SUPPLEMENTARY INFORMATION FILE

A Hydrazine-Free Photoredox Catalytic Synthesis of Azines by Reductive Activation of Readily Available Oxime Esters

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1 General Experimental Information

All commercially available chemicals were purchased in high quality and used without further purification. Dry solvents were bought and stored under a seal with drying agent. All reactions were carried out in dried glassware and under N_2.

All ^{1}H, ^{13}C, ^{19}F NMR data were recorded using an Avance Bruker 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F) or Avance Bruker 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C). Chemical shifts are reported in ppm on the δ-scale. ^{13}C NMR was run in ^{1}H decoupled mode. Data were manipulated using MestReNova version 14.2.0. Multiplicities for coupled signals were denoted as: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet, br. = broad, apt. = apparent. Coupling constants (J) are given in Hz and are uncorrected. Generally, ^{1}H NMR experiments were measured with the signal of residual $CHCl_3$ (7.26 ppm) in $CDCl_3$ as the internal reference, ^{13}C NMR experiments were measured in relative to the signal of $CDCl_3$ (77.16 ppm). In cases where Benzene-d_6 was used, the signals of residual Benzene (7.36 ppm, ^{1}H NMR; 128.37 ppm ^{13}C NMR) were used.

Column chromatography was performed on Merck silica gel 60 (70-230 mesh size) and an appropriate mixture of ethyl acetate/pentane or ethyl acetate/petroleum ether. Mixtures are specified for the specific compounds concerned. Pentane and petroleum ether were freshly distilled prior to use.

High resolution mass spectra (HRMS) were recorded on a Varian MAT 311A, Finnigan MAT 95, Thermoquest Finnigan TSQ 7000 or Agilent Technologies 6540 UHD Accurate-Mass QTOF LC/MS mass spectrometer at the Central Analytical Department (University of Regensburg) and masses observed are accurate to within ±5 ppm.

Thin layer chromatography was done on with silica gel pre-coated aluminium sheets (Merck, silica gel 60 F254, 0.2 mm). For visualization, UV-light (254 nm and 224 nm) and/or a $KMnO_4$ staining solution were employed.

CV measurements were performed with an Autolab PGSTAT302N Metrohm potentiostat. As a working electrode, Glassy Carbon 3.0 mm diameter BASi MF-2012 was used. As the counter electrode, a Platinum wire was used. Silver wire was used as a pseudo reference electrode. As a supporting electrolyte, tetrabutylammonium tetrafluoroborate ($^{n}Bu_4N{\cdot}BF_4$) (0.1 M in MeCN) was used as supplied by Fluka. Prior to the measurement, the electrolyte analyte solution was degassed with Ar. All experiments were performed under Ar atmosphere. Ferrocene was used as an internal reference for determining the reduction and oxidation potentials and setting them vs. SCE.

Samples for steady-state and time-resolved emission experiments were prepared in an oven-dried 1 cm x 1 cm quartz cuvette using dry MeCN as solvent. All samples were inerted by bubbling 3 min with Argon, before sealing and measuring. To ensure comparable extinction coefficients within a set of samples, all samples were examined by UV-vis measurements with Cary 400 and Cary WinUV (v6.2.0.1588) from Agilent© Technologies before Stern Volmer or lifetime experiments aiming for an identical absorption at the designated excitation wavelength. The measurements of quenching and lifetime experiments were conducted using the FloroMax-4 spectrometer, FluorEssence (v3.9), DataStation (v2.7), EzTime TM (v3.3.14.49) and Delta Diode TM LED 370 nm (Model DD-370) all by Horiba© Scientific.

Continuous flow experiments were conducted with Vapourtec UV-150 Photochemical Reactor at 405 nm light irradiation. Temperature was controlled by a N_2 stream and was constant at 25 °C. Pressure was controlled by a back pressure regulator and monitored.

2 MATERIALS

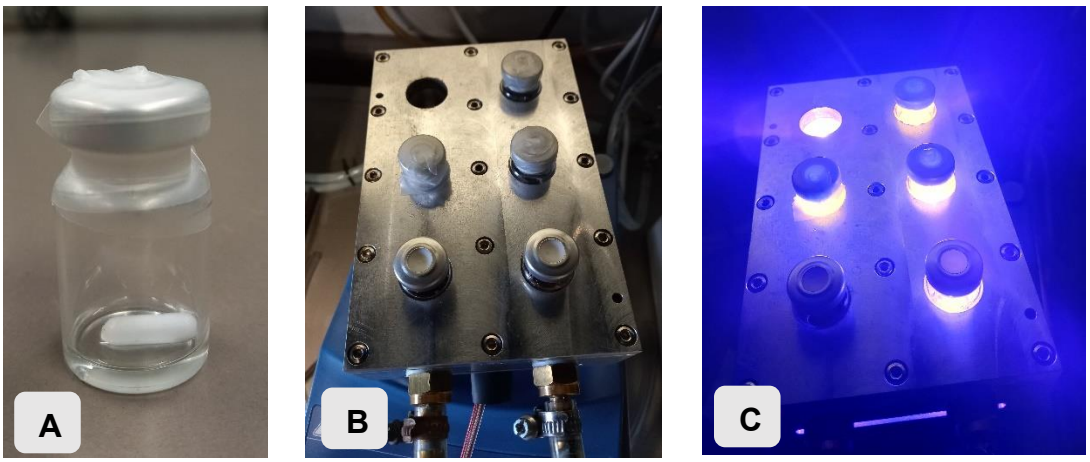


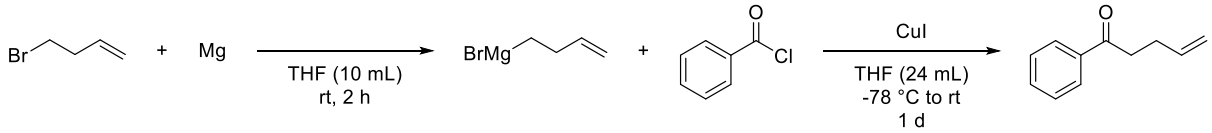
Figure S1. A) Crimp cap vial used to perform photoreactions. B) Cooling mantle used to cool down photoreactions to 25 °C. C) Vials in the cooling mantle on top of a LED.

Photoreactions were performed in oven-dried crimp cap vials equipped with magnetic stirring bars. The vials were inserted into the cooling mantle on top of a LED and the reactions were stirred under cooling, while irradiating with a LED.

3 SYNTHESIS OF STARTING MATERIALS

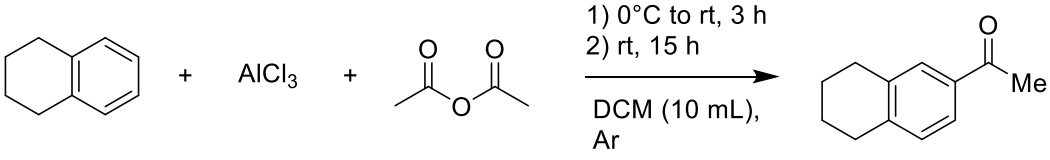
3.1 Synthesis of Ketones

Synthesis of 1-phenylpent-4-en-1-one [3]



In an oven dried Schlenk flask under nitrogen atmosphere, neat 4-bromobut-1-ene (1.91 mmol, 0.2 equiv.) was added to activated magnesium (16.52 mmol, 1.73 equiv.) in dry THF (2 mL). After the Grignard started, a solution of 4-bromobut-1-ene (7.64 mmol, 0.8 equiv.) in dry THF (8 mL) was added dropwise. The Grignard was stirred for 2 h at rt. In a second Schlenk flask equipped with a magnetic stirring bar and a dropping funnel under nitrogen atmosphere, CuI (1.43 mmol, 0.15 equiv.) and benzoyl chloride (9.55 mmol, 1 equiv.) were dissolved in dry THF (10 mL). The solution was stirred for 10 min, then cooled down to -78 °C and the Grignard was added dropwise. After addition of the Grignard, the solution was stirred at rt overnight. Subsequently the reaction was quenched with saturated NH_4Cl solution (40 mL) and then extracted with Et_2O (3 x 50 mL). The collected organic phase was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica with 99:1 Petroleum ether/EtOAc as eluent mixture to give the desired product as a colourless oil. **Yield**: 89% (8.55 mmol). Data consistent with literature [1]

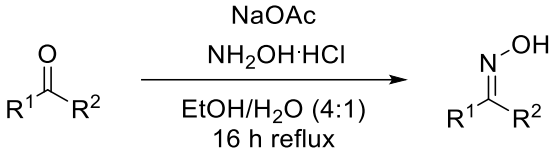
Synthesis of 1-(5,6,7,8-tetrahydronaphthalen-2-yl)ethan-1-one [2]



A mixture of tetralin (3.78 mmol, 1 equiv.) and acetic anhydride (4.54 mmol, 1.20 equiv.) was added dropwise during 3 h to a slurry of $AlCl_3$ (9.08 mmol, 2.40 equiv.) in DCM (5 mL) cooled to 0 °C. The reaction mixture was stirred at rt under an argon flux for 15 h and then poured into ice. The mixture was extracted with DCM (10 mL x 4). The collected organic phase was washed with 5 M HCl (40 mL) and 5% $NaHCO_3$ (40 mL) solution and dried over Na_2SO_4. After filtration the solvent was removed under reduced pressure. The crude product was used in the next step without further purification.

3.2 Synthesis of Oximes

General procedure for synthesis of oximes [3]

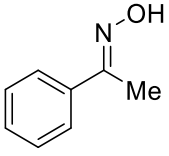


General procedure A (GPA): In a round bottom flask equipped with a stirring bar, the corresponding ketone (1 equiv.) and sodium acetate (1.5 equiv.) were dissolved in EtOH/H_2O (4/1; 0.4 mmol/mL). Hydroxylamine hydrochloride (1.5 equiv.) was added and the resulting mixture was refluxed (97 °C) overnight while stirring. After 16 h, the reaction mixture was cooled to room temperature and the oxime crystallized while cooling down. The crystals were collected and washe_cod with water using suction filtration. The resulting oximes were used in the next reaction without further purification.

General procedure B (GPB): In a round bottom flask equipped with stirring bar the corresponding ketone (1 equiv.) and sodium acetate (1.5 equiv.) were dissolved in EtOH/H_2O (4/1; 0.4 mmol/mL). Hydroxylamine hydrochloride (1.5 equiv.) was added and the resulting mixture was refluxed (97 °C) over night while stirring. After 16 h, the reaction mixture was cooled to room temperature, then water was added to precipitate the oxime as a solid. The solid was collected and washed with water using suction filtration. The resulting oximes were used in the next reaction without further purification.

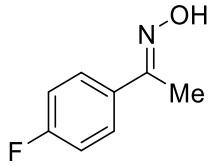
General procedure C (GPC): In a round bottom flask equipped with stirring bar the corresponding Ketone (1 equiv.) and sodium acetate (1.5 equiv.) were dissolved in EtOH/H_2O (4/1; 0.4 mmol/mL). Hydroxylamine hydrochloride (1.5 equiv.) was added and the resulting mixture was refluxed (97 °C) overnight while stirring. After 16 h the reaction mixture was cooled to room temperature, then water was added and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with water (1x volume of solvent used) and brine (1x amount of solvent used) and then dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The resulting oxime were used in the next reaction without further purification.

Synthesis of (*E*)-1-phenylethan-1-one oxime



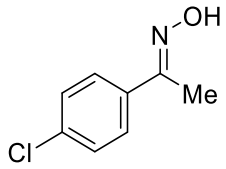
Following **GPB**, the reaction was carried out with acetophenone (30.0 mmol, 1 equiv.), sodium acetate (45.0 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (45.0 mmol, 1.5 equiv.) in EtOH (60 mL)/H_2O (15 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 97% (29.0 mmol).

Synthesis of (*E*)-1-(4-fluorophenyl)ethan-1-one oxime



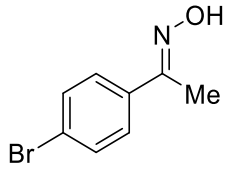
Following **GPB**, the reaction was carried out with 4-fluroacetophenone (20.0 mmol, 1 equiv.), sodium acetate (30.0 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (30.0 mmol, 1.5 equiv.) in EtOH (40 mL)/H_2O (10 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 95% (19.07 mmol).

Synthesis of (*E*)-1-(4-chlorophenyl)ethan-1-one oxime



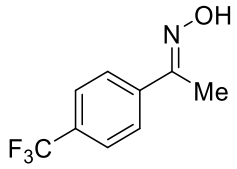
Following **GPB**, the reaction was carried out with 4-chloroacetophenone (10.0 mmol, 1 equiv.), sodium acetate (15.0 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (15.0 mmol, 1.5 equiv.) in EtOH (20 mL)/H_2O (5 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 91% (9.12 mmol).

Synthesis of (*E*)-1-(4-bromophenyl)ethan-1-one oxime



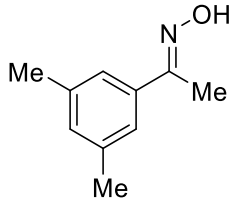
Following **GPB**, the reaction was carried out with 4-bromoacetophenone (10.0 mmol, 1 equiv.), sodium acetate (15.0 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (15.0 mmol, 1.5 equiv.) in EtOH (20 mL)/H_2O (25 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 92% (9.25 mmol).

Synthesis of (*E*)-1-(4-(trifluoromethyl)phenyl)ethan-1-one oxime



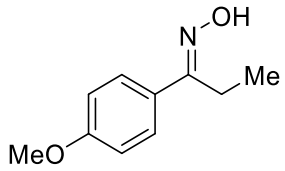
Following **GPB**, the reaction was carried out with 4-trifluoromethylacetophenone (10.0 mmol, 1 equiv.), sodium acetate (15.0 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (15.0 mmol, 1.5 equiv.) in EtOH (20 mL)/H_2O (5 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 96% (9.64 mmol).

Synthesis of (*E*)-1-(3,5-dimethylphenyl)ethan-1-one oxime



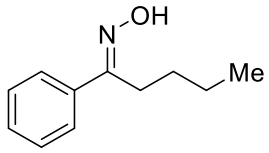
Following **GPB**, the reaction was carried out with 1-(3,5-dimethylphenyl)ethan-1-one (5.0 mmol, 1 equiv.), sodium acetate (7.5 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (7.5 mmol, 1.5 equiv.) in EtOH (10 mL)/H_2O (2.5 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 88% (4.43 mmol).

Synthesis of (*E*)-1-(4-methoxyphenyl)propan-1-one oxime



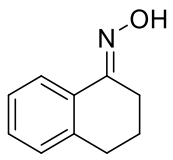
Following **GPC**, the reaction was carried out with 1-(4-methoxyphenyl)propan-1-one (13.0 mmol, 1 equiv.), sodium acetate (19.5 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (19.5 mmol, 1.5 equiv.) in EtOH (26 mL)/H_2O (6.5 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 54% (7.03 mmol).

Synthesis of (*E*)-1-phenylpentan-1-one oxime



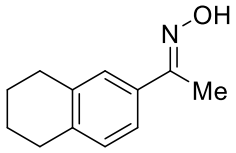
Following **GPC**, the reaction was carried out with valerophenone (10.0 mmol, 1 equiv.), sodium acetate (15.0 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (15.0 mmol, 1.5 equiv.) in EtOH (20 mL)/H_2O (5 mL) to give the crude product. The crude product was purified by flash column chromatography on silica with pentane to 9:1 pentane/EtOAc as eluent mixture to give a yellow oil, which was taken through to the next step. **Yield**: 40% (3.99 mmol).

Synthesis of (*E*)-3,4-dihydronaphthalen-1(2*H*)-one oxime



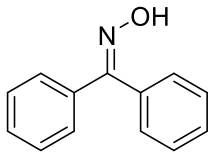
Following **GPB**, the reaction was carried out with tetralone (10.0 mmol, 1 equiv.), sodium acetate (15 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (15.0 mmol, 1.5 equiv.) in EtOH (20 mL)/H_2O (5 mL) to give the product as a pale orange solid, which was taken through to the next step. **Yield**: 88% (8.81 mmol).

Synthesis of (*E*)-1-(5,6,7,8-tetrahydronaphthalen-2-yl)ethan-1-one oxime



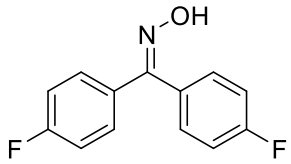
Following **GPC**, the reaction was carried out with 6-acetyltetraline (4.13 mmol, 1 equiv.), sodium acetate (6.20 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (6.20 mmol, 1.5 equiv.) in EtOH (20 mL)/H_2O (5 mL) to give the crude product. The crude product was purified by flash column chromatography on silica with 95:5 to 75:15 pentane/EtOAc as eluent mixture to give the desired product as a yellow oil, which was taken through to the next step. **Yield**: 62% (2.57 mmol).

Synthesis of diphenylmethanone oxime



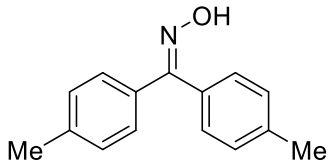
Following **GPA**, the reaction was carried out with benzophenone (35.0 mmol, 1 equiv.), sodium acetate (52.5 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (52.5 mmol, 1.5 equiv.) in EtOH (70 mL)/H_2O (17.5 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 96% (33.67 mmol).

Synthesis of bis(4-fluorophenyl)methanone oxime



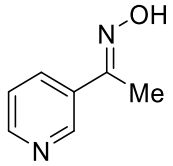
Following **GPA**, the reaction was carried out with bis(4-fluoro)benzophenone (4.34 mmol, 1 equiv.), sodium acetate (6.51 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (6.51 mmol, 1.5 equiv.) in EtOH (9 mL)/H_2O (2 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 90% (3.92 mmol).

Synthesis of bis(4-methylphenyl)methanone oxime



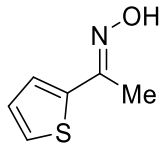
Following **GPA**, the reaction was carried out with 4,4'-dimethylbenzophenone (10.0 mmol, 1 equiv.), sodium acetate (15.0 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (15.0 mmol, 1.5 equiv.) in EtOH (20 mL)/H_2O (5 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 89% (8.92 mmol).

Synthesis of (*E*)-1-(pyridine-3-yl)ethan-1-one oxime



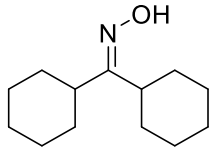
Following **GPC**, the reaction was carried out with 1-(yridine-3-yl)ethan-1-one (5.0 mmol, 1 equiv.), sodium acetate (7.5 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (7.5 mmol, 1.5 equiv.) in EtOH (10 mL)/H_2O (2.5 mL) to give the product as a white solid, which was taken through to the next step. Yield: 85% (4.27 mmol).

Synthesis of (*E*)-1-(thiophen-2-yl)ethan-1-one oxime



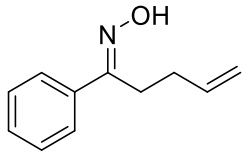
Following **GPB**, the reaction was carried out with 1-(thiophen-2-yl)ethan-1-one (5.0 mmol, 1 equiv.), sodium acetate (7.5 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (7.5 mmol, 1.5 equiv.) in EtOH (10 mL)/H_2O (2.5 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 61% (3.06 mmol).

Synthesis of dicyclohexylmethanone oxime



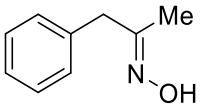
Following **GPC**, the reaction was carried out with di cyclohexyl methyl ketone (10.0 mmol, 1 equiv.), sodium acetate (15.0 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (15.0 mmol, 1.5 equiv.) in EtOH (20 mL)/H_2O (5 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 85% (8.50 mmol)

Synthesis of (*E*)-1-phenylpent-4-en-1-one oxime



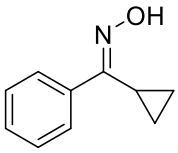
Following **GPB**, the reaction was carried out with 1-phenylpent-4-en-1-one (8.55 mmol, 1 equiv.), sodium acetate (12.82 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (12.82 mmol, 1.5 equiv.) in EtOH (10 mL)/H_2O (2.5 mL) to give the product as a colourless oil, which was taken through to the next step. **Yield**: 96% (8.22 mmol).

Synthesis of 1-phenylpropan-2-one oxime



Following **GPC**, the reaction was carried out with 1-phenylpropan-2-one (10.00 mmol, 1 equiv.), sodium acetate (15.00 mmol, 1.5 equiv.) and hydroxylamine hydrochloride (15.00 mmol, 1.5 equiv.) in EtOH (12 mL)/H_2O (3.5 mL) to give the product as a colourless oil, which was taken through to the next step. **Yield**: 95% (9.52 mmol).

Synthesis of (*E*)-cyclopropyl(phenyl)methanone oxime

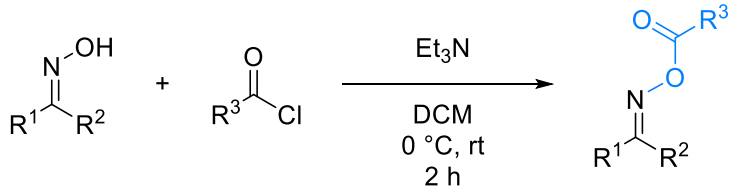


Following GPC, the reaction was carried out with cyclopropyl(phenyl)methanone (5.00 mmol, 1 equiv.), sodium acetate (7.50 mmol, 1.5 equiv. and hydroxylamine hydrochloride (7.50 mmol, 1.5 equiv.) in EtOH (10 mL)/H_2O (2.5 mL) to give the product as a white solid, which was taken through to the next step. **Yield**: 100%, (5.00 mmol)

3.3 Synthesis of Oxime Esters

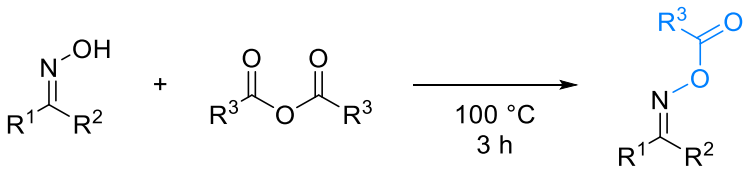
General Procedure for Synthesis of Oxime Esters

General procedure D (GPD) [4]



In a round bottom flask, equipped with a magnetic stirring bar, the corresponding oxime (1 equiv.) and triethylamine (1.5 equiv.) were dissolved in DCM (0.5 mol/L), the resulting mixture was cooled to 0 °C and then corresponding acid chloride (1.5 equiv.) was added. The reaction mixture was stirred for 2 h and then quenched with HCl (1 M) and extracted with DCM (3x volumes of solvent). The combined organic phases were dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. The crude product was purified via column chromatography on silica with pentane/EtOAc eluent mixture.

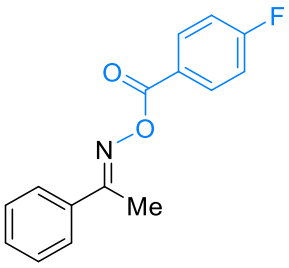
General procedure E (GPE) [5]



Corresponding oxime (1 equiv.) and acid anhydride (2 equiv.) were added into a round bottom flask, equipped with a magnetic stirring bar and a reflux condenser. The resulting mixture was stirred at 100 °C for 3 h and then cooled down to rt. Then EtOAc was added and the organic phase was washed with water (1x 20 mL) and

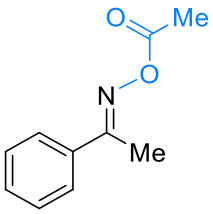
brine (1x 20 mL). The organic phase was dried over Na_2SO_4 and after filtration, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica with pentane/EtOAc eluent mixture.

Synthesis of (*E*)-1-phenylethan-1-one O-(4-fluorobenzoyl) oxime (1a)



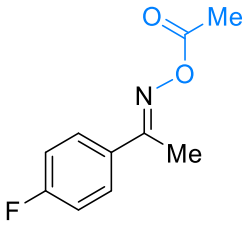
Following **GPD**, the reaction was carried out employing (*E*)-1-phenylethan-1-one oxime (20.0 mmol, 1 equiv.), 4-fluorobenzoyl chloride (30.0 mmol, 1.5 equiv.) and triethylamine (30.0 mmol, 1.5 equiv.) in DCM (40 mL). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a white solid. **Yield**: 71% (14.19 mmol). **R_f** (pentane/EtOAc, 9:1): 0.50. **m.p.** 118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.18 – 8.13 (m, 2H), 7.85 – 7.80 (m, 2H), 7.50 – 7.40 (m, 3H), 7.21 – 7.14 (m, 2H), 2.52 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] = −105.2. **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 163.7, 134.7, 132.3, 132.1, 130.7, 128.6, 127.1, 116.0, 115.7, 14.7. **HRMS** (EI+) Calcd.: $C_{15}H_{12}FNO_2$ $[M]^+$ = 257.0852; Found: $[M]^+$ = 257.0841.

Synthesis of (*E*)-1-phenylethan-1-one O-acetyl oxime (3a)



Following **GPE**, the reaction was carried out using (*E*)-1-phenylethan-1-one oxime (15.0 mmol, 1 equiv.) and acetic anhydride (30.0 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a white solid. **Yield**: 73% (11.0 mmol). **R_f** (pentane/EtOAc, 9:1): 0.58. **m.p.**: 57 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.77 – 7.71 (m, 2H), 7.47 – 7.37 (m, 3H), 2.39 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 169.0, 162.4, 134.8, 130.6, 128.6, 127.0, 77.3, 77.0, 76.7, 22.2, 19.9, 14.4. **HRMS** (EI+) Calcd.: $C_{10}H_{11}NO_2$ $[M]^+$ = 117.0790; Found: $[M]^+$ = 177.0785. Data consistent with the literature. [6]

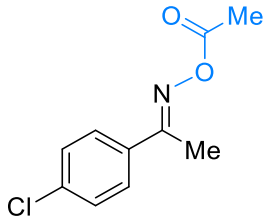
Synthesis of (*E*)-1-(4-fluorophenyl)ethan-1-one O-acetyl oxime (3b)



Following **GPE**, the reaction was carried out using (*E*)-1-(4-fluorophenyl)ethan-1-one oxime (8.0 mmol, 1 equiv.) and acetic anhydride (16.0 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a white solid. **Yield**: 90%

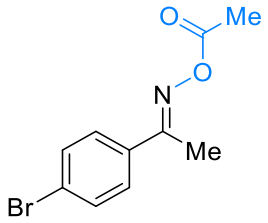
(7.20 mmol). **R_f** (pentane/EtOAc, 9:1): 0.32. **m.p.**: 37 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.78 – 7.72 (m, 2H), 7.12 – 7.06 (m, 2H), 2.37 (s, 3H), 2.27 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] = -110.2. **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 168.7, 165.5, 163.0, 161.4, 131.0 (d, *J* = 3.3 Hz), 129.0 (d, *J* = 8.6 Hz), 115.7, 115.5, 19.8, 14.3. **HRMS** (EI+) Calcd.: $C_{10}H_{10}FNO_2$ $[M]^+$ = 195.0696; Found: $[M]^+$ = 195.0690. Data consistent with the literature. [7]

Synthesis of (*E*)-1-(4-chlorophenyl)ethan-1-one O-acetyl oxime (3c)



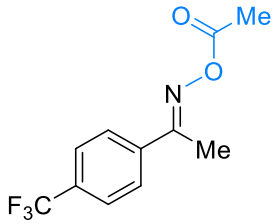
Following **GPE**, the reaction was carried out using (*E*)-1-(4-chlorophenyl)ethan-1-one oxime (9.0 mmol, 1 equiv.) and acetic anhydride (18.0 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a white solid. **Yield**: 84% (7.61 mmol). **R_f** (pentane/EtOAc, 9:1): 0.32. **m.p.**: 95 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.72 – 7.65 (m, 2H), 7.40 – 7.33 (m, 2H), 2.36 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 168.7, 161.3, 136.8, 133.3, 128.8, 128.3, 19.8, 14.2. **HRMS** (EI+) Calcd.: $C_{10}H_{10}ClNO_2$ $[M]^+$ = 211.0400; Found: $[M]^+$ = 211.0399. Data consistent with the literature. [8]

Synthesis of (*E*)-1-(4-bromophenyl)ethan-1-one O-acetyl oxime (3d)



Following **GPE**, the reaction was carried out using (*E*)-1-(4-bromophenyl)ethan-1-one oxime (8.0 mmol, 1 equiv.) and acetic anhydride (16.0 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a pale orange solid. **Yield**: 81% (6.55 mmol). **R_f** (pentane/EtOAc, 9:1): 0.32. **m.p.**: 97 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.65 – 7.59 (m, 2H), 7.57 – 7.51 (m, 2H), 2.36 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ [ppm] = 259.7, 168.7, 161.4, 133.7, 131.8, 128.5, 125.2, 19.8, 14.2. **HRMS** (EI+) Calcd.: $C_{10}H_{10}ClNO_2$ $[M]^+$ = 254.9895; Found: $[M]^+$ = 254.9895. Data consistent with literature. [9]

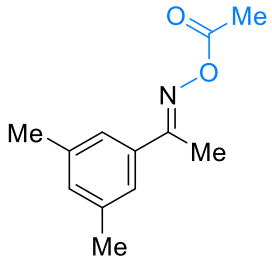
Synthesis of (*E*)-1-(4-(trifluoromethyl)phenyl)ethan-1-one O-acetyl oxime (3e)



Following **GPE**, the reaction was carried out using (*E*)-1-(4-(trifluoromethyl)phenyl)ethan-1-one oxime (9.60 mmol 1 equiv.) and acetic anhydride (19.20 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a white

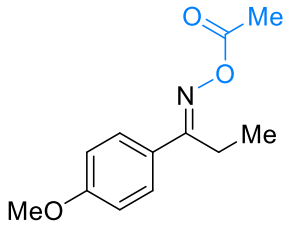
solid. **Yield**: 80% (7.74 mmol). **R_f** (pentane/EtOAc, 9:1): 0.32. **m.p.**: 43 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.87 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 2.41 (s, 3H), 2.28 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] = −63.4. **^{13}C-NMR** (100 MHz, $CDCl_3$, 25 °C): δ [ppm] = 168.6, 161.2, 138.3, 132.3 (q, *J* = 30.4 Hz), 127.4, 125.5 (q, *J* = 3.8 Hz), 125.2, 122.4, 19.7, 14.3. **HRMS** (EI+) Calcd.: $C_{11}H_{10}F_3NO_2$ $[M]^+$ = 245.0664; Found: $[M]^+$ = 245.0674. Data consistent with literature. [9]

Synthesis of (*E*)-1-(3,5-dimethylphenyl)ethan-1-one O-acetyl oxime (3f)



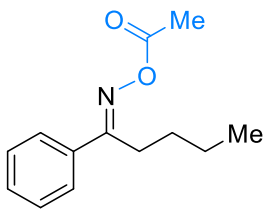
Following **GPE**, the reaction was carried out using (*E*)-1-(3,5-dimethylphenyl)ethan-1-one oxime (3.87 mmol, 1 equiv.) and acetic anhydride (7.74 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a white solid. **Yield**: 71% (2.77 mmol). **R_f** (pentane/EtOAc, 9:1): 0.43. **m.p.**: 107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.34 (s, 2H), 7.08 (s, 1H), 2.36 (s, 3H), 2.34 (s, 6H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 169.0, 162.9, 138.2, 134.7, 132.3, 124.8, 21.3, 19.9, 14.6. **HRMS** (EI+) Calcd.: $C_{12}H_{15}NO_2$ $[M]^+$ = 205.1103; Found: $[M]^+$ = 205.1096.

Synthesis of (*E*)-1-(4-methoxyphenyl)propan-1-one O-acetyl oxime (3g)



Following **GPE**, the reaction was carried out using (*E*)-1-(4-methoxyphenyl)propan-1-one oxime (7.03 mmol, 1 equiv.) and acetic anhydride (14.06 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 7:3 pentane/EtOAc as eluent mixture to give the desired product as a colourless oil. **Yield**: 67% (5.95 mmol). **R_f** (pentane/EtOAc, 7:3) 0.49. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.73 – 7.65 (m, 2H), 6.96 – 6.88 (m, 2H), 3.84 (d, *J* = 3.2 Hz, 3H), 2.82 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 1.18 (t, J = 7.6 Hz, 3H. **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 169.3, 166.8, 161.5, 128.8, 126.0, 114.0, 55.4, 21.50, 19.9, 11.4. **HRMS** (EI+) Calcd.: $C_{12}H_{15}NO_3$ $[M]^+$ = 221.1052; Found: $[M]^+$ = 221.1045.

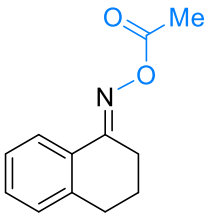
Synthesis of (*E*)-1-phenylpentan-1-one O-acetyl oxime (3h)



Following **GPE**, the reaction was carried out using (*E*)-1-phenylpentan-1-one oxime (3.99 mmol, 1 equiv.) and acetic anhydride (7.99 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a yellow oil. **Yield**: 21% (0.86 mmol).

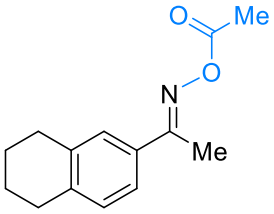
R_f (pentane/EtOAc, 9:1): 0.38. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.64 – 7.52 (m, 2H), 7.34 – 7.19 (m, 3H), 2.76 – 2.62 (m, 2H), 2.11 (s, 3H), 1.46 – 1.33 (m, 2H), 1.25 (dq, *J* = 14.1, 7.0 Hz, 2H), 0.84 – 0.68 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 169.0, 166.4, 134.0, 130.4, 128.8, 127.1, 126.3, 28.7, 27.8, 22.6, 19.8, 13.6. **HRMS** (ESI+) Calcd.: $C_{13}H_{18}NO_2$ $[M+H]^+$ = 220.1338; found $[M+H]^+$ = 220.1330.

Synthesis of (*E*)-3,4-dihydronaphthalen-1(2*H*)-one O-acetyl oxime (3i)



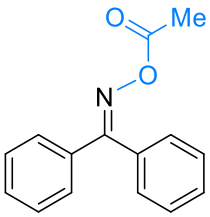
Following **GPE**, the reaction was carried out using (*E*)-3,4-dihydronaphthalen-1(2*H*)-one oxime (8.81 mmol, 1 equiv.) and acetic anhydride (17.62 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a white solid. **Yield**: 67% (5.95 mmol). **R_f** (pentane/EtOAc, 9:1): 0.51. **m.p.**: 150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.14 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.34 (td, *J* = 7.4, 1.4 Hz, 1H), 7.28 – 7.14 (m, 2H), 2.92 – 2.83 (m, 2H), 2.83 – 2.75 (m, 2H), 2.27 (s, 3H), 1.95 – 1.84 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 169.3, 161.3, 140.9, 130.7, 128.8, 126.6, 125.6, 118.1, 29.5, 25.6, 21.3, 19.9. **HRMS** (EI+) Calcd.: $C_{12}H_{13}NO_2$ $[M]^+$ = 203.0946; Found: $[M]^+$ = 203.0937. Data consistent with literature. [9]

Synthesis of (*E*)-1-(5,6,7,8-tetrahydronaphthalen-2-yl)ethan-1-one O-acetyl oxime (3j)



Following **GPE**, the reaction was carried out using (*E*)-1-(5,6,7,8-tetrahydronaphthalen-2-yl)ethan-1-one oxime (2.57 mmol, 1 equiv.) and acetic anhydride (5.15 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a white solid. **Yield**: 45% (1.16 mmol). **R_f** (pentane/EtOAc, 9:1): 0.31. **m.p.**: 69-72 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.44 (dd, J = 10.5, 2.6 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 1H), 2.78 (d, *J* = 3.7 Hz, 4H), 2.35 (s, 3H), 2.26 (s, 3H), 1.85 – 1.71 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 169.3, 162.8, 140.4, 137.6, 132.1, 129.5, 127.8, 124.2, 29.5, 23.2, 20.0, 14.5. **HRMS** (ESI+) Calcd.: $C_{14}H_{18}NO_2$ $[M+H]^+$ = 232.1338; Found: $[M+H]^+$ = 232.1329.

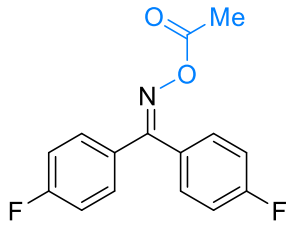
Synthesis of diphenylmethanone O-acetyl oxime (3k)



Following **GPE**, the reaction was carried out using diphenylmethanone oxime (8.00 mmol 1 equiv.) and acetic anhydride (16.00 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent to give the desired product as a white solid. **Yield**: 76% (6.12 mmol). **R_f**

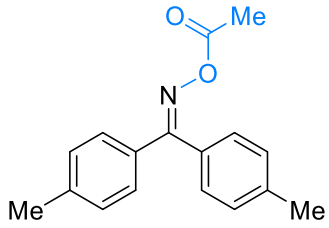
(pentane/EtOAc, 9:1): 0.4. **m.p.**: 103 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.57 (m, 2H), 7.45 (m, 4H), 7.40 – 7.30 (m, 4H), 2.11 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 168.8, 164.7, 134.8, 132.6, 130.9, 129.6, 129.0, 128.8, 128.4, 128.2, 19.7. **HRMS** (EI+) Calcd.: $C_{15}H_{13}NO_2$ $[M]^+$ = 239.0946; Found: $[M]^+$ = 239.0935. Data consistent with literature. [9]

Synthesis of bis(4-fluorophenyl)methanone O-acetyl oxime (3l)



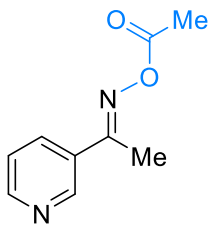
Following **GPE**, the reaction was carried out using bis(4-fluorophenyl)methanone oxime (3.92 mmol, 1 equiv.) and acetic anhydride (7.84 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a white solid. **Yield**: 95% (3.74 mmol). **R_f** (pentane/EtOAc, 9:1): 0.51. **m.p.**: 103 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.59 – 7.54 (m, 2H), 7.35 – 7.29 (m, 2H), 7.20 – 7.13 (m, 2H), 7.10 – 7.03 (m, 2H), 2.11 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] = −109.2, −110.3. **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 168.5, 166.2, 165.0, 162.8, 162.7, 161.7, 131.3 (d, *J* = 1.4 Hz), 131.1 (d, *J* = 1.4 Hz), 130.9 (d, *J* = 2.9 Hz), 128.2 (d, *J* = 3.6 Hz) , 115.9 (d, *J* = 6.6 Hz), 115.6 (d, *J* = 6.6 Hz), 19.6. **HRMS** (EI+) Calcd.: $C_{15}H_{11}F_2NO_2$ $[M]^+$ = 275.0758; Found: $[M]^+$ = 275.0755. Data consistent with literature. [10]

Synthesis of di-*p*-tolylmethanone O-acetyl oxime (3m)



Following **GPE**, the reaction was carried out using di-*p*-tolylmethanone oxime (8.93 mmol, 1 equiv.) and acetic anhydride (17.86 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 75:15 pentane/EtOAc as eluent mixture to give the desired product as a white solid. **Yield**: 57% (5.16 mmol). **R_f** (pentane/EtOAc, 90:10): 0.32. **m.p.**: 114-116 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.50 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.21 (m, 4H), 7.20 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H), 2.14 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ [ppm] = 169.1, 164.9, 141.3, 139.8, 132.3, 129.9, 129.2, 129.2, 129.1, 128.9, 21.6, 19.9. **HRMS** (ESI+) Calcd.: $C_{17}H_{18}NO_2$ $[M]^+$ = 268.1338; Found: $[M]^+$ = 268.1328.

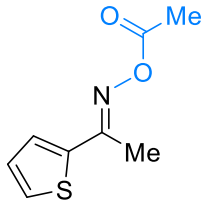
Synthesis of (*E*)-1-(pyridin-3-yl)ethan-1-one O-acetyl oxime (3n)



Following **GPE**, the reaction was carried out using bis (*E*)-1-(pyridin-3-yl)ethan-1-one oxime (4.0 mmol, 1 equiv.) and acetic anhydride (8.0 mmol, 2 equiv.). The crude product was purified by column chromatography

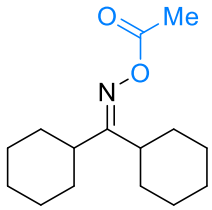
on silica with 1:1 pentane/EtOAc to 100% EtOAc as eluent mixture to give the desired product as a yellow oil. **Yield**: 68% (2.72 mmol). **R_f** (pentane/EtOAc, 1:1): 0.15. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.93 (d, *J* = 1.9 Hz, 1H), 8.73 – 8.64 (m, 1H), 8.11 – 8.06 (m, 1H), 7.39 – 7.31 (m, 1H), 2.41 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 168.6, 160.2, 151.5, 148.1, 134.3, 130.8, 123.4, 19.7, 14.2. **HRMS** (ESI+) Calcd.: $C_9H_{10}N_2O_2$ $[M]^+$ = 178.0742; Found: $[M]^+$ = 178.0738. Data consistent with literature. [6]

Synthesis of (*E*)-1-(thiophen-2-yl)ethan-1-one O-acetyl oxime (3o)



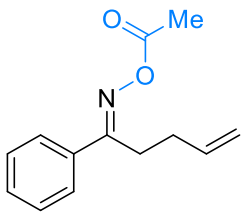
Following **GPE**, the reaction was carried out using (*E*)-1-(thiophen-2-yl)ethan-1-one oxime (2.90 mmol, 1 equiv.) and acetic anhydride (5.80 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as a white solid. **Yield**: 80% (2.32 mmol). **R_f** (pentane/EtOAc, 9:1): 0.32. **m.p.**: 128 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.67 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.57 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.34 (dd, *J* = 5.1, 2.9 Hz, 1H), 2.36 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ [ppm] = 169.0, 158.2, 136.8, 126.8, 126.4, 125.7, 19.9, 14.5. **HRMS** (EI+) Calcd.: $C_8H_9NO_2S$ $[M]^+$ = 183.0354; Found: $[M]^+$ = 183.0349. Data consistent with literature. [11]

Synthesis of €-1-cyclohexylethan-1-one O-acetyl oxime (3p)



Following **GPE**, the reaction was carried out using (*E*)-1-cyclohexylethan-1-one oxime (8.50 mmol, 1 equiv.) and acetic anhydride (17.00 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 95:15 to 90:10 pentane/EtOAc as eluent mixture to give the desired product as white solid. **Yield**: 95% (8..07 mmol). **R_f** (pentane/EtOAc, 9:1): 0.53. **m.p.**:44 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 2.79-2.68 (m, 1H), 2.37-2.26 (m, 1H), 2.16 (s, 3H), 1.83 – 1.52 (m, 12H), 1.53 – 1.10 (m, 8H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ [ppm] = 174.9, 169.5, 42.4, 30.3, 28.7, 26.3, 26.2, 26.0, 25.8, 20.1. **HRMS** (ESI+) Calcd.: $C_{10}H_{17}NO_2$ $[M+Na]^+$ = 274.1782; Found: $[M+Na]^+$ = 274.1785.

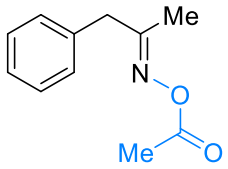
Synthesis of (*E*)-1-phenylpent-4-en-1-one O-acetyl oxime (3q)



Following **GPE**, the reaction was carried o€ut using (*E*)-1-phenylpent-4-en-1-one oxime (8.22 mmol, 1 equiv.) and acetic anhydride (16.44 mmol, 2 equiv.). The crude product was purified using column chromatography on silica with 90:10 pentane/EtOAc as eluent mixture to give the desired product as an orange oil. **Yield**: 71%

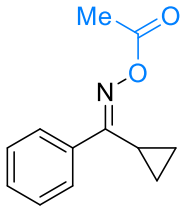
(14.19 mmol). **R_f** (pentane/EtOAc, 9:1): 0.22. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.73 – 7.68 (m, 2H), 7.48 – 7.36 (m, 3H), 5.83 (m, 1H), 5.04 (m, 2H), 2.97 – 2.91 (m, 2H), 2.37 – 2.28 (m, 2H), 2.26 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 169.1, 165.7, 136.5, 133.9, 130.6, 128.6, 127.3, 115.8, 30.7, 27.7, 19.9. **HRMS** (EI+) (m/z) exact mass calc. $[M]^+$ = 217.1103; found $[M]^+$ = 217.1102. **HRMS** (EI+) Calcd.: $C_{13}H_{16}NO_2$ $[M]^+$ = 217.1103; Found: $[M]^+$ = 217.1102. Data consistent with literature. [1]

Synthesis of 1-phenylpropan-2-one O-acetyl oxime (3r)



Following **GPD,** the reaction was carried out using 1-phenylpropan-2-one (9.52 mmol, 1 equiv.), triethylamine (19.04 mmol, 2 equiv.) and acid chloride (11.42 mmol, 1.2 equiv.) in DCM (40 mL). The crude product was purified using column chromatography on silica with 80:20 PE/EtOAc as eluent mixture to give the desired product as an orange oil. The product was obtained as an *E* and *Z* isomeric mixture. **Yield**: 71% (2.14 mmol). **R_f** (pentane/EtOAc, 8:2): 0.36. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.35 – 7.29 (m, 2H), 7.26 (m, 2H), 3.77 (s, 1H), 3.63 (s, 2H), 2.19 (s, 1H), 2.18 (s, 3H), 1.96 (s, 1H), 1.87 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 168.7, 165.2, 164.7, 135.5, 135.0, 129.2, 127.1, 41.9, 36.8, 20.0, 19.7, 15.1. **HRMS** (EI+) Calcd.: $C_{11}H_{14}NO_2$ $[M]^+$ = 191.0946; Found: $[M]^+$ = 191.0937. Data consistent with literature.[12a]

Synthesis of (E)-cyclopropyl(phenyl)methanone O-acetyl oxime (3s)

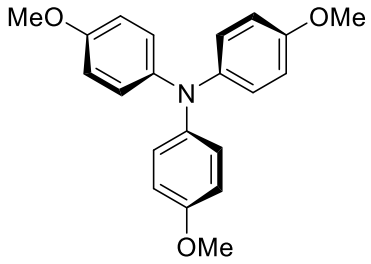


Following **GPE**, the reaction was carried out using (E)-cyclopropyl(phenyl)methanone oxime (5.00 mmol, 1 equiv.) and acetic anhydride (10.00 mmol, 2 equiv.). The crude product was purified by column chromatography on silica with 9:1 pentane/EtOAc as eluent mixture to give the desired product as colorless liquid and as mixture of *E*- and *Z*- isomers. **Yield**: 67% (3.35 mmol). **R_f** (pentane/EtOAc, 8:2): 0.37. **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.42-7.28 (m, 4H), 7.25-7.18 (m, 1H), 2.36 (m, 0.58 H), 2.21 (s, 1.71H), 1.96-1.86 (m, 0.48H), 1.91 (s, 2Hx0.66), 0.92-0.93 (m, 1.18H), 0.93-0.80 (m, 1.71H), 0.70-0.62 (m, 1.13H) **^{13}C NMR** 169.12, 168.9, 168.8, 168.5, 132.2, 131.8, 129.4, 129.1, 128.7, 128.1, 128.0, 127.0, 19.7, 19.4, 15.6, 10.7, 6.4, 6.3. **HRMS** (EI+) Calcd.: $C_{12}H_{13}NO_2$ $[M]^+$ = 203.0946; Found: $[M]^+$ = 203.0942. Data consistent with literature.[12b]

3.4 Synthesis of Photocatalysts

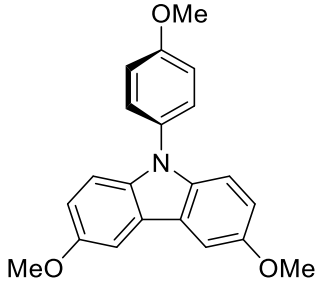
Photocatalysts **TX**, **PTZ**, **Ir(ppy)$_3$**, **TBPA**, ***p*OMe-TPA** and **Phenox-1** were purchased commercially. **Phenox-2** and **Phenthia-1** were prepared as per a previous report from our group (see main manuscript, Ref. 19c)

Synthesis of tris(4-methoxyphenyl)amine (T*p*AA)



To a dried three-necked flask equipped with a reflux condenser and a magnetic stirring bar were added 1-iodo-4-methoxybenzene (23.55 mmol, 3 equiv.), 4-methoxyaniline (7.85 mmol, 1 equiv.), CuI (0.39 mmol, 0.05 equiv.), *t*-BuOK (23.55 mmol, 3 equiv.), and anhydrous toluene (23 mL) under a nitrogen atmosphere. The resulting mixture was stirred overnight at 135 °C. The mixture was cooled to room temperature and filtered over silica plug with EtOAc. The organic phase was washed with H_2O (70 mL x 2) and brine (70 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the crude product was purified by column chromatography with 97.5:2.5 petroleum ether/EtOAc to give the desired product as a pale yellow microcrystalline solid. **Yield**: 72% (5.69 mmol). **M.p.**: 95-97°C. **R_f** (Petroleum ether/EtOAc 97.5:2.5): 0.30. **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 7.14 – 7.05 (m, 6H), 6.78 – 6.69 (m, 6H), 3.32 (s, 9H). **^{13}C NMR** (101 MHz, C_6D_6): δ [ppm] = 155.73, 142.67, 125.38, 115.06, 55.07. **HRMS** (EI+) Calcd.: $C_{21}H_{21}NO_3$ $[M]^+$ = 335.4030; Found: $[M]^+$ = 335.1510. Data consistent with literature. [13]

Synthesis of 3,6-dimethoxy-9-(4-methoxyphenyl)-9H-carbazole (CabZ)



Tris(4-methoxyphenyl)amine **T*p*AA** (1.2 mmol, 1 equiv.) and K_2CO_3 (3.6 mmol, 3 equiv.) were dissolved in MeCN (12 mL) in a 250 mL round bottom flask. The mixture was stirred for 21 h under irradiation with a 405 nm LED. Then H_2O (20 mL) was added and the aqueous phase was extracted with DCM (20 mL x 3). The organic phase was dried over Na_2SO_4 and the solvent was removed after filtration. The product was purified using column chromatography with 97.5:2.5 Petroleum ether/EtOAc as eluent mixture. The desired product was obtained as a brown oil. **Yield**: 24% (284.9 µmol). **R_f** Petroleum ether/EtOAc (95/5): 0.16. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.5 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 7.12 – 7.01 (m, 4H), 3.95 (s, 6H), 3.91 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.64, 153.94, 136.96, 130.90, 128.33, 123.35, 115.28, 115.11, 110.71, 102.94, 56.27, 55.72. **HRMS** (EI+) Calcd.: $C_{21}H_{19}NO_3$ $[M]^+$ = 333.1365; Found: $[M]^+$ = 333.1366. Data is consistent with literature. [14]

4 Optimization of Reaction Conditions

4.1 Screening of Catalysts for Azine Synthesis

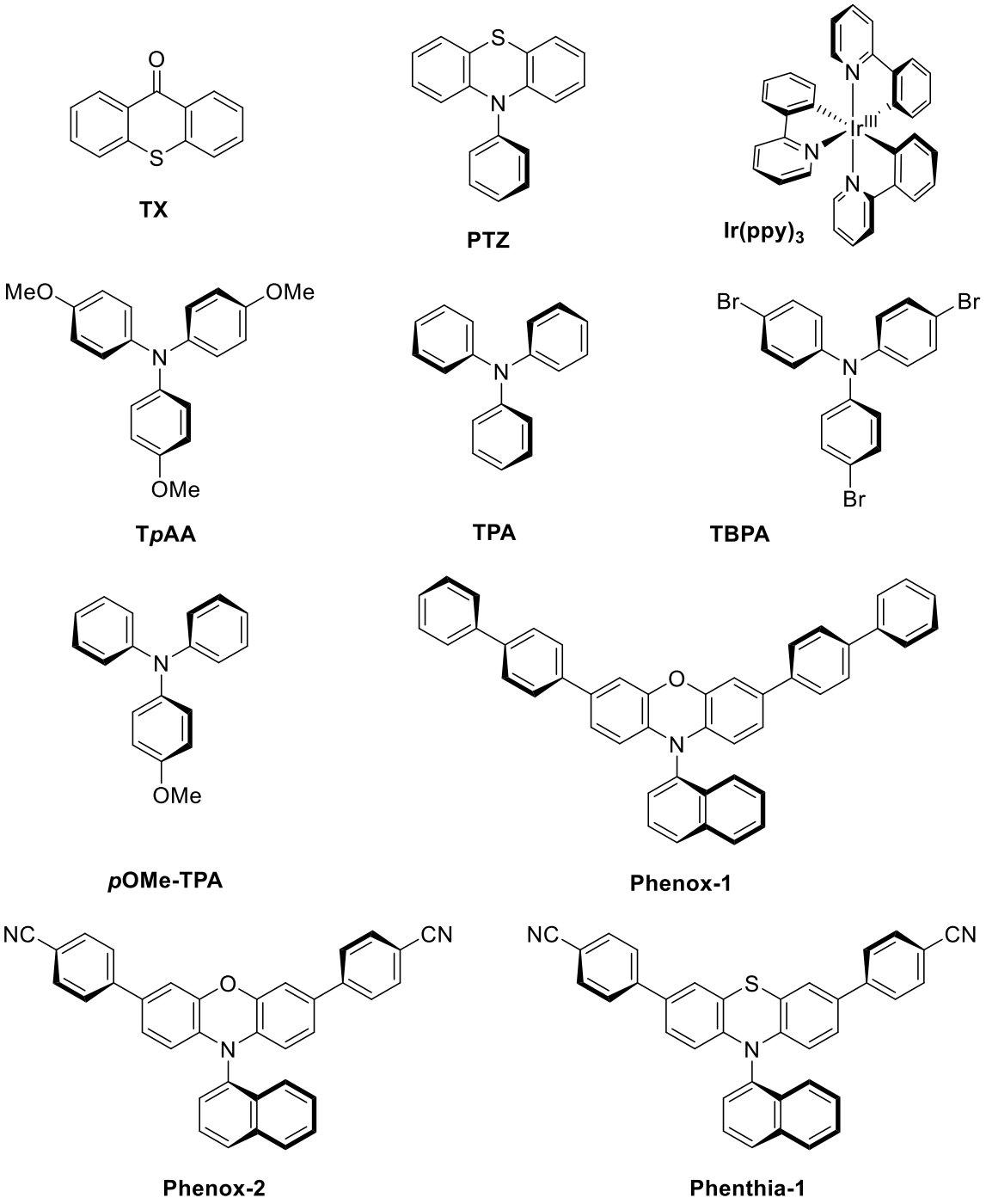
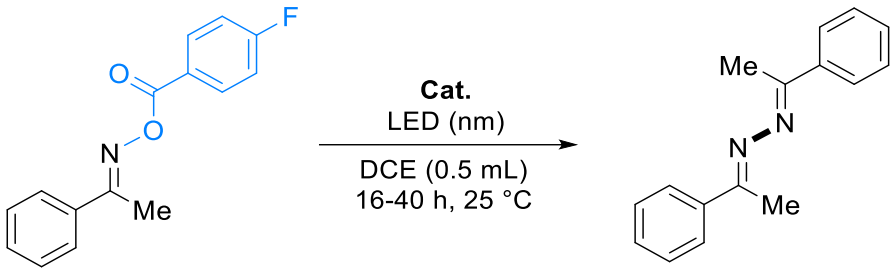


Figure S2. Catalysts employed for the Screening of Catalysts for the formation of azine **2a**

Table S1. Screening of different catalysts



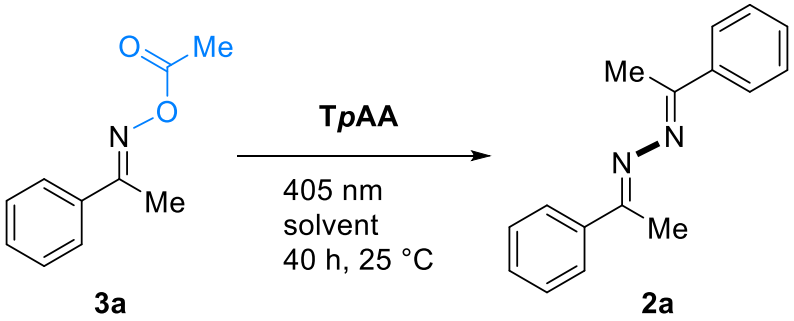
1a **2a**

Entry	Catalyst (mol%)	Reaction time (h)	Wavelength (nm)	Yield of 2a (%)	Conversion of 1a (%)
1	–	40	395	20	50
2	**TX** (5)	16	405	10	100
3	**TX** (5)	16	395	24	100
4	**Ir(ppy)$_3$** (2)	40	450	16	45
5	**PTZ** (10)	40	405	22	68
6	**T*p*AA** (5)	40	405	45	86
7	**T*p*AA** (20)	40	405	59	98
8	**TPA** (20)	40	405	6	50
9	**TBPA** (20)	40	405	5	81
10	***p*OMe-TPA** (20)	40	405	16	50
11	**Phenox-1** (5)	40	450	26	81
12	**Phenox-2** (5)	40	450	37	96
13	**Phenthia-1** (5)	40	405	1	83

All reactions were carried out on a 0.1 mmol scale in dry DCE (0.5 mL) and under nitrogen atmosphere. Conversions/yields determined by ^{1}H NMR of the reaction mixture with CH_2Br_2 as internal standard.

4.2 Screening of Solvents for Azine Synthesis

Table S2. Screening of different solvents

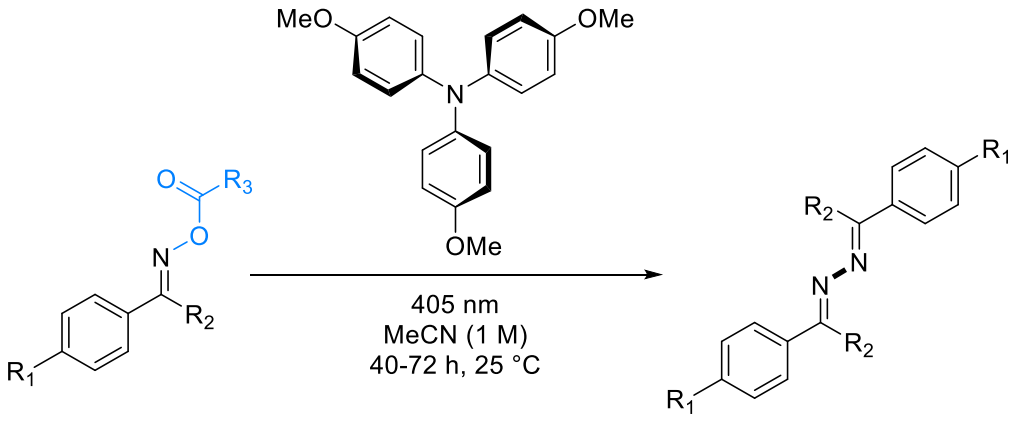


Entry	TpAA (mol%)	Solvent ([M] of 3a)	NMR Yield of 2a (%)	Conversion of 3a (%)[a]
1	20	DCE (0.2)	50	91
2	20	DCE (0.1)	56	90
3	20	DCE (0.07)	52	95
4	20	DCE (0.05)	46	94
5	10	DCE (0.1)	49	76
6	30	DCE (0.1)	58	100
7	20	MeCN (0.2)	68	98
8	20	MeCN (0.1)	86	100
9	20	MeCN (0.07)	76	99
10	20	MeCN (0.05)	81	100
11	10	MeCN (0.1)	65	93
12	15	MeCN (0.1)	74	97
13	25	MeCN (0.1)	75	99
14	–	MeCN (0.1)	–	19
15[b]	20	MeCN (0.1)	23	100
16[c]	20	MeCN (0.1)	2	100
17	20	DMC (0.1)	51	100
18	20	PhMe	48	100
19	20	THF	29	100
20	20	DMA	30	100

[a]All reactions were carried out with (*E*)-1-phenylethan-1-one O-acetyl oxime **3a** (0.1 mmol, 1 equiv.) under irradiation with a 405 nm LED for 40 h. After completion, the solvent was removed under reduced pressure and conversions/yields determined by ^{1}H NMR of the reaction mixture with CH_2Br_2 as internal standard.. [b]Addition of 1 equiv. of TEMPO. [c]Addition of 2 equiv. of TEMPO.

