

ELETRONIC SUPPLEMENTARY INFORMATION for:

Catalytic artificial nitroalkane oxidase – a way towards organocatalytic umpolung

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S1 Experimental

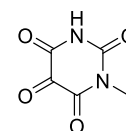
S1.1 General information

Starting materials and reagents were obtained from commercial suppliers and used without further purification. The solvents were purified and dried using standard procedures. NMR spectra were measured on Agilent 400 MR DDR (400 MHz for ^1H and 101 MHz for ^{13}C), Bruker Avance III 600 MHz (600 MHz for ^1H and 151 MHz for ^{13}C), Bruker Avance III 500 MHz (500 MHz for ^1H and 126 MHz for ^{13}C). The spectra were measured in deuterated solvents (chloroform- d , acetonitrile- d_3 and DMSO- d_6). Chemical shifts are given in ppm, using residual solvent as an internal standard. Coupling constants J are reported in Hz. Mass spectroscopy analysis was performed on a LTQ Orbitrap Velos (Thermo Fisher Scientific). UV-Vis spectra were measured on the Agilent Cary 8454 spectrophotometer. Melting points were measured on a Boetius melting point apparatus and are uncorrected. TLC analyses were carried out on a DC Alufolien Kieselgel 60 F254 (Merck). Preparative column chromatography separations were performed on a silica gel Kieselgel 60 (0.040 – 0.063 mm) (Merck).

S1.2 Synthesis of *N*-methylalloxan (**S1**) and sodium nitroalkanides **S2-S3**

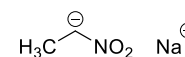
N-Methylalloxan (**S1**)

Compound **S1** was prepared according to a procedure described in literature¹.



Sodium 1-nitroethan-1-ide (**S2**)

Sodium (1.3 g; 56.5 mmol) was dissolved in dry MeOH (60 mL). Solution of nitroethane (**3a**) (4.44 mL; 1.1 eq.; 62.1 mmol) in dry MeOH (25.5 mL) was slowly added. After 10 minutes of stirring, volume of mixture was reduced to 45 mL under reduced pressure. Precipitate was filtered off, washed with EtOH (40 mL) and dried under reduced pressure. Product **S2** was obtained in a form of white crystals (2.58 g, 47%).

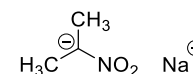


Warning: Heating to high temperatures, especially in the solid state, might be dangerous. Risk of explosion.²

^1H NMR (400 MHz, DMSO- d_6) δ 5.51 (q, $J = 5.6$, 1H, CH-CH $_3$), 1.61 (d, $J = 5.6$, 3H, CH-CH $_3$).

Sodium 2-nitropropan-2-ide (**S3**)

Freshly cut sodium (2.5 g; 109 mmol) was added into dry methanol (200 mL) and stirred under reflux condenser until dissolution. 2-Nitropropane (**3e**) (10.85 mL; 120 mmol; 1.1 eq.) was then poured into the reaction flask and the mixture was stirred for 30 min at RT. Volume of the reaction mixture was reduced to ca. 50 mL and diethyl ether (150 mL) was poured into the residual solution to precipitate the product. Reaction mixture was filtered off and the filtration cake was washed with diethyl ether (100 mL) and dried under vacuum. Product **S3** was obtained in a form of white crystalline solid (6 g; 50%).

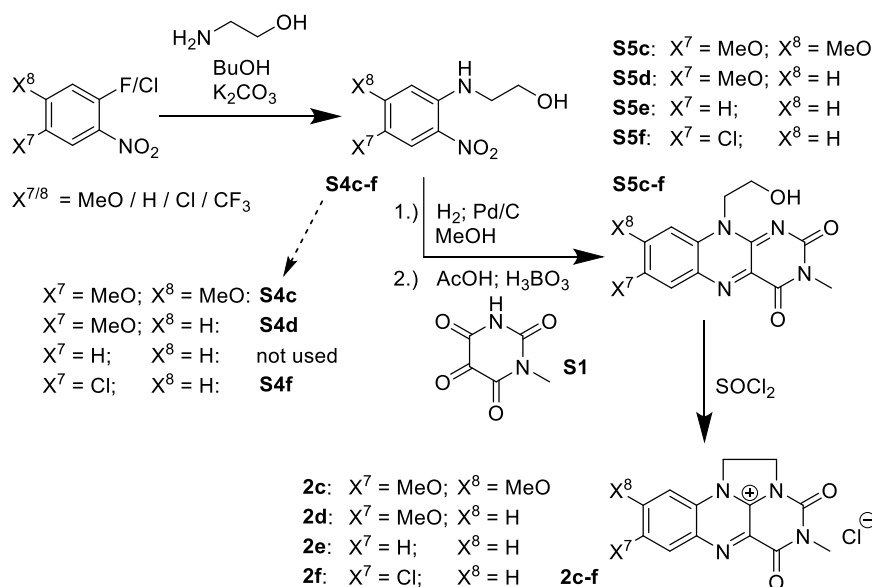


Warning: Heating to high temperatures, especially in the solid state, might be dangerous. Risk of explosion.²

¹H NMR (400 MHz, DMSO-*d*₆) δ 1.80 (s, 6H, 2 × CH₃).

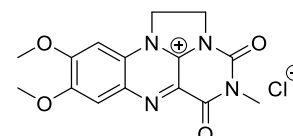
S1.3 Synthesis of 1,10-ethylidene flavinium salts 2c-2g

Synthetic pathway for preparation of flavinium salts 2c-f



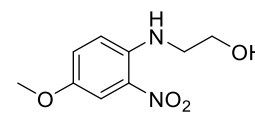
1,10-Ethylidene-7,8-dimethoxy-3-methylisalloxazinium chloride (2c)

Compound **2c** was prepared according to a procedure described in literature¹.



2-[N-(4-Methoxy-2-nitrophenyl)amino]ethan-1-ol (S4d)

1-Fluoro-4-methoxy-2-nitrobenzene (5 g; 29 mmol) was dissolved in butan-1-ol (250 mL). Fine anhydrous K₂CO₃ (8 g; 2 eq.; 58 mmol) and 2-aminoethanol (7.06 mL; 4 eq.; 120 mmol) were added. Mixture was heated to reflux for 40 minutes to achieve full conversion as monitored by TLC (CHCl₃/MeOH 100:3). Mixture was cooled to RT and 1M HCl (300 mL) was slowly added. An extraction with CHCl₃ was performed (300, 200 and 50 mL) and combined organic layers were dried over Na₂SO₄. Solvent was evaporated under reduced pressure and oily residue was left in the fridge overnight. Crude product was recrystallized from CHCl₃ and dried under reduced pressure. Filtrate was evaporated and residue was dissolved in acetone (10 mL). Hexane (50 mL) was added and formed precipitate was filtered off and dried under reduced pressure. Product **S4d** was obtained in a form of red-orange crystalline solid (3.46 g; 56%).



m. p.: 82 – 84 °C (ref.³ 90 – 92 °C)

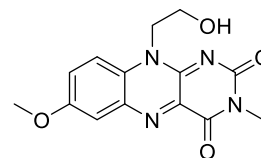
^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 8.16 (s, 1H, N-H), 7.47 (s, 1H, Ar-H), 7.25 (d, $J = 9.3$, 1H, Ar-H), 7.05 (d, $J = 9.3$, 1H, Ar-H), 4.99 – 4.93 (m, 1H, $\text{CH}_2\text{-O-H}$), 3.73 (s, 3H, O- CH_3), 3.68 – 3.61 (m, 2H, CH_2), 3.41 – 3.35 (m, 2H, CH_2).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 148.9, 141.5, 129.8, 127.4, 116.3, 106.3, 59.2, 55.5, 45.0.

HR-MS (APCI+) (m/z): for $[\text{M}+\text{H}]^+$ ($\text{C}_9\text{H}_{13}\text{N}_2\text{O}_4^+$) calc.: 213.08698, found: 213.08690.

10-(2-Hydroxyethyl)-7-methoxy-3-methylisoalloxazine (S5d)

Compound **S4d** (2.1 g; 9.9 mmol) was dissolved in MeOH (200 mL) and Pd/C (0.1 g, 10% Pd) was added. The reaction mixture was stirred under hydrogen atmosphere (balloon) for 4 hours. Colour of reaction mixture changed from yellow to colourless (indication of full conversion). Pd was filtered off through a pad of celite under argon atmosphere and MeOH was evaporated under reduced pressure. Crude phenylenediamine product was used in further reaction without purification.



A solution of *N*-methylalloxan **S1** (1.72 g; 1 eq.; 9.9 mmol) and H_3BO_3 (0.915 g; 1.5 eq.; 14.8 mmol) in hot AcOH (60 mL) was prepared and poured into the stirred solution of crude phenylenediamine in AcOH (60 mL). Reaction mixture was heated to reflux for 30 minutes and then stirred at RT for 22 hours in dark. Precipitate was filtered off, washed with Et_2O (50 mL) and dried under vacuum. Volume of the filtrate was reduced to 10 mL under reduced pressure and Et_2O (50 mL) was added. Mixture was left in the fridge for 20 hours. Precipitate was filtered off, washed with Et_2O (15 mL) and dried under reduced pressure. Product **S5d** was obtained in a form of red-orange crystalline solid (2.35 g; 79%).

Decomposition at 290 °C.

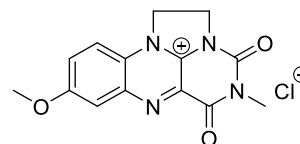
^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 8.05 (d, $J = 9.5$, 1H, Ar-H), 7.67 (d, $J = 2.8$, 1H, Ar-H), 7.61 (dd, $J = 9.5$, 2.8, 1H, Ar-H), 4.74 (t, $J = 5.8$, 2H, CH_2), 3.93 (s, 3H, O- CH_3), 3.82 (t, $J = 5.8$, 2H, CH_2), 3.29 (s, 3H, N- CH_3).

^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 159.6, 157.1, 155.0, 148.3, 137.5, 136.4, 128.3, 125.4, 118.5, 111.1, 57.6, 56.1, 46.8, 28.0.

HR-MS (APCI+) (m/z): for $[\text{M}+\text{H}]^+$ ($\text{C}_{14}\text{H}_{15}\text{N}_4\text{O}_4^+$) calc.: 303.10878, found: 303.10913.

1,10-Ethylidene-7-methoxy-3-methylisoalloxazinium chloride (2d)

Compound **S5d** (1 g; 3.3 mmol) was dissolved in SOCl_2 (15 mL) and stirred at RT in the dark for 2.5 hours. Precipitate was filtered off and washed with Et_2O (10 mL). Crude product was dissolved in the mixture of MeCN (100 mL) and TFA (1 mL). Mixture was filtered and volume of the filtrate was reduced to 25 mL under reduced pressure. Et_2O (110 mL) was added to the mixture. Product precipitated and it was filtered off and dried under reduced pressure. Product **2d** was obtained in the form of orange crystalline solid (0.83 g; 78%).



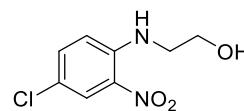
Decomposition at 174 °C.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.29 – 8.25 (m, 1H, Ar-H), 8.14 – 8.09 (m, 2H, 2 \times Ar-H), 5.47 – 5.38 (m, 2H, CH_2), 4.76 – 4.66 (m, 2H, CH_2), 4.05 (s, 3H, O- CH_3), 3.42 (s, 3H, N- CH_3).

^{13}C NMR (151 MHz, DMSO- d_6) δ 159.9, 159.6, 150.6, 143.6, 141.0, 138.2, 130.3, 128.6, 127.6, 107.5, 56.3, 51.3, 39.2, 28.9.

HR-MS (ESI+) (m/z): for $[\text{M}]^+$ ($\text{C}_{14}\text{H}_{13}\text{N}_4\text{O}_3^+$) calc.: 285.09822, found: 285.09845.

2-[*N*-(4-Chloro-2-nitrophenyl)amino]ethan-1-ol (**S4f**)



4-Chloro-1-fluoro-2-nitrobenzene (14.1 g; 80 mmol) was dissolved in butan-1-ol (420 mL). Fine anhydrous K_2CO_3 (13.3 g; 1.2 eq.; 100 mmol) and 2-aminoethanol (9.7 mL; 2 eq.; 0.16 mol) were added. Reaction mixture was refluxed 2 hours and its colour changed from yellow to red. Mixture was cooled to RT and 300 mL of 1M HCl was slowly added. An extraction with CHCl_3 was performed (3 \times 300 mL) and combined organic layers were dried over Na_2SO_4 . Solvent was evaporated and crystalline solid was dried under vacuum. Product **S4f** was obtained as orange crystals (16.6 g; 96%).

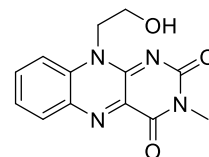
m. p.: 98 – 100 $^\circ\text{C}$ (ref.³ 107 – 108 $^\circ\text{C}$)

^1H NMR (500 MHz, DMSO- d_6) δ 8.27 (bs, 1H, N-H), 8.03 (s, 1H, Ar-H), 7.54 (d, $J = 9.2$, 1H, Ar-H), 7.13 (d, $J = 9.2$, 1H, Ar-H), 4.98 (s, 1H, O-H), 3.67 – 3.61 (m, 2H, CH_2), 3.43 – 3.38 (m, 2H, CH_2).

^{13}C NMR (126 MHz, DMSO- d_6) δ 144.3, 136.3, 130.8, 124.8, 118.3, 116.9, 59.0, 44.9.

HR-MS (APCI+) (m/z): for $[\text{M}+\text{H}]^+$ ($\text{C}_8\text{H}_{10}\text{ClN}_2\text{O}_3^+$) calc.: 217.03745, found: 217.03741.

10-(2-Hydroxyethyl)-3-methylisalloxazine (**S5e**)



Compound **S4f** (10.3 g; 47.6 mmol) was dissolved in MeOH (300 mL). Pd/C (0.53 g, 10% Pd) was added and the reaction mixture was stirred under hydrogen atmosphere (balloon) for 3 hours. Colour of reaction mixture changed from yellow to colourless (indication of full conversion). Pd was filtered off through a pad of celite under argon atmosphere and MeOH was evaporated under reduced pressure. Dehalogenated phenylenediamine was obtained in a form of slightly yellow wax and was used in further reaction without purification.

A solution of *N*-methylalloxan **S1** (8.28 g; 1 eq.; 47.6 mmol) and H_3BO_3 (4.43 g; 1.2 eq.; 71.4 mmol) in hot AcOH (150 mL) was prepared and poured into the stirred solution of phenylenediamine in AcOH (150 mL). Reaction mixture was heated to 50 $^\circ\text{C}$ for 2 hours and then stirred at RT for 20 hours in dark. Precipitate was filtered off, washed with AcOH (30 mL), Et_2O (50 mL) and dried under reduced pressure.

The procedure was originally used with intention to prepare chlorinated derivative **S5f**. Due to dehalogenation in reduction step, we obtained product **S5e** in a form of yellow crystalline solid (3.37 g; 26%).

m. p.: 287 – 290 $^\circ\text{C}$ (ref.⁴ 293 – 298 $^\circ\text{C}$)

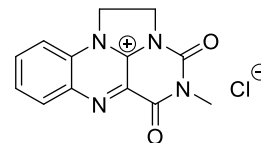
^1H NMR (500 MHz, DMSO- d_6) δ 8.19 (d, $J = 8.1$, 1H, Ar-H), 8.06 (d, $J = 8.7$, 1H, Ar-H), 7.98 (t, $J = 8.0$, 1H, Ar-H), 7.67 (t, $J = 7.7$, 1H, Ar-H), 4.92 (d, $J = 5.9$, 2H, CH_2), 4.45 (d, $J = 5.7$, 2H, CH_2), 3.29 (s, 3H, N- CH_3).

^{13}C NMR (126 MHz, DMSO- d_6) δ 170.3, 159.4, 155.1, 149.3, 137.7, 134.9, 132.8, 131.8, 126.1, 116.5, 60.2, 43.0, 28.0.

HR-MS (APCI+) (m/z): for $[M+H]^+$ ($C_{13}H_{13}N_4O_3^+$) calc.: 273.09822, found: 273.09830.

1,10-Ethylidene-3-methylisoalloxazinium chloride (**2e**)

Compound **S5e** (0.249 g, 0.92 mmol) was dissolved in $SOCl_2$ (7.5 mL) and stirred at RT in the dark for 2 hours. Precipitate was filtered off and washed with 2.5 mL of Et_2O . Crude product was dissolved in the mixture of MeCN (200 mL) and TFA (2.5 mL). Mixture was filtered and its volume was reduced to 100 mL under reduced pressure. Et_2O (150 mL) was added to mixture, and it was left in the fridge overnight to precipitate the product. Precipitate was filtered off and dried under reduced pressure. Product **2e** was obtained in the form of yellow crystalline solid (0.184 g; 69%).



m. p.: 129 – 131 °C

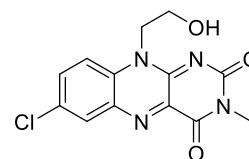
1H NMR (400 MHz, $DMSO-d_6$) δ 8.65 (dd, $J = 8.4, 1.3$, 1H, Ar-H), 8.42 (t, $J = 8.5$, 1H, Ar-H), 8.31 (dd, $J = 8.6, 1.3$, 1H, Ar-H), 8.16 (t, $J = 8.4$, 1H, Ar-H), 5.49 – 5.37 (m, 2H, CH_2), 4.80 – 4.69 (m, 2H, CH_2), 3.43 (s, 3H, N- CH_3).

^{13}C NMR (101 MHz, acetonitrile- d_3) δ 157.3, 146.5, 142.3, 141.00, 140.01, 133.1, 132.0, 131.7, 131.7, 129.7, 50.9, 45.8, 28.8.

HR-MS (ESI+) (m/z): for $[M]^+$ ($C_{13}H_{11}N_4O_2^+$) calc.: 255.08765, found: 255.08702.

7-Chloro-10-(2-hydroxyethyl)-3-methylisoalloxazine (**S5f**)

Nitroaniline **S4f** (6 g; 27.7 mmol) was dissolved in EtOH (100 mL) and $SnCl_2 \cdot 2H_2O$ (31.25 g; 5 eq.; 136 mmol) was added. Reaction mixture was heated to reflux for 15 hours. Volume of mixture was reduced under reduced pressure to 20 mL and pH was adjusted to ca. 11 using 2M NaOH. An extraction with Et_2O (2 \times 100 mL) and EtOAc (2 \times 100 mL) was performed. Organic layers were washed with brine and dried over Na_2SO_4 . Solvent was evaporated under reduced pressure. Crude phenylenediamine in form of slightly brown wax was dissolved in 150 mL of AcOH. To this solution, *N*-methylalloxan **S1** (4.82 g; 1 eq.; 27.7 mmol) and H_3BO_3 (2.57 g; 1.5 eq.; 41.6 mmol) in hot AcOH (150 mL) were added. Reaction mixture was heated to 60 °C for 1 hour and then stirred at RT for 15 hours in dark. Precipitate was filtered off, washed with AcOH (40 mL), Et_2O (40 mL) and dried under vacuum. Product **S5f** was obtained in a form of orange crystalline solid (7.89 g; 93%).



m. p.: 271 – 274 °C

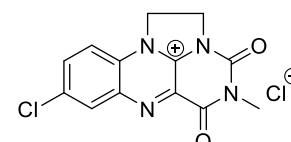
1H NMR (400 MHz, $DMSO-d_6$) δ 8.29 (s, 1H, Ar-H), 8.12 (d, $J = 9.3$, 1H, Ar-H), 7.98 (d, $J = 9.3$, 1H, Ar-H), 4.97 (bs, 1H, CH_2-O-H), 4.71 (t, $J = 5.9$, 2H, CH_2), 3.81 (bs, 2H, CH_2), 3.28 (s, 3H, N- CH_3).

^{13}C NMR (126 MHz, $DMSO-d_6$) δ 159.3, 155.0, 149.1, 138.8, 135.5, 134.2, 132.5, 129.94, 129.86, 119.2, 57.5, 46.8, 28.0.

HR-MS (APCI+) (m/z): for $[M+H]^+$ ($C_{13}H_{12}ClN_4O_3^+$) calc.: 307.05924, found: 307.05969.

7-Chloro-1,10-ethylidene-3-methylisoalloxazinium chloride (**2f**)

Compound **S5f** (1 g; 3.3 mmol) was dissolved in $SOCl_2$ (30 mL) and stirred at RT in the dark for 4 hours. Precipitate was filtered off and washed with



Et₂O (20 mL). Crude product was dissolved in the mixture of MeCN (250 mL) and TFA (3 mL). Mixture was filtered and volume of the filtrate was reduced to 50 mL under reduced pressure. Et₂O (100 mL) was added to the mixture. Product precipitated and it was filtered off and dried under reduced pressure. Product **2f** was obtained in the form of yellow crystalline solid (0.71 g; 67%).

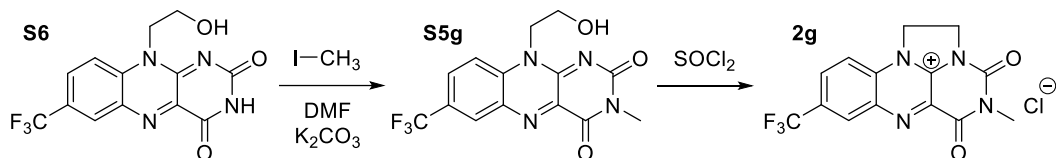
m. p.: 144 – 148 °C

¹H NMR (400 MHz, acetonitrile-*d*₃) δ 8.61 (d, *J* = 2.2, 1H, Ar-*H*), 8.30 (dd, *J* = 9.2, 2.3, 1H, Ar-*H*), 8.05 (d, *J* = 9.1, 1H, Ar-*H*), 5.34 – 5.25 (m, 2H, CH₂), 4.82 – 4.70 (m, 2H, CH₂), 3.47 (s, 3H, N-CH₃) ppm.

¹³C NMR (101 MHz, acetonitrile-*d*₃) δ 157.9, 147.0, 142.9, 141.8, 140.4, 137.7, 133.8, 132.2, 129.2, 119.8, 51.8, 46.6, 29.6.

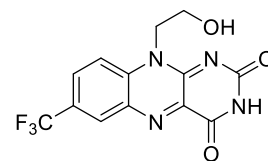
HR-MS (ESI+) (*m/z*): for [M]⁺ (C₁₃H₁₀ClN₄O₂⁺) calc.: 289.04868, found: 289.04935.

Synthetic pathway for preparation of flavinium salt **2g**



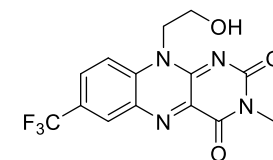
10-(2-Hydroxyethyl)-7-(trifluoromethyl)isoalloxazine (**S6**)

Compound **S6** was prepared according to a procedure described in literature⁵.



10-(2-Hydroxyethyl)-3-methyl-7-(trifluoromethyl)isoalloxazine (**S5g**)

10-(2-Hydroxyethyl)-7-trifluoromethylisoalloxazine (**S6**) (5.87 g; 18 mmol) and MeI (1.68 mL; 1.5 eq.; 27 mmol) were dissolved in dry DMF (250 mL). Fine anhydrous K₂CO₃ (4.98 g; 2 eq.; 36 mmol) was added to the mixture.



Reaction mixture was heated to 95 °C for 4 hours and to 70 °C for 15 hours. Volume of solvent was reduced to 50 mL under reduced pressure and 1M HCl (100 mL) was added. CHCl₃ (50 mL) was added, and precipitate was filtered off and washed with 20 mL of EtOH. Filter cake (product) was dried under reduced pressure and filtrate was extracted with CHCl₃ (2 × 50 mL) and dried over Na₂SO₄. Volume of solvent was reduced under reduced pressure to 20 mL and Et₂O (100 mL) was added. Precipitate was filtered off and dried under reduced pressure. Product **S5g** was obtained in a form of yellow crystalline solid (5.43 g; 89%).

m. p.: 243 – 246 °C (ref.⁶ 234 – 235 °C)

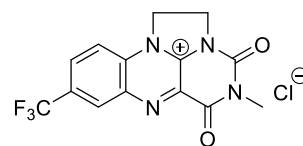
¹H NMR (500 MHz, DMSO-*d*₆) δ 8.53 (s, 1H, Ar-*H*), 8.31 – 8.19 (m, 2H, 2 × Ar-*H*), 4.97 (s, 1H, O-*H*), 4.77 – 4.72 (m, 2H, CH₂), 3.87 – 3.81 (m, 2H, CH₂), 3.29 (s, 3H, N-CH₃).

¹⁹F NMR (376 MHz, DMSO-*d*₆) δ –57.63.

¹³C NMR (126 MHz, DMSO-*d*₆) δ 159.1, 155.1, 149.7, 139.4, 135.9, 134.1, 129.8 (q, *J* = 3.4), 128.7 (q, *J* = 4.3), 125.8 (q, *J* = 33.3), 123.5 (q, *J* = 272.2), 119.0, 57.5, 46.8, 28.1.

HR-MS (APCI+) (*m/z*): for [M+H]⁺ (C₁₄H₁₄F₃N₄O₃⁺) calc.: 341.08560, found: 341.08618.

1,10-Ethylidene-3-methyl-7-(trifluoromethyl)isoalloxazinium chloride (2g)



Compound **S5g** (2 g; 5.9 mmol) was dissolved in SOCl_2 (25 mL) and stirred in the dark for 1.5 hour. Precipitate was filtered off and washed with Et_2O (10 mL). Crude product was dissolved in a mixture of MeCN (200 mL) and TFA (2 mL). The mixture was filtered and volume of the filtrate was reduced under reduced pressure to 50 mL. Et_2O (100 mL) was added to the mixture, and it was stored in the fridge for 2 hours. Product precipitated and it was filtered off and dried under reduced pressure. Product **2g** was obtained in the form of yellow crystalline solid (1.83 g; 87%).

m. p.: 147 – 150 °C (ref.⁶ 186 – 189 °C)

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.08 (s, 1H, Ar-H), 8.69 (d, $J = 8.6$, 1H, Ar-H), 8.50 (d, $J = 8.6$, 1H, Ar-H), 5.59 – 5.37 (m, 2H, CH_2), 4.79 (t, $J = 9.4$, 2H, CH_2), 3.43 (s, 3H, N- CH_3).

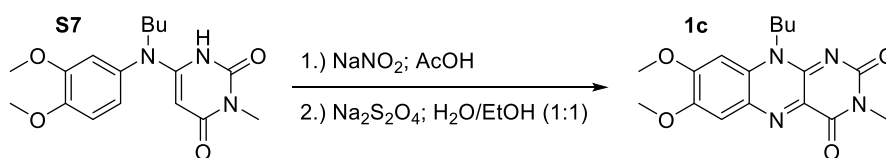
^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -74.87.

^{13}C NMR (101 MHz, acetonitrile- d_3) δ 157.7, 146.9, 144.1, 140.8, 135.5 (q, $J = 3.3$), 134.58, 132.79 (q, $J = 34.3$), 132.23, 131.5 (q, $J = 4.4$), 123.7 (q, $J = 272.5$), 120.2, 51.9, 46.9, 29.7.

HR-MS (ESI+) (m/z): for $[\text{M}]^+$ ($\text{C}_{14}\text{H}_{10}\text{F}_3\text{N}_4\text{O}_2^+$) calc.: 323.07504, found: 323.07520.

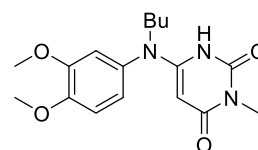
S1.4 Synthesis of isoalloxazines 1c-1h

Synthetic pathway for preparation of isoalloxazine derivative 1c



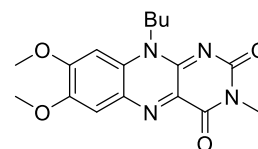
6-(Butyl(3,4-dimethoxyphenyl)amino)-3-methyluracil (S7)

Compound **S7** was prepared according to a procedure described in literature⁷.



10-Butyl-7,8-dimethoxy-3-methylisoalloxazine (1c)

Compound **S7** (300 mg, 0.9 mmol) was suspended in acetic acid (15 mL) and the suspension was cooled to 0 °C in an ice bath. Sodium nitrite (207 mg, 3 mmol) was slowly added. Thick orange precipitate was formed and it was filtered off and washed with EtOH (10 mL). The precipitate was then suspended in mixture of water (20 mL) and ethanol (20 mL) with sodium dithionite (400 mg, 2.3 mmol). After two hours of stirring, crude product was filtered off and washed with diethyl ether (50 mL). Product was recrystallized from mixture of ethanol and chloroform (1:1) to give **1c** (196 mg, 63%).



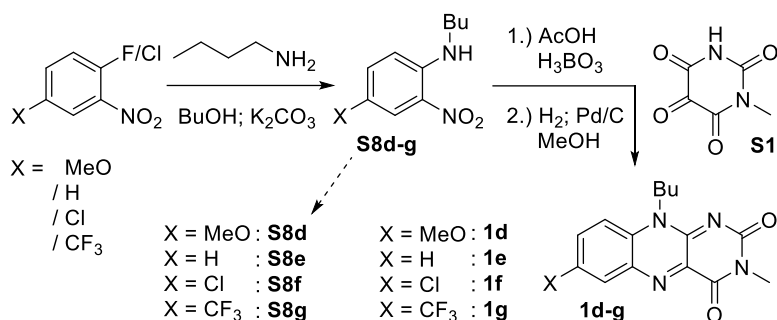
m. p.: 295 – 300 °C with decomposition

^1H NMR (400 MHz, CDCl_3) δ 7.67 (Ar-H, s, 1H), 6.91 (Ar-H, s, 1H), 4.74 (CH_2 , bs, 2H), 4.12 (O- CH_3 , s, 3H), 4.01 (O- CH_3 , s, 3H), 3.52 (CH_3 , s, 3H), 1.88 (CH_2 , p, $J = 7.6$, 2H), 1.56 (CH_2 , h, $J = 7.3$, 2H), 1.04 (CH_3 , t, $J = 7.3$, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 160.7, 157.5, 156.3, 149.4, 148.5, 133.6, 132.5, 130.0, 112.0, 95.6, 57.0, 56.7, 45.0, 29.08, 28.87, 20.3, 14.0.

HR-MS (ESI) (m/z): $[\text{M}+\text{H}]^+$ ($\text{C}_{17}\text{H}_{21}\text{N}_4\text{O}_4+\text{H}^+$) calc.: 345.1563, found: 345.1560.

Synthetic pathway for preparation of isoalloxazines 1d-g



N-Butyl-4-methoxy-2-nitroaniline (**S8d**)

1-Chloro-4-methoxy-2-nitrobenzene (5 g; 27 mmol) was dissolved in butan-1-ol (250 mL). Fine anhydrous K_2CO_3 (7.5 g; 2 eq.; 54 mmol) and butan-1-amine (10.8 mL; 4 eq.; 108 mmol) were added. Mixture was heated to reflux for 9 days to achieve full conversion as monitored by TLC (hexane:EtOAc 10:1). Due to evaporation of butan-1-amine when heating to 120 °C overnight and the cooling water was turned off, another 20 eq. (4 eq. on the 2nd, 3rd, 4th, 5th, and 8th day) of butan-1-amine were added to the mixture. Volume of mixture was reduced to 100 mL under reduced pressure and 1M HCl (210 mL) was slowly added. Mixture was diluted by water (200 mL) and extraction with CHCl_3 (150, 50, 50 mL) was performed. Combined organic layers were dried over Na_2SO_4 . Solvent was evaporated under reduced pressure and residue was dissolved in hexane (200 mL) and left in the fridge overnight. Mixture was washed with water (300, 100, 100 mL) to remove butan-1-ol and organic layer was dried over CaCl_2 . Solvent was evaporated under reduced pressure and crude product was purified by column chromatography (hexane:EtOAc 10:1). Product **S8d** was obtained in the form of red oil (2.86 g; 47%).

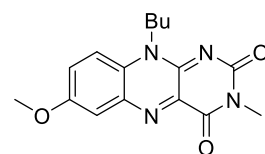
^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.07 (t, $J = 5.4$, 1H, $\text{CH}_2\text{-N-H}$), 7.48 (d, $J = 3.1$, 1H, Ar-H), 7.28 (dd, $J = 9.4$, 3.1, 1H, Ar-H), 7.06 (d, $J = 9.4$, 1H, Ar-H), 3.74 (s, 3H, O- CH_3), 3.38 – 3.29 (m, 2H, N- $\text{CH}_2\text{-CH}_2$), 1.65 – 1.53 (m, 2H, $\text{CH}_2\text{-CH}_2\text{-CH}_3$), 1.43 – 1.30 (m, 2H, $\text{CH}_3\text{-CH}_2$), 0.92 (t, $J = 7.4$, 3H, $\text{CH}_2\text{-CH}_3$).

^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 148.8, 141.3, 129.6, 127.5, 116.1, 106.2, 55.5, 42.1, 30.6, 19.6, 13.6.

HR-MS (APCI+) (m/z): for $[\text{M}+\text{H}]^+$ ($\text{C}_{11}\text{H}_{17}\text{N}_2\text{O}_3^+$) calc.: 225.12337, found: 225.12296.

10-Butyl-7-methoxy-3-methylisoalloxazine (**1d**)

Compound **S8d** (2.16 g; 9.6 mmol) was dissolved in MeOH (200 mL) and Pd/C (0.25 g, 10% Pd) was added. The reaction mixture was stirred under hydrogen atmosphere (balloon) for 1 hour. Colour of reaction mixture



changed from yellow to colourless indicating full conversion. Pd was filtered off through a pad of celite under argon atmosphere and MeOH was evaporated under reduced pressure. Crude 4-methoxybenzene-1,2-diamine was used in further reaction without purification.

A solution of *N*-methylalloxan **S1** (1.68 g; 1 eq.; 9.6 mmol) and H₃BO₃ (0.893 g; 1.5 eq.; 14.5 mmol) in hot AcOH (60 mL) was prepared and poured into the stirred solution of diamine intermediate in AcOH (60 mL). Reaction mixture was heated 5 minutes by heat gun and then stirred at RT for 15 hours in dark. Mixture was diluted by water (120 mL) and precipitate containing impurities was filtered off. Volume of the filtrate was reduced to 15 mL under reduced pressure and TLC was performed (CHCl₃:MeOH 10:1) which showed few spots but no starting material. Mixture was diluted by water (150 mL) and extraction with CHCl₃ (400, 150, 100 mL) was performed. Combined organic layers were dried over Na₂SO₄. Volume of mixture was reduced to 65 mL under reduced pressure and Et₂O (100 mL) was added. Mixture was left in the fridge for 20 hours. Precipitated product was filtered off, washed with Et₂O (30 mL) and dried under reduced pressure. Product **1d** was obtained in a form of red crystalline solid (1.56 g; 52%).

m. p.: 272 – 275 °C

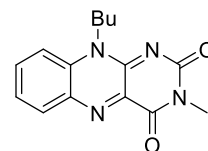
¹H NMR (600 MHz, DMSO-*d*₆) δ 7.96 (d, *J* = 9.4, 1H, Ar-*H*), 7.68 (d, *J* = 2.9, 1H, Ar-*H*), 7.61 (dd, *J* = 9.4, 2.9, 1H, Ar-*H*), 4.62 (t, *J* = 7.8, 2H, N-CH₂), 3.93 (s, 3H, O-CH₃), 3.28 (s, 3H, N-CH₃), 1.75 – 1.67 (m, 2H, CH₂-CH₂-CH₃), 1.51 – 1.42 (m, 2H, CH₂-CH₃), 0.95 (t, *J* = 7.4, 3H, CH₂-CH₃).

