*Supporting Information*

# Synthesis of Sterically Hindered Primary Amines by Concurrent Tandem Photoredox Catalysis

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1. **General Experimental Methods**

Heating of reaction mixtures was performed using a temperature-controlled hotplate equipped with stirring and an active thermocouple. Stirring of reaction mixtures was performed using magnetic stirring, unless noted otherwise. Preparative scale photochemical reactions run in 4 mL vials refer to ChemGlass vials part number CG-4912-01 (1 Dram, 15×45 mm, 13-425 Thread) equipped with pressure relief septa caps (prevents pressure over 150 psig); glass made from 33 expansion borosilicate glass which conforms to ASTM E-438 Type 1-Class A, USP Type 1 and ISO 3585; vials were equipped with a magnetic stir bar (Biotage® Stirbars, part number 355543). Evaporation and concentration *in vacuo* were done using variable vacuum via a vacuum controlled (ca. 400–40 mmHg).
**Materials.** Reagents were purchased in reagent grade from commercial suppliers (Advanced ChemBlocks, Inc.; Alfa Aesar; Angene International Limited; AsaTech, Inc.; AURUM Pharmatech LLC; ChemBridge Corporation; Combi-Blocks, Inc.; Enamine LLC; Key Organics Inc.; Life Chemicals, Inc.; Matrix Scientific; Princeton BioMolecular Research, Inc.; Sigma-Aldrich; TCI America) and used without further purification, unless otherwise described. Anhydrous solvents (acetonitrile, dimethylsulfoxide) were obtained from Sigma-Aldrich as part of their Sure/Seal™ bottles product line. NMR solvents, specifically, $d_6$-DMSO (anhydrous, 99.9% *d*-content, catalog 570672-50G) and $CD_3CN$ (anhydrous, 99.8 % *d*-content, catalog 151807-10X1ML), were purchased from Sigma-Aldrich Isotope Laboratories in sealed ampules and used as received. HPLC and UPLC eluent mixtures made use of HPLC grade MeCN and $H_2O$.

**Instrumentation.** Proton nuclear magnetic resonance ($^1$H NMR) spectra, carbon nuclear magnetic resonance ($^{13}$C NMR) spectra, proton coupled fluorine nuclear magnetic resonance ($^{19}$F NMR), and proton decoupled fluorine nuclear magnetic resonance ($^{19}$F{$^1$H} NMR) were recorded at 25 °C (unless stated otherwise) on a Bruker DRX-500 spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual proton of the NMR solvent according to values reported in the literature.[1] Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent. For samples in $CDCl_3$ the residual solvent signal was referenced to 7.26 ppm for $^1$H and 77.0 ppm for $^{13}$C, for samples in $CD_3CN$ the residual solvent signal was referenced to 1.94 ppm for $^1$H and 1.32 ppm for $^{13}$C, and for samples in $d_6$-DMSO the residual solvent signal was referenced to 2.50 ppm for $^1$H and 39.52 ppm for $^{13}$C. Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dt = doublet of triplets), coupling constants (*J*) in Hertz (Hz). Quantitative $^1$H NMR analysis ($^1$H qNMR) refers to standard $^1$H NMR using the following parameters: d1 = 60 seconds, number of scans = 8. Details of the electrochemistry equipment setup are described below. LRMS data was obtained using a Waters Acquity UPLC interfaced with a Waters Xevo G2 QTof ESI with the source temperature set to 120 °C. UV-vis absorption and emission spectra were collected using a Horiba Duetta Simultaneous EEM Fluorescence and UV-Vis-NIR Spectrophotometer using a 1 cm × 1 cm quartz cuvette.

**Photochemistry Equipment.** Photochemical reactions were conducted on four different scales: 0.01 mmol; 0.1 mmol; 0.3 mmol; and 3.6 mmol, in three separate photoreactor setups. High-throughput experimentation reactions (0.01 mmol scale) were conducted as described by DiRocco *et. al.*[2] The reaction optimization and scope reactions, conducted, at 0.1 mmol and 0.3 mmol respectively, were irradiated for 2.5 hours in a temperature controlled (40 °C) TAK 120 photoreactor with 455 nm light (5 W per vial), enabling up to 10 reactions to be run in parallel at a time.[3] A large scale reaction (3.6 mmol) was conducted in a PennOC m1 photoreactor which can accommodate a 40 mL glass vial.[4]