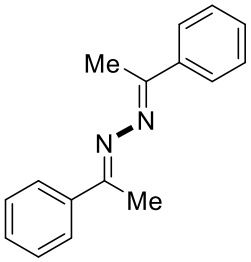
5 PHOTOCATALYTIC REACTIONS TO AZINES

General procedures for photoreactions



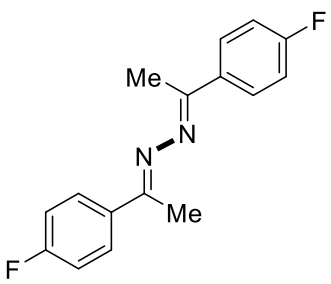
General procedure F (GPF): All solid reactants were added into an oven dried crimp cap vial equipped with a magnetic stirring bar and the vial was capped. Using a high vacuum pump, the vial was evacuated for 2 min and then refilled with N_2. This was repeated for 4 times and the dry solvent was added using a syringe. Then the reaction was put into a cooling mantle on top of a LED and the reaction was stirred under cooling, while irradiating with a LED.

Synthesis of (1*E*,2*E*)-1,2-bis(1-phenylethylidene)hydrazine (2a)



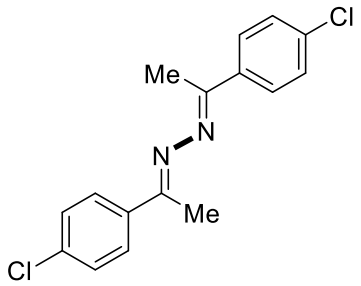
Following **GPF**, the reaction was carried out with **3a** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 9:1 PE/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 80% (39.9 µmol). **R_f** (PE/EtOAc, 9:1): 0.69. **m.p.**: 123 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.96 – 7.90 (m, 4H), 7.48 – 7.40 (m, 6H), 2.34 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 157.7, 138.5, 129.6, 128.34, 126.6, 29.8, 15.0. **HRMS** (ESI) (m/z): exact mass calc. $[M+H]^+$ = 237.1392; found $[M+H]^+$ = 237.1390. **HRMS** (ESI+) Calcd.: $C_{16}H_{17}N_2$ $[M+H]^+$ = 237.1392; Found: $[M+H]^+$ = 237.1390. Data consistent with the literature. [15]

Synthesis of (1*E*,2*E*)-1,2-bis(1-(4-fluorophenyl)ethylidene)hydrazine (2b)



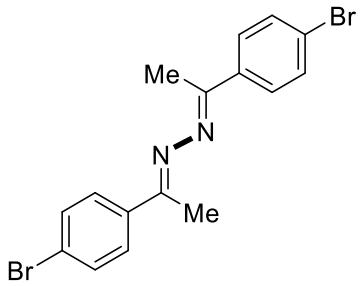
Following **GPF**, the reaction was carried out with **3b** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 9:1 PE/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 70% (34.9 µmol). **R_f** (PE/EtOAc, 9:1: 0.65. **m.p.**: 128 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.99 – 7.86 (m, 4H), 7.17 – 7.07 (m, 4H), 2.33 (s, 6H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ [ppm] = −111.9. **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 165.0, 162.6, 157.4, 134.6 (d, *J* = 3.2 Hz), 128.6 (d, *J* = 8.4 Hz), 115.4115.2, 15.0. **HRMS** (ESI+) Calcd.: $C_{16}H_{15}F_2N_2$ $[M+H]^+$ = 273.1203; Found: $[M+H]^+$ = 273.1201. Data consistent with the literature. [15]

Synthesis of (1E,2E)-1,2-bis(1-(4-chlorophenyl)ethylidene)hydrazine (2c)



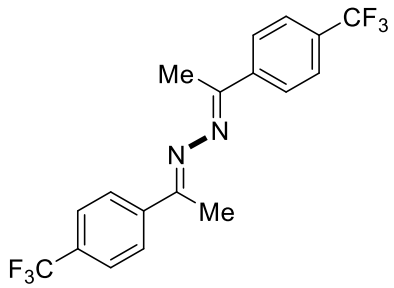
Following **GPF**, the reaction was carried out with **3c** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 9:1 PE/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 77% (38.7 µmol). **R_f** (PE/EtOAc, 9:1): 0.65. **m.p.**: 155 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.88 – 7.83 (m, 4H), 7.42 – 7.37 (m, 4H), 2.31 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 157.3, 136.7, 135.8, 128.6, 128.2, 127.9, 14.9. **HRMS** (ESI+) Calcd.: $C_{16}H_{15}Cl_2N_2$ $[M+H]^+$ = 305.0612; Found: $[M+H]^+$ = 305.0628. Data consistent with the literature. [15]

Synthesis of (1*E*,2*E*)-1,2-bis(1-(4-bromophenyl)ethylidene)hydrazine (2d)



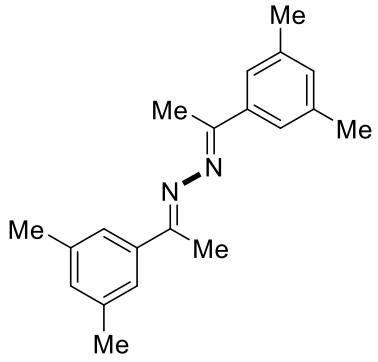
Following **GPF**, the reaction was carried out with **3d** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 9:1 PE/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 43% (21.3 µmol). **R_f** (PE/EtOAc, 9:1): 0.63. **m.p.**: 160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.81 – 7.75 (m, 4H), 7.59 – 7.52 (m, 4H), 2.29 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 157.3, 137.1, 131.5, 128.2, 124.2, 14.9. **HRMS** (ESI+) Calcd.: $C_{16}H_{15}Br_2N_2$ $[M+H]^+$ = 392.9602; Found: $[M+H]^+$ = 392.9601. Data consistent with the literature. [15]

Synthesis of (1*E*,2*E*)-1,2-bis(1-(4-(trifluoromethyl)phenyl)ethylidene)hydrazine (2e)



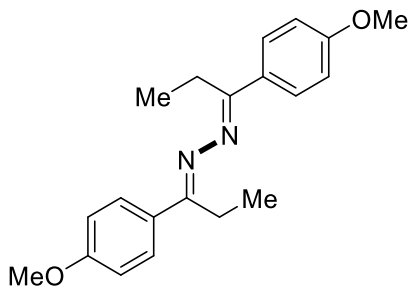
Following **GPF**, the reaction was carried out with **3i** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 9:1 Pe/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 71% (35.8 µmol). **R_f** (Pe/EtOAc, 9:1): 0.72. **m.p.**: 124 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C): δ [ppm] = 8.03 (d, *J* = 8.2 Hz, 4H), 7.69 (d, *J* = 8.3 Hz, 4H), 2.34 (s, 6H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ [ppm] = −63.2. **^{13}C NMR** (101 MHz, $CDCl_3$, 25 °C): δ [ppm] = 156.9, 141.4, 141.3, 131.5 (q, *J* = 29.6), 126.9, 125.4 (q, *J* = 3.7 Hz), 122.7, 15.1. **HRMS** (ESI+) Calcd.: $C_{18}H_{15}F_6N_2$ $[M+H]^+$ = 373.1139; Found: $[M+H]^+$ = 373.1135. Data consistent with the literature. [16]

Synthesis of (1E,2E)-1,2-bis(1-(3,5-dimethylphenyl)ethylidene)hydrazine (2f)



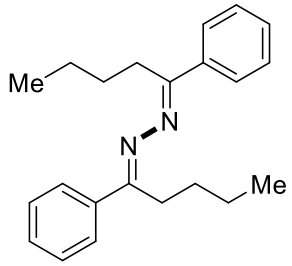
Following **GPF**, the reaction was carried out with **3f** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 9:1 PE/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 45% (22.50 µmol). **R_f** (PE/EtOAc (9:1): 0.62. **m.p.**: 136 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.52 (s, 4H), 7.07 (s, 2H), 2.38 (s, 12H), 2.28 (s, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] = 157.4, 138.5, 137.9, 131.3, 124.4, 21.4, 15.3. **HRMS** (ESI+) Calcd.: $C_{20}H_{25}N_2$ $[M+H]^+$ = 293.2018; Found: $[M+H]^+$ = 293.2016.

Synthesis of (1*E*,2*E*)-1,2-bis(1-(4-methoxyphenyl)propylidene)hydrazine (2g)



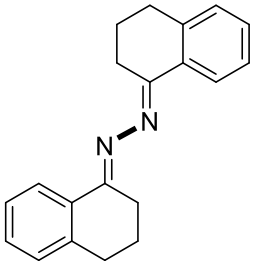
Following **GPF**, the reaction was carried out with **3g** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 9:1 PE/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 62% (30.82 µmol). **R_f** (PE/EtOAc, 8:2): 0.64. **m.p.**: 134 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.90 – 7.85 (m, 4H), 6.97 – 6.92 (m, 4H), 3.86 (s, 6H), 2.89 (q, J = 7.6 Hz, 4H), 1.15 – 1.08 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 162.9, 160.7, 130.2, 128.3, 113.7, 55.3, 21.7, 11.6. **HRMS** (ESI+) Calcd.: $C_{20}H_{15}N_2O_2$ $[M+H]^+$ = 325.1916; Found: $[M+H]^+$ = 325.1912.

Synthesis of (1*E*,2*E*)-1,2-bis(1-phenylpentylidene)hydrazine (2h)



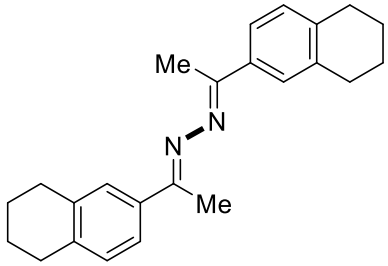
Following **GPF**, the reaction was carried out with **3h** (0.10 mmol, 1 equiv., 75% purity) and **T*p*AA** (0.02 mmol, 0.2 equiv.). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 99:1 PE/EtOAc as eluent mixture to give the desired product as a yellow oil. **Yield**: 80% (0.04 mmol). **R_f** (PE/EtOAc, 99:1): 0.07. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.90 (m, 4H), 7.47 – 7.39 (m, 6H), 2.94 – 2.88 (m, 4H), 1.57 – 1.47 (m, 4H), 1.38 (m, 4H) 0.89 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 162.7, 137.8, 129.5, 128.3, 126.9, 29.1, 28.4, 23.0, 13.9. **HRMS** (ESI+) Calcd.: $C_{22}H_{29}N_2$ $[M+H]^+$ = 321.2331; Found: $[M+H]^+$ = 321.2332.

Synthesis of 1,2-bis((E)-3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine (2i)



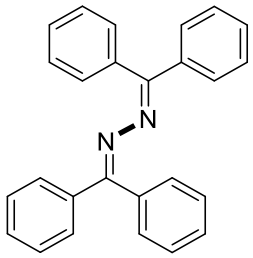
Following **GPF**, the reaction was carried out with **3i** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 17:3 PE/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 31% (15.6 µmol). **R_f** (PE/EtOAc, 17:3): 0.64. **m.p.**: 140 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.36 – 8.25 (m, 2H), 7.38 – 7.22 (m, 4H), 7.23 – 7.13 (m, 2H), 2.91 – 2.70 (m, 8H), 2.00 – 1.85 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 157.1, 140.5, 132.9, 129.5, 128.7, 126.3, 125.5, 29.9, 27.4, 22.1. **HRMS** (ESI+) Calcd.: $C_{20}H_{21}N_2$ $[M+H]^+$ = 289.1705; Found: $[M+H]^+$ = 289.1701. Data consistent with literature.[15]

Synthesis of (1*E*,2*E*)-1,2-bis(1-(5,6,7,8-tetrahydronaphthalen-2-yl)ethylidene)hydrazine (2j)



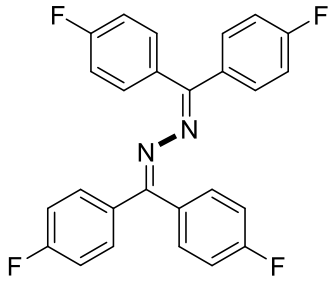
Following **GPF**, the reaction was carried out with **3j** (0.10 mmol, 1 equiv.) and **T*p*AA** (0.02 mmol, 0.2 equiv.). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 95:5 PE/EtOAc as eluent to give the product as a yellow solid. **Yield**: 80% (0.04 mmol). **R_f** (PE/EtOAc, 95:5): 0.47. **m.p.**: 102-104 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 C): δ [ppm] = 7.65 – 7.60 (m, 4H), 7.12 (d, *J* = 7.8 Hz, 2H), 2.87 – 2.76 (m, 8H), 2.28 (s, 6H), 1.87 – 1.78 (m, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 C): δ [ppm] = 157.4, 138.9, 136.9, 135.6, 128.9, 127.1, 123.6, 29.8, 29.1, 23.0, 22.9, 14.9. **HRMS** (ESI+) Calcd.: $C_{24}H_{29}N_2$ $[M+H]^+$ = 345.2331; Found: $[M+H]^+$ = 345.2332. Data consistent with literature.[17]

Synthesis of 1,2-bis(diphenylmethylene)hydrazine (2k)



Following **GPF**, the reaction was carried out with **3k** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 72 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 9:1 PE/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 43% (21.31 µmol). **R_f** (PE/EtOAc, 9:1): 0.65. **m.p.**: 160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.50 – 7.46 (m, 4H), 7.45 – 7.35 (m, 6H), 7.35 – 7.26 (m, 10H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 158.9, 138.2, 135.5, 129.6, 129.3, 128.6, 127.9. **HRMS** (ESI+) Calcd.: $C_{26}H_{21}N_2$ $[M+H]^+$ = 361.1705; Found: $[M+H]^+$ = 361.1707. Data consistent with literature. [18]

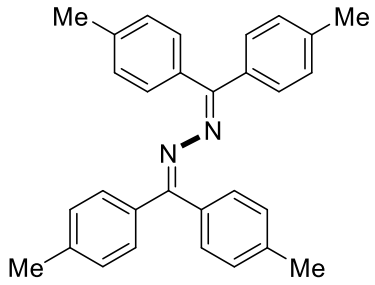
Synthesis of 1,2-bis(bis(4-fluorophenyl)methylene)hydrazine (2l)



Following **GPF**, the reaction was carried out with **3l** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 72 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 9:1 PE/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 40% (20.10 µmol). **R_f** (PE/EtOAc, 9:1): 0.62. **m.p.**: 184 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.51 – 7.43 (m, 4H), 7.36 – 7.28 (m, 4H), 7.16 – 7.08 (m, 4H), 7.04 – 6.96 (m, 4H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ [ppm] = −111.0, −111.8. **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 165.2, 164.0, 162.7, 161.6,

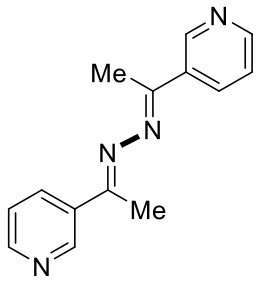
158.8, 134.0 (d, *J* = 3.1 Hz), 131.4 (d, *J* = 8.2 Hz), 131.1 (d, *J* = 3.6 Hz), 130.6 (d, *J* = 8.4 Hz), 115.3 (d, *J* = 14.7 Hz), 115.1 (d, *J* =15.7 Hz) . **HRMS** (ESI+) Calcd.: $C_{26}H_{17}F_4N_2$ $[M+H]^+$ = 433.1329; Found: $[M+H]^+$ = 433.1326. Data consistent with literature. [19]

Synthesis of 1,2-bis(di-*p*-tolylmethylene)hydrazine (2m)



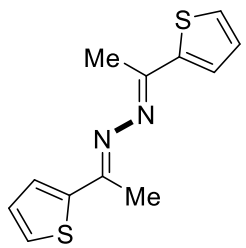
Following **GPF,** the reaction was carried out with **3m** (0.10 mmol, 1 equiv.) and **T*p*AA** (0.02 mmol, 0.2 equiv.). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 95:5 PE/EtOAc as eluent to give the desired product as a yellow solid. **Yield**: 80% (0.04 mmol). $\mathbf{R_f}$ (Pe/EtOAc, 95:5): 0.20. **m.p**: 186-188 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 C): δ [ppm] = 7.40 (m, 4H), 7.21 (m, 8H), 7.09 (m, 4H), 2.38 (s, 6H), 2.34 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 C): δ [ppm] = 159.0, 139.5, 138.5, 135.9, 132.7, 129.6, 128.8, 128.7, 128.4, 29.7, 21.4, 21.3. **HRMS** (ESI+) Calcd.: $C_{30}H_{29}N_2$ $[M+H]^+$ = 417.2324; Found: $[M+H]^+$ = 417.2344. Data consistent with literature.[20]

Synthesis of (1*E*,2*E*)-1,2-bis(1-(pyridin-3-yl)ethylidene)hydrazine (2n)



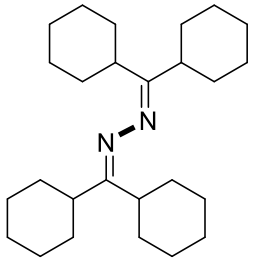
Following **GPF**, the reaction was carried out with **3n** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 50% (25.01 µmol). $\mathbf{R_f}$ (EtOAc): 0.05. **m.p.**: 104 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 9.10 (d, *J* = 1.8 Hz, 2H), 8.65 (dd, *J* = 4.8, 1.6 Hz, 2H), 8.25 – 8.17 (m, 2H), 7.42 – 7.32 (m, 2H), 2.35 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 156.8, 150.7, 148.2, 133.9, 133.6, 123.3, 14.9. **HRMS** (ESI+) Calcd.: $C_{14}H_{15}N_4$ $[M+H]^+$ = 239.1297; Found: $[M+H]^+$ = 239.1294. Data consistent with literature.[21]

Synthesis of (1*E*,2*E*)-1,2-bis(1-(thiophen-2-yl)ethylidene)hydrazine (2o)



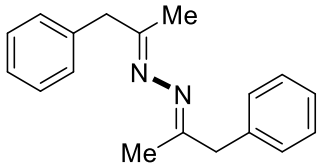
Following **GPF**, the reaction was carried out with **3o** (0.1 mmol, 1 equiv.) and **T*p*AA** (20.0 µmol, 0.2 equiv.) in dry MeCN (1 mL). The reaction mixture was irradiated for 40 h with a 405 nm LED. The crude product was purified by column chromatography on silica with 9:1 PE/EtOAc as eluent mixture to give the desired product as a yellow solid. **Yield**: 54% (26.98 µmol). **R_f** (PE/EtOAc, 9:1): 0.69. **m.p.**: 117 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.71 (dd, *J* = 5.1, 1.2 Hz, 2H), 7.64 (dd, *J* = 2.9, 1.2 Hz, 2H), 7.33 (dd, *J* = 5.1, 2.9 Hz, 2H), 2.33 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 155.2, 142.1, 126.2, 125.7, 125.0, 15.5. **HRMS** (ESI+) Calcd.: $C_{12}H_{13}N_2S_2$ $[M+H]^+$ = 249.0520; Found: $[M+H]^+$ = 249.0516. Data consistent with literature.[22]

Attempted synthesis of 1,2-bis(dicyclohexylmethylene)hydrazine (2p)



Following **GPF**, the reaction was carried out with **3p** (0.10 mmol) and **T*p*AA** (0.02 mmol, 0.2 equiv.). The reaction mixture was irradiated for 40 h with a 405 nm LED. No product was formed, 76% conversion of **3p** was observed.

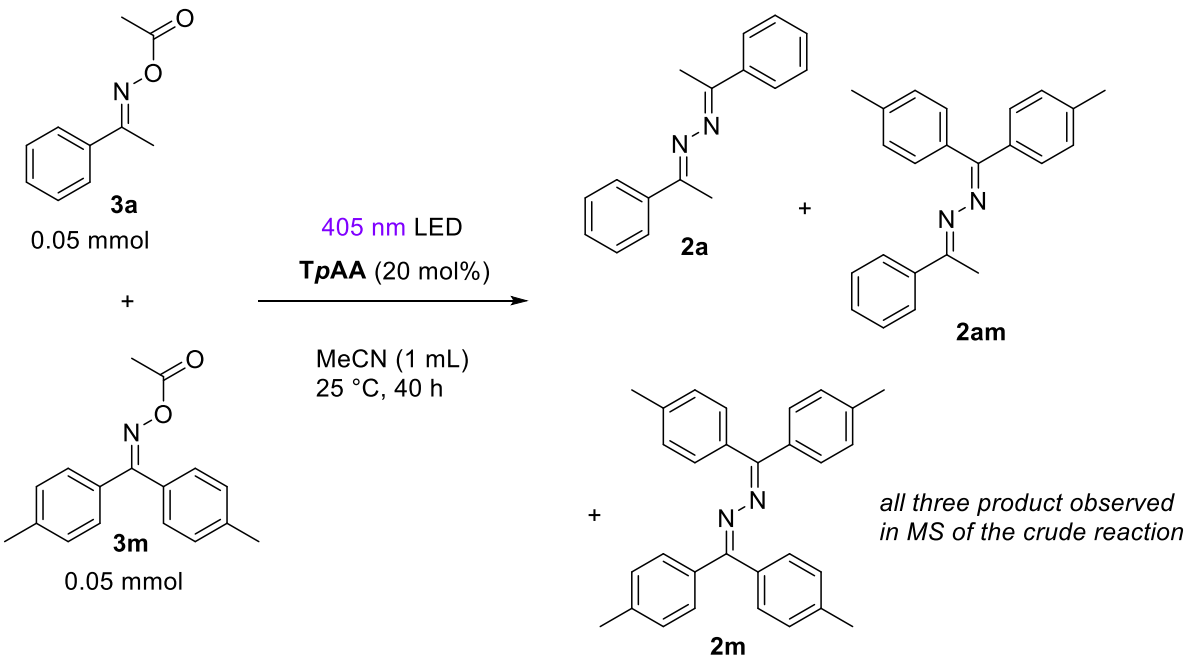
Attempted synthesis of (1*E*,2*E*)-1,2-bis(1-phenylpropan-2-ylidene)hydrazine (2r)

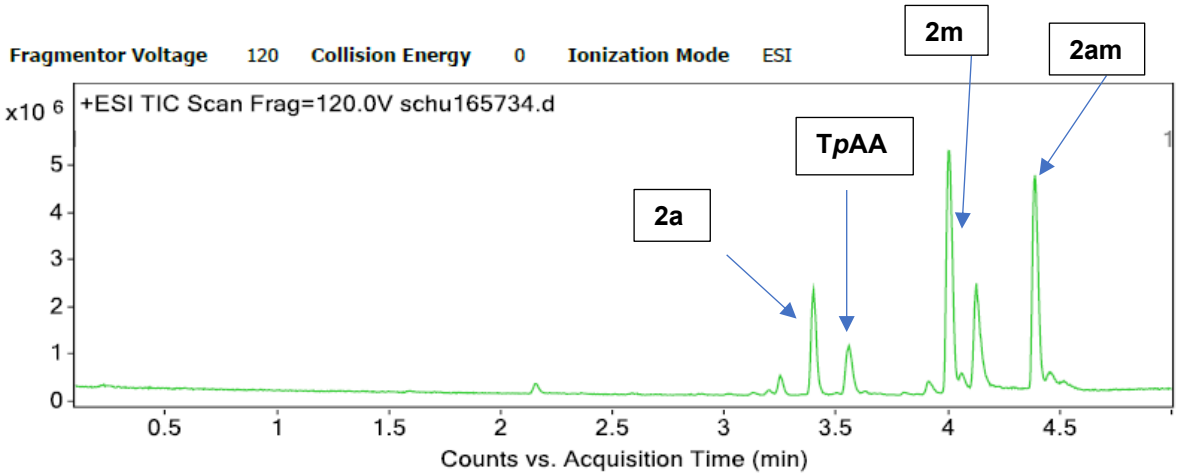


Following **GPF**, the reaction was carried out with **3r** (0.10 mmol) and **T*p*AA** (0.02 mmol, 0.2 equiv.). The reaction mixture was irradiated for 40 h with a 405 nm LED. No product was formed, 64% conversion of **3r** was observed.

Attempted cross-coupling of different iminyl radicals

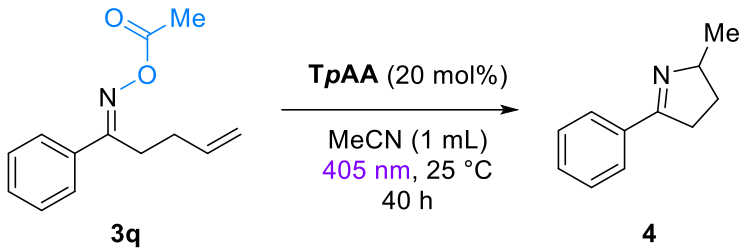
Following GPF, the reaction was carried out with both **3a** (0.05 mmol) and **3m** (0.05 mmol) with **TpAA** (0.02 mmol). The mixture was irradiated for 40 h with a 405 nm LED. A mixture of homocoupled and heterocoupled products was formed in the LC-MS:





6 Mechanistic Studies

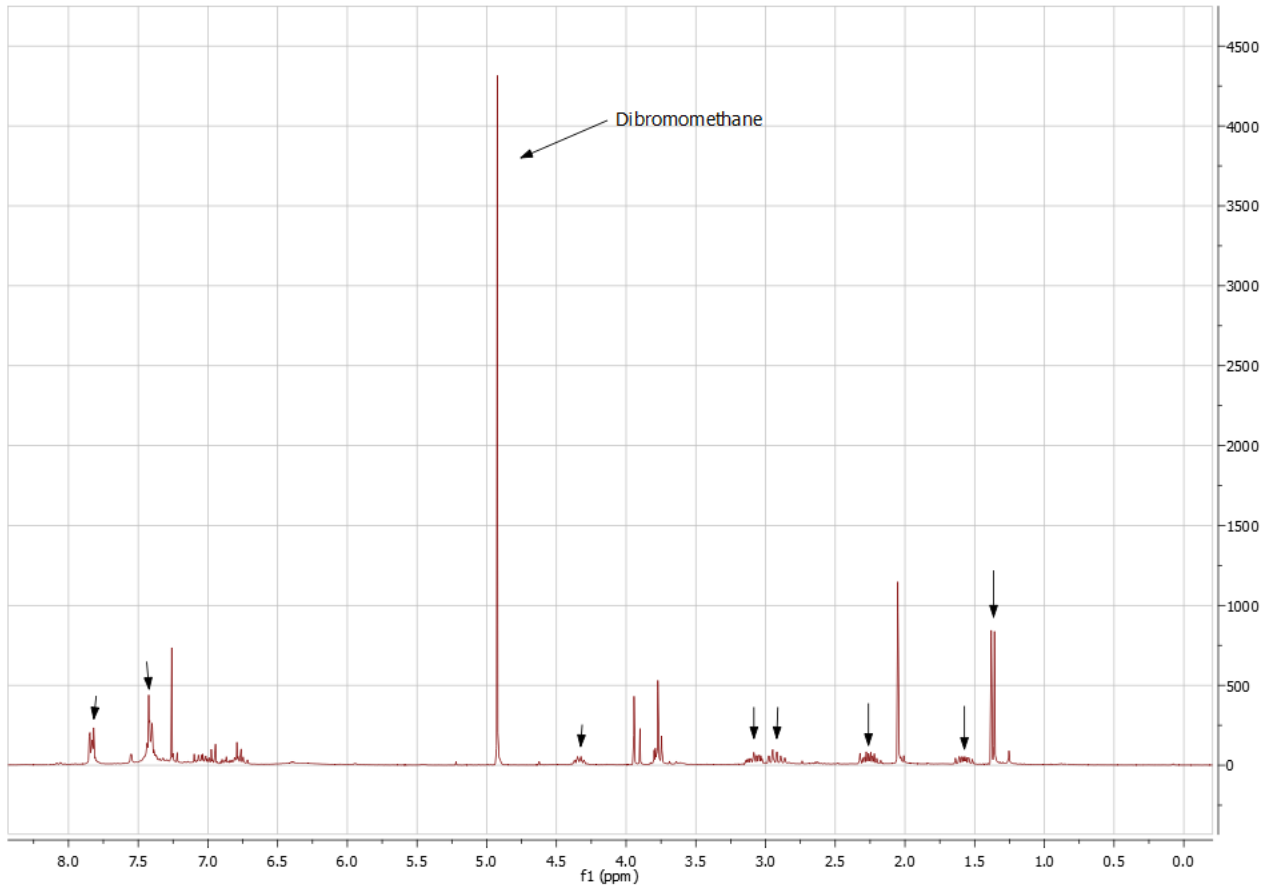
6.1 Iminyl radical cyclization study



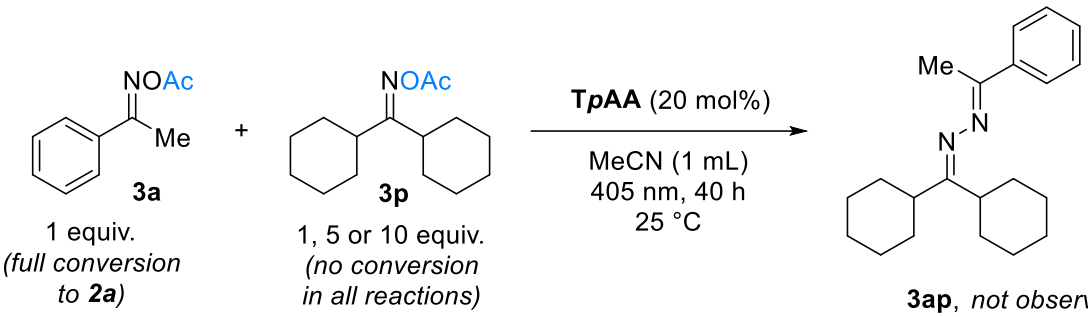
To prove the existence of a N-centered radical (NCR) the following cyclization reaction was carried out following **GPF** with **3q** (0.10 mmol, 1 equiv. SM only 75% purity) and **TpAA** (0.02 mmol, 0.2 equiv.). **NMR Yield**: 37%, 100% conversion. Yield was determined by ^{1}H NMR following addition of 0.1 mmol of CH_2Br_2 to the crude

reaction mixture. Product **4** was not isolated. The formation of product **4** proves that an NCR is formed during the reaction.

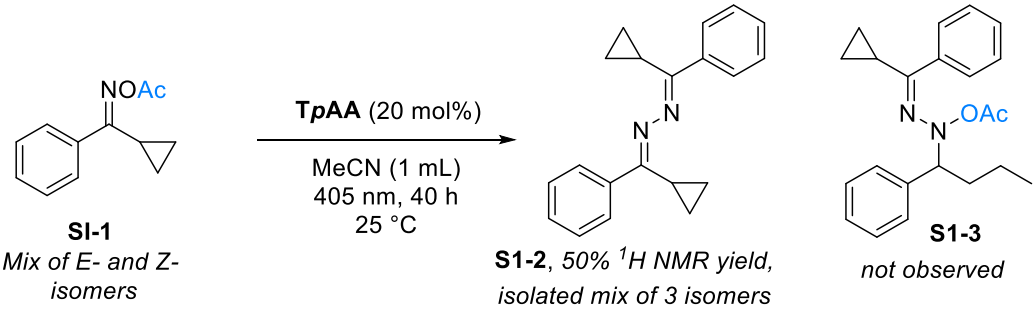
^{1}H NMR (300 MHz, $CDCl_3$)



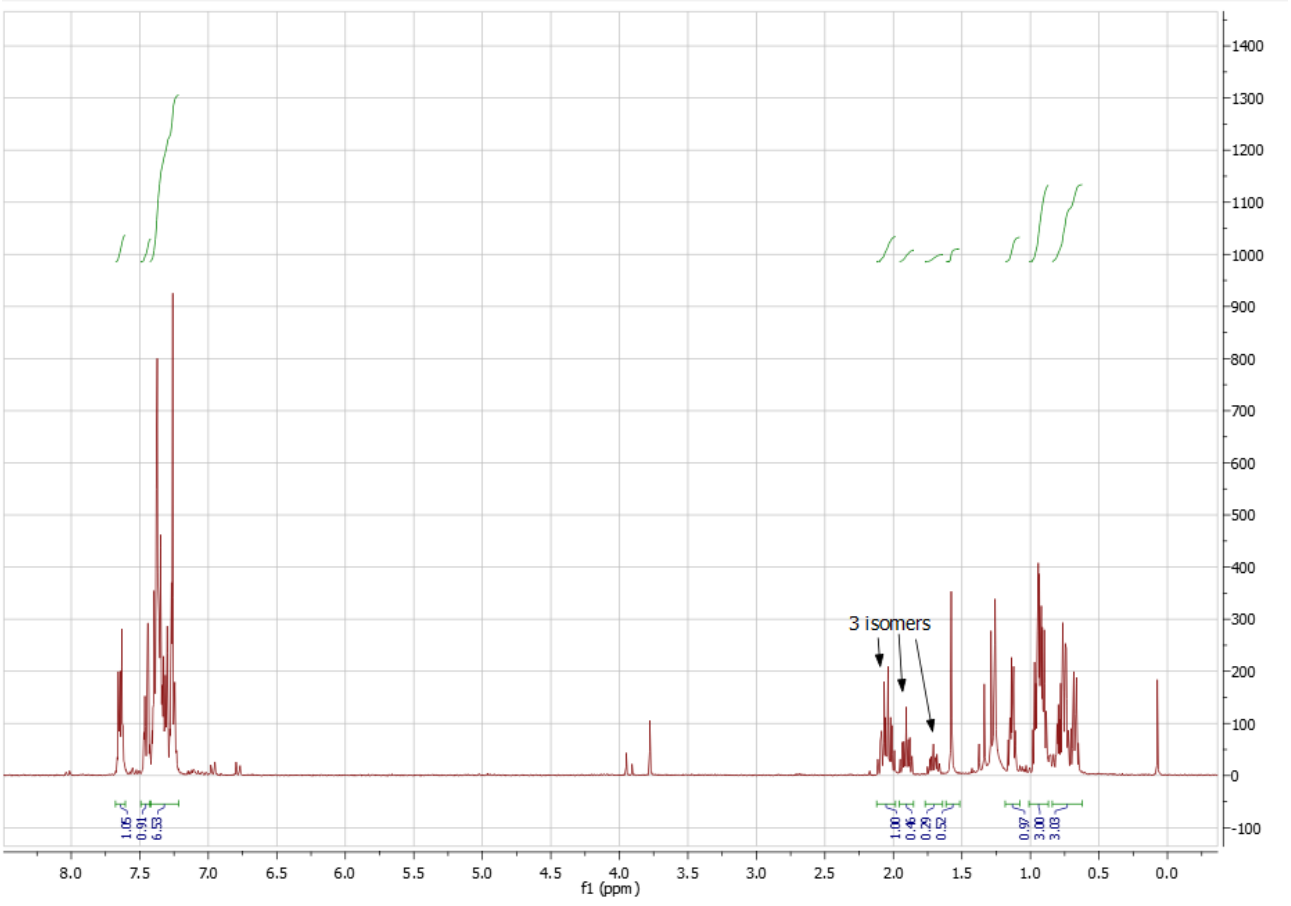
6.2 Probing Addition-Elimination Pathway for the Reaction



When reaction oxime esters **3a** and **3p** (1, 5 and 10 equiv. respectively) together no conversion of **3p** was observed and 82% of azine **2a** (100% conversion of **3a** occurred). This result suggests *against* an addition-elimination mechanism (considering the iminyl radical adding to the N atom of an oxime ester, followed by fragmentation of a carboxyl radical from the incipient carbon-centered radical).

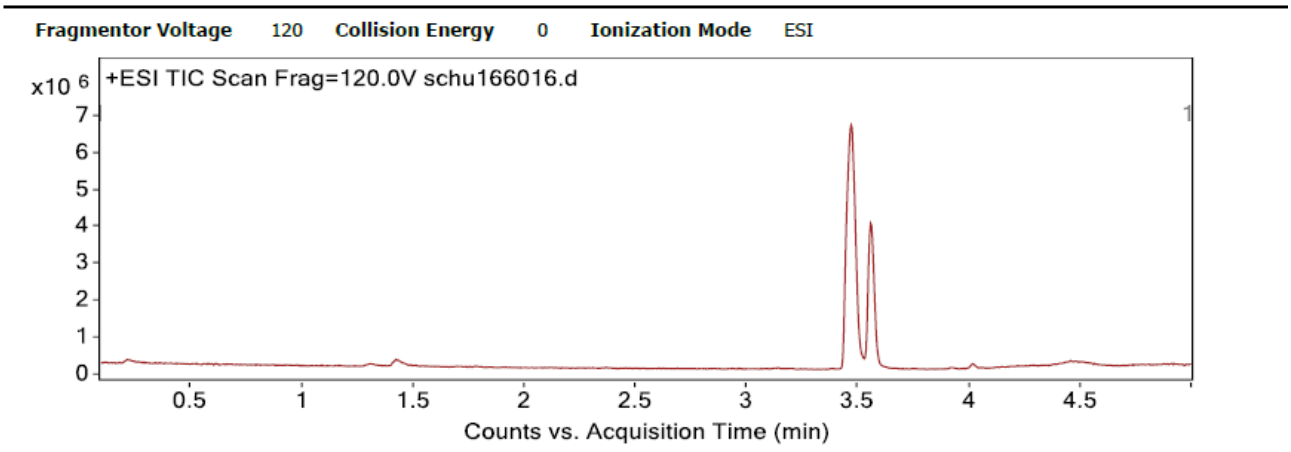


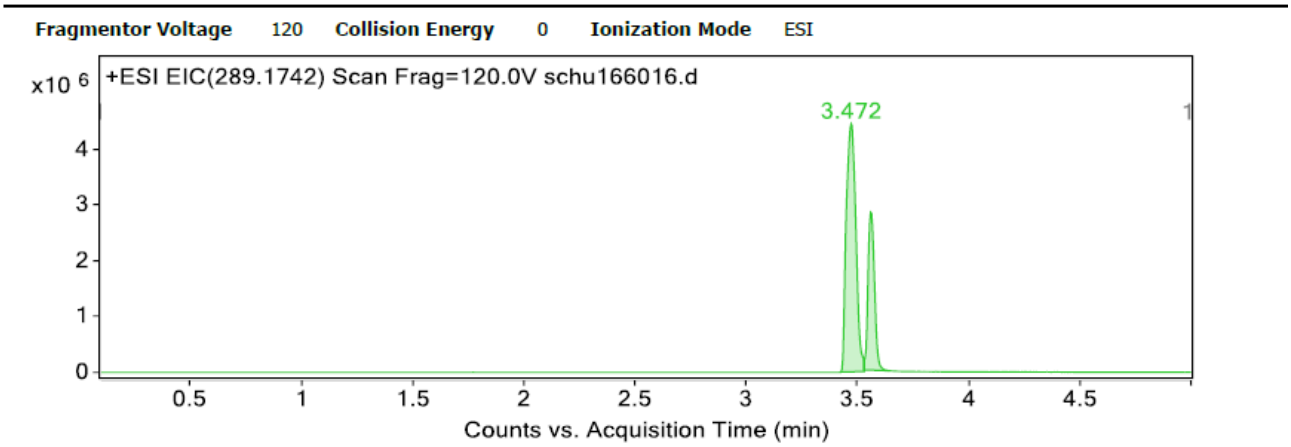
^{1}H-NMR of 3 isolated isomers of cyclopropyl azine.

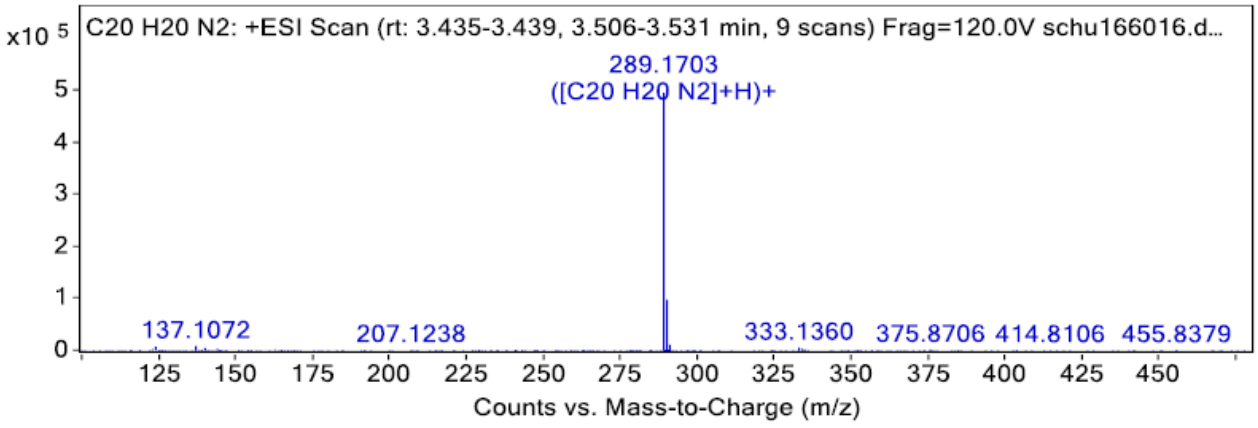


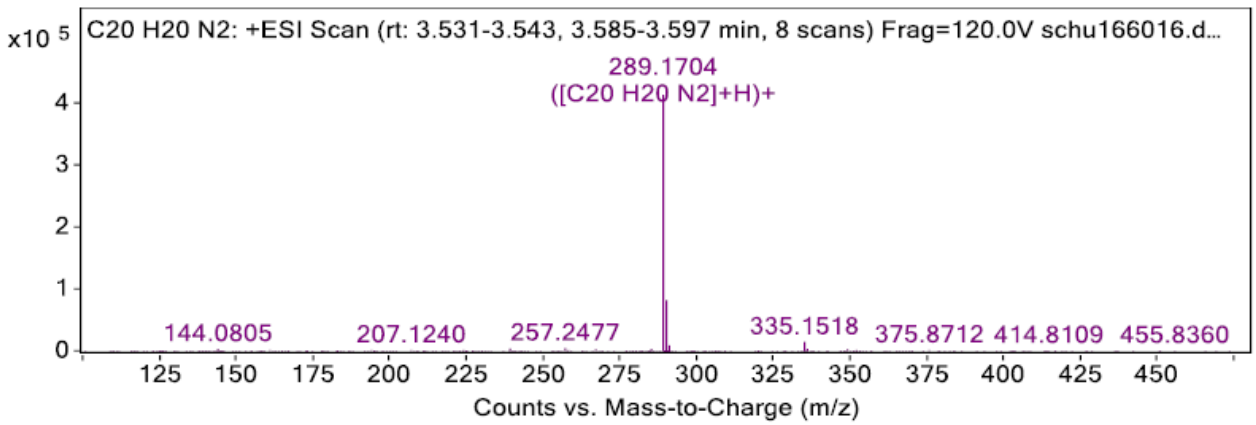
In another test phenyl, cyclopropyl oxime ester (**3s**, as a mixture of its *E*- and *Z*- isomers) was subjected to the reaction conditions. If the iminyl radical added to the N atom, an intermediate benzylic radical should form, which would subsequently open the cyclopropyl ring, retaining the acetate group (i.e. product **S2**). However, this was not the case – as the cyclopropyl azine (product **S1**) was clearly detected in the crude ^{1}H NMR (50% yield) and then isolated (as a mixture of 3 isomers), see above spectrum. Furthermore, no ring opening product could be detected in the crude ^{1}H NMR or in the MS.

The isolated fraction of **S2** separates into two peaks in LC-MS both having the same mass. **HRMS** (ESI+) Calcd.: $C_{13}H_{16}N_2$ $[M+H]^+$ = 289.1643; Found: $[M+H]^+$ = 289.1703 and $[M+H]^+$ = 289.1704.

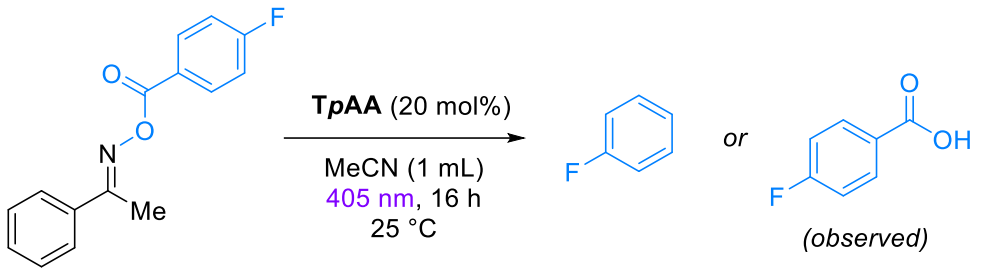








6.3 NMR investigation of the fate of the O-auxiliary of the oxime ester

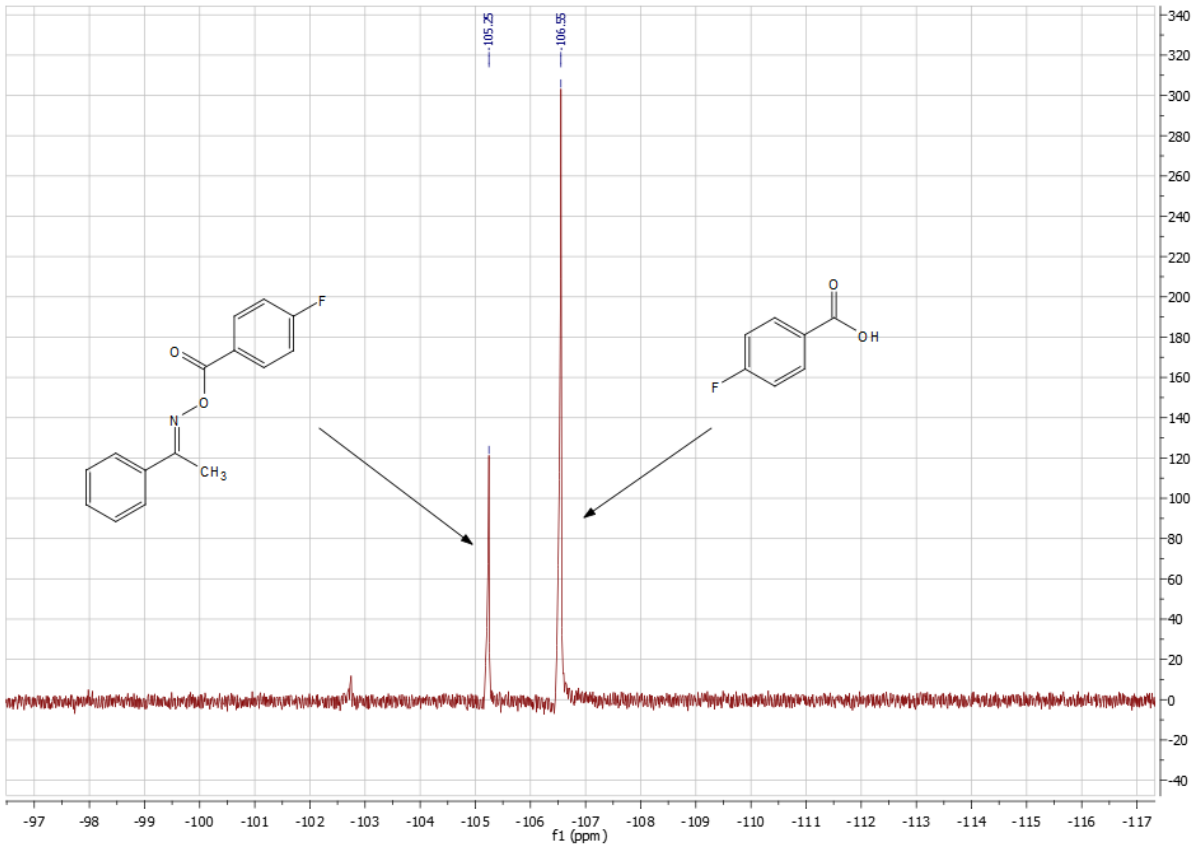


1a

The fate of the O-auxiliary of substrate **1a** was examined. An EnT mechanism would afford N−O bond homolysis and therefore the O-centered radical. According to Glorius and co-workers (see main manuscript, Ref. 17) this decarboxylates to a C-centered radical when generated by an EnT process. However, no fluorobenzene was observed by ^{19}F-NMR of the reaction. In the ^{19}F-NMR, 4-fluorocarboxylic acid was observed.

The reaction was performed following **GPF** on a 0.1 mmol scale. The reaction run for 16 h, then 0.2 mL were taken and added into a NMR tube. Another 0.4 mL $CDCl_3$ were added and ^{19}F-NMR was measured.

^{19}F NMR (377 MHz, $CDCl_3$)



^{19}F-NMR shows partial conversion of substrate **1a** in 4-fluorobenzoid acid (−106.55 ppm). Fluorobenzene was not observed in the NMR.

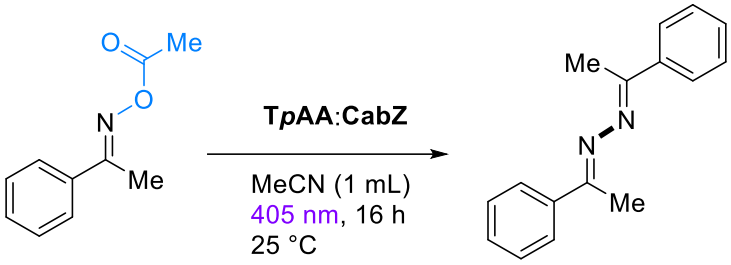
Note: As a spiking experiment, addition of authentic 4-fluorobenzoic acid increased the size of the peak at −106.5 ppm confirming its generation in the reaction.

Since no protic source is added, the fate of the O-auxiliary is the acid form not the carboxylate, suggesting that the carboxylate provides an electron to effect photocatalyst turnover. Presumably, the resulting O-centered radical engages MeCN in HAT to generate the acid form which we detect.

6.4 Carbazole study

It was discovered spectroscopically and by NMR of the reaction mixture that **T*p*AA** transforms into 3,6-dimethoxy-9-(4-methoxyphenyl)-9H-carbazole (**CabZ**) during the reaction. At the end of the reaction a ratio of 7:3 (**T*p*AA**:**CabZ**) was observed. Speculating that **CabZ** might be the active SET photocatalyst, a series of test reactions were performed using different ratios of **T*p*AA**:**CabZ** (Table S3).

Table S3. Carbazole vs T*p*AA photocatalyst efficiency test reactions



3a **2a**

Entry	T*p*AA:CabZ	Time (h)	Yield of 2a (%)	Conversion of 3a (%)
1	100:0	16	54	75
2	90:10	16	53	100
3	80:20	16	68	96
4	65:35	16	76	97
5[a]	65:35	16	–	–
6	50:50	16	75	97
7	35:65	16	72	98
8	20:80	16	63	98
9	0:100	16	59	96
10	100:0	40	86	100
11	0:0	16	–	–

All reactions were carried out following **GPF** on a 0.1 mmol scale of oxime ester **3a** in MeCN (1 mL). The mixture of **T*p*AA** and **CabZ** corresponds to 0.02 mmol. Conversions/yields determined by ^{1}H NMR of the reaction mixture with CH_2Br_2 as internal standard. [a]Without light.

A control reaction without light irradiation (Table S3, Entry 5) gave no conversion of oxime ester **3a** to the desired product **2a**.

It can be observed that different ratios of **T*p*AA** and **CabZ** can lead to the formation of product **2a** in similar yields (Table S3, Entry 2-4,6). The conversion of oxime ester **3a** is higher with **CabZ** as the catalyst after a given time, however, yields could not match the 86% product formation with 100% **T*p*AA** after 40 h. This suggests **CabZ** is catalytically active, but is less selective. Greater conformational flexibility in **T*p*AA** may favour its preassembly with **3a**.

6.5 Steady-state Luminescence quenching experiments and Stern-Volmer plots

We investigated the quenching effect of substrate **3a** on the luminescence of **T*p*AA** (SV-1, SV-2, SV-3), **CabZ** (SV-4, SV-5), and a 70:30 mixture of **T*p*AA** and **CabZ** (SV-6, SV-7) as shown in Table S4. For both steady-state and time resolved luminescence measurements, samples were prepared in an oven-dried 1 cm x 1 cm quartz cuvette. Dry MeCN was used as solvent. All samples were prepared under Ar atmosphere (Ar bubbling for 3 min) before starting the measurement. To ensure identical absorption of λ(Exi) = 370 nm all samples were examined with UV-vis by Cary 400 and Cary WinUV (v6.2.0.1588) from Agilent© Technologies before the measurement of the emission intensity aiming for a coherent absorption at 370 nm. The measurements were

using the FluoroMax-4 spectrometer, FluorEssence (v3.9) all by Horiba© Scientific. The emission spectra was recorded from 380 nm to 700 nm in increments of 1 nm. The addition of quencher **3a** was carried out in steps of 20% in ratio to the catalyst leading to six samples in total (Sample A-F) if not mentioned in a different way.

Standard sample preparation:
Sample A: 1 equiv. catalyst
Sample B: 1 equiv. catalyst + 0.2 equiv. substrate
Sample C: 1 equiv. catalyst + 0.4 equiv. substrate
Sample D: 1 equiv. catalyst + 0.6 equiv. substrate
Sample F: 1 equiv. catalyst + 0.8 equiv. substrate
Sample G: 1 equiv. catalyst + 1 equiv. substrate

Table S4. overview of steady-state luminescence experiments

Experiment name	*Catalyst*	*Catalyst conc. [mM]*
SV-1	**T*p*AA**	0.1
SV-2	**T*p*AA**	1.0
SV-3	**T*p*AA**	0.1
SV-4	**CabZ**	0.1
SV-5	**CabZ**	0.01
SV-6	**T*p*AA** + **CabZ (70:30)**	0.023 (**T*p*AA**), 0.010 (**CabZ**)
SV-7	**T*p*AA** + **CabZ (70:30)**	0.023 (**T*p*AA**), 0.010 (**CabZ**)

Stern-Volmer experiment no. 1 (SV-1, 0.1 mM T*p*AA):

In SV-1 we examined the behaviour of **T*p*AA** and **3a**. We were aiming for a concentration of 0.1 mM for **T*p*AA**. The slit width was 1.3 nm on for both monocromators. We found a maximum in the emission spectra at 395 nm for **T*p*AA** in sample A (Figure S4, right). Processing the date (Table S5) we saw that the Stern-Volmer plot of SV-1 (Figure S4) shows no quenching of ***T*p*AA** by **3a**.

An additional experiment discovered that the luminescence intensity of **T*p*AA** increased over time upon continuous light irradiation of the sample at 370 nm (Figure S5). For this, a fresh prepared sample A of SV-1 was placed in the FluoroMax device and while the shutter was manually opened (disabling the closing of the shutter) an emission spectra was recorded every 5 min for 25 min. During this period 370 nm would constantly irradiated. We found an approximately linear growth of intensity in this period for the emission of **T*p*AA** but no change in the absorption spectra (Figure S5, red line). A control experiment done in the dark with only a short initial light irradiation of 370 nm for 1 min at the beginning showed that this effect described above can only be observed when constant light irradiation takes place (Figure S5, black line). No photo bleaching was observed. This effect was future investigated and explained in SV-3 by creating a time resolved steady-state emission experiment for an identical sample row as SV-1.

Stern-Volmer experiment no. 2 (SV-2, 1.0 mM T*p*AA):

The experiment of SV-2 used **T*p*AA** and **3a** at a concentration for **T*p*AA** of 1.0 mM. Therefore, we aimed for an absorption of 0.95 – 1.02 at 370 nm. In all other aspects, the procedure was identical to SV-1. This high concentration (closer to standard reaction conditions) was suspected to allow the observation of concentration dependent effects by changes in UV-vis or emission spectra. Due to the high absorption at λ(Exi) this results need to be interpreted with care.

The Stern-Volmer plot of SV-2 found no evidence for quenching (Table S6, Figure S7). We observed no changes in the UV-vis or emission spectra of SV-2 (Figure S6). This indicates no concentration depended effects that would alternate the reaction, absorption spectra or emission spectra take place. In conclusion of SV-1 and SV-2 **T*p*AA** was ruled out as active catalyst species.

Stern-Volmer experiment no. 3 (SV-3, 0.1 mM T*p*AA):

As we were interested in the light-induced behaviour of **T*p*AA** (Figure S5) we decided to investigate this in SV-3 by preparing the samples identical to SV-1 with a conc. of 0.1 mM for **T*p*AA** and added the substrate **3a** in steps of 0%, 5%, 15%, 25% 50%, 75% and 100% (Sample A – Sample G).

Sample A: 1 equiv. **T*p*AA**
Sample B: 1 equiv. **T*p*AA** + 0.05 equiv. **3a**
Sample C: 1 equiv. **T*p*AA** + 0.15 equiv. **3a**
Sample D: 1 equiv. **T*p*AA** + 0.25 equiv. **3a**
Sample E: 1 equiv. **T*p*AA** + 050 equiv. **3a**
Sample F: 1 equiv. **T*p*AA** + 0.75 equiv. **3a**
Sample G: 1 equiv. **T*p*AA** + 1.00 equiv. **3a**

Samples were examined for 185 min with emission spectra being recorded every 5 min under constant irradiation of 370 nm (Figure S9). During this time of 185 min the light source of the FluoroMax device and the manual shutter control were used. This procedure was identical to the experiment shown in Figure S5 of SV-1. We chose a slid width of 1.0 for the monocromators (low starting intensity) to allow the intensity to grow within the detector range. Before and after the time resolved measurements an absorption spectra of the sample was recorded (Figure S8). During this experiment, several noteworthy observations were found.

(I) We saw that the UV-vis after the time resolved emission measurements changed (Figure S8, right). Hereby absorption maxima at 310 nm, 355 nm, and 370 nm appeared in in all samples. This suggested the formation of a new species from **T*p*AA**. As **3a** was not needed for this effect, it is seen as a process independent by substrate.

(II) The new species generated from **T*p*AA** shows assumedly a substantially higher absorption at 370 nm (Figure S8, right)

(III) The emission intensity at 395 nm of sample A grew approximately linearly within the first 60 min (Figure S10, left). After 185 min, it grew as a logarithmic function.

(IV) After 10 – 15 min the emission intensity increased if **3a** was present (sample B – G, Figure S10, left). No correlation between the ratio of **T*p*AA** and **3a** was found in regards of emission intensity and added equiv. of **3a**.

(V) Despite the development of new UV-vis peaks (Figure S8, right), the shape of the emission spectra did not change regardless of time and added quencher (Figure S10, right). No new emission maxima was identified. (SV-4 and SV-5 found an emission maximum at 393 nm for **CabZ**)

(VI) No quenching was found in beginning of the experiment, being coherent with SV-1 (Figure S10, left).

Two major conclusions can be drawn from these observations.

The new species suggested by (I) was assumed to be the carbazole (**CabZ**) being photochemicaly generated from **T*p*AA**. The observed absorption maxima at 310 nm, 355 nm, and 370 nm is also coherent with the absorption spectra of synthesized **CabZ** (compare Figure S11, left). Experiments proved this assumption by finding the **CabZ** in crude reaction mixtures with only **T*p*AA** as added catalyst. Hereby we for example found a ratio of **T*p*AA** to **CabZ** of 66:34 for the remaining cat. load at the end of the reaction in Table S6. As **T*p*AA** was excluded as single active catalyst in the reaction by SV-1 and SV-2, we decided to do Stern-Volmer experiments focusing on **CabZ** and **3a** (see SV-4 and SV-5).

Furthermore, the observation of (IV) may explained by **3a** having an influence on the ratio between **T*p*AA** and low quantities of photochemical generated **CabZ** or generally on the efficiency of photochemical reaction of **T*p*AA** to **CabZ**. This is indirectly reflected by the higher extinction coefficient of **CabZ** at 370 nm (approximately factor 7 compared to **T*p*AA**, compare Figure S3 left and Table S5 to Figure S11 left and Table S7) that causes the observations of SV-3 (II). The higher extinction coefficient of **CabZ** could lead to the higher emission intensity observed in (IV) (also see SV-4 and SV-5 compared to SV-1, SV-2). Assuming that traces of **3a** can facilitate the formation from **T*p*AA** to **CabZ**, we would see a sudden rise in emission intensity and find an indicator for interaction of **T*p*AA**, **3a**, and possible also **CabZ**. This explains the observation (IV) and maybe possible competing side reactions consuming **T*p*AA**, depending on the role identified for the **CabZ**.

Stern-Volmer experiment no. 4 (SV-4, 0.1 mM CabZ):

Due to the long reaction time found under optimal conditions (adding **T*p*AA** only), we suspected that the **CabZ** maybe was the active catalyst in this reaction. The carbazole might be photochemicaly generated only slowly in the first hours from **T*p*AA** due to the low absorbance at 405 nm. This would allow an effective catalytic cycle only once enough **CabZ** was generated. Therefore, we decided to do a Stern-Volmer experiment with the **CabZ** and **3a** (SV-4). We started with a conc. of 0.1 mM for SV-4 (identical to SV-1) observing an absorption around 0.72 - 0.88 and a slid width of 0.75 nm on both light paths sides.

Hereby we identified an emission maximum of 393 nm for **CabZ** (Figure S11, right). Additionally in comparison to **T*p*AA** (comparing to SV-1) we so no rising fluorescence intensity effect but weak photo bleaching after several minutes under irradiation of 370 nm light. Processing the data of SV-4 in Table S7 we found no evidence for quenching between **CabZ** and **3a** (Figure S12).

