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1. Instrumentation and chemicals

NMR-Spectroscopy: ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR were recorded at 223 K and 229 K using a Bruker Avance II 300, Bruker NEO 400, Agilent DD2 500 and an Agilent DD2 600 spectrometer. Chemical shifts (δ in ppm) were referenced to the solvent residual peak of $CDCl_3$ (δ_H = 7.26; δ_C = 77.16), DMSO-d_6 (δ_H = 2.50; δ_C = 39.52), C_6D_6 (δ_H = 7.16; δ_C = 128.06), and acetone-d_6 (δ_H = 2.05; δ_C = 206.26). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. The multiplets of the observed signals were given as s (singlet), br (broad singlet), d (doublet), t (triplet), q (quartet), hept (heptet), m (multiplet) and combination of the above.

Mass Spectroscopy: High-resolution (HRMS) ESI (*m/z*) spectra were measured on a Thermo Fisher Scientific LTQ XL Orbitrap and Thermo Fisher Scientific Orbitrap Velos Pro. High-resolution EI (*m/z*) spectra were measured on a Thermo Fischer Scientific Exactive GC Orbitrap GC-MS system. MassLinx 4.0 of Water-Micromass was used for data analysis.

Chromatography: For analytical thin layer chromatography (TLC) *Merck silica gel 60 F254*-plates were used and detection was carried out using UV-light (254 nm) or $KMnO_4$-stain (1.5 g $KMnO_4$, 5 g $NaHCO_3$ in 250 mL water). Flash coloumn chromatography was carried out on *VWR* silica gel (40 – 63 μm). Solvents for chromatography and liquid-liquid extractions were purchased in technical grad and purified by distillation. Diethylether (Et_2O) was distilled over ferrous sulfate heptahydrate. Reversed phase medium pressure liquid chromatography (RP-MPLC) was carried out on an automatic flash system by *Büchi C-850 Flashprep* using commercially available 4 g *Reveleris*-C_{18}-flash catridges as the stationary phase. As mobile phase, water (*Milli-Q* grade) and acetonitrile (HPLC grade) were used. Detection was performed by UV-absorption (λ = 210, 230, 254, 320 nm).

Infrared Spectroscopy: IR spectra were recorded on a *FTIR-4600LE Fourier-Transfrom Infrared Spectrometer Jasco*. The absorption signals are given *via* wavenumber (cm^{-1}). Signals are categorized as strong (*s*), medium (*m*) and weak (*w*).

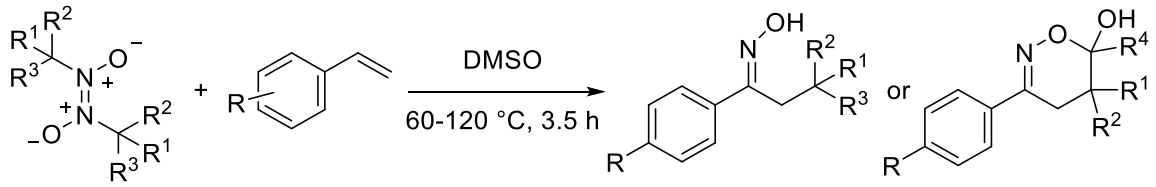
Melting Points: Melting points are measured on a *Büchi M560* and are uncorrected.

Experimental procedures, reagents and glassware: Unless stated otherwise, all reactions with air or moisture sensitive reagents or intermediates were performed under argon atmosphere using standard *Schlenk* technique and all glassware was pre-dried in an oven at 100 °C. Diethylether (Et_2O) was distilled over an Na/K-alloy. Dichloromethane (CH_2Cl_2) was distilled over phosphorous pentoxide (P_2O_5). Tetrahydrofuran (THF) was distilled over sodium and then freshly distilled over potassium prior to use. Anhydrous methanol (MeOH), acetone, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were purchased in extra-dry grade from *Acros Organics* and stored over molecular sieves. Unless stated otherwise, all reagents were purchased at *Sigma Aldrich*, *Acros Organics*, *Alfa Aesar*, *ABCR*, *TCI*, *Fluorochem* and *BLDPharm* and were used without further purification. Styrenes **2c**, **2d**, **2f**, **2g**, **2h**, **2p**,

2q, **2s**, **2t** were prepared by Wittig olefination from the corresponding aldehyde. Styrene **2l** was synthesized from **2f**.[1]

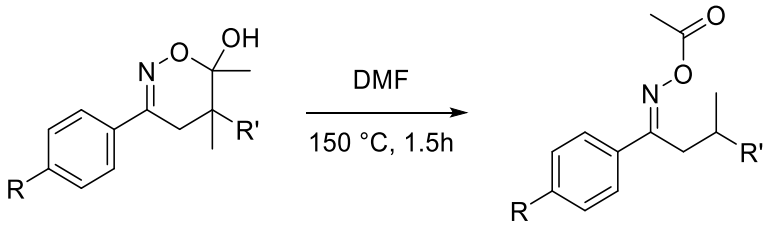
2. General procedures

General procedure I (GPI)



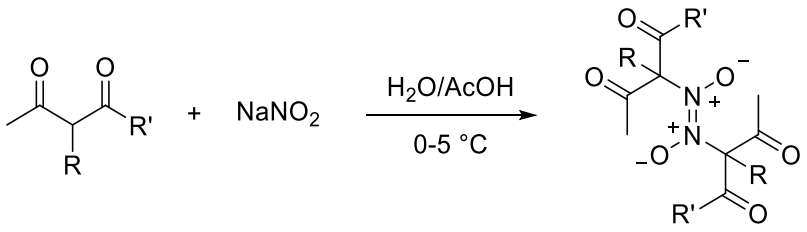
A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. Afterwards, styrene (0.60 mmol, 3.0 equiv.) and DMSO (2 mL) were added and the mixture was heated to a specific temperature. The azodioxy compound (0.10 mmol) was added to the reaction mixture in six portions every 30 min. One hour after the final addition, the reaction was quenched by the addition of water (3 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography.

General procedure II (GPII)



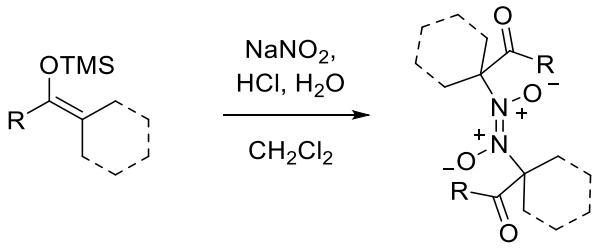
A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. Afterwards, the 5,6-dihydro-4*H*-1,2-oxazine (0.15 mmol) was dissolved in DMF (2 mL) and heated to 150 °C for 1.5 h. The reaction mixture was cooled to room temperature, treated with water (4 mL) and extracted with EtOAc (3x 10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography.

General procedure III (GPIII)



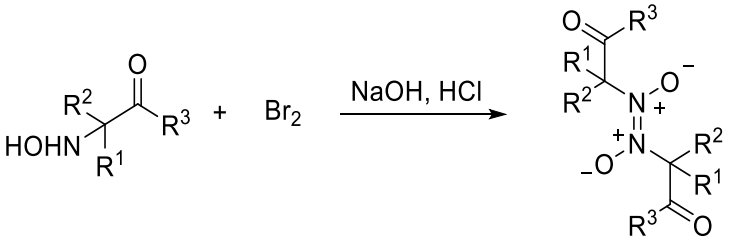
The ketone (4.0 mmol, 1.0 equiv.) was dissolved in acetic acid (1 mL) and cooled to approximately 0 °C. Sodium nitrite (4.8 mmol, 1.2 equiv.) was dissolved in water (0.5 mL) and added dropwise to the solution. Initially, the mixture became blue-green and then colourless crystals deposited. The mixture was stirred for 1 h to complete dimerization of the monomer, before the crystals that had deposited were separated off and washed with water and n-hexane.

General procedure IV (GPIV)



A 100 mL three-neck round bottom flask was evacuated and backfilled with argon 3 times. Then, it was equipped with a tube capped with a needle and connected through a septum with a two-neck round bottom flask filled with argon. With a constant stream of argon bubbling through the apparatus, the two-neck round bottom flask was attached to a bubbler filled with water. CH_2Cl_2 (2 mL) was added to the two-neck round bottom flask, cooled to 0 °C and conc. HCl (8.3 mL) was added to the three-neck round bottom flask. The argon stream was stopped, the needle that connects the three-neck with the two-neck round bottom flask was immersed into the CH_2Cl_2 and a solution of $NaNO_2$ (1.0 g, 15 mmol, 15 equiv.) in water was slowly added to the conc. HCl *via* syringe pump (240 µL/min). Once the CH_2Cl_2 was saturated by NOCl and turned brown, the needle was removed out of the two-neck round bottom flask and the silyl enol ether (1.0 mmol, 1.0 equiv.) was added to the CH_2Cl_2 (Caution! The excess NOCl in the three-neck round bottom flask has to be neutralized). The mixture turned blue-green immediately and the solvent and excess NOCl were directly removed under reduced pressure. The resulting colourless, dimeric solid was washed with pentane and dried under vacuum.

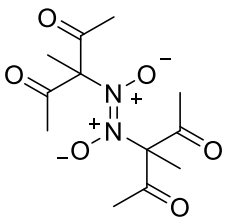
General procedure V (GPIV)



Hydroxylamine (1.0 equiv.) was dissolved in HCl (2 mol/L) and cooled to 0 °C. Br_2 (0.93 equiv.) was dissolved in aqueous NaOH (2.5 mol/L) and added dropwise to the hydroxylamine solution. With the addition of the first portion of the bromine solution, the mixture became blue-green, and then colorless crystals deposited. The solution was stirred for 1 h at 0 °C to complete dimerization of the nitroso-compound. Then, the precipitated product was separated off and washed with water and n-hexane.

3. Synthesis of starting materials

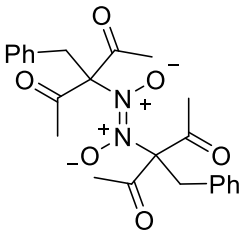
(*E*)-1,2-Bis(3-methyl-2,4-dioxopentan-3-yl)diazene 1,2-dioxide (**1a**)



(*E*)-1,2-Bis(3-methyl-2,4-dioxopentan-3-yl)diazene 1,2-dioxide (**1a**) was prepared according to **GPIII** using 3-methyl-2,4-pentanedione (3.36 g, 29.4 mmol, 1.0 equiv.), sodium nitrite (2.44 g, 35.3 mmol, 1.2 equiv.), acetic acid (7.4 mL) and water (3.5 mL). Colourless (*E*)-1,2-bis(3-methyl-2,4-dioxopentan-3-yl)diazene 1,2-dioxide (2.96 g, 10.4 mmol, 70%) was separated off and washed with water and n-hexane.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 2.39 (s, 12H), 1.74 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 197.4 (C_q), 90.0 (C_q), 27.4 (CH_3), 19.0 (CH_3). **FTIR** (neat): ν (cm^{-1}): 3015*w*, 2946*w*, 1738*s*, 1725*s*, 1436*m*, 1365*s*, 1292*m*, 1227*s*, 1217*s*, 1099*w*, 974*w*, 910*w*, 728*w*, 580*w*. **HRMS** (ESI) exact mass calculated for $C_{12}H_{18}N_2O_6Na^+$ $[2M+Na]^+$: *m/z* = 309.10571; found 309.10562. **M.p.**: 121 – 122 °C.

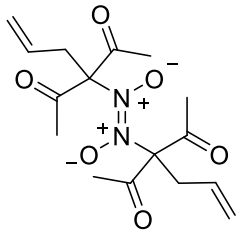
(*E*)-1,2-Bis(3-benzyl-2,4-dioxopentan-3-yl)diazene 1,2-dioxide (**1v**)



(*E*)-1,2-Bis(3-benzyl-2,4-dioxopentan-3-yl)diazene 1,2-dioxide (**1v**) was prepared according to **GPIII** using 3-benzylpentane-2,4-dione (0.48 g, 2.5 mmol, 1.0 equiv.), sodium nitrite (0.21 g, 3.0 mmol, 1.2 equiv.), acetic acid (0.6 mL) and water (0.3 mL). Colourless (*E*)-1,2-bis(3-benzyl-2,4-dioxopentan-3-yl)diazene 1,2-dioxide (0.44 g, 1.0 mmol, 80%) was separated off and washed with water and n-hexane.

^{1}H-NMR (300 MHz, C_6D_6, 299 K) δ (ppm) = 6.99 – 6.90 (m, 10H), 3.33 (s, 4H), 2.23 (s, 12H). **^{13}C-NMR** (75 MHz, C_6D_6, 299 K) δ (ppm) = 197.3 (C_q), 131.4 (CH), 128.6 (CH), 128.1 (CH), 92.7 (C_q), 39.9 (CH_2), 29.1 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2311*w*, 1725*m*, 1703*s*, 1498*w*, 1432*w*, 1359*w*, 1285*s*, 1249*w*, 1165*m*, 1086*w*, 1035*w*, 913*m*, 749*s*, 705*m*, 603*w*, 586*w*. **HRMS** (ESI) exact mass calculated for $C_{24}H_{26}N_2O_6Na^+$ $[2M+Na]^+$: *m/z* = 461.16831; found 461.16797. **M.p.**: 88 – 90 °C.

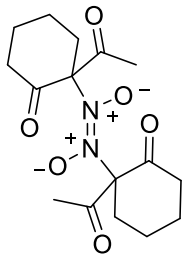
(*E*)-1,2-Bis(3-acetyl-2-oxohex-5-en-3-yl)diazene 1,2-dioxide (**1w**)



(*E*)-1,2-Bis(3-acetyl-2-oxohex-5-en-3-yl)diazene 1,2-dioxide (**1w**) was prepared according to **GPIII** using 3-allylhexane-2,4-dione (1.90 g, 13 mmol, 1.0 equiv.), sodium nitrite (1.08 g, 16 mmol, 1.2 equiv.), acetic acid (3.3 mL) and water (1.6 mL). Colourless (*E*)-1,2-bis(3-acetyl-2-oxohex-5-en-3-yl)diazene 1,2-dioxide (1.05 g, 2.9 mmol, 44%) was isolated.

^{1}H-NMR (300 MHz, C_6D_6, 299 K) δ (ppm) = 5.70 (ddt, *J* = 16.7, 10.5, 7.1 Hz, 2H), 4.89 – 4.78 (m, 4H), 2.66 (dt, *J* = 7.1, 1.2 Hz, 4H), 2.28 (s, 12H). **^{13}C-NMR** (75 MHz, C_6D_6, 299 K) δ (ppm) = 196.8 (C_q), 130.2 (CH_2), 121.2 (CH), 92.9 (C_q), 38.4 (CH_2), 28.6 (CH_3). **FTIR** (neat): ν (cm^{-1}): 1719*s*, 1708*s*, 1641*m*, 1557*m*, 1416*m*, 1359*s*, 1299*s*, 1280*s*, 1182*s*, 1128*w*, 993*w*, 941*m*, 851*w*, 750*w*, 717*w*, 637*w*, 608*m*, 585*m*. **HRMS** (ESI) exact mass calculated for $C_{16}H_{22}N_2O_6Na^+$ $[2M+Na]^+$: *m/z* = 361.13701; found 361.13709. **M.p.**: 87 – 88 °C.

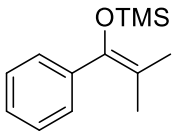
(*E*)-1,2-Bis(1-acetyl-2-oxocyclohexyl)-diazene 1,2-dioxide (**1x**)



(*E*)-1,2-Bis(1-acetyl-2-oxocyclohexyl)-diazene 1,2-dioxide (**1x**) was prepared according to **GPIII** using 2-acetylcyclohexan-1-one (0.33 mL, 2.5 mmol, 1.0 equiv.), sodium nitrite (0.21 g, 3.0 mmol, 1.2 equiv.), acetic acid (0.6 mL) and water (0.3 mL). Colourless (*E*)-1,2-bis(1-acetyl-2-oxocyclohexyl)-diazene 1,2-dioxide (0.23 g, 0.70 mmol, 54%) was isolated as a mixture of diastereoisomers.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 2.95 – 2.75 (m, 4H), 2.72 – 2.58 (m, 2H), 2.45 – 2.29 (m, 8H), 2.01 – 1.85 (m, 6H), 1.76 – 1.60 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 198.8 (C_q), 198.8 (C_q), 196.3 (C_q), 91.8 (C_q), 91.8 (C_q), 41.5 (CH_2), 41.4 (CH_2), 33.0 (CH_2), 32.9 (CH_2), 27.5 (CH_2), 27.3 (CH_2), 26.9 (CH_3), 26.8 (CH_3), 20.7 (CH_2), 20.7 (CH_2). **FTIR** (neat): ν (cm^{-1}): 1719*s*, 1423*w*, 1362*w*, 1311*w*, 1280*s*, 1194*w*, 1132*w*, 1085*w*, 913*m*, 743*m*, 601*w*, 560*w*. **HRMS** (ESI) exact mass calculated for $C_{16}H_{22}N_2O_6Na^+$ $[2M+Na]^+$: *m/z* = 361.13701; found 361.13688. **M.p.**: 100 – 101 °C.

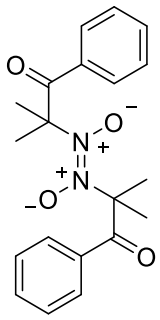
Trimethyl((2-methyl-1-phenylprop-1-en-1-yl)oxy)silane



A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. Isobutyrophenone (2.3 mL, 15 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (12 mL) and NEt_3 (9.0 mL) and cooled to 0 °C. Then, trimethylsilyl trifluoromethanesulfonate (4.1 mL, 23 mmol, 1.5 equiv.) was slowly added. The reaction mixture was gradually warmed to room temperature and stirred overnight. Saturated $NaHCO_3$ (10 mL) was carefully added, the phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x10 mL). The combined organic phases were washed with brine (10 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (pentane/EtOAc 100:1) to yield trimethyl((2-methyl-1-phenylprop-1-en-1-yl)oxy)silane (2.2 g, 10 mmol, 68%) as colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.40 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 1.85 (s, 3H), 1.74 (s, 3H), 0.04 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 143.7 (C_q), 139.2 (C_q)), 129.3 (2xCH), 127,8 (2xCH), 127.2 (CH), 113.1 (C_q), 19.9 (CH_3), 18.4 (CH_3), 0.5 (3xCH_3). The spectroscopic data are in accordance with the literature.[2]

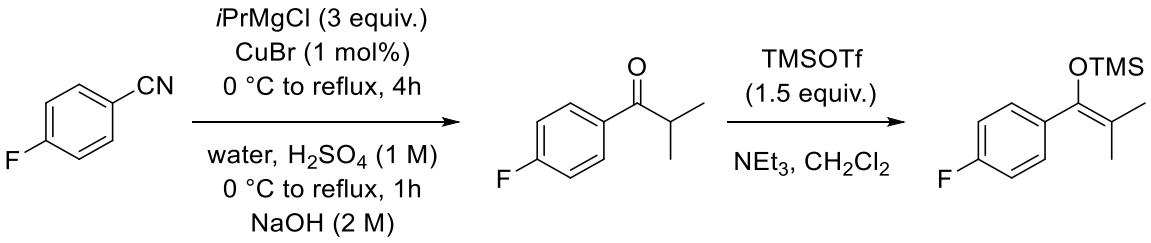
(*E*)-1,2-Bis(2-methyl-1-oxo-1-phenylpropan-2-yl)diazene 1,2-dioxide (**1y**)



(*E*)-1,2-Bis(2-methyl-1-oxo-1-phenylpropan-2-yl)diazene 1,2-dioxide (**1y**) was prepared according to **GPIV** using trimethyl((2-methyl-1-phenylprop-1-en-1-yl)oxy)silane (0.331 g, 1.50 mmol, 1.0 equiv.), sodium nitrite (1.55 g, 23.0 mmol, 15 equiv.), conc. HCl (12.5 mL) and CH_2Cl_2 (3 mL). Colourless (*E*)-1,2-bis(2-methyl-1-oxo-1-phenylpropan-2-yl)diazene 1,2-dioxide (0.232 g, 0.65 mmol, 87%) was obtained.

^{1}H-NMR (500 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.82 – 7.79 (m, 4H), 7.54 (ddt, *J* = 7.9, 7.0, 1.3 Hz, 2H), 7.43 – 7.39 (m, 4H), 1.52 (s, 12H). **^{13}C-NMR** (126 MHz, $CDCl_3$, 223 K) δ (ppm) = 191.7 (C_q), 133.5 (CH), 132.9 (C_q), 128.7 (CH), 128.2 (CH), 79.9 (C_q), 77.4 (C_q), 23.6 (CH_3), 18.6 (CH_3). **FTIR** (neat): ν (cm^{-1}): 3014*m*, 2970*w*, 2360*w*, 1738*s*, 1684*w*, 1446*w*, 1365*m*, 1281*w*, 1228*m*, 1217*s*, 911*w*, 791*w*, 742*w*, 702*w*, 653*w*, 527*w*. **HRMS** (ESI) exact mass calculated for $C_{20}H_{22}N_2O_4Na^+$ $[2M+Na]^+$: *m/z* = 377.14718; found 377.14710. **M.p.**: 139 – 141 °C.

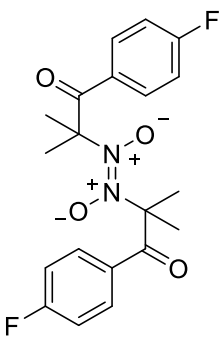
((1-(4-Fluorophenyl)-2-methylprop-1-en-1-yl)oxy)trimethylsilane



Step 1: A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. 4-Fluorobenzonitrile (1.2 g, 10 mmol, 1.0 equiv.) was dissolved in THF (10 mL) and *i*PrMgCl (15.0 mL, 30 mmol, 3.0 equiv., 2 mol/L in THF) was added dropwise. Then, CuBr (0.014 g, 0.10 mmol, 1 mol%) was added and the reaction mixture was refluxed for 4 h before it was cooled to 0 °C and quenched by the dropwise addition of water (11 mL). H_2SO_4 (36 mL, 1 mol/L) was added and the mixture was refluxed for 1 h before it was cooled to 0 °C again and basified with aqueous NaOH (2 mol/L) until pH ca. 10. The mixture was then extracted with EtOAc (3x80 mL) and the combined organic phases were washed with brine (150 mL) and dried with Na_2SO_4. Evaporation of the solvent delivered 1-(4-fluorophenyl)-2-methylpropan-1-one (1.2 g, 7.7 mmol, 77%) as a colourless oil that was used without further purification. **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.03 – 7.94 (m, 2H), 7.18 – 7.09 (m, 2H), 3.51 (hept, *J* = 6.9 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 203.0 (C_q), 165.7 (d, *J* = 254.2 Hz, C_q), 132.7 (d, *J* = 3.2 Hz, C_q), 131.1 (d, *J* = 9.2 Hz, 2xCH), 115.8 (d, *J* = 21.8 Hz, 2xCH), 35.5 (CH), 19.3 (2xCH_3). **^{19}F-NMR** (282 MHz, $CDCl_3$, 299 K) δ (ppm) = –105.9. The spectroscopic data are in accordance with the literature.[7]

Step 2: A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. 1-(4-fluorophenyl)-2-methylpropan-1-one (1.2 g, 7.7 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (6.0 mL) and NEt_3 (5.1 mL) and cooled to 0 °C. Then, trimethylsilyl trifluoromethanesulfonate (2.1 mL, 12 mmol, 1.5 equiv.) was slowly added. The reaction mixture was gradually warmed to room temperature and stirred overnight. Saturated $NaHCO_3$ (10 mL) was carefully added, the phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x10 mL). The combined organic phases were washed with brine (10 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (pentane/EtOAc 100:1) to yield ((1-(4-fluorophenyl)-2-methylprop-1-en-1-yl)oxy)trimethylsilane (1.2 g, 5.4 mmol, 70%) as colourless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.33 – 7.23 (m, 2H), 7.04 – 6.95 (m, 2H), 1.77 (s, 3H), 1.65 (s, 3H), -0.03 (s, 9H). **^{13}C-NMR** (126 MHz, $CDCl_3$, 299 K) δ (ppm) = 161.9 (d, *J* = 246.1 Hz, C_q), 142.7 (C_q), 135.3 (d, *J* = 3.4 Hz, C_q), 130.9 (d, *J* = 8.1 Hz, CH), 114.7 (d, *J* = 21.3 Hz, CH), 113.2 (C_q), 19.8 (CH_3), 18.4 (CH_3), 0.5 (d, *J* = 7.6 Hz, CH_3). **^{19}F-NMR** (470 MHz, $CDCl_3$, 299 K) δ (ppm) = –-114.87 (tt, *J* = 8.8, 5.5 Hz). **FTIR** (neat): ν (cm^{-1}): 2974*m*, 2360*w*, 1684*s*, 1598*s*, 1505*m*, 1467*w*, 1410*w*, 1383*w*, 1224*s*, 1154*s*, 1035*w*, 982*m*, 846*s*, 758*m*, 592*w*. **HRMS** (EI) exact mass calculated for $C_{13}H_{19}OFSi^+$ $[M]^+$: *m/z* = 238.11837; found 238.11763.

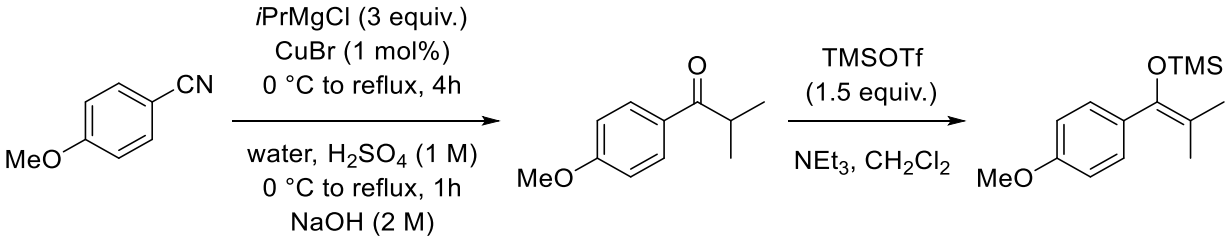
(*E*)-1,2-Bis(1-(4-fluorophenyl)-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (**1z**)



(*E*)-1,2-Bis(1-(4-fluorophenyl)-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (**1z**) was prepared according to **GPIV** using ((1-(4-fluorophenyl)-2-methylprop-1-en-1-yl)oxy)trimethylsilane (0.23 g, 0.97 mmol, 1.0 equiv.), sodium nitrite (1.0 g, 14 mmol, 15 equiv.), conc. HCl (8.3 mL) and CH_2Cl_2 (2 mL). Colourless (*E*)-1,2-bis(1-(4-fluorophenyl)-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (0.15 g, 0.38 mmol, 77%) was obtained.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.89 – 7.77 (m, 4H), 7.14 – 7.02 (m, 4H), 1.54 (s, 12H). **^{13}C-NMR** (151 MHz, $CDCl_3$, 299 K) δ (ppm) = 190.4 (C_q), 165.6 (d, *J* = 255.6 Hz, C_q), 133.0 (d, *J* = 9.8 Hz, C_q), 131.2 (d, *J* = 9.2 Hz, CH), 115.8 (d, *J* = 21.9 Hz, CH), 80.4 (C_q). The ^{13}C-NMR signals of the methyl groups are very broad and cannot be seen at room temperature. **^{19}F-NMR** (282 MHz, $CDCl_3$, 299 K) = –104.6 (s). **FTIR** (neat): ν (cm^{-1}): 1690*s*, 1599*m*, 1507*w*, 1459*w*, 1281*s*, 1264*s*, 1231*m*, 1158*m*, 990*w*, 912*s*, 850*m*, 750*s*, 605*m*. **HRMS** (ESI) exact mass calculated for $C_{20}H_{20}N_2O_4F_2Na^+$ $[2M+Na]^+$: *m/z* = 413.12833; found 413.12833. **M.p.**: 138 – 139 °C.

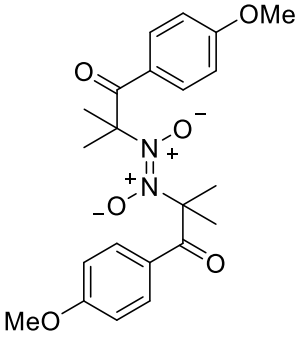
((1-(4-methoxyphenyl)-2-methylprop-1-en-1-yl)oxy)Trimethylsilane



Step 1: A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. 4-Methoxybenzonitrile (1.32 g, 10 mmol, 1.0 equiv.) was dissolved in THF (10 mL) and *i*PrMgCl (15.0 mL, 30 mmol, 3.0 equiv., 2 mol/L in THF) was added dropwise. Then, CuBr (0.014 g, 0.10 mmol, 1 mol%) was added and the reaction mixture was refluxed for 4 h before it was cooled to 0 °C and quenched by the dropwise addition of water (11 mL). H_2SO_4 (36 mL, 1 mol/L) was added and the mixture was refluxed for 1 h before it was cooled to 0 °C again and basified with aqueous NaOH (2 mol/L) until pH ca. 10. The mixture was then extracted with EtOAc (3x80 mL) and the combined organic phases were washed with brine (150 mL) and dried with Na_2SO_4. Evaporation of the solvent delivered 1-(4-methoxyphenyl)-2-methylpropan-1-one (1.75 g, 9.9 mmol, 98%) as a colourless oil that was used without further purification. **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.98 – 7.92 (m, 2H), 6.97 – 6.90 (m, 2H), 3.87 (s, 3H), 3.52 (hept, *J* = 6.8 Hz, 1H), 1.20 (d, *J* = 6.8 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 203.3 (C_q), 163.4 (C_q), 130.7 (2xCH), 129.3 (C_q), 113.9 (2xCH_3), 55.6 (CH_3), 35.1 (CH), 19.4 (2xCH_3). The spectroscopic data are in accordance with the literature.[7]

Step 2: A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. 1-(4-methoxyphenyl)-2-Methylpropan-1-one (1.75 g, 9.9 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (8.0 mL) and NEt_3 (5.7 mL) and cooled to 0 °C. Then, trimethylsilyl trifluoromethanesulfonate (2.7 mL, 15 mmol, 1.5 equiv.) was slowly added. The reaction mixture was gradually warmed to room temperature and stirred overnight. Saturated $NaHCO_3$ (10 mL) was carefully added, the phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x10 mL). The combined organic phases were washed with brine (10 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (pentane/EtOAc 100:1) to yield ((1-(4-methoxyphenyl)-2-methylprop-1-en-1-yl)oxy)trimethylsilane (2.2 g, 8.3 mmol, 85%) as colourless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.28 – 7.19 (m, 2H), 6.88 – 6.80 (m, 2H), 3.81 (s, 3H), 1.77 (s, 3H), 1.66 (s, 3H), -0.02 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 158.7 (C_q), 143.4 (C_q), 131.7 (C_q), 130.5 (2xCH), 113.1 (2xCH), 112.2 (C_q), 55.3 (CH_3), 19.9 (CH_3), 18.4 (CH_3), 0.6 (3xCH_3). **FTIR** (neat): ν (cm^{-1}): 2957*w*, 1676*w*, 1606*m*, 1509*s*, 1464*w*, 1300*w*, 1282*w*, 1247*s*, 1151*s*, 1107*w*, 1031*m*, 1010*w*, 899*m*, 871*s*, 840*s*, 801*w*, 756*w*, 637*w*, 600*w*. **HRMS** (EI) exact mass calculated for $C_{14}H_{22}O_2Si^+$ $[M]^+$: *m/z* = 250.13826; found 250.13820.

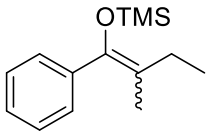
(*E*)-1,2-Bis(1-(4-methoxyphenyl)-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (**1aa**)



(*E*)-1,2-Bis(1-(4-methoxyphenyl)-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (**1aa**) was prepared according to **GPIV** using ((1-(4-methoxyphenyl)-2-methylprop-1-en-1-yl)oxy)trimethylsilane (0.25 g, 1.0 mmol, 1.0 equiv.), sodium nitrite (1.0 g, 15 mmol, 15 equiv.), conc. HCl (8.3 mL) and CH_2Cl_2 (2 mL). Colourless (*E*)-1,2-bis(1-(4-methoxyphenyl)-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (0.12 g, 0.30 mmol, 59%) was obtained.

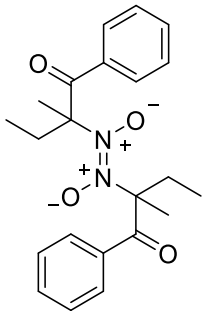
^{1}H-NMR (599 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.83 – 7.78 (m, 4H), 6.89 – 6.84 (m, 4H), 3.85 (s, 6H), 1.55 (s, 12H). **^{13}C-NMR** (151 MHz, $CDCl_3$, 299 K) δ (ppm) = 190.4 (C_q), 163.5 (C_q), 130.9 (CH), 126.7 (C_q), 113.8 (CH), 80.4 (C_q), 55.6 (CH_3), 21.8 (br, CH_3). **FTIR** (neat): ν (cm^{-1}): 1674*s*, 1598*s*, 1510*w*, 1453*w*, 1384*w*, 1308*w*, 1283*m*, 1262*s*, 1162*s*, 1031*w*, 989*w*, 912*s*, 848*m*, 729*s*, 703*w*, 604*m*. **HRMS** (ESI) exact mass calculated for $C_{44}H_{52}N_4O_{12}Na^+$ $[4M+Na]^+$: *m/z* = 851.34739; found 851.34857. **M.p.**: 140 – 142 °C.

Trimethyl((2-methyl-1-phenylbut-1-en-1-yl)oxy)silane



Trimethyl((2-methyl-1-phenylbut-1-en-1-yl)oxy)silane was prepared according to a literature procedure.[8] 2-Methyl-1-phenylbutan-1-one (1.4 g, 8.5 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (6.8 mL) and NEt_3 (5.1 mL) under an argon atmosphere. At 0 °C trimethylsilyl trifluoromethanesulfonate (2.3 mL, 13 mmol, 1.5 equiv.) was slowly added and the reaction mixture was warmed to room temperature and stirred overnight. Then, saturated aqueous $NaHCO_3$-solution (15 mL) was added and the mixture was extracted with CH_2Cl_2 (3x10 mL). The combined organic phases were washed with brine (20 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (pentane/EtOAc 100:1) to yield trimethyl((2-methyl-1-phenylbut-1-en-1-yl)oxy)silane (1.4 g, 6.0 mmol, 70%) as colourless oil as a mixture of *E*/*Z*-isomers. **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.38 – 7.28 (m, 5H), 2.31 (q, *J* = 7.5 Hz, 1H), 2.08 (q, *J* = 7.5 Hz, 1H), 1.83 (s, 1.5H), 1.71 (s, 1.5H), 1.12 (t, *J* = 7.5 Hz, 1.5H), 1.06 (t, *J* = 7.5 Hz, 1.5H), 0.03 (s, 4.5H), 0.03 (s, 4.5H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 129.4 (2xCH), 129.1 (2xCH), 127.9 (2xCH), 127.8 (2xCH), 127.3 (CH), 127.2 (CH), 26.3 (CH_2), 24.7 (CH_2), 16.9 (CH_3), 15.2 (CH_3), 13.6 (CH_3), 12.4 (CH_3), 0.5 (CH_3), 0.5 (CH_3). Not all quaternary ^{13}C-signals could be detected. The spectroscopic data are in accordance with the literature.[8]

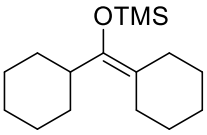
(*E*)-1,2-Bis(2-methyl-1-oxo-1-phenylbutan-2-yl)diazene 1,2-dioxide (**1ab**)



(*E*)-1,2-Bis(2-methyl-1-oxo-1-phenylbutan-2-yl)diazene 1,2-dioxide (**1ab**) was prepared according to **GPIV** using trimethyl((2-methyl-1-phenylbut-1-en-1-yl)oxy)silane (0.35 g, 1.5 mmol, 1.0 equiv.), sodium nitrite (1.5 g, 23 mmol, 15 equiv.), conc. HCl (12 mL) and CH_2Cl_2 (3 mL). Colourless (*E*)-1,2-bis(2-methyl-1-oxo-1-phenylbutan-2-yl)diazene 1,2-dioxide (0.24 g, 0.65 mmol, 84%) was obtained as mixture of diastereoisomers (dr = 2:1).

^{1}H-NMR both isomers (599 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.88 – 7.77 (m, 4H), 7.56 – 7.48 (m, 2H), 7.43 – 7.36 (m, 4H), 2.33 – 2.03 (m, 4H), 1.52 (s, 2H), 1.43 (s, 4H), 0.66 (t, *J* = 7.6 Hz, 4H), 0.47 (t, *J* = 7.5 Hz, 2H). **^{13}C-NMR** both isomers (151 MHz, $CDCl_3$, 299 K) δ (ppm) = 192.0 (C_q), 191.6 (C_q) 134.9 (C_q), 134.9 (C_q), 132.9 (CH), 132.9 (CH), 128.6 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 83.6 (C_q), 83.6 (C_q), 27.9 (CH_2), 27.8 (CH_2), 16.7 (CH_3), 16.6 (CH_3), 7.8 (CH_3), 7.3 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2991*w*, 1682*s*, 1595*w*, 1578*w*, 1446*w*, 1366*w*, 1309*w*, 1274*s*, 1247*m*, 1231*m*, 1163*m*, 1119*w*, 1083*w*, 1001*w*, 970*w*, 955*w*, 904*w*, 829*w*, 792*w*, 740*w*, 699*s*, 650*s*, 574*w*. **HRMS** (ESI) exact mass calculated for $C_{22}H_{26}N_2O_4Na^+$ $[2M+Na]^+$: *m/z* = 405.17848; found 405.17859. **M.p.**: 112 – 134 °C.

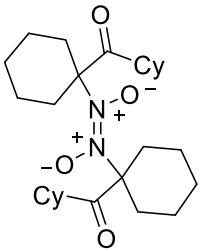
(Cyclohexyl(cyclohexylidene)methoxy)trimethylsilane



(Cyclohexyl(cyclohexylidene)methoxy)trimethylsilane was prepared according to a literature procedure.[9] Dicyclohexylketone (1.6 mL, 8.0 mmol, 1.0 equiv.) was dissolved in THF (31 mL) under argon atmosphere. LiHMDS (9.2 mL, 12 mmol, 1.5 equiv., 1.3 mol/L) was added and the mixture was stirred for 30 min. Then, chlorotrimethylsilane (1.2 mL, 9.6 mmol, 1.2 equiv.) was added and the mixture was stirred for another 30 min before being carefully quenched with water (20 mL) and extraced with CH_2Cl_2 (3x 15 mL). The combined organic phases were washed with brine (20 mL), dried with Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (pentane/EtOAc 100:2) to yield (cyclohexyl(cyclohexylidene)methoxy)trimethylsilane (2.0 g, 7.4 mmol, 93%) as colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 2.49 – 2.36 (m, 1H), 2.13 – 2.06 (m, 3H), 1.80 – 1.60 (m, 4H), 1.57 – 1.41 (m, 8H), 1.41 – 1.18 (m, 5H), 0.20 (s, 6H), 0.18 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 146.4 (C_q), 116.5 (C_q), 39.6 (CH), 30.8 (CH_2), 29.4 (CH_2), 28.8 (CH_2) 28.4 (CH_2), 28.3 (CH_2), 27.5 (CH_2), 27.1 (CH_2), 26.8 (CH_2), 26.3 (CH_2), 25.9 (CH_2), 5.6 (CH_3), 1.3 (CH_3). The analytical data are in accordance with the literature.[9]

(*E*)-1,2-Bis(1-(cyclohexanecarbonyl)cyclohexyl)-diazene 1,2-dioxide (**1ac**)

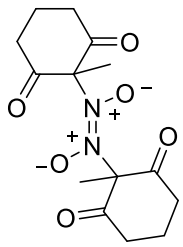


A 100 mL three-neck round bottom flask was evacuated and backfilled with argon 3 times. Then, it was equipped with a tube capped with a needle and connected through a septum with a two-neck round bottom flask filled with argon. With a constant stream of argon bubbling through the apparatus, the two-neck round bottom flask was attached to a bubbler filled with water. *n*-Pentane (2.5 mL) and (cyclohexyl(cyclohexylidene)methoxy)trimethylsilane (0.37 g, 1.4 mmol, 1.0 equiv.) were added to the two-neck round bottom flask, cooled to 0 °C and conc. HCl (12.5 mL) was added to the three-neck round bottom flask. The argon stream was stopped, the needle that connects the three-neck with the two-neck round bottom flask was immersed into the *n*-pentane solution and a solution of $NaNO_2$ (1.5 g, 23 mmol, 16 equiv.) in water (3 mL) was slowly added to the conc. HCl *via* syringe pump (240 µL/min). The *n*-pentane solution turned blue-green upon NOCl addition. Once the colour started to turn brown and the gas phase above the solution turned brown, the needle was removed out of the two-neck round bottom flask (Caution! The excess NOCl in the three-neck round bottom flask has to be neutralized). The solvent and excess NOCl were directly removed under reduced pressure. The resulting colourless (*E*)-1,2-bis(1-(cyclohexanecarbonyl)cyclohexyl)-diazene 1,2-dioxide (0.088 g, 0.20 mmol, 28%) was washed with pentane and dried under vacuum.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 2.68 – 2.55 (m, 2H), 2.47 – 2.33 (m, 4H), 1.88 – 1.53 (m, 24H), 1.49 – 1.17 (m, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 205.9 (C_q), 83.4 (C_q),

45.5 (CH), 29.8 (CH_2), 28.8 (CH_2), 25.9 (CH_2), 25.7 (CH_2), 24.9 (CH_2), 21.9 (CH_2). **FTIR** (neat): ν (cm^{-1}): 2928*s*, 2854*m*, 1716*m*, 1702*s*, 1450*m*, 1426*w*, 1370*w*, 1325*w*, 1279*s*, 1257*w*, 1240*w*, 1210*w*, 1147*w*, 1038*w*, 988*m*, 911*m*, 731*s*, 648*w*, 581*w*. **HRMS** (ESI) exact mass calculated for $C_{26}H_{42}N_2O_4Na^+$ $[2M+Na]^+$: *m/z* = 469.30368; found 469.30365. **M.p.**: 115 – 117 °C.

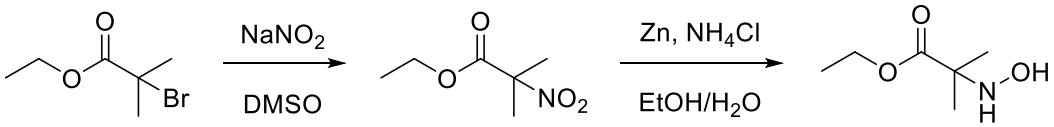
(*E*)-1,2-Bis(1-methyl-2,6-dioxocyclohexyl)-diazene 1,2-dioxide (**1ad**)



(*E*)-1,2-Bis(1-methyl-2,6-dioxocyclohexyl)-diazene 1,2-dioxide (**1ad**) was prepared according to a literature procedure with slight modifications.[10] 2-Methyl-cyclohexan-1,3-dione (1.3 g, 10 mmol, 1.0 equiv) was dissolved in aqueous 10% KOH (10 mL). At 0 °C, sodium nitrite (0.70 g, 10 mmol, 1.0 equiv.) in water (10 mL) was added. Under vigorous stirring 20% HCl is added dropwise until an acidic pH is obtained. The reaction mixture is stirred for 1 h at 0 °C, the formed crystals are filtered off and washed with H_2O, hot EtOH and pentane. Colourless (*E*)-1,2-bis(1-methyl-2,6-dioxocyclohexyl)-diazene 1,2-dioxide (0.39 g, 1.3 mmol, 25%) was obtained.

^{1}H-NMR (500 MHz, d-TFA/acetone-d_6, 299 K) δ (ppm) = 2.51 – 2.43 (m,4H), 2.33 – 2.25 (m, 4H), 1.86 – 1.75 (m, 2H), 1.68 – 1.59 (m, 2H), 1.33 (s, 0.8H), 1.17 (s, 5.2). **^{13}C-NMR** (126 MHz, d-TFA/acdetone-d_6, 299 K) δ (ppm) = 203.6 (C_q), 86.8 (C_q), 37.3 (CH_2), 17.8 (CH_3), 16.5 (CH_2). **HRMS** (ESI) exact mass calculated for $C_{14}H_{18}N_2O_6Na^+$ $[2M+Na]^+$: *m/z* = 333.10571; found 333.10542. **M.p.**: 150 – 152 °C.

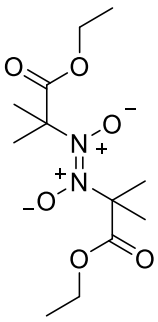
Ethyl 2-(hydroxyamino)-2-methylpropanoate



Step 1: To a stirred suspension of sodium nitrite (5.17 g, 75.0 mmol, 1.5 equiv.) in DMSO (50 mL) ethyl 2-bromo-2-methylpropanoate (7.3 mL, 50.0 mmol, 1.0 equiv.) was added. The mixture was stirred at 80 °C for 3 h. Then, the reaction mixture was poured into ice/water and extracted with Et_2O (3x 50 mL). The combined organic phases were washed with brine (50 mL), dried with Na_2SO_4 and concentrated under reduced pressure to give ethyl 2-methyl-2-nitropropanoate (6.51 g, 40.4 mmol, 81%) as a slight yellow oil in sufficient purity. **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 4.26 (q, *J* = 7.1 Hz, 2H), 1.81 (s, 6H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 167.9 (C_q), 89.5 (C_q), 63.0 (CH_2), 24.1 (2xCH_3), 13.9 (CH_3). The spectroscopic data are in accordance with the literature.[3]

Step 2: To a stirred suspension of ethyl 2-methyl-2-nitropropanoate (6.45 g, 40.0 mmol, 1.0 equiv.) and NH_4Cl (9.63 g, 180 mmol, 4.0 equiv.) in ethanol (14.5 mL) and water (29 mL), zinc (8.83 g, 135 mmol, 3.0 equiv.) was added in several portions while maintaining at a temperature under 40 °C. After the final addition, the suspension was stirred at 35 °C for 5 h. Then, the mixture was filtered and the filtrate concentrated. The residue was dissolved in Et_2O (10 mL) and water (10 mL). The organic layer was separated and washed with HCl (2 mol/L). The combined aqueous phases were washed with Et_2O (10 mL) and its pH was adjusted to 10 with K_2CO_3. The aqueous layer was then extracted with EtOAc (2x10 mL). The combined organic phases were washed brine (20 mL), dried with Na_2SO_4 and concentrated under reduced pressure to give ethyl 2-(hydroxyamino)-2-methylpropanoate (2.46 g, 17.0 mmol, 42%) as a slight yellow oil in sufficient purity. **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 5.59 (br, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.32 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 175.3 (C_q), 62.6 (CH_2), 61.0 (C^q), 21.9 (2xCH_3), 14.0 (CH_3). The spectroscopic data are in accordance with the literature.[3]

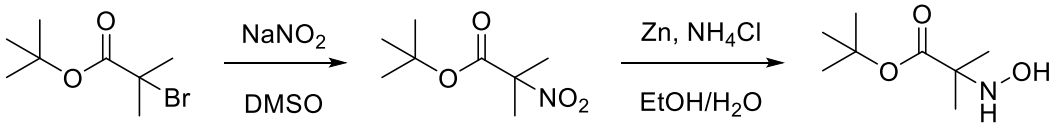
(*E*)-1,2-Bis(1-ethoxy-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (**1ae**)



(*E*)-1,2-Bis(1-ethoxy-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (**1ae**) was prepared according to **GPV** using ethyl 2-(hydroxyamino)-2-methylpropanoate (0.15 g, 1.0 mmol, 1.0 equiv.), bromine (48 µL, 0.93 mmol, 0.93 equiv.), aqueous NaOH (2.5 mol/L, 1.0 mL) and HCl (2.0 mol/L, 2.3 mL). Colourless (*E*)-1,2-bis(1-ethoxy-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (0.10 g, 0.35 mmol, 70%) was obtained.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 4.21 (q, *J* = 7.1 Hz, 4H), 1.62 (s, 12H), 1.25 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 168.3 (C_q), 75.4 (C_q), 62.0 (CH_2), 20.8 (CH_3), 14.2 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2988*w*, 2944*w*, 1737*s*, 1471*w*, 1446*w*, 1385*w*, 1365*w*, 1271*s*, 1173*s*, 1148*s*, 1110*w*, 1023*m*, 913*w*, 860*w*, 742*m*, 681*m*, 648*w*, 571*w*. **HRMS** (ESI) exact mass calculated for $C_6H_{11}NO_3Na^+$ $[M+Na]^+$: *m/z* = 168.06311; found 168.06312. The spectroscopic data are in accordance with the literature.[4]

***tert*-Butyl 2-(hydroxyamino)-2-methylpropanoate**

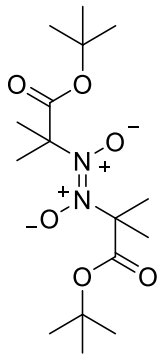


Step 1: To a stirred suspension of sodium nitrite (5.17 g, 75.0 mmol, 1.5 equiv.) in DMSO (50 mL) *tert*-butyl 2-bromo-2-methylpropanoate (9.3 mL, 50.0 mmol, 1.0 equiv.) was added. The mixture was stirred at 80 °C for 3 h. Then, the reaction mixture was poured into ice/water and extracted with Et_2O (3x

50 mL). The combined organic phases were washed with brine (50 mL), dried with Na_2SO_4 and concentrated under reduced pressure to give *tert*-butyl 2-methyl-2-nitropropanoate (8.87 g, 46.9 mmol, 94%) as a colourless oil in sufficient purity. **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 1.76 (s, 6H), 1.47 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 166.7 (C_q), 89.9 (C_q), 83.8 (C_q), 27.5 (3xCH_3), 23.9 (2xCH_3). **FTIR** (neat): ν (cm^{-1}): 2982*w*, 1742*s*, 1550*s*, 1458*w*, 1396*w*, 1370*m*, 1349*w*, 1288*m*, 1258*w*, 1197*w*, 1140*s*, 1038*w*, 960*w*, 876*w*, 840*m*, 756*w*, 723*w*, 683*w*. **HRMS** (ESI) exact mass calculated for $C_8H_{15}NO_4Na^+$ $[M+Na]^+$: *m/z* = 212.08933; found 212.08915.

Step 2: To a stirred suspension of *tert*-butyl 2-methyl-2-nitropropanoate (8.87 g, 46.9 mmol, 1.0 equiv.) and NH_4Cl (10.1 g, 188 mmol, 4.0 equiv.) in ethanol (15 mL) and water (29 mL), zinc (9.22 g, 141 mmol, 3.0 equiv.) was added in several portions while maintaining at a temperature under 40 °C. After the final addition, the suspension was stirred at 35 °C for 5 h. Then, the mixture was filtered and the filtrate concentrated. The residue was dissolved in Et_2O (10 mL) and water (10 mL). The organic layer was separated and washed with HCl (2 mol/L). The combined aqueous phases were washed with Et_2O (10 mL) and its pH was adjusted to 10 with K_2CO_3. The aqueous layer was then extracted with EtOAc (2x10 mL). The combined organic phases were washed brine (20 mL), dried with Na_2SO_4 and concentrated under reduced pressure to give *tert*-butyl 2-(hydroxyamino)-2-methylpropanoate (4.73 g, 27.0 mmol, 57%) as a colourless solid in sufficient purity. **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 5.59 (br, 2H), 1.46 (s, 9H), 1.27 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 175.0 (C_q), 81.5 (C_q), 63.3 (C_q), 28.1 (3xCH_3), 22.2 (2xCH_3). **FTIR** (neat): ν (cm^{-1}): 2979*w*, 1729*s*, 1460*w*, 1368*m*, 1286*w*, 1249*w*, 1146*s*, 917*w*, 849*w*, 749*w*. **HRMS** (ESI) exact mass calculated for $C_8H_{17}NO_3Na^+$ $[M+Na]^+$: *m/z* = 198.11006; found 198.10973. **M.p.**: 71 – 75 °C.

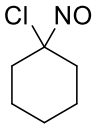
(*E*)-1,2-Bis(1-(*tert*-butoxy)-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (**1af**)



(*E*)-1,2-Bis(1-(*tert*-butoxy)-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (**1af**) was prepared according to **GPV** using *tert*-butyl 2-(hydroxyamino)-2-methylpropanoate (0.53 g, 3.0 mmol, 1.0 equiv.), bromine (95 µL, 2.8 mmol, 0.93 equiv.), aqueous NaOH (2.5 mol/L, 3.0 mL) and HCl (2.0 mol/L, 6.6 mL). Colourless (*E*)-1,2-bis(1-(*tert*-butoxy)-2-methyl-1-oxopropan-2-yl)diazene 1,2-dioxide (0.34 g, 1.0 mmol, 66%) was obtained.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 1.59 (s, 12H), 1.43 (s, 18H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 167.2 (C_q), 82.4 (C_q), 75.6 (C_q), 27.9 (CH_3), 20.8 (CH_3). **FTIR** (neat): ν (cm^{-1}): 310*w*, 2321*w*, 1739*s*, 1454*w*, 1390*w*, 1365*m*, 1301*m*, 1277*s*, 1173*s*, 1141*s*, 913*w*, 849*w*, 745*m*, 685*w*, 566*w*. **HRMS** (ESI) exact mass calculated for $C_8H_{15}NO_3Na^+$ $[M+Na]^+$: *m/z* = 196.09441; found 196.09441. **M.p.**: 110 – 112 °C.

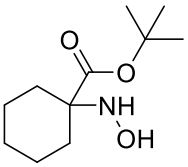
1-Chloro-1-nitrosocyclohexane



Cyclohexanone oxime (0.28 g, 2.5 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (13 mL) in an argon atmosphere. At 0 °C Willgerodt reagent ($PhICl_2$) (0.69 g, 2.5 mmol, 1.0 equiv.) was added and the mixture was stirred for 1 h. Then, the solvent was carefully removed under reduced pressure. The crude product was purified by two flash column chromatographies (CH_2Cl_2 100%; then pentane 100%) and 1-chloro-1-nitrosocyclohexane (0.23 g, 1.5 mmol, 61%) was obtained as deep blue oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 2.70–2.57 (m, 2H), 1.95 – 1.77 (m, 5H), 1.75 – 1.63 (m, 2H), 1.59 – 1.46 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 33.5 (2xCH_2), 24.8 (CH_2), 21.9 (2xCH_2). The quaternary ^{13}C-signal could not be observed. **FTIR** (neat): ν (cm^{-1}): 2941*s*, 2864*m*, 2359*w*, 1739*m*, 1574*s*, 1448*s*, 1365*w*, 1252*w*, 1217*w*, 1143*w*, 1021*w*, 913*m*, 873*m*, 800*w*, 747*w*, 665*w*, 570*w*, 511*w*. The product mass could not be detected by HRMS (ESI) nor EI-MS.

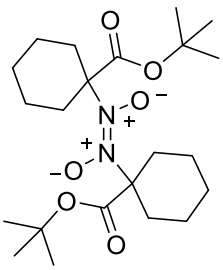
***tert*-Butyl 1-(hydroxyamino)cyclohexane-1-carboxylate**



To a stirred solution of diisopropylamine (0.16 mL, 1.1 mmol, 1.1 equiv.) in THF (1.5 mL) *n*BuLi (1.6 mol/L in hexane, 0.68 mL, 1.1 mmol, 1.1 equiv.) and DMPU (0.13 mL, 1.1 mmol, 1.1 equiv.) were added at –78 °C under an argon atmosphere. The reaction was stirred at the same temperature for 1 h. Then, *tert*-butyl cyclohexanecarboxylate (0.18 g, 1.0 mmol, 1.0 equiv.) was added at –78 °C and stirring was continued for 1 h at the same temperature. 1-Chloro-1-nitrosocyclohexane (0.16 g, 1.1 mmol, 1.1 equiv.) was added and the reaction mixture was stirred for 1 h at at –78 °C. Finally, HCl (1 mol/L, 1 mL) was added and the mixture was stirred at room temperature for 3 h. The phases were separated and the organic phase was washed with HCl (1 mol/L, 2 mL). The combined aqueous phases were extracted with Et_2O (5 mL), basified with $NaHCO_3$ to pH 9 and extracted with EtOAc (2x5 mL). The combined organic phases were washed with brine (10 mL), dried with Na_2SO_4 and concentrated. The crude prodcut was purified by flash column chromatography (pentane/EtOAc 4:1) and *tert*-butyl 1-(hydroxyamino)cyclohexane-1-carboxylate (0.088 g, 0.21 mmol, 41%) was isolated as colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 5.54 (s, 2H), 1.92 – 1.81 (m, 2H), 1.68 – 1.51 (m, 5H), 1.48 (s, 9H), 1.46 – 1.39 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 174.5 (C_q), 81.4 (C_q), 65.9 (C_q), 30.5 (CH_2), 28.2 (CH_3), 25.7 (CH_2), 21.9 (CH_2). **FTIR** (neat): ν (cm^{-1}): 2932*s*, 2857*m*, 1721*s*, 1452*w*, 1392*w*, 1367*m*, 1249*m*, 1174*m*, 1151*s*, 1138*s*, 1069*w*, 1032*w*, 956*w*, 913*w*, 889*w*, 847*m*, 744*w*. **HRMS** (ESI) exact mass calculated for $C_{11}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 238.14136; found 238.14114. **M.p.**: 73 – 75 °C.

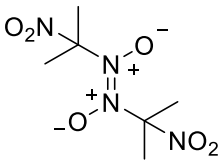
(*E*)-1,2-Bis(1-(*tert*-butoxycarbonyl)cyclohexyl)-diazene 1,2-dioxide (1ag)



(*E*)-1,2-Bis(1-(*tert*-butoxycarbonyl)cyclohexyl)-diazene 1,2-dioxide (**1ag**) was prepared according to **GPV** using *tert*-butyl 1-(hydroxyamino)cyclohexane-1-carboxylate (0.42 g, 2.0 mmol, 1.0 equiv.), bromine (97 µL, 1.9 mmol, 0.93 equiv.), aqueous NaOH (2.5 mol/L, 2.0 mL) and HCl (2.0 mol/L, 4.5 mL). Colourless (*E*)-1,2-bis(1-(*tert*-butoxycarbonyl)cyclohexyl)-diazene 1,2-dioxide (0.35 g, 0.80 mmol, 81%) was obtained.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 2.21 – 1.97 (m, 8H), 1.78 – 1.62 (m, 8H), 1.52 – 1.42 (m, 4H), 1.46 (s, 18H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 82.2 (C_q), 78.6 (C_q), 29.4 (CH_2), 28.0 (CH_3), 25.0 (CH_2), 21.9 (CH_2). Not all quaternary ^{13}C-signals could be detected. **FTIR** (neat): ν (cm^{-1}): 2931*m*, 2867*w*, 1742*s*, 1455*w*, 1393*w*, 1368*m*, 1318*w*, 1291*s*, 1248*m*, 1169*m*, 1139*s*, 1067*w*, 1033*w*, 912*w*, 846*w*, 743*w*, 715*w*, 695*w*. **HRMS** (ESI) exact mass calculated for $C_{11}H_{19}NO_3Na^+$ $[M+Na]^+$: *m/z* = 236.12571; found 236.12535. **M.p.**: 101 – 103 °C.

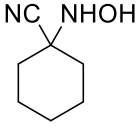
(*E*)-1,2-Bis(2-nitropropan-2-yl)diazene 1,2-dioxide (1ah)



(*E*)-1,2-Bis(2-nitropropan-2-yl)diazene 1,2-dioxide (**1ah**) was prepared according to a procedure by *Cheng et al.*[5]. 2-Nitropropane (2.7 mL, 30 mmol, 1.0 equiv.) was dissolved in a solution of KOH (2.5 g, 45 mmol, 1.5 equiv.) in water (9 mL) at 0 °C until the nitropropane layer had disappeared. The solution was cooled to -10 °C and sodium nitrite (2.3 g, 33 mmol, 1.1 equiv.) was added. The solution was added at once to a stirred solution of conc. H_2SO_4 (3.0 mL) in water (18 mL) at -10 °C. The mixture was stirred for 30 min in the dark until the monomer dimerized. The crude product was filtered and carefully washed with water. Recrystallization from ether afforded pure (*E*)-1,2-bis(2-nitropropan-2-yl)diazene 1,2-dioxide (2.8 g, 12 mmol, 80%).

^{1}H-NMR (300 MHz, DMSO-d_6, 299 K) δ (ppm) = 1.73 (s, 6H). **^{13}C-NMR** (75 MHz, DMSO-d_6, 299 K) δ (ppm) = 30.7 (C_q), 19.3 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2924*w*, 1573*m*, 1557*m*, 1377*w*, 1340*w*, 1301*s*, 1231*w*, 1188*w*, 1149*w*, 856*w*, 666*w*, 584*w*, 530*w*. The product mass could not be detected via HRMS (ESI) nor EI-MS. **M.p.**: 73 – 74 °C.

1-(Hydroxyamino)cyclohexane-1-carbonitrile

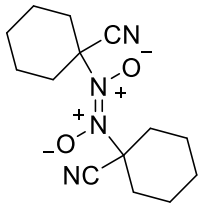


Cyclohexanone (4.1 mL, 40 mmol, 1.0 equiv.) and hydroxylamine hydrochloride (3.1 g, 44 mmol, 1.1 equiv.) were dissolved in water (6.0 mL) and ethanol (10 mL). With vigorous stirring a solution of sodium cyanide (2.0 g, 40 mmol, 1.0 equiv.) in water (7.8 mL) was added over a period of 30 min. Stirring was continued for 3 d at room temperature. Then,

crystalline 1-(hydroxyamino)cyclohexane-1-carbonitrile (4.0 g, 29 mmol, 72%) was filtered and washed with water.

^{1}H-NMR (300 MHz, DMSO-d_6, 299 K) δ (ppm) = 7.74 (d, *J* = 3.4 Hz, 1H), 6.33 (d, *J* = 3.4 Hz, 1H), 1.98 – 1.87 (m 2H), 1.76 – 1.64 (m, 2H), 1.61 – 1.51 (m, 1H), 1.45 – 1.29 (m, 4H), 1.27 – 1.15 (m, 1H). **^{13}C-NMR** (75 MHz, DMSO-d_6, 299 K) δ (ppm) = 122.4 (C_q), 59.9 (C_q), 32.4 (2xCH_2), 24.8 (CH_2), 21.7 (2xCH_2). **FTIR** (neat): ν (cm^{-1}): 3255*w*, 2944*w*, 2961*w*, 1738*s*, 1444*w*, 1365*s*, 1228*m*, 1217*s*, 1165*w*, 1028*w*, 968*w*, 910*w*, 742*m*, 512*w*. **HRMS** (ESI) exact mass calculated for $C_7H_{12}N_2ONa^+$ $[M+Na]^+$: *m/z* = 163.08418; found 163.08409. **M.p.**: 122 – 124 °C.

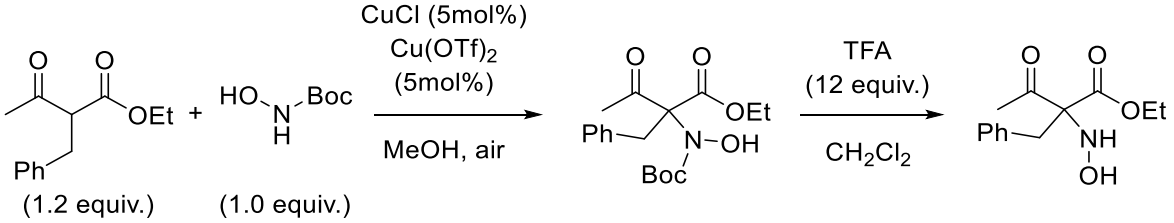
(*E*)-1,2-Bis(1-cyanocyclohexyl)diazene 1,2-dioxide (**1ai**)



(*E*)-1,2-Bis(1-cyanocyclohexyl)diazene 1,2-dioxide (**1ai**) was prepared according to **GPV** using 1-(hydroxyamino)cyclohexane-1-carbonitrile (0.20 g, 1.4 mmol, 1.0 equiv.), bromine (67 µL, 1.3 mmol, 0.93 equiv.), aqueous NaOH (2.5 mol/L, 1.4 mL) and HCl (2.0 mol/L, 3.1 mL). (*E*)-1,2-bis(1-cyanocyclohexyl)diazene 1,2-dioxide (0.093 g, 0.33 mmol, 48%) was obtained as deep blue solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 2.54 (td, *J* = 12.9, 4.0 Hz, 2H), 2.12 – 2.00 (m, 2H), 1.93 – 1.78 (m, 3H), 1.72 – 1.45 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 30.5 (CH_2), 24.5 (CH_2), 22.1 (CH_2). The quaternary ^{13}C-signals couldn't be observed. The spectroscopic data are in accordance with the literature.[6]

Ethyl 2-benzyl-2-(hydroxyamino)-3-oxobutanoate



Step 1: Based on a literature procedure[12], a round bottom flask was charged with *N*-Boc-hydroxylamine (0.56 g, 4.2 mmol, 1.2 equiv.), CuCl (0.021 g, 0.21 mmol, 5 mol%) and $Cu(OTf)_2$ (0.075 g, 0.21 mmol, 5 mol%). MeOH (30 mL) and ethyl 2-benzyl-3-oxobutanoate (1.1 g, 5.1 mmol, 1.2 equiv.) were added and the reaction mixture was vigorously stirred at room temperature open to air using two cannulas (0.9 x 40 mm) for 3 d. The solvent was removed under reduced pressure. The residue was taken up in EtOAc (45 mL) and quenched with EDTA (0.5 mol/L). The solution was stirred until the colour no longer persisted in the organic layer (approx. 40 min). The reaction was filtered and the filtrate was extracted with EtOAc (3x 30 mL). The combined organic phases were washed with brine (40 mL), dried with

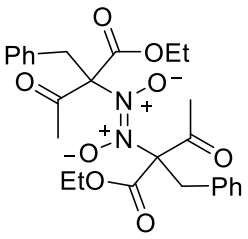
Na_2SO_4 and concentrated. The crude product was purified by flash coloumn chromatography (pentane/EtOAc 10:1 to 6:1) and ethyl 2-benzyl-2-((*tert*-butoxycarbonyl)(hydroxy)amino)-3-oxobutanoate (0.47 g, 1.3 mmol, 32%) was obtained as colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.41 – 7.35 (m, 2H), 7.30 – 7.20 (m, 3H), 6.19 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.64 – 3.45 (m, 2H), 2.10 (s, 3H), 1.36 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 167.9 (C_q), 156.7 (C_q), 131.1 (2xCH), 128.4 (2xCH), 127.2 (CH), 82.2 (C_q), 77.4 (C_q), 62.7 (CH_2), 37.0 (CH_2), 28.0 (CH_3), 27.0 (CH_3), 14.0 (CH_3). Not all quaternary ^{13}C-signals could be detected. **FTIR** (neat): ν (cm^{-1}): 2986*w*, 1730*s*, 1456*w*, 1370*m*, 1299*m*, 1256*m*, 1156*s*, 1032*w*, 913*w*, 852*w*, 742*m*, 702*m*. **HRMS** (ESI) exact mass calculated for $C_{18}H_{25}NO_6Na^+$ $[M+Na]^+$: *m/z* = 374.15741; found 374.15795.

Step 2: To an ice-cold stirred solution of ethyl 2-benzyl-2-((*tert*-butoxycarbonyl)(hydroxy)amino)-3-oxobutanoate (0.61 g, 1.7 mmol, 1.0 equiv.) in CH_2Cl_2 (18 mL) was added trifluoroacetic acid (1.6 mL, 21 mmol, 12 equiv.) dropwise. The reaction was stirred for 30 min and then transferred to a separatory funnel containing saturated $NaHCO_3$ (15 mL). The reaction was extracted with CH_2Cl_2 (3x10 mL). The combined organic phases were washed with brine (10 mL) and dried with Na_2SO_4. Evaporation of the solvent under reduced pressure gave ethyl 2-benzyl-2-(hydroxyamino)-3-oxobutanoate (0.42 g, 1.7 mmol, 99%) as colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.32 – 7.23 (m, 3H), 7.22 – 7.17 (m, 2H), 5.10 (br, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.36 (s, 2H), 2.28 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 202.9 (C_q), 168.9 (C_q), 134.9 (C_q), 130.2 (2xCH), 128.7 (2xCH), 127.4 (CH), 78.8 (C_q), 62.2 (CH_2), 36.4 (CH_2), 26.7 (CH_3), 14.1 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2970*w*, 1737*s*, 1655*w*, 1496*w*, 1455*w*, 1366*m*, 1228*m*, 1217*m*, 1092*w*, 1056*w*, 913*w*, 851*w*, 744w, *700*w, *527*w. **HRMS** (ESI) exact mass calculated for $C_{13}H_{17}NO_4Na^+$ $[M+Na]^+$: *m/z* = 274.10498; found 274.10486.

(*E*)-1,2-Bis(2-benzyl-1-ethoxy-1,3-dioxobutan-2-yl)-diazene 1,2-dioxide (**1aj**)

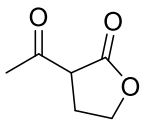


(*E*)-1,2-Bis(2-benzyl-1-ethoxy-1,3-dioxobutan-2-yl)-diazene 1,2-dioxide (**1aj**) was prepared according to **GPV** using ethyl 2-benzyl-2-(hydroxyamino)-3-oxobutanoate (0.33 g, 1.3 mmol, 1.0 equiv.), bromine (62 µL, 1.2 mmol, 0.93 equiv.), aqueous NaOH (2.5 mol/L, 1.0 mL) and HCl (2.0 mol/L, 2.2 mL). Colourless (*E*)-1,2-bis(2-benzyl-1-ethoxy-1,3-dioxobutan-2-yl)-diazene 1,2-dioxide (0.14 g, 0.28 mmol, 43%) was obtained as a mixture of diastereoisomers (dr = 1:5.5).

^{1}H-NMR (599 MHz, C_6D_6, 299 K) δ (ppm) = 7.09 – 6.94 (m, 10H), 4.19 (dq, *J* = 10.5, 7.1 Hz, 1.7H), 4.08 (dq, *J* = 10.5, 7.1 Hz, 1.7H), 3.73 (q, *J* = 7.1 Hz, 0.6H), 3.66 – 3.58 (m, 3.4H), 3.28 (d, *J* = 14.4 Hz, 0.3H), 3.21 (d, *J* = 14.4 Hz, 0.3H), 2.47 (s, 5.1H), 2.09 (s, 0.9H), 1.16 (t, *J* = 7.1 Hz, 5.1H), 0.67 (t, *J* = 7.1 Hz, 0.9H). **^{13}C-NMR** (151 MHz, C_6D_6, 299 K) δ (ppm) = 196.1 (C_q), 163.8 (C_q), 132.6 (C_q), 131.1

(CH), 130.8 (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 127.4 (CH), 86.8 (C_q), 62.7 (CH_2), 62.2 (CH_2), 40.5 (CH_2), 37.6 (CH_2), 31.0 (CH_3), 30.2 (CH_3), 13.8 (CH_3), 13.6 (CH_3). Not all ^{13}C-signals could be detected. **FTIR** (neat): ν (cm^{-1}): 2970*w*, 1726*s*, 1657*w*, 1556*m*, 1496*w*, 1455*w*, 1365*m*, 1267*m*, 1217*m*, 1121*w*, 1057*w*, 1014*w*, 855*w*, 750*w*, 701*m*, 527*w*. **HRMS** (ESI) exact mass calculated for $C_{13}H_{15}NO_4Na^+$ $[M+Na]^+$: *m/z* = 272.08933; found 272.08922. **M.p.**: 59 – 61 °C.

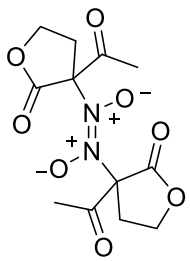
3-Acetyldihydrofuran-2(3*H*)-one



To a stirred solution of γ-butyrolactone (1.7 mL, 23 mmol, 1.0 equiv.) in THF (45 mL) at –78 °C was added LiHMDS (1 mol/L in THF, 47 mL, 47 mmol, 2.1 equiv.) dropwise under argon. The reaction mixture was stirred for 10 min at the same temperature, acetic anhydride (2.1 mL, 23 mmol, 1.0 equiv.) was added dropwise and the mixture was stirred for 1 h. To stop the reaction HCl (2 mol/L, 25 mL) was carefully added and the mixture was warmed to room temperature. The reaction was extracted with EtOAc (3x20 mL) and the combined organic phases were washed with brine and dried with Na_2SO_4. The crude product was purified by flash coloumn chromatography (pentane/EtOAc 2:1) and 3-acetyldihydrofuran-2(3*H*)-one (1.8 g, 14 mmol, 63%) was obtained as colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 4.39 – 4.28 (m, 2H), 3.69 (dd, *J* = 9.3, 6.7 Hz, 1H), 2.78 (ddt, *J* = 13.2, 8.1, 6.6 Hz, 1H), 2.44 (s, 3H), 2.34 – 2.22 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 200.2 (C_q), 67.5 (CH_2), 53.2 (CH), 29.5 (CH_3), 23.8 (CH_2). Spectroscopic data are in accordance with the literature.[13]

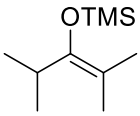
(*E*)-1,2-Bis(3-acetyl-2-oxotetrahydrofuran-3-yl)-diazene 1,2-dioxide (**1ak**)



(*E*)-1,2-Bis(3-acetyl-2-oxotetrahydrofuran-3-yl)-diazene 1,2-dioxide (**1ak**) was prepared according to **GPIII** using 3-acetyldihydrofuran-2(3*H*)-one (0.51 g, 4.0 mmol, 1.0 equiv.), sodium nitrite (0.33 g, 4.8 mmol, 1.2 equiv.), acetic acid (1 mL) and water (0.5 mL). Colourless (*E*)-1,2-bis(3-acetyl-2-oxotetrahydrofuran-3-yl)-diazene 1,2-dioxide (0.18 g, 0.55 mmol, 28%) was isolated.

^{1}H-NMR and ^{13}C-NMR spectra could not be recorded due to fast decomposition in solution. **FTIR** (KBr): ν (cm^{-1}): 3256*m*, 1789*s*, 1470*w*, 1379*m*, 1292*s*, 1233*w*, 1146*s*, 1111*w*, 1051*w*, 1013*m*, 982*m*, 943*w*, 868*w*, 704*m*, 673*w*, 625*m*, 598*w*, 528*m*. **HRMS** (ESI) exact mass calculated for $C_6H_7NO_4Na^+$ $[M+Na]^+$: *m/z* = 180.02673; found 180.02666. **M.p.**: 88 – 89 °C.

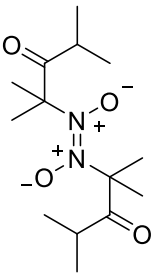
((2,4-Dimethylpent-2-en-3-yl)oxy)trimethylsilane



A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. To a solution of diisopropylamine (0.91 mL, 6.5 mmol, 1.3 equiv.) in THF (30 mL) *n*BuLi (1.6 mol/L in hexane, 4.4 mL, 7.0 mmol, 1.4 equiv.) was added at –78 °C. The reaction mixture was stirred at –78 °C for 10 min and at room temperature for 10 min. Then, 2,4-dimethylpentan-3-one (0.70 mL, 5.0 mmol, 1.0 equiv.) was added at –78 °C, the mixture was stirred for 30 min at the same temperature and trimethylsilyl chloride (0.89, 7.0 mmol, 1.4 equiv.) was added. The reaction mixture was allowed to warm to room temperature overnight. Saturated, aqueous $NaHCO_3$ (20 mL) was added and the mixture was extracted with Et_2O (3x20 mL). The combined organic phases were washed with brine (20 mL), dried with Na_2SO_4 and concentrated. The crude product was purified by column chromatography on deactivated SiO_2 (silica gel treated with 2.5% NEt_3 prior to use) (pentane/EtOAc 100:2) and ((2,4-dimethylpent-2-en-3-yl)oxy)trimethylsilane (0.74 g, 4.0 mmol, 79%) was obtained as colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 2.80 (hept, *J* = 6.9 Hz, 1H), 1.62 (s, 3H), 1.58 (s, 3H), 0.97 (d, *J* = 6.9 Hz, 6H), 0.20 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 149.2, 107.3, 29.1, 20.3, 19.0, 18.6, 1.1. The spectroscopic data are in accordance with the literature.[11]

(*E*)-1,2-Bis(2,4-dimethyl-3-oxopentan-2-yl)diazene 1,2-dioxide (**1al**)

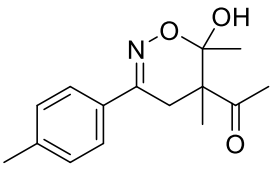


(*E*)-1,2-Bis(2,4-dimethyl-3-oxopentan-2-yl)diazene 1,2-dioxide (**1al**) was prepared according to **GPIV** using ((2,4-dimethylpent-2-en-3-yl)oxy)trimethylsilane (0.19 g, 1.0 mmol, 1.0 equiv.), sodium nitrite (1.0 g, 15 mmol, 15 equiv.), conc. HCl (8.3 mL) and CH_2Cl_2 (2 mL). After the NOCl addition, the solvent and excess NOCl were carefully removed with a rotavap (prior to dimerization, monomeric 2,4-dimethyl-2-nitrospentan-3-one is volatile). The resulting solid was washed with pentane and dried in vacuum. Colourless (*E*)-1,2-bis(2,4-dimethyl-3-oxopentan-2-yl)diazene 1,2-dioxide (0.091 g, 0.32 mmol, 64%) was obtained.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 2.95 (hept, *J* = 6.8 Hz, 2H), 1.59 (s, 12H), 1.14 (d, *J* = 6.8 Hz, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 206.5 (C_q), 80.5 (C_q), 35.1 (CH), 20.8 (CH_3), 19.9 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2976*w*, 1706*s*, 1456*w*, 1381*w*, 1274*s*, 1195*w*, 1149*w*, 1092*w*, 1005*m*, 967*w*, 913*w*, 737*w*, 642*w*, 565*w*. **HRMS** (ESI) exact mass calculated for $C_{14}H_{26}N_2O_4Na^+$ $[2M+Na]^+$: *m/z* = 309.17958; found 309.17833. **M.p.**: 108 – 110 °C.

4. Synthesis and characterization of products

1-(6-Hydroxy-5,6-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3a**)



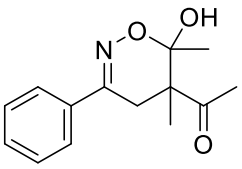
1-(6-Hydroxy-5,6-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3a**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-5,6-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.038 g, 0.15 mmol, 73%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.64 – 7.56 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.99 (br, 1H), 3.36 (d, *J* = 17.5 Hz, 1H), 2.44 – 2.34 (m, 4H), 1.54 (s, 3H), 1.23 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.9 (C_q), 154.1 (C_q), 140.2 (C_q), 132.5 (C_q), 129.3 (2xCH), 125.5 (2xCH), 97.7 (C_q), 49.1 (C_q), 30.8 (CH_2), 28.1 (CH_3), 22.6 (CH_3), 21.4 (CH_3), 19.8 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.64 – 7.56 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.99 (br, 1H), 2.94 (d, *J* = 18.8 Hz, 1H), 2.61 (d, *J* = 18.8 Hz, 1H), 2.26 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.5 (C_q), 156.1 (C_q), 140.2 (C_q), 132.1 (C_q), 129.4 (2xCH), 125.6 (2xCH), 97.8 (C_q), 50.2 (C_q), 31.4 (CH_2), 27.8 (CH_3), 22.5 (CH_3), 21.4 (CH_3), 19.7 (CH_3).

FTIR (neat): ν (cm^{-1}): 3400*m*, 3100*w*, 2900*w*, 1721*w*, 1698*s*, 1641*w*, 1614*m*, 1514*w*, 1461*w*, 1414*w*, 1382*m*, 1356*m*, 1283*w*, 1209*w*, 1151*m*, 1124*w*, 1088*m*, 1042*m*, 1020*w*, 979*w*, 938*w*, 904*s*, 864*m*, 815*s*, 778*w*, 732*m*, 600*m*. **HRMS** (ESI) exact mass calculated for $C_{15}H_{19}NO_3Na^+$ $[M+Na]^+$: *m/z* = 284.12571; found 284.12555.

1-(6-Hydroxy-5,6-dimethyl-3-phenyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3b**)



1-(6-Hydroxy-5,6-dimethyl-3-phenyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3b**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (69 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-5,6-dimethyl-3-phenyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.037 g, 0.15 mmol, 74%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

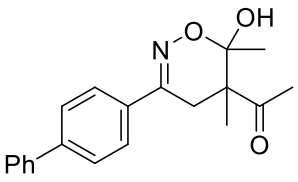
For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.75 – 7.67 (m, 2H), 7.43 – 7.34 (m, 2H), 3.96 (br, 1H), 3.37 (d, *J* = 17.5 Hz, 1H), 2.42 (d, *J* = 17.5 Hz, 1H), 2.37 (s, 3H), 1.56 (s, 2H), 1.24

(s, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.8 (C_q), 154.2 (C_q), 135.4 (C_q), 130.0 (CH), 128.7 (2xCH), 125.6 (2xCH), 97.7 (C_q), 49.1 (C_q), 30.8 (CH_2), 28.1 (CH_3), 22.6 (CH_3), 19.8 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.75 – 7.67 (m, 2H), 7.43 – 7.34 (m, 2H), 3.96 (br, 1H), 2.96 (d, *J* = 18.7 Hz, 1H), 2.62 (d, *J* = 18.7 Hz, 1H), 2.27 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H).**^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.4 (C_q), 156.2 (C_q), 135.0 (C_q), 130.1 (CH), 128.7 (2xCH), 125.7 (2xCH), 97.9 (C_q), 31.4 (CH_2), 27.8 (CH_3), 22.5 (CH_3), 19.7 (CH_3).

FTIR (neat): ν (cm^{-1}): 3382*s*, 2998*w*, 1698*s*, 1496*w*, 1444*w*, 1383*m*, 1355*m*, 1282*w*, 1209*w*, 1156*m*, 1090*m*, 1043*w*, 942*w*, 906*s*, 863*w*, 760*s*, 732*w*, 693*s*, 604*w*. **HRMS** (ESI) exact mass calculated for $C_{14}H_{17}NO_3Na^+$ $[M+Na]^+$: *m/z* = 207.11006; found 270.10989.

1-(3-([1,1'-Biphenyl]-4-yl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (3c)



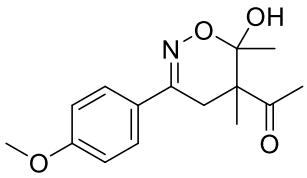
1-(3-([1,1'-Biphenyl]-4-yl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3c**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), 4-Vinylbiphenyl (0.11 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(3-([1,1'-biphenyl]-4-yl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.045 g, 0.14 mmol, 69%) was isolated as a colourless solid and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.86 – 7.76 (m, 2H), 7.67 – 7.57 (m, 4H), 7.50 – 7.41 (m, 2H), 7.40 – 7.33 (m, 1H), 3.97 (br, 1H), 3.42 (d, *J* = 17.5 Hz, 1H), 2.47 (d, *J* = 17.5 Hz, 1H), 2.39 (s, 3H), 1.60 (s, 3H), 1.27 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.8 (C_q), 153.8 (C_q), 142.7 (C_q), 140.3 (C_q), 134.2 (C_q), 129.0 (2xCH), 127.8 (CH), 127.3 (2xCH), 127.2 (2xCH), 126.1 (2xCH), 97.8 (C_q), 49.1 (C_q), 30.8 (CH_2), 28.2 (CH_3), 22.6 (CH_3), 19.8 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.86 – 7.76 (m, 2H), 7.67 – 7.57 (m, 4H), 7.50 – 7.41 (m, 2H), 7.40 – 7.33 (m, 1H), 3.97 (br, 1H), 3.01 (d, *J* = 18.6 Hz, 3H), 2.67 (d, *J* = 18.6 Hz, 3H), 2.30 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.4 (C_q), 155.8 (C_q), 142.8 (C_q), 133.8 (C_q), 127.3 (2xCH), 126.1 (2xCH), 98.0 (C_q), 50.2 (C_q), 31.4 (CH_2), 27.8 (CH_3), 22.5 (CH_3), 19.7 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3370*m*, 3100*w*, 2980*w*, 2970*w*, 2015*w*, 1699*s*, 1600*m*, 1580*w*, 1488*m*, 1448*m*, 1383*m*, 1357*m*, 1282*m*, 1210*m*, 1155*m*, 1121*m*, 1089*s*, 1007*m*, 940*m*, 907*s*, 839*s*, 765*s*, 728*s*, 697*s*, 648*m*, 604*m*, 570*m*. **HRMS** (ESI) exact mass calculated for $C_{20}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 346.14136; found 346.14138. **M.p.**: 146 – 147 °C.

1-(6-Hydroxy-3-(4-methoxyphenyl)-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3d**)



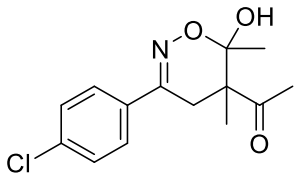
1-(6-Hydroxy-3-(4-methoxyphenyl)-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3d**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (81 mL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-3-(4-methoxyphenyl)-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.042 g, 0.15 mmol, 75%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.71 – 7.62 (m, 2H), 6.94 – 6.86 (m, 2H), 3.82 (s, 3H), 3.34 (d, *J* = 17.5 Hz, 1H), 2.40 (d, *J* = 17.5 Hz, 1H), 2.37 (s, 3H), 1.55 (s, 3H), 1.24 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.9 (C_q), 161.0 (C_q), 153.6 (C_q), 127.8 (C_q), 127.0 (2xCH), 114.0 (2xCH), 97.6 (C_q), 55.5 (CH_3), 49.2 (C_q), 30.8 (CH_2), 27.8 (CH_3), 22.6 (CH_3), 19.9 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.71 – 7.62 (m, 2H), 6.94 – 6.86 (m, 2H), 3.82 (s, 3H), 2.93 (d, *J* = 18.6 Hz, 1H), 2.60 (d, *J* = 18.6 Hz, 1H), 2.26 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.5 (C_q), 161.1 (C_q), 155.8 (C_q), 127.4 (C_q), 127.1 (2xCH), 114.0 (2xCH), 97.7 (C_q), 50.2 (C_q), 31.3 (CH_2), 27.8 (CH_3), 22.5 (CH_3), 19.7 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3393*s*, 2938*w*, 1698*s*, 1609*m*, 1570*w*, 1513*m*, 1456*w*, 1416*w*, 1357*w*, 1299*w*, 1249*s*, 1178*m*, 1087*m*, 1044*m*, 1027*w*, 904*s*, 864*w*, 931*s*, 801*w*, 731*m*, 663*w*, 600*w*. **HRMS** (ESI) exact mass calculated for $C_{15}H_{19}NO_4Na^+$ $[M+Na]^+$: *m/z* = 300.12063; found 300.12042.

1-(3-(4-Chlorophenyl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3e**)



1-(3-(4-Chlorophenyl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3e**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (72 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(3-(4-chlorophenyl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.038 g, 0.13 mmol, 67%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

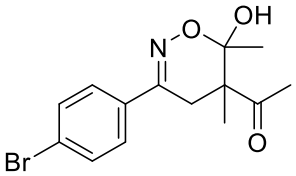
For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.68 – 7.61 (m, 2H), 7.39 – 7.31 (m, 2H), 3.58 (br, 1H), 3.33 (d, *J* = 17.4 Hz, 1H), 2.36 (s, 3H), 2.36 (d, *J* = 17.4 Hz, 1H), 1.57 (s, 3H), 1.24

(s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.5 (C_q), 153.2 (C_q), 136.0 (C_q), 133.8 (C_q), 128.9 (2xCH), 126.9 (2xCH), 97.8 (C_q), 49.0 (C_q), 30.7 (CH_2), 28.1 (CH_3), 22.6 (CH_3), 19.8 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.68 – 7.61 (m, 2H), 7.39 – 7.31 (m, 2H), 3.58 (br, 1H), 2.92 (d, *J* = 18.6 Hz, 1H), 2.56 (d, *J* = 18.6 Hz, 1H), 2.26 (s, 3H), 1.46 (s, 3H), 1.37 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.0 (C_q), 155.2 (C_q), 136.1 (C_q), 133.4 (C_q), 128.9 (2xCH), 126.9 (2xCH), 98.0 (C_q), 50.1 (C_q), 31.3 (CH_2), 27.7 (CH_3), 22.6 (CH_3), 19.6 (CH_3).

FTIR (neat): ν (cm^{-1}): 3386*s*, 2992*w*, 1697*s*, 1601*w*, 1493*w*, 1358*m*, 1277*w*, 1215*w*, 1153*m*, 1088*s*, 1041*w*, 906*s*, 825*s*, 783*w*, 729*s*, 640*w*, 598*w*. **HRMS** (ESI) exact mass calculated for $C_{14}H_{16}NO_3ClNa^+$ $[M+Na]^+$: *m/z* = 304.07109; found 304.07080.

1-(3-(4-Bromophenyl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3f**)



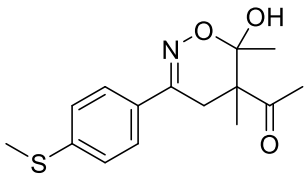
1-(3-(4-Bromophenyl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3f**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (0.11 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(3-(4-bromophenyl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.049 g, 0.15 mmol, 75%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.62 – 7.54 (m, 2H), 7.54 – 7.48 (m, 2H), 3.63 (br, 1H), 3.33 (d, *J* = 17.4 Hz, 1H), 2.36 (s, 3H), 2.35 (d, *J* = 17.4 Hz, 1H), 1.57 (s, 3H), 1.24 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.4 (C_q), 153.3 (C_q), 134.2 (C_q), 131.8 (2xCH), 127.2 (2xCH), 124.3 (C_q), 97.8 (C_q), 49.0 (C_q), 30.6 (CH_2), 28.1 (CH_3), 22.6 (CH_3), 19.8 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.62 – 7.54 (m, 2H), 7.54 – 7.48 (m, 2H), 3.63 (br, 1H), 2.91 (d, *J* = 18.6 Hz, 1H), 2.56 (d, *J* = 18.6 Hz, 1H), 2.26 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.0 (C_q), 155.2 (C_q), 133.9 (C_q), 131.9 (2xCH), 127.2 (2xCH), 124.4 (C_q), 98.0 (C_q), 50.1 (C_q), 31.2 (CH_2), 27.7 (CH_3), 22.6 (CH_3), 19.7 (CH_3).

FTIR (neat): ν (cm^{-1}): 3384*s*, 2993*w*, 1697*s*, 1588*w*, 1488*w*, 1449*w*, 1416*w*, 1384*w*, 1355*m*, 1283*w*, 1209*w*, 1152*m*, 1073*s*, 1040*w*, 1009*m*, 938*w*, 904*s*, 862*w*, 821*s*, 783*w*, 730*s*, 648*w*, 594*m*. **HRMS** (ESI) exact mass calculated for $C_{14}Na^+$ $[M+Na]^+$: *m/z* = 348.02058; found 348.02050.

1-(6-Hydroxy-5,6-dimethyl-3-(4-(methylthio)phenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3g**)



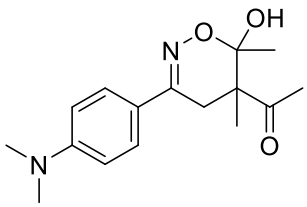
1-(6-Hydroxy-5,6-dimethyl-3-(4-(methylthio)phenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3g**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (0.090 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-5,6-dimethyl-3-(4-(methylthio)phenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.046 g, 0.16 mmol, 78%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.65 – 7.60 (m, 2H), 7.24 – 7.20 (m, 2H), 3.33 (d, *J* = 17.5 Hz, 1H), 2.48 (s, 3H), 2.37 (d, *J* = 17.5 Hz, 1H), 2.35 (s, 3H), 1.55 (s, 3H), 1.22 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.6 (C_q), 153.6 (C_q), 141.2 (C_q), 131.8 (C_q), 126.0 (2xCH), 125.9 (2xCH), 97.8 (C_q), 49.1 (C_q), 30.7 (CH_2), 28.1 (CH_3), 22.6 (CH_3), 19.8 (CH_3), 15.4 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) =7.65 – 7.60 (m, 2H), 7.24 – 7.20 (m, 2H), 2.92 (d, *J* = 18.6 Hz, 1H), 2.58 (d, *J* = 18.6 Hz, 1H), 2.48 (s, 3H), 2.25 (s, 3H), 1.44 (s, 3H), 1.35 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.3 (C_q), 155.7 (C_q), 141.3 (C_q), 131.4 (C_q), 126.0 (2xCH), 97.9 (C_q), 49.1 (C_q), 31.3 (CH_2), 27.7 (CH_3), 22.5 (CH_3), 19.7 (CH_3), 15.4 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3300*m*, 2991*w*, 2922*w*, 1699*s*, 1591*m*, 1494*m*, 1426*m*, 1383*m*, 1356*s*, 1284*m*,1156*m*, 1091*s*, 1040*m*, 1013*w*, 938*m*, 906*s*, 863*m*, 818*s*, 731*m*, 596*m*. **HRMS** (ESI) exact mass calculated for $C_{15}H_{19}NO_3SNa^+$ $[M+Na]^+$: *m/z* = 316.09779; found 316.09780.

