Supporting Information

Palladium-Catalyzed Distal γ– and ε–Benzylation, Allylation and Allenylation of Enones

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Experimental:

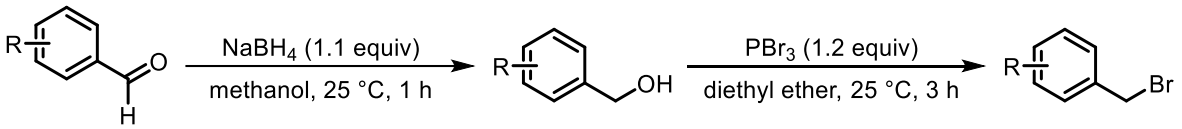
(1) General Methods:

All commercially available compounds were used without purification. Unless otherwise noted, all reactions were performed in oven-dried glassware. All reactions were run under 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 dichloromethane and dichloroethane were distilled from CaH_2. Petroleum ether with a boiling range of 40−60 °C was used. Melting points are uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR: Recorded on 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). IR: Perkin Elmer Spectrum BX FTIR, Shimadzu IRAffinity-1 FTIR and were recorded on an FT-IR Spectrometer System (PerkinElmer Spectrum Two) and are reported in the frequency of absorption (cm^{-1}). Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at different low temperatures for each crystal.

(1) Preparation of silylenol ethers: All silyldienol and silyltrienol ethers were prepared according to previously reported literature procedure.[1,2]

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

Scheme S1: General procedure (A) for the synthesis of benzyl bromide:[1]

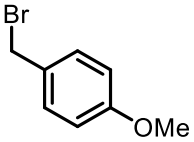


Procedure A: In an oven-dried round bottom flask equipped with a magnetic stir bar, the benzaldehyde (3.2 mmol, 1.0 equiv) was dissolved in methanol (20 mL) followed by the slow addition of $NaBH_4$ (4.8 mmol, 1.5 equiv) at 0 °C. The reaction mixture was stirred at room temperature for an hour. After completion of the reaction, it was quenched with ice-cold water and concentrated under reduced pressure. The resulting aqueous phase was extracted with EtOAc (2 x 10 mL). The combined organic extract was dried over anhyd. Na_2SO_4. Upon filtration and concentration under reduced pressure, the crude product was used as such without further purification.

Tribromophosphine (3.79 mmol, 1.2 equiv) was added dropwise to a stirred solution of the benzyl alcohol in dry DCM (15 mL) at 0 °C. The reaction mixture was stirred for 3 hours at room temperature (25 °C). After the completion, the reaction mixture was quenched with aq. $NaHCO_3$ and extracted with

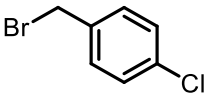
DCM (30 mL). The combined organic extract was dried over anhyd. Na_2SO_4 and filtered. After concentration under reduced pressure, the residue was good enough to be used for the next step without any purification.

1-(bromomethyl)-4-methoxybenzene (2c):[3]



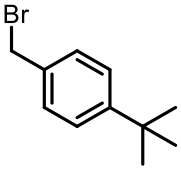
Reaction performed on 3.16 mmol scale (500 mg); Yield: 96% (696 mg); Physical appearance: Colorless gel; TLC R_f 0.3 (5:1 Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.7 Hz, 1H, merged with $CHCl_3$ peak), 6.89 (d, J = 8.7 Hz, 2H), 4.53 (s, 2H), 3.83 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.

1-(bromomethyl)-4-chlorobenzene (2d):[3]



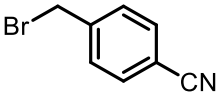
Reaction performed on 2.10 mmol scale (300 mg); Yield: 91% (393 mg); Physical appearance: Brown gel; TLC R_f 0.5 (5:1 Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 4.48 (s, 2H). Spectral data obtained were in good agreement with those reported in the literature.

1-(bromomethyl)-4-(tert-butyl)benzene (2e):[3]



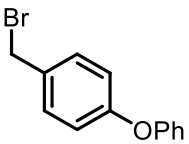
Reaction performed on 3.04 mmol scale (400 mg); Yield: 96% (661 mg); Physical appearance: Brown gel; TLC R_f 0.5 (5:1 Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 4H), 4.52 (s, 2H), 1.34 (s, 9H). Spectral data obtained were in good agreement with those reported in the literature.

4-(bromomethyl)benzonitrile (2f):[3]



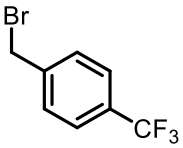
Reaction performed on 2.25 mmol scale (300 mg); Yield: 83% (367 mg); Physical appearance: Brown gel; TLC R_f 0.3 (5:1 Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 4.50 (s, 2H). Spectral data obtained were in good agreement with those reported in the literature.

1-(bromomethyl)-4-phenoxybenzene (2g):[3]



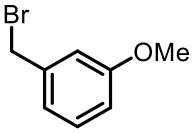
Reaction performed on 2.50 mmol scale (500 mg); Yield: 97% (449 mg); Physical appearance: Brown gel; TLC R_f 0.3 (5:1 Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.32 (t, J = 7.9 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.08 – 7.03 (m, 3H), 6.98 – 6.94 (m, 1H), 4.47 (s, 2H). Spectral data obtained were in good agreement with those reported in the literature.

1-(bromomethyl)-4-(trifluoromethyl)benzene (2h):[3]



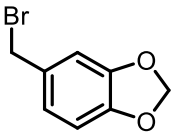
Reaction performed on 2.84 mmol scale (500 mg); Yield: 91% (613 mg); Physical appearance: colorless gel; TLC R_f 0.3 (5:1 Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 4.53 (s, 2H). Spectral data obtained were in good agreement with those reported in the literature.

1-(bromomethyl)-3-methoxybenzene (2i):[3]



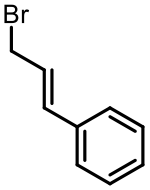
Reaction performed on 3.16 mmol scale (500 mg); Yield: 97% (701 mg); Physical appearance: Brown gel; TLC R_f 0.3 (5:1 Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.96 (t, J = 2.2 Hz, 1H), 6.87 (dd, J = 8.3, 2.3 Hz, 1H), 4.49 (s, 2H), 3.84 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.

5-(bromomethyl)benzo[d][1,3]dioxole (2j):[3]



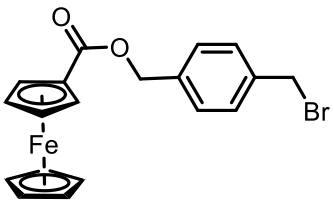
Reaction performed on 3.29 mmol scale (500 mg); Yield: 92% (650 mg); Physical appearance: Brown gel; TLC R_f 0.3 (5:1 Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.92 – 6.87 (m, 2H), 6.77 (d, J = 7.7 Hz, 1H), 5.99 (s, 2H), 4.48 (s, 2H). Spectral data obtained were in good agreement with those reported in the literature.

(*E*)-(3-bromoprop-1-en-1-yl)benzene (2k):[3]

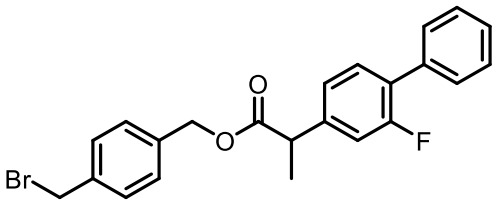


Reaction performed on 3.73 mmol scale (500 mg); Yield: 59% (434 mg); Physical appearance: Brown gel; TLC R_f 0.3 (5:1 Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.36 (d, J = 7.2 Hz, 2H), 7.31 (d, J = 7.2 Hz, 1H), 6.68 (d, J = 15.8 Hz, 1H), 6.48 – 6.38 (m, 1H), 4.19 (d, J = 7.8 Hz, 2H). Spectral data obtained were in good agreement with those reported in the literature.

Compound (2l): Reaction performed on 0.87 mmol scale (200 mg); Yield: 64% (230 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 4H), 5.28 (s, 2H), 4.85 (t, J = 1.8 Hz, 2H), 4.52 (s, 2H), 4.43 (t, J = 1.8 Hz, 2H), 4.14 (s, 5H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.50, 137.78, 136.93, 129.26, 128.81, 128.64, 128.59, 71.47, 70.89, 70.24, 69.76, 65.35; **HRMS** (ESI-ToF) *m/z*: [M] Calcd. for $C_{19}H_{17}BrFeO_2$ 411.9758 and 413.9736; Found 411.9752 and 413.9747; **IR** (Thin Film, neat, cm^{-1}): 3091, 2921, 2875, 1720, 1341, 1268, 1157, 1102, 1086, 992, 739, 602.

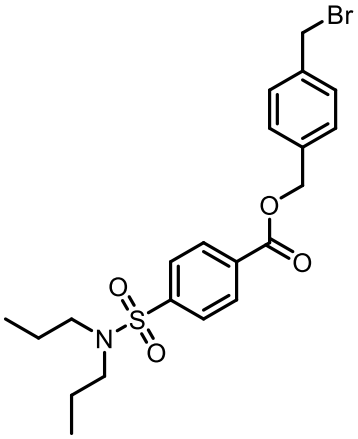


3-(4-nitrophenethyl)cyclohex-2-en-1-one (2m):[4a]



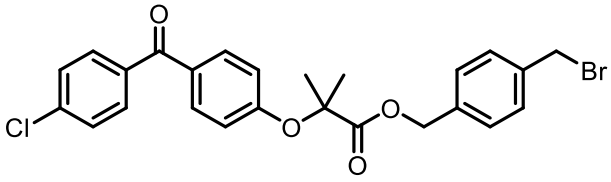
Reaction performed on 0.81 mmol scale (200 mg); Yield: 46% (160 mg); Physical appearance: colorless solid; M.p. 72–74 °C; TLC R_f 0.4 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.50 – 7.42 (m, 2H), 7.42 – 7.36 (m, 4H), 7.26 (s, 2H), 7.18 – 7.10 (m, 2H), 5.16 (dd, J = 12.5 Hz, 2H), 4.50 (s, 2H), 3.83 (q, J = 7.2 Hz, 1H), 1.57 (d, J = 7.1 Hz, 3H, merged with H_2O); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.70, 141.52, 137.79, 136.09, 135.47, 130.80, 129.22, 128.95 (d, $J_{C\text{-}F}$ = 2.98 Hz), 128.42 (d, $J_{C\text{-}F}$ = 9.54 Hz), 127.82, 127.69, 123.58 (d, $J_{C\text{-}F}$ = 3.24 Hz), 115.27 (d, $J_{C\text{-}F}$ = 23.74 Hz), 99.99, 66.17, 45.03, 32.97, 18.31; **^{19}F NMR** (471 MHz, $CDCl_3$) –117.41; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{23}H_{20}BrFO_2$ 449.0523 and 451.0504; Found 449.0509 and 451.0496; **IR** (Thin Film, neat, cm^{-1}): 2926, 2821, 1701, 1641, 1322, 1317, 1160, 1128, 1037, 1016, 807, 821.

4-(bromomethyl)benzyl 4-(*N*,*N*-dipropylsulfamoyl)cyclohexa-1,5-diene-1-carboxylate (2n):[4b]



Reaction performed on 0.70 mmol scale (200 mg); Yield: 43% (141 mg); Physical appearance: colorless solid; M.p. 92–94 °C, TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.45 (s, 4H), 5.40 (s, 2H), 4.53 (s, 2H), 3.16 – 3.05 (m, 4H), 1.65 – 1.49 (m, 4H), 0.89 (t, J = 7.4 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.03, 144.46, 138.16, 135.75, 133.27, 130.34, 129.39, 128.81, 127.04, 66.81, 49.91, 32.88, 21.92, 11.16; **HRMS** (ESI-ToF) *m/z*: $[M-H]^+$ Calcd. for $C_{21}H_{28}BrNO_4S$ 468.0839 and 470.0819; Found 468.0830 and 470.0842; **IR** (Thin Film, neat, cm^{-1}): 2965, 2933, 2875, 1720, 1341, 1268, 1157, 1102, 1086, 992, 739, 602.

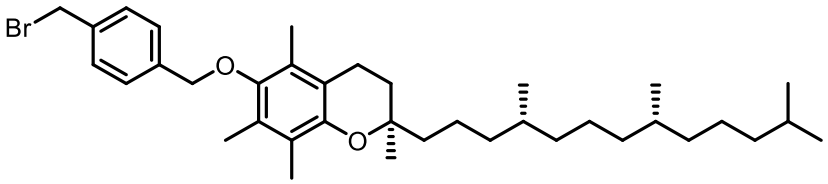
4-(bromomethyl)benzyl-2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (2o):[4b]



Reaction performed on 0.33 mmol scale (100 mg); Yield: 57% (92 mg); Physical appearance: colorless solid, M.p. 75–77 °C ; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.9 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 5.20 (s, 2H), 4.46 (s, 2H), 1.70 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.57, 194.17, 173.49, 159.53, 153.41, 139.41, 138.47, 136.33, 133.39,

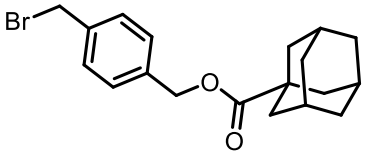
131.96, 131.18, 130.35, 129.43, 129.24, 128.79, 128.58, 117.30, 79.45, 67.11, 40.55, 37.83, 36.74, 28.60, 25.45, 25.42; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{55}H_{22}BrClO_4$ 525.0262 and 527.0247; Found 525.0237 and 527.0309; **IR** (Thin Film, neat, cm^{-1}): 2923, 2864, 1457, 1410, 1372, 1255, 1157, 1017, 814.

4-(bromomethyl)benzyl 4-(*N*,*N*-dipropylsulfamoyl)cyclohexa-1,5-diene-1-carboxylate (2p):[4b]



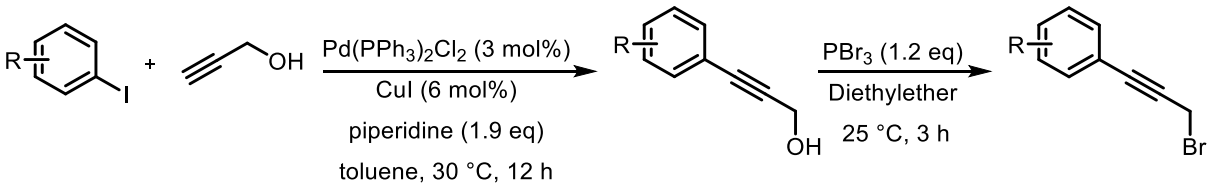
Reaction performed on 0.46 mmol scale (200 mg); Yield: 57% (163 mg); Physical appearance: colorless solid, M.p. 84–86 °C; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 4.71 (s, 2H), 4.55 (s, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.23 (s, 3H), 2.18 (s, 3H), 2.13 (s, 3H), 1.91 – 1.74 (m, 2H), 1.60 – 1.54 (m, 6H), 1.45 – 1.35 (m, 4H), 1.32 – 1.26 (m, 10H), 1.19 – 1.06 (m, 6H), 0.91 – 0.84 (m, 13H). Spectral data obtained were in good agreement with those reported in the literature.

4-(bromomethyl)benzyl (3r,5r,7r)-adamantane-1-carboxylate (2q):[4b]



Reaction performed on 1.1 mmol scale (200 mg); Yield: 74% (301 mg); Physical appearance: colorless solid, M.p. 62–64 °C; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.11 (s, 2H), 4.52 (s, 2H), 2.08 – 2.01 (m, 5H), 1.94 (s, 3H), 1.76 – 1.73 (m, 7H). Spectral data obtained were in good agreement with those reported in the literature.

Scheme S2: General procedure (B) for the synthesis of propargyl bromides:[6]

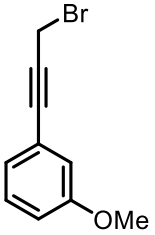


Procedure B: To a solution of the iodobenzene (4.90 mmol, 1.0 equiv) in toluene (1 mL/mmol), $Pd(PPh_3)_2Cl_2$ (0.14 mmol, 0.03 equiv), CuI (0.29 mmol, 0.06 equiv) and piperidine (9.36 mmol, 1.91 equiv) were added. This was followed by a dropwise addition of the propargyl alcohol (5.0 mmol, 1.02 equiv) (Caution: exothermic reaction). The reaction mixture turned brown and was then stirred at room temperature (25 °C) for overnight. Then, the reaction mixture was filtered through Celite and washed with Et_2O. The solvent was evaporated under reduced pressure giving an oily mixture, which was

purified by silica gel flash column chromatography. Analytical data of the propargyl alcohols (**4a**–**4f)** matched well with that reported in the literature.

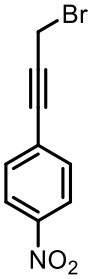
Tribromophosphine (1.2 equiv) was added dropwise to a stirred solution of the propargylic alcohol in freshly distilled DCM (15 ml) at 0 °C. The reaction mixture was stirred for 3 hours at room temperature (25 °C). After the completion, the reaction mixture was carefully quenched with aq. $NaHCO_3$ and extracted with DCM (30 mL). The combined organic extract was dried over anhyd. Na_2SO_4 and filtered. After concentration under reduced pressure, the crude product was used as it is without further purification.

1-(3-bromoprop-1-yn-1-yl)-3-methoxybenzene (4a):[6]



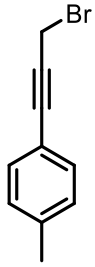
Reaction performed on 1.85 mmol scale (300 mg); Yield: 49% (205 mg); Physical appearance: colorless gel; TLC R_f 0.3 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 8.0 Hz, 1H), 7.08 – 7.04 (m, 1H), 7.01 - 6.98 (m, 1H), 6.94 – 6.90 (m, 1H), 4.18 (s, 2H), 3.82 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.

1-(3-bromoprop-1-yn-1-yl)-4-nitrobenzene (4b):[6]



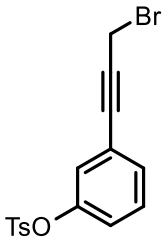
Reaction performed on 1.69 mmol scale (300 mg); Yield: 50% (301 mg); Physical appearance: colorless gel; TLC R_f 0.3 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 4.56 (s, 2H). Spectral data obtained were in good agreement with those reported in the literature.

1-(3-bromoprop-1-yn-1-yl)-4-methylbenzene (4c):[6]



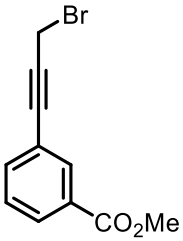
Reaction performed on 2.74 mmol scale (400 mg); Yield: 55% (235 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 4.19 (s, 2H), 2.38 (s, 2H). Spectral data obtained were in good agreement with those reported in the literature.

3-(3-bromoprop-1-yn-1-yl)phenyl 4-methylbenzenesulfonate (4d):[6]



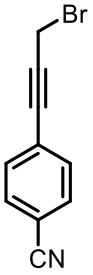
Reaction performed on 0.99 mmol scale (300 mg); Yield: 51% (122 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.7 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.25 (t, J = 7.8 Hz, 1H), 7.12 (t, J = 1.8 Hz, 1H), 6.98 (dd, J = 8.2, 2.1 Hz, 1H), 4.14 (s, 2H), 2.48 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.

methyl 3-(3-bromoprop-1-yn-1-yl)benzoate (4e):[6]



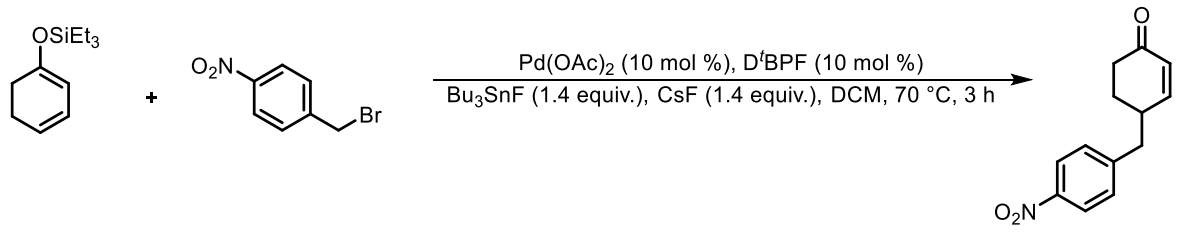
Reaction performed on 1.58 mmol scale (300 mg); Yield: 64% (197 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.9, 1.4 Hz, 1H), 7.57 (dd, J = 7.9, 1.4 Hz, 1H), 7.49 (td, J = 7.5, 1.4 Hz, 1H), 7.40 (td, J = 7.5, 1.4 Hz, 1H), 4.57 (s, 2H), 3.94 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.

4-(3-bromoprop-1-yn-1-yl)benzonitrile (4f):[6]



Reaction performed on 1.91 mmol scale (300 mg); Yield: 63% (265 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 4.17 (s, 2H), 1.58 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.

(2) Scheme S3: Optimization studies for the γ-alkylation of silyldienol ethers:

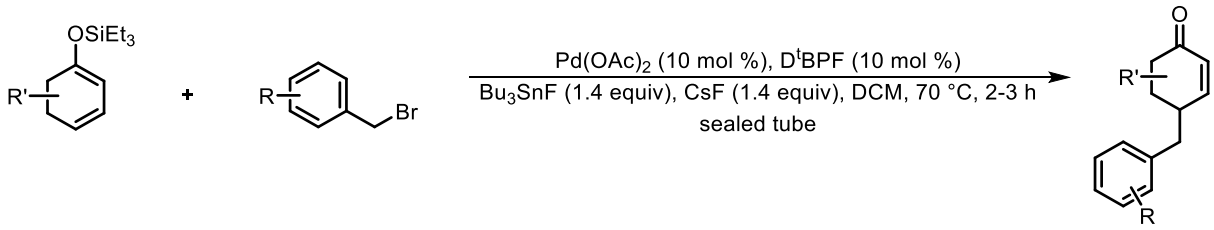


Sr. No.	Deviation from standard condition	Yield
1.	None	75%
2.	[Pd(Cl)$_2$], D^{t}BPF	14%
3.	[Pd(TFA)$_2$], D^{t}BPF	19%
4.	[Pd(OPiv)$_2$], D^{t}BPF	<5%
5.	[Pd(acac)$_2$], D^{t}BPF	<5%

6.	[$Pd(CH_3CN)_2Cl_2$], D^{t}BPF	18%
7.	[$Pd(PPh_3)_4$]	Trace
8.	Only Bu_3SnF (2.8 equiv)	0%
9.	Only CsF (2.8 equiv)	0%
10.	Only ZnF_2 (2 equiv)	0%
11.	Only AgF (2 equiv)	0%
12.	Only TBAF (2 equiv)	0%
13.	(*R*)-BINAP as a ligand	0%
14.	dppp as a ligand	<10%
15.	PPh_3 (20 mol%) as a ligand	37%
16.	Toluene as the solvent	Trace
17.	THF as the solvent	0%
18.	DCE as the solvent	Trace
19.	DMF as the solvent	0%
20.	at 50 °C	<5%
21.	at 90 °C	Trace
22.	With benzyl chloride as a benzyl source	58%

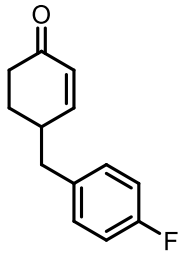
(4) General procedures and analytical data of the γ- alkylation of di- and trienones:

Scheme S4: Procedure for the γ- alkylation of silyldi- and trienol ethers:



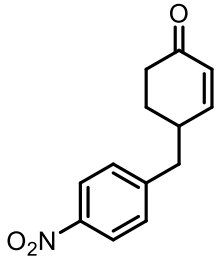
In a pressure tube equipped with a magnetic stir bar, the silyldienol ether (0.41 mmol, 2.8 equiv) and benzyl bromide (0.15 mmol, 1 equiv) were dissolved in dry DCM (2 mL) and the solution was degassed for 10 min with argon. The tube was sealed and moved into a glovebox. This was followed by the addition of $Pd(OAc)_2$ (3.3 mg, 0.015 mmol, 0.1 equiv), D^{t}BPF (7.8 mg, 0.015 mmol, 0.1 equiv), CsF (31 mg, 0.21 mmol, 1.4 equiv) and Bu_3SnF (64 mg, 0.21 mmol, 1.4 equiv). The tube was fitted tightly with a Teflon screw cap and moved out of the glovebox. The reaction mixture was heated to 70 ^{o}C in an oil bath and maintained at that temperature for 3 hours. Upon cooling to room temperature, the reaction mixture was diluted with about 20 mL of DCM, and the resulting slurry was filtered through a pad of Celite, eluting with DCM. The filtrate was washed successively with 1 M NaOH and water. The combined organic extract was dried over anhyd. Na_2SO_4 and filtered. Upon concentration under reduced pressure, the crude product was purified by silica gel flash column chromatography.

4-(4-fluorobenzyl)cyclohex-2-en-1-one (3a):



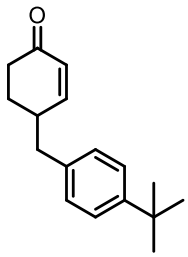
Reaction performed on 0.20 mmol scale (40 mg); Yield: 93% (40 mg); Physical appearance: colorless gel; TLC R_f 0.5 (9:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) 7.22 – 7.15 (m, 2H), 7.07 – 7.00 (m, 2H), 6.84 (d, J = 10.3 Hz, 2H), 6.02 (d, J = 10.3 Hz, 2H), 2.84 – 2.77 (m, 1H), 2.76 - 2.65 (m, 2H), 2.58 – 2.47 (m, 1H), 2.43 – 2.31 (m, 1H), 2.12 – 2.03 (m, 1H), 1.79 – 1.67 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.53, 161.59 (d, $J_{C\text{-}F}$ = 245.33 Hz), 153.36, 134.5 (d, $J_{C\text{-}F}$ = 3.22 Hz), 130.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 129.46, 115.4 (d, $J_{C\text{-}F}$ = 21.2 Hz), 40.10, 38.02, 36.76, 28.55; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –116.48; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{13}FO$ 205.1023; Found 205.1032; **IR** (Thin Film, neat, cm^{-1}): 2925, 1663, 1625, 1508, 1157, 1219, 885, 832, 531.

4-(4-nitrobenzyl)cyclohex-2-en-1-one (3b):



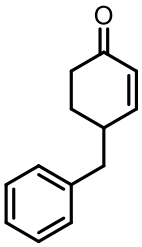
Reaction performed on 0.093 mmol scale (20 mg); Yield: 75% (16 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.23 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 6.83 – 6.79 (m, 1H), 6.07 – 6.03 (m, 1H), 2.99 – 293 (m, 1H), 2.89 – 2.84 (m, 1H), 2.83 – 2.76 (m, 1H), 2.58 – 2.51 (m, 1H), 2.43 – 2.35 (m, 1H), 2.12 – 2.05 (m, 1H), 1.81 – 1.72 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.96, 152.19, 146.66, 129.94, 129.88, 123.92, 40.74, 37.59, 36.63, 28.57; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{13}NO_3$ 232.0968; Found 232.0942; **IR** (Thin Film, neat, cm^{-1}): 2981, 2911, 1732, 1612, 1587, 1517, 1463, 1356, 1219, 1040,769.

4-(4-(tert-butyl)benzyl)cyclohex-2-en-1-one (3c):



Reaction performed on 0.18 mmol scale (40 mg); Yield: 65% (27 mg); Physical appearance: colorless gel; TLC R_f 0.5 (9:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.89 (dt, J = 10.0, 1.8 Hz, 1H), 6.01 (dd, J = 10.4, 1.03 Hz, 1H), 2.80 – 2.69 (m, 3H), 2.58 – 2.48 (m, 1H), 2.43 – 2.32 (m, 1H), 2.14 – 2.05 (m, 1H), 1.82 – 1.69 (m, 1H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.87, 154.11, 149.41, 135.85, 129.20, 128.71, 125.46, 40.38, 38.01, 36.85, 34.44, 31.38, 28.70; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{22}O$ 243.1743; Found 243.1725; **IR** (Thin Film, neat, cm^{-1}): 2958, 1920, 1864, 1680, 1510, 1461, 1388, 1109, 853.

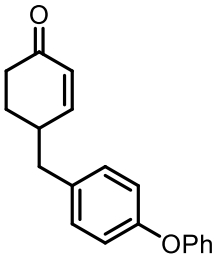
4-benzylcyclohex-2-en-1-one (3d):



Reaction performed on 0.12 mmol scale (20 mg, Benzyl bromide); Yield: 64% (19 mg); Physical appearance: brown gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.1 Hz, 2H), 6.87 (d, *J* = 10.0 Hz, 1H), 6.01 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.87 – 2.70 (m, 3H), 2.53 (dt, *J* = 16.8, 4.8 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.13 – 2.05 (m, 1H), 1.80 – 1.71 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.72, 153.79, 138.96, 129.32, 129.05, 128.61, 126.55, 40.93, 38.00, 36.81, 28.65; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{14}O$ 186.1117; Found 186.1134; **IR** (Thin Film, neat, cm^{-1}): 2961, 2920, 1653, 1619, 1577, 1507, 1363, 1326, 1215, 1030,769.

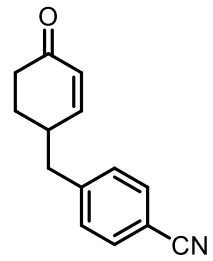
Reaction performed on 0.16 mmol scale (20 mg, Benzyl chloride); Yield: 58% (17 mg)

4-(4-phenoxybenzyl)cyclohex-2-en-1-one (3e):



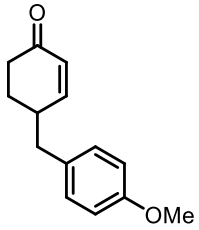
Reaction performed on 0.76 mmol scale (20 mg); Yield: 61% (13 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.07 – 7.00 (m, 2H), 6.96 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.92 – 6.88 (m, 2H), 6.87 – 6.83 (m, 1H), 6.03 – 5.99 (m, 1H), 2.84 – 2.76 (m, 1H), 2.76 – 2.68 (m, 2H), 2.56 – 2.48 (m, 1H), 2.42 – 2.32 (m, 1H), 2.13 – 2.05 (m, 1H), 1.79 – 1.69 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.60, 157.54, 157.07, 153.50, 141.01, 129.85, 129.80, 129.43, 123.92, 123.38, 119.38, 118.94, 116.88, 40.74, 37.83, 36.79, 28.61; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{19}H_{18}O_2$ 279.1380; Found 279.1358; **IR** (Thin Film, neat, cm^{-1}): 3031, 2921, 1675, 1581, 1485, 1247, 1212, 1162, 1143, 758, 692.

4-((4-oxocyclohex-2-en-1-yl)methyl)benzonitrile (3f):



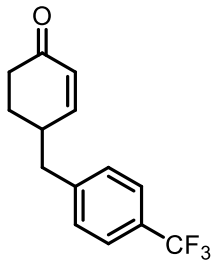
Reaction performed on 0.15 mmol scale (30 mg); Yield: 59% (19 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 9.6 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 1H), 2.96 – 2.85 (m, 1H), 2.84 – 2.72 (m, 2H), 2.59 – 2.17 (m, 1H), 2.43 – 2.33 (m, 1H), 2.13 – 2.00 (m, 1H), 1.82 – 1.69 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.04, 152.39, 144.54, 132.44, 129.83, 118.73, 110.65, 40.98, 37.54, 36.63, 28.55; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{13}NO$ 212.1070; Found 212.1057; **IR** (Thin Film, neat, cm^{-1}): 2918, 1677, 1322, 1160, 1107, 1066, 1018, 855, 821.

4-(4-methoxybenzyl)cyclohex-2-en-1-one (3g):



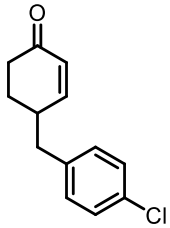
Reaction performed on 0.20 mmol scale (40 mg); Yield: 58% (25 mg); Physical appearance: Brown gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.13 (d, J = 8.6 Hz, 2H), 6.92 – 6.83 (m, 3H), 6.01 (dd, J = 10.1, 1.3 Hz, 1H), 3.83 (s, 3H), 2.80 – 2.65 (m, 3H), 2.57 - 2.46 (m, 1H), 2.41 – 2.31 (m, 1H), 2.13 – 2.03 (m, 1H), 1.81 – 1.67 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.78, 158.27, 153.94, 130.95, 129.97, 129.25, 113.98, 55.29, 40.04, 38.18, 36.83, 28.60; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{16}O_2$ 217.1223; Found 217.1227; **IR** (Thin Film, neat, cm^{-1}): 2918, 1850, 1674, 1511, 1244, 1177, 848, 563.

4-(4-(trifluoromethyl)benzyl)cyclohex-2-en-1-one (3h):



Reaction performed on 0.17 mmol scale (40 mg); Yield: 54% (23 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.85 – 6.80 (m, 1H), 6.06 – 6.01 (m, 1H), 2.93 – 2.86 (m, 1H), 2.84 – 2.79 (m, 1H), 2.79 – 2.73 (m, 1H), 2.53 (dt, J = 16.8, 4.8 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.12 – 2.04 (m, 1H), 1.80 – 1.70 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.27, 152.83, 143.06, 129.67, 129.37, 129.02 (d, $J_{C\text{-}F}$ = 32.77 Hz), 125.57 (q, $J_{C\text{-}F}$ = 4.37 Hz), 124.09 (d, $J_{C\text{-}F}$ = 271.00 Hz), 40.71, 37.71, 36.70, 28.58; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –62.43; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{13}F_3O$ 255.0991; Found 255.1002; **IR** (Thin Film, neat, cm^{-1}): 2924, 2858, 1677, 1322, 1161, 1108, 1018, 855, 637.

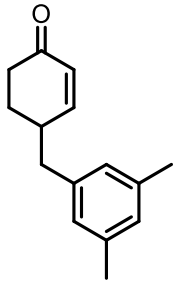
4-(4-chlorobenzyl)cyclohex-2-en-1-one (3i):



Reaction performed on 0.19 mmol scale (40 mg); Yield: 49% (27 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 10.1 Hz, 1H), 6.01 (d, J = 10.1 Hz, 1H), 2.84 – 2.67 (m, 3H), 2.57 – 2.47 (m, 1H), 2.42 – 2.30 (m, 1H), 2.12 – 2.03 (m, 1H), 1.79 – 1.66 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.45, 153.21, 137.38, 132.40, 130.36, 129.52, 128.75, 40.25, 37.85, 36.73, 28.55; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{13}ClO$ 221.0728; Found 221.0720; **IR** (Thin Film, neat, cm^{-1}): 2923, 1849, 1656, 1501, 1234, 1169, 845, 561.

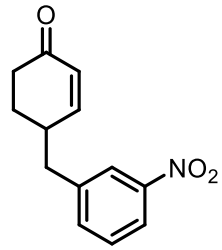
Reaction performed on 0.12 mmol scale (20 mg, 4-chlorobenzyl chloride); Yield: 40% (11 mg).

4-(3,5-dimethylbenzyl)cyclohex-2-en-1-one (3j):



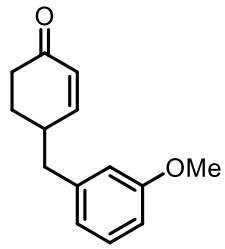
Reaction performed on 0.20 mmol scale (40 mg); Yield: 93% (40 mg); Physical appearance: colorless gel; TLC R_f 0.5 (9:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.91 (s, 1H), 6.90 – 6.86 (m, 1H), 6.84 (s, 2H), 6.01 (dd, *J* = 10.2, 1.4 Hz, 1H), 2.76 – 2.63 (m, 3H), 2.53 (dt, *J* = 16.8, 4.1 Hz, 1H), 2.43 – 2.36 (m, 1H), 2.34 (s, 6H), 2.15 – 2.03 (m, 1H), 1.85 – 1.68 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.82, 154.11, 138.88, 138.06, 129.16, 128.13, 126.87, 40.78, 38.02, 36.88, 28.76, 21.30; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{18}O$ 215.1430; Found 215.1417; **IR** (Thin Film, neat, cm^{-1}): 3014, 2916, 2859, 1673, 1604, 1387, 1450, 1208, 850, 702.

4-(3-nitrobenzyl)cyclohex-2-en-1-one (3k):



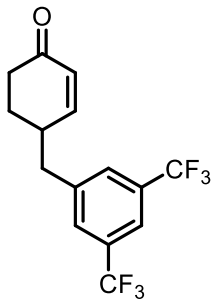
Reaction performed on 0.20 mmol scale (40 mg); Yield: 51% (22 mg); Physical appearance: colorless gel; TLC R_f 0.5 (4:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.5 Hz, 1H), 8.12 (s, 1H), 7.59 – 7.50 (m, 2H), 6.82 (d, *J* = 10.4 Hz, 1H), 6.06 (d, *J* = 10.4 Hz, 1H), 3.01 – 2.92 (m, 1H), 2.91 – 2.76 (m, 2H), 2.60 – 2.50 (m, 1H), 2.46 – 2.34 (m, 1H), 2.15 – 2.05 (m, 1H), 1.84 – 1.73 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.04, 152.22, 140.97, 135.24, 129.95, 129.60, 123.80, 121.86, 40.52, 37.63, 36.65, 28.53; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{13}NO_3$ 232.0968; Found 232.0966; **IR** (Thin Film, neat, cm^{-1}): 2961, 2901, 1715, 1602, 1577, 1501, 1421, 1354, 1209, 1011,769.

4-(3-methoxybenzyl)cyclohex-2-en-1-one (3l):



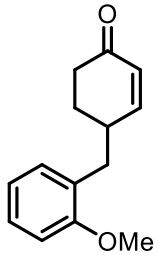
Reaction performed on 0.20 mmol scale (40 mg); Yield: 33% (14.5 mg); Physical appearance: colorless gel; TLC R_f 0.5 (4:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 6.87 (d, *J* = 10.2 Hz, 1H), 6.83-6.87 (m, 2H), 6.76 (s, 1H), 6.00 (d, *J* = 10.2 Hz, 1H), 3.83 (s, 3H), 2.80 – 2.67 (m, 3H), 2.59 – 2.40 (m, 1H), 2.42 – 2.29 (m, 1H), 2.14 – 2.02 (m, 1H), 1.79 – 1.69 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.69, 159.78, 153.79, 140.56, 129.58, 129.28, 121.41, 115.00, 111.56, 55.19, 40.93, 37.90, 36.82, 28.67; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{16}O_2$ 217.2223; Found 217.2222; **IR** (Thin Film, neat, cm^{-1}): 2923, 1849, 1656, 1501, 1234, 1169, 845, 561.

4-(3,5-bis(trifluoromethyl)benzyl)cyclohex-2-en-1-one (3m):



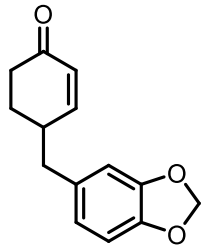
Reaction performed on 0.098 mmol scale (30 mg); Yield: 37% (12 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.69 (s, 2H), 6.83 – 6.76 (m, 1H), 6.07 (dd, J = 10.2, 2.2 Hz, 1H), 3.05 – 2.95 (m, 1H), 2.93 – 2.85 (m, 1H), 2.85 – 2.77 (m, 1H), 2.60 – 2.50 (m, 1H), 2.46 – 2.36 (m, 1H), 2.14 – 2.05 (m, 1H), 1.83 – 1.72 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.82, 151.73, 141.41, 132.0 (d, $J_{C\text{-}F}$ = 34.8 Hz), 130.10, 129.09, 123.17 (d, $J_{C\text{-}F}$ = 273.89 Hz), 120.84 (q, $J_{C\text{-}F}$ = 4.03 Hz), 40.60, 37.54, 36.60, 28.55; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –62.85; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{12}F_6O$ 323.0865; Found 323.0889; **IR** (Thin Film, neat, cm^{-1}): 2956, 2924, 2855, 1681, 1382, 1277, 1106, 988, 532.

4-(2-methoxybenzyl)cyclohex-2-en-1-one (3n):



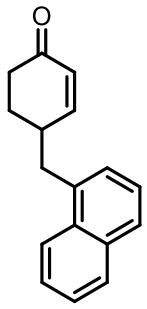
Reaction performed on 0.20 mmol scale (40 mg); Yield: 26% (11 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (dt, J = 7.4, 1.7 Hz, 1H, merged with $CHCl_3$), 7.14 (dd, J = 7.4, 1.7 Hz, 1H), 6.97 – 6.86 (m, 3H), 5.99 (dd, J = 10.3, 1.9 Hz, 1H), 3.86 (s, 3H), 2.86 – 2.73 (m, 3H), 2.58 – 2.49 (m, 1H), 2.41 – 2.30 (m, 1H), 2.11 – 2.00 (m, 1H), 1.81 – 1.68 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.12, 157.62, 154.84, 130.92, 128.85, 127.88, 127.37, 120.41, 110.45, 55.23, 36.92, 36.42, 35.42, 28.74; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{16}O_2$ 217.1223; Found 217.1220; **IR** (Thin Film, neat, cm^{-1}): 2917, 2836, 1672, 1493, 1463, 1242, 1110, 1026, 752.

4-(benzo[*d*][1,3]dioxol-5-ylmethyl)cyclohex-2-en-1-one (3o):



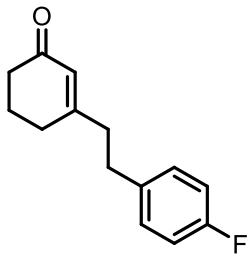
Reaction performed on 0.093 mmol scale (20 mg); Yield: 75% (16 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.88 – 6.83 (m, 1H), 6.78 (d, J = 7.8 Hz, 1H), 6.70 (s, 1H), 6.66 (dd, J = 7.9, 1.7 Hz, 1H), 6.00 (d, J = 10.3 Hz, 1H), 5.97 (s, 2H), 2.76 – 2.62 (m, 3H), 2.56- 2.48 (m, 1H), 2.41 – 2.31 (m, 1H), 2.13 – 2.02 (m, 1H), 1.79 – 1.67 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.70, 153.69, 147.80, 146.19, 132.66, 129.32, 121.99, 109.24, 108.29, 100.96, 40.64, 38.15, 36.80, 28.56; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{14}O_3$ 231.1016; Found 231.1022; **IR** (Thin Film, neat, cm^{-1}): 2919, 1674, 1502, 1488, 1441, 1244, 1207, 1189, 1036, 923, 808.

4-(naphthalen-1-ylmethyl)cyclohex-2-en-1-one (3p):



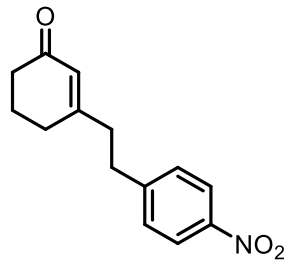
Reaction performed on 0.090 mmol scale (20 mg); Yield: 41% (8 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.39 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.49 – 7.43 (m, 1H), 7.39 – 7.34 (m, 1H), 6.95 – 6.90 (m, 1H), 6.03 (dd, *J* = 10.2, 2.3 Hz, 1H), 3.29 (dd, *J* = 13.4, 7.7 Hz, 1H), 3.19 (dd, *J* = 13.4, 7.7 Hz, 1H), 3.01 – 2.87 (m, 1H), 2.63 – 2.49 (m, 1H), 2.43 – 2.31 (m, 1H), 2.18 – 2.06 (m, 1H), 1.94 – 1.78 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.88, 153.81, 129.20, 129.07, 127.49, 126.17, 125.71, 125.39, 123.46, 99.97, 38.08, 37.11, 36.88, 29.17; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{17}H_{16}O$ 259.1093; Found 259.1111; **IR** (Thin Film, neat, cm^{-1}): 3042, 2924, 2861, 1675, 1390, 1251, 1211, 800, 780.

3-(4-fluorophenethyl)cyclohex-2-en-1-one (3q):



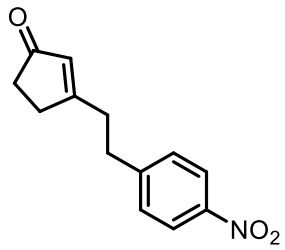
Reaction performed on 0.21 mmol scale (40 mg); Yield: 70% (31 mg); Physical appearance: Brown gel; TLC R_f 0.3 (5:1 Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) 7.19 – 7.10 (m, 2H), 6.99 (t, *J* = 8.5 Hz, 2H), 5.90 (s, 1H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.52 (t, *J* = 8.0 Hz, 2H), 2.37 (t, *J* = 6.7 Hz, 2H), 2.30 (t, *J* = 5.9 Hz, 2H), 2.04 – 1.96 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.71, 164.92, 161.42 (d, J_{C-F} = 244.49 Hz), 136.29 (d, J_{C-F} = 3.3 Hz), 129.60 (d, J_{C-F} = 7.9 Hz), 126.13, 115.31 (d, *J* = 21.2 Hz), 39.70, 37.31, 32.56, 29.90, 22.67; **^{19}F NMR** (471 MHz, $CDCl_3$) δ −116.95; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{15}FO$ 219.1180; Found 219.1181; **IR** (Thin Film, neat, cm^{-1}): 2925, 1663, 1625, 1508, 1219, 1157, 885, 832, 531.

3-(4-nitrophenethyl)cyclohex-2-en-1-one (3r):



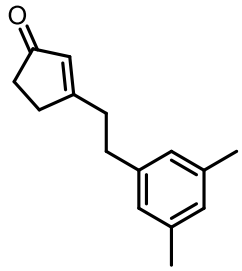
Reaction performed on 0.14 mmol scale (30 mg); Yield: 68% (23 mg, *rotational isomers* 1:0.11); Physical appearance: brown gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 5.91 (s, 1H), 2.97 (t, *J* = 7.8 Hz, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.39 (t, *J* = 6.4 Hz, 2H), 2.33 (t, *J* = 6.1 Hz, 2H), 2.07 – 1.98 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.47, 163.71, 148.37, 129.10, 126.34, 123.88, 38.78, 37.28, 33.08, 29.88, 22.63; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{15}NO_3$ 246.1125; Found 246.1100; **IR** (Thin Film, neat, cm^{-1}): 2932, 1669, 1615, 1498, 1231, 1210, 1137, 874, 829, 533.

3-(4-nitrophenethyl)cyclopent-2-en-1-one (3s):



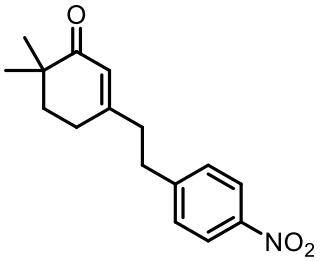
Reaction performed on 0.093 mmol scale (20 mg); Yield: 70% (15 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) 8.20 (t, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 6.01 (s, 1H), 3.06 (t, J = 7.6 Hz, 2H), 2.80 (t, J = 7.9 Hz, 2H), 2.67 – 2.60 (m, 2H), 2.48 – 2.41 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.43, 179.99, 148.10, 146.76, 130.17, 129.04, 123.93, 35.26, 34.31, 33.08, 31.71; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{13}NO_3$ 232.0968; Found 232.0965; **IR** (Thin Film, neat, cm^{-1}): 2915, 1711, 1637, 1518, 1467, 1127, 1209, 855, 832, 521.

3-(3,5-dimethylphenethyl)cyclopent-2-en-1-one (3t):



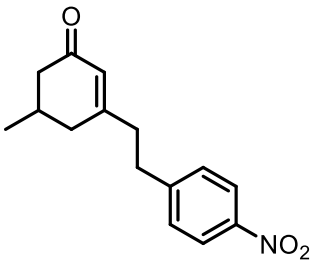
Reaction performed on 0.15 mmol scale (30 mg); Yield: 65% (21 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.88 (s, 1H), 6.84 (s, 2H), 6.02 (s, 1H), 2.89 – 2.82 (m, 2H), 2.77 – 2.70 (m, 2H), 2.64 – 2.58 (m, 2H), 2.45 – 2.40 (m, 2H), 2.32 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.04, 182.02, 140.47, 138.10, 129.73, 127.98, 125.99, 35.30, 35.16, 33.16, 31.72, 21.27; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{18}O$ 215.1430; Found 215.1417; **IR** (Thin Film, neat, cm^{-1}): 2918, 1705, 1674, 1614, 1437, 1183, 843, 676.

6,6-dimethyl-3-(4-nitrophenethyl)cyclohex-2-en-1-one (3u):



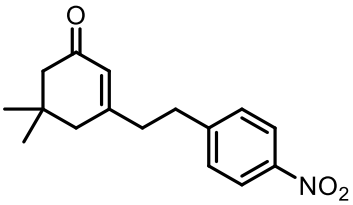
Reaction performed on 0.093 mmol scale (20 mg); Yield: 67% (17 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 5.80 (s, 1H), 2.96 (t, J = 7.9 Hz, 2H), 2.56 (t, J = 7.9 Hz, 2H), 2.33 (t, J = 6.1 Hz, 2H), 1.83 (t, J = 6.1 Hz, 2H), 1.10 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.27, 161.36, 148.47, 146.65, 129.11, 124.83, 123.84, 40.46, 38.43, 36.24, 33.22, 27.29, 24.10; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{19}NO_3$ 274.1438; Found 274.1427; **IR** (Thin Film, neat, cm^{-1}): 2941, 1672, 1516, 1343, 1240,1135, 855.

5-methyl-3-(4-nitrophenethyl)cyclohex-2-en-1-one (3v):



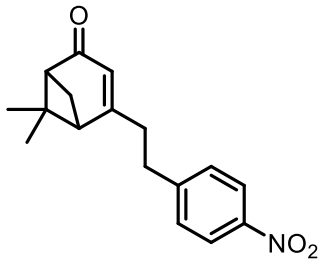
Reaction performed on 0.14 mmol scale (20 mg); Yield: 64% (15.4 mg, mixture of rotamers, 1:1); Physical appearance: red solid; M.p. 89–91 °C; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 5.88 (s, 1H), 3.31 – 3.16 (m, 2H), 2.95 (t, *J* = 7.7 Hz, 2H), 2.56 (t, *J* = 8.2 Hz, 2H), 2.53 – 2.41 (m, 3H), 2.41 – 2.30 (m, 3H), 2.23 – 2.13 (m, 4H), 2.10 – 2.02 (m, 4H), 1.10 – 1.05 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.67, 161.30, 148.34, 146.68, 129.31, 129.12, 125.26, 123.87, 51.00, 44.13, 38.75, 33.65, 32.96, 28.32; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{17}NO_3$ 260.1281; Found 260.1273; **IR** (Thin Film, neat, cm^{-1}): 2923, 1671, 1566, 1373, 1230, 1125, 845.

5,5-dimethyl-3-(4-nitrophenethyl)cyclohex-2-en-1-one (3w):



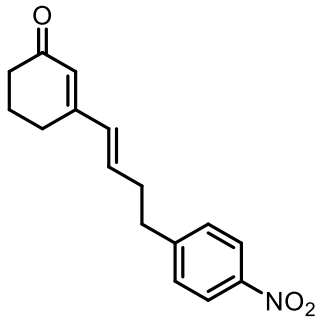
Reaction performed on 0.093 mmol scale (20 mg); Yield: 63% (16 mg, mixture of rotamers, 1.0:0.2); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 5.91 (s, 1H), 2.96 (t, *J* = 7.8 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.27 – 2.19 (m, 4H), 1.06 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.67, 161.30, 148.34, 146.68, 129.31, 129.12, 125.26, 123.96, 123.87, 123.82, 51.00, 44.13, 38.75, 33.65, 32.96, 28.32; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{19}NO_3$ 274.1438; Found 274.1418; **IR** (Thin Film, neat, cm^{-1}): 2942, 1675, 1509, 1453, 1239,1145, 845.

6,6-dimethyl-4-(4-nitrophenethyl)bicyclo[3.1.1]hept-3-en-2-one (3x):



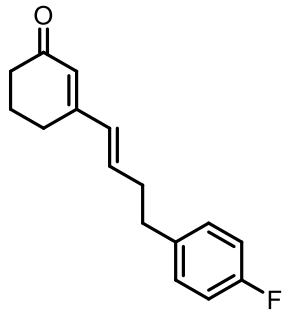
Reaction performed on 0.093 mmol scale (20 mg); Yield: 57% (14.3 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 5.77 (s, 1H), 2.95 (t, *J* = 7.9 Hz, 2H), 2.90 – 2.80 (m, 1H), 2.73 – 2.59 (m, 3H), 2.52 (t, *J* = 5.8 Hz, 1H), 2.07 (d, *J* = 9.2 Hz, 1H), 1.54 (s, 3H), 1.02 (s, 3H): **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.56, 170.93, 148.30, 146.68, 129.08, 123.86, 120.72, 57.83, 54.03, 48.76, 40.97, 37.76, 32.50, 26.59, 22.34; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{19}NO_3$ 286.1438; Found 286.1425; **IR** (Thin Film, neat, cm^{-1}): 2956, 1681, 1516, 1463, 1140, 1125, 755.

(*E*)-3-(4-(4-nitrophenyl)but-1-en-1-yl)cyclohex-2-en-1-one (3y):



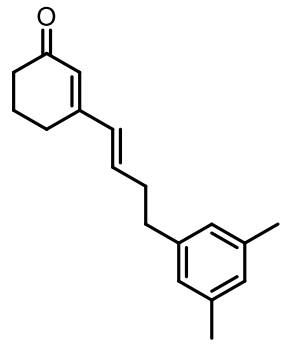
Reaction performed on 0.19 mmol scale (40 mg); Yield: 64% (32 mg); ^{1}H NMR analysis of the crude mixture of the products shows only the ε–product (*E* isomer); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 6.24 – 6.13 (m, 2H), 5.87 (s, 1H), 2.89 (t, J = 7.7 Hz, 2H), 2.62 – 2.52 (m, 2H), 2.47 – 2.36 (m, 4H), 2.08 – 1.98 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.26, 156.78, 148.83, 146.55, 136.15, 132.71, 132.68, 129.20, 129.17, 127.12, 123.75, 123.72, 37.66, 35.08, 34.24, 25.04, 22.28; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{17}NO_3$ 272.1281; Found 272.1272; **IR** (Thin Film, neat, cm^{-1}): 3384. 2941, 1660, 1598, 1513, 1341, 1255, 1191, 1133, 854.

(*E*)-3-(4-(4-fluorophenyl)but-1-en-1-yl)cyclohex-2-en-1-one (3z):



Reaction performed on 0.21 mmol scale (40 mg); Yield: 54% (23 mg); ^{1}H NMR analysis of the crude mixture of the products shows only the ε–product (*E* isomer); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (dd, J = 8.4, 5.5 Hz, 2H), 7.00 (t, J = 8.4 Hz, 2H), 6.24 – 6.20 (m, 2H), 5.90 (s, 1H), 2.76 (t, J = 7.7 Hz, 2H), 2.55 – 2.49 (m, 2H), 2.47 – 2.41 (m, 4H), 2.08 – 2.01 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.41, 161.41 (d, $J_{C\text{-}F}$ = 244.69 Hz), 157.18, 137.31, 136.65, 132.21, 129.70 (d, $J_{C\text{-}F}$ = 8.66 Hz), 128.70 (d, $J_{C\text{-}F}$ = 15.1 Hz), 126.86, 115.22 (d, $J_{C\text{-}F}$ = 21.1 Hz), 37.70, 35.05, 34.47, 25.07, 22.33; **^{19}F NMR** (471 MHz, $CDCl_3$) –116.71; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{17}OF$ 245.1336; Found 245.1312; **IR** (Thin Film, neat, cm^{-1}): 3371. 2931, 1657, 1578, 1510, 1311, 1155, 1111, 1101, 854.

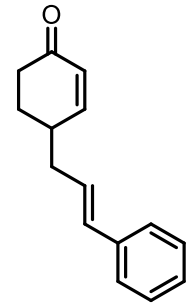
(*E*)-3-(4-(3,5-dimethylphenyl)but-1-en-1-yl)cyclohex-2-en-1-one (3aa):



Reaction performed on 0.10 mmol scale (20 mg); Yield: 27% (7 mg, *E*:*Z* 1.0:0.16); ^{1}H NMR analysis of the crude mixture of the products shows only the ε–product; Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.83 (s, 2H), 6.28 – 6.23 (m, 2H), 5.90 (s, 1H), 2.71 (t, J = 7.5 Hz, 1H), 2.56 – 2.51 (m, 1H), 2.49 – 2.45 (m, 2H), 2.42 (t, J = 6.7 Hz, 2H), 2.32 (s, 6H), 2.10 – 2.01 (m, 3H), 1.91 (d, J = 5.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.45, 157.51, 157.42, 141.02, 138.04, 137.94, 133.81, 132.80, 131.85, 127.72, 126.72, 126.30, 126.18, 37.73, 35.17, 35.09, 25.09, 25.05, 22.38, 22.36, 21.29, 18.90; **HRMS**

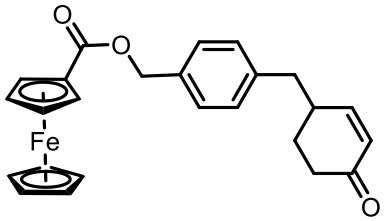
(ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{18}H_{22}O$ 255.1743; Found 255.1713; **IR** (Thin Film, neat, cm^{-1}): 3427, 2921, 2852, 1667, 1605, 1454, 1190, 1133, 1039, 966, 846, 702.

4-cinnamylcyclohex-2-en-1-one (3ab):



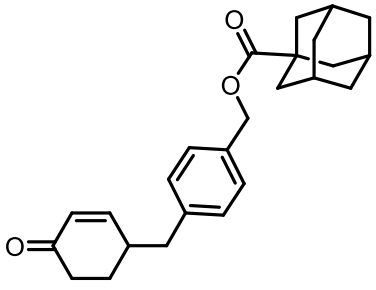
Reaction performed on 0.10 mmol scale (20 mg); Yield: 51% (11 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 6.98 – 6.91 (m, 1H), 6.53 – 6.46 (m, 1H), 6.28 – 6.18 (m, 1H), 6.04 (dd, *J* = 10.2, 2.4 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.59 – 2.49 (m, 1H), 2.48 – 2.34 (m, 3H), 2.24 – 2.12 (m, 1H), 1.88 – 1.73 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.85, 154.04, 132.73, 129.43, 128.60, 127.39, 126.87, 126.08, 38.15, 36.94, 36.34, 28.69; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{16}O$ 213.1274; Found 213.1275; **IR** (Thin Film, neat, cm^{-1}): 3417, 2911, 2752, 1777, 1601, 1464, 1180, 1123, 1019, 956, 841, 701.

Compound 3ac: Reaction performed on 0.097 mmol scale (40 mg); Yield: 80% (33 mg); Physical



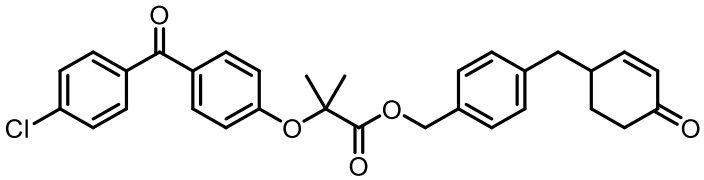
appearance: red gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.1 Hz, 2H), 7.24 (d, *J* = 7.1 Hz, 2H), 6.84 (d, *J* = 9.8 Hz, 1H), 5.98 (d, *J* = 9.9 Hz, 1H), 5.27 (s, 2H), 4.85 (s, 2H), 4.42 (s, 2H), 4.11 (s, 5H), 2.87 – 2.67 (m, 3H), 2.55 – 2.42 (m, 1H), 2.39 – 2.25 (m, 1H), 2.13 – 2.01 (m, 1H), 1.80 – 1.64 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.61, 171.50, 153.61, 139.08, 134.97, 129.38, 129.25, 128.81, 71.46, 71.03, 70.25, 69.73, 65.56, 40.63, 37.96, 36.77, 28.61; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{25}H_{24}FeO_3$ 451.0967; Found 451.0959; **IR** (Thin Film, neat, cm^{-1}): 3095, 3026, 2920, 1706, 1673, 1456, 1378, 1270, 1124, 1105, 819.

4-((4-oxocyclohex-2-en-1-yl)methyl)benzyl (3r,5r,7r)-adamantane-1-carboxylate (3ad):



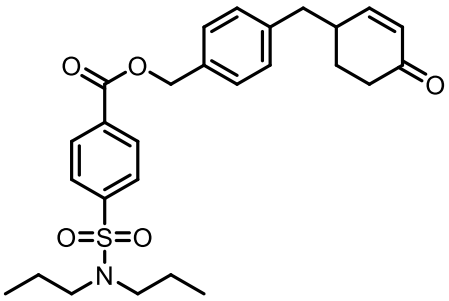
Reaction performed on 0.11 mmol scale (20 mg); Yield: 75% (13 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 10.0 Hz, 1H), 6.01 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.10 (s, 2H), 2.88 – 2.68 (m, 3H), 2.57 – 2.47 (m, 1H), 2.43 – 2.31 (m, 1H), 2.14 – 2.06 (m, 1H), 2.06 – 2.01 (m, 3H), 1.98 – 1.92 (m, 6H), 1.79 – 1.69 (m, 7H): **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.61, 177.49, 153.63, 138.68, 134.90, 129.36, 129.17, 127.96, 65.47, 40.79, 40.63, 38.85, 37.93, 36.81, 36.49, 28.65, 27.95; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{25}H_{30}O_3$ 379.2268; Found 379.2265; **IR** (Thin Film, neat, cm^{-1}): 2904, 2850, 1723, 1675, 1451, 1225, 1181, 1071, 976.

4-((4-oxocyclohex-2-en-1-yl)methyl)benzyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (3ae):



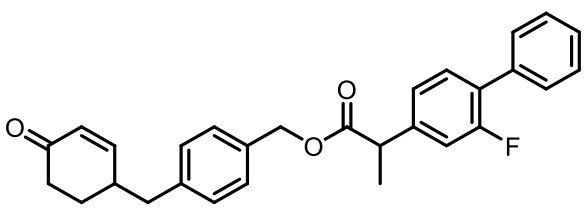
Reaction performed on 0.36 mmol scale (76 mg); Yield: 66% (44 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.85 – 6.77 (m, 3H), 6.00 (dd, *J* = 10.1, 1.7 Hz, 1H), 5.20 (s, 2H), 2.82 – 2.67 (m, 3H), 2.50 (dt, *J* = 16.8, 4.8 Hz, 1H), 2.35 (ddd, *J* = 17.0, 12.4, 4.9 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.76 – 1.71 (m, 1H), 1.70 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.57, 194.17, 173.49, 159.53, 153.41, 139.41, 138.47, 136.33, 133.39, 131.96, 131.18, 130.35, 129.43, 129.24, 128.79, 128.58, 117.30, 79.45, 67.11, 40.55, 37.83, 36.74, 28.60, 25.45, 25.42; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{31}H_{29}ClO_5$ 517.1776; Found 517.1758; **IR** (Thin Film, neat, cm^{-1}): 2923, 2854, 1736, 1653, 1596, 1282, 1248, 1131, 926, 762.

4-((4-oxocyclohex-2-en-1-yl)methyl)benzyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (3af):



Reaction performed on 0.64 mmol scale (30 mg); Yield: 56% (18 mg); Physical appearance: brown gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 10.5 Hz, 1H), 6.02 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.40 (s, 2H), 3.11 (t, *J* = 7.3 Hz, 4H), 2.87 – 2.70 (m, 3H), 2.53 (dt, *J* = 16.7, 4.8 Hz, 1H), 2.37 (ddd, *J* = 17.0, 12.4, 4.9 Hz, 1H), 2.14 – 2.04 (m, 1H), 1.80 – 1.70 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.55, 165.11, 153.46, 144.41, 139.43, 133.81, 133.39, 130.34, 129.44, 129.40, 128.78, 127.03, 67.08, 49.93, 40.64, 37.90, 36.79, 28.63, 21.93, 11.17; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{27}H_{33}NO_5S$ 506.1972; Found 506.1966; **IR** (Thin Film, neat, cm^{-1}): 2924, 1732, 1676, 1623, 1484, 1417, 1222, 1170, 1132, 1075, 766, 698.

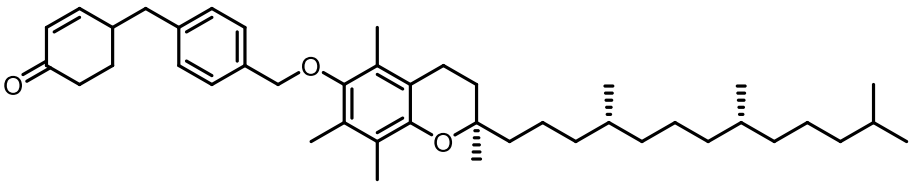
4-((4-oxocyclohex-2-en-1-yl)methyl)benzyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (3ag):



Reaction performed on 0.70 mmol scale (30 mg); Yield: 55% (17 mg); Physical appearance: colorless gel; TLC R_f 0.2 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.21 – 7.16 (m, 3H), 7.12 (dd, *J* = 11.5, 1.7 Hz, 1H), 6.84 (dt, *J*

= 10.0, 1.7 Hz, 1H), 6.00 (dd, *J* = 10.2, 1.9 Hz, 1H), 5.16 (dd, *J* = 12.3 Hz, 2H), 3.83 (q, *J* = 7.1 Hz, 1H), 2.86 – 2.68 (m, 3H), 2.51 (dt, *J* = 16.9, 4.8 Hz, 1H), 2.35 (ddd, *J* = 17.0, 12.4, 4.9 Hz, 1H), 2.11 – 2.01 (m, 1H), 1.78 – 1.67 (m, 1H), 1.58 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.59, 173.77, 159.61 (d, J_{C-F} = 248.29 Hz), 153.52, 141.66 (d, J_{C-F} = 7.6 Hz), 139.06, 135.47, 134.12, 130.77 (d, J_{C-F} = 4.2 Hz), 129.38, 129.20, 128.92 (d, J_{C-F} = 3.0 Hz), 128.48, 128.36, 127.90, 127.72, 123.62, 115.27 (d, J_{C-F} = 23.5 Hz), 66.42, 45.05, 40.61, 37.90, 36.78, 28.63, 18.33; **^{19}F NMR** (471 MHz, $CDCl_3$) δ −117.65; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{29}H_{27}O_3F$ 465.1836; Found 465.1827; **IR** (Thin Film, neat, cm^{-1}): 2964, 2932, 2875, 1720, 1675, 1341, 1269, 1157, 1102, 991, 739, 602.

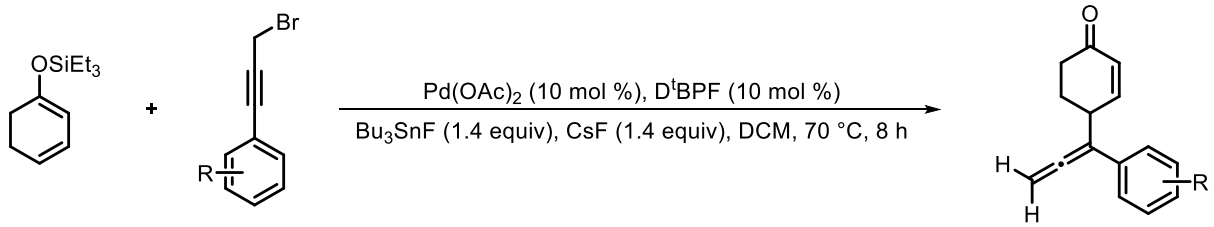
4-(4-((((*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)benzyl)cyclohex-2-en-1-one (3ah):



Reaction performed on 0.49 mmol scale (30 mg); Yield: 65% (20 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 10.2 Hz, 1H), 6.02 (d, *J* = 10.3 Hz, 1H), 4.70 (s, 2H), 2.89 – 2.73 (m, 3H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.58 – 2.50 (m, 1H), 2.44- 2.32 (m, 2H), 2.25 (s, 3H), 2.20 (s, 3H), 2.13 (s, 3H), 1.91 – 1.74 (m, 3H), 1.68 – 1.48 (m, 6H), 1.46 – 1.38 (m, 4H), 1.32 – 1.23 (m, 9H), 1.20 – 1.05 (m, 7H), 0.91 – 0.85 (m, 11H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.68, 153.74, 148.04, 138.53, 136.37, 129.35, 129.14, 128.09, 127.89, 125.92, 122.96, 117.62, 74.85, 74.43, 40.68, 39.38, 38.04, 37.41, 36.82, 32.79, 32.72, 28.66, 27.99, 24.82, 24.46, 23.91, 22.74, 22.64, 21.06, 20.70, 19.70, 12.89, 12.02, 11.84; **HRMS** (ESI-ToF) *m/z*: $[M]^+$ Calcd. for $C_{43}H_{65}O_3$ 629.4928; Found 629.4918; **IR** (Thin Film, neat, cm^{-1}): 2923, 2855, 1680, 1457, 1375, 1411, 1252, 1086, 1016, 809.

(5) General procedures and analytical data of the γ-allenylated enones:

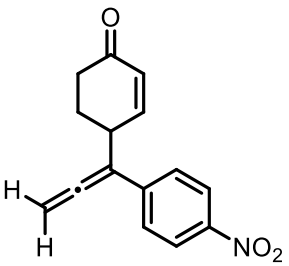
Scheme S5: Procedure for the γ-allenylation of silyldienol ethers:



In a pressure tube equipped with a magnetic stir bar, the silyldienol ether (0.41 mmol, 2.8 equiv.) and benzyl bromide (0.15 mmol, 1 equiv.) were dissolved in dry DCM (2 mL) and the solution was degassed for 10 min with argon. The tube was sealed and moved into the glovebox. This was followed by the addition of $Pd(OAc)_2$ (3.3 mg, 0.015 mmol, 0.1 equiv), D^{t}BPF (7.8 mg, 0.015 mmol, 0.1 equiv), CsF

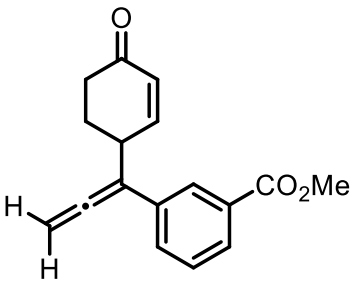
(31 mg, 0.21 mmol, 1.4 equiv) and Bu_3SnF (64 mg, 0.21 mmol, 1.4 equiv). The tube was fitted tightly with a Teflon screw cap and moved out of the glovebox. The reaction mixture was heated to 70 °C in an oil bath and maintained at that temperature for 8 h. Upon cooling to room temperature, the reaction mixture was diluted with about 20 mL of DCM, and the resulting slurry was filtered through a pad of Celite, eluting with DCM. The filtrate was extracted with DCM and washed successively with 1 M NaOH and water. The combined organic extract was dried over anhyd. Na_2SO_4 and filtered. Upon concentration under reduced pressure, the crude product was purified by silica gel flash column chromatography.

4-(1-(4-nitrophenyl)propa-1,2-dien-1-yl)cyclohex-2-en-1-one (5a):



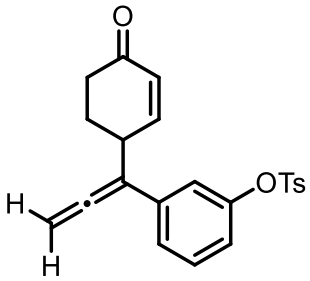
Reaction performed on 0.12 mmol scale (30 mg); Yield: 81% (26 mg, allenyl:propargyl 1.0:0.13); Physical appearance: brown gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 6.94 – 6.90 (m, 1H), 6.13 (dd, *J* = 10.2, 2.4 Hz, 1H), 5.39 – 5.29 (m, 2H), 3.75 – 3.69 (m, 1H), 2.66 – 2.58 (m, 1H), 2.55 – 2.46 (m, 1H), 2.40 – 2.33 (m, 1H), 2.13 – 2.02 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.64, 198.76, 150.51, 141.84, 130.07, 126.90, 124.03, 106.04, 81.46, 36.50, 35.62, 28.48; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{13}NO_3$ 256.0968; Found 256.0962; **IR** (Thin Film, neat, cm^{-1}): 3441, 2960, 2871, 1719, 1654, 1511, 1462, 1365, 1266, 1038, 850, 569.

methyl 3-(1-(4-oxocyclohex-2-en-1-yl)propa-1,2-dien-1-yl)benzoate (5b):



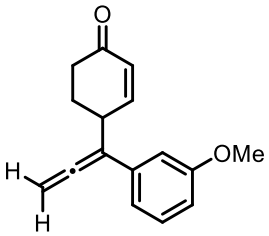
Reaction performed on 0.14 mmol scale (30 mg); Yield: 77% (25 mg); Physical appearance: brown gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.96 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.64 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 6.10 (dd, *J* = 10.2, 2.3 Hz, 1H), 5.30 – 5.20 (m, 2H), 3.96 (s, 3H), 3.77 – 3.69 (m, 1H), 2.67 – 2.58 (m, 1H), 2.53 – 2.45 (m, 1H), 2.38 – 2.30 (m, 1H), 2.12 – 2.02 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.51, 199.28, 166.90, 151.39, 135.30, 131.01, 130.72, 129.67, 128.83, 128.38, 127.15, 106.19, 80.84, 52.30, 36.58, 35.78, 28.42; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{16}O_3$ 269.1172; Found 269.1180; **IR** (Thin Film, neat, cm^{-1}): 3439, 2951, 2771, 1619, 1632, 1491, 1443, 1395, 1216, 1018, 840, 579.

3-(1-(4-oxocyclohex-2-en-1-yl)propa-1,2-dien-1-yl)phenyl 4-methylbenzenesulfonate (5c):



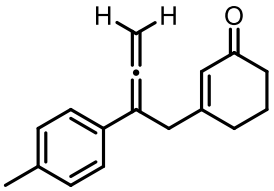
Reaction performed on 0.82 mmol scale (30 mg); Yield: 77% (24 mg, allenyl:propargyl 1.0:0.07); Physical appearance: brown gel; TLC R_f 0.2 (4:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.00 (t, *J* = 1.9 Hz, 1H), 6.90 (dt, *J* = 7.4, 1.9 Hz, 1H), 6.87 – 6.82 (m, 1H), 6.07 (dd, *J* = 10.2, 2.3 Hz, 1H), 5.23 – 5.13 (m, 2H), 3.56 – 3.48 (m, 1H), 2.63 – 2.52 (m, 1H), 2.47 (s, 3H), 2.45 – 2.39 (m, 1H), 2.29 – 2.17 (m, 1H), 2.05 – 1.90 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.47, 199.05, 151.13, 150.05, 145.41, 136.76, 132.45, 129.77, 128.59, 125.07, 121.01, 120.25, 105.82, 80.86, 36.55, 35.67, 28.33, 21.74; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{22}H_{20}O_4S$ 381.1155; Found 381.1173; **IR** (Thin Film, neat, cm^{-1}): 2933, 1713, 1445, 1269, 1174, 1161, 1053, 961, 793, 730.

4-(1-(3-methoxyphenyl)propa-1,2-dien-1-yl)cyclohex-2-en-1-one (5d):



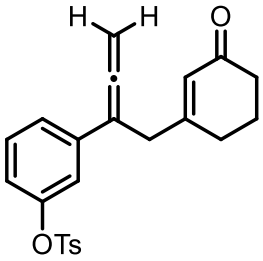
Reaction performed on 0.13 mmol scale (30 mg); Yield: 75% (24 mg); Physical appearance: brown gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.83 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.08 (dd, *J* = 10.2, 2.3 Hz, 1H), 5.24 – 5.13 (m, 2H), 3.85 (s, 3H), 3.70 – 3.62 (m, 1H), 2.65 – 2.56 (m, 1H), 2.51 – 2.42 (m, 1H), 2.38 – 2.28 (m, 1H), 2.13 – 2.01 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.40, 199.44, 159.94, 151.89, 136.25, 129.68, 129.44, 118.72, 112.55, 112.41, 106.63, 80.29, 55.29, 36.66, 35.98, 28.50; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{16}H_{16}O_2$ 263.1043; Found 263.1074; **IR** (Thin Film, neat, cm^{-1}): 3443, 2955, 2923, 2852, 1713, 1677, 1597, 1581, 1487, 1430, 1377, 1260, 1167, 783, 699.

3-(2-(*p*-tolyl)buta-2,3-dien-1-yl)cyclohex-2-en-1-one (5e):



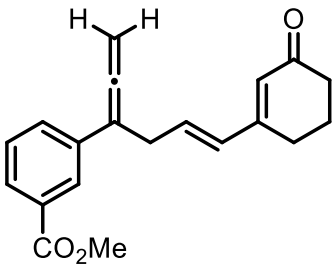
Reaction performed on 0.096 mmol scale (20 mg); Yield: 53% (12 mg); Physical appearance: colorless gel; TLC R_f 0.3 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.01 (s, 1H), 5.11 (t, *J* = 2.5 Hz, 2H), 3.39 – 3.35 (m, 2H), 2.41 – 2.35 (m, 4H), 2.35 (s, 3H), 2.04 – 1.96 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.23, 199.87, 164.35, 163.41, 136.84, 132.11, 129.27, 127.37, 127.02, 125.76, 100.93, 78.20, 39.27, 37.34, 29.39, 22.61, 21.07; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{18}O$ 239.1430; Found 239.1424; **IR** (Thin Film, neat, cm^{-1}): 3440, 2925, 1718, 1556, 1607, 1411, 1351, 1182, 817.

3-(1-(3-oxocyclohex-1-en-1-yl)buta-2,3-dien-2-yl)phenyl 4-methylbenzenesulfonate (5f):



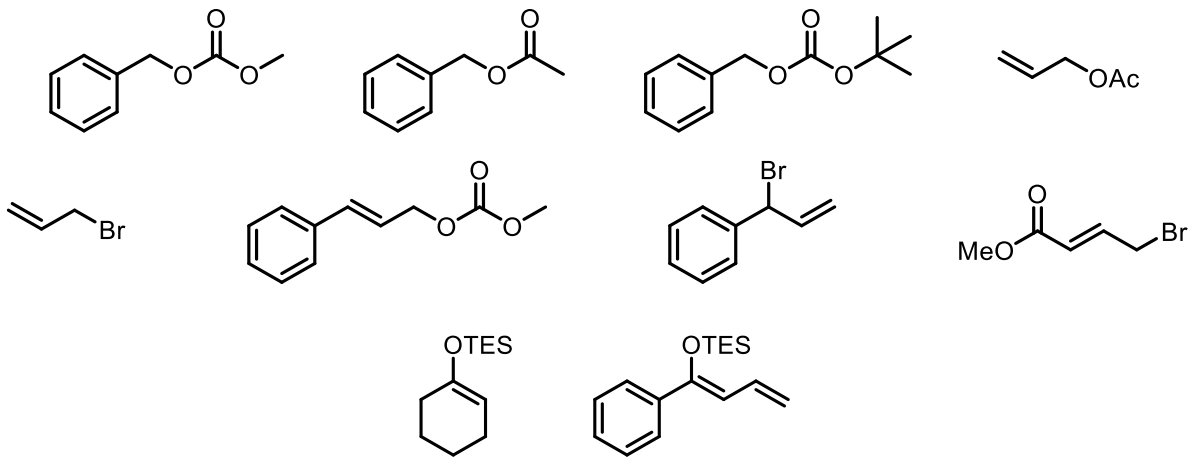
Reaction performed on 0.57 mmol scale (20 mg); Yield: 40% (8 mg); Physical appearance: colorless gel; TLC R_f 0.2 (4:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.0 (s, 1H), 6.78 (dt, *J* = 7.1, 2.1 Hz, 1H), 5.92 (s, 1H), 5.12 (t, *J* = 8.4 Hz, 2H), 3.29 (s, 2H), 2.47 (s, 3H), 2.42 – 2.34 (m, 4H), 2.07 – 1.97 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.45, 199.63, 162.40, 149.96, 145.34, 137.23, 132.34, 129.76, 129.52, 128.55, 127.32, 124.46, 120.60, 119.86, 100.25, 78.90, 38.80, 37.31, 29.56, 22.58, 21.72; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{23}H_{22}O_4S$ 395.1312; Found 395.1295; **IR** (Thin Film, neat, cm^{-1}): 2931, 1711, 1435, 1271, 1184, 1171, 1063, 965, 794, 731.

methyl (*E*)-3-(6-(3-oxocyclohex-1-en-1-yl)hexa-1,2,5-trien-3-yl)benzoate (5g):



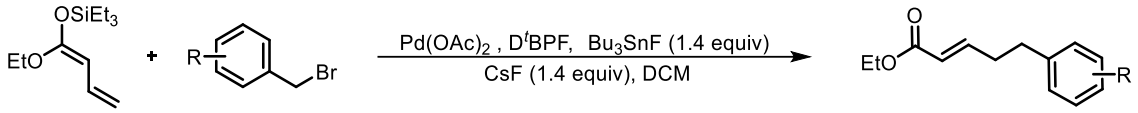
Reaction performed on 0.057 mmol scale (40 mg); Yield: 31% (8.2 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49 (td, *J* = 7.6, 1.4 Hz, 1H), 7.38 – 7.31 (m, 2H), 6.32 – 6.23 (m, 2H), 5.91 (s, 1H), 4.90 (t, *J* = 3.1 Hz, 2H), 3.91 (s, 3H), 3.20 – 3.24 (m, 2H), 2.47 (t, *J* = 6.0 Hz, 2H), 2.42 (t, *J* = 6.6 Hz, 2H), 2.09 – 2.00 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.29, 198.89, 180.68, 157.22, 135.14, 132.76, 131.66, 130.20, 129.60, 127.32, 127.00, 52.25, 37.68, 36.98, 25.10, 22.31; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{20}H_{20}O_3$ 309.1485; Found 309.1458 mass data; **IR** (Thin Film, neat, cm^{-1}): 2924, 1715, 1433, 1259, 1192, 1131, 1082, 965, 762, 734.

Unsuccessful substrates:



(6) General procedures and analytical data of the γ-alkylation and allenylation of α,β-unsaturated esters:

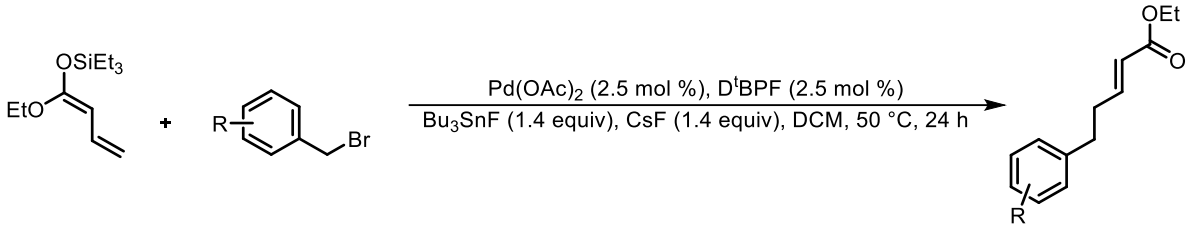
Scheme S6: Optimization studies for the γ-alkylation of silyl ketene acetals:



Sr. No.	Condition	Yield
1.	$Pd(OAc)_2$ (2.5 mol%), D^{t}BPF (2.5 mol%), 70 °C, 8 h	Trace
2.	$Pd(OAc)_2$ (2.5 mol%), D^{t}BPF (2.5 mol%), 25 °C, 12 h	Trace
3.	$Pd(OAc)_2$ (2.5 mol%), D^{t}BPF (2.5 mol%), 60 °C, 6 h, toluene or THF	Trace
4.	$Pd(OAc)_2$ (5 mol%), D^{t}BPF (5 mol%), 50 °C, 24 h	50%
5.	$Pd(OAc)_2$ (2.5 mol%), D^{t}BPF (2.5 mol%), 50 °C, 20–24 h	87%

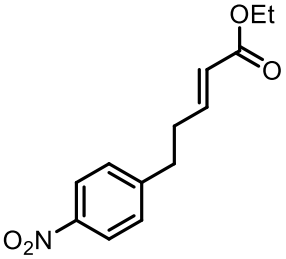
(7) General procedures and analytical data of the γ-alkylation and allenylation of α,β-unsaturated esters:

Scheme S7: Procedure for the γ-alkylation and allenylation of silyl ketene acetal:



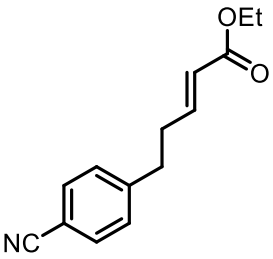
In a pressure tube equipped with a magnetic stir bar, the silyl ketene acetal (0.39 mmol, 2.8 equiv) and benzyl bromide (0.14 mmol, 1.0 equiv) were dissolved in dry DCM (2 mL) and the solution was degassed for 10 min with argon. The tube was sealed and moved into the glovebox. This was followed by the addition of $Pd(OAc)_2$ (3.3 mg, 0.0035 mmol, 0.025 equiv), D^{t}BPF (3.9 mg, 0.0035 mmol, 0.025 equiv), CsF (29 mg, 0.19 mmol, 1.4 equiv) and Bu_3SnF (60 mg, 0.19 mmol, 1.4 equiv). The tube was tightly fitted with a Teflon screw cap and moved out of the glovebox. The reaction mixture was heated to 50 ^{o}C in an oil bath and maintained at that temperature for 24 hours. Upon cooling to room temperature, the reaction mixture was diluted with about 20 mL of DCM, and the resulting slurry was filtered through a pad of Celite, eluting with DCM. The filtrate was extracted with DCM and washed successively with 1 M NaOH and water. The combined organic extract was dried over anhyd. Na_2SO_4 and filtered. Upon concentration under reduced pressure, the crude product was purified by silica gel flash column chromatography.

ethyl (*E*)-5-(4-nitrophenyl)pent-2-enoate (7a):



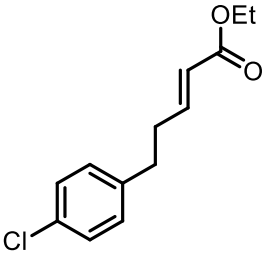
Reaction performed on 0.093 mmol scale (20 mg); Yield: 87% (20 mg); Physical appearance: colorless gel; TLC R_f 0.4 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.02 – 6.91 (m, 1H), 5.86 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.63 – 2.54 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.28, 148.42, 146.64, 146.50, 129.19, 123.81, 122.64, 60.38, 34.17, 33.12, 14.25; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{15}NO_4$ 274.1074; Found 274.1067; **IR** (Thin Film, neat, cm^{-1}): 2917, 1717, 1655, 1530, 1350, 1278, 1037, 853.

ethyl (*E*)-5-(4-cyanophenyl)pent-2-enoate (7b):



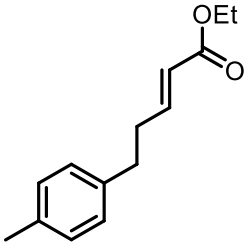
Reaction performed on 0.10 mmol scale (20 mg); Yield: 70% (17.5 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.96 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.85 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.60 – 2.51 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.33, 146.68, 146.30, 132.37, 129.18, 122.54, 118.93, 110.23, 60.37, 34.42, 33.14, 14.25; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{15}NO_2$ 230.1176; Found 230.1188; **IR** (Thin Film, neat, cm^{-1}): 2961, 2924, 2852, 1718, 1033, 801, 762. 635.

ethyl (*E*)-5-(4-chlorophenyl)pent-2-enoate (7c):



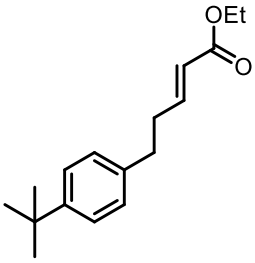
Reaction performed on 0.097 mmol scale (20 mg); Yield: 65% (14 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H, merged with chloroform peak), 7.13 (d, *J* = 8.2 Hz, 2H), 6.99 (dt, *J* = 15.6, 6.7 Hz, 1H), 5.85 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.56 – 2.45 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.48, 147.45, 139.17, 131.93, 129.68, 128.59, 122.14, 99.98, 60.27, 33.70, 33.69, 14.26; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{15}ClO_2$ 239.0833; Found 239.0815; **IR** (Thin Film, neat, cm^{-1}): 2981, 2932, 1715, 1653, 1492, 1367, 1311, 1266, 1194, 1148, 1091, 1038, 1014, 807.

ethyl (*E*)-5-(*p*-tolyl)pent-2-enoate (7d):



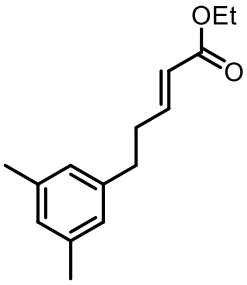
Reaction performed on 0.11 mmol scale (20 mg); Yield: 61% (14.5 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.06 (m, 4H), 7.07 – 6.98 (m, 1H), 5.87 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.57 – 2.48 (m, 2H), 2.35 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.62, 148.20, 137.74, 135.63, 135.60, 129.15, 128.19, 121.77, 60.19, 34.04, 33.92, 21.00, 14.28; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{18}O_2$ 219.1380; Found 219.1383; **IR** (Thin Film, neat, cm^{-1}): 2927, 1718, 1654, 1515, 1446, 1367, 1147, 973, 807.

ethyl (*E*)-5-(4-(*tert*-butyl)phenyl)pent-2-enoate (7e):



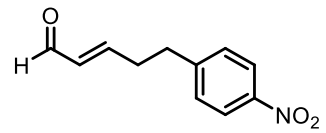
Reaction performed on 0.088 mmol scale (20 mg); Yield: 44% (10 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.09 – 7.00 (m, 1H), 5.89 (dt, *J* = 15.7, 1.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.59 – 2.49 (m, 2H), 1.34 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.65, 148.99, 148.31, 137.76, 127.96, 125.37, 121.71, 60.20, 34.39, 33.88, 33.79, 31.39, 14.28; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{17}H_{24}O_2$ 283.1669; Found 283.1682; **IR** (Thin Film, neat, cm^{-1}): 2971, 2934, 1712, 1651, 1482, 1357, 1260, 1168, 1097, 1026, 817, 806.

ethyl (*E*)-5-(3,5-dimethylphenyl)pent-2-enoate (7f):



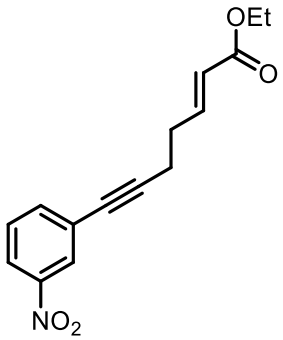
Reaction performed on 0.10 mmol scale (20 mg); Yield: 80% (18.5 mg); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (dt, *J* = 15.7, 6.8 Hz, 1H), 6.87 (s, 1H), 6.83 (s, 2H), 5.87 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.72 (t, *J* = 7.1 Hz, 2H), 2.56 – 2.49 (m, 2H), 2.32 (s, 6H), 1.31 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.68, 148.33, 140.78, 137.99, 127.80, 126.15, 121.68, 60.20, 34.21, 34.00, 21.27, 14.28; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{20}O_2$ 233.1536; Found 233.1528; **IR** (Thin Film, neat, cm^{-1}): 2980, 2935, 1716, 1654, 1492, 1367, 1266, 1178, 1092, 1036, 837, 807.

(*E*)-5-(4-nitrophenyl)pent-2-enal (7g):



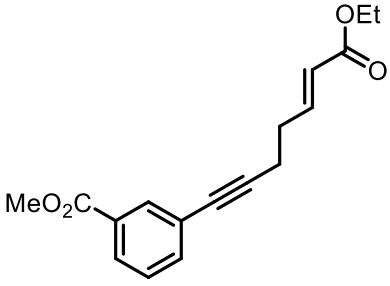
Reaction performed on 0.093 mmol scale (20 mg); Yield: 30% (6 mg); Rotational isomer: 1:0.1; Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.53 (d, *J* = 7.8 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.85 (dt, *J* = 15.7, 6.7 Hz, 1H), 6.20 – 6.13 (m, 1H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.77 – 2.71 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$)) δ 193.50, 155.39, 147.87, 133.84, 129.18, 123.94, 33.88, 33.50; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{11}H_{11}NO_3$ 206.0812; Found 206.0825; **IR** (Thin Film, neat, cm^{-1}): 3152, 2950, 1716, 1634, 1482, 1354, 1260, 1138, 1042, 1026, 830, 807.

ethyl (*E*)-7-(3-nitrophenyl)hept-2-en-6-ynoate (7h):



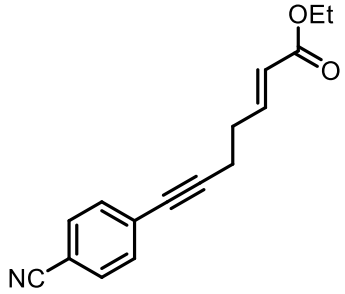
Reaction performed on 0.083 mmol scale (20 mg); Yield: 78% (16.7 mg, propagyl:allenyl 1.0:0.1); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (t, *J* = 1.9 Hz, 1H), 8.15 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.70 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.05 (dt, *J* = 15.6, 6.7 Hz, 1H), 5.97 (dt, *J* = 15.6, 1.7 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 6.7 Hz, 2H), 2.58 – 2.53 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.37, 146.14, 137.36, 129.22, 126.47, 125.40, 122.79, 122.57, 91.36, 79.58, 60.42, 31.00, 18.38, 14.27; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{15}NO_4$ 274.1074; Found 274.1067; **IR** (Thin Film, neat, cm^{-1}): 2947, 1710, 1651, 1437, 1297, 1221, 1203, 754.

methyl (*E*)-3-(7-ethoxy-7-oxohept-5-en-1-yn-1-yl)benzoate (7i):



Reaction performed on 0.079 mmol scale (20 mg); Yield: 73% (16.5 mg, propargyl:allenyl, 1.0:0.22); Physical appearance: colorless gel; TLC R_f 0.5 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.99 – 7.94 (m, 1H), 7.61 – 7.56 (m, 1H), 7.39 (t, *J* = 7.7 Hz 1H), 7.12 – 6.99 (m, 1H), 5.99 – 5.92 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 2.64 – 2.58 (m, 2H), 2.58 – 2.50 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.50, 166.43, 146.49, 135.79, 132.72, 130.30, 128.81, 128.36, 124.00, 122.57, 122.34, 89.38, 80.69, 60.35, 52.25, 31.26, 18.40, 14.27; **HRMS** (ESI-ToF) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{18}NO_4$ 287.1278; Found 287.1290; **IR** (Thin Film, neat, cm^{-1}): 2953, 1720, 1655, 1438, 1296, 1229, 1202, 755.

ethyl (*E*)-7-(4-cyanophenyl)hept-2-en-6-ynoate (7j):

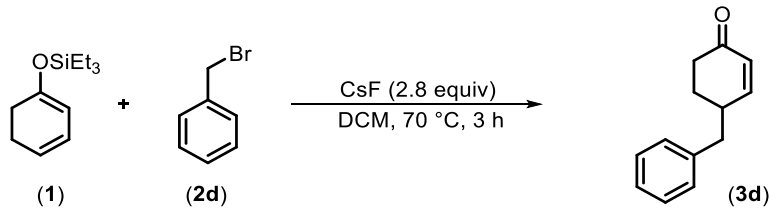


Reaction performed on 0.087 mmol scale (20 mg); Yield: 70% (16 mg, propagyl:allenyl 1:0.1); Physical appearance: colorless gel; TLC R_f 0.4 (5:1 Petroleum ether:EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.04 (dt, J = 15.6, 6.7 Hz, 1H), 5.96 (d, J = 15.6 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 2.63 (t, J = 7.0 Hz, 2H), 2.54 (q, J = 6.9 Hz, 2H), 1.31 (t, J = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.33, 146.11, 132.15, 131.95, 128.56, 126.40, 122.76, 118.55, 111.16, 93.32, 80.45, 60.39, 30.98, 18.50, 14.27; **HRMS** (ESI-ToF) *m/z*: $[M+Na]^+$ Calcd. for $C_{16}H_{15}NO_2$ 276.0995; Found 276.1017; **IR** (Thin Film, neat, cm^{-1}): 3468, 2925, 2229, 1720, 1607, 1405, 1370, 1212, 1095, 1019, 842.

(8) Control experiments (*via* GC):

We performed these studies to assess the role of the Pd-catalyst and exclude the possibility of a fluoride-mediated vinylogous Mukaiyama-type alkylation.

(I) In a pressure tube equipped with a magnetic stir bar, the silyldienol ether (0.41 mmol, 2.8 equiv) and benzyl bromide (0.15 mmol, 1.0 equiv) were dissolved in dry DCM (2 mL) and the solution was degassed for 10 min with argon. The tube was sealed and moved into the glovebox. This was followed by the addition of CsF (62 mg, 0.42 mmol, 2.8 equiv) and dodecane (0.075 mmol, 0.5 equiv) as the internal standard. The tube was fitted tightly with a Teflon screw cap and moved out of the glovebox. The reaction mixture was heated to 70 °C in an oil bath. Aliquots were drawn at 15-minute intervals, and conversions were checked by GC-MS. The consumption of starting material(s) and the formation of product(s) was plotted with time (average of 3 runs).



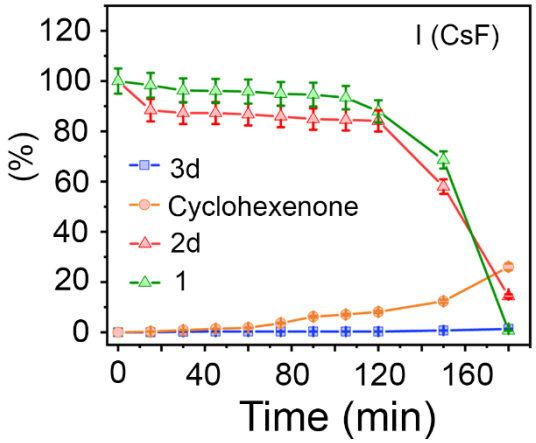
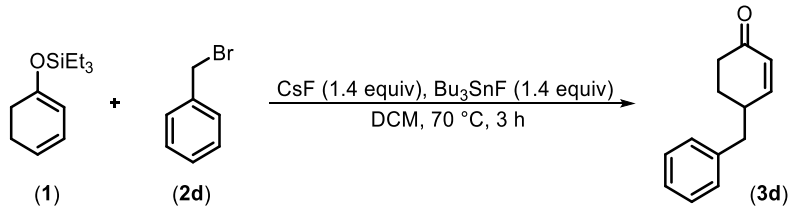


Figure S1: Consumption of starting material(s) and product(s) formation

(II) In a pressure tube equipped with a magnetic stir bar, the silyldienol ether (0.41 mmol, 2.8 equiv) and benzyl bromide (0.15 mmol, 1 equiv) were dissolved in dry DCM (2 mL) and the solution was degassed for 10 min with argon. The tube was sealed and moved into the glovebox. This was followed by the addition of CsF (31 mg, 0.21 mmol, 1.4 equiv), Bu_3SnF (64 mg, 0.21 mmol, 1.4 equiv) and dodecane (0.075 mmol, 0.5 equiv) as the internal standard. The tube was fitted tightly with a Teflon screw cap and moved out of the glovebox. The reaction mixture was heated to 70 °C. Aliquots were drawn at 15-minute intervals, and conversions were checked by GC-MS. The consumption of starting material(s) and formation of product(s) was plotted with time (average of 3 runs).



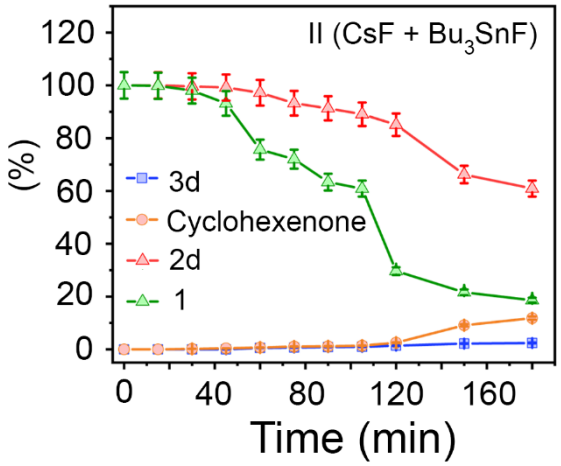


Figure S2: Consumption of starting material and product formation

(III) In a pressure tube equipped with a magnetic stir bar, the silyl dienolether (0.41 mmol, 2.8 equiv) and benzyl bromide (0.15 mmol, 1 equiv) were dissolved in dry DCM (2 mL) and the solution was degassed for 10 min with argon. The tube was sealed and moved into the glovebox. This was followed by the addition of $Pd(OAc)_2$ (3.3 mg, 0.015 mmol, 0.1 equiv), D^{t}BPF (7.8 mg, 0.015 mmol, 0.1 equiv), CsF (31 mg, 0.21 mmol, 1.4 equiv), Bu_3SnF (64 mg, 0.21 mmol, 1.4 equiv) and dodecane (0.075 mmol, 0.5 equiv) as the internal standard. The tube was fitted tightly with a Teflon screw cap and moved out of the glovebox. The reaction mixture was heated to 70 °C in an oil bath. Aliquots were drawn at 15-minute intervals, and conversions were checked by GC-MS. The consumption of starting material(s) and formation of product(s) was plotted with time (average of 3 runs).

