Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 657–658

Nucleophilic ring opening of imidazolone activated donor–acceptor cyclopropanes with alcohols

Viktoria A. Ikonnikova, Ekaterina A. Zhigileva, Andrei V. Kuleshov, Vasilissa V. Shirokova, Mikhail S. Baranov and Andrey A. Mikhaylov

Reagents and methods: Solvents and reagents were distilled over the specified drying agents prior use: 1,2-dichloroethane, DMSO (CaH_2), ethyl acetate (K_2CO_3). Alcohols were eluted through a column with Al_2O_3 and distilled afterwards. Trimethylsulfoxonium iodide (Acros) and *N*,*N*,*N*',*N*'-tetramethylguanidine (TMG, Merck) were used as received. 4-(2,4-Dimethoxybenzylidene)-1,2-dimethyl-1*H*-imidazol-5-one [S1], 4-(2,5-dimethoxybenzylidene)-1,2-dimethyl-1*H*-imidazol-5-one [S2] and cyclopropanes **1a,b,e-g** [S3] were prepared according literature procedures.

Analytical thin-layer chromatography (TLC) was performed using aluminum plates pre-coated with silica gel (silica gel 60 F_{254}, Merck). TLC plates were visualized by exposure to 254 nm ultraviolet light (UV) or were stained by submersion in acidic ethanolic solution of vanillin followed by brief heating (vanillin) or submersion in aqueous potassium permanganate solution followed by extensive washing with water ($KMnO_4$). Flash-column chromatography was carried out on silica gel (60 Å, 230–400 mesh, Sigma-Aldrich).

NMR spectra were recorded using Bruker Fourier 300, Bruker Avance II 700 instruments at indicated temperature. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant (J) in Hertz, integration. Proton chemical shifts are expressed in ppm (δ scale) and are referenced to residual protium in the NMR solvents ($CHCl_3$, δ 7.26 ppm). Carbon chemical shifts are expressed in ppm (δ scale) and are referenced to the carbon resonances of the NMR solvents ($CDCl_3$, δ 77.16 ppm).

High-resolution mass spectra were recorded on a Bruker micrOTOF-Q II mass spectrometer using electrospray ionization (ESI–TOF). Melting points were determined on Kofler melting point apparatus and are uncorrected.

Cyclopropanation procedure. Sodium hydride (60% dispersion in mineral oil, 177 mg, 4.43 mmol, 1.15 equiv) was added to a stirred solution of trimethyl sulfoxonium iodide (1.10 g, 5.01 mmol, 1.30 equiv) in dry DMSO (8 mL) at room temperature. The resulting mixture was stirred for 30 min until a clear solution was formed (resulting ylide partially precipitates). Then, the corresponding 4-benzyline-1,2-dimethyl-1*H*-imidazol-5-one (1.00 g, 3.9 mmol, 1 equiv) was added in a single portion. The mixture was stirred for 1.5 h at r.t. and then poured into a mixture of EtOAc (70 mL) and H_2O (60 mL). The aqueous layer was back-extracted with EtOAc (20 mL). The combined organic phase was washed with brine (60 mL), dried over Na_2SO_4 and evaporated in vacuo. Cyclopropane **1c** (545 mg, 2.00 mmol, 52%) was obtained by recrystallization of the residue from hexane/EtOAc (40 mL of 1:1 mixture); cyclopropane **1d** (538 mg, 1.96 mmol, 51%) was obtained by column chromatography on silica, using EtOAc as eluent.

***cis*-1-(2,4-Dimethoxyphenyl)-5,6-dimethyl-4,6-diazaspiro[2.4]hept-4-en-7-one 1c:**

Mp 177–179 °C, R_f = 0.17 (EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.17 (d, *J* = 8.4 Hz, 1H), 6.45 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.39 (d, *J* = 2.4 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.17–3.11 (m, 1H), 3.14 (s, 3H), 2.17 (s, 3H), 2.12 (dd, *J* = 8.8, 4.8 Hz, 1H), 2.01 (dd, *J* = 9.5, 4.8 Hz, 1H);

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 181.5 (C=O), 160.0 (C=N), 159.9 (C-O), 159.6 (C-O), 128.9 (CH_{Ar}), 117.2 (C_{Ar}), 104.0 (CH_{Ar}), 98.4 (CH_{Ar}), 56.1 (C), 55.4 (OCH_3), 55.4 (OCH_3), 30.9 and 26.9 (CH and NCH_3), 22.3 (CH_2), 15.8 (CH_3);

HRMS (ESI+): calculated for $C_{15}H_{19}N_2O_3$ ($M+H^+$): 275.1390, found: 275.1393.

***cis*-1-(2,5-Dimethoxyphenyl)-5,6-dimethyl-4,6-diazaspiro[2.4]hept-4-en-7-one 1d:**

Mp 128–130 °C (hexane/EtOAc), R_f = 0.20 (EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 6.88 (t, *J* = 1.7 Hz, 1H), 6.73 (d, *J* = 1.7 Hz, 2H), 3.76 (s, 3H), 3.68 (s, 3H), 3.28 (t, *J* = 9.1 Hz, 1H), 3.15 (s, 3H), 2.18 (s, 3H), 2.12 (dd, *J* = 8.8, 4.8 Hz, 1H), 2.03 (dd, *J* = 9.5, 4.8 Hz, 1H);

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 181.5 (C=O), 160.1 (C=N), 153.5 (C-O), 153.2 (C-O), 126.1 (C_{Ar}), 115.3 (CH_{Ar}), 112.5 (CH_{Ar}), 111.4 (CH_{Ar}), 56.2 (OCH_3), 56.1 (C), 55.8 (OCH_3), 31.2 and 27.0 (CH and NCH_3), 22.5 (CH_2), 15.8 (CH_3);

HRMS (ESI+): calculated for $C_{15}H_{19}N_2O_3$ ($M+H^+$): 275.1390, found: 275.1395.

Cyclopropane opening with alcohols (general procedure)

Alcohol **2** (7.5 mmol, 10 equiv for **2a-c**; or 3.8 mmol, 5 equiv for **2d,e**) and $TsOH\cdot H_2O$ (158 mg, 0.83 mmol, 1.1 equiv) were added successively to a solution of cyclopropane **1** (0.75 mmol, 1 equiv) in 1,2-dichloroethane (4 ml). The reaction mixture was stirred at room temperature for 1–3 h (7 days for **1g**) until the full conversion of cyclopropane **1** was reached (TLC control, EtOAc). The mixture was then neutralized with *N,N,N',N'*-tetramethylguanidine (0.14 ml, 130 mg, 1.13 mmol, 1.5 equiv). After stirring for additional 15 min, the mixture was poured into separatory funnel containing EtOAc (20 ml) and H_2O (40 ml), the flask was rinsed with EtOAc (20 ml). The combined organic phase was washed with brine, dried over Na_2SO_4 and evaporated *in vacuo* to provide desired product **3** in 75-99% in >95% purity (except for **3ga**).

5-[2-Methoxy-2-(4-methoxyphenyl)ethyl]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 3aa:

Yield 166 mg (0.60 mmol, 80%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 7.27 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 1H), 6.88 (d, *J* = 8.6 Hz 1H), 6.87 (d, *J* = 8.6 Hz 1H), 4.50 (dd, *J* = 9.4, 4.7 Hz, 0.5H), 4.35 (dd, *J* = 8.8, 5.8 Hz, 0.5H), 4.21 (ddq, *J* = 9.4, 4.8, 2.2 Hz, 0.5H), 3.95 (tq, *J* = 6.2, 2.2 Hz, 0.5H), 3.80 (s, 3H), 3.21 (s, 1.5H), 3.09 (s, 1.5H), 3.07 (s, 1.5H), 2.98 (s, 1.5H), 2.36 (ddd, *J* = 14.0, 9.4, 4.9 Hz, 0.5H), 2.32–2.18 (m, 0.5H), 2.23 (d, *J* = 2.2 Hz, 1.5H), 2.22 (d, *J* = 2.2 Hz, 1.5H), 2.13 (dt, *J* = 14.0, 6.0 Hz, 0.5H), 1.68 (ddd, *J* = 14.0, 9.4, 4.7 Hz, 0.5H);

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 183.8 and 183.5 (C=O), 161.9 and 161.6 (C=N), 159.4 (2×OC_{Ar}), 133.5 and 133.2 (C_{Ar}), 128.3 and 128.3 (2×CH_{Ar}), 114.0 and 113.9 (2×CH_{Ar}), 80.0 and 79.5 (OCH), 65.1 and 65.1 (CH), 56.5 and 56.4 (OCH_3), 55.4 (OCH_3), 39.7 and 39.2 (CH_2), 26.6 (CH_3), 15.9 (CH_3);

HRMS (ESI+): calculated for $C_{15}H_{21}N_2O_3$ ($M+H^+$): 277.1547, found: 277.1545.

5-[2-Ethoxy-2-(4-methoxyphenyl)ethyl]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 3ab:

Yield 215 mg (0.74 mmol, 99%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 7.27 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz 1H), 6.86 (d, *J* = 8.6 Hz 1H), 4.60 (dd, *J* = 9.6, 4.5 Hz, 0.5H), 4.46 (dd, *J* = 9.1, 5.4 Hz, 0.5H), 4.25 (ddq, *J* = 9.1, 4.4, 2.2 Hz, 0.5H), 3.93 (tq, *J* = 6.2, 2.2 Hz, 0.5H), 3.79 (s, 3H), 3.43−3.21 (m, 1.5H), 3.15 (dq, *J* = 9.4, 7.0 Hz, 0.5H), 3.07 (s, 1.5H), 2.98 (s, 1.5H), 2.35 (ddd, *J* = 14.0, 9.1, 4.4 Hz, 0.5H), 2.32–2.18 (m, 0.5H), 2.22 (d, *J* = 2.2 Hz, 1.5H), 2.22 (d, *J* = 2.2 Hz, 1.5H), 2.13 (ddd, *J* = 14.0, 6.6, 5.4 Hz, 0.5H), 1.68 (ddd, *J* = 14.0, 9.6, 5.4 Hz, 0.5H), 1.14 (t, *J* = 7.0 Hz, 1.5H), 1.05 (t, *J* = 7.0 Hz, 1.5H);

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 183.5 and 183.4 (C=O), 161.7 and 161.4 (C=N), 159.1 and 159.1 (OC_{Ar}), 134.2 and 133.9 (C_{Ar}), 128.0 and 128.0 (2×CH_{Ar}), 113.7 and 113.7 (2×CH_{Ar}), 77.7 and 77.6 (O-CH), 65.0 and 64.9 (CH), 63.9 and 63.6 (OCH_2), 55.2 (OCH_3), 39.8 and 39.0 (CH_2), 26.5 and 26.4 (CH_3), 15.8 (CH_3), 15.3 and 15.2 (CH_3);

HRMS (ESI+): calculated for $C_{16}H_{23}N_2O_3$ ($M+H^+$): 291.1703, found: 291.1704.

5-[2-Isopropoxy-2-(4-methoxyphenyl)ethyl]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 3ac:
Yield 216 mg (0.71 mmol, 94%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 7.27 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz 1H), 6.85 (d, *J* = 8.6 Hz 1H), 4.71 (dd, *J* = 9.6, 4.4 Hz, 0.5H), 4.61 (dd, *J* = 9.4, 4.9 Hz, 0.5H), 4.21 (ddq, *J* = 9.0, 4.5, 2.1 Hz, 0.5H), 3.94 (ddq, *J* = 7.3, 4.7, 2.2 Hz, 0.5H), 3.78 (s, 3H), 3.52 (hept, *J* = 6.1 Hz, 0.5H), 3.37 (hept, *J* = 6.1 Hz, 0.5H), 3.06 (s, 1.5H), 2.97 (s, 1.5H), 2.34–2.16 (m, 1H), 2.21 (d, *J* = 2.2 Hz, 3H), 2.06 (ddd, *J* = 14.0, 7.3, 4.4 Hz, 0.5H), 1.63 (ddd, *J* = 14.0, 9.6, 4.5 Hz, 0.5H), 1.16 (d, *J* = 6.0 Hz, 1.5H), 1.03 (d, *J* = 6.1 Hz, 1.5H), 1.01 (d, *J* = 6.1 Hz, 1.5H), 0.97 (d, *J* = 6.2 Hz, 1.5H);

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 183.3 and 183.3 (C=O), 161.7 and 161.2 (C=N), 158.9 and 158.8 (OC_{Ar}), 135.0 and 134.4 (C_{Ar}), 127.8 and 127.8- ($2\times CH_{Ar}$), 113.6 and 113.4 ($2\times CH_{Ar}$), 74.8 and 74.3 (OCH), 68.8, 67.7, 64.9 and 64.7 (OCH and CH), 55.0 (OCH_3), 40.1 and 39.2 (CH_2), 26.3 and 26.3 (CH_3), 23.4, 23.3, 21.4 and 20.8 (CH_3 and CH_3), 15.7 and 15.6 (CH_3);

HRMS (ESI+): calculated for $C_{17}H_{25}N_2O_3$ ($M+H^+$): 305.1860, found: 305.1864.

5-[2-(4-Methoxyphenyl)-2-propoxyethyl]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 3ad:
Yield 170 mg (0.56 mmol, 75%).

^{1}H NMR(300 MHz, $CDCl_3$, 300 K): δ (for isomers mixture)= 7.26 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 1H), 4.58 (dd, *J* = 9.7, 4.3 Hz, 0.5H), 4.46 (dd, *J* = 9.1, 5.4 Hz, 0.5H), 4.31−4.21 (m, 0.5H), 4.00−3.87 (m, 0.5H), 3.79 (s, 3H), 3.25 (t, *J* = 6.6 Hz, 1H), 3.20−3.01 (m, 1H), 3.06 (s, 1.5H), 2.99 (s, 1.5H), 2.40–2.16 (m, 4H), 2.10 (dt, *J* = 14.0, 6.3 Hz, 0.5H), 1.70−1.38 (m, 2.5H), 0.86 (t, *J* = 7.3 Hz, 1.5H), 0.82 (t, *J* = 7.4 Hz, 1.5H);

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 183.7 (C=O), 161.9 and 161.5 (C=N), 159.2 (OC_{Ar}), 134.4 and 134.1 (C_{Ar}), 128.2 and 128.1 ($2\times CH_{Ar}$), 113.9 and 113.8 ($2\times CH_{Ar}$), 77.9 and 77.7 (OCH), 70.4 and 70.3 (OCH_2), 65.1 and 65.0 (CH), 55.3 (OCH_3), 40.1 and 39.2 (CH_2), 26.6 (CH_3), 23.2 (CH_2), 15.9 (CH_3), 10.8 and 10.7 (CH_3);

HRMS (ESI+): calculated for $C_{17}H_{25}N_2O_3$ ($M+H^+$): 305.1860, found: 305.1863.

5-[2-Allyloxy-2-(4-methoxyphenyl)ethyl]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 3ae:
Yield 208 mg (contains 7% EtOAc, corrected yield 192 mg, 0.64 mmol, 85%), *dr* 1.4:1

^{1}H NMR (700 MHz, $CDCl_3$, 300 K): δ (*isomer 1*) = 7.26 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.78 (dddd, *J* = 17.3, 10.6, 6.0, 4.9 Hz, 1H), 5.17 (dq, *J* = 17.3, 1.8 Hz, 1H), 5.08 (dq, *J* = 10.6, 1.5 Hz, 1H), 4.50 (dd, *J* = 9.5, 5.1 Hz, 1H), 3.95 (ddq, *J* = 6.8, 5.1, 2.3 Hz, 1H), 3.89–3.84 (m, 4H), 3.58 (ddt, *J* = 12.9, 6.0, 1.4 Hz, 1H), 3.03 (s, 3H), 2.32 (ddd, *J* = 14.2, 9.5, 5.1 Hz, 1H), 2.21 (d, *J* = 2.3 Hz, 3H), 2.17 (ddd, *J* = 14.1, 6.8, 5.1 Hz, 1H); δ (*isomer 2*) = 7.27 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.87 (dddd, *J* = 17.2, 10.7, 5.8, 5.2 Hz, 1H), 5.22 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.10 (dq, *J* = 10.7, 1.5 Hz, 1H), 4.66 (dd, *J* = 9.4, 4.7 Hz, 1H), 4.24 (ddq, *J* = 9.4, 4.8, 2.2 Hz, 1H), 3.87 (ddt, *J* = 12.7, 5.2, 1.6 Hz, 1H), 3.89–3.84 (m, 4H), 2.97 (s, 3H), 2.39 (ddd, *J* = 14.1, 9.4, 4.8 Hz, 1H), 2.20 (d, *J* = 2.3 Hz, 3H), 1.72 (ddd, *J* = 14.1, 9.4, 4.7 Hz, 1H);

^{13}C NMR (175 MHz, $CDCl_3$, 300 K): δ (*for isomers mixture*) = 183.7 and 183.5 (C=O), 162.0 and 161.5 (C=N), 159.4 (OC_{Ar}) 135.2, 135.0, 133.7 and 133.5 ($\underline{C}H_2$= and C_{Ar}), 128.3 and 128.2 ($2\times CH_{Ar}$), 116.4 and 115.8 (=$\underline{C}$H), 114.0 and 113.9 ($2\times CH_{Ar}$), 77.6 and 77.4 (OCH), 69.4 and 69.3 (CH), 65.1 and 65.0 (CH_2), 55.3 (OCH_3), 39.7 and 39.1 (CH_2), 26.7 and 26.5 (CH_3), 15.9 and 15.9 (CH_3);

HRMS (ESI+): calculated for $C_{17}H_{23}N_2O_3$ ($M+H^+$): 303.1703, found: 303.1703.