1-(3-(4-(Dimethylamino)phenyl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3h**)



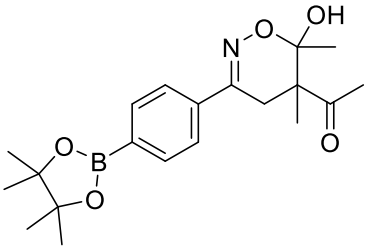
1-(3-(4-(Dimethylamino)phenyl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3h**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (0.088 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(3-(4-(dimethylamino)phenyl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.045 g, 0.15 mmol, 77%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.66 – 7.58 (m, 2H), 6.73 – 6.66 (m, 2H), 3.88 (br, 1H), 3.32 (d, *J* = 17.3 Hz, 1H), 2.99 (s, 6H), 2.41 (d, *J* = 17.3 Hz, 1H), 2.37 (s, 3H), 1.53 (s, 3H), 1.23 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 211.3 (C_q), 153.7 (C_q), 151.4 (C_q), 126.6 (2xCH), 123.0 (C_q), 111.9 (2xCH), 97.5 (C_q), 49.2 (C_q), 40.4 (2xCH_3), 30.7 (CH_2), 28.2 (CH_3), 22.7 (CH_3), 19.9 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.66 – 7.58 (m, 2H), 6.73 – 6.66 (m, 2H), 3.88 (br, 1H), 2.99 (s, 6H), 2.91 (d, *J* = 18.6 Hz, 1H), 2.62 (d, *J* = 18.6 Hz, 1H), 2.26 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.9 (C_q), 155.9 (C_q), 151.5 (C_q), 126.7 (2xCH), 122.5 (C_q), 97.5 (C_q), 50.3 (C_q), 31.1 (CH_2), 27.8 (CH_3), 22.5 (CH_3), 19.8 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3380*m*, 3000*w*, 2928*m*, 2804*w*, 1703*s*, 1611*s*, 1528*s*, 1446*w*, 1365*s*, 1285*m*, 1225*m*, 1199*m*, 1168*m*, 1129*m*, 1089*m*, 1042*m*, 1004*w*, 947*m*, 904*s*. **HRMS** (ESI) exact mass calculated for $C_{16}H_{22}N_2O_3K^+$ $[M+K]^+$: *m/z* = 329.12620; found 329.12619.

1-(6-Hydroxy-5,6-dimethyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3i**)



1-(6-Hydroxy-5,6-dimethyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3i**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (0.14 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-5,6-dimethyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.045 g, 0.12 mmol, 60%) was isolated as a colourless solid and inseperable mixture of diastereoisomers (dr = 3:1).

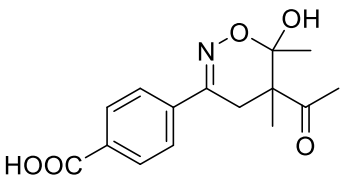
For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.83 (d, *J* = 7.9 Hz, 2H), 7.75 – 7.67 (m, 2H), 3.80 (s, 1H), 3.36 (d, *J* = 17.5 Hz, 1H), 2.42 (d, *J* = 17.5 Hz, 1H), 2.37 (s, 3H), 1.56 (s, 3H), 1.35 (s, 12H), 1.24 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.7 (C_q), 154.0 (C_q), 137.8 (C_q), 135.1 (2xCH), 124.8 (2xCH), 97.8 (C_q), 84.1 (2xC_q), 49.0 (C_q), 30.8 (CH_2), 28.1 (CH_3), 25.0 (4xCH_3), 22.7 (CH_3), 19.8 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.83 (d, *J* = 7.9 Hz, 2H), 7.75 – 7.67 (m, 2H), 3.48 (s, 1H), 2.96 (d, *J* = 18.8 Hz, 1H), 2.62 (d, *J* = 18.8 Hz, 1H), 2.26 (s, 3H), 1.45 (s, 3H), 1.36 (s, 3H), 1.35 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.3 (C_q), 137.4 (C_q), 135.1

(2xCH), 124.8 (2xCH), 84.1 (2xC_q), 50.1 (C_q), 31.3 (CH_2), 27.7 (CH_3), 25.0 (4xCH_3), 19.7 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3403*m*, 2980*m*, 2250*w*, 1700*s*, 1613*w*, 1516*w*, 1448*w*, 1396*m*, 1355*s*, 1321*m*, 1268*w*, 1212*w*, 1142*s*, 1089*s*, 1038*w*, 1018*w*, 961*w*, 940*w*, 906*s*, 856*m*, 825*m*, 783*w*, 729*s*, 670*w*, 655*s*, 605*w*, 579*w*. **HRMS** (ESI) exact mass calculated for $C_{20}H_{28}NO_5BNa^+$ $[M+Na]^+$: *m/z* = 396.19564; found 396.19570. **M.p.**: 112 – 114 °C.

4-(5-Acetyl-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-3-yl)benzoic acid (**3j**)



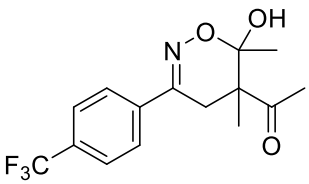
4-(5-Acetyl-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-3-yl)benzoic acid (**3j**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (89 mg, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc/HOAc 100:100:1) and 4-(5-acetyl-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-3-yl)benzoic acid (0.040 g, 0.14 mmol, 69%) was isolated as a colourless solid and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, acetone-d_6, 299 K) δ (ppm) = 8.10 – 8.04 (m, 2H), 7.96 – 7.88 (m, 2H), 6.02 (br, 1H), 3.49 (d, *J* = 17.6 Hz, 1H), 2.68 (d, *J* = 17.6 Hz, 1H), 2.39 (s, 2H), 1.55 (s, 3H), 1.16 (s, 3H). **^{13}C-NMR** (75 MHz, acetone-d_6, 299 K) δ (ppm) = 209.6 (C_q), 167.2 (C_q), 153.6 (C_q), 141.3 (C_q), 131.9 (C_q), 130.5 (2xCH), 126.3 (2xCH), 98.5 (C_q), 49.7 (C_q), 30.6 (CH_2), 28.3 (CH_3), 22.3 (CH_3), 19.6 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, acetone-d_6, 299 K) δ (ppm) = 8.10 – 8.04 (m, 2H), 7.96 – 7.88 (m, 2H), 6.02 (br, 1H), 3.11 (d, *J* = 18.8 Hz, 1H), 2.63 (d, *J* = 18.8 Hz, 1H), 2.24 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H). **^{13}C-NMR** (75 MHz, acetone-d_6, 299 K) δ (ppm) = 209.0 (C_q), 155.4 (C_q), 140.9 (C_q), 132.0 (C_q) 130.6 (2xCH), 128.9 (2xCH), 98.5 (C_q), 50.8 (C_q), 31.4 (CH_2), 27.8 (CH_3), 22.2 (CH_3), 20.0 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected.

FTIR (neat): ν (cm^{-1}): 2996*s*, 1688*s*, 1613*w*, 1598*w*, 1563*w*, 1509*w*, 1419*m*, 1384*w*, 1357*w*, 1317*w*, 1282*m*, 1248*m*, 1161*w*, 1119*w*, 1090*m*, 1042*w*, 941*m*, 911*s*, 859*s*, 773*m*, 698*w*, 596*w*. **HRMS** (ESI) exact mass calculated for $C_{15}H_{16}NO_5^-$ $[M-H]^-$: *m/z* = 290.10340; found 290.10280. **M.p.**: 130 – 131 °C.

1-(6-Hydroxy-5,6-dimethyl-3-(4-(trifluoromethyl)phenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3k**)



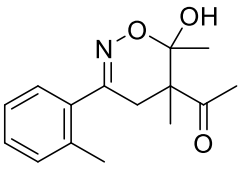
1-(6-Hydroxy-5,6-dimethyl-3-(4-(trifluoromethyl)phenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3k**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (89 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-5,6-dimethyl-3-(4-(trifluoromethyl)phenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.038 g, 0.12 mmol, 60%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.89 – 7.78 (m, 2H), 7.68 – 7.59 (m, 2H), 3.45 (br, 1H), 3.37 (d, *J* = 17.6 Hz, 1H), 2.40 (d, *J* = 17.6 Hz, 1H), 2.38 (s, 3H), 1.60 (s, 3H), 1.26 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.3 (C_q), 153.1 (C_q), 138.7 (C_q), 131.7 (q, *J* = 32.7 Hz, C_q), 126.0 (2xCH), 125.7 (q, *J* = 3.8 Hz, 2xCH), 124.0 (q, *J* = 272.2 Hz, C_q), 98.0 (C_q), 48.9 (C_q), 30.7 (CH_2), 28.1 (CH_3), 22.8 (CH_3), 19.8 (CH_3). **^{19}F-NMR** (282 MHz, $CDCl_3$, 299 K) δ (ppm) = 62.8.

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.89 – 7.78 (m, 2H), 7.68 – 7.59 (m, 2H), 3.45 (br, 1H), 2.97 (d, *J* = 18.6 Hz, 1H), 2.60 (d, *J* = 18.6 Hz, 1H), 2.28 (s, 3H), 1.50 (s, 3H), 1.39 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.8 (C_q), 155.0 (C_q), 138.4 (C_q), 126.0 (2xCH), 98.2 (C_q), 31.3 (CH_2), 27.7 (CH_3), 19.6 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected. **^{19}F-NMR** (282 MHz, $CDCl_3$, 299 K) δ (ppm) = 62.8.

FTIR (neat): ν (cm^{-1}): 3383*m*, 2292*w*, 1698*m*, 1604*w*, 1409*w*, 1385*w*, 1356*w*, 1322*s*, 1210*w*, 1164*m*, 1114*s*, 1089*m*, 1068*s*, 1040*m*, 1014*w*, 940*w*, 908*s*, 839*s*, 789*w*, 769*w*, 732*m*, 648*w*, 601*m*. **HRMS** (ESI) exact mass calculated for $C_{15}H_{16}NO_3F_3Na^+$ $[M+Na]^+$: *m/z* = 338.09745; found 338.09714.

1-(6-Hydroxy-5,6-dimethyl-3-(*o*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3l**)



1-(6-Hydroxy-5,6-dimethyl-3-(*o*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3l**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (76 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-5,6-dimethyl-3-(*o*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.031 g, 0.16 mmol, 66%) was isolated as a colourless solid and inseperable mixture of diastereoisomers (dr = 3:1).

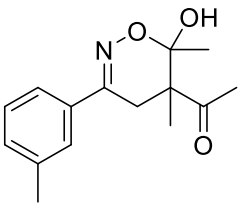
For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.30 – 7.19 (m, 4H), 3.73 (br, 1H), 3.27 (d, *J* = 17.9 Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H), 2.16 (d, *J* = 17.9 Hz, 1H), 1.55 (s, 3H), 1.31 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.5 (C_q), 157.5 (C_q), 136.1 (C_q), 136.0 (C_q), 130.9

(CH), 129.1 (CH), 128.0 (CH), 126.0 (CH), 97.2 (C_q), 49.2 (C_q), 34.5 (CH_2), 28.1 (CH_3), 22.6 (CH_3), 19.9 (CH_3), 19.8 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.30 – 7.19 (m, 4H), 3.73 (br, 1H), 2.72 (d, *J* = 19.1 Hz, 1H), 2.46 (d, *J* = 19.1 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.2 (C_q), 159.9 (C_q), 136.1 (C_q), 135.8 (C_q), 130.9 (CH), 127.9 (CH), 126.0 (CH), 97.2 (C_q), 50.5 (C_q), 34.9 (CH_2), 27.9 (CH_3), 22.6 (CH_3), 20.0 (CH_3), 19.7 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3400*m*, 2930*w*, 2800*w*, 1699*s*, 1492*w*, 1454*m*, 1413*m*, 1382*m*, 1354*m*, 1276*w*, 1211*m*, 1154*m*, 1088*s*, 895*s*, 757*s*, 725*s*, 607*s*. **HRMS** (ESI) exact mass calculated for $C_{15}H_{19}NO_3Na^+$ $[M+Na]^+$: *m/z* = 284.12571; found 284.12565. **M.p.**: 99 – 100 °C.

1-(6-Hydroxy-5,6-dimethyl-3-(*m*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3m**)



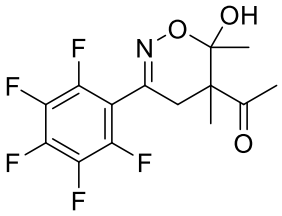
1-(6-Hydroxy-5,6-dimethyl-3-(*m*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3m**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (80 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-5,6-dimethyl-3-(*m*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.037 g, 0.14 mmol, 70%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.57 – 7.46 (m, 2H), 7.33 – 7.19 (m, 2H), 3.36 (d, *J* = 17.5 Hz, 1H), 2.46 – 2.34 (m, 3H), 1.55 (s, 3H), 1.24 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.9 (C_q), 154.3 (C_q), 138.4 (C_q), 135.3 (C_q), 130.7 (CH), 128.6 (CH), 126.3 (CH), 122.8 (CH), 97.7 (C_q), 49.1 (C_q), 30.9 (CH_2), 28.2 (CH_3), 22.6 (CH_3), 21.6 (CH_3), 19.8 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.57 – 7.46 (m, 2H), 7.33 – 7.19 (m, 2H), 2.96 (d, *J* = 18.8 Hz, 1H), 2.62 (d, *J* = 18.8 Hz, 1H), 2.28 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.5 (C_q), 156.4 (C_q), 138.4 (C_q), 134.9 (C_q), 130.8 (CH), 128.6 (CH), 122.8 (CH), 97.9 (C_q), 50.2 (C_q), 31.5 (CH_2), 27.8 (CH_3), 22.5 (CH_3), 19.6 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3383*s*, 2924*w*, 1697*s*, 1578*w*, 1449*w*, 1420*w*, 1381*w*, 1354*m*, 1285*w*, 1217*w*, 1148*m*, 1086*s*, 904*s*, 865*m*, 828*w*, 781*m*, 728*s*, 694*s*, 647*w*, 606*m*, 584*m*. **HRMS** (ESI) exact mass calculated for $C_{15}H_{19}NO_3Na^+$ $[M+Na]^+$: *m/z* = 284.12571; found 284.12542.

1-(6-Hydroxy-5,6-dimethyl-3-(perfluorophenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3n**)



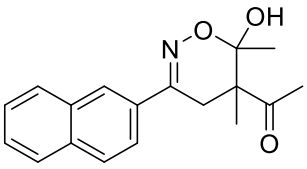
1-(6-Hydroxy-5,6-dimethyl-3-(perfluorophenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3n**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (83 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-5,6-dimethyl-3-(perfluorophenyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.016 g, 0.046 mmol, 23%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (500 MHz, $CDCl_3$, 299 K) δ (ppm) = 3.50 (br, 1H), 3.30 (d, *J* = 17.9 Hz, 1H), 2.33 (s, 3H), 2.20 (d, *J* = 17.9 Hz, 1H), 1.62 (s, 3H), 1.30 (s, 3H). **^{13}C-NMR {^{19}F}** (126 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.4 (C_q), 146.5 (C_q), 144.7 (C_q), 142.0 (C_q), 137.9 (C_q), 111.5 (C_q), 98.6 (C_q), 48.7 (C_q), 33.8 (CH_2), 28.0 (CH_3), 22.6 (CH_3), 19.4 (CH_3). **^{19}F-NMR** (470 MHz, $CDCl_3$, 299 K) δ (ppm) = -141.5 – -141.4 (m, 2F), -152.1 – -151.9 (m, 1F), -160.9 – -160.7 (m, 2F).

For minor isomer: **^{1}H-NMR** (500 MHz, $CDCl_3$, 299 K) δ (ppm) = 3.50 (br, 1H), 2.83 (d, *J* = 19.4 Hz, 1H), 2.45 (d, *J* = 19.4 Hz, 1H), 2.33 (s, 3H), 1.52 (s, 3H), 1.38 (s, 3H). **^{13}C-NMR {^{19}F}** (126 MHz, $CDCl_3$, 299 K) δ (ppm) = 208.1 (C_q), 148.6 (C_q), 144.8 (C_q), 111.2 (C_q), 98.7 (C_q), 50.0 (C_q), 34.4 (CH_2), 27.6 (CH_3), 19.3 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected. **^{19}F-NMR** (470 MHz, $CDCl_3$, 299 K) δ (ppm) = -141.4 – 141.3 (m, 2F), -152.1 – -151.9 (m, 1F), -160.9 – -160.7 (m, 2F).

FTIR (neat): ν (cm^{-1}): 3335*s*, 1703*s*, 1656*w*, 1523*m*, 1496*s*, 1441*w*, 1385*w*, 1355*w*, 1317*w*, 1225*w*, 1149*w*, 1065*s*, 990*s*, 953*w*, 903*w*, 860*m*, 819*w*, 767*w*, 590*w*. **HRMS** (ESI) exact mass calculated for $C_{14}H_{12}NO_3F_5Na^+$ $[M+Na]^+$: *m/z* = 360.06296; found 360.06298.

1-(6-Hydroxy-5,6-dimethyl-3-(naphthalen-2-yl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3o**)



1-(6-Hydroxy-5,6-dimethyl-3-(naphthalen-2-yl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3o**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (0.093 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-5,6-dimethyl-3-(naphthalen-2-yl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.050 g, 0.17 mmol, 84%) was isolated as a colourless solid and inseperable mixture of diastereoisomers (dr = 3:1).

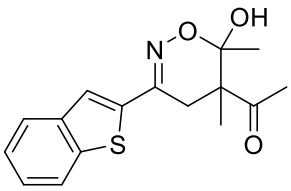
For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.05 (d, *J* = 1.8 Hz, 1H), 8.00 – 7.95 (m, 1H), 7.88 – 7.79 (m, 3H), 7.55 – 7.45 (m, 2H), 3.79 (br, 1H), 3.49 (d, *J* = 17.4 Hz, 1H), 2.58 (d, *J* = 17.4 Hz, 1H), 2.41 (s, 3H), 1.61 (s, 3H), 1.29 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.8 (C_q), 153.9 (C_q), 134.0 (C_q), 133.1 (C_q), 132.8 (C_q), 128.6 (CH), 128.4 (CH), 127.8 (CH),

127.1 (CH), 126.6 (CH), 125.3 (CH), 122.9 (CH), 97.9 (C_q), 49.2 (C_q), 30.7 (CH_2), 28.2 (CH_3), 22.7 (CH_3), 19.9 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.08 (d, *J* = 1.8 Hz, 1H), 8.00 – 7.95 (m, 1H), 7.88 – 7.79 (m, 3H), 7.55 – 7.45 (m, 2H), 3.79 (br, 1H), 3.12 (d, *J* = 18.6 Hz, 1H), 2.76 (d, *J* = 18.6 Hz, 1H), 2.31 (s, 3H), 1.50 (s, 3H), 1.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.4 (C_q), 155.9 (C_q), 134.1 (C_q), 132.4 (C_q), 128.7 (CH), 127.1 (CH), 125.5 (CH), 122.9 (CH), 98.1 (C_q), 50.2 (C_q), 31.3 (CH_2), 27.8 (CH_3), 22.6 (CH_3), 19.7 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3302*s*, 2988*w*, 2254*w*, 1696*s*, 1600*w*, 1503*w*, 1450*w*, 1354*w*, 1276*m*, 1261*w*, 1208*w*, 1151*w*, 1131*w*, 1087*m*, 1034*w*, 960*w*, 904*s*, 857*m*, 820*m*, 749*s*, 725*s*, 648*m*, 598*m*. **HRMS** (ESI) exact mass calculated for $C_{18}H_{19}NO_3Na^+$ $[M+Na]^+$: *m/z* = 320.12571; found 320.12558.

1-(3-(Benzo[*b*]thiophen-2-yl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3p**)



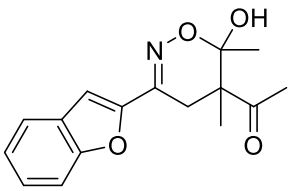
1-(3-(Benzo[*b*]thiophen-2-yl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3p**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), 2-vinylbenzothiophene (0.096 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(3-(benzo[*b*]thiophen-2-yl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.023 g, 0.076 mmol, 38%) was isolated as a colourless solid and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.83 – 7.71 (m, 2H), 7.50 (s, 1H), 7.39 – 7.29 (m, 2H), 3.45 (d, *J* = 17.1 Hz, 1H), 2.57 (d, *J* = 17.1 Hz, 1H), 2.40 (s, 3H), 1.62 (s, 3H), 1.28 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.1 (C_q), 151.2 (C_q), 140.2 (C_q), 139.7 (C_q), 139.3 (C_q), 125.9 (CH), 124.6 (CH), 124.2 (CH), 123.1 (CH), 122.5 (CH), 98.7 (C_q), 49.0 (C_q), 30.6 (CH_2), 28.1 (CH_3), 22.7 (CH_3), 19.8 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.83 – 7.71 (m, 2H), 7.52 (s, 1H), 7.39 – 7.29 (m, 2H), 3.11 (d, *J* = 18.4 Hz, 1H), 2.72 (d, *J* = 18.4 Hz, 1H), 2.31 (s, 3H), 1.51 (s, 3H), 1.40 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 208.9 (C_q), 153.1 (C_q), 139.3 (C_q), 139.2 (C_q), 126.0 (CH), 124.7 (CH), 124.2 (CH), 123.5 (CH), 122.5 (CH), 98.9 (C_q), 50.0 (C_q), 31.2 (CH_2), 27.8 (CH_3), 22.7 (CH_3), 19.6 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 2988*w*, 2362*w*, 1698*s*, 1581*w*, 1508*w*, 1456*w*, 1357*m*, 1282*w*, 1246*w*, 1203*m*, 1155*m*, 1088*m*, 1016*w*, 997*w*, 973*w*, 939*w*, 904*s*, 861*m*, 825*m*, 726*s*, 648*w*, 594*w*. **HRMS** (ESI) exact mass calculated for $C_{16}H_{17}NO_3SNa^+$ $[M+Na]^+$: *m/z* = 326.08214; found 326.08209. **M.p.**: 136 – 137 °C.

1-(3-(Benzofuran-2-yl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3q**)



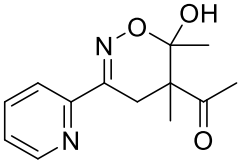
1-(3-(Benzofuran-2-yl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3q**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), 2-vinylbenzofuran (0.087 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(3-(benzofuran-2-yl)-6-hydroxy-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.030 g, 0.010 mmol, 52%) was isolated as a yellow oil and inseperable mixture of diastereoisomers (dr = 3:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.62 – 7.56 (m, 1H), 7.54 – 7.48 (m, 1H), 7.37 – 7.30 (m, 1H), 7.28 – 7.21 (m, 1H), 7.11 (s, 1H), 3.40 (d, *J* = 17.6 Hz, 1H), 3.40 (br, 1H), 2.55 (d, *J* = 17.6 Hz, 1H), 2.40 (s, 3H), 1.61 (s, 3H), 1.27 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.3 (C_q), 155.1 (C_q), 150.7 (C_q), 147.9 (C_q), 127.9 (C_q), 125.9 (CH), 123.5 (CH), 121.8 (CH), 111.7 (CH), 106.0 (CH), 98.7 (C_q), 48.7 (C_q), 29.7 (CH_2), 28.1 (CH_3), 22.7 (CH_3), 19.7 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.62 – 7.56 (m, 1H), 7.54 – 7.48 (m, 1H), 7.37 – 7.30 (m, 1H), 7.28 – 7.21 (m, 1H), 7.11 (s, 1H), 3.40 (br, 1H), 3.06 (d, *J* = 18.8 Hz, 1H), 2.66 (d, *J* = 18.8 Hz, 1H), 2.31 (s, 3H), 1.51 (s, 3H), 1.40 (s, 3H). The ^{13}C-signals of the minor isomer could not be detected.

FTIR (neat): ν (cm^{-1}): 3360*s*, 2996*w*, 2251*w*, 1698*s*, 1614*w*, 1558*w*, 1450*m*, 1417*w*, 1382*m*, 1355*m*, 1297*w*, 1257*m*, 1223*w*, 1201*w*, 1173*m*, 1144*m*, 1109*w*, 1088*m*, 1049*w*, 1008*w*, 956*m*, 896*s*, 876*s*, 856*w*, 812*w*, 750*s*, 728*s*, 664*w*, 647*w*, 595*w*. **HRMS** (ESI) exact mass calculated for $C_{16}H_{17}NO_4Na^+$ $[M+Na]^+$: *m/z* = 310.10498; found 310.10458.

1-(6-Hydroxy-5,6-dimethyl-3-(pyridin-2-yl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3r**)



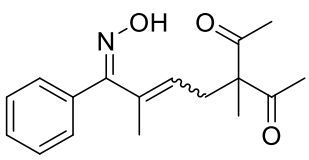
1-(6-Hydroxy-5,6-dimethyl-3-(pyridin-2-yl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3r**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), 2-vinylpyridine (65 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(6-hydroxy-5,6-dimethyl-3-(pyridin-2-yl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.037 g, 0.15 mmol, 74%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 4:1).

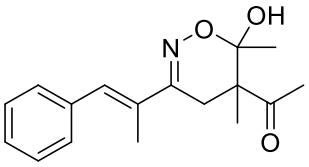
For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.61 – 8.55 (m, 1H), 8.05 – 7.98 (m, 1H), 7.75 – 7.66 (m, 1H), 7.33 – 7.27 (m, 1H), 4.26 (br, 1H), 3.28 (d, *J* = 18.3 Hz, 1H), 2.97 (d, *J* = 18.3 Hz, 1H), 2.37 (s, 3H), 1.58 (s, 3H), 1.23 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 211.9 (C_q), 155.0 (C_q), 153.2 (C_q), 148.7 (CH), 136.7 (CH), 124.5 (CH), 120.7 (CH), 98.6 (C_q), 48.6 (C_q), 29.7 (CH_2), 28.0 (CH_3), 22.4 (CH_3), 19.7 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.61 – 8.55 (m, 1H), 8.05 – 7.98 (m, 1H), 7.75 – 7.66 (m, 1H), 7.33 – 7.27 (m, 1H), 4.26 (br, 1H), 3.25 (d, *J* = 19.5 Hz, 1H), 2.79 (d, *J* = 19.5 Hz, 1H), 2.24 (s, 3H), 1.51 (s, 3H), 1.37 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 153.1 (C_q), 148.9 (CH), 136.7 (CH), 120.6 (CH), 49.8 (C_q), 30.0 (CH_2), 27.7 (CH_3), 22.6 (CH_3), 19.9 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3001*s*, 2943*w*, 1738*m*, 1699*s*, 1581*w*, 1567*w*, 1469*w*, 1435*m*, 1355*s*, 1286*w*, 1216*s*, 1151*m*, 1121*w*, 1087*m*, 1041*w*, 994*w*, 942*m*, 913*s*, 859*m*, 780*s*, 730*s*, 681*w*, 647*w*, 605*m*. **HRMS** (ESI) exact mass calculated for $C_{13}H_{16}N_2O_3Na^+$ $[M+Na]^+$: *m/z* = 271.10531; found 271.10509.

3-((4*E*)-4-(Hydroxyimino)-3-methyl-4-phenylbut-2-en-1-yl)-3-methylpentane-2,4-dione (**3s'**) **and (*E*)-1-(6-Hydroxy-5,6-dimethyl-3-(1-phenylprop-1-en-2-yl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one** (**3s**)





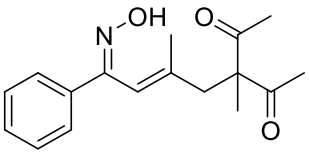
3-((4*E*)-4-(Hydroxyimino)-3-methyl-4-phenylbut-2-en-1-yl)-3-methylpentane-2,4-dione (**3s'**) and (*E*)-1-(6-Hydroxy-5,6-dimethyl-3-(1-phenylprop-1-en-2-yl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3s**) were prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (0.087 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and the product (0.047 g, 0.17 mmol, 81%) was isolated as a colourless oil and mixture of 3 isomers. Further separation provided **3s'** (61%, E/Z: 1.6:1) and **3s** (20%, dr = 3:1).

For **3s'** (The ratio between both isomers changed from 1.6:1 to 1:1 upon separation from **3s**): **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) both isomers = 8.41 (br, 1H), 7.54 – 7.49 (m, 1H), 7.43 – 7.32 (m, 3H), 7.17 – 7.12 (m, 1H), 5.24 (tq, *J* = 7.5, 1.5 Hz, 0.5H), 5.15 (tq, *J* = 7.6, 1.4 Hz, 0.5H), 2.79 (d, *J* = 7.5 Hz, 1H), 2.70 (d, *J* = 7.6 Hz, 1H), 2.14 (s, 3H), 2.03 (s, 3H), 1.97 – 1.91 (m, 5H), 1.40 (s, 1.5H), 1.21 (s, 1.5H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) both isomers = 207.0 (C_q), 206.6 (C_q), 160.9 (C_q), 160.3 (C_q), 136.4 (C_q), 134.9 (C_q), 132.9 (C_q), 132.5 (C_q), 131.0 (CH), 129.6 (CH), 128.8 (CH), 128.6 (2xCH), 128.6 (2xCH), 128.3 (2xCH), 127.2 (2xCH), 126.5 (CH), 66.7 (C_q), 66.6 (C_q), 33.4 (CH_2), 32.8 (CH_2), 26.8 (2xCH_3), 26.7 (2xCH_3), 18.4 (CH_3), 18.3 (CH_3), 15.8 (CH_3), 13.4 (CH_3). **FTIR**

(neat): ν (cm^{-1}): 3383*w*, 2991*w*, 2923*w*, 1694*s*, 1494*w*, 1444*w*, 1356*m*, 1320*w*, 1211*m*, 1157*w*, 1091*w*, 1018*w*, 961*m*, 914*m*, 849*w*, 771*m*, 730*m*, 697*s*, 665*w*, 644*w*, 618*w*. **HRMS** (ESI) exact mass calculated for $C_{17}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 310.14136; found 310.14120.

For **3s**: Major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.39 – 7.28 (m, 5H), 6.90 (s, 1H), 3.43 (br, 1H), 3.19 (d, *J* = 17.1 Hz, 1H), 2.39 (d, *J* = 17.1 Hz, 1H), 2.37 (s, 3H), 2.16 – 2.12 (m, 3H), 1.58 (s, 3H), 1.26 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 211.2 (C_q), 155.7 (C_q), 136.9 (C_q), 134.8 (C_q), 130.3 (CH), 129.5 (2xCH), 128.4 (2xCH), 126.6 (CH), 97.8 (C_q), 49.0 (C_q), 29.7 (CH_2), 28.1 (CH_3), 22.8 (CH_3), 20.0 (CH_3), 14.2 (CH_3).
For **3s**: Minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.39 – 7.28 (m, 5H), 6.94 (s, 1H), 2.93 (d, *J* = 18.3 Hz, 1H), 2.83 (br, 1H), 2.54 (d, *J* = 18.3 Hz, 1H), 2.28 (s, 3H), 2.16 – 2.12 (m, 3H), 1.47 (s, 3H), 1.36 (s, 3H).**^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 153.9 (C_q), 129.6 (2xCH), 126.6 (CH), 97.9 (C_q), 50.1 (C_q), 30.3 (CH_2). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.
FTIR (neat): ν (cm^{-1}): 3393*m*, 2996*w*, 2925*w*, 1697*s*, 1492*w*, 1445*w*, 1356*m*, 1255*w*, 1208*w*, 1154*m*, 1090*m*, 1013*w*, 970*w*, 94,3*m*, 915*s*, 865*m*, 759*w*, 722*m*, 697*s*, 647*w*, 603*w*. **HRMS** (ESI) exact mass calculated for $C_{17}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 310.14136; found 310.14094. **M.p.**: 112 – 134 °C.

3-((2*E*,4*E*)-4-(Hydroxyimino)-2-methyl-4-phenylbut-2-en-1-yl)-3-methylpentane-2,4-dione (**3t'**)

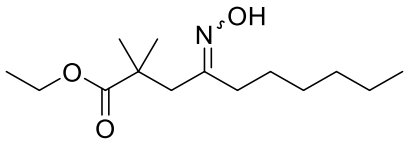


3-((2*E*,4*E*)-4-(Hydroxyimino)-2-methyl-4-phenylbut-2-en-1-yl)-3-methylpentane-2,4-dione (**3t'**) was prepared according to **GPI** using **1a** (0.029 g, 0.10 mmol), styrene (0.087 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 8:1) and 3-((2*E*,4*E*)-4-(hydroxyimino)-2-methyl-4-phenylbut-2-en-1-yl)-3-methylpentane-2,4-dione (0.049 g, 0.17 mmol, 86%) was isolated as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.62 (br, 1H), 7.54 – 7.48 (m, 2H), 7.38 – 7.34 (m, 3H), 6.00 (q, *J* = 1.1 Hz, 1H), 2.86 (d, *J* = 1.1 Hz, 2H), 2.18 (s, 6H), 1.46 (s, 3H), 1.37 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K)) δ (ppm) = 207.0 (C_q), 155.9 (C_q), 141.7 (C_q), 135.4 (C_q), 129.5 (CH), 128.7 (CH), 127.1 (CH), 120.4 (CH), 66.8 (C_q), 43.7 (CH_2), 26.9 (CH_3), 21.1 (CH_3), 18.4 (CH_3).

FTIR (neat): ν (cm^{-1}): 3371*s*, 2982*w*, 1693*s*, 1494*w*, 1445*m*, 1382*w*, 1356*s*, 1279*w*, 1205*m*, 1092*m*, 1024*w*, 947*s*, 919*m*, 760*s*, 732*w*, 696*s*, 668*w*, 620*w*, 588*w*. **HRMS** (ESI) exact mass calculated for $C_{17}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 310.14136; found 310.14127.

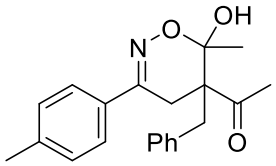
Ethyl 4-(hydroxyimino)-2,2-dimethyldecanoat (**3u'**)



A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. Afterwards, oct-1-ene (1.3 mL, 8.0 mmol, 40 equiv.) and DMSO (1.0 mL) were added and the mixture was heated to 120 °C. **1ae** (0.029 g, 0.10 mmol) was dissolved in DMSO (1 mL) and added to the reaction over 2.5 h by syringe pump. 30 Min after, the reaction was cooled to room temperature and quenched by the addition of water (3 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by flash column chromatography (pentane/EtOAc 10:1) and ethyl 4-(hydroxyimino)-2,2-dimethyldecanoat (0.0095 g, 0.037 mmol, 18%, E/Z: 1:1.67) was isolated as colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 4.12 (qd, *J* = 7.1, 3.9 Hz, 2H), 2.70 (s, 0.75H), 2.44 (s, 1.25H), 2.28 – 2.21 (m, 1.25H), 2.11 – 2.03 (m, 0.75H), 1.52 – 1.41 (m, 2H), 1.32 – 1.20 (m, 15H), 0.92 – 0.84 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 60.6 (CH_2), 43.9 (CH_2), 41.3 (CH_2), 31.7 (CH_2), 29.6 (CH_2), 29.1 (CH_2), 28.6 (CH_2), 26.5 (CH_2), 26.0 (CH_3), 25.9 (CH_3), 25.7 (CH_2), 22.7 (CH_2), 14.2 (CH_3), 14.2 (CH_3). Neither the ^{13}C-signals nor all the signals of the minor isomer could be detected. **FTIR** (neat): ν (cm^{-1}): 2930*m*, 1728*s*, 1469*w*, 1366*m*, 1216*m*, 1132*w*, 1027*w*, 913*m*, 744*m*. **HRMS** (ESI) exact mass calculated for $C_{14}H_{27}NO_3Na^+$ $[M+Na]^+$: *m/z* = 280.18831; found 280.18817.

1-(5-Benzyl-6-hydroxy-6-methyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3v**)



1-(5-Benzyl-6-hydroxy-6-methyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3v**) was prepared according to **GPI** using **1v** (0.044 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-(5-benzyl-6-hydroxy-6-methyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.038 g, 0.11 mmol, 57%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

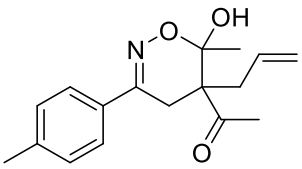
For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.53 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.15 (m, 5H), 6.97 – 6.88 (m, 2H), 3.62 (d, *J* = 13.4 Hz, 1H), 3.17 (d, *J* = 17.3 Hz, 1H), 2.59 (d, *J* = 17.3 Hz, 1H), 2.49 (d, *J* = 13.4 Hz, 1H), 2.38 (s, 3H), 2.14 (s, 3H), 1.67 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.9 (C_q), 154.2 (C_q), 140.2 (C_q), 136.7 (C_q), 132.2 (C_q), 130.3 (2xCH), 129.4 (2xCH), 128.7 (2xCH), 127.0 (CH), 125.7 (2xCH), 98.8 (C_q), 53.3 (C_q), 38.1 (CH_2), 30.2 (CH_3), 26.1 (CH_2), 22.5 (CH_3), 21.5 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.53 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.15 (m, 5H), 7.09 – 7.04 (m, 2H), 3.70 (d, *J* = 13.3 Hz, 1H), 2.89 – 2.78 (m, 2H), 2.63 – 2.46 (m, 1H), 2.36

(s, 3H), 2.12 (s, 3H), 1.60 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.4 (C_q), 132.1 (C_q), 130.3 (2xCH), 127.0 (CH), 125.6 (2xCH), 98.2 (C_q), 54.6 (C_q), 38.6 (CH_2), 29.1 (CH_3), 28.5 (CH_2), 22.9 (CH_3), 21.5 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3381*s*, 3029*w*, 1699*s*, 1604*w*, 1514*w*, 1495*w*, 1454*w*, 1383*m*, 1351*m*, 1202*m*, 1142*m*, 1081*w*, 1035*w*, 986*w*, 940*w*, 907*s*, 861*w*, 815*s*, 759*m*, 731*s*, 706*s*, 648*w*, 603*w*. **HRMS** (ESI) exact mass calculated for $C_{21}H_{23}NO_3Na^+$ $[M+Na]^+$: *m/z* = 360.15701; found 360.15694. **M.p.**: 115 – 117 °C.

1-(5-Allyl-6-hydroxy-6-methyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3w**)



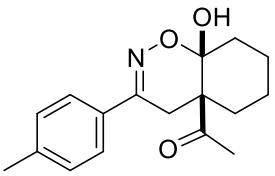
1-(5-Allyl-6-hydroxy-6-methyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3w**) was prepared according to **GPI** using **1w** (0.034 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 6:1) and 1-(5-allyl-6-hydroxy-6-methyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (0.032 g, 0.11 mmol, 56%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 2:1).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.66 – 7.54 (m, 2H), 7.24 – 7.16 (m, 2H), 5.67 – 5-46 (m, 1H), 5.17 – 4.93 (m, 2H), 3.61 (br, 1H), 3.29 (dd, *J* = 17.6, 1.7 Hz, 1H), 2.94 – 2.82 (m, 1H), 2.76 (d, *J* = 17.6 Hz, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 2.07 – 1.96 (m, 1H), 1.56 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.8 (C_q), 154.5 (C_q), 140.1 (C_q), 133.0 (CH), 132.5 (C_q), 129.4 (2xCH), 125.7 (2xCH), 120.0 (CH_2), 98.0 (C_q), 52.5 (C_q), 36.9 (CH_2), 29.6 (CH_3), 26.5 (CH_2), 22.5 (CH_3), 21.4 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.66 – 7.54 (m, 2H), 7.24 – 7.16 (m, 2H), 5.67 – 5-46 (m, 1H), 5.17 – 4.93 (m, 2H), 3.45 (br, 1H), 3.09 – 2.98 (m, 1H), 2.94 – 2.82 (m, 1H), 2.76 – 2.64 (m, 1H), 2.37 (s, 3H), 2.24 (s, 3H), 2.07 – 1.96 (m, 1H), 1.46 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 208.7 (C_q), 156.7 (C_q), 140.3 (C_q), 132.6 (CH), 132.2 (C_q), 125.6 (2xCH), 119.8 (CH_2), 97.8 (C_q), 53.8 (C_q), 37.1 (CH_2), 28.5 (CH_3), 28.3 (CH_2), 22.8 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3384*m*, 3003*w*, 1760*w*, 1699*s*, 1639*w*, 1614*w*, 1514*w*, 1437*w*, 1415*w*, 1383*w*, 1354*m*, 1297*w*, 1203*m*, 1142*m*, 1038*w*, 996*w*, 906*s*, 855*w*, 815*w*, 786*w*, 731*m*, 648*w*, 600*m*. **HRMS** (ESI) exact mass calculated for $C_{17}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 310.14136; found 310.14108.

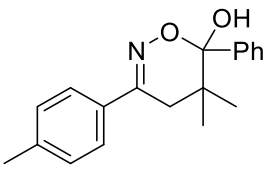
1-((4a*R*,8a*R*)-8a-Hydroxy-3-(*p*-tolyl)-6,7,8,8a-tetrahydro-4*H*-benzo[*e*][1,2]oxazin-4a(5*H*)-yl)ethan-1-one (**3x**)



1-((4a*R*,8a*S*)-8a-Hydroxy-3-(*p*-tolyl)-6,7,8,8a-tetrahydro-4*H*-benzo[*e*][1,2]oxazin-4a(5*H*)-yl)ethan-1-one (**3x**) was prepared according to **GPI** using **1x** (0.034 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and 1-((4a*R*,8a*S*)-8a-hydroxy-3-(*p*-tolyl)-6,7,8,8a-tetrahydro-4*H*-benzo[*e*][1,2]oxazin-4a(5*H*)-yl)ethan-1-one (0.044 g, 0.15 mmol, 76%) was isolated as colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.63 – 7.56 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 3.76 (br, 1H), 2.86 (d, *J* = 17.4 Hz, 1H), 2.47 (d, *J* = 17.4 Hz, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.09 – 1.91 (m, 3H), 1.77 – 1.58 (m, 4H), 1.29 – 1.13 (m, 1H). **^{13}C-NMR** (76 MHz, $CDCl_3$, 299 K) δ (ppm) = 212.1 (C_q), 152.4 (C_q), 140.0 (C_q), 132.4 (C_q), 129.3 (2xCH), 125.4 (2xCH), 96.0 (C_q), 50.3 (C_q), 34.0 (CH_2), 32.1 (CH_2), 29.1 (CH_2), 26.6 (CH_3), 22.9 (CH_2), 22.1 (CH_2), 21.4 (CH_3). **FTIR** (neat): ν (cm^{-1}): 3211*w*, 2922*w*, 2861*w*, 1738*m*, 1699*s*, 1618*w*, 1514*w*, 1444*m*, 1354*s*, 1301*w*, 1217*m*, 1173*m*, 1154*w*, 1120*m*, 1086*m*, 1045*w*, 976*w*, 948*m*, 909*s*, 860*w*, 841*w*, 812*s*, 792*w*, 731*s*, 595*w*, 575*w*. **HRMS** (ESI) exact mass calculated for $C_{17}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 310.14136; found 310.14115. **M.p.**: 158 – 159 °C.

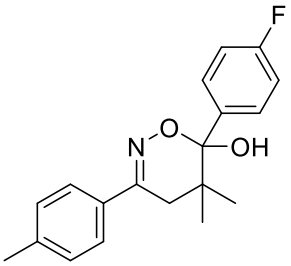
5,5-Dimethyl-6-phenyl-3-(p-tolyl)-5,6-dihydro-4H-1,2-oxazin-6-ol (**3y**)



5,5-Dimethyl-6-phenyl-3-(p-tolyl)-5,6-dihydro-4H-1,2-oxazin-6-ol (**3y**) was prepared according to **GPI** using **1y** (0.035 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 120 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 10:1) and 5,5-dimethyl-6-phenyl-3-(p-tolyl)-5,6-dihydro-4H-1,2-oxazin-6-ol (0.035 g, 0.12 mmol, 59%) was isolated as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.69 – 7.63 (m, 4H), 7.40 – 7.35 (m, 3H), 7.24 – 7.17 (m, 2H), 2.93 (d, *J* = 17.5 Hz, 1H), 2.74 (br, 1H), 2.41 – 2.31 (m, 2H), 1.07 (s, 3H), 0.88 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$, 299 K) δ (ppm) = 155.4 (C_q), 138.7 (C_q), 139.2 (C_q), 133.1 (C_q), 129.3 (2xCH), 128.6 (CH), 128.0 (2xCH), 127.6 (2xCH), 125.5 (2xCH), 101.0 (C_q), 34.9 (CH_2), 33.2 (C_q), 24.5 (CH_3), 24.2 (CH_3), 21.4 (CH_3). **FTIR** (neat): ν (cm^{-1}): 3380*s*, 2975*w*, 1613*w*, 15144*w*, 1493*w*, 1473*w*, 1446*m*, 1415*w*, 1365*m*, 1277*m*, 1214*w*, 1147*w*, 1095*w*, 1068*m*, 1035*w*, 1017*s*, 944*s*, 903*s*, 840*w*, 814*m*, 791*w*, 760*s*, 733*m*, 704*s*, 670*w*, 647*w*, 576*w*. **HRMS** (ESI) exact mass calculated for $C_{19}H_{21}NO_2Na^+$ $[M+Na]^+$: *m/z* = 318.14645; found 318.14648. **M.p.**: 193 – 194 °C.

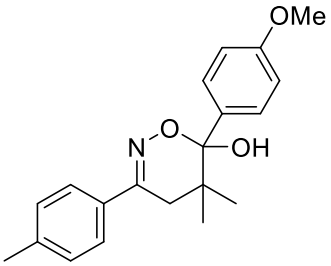
6-(4-Fluorophenyl)-5,5-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (**3z**)



6-(4-Fluorophenyl)-5,5-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (**3z**) was prepared according to **GPI** using **1z** (0.039 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 120 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 8:1) and 6-(4-fluorophenyl)-5,5-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (0.034 g, 0.11 mmol, 54%) was isolated as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.66 – 7.58 (m, 4H), 7.22 – 7.17 (m, 2H), 7.07 – 7.00 (m, 2H), 2.91 (d, *J* = 17.6 Hz, 1H), 2.77 (br, 1H), 2.38 (s, 3H), 2.35 (d, *J* = 17.6 Hz, 1H), 1.05 (s, 3H), 0.85 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$, 299 K) δ (ppm) = 163.0 (d, *J* = 247.3 Hz, C_q), 155.7 (C_q), 139.9 (C_q), 135.0 (d, *J* = 3.2 Hz, C_q), 132.9 (C_q), 129.9 (d, *J* = 8.3 Hz, 2xCH), 129.3 (2xCH), 125.6 (2xCH), 146.5 (d, *J* = 21.4 Hz, 2xCH), 100.8 (C_q), 34.9 (CH_2), 33.3 (C_q), 24.5 (CH_3), 24.2 (CH_3), 21.4 (CH_3). **^{19}F-NMR** (282 MHz, $CDCl_3$, 299 K) δ (ppm) = -114.0 (d, *J* = 1.5 Hz, 1F). **FTIR** (neat): ν (cm^{-1}): 3228*m*, 1604*w*, 1508*w*, 1373*w*, 1223*m*, 1153*w*, 1092*m*, 1014*w*, 933*s*, 818*s*, 752*s*, 660*w*. **HRMS** (ESI) exact mass calculated for $C_{19}H_{20}NO_2Na^+$ $[M+Na]^+$: *m/z* = 336.13703; found 336.13697. **M.p.**: 185 – 188 °C.

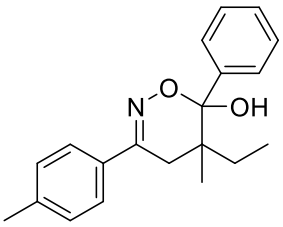
6-(4-Methoxyphenyl)-5,5-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (**3aa**)



6-(4-Methoxyphenyl)-5,5-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (**3aa**) was prepared according to **GPI** using **1aa** (0.041 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 120 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 8:1) and 6-(4-methoxyphenyl)-5,5-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (0.026 g, 0.08 mmol, 40%) was isolated as colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.66 – 7.61 (m, 2H), 7.59 – 7.54 (m, 2H), 7.22 – 7.17 (m, 2H), 6.90 – 6.85 (m, 2H), 3.83 (s, 3H), 2.90 (d, *J* = 17.5 Hz, 1H), 2.38 (s, 3H), 2.34 (d, *J* = 17.5 Hz, 1H), 1.05 (s, 3H), 0.86 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 159.7 (C_q), 155.4 (C_q), 139.7 (C_q), 133.1 (C_q), 131.3 (C_q), 129.3 (2xCH), 129.2 (2xCH), 125.5 (2xCH), 112.8 (2xCH), 101.0 (C_q), 55.4 (CH_3), 34.9 (CH_2), 33.4 (C_q), 24.5 (CH_3), 24.2 (CH_3), 21.4 (CH_3). **FTIR** (neat): ν (cm^{-1}): 3418*m*, 2967*m*, 2835*w*, 1609*m*, 1583*w*, 1508*s*, 1463*w*, 1415*w*, 1364*w*, 1302*m*, 1279*w*, 1246*s*, 1216*w*, 1176*s*, 1079*m*, 1037*m*, 1019*s*, 980*w*, 940*s*, 905*s*, 828*s*, 813*s*, 785*m*, 730*s*, 646*w*, 627*m*, 578*m*. **HRMS** (ESI) exact mass calculated for $C_{20}H_{23}NO_3Na^+$ $[M+Na]^+$: *m/z* = 348.15701; found 348.15692. **M.p.**: 153 – 155 °C.

5-Ethyl-5-methyl-6-phenyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (**3ab**)



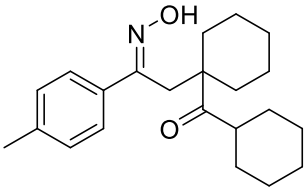
5-Ethyl-5-methyl-6-phenyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (**3ab**) was prepared according to **GPI** using **1ab** (0.038 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 120 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 8:1) and 5-ethyl-5-methyl-6-phenyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (0.039 g, 0.13 mmol, 63%) was isolated as colourless oil and inseperable mixture of diastereoisomers (dr = 3:2).

For major isomer: **^{1}H-NMR** (500 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.67 – 7.63 (m, 4H), 7.38 – 7.33 (m, 3H), 7.22 – 7.18 (m, 2H), 2.97 (br, 1H), 2.79 (d, *J* = 17.5 Hz, 1H), 2.43 – 2.37 (m, 4H), 1.81 (dq, *J* = 13.5, 7.6 Hz, 1H), 1.22 – 1.13 (m, 1H), 0.87 – 0.82 (m, 6H). **^{13}C-NMR** (126 MHz, $CDCl_3$, 299 K) δ (ppm) = 155.5 (C_q), 139.6 (C_q), 139.3 (C_q), 133.4 (C_q), 129.2 (2xCH), 128.5 (CH), 128.1 (2xCH), 127.5 (2xCH), 125.6 (2xCH), 101.3 (C_q), 36.1 (C_q), 31.7 (CH_2), 28.7 (CH_2), 21.4 (CH_3), 19.9 (CH_3), 7.5 (CH_3).

For minor isomer: **^{1}H-NMR** (500 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.67 – 7.63 (m, 4H), 7.38 – 7.33 (m, 3H), 7.22 – 7.18 (m, 2H), 2.97 (br, 1H), 2.73 (dd, *J* = 17.8, 1.6 Hz, 1H), 2.59 (d, *J* = 17.8 Hz, 1H), 2.38 (s, 3H), 1.57 – 1.48 (m, 1H), 1.06 – 0.98 (m, 4H), 0.72 (t, *J* = 7.6 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$, 299 K) δ (ppm) = 155.6 (C_q), 139.7 (C_q), 139.3 (C_q), 133.1 (C_q), 129.3 (2xCH), 128.5 (CH), 128.2 (2xCH), 127.5 (2xCH), 125.6 (2xCH), 101.3 (C_q), 36.0 (C_q), 29.4 (CH_2), 26.7 (CH_2), 21.4 (CH_3), 20.5 (CH_3), 8.0 (CH_3).

FTIR (neat): ν (cm^{-1}): 3396*m*, 2967*m*, 2881*w*, 1614*w*, 1513*w*, 1446*m*, 1360*w*, 1254*w*, 1185*w*, 1148*w*, 1070*m*, 1034*w*, 1006*w*, 961*s*, 909*s*, 812*m*, 788*w*, 760*s*, 730*s*, 702*s*, 669*w*, 647*w*, 607*w*, 592*w*. **HRMS** (ESI) exact mass calculated for $C_{20}H_{23}NO_2Na^+$ $[M+Na]^+$: *m/z* = 332.16210; found 332.16198.

(*E*)-Cyclohexyl(1-(2-(hydroxyimino)-2-(*p*-tolyl)ethyl)cyclohexyl)methanone (**3ac'**)

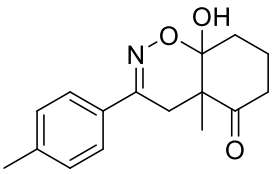


(*E*)-Cyclohexyl(1-(2-(hydroxyimino)-2-(*p*-tolyl)ethyl)cyclohexyl)methanone (**3ac'**) was prepared according to **GPI** using **1ac** (0.044 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 120 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 8:1) and (*E*)-cyclohexyl(1-(2-(hydroxyimino)-2-(*p*-tolyl)ethyl)cyclohexyl)methanone (0.032 g, 0.09 mmol, 47%) was isolated as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.42 – 7.37 (m, 2H), 7.20 – 7.16 (m, 2H), 2.99 (s, 2H), 2.94 (tt, *J* = 11.5, 3.3 Hz, 1H), 2.36 (s, 3H), 2.04 – 1.93 (m, 2H), 1.78 – 1.72 (m, 2H), 1.69 – 1.59 (m, 4H), 1.51 – 1.36 (m, 5H), 1.31 – 1.16 (m, 8H). **^{13}C-NMR** (101 MHz, $CDCl_3$, 299 K) δ (ppm) = 217.8

(C_q), 157.5 (C_q), 139.3 (C_q), 134.6 (C_q), 129.4 (2xCH), 126.8 (2xCH), 53.2 (C_q), 45.4 (CH), 33.1 (2xCH_2), 32.9 (CH_2), 30.5 (2xCH_2), 26.0 (2xCH_2), 25.9 (CH_2), 25.9 (CH_2), 23.7 (2xCH_2), 21.4 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2926*s*, 2853*m*, 1691*m*, 1600*w*, 1514*w*, 1447*m*, 1318*w*, 1239*w*, 1173*w*, 1140*w*, 1047*w*, 998*w*, 957*m*, 907*s*, 817*m*, 728*s*, 647*w*, 590*w*. **HRMS** (ESI) exact mass calculated for $C_{22}H_{31}NO_2Na^+$ $[M+Na]^+$: *m/z* = 364.22470; found 364.22464. **M.p.**: 124 – 127 °C.

8a-Hydroxy-4a-methyl-3-(*p*-tolyl)-4,4a,6,7,8,8a-hexahydro-5*H*-benzo[*e*][1,2]oxazin-5-one (**3ad**)



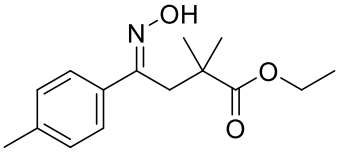
8a-Hydroxy-4a-methyl-3-(*p*-tolyl)-4,4a,6,7,8,8a-hexahydro-5*H*-benzo[*e*][1,2]oxazin-5-one (**3ad**) was prepared according to **GPI** using **1ad** (0.031 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 80 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 3:1) and 8a-hydroxy-4a-methyl-3-(*p*-tolyl)-4,4a,6,7,8,8a-hexahydro-5*H*-benzo[*e*][1,2]oxazin-5-one (0.042 g, 0.15 mmol, 68%) was isolated as colourless solid and inseperable mixture of diasteroisomers (dr = 7:3).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.67 – 7.56 (m, 2H), 7.22 – 7.11 (m, 2H), 3.89 (br, 1H), 3.18 (d, *J* = 17.7 Hz, 1H), 2.71 – 2.53 (m, 1H), 2.36 (s, 3H), 2.44 – 2.22 (m, 3H), 2.07 – 1.79 (m, 3H), 1.38 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.5 (C_q), 156.0 (C_q), 139.3 (C_q), 132.3 (C_q), 129.2 (2xCH), 125.7 (2xCH), 98.9 (C_q), 49.1 (C_q), 35.3 (CH_2), 31.5 (CH_2), 26.2 (CH_2), 22.2 (CH_3), 21.4 (CH_3), 19.6 (CH_2).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.67 – 7.56 (m, 2H), 7.22 – 7.11 (m, 2H), 3.62 (br, 1H), 3.17 (d, *J* = 18.0 Hz, 1H), 2.71 – 2.53 (m, 1H), 2.36 (s, 3H), 2.44 – 2.22 (m, 3H), 2.07 – 1.79 (m, 3H), 1.23 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.8 (C_q), 156.4 (C_q), 140.1 (C_q), 132.9 (C_q), 129.3 (2xCH), 125.6 (2xCH), 99.1 (C_q), 47.0 (C_q), 35.8 (CH_2), 29.3 (CH_2), 27.5 (CH_2), 21.8 (CH_3), 21.4 (CH_3), 19.7 (CH_2).

FTIR (neat): ν (cm^{-1}): 3455*w*, 3015*m*, 2970*m*, 2251*w*, 1738*s*, 1616*w*, 1515*w*, 1441*m*, 1424*m*, 1365*s*, 1317*w*, 1272*w*, 1228*m*, 1216*s*, 1160*w*, 1114*w*, 1070*w*, 1039*w*, 1015*m*, 962*w*, 903*s*, 833*w*, 815*m*, 793*w*, 726*s*, 648*w*, 574*w*, 541*m*. **HRMS** (ESI) exact mass calculated for $C_{16}H_{19}NO_3Na^+$ $[M+Na]^+$: *m/z* = 296.12571; found 296.12514. **M.p.**: 136 – 138 °C.

Ethyl (*E*)-4-(hydroxyimino)-2,2-dimethyl-4-(*p*-tolyl)butanoate (**3ae'**)

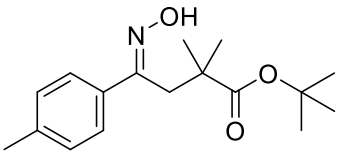


A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. Afterwards, *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (1.5 mL) were added and the mixture was heated to 120 °C. **1ae** (0.029 g, 0.10 mmol) was dissolved in DMSO

(1 mL) and added to the reaction over 2.5 h by syringe pump. 30 Min after, the reaction was cooled to room temperature and quenched by the addition of water (3 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by flash column chromatography (pentane/EtOAc 10:1) and ethyl (*E*)-4-(hydroxyimino)-2,2-dimethyl-4-(*p*-tolyl)butanoate (0.037 g, 0.14 mmol, 71%) was isolated as colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 9.64 (br, 1H), 7.69 – 7.60 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.41 (s, 2H), 2.61 (s, 3H), 1.43 (s, 6H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 177.2 (C_q), 157.8 (C_q), 139.3 (C_q), 133.8 (C_q), 129.2 (2xCH), 126.9 (2xCH), 60.6 (CH_2), 42.2 (C_q), 35.3 (CH_2), 25.7 (2xCH_3), 21.4 (CH_3), 14.0 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2977*m*, 1724*s*, 1684*m*, 1606*w*, 1563*m*, 1513*w*, 1474*w*, 1446*w*, 1407*w*, 1385*w*, 1301*m*, 1228*m*, 1180*s*, 1127*s*, 1027*m*, 973*w*, 920*w*, 904*w*, 863*w*, 808*s*, 774*m*, 597*w*. **HRMS** (ESI) exact mass calculated for $C_{15}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 286.14136; found 286.14136. **M.p.**: 50 – 52 °C.

***Tert*-butyl (*E*)-4-(hydroxyimino)-2,2-dimethyl-4-(*p*-tolyl)butanoate (3af')**

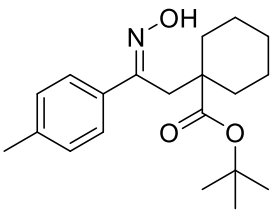


Tert-butyl (*E*)-4-(hydroxyimino)-2,2-dimethyl-4-(*p*-tolyl)butanoate (**3af'**) was prepared according to **GPI** using **1af** (0.035 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 120 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 10:1) and *tert*-butyl (*E*)-4-(hydroxyimino)-2,2-dimethyl-4-(*p*-tolyl)butanoate (0.034 g, 0.12 mmol, 59%) was isolated as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.44 – 7.37 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 3.14 (s, 2H), 2.34 (s, 3H), 1.28 (s, 9H), 1.10 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 176.6 (C_q), 158.2 (C_q), 139.3 (C_q), 134.1 (C_q), 129.3 (2xCH), 127.1 (2xCH), 80.3 (C_q), 42.9 (C_q), 34.7 (CH_2), 27.8 (3xCH_3), 26.0 (2xCH_3), 21.4 (CH_3). **FTIR** (neat): ν (cm^{-1}): 3241*m*, 2976*m*, 2927*w*, 2361*w*, 1719*s*, 1611*w*, 1562*w*, 1514*w*, 1472*w*, 1449*w*, 1390*w*, 1367*m*, 1316*w*, 1252*m*, 1132*s*, 1063*w*, 976*w*, 926*m*, 849*m*, 815*s*, 774*w*, 732*s*, 647*w*, 589*w*. **HRMS** (ESI) exact mass calculated for $C_{17}H_{25}NO_3Na^+$ $[M+Na]^+$: *m/z* = 314.17266; found 314.17254.

***Tert*-butyl (*E*)-1-(2-(hydroxyimino)-2-(*p*-tolyl)ethyl)cyclohexane-1-carboxylate (3ag')**

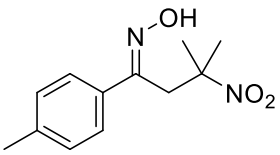
Tert-butyl (*E*)-1-(2-(hydroxyimino)-2-(*p*-tolyl)ethyl)cyclohexane-1-carboxylate (**3ag'**) was prepared according to **GPI** using **1ag** (0.043 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 120 °C. The crude product was purified by flash column chromatography



(pentane/EtOAc 20:1) and *tert*-butyl (*E*)-1-(2-(hydroxyimino)-2-(*p*-tolyl)ethyl)cyclohexane-1-carboxylate (0.031 g, 0.094 mmol, 47%) was isolated as colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.74 (s, 1H), 7.45 – 7.36 (m, 2H), 7.19 – 7.12 (m, 2H), 3.02 (s, 2H), 2.35 (s, 3H), 2.07 – 1.96 (m, 2H), 1.59 – 145 (m, 3H), 1.27 (s, 9H), 1.26 – 1.04 (m, 5H). **^{13}C-NMR** (76 MHz, $CDCl_3$, 299 K) δ (ppm) = 174.9 (C_q), 157.5 (C_q), 139.1 (C_q), 134.6 (C_q), 129.3 (2xCH), 126.9 (2xCH), 80.3 (C_q), 47.7 (C_q), 35.9 (CH_2), 35.3 (2xCH_2), 27.9 (CH_3), 25.7 (CH_2), 23.6 (2xCH_2), 21.4 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2928*m*, 2857*w*, 1737*s*, 1685*w*, 1607*w*, 1564 *m*, 1450*m*, 1366*s*, 1228*s*, 1217*s*, 1151*m*, 1130*s*, 1066*w*, 1037*w*, 973*w*, 895*w*, 849*m*, 816*w*, 741*w*, 637*w*, 571*w*. **HRMS** (ESI) exact mass calculated for $C_{20}H_{29}NO_3Na^+$ $[M+Na]^+$: *m/z* = 354.20396; found 354.20360.

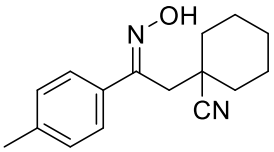
(*E*)-3-Methyl-3-nitro-1-(*p*-tolyl)butan-1-one oxime (**3ah'**)



A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. Afterwards, *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (1.5 mL) were added and the mixture was heated to 80 °C. **1ah** (0.024 g, 0.10 mmol) was dissolved in DMF (1 mL) and the blue solution was added to the reaction over 2.5 h by syringe pump. 30 Min after, the reaction was quenched by the addition of water (3 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by flash column chromatography (pentane/EtOAc 20:5) and (*E*)-3-methyl-3-nitro-1-(*p*-tolyl)butan-1-one oxime (0.023 g, 0.10 mmol, 48%) was isolated as colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.43 – 7.38 (m, 2H), 7.21 – 7.16 (m, 2H), 3.56 (s, 2H), 2.36 (s, 3H), 1.55 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 155.6 (C_q), 140.3 (C_q), 132.3 (C_q), 129.6 (2xCH), 126.7 (2xCH), 87.3 (C_q), 35.5 (CH_2), 26.6 (2xCH_3), 21.5 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2925*w*, 1685*s*, 1607*m*, 1542*s*, 1470*w*, 1454*w*, 1406*m*, 1371*s*, 1349*s*, 1311*w*, 1228*m*, 1184*w*, 1012*w*, 976*w*, 809*s*, 569*w*. **HRMS** (ESI) exact mass calculated for $C_{12}H_{16}N_2O_3Na^+$ $[M+Na]^+$: *m/z* = 259.10531; found 259.10529. **M.p.**: 146 – 148 °C.

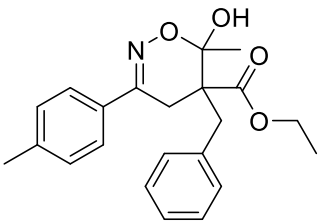
(*E*)-1-(2-(Hydroxyimino)-2-(*p*-tolyl)ethyl)cyclohexane-1-carbonitrile (**3ai'**)



A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. Afterwards, *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (1.5 mL) were added and the mixture was heated to 120 °C. **1ai** (0.028 g, 0.10 mmol) was dissolved in DMSO (1 mL) and added to the reaction over 2.5 h by syringe pump. 30 Min after, the reaction was quenched by the addition of water (3 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by flash column chromatography (pentane/EtOAc 10:1) and (*E*)-1-(2-(hydroxyimino)-2-(*p*-tolyl)ethyl)cyclohexane-1-carbonitrile (0.020 g, 0.08 mmol, 38%) was isolated as colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.73 (s, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 3.17 (s, 2H), 2.37 (s, 3H), 1.91 (d, *J* = 13.2 Hz, 2H), 1.74 – 1.48 (m, 6H), 1.36 (td, *J* = 12.9, 3.6 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 155.6 (C_q), 140.0 (C_q), 133.1 (C_q), 129.5 (2xCH), 126.8 (2xCH), 123.0 (C_q), 38.3 (C_q), 36.2 (2xCH_2), 34.9 (CH_2), 25.1 (CH_2), 23.1 (2xCH_2), 21.5 (CH_3). **FTIR** (neat): ν (cm^{-1}): 3363*m*, 2933*s*, 2860*m*, 1685*w*, 1609*w*, 1558*w*, 1513*w*, 1449*m*, 1330*w*, 1291*w*, 1187*w*, 1046*w*, 983*m*, 911*s*, 818*s*, 730*s*, 648*w*, 589*w*. **HRMS** (ESI) exact mass calculated for $C_{16}H_{19}N_2O^-$ [M-H]$^-$: *m/z* = 255.14919; found 255.15022. **M.p.**: 122 – 125 °C.

Ethyl 5-benzyl-6-hydroxy-6-methyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazine-5-carboxylate (**3aj**)



Ethyl 5-benzyl-6-hydroxy-6-methyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazine-5-carboxylate (**3aj**) was prepared according to **GPI** using **1aj** (0.050 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 6:1) and ethyl 5-benzyl-6-hydroxy-6-methyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazine-5-carboxylate (0.047 g, 0.13 mmol, 64%) was isolated as a colourless oil and inseperable mixture of diastereoisomers (dr = 3:1).

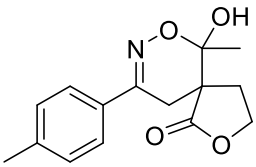
For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.55 – 7.49 (m, 2H), 7.25 – 7.09 (m, 5H), 6.99 – 6.92 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.86 (br, 1H), 3.46 (d, *J* = 13.5 Hz, 1H), 3.12 (d, *J* = 18.3 Hz, 1H), 2.62 (d, *J* = 13.5 Hz, 1H), 2.46 (d, *J* = 18.3 Hz, 1H), 2.34 (s, 3H), 1.78 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 172.6 (C_q), 154.9 (C_q), 140.0 (C_q), 136.2 (C_q), 132.3 (C_q), 130.1 (2xCH), 129.3 (2xCH), 128.6 (2xCH), 127.2 (CH), 125.7 (2xCH), 98.9 (C_q), 61.8 (CH_2), 49.8 (C_q), 39.2 (CH_2), 26.0 (CH_2), 22.5 (CH_3), 21.4 (CH_3), 14.1 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.47 – 7.42 (m, 2H), 7.25 – 7.09 (m, 5H), 4.09 (qd, *J* = 7.1, 2.9 Hz, 1H), 3.86 (br, 1H), 3.57 (d, *J* = 13.2 Hz, 1H), 2.86 (d, *J* = 13.2 Hz, 1H),

2.67 (d, *J* = 17.6 Hz, 1H), 2.49 (d, *J* = 17.6 Hz, 1H), 2.31 (s, 3H), 1.76 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 171.9 (C_q), 157.2 (C_q), 139.7 (C_q), 136.3 (C_q), 132.3 (C_q), 130.1 (2xCH), 129.2 (2xCH), 128.6 (2xCH), 127.0 (CH), 125.8 (2xCH), 97.6 (C_q), 61.5 (CH_2), 50.9 (C_q), 39.2 (CH_2), 28.3 (CH_2), 22.9 (CH_3), 21.4 (CH_3), 14.0 (CH_3).

FTIR (neat): ν (cm^{-1}): 3430*w*, 3030*w*, 2984*w*, 1724*s*, 1604*w*, 1514*w*, 1496*w*, 1454*w*, 1417*w*, 1383*w*, 1366*w*, 1302*w*, 1192*m*, 1146*m*, 1082*m*, 1039*m*, 948*w*, 908*s*, 863*w*, 814*s*, 795*w*, 729*s*, 701*s*, 649*w*. **HRMS** (ESI) exact mass calculated for $C_{22}H_{25}NO_4Na^+$ $[M+Na]^+$: *m/z* = 390.16758; found 390.16728. **M.p.**: 57 – 60 °C.

6-Hydroxy-6-methyl-9-(*p*-tolyl)-2,7-dioxa-8-azaspiro[4.5]dec-8-en-1-one (**3ak**)



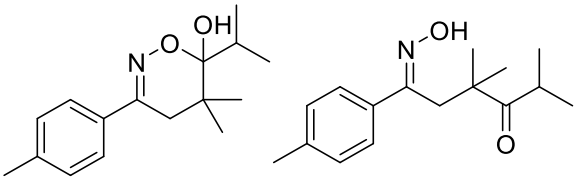
6-Hydroxy-6-methyl-9-(*p*-tolyl)-2,7-dioxa-8-azaspiro[4.5]dec-8-en-1-one (**3ak**) was prepared according to **GPI** using **1ak** (0.031 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 60 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 6:1) and 6-hydroxy-6-methyl-9-(*p*-tolyl)-2,7-dioxa-8-azaspiro[4.5]dec-8-en-1-one (0.039 g, 0.14 mmol, 70%) was isolated as a colourless solid and inseperable mixture of diastereoisomers (dr = 3:2).

For major isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.58 (dd, *J* = 8.3, 3.5 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 4.42 – 4.30 (m, 2H), 3.64 (br, 1H), 3.34 (d, *J* = 17.6 Hz, 1H), 3.02 (d, *J* = 18.3 Hz, 1H), 2.53 (d, *J* = 17.6 Hz, 1H), 2.57 – 2.44 (m, 1H), 2.36 (s, 3H), 2.15 – 2.01 (m, 1H), 1.63 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 177.9 (C_q), 153.4 (C_q), 140.5 (C_q), 132.0 (C_q), 129.5 (2xCH), 125.5 (2xCH), 95.5 (C_q), 65.6 (CH_2), 44.9 (C_q), 31.7 (CH_2), 30.0 (CH_2), 22.7 (CH_3), 21.4 (CH_3).

For minor isomer: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.58 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 4.42 – 4.30 (m, 2H), 3.64 (br, 1H), 3.02 (d, *J* = 18.3 Hz, 1H), 2.85 (ddd, *J* = 13.5, 7.6, 3.5 Hz, 1H), 2.72 (d, *J* = 18.3 Hz, 1H), 2.36 (s, 3H), 2.15 – 2.01 (m, 1H), 1.61 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 176.8 (C_q), 153.2 (C_q), 140.3 (C_q), 131.8 (C_q), 129.4 (2xCH), 125.5 (2xCH), 98.0 (C_q), 66.3 (CH_2), 45.3 (C_q), 32.4 (CH_2), 32.2 (CH_2), 22.2 (CH_3). Not all ^{13}C-signals of the minor isomer could be detected, probably due to an overlap with the major isomer.

FTIR (neat): ν (cm^{-1}): 3415*m*, 2995*w*, 2922*w*, 1751*s*, 1613*w*, 1513*w*, 1451*w*, 1418*w*, 1381*m*, 1277*w*, 1208*m*, 1176*m*, 1153*m*, 1114*m*, 1096*w*, 1029*s*, 985*w*, 944*w*, 907*s*, 816*m*, 791*w*, 728*s*, 647*w*, 580*w*. **HRMS** (ESI) exact mass calculated for $C_{15}H_{17}NO_4Na^+$ $[M+Na]^+$: *m/z* = 298.10498; found 298.10488. **M.p.**: 74 – 76 °C.

6-Isopropyl-5,5-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (**3al**) **and (*E*)-6-(hydroxyimino)-2,4,4-Trimethyl-6-(*p*-tolyl)hexan-3-one** (**3al'**)



6-Isopropyl-5,5-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-6-ol (**3al**) and (*E*)-6-(hydroxyimino)-2,4,4-Trimethyl-6-(*p*-tolyl)hexan-3-one (**3al'**) were prepared according to **GPI** using **1al** (0.029 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) at 80 °C. The crude product was purified by flash column chromatography (pentane/EtOAc 10:1) and **3al** and **3al'** (0.026 g, 0.10 mmol, 49%) were isolated as colourless solid and inseperable mixture of isomers (**3al**:**3al'** = 1:1.1).

For **3al**: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.65 – 7.58 (m, 2H), 7.21 – 7.14 (m, 2H), 2.78 (d, *J* = 17.7 Hz, 1H), 2.49 (s, 1H), 2.43 – 2.27 (m, 4H), 2.12 (d, *J* = 17.7 Hz, 1H), 1.22 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.07 (s, 3H).

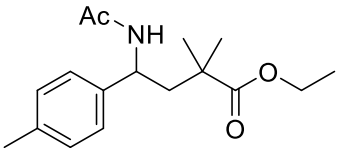
For **3al'**: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.22 (br, 1H), 7.44 – 7.37 (m, 2H), 7.21 – 7.14 (m, 2H), 3.18 – 3.06 (m, 1H), 3.12 (s, 3H), 2.43 – 2.27 (m, 3H), 1.08 (s, 6H), 0.99 (d, *J* = 6.7 Hz, 6H).

For **3al** and **3al'**: **^{13}C-NMR** (76 MHz, $CDCl_3$, 299 K) δ (ppm) = 218.9 (C_q), 158.3 (C_q), 155.3 (C_q), 139.6 (C_q), 139.3 (C_q), 134.5 (C_q), 133.1 (C_q), 129.3 (2xCH), 129.2 (2xCH), 126.9 (2xCH), 125.3 (2xCH), 101.8 (C_q), 48.2 (C_q), 36.6 (CH_2), 34.4 (CH), 33.8 (C_q), 32.9 (CH), 32.8 (CH_2), 26.1 (CH_3), 24.7 (CH_3), 24.4 (CH_3), 21.4 (CH_3), 21.4 (CH_3), 20.2 (CH_3), 19.5 (CH_3), 18.0 (CH_3).

FTIR (neat): ν (cm^{-1}): 2970*m*, 1739*s*, 1609*w*, 1577*w*, 1513*w*, 1446*m*, 1366*s*, 1288*s*, 1217*s*, 1206*s*, 1149*w*, 1110*w*, 1034*w*, 933*w*, 908*w*, 818*m*, 722*w*, 659*w*. **HRMS** (ESI) exact mass calculated for $C_{16}H_{23}NO_2Na^+$ $[M+Na]^+$: *m/z* = 284.16210; found 284.16178. **M.p.**: 124 – 126 °C.

5. Synthetic applications

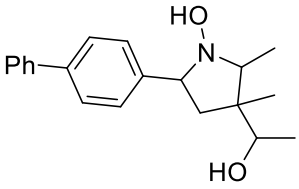
Ethyl 4-acetamido-2,2-dimethyl-4-(*p*-tolyl)butanoate (**4**)



To a stirred ice-cold solution of **3ae'** (0.053 g, 0.20 mmol, 1.0 eq.) in Ac_2O (0.4 mL) Zn powder (0.065 g, 1.0 mmol, 5.0 eq.) was added in small portions. Then, glacial acetic acid (0.11 mL, 2.0 mmol, 10 eq.) was added dropwise at 0 °C. The reaction mixture was stirred at 68 °C overnight. The mixture was cooled to ambient temperature, filtered and the residue was washed with CH_2Cl_2 (5 mL). The filtrate was treated with saturated $NaHCO_3$ and extracted with CH_2Cl_2 (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by flash column chromatography (pentane/EtOAc 1:1 to 1:2) and ethyl 4-acetamido-2,2-dimethyl-4-(*p*-tolyl)butanoate (0.036 g, 0.12 mmol, 58%) was isolated as colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.18 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.01 (d, *J* = 8.5 Hz, 1H), 5.06 (ddd, *J* = 10.6, 8.5, 4.6 Hz, 1H), 4.14 – 3.96 (m, 2H), 2.41 – 2.32 (m, 1H), 2.31 (s, 3H), 1.88 (s, 3H), 1.74 (dd, *J* = 14.5, 4.6 Hz, 1H), 1.29 – 1.18 (m, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 178.8 (C_q), 168.9 (C_q), 140.2 (C_q), 137.0 (C_q), 129.3 (2xCH), 126.4 (2xCH), 60.8 (CH_2), 50.4 (CH), 45.9 (CH_2), 41.3 (C_q), 28.3 (CH_3), 23.4 (CH_3), 23.4 (CH_3), 21.1 (CH_3), 14.2 (CH_3). **FTIR** (neat): ν (cm^{-1}): 3283*w*, 2970*m*, 2247*w*, 1737*s*, 1645*m*, 1545*w*, 1515*w*, 1474*w*, 1444*w*, 1367*s*, 1308*w*, 1279*w*, 1228*m*, 1217*s*, 1141*m*, 1113*w*, 1093*w*, 1025*w*, 909*w*, 861*w*, 808*w*, 771*w*, 729*m*, 647*w*, 600*w*, 527*w*, 515*w*. **HRMS** (ESI) exact mass calculated for $C_{17}H_{25}NO_3Na^+$ $[M+Na]^+$: *m/z* = 314.17266; found 314.17276.

5-([1,1'-Biphenyl]-4-yl)-3-(1-hydroxyethyl)-2,3-dimethylpyrrolidin-1-ol (**5**)

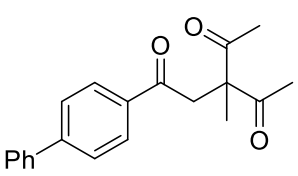


A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. **3c** (0.049 g, 0.15 mmol, 1.0 eq.) was dissolved in glacial acetic acid (1 mL) and $NaCNBH_3$ (0.030 g, 0.48 mmol, 3.2 eq.) was carefully added at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was then poured into a saturated solution of Na_2CO_3 (15 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was dissolved in $CHCl_3$ (0.5 mL). After adding two drops of NEt_3, the mixture was heated to 60 °C and stirred for 3 h. Then, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (pentane/EtOAc 4:1 to 2:1) and 5-([1,1'-biphenyl]-4-yl)-

3-(1-hydroxyethyl)-2,3-dimethylpyrrolidin-1-ol (0.023 g, 0.074 mmol, 49%) was isolated as colourless solid and mixture of diastereoisomers.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.61 – 7.54 (m, 4H), 7.49 – 7.40 (m, 4H), 7.37 – 7.30 (m, 1H), 4.70 (br, 1H), 3.87 – 3.61 (m, 2H), 3.02 – 2.92 (m, 1H), 2.45 (dd, *J* = 13.3, 8.7 Hz, 0.7H, major isomer), 2.20 (dd, *J* = 13.3, 8.5 Hz, 0.3H, minor isomer), 1.42 – 1.28 (m, 1H), 1.27 – 1.15 (m, 6H), 1.05 (s, 0.9H, minor isomer), 1.00 (s, 2.1H, major isomer). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 141.7 (C_q, major), 141.5 (C_q, minor), 141.2 (C_q, major), 141.2 (C_q, minor), 140.4 (C_q, minor), 140.4 (C_q, minor), 128.9 (2xCH), 128.1 (2xCH), 127.4 (2xCH), 127.3 (CH), 127.2 (2xCH), 75.3 (CH, mino), 72.0 (CH, major), 70.9 (CH, minor), 70.8 (CH, major), 68.7 (CH, minor), 67.0 (CH, major), 43.7 (CH_2, major), 43.3 (CH_2, minor), 43.0 (CH_2, minor), 40.3 (CH_2, major), 20.4 (CH_3, major), 19.7 (CH_3, minor), 19.0 (CH_3, minor), 18.9 (CH_3, major), 15.0 (CH_3, minor), 13.4 (CH_3, major). **FTIR** (neat): ν (cm^{-1}): 3365*s*, 3029*w*, 2970*m*, 2873*w*, 2246*w*, 1739*s*, 1599*w*, 1520*w*, 1488*m*, 1447*w*, 1373*m*, 1307*w*, 1228*w*, 1217*w*, 1091*m*, 1008*w*, 980*w*, 907*m*, 835*m*, 793*w*, 764*s*, 729*s*, 696*s*, 647*w*, 617*w*, 581*w*, 541*w*. **HRMS** (ESI) exact mass calculated for $C_{20}H_{25}NO_2Na^+$ $[M+Na]^+$: *m/z* = 334.17775; found 334.17773. **M.p.**: 134 – 136 °C.

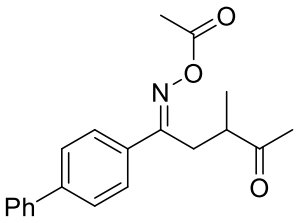
1-([1,1'-Biphenyl]-4-yl)-3-acetyl-3-methylpentane-1,4-dione (**6**)



To a solution of **3c** (0.032 g, 0.10 mmol, 1.0 equiv.) in ethanol (1 mL) and formaldehyde (37%, 1 mL) HCl (3 mol/L, 1 mL) was added under stirring and the mixture was heated to reflux for 3 h. After complete consumption of the starting material, ethanol was evaporated from the reaction mixture and the residue was extracted with EtOAc (3x 10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by flash column chromatography (pentane/EtOAc 8:1 to 3:1) and 1-([1,1'-biphenyl]-4-yl)-3-acetyl-3-methylpentane-1,4-dione (0.021 g, 0.068 mmol, 68%) was isolated as colourless solid.

^{1}H-NMR (599 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.06 – 8.02 (m, 2H), 7.71 – 7.68 (m, 2H), 7.64 – 7.61 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.39 (m, 1H), 3.73 (s, 2H), 2.24 (s, 6H), 1.57 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$, 299 K) δ (ppm) = 206.4 (2xC_q), 197.0 (C_q), 146.4 (C_q), 139.9 (C_q), 135.3 (C_q), 129.1 (2xCH), 128.9 (2xCH), 128.5 (CH), 127.5 (2xCH), 127.4 (2xCH), 64.7 (C_q), 45.0 (CH_2), 26.6 (2xCH_3), 19.8 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2999*w*, 2970*w*, 2944*w*, 1738*s*, 1696*s*, 1677*s*, 16003*m*, 1582*w*, 1559*w*, 1518*w*, 1448*w*, 1403*m*, 1353*s*, 1272*w*, 1227*s*, 1217*s*, 1203*s*, 1172*m*, 1092*w*, 1027*w*, 1006*m*, 922*w*, 855*w*, 833*w*, 765*m*, 750*w*, 737*w*, 723*w*, 693*m*, 606*w*, 585*w*, 570*w*. **HRMS** (ESI) exact mass calculated for $C_{20}H_{20}O_3Na^+$ $[M+Na]^+$: *m/z* = 331.13047; found 331.13055. **M.p.**: 102 – 104 °C.

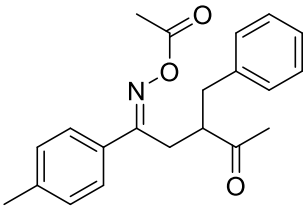
(*E*)-5-([1,1'-Biphenyl]-4-yl)-5-(acetoxyimino)-3-methylpentan-2-one (**7a**)



(*E*)-5-([1,1'-Biphenyl]-4-yl)-5-(acetoxyimino)-3-methylpentan-2-one (**7a**) was prepared according to **GPII** using **3c** (0.050 g, 0.15 mmol, 1.0 equiv.) and DMF (2 mL). The crude product was purified by flash column chromatography (pentane/EtOAc 3:1) and (*E*)-5-([1,1'-biphenyl]-4-yl)-5-(acetoxyimino)-3-methylpentan-2-one (0.036 g, 0.11 mmol, 74%) was isolated as a colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.82 – 7.75 (m, 2H), 7.67 – 7.58 (m, 4H), 7.49 – 7.42 (m, 2H), 7.41 – 7.34 (m,1H), 3.17 (dd, *J* = 13.6, 5.8 Hz, 1H), 3.04 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.92 – 2.78 (m, 1H), 2.27 (s, 3H), 2.16 (s, 3H), 1.16 (d, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.1 (C_q), 168.8 (C_q), 164.4 (C_q), 143.7 (C_q), 140.1 (C_q), 132.6 (C_q), 129.0 (2xCH), 128.1 (CH), 128.0 (2xCH), 127.6 (2xCH), 127.2 (2xCH), 44.6 (CH), 30.2 (CH_2), 28.5 (CH_3), 20.2 (CH_3), 16.6 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2975*w*, 1766*s*, 1711*s*, 1600*w*, 1579*w*, 1488*w*, 1458*w*, 1403*w*, 1364*m*, 1328*w*, 1269*w*, 1194*s*, 1109*w*, 1041*w*, 1003*m*, 939*m*, 906*m*, 906*m*, 846*m*, 767*s*, 732*w*, 698*m*, 634*w*, 596*w*. **HRMS** (ESI) exact mass calculated for $C_{20}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 346.14136; found 346.14225. **M.p.**: 60 – 62 °C.

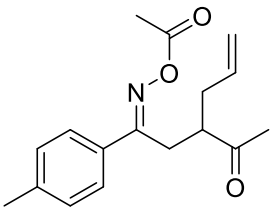
(*E*)-5-(Acetoxyimino)-3-benzyl-5-(*p*-tolyl)pentan-2-one (**7b**)



(*E*)-5-(Acetoxyimino)-3-benzyl-5-(*p*-tolyl)pentan-2-one (**7b**) was prepared according to **GPII** using **3v** (0.051 g, 0.15 mmol, 1.0 equiv.) and DMF (2 mL). The crude product was purified by flash column chromatography (pentane/EtOAc 5:1) and (*E*)-5-(acetoxyimino)-3-benzyl-5-(*p*-tolyl)pentan-2-one (0.035 g, 0.10 mmol, 69%) was isolated as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.48 – 7.43 (m, 2H), 7.31 – 7.20 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.08 (m, 2H), 3.15 (dd, *J* = 12.8, 8.3 Hz, 1H), 3.11 – 3.03 (m, 1H), 2.98 – 2.89 (m, 2H), 2.68 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.37 (s, 3H), 2.18 (s, 3H), 1.90 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.3 (C_q), 168.7 (C_q), 164.4 (C_q), 141.3 (C_q), 138.5 (C_q), 130.6 (C_q), 129.6 (2xCH), 129.1 (2xCH), 128.8 (2xCh), 127.4 (2xCH), 126.9 (CH), 51.8 (CH), 38.3 (CH_2), 31.0 (CH_3), 29.5 (CH_2), 21.5 (CH_3), 19.8 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2921*w*, 1762*s*, 1712*s*, 1603*w*, 1564*w*, 1513*w*, 1496*w*, 1454*w*, 1364*m*, 1327*w*, 1194*s*, 1042*w*, 999*m*, 932*m*, 892*m*, 821*m*, 747*m*, 701*s*, 643*w*, 622*w*, 596*w*, 571*w*. **HRMS** (ESI) exact mass calculated for $C_{21}H_{23}NO_3Na^+$ $[M+Na]^+$: *m/z* = 360.15701; found 360.15731.

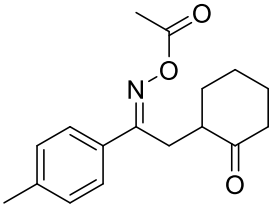
(*E*)-3-(2-(Acetoxyimino)-2-(*p*-tolyl)ethyl)hex-5-en-2-one (**7c**)



(*E*)-3-(2-(Acetoxyimino)-2-(*p*-tolyl)ethyl)hex-5-en-2-one (**7c**) was prepared according to **GPII** using **3w** (0.043 g, 0.15 mmol, 1.0 equiv.) and DMF (2 mL). The crude product was purified by flash column chromatography (pentane/EtOAc 5:1) and (*E*)-3-(2-(acetoxyimino)-2-(*p*-tolyl)ethyl)hex-5-en-2-one (0.025 g, 0.09 mmol, 58%) was isolated as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.61 – 7.54 (m, 2H), 7.23 – 7.18 (m, 2H), 5.67 (ddt, *J* = 16.4, 10.9, 7.0 Hz, 1H), 5.10 – 5.00 (m, 2H), 3.10 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.98 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.90 – 2.80 (m, 1H), 2.38 (s, 3H), 2.42 – 2.31 (m, 1H), 2.25 (s, 3H), 2.28 – 2.17 (m, 1H), 2.06 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 209.6 (C_q), 168.8 (C_q), 164.6 (C_q), 141.3 (C_q), 134.3 (CH), 130.8 (C_q), 129.6 (2xCH), 127.5 (2xCH), 118.3 (CH_2), 49.6 (CH), 35.8 (CH_2), 30.1 (CH_3), 28.9 (CH_2), 21.5 (CH_3), 20.0 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2921*w*, 1763*s*, 1712*s*, 1640*w*, 1604*w*, 1564*w*, 1514*w*, 1443*w*, 1365*m*, 1326*w*, 1196*s*, 1043*w*, 9999*m*, 925*s*, 892*m*, 822*m*, 744*w*, 644*w*, 621*w*, 595*w*, 572*w*. **HRMS** (ESI) exact mass calculated for $C_{17}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 310.14136; found 310.14150.

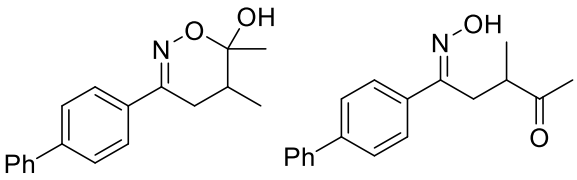
(*E*)-2-(2-(Acetoxyimino)-2-(*p*-tolyl)ethyl)cyclohexan-1-one (**7d**)



(*E*)-2-(2-(Acetoxyimino)-2-(*p*-tolyl)ethyl)cyclohexan-1-one (**7d**) was prepared according to **GPII** using **3x** (0.043 g, 0.15 mmol, 1.0 equiv.) and DMF (2 mL). The crude product was purified by flash column chromatography (pentane/EtOAc 5:1) and (*E*)-2-(2-(acetoxyimino)-2-(*p*-tolyl)ethyl)cyclohexan-1-one (0.043 g, 0.15 mmol, 99%) was isolated as a colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.61 – 7.56 (m, 2H), 7.22 – 7.16 (m, 2H), 3.24 (dd, *J* = 13.8, 4.2 Hz, 1H), 2.99 (dd, *J* = 13.8, 9.9 Hz, 1H), 2.60 – 2.40 (m, 2H), 2.37 (s, 3H), 2.33 – 2.25 (m, 1H), 2.23 (s, 3H), 2.11 – 1.97 (m, 2H), 1.85 – 1.76 (m, 1H), 1.72 – 1.35 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 210.8 (C_q), 169.0 (C_q), 165.3 (C_q), 141.1 (C_q), 131.0 (C_q), 129.6 (2xCH), 127.3 (2xCH), 48.4 (CH), 42.0 (CH_2), 33.6 (CH_2), 27.7 (CH_2), 27.6 (CH_2), 25.1 (CH_2), 21.5 (CH_3), 20.2 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2934*w*, 2861*w*, 1761*s*, 1707*s*, 1604*w*, 1565*w*, 1514*w*, 1447*w*, 1365*m*, 1326*w*, 1195*s*, 1129*w*, 1043*w*, 1001*w*, 945*w*, 918*m*, 893*m*, 821*m*, 766*w*, 728*s*, 647*w*, 620*w*, 597*w*, 559*w*. **HRMS** (ESI) exact mass calculated for $C_{17}H_{21}NO_3Na^+$ $[M+Na]^+$: *m/z* = 310.14136; found 310.14152. **M.p.**: 108 – 109 °C.

