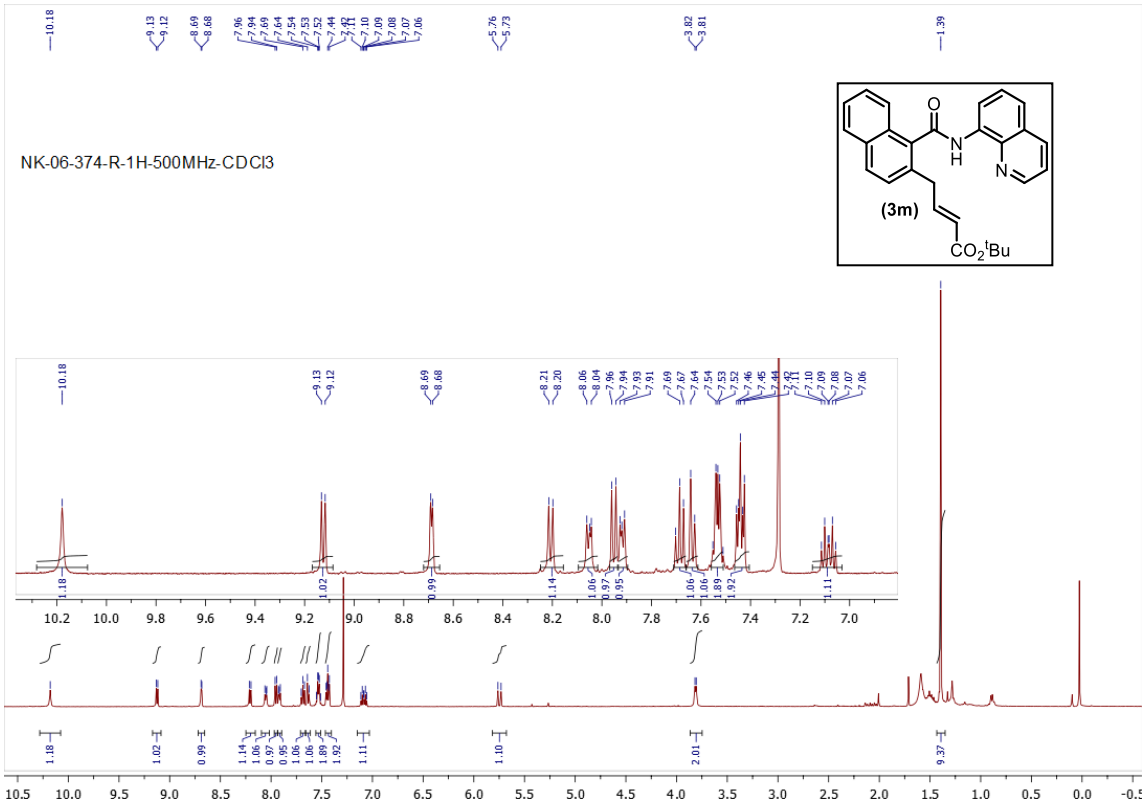
Analysis Info

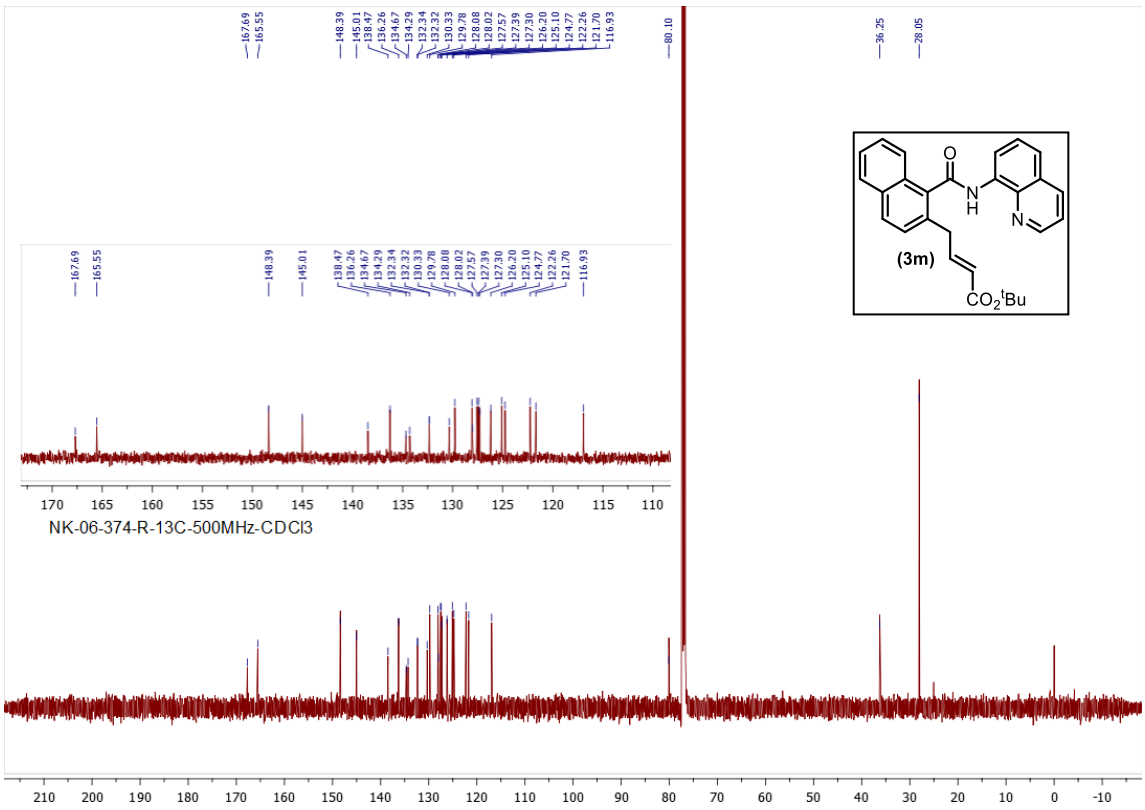
Acquisition Date	4/1/2022 2:26:07 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\April-2022\01-April\Dr.M.Kapur-NK-06-388_1-B,2_01_11620.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr.M.Kapur-NK-06-388	Instrument	micrOTOF-Q II 10330
Comment			

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




NK-06-374-R-1H-500MHz-CDCl3
(3m)
CO2tBu


NK-06-374-R-13C-500MHz-CDCl3
(3m)
CO2tBu

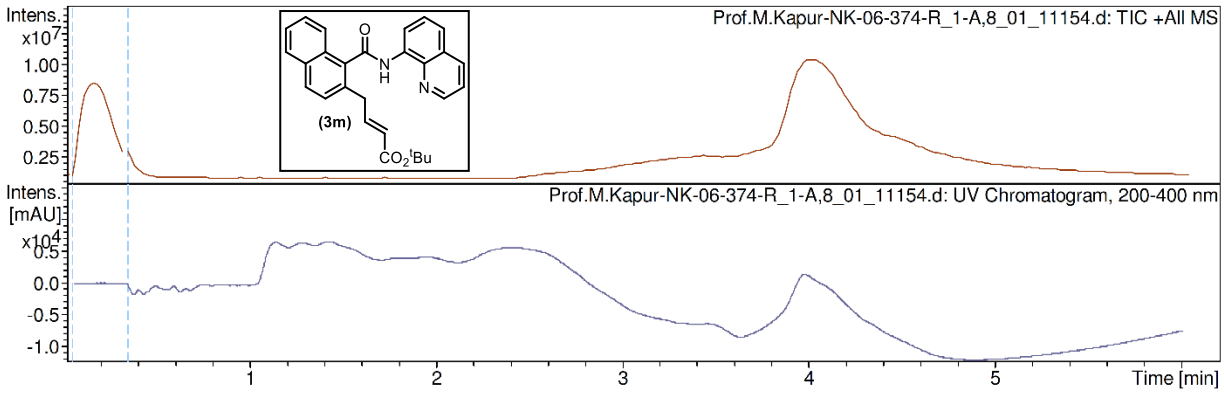
Display Report

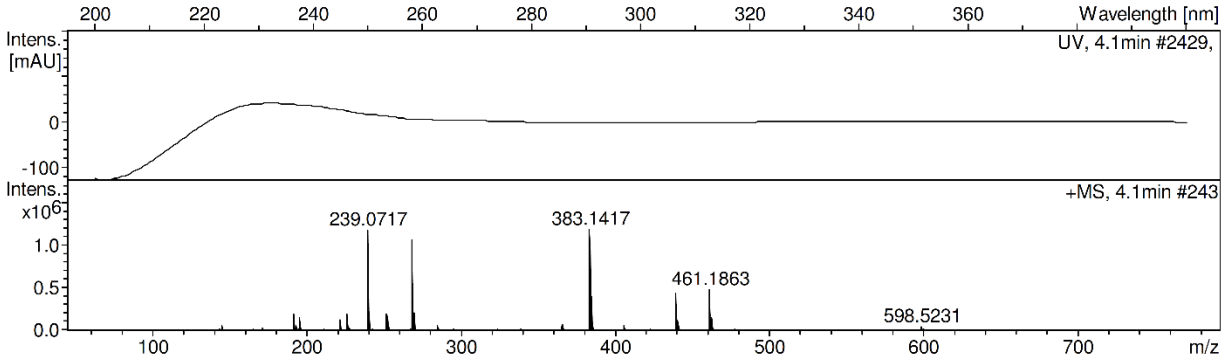
Analysis Info

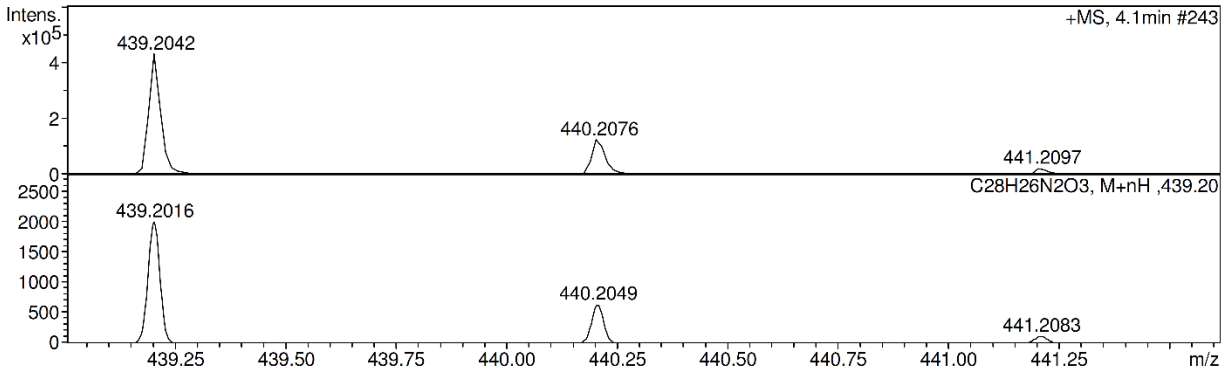
Acquisition Date	2/16/2022 1:10:39 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\fe-2022\16-feb-2022\Prof.M.Kapur-NK-06-374-R_1-A,8_01_11154.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Prof.M.Kapur-NK-06-374-R	Instrument	micrOTOF-Q II 10330
Comment			

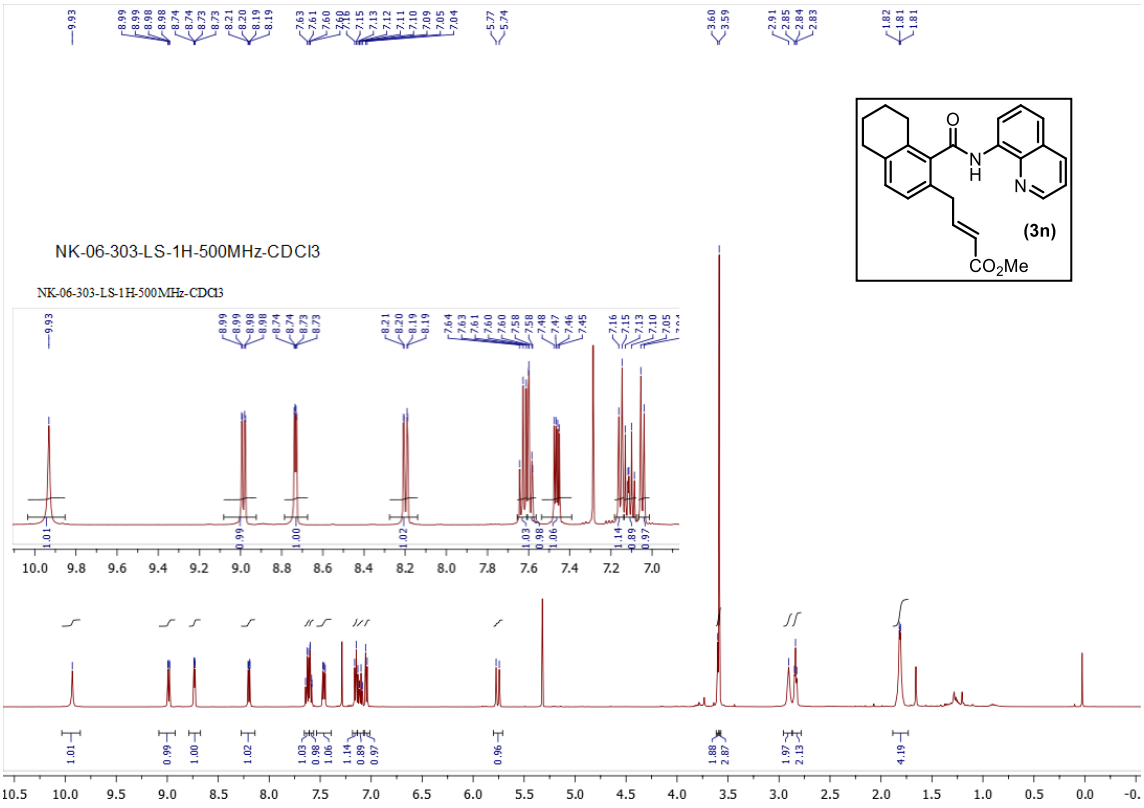
Acquisition Parameter

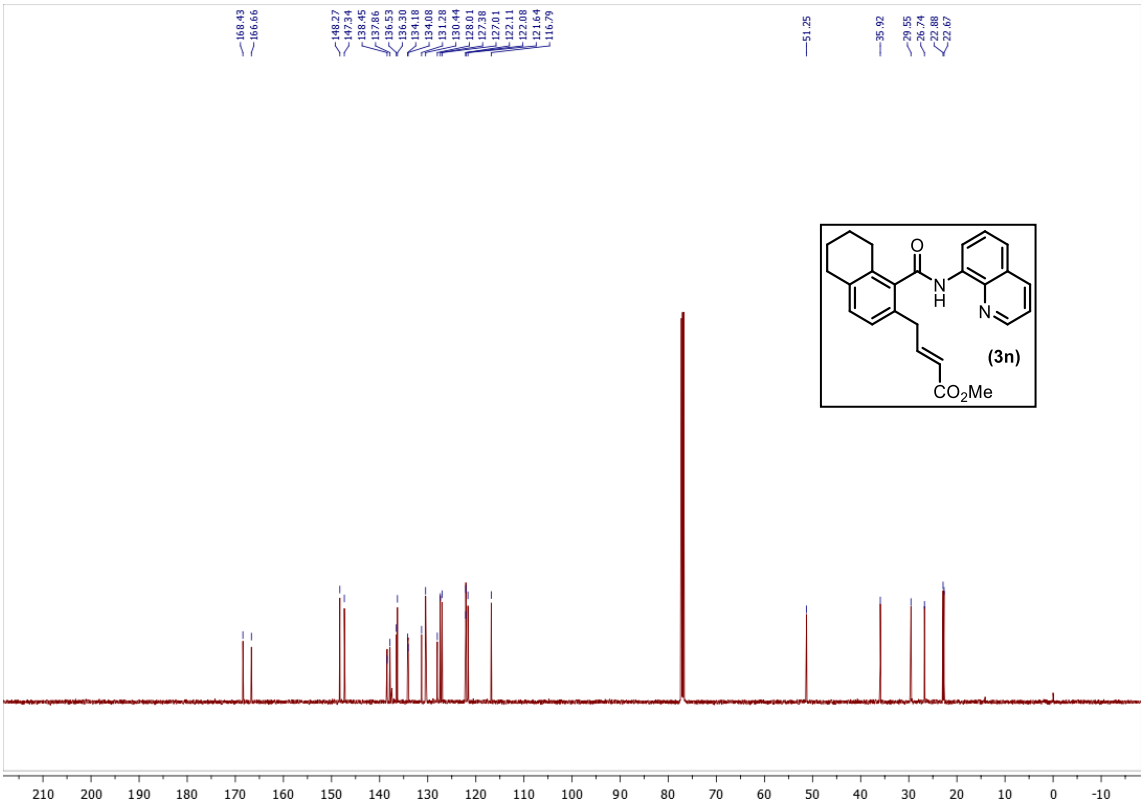
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








NK-06-303-LS-1H-500MHz-CDCl3
(3n)


(3n)

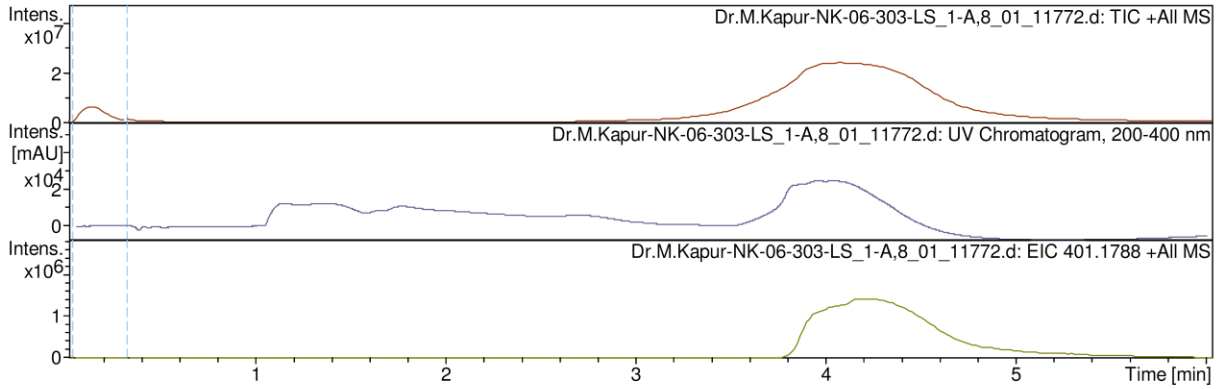
Display Report

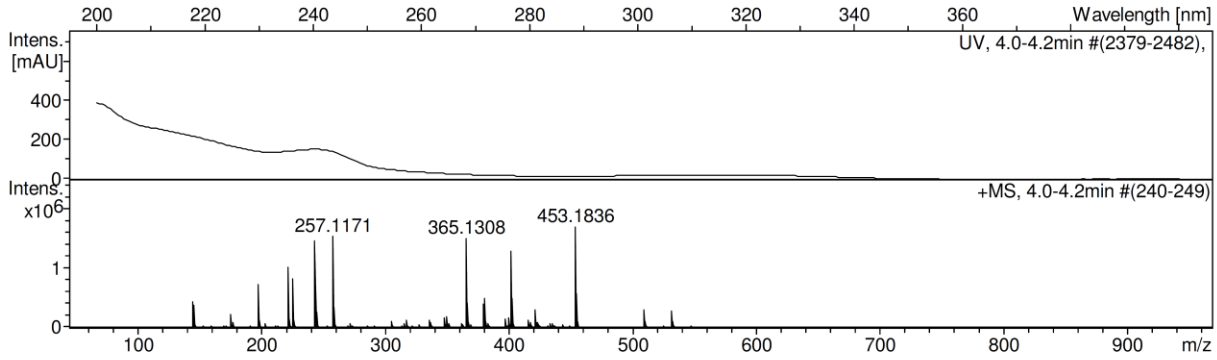
Analysis Info

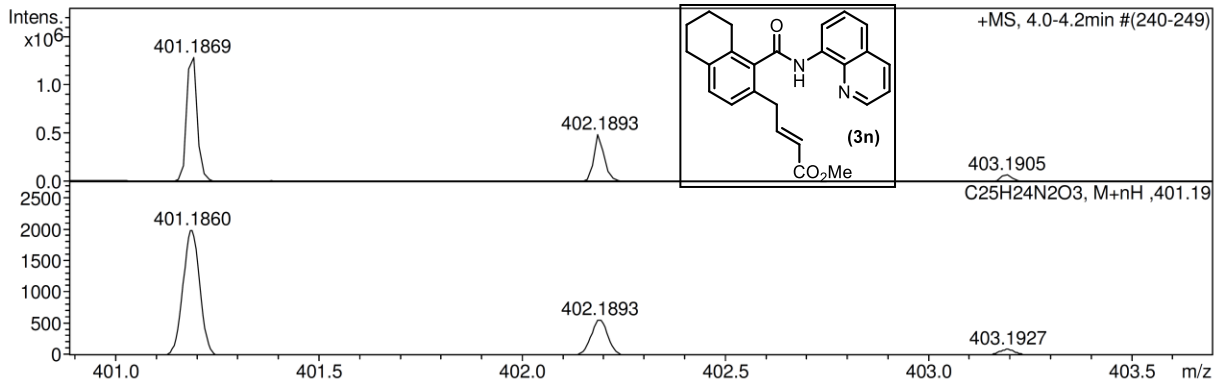
Acquisition Date	4/18/2022 1:11:38 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\April-2022\18-april\Dr.M.Kapur-NK-06-303-LS_1-A,8_01_11772.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr.M.Kapur-NK-06-303-LS	Instrument	micrOTOF-Q II 10330
Comment			

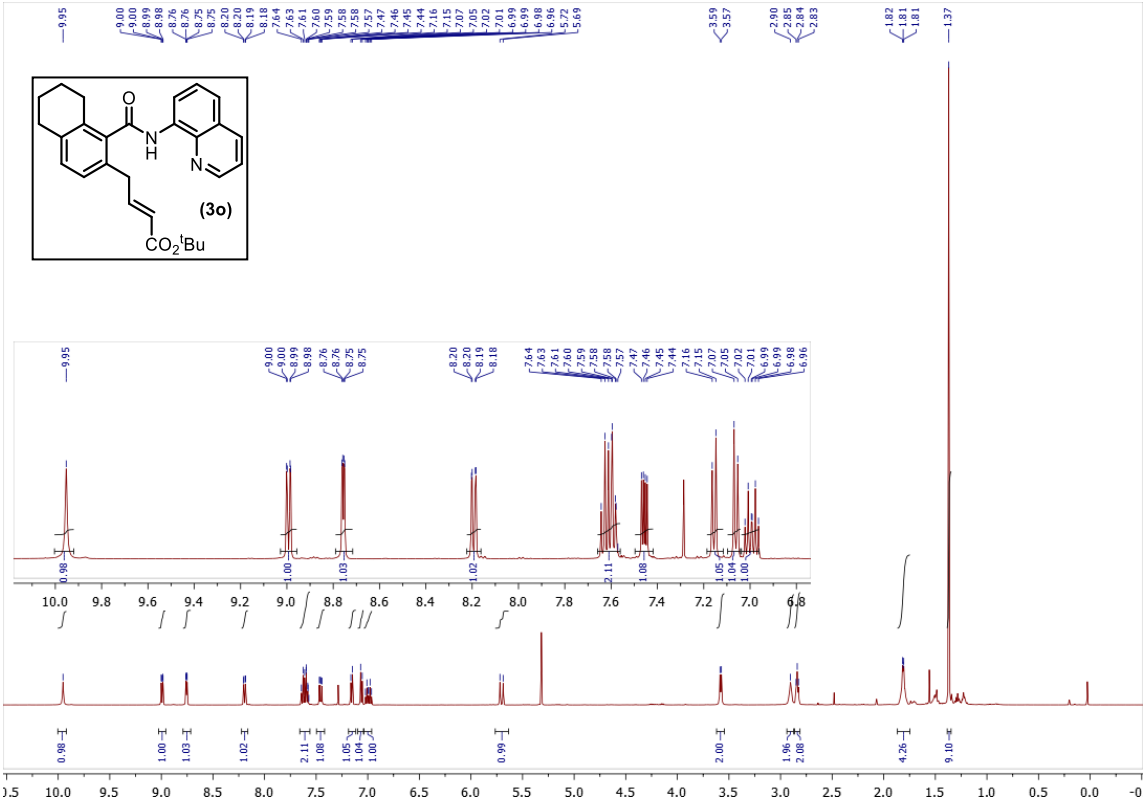
Acquisition Parameter

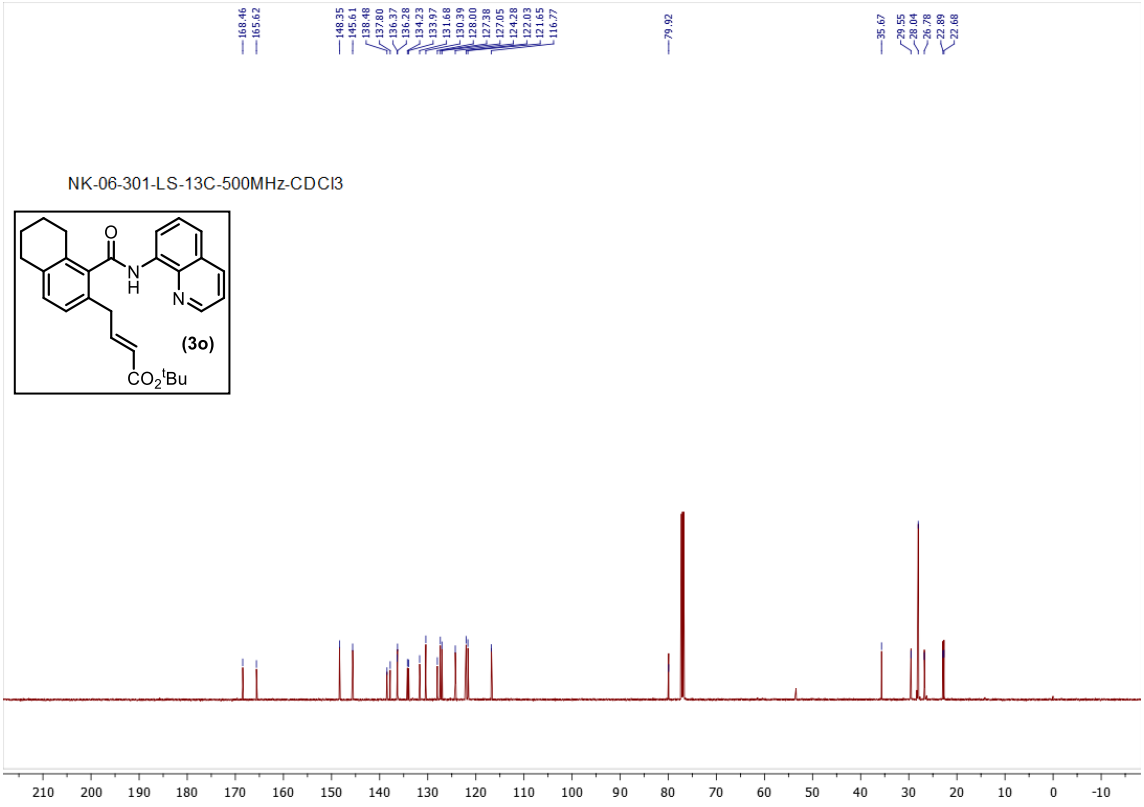
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