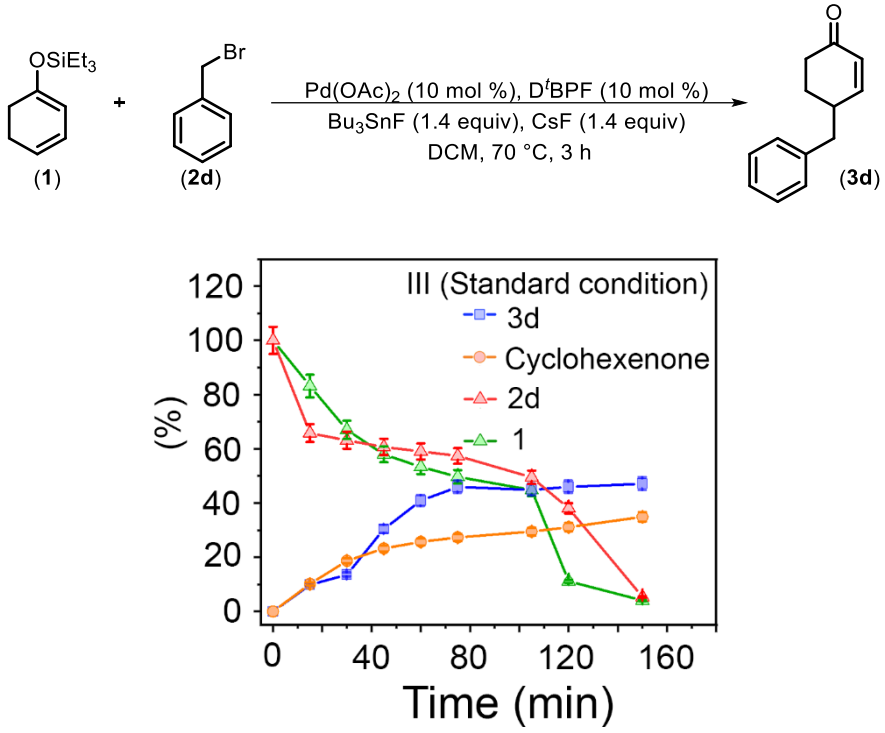


Figure S3: Consumption of starting material and product formation

(9) X-ray Crystallographic Data:

X-ray crystallographic study of compound 3v

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

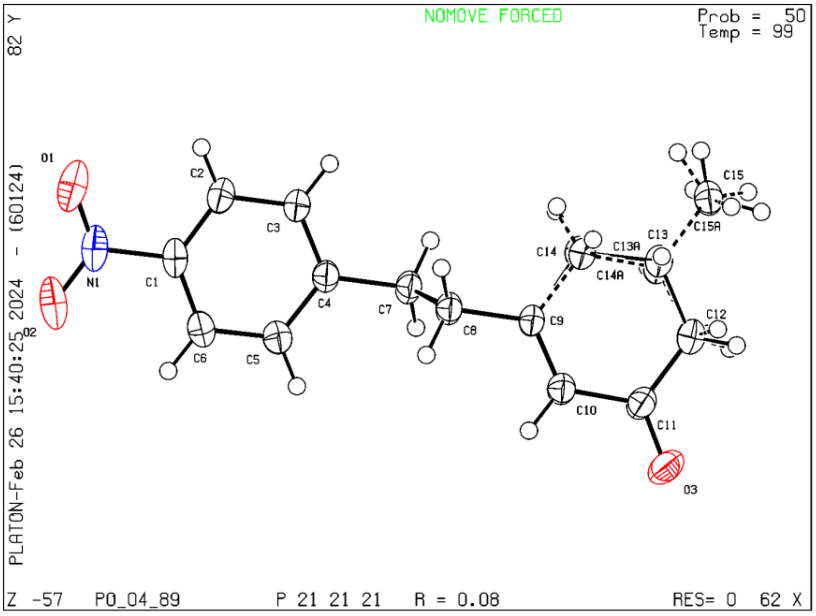


Figure 1: Crystal structure of **3v** (CCDC 2343455), showing thermal ellipsoid at 50% probability level

Identification code	**3v**
Empirical formula	C15 H17 N O3
Formula weight	259.29
Temperature/K	99.00
Crystal system, space group	Orthorhombic, *P* 2_1 2_1 2_1
a/Å	7.1533(11)
b/Å	12.457(3)
c/Å	14.899(2)
α/°	90
β/°	90
γ/°	90
Volume/Å	1327.6(4)
Z	4
ρ_{calc}g/cm^3	1.297
μ/mm^{-1}	0.090
F(000)	552.0
Crystal size/mm^3	0.153×0.136×0.124
Radiation Mo Kα	0.71073
2Θ range for data collection/°	4.262 to 67.1
Index ranges	$-10 \leq h \leq 9$, $-17 \leq k \leq 18$, $-23 \leq l \leq 20$
Reflections collected	10550

Independent reflections	4670 [R_{int} = 0.0818, R_{sigma} = 0.1163]
Data/restraints/parameters	4670/194/202
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0753, wR_2 = 0.1722
Final R indexes [all data]	R_1 = 0.1317, wR_2 = 0.2104
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.24

X-ray crystallographic study of compound 5a

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

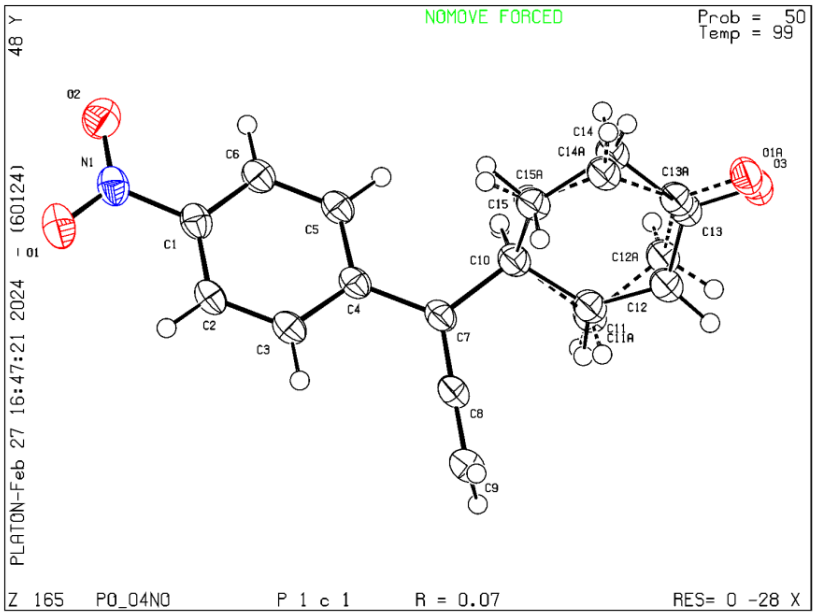


Figure 2: Crystal structure of **5a** (CCDC 2343452), showing thermal ellipsoid at 50% probability level

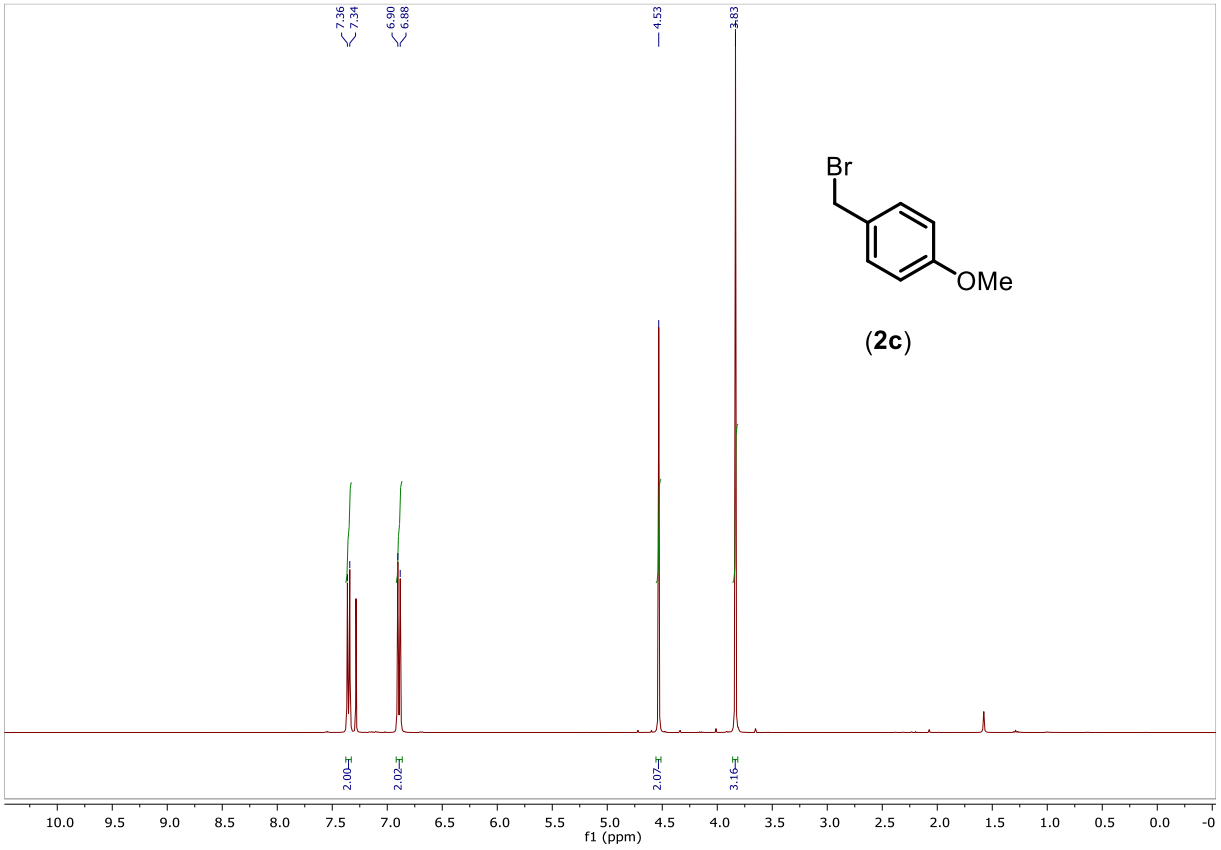
Identification code	**5a**
Empirical formula	C15 H13 N O3
Formula weight	255.26
Temperature/K	99.00
Crystal system, space group	Monoclinic, Pc
a/Å	6.151(3)
b/Å	14.019(7)

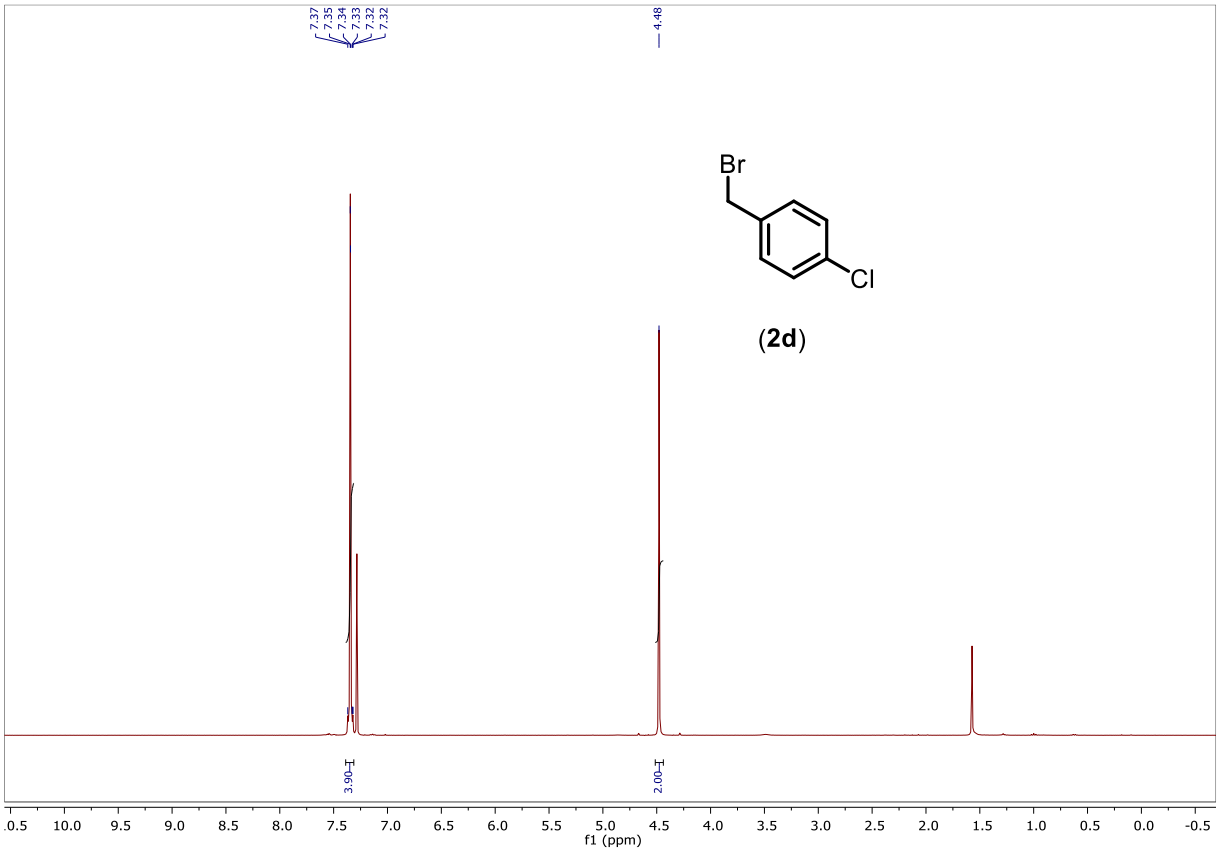
c/Å	7.211(3)
α/°	90
β/°	95.579(17)
γ/°	90
Volume/Å	618.9(5)
Z	2
ρ_{calc}g/cm^3	1.370
μ/mm^{-1}	0.096
F(000)	268.0
Crystal size/mm^3	0.23×0.216×0.189
Radiation Mo Kα	0.71073
2Θ range for data collection/°	5.812 to 60.488
Index ranges	$-8 \leq h \leq 6$, $-19 \leq k \leq 19$, $-9 \leq l \leq 10$
Reflections collected	10262
Independent reflections	2984 [R_{int} = 0.1178, R_{sigma} = 0.1163]
Data/restraints/parameters	2984/274/235
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0684, wR_2 = 0.1446
Final R indexes [all data]	R_1 = 0.1289, wR_2 = 0.1762
Largest diff. peak/hole / e Å^{-3}	0.31/-0.28

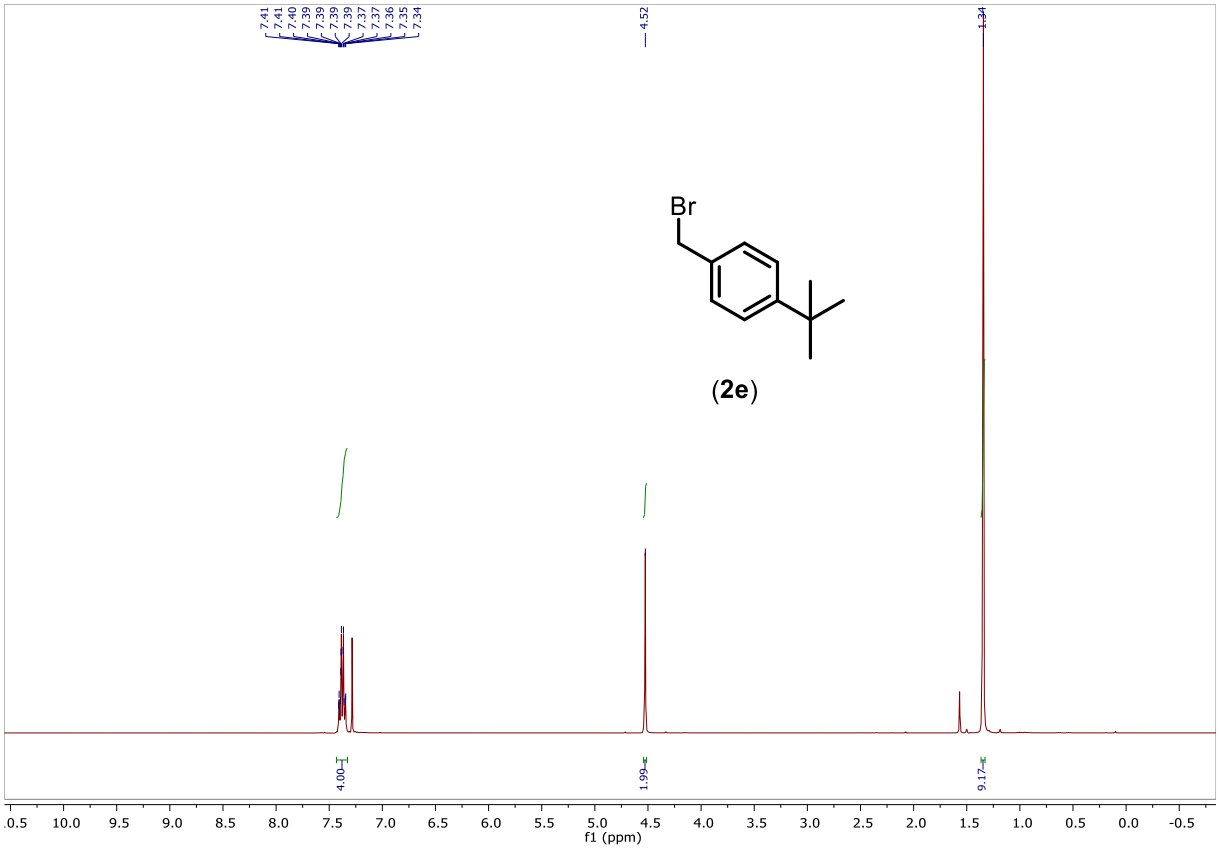
(10) References:

1. (a) G. Saini, A. Mondal and M. Kapur, *Org. Lett.*, 2019, **21**, 9071; (b) T. Q. Davies, J. J. Murphy, M. Dousset and A. Fürstner, *J. Am. Chem. Soc.*, 2021, **143**, 13489.
2. D. S. Huang and J. F. Hartwig, *Angew. Chem., Int. Ed*., 2010, **49**, 5757.
3. (a) S. Y. Min, H. X. Song, S. S. Yan, R. Yuan, J. H. Ye, B. Q. Wang, Y. Y. Gui and D. G. Yu, *Green Chem.*, 2023, **25**, 6194. (b) Y. Gao, L. Y. Wang, T. Zhang, B. M. Yang and Y. Zhao, *Angew. Chem., Int. Ed*., 2022, **61**, e202200371, DOI: 10.1002/anie.202200371. (c) S. Kim, Y. Lee and E. J. Cho, *J. Org. Chem*. 2023, **88**, 6382. (d) Z. Xiong, F. Xu, Y. Zhou, R. Zhang, Y. Zhang, Y. Chen, W. Yao and Z. Wang, *Org. Lett.* 2023, **25**, 8302.
4. M. Yang, J. Fang, H. Liu, X. Lu, J. Zhou, Z. Mou and H. Wang, *Adv. Synth. Catal.*, 2023, **365**, 1806.
5. H. J. Zhang, Y. C. Xie and L. Yin, *Nat. Commun.*, 2019, **10**, 1.
6. Q. L. Yang, R. C. Ma, Z. H. Li, W. W. Li, G. R. Qu and H. M. Guo, *Org. Chem. Front.*, 2022, **9**, 4990.

(11) Copies of ^{1}H, ^{13}C, ^{19}F NMR and HRMS spectra:



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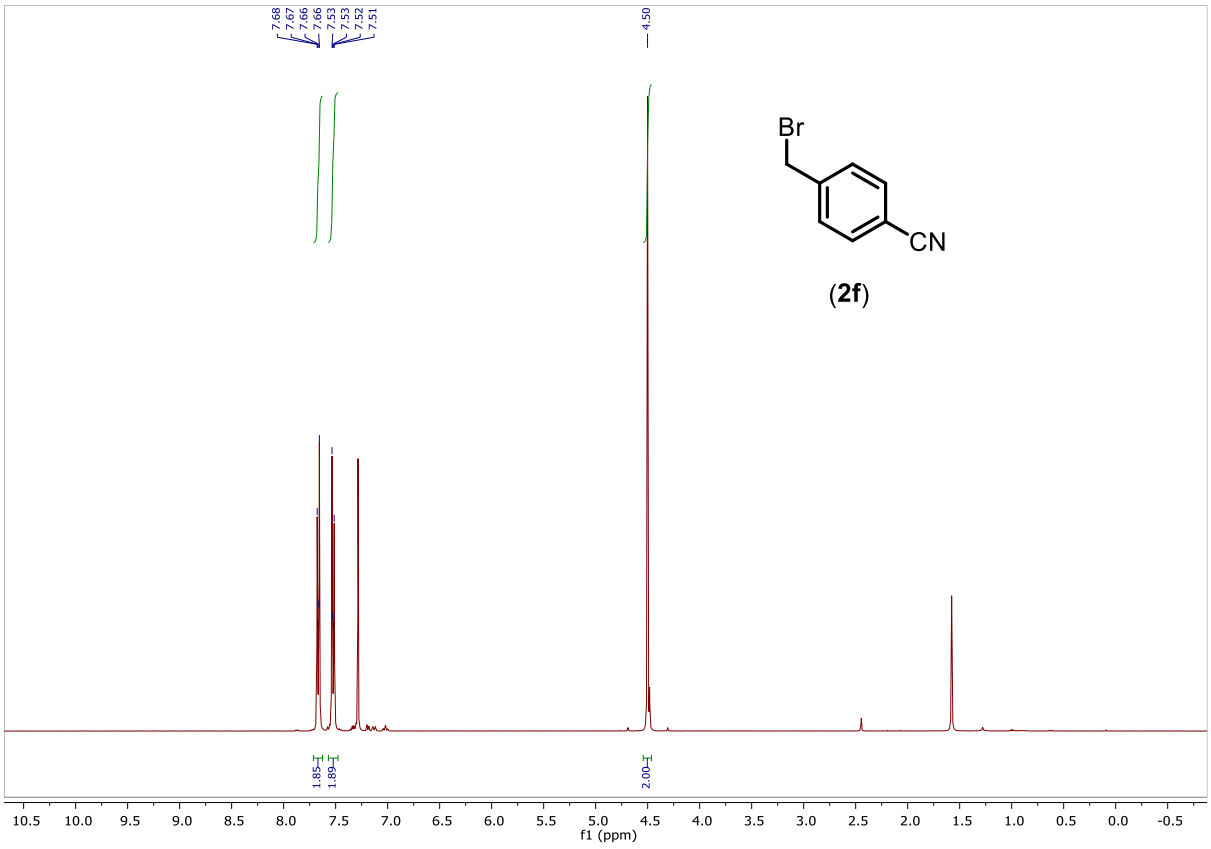
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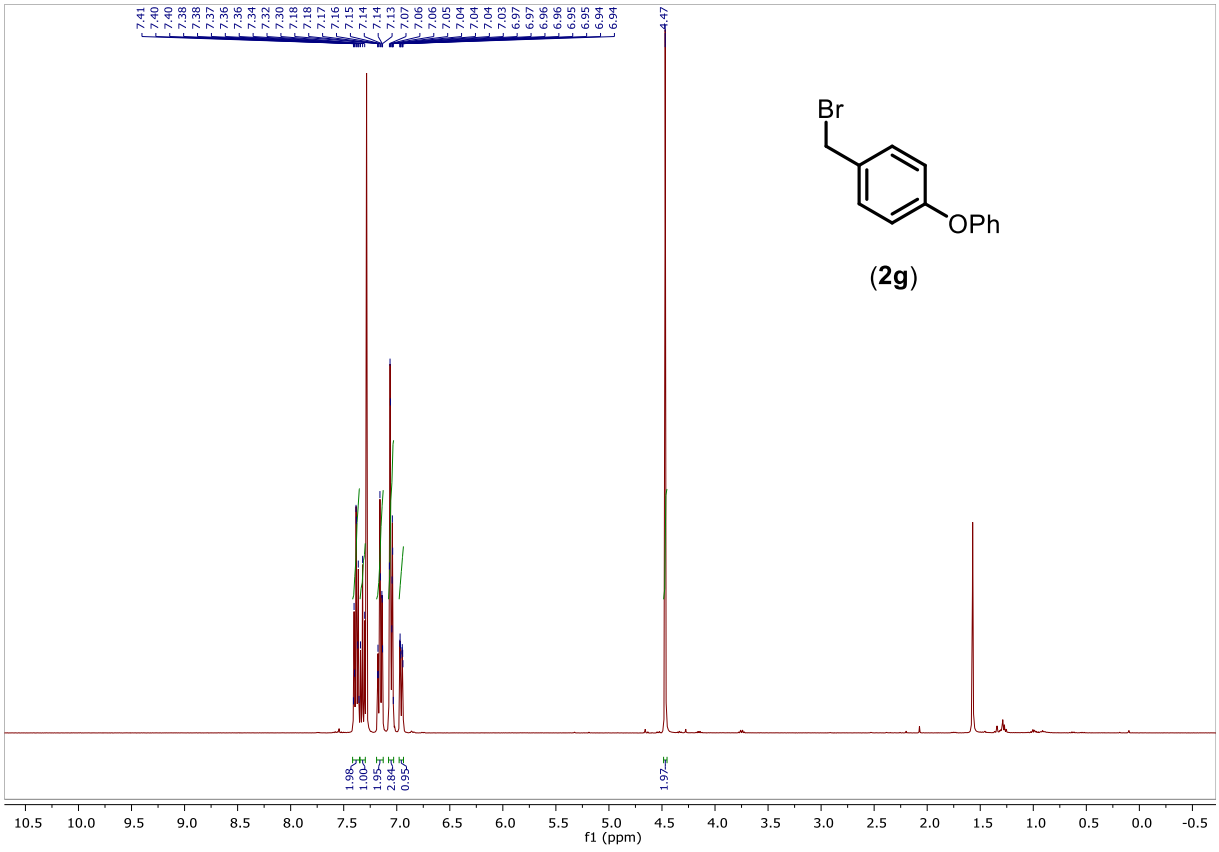
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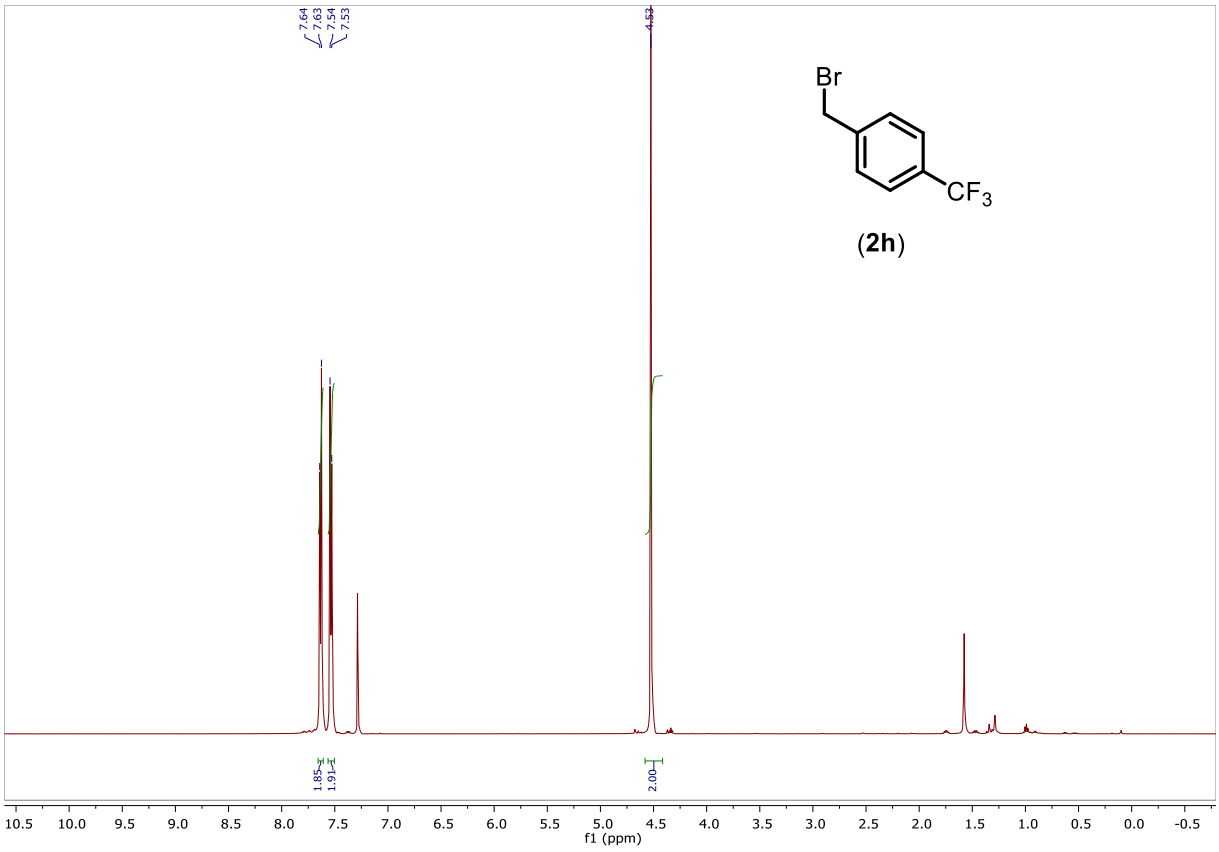
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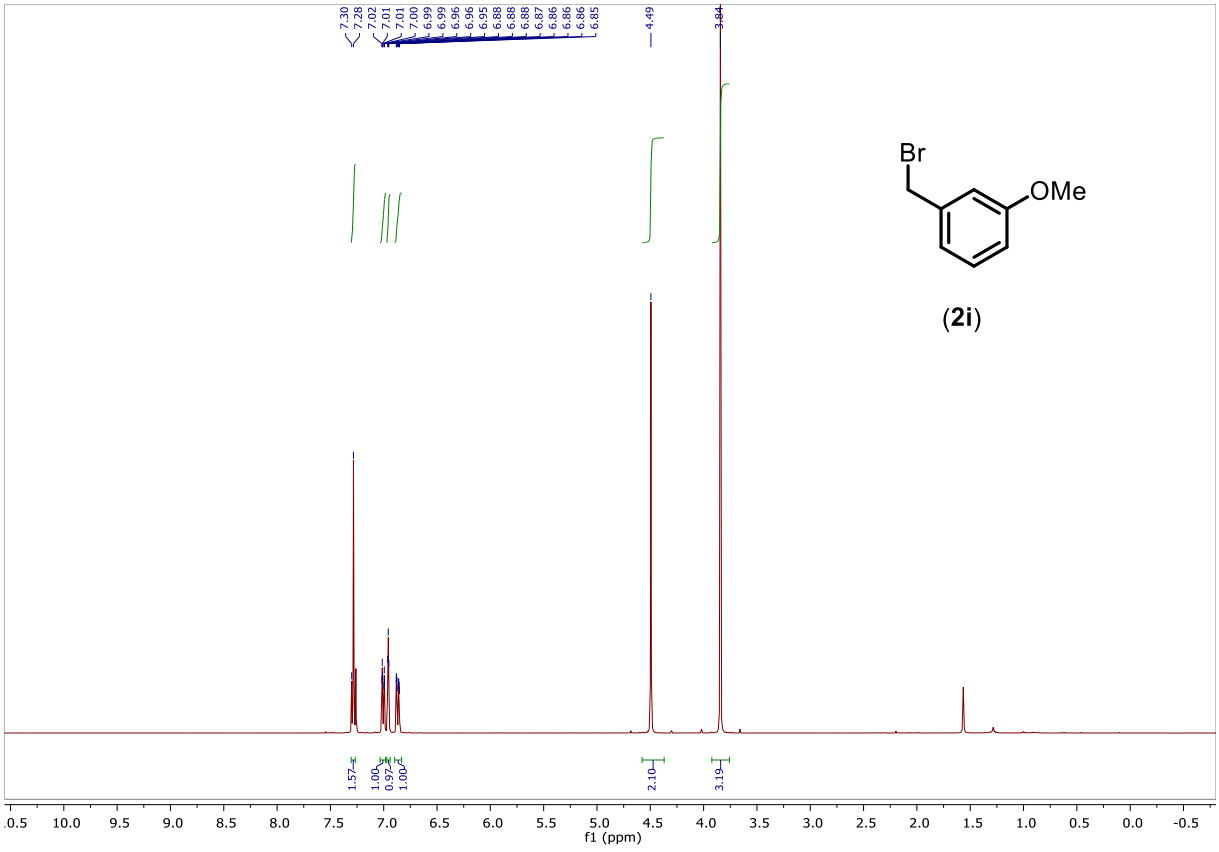
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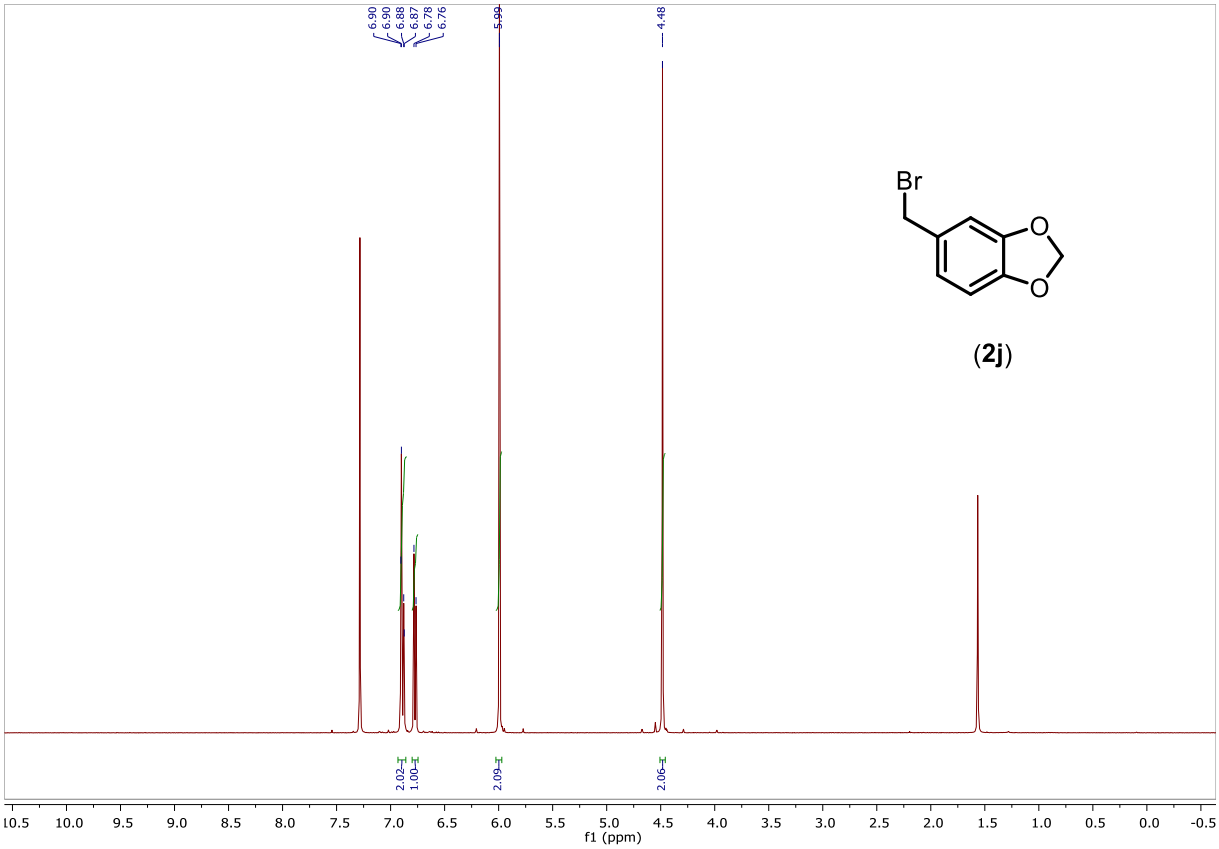
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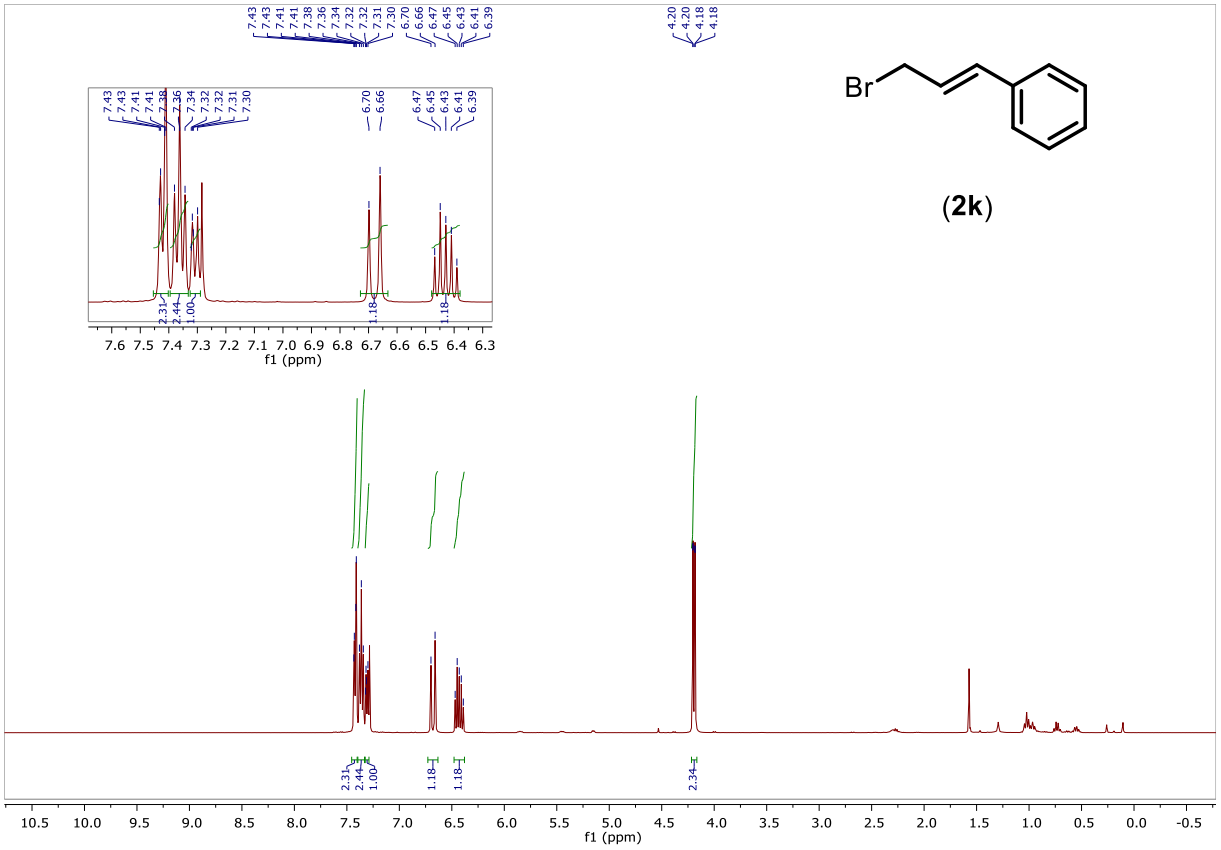
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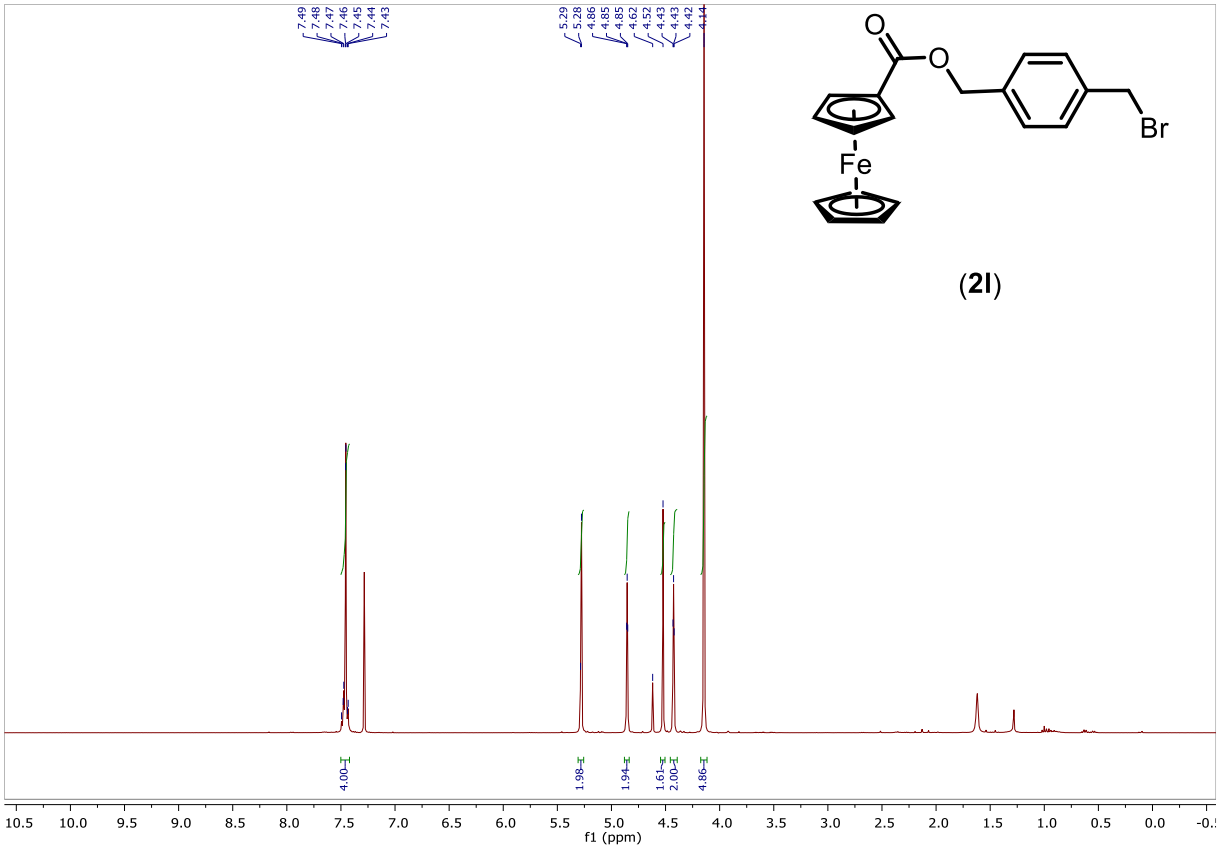
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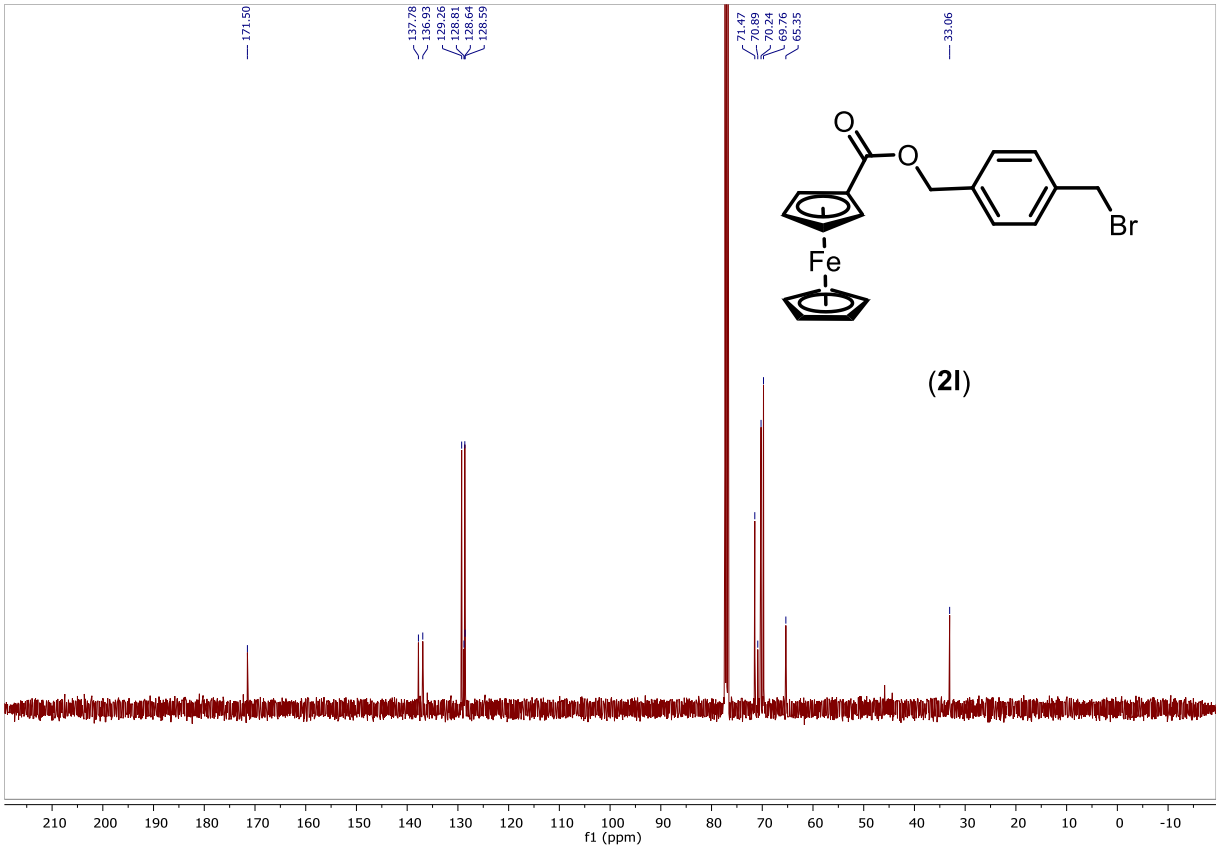
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Display Report

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Comment			

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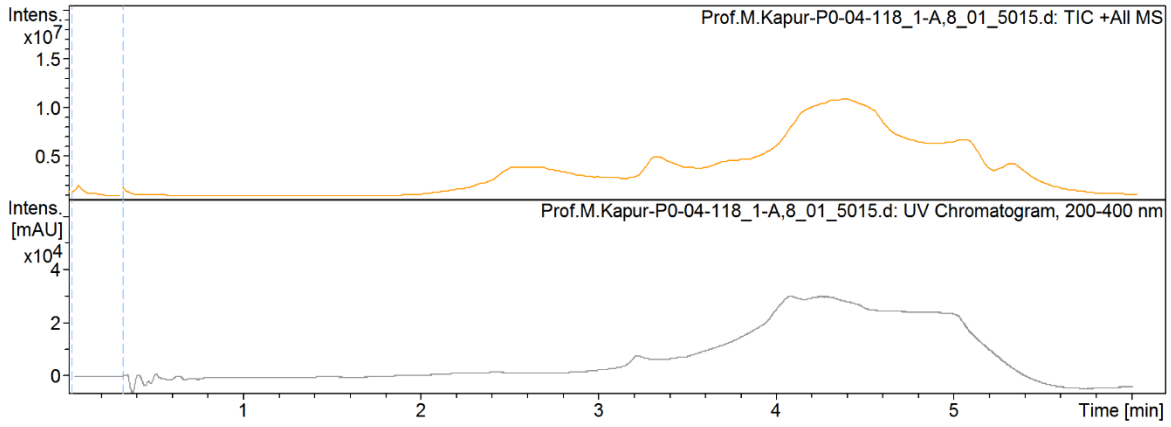

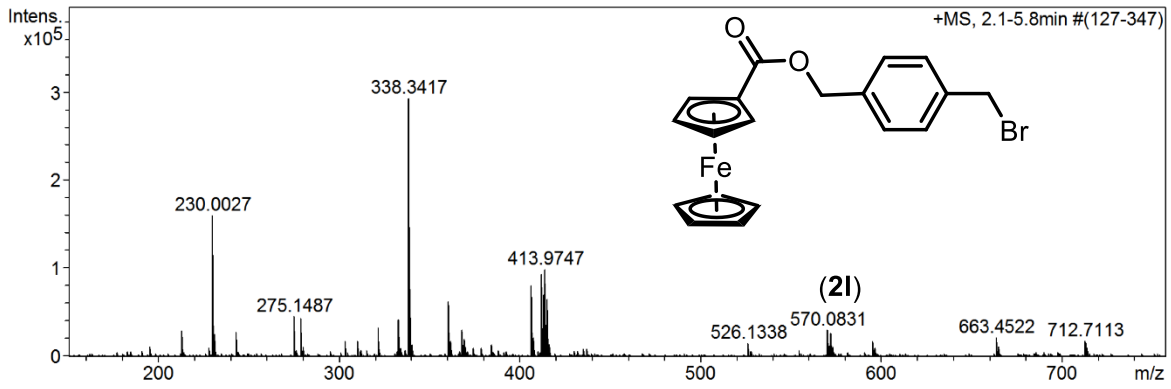

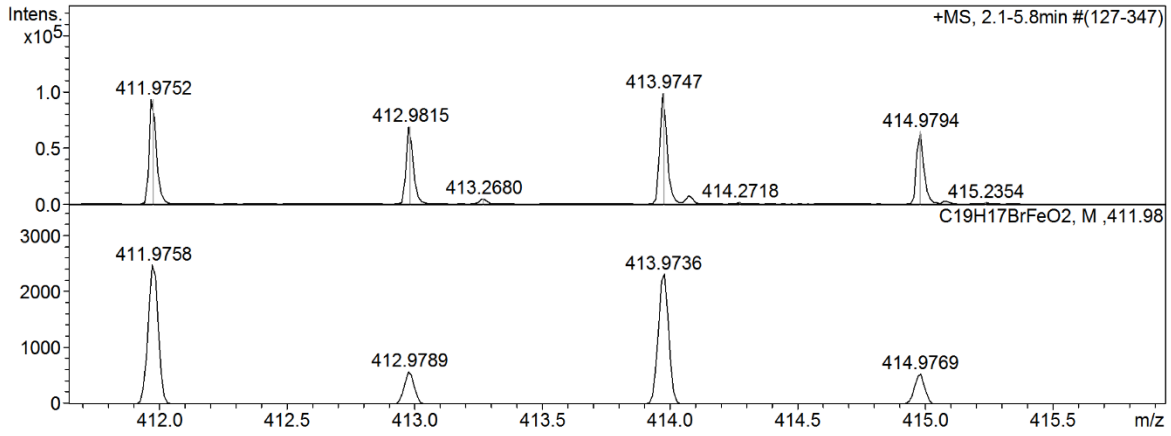

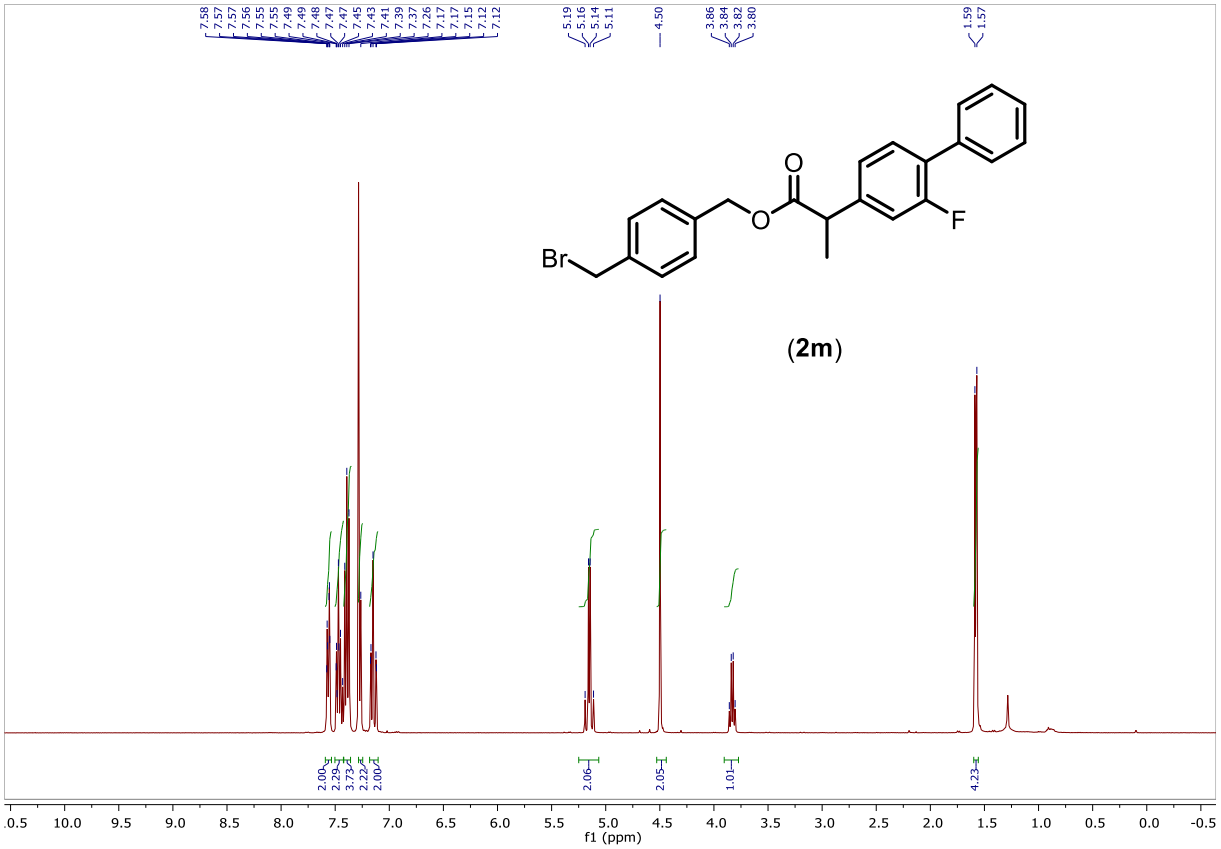
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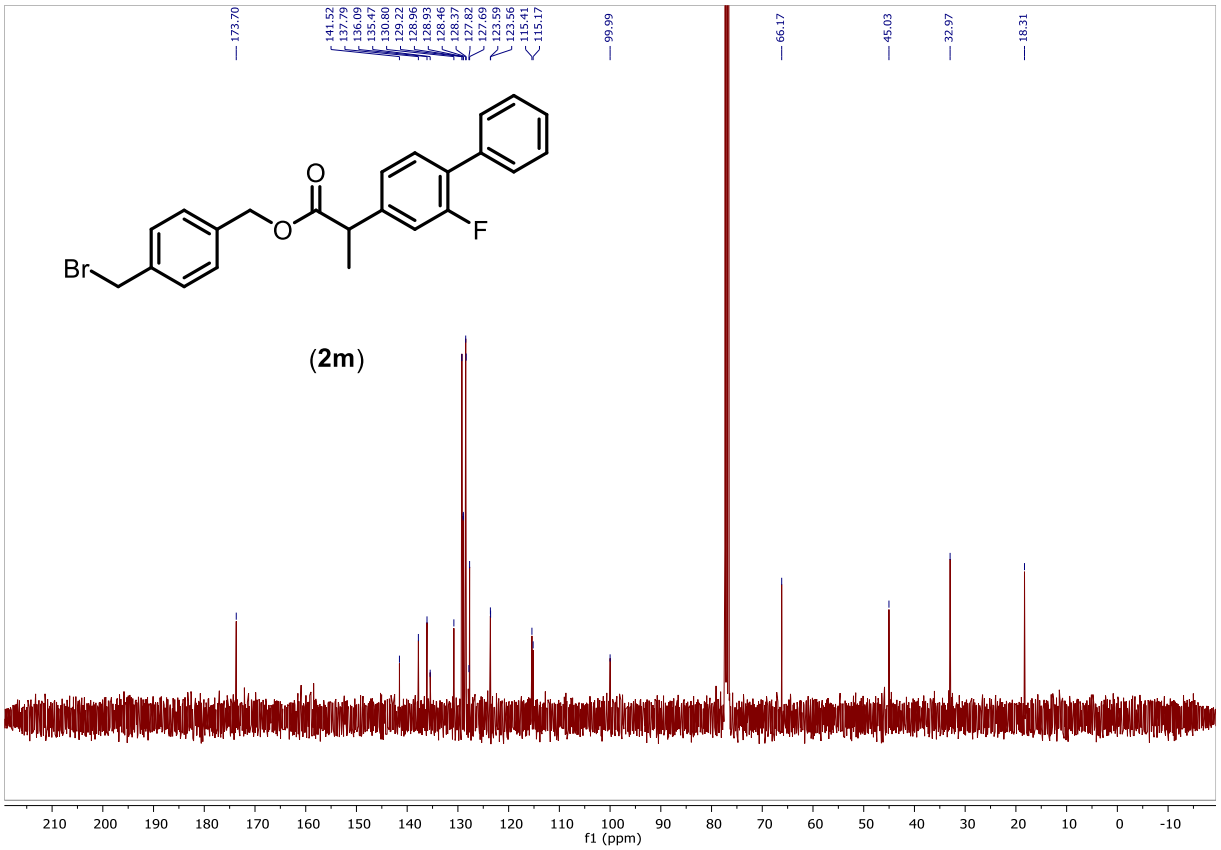
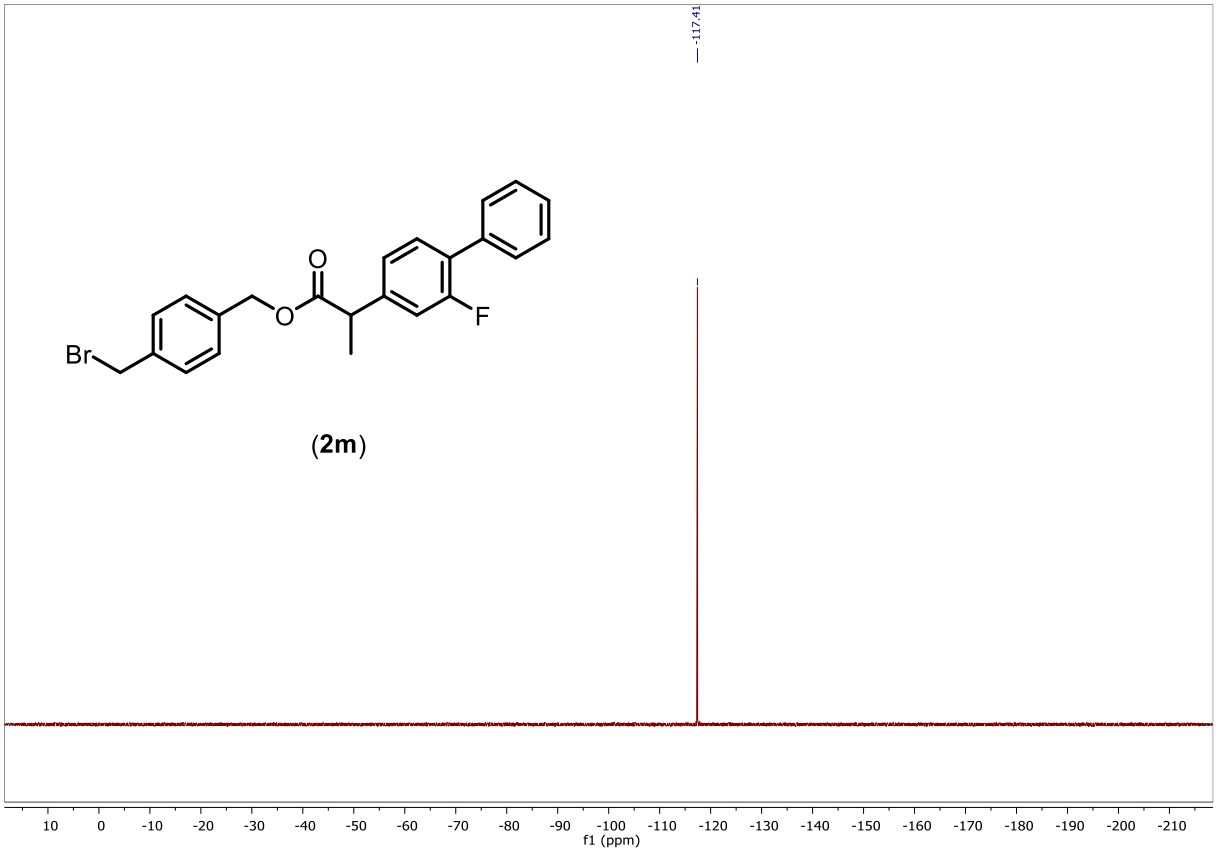
F
Br
(2m)
2.00
2.29
3.73
2.22
2.00
2.06
2.05
1.01
4.23
f1 (ppm)


173.70
141.52
137.79
136.09
135.47
130.80
129.22
128.96
128.93
128.46
128.37
127.82
127.69
123.59
123.56
115.41
115.17
99.99
66.17
45.03
32.97
18.31
O
O
F
Br
(2m)
f1 (ppm)


-117.41
O
O
F
Br
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

(**2m**)

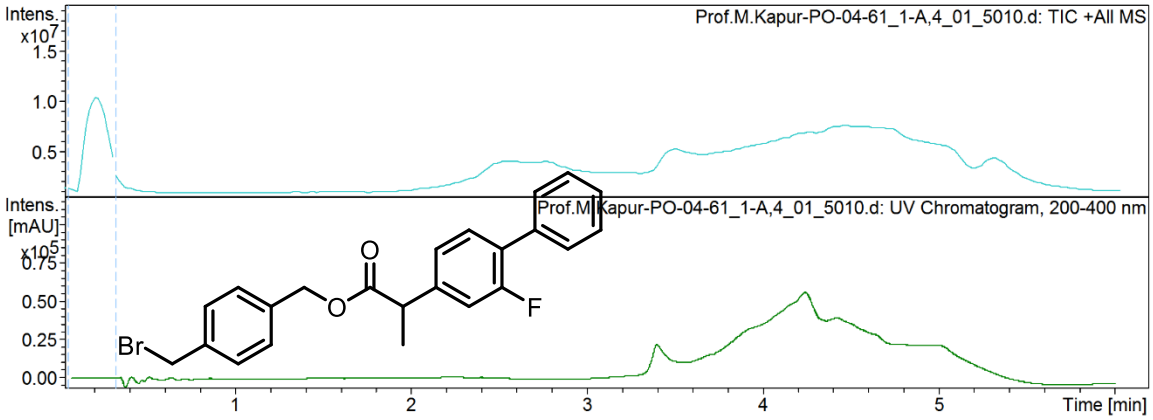
Display Report

Analysis Info

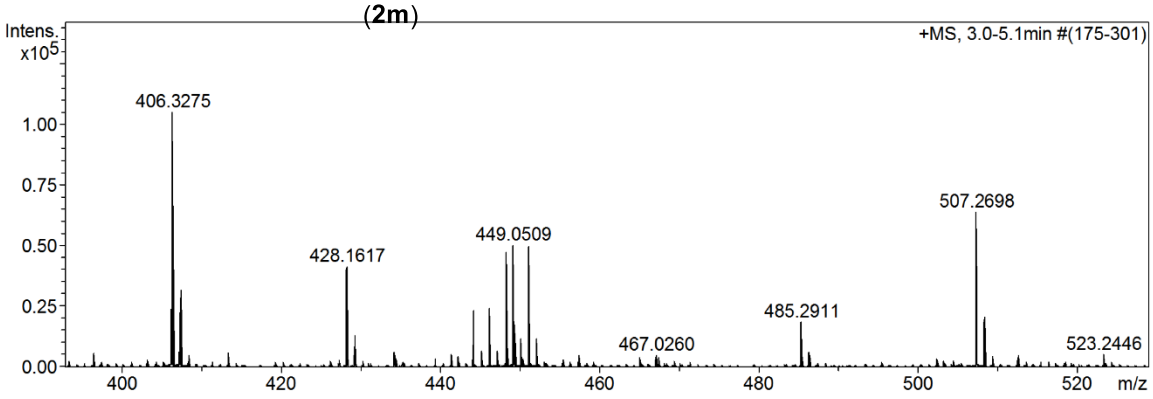
Acquisition Date	13-05-2024 12:00:47		
Analysis Name	D:\Data\USER DATA 2024\May-2024\13-may\Prof.M.Kapur-PO-04-61_1-A,4_01_5010.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-61	Instrument	micrOTOF-Q 10330
Comment			

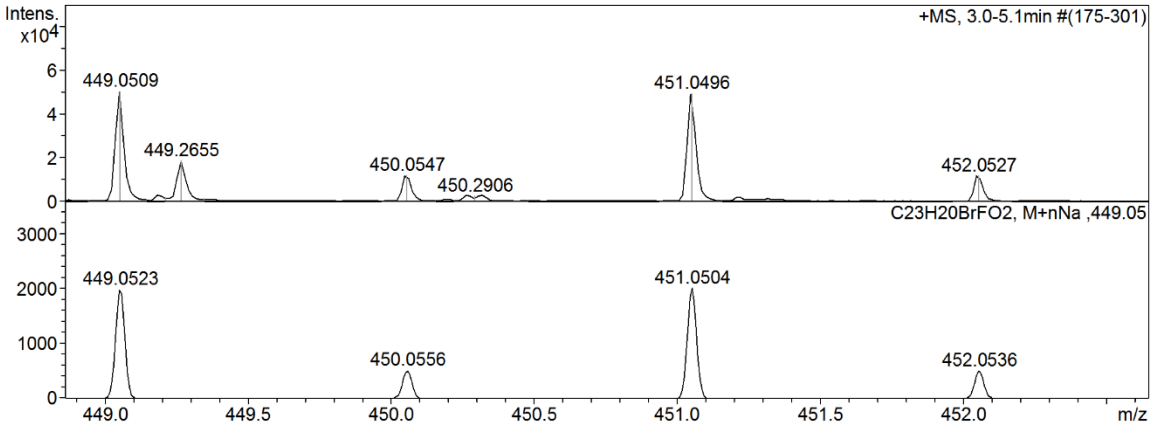
Acquisition Parameter

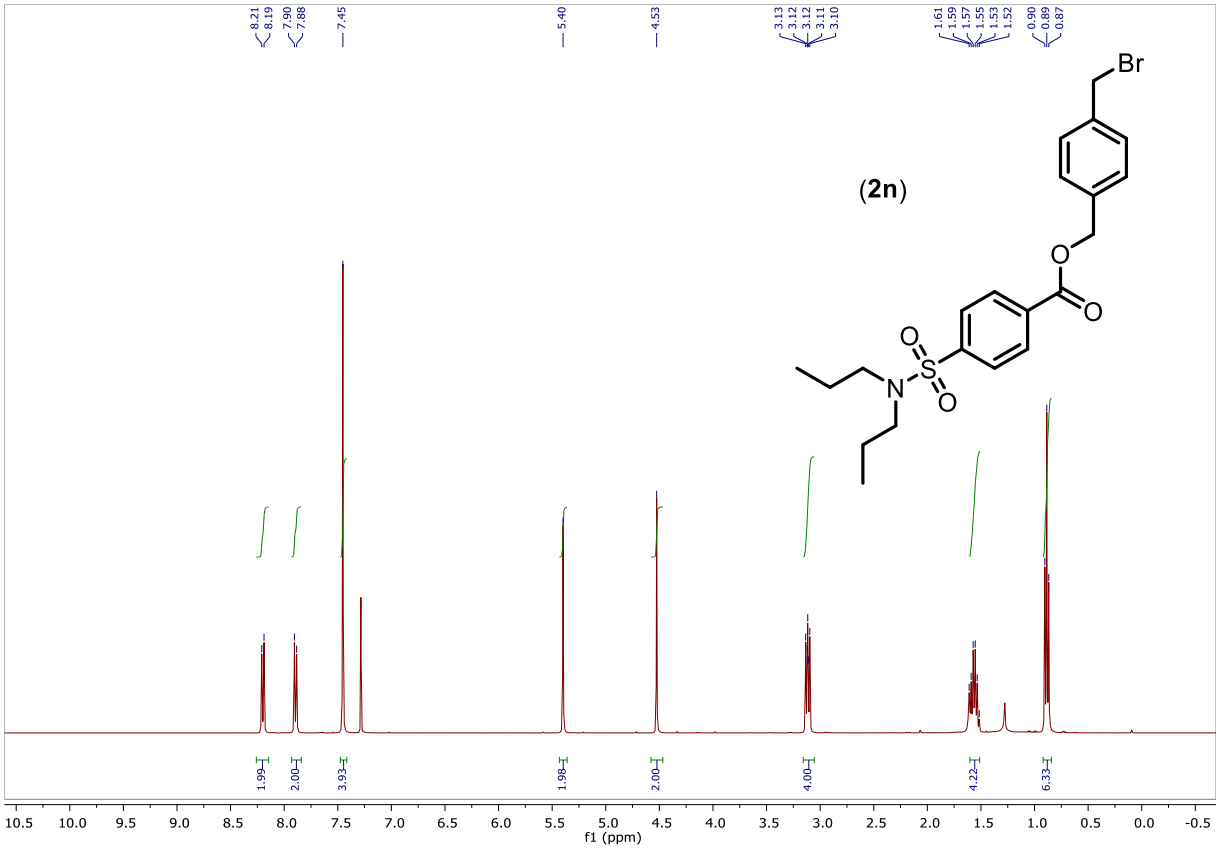
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	17.4 psi
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

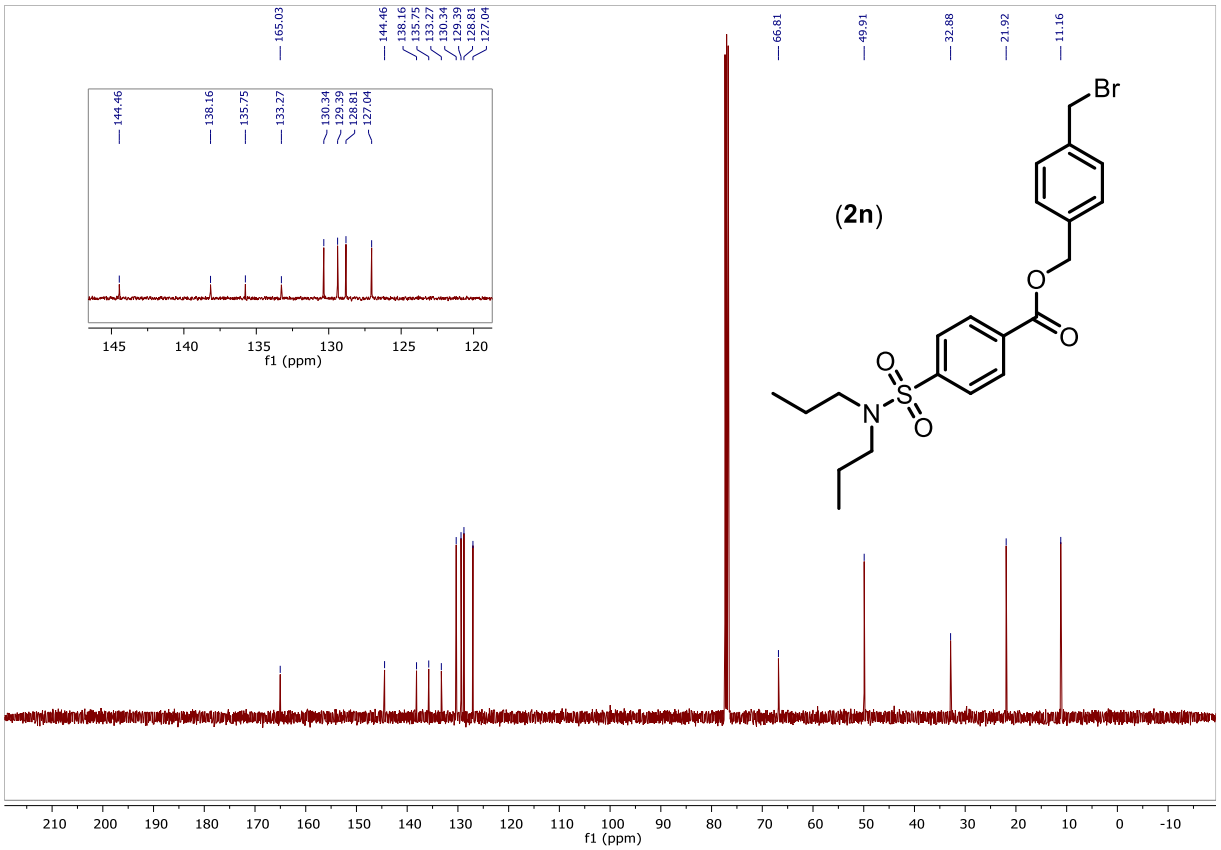


(**2m**)






8.21
8.19
7.90
7.88
7.45
5.40
4.53
3.13
3.12
3.12
3.11
3.10
1.61
1.59
1.57
1.55
1.53
1.52
0.90
0.89
0.87
Br
(2n)
O
O
O
S
O
N
1.99
2.00
3.93
1.98
2.00
4.00
4.22
6.33
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


165.03
144.46
138.16
135.75
133.27
130.34
129.39
128.81
127.04
66.81
49.91
32.88
21.92
11.16
Br
(2n)
O
O
O
S
O
N
145 140 135 130 125 120
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

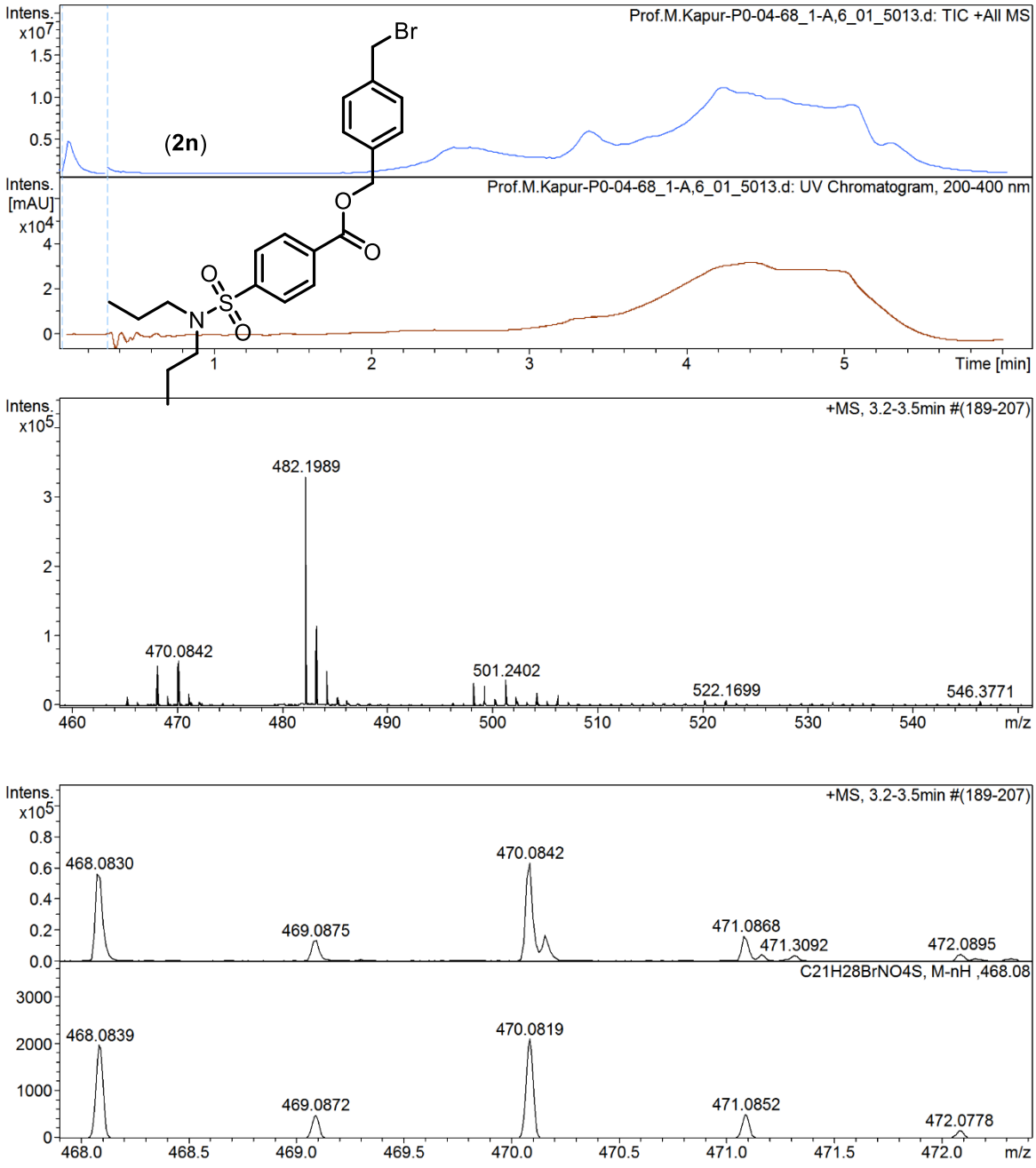
Display Report

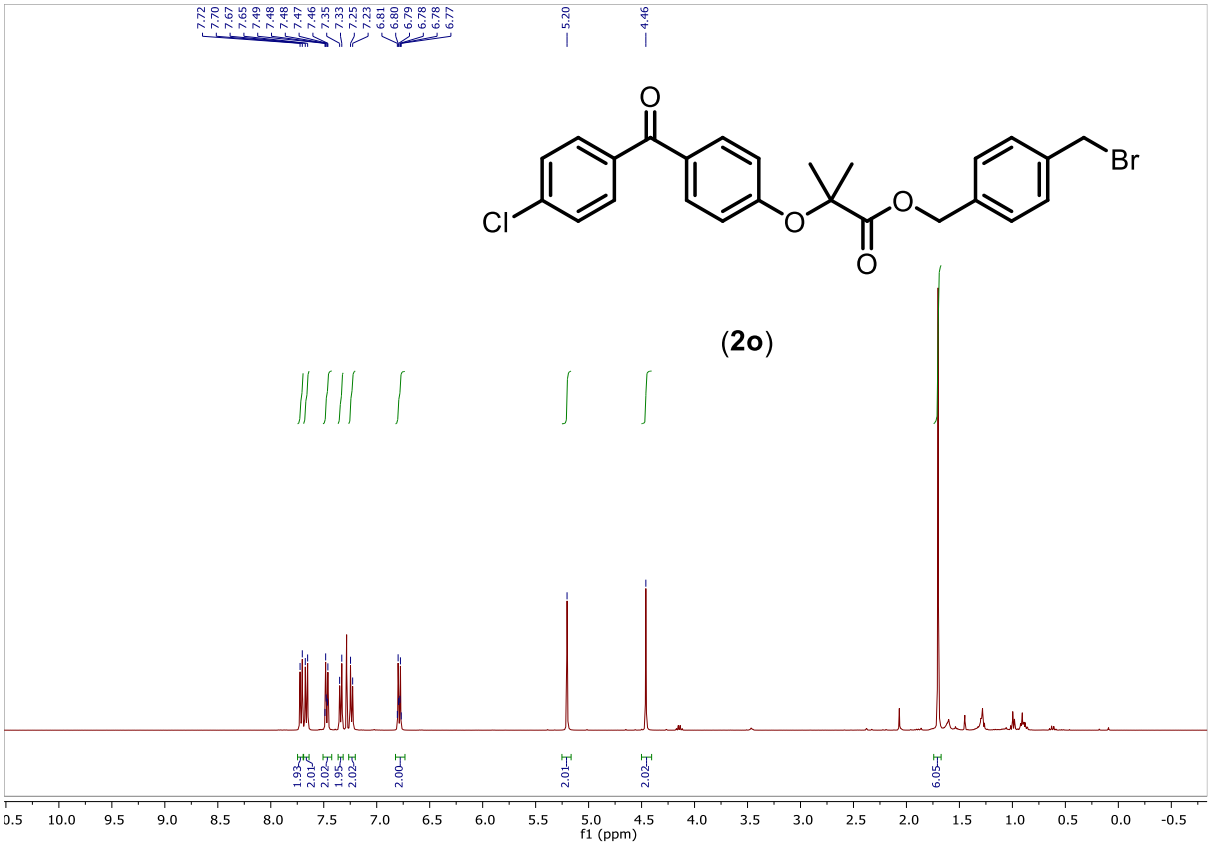
Analysis Info

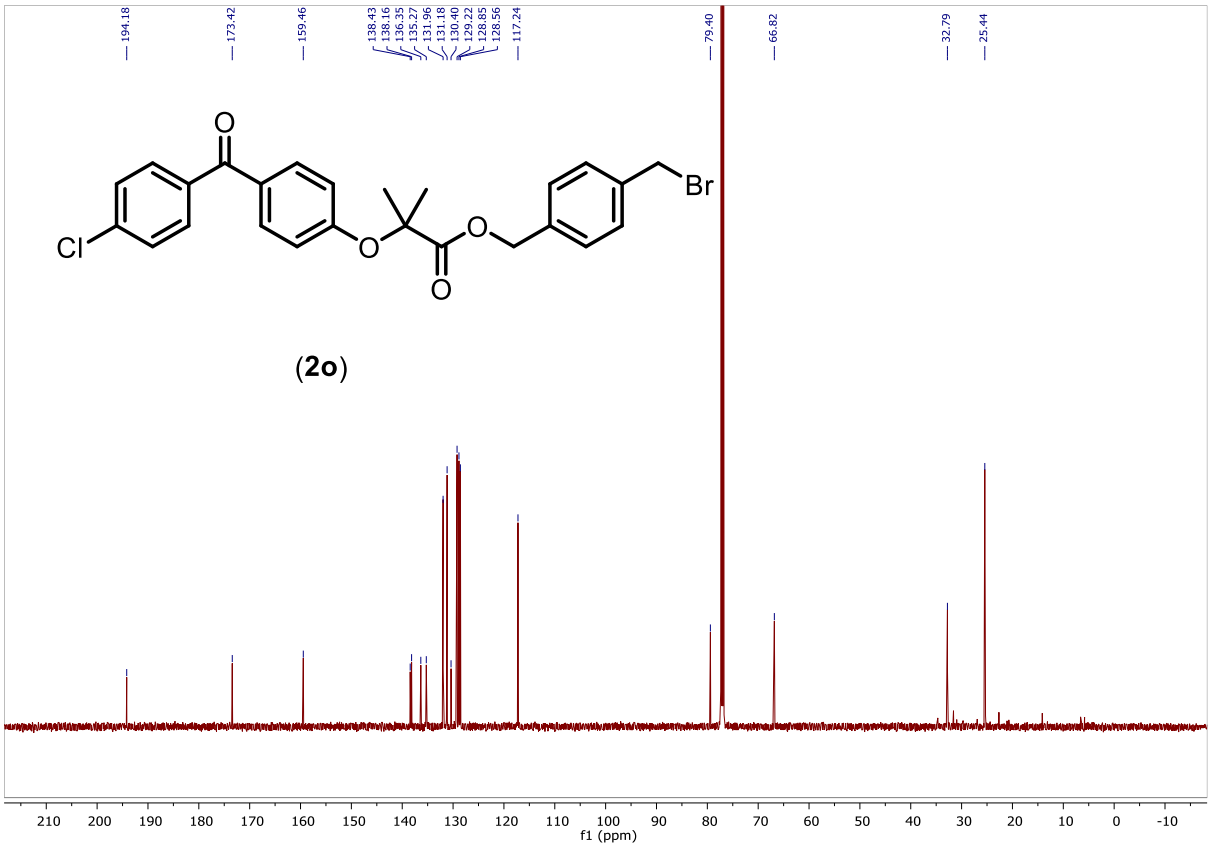
Analysis Name	D:\Data\USER DATA 2024\May-2024\13-may\Prof.M.Kapur-P0-04-68_1-A,6_01_5013.d	Acquisition Date	13-05-2024 12:22:29
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-P0-04-68	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	17.4 psi
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

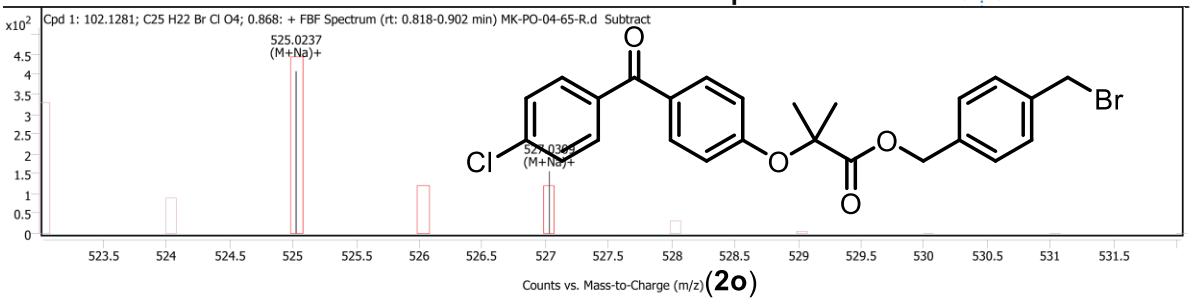



7.72
7.70
7.67
7.65
7.49
7.48
7.48
7.47
7.46
7.35
7.33
7.25
7.23
6.81
6.80
6.79
6.78
6.78
6.77
5.20
4.46
O
Cl
O
O
O
Br
(2o)
1.93
2.01
2.02
1.95
2.02
2.00
2.01
2.02
6.05
f1 (ppm)


194.18
173.42
159.46
138.43
138.16
136.35
135.27
131.96
131.18
130.40
129.22
128.85
128.56
117.24
79.40
66.82
32.79
25.44
O
Cl
O
O
O
Br
(2o)
f1 (ppm)

Custom Workflow Report

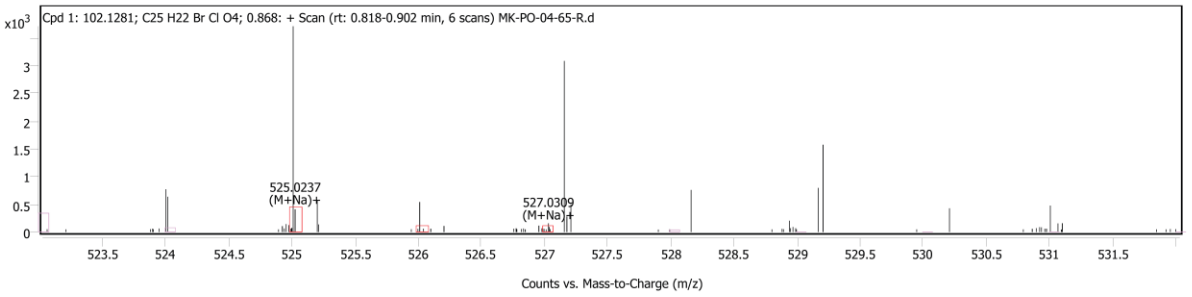
Agilent | Trusted Answers



(2o)

Spectrum Peaks

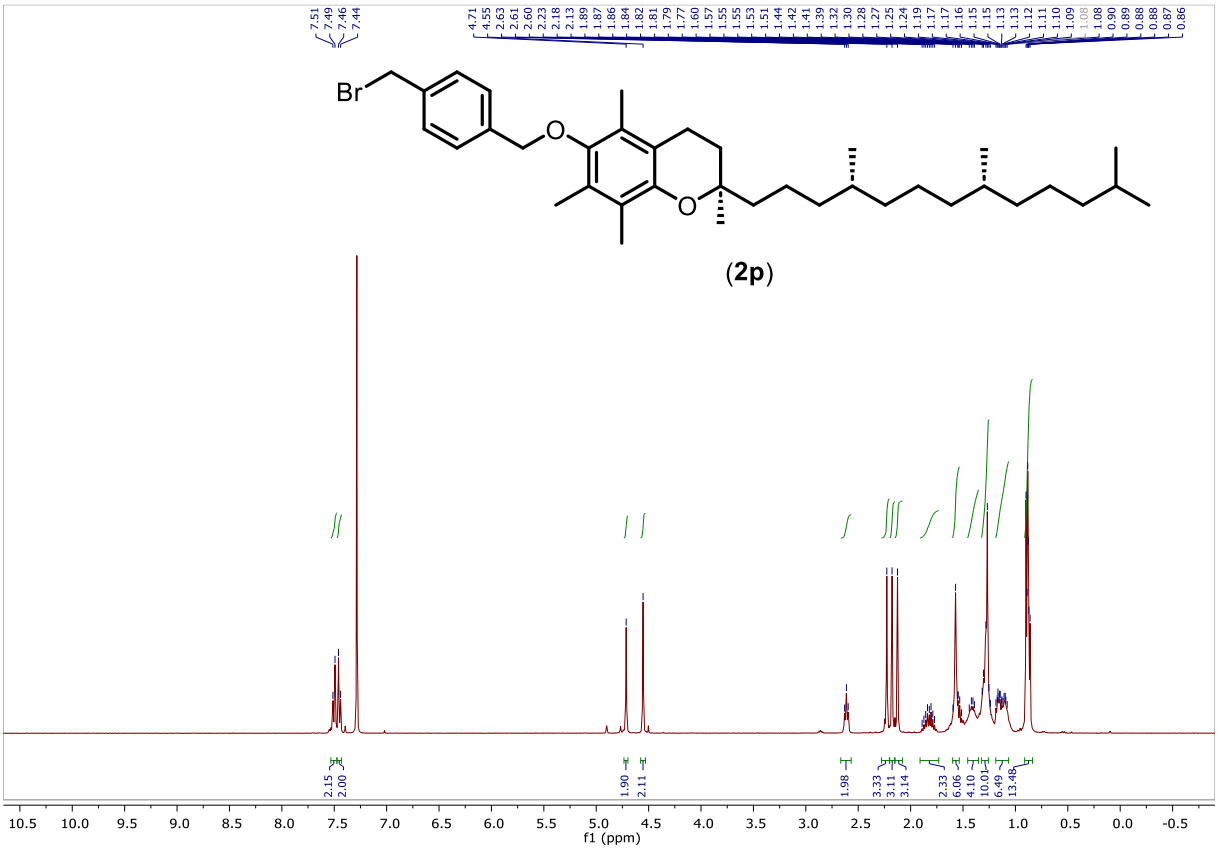
m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
525.0237	525.0262	-4.87	408	100.00	100.00	(M+Na)+	1
527.0309	527.0247	11.90	156	38.26	27.61	(M+Na)+	1



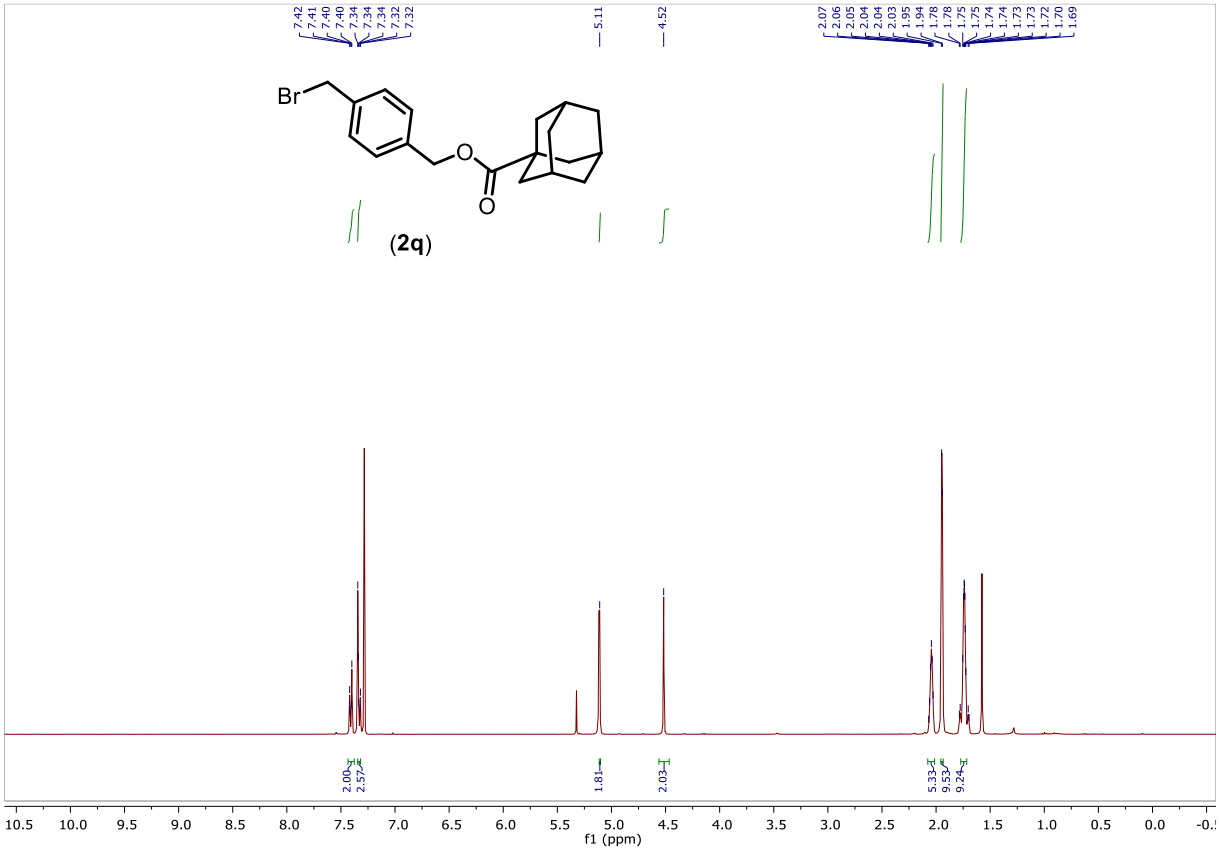
Spectrum Peaks

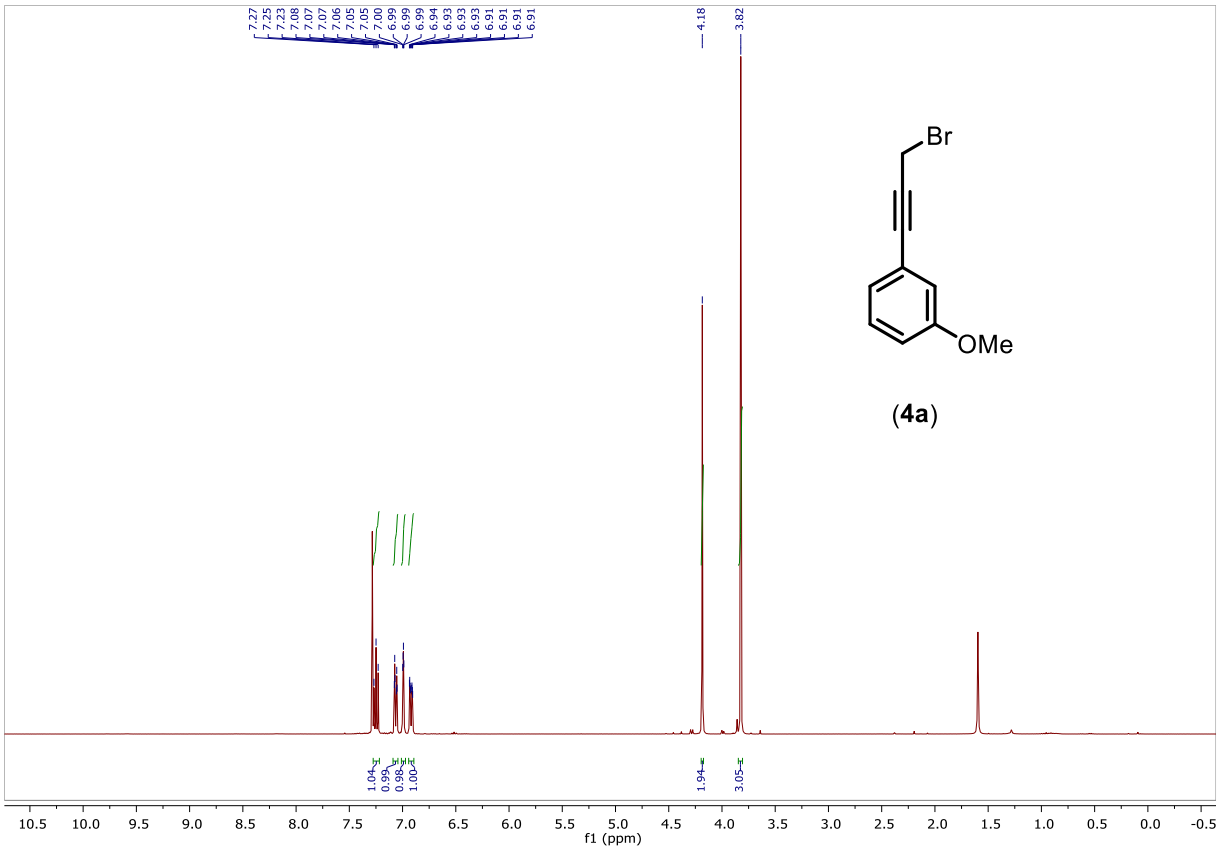
m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
525.0237	525.0262	-4.87	408	100.00	100.00	(M+Na)+	1
527.0309	527.0247	11.90	156	38.26	27.61	(M+Na)+	1

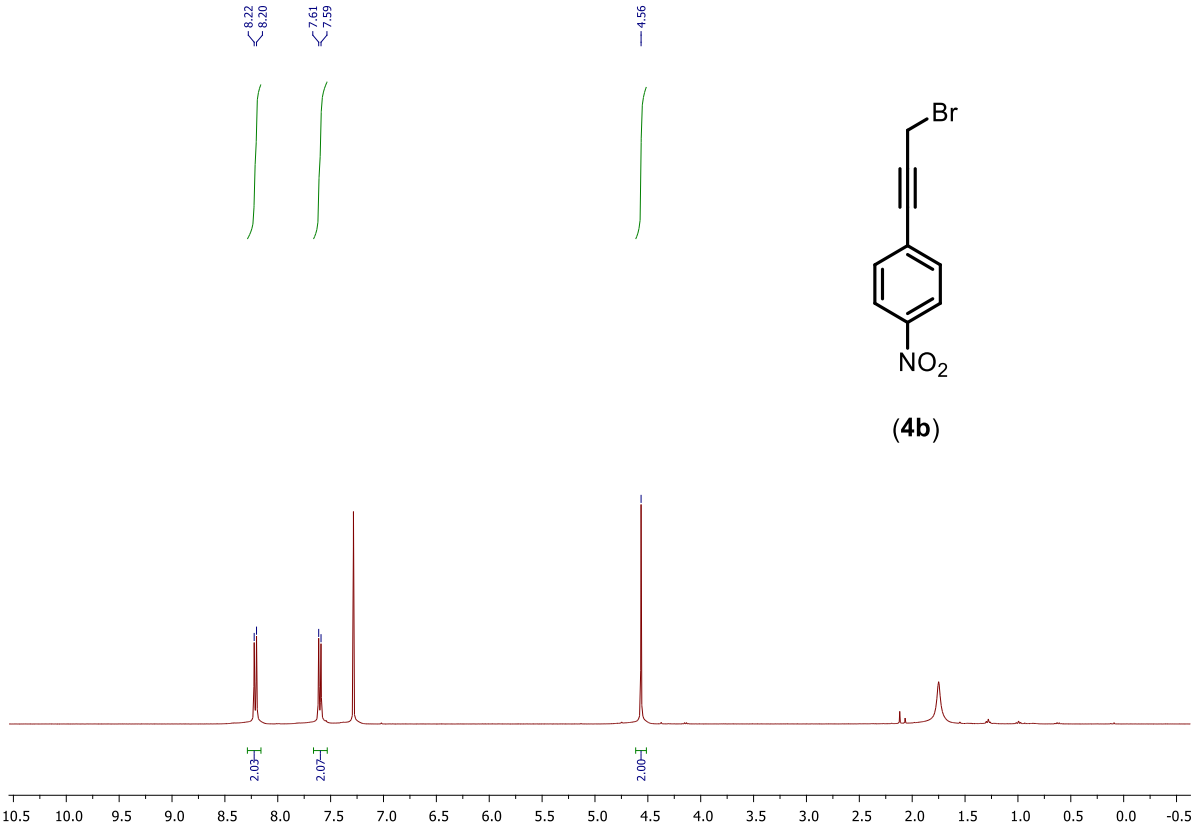
MassHunter Qual 10.0
(End of Report)



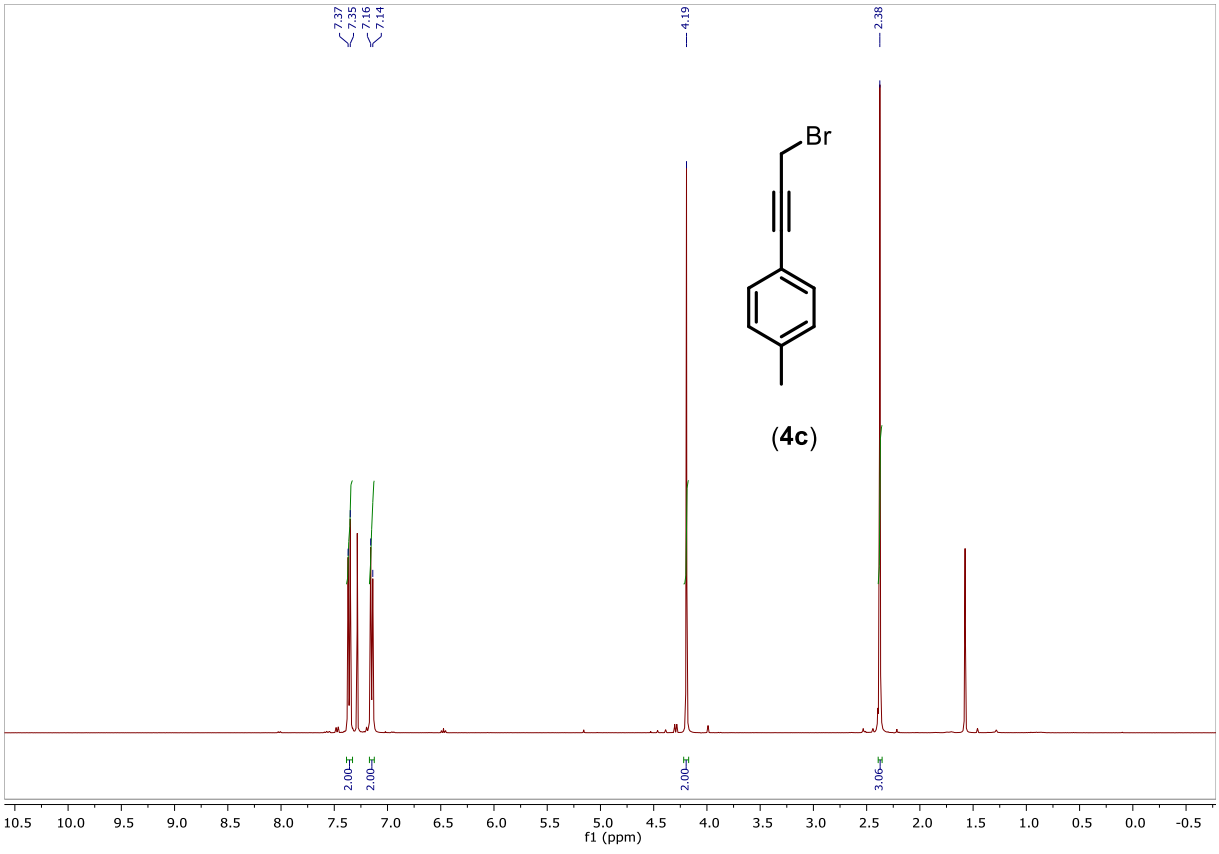
(2p)