¹³C NMR (151 MHz, DMSO-*d*₆) δ 159.6, 157.1, 155.1, 148.0, 137.7, 136.5, 127.1, 125.6, 117.6, 111.5, 56.1, 44.1, 28.9, 28.0, 19.5, 13.7.

HR-MS (APCI+) (m/z): for [M+H]⁺ (C₁₆H₁₉N₄O₃⁺) calc.: 315.14517, found: 315.14542.

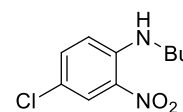
10-Butyl-3-methylisalloxazine (1e)

Compound **1e** was prepared according to a procedure described in literature⁸. The procedure corresponds to the synthetic pathway displayed in general scheme.



N-Butyl-4-chloro-2-nitroaniline (S8f)

4-Chloro-1-fluoro-2-nitrobenzene (10 g; 57 mmol) was dissolved in butan-1-ol (250 mL), 2 eq. of butan-1-amine (11.3 mL; 114 mmol) and 2 eq. of K₂CO₃ (15.8 g; 114 mmol) were added. Reaction mixture was heated to reflux and it was monitored by TLC (hexane:EtOAc; 10:1). After 30 minutes, it was left to cool down and water (250 mL) and concentrated HCl (50 mL) was added. Then the mixture was extracted by CH₂Cl₂ (3 × 100 mL). Combined organic layers were treated by Na₂SO₄, filtered and dried under vacuum. Product **S8f** was obtained in a form of red oil (12.8 g; 98%).



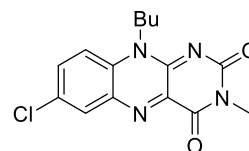
¹H NMR (400 MHz, CDCl₃): δ 8.16 (dd, *J* = 2.6, 0.4, 1H), 8.02 (brs, 1H), 7.37 (dd, *J* = 9.2, 2.6, 1H), 6.81 (dd, *J* = 9.2, 0.5, 1H), 3.29 (t, *J* = 7.1, 2H), 1.77 – 1.65 (m, 2H), 1.54 – 1.41 (m, 2H), 0.98 (t, *J* = 7.3, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 144.4, 136.5, 131.6, 126.0, 119.9, 115.4, 43.0, 31.0, 20.3, 13.9.

HR-MS (APCI+): Calculated for C₁₀H₁₄ClN₂O₂+H⁺ (M+H⁺): 229.07383; Found: 229.07324.

10-Butyl-7-chloro-3-methylisalloxazine (1f)

Compound **S8f** (10 g; 44 mmol) was dissolved in ethanol (200 mL) and 5 eq. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (49 g; 220 mmol). Reaction mixture was heated near to its boiling point (ca. 75 °C) overnight. Majority of solvent was evaporated and residual mixture was diluted by water (100 mL) and solution of NaOH (19 g) in water (100 mL) was added. Then it was extracted by CH_2Cl_2 (3 × 100 mL). Combined organic layers were treated by Na_2SO_4 , filtered and evaporated in vacuum evaporator. Resulting crude phenylenediamine (in a form of brown oil) was immediately used in another reaction step: it was dissolved in acetic acid (100 mL). Into this solution was poured a solution of 1.1 eq. of *N*-methylalloxan **S1** (7.7 g; 44 mmol) and 1.1 eq. of boric acid (2.7 g; 44 mmol) in hot acetic acid (200 mL). Reaction mixture was then heated to reflux for 5 minutes and then it was stirred without heating overnight. Product precipitated and water (200 mL) was added into the mixture and let to settle overnight. Then it was filtered off, washed by water (200 mL) and dried under vacuum to afford product **1f** in form of yellow crystals (9.1 g; 65%).



m. p.: 260 – 261 °C with crystal rearrangement at 211 – 217 °C

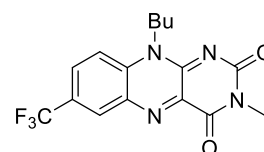
^1H NMR (400 MHz, CDCl_3): δ 8.29 (d, $J = 2.4$, 1H), 7.82 (dd, $J = 9.2$, 2.4, 1H), 7.57 (d, $J = 9.2$, 1H), 4.67 (t, $J = 8.1$, 2H), 3.51 (s, 3H), 1.82 (tt, $J = 8.1$, 6.4, 2H), 1.55 (dt, $J = 15.3$, 7.5, 2H), 1.01 (t, $J = 7.4$, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 159.5, 155.8, 148.7, 138.1, 136.3, 135.8, 132.23, 132.16, 131.3, 116.5, 45.1, 29.28, 29.02, 20.3, 13.9.

HR-MS (APCI+): Calculated for $\text{C}_{15}\text{H}_{15}\text{ClN}_4\text{O}_2 + \text{H}^+$ ($\text{M} + \text{H}^+$): 319.09563; Found: 319.09644.

10-Butyl-7-(trifluoromethyl)-3-methylisalloxazine (1g)

Compound **1g** was prepared according to a procedure described in literature⁹. The procedure corresponds to the synthetic pathway displayed in general scheme.

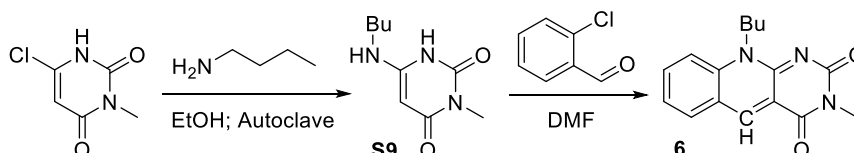


Riboflavin tetraacetate (1h)

Compound **1h** was prepared according to a procedure described in literature¹⁰.

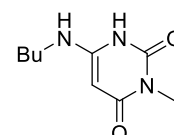
S1.5 Synthesis of 5-deazaisalloxazine 6

Synthetic pathway for preparation of 5-deazaisalloxazine 6



6-(*N*-Butylamino)-3-methyluracil (S9)

6-Chloro-3-methyluracil (5 g; 31 mmol) and butan-1-amine (12.4 mL; 4 eq.; 125 mmol) were dissolved in EtOH (13 mL) and mixture was placed in an autoclave.



Reaction mixture was heated to 120 °C for 12 hours. Solvent was evaporated under reduced pressure and water (20 mL) was added. Crude products precipitated and it was filtered off, recrystallized from water, and dried under reduced pressure. Product **S9** was obtained in form of beige crystalline solid (2.23 g; 36%).

m. p.: 238 – 240 °C (ref.¹¹ 242 – 244 °C)

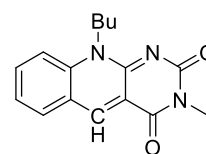
¹H NMR (400 MHz, DMSO-*d*₆) δ 10.12 (s, 1H, O=C-N-H), 6.06 (s, 1H, CH₂-NH), 4.56 (s, 1H, C=C-H), 3.02 (s, 3H, N-CH₃), 3.01 – 2.96 (m, 2H, N-CH₂), 1.51 – 1.40 (m, 2H, CH₂-CH₂-CH₃), 1.36 – 1.25 (m, 2H, CH₂-CH₃), 0.89 (t, *J* = 7.3, 3H, CH₂-CH₃).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 163.1, 152.5, 151.0, 72.4, 40.9, 30.3, 25.9, 19.4, 13.6.

HR-MS (APCI+) (m/z): for [M+H]⁺ (C₉H₁₆N₃O₂⁺) calc.: 198.12370, found: 198.12373.

10-Butyl-3-methyl-5-deazaisoalloxazine (6)

Compound **S9** (1.73 g; 8.75 mmol) and 2-chlorobenzaldehyde (1 mL; 8.75 mmol) were dissolved in DMF (100 mL). Mixture was heated to 180 °C for 3 days and monitored by TLC (CHCl₃:MeOH 10:1) which showed not full conversion and 2 by-products. Reaction mixture was cooled to RT and crystals precipitated. Precipitate was filtered off. Crude product was recrystallized from MeOH. Precipitate was filtered off, washed with Et₂O (15 mL) and dried under reduced pressure. Volume of filtrate was reduced under reduced pressure. Product precipitated and it was filtered off and dried under reduced pressure. Product **6** was obtained in a form of yellow crystals (1.28 g; 51%).



m. p.: 244 – 247 °C (ref.¹² 245 °C)

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.06 (s, 1H, C=CH), 8.26 – 8.22 (m, 1H, Ar-H), 8.00 – 7.95 (m, 2H, 2 × Ar-H), 7.58 – 7.52 (m, 1H, Ar-H), 4.70 (s, 2H, N-CH₂), 3.26 (s, 3H, N-CH₃), 1.78 – 1.62 (m, 2H, CH₂-CH₂-CH₃), 1.54 – 1.42 (m, 2H, CH₂-CH₃), 0.96 (t, *J* = 7.3 Hz, 3H, CH₂-CH₃).

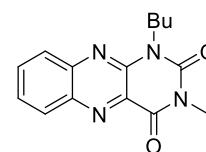
¹³C NMR (151 MHz, DMSO-*d*₆) δ 161.6, 156.0, 155.4, 142.1, 139.8, 135.5, 131.9, 124.3, 121.3, 116.5, 114.4, 43.9, 29.0, 27.5, 19.5, 13.7.

HR-MS (APCI+) (m/z): for [M+H]⁺ (C₁₆H₁₈N₃O₂⁺) calc.: 284.13935, found: 284.13974.

S1.6 Synthesis of alloxazine 5

1-Butyl-3-methyl-isoalloxazine (5)

Compound **5** was prepared according to a procedure described in literature¹³.



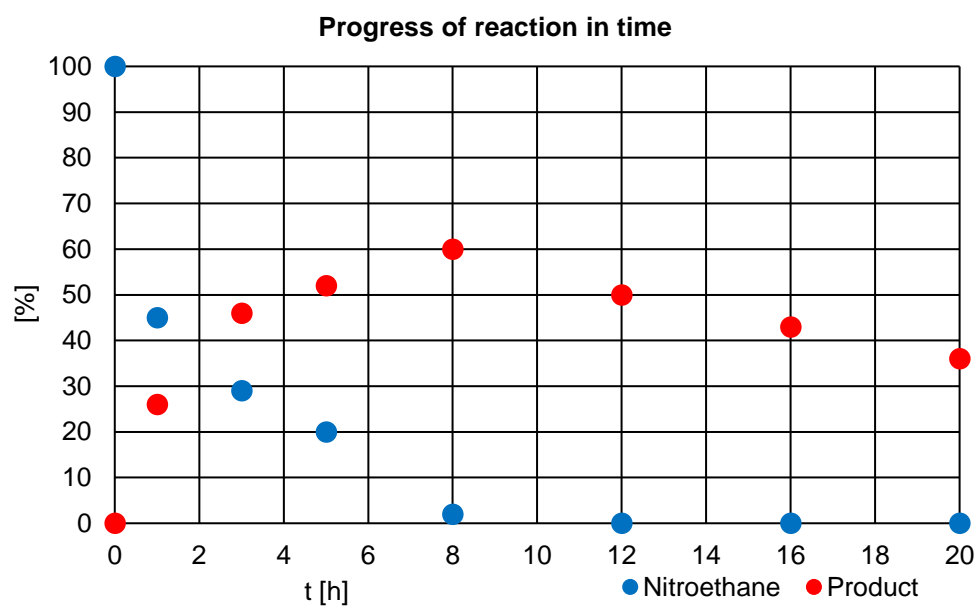
S1.7 Optimization of catalytic system

S1.7.1 Preliminary experiments

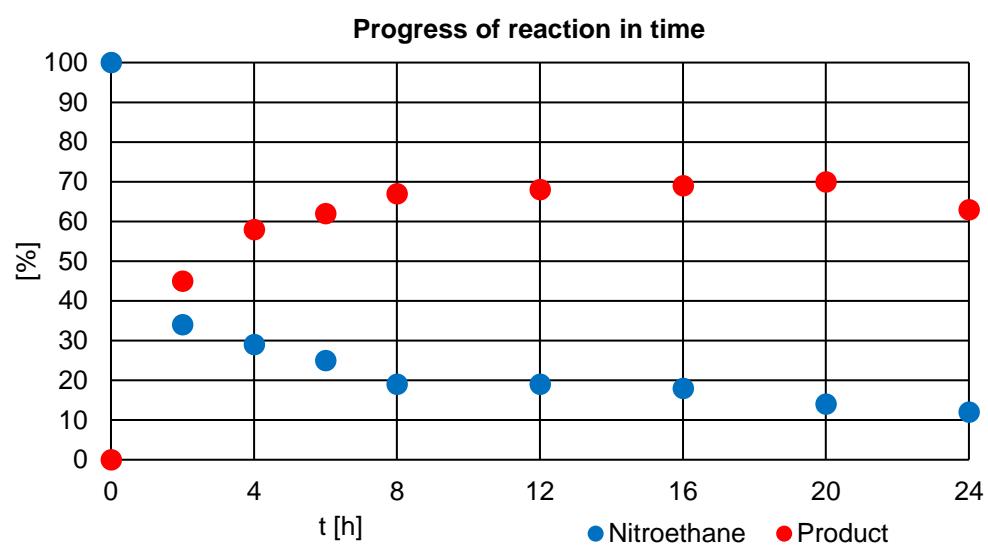
Flavinium salt **2c** (21 mg; 10 mol% or 10 mg; 5 mol%) was dissolved in water (1 mL) in Schlenk tube. Nitroethane (**3a**) (43 μ L; 0.6 mmol) and 0.55 eq. of base ($\text{Bu}_4\text{N}^+\text{OH}^-$ / Na_2CO_3 / NaHCO_3 / Li_2CO_3 /dimethylaniline /DIPEA / Et_3N) or none were added. Schlenk tube was 3x flushed and pressurized by oxygen at 2.5 or 4.5 atm. Alternatively, Schlenk tube was 3x degassed by Schlenk procedure and kept under argon atmosphere. Schlenk tube was placed into thermostat set on 5 or 25 or 45 $^\circ\text{C}$ and reaction mixture was stirred for estimated time. Solution of HCl (1M; 1 mL) and standard solution of dimethyl sulfone in $\text{DMSO-}d_6$ (100 μ L) were added. Sample of the mixture (100 μ L) was dissolved in $\text{DMSO-}d_6$ (500 μ L) and conversion of **3a** product **4a** was estimated by ^1H NMR spectroscopy.

Base (0.55 eq.)	Atmosphere	2c (mol%)	Temp. ($^\circ\text{C}$)	Time (h)	3a (%)	4a (%)
$\text{Bu}_4\text{N}^+\text{OH}^-$	O_2 (2.5 atm.)	10	25	16	15	46
Na_2CO_3	O_2 (2.5 atm.)	10	25	16	7	54
NaHCO_3	O_2 (2.5 atm.)	10	25	16	54	31
Li_2CO_3	O_2 (2.5 atm.)	10	25	16	2	50
Dimethylaniline	O_2 (2.5 atm.)	10	25	16	71	0
DIPEA	O_2 (2.5 atm.)	10	25	16	37	52
Et_3N	O_2 (2.5 atm.)	10	25	16	19	56
-	O_2 (2.5 atm.)	10	25	16	78	0
Et_3N	H_2O_2 (2 eq.)	10	25	16	51	9
Et_3N	O_2 (1 atm.)	10	25	16	11	52
Et_3N	O_2 (4.5 atm.)	10	25	16	18	68
Et_3N	Ar (1 atm.)	10	25	16	45	15
Na_2CO_3	O_2 (4.5 atm.)	10	25	8	2	60
Na_2CO_3	O_2 (4.5 atm.)	10	25	20	0	36
Et_3N	O_2 (4.5 atm.)	10	25	8	19	67
Et_3N	O_2 (4.5 atm.)	10	25	20	14	70
Et_3N	O_2 (4.5 atm.)	10	5	16	40	43
Et_3N	O_2 (4.5 atm.)	10	5	40	31	49
Et_3N	O_2 (4.5 atm.)	10	45	16	4	54
Et_3N	O_2 (4.5 atm.)	10	45	2	20	61
Et_3N	O_2 (4.5 atm.)	5	45	2	13	61
Et_3N	O_2 (4.5 atm.)	-	45	2	51	5

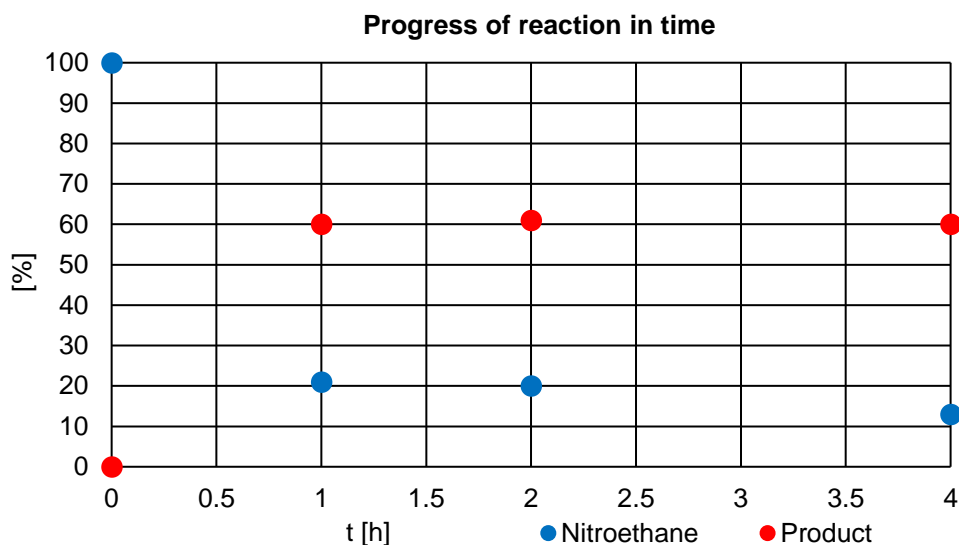
Reaction of 3a in water, in a presence of 10 mol% of 2c, 0.55 eq. Na_2CO_3 at 25 °C under oxygen.



Reaction of 3a in water, in a presence of 10 mol% of 2c, 0.55 eq. Et_3N at 25 °C under oxygen.



Reaction of **3a** in water, in a presence of 10 mol% of **2c**, 0.55 eq. Et₃N at 45 °C under oxygen.



S1.7.2 Solvent screening

Flavinium salt **2c** (21 mg; 10 mol%) was dissolved in mixture of water (1 mL) and methanol (1 mL)/ acetonitrile (1 mL)/ dioxane (1 mL)/ DMSO (1 or 2 mL) in Schlenk tube. Nitroethane (43 μ L; 0.6 mmol) and Et₃N (46 μ L; 0.55 eq.) were added. Schlenk tube was 3x flushed and pressurized by O₂ at 4.5 atm. and placed into thermostat. Reaction mixture stirred for 2 h at 45 °C. After 2 h, solution of HCl (1M; 1 mL) and standard solution of dimethyl sulfone in DMSO-*d*₆ (100 μ L) were added. Sample of the mixture (100 μ L) was dissolved in DMSO-*d*₆ (500 μ L) and conversion of **3a** to **4a** was estimated by ¹H NMR spectroscopy.

Solvent	3a (%)	4a (%)
H ₂ O (1 mL)	20	61
H ₂ O (1 mL) + CH ₃ OH (1 mL)	32	42
H ₂ O (1 mL) + CH ₃ CN (1 mL)	23	55
H ₂ O (1 mL) + dioxane (1 mL)	25	52
H ₂ O (1 mL) + DMSO (1 mL)	36	57
H ₂ O (1 mL) + DMSO (2 mL)	18	36

S1.7.3 Catalyst screening

Catalyst (10 mol%) was dissolved in water (1 mL) or in mixture of water (1 mL) and DMSO (2 mL) in Schlenk tube. Nitroethane (**3a**) (43 μ L; 0.6 mmol) and Et₃N (46 μ L; 0.55 eq.) were added. Schlenk tube was 3x flushed and pressurized by O₂ at 4.5 atm. and placed into thermostat. Reaction mixture stirred for 4 h at 45 °C. After 4 h, solution of HCl (1M; 1 mL) and standard solution of dimethyl

sulfone in DMSO-*d*₆ (100 μL) were added. Sample of the mixture (100 μL) was dissolved in DMSO-*d*₆ (500 μL) and conversion of **3a** to **4a** was estimated by ¹H NMR spectroscopy.

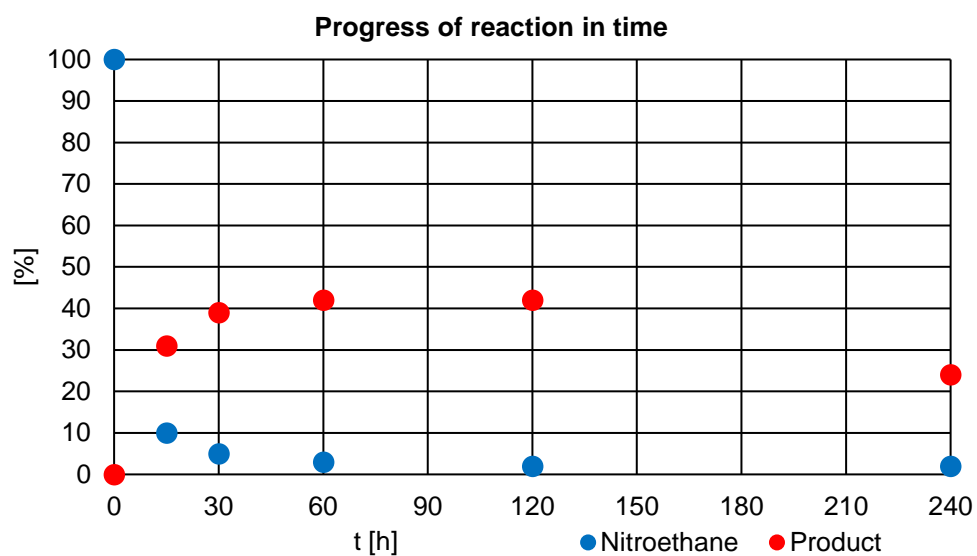
Catalyst	Solvent	3a (%)	4a (%)
2e	H ₂ O + DMSO (1:2)	17	36
2e	H ₂ O	12	66
1e	H ₂ O + DMSO (1:2)	21	50
5	H ₂ O + DMSO (1:2)	81	11
6	H ₂ O + DMSO (1:2)	60	10
2c	H ₂ O + DMSO (1:2)	15	35
2c	H ₂ O	15	61
2d	H ₂ O	22	51
2f	H ₂ O	14	64
2g	H ₂ O	33	41
1c	H ₂ O + DMSO (1:2)	68	15
1d	H ₂ O + DMSO (1:2)	35	45
1f	H ₂ O + DMSO (1:2)	17	61
1f	H ₂ O	29	45
1g	H ₂ O + DMSO (1:2)	16	51

S1.7.4 Optimization of protocol for preparative experiments

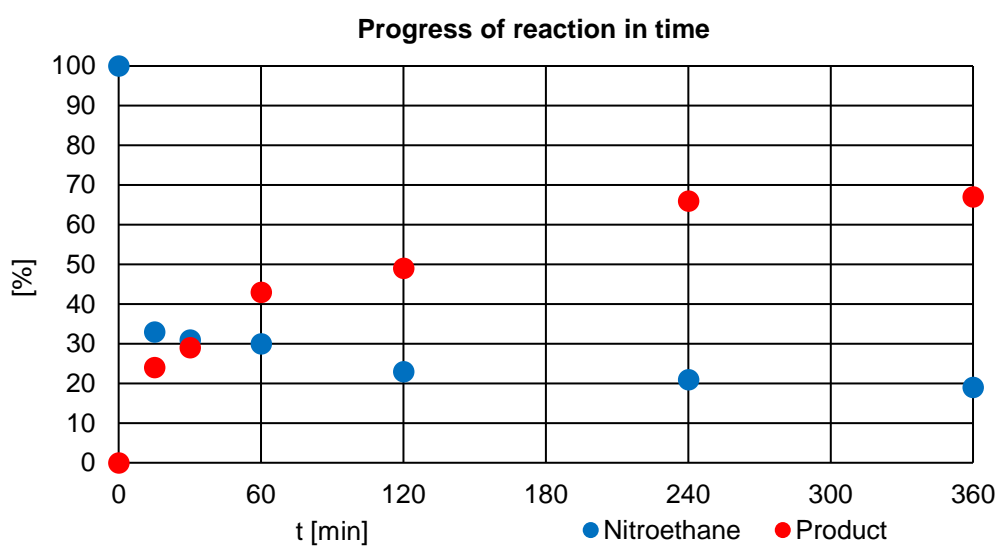
Catalyst **2c** (21 mg; 10 mol%) was dissolved in water (1 mL) or **1f** (20 mg; 10 mol%) was dissolved in mixture of water (1 mL) and DMSO (2 mL) in Schlenk tube. Nitroethane (**3a**) (43 μL; 0.6 mmol) and Et₃N (46 μL; 0.55 eq. or 92 μL; 1.1 eq.) were added. Schlenk tube was 3× flushed and pressurized by O₂ at 4.5 atm., it was placed into thermostat set on 5 or 25 or 45 °C and reaction mixture was stirred for estimated time. Solution of HCl (1M; 1 mL) and standard solution of dimethyl sulfone in DMSO-*d*₆ (100 μL) were added. Sample of the mixture (100 μL) was dissolved in DMSO-*d*₆ (500 μL) and conversion of **3a** to **4a** was estimated by ¹H NMR spectroscopy.

Catalyst	Base (eq.)	Solvent	Time (h)	3a (%)	4a (%)
1f	0.55	H ₂ O + DMSO (1:2)	4	23	66
1f	1.10	H ₂ O + DMSO (1:2)	4	4	69
1f	1.10	H ₂ O + DMSO (1:2)	6	3	70
2c	0.55	H ₂ O	2	20	61
2c	1.10	H ₂ O	2	2	42

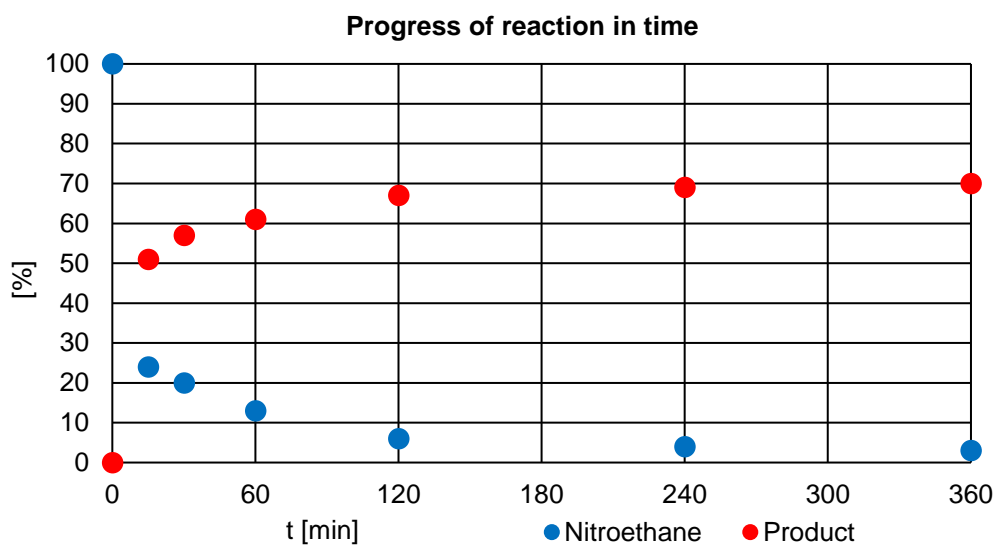
Reaction of 3a in water, in a presence of 10 mol% of 2c, 1.1 eq. Et₃N at 45 °C under oxygen.



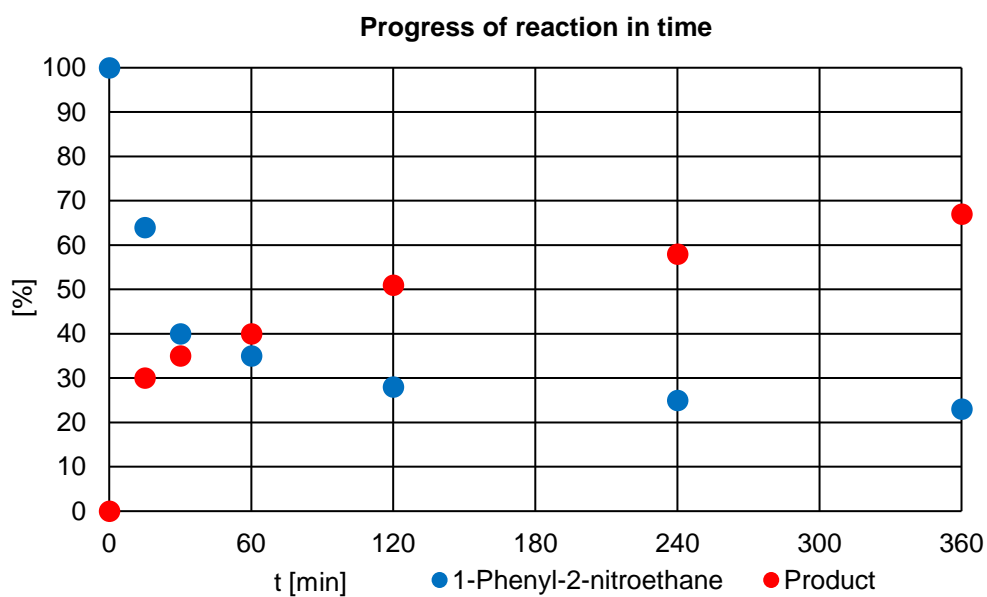
Reaction of 3a in water/DMSO (1:2) mixture, in a presence of 10 mol% of 1f, 0.55 eq. Et₃N at 45 °C under oxygen.



Reaction of 3a in water/DMSO (1:2) mixture, in a presence of 10 mol% of 1f, 1.1 eq. Et₃N at 45 °C under oxygen.

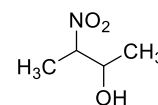


Reaction of 3f in water/DMSO (1:2) mixture, in a presence of 10 mol% of 1f, 0.55 eq. Et₃N at 45 °C under oxygen.



S1.8 Preparative experiments

Preparative experiment based on catalyst **2c** – preparation of 3-nitrobutan-2-ol (**4a**)



Catalyst **2c** (210 mg; 10 mol%) was dissolved in water (10 mL) in Schlenk tube. Nitroethane (**3a**) (430 μ L; 6 mmol) and Et₃N (460 μ L; 0.55 eq.) were added. Schlenk tube was 3 \times flushed and pressurized by O₂ at 4.5 atm. and reaction mixture was stirred at RT for 20 h. Solution of HCl (1M; 40 mL) and water (20 mL) were added. Mixture was extracted by chloroform (3 \times 40 mL). Combined organic layers were dried over Na₂SO₄ and evaporated by RVE. Residue was dissolved in EtOAc (10 mL) and poured on a short silicagel column (30 g). Product was then washed out by 4:1 mixture of hexane and EtOAc (200 mL). Solvents were evaporated by RVE and product was dried under vacuum. Product **4a** was obtained in a form of slightly yellow oil (221 mg; 62%).

Diastereomer A (60%):

¹H NMR (400 MHz, CDCl₃) δ 4.55 – 4.42 (m, 1H), 4.14 (dq, J = 7.5, 6.4, 1H), 1.54 (d, J = 6.9, 3H), 1.28 (d, J = 6.5, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 88.9, 69.3, 19.5, 16.3.

Diastereomer B (40%):

¹H NMR (400 MHz, CDCl₃) δ 4.55 – 4.42 (m, 1H), 4.35 (qd, J = 6.5, 3.2, 1H), 1.56 (d, J = 6.9, 3H), 1.24 (d, J = 6.5, 3H).

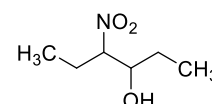
¹³C NMR (101 MHz, CDCl₃) δ 87.2, 68.3, 19.0, 12.8.

HR-MS (APCI-) (m/z): for [M-H]⁻ (C₄H₈NO₃)⁻ calc.: 118.05097, found: 118.05030.

General procedure of preparative experiments based on catalyst **1f**

Catalyst **1f** (64 mg; 10 mol%) was dissolved in water/DMSO (1:2) mixture (10 mL) in Schlenk tube. Starting material (2 mmol) and Et₃N (307 μ L; 1.1 eq.) were added. Schlenk tube was 3 \times flushed and pressurized by O₂ at 4.5 atm. Schlenk tube was placed into water bath heated to 45 °C. The temperature was kept, and reaction mixture was stirred for 4 h. Solution of HCl (1M; 20 mL) and water (20 mL) were added. Mixture was extracted by chloroform (3 \times 40 mL). Combined organic layers were dried over Na₂SO₄ and evaporated by RVE. Crude product was purified by column chromatography using silicagel (100 g) and 5:1 mixture of hexane and EtOAc.

Preparation of 4-nitrohexan-3-ol (**4c**)



Product **4c** was obtained from 1-nitropropane (**3c**) (179 μ L, 2 mmol) via general procedure using **1f** in a form of oil (90 mg, 61%).

Diastereomer A (70%):

¹H NMR (400 MHz, CDCl₃) δ 4.46 – 4.32 (m, 1H), 3.89 – 3.77 (m, 1H), 2.34 – 2.24 (m, 1H), 1.96 – 1.78 (m, 2H), 1.54 – 1.40 (m, 2H), 1.09 – 0.92 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 94.1, 73.2, 26.7, 24.0, 10.3, 9.8.

Diastereomer B (30%):

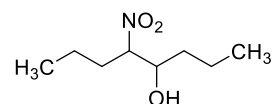
^1H NMR (400 MHz, CDCl_3) δ 4.46 – 4.32 (m, 1H), 3.99 – 3.89 (m, 1H), 2.40 (dd, $J = 4.9, 1.8$, 1H), 2.09 – 2.07 (m, 2H), 1.68 – 1.54 (m, 2H), 1.09 – 0.92 (m, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 93.7, 73.7, 26.4, 21.6, 10.6, 10.2.