Stern-Volmer experiment no. 5 (SV-5, 0.01 mM CabZ):

As we suspected that, the absorption at 370 nm was too high in SV-4 (Figure S11, left) we decided to do a Stern-Volmer experiment with 0.01 mM for **CabZ** (SV-5). The absorbance was now more comparable to SV-1 (Figure S13, left) We set a slid width of 1.3 nm for both light paths, being identical to SV-1.

In this experiment, we found no evidence for quenching (Figure S13 right, Table S8, Figure S14). This provided the information, that ***CabZ** alone is not quenched by **3a**.

Stern-Volmer experiment no. 6 (SV-6, 0.023 mM T*p*AA and 0.010 mM CabZ):

As **T*p*AA** as well **CabZ** were not identified as single active catalyst in this series of quenching experiments, we wondered if both catalysts would be need to form the full catalytic cycle. Hereby the final ratio of **T*p*AA**:**CabZ** found in the reaction conditions with the highest yield were taken as starting point (see table 3). Therefore we prepared a mixed stock solution of **T*p*AA**:**CabZ** (70:30) and used a slid width of 1.0 on both light paths. Due to the absorbance of this mixture at 370 nm being too high for the spectrometer, we diluted the mixture in comparison to prior experiments to a final conc. of 0.023 mM for **T*p*AA** as well as 0.010 mM for **CabZ**.

To our surprise, the UV-vis measured before the steady-state emission experiment showed no constant spectra at 300 nm but a shift leading to an overall shrinking absorption similar to decomposition (Figure S15 left). This leaded in consequence to a lower emission intensity at 395 nm (figure 13 right). The SV-6 graph in Figure S16 and Table S9 therefore could lead to the wrong impression of prove of quenching. As the absorption spectra is influenced by the addition of **3a** (influencing **T*p*AA** and **CabZ**) or by an instable stock solution, we are not able to tell what ratio of **T*p*AA** and **CabZ** present when measuring the emission. As reason we suspected the altering stock solution of **T*p*AA** and **CabZ** (stock solution of mixture) used during sample preparations.

Stern-Volmer experiment no. 7 (SV-7, 0.1 mM T*p*AA and 0.1 mM CabZ):

As we suspected the mixed stock solution, we prepared Sample A and Sample F of SV-6 as prior described but used separated catalyst stock solutions, allowing alternating effects only directly before the measurements. We again found non-consistent absorption spectra (Figure S17, left). This indicates that **3a** influences the ratio of **T*p*AA** and **CabZ** as suggested in SV-3 observation (IV). The changes in intensity of absorption matched those of emission, such that conclusions could not be drawn about quenching.

Summary:

We discovered that **CabZ** is photochemicaly generated from **T*p*AA**. This process is influenced by the substrate **3a**, as evidence of a stabilizing interaction between **T*p*AA** and **3a**. The character of this interaction is not yet known, and we propose a combination of N-lone-pair---C=N and $\pi-\pi$ stacking interactions, based on the known interactions of neutral Ar_3N with ketones and of the known propensity of Ar_3N and their radical cations to participate in $\pi-\pi$ interactions with aryl-containing substrates in the literature (see Ref. 21, main manuscript).

While quenching of ***T*pAA** by **3a** could not be directly proven due to the simultaneous transformation of **T*p*AA** to **CabZ** during irradiation (where the latter exhibits stronger emission at the same wavelength), we can rely on the *lack* of Stern-Volmer quenching of (authentically-prepared) ***CabZ** by **3a** (see SV-4 and SV-5) to conclude that ***TpAA** is the more likely candidate of the two for the initial PET step. Higher concentrations (excesses) of quenchers might be needed for quenching to become detectable, since our maximum ratio was 1 equiv w.r.t **T*p*AA**. However, we elected not to commit further **3a** to such investigations due to the clear transformation of **T*p*AA** to **CabZ** occluding analysis.

Data for Stern-Volmer 1 (SV-1):

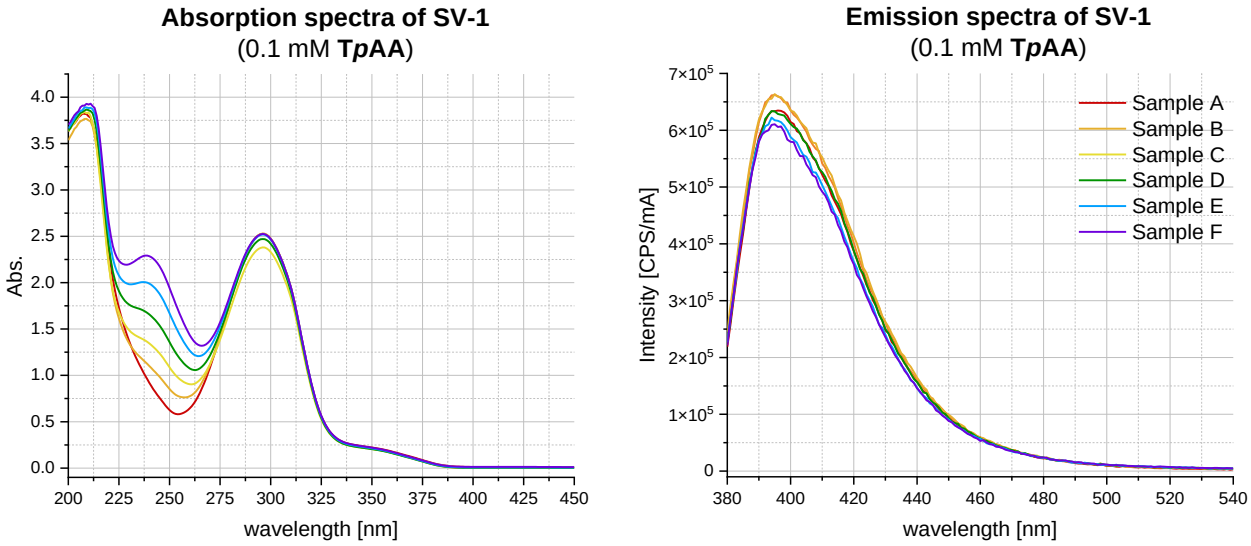


Figure S3. UV-vis spectra of SV-1 (left) and emission spectra of SV-1 (right)

Table S5. Absorption at 370 nm before Steady-state emission experiment and emission intensity of 395 nm, both taken from data shown in Figure S3

Sample Name	*Sample A*	*Sample B*	*Sample C*	*Sample D*	*Sample E*	*Sample F*
OD of 370 nm (UV-vis)	0.1188	0.1038	0.1068	0.1018	0.1073	0.1135
I [CPS/mA] (at 395 nm)	633435	662127	663714	633227	617716	610502

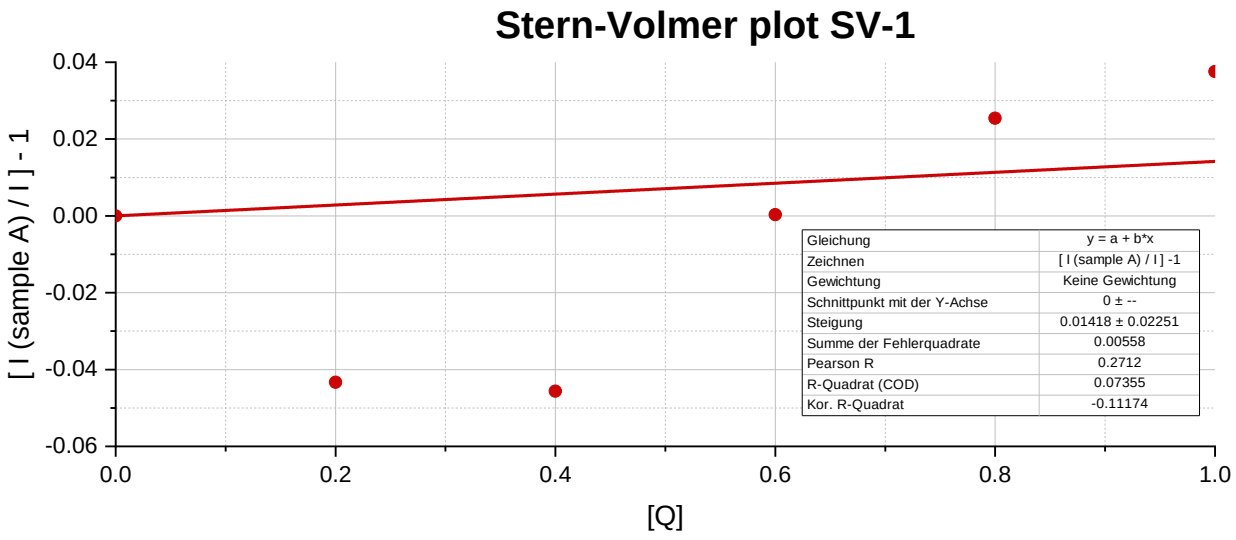


Figure S4. Stern-Volmer plot of experiment SV-1 based on Table S5.

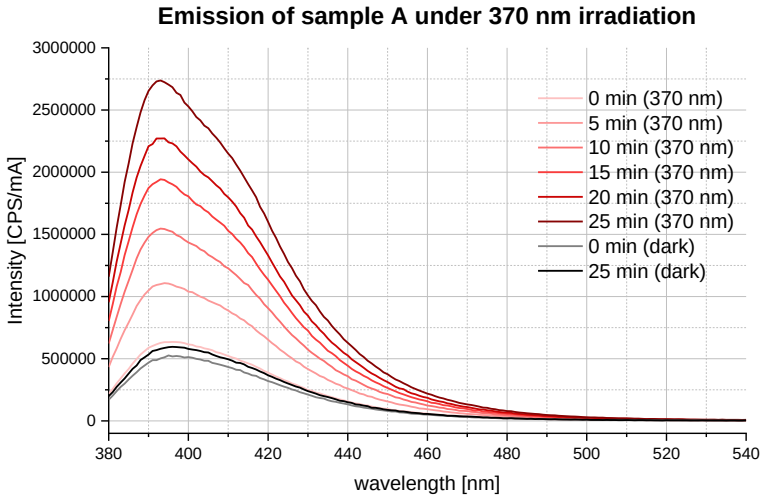


Figure S5. Emission intensity of Sample A in case of constant light irradiation (370 nm) over a period of 25 min (red graphs) and emission intensity of Sample A in case of initial 1 min light irradiation (370 nm) at 0 min and 25 min (control experiment, black and grey graph).

Data for Stern-Volmer 2 (SV-2):

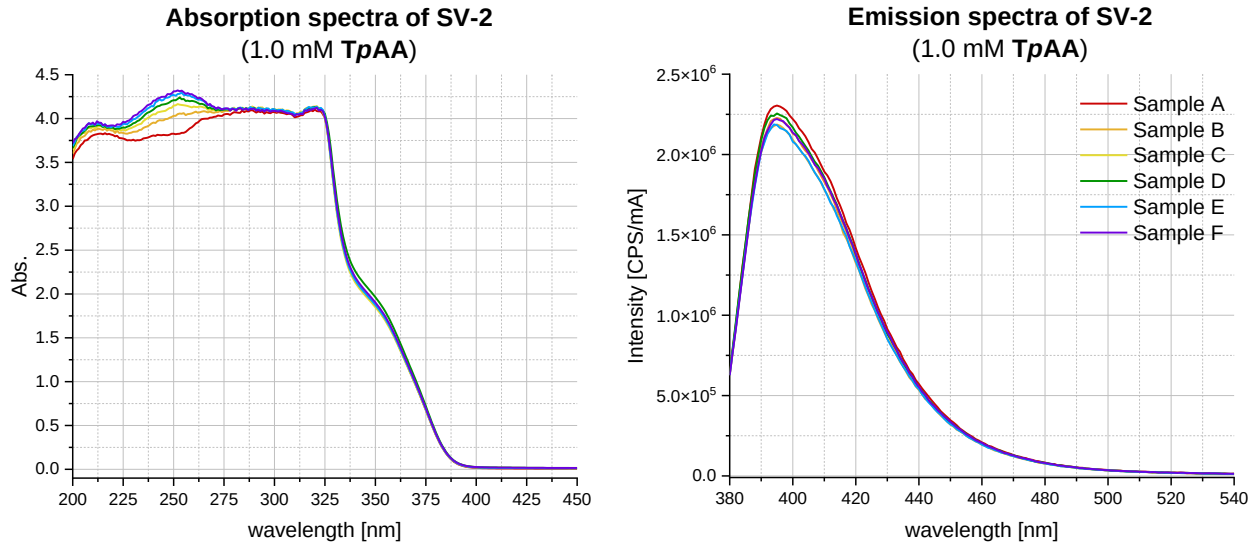


Figure S6. UV-vis spectra of SV-2 (left), emission spectra of SV-2 (right)

Table S6. Absorption at 370 nm before steady-state emission experiment and emission intensity of 395 nm, both taken from data shown in Figure S6.

Sample Name	*Sample A*	*Sample B*	*Sample C*	*Sample D*	*Sample E*	*Sample F*
OD of 370 nm (UV-vis)	0.9595	0.9649	0.9558	1.0167	0.9698	0.9825
I [CPS/mA] (at 395 nm)	2304774	2227135	2186765	2255652	2183242	2221166

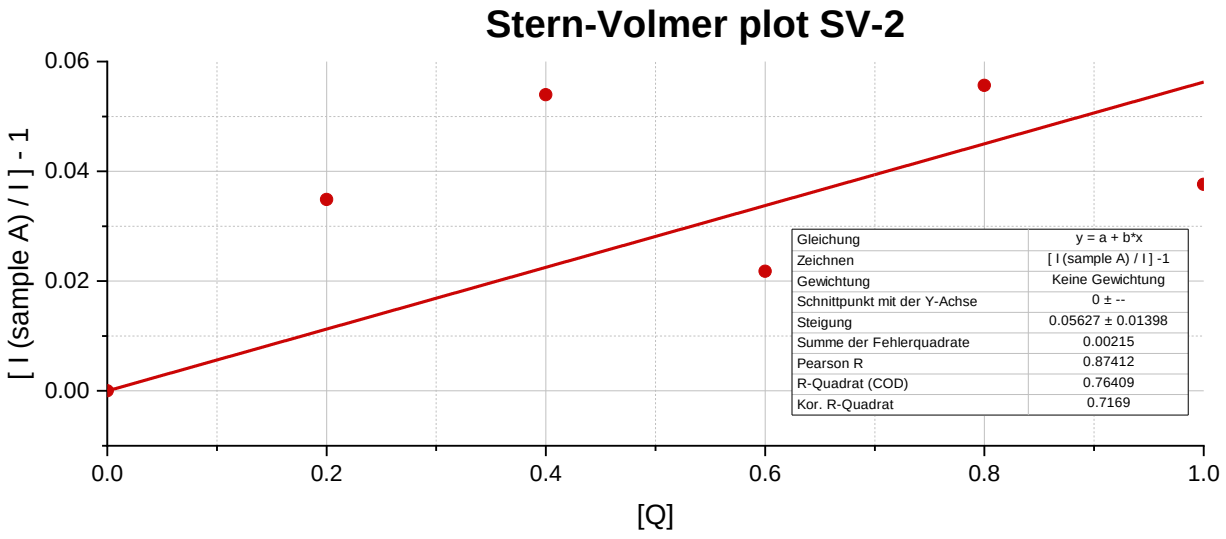


Figure S7. Stern-Volmer plot of experiment SV-2 based on Table S6

Data of Stern-Volmer 3 (SV-3):

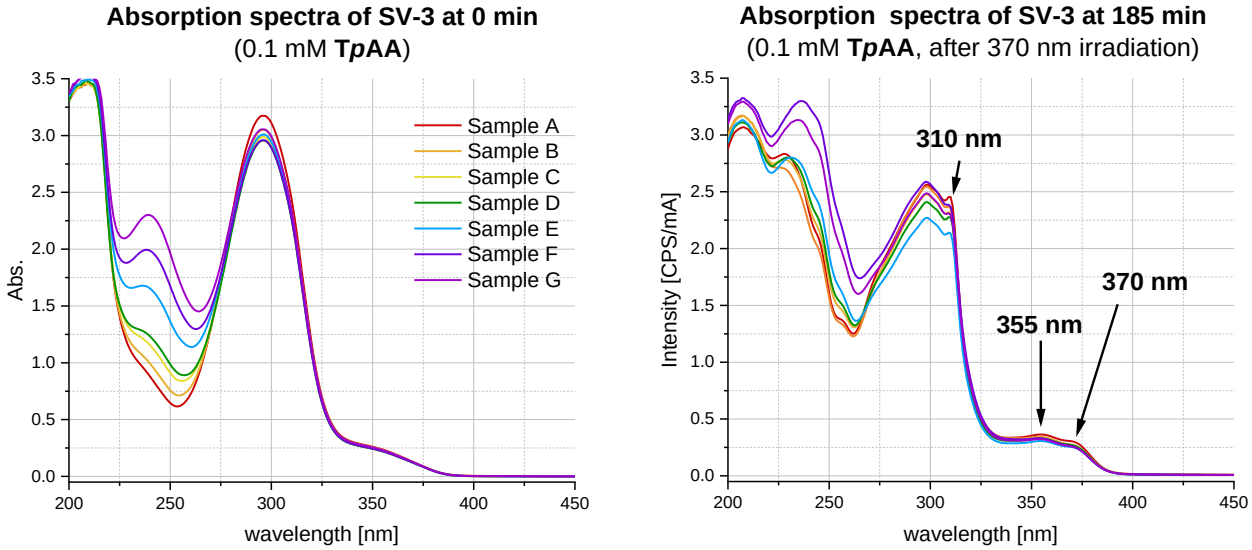
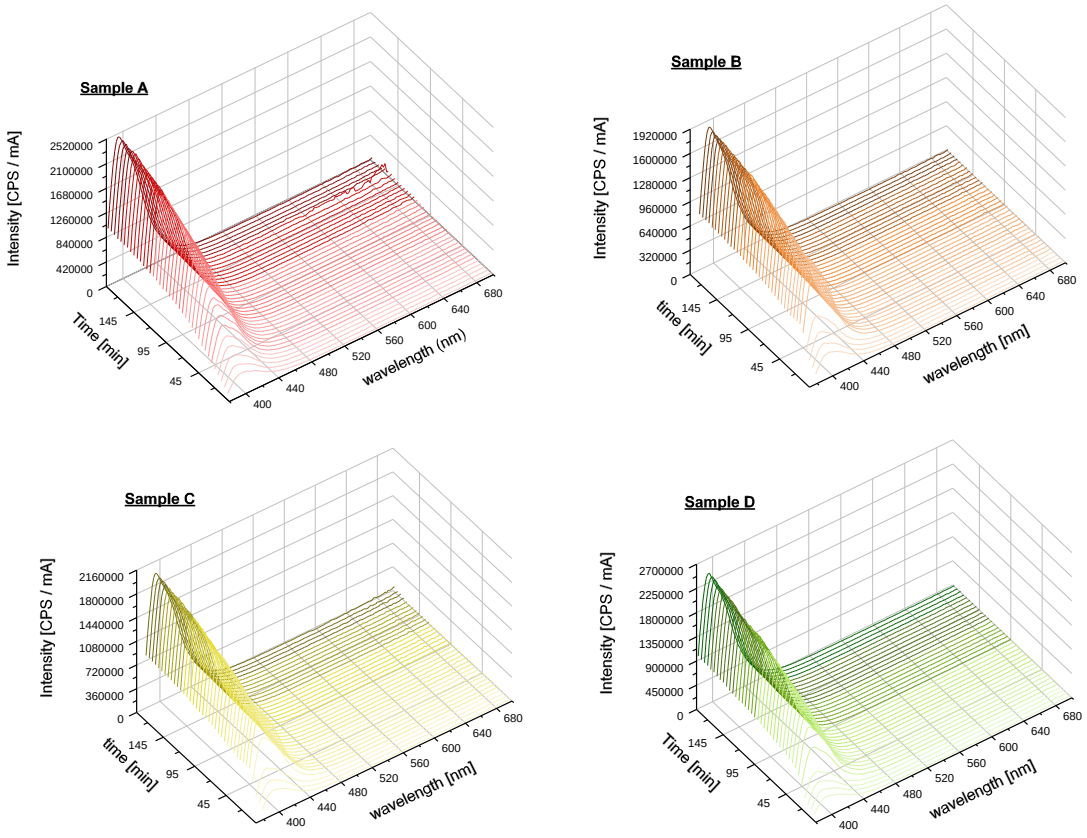


Figure S8. Absorption spectra of SV-3 samples before (left) and after (right) the time resolved steady-state emission experiment



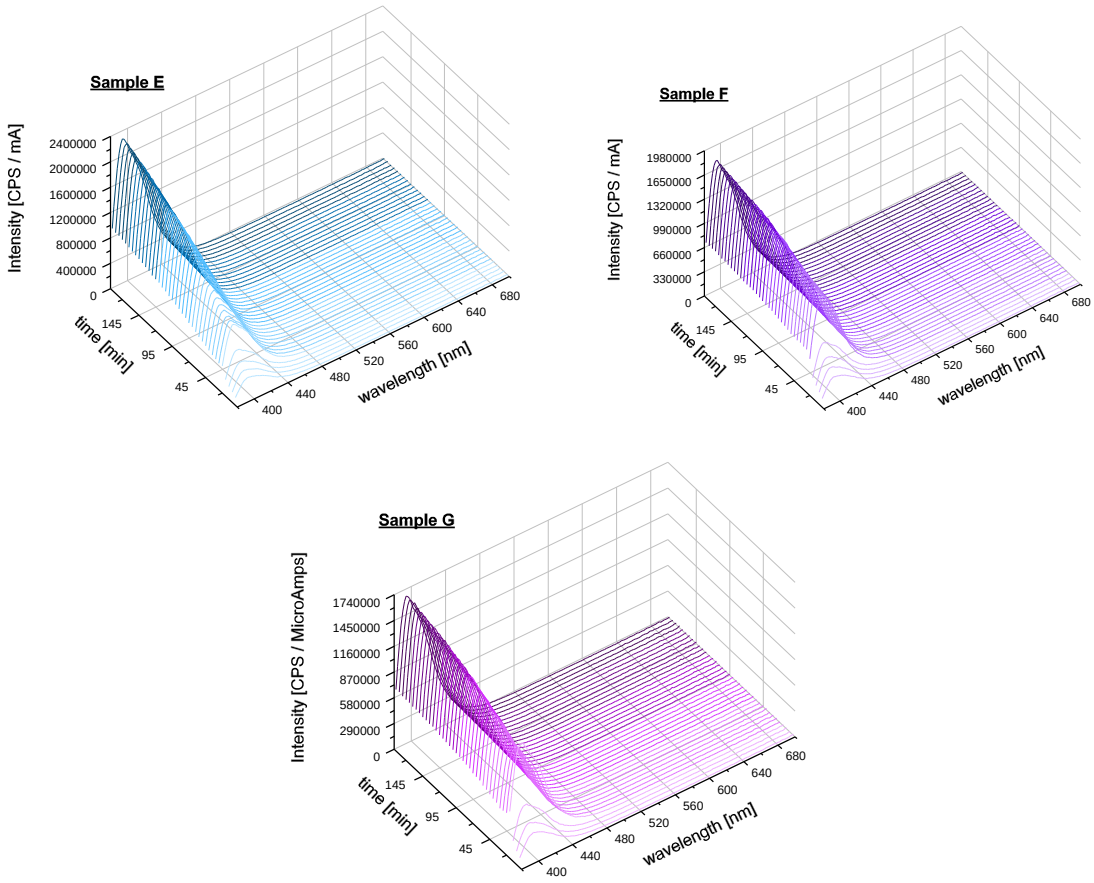


Figure S9. Time resolved emission spectra of SV-3 of each sample

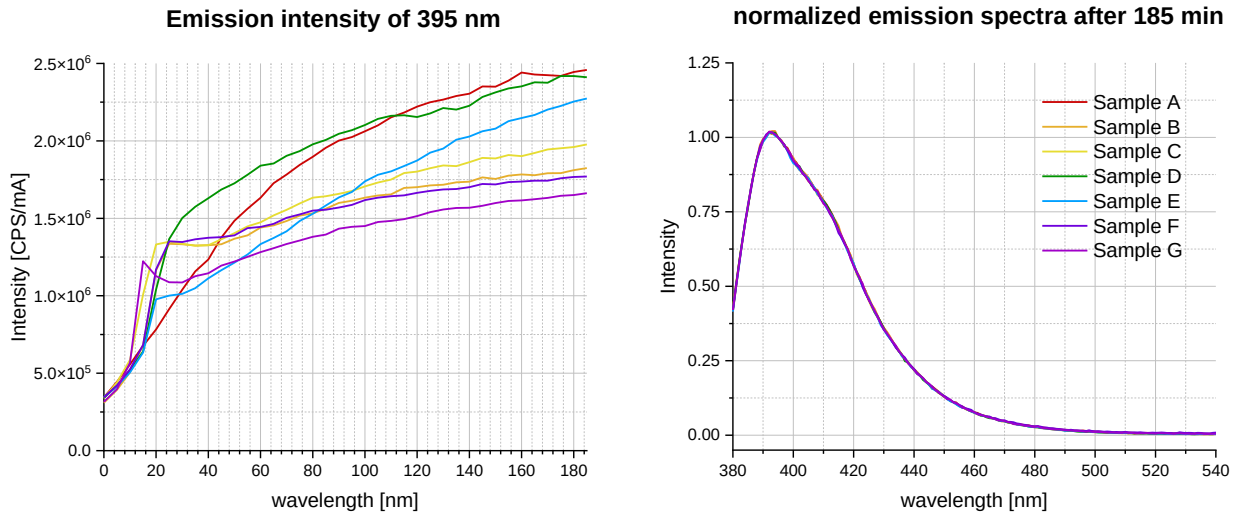


Figure S10. Time tracing of emission wavelength 395 nm of SV-3 (left), overlay of emission spectra of SV-3 at 185 min while normalizing maxima at 395 nm to 1.

Data of Stern-Volmer 4 (SV-4):

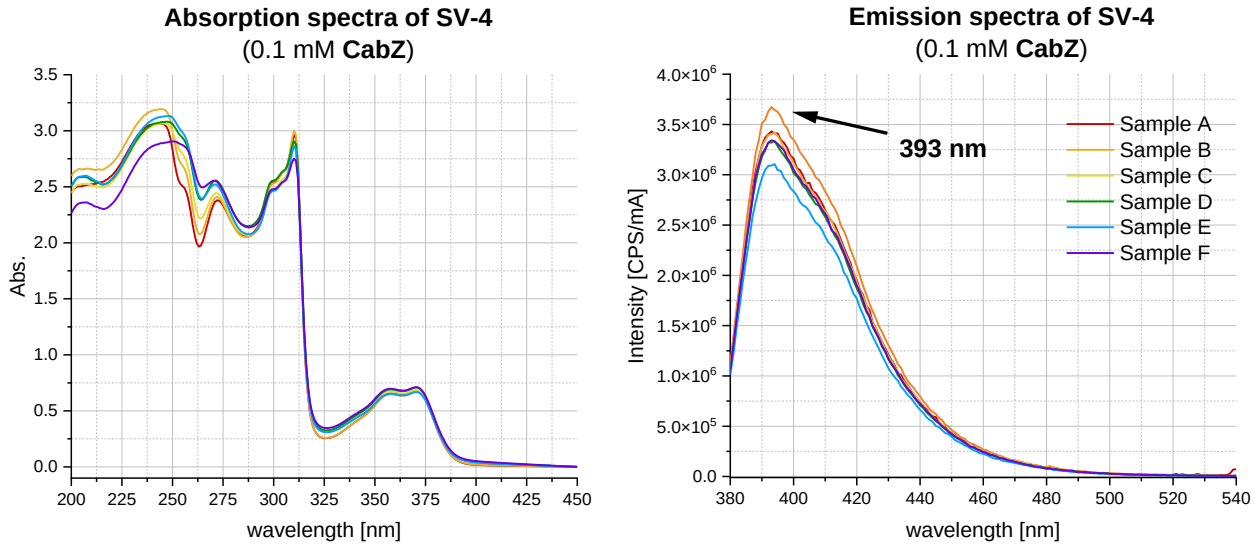


Figure S11. UV-vis spectra of SV-4 (left) and emission spectra of SV-4 (right)

Table S7. Absorption at 370 nm before steady-state emission experiment and emission intensity of 395 nm, both taken from data shown in Figure S11.

Sample Name	*Sample A*	*Sample B*	*Sample C*	*Sample D*	*Sample E*	*Sample F*
OD 370 nm (UV-vis)	0.7192	0.7191	0.8252	0.8234	0.7854	0.8802
I [CPS/mA] (at 393 nm)	3431044	3673073	3403407	3319160	3092635	3342495

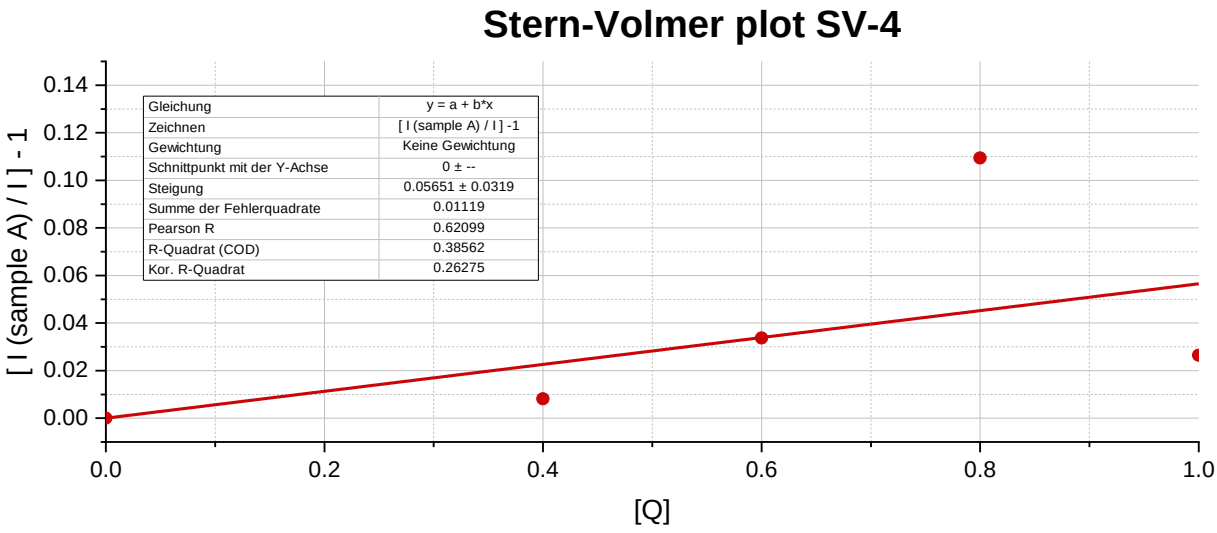


Figure S12. Stern-Volmer plot of experiment SV-4 based on Table S7.

Data of Stern-Volmer 5 (SV-5):

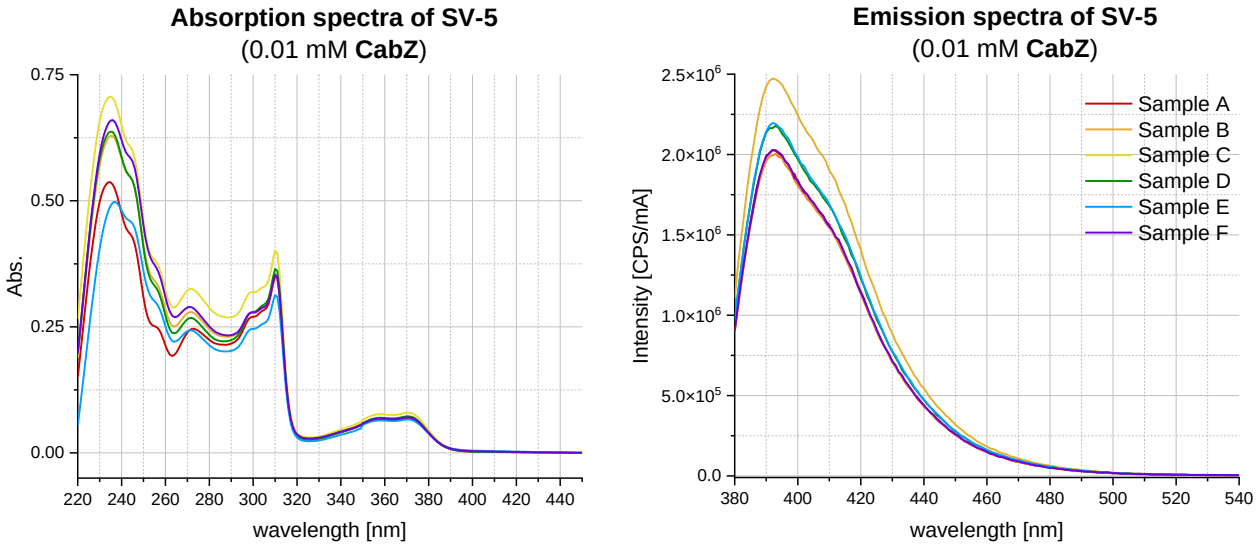


Figure S13. UV-vis spectra of SV-5 (left) and emission spectra of SV-5 (right)

Table S8. Absorption at 370 nm before steady-state emission experiment and emission intensity of 395 nm, both taken from data shown in Figure S13.

Sample Name	*Sample A*	*Sample B*	*Sample C*	*Sample D*	*Sample E*	*Sample F*
OD of 370 nm (UV-vis)	0.0782	0.0824	0.0905	0.0803	0.0814	0.0814
I [CPS/mA] (at 393 nm)	2021165	2003317	2467047	2178074	2189393	2027290

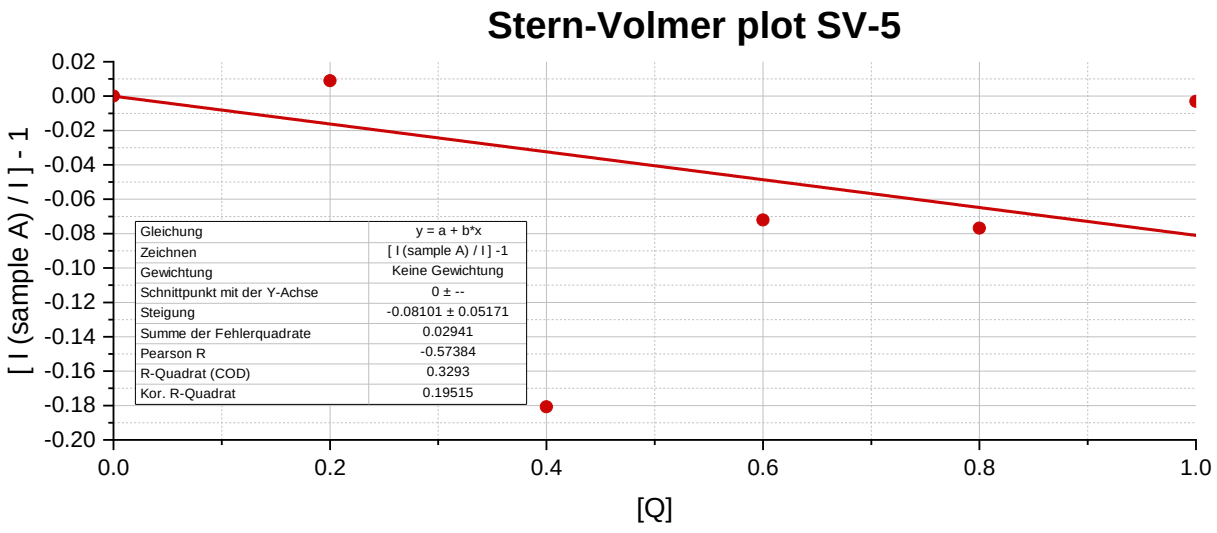


Figure S14. Stern-Volmer plot of experiment SV-5 based on Table S8.

Data Stern-Volmer 6 (SV-6):

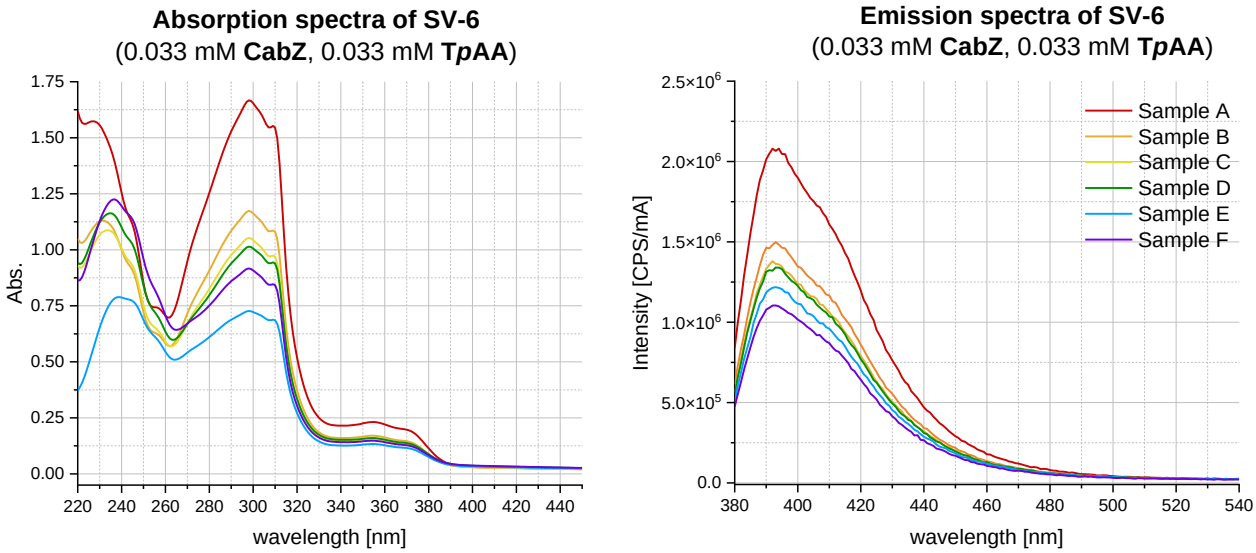


Figure S15. UV-vis spectra of SV-6 (left) and emission spectra of SV-6 (right)

Table S9. Absorption at 370 nm before steady-state emission experiment and emission intensity of 395 nm, both taken from data shown in Figure S15.

Sample Name	*Sample A*	*Sample B*	*Sample C*	*Sample D*	*Sample E*	*Sample F*
OD of 370 nm (UV-vis)	0.1972	0.1456	0.1340	0.1376	0.1109	0.1278
I [CPS/mA] (at 395 nm)	2065756	1498820	1362852	1340923	1218006	1104328

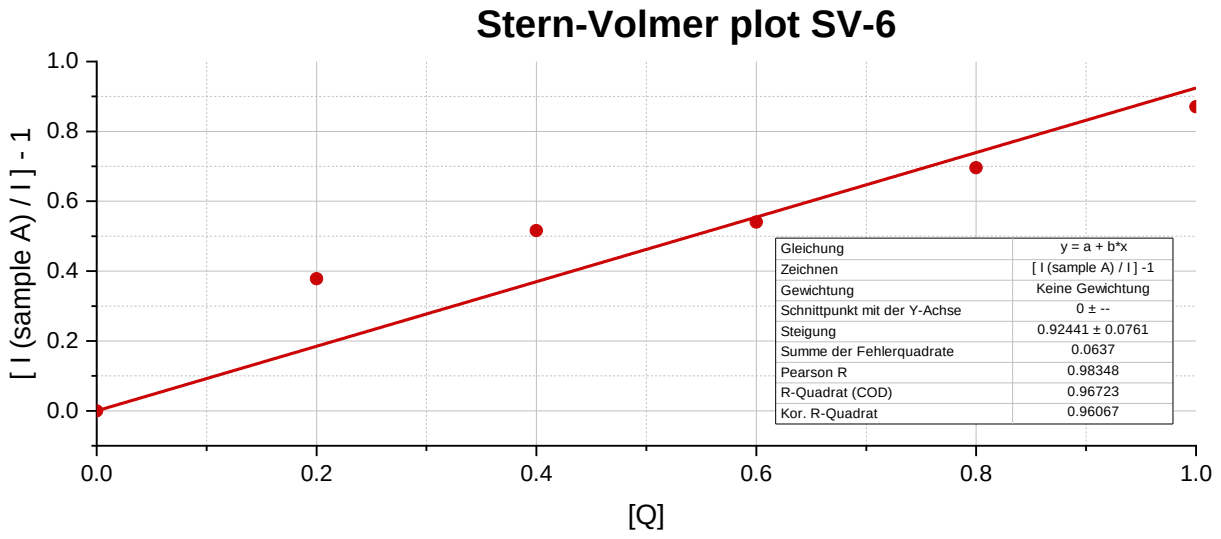


Figure S16. Stern-Volmer plot of experiment SV-6 based on Table S9.

Data Stern-Volmer (SV-7):

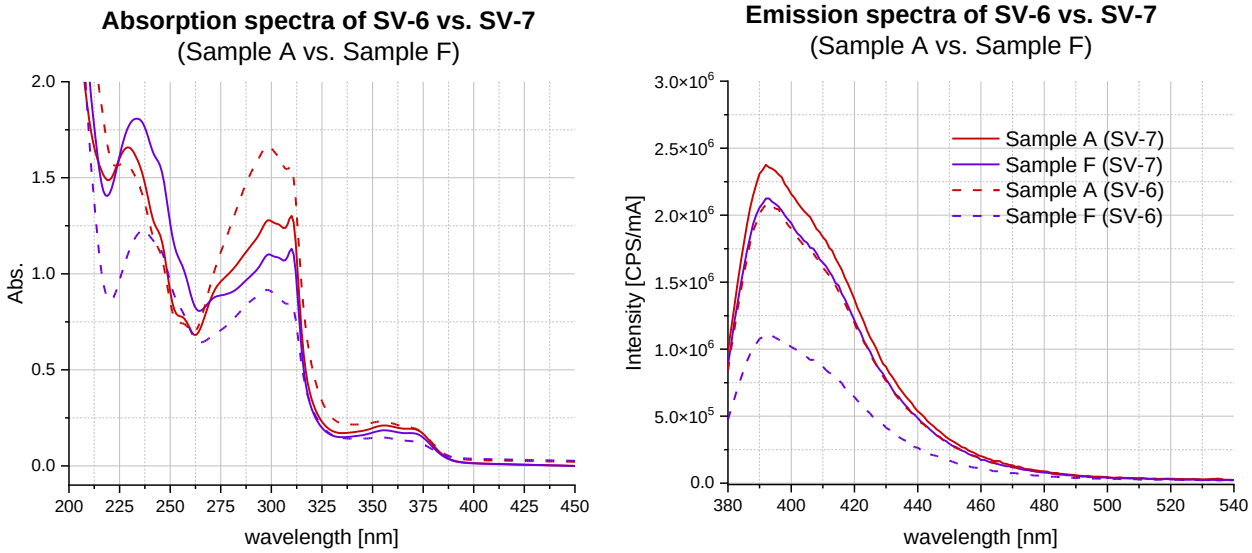


Figure S17. Comparison of absorption (left) as well as emission (right) spectra of Sample A and Sample F of SV-6 (dashed lines) and SV-7 (continuous line).

6.6 Lifetime measurements: Time-correlated single photon counting

The time-correlated single photon counting (TCSPC) measurements used the FluoroMax-4 spectrometer, DataStation (v2.7), EzTime TM (v3.3.14.49) and Delta Diode TM LED 370 nm (Model DD-370) all by Horiba© Scientific. Preparation of samples was identical to that of the steady-state luminescence experiments, using the exact same nomenclature when referring to a sample (e.g. Sample A of SV-1 is identical to Sample A of TCSPC experiment no.1). For the examination of the lifetime we used a measurement range of 200 ns and a band pass of 3 nm. Experiments were run until 10000 counts were reached. The fitting range was determined by examining Sample A of SV-1. A bin range of 950 - 2000 was set for the decays and 900 - 2000 for the IRF (Prompt) during fitting. ChiSq values were typically ~1.1 when fitting with two exponentials. A sufficiently good ChiSq (~1) was not found for single exponential fitting in any case (always >2).

TCSPC experiment no. 1 (identical sample preparation to SV-1, 0.1 mM T*p*AA):

The lifetime for ***T*pAA** was biexponential with 2.29 ns (32%) for τ_1 and 8.19 ns (68%) for τ_2 (Table S10). The previously reported lifetime was a single value of 3.6 ns,[23] which is close to the weighted average of the two values of our exponential decay (3.15 ns). We assume a monoexponential fitting was used in the previous literature with a sub-optimal fit.

In presence of 1 equiv. **3a** (Sample F) we found lifetimes of 2.30 ns (37%) for τ_1 and 8.31 ns (63%) for τ_2. The comparison of the calculated lifetimes of Sample A and Sample F clearly show no quenching (quenching fraction for τ_1: <0.5% for τ_2: 1.5%).

TCSPC experiment no. 2 (identical sample preparation to SV-2, 1.0 mM T*p*AA):

At the higher concentration (1.0 mM), the lifetime was biexponential with 2.28 ns for τ_1 (36%) and 8.04 ns (64%) for τ_2 (Table S11). Results of Sample A were exactly consistent with the lower concentration results (no. 1). In Sample F, we found 2.23 ns (39%) for τ_1 and 7.74 ns (61%) for τ_2.Therefore, a very minor quenching of the second decay component of the lifetime was observed (quenching fraction for τ_1: 2% for τ_2: 4%).

Although the values in Sample F were consistently lower than Sample A (both experiments no. 1 and no. 2), the differences in numbers are likely within the expected error of fitting in TCSPC.

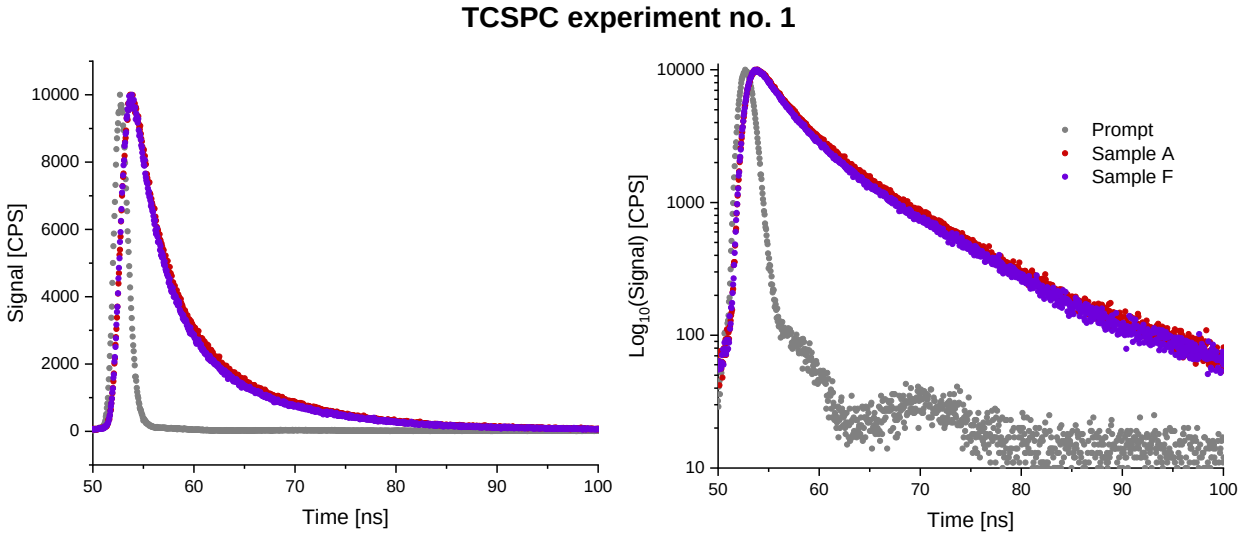


Figure S18. Decay of TCSPC experiment no. 1 showing Prompt (grey), Sample A (**T*p*AA**, red) and Sample F (**T*p*AA** + 1 equiv. **3a**, purple) in linear (left) and logarithmic (right) plot.

Table S10. Results of TCSPC experiment no. 1 (0.1 mM T*p*AA)

Sample Name	*Sample A*	*Sample F*
chi-square	1.09	1.08
Lifetime τ_1 [ns]	2.29	2.30
Relative amplitude τ_1	31.82%	36.59%
Lifetime τ_2 [ns]	8.19	8.31
Relative amplitude τ_2	68.18%	63.41%

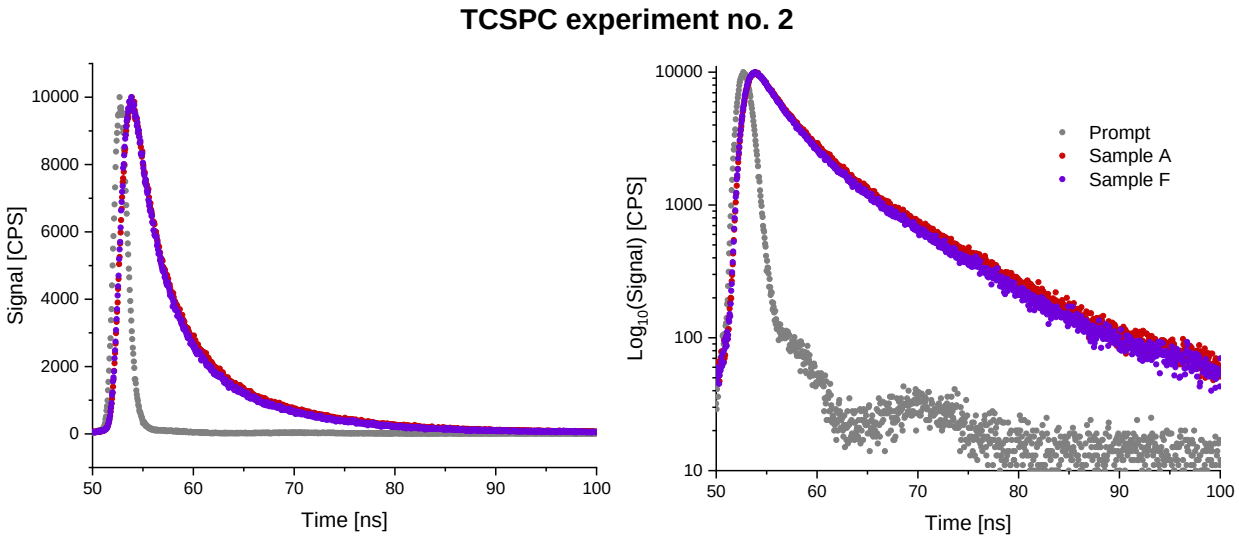


Figure S19. Decay of TCSPC experiment no. 1 showing Prompt (grey), Sample A (**T*p*AA,** red) and Sample F (**T*p*AA** + 1 equiv. **3a**, purple) in linear (left) and logarithmic (right) plot.

Table S11. Results of TCSPC experiment no. 2 (1.0 mM T*p*AA)

Sample Name	*Sample A*	*Sample F*
chi-square	1.12	1.06
Lifetime τ_1 [ns]	2.28	2.23
Relative amplitude τ_1	36.44%	38.74%
Normalized τ_1	0.67	0.69
Lifetime τ_2 [ns]	8.04	7.74
Relative amplitude τ_2	63.56%	61.26%
Normalized τ_2	0.33	0.31

7 OTHER CHARACTERIZATION DATA

7.1 Cyclic Voltammetry

The cyclic voltammetry data was collected with Autolab device (PGSTAT302N Metrohm) and the program Nova (version 1.11). Glassy carbon (3.0 mm diameter BASi MF-2012) was used as a working electrode and as counter electrode a Pt wire. An Ag wire was connected to the set up as a reference electrode (pseudo reference electrode). For all measurements was used commercial MeCN, $^{n}Bu_4N \cdot PF_6$ (0.10 M, > 98% purity) as electrolyte and $Fe(Cp)_2$ as internal standard. Before each experiment, the sample was degassed by bubbling argon through the mixture for 3 min. The data considered the shift of Fc^+/Fc and corrected the $E_{1/2}$ of $Fe(Cp)_2$ to +0.45 V, resulting in all data shown being as they would be versus SCE as reference electrode.

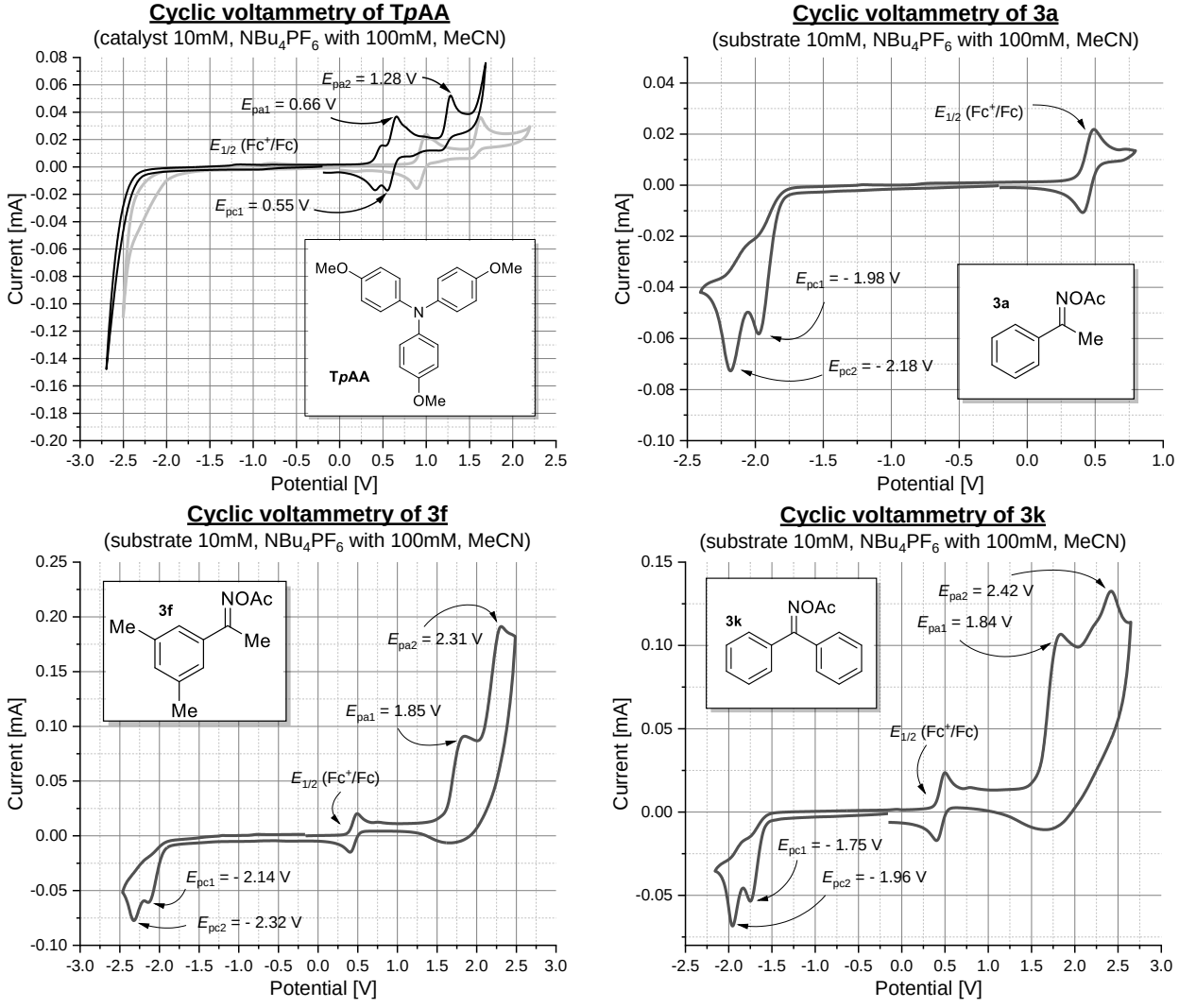


Figure S20. CV data of catalyst **T*p*AA** and oxime esters **3a**, **3f**, and **3k**. In gray, the CV experiment of **T*p*AA** (see top left) without $Fe(Cp)_2$ is shown to distinguish between the first reversible oxidation and $Fe(Cp)_2$.

7.2 X-ray structure of azine 2a

Crystal data were collected using a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer equipped with an Oxford Cryosystems Cryostream 700 low-temperature device operating at T = 126.06(10) K by the X-Ray structure analysis department of the University of Regensburg. Data were measured using ω scans with Cu K_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.42.73a.[24] The maximum resolution that was achieved was Θ = 73.812° (0.80 Å). The unit cell was refined using CrysAlisPro 1.171.42.73a[24] on 11814 reflections, 70% of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.42.73a.[24] The final completeness is 99.90 % out to 73.812° in Θ. A gaussian absorption correction was performed using CrysAlisPro 1.171.42.73a.[24] Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[25] The absorption coefficient μ of this material is 0.570 mm^{-1} at this wavelength (λ = 1.54184Å) and the minimum and maximum transmissions are 0.462 and 1.000. The structure was solved and the space group P21/n (# 14) determined by the ShelXT 2018/2 structure solution program[26] using dual methods and by using Olex2 1.5-alpha as the graphical interface.[27] The model was refined with ShelXL 2018/3[26] using full matrix least squares minimization on $\mathbf{F^2}$. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

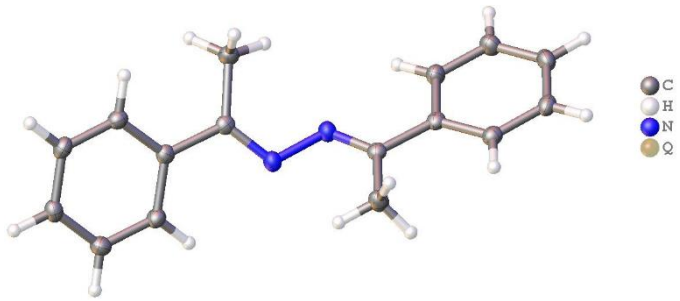


Figure S21. Crystal structure of azine **2a**. CCDC deposition number: 2288426

Single clear colorless prism-shaped crystals of **2a** were used. A suitable crystal with dimensions 0.26 × 0.20 × 0.07 mm^3 was selected and mounted on a MITIGEN holder inert oil on a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The crystal was kept at a steady T = 126.06(10) K during data collection.

Table S12. Summary of results of crystal structure of azine 2a

Formula	$C_{16}H_{16}N_2$
$D_{calc.}$/ g cm^{-3}	1.246
μ/mm^{-1}	0.570
Formula Weight	236.31
Colour	clear colourless
Shape	prism-shaped
Size/mm^3	0.26×0.20×0.07
T/K	126.06(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	11.58810(10)
b/Å	7.38790(10)
c/Å	14.8464(2)
α/°	90
β/°	97.5220(10)
γ/°	90
V/Å^3	1260.09(3)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_α
θ_{min}/°	4.562
θ_{max}/°	73.812
Measured Refl's.	16836
Indep't Refl's	2468
Refl's I≥2 σ(I)	2351
R_{int}	0.0159
Parameters	227
Restraints	0
Largest Peak	0.203
Deepest Hole	-0.187
GooF	1.080
wR_2 (all data)	0.0938
wR_2	0.0928
R_1 (all data)	0.0335
R_1	0.0324

Table S13. Structure Quality Indicators

Reflections:	d min (Cu\a) 2Θ=147.6° 0.80	I/σ(I) 115.1	Rint 1.59%	Full 135.4° 97% to 147.6° 99.9
Refinement:	Shift -0.001	Max Peak 0.2	Min Peak -0.2	GooF 1.080

There is a single formula unit in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1. The moiety formula is $C_{16}H_{16}N_2$.