5-[2-Methoxy-2-(2-methoxyphenyl)ethyl]-2,3-dimethyl-3,5-dihydro-4*H*-im-4-one 3ba:
Yield 175 mg (0.63 mmol, 84%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 7.40 (dd, *J* = 7.6, 2.2 Hz, 0.5H), 7.19 (dd, *J* = 7.6, 2.2 Hz, 0.5H), 7.23 (td, *J* = 7.9, 2.0 Hz, 1H), 6.97 (td, *J* = 7.4, 1.1 Hz, 0.5H), 6.96 (td, *J* = 7.4, 1.1 Hz, 0.5H), 6.85 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.97 (dd, *J* = 9.7, 3.7 Hz, 0.5H), 4.80 (dd, *J* = 9.7, 4.3 Hz, 0.5H), 4.30 (ddq, *J* = 10.3, 4.3, 2.2 Hz, 0.5H), 4.04 (tq, *J* = 6.7, 4.4, 2.2 Hz, 0.5H), 3.82 (s, 1.5H), 3.81 (s, 1.5H), 3.28 (s, 1.5H), 3.11 (s, 1.5H), 3.09 (s, 1.5H), 2.99 (s, 1.5H), 2.32–2.12 (m, 1.5H), 2.25 (d, *J* = 2.2 Hz, 1.5H), 2.23 (d, *J* = 2.2 Hz, 1.5H), 1.74 (ddd, *J* = 14.0, 10.3, 3.7 Hz, 0.5H);

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 184.1 and 183.7 (C=O), 161.8 and 161.4 (C=N), 157.3 and 157.2 (C_{Ar}), 129.6 and 129.6 (C_{Ar}), 128.5 and 128.5 (CH_{Ar}), 127.2 and 127.0 (CH_{Ar}), 120.8 and 120.8 (CH_{Ar}), 110.5 and 110.4 (CH_{Ar}), 74.5 and 74.4 (OCH), 65.3 and 65.2 (CH), 57.0 and 56.7 (OCH_3), 55.5 and 55.4 (OCH_3), 38.3 and 37.6 (CH_2), 26.6 (CH_3), 15.9 (CH_3);

HRMS (ESI+): calculated for $C_{15}H_{21}N_2O_3$ ($M+H^+$): 277.1547, found: 277.1544.

5-[2-(2,4-Dimethoxyphenyl)-2-methoxyethyl]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 3ca:

Yield 225 mg (0.73 mmol, 98%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 7.17 (d, *J* = 8.1 Hz, 1H), 6.39 (d, *J* = 8.1, 1H), 6.33 (s, 1H), 4.79 (dd, *J* = 9.6, 4.0 Hz, 0.5H), 4.63 (dd, *J* = 9.2, 4.9 Hz, 0.5H), 4.23–4.08 (m, 0.5H), 3.97–3.85 (m, 0.5H), 3.69 (s, 6H), 3.14 (s, 1.5H), 2.99 (s, 1.5H), 2.98 (s, 1.5H), 2.87 (s, 1.5H), 2.27–2.02 (m, 4.5H), 1.63 (ddd, *J* = 14.0, 10.2, 4.1 Hz, 0.5H);

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 183.8 and 183.4 (C=O), 161.5, 161.2, 160.1, 160.0, 158.2 and 158.1 (C=N, OC_{Ar} and OC_{Ar}), 127.9 and 127.6 (CH_{Ar}), 121.6 and 121.6 (C_{Ar}), 104.2 and 104.2 (CH_{Ar}), 98.1 and 98.1 (CH_{Ar}), 73.9 and 73.8 (OCH), 65.1 and 65.0 (CH), 56.4 and 56.2 (OCH_3), 55.2 and 55.2 (OCH_3), 55.1 (OCH_3), 38.1 and 37.5 (CH_2), 26.3 (CH_3), 15.6 and 15.6 (CH_3);

HRMS (ESI+): calculated for $C_{16}H_{23}N_2O_3$ ($M+H^+$): 307.1652, found: 307.1655.

5-[2-(2,5-Dimethoxyphenyl)-2-methoxyethyl]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 3da:

Yield 214 mg (0.70 mmol, 93%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 6.99 (d, *J* = 2.7 Hz, 0.5H), 6.98 (d, *J* = 2.8 Hz, 0.5H), 6.83−6.70 (m, 2H), 4.95 (dd, *J* = 9.8, 3.6 Hz, 0.5H), 4.77 (dd, *J* = 9.8, 4.2 Hz, 0.5H), 4.30 (ddq, *J* = 10.3, 4.2, 2.2 Hz, 0.5H), 4.05 (ddq, *J* = 6.7, 4.4, 2.4 Hz, 0.5H), 3.77 (s, 3H), 3.76 (s, 1.5H), 3.76 (s, 1.5H), 3.29 (s, 1.5H), 3.13 (s, 1.5H), 3.09 (s, 1.5H), 3.00 (s, 1.5H), 2.35–2.09 (m, 4.5H), 1.71 (ddd, *J* = 14.0, 10.4, 3.6 Hz, 0.5H);

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 183.8 and 183.5 (C=O), 161.7 and 161.4 (C=N), 153.9 and 153.8 (OC_{Ar}), 151.3 and 151.2 (OC_{Ar}), 130.8 and 130.7 (C_{Ar}), 113.3 and 113.3 (CH_{Ar}), 112.3 and 112.0 (CH_{Ar}), 111.7 and 111.5 (CH_{Ar}), 74.3 and 74.1 (OCH), 65.1 and 65.0 (CH), 56.9 and 56.7 (OCH_3), 56.0 and 55.9 (OCH_3), 55.7 and 55.7 (OCH_3), 38.3 and 37.5 (CH_2), 26.4 (CH_3), 15.7 and 15.7 (CH_3);

HRMS (ESI+): calculated for $C_{16}H_{23}N_2O_3$ ($M+H^+$): 307.1652, found: 307.1657.

5-[2-(3,4-Dimethoxyphenyl)-2-methoxyethyl]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 3ea:

Yield 174 mg (0.57 mmol, 76%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 6.92−6.76 (m, 3H), 4.50 (dd, *J* = 9.5, 4.5 Hz, 0.5H), 4.34 (dd, *J* = 9.0, 5.4 Hz, 0.5H), 4.22 (ddq, *J* = 9.7, 4.8, 2.2 Hz, 0.5H), 3.95 (tq, *J* = 6.1, 2.2 Hz, 0.5H), 3.89 (s, 1.5H), 3.88 (s, 1.5H), 3.87 (s, 3H), 3.23 (s, 1.5H), 3.11 (s, 1.5H), 3.08 (s, 1.5H), 3.00 (s, 1.5H), 2.35 (ddd, *J* = 14.0, 9.7, 4.8 Hz, 0.5H), 2.30–2.20 (m, 0.5H), 2.25 (d, *J* = 2.2 Hz, 1.5H), 2.22 (d, *J* = 2.2 Hz, 1.5H), 2.14 (dt, *J* = 13.9, 5.8 Hz, 0.5H), 1.68 (ddd, *J* = 14.0, 9.5, 4.5 Hz, 0.5H);

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 183.8 and 183.6 (C=O), 162.0 and 161.7 (C=N), 149.4 and 149.3 (OC_{Ar}), 148.7 (OC_{Ar}), 134.1 and 133.8 (C_{Ar}), 119.7 and 119.6 (CH_{Ar}), 110.9 and 110.9 (CH_{Ar}), 109.5 and 109.4 (CH_{Ar}), 80.3 and 79.8 (OCH), 65.1 and 65.0 (CH), 56.6 and 56.5 (OCH_3), 56.0 ($2\times OCH_3$), 39.8 and 39.3 (CH_2), 26.6 (CH_3), 15.9 (CH_3);

HRMS (ESI+): calculated for $C_{16}H_{23}N_2O_3$ ($M+H^+$): 307.1652, found: 307.1655.

5-[2-Methoxy-2-(thiophen-2-yl)ethyl]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 3fa:

Yield 177 mg (0.70 mmol, 94%), *dr* 1.1:1

^{1}H NMR (700 MHz, $CDCl_3$, 300 K): δ (*isomer 1*) = 7.29–7.26 (m, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.97–6.94 (m, 1H), 4.73 (dd, *J* = 8.8, 5.7 Hz, 1H), 3.97 (tq, *J* = 6.3, 2.2 Hz, 1H), 3.17 (s, 3H), 3.07 (s, 3H), 2.35 (ddd, *J* = 13.6, 8.8, 6.3 Hz, 1H), 2.37–2.22 (m, 1H), 2.23 (d, *J* = 2.2 Hz, 3H); δ (*isomer 2*) = 7.29–7.26 (m, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.97–6.94 (m, 1H), 4.85 (dd, *J* = 9.4, 4.7 Hz, 1H), 4.22 (ddq, *J* = 9.7, 4.9, 2.2 Hz, 1H), 3.29 (s, 3H), 3.01 (s, 3H), 2.46 (ddd, *J* = 14.1, 9.4, 4.9 Hz, 1H), 2.22 (d, *J* = 2.2 Hz, 3H), 1.81 (ddd, *J* = 14.1, 9.7, 4.7 Hz, 1H);

^{13}C NMR (175 MHz, $CDCl_3$, 300 K): δ (for isomers mixture) = 183.4 and 183.3 (C=O), 162.1 and 161.8 (C=N), 145.3 and 144.9 (C_{Ar}), 126.5, 126.5, 126.0, 125.8, 125.4 and 125.3 (3×CH_{Ar}), 75.9 and 75.4 (OCH), 64.9 and 64.8 (CH), 56.6 and 56.4 (O-CH_3), 40.1 and 39.5 (CH_2), 26.6 (CH_3), 15.9 (CH_3);

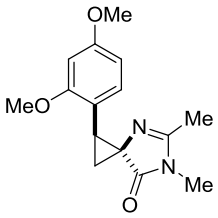
HRMS (ESI+): calculated for $C_{12}H_{17}N_2O_2S$ ($M+H^+$): 253.1005, found: 253.1010.

References

[S1] T. Chatterjee, M. Mandal, A. Das, K. Bhattacharyya, A. Datta P. K. Mandal *J. Phys. Chem. B*, 2016, **120**, 3503.

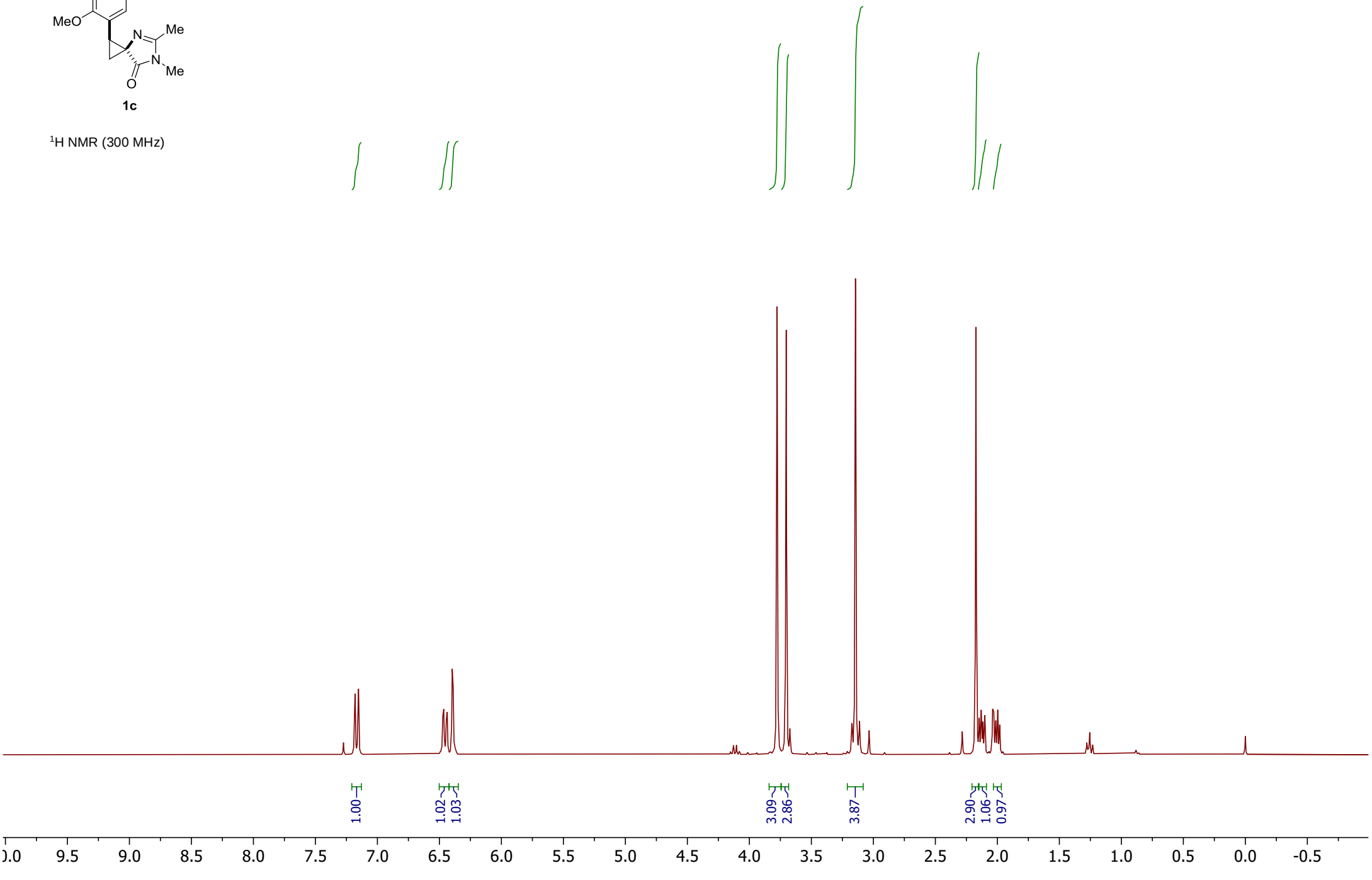
[S2] N. V. Povarova, S. O. Zaitseva, N. S. Baleeva. A. Yu. Smirnov, I. N. Myasnyanko, M. B. Zagudaylova, N. G. Bozhanova, D. A. Gorbachev, K. K. Malyshevskaya, A. S. Gavrikov, A. S. Mishin and M. S. Baranov, *Chem. Eur. J.*, 2019, **25**, 9592.

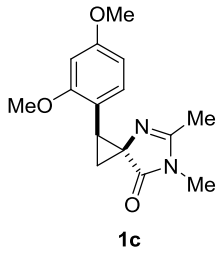
[S3] A. A. Mikhaylov, A. V. Kuleshov, P. N. Solyev, A. A. Korlyukov, P. V. Dorovatovskii, K. S. Mineev and M. S. Baranov, *Org. Lett.*, 2020, **22**, 2740.



1c

^{1}H NMR (300 MHz)

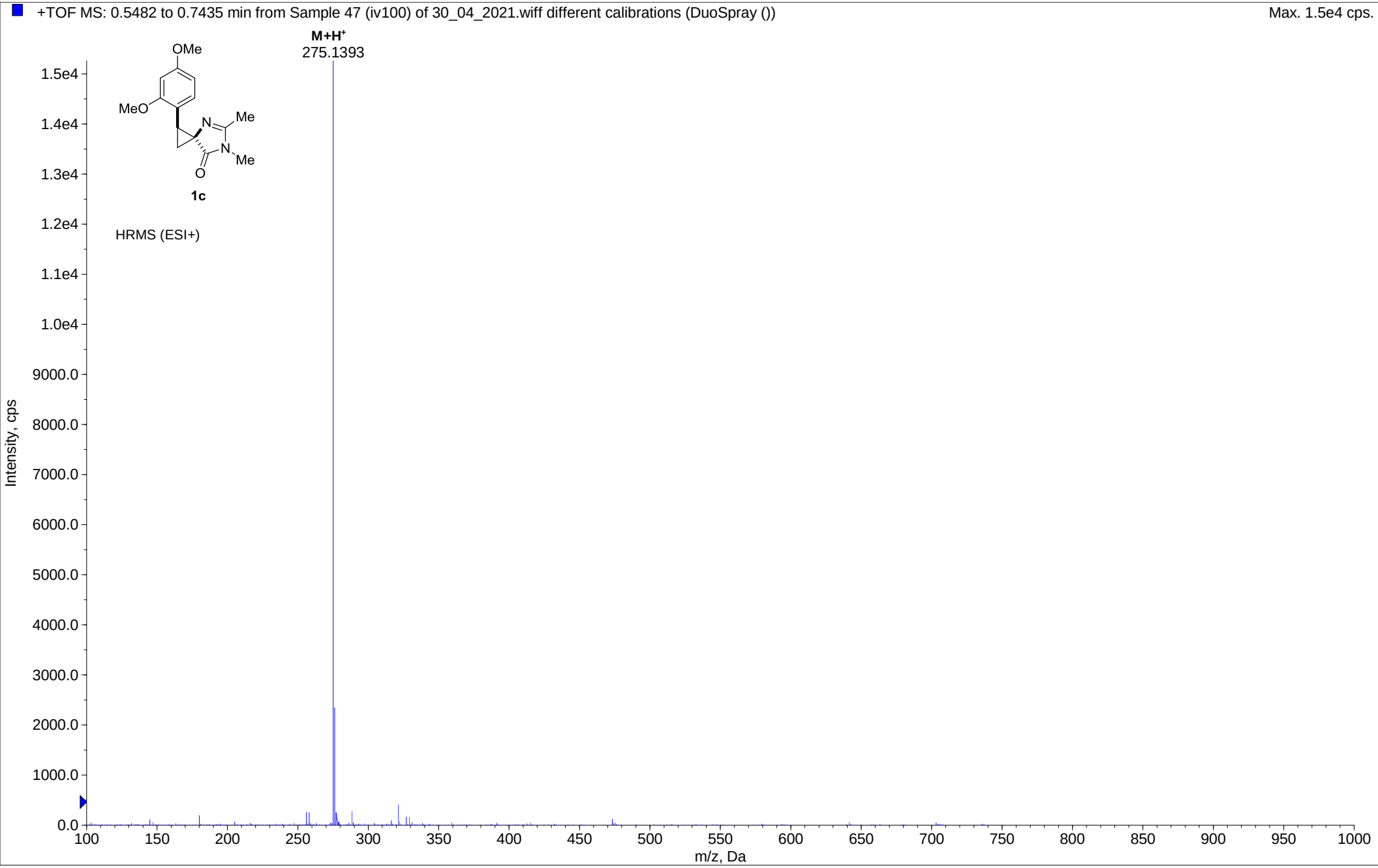


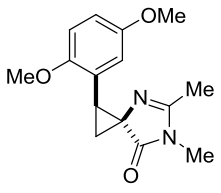


1c

^{13}C NMR (75 MHz)