(3o)
CO2tBu


NK-06-301-LS-13C-500MHz-CDCl3
(3o)
CO2tBu

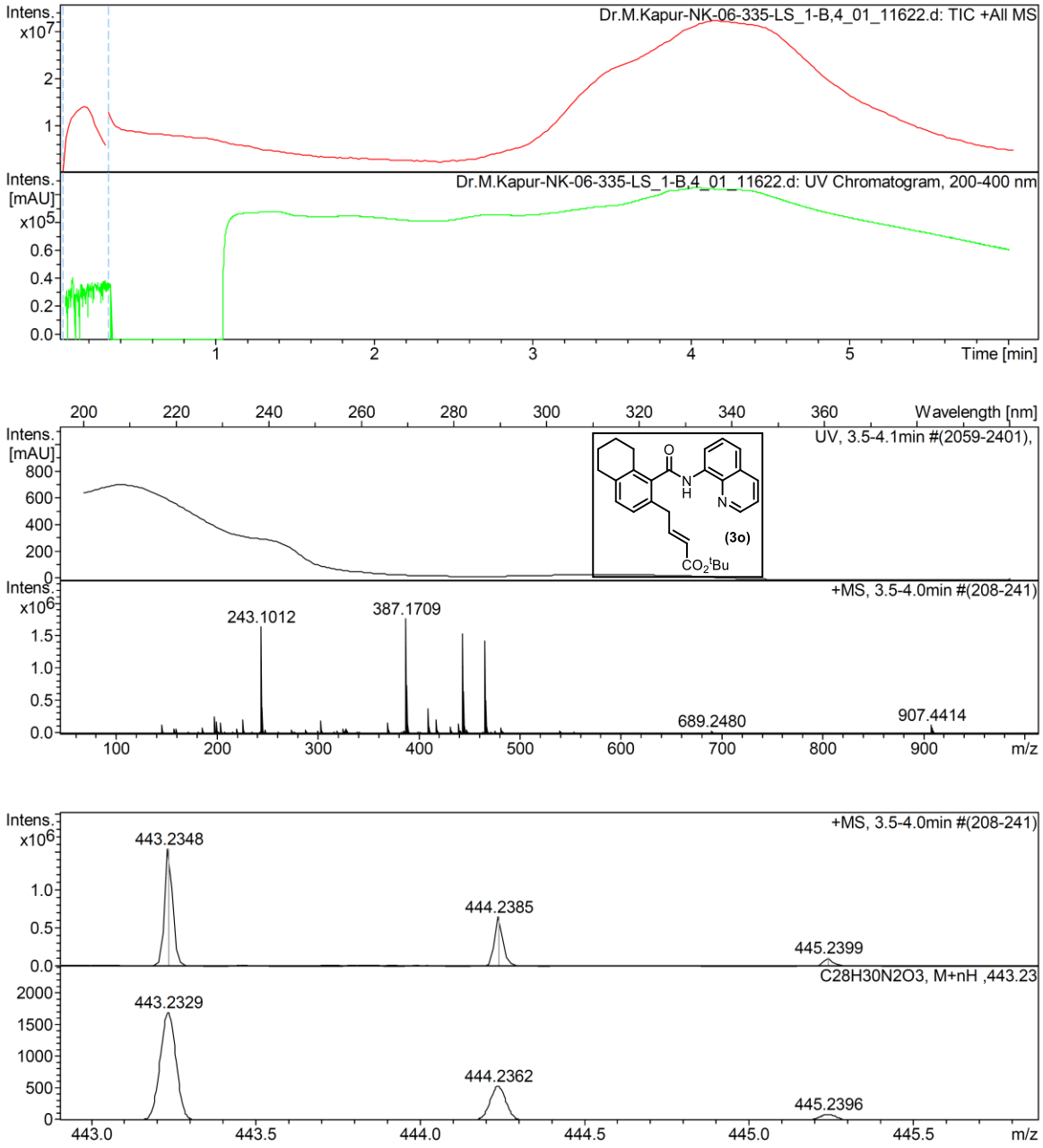
Display Report

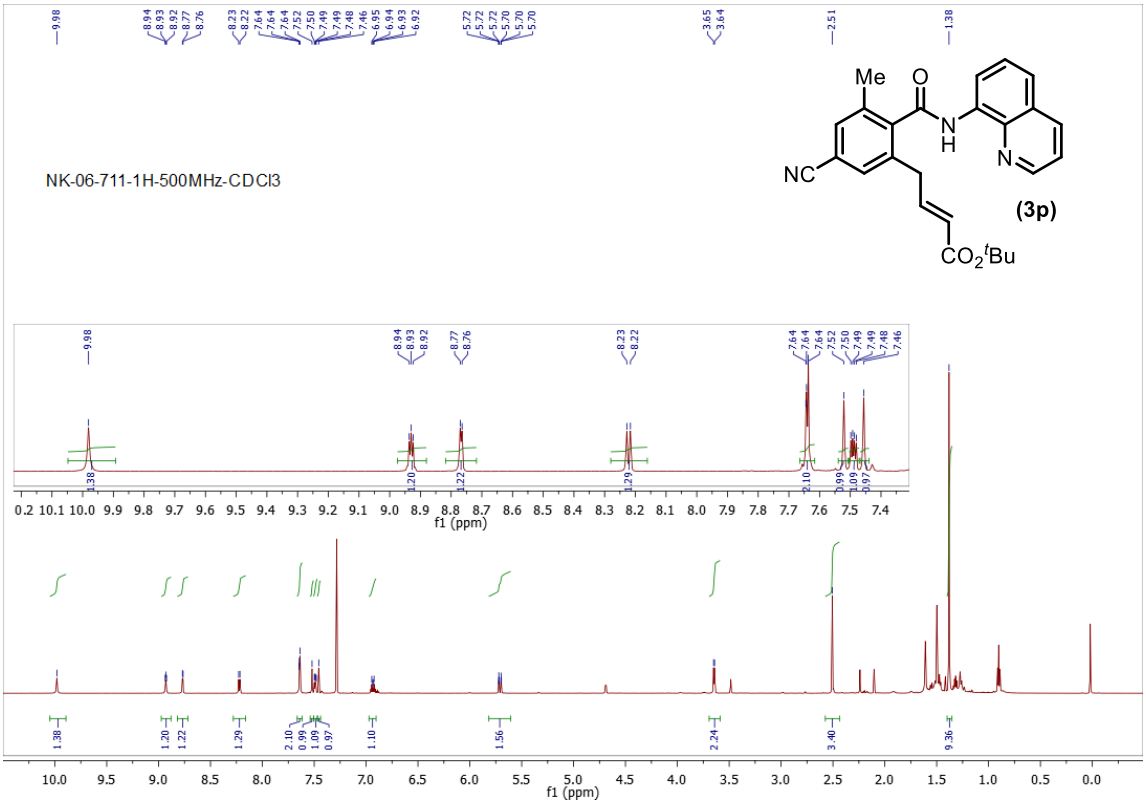
Analysis Info

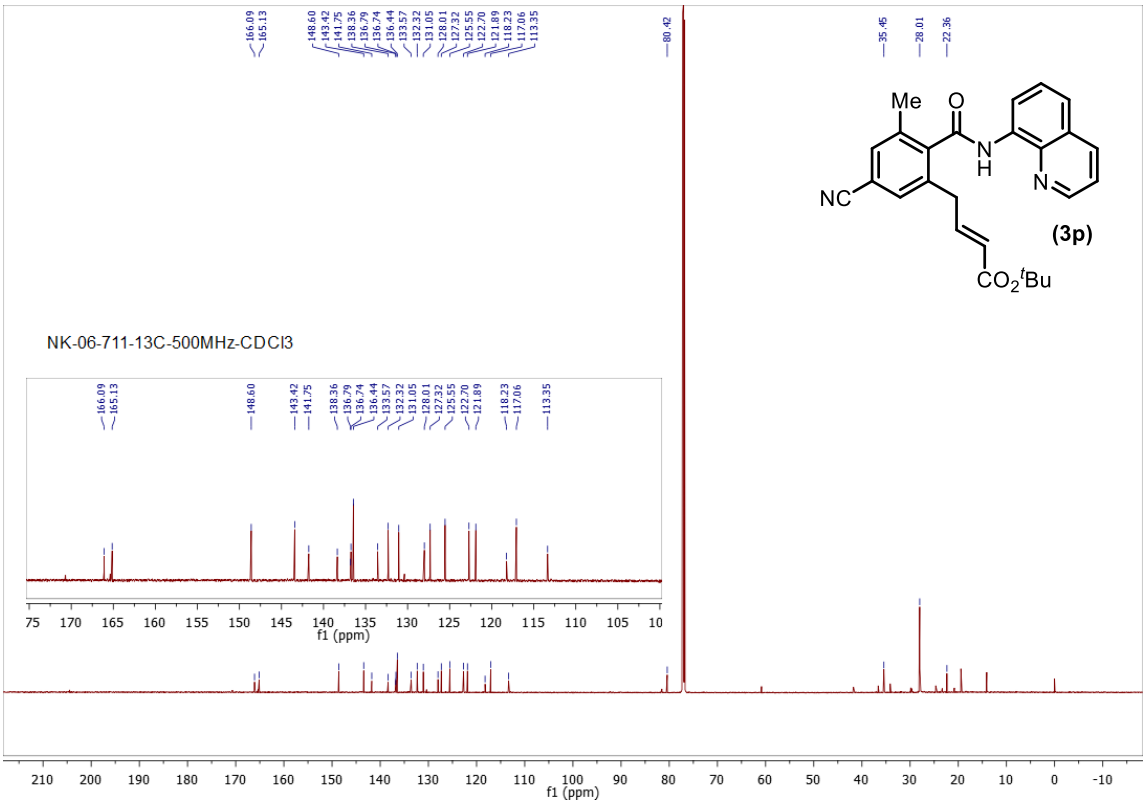
Analysis Name	G:\HRMS-DATA-27-04-22\LC-HRMS- 2022\NEW USER DATA 2022\April 2022\01-April\Dr.M.Kapur-NK-06-335-LS_1-B,4_01_11622.d	Acquisition Date	01-04-2022 14:40:27
Method	hrcms-20 septan	Operator	RUCHI
Sample Name	Dr.M.Kapur-NK-06-335-LS	Instrument	micrOTOF-Q II 10330
Comment			

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




NK-06-711-1H-500MHz-CDCl3
Me
O
N
H
N
NC
(3p)
CO2tBu
f1 (ppm)


NK-06-711-13C-500MHz-CDCl3
Me
O
N
H
N
NC
(3p)
CO2tBu
f1 (ppm)

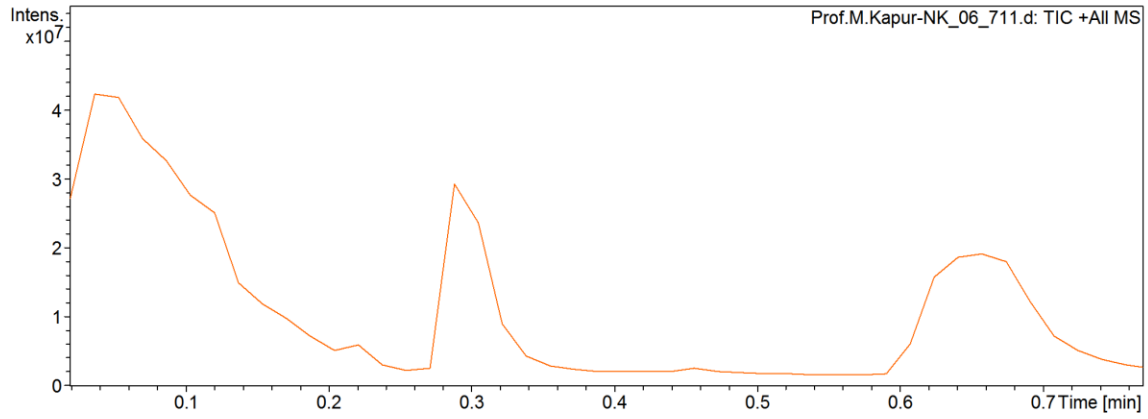
Display Report

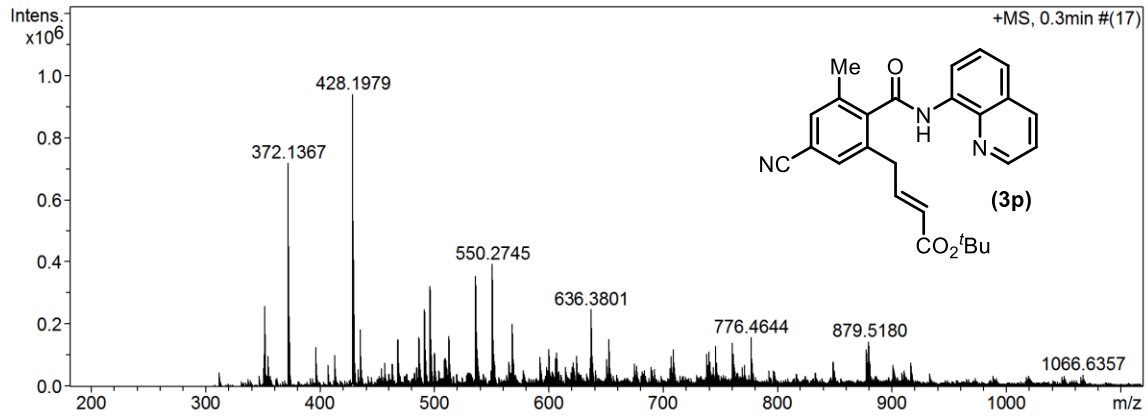
Analysis Info

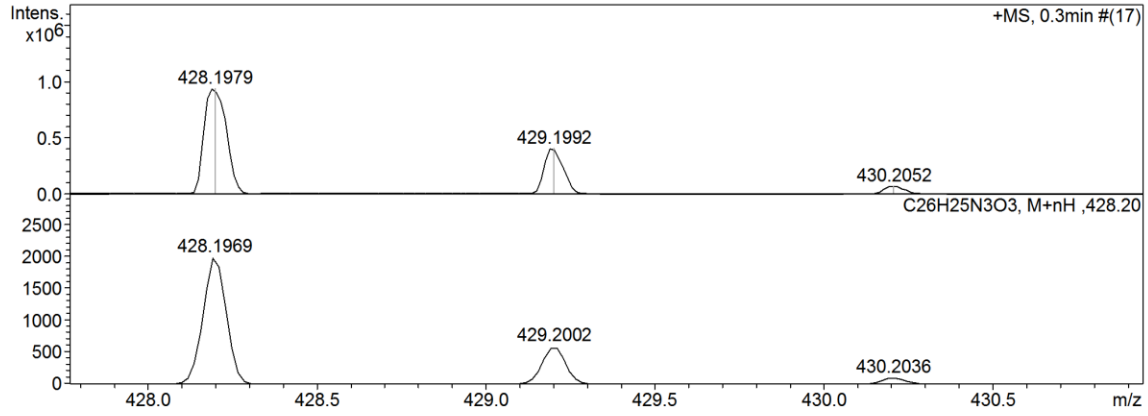
Analysis Name	D:\Data\USER DATA 2022\Nov-2022\21-11-2022\Prof.M.Kapur-NK_06_711.d	Acquisition Date	21-11-2022 09:56:32
Method	tune_wide.m	Operator	Bruker
Sample Name	NK_06_711	Instrument	micrOTOF-Q 10330
Comment			

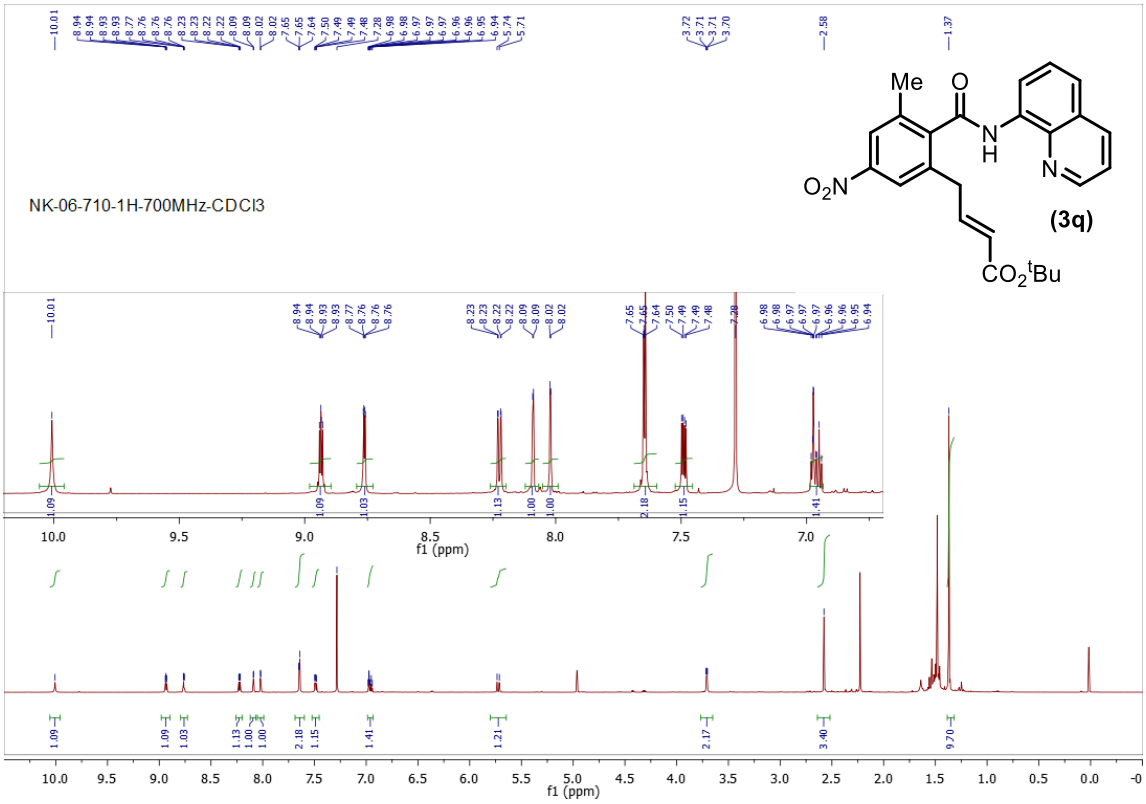
Acquisition Parameter

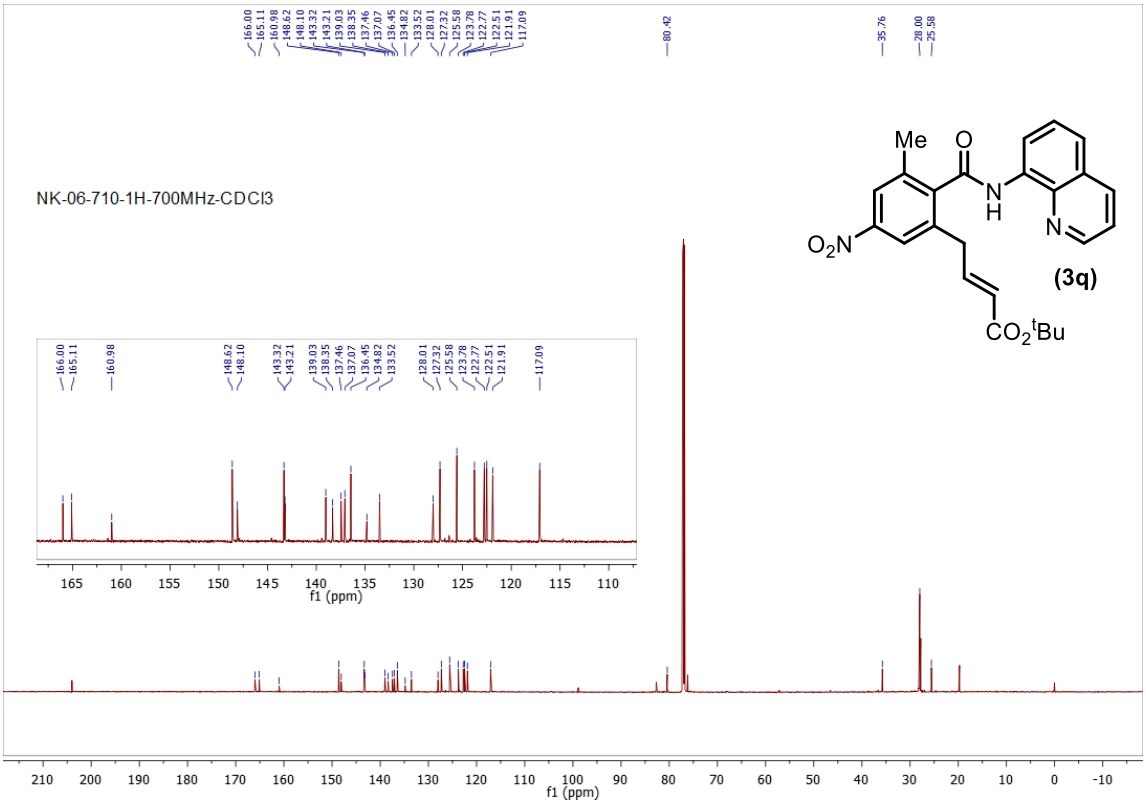
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source








NK-06-710-1H-700MHz-CDCl3
Me
O
N
H
N
O_2N
$CO_2{}^tBu$
(3q)
f1 (ppm)


NK-06-710-1H-700MHz-CDCl3
Me
O
N
H
N
O_2N
$CO_2{}^tBu$
(3q)
f1 (ppm)

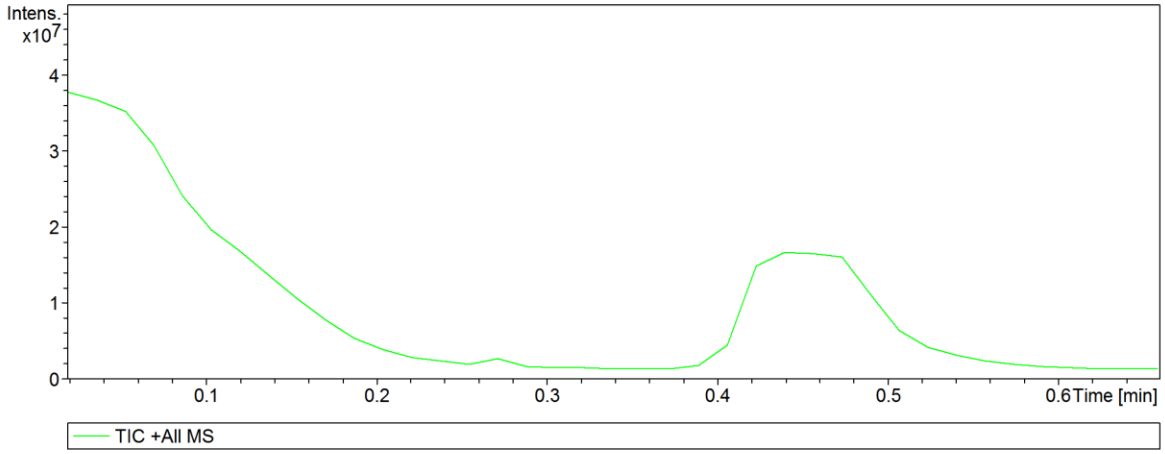
Display Report

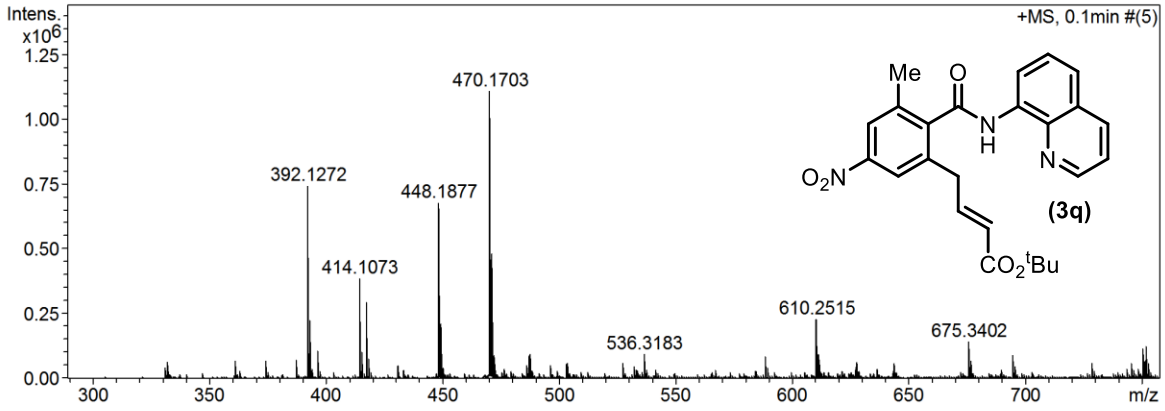
Analysis Info

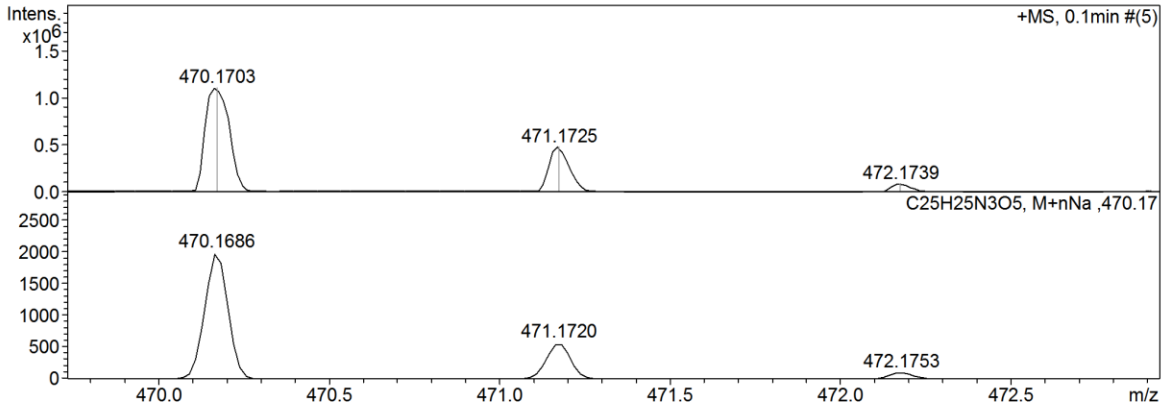
Analysis Name	D:\Data\USER DATA 2022\Nov-2022\21-11-2022\Prof.M.Kapur-NK_06_710-1.d	Acquisition Date	21-11-2022 09:54:17
Method	tune_wide.m	Operator	Bruker
Sample Name	NK_06_710-1	Instrument	micrOTOF-Q 10330
Comment			