Br
O
O
(2q)
f1 (ppm)

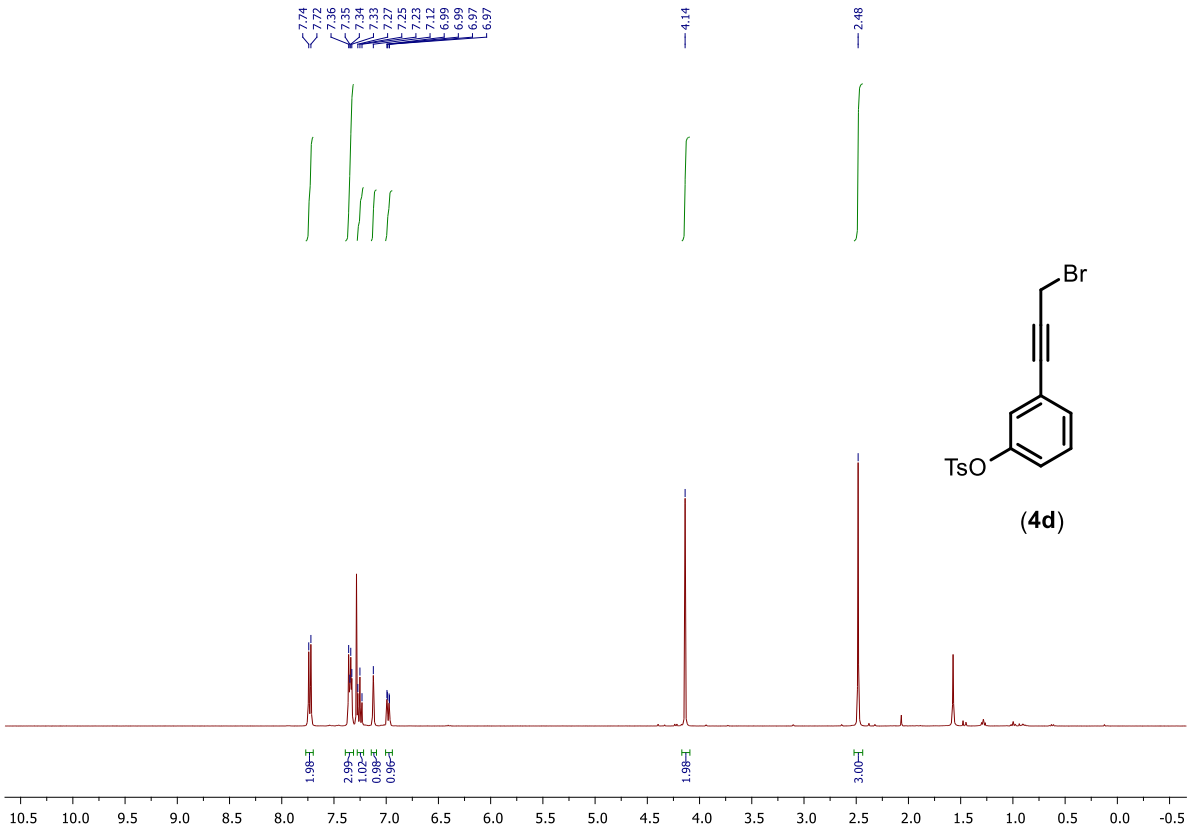

Br
OMe
(4a)
f1 (ppm)


8.22
8.20
7.61
7.59
4.56
Br
NO2
2.03
2.07
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

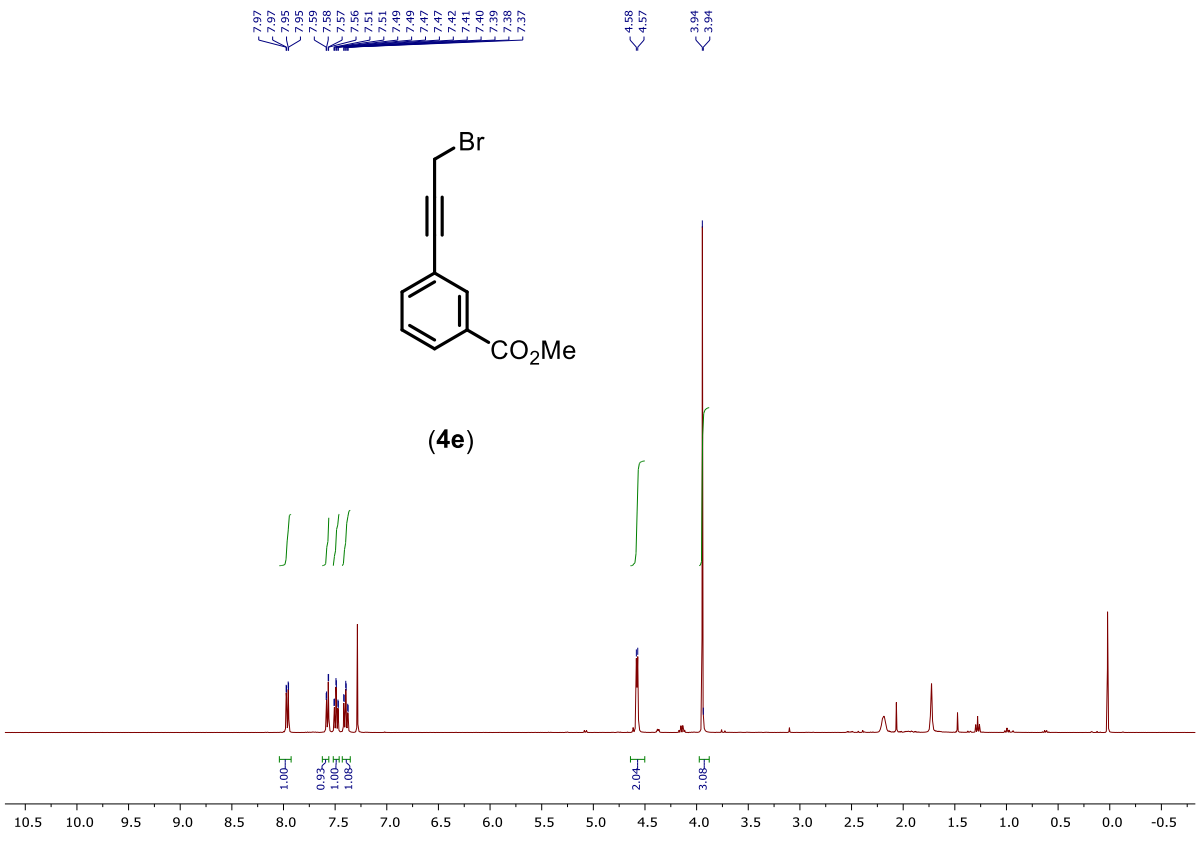
(**4b**)


7.37
7.35
7.16
7.14
4.19
2.38
Br
2.00
2.00
2.00
3.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

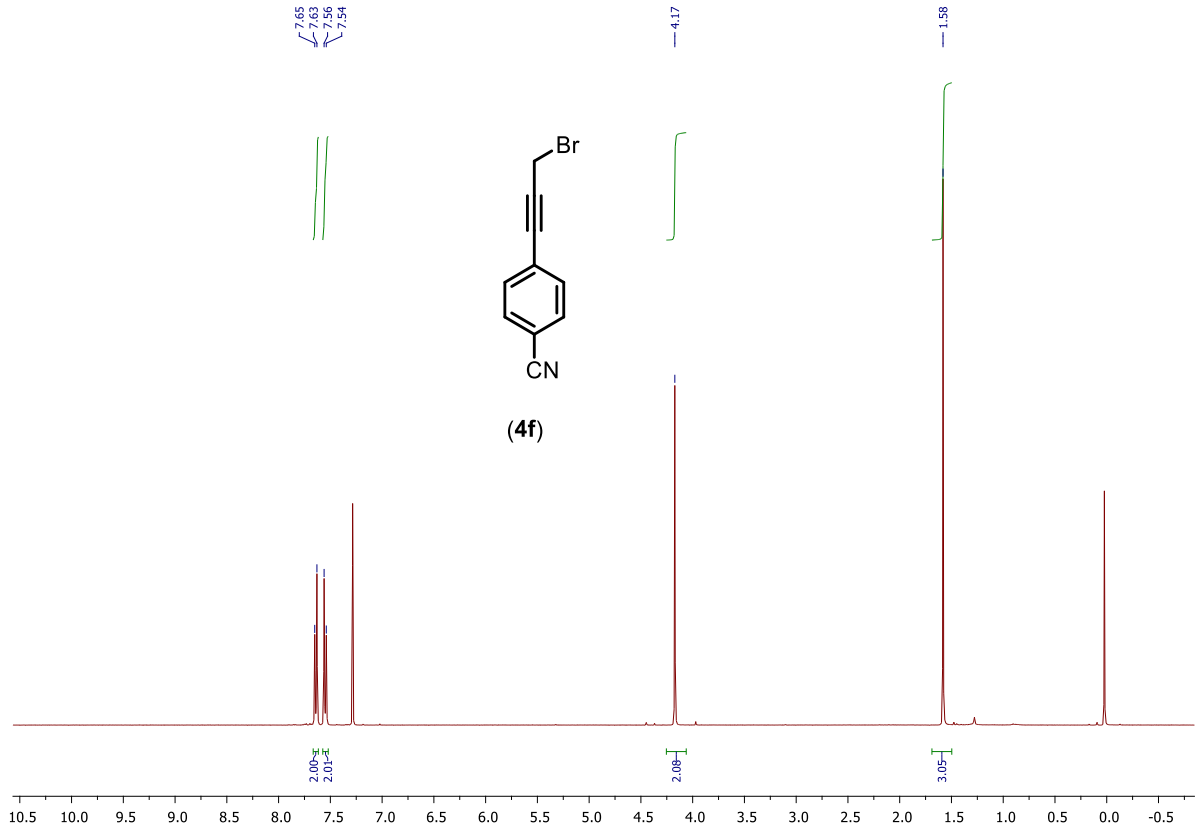
(**4c**)

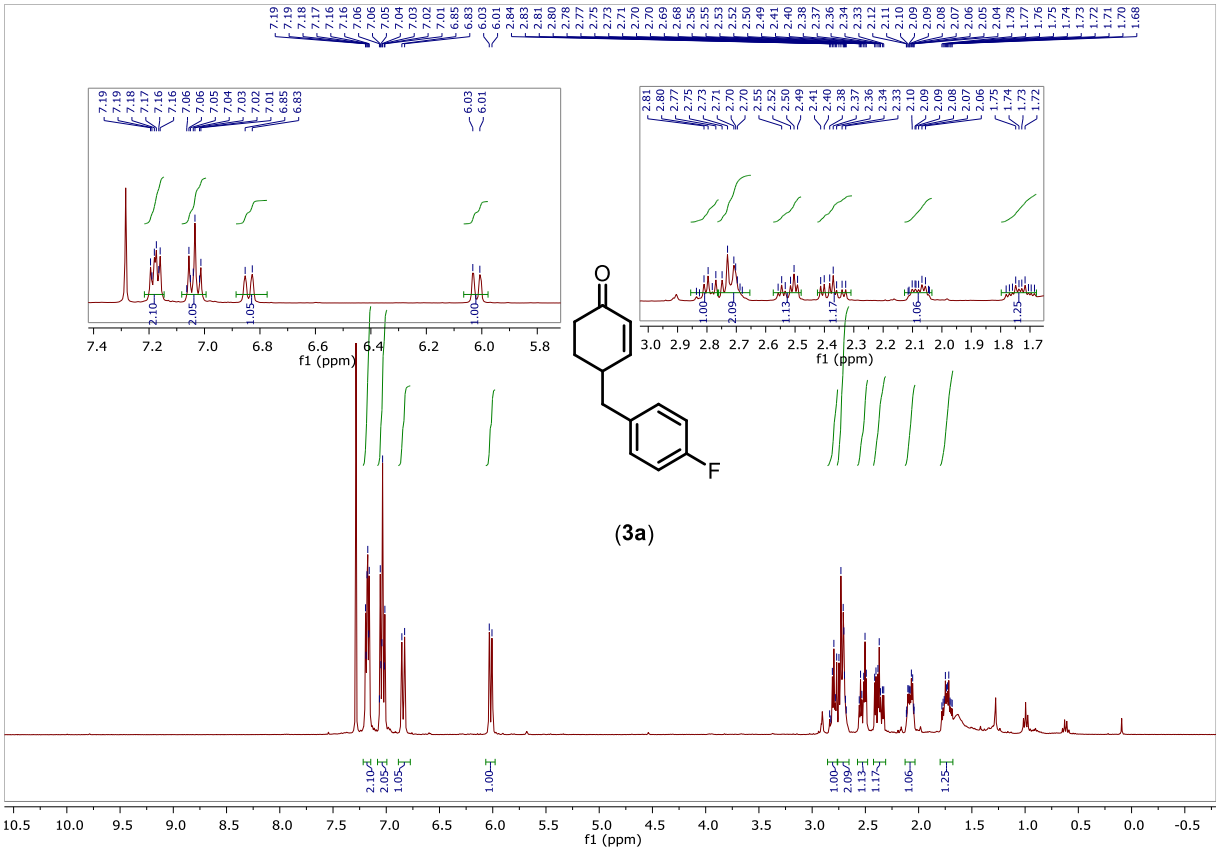

7.74
7.72
7.36
7.35
7.34
7.33
7.27
7.25
7.23
7.12
6.99
6.97
6.97
4.14
2.48
Br
TsO
1.98
2.99
1.02
0.98
0.96
1.98
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

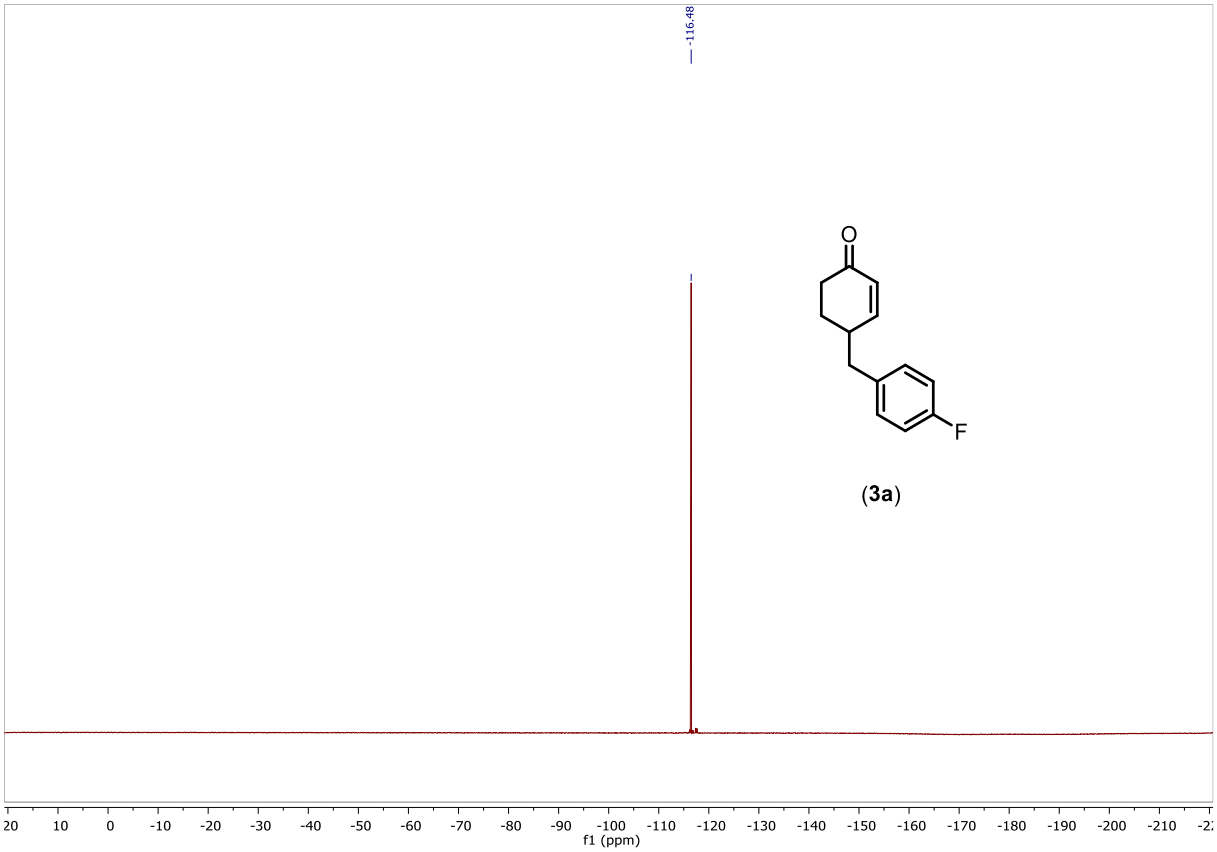
(**4d**)

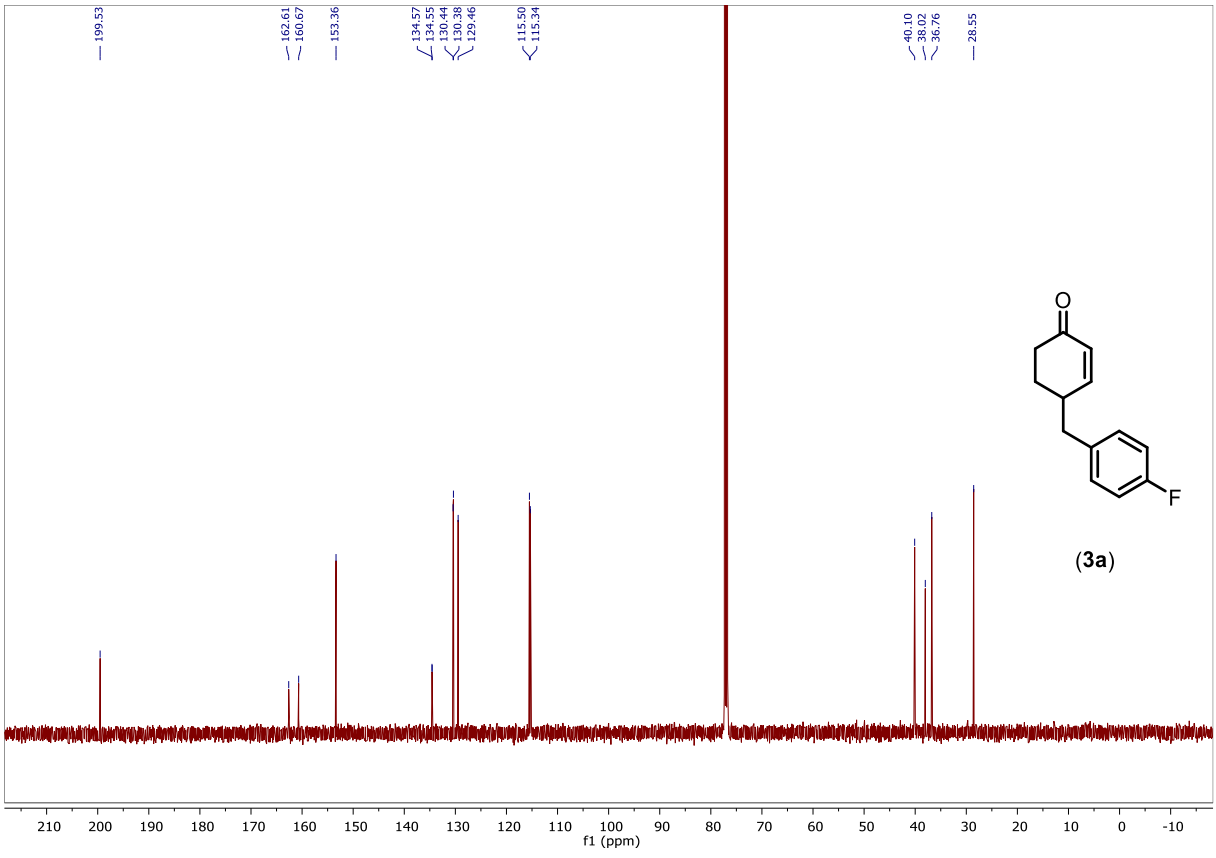

7.97
7.97
7.95
7.95
7.59
7.58
7.57
7.56
7.51
7.51
7.49
7.49
7.47
7.47
7.42
7.41
7.40
7.39
7.38
7.37
4.58
4.57
3.94
3.94
Br
CO2Me
1.00
0.93
1.00
1.08
2.04
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

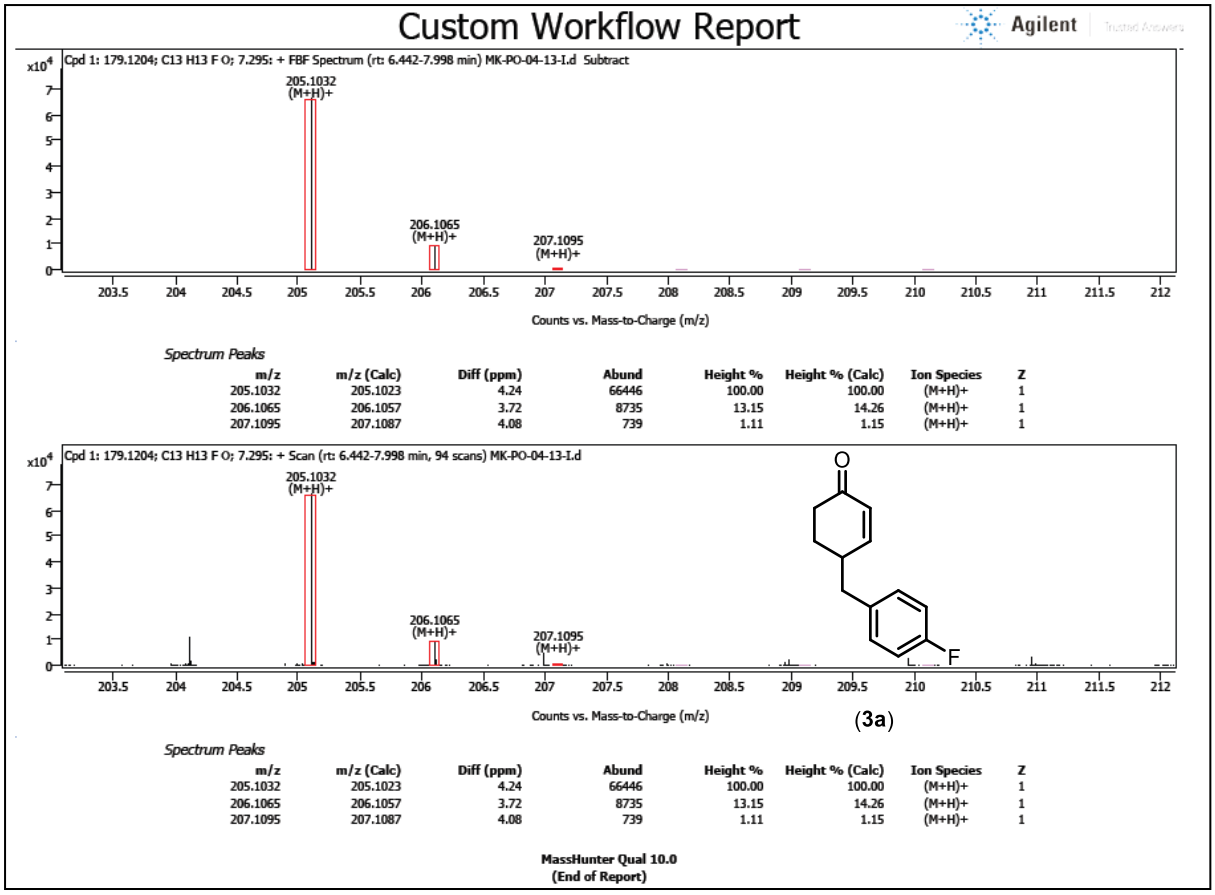
(**4e**)

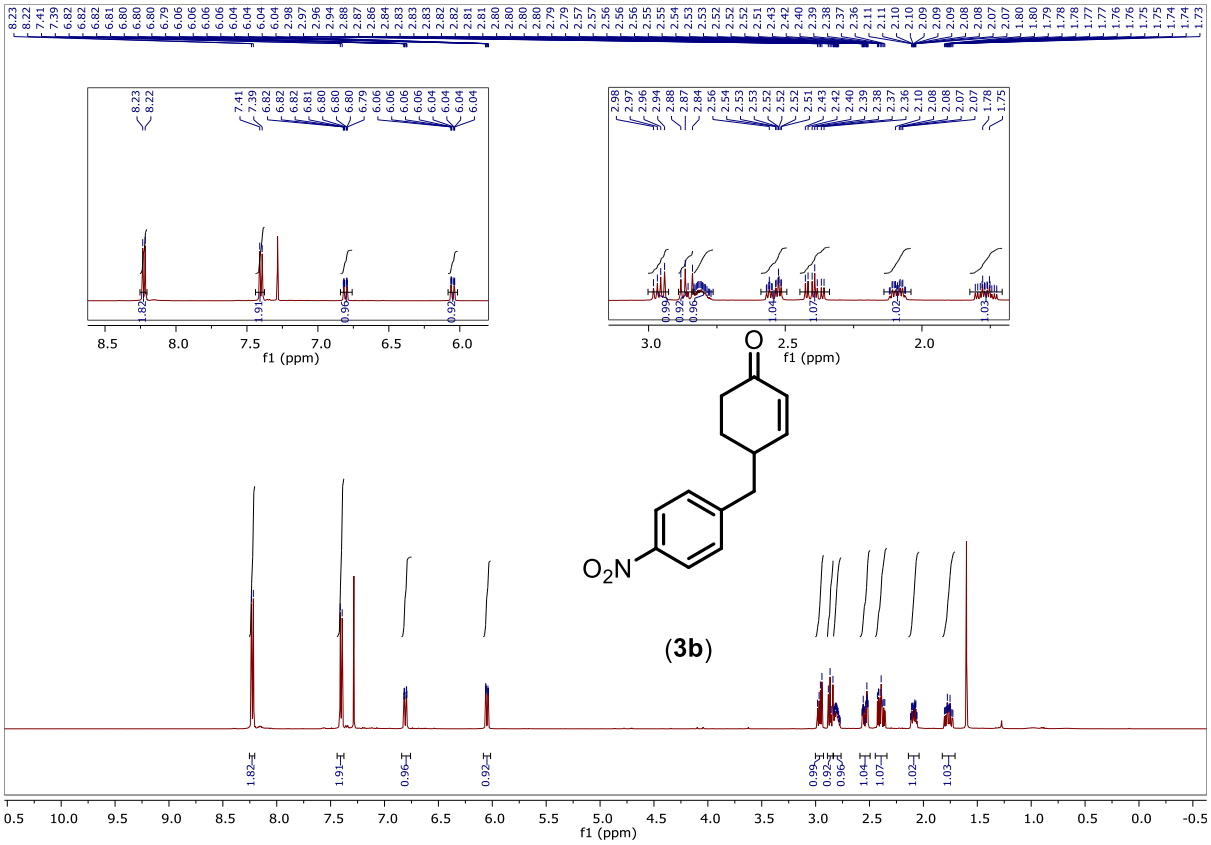

Br
CN
(4f)

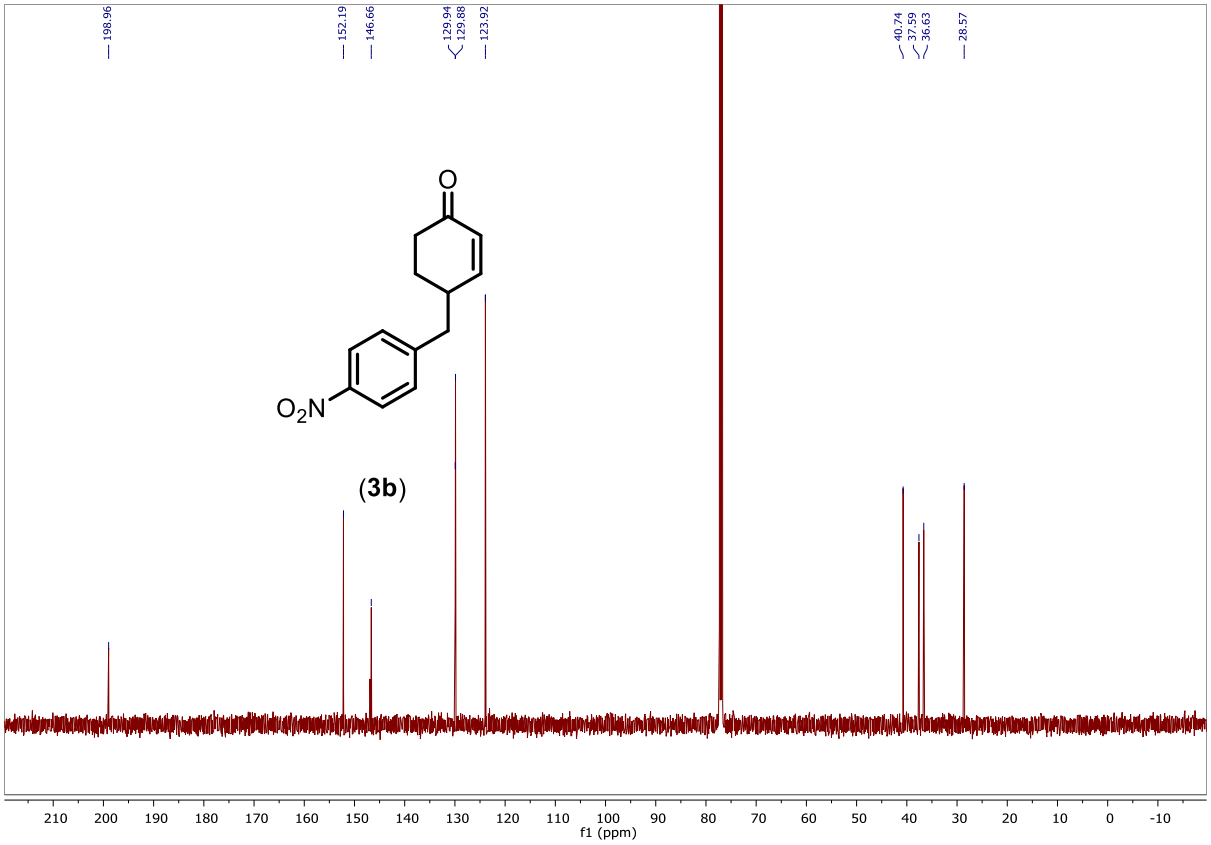

O
F
(3a)
f1 (ppm)


-116.48
O
F
(3a)
f1 (ppm)


199.53
162.61
160.67
153.36
134.57
134.55
130.44
130.38
129.46
115.50
115.34
40.10
38.02
36.76
28.55
O
F
(3a)
f1 (ppm)


Custom Workflow Report
Agilent
Cpd 1: 179.1204; C13 H13 F O; 7.295: + FBF Spectrum (rt: 6.442-7.998 min) MK-PO-04-13-I.d Subtract
205.1032 (M+H)+
206.1065 (M+H)+
207.1095 (M+H)+
Counts vs. Mass-to-Charge (m/z)
Spectrum Peaks
m/z | m/z (Calc) | Diff (ppm) | Abund | Height % | Height % (Calc) | Ion Species | Z
205.1032 | 205.1023 | 4.24 | 66446 | 100.00 | 100.00 | (M+H)+ | 1
206.1065 | 206.1057 | 3.72 | 8735 | 13.15 | 14.26 | (M+H)+ | 1
207.1095 | 207.1087 | 4.08 | 739 | 1.11 | 1.15 | (M+H)+ | 1
Cpd 1: 179.1204; C13 H13 F O; 7.295: + Scan (rt: 6.442-7.998 min, 94 scans) MK-PO-04-13-I.d
(3a)
MassHunter Qual 10.0
(End of Report)


f1 (ppm)
(3b)


198.96
152.19
146.66
129.94
129.88
123.92
40.74
37.59
36.63
28.57
O
O2N
(3b)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

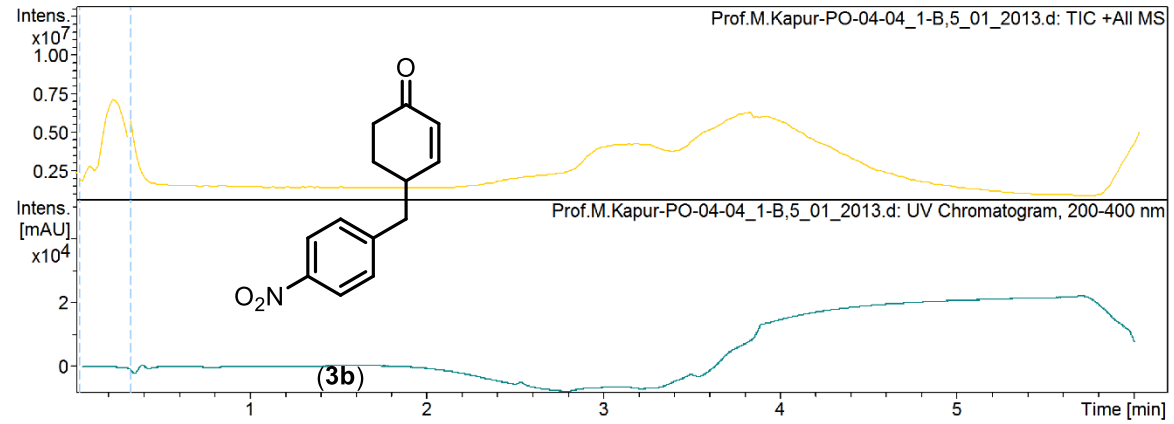
Display Report

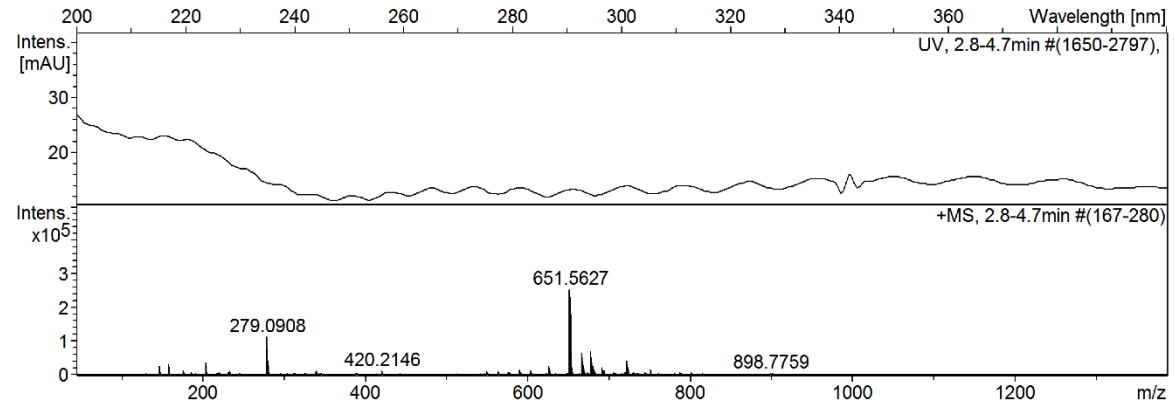
Analysis Info

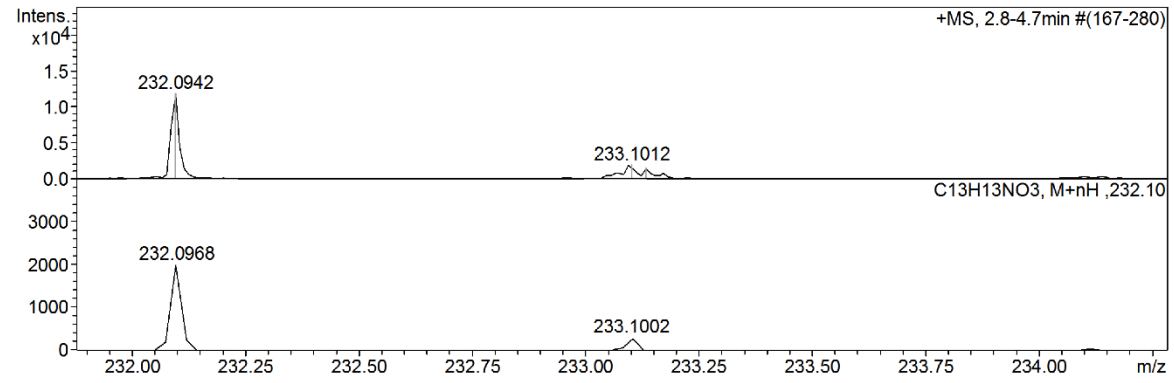
Acquisition Date	21-06-2023 12:51:30		
Analysis Name	D:\Data\USER DATA 2023\June\21-june\Prof.M.Kapur-PO-04-04_1-B,5_01_2013.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-04	Instrument	micrOTOF-Q 10330
Comment			

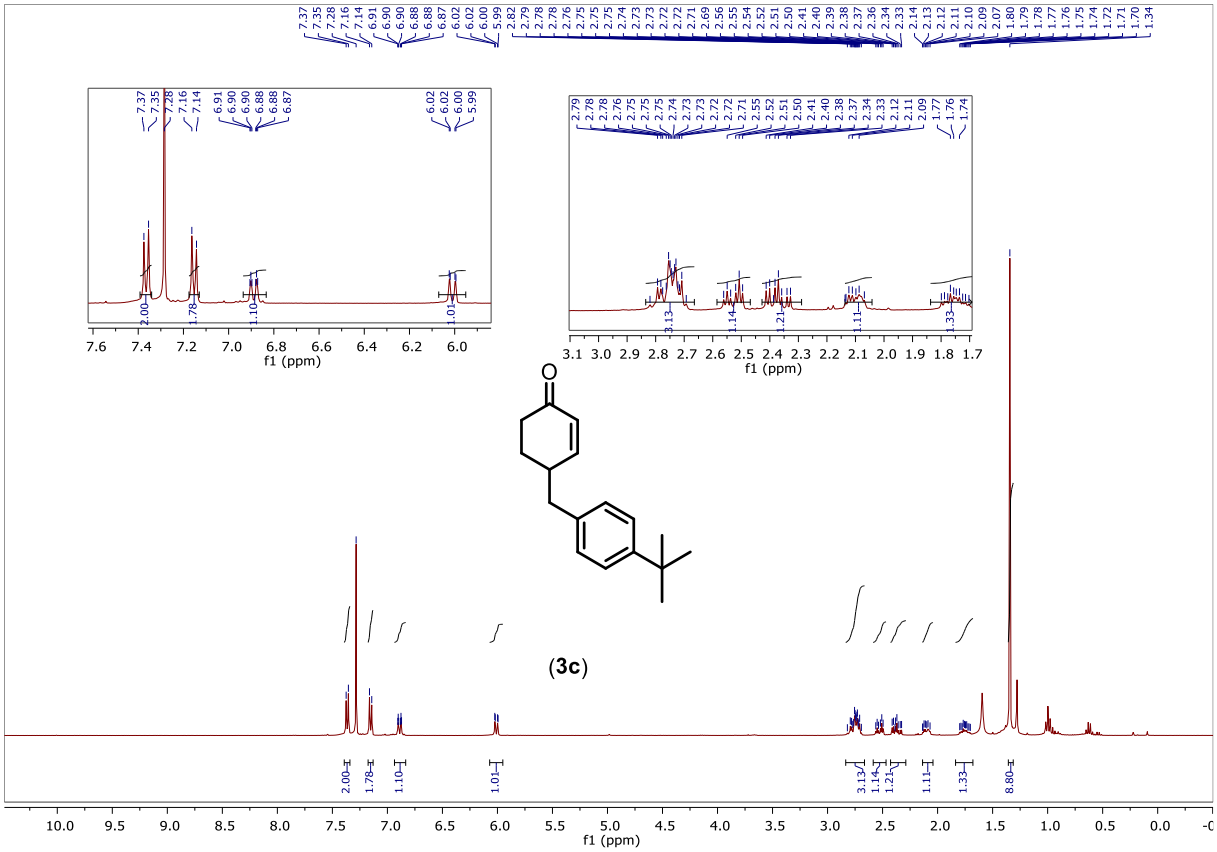
Acquisition Parameter

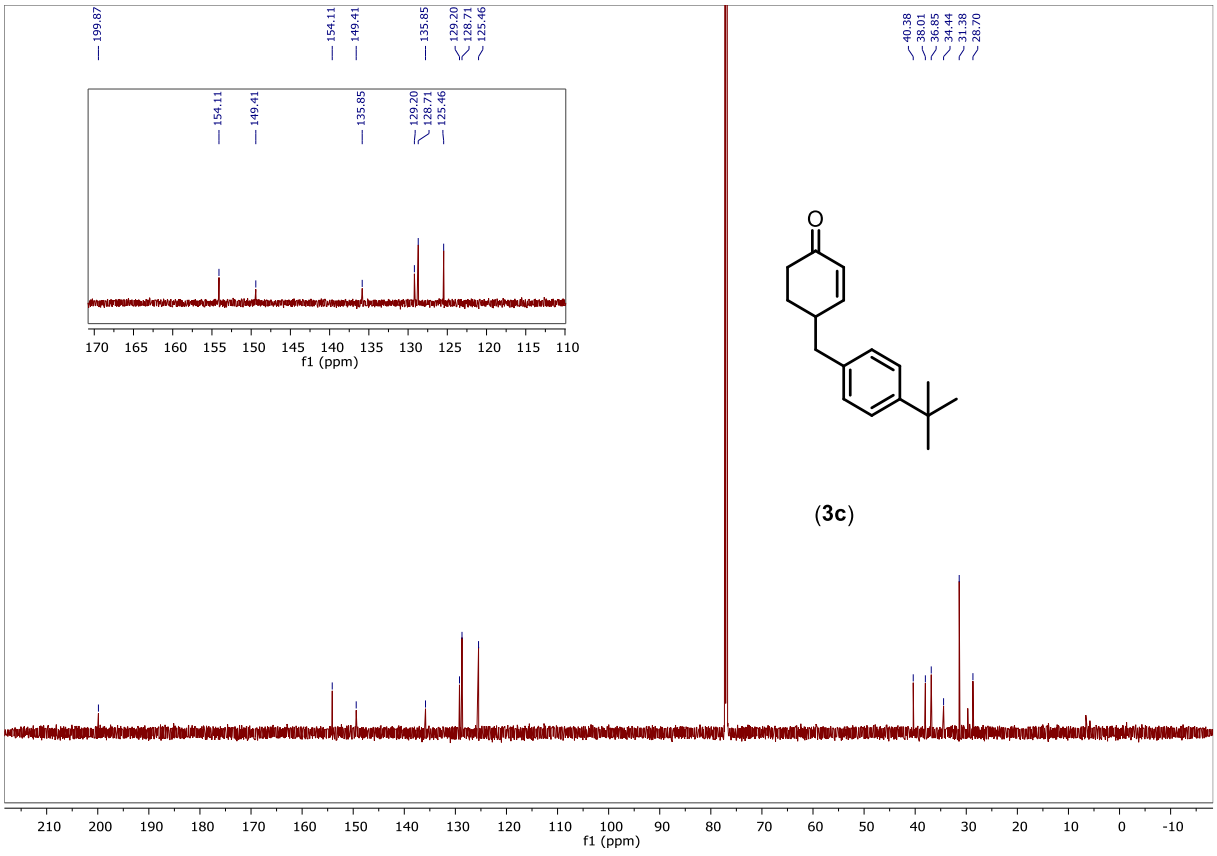
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








(3c)
f1 (ppm)


(3c)
f1 (ppm)

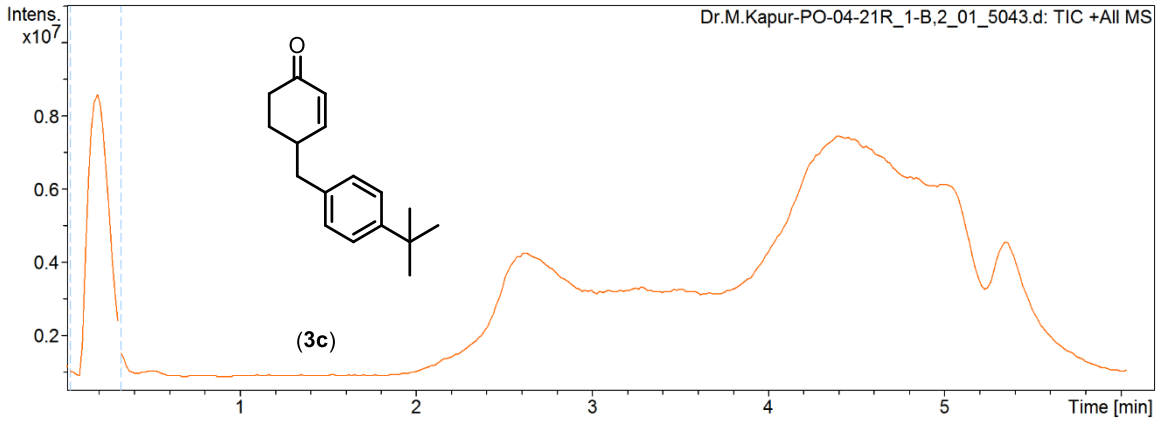
Display Report

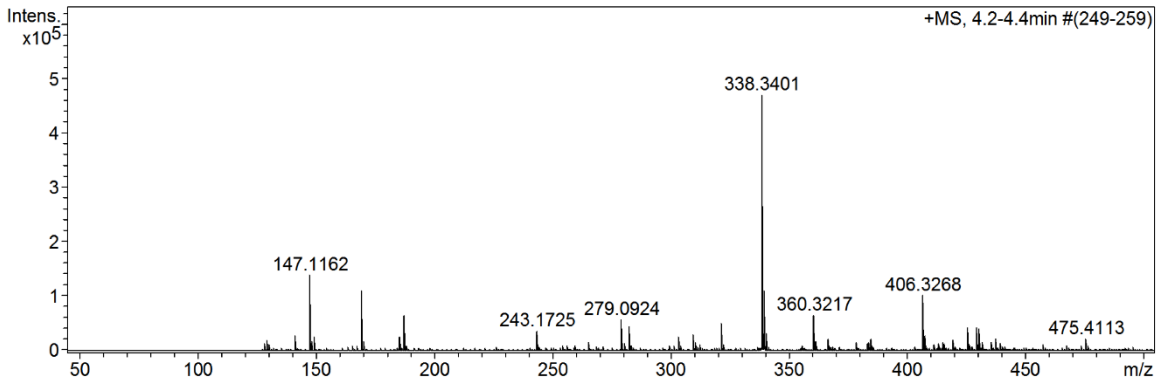
Analysis Info

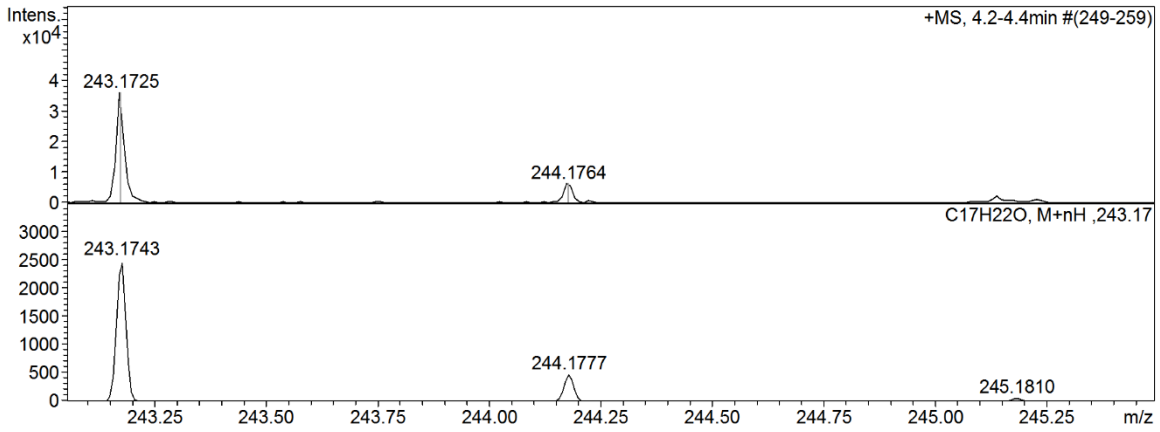
Acquisition Date	14-05-2024 13:26:27		
Analysis Name	D:\Data\USER DATA 2024\May-2024\14-may\Dr.M.Kapur-PO-04-21R_1-B,2_01_5043.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Dr.M.Kapur-PO-04-21R	Instrument	micrOTOF-Q 10330
Comment			

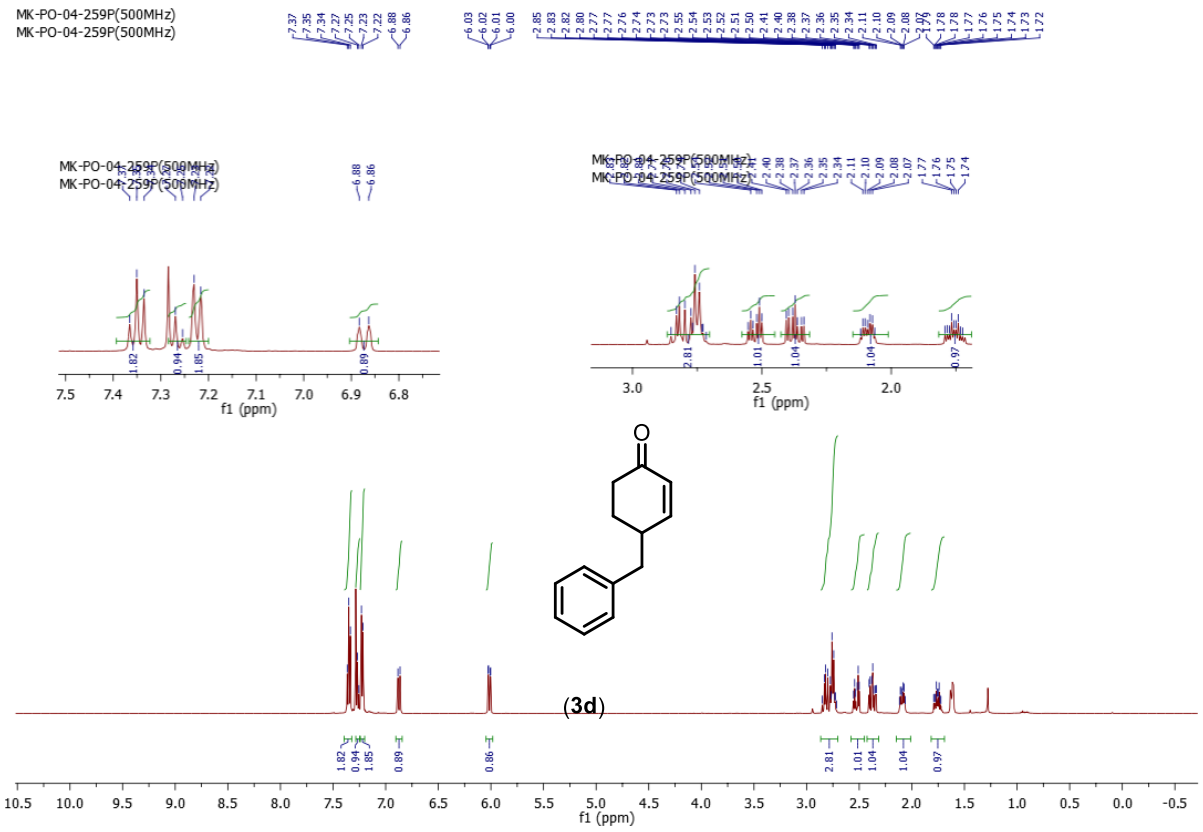
Acquisition Parameter

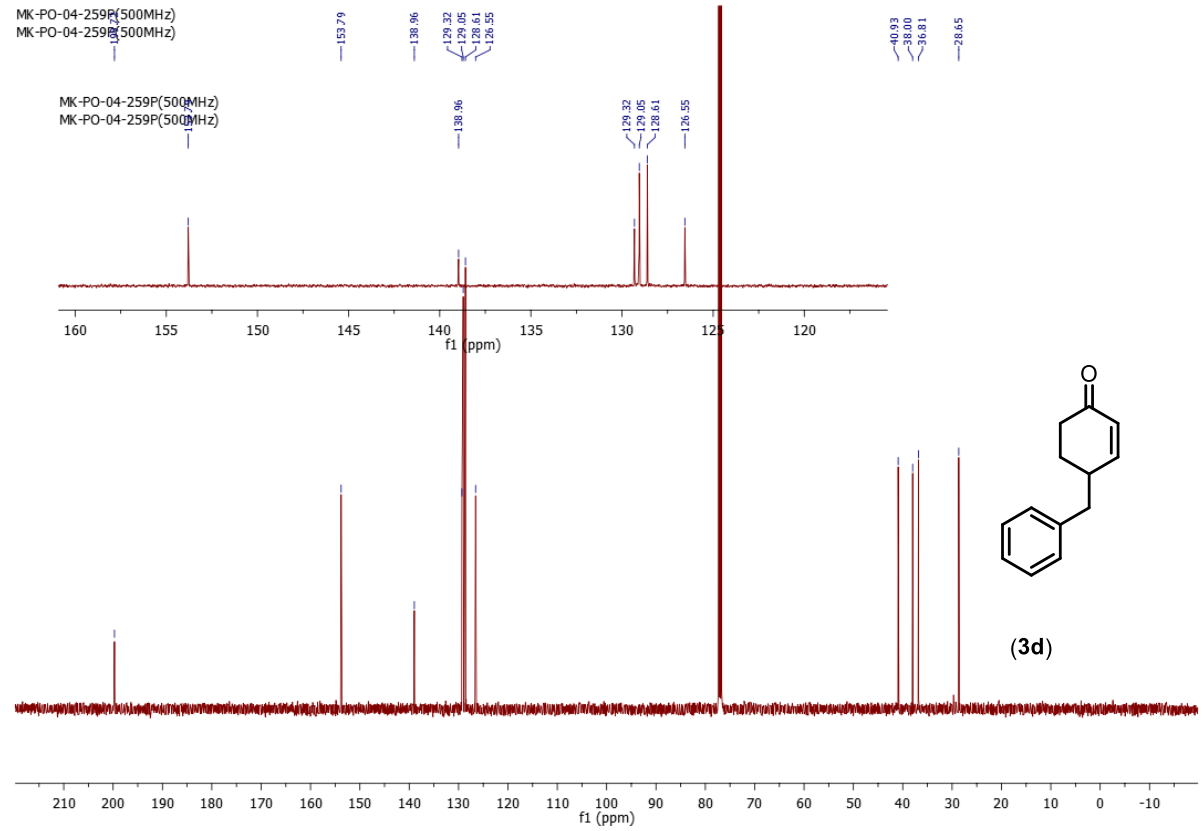
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	17.4 psi
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








MK-PO-04-259P(500MHz)
MK-PO-04-259P(500MHz)
(3d)
f1 (ppm)


MK-PO-04-259P(500MHz)
MK-PO-04-259P(500MHz)
(3d)
f1 (ppm)

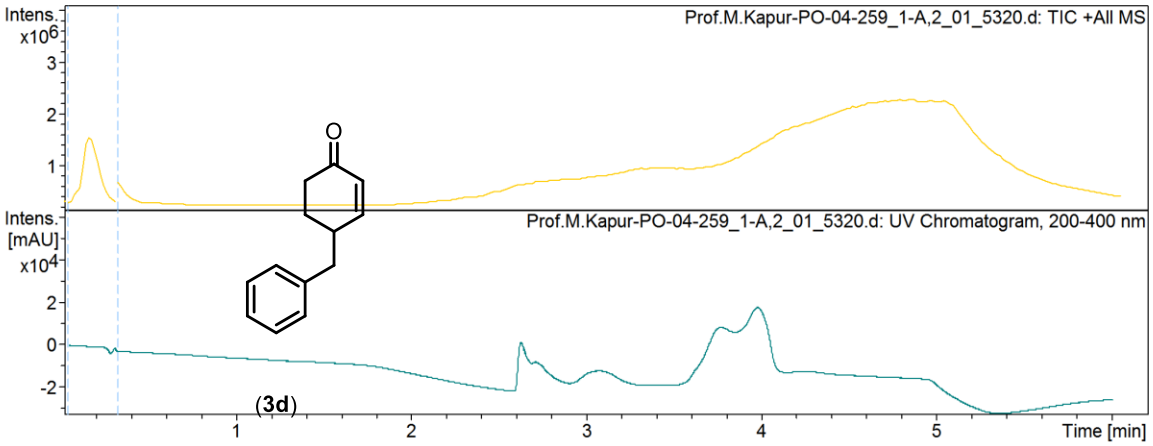
Display Report

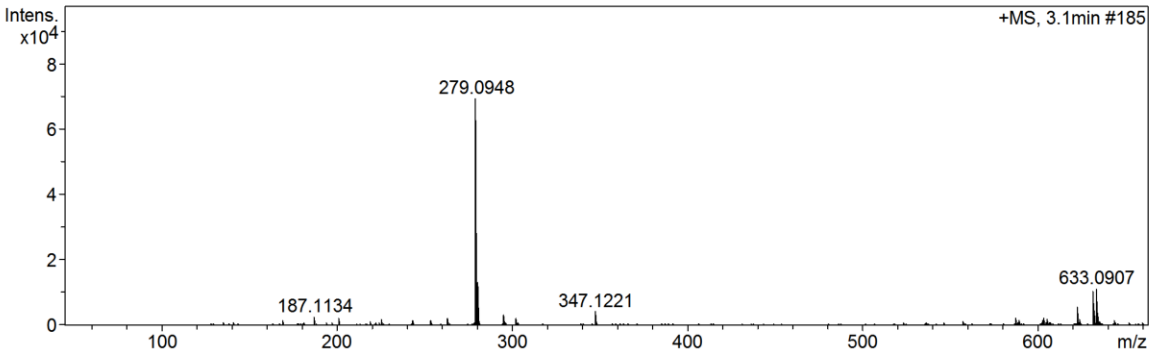
Analysis Info

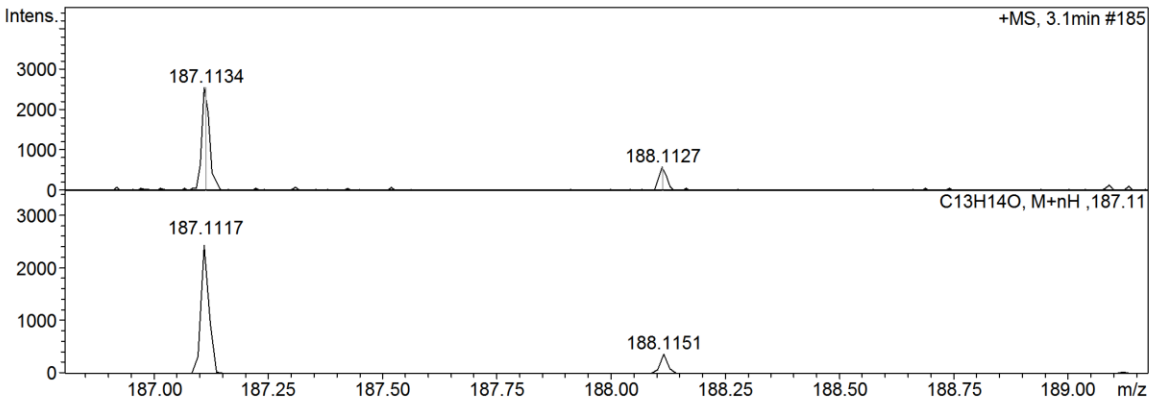
Analysis Name	D:\Data\USER DATA 2024\Sept-2024\18-sept-24\Prof.M.Kapur-PO-04-259_1-A,2_01_5320.d	Acquisition Date	18-09-2024 11:42:45
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-259	Instrument	micrOTOF-Q 10330
Comment			

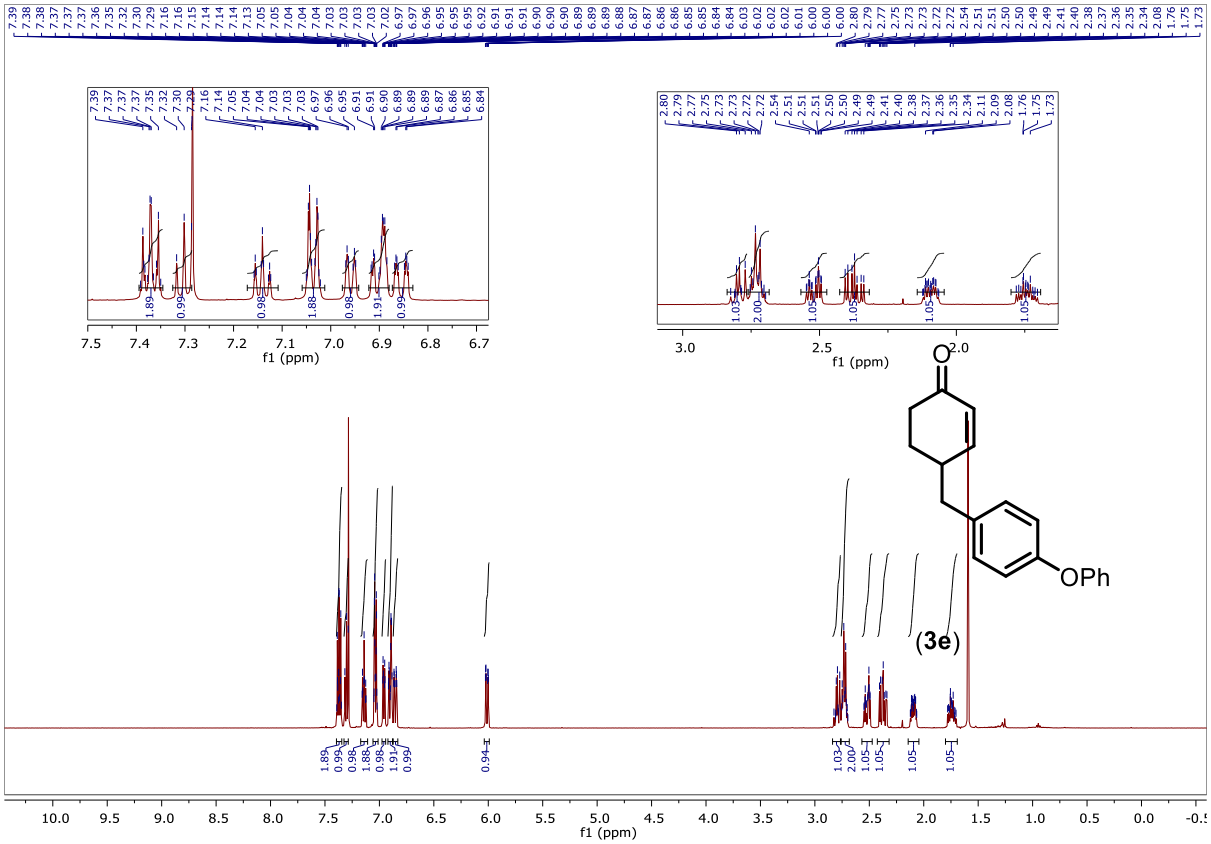
Acquisition Parameter

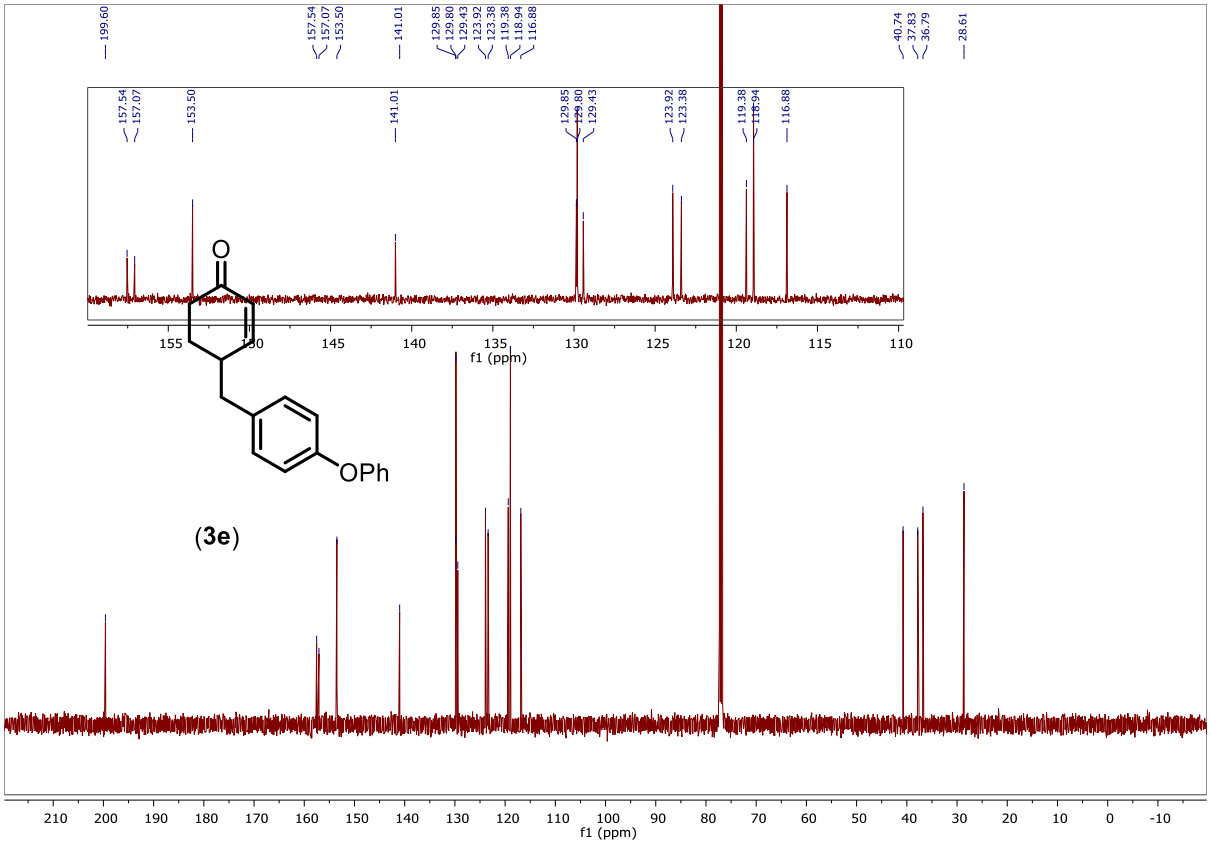
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	17.4 psi
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








f1 (ppm)
O
OPh
(3e)


f1 (ppm)
O
OPh
(3e)

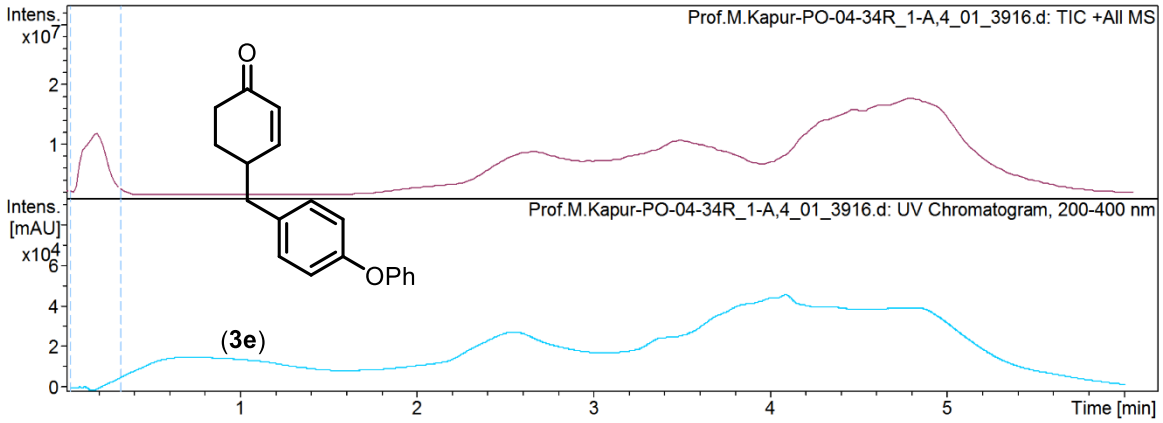
Display Report

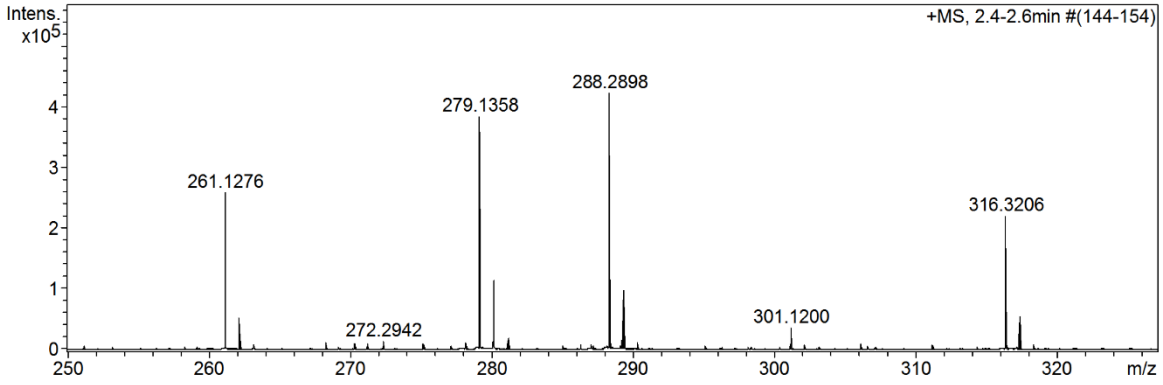
Analysis Info

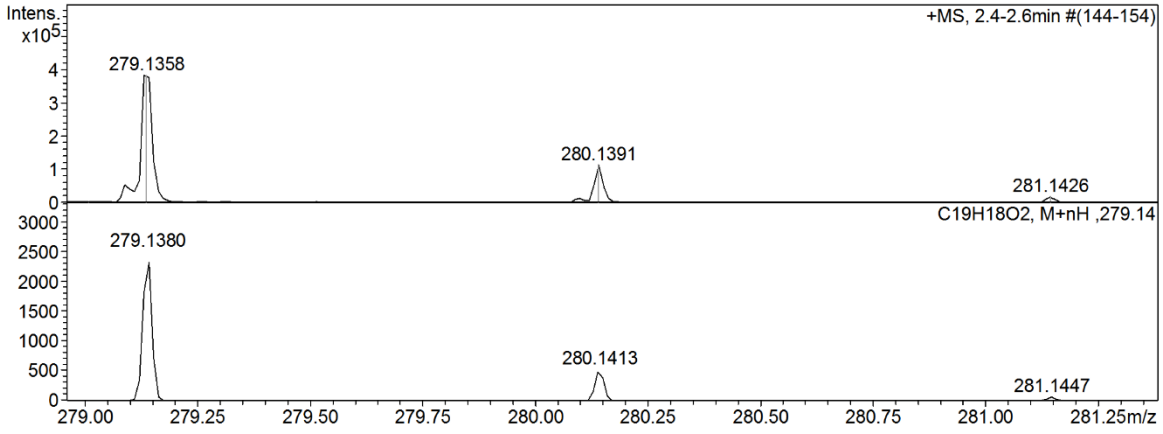
Acquisition Date	24-01-2024 12:52:25		
Analysis Name	D:\Data\USER DATA 2024\Jan2024\24-Jan\Prof.M.Kapur-PO-04-34R_1-A,4_01_3916.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-34R	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

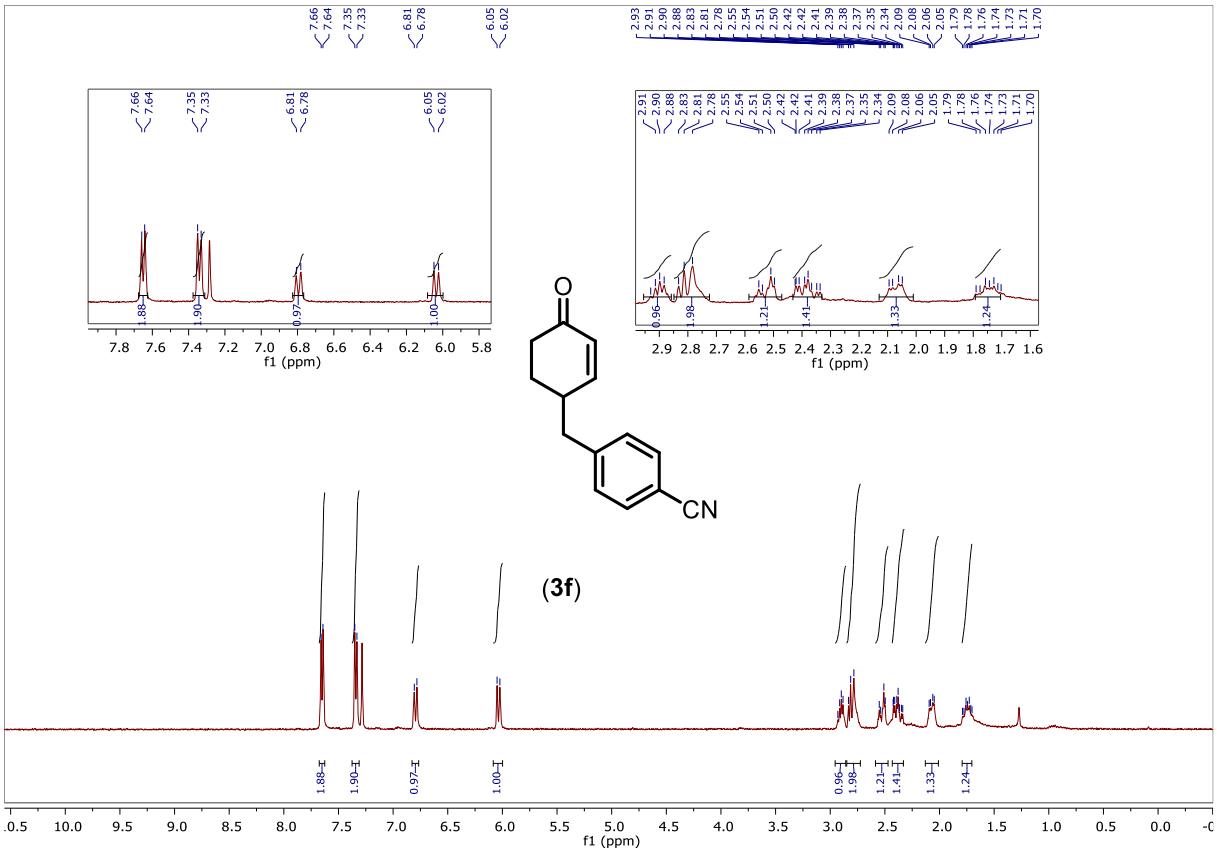
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

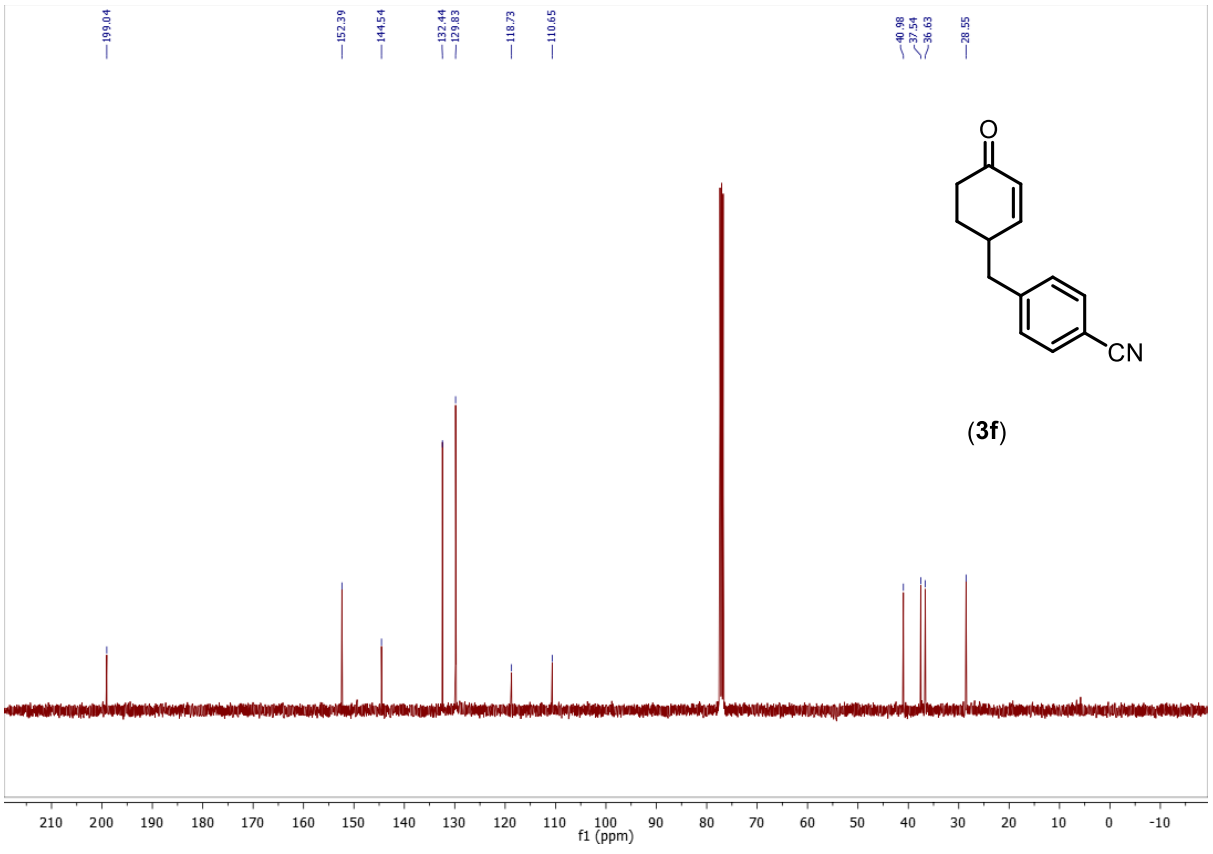






Bruker Compass DataAnalysis 4.0 printed: 24-01-2024 14:40:34 Page 1 of 1


O
CN
(3f)
f1 (ppm)


O
CN
(3f)
f1 (ppm)

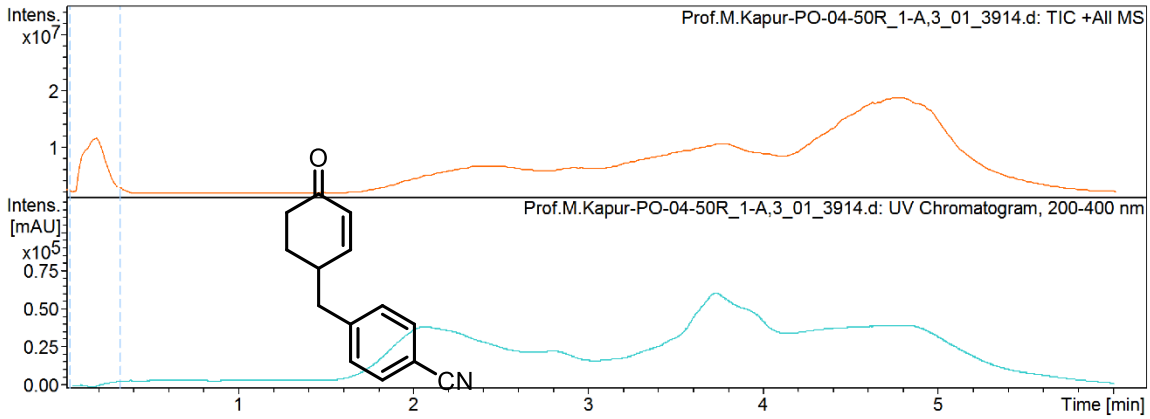
Display Report

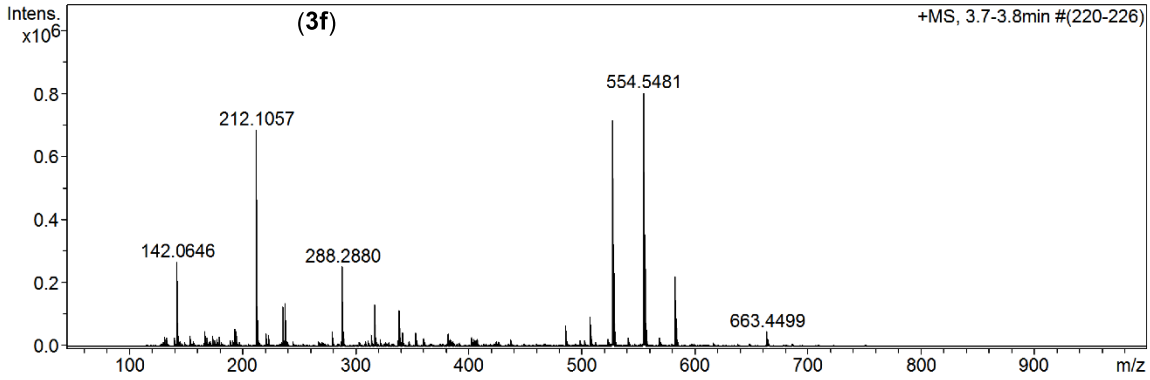
Analysis Info

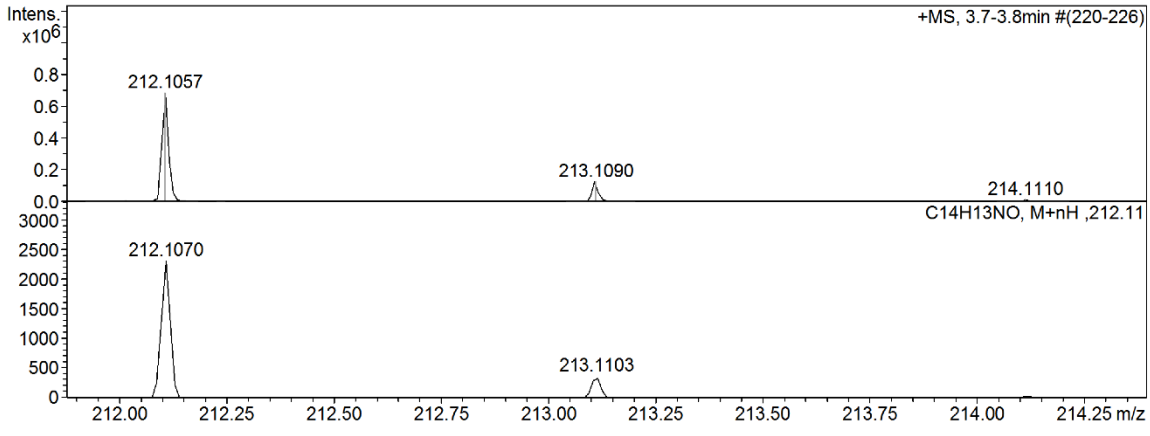
Acquisition Date	24-01-2024 12:37:55		
Analysis Name	D:\Data\USER DATA 2024\Jan2024\24-Jan\Prof.M.Kapur-PO-04-50R_1-A,3_01_3914.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-50R	Instrument	micrOTOF-Q 10330
Comment			

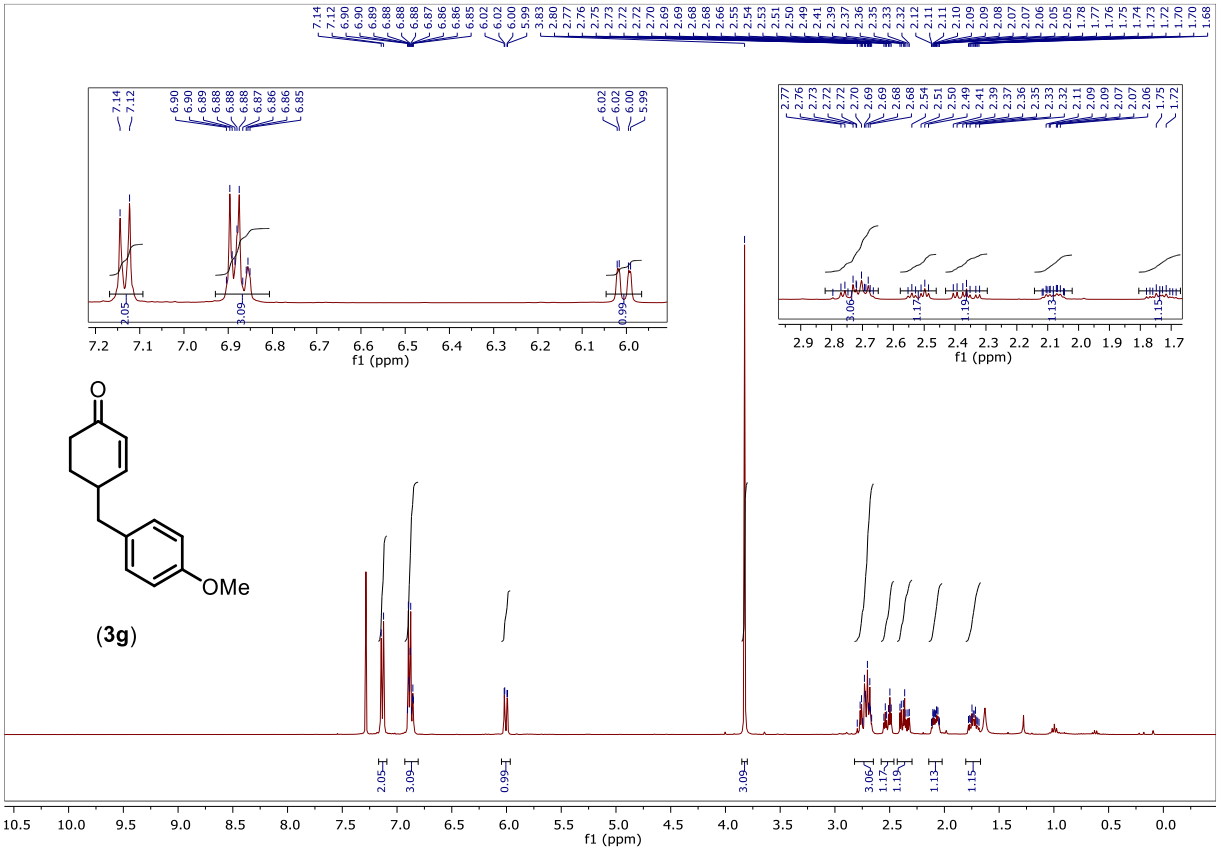
Acquisition Parameter

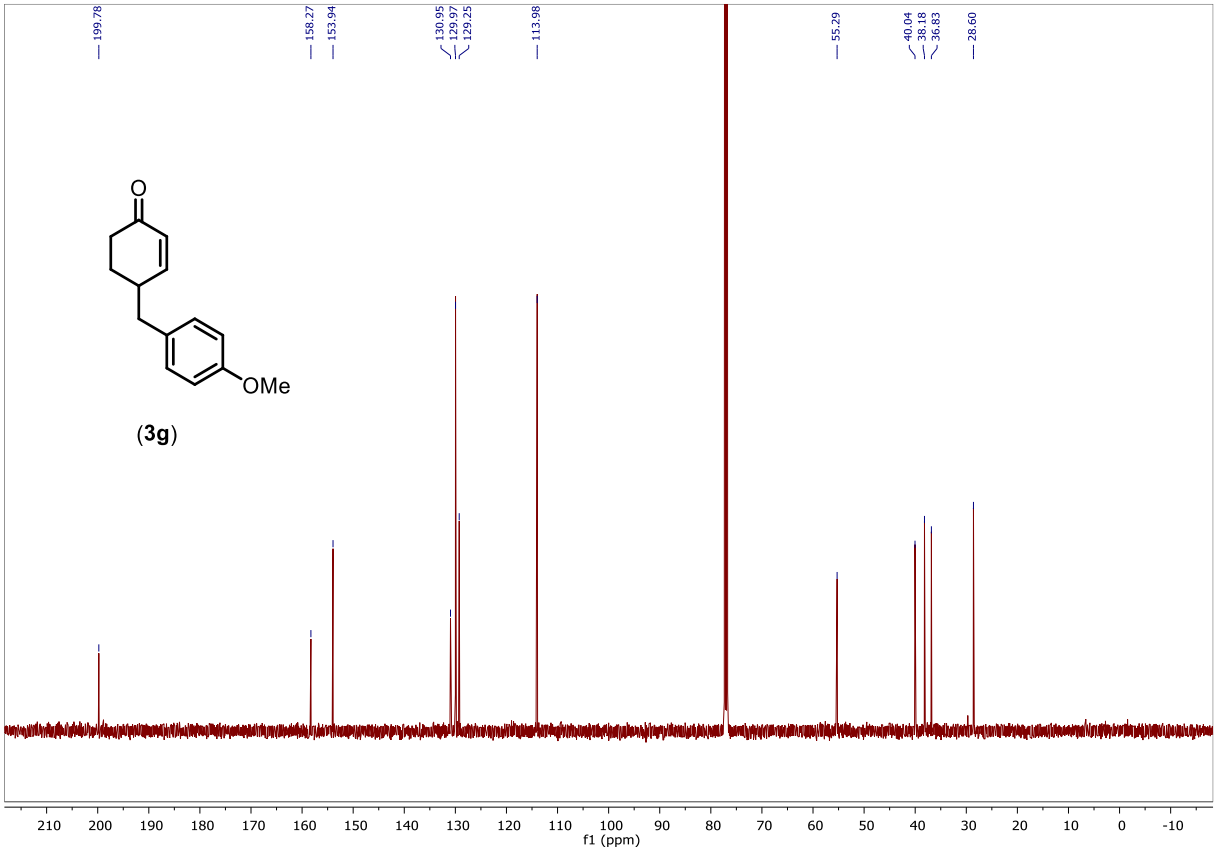
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








OMe
(3g)
f1 (ppm)


OMe
(3g)
f1 (ppm)

Custom Workflow Report

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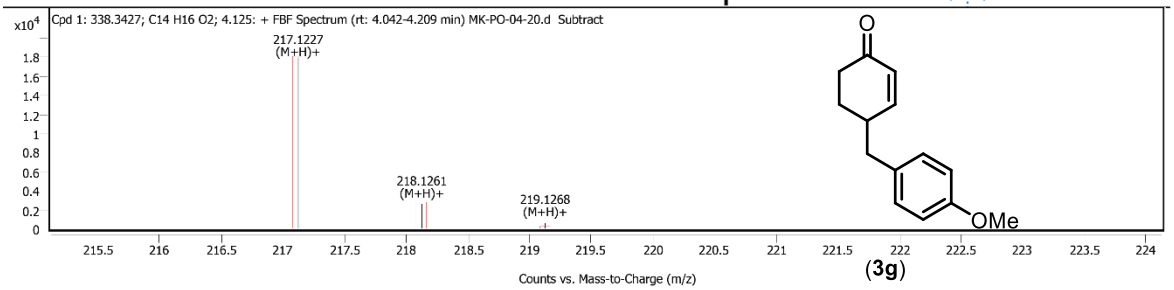
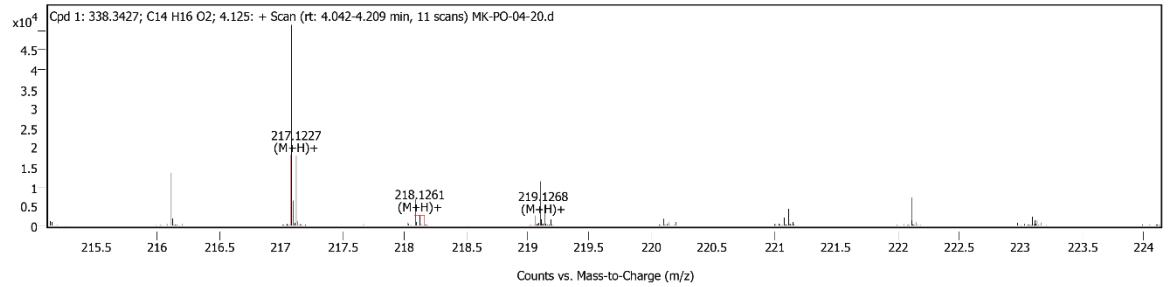


(**3g**)

Spectrum Peaks

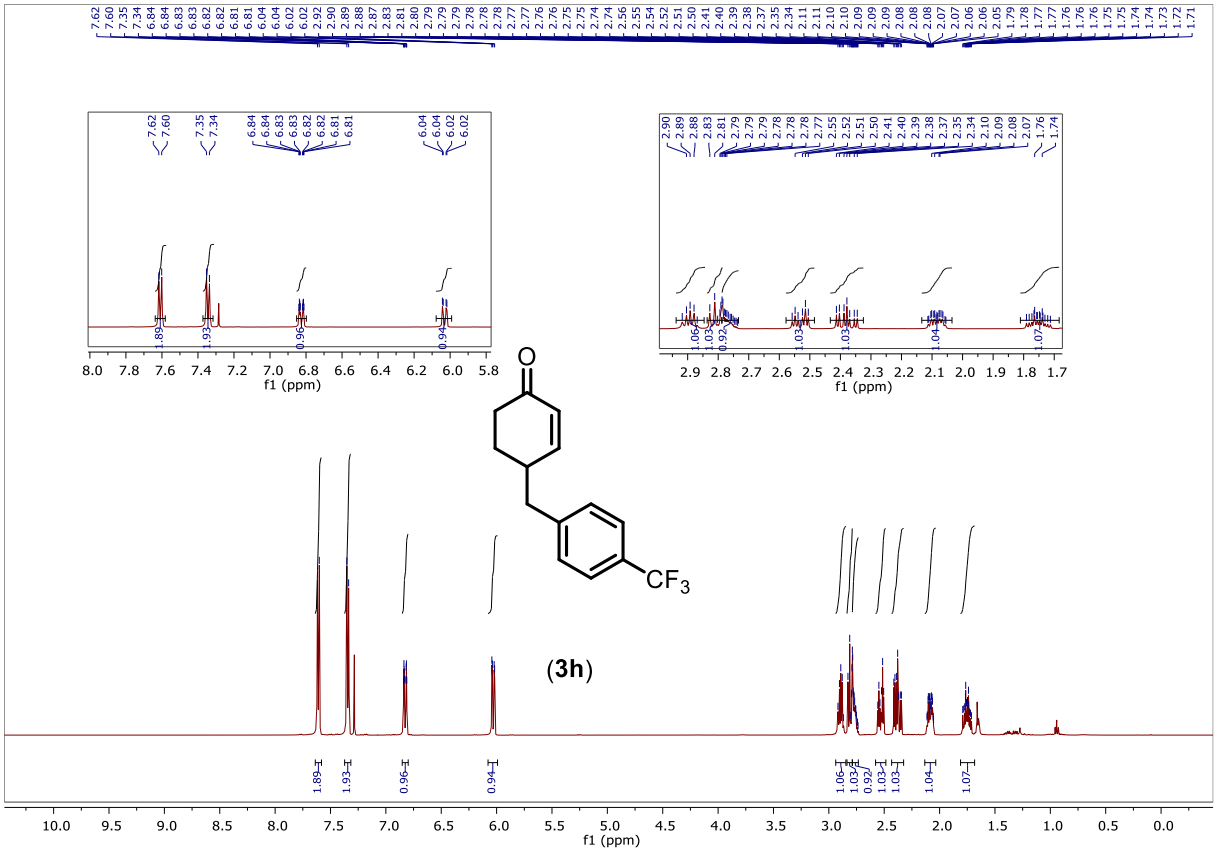
m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
217.1227	217.1223	1.64	17933	100.00	100.00	(M+H)+	1
218.1261	218.1257	1.89	2548	14.21	15.41	(M+H)+	1
219.1268	219.1284	-7.18	526	2.93	1.52	(M+H)+	1

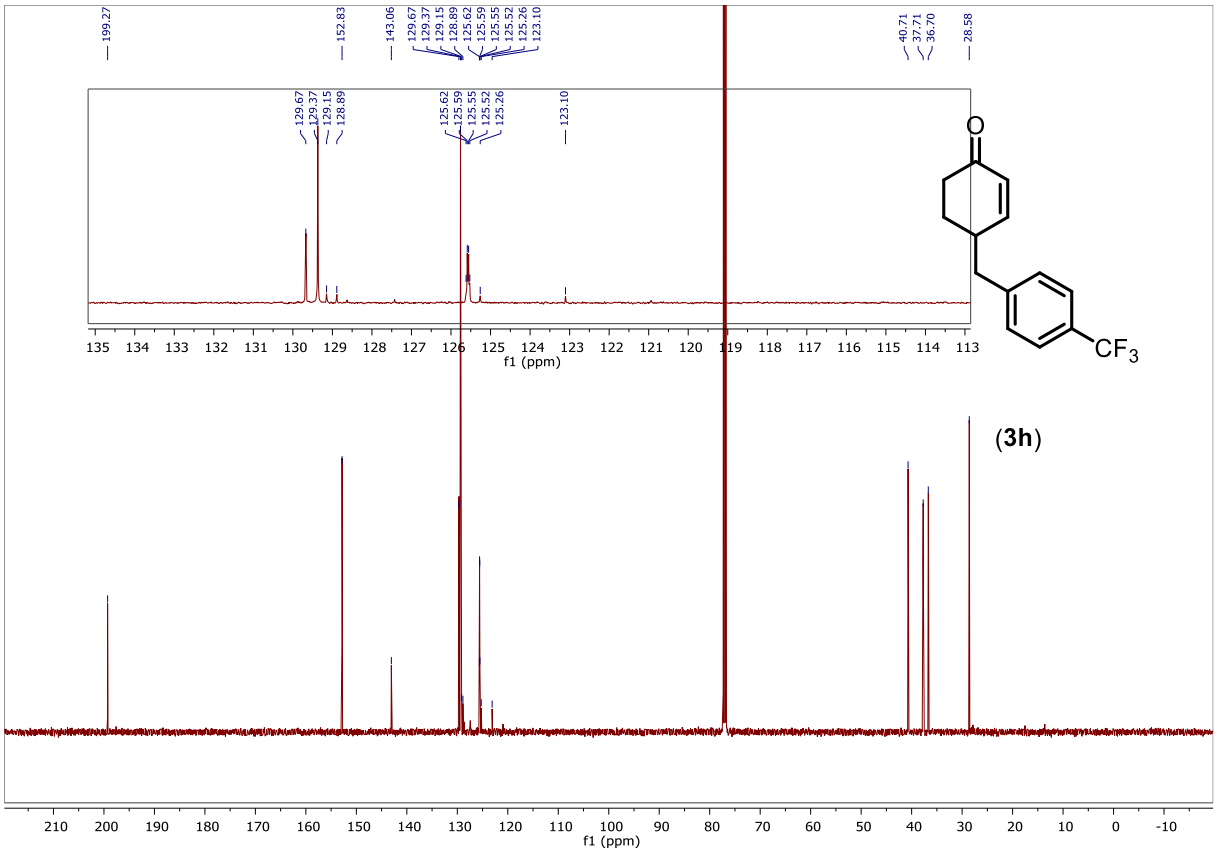


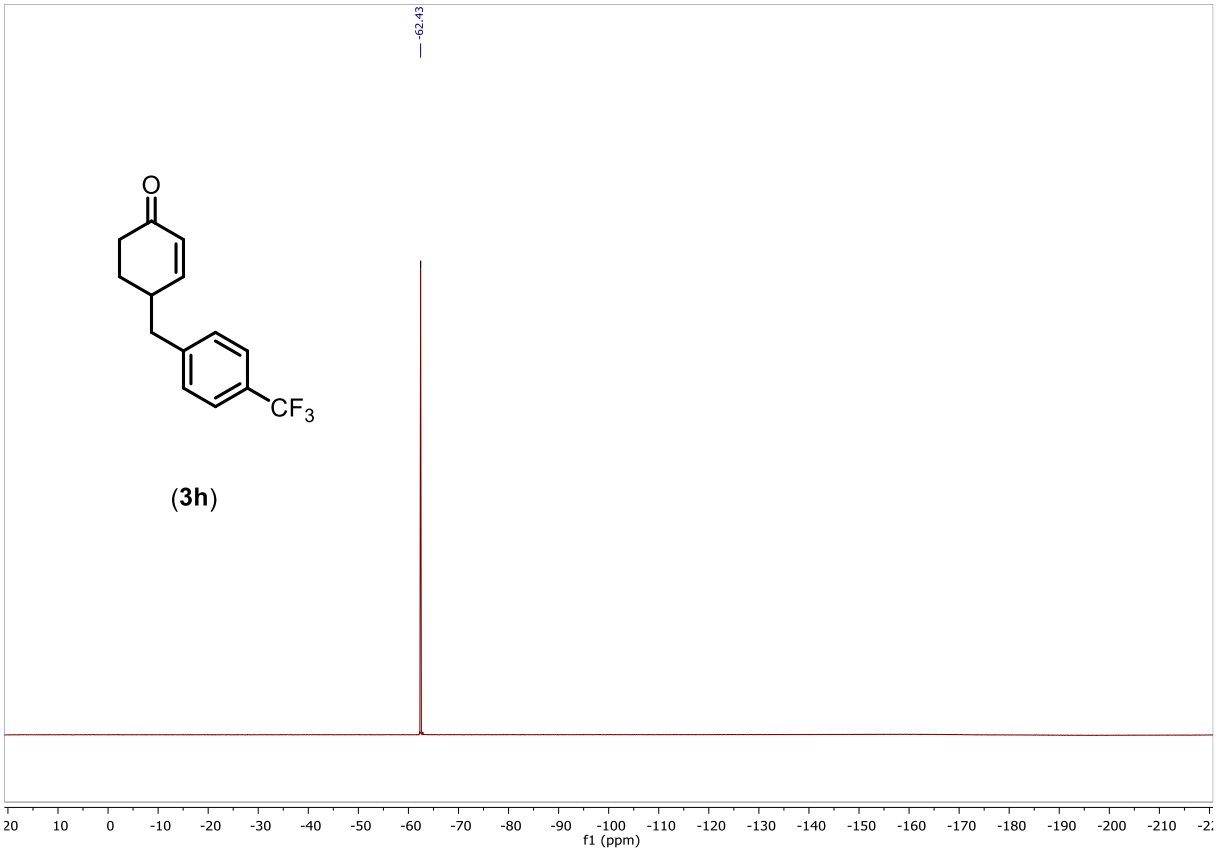
Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
217.1227	217.1223	1.64	17933	100.00	100.00	(M+H)+	1
218.1261	218.1257	1.89	2548	14.21	15.41	(M+H)+	1
219.1268	219.1284	-7.18	526	2.93	1.52	(M+H)+	1