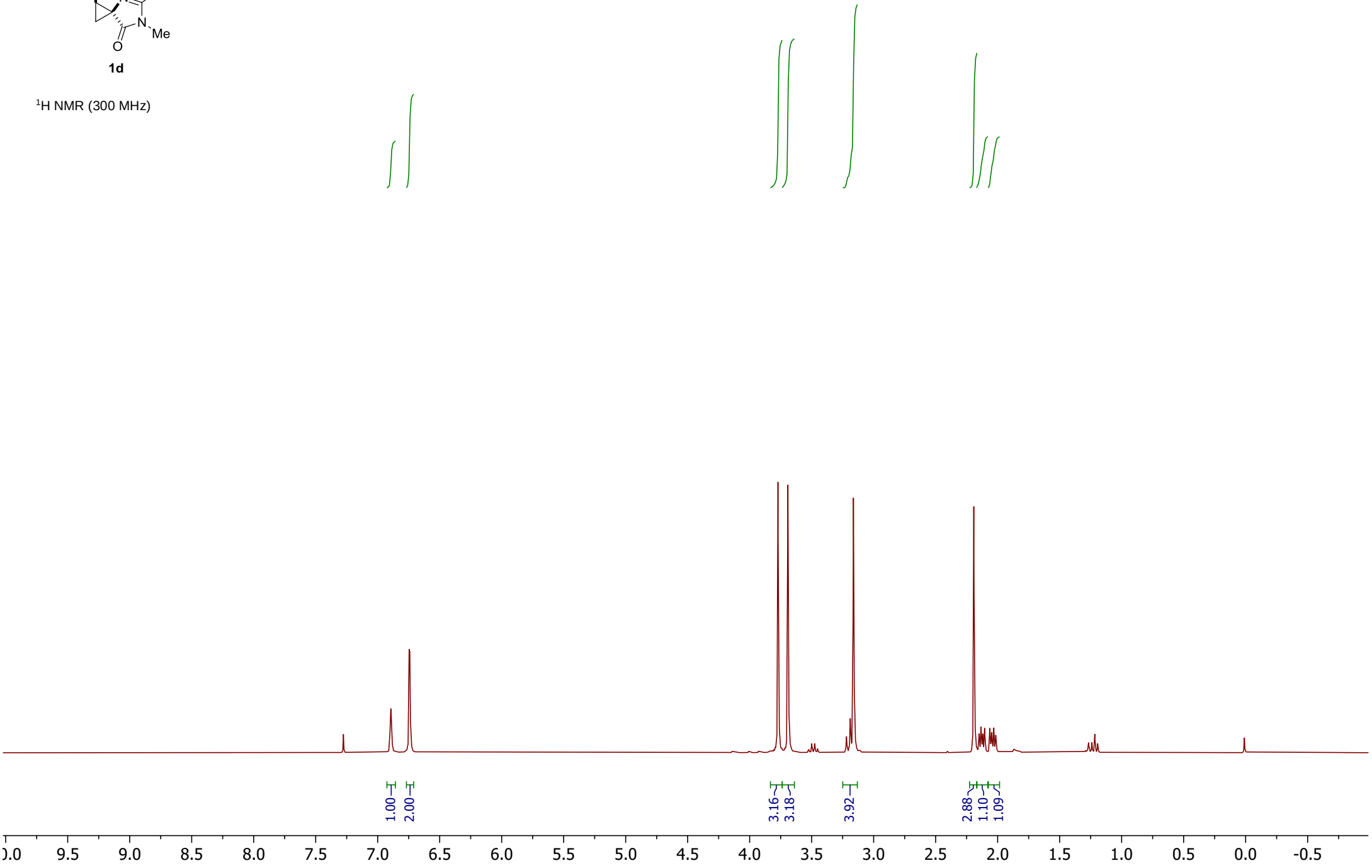
181.49
160.01
159.89
159.60
128.92
117.22
104.00
98.42
56.09
55.43
55.38
30.86
26.92
22.27
15.77

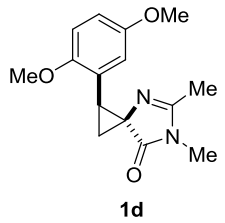

+TOF MS: 0.5482 to 0.7435 min from Sample 47 (iv100) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 1.5e4 cps.
M+H+
275.1393
OMe
MeO
N
Me
N
Me
O
1c
HRMS (ESI+)
Intensity, cps
1.5e4
1.4e4
1.3e4
1.2e4
1.1e4
1.0e4
9000.0
8000.0
7000.0
6000.0
5000.0
4000.0
3000.0
2000.0
1000.0
0.0
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
m/z, Da



1d

^{1}H NMR (300 MHz)



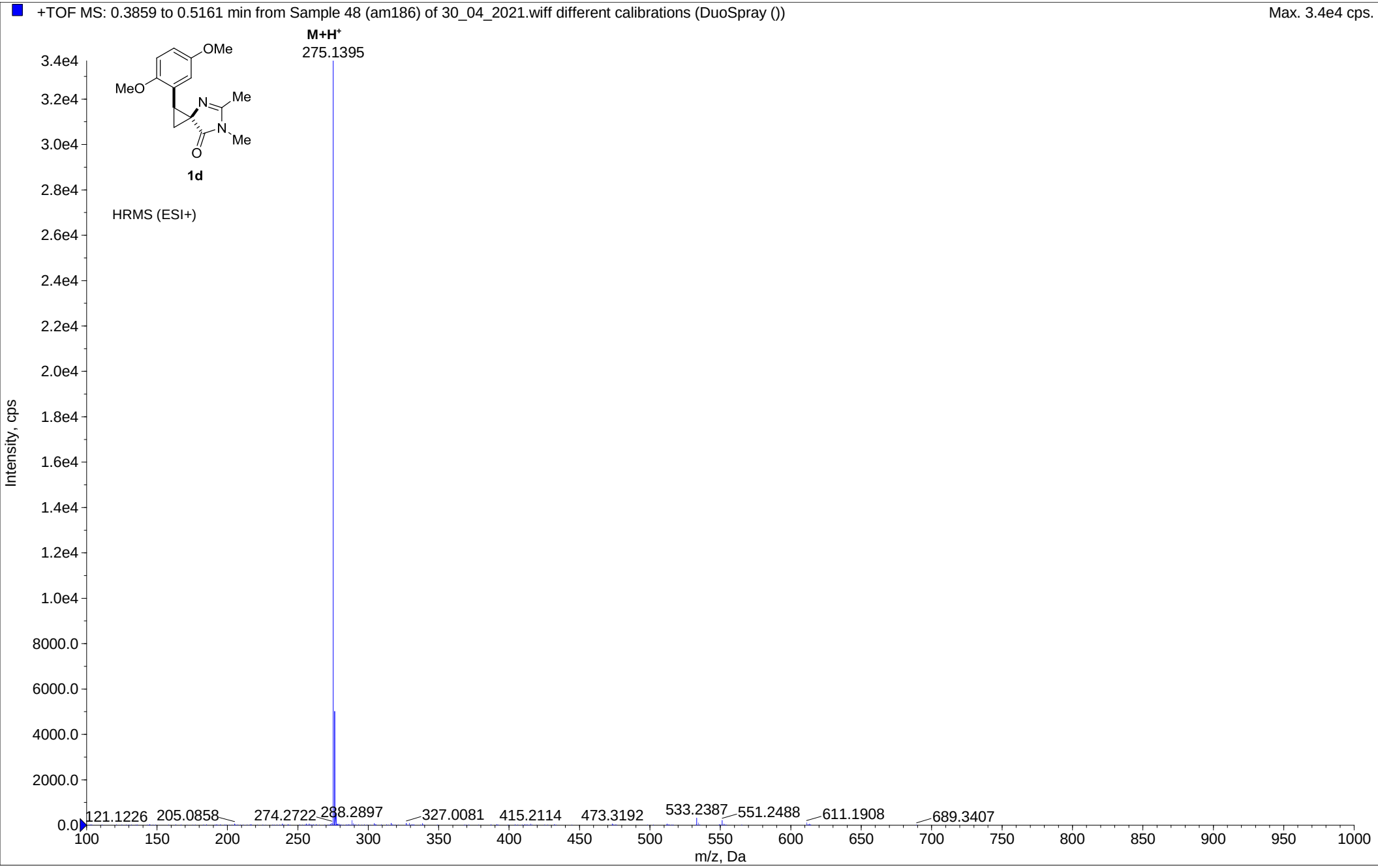


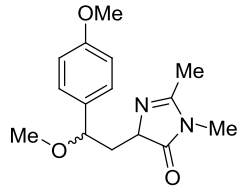
1d

^{13}C NMR (75 MHz)

181.47
160.14
153.48
153.16
126.06
115.28
112.52
111.38
56.18
56.05
55.76
31.22
27.01
22.48
15.82

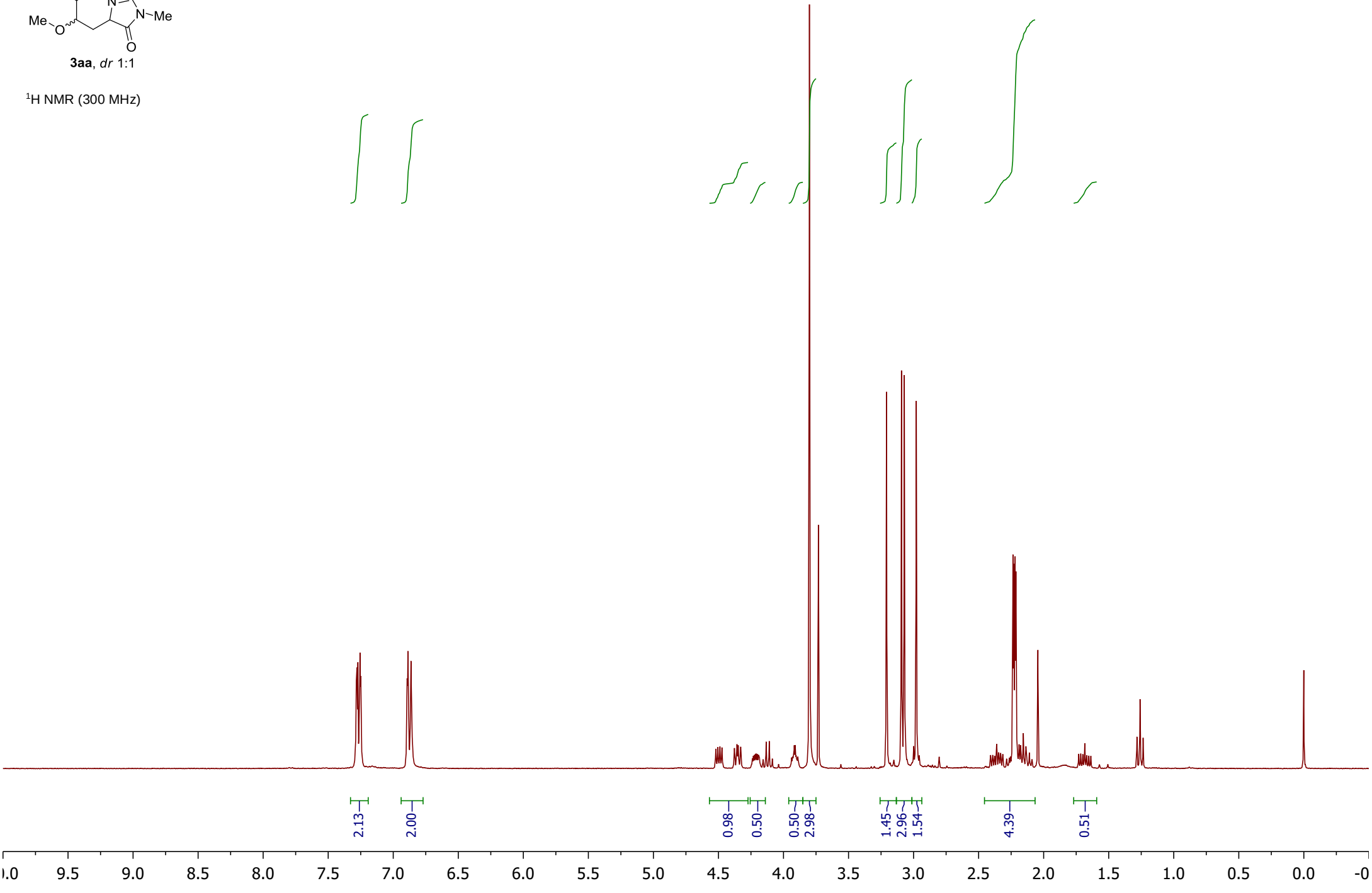
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2

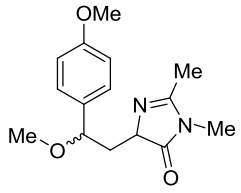

+TOF MS: 0.3859 to 0.5161 min from Sample 48 (am186) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 3.4e4 cps.
M+H+
275.1395
OMe
MeO
N
Me
N
Me
O
1d
HRMS (ESI+)
Intensity, cps
3.4e4
3.2e4
3.0e4
2.8e4
2.6e4
2.4e4
2.2e4
2.0e4
1.8e4
1.6e4
1.4e4
1.2e4
1.0e4
8000.0
6000.0
4000.0
2000.0
0.0
121.1226
205.0858
274.2722
288.2897
327.0081
415.2114
473.3192
533.2387
551.2488
611.1908
689.3407
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
m/z, Da



3aa, *dr* 1:1

^{1}H NMR (300 MHz)



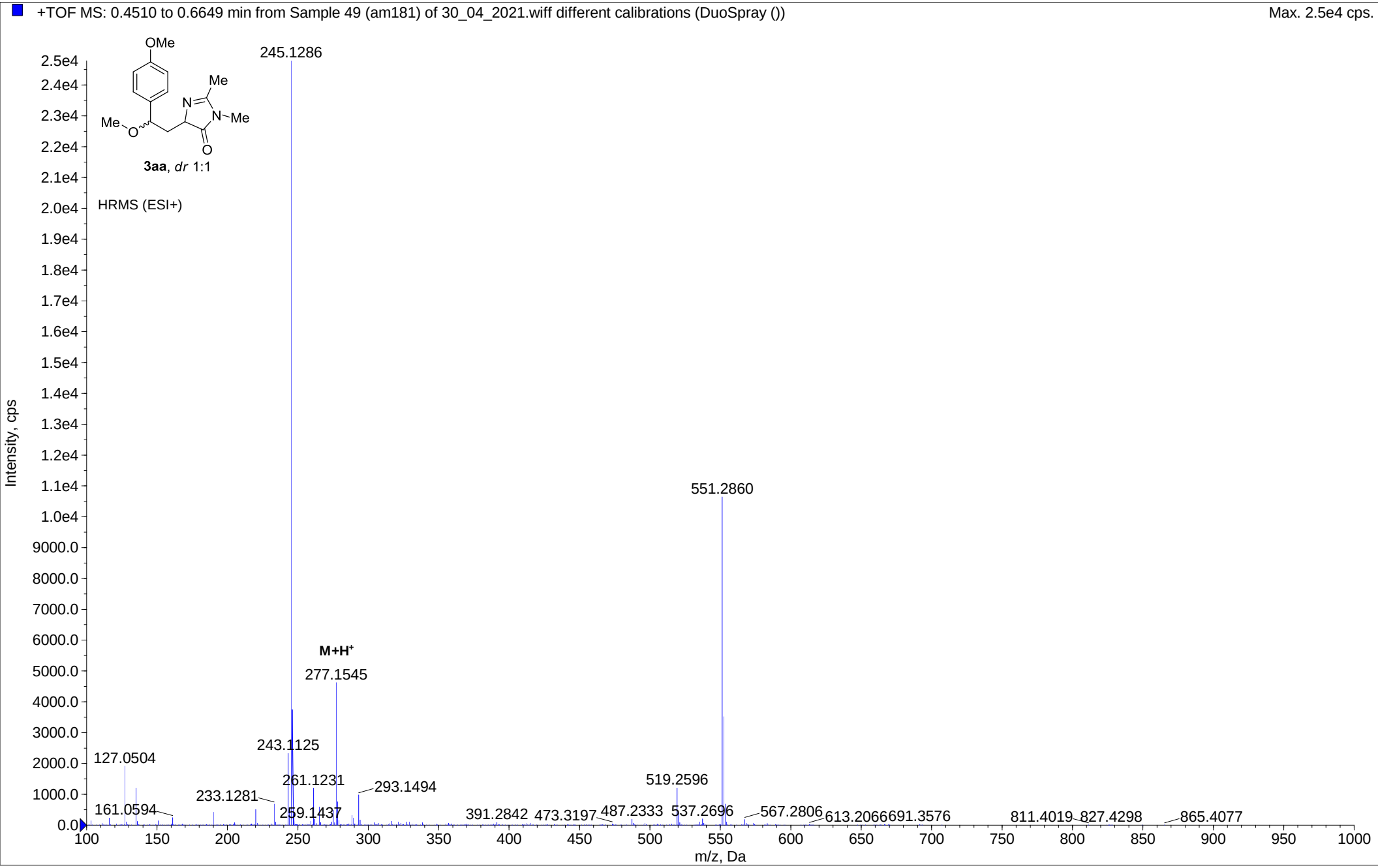


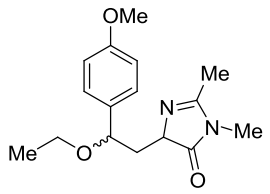
3aa, *dr* 1:1

^{13}C NMR (75 MHz)

183.81
183.54
161.88
161.58
159.39
133.48
133.18
128.32
128.30
113.96
113.87
80.00
79.49
65.12
65.05
56.50
56.37
55.38
39.70
39.22
26.59
15.94