3-([1,1'-Biphenyl]-4-yl)-5,6-dimethyl-5,6-dihydro-4*H*-1,2-oxazin-6-ol (**8**) **and (*E*)-5-([1,1'-Biphenyl]-4-yl)-5-(hydroxyimino)-3-methylpentan-2-one** (**8'**)

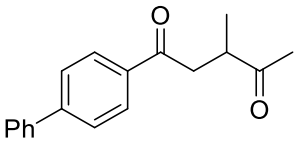


A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. **7a** (0.049 g, 0.15 mmol, 1.0 eq.) was dissolved in Et_2O (1.5 mL) and $Co_2(CO)_8$ (0.051 g, 0.15 mmol, 1.0 eq.) and NEt_3 (21 µL, 0.15 mmol, 1.0 eq.) were added successively. The mixture was stirred for 15 min at r.t and the solvent was evaporated. The residue was dissolved in H_2O/MeOH (1.5 mL, 1:2) and stirred for 30 min at r.t. Then, the mixture was diluted with H_2O and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by flash column chromatography (pentane/EtOAc 4:1) and **8** and **8'** (0.037 g, 0.13 mmol, 87%) were isolated as colourless solid as a inseperable mixture of isomers (**8**:**8'** = 5:1; whereas **8** itself is a mixture of two diastereoisomers with dr = 2.1:1).

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.82 – 7.77 (m, 1.7H), 7.70 – 7.66 (m, 0.3H), 7.65 – 7.58 (m, 4H), 7.48 – 7.41 (m, 2H), 7.40 – 7.32 (m, 1H), 3.09 (dd, *J* = 17.8, 7.1 Hz, 0.33H), 3.02 – 2.96 (m, 0.25H), 2.62 (d, *J* = 6.5 Hz, 0.18H), 2.58 – 2.48 (m, 1H), 2.44 (d, *J* = 11.8 Hz, 0.18H), 2.34 (dd, *J* = 17.7, 2.1 Hz, 0.3H), 2.24 (qd, *J* = 7.1, 2.2 Hz, 0.5H), 2.17 (s, 0.5H, **8'**), 2.13 – 2.00 (m, 0.6H), 1.62 (s, 1.7H, **8**), 1.57 (s, 0.8H, **8**), 1.18 (d, *J* = 6.7 Hz, 1.7H, **8**), 1.14 (d, *J* = 6.7 Hz, 0.5H, **8'**), 1.05 (d, *J* = 7.0 Hz, 0.8H, **8**). **^{13}C-NMR** (75MHz, $CDCl_3$, 299 K) δ (ppm) = 211.6 (C_q), 157.5 (C_q), 155.6 (C_q), 153.9 (C_q), 143.3 (C_q), 142.3 (C_q), 142.3 (C_q), 140.6 (C_q), 140.5 (C_q), 140.3 (C_q), 134.7 (C_q), 134.7 (C_q), 129.1 (CH), 129.0 (CH), 128.8 (CH), 128.5 (CH), 128.1 (CH), 127.7 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 127.2 (CH), 127.2 (CH), 127.0 (CH), 126.0 (CH), 126.0 (CH), 97.7 (C_q), 97.5 (C_q), 44.3 (CH), 32.1 (CH), 30.8 (CH), 29.0 (CH_2), 28.5 (CH_3), 27.8 (CH_2), 27.1 (CH_2), 24.8 (CH_3), 16.7 (CH_3), 16.6 (CH_3), 15.9 (CH_3), 14.3 (CH_3). Not all ^{13}C-signals of the minor isomers could be detected, probably due to an overlap.

FTIR (neat): ν (cm^{-1}): 3445*w*, 3029*w*, 2937*w*, 1739*s*, 1600*w*, 1488*w*, 1448*m*, 1635*s*, 1259*w*, 1228*s*, 1217*s*, 1204*s*, 1111*w*, 1075*w*, 1044*w*, 1021*w*, 1007*w*, 935*w*, 903*s*, 841*m*, 765*s*, 729*s*, 696*m*, 647*w*, 563*w*. **HRMS** (ESI) exact mass calculated for $C_{18}H_{19}NO_2Na^+$ $[M+Na]^+$: *m/z* = 304.13080; found 304.13086. **M.p.**: 115 – 118 °C.

1-([1,1'-Biphenyl]-4-yl)-3-methylpentane-1,4-dione (**9**)

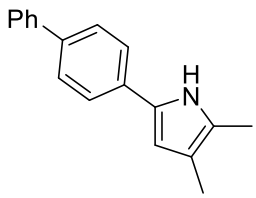


A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. **7a** (0.049 g, 0.15 mmol, 1.0 eq.) was dissolved in Et_2O (1.5 mL) and $Co_2(CO)_8$ (0.051 g, 0.15 mmol, 1.0 eq.) and

NEt_3 (21 µL, 0.15 mmol, 1.0 eq.) were added successively. The mixture was stirred for 15 min at r.t and the solvent was evaporated. The residue was dissolved in H_2O/MeOH (1.5 mL, 1:2) and stirred for 30 min at r.t. Then, the mixture was diluted with H_2O and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was redissolved in ethanol (1 mL) and formaldehyde (37%, 1 mL). HCl (3 mol/L, 1 mL) was added under stirring and the mixture was heated to reflux for 3 h. After complete consumption of the starting material, ethanol was evaporated from the reaction mixture and the residue was extracted with EtOAc (3x 10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by RP-MPLC (MeCN/H_2O, gradient from 5% to 60% within 30 min) and 1-([1,1'-biphenyl]-4-yl)-3-methylpentane-1,4-dione (0.032 g, 0.12 mmol, 81%) was isolated as colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.03 (dd, *J* = 8.5, 1.6 Hz, 2H), 7.70 – 7.59 (m, 4H), 7.51 – 7.35 (m, 3H), 3.64 – 3.50 (m, 2H), 3.35 – 3.18 (m, 1H), 2.96 (ddd, *J* = 17.9, 4.5, 1.4 Hz, 2H), 2.32 (s, 3H), 1.23 (dd, *J* = 7.2, 1.4 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 211.7 (C_q), 198.3 (C_q), 146.0 (C_q), 140.0 (C_q), 135.5 (C_q), 129.1 (2xCH), 128.8 (2xCH), 128.4 (CH), 127.4 (2xCH), 127.4 (2xCH), 42.0 (CH), 28.8 (CH_3), 16.9 (CH_3). **FTIR** (neat): ν (cm^{-1}): 2970*w*, 2359*w*, 1738*s*, 1657*w*, 1365*m*, 1228*m*, 1217*m*, 1057*w*, 913*w*, 837*w*, 742*w*, 699*w*, 576*w*, 537*w*, 526*w*. **HRMS** (ESI) exact mass calculated for $C_{18}H_{18}O_2Na^+$ $[M+Na]^+$: *m/z* = 289.11990; found 289.11968. **M.p.**: 74 – 75 °C.

5-([1,1'-Biphenyl]-4-yl)-2,3-dimethyl-1*H*-pyrrole (**10**)



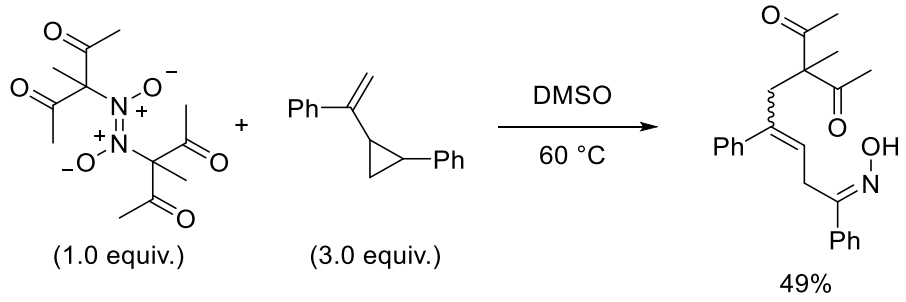
A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. **9** (0.027 g, 0.10 mmol, 1.0 eq.) was dissolved in EtOH (1 mL) and NH_4OAc (0.059 g, 0.76 mmol, 7.6 eq.) was added and the reaction mixture was refluxed for 4 h. After complete consumption of the starting material, CH_2Cl_2 was added and the resulting solution was poured into 1:1 saturated NH_4Cl/H_2O (10 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by flash column chromatography (pentane/EtOAc 50:1) and 5-([1,1'-biphenyl]-4-yl)-2,3-dimethyl-1*H*-pyrrole (0.020 g, 0.080 mmol, 80%) was isolated as colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.97 (s, 1H), 7.65 – 7.54 (m, 4H), 7.51 – 7.40 (m, 4H), 7.38 – 7.30 (m, 1H), 6.35 (d, *J* = 2.9 Hz, 1H), 2.26 (s, 3H), 2.08 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 140.9 (C_q), 138.2 (C_q), 132.1 (C_q), 129.1 (C_q), 128.9 (2xCH), 127.6 (2xCH), 127.2 (CH), 126.9 (2xCH), 125.6 (C_q), 123.6 (2xCH), 116.6 (C_q), 108.2 (CH), 11.3 (CH_3), 11.1 (CH_3).

FTIR (neat): ν (cm^{-1}): 3440*w*, 2970*w*, 1739*s*, 1536*w*, 1420*w*, 1365*s*, 1228*m*, 1217*m*, 912*w*, 835*w*, 804*w*, 763*m*, 692*w*, 658*w*, 527*w*. **HRMS** (ESI) exact mass calculated for $C_{18}H_{16}N^-$ $[M-H]^-$: *m/z* = 246.12882; found 246.12861. **M.p.**: 210 – 213 °C.

6. Mechanistic studies and complementary reactivity experiment

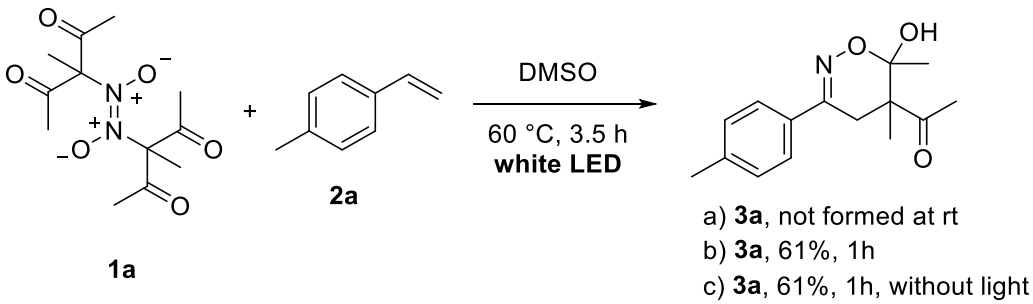
Ring opening experiment on **2v**:



A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. (1-(2-phenylcyclopropyl)vinyl)benzene (**2v**) (0.13 g, 0.60 mmol, 3.0 equiv.) and DMSO (2 mL) were added and the mixture was heated to 60 °C. **1a** (0.029 g, 0.10 mmol) was added to the reaction in six portions every 30 min. One hour after the final addition, the reaction was quenched by the addition of water (3 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The crude product was purified by flash column chromatography (pentane/EtOAc 5:1 to 2:1) and 3-((5*E*)-5-(hydroxyimino)-2,5-diphenylpent-2-en-1-yl)-3-methylpentane-2,4-dione (**11**) (0.036 g, 0.099 mmol, 49%) was isolated as a colourless oil as mixture of diastereoisomers (dr = 2:1).

^{1}H-NMR (major isomer) (500 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.61 – 7.58 (m, 1H), 7.39 – 7.27 (m, 5H), 7.23 – 7.07 (m, 4H), 5.62 (t, *J* = 7.1 Hz, 1H), 3.68 (d, *J* = 7.1 Hz, 2H), 3.29 (s, 2H), 1.89 (s, 6H), 1.27 (s, 3H). **^{1}H-NMR** (minor isomer) (500 MHz, $CDCl_3$, 299 K) δ (ppm) = 7.61 – 7.58 (m, 1H), 7.39 – 7.27 (m, 5H), 7.23 – 7.07 (m, 4H), 5.55 (t, *J* = 7.1 Hz, 1H), 3.46 (d, *J* = 7.1 Hz, 2H), 2.98 (s, 2H), 1.82 (s, 6H), 1.19 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$, 299 K) δ (ppm) = 207.3 (C_q, major), 206.8 (C_q, minor), 157.9 (C_q, minor), 157.6 (C_q, major), 143.0 (C_q, major), 139.4 (C_q, minor), 139.0 (C_q, major), 138.5 (C_q, minor), 135.4 (C_q, major), 135.3 (C_q, minor), 129.6 (CH), 129.4 (CH, minor), 129.1 (CH), 128.8 (2xCH, major), 128.5 (CH), 128.4 (CH), 128.3 (2xCH, major), 127.7 (2xCH, major), 127.6 (CH), 127.6 (CH, minor), 127.5 (CH), 126.6 (2xCH, major), 126.6 (CH), 126.2 (CH, minor), 66.9 (C_q, minor), 66.5 (C_q, major), 43.6 (CH_2, minor), 34.5 (CH_2, major), 26.9 (CH_3, major), 26.9 (CH_2, minor), 26.8 (CH_2, major), 26.6 (CH_3, minor), 18.2 (CH_3, major). **FTIR** (neat): ν (cm^{-1}): 3382*m*, 2930*w*, 1696*s*, 1493*w*, 1445*w*, 1357*m*, 1282*w*, 1207*w*, 1094*w*, 958*w*, 914*m*, 763*m*, 735*w*, 699*m*. **HRMS** (ESI) exact mass calculated for $C_{23}H_{25}NO_3Na^+$ $[M+Na]^+$: *m/z* = 386.17266; found 386.17257.

White LED irradiation experiments:



A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. *p*-Methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) was dissolved in DMSO (2 mL) and **1a** (0.029 g, 0.10 mmol) was added at once.

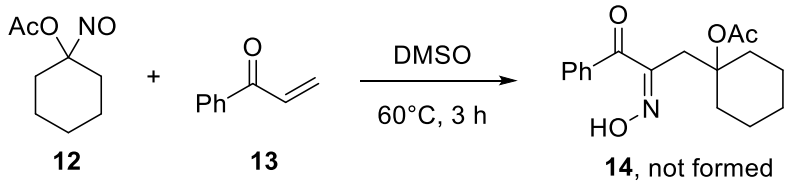
For a): The reaction was stirred at room temperature (in a water bath to prevent heating through irradiation) and irradiated with a 10 W white LED for 3,5 h.

For b): The reaction was stirred at 60 °C and irradiated with a 10 W white LED for 1 h.

For c): The reaction was stirred at 60 °C for 1 h.

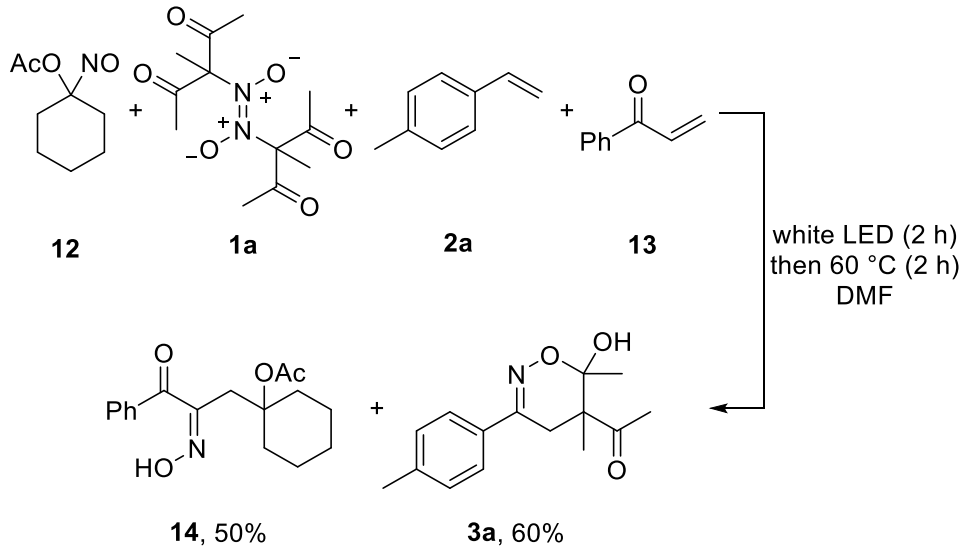
After the given times, the reactions were diluted with water (3 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The yields of **3a** were determined by ^{1}H-NMR spectroscopy using CH_2Br_2 as internal standard.

α-Acetoxy nitroso compounds as thermal radical precursors:



A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. 1-Phenylprop-2-en-1-one (0.079 g, 0.60 mmol, 3.0 equiv.) was dissolved in DMSO (2 mL) and heated to 60 °C (120 °C respectively). 1-Nitrosocyclohexyl acetate (0.034 g, 0.20 mmol, 1.0 equiv.) was added to the reaction portionwise for three times ever 30 min. Half an hour after the final addition, the reaction was diluted with water (3 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The formation of **14** was checked by ^{1}H-NMR analysis.

Complementary reactivity experiment with (*E*)-1,2-bis(3-methyl-2,4-dioxopentan-3-yl)diazene 1,2-dioxide (**1a**) and 1-nitrosocyclohexyl acetate (**12**):



12 **1a** **2a** **13**

14, 50% **3a**, 60%

A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with argon 3 times. 1-Nitrosocyclohexyl acetate (0.034 g, 0.20 mmol, 1.0 equiv.), **1a** (0.029 g, 0.10 mmol), *p*-methylstyrene (79 µL, 0.60 mmol, 3.0 equiv.) and 1-phenylprop-2-en-1-one (0.079 g, 0.60 mmol, 3.0 equiv.) were dissolved in DMF (2 mL). The reaction mixture was irradiated with a 10 W white LED (the distance between the tube and the light source was about 4 cm) for 2 h. Then, irradiation was stopped and the mixture was heated to 60 °C. After two hours, the mixture was quenched with water (3 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine (15 mL) and dried with Na_2SO_4. The crude product was purified by flash column chromatography (pentane/EtOAc 25:1 to 3:2) and (*Z*)-1-(2-(hydroxyimino)-3-oxo-3-phenylpropyl)cyclohexyl acetate (**14**, 0.030 g, 0.10 mmol, 50%) and 1-(6-hydroxy-5,6-dimethyl-3-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazin-5-yl)ethan-1-one (**3a**, 0.031 g, 0.12 mmol, 60%) were isolated.

For **14**: **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K) δ (ppm) = 8.37 (br, 1H), 7.96 – 7.89 (m, 2H), 7.60 – 7.53 (m, 1H), 7.48 – 7.41 (m, 2H), 3.42 (s, 2H), 2.37 – 2.25 (m, 2H), 1.81 (s, 3H), 1.59 – 1.22 (m, 8H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K) δ (ppm) = 170.7 (C_q), 157.5 (C_q), 136.3 (C_q), 133.1 (CH), 130.6 (2xCH), 128.3 (2xCH), 83.3 (C_q), 35.4 (CH_2), 32.1 (CH_2), 25.4 (CH_2), 22.4 (CH_3), 22.0 (CH_2). The spectroscopic data are in accordance with the literature.[14] **HRMS** (ESI) exact mass calculated for $C_{17}H_{21}NO_4Na^+$ $[M+Na]^+$: *m/z* = 326.13628; found 326.13596.

7. X-ray crystal structure analysis of **3x** and **3y**

X-Ray diffraction: Data sets for compounds **3x** and **3y** were collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: APEX3 V2019.1-0[15] (Bruker AXS Inc., **2019**); cell refinement: SAINT V8.40A (Bruker AXS Inc., **2019**); data reduction: SAINT V8.40A (Bruker AXS Inc., **2019**); absorption correction, SADABS V2016/2 (Bruker AXS Inc., **2019**); structure solution *SHELXT-2015*[16] (Sheldrick, G. M. *Acta Cryst.*, **2015**, *A71*, 3-8); structure refinement *SHELXL-2015*[17] (Sheldrick, G. M. *Acta Cryst.*, **2015**, *C71* (1), 3-8) and graphics, *XP*[18] (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and *w*R^2 values are given for all reflections.

X-ray crystal structure analysis of 3x: A colorless, needle-like specimen of $C_{17}H_{21}NO_3$, approximate dimensions 0.030 mm x 0.037 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1229 frames were collected. The total exposure time was 19.72 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 20794 reflections to a maximum θ angle of 67.26° (0.84 Å resolution), of which 2612 were independent (average redundancy 7.961, completeness = 99.5%, R_{int} = 42.48%, R_{sig} = 16.44%) and 1110 (42.50%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 11.1765(17) Å, $\underline{b}$ = 14.187(3) Å, $\underline{c}$ = 9.571(2) Å, β = 105.211(13)°, volume = 1464.4(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 948 reflections above 20 σ(I) with 8.198° < 2θ < 130.1°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.681. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9190 and 0.9790. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{17}H_{21}NO_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 196 variables converged at R1 = 8.17%, for the observed data and wR2 = 22.29% for all data. The goodness-of-fit was 0.962. The largest peak in the final difference electron density synthesis was 0.374 $e^-/Å^3$ and the largest hole was -0.326 $e^-/Å^3$ with an RMS deviation of 0.096 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.303 g/cm^3 and F(000), 616 e^-. The hydrogen at O2 atom was refined freely. CCDC Nr.: 2178220.

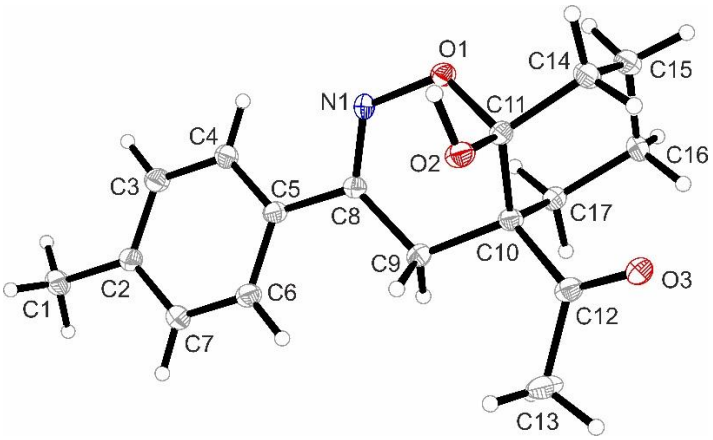


Figure S1: Crystal structure of compound **3x**.
Thermal ellipsoids are shown at 30% probability.

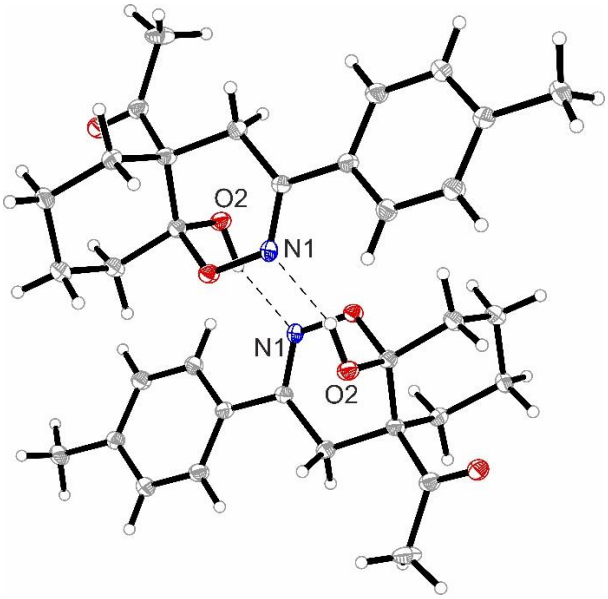


Figure S1a: Formation of dimeric units involving the O-H···N hydrogen bond interactions between the molecules of compound **3x**.
Thermal ellipsoids are shown at 30% probability.

Table S1. Non-covalent intermolecular interactions in compound **3x** (Å and deg)

D-H···*A*	*d*(*D*-H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*DHA*)
O2-H2···N1$^{\#1}$	1.00(6)	1.81(6)	2.765(6)	158.0(5)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1, -y+1, -z+1.

X-ray crystal structure analysis of 3y: A colorless, plate-like specimen of $C_{19}H_{21}NO_2$, approximate dimensions 0.050 mm x 0.074 mm x 0.148 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1763 frames were collected. The total exposure time was 22.20 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 33198 reflections to a maximum θ angle of 68.26° (0.83 Å resolution), of which 2798 were independent (average redundancy 11.865, completeness = 99.7%, R_{int} = 5.37%, R_{sig} = 2.20%) and 2405 (85.95%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.0815(2) Å, b = 11.6927(2) Å, c = 14.7988(3) Å, β = 102.0500(10)°, volume = 1536.82(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 9923 reflections above 20 σ(I) with 9.724° < 2θ < 136.5°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.886. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9100 and 0.9680. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{19}H_{21}NO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 206 variables converged at R1 = 3.37%, for the observed data and wR2 = 8.61% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.280 $e^-/Å^3$ and the largest hole was -0.195 $e^-/Å^3$ with an RMS deviation of 0.038 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.277 g/cm^3 and F(000), 632 e^-. The hydrogen at O2 atom was refined freely. CCDC Nr.: 2178219.

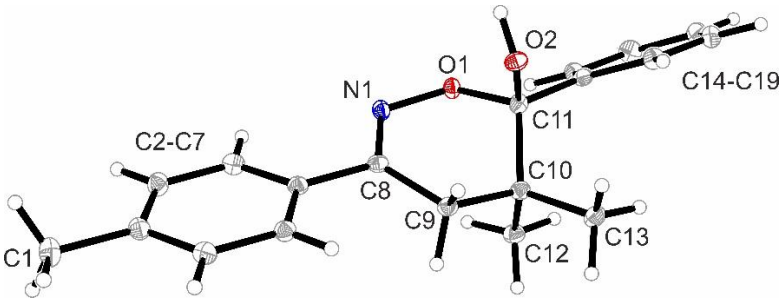


Figure S2: Crystal structure of compound **3y**.
Thermal ellipsoids are shown at 50% probability.

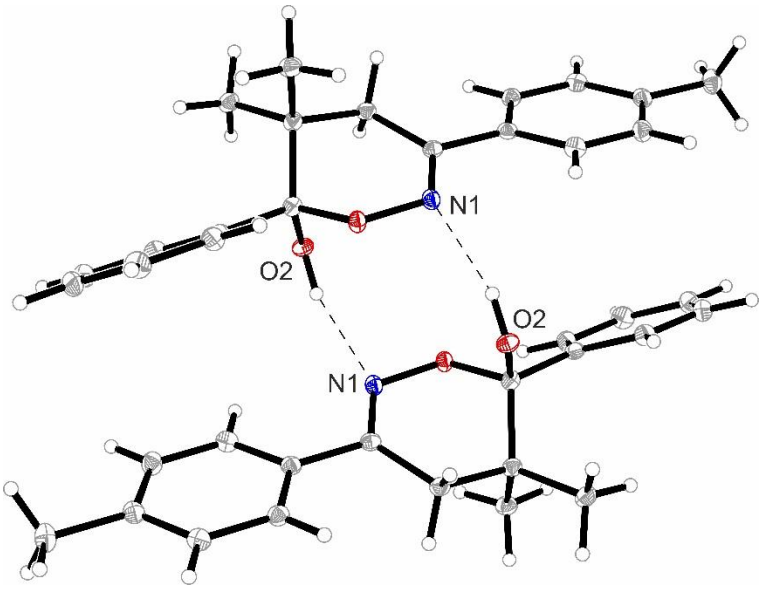


Figure S2a: Formation of dimeric units involving the O-H···N hydrogen bond interactions between the molecules of compound **3y**. Thermal ellipsoids are shown at 50% probability.

Table S2. Non-covalent intermolecular interactions in compound **3y** (Å and deg)

D-H···*A*	*d*(*D*-H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*H*A*)
O2-H2···N1$^{\#1}$	0.90(2)	1.98(2)	2.854(1)	164.5(2)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1, -y+1, -z+1.

8. DFT Calculations

8.1 Methods

All structures were optimized without geometry constraints using the PBE0 hybrid functional[19,20] and an atom-pairwise dispersion correction (D3).[21,22] A flexible triple zeta basis set (def2-TZVP)[23] was used in all calculations. The nature of the optimized stationary points was proven by the presence of either 0 (minimum) or 1 (transition structure) imaginary vibrational frequency. For the determination of the free enthalpy contributions at 298 K (G^{RRHO}), a rotor approximation was applied for vibrational modes with wave numbers below 100 cm^{-1}.[24] Electronic energies were recalculated with the hybrid meta-GGA functional PW6B95(-D3)[25] using the structures optimized with PBE0-D3. Solvation free energies (G_{solv}) for T = 298.15 K in acetone were obtained with COSMO-RS[26,27] using the COSMOtherm program package.[28] The final value for the free enthalpy of dimerization and NO dissociation in solution (ΔG_{298}) was obtained using the sum of the differences in PW6B95-D3 electronic energies, G^{RRHO}(298K), and G_{solv} as

$$\Delta G_{298} = \Delta E(\text{PW6B95-D3}) + \Delta G^{rrho} + \Delta G_{solv}$$

All quantum chemical calculations were performed with the TURBOMOLE program.[29] The preferred conformers of nitroso compounds and dimers (**1a**, **12**, **S1**-**S6**) were selected in a conformational search using semiempirical DFT method GFN2-xTB.[30,31]

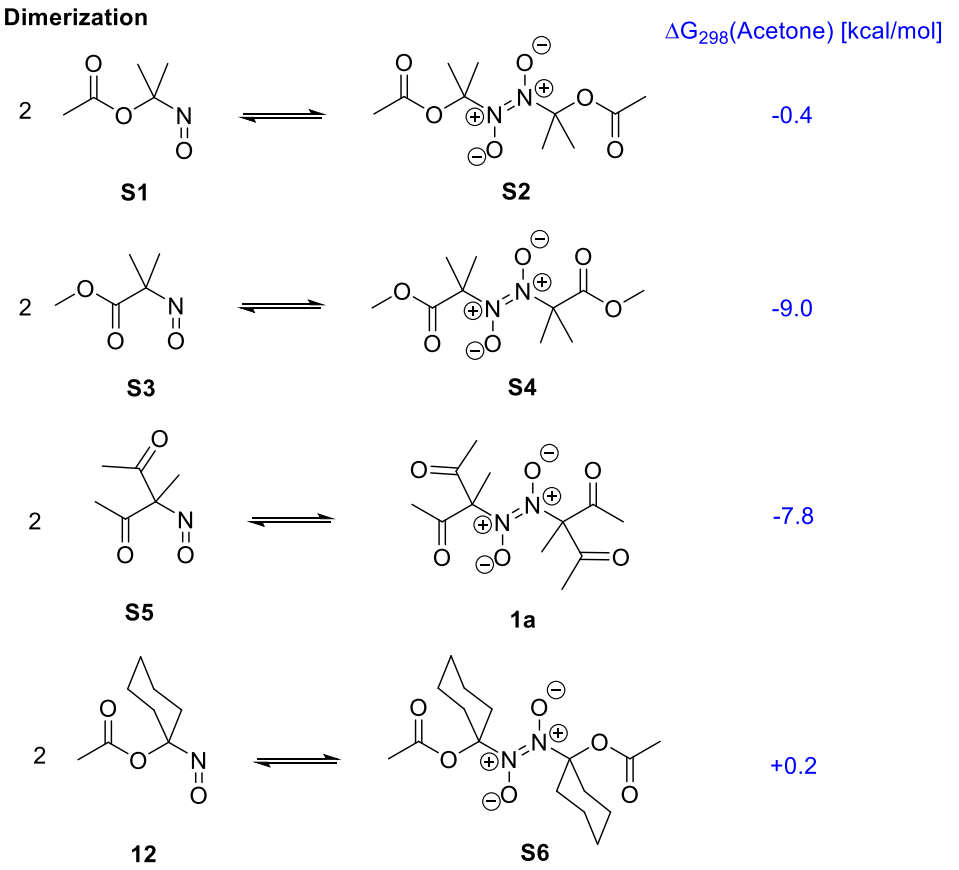
8.2 Results

Calculated electronic energies, G^{RRHO}(298K) and G_{solv} of all optimized structures are reported in Table S1. The calculated free energies of dimerization and energies / free energies of C-NO dissociation are given in Scheme S1. Optimized structures are depicted in Figure S1.

Table S1 DFT energies, thermostatistical free energy contributions at 298 K (G^{rrho}), solvation free energies (G_{solv}, COSMO-RS, 298K, Acetone) for nitroso compounds **12**, **S1**, **S3**, **S5**, dimers **1a**, **S2**, **S4**, **S6**, and NO dissociation products **S7**-**S10**.[a]

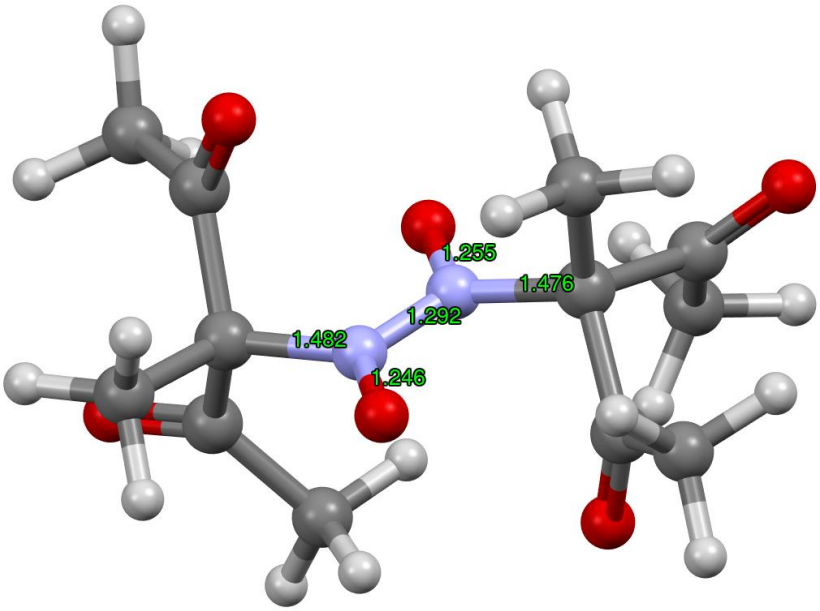
Compound	E(PBE0-D3) [E_h]	G^{rrho}(298K) [kcal/mol]	E(PW6B95-D3)[b] [E_h]	G_{solv} [kcal/mol]
1a	-1028.103292	158.409	-1030.474042	-7.720
12	-592.625763	108.323	-594.006198	-4.059
S1	-475.976861	67.542	-477.070093	-2.371
S2	-951.988785	154.172	-954.167148	-7.268
S3	-475.966941	67.769	-477.060161	-2.209
S4	-951.983961	155.626	-954.161597	-7.557
S5	-514.025786	68.944	-515.214907	-3.602
S6	-1185.284924	235.442	-1188.038061	-10.573
S7	-346.108771	61.808	-346.916897	-0.997
S8	-346.115535	62.549	-346.924475	-1.175
S9	-384.180831	64.621	-385.086517	-2.865
S10	-462.753859	103.059	-463.849317	-2.915
NO	-129.806956	-9.216	-130.093050	3.686

[a] all DFT energies were obtained with the def2-TZVP basis set
[b] single point energies with PBE0-D3 optimized molecular structures

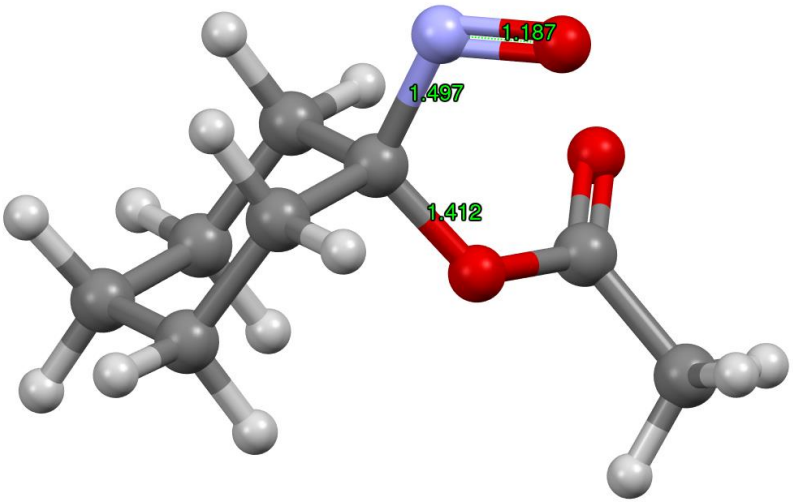


Scheme S1

Figure S1 Optimized molecular structures (PBE0-D3/def2-TZVP)

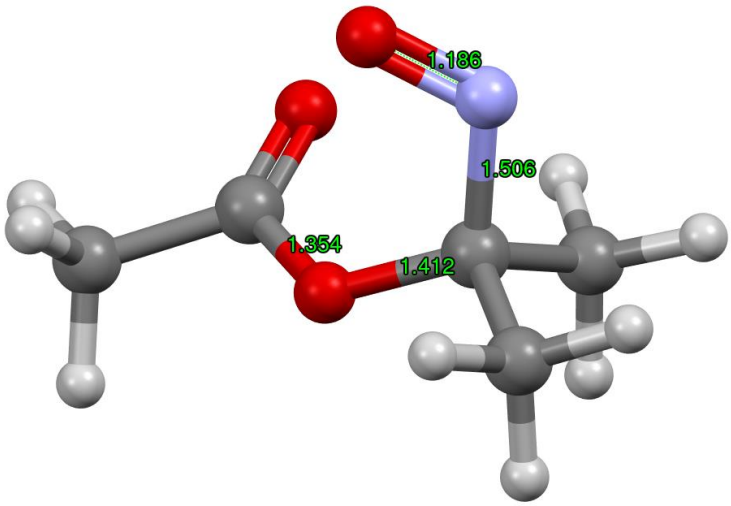


1a

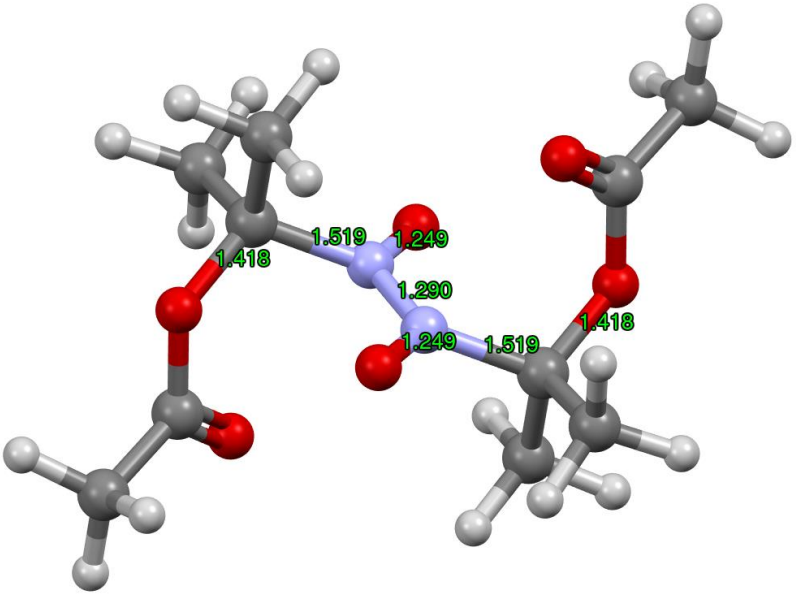


12

Figure S1 (continued) Optimized molecular structures (PBE0-D3/def2-TZVP)

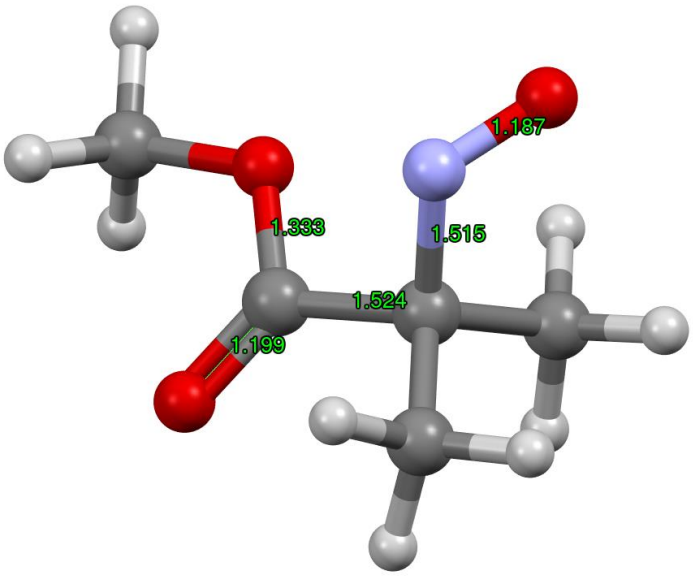


S1

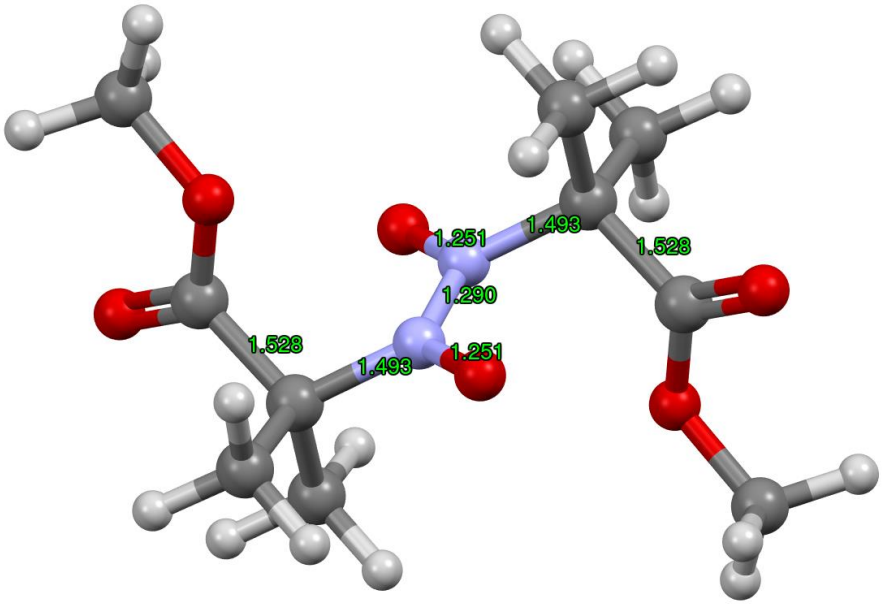


S2

Figure S1 (continued) Optimized molecular structures (PBE0-D3/def2-TZVP)

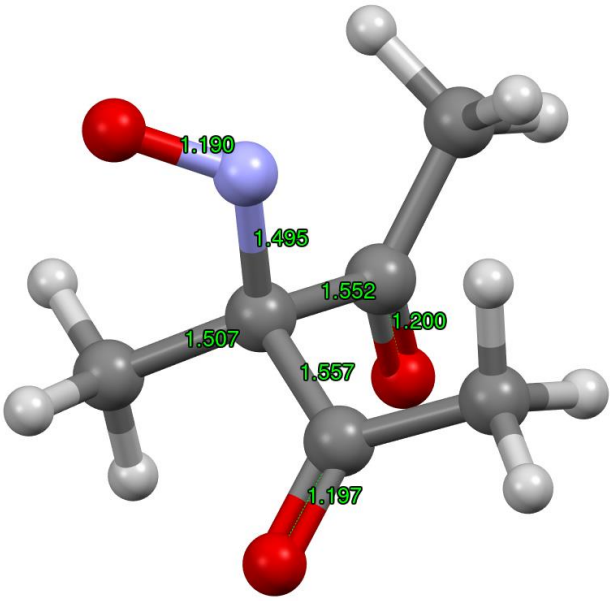


S3

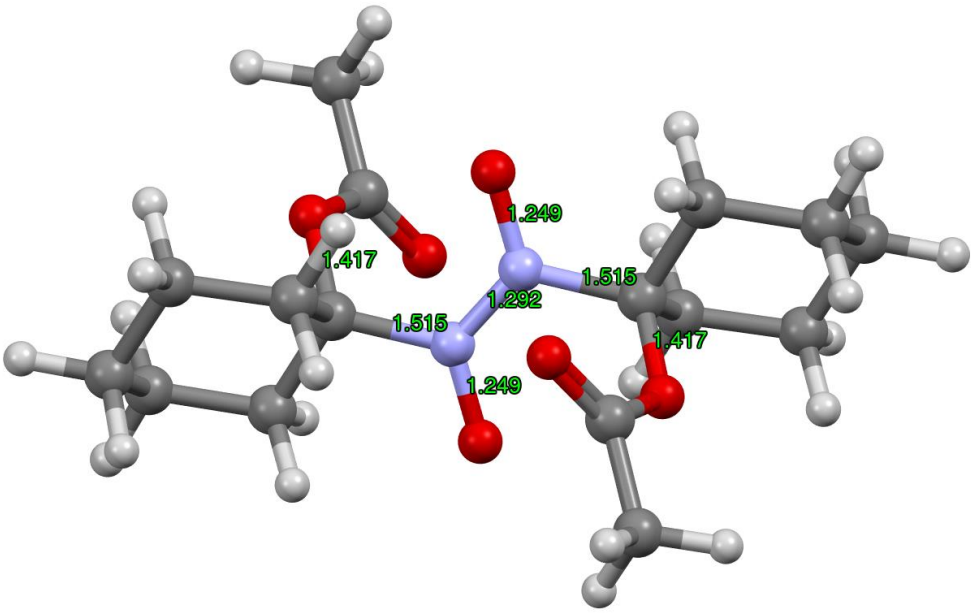


S4

Figure S1 (continued) Optimized molecular structures (PBE0-D3/def2-TZVP)

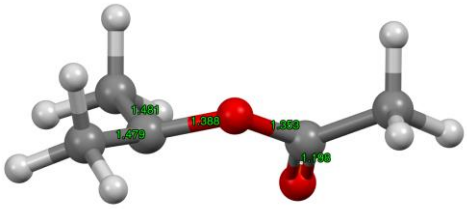


S5

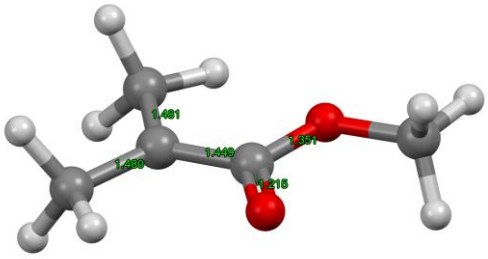


S6

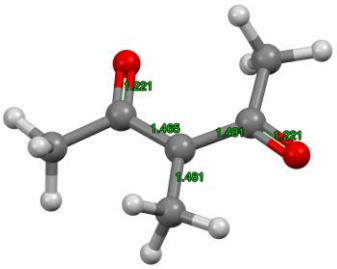
Figure S1 (continued) Optimized molecular structures (PBE0-D3/def2-TZVP)



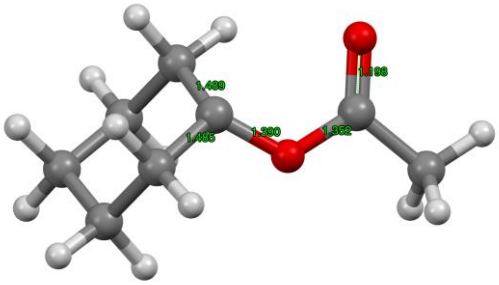
S7



S8



S9



S10

8.3 Cartesian coordinates (Å) of all DFT-optimized species

S1

```
E(PBE0-D3/def2-TZVP) = -475.9768612600 (conv)
Lowest Freq. =    62.63 cm^-1
18
S1 (003conf/opt/s000)
C    -0.8671482    0.1223472    0.0581500
N    -1.1013875    1.6083460    0.1371167
O    -0.2406264    2.2772839   -0.3285877
C    -1.8473534   -0.3467630   -1.0027842
H    -2.8583727   -0.0315741   -0.7452580
H    -1.8179312   -1.4354267   -1.0609529
H    -1.5773413    0.0692810   -1.9742421
C    -1.1856497   -0.4665880    1.4188930
H    -1.0766543   -1.5513272    1.3705658
H    -2.2195272   -0.2313890    1.6737541
H    -0.5273585   -0.0717393    2.1878989
O     0.4178518   -0.1932703   -0.4352891
C     1.5233852    0.1888053    0.2460257
O     1.5124979    0.6813948    1.3376721
C     2.7465694   -0.1055106   -0.5631851
H     2.7561695    0.5458496   -1.4395927
H     2.7303827   -1.1361949   -0.9196535
H     3.6324940    0.0764754    0.0394690
```

S2

```
E(PBE0-D3/def2-TZVP) = -951.9887851671 (conv)
Lowest Freq. =    36.36 cm^-1
36
S2 (004conf/opt/s000)
C    -1.3564331    1.3465818   -0.0948678
C    -1.7206923    2.2681968    1.0456318
H    -2.5940222    2.8388711    0.7273382
H    -1.9589530    1.6978336    1.9407922
H    -0.9042652    2.9498748    1.2692253
C    -0.9251304    2.0866003   -1.3425232
H    -0.0610465    2.7101085   -1.1139687
H    -1.7489427    2.7183137   -1.6759263
H    -0.6661003    1.3831778   -2.1312393
O    -2.4825203    0.5640553   -0.4568679
C    -2.8424201   -0.4958396    0.2887058
O    -2.3096012   -0.8038458    1.3191517
C    -3.9661276   -1.2298812   -0.3678798
H    -4.7444633   -0.5368239   -0.6879598
H    -3.5751093   -1.7244880   -1.2596501
H    -4.3686102   -1.9705299    0.3183597
N    -0.1778011    0.5040412    0.3609527
O     0.4844958    0.8916598    1.3459537
N     0.1778011   -0.5040412   -0.3609527
O    -0.4844958   -0.8916598   -1.3459537
C     1.3564331   -1.3465818    0.0948678
C     0.9251304   -2.0866003    1.3425232
H     0.6661003   -1.3831778    2.1312393
H     0.0610465   -2.7101085    1.1139687
H     1.7489427   -2.7183137    1.6759263
C     1.7206923   -2.2681968   -1.0456318
H     2.5940222   -2.8388711   -0.7273382
H     1.9589530   -1.6978336   -1.9407922
H     0.9042652   -2.9498748   -1.2692253
O     2.4825203   -0.5640553    0.4568679
```

```
C     2.8424201    0.4958396   -0.2887058
O     2.3096012    0.8038458   -1.3191517
C     3.9661276    1.2298812    0.3678798
H     4.3686102    1.9705299   -0.3183597
H     3.5751093    1.7244880    1.2596501
H     4.7444633    0.5368239    0.6879598
```

S3

```
E(PBE0-D3/def2-TZVP) = -475.9669412053 (conv)
Lowest Freq. =    38.70 cm^-1
18
S3 (005conf/opt/s002)
C     0.8116789   -0.0493619    0.1158990
N     1.0571658    1.0962348    1.0762883
O     1.6043046    2.0349198    0.5995138
C    -0.6766955   -0.3594515    0.2269632
O    -1.1462137   -1.4525236    0.3770009
O    -1.3958482    0.7552350    0.0993084
C    -2.8099776    0.5873919    0.1652392
H    -3.0951391    0.1419162    1.1186420
H    -3.1545222   -0.0565632   -0.6446865
H    -3.2309515    1.5848035    0.0669865
C     1.6227435   -1.2023079    0.6824476
H     2.6885485   -1.0085582    0.5505837
H     1.3557871   -2.1234874    0.1651106
H     1.4150820   -1.3364721    1.7445733
C     1.1676113    0.2865989   -1.3177030
H     2.2284431    0.5286536   -1.3916819
H     0.5978522    1.1442820   -1.6750765
H     0.9601310   -0.5713099   -1.9594086
```

S4

```
E(PBE0-D3/def2-TZVP) = -951.9839610660 (conv)
Lowest Freq. =    37.58 cm^-1
36
S4 (006conf/opt/s000)
C    -1.4238333   -1.2127564   -0.0986852
C    -1.8296526   -1.9822860   -1.3452026
H    -1.9838381   -1.3129922   -2.1900637
H    -1.0600550   -2.7051084   -1.6094837
H    -2.7599840   -2.5088190   -1.1277426
C    -1.1409042   -2.1389212    1.0709435
H    -2.0536164   -2.6786668    1.3197120
H    -0.8266812   -1.5757316    1.9478227
C     1.8296526    1.9822860    1.3452026
C     1.4238333    1.2127564    0.0986852
C     1.1409042    2.1389212   -1.0709435
H     0.3649347    2.8512440   -0.7873366
H     2.0536164    2.6786668   -1.3197120
H     0.8266812    1.5757316   -1.9478227
C     2.5462876    0.2306665   -0.2344727
O     3.3988657    0.4461137   -1.0465418
O     2.5307820   -0.8135588    0.5949888
C     3.5402442   -1.7892666    0.3556687
H     3.4334762   -2.1966413   -0.6502972
H     3.3858112   -2.5653510    1.1014412
H     4.5319600   -1.3482895    0.4605634
N     0.1759773    0.4579587    0.4186607
O    -0.5339030    0.7499388    1.4060224
N    -0.1759773   -0.4579587   -0.4186607
O     0.5339030   -0.7499388   -1.4060224
```

```
H     2.7599840    2.5088190    1.1277426
H     1.9838381    1.3129922    2.1900637
H     1.0600550    2.7051084    1.6094837
H    -0.3649347   -2.8512440    0.7873366
C    -2.5462876   -0.2306665    0.2344727
O    -3.3988657   -0.4461137    1.0465418
O    -2.5307820    0.8135588   -0.5949888
C    -3.5402442    1.7892666   -0.3556687
H    -3.4334762    2.1966413    0.6502972
H    -4.5319600    1.3482895   -0.4605634
H    -3.3858112    2.5653510   -1.1014412
```

S5

```
E(PBE0-D3/def2-TZVP) = -514.0257859907 (conv)
Lowest Freq. =    28.92 cm^-1
19
S5 (013conf/opt/s001)
C    -0.2343889   -0.5108125    0.2740515
N    -0.0666019   -1.1871823   -1.0485226
O    -0.2274481   -2.3662874   -1.0237765
C    -0.4998261   -1.4436725    1.4272410
H     0.3071701   -2.1718951    1.5213755
H    -0.5676432   -0.8605606    2.3429731
H    -1.4359003   -1.9783120    1.2778262
C    -1.4085986    0.4892052    0.0593220
O    -2.3765956    0.4167492    0.7598732
C    -1.2493347    1.5043288   -1.0290820
H    -0.9356641    1.0187224   -1.9560079
H    -0.4671791    2.2170338   -0.7500298
H    -2.1856613    2.0399663   -1.1704287
C     1.0338061    0.3436962    0.5413542
O     1.1233933    0.9157714    1.5928403
C     2.1015938    0.3975030   -0.5063935
H     2.8919549    1.0721659   -0.1835255
H     1.6888346    0.7101682   -1.4672394
H     2.5080889   -0.6065879   -0.6618509
```

1a

```
E(PBE0-D3/def2-TZVP) = -1028.103292113 (conv)
Lowest Freq. =    32.83 cm^-1
38
1a (012conf/opt/s000)
C    -1.9078232    0.1764399    0.4921103
N    -0.4451751    0.3387573    0.6636785
N     0.2605006    0.1160108   -0.3958718
O    -0.2919869   -0.2018698   -1.4772269
C     1.6968324    0.4397171   -0.2944380
C     1.8189191    1.9506113   -0.3684941
H     1.3749459    2.2996793   -1.3010411
H     2.8685959    2.2337076   -0.3675109
H     1.3027938    2.4188106    0.4679554
C     2.2515916   -0.2316745    0.9949007
O     1.9888753   -1.3877447    1.2049776
C     3.2064411    0.5627135    1.8205464
H     4.0715272    0.8445798    1.2130978
H     3.5307756   -0.0403729    2.6656029
H     2.7335331    1.4808956    2.1698741
C     2.5047602   -0.2374178   -1.4371514
O     3.4493679    0.3670252   -1.8701693
C     2.1609276   -1.6249128   -1.8721123
H     1.3391237   -1.5731266   -2.5875818
```

```
H     1.8298166   -2.2288187   -1.0272107
H     3.0364953   -2.0653122   -2.3460869
O     0.0755180    0.6872351    1.7409988
C    -2.5941082    0.7219564    1.7368325
H    -2.2865357    0.1702519    2.6245688
H    -2.3386866    1.7720623    1.8653187
H    -3.6697915    0.6118298    1.6016750
C    -2.2920595   -1.3100421    0.3623547
O    -3.4430541   -1.5746238    0.1336343
C    -1.2536829   -2.3548014    0.6148522
H    -0.6384122   -2.1191736    1.4859084
H    -0.5819924   -2.4019142   -0.2458477
H    -1.7467152   -3.3161348    0.7411730
C    -2.2976168    1.0985395   -0.7064431
O    -1.8228221    2.2032236   -0.7022257
C    -3.2900912    0.6347961   -1.7162369
H    -4.2387981    0.3900200   -1.2357716
H    -2.9366106   -0.2772001   -2.1981162
H    -3.4253786    1.4262774   -2.4505236
```

12

```
E(PBE0-D3/def2-TZVP) = -592.6257629343 (conv)
Lowest Freq. =    53.45 cm^-1
25
12 (014conf/opt/s000)
C    -0.1913820   -0.8885002   -0.1612970
N    -0.8159514   -2.2129783   -0.4705215
O    -1.9094368   -2.3689609   -0.0357929
C     0.4291404   -0.3455710   -1.4440720
H     1.0314317   -1.1574320   -1.8638092
H    -0.3554062   -0.1135694   -2.1612529
C     1.3071683    0.8640279   -1.1620009
H     0.6851767    1.6900755   -0.8001385
H     1.7589606    1.2034502   -2.0975374
C     2.3829113    0.5475915   -0.1337056
H     3.0750461   -0.1934135   -0.5522589
H     2.9745503    1.4403289    0.0857644
C     1.7695242   -0.0023965    1.1451062
H     2.5501188   -0.2828733    1.8573043
C     0.8919078   -1.2134308    0.8663078
H     1.4920518   -2.0366973    0.4683611
H     0.4042310   -1.5690293    1.7775771
H     1.1655102    0.7731567    1.6265680
O    -1.0861864   -0.0078442    0.4857223
C    -2.2109942    0.4094620   -0.1389806
O    -2.4706044    0.1965226   -1.2887109
C    -3.0649791    1.1819351    0.8162688
H    -3.9120236    1.6066167    0.2840457
H    -2.4822032    1.9695003    1.2962287
H    -3.4185616    0.5100294    1.6008239
```

S6

```
E(PBE0-D3/def2-TZVP) = -1185.284924418 (conv)
Lowest Freq. =    27.32 cm^-1
50
S6 (015conf/opt/s000)
C     1.9077193    0.0011408    0.1005883
O     2.1902042   -1.3079207   -0.3641224
C     1.6394936   -2.3788115    0.2324590
O     0.9520068   -2.3227168    1.2146602
C     1.9862714   -3.6217312   -0.5215929
```

```
H     1.6907589   -4.4938566    0.0558901
H     1.4473962   -3.6052918   -1.4713609
H     3.0527824   -3.6514178   -0.7464252
C     2.7134895    0.2946565    1.3545415
C     4.2033753    0.2402099    1.0431950
C     4.5732998    1.2030071   -0.0758989
C     3.7505132    0.9281902   -1.3255856
C     2.2575746    0.9571907   -1.0302580
H     1.9519105    1.9566308   -0.7079968
H     1.6680945    0.6966556   -1.9087492
H     3.9714980    1.6642097   -2.1028426
H     4.0173618   -0.0511003   -1.7347756
H     5.6408719    1.1310653   -0.3013613
H     4.3907112    2.2313148    0.2595449
H     4.7605807    0.4776586    1.9529014
H     4.4879281   -0.7782605    0.7593384
H     2.4389905    1.2882645    1.7082210
H     2.4318309   -0.4131089    2.1342597
N     0.4411285    0.1952604    0.4292823
N    -0.4411285   -0.1952604   -0.4292823
O    -0.1376579   -0.8381531   -1.4562327
C    -1.9077193   -0.0011408   -0.1005883
O    -2.1902042    1.3079207    0.3641224
C    -1.6394936    2.3788115   -0.2324590
O    -0.9520068    2.3227168   -1.2146602
C    -1.9862714    3.6217312    0.5215929
H    -1.6907589    4.4938566   -0.0558901
H    -1.4473962    3.6052918    1.4713609
H    -3.0527824    3.6514178    0.7464252
C    -2.2575746   -0.9571907    1.0302580
C    -3.7505132   -0.9281902    1.3255856
C    -4.5732998   -1.2030071    0.0758989
C    -4.2033753   -0.2402099   -1.0431950
C    -2.7134895   -0.2946565   -1.3545415
H    -2.4389905   -1.2882645   -1.7082210
H    -2.4318309    0.4131089   -2.1342597
H    -4.7605807   -0.4776586   -1.9529014
H    -4.4879281    0.7782605   -0.7593384
H    -5.6408719   -1.1310653    0.3013613
H    -4.3907112   -2.2313148   -0.2595449
H    -3.9714980   -1.6642097    2.1028426
H    -4.0173618    0.0511003    1.7347756
H    -1.9519105   -1.9566308    0.7079968
H    -1.6680945   -0.6966556    1.9087492
O     0.1376579    0.8381531    1.4562327
```

S7

```
E(PBE0-D3/def2-TZVP) = -346.1087707805 (conv)
Lowest Freq. =    49.40 cm^-1
16
S7 (009c1/opt)
C    -0.9426323    0.1112709    0.0351503
C    -1.9566192    0.0303605   -1.0381823
H    -2.9315167    0.3463911   -0.6642172
H    -2.0660728   -0.9970093   -1.4200996
H    -1.6836074    0.6631257   -1.8853647
C    -1.2138193   -0.3657355    1.4108464
H    -1.0953797   -1.4586745    1.4811442
H    -2.2421469   -0.1292191    1.6872845
H    -0.5414072    0.0911873    2.1365564
O     0.3407665   -0.0590962   -0.4647603
C     1.4007078    0.4948831    0.1674159
```

```
O     1.3151274    1.2065090    1.1273566
C     2.6733218    0.0960457   -0.5132027
H     2.6331889    0.3681600   -1.5692875
H     2.7977656   -0.9873801   -0.4612876
H     3.5123235    0.5891813   -0.0293526
```

S8

```
E(PBE0-D3/def2-TZVP) = -346.1155345185 (conv)
Lowest Freq. =    47.30 cm^-1
16
S8 (010c1/opt)
C     0.8341831   -0.2531226   -0.0275780
C    -0.5293238   -0.1648273    0.4535191
O    -0.9660110   -0.7784951    1.4066529
O    -1.2933708    0.6819266   -0.2704747
C    -2.6368213    0.7984801    0.1709419
H    -2.6771030    1.1695326    1.1965351
H    -3.1425745   -0.1678436    0.1325847
H    -3.1137773    1.5036672   -0.5067049
C     1.7630904   -1.1682729    0.6717396
H     2.6265146   -0.6175142    1.0642722
H     2.1684721   -1.9140105   -0.0230412
H     1.2661769   -1.6805221    1.4933689
C     1.3162886    0.5082783   -1.2033405
H     2.2765839    0.9872234   -0.9832446
H     0.6054629    1.2645577   -1.5275237
H     1.5022092   -0.1690577   -2.0477067
```

S9

```
E(PBE0-D3/def2-TZVP) = -384.1808312140 (conv)
Lowest Freq. =    22.06 cm^-1
17
S9 (017c1/opt)
C    -0.1643878    0.2917220   -0.2007304
C     0.2147855    1.3980350   -1.1092822
H     0.9755935    2.0414921   -0.6561234
H     0.6559079    1.0105254   -2.0350869
H    -0.6600674    1.9923880   -1.3621447
C    -1.6047731    0.1372212    0.1066873
O    -2.3876101    0.9204427   -0.4074158
C    -2.1073263   -0.9413990    1.0174173
H    -1.8374829   -1.9280437    0.6385128
H    -3.1888767   -0.8418424    1.0918479
H    -1.6449475   -0.8674453    2.0025402
C     0.8696896   -0.5957837    0.3372227
O     0.6033369   -1.5276622    1.0806280
C     2.3000352   -0.3263078   -0.0537040
H     2.9333983   -1.0931700    0.3869371
H     2.6202230    0.6566200    0.3021383
H     2.4225019   -0.3267923   -1.1394442
```

S10

```
E(PBE0-D3/def2-TZVP) = -462.7538594888 (conv)
Lowest Freq. =    48.21 cm^-1
23
S10 (016c1/opt)
C     0.0131789   -0.8754621   -0.1046043
C     0.5496312   -0.2423023   -1.3408019
H     1.3071224   -0.9115569   -1.7642407
H    -0.2277907   -0.1229854   -2.0942471
```

```
C     1.2127860    1.1002824   -0.9941207
H     0.4390790    1.8091295   -0.6771868
H     1.6804452    1.5229951   -1.8882222
C     2.2376784    0.9390444    0.1210968
H     3.0607616    0.3066638   -0.2357057
H     2.6774616    1.9090111    0.3709467
C     1.6245297    0.3079510    1.3643735
H     2.3827007    0.1667551    2.1402313
C     0.9635852   -1.0375188    1.0248780
H     1.7430510   -1.7470522    0.7244625
H     0.4542858   -1.4560960    1.8955634
H     0.8651644    0.9802985    1.7789122
O    -1.2475695   -0.4884768    0.3334161
C    -2.3279048   -0.7084533   -0.4491319
O    -2.2899066   -1.2774113   -1.5028347
C    -3.5572290   -0.1504638    0.1987457
H    -4.4230327   -0.3661193   -0.4217898
H    -3.4516329    0.9283450    0.3294060
H    -3.6863951   -0.5865778    1.1908535
```

NO

```
E(PBE0-D3/def2-TZVP) = -129.8069561517 (conv)
Lowest Freq. =  2030.61 cm^-1
2
NO (011c1/opt)
N     0.0000000    0.0000000    0.5698763
O     0.0000000    0.0000000   -0.5698763
```

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[28] COSMOtherm, Release 19; © **2019** COSMOlogic GmbH & Co. KG, a Dassault Systèmes company.

[29] TURBOMOLE V7.5.1 (2021), a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from *http://www.turbomole.com*.

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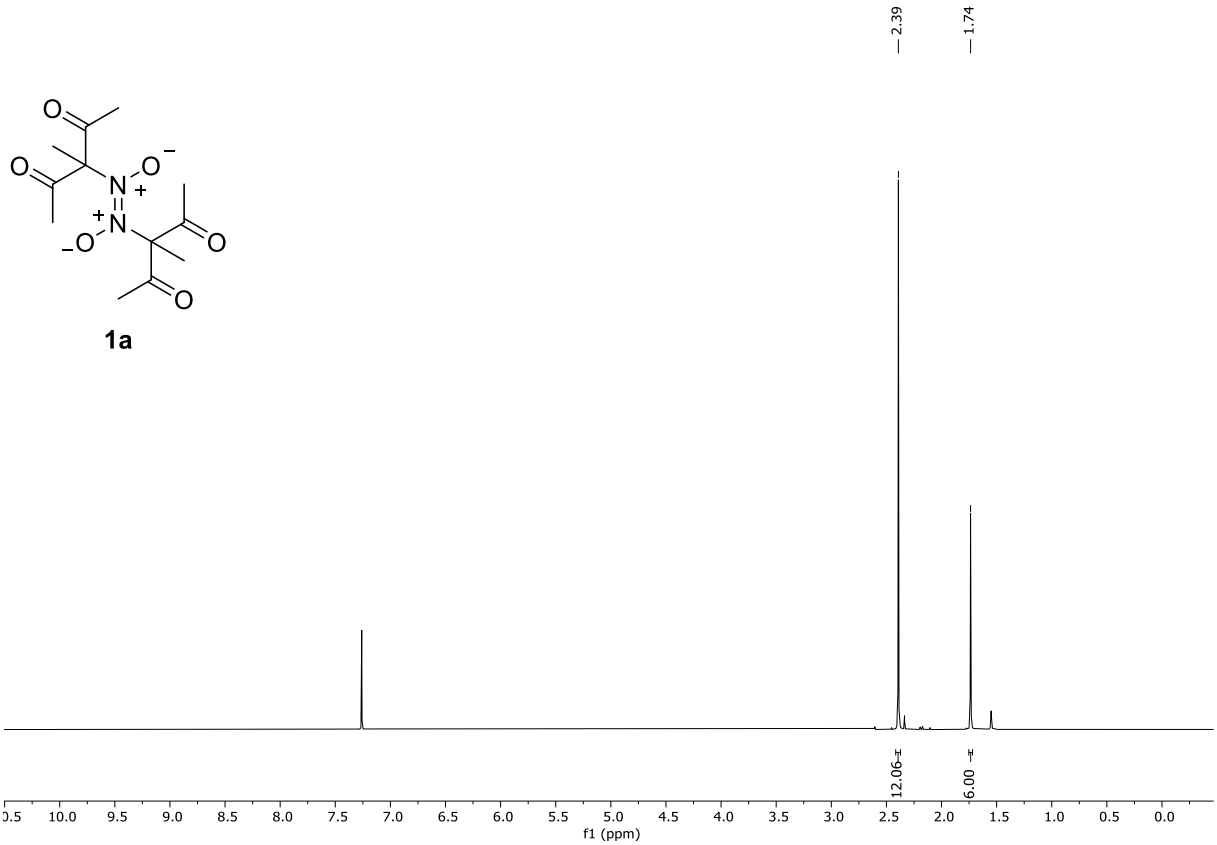
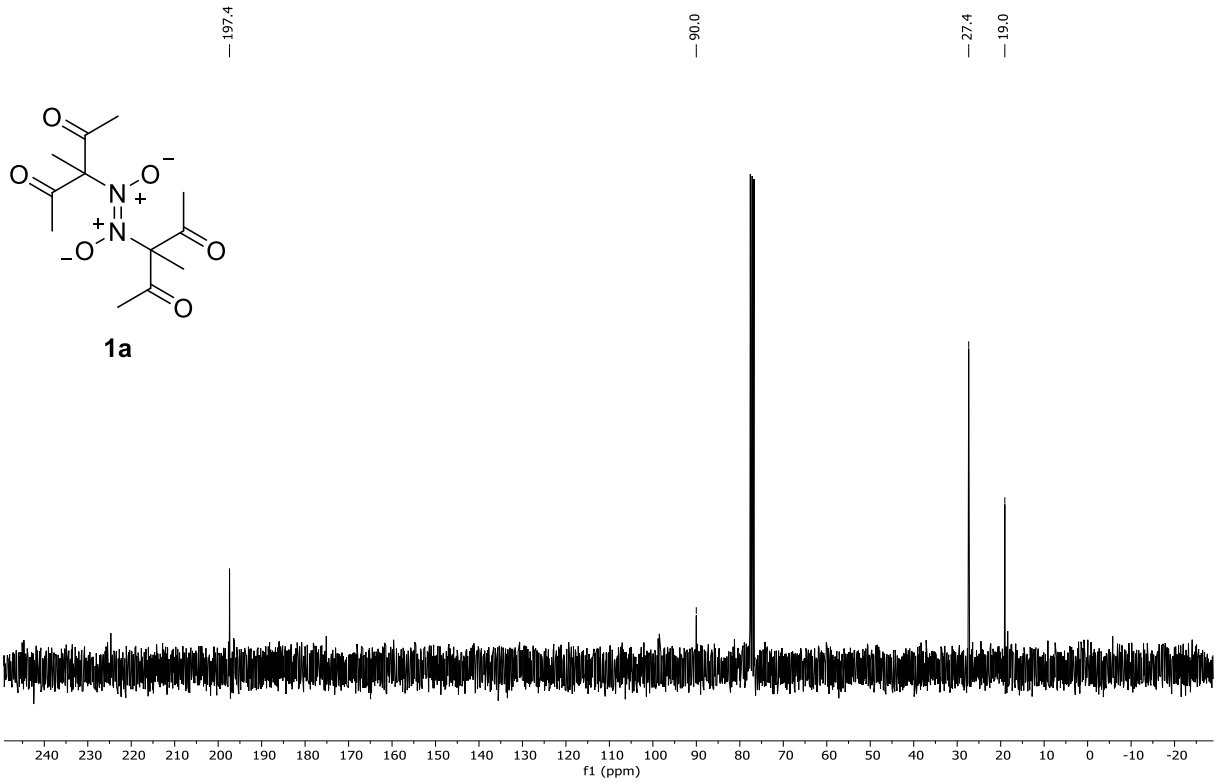
10. NMR spectra of novel compounds

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



1a

^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



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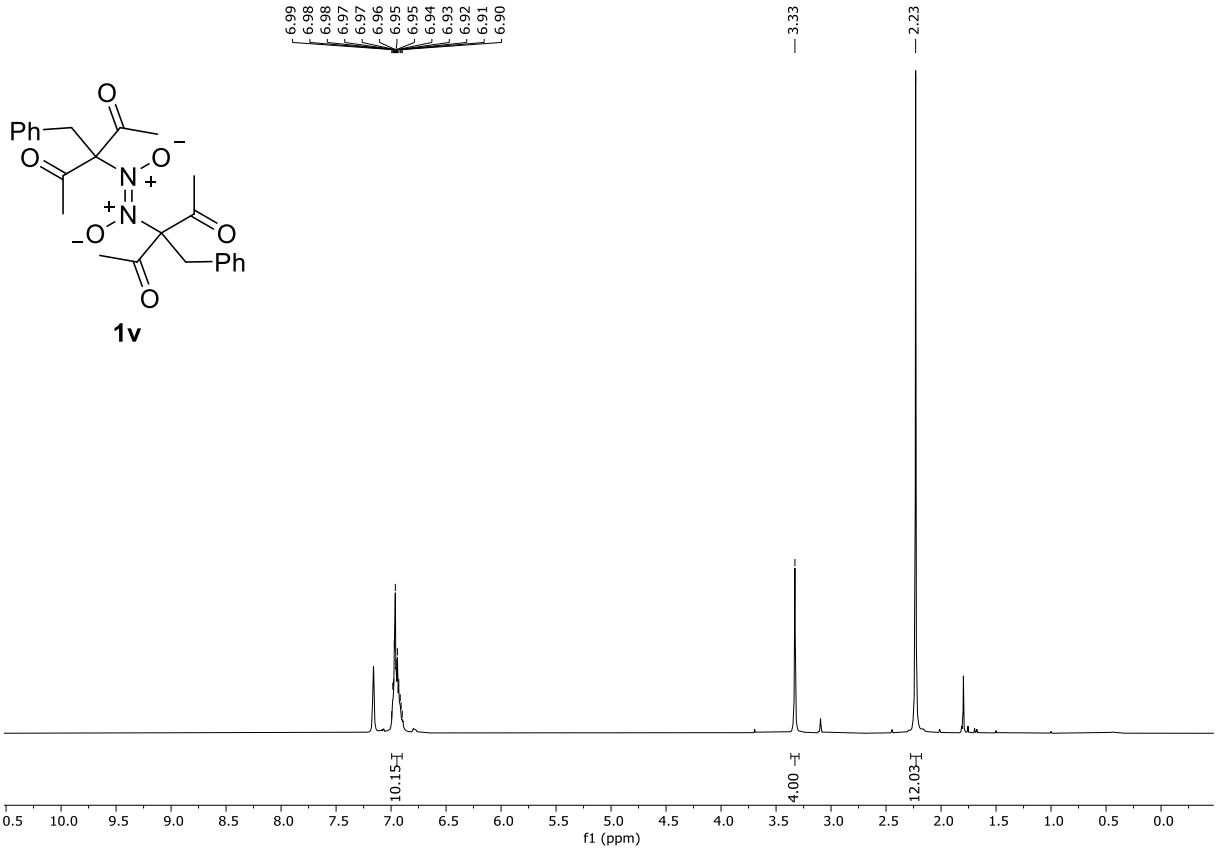
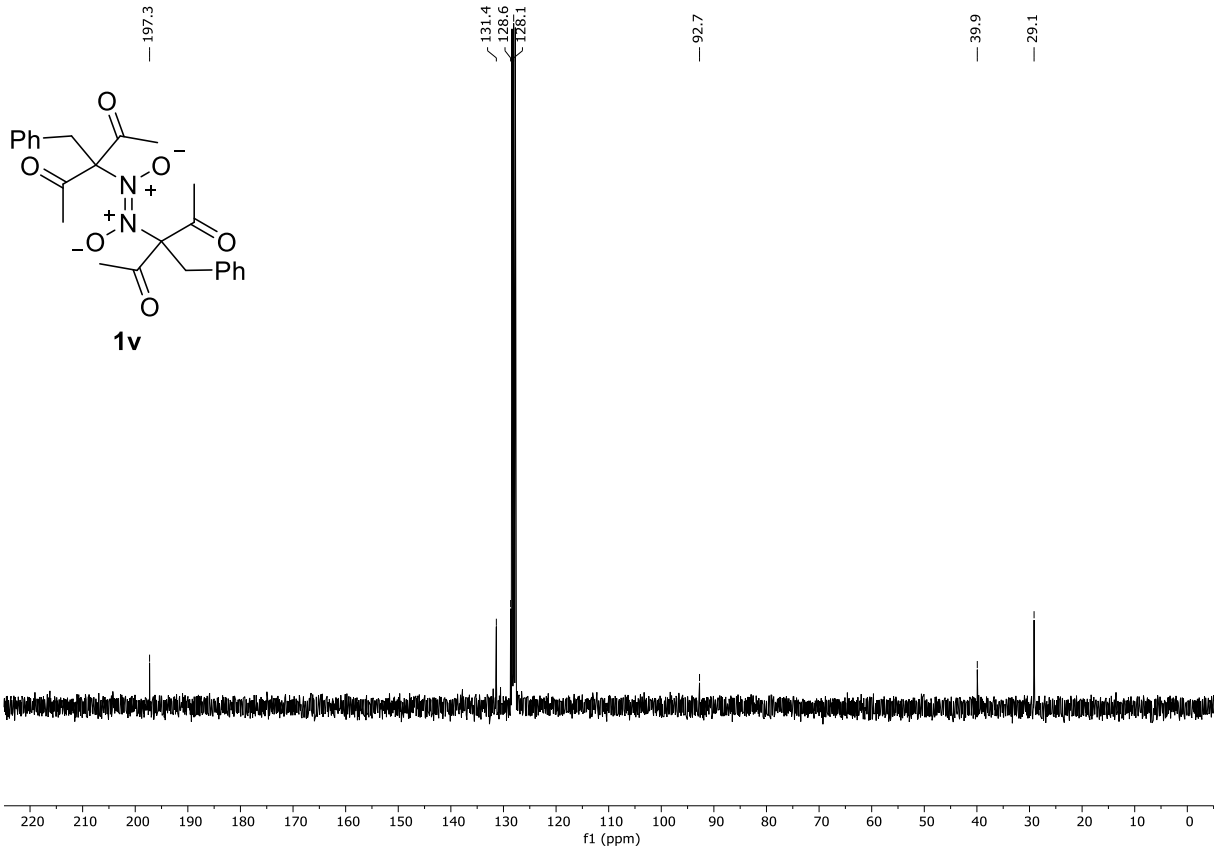
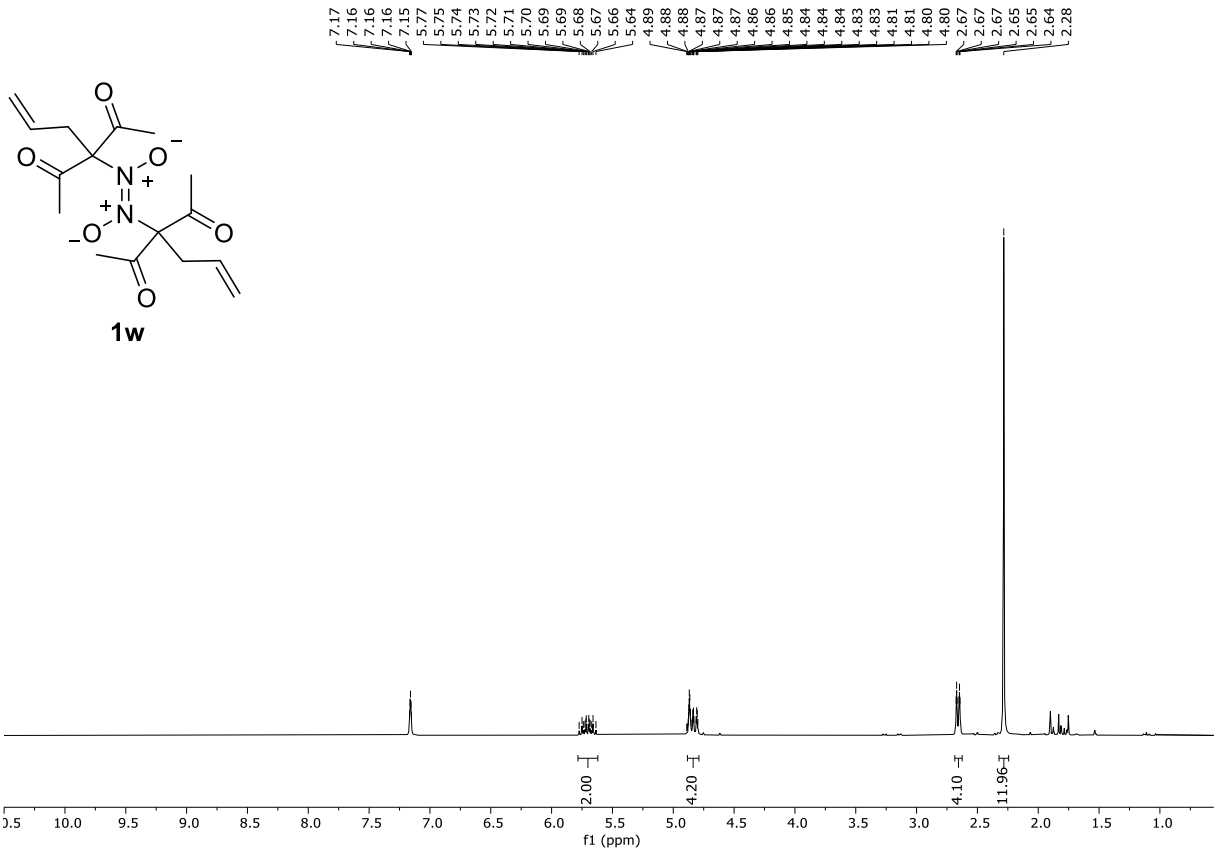
^{1}H-NMR (300 MHz, C_6D_6, 299 K)



^{13}C-NMR (75 MHz, C_6D_6, 299 K)



^{1}H-NMR (300 MHz, C_6D_6, 299 K)



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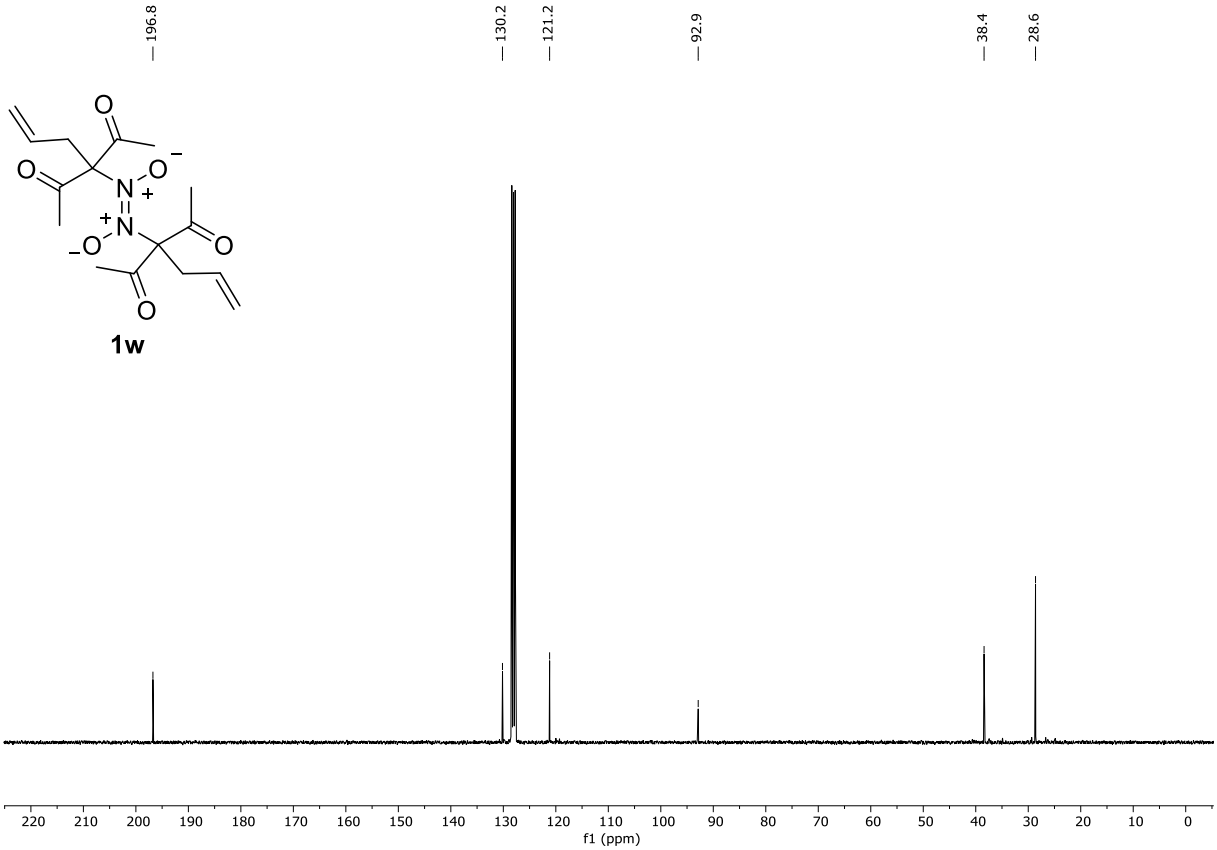

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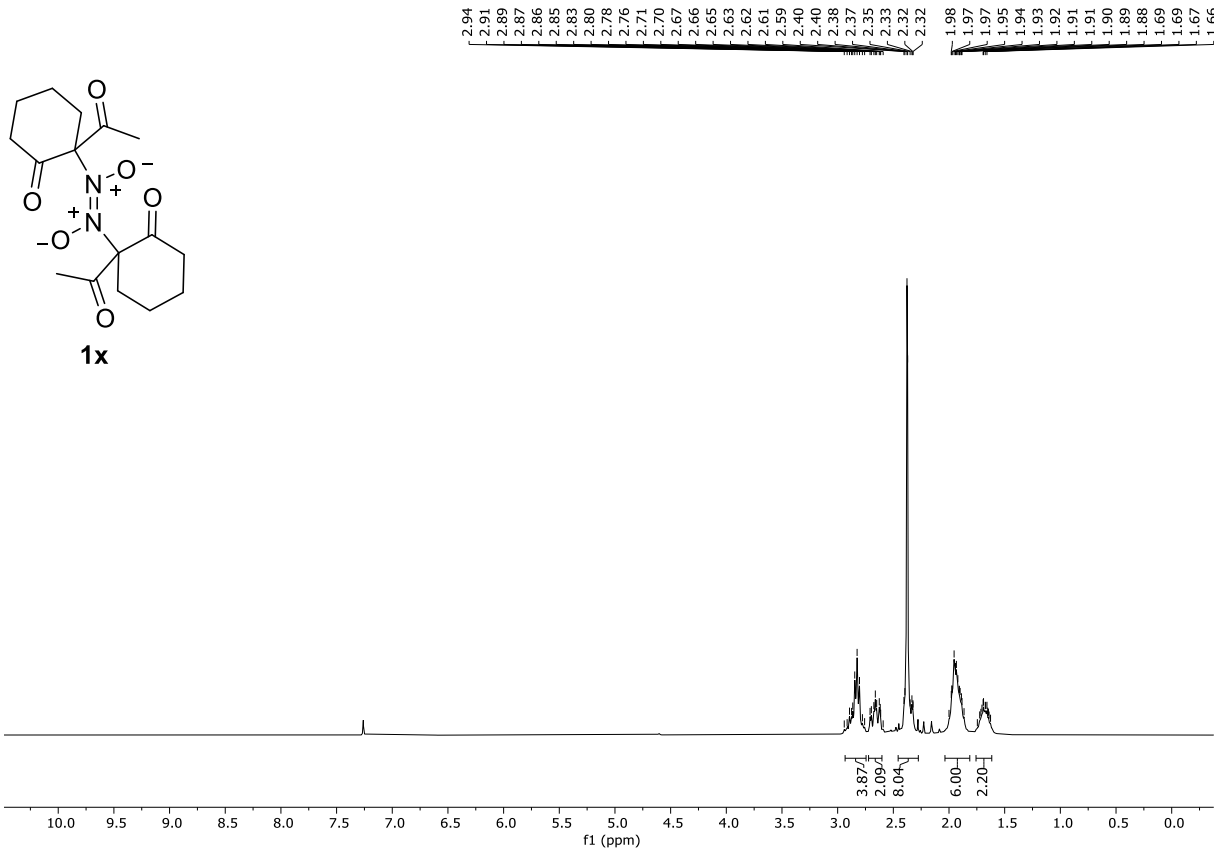
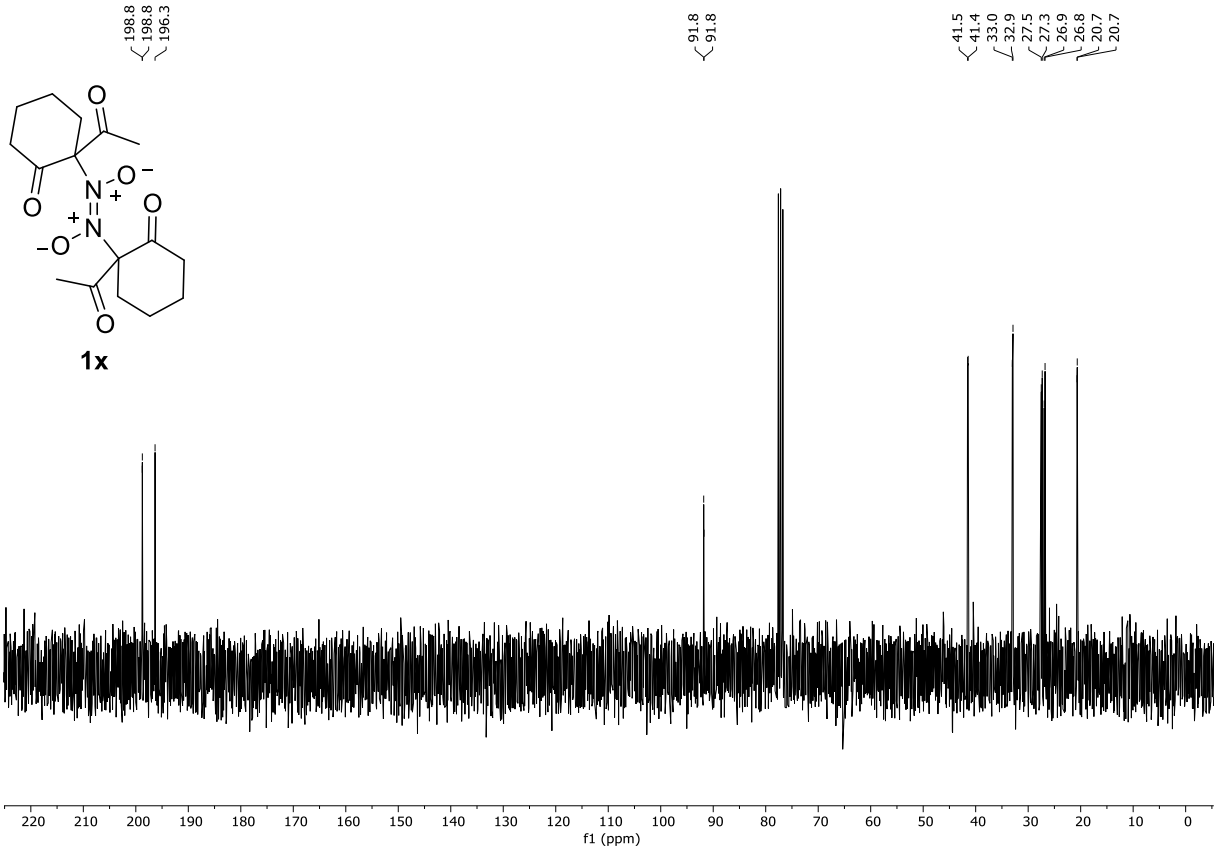
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