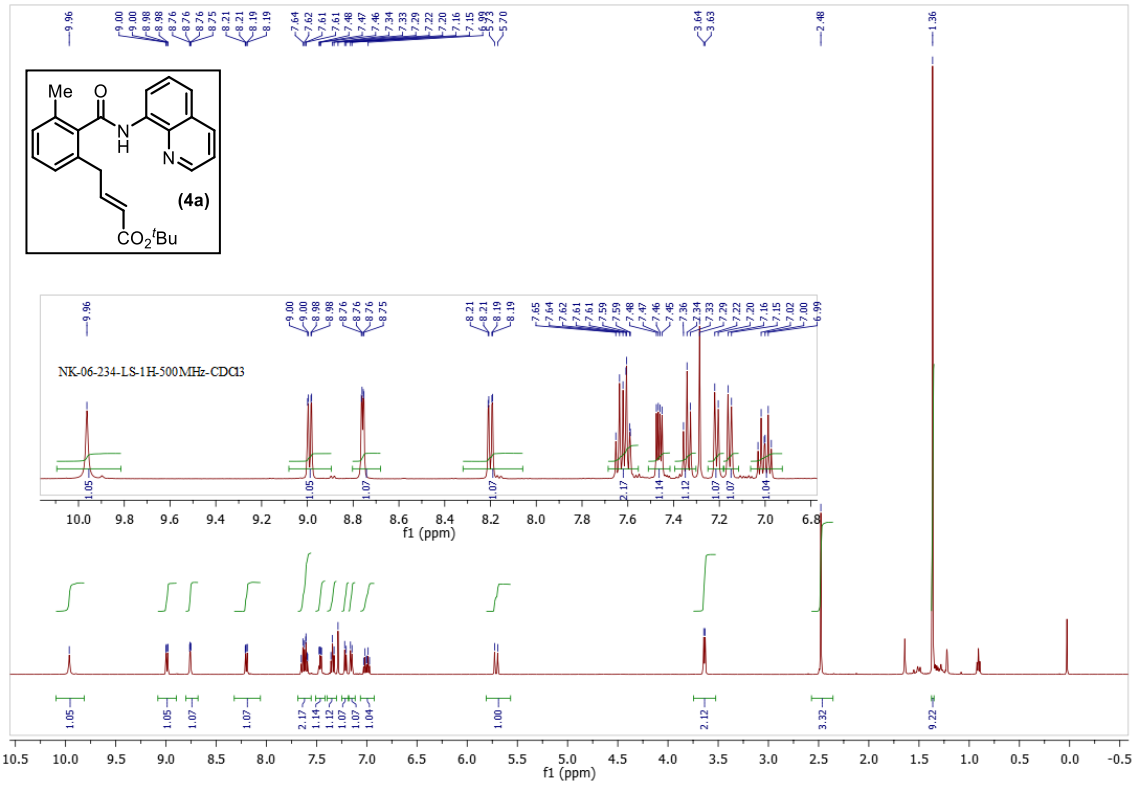
Acquisition Parameter

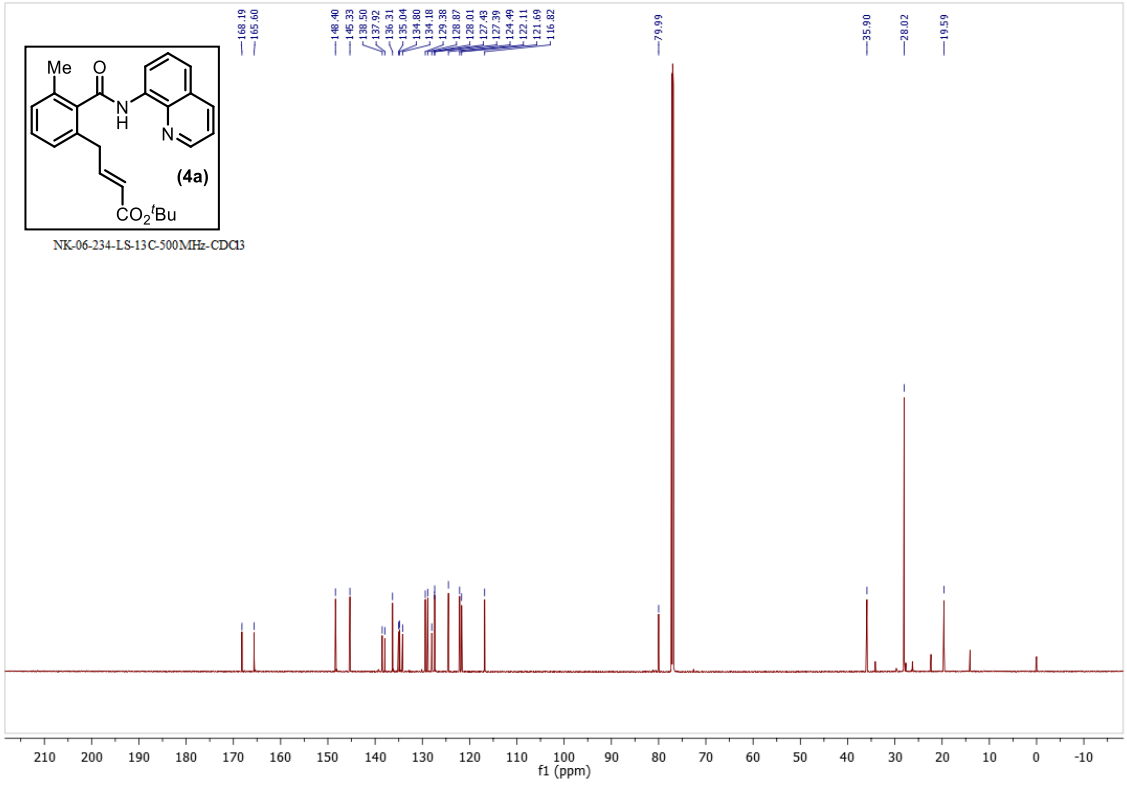
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source








Me
O
N
H
N
(4a)
CO2tBu
NK-06-234-LS-1H-500MHz-CDCl3
f1 (ppm)


Me
O
N
H
N
(4a)
CO2tBu
NK-06-234-LS-13C-500MHz-CDCl3
f1 (ppm)

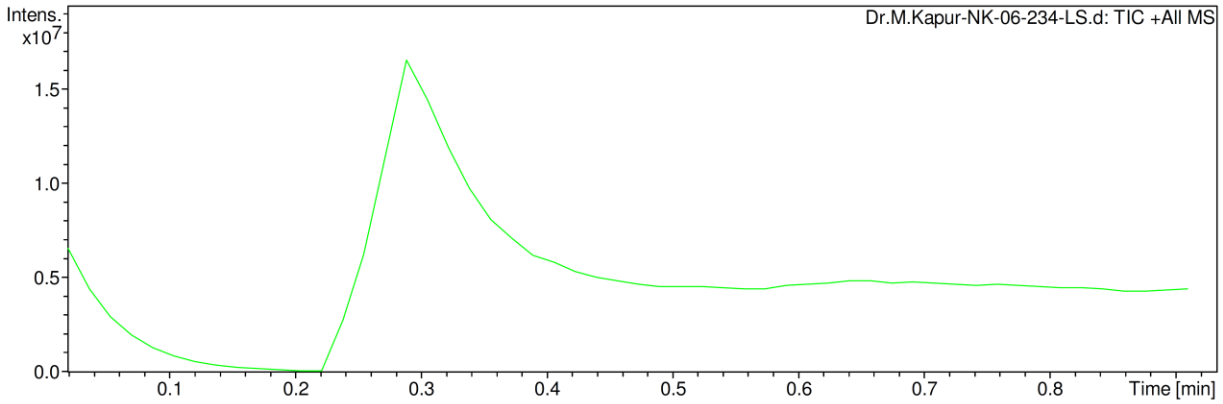
Display Report

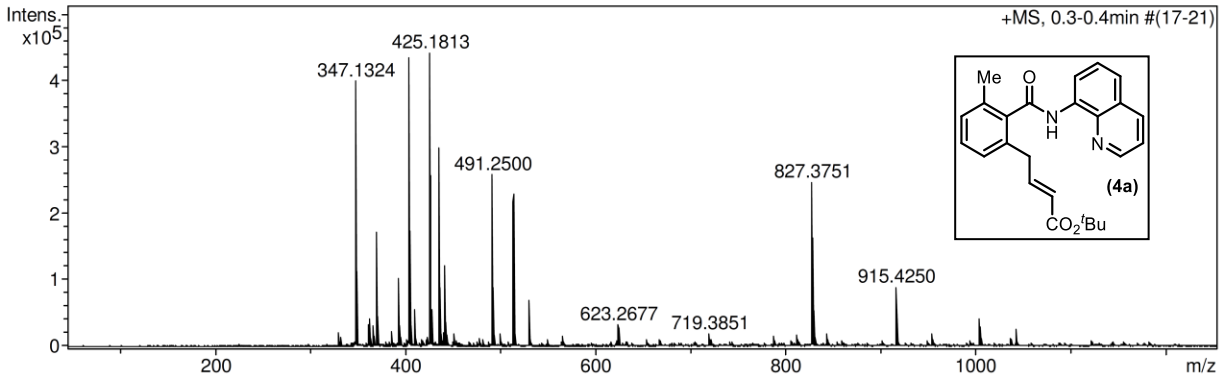
Analysis Info

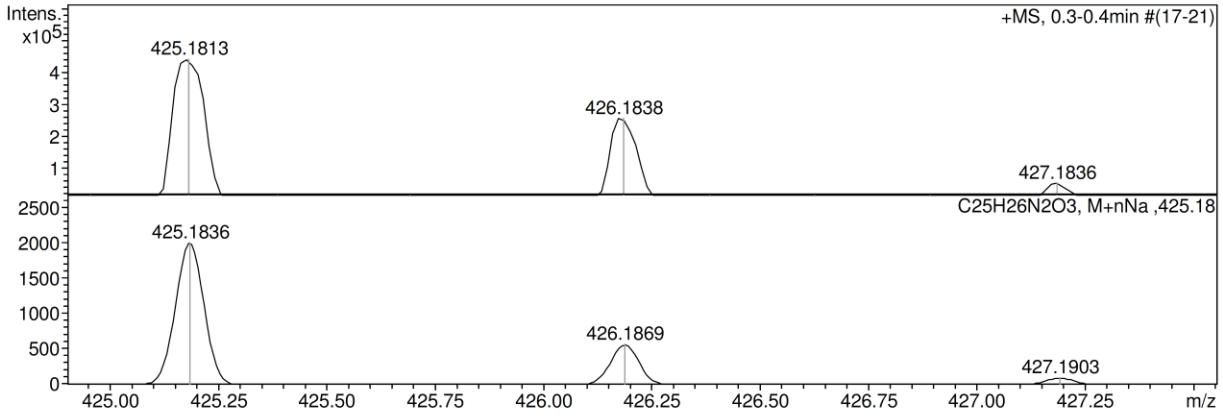
Analysis Name	D:\Data\new user data 2021\August-2021\23 Aug\Dr.M.Kapur-NK-06-234-LS.d	Acquisition Date	8/23/2021 4:10:26 PM
Method	tune_wide.m	Operator	RUCHI
Sample Name	NK-06-234-LS	Instrument	micrOTOF-Q II 10330
Comment			

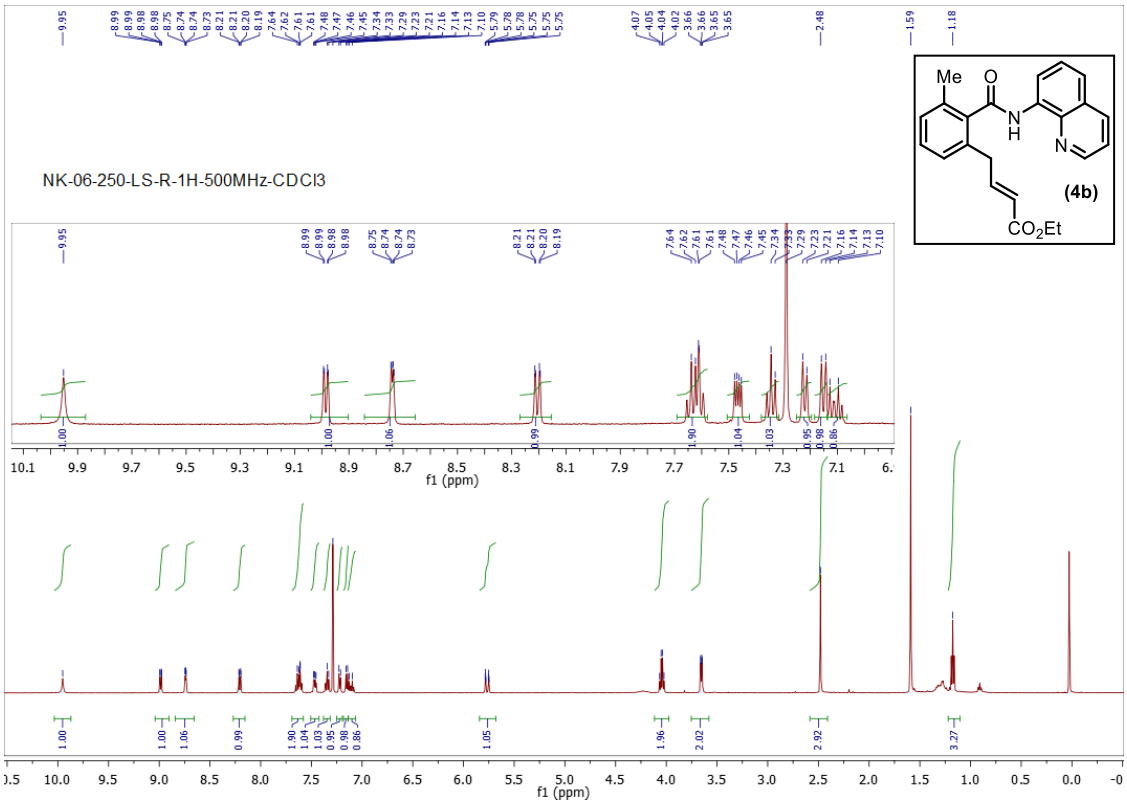
Acquisition Parameter

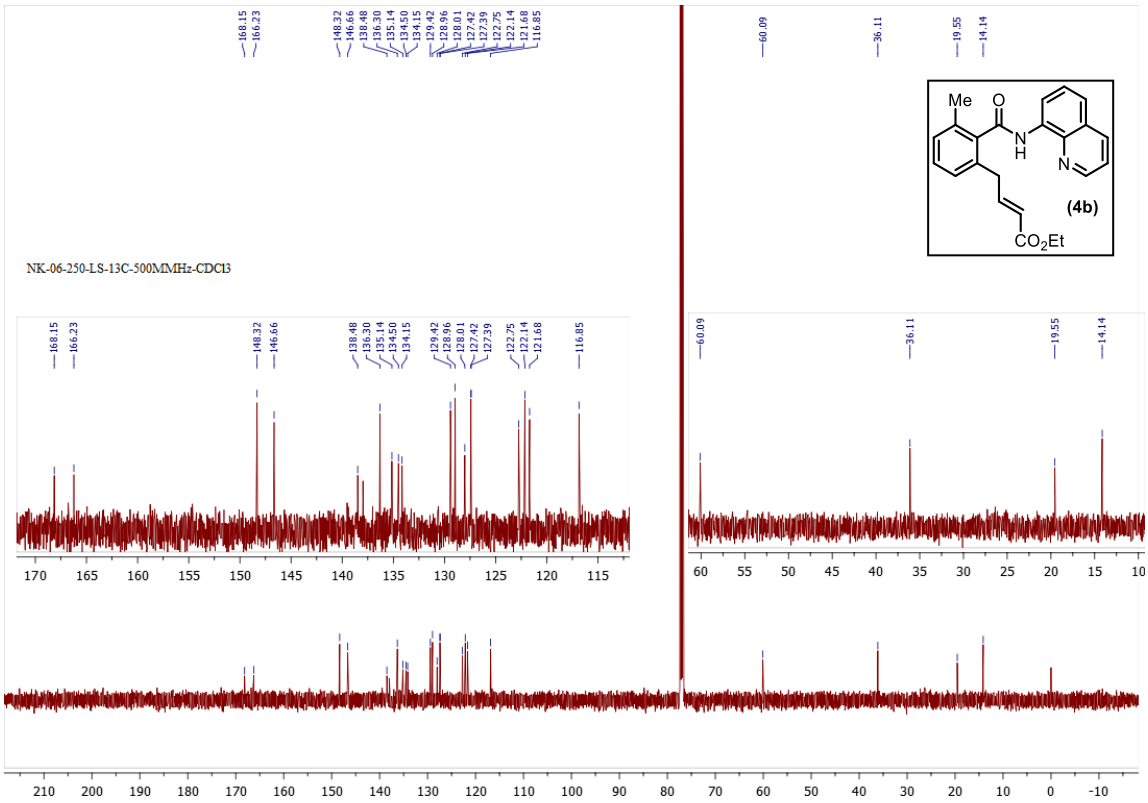
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste








NK-06-250-LS-R-1H-500MHz-CDCl3
Me
O
N
H
N
(4b)
CO2Et
f1 (ppm)


NK-06-250-LS-13C-500MMHz-CDCl3
Me
O
N
H
N
(4b)
CO2Et

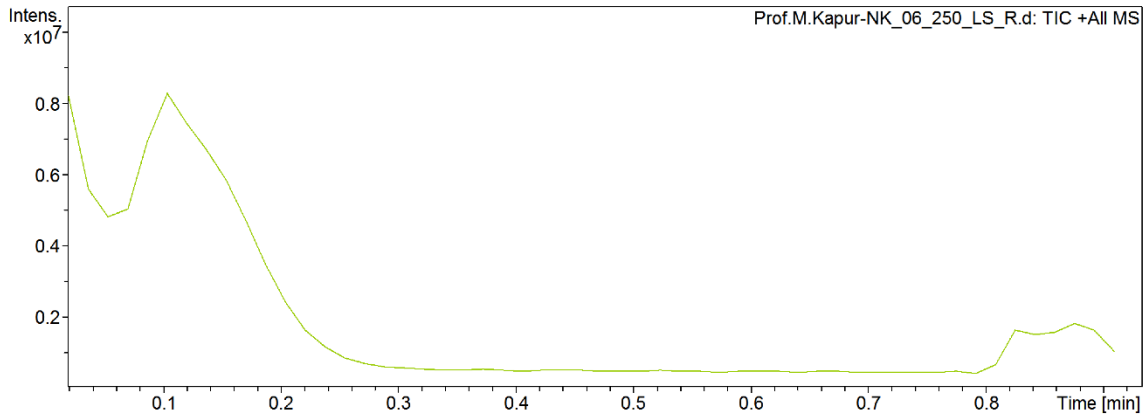
Display Report

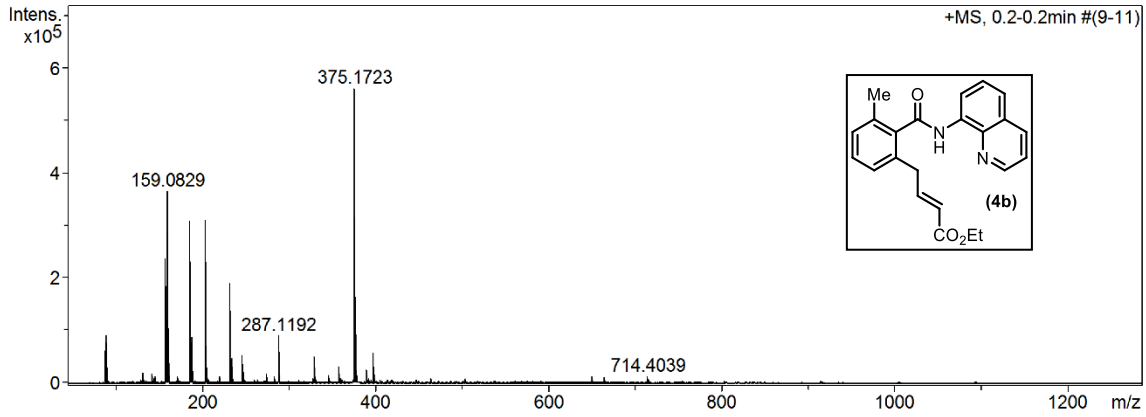
Analysis Info

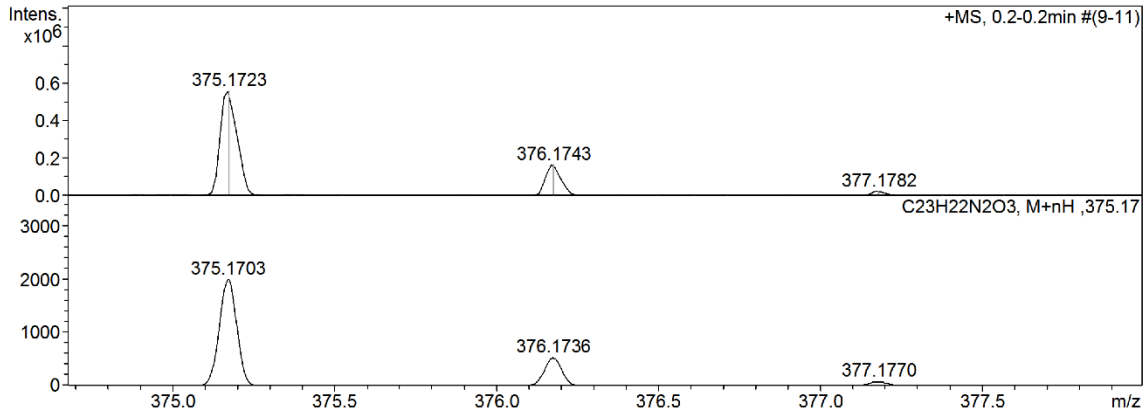
Acquisition Date	22-06-2022 10:43:06		
Analysis Name	D:\Data\USER DATA 2022\JUNE2022\22-06-22\Prof.M.Kapur-NK_06_250_LS_R.d		
Method	tune mix_low.New.021117.m	Operator	Bruker
Sample Name	NK_06_250_LS_R	Instrument	micrOTOF-Q 10330
Comment			