**Abbreviations.** DMSO = dimethylsulfoxide, ESI = electrospray ionization ($ESI^+$ and $ESI^-$ denote positive or negative mode, respectively), EtOAc = ethyl acetate, GC = gas chromatography, HPLC = high pressure liquid chromatography, UPLC = ultrahigh pressure liquid chromatography, UPLC-MS = HR = high resolution, LC = liquid chromatography, LED = light emitting diode, LR = low-resolution, MeCN = acetonitrile, MeOH = methanol, MS = mass spectrometry, NA = not available, ND = not detected, PTFE = polytetrafluoroethylene, qNMR = quantitative NMR, QToF = quadrupole time of flight, RBF = round bottom flask, rpm = rounds per minute, RT = room temperature (ca. 25 °C), THF = tetrahydrofuran, v/v = volume per volume percent, w/v = weight per volume percent, DIPA = diisopropylamine, DIPEA = diisopropylethylamine, BzOH = benzoic acid.

**Symbols.** δ = parts per million (ppm), $T$ = time, $t_r$ = retention time, $t_{rr}$ = relative retention time, $[compound]_o$ = initial concentration of specific *compound*, $[compound]_T$ = total initial concentration of specific *compound* assuming no speciation of the compound has occurred.

**UPLC MS Method for Assay Yield and LRMS Determination.** Samples were dissolved in MeCN and 1 µL injection volumes were used. The Waters UPLC was equipped with an ACQUITY UPLC™ BEH C18 VanGuard Pre-column (130 Å pore size, 1.7 µm particle size, 2.1 mm × 5 mm length; part number for 3/pkg: 186003975) flowing into an ACQUITY UPLC™ HSS T3 Column (100 Å pore size, 1.8 µm particle size, 2.1 mm internal diameter × 50 mm length; part number 186003538) operating at 55 °C with a 0.8 mL/min flow rate of a binary eluent mixture (eluent A and B, prepared as described below). The 4 min method used the following eluent gradient: gradient from 95%A, 5%B at $t$ = 0 min to 80%A, 20%B at $t$ = 1.50 min, followed by a gradient to reach 0.1%A, 99.9%B at $t$ = 3.90 min, and a subsequent change to 95%A, 5%B at $t$ = 3.91 min until $t$ = 4.00 min. Two different eluent systems were used: (system 1) eluent A = aqueous mobile phase (3960 mL $H_2O$, 40 mL pH 3.5 buffer, details below), eluent B = organic mobile phase (3600 mL MeCN, 360 mL $H_2O$, 40 mL pH 3.5 buffer, details below. The pH 3.5 buffer is prepared by dissolving ammonium formate (12.6 g, 0.200 mol) and formic acid (7.9 mL, 9.6 g, 0.21 mol) in 1000 mL $H_2O$. For analysis of the reaction mixture containing product **5s** derived via the oxime photochemistry, a different mobile phase gradient in the context of a 6 min method. The 6 min method used the following eluent gradient: gradient from 95%A, 5%B at $t$ = 0 min to 80%A, 20%B at $t$ = 2.25 min, followed by a gradient to reach 0.1%A, 99.9%B at $t$ = 5.85 min, and a subsequent change to 95%A, 5%B at $t$ = 5.87 min until $t$ = 6.00 min.

**UPLC-MS Method for Yield Determination.** Reactions were diluted in volumetric flasks with a known amount of biphenyl (Sigma Aldrich, B34656) as an internal standard ratio. Aliquots of this reaction-internal standard mixture were then diluted in vials for UPLC-MS analysis. Samples were then analyzed by the **UPLC MS Method for Assay Yield and LRMS Determination**. Analysis of the chromatograph for each reaction mixture yielded LRMS data for product identification and a corresponding peak which was analyzed for UV-Vis absorption. The raw area under the curve for the product peak at 210 nm was then compared to the raw area under the curve for the biphenyl internal standard. The ratio between these two values was then utilized to determine yield via calibration of the UPLC-MS from an authentic sample isolated from the reaction mixtures, or obtained from other chemical syntheses.

Reactions were diluted with MeCN in a 25 mL flask containing 5 mL of a 12.5 mM biphenyl solution in MeCN. The theoretical yield in mmol was then utilized to calculate the concentration of product in the 25 mL flask when the reaction was quantitative. Authentic sample was then utilized to develop a calibration curve between a concentration range which encompassed 0% to > 100% yield. The yield of the reaction was then determined by comparing the obtained product to internal standard ratio vs. the calibration curve.