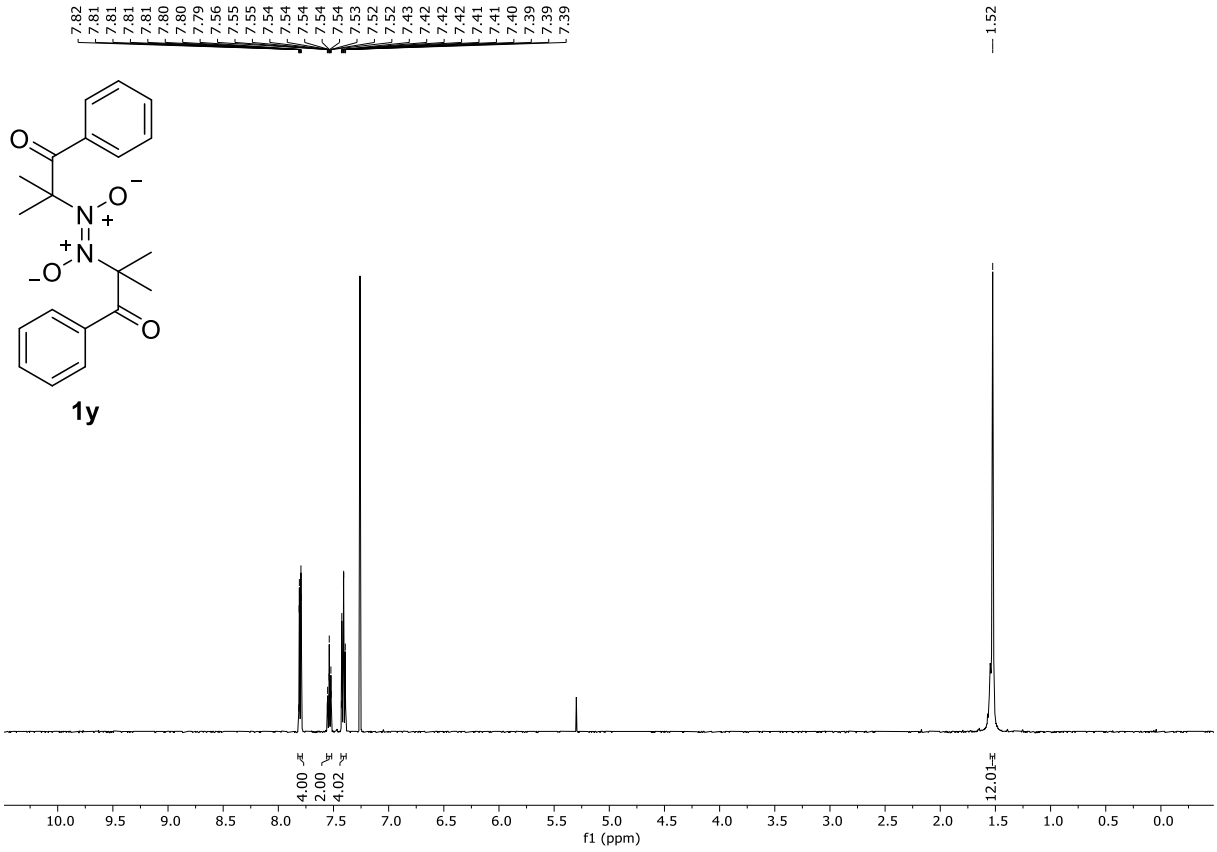
1x

^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



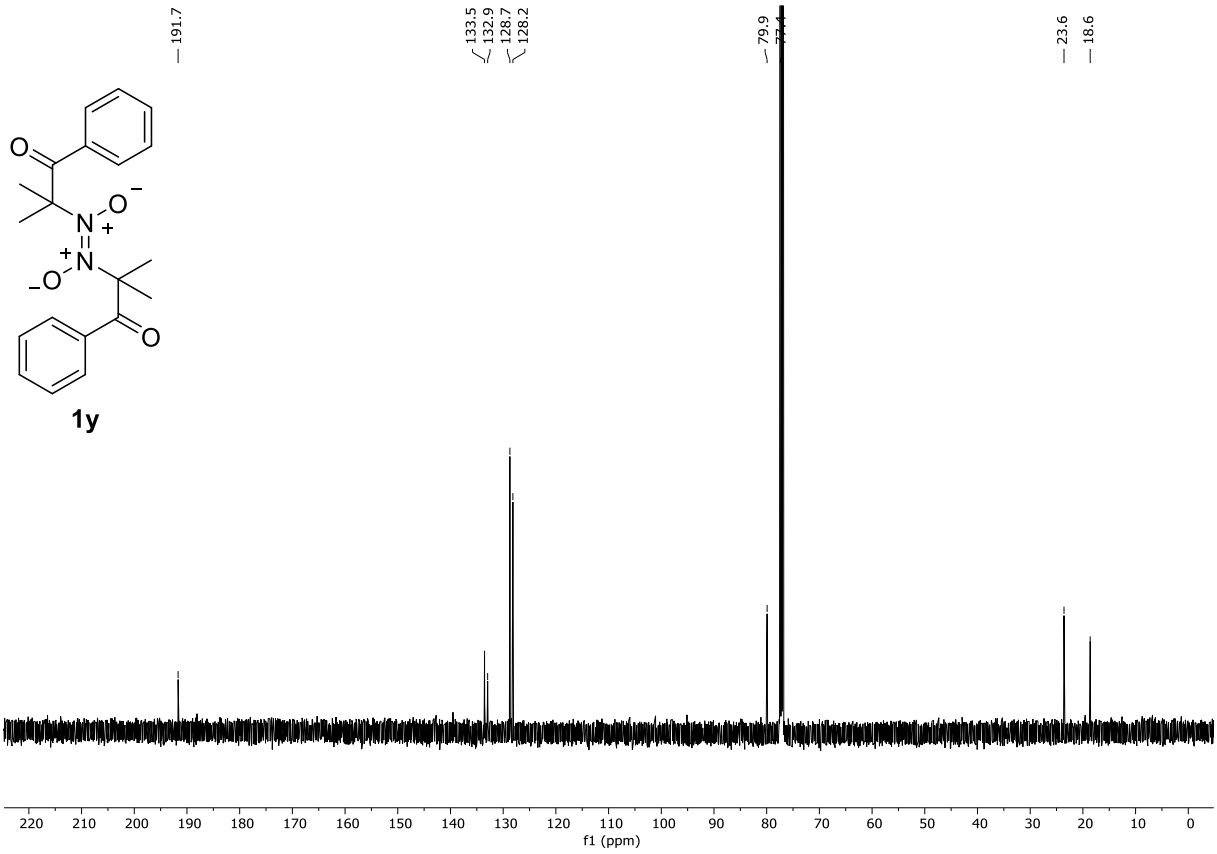
1x

^{1}H-NMR (500 MHz, $CDCl_3$, 299 K)



1y

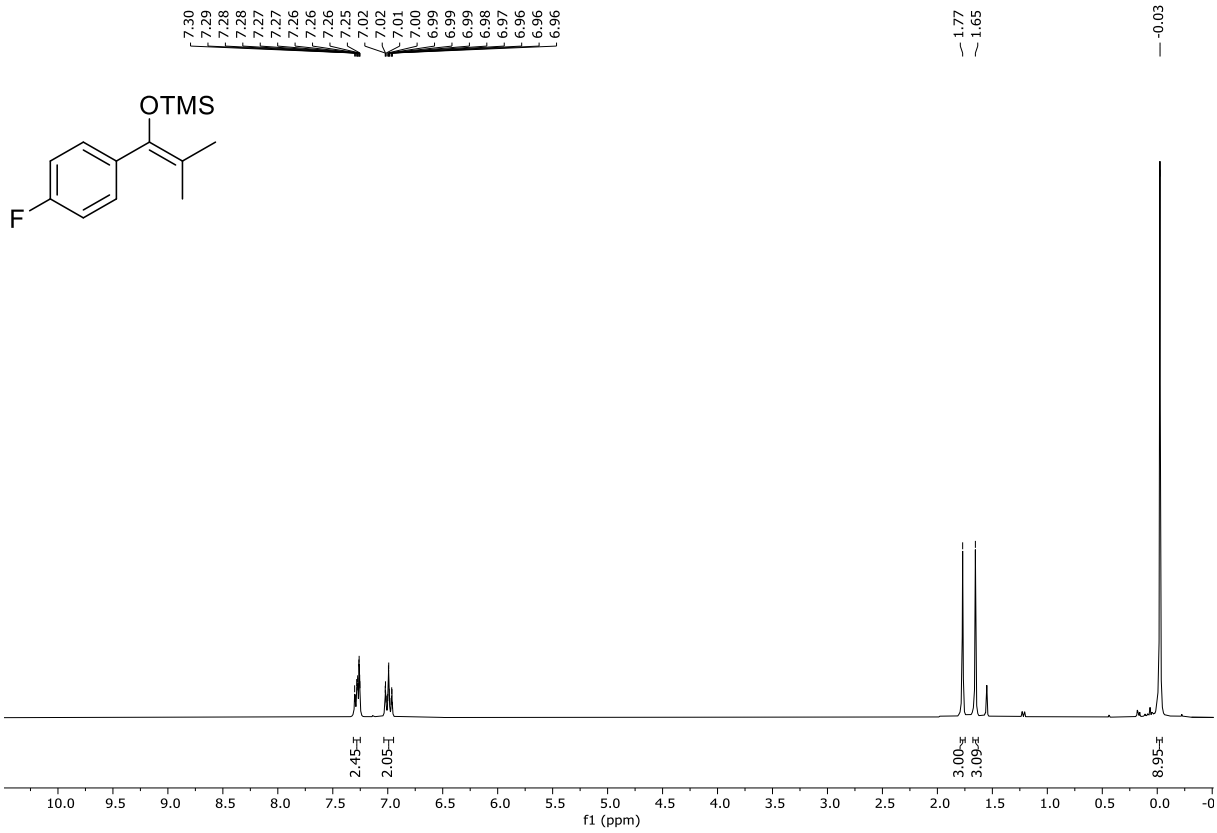
^{13}C-NMR (126 MHz, $CDCl_3$, 223 K)



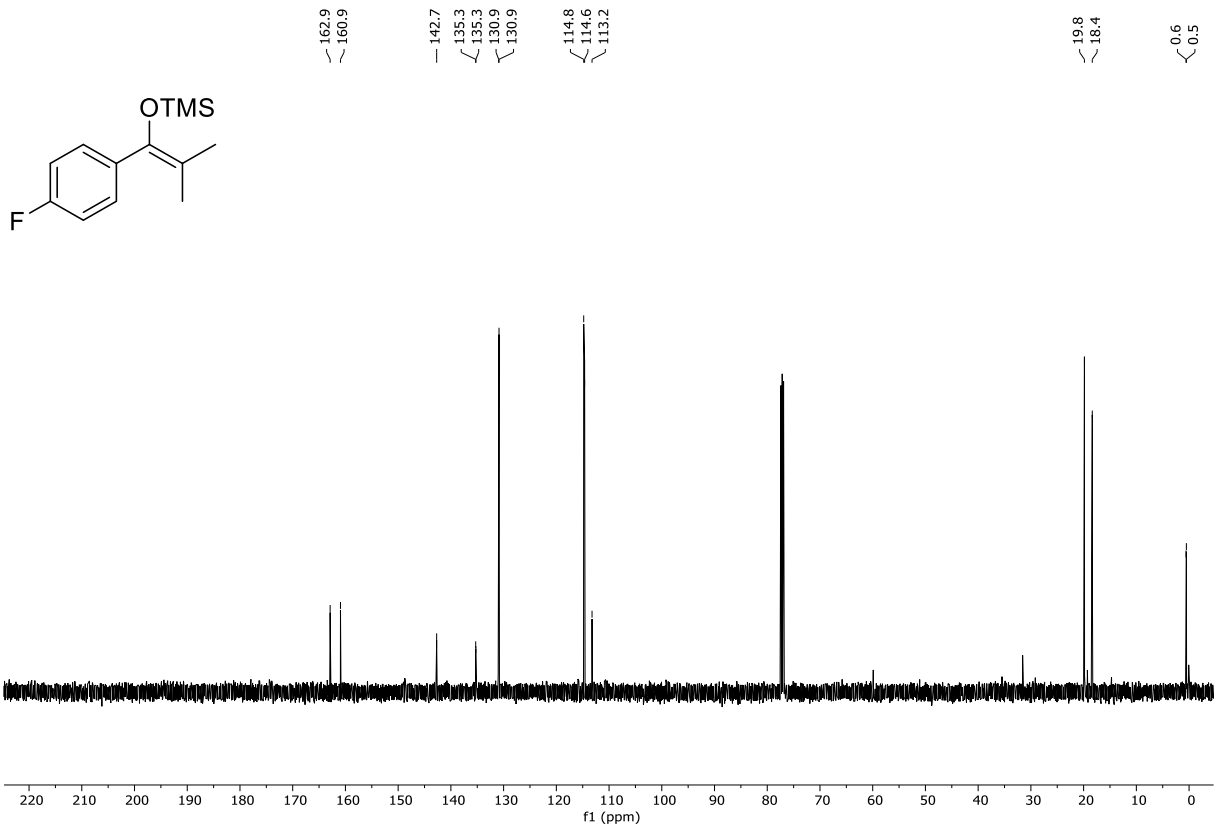
1y

((1-(4-fluorophenyl)-2-methylprop-1-en-1-yl)oxy)Trimethylsilane

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



^{13}C-NMR (126 MHz, $CDCl_3$, 299 K)



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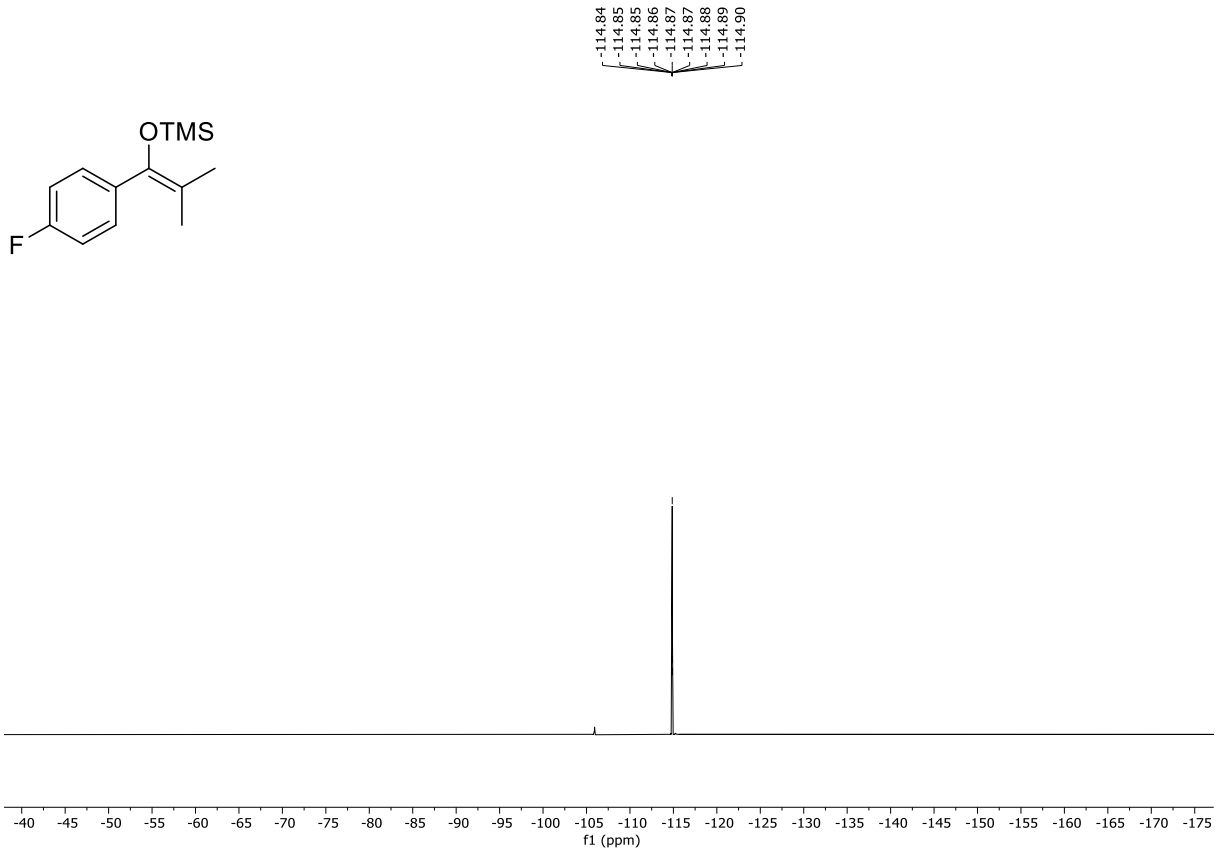
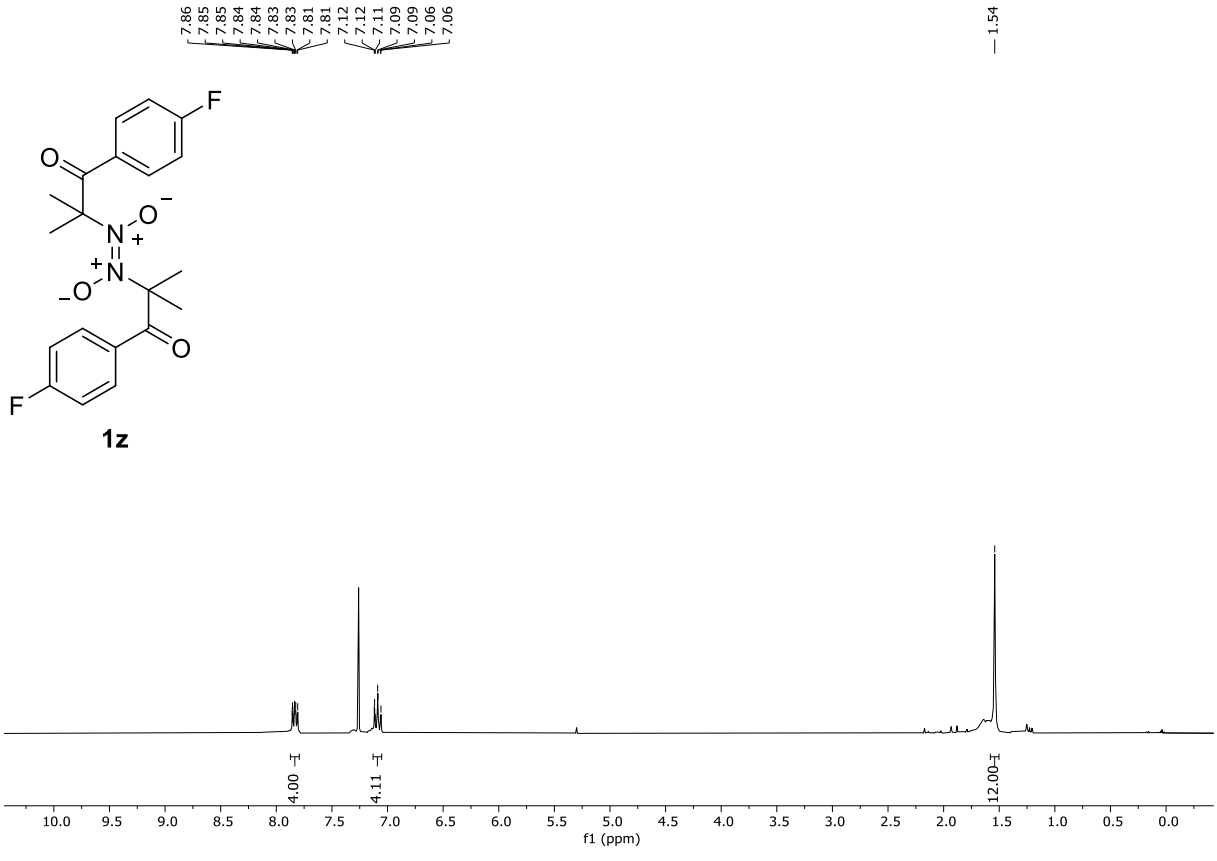
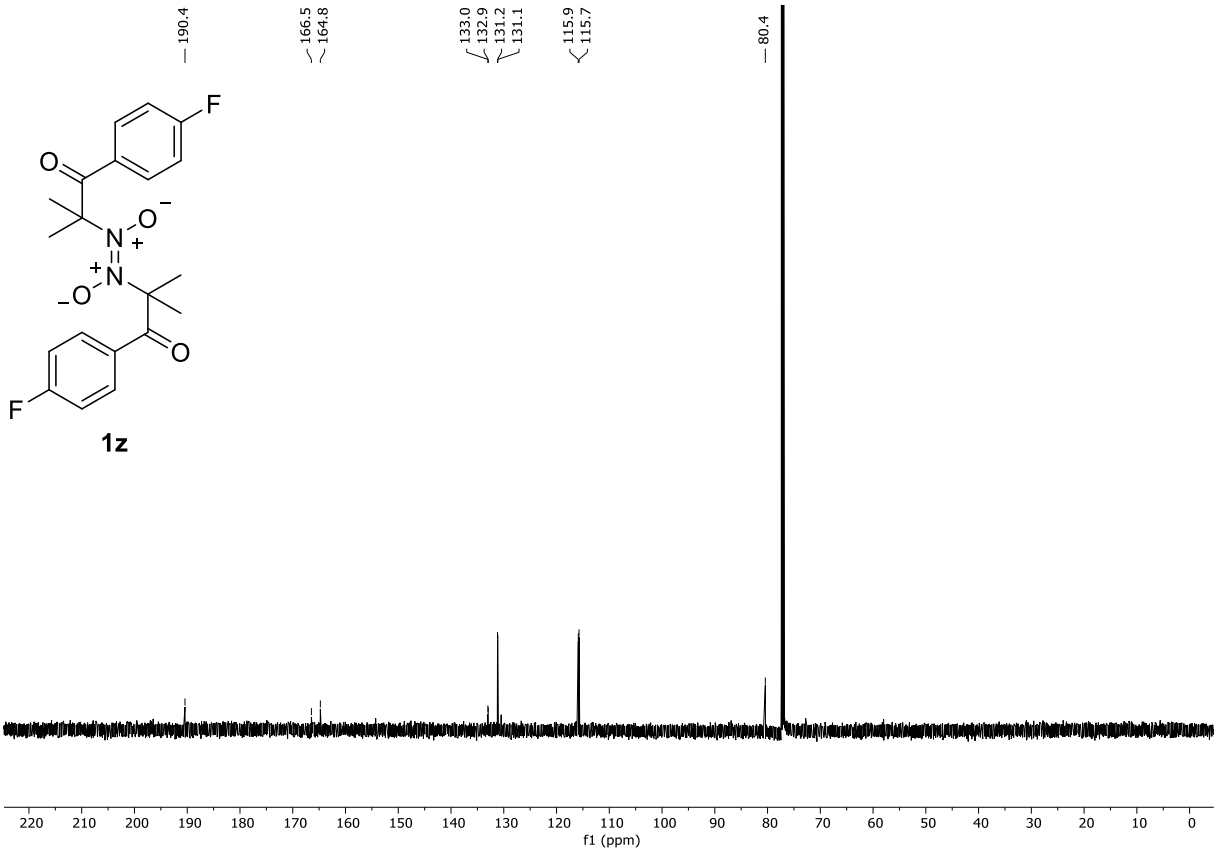


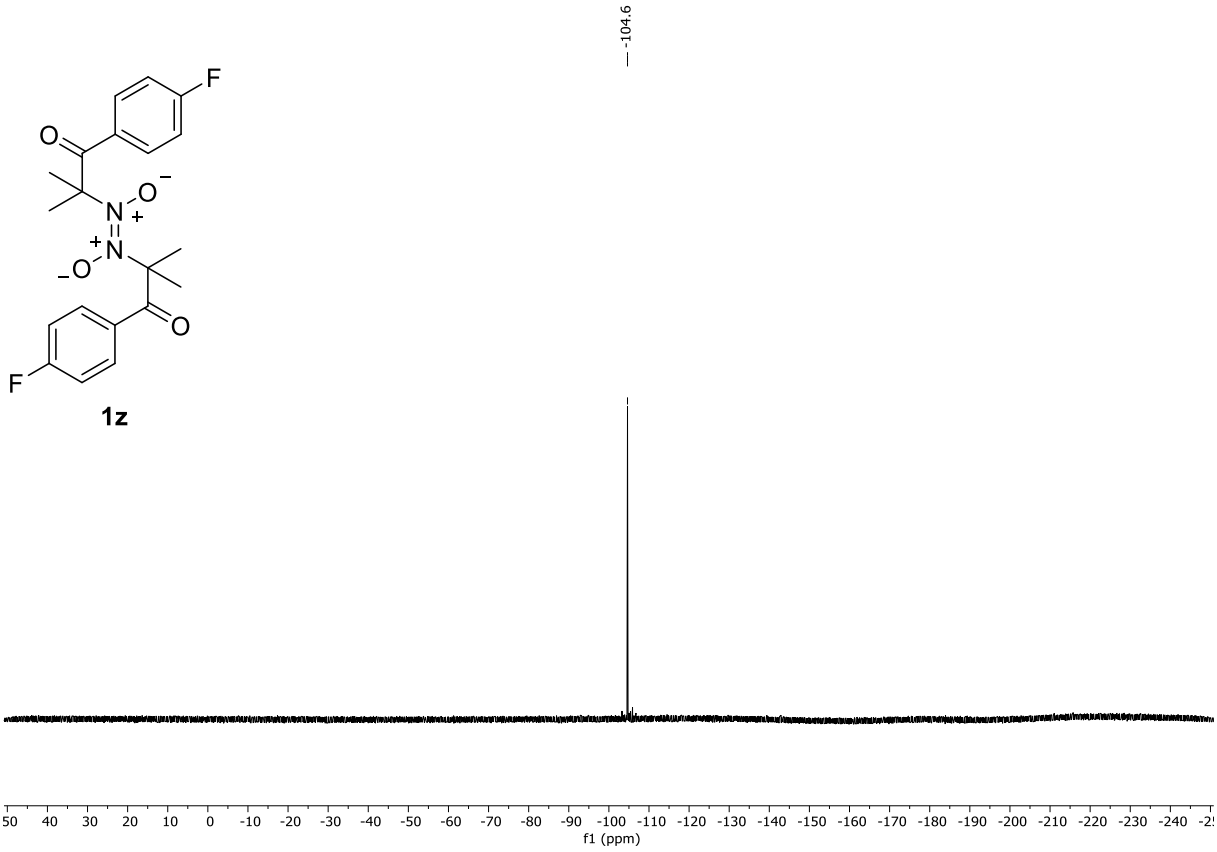
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



^{13}C-NMR (151 MHz, $CDCl_3$, 299 K)

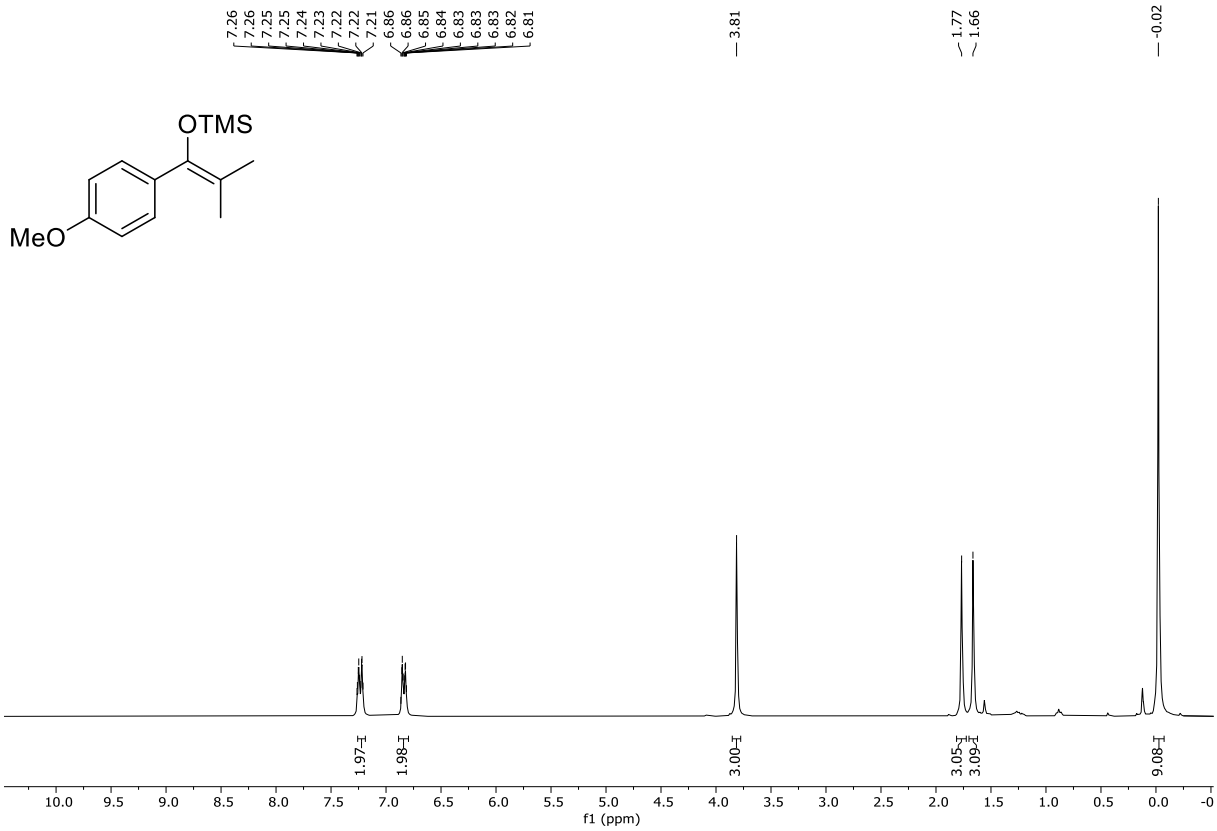


^{19}F-NMR (282 MHz, $CDCl_3$, 299 K)

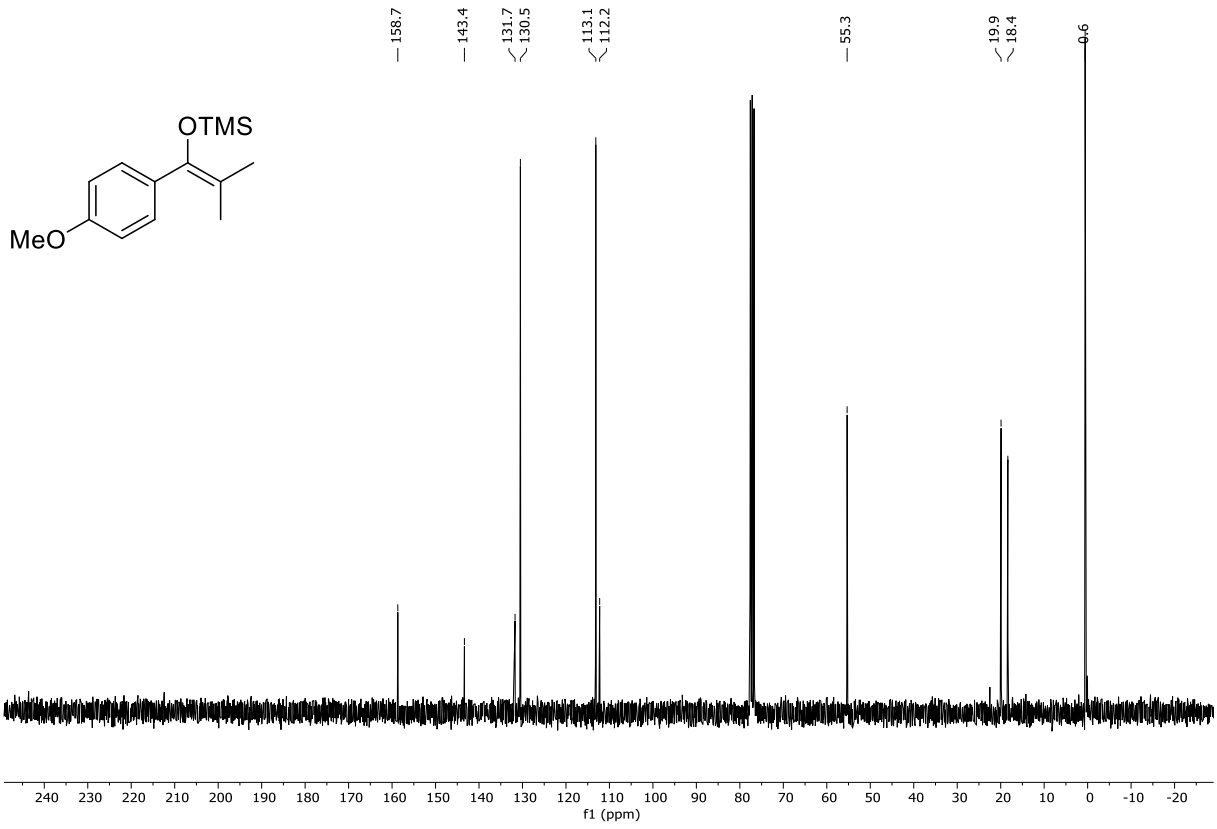


((1-(4-methoxyphenyl)-2-methylprop-1-en-1-yl)oxy)Trimethylsilane

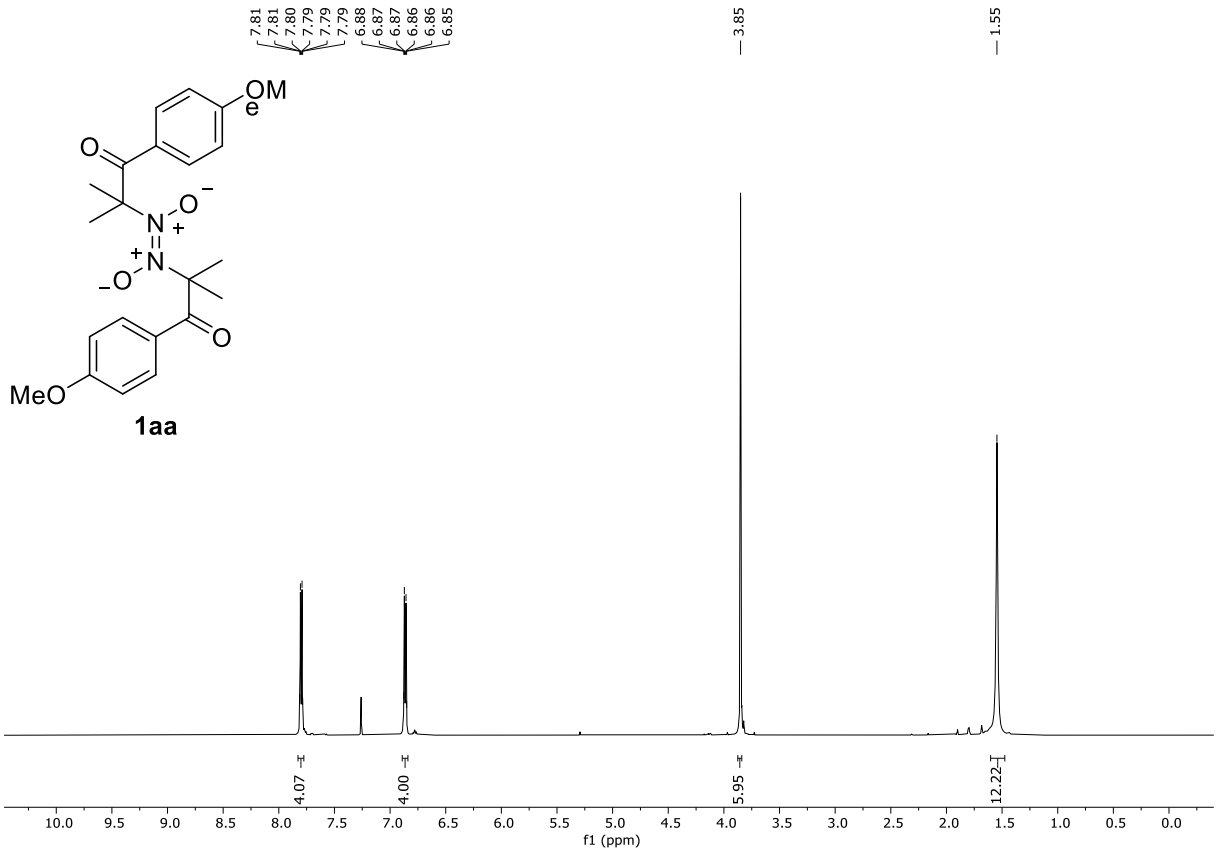
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



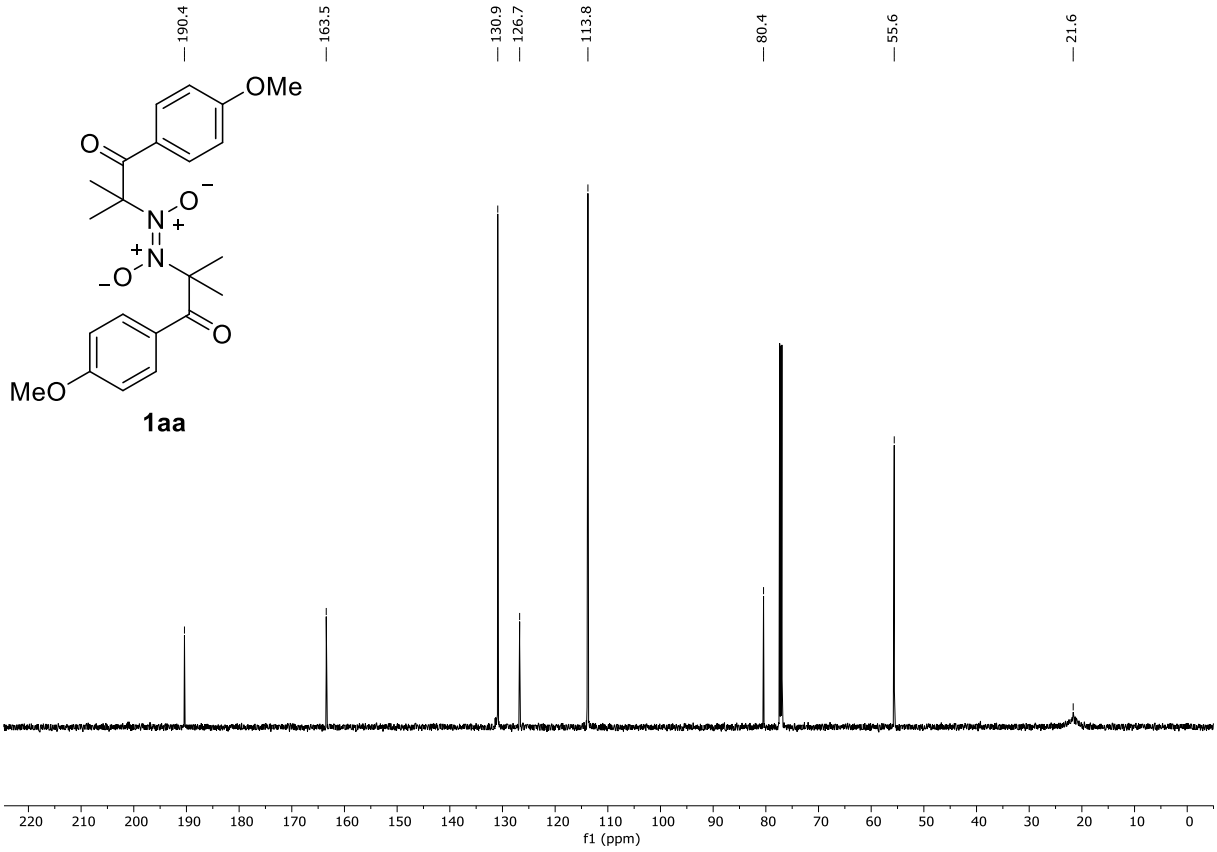
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



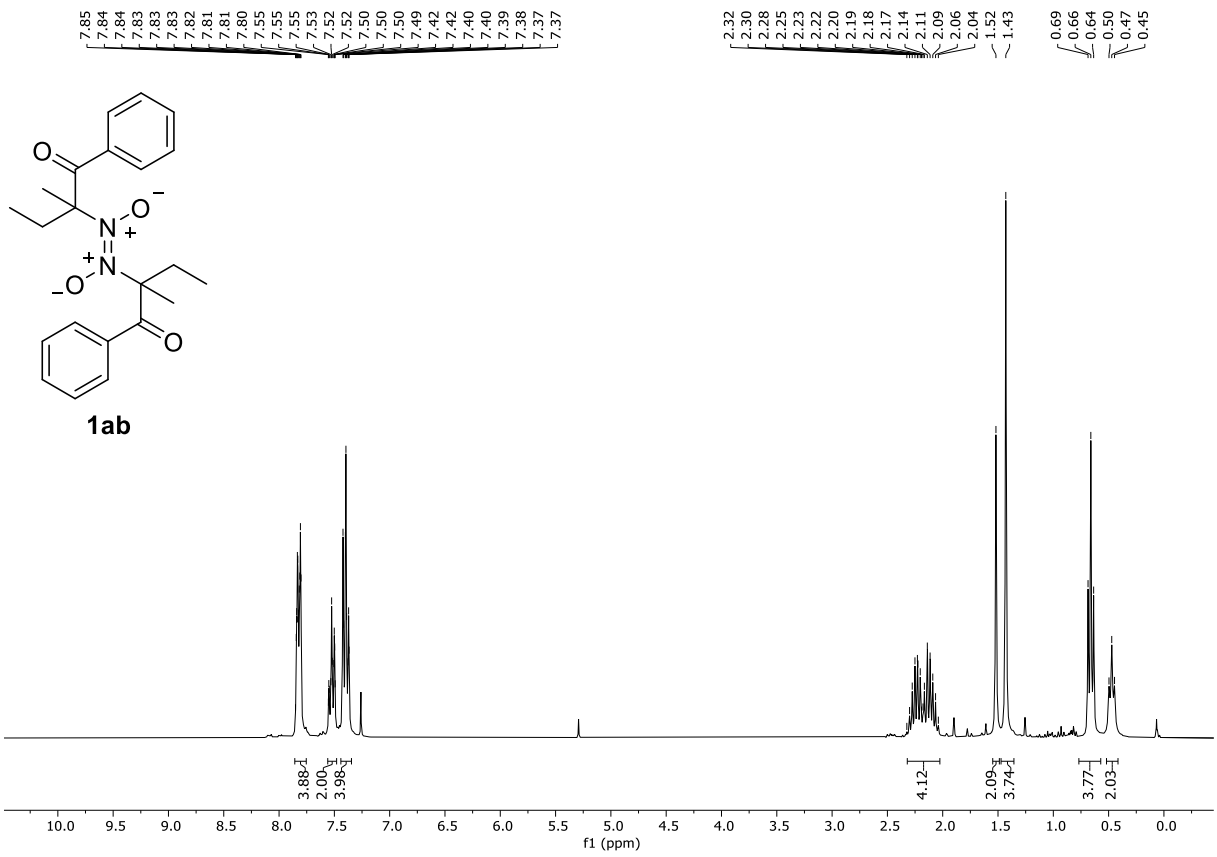
^{1}H-NMR (599 MHz, $CDCl_3$, 299 K)



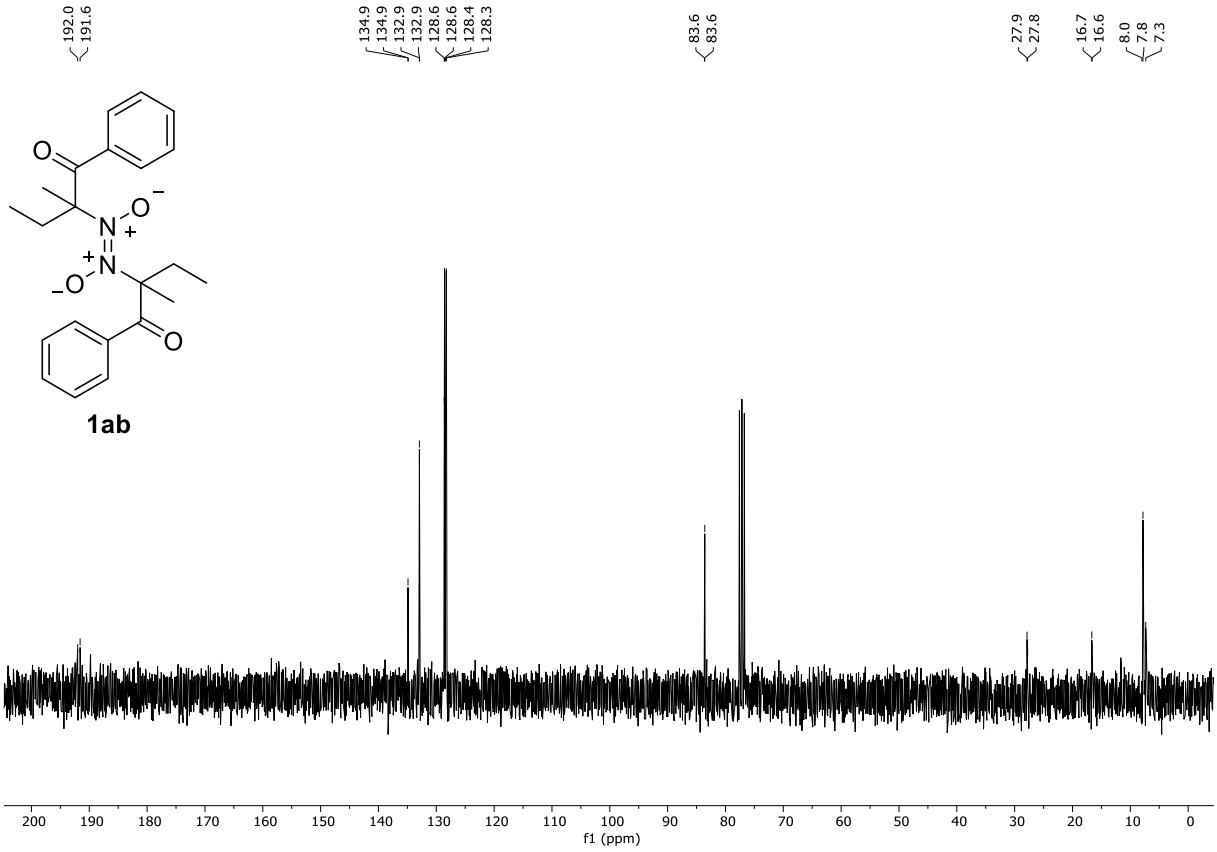
^{13}C-NMR (151 MHz, $CDCl_3$, 299 K)



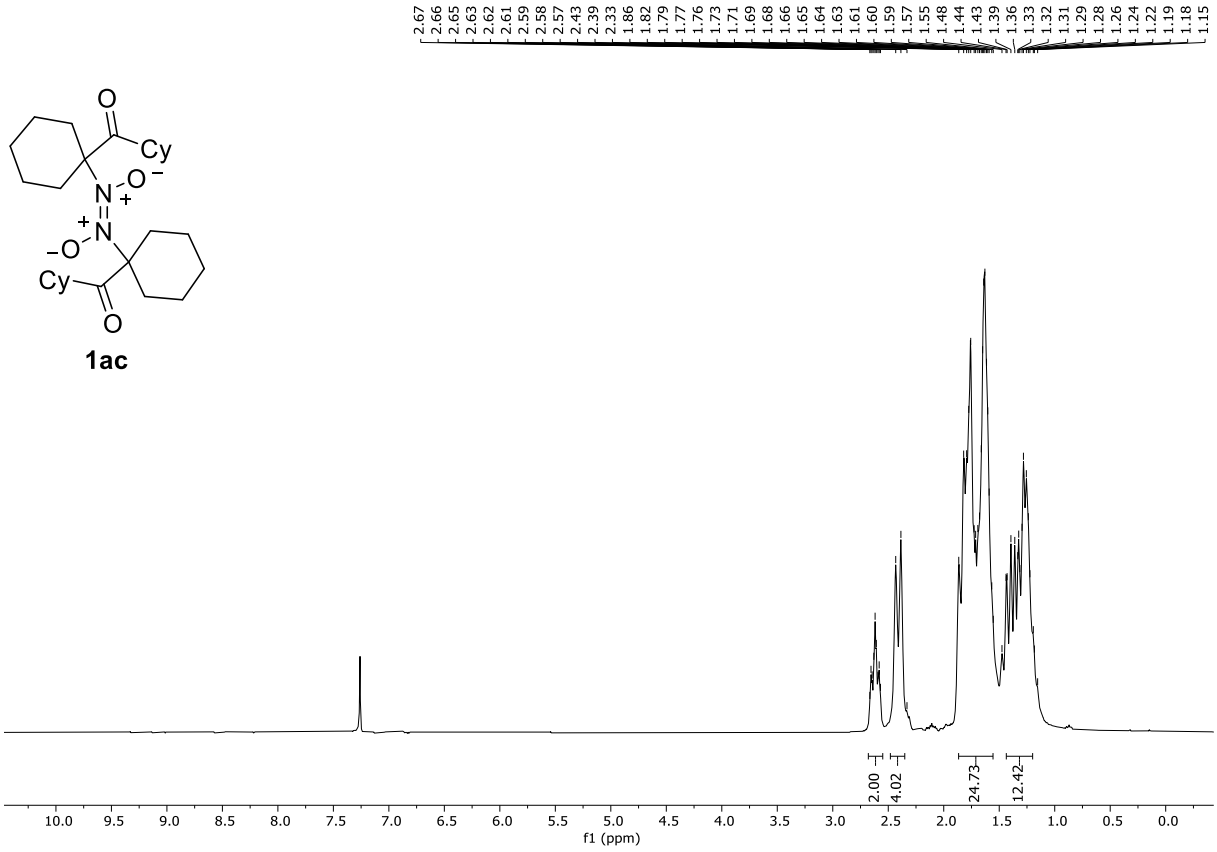
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)

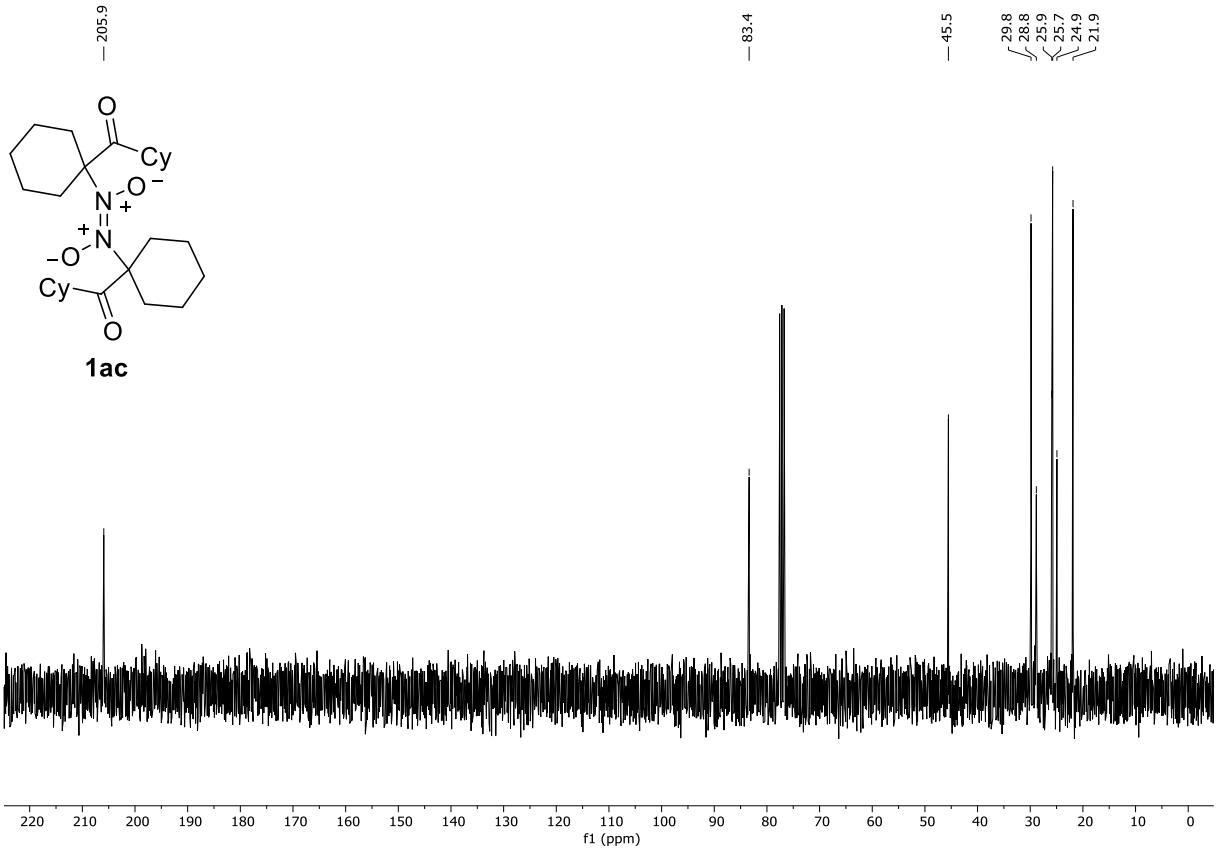


^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



1ac

^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



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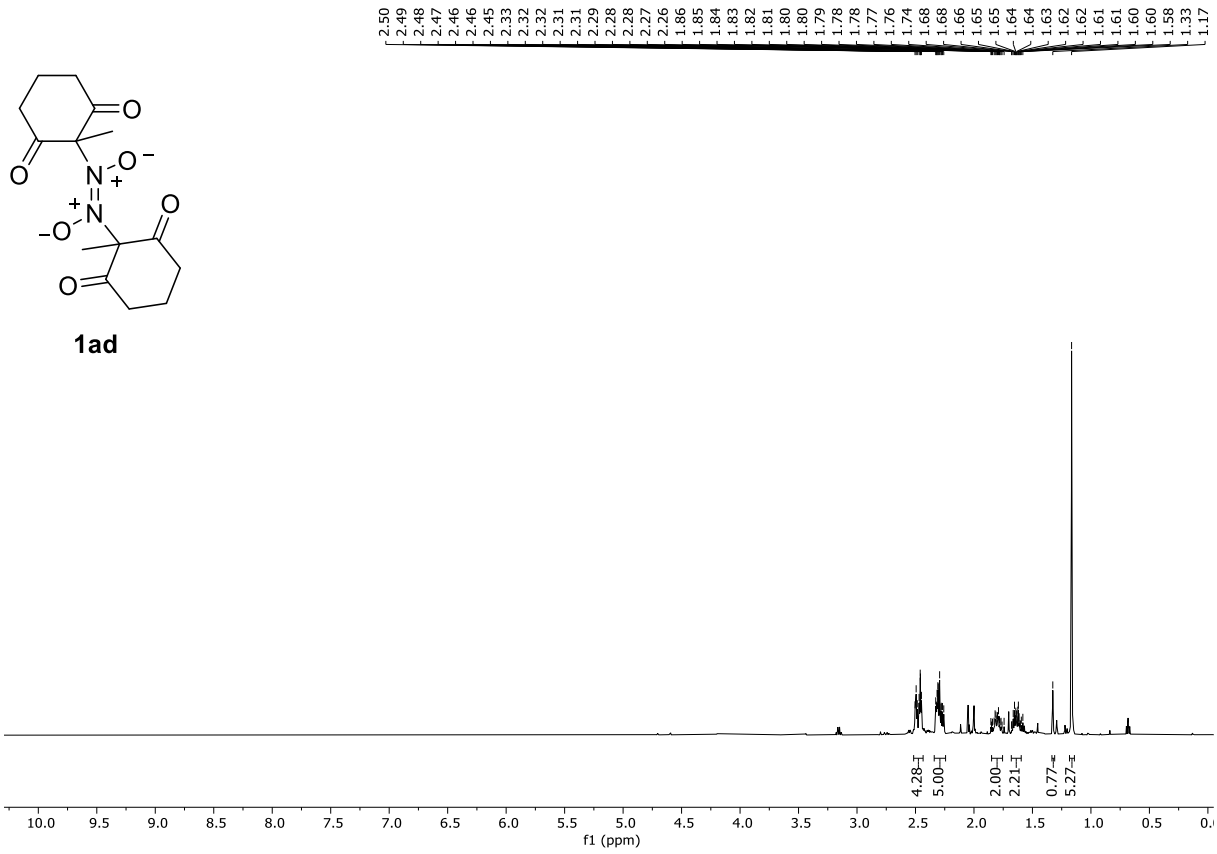
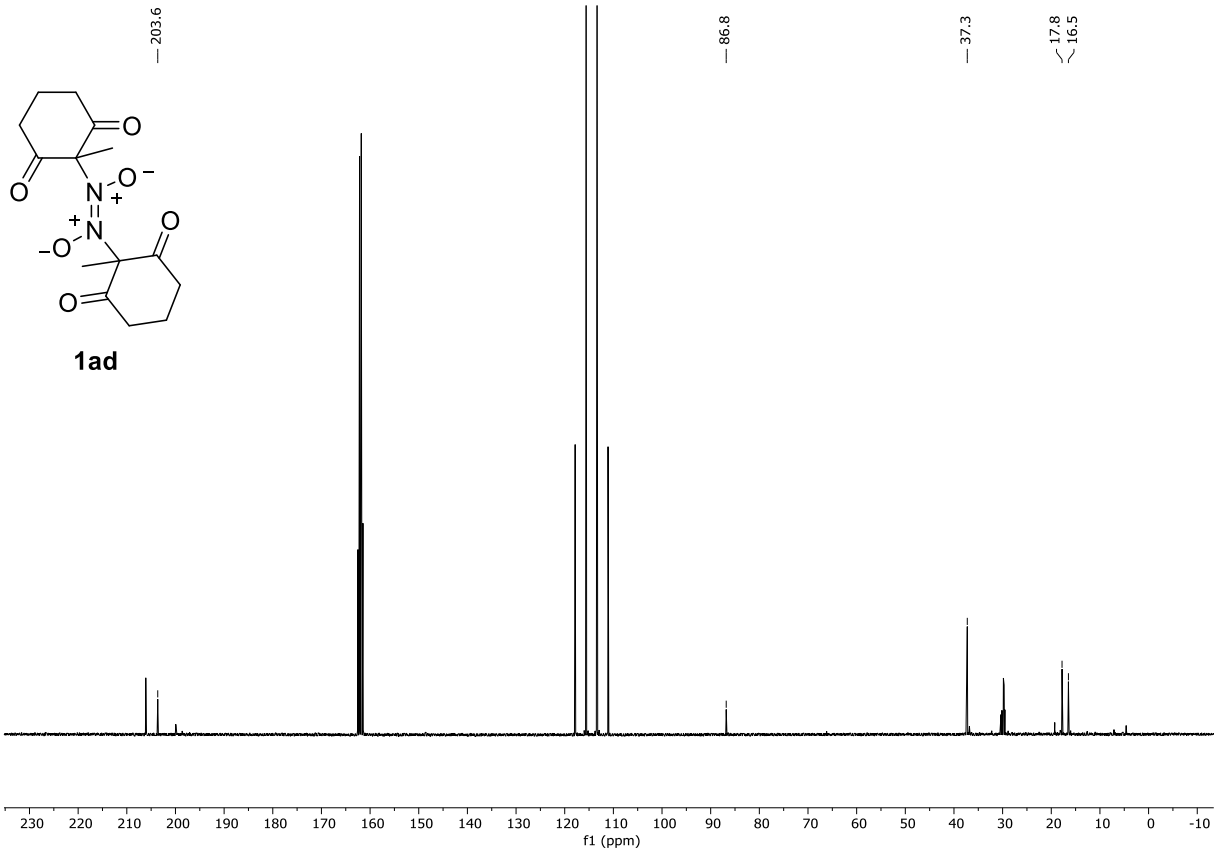
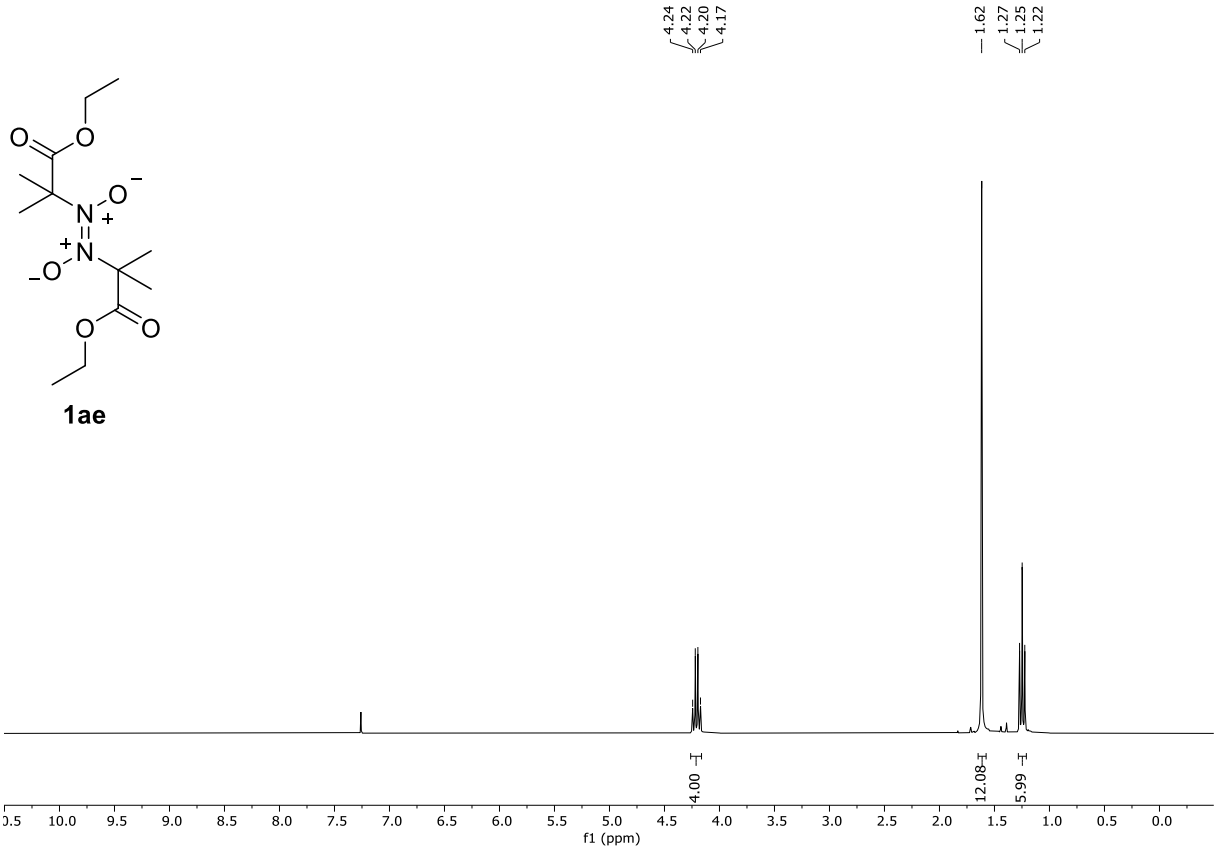
^{1}H-NMR (500 MHz, d-TFA/acetone-d_6, 299 K)



^{13}C-NMR (126 MHz, d-TFA/acetone-d_6, 299 K)

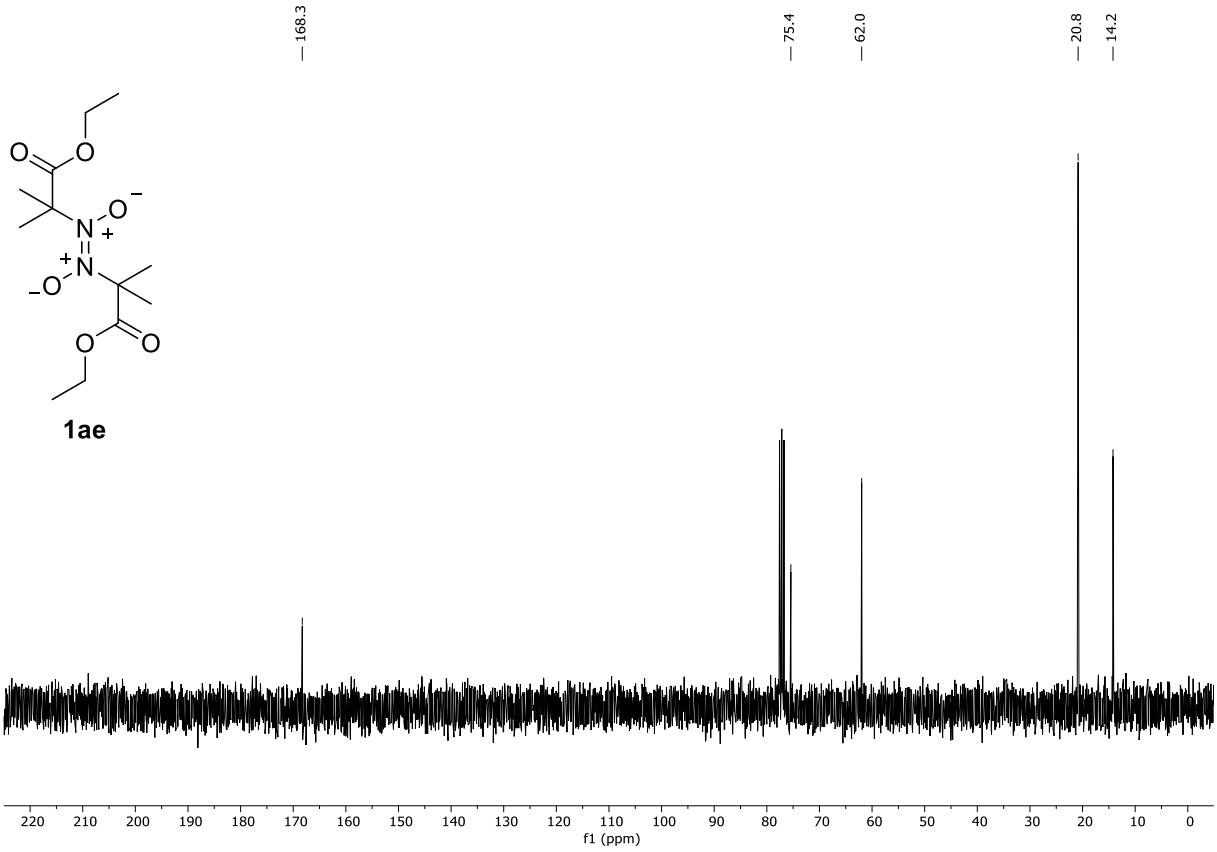


^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



1ae

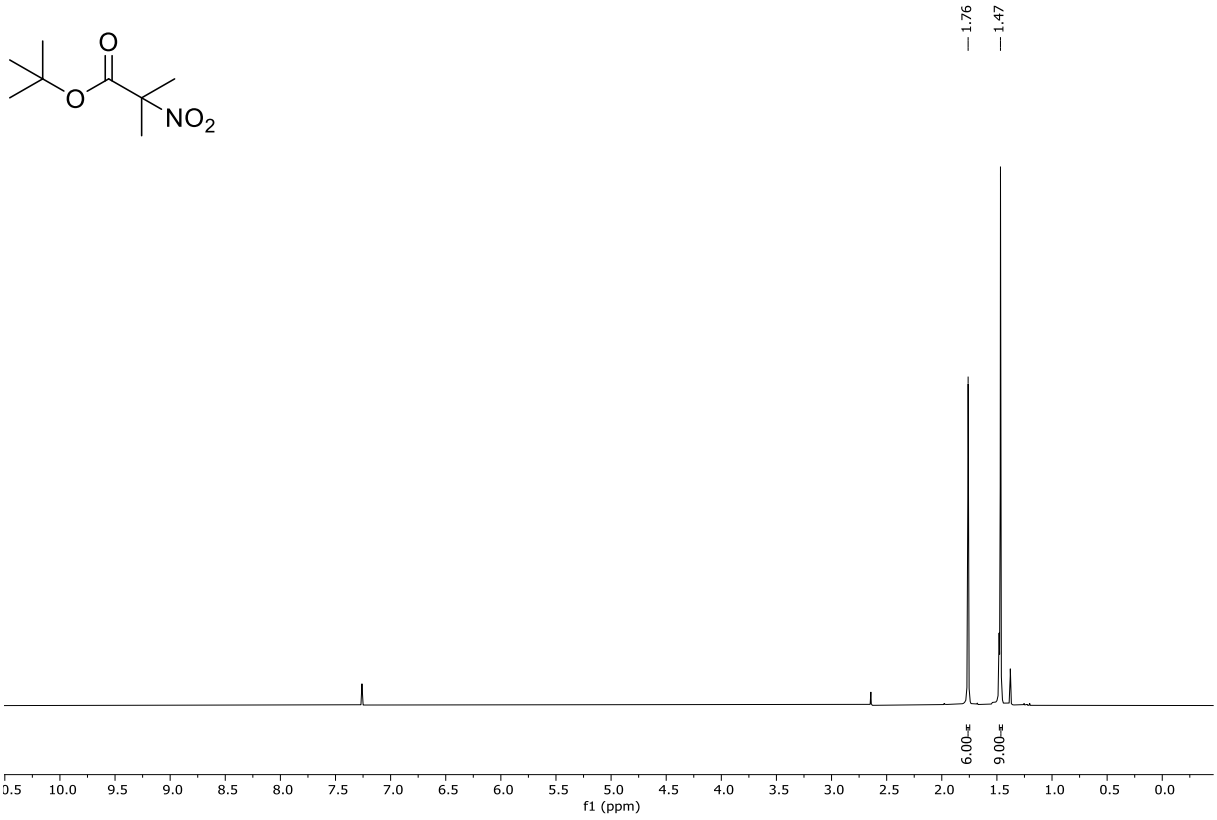
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



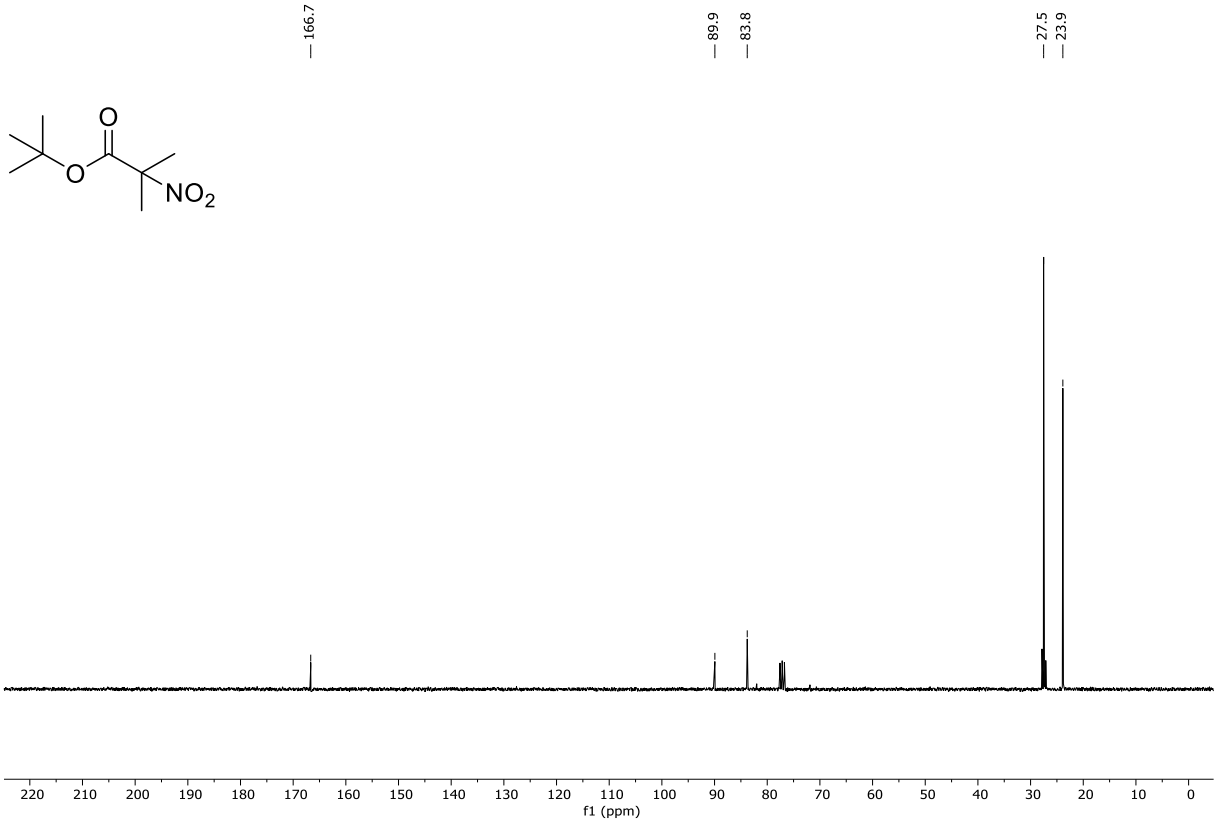
1ae

Tert-butyl 2-methyl-2-nitropropanoate

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)

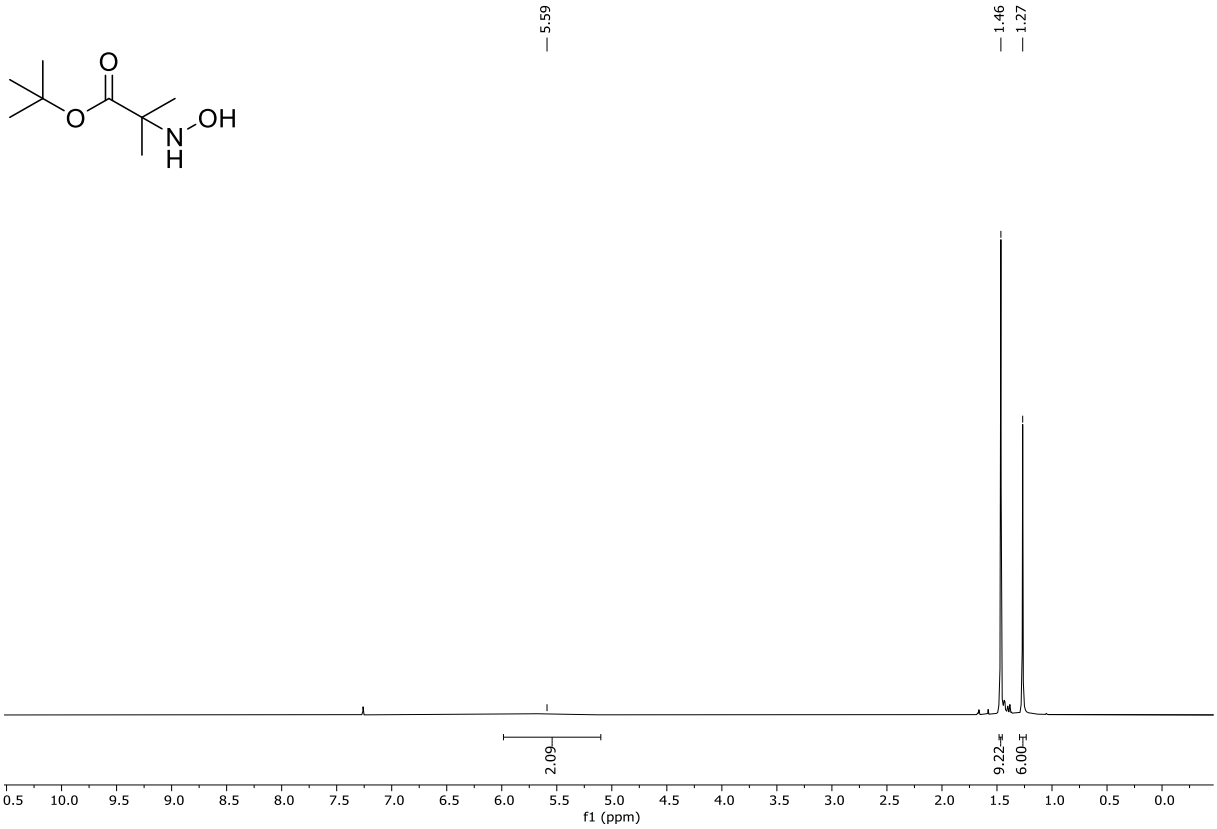


^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)

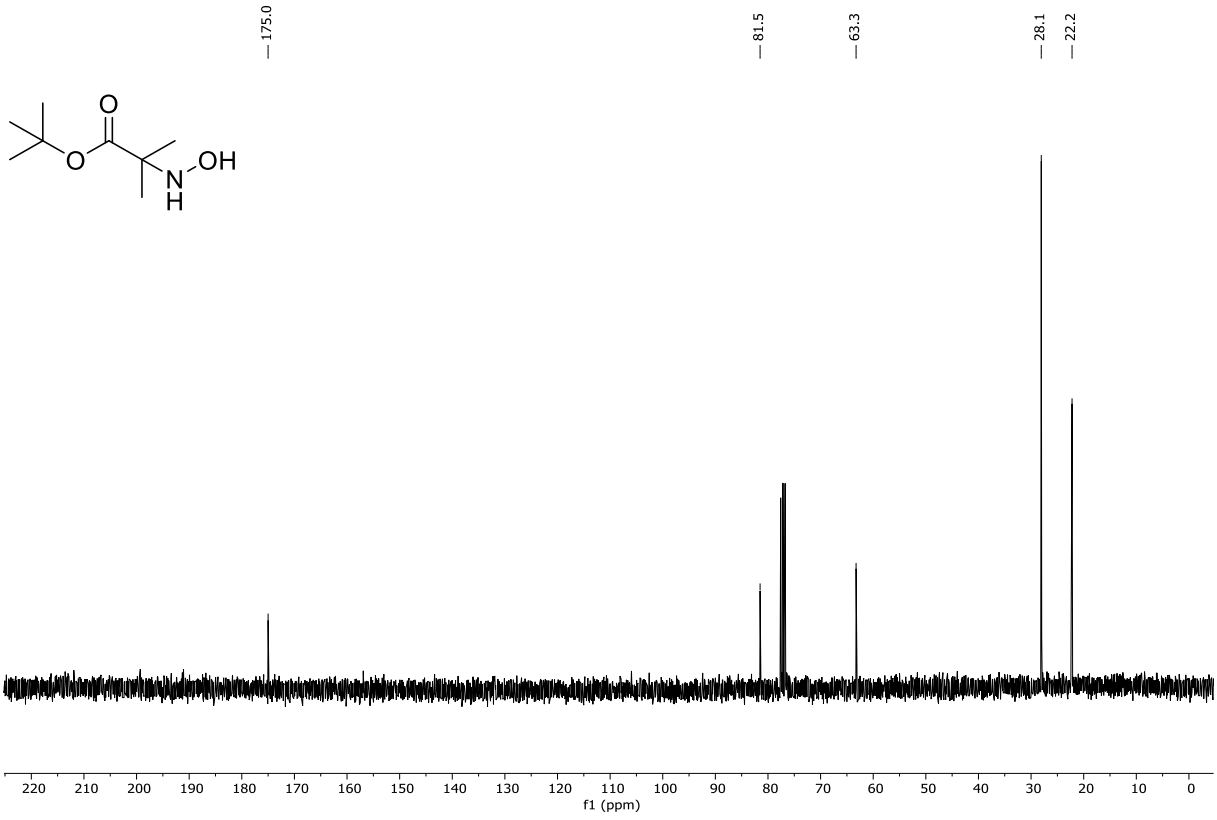


Tert-butyl 2-(hydroxyamino)-2-methylpropanoate

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



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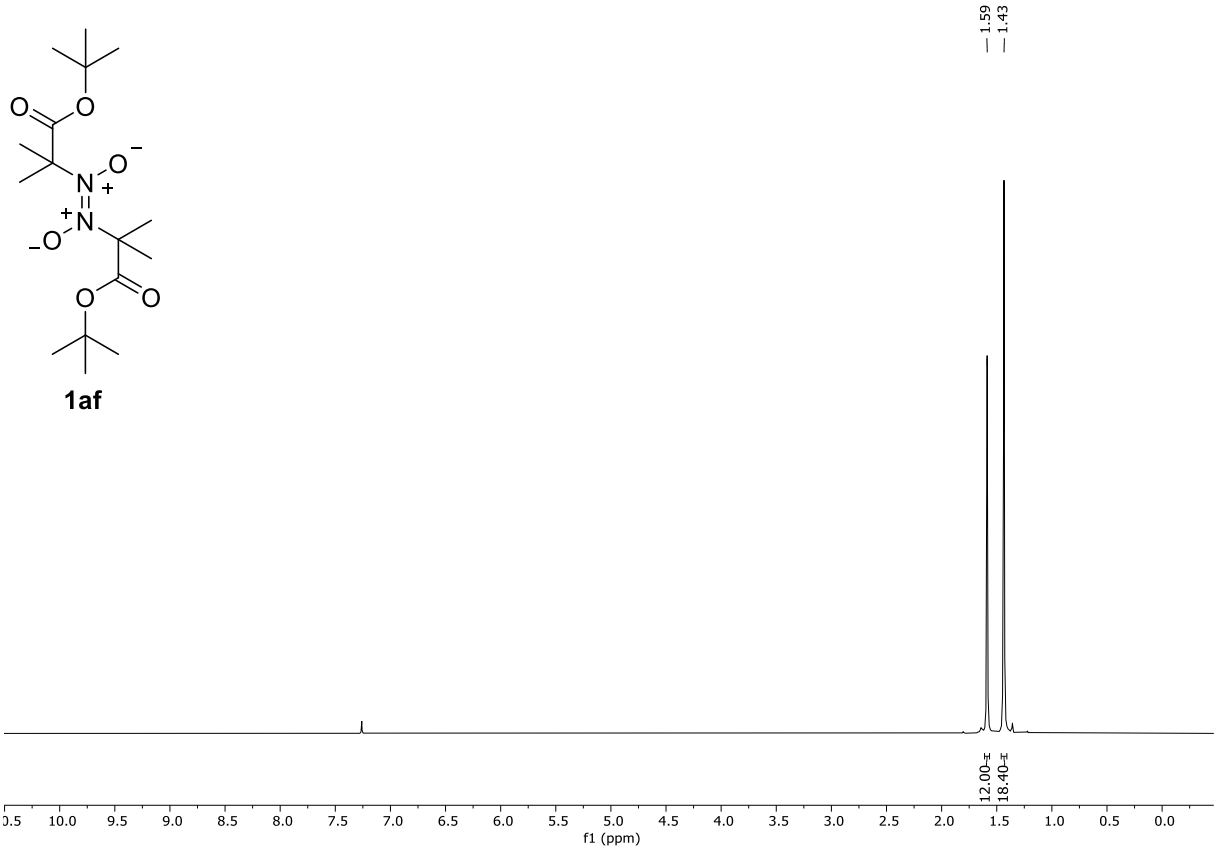

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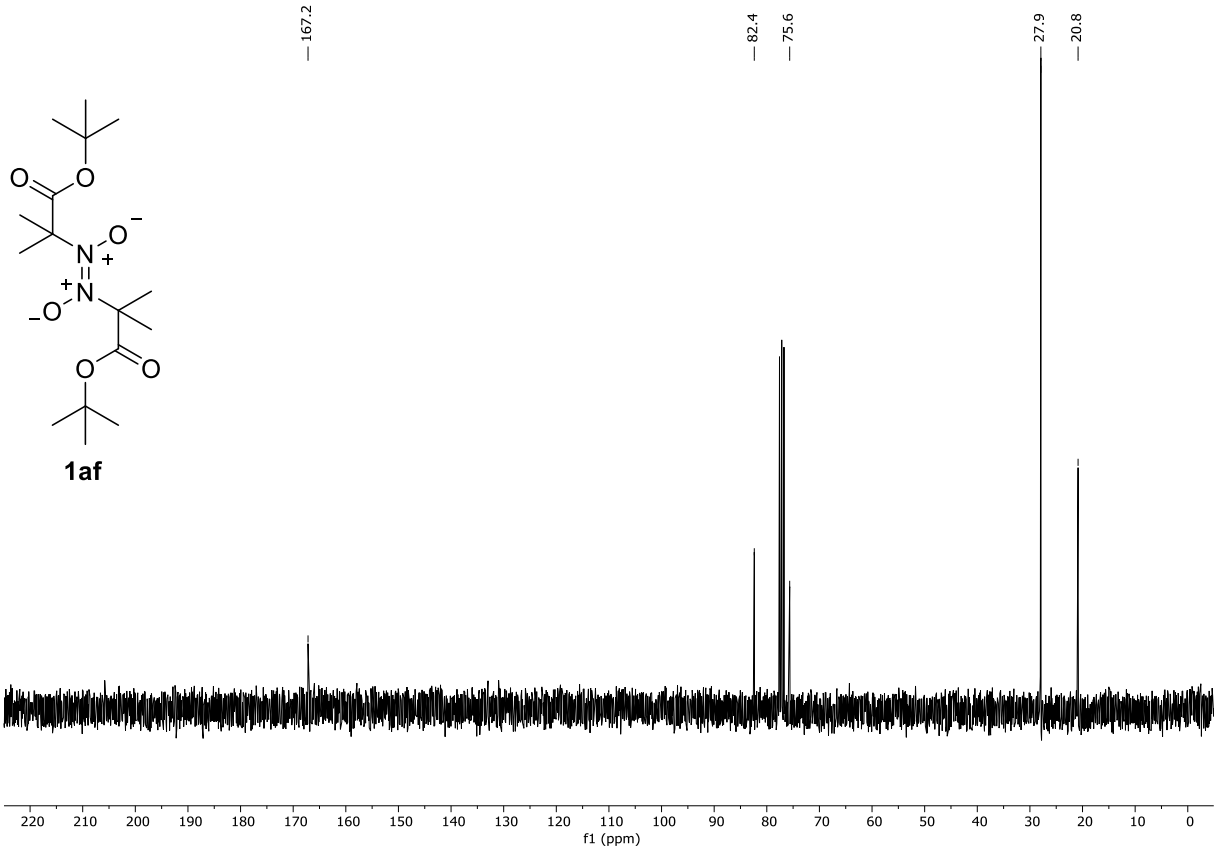
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



1af

1-Chloro-1-nitrosocyclohexane

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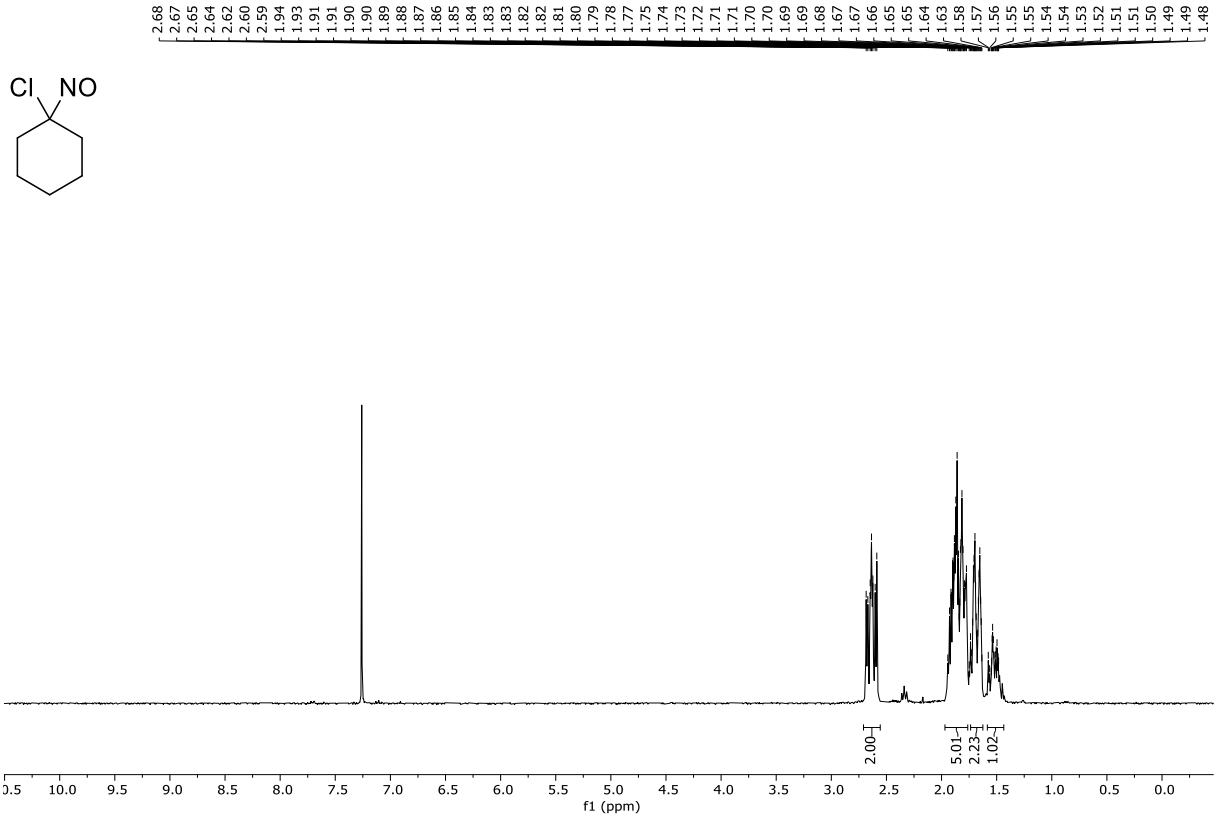
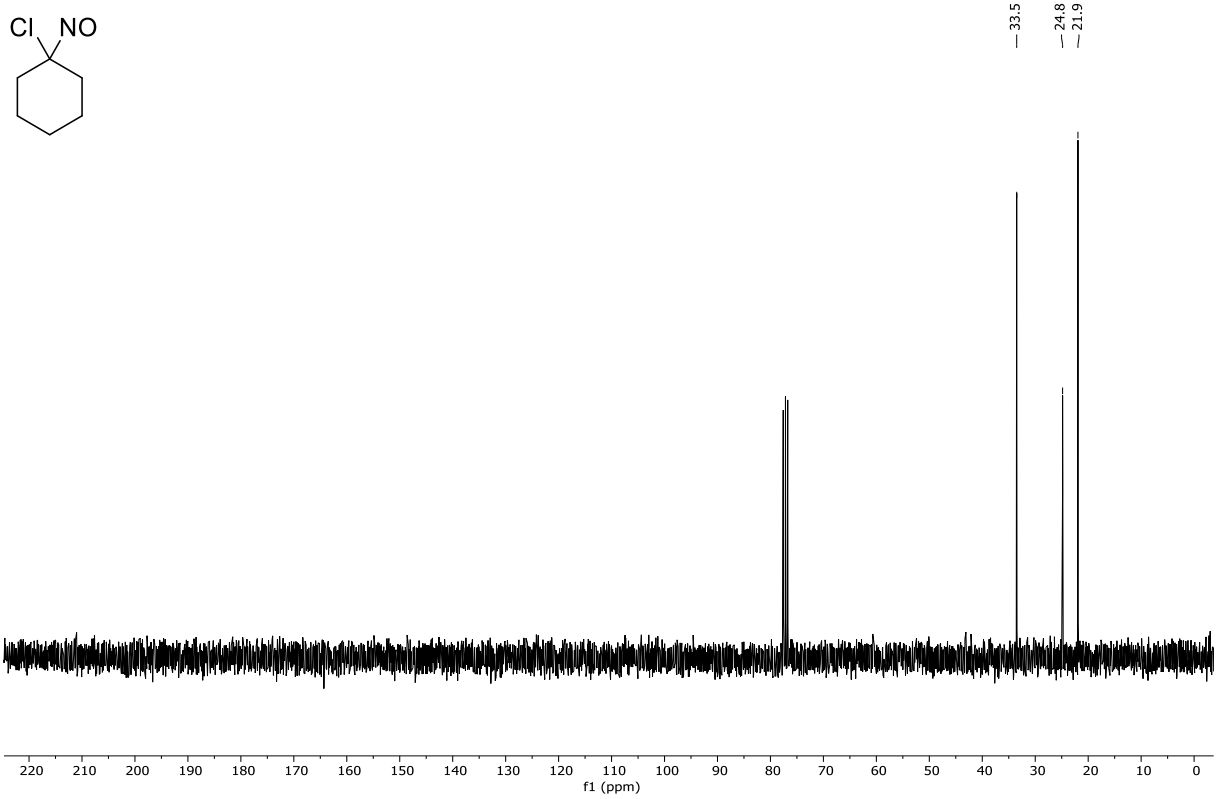
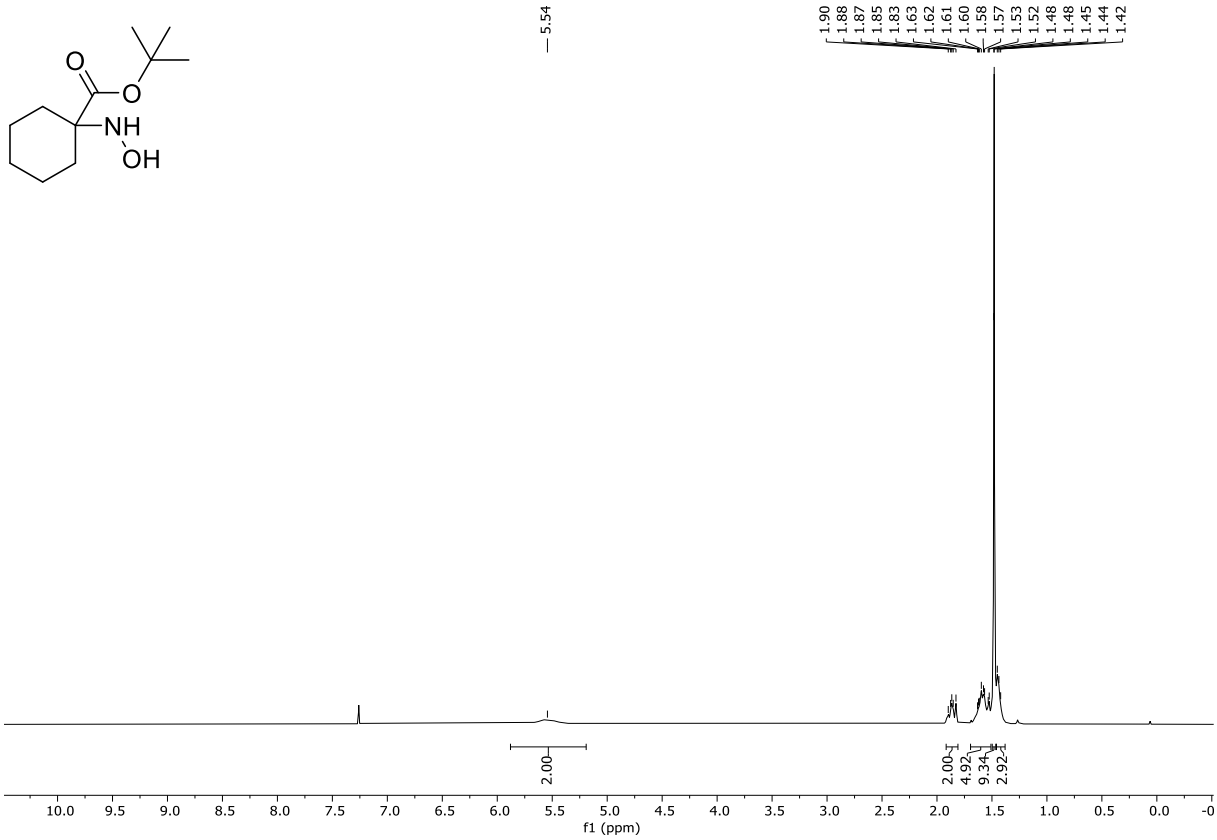