MassHunter Qual 10.0
(End of Report)


f1 (ppm)
(3h)


f1 (ppm)
(3h)


-62.43
O
CF3
(3h)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

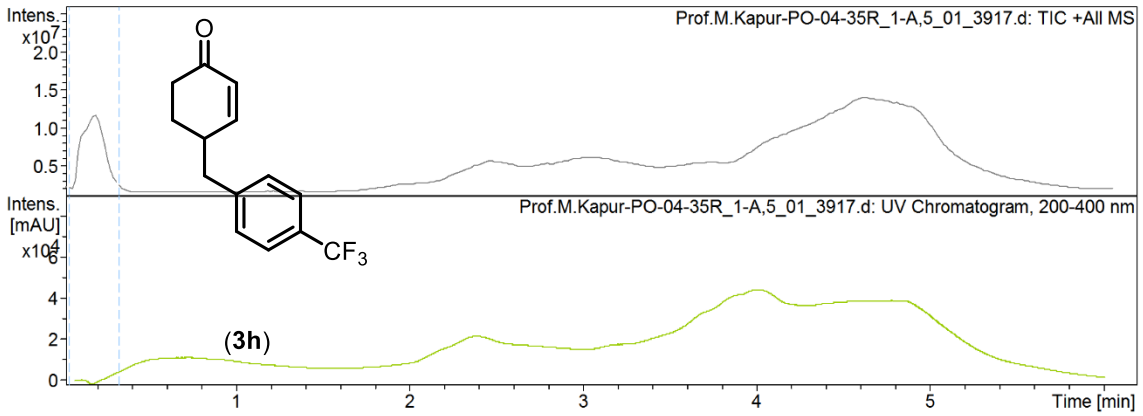
Display Report

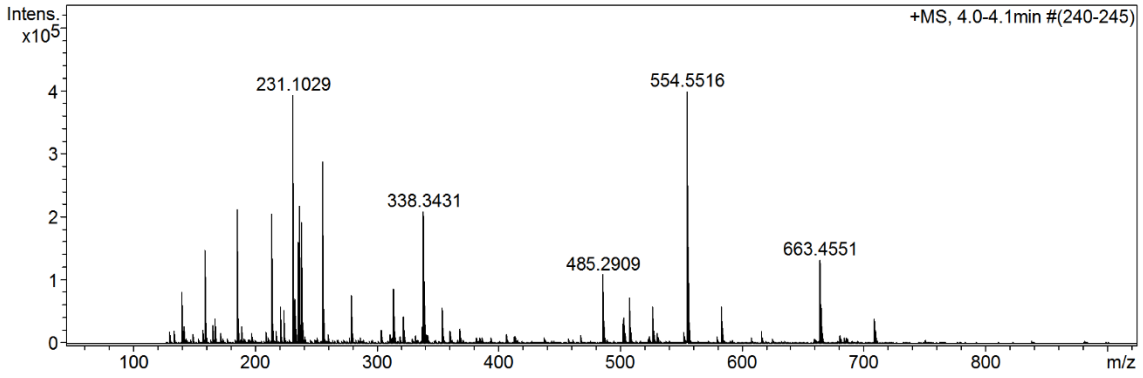
Analysis Info

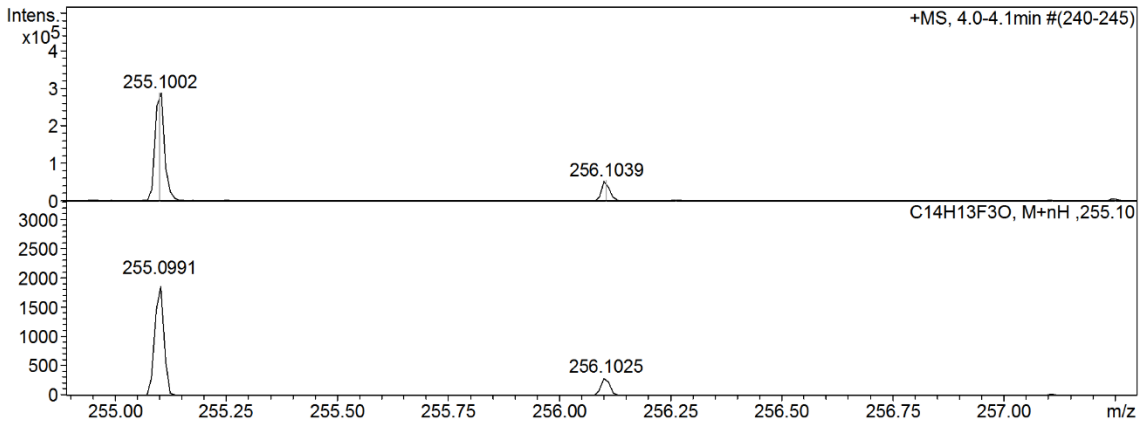
Analysis Name	D:\Data\USER DATA 2024\Jan2024\24-Jan\Prof.M.Kapur-PO-04-35R_1-A,5_01_3917.d	Acquisition Date	24-01-2024 12:59:43
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-35R	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

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







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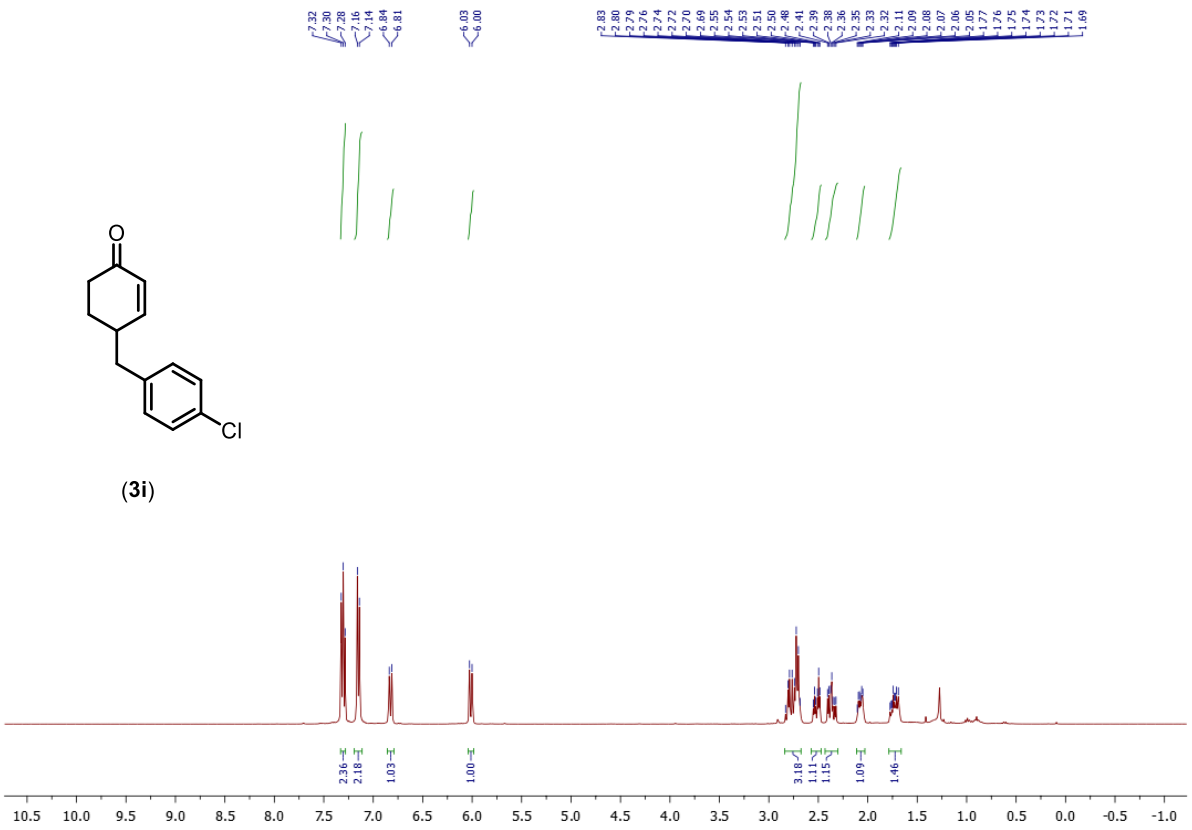
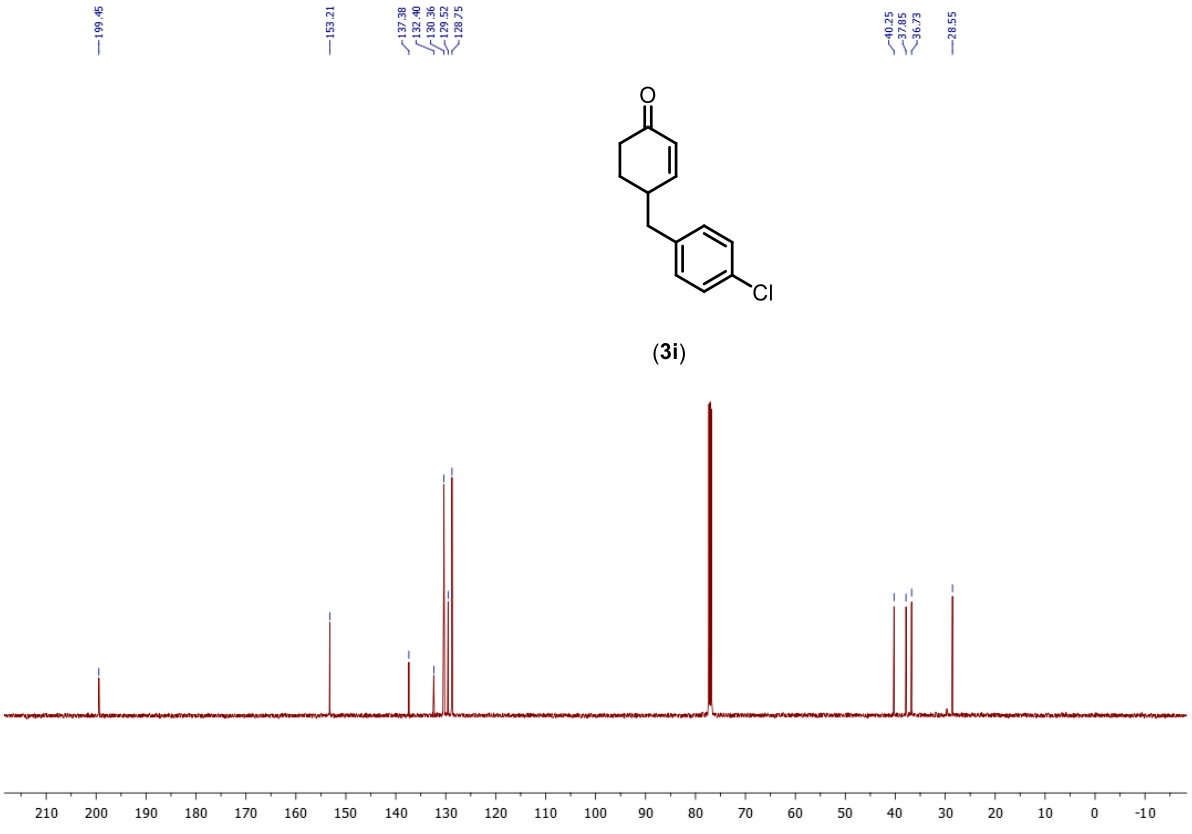

7.32
7.30
7.28
7.16
7.14
6.84
6.81
6.03
6.00
2.83
2.80
2.79
2.76
2.74
2.72
2.70
2.69
2.55
2.54
2.53
2.51
2.50
2.48
2.41
2.39
2.38
2.36
2.35
2.33
2.32
2.11
2.09
2.08
2.07
2.06
2.05
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.69
O
Cl
2.36
2.18
1.03
1.00
3.18
1.11
1.15
1.09
1.46
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

(**3i**)


199.46
153.21
137.38
132.40
130.36
129.52
128.75
40.25
37.85
36.73
28.55
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

(**3i**)

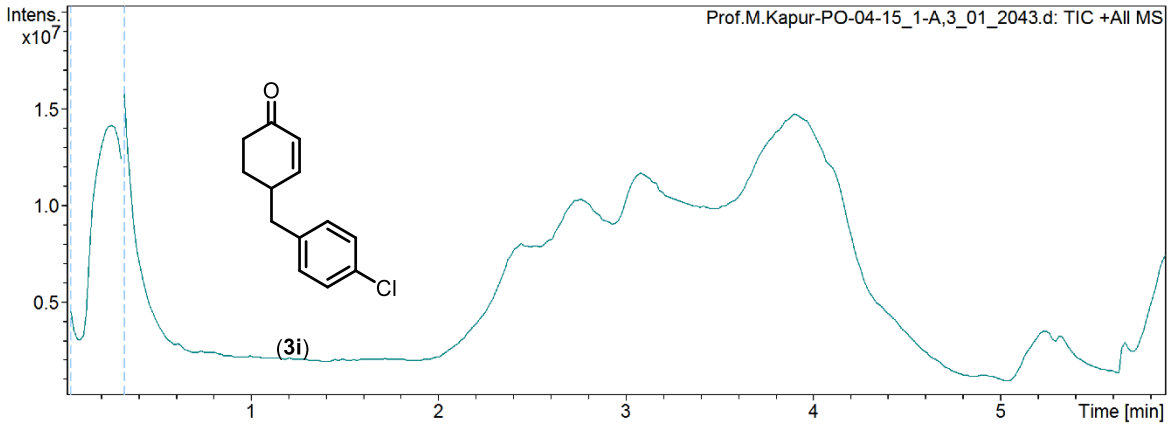
Display Report

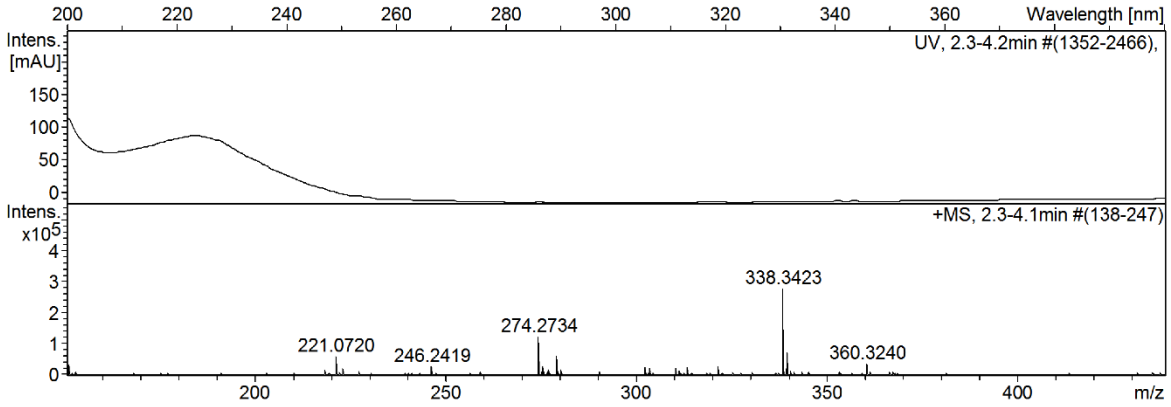
Analysis Info

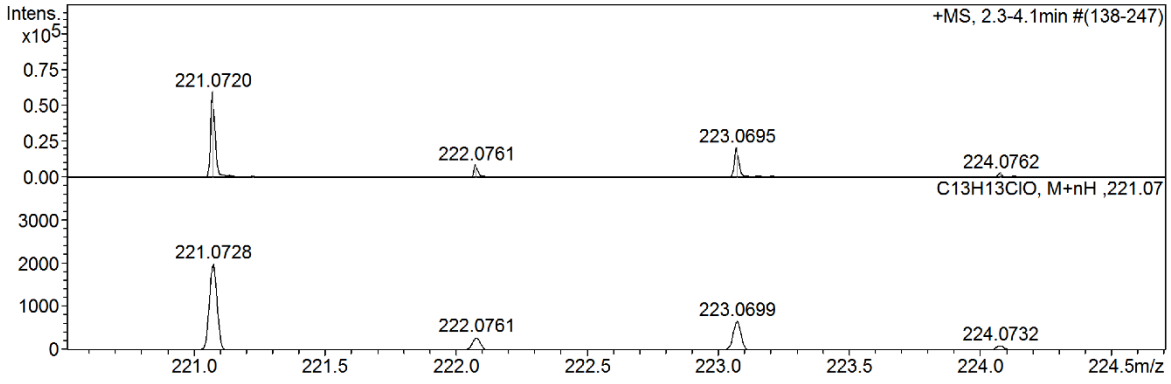
Acquisition Date	23-06-2023 10:23:23		
Analysis Name	D:\Data\USER DATA 2023\June\22-june\Prof.M.Kapur-PO-04-15_1-A,3_01_2043.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-15	Instrument	micrOTOF-Q 10330
Comment			

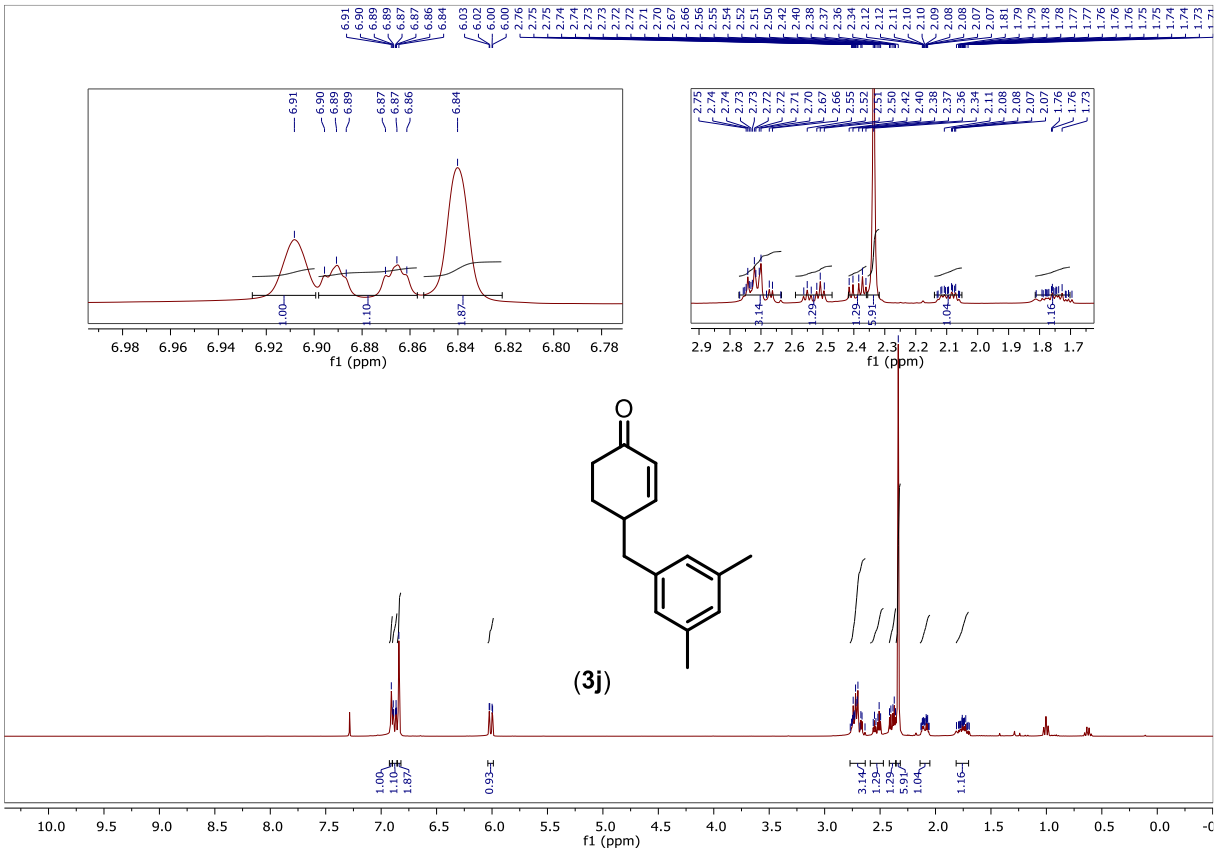
Acquisition Parameter

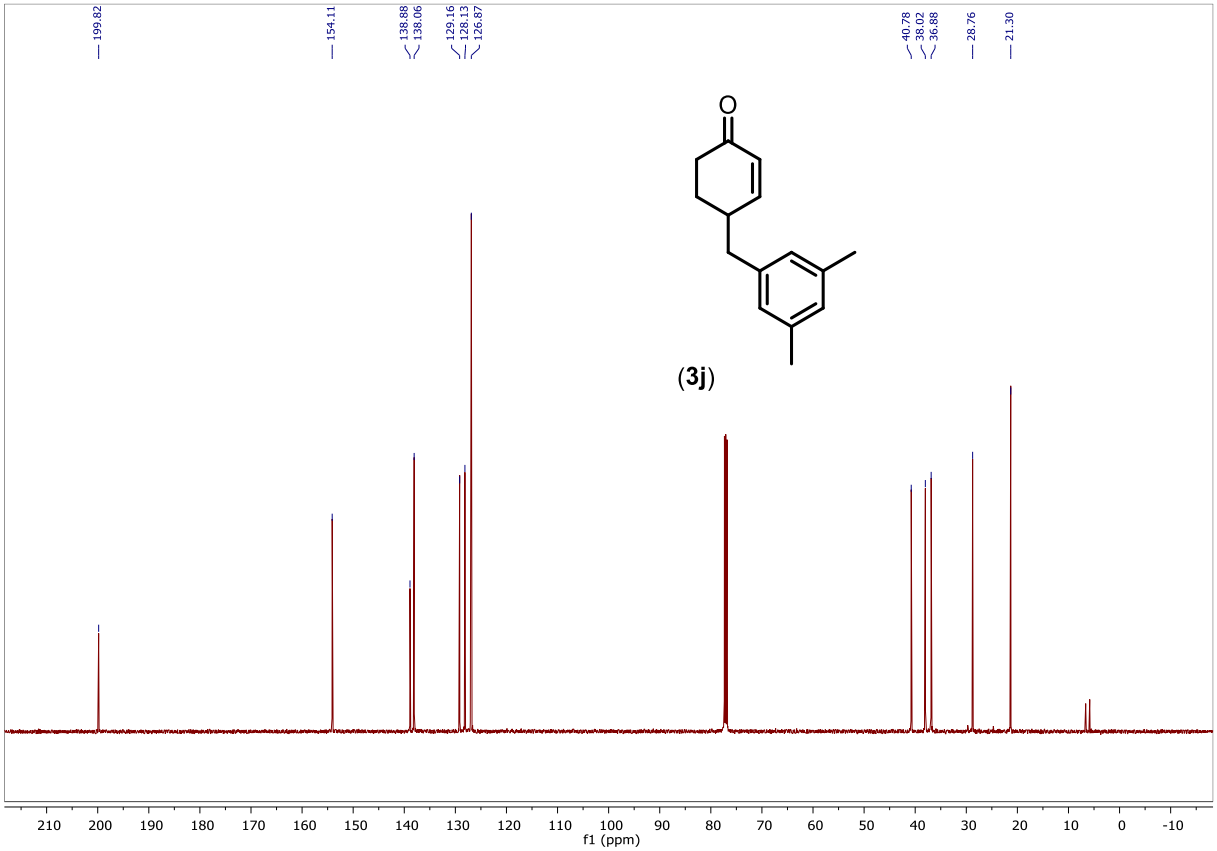
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








(3j)
f1 (ppm)


(3j)
f1 (ppm)

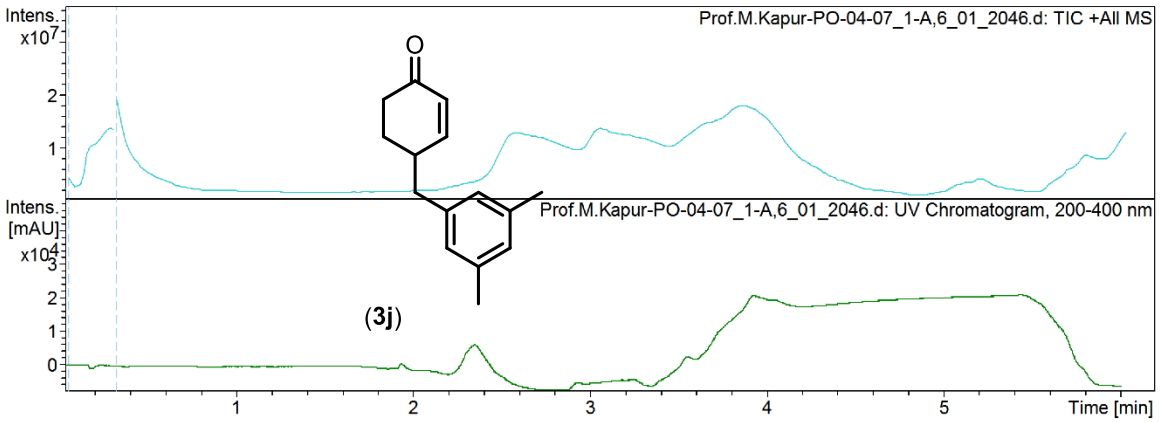
Display Report

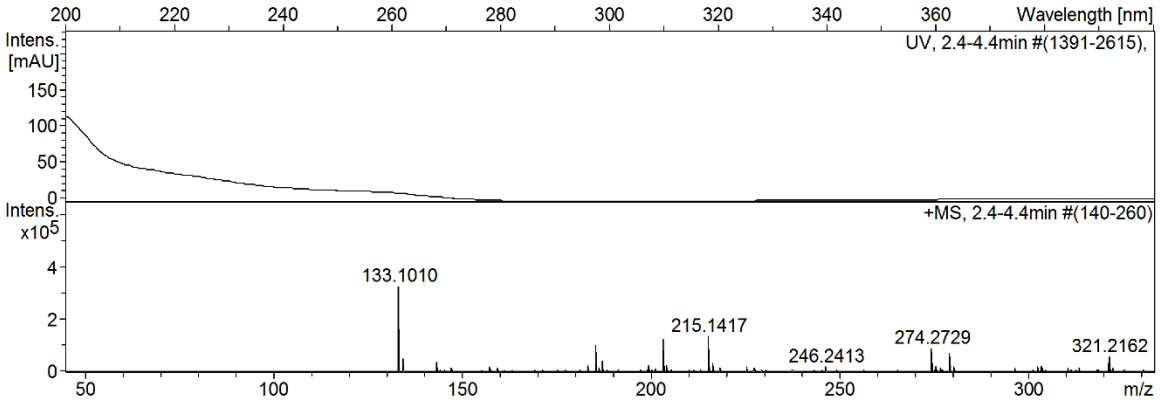
Analysis Info

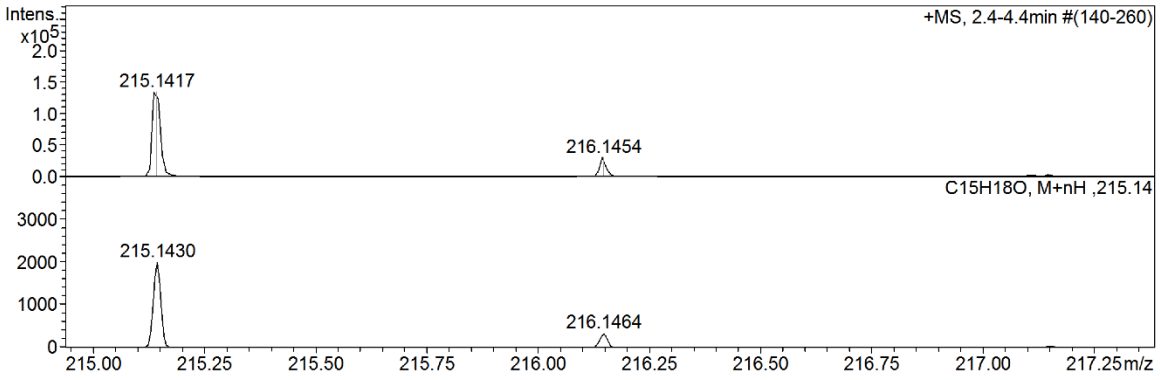
Acquisition Date	23-06-2023 10:45:06		
Analysis Name	D:\Data\USER DATA 2023\June\22-june\Prof.M.Kapur-PO-04-07_1-A,6_01_2046.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-07	Instrument	micrOTOF-Q 10330
Comment			

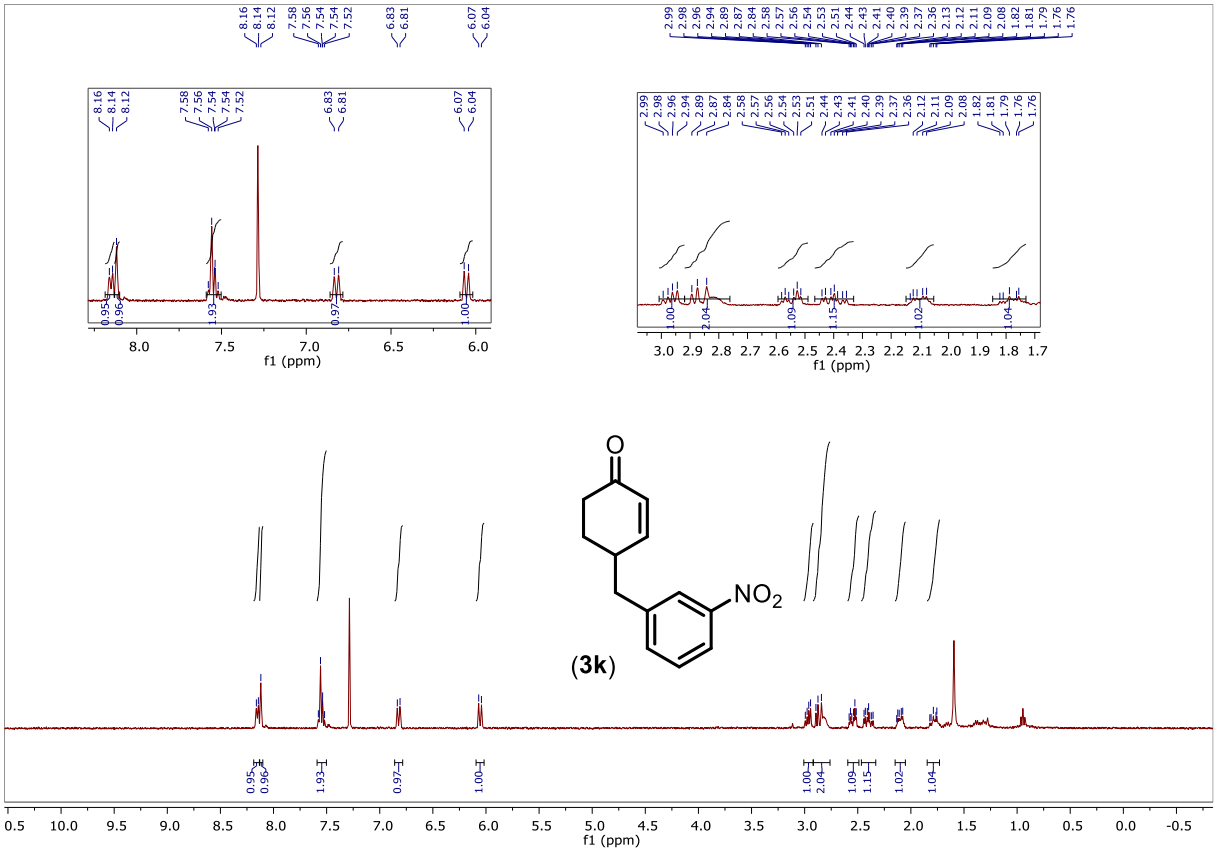
Acquisition Parameter

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








8.16
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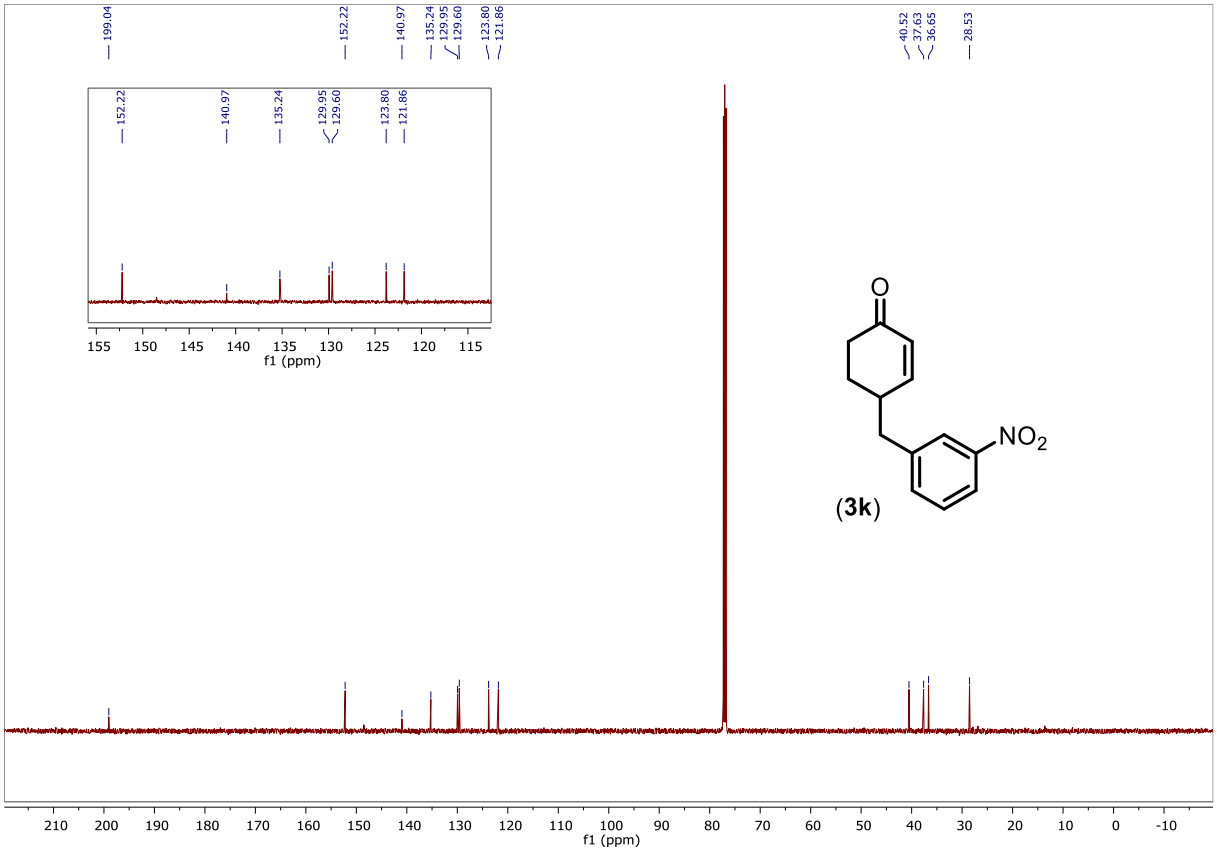
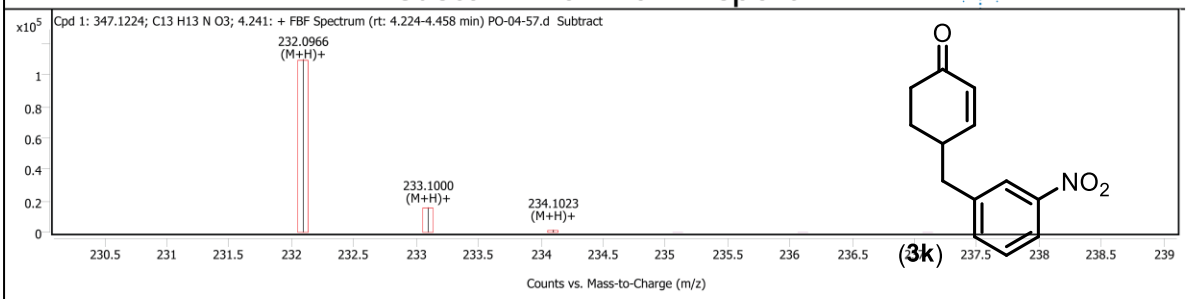
8.12
7.58
7.56
7.54
7.54
7.52
6.83
6.81
6.07
6.04
2.99
2.98
2.96
2.94
2.89
2.87
2.84
2.58
2.57
2.56
2.54
2.53
2.51
2.44
2.43
2.41
2.40
2.39
2.37
2.36
2.12
2.11
2.09
2.08
1.82
1.81
1.79
1.76
1.76
0.95
0.96
1.93
0.97
1.00
1.00
2.04
1.09
1.15
1.02
1.04
f1 (ppm)
O
NO2
(3k)


199.04
152.22
140.97
135.24
129.95
129.60
123.80
121.86
40.52
37.63
36.65
28.53
f1 (ppm)
O
NO2
(3k)

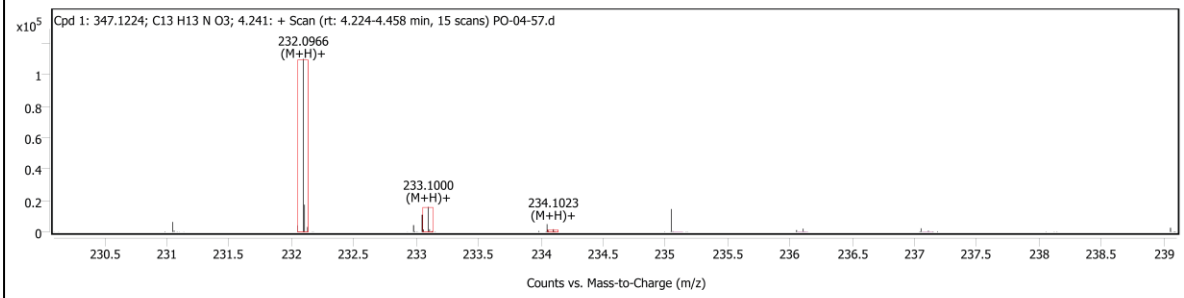
Custom Workflow Report

Agilent Trusted Answers



Spectrum Peaks

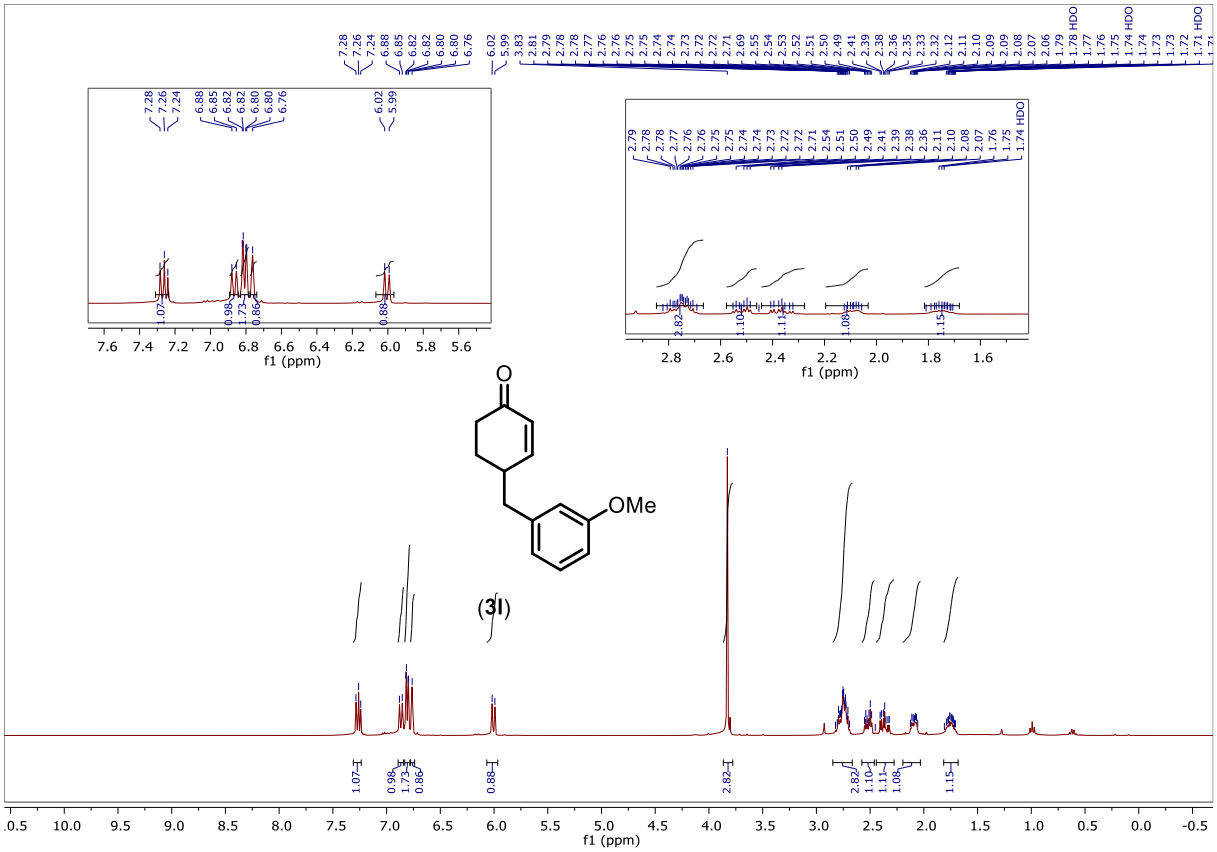
m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
232.0966	232.0968	-0.83	110075	100.00	100.00	(M+H)+	1
233.1000	233.1001	-0.32	15926	14.47	14.70	(M+H)+	1
234.1023	234.1024	-0.39	1614	1.47	1.62	(M+H)+	1

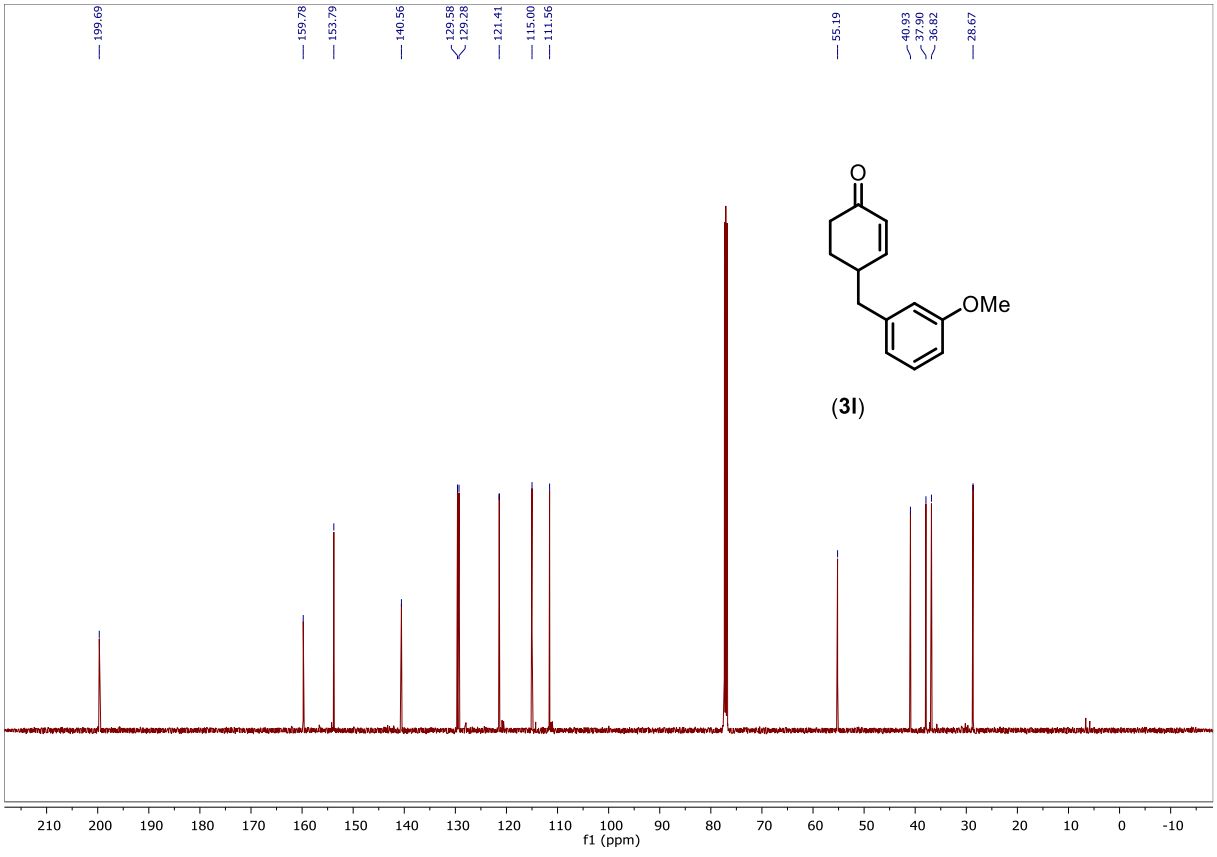


Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
232.0966	232.0968	-0.83	110075	100.00	100.00	(M+H)+	1
233.1000	233.1001	-0.32	15926	14.47	14.70	(M+H)+	1
234.1023	234.1024	-0.39	1614	1.47	1.62	(M+H)+	1

MassHunter Qual 10.0
(End of Report)


OMe
(3l)
f1 (ppm)


OMe
(3l)
f1 (ppm)

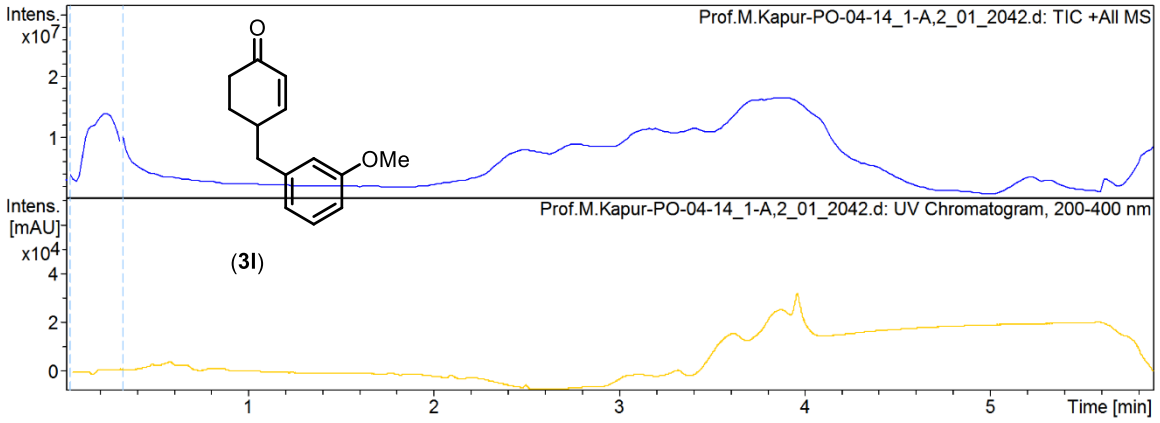
Display Report

Analysis Info

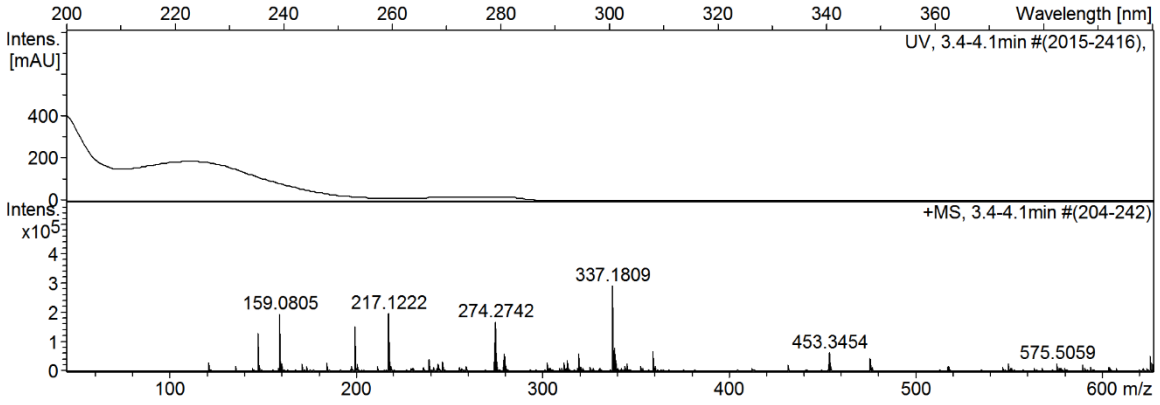
Acquisition Date	23-06-2023 10:16:08		
Analysis Name	D:\Data\USER DATA 2023\June\22-june\Prof.M.Kapur-PO-04-14_1-A,2_01_2042.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-14	Instrument	micrOTOF-Q 10330
Comment			

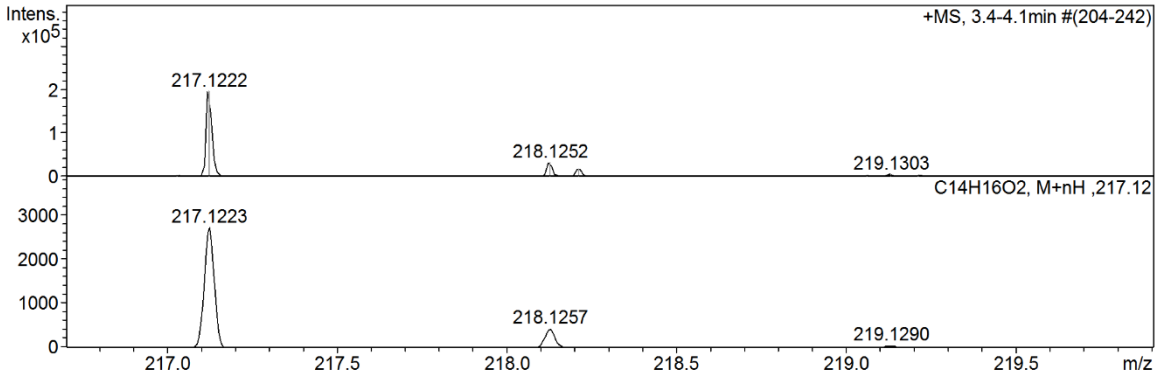
Acquisition Parameter

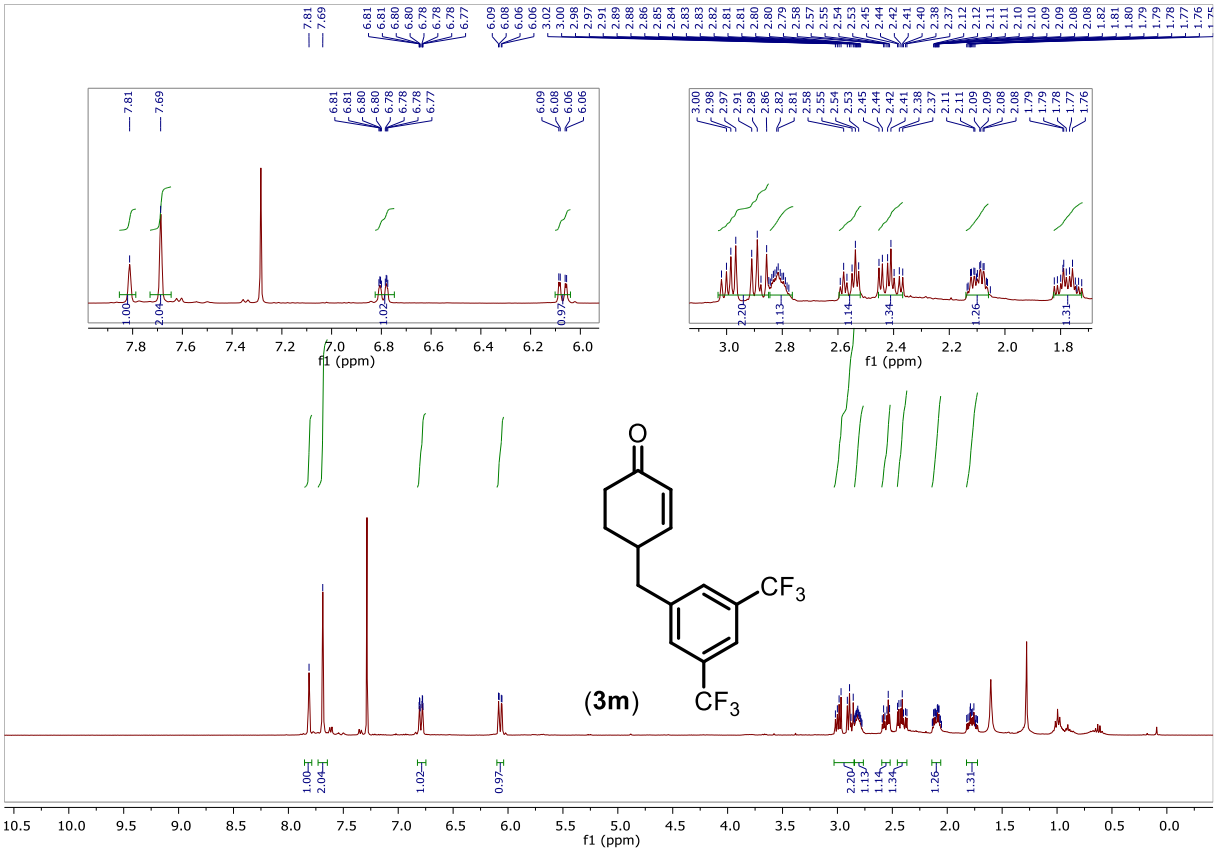
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

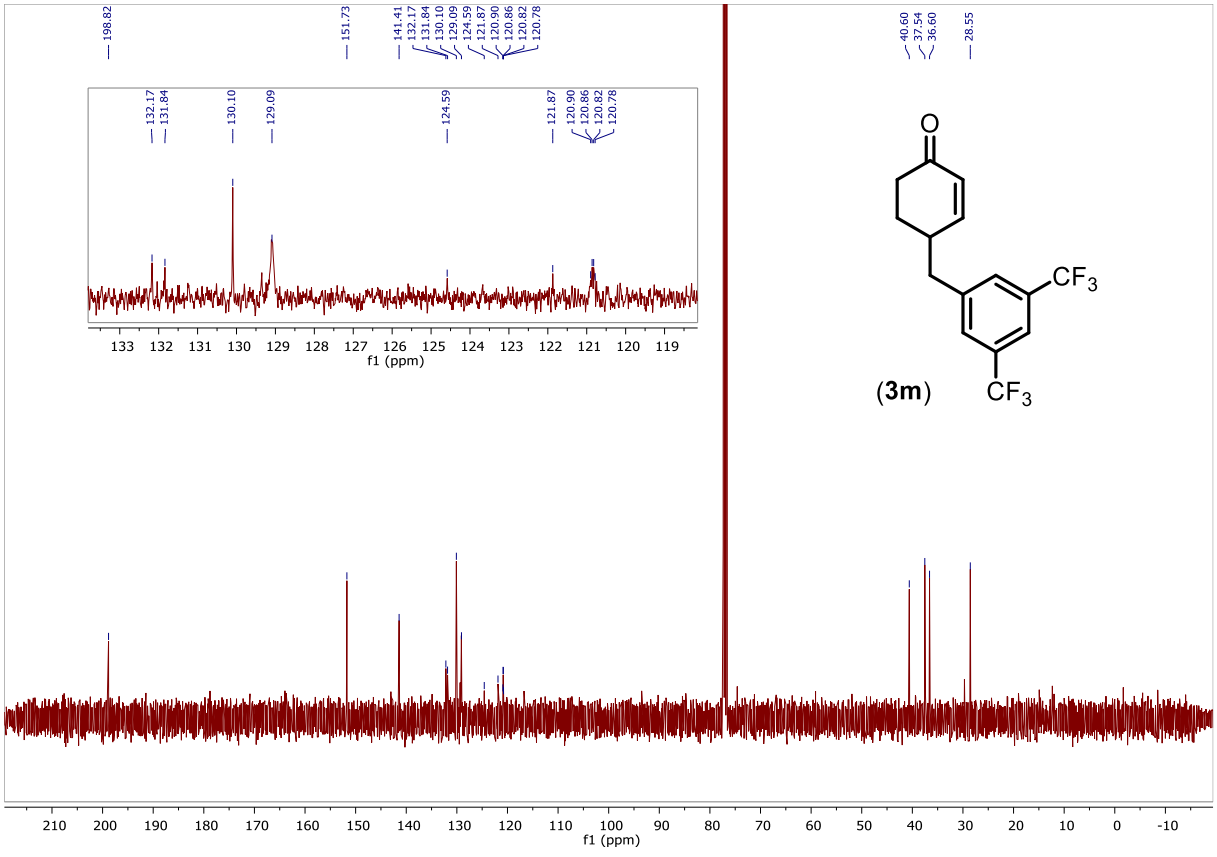


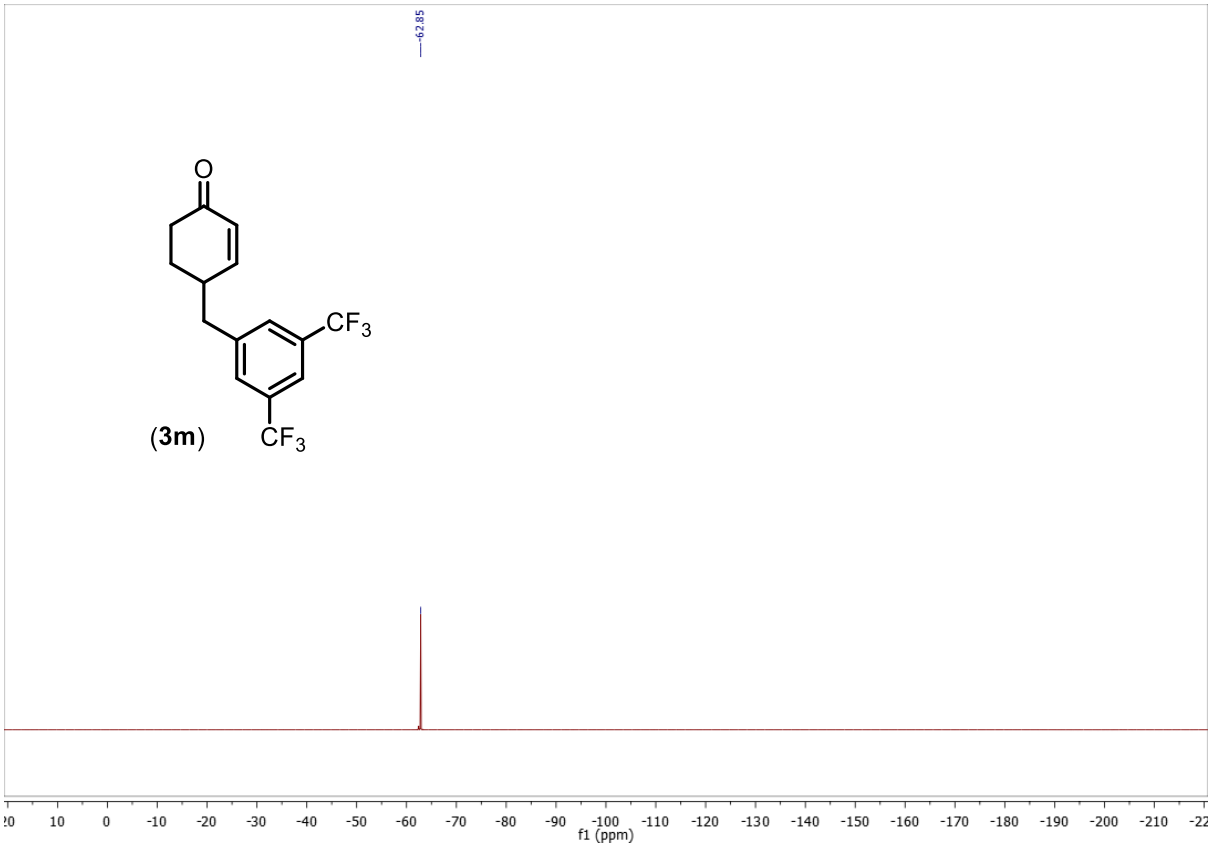
(**3l**)






f1 (ppm)
(3m)
CF3
CF3


f1 (ppm)
(3m)
CF3
CF3


-62.85
O
CF3
CF3
(3m)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

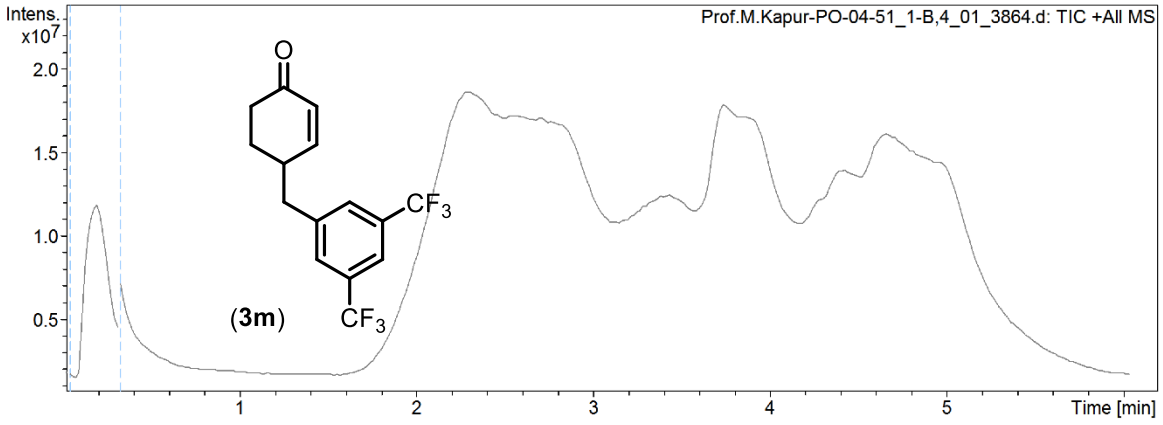
Display Report

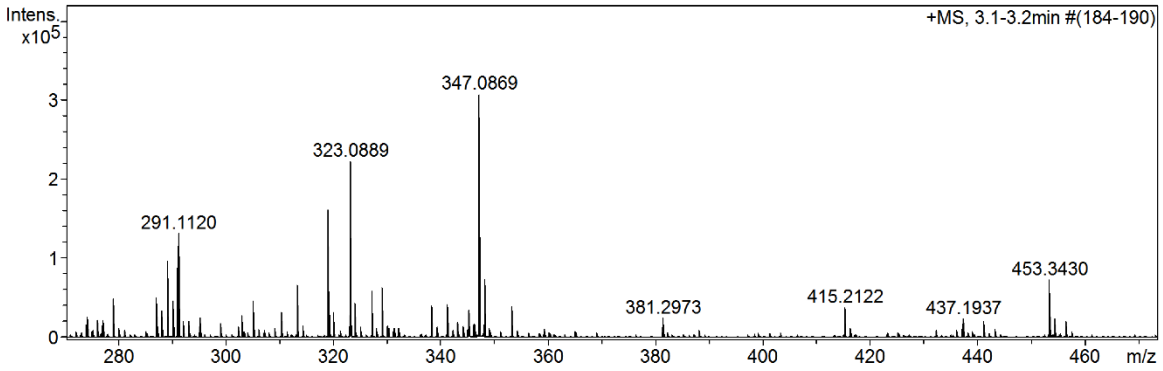
Analysis Info

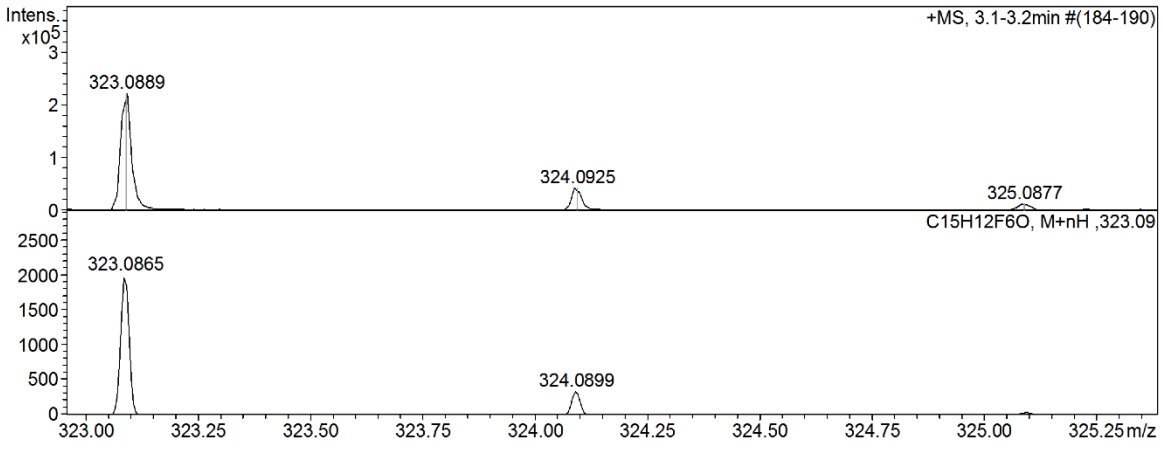
Acquisition Date	17-01-2024 17:57:30		
Analysis Name	D:\Data\USER DATA 2024\17-jan\Prof.M.Kapur-PO-04-51_1-B,4_01_3864.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-51	Instrument	micrOTOF-Q 10330
Comment			

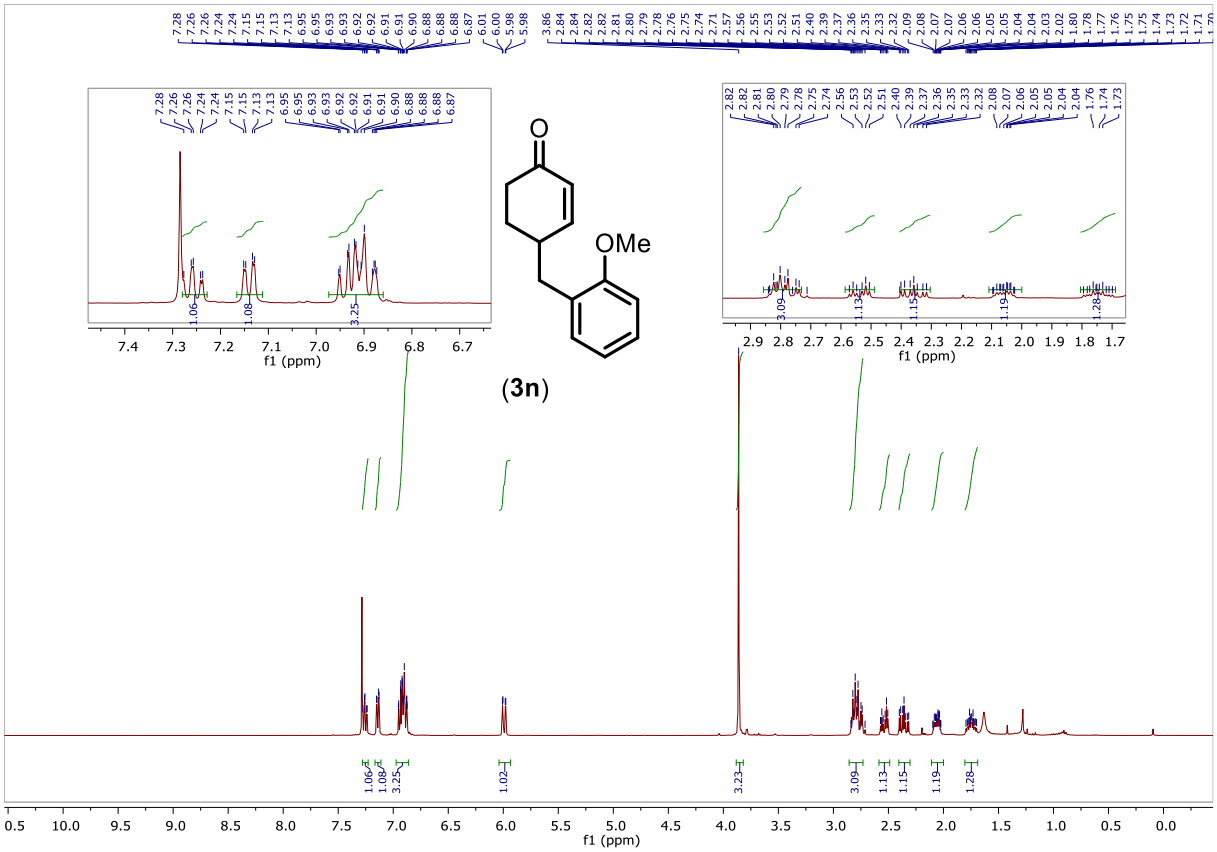
Acquisition Parameter

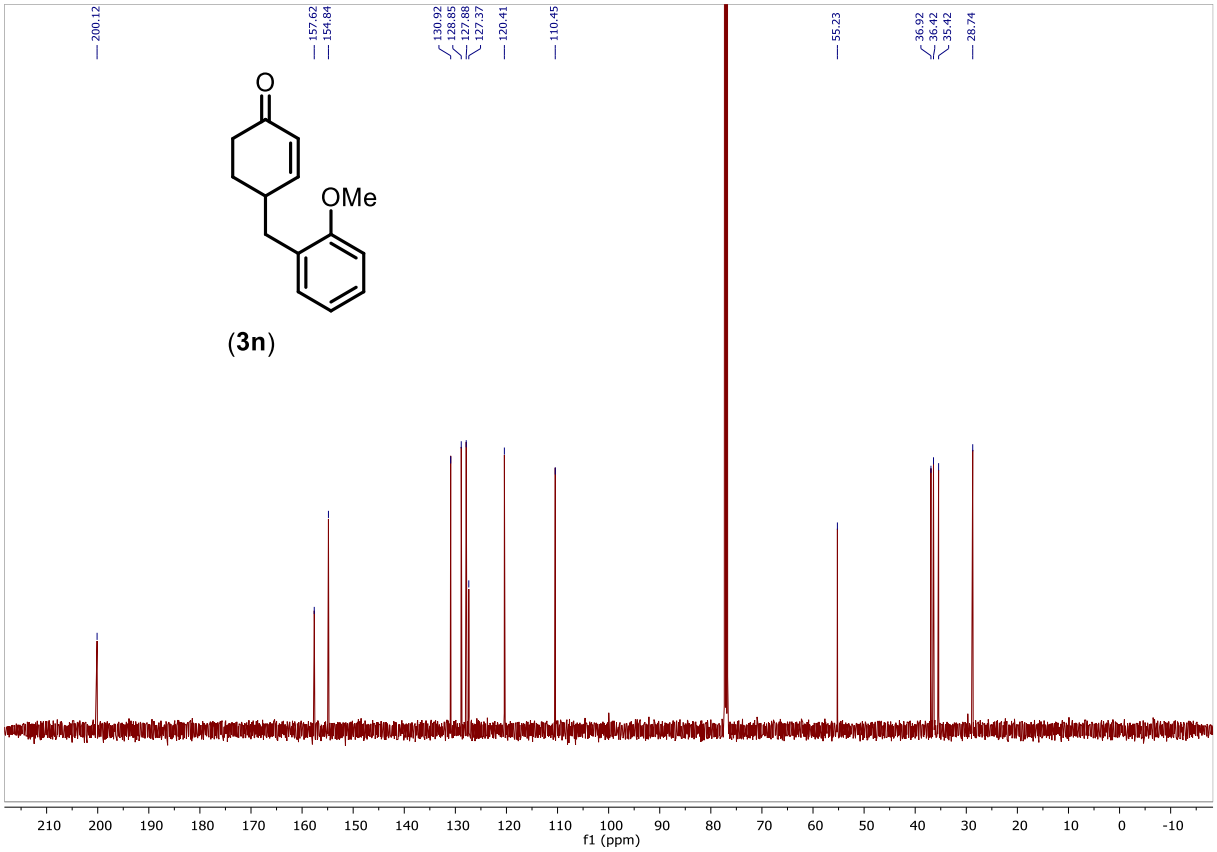
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



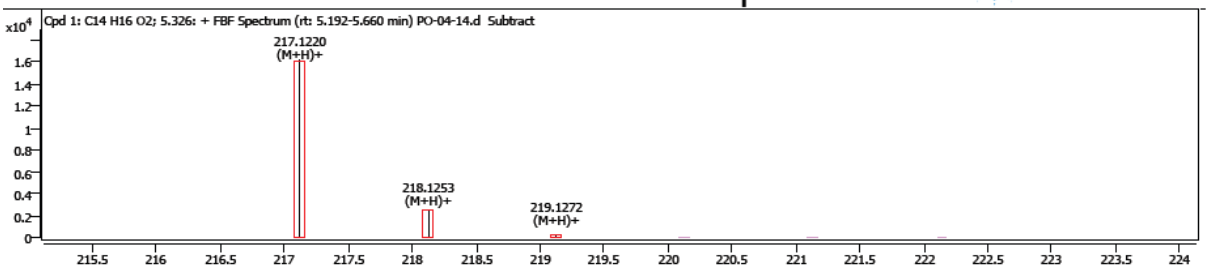





OMe
(3n)
f1 (ppm)

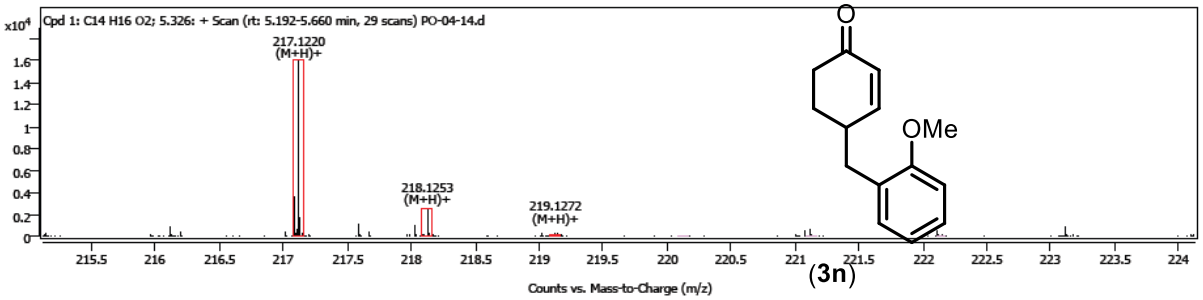

OMe
(3n)
f1 (ppm)

Custom Workflow Report



Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
217.1220	217.1223	-1.38	16128	100.00	100.00	(M+H)+	1
218.1253	218.1257	-2.05	2431	15.07	15.41	(M+H)+	1
219.1272	219.1284	-5.64	260	1.61	1.52	(M+H)+	1

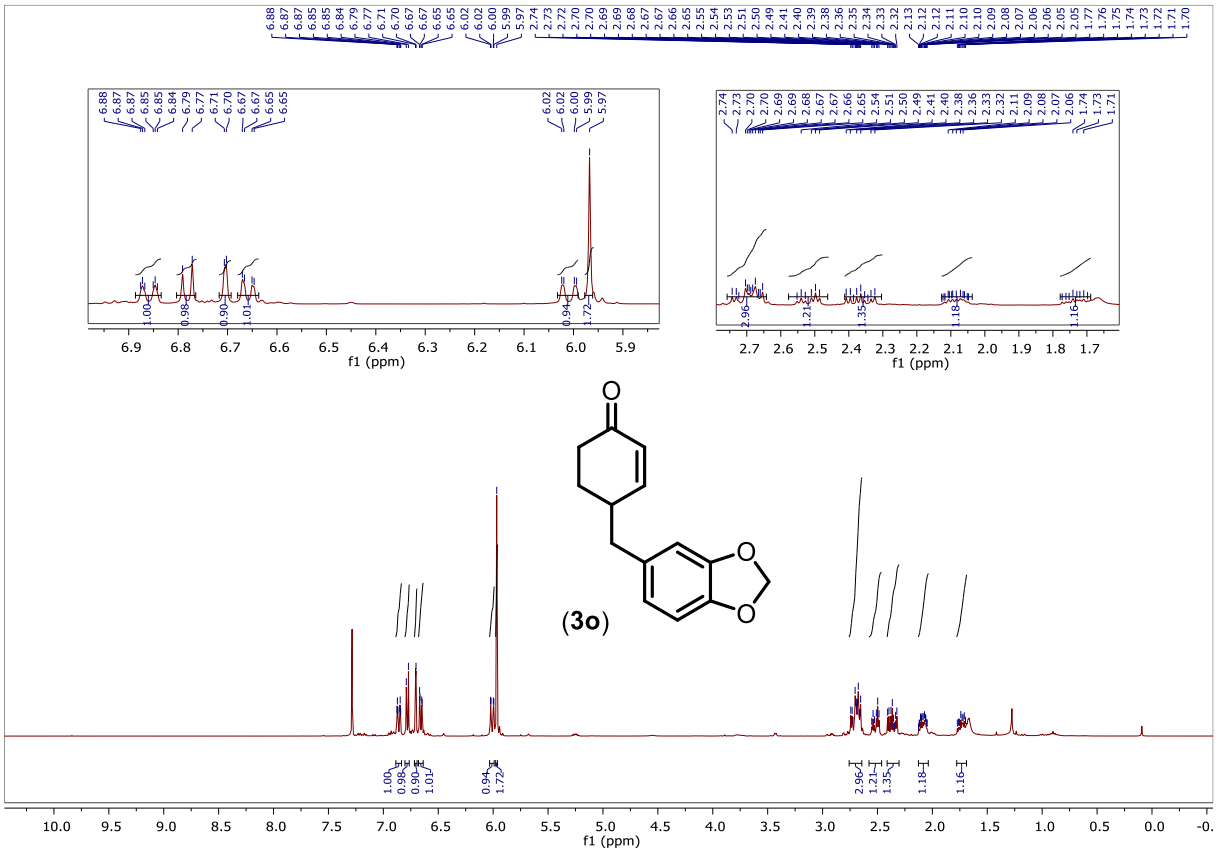


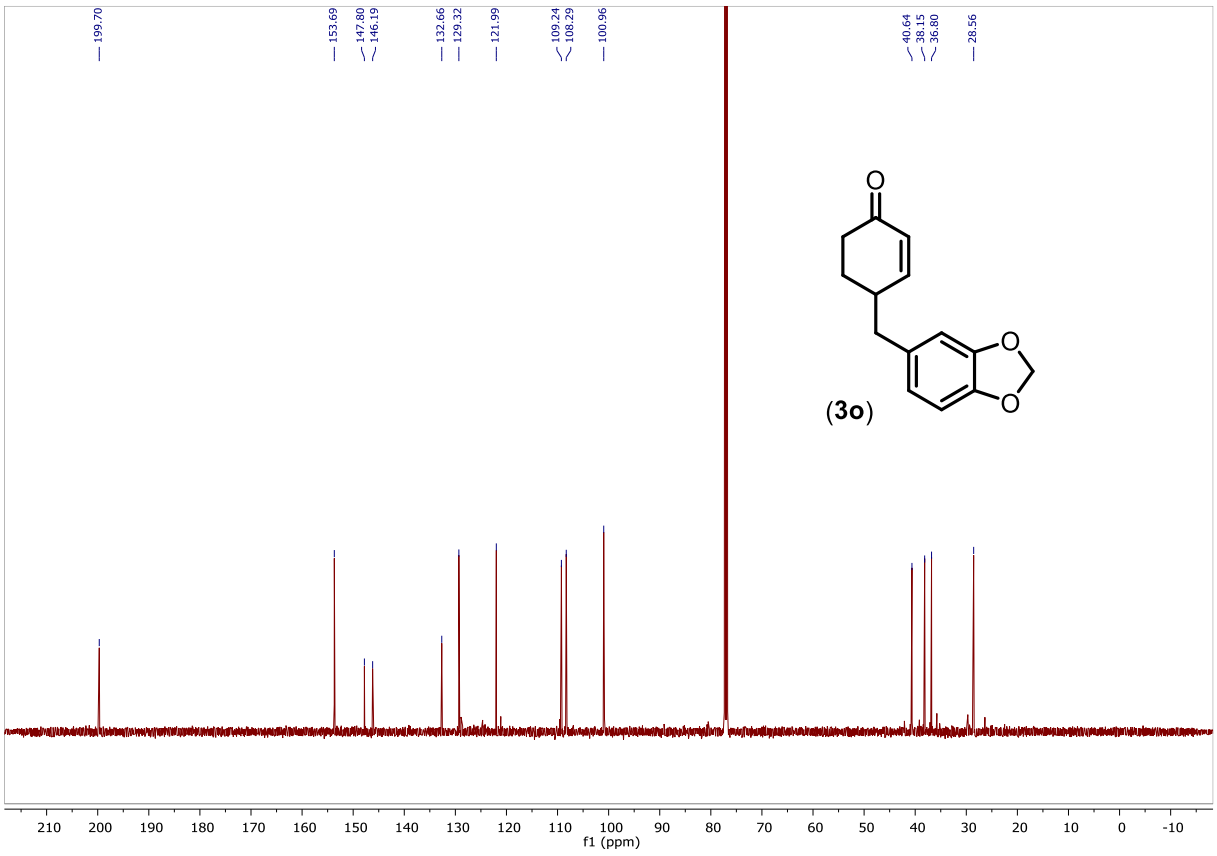
(3n)

Spectrum Peaks

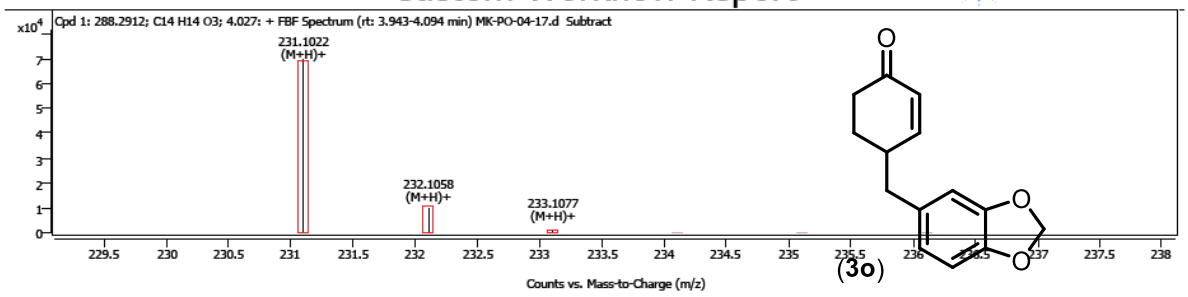
m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
217.1220	217.1223	-1.38	16128	100.00	100.00	(M+H)+	1
218.1253	218.1257	-2.05	2431	15.07	15.41	(M+H)+	1
219.1272	219.1284	-5.64	260	1.61	1.52	(M+H)+	1

MassHunter Qual 10.0
(End of Report)


(3o)
f1 (ppm)


(3o)
f1 (ppm)

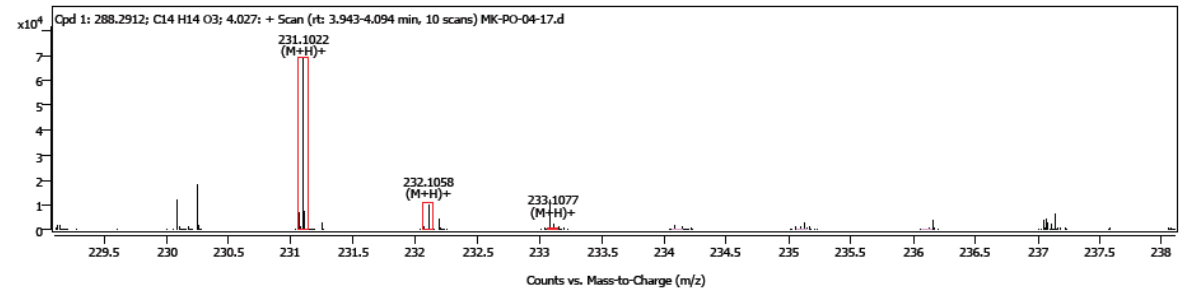
Custom Workflow Report



(3o)

Spectrum Peaks

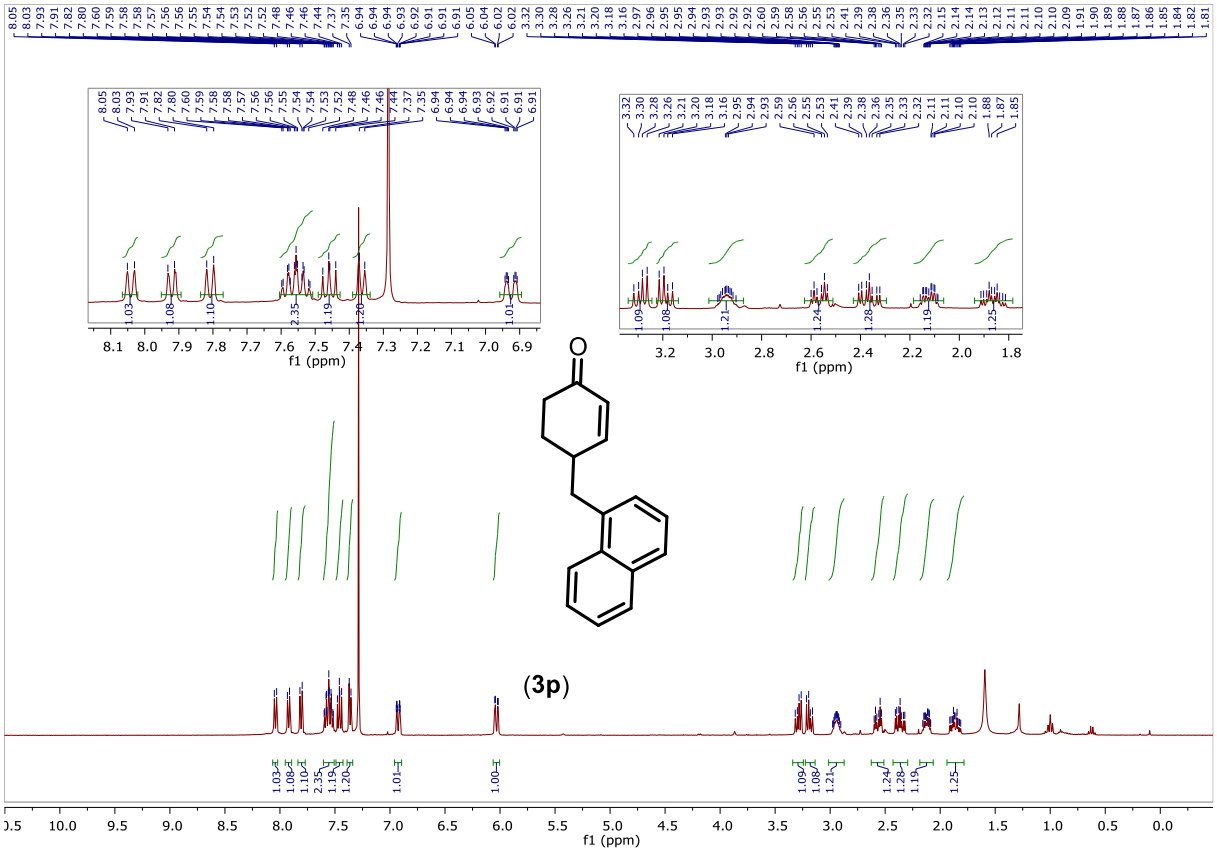
m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
231.1022	231.1016	2.82	69667	100.00	100.00	(M+H)+	1
232.1058	232.1050	3.44	10020	14.38	15.43	(M+H)+	1
233.1077	233.1075	1.24	436	0.63	1.72	(M+H)+	1

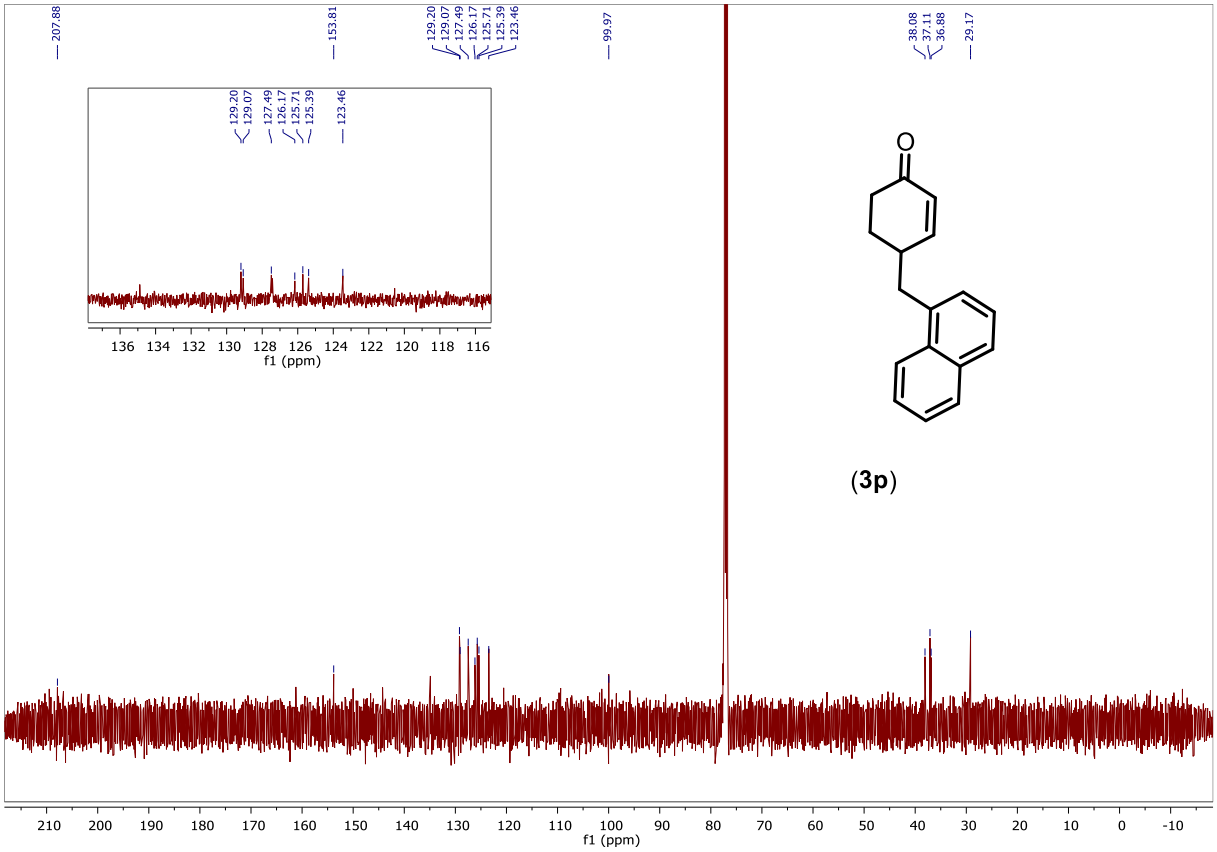


Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
231.1022	231.1016	2.82	69667	100.00	100.00	(M+H)+	1
232.1058	232.1050	3.44	10020	14.38	15.43	(M+H)+	1
233.1077	233.1075	1.24	436	0.63	1.72	(M+H)+	1

MassHunter Qual 10.0
(End of Report)


(3p)
f1 (ppm)


(3p)
f1 (ppm)

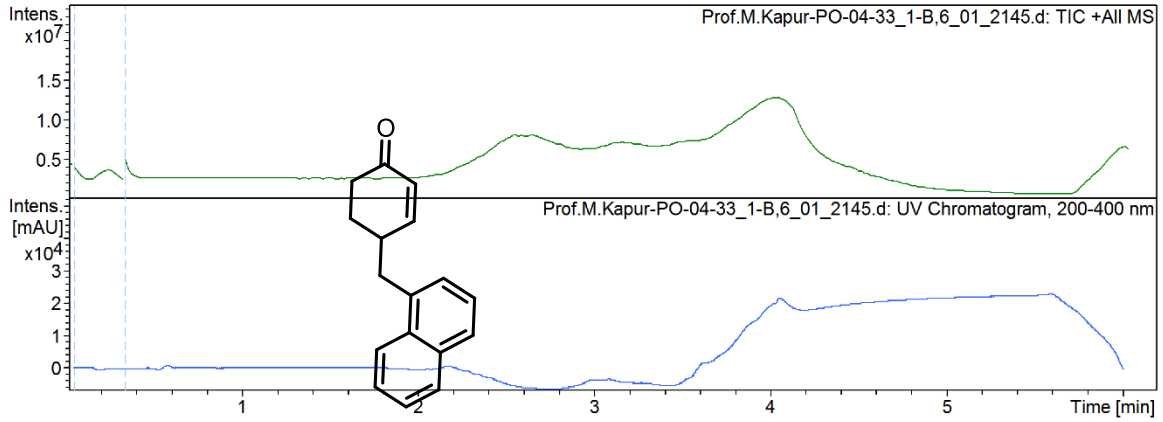
Display Report

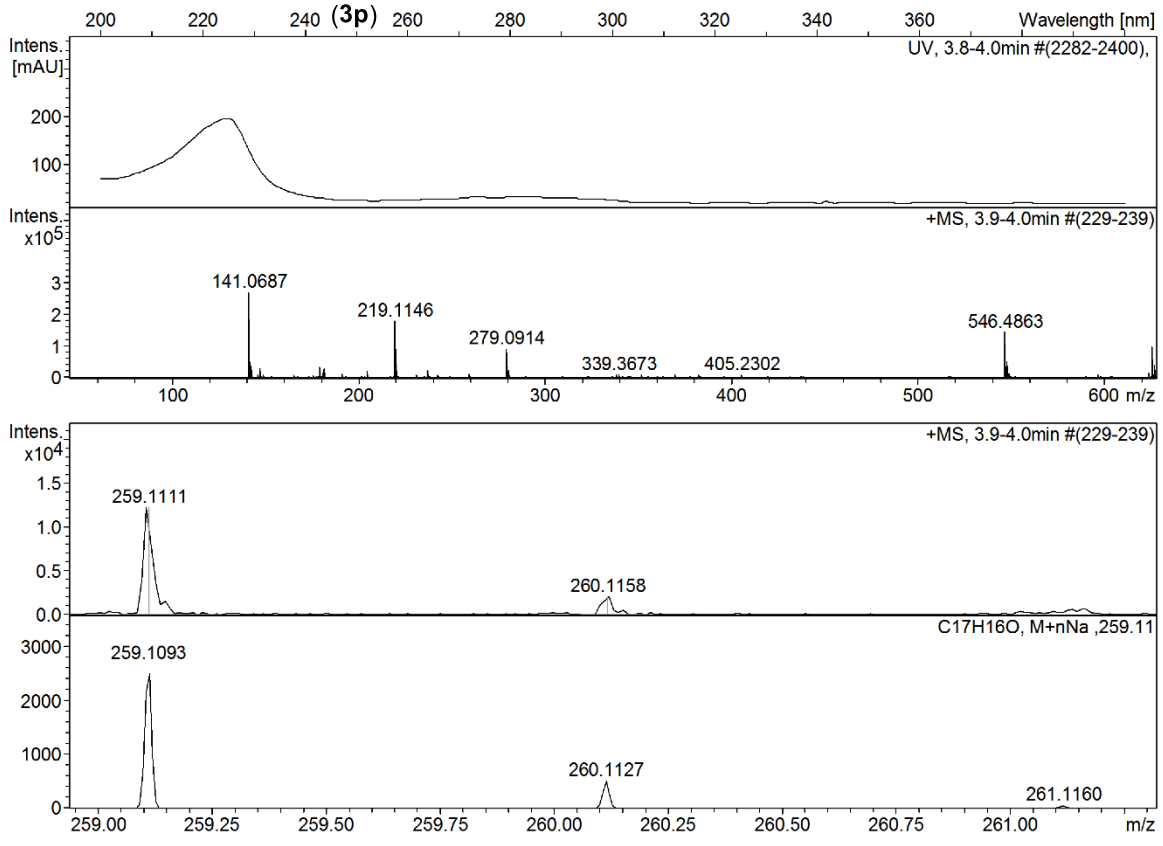
Analysis Info

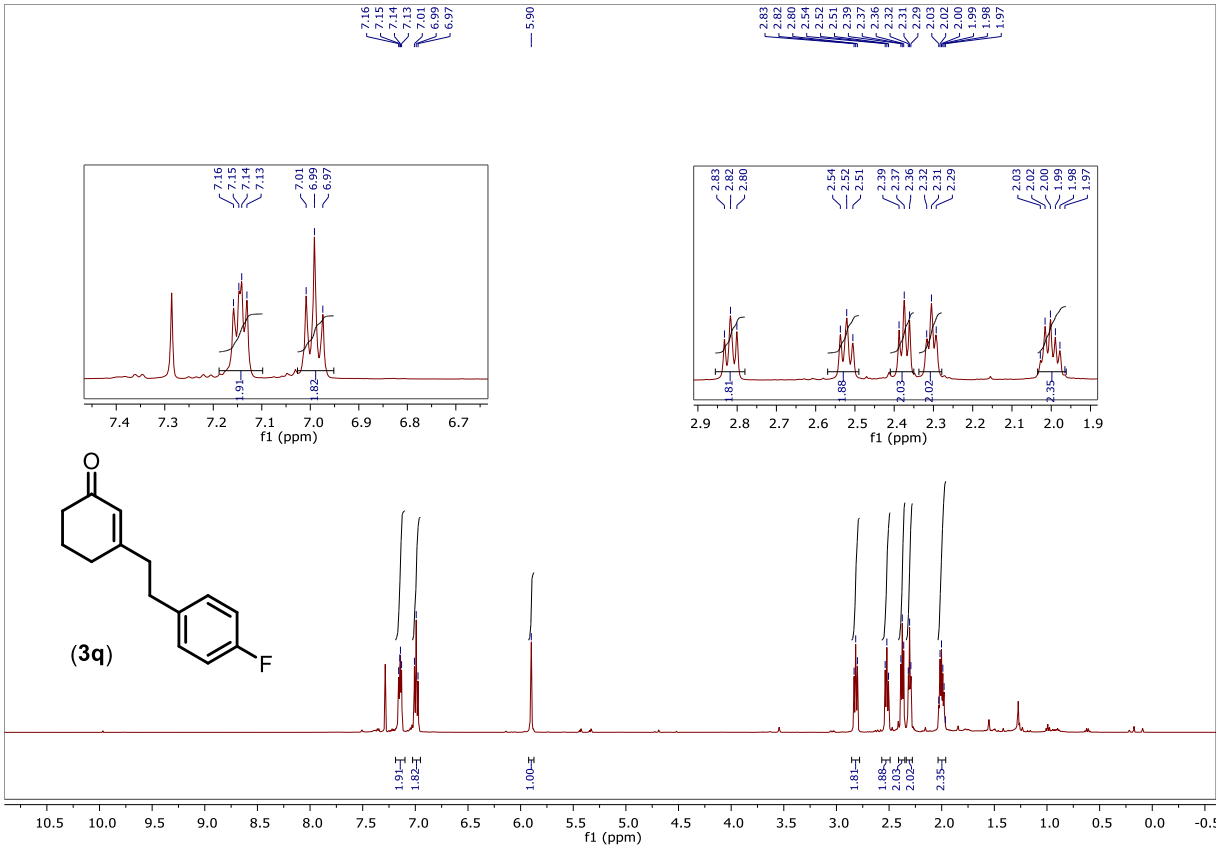
Acquisition Date	27-06-2023 13:45:27		
Analysis Name	D:\Data\USER DATA 2023\June\27-june\Prof.M.Kapur-PO-04-33_1-B,6_01_2145.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-33	Instrument	micrOTOF-Q 10330
Comment			