***Caution!*** *Cyanide may be produced as a byproduct in these reactions. Cyanide is toxic and could lead to the release of HCN gas (extremely toxic). Reactions and their aqueous work-up should be conducted in well-ventilated enclosures (e.g. fumehood) and aqueous cyanide-containing waste should be kept basic and disposed of in accordance with local guidelines.*

## 2. Optimization of Reaction Conditions

### 2.1 High-throughput Experimentation: Photocatalyst Screen (Selected Data)

In a glove box under a nitrogen atmosphere, the components of the reaction were added to a 20 mL vial containing a stir bar. The oxime **3a** (0.66 mmol, 2.2 equiv.) was added followed by 4-cyanopyridine (**4a**) (0.3 mmol, 1 eq). The contents of the vial were then dissolved in DMSO (3 mL, 0.1 M) and stirred until homogeneous. After stirring, DIPA (157 µL, 0.9 mmol, 3.6 equiv.). The reaction was stirred for 10 minutes until the reaction solution was homogeneous. This was repeated three further times, where acetone, acetonitrile, and 1,2-dichloroethane were used as the reaction solvent. Pre-dosed photocatalysts (22 photocatalysts and 2 control reactions consisting of well with no catalyst and either the presence or absence of light) in 1 mL titer vials for a subtotal of 24 different conditions. These 24 conditions were screened with the stock solutions created in 4 different solvents (DMSO, MeCN, DMF, 1,2-dichloroethane) in a single 96-well plate array. The reactions were irradiated with blue light (455 nm, 30 mA LED, 37 °C) for 20 h. The reactions were quenched by opening the vials and exposing the contents to oxygen. Triethylamine (100 µL) was added to each reaction to quench any potential hydrogencyanide that was evolved in the reaction. An aliquot from each reaction (100 µL) was diluted into a solution of biphenyl in acetonitrile (500 µL, 2 mM biphenyl). Each reaction was analyzed by UPLC-MS. The reaction yield was determined via calibration of the UV-Vis absorption signal for product.

***Caution!*** *Cyanide may be produced as a byproduct in these reactions. Cyanide is toxic and could lead to the release of HCN gas (extremely toxic). Reactions and their aqueous work-up should be conducted in well-ventilated enclosures (e.g. fumehood) and aqueous cyanide-containing waste should be kept basic and disposed of in accordance with local guidelines.*

Results can be found on the following page.

**Table S1.** Selected results of reaction discovery via high-throughput experimentation

| Photocatalyst | Solvent | Reductant | Yield |
|---|---|---|---|
| 4-Cz-IPN | Acetone | DIPA | 30% |
| 4-DPA-IPN | Acetone | DIPA | 0% |
| Mes-Acri | Acetone | DIPA | 0% |
| tBu-Acri-N-Ph | Acetone | DIPA | 0% |
| tetraMeO-Acri-N-Ph | Acetone | DIPA | 0% |
| tetraMeO-Acri-N-diMeOPh | Acetone | DIPA | 0% |
| $Ru(bpz)_3(PF_6)_2$ | Acetone | DIPA | 0% |
| $Ru(bpy)_3(PF_6)_2$ | Acetone | DIPA | 0% |
| $Ru(bpm)_3(Cl)_2$ | Acetone | DIPA | 0% |
| $Ru(phen)_3Cl_2\ xH_2O$ | Acetone | DIPA | 0% |
| $Ru(p\text{-}CF_3\text{-}bpy)_3\ (BF_4)_2$ | Acetone | DIPA | 0% |
| $Ir(ppy)_2(dtbpy)(PF_6)$ | Acetone | DIPA | 0% |
| $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ | Acetone | DIPA | 0% |
| $Ir(ppy)_3$ | Acetone | DIPA | 0% |
| $Ir(dF\text{-}ppy)_3$ | Acetone | DIPA | 0% |
| $Ir[dF(F)ppy]_2(dtbpy)PF_6$ | Acetone | DIPA | 0% |
| $Ir[dF(H)ppy]_2(dtbpy)PF_6$ | Acetone | DIPA | 0% |
| $Ir[dF(Me)ppy]_2(dtbpy)PF_6$ | Acetone | DIPA | 0% |
| Rhodamine 6G | Acetone | DIPA | 0% |
| N-Et-Flavinium | Acetone | DIPA | 5% |
| Ph-phenathiazine | Acetone | DIPA | 0% |
| DCA | Acetone | DIPA | 0% |
| No cat | Acetone | DIPA | 0% |
| No cat/ no light | Acetone | DIPA | 0% |
| 4-Cz-IPN | DMSO | DIPA | 2% |
| 4-DPA-IPN | DMSO | DIPA | 4% |
| Mes-Acri | DMSO | DIPA | 0% |
| tBu-Acri-N-Ph | DMSO | DIPA | 0% |
| tetraMeO-Acri-N-Ph | DMSO | DIPA | 0% |
| tetraMeO-Acri-N-diMeOPh | DMSO | DIPA | 0% |
| $Ru(bpz)_3(PF_6)_2$ | DMSO | DIPA | 0% |
| $Ru(bpy)_3(PF_6)_2$ | DMSO | DIPA | 0% |
| $Ru(bpm)_3(Cl)_2$ | DMSO | DIPA | 0% |
| $Ru(phen)_3Cl_2\ xH_2O$ | DMSO | DIPA | 0% |
| $Ru(p\text{-}CF_3\text{-}bpy)_3\ (BF_4)_2$ | DMSO | DIPA | 0% |
| $Ir(ppy)_2(dtbpy)(PF_6)$ | DMSO | DIPA | 43% |
| $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ | DMSO | DIPA | 50% |
| $Ir(ppy)_3$ | DMSO | DIPA | 3% |
| $Ir(dF\text{-}ppy)_3$ | DMSO | DIPA | 0% |
| $Ir[dF(F)ppy]_2(dtbpy)PF_6$ | DMSO | DIPA | 7% |
| $Ir[dF(H)ppy]_2(dtbpy)PF_6$ | DMSO | DIPA | 68% |
| $Ir[dF(Me)ppy]_2(dtbpy)PF_6$ | DMSO | DIPA | 71% |
| Rhodamine 6G | DMSO | DIPA | 0% |
| N-Et-Flavinium | DMSO | DIPA | 0% |
| Ph-phenathiazine | DMSO | DIPA | 0% |
| DCA | DMSO | DIPA | 0% |