Table S14. Data Plots: Diffraction Data

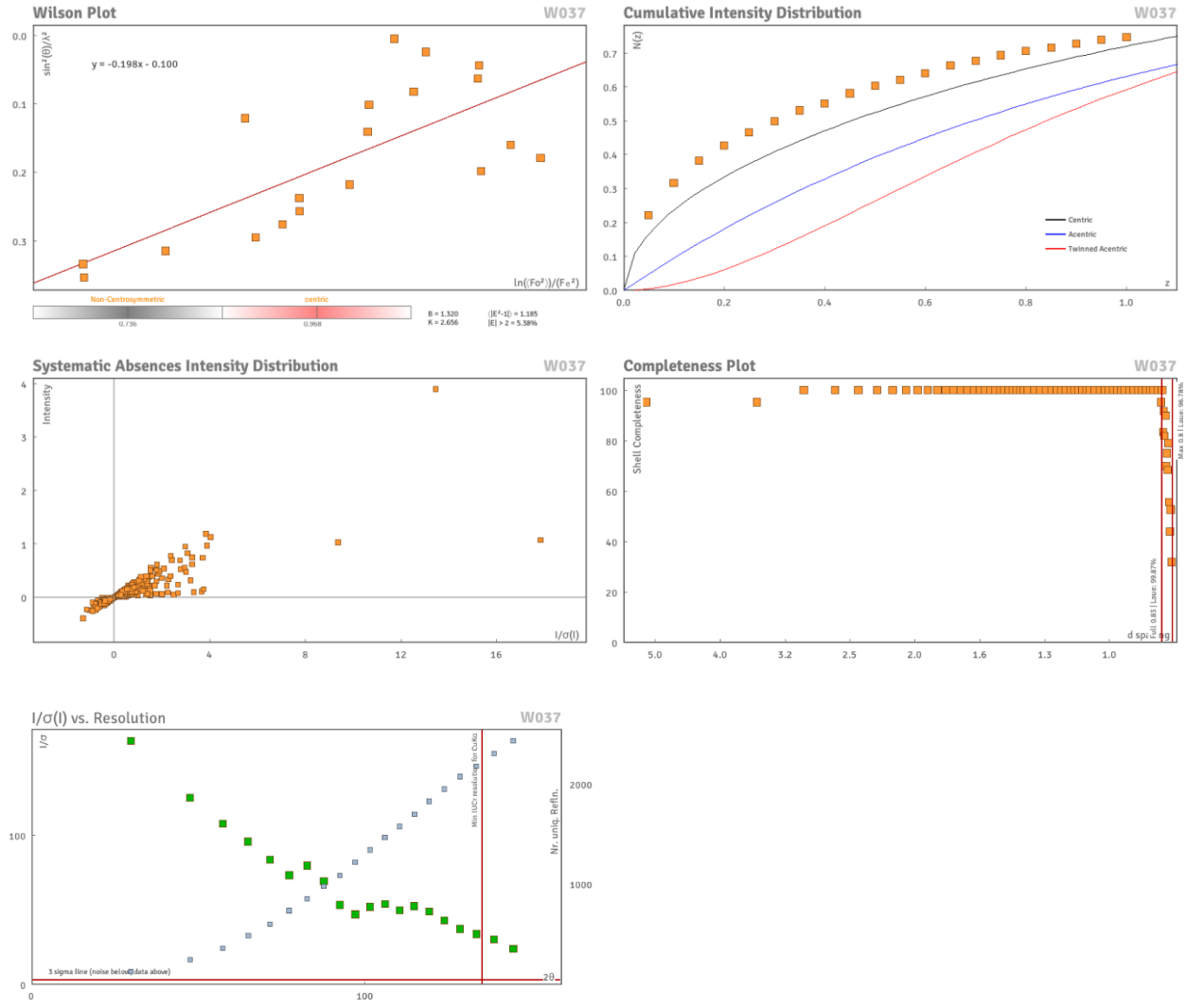


Table S15. Data Plots: Refinement and Data

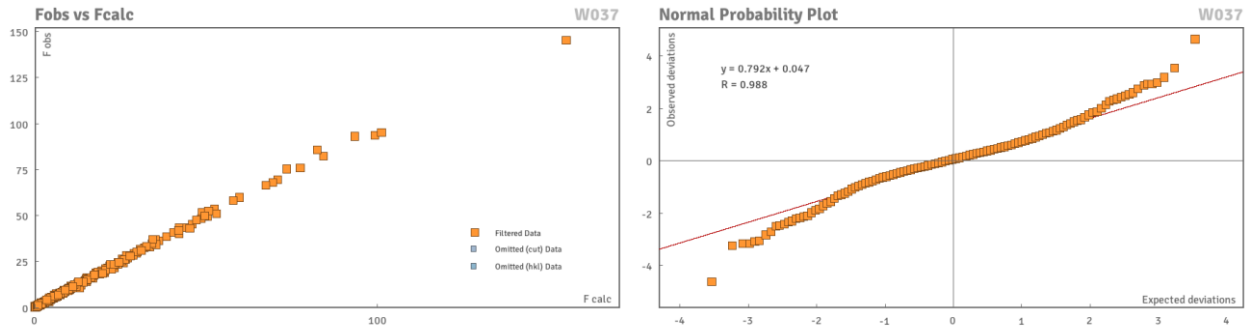


Table S16. Reflection Statistics

Total reflections (after filtering)	17841	Unique reflections	2468
Completeness	0.968	Mean I/σ	67.42
hkl_{max} collected	(14, 9, 15)	hkl_{min} collected	(-12, -8, -18)
hkl_{max} used	(14, 9, 18)	hkl_{min} used	(-14, 0, 0)

Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	14.72	d_{min} used	0.8
Friedel pairs	2152	Friedel pairs merged	1
Inconsistent equivalents	4	R_{int}	0.0159
R_{sigma}	0.0087	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(2119, 1801, 1116, 618, 378, 199, 103, 100, 65, 38, 20, 20, 10, 2, 2, 3, 2)	Maximum multiplicity	26
Removed systematic absences	1005	Filtered off (Shel/OMIT)	0

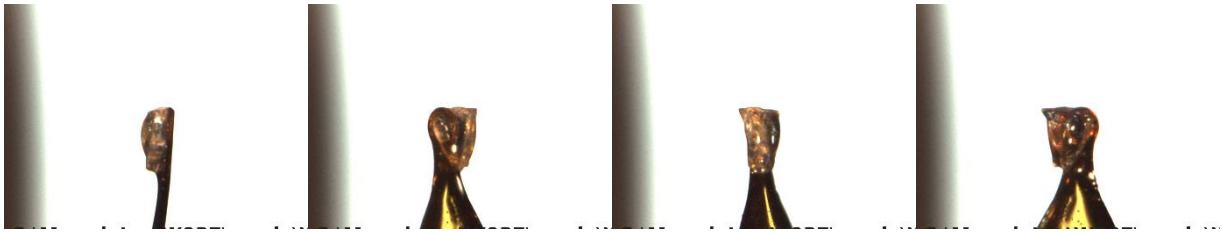


Figure S22. Single clear colorless prism-shaped crystals

Table S17. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
N1	6337.9(6)	2001.6(10)	4889.3(5)	20.13(19)
N2	5952.7(6)	2018.2(10)	3958.4(5)	20.72(19)
C7	5531.0(7)	2254.6(11)	5396.7(6)	17.7(2)
C15	6623.2(7)	2832.4(11)	3464.1(6)	17.8(2)
C14	6856.5(7)	3777.1(12)	1869.3(6)	20.4(2)
C9	6233.9(7)	2838.2(11)	2467.3(6)	17.9(2)
C1	5890.0(7)	2197.8(11)	6393.7(6)	17.4(2)
C13	6461.6(8)	3828.3(12)	942.1(6)	22.4(2)
C5	5566.5(8)	3010.4(12)	7921.1(6)	22.0(2)
C6	5204.8(8)	2999.6(12)	6990.7(6)	20.5(2)
C10	5208.2(8)	1939.3(12)	2112.8(6)	21.4(2)
C2	6941.3(7)	1385.7(12)	6755.1(6)	20.4(2)
C8	4282.0(8)	2647.2(13)	5037.2(6)	22.9(2)
C4	6604.2(8)	2182.5(12)	8271.2(6)	21.9(2)
C3	7287.9(8)	1365.2(13)	7684.0(6)	22.9(2)
C16	7729.0(8)	3789.7(13)	3827.2(6)	24.6(2)
C12	5447.8(8)	2928.5(13)	600.9(6)	23.8(2)
C11	4826.3(8)	1980.2(13)	1189.1(6)	24.7(2)

Table S18. Anisotropic Displacement Parameters (×10^4) for 2a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	21.8(4)	22.1(4)	16.5(4)	0.4(3)	2.3(3)	-0.5(3)
N2	21.7(4)	23.9(4)	16.5(4)	0.2(3)	2.5(3)	-0.4(3)
C7	19.5(4)	13.7(4)	20.0(4)	0.8(3)	3.0(3)	-1.5(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C15	17.9(4)	15.9(4)	19.8(4)	-0.3(3)	3.0(3)	3.0(3)
C14	19.7(4)	18.8(4)	23.1(4)	0.7(3)	4.8(3)	1.1(3)
C9	18.6(4)	15.9(4)	19.7(4)	0.0(3)	4.1(3)	3.3(3)
C1	18.8(4)	14.9(4)	19.0(4)	0.8(3)	3.8(3)	-2.2(3)
C13	24.7(4)	22.0(4)	21.9(4)	3.7(3)	8.8(3)	4.2(3)
C5	22.7(4)	23.0(5)	21.5(4)	-2.3(3)	7.8(3)	-1.2(3)
C6	18.8(4)	20.2(4)	22.9(4)	0.8(3)	4.1(3)	1.2(3)
C10	20.8(4)	23.2(5)	20.4(4)	2.3(3)	3.9(3)	-1.1(3)
C2	20.7(4)	20.4(4)	20.9(4)	-0.2(3)	5.1(3)	2.3(3)
C8	18.8(4)	28.1(5)	21.7(4)	1.2(4)	1.5(3)	0.1(3)
C4	25.1(4)	22.7(5)	17.8(4)	0.6(3)	2.4(3)	-3.3(3)
C3	20.8(4)	24.3(5)	23.1(4)	1.8(3)	1.2(3)	2.3(3)
C16	21.8(4)	30.7(5)	20.6(4)	1.9(4)	0.4(3)	-4.4(4)
C12	27.6(5)	27.1(5)	16.7(4)	1.5(3)	2.1(3)	5.3(3)
C11	23.1(4)	28.4(5)	22.0(5)	0.1(4)	0.2(4)	-1.6(4)

Table S19. Bond Lengths in Å for 2a.

Atom	Atom	Length/Å
N1	N2	1.3957(10)
N1	C7	1.2888(11)
N2	C15	1.2858(11)
C7	C1	1.4848(11)
C7	C8	1.5039(12)
C15	C9	1.4896(12)
C15	C16	1.5007(12)
C14	C9	1.3991(12)
C14	C13	1.3931(12)
C9	C10	1.4025(12)
C1	C6	1.3969(12)
C1	C2	1.4003(12)
C13	C12	1.3867(13)
C5	C6	1.3900(12)
C5	C4	1.3880(13)
C10	C11	1.3851(12)
C2	C3	1.3851(12)
C4	C3	1.3903(13)
C12	C11	1.3917(13)

Table S20. Bond Angles in ° for 2a.

Atom	Atom		Angle/Å
C7	N1	N2	114.52(7)
C15	N2	N1	115.49(7)
N1	C7	C1	116.65(7)
N1	C7	C8	123.97(8)
C1	C7	C8	119.36(7)
N2	C15	C9	116.19(8)
N2	C15	C16	124.53(8)
C9	C15	C16	119.26(7)
C13	C14	C9	120.70(8)
C14	C9	C15	121.17(8)
C14	C9	C10	118.60(8)
C10	C9	C15	120.20(8)
C6	C1	C7	120.81(8)
C6	C1	C2	118.48(8)
C2	C1	C7	120.68(8)

Atom	Atom		Angle/Å
C12	C13	C14	120.06(8)
C4	C5	C6	120.22(8)
C5	C6	C1	120.70(8)
C11	C10	C9	120.43(8)
C3	C2	C1	120.70(8)
C5	C4	C3	119.57(8)
C2	C3	C4	120.31(8)
C13	C12	C11	119.69(8)
C10	C11	C12	120.52(9)

Table S21. Torsion Angles in ° for 2a

Atom	Atom	Atom	Atom	Angle/°
N1	N2	C15	C9	179.09(7)
N1	N2	C15	C16	-2.48(12)
N1	C7	C1	C6	159.45(8)
N1	C7	C1	C2	-18.62(11)
N2	N1	C7	C1	178.34(7)
N2	N1	C7	C8	-3.44(12)
N2	C15	C9	C14	176.04(8)
N2	C15	C9	C10	-2.01(12)
C7	N1	N2	C15	139.66(8)
C7	C1	C6	C5	-177.30(7)
C7	C1	C2	C3	178.66(8)
C15	C9	C10	C11	178.31(8)
C14	C9	C10	C11	0.22(13)
C14	C13	C12	C11	0.19(13)
C9	C14	C13	C12	-0.64(13)
C9	C10	C11	C12	-0.66(14)
C1	C2	C3	C4	-1.17(13)
C13	C14	C9	C15	-177.65(7)
C13	C14	C9	C10	0.43(12)
C13	C12	C11	C10	0.46(14)
C5	C4	C3	C2	0.42(13)
C6	C1	C2	C3	0.55(12)
C6	C5	C4	C3	0.93(13)
C2	C1	C6	C5	0.81(12)
C8	C7	C1	C6	-18.86(11)
C8	C7	C1	C2	163.07(8)
C4	C5	C6	C1	-1.56(13)
C16	C15	C9	C14	-2.48(12)
C16	C15	C9	C10	179.47(8)

Table S22. Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2	7425(9)	817(16)	6347(7)	26(3)
H6	4484(10)	3607(16)	6749(7)	26(3)
H14	7563(10)	4435(17)	2098(7)	26(3)
H13	6891(9)	4506(16)	528(7)	27(3)
H12	5168(10)	2950(16)	-47(8)	30(3)
H10	4784(9)	1273(16)	2515(8)	26(3)
H4	6842(9)	2171(15)	8936(8)	24(3)
H3	8015(10)	780(16)	7922(8)	29(3)
H5	5093(10)	3621(16)	8336(8)	27(3)
H11	4106(10)	1349(17)	961(8)	33(3)

Atom	x	y	z	U_{eq}
H8A	3741(11)	2100(17)	5428(8)	35(3)
H16A	7644(11)	5113(19)	3757(8)	43(3)
H8B	4122(10)	3953(19)	5020(8)	38(3)
H8C	4099(11)	2188(18)	4410(9)	40(3)
H16B	8373(11)	3437(19)	3490(9)	40(3)
H16C	7958(11)	3490(20)	4462(9)	47(4)

8 CONTINUOUS FLOW EXPERIMENTS

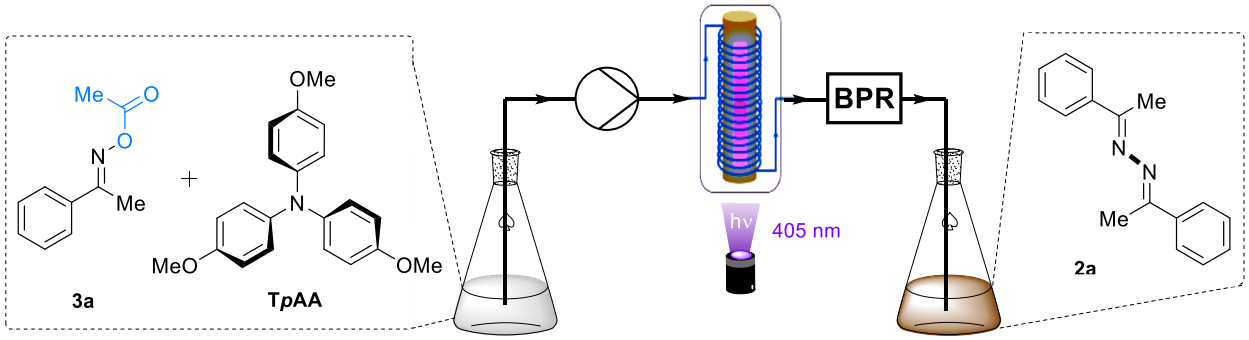
Figure S23. Vapourtec UV-150 Photochemical Reactor

To a vial equipped with a septum, dry MeCN (10 mL) was added different amounts of oxime ester **3a** and photocatalyst **T*p*AA**, as shown in Table S23.

The flow reactions were carried out on the Vapourtec UV-150 Photochemical Reactor at 405 nm. Temperature was controlled by a N_2 stream and was constant at 25 °C, with a reactor volume of 8.2 mL. Pressure was controlled by a back pressure regulator and monitored. First, the reactor was rinsed with MeCN (10 mL), then the reaction mixture was introduced to the reactor for 82 to 410 min (Entry 1-6, Table S23). The pressure was stable for this time. The product was collected as a brown solution.

Scale up synthesis of azine **2a** (657 mg, 40% isolated yield) was achieved via continuous recirculation through the reactor under irradiation with a 405 nm LED for 70 h, with a 0.1 mL/min flow rate.

Table S23. Continuous flow experiments



Entry	Scale (mmol)	Concentration (M)	Flow rate (mL/min)	R_T (min)	Conversion (%)	Yield of 2a (%)[a]	Productivity (mg/h)
1	1	0.1	0.02	410	80	61	8.6
2	1	0.1	0.05	164	64	37	13.1
3	1	0.1	0.1	82	34	34	24.1
4[b]	1	0.1	0.1	246	58	58	13.2
5	0.75	0.075	0.1	82	39	39	20.7
6	0.50	0.05	0.1	82	54	49	17.4
7	6.95	0.1	0.1	(70 h)	-	40 (0.66 g)[c]	-
8[d]	1	0.1	0.1	82	67	43	37.1

All reactions were carried out with (*E*)-1-phenylethan-1-one-O-acetyl oxime **3a** (1 equiv.) in MeCN (10 mL) under irradiation with a 405 nm LED. [a]After completion, the solvent was simply removed under reduced pressure and yield was determined by ^{1}H NMR of the reaction mixture with CH_2Br_2 as internal standard. [b]Mixture circulated through the reactor continuously under irradiation for three passes. [c]Isolated yield. [d]Reaction was performed with 100% **CabZ** as the Catalyst (no **T*p*AA**)

9 GREEN CHEMISTRY METRICS AND SAFETY DATA SHEET

9.1 Green Chemistry Metrics

Atom economy (AE)[28] and Hudlicky's Effective Mass Yield (EMY)[29] were employed as green chemistry metrics to characterize the reactions of the substrate scope herein. AE was calculated using Formula (1) and EMY was calculated with Formula (2):

$$1) \quad AE = \frac{MW(Product)x100}{\sum MW(Raw\ materials)+\sum MW(Reagents)}$$

$$2) \quad EMY = \frac{m(Product)x100}{\sum m(Raw\ materials)+\sum m(reagents)}$$

According to Sanofi's Solvent Selection Guide,[30] MeCN can be omitted as the most favourable (first choice) solvent from the family of polar aprotic solvents. Acetate was considered a benign side product, which is valuable and could be collected from aqueous extraction and further processed. As **T*p*AA** is consumed during the reaction we considered it within our calculations for EMY values. In Table S24, we present AE and EMY with and without acetate/with and without **T*p*AA**. For AE values, two times the molecular weight of the oxime ester was used to account for the reaction stoichiometry.

Table S24. Calculated Green Metric values

Azine	*Atom economy*		*EMY without **TpAA***		*EMY with **TpAA***	
	No acetate	With acetate	No acetate	With acetate	No acetate	With acetate
2a	67	100	57	86	42	62
2b	70	100	52	74	38	55
2c	72	100	58	81	44	62
2d	77	100	38	49	30	39
2e	76	100	63	83	50	65
2f	71	100	41	57	31	43
2g	72	100	50	70	38	53
2h	73	100	63	86	48	66
2i	71	100	45	63	34	47
2j	74	100	45	60	35	47
2k	75	100	34	45	26	35
2l	78	100	31	40	25	32
2m	78	100	49	63	39	50
2n	67	100	41	62	30	45
2o	68	100	40	59	29	43

When considering acetate as a benign by-product the AE and EMY are very high, as no CO_2 is released in the reaction, most of the input atoms/mass is actually utilized in the reaction. As **T*p*AA** as a catalyst is slowly converted into **CabZ** and cannot be fully recovered we consider EMY with **T*p*AA** as the most representative values and were also used in the Substrate Scope of the manuscript.

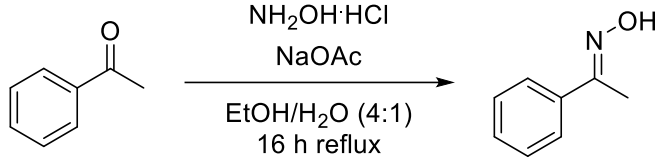
9.2 Safety/Risk Assessments

Safety data were taken from their respective data sheet provided by a supplier of the chemicals. Example risk assessments provided here are for the model reaction with the acetophenone derived oxime ester and show a typical scale for these reactions.

RISK ASSESSMENT FORM

Oxime Synthesis (model Substrate)

Reaction scheme or description of process



Materials and Hazards

Substance	Quantity	Hazards	Precautions
Acetophenone	1.17 mL	302-319	264-270-280-301-305+351+338-337+313
NaOAc	1.23 g	none	
Hydroxylamine Hydrochloride	1.04 g	290-302+312-315-317-319-351-373-410	273-280-301+312-302+352+312-305+351+338
EtOH	7.5 mL	225-319	210-233-240-241-242-305+351+338

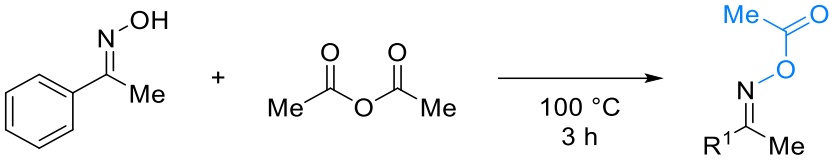
Type of protection device	Yes/No
• Goggles	Yes
• Lab coat	Yes
• Mask	No
• Gloves	Yes
• Other	No

The experiment is to run at °C: 100°C	FROM (Time/Date): xxx TO (Time/Date): yyy
Building: Chemistry	Room: zzz
Type of glassware used:	Round bottom flask (50 mL)

RISK ASSESSMENT FORM

Oxime ester Synthesis (Model Substrate)

Reaction scheme or description of process



Materials and Hazards

Substance	Quantity	Hazards	Precautions
Acetophenone Oxime	1.35 g	302-315-319-335	280-305+351+338
Acetic Anhydride	1.89 g	226-302-314-332	210-280-301+312-303+361+353-304+340+310-305+351+338

Type of protection device	Yes/No
• Goggles	Yes
• Lab coat	Yes
• Mask	No
• Gloves	Yes
• Other	No

The experiment is to run at °C: 100°C

FROM (Time/Date): xxx
TO (Time/Date): yyy

Building: Chemistry

Room: zzz

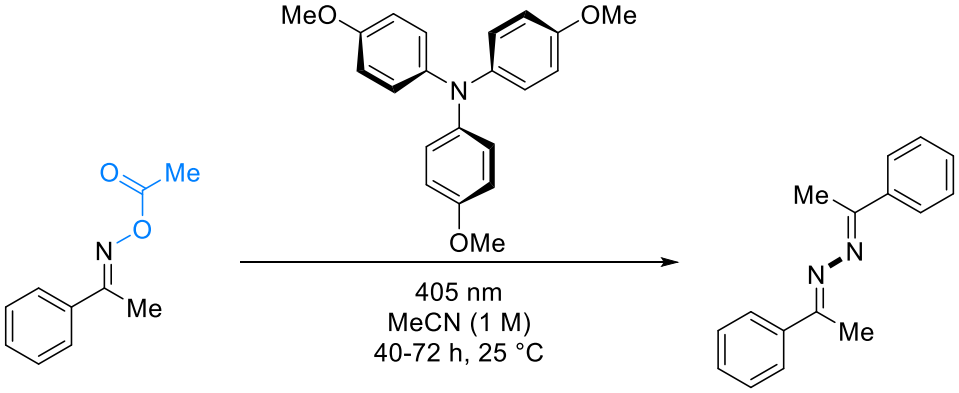
Type of glassware used:

Round bottom flask (50 mL)

RISK ASSESSMENT FORM

Typical Photo reaction (Model Substrate)

Reaction scheme or description of process



Materials and Hazards

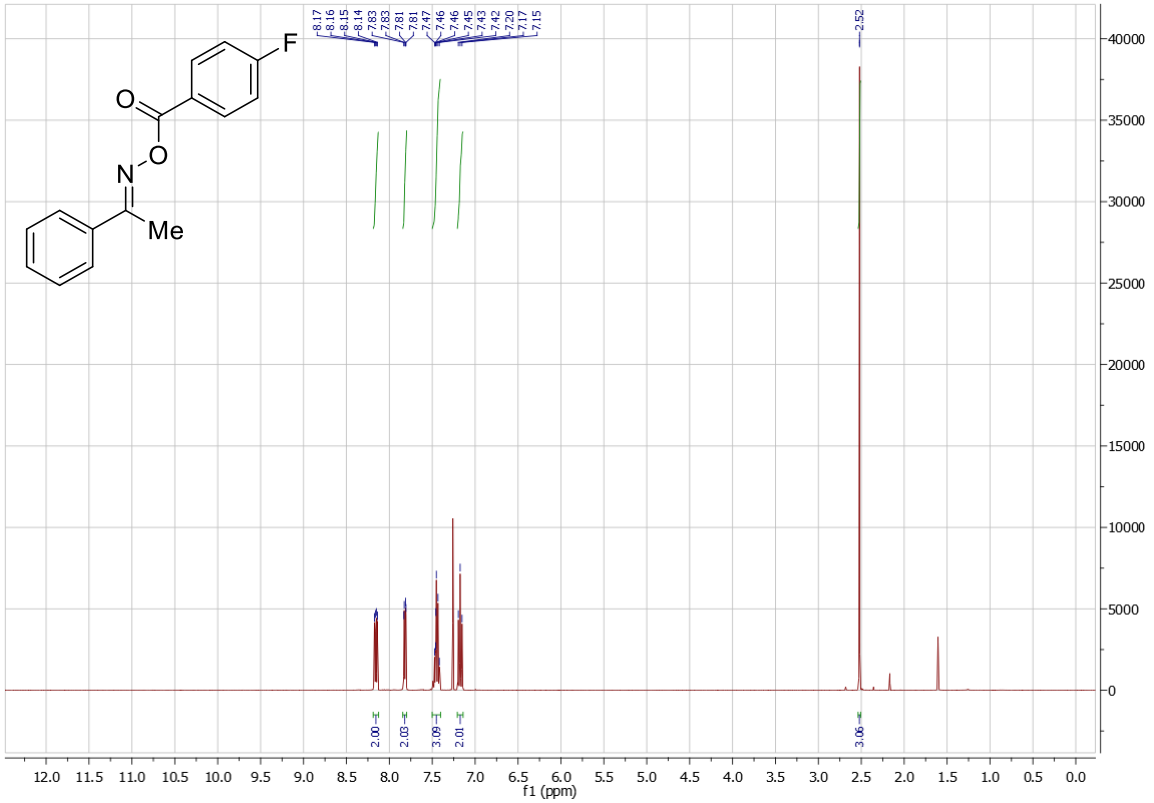
Substance	Quantity	Hazards	Precautions
Acetophenone Oxime ester	35.4 mg	Non found	Treat as toxic
T*p*AA	6.7 mg	302-315-319-335	280-305+351+338
MeCN	1 mL	225-302-312-319-332	210-280-305+351+338

Type of protection device	Yes/No
• Goggles	Yes (UV/goggles)
• Lab coat	Yes
• Mask	No
• Gloves	Yes
• Other	LEDs (covered in an enclosure)

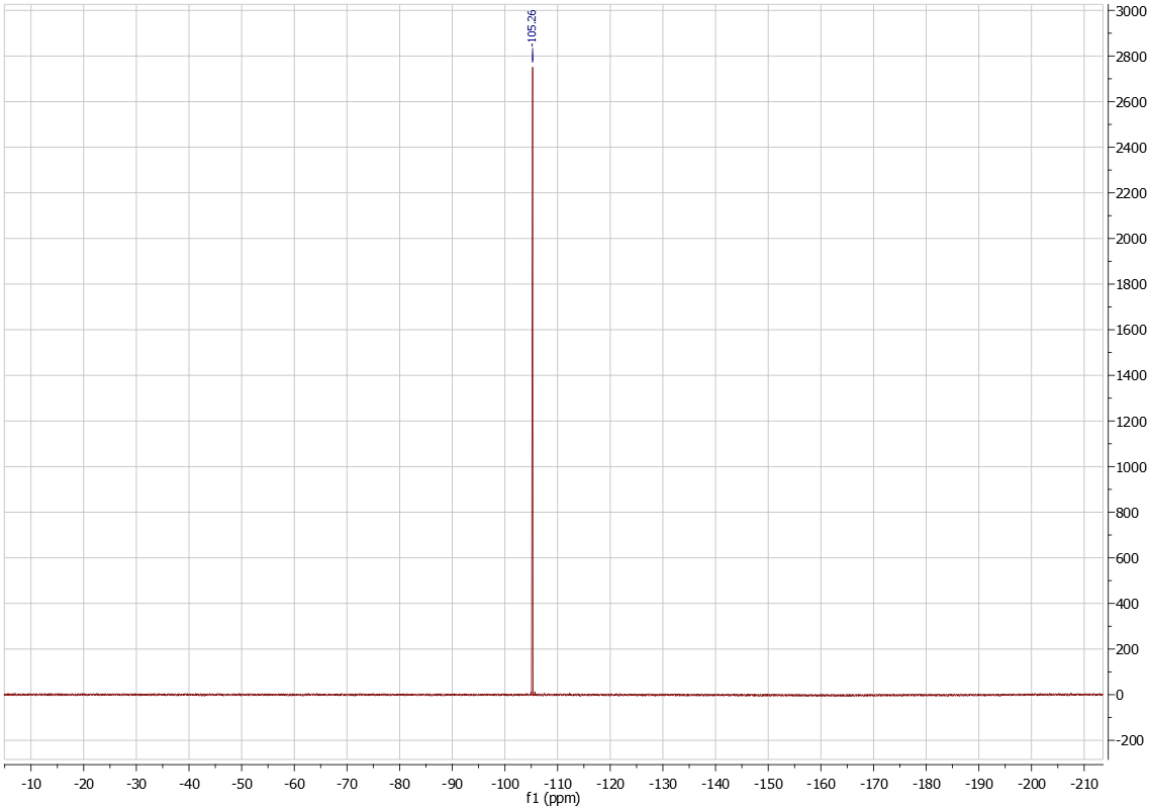
The experiment is to run at °C: 25°C with 405 nm light irradiation	FROM (Time/Date): xxx TO (Time/Date): yyy
Building: Chemistry	Room: zzz
Type of glassware used:	Crimp cap vial (5 mL)

10 ^{1}H NMR AND ^{13}C NMR SPECTRA

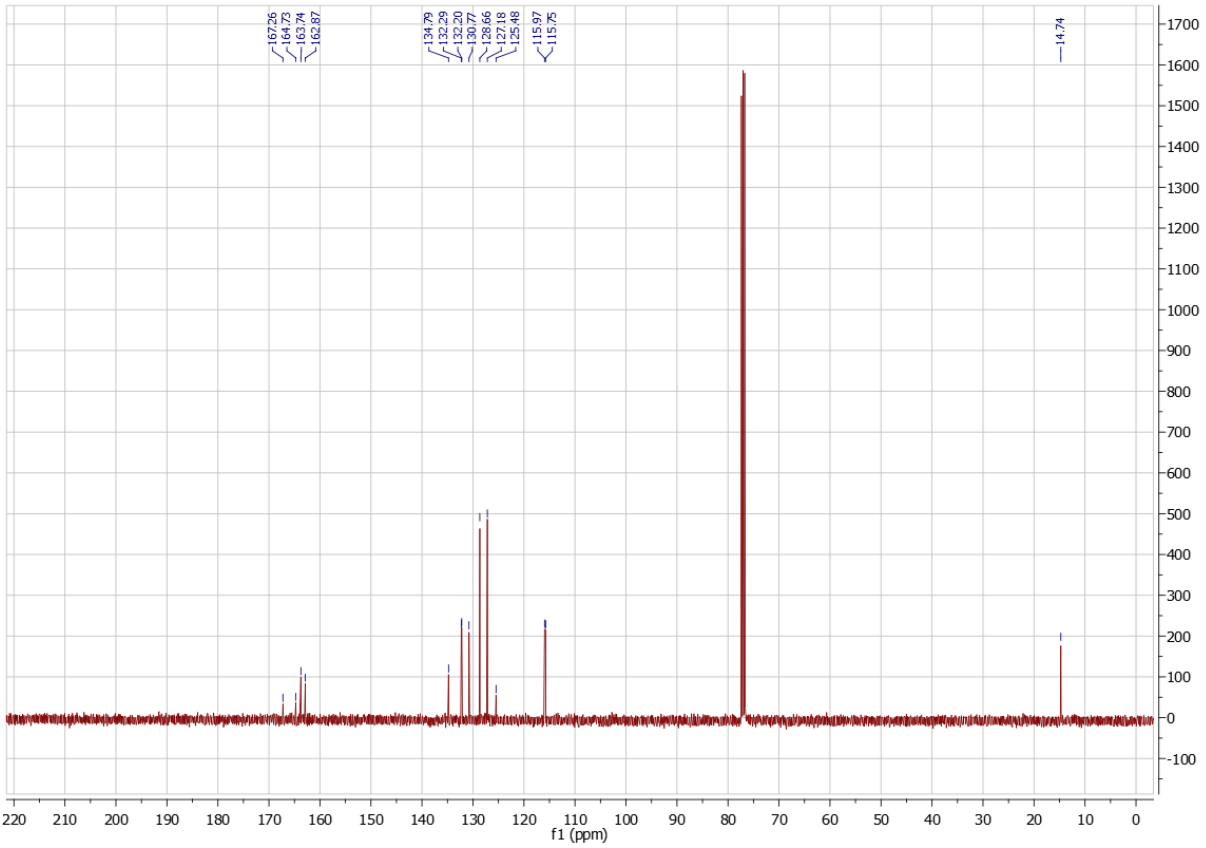
^{1}H-NMR (400 MHz, $CDCl_3$): **(*E*)-1-phenylethan-1-one O-(4-fluorobenzoyl) oxime (1a)**



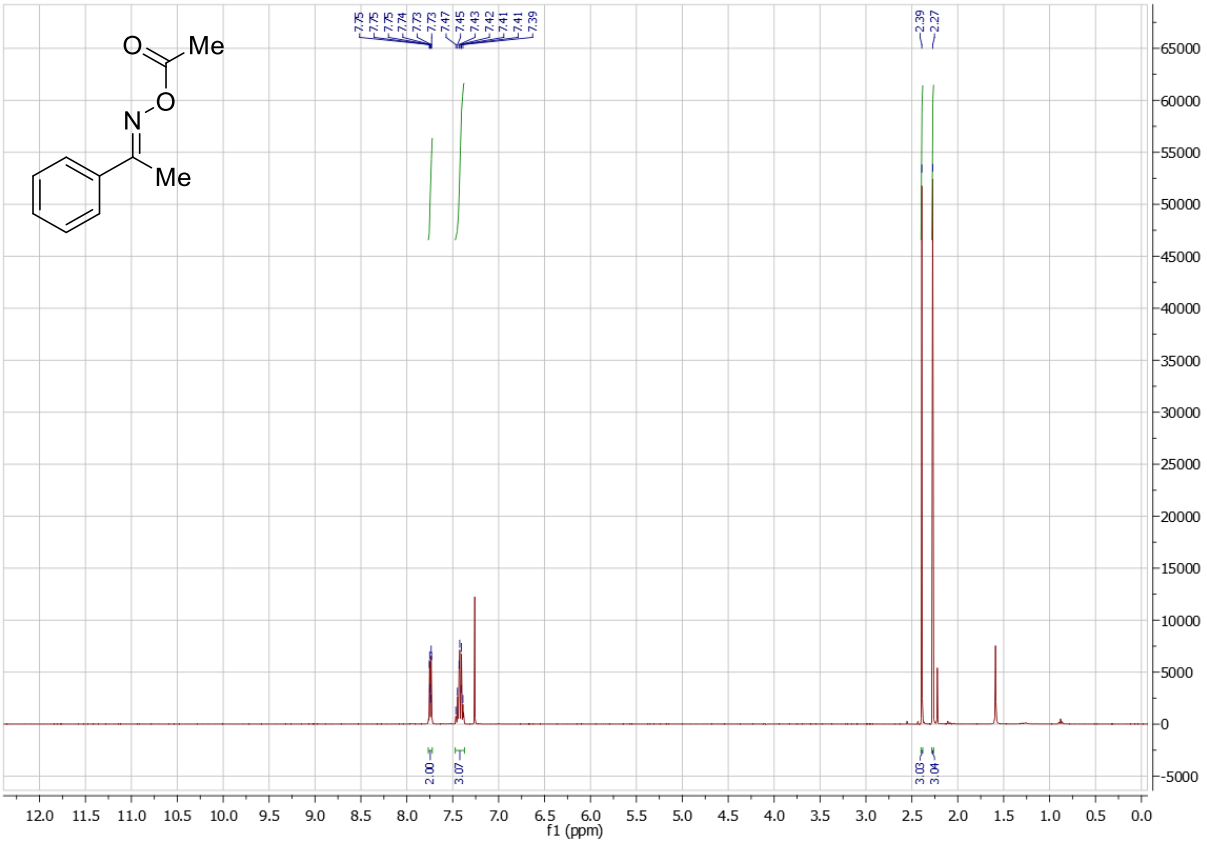
^{19}F NMR (377 MHz, $CDCl_3$)



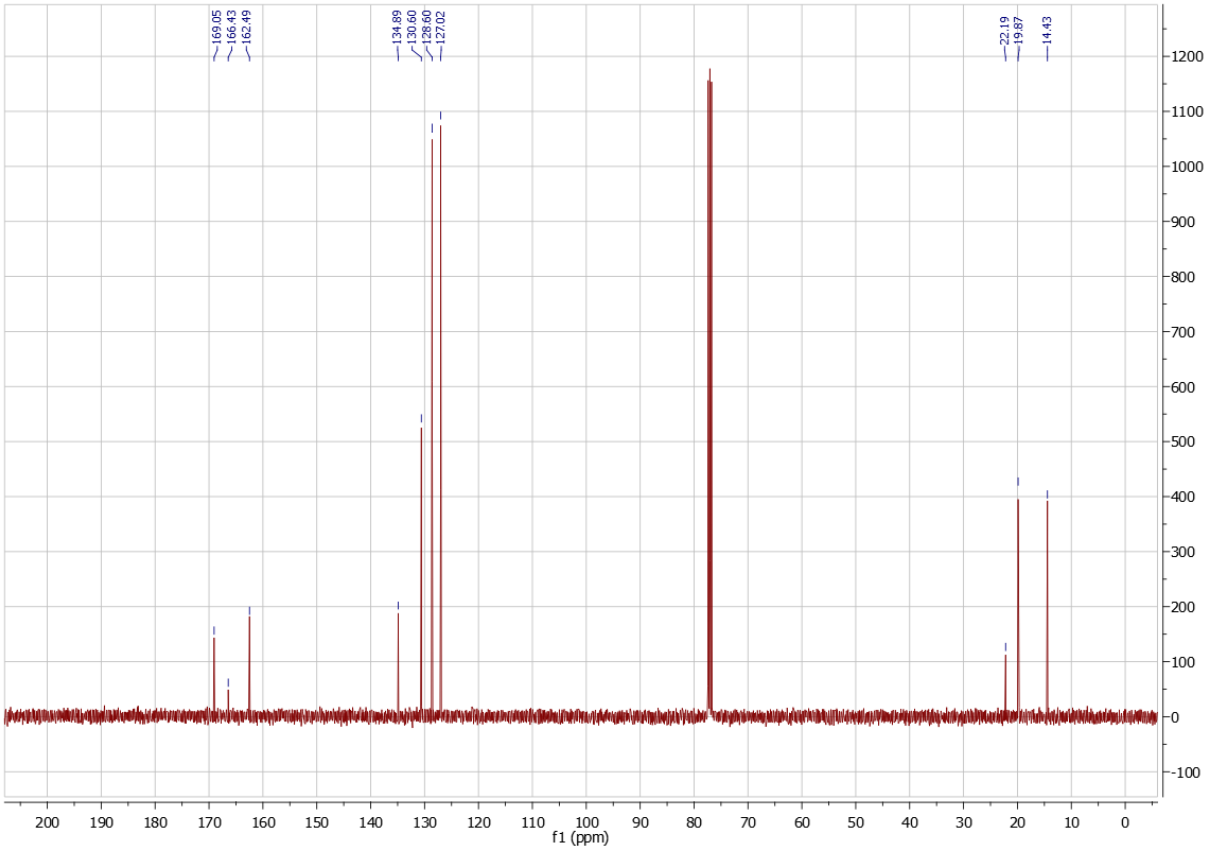
^{13}C NMR (75 MHz, $CDCl_3$)



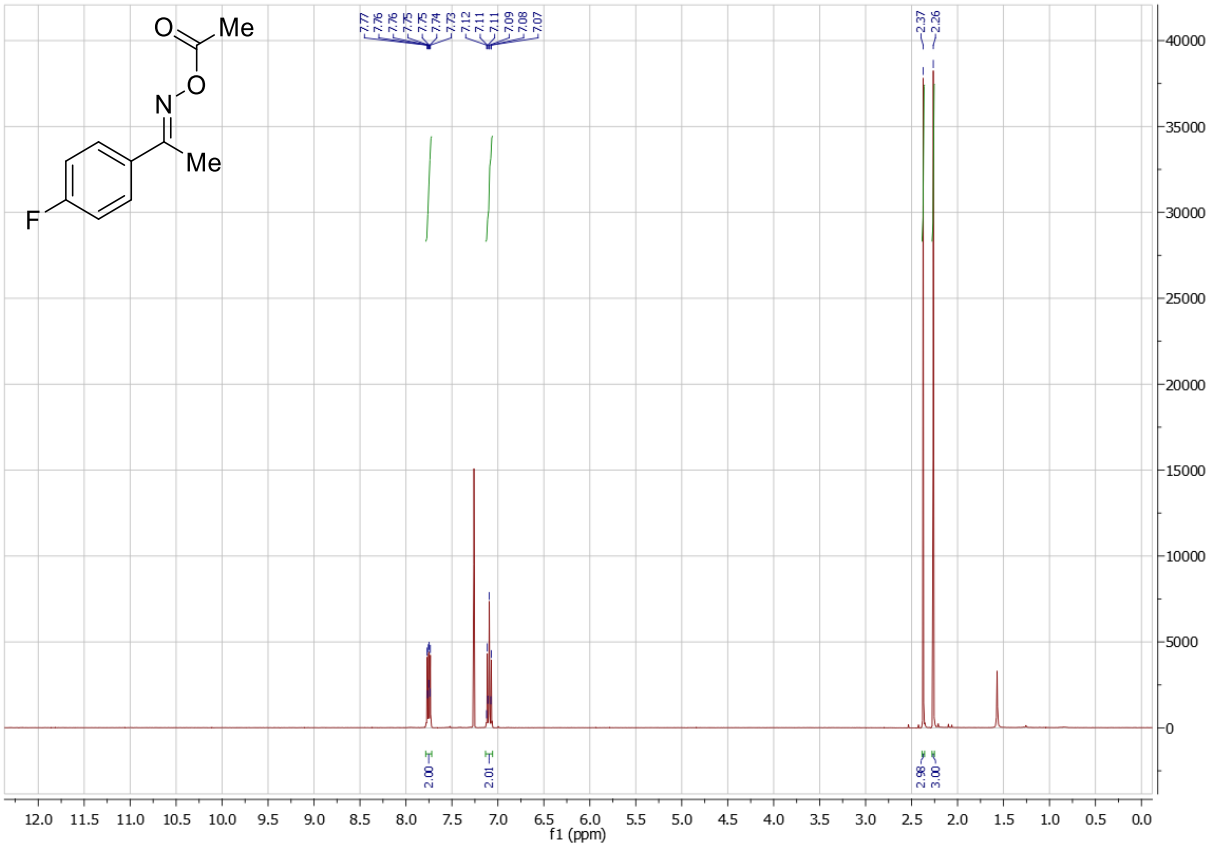
^{1}H NMR (400 MHz, $CDCl_3$): **(*E*)-1-phenylethan-1-one O-acetyl oxime (3a)**



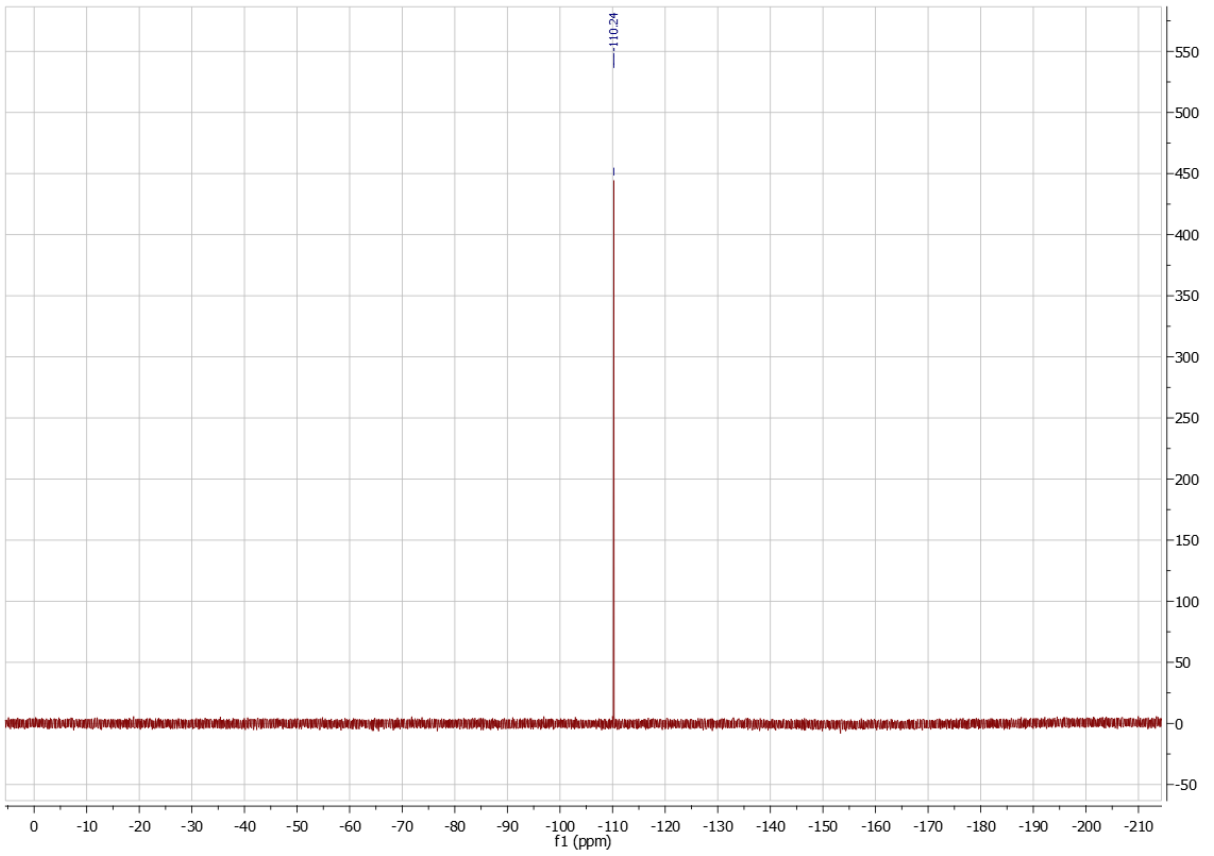
^{13}C NMR (101 MHz, $CDCl_3$)



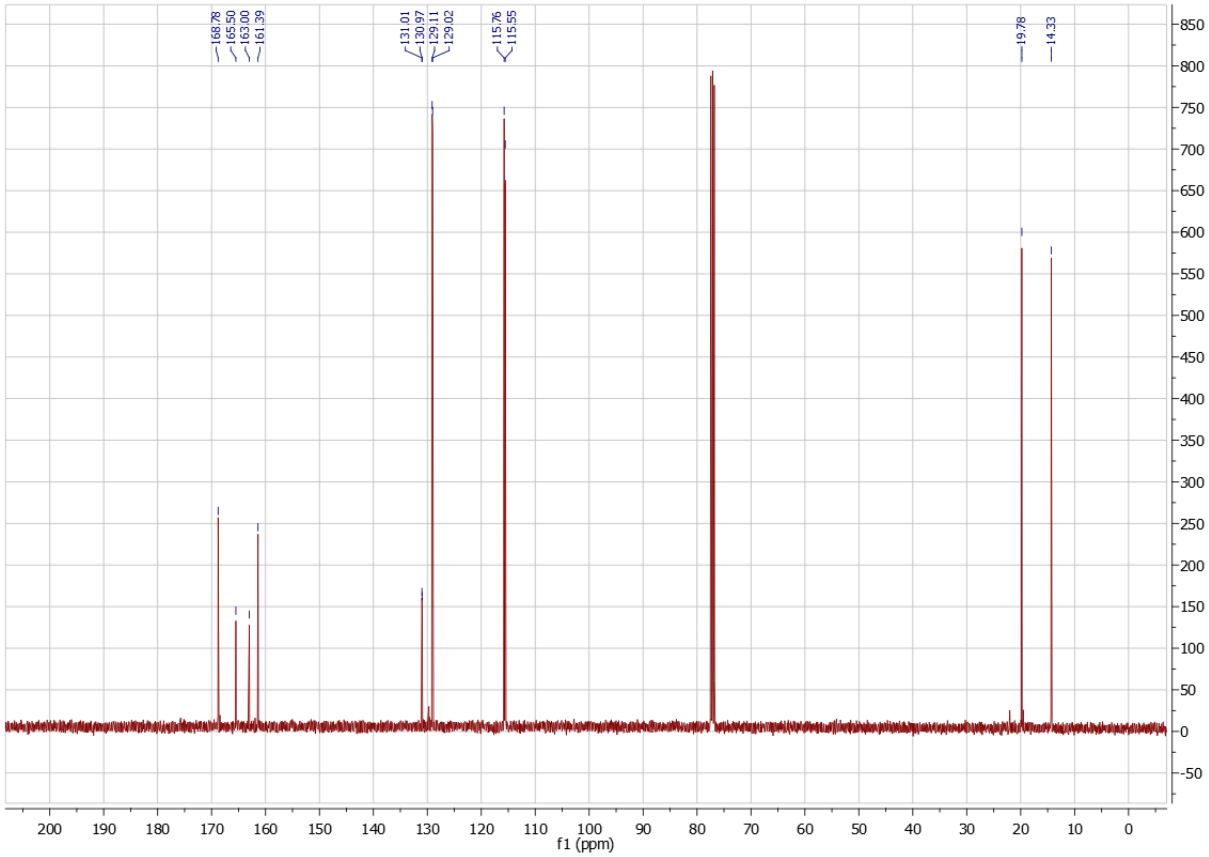
^{1}H NMR (400 MHz, $CDCl_3$): **(*E*)-1-(4-fluorophenyl)ethan-1-one O-acetyl oxime (3b)**



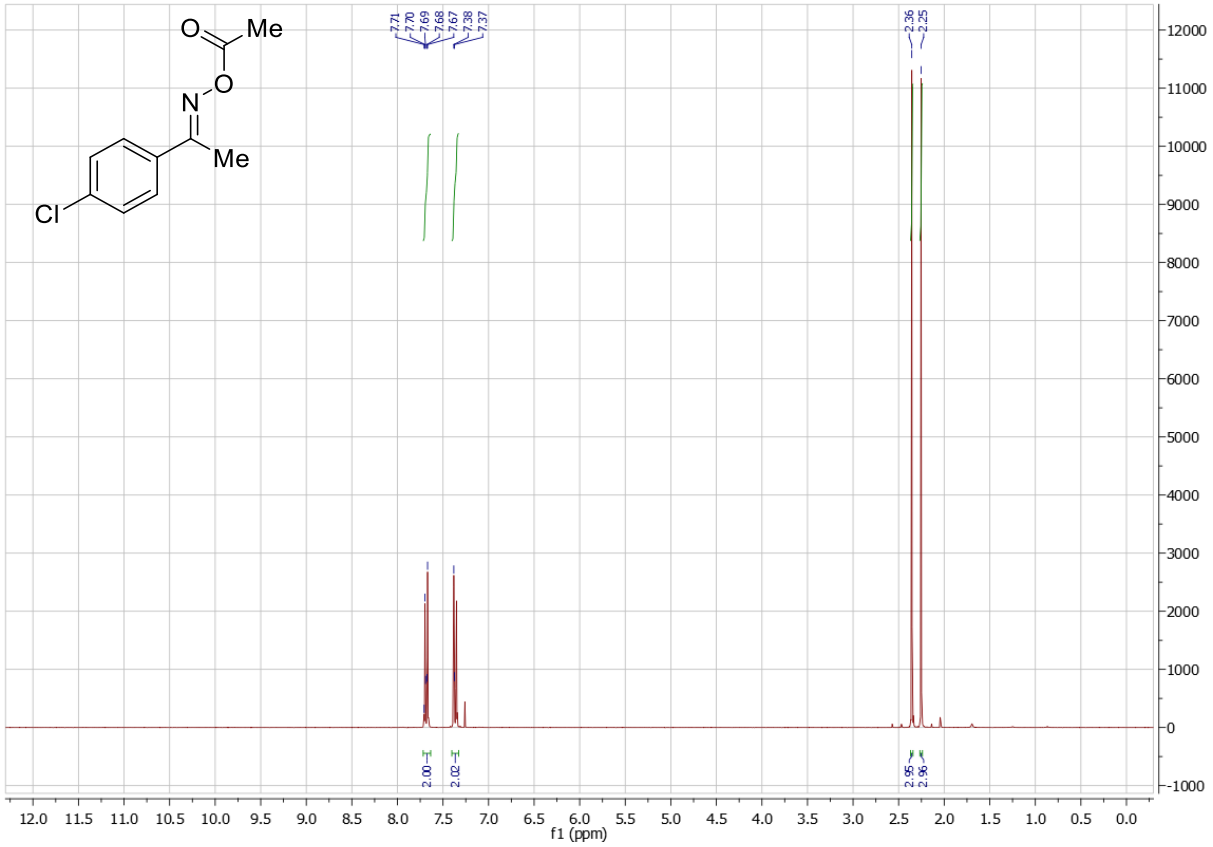
^{19}F NMR (377 MHz, $CDCl_3$)



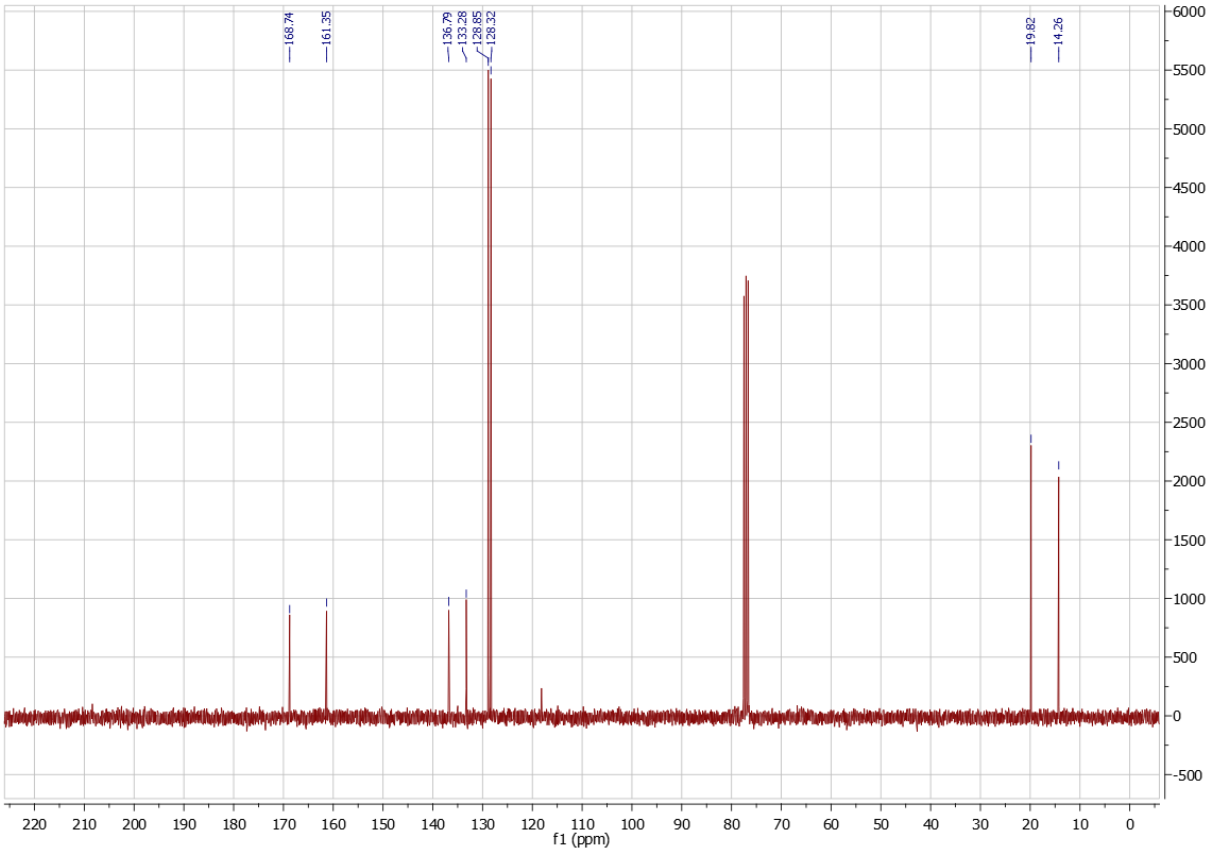
^{13}C NMR (101 MHz, $CDCl_3$)



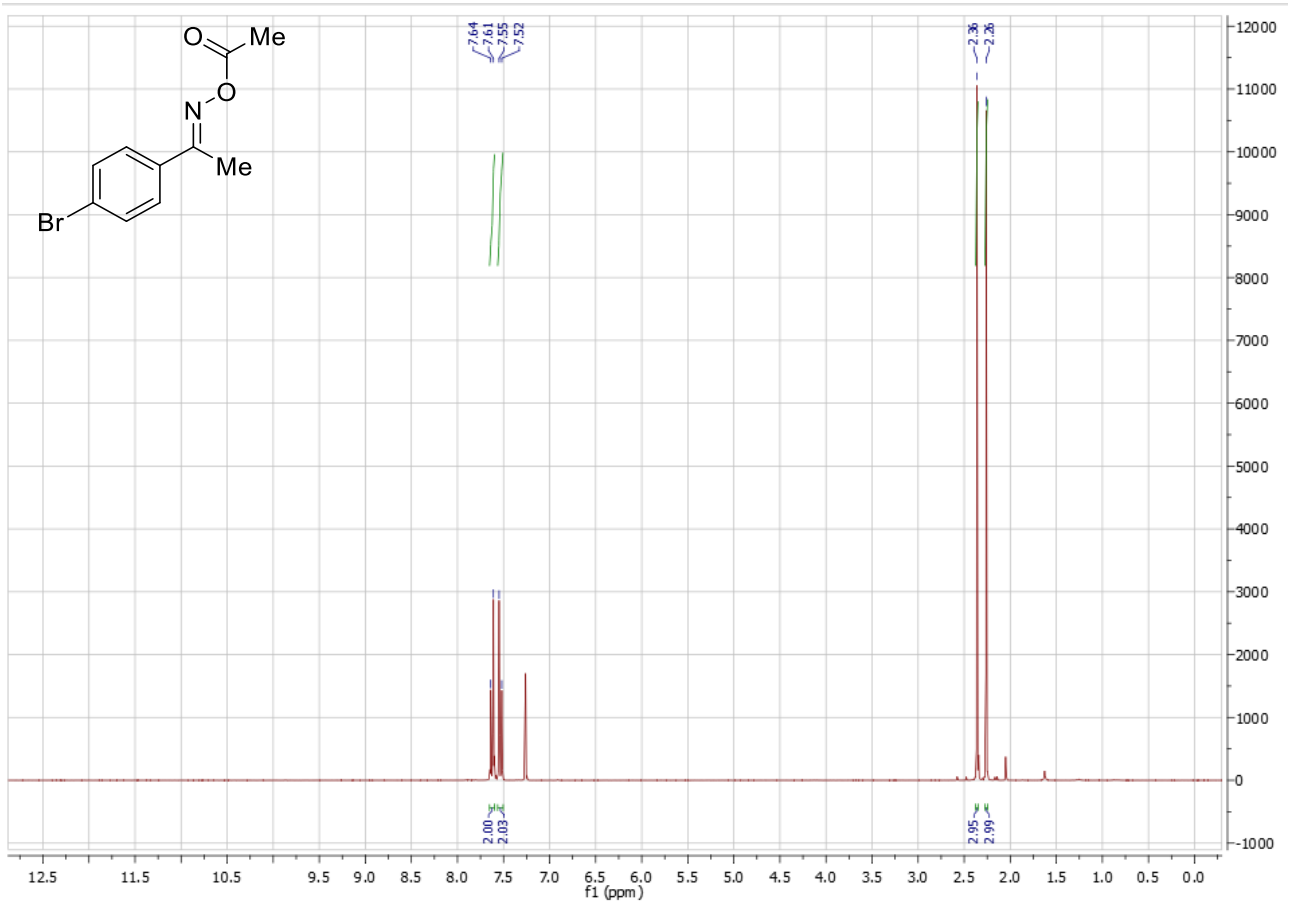
^{1}H NMR (400 MHz, $CDCl_3$): **(*E*)-1-(4-chlorophenyl)ethan-1-one O-acetyl oxime (3c)**