HR-MS (APCI-) (m/z): for $[\text{M}-\text{H}]^-$ ($\text{C}_6\text{H}_{12}\text{NO}_3^-$) calc.: 146.08227, found: 146.0171.

Preparation of 5-nitrooctan-4-ol (**4d**)

Product **4d** was obtained from 1-nitrobutane (**3d**) (212 μL , 2 mmol) via general procedure using **1f** in a form of oil (99 mg, 57%).



Diastereomer A (65%):

^1H NMR (400 MHz, CDCl_3) δ 4.51 – 4.42 (m, 1H), 3.88 (d, $J = 7.5$, 1H), 2.19 – 1.98 (m, 2H), 2.16 – 2.11 (m, 1H), 1.81 – 1.30 (m, 6H), 0.95 (m, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 92.8, 72.0, 35.8, 32.6, 19.2, 18.7, 14.0, 13.6.

Diastereomer B (35%):

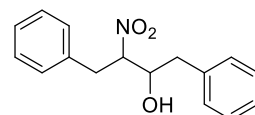
^1H NMR (400 MHz, CDCl_3) δ 4.50 – 4.42 (m, 1H), 4.03 (dd, $J = 8.1, 4.0$, 1H), 2.33 – 2.28 (m, 1H), 2.19 – 1.98 (m, 2H), 1.81 – 1.30 (m, 6H), 0.95 (m, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 92.2, 72.2, 35.3, 30.0, 19.5, 19.0, 13.9, 13.6.

HR-MS (APCI-) (m/z): for $[\text{M}-\text{H}]^-$ ($\text{C}_8\text{H}_{16}\text{NO}_3^-$) calc.: 174.11357, found: 174.11311.

Preparation of 3-nitro-1,4-diphenylbutan-2-ol (**4f**).

Product **4f** was obtained from 2-phenylnitroethane (**3f**) (268 μL , 2 mmol) via general procedure using **1f** in a form of white oily compound (160 mg, 59%).



Diastereomer A (60%):

^1H NMR (400 MHz, CDCl_3) δ 7.56 – 6.98 (m, 10H), 4.73 (m, 1H), 4.12 (tt, $J = 7.7, 5.2$, 1H), 3.62 – 3.10 (m, 2H), 3.09 – 2.72 (m, 2H), 2.38 (d, $J = 7.4$, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 136.2, 135.0, 129.5, 129.06, 129.03, 128.98, 127.7, 127.4, 92.4, 72.5, 40.4, 36.6.

Diastereomer B (40%):

^1H NMR (400 MHz, CDCl_3) δ 7.56 – 6.98 (m, 10H), 4.73 (m, 1H), 4.34 (dq, $J = 8.6, 4.5$, 1H), 3.62 – 3.10 (m, 2H), 3.09 – 2.72 (m, 2H), 2.29 (d, $J = 4.1$, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 136.2, 135.7, 129.5, 129.12, 129.00, 128.96, 127.56, 127.45, 92.7, 73.0, 39.8, 34.8.

HR-MS (APCI-) (m/z): for $[\text{M}-\text{H}]^-$ ($\text{C}_{16}\text{H}_{16}\text{NO}_3^-$) calc.: 270.11357, found: 270.11365.

Preparation of 3,4,5-triphenyl-4,5-dihydroisoxazole 2-oxide (7)

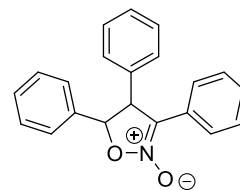
Product **7** was obtained from (nitromethyl)benzene (**3g**) (237 μ L, 2 mmol) via general procedure using **1f** in a form of white crystalline solid (110 mg, 52%).

m. p.: 161.5 – 163.0 $^{\circ}$ C (lit.¹⁴ 162 – 163 $^{\circ}$ C)

1 H NMR (400 MHz, CDCl₃) δ 7.90 – 7.82 (m, 2H), 7.47 – 7.23 (m, 13H), 5.43 (d, J = 4.4, 1H), 4.83 (d, J = 4.4, 1H).

13 C NMR (101 MHz, CDCl₃) δ 139.22, 139.12, 129.7, 129.45, 129.25, 129.0, 128.7, 128.5, 127.5, 126.9, 126.3, 125.3, 116.1, 83.9, 59.9.

HR-MS (APCI+) (m/z): for [M+H]⁺ (C₂₁H₁₈NO₂⁺) calc.: 316,13321, found: 316,13354.



S1.9 Quantum chemical calculations

Calculations were performed using ORCA 4.2.0¹⁵ using the CESNET Metacentrum grid infrastructure¹⁶. Preoptimizations of structures' geometries were done using semiempirical GFN2-xTB¹⁷ calculation method. The most stable conformers of the molecules were found by CREST¹⁸ software with default options. The geometries of the three most stable conformers have been optimized at the B3LYP¹⁹/def2-TZVP²⁰ level with def2/J auxiliary basis²¹ and the RIJCOSX approximation²². B3LYP functional is commonly used for calculations on flavins.²³ For the long-range interactions the D3BJ²⁴ dispersion correction with the Becke-Johnson damping was added. The gas phase Gibbs energies at 298 K were computed at the B3LYP¹⁹/def2-TZVP²⁰ level and were not scaled. Solvation free energies were computed using CPCM²⁵ formalism and parameters for DMSO. Single point energies of all structures were calculated using DLPNO-CCSD(T) method²⁶ with def2-QZVP basis set²⁰ with def2-QZVPP/C²⁷ and def2/J auxiliary basis²¹ and the RIJCOSX approximation²². Basis set superposition error (BSSE) effect on the geometries was excluded by optimizing geometries of (description of test set) at def2-QZVP level and finding the geometries being unchanged from the def2-TZVP level. The energetic effect of BSSE was treated by calculation of final energies using DLPNO-CCSD(T)²⁸ with sufficiently large basis set.

The final composite energy of the most stable conformer was calculated as:

$$E_{\text{composite}} = E_{\text{DLPNO-CCSD(T)}} + dG_{\text{thermal}} + dG_{\text{solvation}}.$$

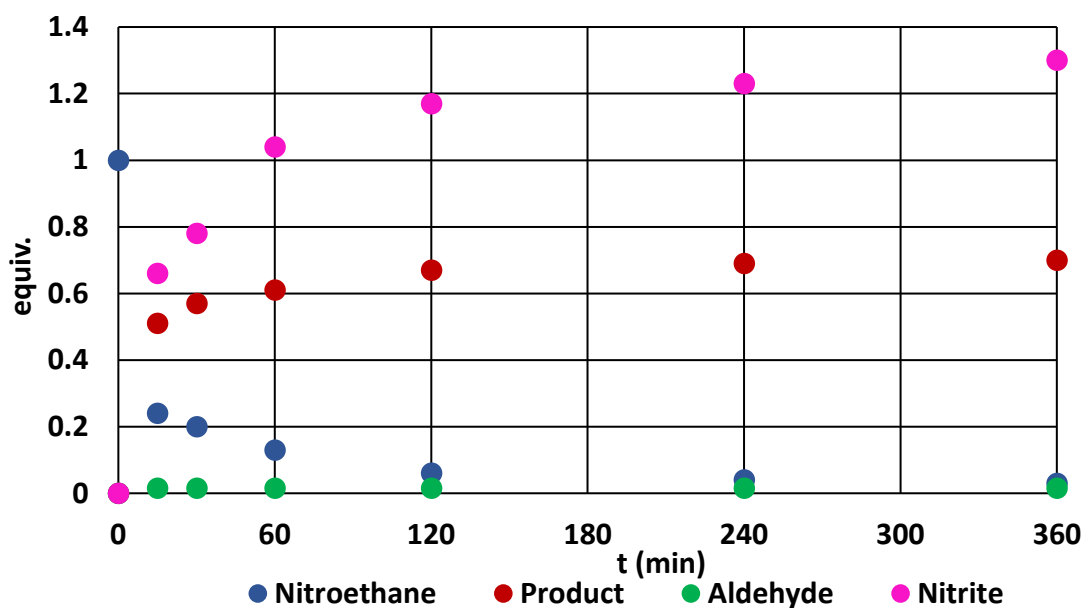
S2 Mechanistic studies

S2.1 Measurement of reaction course

1f (20 mg; 10 mol%) was dissolved in water/DMSO (1:2) mixture (3 mL) in Schlenk tube. Nitroethane (**3a**) (43 μ L; 0.6 mmol) and Et₃N (92 μ L; 1.1 eq.) were added. Schlenk tube was 3 \times flushed and pressurized by O₂ at 4.5 atm. Schlenk tube was stirred and placed into thermostat set on 45 °C. Reaction was interrupted after 15/30/60/120/240/360 minutes.

Concentration of nitroethane (**3a**), 3-nitrobutan-2-ol (**4a**) and acetaldehyde was estimated by ¹H NMR spectroscopy after addition of dimethyl sulfone in DMSO-*d*₆ as an internal standard.

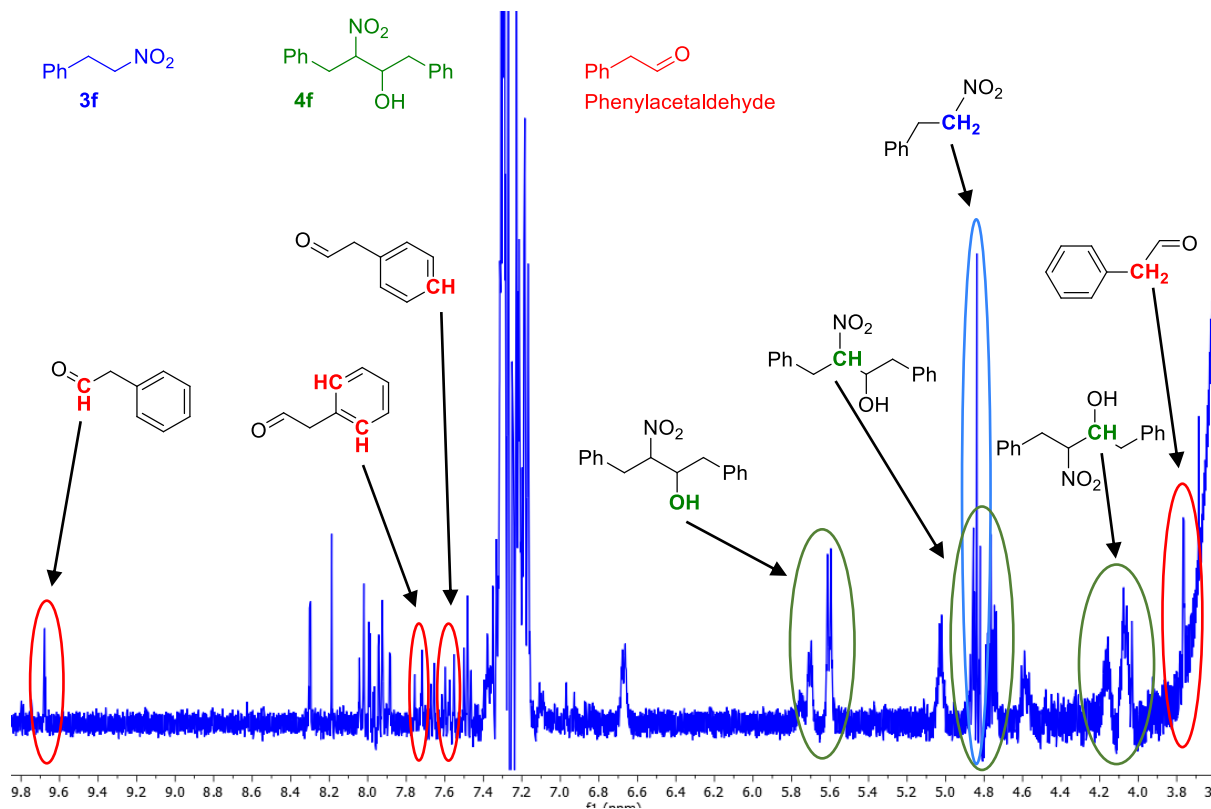
Modified method of Griess colorimetric analysis published in lit.²⁹ was used. Reaction mixture was diluted by water to a volume of 100 mL. Then it was extracted by EtOAc (3 \times 50 mL) and by diethyl ether (3 \times 50 mL). Aliquot of water layer was treated by Griess reagent and analysed by UV/Vis spectroscopy.



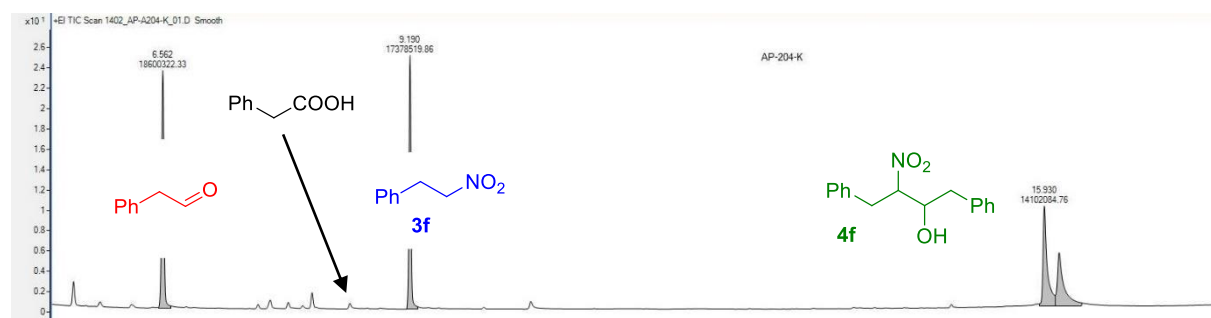
S2.2 Analysis of sideproducts

Catalyst **1f** (20 mg; 10 mol%) was dissolved in water/DMSO (1:2) mixture (3 mL) in Schlenk tube. 2-Phylnitroethane (**3f**) (80 μ L; 0.6 mmol) and Et₃N (92 μ L; 1.1 eq.) were added. Schlenk tube was 3 \times flushed and pressurized by O₂ at 4.5 atm. and placed into thermostat. Reaction mixture was stirred for 4 h at 45 $^{\circ}$ C. After 4 h, reaction mixture was analysed by GCMS and ¹H NMR spectroscopy.

NMR analysis of reaction mixture



GCMS analysis of reaction mixture



S2.3 Reaction of nitromethane (3b)

Analysis of products

Catalyst **2c** (21 mg; 10 mol%) was dissolved in water (1 mL) in Schlenk tube. Nitromethane (**3b**) (32 μ L; 0.6 mmol) and Et₃N (46 μ L; 0.55 eq.) were added. Schlenk tube was 3 \times flushed and pressurized by O₂ at 4.5 atm. Reaction mixture was stirred at RT for 16 h. Then, it was evaporated by RVE and dried under vacuum. Residue was dissolved in D₂O (600 μ L) and analysed by ¹H NMR spectroscopy.

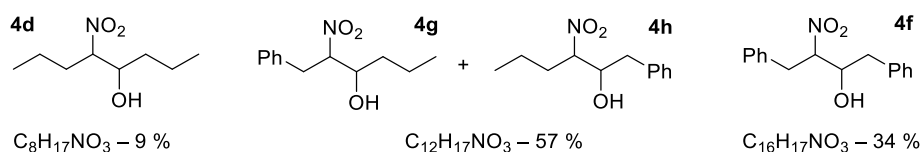
Presence of 2-nitropropane-1,3-diol and 2-(hydroxymethyl)-2-nitropropane-1,3-diol was confirmed by comparison of the obtained NMR spectra with literature³⁰.

Detection of formaldehyde in reaction mixture

Catalyst **2c** (21 mg; 10 mol%) was dissolved in water (1 mL) in Schlenk tube. Nitromethane (**3b**) (32 μ L; 0.6 mmol) and Et₃N (46 μ L; 0.55 eq.) were added. Schlenk tube was 3 \times flushed and pressurized by O₂ at 4.5 atm. Reaction mixture was stirred at RT for 90 min. Then, semicarbazide hydrochloride (34 mg, 0.3 mmol) was added. Reaction mixture was stirred for additional 30 min. Sample of the mixture (100 μ L) was dissolved in DMSO-*d*₆ (500 μ L) and analysed by ¹H NMR spectroscopy. Presence of formaldehyde semicarbazone was confirmed by comparison of the obtained NMR spectra with literature³¹.

S2.4 Crossed experiment

Catalyst **1f** (20 mg; 10 mol%) was dissolved in water/DMSO (1:2) mixture (3 mL) in Schlenk tube. 1-Nitrobutane (**3d**) (32 μ L; 0.3 mmol), 2-phenylnitroethane (**3f**) (40 μ L; 0.3 mmol) and Et₃N (92 μ L; 0.66 mmol) were added. Schlenk tube was 3 \times flushed and pressurized by O₂ at 4.5 atm. and placed into thermostat. Reaction mixture was stirred for 4 h at 45 °C. After 4 h, solution of HCl (1M; 1 mL) and water (20 mL) were added. Mixture was extracted by CHCl₃ (3 \times 25 mL). Combined organic layers were extracted by water (3 \times 50 mL), dried by Na₂SO₄ and solvent was removed under reduced pressure. Residue was analysed by LCMS. Relative composition of reaction mixture was:



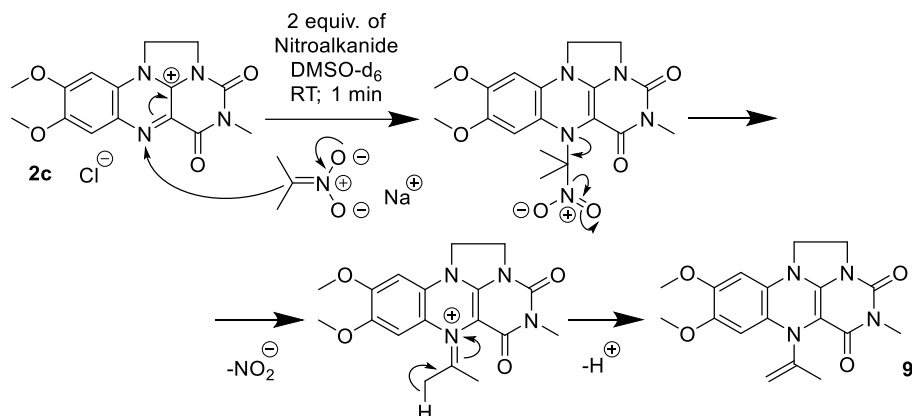
S2.5 Experiment under irradiation

Catalyst **1f** (10 mg; 10 mol%) was dissolved in water/DMSO (1:2) mixture (4.5 mL) in Schlenk tube. 2-Phenyl-1-nitroethane (**3f**) (40 μ L; 0.3 mmol) and Et₃N (46 μ L; 1.1 eq.) were added. Schlenk tube was 3 \times flushed and pressurized by O₂ at 4.5 atm. and placed into thermostat. Reaction mixture was irradiated by 447 nm LED and stirred for 4 h at 45 °C. After 4 h, solution of HCl (1M; 0.5 mL) and standard solution of dimethyl sulfone in DMSO-*d*₆ (100 μ L) were added. Sample of the mixture (100 μ L) was dissolved in DMSO-*d*₆ (500 μ L) and analysed by ¹H NMR spectroscopy.

S2.6 Detection of adducts by NMR and MS

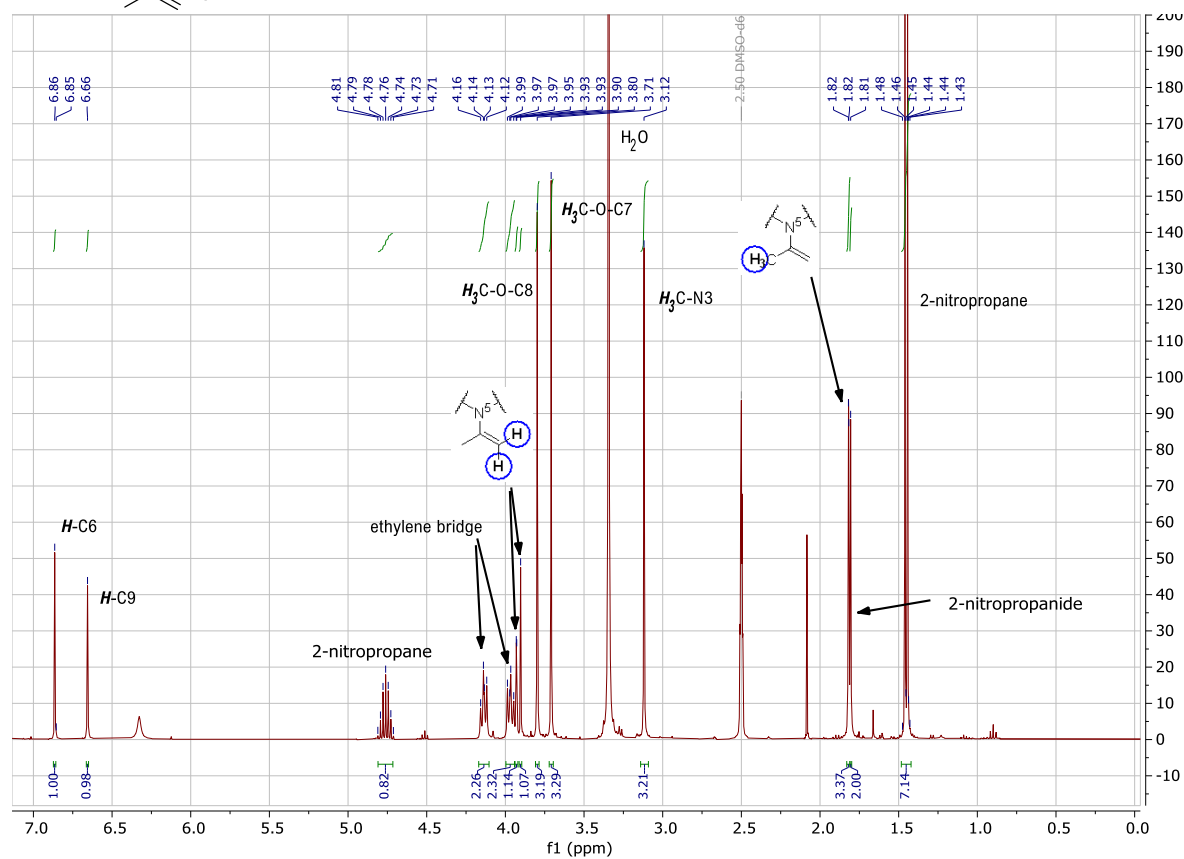
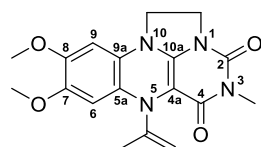
Addition of 2-nitropropan-2-ide (**S3**) to position N(5) of **2c** – adduct **9**

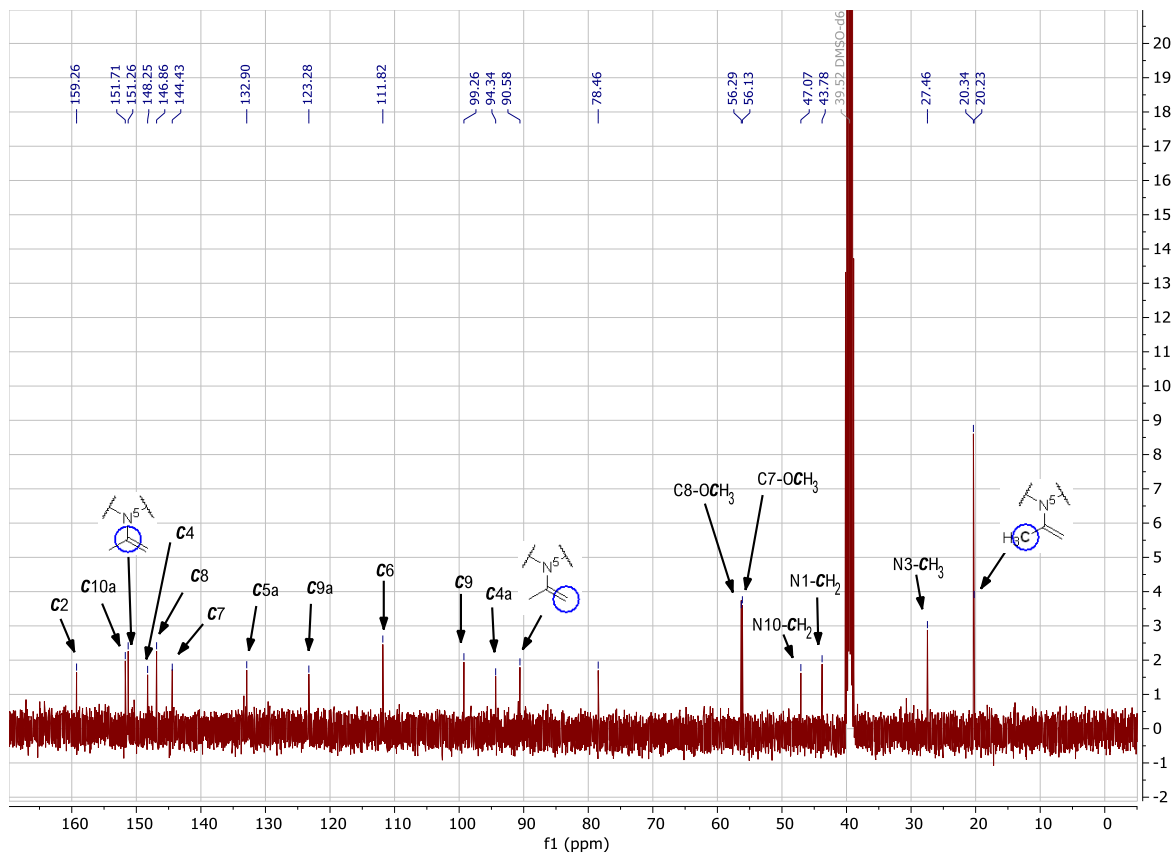
Mechanism of formation of adduct **9**:



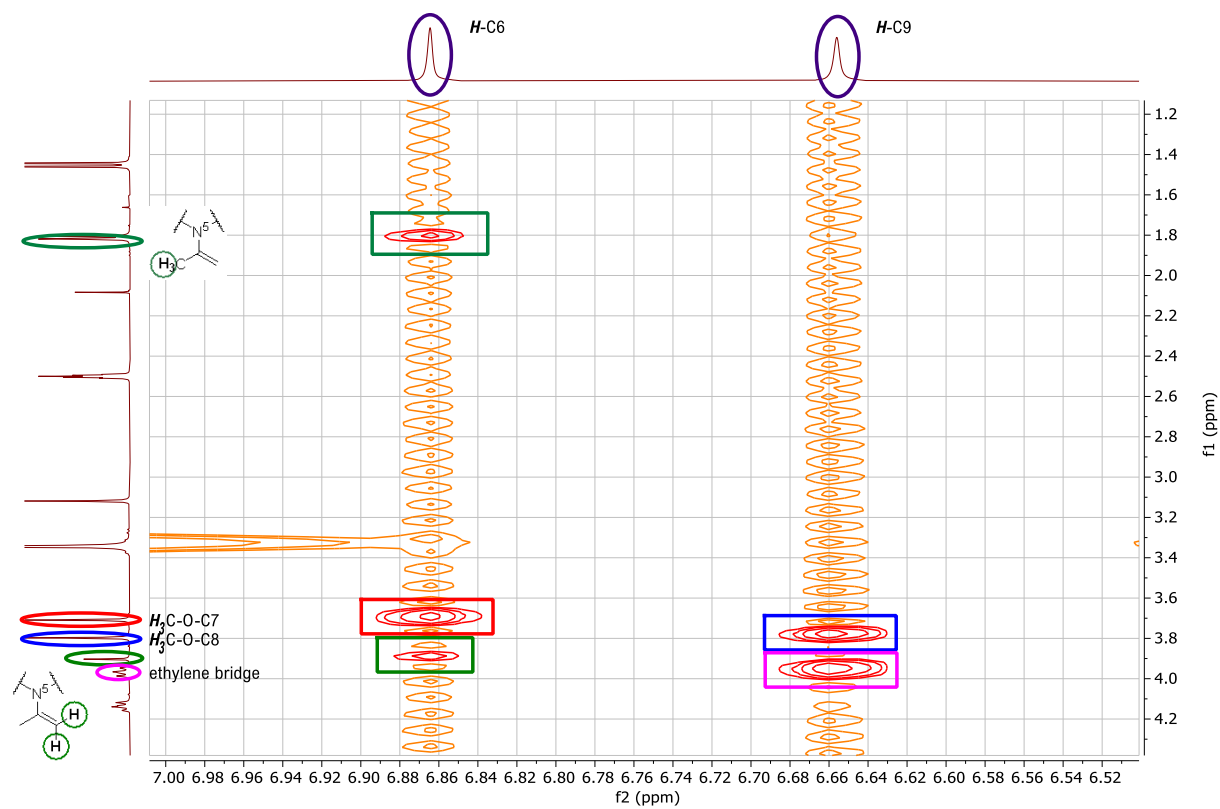
NMR analysis of adduct **9**:

2c (3.5 mg; 0.01 mmol) and **S3** (2.2 mg, 0.02 mmol) were dissolved in DMSO- d_6 (0.75 mL) in NMR tube. The mixture was shaken and sonicated until all material was dissolved. The mixture was then analysed by NMR spectroscopy.



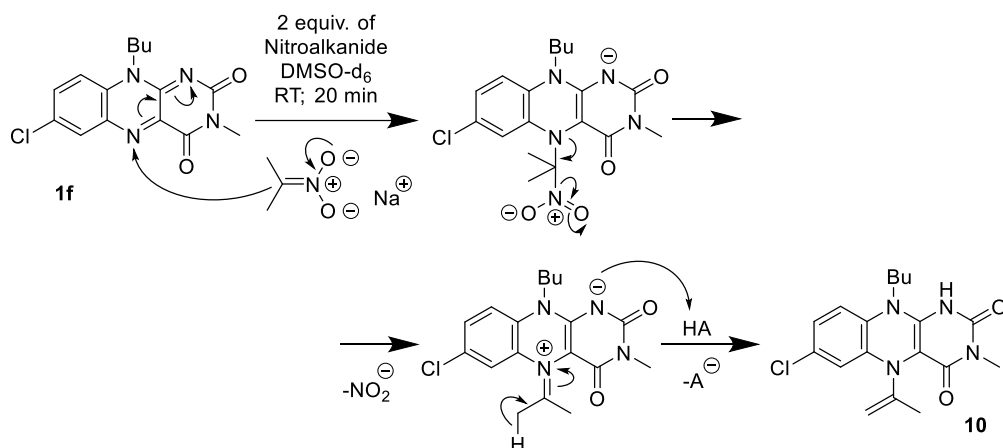


NOESY:



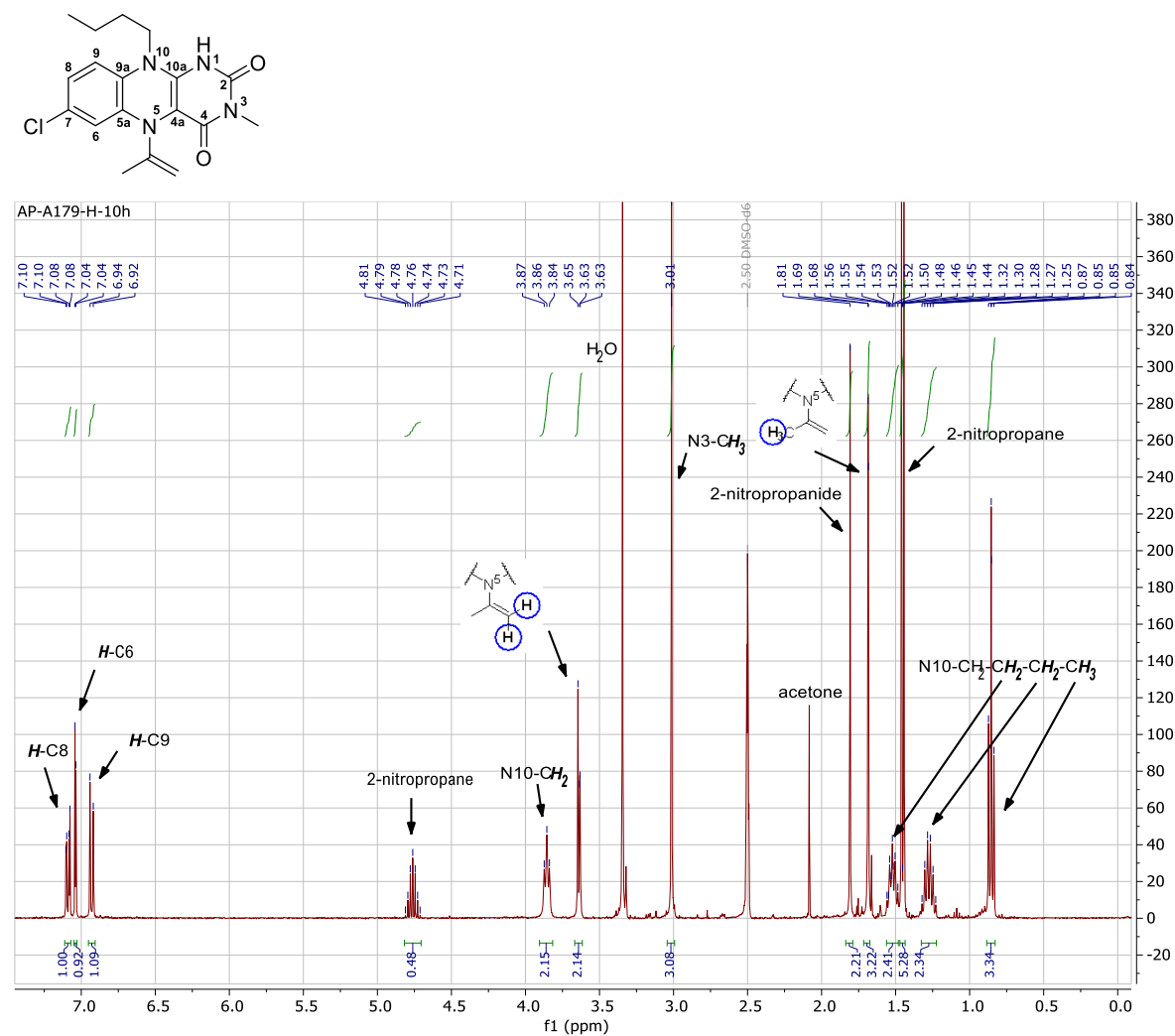
Addition of 2-nitropropan-2-ide (**S3**) to position N(5) of **1f** – adduct **10**