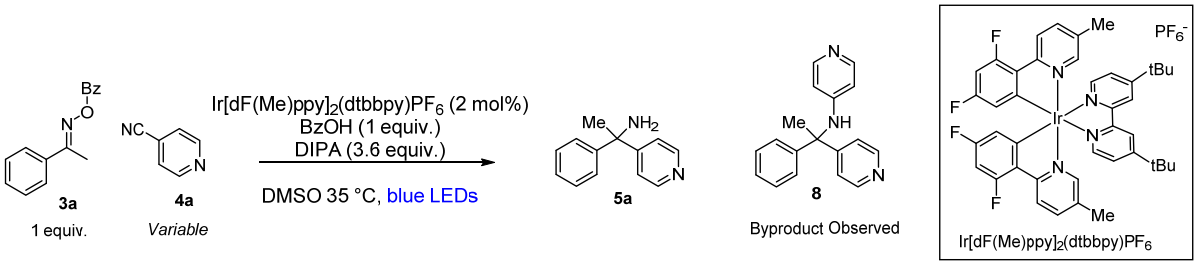
| | | | |
|---|---|---|---|
| No cat | DMSO | DIPA | 0% |
| No cat/ no light | DMSO | DIPA | 0% |
| 4-Cz-IPN | MeCN | DIPA | 4% |
| 4-DPA-IPN | MeCN | DIPA | 0% |
| Mes-Acri | MeCN | DIPA | 0% |
| tBu-Acri-N-Ph | MeCN | DIPA | 0% |
| tetraMeO-Acri-N-Ph | MeCN | DIPA | 0% |
| tetraMeO-Acri-N-diMeOPh | MeCN | DIPA | 0% |
| $Ru(bpz)_3(PF_6)_2$ | MeCN | DIPA | 0% |
| $Ru(bpy)_3(PF_6)_2$ | MeCN | DIPA | 0% |
| $Ru(bpm)_3(Cl)_2$ | MeCN | DIPA | 0% |
| $Ru(phen)_3Cl_2$ $xH_2O$ | MeCN | DIPA | 0% |
| $Ru(p\text{-}CF_3\text{-}bpy)_3$ $(BF_4)_2$ | MeCN | DIPA | 0% |
| $Ir(ppy)_2(dtbpy)(PF_6)$ | MeCN | DIPA | 0% |
| $Ir[dF(CF3)ppy]_2(dtbpy)PF_6$ | MeCN | DIPA | 0% |
| $Ir(ppy)_3$ | MeCN | DIPA | 0% |
| $Ir(dF\text{-}ppy)_3$ | MeCN | DIPA | 0% |
| $Ir[dF(F)ppy]_2(dtbpy)PF_6$ | MeCN | DIPA | 6% |
| $Ir[dF(H)ppy]_2(dtbpy)PF_6$ | MeCN | DIPA | 7% |
| $Ir[dF(Me)ppy]_2(dtbpy)PF_6$ | MeCN | DIPA | 0% |
| Rhodamine 6G | MeCN | DIPA | 0% |
| N-Et-Flavinium | MeCN | DIPA | 0% |
| Ph-phenathiazine | MeCN | DIPA | 0% |
| DCA | MeCN | DIPA | 0% |
| No cat | MeCN | DIPA | 0% |
| No cat/ no light | MeCN | DIPA | 0% |
| 4-Cz-IPN | 1,2-dichloroethane | DIPA | 4% |
| 4-DPA-IPN | 1,2-dichloroethane | DIPA | 0% |
| Mes-Acri | 1,2-dichloroethane | DIPA | 0% |
| tBu-Acri-N-Ph | 1,2-dichloroethane | DIPA | 0% |
| tetraMeO-Acri-N-Ph | 1,2-dichloroethane | DIPA | 0% |
| tetraMeO-Acri-N-diMeOPh | 1,2-dichloroethane | DIPA | 0% |
| $Ru(bpz)_3(PF_6)_2$ | 1,2-dichloroethane | DIPA | 0% |
| $Ru(bpy)_3(PF_6)_2$ | 1,2-dichloroethane | DIPA | 0% |
| $Ru(bpm)_3(Cl)_2$ | 1,2-dichloroethane | DIPA | 0% |
| $Ru(phen)_3Cl_2$ $xH_2O$ | 1,2-dichloroethane | DIPA | 0% |
| $Ru(p\text{-}CF_3\text{-}bpy)_3$ $(BF_4)_2$ | 1,2-dichloroethane | DIPA | 0% |
| $Ir(ppy)_2(dtbpy)(PF_6)$ | 1,2-dichloroethane | DIPA | 2% |
| $Ir[dF(CF3)ppy]_2(dtbpy)PF_6$ | 1,2-dichloroethane | DIPA | 0% |
| $Ir(ppy)_3$ | 1,2-dichloroethane | DIPA | 0% |
| $Ir(dF\text{-}ppy)_3$ | 1,2-dichloroethane | DIPA | 0% |
| $Ir[dF(F)ppy]_2(dtbpy)PF_6$ | 1,2-dichloroethane | DIPA | 0% |
| $Ir[dF(H)ppy]_2(dtbpy)PF_6$ | 1,2-dichloroethane | DIPA | 19% |
| $Ir[dF(Me)ppy]_2(dtbpy)PF_6$ | 1,2-dichloroethane | DIPA | 0% |
| Rhodamine 6G | 1,2-dichloroethane | DIPA | 0% |
| N-Et-Flavinium | 1,2-dichloroethane | DIPA | 0% |
| Ph-phenathiazine | 1,2-dichloroethane | DIPA | 0% |
| DCA | 1,2-dichloroethane | DIPA | 0% |