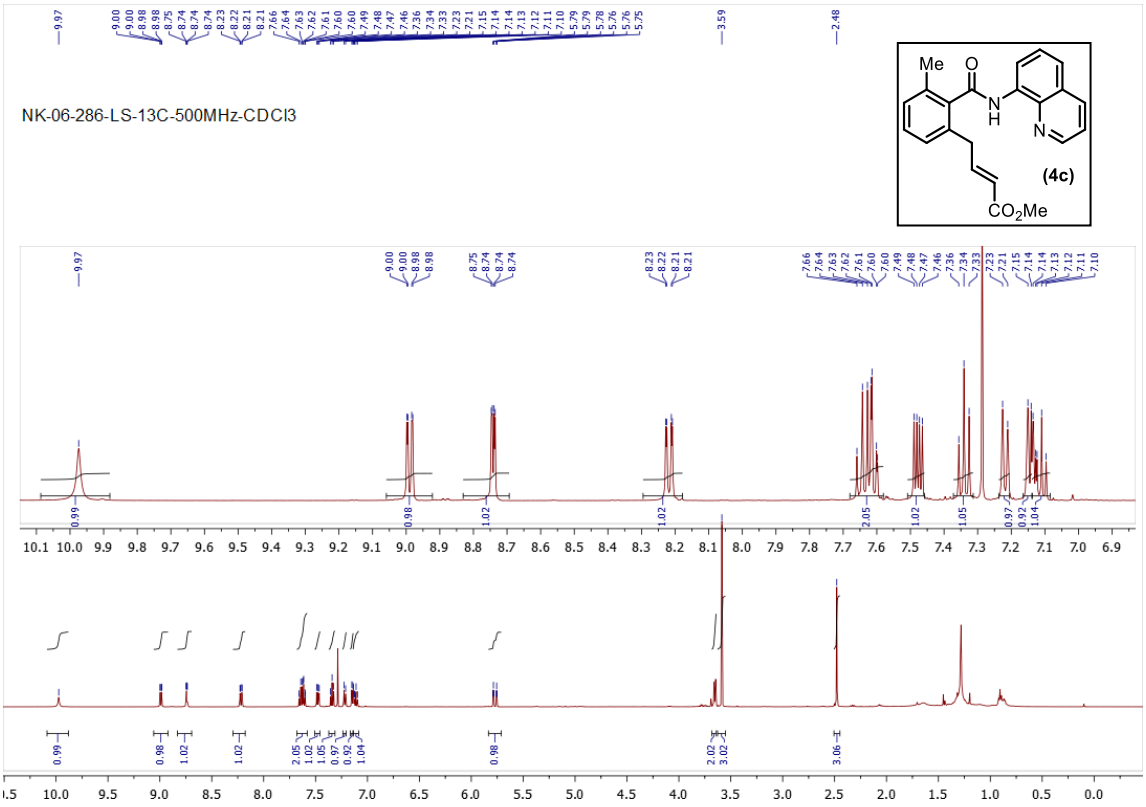
Acquisition Parameter

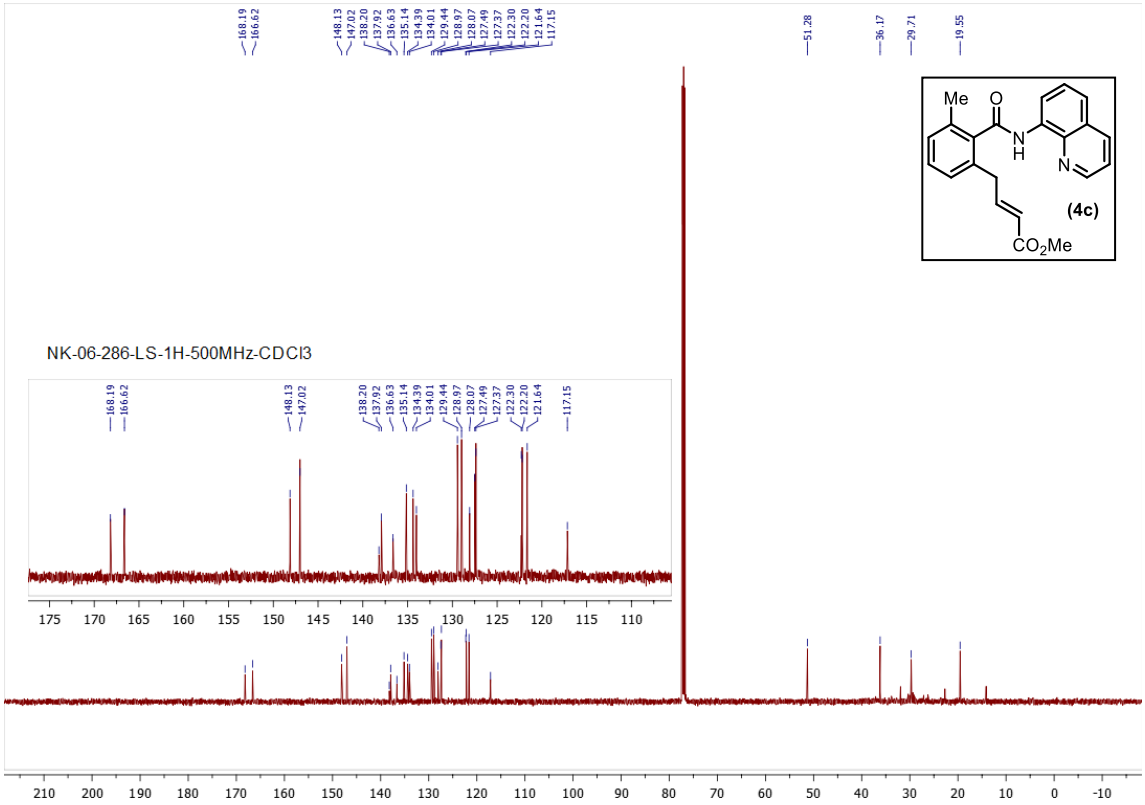
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source








NK-06-286-LS-13C-500MHz-CDCl3
Me
O
N
H
N
(4c)
CO2Me


NK-06-286-LS-1H-500MHz-CDCl3
Me
O
N
H
N
(4c)
CO2Me

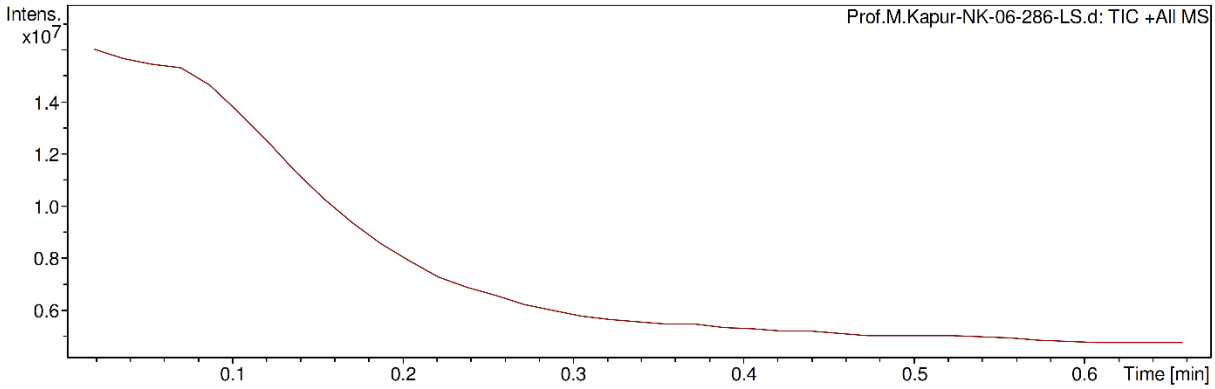
Display Report

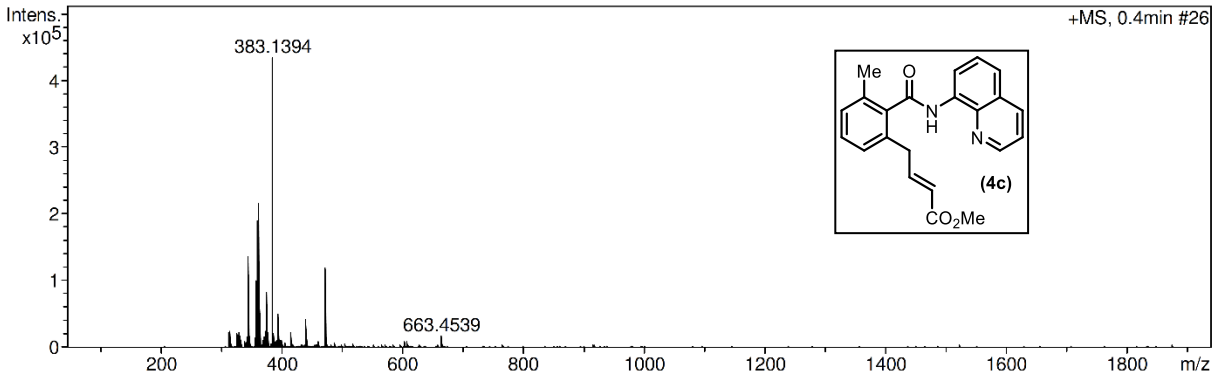
Analysis Info

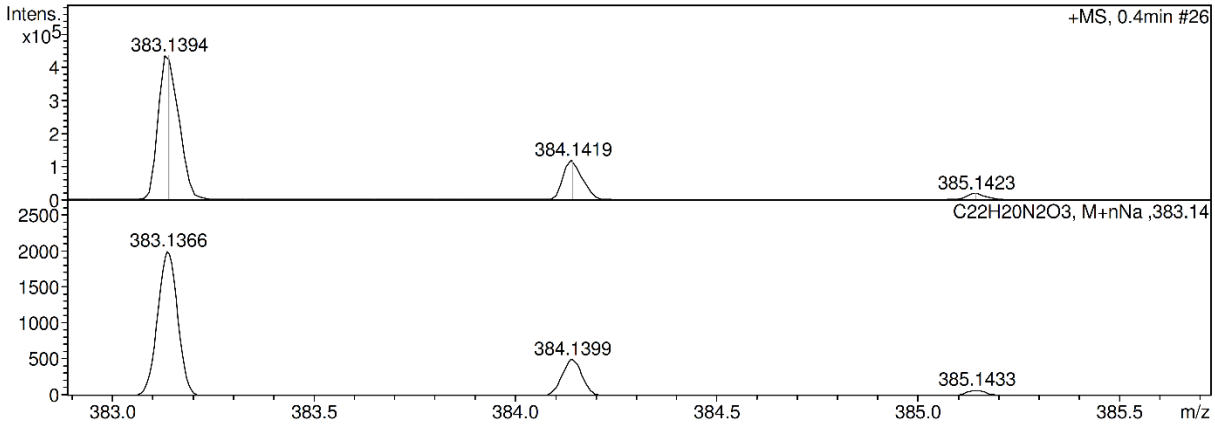
Acquisition Date	3/31/2022 2:53:59 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\March-2022\31march\Prof.M.Kapur-NK-06-286-LS.d		
Method	tune_wide _APCI_23.06.m	Operator	RUCHI
Sample Name	NK-06-286-LS	Instrument	micrOTOF-Q II 10330
Comment			

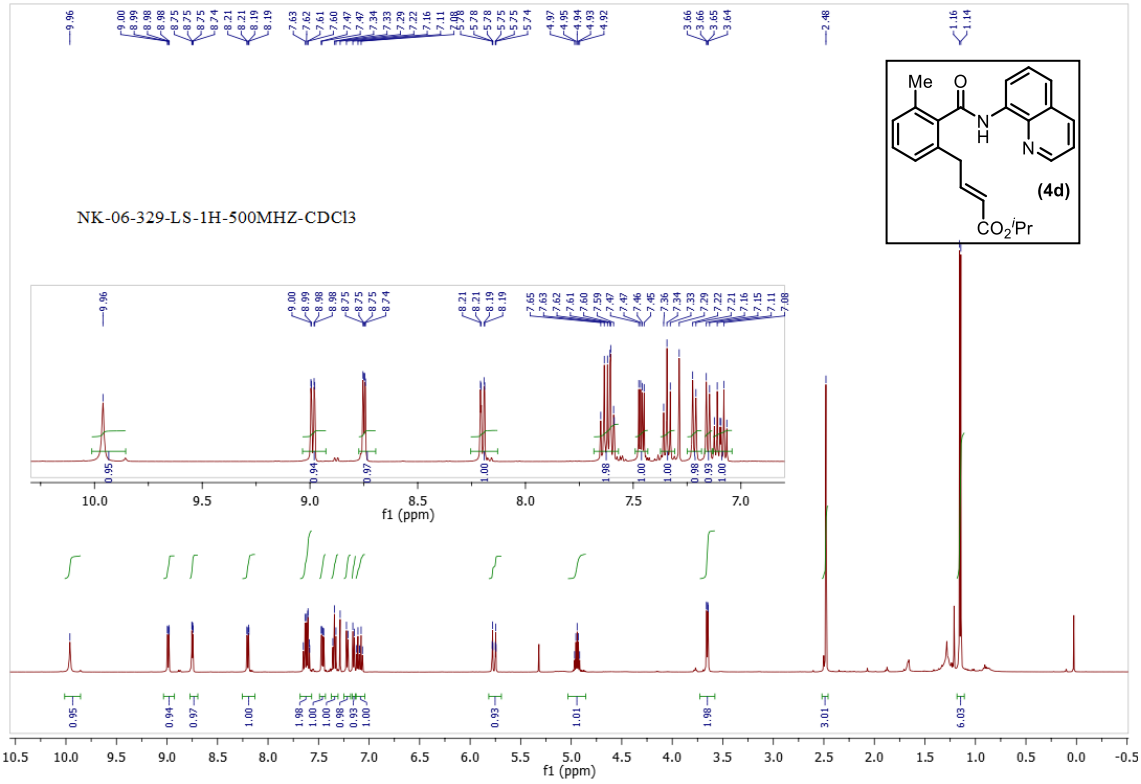
Acquisition Parameter

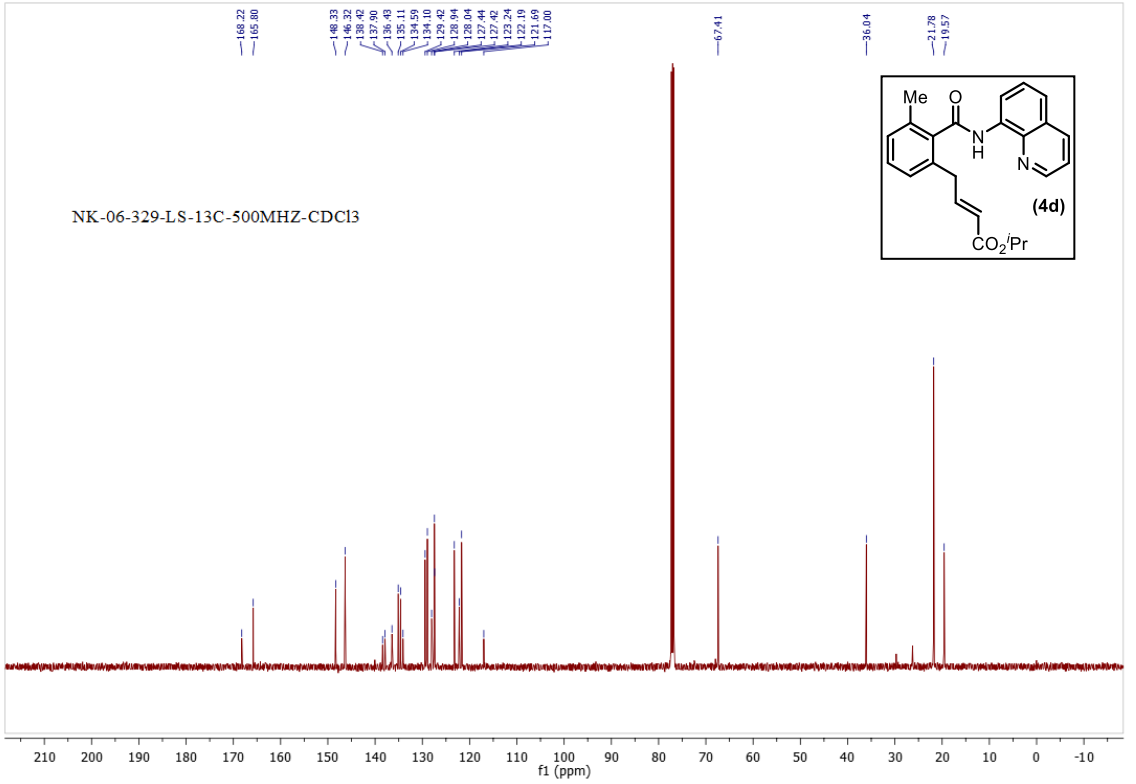
Source Type	Multi Mode	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	2500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source








NK-06-329-LS-1H-500MHZ-CDCl3
Me
O
N
H
N
(4d)
CO2iPr
f1 (ppm)


NK-06-329-LS-13C-500MHZ-CDCl3
Me
O
N
H
N
(4d)
CO2iPr
f1 (ppm)

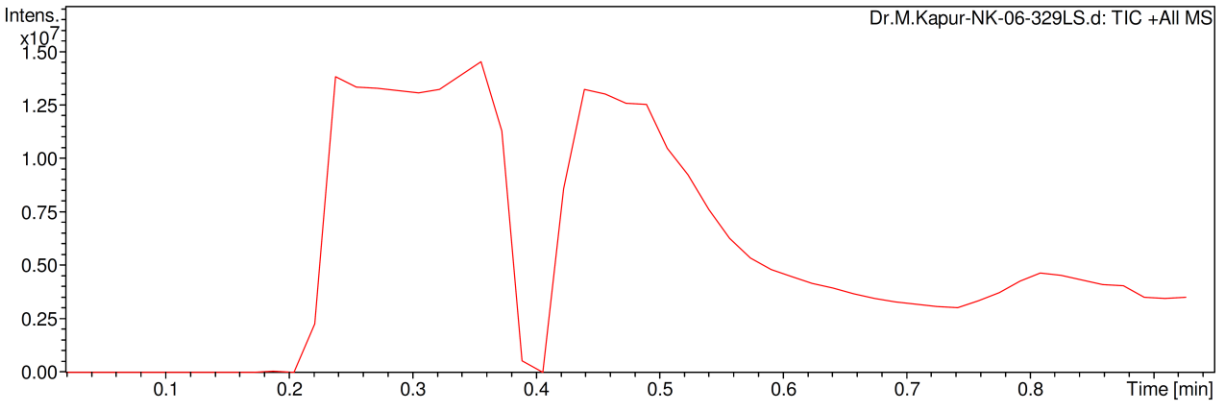
Display Report

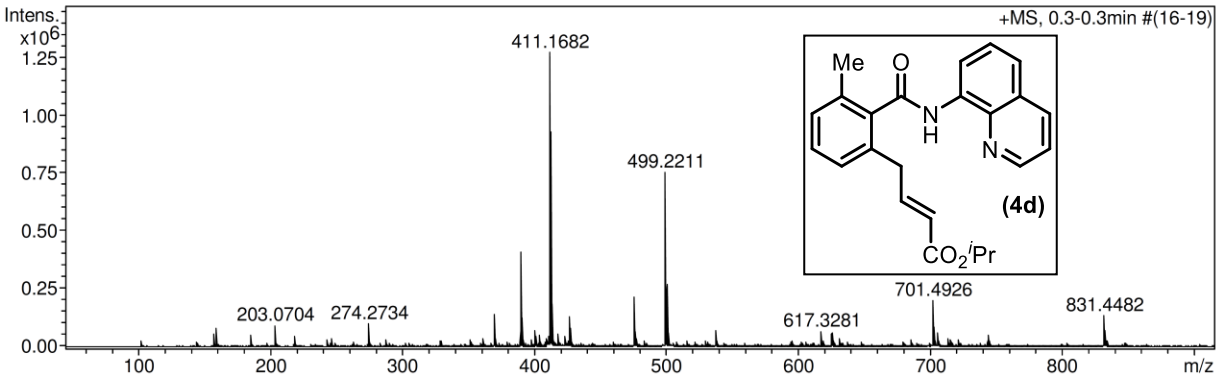
Analysis Info

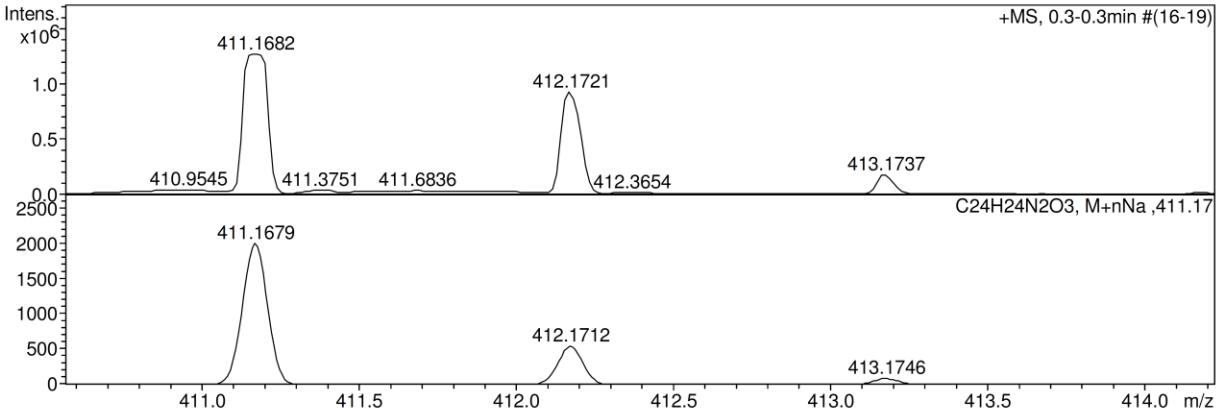
Analysis Name	D:\Data\new user data 2021\Nov-2021\17-Nov\Dr.M.Kapur-NK-06-329LS.d	Acquisition Date	11/17/2021 3:54:02 PM
Method	tune mix_low.New.021117.m	Operator	RUCHI
Sample Name	NK-06-329LS	Instrument	micrOTOF-Q II 10330
Comment			

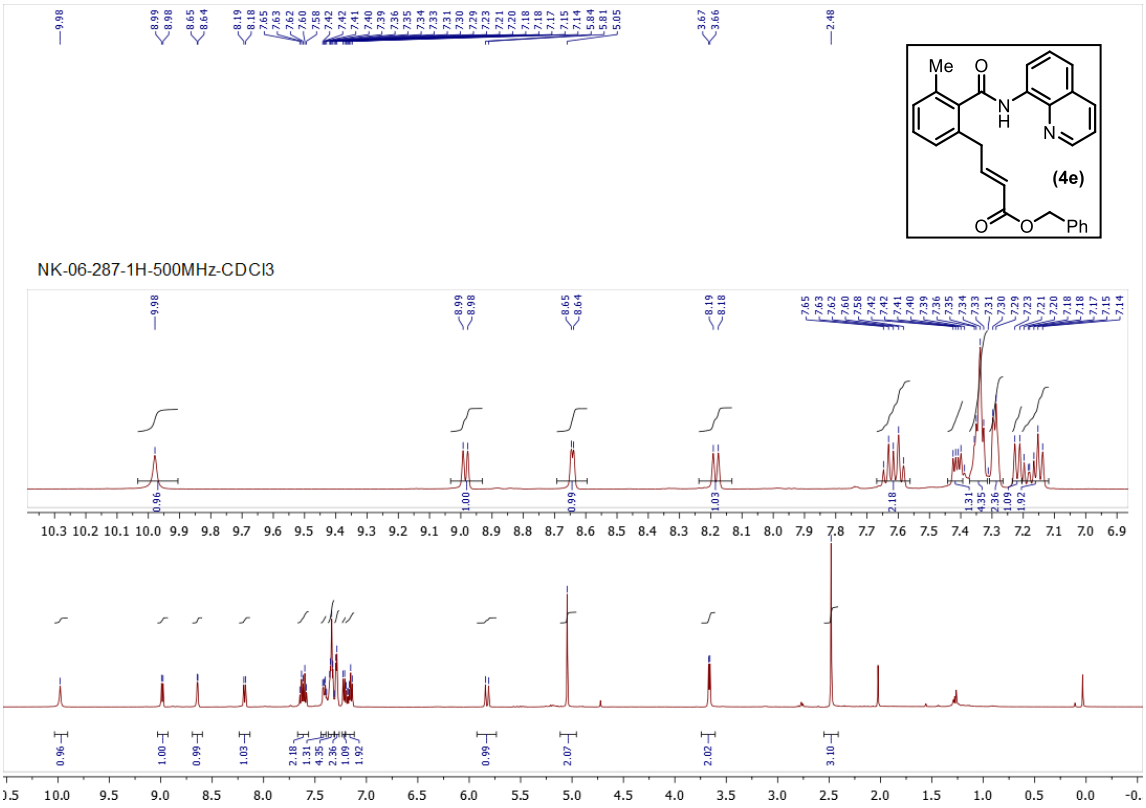
Acquisition Parameter

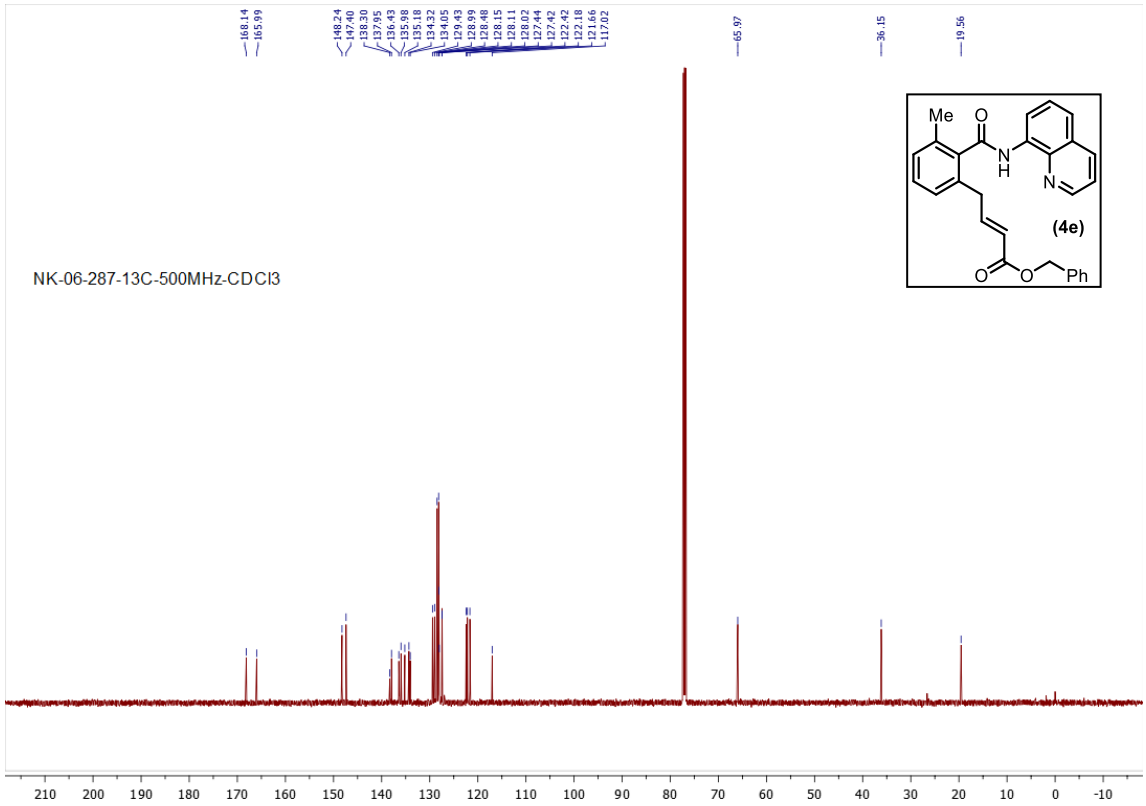
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste








Me
O
N
H
N
(4e)
O
O
Ph
NK-06-287-1H-500MHz-CDCl3


Me
O
N
H
N
(4e)
O
O
Ph
NK-06-287-13C-500MHz-CDCl3

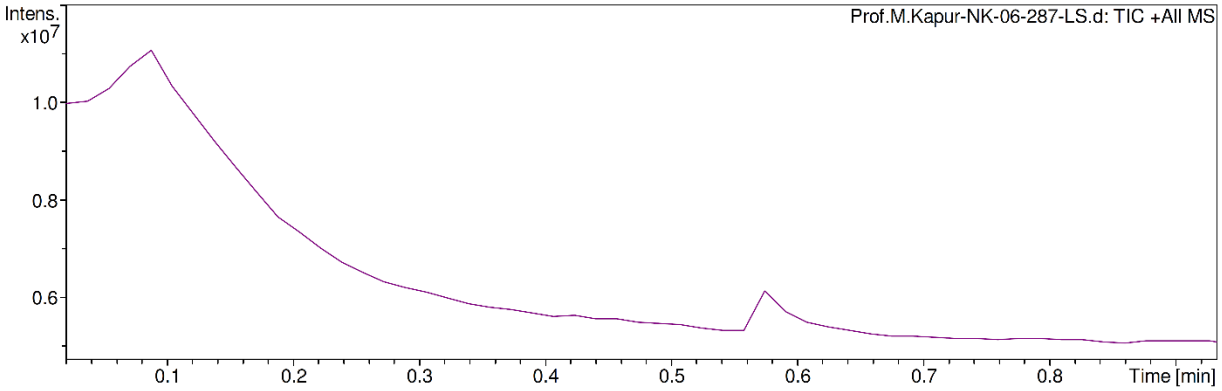
Display Report

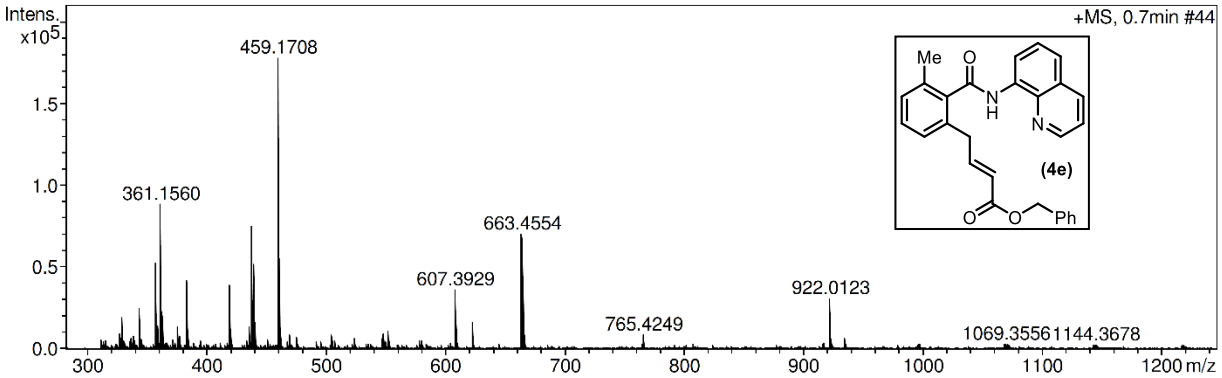
Analysis Info

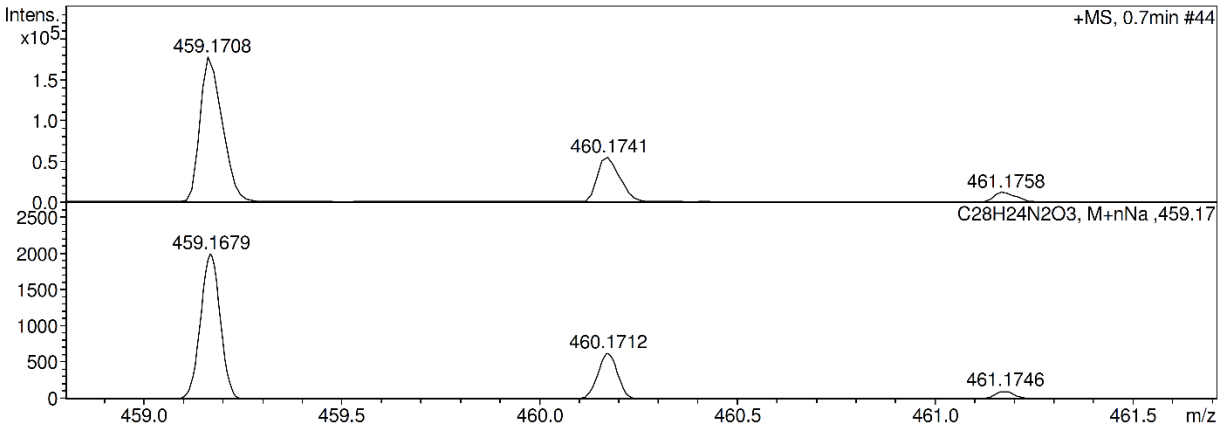
Analysis Name	D:\Data\NEW USER DATA 2022\March-2022\31march\Prof.M.Kapur-NK-06-287-LS.d	Acquisition Date	3/31/2022 2:40:40 PM
Method	tune_wide _APCI_23.06.m	Operator	RUCHI
Sample Name	NK-06-287-LS	Instrument	micrOTOF-Q II 10330
Comment			

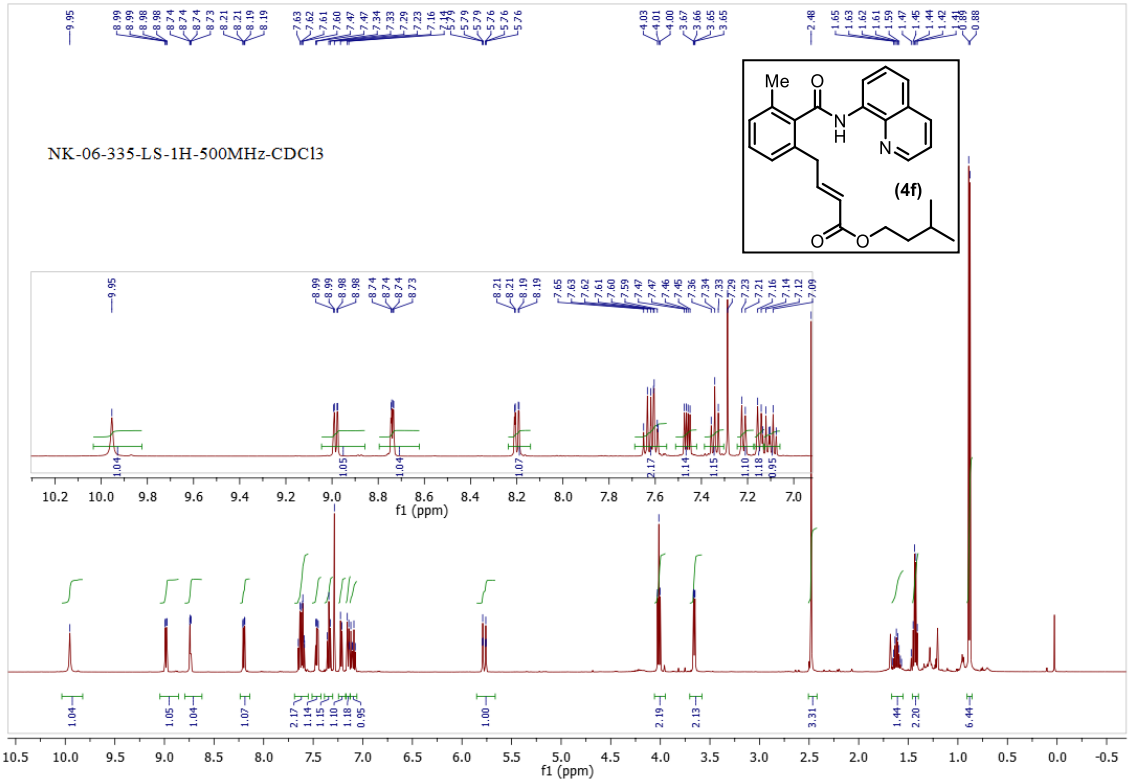
Acquisition Parameter

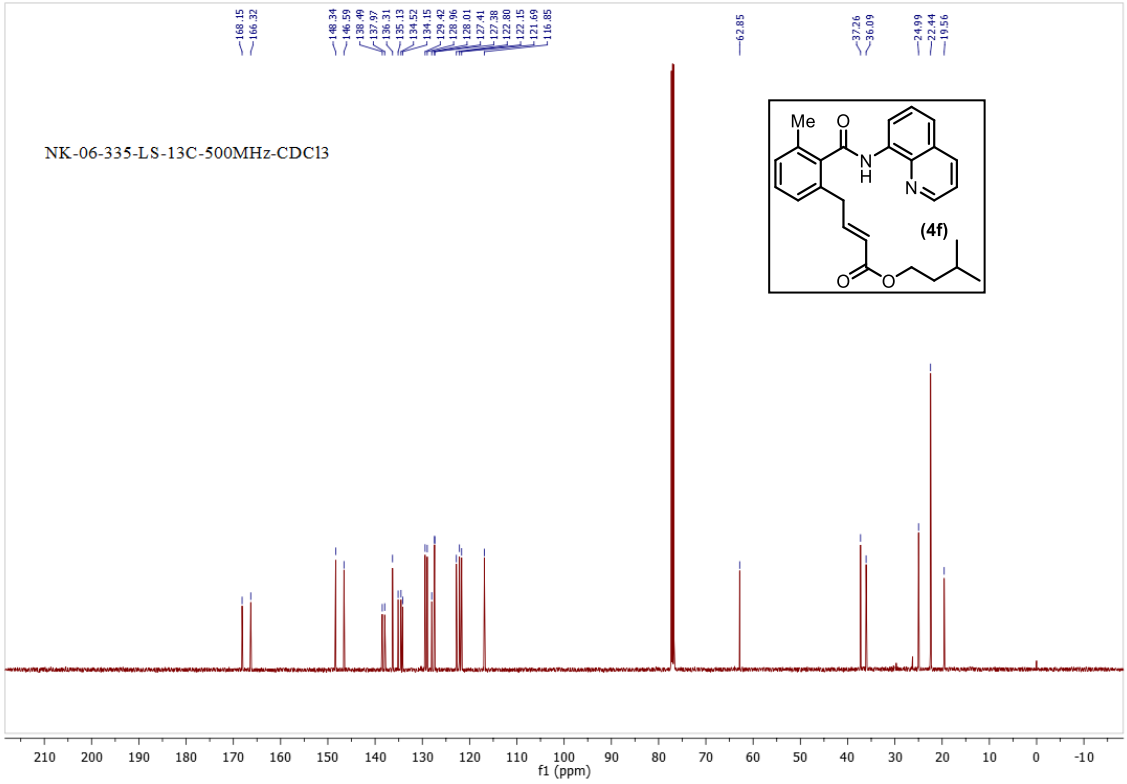
Source Type	Multi Mode	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	2500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source








NK-06-335-LS-1H-500MHz-CDCl3
Me
O
N
H
N
(4f)
O
O
f1 (ppm)


NK-06-335-LS-13C-500MHz-CDCl3
Me
O
N
H
N
(4f)
O
O
f1 (ppm)

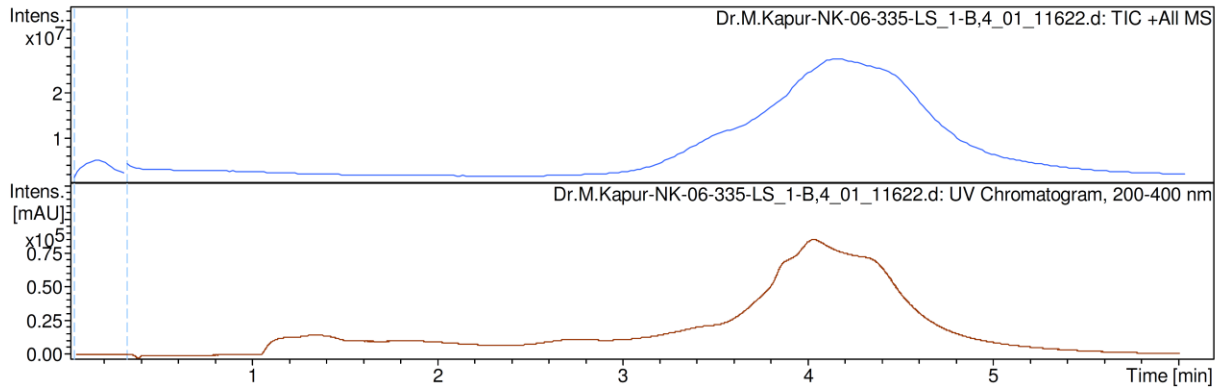
Display Report

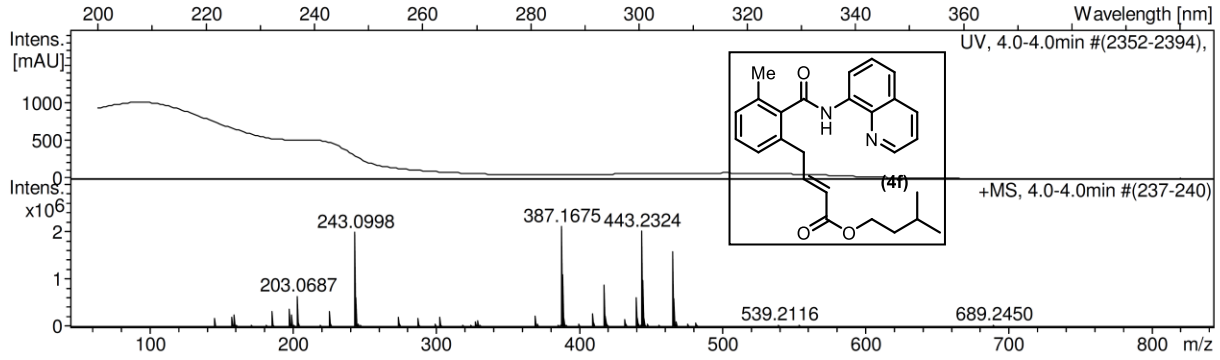
Analysis Info

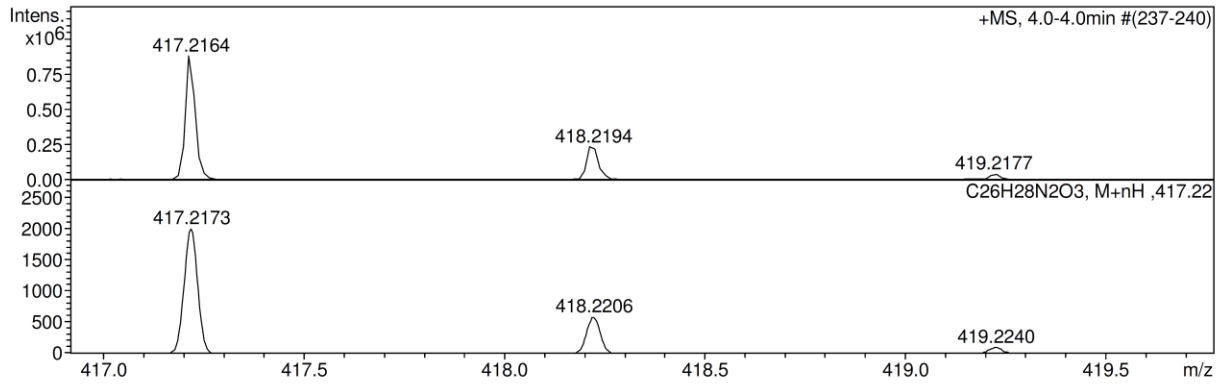
Acquisition Date	4/1/2022 2:40:27 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\April-2022\01-April\Dr.M.Kapur-NK-06-335-LS_1-B,4_01_11622.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr.M.Kapur-NK-06-335-LS	Instrument	micrOTOF-Q II 10330
Comment			

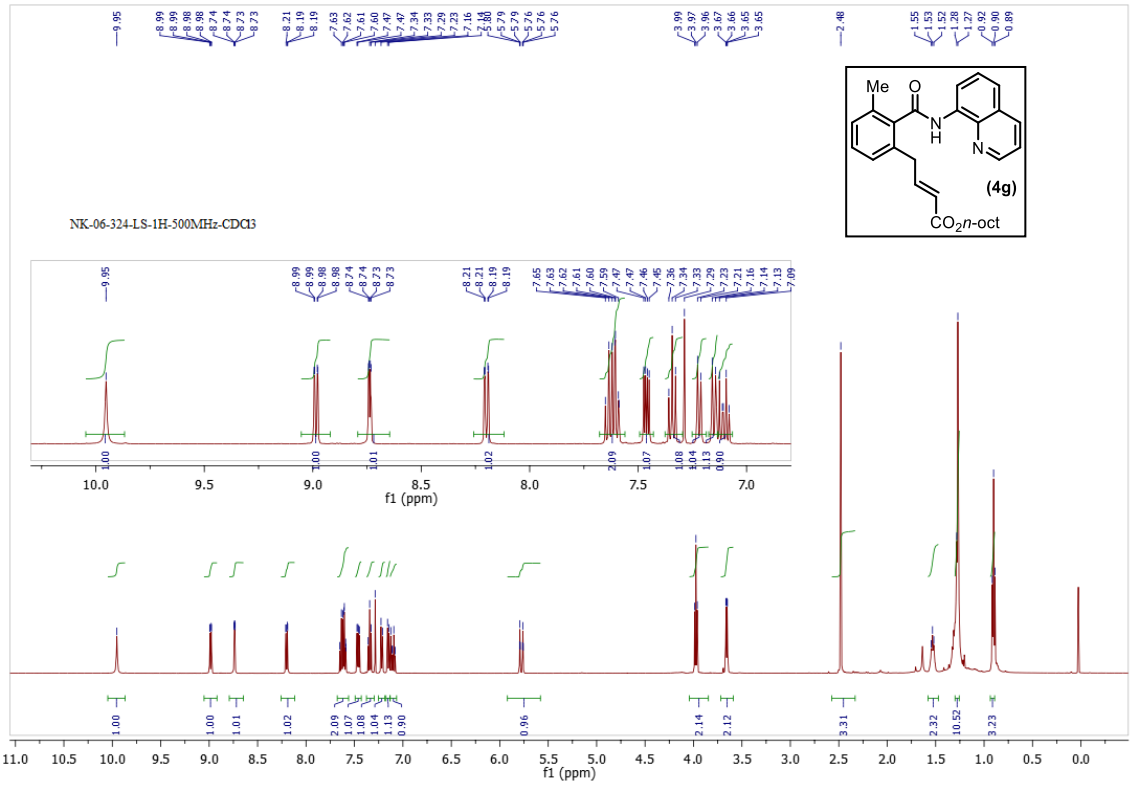
Acquisition Parameter

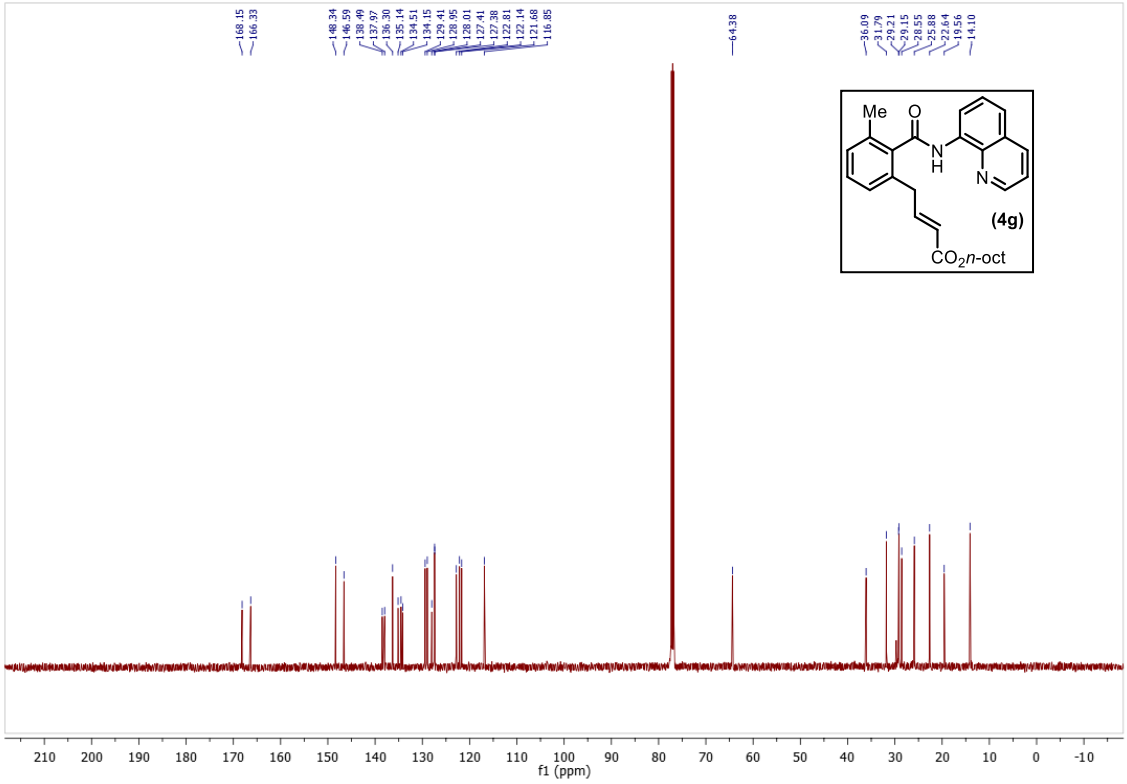
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








NK-06-324-LS-1H-500MHz-CDCl3
Me
O
N
H
N
(4g)
CO2n-oct
f1 (ppm)


Me
O
N
H
N
(4g)
CO2n-oct
f1 (ppm)

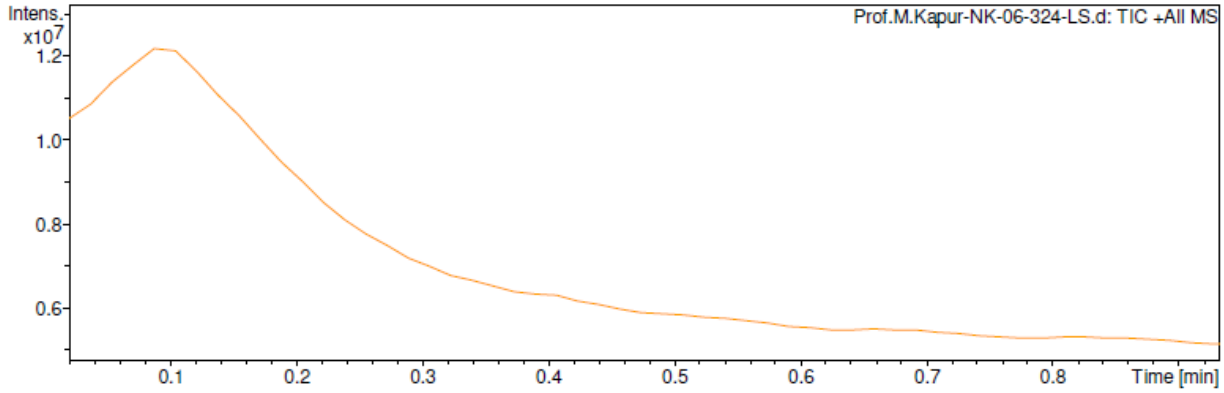
Display Report

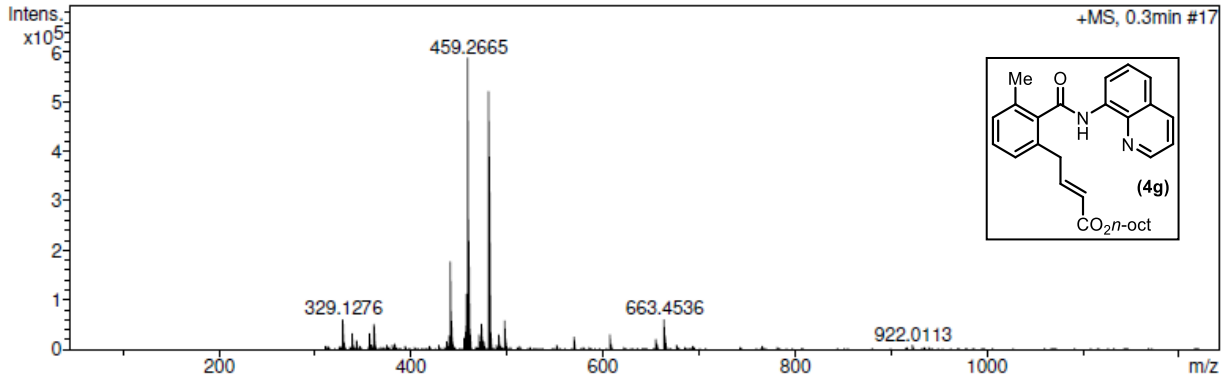
Analysis Info

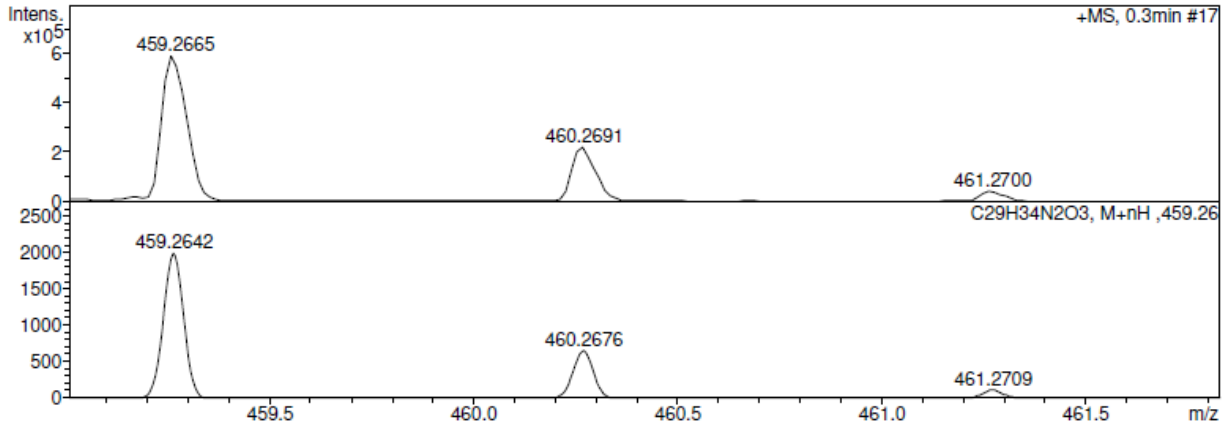
Acquisition Date	3/31/2022 2:43:28 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\March-2022\31march\Prof.M.Kapur-NK-06-324-LS.d		
Method	tune_wide _APCI_23.06.m	Operator	RUCHI
Sample Name	NK-06-324-LS	Instrument	micrOTOF-Q II 10330
Comment			