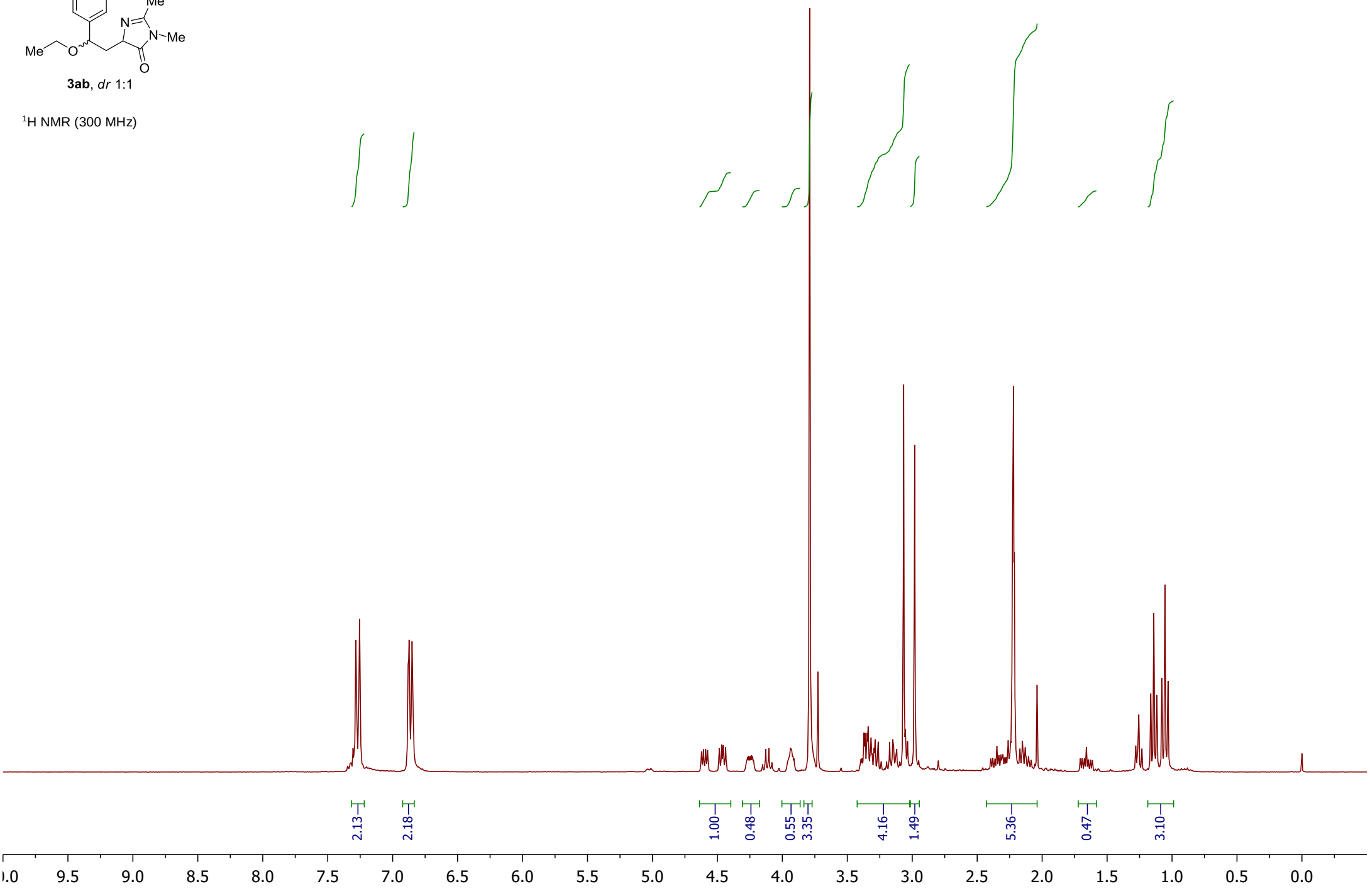
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60

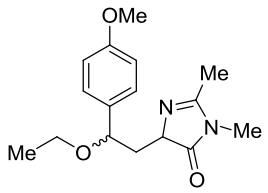

+TOF MS: 0.4510 to 0.6649 min from Sample 49 (am181) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 2.5e4 cps.
OMe
Me
N
N
Me
Me
O
O
3aa, dr 1:1
HRMS (ESI+)
245.1286
M+H+
277.1545
551.2860
243.1125
127.0504
261.1231
293.1494
519.2596
233.1281
161.0594
259.1437
391.2842
473.3197
487.2333
537.2696
567.2806
613.2066
691.3576
811.4019
827.4298
865.4077
Intensity, cps
m/z, Da



3ab, *dr* 1:1

^{1}H NMR (300 MHz)



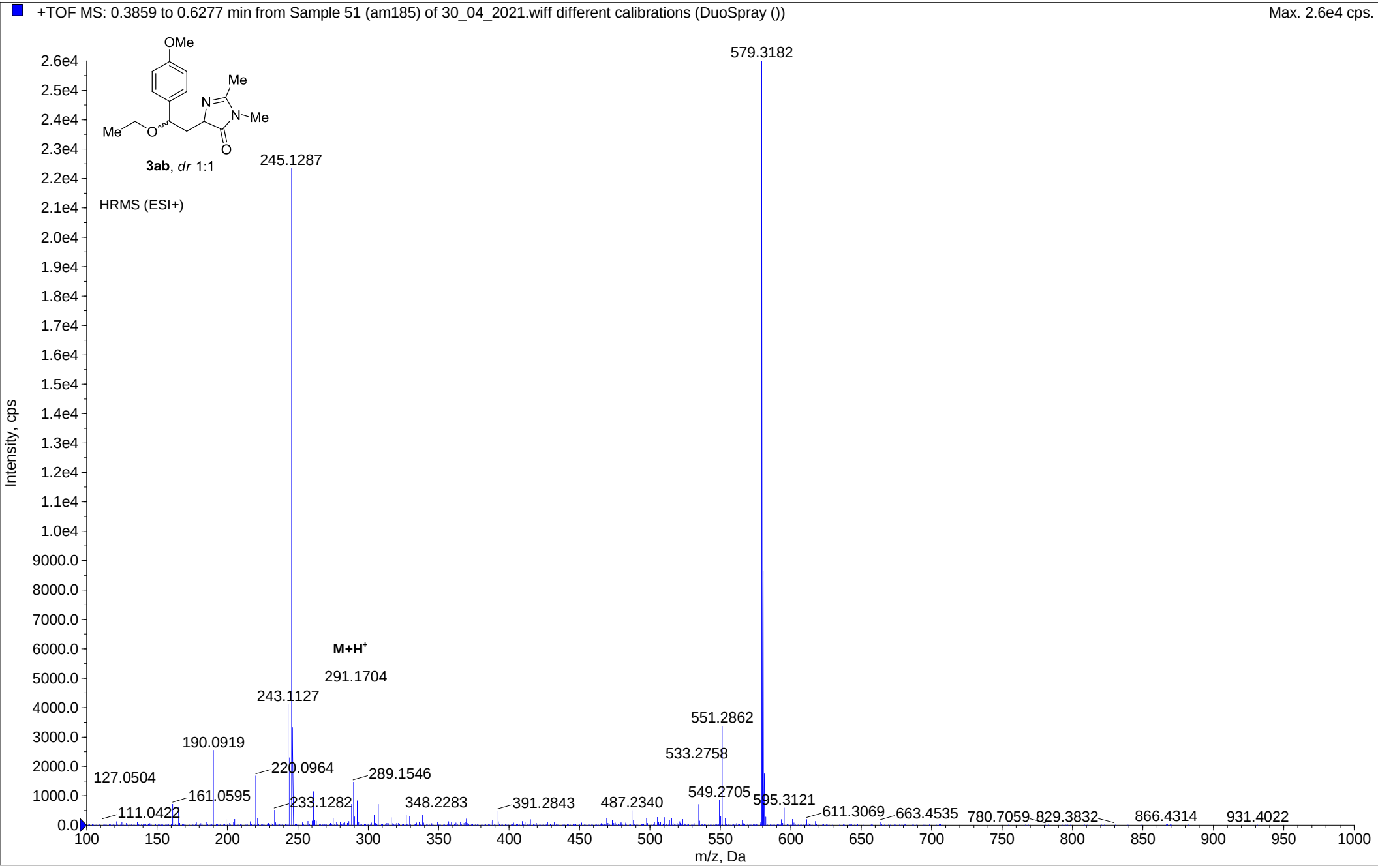


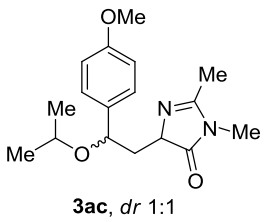
3ab, *dr* 1:1

^{13}C NMR (75 MHz)

183.54
183.43
161.73
161.40
159.10
159.08
134.21
133.85
128.00
127.97
113.74
113.65
77.69
77.53
64.95
64.90
63.85
63.62
55.19
39.81
38.98
26.47
26.42
15.77
15.33
15.24

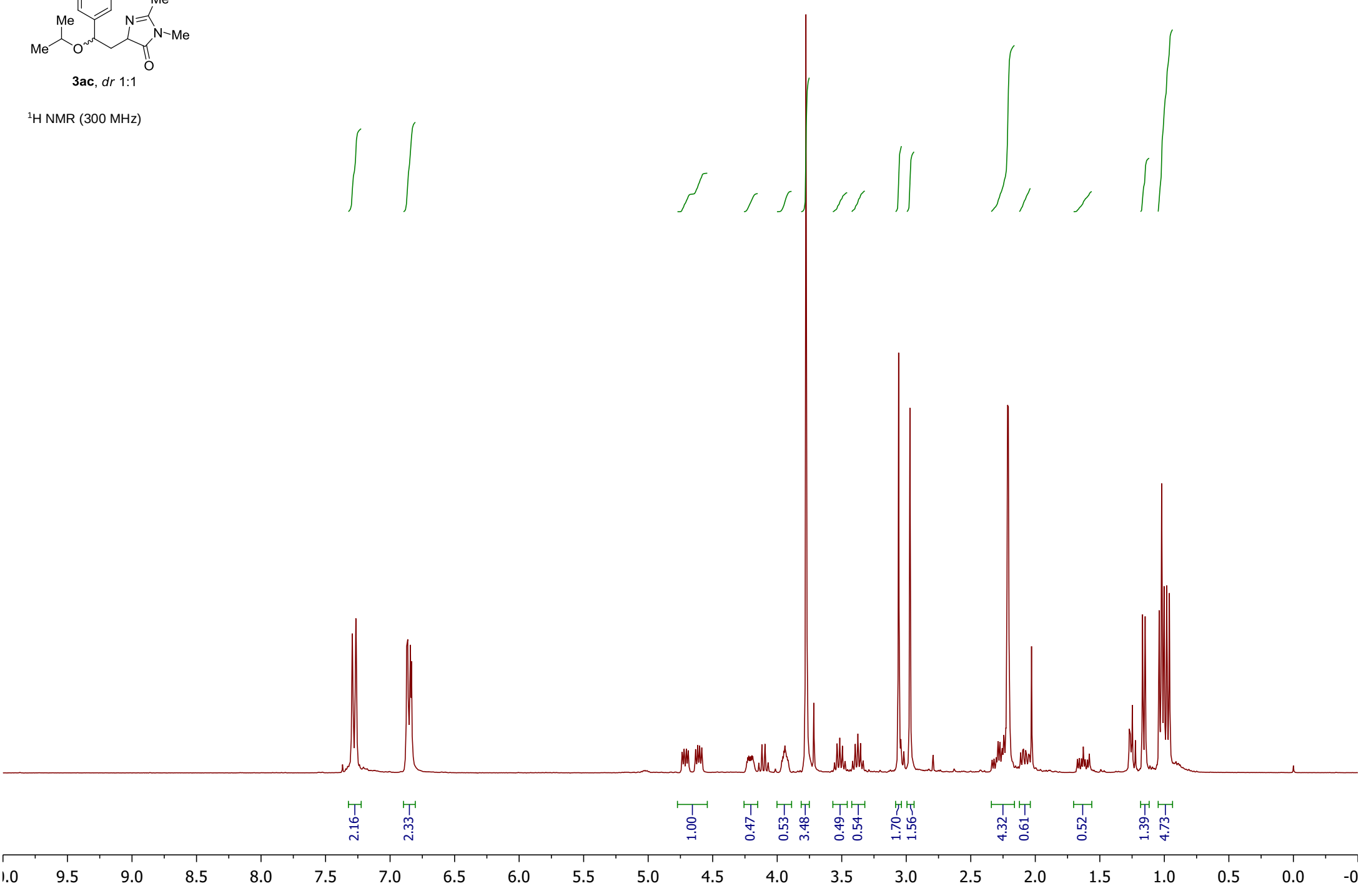
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60

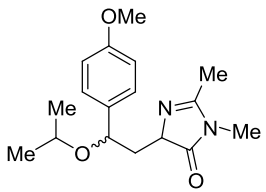

+TOF MS: 0.3859 to 0.6277 min from Sample 51 (am185) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 2.6e4 cps.
OMe
Me
N
N
Me
Me
O
O
3ab, dr 1:1
HRMS (ESI+)
579.3182
245.1287
M+H+
291.1704
243.1127
551.2862
190.0919
533.2758
220.0964
289.1546
127.0504
161.0595
549.2705
595.3121
233.1282
348.2283
391.2843
487.2340
611.3069
663.4535
780.7059
829.3832
866.4314
931.4022
111.0422
Intensity, cps
m/z, Da



3ac, *dr* 1:1

^{1}H NMR (300 MHz)



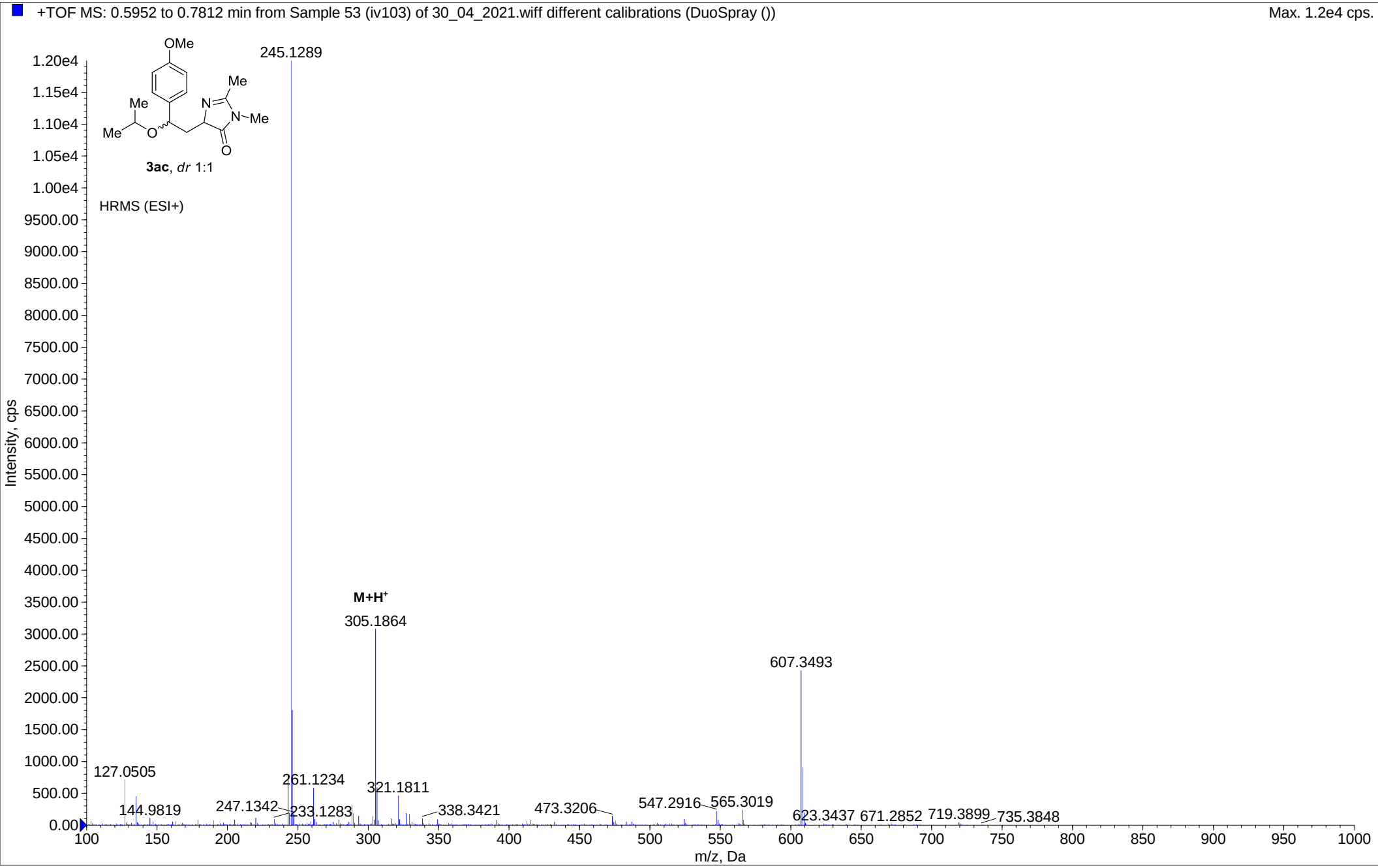


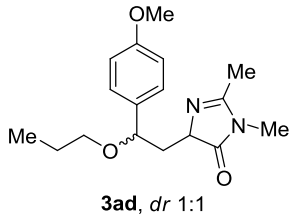
3ac, *dr* 1:1

^{13}C NMR (75 MHz)

183.33
183.26
161.67
161.19
158.89
158.83
134.95
134.44
127.84
127.76
113.56
113.43
74.83
74.30
68.80
67.71
64.87
64.69
55.02
40.14
39.17
26.30
26.26
23.37
23.34
21.40
20.81
15.69
15.60