^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)

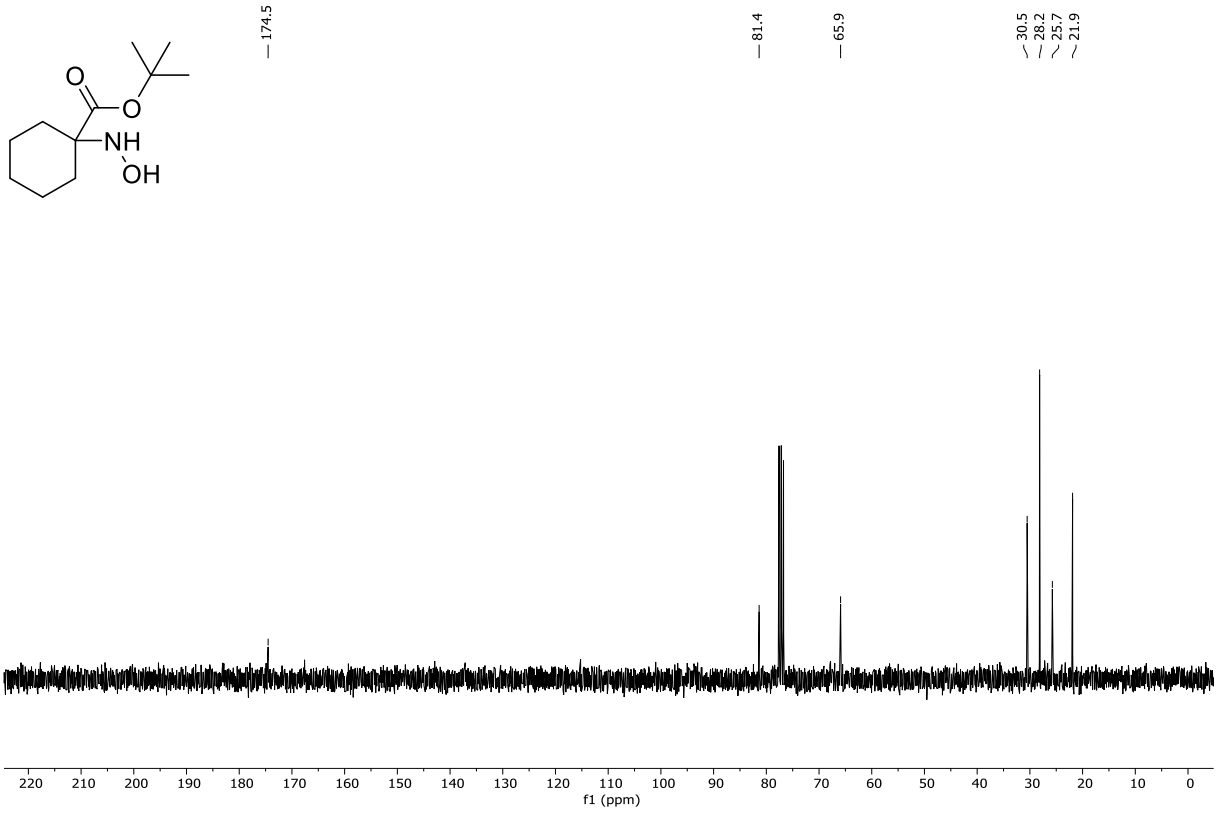


Tert-butyl 1-(hydroxyamino)cyclohexane-1-carboxylate

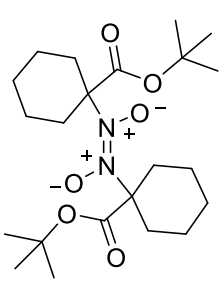
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



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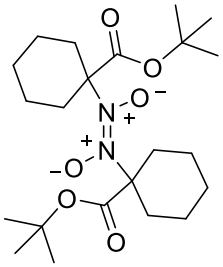
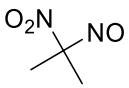
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



1ag

^{1}H-NMR (300 MHz, DMSO-d_6, 299 K)



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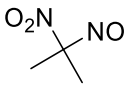
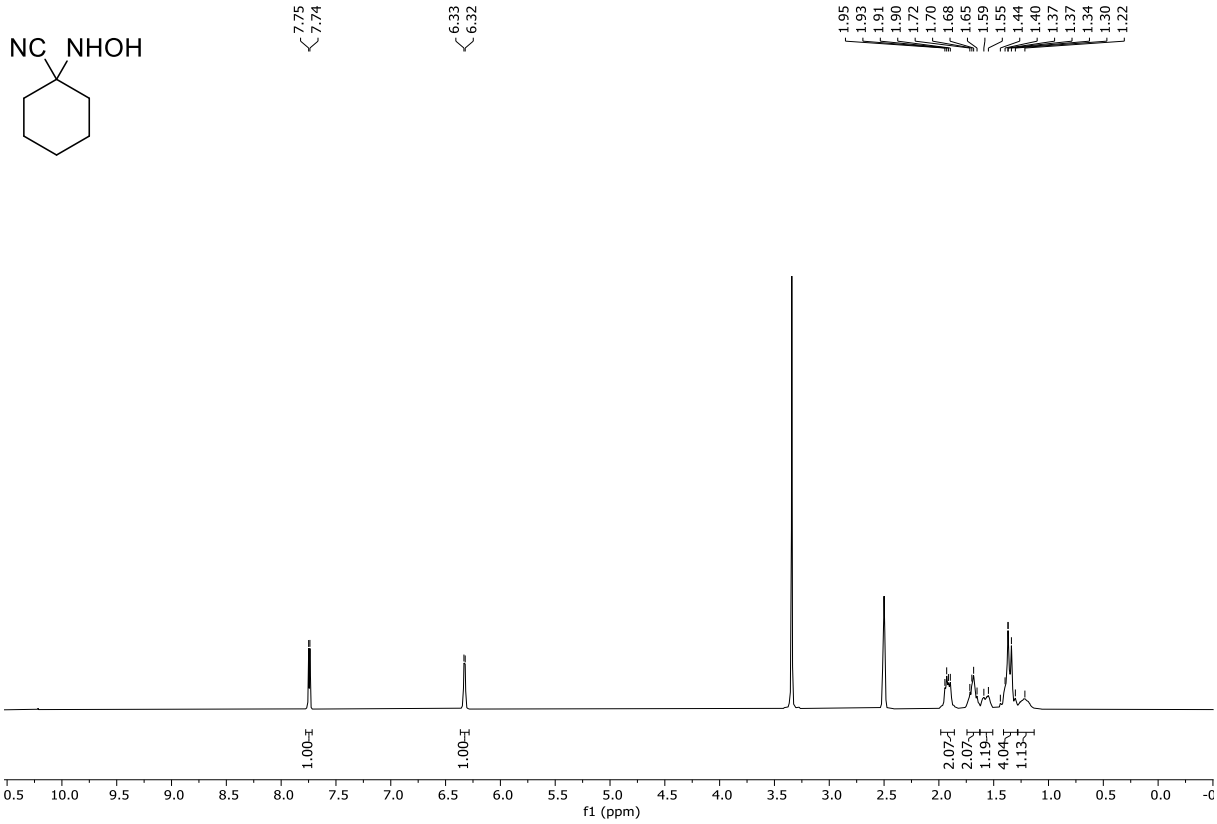
^{13}C-NMR (75 MHz, DMSO-d_6, 299 K)



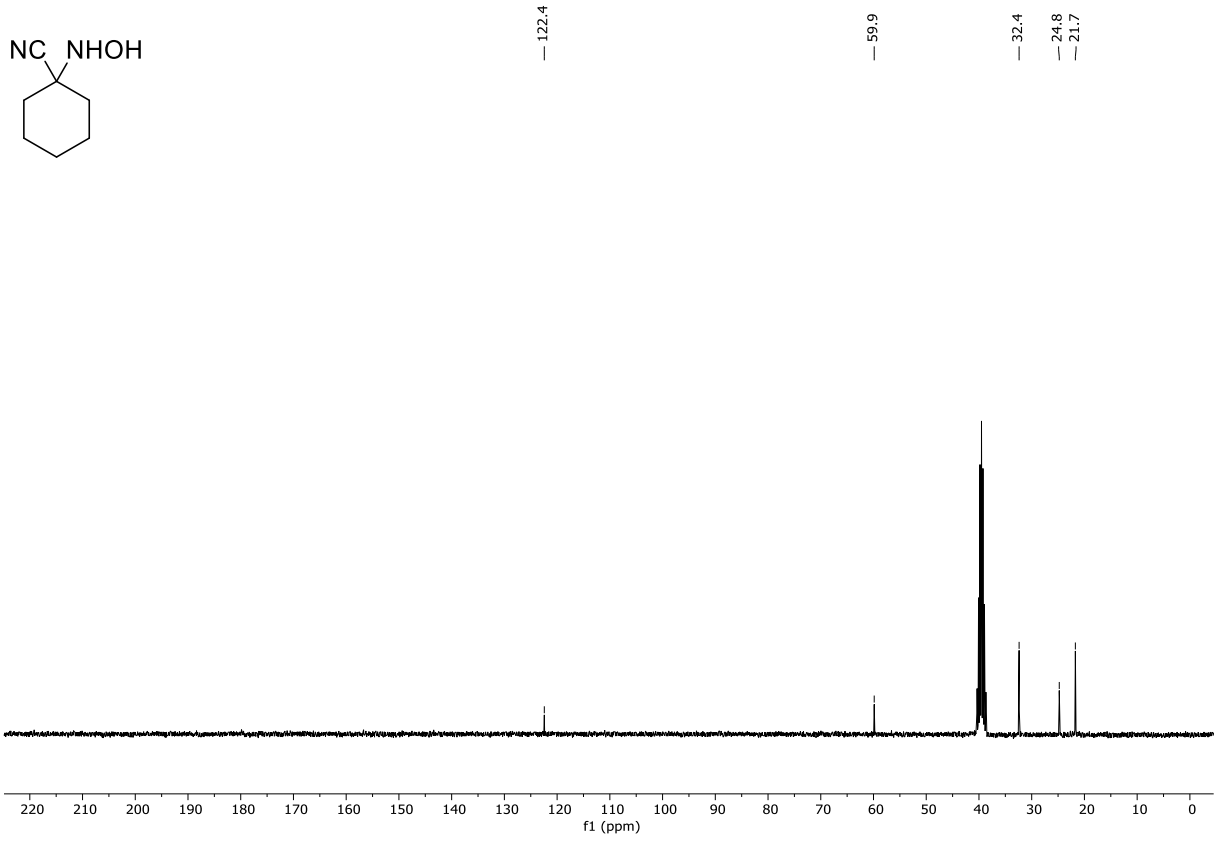
1ah

1-(hydroxyamino)Cyclohexane-1-carbonitrile

^{1}H-NMR (300 MHz, DMSO-d_6, 299 K)

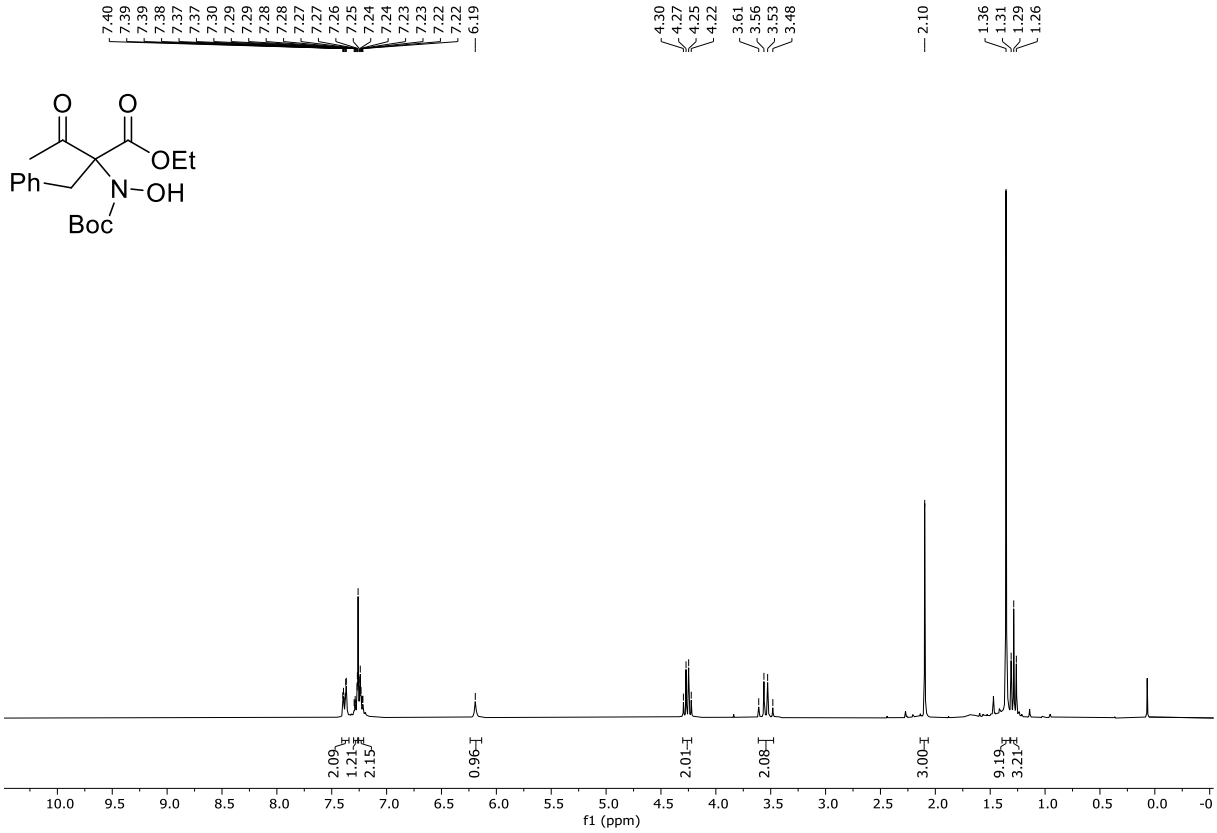


^{13}C-NMR (75 MHz, DMSO-d_6, 299 K)

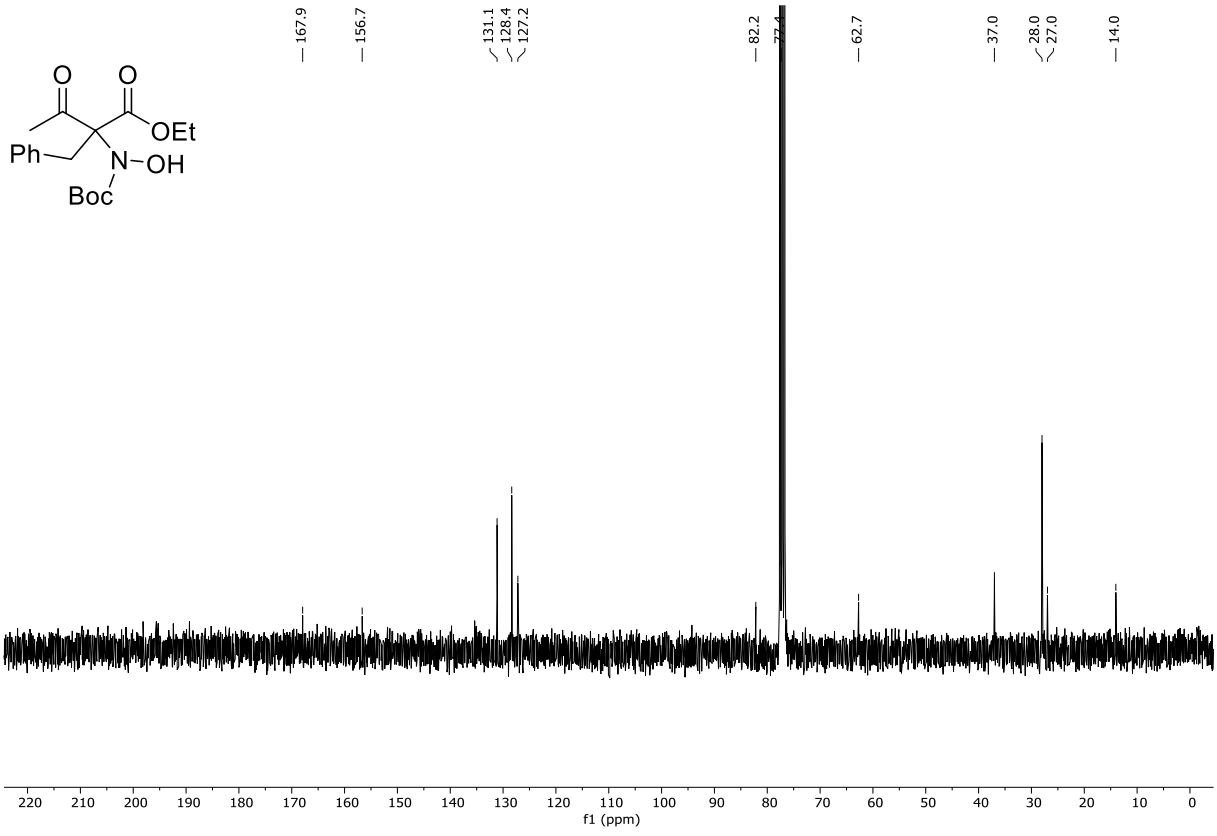


Ethyl 2-benzyl-2-((*tert*-butoxycarbonyl)(hydroxy)amino)-3-oxobutanoate

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)

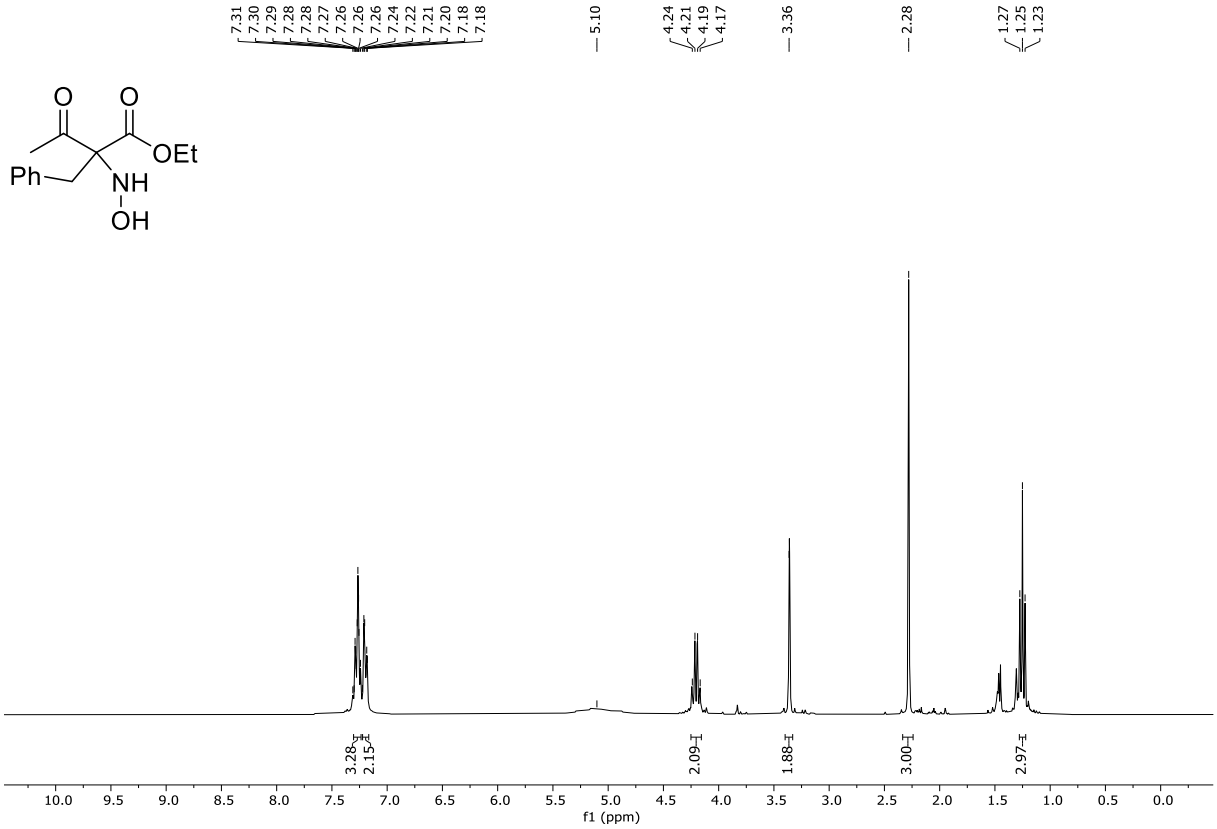


^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)

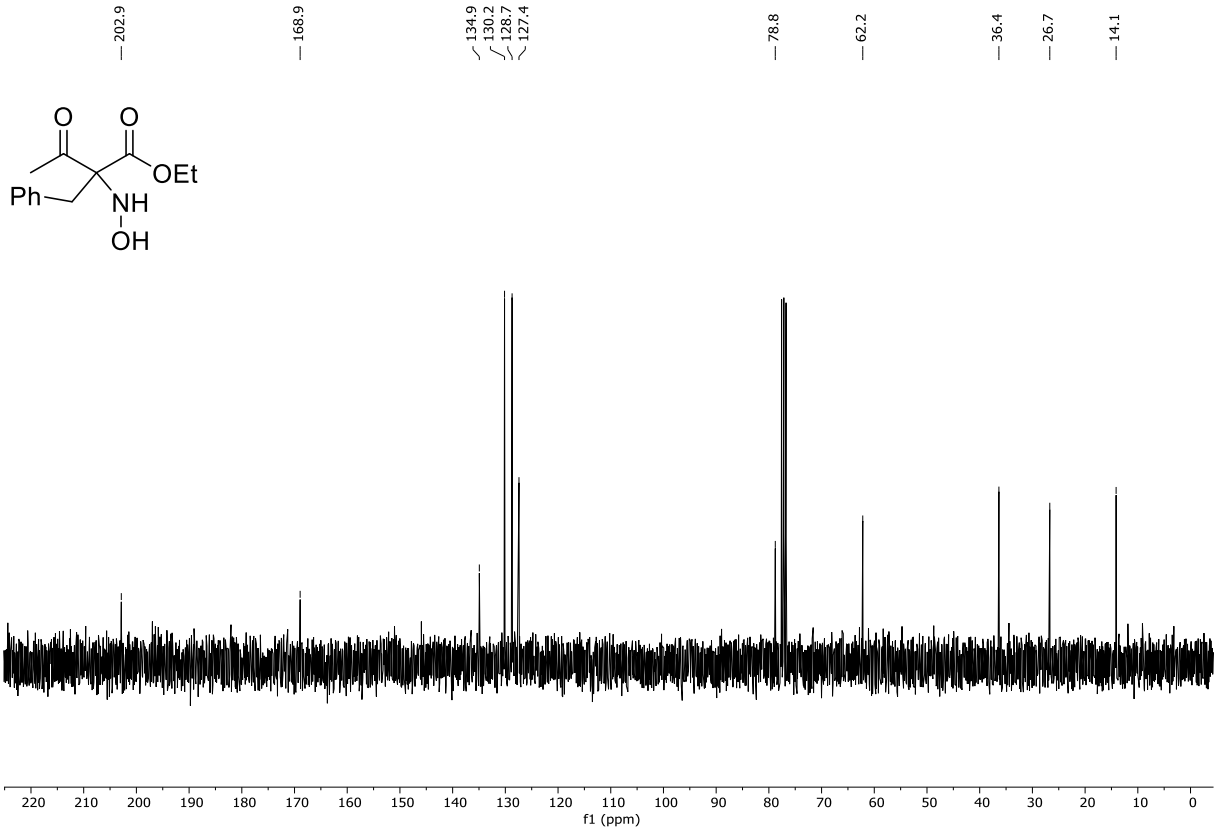


Ethyl 2-benzyl-2-(hydroxyamino)-3-oxobutanoate

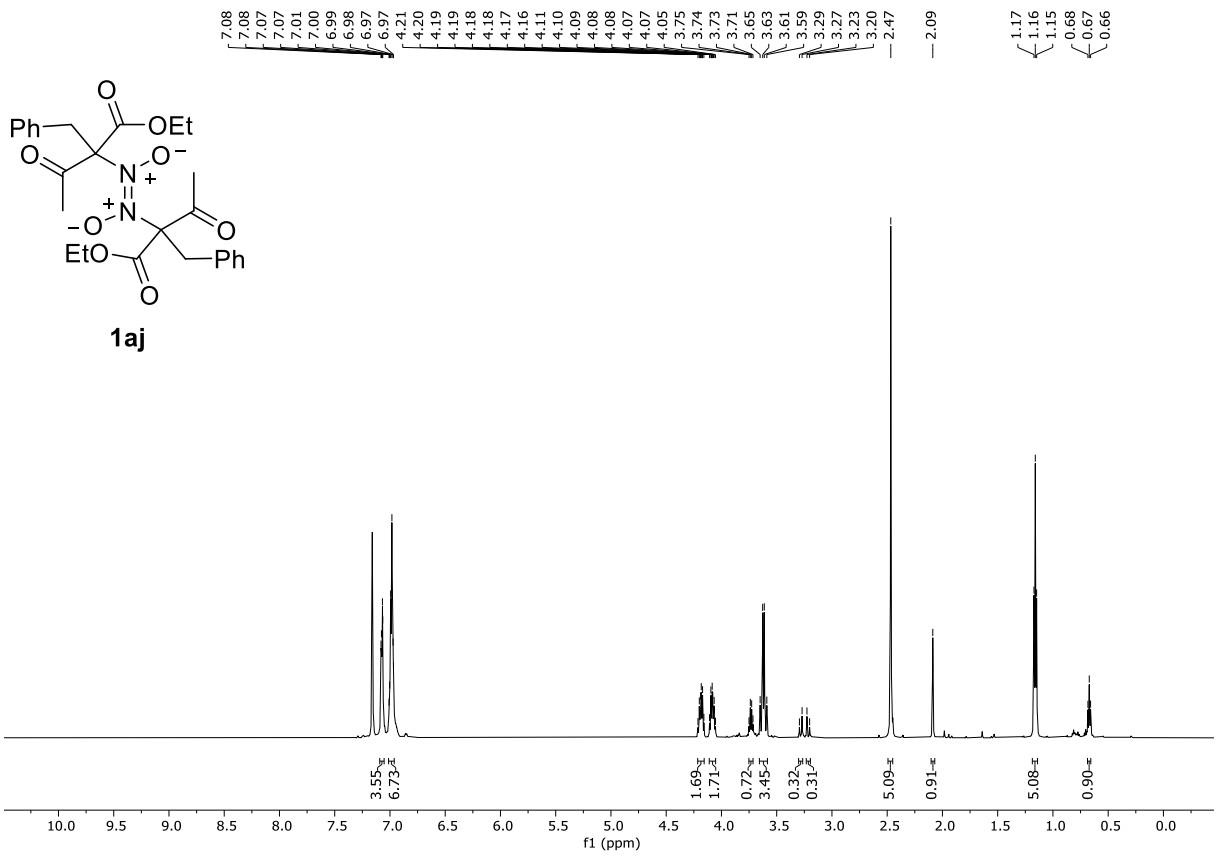
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



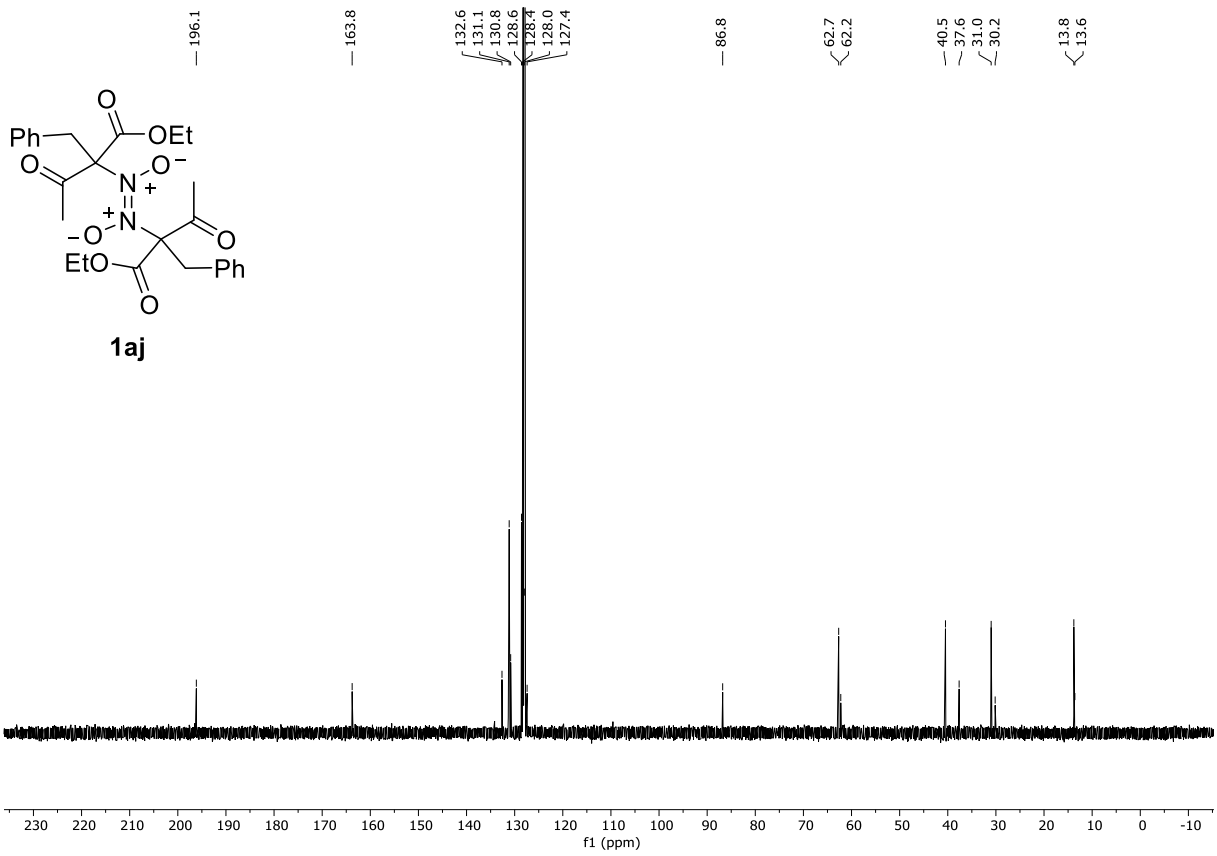
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



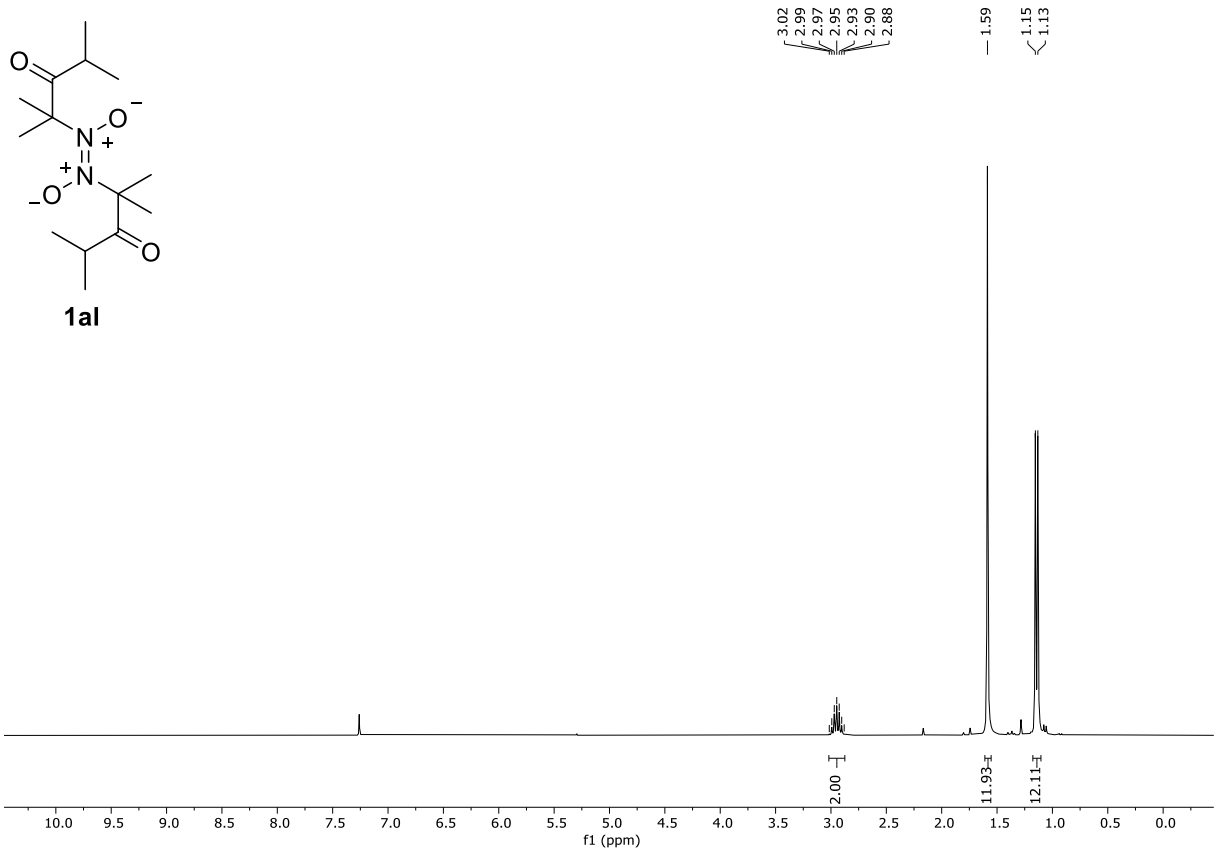
^{1}H-NMR (599 MHz, C_6D_6, 299 K)



^{13}C-NMR (151 MHz, C_6D_6, 299 K)

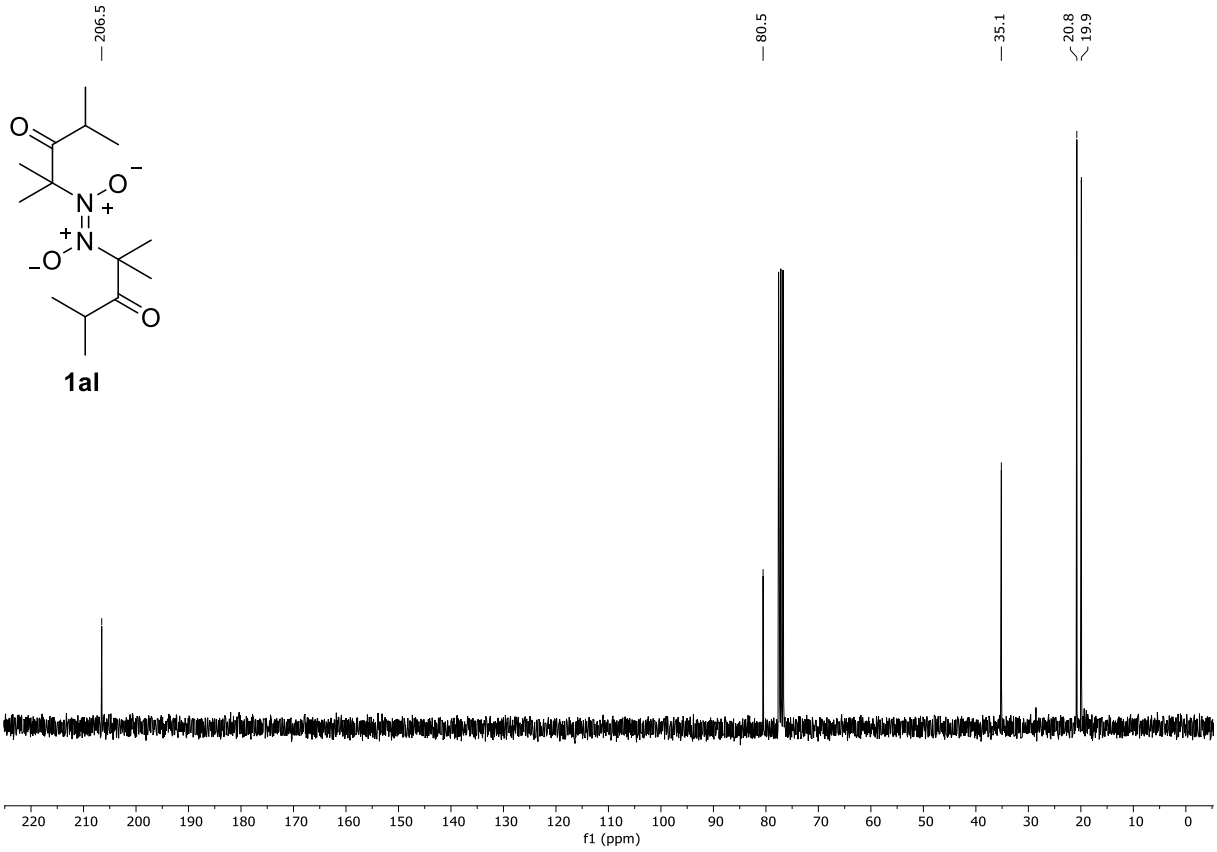


^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



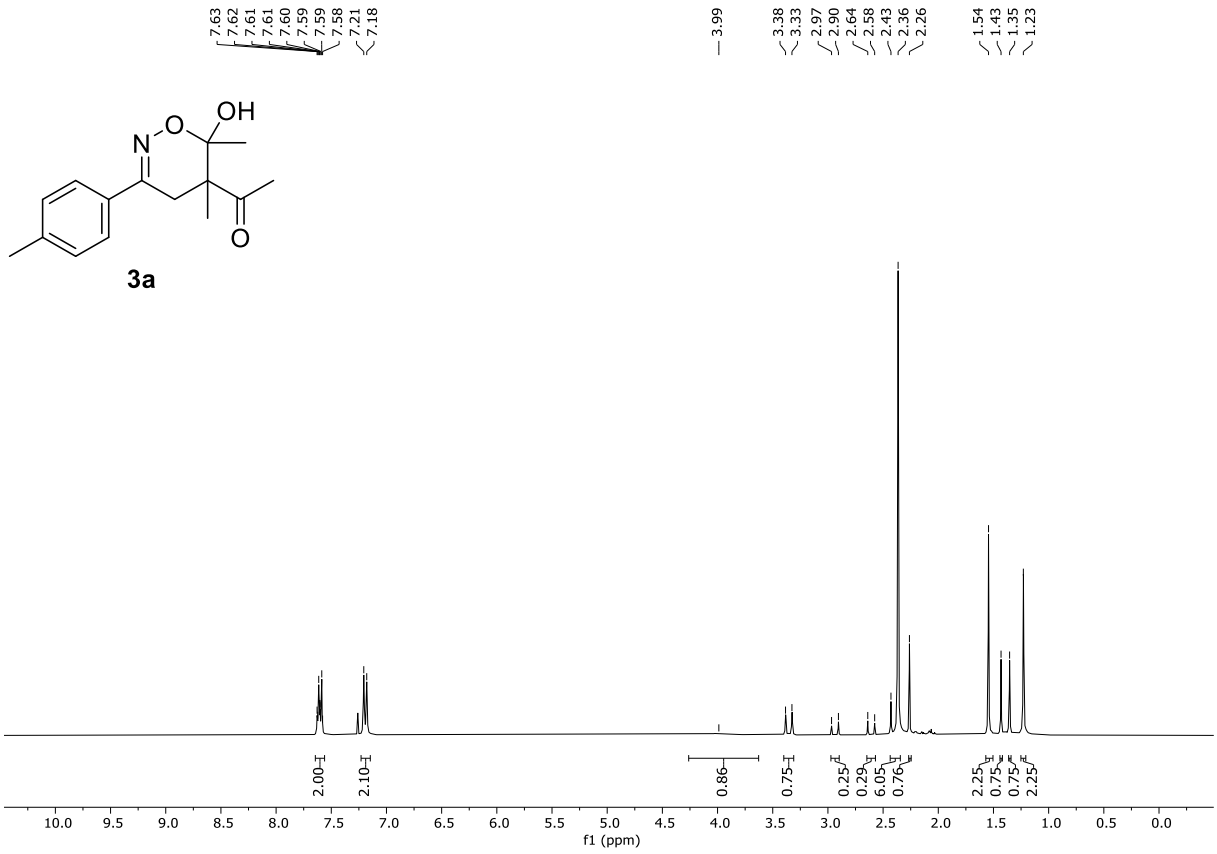
1al

^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)

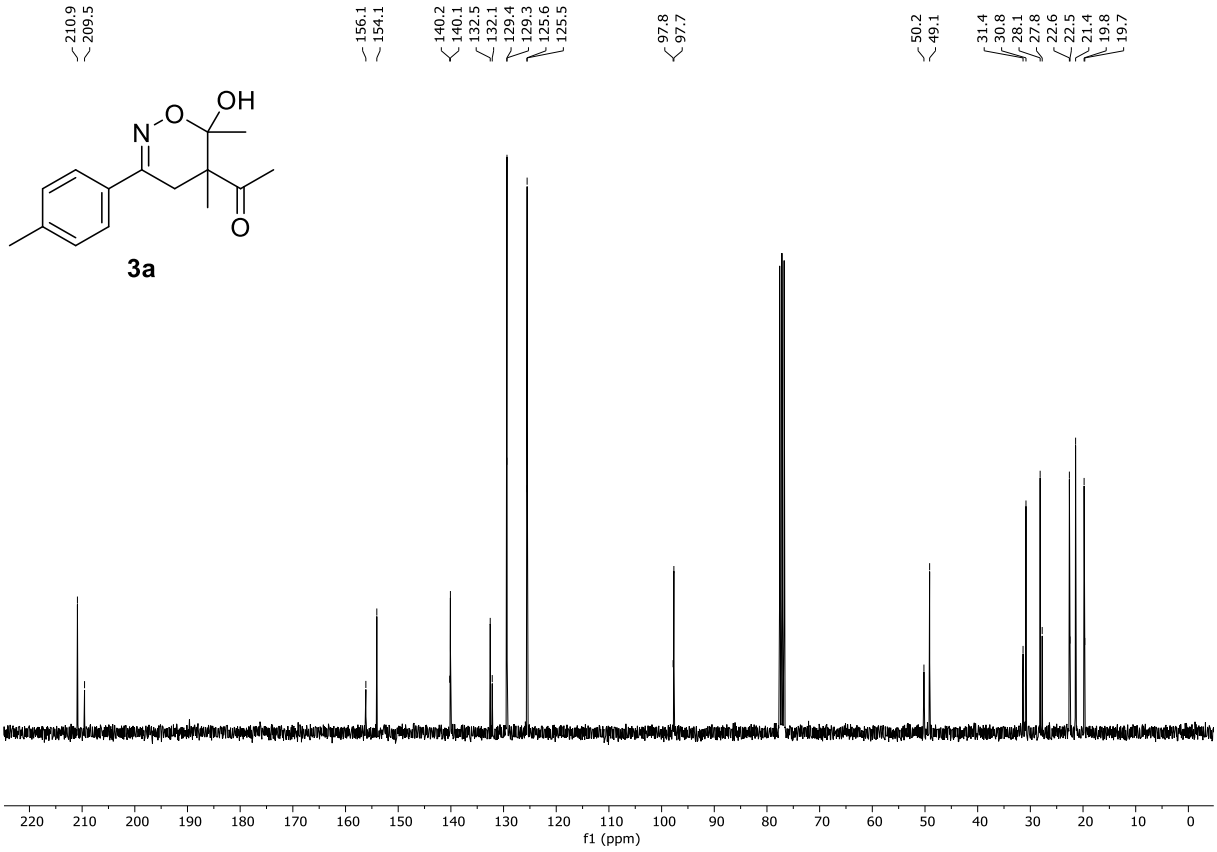


1al

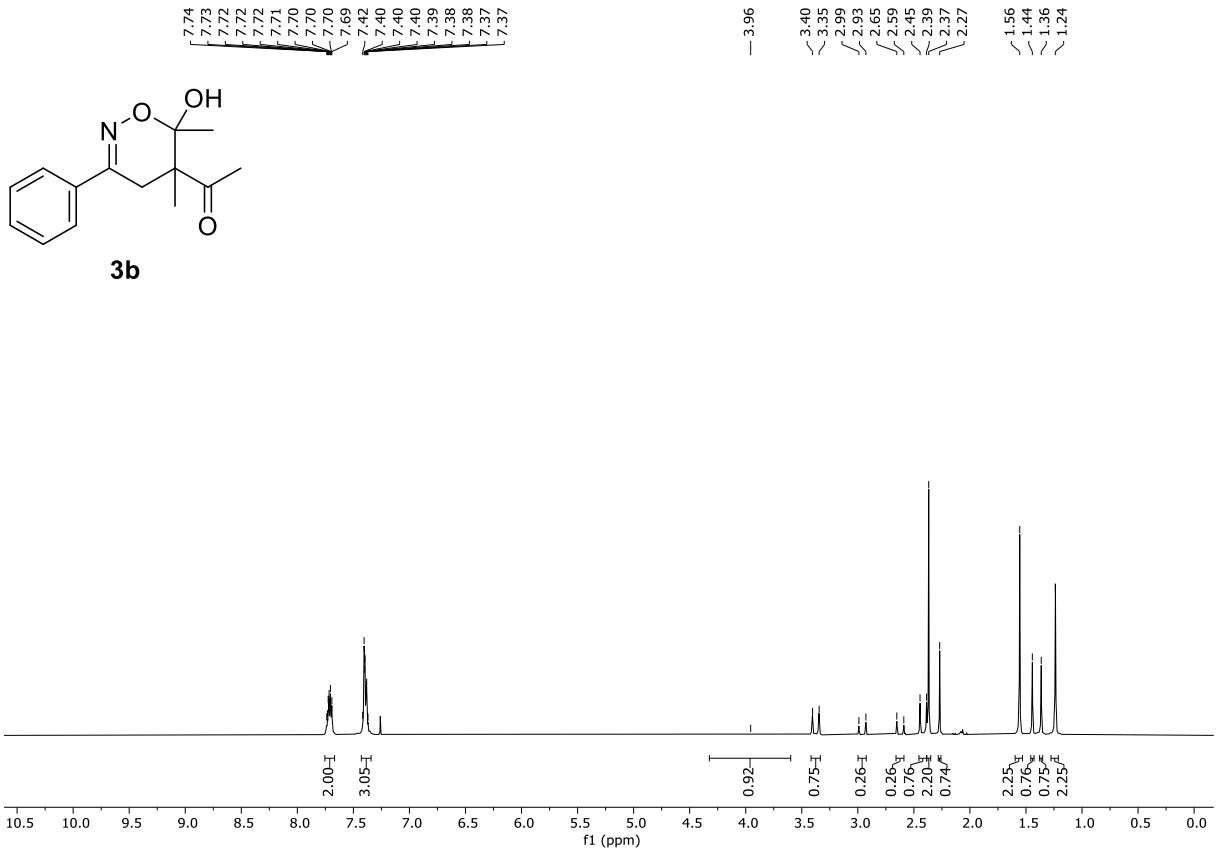
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



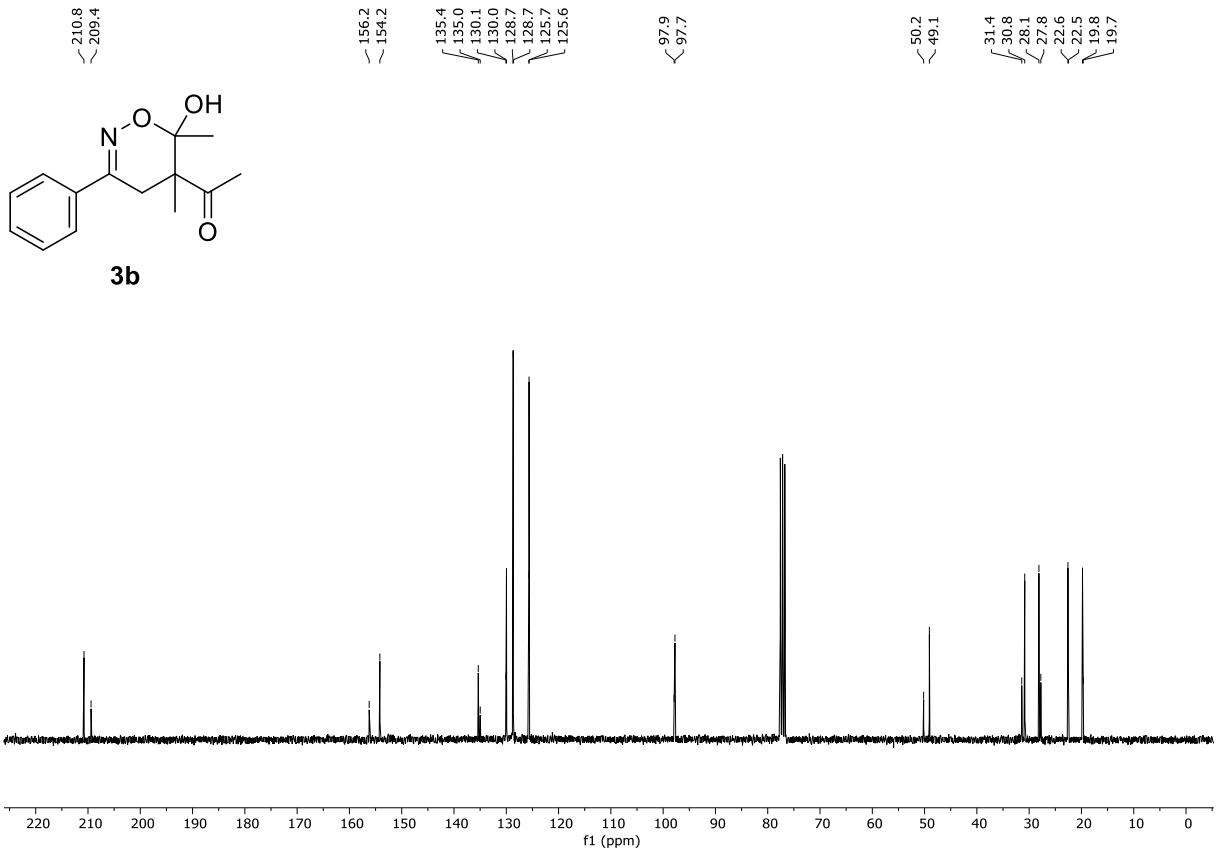
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



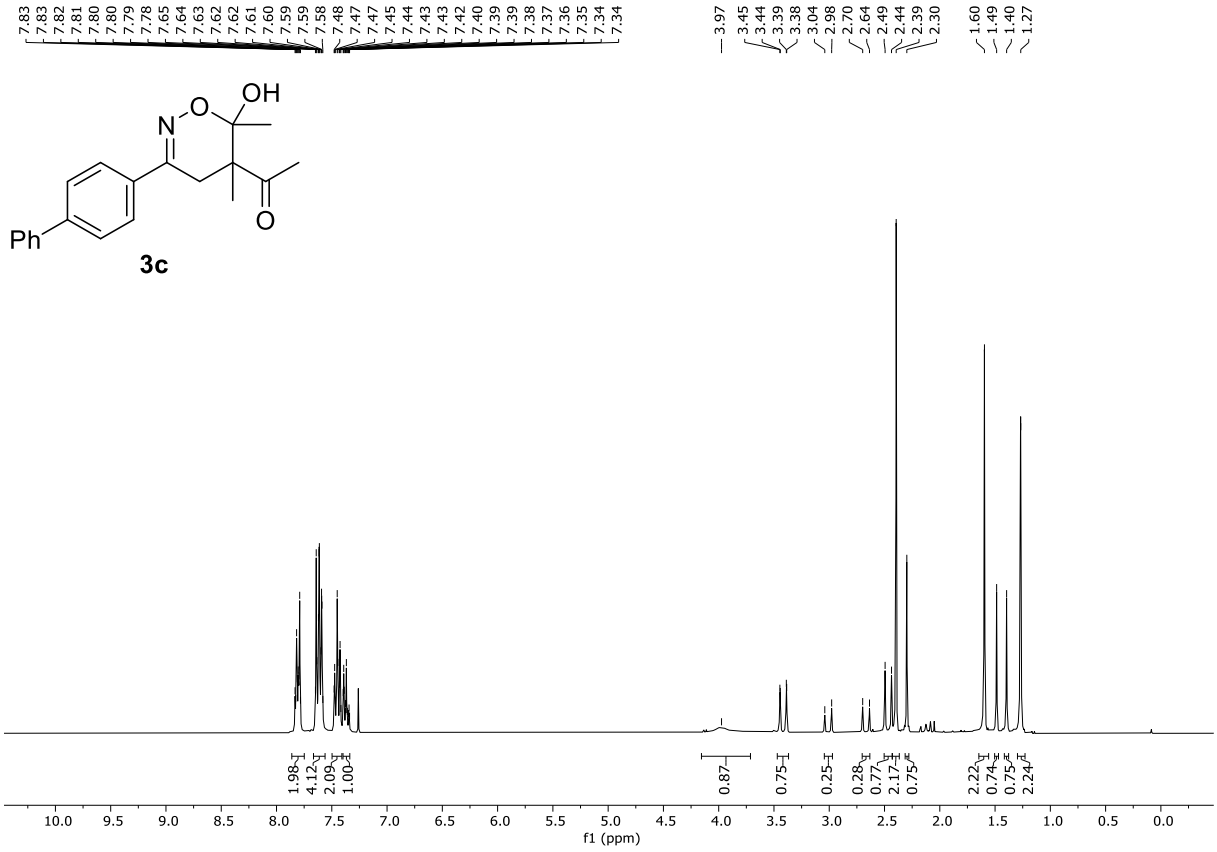
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



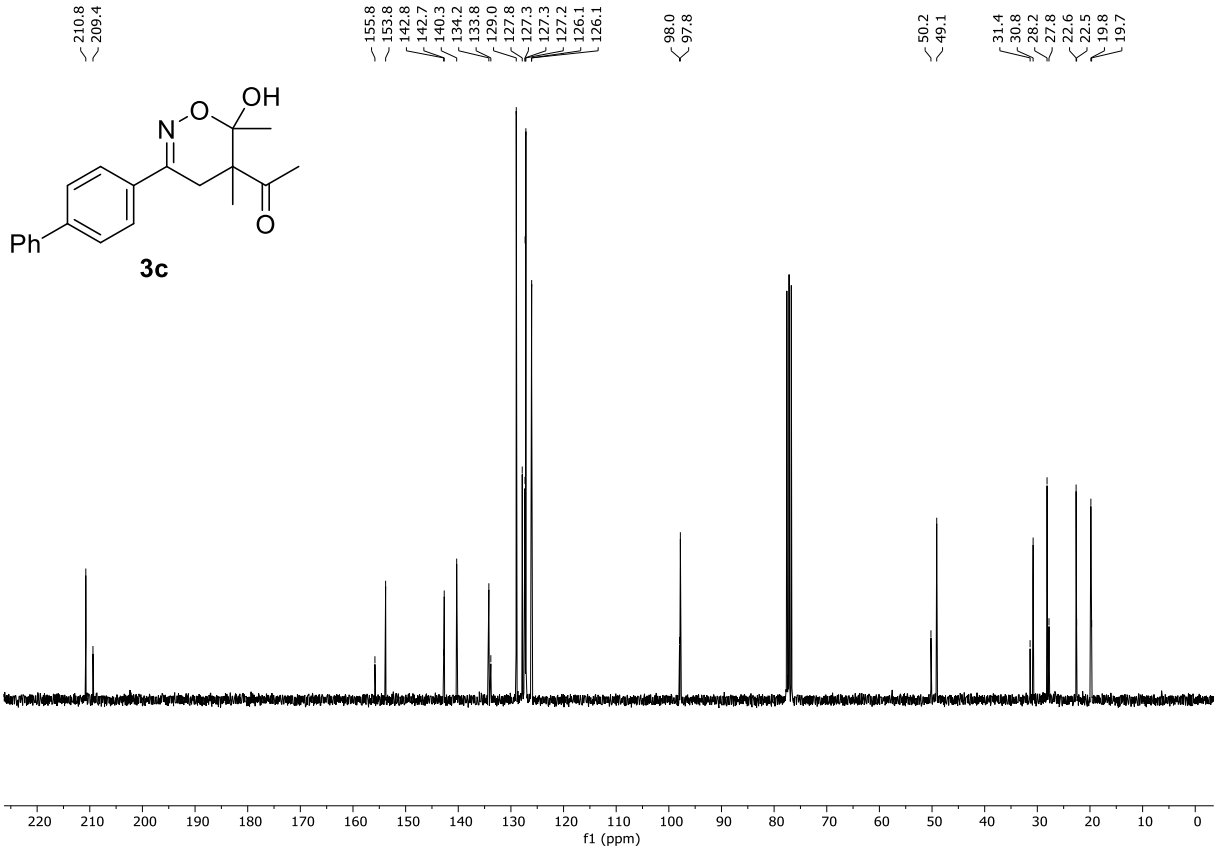
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



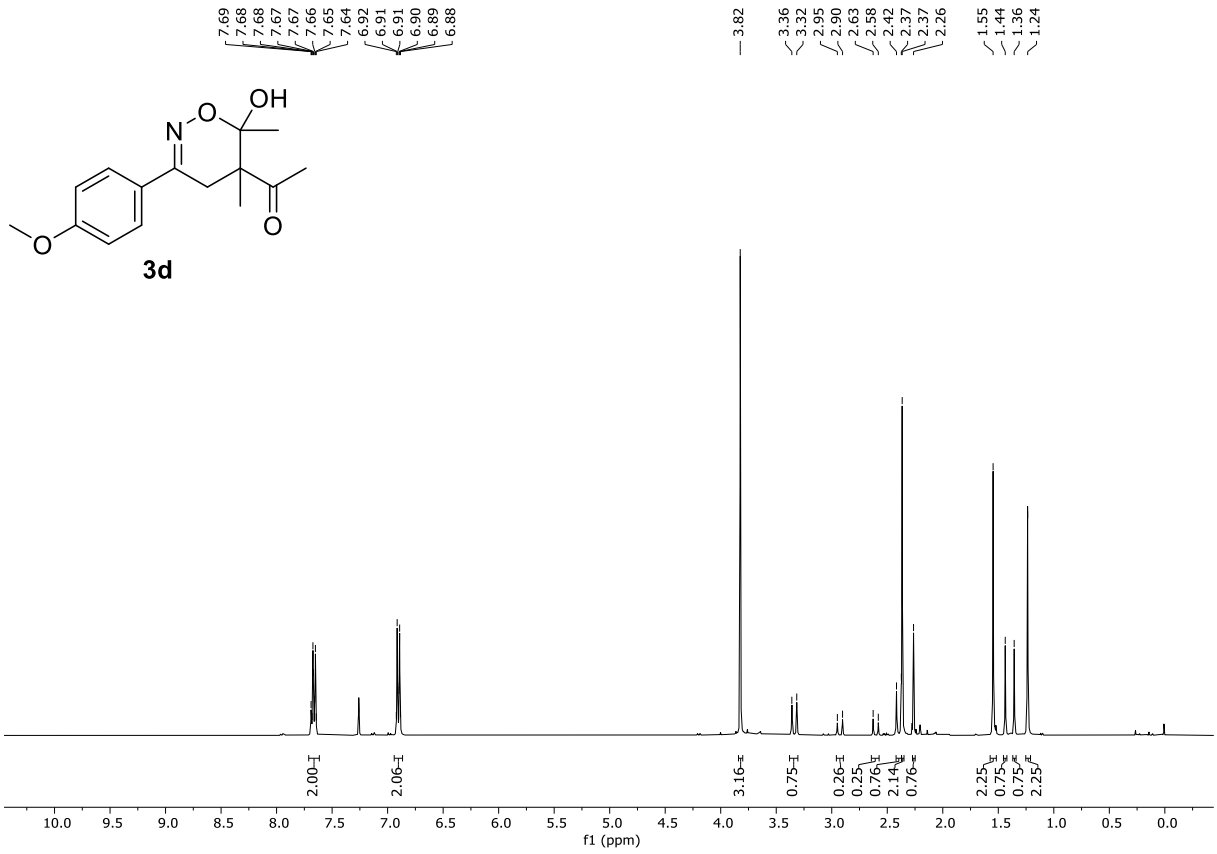
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



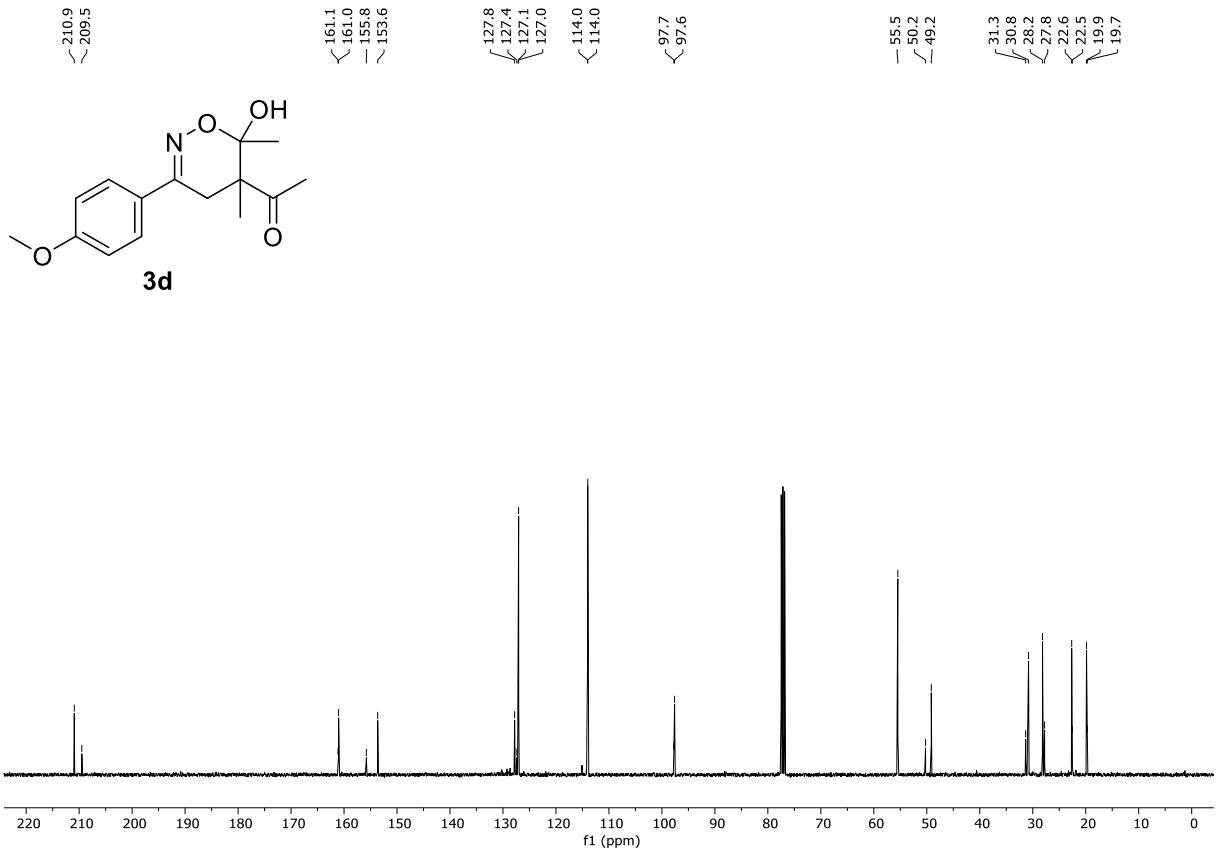
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



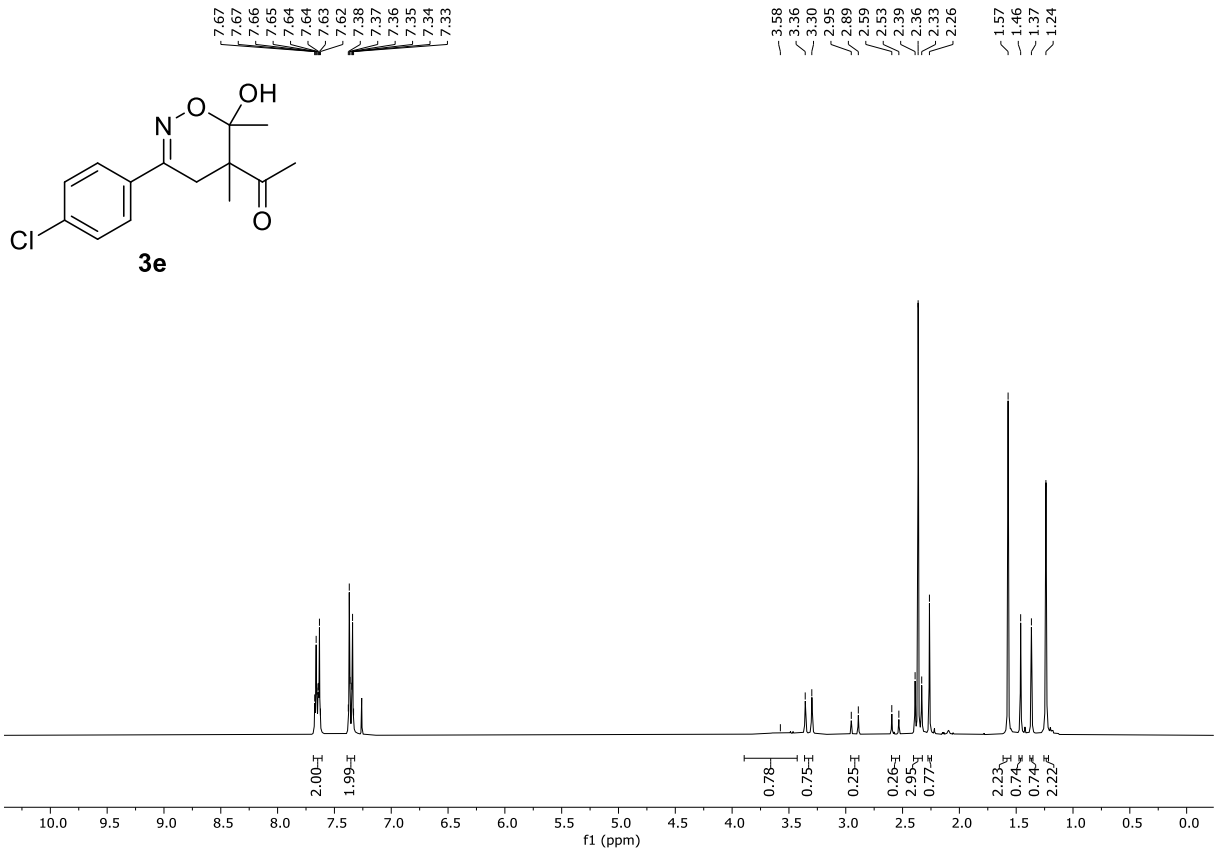
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



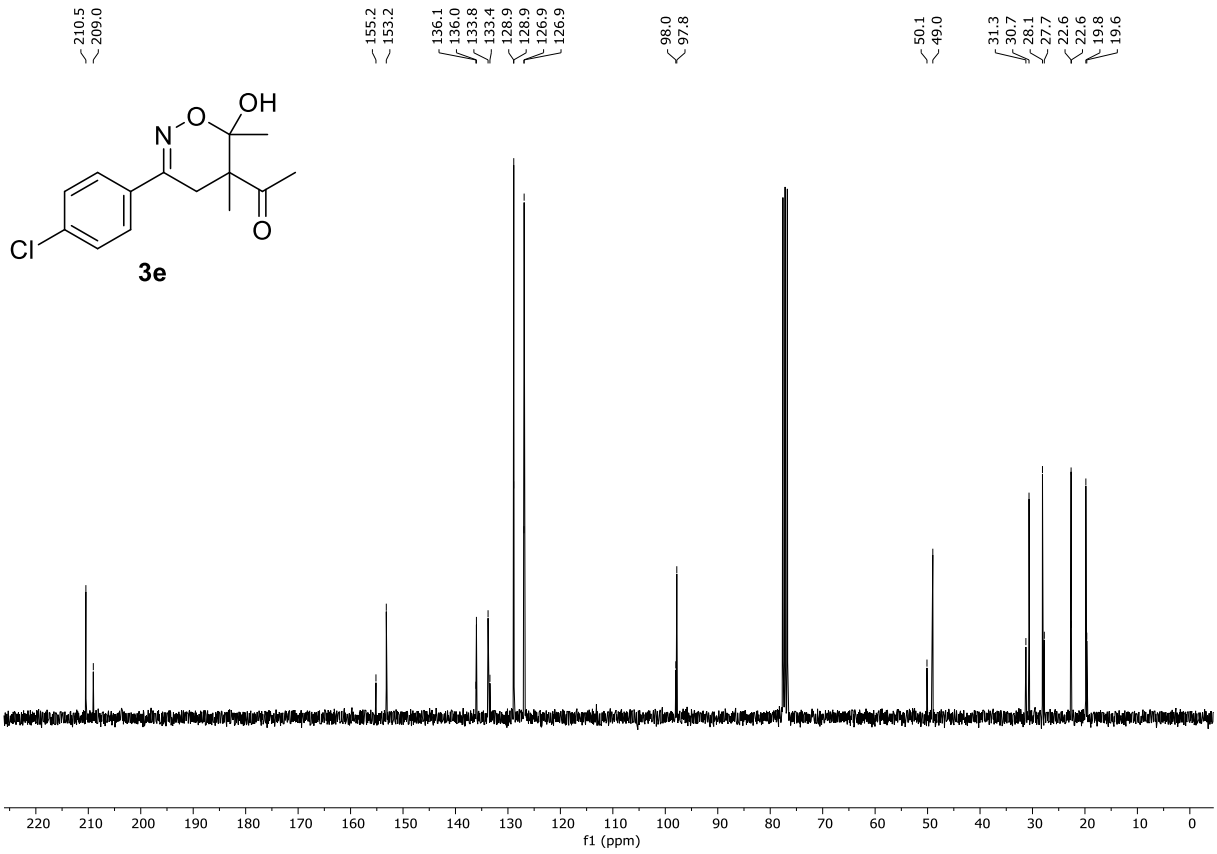
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



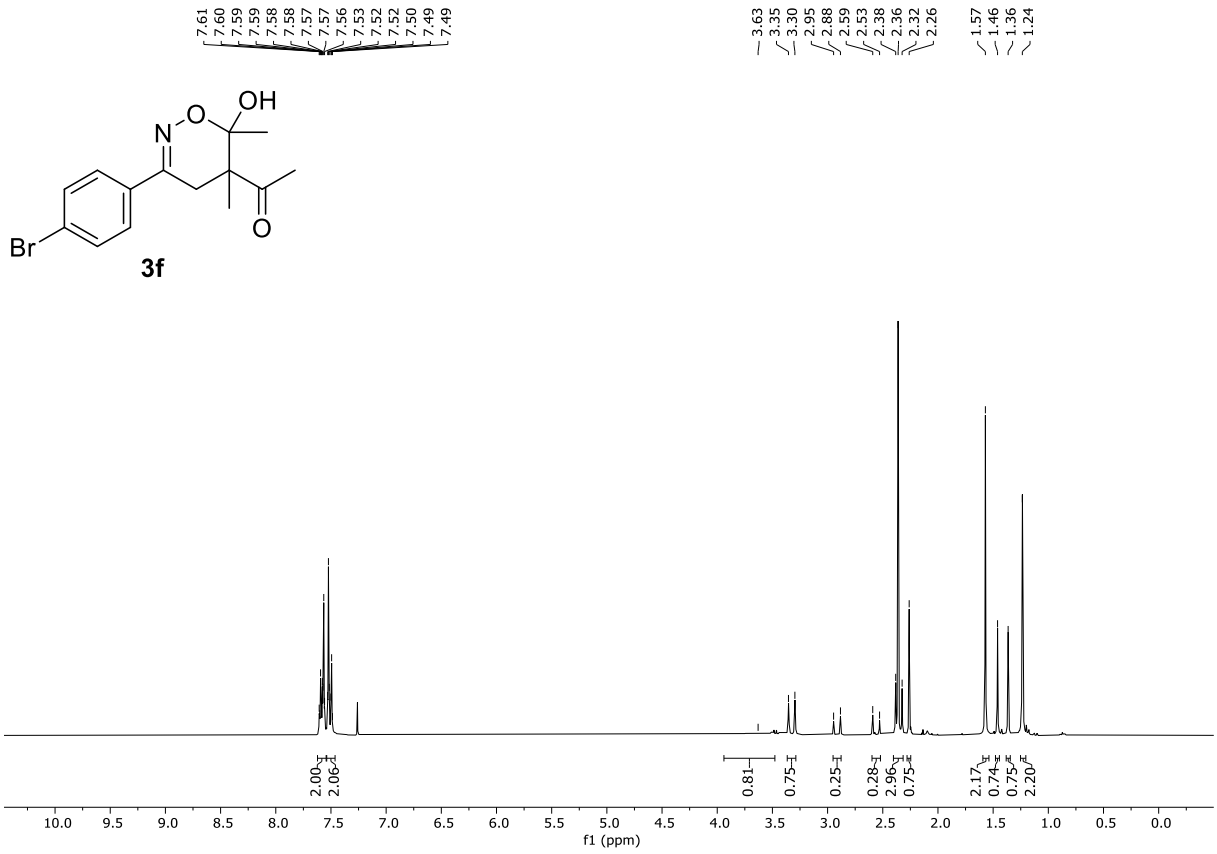
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



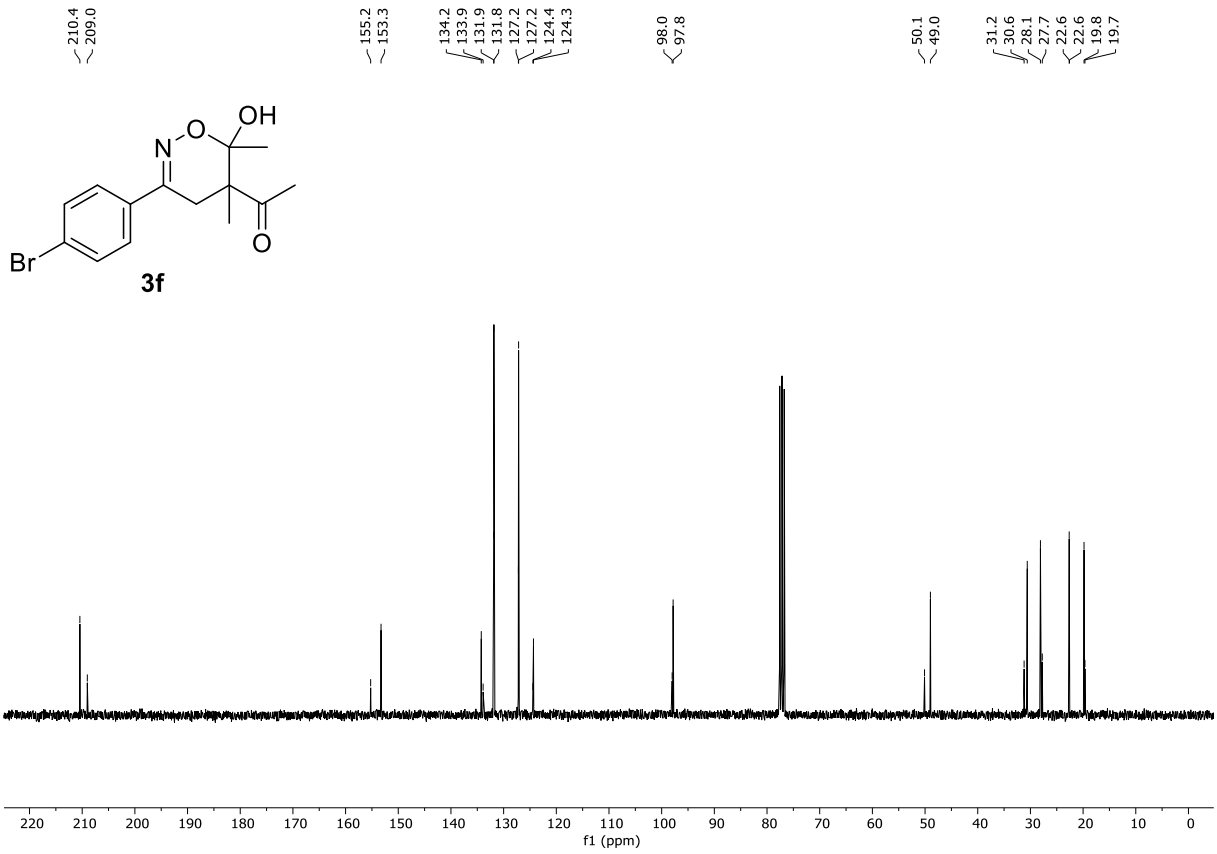
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



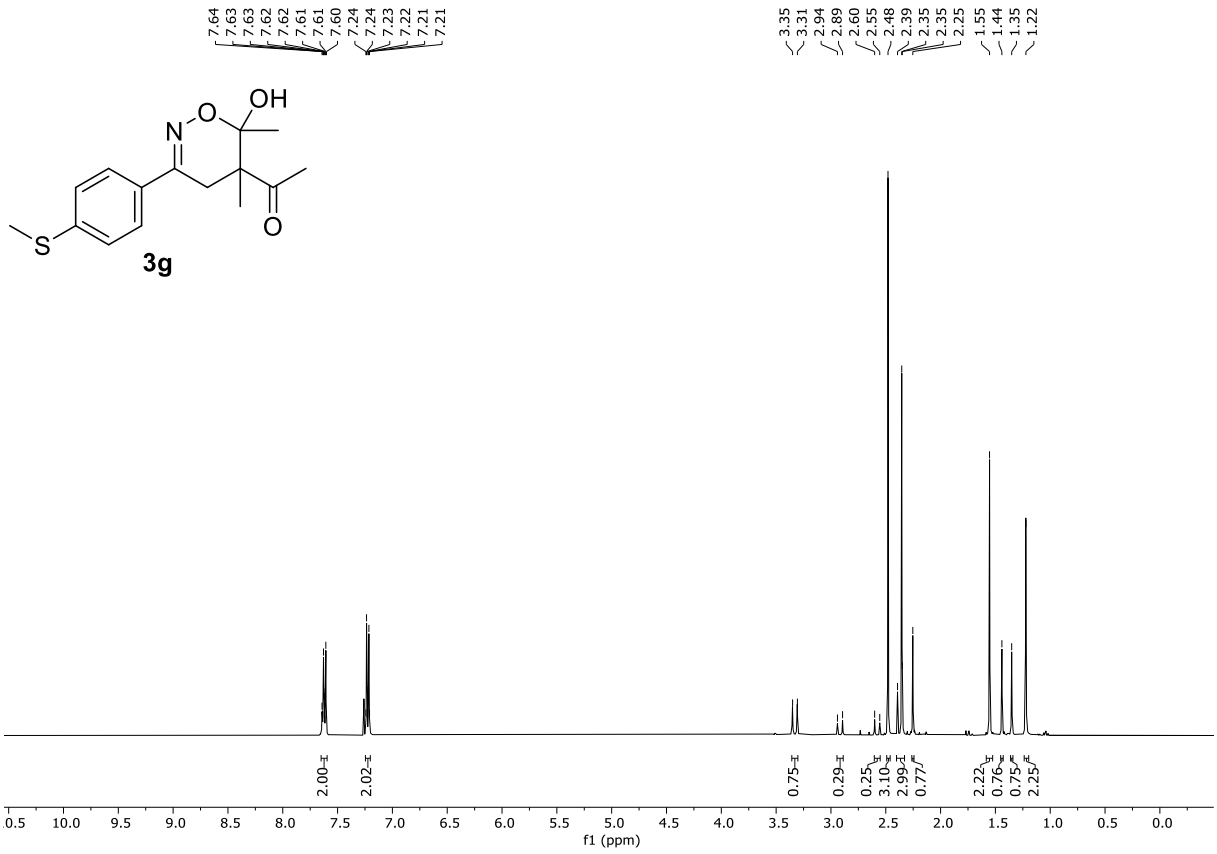
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



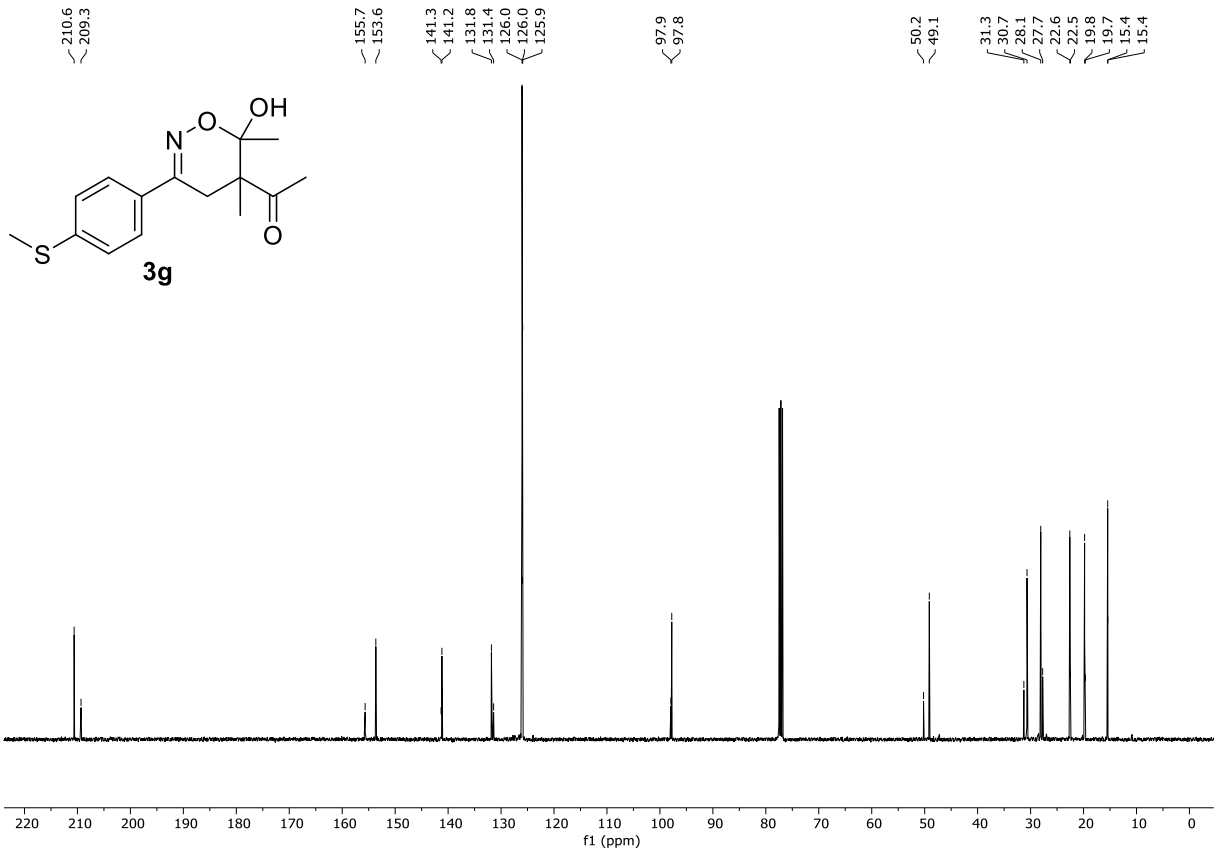
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



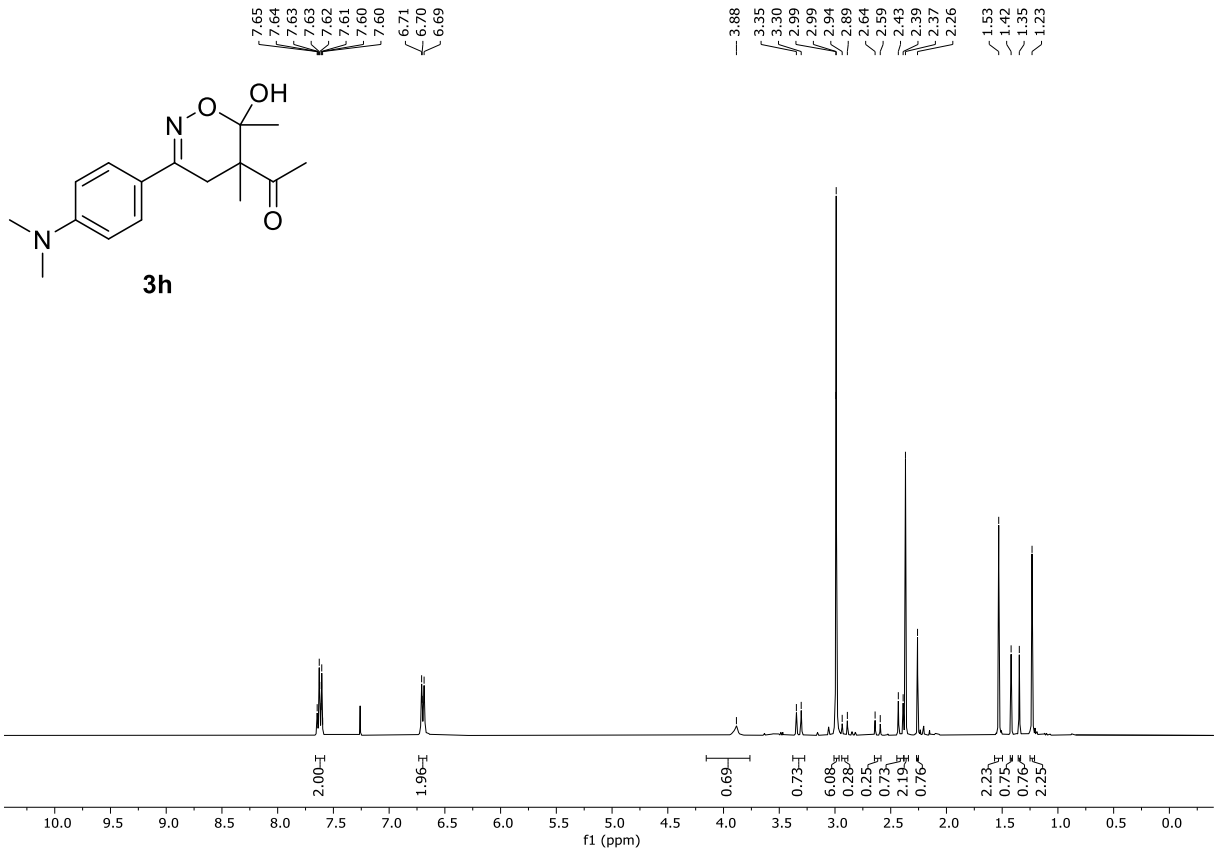
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



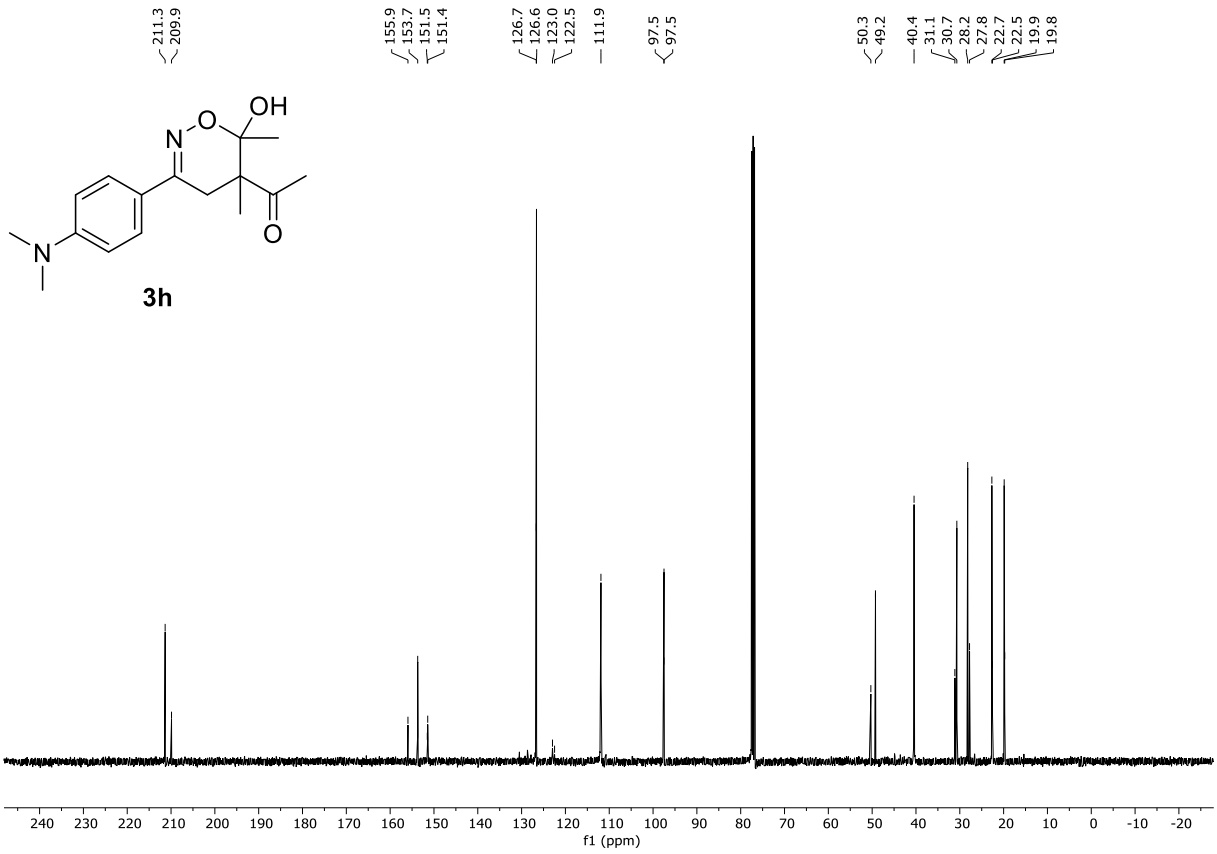
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