| | | | |
|---|---|---|---|
| No cat | 1,2-dichloroethane | DIPA | 0% |
| No cat/ no light | 1,2-dichloroethane | DIPA | 0% |
| 4-Cz-IPN | DMSO | DIPEA | 9% |
| Eosin Y | DMSO | DIPA | 0% |
| Eosin Y | 1,2-dichloroethane | DIPA | 0% |
| Eosin Y | MeCN | DIPA | 0% |
| Eosin Y | Acetone | DIPA | 0% |
| 4-DPA-IPN | DMSO | DIPEA | 16% |
| Mes-Acri | DMSO | DIPEA | 2% |
| tBu-Acri-N-Ph | DMSO | DIPEA | 0% |
| tetraMeO-Acri-N-Ph | DMSO | DIPEA | 3% |
| tetraMeO-Acri-N-diMeOPh | DMSO | DIPEA | 0% |
| Ru(bpz)3(PF6)2 | DMSO | DIPEA | 0% |
| Ru(bpy)3(PF6)2 | DMSO | DIPEA | 11% |
| Ru(bpm)3(Cl)2 | DMSO | DIPEA | 0% |
| Ru(phen)3Cl2 xH2O | DMSO | DIPEA | 2% |
| Ru(p-CF3-bpy)3 (BF4)2 | DMSO | DIPEA | 0% |
| Ir(ppy)2(dtbpy)(PF6) | DMSO | DIPEA | 3% |
| Ir[dF(CF3)ppy]2(dtbpy)PF6 | DMSO | DIPEA | 13% |
| Ir(ppy)3 | DMSO | DIPEA | 7% |
| Ir(dF-ppy)3 | DMSO | DIPEA | 4% |
| Ir[dF(F)ppy]2(dtbpy)PF6 | DMSO | DIPEA | 5% |
| Ir[dF(H)ppy]2(dtbpy)PF6 | DMSO | DIPEA | 5% |
| Ir[dF(Me)ppy]2(dtbpy)PF6 | DMSO | DIPEA | 7% |
| Rhodamine 6G | DMSO | DIPEA | 0% |
| N-Et-Flavinium | DMSO | DIPEA | 0% |
| Ph-phenathiazine | DMSO | DIPEA | 0% |
| DCA | DMSO | DIPEA | 0% |
| No cat | DMSO | DIPEA | 0% |
| No cat/ no light | DMSO | DIPEA | 0% |