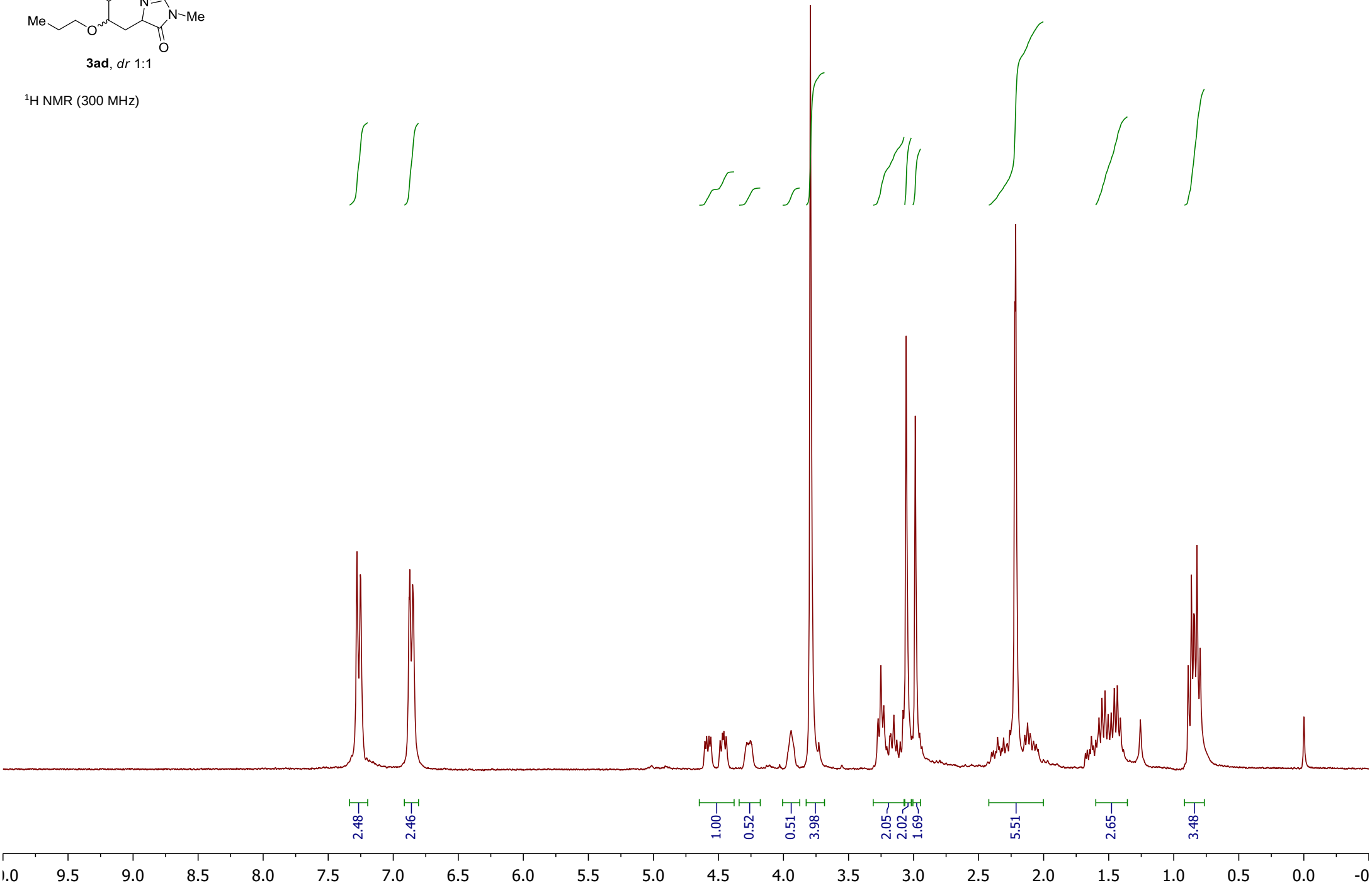
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

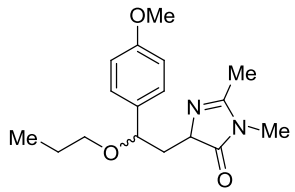

+TOF MS: 0.5952 to 0.7812 min from Sample 53 (iv103) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 1.2e4 cps.
OMe
Me
Me
Me
N
N
Me
O
O
3ac, dr 1:1
HRMS (ESI+)
245.1289
M+H+
305.1864
607.3493
127.0505
144.9819
247.1342
233.1283
261.1234
321.1811
338.3421
473.3206
547.2916
565.3019
623.3437
671.2852
719.3899
735.3848
Intensity, cps
m/z, Da



3ad, *dr* 1:1

^{1}H NMR (300 MHz)

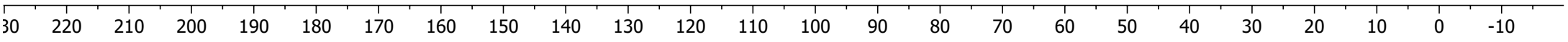


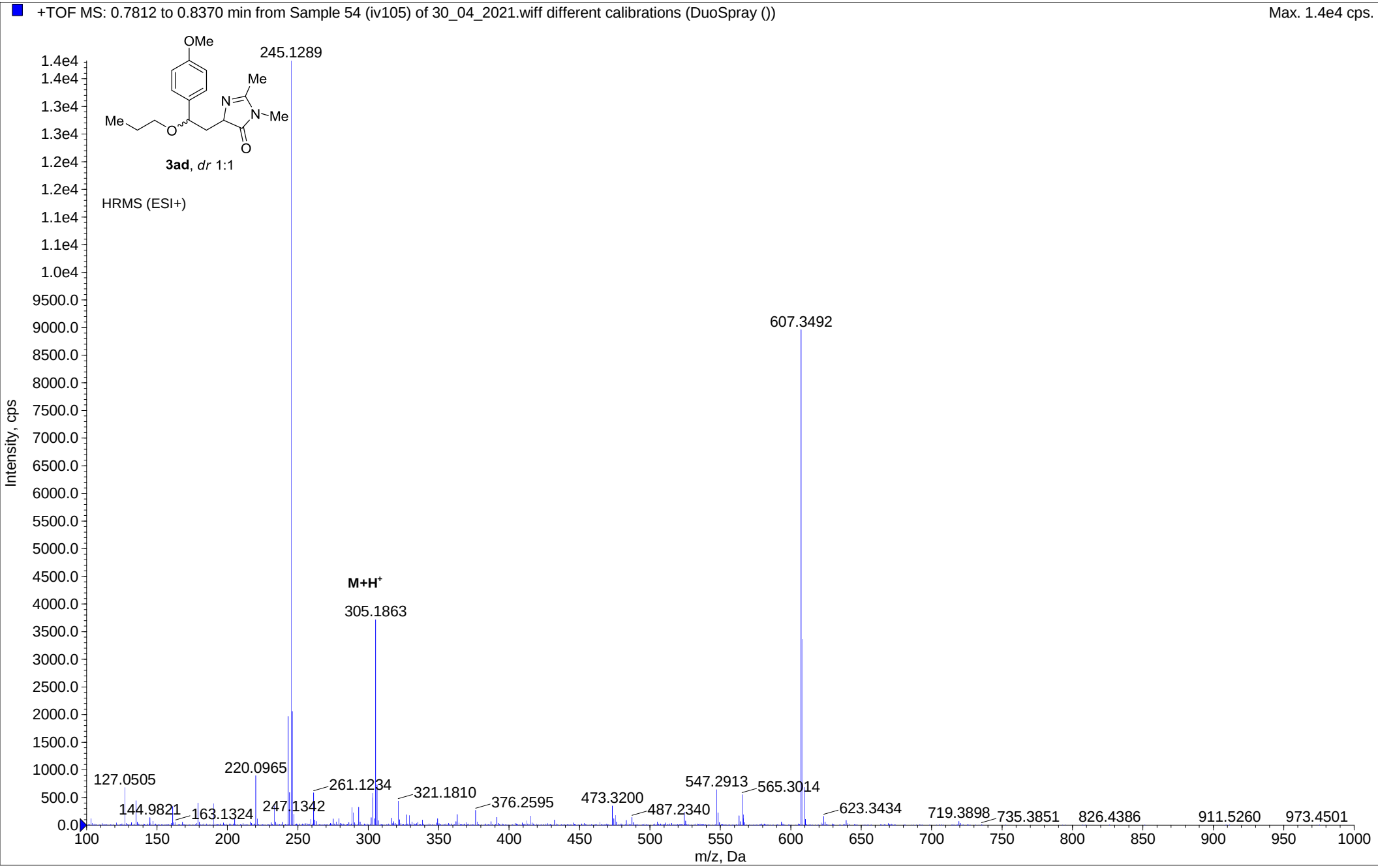


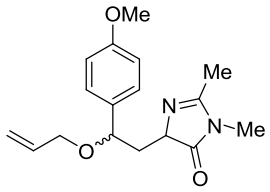
3ad, *dr* 1:1

^{13}C NMR (75 MHz)

183.65
161.85
161.51
159.21
134.43
134.09
128.15
128.10
113.85
113.76
77.94
77.71
70.37
70.26
65.11
65.01
55.32
40.09
39.19
26.59
23.19
15.89
10.78
10.74

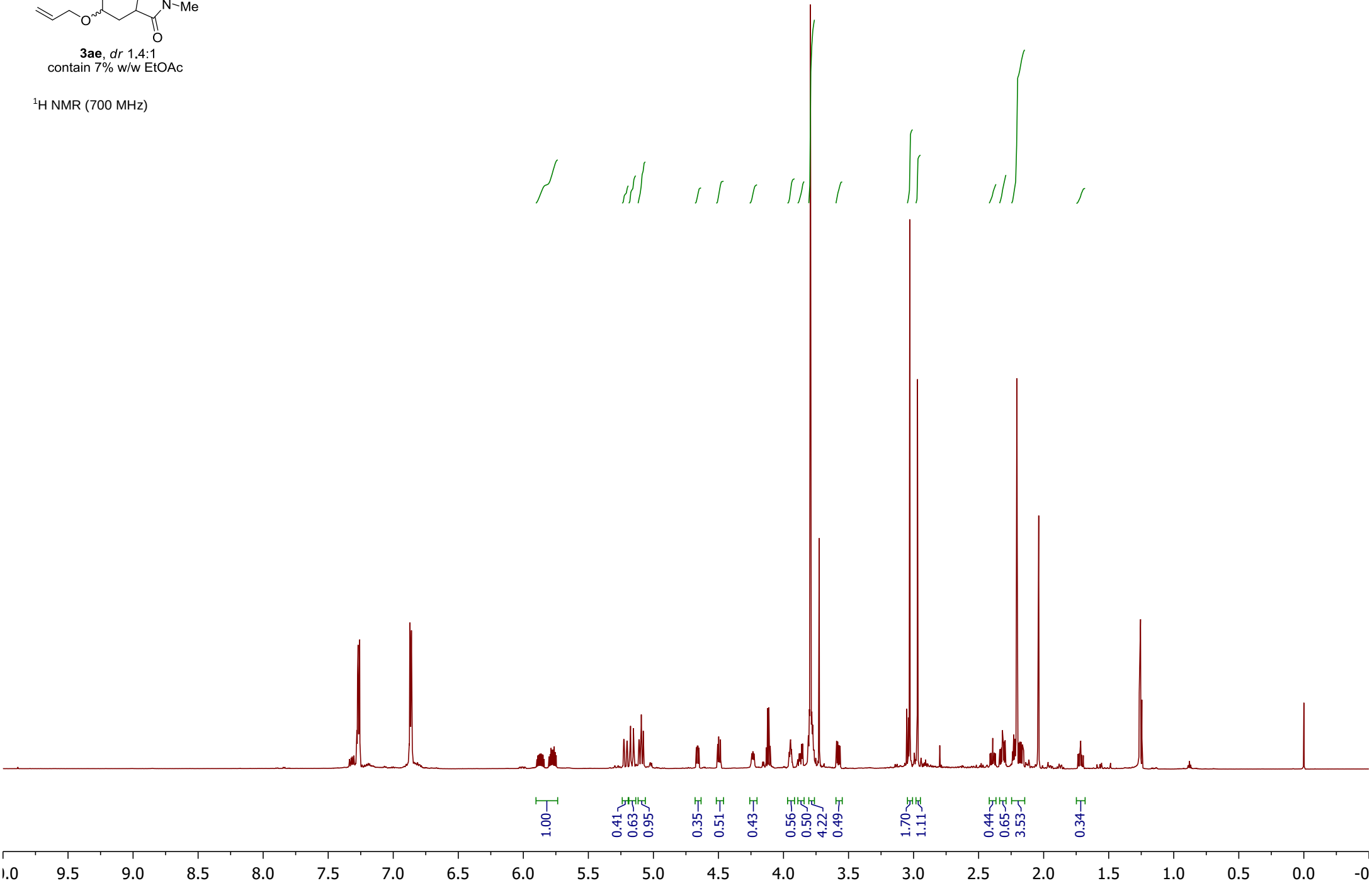



+TOF MS: 0.7812 to 0.8370 min from Sample 54 (iv105) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 1.4e4 cps.
OMe
Me
N
N
Me
Me
O
O
3ad, dr 1:1
HRMS (ESI+)
245.1289
607.3492
M+H+
305.1863
127.0505
220.0965
144.9821
163.1324
247.1342
261.1234
321.1810
376.2595
473.3200
487.2340
547.2913
565.3014
623.3434
719.3898
735.3851
826.4386
911.5260
973.4501
Intensity, cps
m/z, Da



3ae, *dr* 1.4:1
contain 7% w/w EtOAc

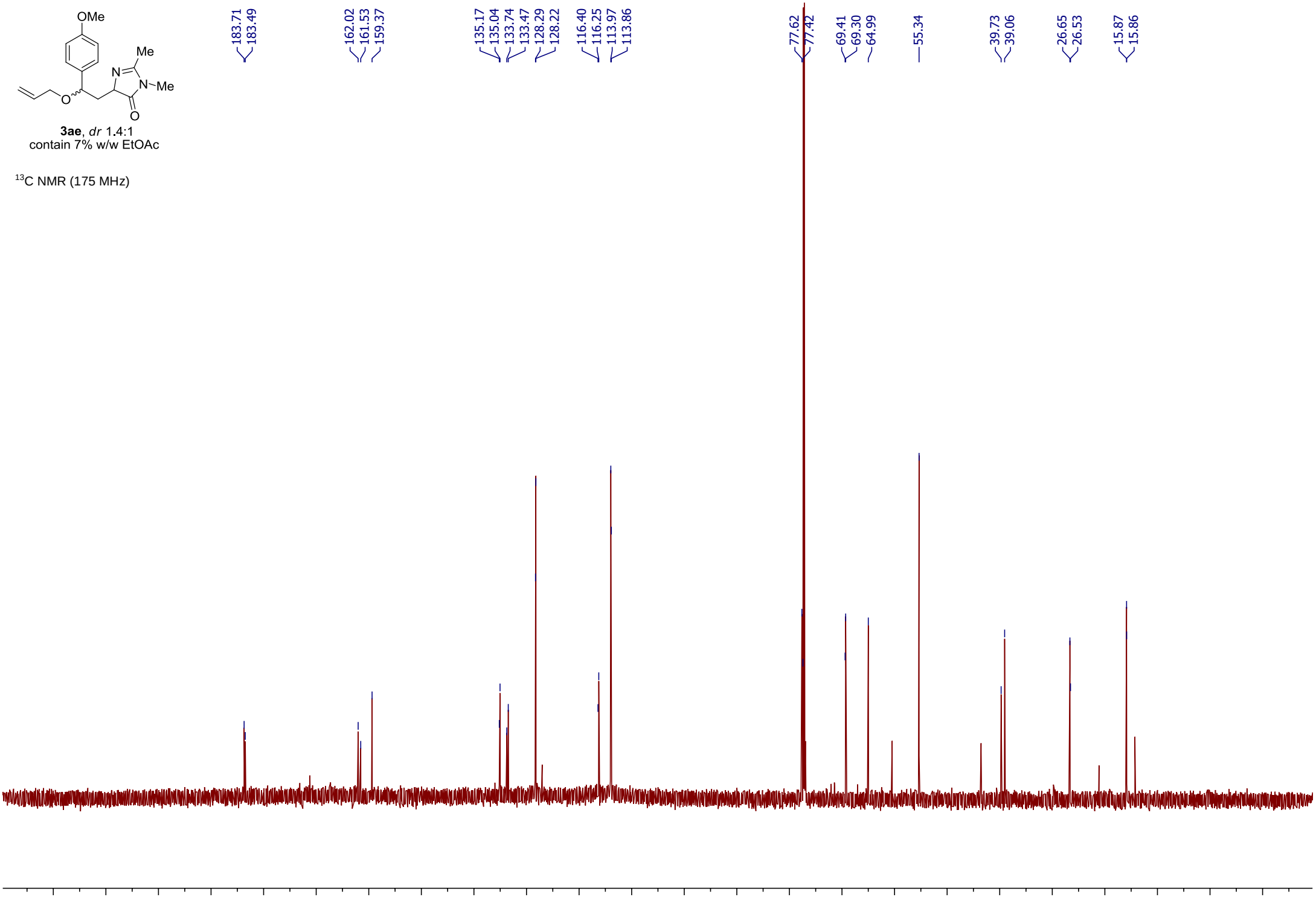
^{1}H NMR (700 MHz)