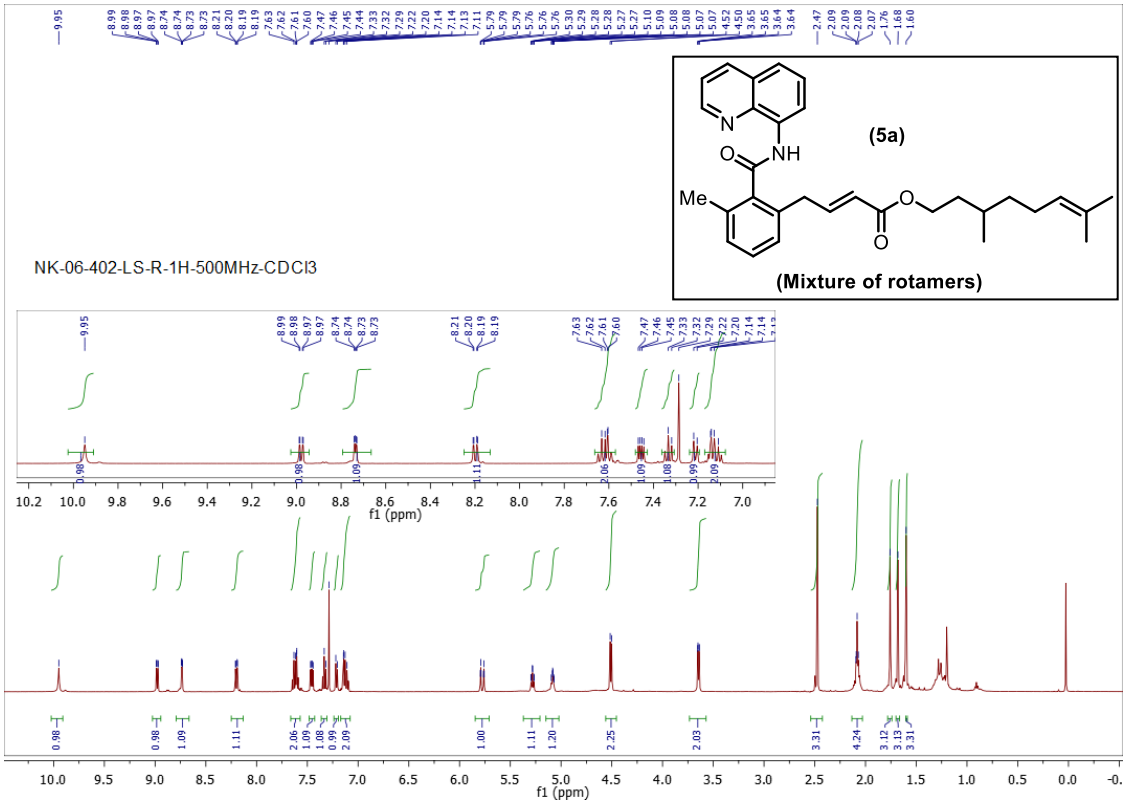
Acquisition Parameter

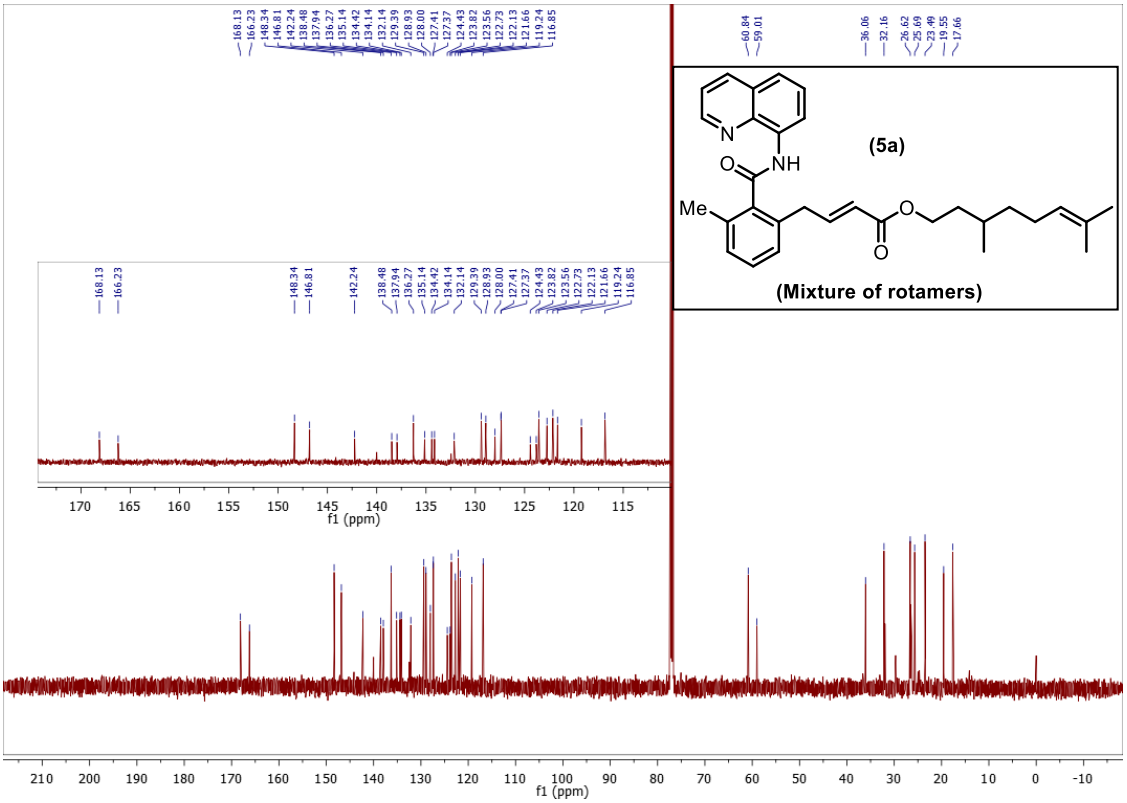
Source Type	Multi Mode	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	2500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source








NK-06-402-LS-R-1H-500MHz-CDCl3
(5a)
(Mixture of rotamers)
f1 (ppm)


(5a)
(Mixture of rotamers)
f1 (ppm)

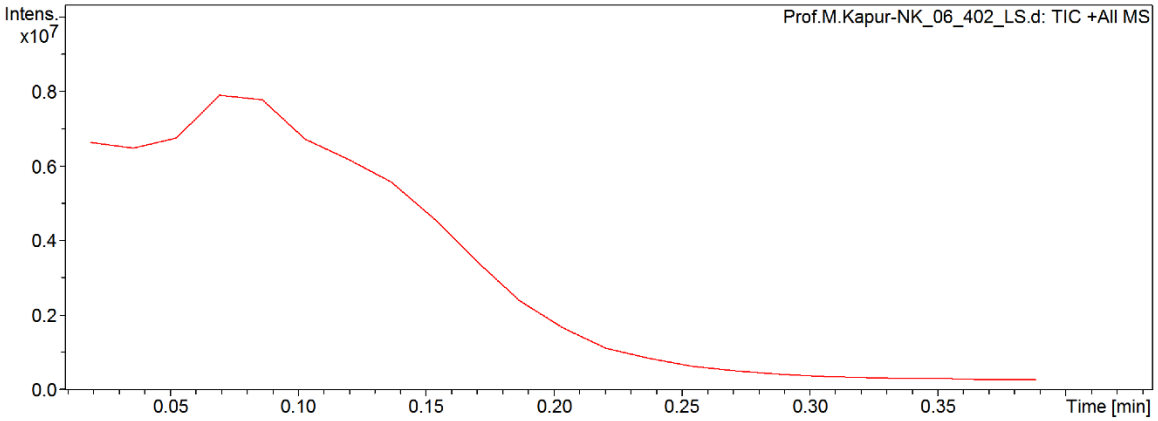
Display Report

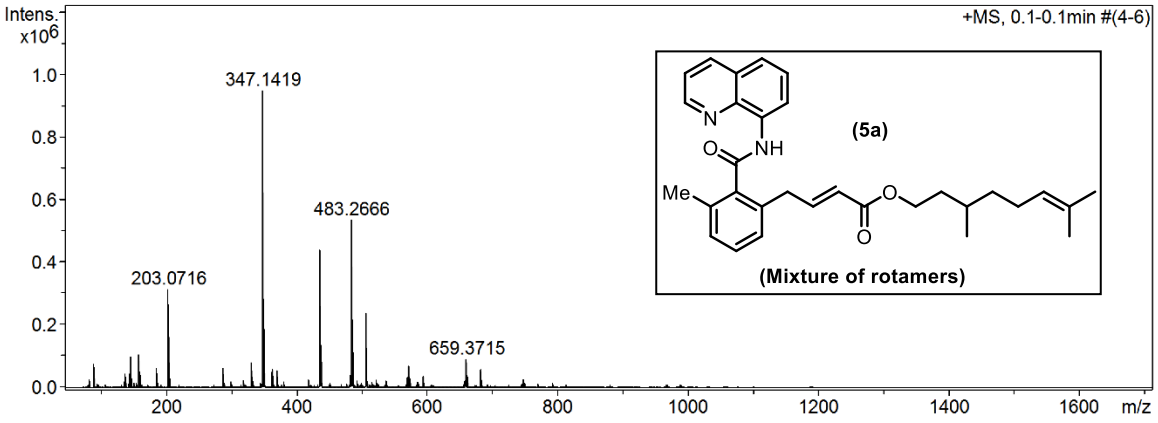
Analysis Info

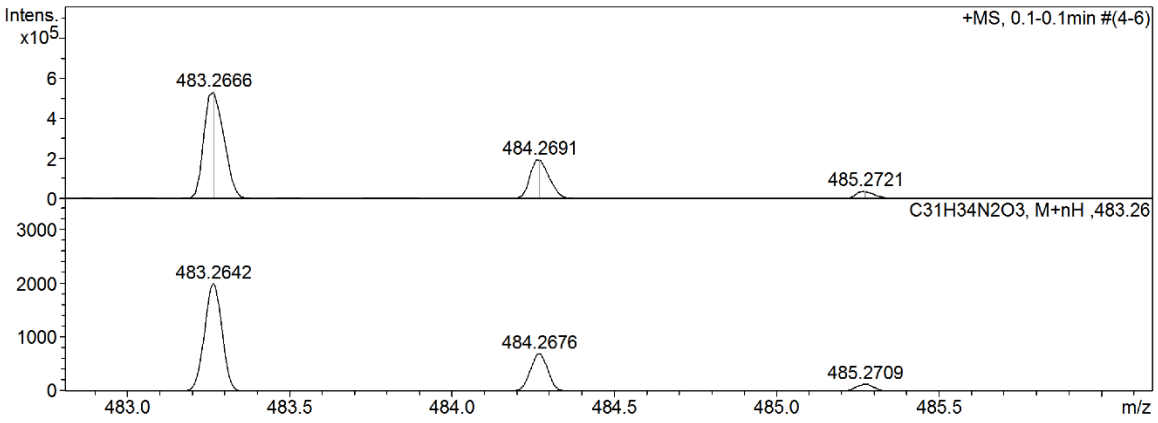
Analysis Name	D:\Data\USER DATA 2022\JUNE2022\21-06-22\Prof.M.Kapur-NK_06_402_LS.d	Acquisition Date	21-06-2022 14:21:21
Method	tune mix_low.New.021117_1.m	Operator	Bruker
Sample Name	NK_06_402_LS	Instrument	micrOTOF-Q 10330
Comment			

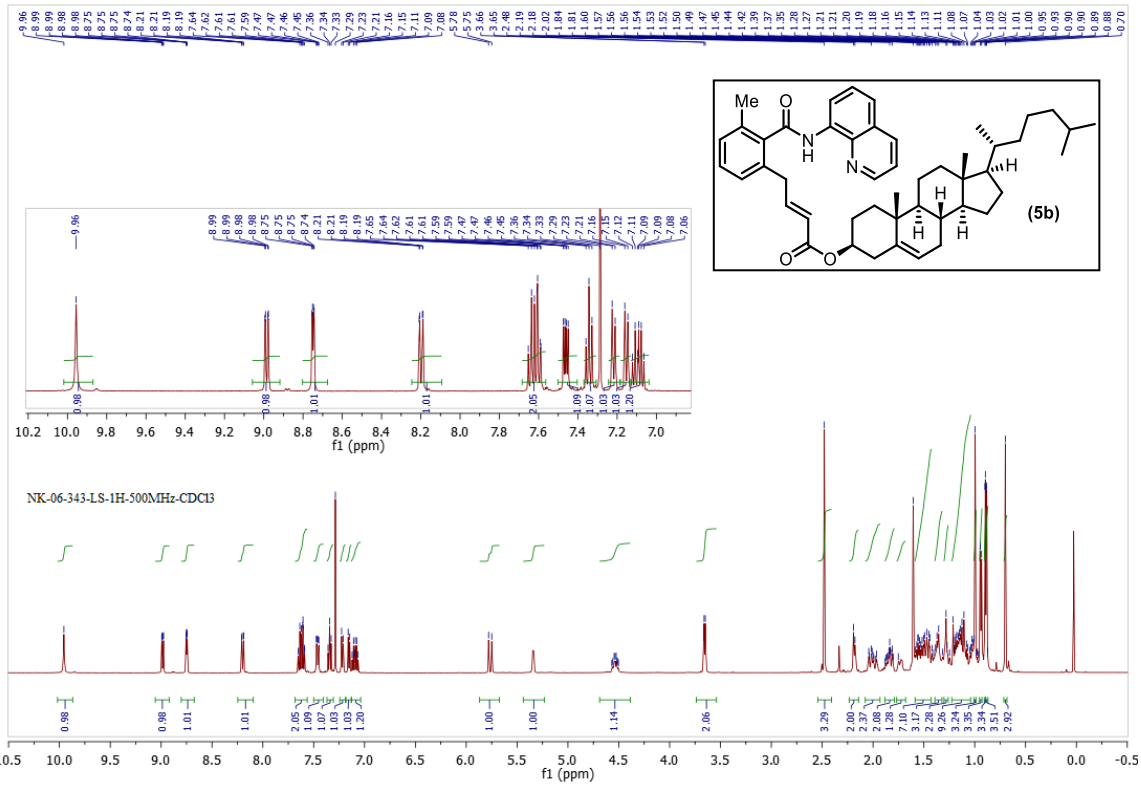
Acquisition Parameter

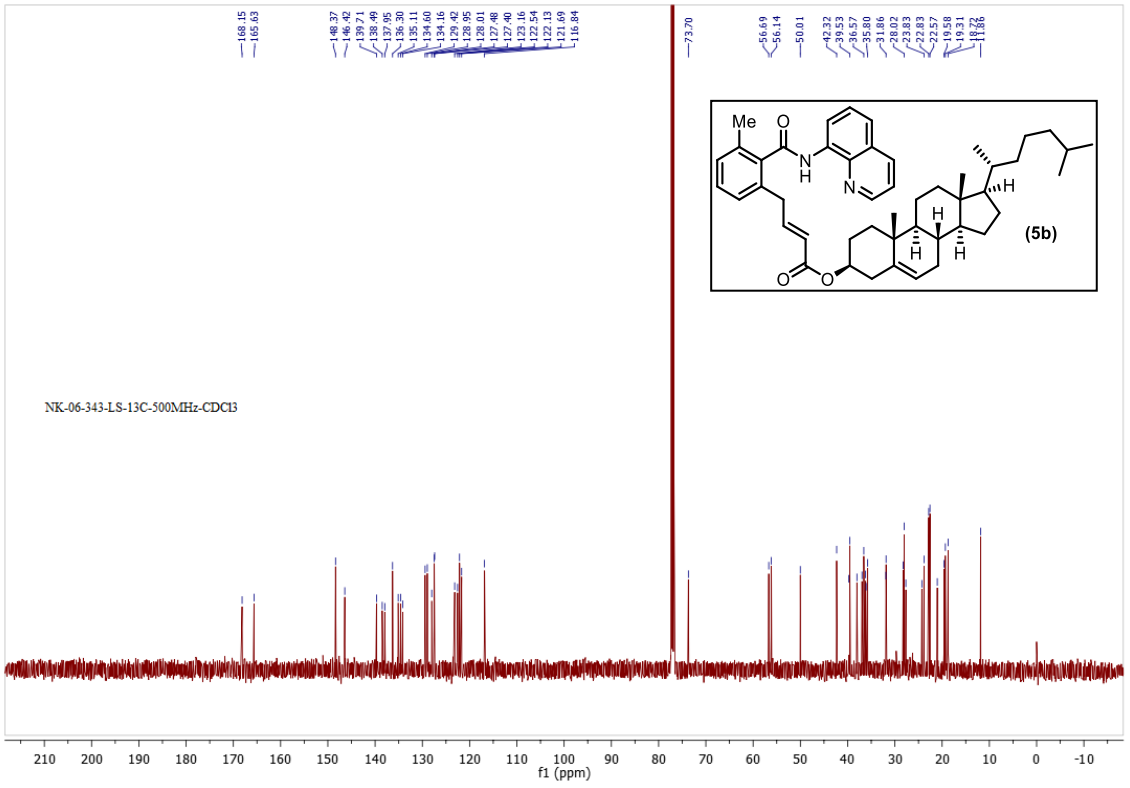
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source








Me
O
N
H
N
H
H
H
O
O
(5b)
f1 (ppm)
NK-06-343-LS-1H-500MHz-CDCl3
f1 (ppm)


Me
O
N
H
N
H
H
H
O
O
(5b)
NK-06-343-LS-13C-500MHz-CDCl3
f1 (ppm)

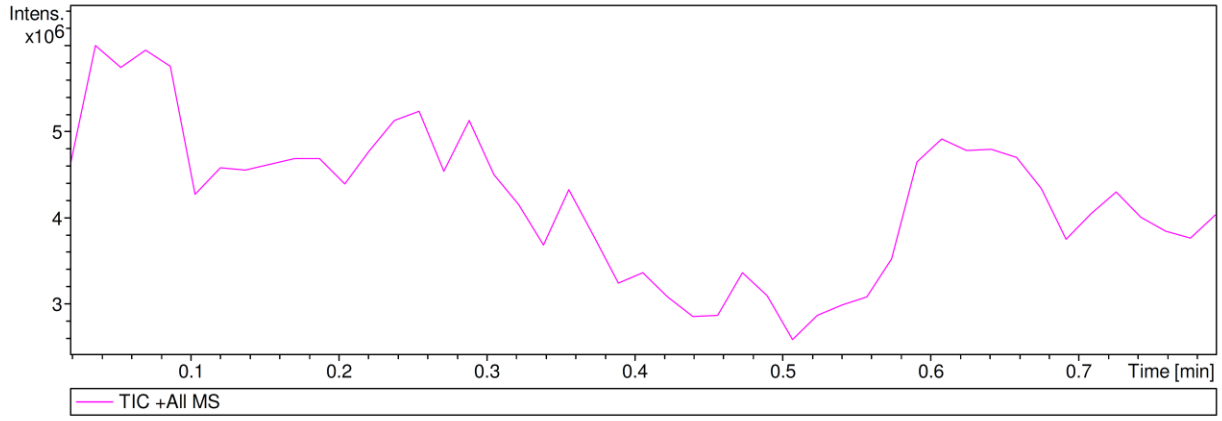
Display Report

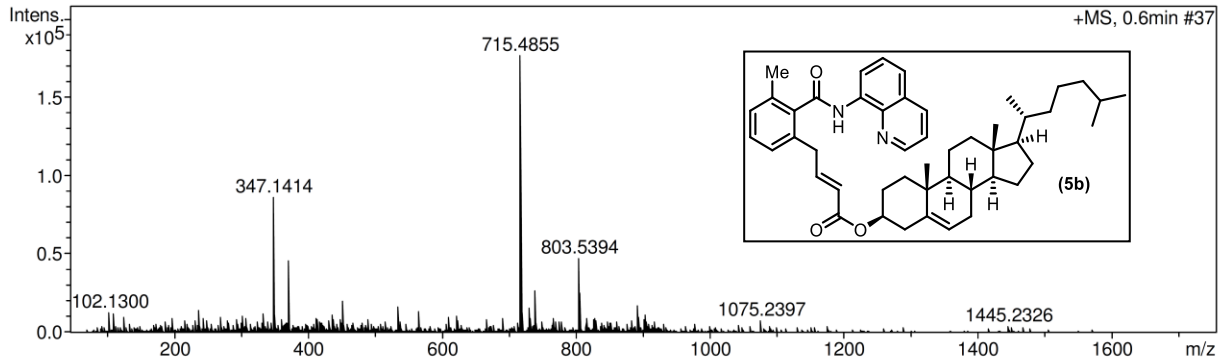
Analysis Info

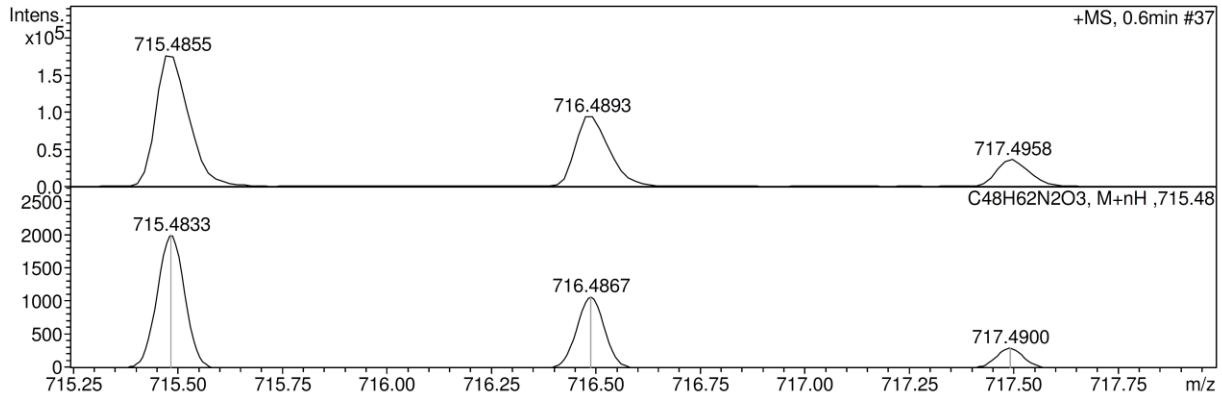
Acquisition Date	1/31/2022 10:46:03 AM		
Analysis Name	D:\Data\NEW USER DATA 2022\Jan-2022\31-jan-2022\Prof.M.Kapur-NK-06-343-LS.d		
Method	tune mix_low.New.021117.m	Operator	RUCHI
Sample Name	NK-06-343-LS	Instrument	micrOTOF-Q II 10330
Comment			

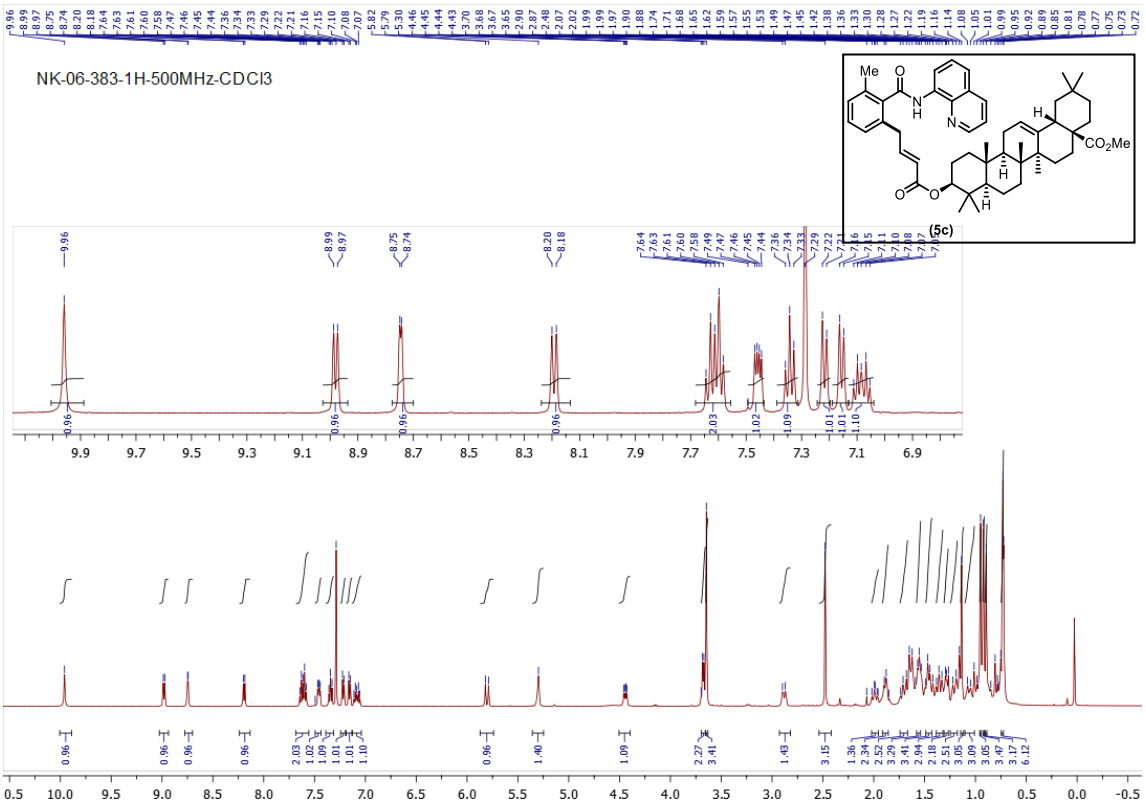
Acquisition Parameter

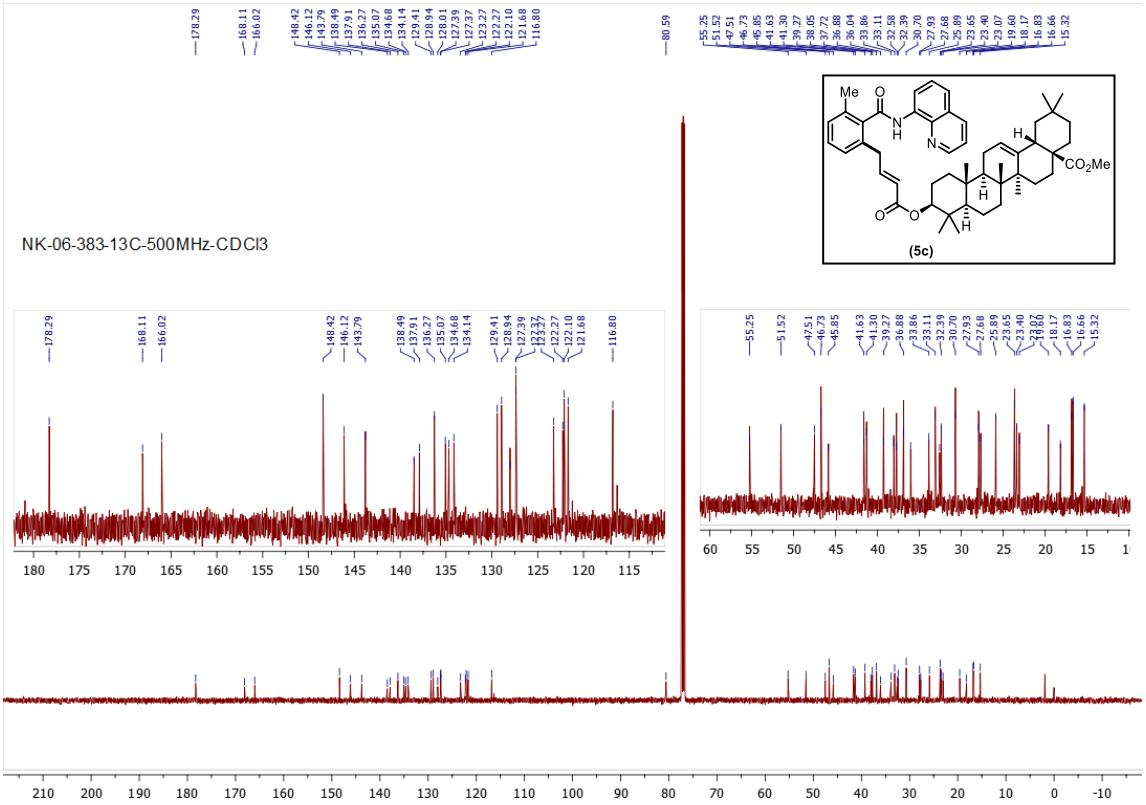
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source