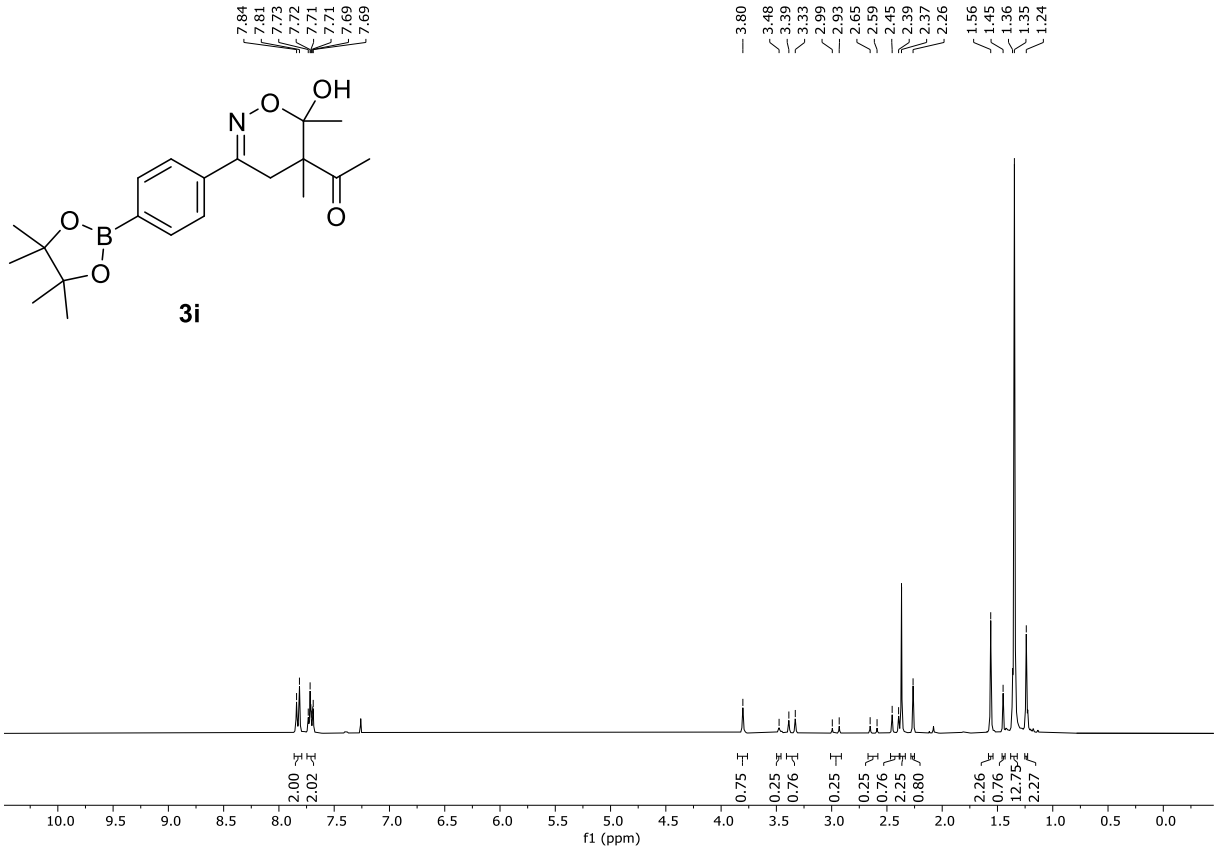
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



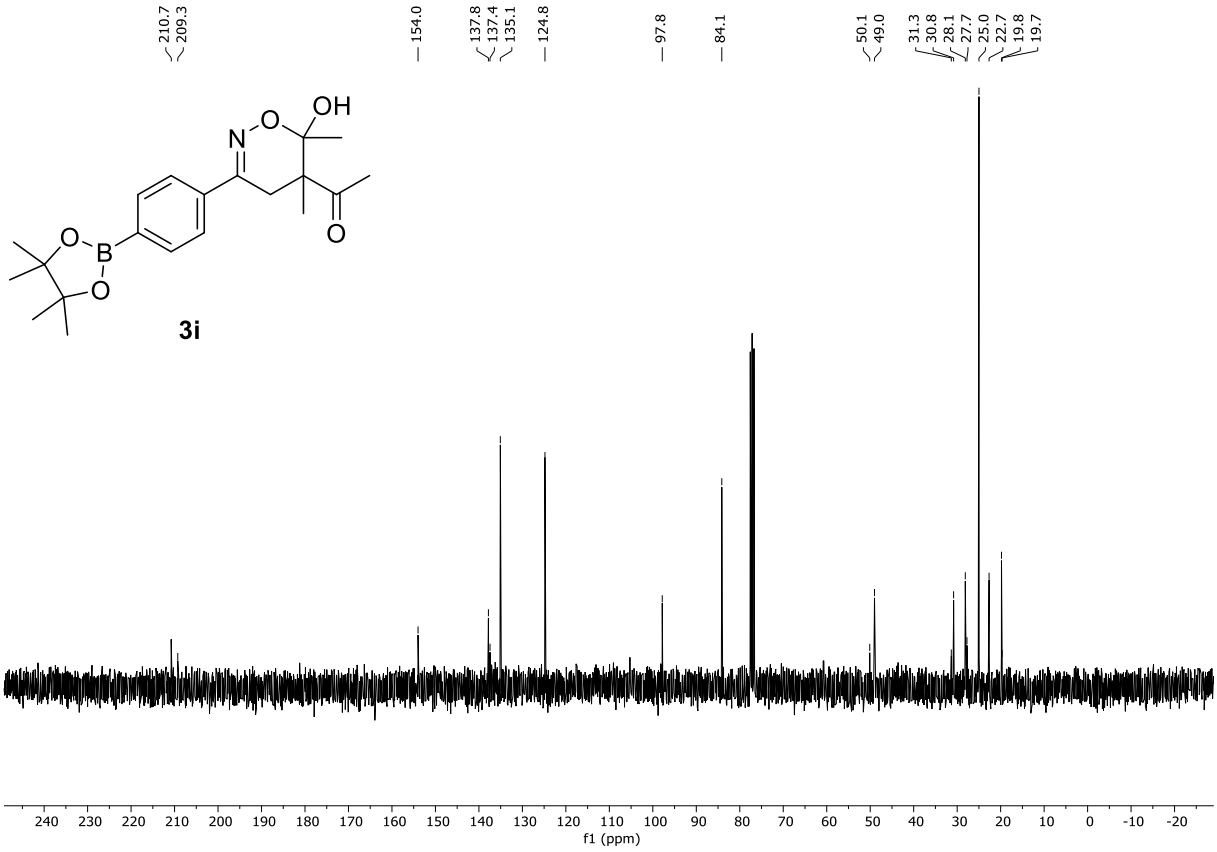
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



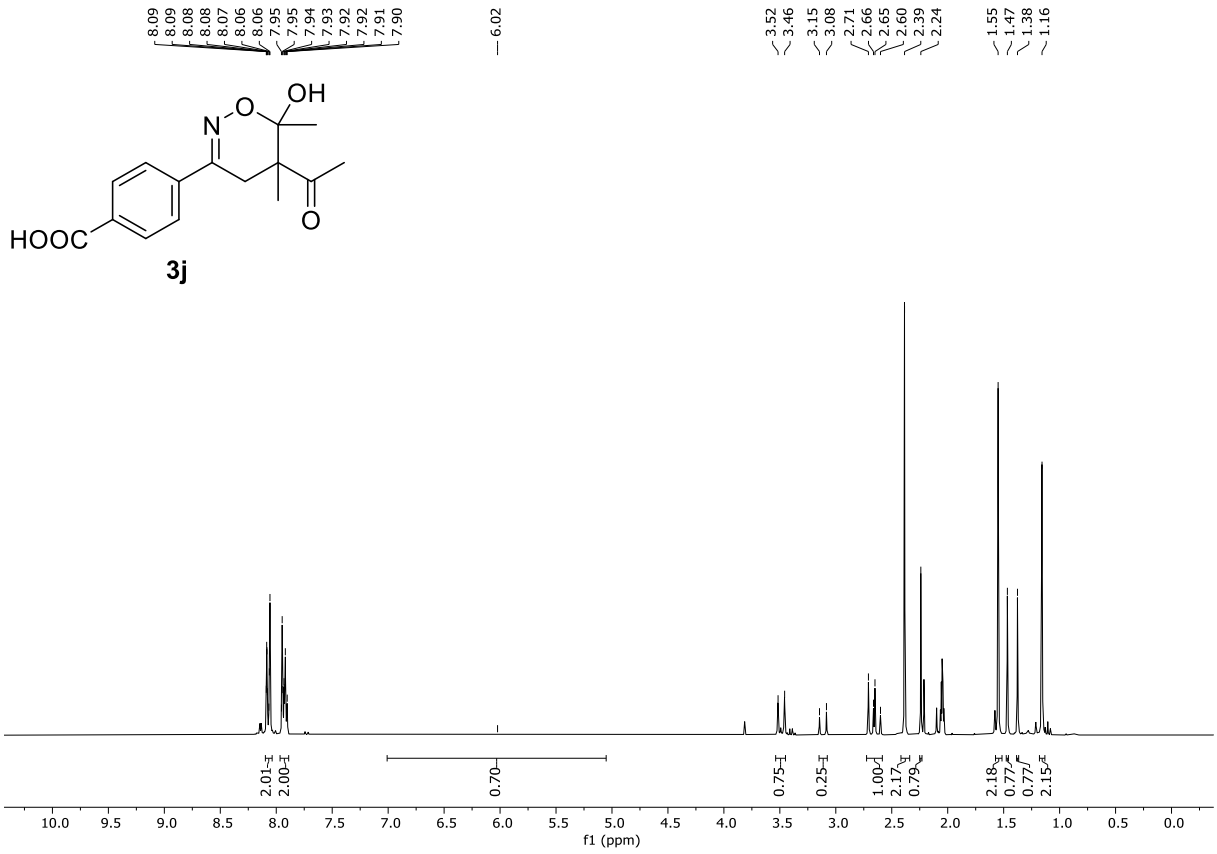
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



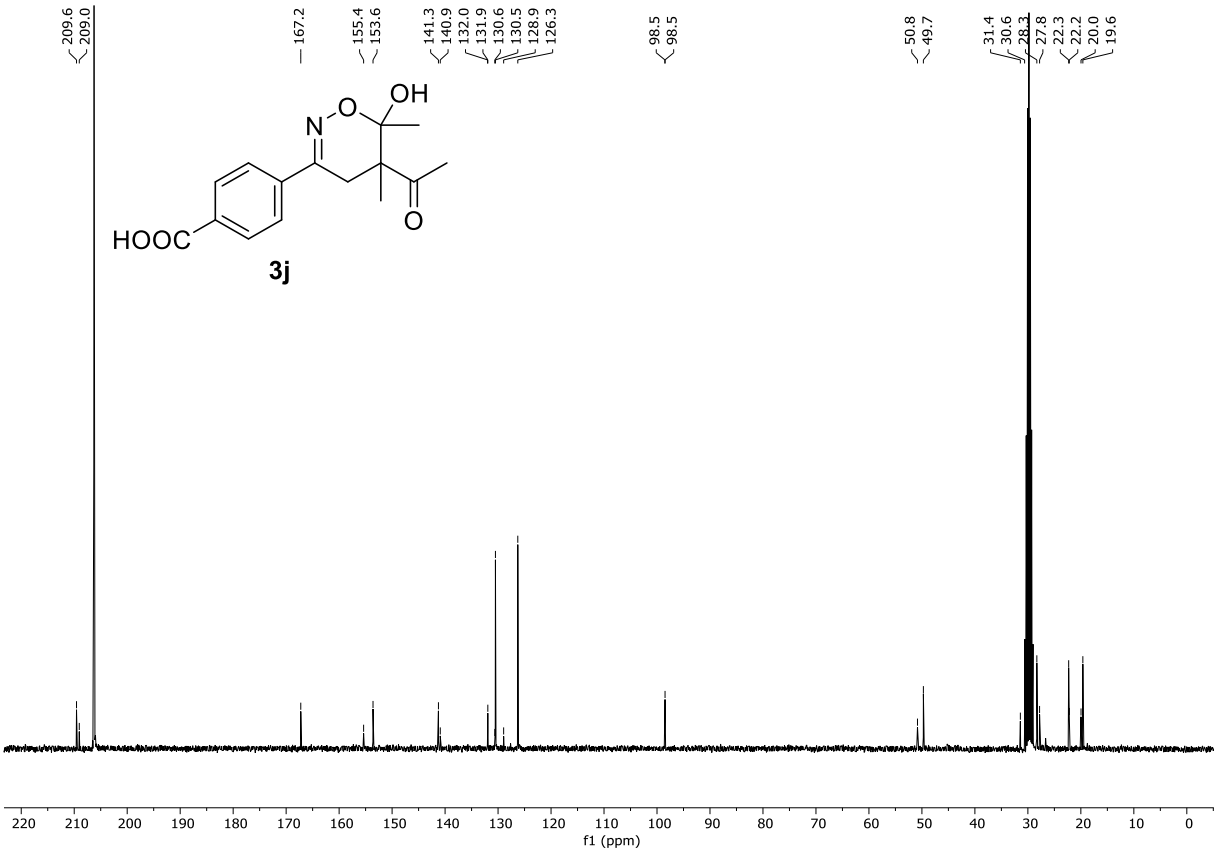
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



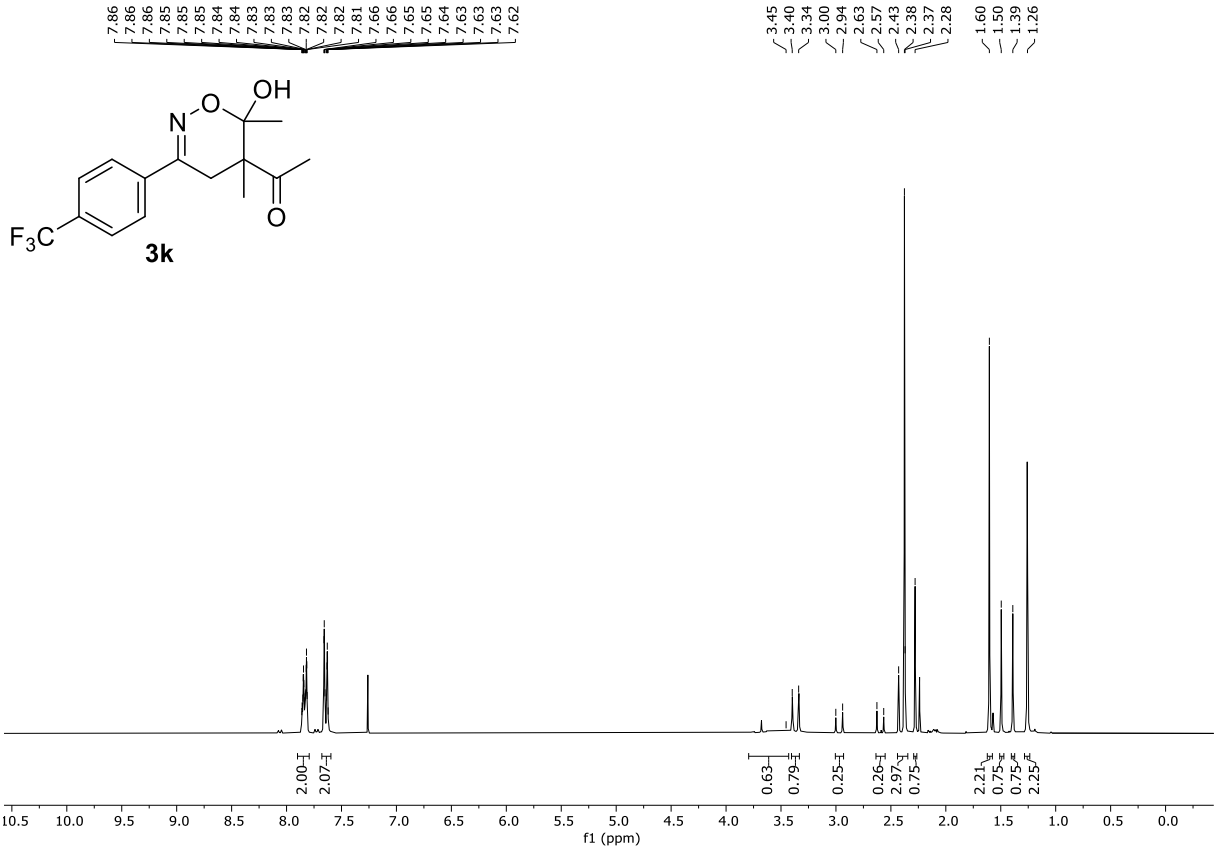
^{1}H-NMR (300 MHz, acetone-d_6, 299 K)



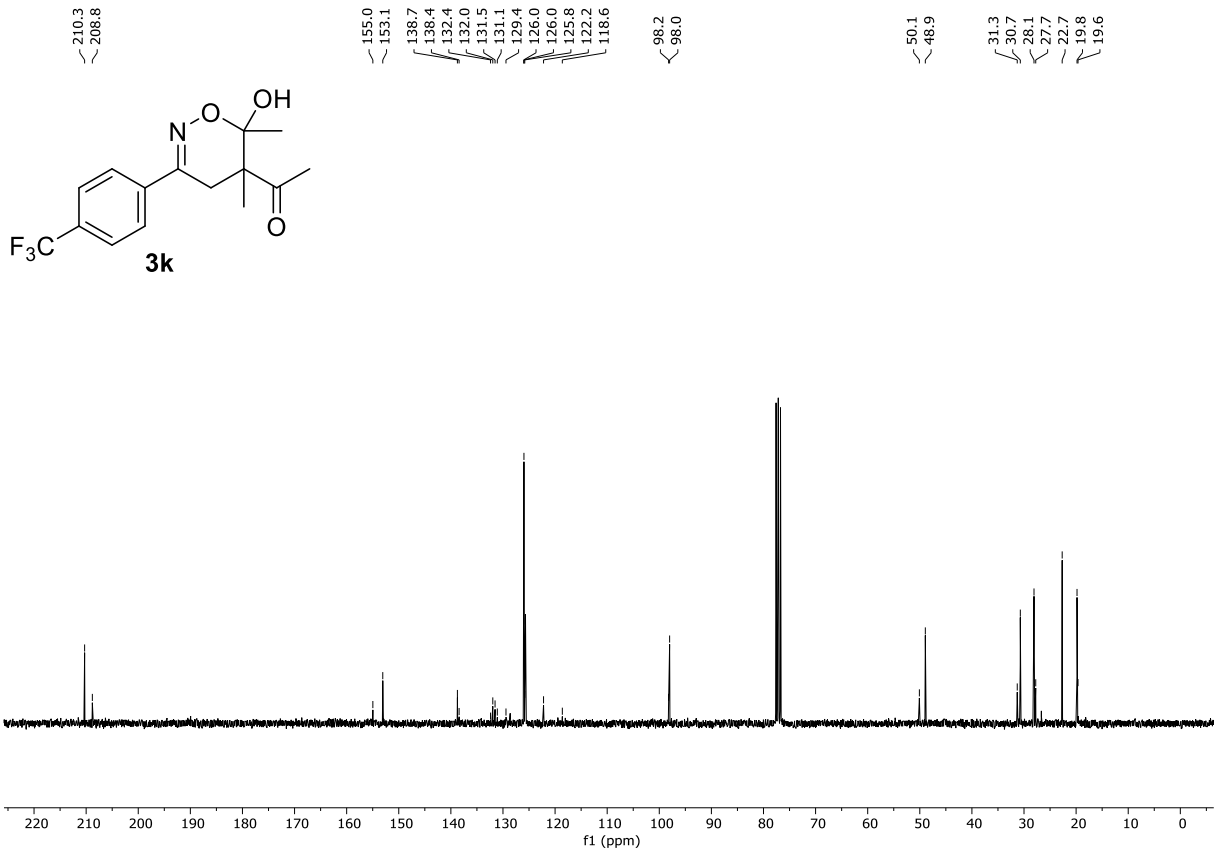
^{13}C-NMR (75 MHz, acetone-d_6, 299 K)



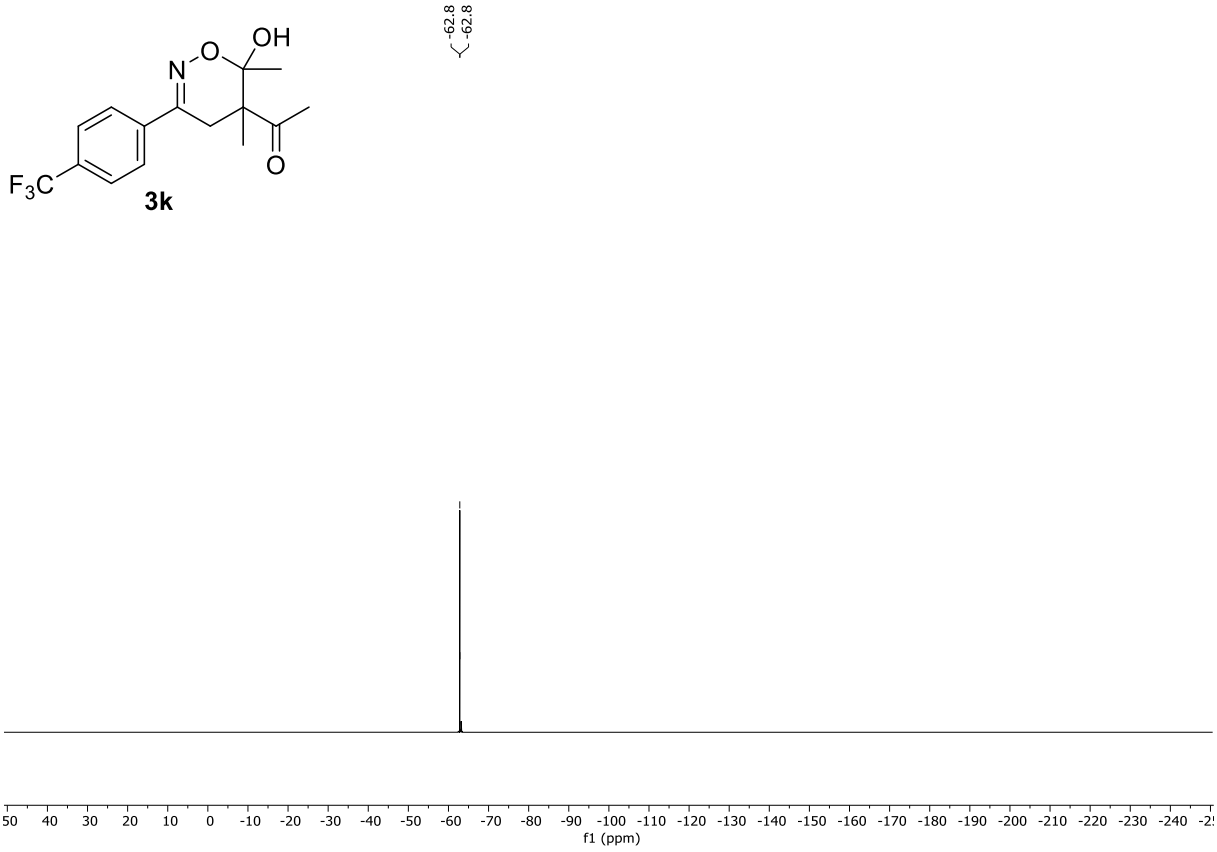
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



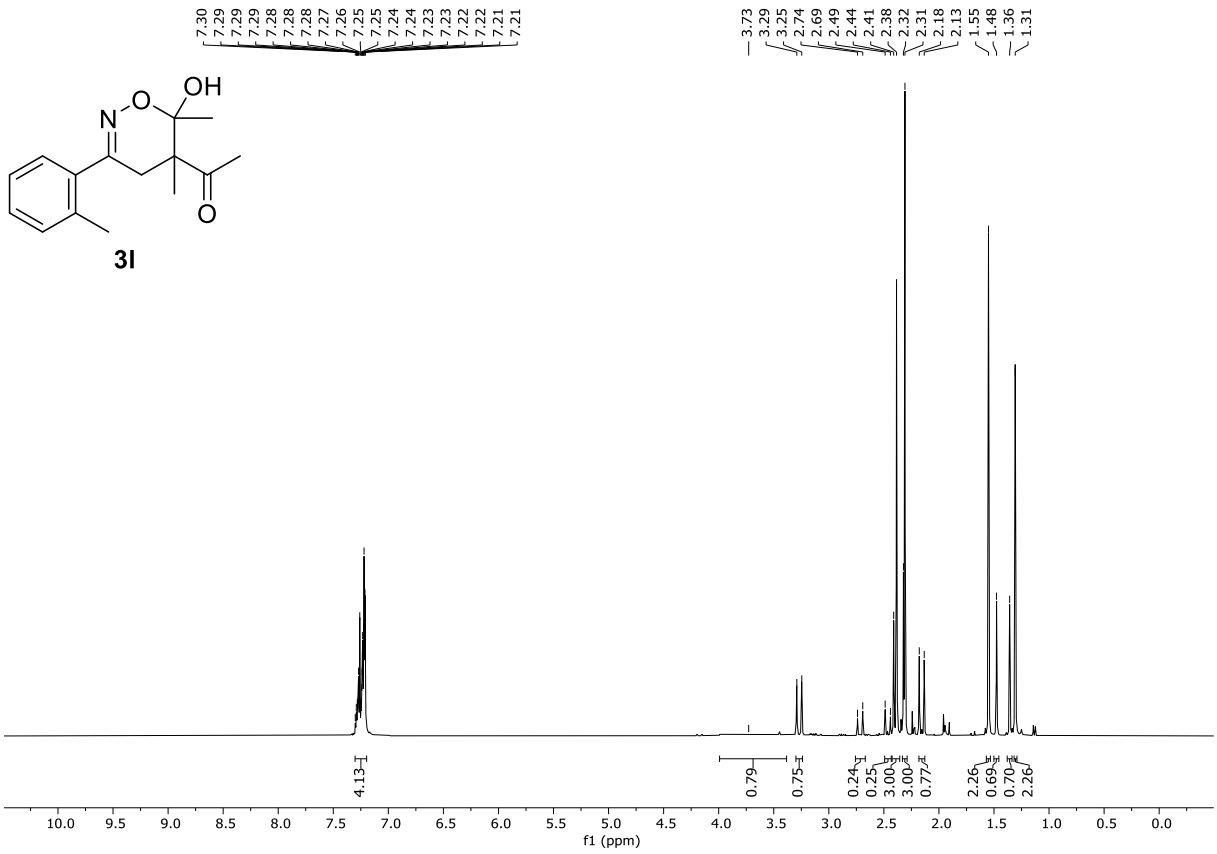
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



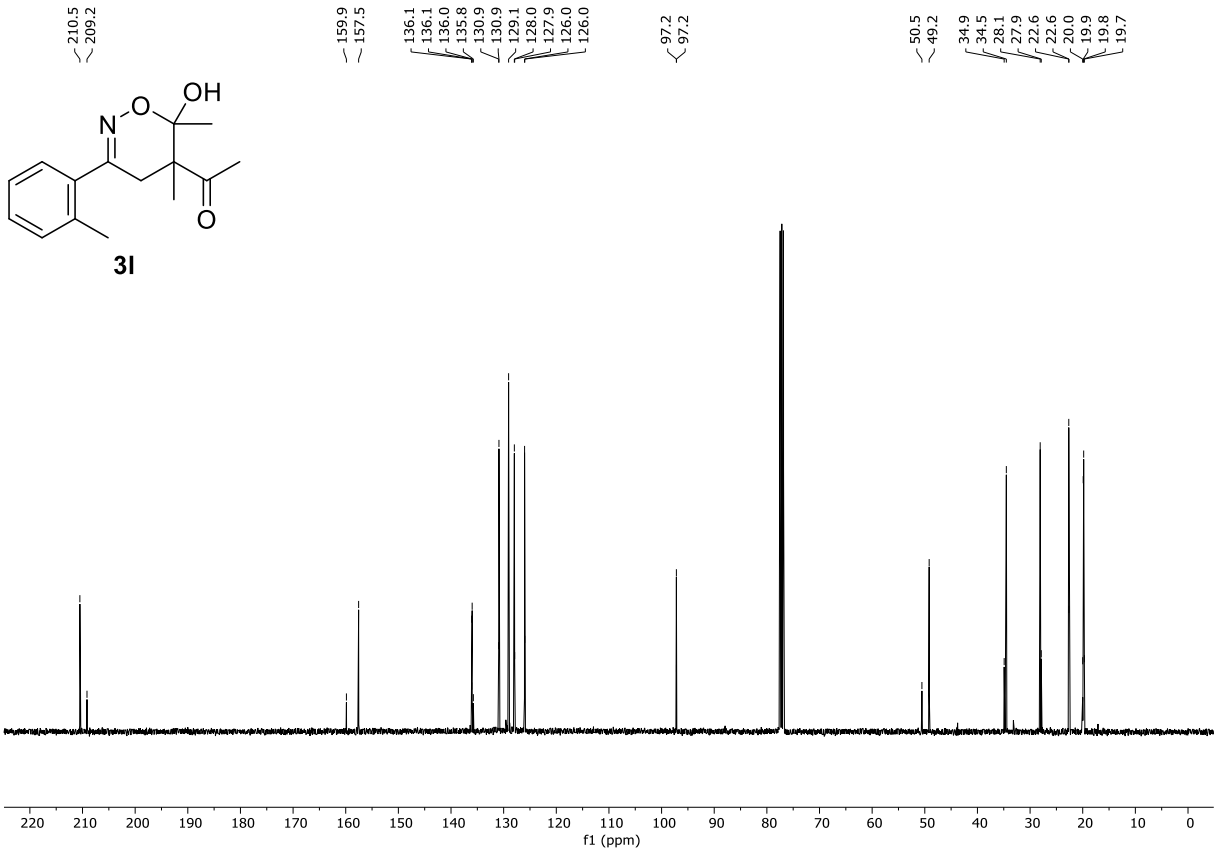
^{19}F-NMR (282 MHz, $CDCl_3$, 299 K)



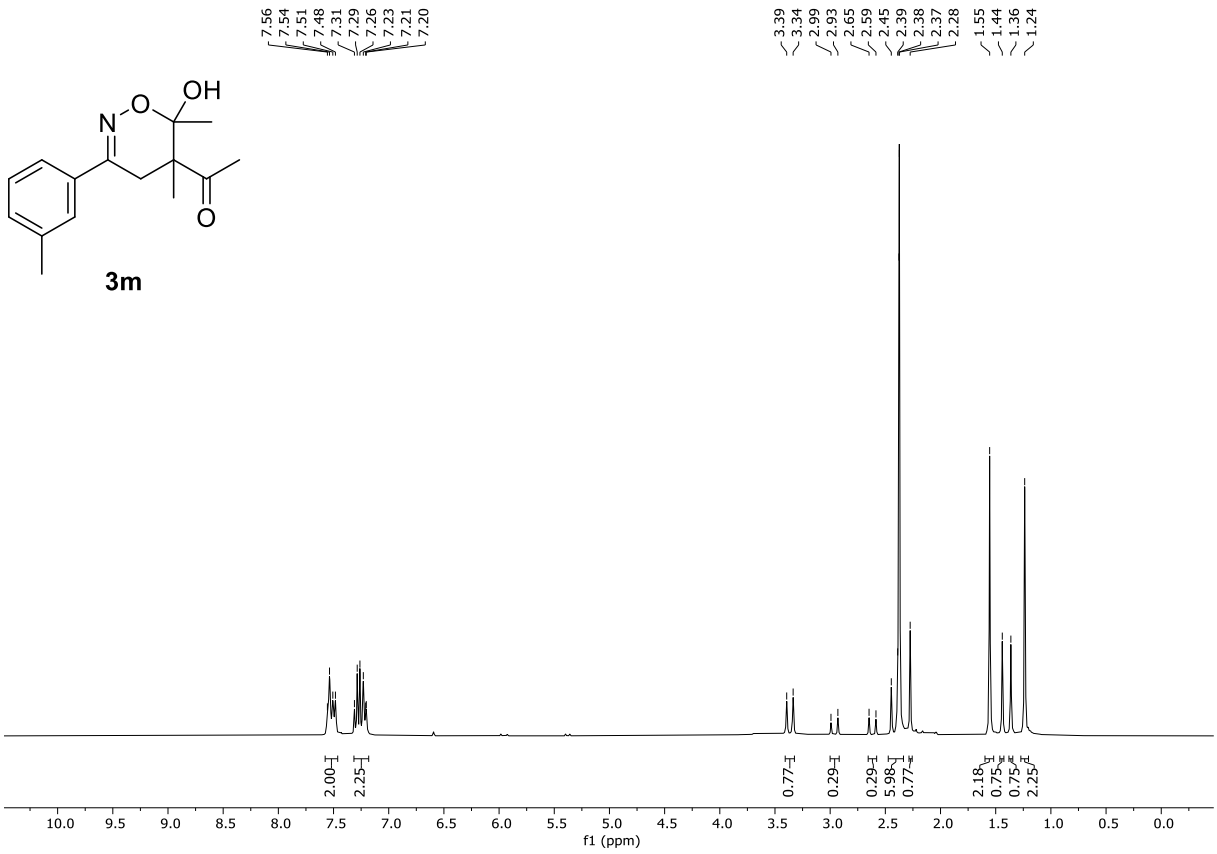
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



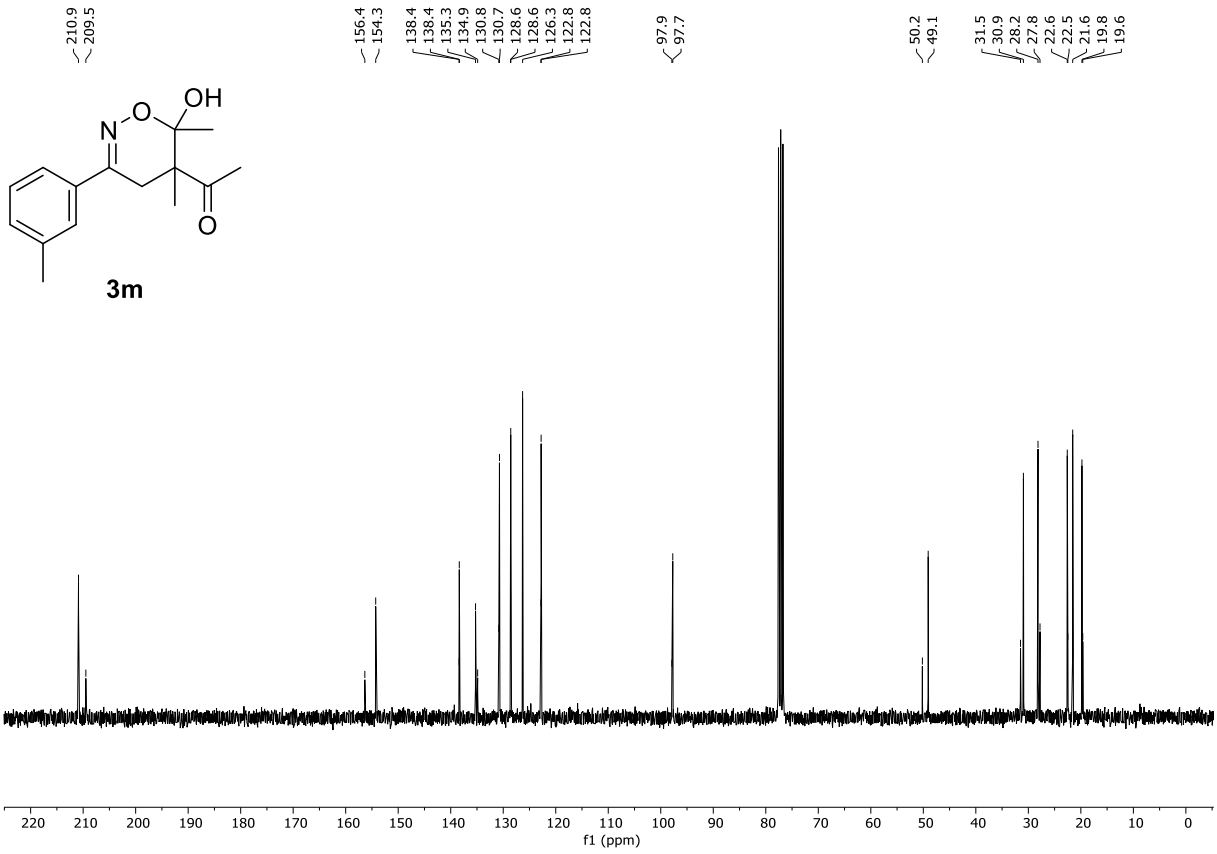
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



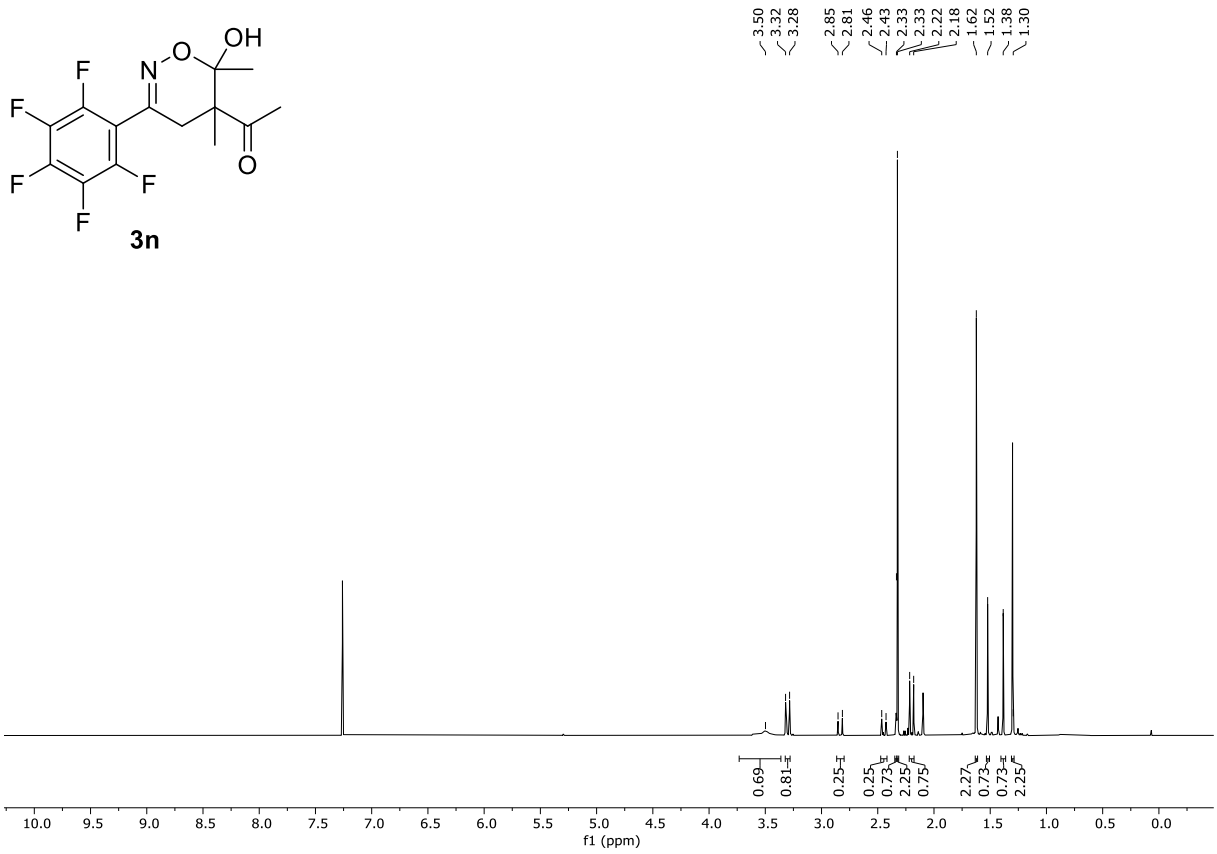
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



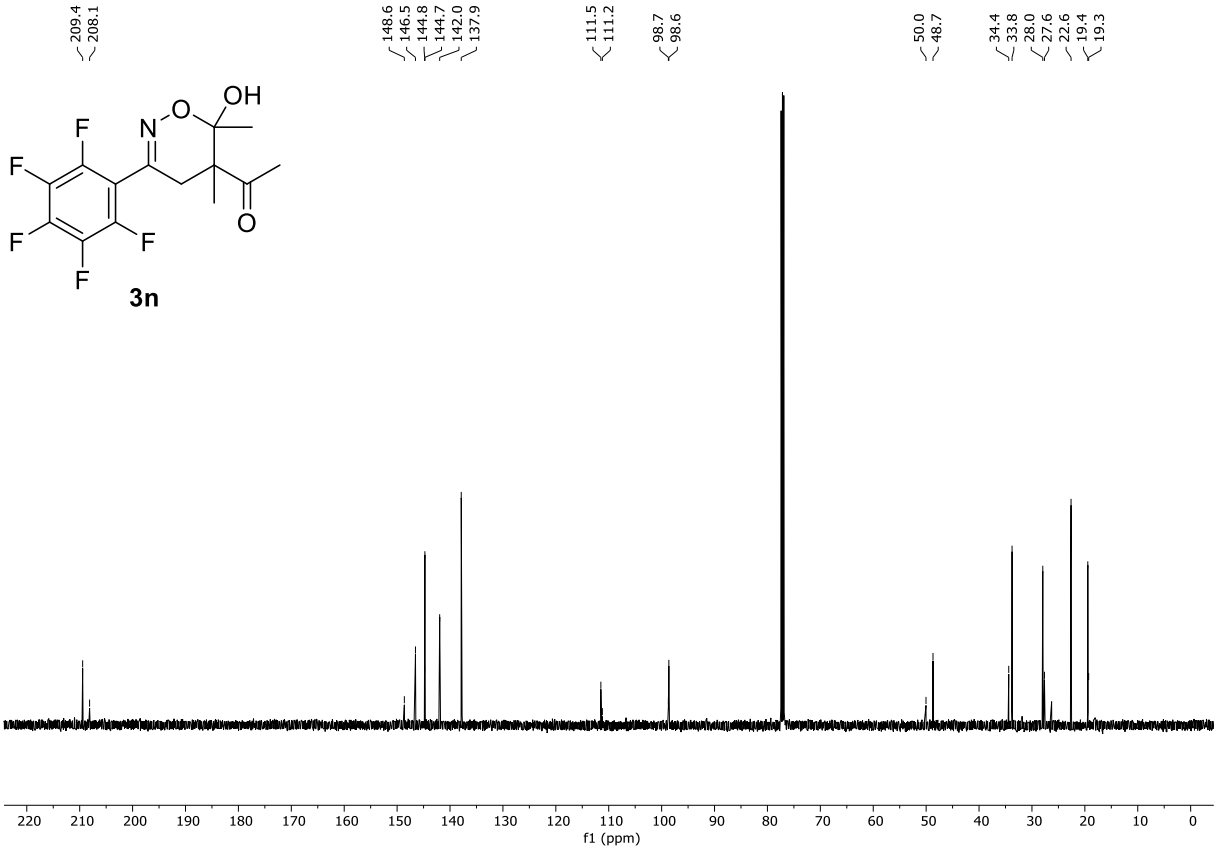
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



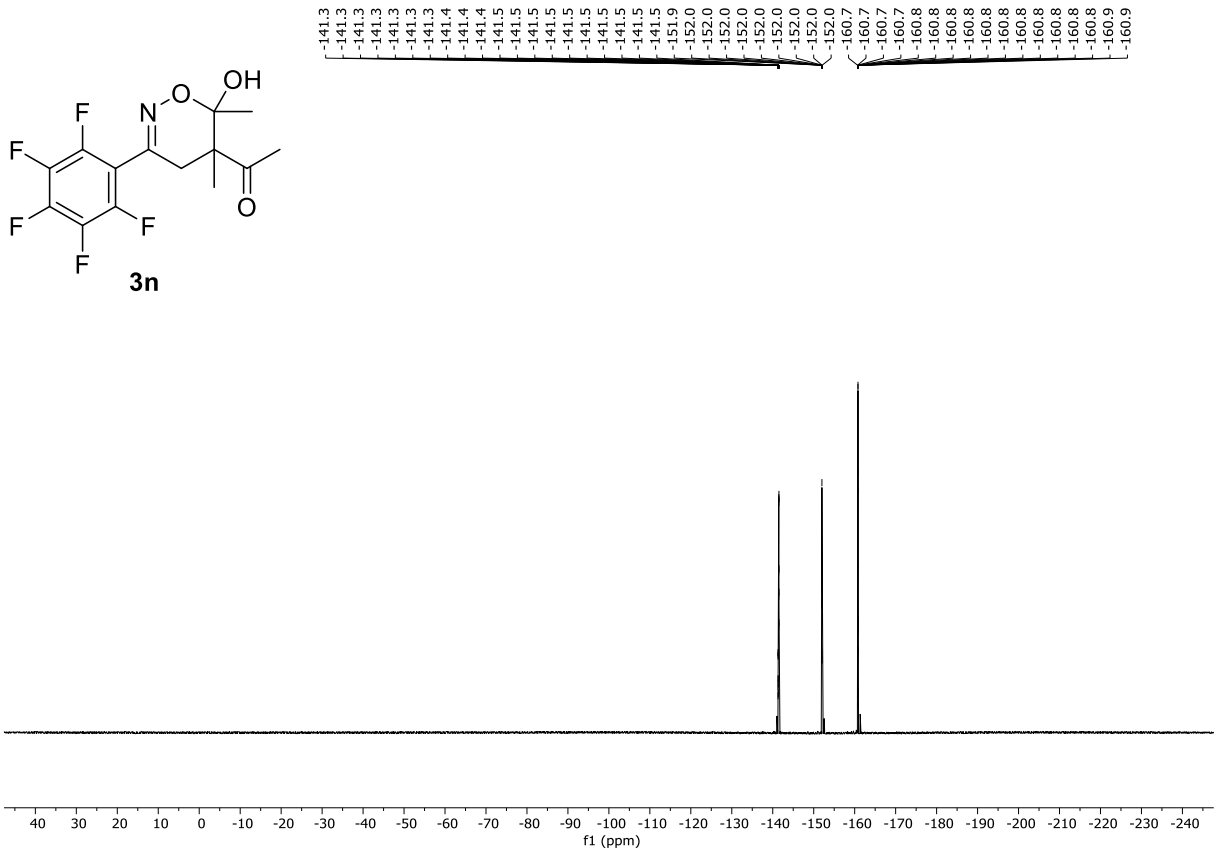
^{1}H-NMR (500 MHz, $CDCl_3$, 299 K)



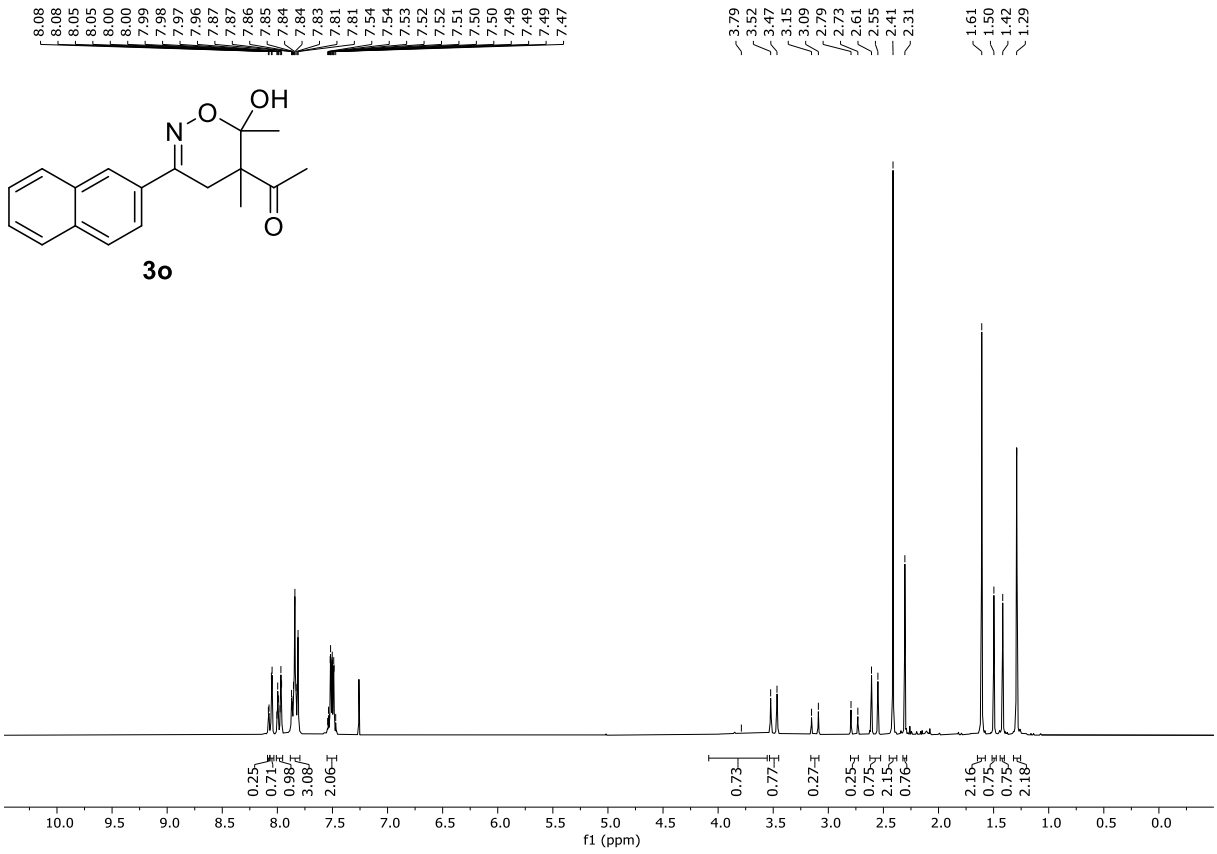
^{13}C-NMR {^{19}F} (126 MHz, $CDCl_3$, 299 K)



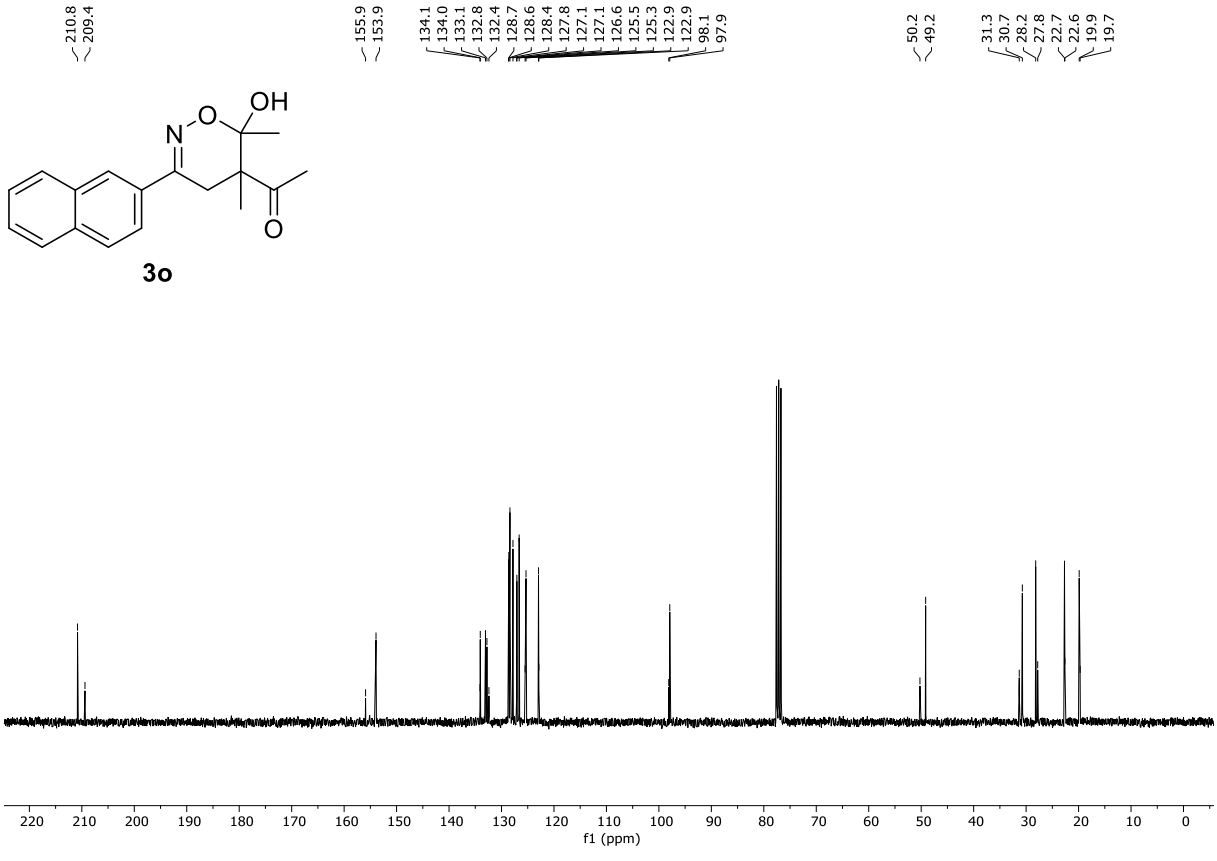
^{19}F-NMR (470 MHz, $CDCl_3$, 299 K)



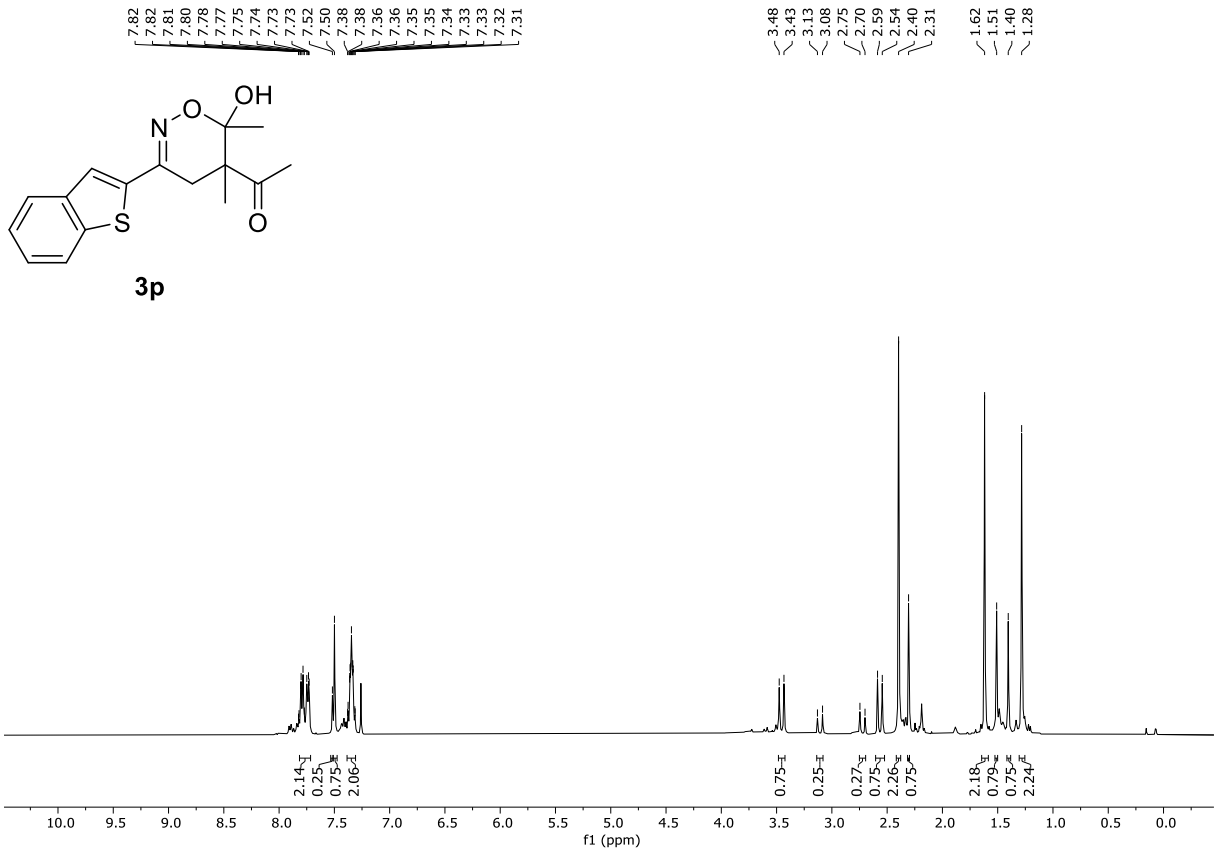
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



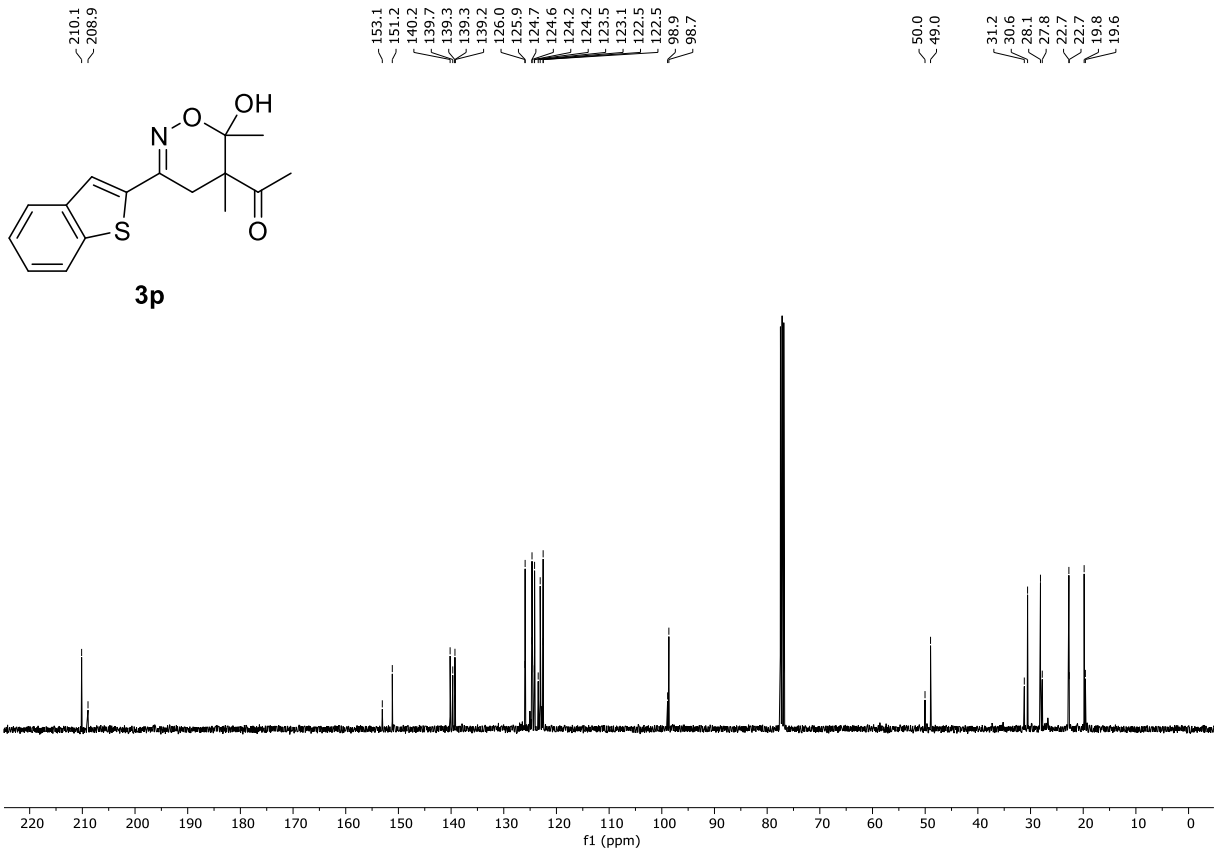
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



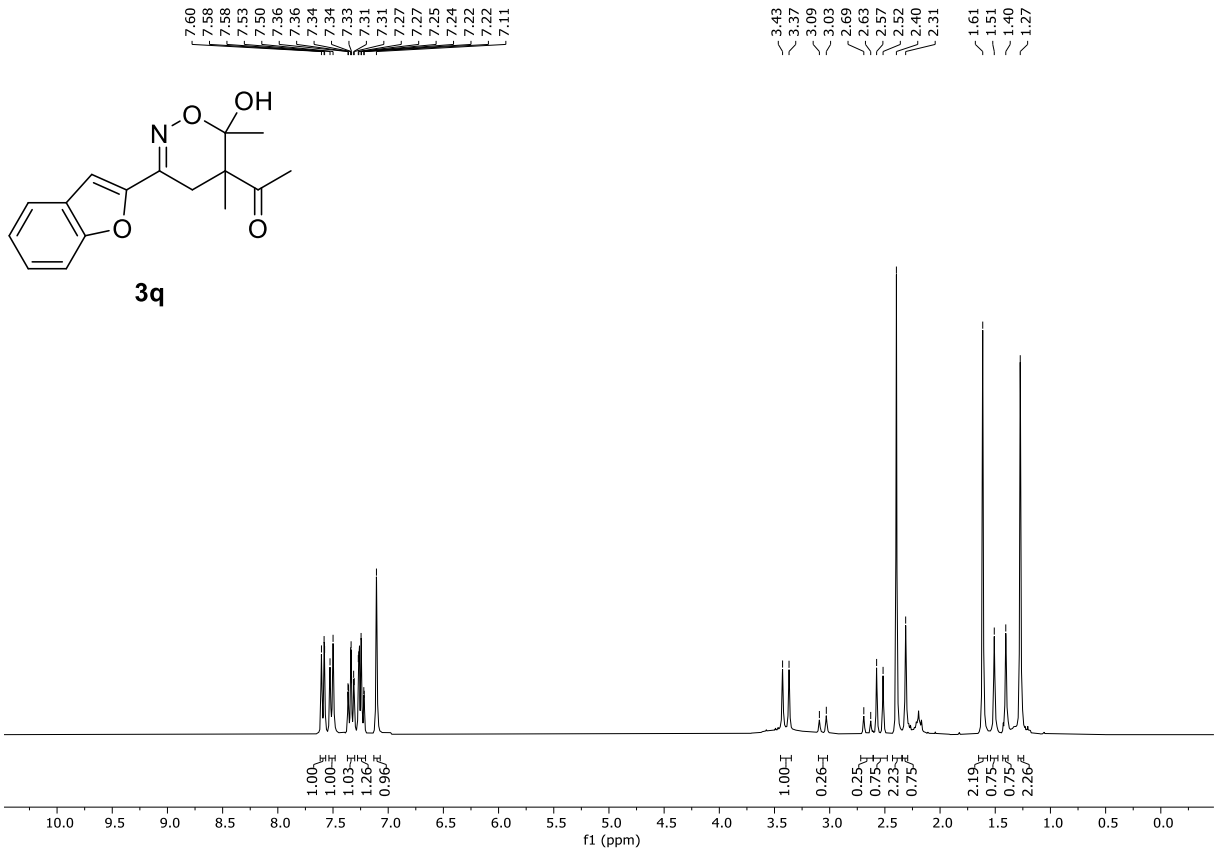
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)

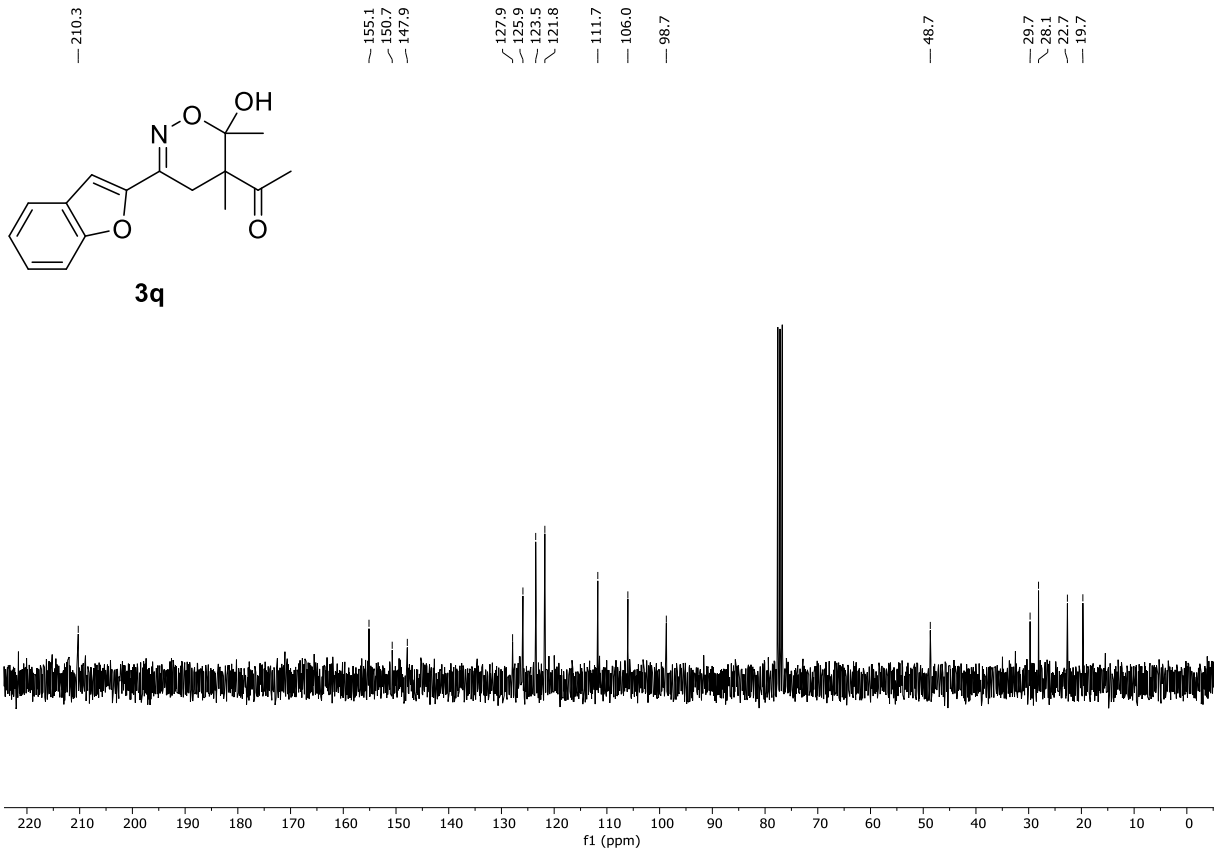


^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



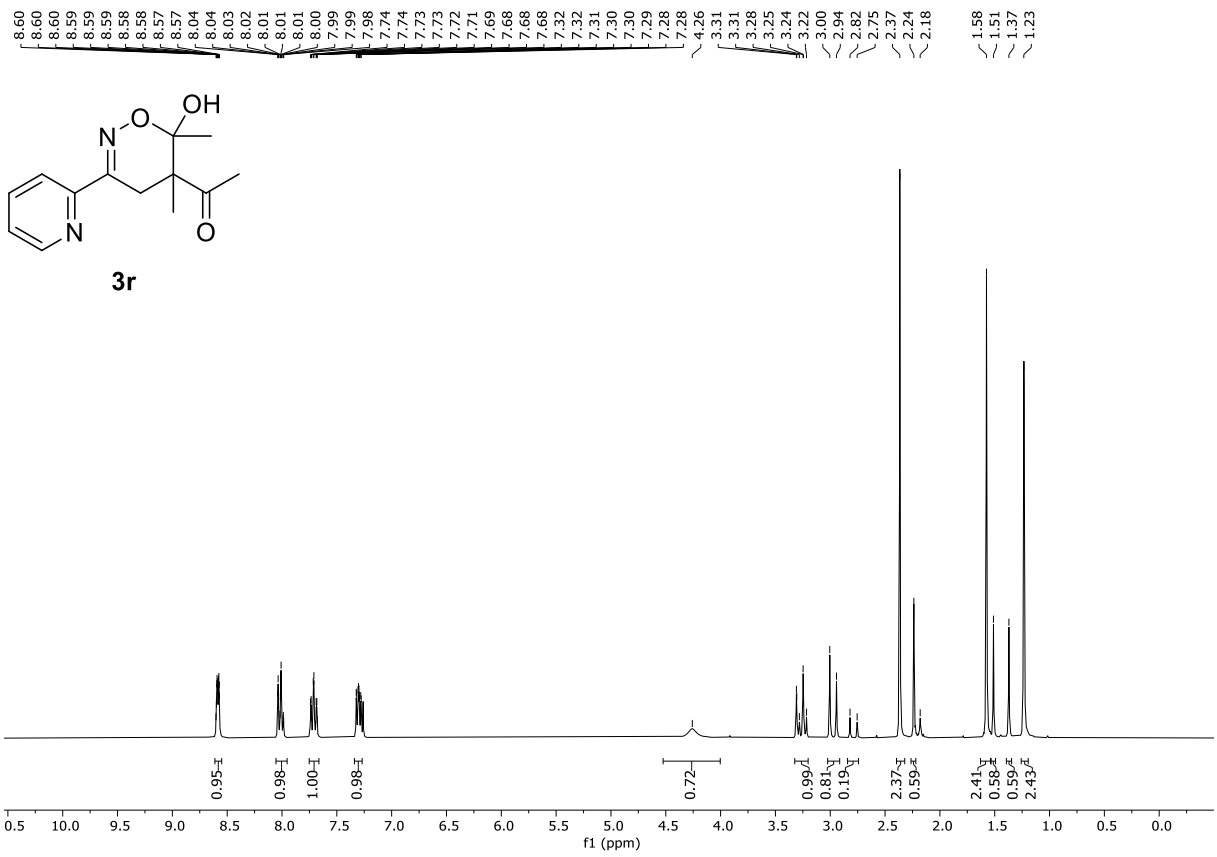
3q

^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



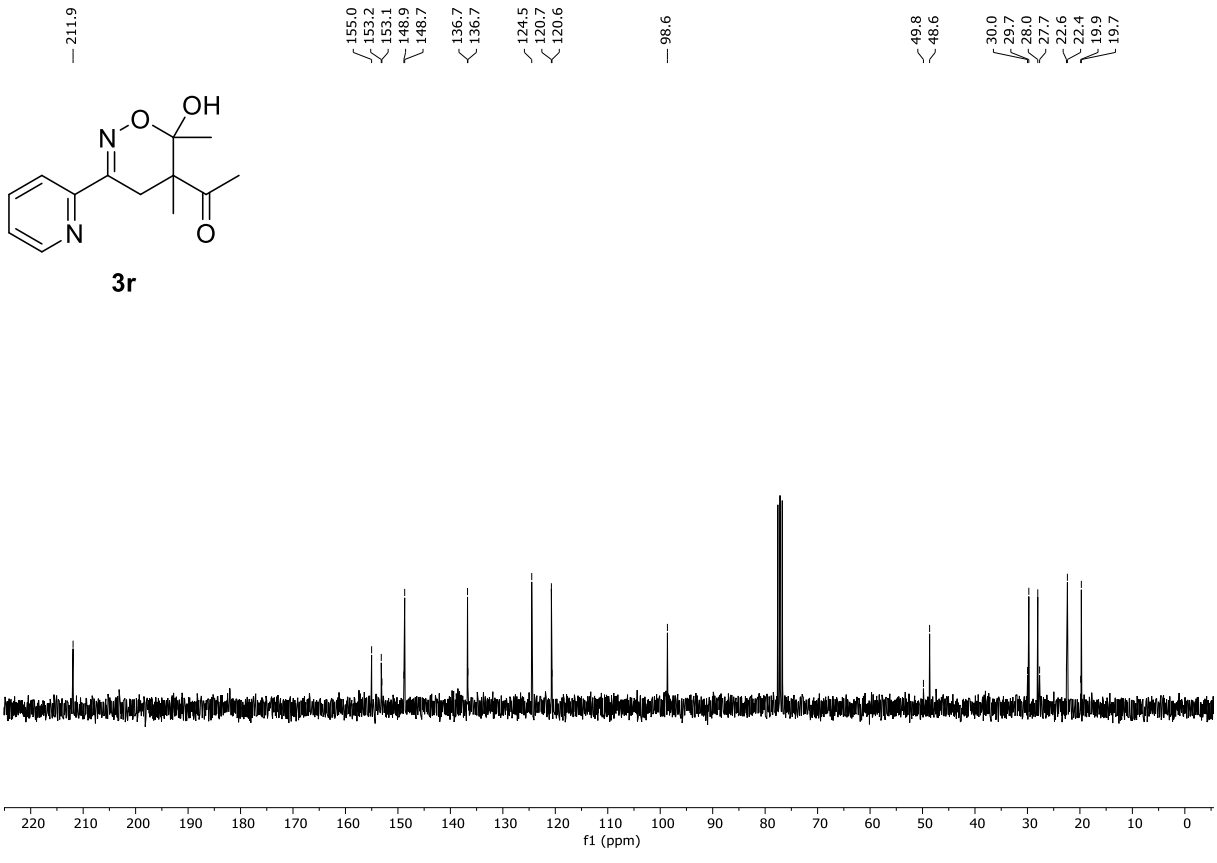
3q

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



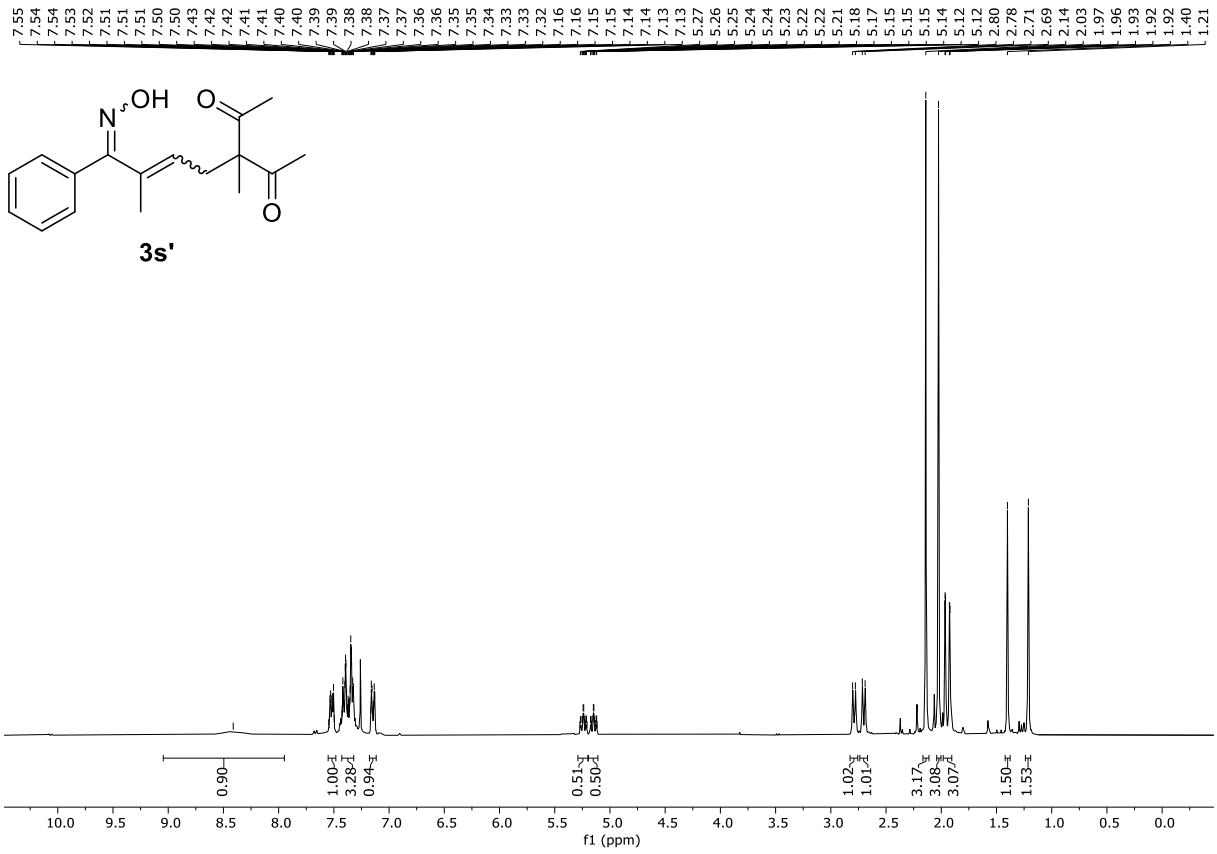
3r

^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)

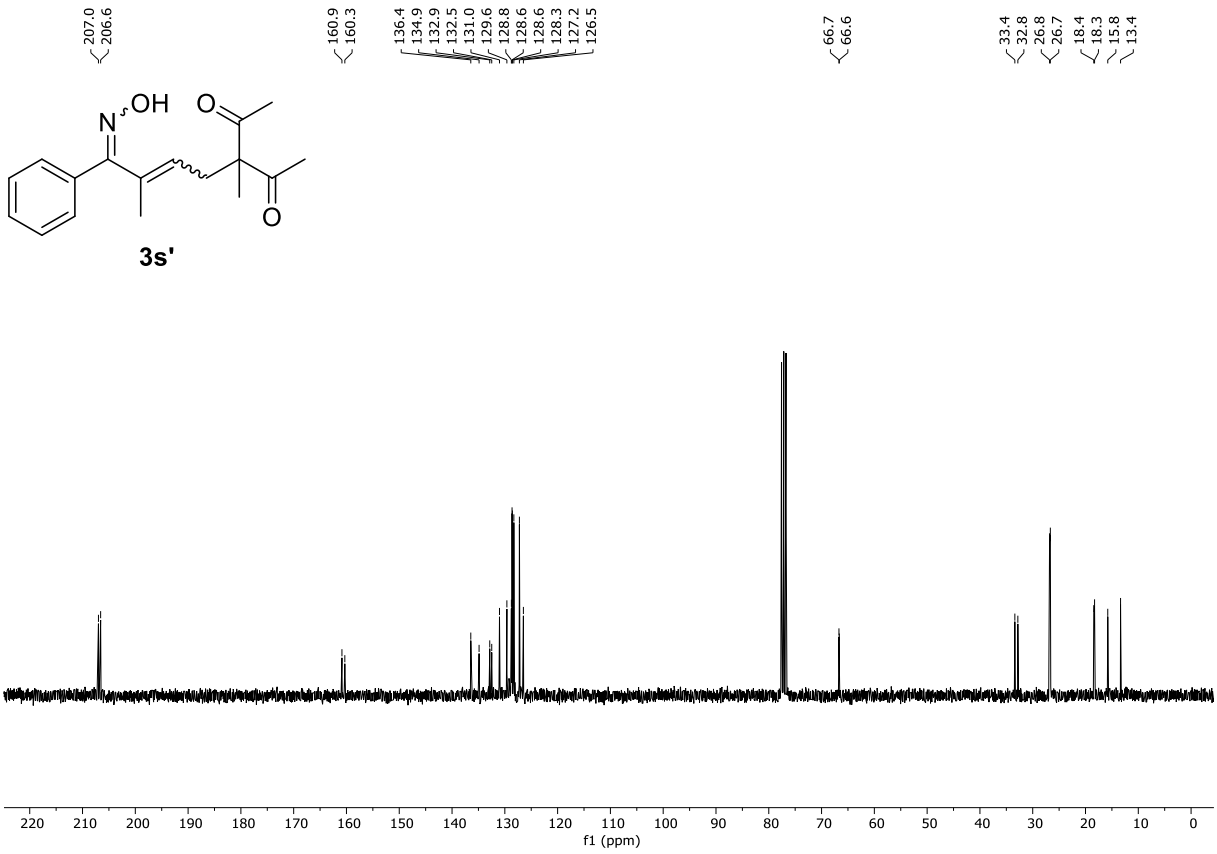


3r

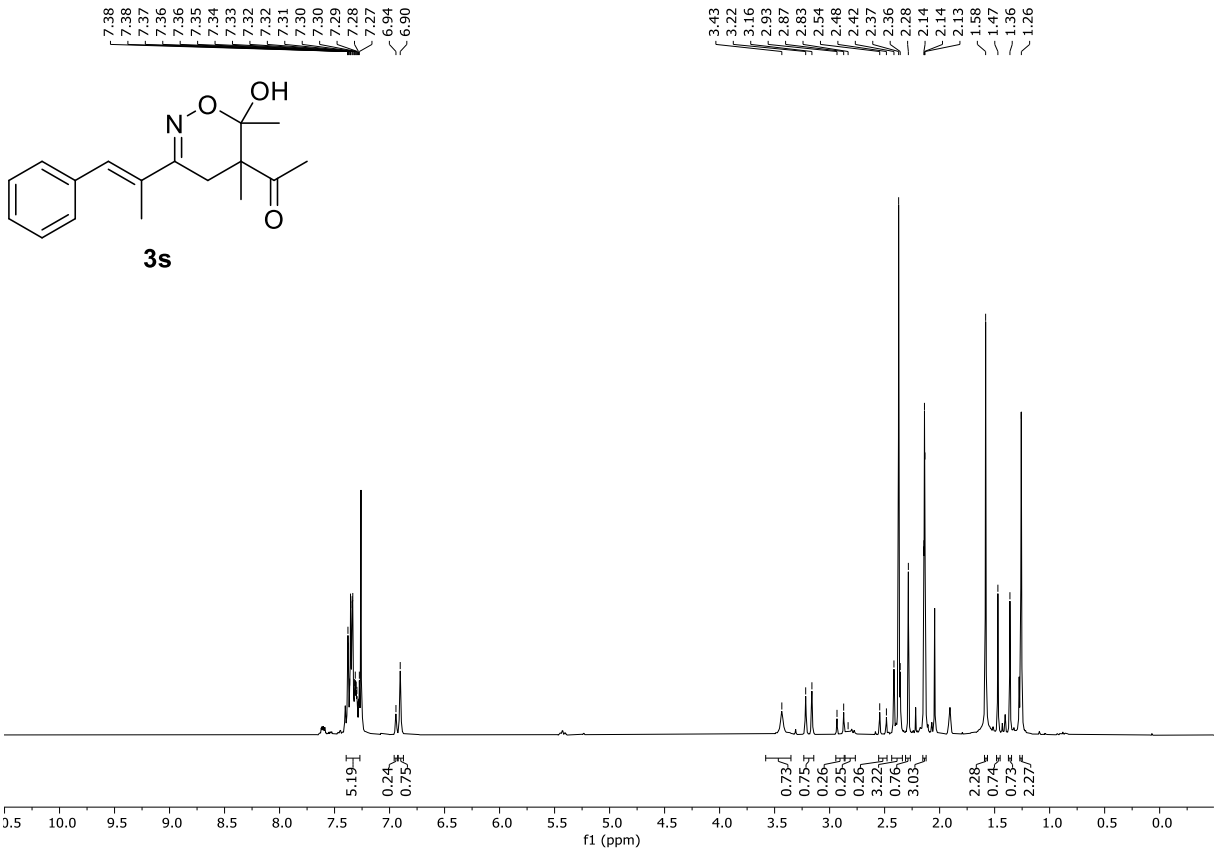
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



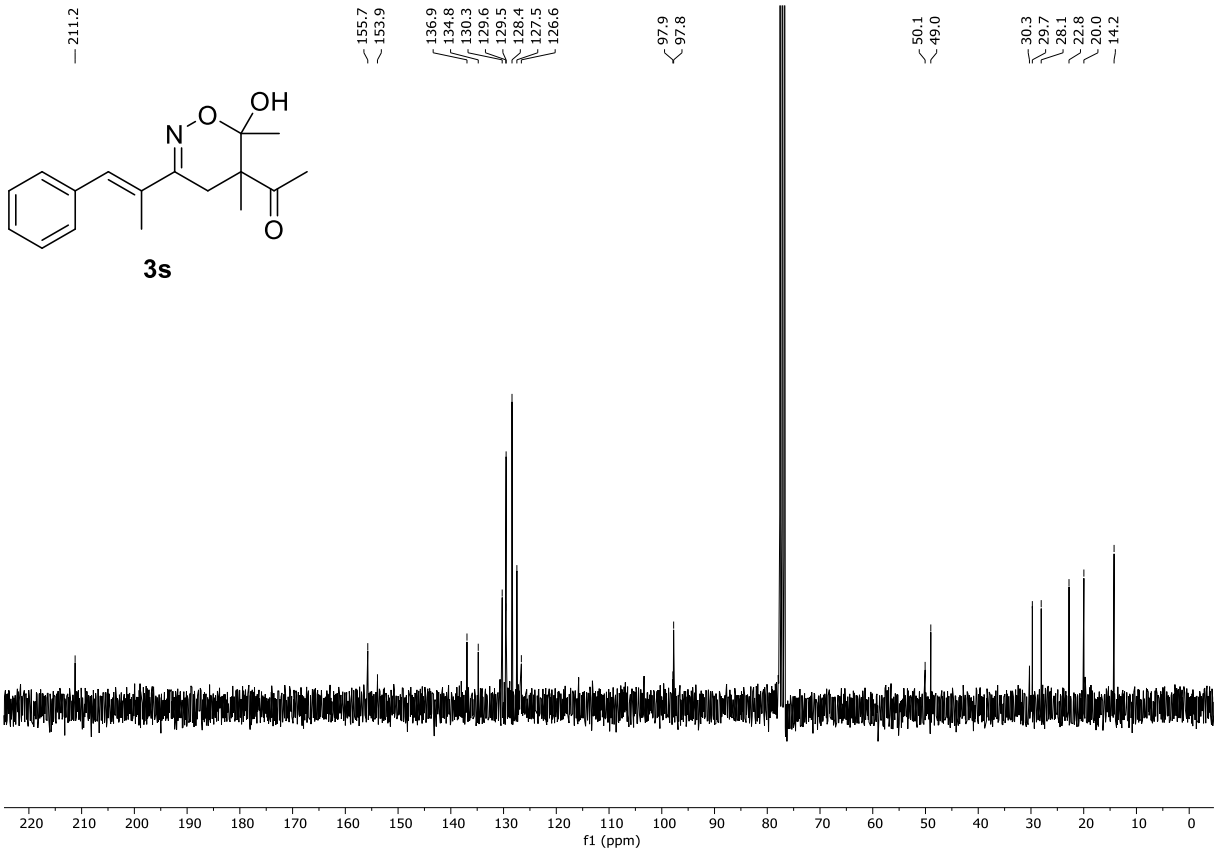
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



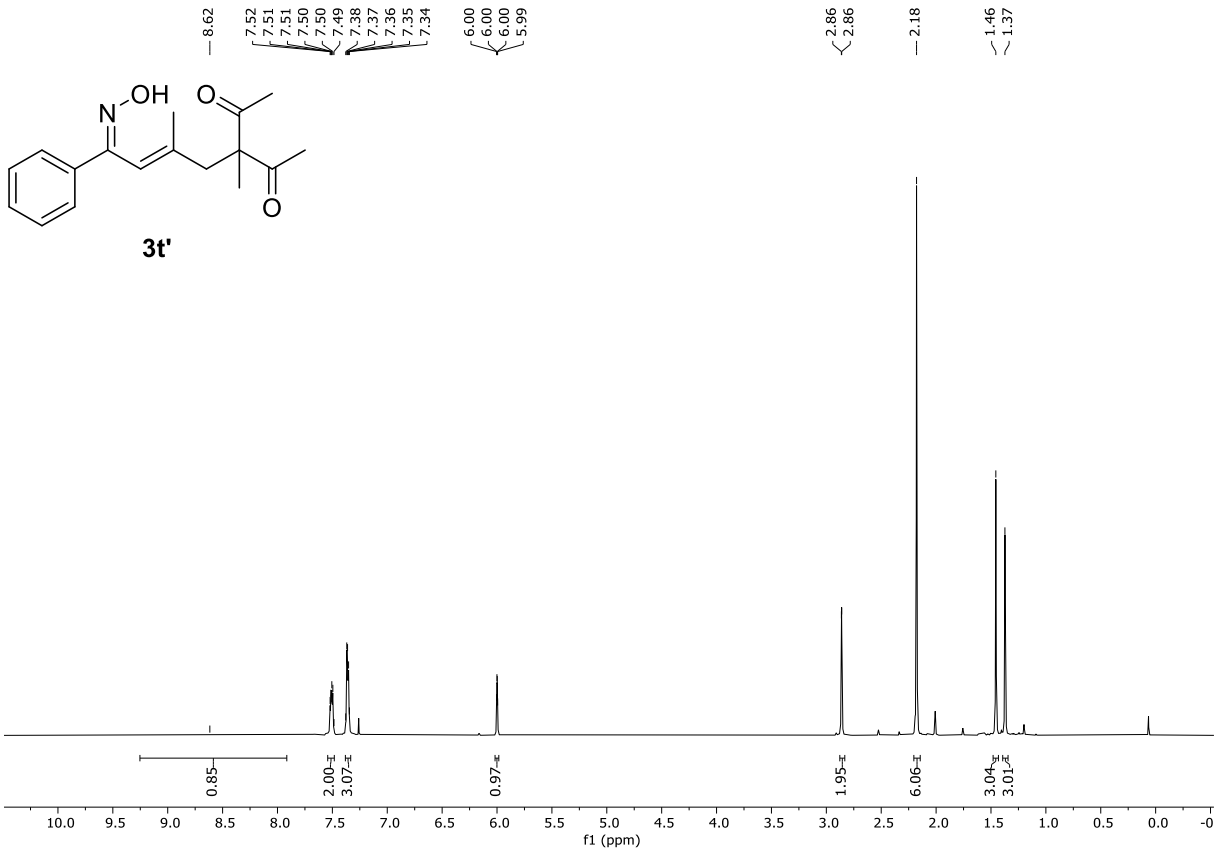
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



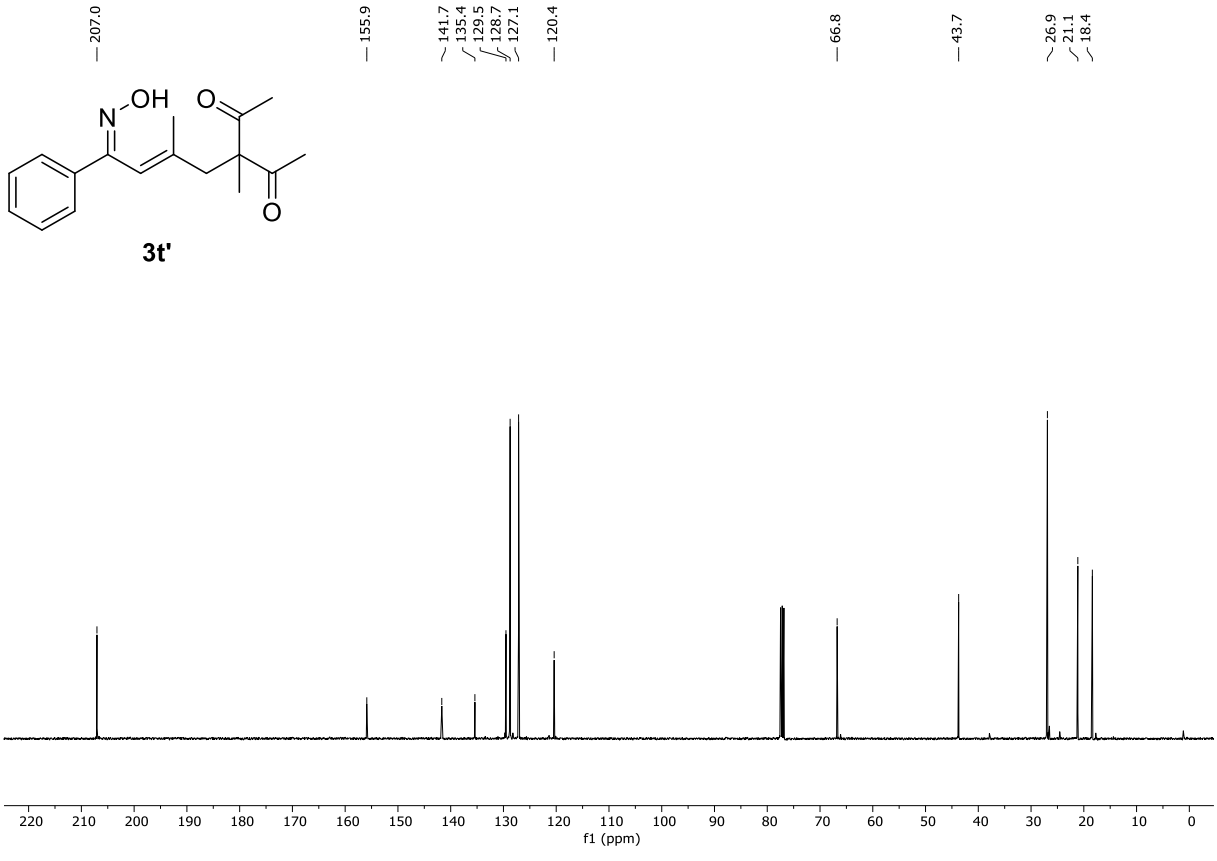
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