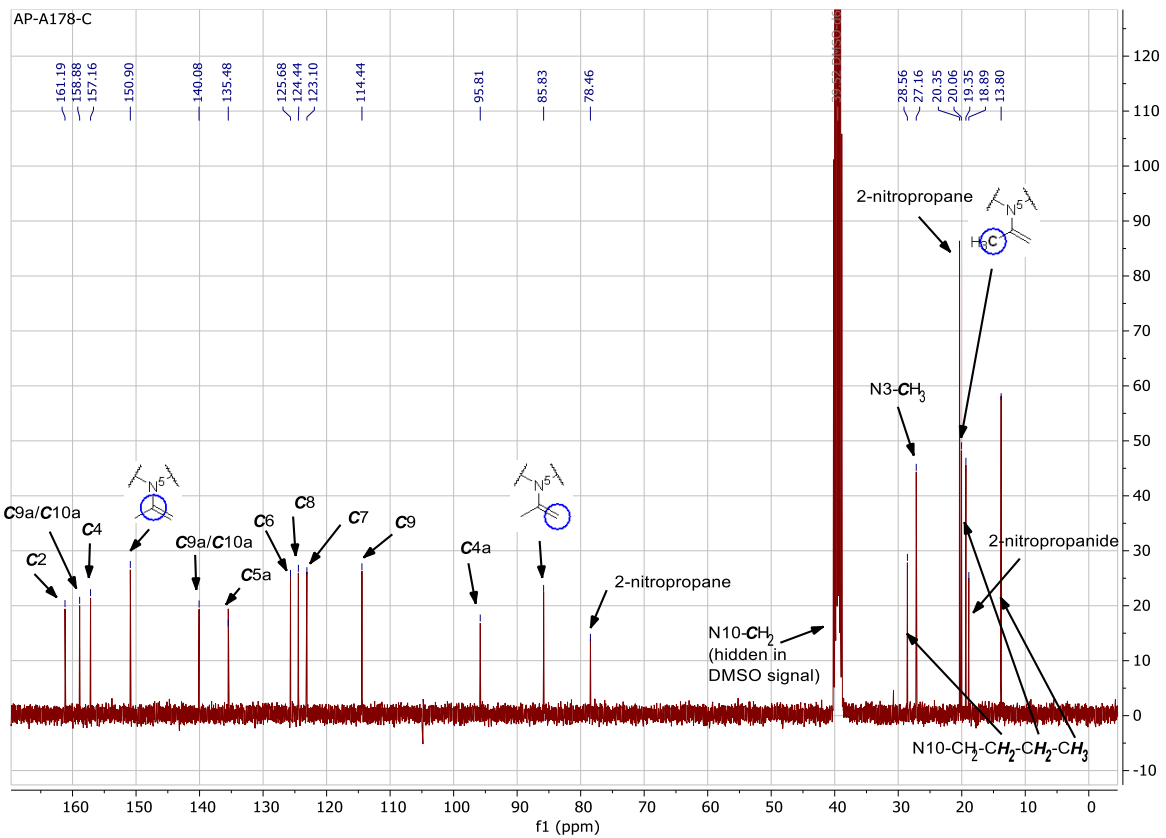
Mechanism of formation of adduct **10**:



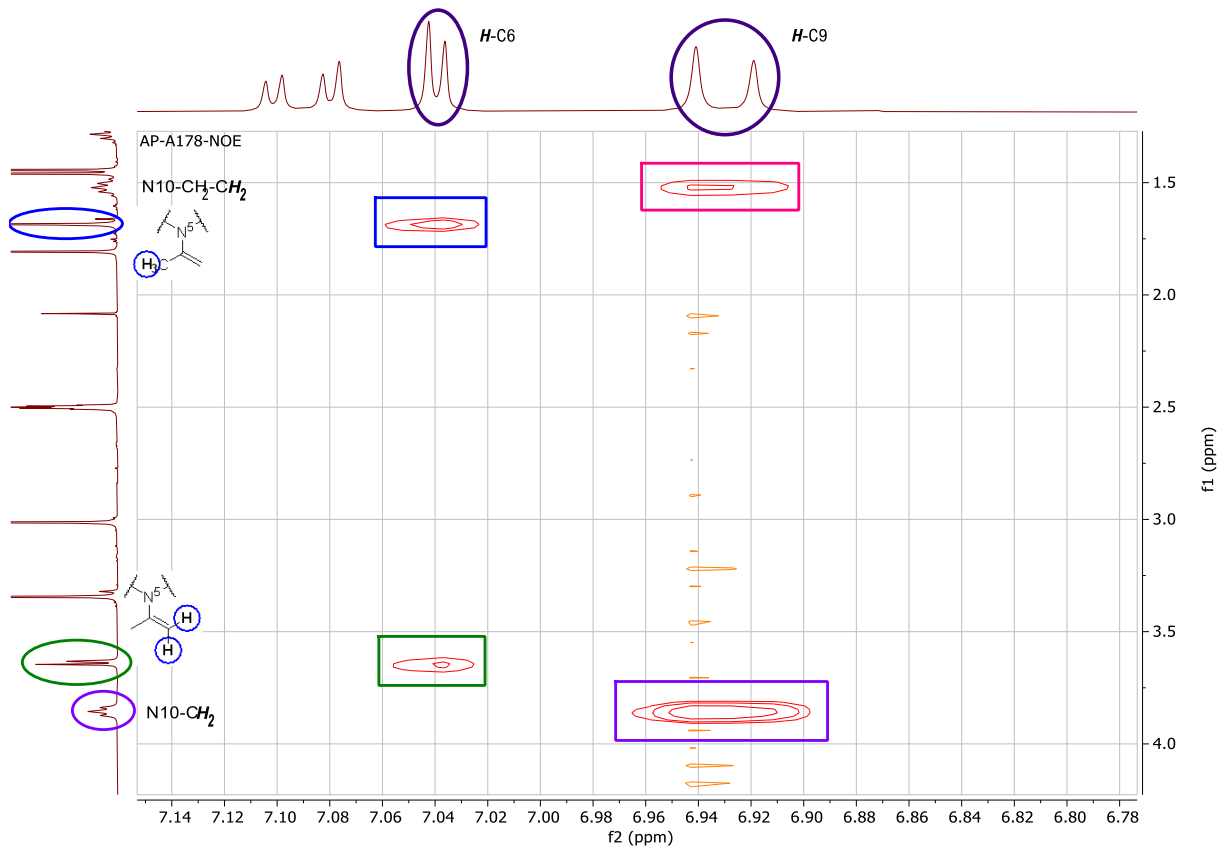
NMR analysis of adduct **10**:

1f (3.2 mg; 0.01 mmol) and **S3** (2.2 mg, 0.02 mmol) were dissolved in DMSO- d_6 (0.75 mL) in NMR tube. The mixture was shaken and sonicated until all material was dissolved. After 20 minutes, the mixture was analysed by NMR spectroscopy.



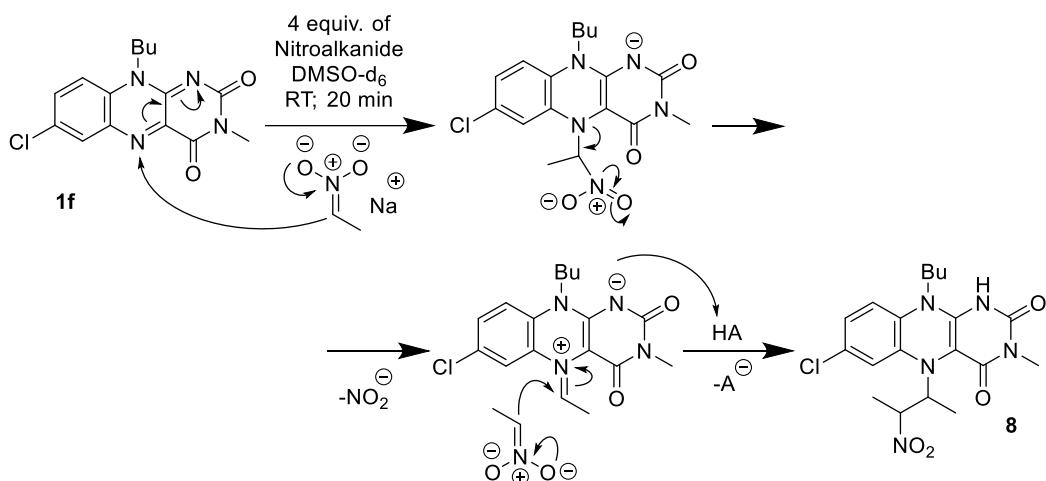


NOESY:



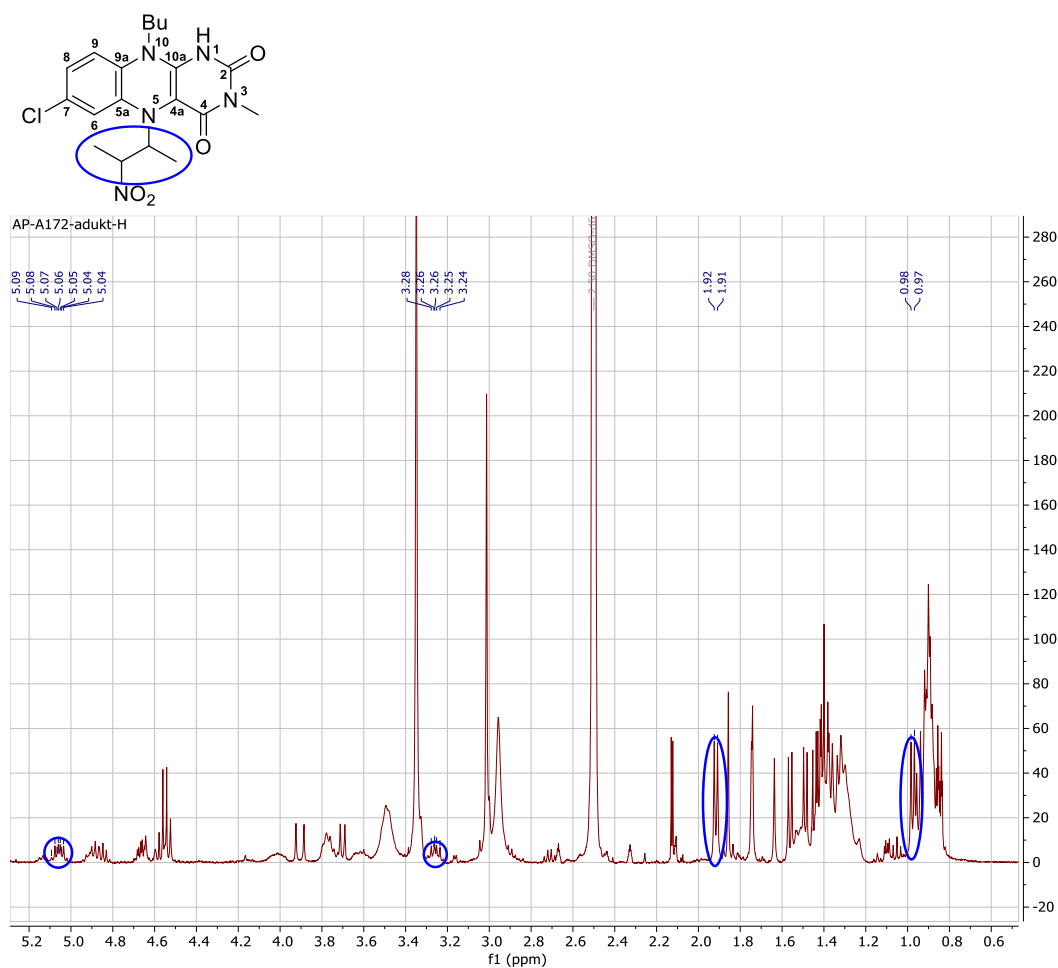
Interaction of 1-nitroethan-1-ide (**S2**) with **1f** – 3-nitrobut-2-yl adduct **9**

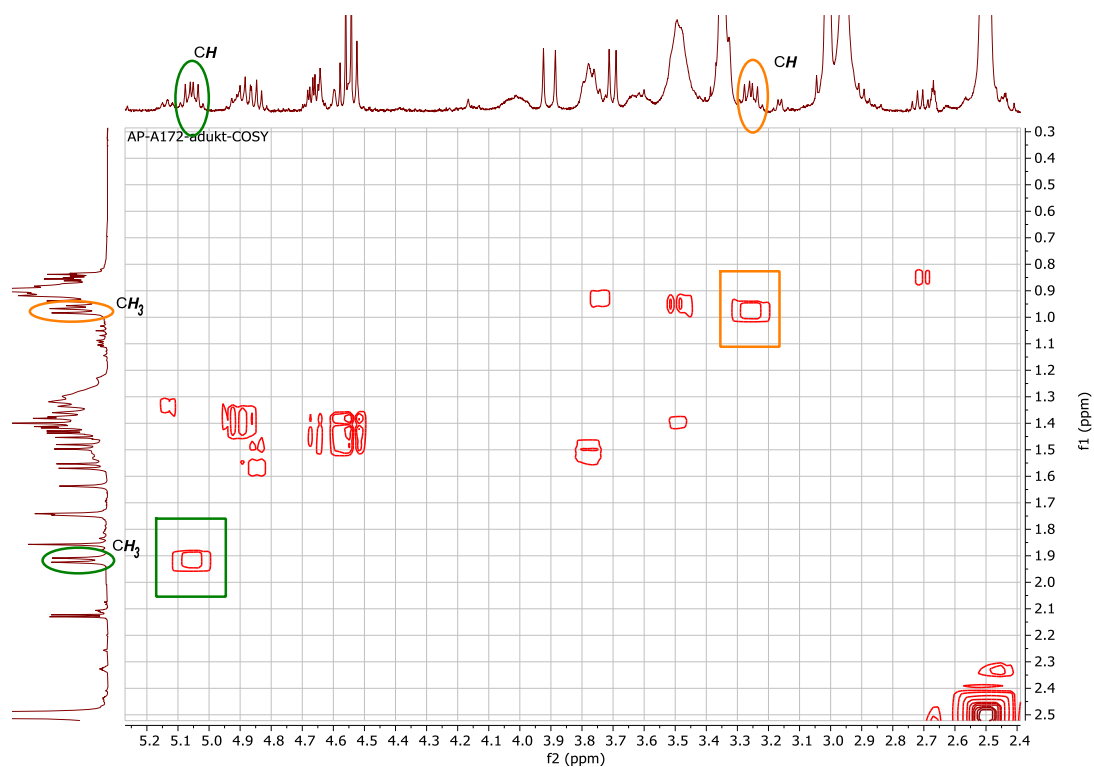
Mechanism of formation of adduct **8**:



NMR analysis of adduct **8**:

1f (3.2 mg; 0.01 mmol) and **S2** (4 mg, 0.04 mmol) were dissolved in DMSO- d_6 (0.75 mL) in NMR tube. The mixture was shaken and sonicated until all material was dissolved. After 20 minutes, the mixture was analysed by NMR spectroscopy.

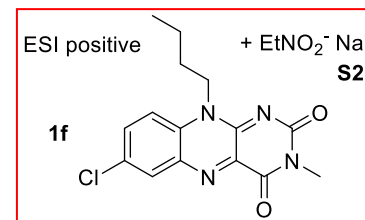
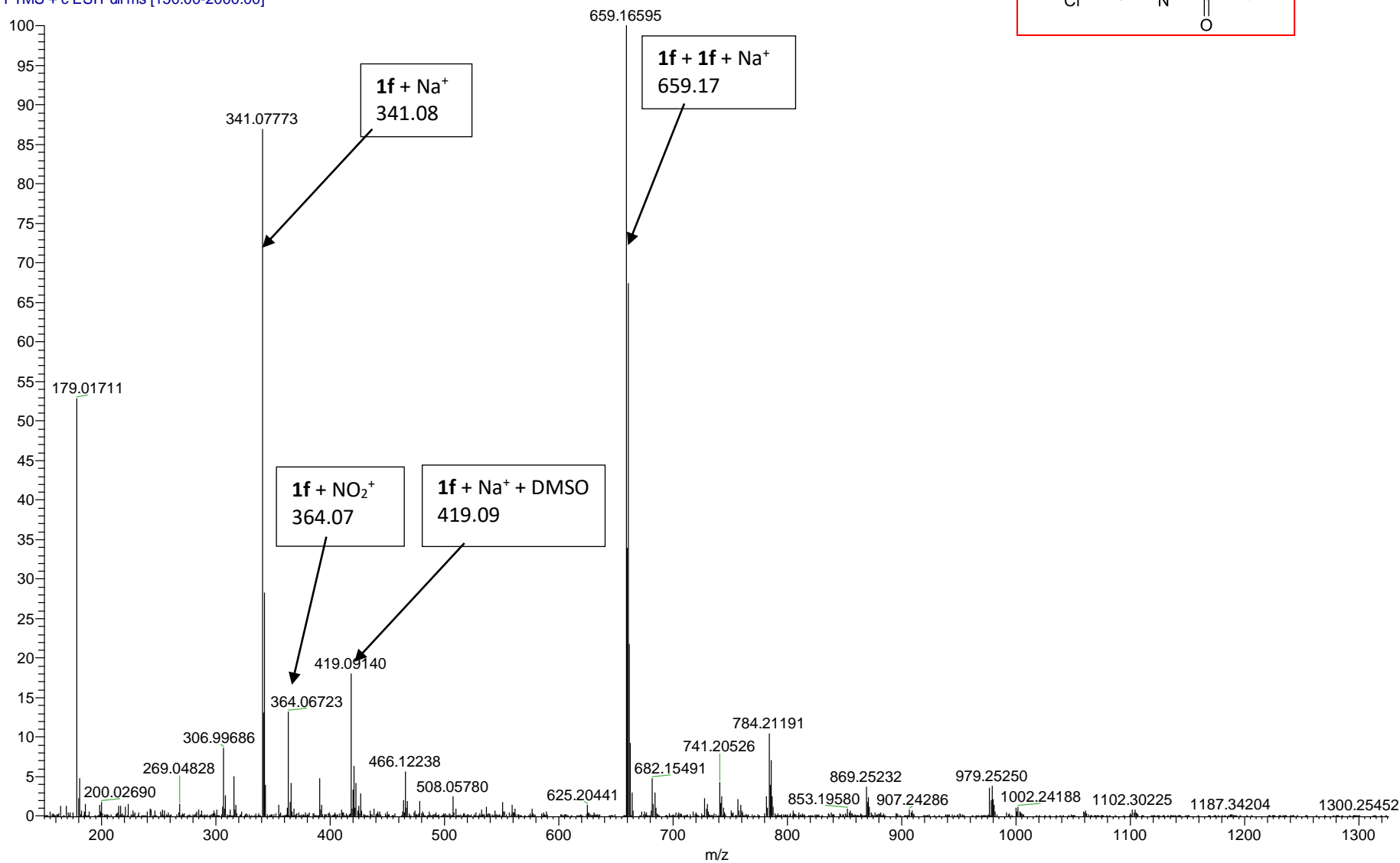




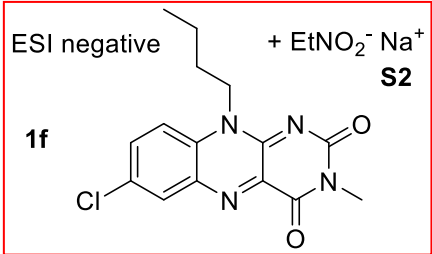
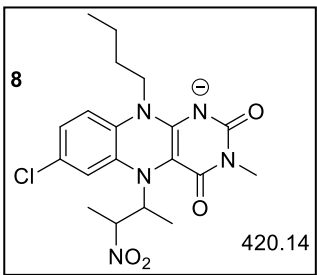
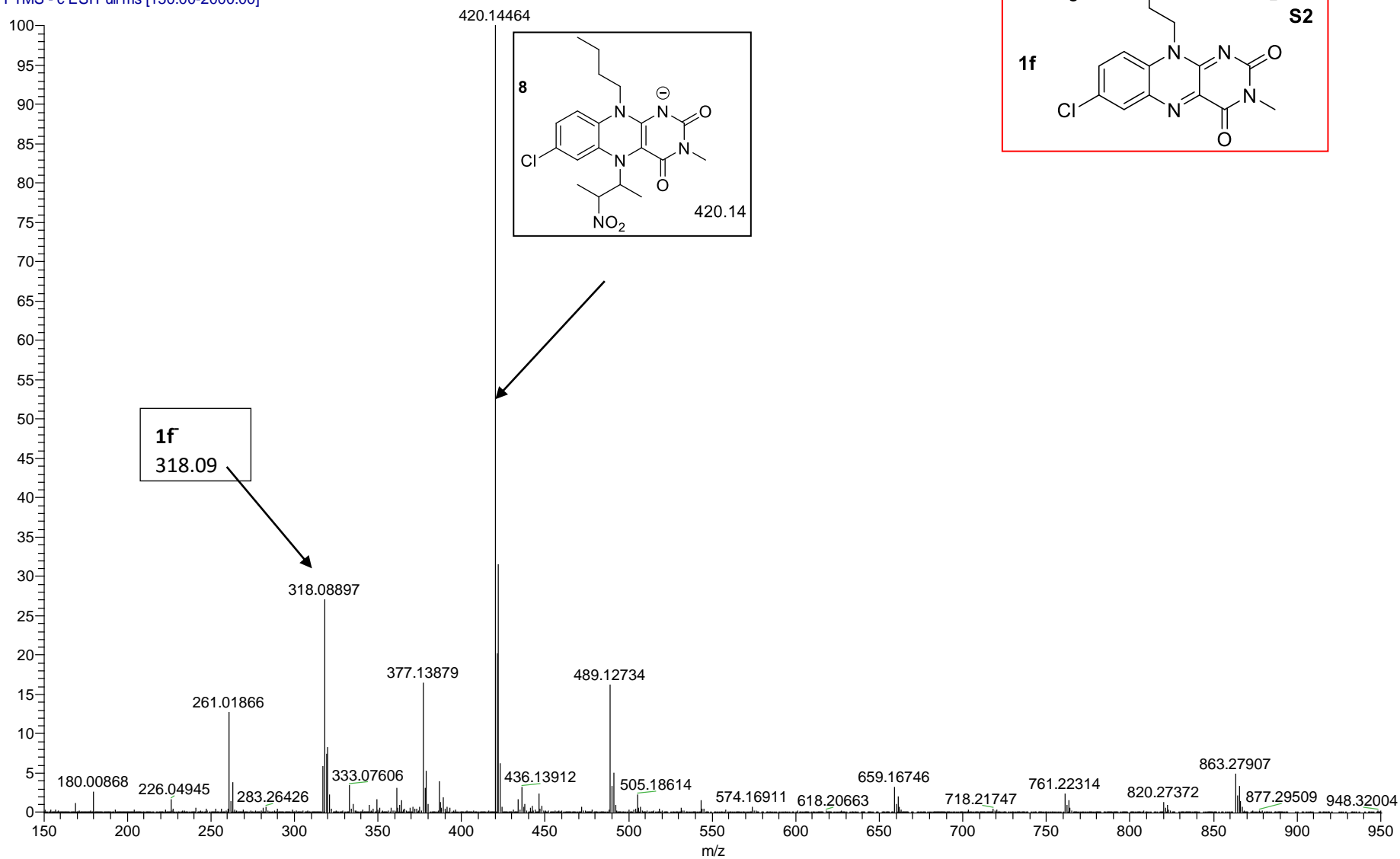
MS analysis of adducts **8**, **9** and **10**

1f (3.2 mg; 0.01 mmol) or **2c** (3.5 mg; 0.01 mmol) and **S2** (4 mg, 0.04 mmol) or **S3** (2.2 mg, 0.02 mmol) were dissolved in DMSO (1 mL). The solution was sonicated until all material was dissolved. The mixture was kept at RT for 15 minutes and then it was diluted by acetonitrile and analysed by HR-MS using ESI positive or ESI negative ionization.

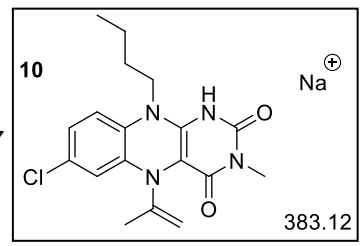
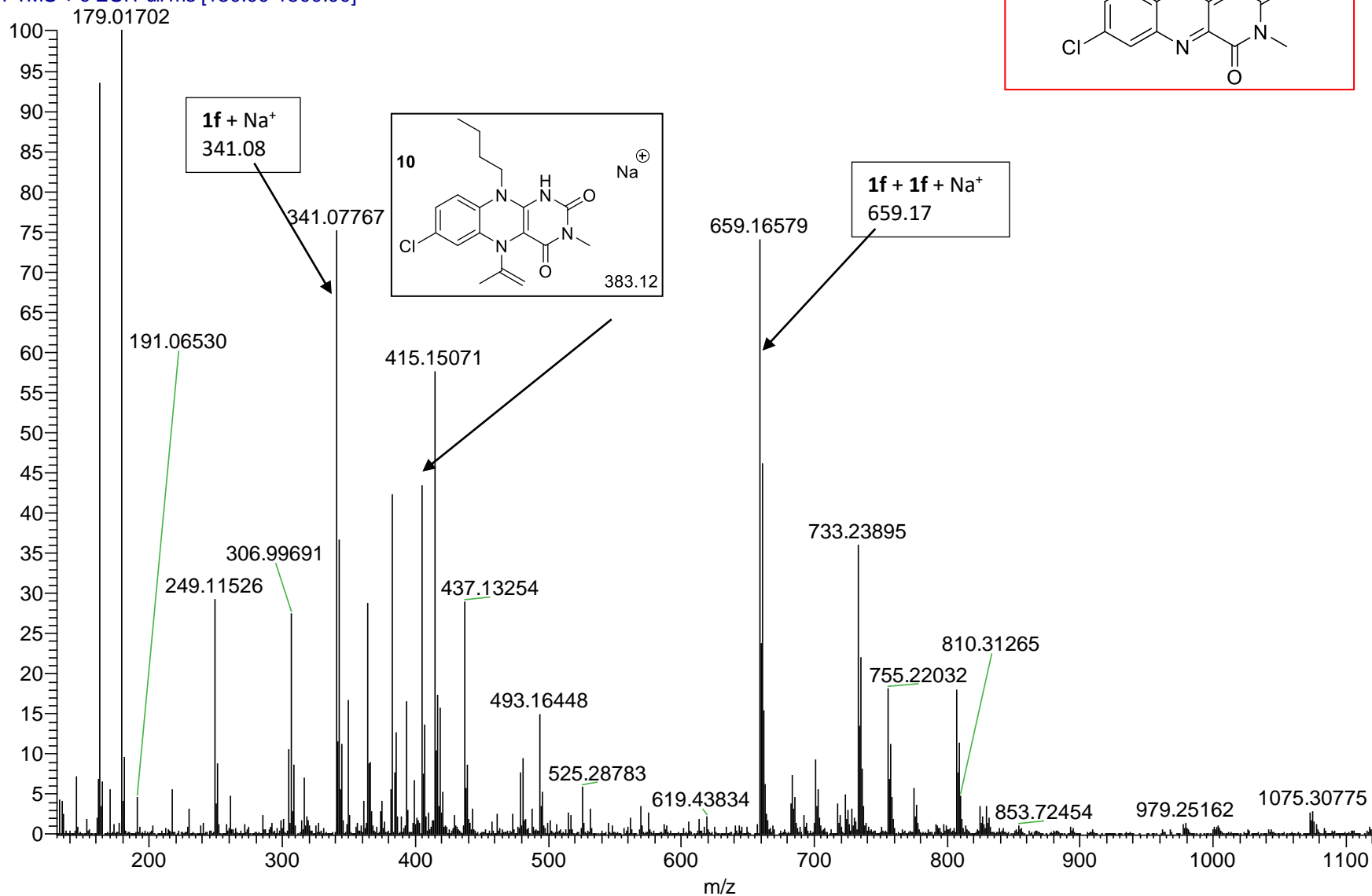
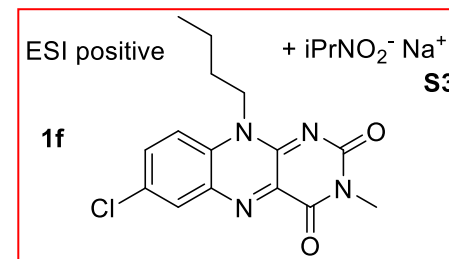
208_Pokluda_ESIpos_vz_15min_1 #83 RT: 1.82 AV: 1 NL: 4.58E6
T: FTMS + c ESI Full ms [150.00-2000.00]



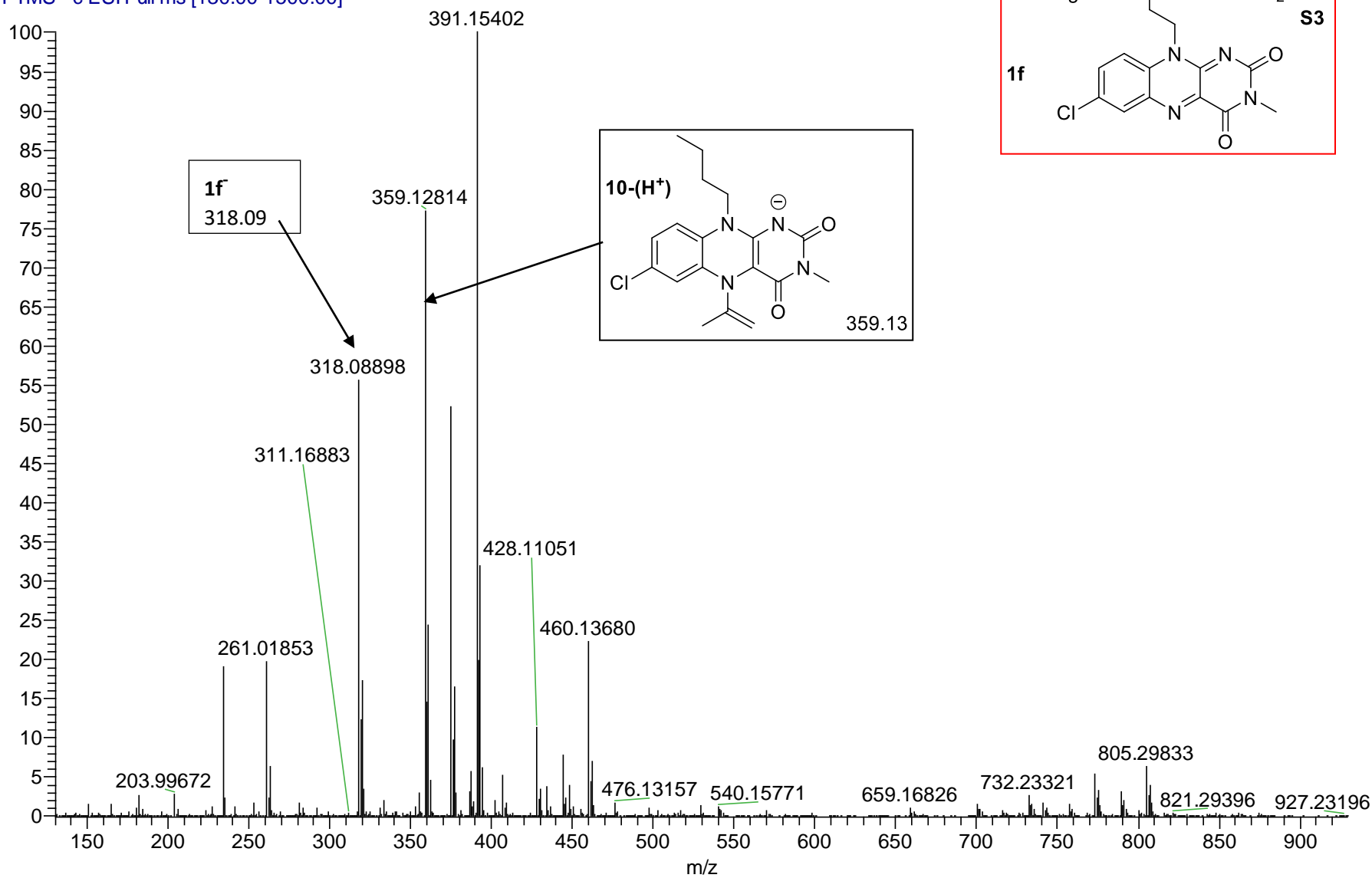
208_Pokluda_ESIheg_vz_15min_1 #8-22 RT: 0.19-0.55 AV: 15 NL: 8.27E6
T: FTMS - c ESI Full ms [150.00-2000.00]