NK-06-383-1H-500MHz-CDCl3
Me
O
N
H
N
H
CO2Me
O
O
H
(5c)


NK-06-383-13C-500MHz-CDCl3
Me
O
N
H
N
H
CO2Me
O
O
H
(5c)

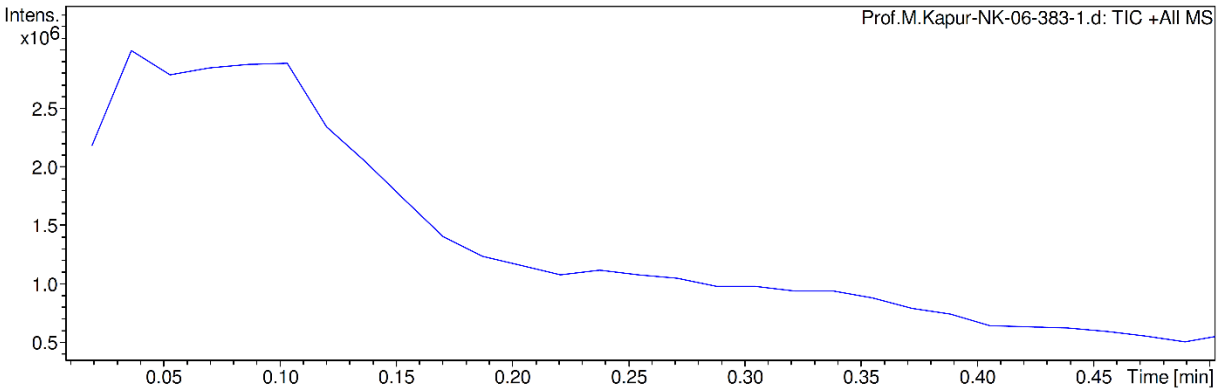
Display Report

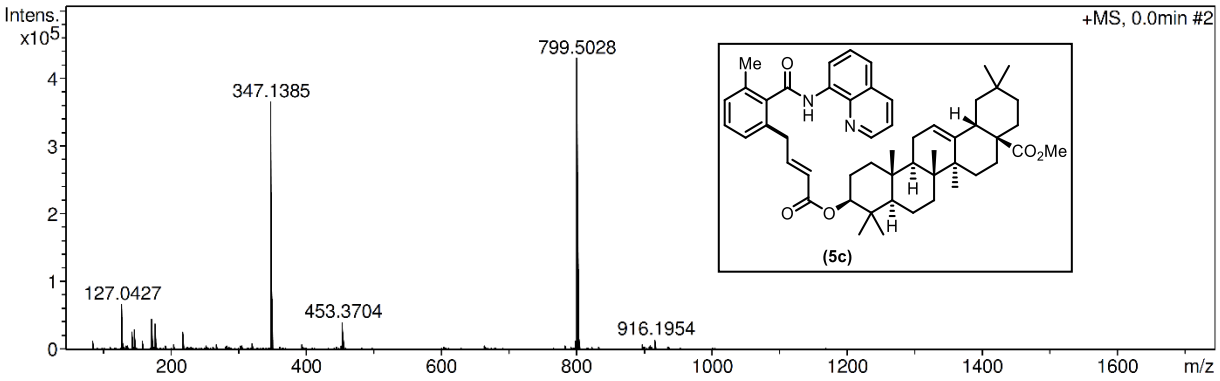
Analysis Info

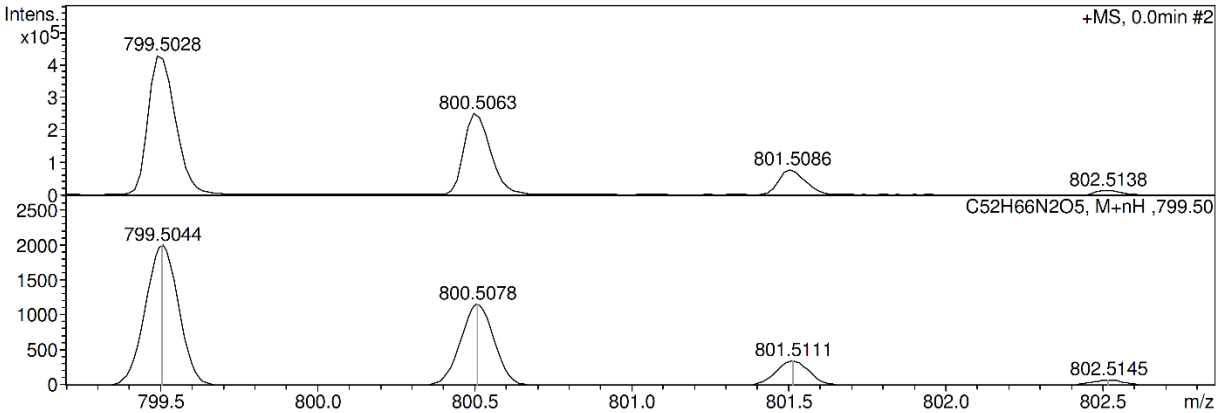
Acquisition Date	2/23/2022 3:52:42 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\fe-2022\23-feb-2022\Prof.M.Kapur-NK-06-383-1.d		
Method	tune mix_low.New.021117.m	Operator	RUCHI
Sample Name	NK-06-383-1	Instrument	micrOTOF-Q II 10330
Comment			

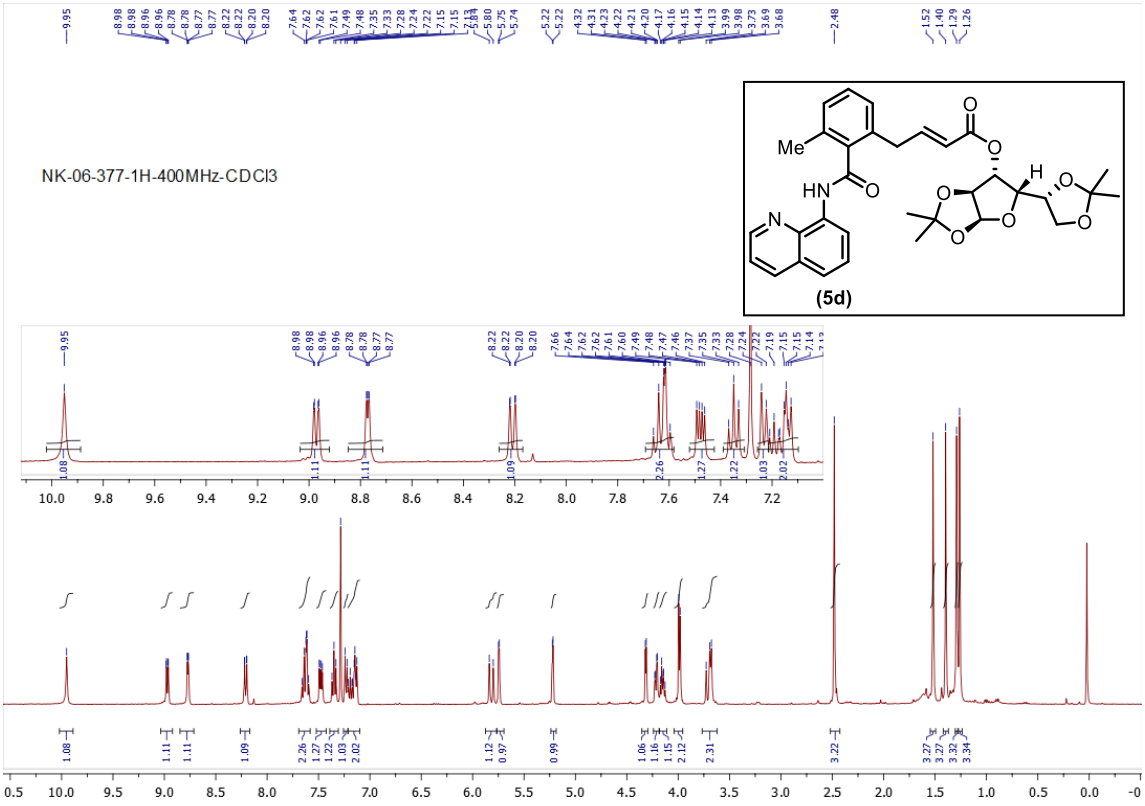
Acquisition Parameter

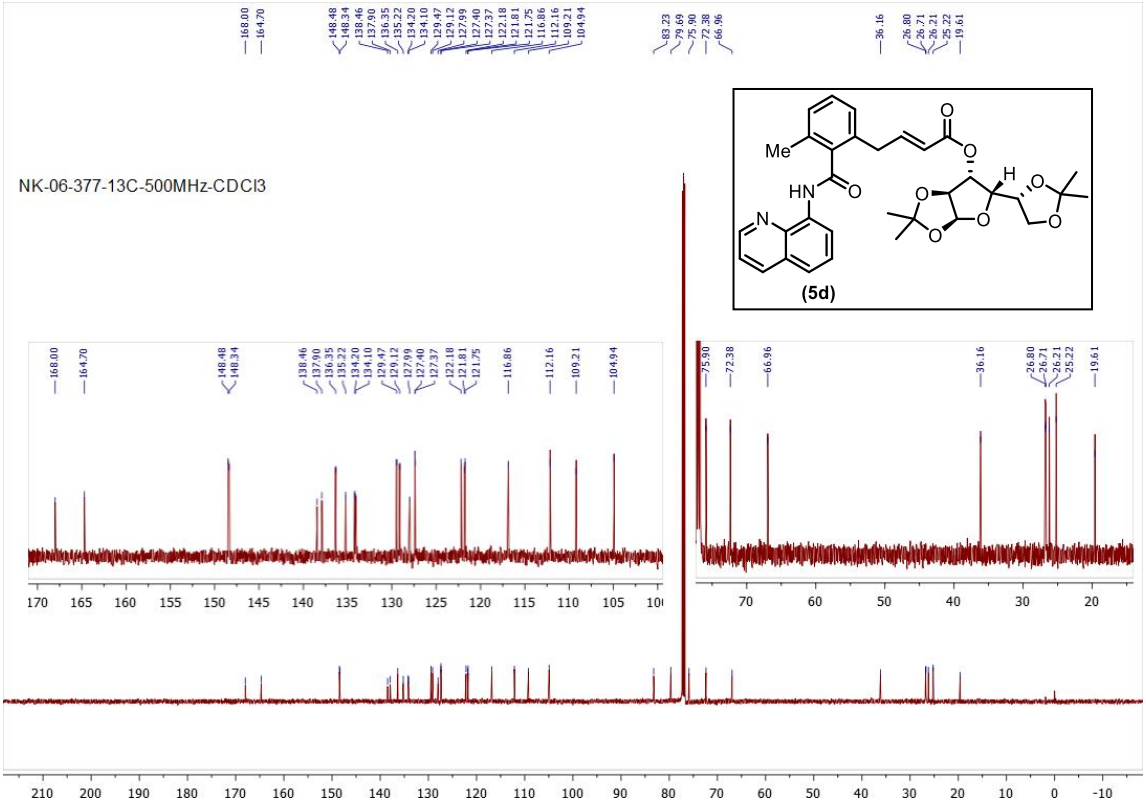
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source








NK-06-377-1H-400MHz-CDCl3
(5d)


NK-06-377-13C-500MHz-CDCl3
(5d)

Display Report

Analysis Info

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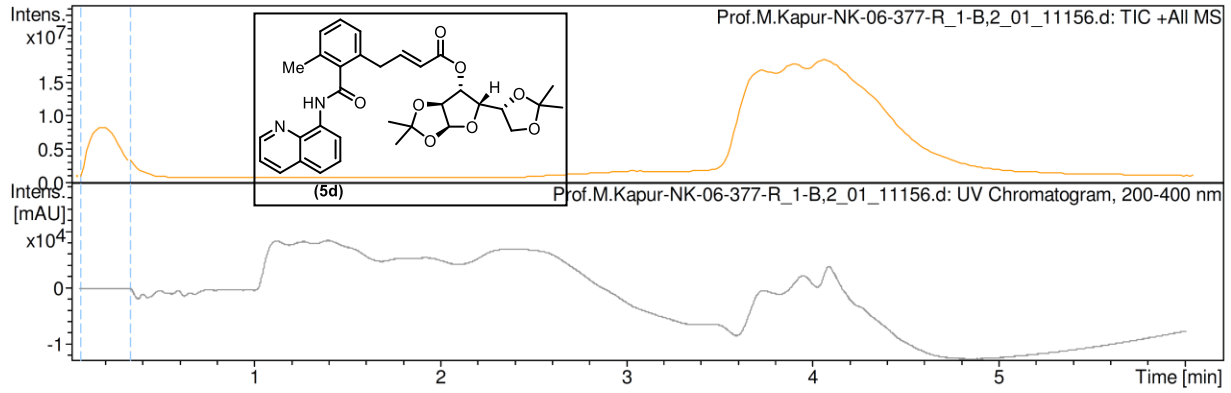
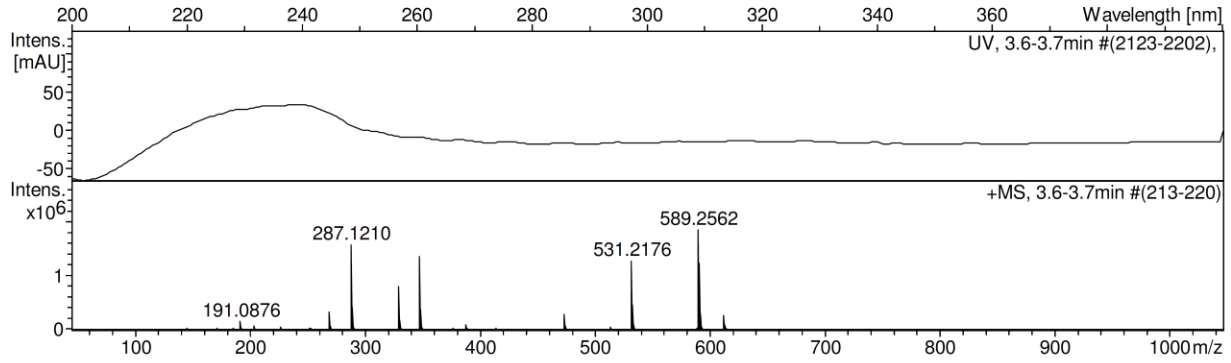
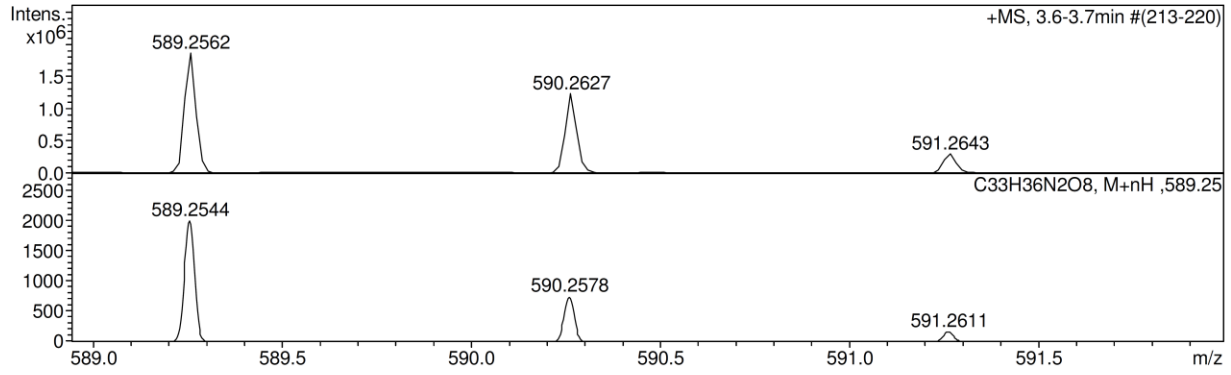
Analysis Name	D:\Data\NEW USER DATA 2022\fe-2022\16-feb-2022\Prof.M.Kapur-NK-06-377-R_1-B,2_01_11156.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Prof.M.Kapur-NK-06-377-R	Instrument	micrOTOF-Q II 10330
Comment			

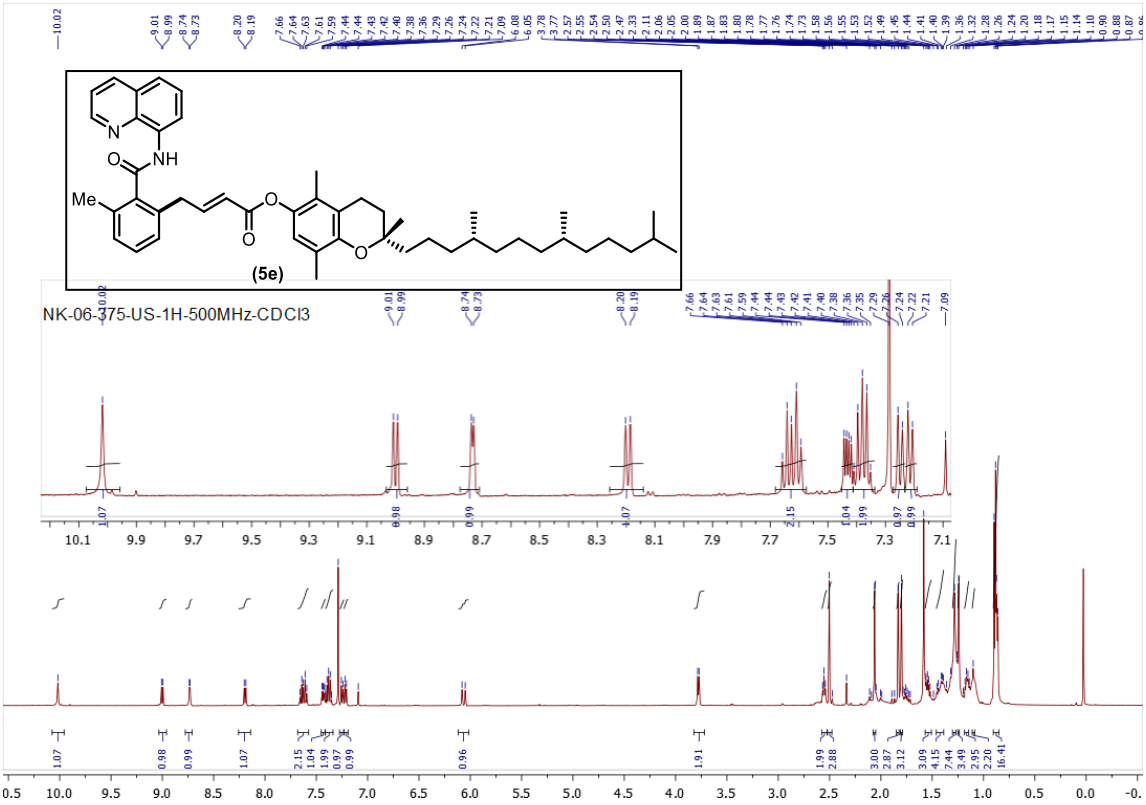
Acquisition Parameter

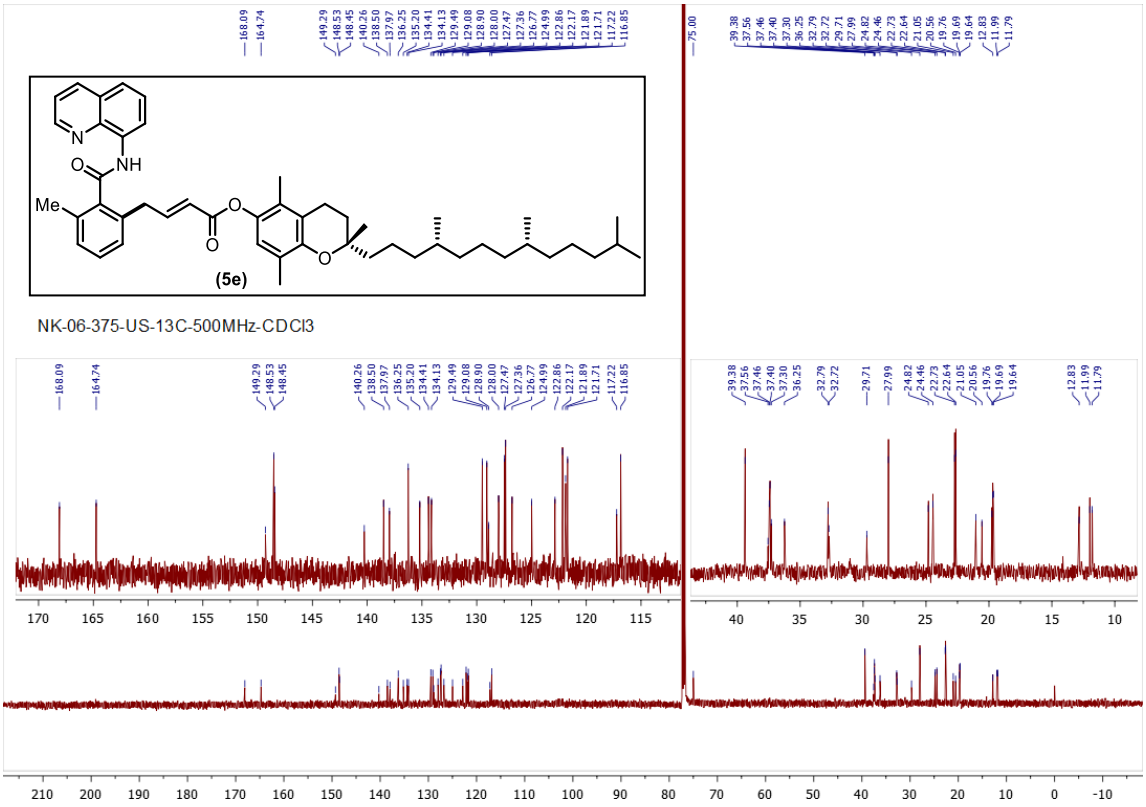
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








(5e)
NK-06-375-US-1H-500MHz-CDCl3


(5e)
NK-06-375-US-13C-500MHz-CDCl3

Display Report

Analysis Info

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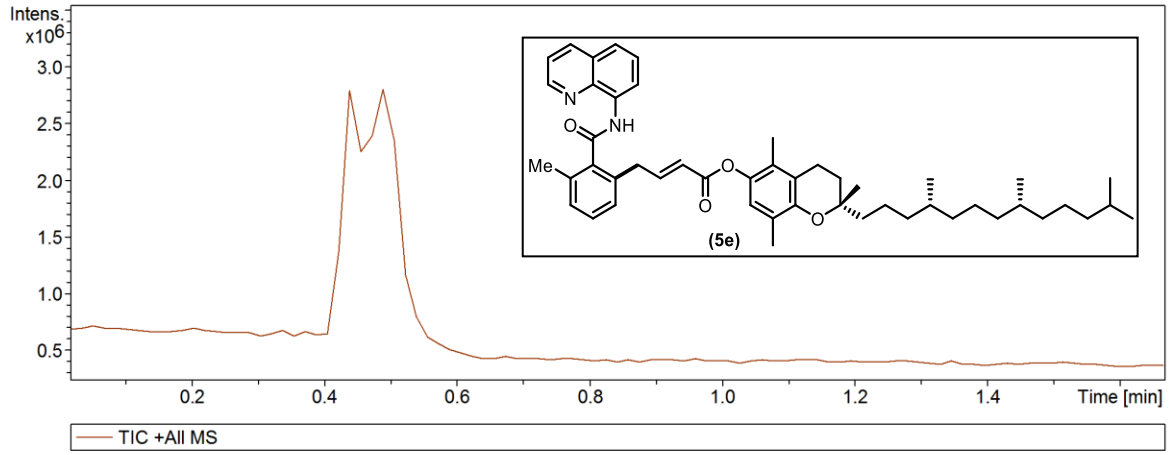
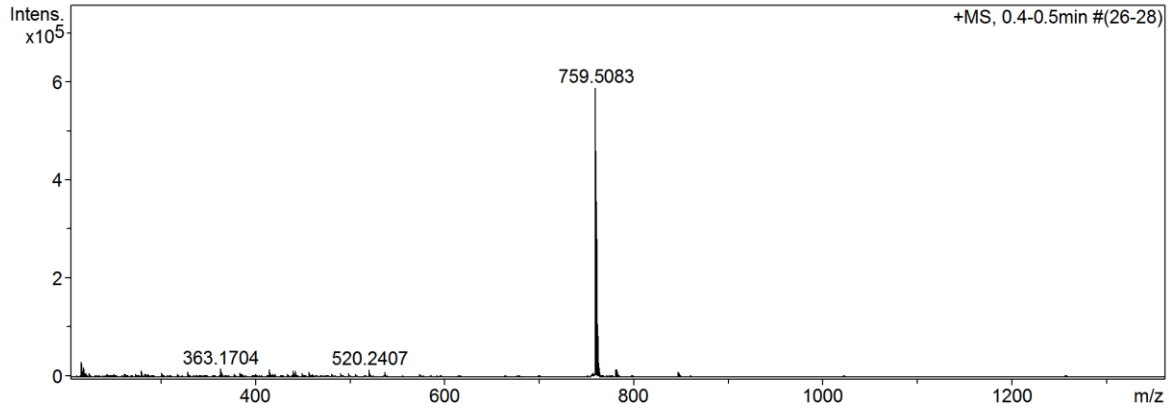
Analysis Name	D:\Data\USER DATA 2022\AUG2022\30-08-2022\Prof.M.Kapur-NK_06_375_US_R_2.d		
Method	tune mix_low.New.021117.m	Operator	Bruker
Sample Name	NK_06_375_US_R_2	Instrument	micrOTOF-Q 10330
Comment			