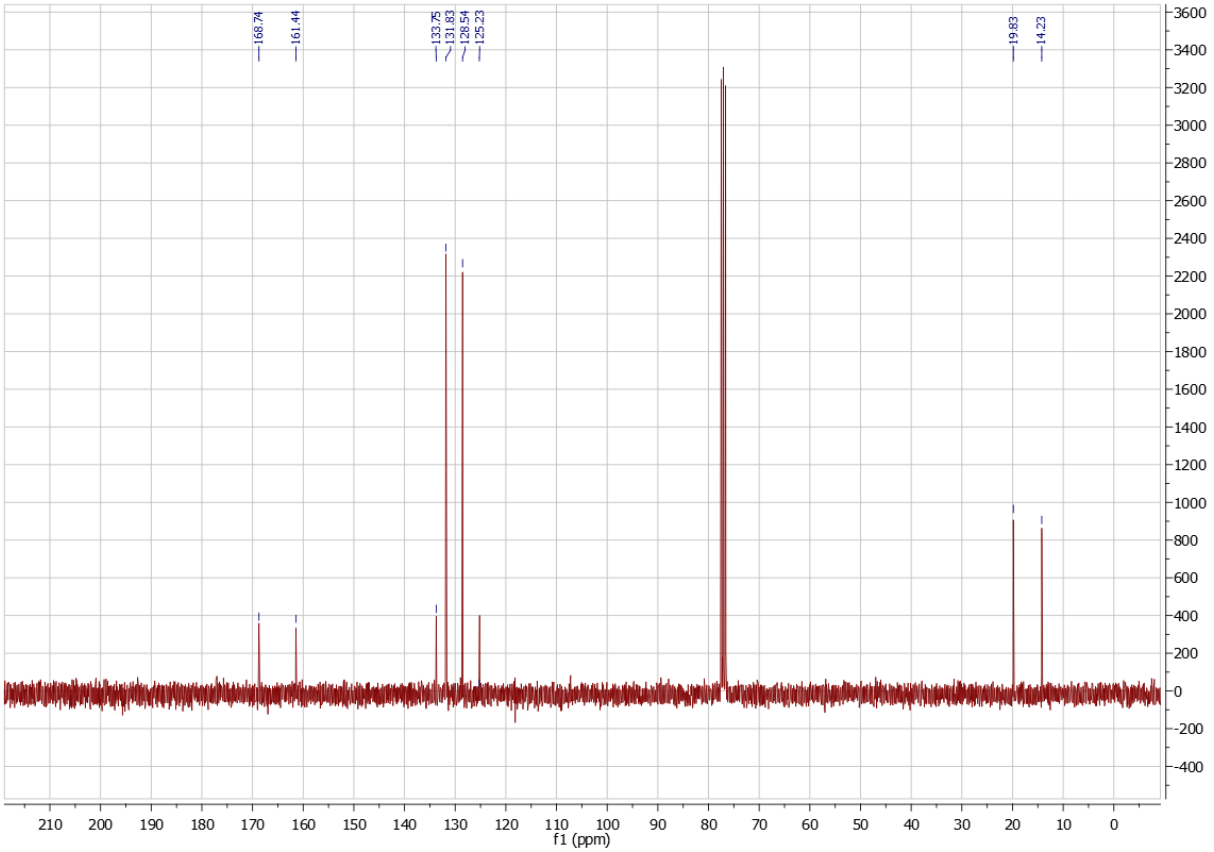
^{13}C NMR (75 MHz, $CDCl_3$):



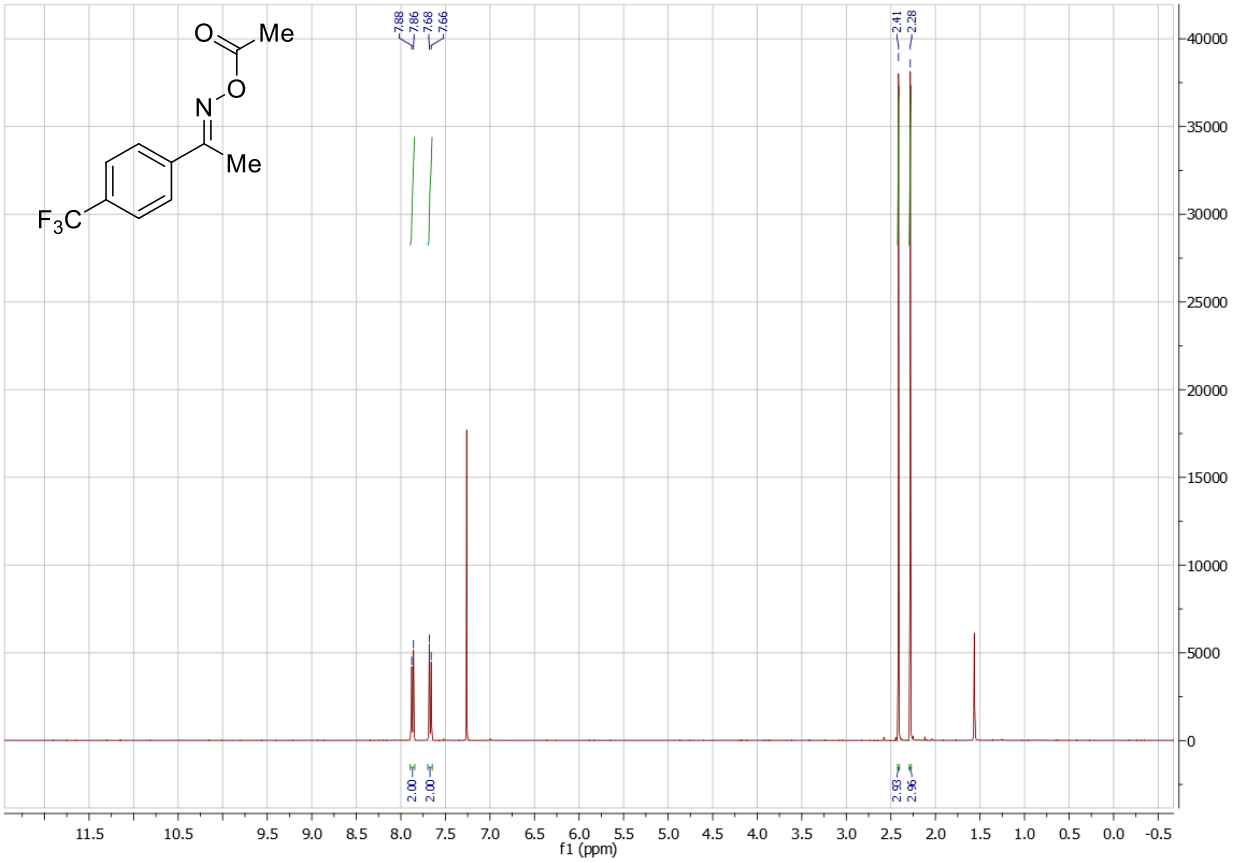
^{1}H NMR (300 MHz, $CDCl_3$): **(*E*)-1-(4-bromophenyl)ethan-1-one O-acetyl oxime (3d)**



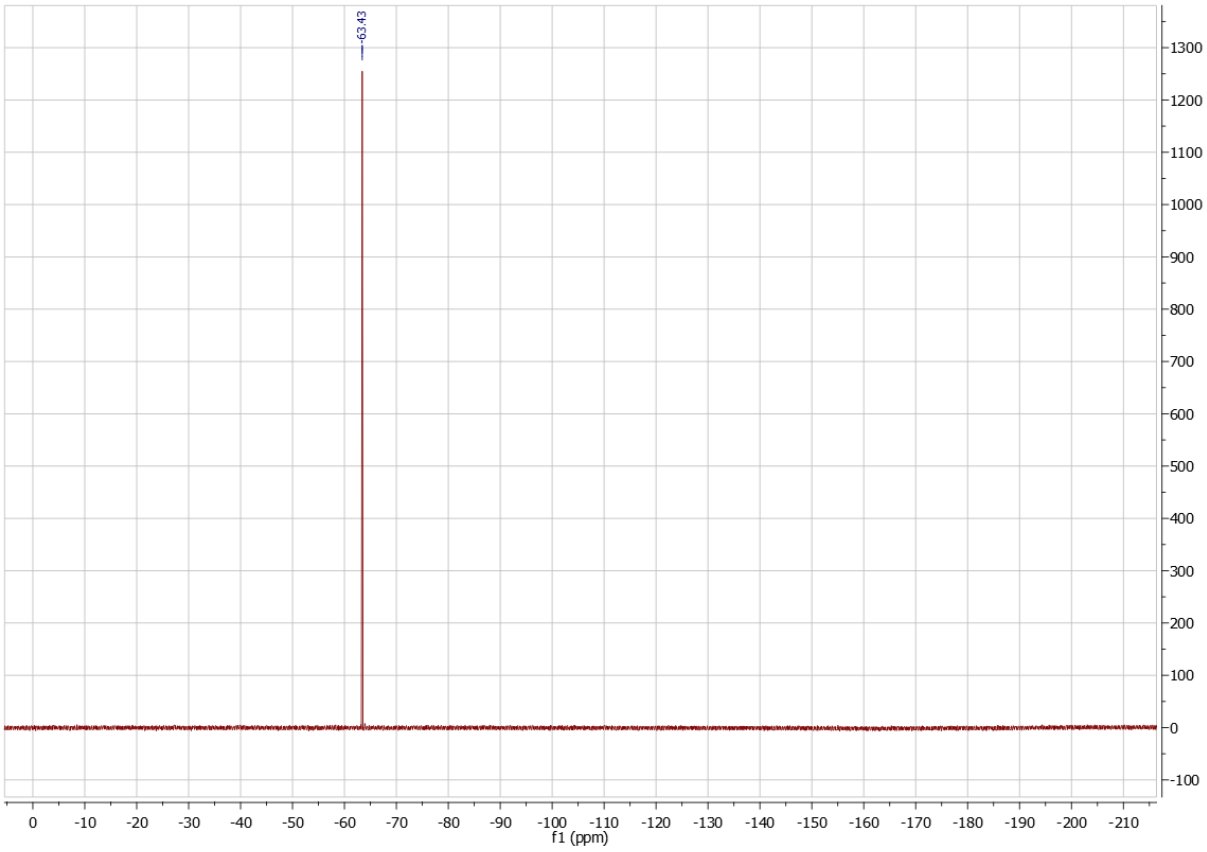
^{13}C NMR (75 MHz, $CDCl_3$)



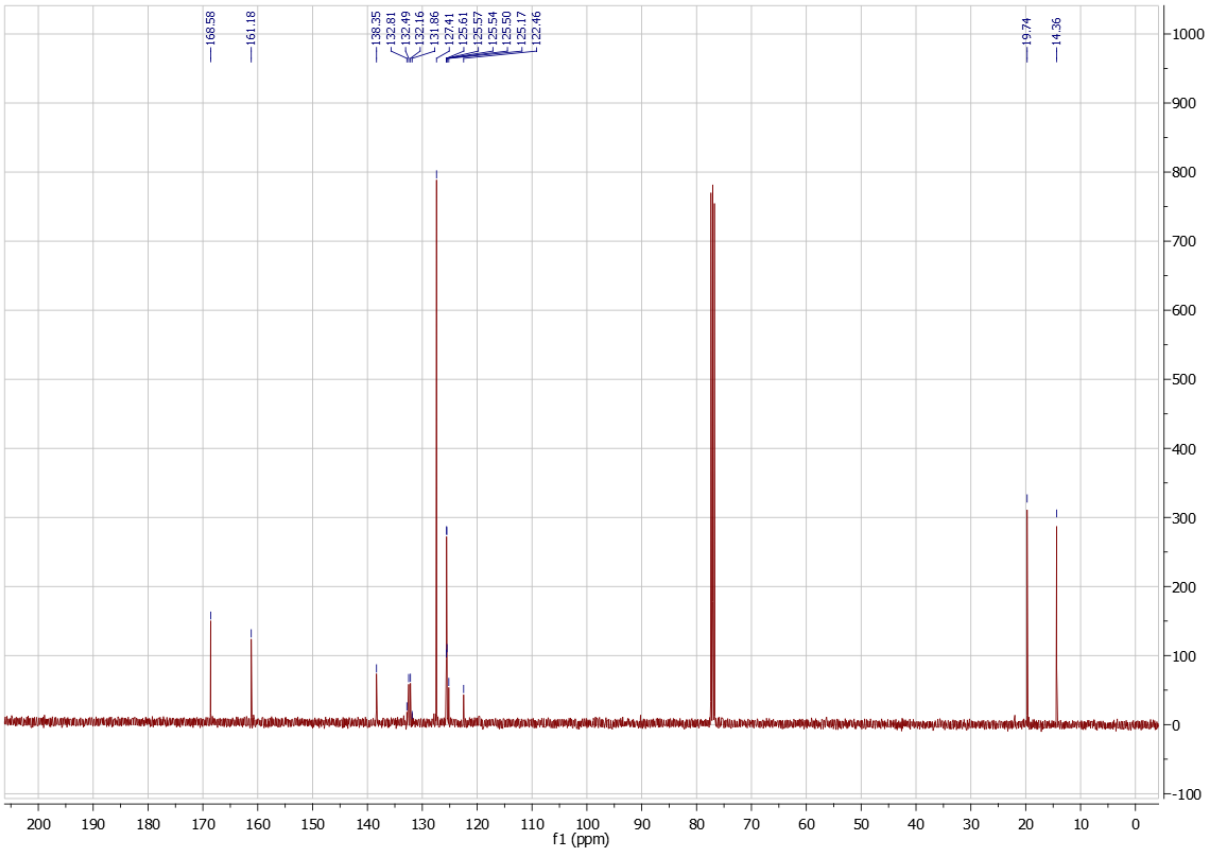
^{1}H NMR (400 MHz, $CDCl_3$): **(*E*)-1-(4-(trifluoromethyl)phenyl)ethan-1-one O-acetyl oxime (3e)**



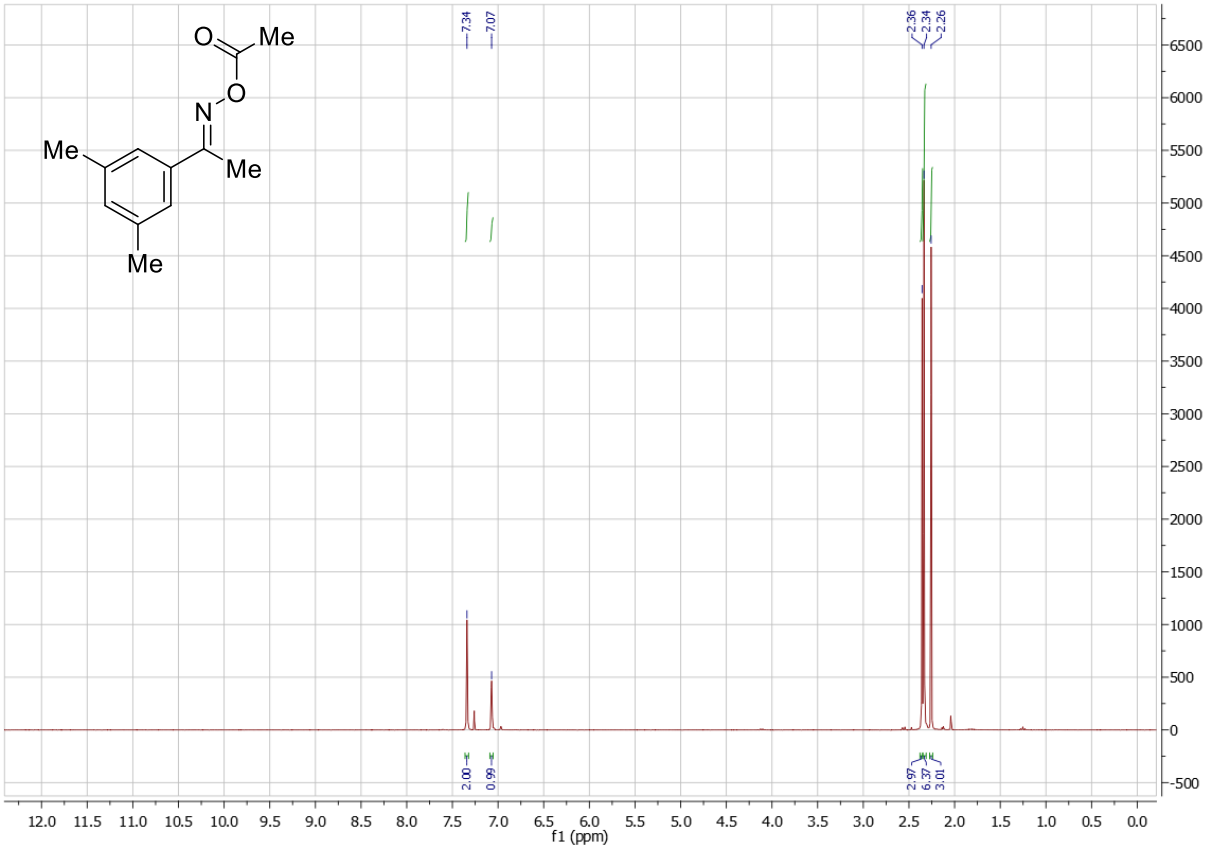
^{19}F NMR (377 MHz, $CDCl_3$)



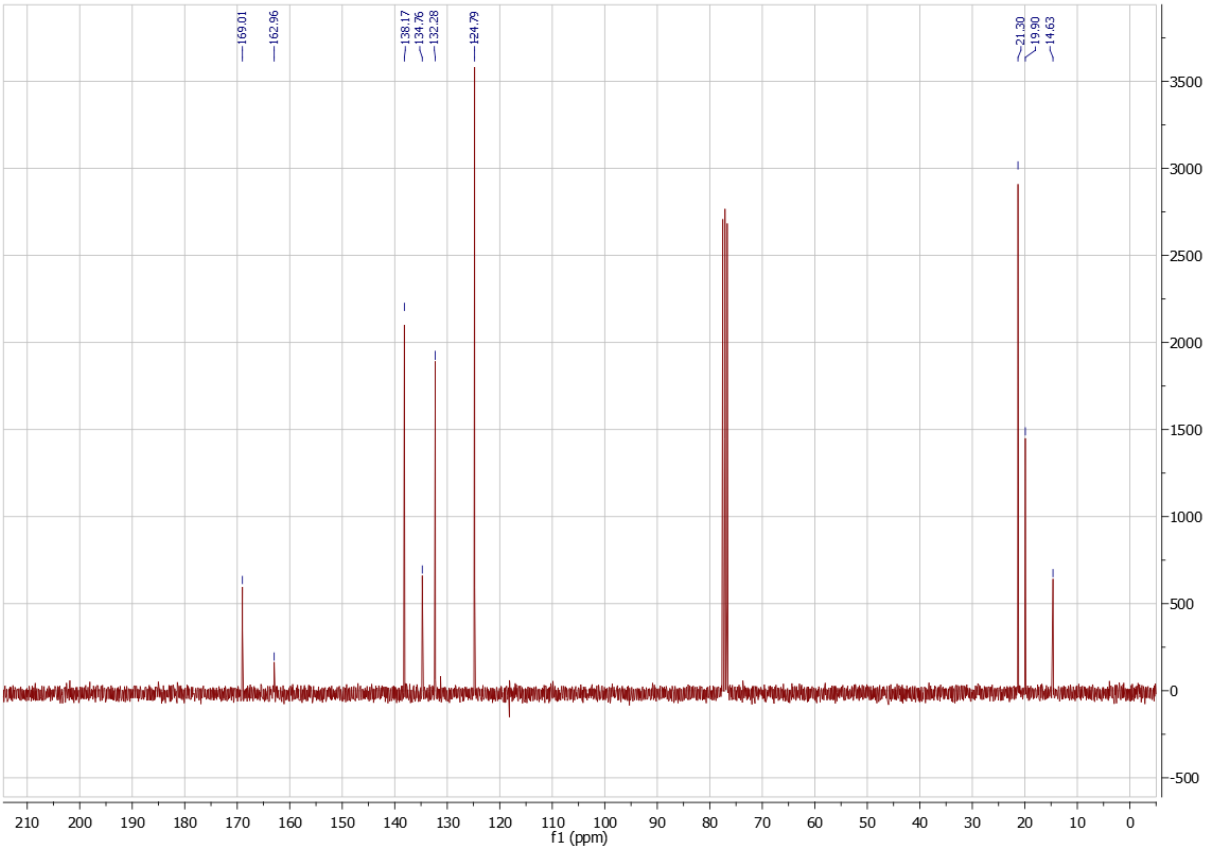
^{13}C NMR (101 MHz, $CDCl_3$):



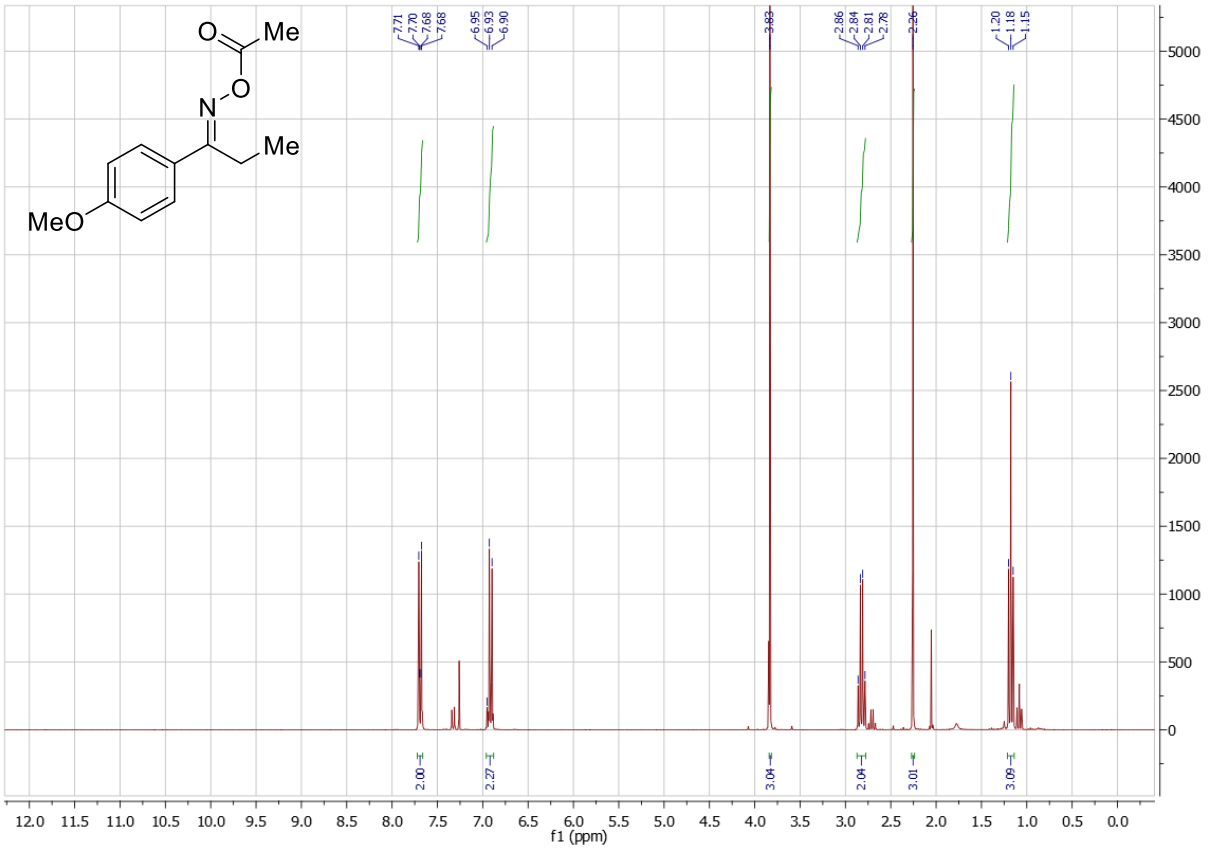
^{1}H NMR (300 MHz, $CDCl_3$): **(*E*)-1-(3,5-dimethylphenyl)ethan-1-one O-acetyl oxime (3f)**



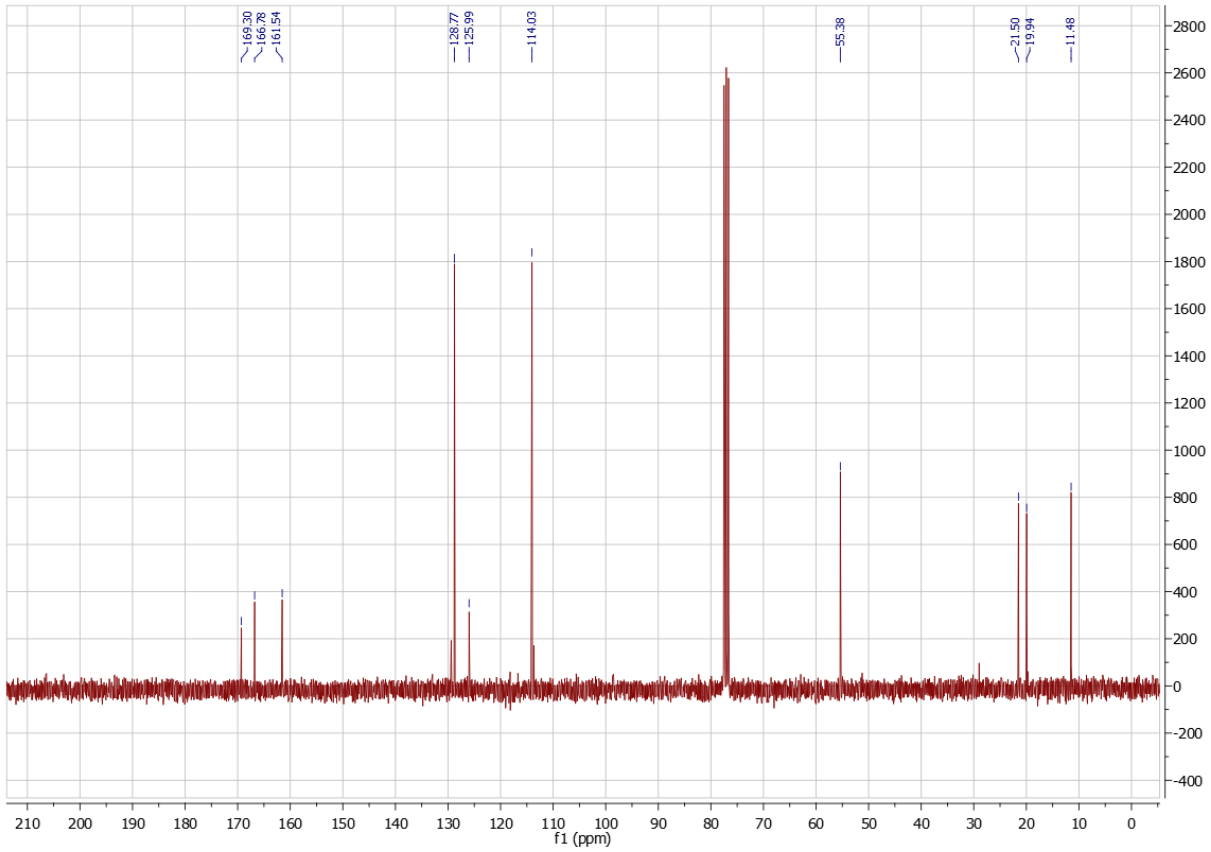
^{13}C NMR (75 MHz, $CDCl_3$):



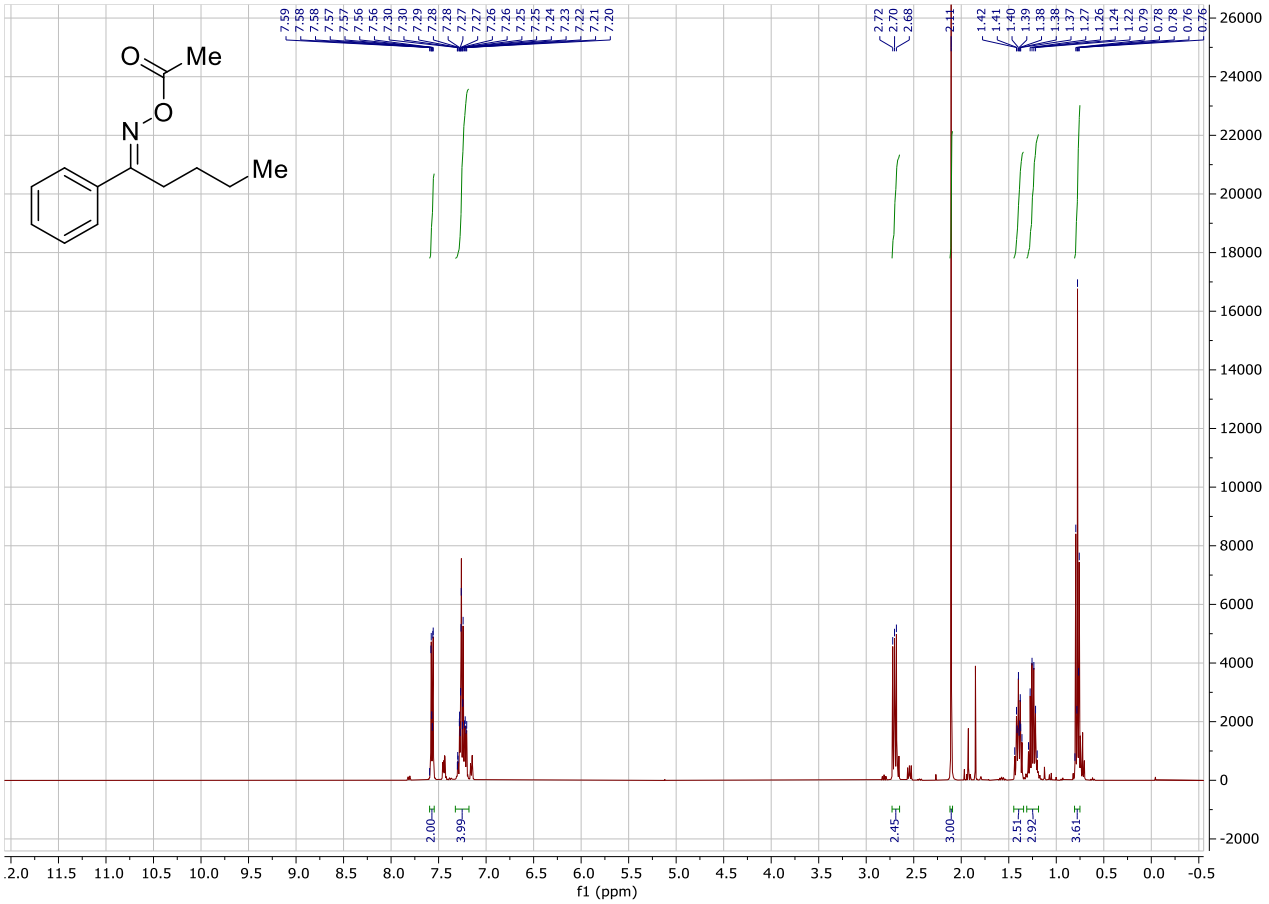
^{1}H NMR (400 MHz, $CDCl_3$): **(*E*)-1-(4-methoxyphenyl)propan-1-one O-acetyl oxime (3g)**



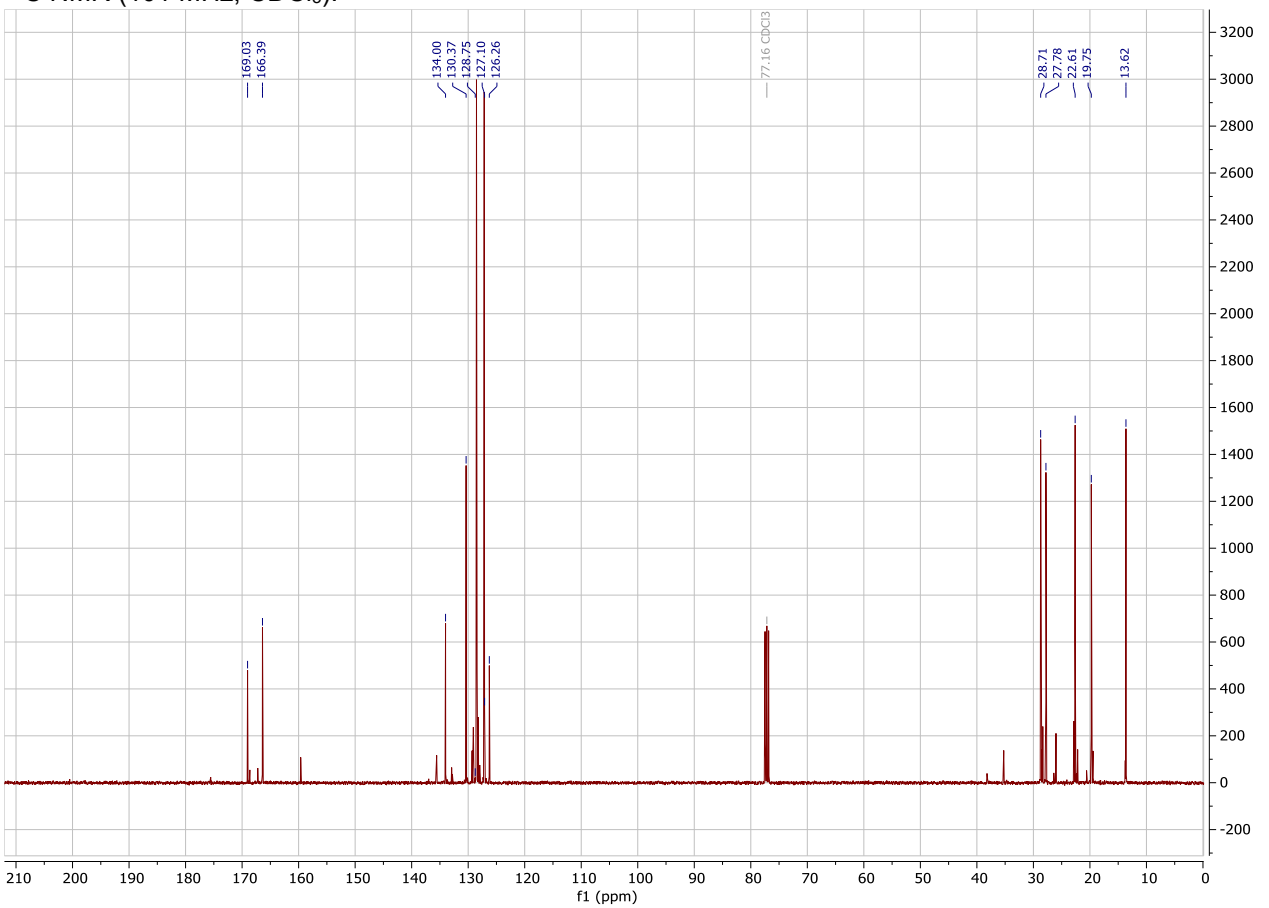
^{13}C NMR (101 MHz, $CDCl_3$):



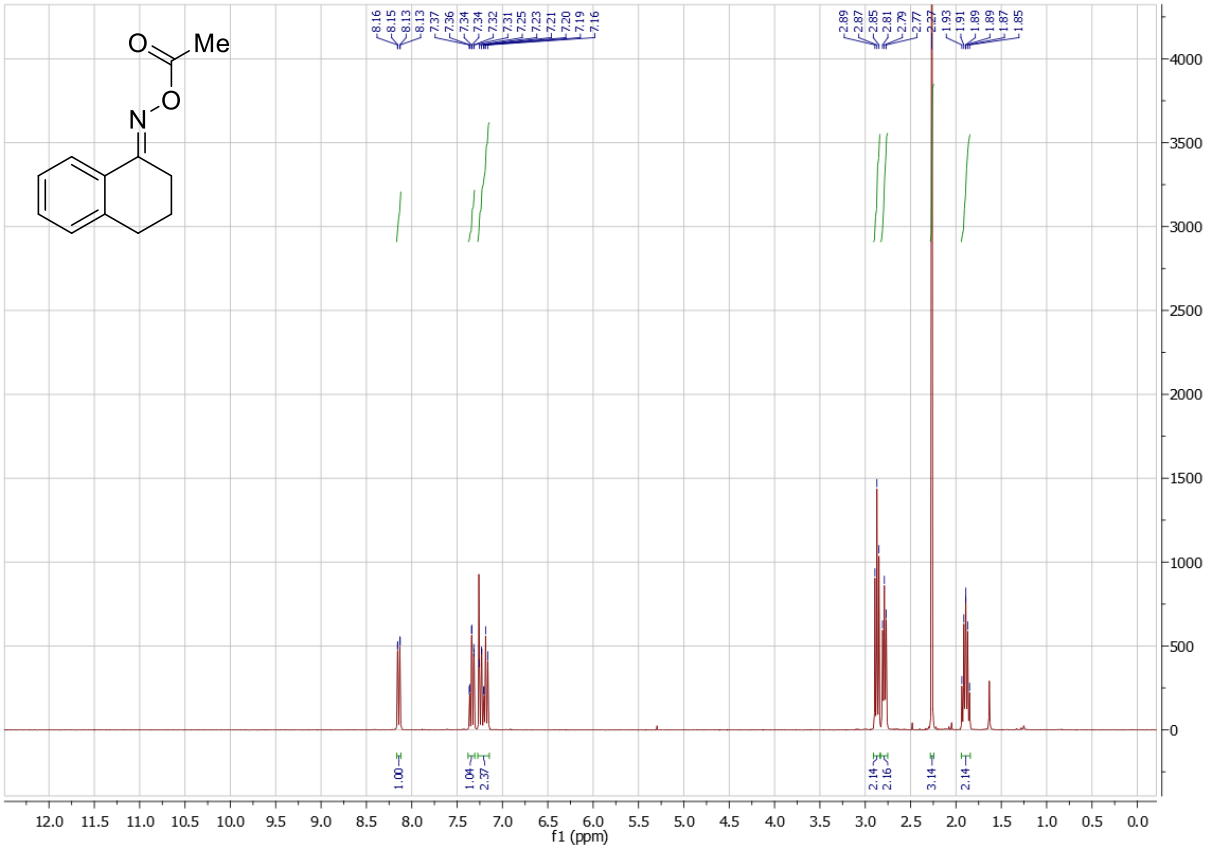
^{1}H NMR (400 MHz, $CDCl_3$): **(*E*)-1-phenylpentan-1-one O-acetyl oxime (3h)**



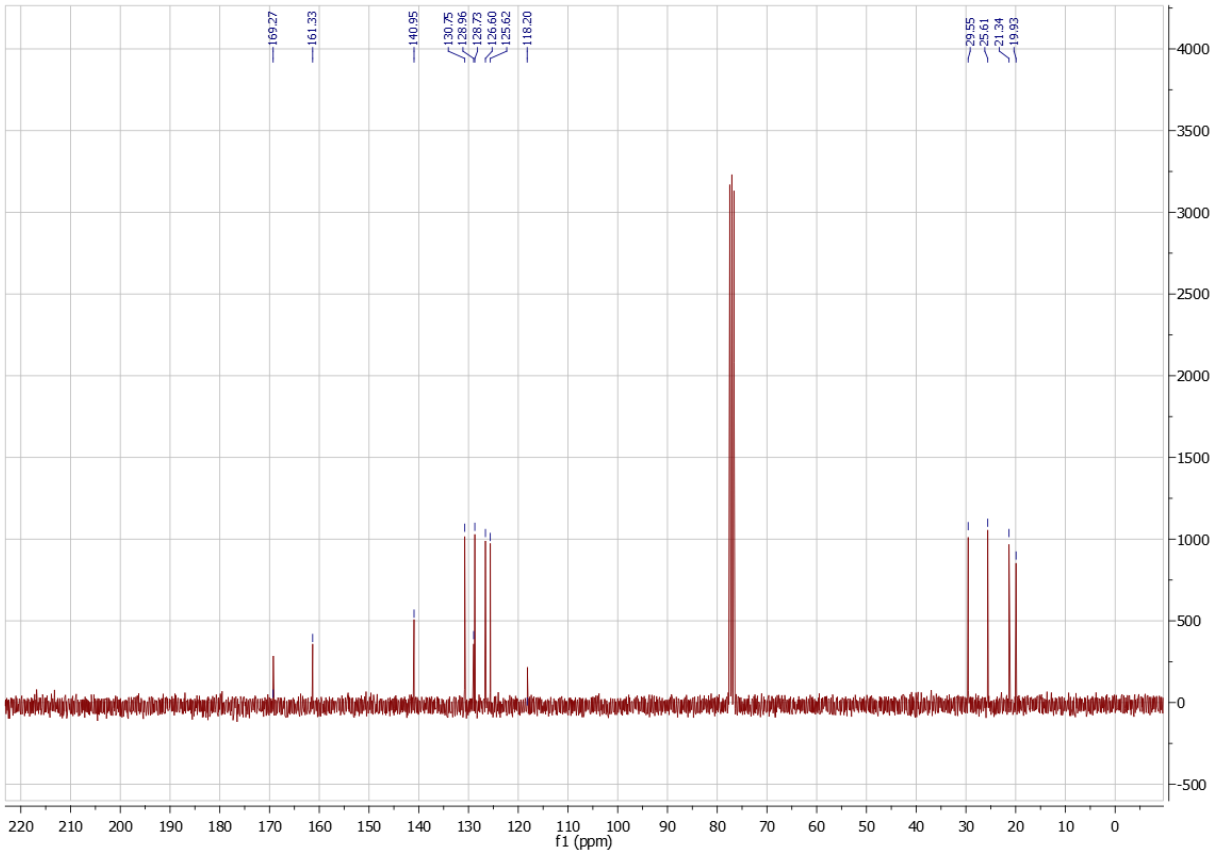
^{13}C NMR (101 MHz, $CDCl_3$):



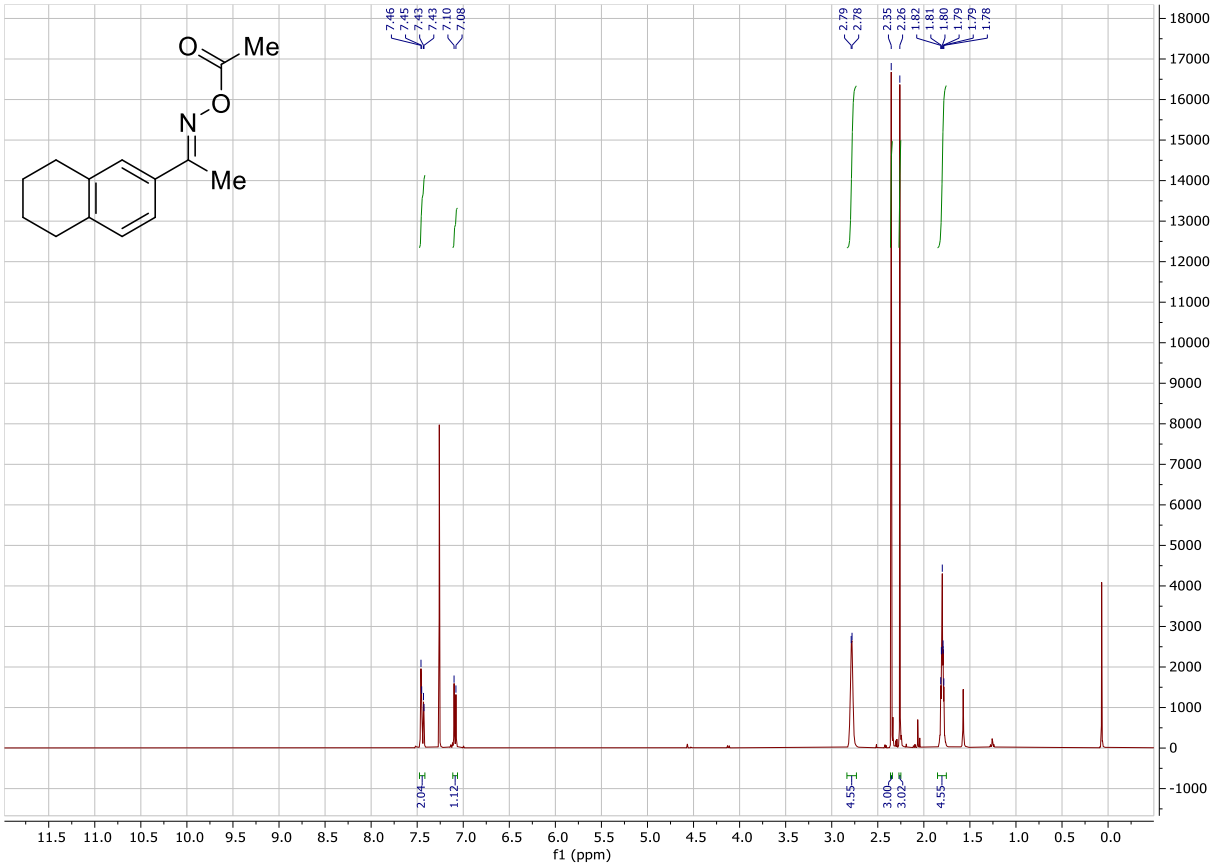
^{1}H NMR (300 MHz, $CDCl_3$): **(*E*)-3,4-dihydronaphthalen-1(2*H*)-one O-acetyl oxime (3i)**



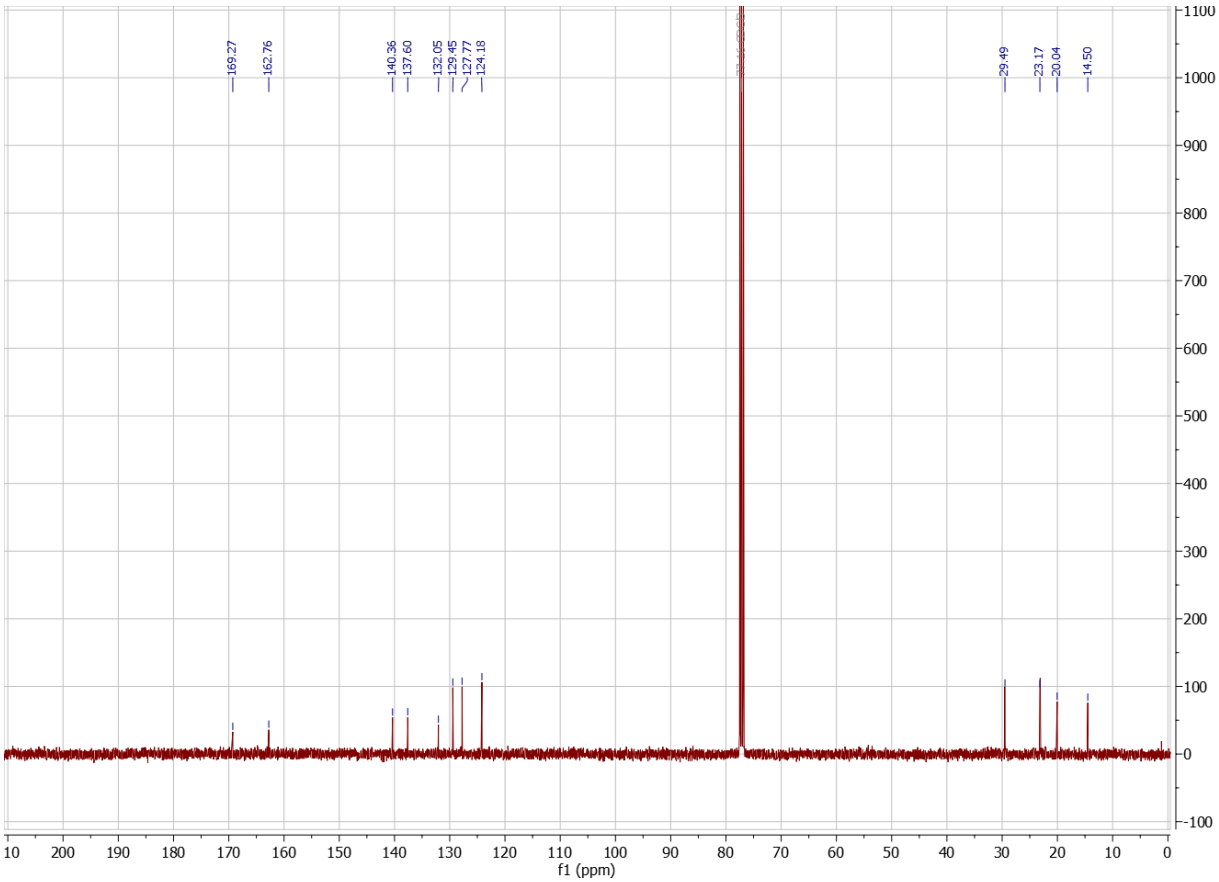
^{13}C NMR (75 MHz, $CDCl_3$):



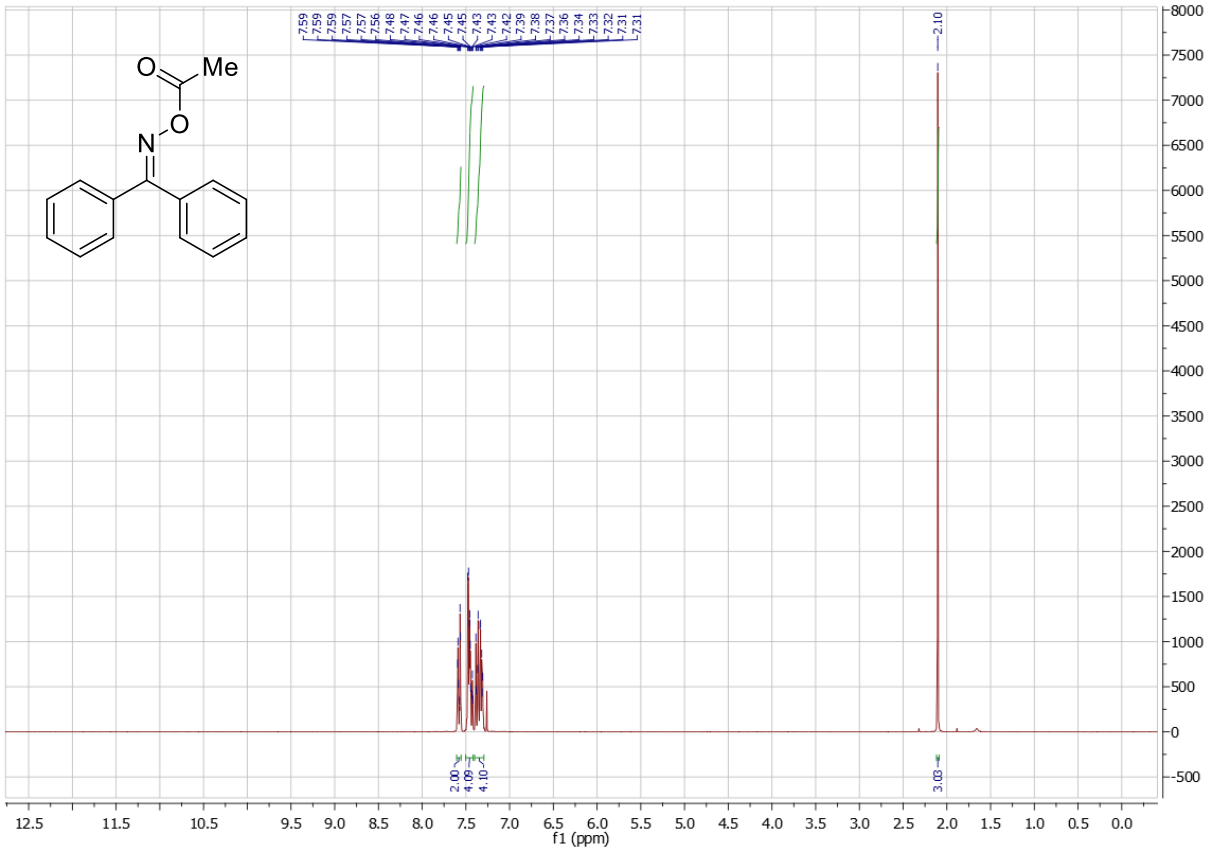
^{1}H NMR (400 MHz, $CDCl_3$): **(*E*)-1-(5,6,7,8-tetrahydronaphthalen-2-yl)ethan-1-one O-acetyl oxime (3j)**



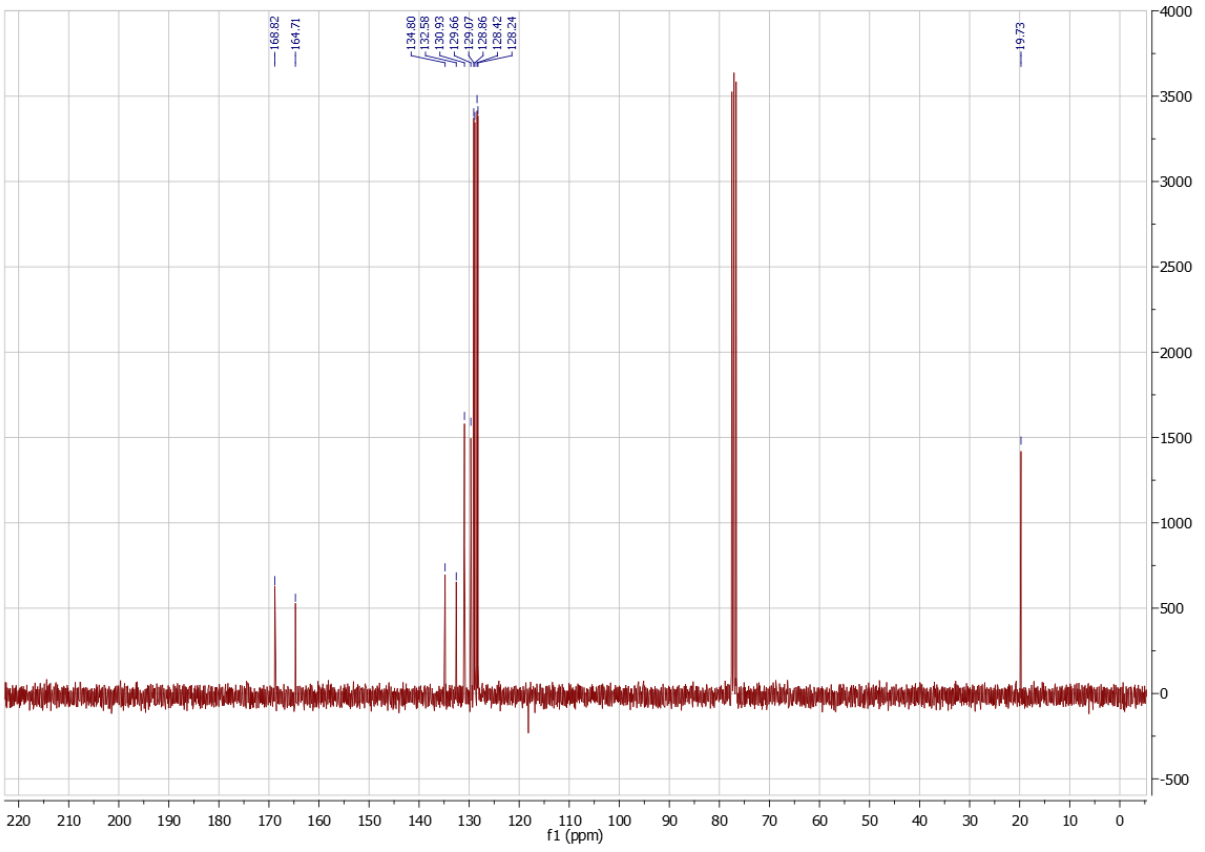
^{13}C NMR (101 MHz, $CDCl_3$):



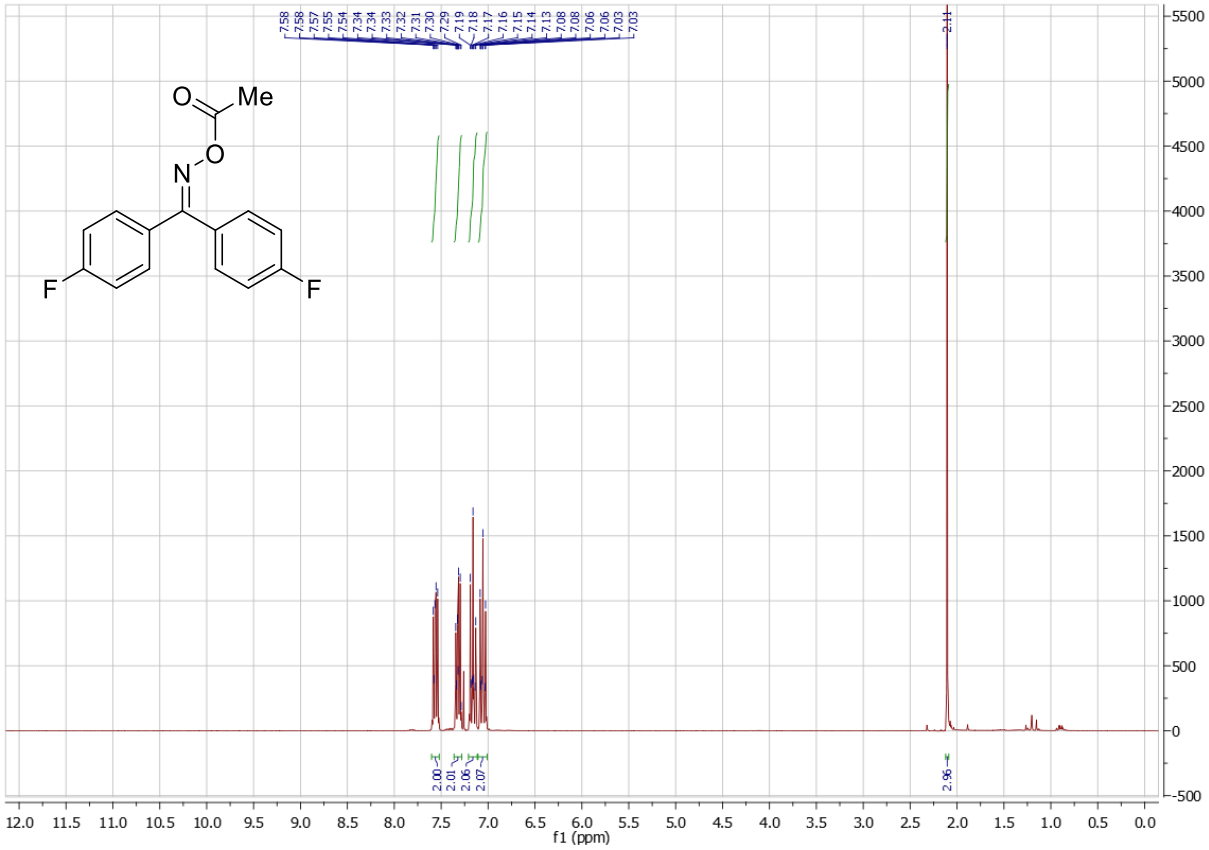
^{1}H NMR (300 MHz, $CDCl_3$): **Diphenylmethanone O-acetyl oxime (3k)**