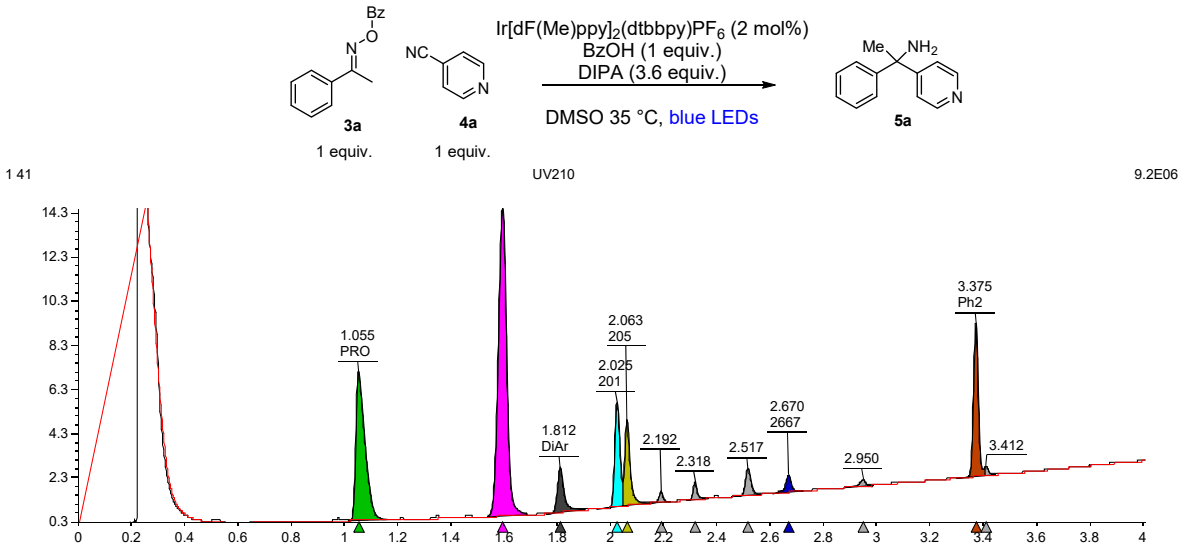
**2.2** The Effect of Super-Stoichiometric Equivalents of 4-Cyanopyridine

A stock solution of 4-cyanopyridine **4a** was made in DMSO (344 mg in 2.2 mL DMSO, 0.5 M) in a 20 mL vial containing a stir bar. In separate vials, stock solutions of the photocatalyst (36 mg in 1200 µL, 6E-3 mmol per 200 µL), benzoic acid (220 mg in 1200 µL, 0.1 mmol in 200 µL), and model oxime **3a** (431 mg in 4.5 mL, 0.4 M) were made in DMSO. Each component of the reaction was added to a 4 mL vial: 200 µL of photocatalyst solution, 200 µL benzoic acid solution, 750 µL of oxime solution, and 200 µL per equivalent of 4-cyanopyridine solution. DMSO was added to each reaction to yield a final reaction volume of 3 mL. The reaction was stirred in the glovebox for 10 minutes yielding a homogeneous solution. DIPA (153 µL, 1.1 mmol, 3.6 equiv) was added to the vial. The reaction was stirred for 10 minutes before being removed from the glovebox and having its cap sealed by parafilm. The reaction was placed into the photoreactor and irradiated with blue light (455 nm, 5W per reaction) for two hours. After the two hours, the reaction was quenched by opening the vial and exposing the contents to oxygen. Triethylamine was added to each reaction to quench any hydrogen cyanide that was evolved in the reaction. An aliquot from each reaction (100 µL) was diluted into a solution of biphenyl in acetonitrile (500 µL, 2 mM biphenyl). Each reaction was analyzed by UPLC-MS. The reaction yield was determined via calibration of the UV-Vis absorption signal for product.