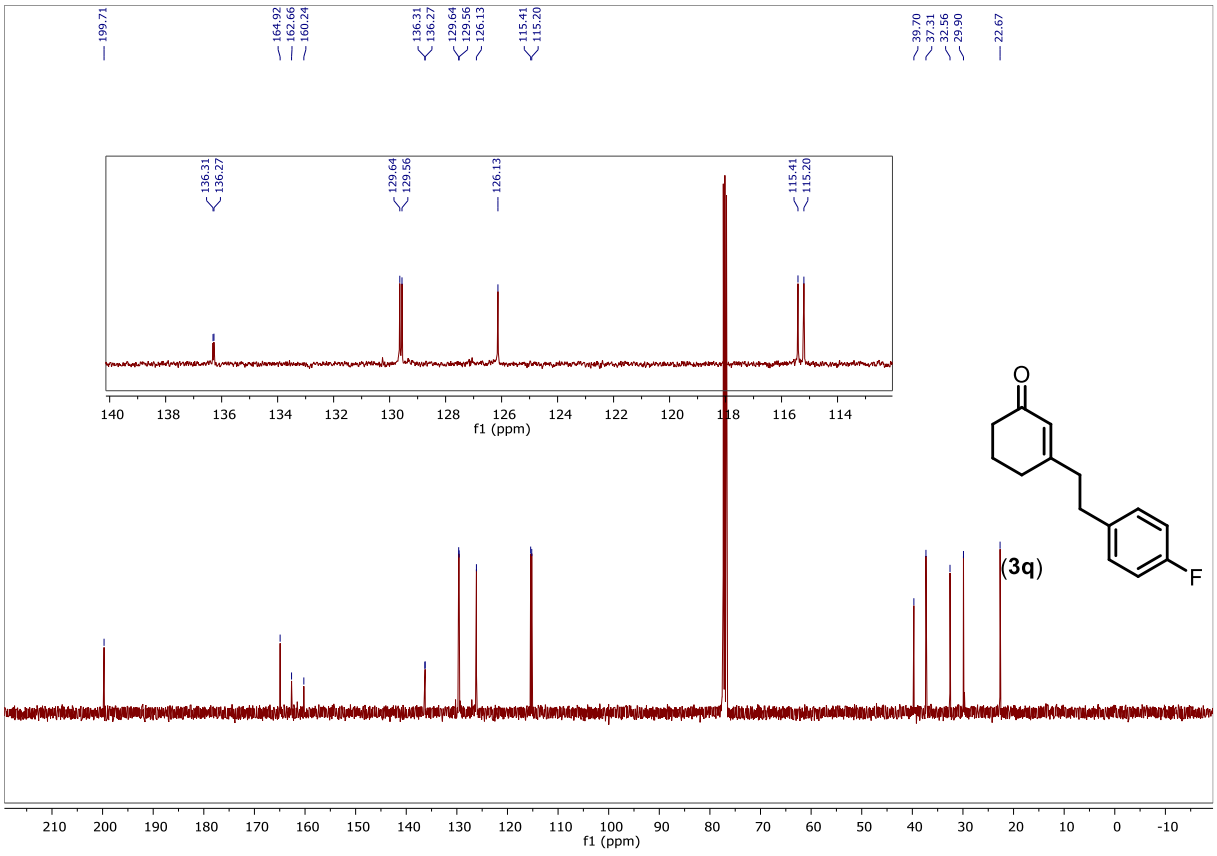
Acquisition Parameter

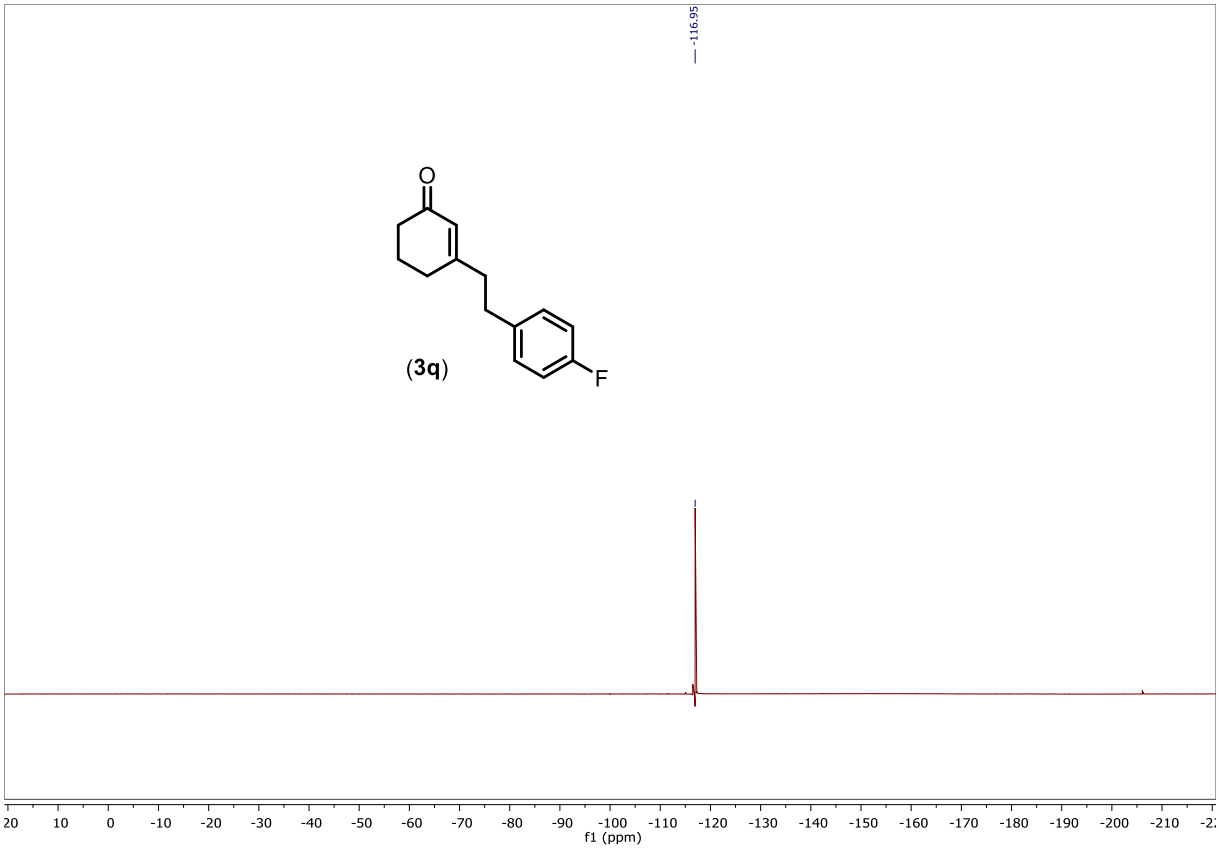
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste






(3q)
F
f1 (ppm)


(3q)
F
f1 (ppm)


-116.95
O
F
(3q)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

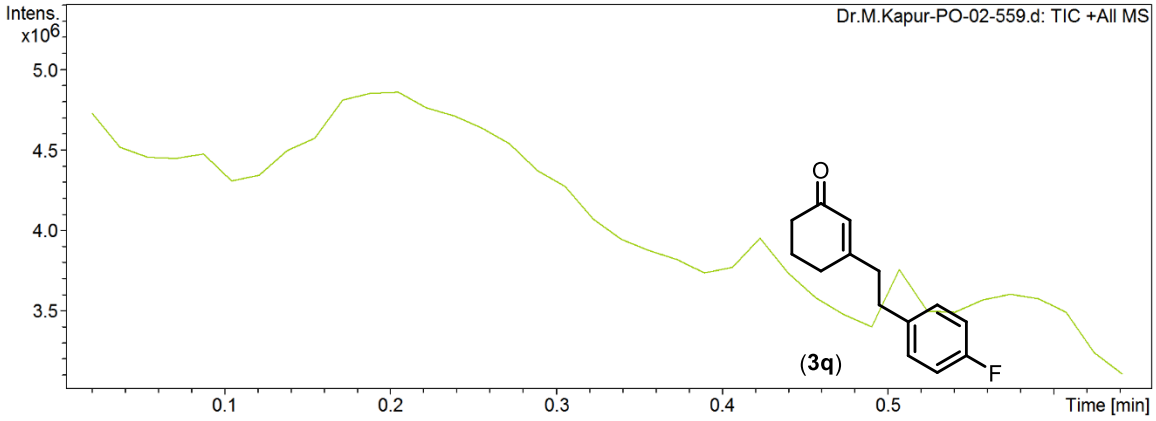
Display Report

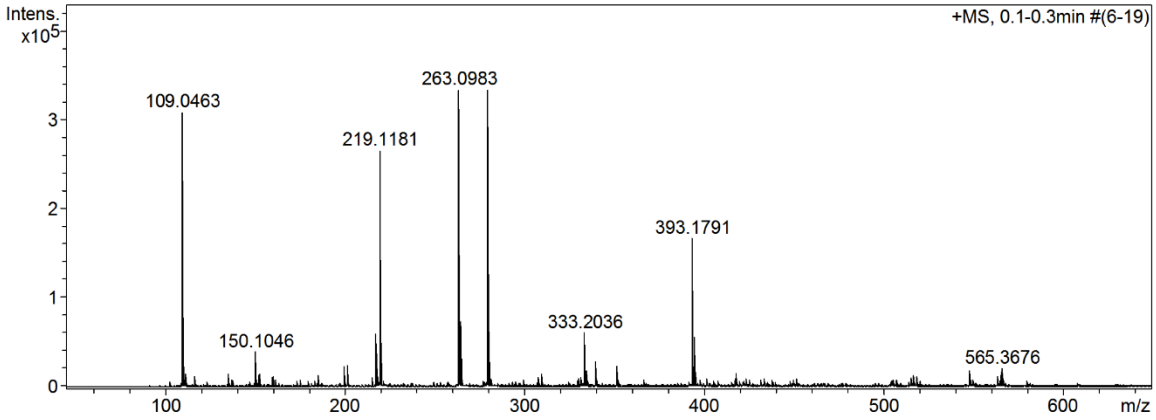
Analysis Info

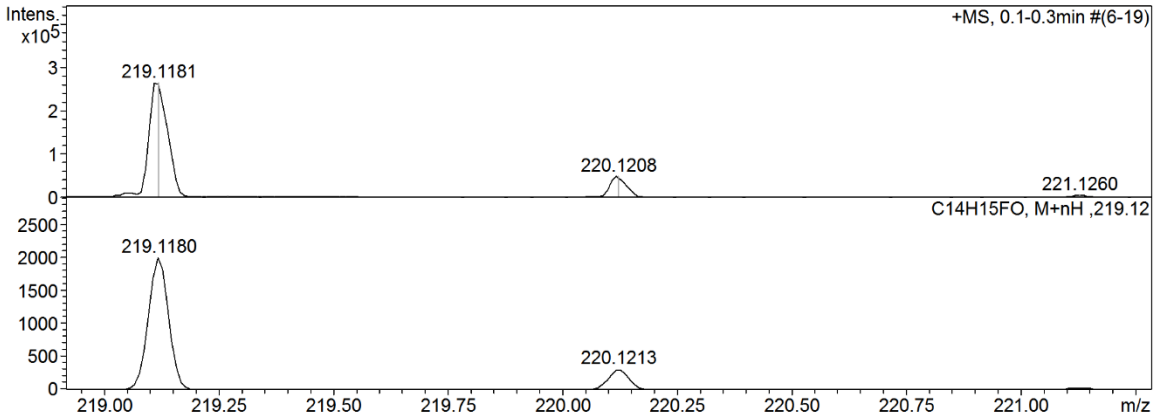
Analysis Name	D:\Data\USER DATA 2023\April\06-april\Dr.M.Kapur-PO-02-559.d	Acquisition Date	06-04-2023 14:43:38
Method	tune_low_APCI.m	Operator	Bruker
Sample Name	PO-02-559	Instrument	micrOTOF-Q 10330
Comment			

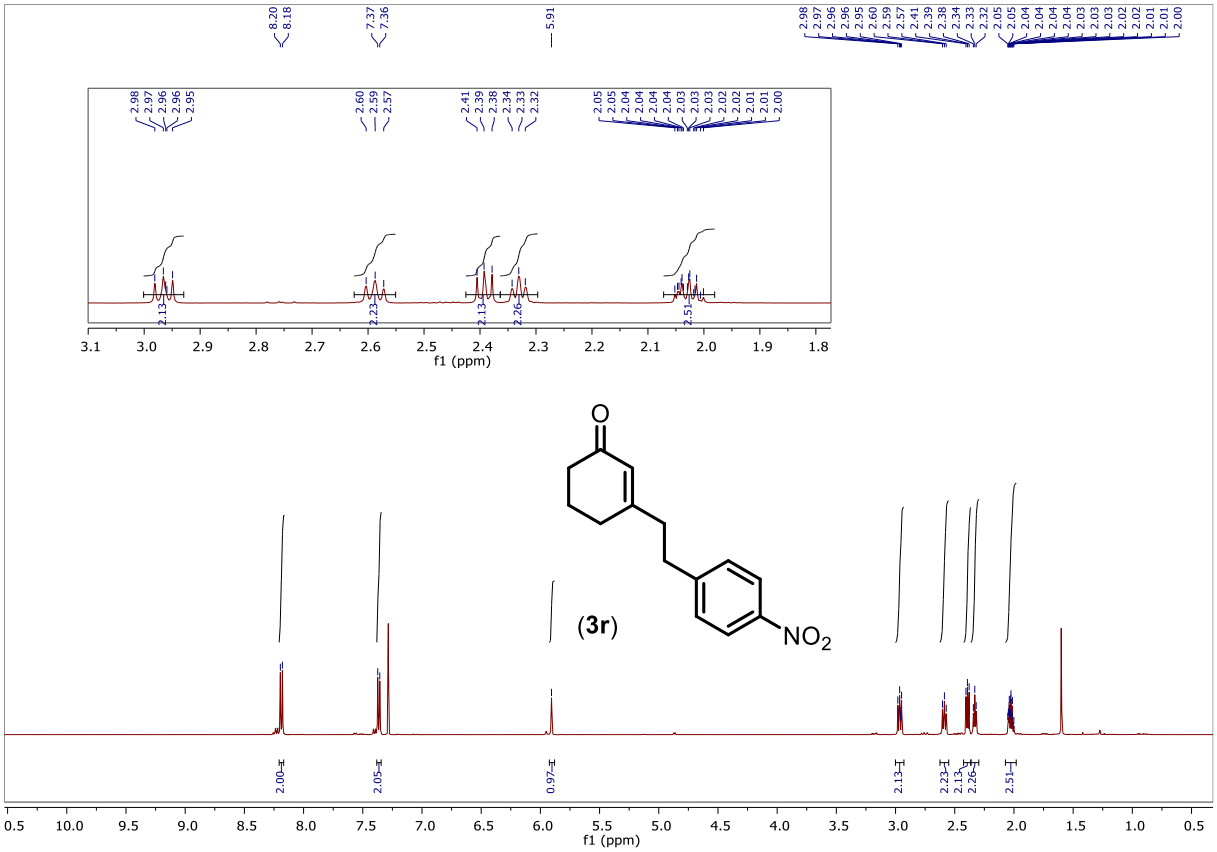
Acquisition Parameter

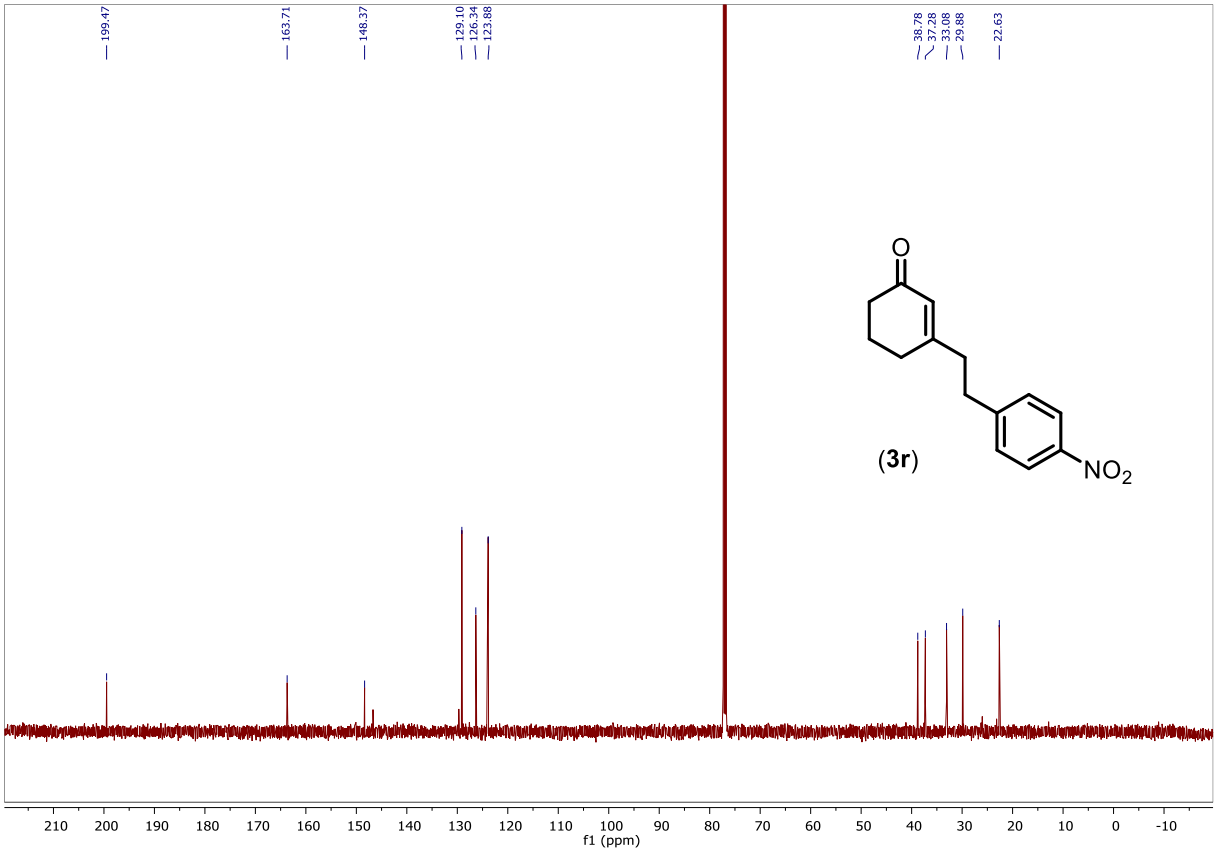
Source Type	Multi Mode	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	2500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source








8.20
8.18
7.37
7.36
5.91
f1 (ppm)
(3r)
NO2
f1 (ppm)


199.47
163.71
148.37
129.10
126.34
123.88
38.78
37.28
33.08
29.88
22.63
(3r)
NO2
f1 (ppm)

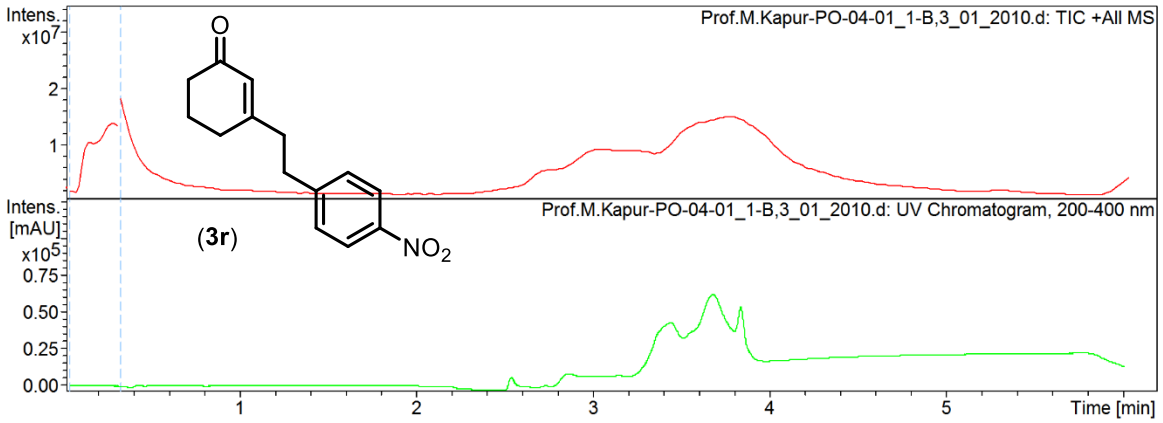
Display Report

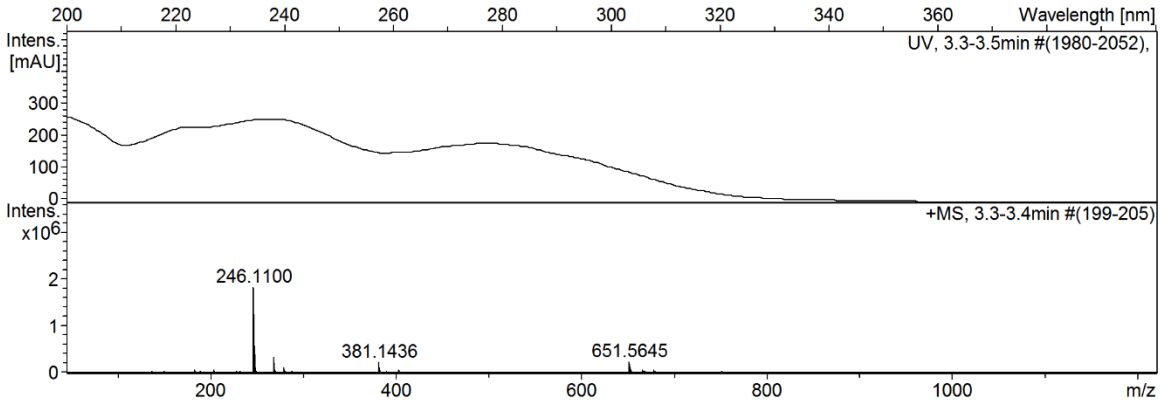
Analysis Info

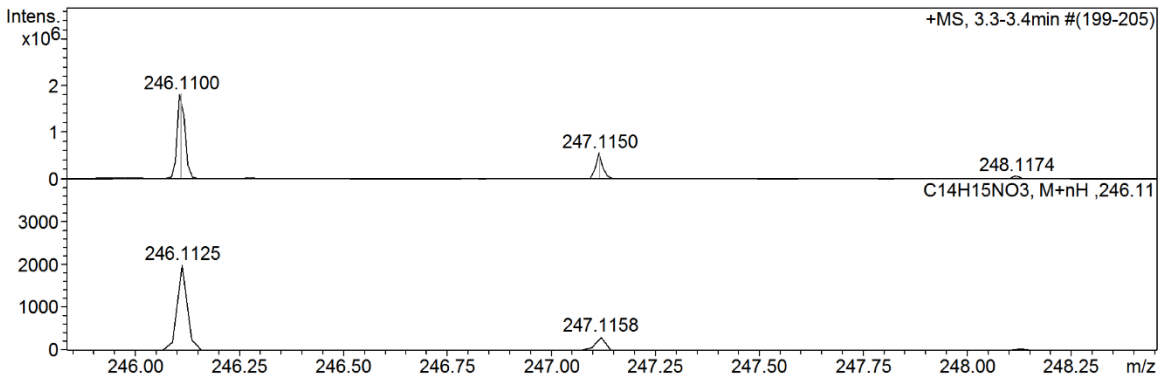
Acquisition Date	21-06-2023 12:29:48		
Analysis Name	D:\Data\USER DATA 2023\June\21-june\Prof.M.Kapur-PO-04-01_1-B,3_01_2010.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-01	Instrument	micrOTOF-Q 10330
Comment			

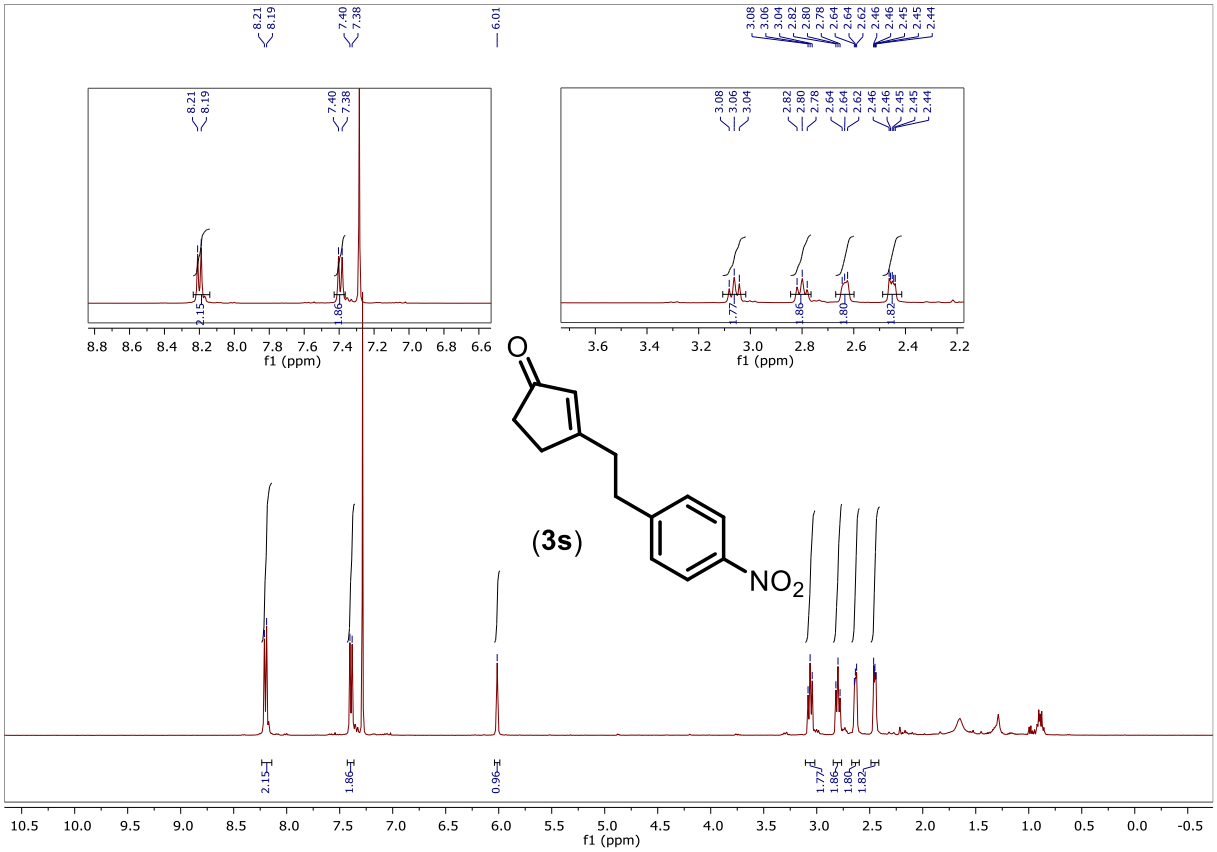
Acquisition Parameter

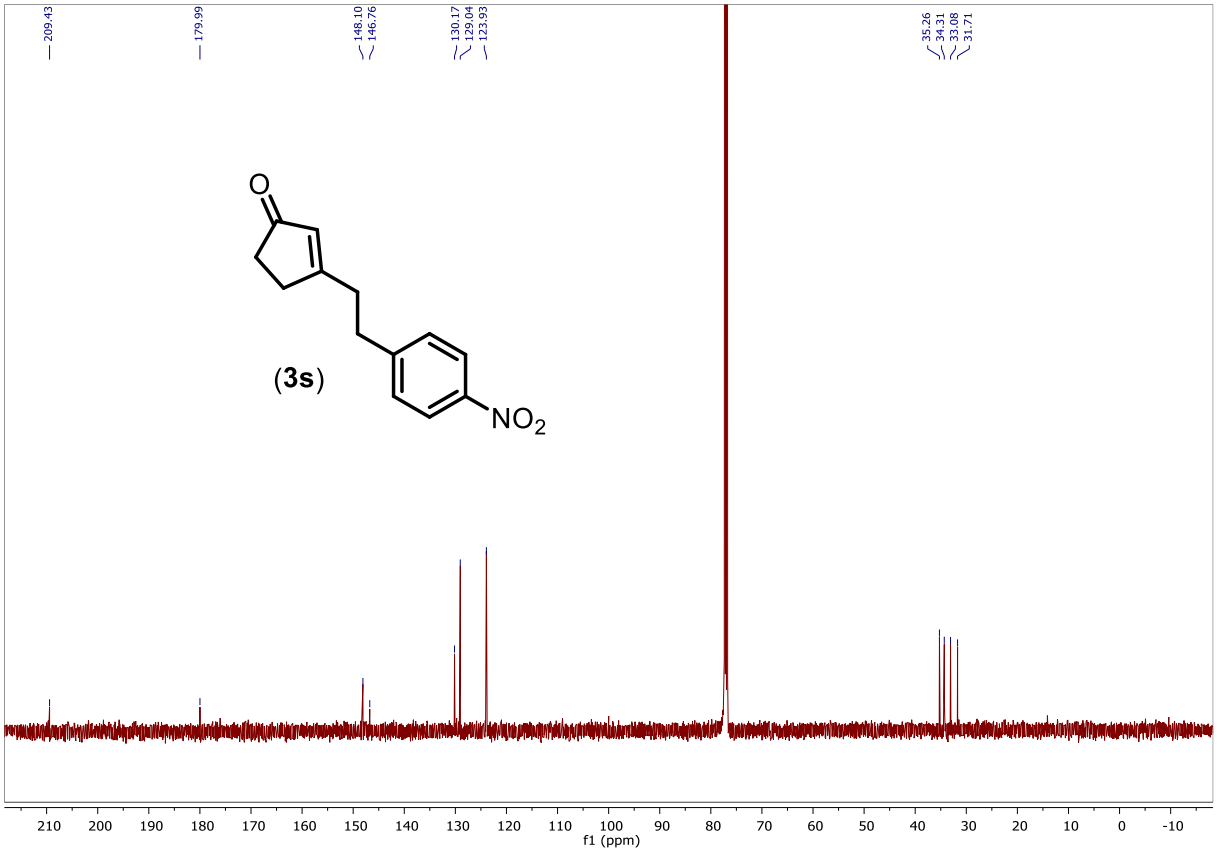
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








8.21
8.19
7.40
7.38
6.01
3.08
3.06
3.04
2.82
2.80
2.78
2.64
2.64
2.62
2.46
2.46
2.45
2.45
2.44
f1 (ppm)
(3s)
NO2
2.15
1.86
0.96
1.77
1.86
1.80
1.82


209.43
179.99
148.10
146.76
130.17
129.04
123.93
35.26
34.31
33.08
31.71
f1 (ppm)
(3s)
NO2

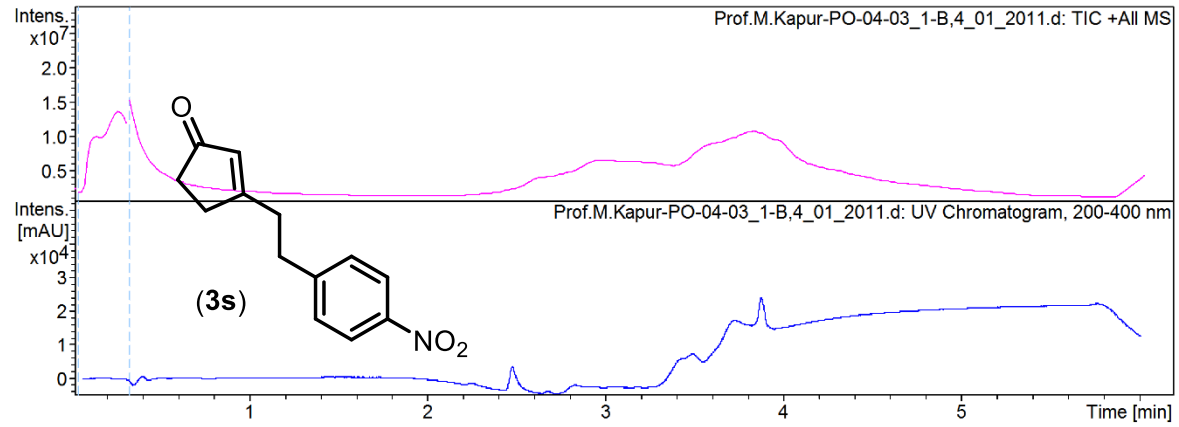
Display Report

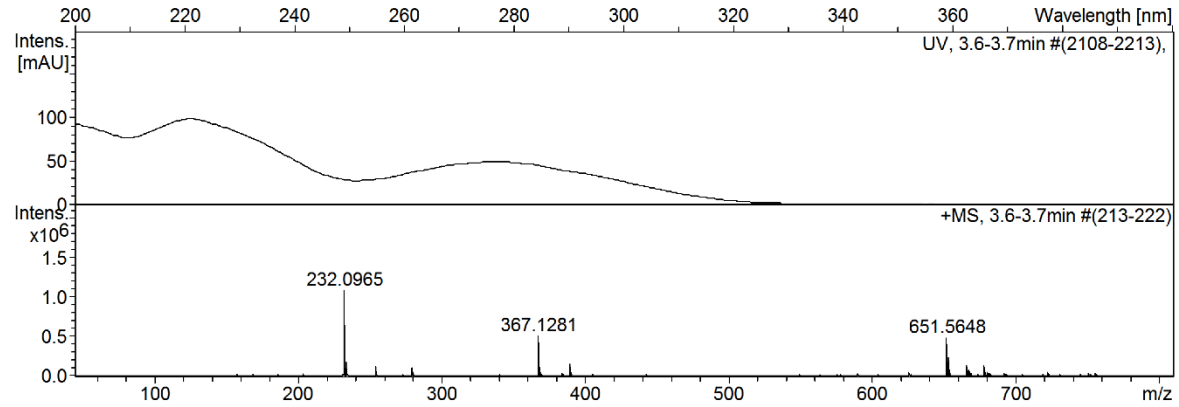
Analysis Info

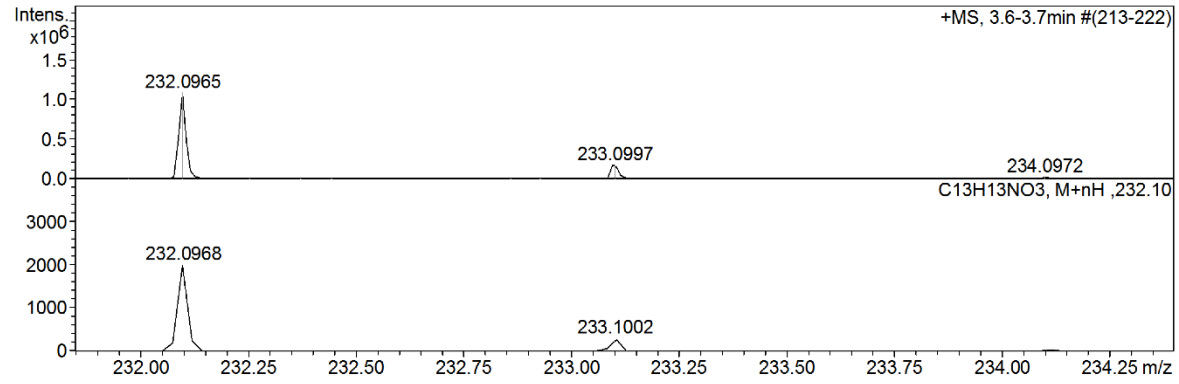
Acquisition Date	21-06-2023 12:37:02		
Analysis Name	D:\Data\USER DATA 2023\June\21-june\Prof.M.Kapur-PO-04-03_1-B,4_01_2011.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-03	Instrument	micrOTOF-Q 10330
Comment			

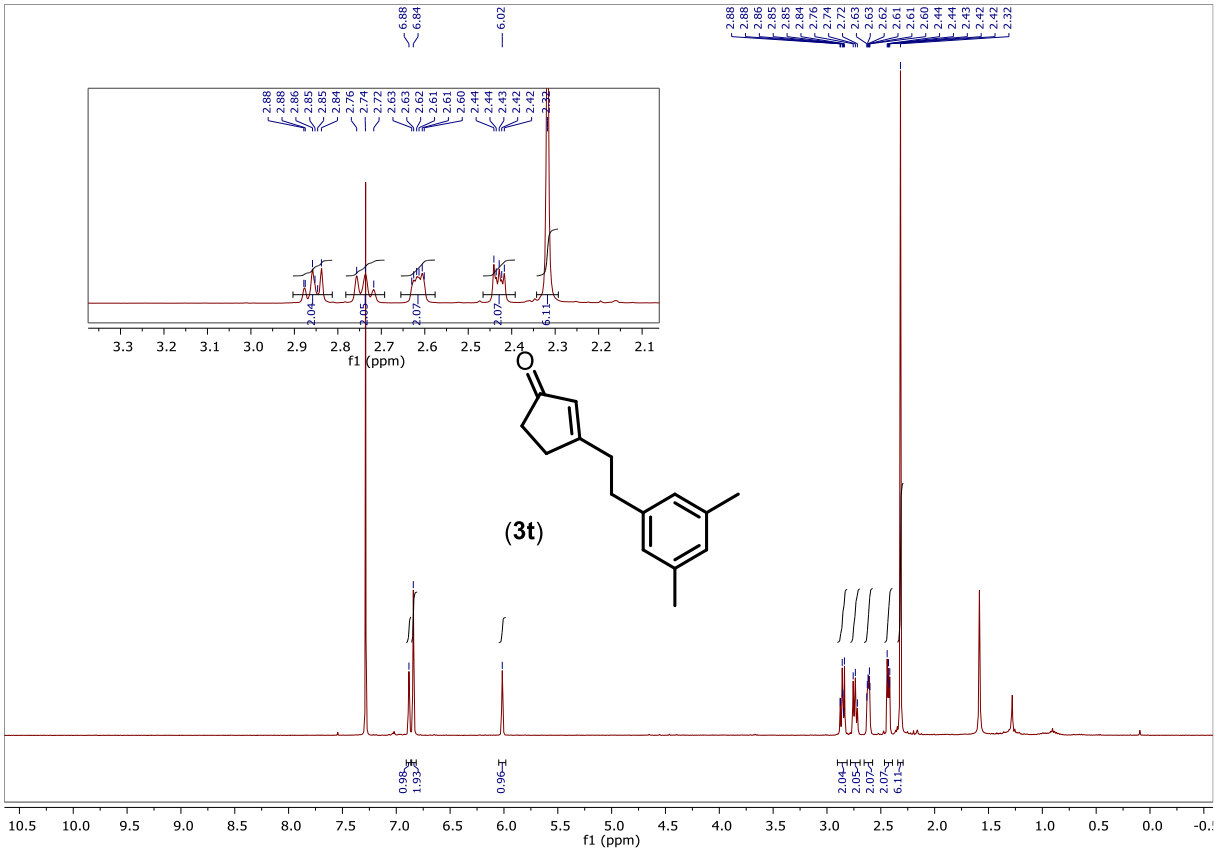
Acquisition Parameter

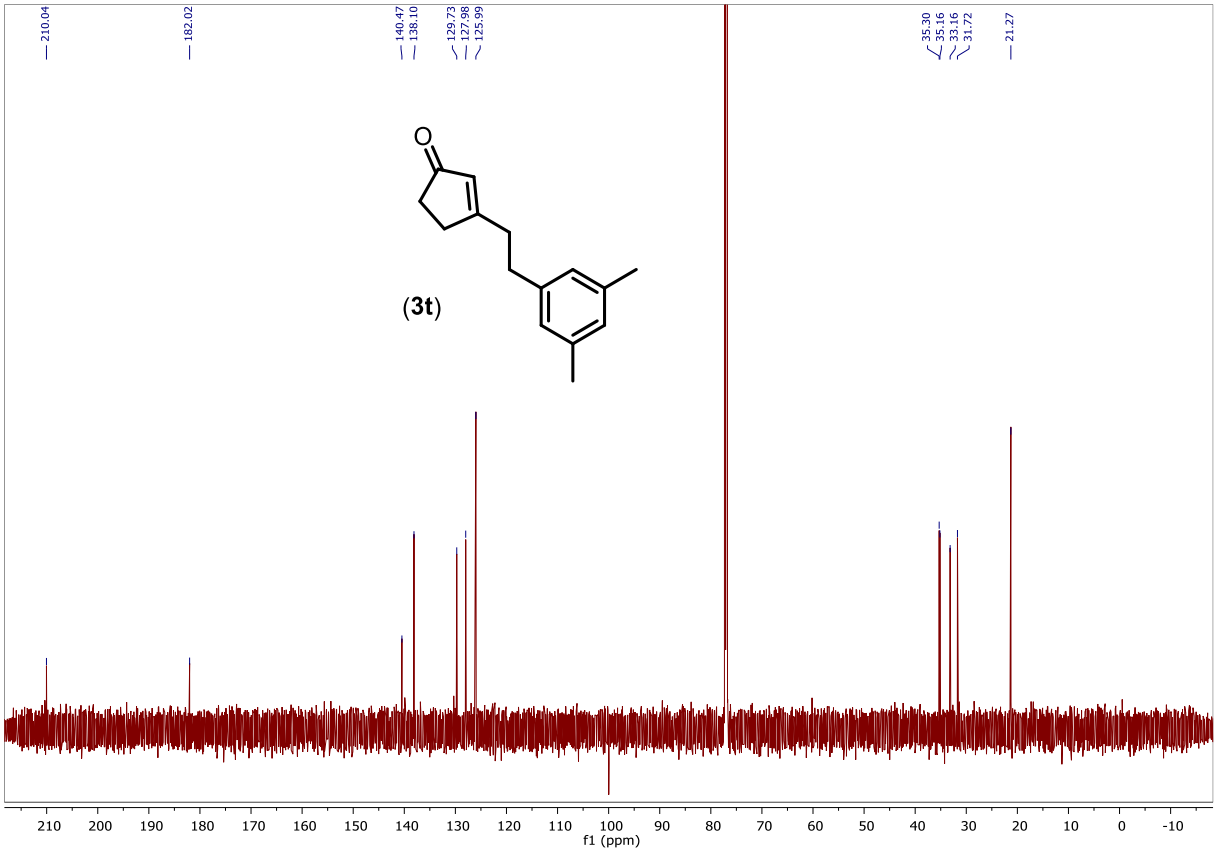
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








(3t)
f1 (ppm)


(3t)
f1 (ppm)

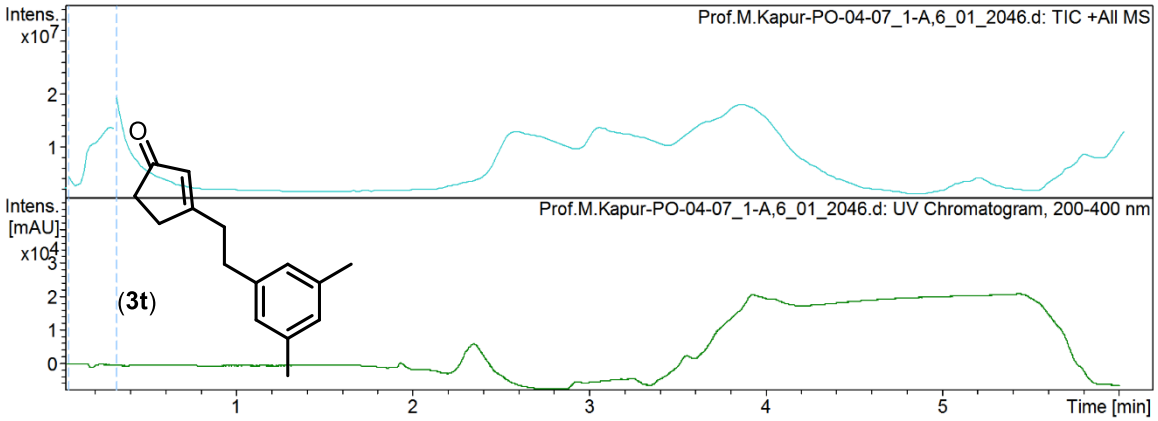
Display Report

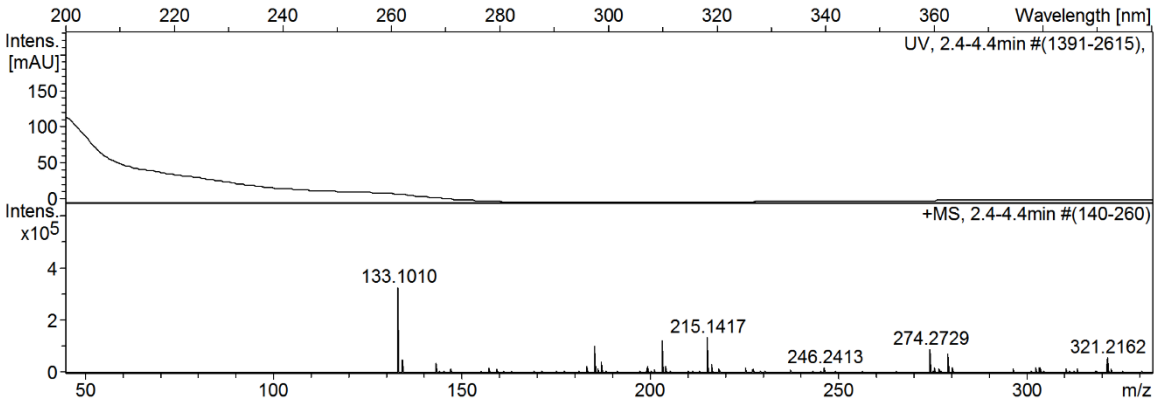
Analysis Info

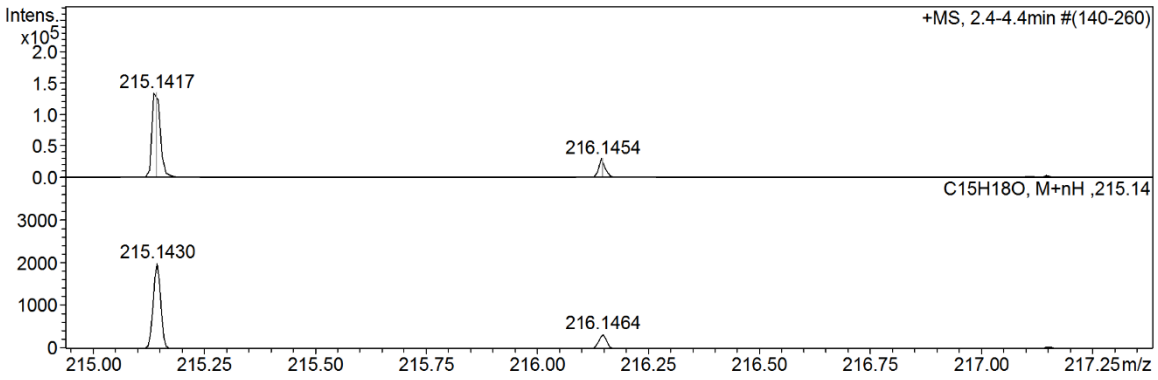
Analysis Name	D:\Data\USER DATA 2023\June\22-june\Prof.M.Kapur-PO-04-07_1-A,6_01_2046.d	Acquisition Date	23-06-2023 10:45:06
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-07	Instrument	micrOTOF-Q 10330
Comment			

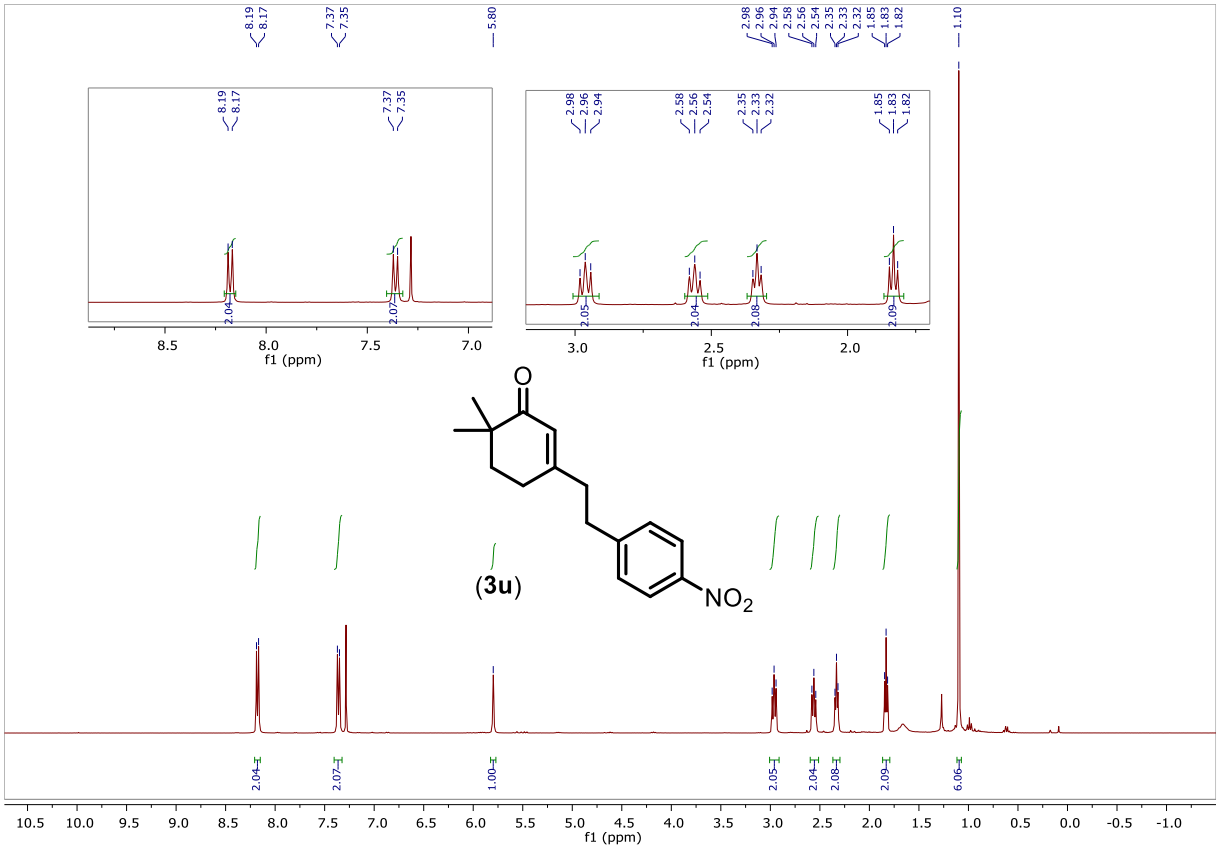
Acquisition Parameter

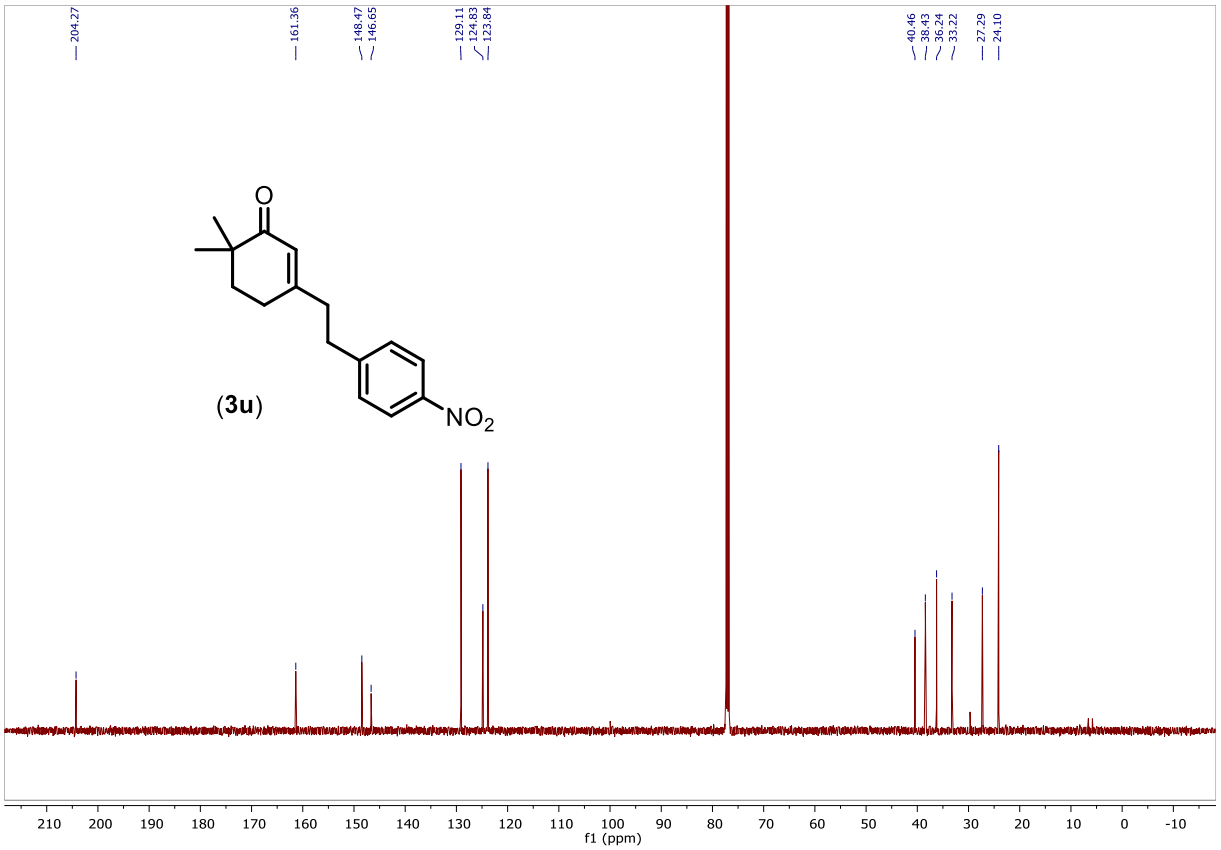
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








8.19
8.17
7.37
7.35
5.80
2.98
2.96
2.94
2.58
2.56
2.54
2.35
2.33
2.32
1.85
1.83
1.82
1.10
f1 (ppm)
O
NO2
(3u)


204.27
161.36
148.47
146.65
129.11
124.83
123.84
40.46
38.43
36.24
33.22
27.29
24.10
f1 (ppm)
O
NO2
(3u)

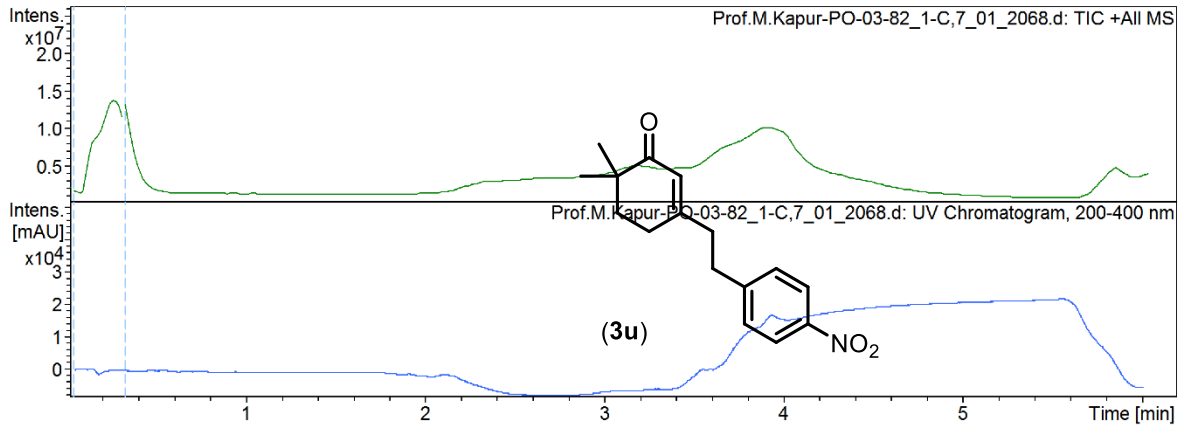
Display Report

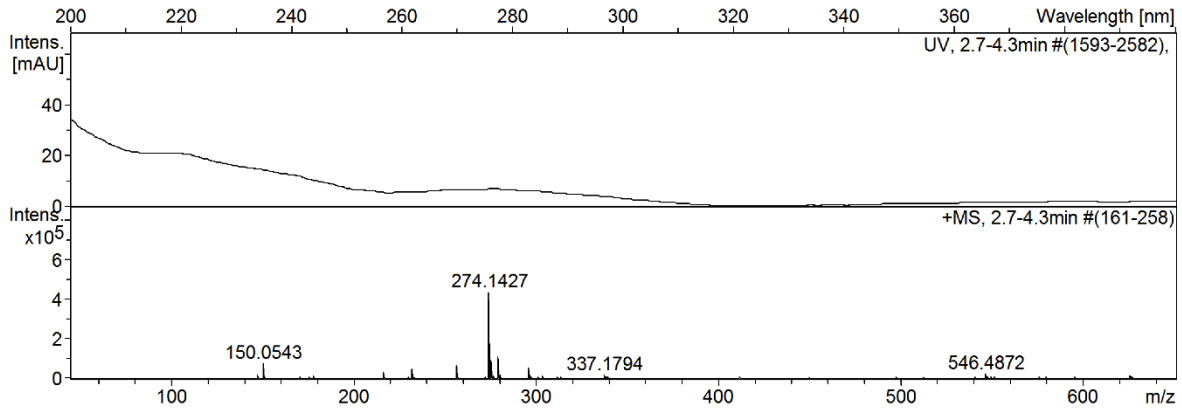
Analysis Info

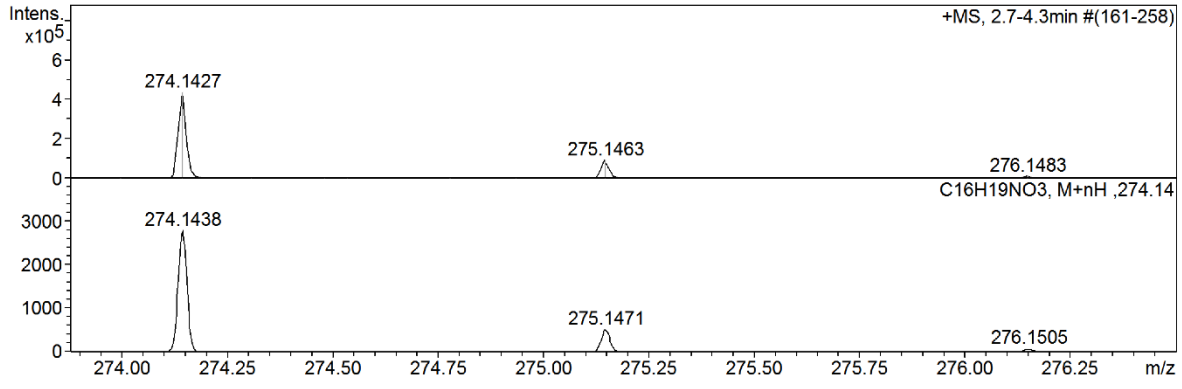
Acquisition Date	23-06-2023 14:08:57		
Analysis Name	D:\Data\USER DATA 2023\June\22-june\Prof.M.Kapur-PO-03-82_1-C,7_01_2068.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-03-82	Instrument	micrOTOF-Q 10330
Comment			

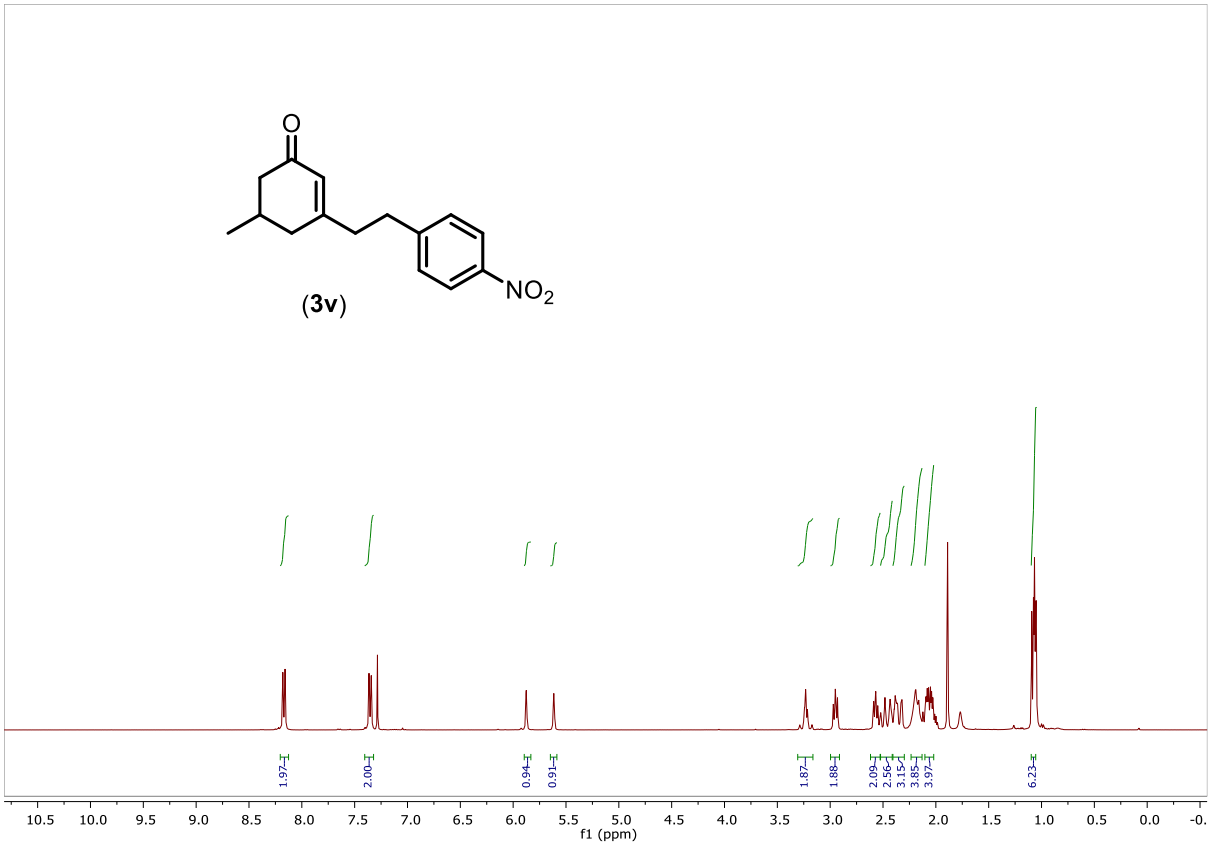
Acquisition Parameter

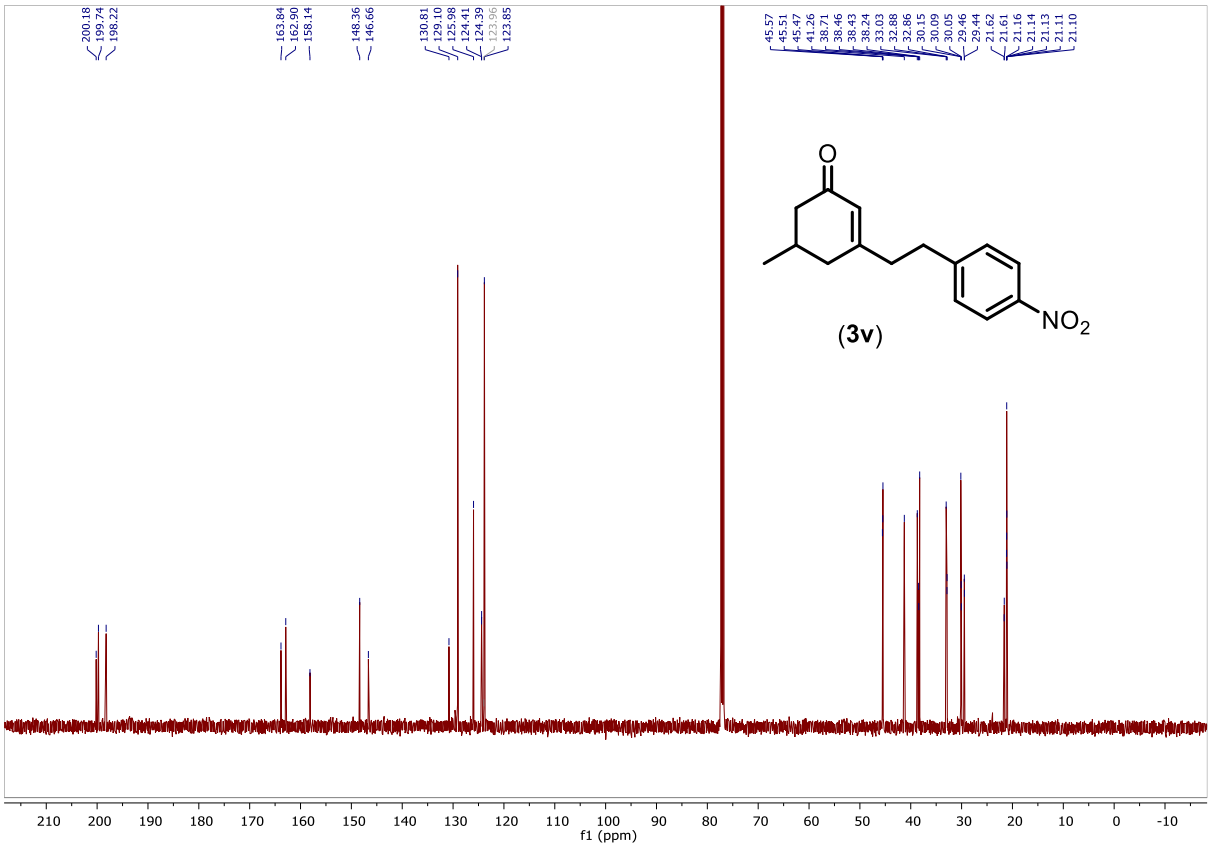
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








O
NO2
(3v)
1.97
2.00
0.94
0.91
1.87
1.68
2.09
2.56
3.15
3.85
3.97
6.23
f1 (ppm)


200.18
199.74
198.22
163.84
162.90
158.14
148.36
146.66
130.81
129.10
125.98
124.41
124.39
123.96
123.85
45.57
45.51
45.47
41.26
38.71
38.46
38.43
38.24
33.03
32.88
32.86
30.15
30.09
30.05
29.46
29.44
21.62
21.61
21.16
21.14
21.13
21.11
21.10
O
NO2
(3v)
f1 (ppm)

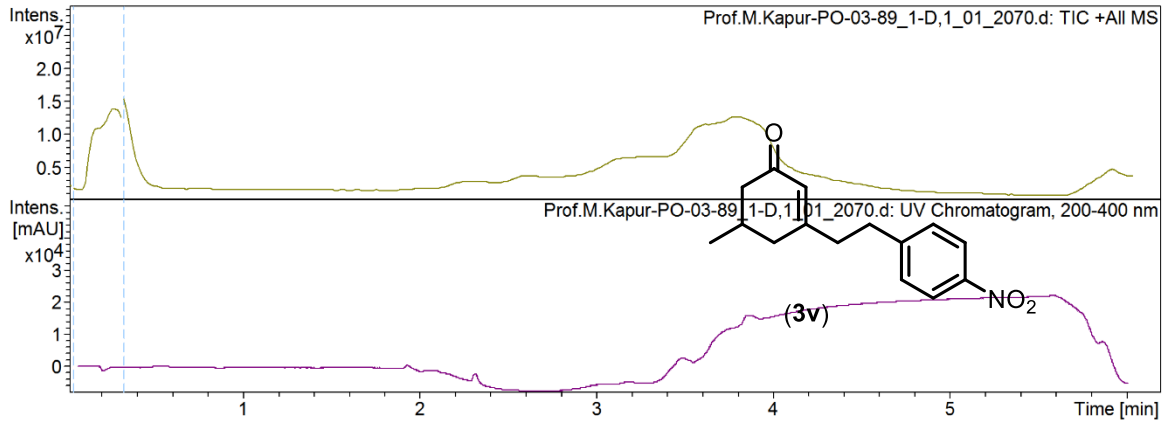
Display Report

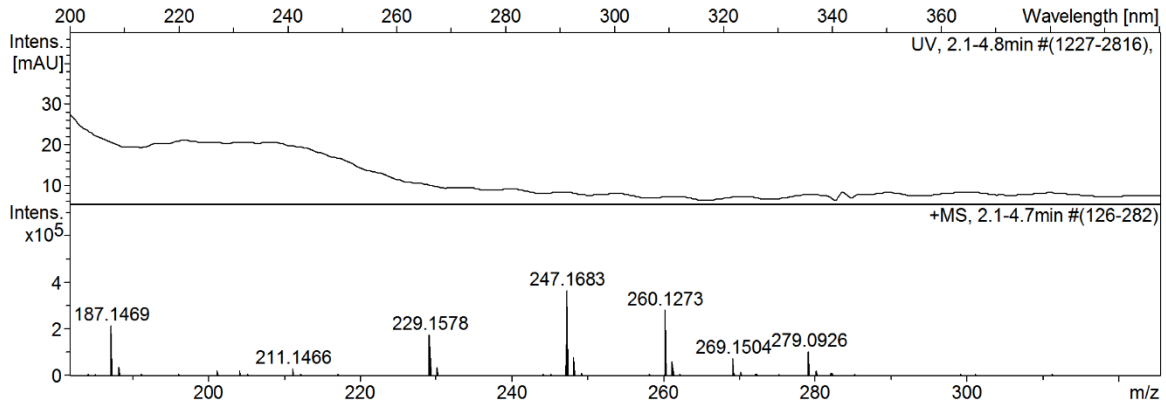
Analysis Info

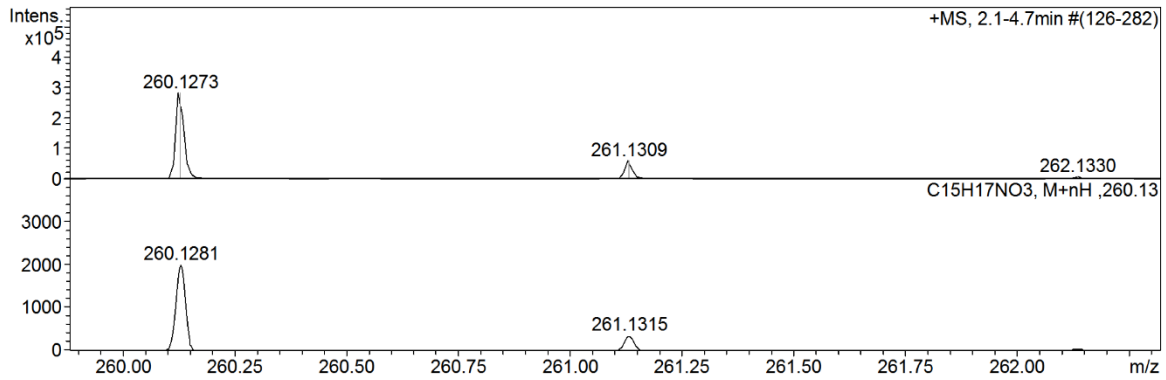
Acquisition Date	23-06-2023 14:23:26		
Analysis Name	D:\Data\USER DATA 2023\June\22-june\Prof.M.Kapur-PO-03-89_1-D,1_01_2070.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-03-89	Instrument	micrOTOF-Q 10330
Comment			

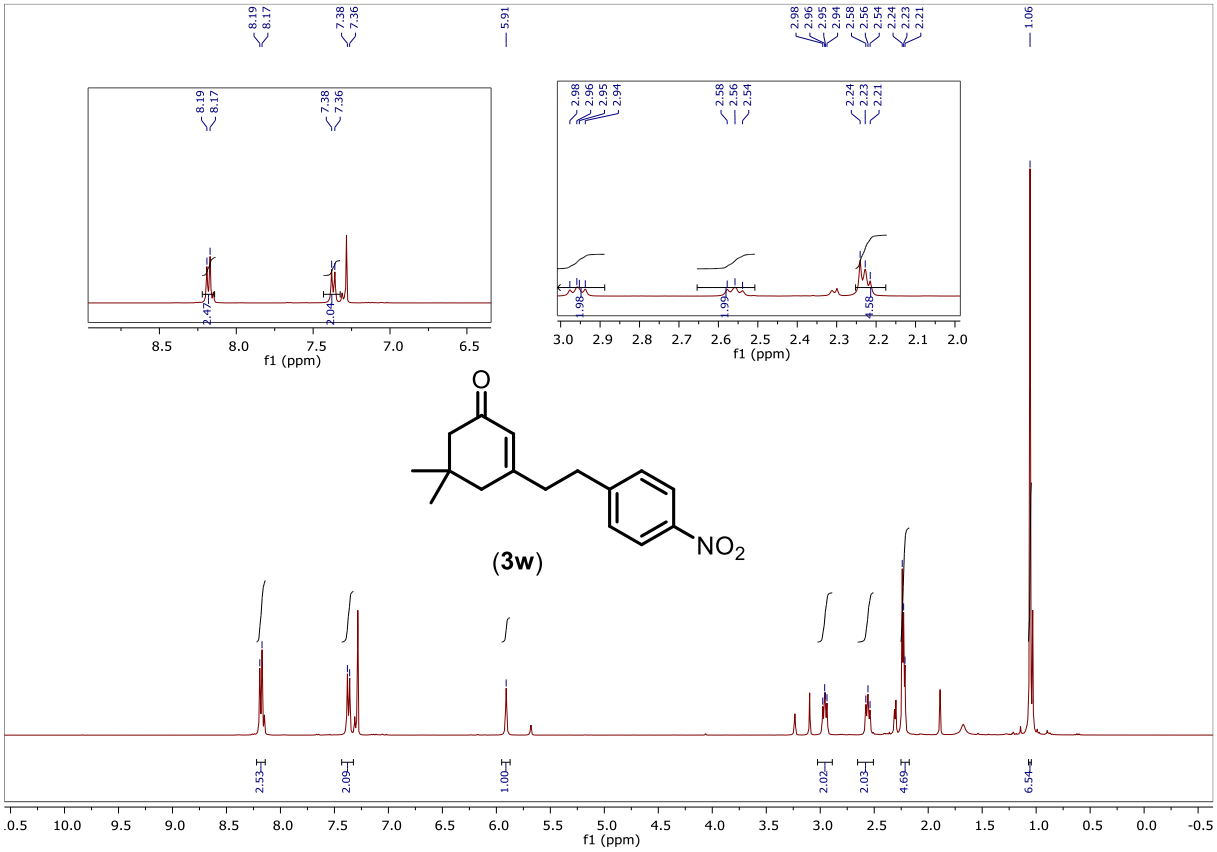
Acquisition Parameter

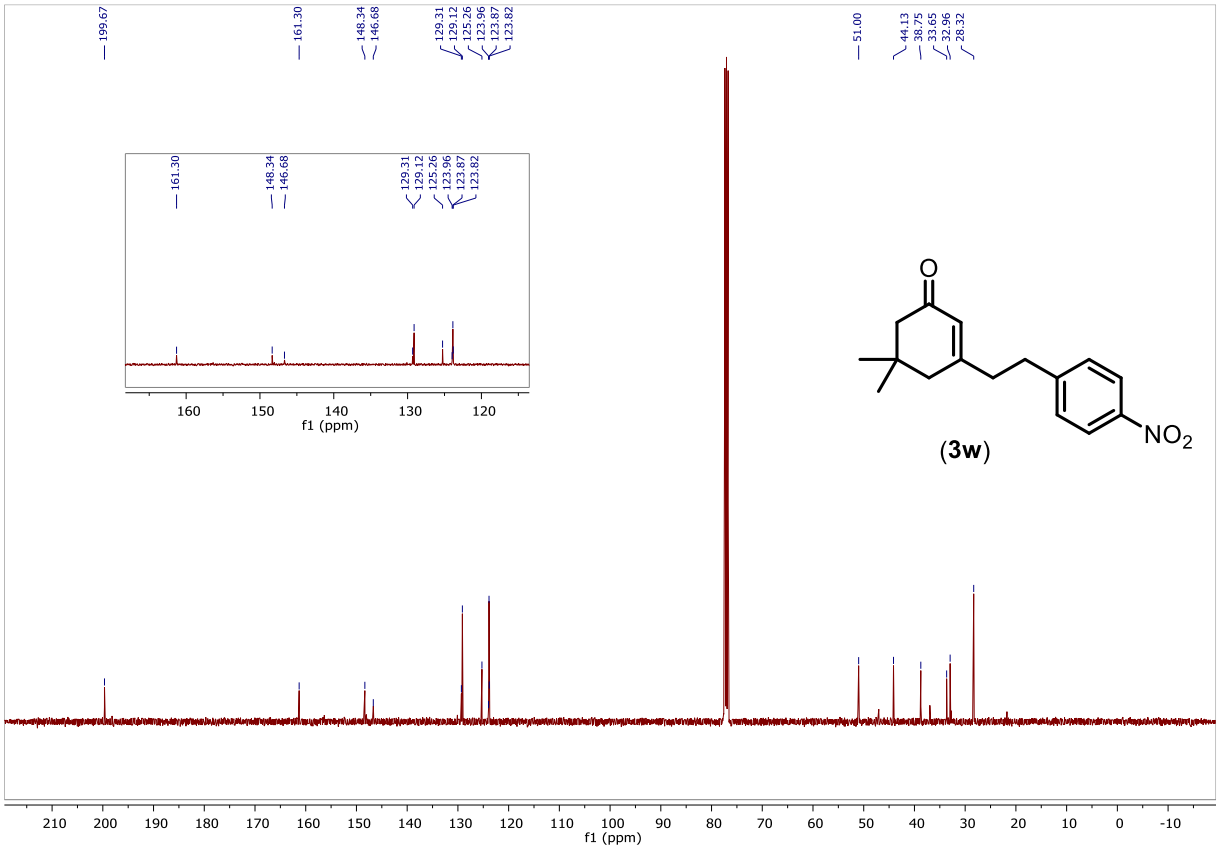
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








8.19
8.17
7.38
7.36
5.91
2.98
2.96
2.95
2.94
2.58
2.56
2.54
2.24
2.23
2.21
1.06
f1 (ppm)
O
NO2
(3w)


199.67
161.30
148.34
146.68
129.31
129.12
125.26
123.96
123.87
123.82
51.00
44.13
38.75
33.65
32.96
28.32
f1 (ppm)
O
NO2
(3w)

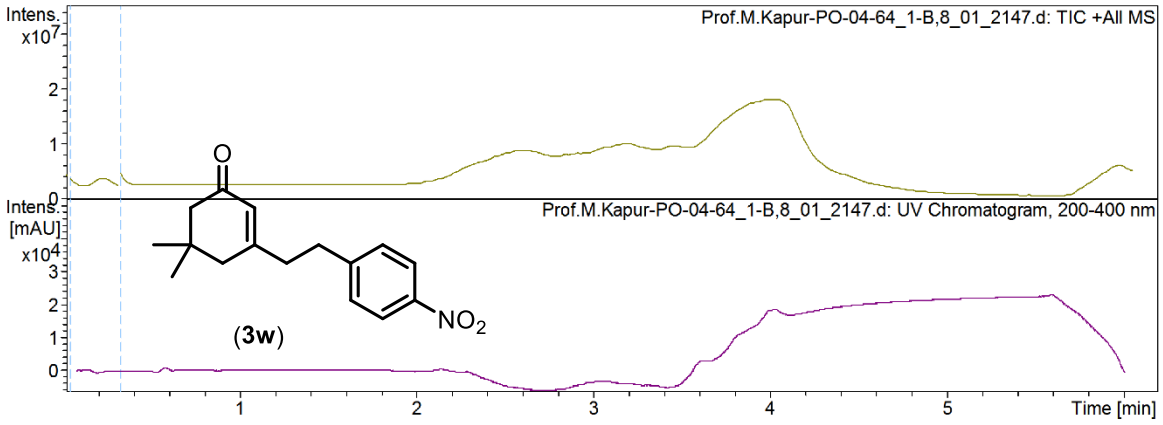
Display Report

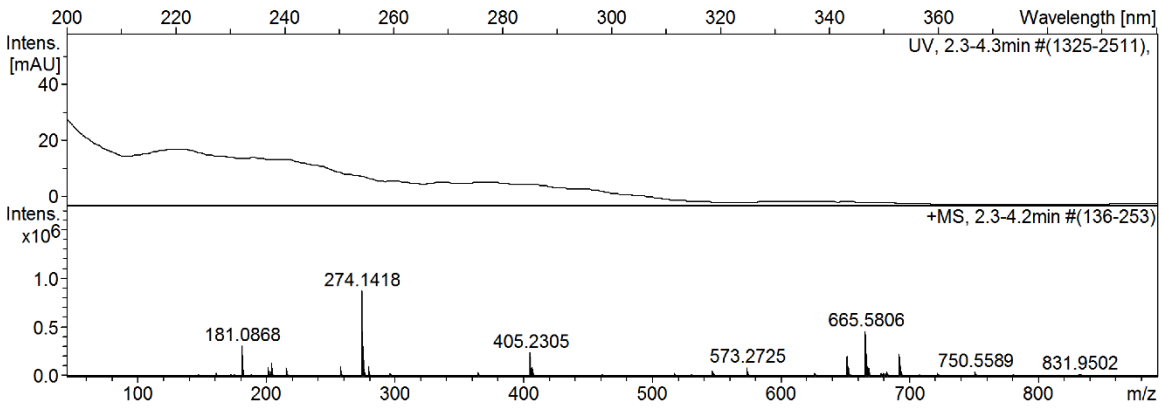
Analysis Info

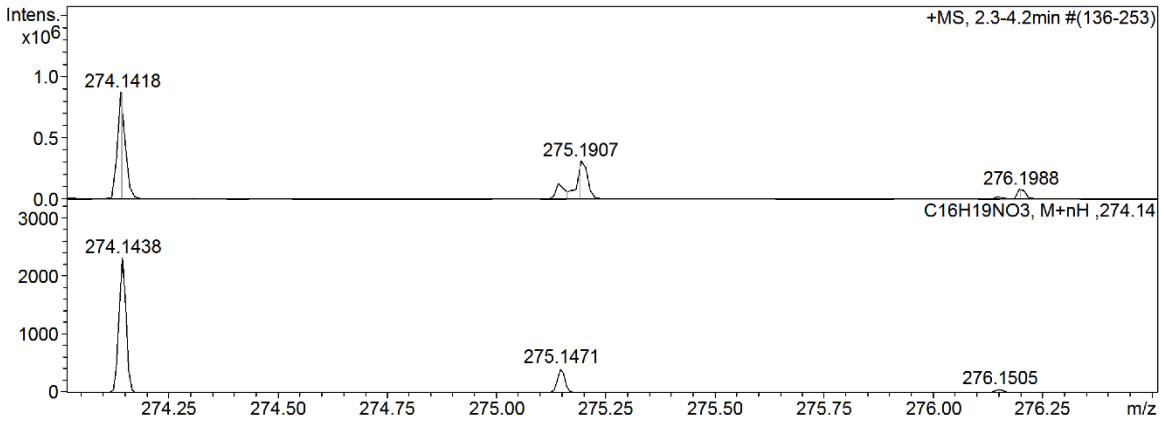
Acquisition Date	27-06-2023 13:59:54		
Analysis Name	D:\Data\USER DATA 2023\June\27-june\Prof.M.Kapur-PO-04-64_1-B,8_01_2147.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-64	Instrument	micrOTOF-Q 10330
Comment			

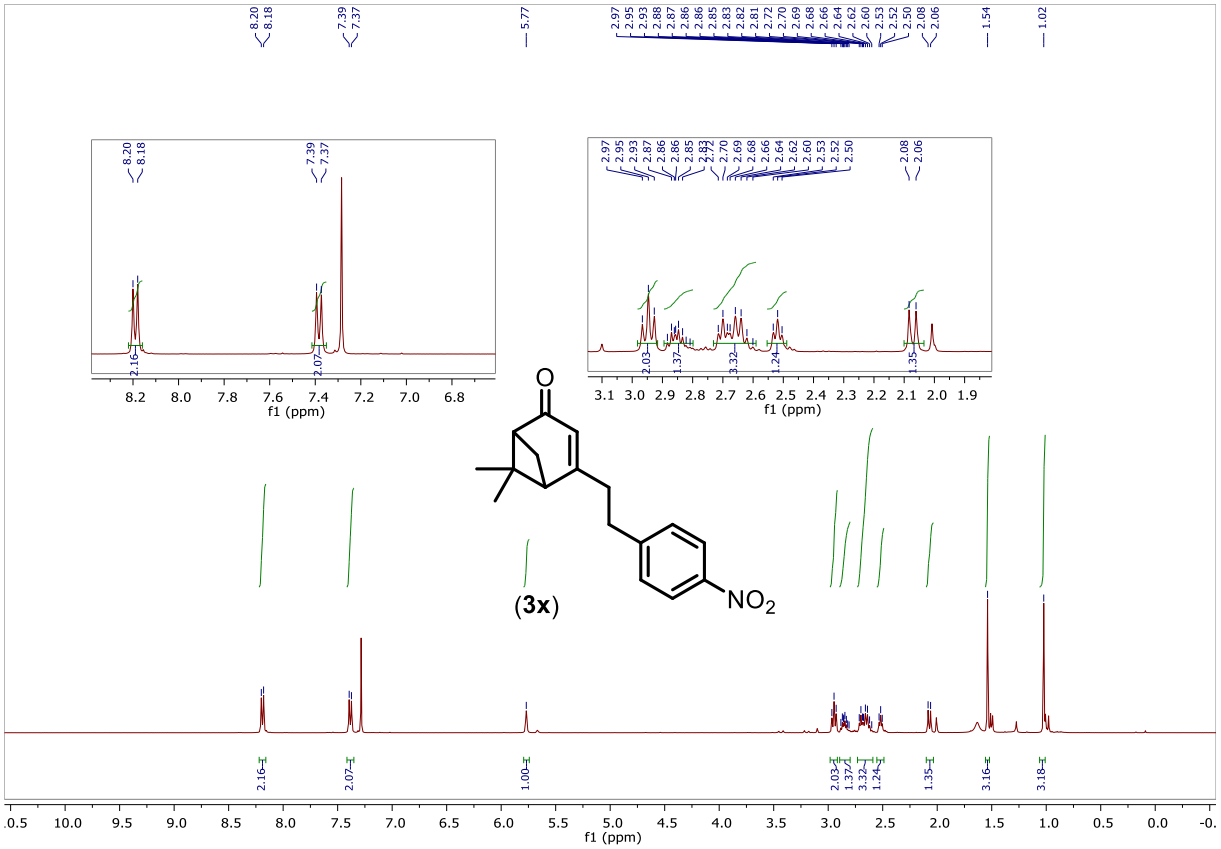
Acquisition Parameter

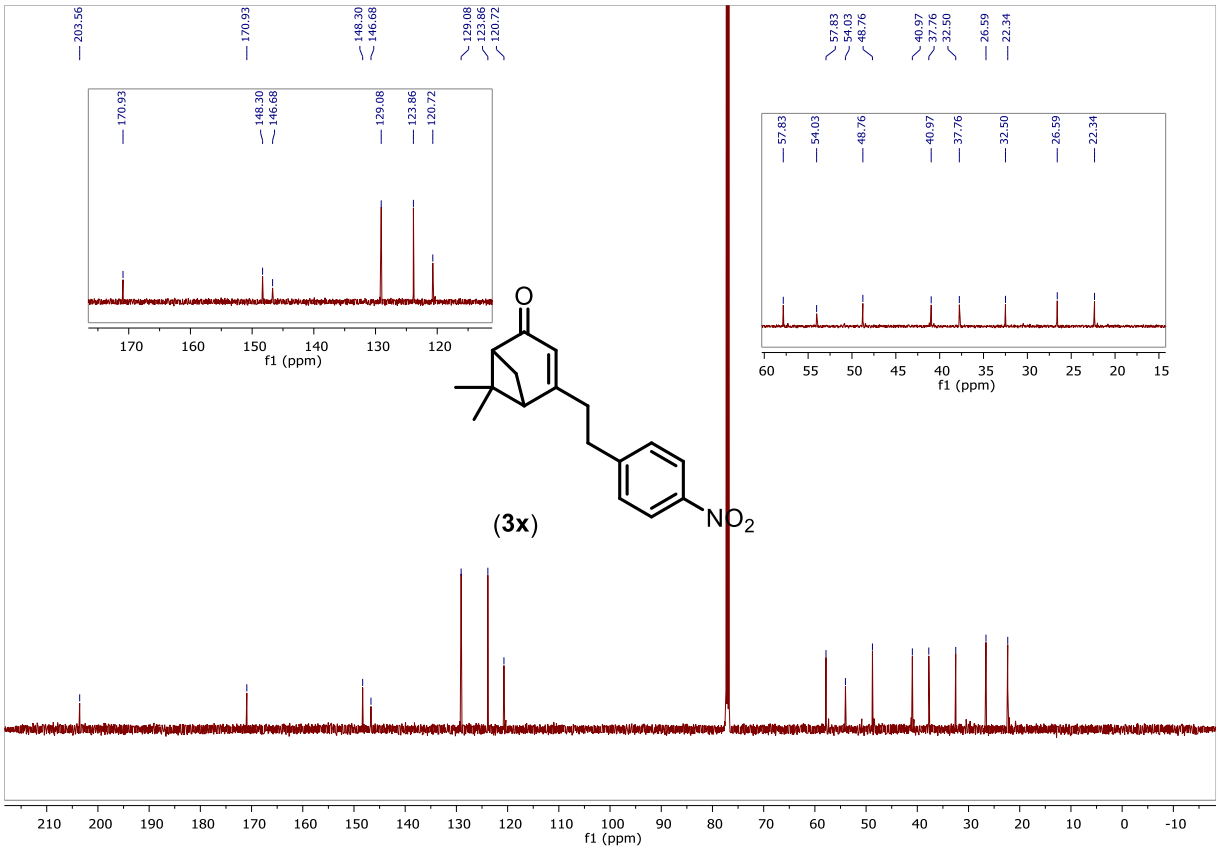
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








8.20
8.18
7.39
7.37
5.77
2.97
2.95
2.93
2.88
2.87
2.86
2.86
2.86
2.85
2.83
2.82
2.81
2.72
2.70
2.69
2.68
2.66
2.64
2.62
2.60
2.53
2.52
2.50
2.08
2.06
1.54
1.02
f1 (ppm)
O
NO2
(3x)


203.56
170.93
148.30
146.68
129.08
123.86
120.72
57.83
54.03
48.76
40.97
37.76
32.50
26.59
22.34
f1 (ppm)
O
NO2
(3x)

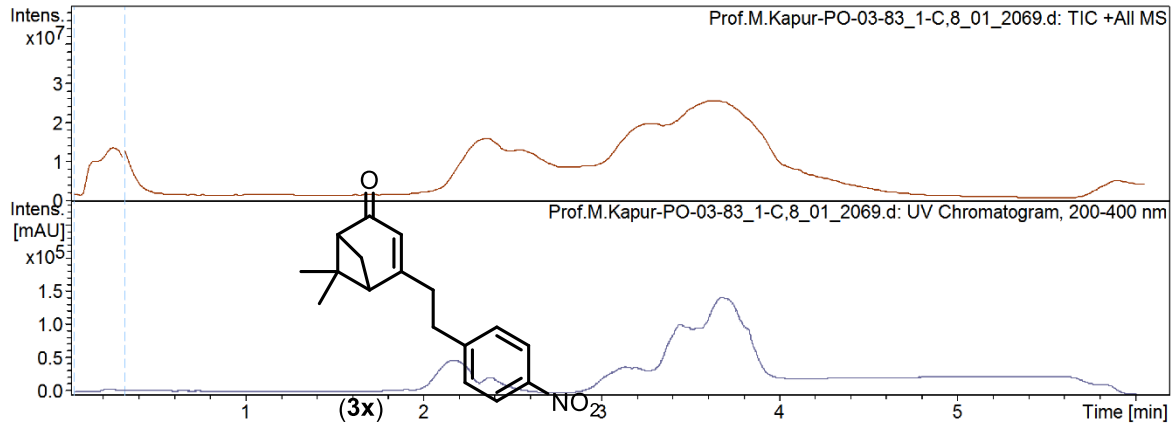
Display Report

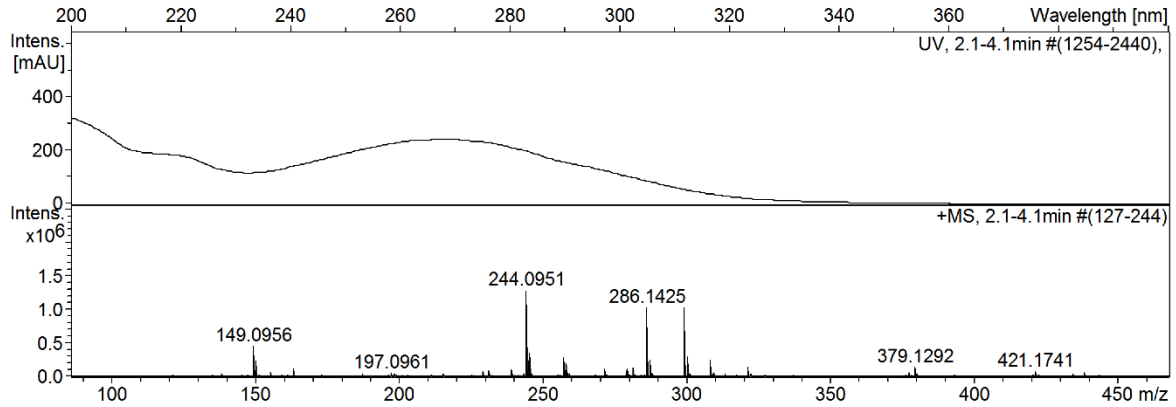
Analysis Info

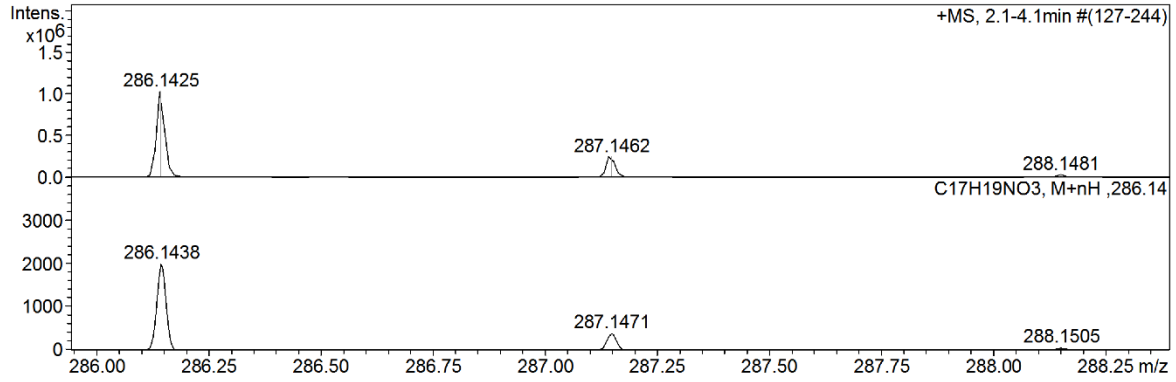
Acquisition Date	23-06-2023 14:16:12		
Analysis Name	D:\Data\USER DATA 2023\June\22-june\Prof.M.Kapur-PO-03-83_1-C,8_01_2069.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-03-83	Instrument	micrOTOF-Q 10330
Comment			

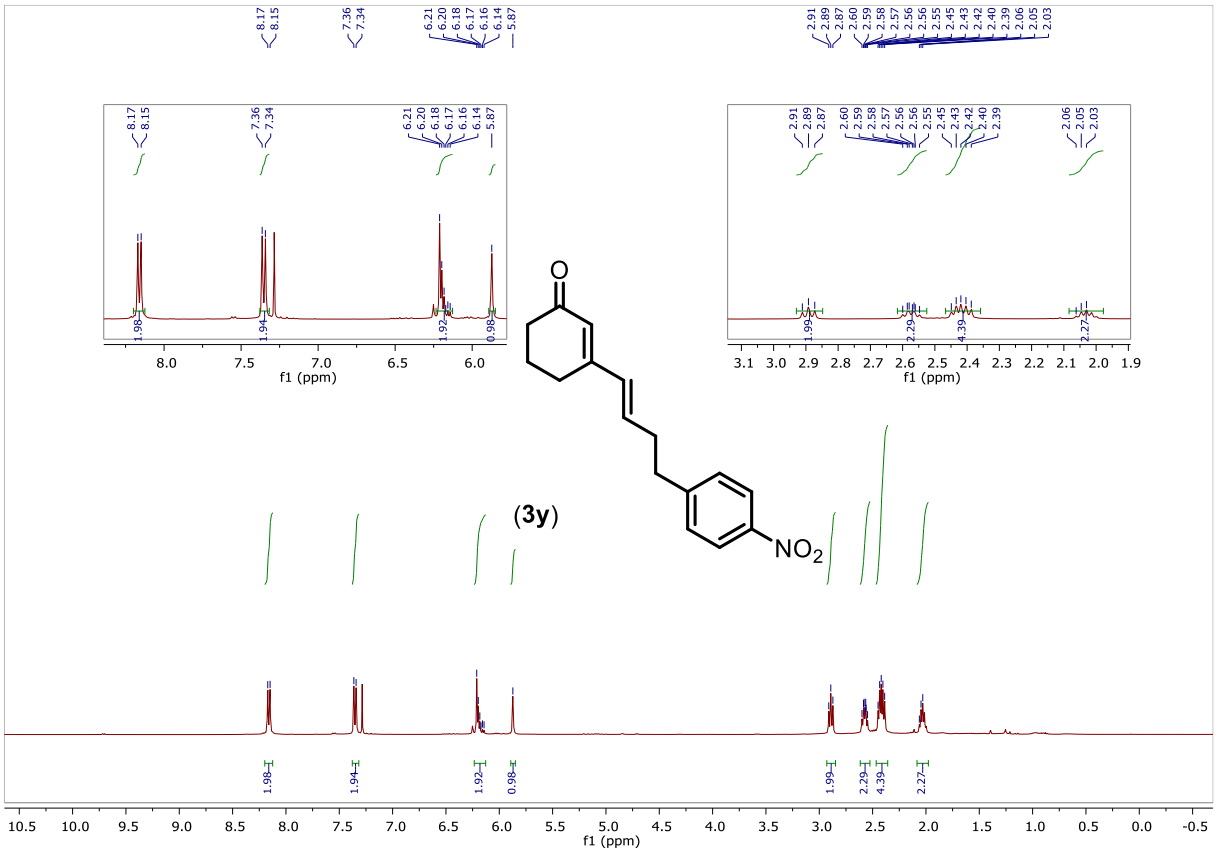
Acquisition Parameter

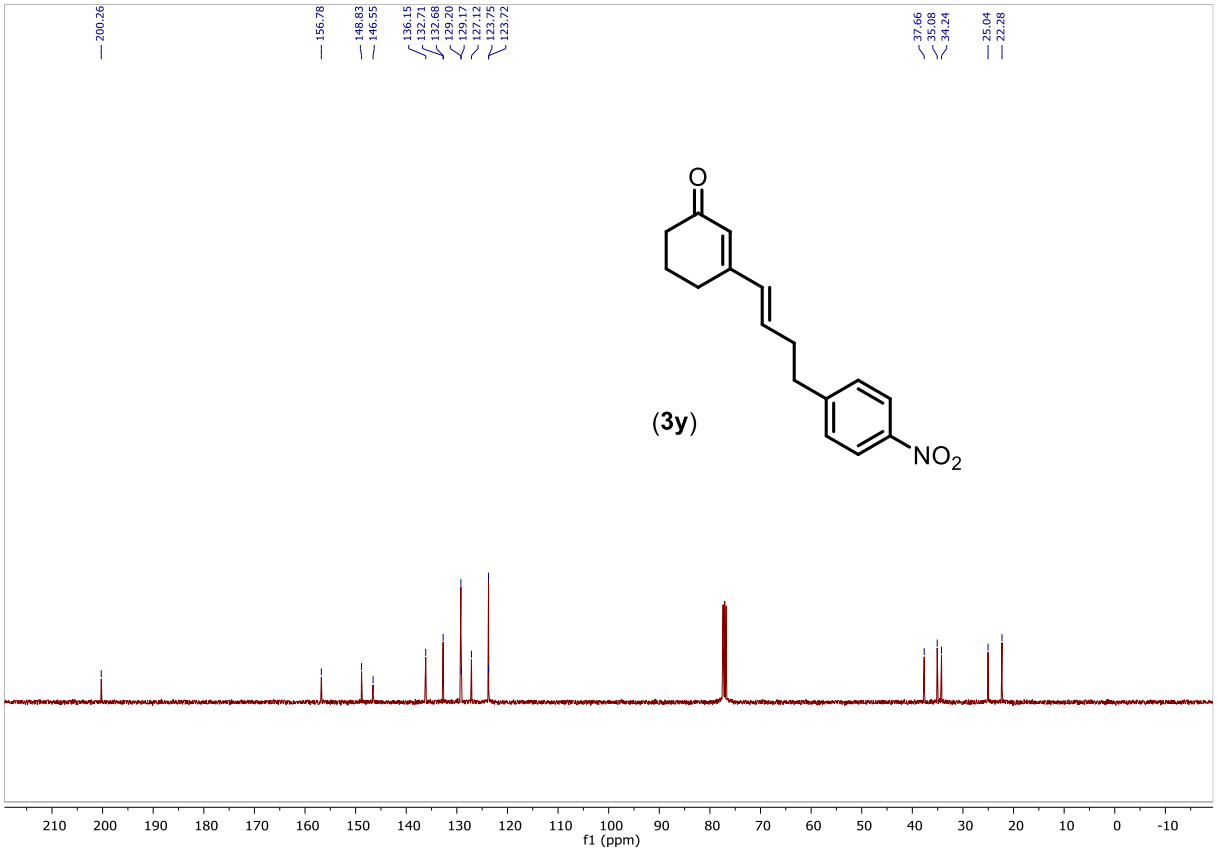
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








8.17
8.15
7.36
7.34
6.21
6.20
6.18
6.17
6.16
6.14
5.87
2.91
2.89
2.87
2.60
2.59
2.58
2.57
2.56
2.56
2.55
2.45
2.43
2.42
2.40
2.39
2.06
2.05
2.03
1.98
1.94
1.92
0.98
1.99
2.29
4.39
2.27
f1 (ppm)
O
(3y)
NO2


200.26
156.78
148.83
146.55
136.15
132.71
132.68
129.20
129.17
127.12
123.75
123.72
37.66
35.08
34.24
25.04
22.28
O
(3y)
NO2
f1 (ppm)