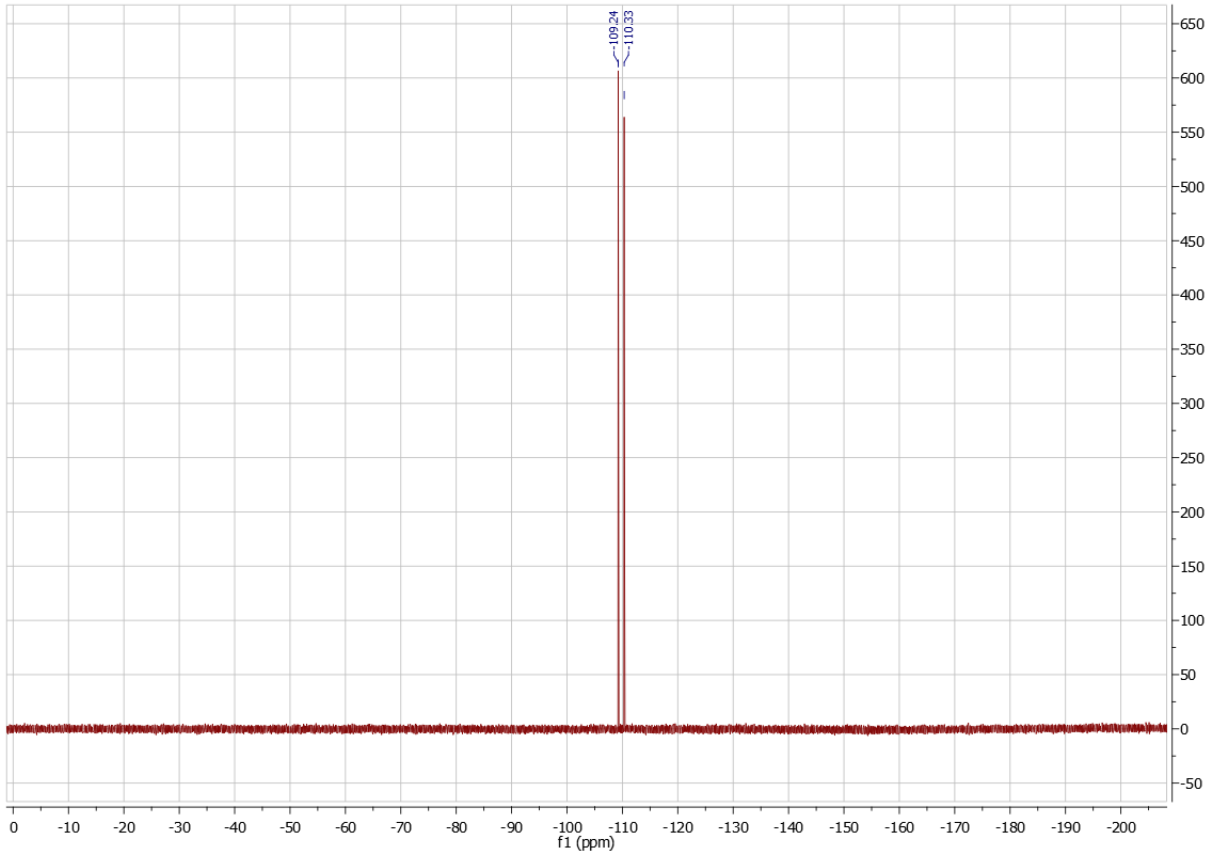
^{13}C NMR (75 MHz, $CDCl_3$):



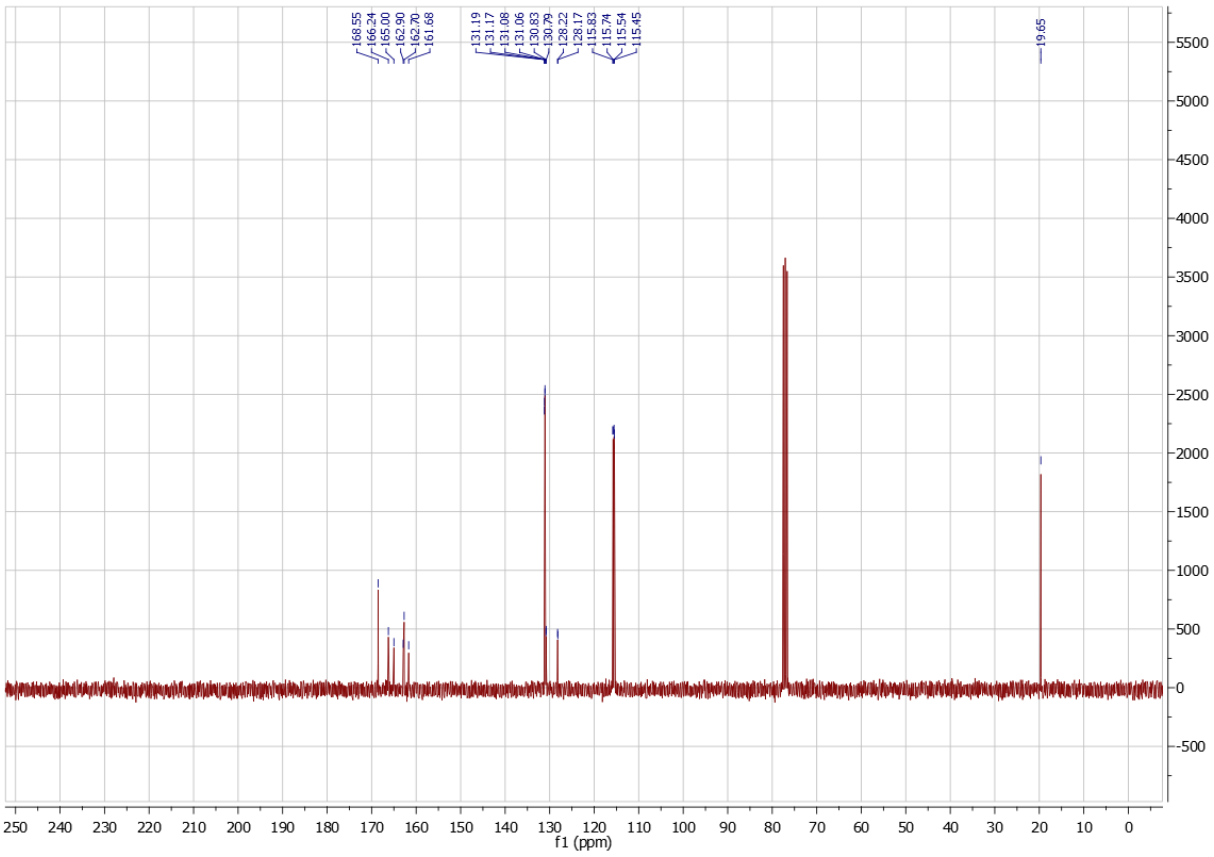
^{1}H NMR (400 MHz, $CDCl_3$): **Bis(4-fluorophenyl)methanone O-acetyl oxime (3l)**



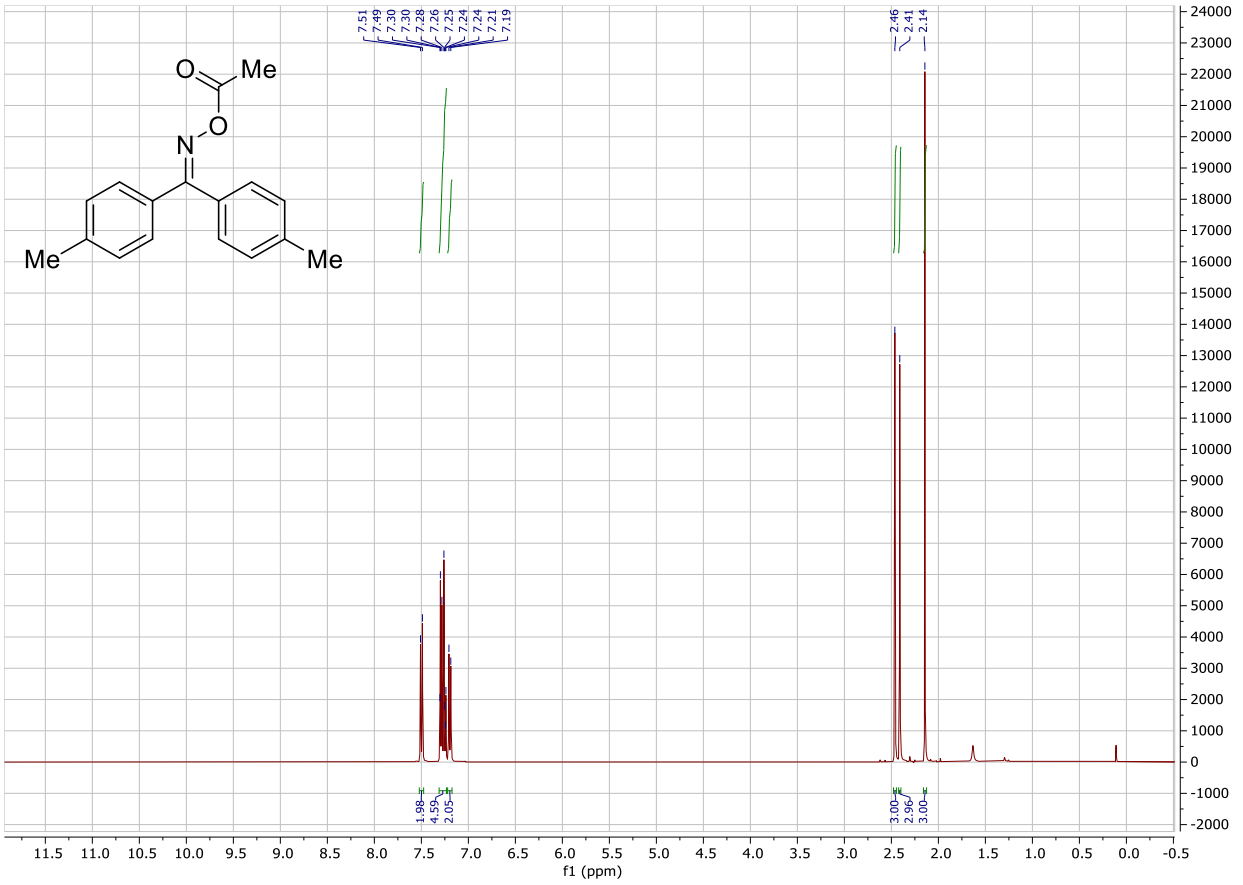
^{19}F NMR (377 MHz, $CDCl_3$):



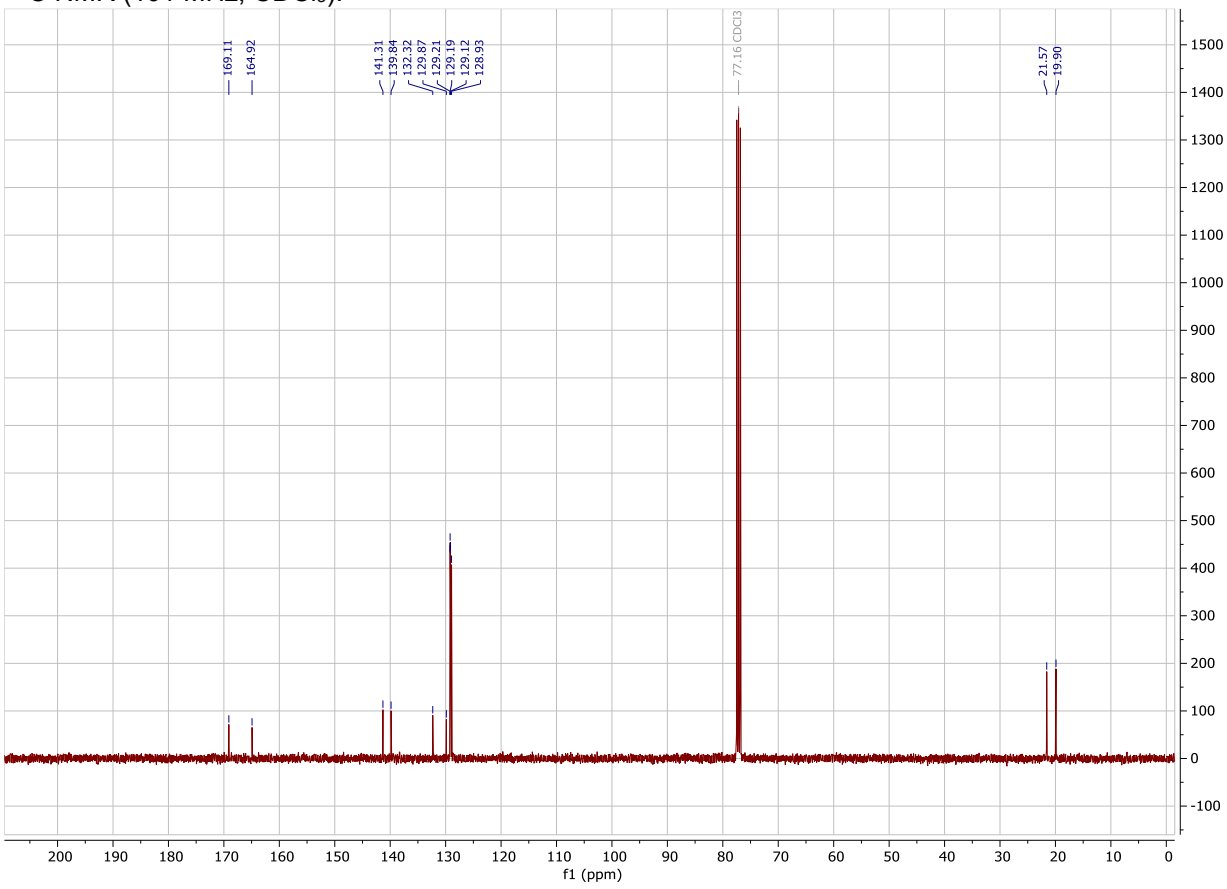
^{13}C NMR (101 MHz, $CDCl_3$):



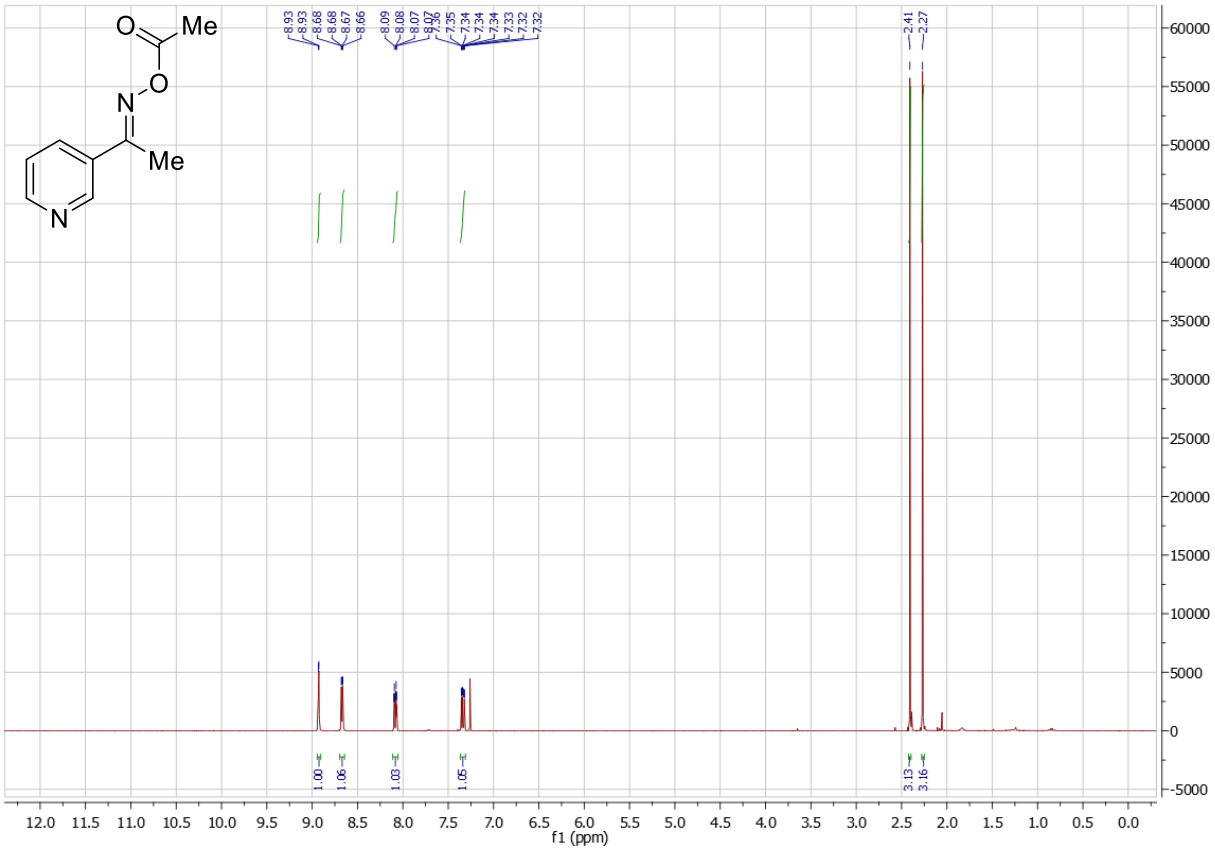
^{1}H NMR (400 MHz, $CDCl_3$): **Di-*p*-tolylmethanone O-acetyl oxime (3m)**



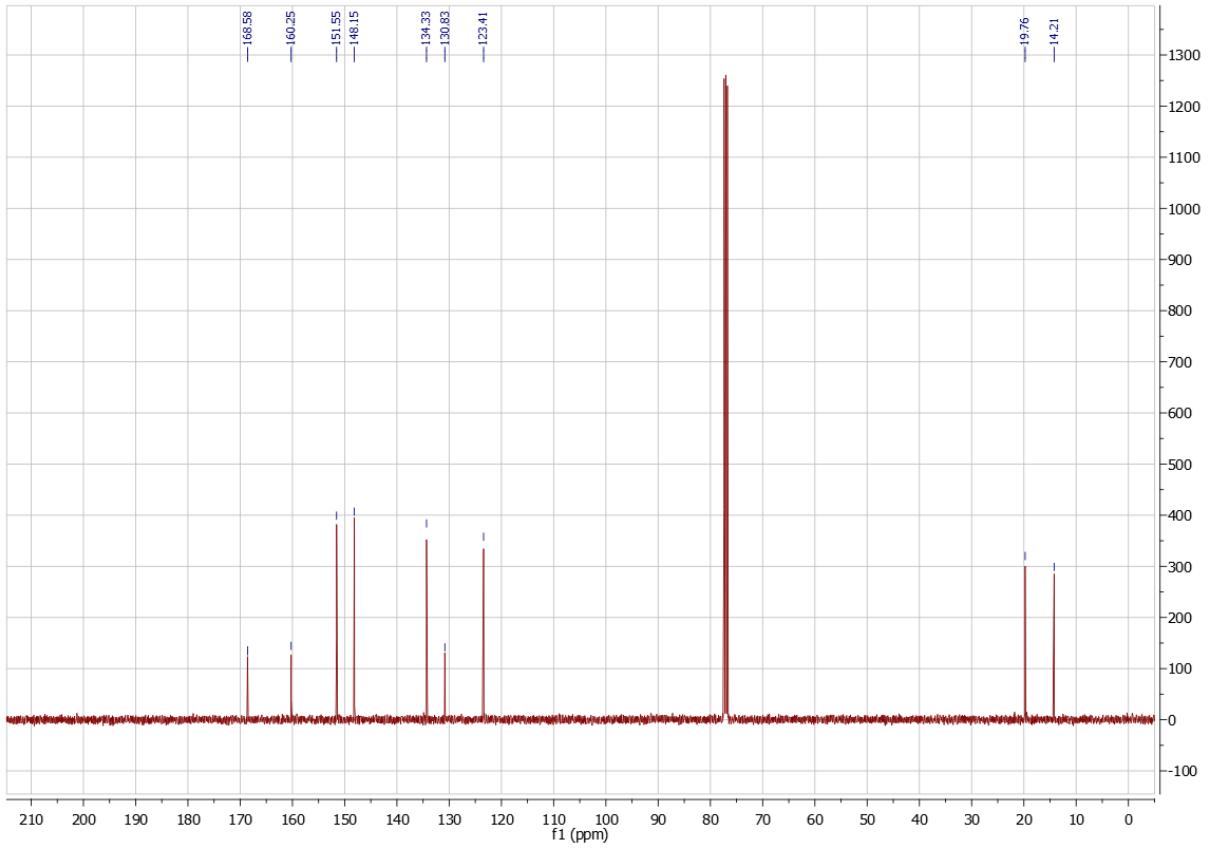
^{13}C NMR (101 MHz, $CDCl_3$):



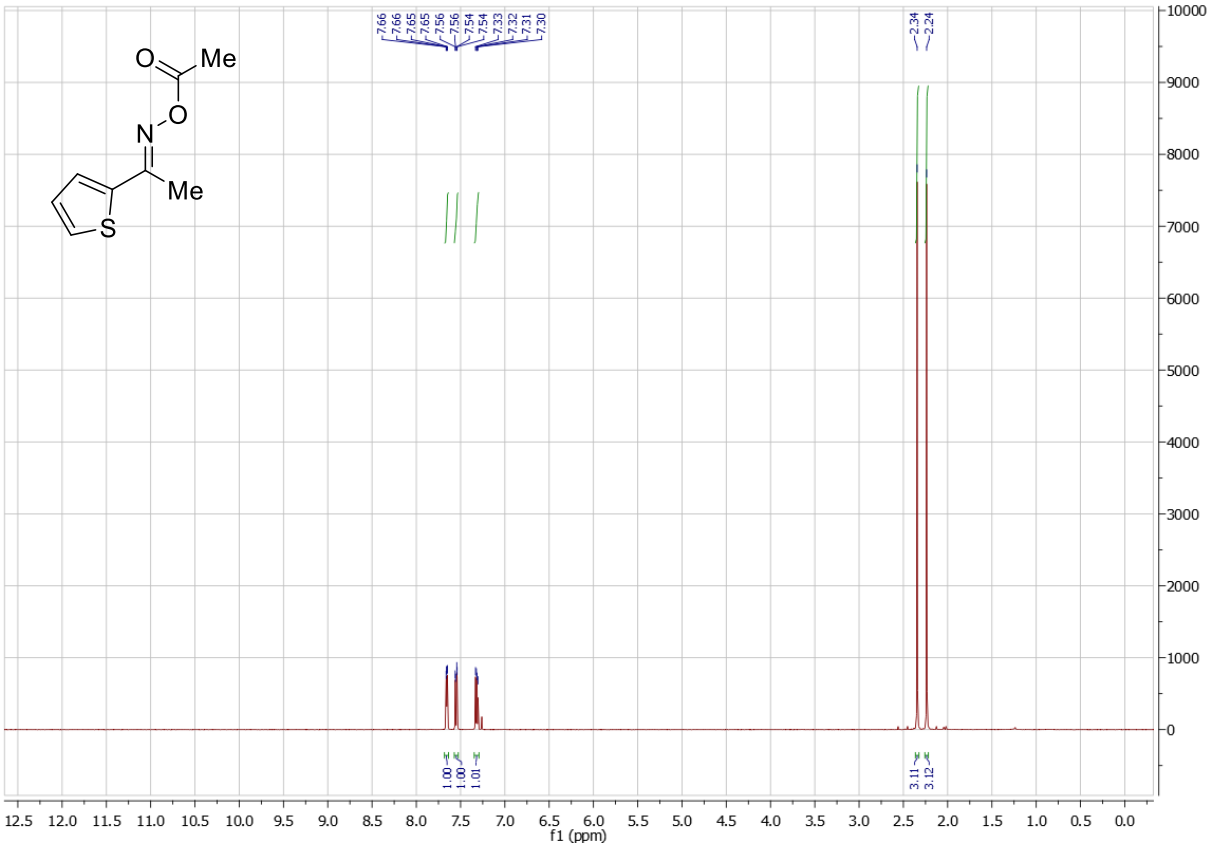
^{1}H NMR (300 MHz, $CDCl_3$): **(*E*)-1-(pyridin-3-yl)ethan-1-one O-acetyl oxime (3n)**



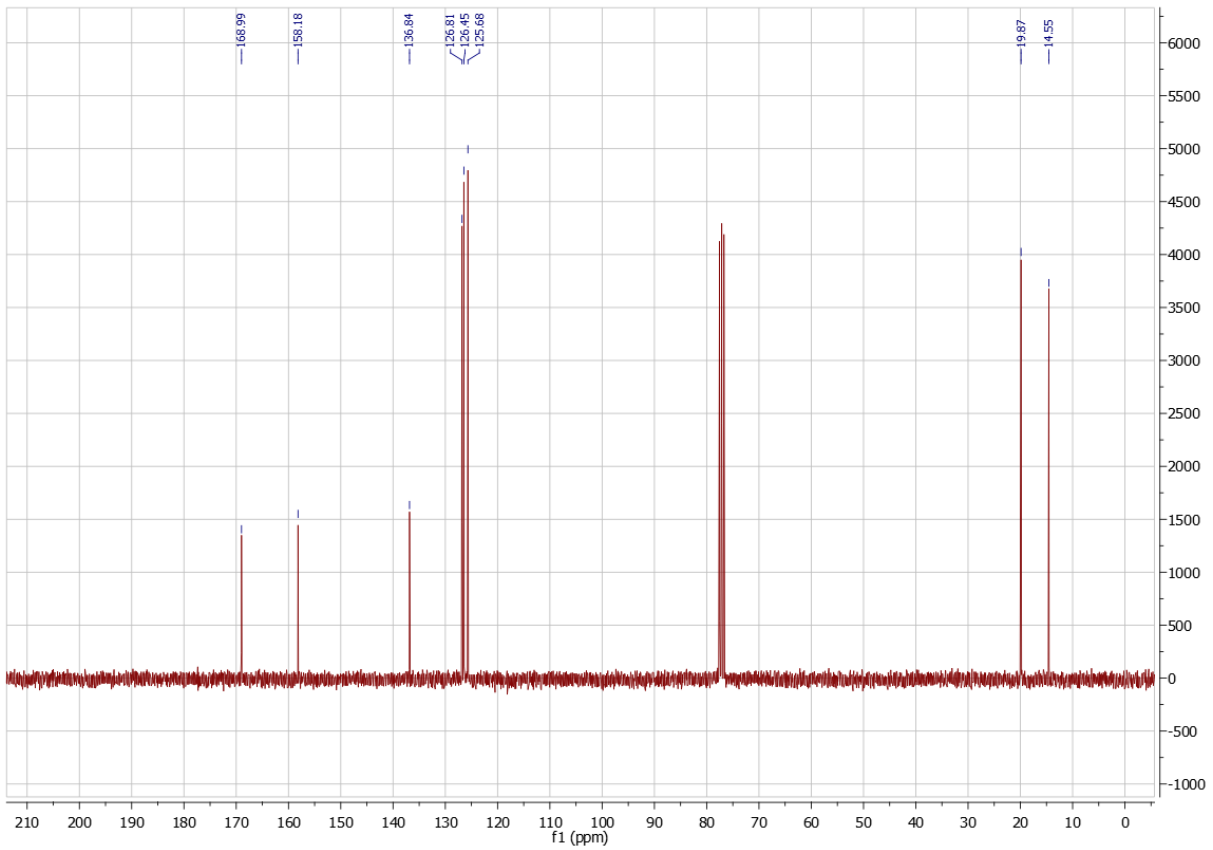
^{13}C NMR (75 MHz, $CDCl_3$):



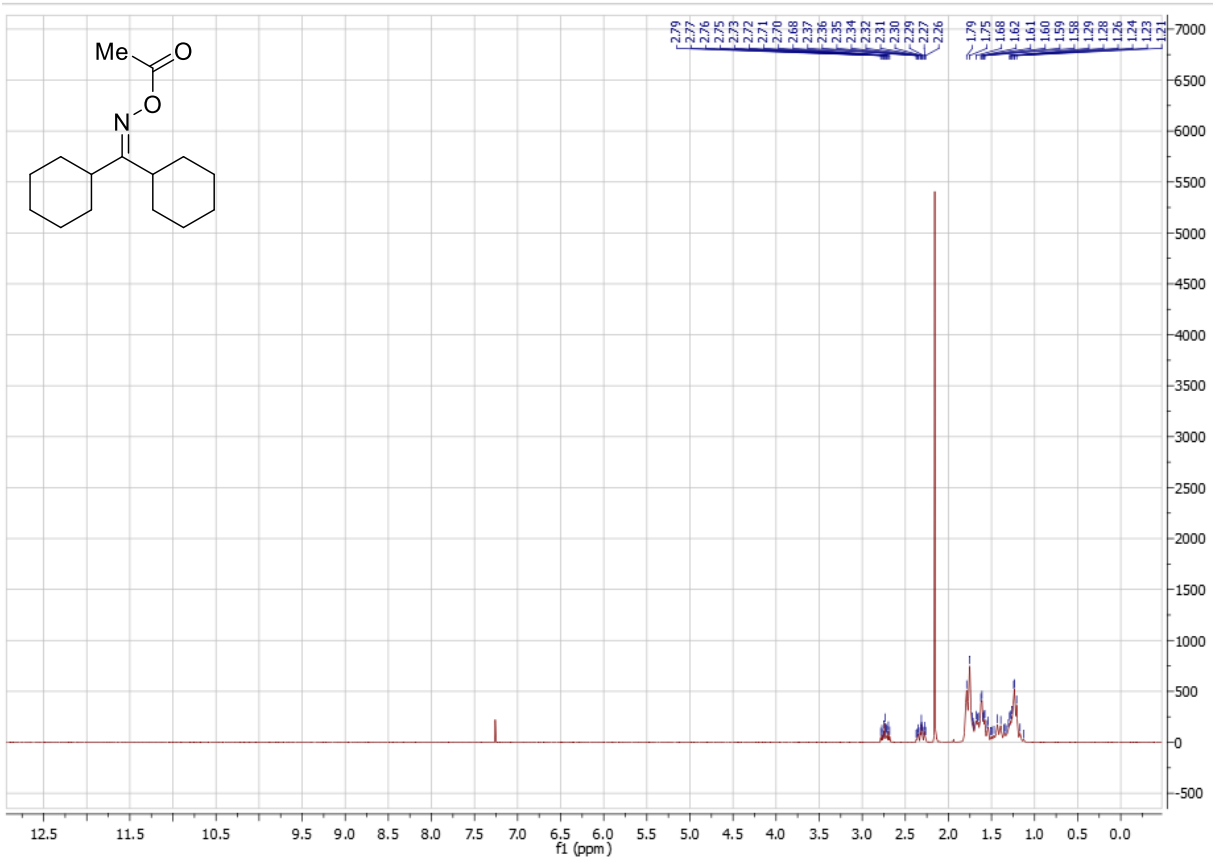
^{1}H NMR (300 MHz, $CDCl_3$): **(*E*)-1-(thiophen-2-yl)ethan-1-one O-acetyl oxime (3o)**



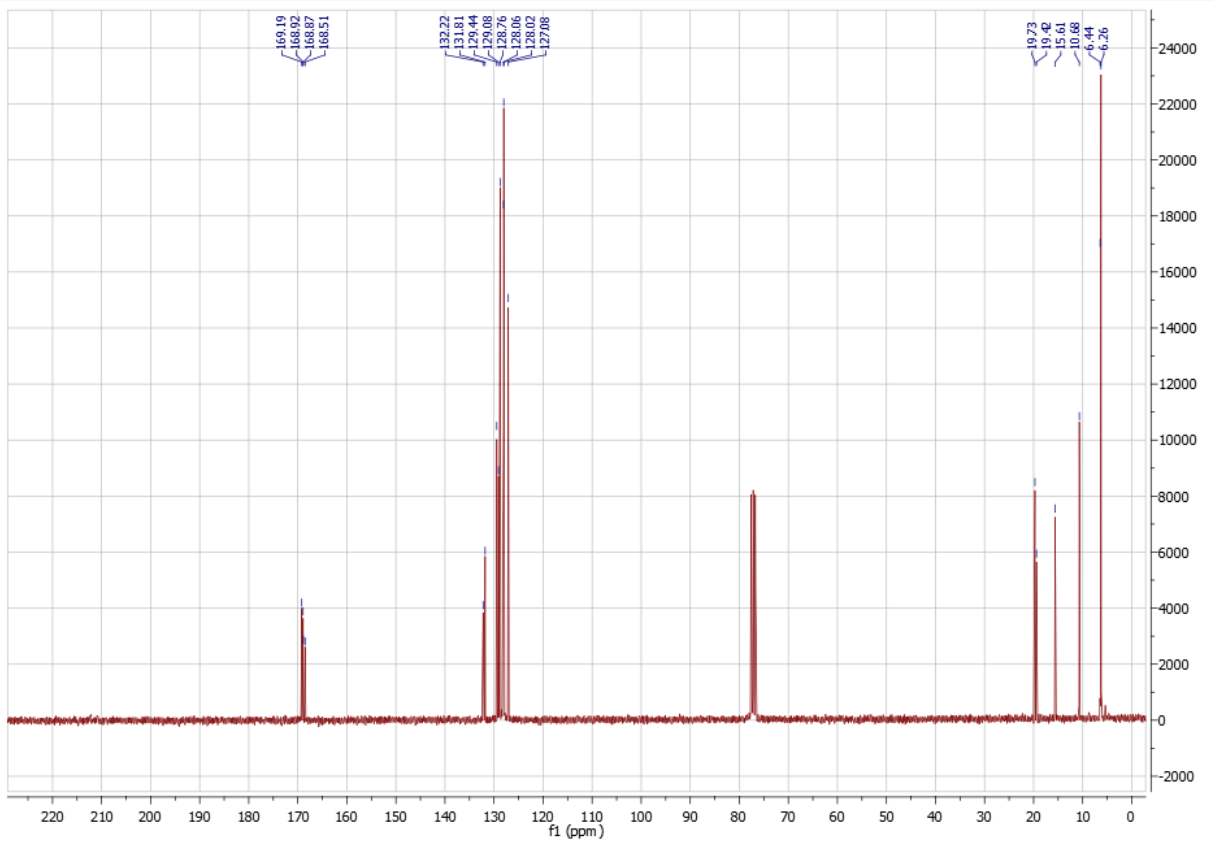
^{13}C NMR (75 MHz, $CDCl_3$):



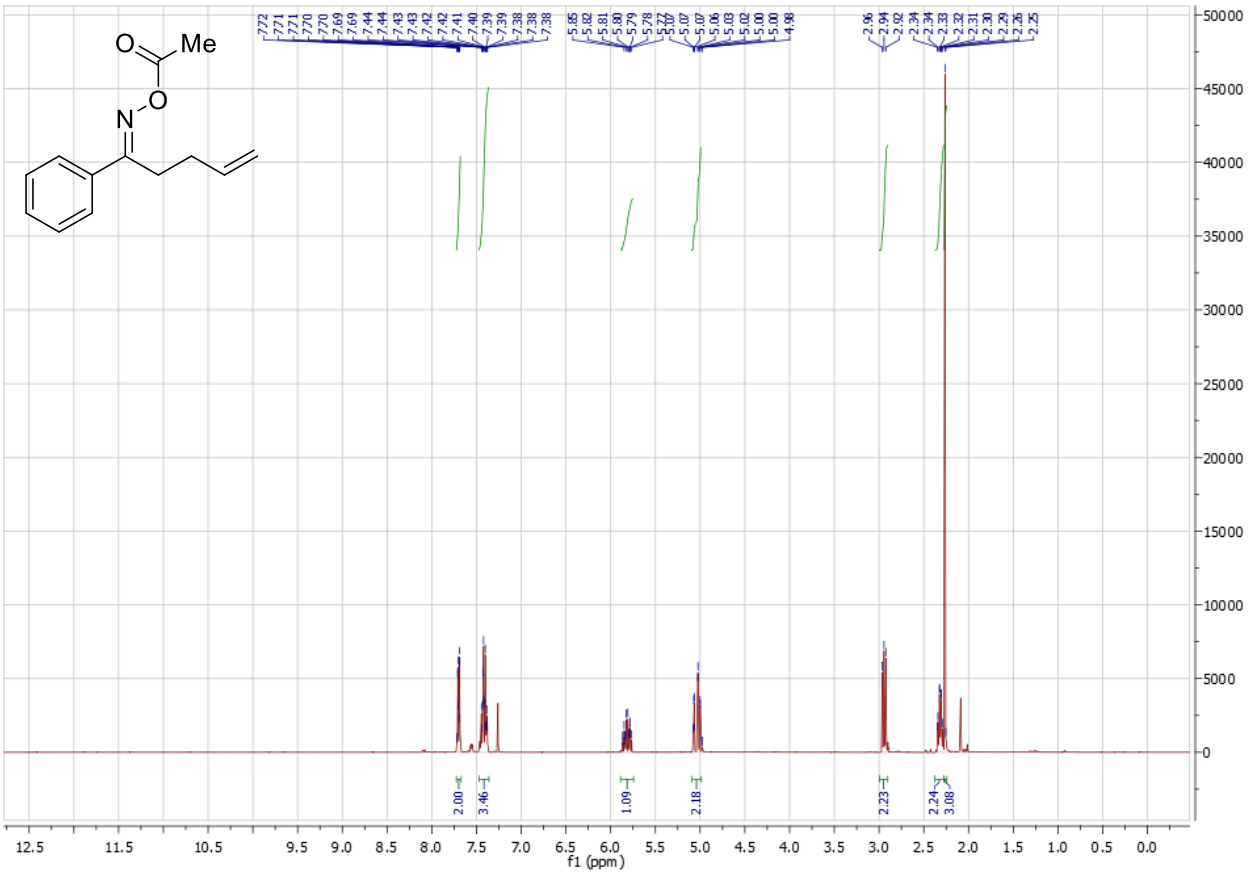
^{1}H NMR (300 MHz, $CDCl_3$): **(*E*)-dicyclohexylmethanone O-acetyl oxime (3p)**



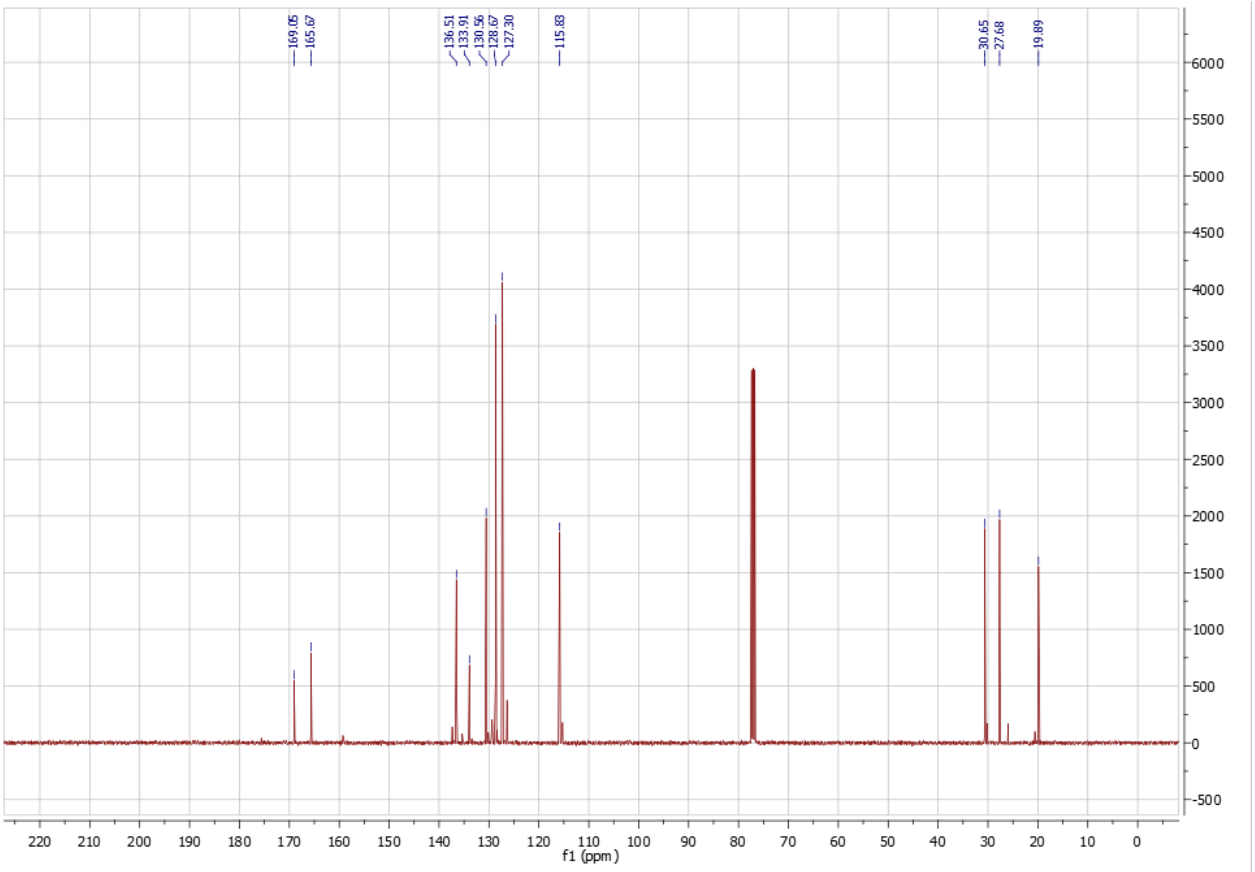
^{13}C NMR (75 MHz, $CDCl_3$):



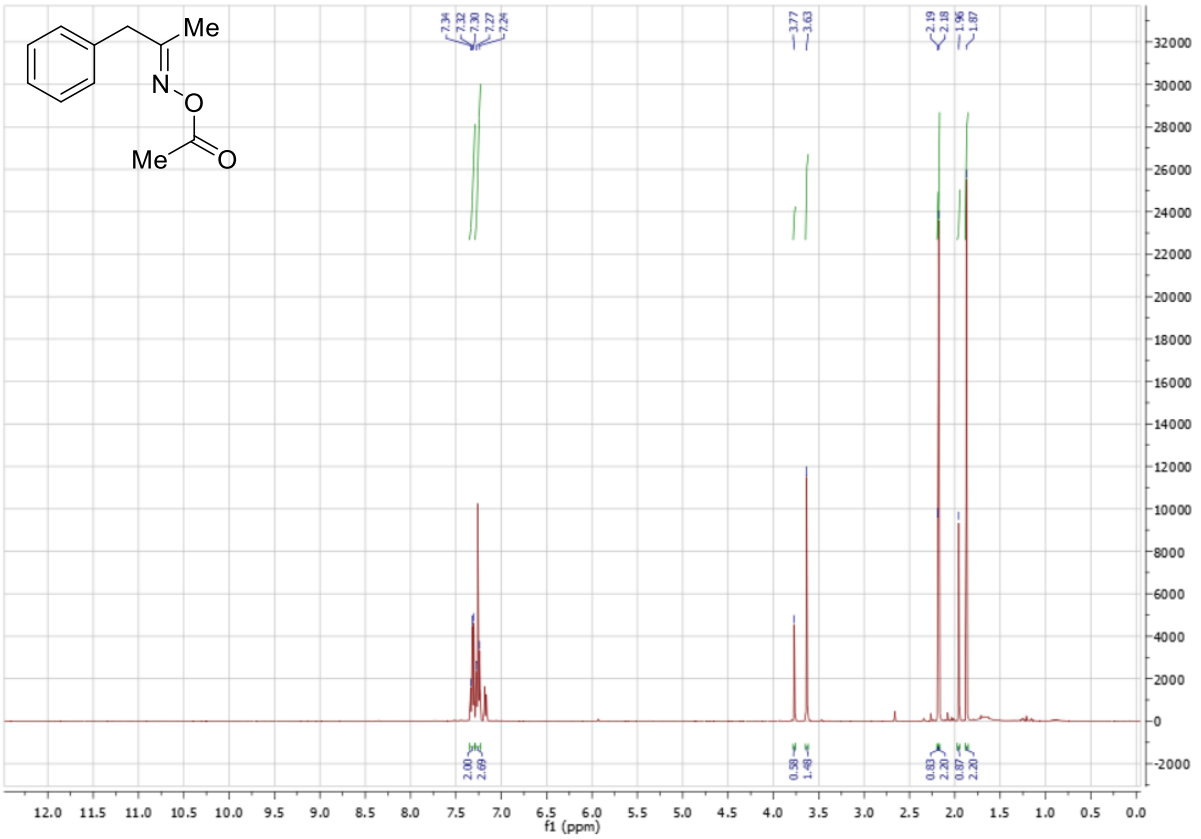
^{1}H NMR (400 MHz, $CDCl_3$): **(*E*)-1-phenylpent-4-en-1-one O-acetyl oxime (3q)**



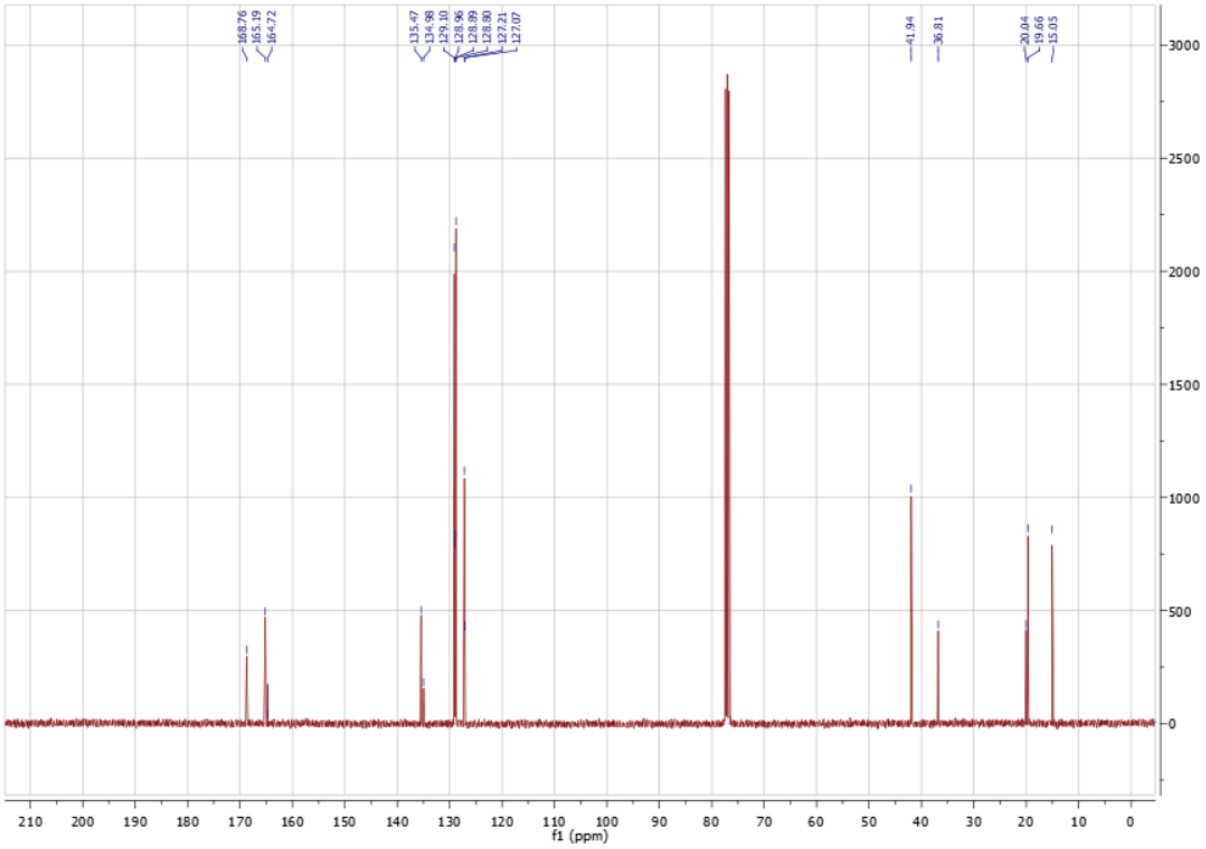
^{13}C NMR (101 MHz, $CDCl_3$):



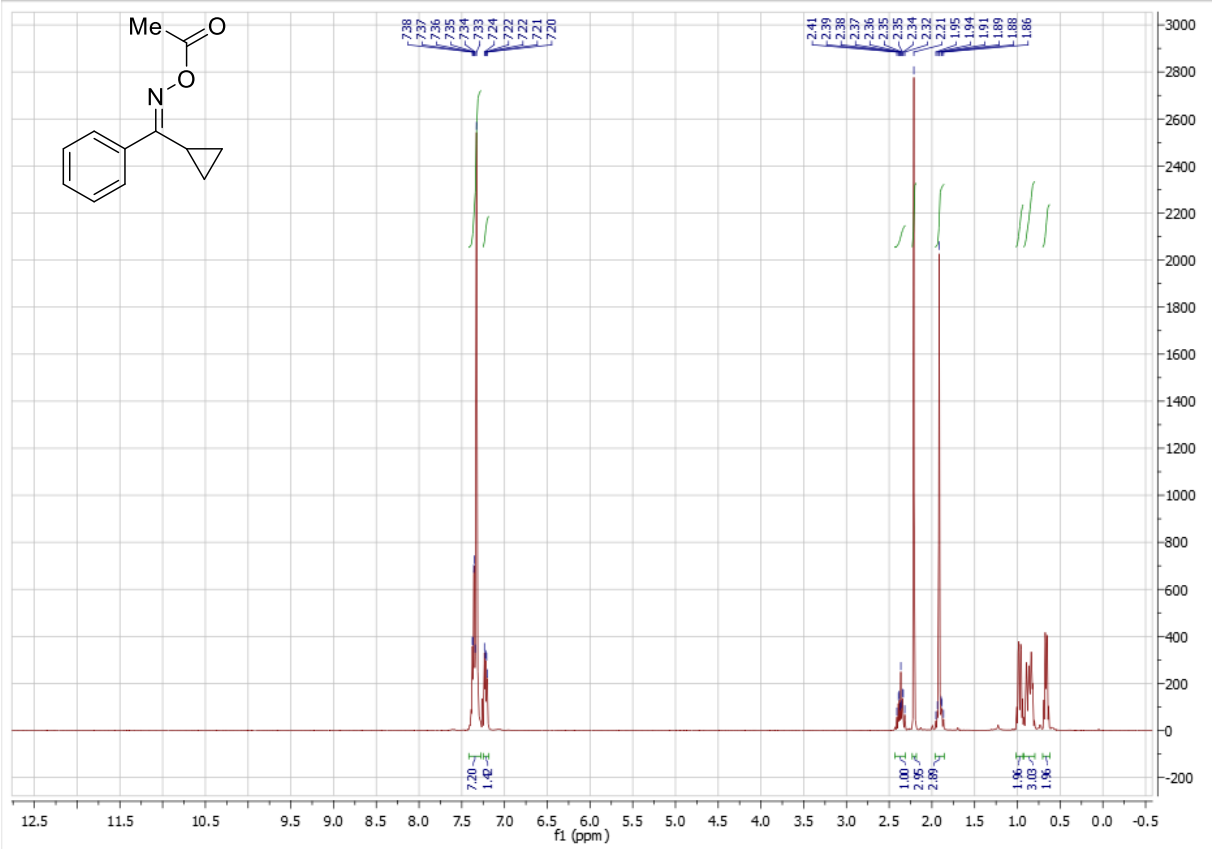
^{1}H NMR (400 MHz, $CDCl_3$): **1-phenylpropan-2-one O-acetyl oxime (3r)**



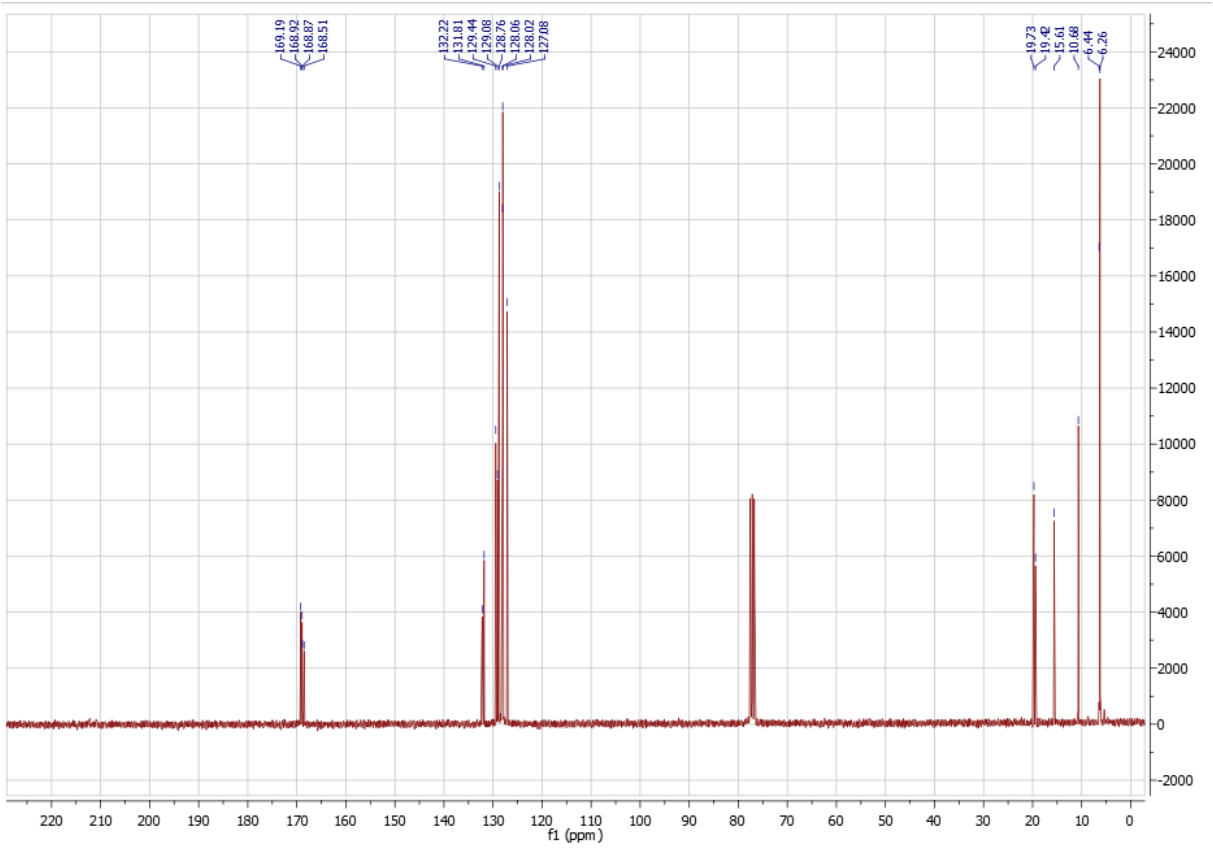
^{13}C NMR (101 MHz, $CDCl_3$):



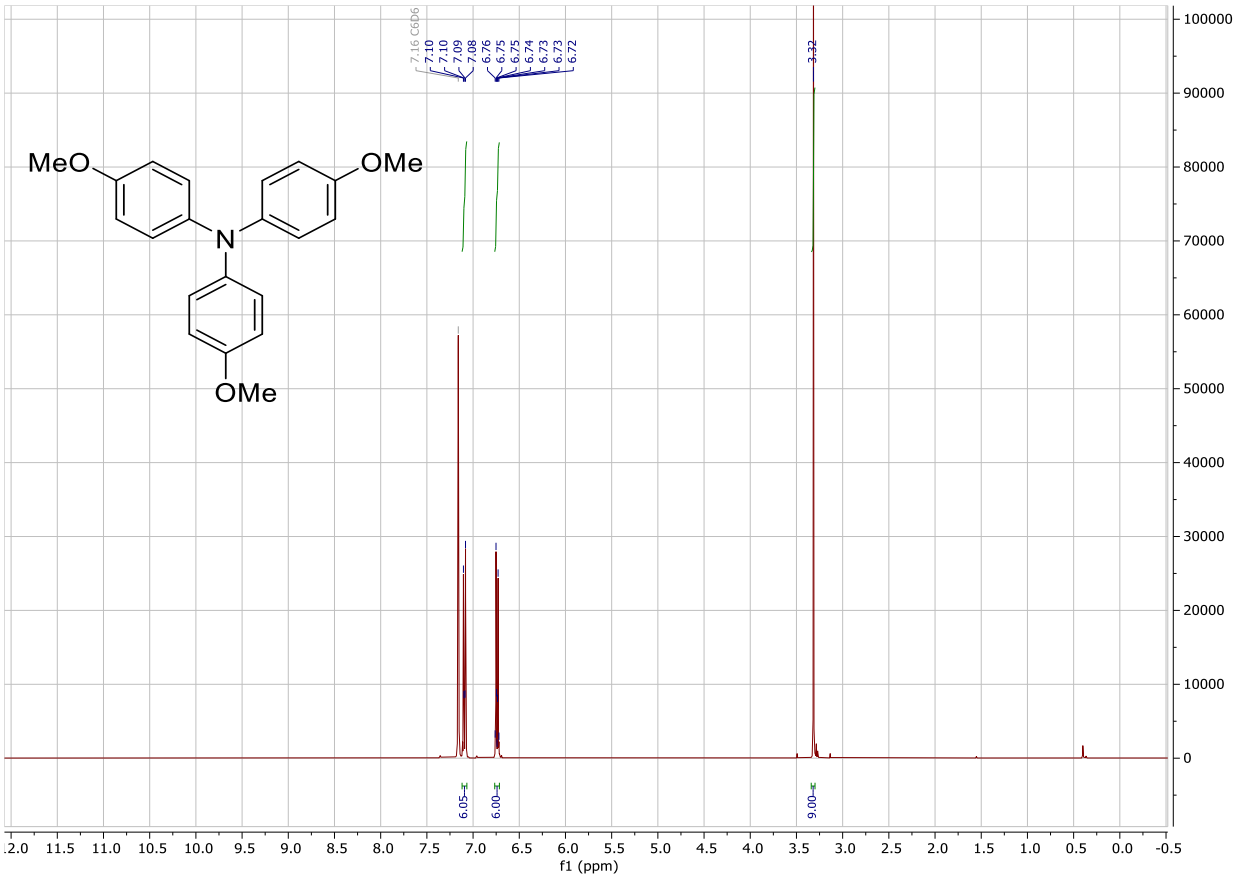
^{1}H NMR (400 MHz, $CDCl_3$): **Cyclopropyl(phenyl)methanone O-acetyl oxime (mixture of (E)- and (Z)-isomers) (3s)**



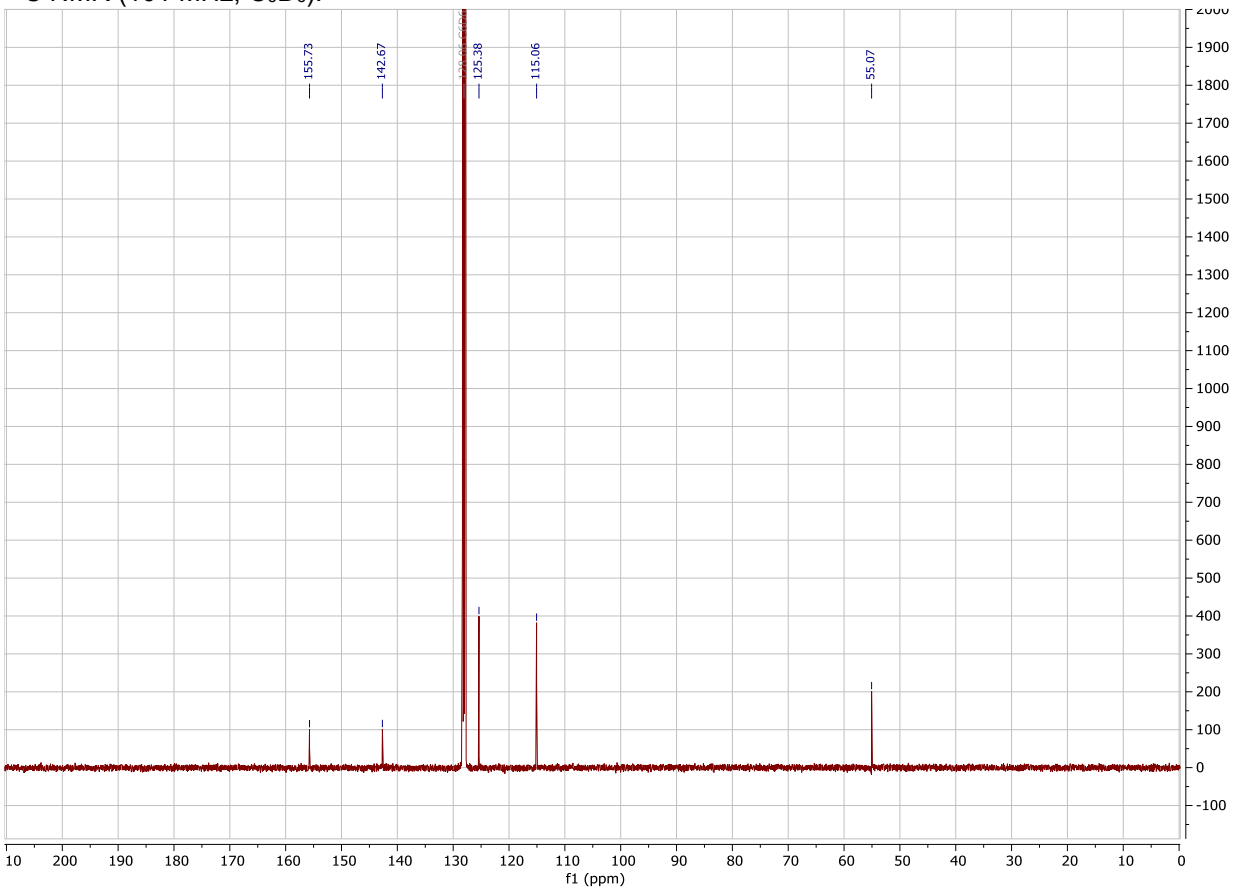
^{13}C NMR 101 MHz, $CDCl_3$):