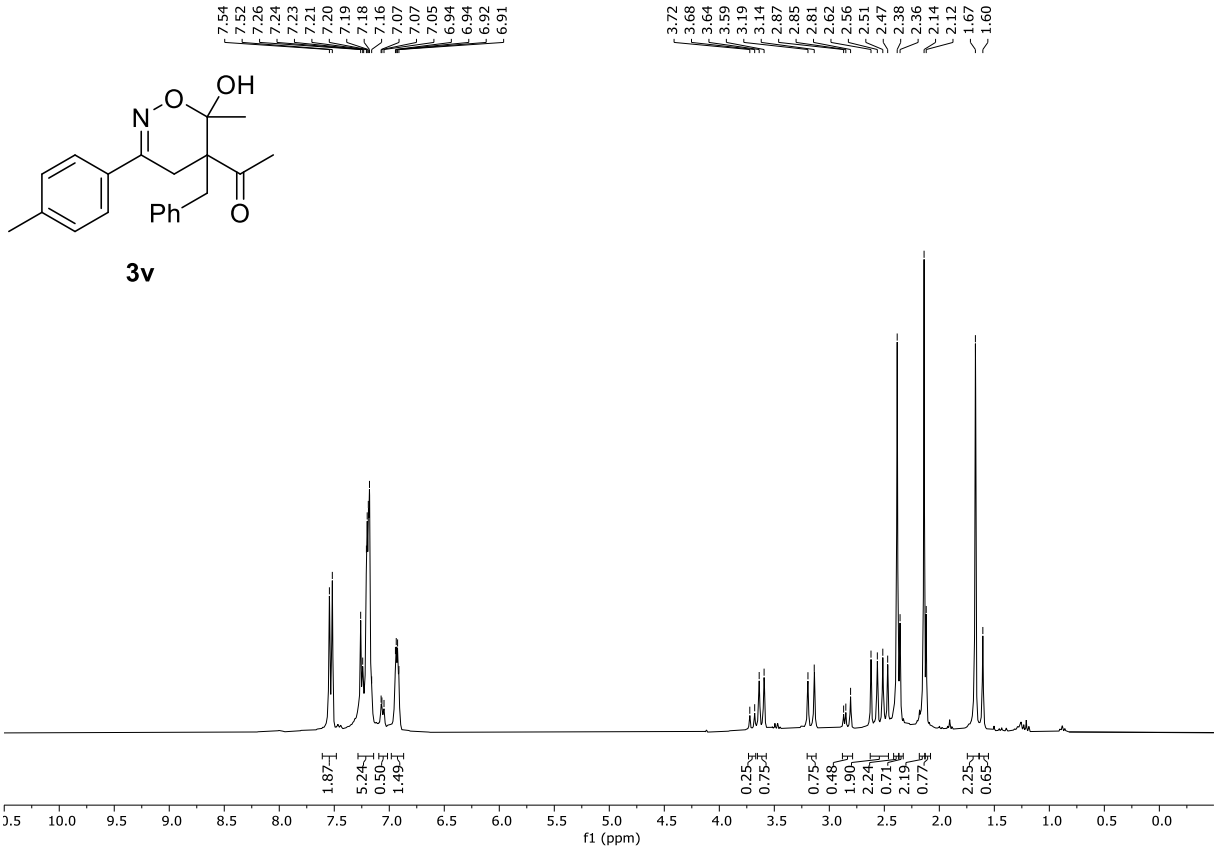
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



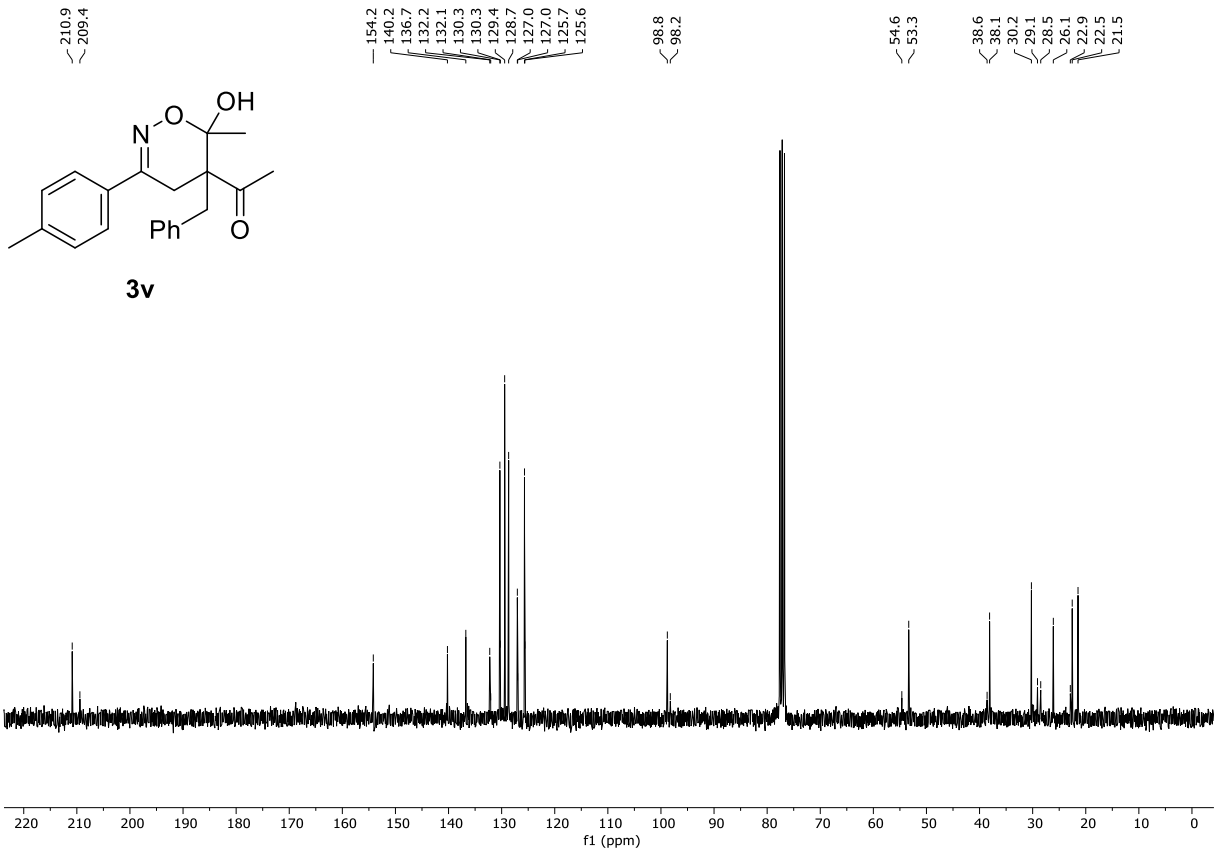
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



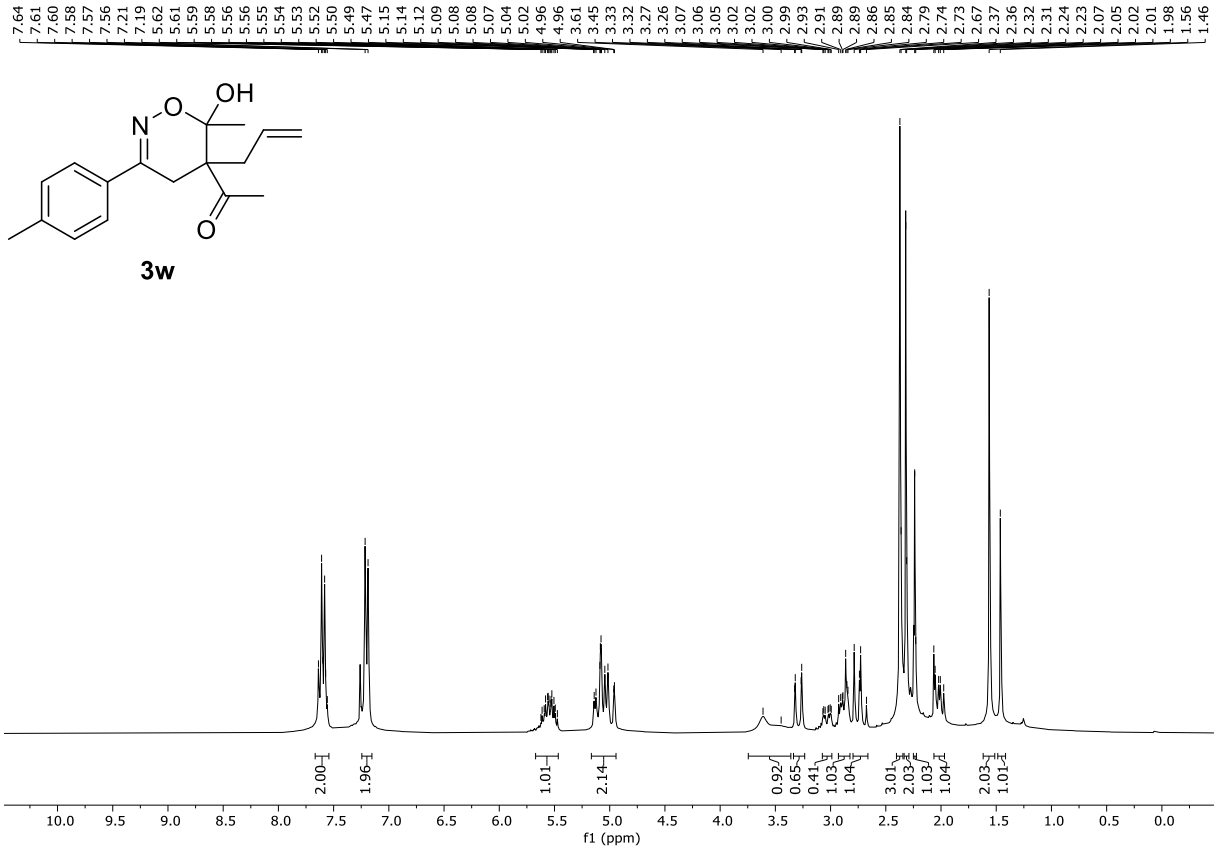
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



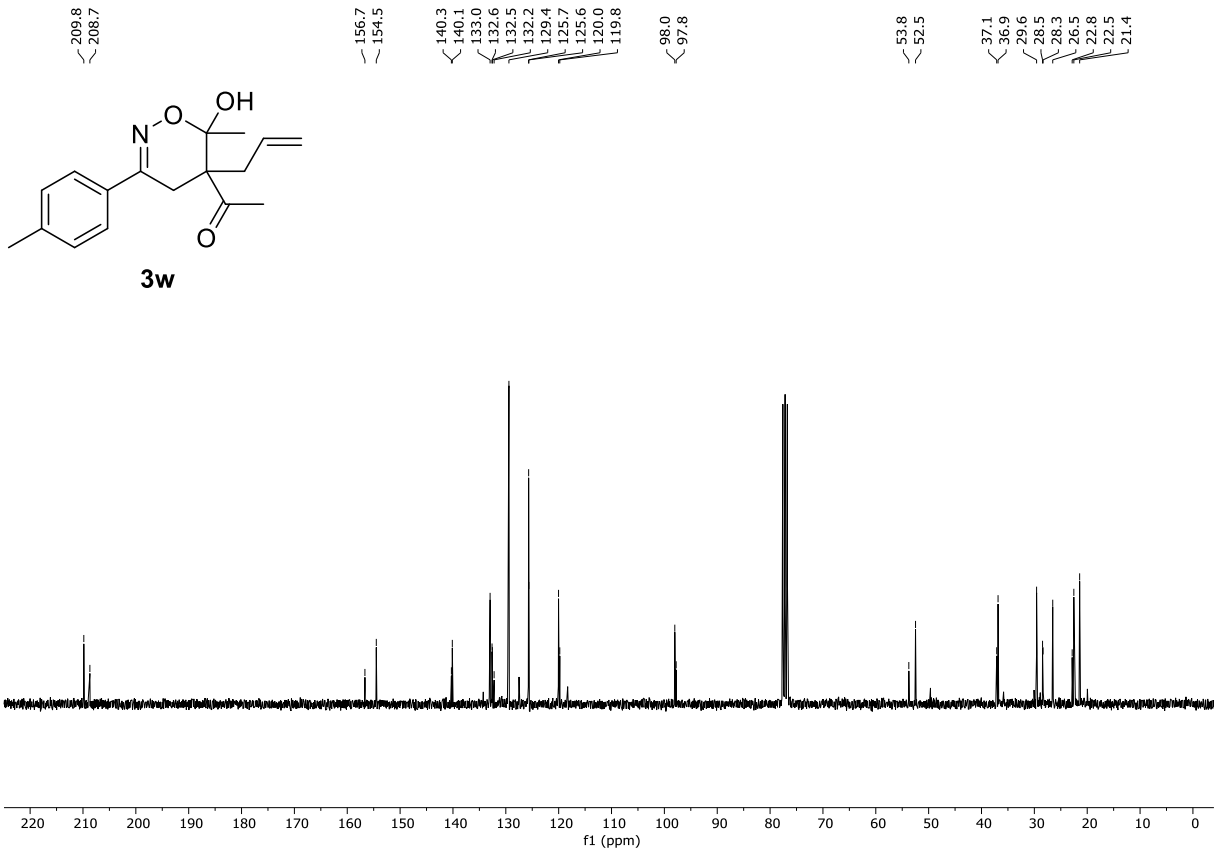
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



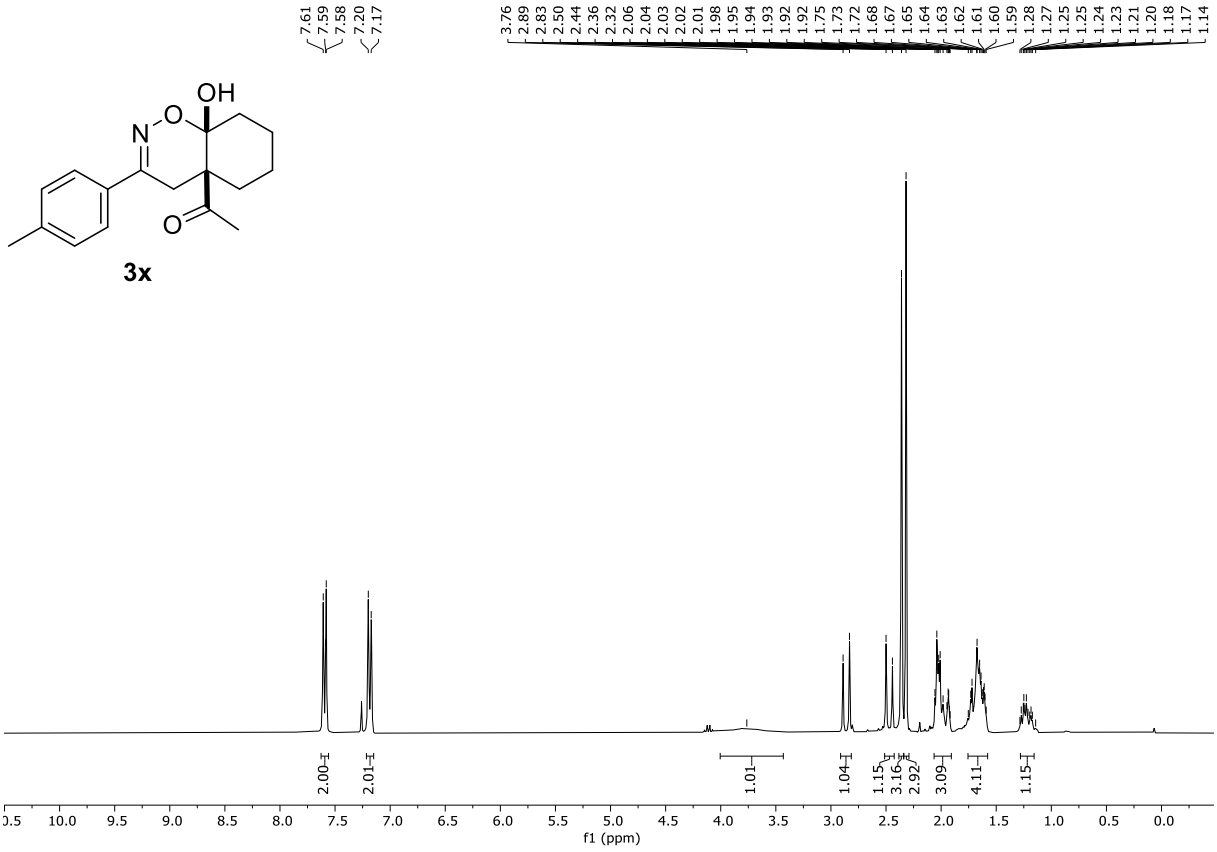
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



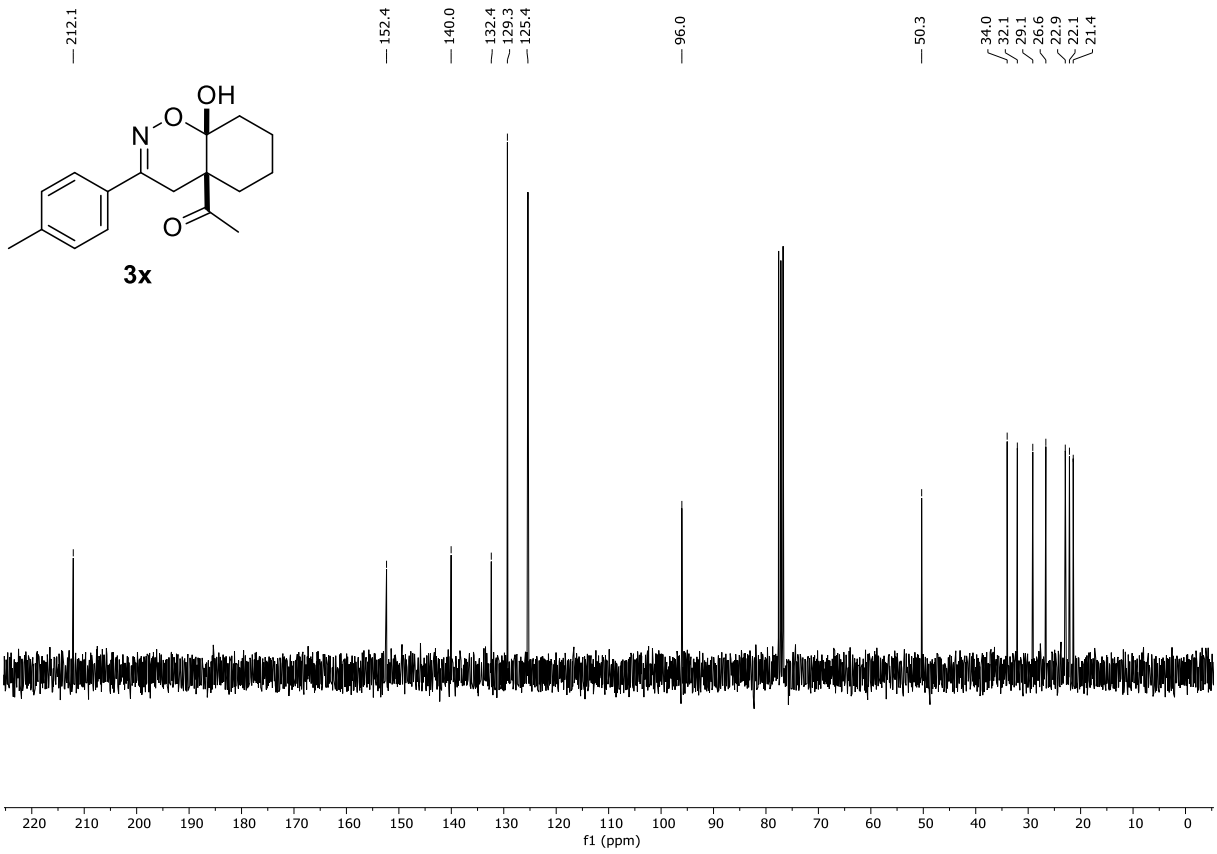
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



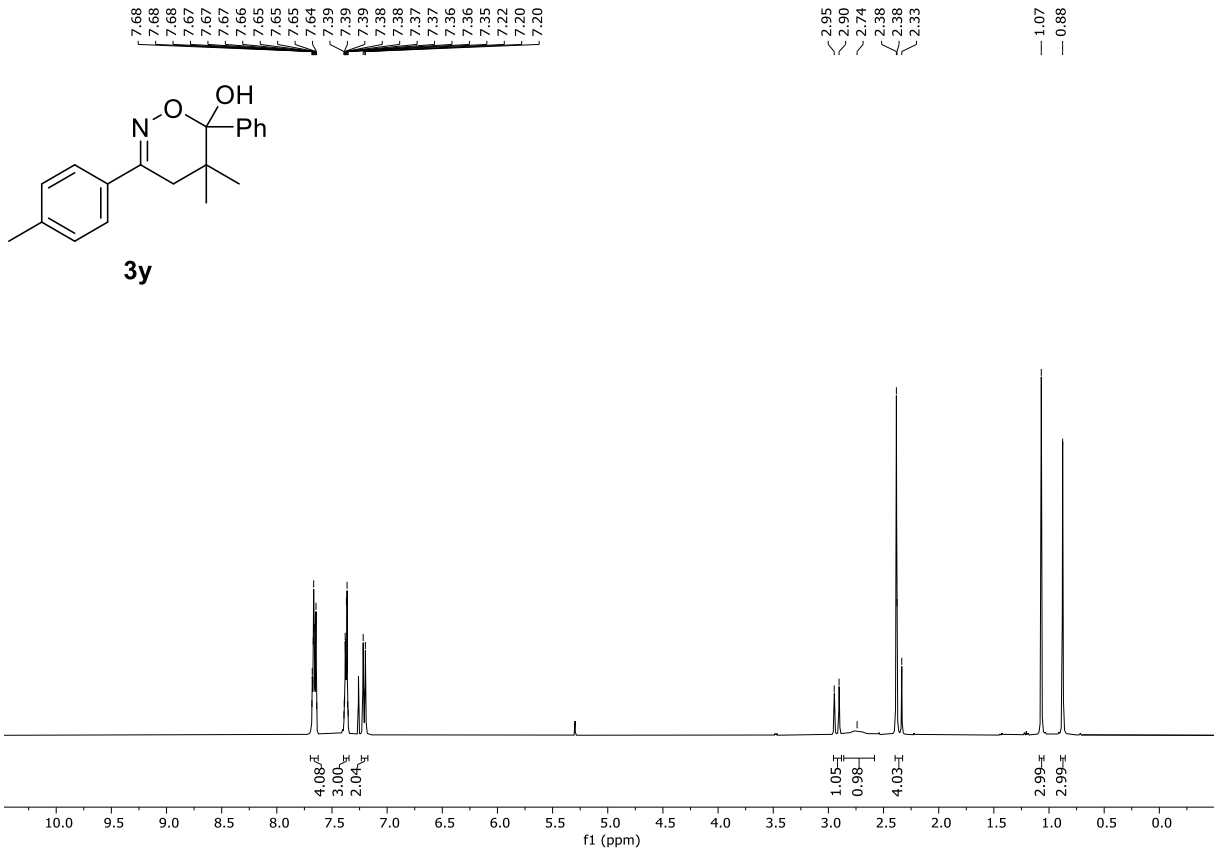
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



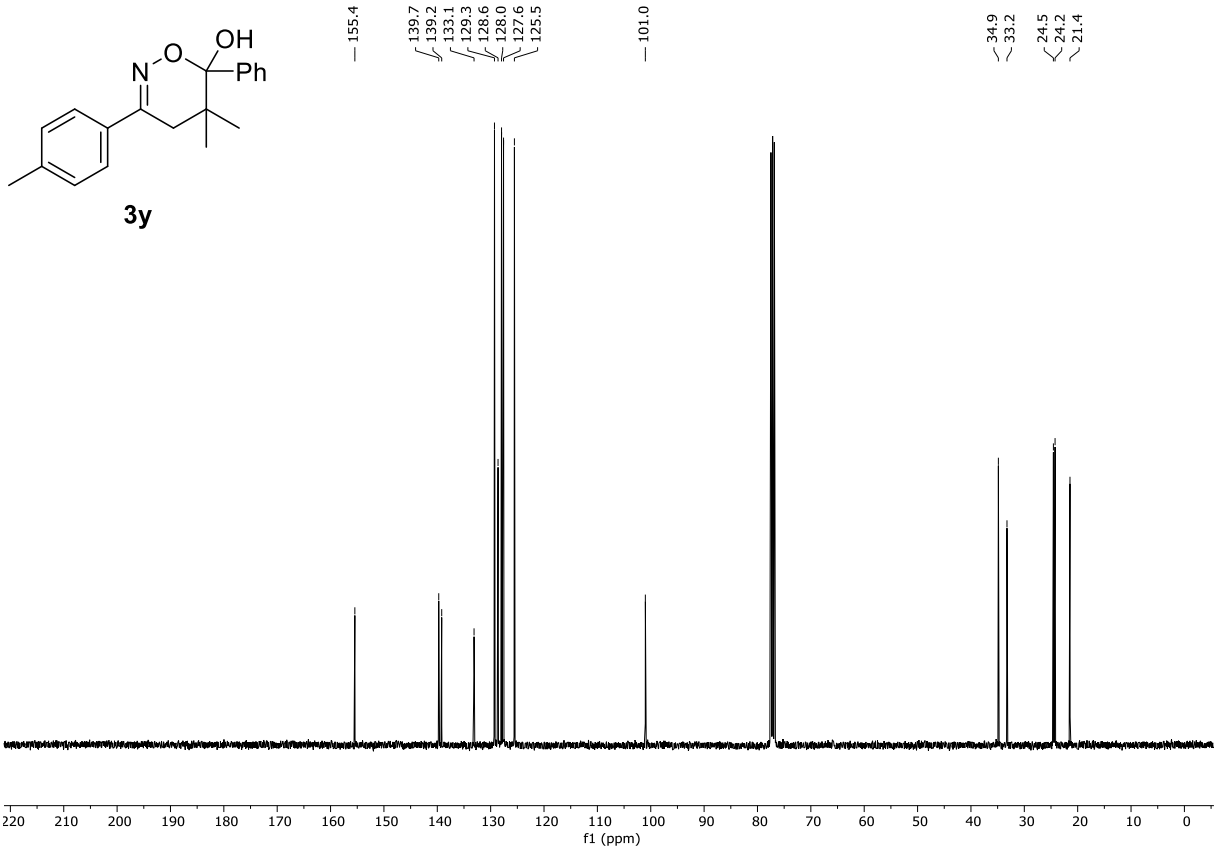
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



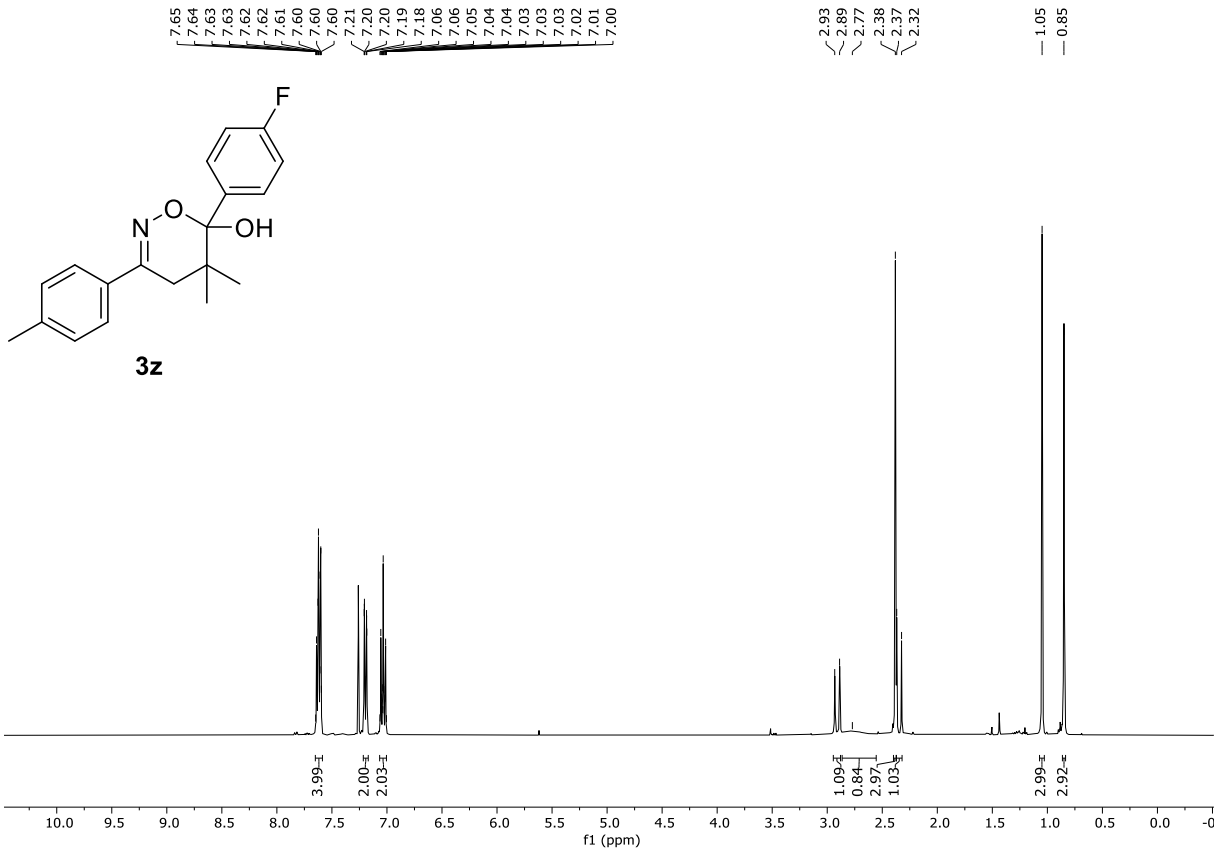
^{1}H-NMR (400 MHz, $CDCl_3$, 299 K)



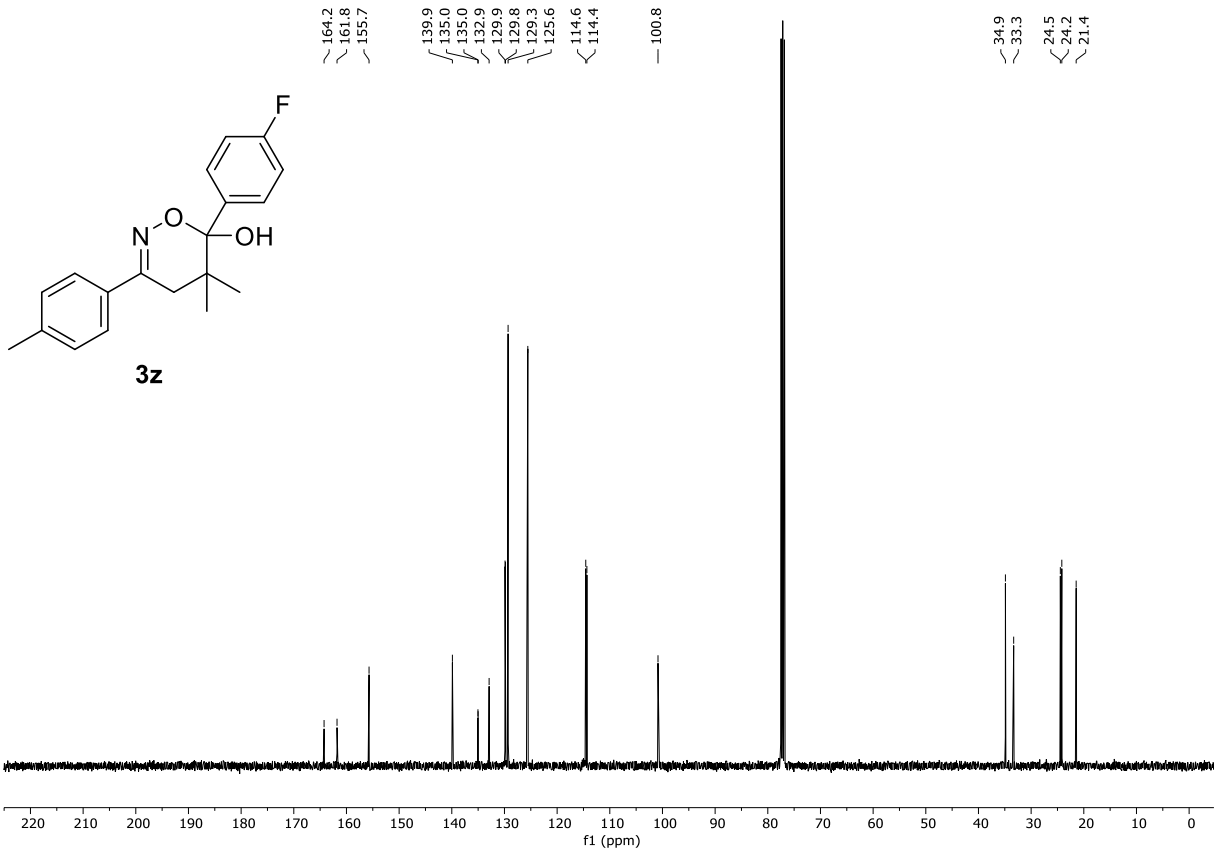
^{13}C-NMR (101 MHz, $CDCl_3$, 299 K)



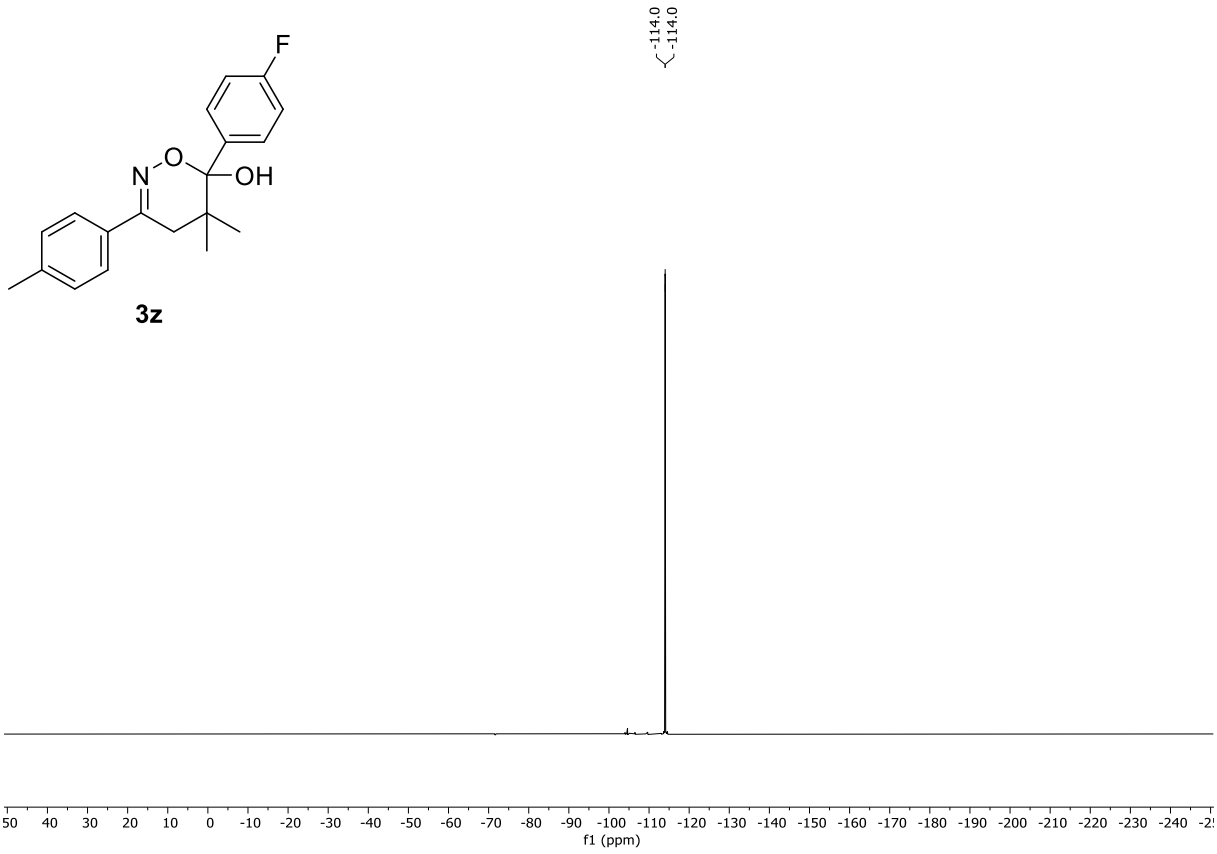
^{1}H-NMR (400 MHz, $CDCl_3$, 299 K)



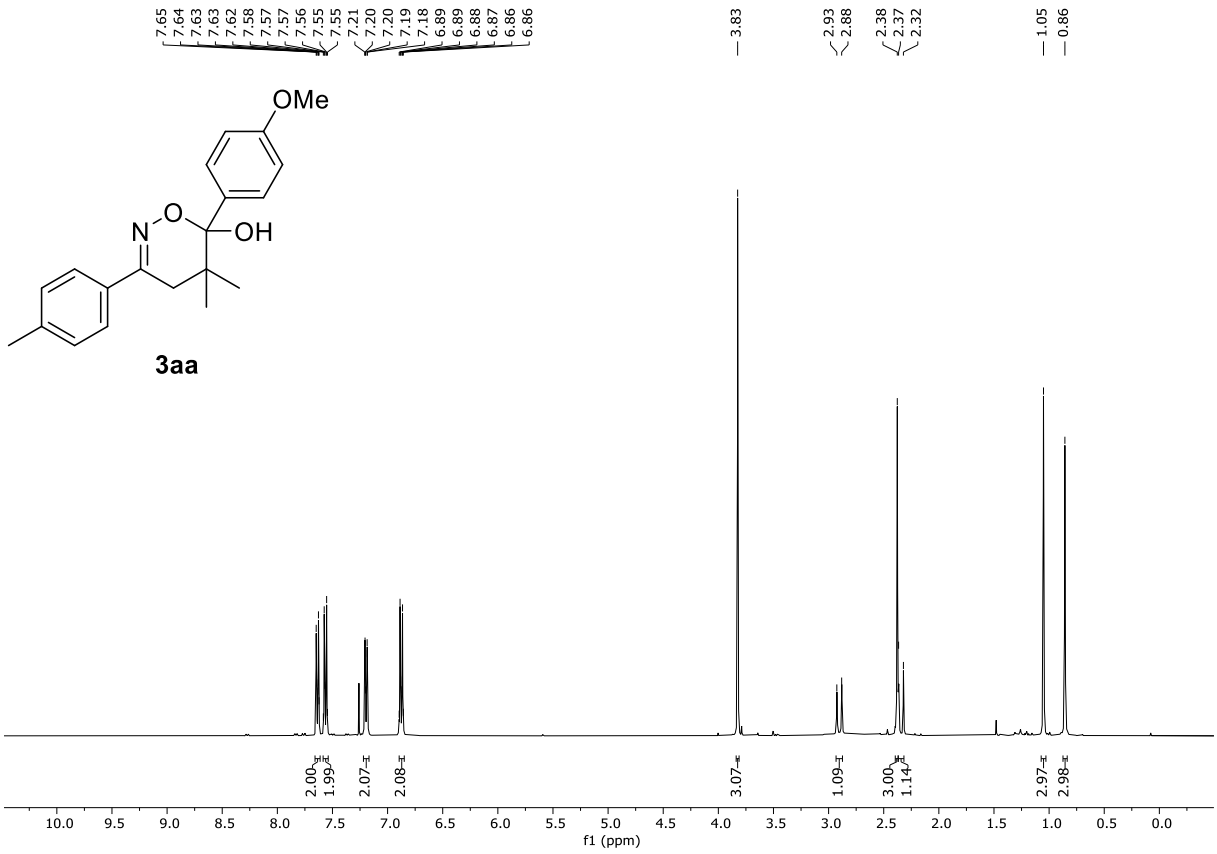
^{13}C-NMR (101 MHz, $CDCl_3$, 299 K)



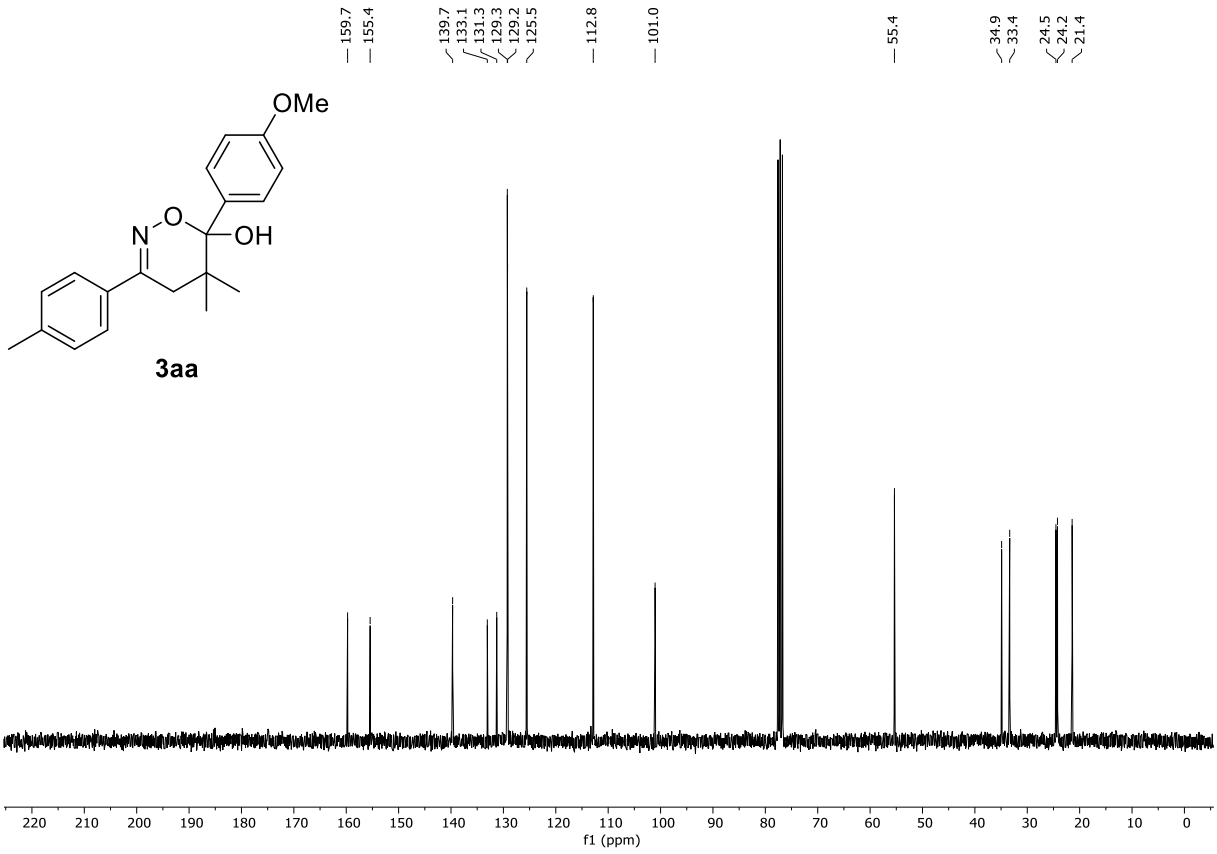
^{19}F-NMR (282 MHz, $CDCl_3$, 299 K)



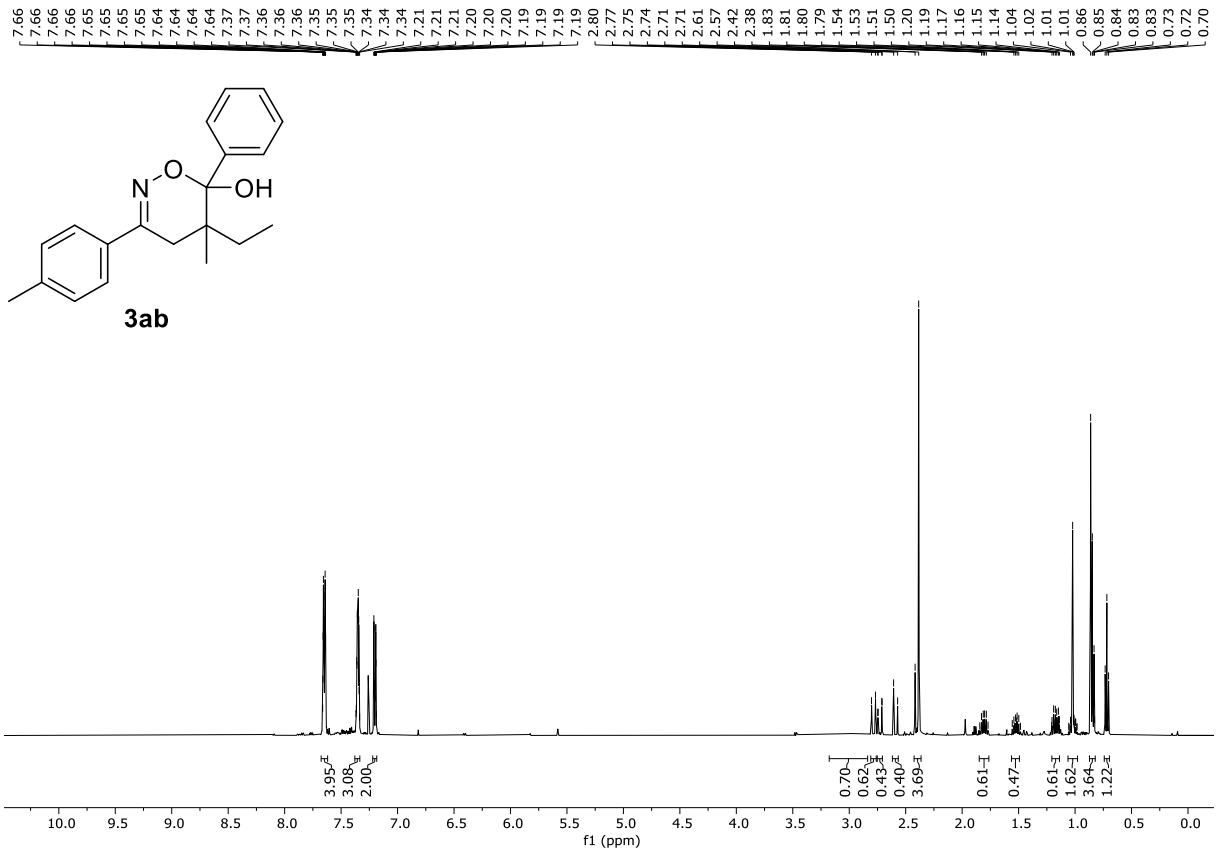
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



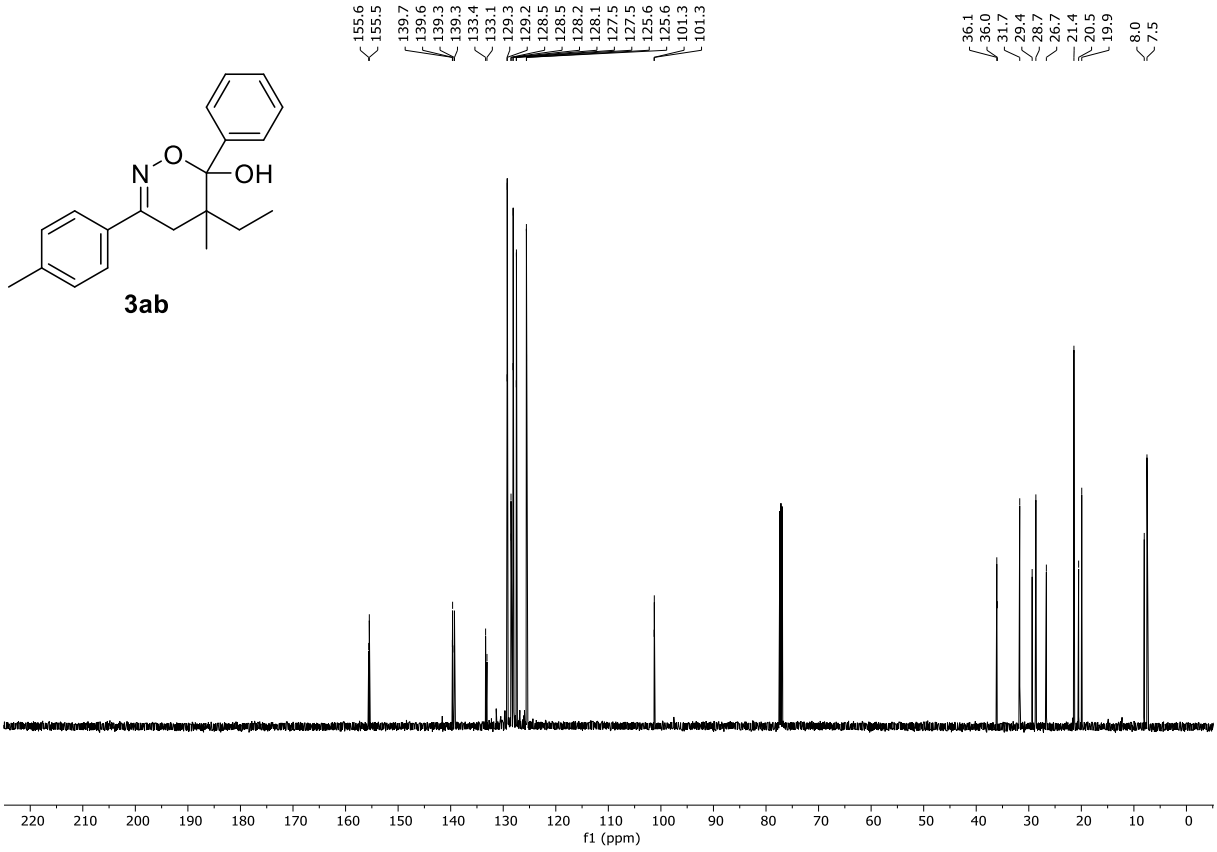
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



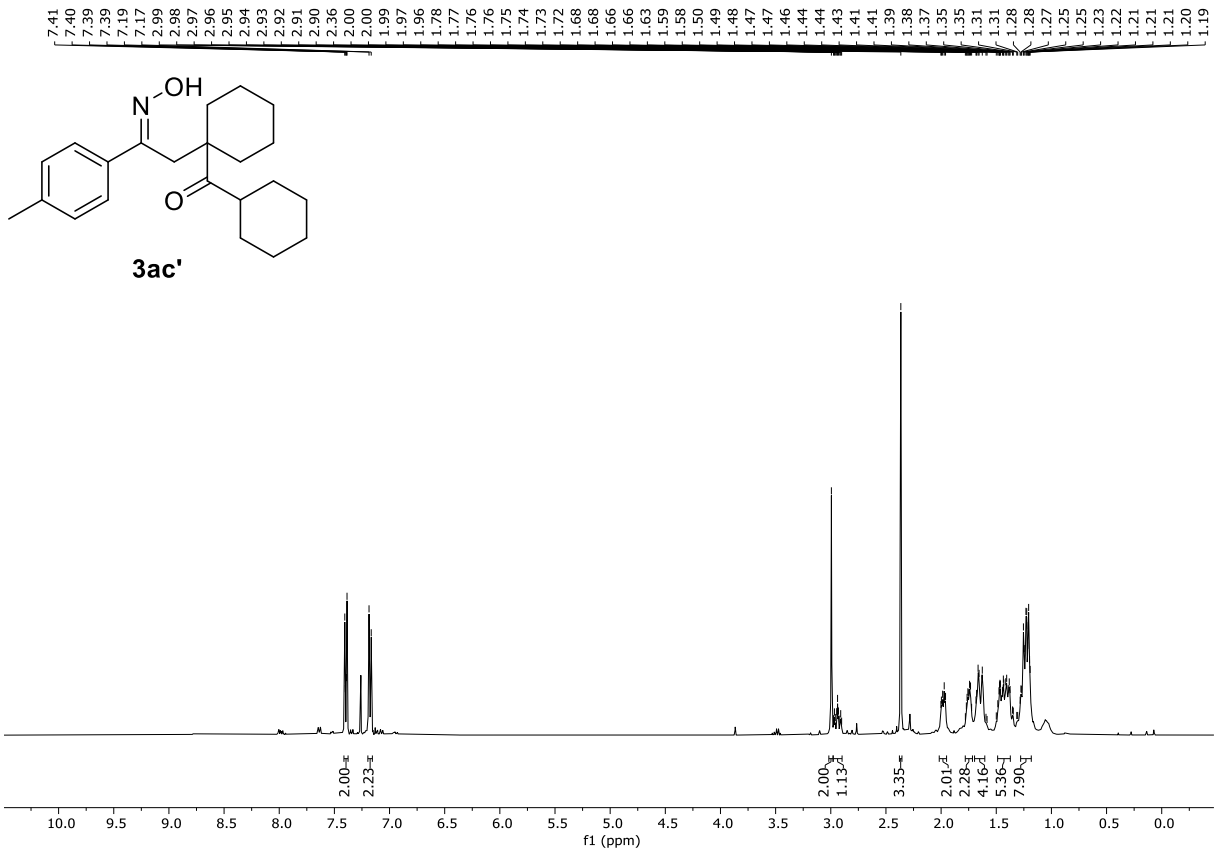
^{1}H-NMR (500 MHz, $CDCl_3$, 299 K)



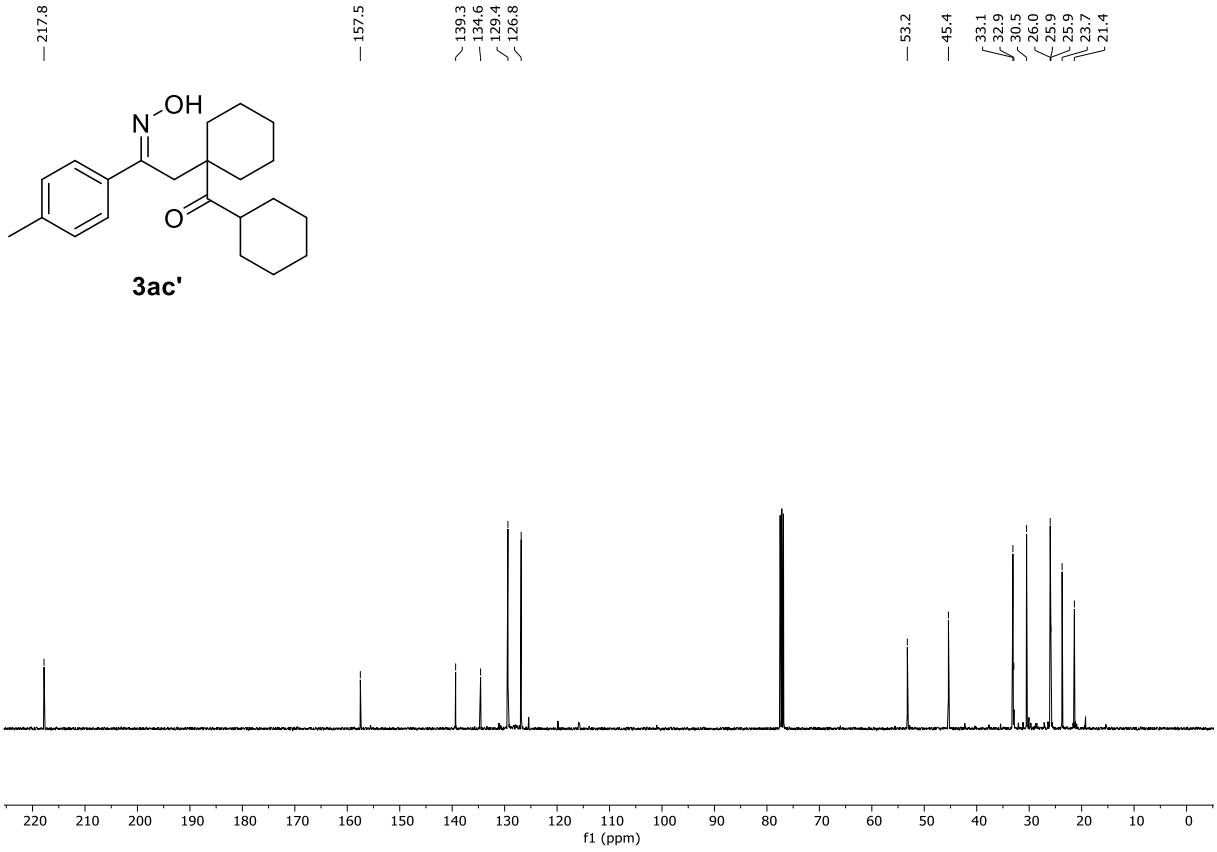
^{13}C-NMR (126 MHz, $CDCl_3$, 299 K)



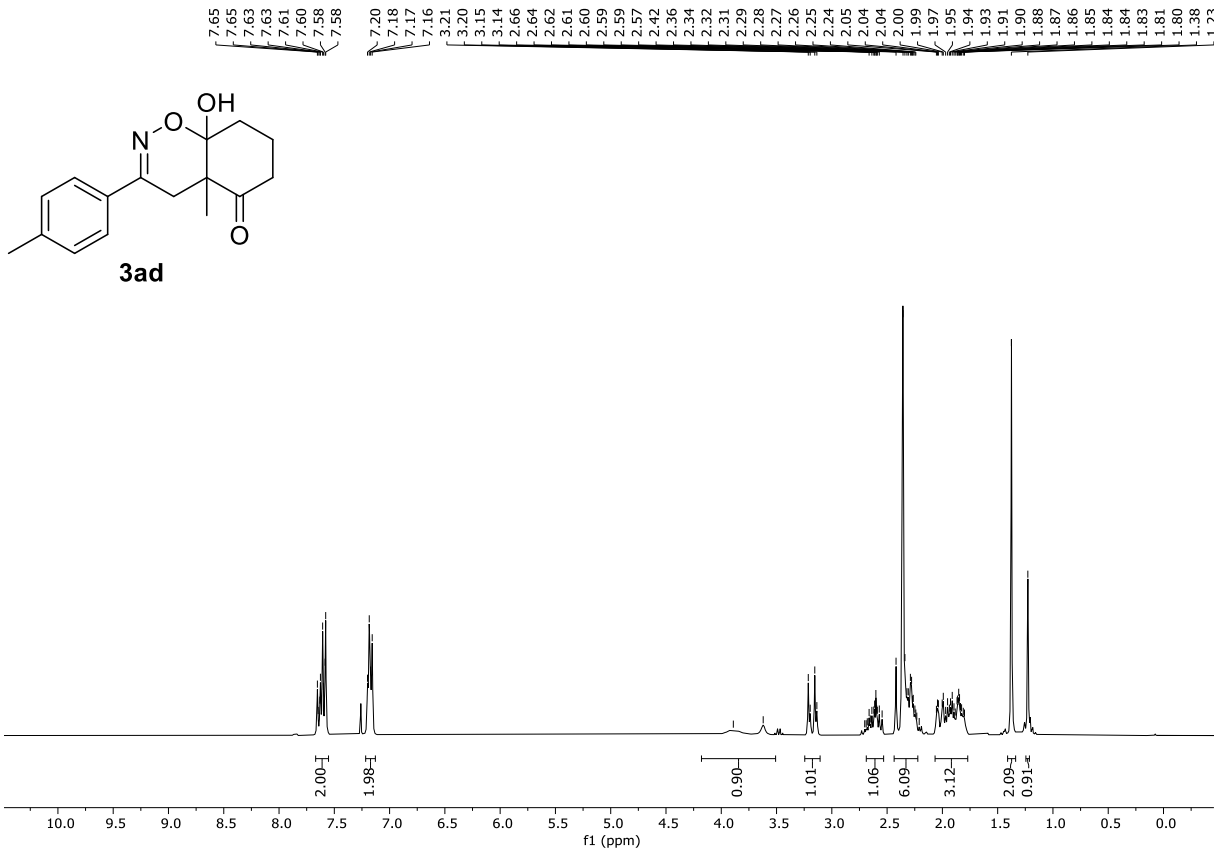
^{1}H-NMR (400 MHz, $CDCl_3$, 299 K)



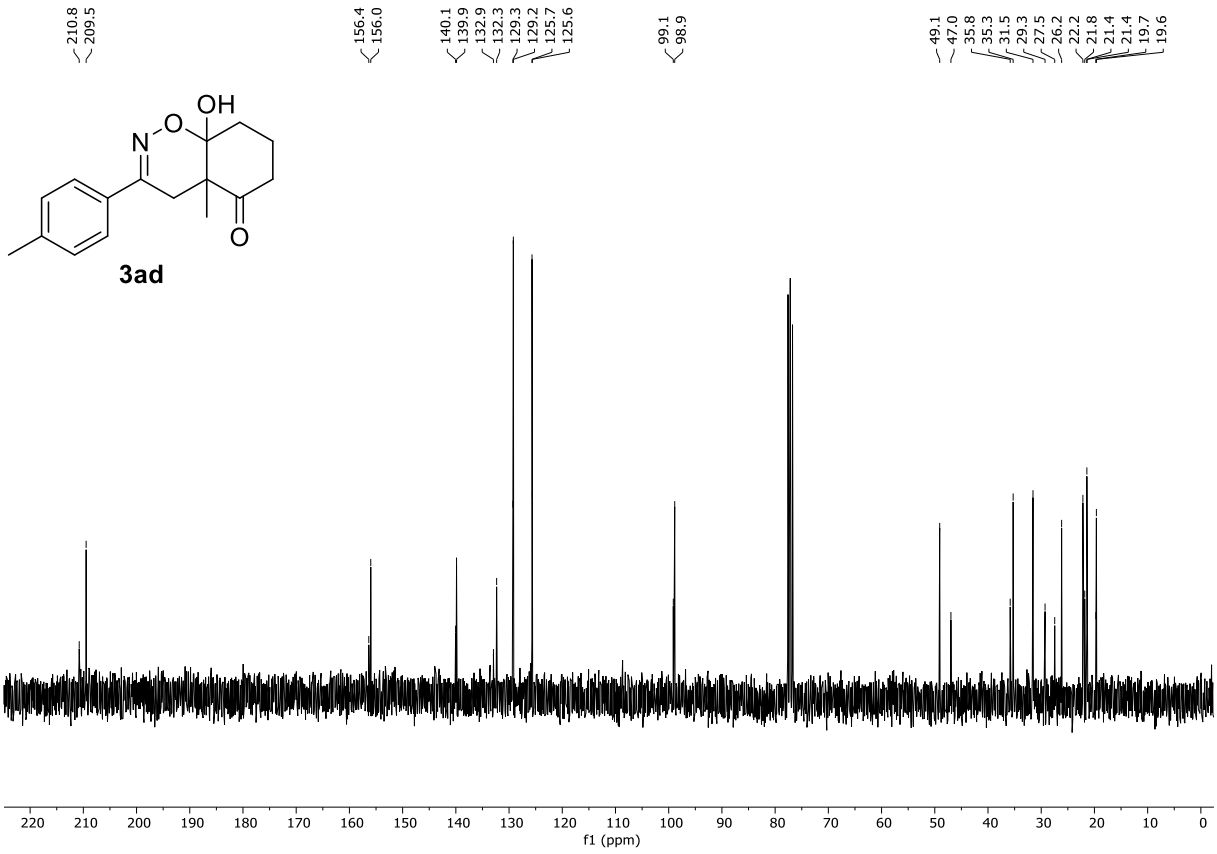
^{13}C-NMR (101 MHz, $CDCl_3$, 299 K)



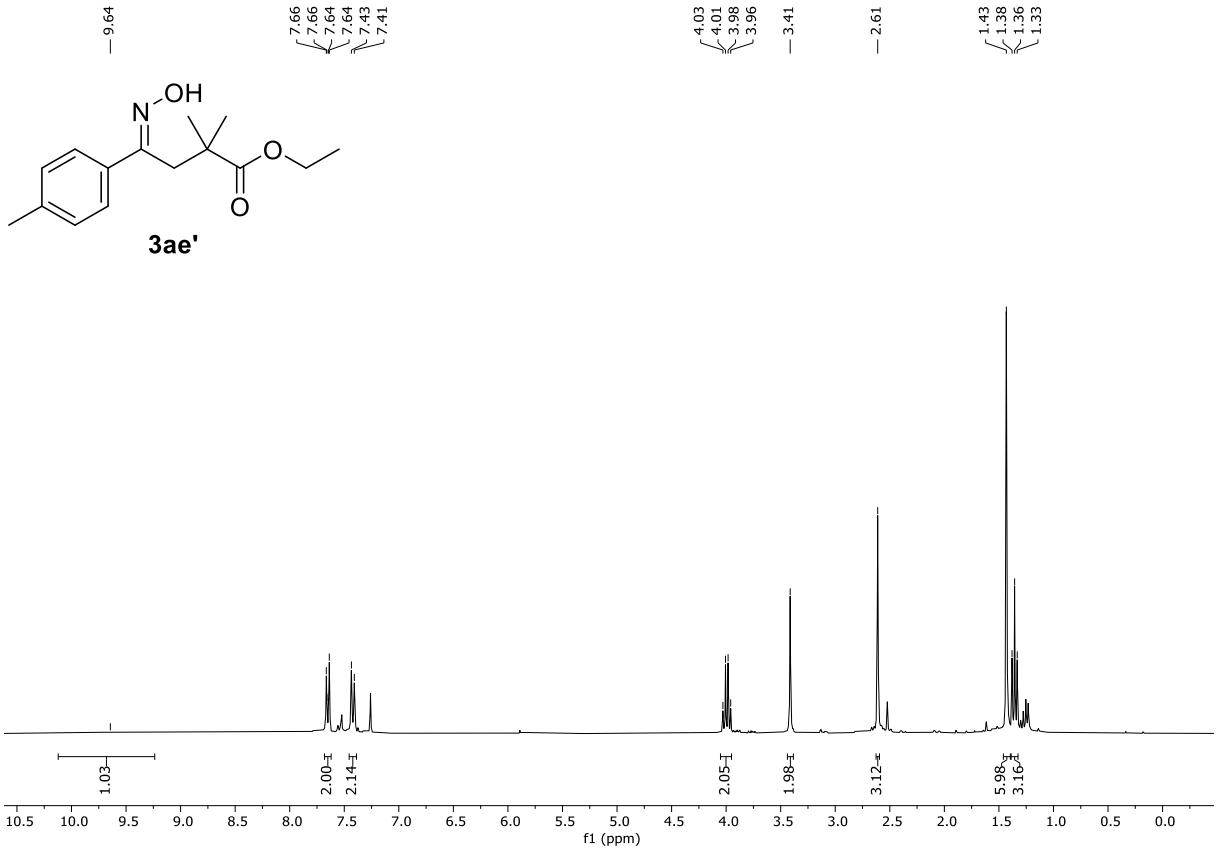
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



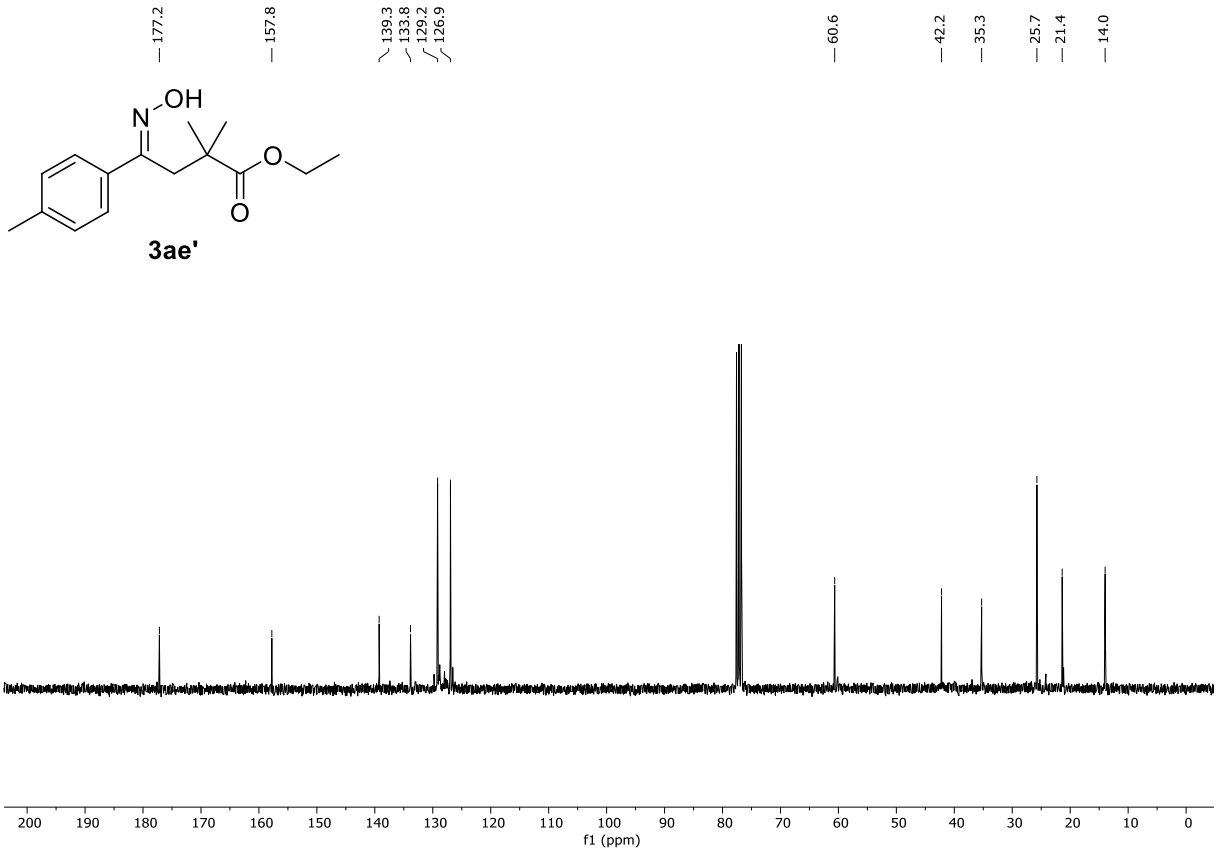
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



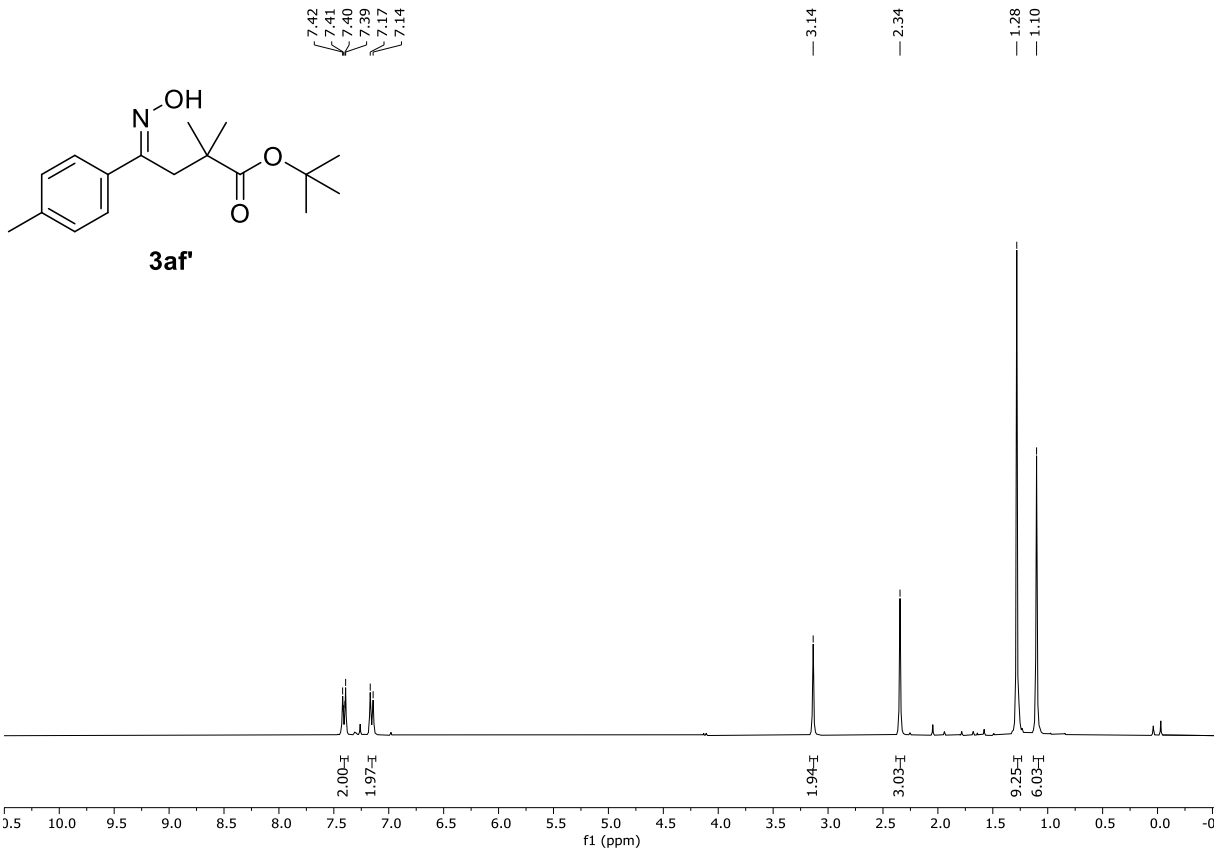
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



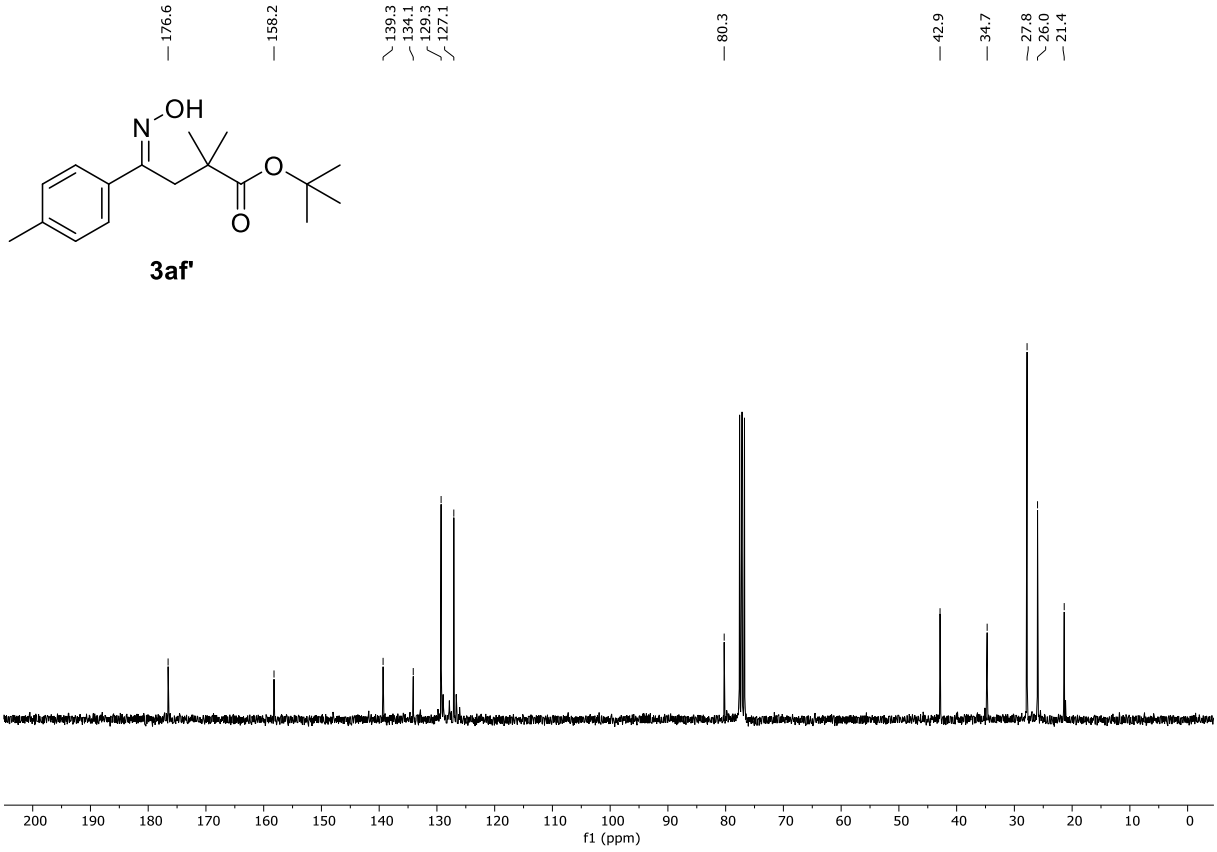
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



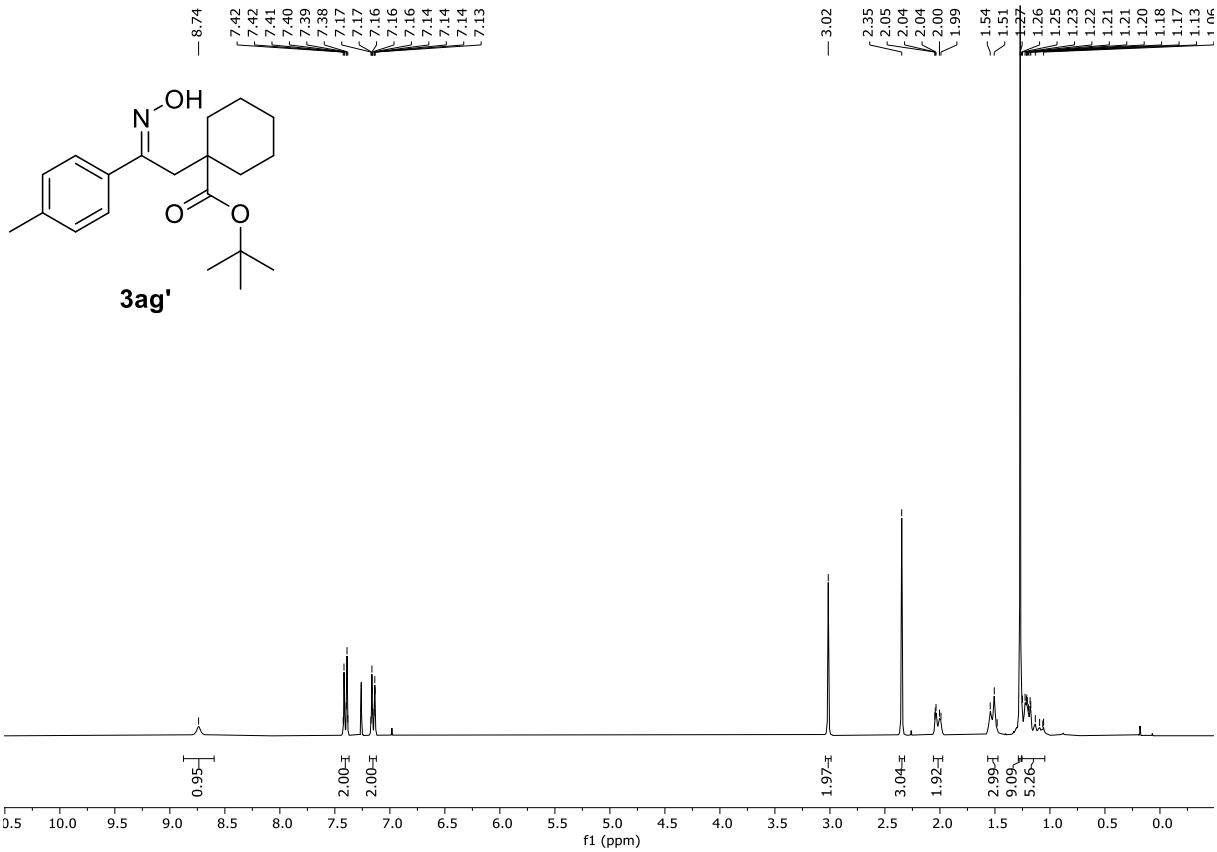
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



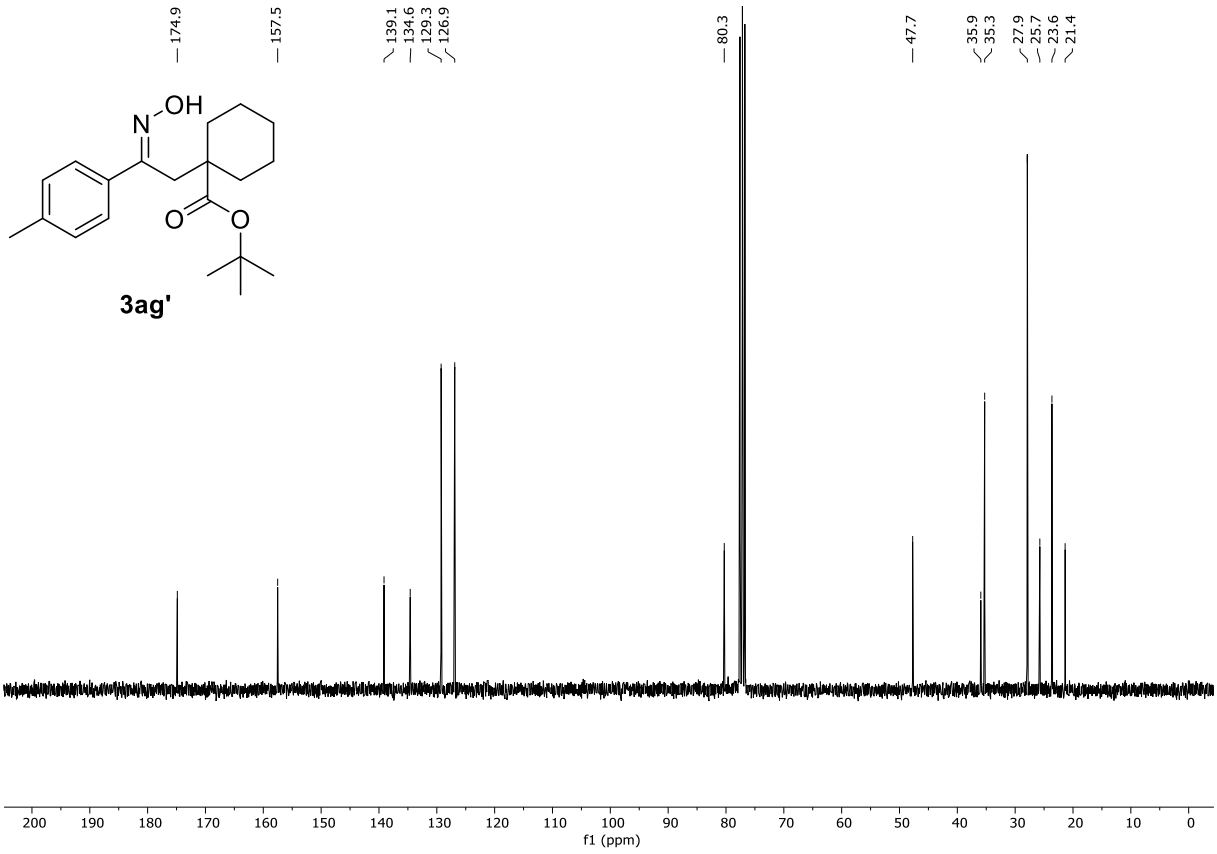
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



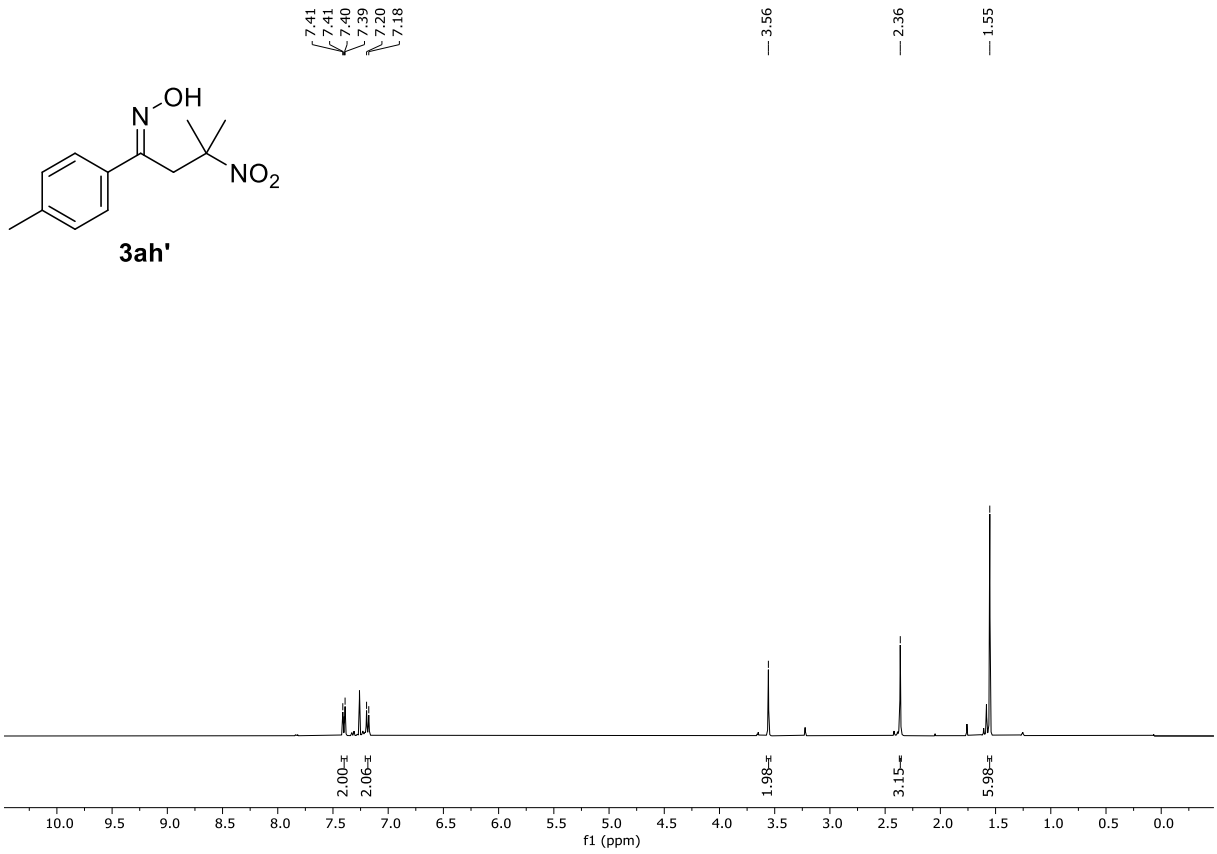
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



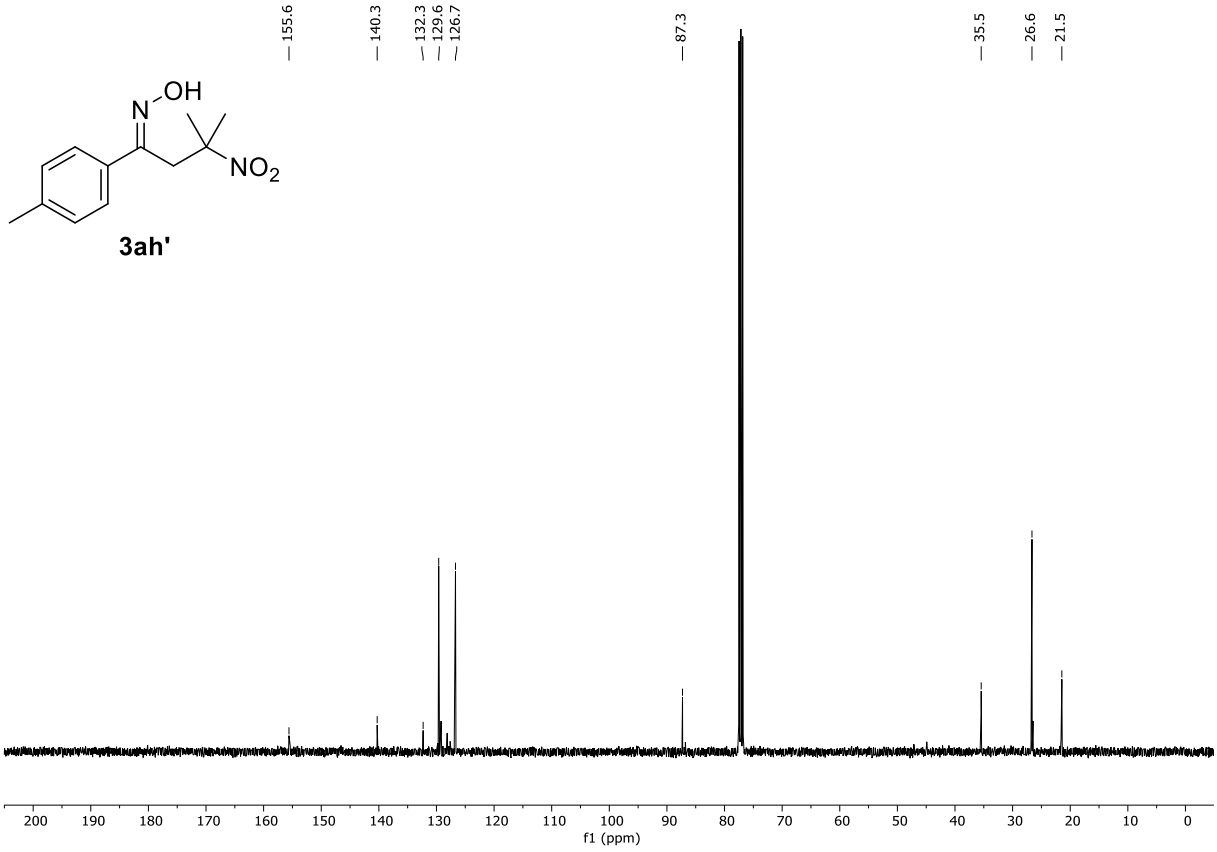
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



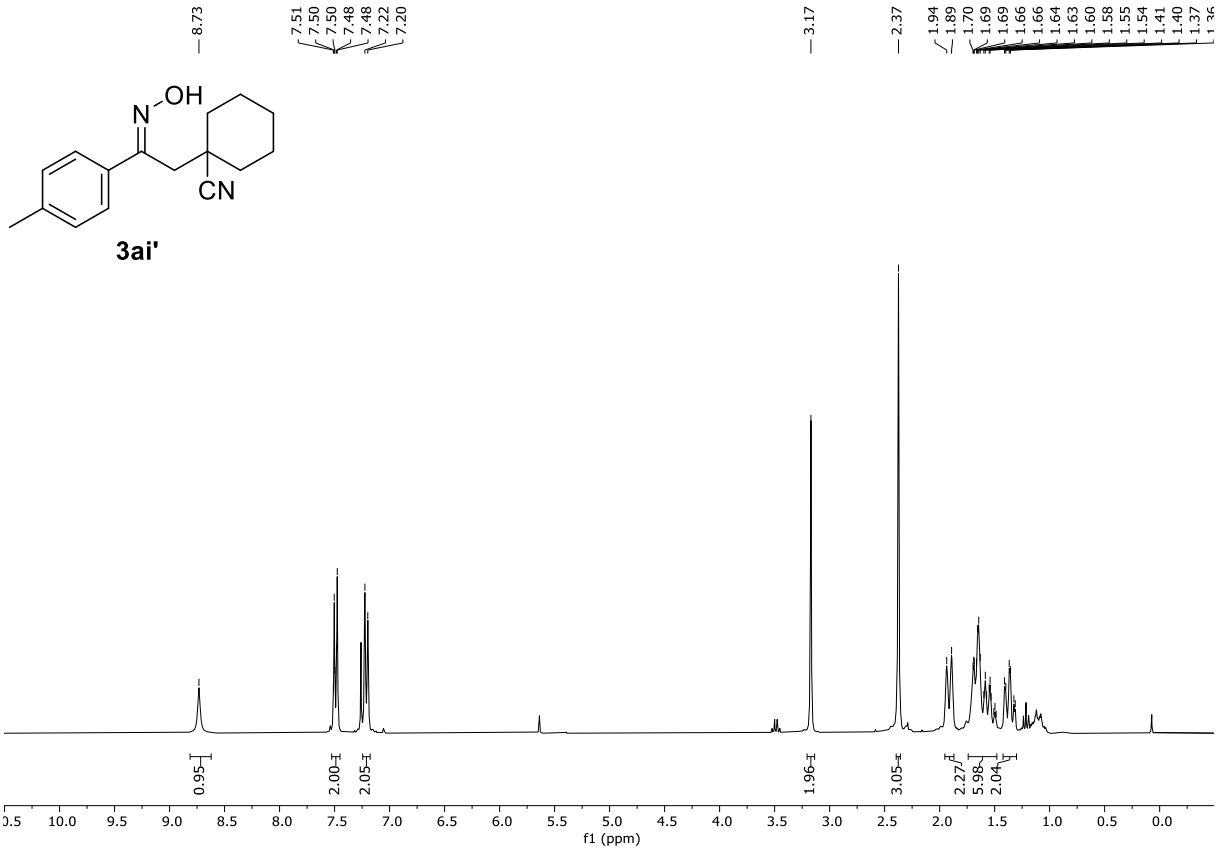
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