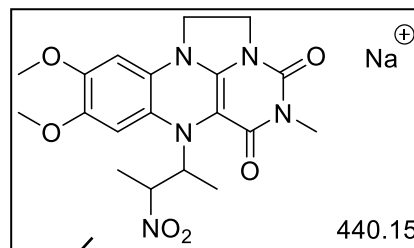
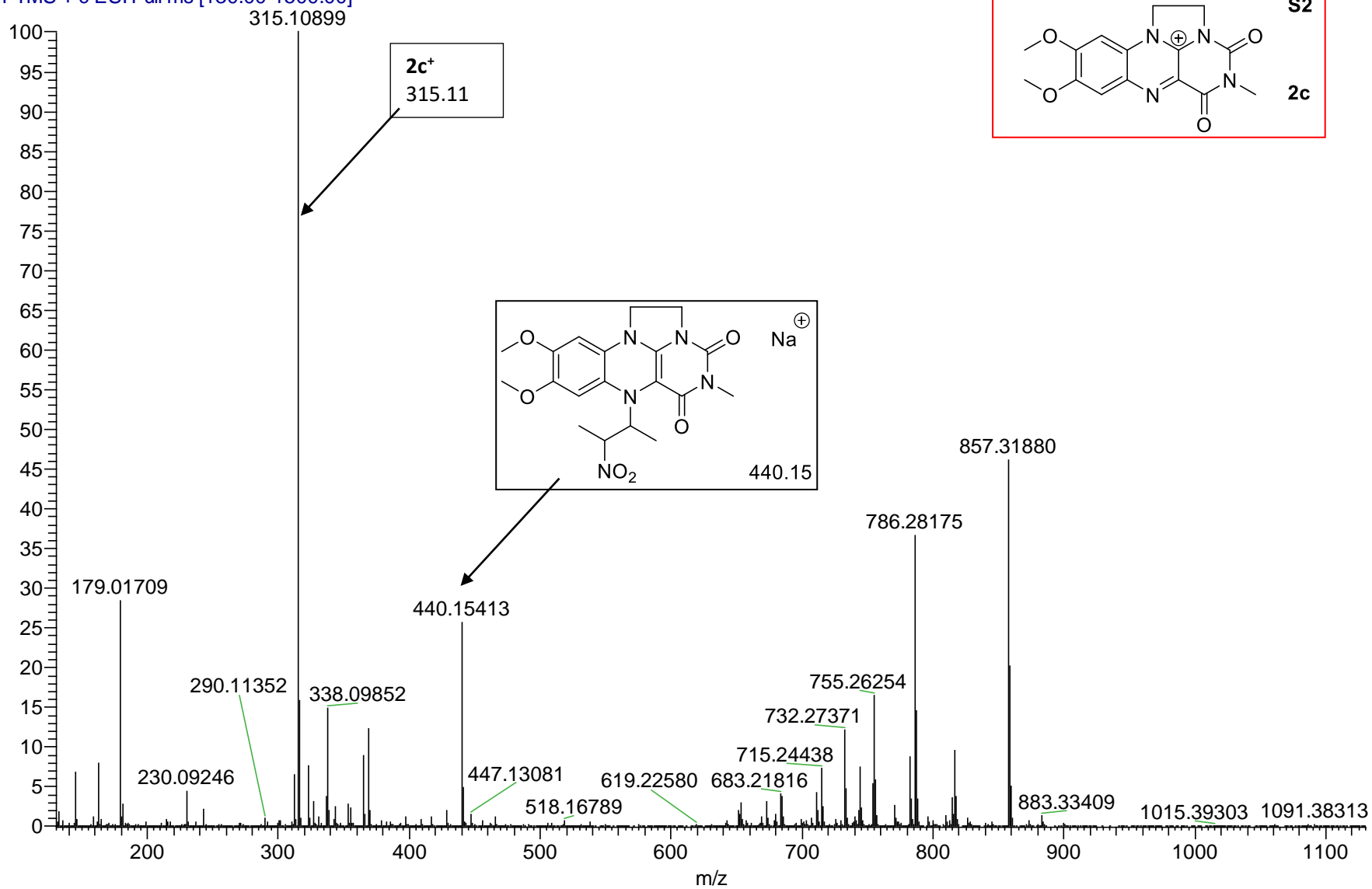
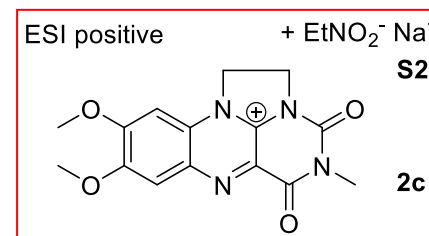
277_Pokluda_ESIpos_A-141-1_1 #33-36 RT: 0.48-0.52 AV: 4 NL: 7.43E6
T: FTMS + c ESI Full ms [130.00-1500.00]



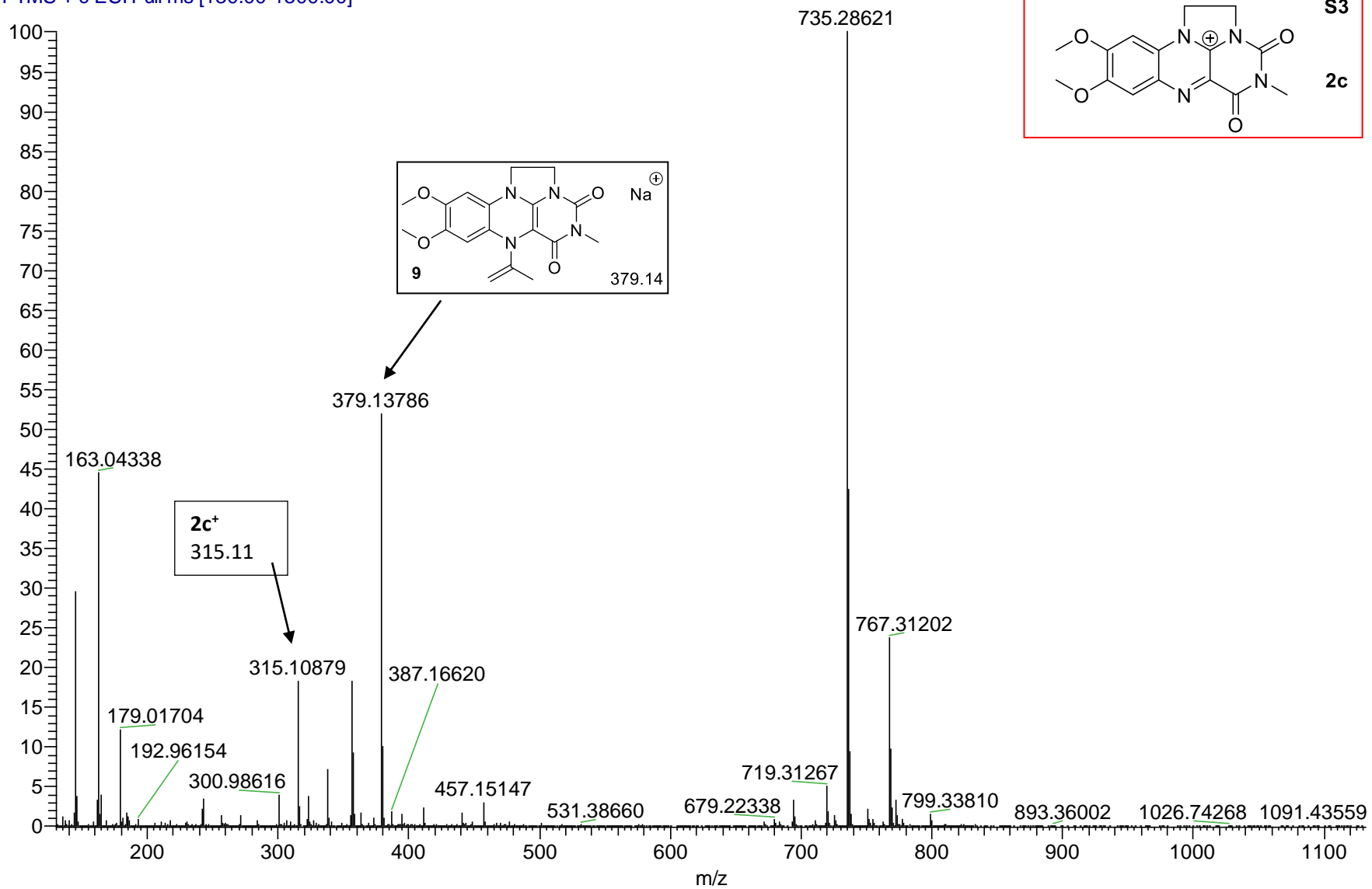
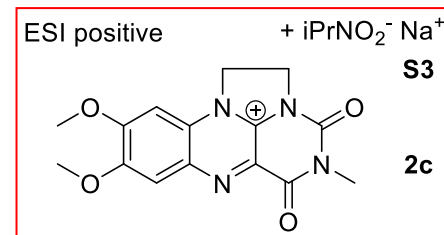
277_Pokluda_ESIneg_A-141_1 #19-22 RT: 0.47-0.55 AV: 4 NL: 1.02E7
T: FTMS - c ESI Full ms [130.00-1500.00]



277_Pokluda_ESIpos_A-142-1_1 #30-39 RT: 0.43-0.56 AV: 10 NL: 2.20E7
T: FTMS + c ESI Full ms [130.00-1500.00]

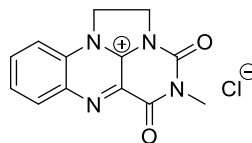


277_Pokluda_ESIpos_A-143-1_1 #97-109 RT: 1.42-1.59 AV: 13 NL: 2.42E7
T: FTMS + c ESI Full ms [130.00-1500.00]

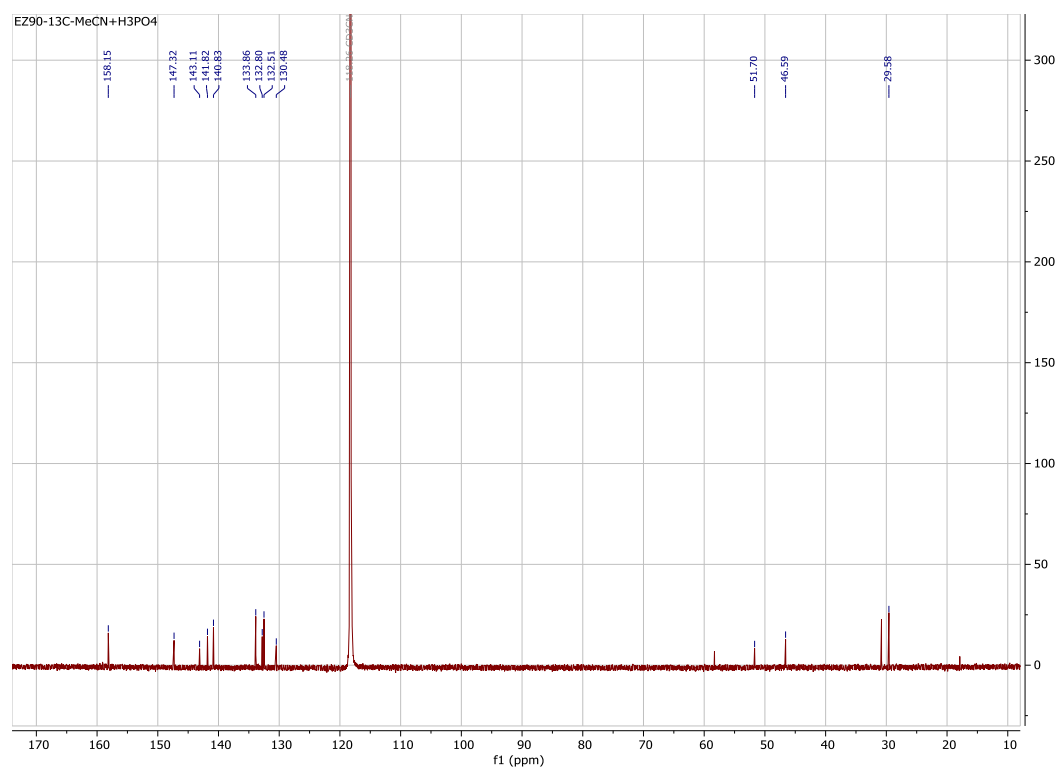
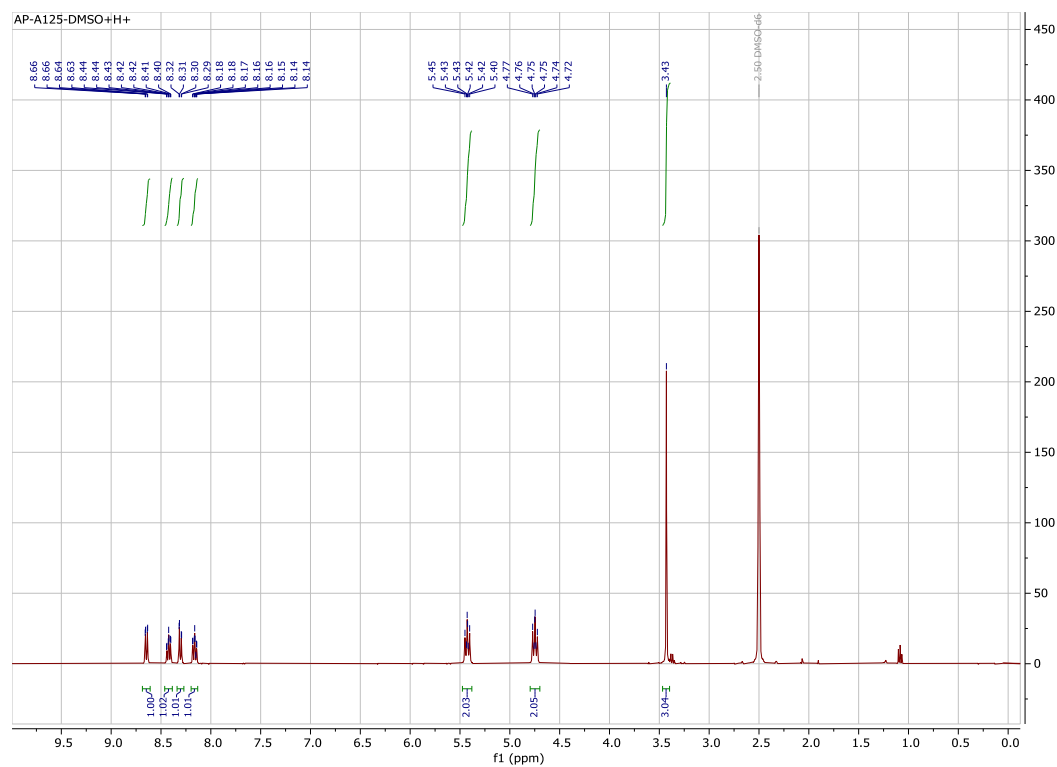


S3 NMR spectra

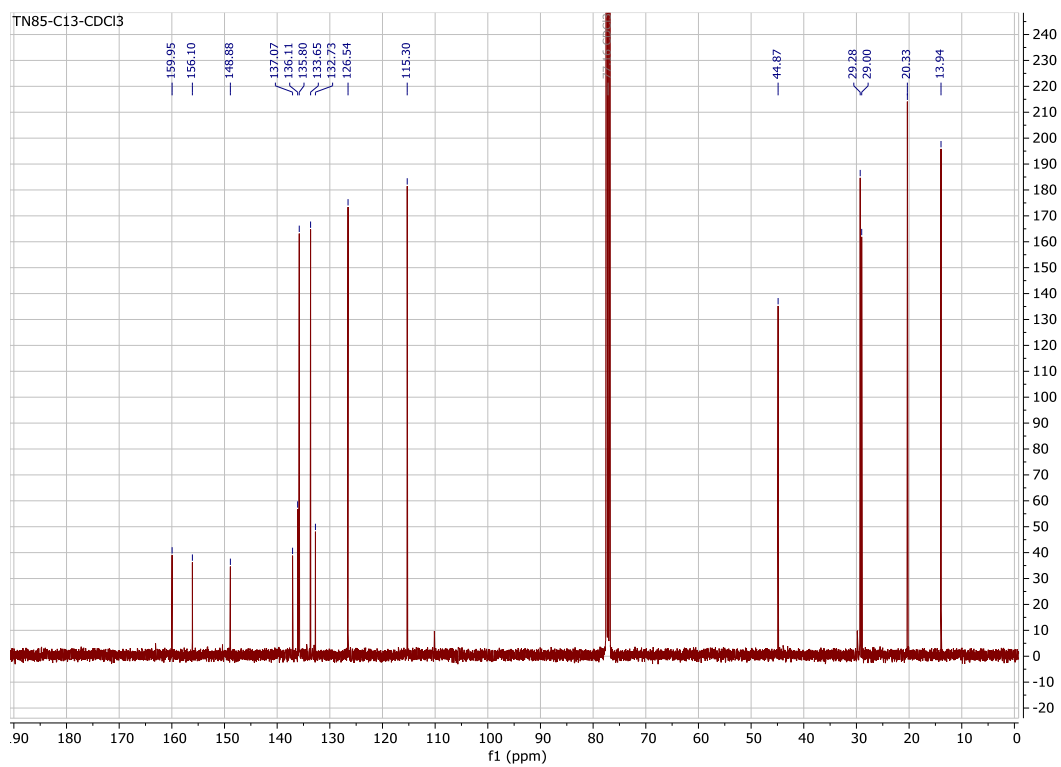
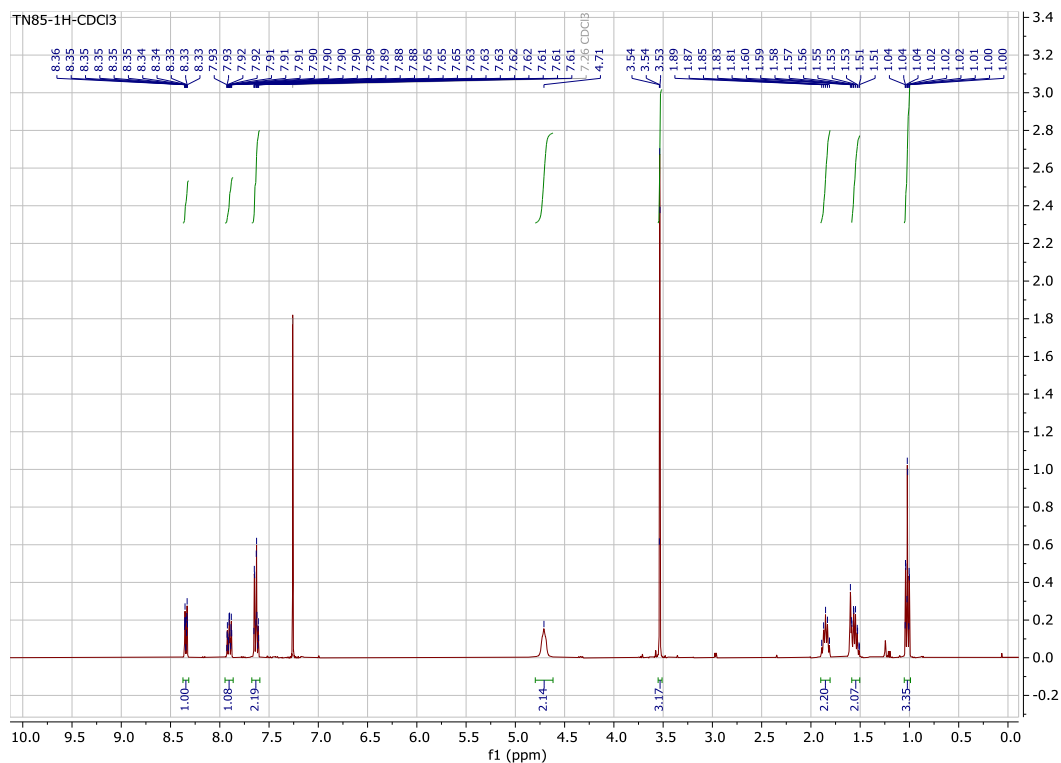
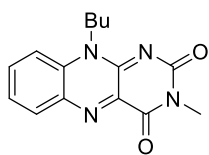
S3.1 NMR spectra of flavin derivatives



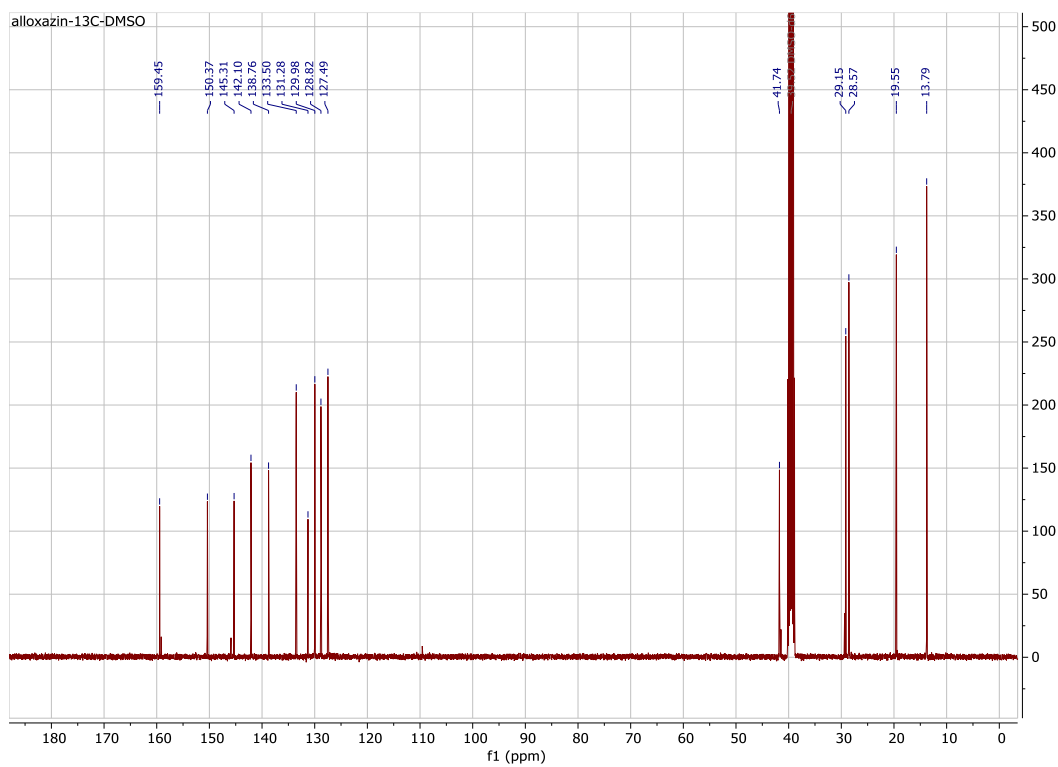
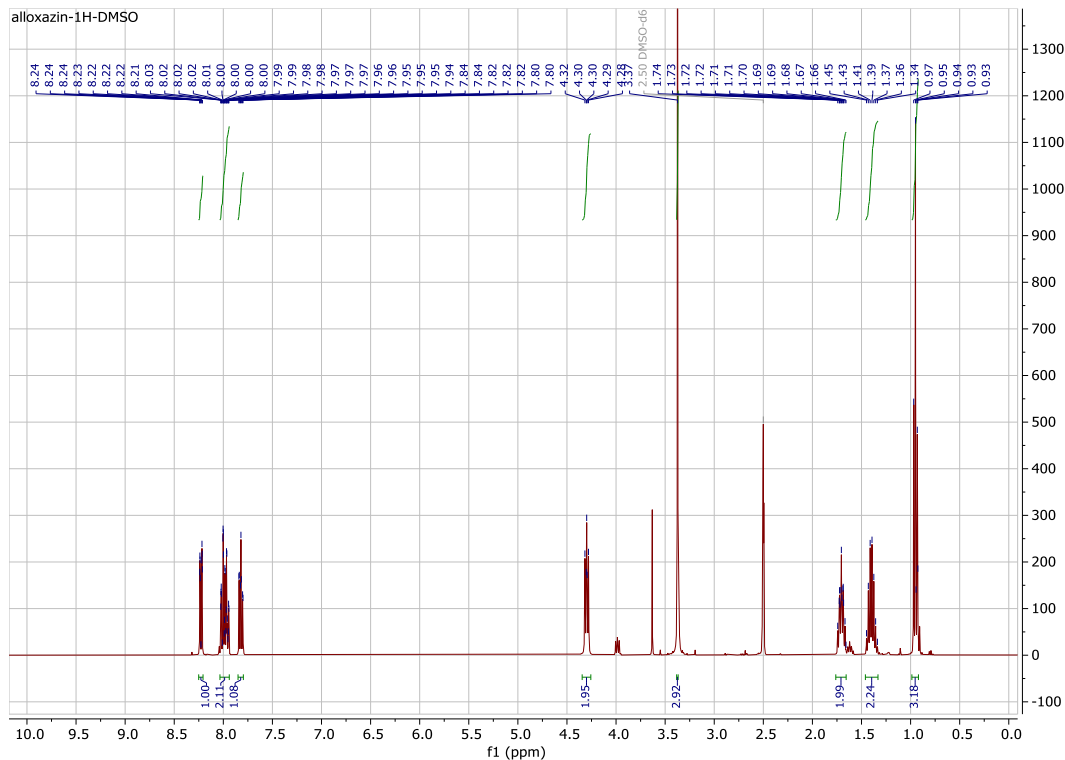
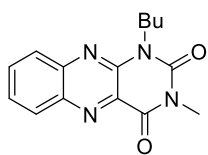
1,10-Ethylidene-3-methylisalloxazinium chloride (1e)



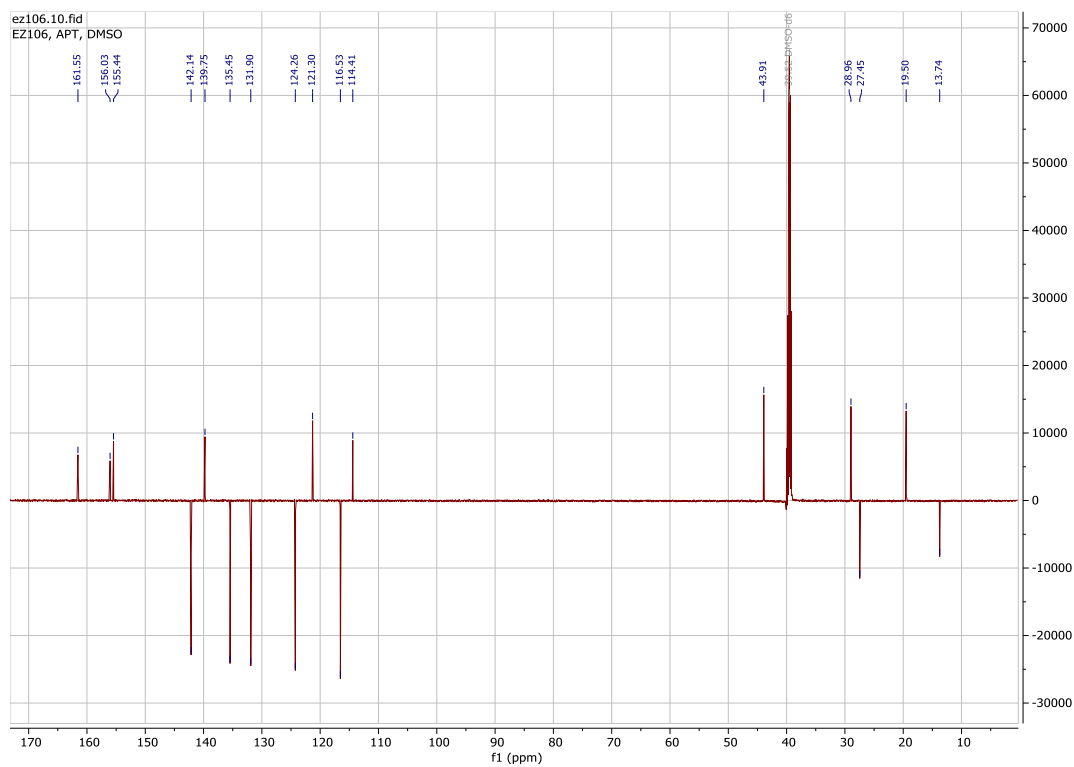
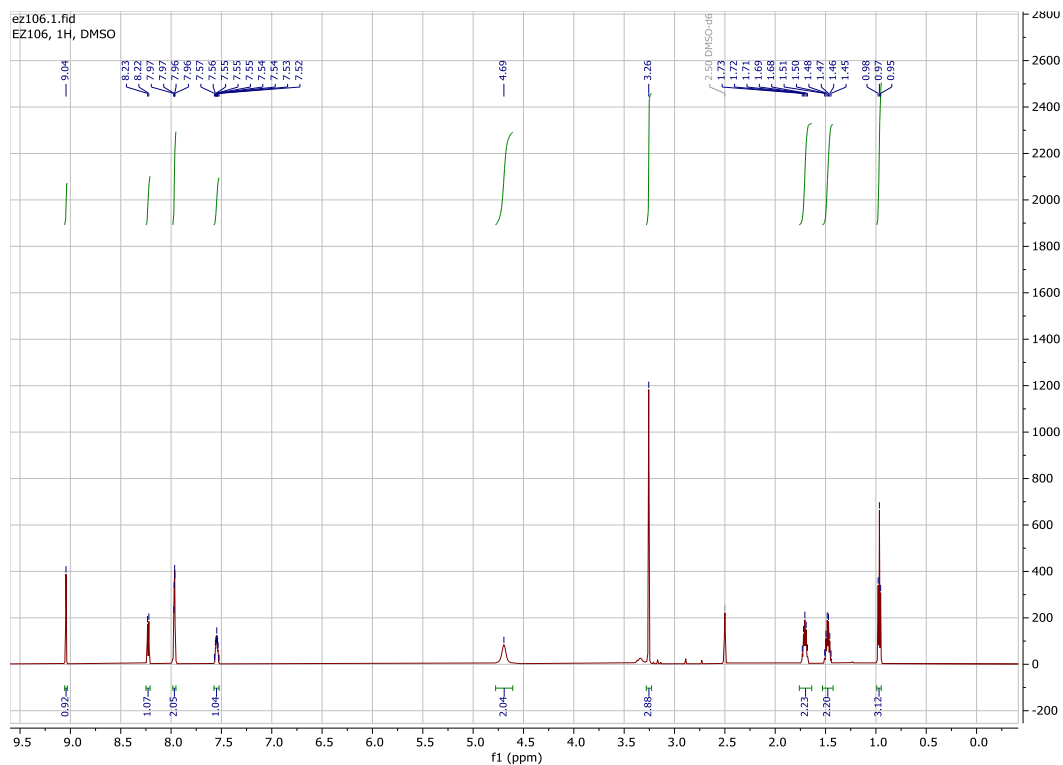
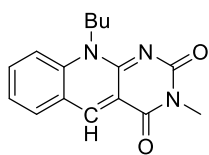
10-Butyl-3-methylisoalloxazine (2e)



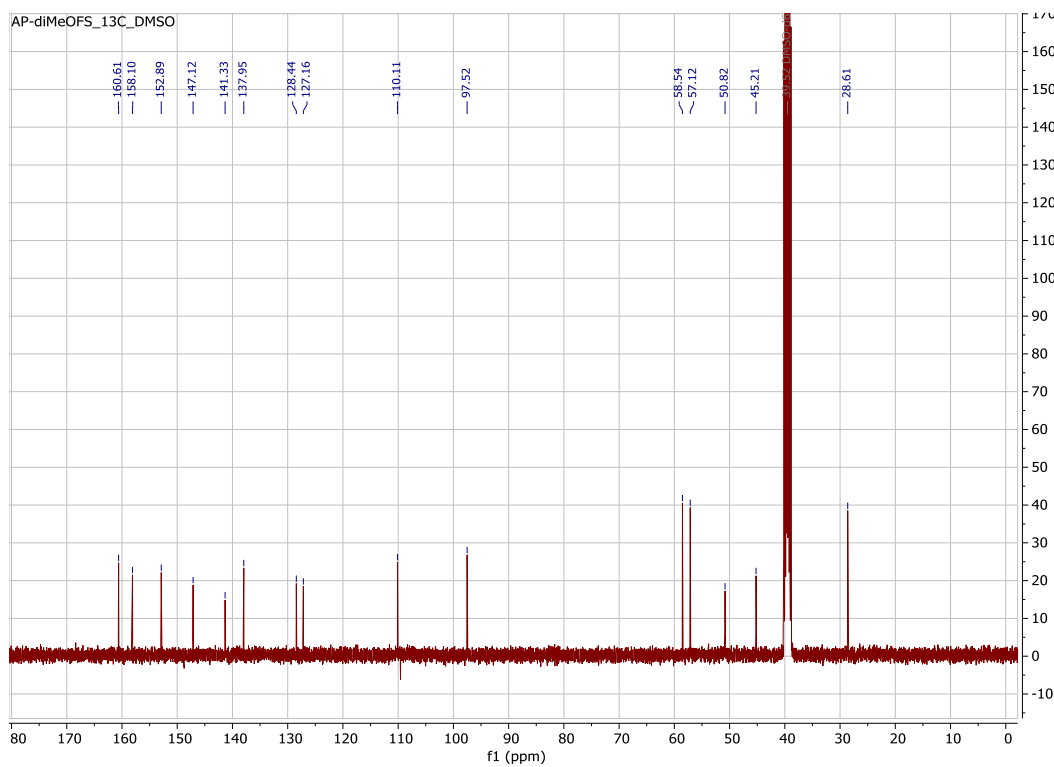
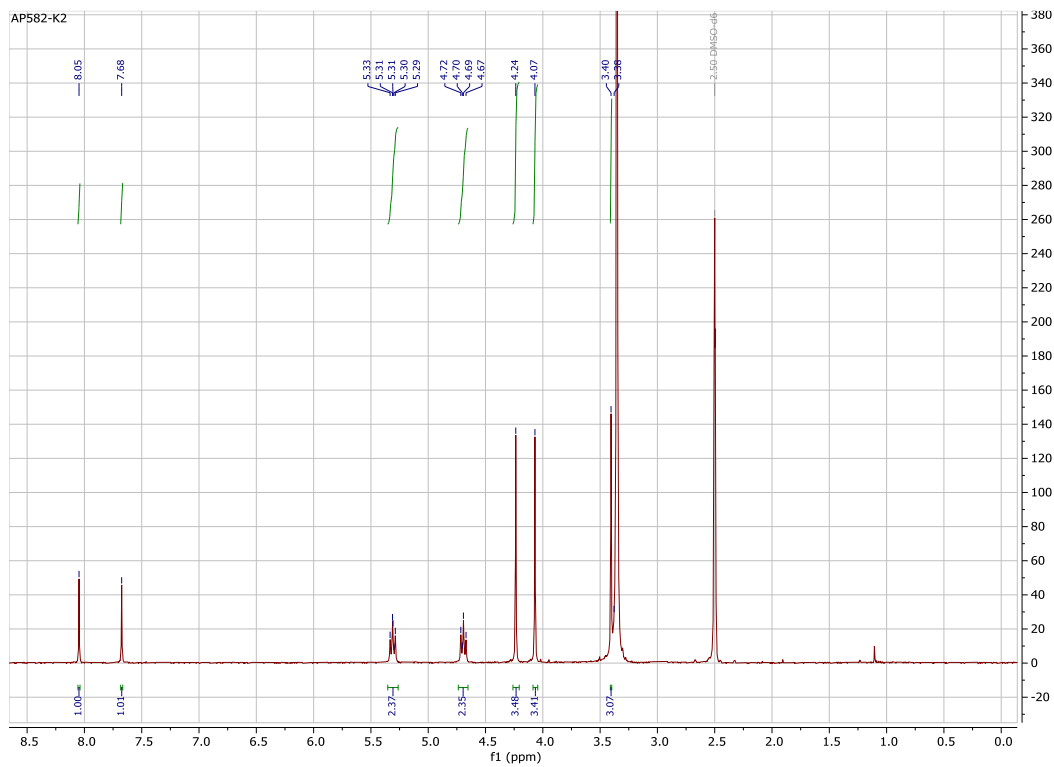
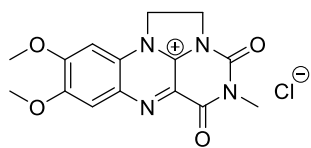
1-Butyl-3-methyl-isoalloxazine (5)