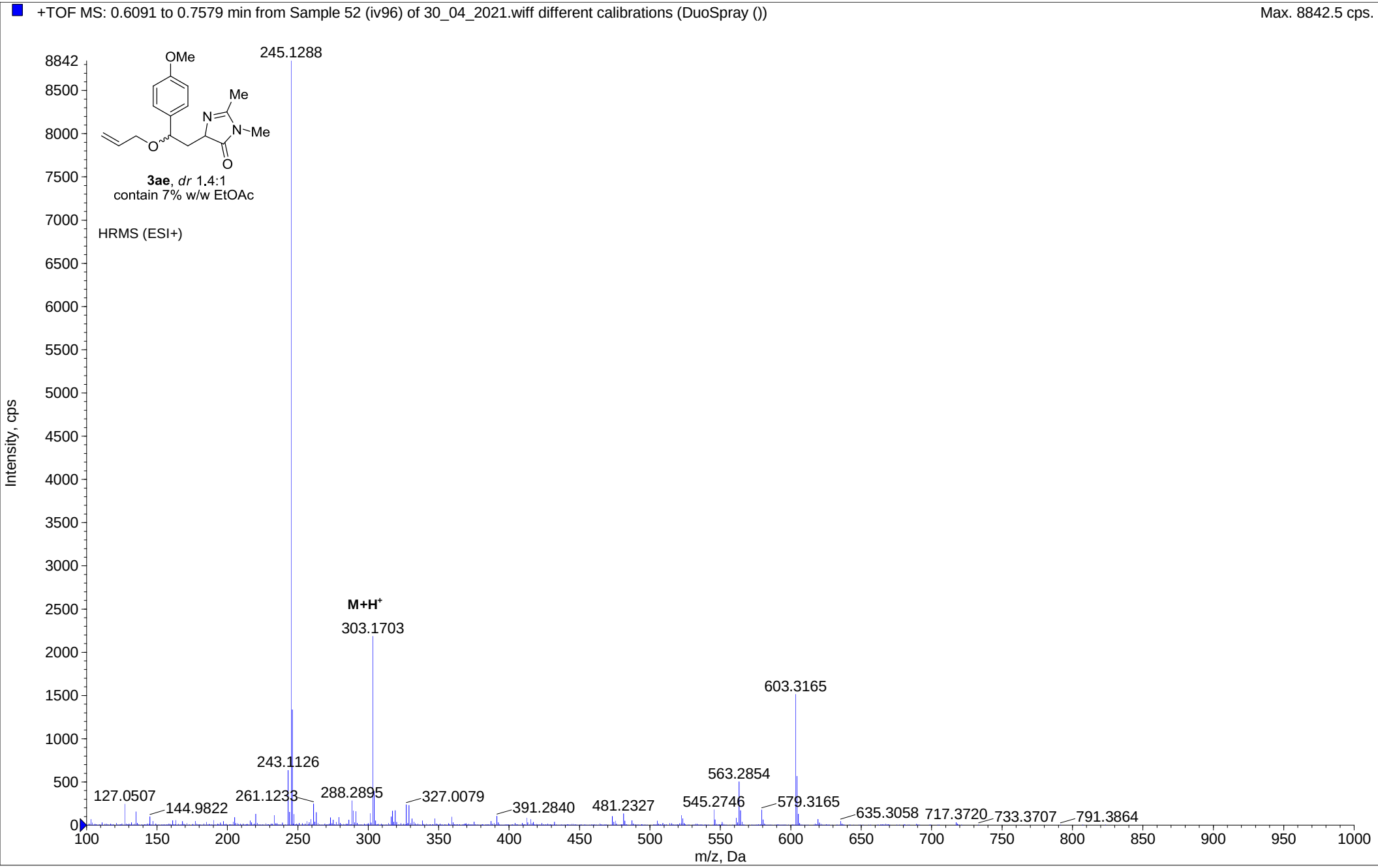


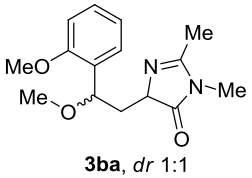
3ae, *dr* 1.4:1
contain 7% w/w EtOAc

^{13}C NMR (175 MHz)

183.71
183.49
162.02
161.53
159.37
135.17
135.04
133.74
133.47
128.29
128.22
116.40
116.25
113.97
113.86
77.62
77.42
69.41
69.30
64.99
55.34
39.73
39.06
26.65
26.53
15.87
15.86

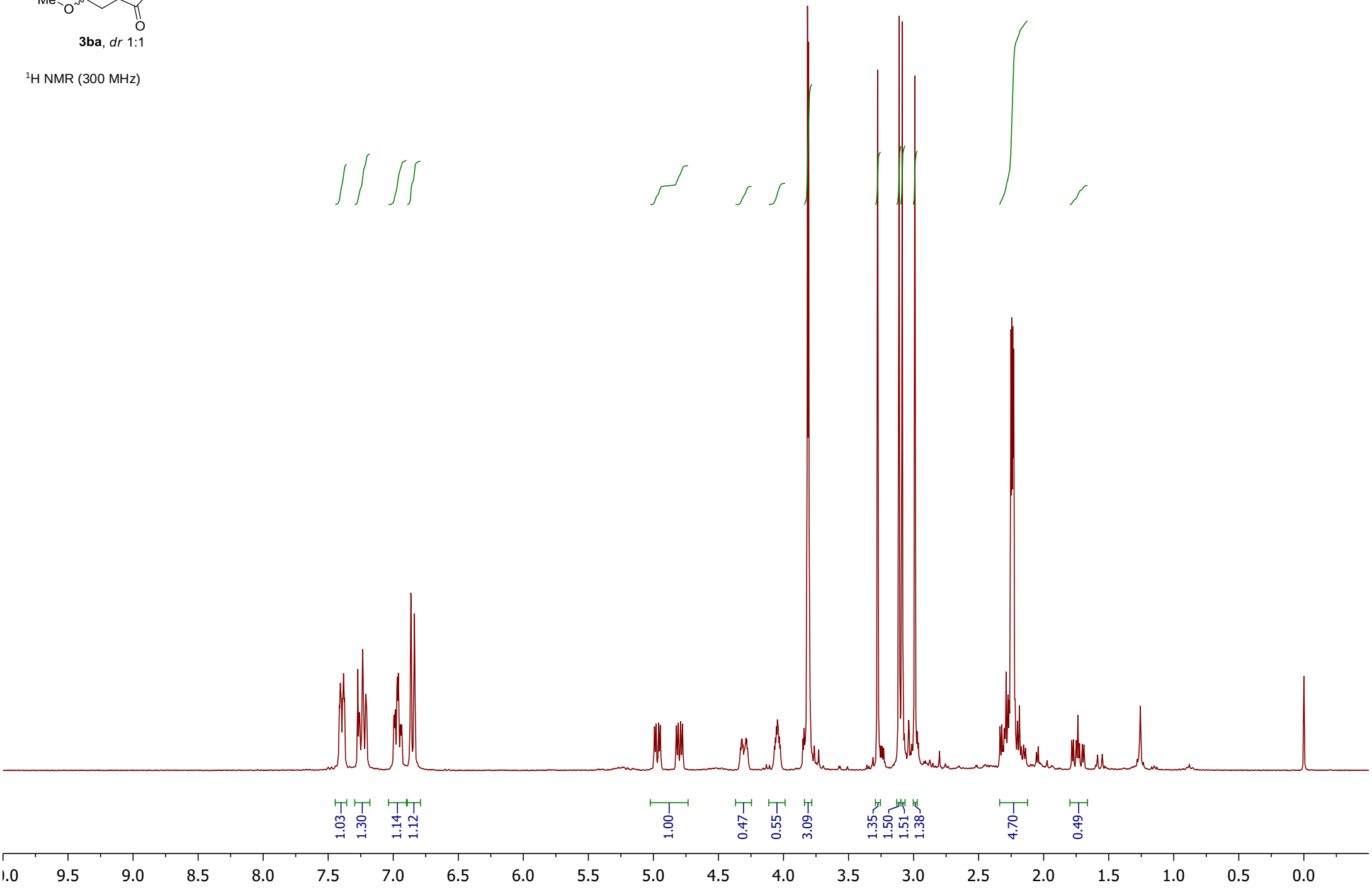


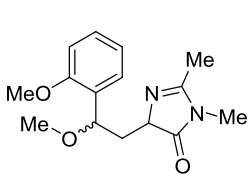

+TOF MS: 0.6091 to 0.7579 min from Sample 52 (iv96) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 8842.5 cps.
OMe
Me
N
N
Me
O
O
3ae, dr 1.4:1
contain 7% w/w EtOAc
HRMS (ESI+)
245.1288
M+H+
303.1703
603.3165
243.1126
563.2854
127.0507
144.9822
261.1233
288.2895
327.0079
391.2840
481.2327
545.2746
579.3165
635.3058
717.3720
733.3707
791.3864
Intensity, cps
m/z, Da



3ba, *dr* 1:1

^{1}H NMR (300 MHz)

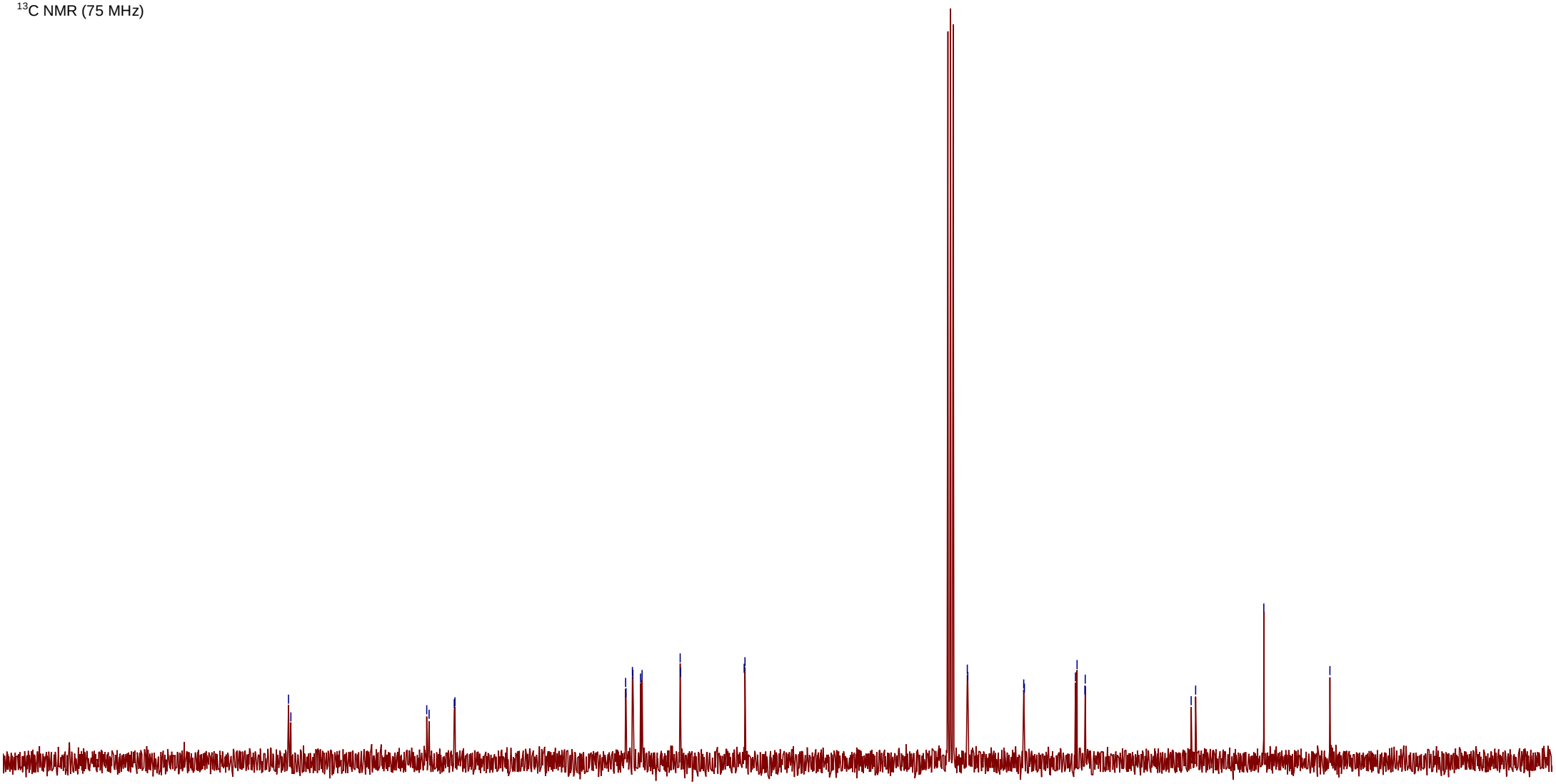




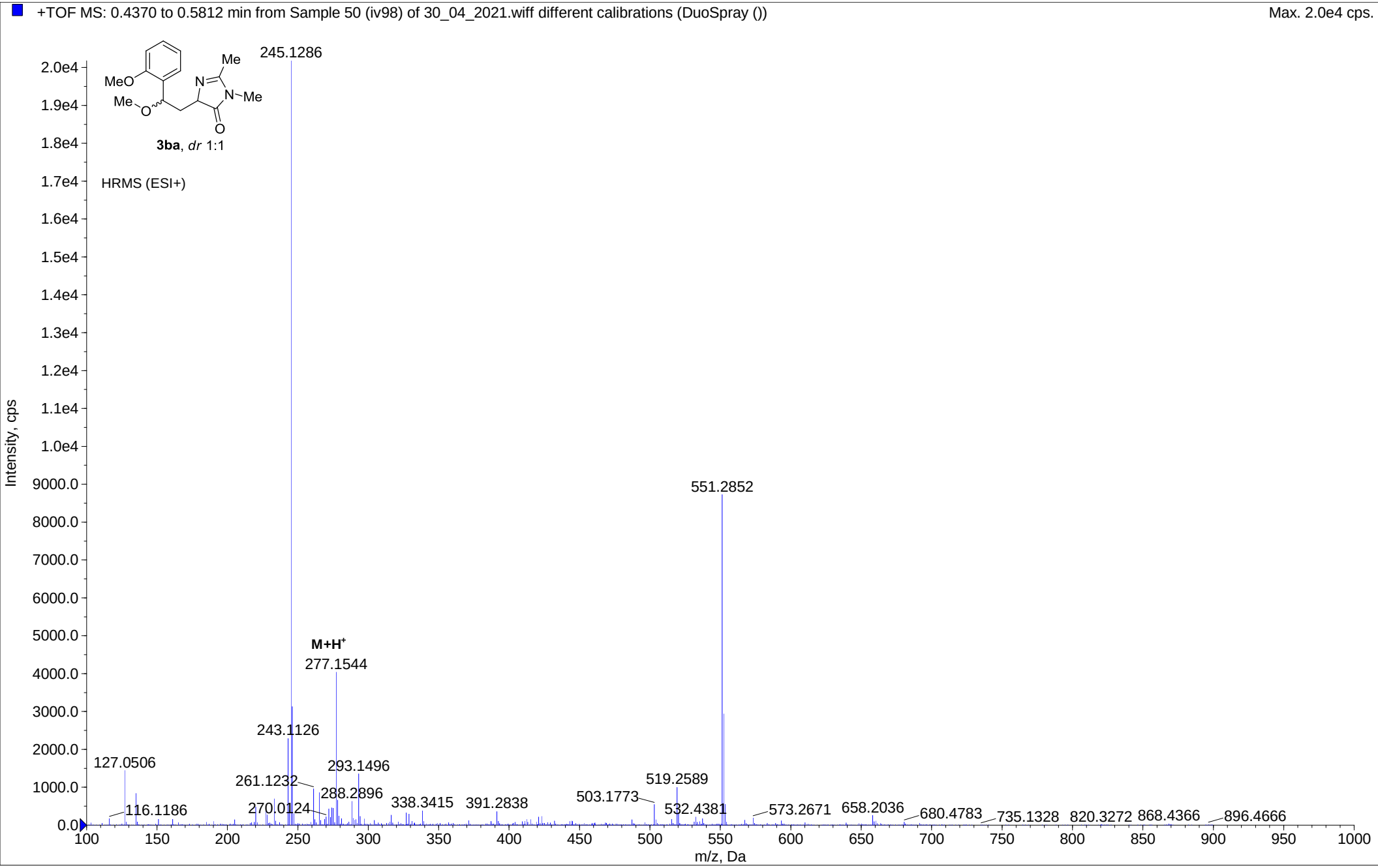
3ba, *dr* 1:1

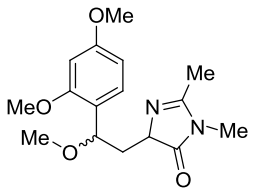
^{13}C NMR (75 MHz)

184.09
183.71
161.76
161.38
157.32
157.21
129.64
129.58
128.54
128.47
127.23
126.98
120.83
120.76
110.49
110.36
74.45
74.37
65.34
65.23
56.98
56.72
55.46
55.40
38.29
37.57
26.56
15.88



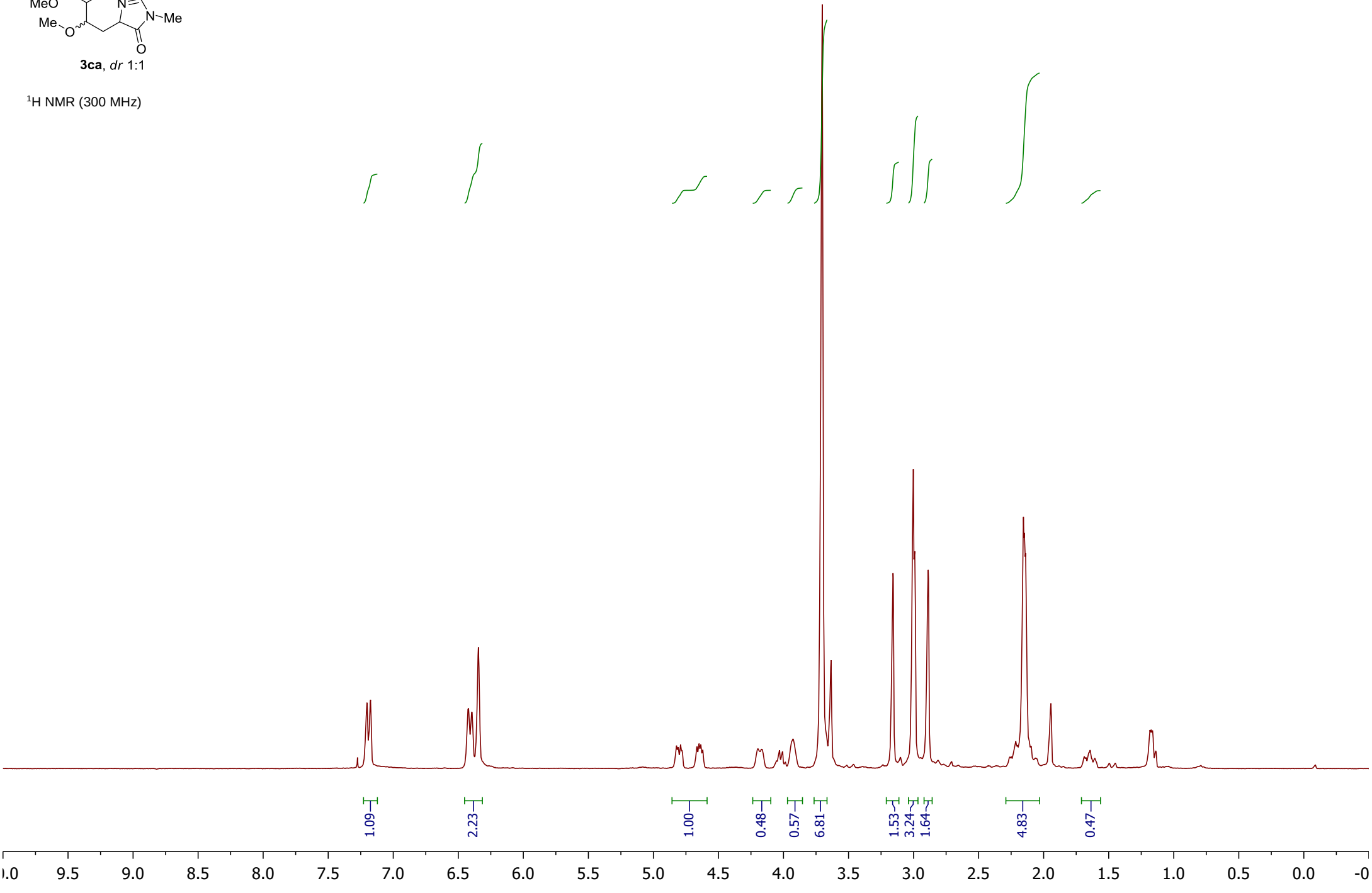
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