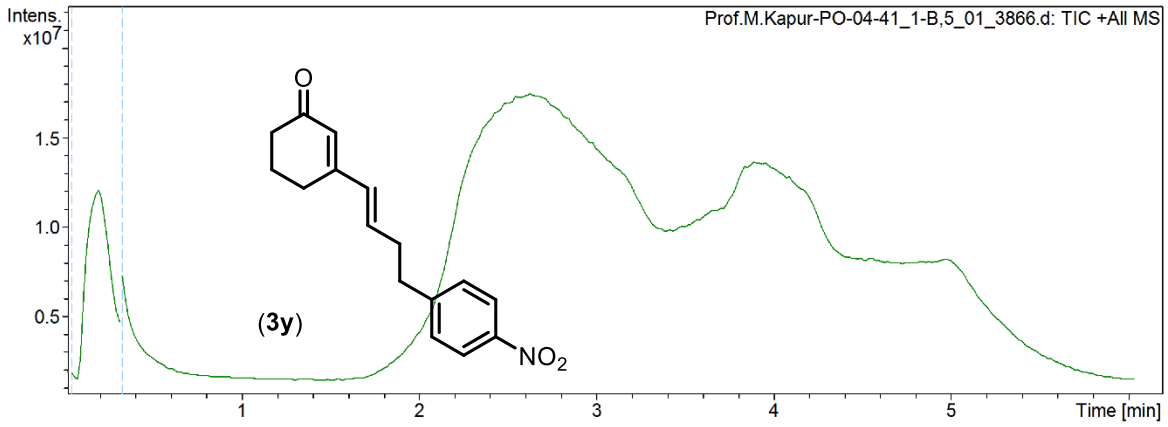
Display Report

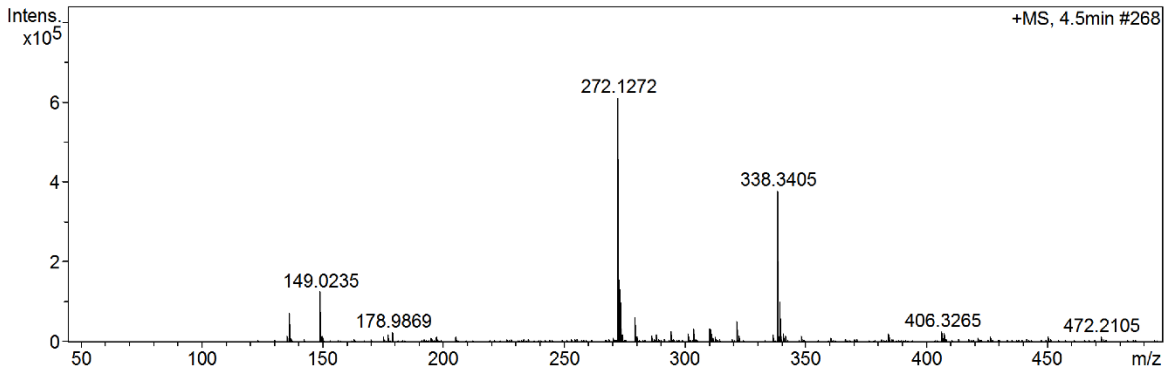
Analysis Info

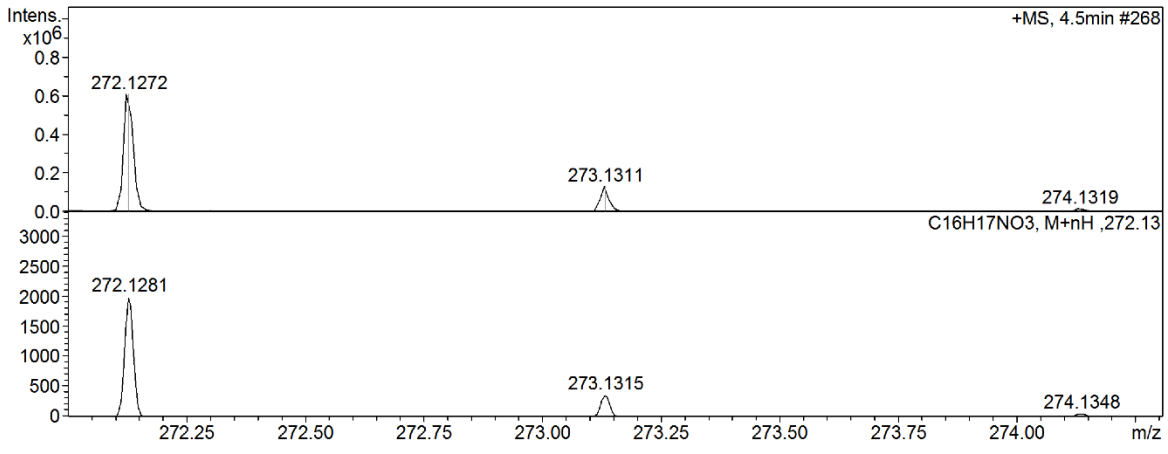
Acquisition Date	17-01-2024 18:12:05		
Analysis Name	D:\Data\USER DATA 2024\17-jan\Prof.M.Kapur-PO-04-41_1-B,5_01_3866.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-41	Instrument	micrOTOF-Q 10330
Comment			

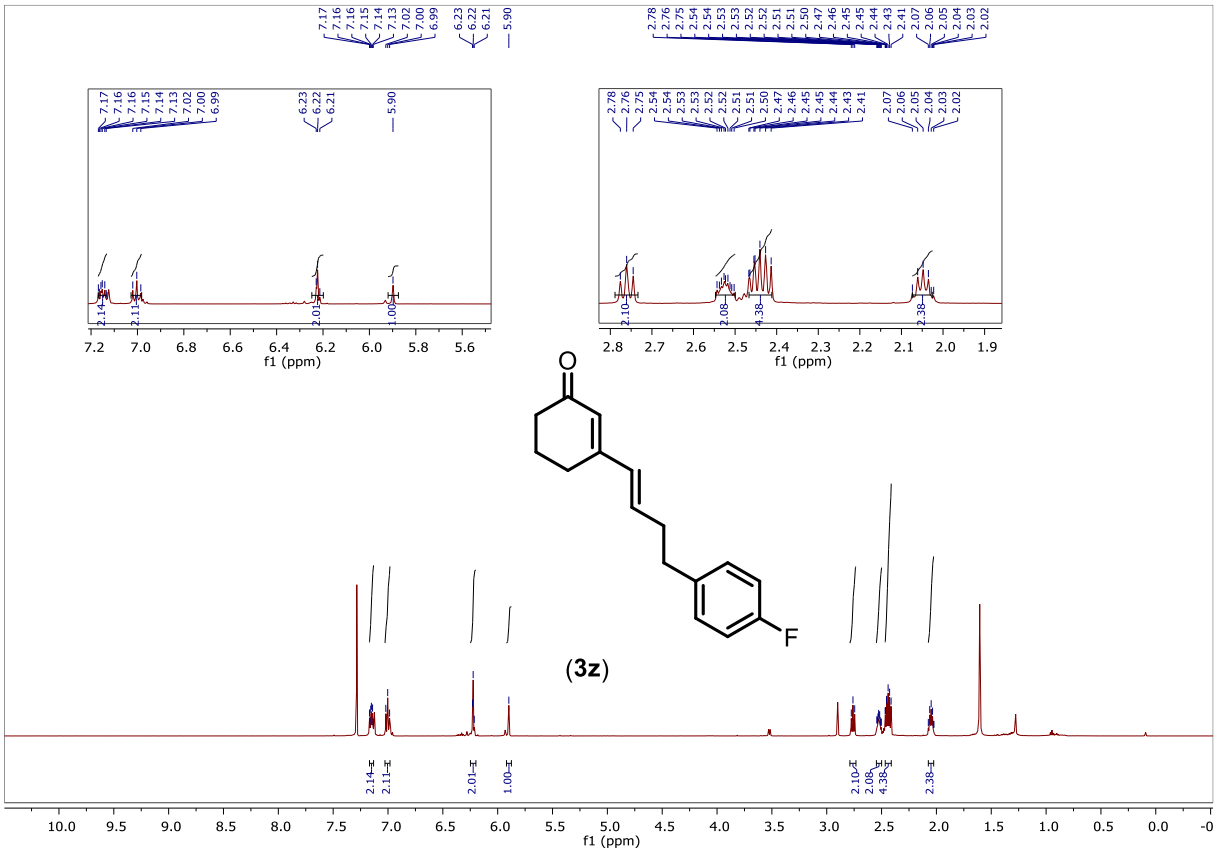
Acquisition Parameter

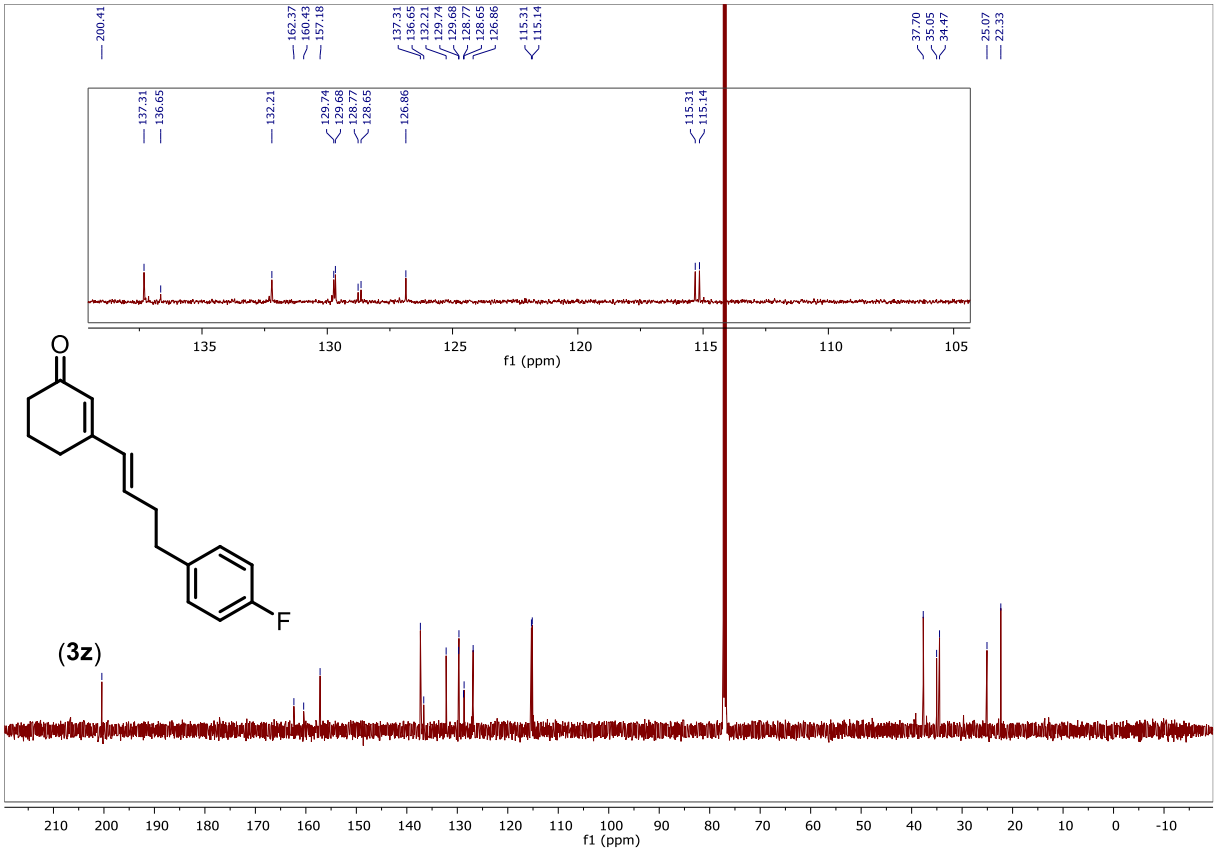
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

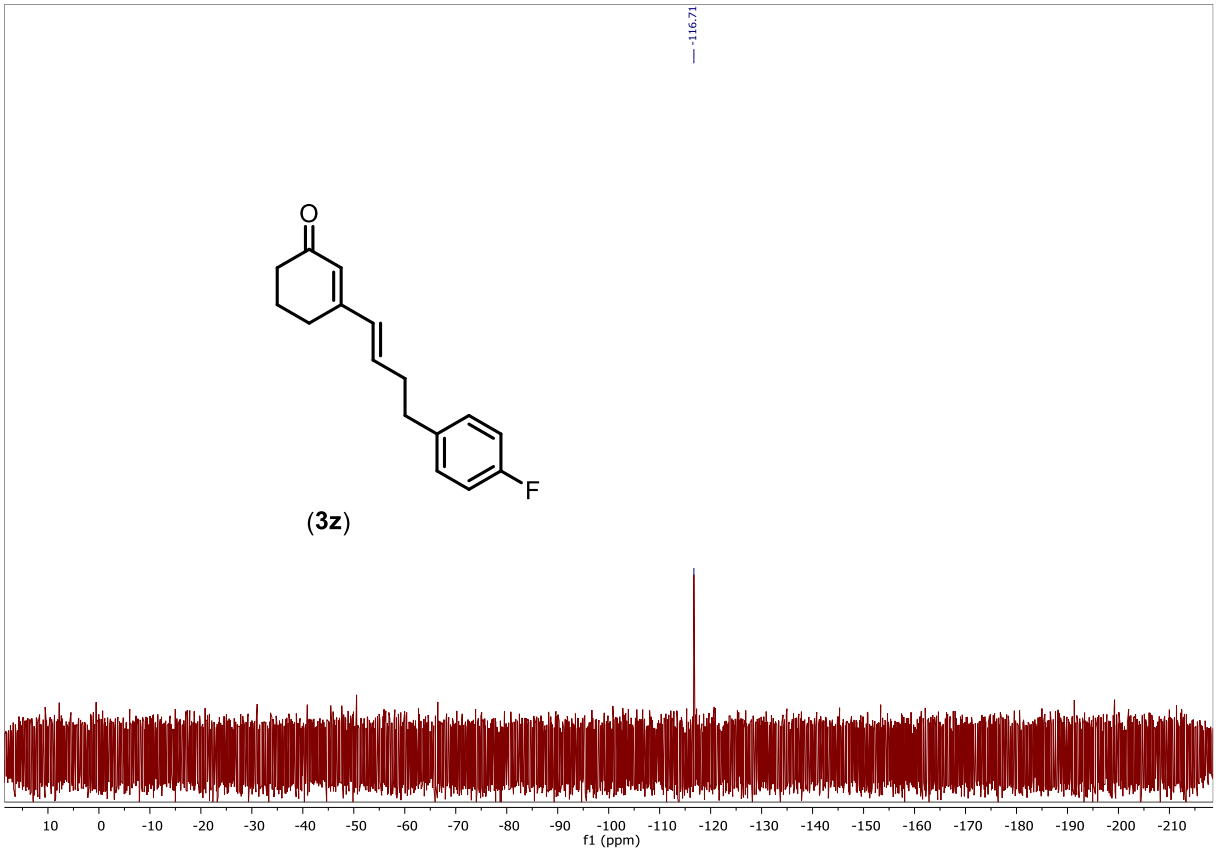







(3z)
F
f1 (ppm)


(3z)
F
f1 (ppm)


-116.71
O
F
(3z)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

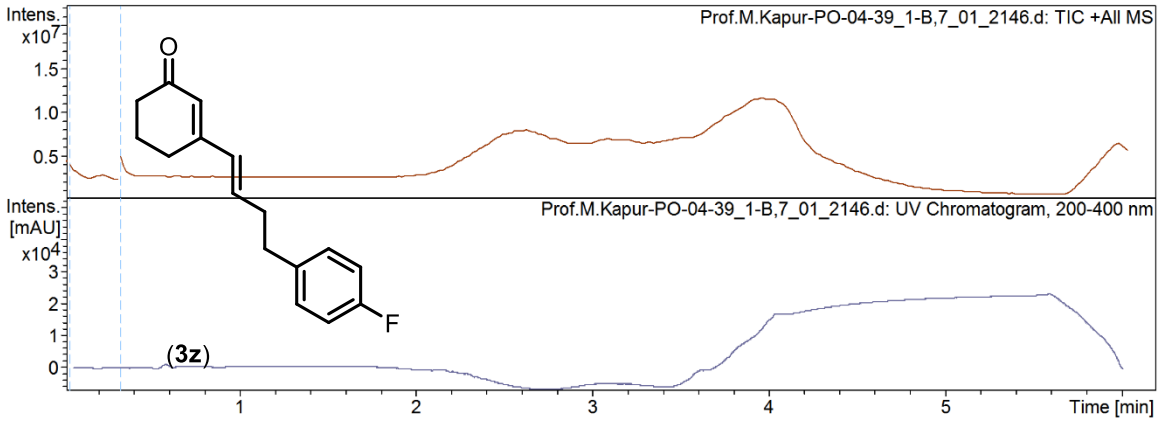
Display Report

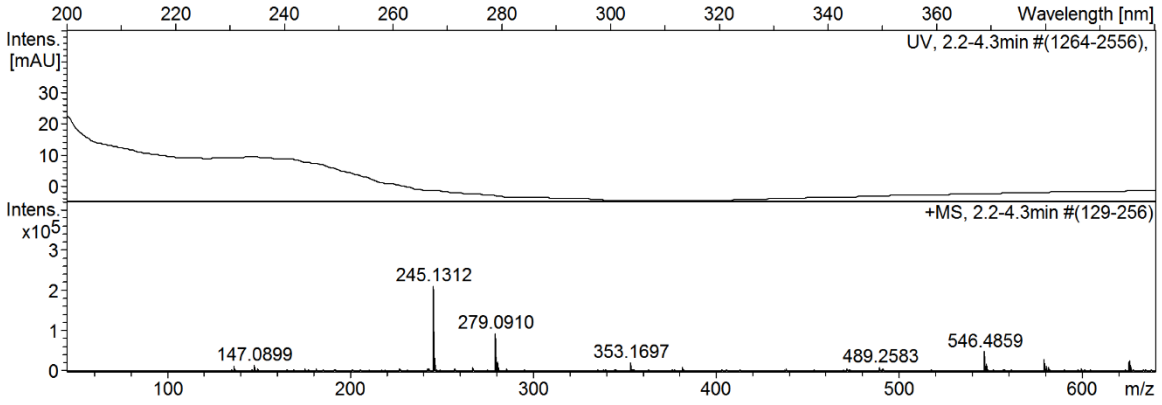
Analysis Info

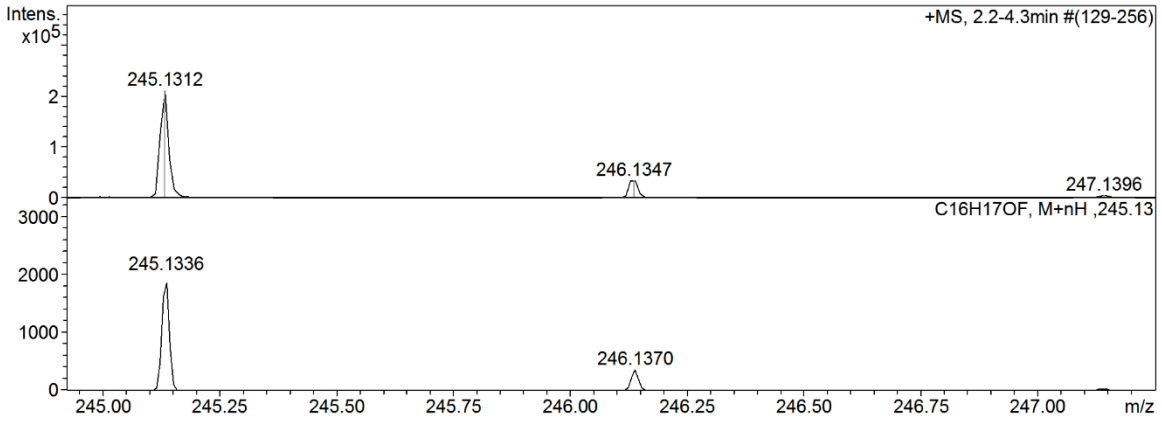
Acquisition Date	27-06-2023 13:52:39		
Analysis Name	D:\Data\USER DATA 2023\June\27-june\Prof.M.Kapur-PO-04-39_1-B,7_01_2146.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-39	Instrument	micrOTOF-Q 10330
Comment			

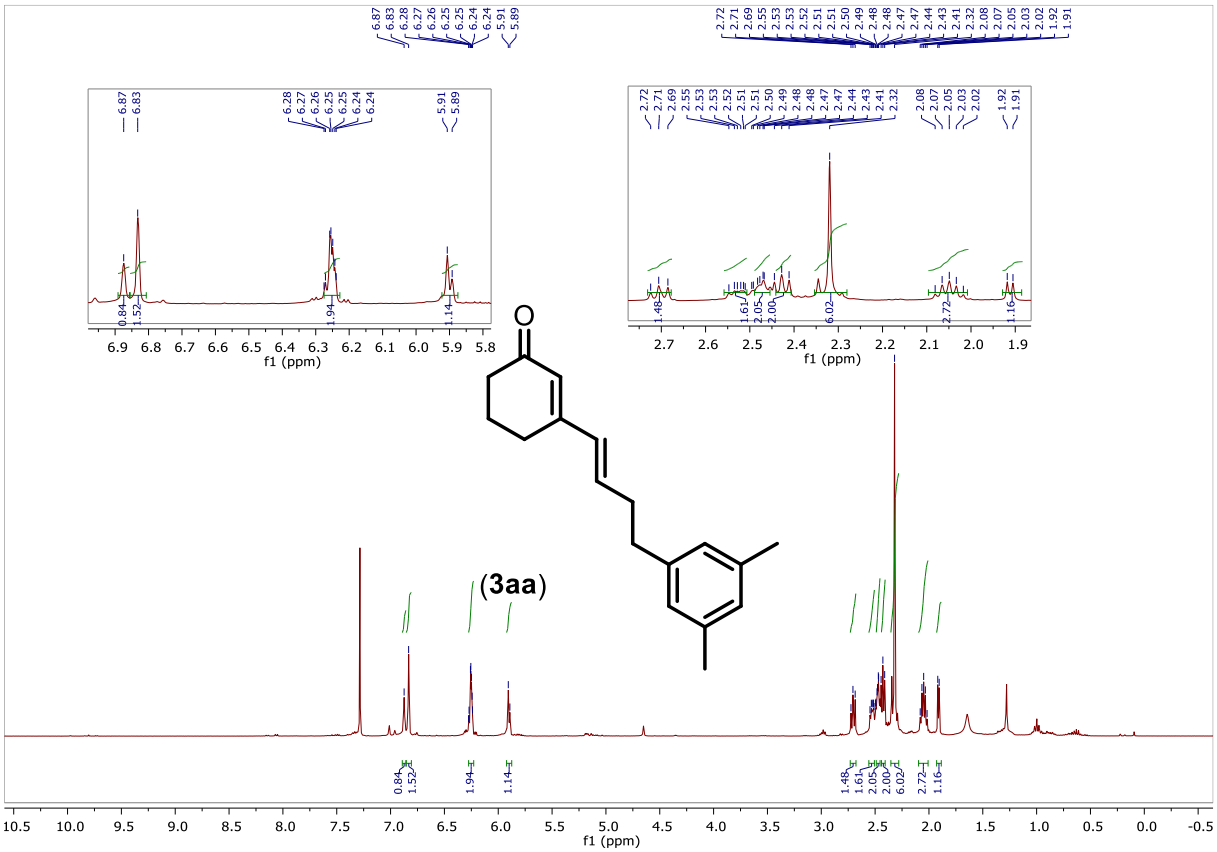
Acquisition Parameter

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





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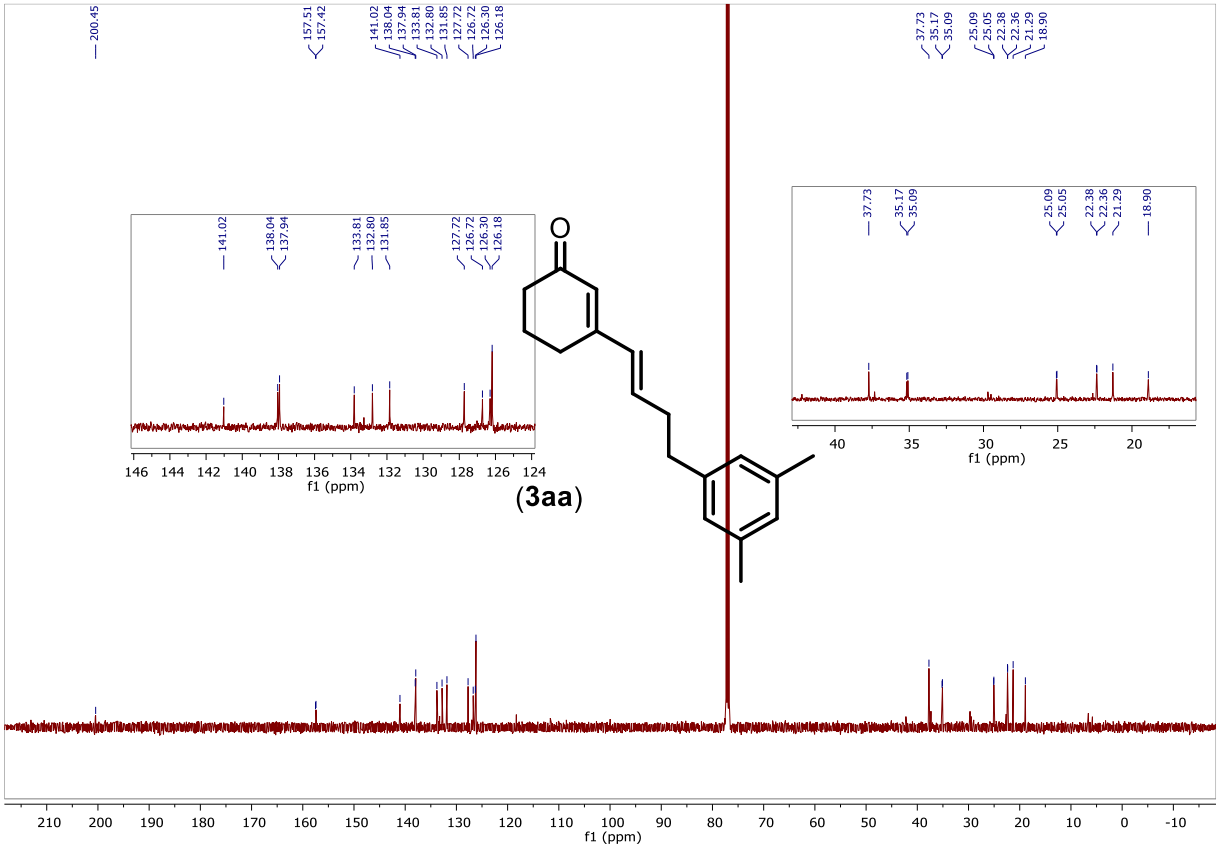
f1 (ppm)


(3aa)
f1 (ppm)

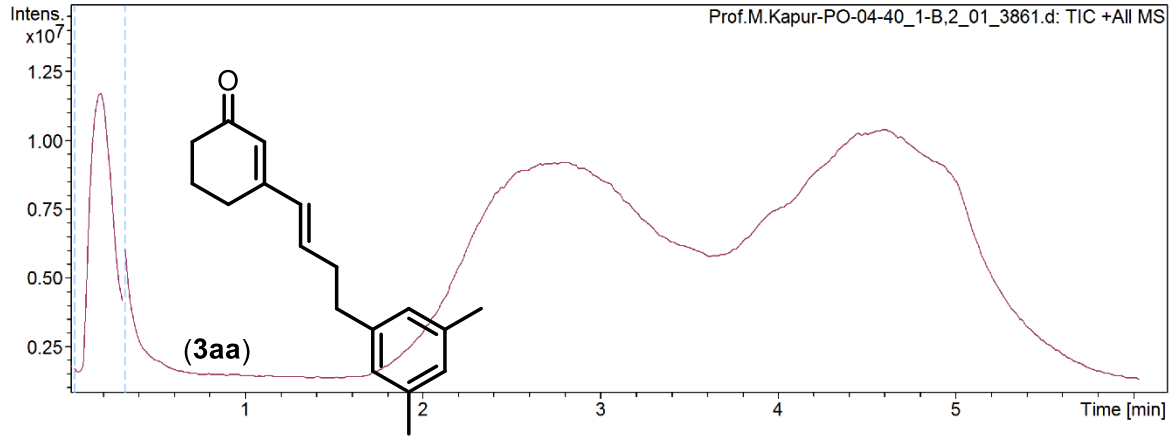
Display Report

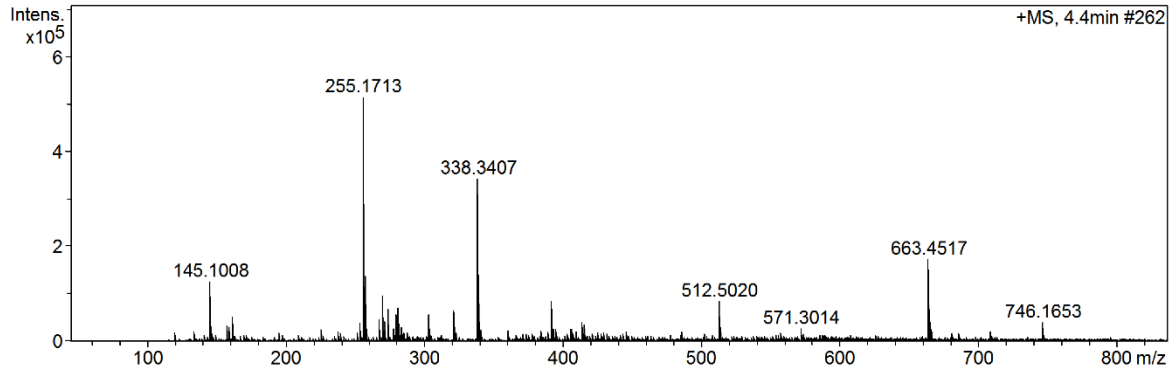
Analysis Info

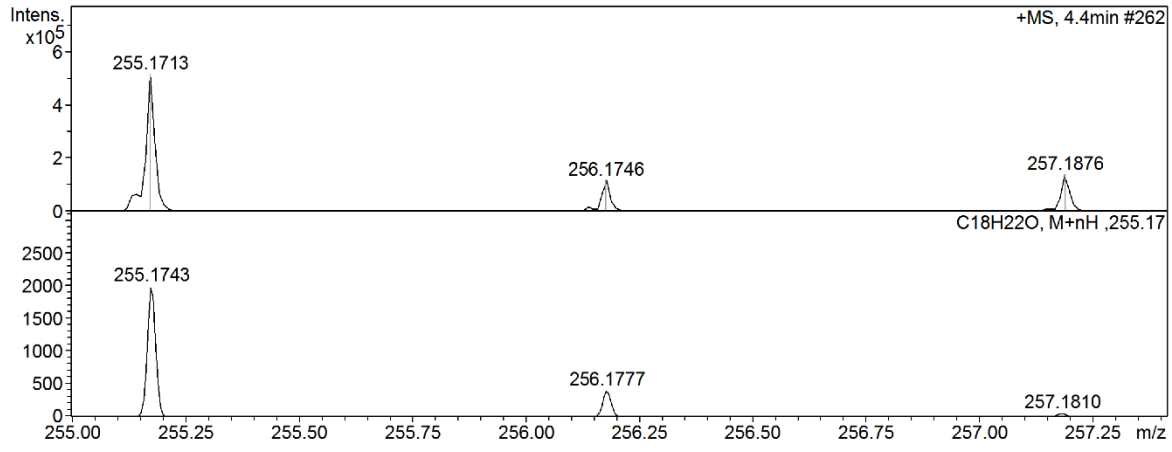
Analysis Name	D:\Data\USER DATA 2024\17-jan\Prof.M.Kapur-PO-04-40_1-B,2_01_3861.d	Acquisition Date	17-01-2024 17:35:40
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-40	Instrument	micrOTOF-Q 10330
Comment			

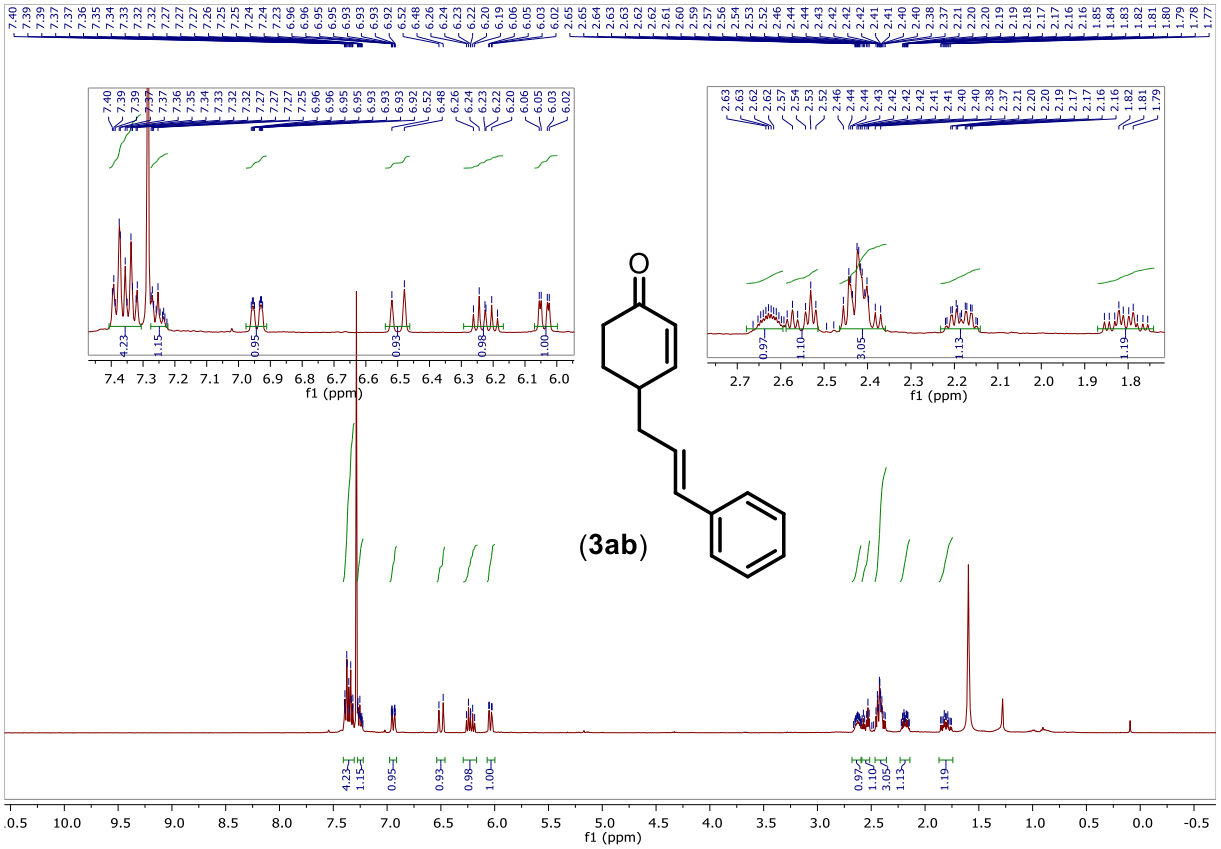
Acquisition Parameter

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





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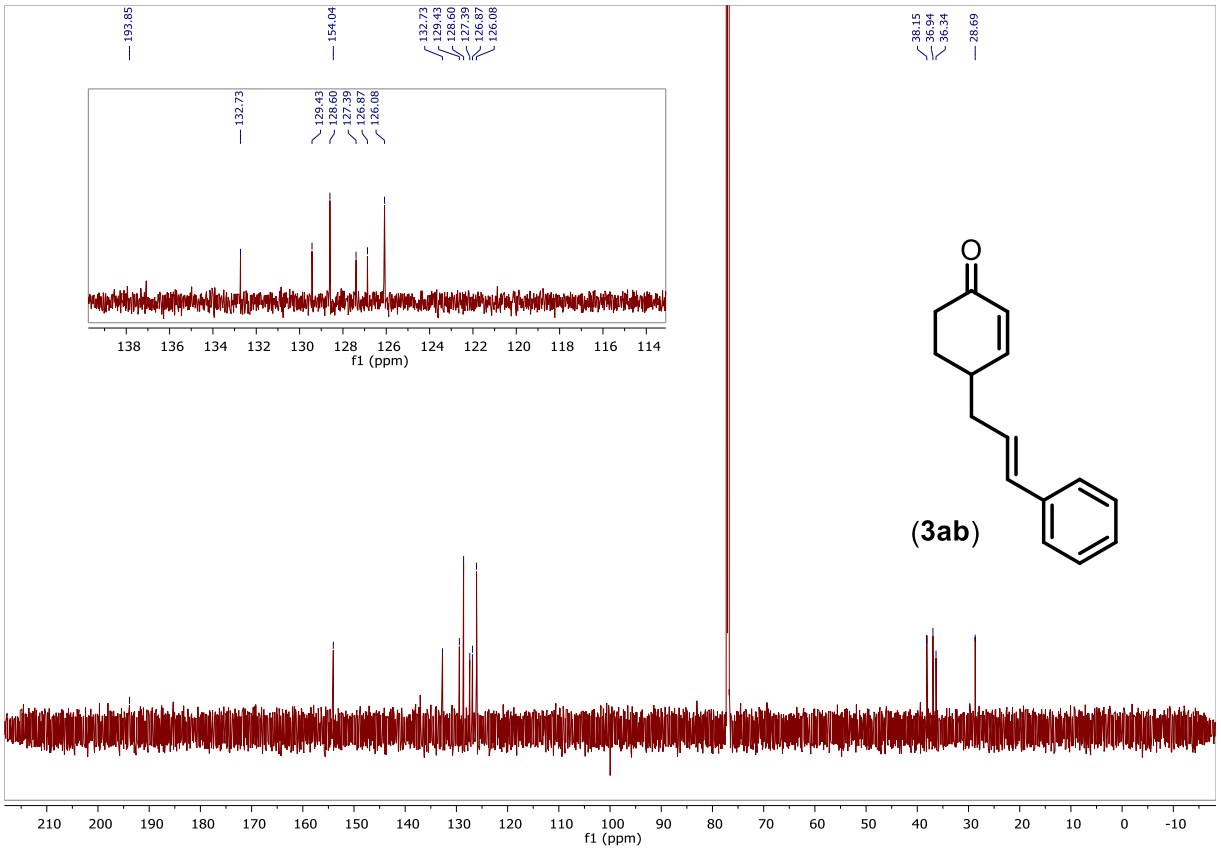
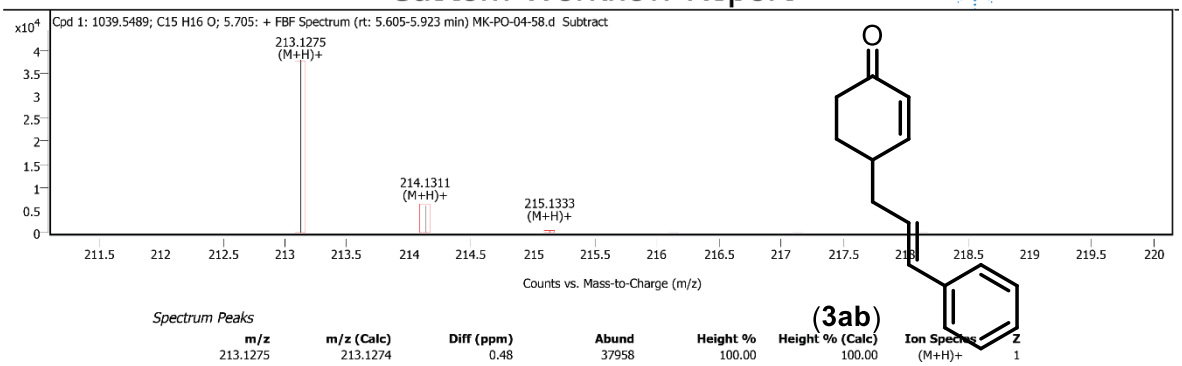
f1 (ppm)


(3ab)
f1 (ppm)

Custom Workflow Report

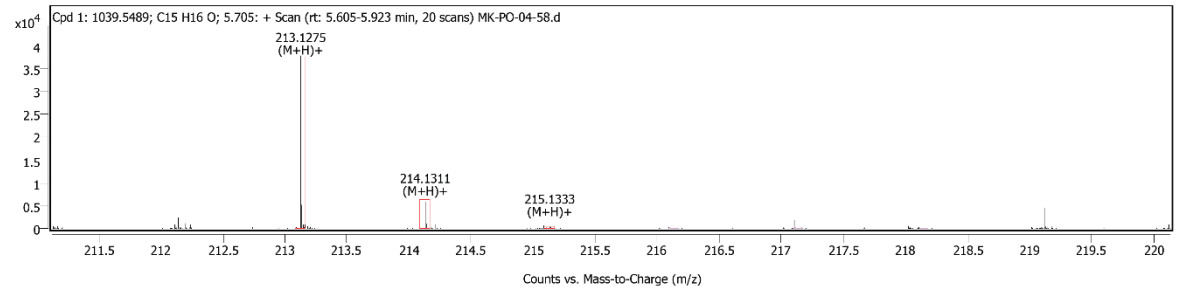
Agilent Trusted Answers



(**3ab**)

Spectrum Peaks

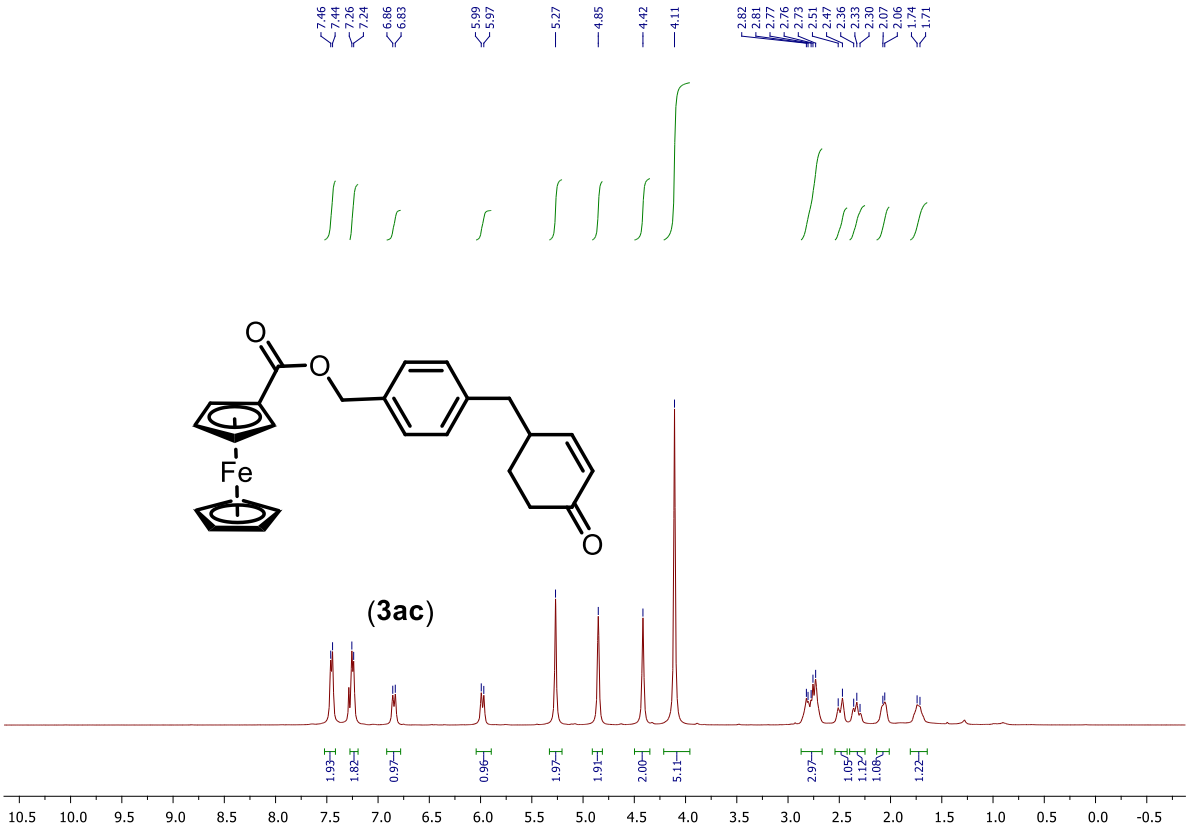
m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
213.1275	213.1274	0.48	37958	100.00	100.00	(M+H)+	1
214.1311	214.1308	1.56	5884	15.50	16.46	(M+H)+	1
215.1333	215.1338	-2.57	423	1.11	1.47	(M+H)+	1



Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
213.1275	213.1274	0.48	37958	100.00	100.00	(M+H)+	1
214.1311	214.1308	1.56	5884	15.50	16.46	(M+H)+	1
215.1333	215.1338	-2.57	423	1.11	1.47	(M+H)+	1

MassHunter Qual 10.0
(End of Report)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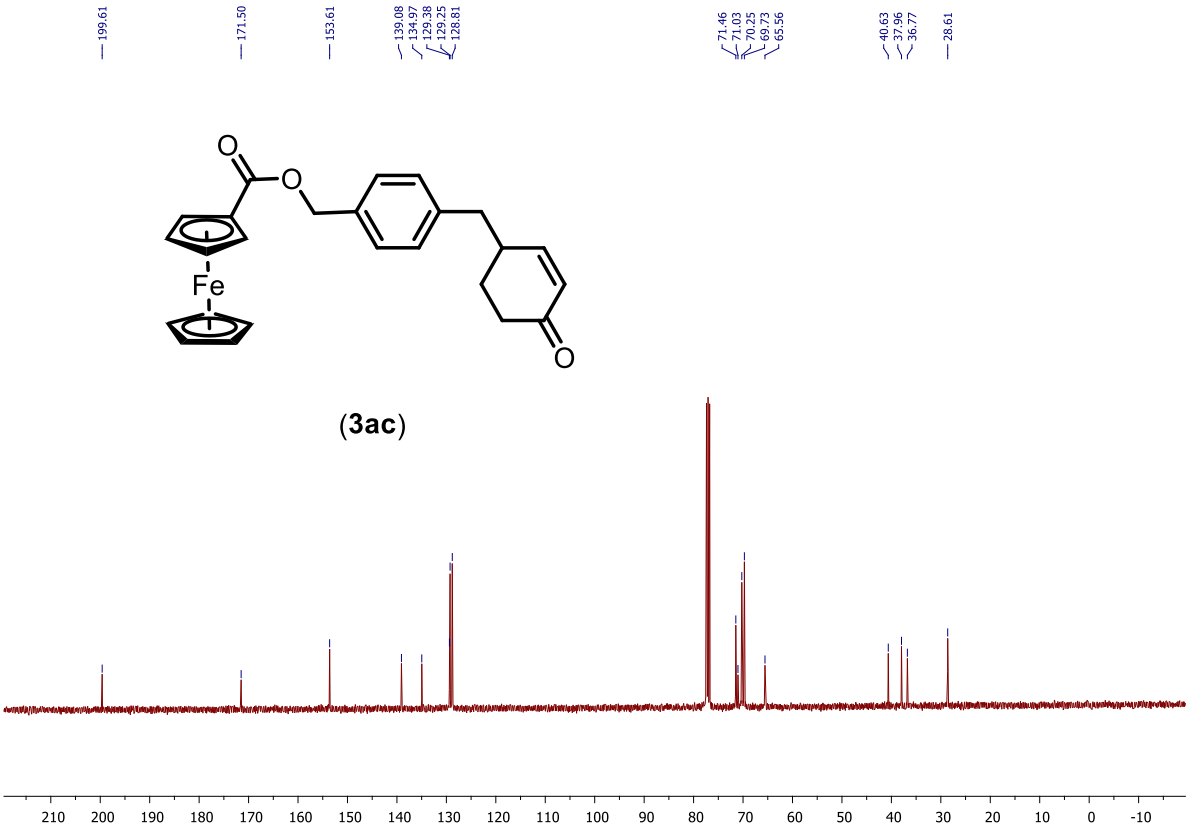
7.44
7.26
7.24
6.86
6.83
5.99
5.97
5.27
4.85
4.42
4.11
2.82
2.81
2.77
2.76
2.73
2.51
2.47
2.36
2.33
2.30
2.07
2.06
1.74
1.71
O
O
Fe
O
(3ac)
1.93
1.82
0.97
0.96
1.97
1.91
2.00
5.11
2.97
1.05
1.12
1.08
1.22
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


199.61
171.50
153.61
139.08
134.97
129.38
129.25
128.81
71.46
71.03
70.25
69.73
65.56
40.63
37.96
36.77
28.61
O
O
Fe
O
(3ac)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

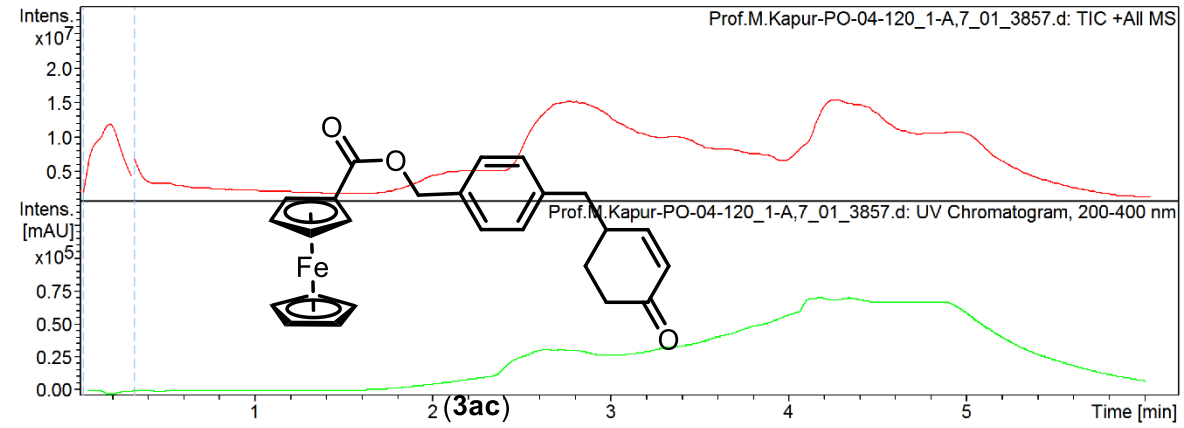
Display Report

Analysis Info

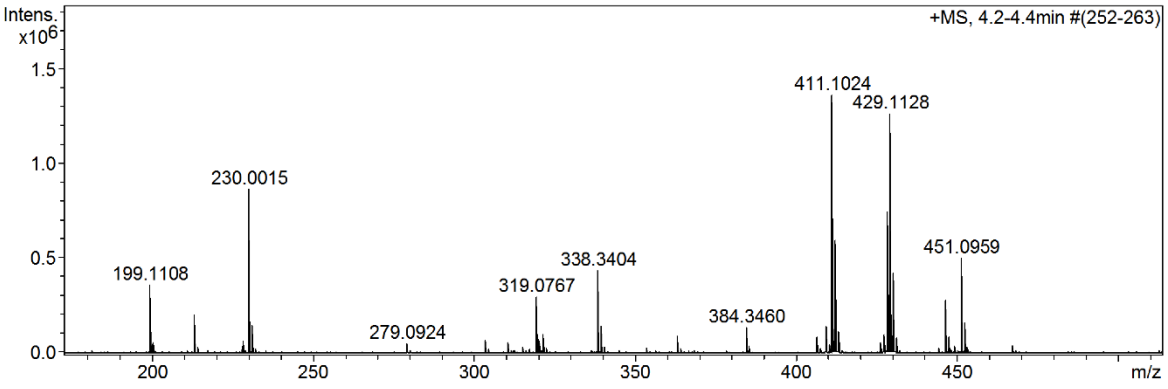
Analysis Name	D:\Data\USER DATA 2024\17-jan\Prof.M.Kapur-PO-04-120_1-A,7_01_3857.d	Acquisition Date	17-01-2024 17:06:32
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-120	Instrument	micrOTOF-Q 10330
Comment			

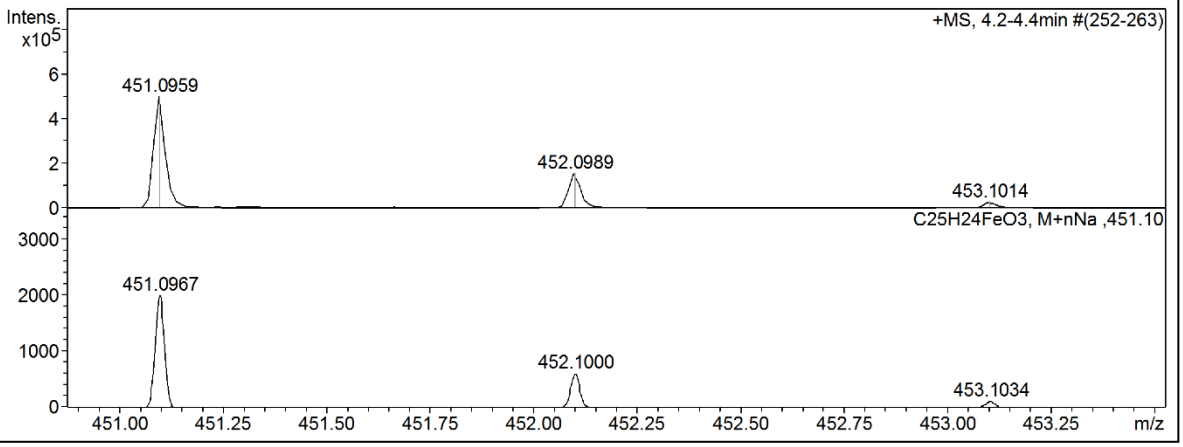
Acquisition Parameter

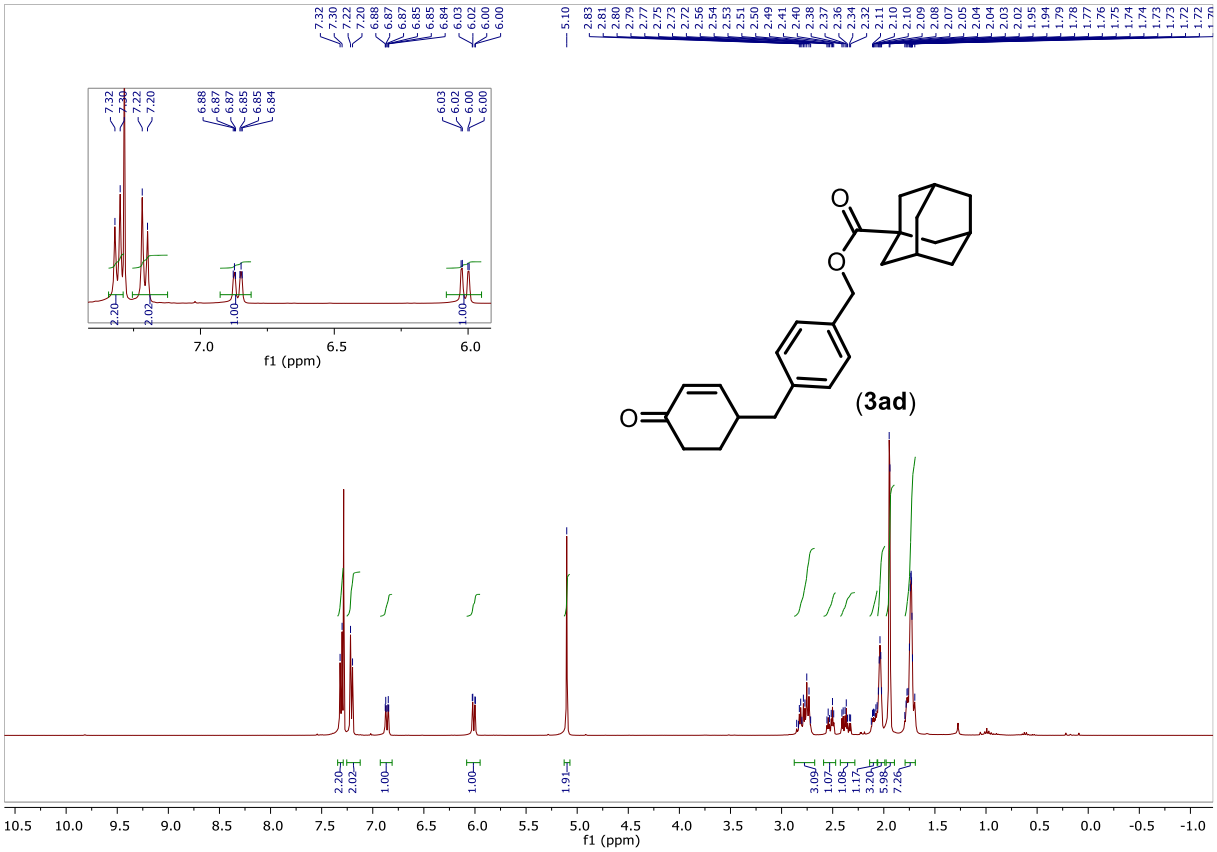
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

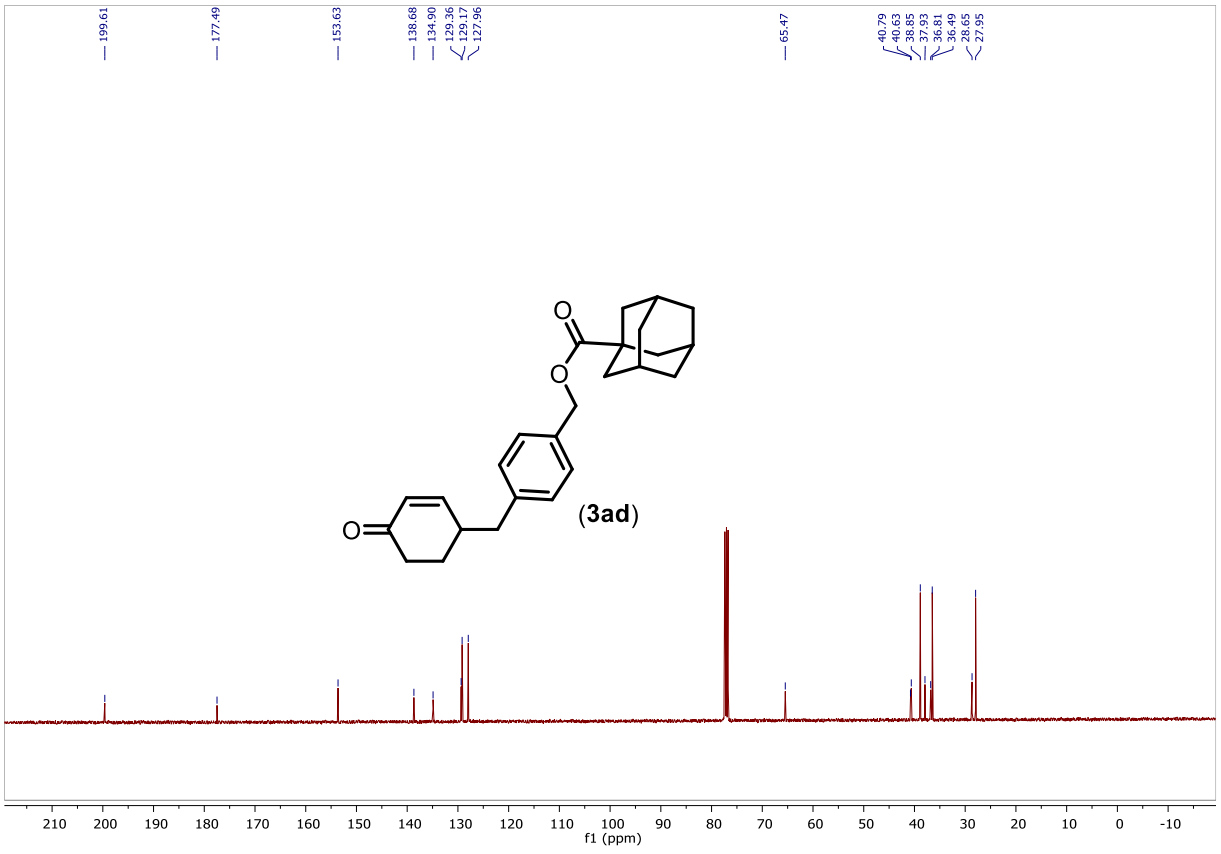


(3ac)






(3ad)
f1 (ppm)


(3ad)
f1 (ppm)

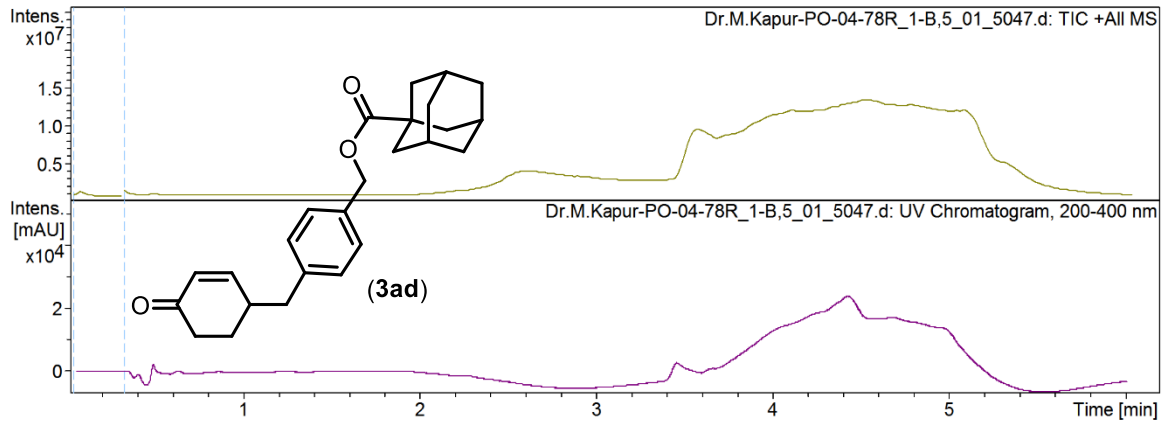
Display Report

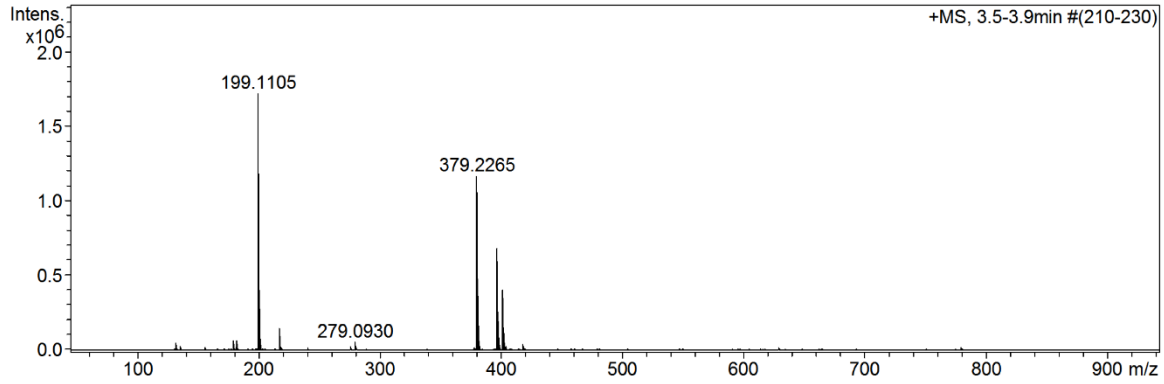
Analysis Info

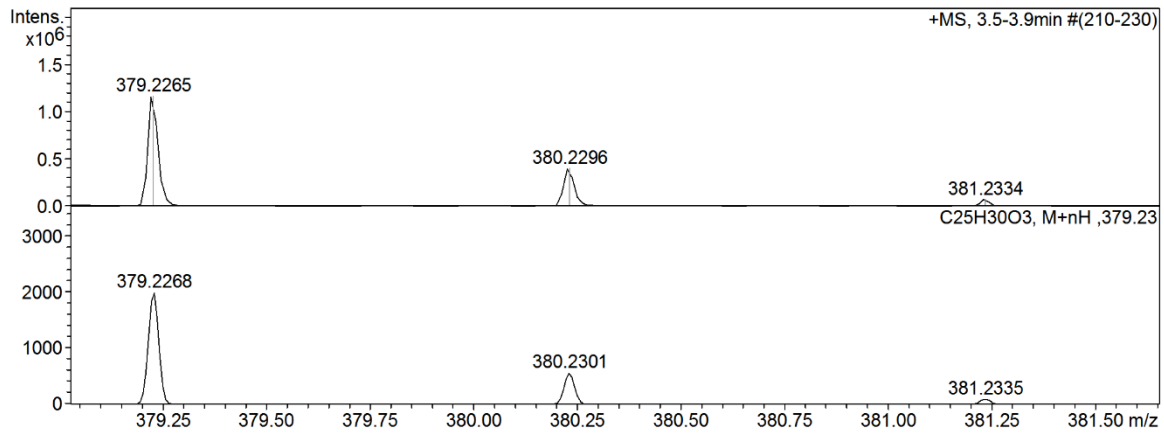
Analysis Name	D:\Data\USER DATA 2024\May-2024\14-may\Dr.M.Kapur-PO-04-78R_1-B,5_01_5047.d	Acquisition Date	14-05-2024 13:55:23
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Dr.M.Kapur-PO-04-78R	Instrument	micrOTOF-Q 10330
Comment			

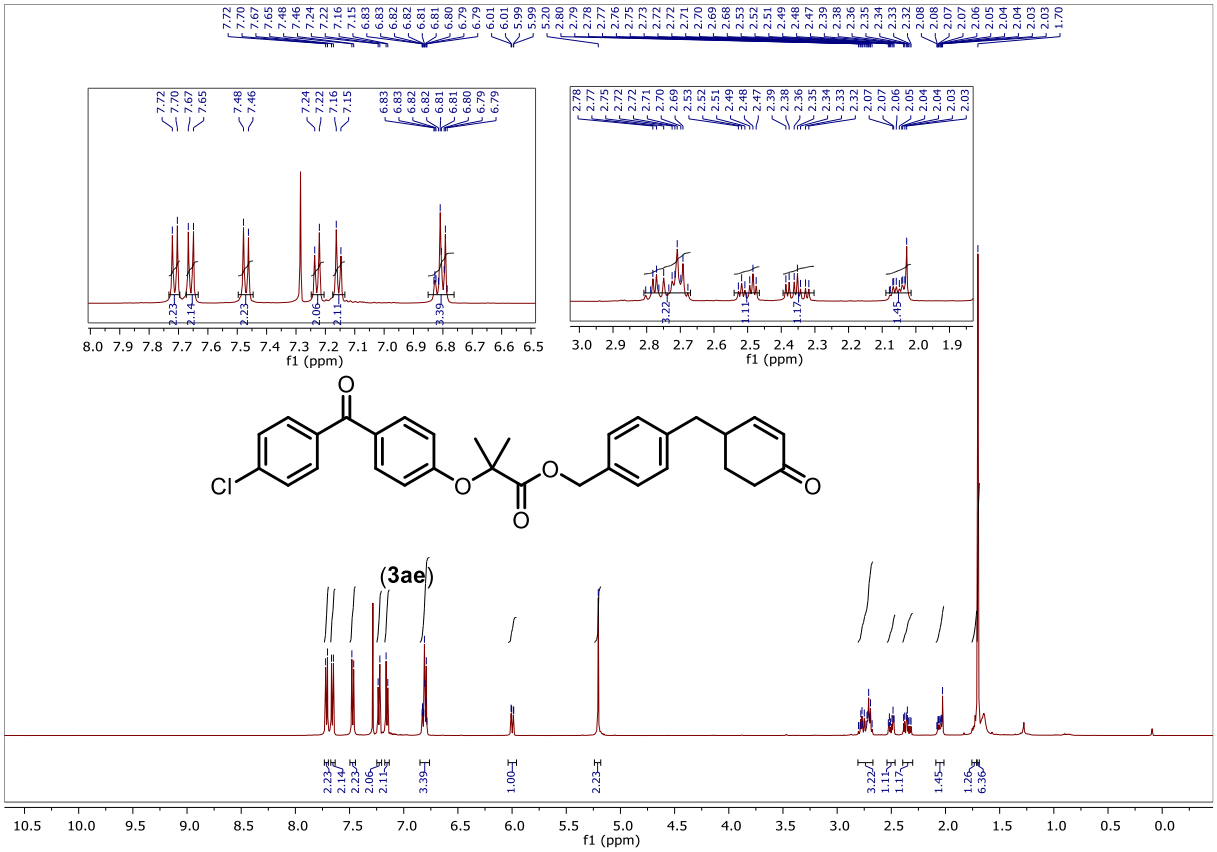
Acquisition Parameter

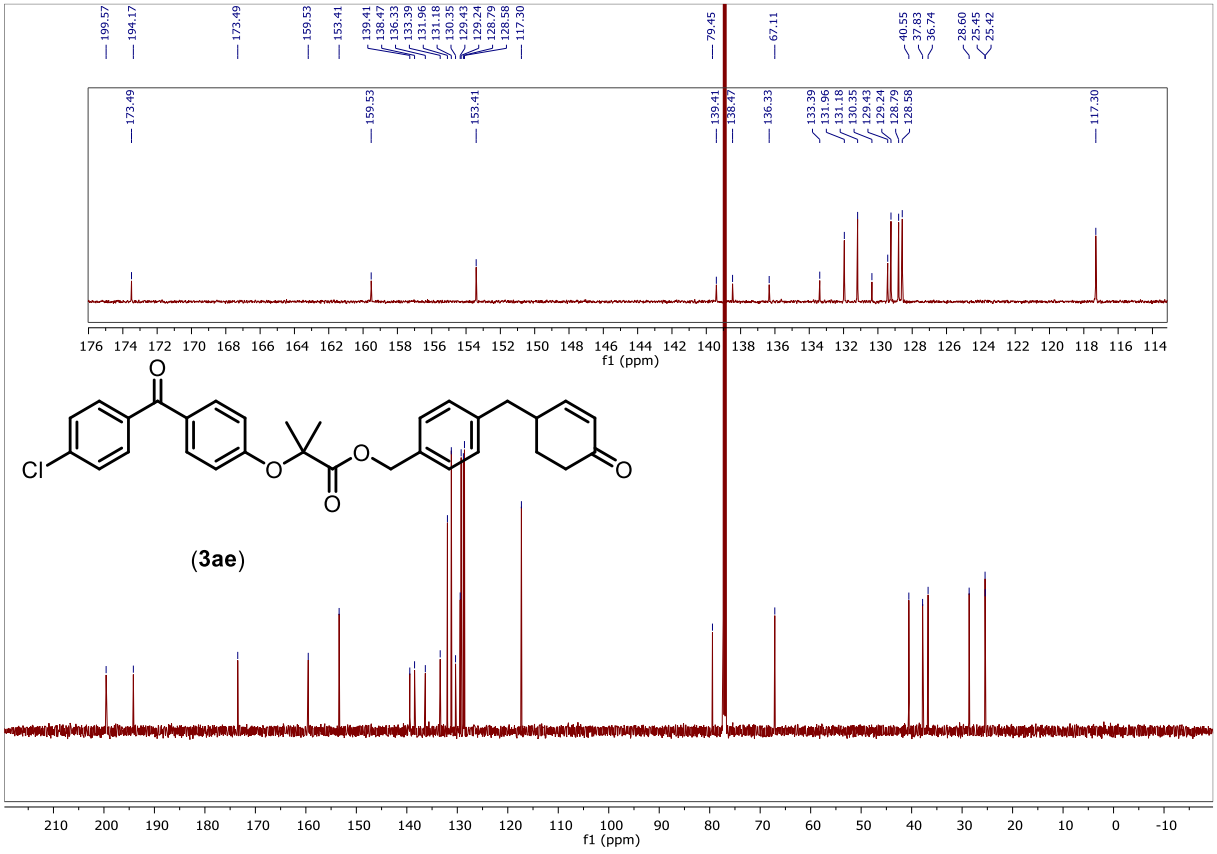
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	17.4 psi
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








f1 (ppm)
(3ae)


f1 (ppm)
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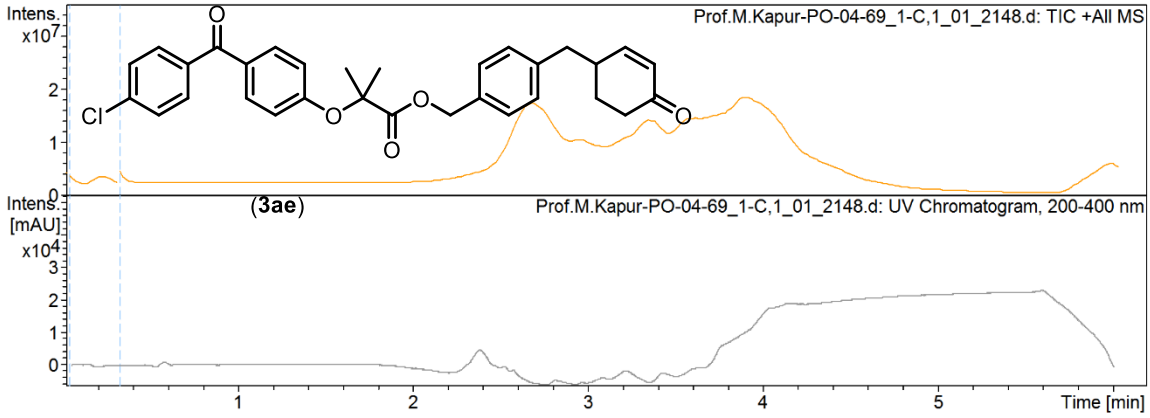
Display Report

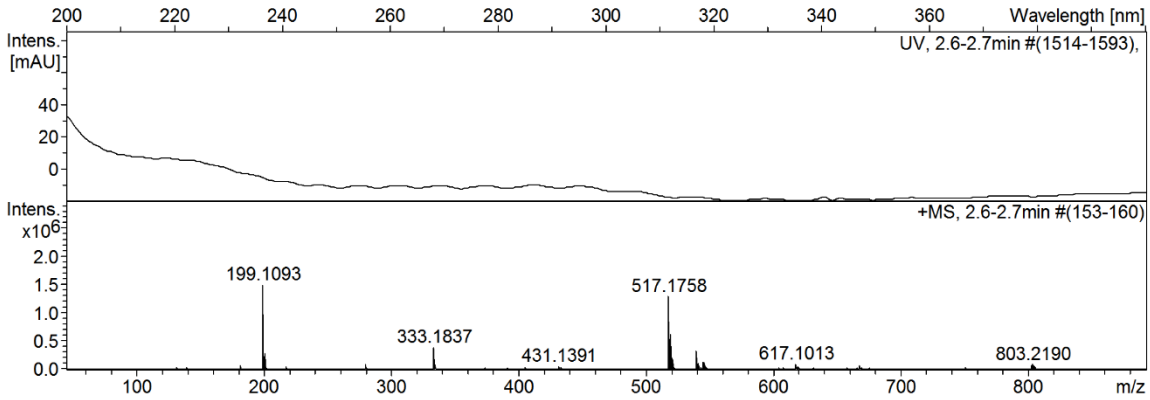
Analysis Info

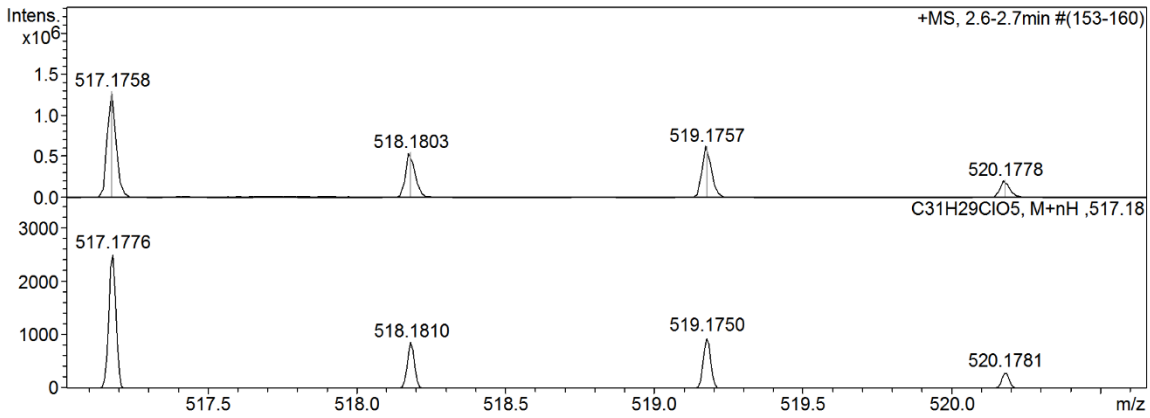
Acquisition Date	27-06-2023 14:07:08		
Analysis Name	D:\Data\USER DATA 2023\June\27-june\Prof.M.Kapur-PO-04-69_1-C,1_01_2148.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-69	Instrument	micrOTOF-Q 10330
Comment			

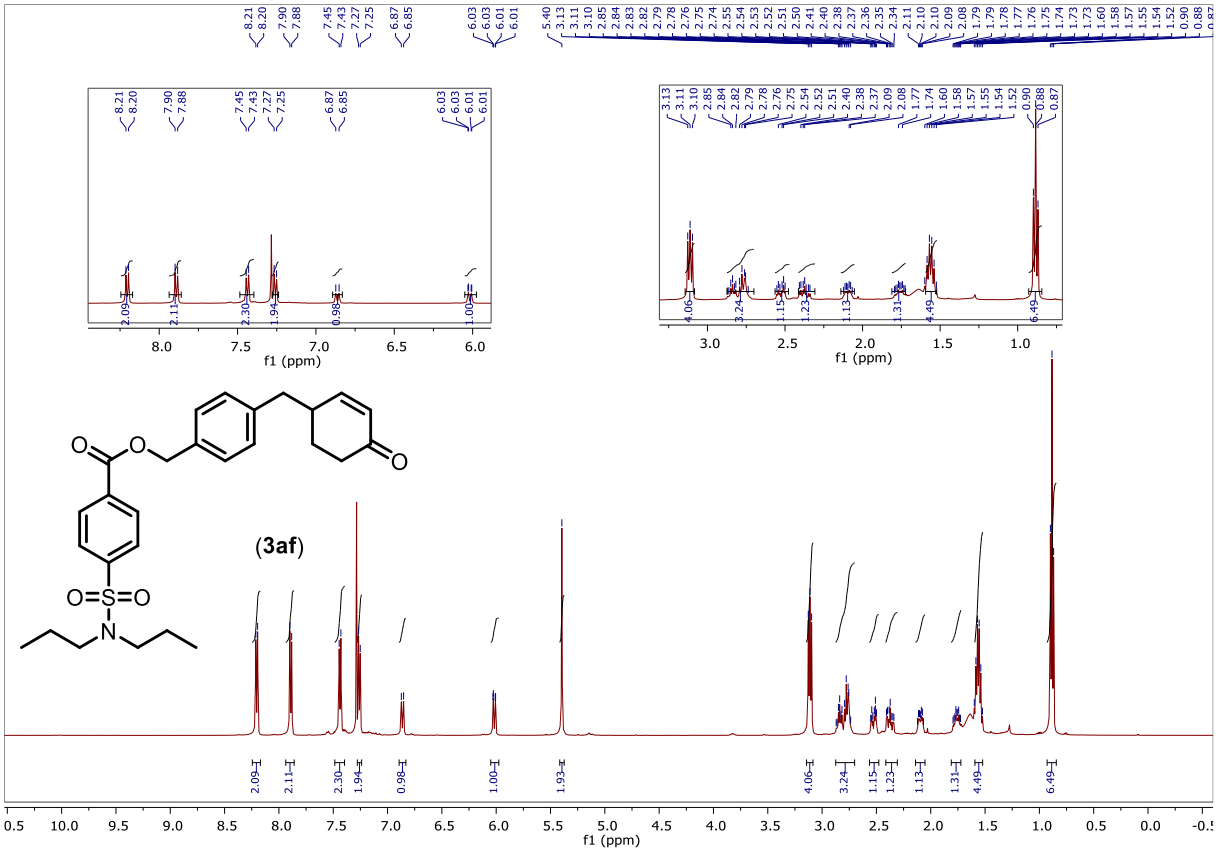
Acquisition Parameter

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





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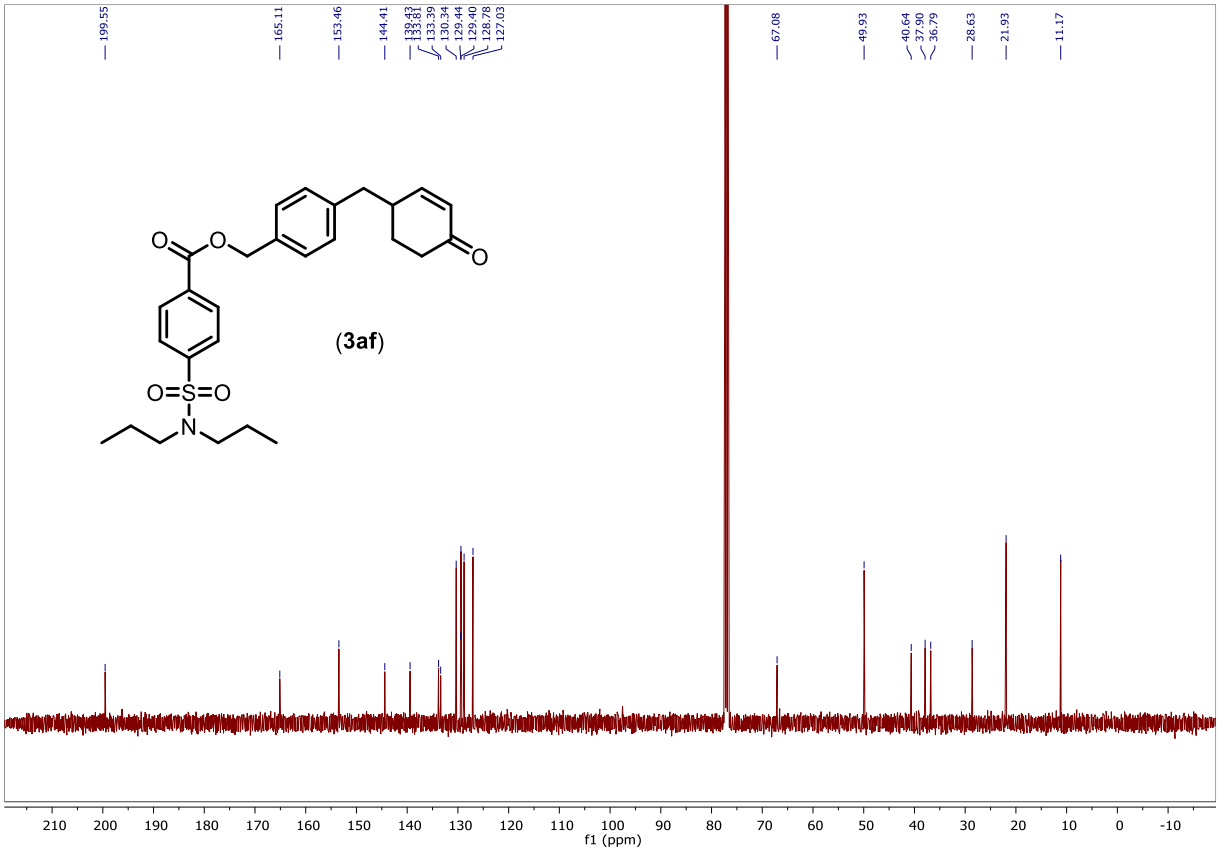
f1 (ppm)


(3af)
f1 (ppm)

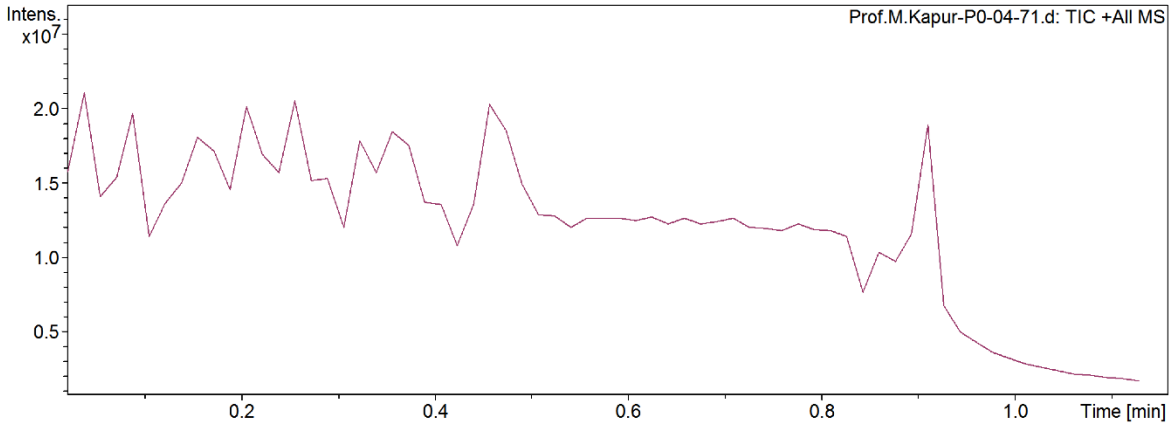
Display Report

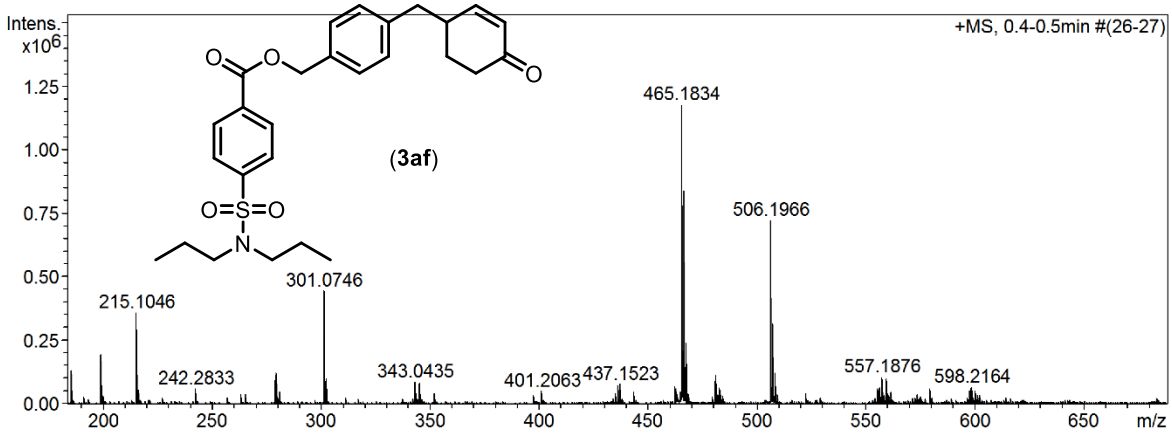
Analysis Info

Analysis Name	D:\Data\USER DATA 2023\June\16-june\Prof.M.Kapur-P0-04-71.d	Acquisition Date	16-06-2023 16:37:58
Method	tune_low_APR23.m	Operator	Bruker
Sample Name	P0-04-71	Instrument	micrOTOF-Q 10330
Comment			

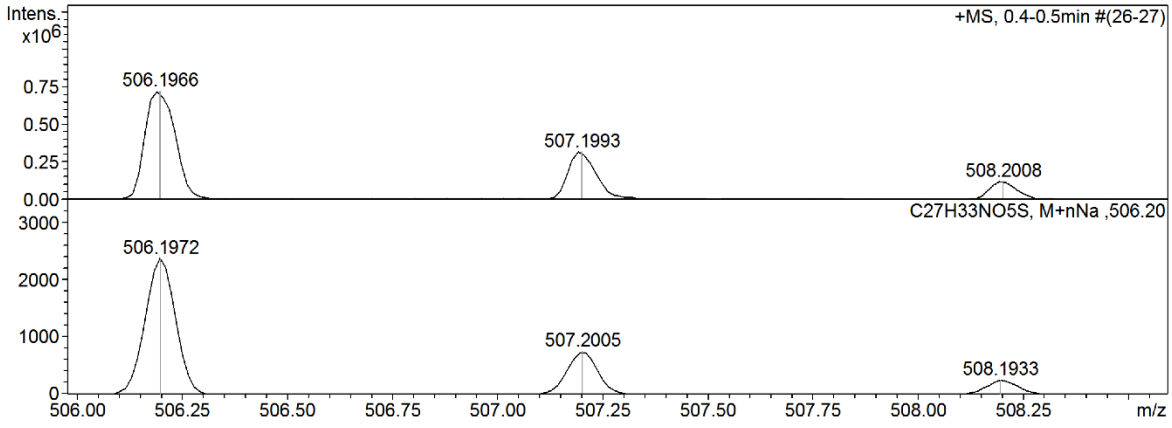
Acquisition Parameter

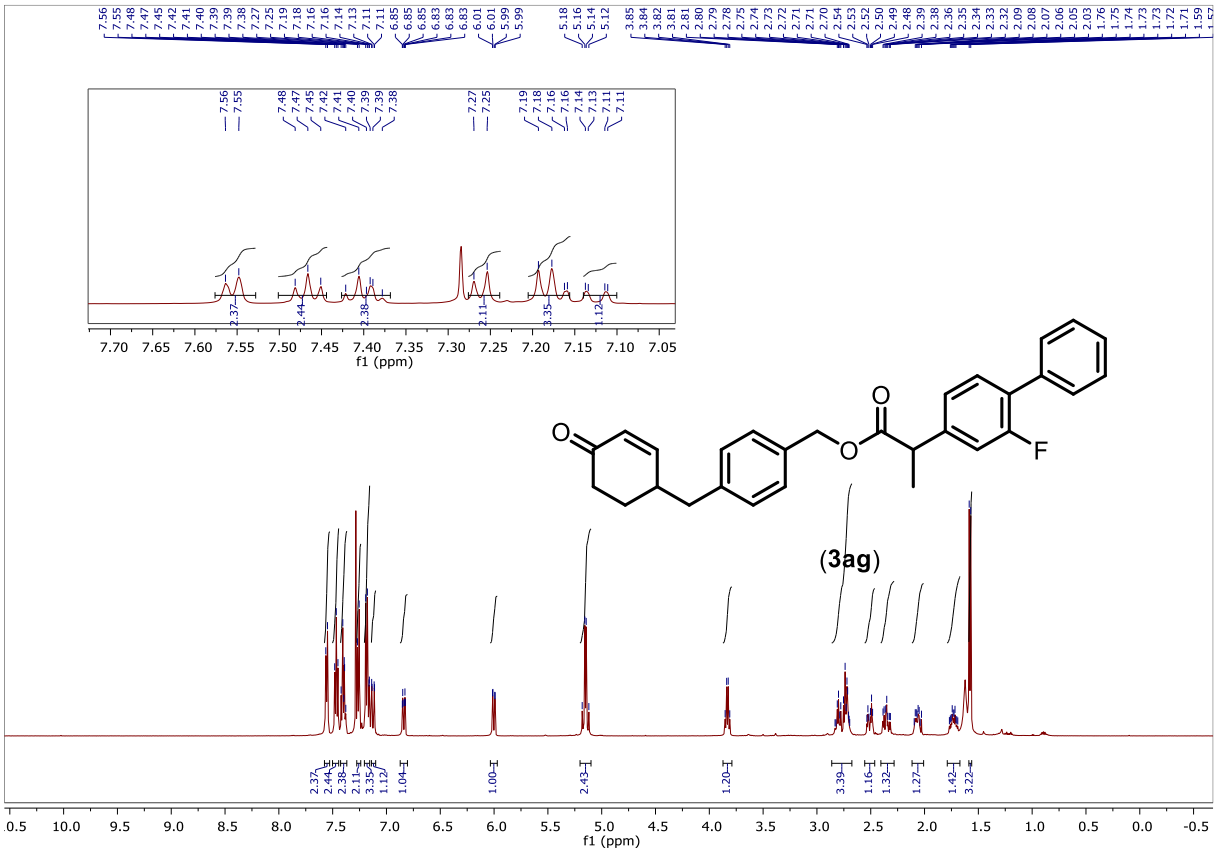
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste





(**3af**)

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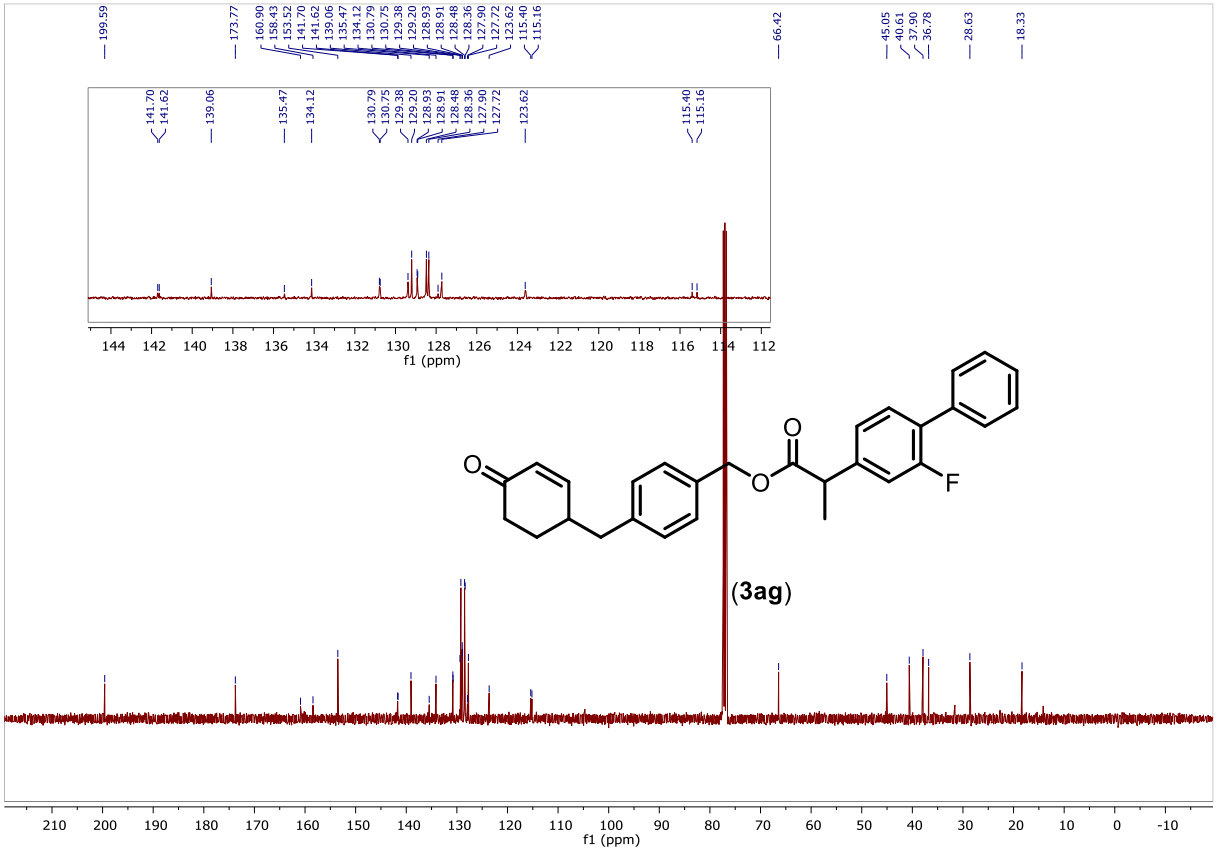
f1 (ppm)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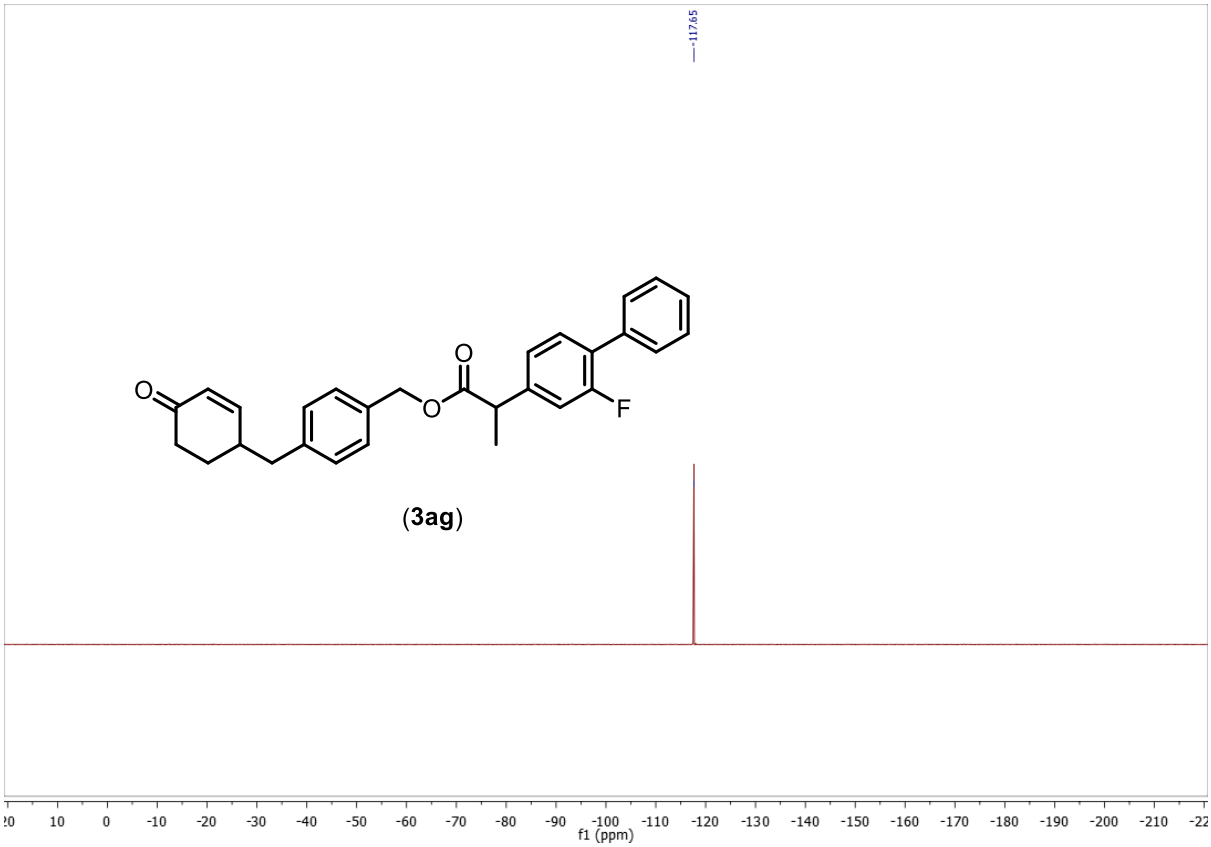
f1 (ppm)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O
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f1 (ppm)

(**3ag**)

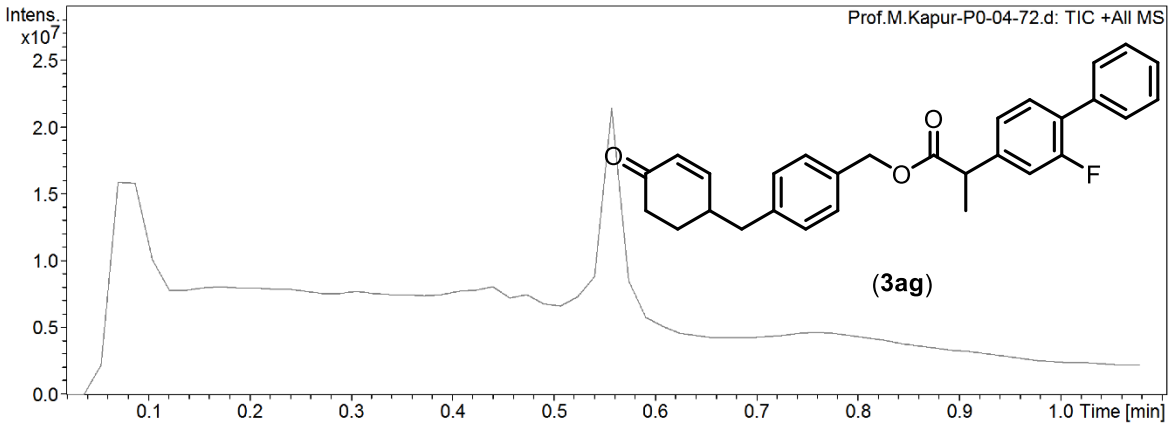
Display Report

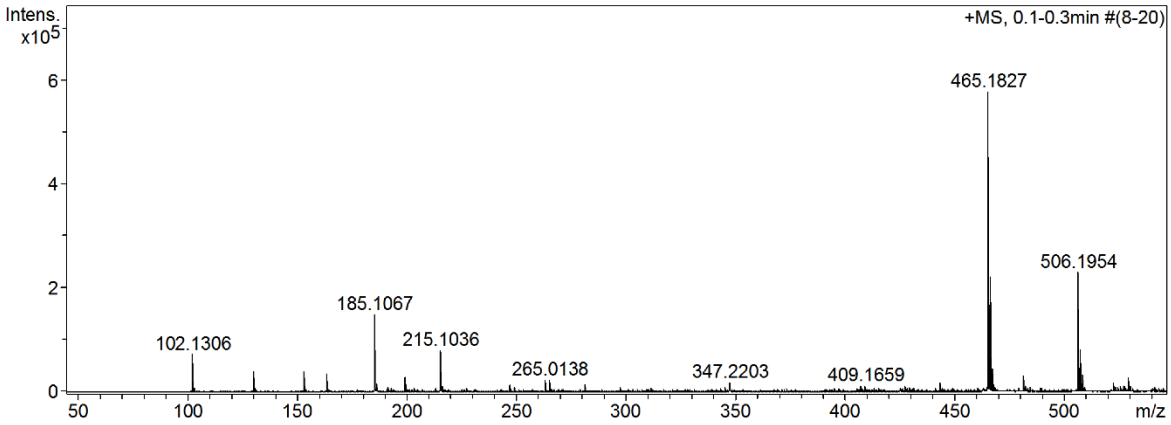
Analysis Info

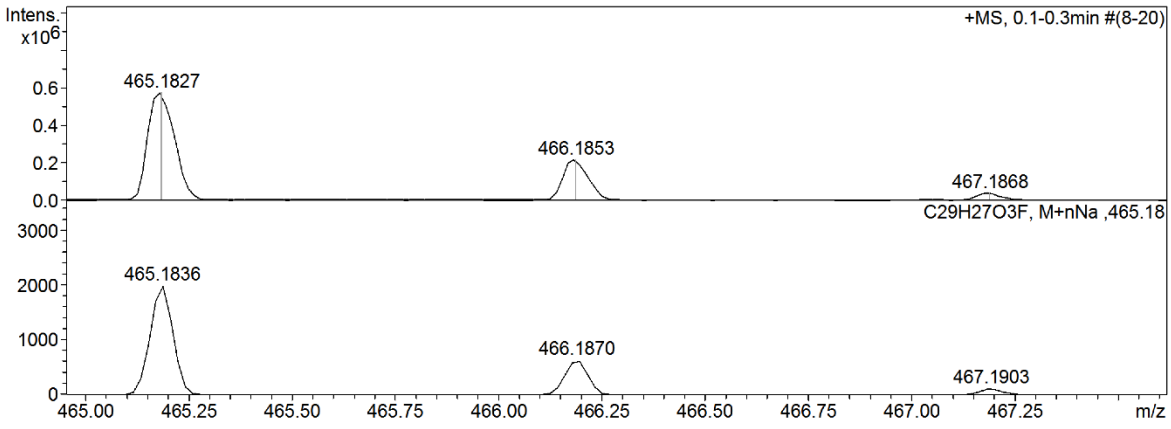
Acquisition Date	16-06-2023 16:41:14		
Analysis Name	D:\Data\USER DATA 2023\June\16-june\Prof.M.Kapur-P0-04-72.d		
Method	tune_low_APR23.m	Operator	Bruker
Sample Name	P0-04-72	Instrument	micrOTOF-Q 10330
Comment			