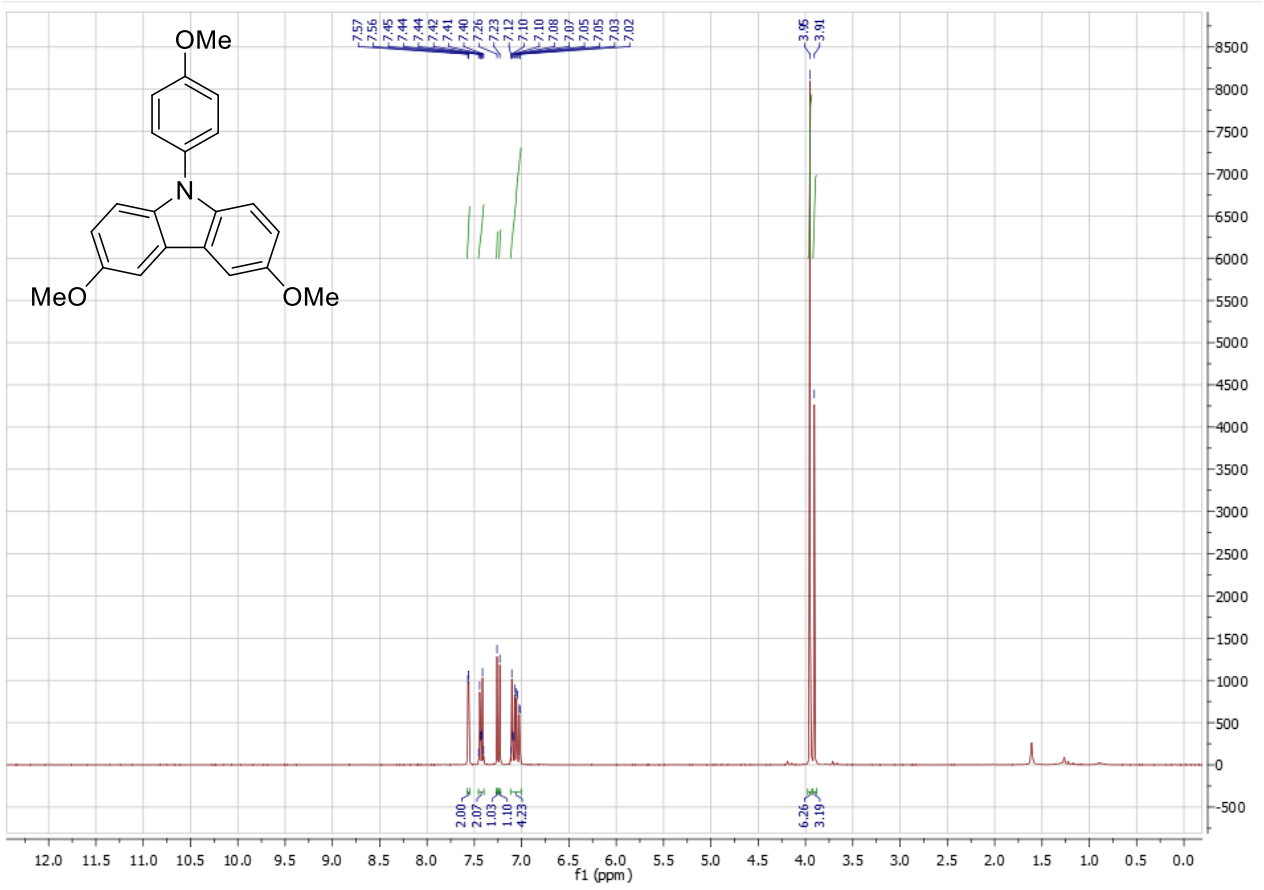
^{1}H NMR (400 MHz, C_6D_6): **Tris(4-methoxyphenyl)amine (T*p*AA)**



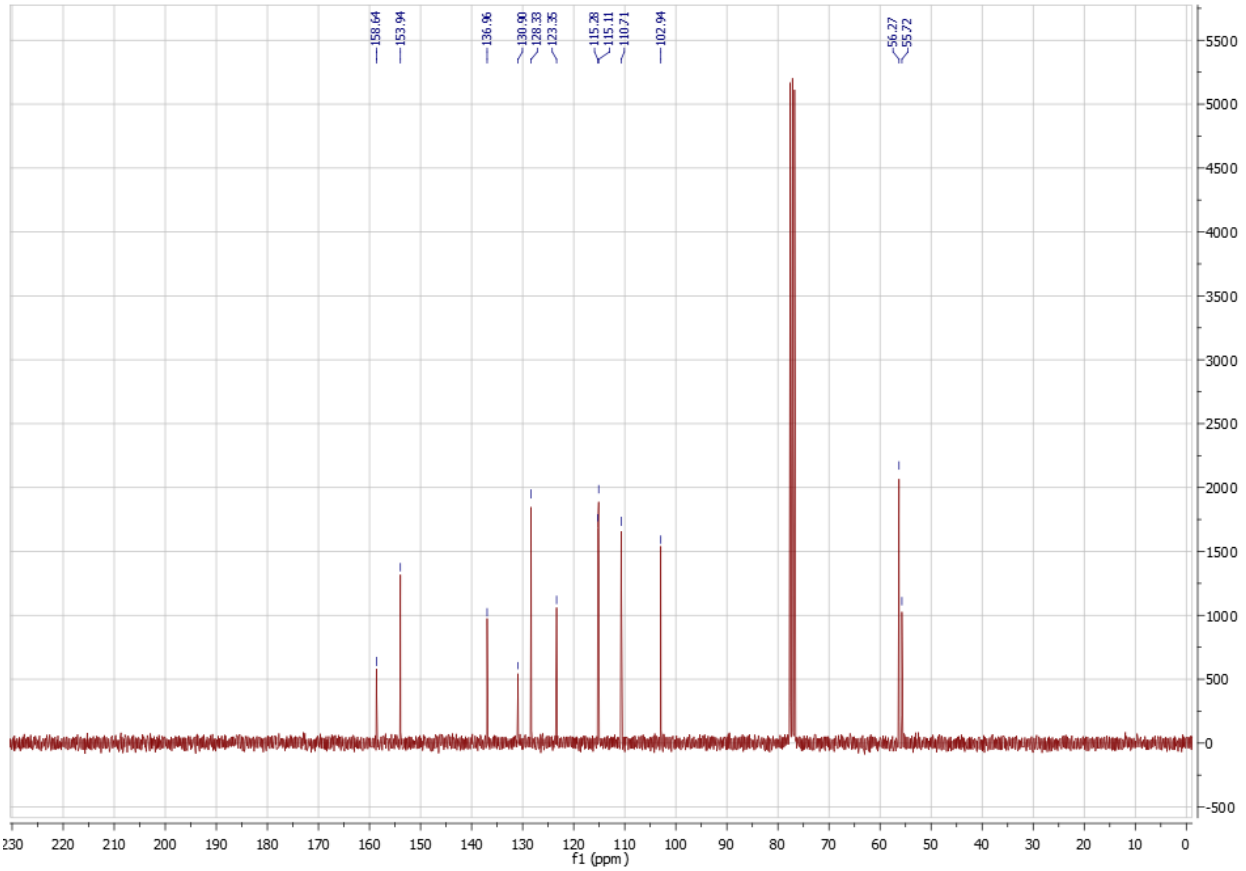
^{13}C NMR (101 MHz, C_6D_6):



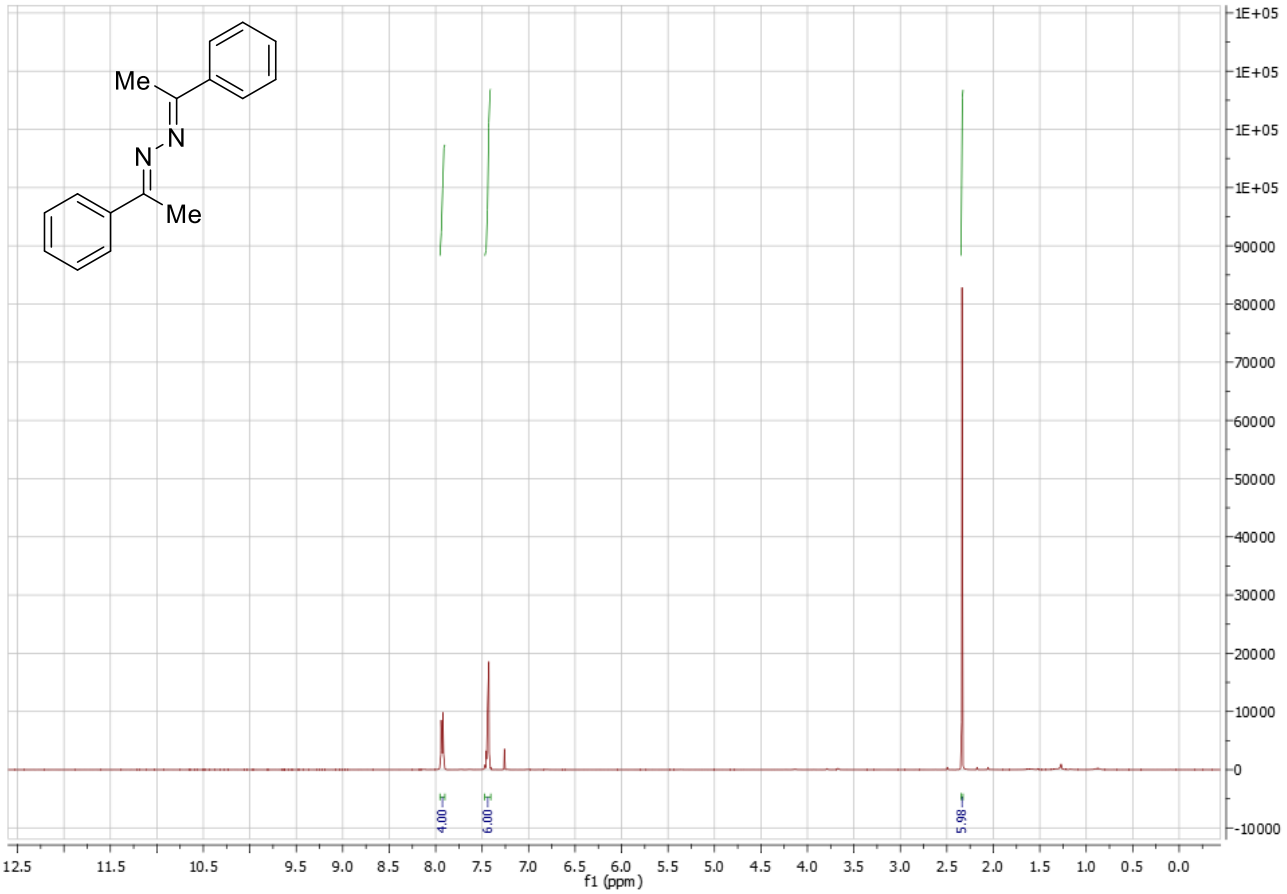
^{1}H NMR (400 MHz, $CDCl_3$): **3,6-dimethoxy-9-(4-methoxyphenyl)-9H-carbazole (CabZ)**



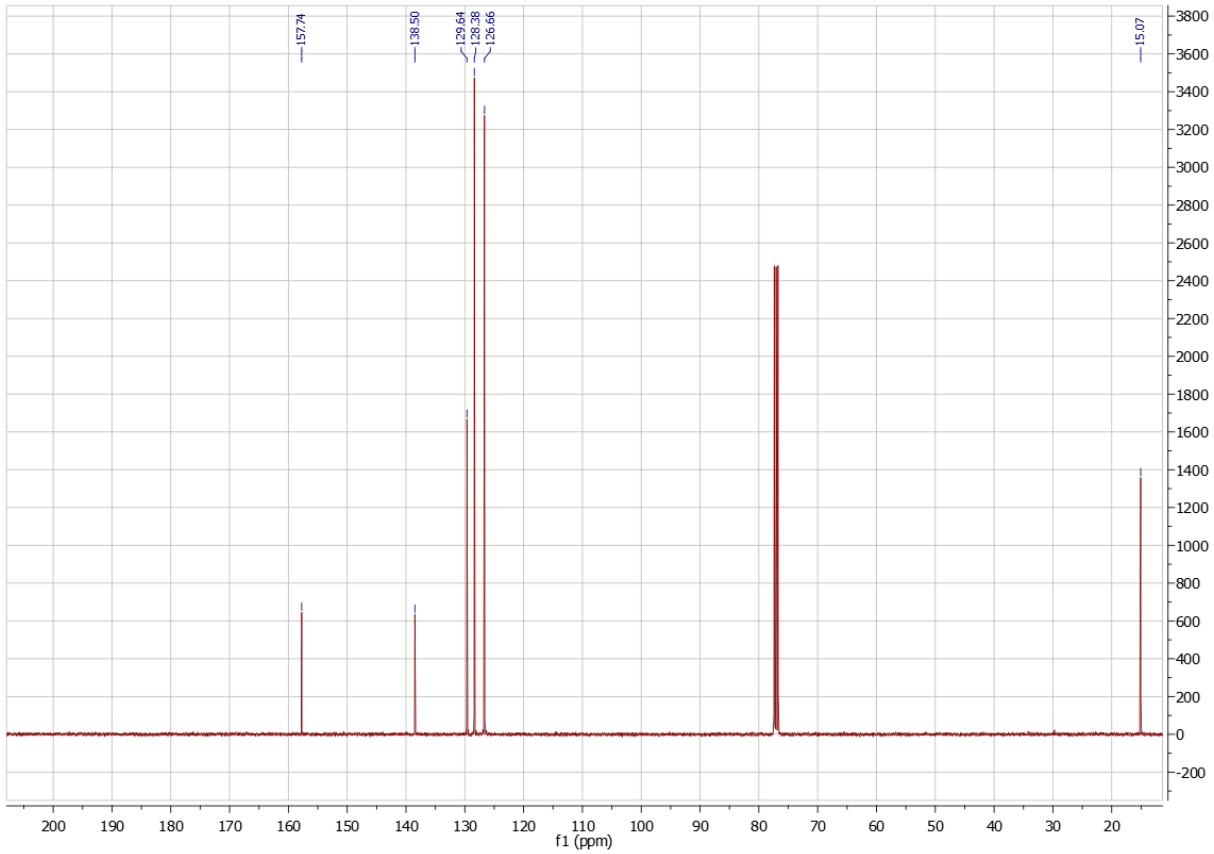
^{13}C NMR (101 MHz, $CDCl_3$):



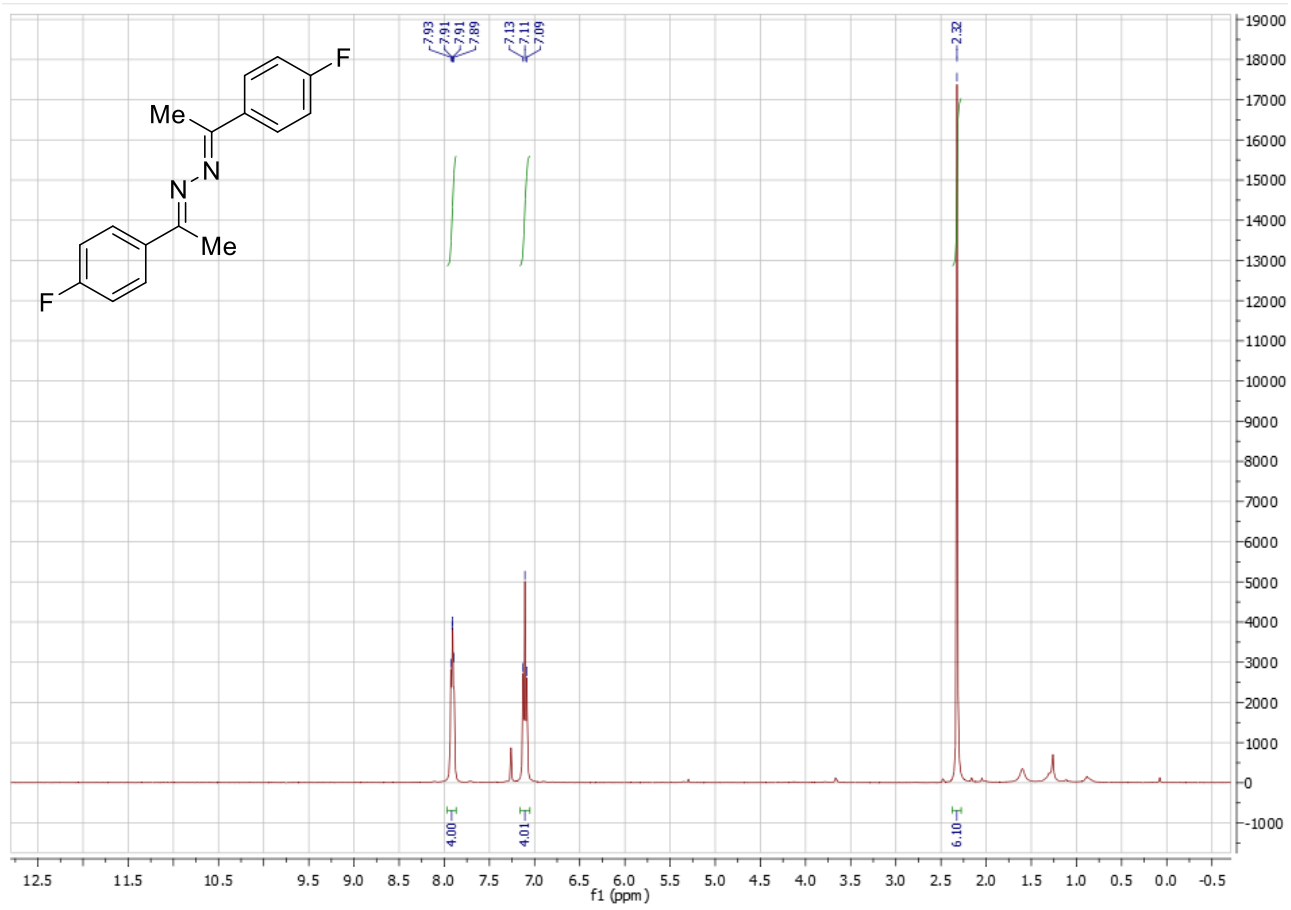
^{1}H NMR (400 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-phenylethylidene)hydrazine (2a)**



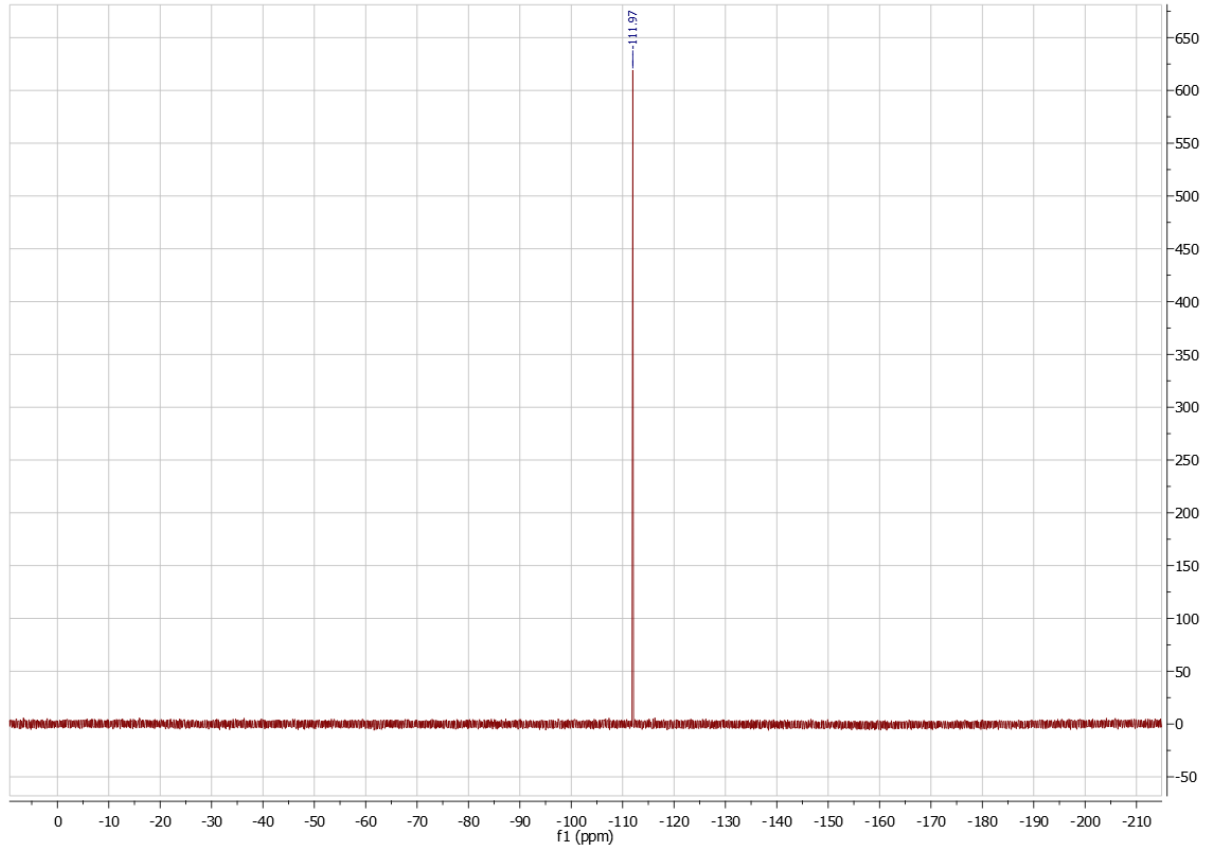
^{13}C NMR (101 MHz, $CDCl_3$):



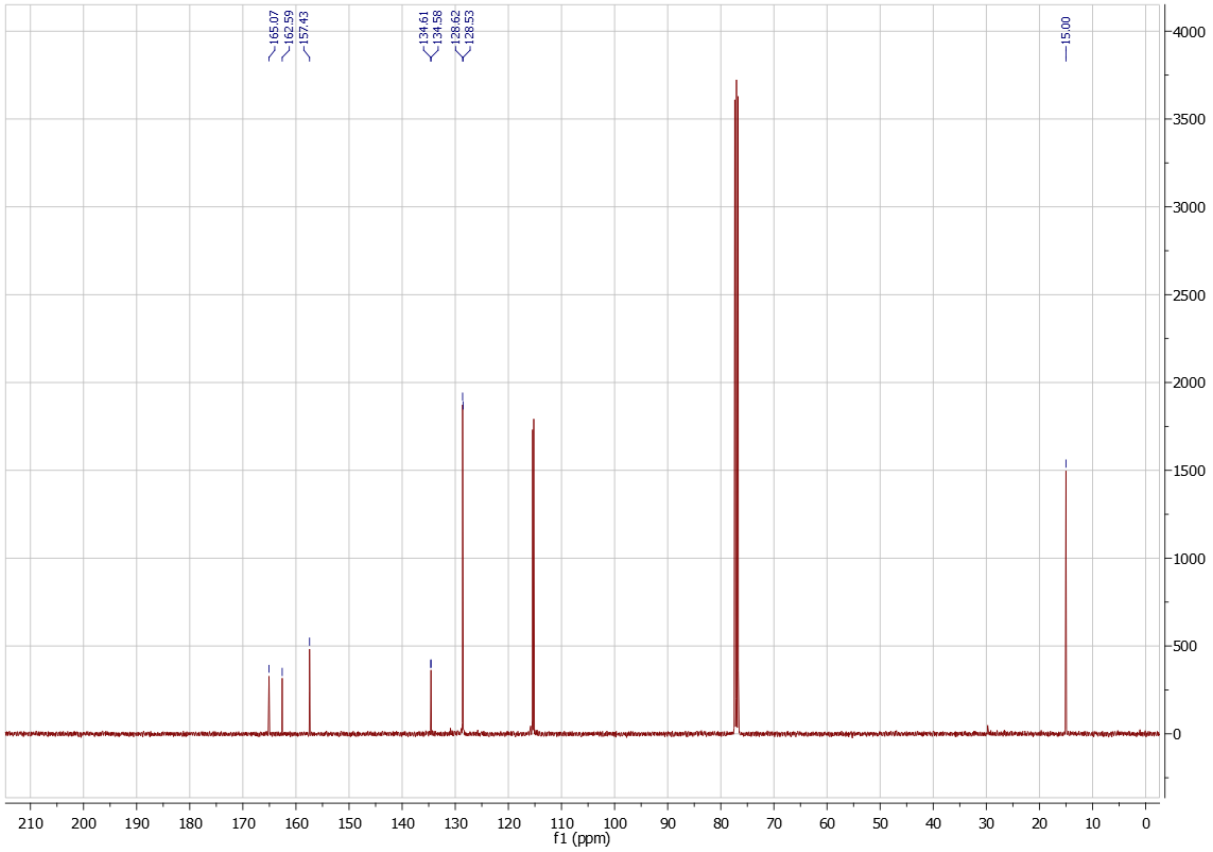
^{1}H NMR (400 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-(4-fluorophenyl)ethylidene)hydrazine (2b)**



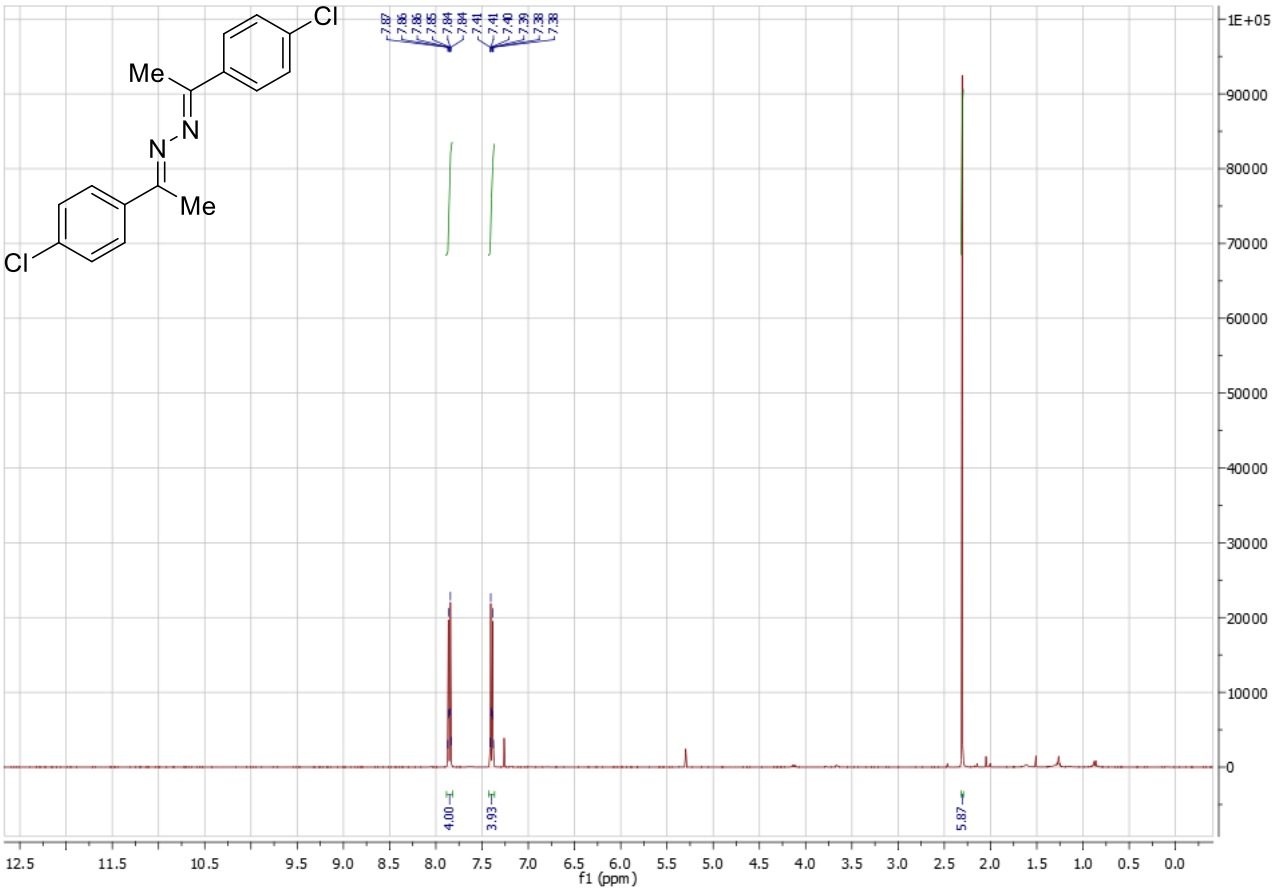
^{19}F NMR (377 MHz, $CDCl_3$):



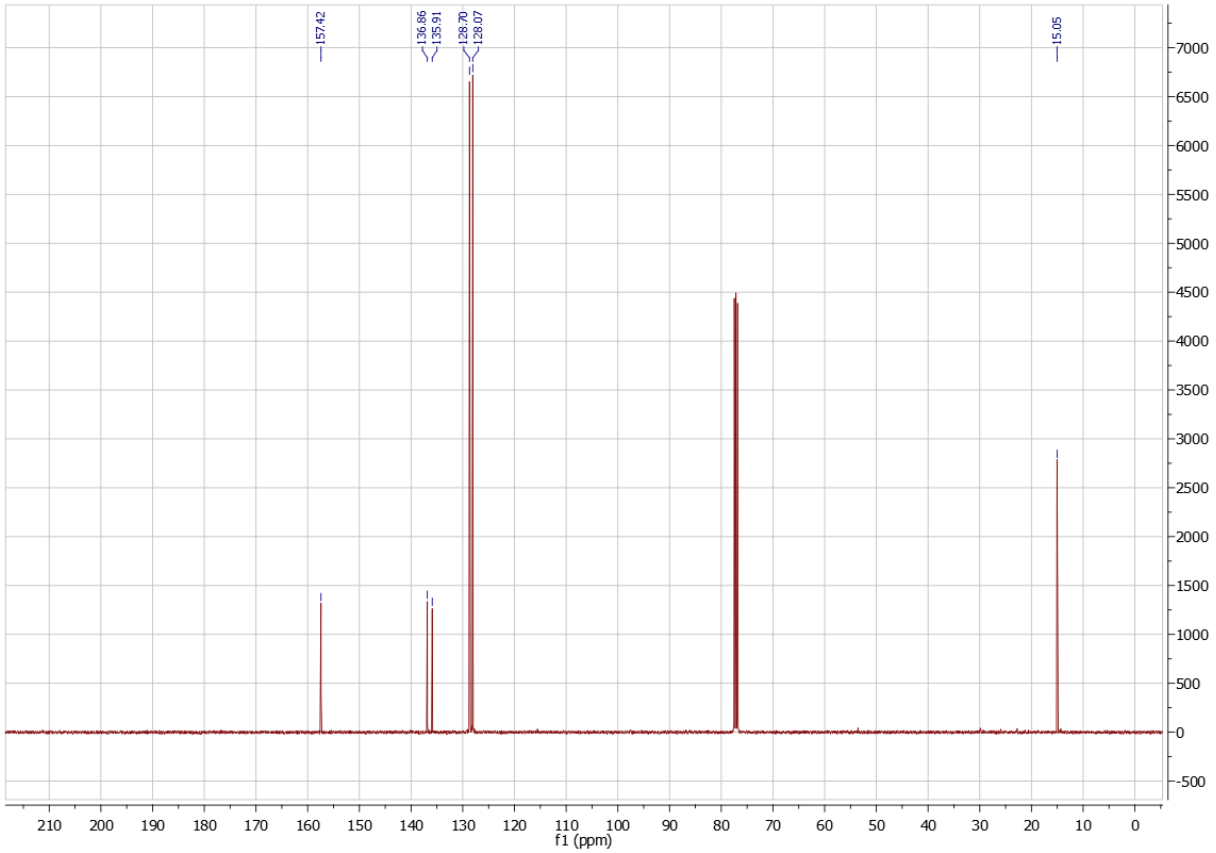
^{13}C NMR (101 MHz, $CDCl_3$):



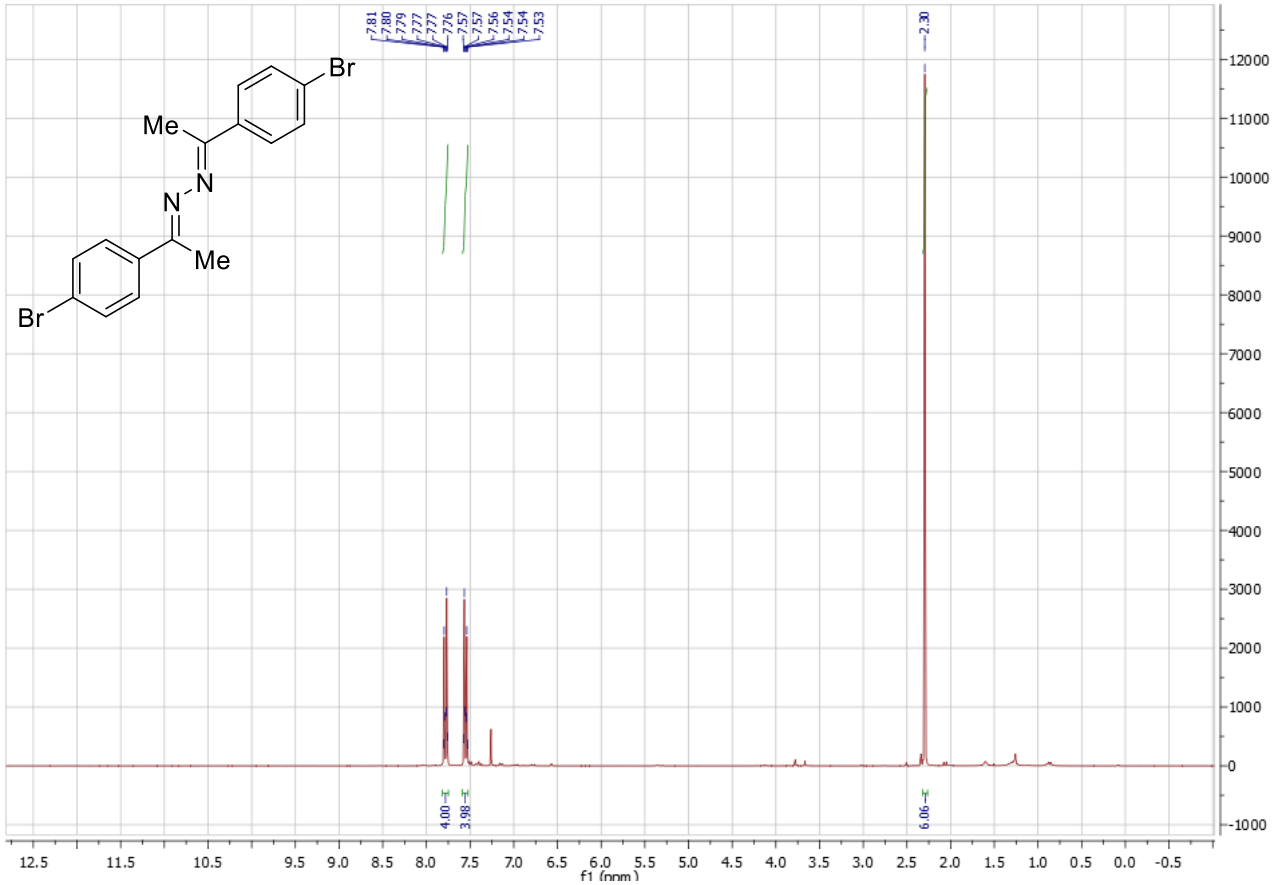
^{1}H NMR (400 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-(4-chlorophenyl)ethylidene)hydrazine (2c)**



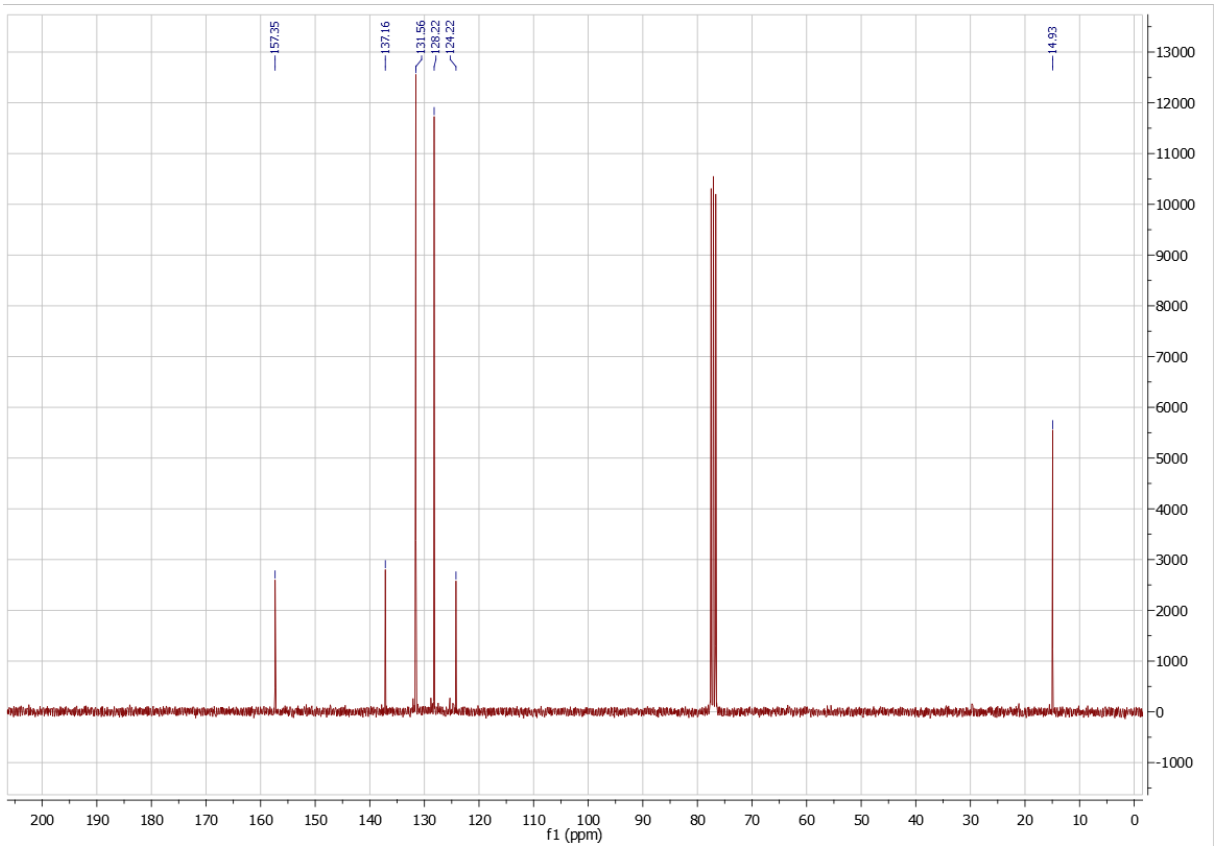
^{13}C NMR (101 MHz, $CDCl_3$):



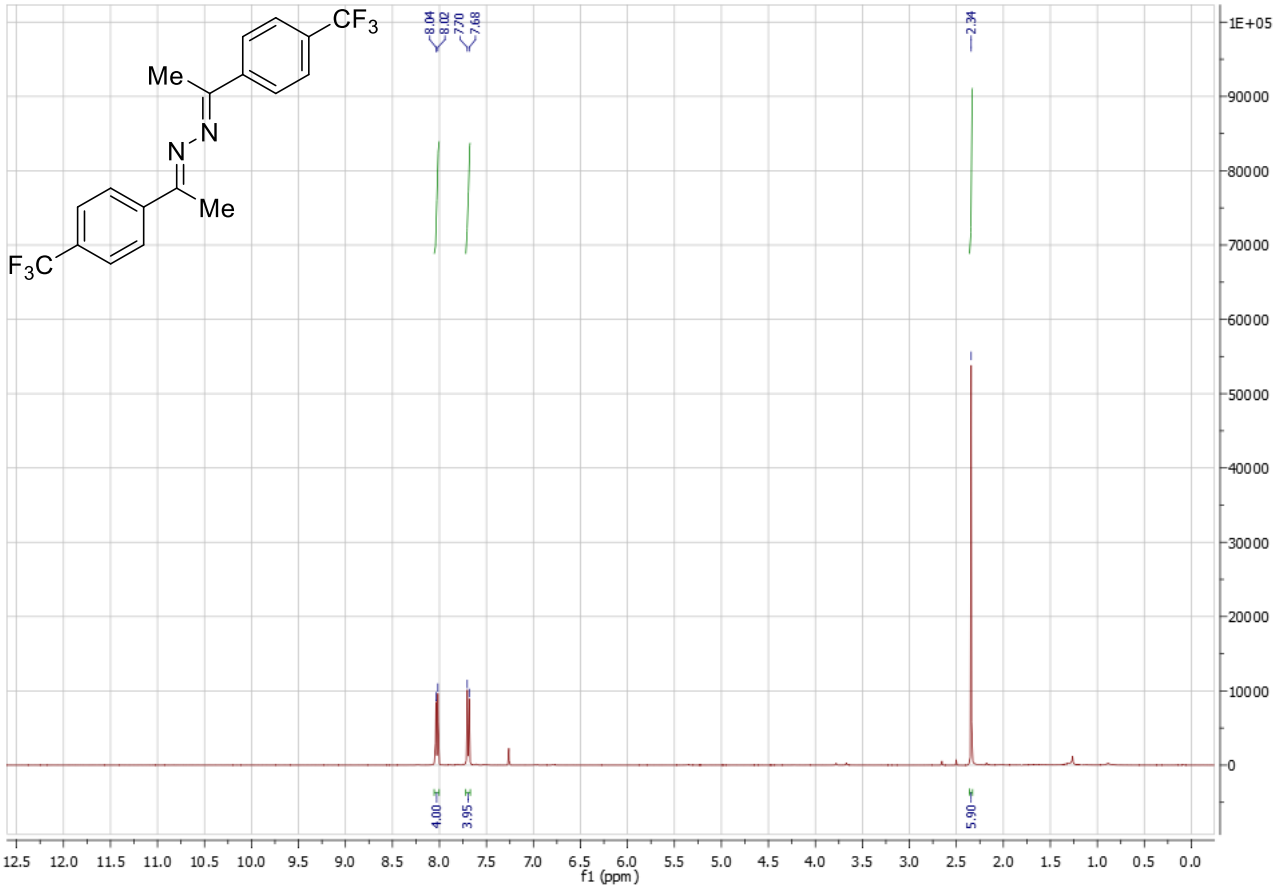
^{1}H NMR (300 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-(4-bromophenyl)ethylidene)hydrazine (2d)**



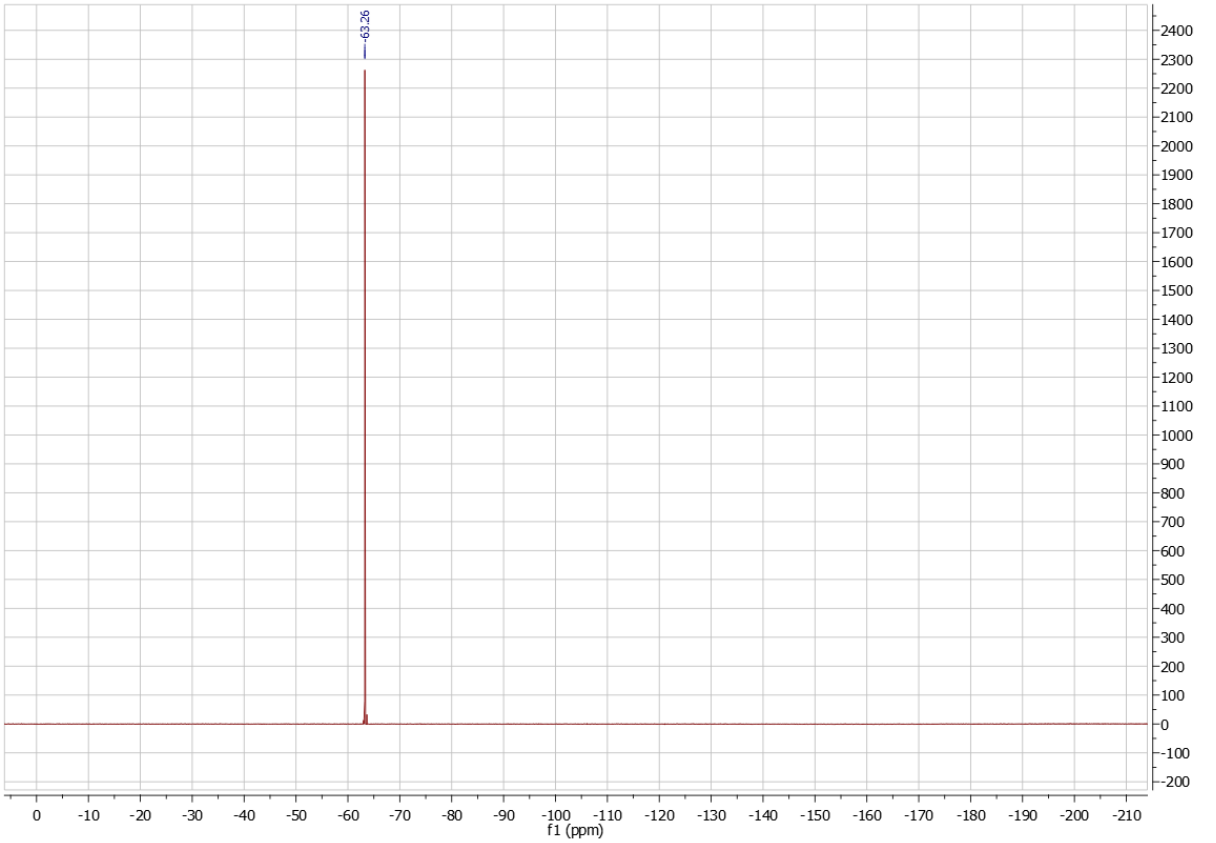
^{13}C NMR (75 MHz, $CDCl_3$):



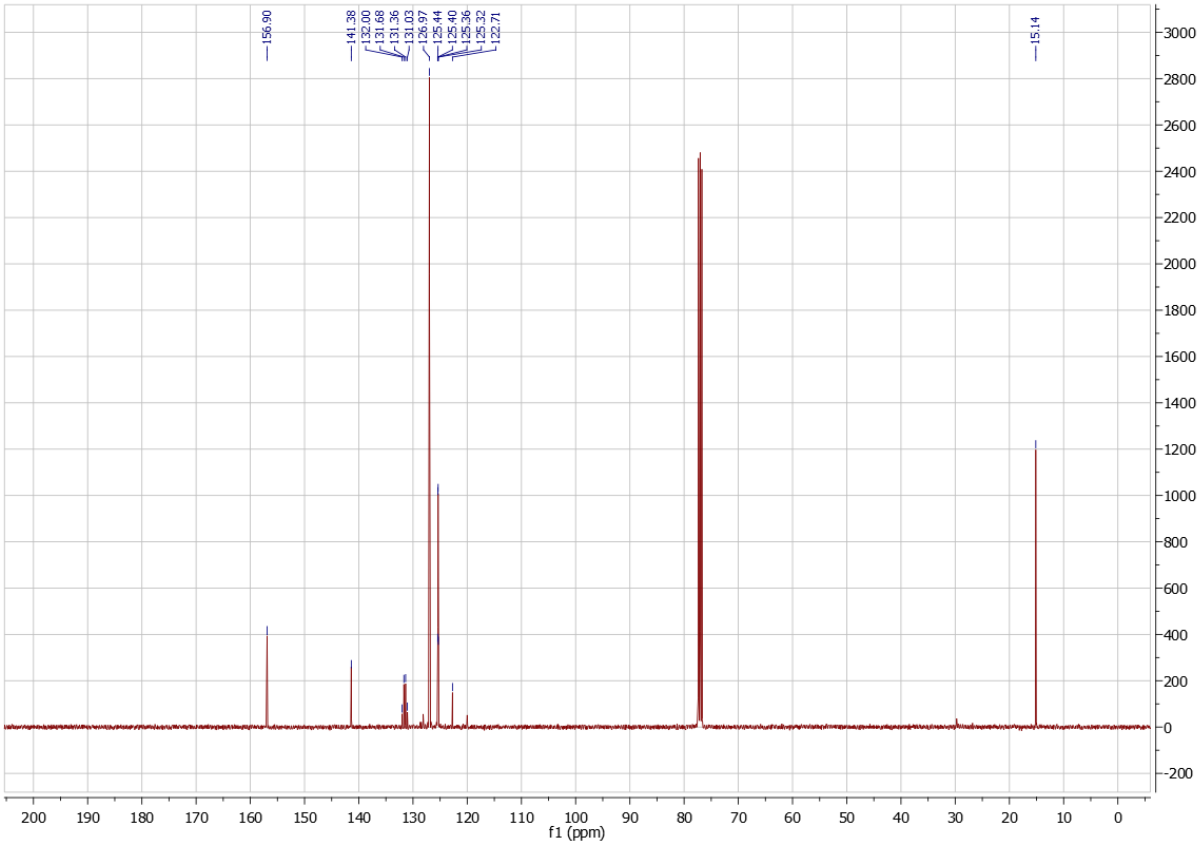
^{1}H NMR (400 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-(4-(trifluoromethyl)phenyl)ethylidene)hydrazine (2e)**



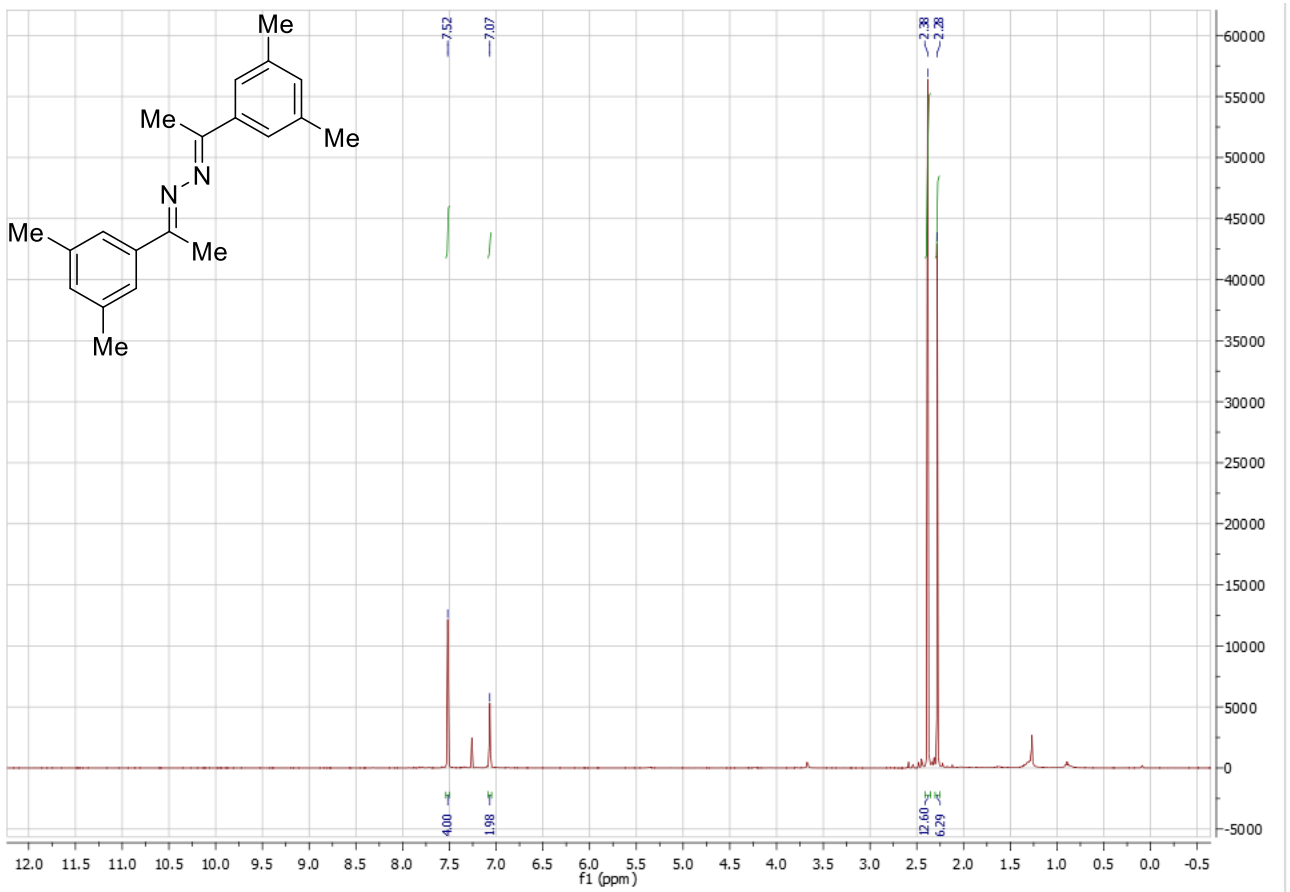
^{19}F NMR (377 MHz, $CDCl_3$):



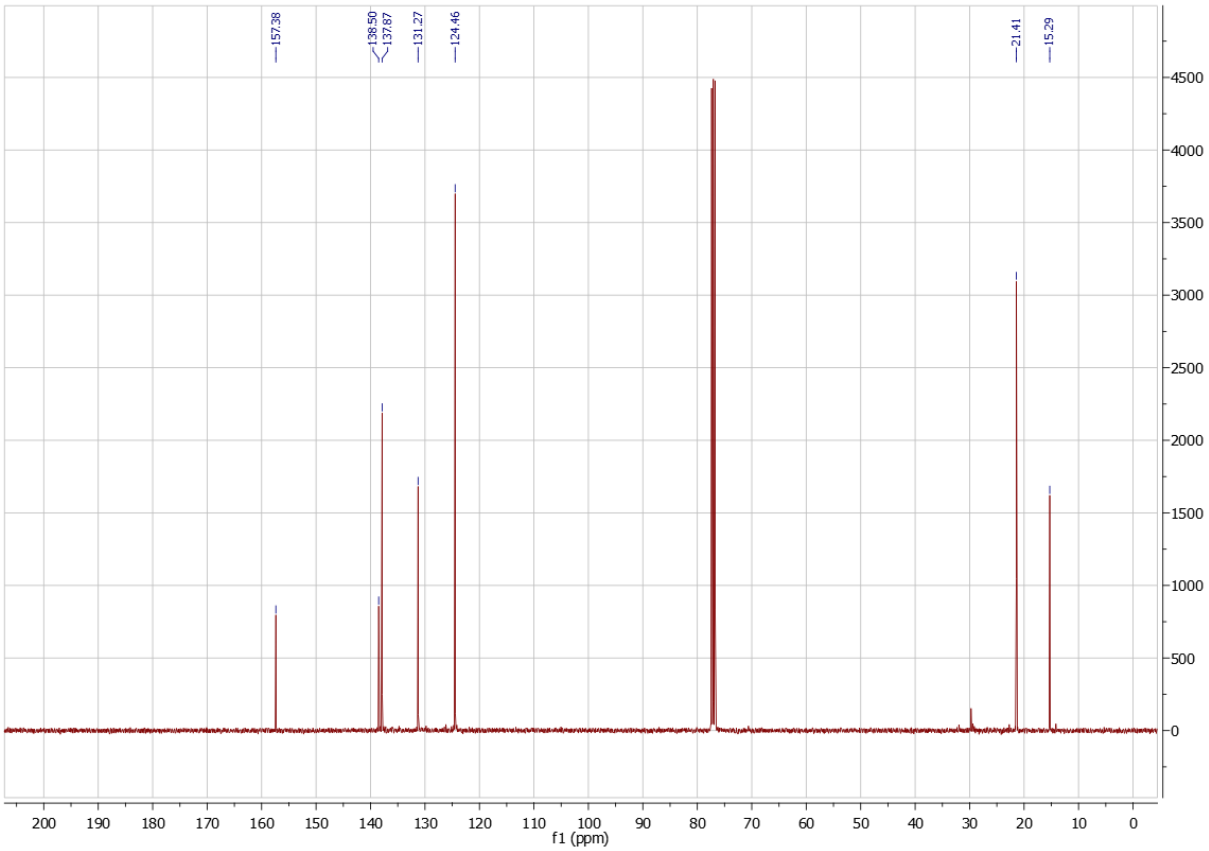
^{13}C NMR (101 MHz, $CDCl_3$):



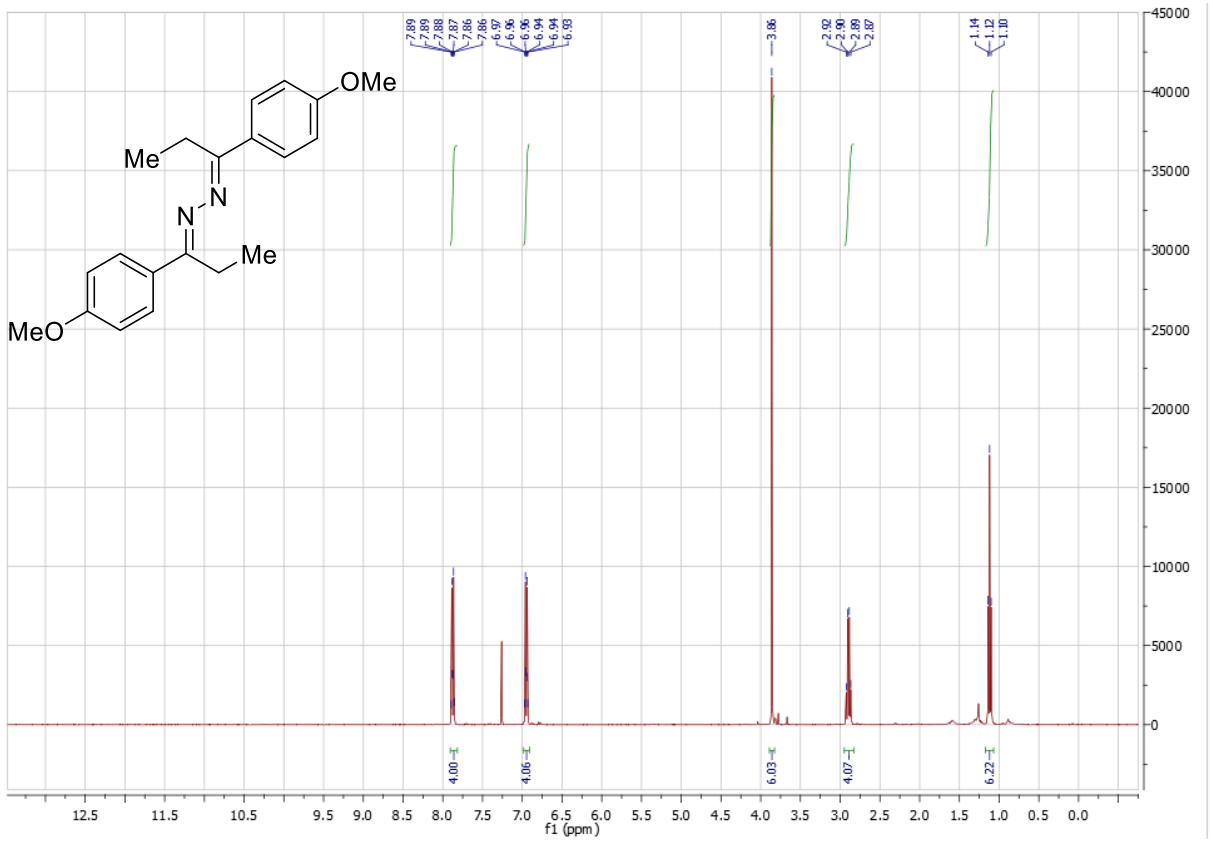
^{1}H NMR (400 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-(3,5-dimethylphenyl)ethylidene)hydrazine (2f)**