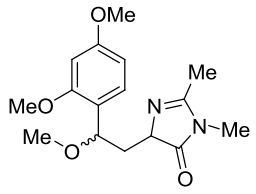

+TOF MS: 0.4370 to 0.5812 min from Sample 50 (iv98) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 2.0e4 cps.
3ba, dr 1:1
HRMS (ESI+)
Intensity, cps
m/z, Da
M+H+
245.1286
277.1544
551.2852
243.1126
293.1496
261.1232
288.2896
519.2589
127.0506
116.1186
270.0124
338.3415
391.2838
503.1773
532.4381
573.2671
658.2036
680.4783
735.1328
820.3272
868.4366
896.4666



3ca, *dr* 1:1

^{1}H NMR (300 MHz)

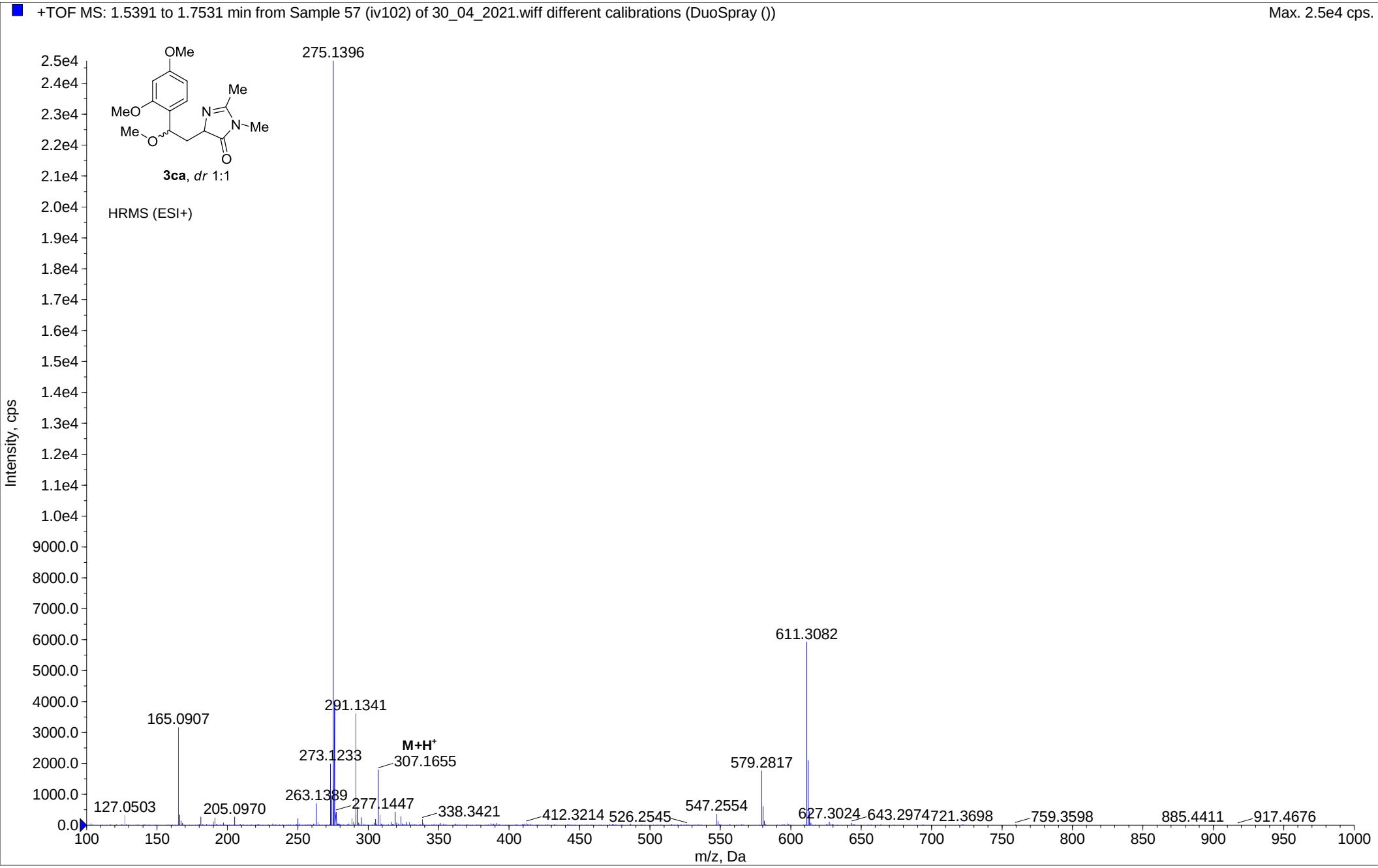


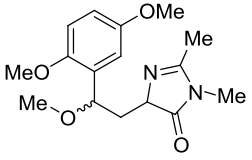


3ca, *dr* 1:1

^{13}C NMR (75 MHz)

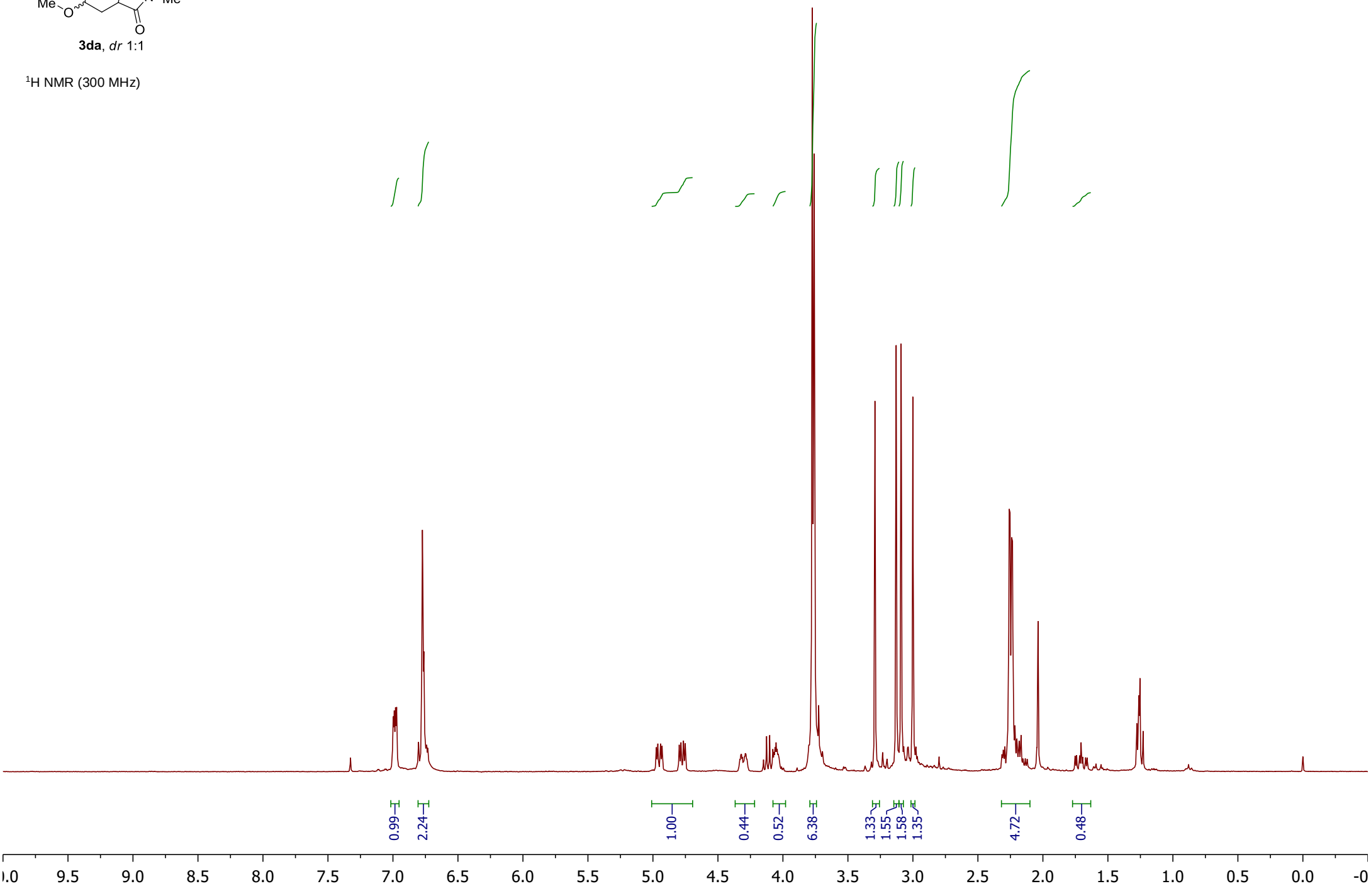
183.78
183.41
161.51
161.16
160.08
160.03
158.22
158.11
127.87
127.57
121.59
121.55
104.24
104.17
98.13
98.08
73.93
73.81
65.06
64.97
56.40
56.19
55.21
55.17
55.13
38.05
37.46
26.26
15.62
15.59

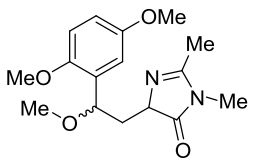

+TOF MS: 1.5391 to 1.7531 min from Sample 57 (iv102) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 2.5e4 cps.
OMe
MeO
Me
Me
N
N
Me
O
O
3ca, dr 1:1
HRMS (ESI+)
275.1396
611.3082
291.1341
165.0907
M+H+
273.1233
307.1655
579.2817
263.1389
277.1447
127.0503
205.0970
338.3421
412.3214
526.2545
547.2554
627.3024
643.2974
721.3698
759.3598
885.4411
917.4676
Intensity, cps
m/z, Da



3da, *dr* 1:1

^{1}H NMR (300 MHz)



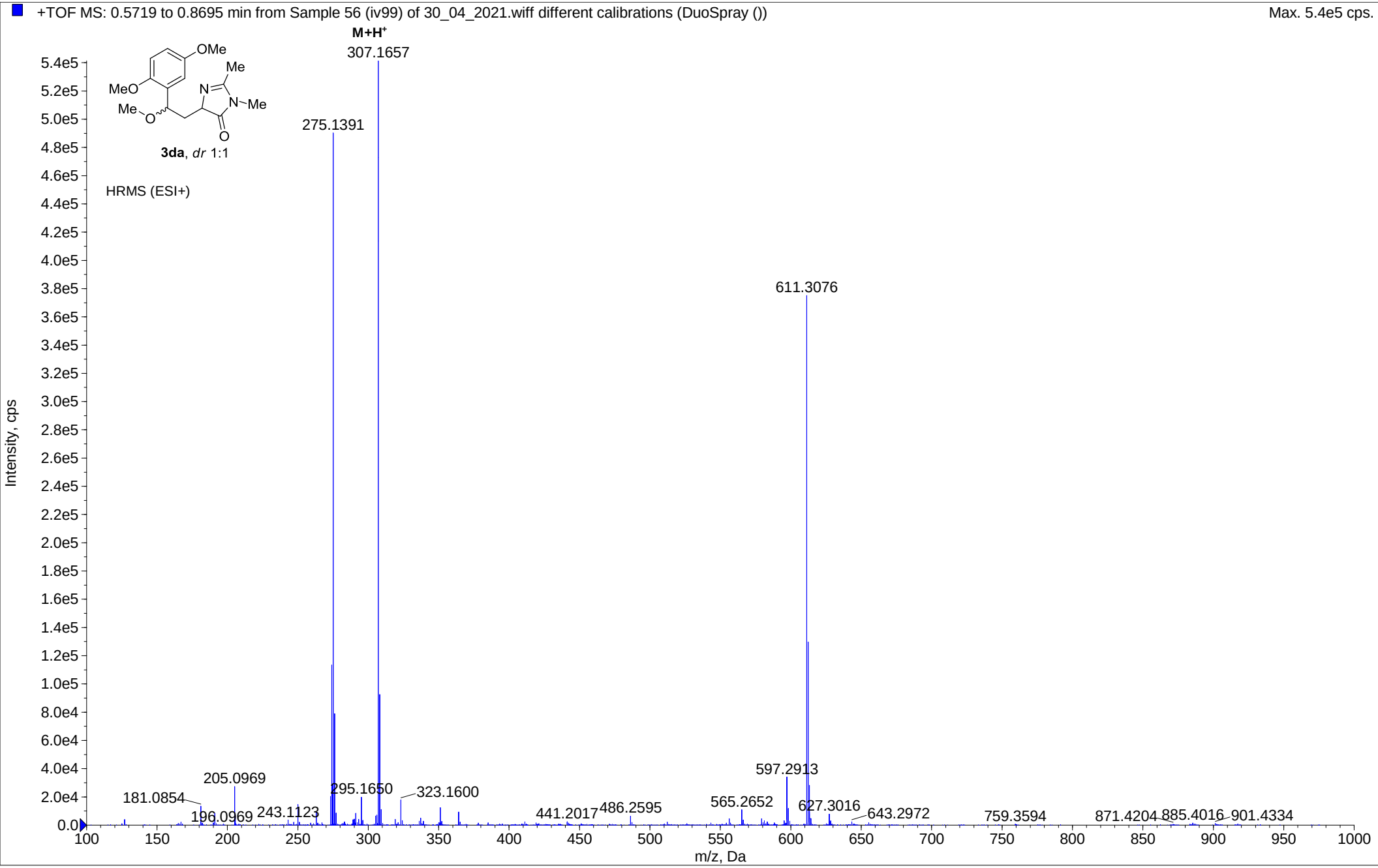


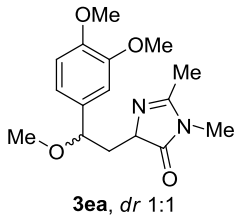
3da, *dr* 1:1

^{13}C NMR (75 MHz)

183.84
183.49
161.73
161.36
153.94
153.88
151.31
151.20
130.81
130.68
113.30
113.26
112.33
112.01
111.66
111.50
74.30
74.13
65.11
65.00
56.90
56.68
55.97
55.87
55.70
55.66
38.34
37.52
26.40
15.73
15.70

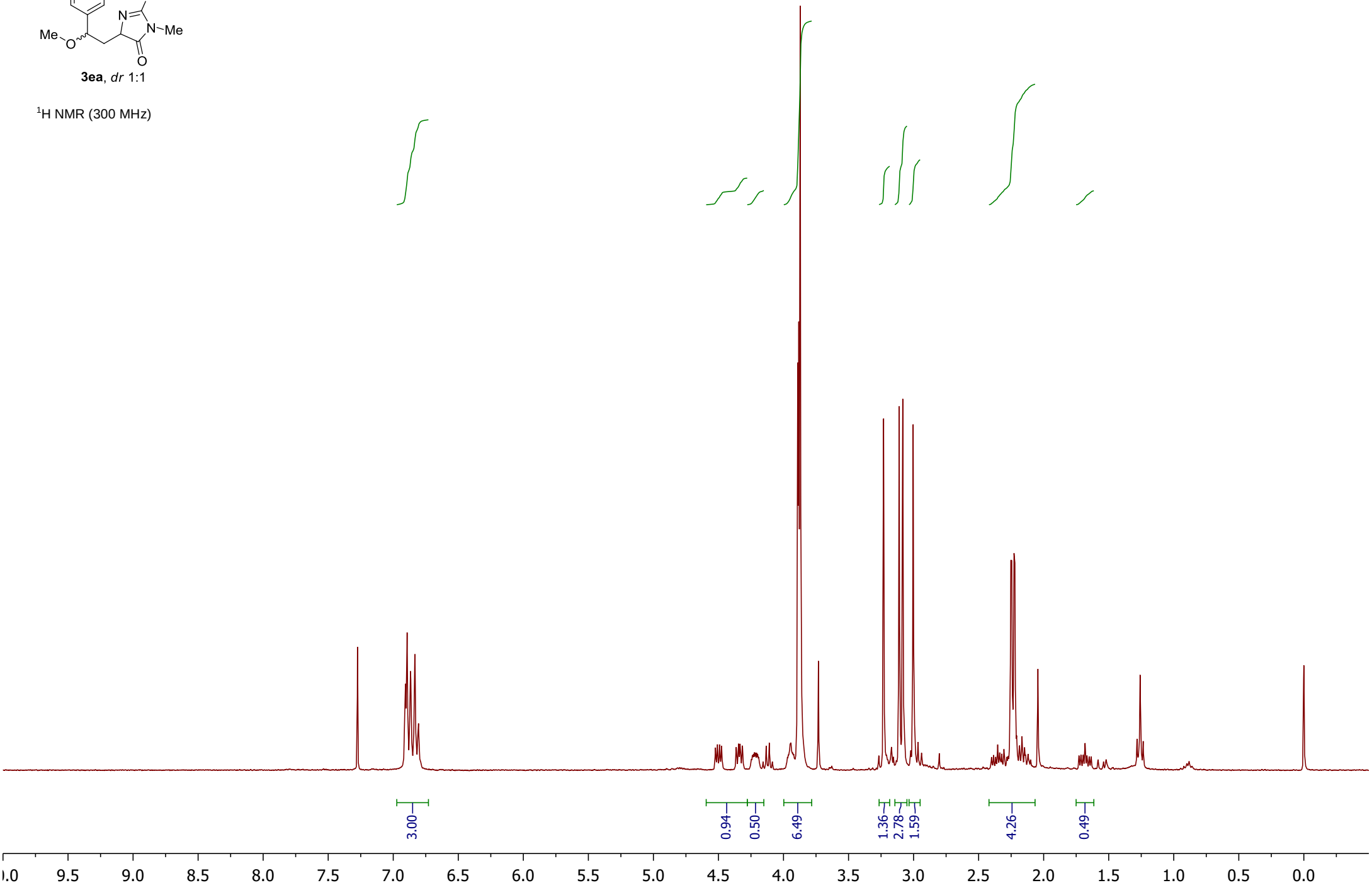
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2