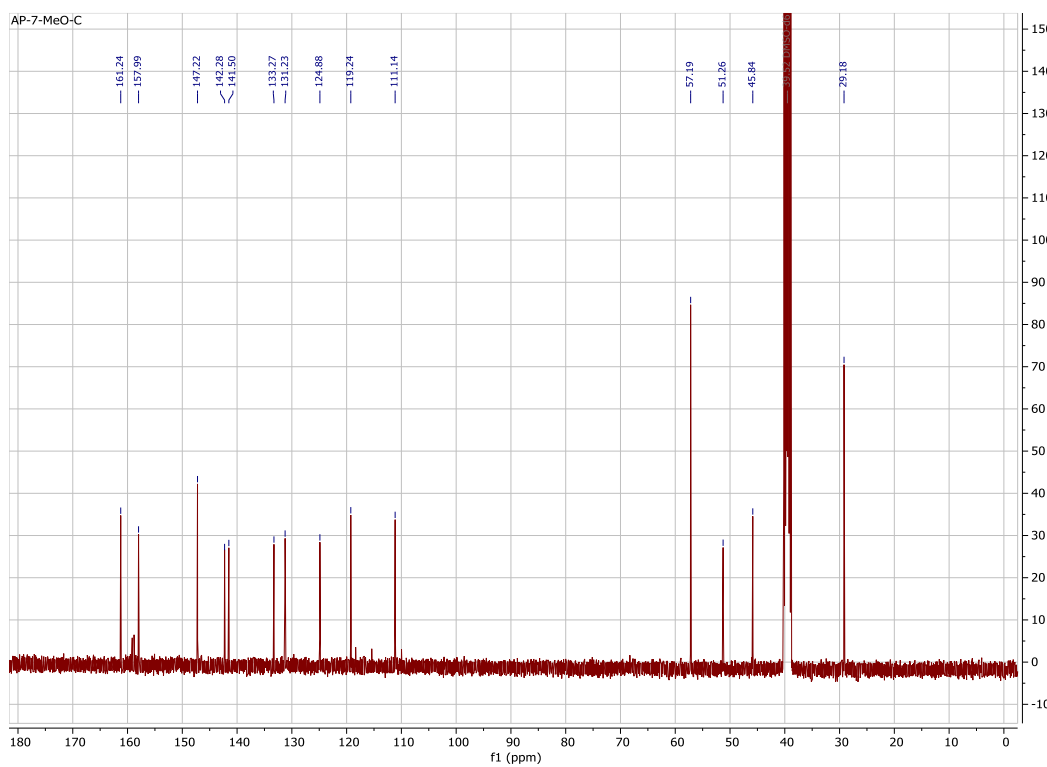
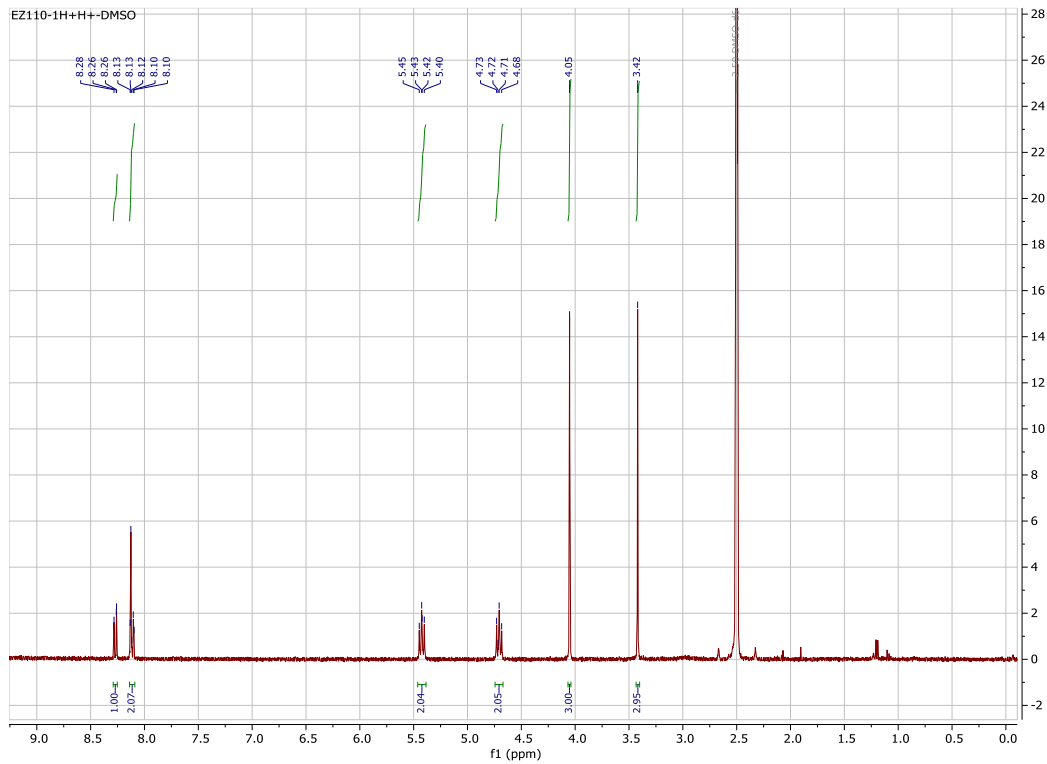
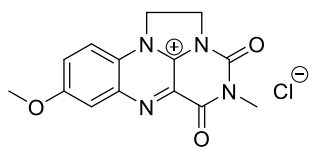
10-Butyl-3-methyl-5-deazaalloxazine (6)



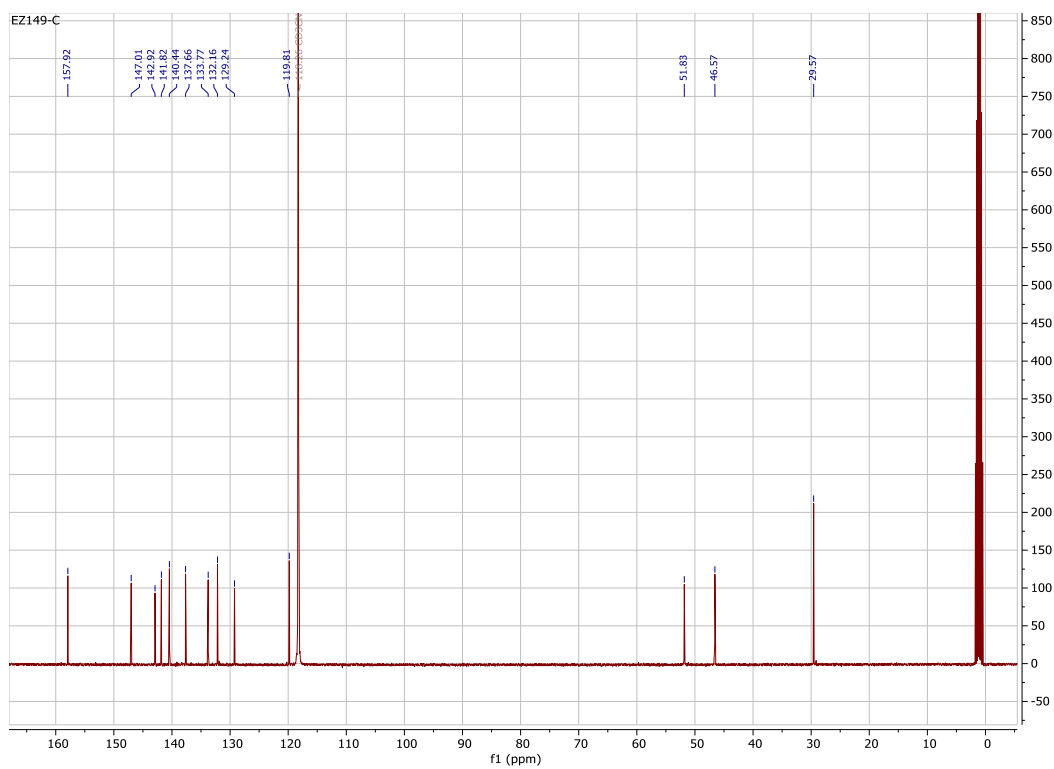
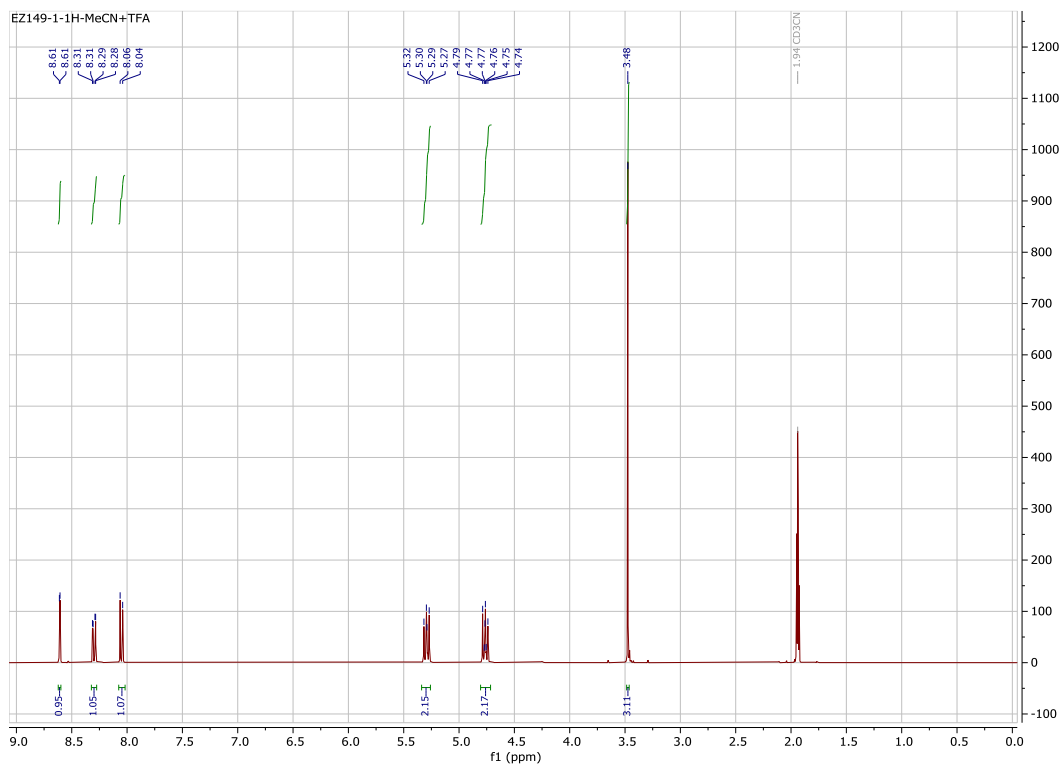
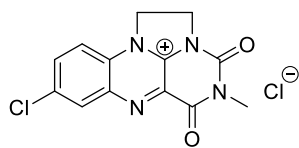
1,10-Ethylidene-7,8-dimethoxy-3-methylisoalloxazinium chloride (**2c**)



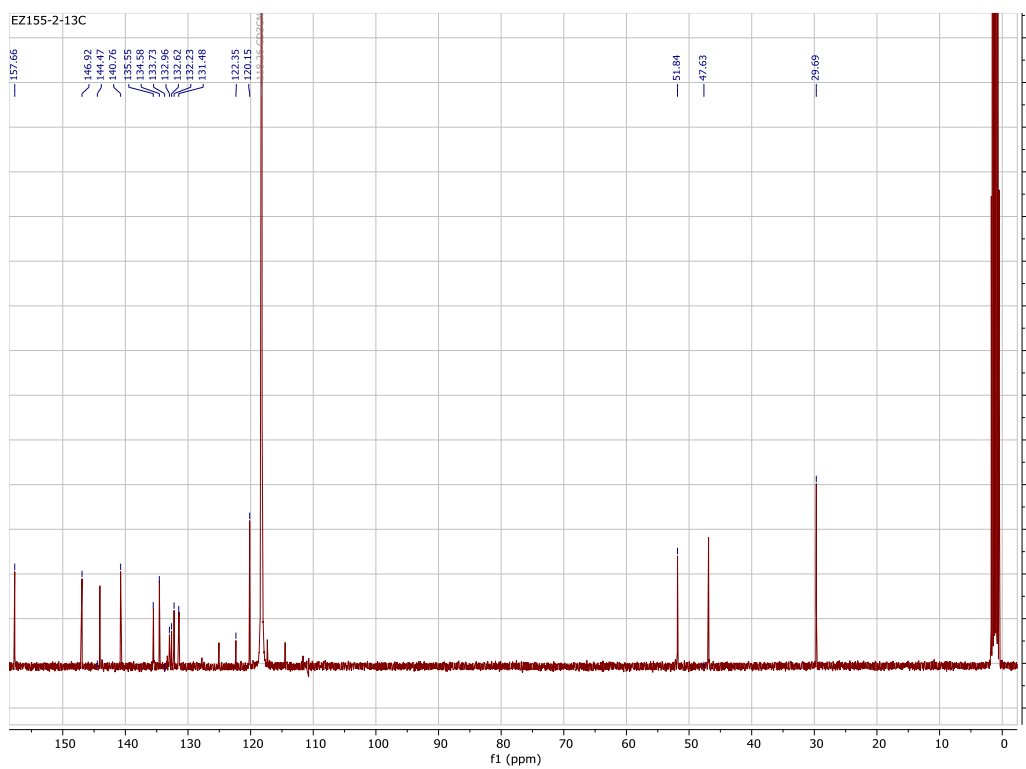
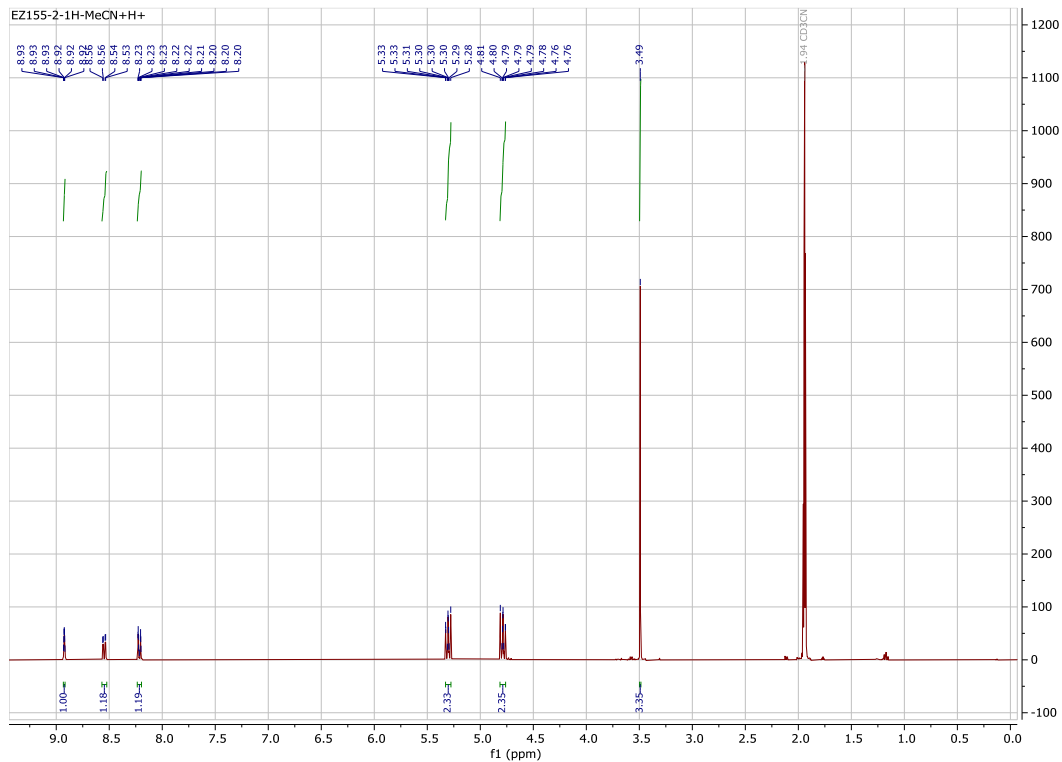
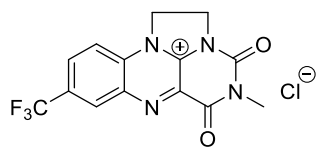
1,10-Ethylidene-7-methoxy-3-methylisoalloxazinium chloride (2d)



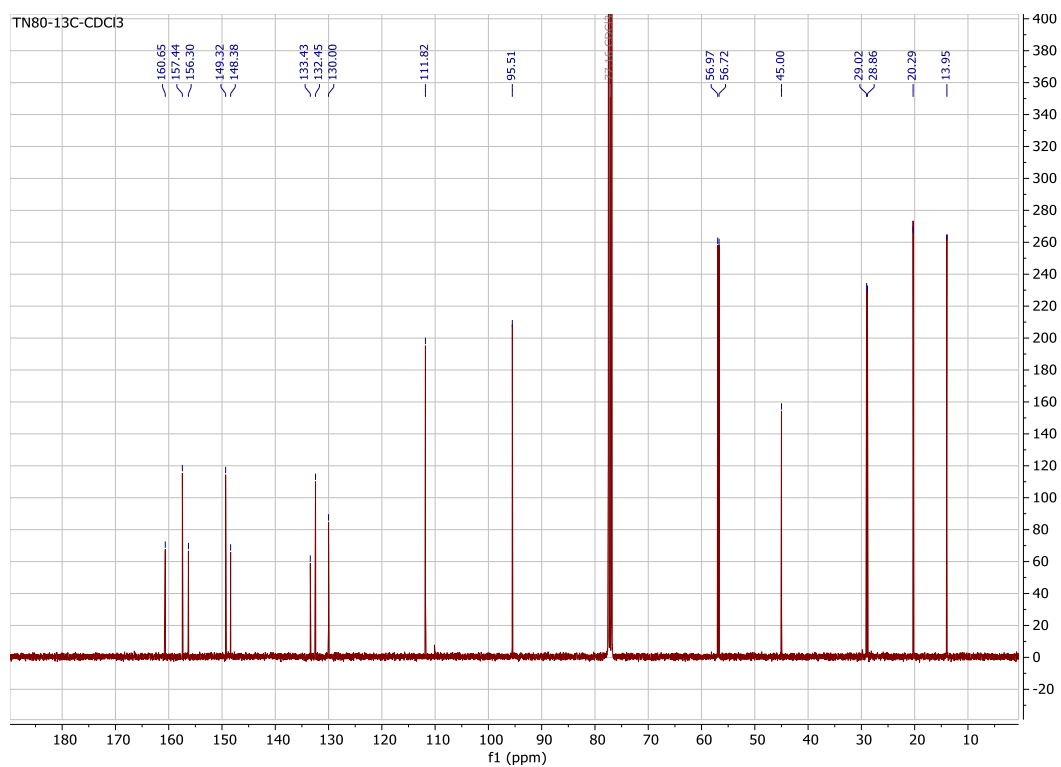
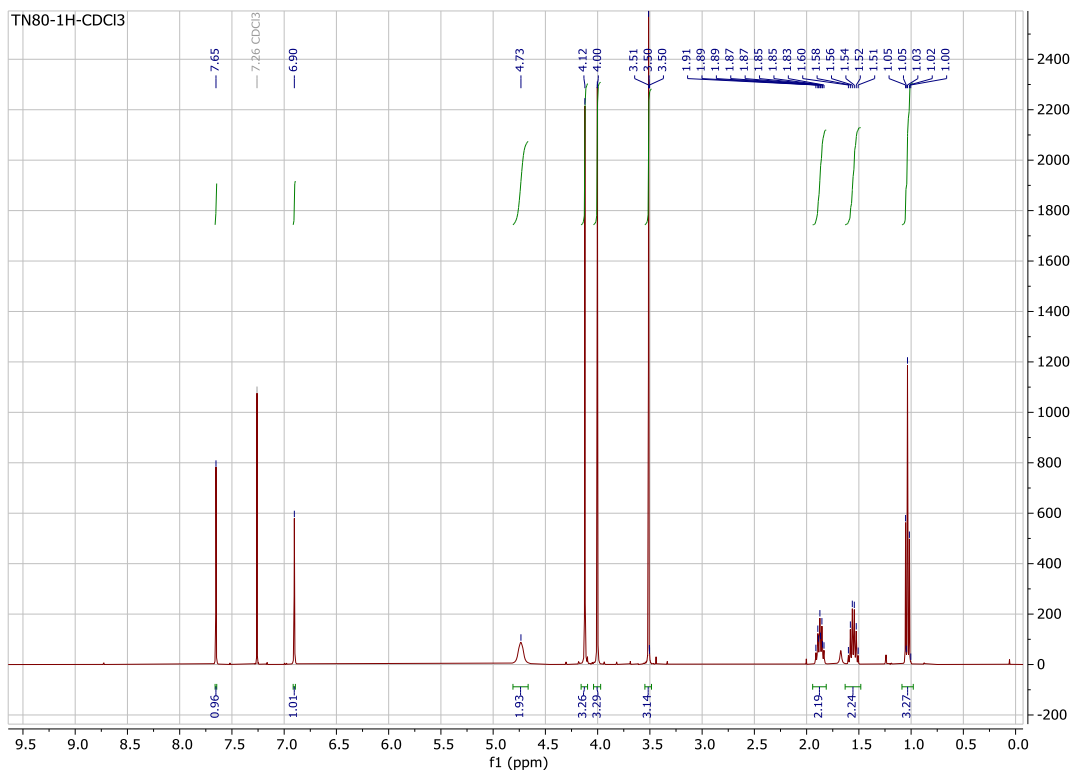
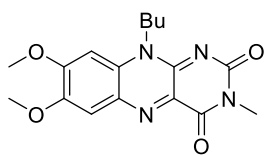
7-Chloro-1,10-ethylidene-3-methylisoalloxazinium chloride (**2f**)



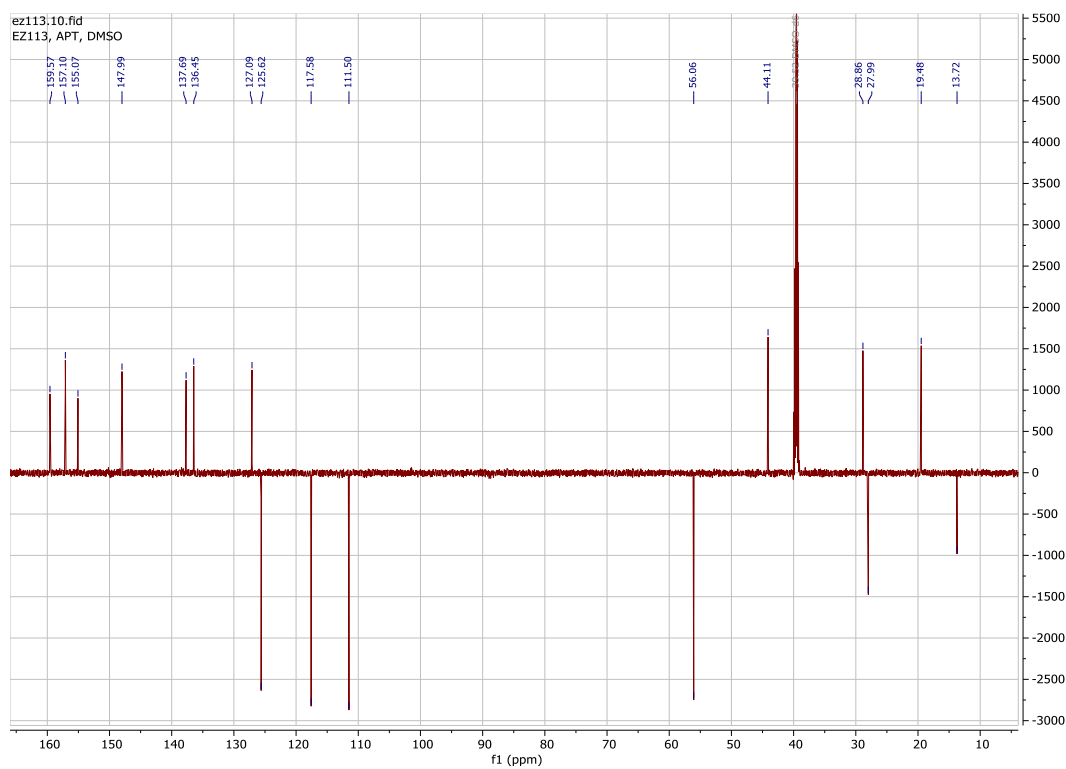
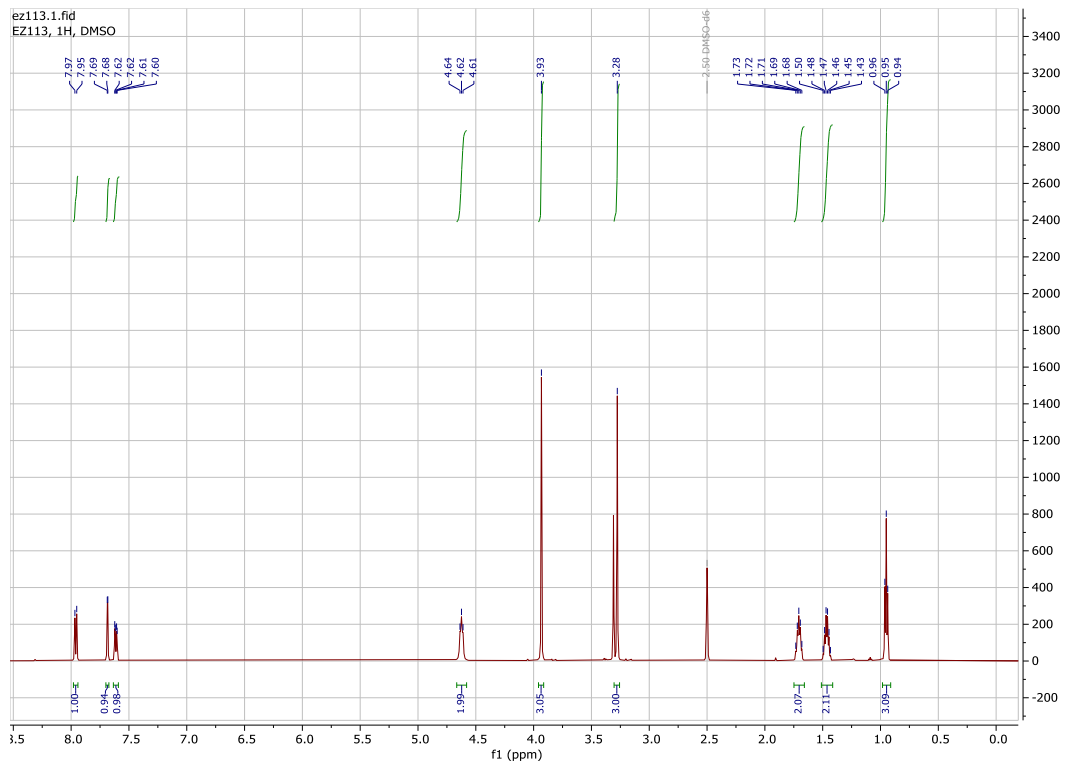
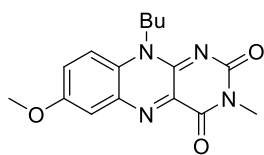
1,10-Ethylidene-3-methyl-7-(trifluoromethyl)isoalloxazinium chloride (**2g**)



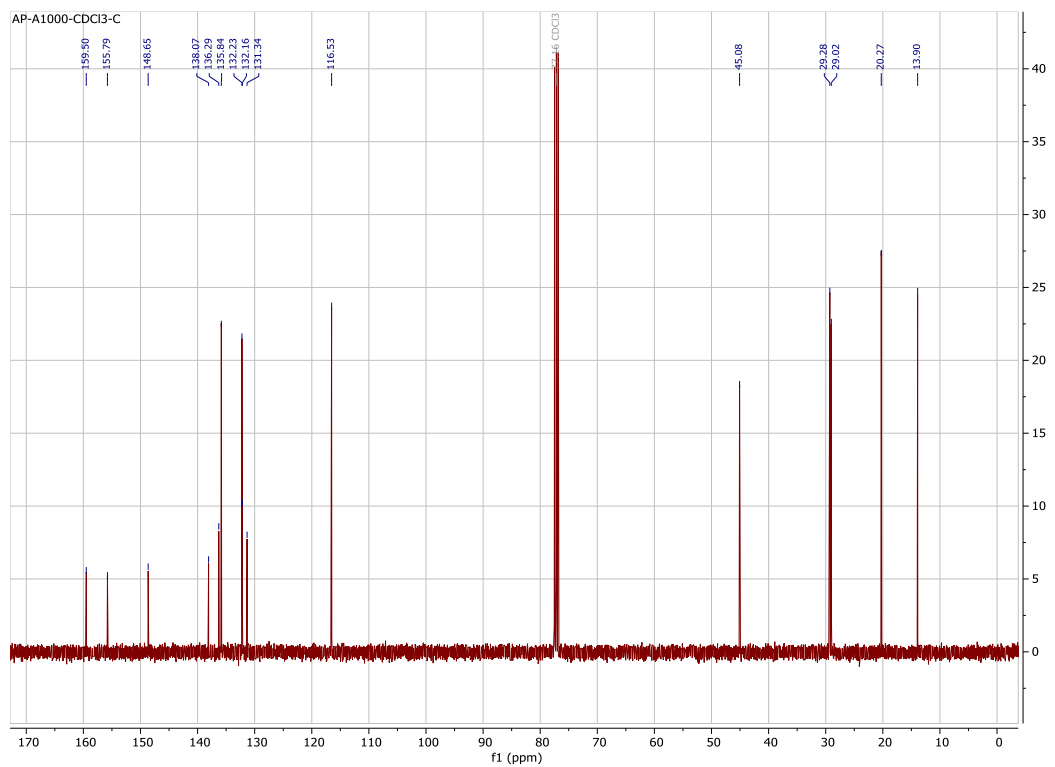
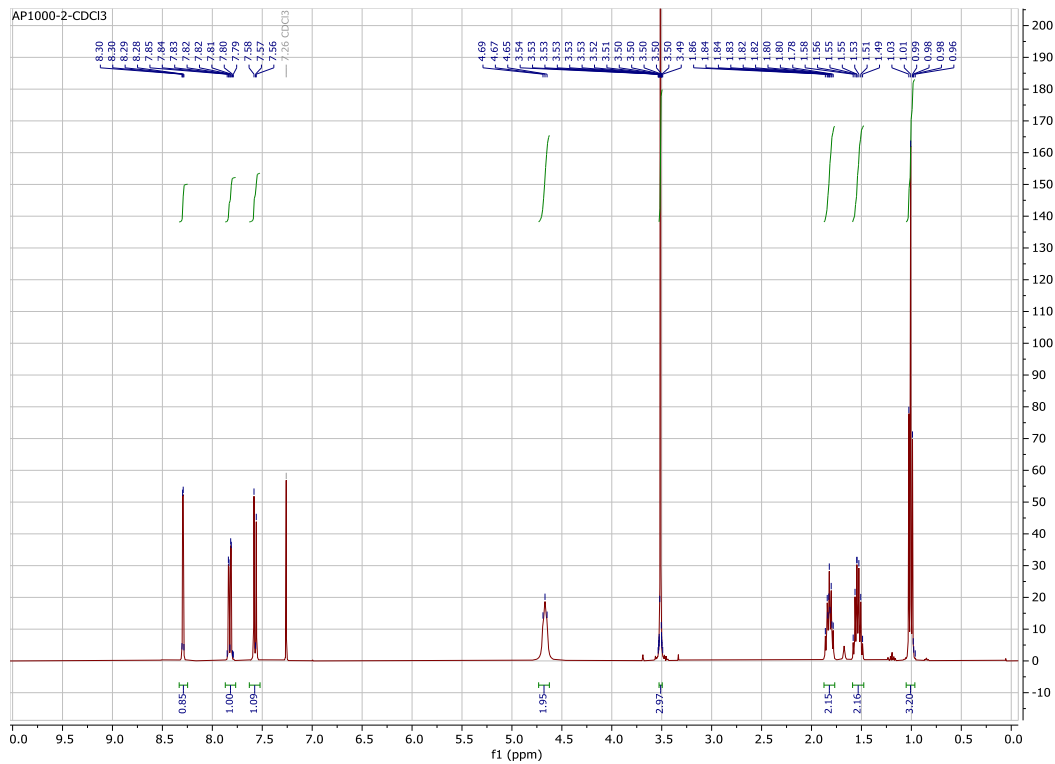
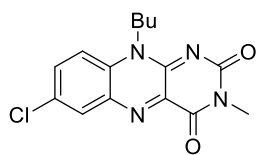
10-Butyl-7,8-dimethoxy-3-methylisoalloxazine (1c)