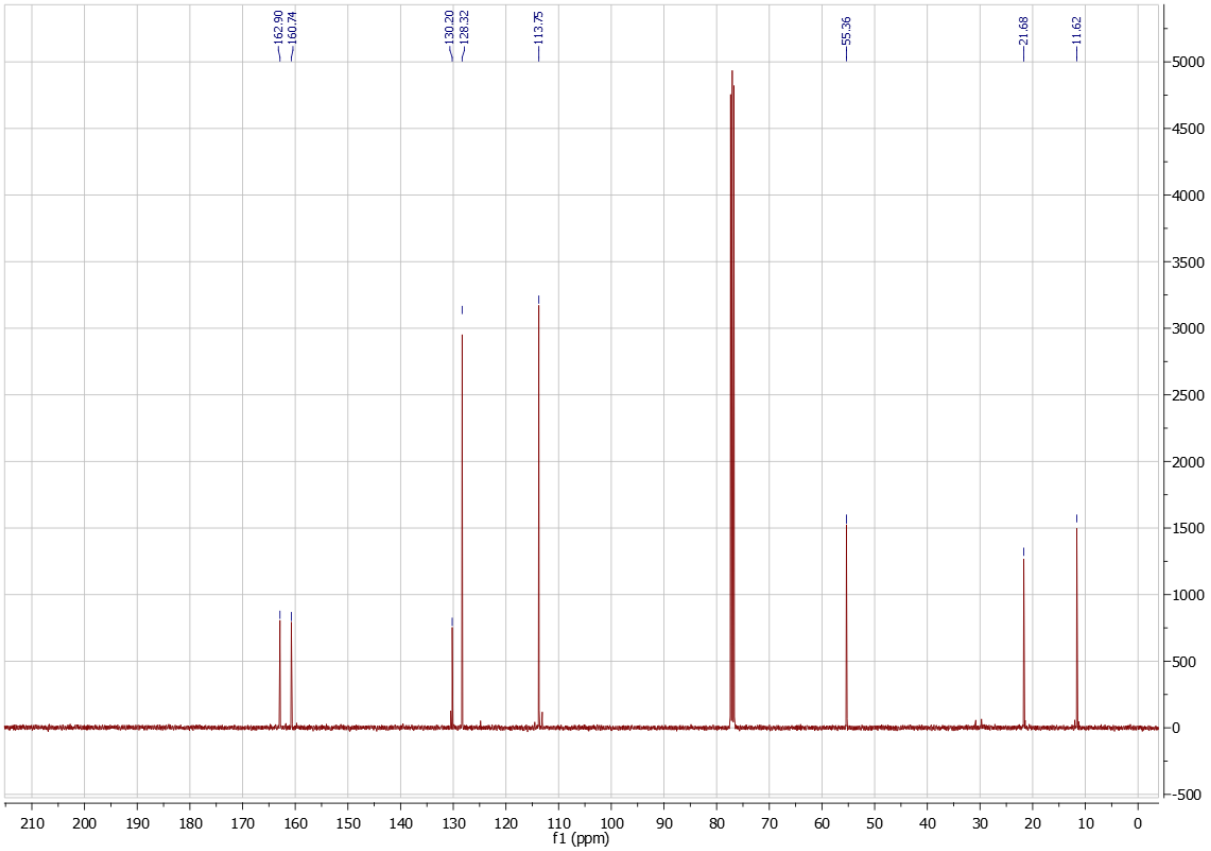
^{13}C NMR (101 MHz, $CDCl_3$):



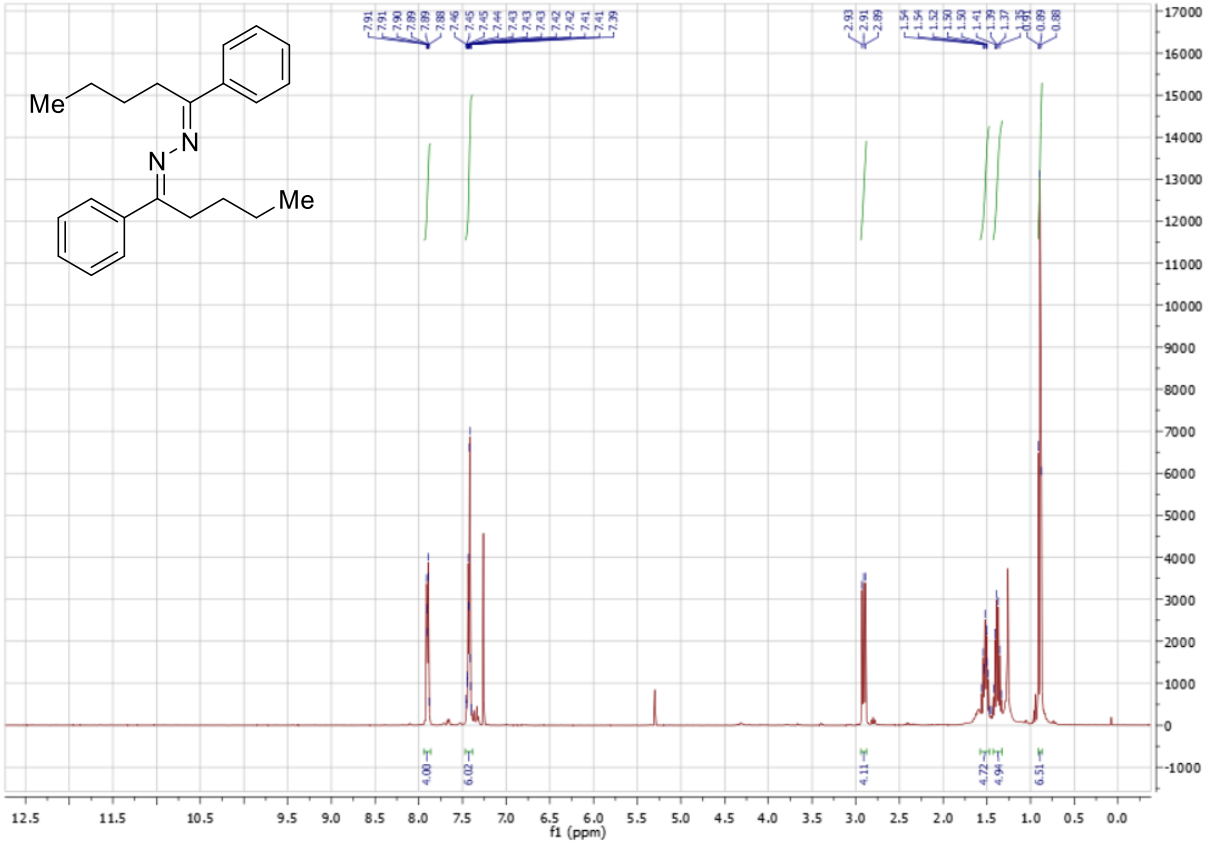
^{1}H NMR (400 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-(4-methoxyphenyl)propylidene)hydrazine (2g)**



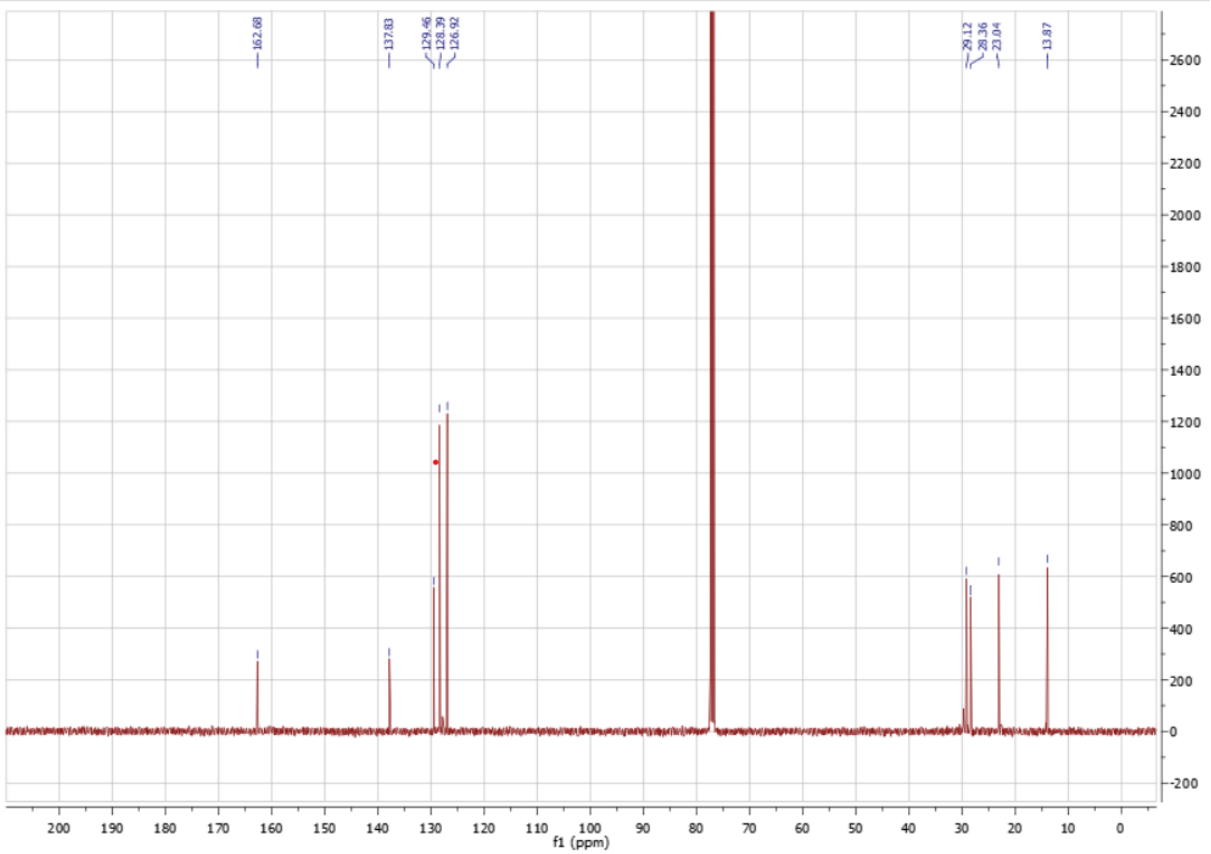
^{13}C NMR (101 MHz, $CDCl_3$):



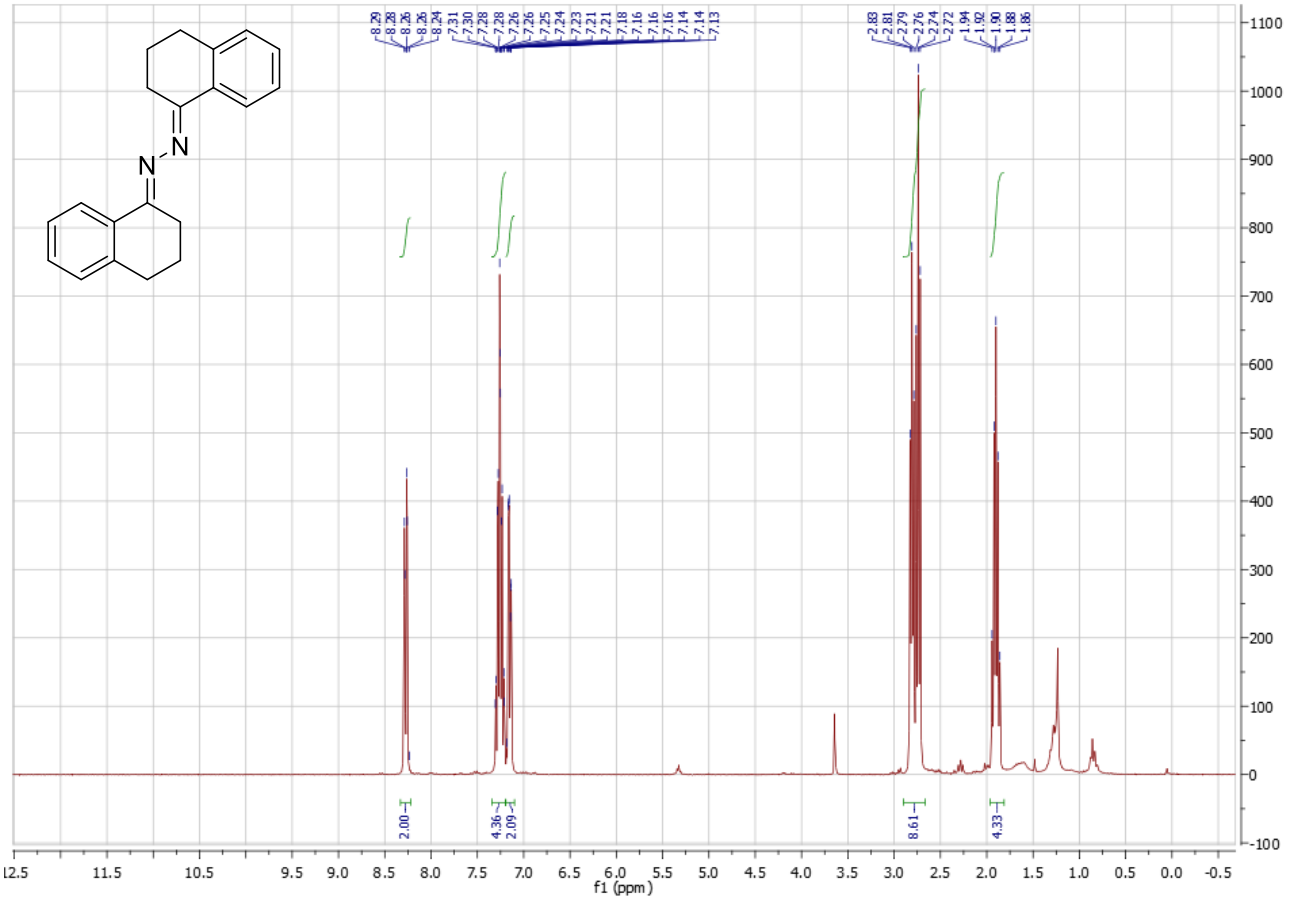
^{1}H NMR (400 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-phenylpentylidene)hydrazine (2h)**



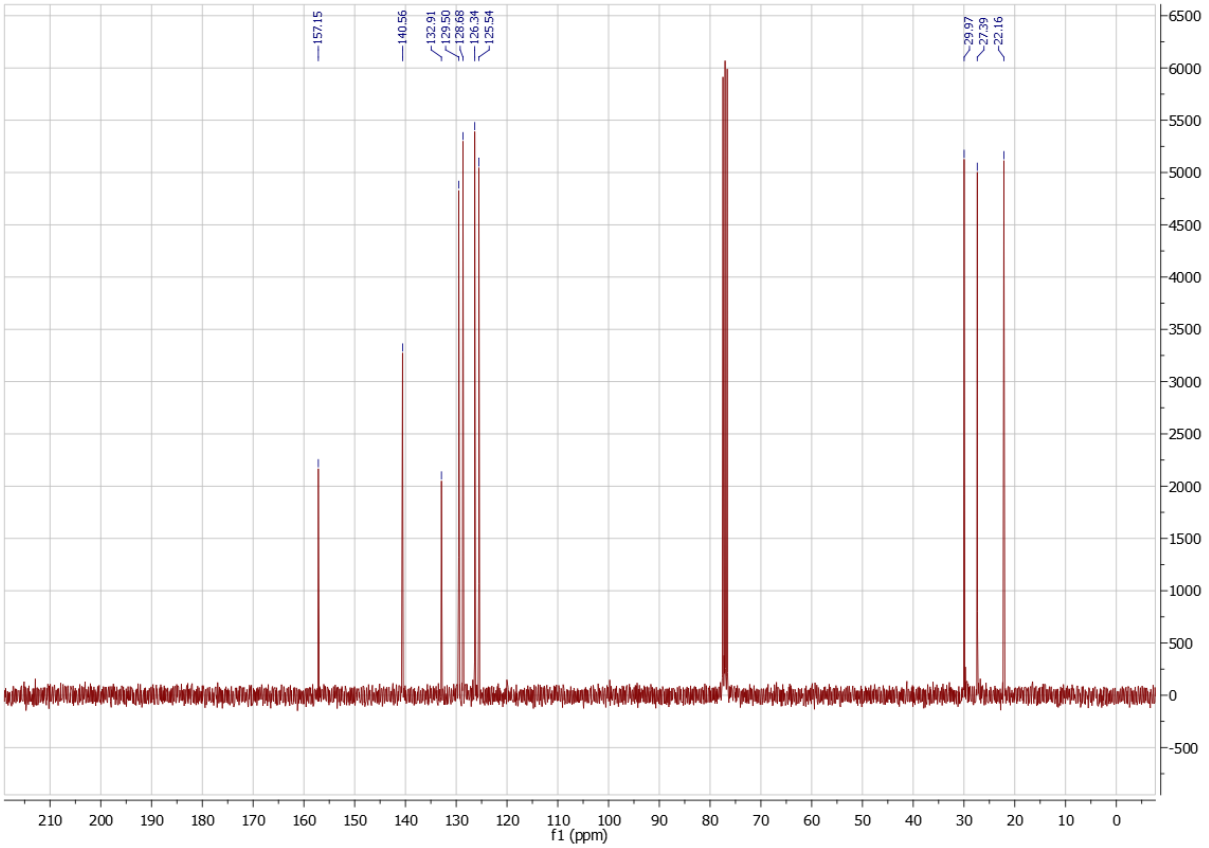
^{13}C NMR (101 MHz, $CDCl_3$):



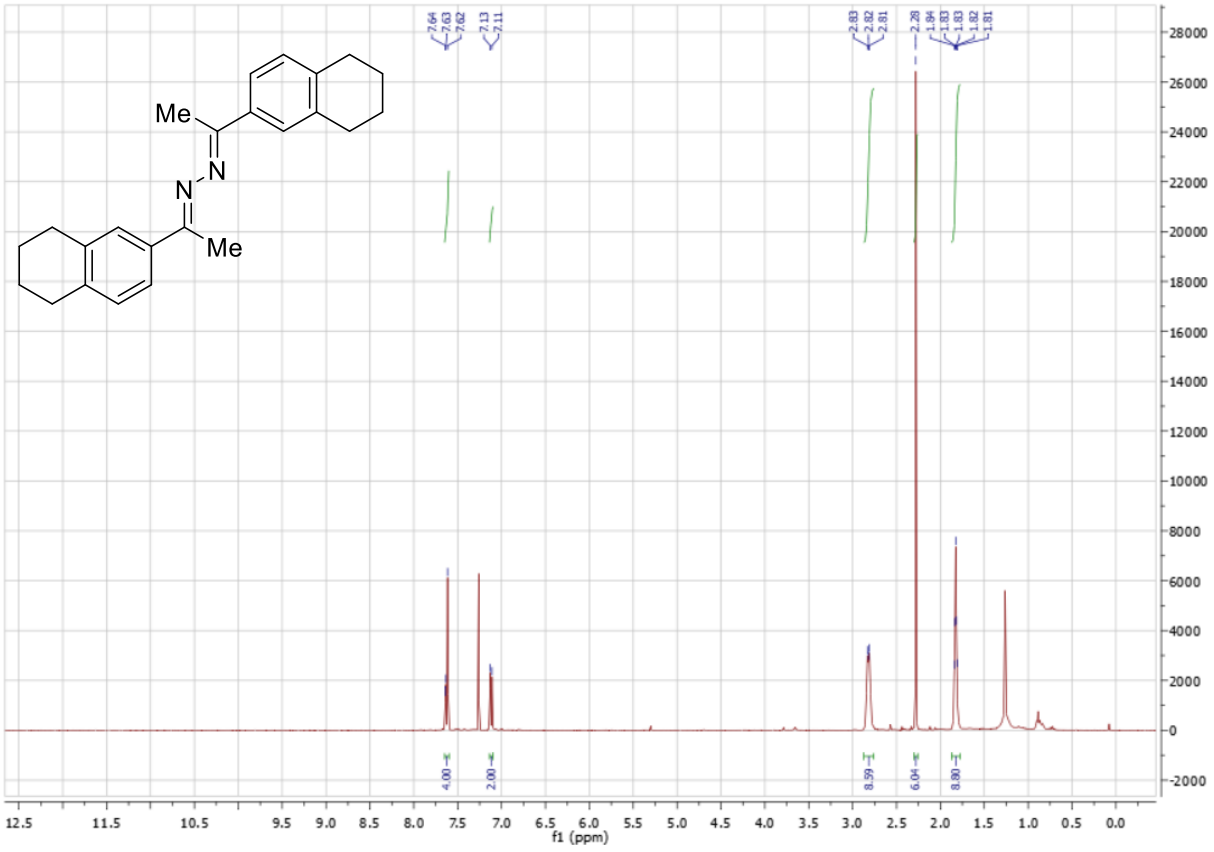
^{1}H NMR (300 MHz, $CDCl_3$): **1,2-bis((E)-3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine (2i)**



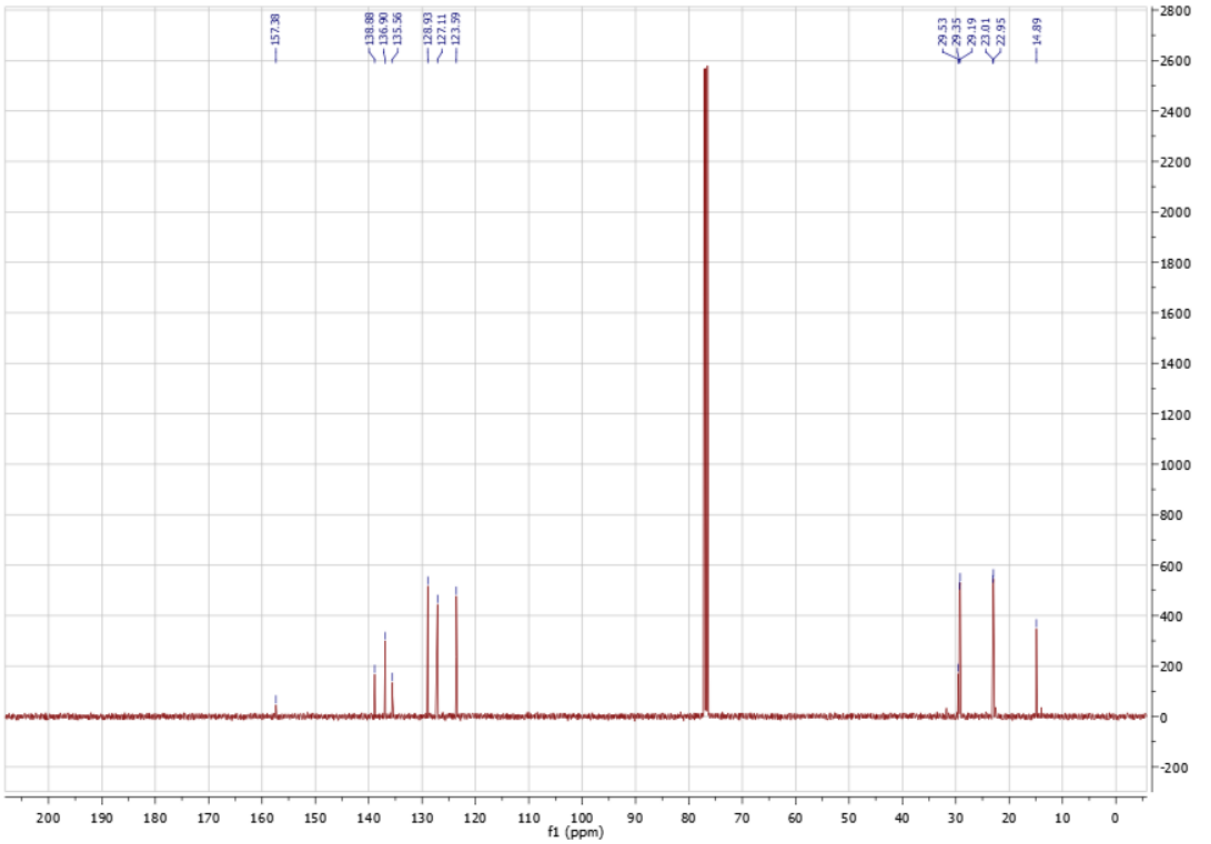
^{13}C NMR (75 MHz, $CDCl_3$):



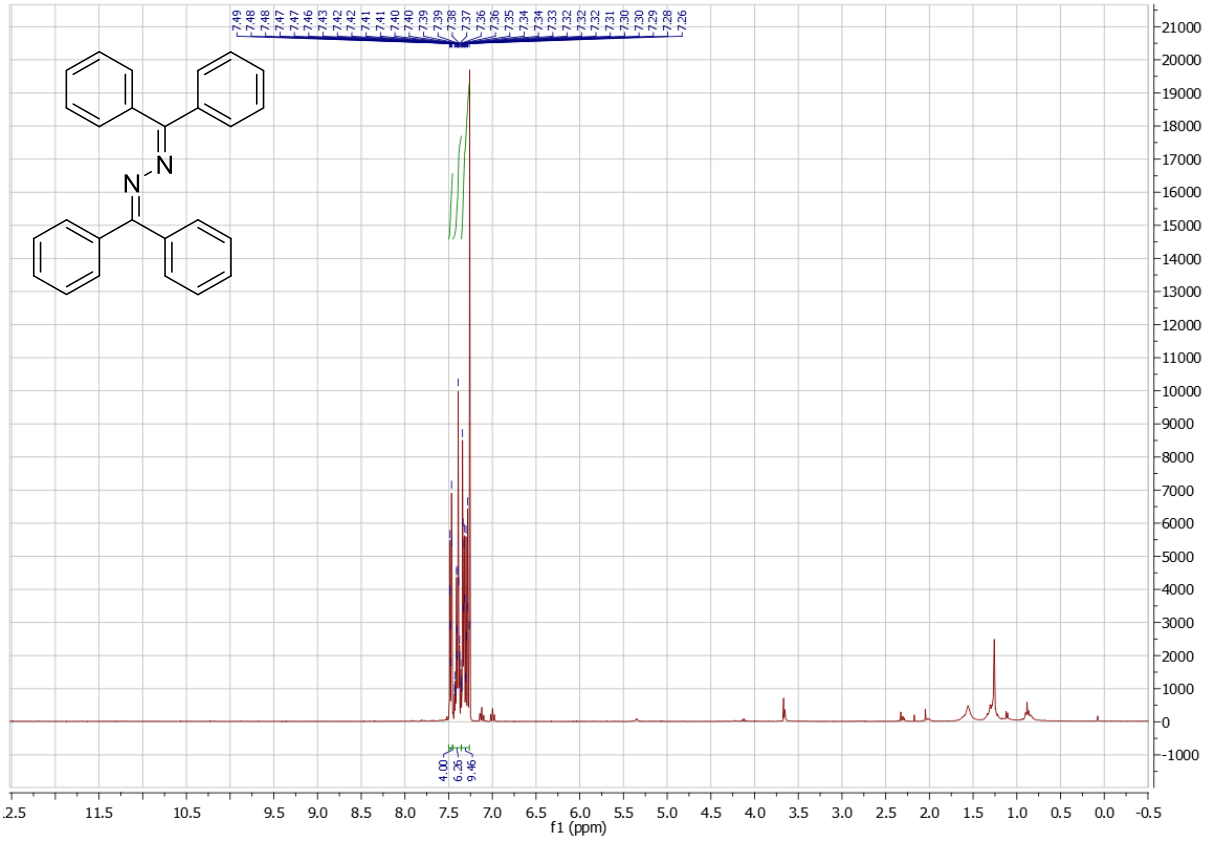
^{1}H NMR (400 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-(5,6,7,8-tetrahydronaphthalen-2-yl)ethylidene)hydrazine (2j)**



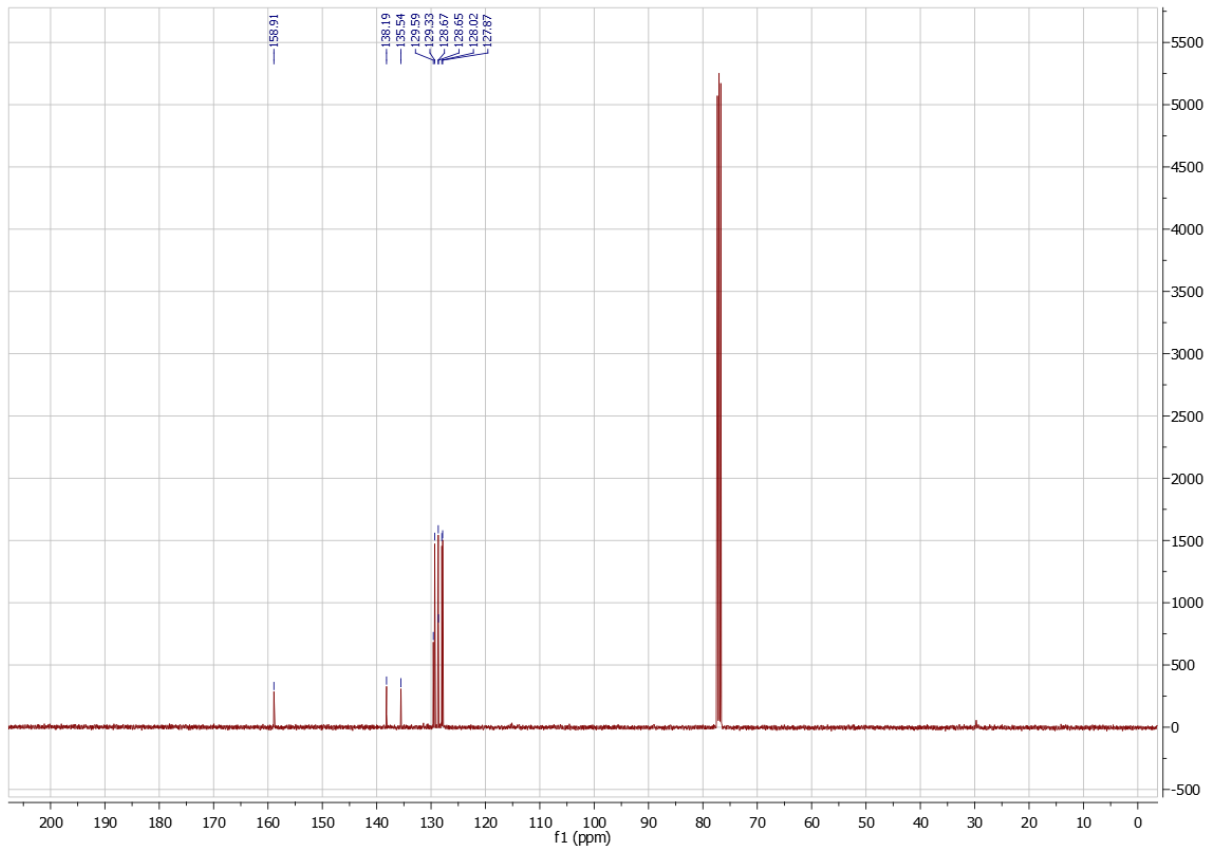
^{13}C NMR (101 MHz, $CDCl_3$):



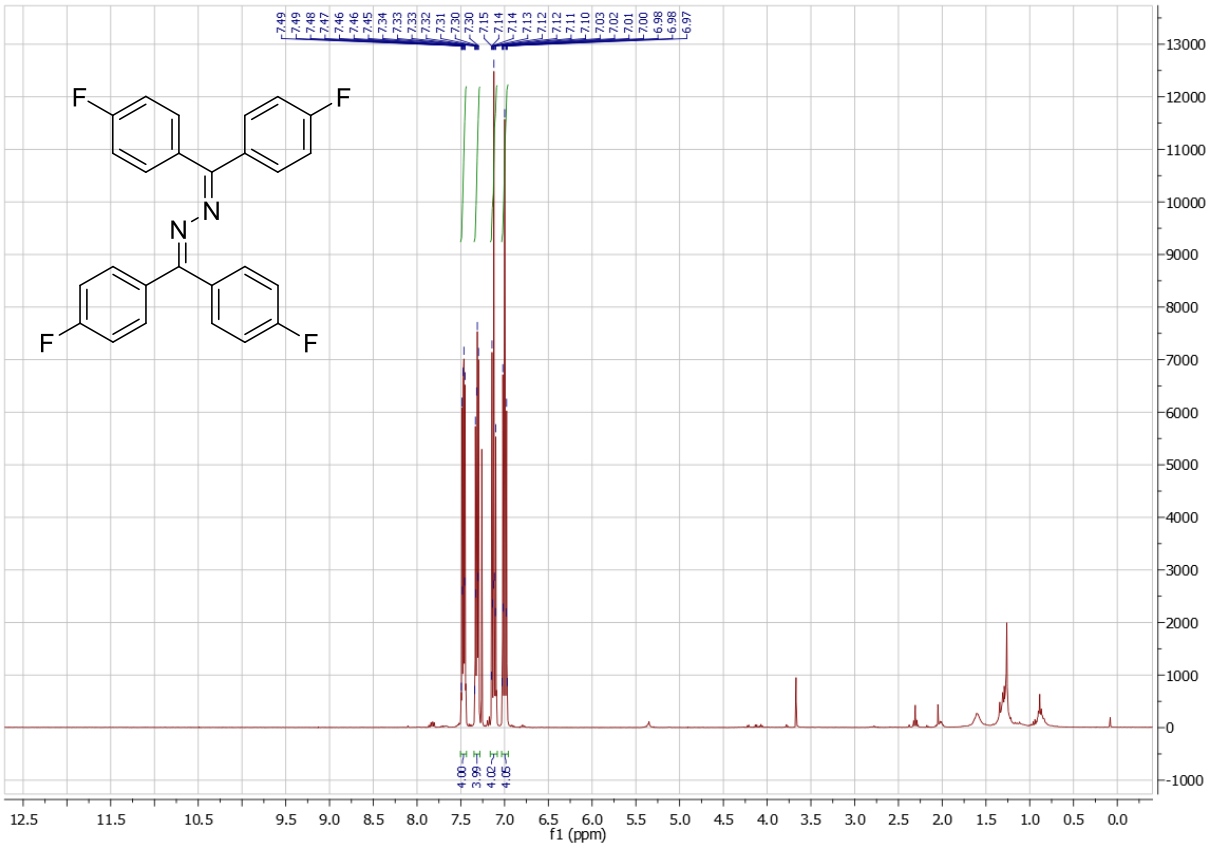
^{1}H NMR (400 MHz, $CDCl_3$): **1,2-bis(diphenylmethylene)hydrazine (2k)**



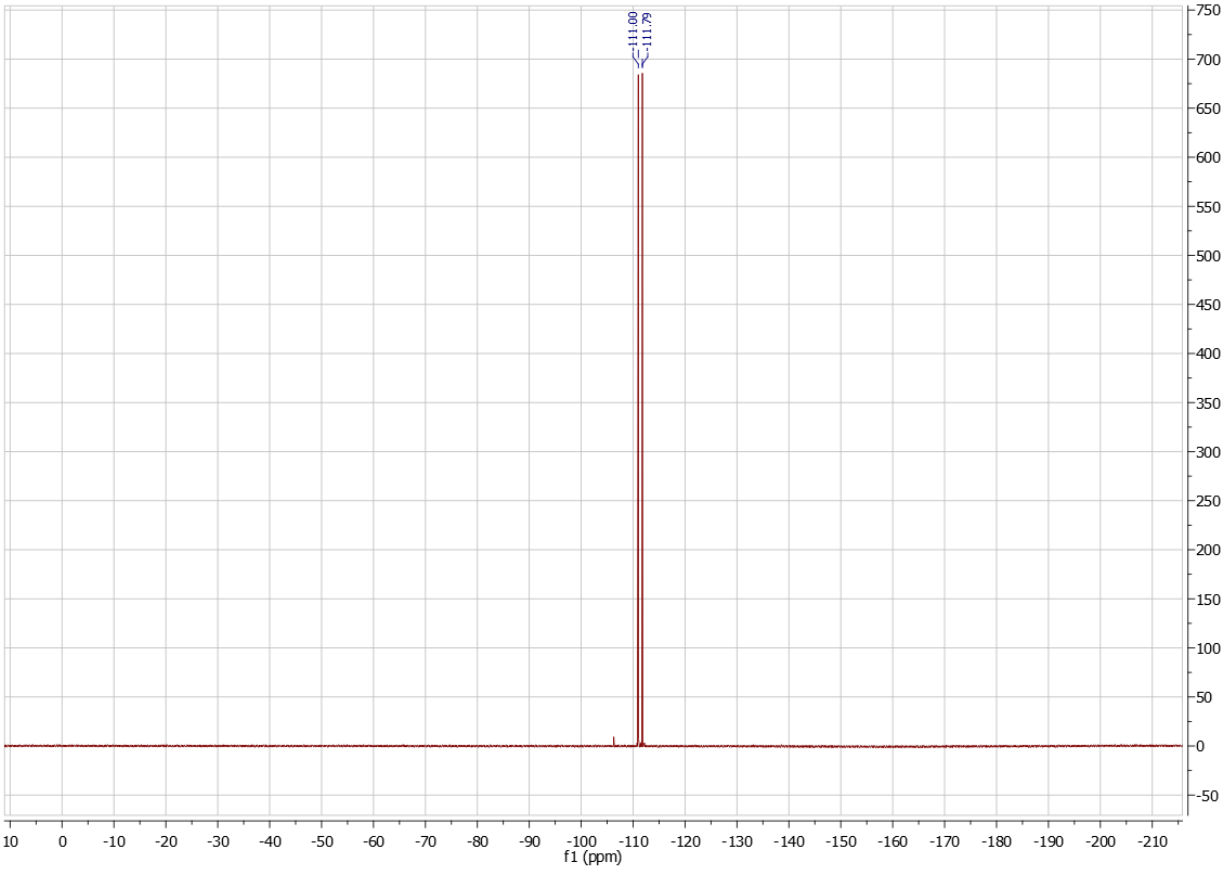
^{13}C NMR (101 MHz, $CDCl_3$):



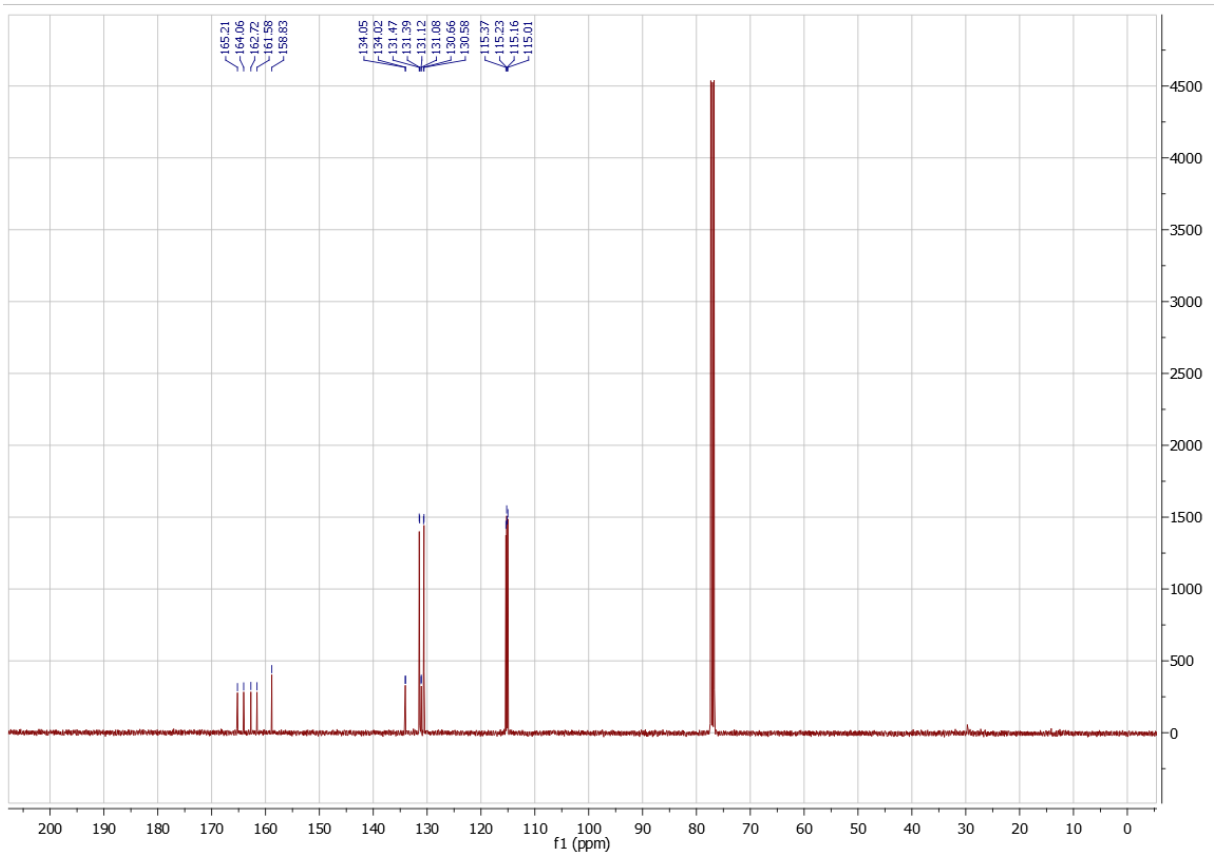
^{1}H NMR (400 MHz, $CDCl_3$): **1,2-bis(bis(4-fluorophenyl)methylene)hydrazine (2l)**



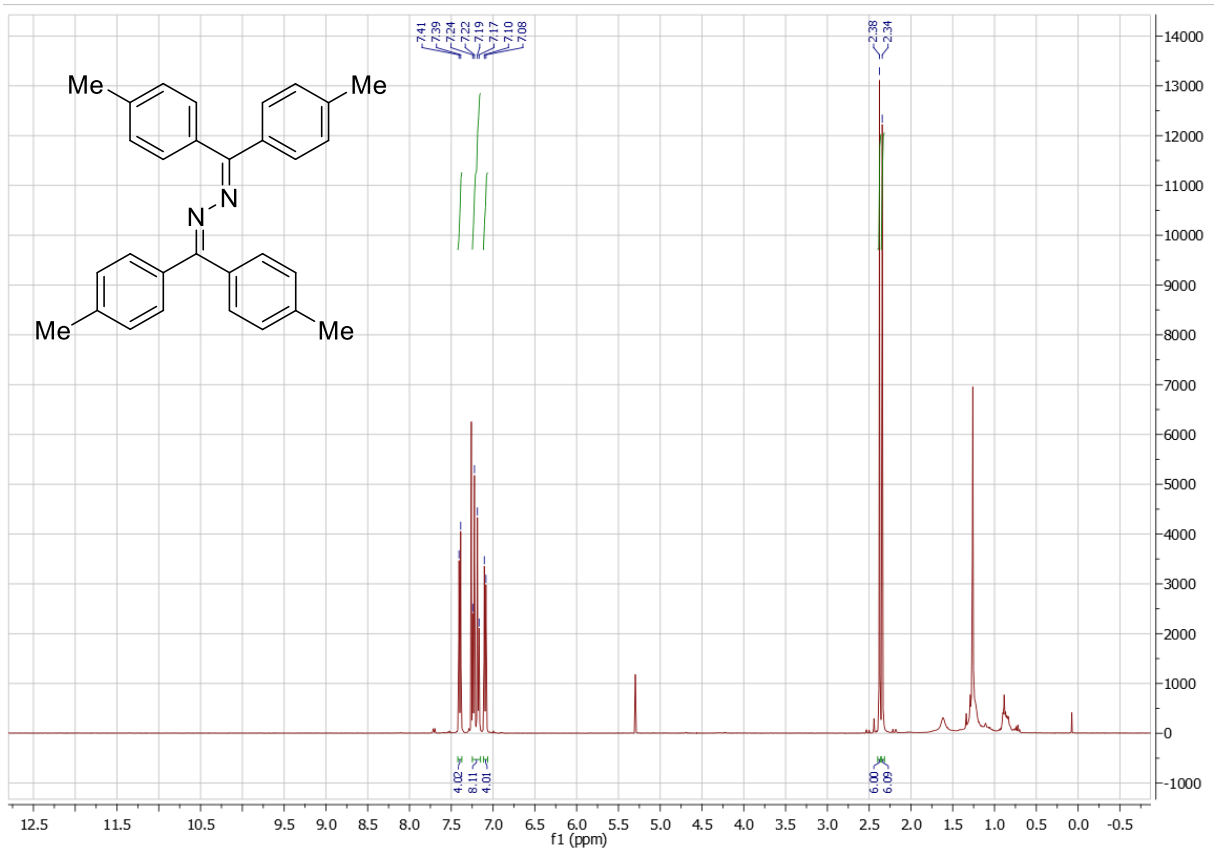
^{19}F NMR (377 MHz, $CDCl_3$):



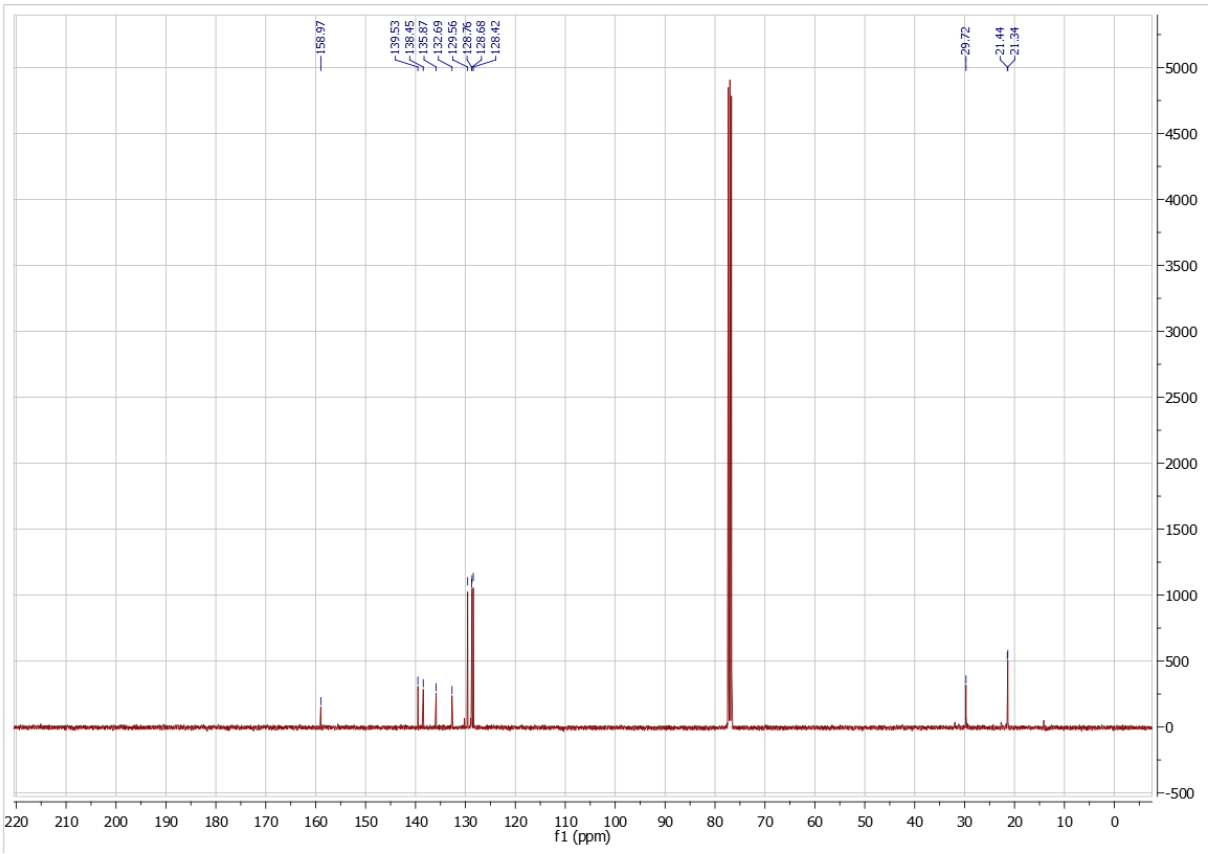
^{13}C NMR (101 MHz, $CDCl_3$):



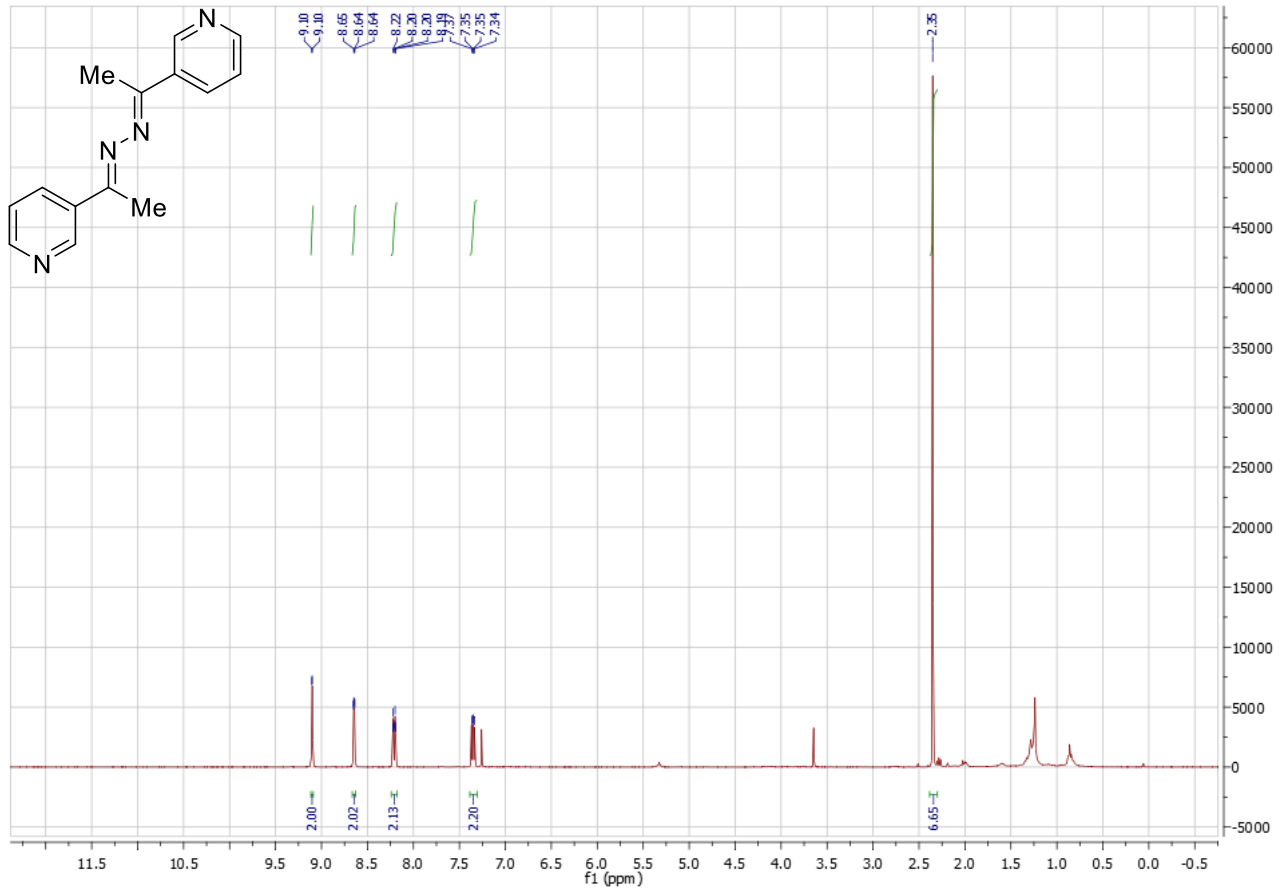
^{1}H NMR (400 MHz, $CDCl_3$): **1,2-bis(di-*p*-tolylmethylene)hydrazine (2m)**



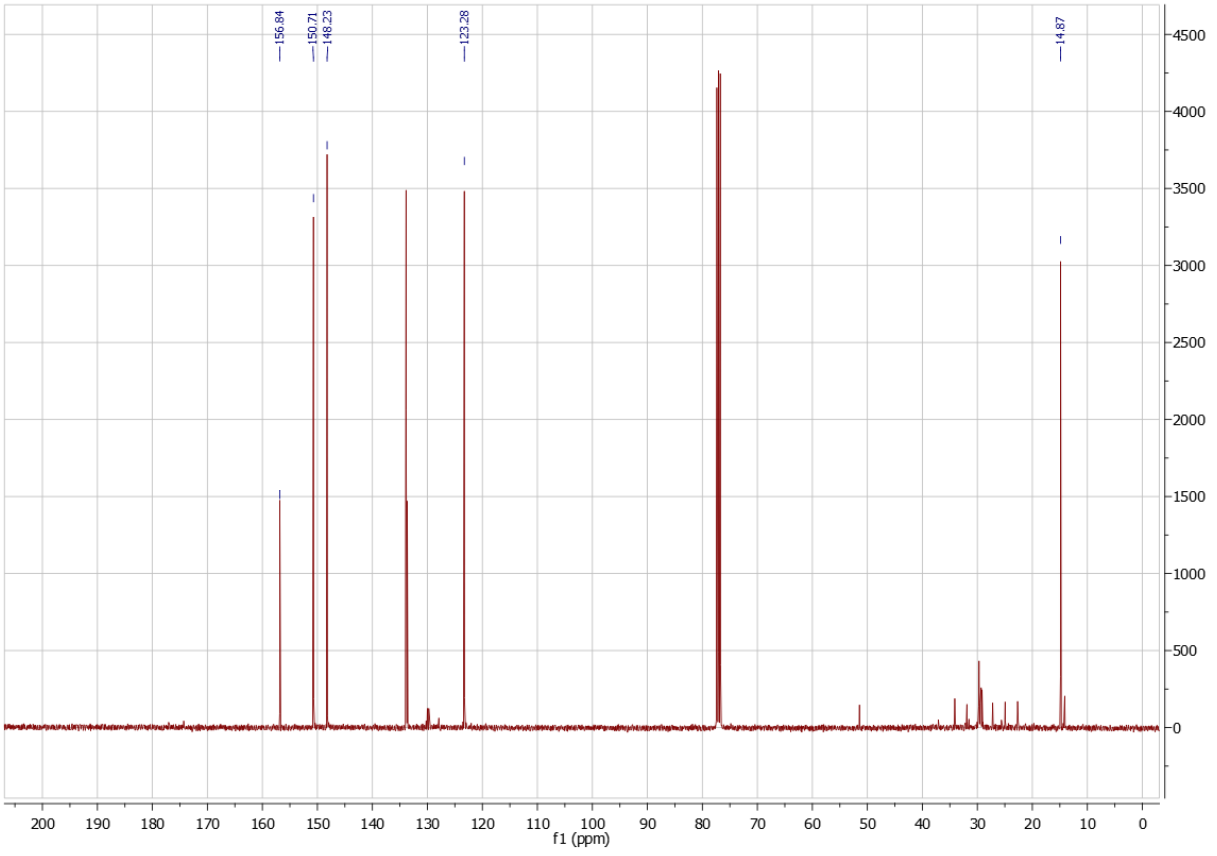
^{13}C NMR (101 MHz, $CDCl_3$):



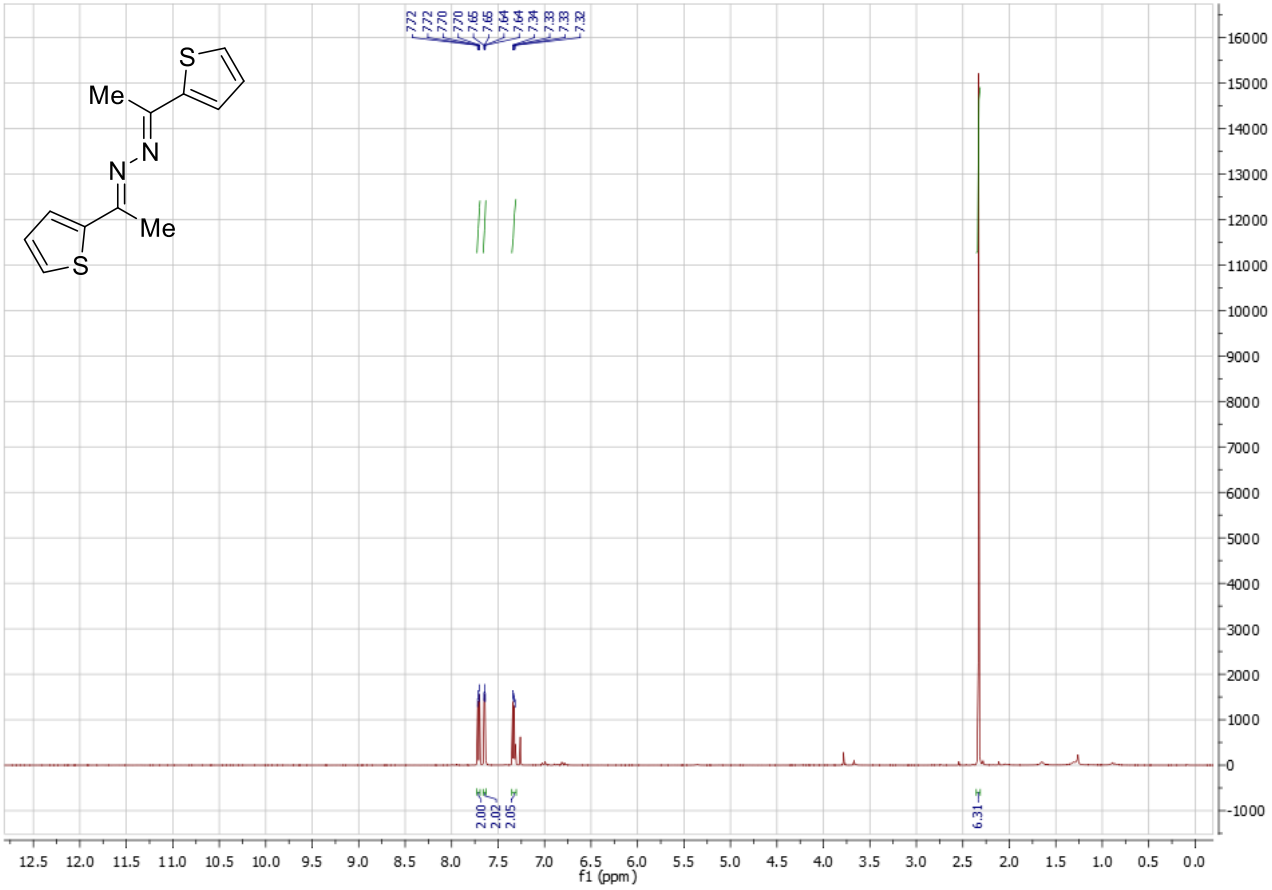
^{1}H NMR (400 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-(pyridin-3-yl)ethylidene)hydrazine (2n)**



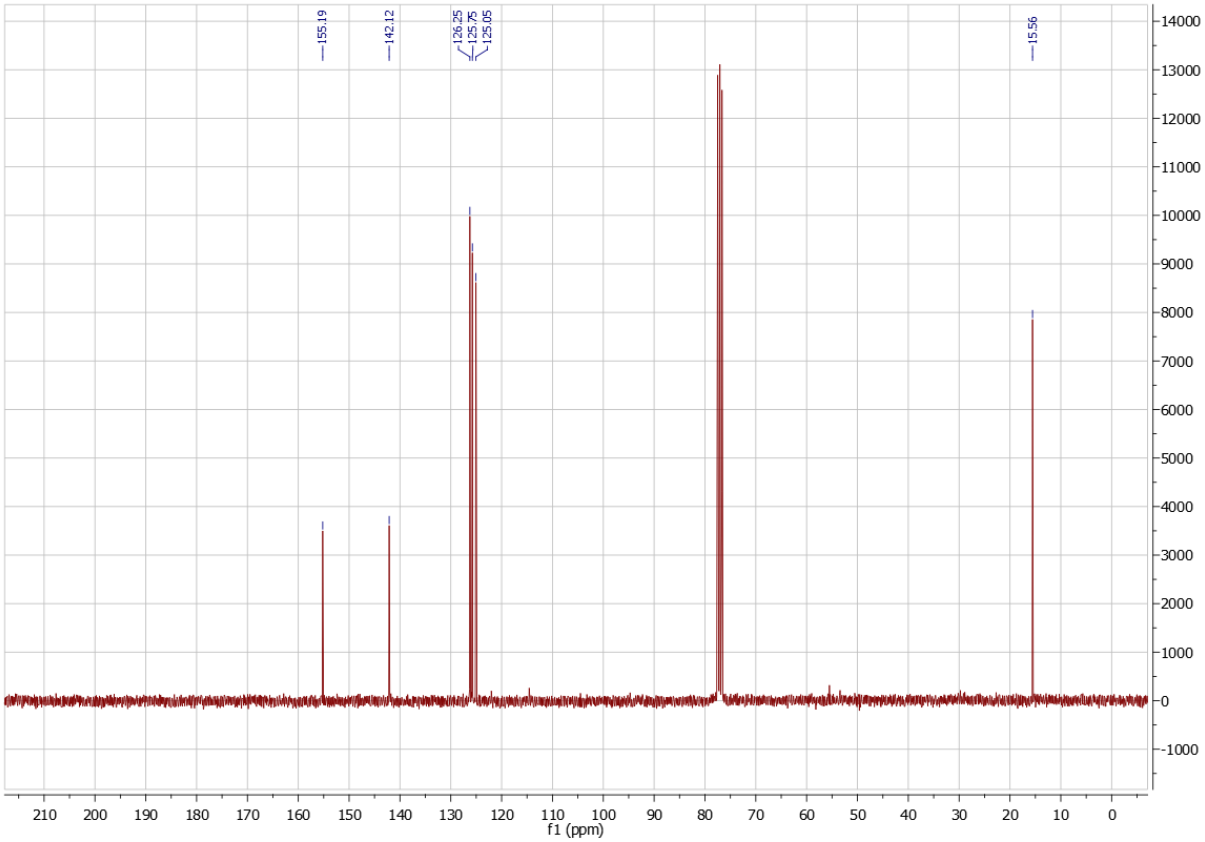
^{13}C NMR (101 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$): **(1*E*,2*E*)-1,2-bis(1-(thiophen-2-yl)ethylidene)hydrazine (2o)**



^{13}C NMR (75 MHz, $CDCl_3$):



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