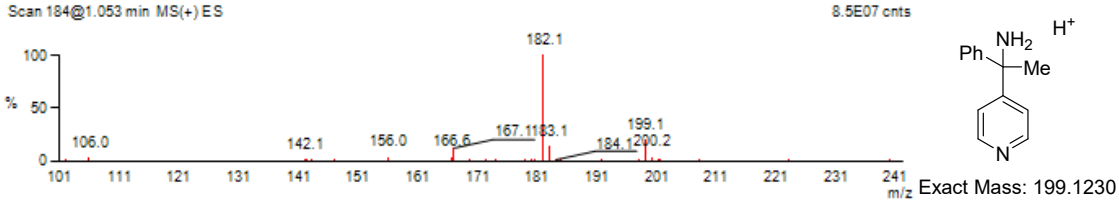
**Table S2.** Testing the role of cyanoarene stoichiometry



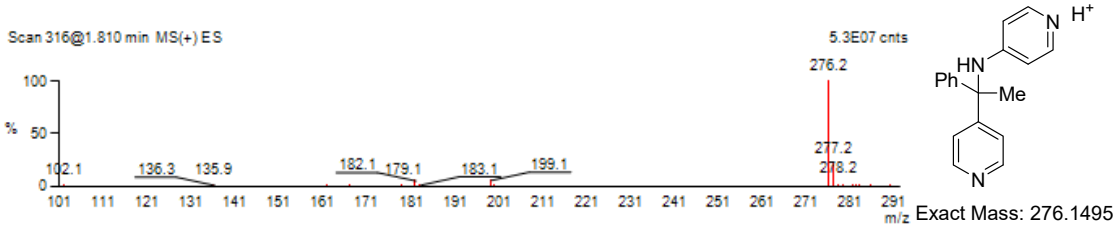

| Equivalents of 4-cyanopyridine | Yield | 4-cyanopyridine to IS | Byproduct to IS | Byproduct to Product |
|---|---|---|---|---|
| 1 | 39% | 0.00 | 0.40 | 0.22 |
| 1.5 | 64% | 0.00 | 0.67 | 0.23 |
| 2 | 86% | 0.00 | 0.98 | 0.25 |
| 2.5 | 89% | 0.49 | 1.05 | 0.26 |
| 3 | 89% | 1.92 | 1.09 | 0.27 |




Product ($t$ = 1.055). Theoretical m/z [M+H] = 199.1230. Observed: [M+H]199.1, [M-$NH_2$] 182.1 (fragment).




DiAr ($t$ = 1.81). Theoretical m/z [M+H] = 276.1495. Observed: [M+H]276.2, [M- 4pyr] 199.1 (fragment) [M-$NH_2$-4pyr] 182.1 (fragment).




(201) & (205) ($t$ = 2.01 & $t$ = 2.05) Theoretical m/z [M+H] = 224.1182. Observed: [M+H]224.2, [M-$NH_2$] 202.2 (fragment). Masses consistent for both observed byproducts.