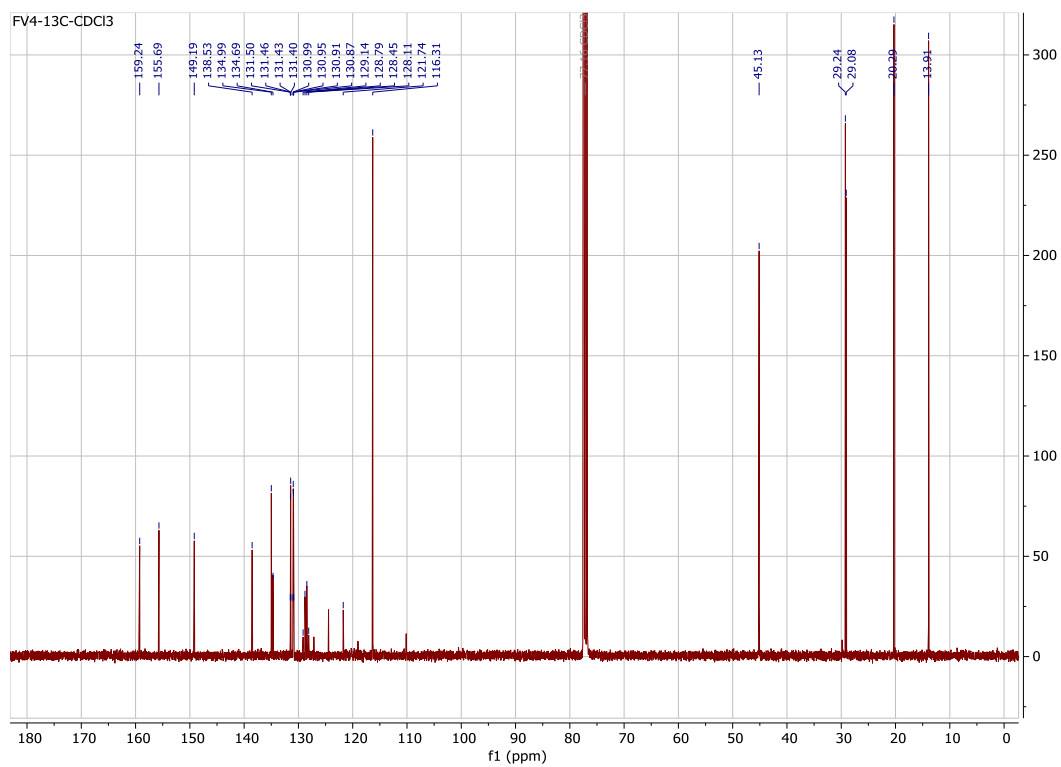
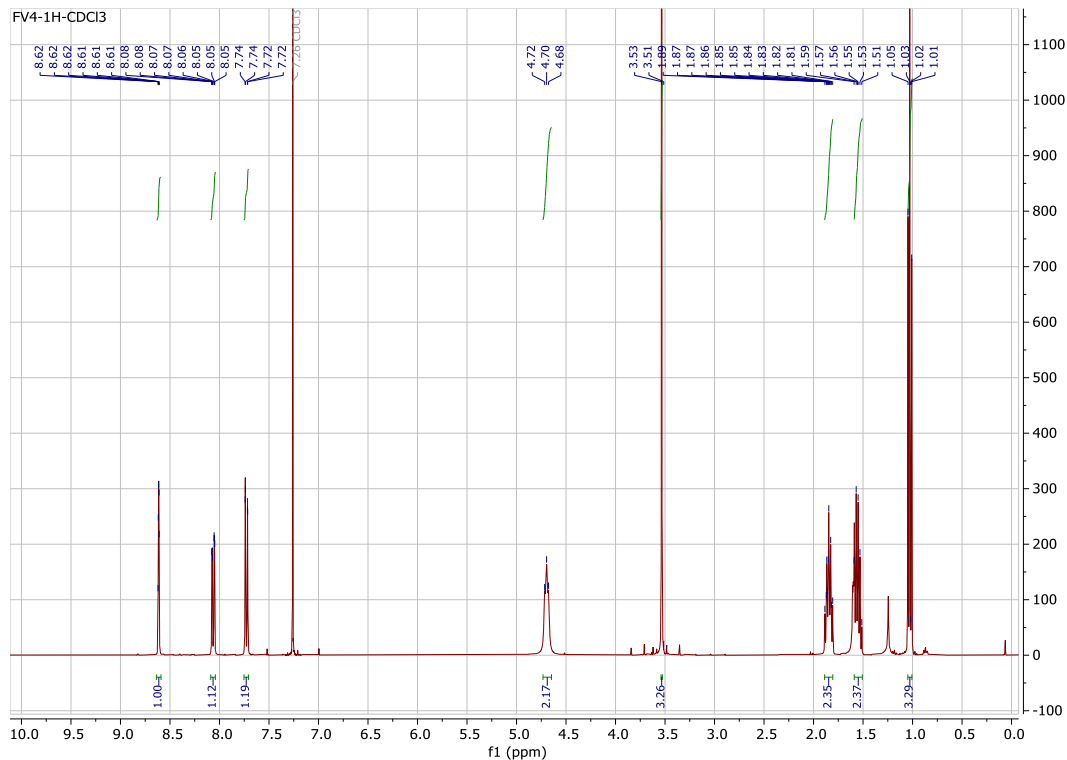
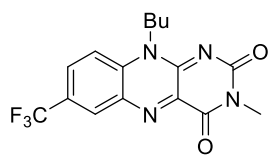
10-Butyl-7-methoxy-3-methylisoalloxazine (**1d**)



10-Butyl-7-chloro-3-methylisoalloxazine (1f)

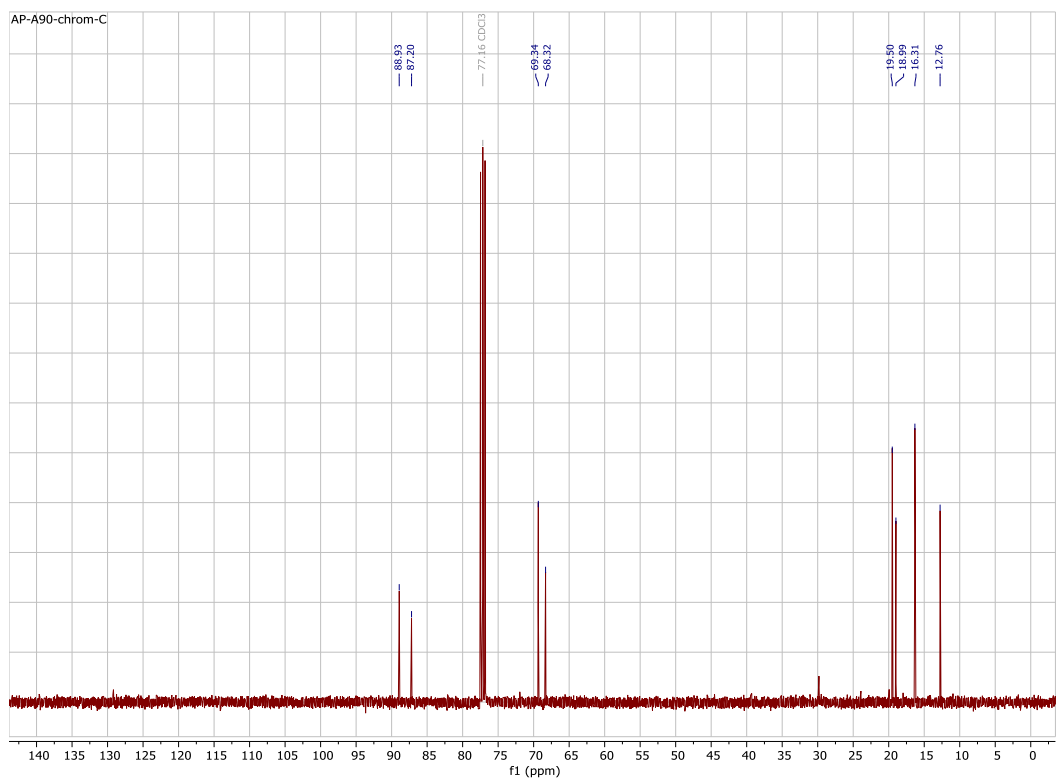
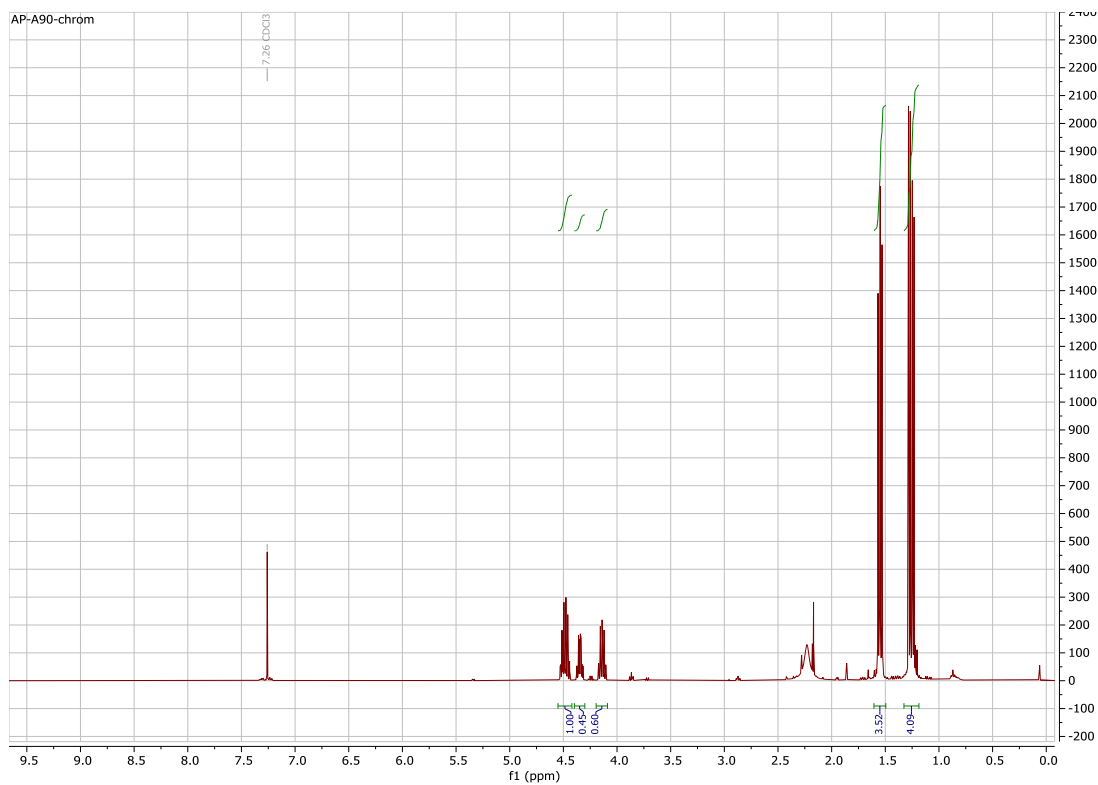
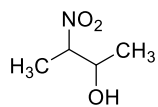


10-Butyl-7-(trifluoromethyl)-3-methylisoalloxazine (**1g**)

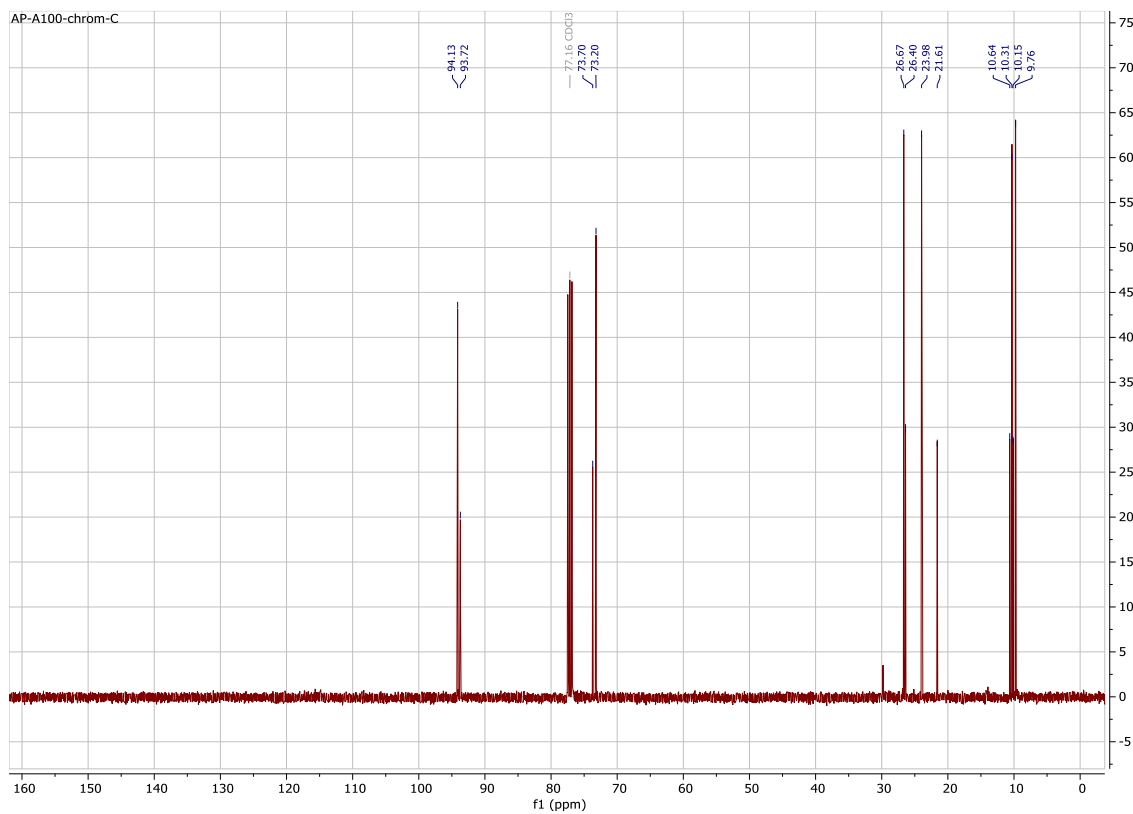
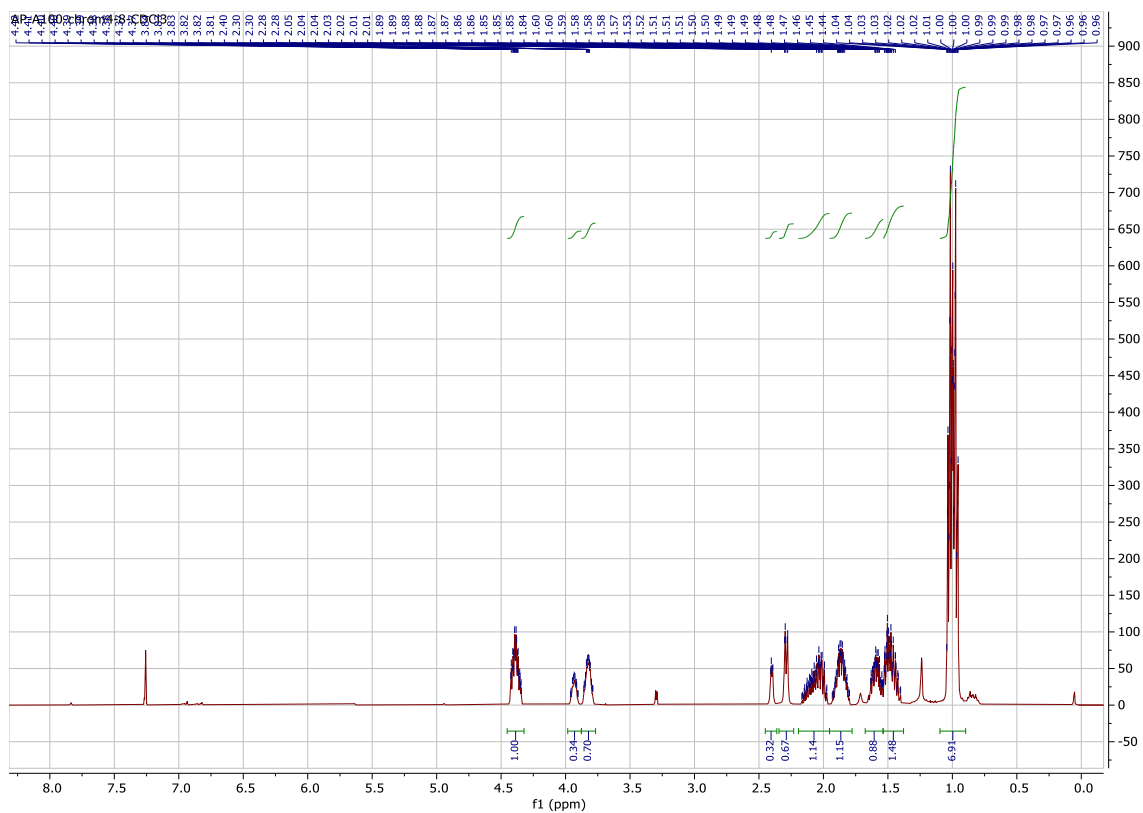
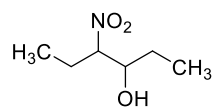


S3.2 NMR spectra of coupling reaction products

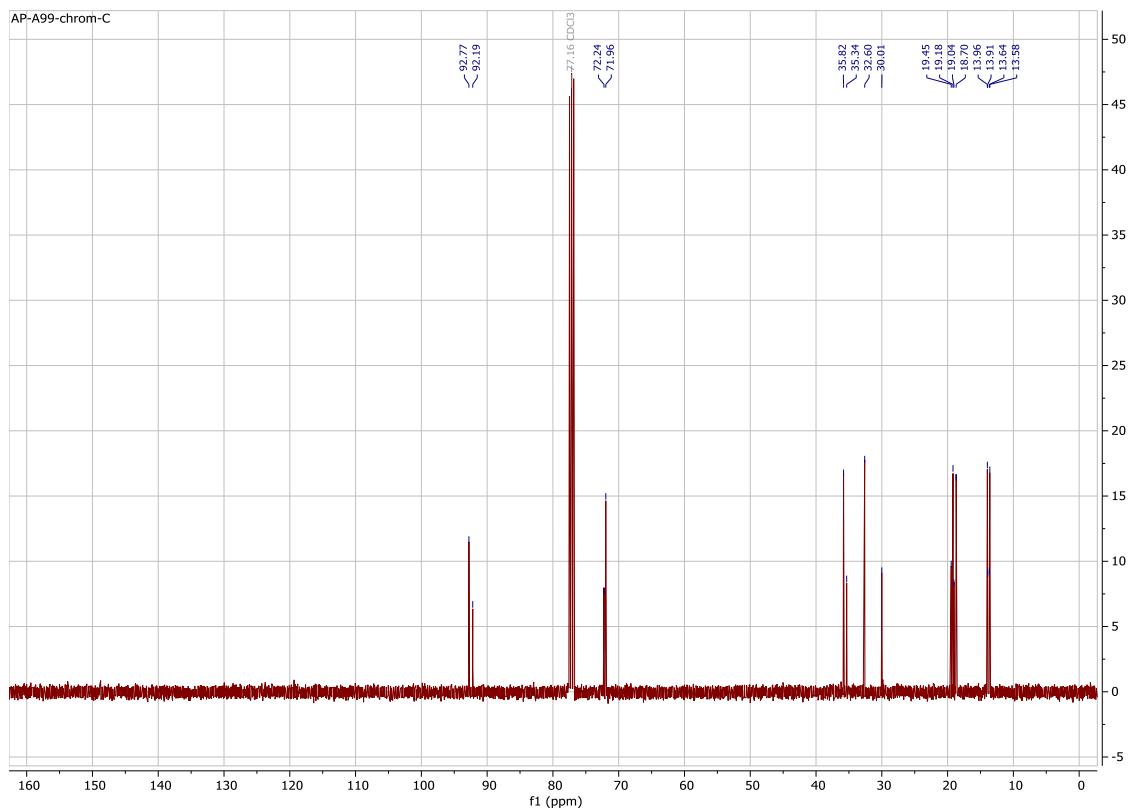
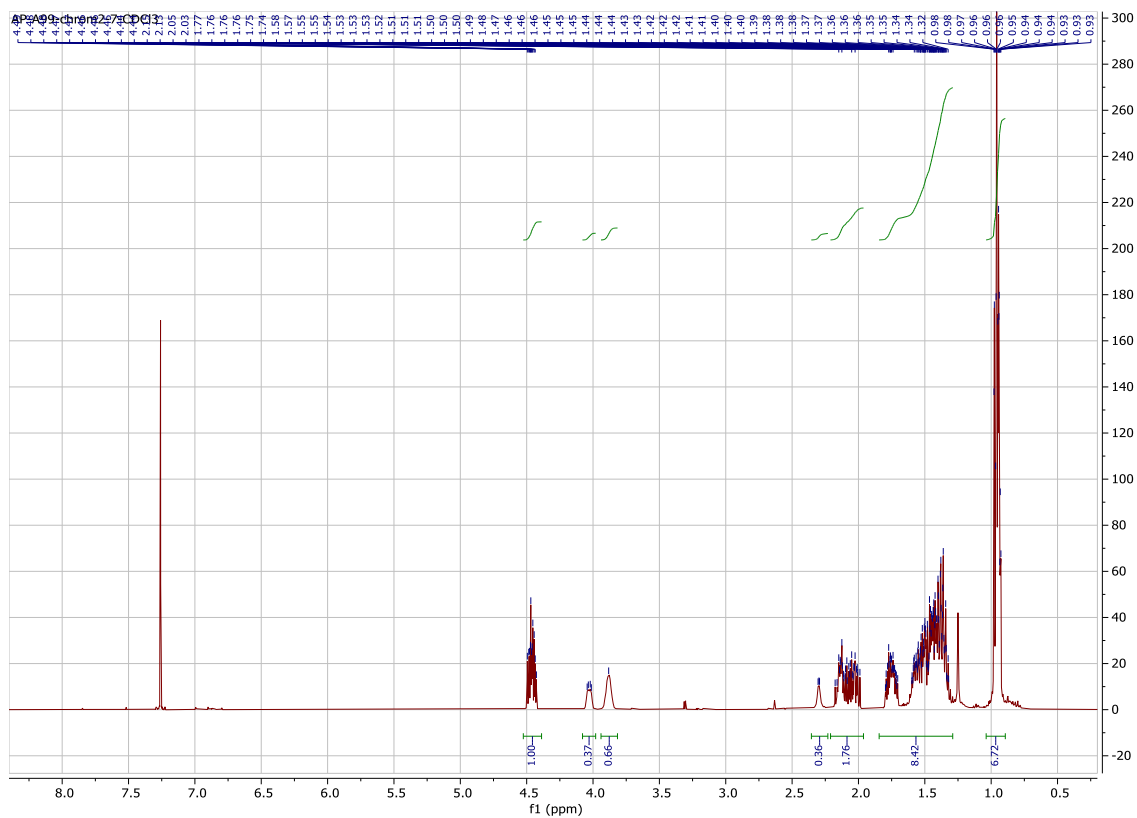
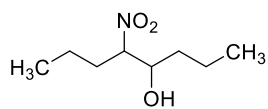
3-Nitrobutan-2-ol (4a)



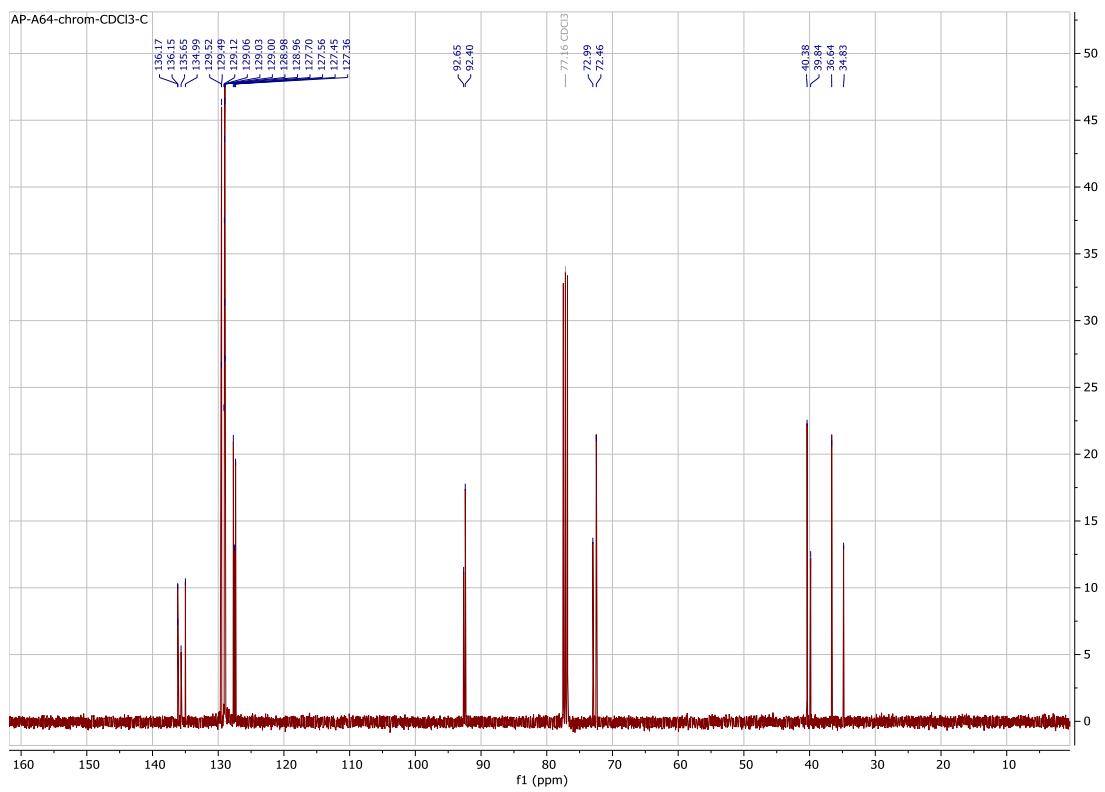
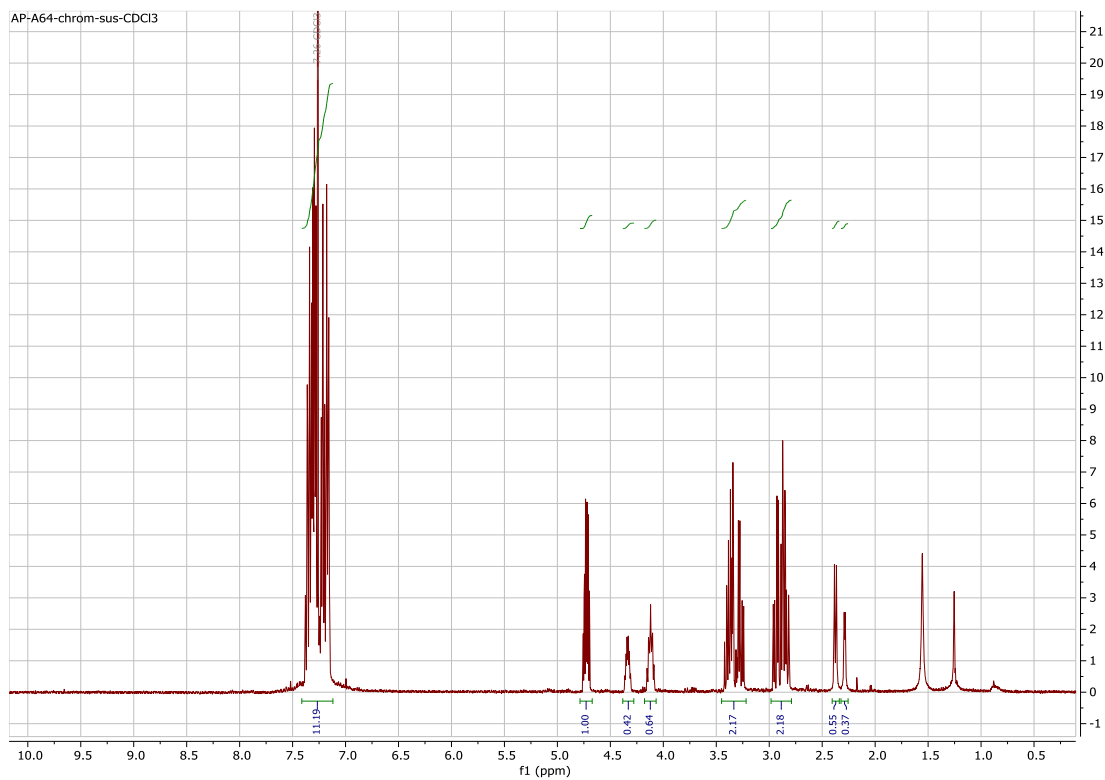
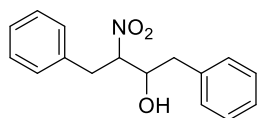
4-Nitrohexan-3-ol (**4c**)



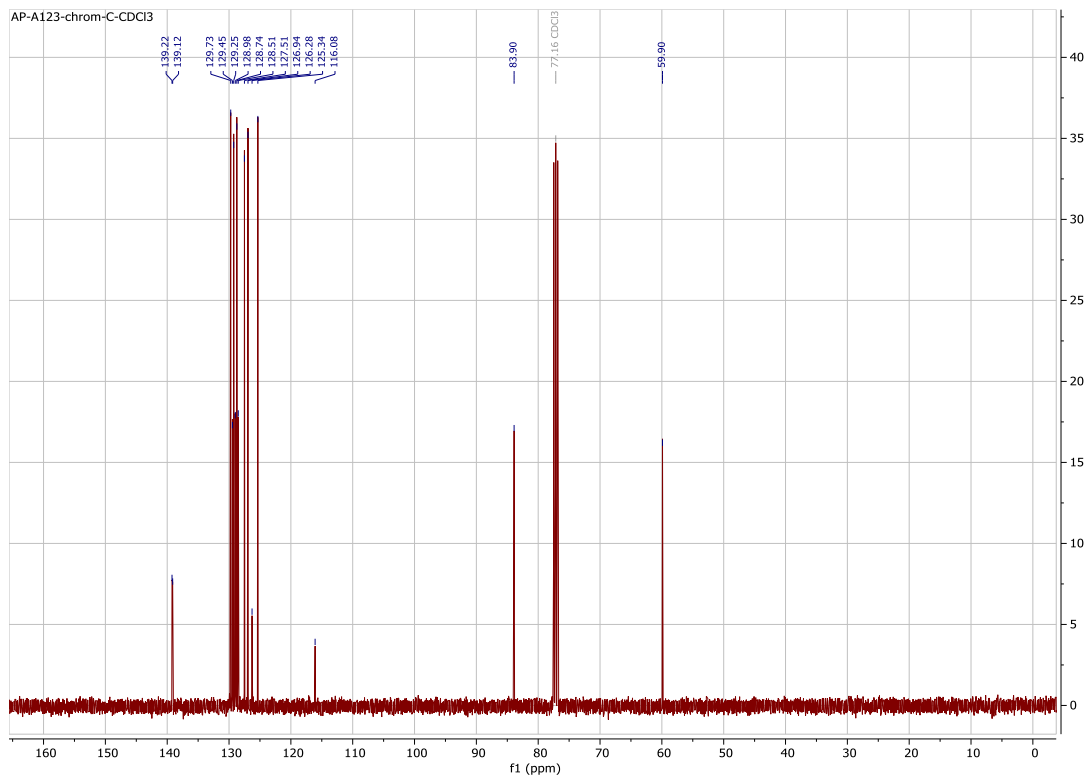
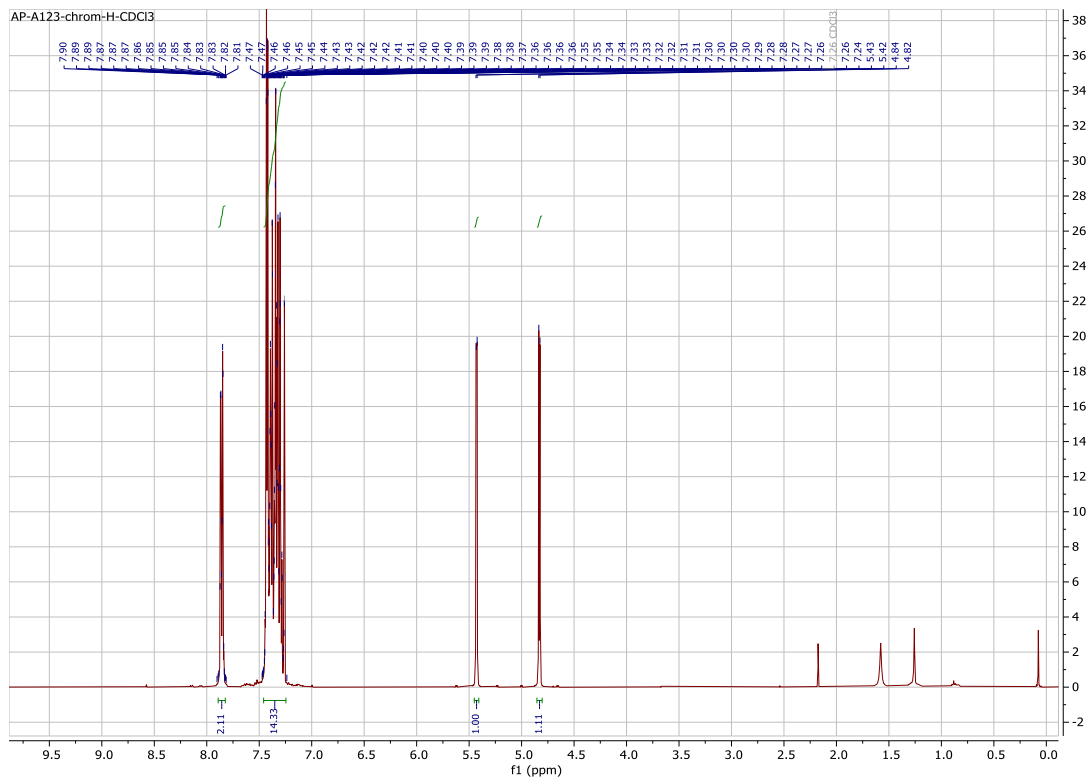
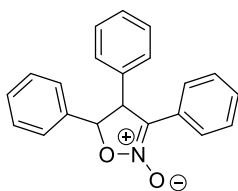
5-Nitrooctan-4-ol (4d)



3-Nitro-1,4-diphenylbutan-2-ol (4f)



3,4,5-Triphenyl-4,5-dihydroisoxazole 2-oxide (7)



S4 Energies and cartesian coordinates of the optimized structures

All contributions to the final composite energies. The labels correspond to molecules A-L in the Figure 3 of the article and auxiliary species therein.

Cartesian coordinates are reported in ångströms, energies are reported in hartree.