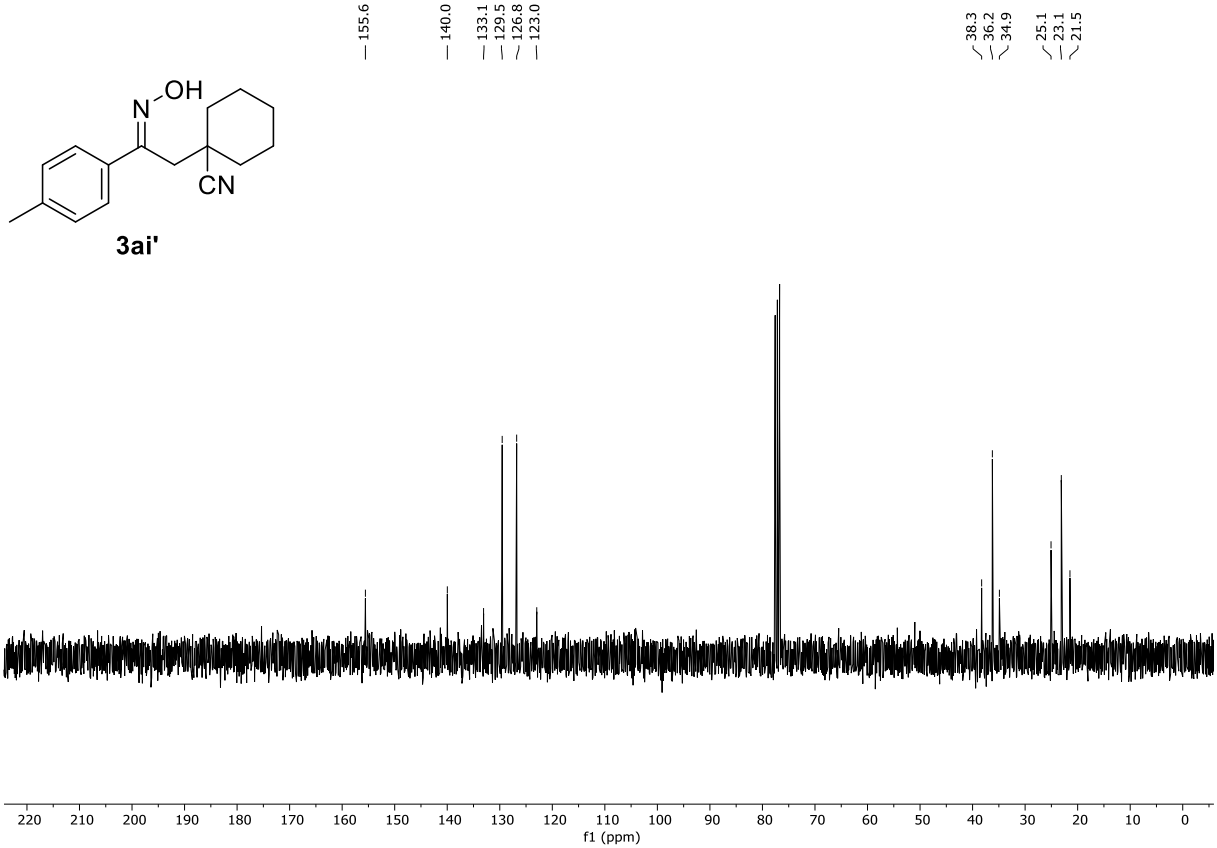
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



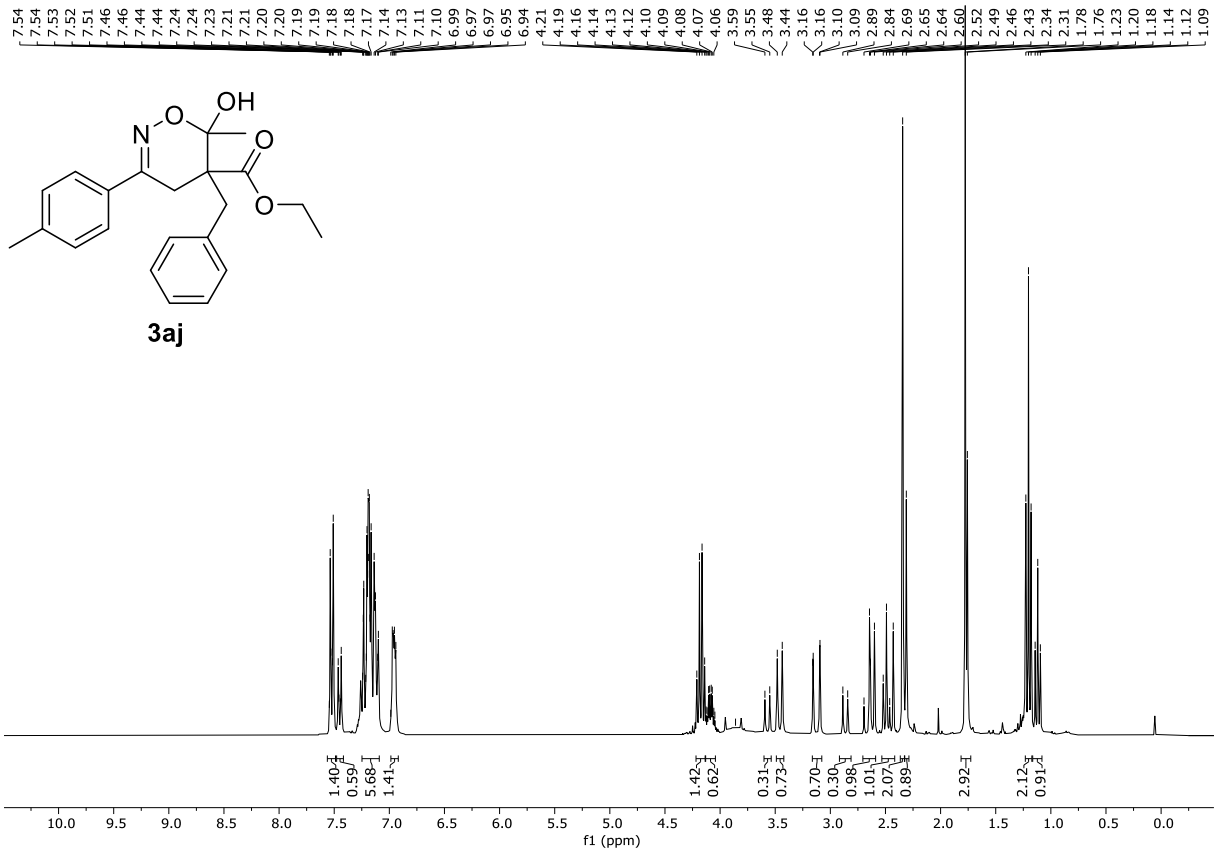
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



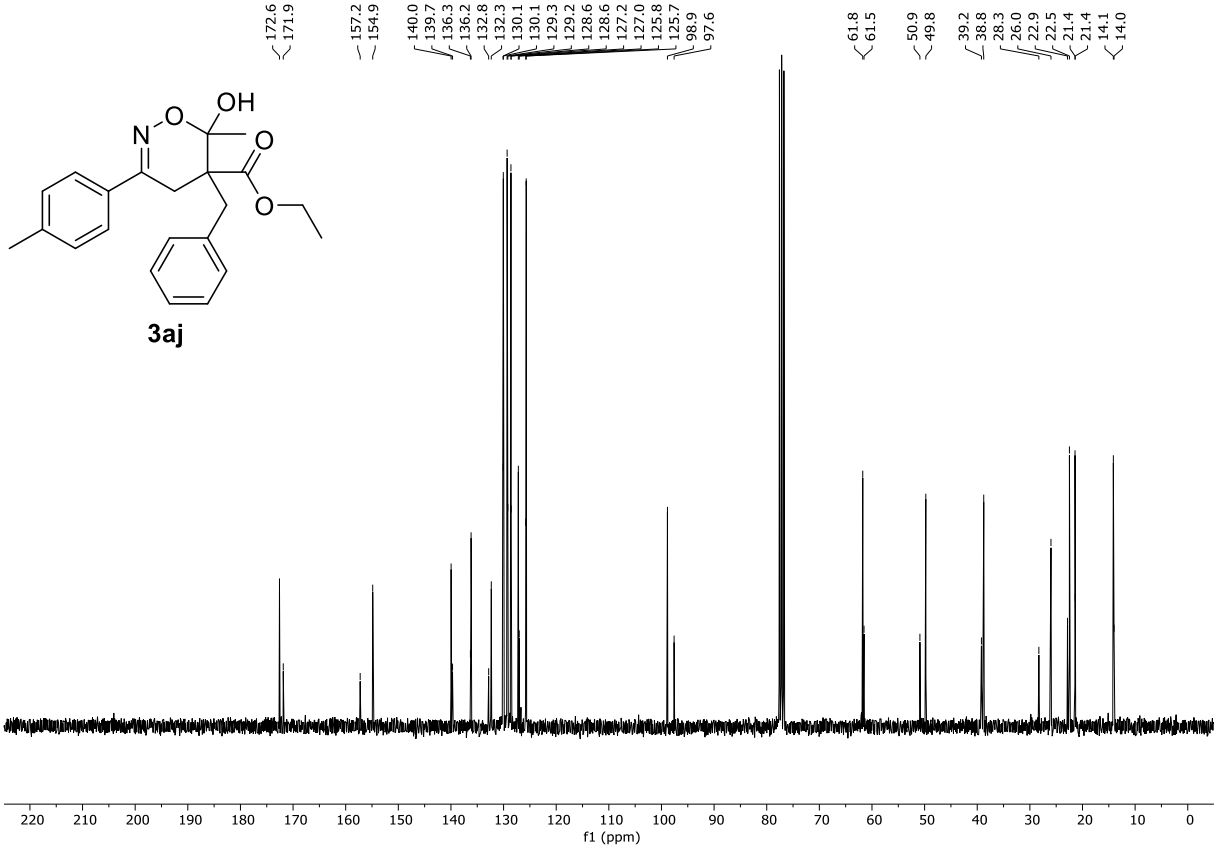
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



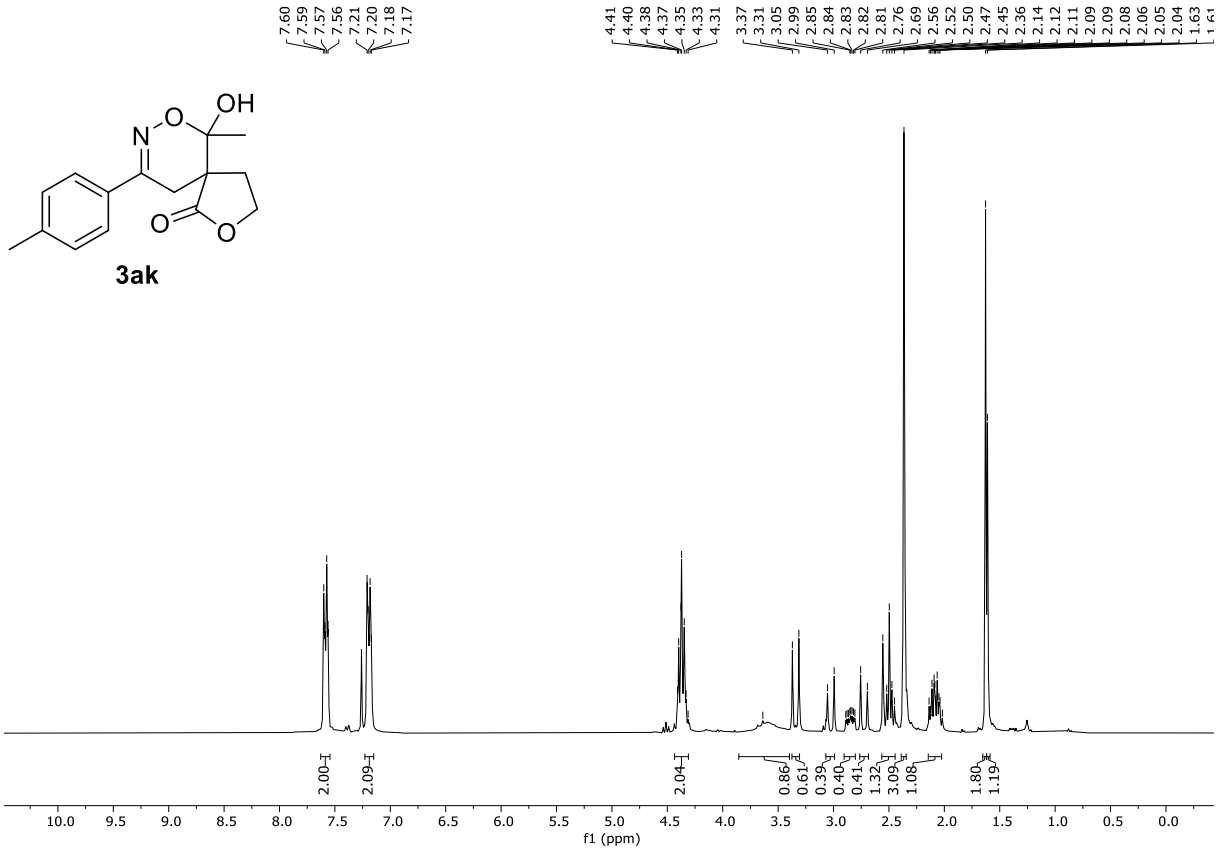
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



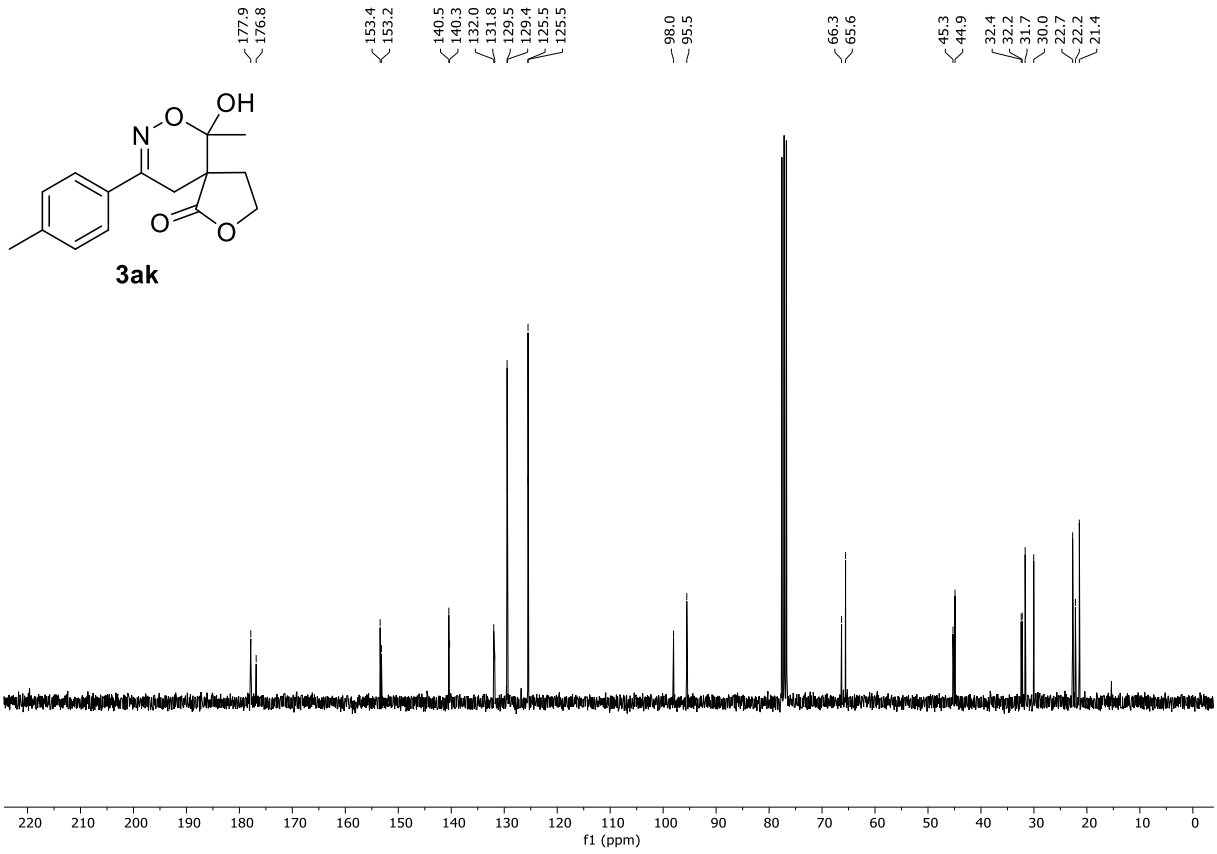
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



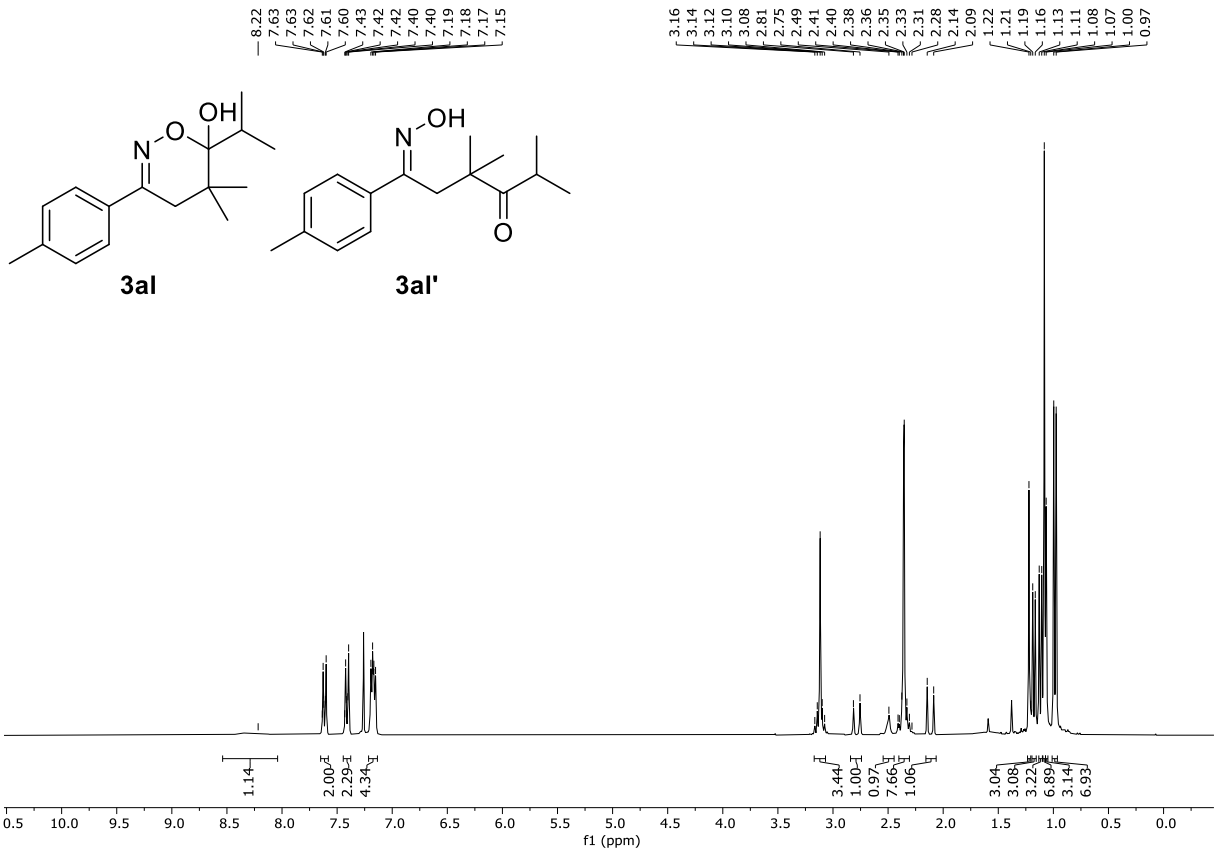
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



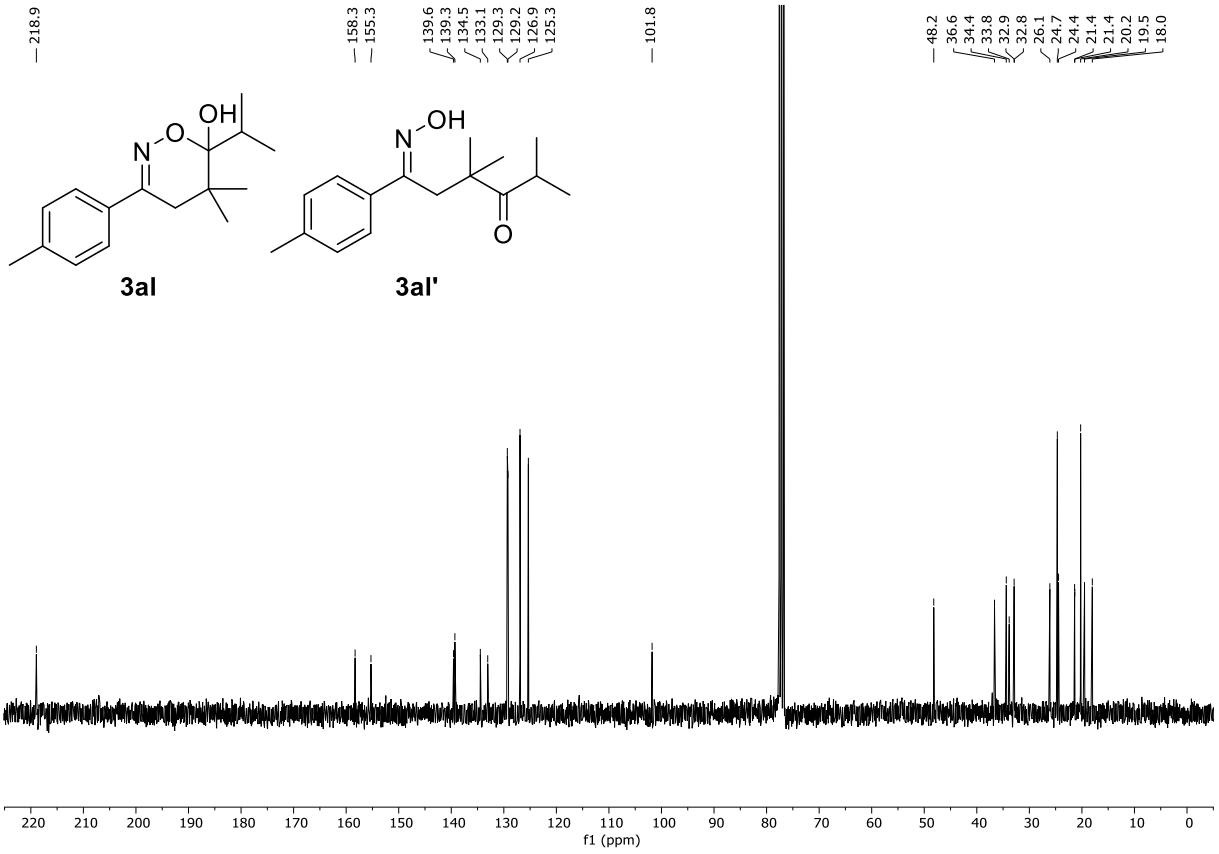
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



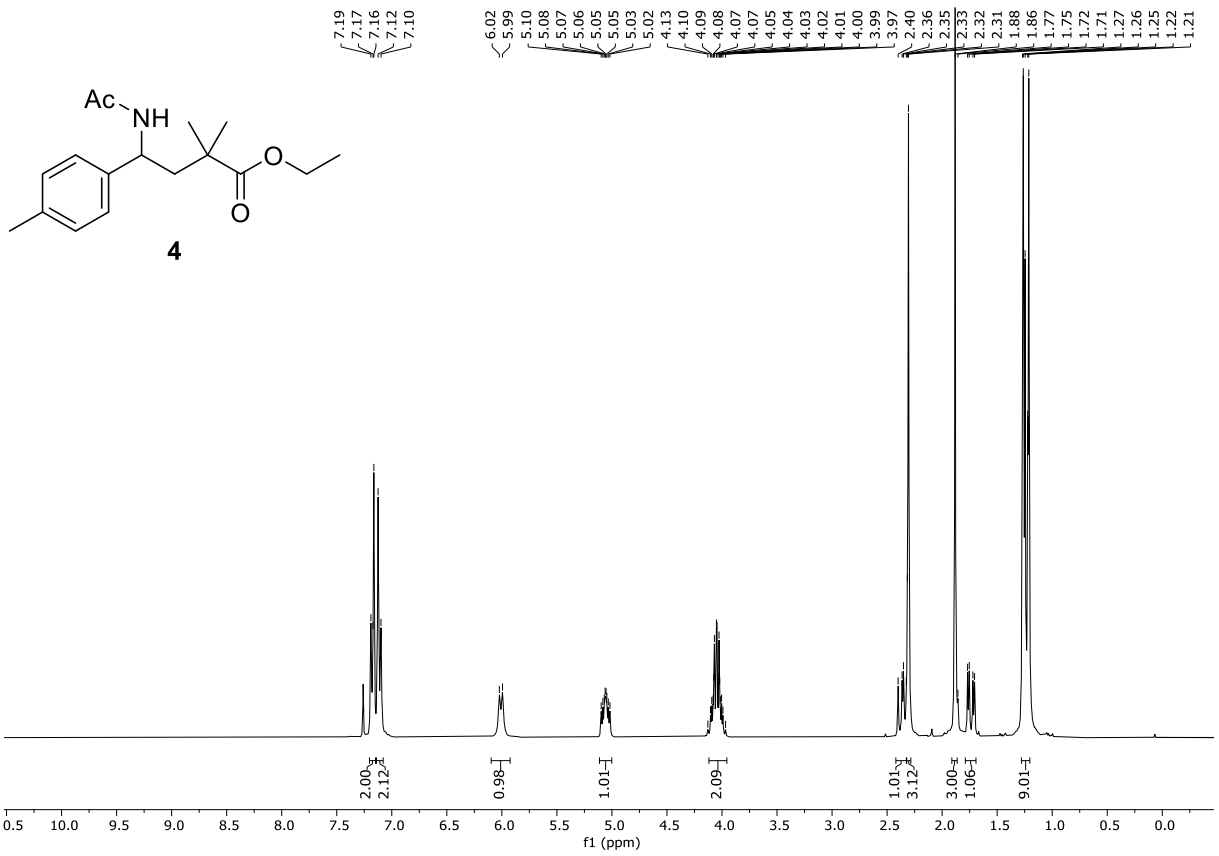
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



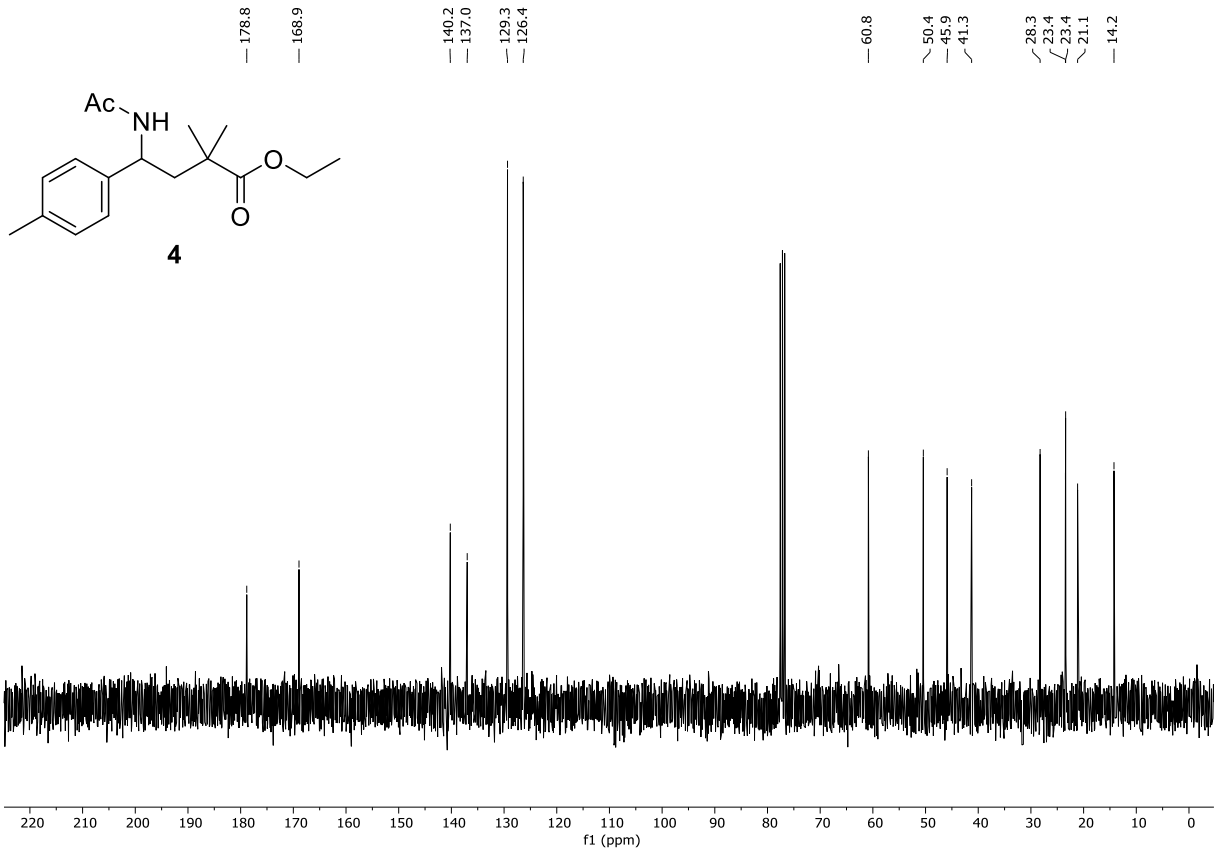
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



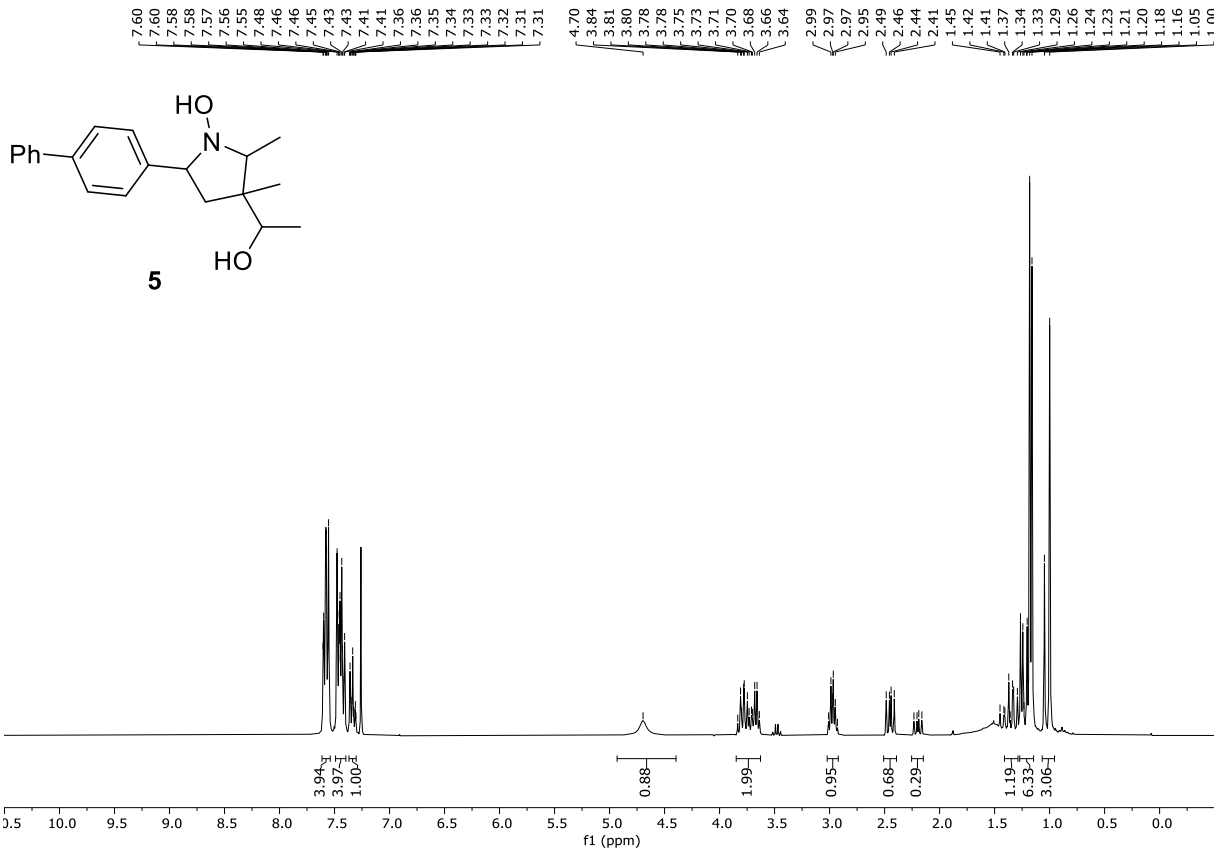
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



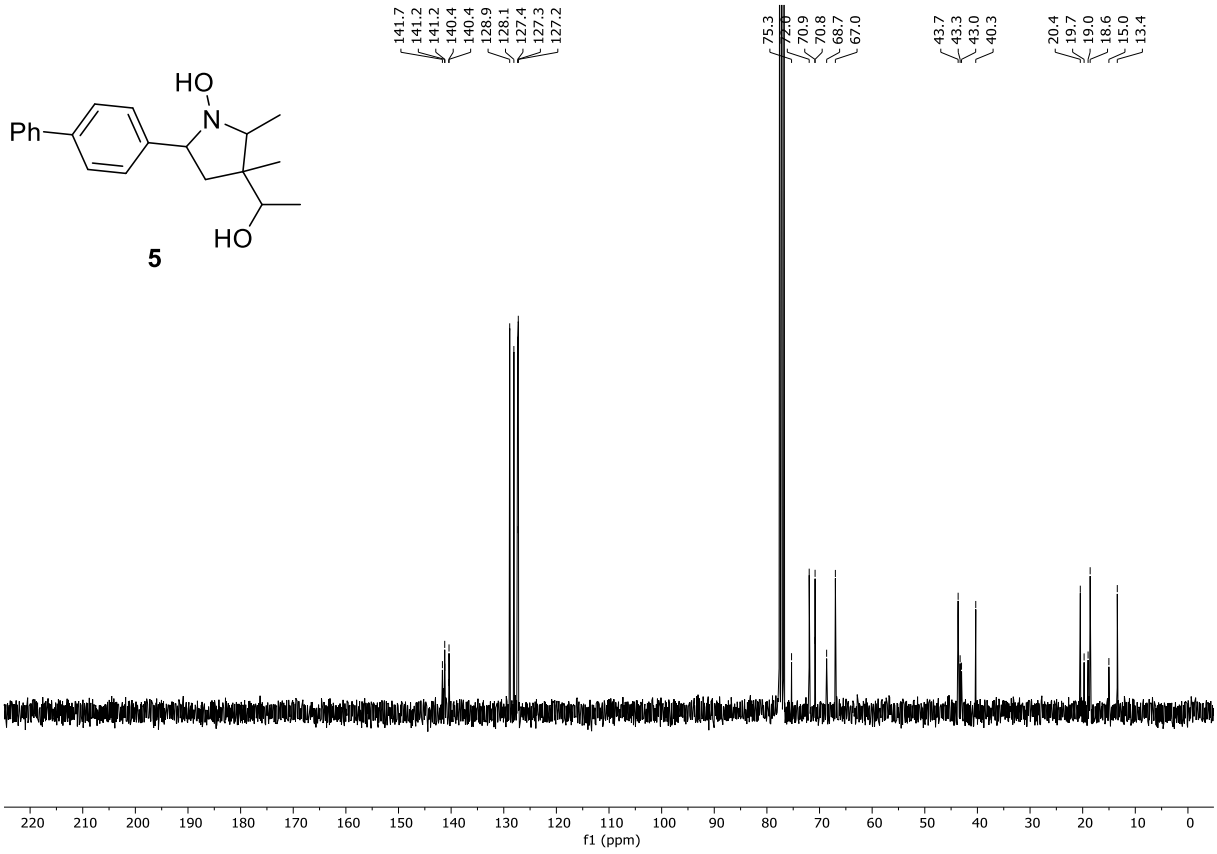
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



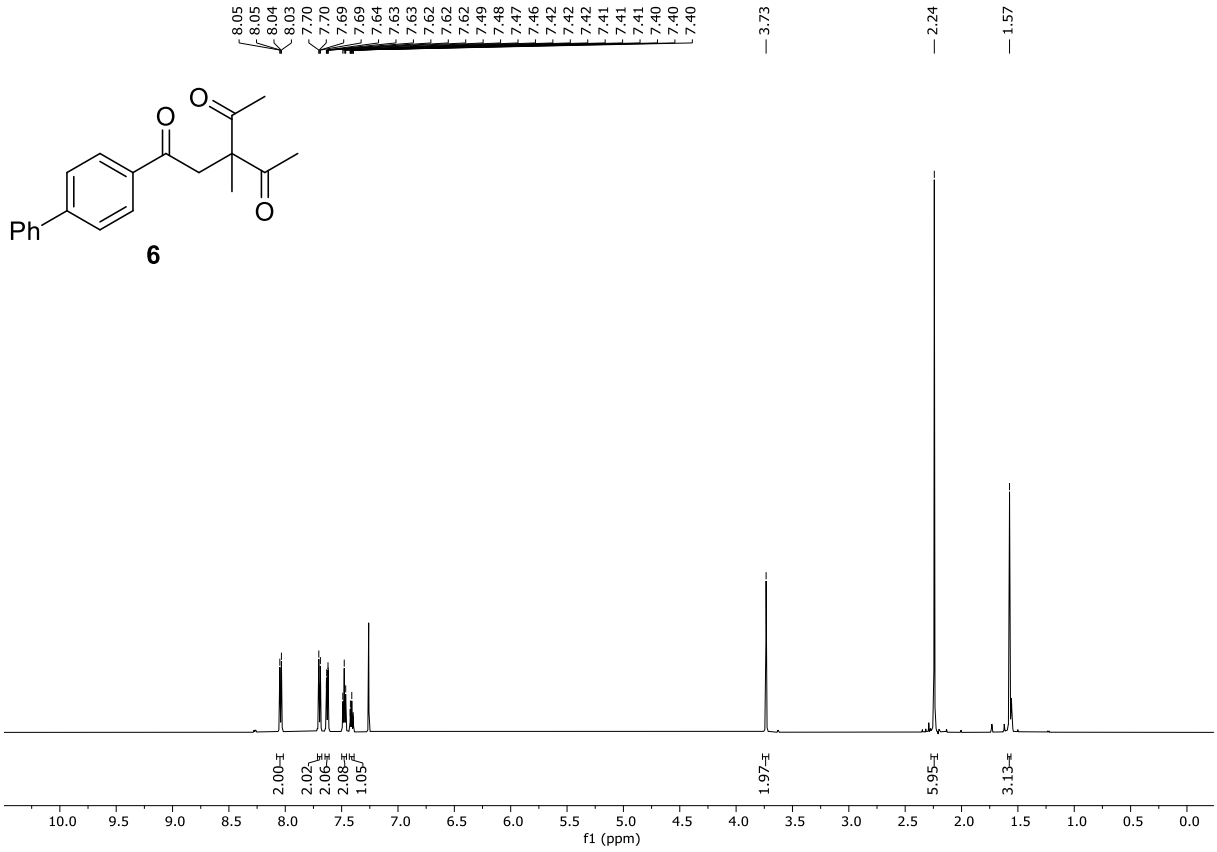
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



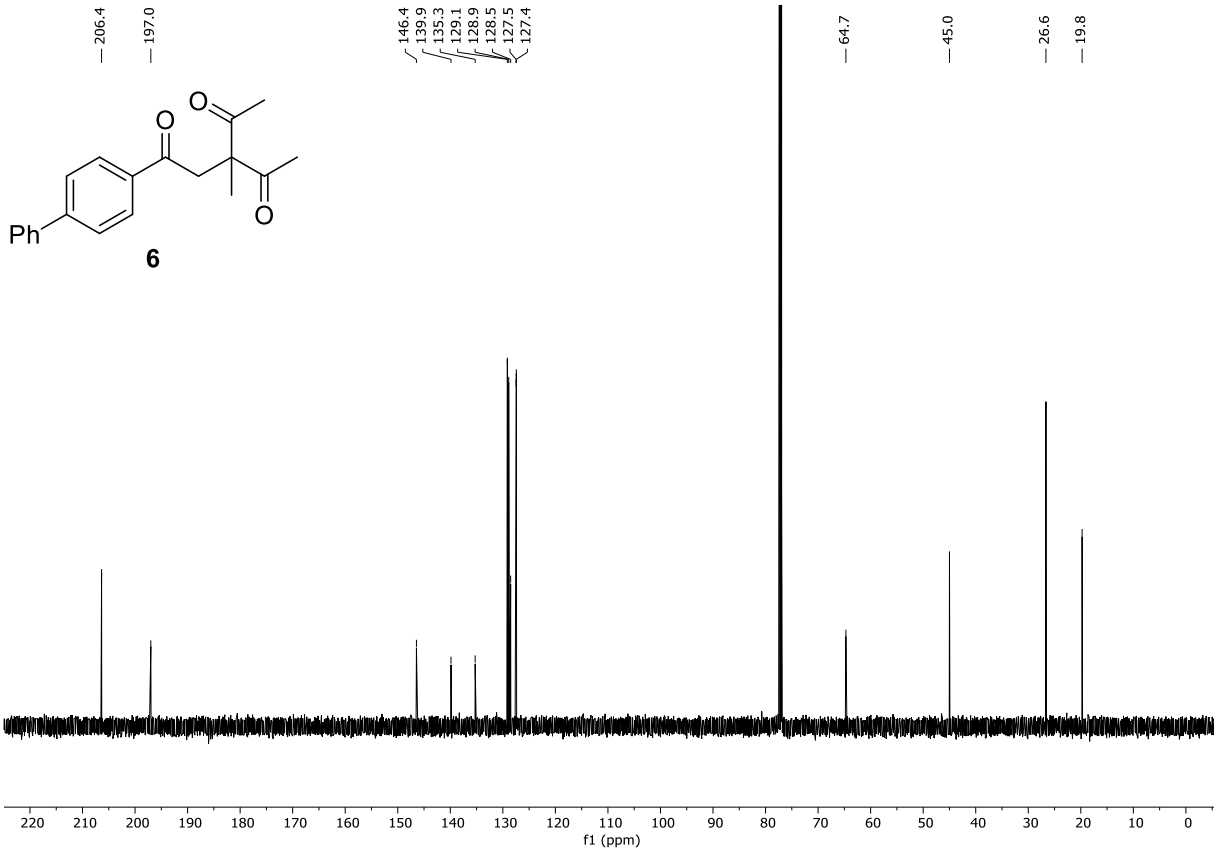
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



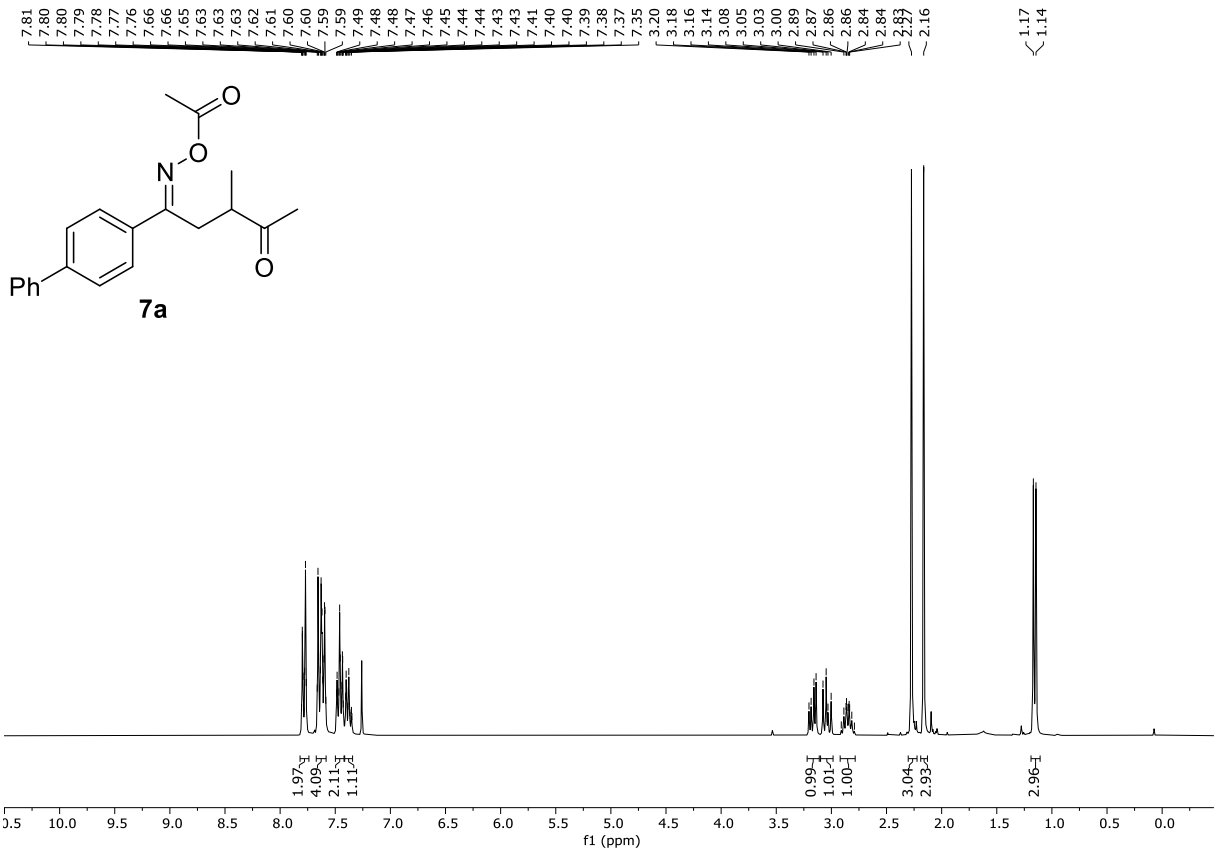
^{1}H-NMR (599 MHz, $CDCl_3$, 299 K)



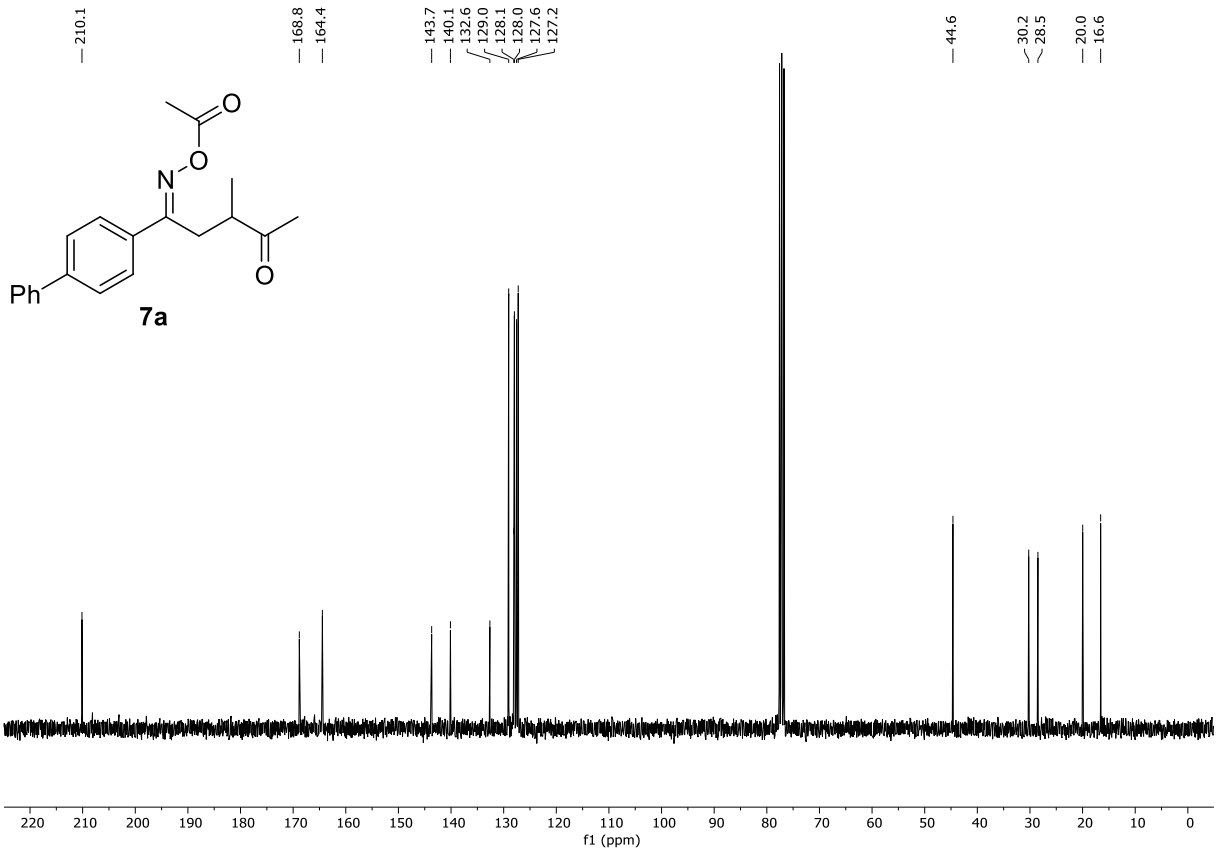
^{13}C-NMR (151 MHz, $CDCl_3$, 299 K)



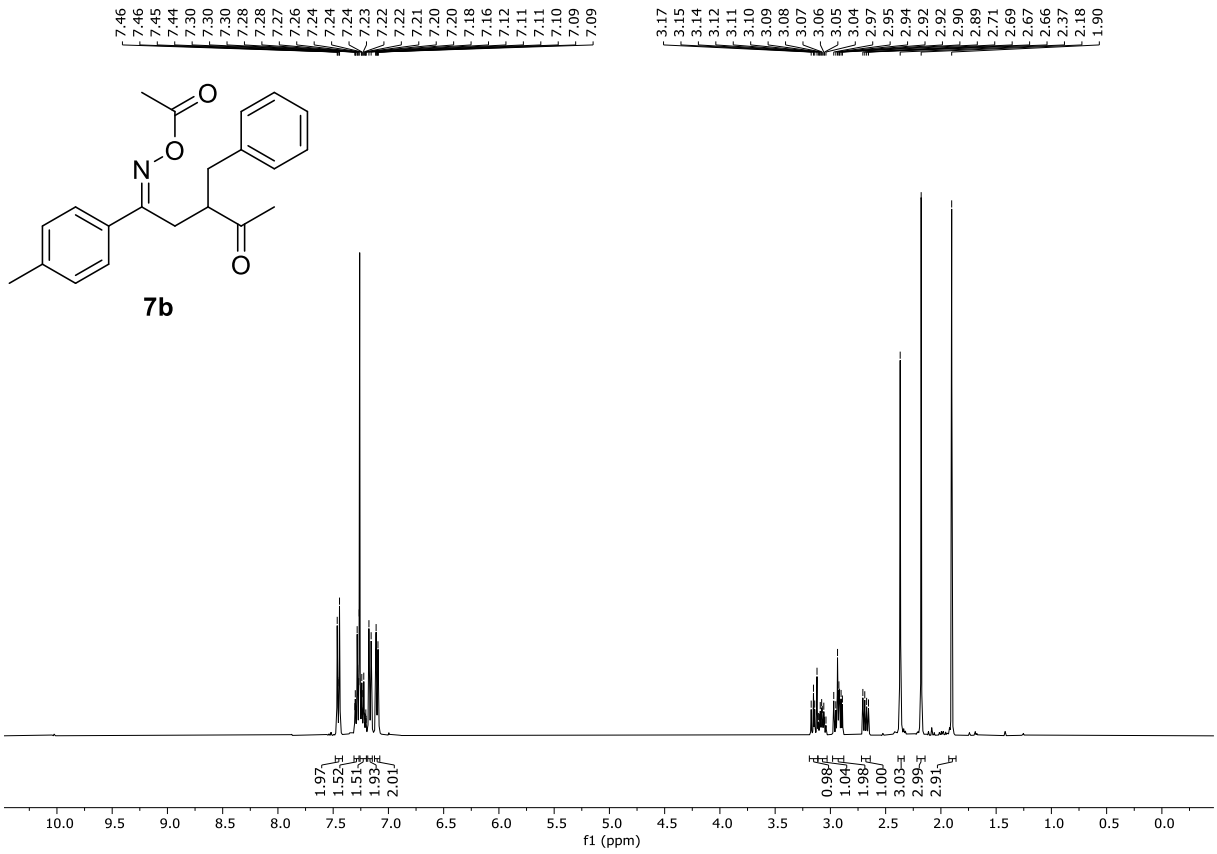
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



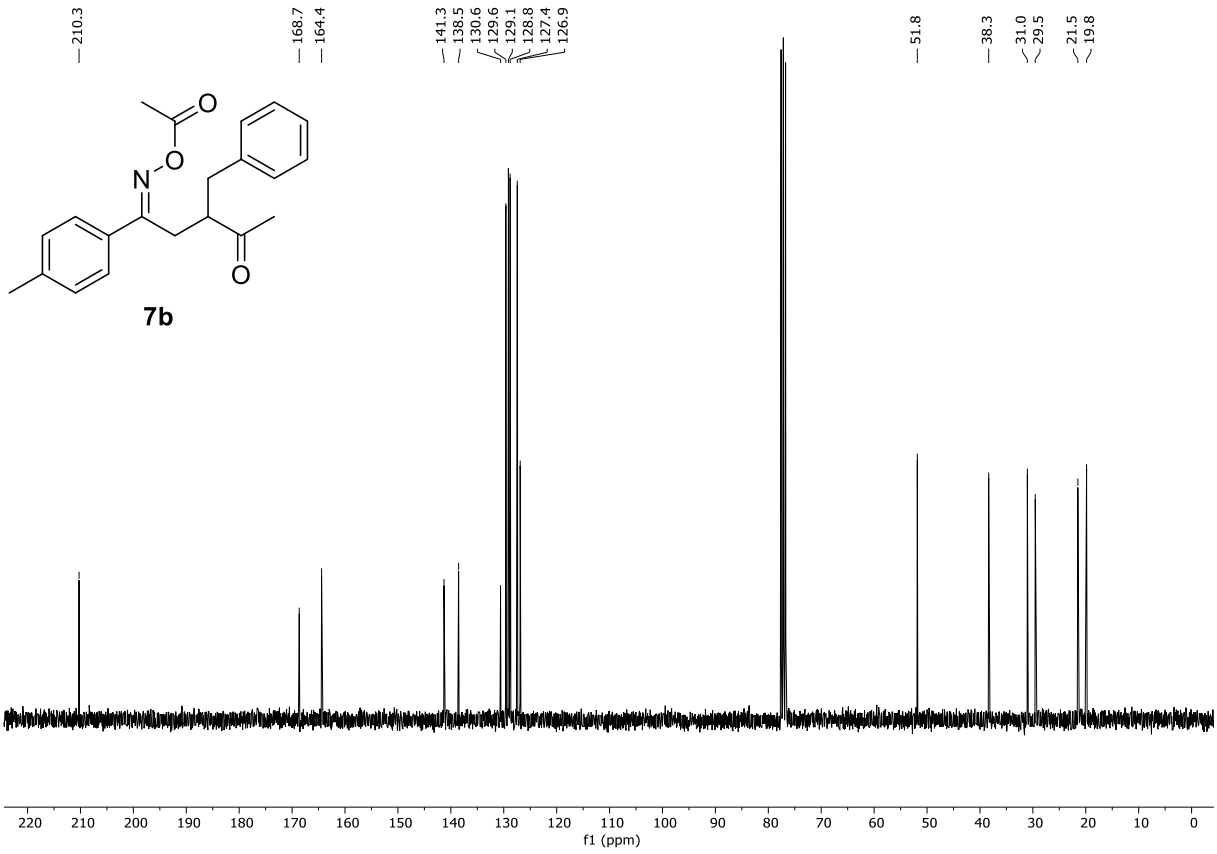
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



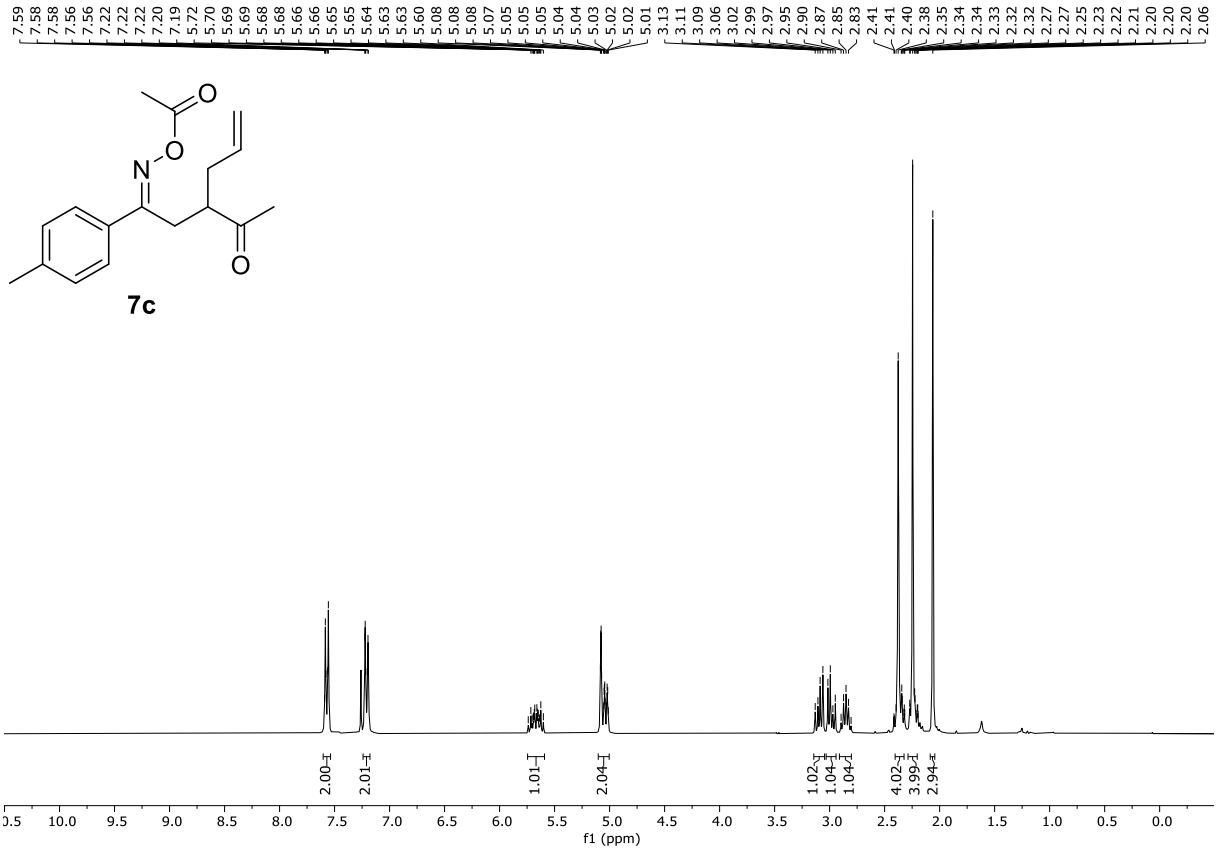
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



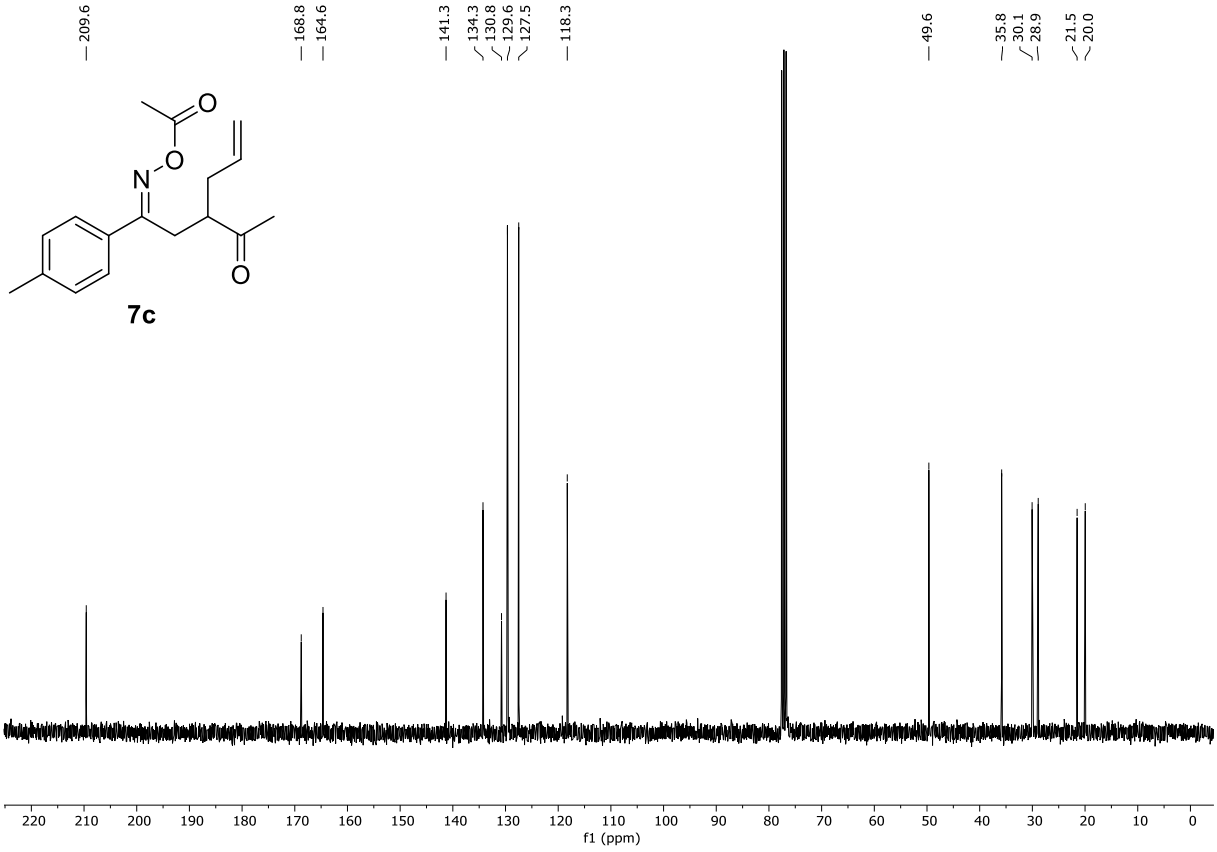
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



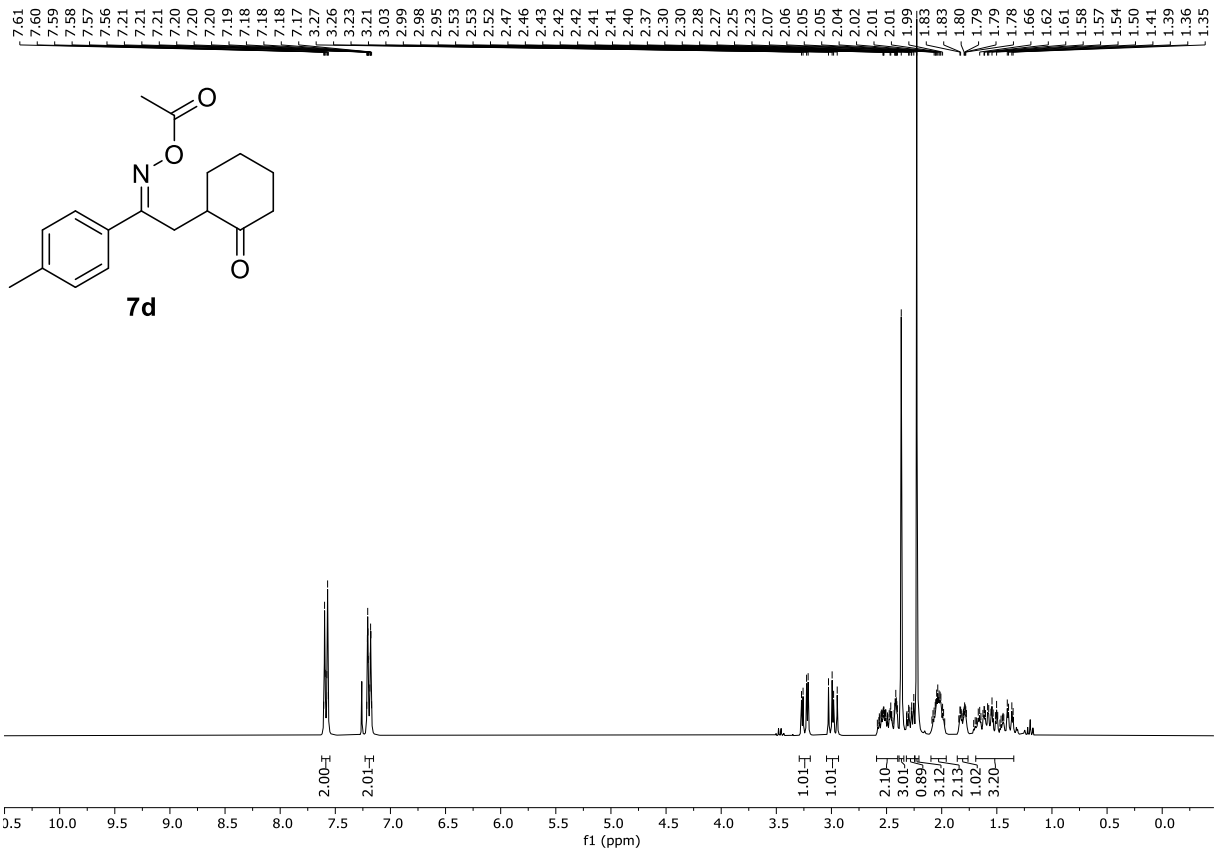
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



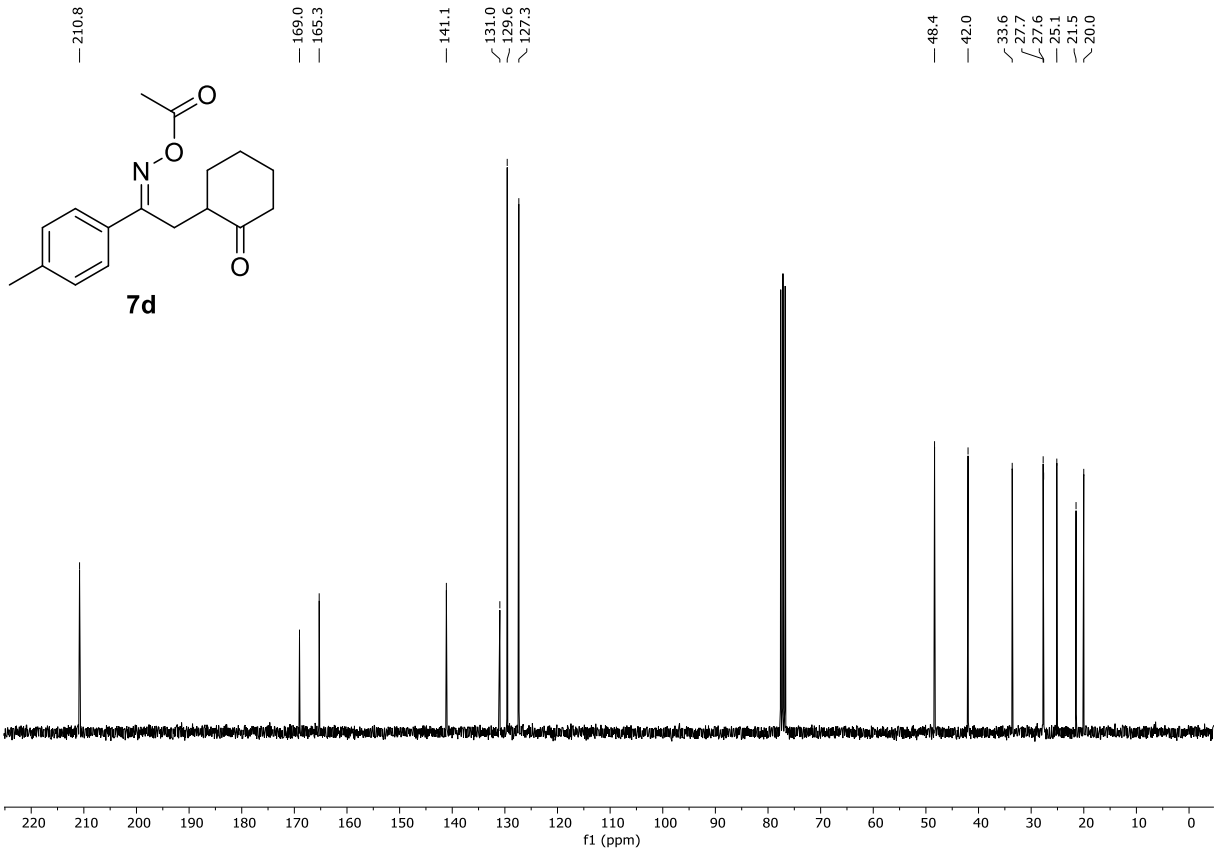
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



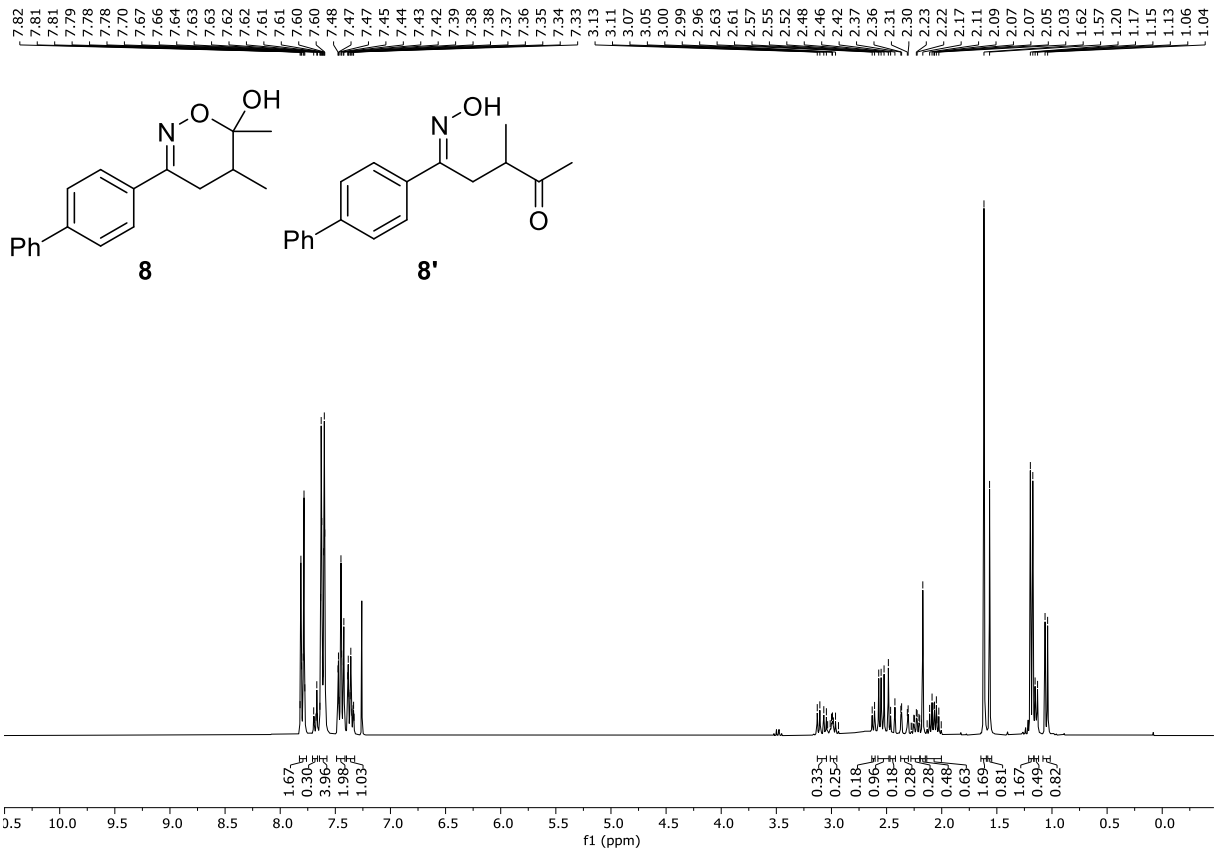
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



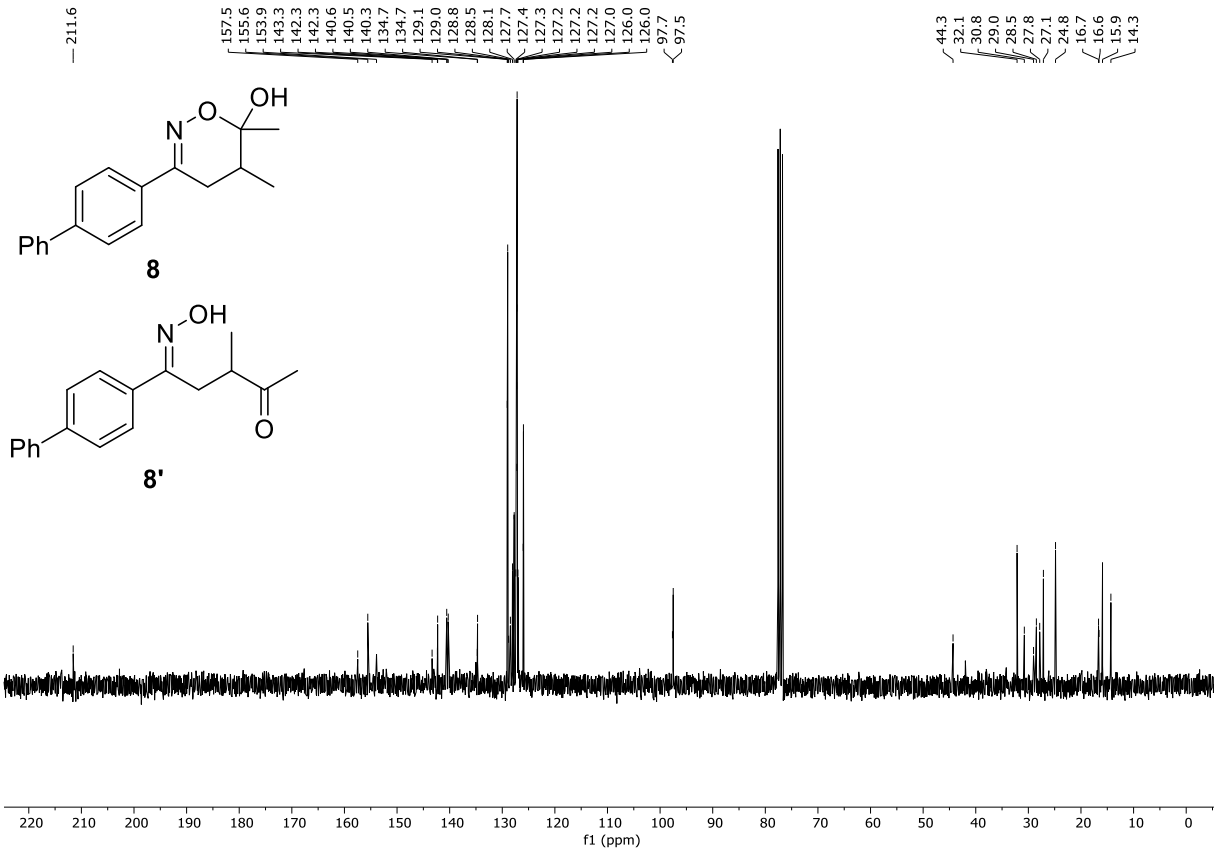
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



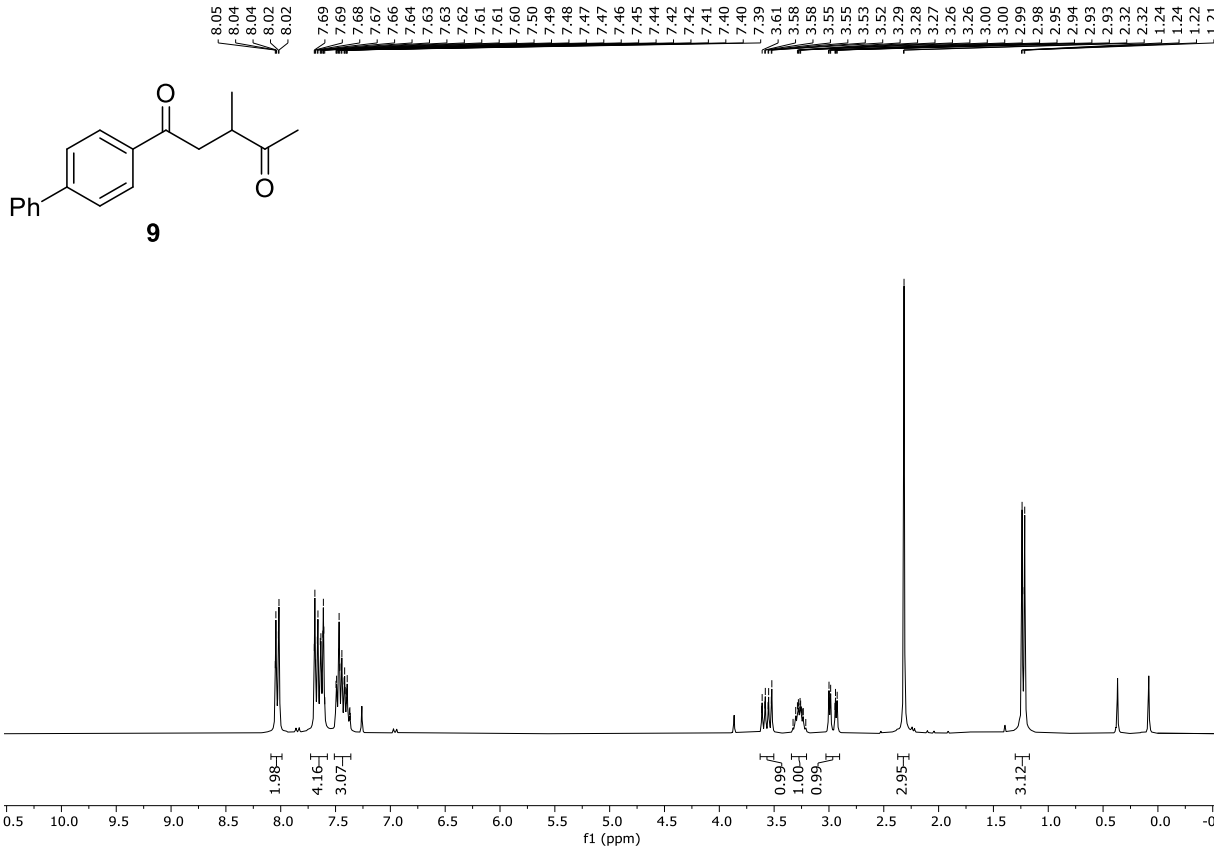
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



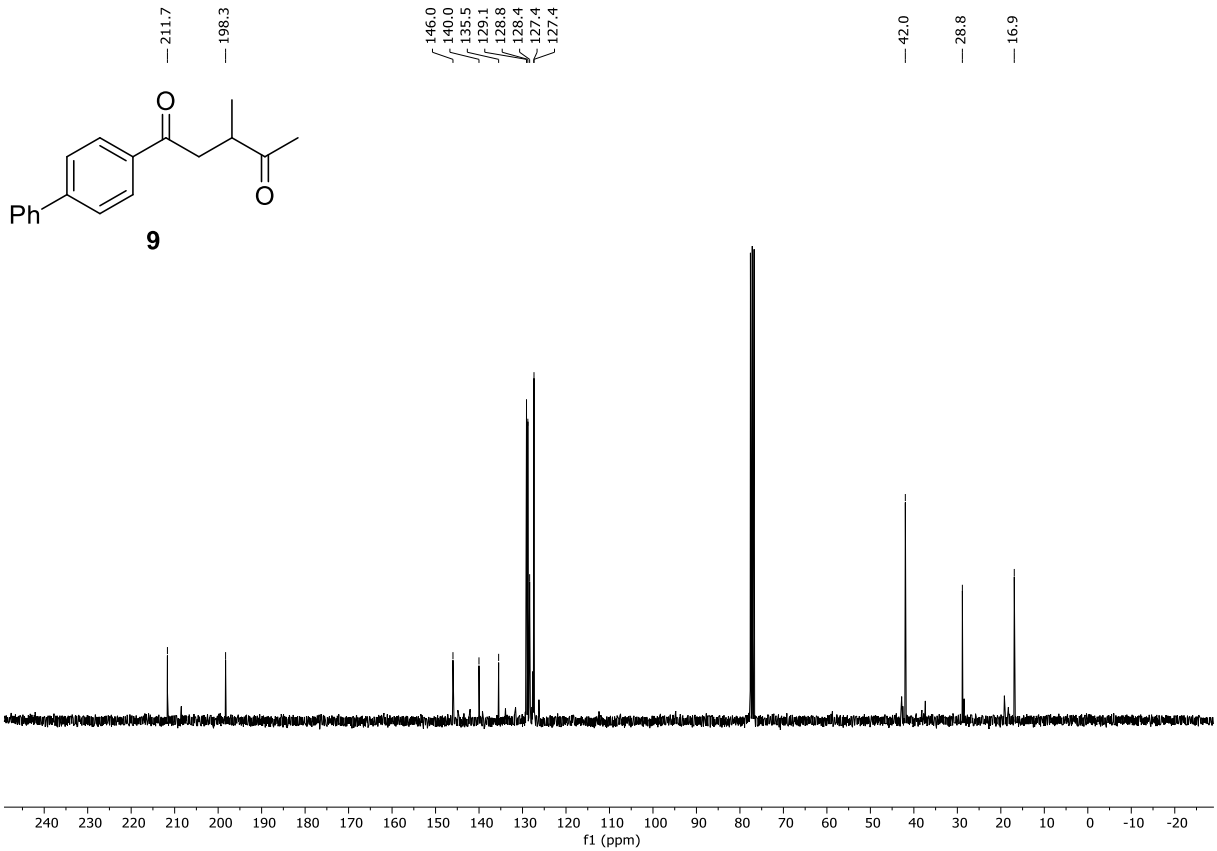
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



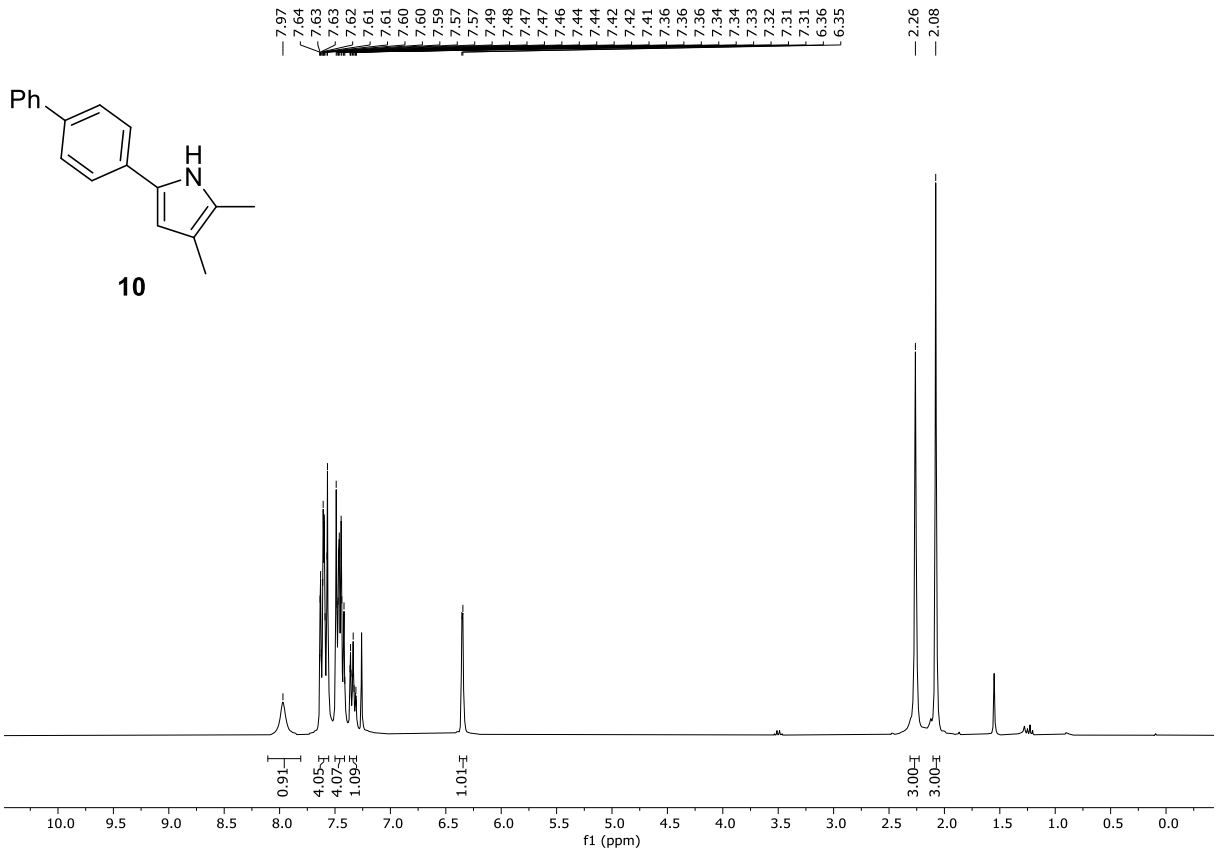
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



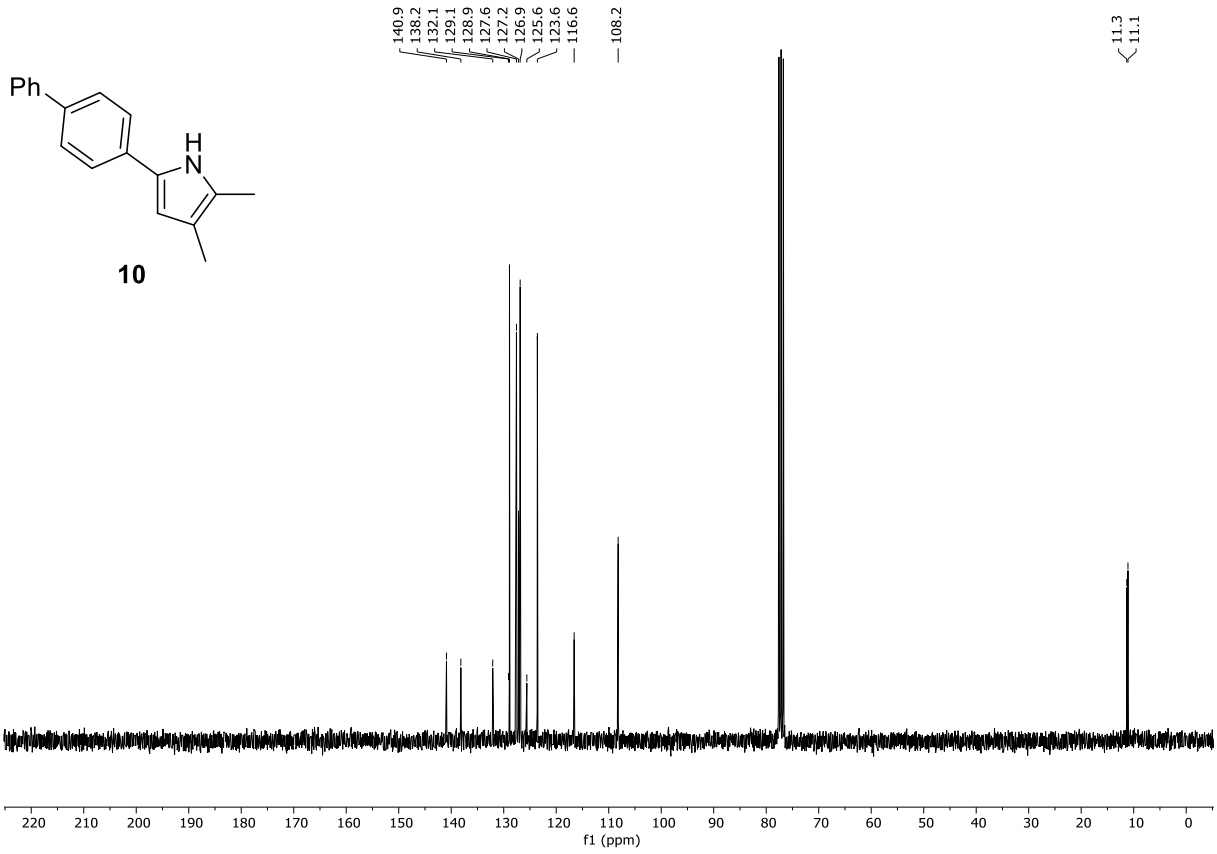
^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



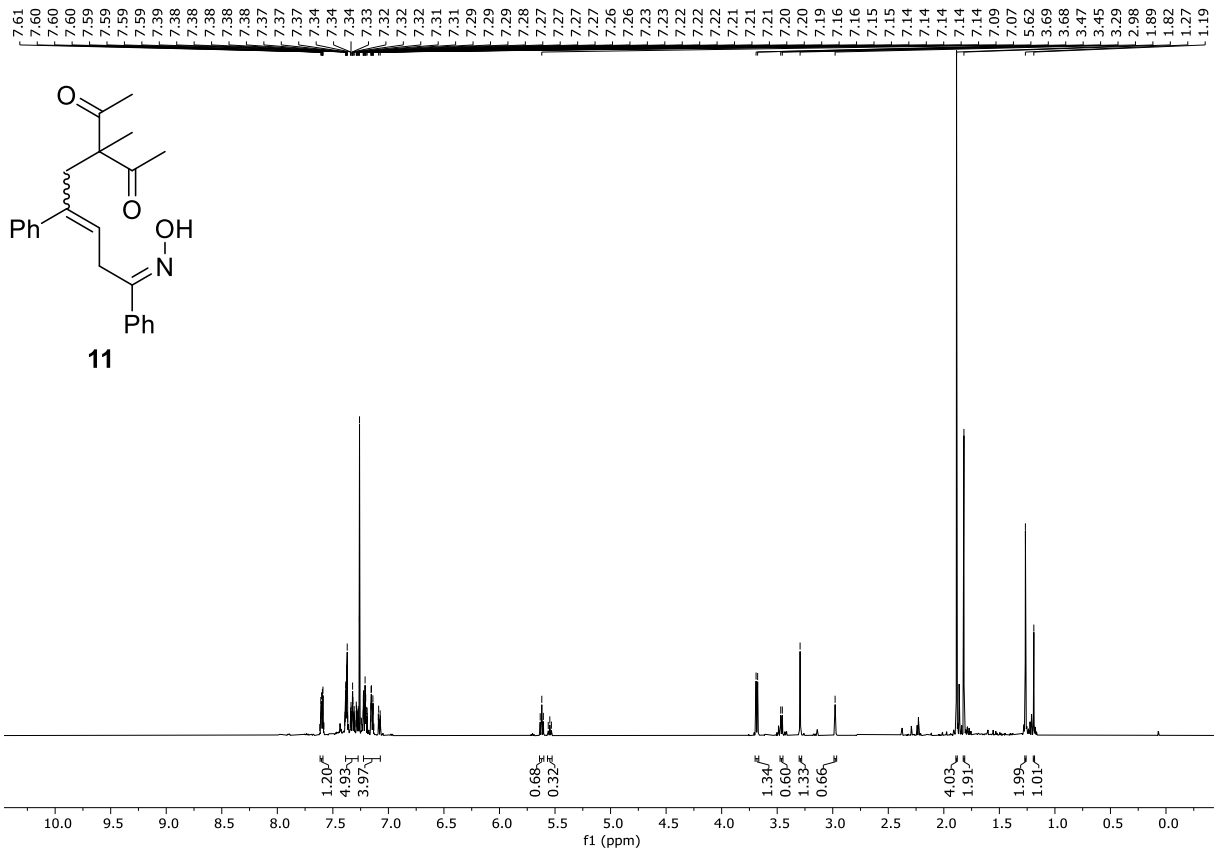
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K)



^{13}C-NMR (75 MHz, $CDCl_3$, 299 K)



^{1}H-NMR (500 MHz, $CDCl_3$, 299 K)



^{13}C-NMR (126 MHz, $CDCl_3$, 299 K)