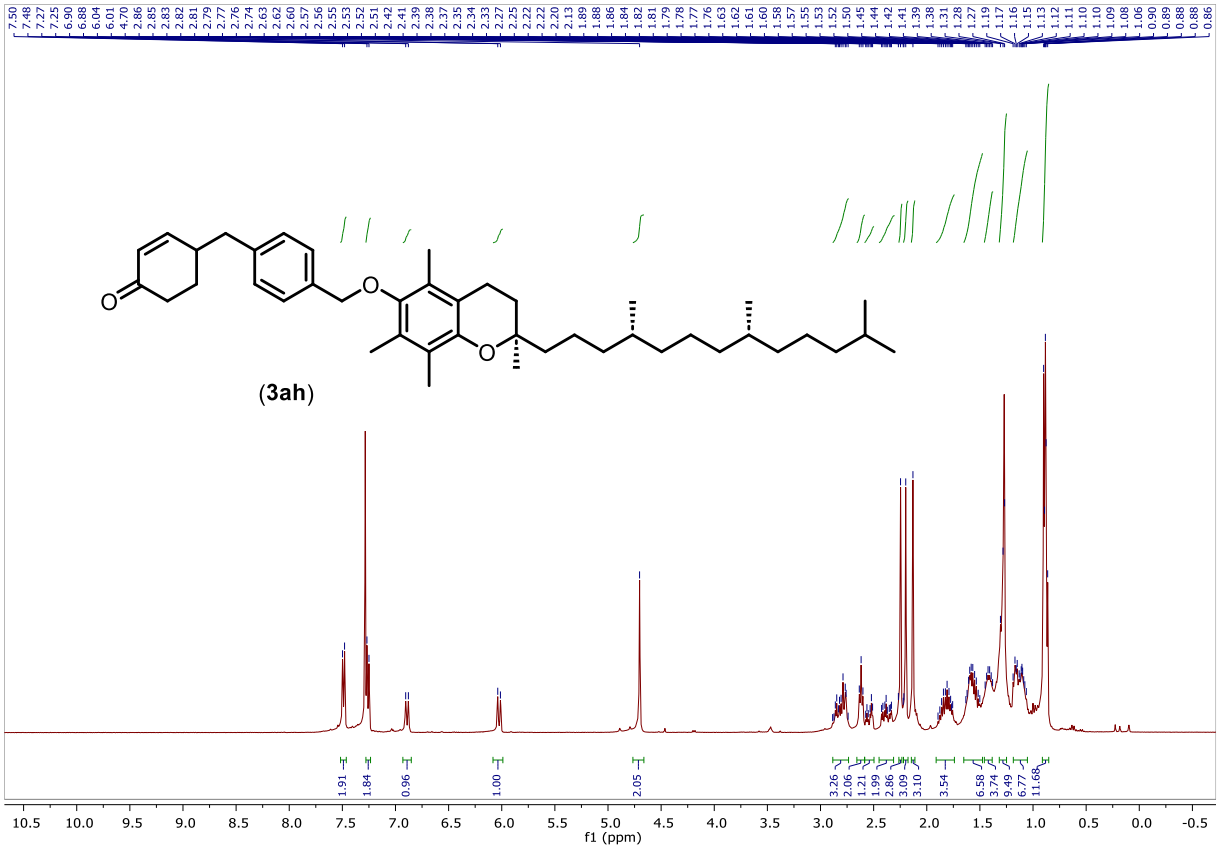
Acquisition Parameter

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





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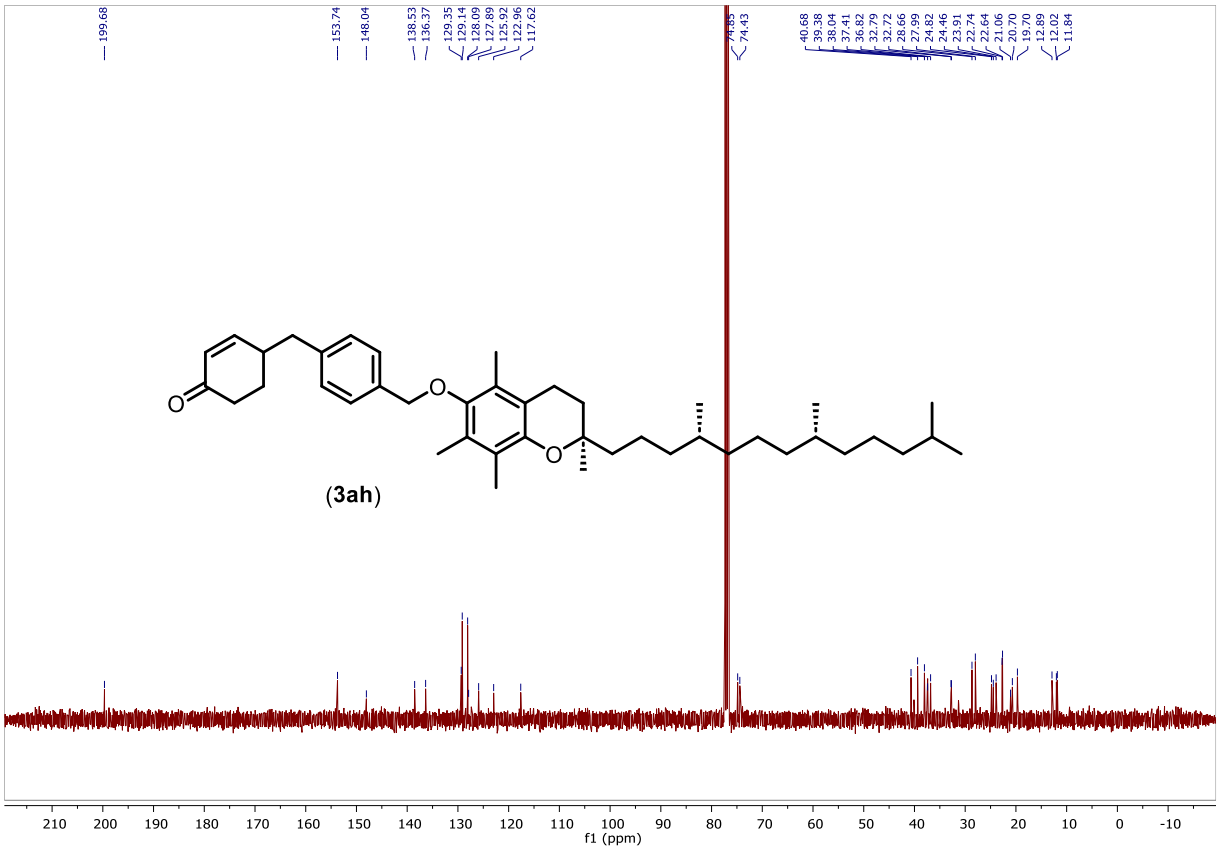
f1 (ppm)


(3ah)
f1 (ppm)

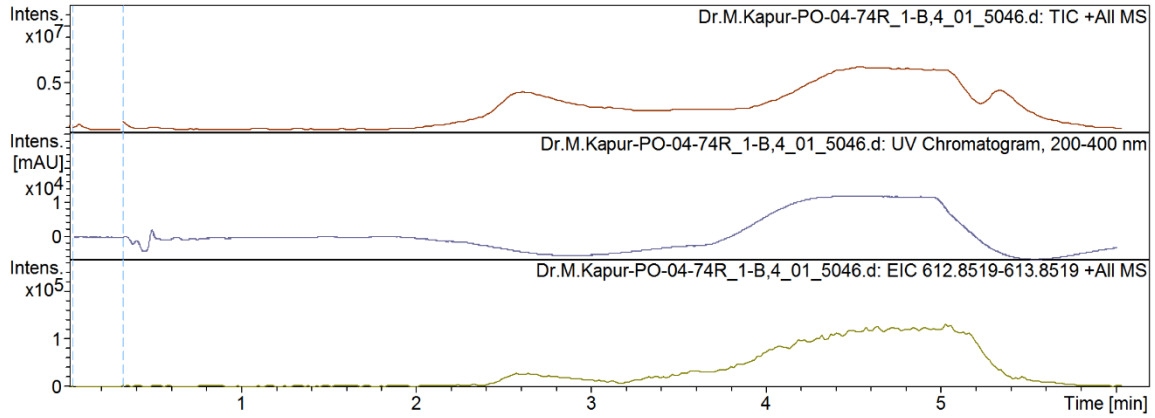
Display Report

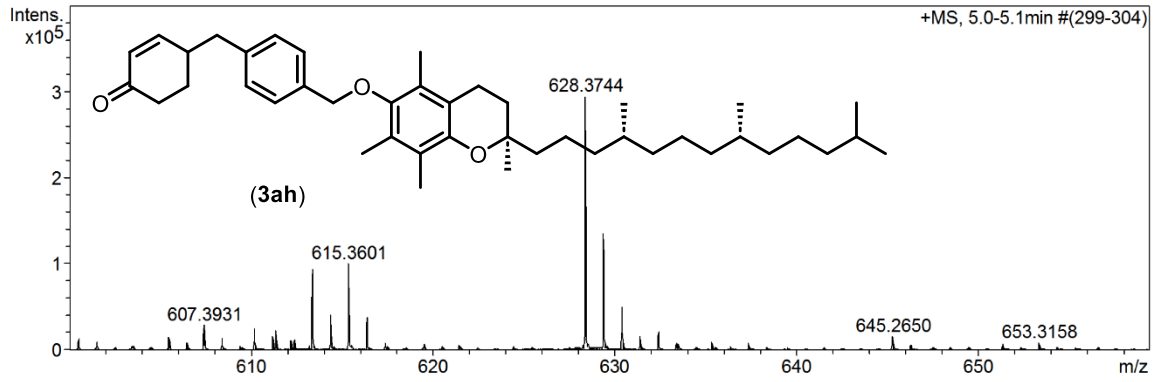
Analysis Info

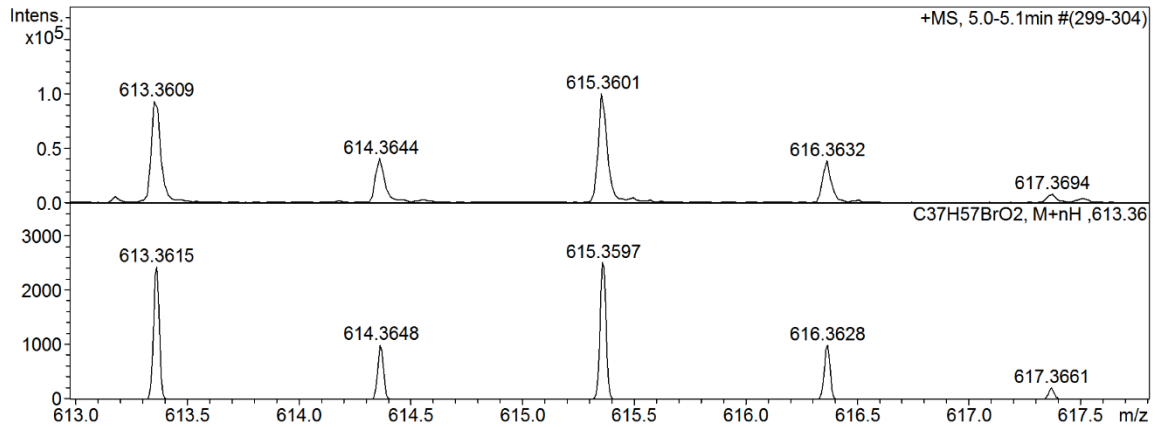
Acquisition Date	14-05-2024 13:48:10		
Analysis Name	D:\Data\USER DATA 2024\May-2024\14-may\Dr.M.Kapur-PO-04-74R_1-B,4_01_5046.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Dr.M.Kapur-PO-04-74R	Instrument	micrOTOF-Q 10330
Comment			

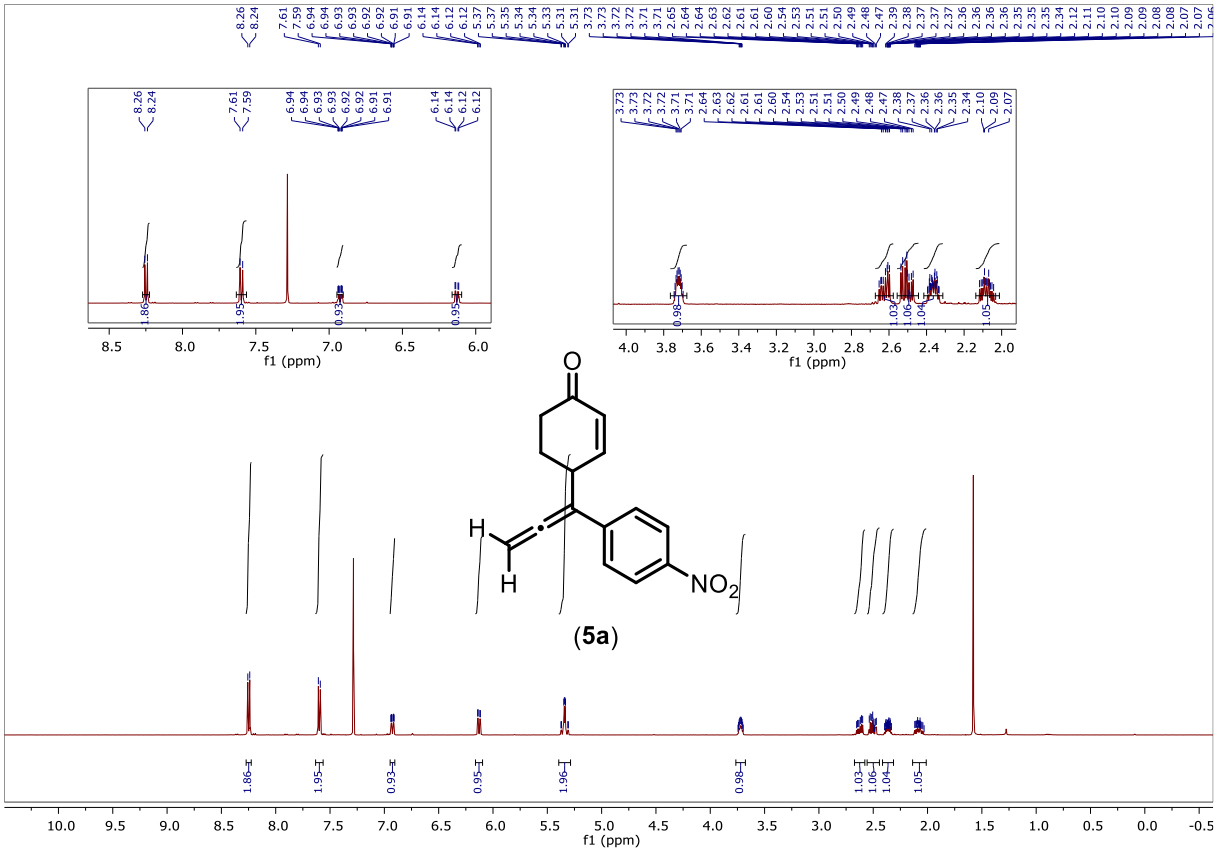
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	17.4 psi
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

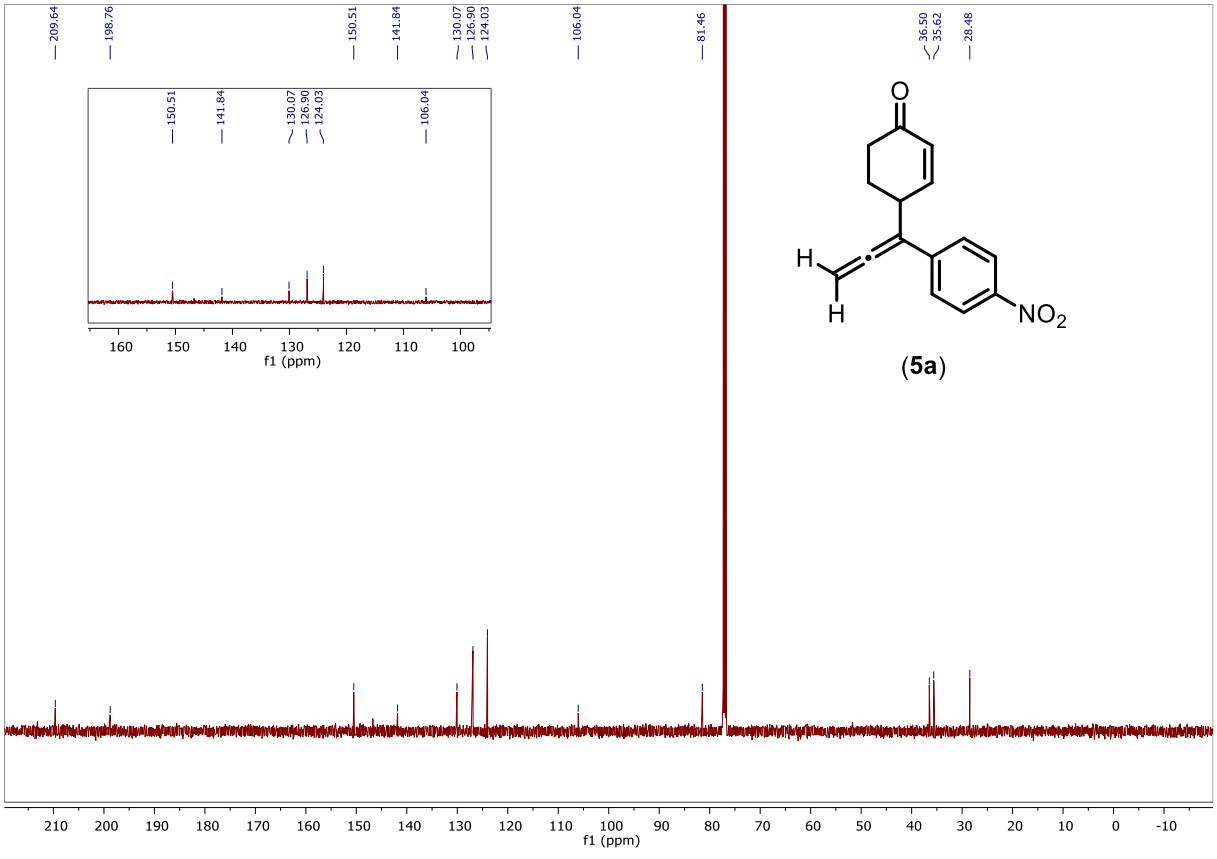








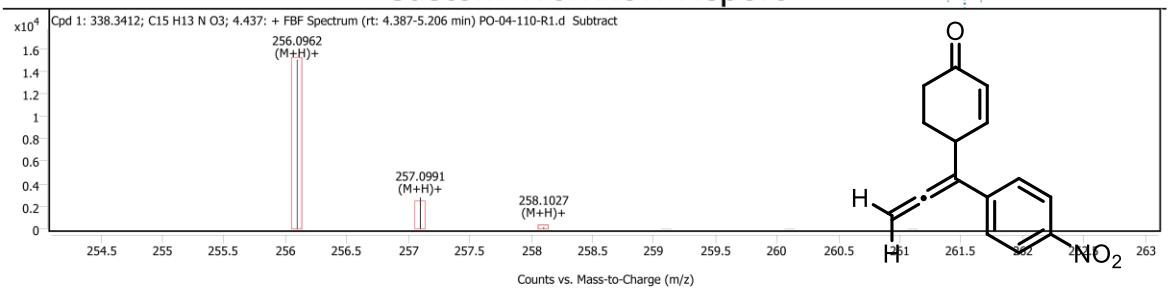
(**5a**)



(**5a**)

Custom Workflow Report

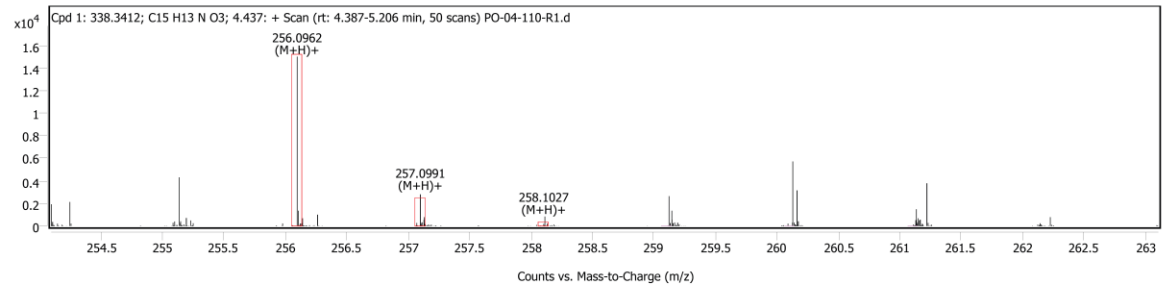
Agilent | Trusted Answers



(**5a**)

Spectrum Peaks

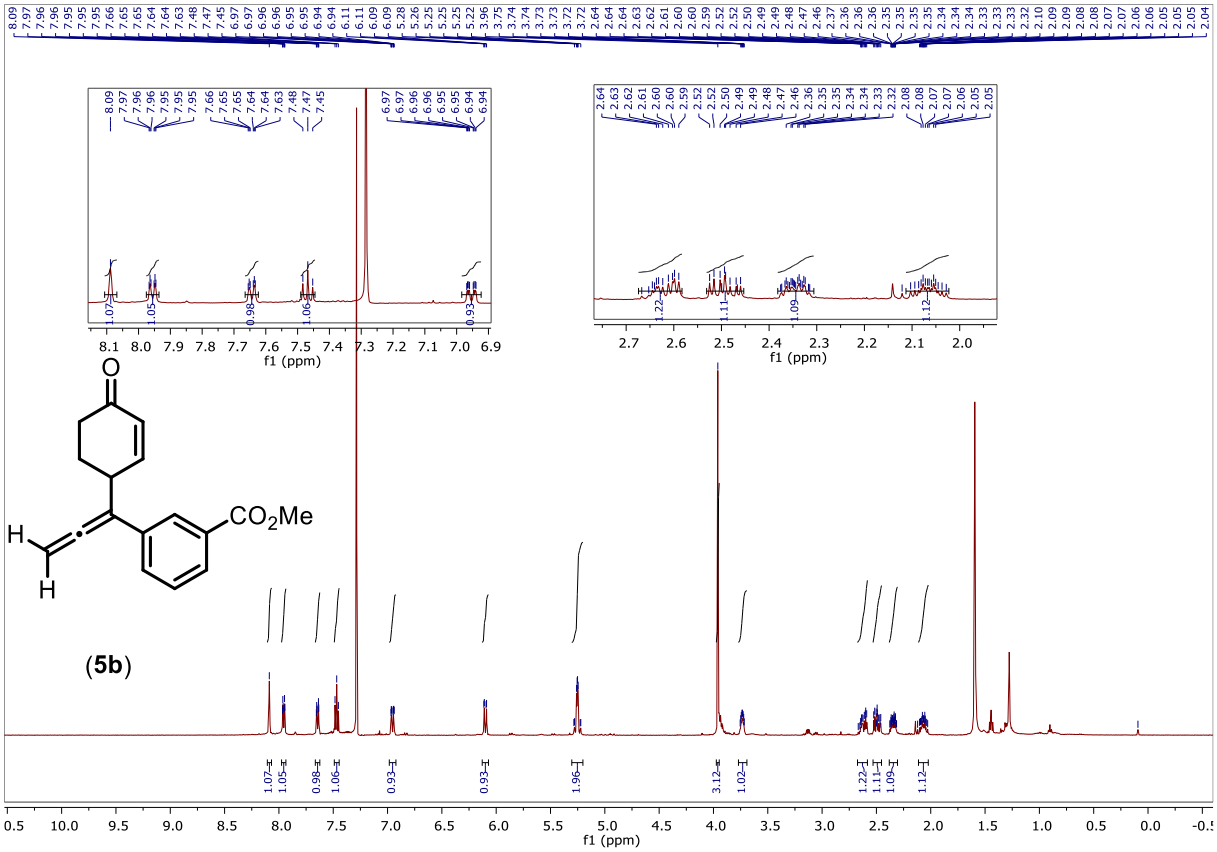
m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
256.0962	256.0968	-2.32	14984	100.00	100.00	(M+H)+	1
257.0991	257.1001	-3.75	2797	18.67	16.86	(M+H)+	1
258.1027	258.1026	0.38	175	1.17	1.95	(M+H)+	1

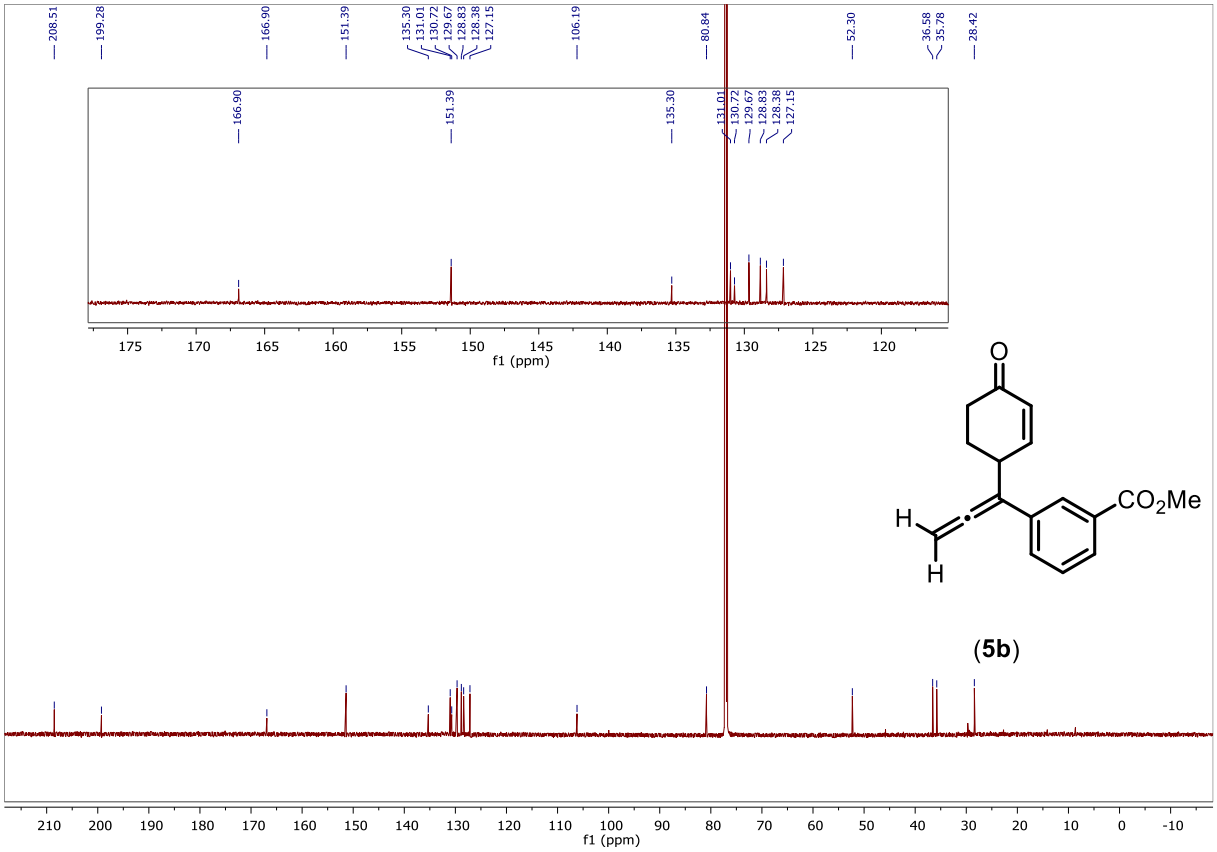


Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
256.0962	256.0968	-2.32	14984	100.00	100.00	(M+H)+	1
257.0991	257.1001	-3.75	2797	18.67	16.86	(M+H)+	1
258.1027	258.1026	0.38	175	1.17	1.95	(M+H)+	1

MassHunter Qual 10.0
(End of Report)


f1 (ppm)
(5b)


f1 (ppm)
(5b)

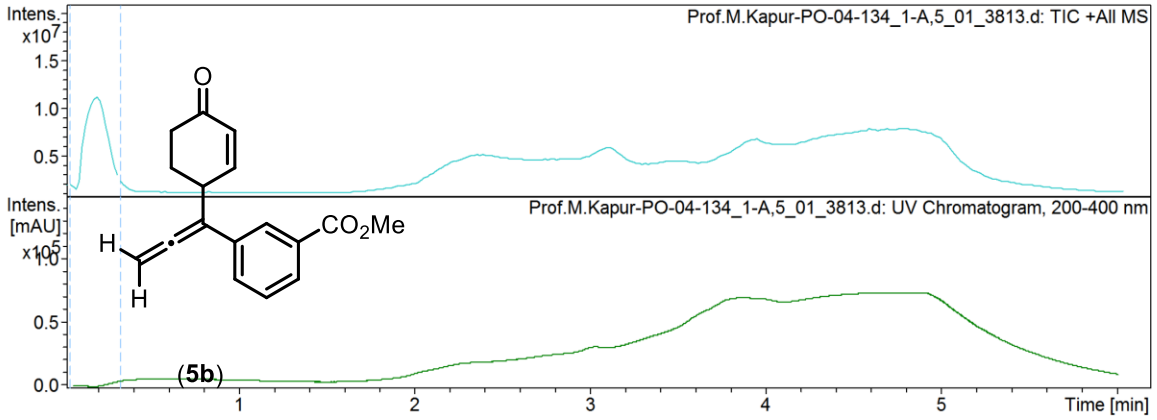
Display Report

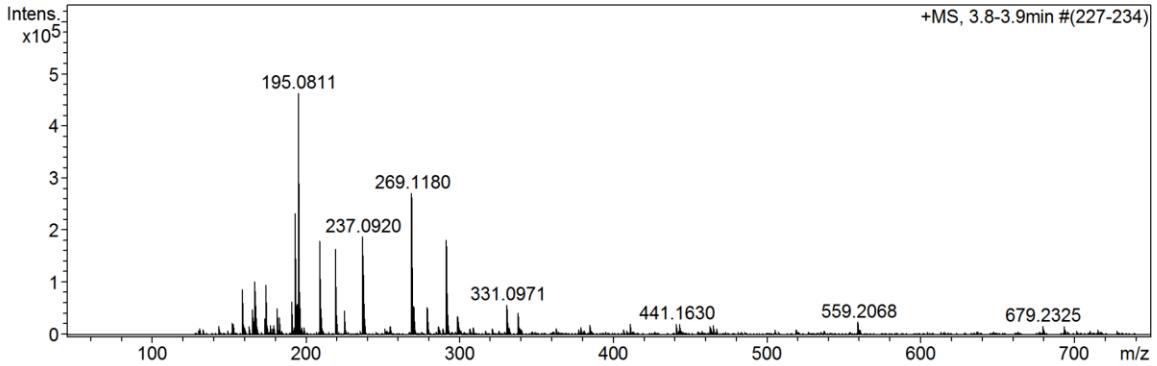
Analysis Info

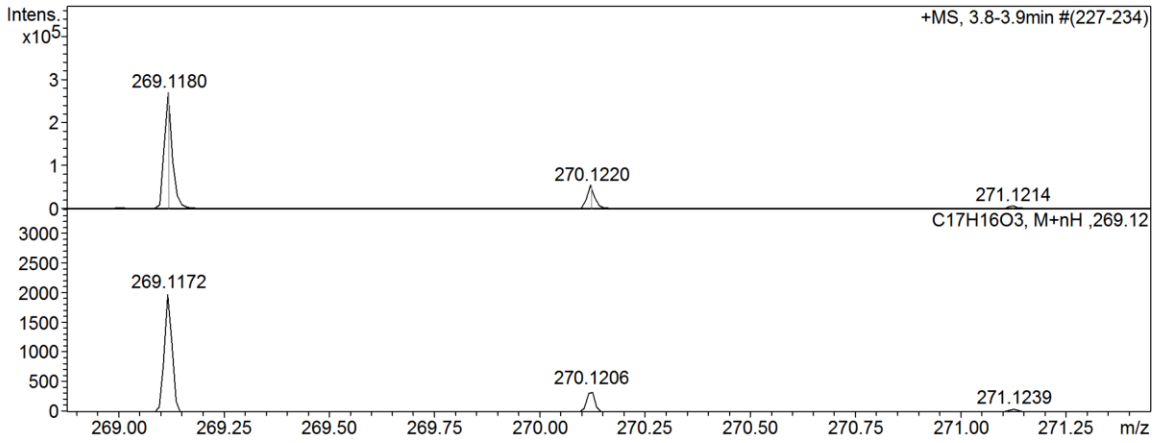
Analysis Name	D:\Data\USER DATA 2024\16-jan\Prof.M.Kapur-PO-04-134_1-A,5_01_3813.d	Acquisition Date	16-01-2024 12:57:56
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-134	Instrument	micrOTOF-Q 10330
Comment			

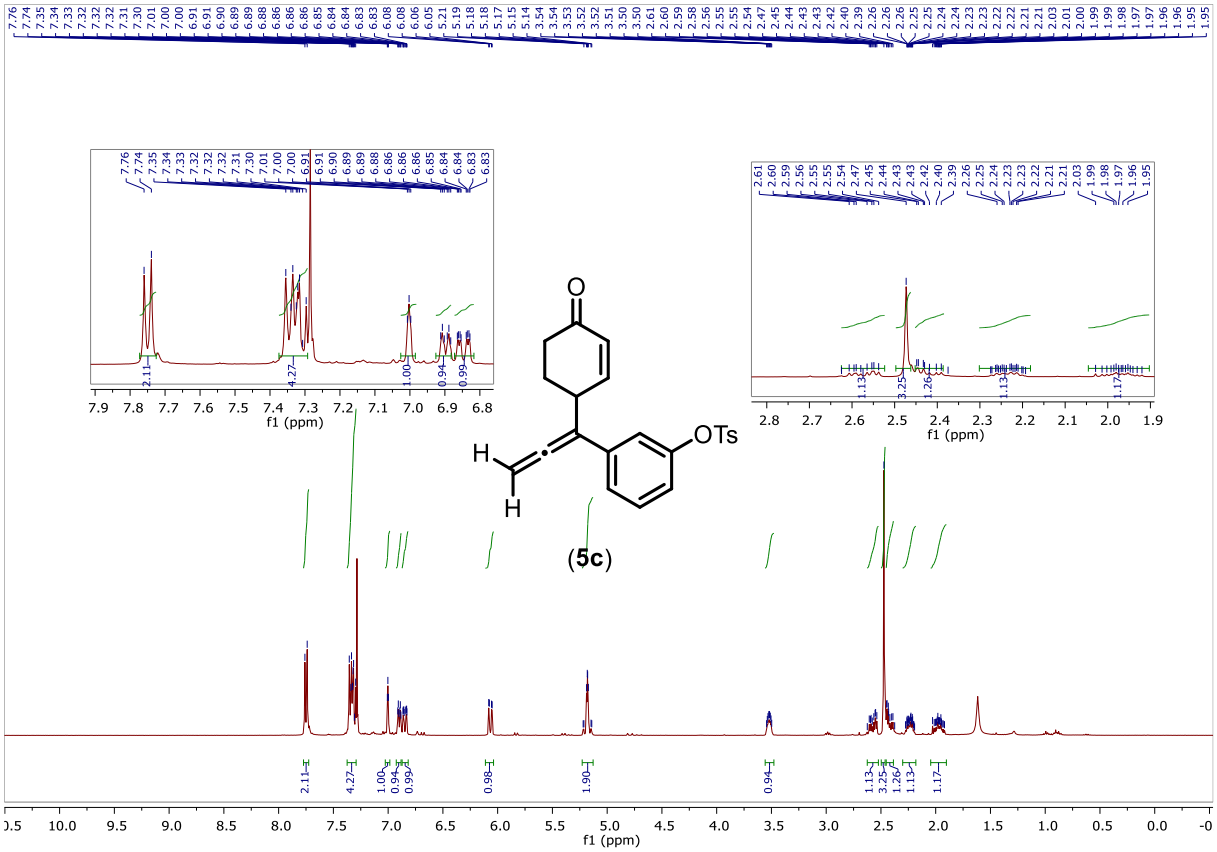
Acquisition Parameter

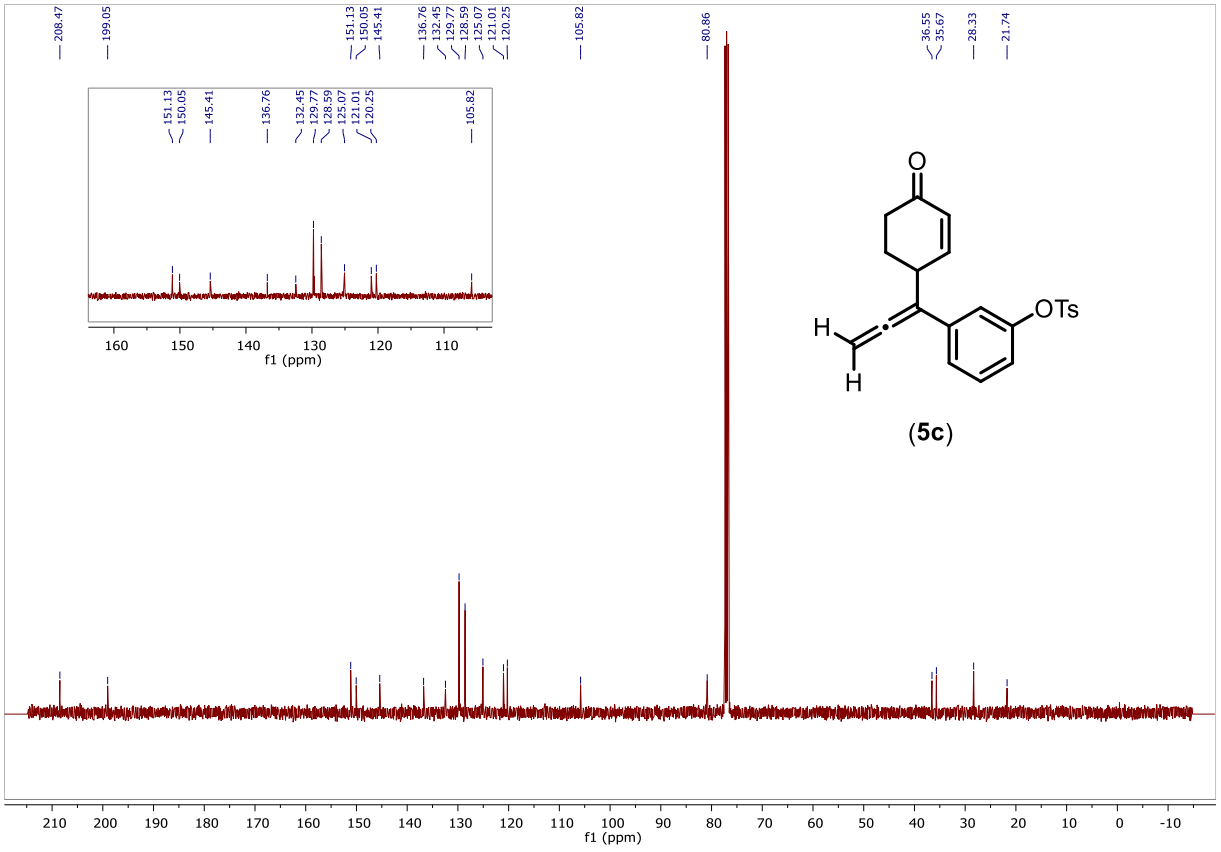
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








O
H
H
OTs
(5c)
f1 (ppm)


O
H
H
OTs
(5c)
f1 (ppm)

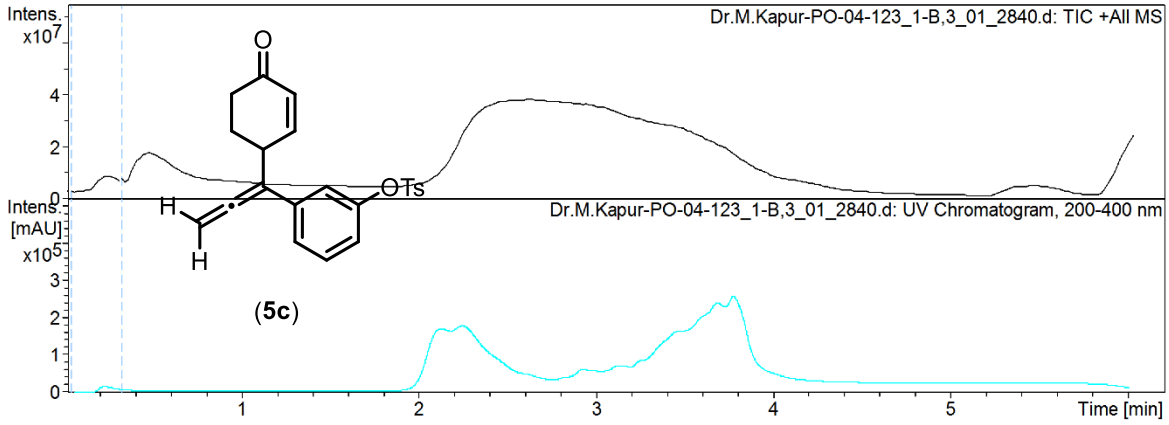
Display Report

Analysis Info

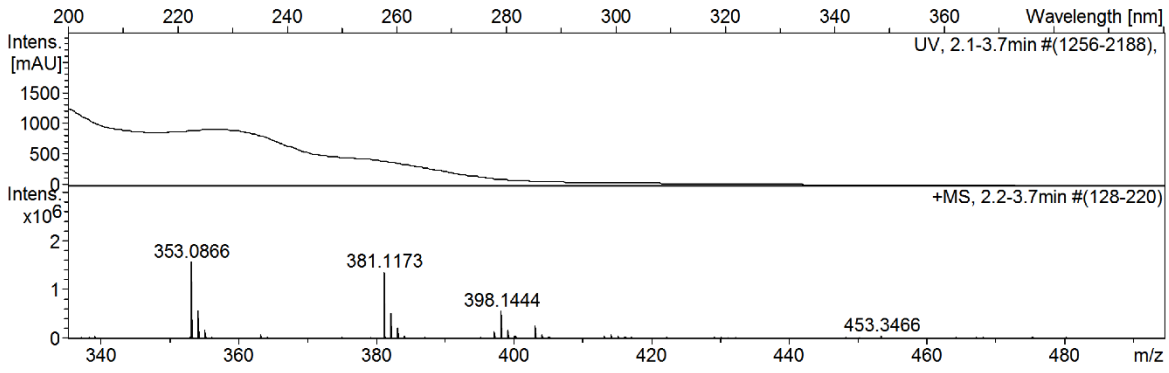
Acquisition Date	25-08-2023 12:40:02		
Analysis Name	D:\Data\USER DATA 2023\Aug-23\25-aug\Dr.M.Kapur-PO-04-123_1-B,3_01_2840.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Dr.M.Kapur-PO-04-123	Instrument	micrOTOF-Q 10330
Comment			

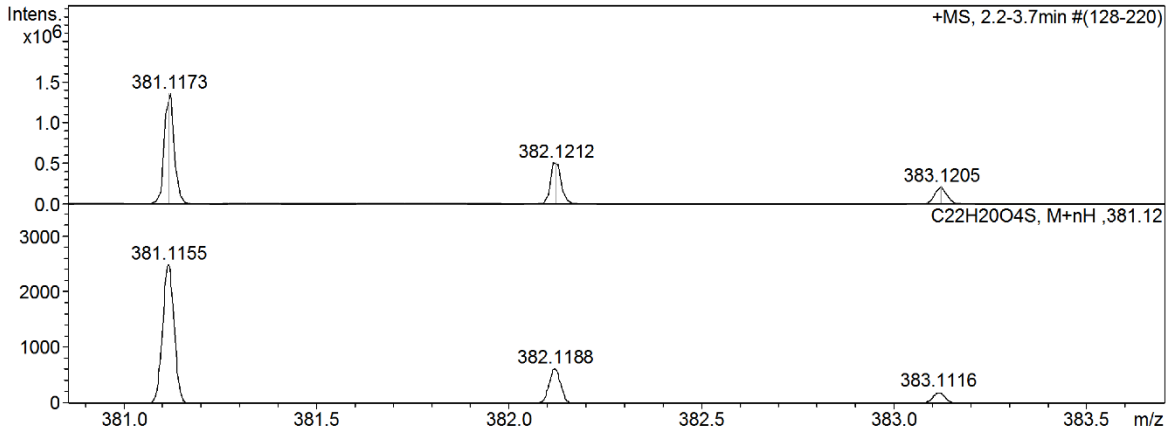
Acquisition Parameter

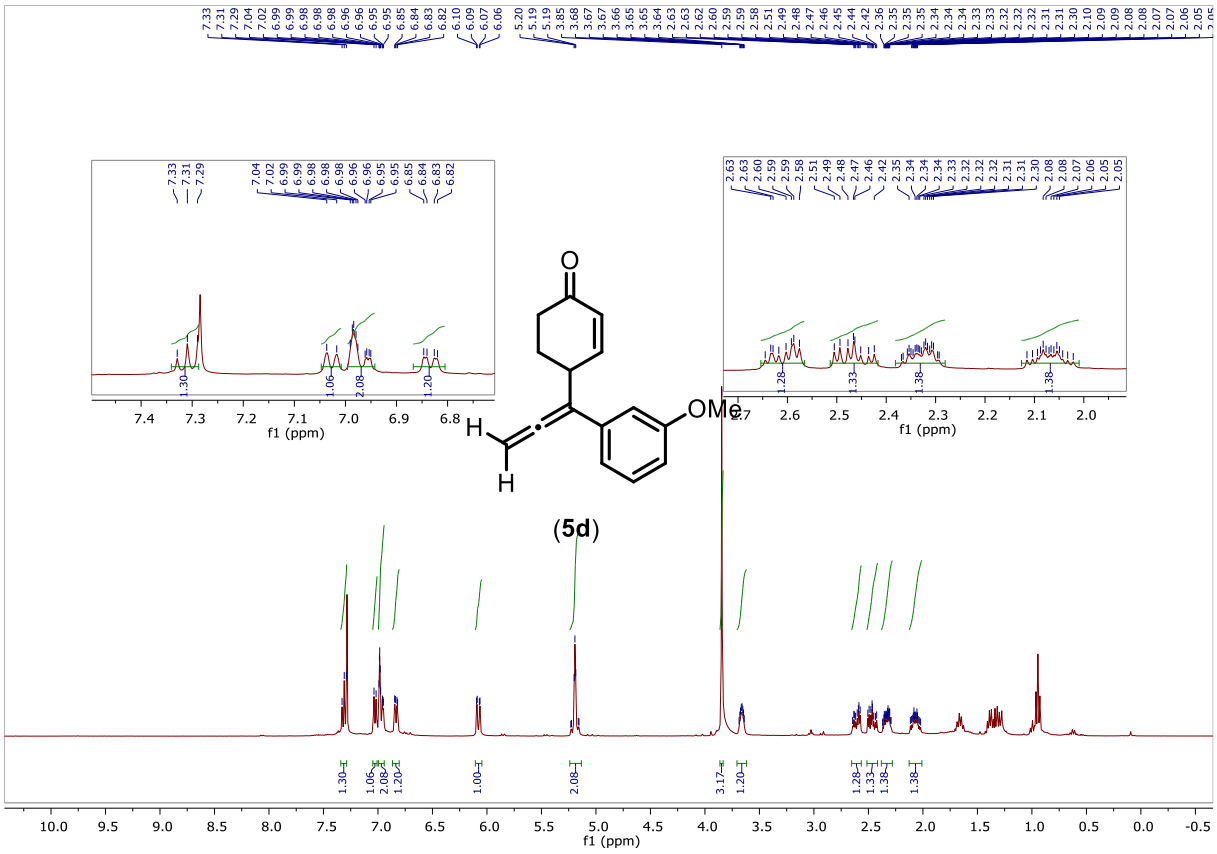
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

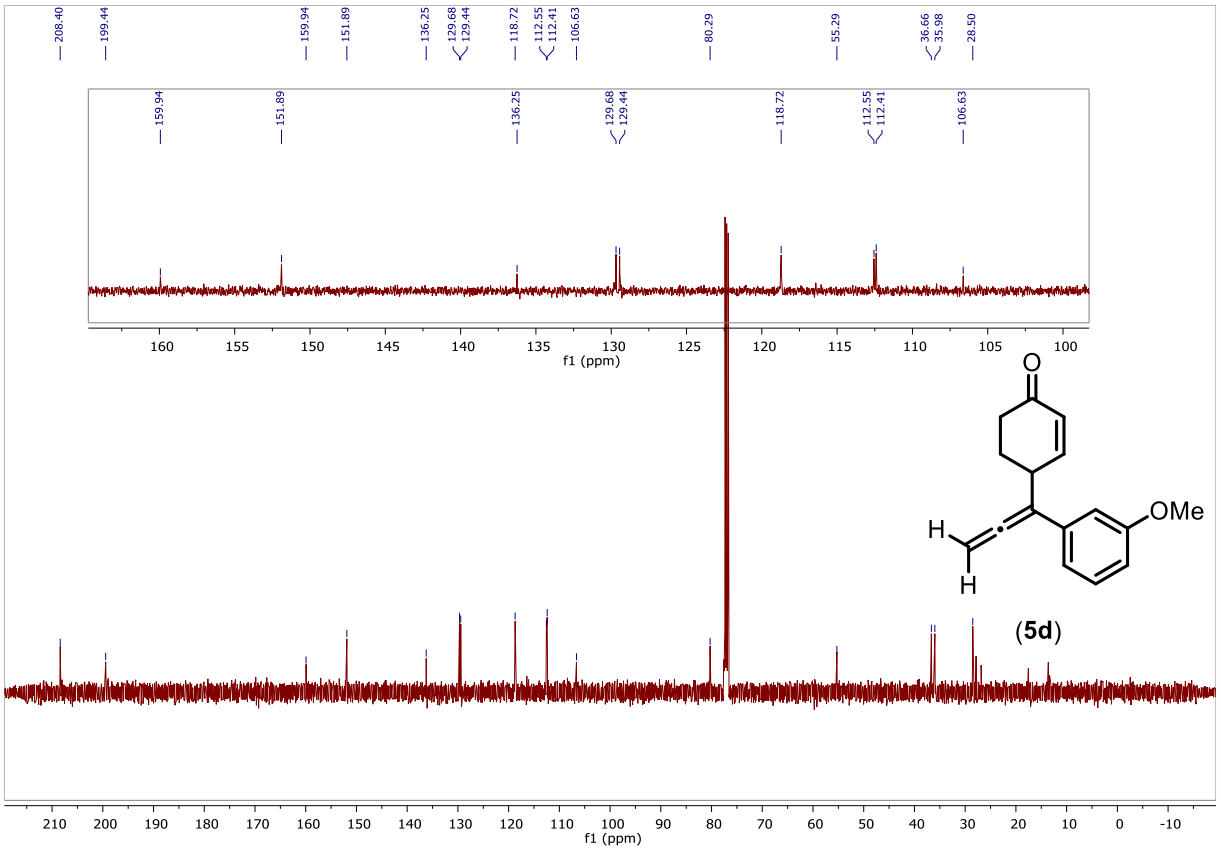


(**5c**)






O
OMe
H
H
(5d)
f1 (ppm)


O
OMe
H
H
(5d)
f1 (ppm)

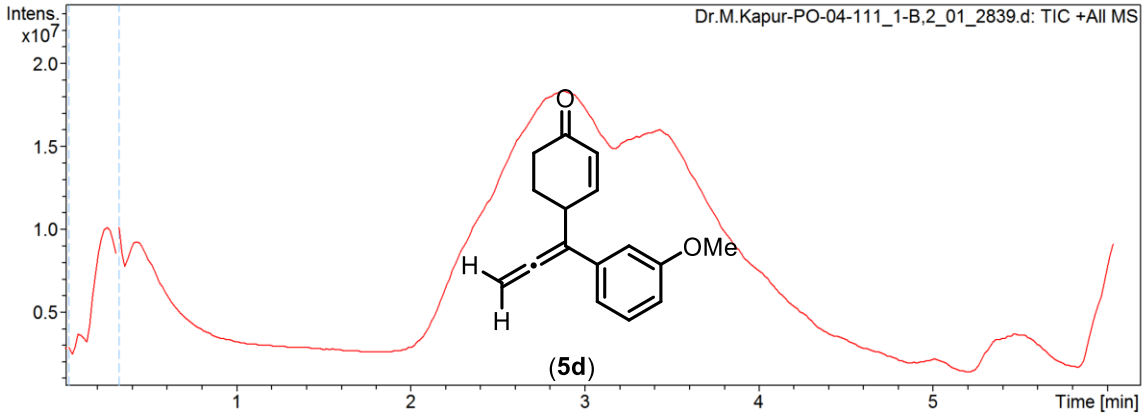
Display Report

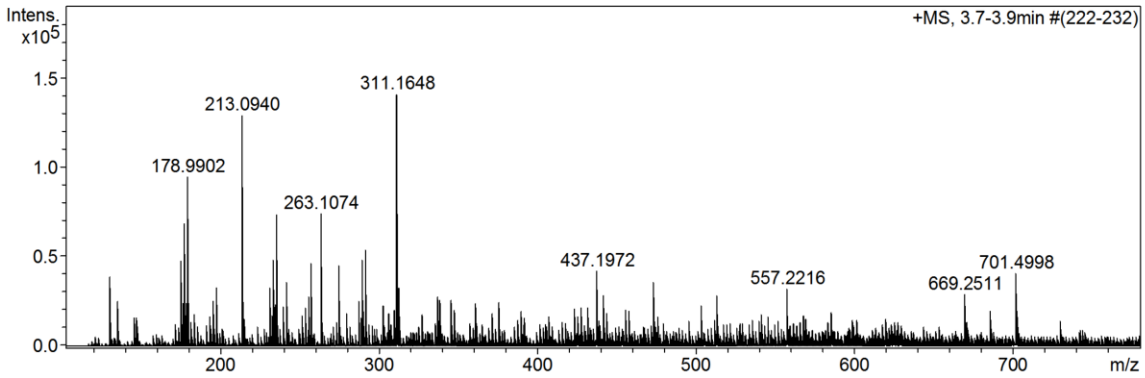
Analysis Info

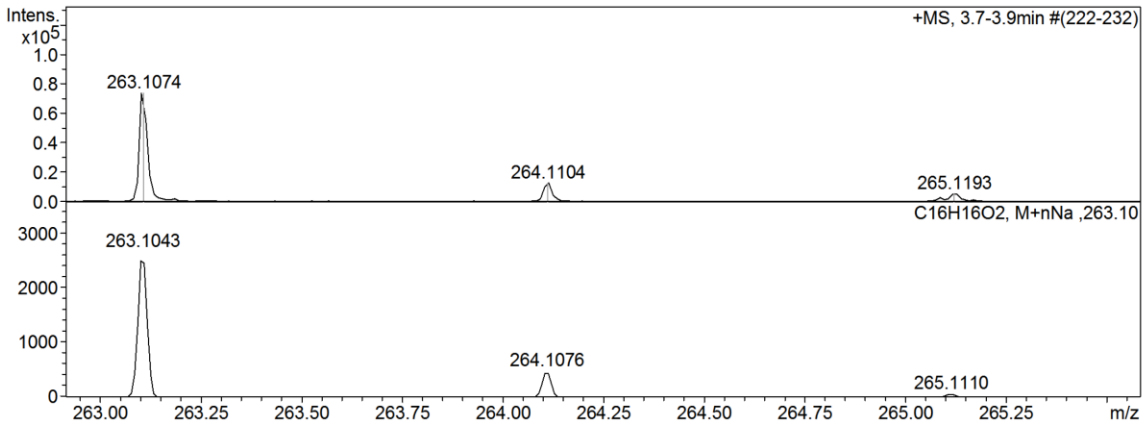
Acquisition Date	25-08-2023 12:32:50		
Analysis Name	D:\Data\USER DATA 2023\Aug-23\25-aug\Dr.M.Kapur-PO-04-111_1-B,2_01_2839.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Dr.M.Kapur-PO-04-111	Instrument	micrOTOF-Q 10330
Comment			

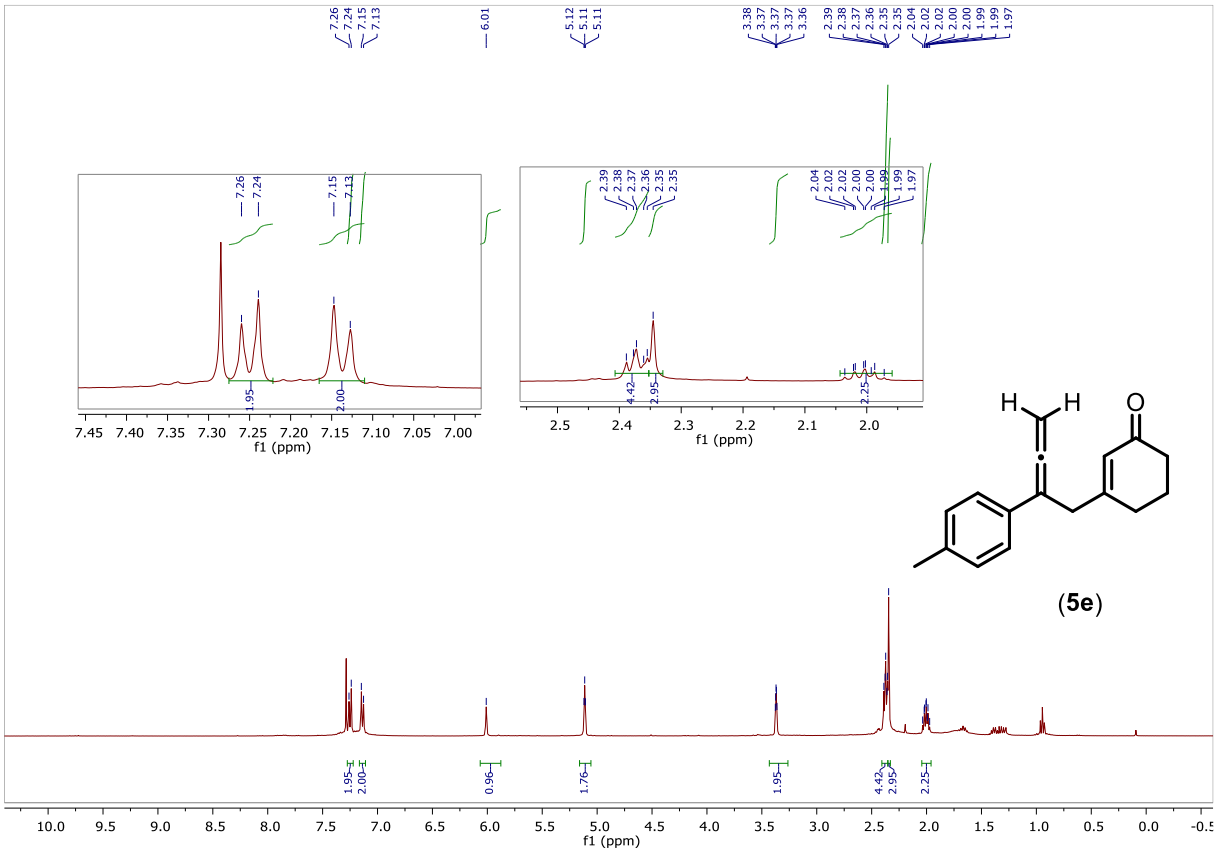
Acquisition Parameter

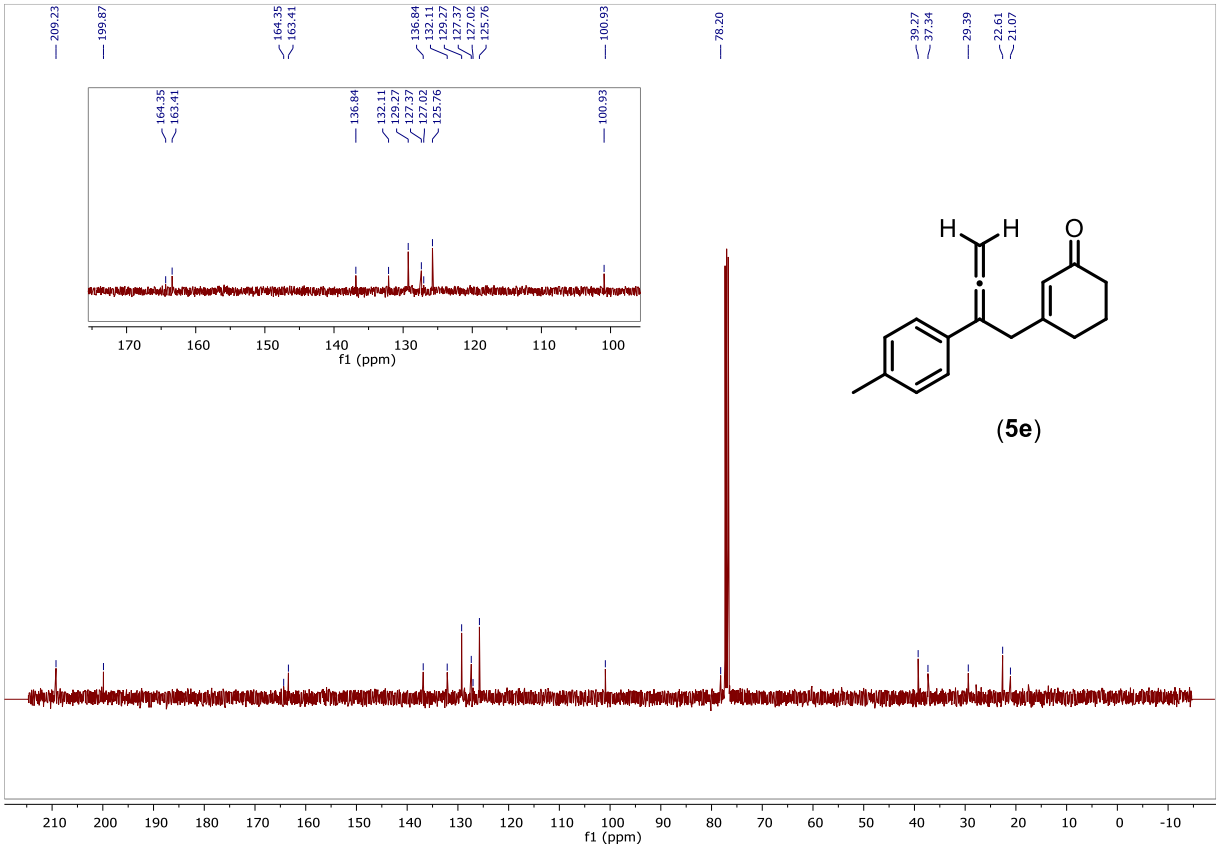
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








f1 (ppm)
H
H
O
(5e)


f1 (ppm)
H
H
O
(5e)

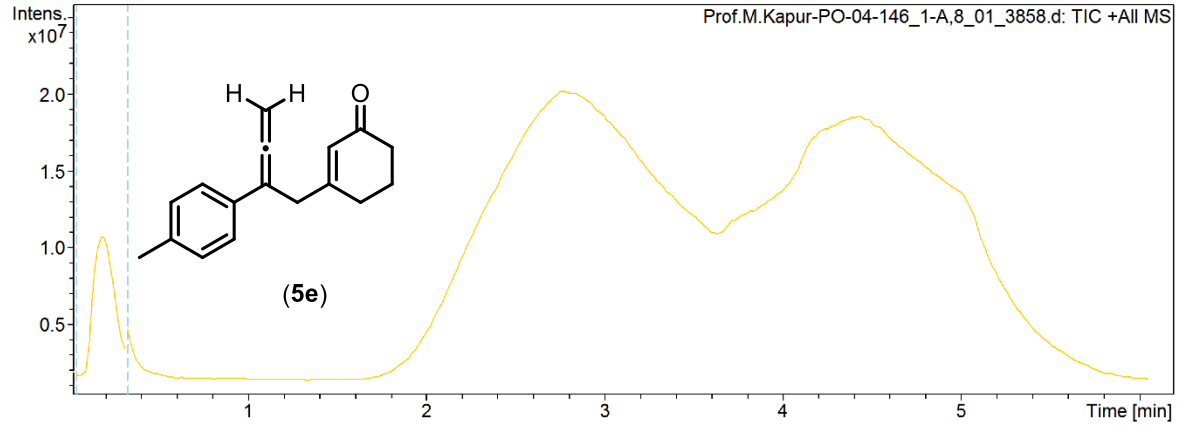
Display Report

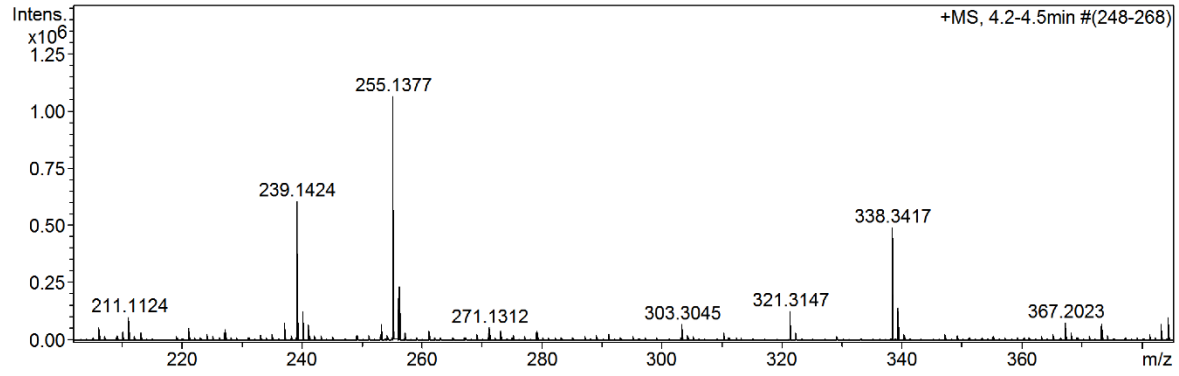
Analysis Info

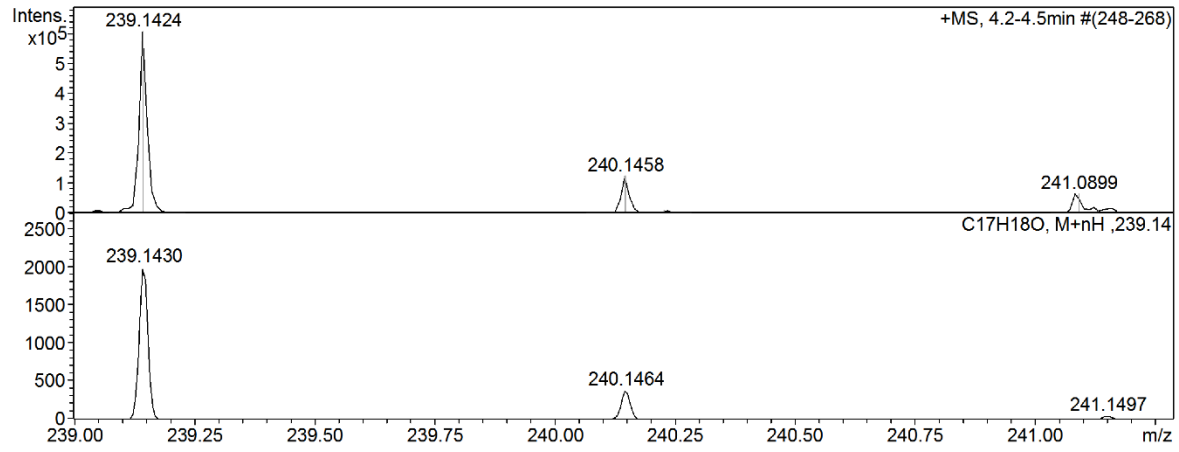
Analysis Name	D:\Data\USER DATA 2024\17-jan\Prof.M.Kapur-PO-04-146_1-A,8_01_3858.d	Acquisition Date	17-01-2024 17:13:52
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-146	Instrument	micrOTOF-Q 10330
Comment			

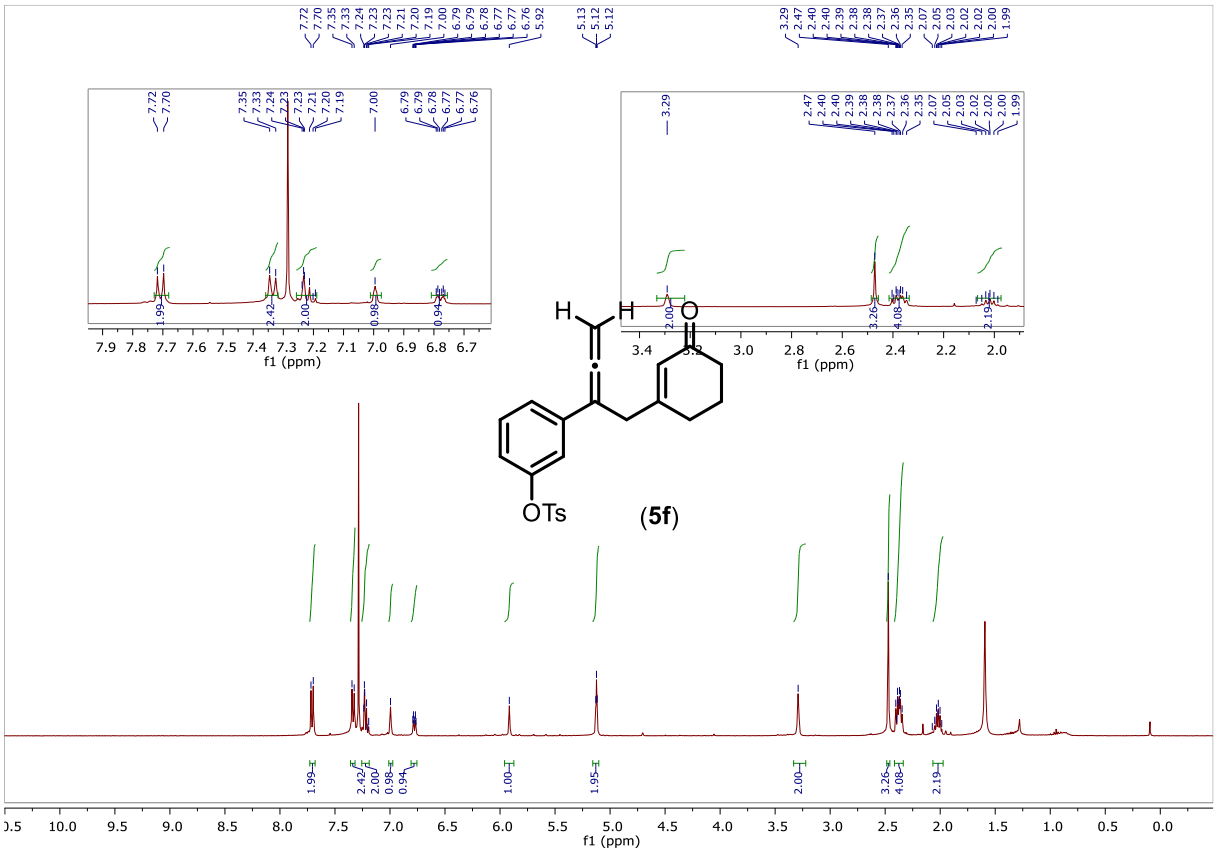
Acquisition Parameter

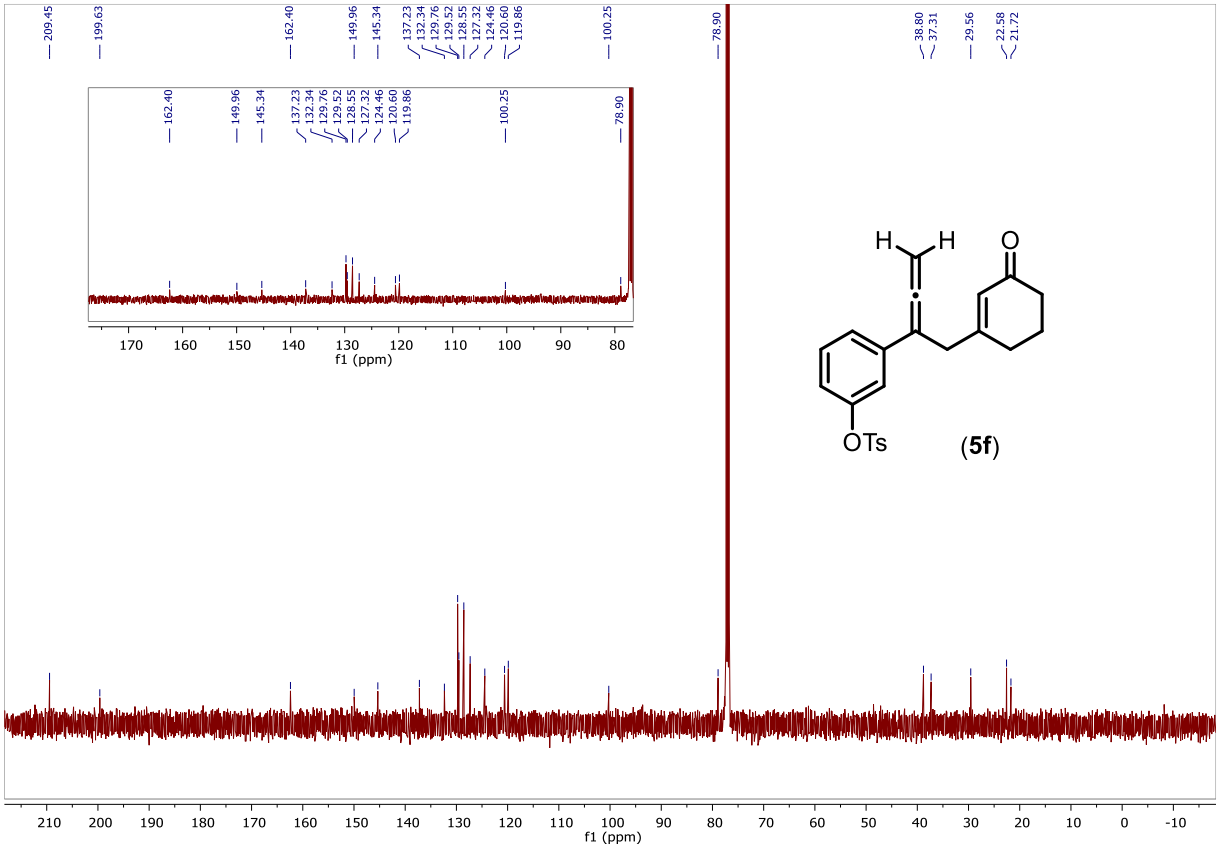
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








f1 (ppm)
OTs
(5f)


f1 (ppm)
OTs
(5f)

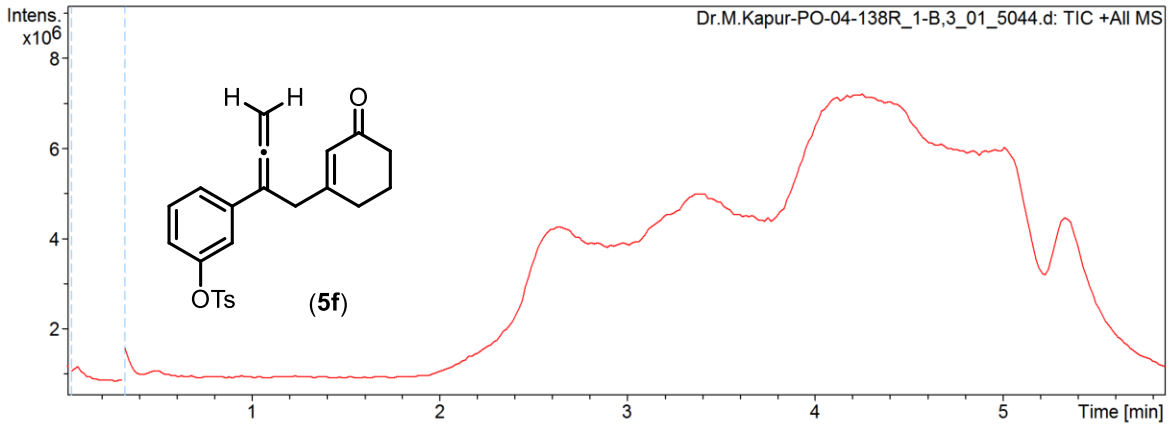
Display Report

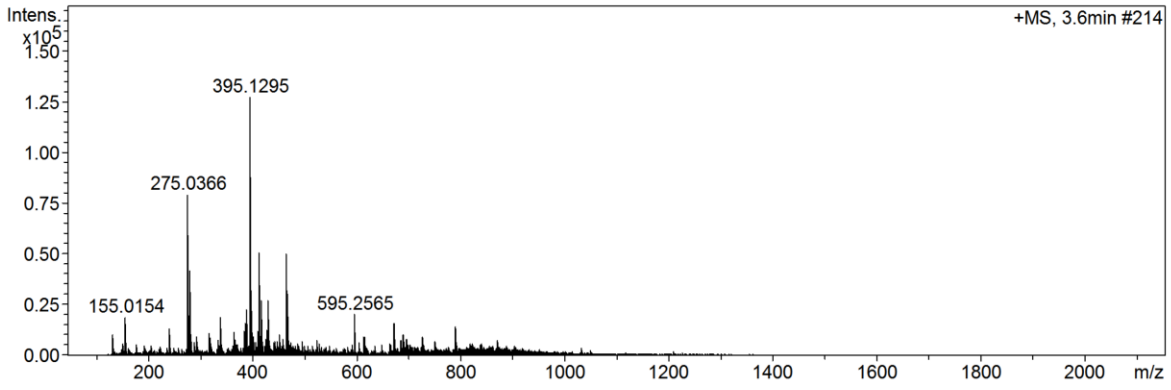
Analysis Info

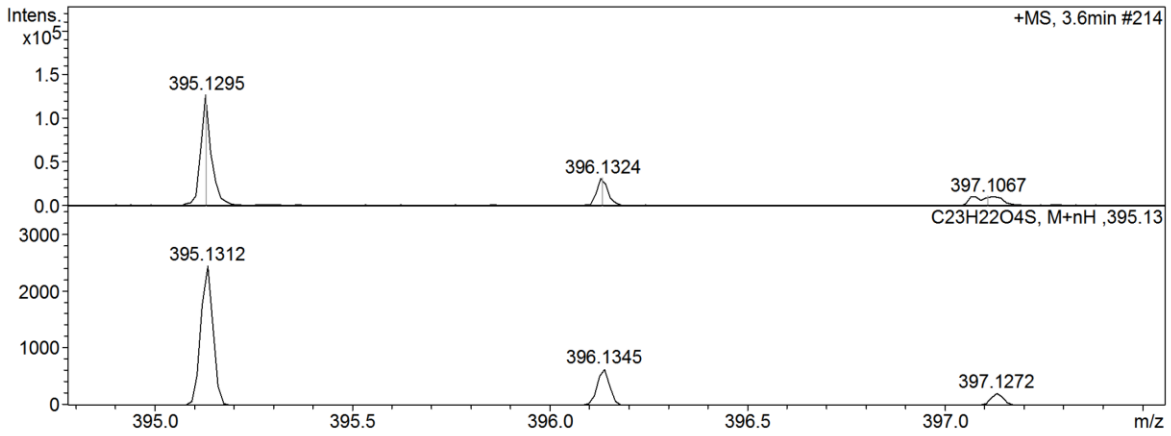
Acquisition Date	14-05-2024 13:33:40		
Analysis Name	D:\Data\USER DATA 2024\May-2024\14-may\Dr.M.Kapur-PO-04-138R_1-B,3_01_5044.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Dr.M.Kapur-PO-04-138R	Instrument	micrOTOF-Q 10330
Comment			

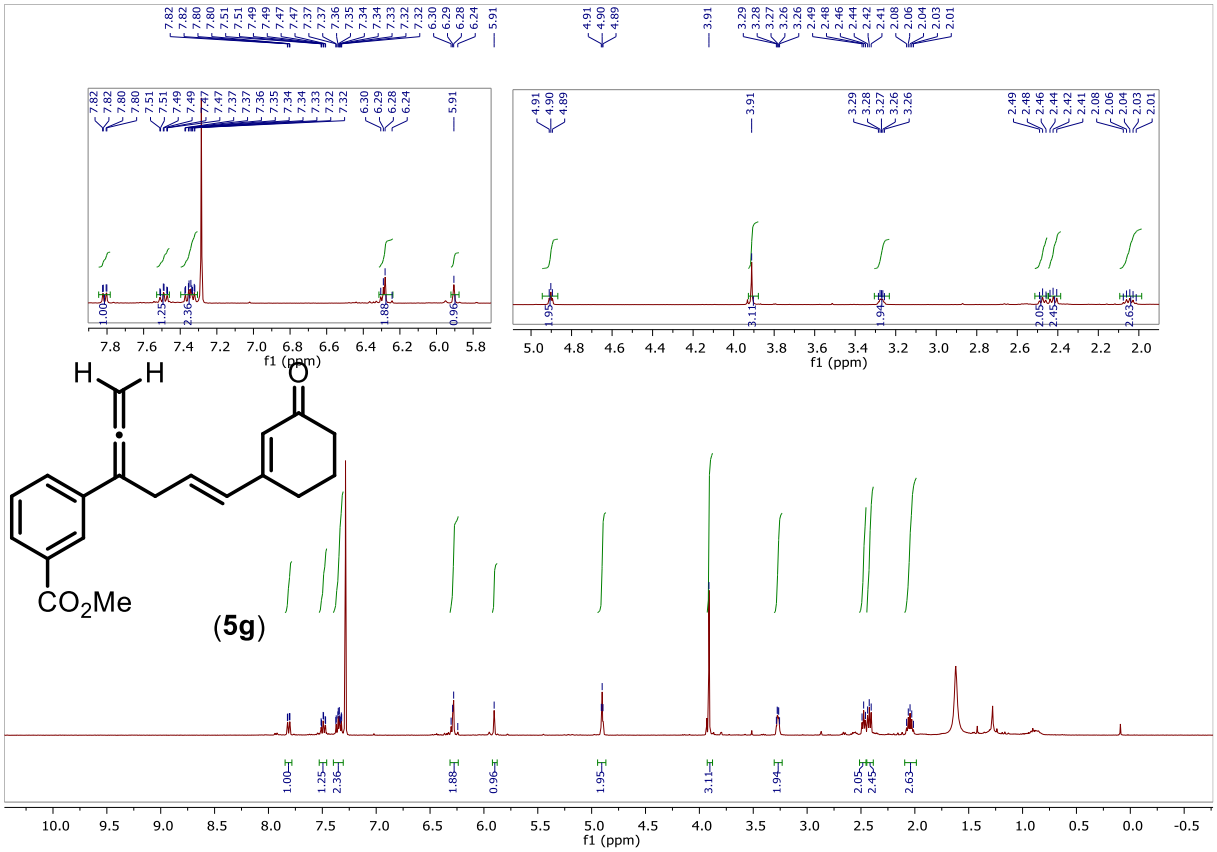
Acquisition Parameter

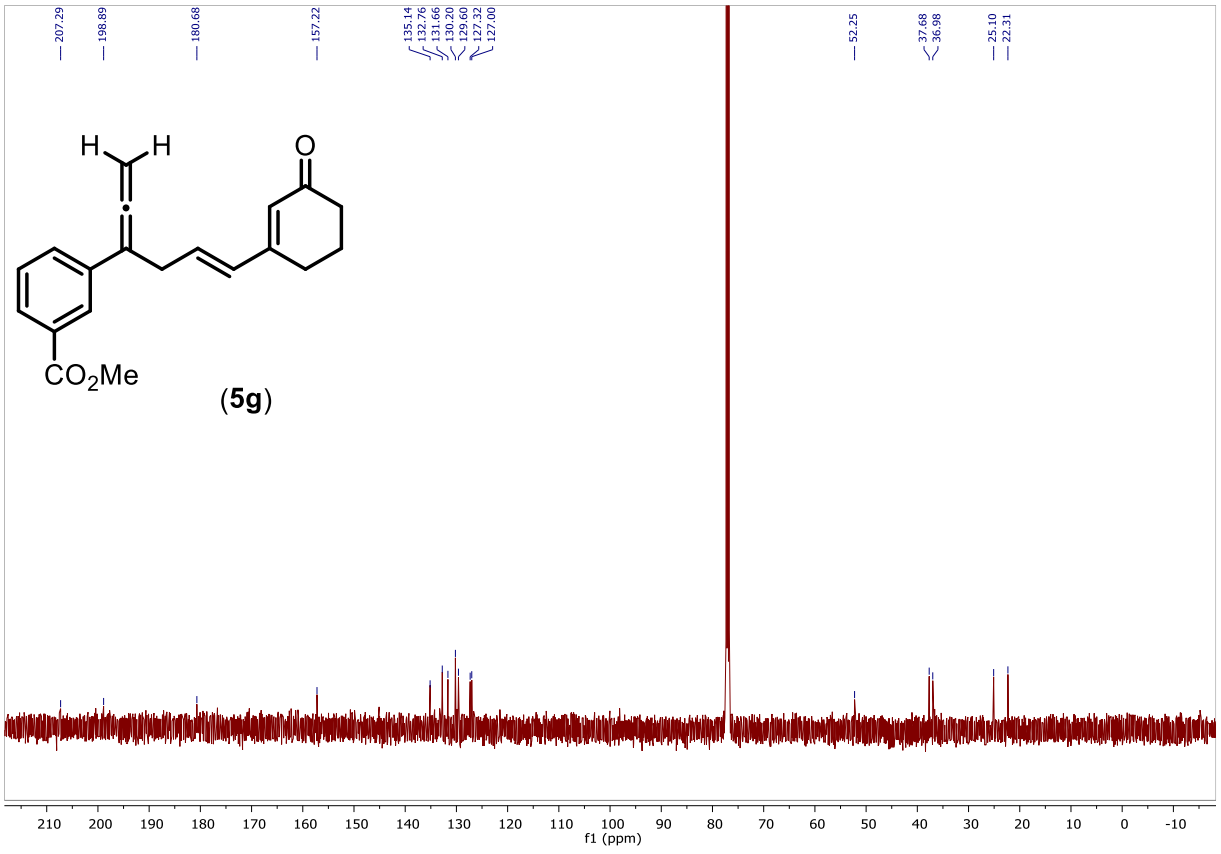
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	17.4 psi
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








H
H
O
CO2Me
(5g)
f1 (ppm)


H
H
O
CO2Me
(5g)
f1 (ppm)

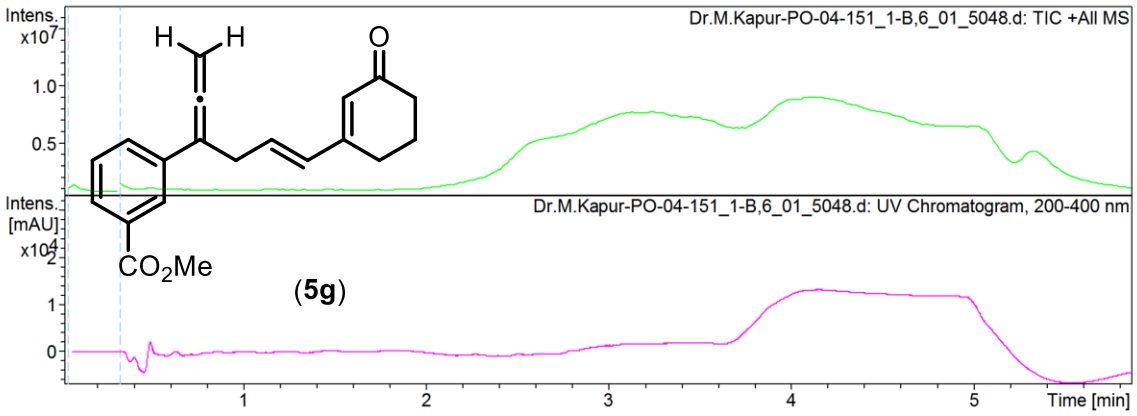
Display Report

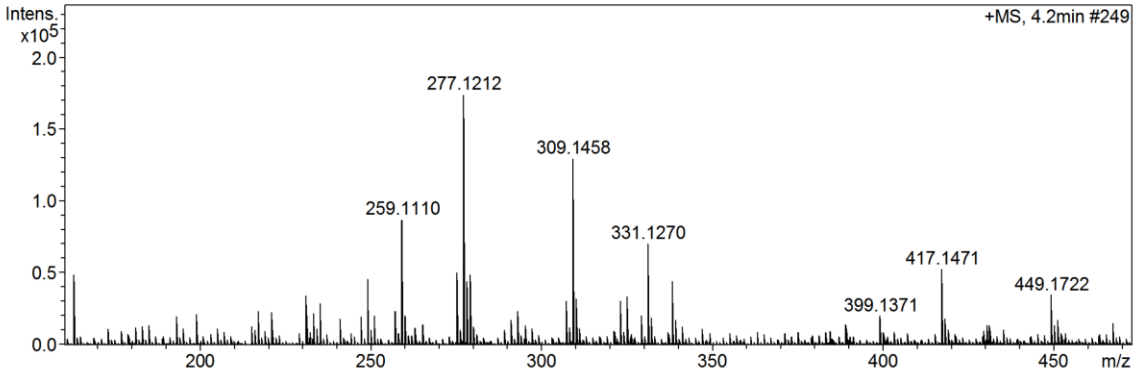
Analysis Info

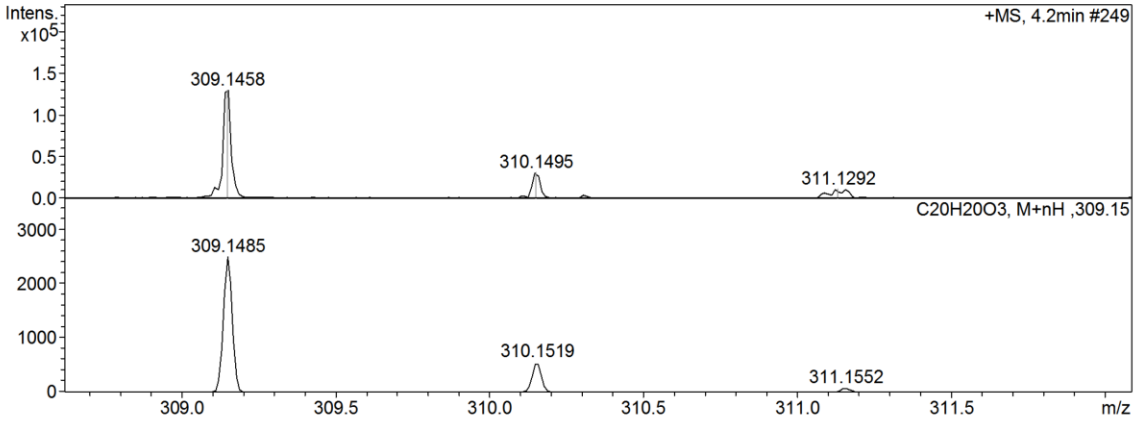
Acquisition Date	14-05-2024 14:02:36		
Analysis Name	D:\Data\USER DATA 2024\May-2024\14-may\Dr.M.Kapur-PO-04-151_1-B,6_01_5048.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Dr.M.Kapur-PO-04-151	Instrument	micrOTOF-Q 10330
Comment			

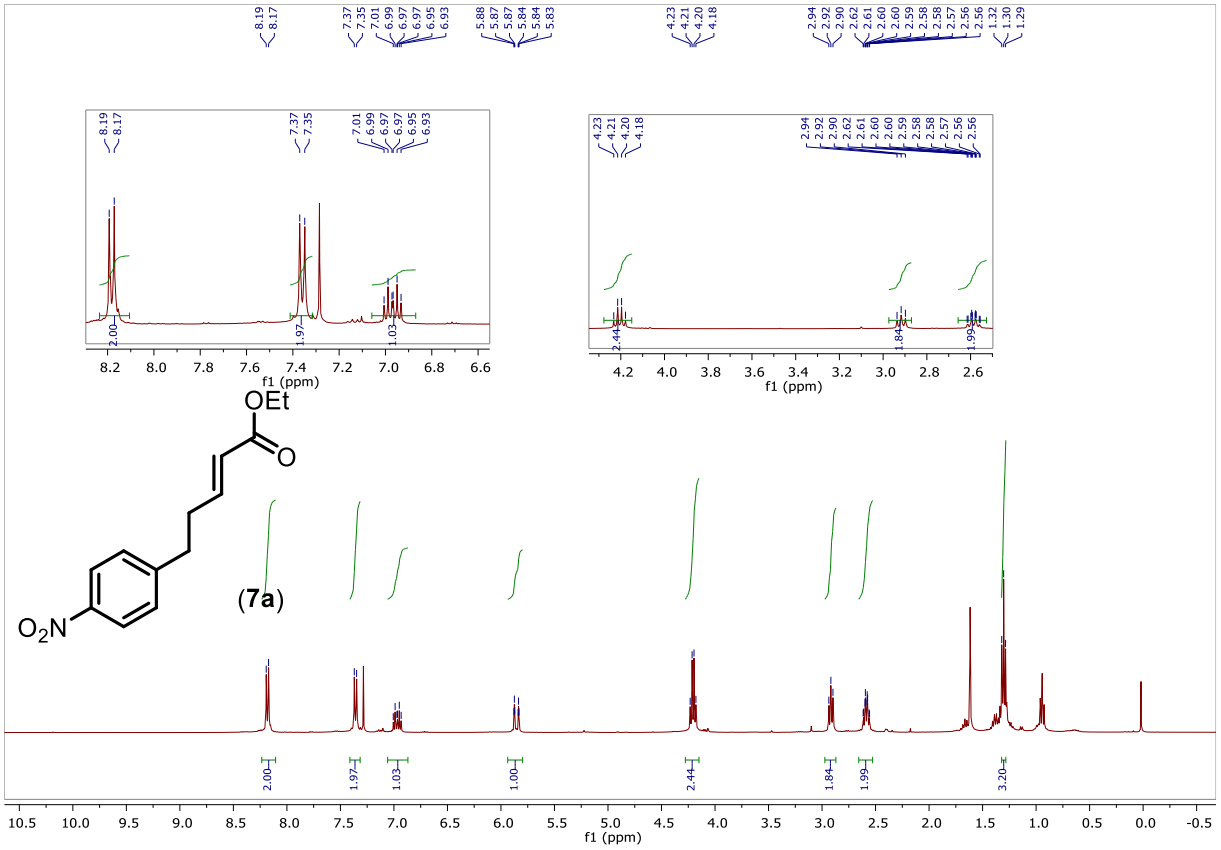
Acquisition Parameter

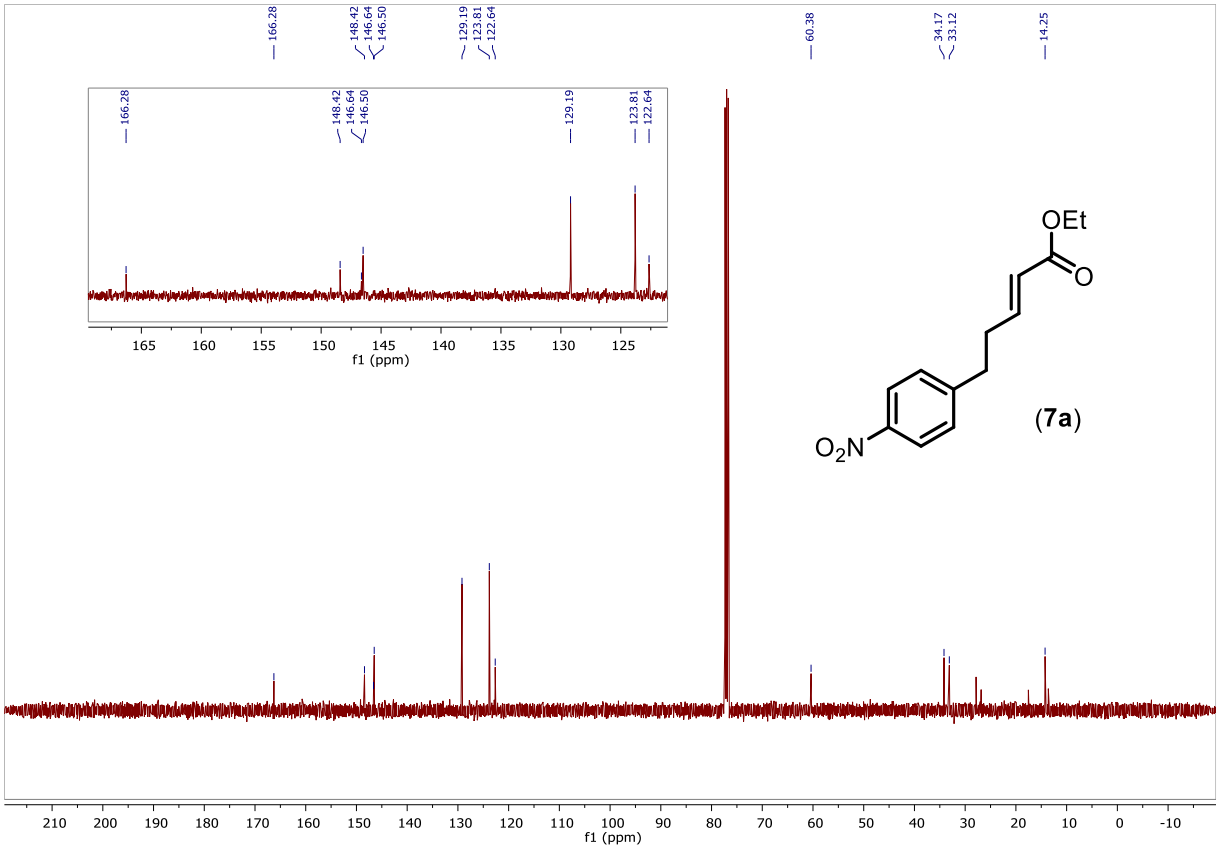
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	17.4 psi
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








OEt
O
O_2N
(7a)
f1 (ppm)


OEt
O
O_2N
(7a)
f1 (ppm)

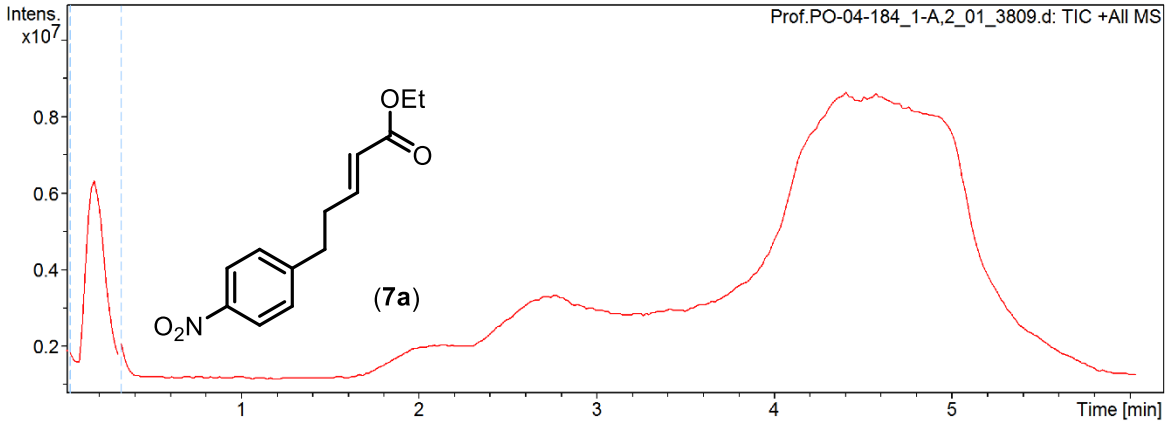
Display Report

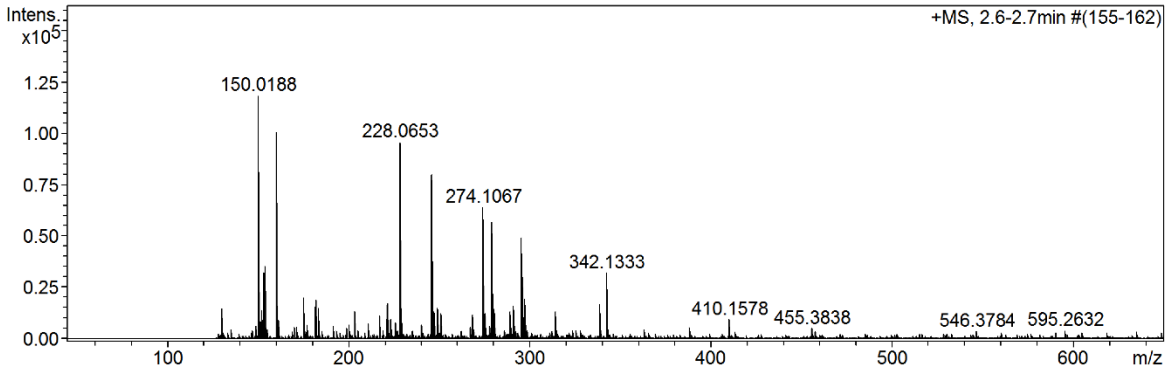
Analysis Info

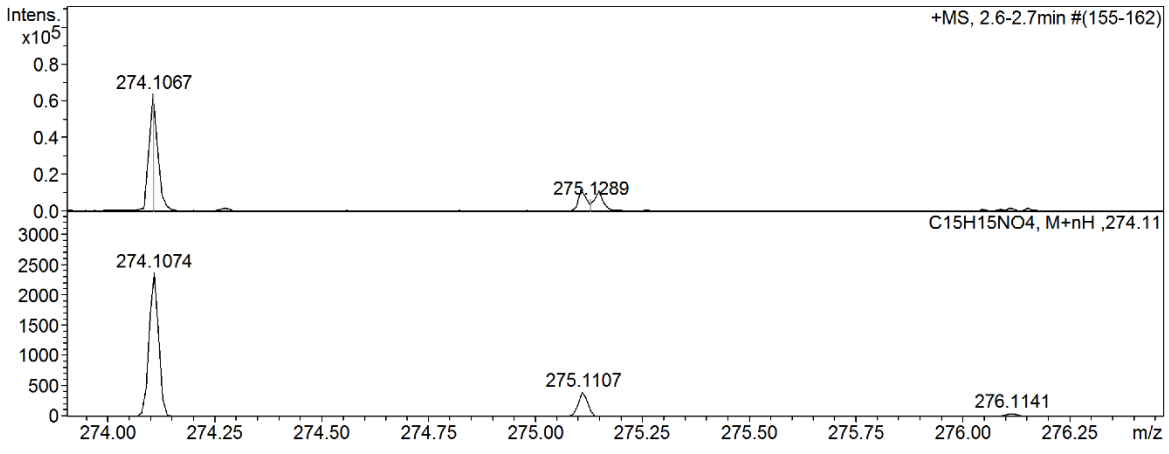
Analysis Name	D:\Data\USER DATA 2024\16-jan\Prof.PO-04-184_1-A,2_01_3809.d	Acquisition Date	16-01-2024 12:28:58
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.PO-04-184	Instrument	micrOTOF-Q 10330
Comment			