	$E(\text{CC})$	$E(\text{therm})$	$E(\text{solvation})$	$E(\text{composite})$
4a	-437.64831	0.10587	-0.01761	-437.56005
acetaldehyde	-153.63273	0.03023	-0.00778	-153.61028
1-nitroethan-1-ide	-283.40597	0.03512	-0.11186	-283.48271
H ₂ O	-76.36142	0.00348	-0.01074	-76.36868
NO ₂ ⁻	-204.93564	-0.01514	-0.10883	-205.05961
OH ⁻	-75.71539	-0.00800	-0.14967	-75.87306
A	-1098.82340	0.25056	-0.09987	-1098.67271
B	-1382.44320	0.31398	-0.03770	-1382.16692
C	-1177.31418	0.30490	-0.08864	-1177.09792
D	-1253.30724	0.31890	-0.03219	-1253.02053
E	-1099.64969	0.26098	-0.03199	-1099.42070
F	-1460.94057	0.36853	-0.04050	-1460.61254
G	-1099.06960	0.24433	-0.11156	-1098.93683
H	-1290.77750	0.16014	-0.03126	-1290.64862
I	-1574.26326	0.22174	-0.08958	-1574.13110
J	-1369.24940	0.21291	-0.03707	-1369.07356
K	-1445.12097	0.22857	-0.08233	-1444.97473
L	-1652.75815	0.27717	-0.09241	-1652.57339

4a

17

Coordinates from ORCA-job opt-00

C	2.56512852085996	-0.28508496457923	0.02511455529703
H	2.76217336449314	-0.18336338300721	1.09689338493090
H	2.70560929301982	-1.32943999608657	-0.25708627371917
H	3.29924746472971	0.31262292921812	-0.51339419896710
C	1.17271272837550	0.22067435582112	-0.32670412201036
H	0.98350395817313	0.07355108897884	-1.39148359801825
C	0.06226858950160	-0.50325394073439	0.44654034628059
H	0.13195270418378	-0.26169947206348	1.50716000942441
C	-0.01328798074658	-2.00433198984564	0.22391686400689
H	0.88093322945478	-2.48234386851997	0.62138028214897
H	-0.87427165957149	-2.42448236378279	0.74428151750602
H	-0.10301502935255	-2.23782286982348	-0.83610388152428
N	-1.26120950412546	0.11233285591464	0.01572749626625
O	-1.61405275632592	-0.08703266515149	-1.13341779281794
O	-1.87818409391913	0.75673553139753	0.84188807218685
O	1.07017781352208	1.62492403192152	-0.12921467356075
H	1.28673586382762	1.83425465694249	0.78747239496993

acetaldehyde

7

Coordinates from ORCA-job opt-0

C	0.12883447956144	0.41583906278677	0.00126109595308
H	0.16982042872705	1.52746128166560	-0.00075862155264
C	-1.25440045290740	-0.16910880896927	0.00023782799344
H	-1.80103581196962	0.19353916043721	-0.87597983206757
H	-1.22342701161278	-1.25752051927065	-0.00024678771529
H	-1.80181223206503	0.19272285041282	0.87630279234918
O	1.14760095996634	-0.22518718276247	-0.00061500296021

1-nitroethan-1-ide

9

Coordinates from ORCA-job opt-1

C	-1.97229671771536	0.00532378610538	-0.04817460102292
H	-2.05274287519884	-0.88825653309332	-0.68498189052101
H	-2.76870145376289	0.69831622276563	-0.34476832999812
H	-2.18345435443849	-0.34476204048629	0.97200104246015
C	-0.65461273530612	0.68765232425938	-0.16430510379527
H	-0.53868112427918	1.68302655413887	-0.56131128416289
N	0.47350254756890	0.05994797352736	0.16915453044569
O	0.41487977554610	-1.13449498723713	0.63199713737264
O	1.60907845568590	0.63987683332011	0.03433769532174

H₂O

3

Coordinates from ORCA-job opt-0

O	0.00000132379872	0.07509195731003	-0.00000000011069
H	-0.76300704213715	-0.51332225214627	0.00000000070171

H	0.76301956233844	-0.51330973716376	0.00000000020899
NO₂⁻			
3			
Coordinates from ORCA-job opt-0			
N	-0.00000008293055	-0.45415930131061	-0.00000000013622
O	-1.06969377230669	0.20848190401044	0.00000000001811
O	1.06969385253724	0.20848193600017	0.00000000001811
OH⁻			
2			
Coordinates from ORCA-job opt-0			
O	-1.96446959135153	0.91245687182019	0.00000000000000
H	-2.28856873644847	1.82768460757981	0.00000000000000
A			
38			
Coordinates from ORCA-job opt-0			
C	-3.34552165584306	-0.84272313829444	0.00137793036109
C	-2.16021320830388	-1.52931089309726	0.00100850313538
C	-0.92364165033569	-0.84407083331646	0.00021335920940
C	-0.94057744993995	0.59507727430229	-0.00077950745614
C	-2.13630849480569	1.30430975641911	-0.00088286433565
C	-3.33536068348127	0.60426533189047	0.00044613933343
C	1.40206636033002	0.47107220062675	-0.00003628960030
C	1.37118756952508	-0.91894355626693	0.00086749010502
C	2.68584489651865	-1.60853888582451	0.00225706080936
C	3.79662302762246	0.65265700752995	0.00266924404109
H	-2.12217928741189	-2.60753031687753	0.00171390637637
H	-2.13615267382857	2.38286132881907	-0.00162169863971
N	0.21673013703390	-1.55359357588866	0.00092603552044
N	0.28524223540775	1.20254927286589	-0.00112004086147
N	2.51146261934991	1.21789893545575	0.00055697706932
N	3.80444884799780	-0.74170410646757	0.00288926861663
C	5.11657231155570	-1.40631329772022	0.00475918283471
H	5.20128498538900	-2.03752047951878	-0.87704705923521
H	5.88289918258427	-0.64008487199258	0.00200094163138
H	5.20211248912115	-2.03163223514160	0.89073501487875
C	0.62320313155949	2.64590242870667	-0.00121159373153
H	0.20101581552869	3.11557286498507	0.88599481283943
H	0.20164494273136	3.11547424481160	-0.88875734204909
C	2.18100391954646	2.65340947897193	-0.00068731874973
H	2.59456292765290	3.13499245849450	0.88256879268029
H	2.59507038390198	3.13347855836053	-0.88454942115939
O	4.77478429101166	1.35365063859034	0.00387325932858
O	2.81692560785370	-2.80333956891643	0.00327785937963
O	-4.55919203838247	-1.38354392929391	0.00279833621263
O	-4.52868098478509	1.16339505142583	0.00123253708310
C	-4.66277425580837	2.58912734768092	0.00040260796291
H	-5.73121403294474	2.77970370342690	0.00164622277634
H	-4.20912595762413	3.01687503393232	0.89663115204827
H	-4.21143816135166	3.01558949369978	-0.89761898662843
C	-4.67663271442199	-2.81005381381079	0.00465864546511
H	-5.74228723987252	-3.01568868283109	0.00664608255014
H	-4.21717150708795	-3.23440705380619	-0.89056288617562

H -4.21426703449299 -3.23229726213069 0.89937689147343

B

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Coordinates from ORCA-job opt-00

C 3.41842764154527 -0.30250959759514 0.64098471578718
C 2.23769287071239 -1.02794249087480 0.69999410105082
C 1.01672808974709 -0.47281966349573 0.32255375510106
C 0.98682178157745 0.87379374557890 -0.05962204855482
C 2.15911264222816 1.62779460191222 -0.08085067111344
C 3.37811686881247 1.05100394248059 0.25131208308641
C -1.36034963733234 0.78553932977153 0.08683705133175
C -1.36992996420355 -0.50380784848620 0.48403350944907
C -2.61924624718802 -1.06771786026390 0.91298528433051
C -3.70407950628269 1.15499635823125 0.46354350336834
H 2.24858549498463 -2.04745255638059 1.04365482490360
H 2.11588008743381 2.66222164532605 -0.38257479086635
N -0.17959532850969 -1.27312249654772 0.31148937165673
N -0.26287088907210 1.44936221854816 -0.36396977507032
N -2.43844872689591 1.60954462161415 0.13334226172366
N -3.73045057124983 -0.17395654571916 0.87051953688055
C -5.03027708844865 -0.74367308076752 1.22606539548364
H -5.79448286451778 -0.02228029476969 0.95868556658473
H -5.17219957873123 -1.67727303647418 0.68804434476395
H -5.07111820639795 -0.95710254449534 2.29459398977101
C -0.55985345461440 2.87817983630821 -0.47859700434673
H -0.17541719724208 3.28396898282020 -1.41386198724666
H -0.10963857766741 3.42795630737077 0.35386555965073
C -2.10742614455538 2.92517490036373 -0.42109924176459
H -2.55237684730792 3.03600117757135 -1.41058185239485
H -2.48289143057602 3.71832220039441 0.22044965011149
O -4.67738801697368 1.88042461422536 0.40092500052219
O -2.79220885290197 -2.22957250877479 1.24807216424008
C -0.31641011186018 -2.28724830603546 -0.72750213728889
H -1.33106215943999 -2.66500340579459 -0.65765158581284
C 0.68511619412725 -3.41267146952714 -0.69922789134199
H 0.65465966329533 -3.87348729584500 0.28791323780372
H 0.40904930867748 -4.16217919236212 -1.44116044828172
H 1.68984679939264 -3.06420437114636 -0.91926213002192
N -0.26244648415899 -1.55617845438432 -2.08553632414206
O -1.31251250882603 -1.07589728003720 -2.49097559387391
O 0.83332425206192 -1.37659200905823 -2.59469880180993
O 4.64383084502384 -0.80263636986375 0.94625357664732
C 4.73135630618201 -2.17990853124779 1.26976908828215
H 4.17499836814706 -2.41579855230895 2.18215611961857
H 4.36041452451551 -2.80327332535399 0.45006869470643
H 5.78733444583275 -2.38439856874587 1.43037421330850
O 4.56264466172193 1.70842816715704 0.25319958275168
C 4.58621934095731 3.06090090739886 -0.16436398741551
H 3.93860454325452 3.68504020245679 0.45815887955024
H 5.61642018559072 3.38972145327358 -0.04998039548655
H 4.28484392743222 3.16029064855237 -1.21246578143304

C

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Coordinates from ORCA-job opt-00

C	-3.37012533069931	0.67566214660324	0.19776326455704
C	-2.18045260862551	1.36285999736273	0.03014156935011
C	-0.99806071523242	0.67889564039496	-0.27389175381146
C	-1.00967004472724	-0.71057759298917	-0.39504174624123
C	-2.20918946115801	-1.41072772148320	-0.24999167040557
C	-3.38716481260242	-0.74104102654631	0.03981857067531
C	1.33005187719329	-0.70120095014994	-0.36338397341004
C	1.42280518142351	0.65659243209819	-0.25782694340424
C	2.62203142781928	1.21513615998020	0.34356665407548
C	3.60346374687785	-1.08558661662068	0.32925289960460
H	-2.16075301067095	2.43052032377733	0.18122534539572
H	-2.21091402756310	-2.48315609110147	-0.36111431630979
N	0.23669382585238	1.38902324400390	-0.54637060654236
N	0.19780922624060	-1.38659320929284	-0.61947239675128
N	2.36265861721403	-1.52869400664177	-0.12573264012462
N	3.68546963374862	0.29337791167852	0.49561261709806
C	4.96047051727949	0.79965885424061	1.02535172990027
H	5.77022395205682	0.24827510869242	0.55871630154259
H	5.02522394136023	1.85745596324193	0.79268324272723
H	5.00901193129285	0.65851880772935	2.10529773113538
C	0.42924302271367	-2.83054811769213	-0.40382729135880
H	0.02589181083005	-3.41313917051733	-1.22879876008995
H	-0.05353582104628	-3.14172910957546	0.52488415237746
C	1.97051188560503	-2.93089340564691	-0.31423110106497
H	2.41543593936447	-3.31912929384550	-1.22964486209801
H	2.31427096906424	-3.53299769385016	0.52234583557460
O	4.49215713150196	-1.86326680082398	0.57000490559879
O	2.72754591435696	2.36723370607225	0.71594841393882
C	0.23279375407588	2.57108045485392	-1.09626581395177
H	-0.74911520255971	2.99579998531819	-1.24507115960520
C	1.40933965035267	3.29996967547204	-1.59437770567328
H	2.15902988596315	2.61234993333135	-1.99093216790162
H	1.09315424500339	3.99614395349230	-2.36963856057077
H	1.89754446713314	3.86018731459053	-0.79158002867111
O	-4.54581896033238	1.22986575637328	0.52018788506550
C	-4.60168095404397	2.62818911442262	0.79154515163074
H	-5.62275475002906	2.82738040479803	1.10326971466846
H	-3.91508233515903	2.89782648471133	1.59754587154929
H	-4.37257110538772	3.20900164779227	-0.10556576947566
O	-4.57176332168449	-1.32676468618516	0.22394257085695
C	-4.66732169671918	-2.74653360295417	0.12541064748047
H	-4.00916631789844	-3.23129142135141	0.84988079899432
H	-5.70030971379411	-2.98992365602137	0.35384048313378
H	-4.42337384509023	-3.08506744684255	-0.88503110026922

D

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Coordinates from ORCA-job opt-00

C	3.42166415356705	-0.50828448489238	0.23301681190594
C	2.20974377746401	-1.18373818603089	0.16170219675673

C	1.01393233864553	-0.51767838709775	-0.11623388351895
C	1.05645349246716	0.87234272450861	-0.28766065467601
C	2.26063186367458	1.56341072687635	-0.17973248624433
C	3.45005730349246	0.88788828633812	0.07254039777736
C	-1.30625209192138	0.86708855502951	-0.26622011425882
C	-1.38161270311460	-0.47103835455711	-0.08395996239929
C	-2.62196204668816	-0.99101991112137	0.41727325066314
C	-3.62063694722498	1.29757327291202	0.23900078399794
H	2.16958625156209	-2.24489100666449	0.34811697228995
H	2.26997192590627	2.63293822206399	-0.32486317784600
N	-0.19803562214741	-1.22306584619747	-0.24398297351368
N	-0.16368054361030	1.55673635390122	-0.57100299193471
N	-2.34060441529125	1.72535060999412	-0.05505910871466
N	-3.70612594606597	-0.07368133171090	0.44730318374052
C	-5.02383670322308	-0.63242609355872	0.75265522420730
H	-5.19126745433907	-1.50802694679019	0.13072402681272
H	-5.07889116024710	-0.94096998451994	1.79657636653969
H	-5.76414601842398	0.13400392204759	0.55009796993746
C	-0.38401883790563	2.97671915478649	-0.26159794864140
H	0.09832404911365	3.62085657561575	-0.99498351355065
H	0.01750268642607	3.21428669505724	0.73045967312442
C	-1.92089834278488	3.10675789892750	-0.29337737397771
H	-2.28754293852866	3.45194932717216	-1.26159224767653
H	-2.31005556319181	3.76448457641243	0.47931022562963
O	-4.55729437195601	2.07043468399505	0.30905265052644
O	-2.82150014389081	-2.15455953992462	0.76503900837136
C	-0.22342143687987	-2.56719160546866	-0.81400220493651
H	0.77584840441924	-2.74265789868864	-1.20961235763550
C	-1.21658729004589	-2.68203821662264	-1.96550817046306
H	-1.11861977564553	-3.66965750786132	-2.41601050831011
H	-2.24326620536276	-2.57001076004715	-1.62214525771961
H	-1.00526434889876	-1.92699478064140	-2.72568304502256
O	4.61650348219963	-1.10769447026952	0.47120102928957
C	4.62684230941371	-2.51252064845492	0.65858626212160
H	5.66253732738546	-2.78153117117704	0.85221129478338
H	4.00956493974684	-2.80978932595412	1.51126845489869
H	4.27390606145452	-3.03532511469531	-0.23572284751650
O	4.66777496017478	1.48204259194491	0.19837380748774
C	4.75479156722104	2.87687703647097	-0.00202140328032
H	5.79428890316147	3.14295641926186	0.17648431162465
H	4.47875476606014	3.15441465076453	-1.02558622892936
H	4.11874191224307	3.42516392908133	0.69994417752380
O	-0.41682534534361	-3.55953248273139	0.17044549940285
H	-1.27303036046727	-3.35592447938380	0.58863985755338

E

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Coordinates from ORCA-job opt-00

C	3.35539948463846	0.80207195787725	-0.02311647792172
C	2.17338608492362	1.50802924938040	-0.22323388783000
C	0.95847233843820	0.85533962808784	-0.43317687337179
C	0.94304536945744	-0.54493520008110	-0.42114948625011
C	2.12012577431569	-1.25836985492453	-0.21880368030191

C	3.33136354915249	-0.60329056156867	-0.02568292865837
C	-1.40654944798111	-0.43778848196387	-0.37660438556855
C	-1.42599930212745	0.90520957382345	-0.39094570382962
C	-2.65296728018804	1.57553122318491	-0.08369572650307
C	-3.71868709198910	-0.67657131921831	0.22525221674336
H	2.18204203023564	2.58884015563866	-0.21922670969067
H	2.08517436525536	-2.33688573904787	-0.21734720562121
N	-0.22305753705497	1.58475437258566	-0.69186029892028
N	-0.30117267634018	-1.21768670360040	-0.61819037566612
N	-2.48043595003843	-1.20969154936338	-0.06511419748557
N	-3.75866384234588	0.71108204696957	0.17711817145794
C	-5.05105492198960	1.32211435747868	0.48557516675738
H	-4.99635198338482	2.36726226629996	0.19910361561064
H	-5.83495057149541	0.80632951075232	-0.06265920660830
H	-5.26704964913889	1.24235996151734	1.55207242072577
C	-0.58064985852187	-2.56880440918342	-0.10988500716629
H	-0.17388822335872	-2.69033767015709	0.90132348599084
H	-0.14626829336949	-3.33050929628793	-0.75506255746511
C	-2.12442054894877	-2.62697097963971	-0.10362270390335
H	-2.53008357742948	-3.14676490580753	0.76052655514361
H	-2.52358081123478	-3.09050506060067	-1.00734977138072
O	-4.67375020838911	-1.37722040304851	0.50403104988054
O	-2.77282274851402	2.79279271613852	-0.03328935326080
O	4.56738297084805	1.37709806702156	0.19003791194922
C	4.62187181589408	2.78386416738422	0.34027367353651
H	3.97071906920478	3.12419517708775	1.15103402474442
H	5.65471430504903	3.02018863359595	0.58585280881097
H	4.34091271073989	3.29762445956287	-0.58442747976796
O	4.52301106703252	-1.22941314638253	0.17686669830977
C	4.51696013320027	-2.63762768087489	0.29124466339727
H	5.54010180581555	-2.92795403645986	0.51836346233499
H	3.85943336753560	-2.97162616277873	1.10051595457540
H	4.20267272795003	-3.11576031433100	-0.64284504420035
H	-0.22780708494661	2.54204095053309	-0.36874720089674

F

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Coordinates from ORCA-job opt-00

C	-3.73992406292675	0.51286315199994	-0.45791326690968
C	-2.48704428713968	1.06753030203977	-0.68011299785550
C	-1.30965490663077	0.37244527496895	-0.39186716991235
C	-1.42722255429663	-0.90790644008918	0.15468003618285
C	-2.67598674570859	-1.51115458931321	0.29997129190242
C	-3.83669497304020	-0.82084669157221	-0.01865389068939
C	0.90529225642829	-1.13163356737232	-0.04978065682813
C	1.05137416554509	0.05796055494154	-0.67597409794754
C	2.29086896156435	0.25817325732064	-1.39871575517727
C	3.14551359574606	-1.90250883819164	-0.44448246391886
H	-2.40675465553064	2.05706848571364	-1.10343896841728
H	-2.73558926489795	-2.51356919864543	0.69280960979581
N	-0.03974823050733	0.98273782083487	-0.62774390622198
N	-0.24339375993191	-1.57065384970261	0.54781759508734
N	1.85144702887176	-2.10364907742583	-0.00251835863098

N	3.31764311478812	-0.69164988929105	-1.08885205096453
C	4.67058580102421	-0.37342152481259	-1.54285281727034
H	5.36722964173153	-0.94887110459031	-0.94278761831814
H	4.80258588618534	-0.62860371733238	-2.59533560855780
H	4.83401273359578	0.69270720808848	-1.40960031622257
C	-0.13941947724475	-3.01217542701478	0.79318353788380
H	-0.65360881661366	-3.56792520067980	0.00154906798257
H	-0.57824339393903	-3.28234528533005	1.75281103700866
C	1.38131217909669	-3.26021030061944	0.75515567247075
H	1.65115585692085	-4.18493215011750	0.25141232491965
H	1.82561924941909	-3.25962277816991	1.75172263591668
O	4.01035263221817	-2.74159438122447	-0.28365698313059
O	2.53677241825896	1.15649484843001	-2.18125456811706
C	0.18632090997031	2.24772861819044	0.10977411131429
H	-0.81358324882170	2.60491778870456	0.36055911316728
C	0.83226395472174	3.31833227285098	-0.76239633102854
H	0.18868382812564	3.47998691779638	-1.62731103122354
H	0.92301876776119	4.25913036342467	-0.21844758808366
H	1.80762560672543	3.02136815341797	-1.12793513160226
O	-4.91620295037678	1.16449136828206	-0.64991405269290
C	-4.86953272808838	2.56664779726046	-0.83601850367074
H	-4.43597829403936	2.83371193241975	-1.80514343044418
H	-5.90073743308187	2.90968264986049	-0.79706942759860
H	-4.29433496246822	3.05113082461951	-0.04138287077206
O	-5.08790278509493	-1.33885769930390	0.06452579529458
C	-5.22122123648010	-2.71030201870900	0.38824633753043
H	-6.27668135611348	-2.94572676411507	0.27267679587942
H	-4.63489373970167	-3.33751634933940	-0.28964251566115
H	-4.91317033893940	-2.91153334214374	1.41972825107191
C	0.79755190627063	2.01684811754821	1.51235475275180
H	0.26415157601128	1.19723976228109	1.98879912675169
C	0.75341761678076	3.25841772976890	2.39474817402609
H	1.11789649363865	3.02738313575786	3.39626626611155
H	1.36274372478471	4.05646039746005	1.97534272432262
H	-0.27658440940206	3.60757531315337	2.47396915242472
N	2.23971901649859	1.54122267670617	1.50362475255257
O	3.05787110325438	2.22069015411813	0.91059309363583
O	2.49929408957832	0.53681084814692	2.15062790998233

G

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Coordinates from ORCA-job opt-0

C	3.37534347219487	0.78692189150553	-0.06148046126238
C	2.19347285491061	1.51128356284645	-0.18159445063793
C	0.92154323390893	0.90304328235767	-0.33843571072640
C	0.95135824706404	-0.52917771364914	-0.36628646353786
C	2.12394494721084	-1.25041366256723	-0.24152120570986
C	3.35793188765968	-0.60926174599086	-0.08795945608326
C	-1.40192703996565	-0.39492280924253	-0.31281955685817
C	-1.37326457749433	0.96145684519864	-0.28261760099368
C	-2.66368983610297	1.59572637147036	-0.06754487460911
C	-3.72725558183400	-0.69376125782674	0.20043889618163
H	2.19608419327938	2.59010351638086	-0.12708490048441

H	2.08094379729756	-2.33010731163988	-0.28574469717431
N	-0.19527561927689	1.66854942853746	-0.41928483131784
N	-0.30013910930706	-1.19787514448081	-0.58201961517431
N	-2.48448782490553	-1.19521151988052	-0.05238852429159
N	-3.77732630565850	0.68559509951139	0.14580549596935
C	-5.08325834792393	1.27679179930726	0.40253650673847
H	-5.03725653429682	2.31464982181031	0.08786989157070
H	-5.84696981928063	0.72859863174139	-0.14474907462470
H	-5.33055263858465	1.22918566700277	1.46651491935298
C	-0.57582197020953	-2.52757479308400	-0.04853695245551
H	-0.20199027823897	-2.62229396518917	0.98430967262580
H	-0.10929933545695	-3.30708634776818	-0.65191233231243
C	-2.11478254800083	-2.60345957327436	-0.08895037396241
H	-2.54199346935200	-3.13591602362714	0.75864229635966
H	-2.48122349544598	-3.06967486702152	-1.00768442958503
O	-4.69269187727616	-1.41617045000113	0.45255425877369
O	-2.88808665610814	2.79772109366912	-0.05417350197125
O	4.61379754118148	1.37005090623508	0.10615441081657
C	4.65099213806559	2.76192485232683	0.31298463093126
H	4.03272744447584	3.06286412901517	1.16579311088522
H	5.69258161801893	3.01230730387625	0.51775027778353
H	4.31140552794416	3.31664353342071	-0.56897024875943
O	4.57162564612265	-1.27371918318677	0.03280845005378
C	4.51319041016247	-2.65599327347066	0.25124800362630
H	5.53567766369593	-2.98668576704015	0.43788431751428
H	3.89028711723403	-2.90938274962100	1.11931414848941
H	4.11876958429248	-3.19875550765145	-0.61894722514077

H

28

Coordinates from ORCA-job opt-0

C	3.62923582586161	0.23534451571563	-0.00085881901904
C	2.48860511770518	1.00677371492247	-0.00137561448762
C	1.22927546803222	0.38988296259715	0.00113887216409
C	1.13422305309981	-1.02276505468868	0.00374886241643
C	2.30996731756425	-1.78574825693222	0.00530894263470
C	3.54126847555798	-1.16100311344295	0.00286256704453
C	-1.25532282048833	-0.81811764913781	0.00113883819218
C	-1.04514959346969	0.62055934186454	0.00181315484541
C	-2.26965398829438	1.48167999187546	0.00394056608913
C	-3.57228600802638	-0.63115486912099	-0.00611923595406
H	2.52788933454086	2.08667442026068	-0.00400025435549
H	2.26579485378946	-2.86384062918612	0.00820662884938
N	0.11353523831211	1.18477833737716	0.00125848818414
N	-0.11975684093097	-1.59748527278588	0.00399917416278
N	-2.41756860748883	-1.38606257323134	-0.00254960846028
N	-3.46121707543871	0.78650507506130	0.00060771489016
C	-4.68312771909799	1.59065158375294	0.00251756820143
H	-4.70553501847797	2.22417593337946	0.88873785596382
H	-4.69990226354621	2.23686915762434	-0.87452088150037
H	-5.52743290314905	0.91184238828736	-0.00489010199319
O	-4.66559571447516	-1.14993566888563	-0.01470179637735
O	-2.22170912950595	2.69257730477302	0.00727604324299

H	4.44612899133973	-1.75217803122047	0.00371996476645
Cl	5.19750418216739	0.98689941232340	-0.00506651256867
C	-0.26043360674209	-3.05285875052621	0.00580091980867
H	0.21380932992848	-3.47231199923127	-0.88172001999517
H	-1.31938810929538	-3.28464562198381	0.00170185309271
H	0.20614778142799	-3.46926560554150	0.89893204026225

I

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Coordinates from ORCA-job opt-00

C	3.52144254186996	-1.22786390135370	-1.24167287266996
C	2.27595631918299	-1.74251143627278	-0.90258418961168
C	1.24363405855087	-0.87857606881140	-0.57763179911715
C	1.42369196891955	0.51841446061039	-0.65781406706501
C	2.69043130584906	1.00829605291711	-0.99156297429268
C	3.73981655660350	0.13809750058105	-1.26932736874664
C	-0.95695339500709	0.81287054610908	-0.67800016280565
C	-1.10905105359404	-0.56048867584705	-0.57620739311416
C	-2.30492926314857	-1.15241799874781	-1.08024680770721
C	-3.10634239538551	1.19157096568160	-1.42766056318975
H	2.86661373399816	2.07319269787546	-1.04021642670663
N	-0.01109049382651	-1.35646206098723	-0.11756672110961
N	0.32997401255065	1.33639505856484	-0.41279013708176
N	-1.88300993910714	1.66959418513849	-1.06903693645932
N	-3.26991772669695	-0.21718066292982	-1.48878784237706
C	-4.53180010666945	-0.75390436805227	-1.97205622027833
H	-5.10118538875764	0.07312942132953	-2.38372768855116
H	-4.34428925975420	-1.51838893722637	-2.72548240603335
H	-5.09139347431332	-1.22444339285108	-1.15915941740946
O	-4.04951709807989	1.92104688277500	-1.72882775851797
O	-2.55069572157710	-2.36389998389578	-1.15343215400832
C	0.50227888995180	2.77135033863399	-0.35263313147561
H	-0.44343007797942	3.20952777213033	-0.05272845024379
H	0.77942588984916	3.19887226202401	-1.32302356097269
C	-0.02019301213834	-1.91272889630405	1.20394900160402
H	0.81179481678698	-2.60625454394107	1.30114278254806
C	-1.33972956217789	-2.50737522146819	1.62326674610616
H	-1.65414940533073	-3.23227401662858	0.87638787416574
H	-1.24240614148194	-2.97604616336090	2.60406726342197
H	-2.09717153917089	-1.72846816121637	1.67840155050348
N	0.38223091715474	-0.81133160741504	2.26177303766155
O	1.56966960093531	-0.75128932686561	2.56072736292209
O	-0.47366028547635	-0.03452977238964	2.65075584501655
H	2.10541859896913	-2.80953250705240	-0.87632235191605
H	4.71575886222099	0.52694123161792	-1.52420511998879
Cl	4.82674652519409	-2.32914616270701	-1.65900986895905
H	1.27740184108602	3.01227222033535	0.37716280645921

J

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Coordinates from ORCA-job opt-0

C	3.57175268113549	-1.21490318442373	-1.06707065434517
C	2.31581742991746	-1.71247050539369	-0.75261334032587
C	1.27986062492701	-0.82593538873650	-0.50796913776658

C	1.44691493369409	0.56267140121519	-0.63760878595666
C	2.73499061227857	1.03370203277183	-0.92333981812309
C	3.78731313431664	0.15607864682932	-1.12366894676451
C	-0.91507393345275	0.86716594168806	-0.73408899522435
C	-1.08348380880224	-0.52093138537652	-0.57351787122637
C	-2.31167535168570	-1.13082395976394	-1.00840294429759
C	-3.12859066428430	1.19107722160421	-1.33888522763334
H	2.91049482307218	2.09481412132255	-1.01711904531482
N	-0.01402410408060	-1.27855427639341	-0.07342073219595
N	0.35440572498454	1.40029287585566	-0.50226689429851
N	-1.87162661431838	1.68278547207335	-1.07407429086075
N	-3.28959823894081	-0.22111670614430	-1.38587404285367
C	-4.57016594188327	-0.76911521528811	-1.82556669246239
H	-5.14987752876646	0.04674255861912	-2.24287702909485
H	-4.39842704961540	-1.54738950418634	-2.56629146281542
H	-5.10702970761734	-1.21297501018356	-0.98541639258352
O	-4.07675104869830	1.91652465807021	-1.56546562233127
O	-2.50036785485245	-2.34680316152439	-1.07596765341335
C	0.52622278531556	2.84541687640026	-0.50993806731101
H	-0.42558063377366	3.29407202855886	-0.24842185532247
H	0.81799075960259	3.21333609272068	-1.49684319344441
C	-0.12838371629847	-2.27185796044856	0.77093923052136
H	0.79316868466241	-2.78095177885451	1.01232097485315
C	-1.37441779763065	-2.62565129445930	1.46380573200357
H	-2.01739284775121	-3.25026502287714	0.83539062853061
H	-1.14337464645159	-3.14208615484309	2.39433487015154
H	-1.95367187316053	-1.71860722324394	1.66590704566522
H	2.14663371968487	-2.77870154778475	-0.71710643844938
H	4.77121445532890	0.53709219348094	-1.35709407488426
Cl	4.87109044640528	-2.31856273495351	-1.41853001375799
H	1.28555445673855	3.12139982366905	0.22069665133212

K

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Coordinates from ORCA-job opt-0

C	3.57541280284472	-1.23225947671290	-1.20584519778651
C	2.32352210894293	-1.76484245599032	-0.91587201455007
C	1.26910726122305	-0.92394070436242	-0.59412866196924
C	1.44924962655832	0.47679770902323	-0.62510632308399
C	2.71611340288074	0.98572915592706	-0.92399777895518
C	3.78303760355361	0.13417199655725	-1.19974662140875
C	-0.93481757474488	0.76591462280069	-0.62011355603596
C	-1.08161074438784	-0.61039369541730	-0.56992351714565
C	-2.30173238169566	-1.17062660577011	-1.06123875873215
C	-3.10322109756920	1.18790767097758	-1.29767358061769
H	2.88467052435662	2.05288318696476	-0.93851078008570
N	0.02006614638693	-1.44818495284066	-0.17840222995772
N	0.35440983952310	1.29050375770924	-0.35364812271848
N	-1.86965590783551	1.64291062883331	-0.95230434529345
N	-3.27873473300445	-0.21410092437147	-1.39763713606406
C	-4.56000349173898	-0.72847975823179	-1.85329614150167
H	-5.13322741946803	0.11110262748803	-2.23302826690392
H	-4.40261957602221	-1.48173280414610	-2.62464386949365

H	-5.10124109854464	-1.20913259246331	-1.03345904415685
O	-4.04715106033792	1.93814153894807	-1.54791658686033
O	-2.56264979816568	-2.37343571203342	-1.17757805475214
C	0.52431658684590	2.72699832670520	-0.32396064806438
H	-0.42537176683658	3.17067609062152	-0.04522779426269
H	0.80904398422427	3.13247815184731	-1.30227622434977
C	0.03176551676004	-1.93380584555111	1.20003534066476
H	0.86325004731421	-2.63545339585074	1.28287814815470
C	-1.27323707087028	-2.61068662284238	1.57723187484245
H	-1.55263193502764	-3.35814701813914	0.83845734382144
H	-1.16709040303537	-3.06002230255933	2.56588505746566
H	-2.07734122920781	-1.87336085156683	1.61521156786231
H	2.15876954272747	-2.83303350339136	-0.92580211059080
H	4.75979108901654	0.53953257410054	-1.42406655814322
Cl	4.90373859211350	-2.31332825873381	-1.61329034797925
H	1.29562317456305	2.98904448406041	0.40310584612811
O	0.36189400957876	-0.91065326979782	2.15890280361076
H	-0.27636612092104	-0.19584743179181	2.03157932891309

L

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Coordinates from ORCA-job opt-01

C	3.65726209058259	0.42123112031738	-0.07875947049852
C	2.54009820638112	-0.34944155039605	0.21864948534573
C	1.25694875825978	0.14733328164738	-0.00088340765147
C	1.10834669243573	1.48783826721558	-0.45423476727732
C	2.25152186075894	2.24734031938937	-0.69324399439319
C	3.53378371391652	1.71649938107394	-0.53270249012327
C	-1.24135146428171	1.43026122830095	0.06083325699597
C	-1.07484376373649	0.13754414847842	0.52261864060821
C	-2.01428456686463	-0.38476613276882	1.44840029990932
C	-3.31249195227974	1.70275089402024	1.03546146805652
H	2.67319856802111	-1.34704886895183	0.59865294322811
H	2.15375661263806	3.26223116683512	-1.04698504771169
H	4.40808675887063	2.30817646879804	-0.76243475189054
N	0.09988665147007	-0.59927198392502	0.17745666985378
N	-0.17441983165564	1.98513256194368	-0.67731979299417
N	-2.28407255934157	2.20672630151792	0.29867008024516
N	-3.13885300407415	0.43473643436347	1.63560528648728
C	-4.23396638877649	-0.05866727070049	2.45131911321269
H	-4.48370915330681	0.67012736448160	3.22216075027367
H	-5.12517349093542	-0.20681705631840	1.83761442609829
H	-3.91742920716581	-0.99834098865076	2.89504328960878
O	-4.37193076347715	2.30007842826794	1.22913460809549
O	-1.91169786851192	-1.48064763651288	2.03130335190951
Cl	5.25634361238208	-0.28867094271446	0.13153894049718
C	-0.33865592661133	3.29953299842841	-1.26285503169199
H	0.00459030135916	4.09774647355378	-0.59266263860610
H	-1.39624542323920	3.45388364063364	-1.44906969605142
H	0.22367262437581	3.35358050536468	-2.19707751482301
C	-0.06995936490948	-1.99437157037502	-0.19724658926260
H	-1.13142474327437	-2.17792166169807	-0.05128577312842
C	0.62724929410241	-3.00814245972938	0.71481432738067

H	1.70248996152197	-3.08060250718477	0.54985358512309
H	0.43031164389683	-2.71565212178508	1.74444168909051
H	0.19520310087998	-3.99868113109467	0.55208960301303
C	0.20054113802890	-2.33568773488554	-1.69383387838150
H	-0.04412376160432	-3.39091261582177	-1.80537834788758
C	1.57362592026172	-2.05354780040292	-2.27978680800676
H	1.63710906157213	-2.46071298152679	-3.29115039973387
H	1.78651955389187	-0.99123714171409	-2.31770333411245
H	2.33695967896056	-2.53692055586093	-1.67242561975419
N	-0.86819508367661	-1.65184328867724	-2.52084870919247
O	-0.63438945685946	-0.53979394805612	-2.96026779819399
O	-1.91985734158566	-2.26043098118041	-2.67288768466642

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