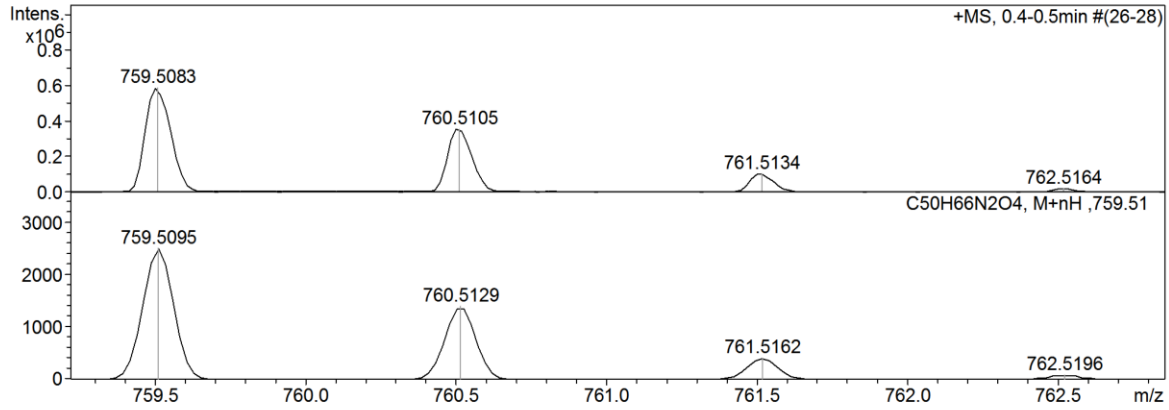
Acquisition Parameter

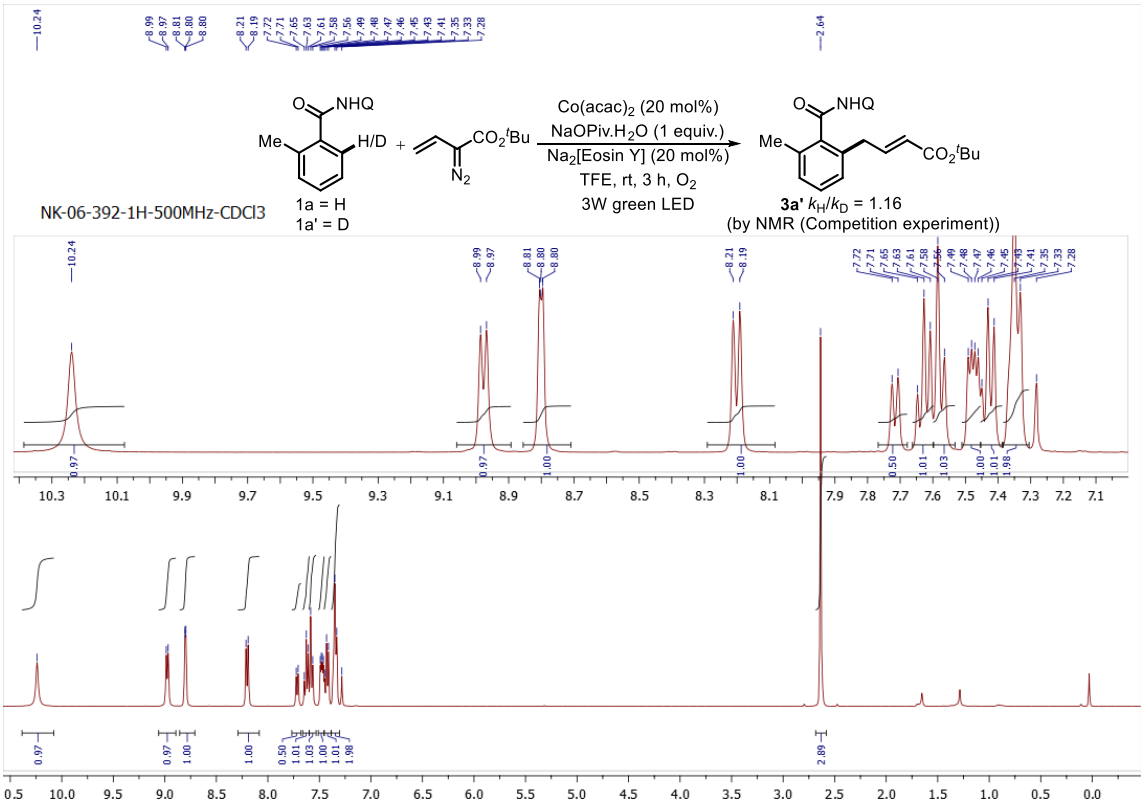
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

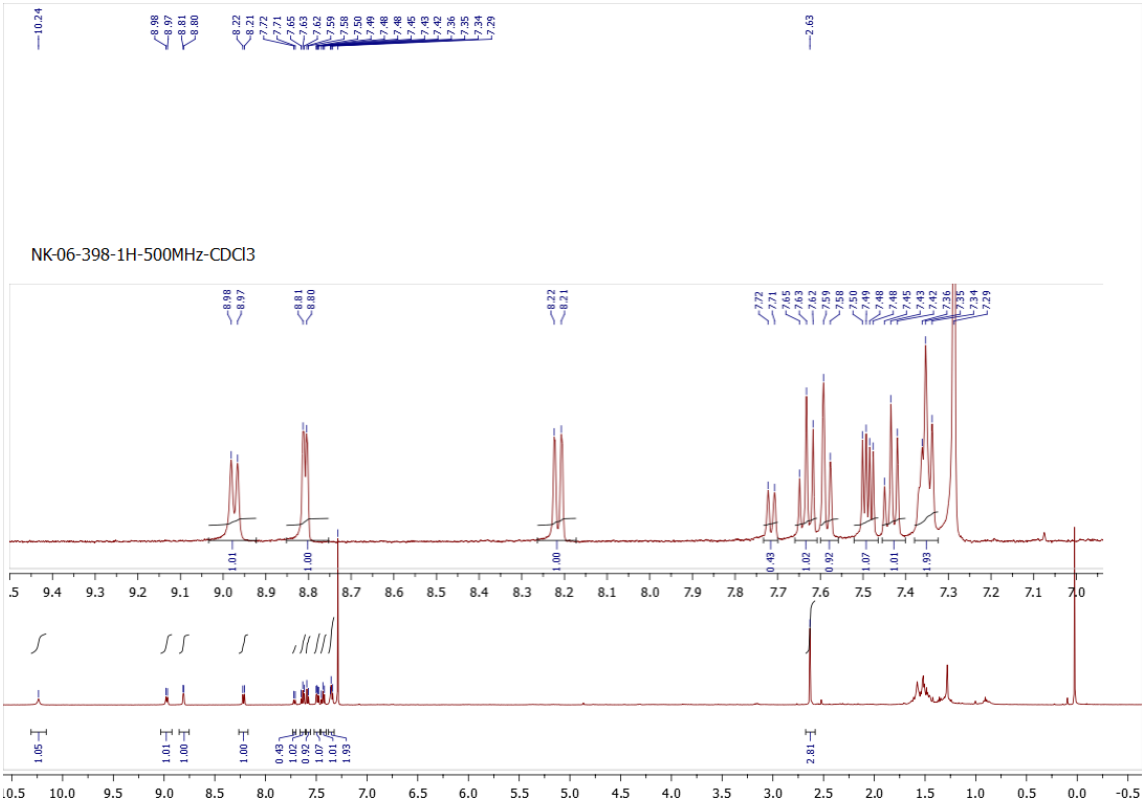


TIC +All MS






NHQ
Me
H/D
CO2tBu
N2
Co(acac)2 (20 mol%)
NaOPiv.H2O (1 equiv.)
Na2[Eosin Y] (20 mol%)
TFE, rt, 3 h, O2
3W green LED
1a = H
1a' = D
3a' kH/kD = 1.16
(by NMR (Competition experiment))
NK-06-392-1H-500MHz-CDCl3


NK-06-398-1H-500MHz-CDCl3

(7) ESI-HRMS for Cobaltacycle Intermediate (6a):

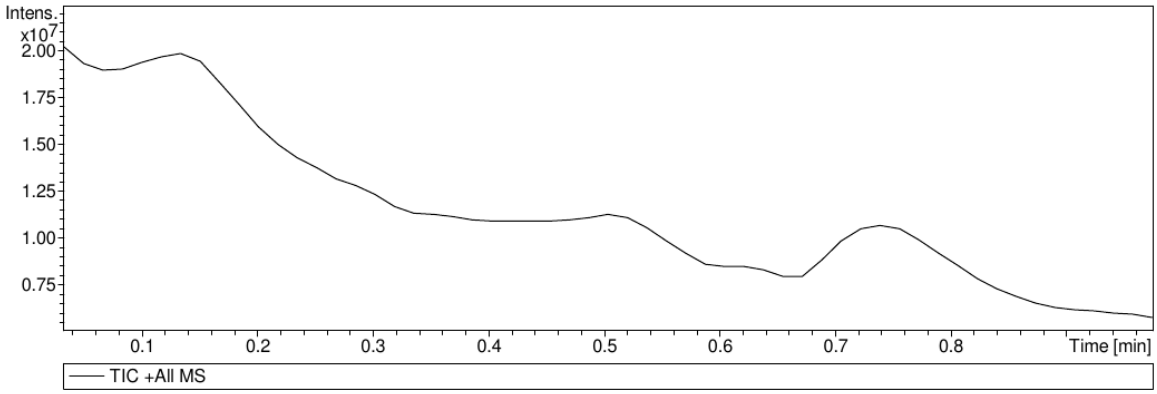
Display Report

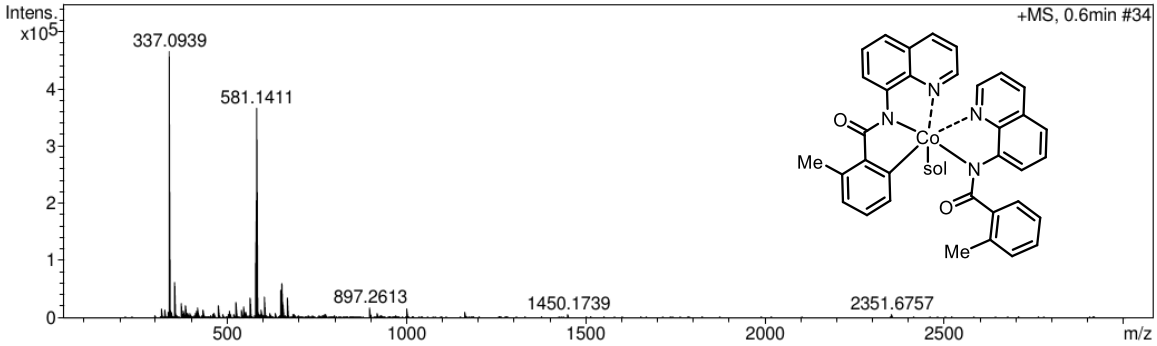
Analysis Info

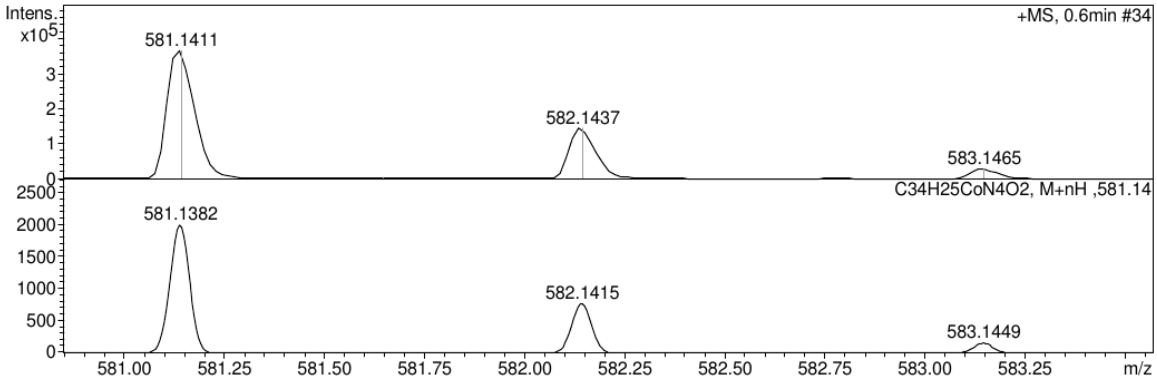
Acquisition Date	2/28/2022 2:46:25 PM		
Analysis Name	D:\Data\NEW USER DATA 2022\fe-2022\28-feb-2022\Prof.M.Kapur-ND-01-219.d		
Method	tune_wide.m	Operator	RUCHI
Sample Name	ND-01-219	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

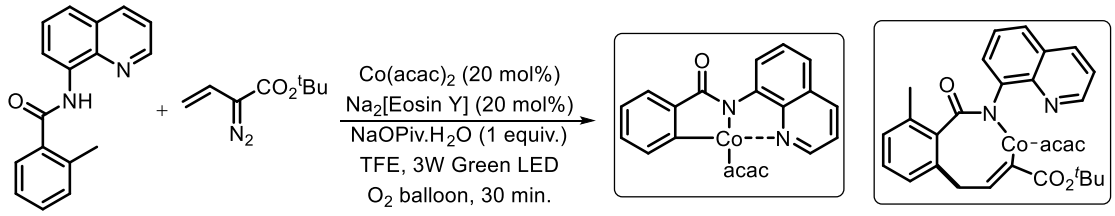
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source





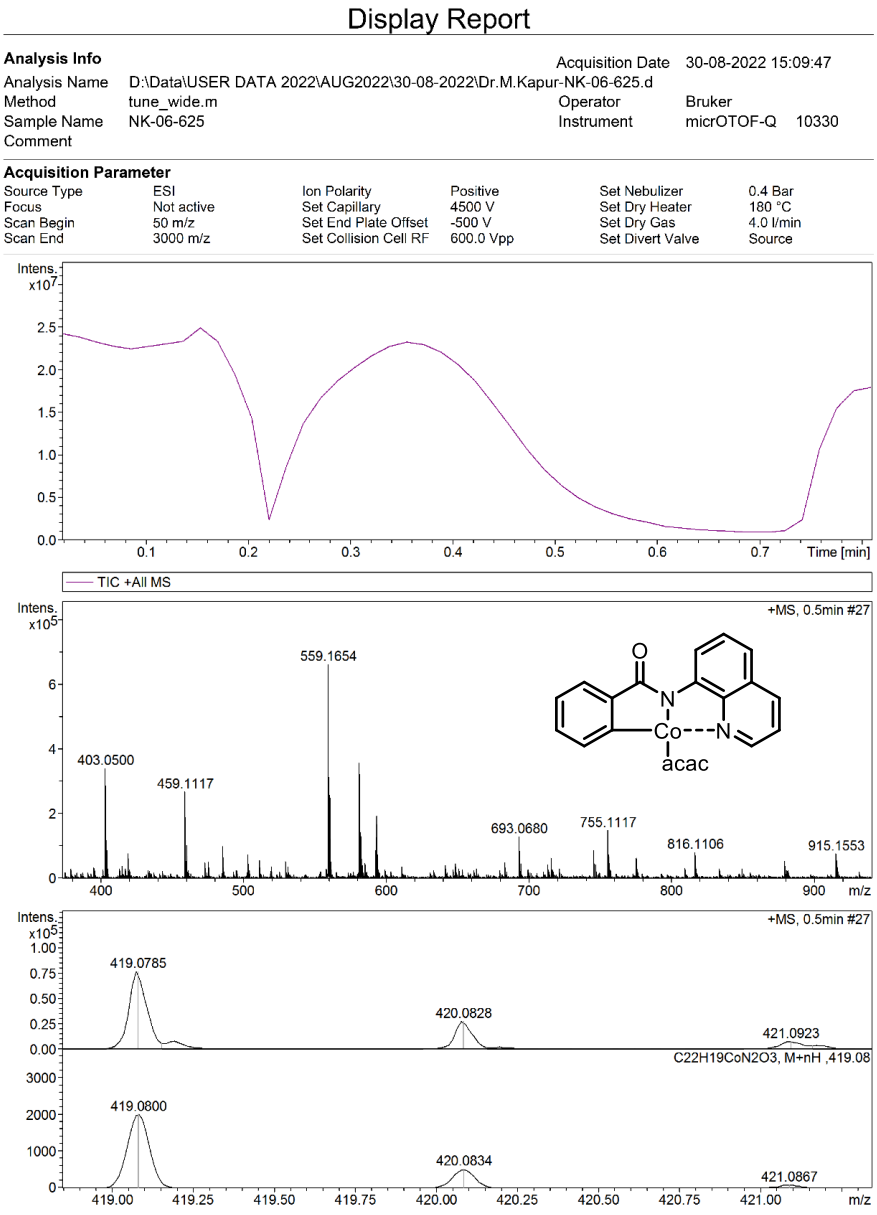


(8) Detection of intermediates by mass spectrometry



ESI-HRMS for C'
calcd. [M+H] 419.0800
found [M+H] 419.0785

ESI-HRMS for F
calcd. [M+H] 559.1638
found [M+H] 559.1645



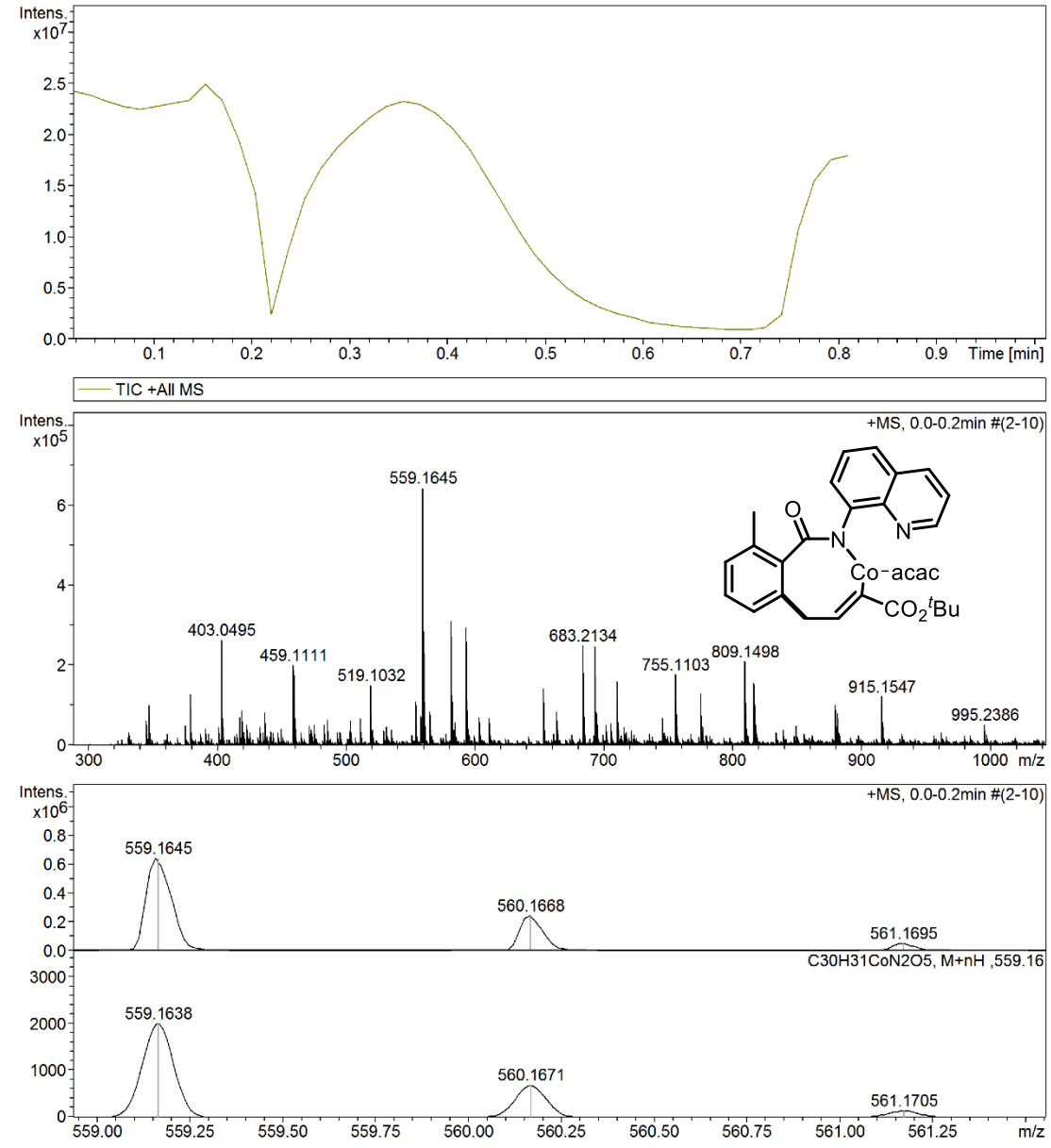
Display Report

Analysis Info

Analysis Name	D:\Data\USER DATA 2022\AUG2022\30-08-2022\Dr.M.Kapur-NK-06-625.d	Acquisition Date	30-08-2022 15:09:47
Method	tune_wide.m	Operator	Bruker
Sample Name	NK-06-625	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 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	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



(9) X-ray diffraction structural analysis data of 3j:

Sample Preparation: 5 mg of **3j** (white solid) was taken in a 10 mL beaker and dissolved in a minimum amount of chloroform. Hexane (3 mL) was added to the beaker along the wall. The beaker was capped loosely and kept at room temperature for slow evaporation. After 5 days single crystal was obtained which was subjected to X-ray diffraction.

Table S5: Crystal data and structure refinement for 3j.

Identification code	3j
Empirical formula	$C_{26}H_{28}N_2O_3$
Formula weight	416.52
Temperature/K	290.0
Crystal system	triclinic
Space group	P-1
a/Å	5.3986(8)
b/Å	11.9982(17)
c/Å	18.382(3)
α/°	104.537(6)
β/°	91.863(6)
γ/°	98.368(5)
Volume/Å^3	1137.3(3)
Z	2
ρ_{calc}g/cm^3	1.2162
μ/mm^{-1}	0.080
F(000)	444.2
Crystal size/mm^3	1 × 0.8 × 0.6
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.7 to 57.4

Index ranges	$-7 \leq h \leq 7, -16 \leq k \leq 16, -24 \leq l \leq 24$
Reflections collected	33092
Independent reflections	5871 [R_{int} = 0.0649, R_{sigma} = 0.0504]
Data/restraints/parameters	5871/0/285
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0538, wR_2 = 0.1303
Final R indexes [all data]	R_1 = 0.0910, wR_2 = 0.1558
Largest diff. peak/hole / e $Å^{-3}$	0.29/-0.27

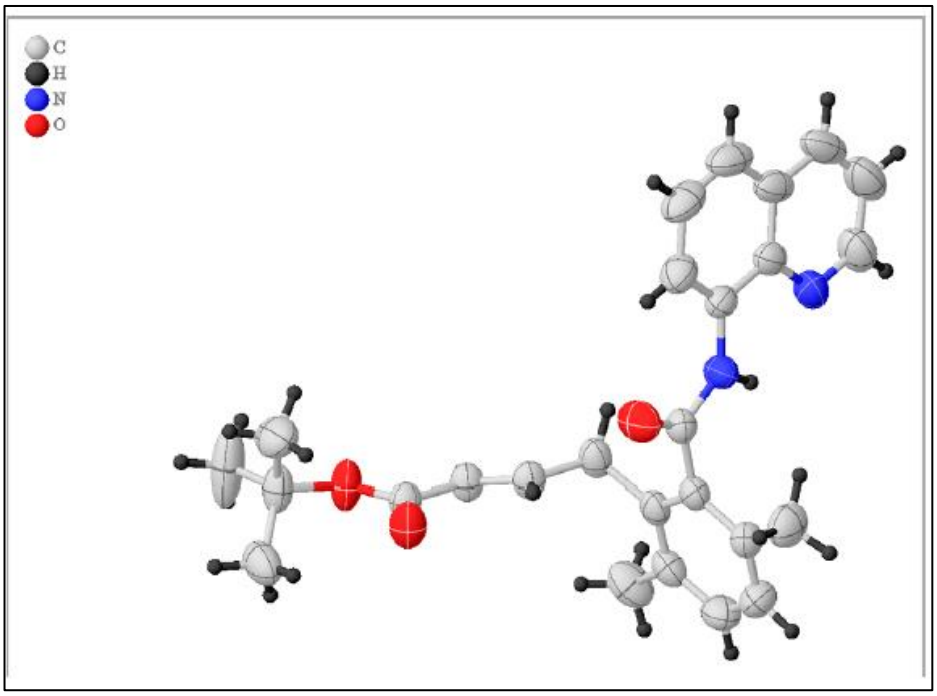


Fig. S1. X-ray structure of *tert*-butyl (*E*)-4-(3,6-dimethyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (**3j**) (*ORTEP* view at 50% ellipsoidal probability).