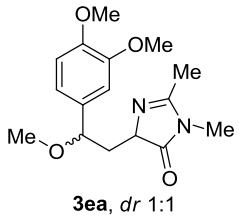

+TOF MS: 0.5719 to 0.8695 min from Sample 56 (iv99) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 5.4e5 cps.
M+H+
307.1657
275.1391
611.3076
597.2913
205.0969
181.0854
196.0969
243.1123
295.1650
323.1600
441.2017
486.2595
565.2652
627.3016
643.2972
759.3594
871.4204
885.4016
901.4334
OMe
Me
MeO
N
N
Me
Me
O
O
3da, dr 1:1
HRMS (ESI+)
Intensity, cps
m/z, Da



3ea, *dr* 1:1

^{1}H NMR (300 MHz)



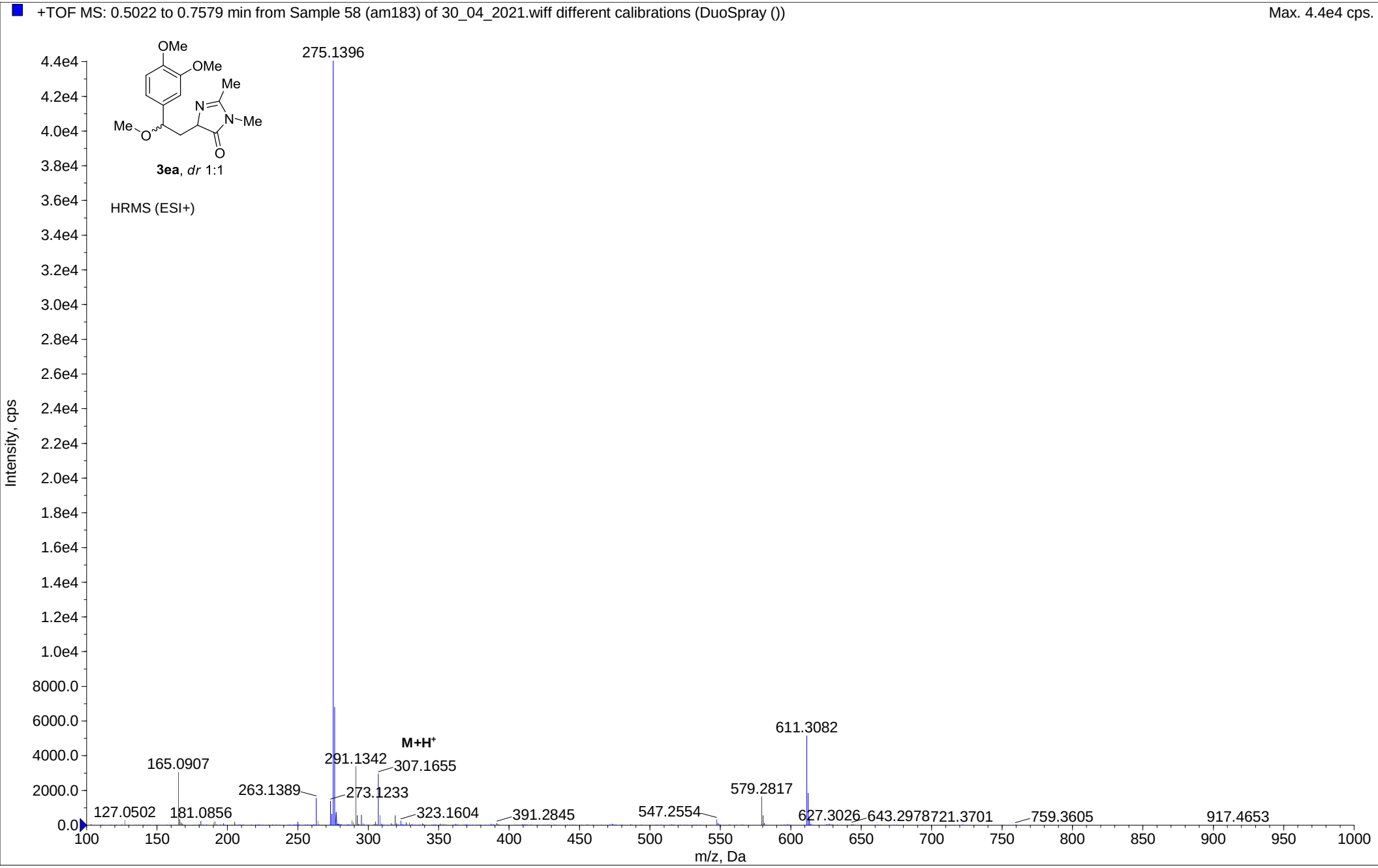


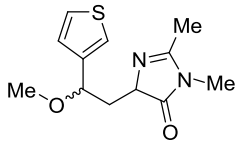
3ea, *dr* 1:1

^{13}C NMR (75 MHz)

183.82
183.55
161.97
161.65
149.35
149.30
148.73
134.07
133.77
119.66
119.62
110.94
110.85
109.54
109.43
80.29
79.79
65.10
65.04
56.59
56.48
56.01
39.81
39.30
26.61
15.94

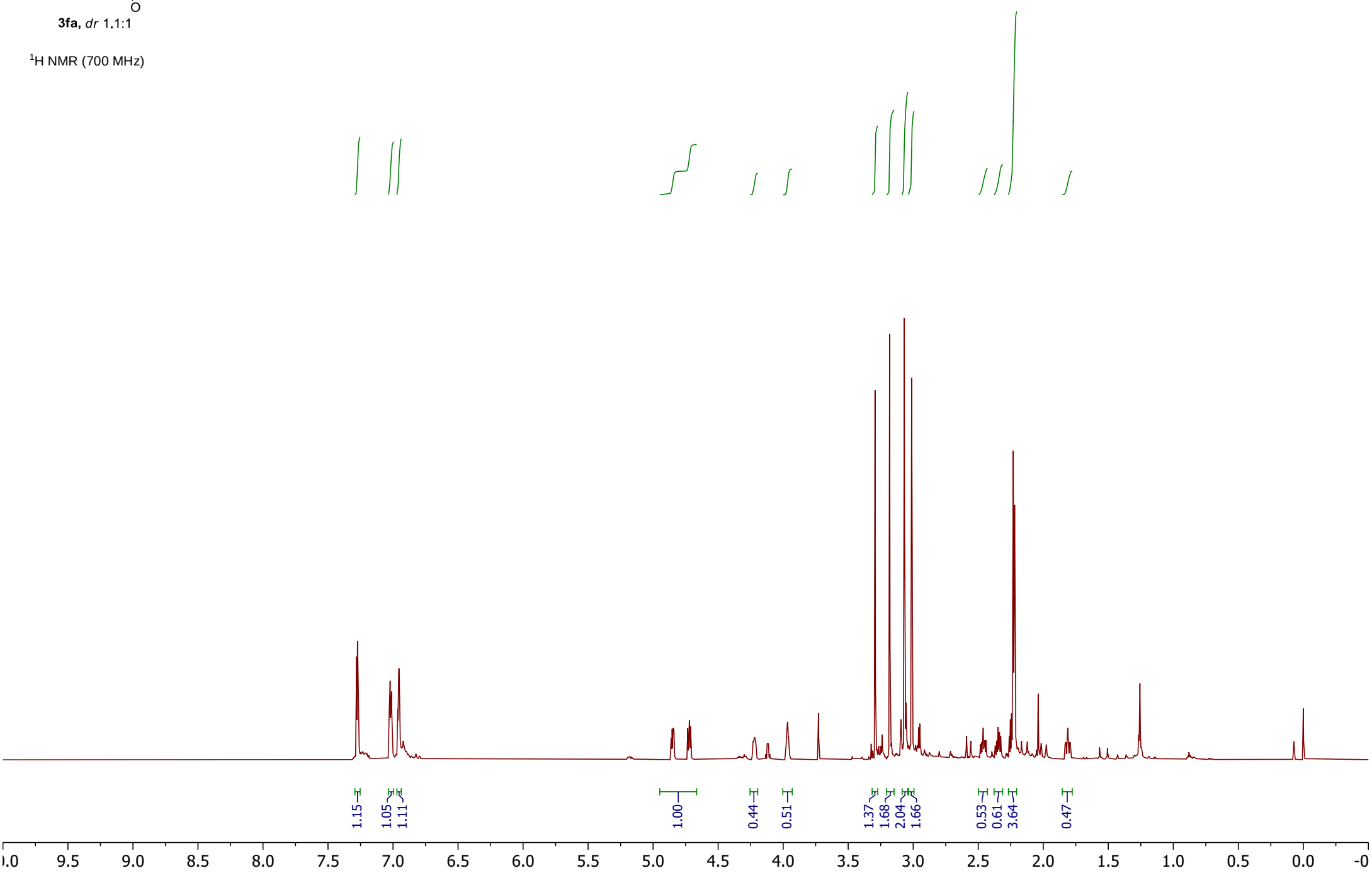
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60

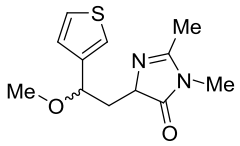

+TOF MS: 0.5022 to 0.7579 min from Sample 58 (am183) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 4.4e4 cps.
OMe
OMe
Me
N
N
Me
Me
O
O
3ea, dr 1:1
HRMS (ESI+)
275.1396
M+H+
611.3082
165.0907
291.1342
307.1655
263.1389
273.1233
579.2817
127.0502
181.0856
323.1604
391.2845
547.2554
627.3026
643.2978
721.3701
759.3605
917.4653
Intensity, cps
m/z, Da



3fa, *dr* 1.1:1

^{1}H NMR (700 MHz)

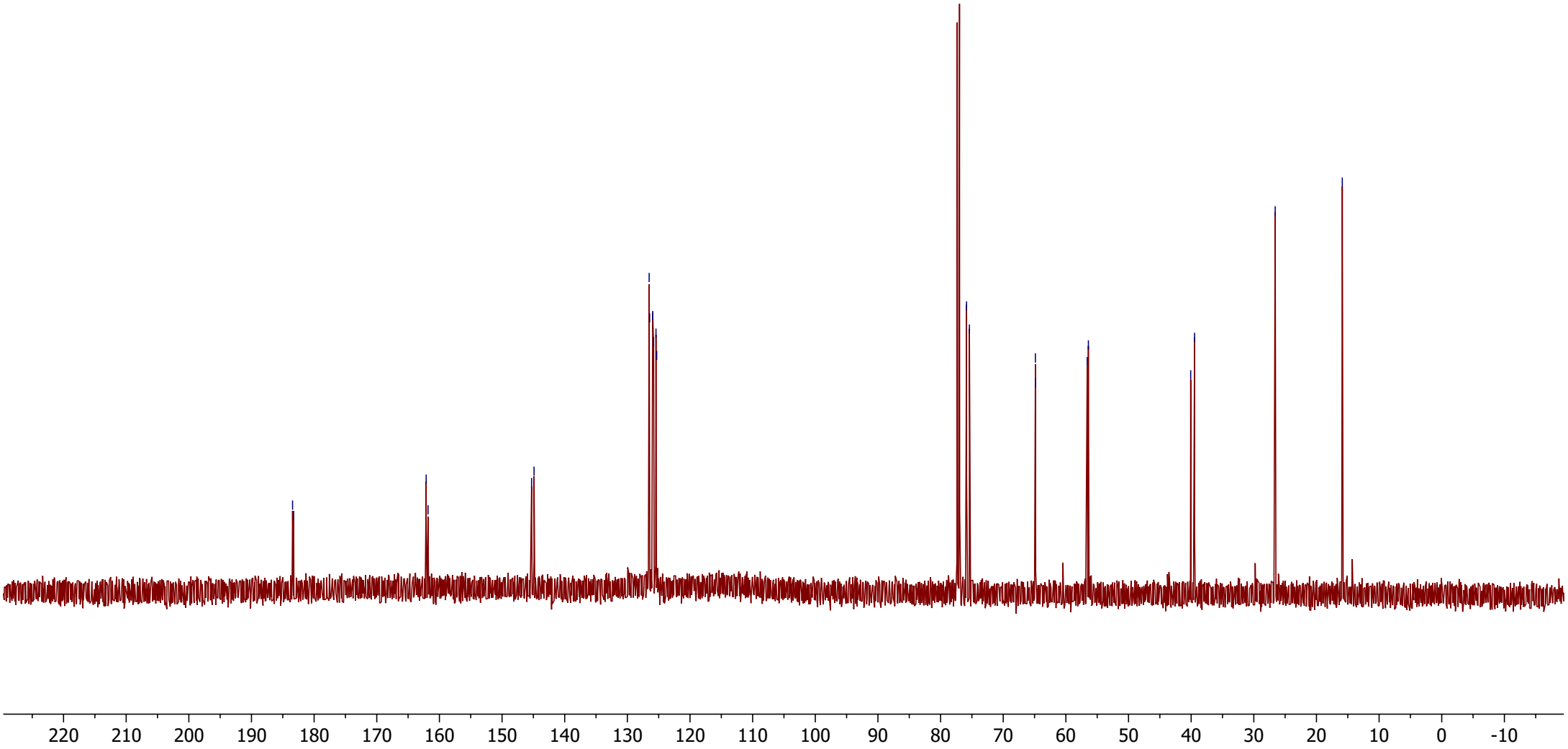


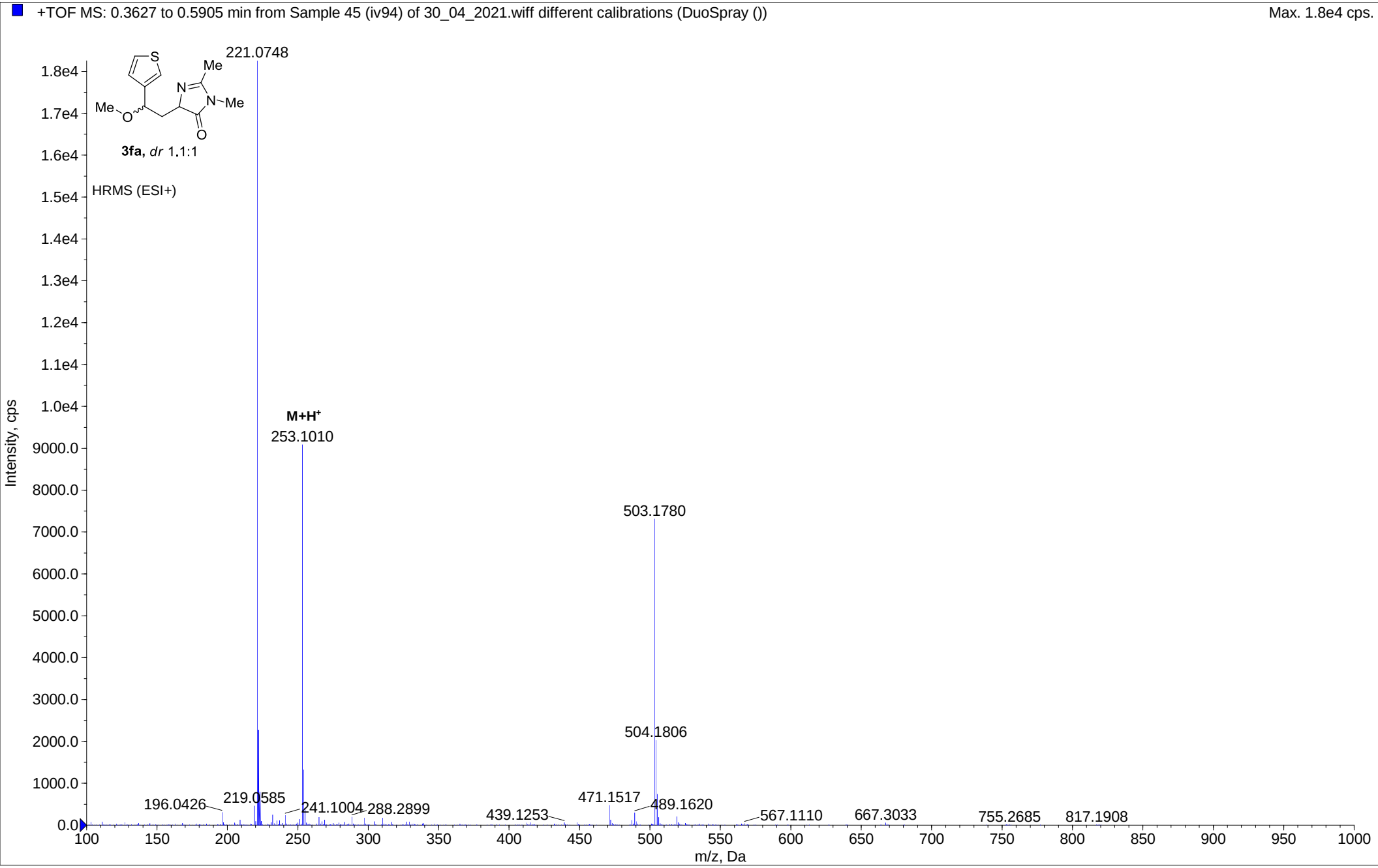


3fa, *dr* 1.1:1

^{13}C NMR (175 MHz)

183.44
183.26
162.11
161.82
145.29
144.89
126.52
126.45
125.96
125.81
125.43
125.32
75.85
75.40
64.86
64.84
56.59
56.41
40.07
39.46
26.59
15.88




+TOF MS: 0.3627 to 0.5905 min from Sample 45 (iv94) of 30_04_2021.wiff different calibrations (DuoSpray ())
Max. 1.8e4 cps.
3fa, dr 1.1:1
HRMS (ESI+)
M+H+
253.1010
221.0748
503.1780
504.1806
196.0426
219.0585
241.1004
288.2899
439.1253
471.1517
489.1620
567.1110
667.3033
755.2685
817.1908
Intensity, cps
m/z, Da