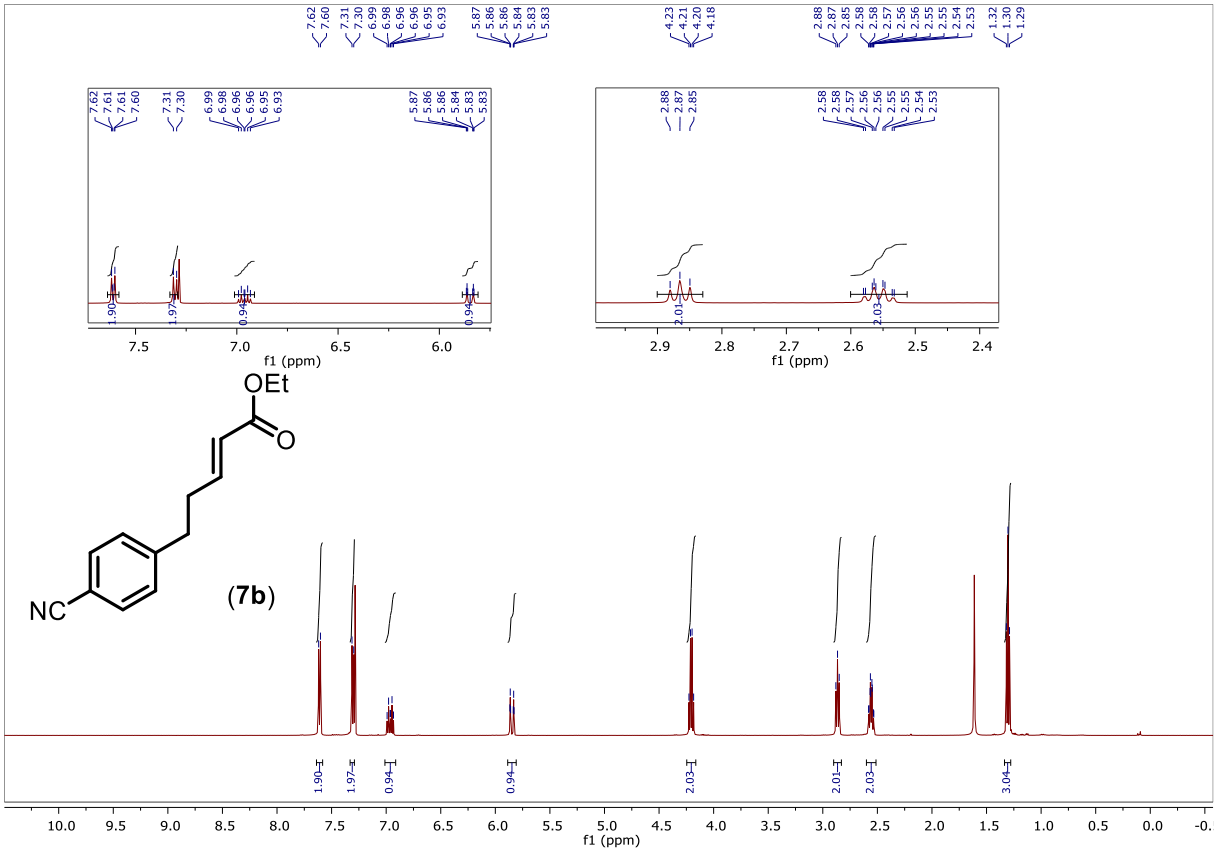
Acquisition Parameter

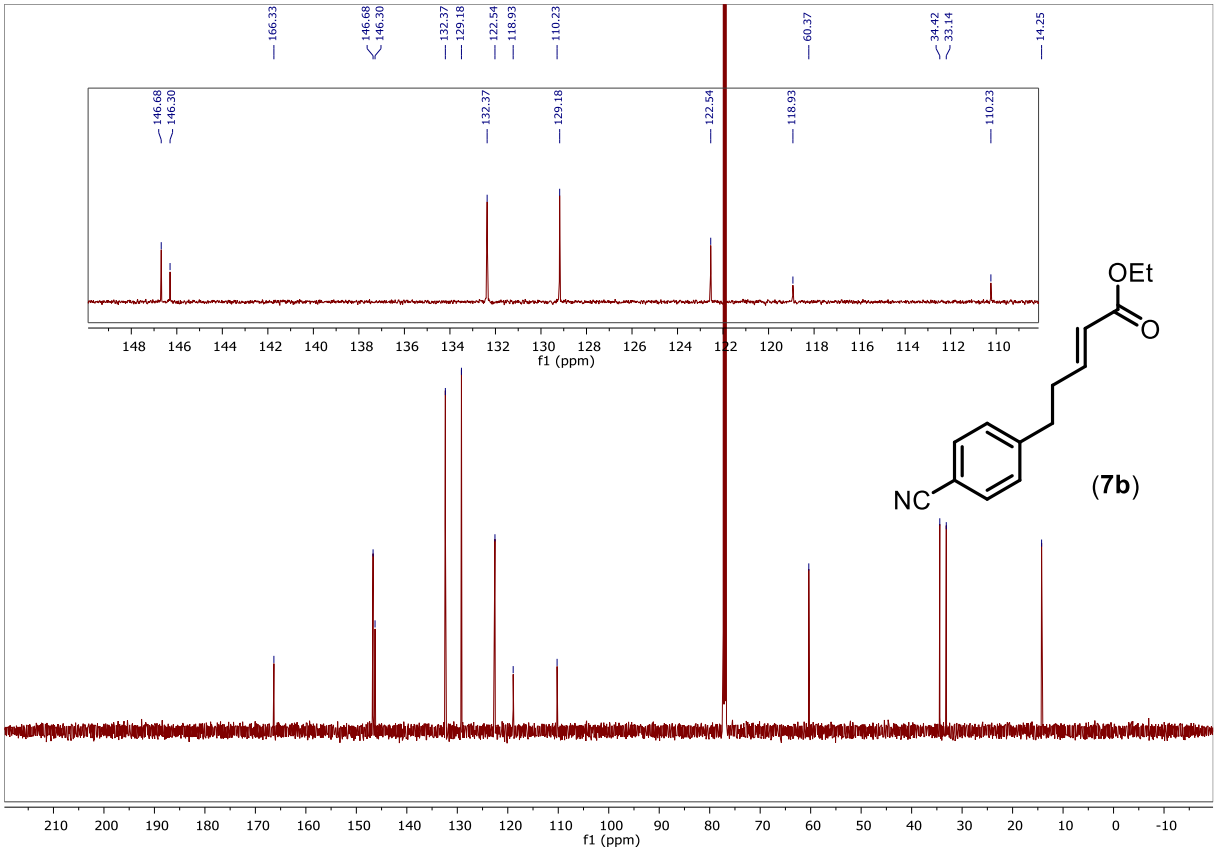
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








OEt
O
NC
(7b)
f1 (ppm)


OEt
O
NC
(7b)
f1 (ppm)

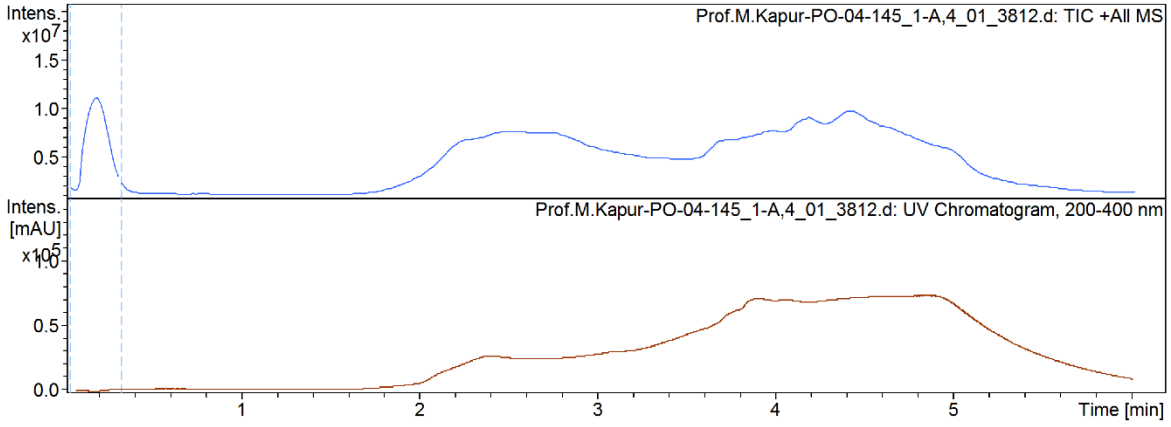
Display Report

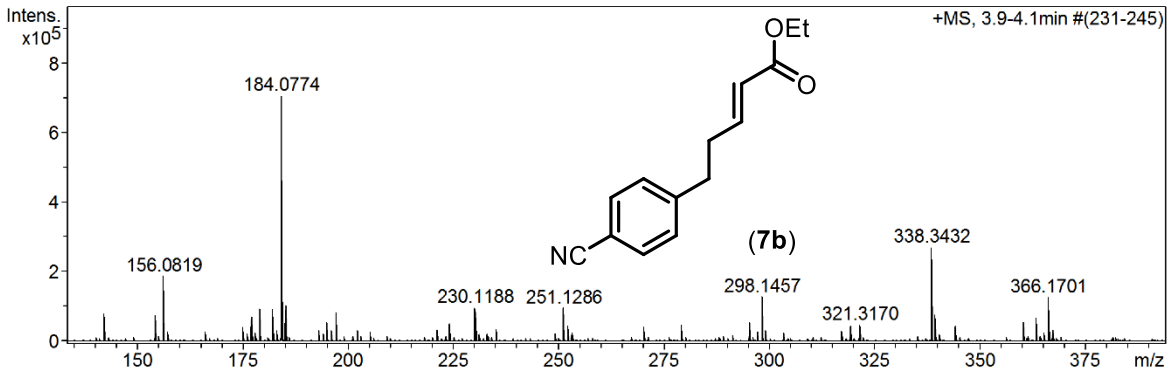
Analysis Info

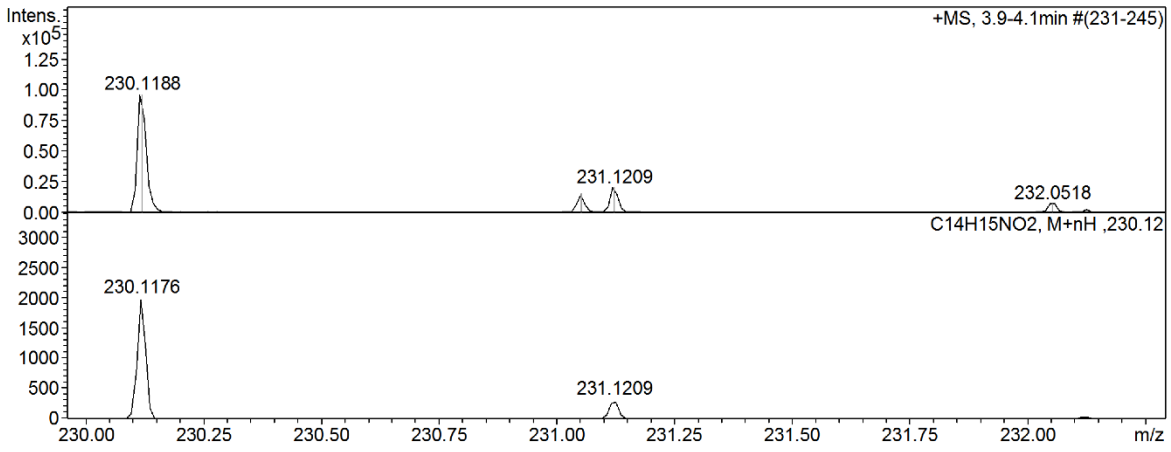
Analysis Name	D:\Data\USER DATA 2024\16-jan\Prof.M.Kapur-PO-04-145_1-A,4_01_3812.d	Acquisition Date	16-01-2024 12:50:41
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-145	Instrument	micrOTOF-Q 10330
Comment			

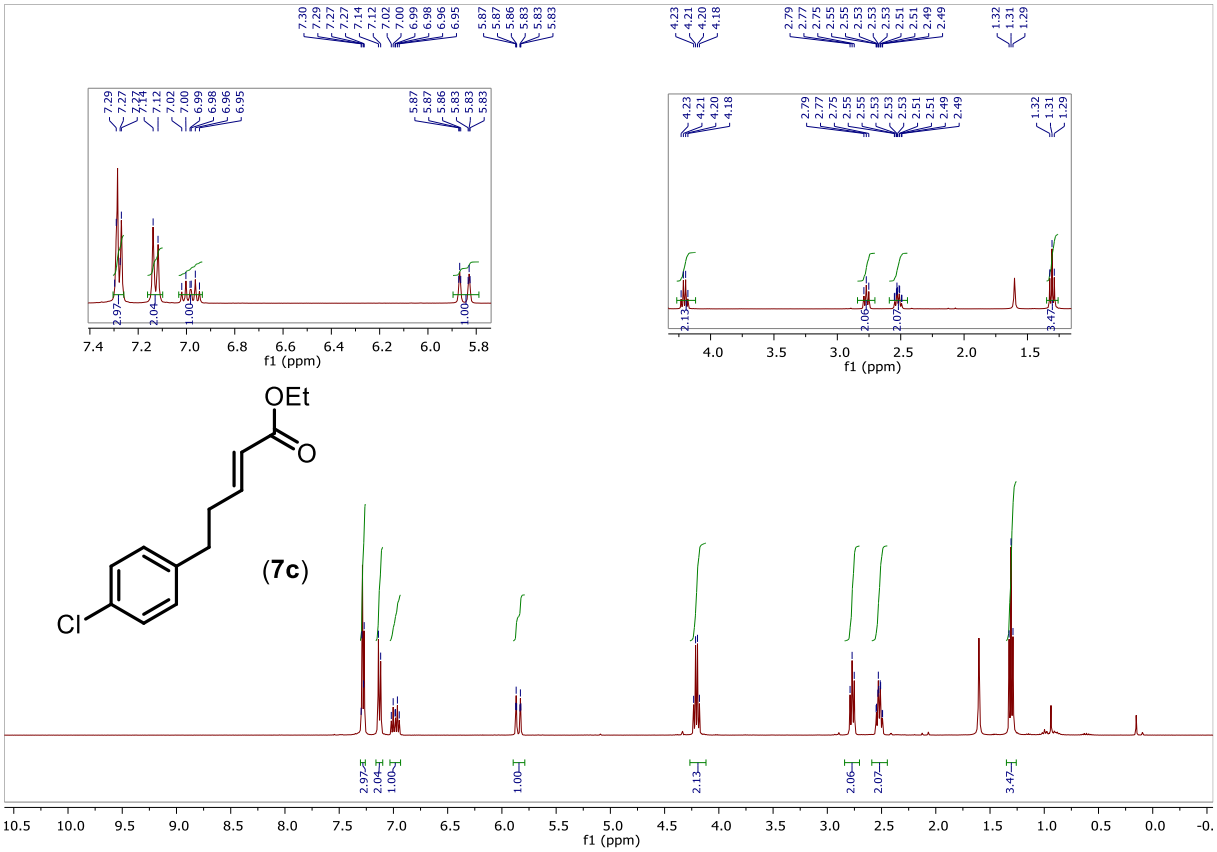
Acquisition Parameter

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





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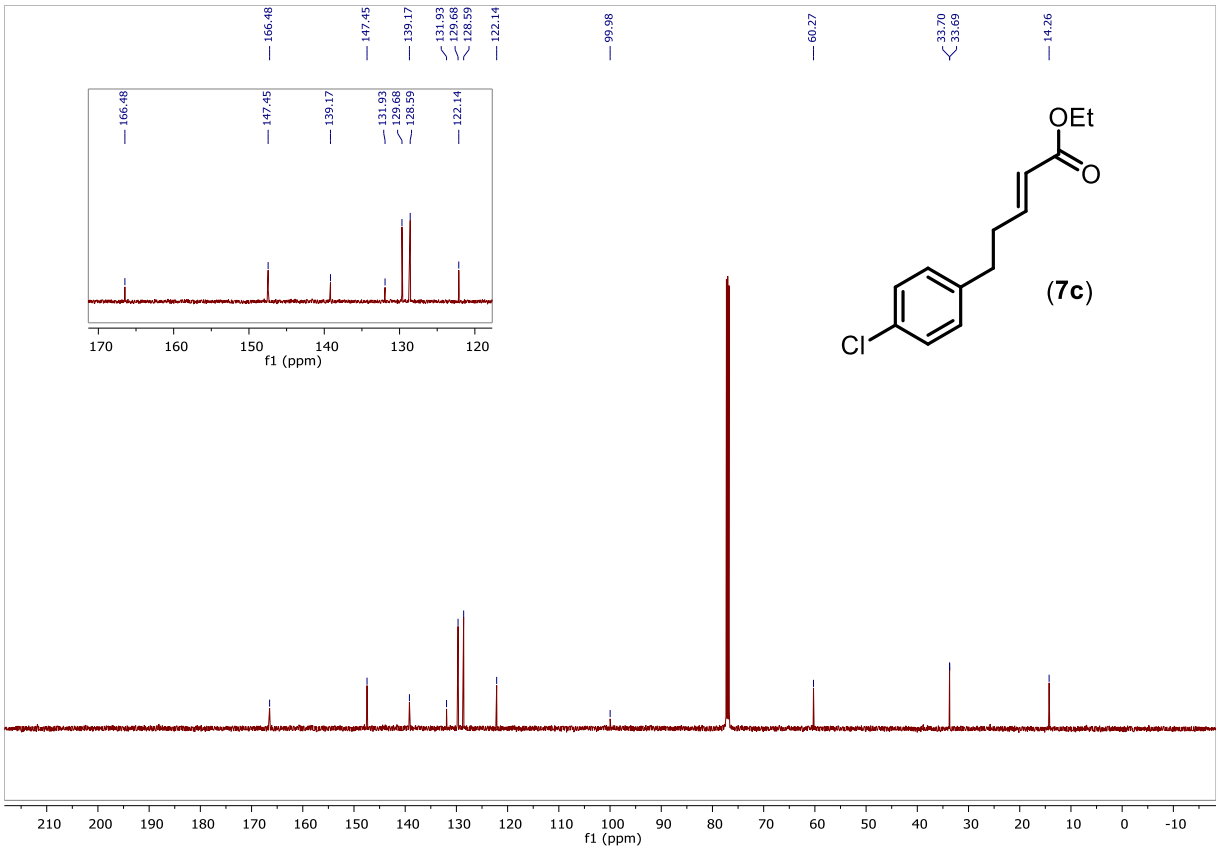
(7c)
f1 (ppm)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(7c)
f1 (ppm)

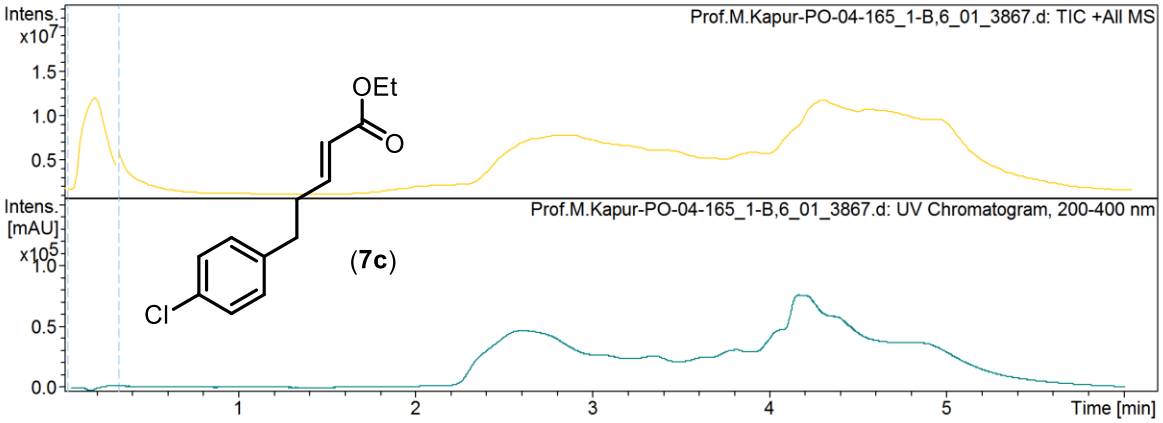
Display Report

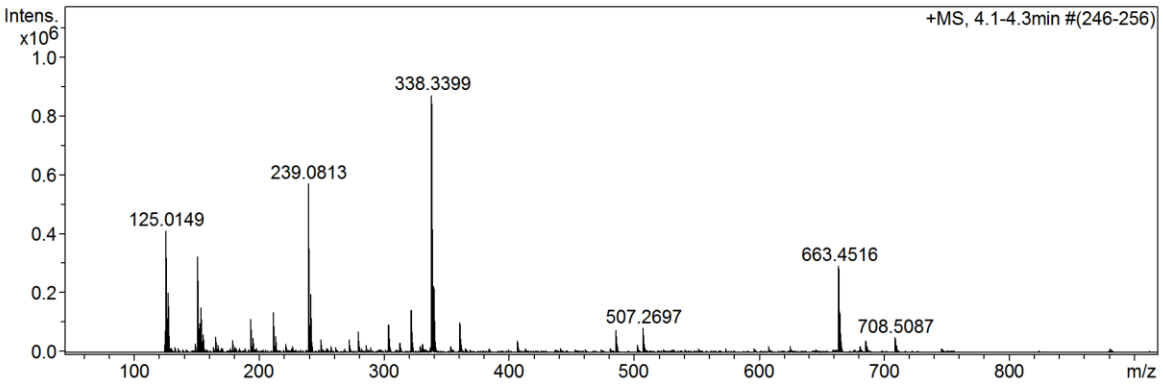
Analysis Info

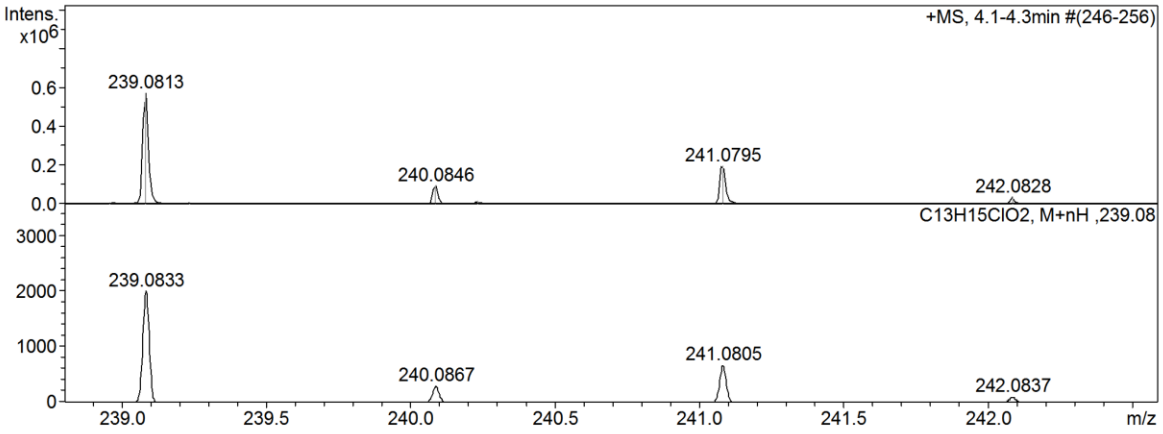
Analysis Name	D:\Data\USER DATA 2024\17-jan\Prof.M.Kapur-PO-04-165_1-B,6_01_3867.d	Acquisition Date	17-01-2024 18:19:24
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-165	Instrument	micrOTOF-Q 10330
Comment			

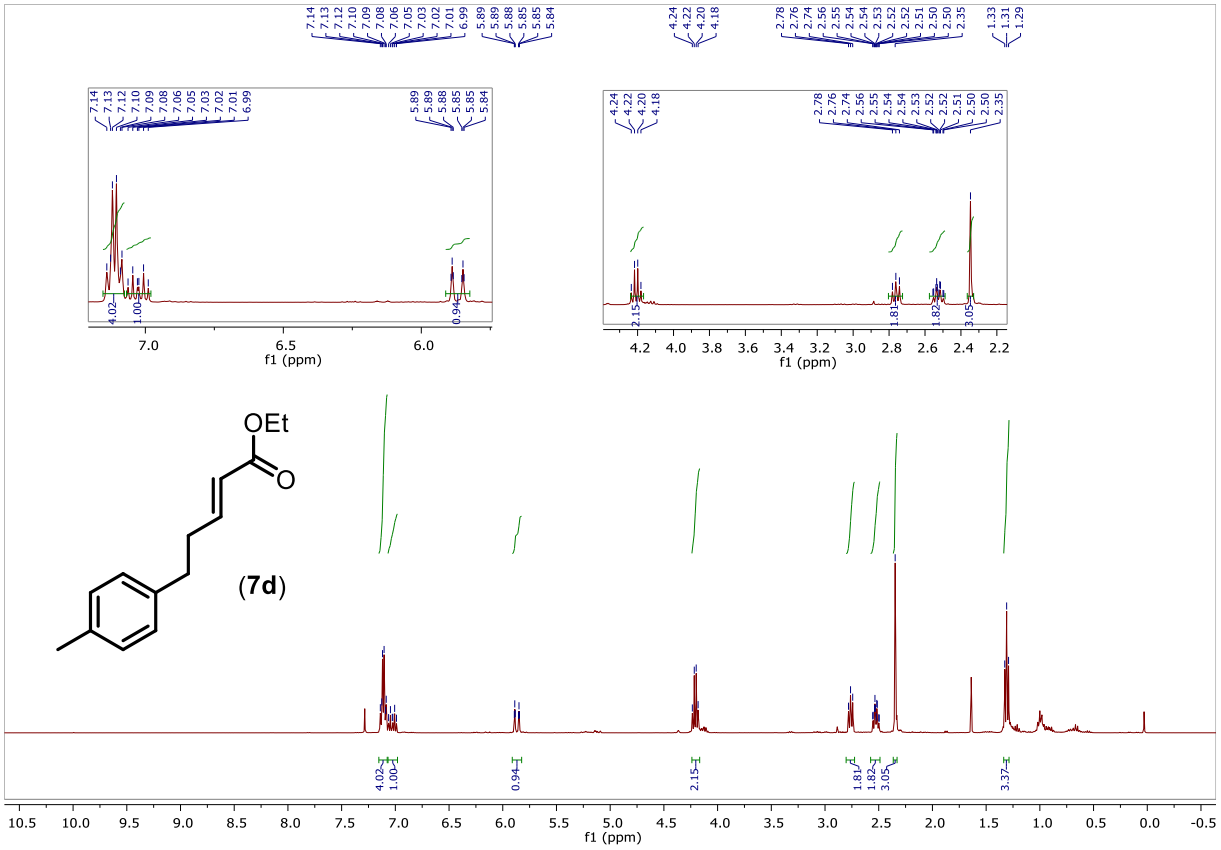
Acquisition Parameter

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





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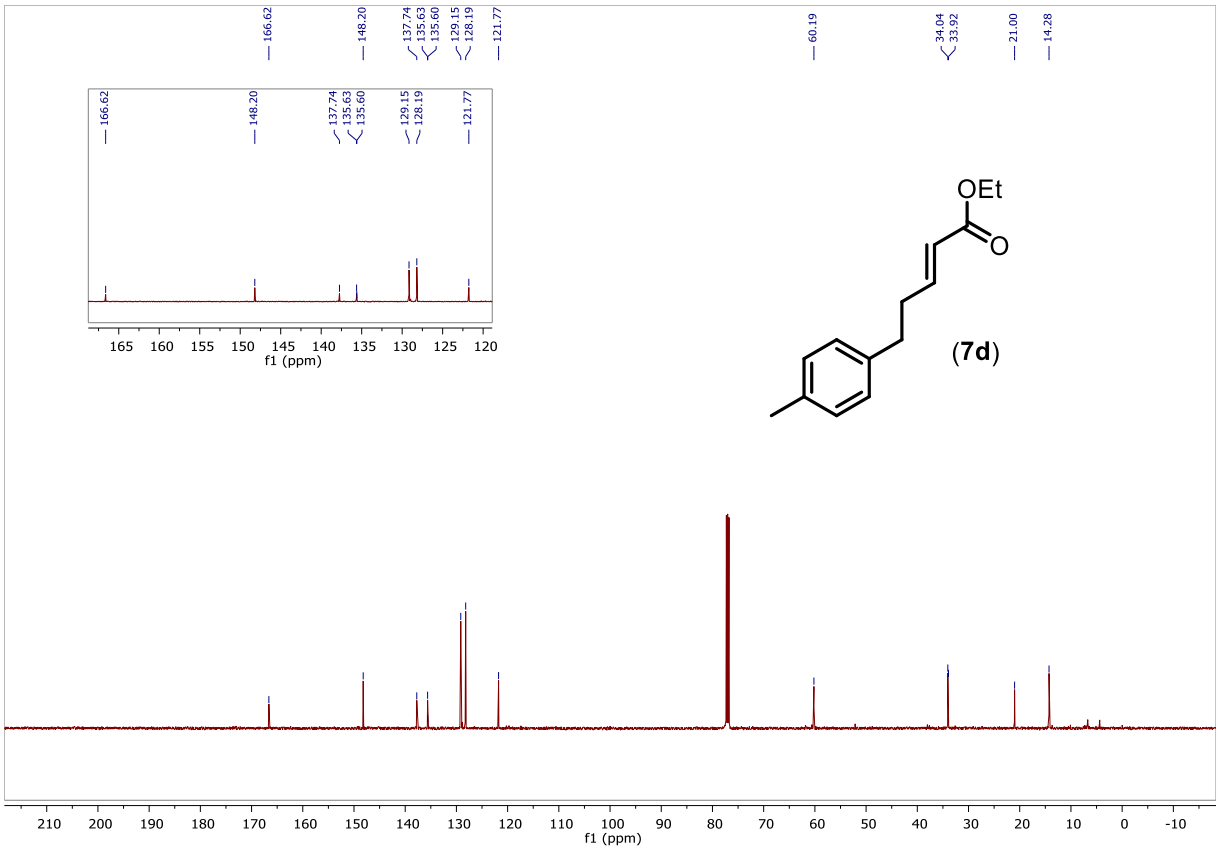
f1 (ppm)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f1 (ppm)

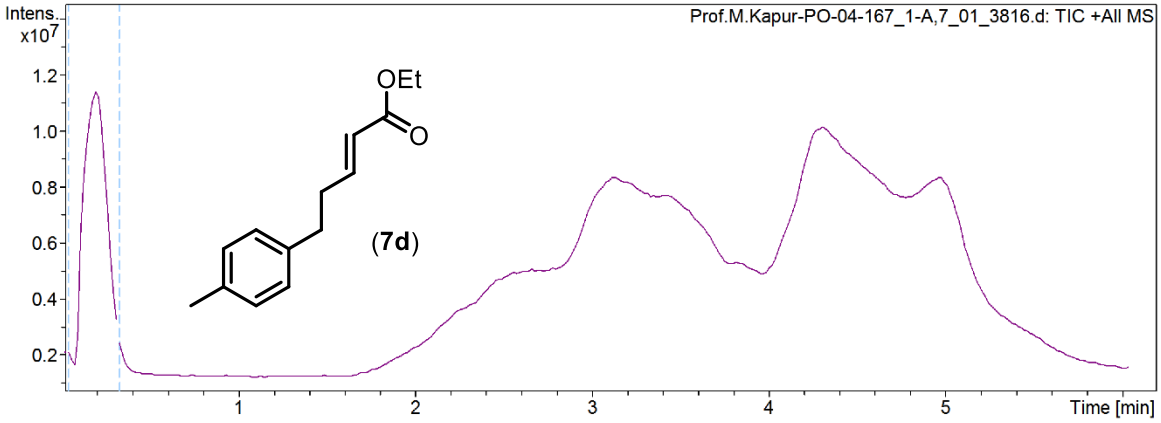
Display Report

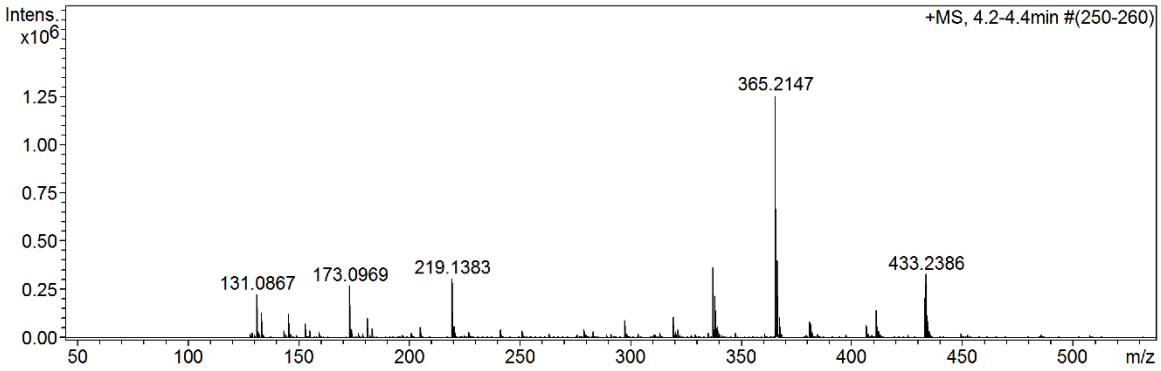
Analysis Info

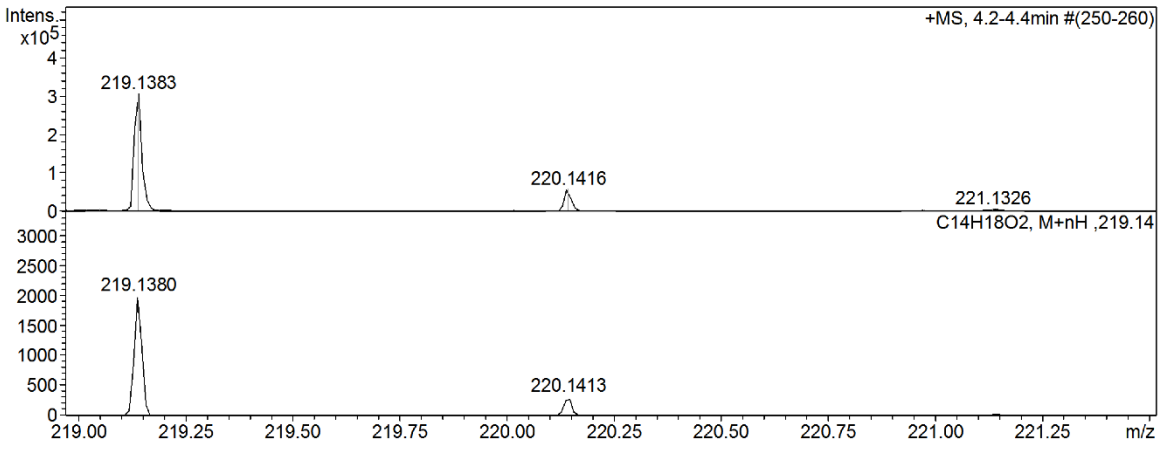
Analysis Name	D:\Data\USER DATA 2024\16-jan\Prof.M.Kapur-PO-04-167_1-A,7_01_3816.d	Acquisition Date	16-01-2024 13:19:42
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-167	Instrument	micrOTOF-Q 10330
Comment			

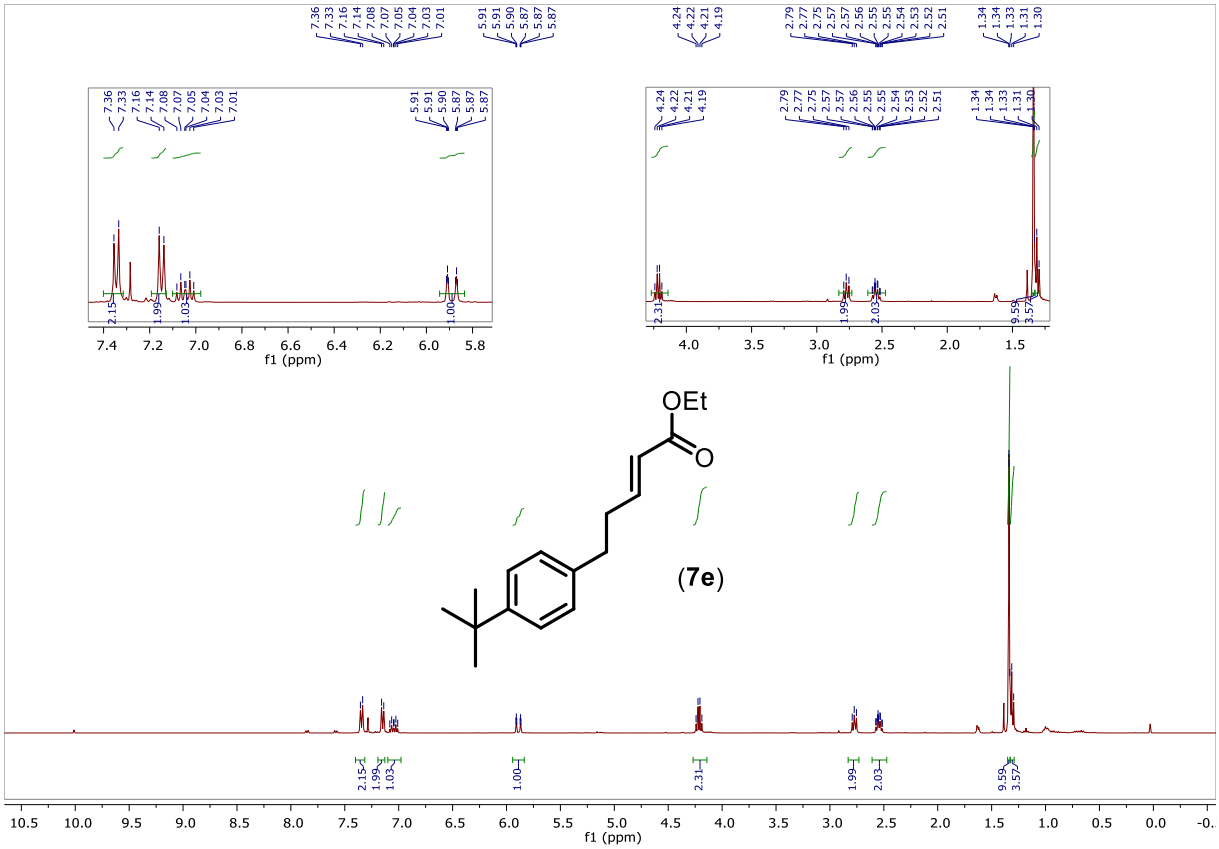
Acquisition Parameter

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





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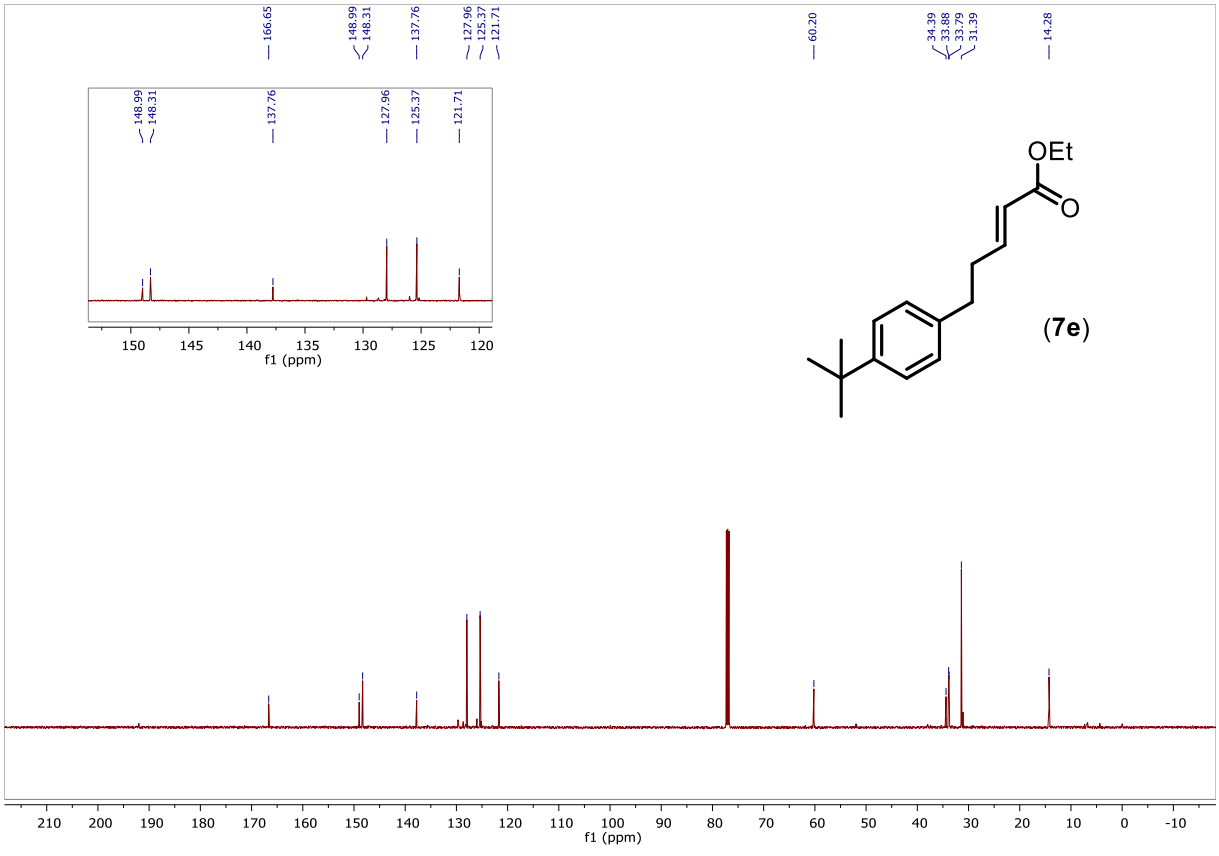
(7e)
f1 (ppm)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(7e)
f1 (ppm)

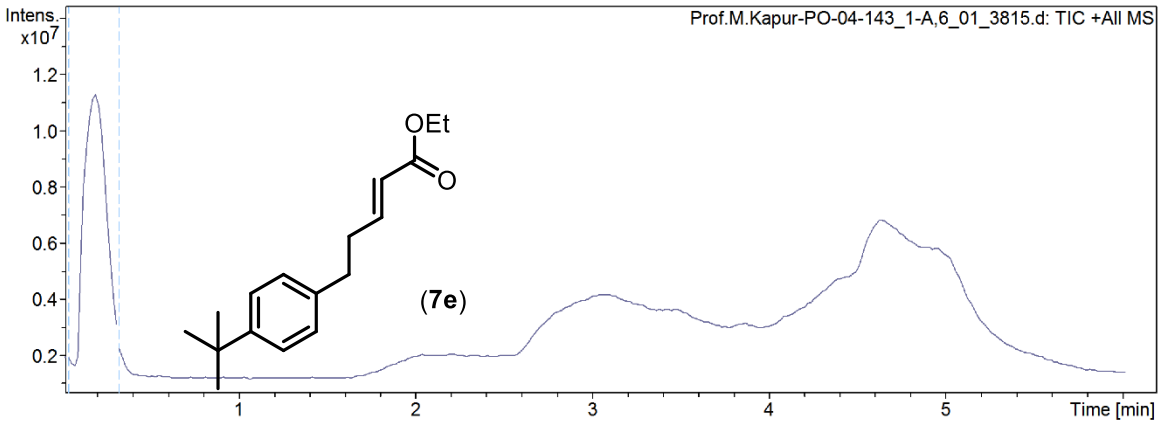
Display Report

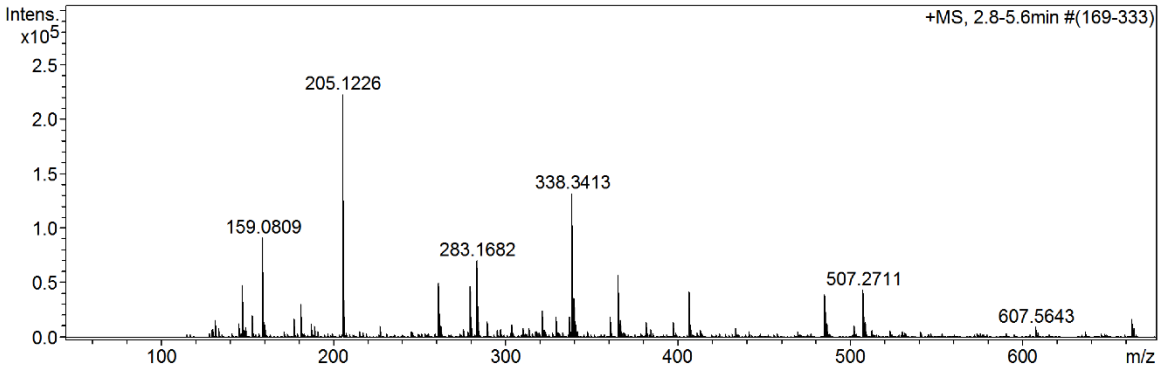
Analysis Info

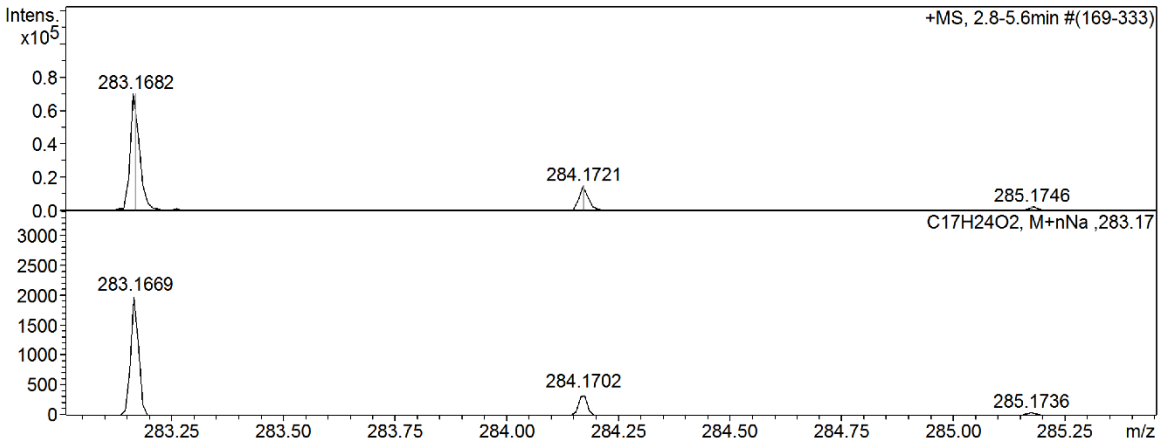
Analysis Name	D:\Data\USER DATA 2024\16-jan\Prof.M.Kapur-PO-04-143_1-A,6_01_3815.d	Acquisition Date	16-01-2024 13:12:25
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-143	Instrument	micrOTOF-Q 10330
Comment			

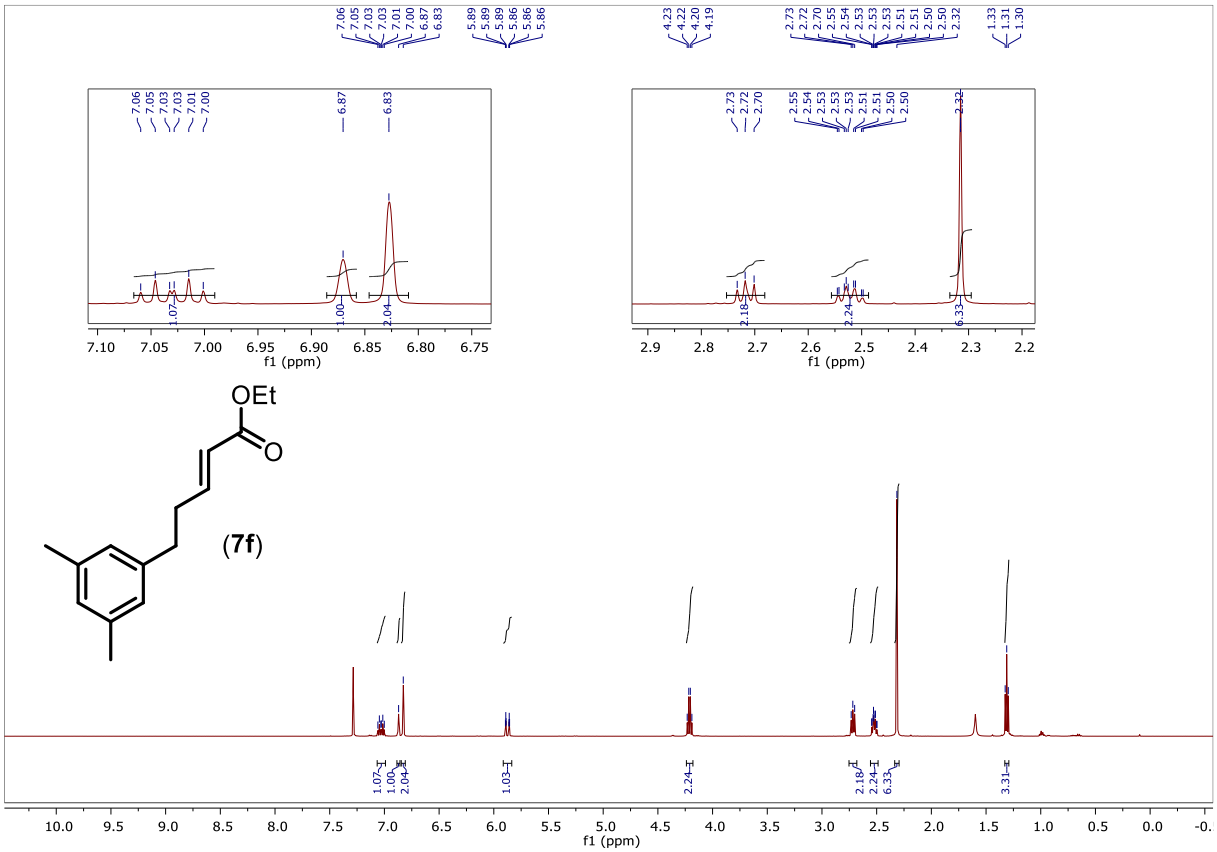
Acquisition Parameter

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





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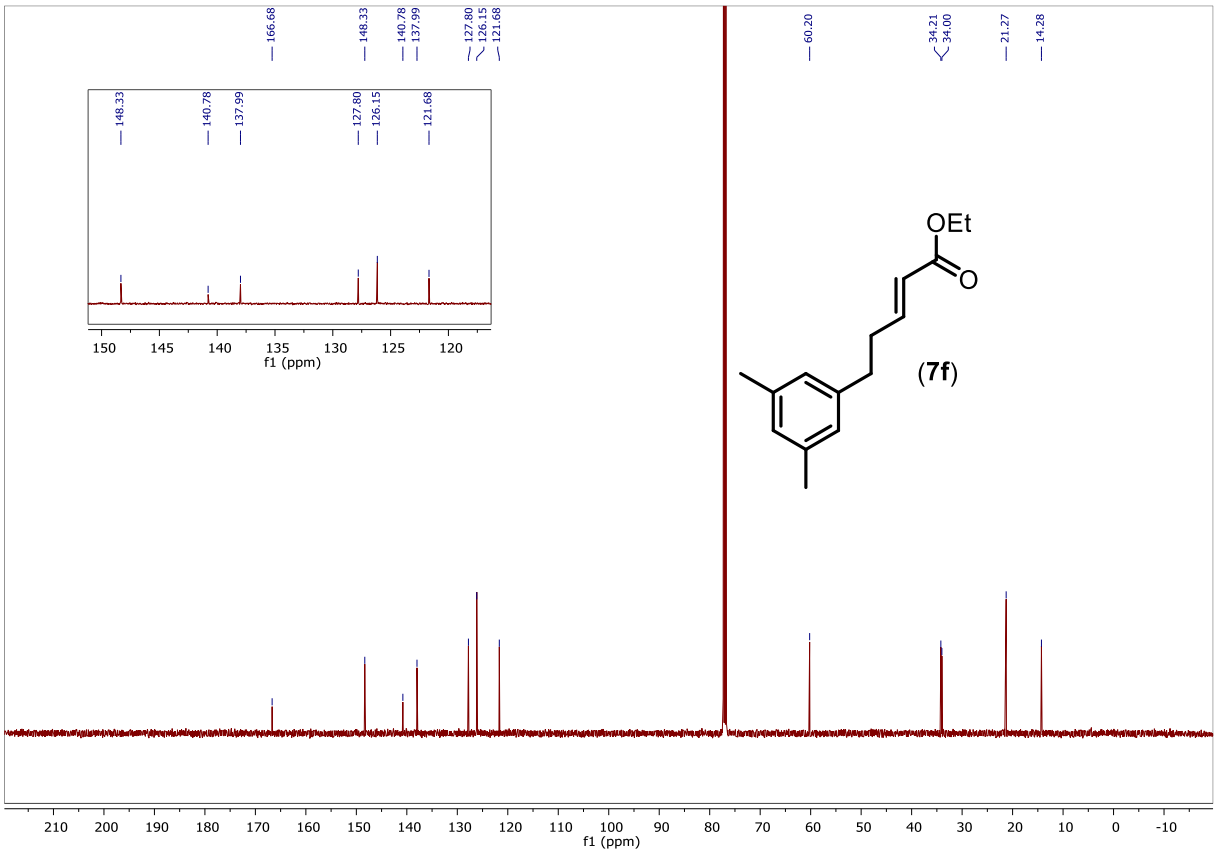
(7f)
f1 (ppm)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O
(7f)
f1 (ppm)

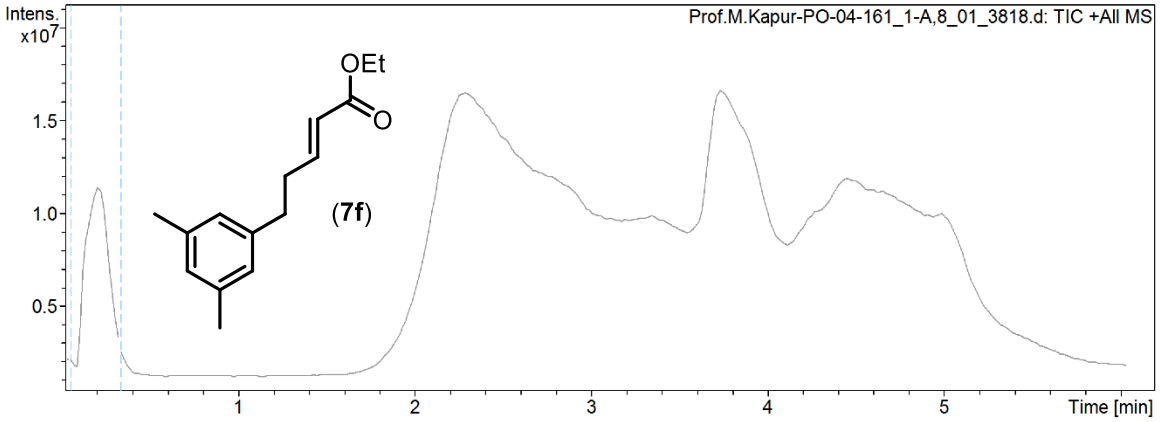
Display Report

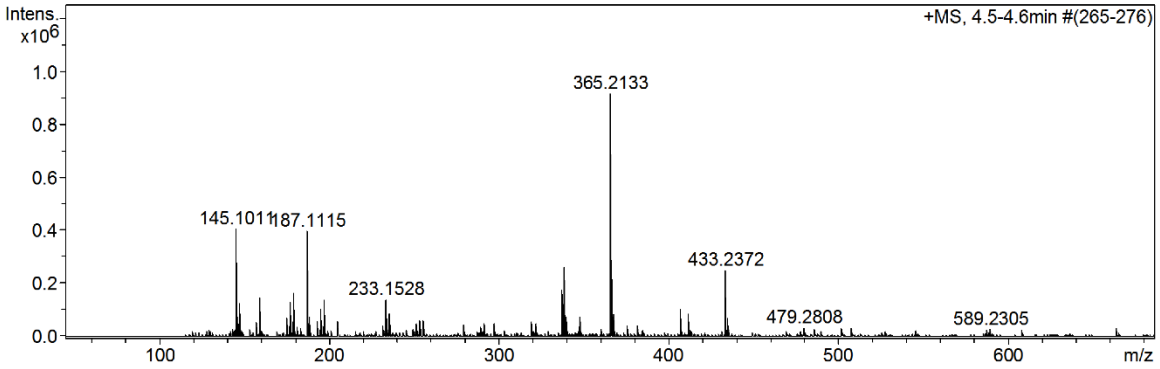
Analysis Info

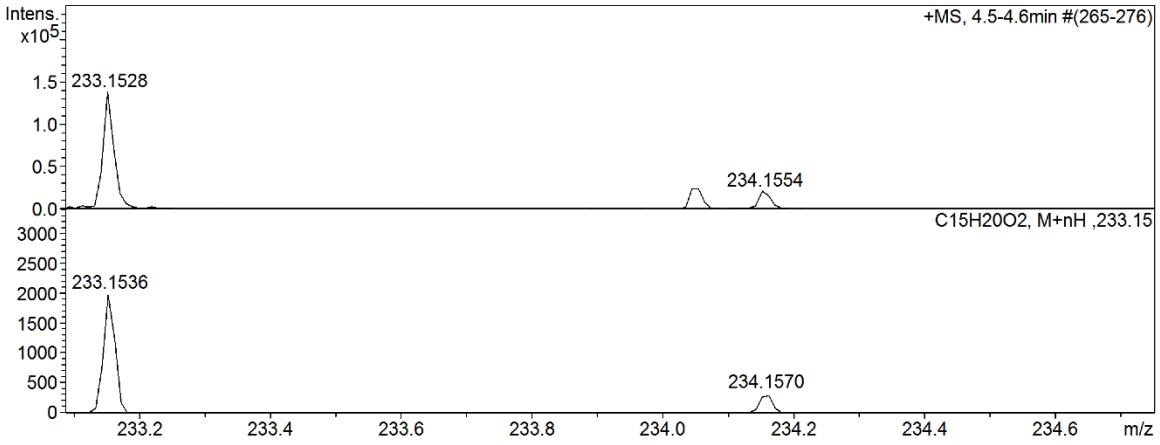
Acquisition Date	16-01-2024 13:34:12		
Analysis Name	D:\Data\USER DATA 2024\16-jan\Prof.M.Kapur-PO-04-161_1-A,8_01_3818.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-161	Instrument	micrOTOF-Q 10330
Comment			

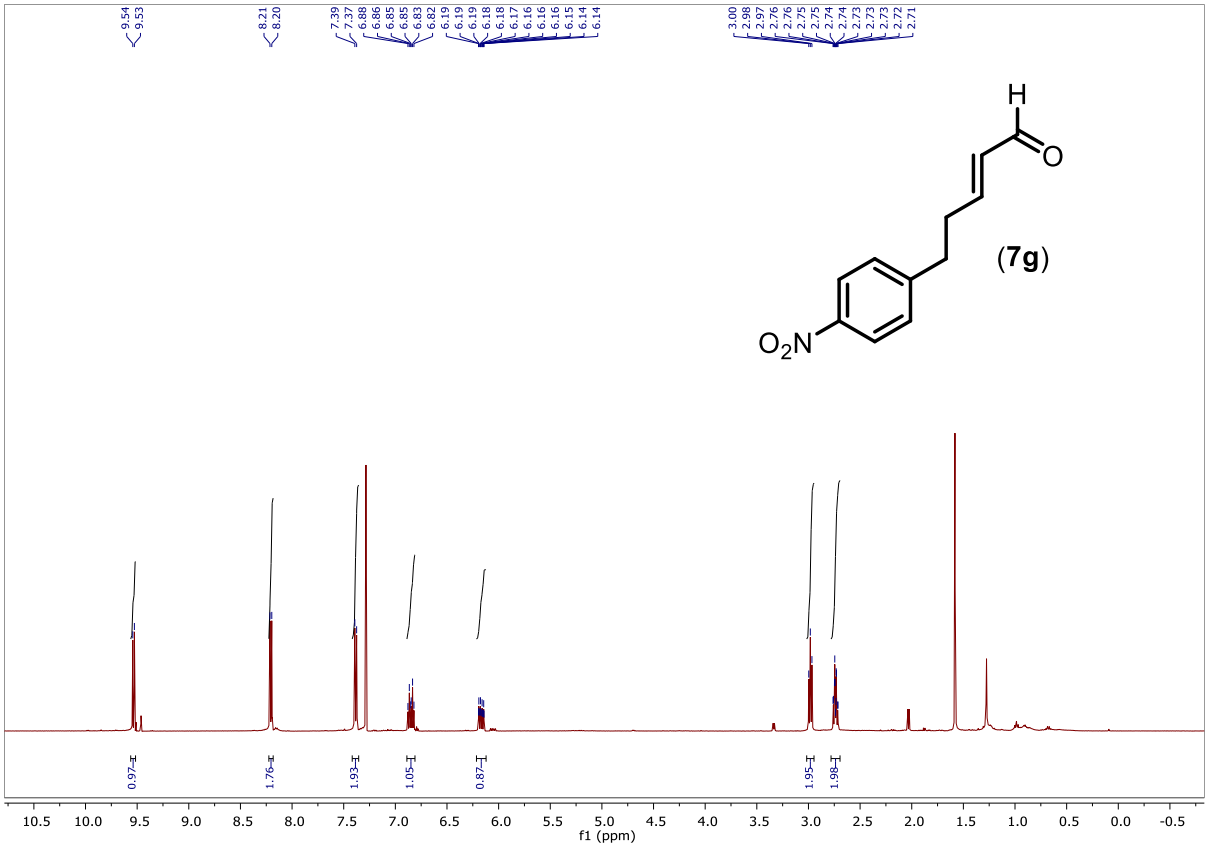
Acquisition Parameter

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





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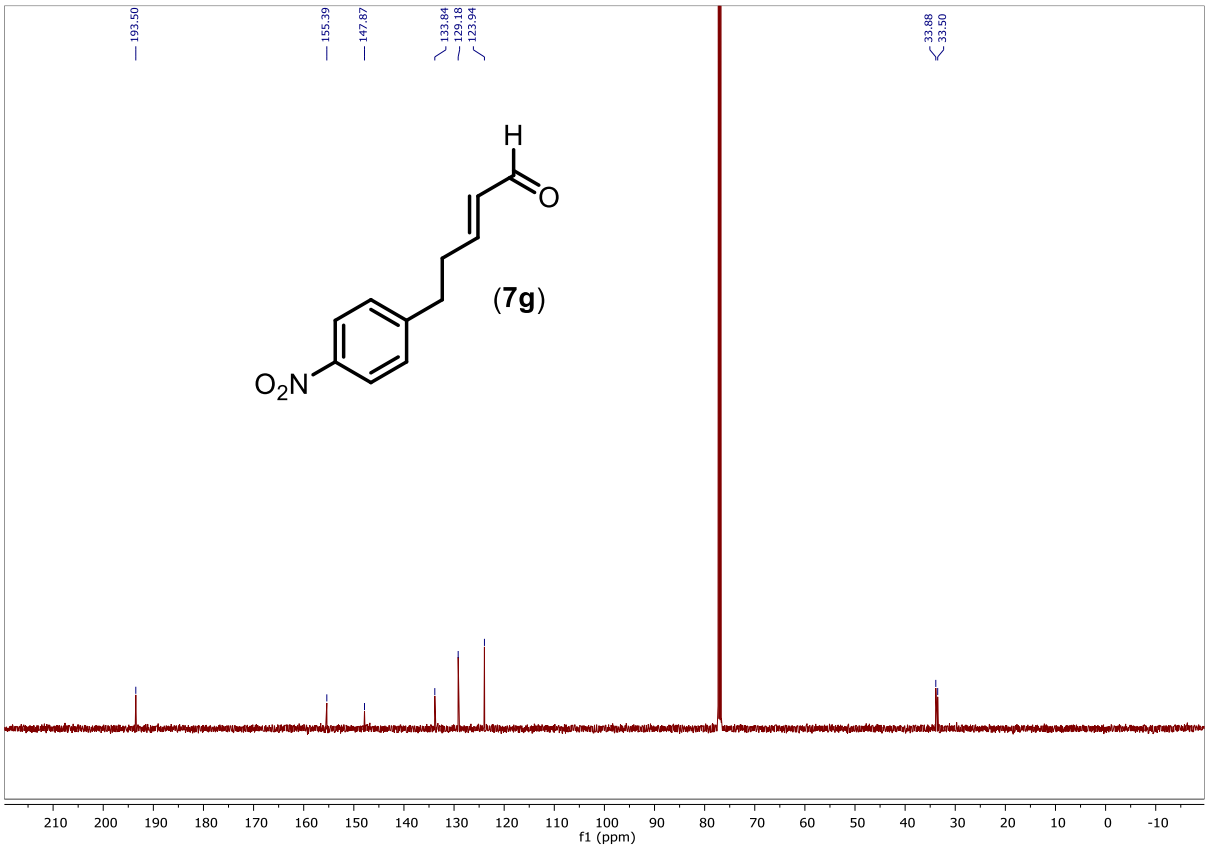
7.37
6.88
6.86
6.85
6.85
6.83
6.82
6.19
6.19
6.19
6.18
6.18
6.17
6.16
6.16
6.16
6.15
6.14
6.14
3.00
2.98
2.97
2.76
2.76
2.75
2.75
2.74
2.74
2.73
2.73
2.73
2.72
2.71
H
O
(7g)
O2N
0.97
1.76
1.93
1.05
0.87
1.95
1.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


193.50
155.39
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129.18
123.94
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33.50
H
O
(7g)
O2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

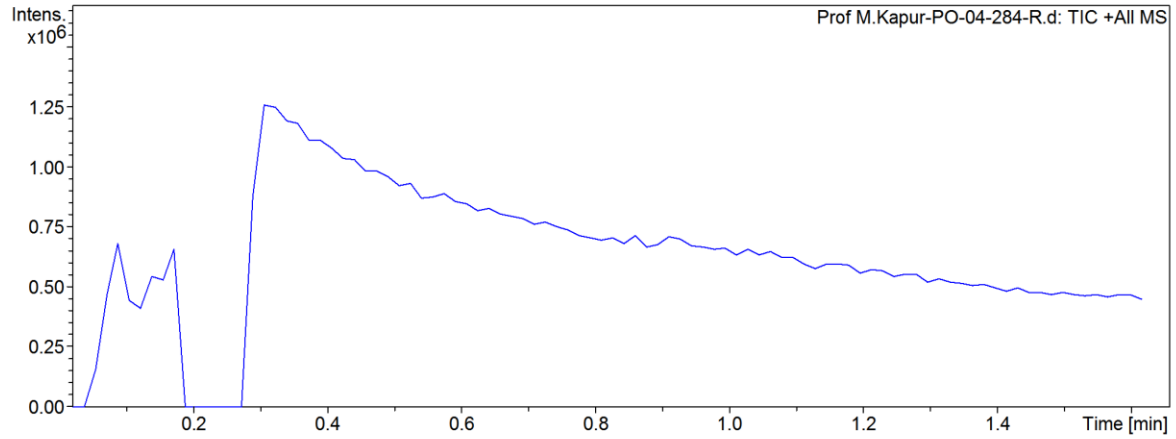
Display Report

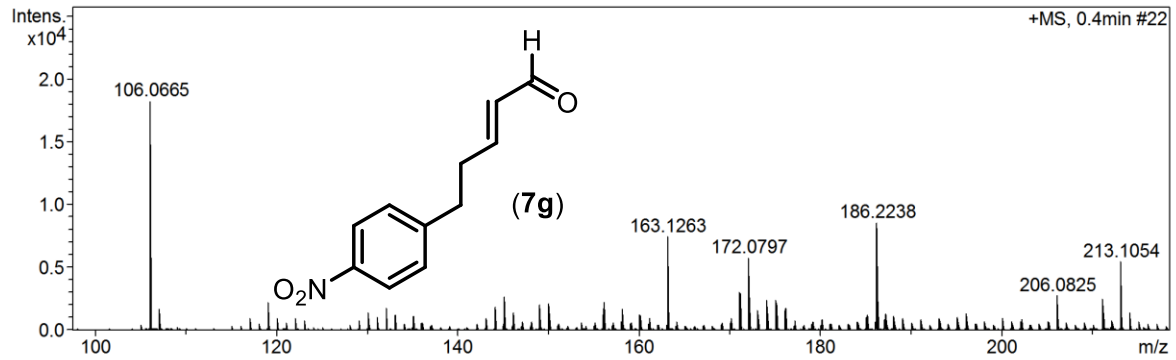
Analysis Info

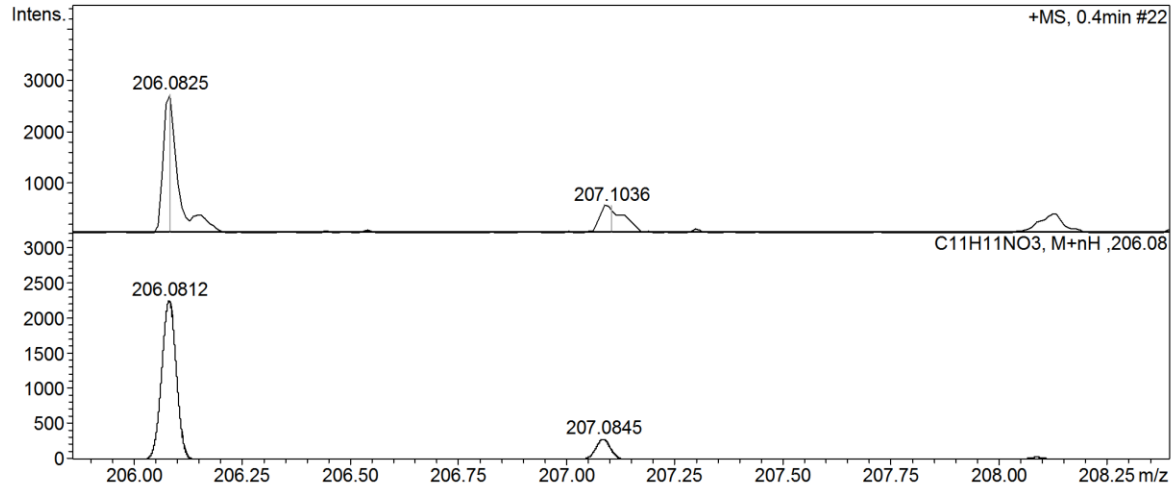
Analysis Name	D:\Data\USER DATA 2024\Dec-2024\19-dec\Prof M.Kapur-PO-04-284-R.d	Acquisition Date	20-12-2024 10:13:18
Method	tune_low.m	Operator	Bruker
Sample Name	PO-04-284-R	Instrument	micrOTOF-Q 10330
Comment			

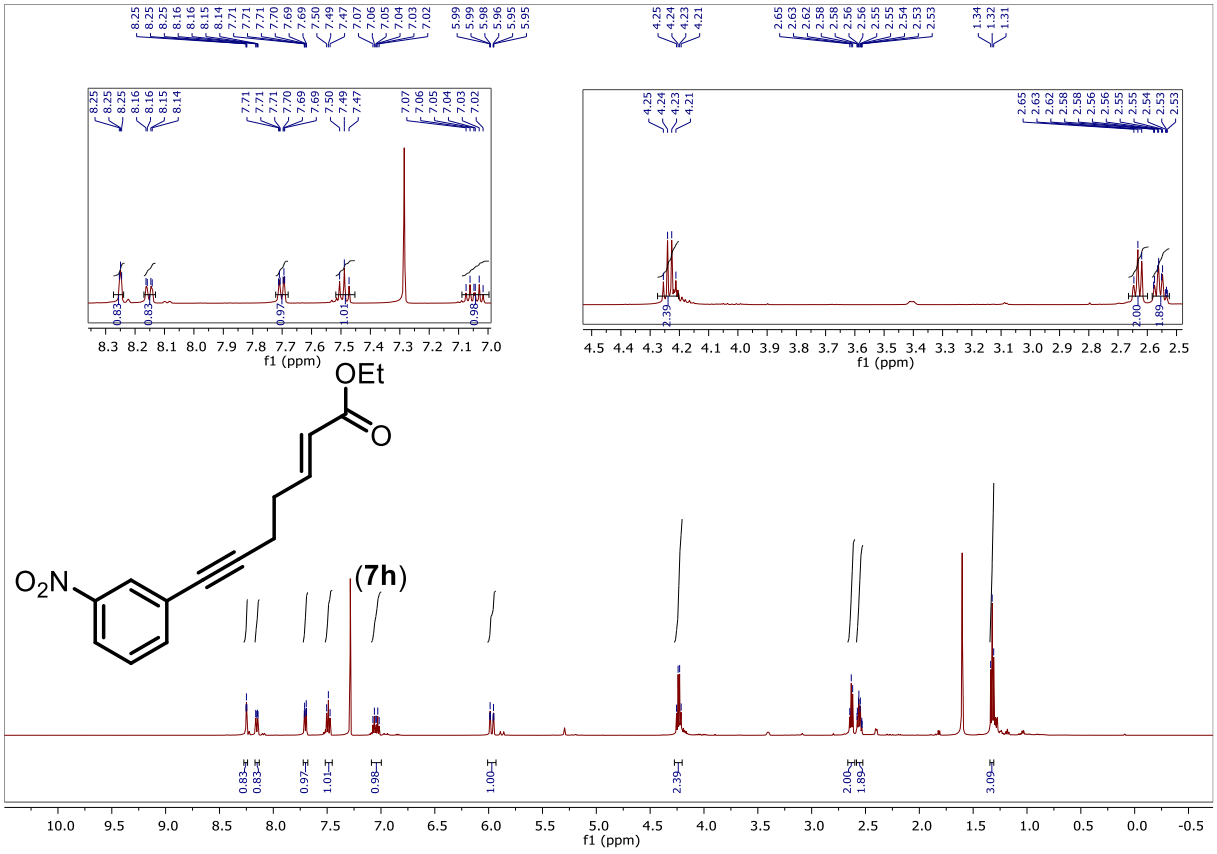
Acquisition Parameter

Source Type	Multi Mode	Ion Polarity	Positive	Set Nebulizer	29.0 psi
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	150.0 Vpp	Set Divert Valve	Waste





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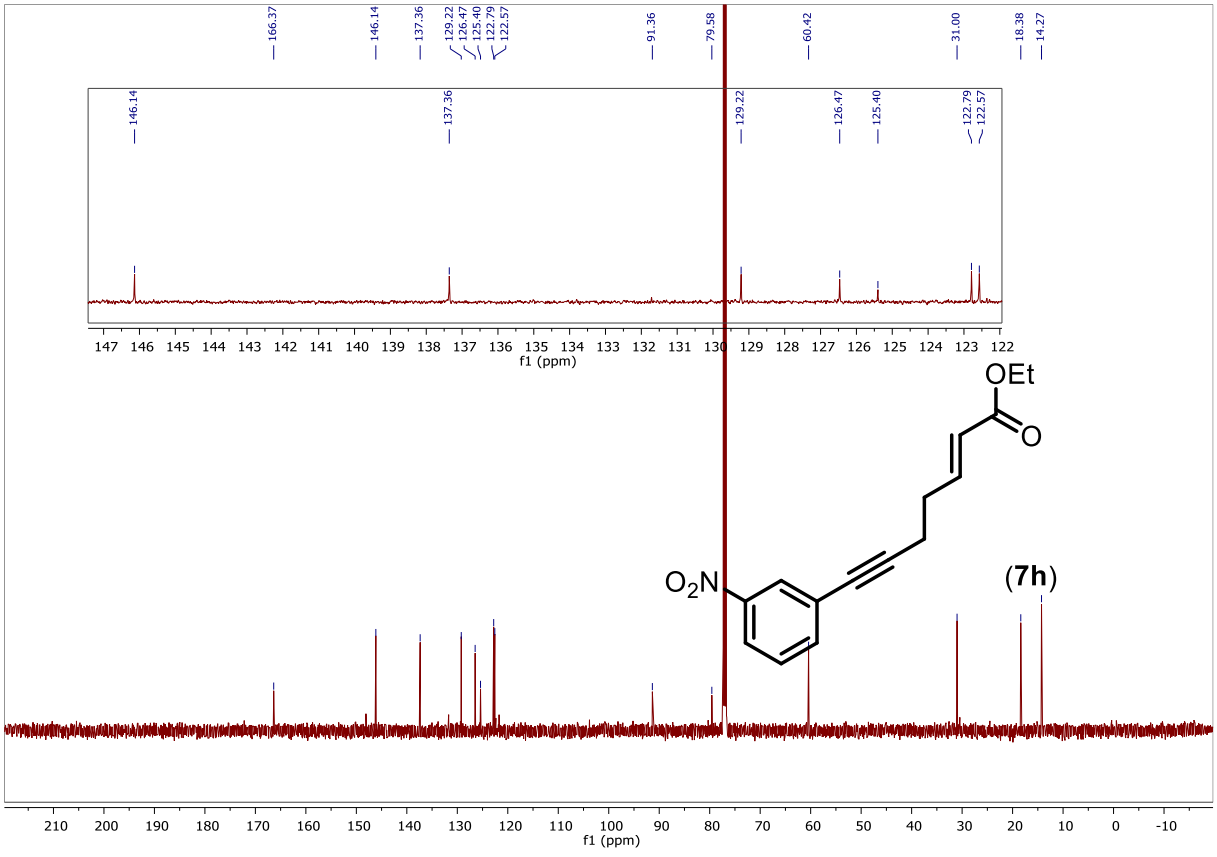
(7h)
f1 (ppm)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(7h)
f1 (ppm)

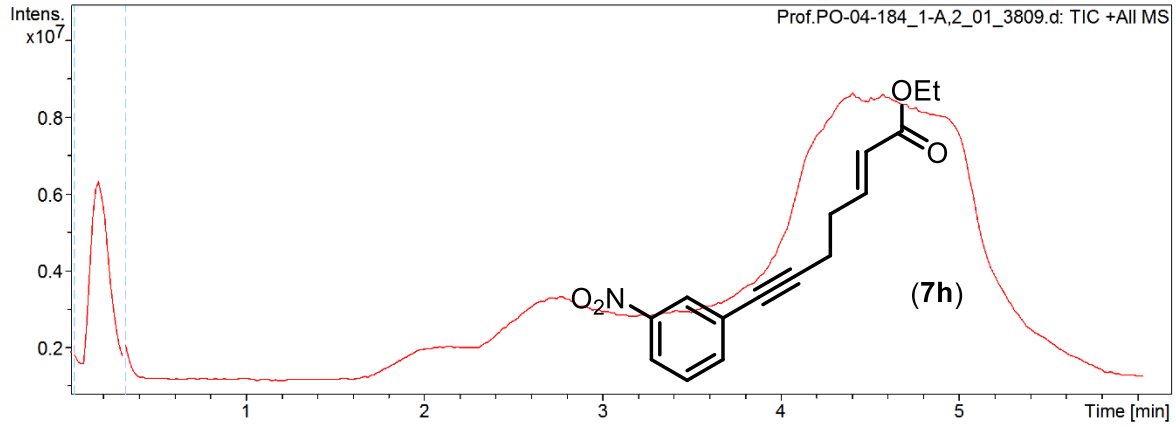
Display Report

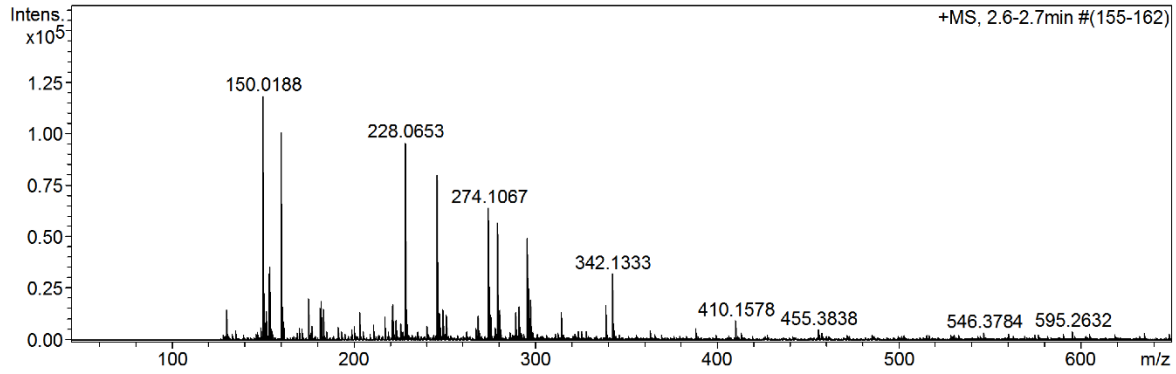
Analysis Info

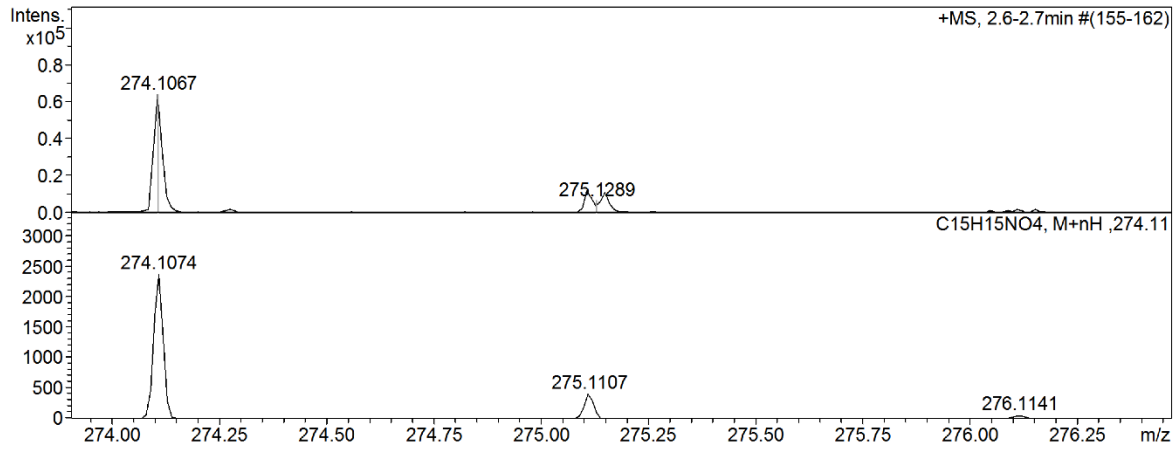
Analysis Name	D:\Data\USER DATA 2024\16-jan\Prof.PO-04-184_1-A,2_01_3809.d	Acquisition Date	16-01-2024 12:28:58
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.PO-04-184	Instrument	micrOTOF-Q 10330
Comment			

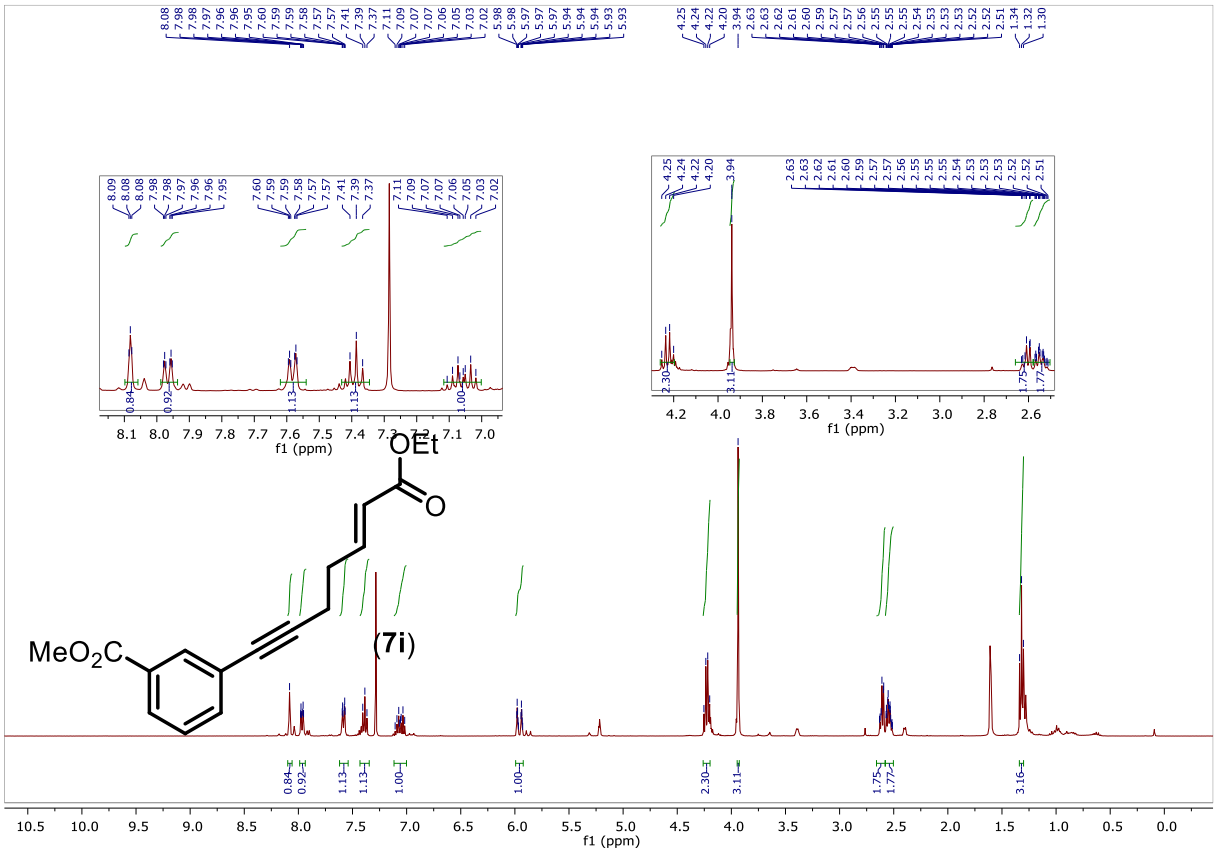
Acquisition Parameter

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





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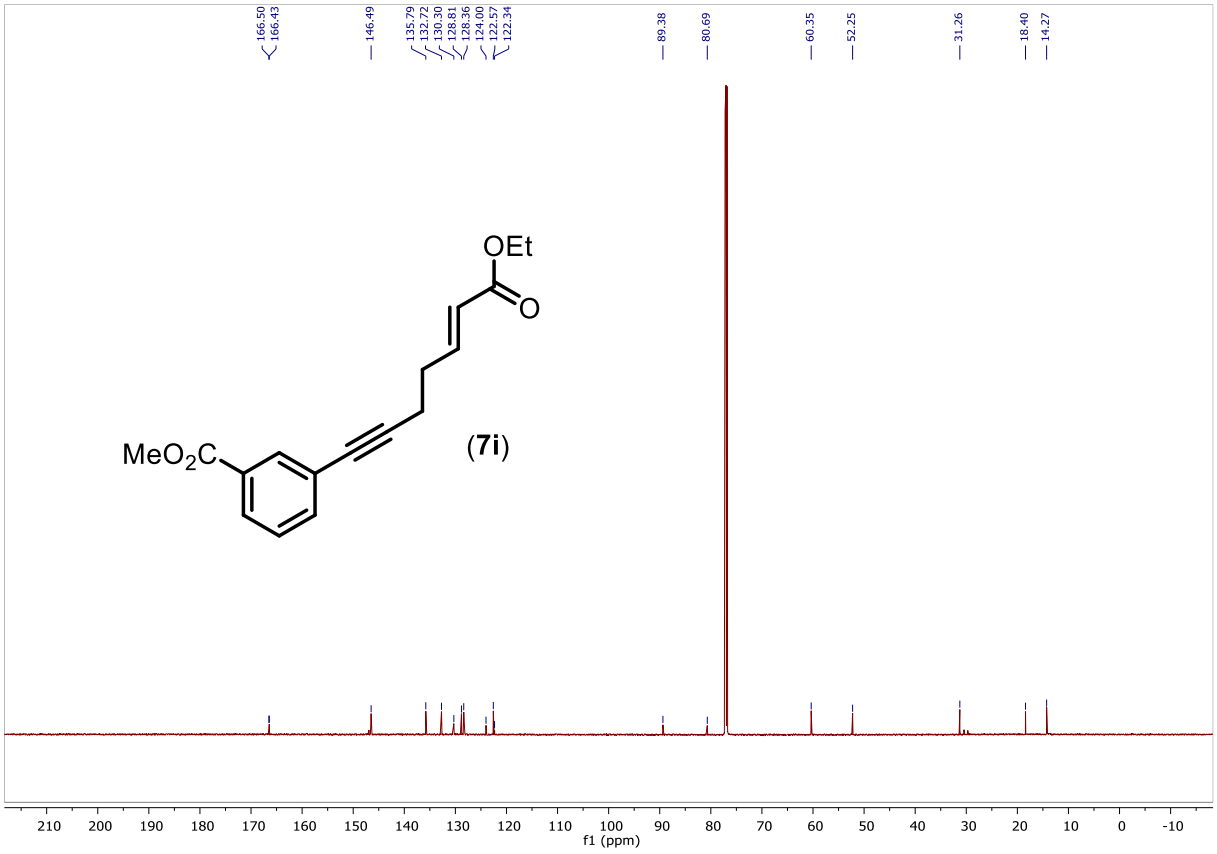
(7i)
f1 (ppm)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O
MeO2C
(7i)
f1 (ppm)

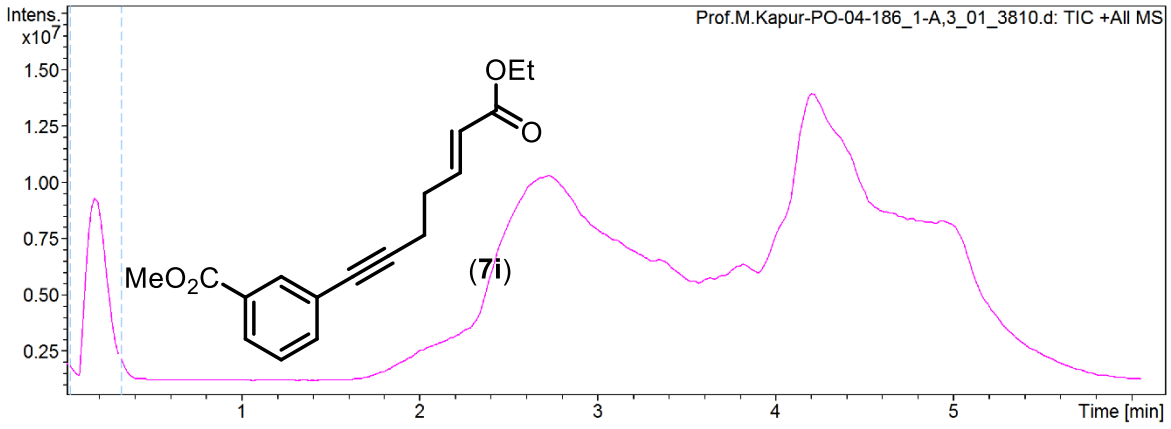
Display Report

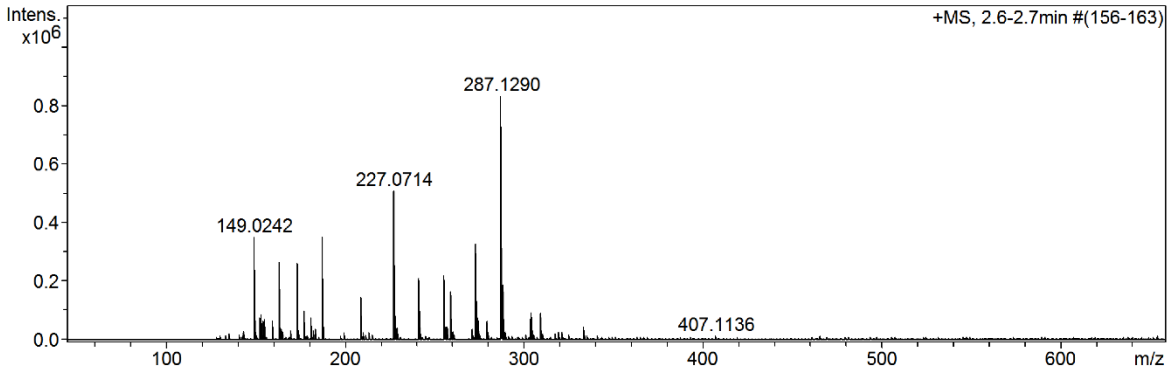
Analysis Info

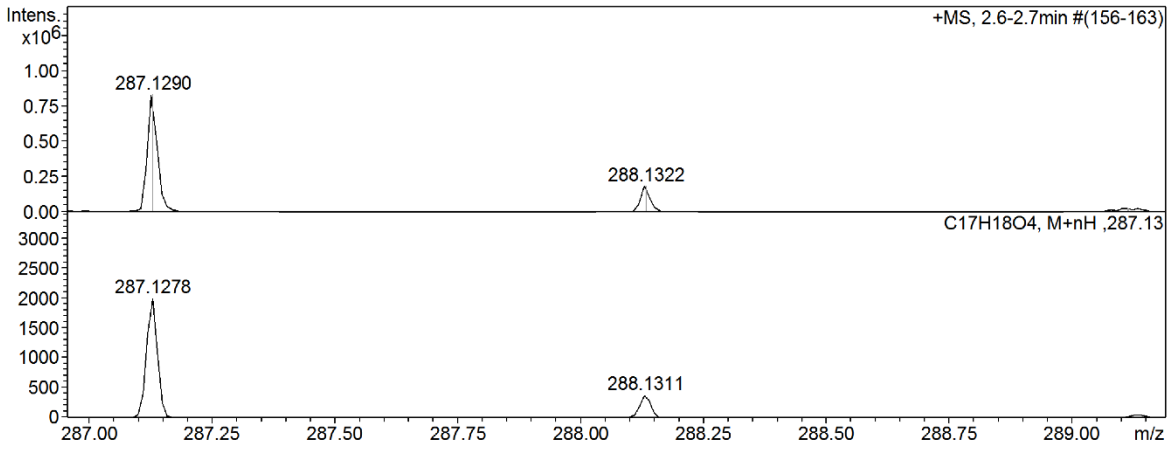
Acquisition Date	16-01-2024 12:36:10		
Analysis Name	D:\Data\USER DATA 2024\16-jan\Prof.M.Kapur-PO-04-186_1-A,3_01_3810.d		
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.M.Kapur-PO-04-186	Instrument	micrOTOF-Q 10330
Comment			

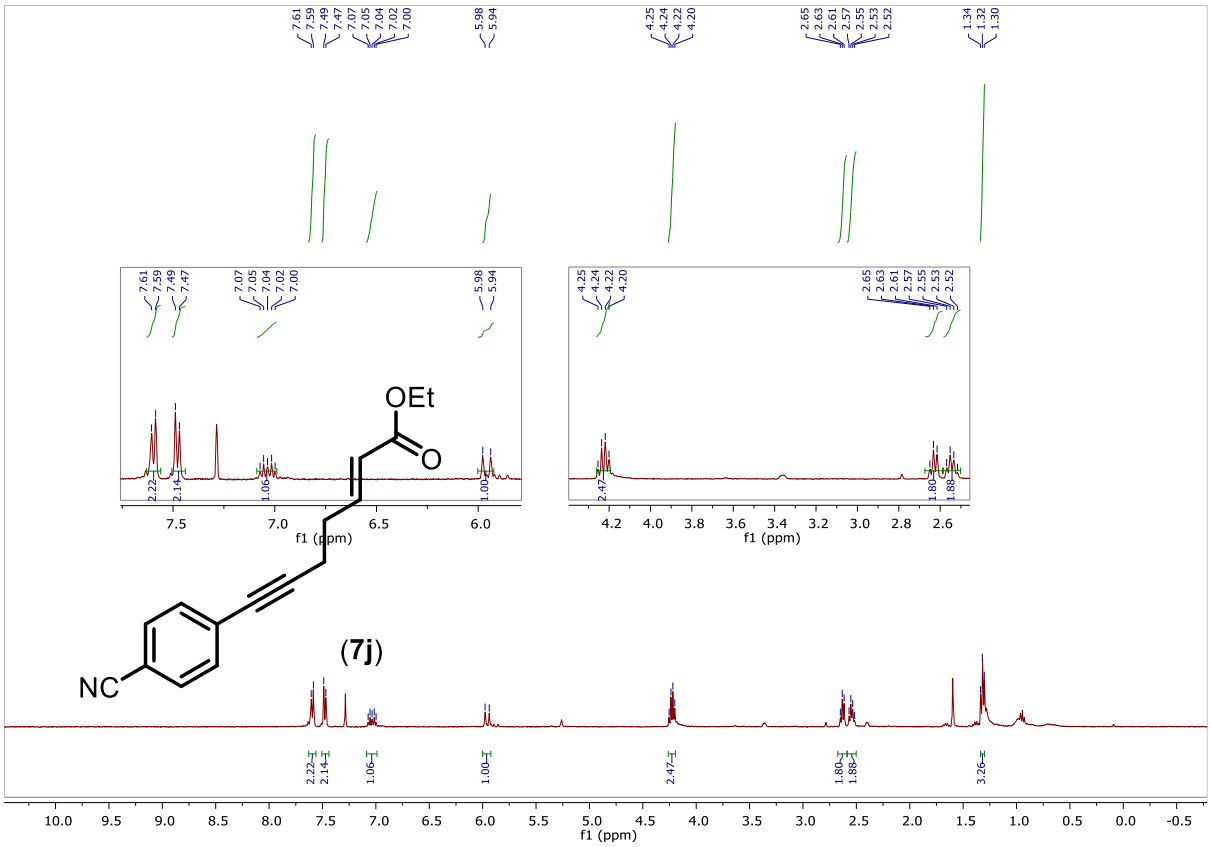
Acquisition Parameter

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





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7.07
7.05
7.04
7.02
7.00
5.98
5.94
4.25
4.24
4.22
4.20
2.65
2.63
2.61
2.57
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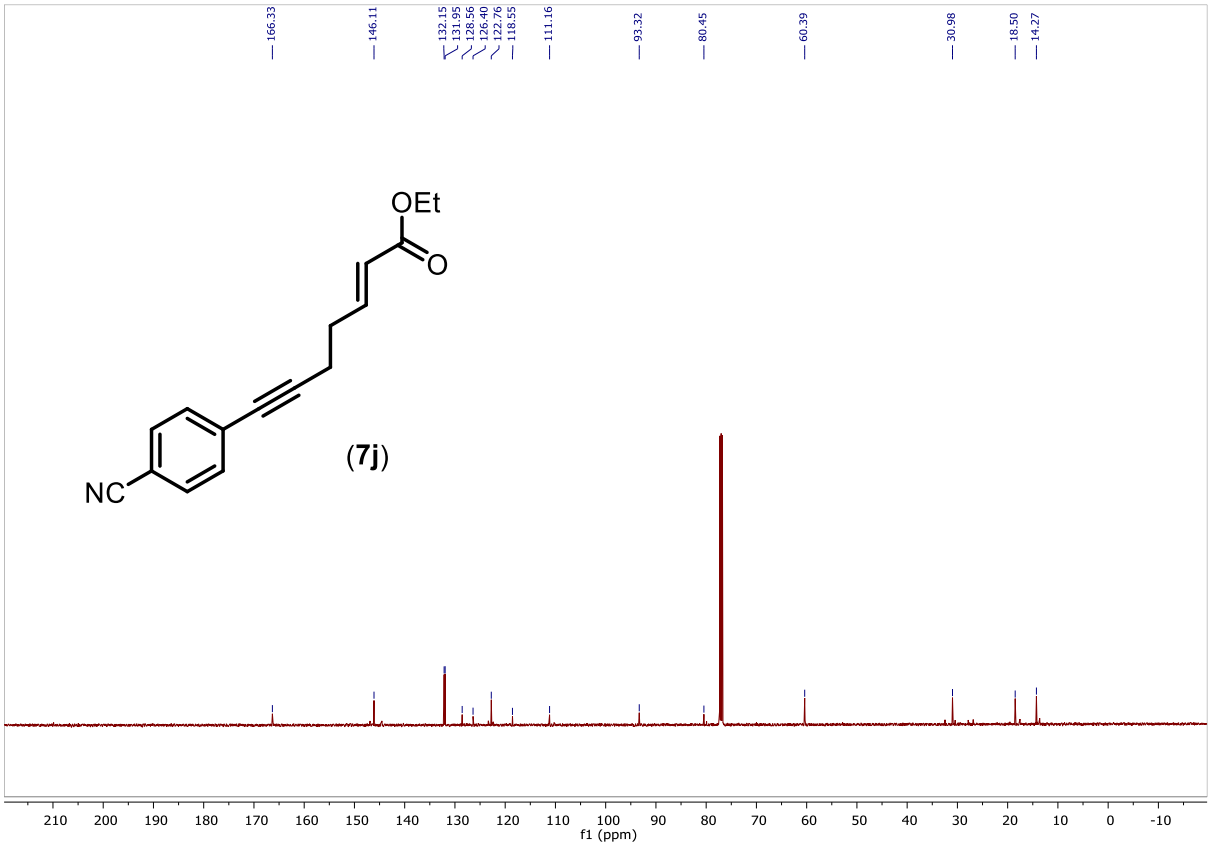
2.53
2.52
1.34
1.32
1.30
OEt
O
NC
(7j)
f1 (ppm)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132.15
131.95
128.56
126.40
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118.55
111.16
93.32
80.45
60.39
30.98
18.50
14.27
OEt
O
NC
(7j)
f1 (ppm)

Display Report

Analysis Info

Analysis Name	D:\Data\USER DATA 2024\Aug-2024\14-aug\Prof.M.Kapur-PO_04_270-1.d	Acquisition Date	14-08-2024 12:39:18
Method	tune_low_8Aug2024.m	Operator	Bruker
Sample Name	PO_04_270-1	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

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