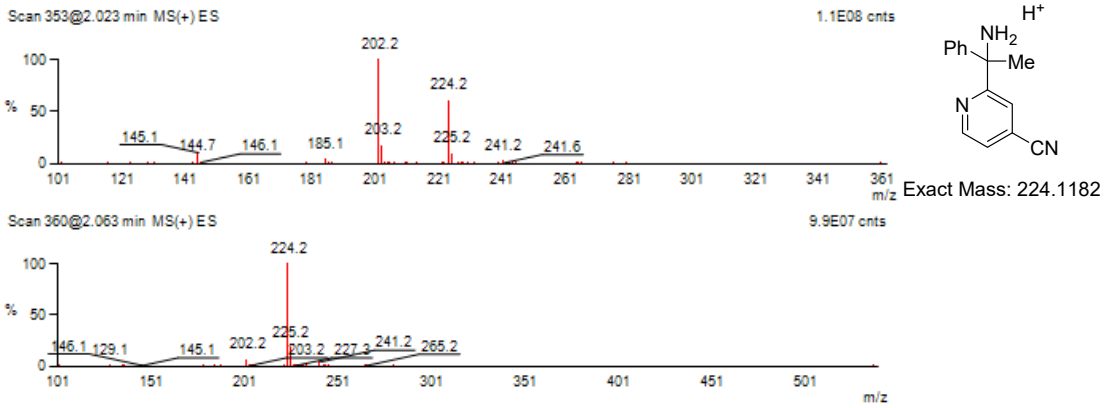
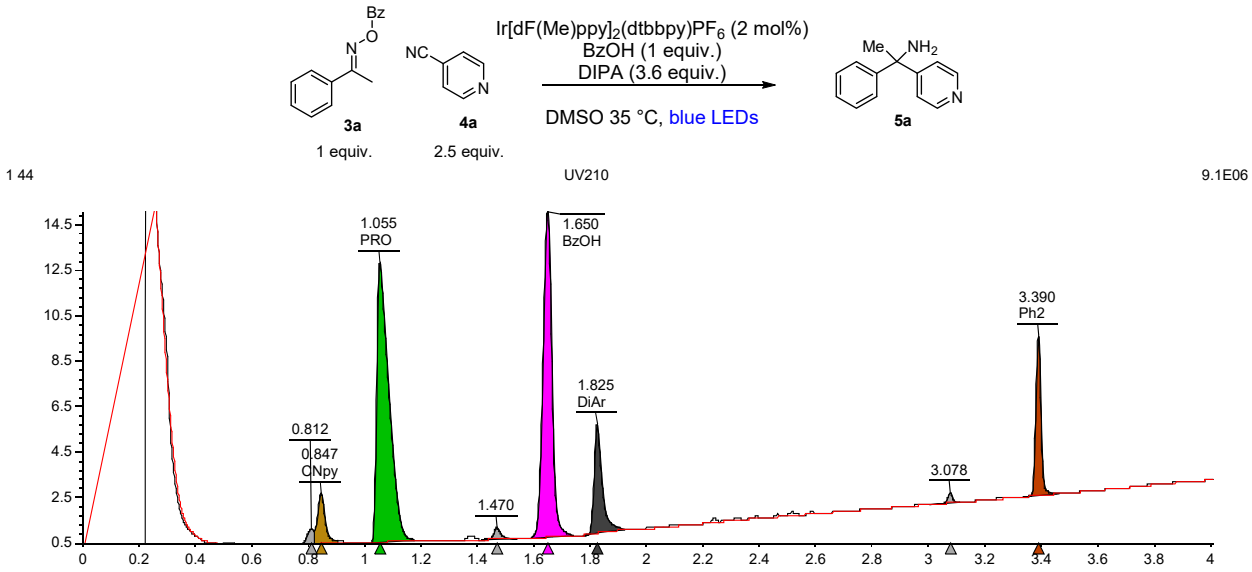
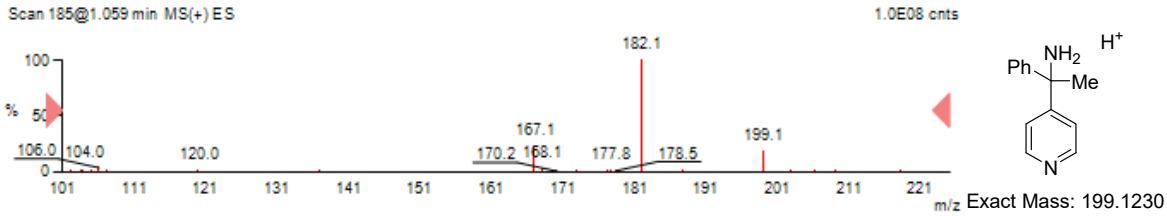



**Figure S1**. UPLC-MS analysis of a coupling reaction with 1:1 stoichiometry of **3a**:**4a**




Product ($t$ = 1.055). Theoretical m/z [M+H] = 199.1230. Observed: [M+H]199.1, [M-$NH_2$] 182.1 (fragment).




DiAr ($t$ = 1.81). Theoretical m/z [M+H] = 276.1495. Observed: [M+H]276.2, [M- 4pyr] 199.1 (fragment) [M-$NH_2$-4pyr] 182.1 (fragment).

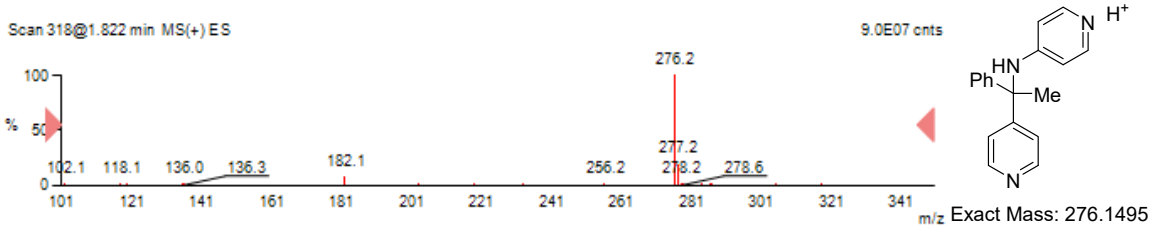
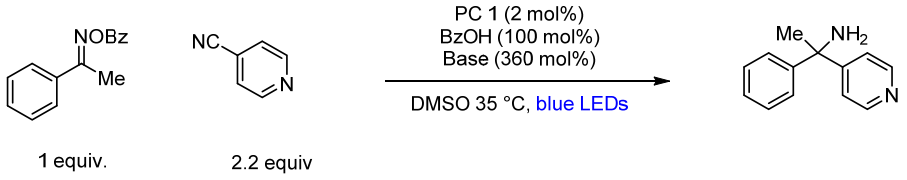


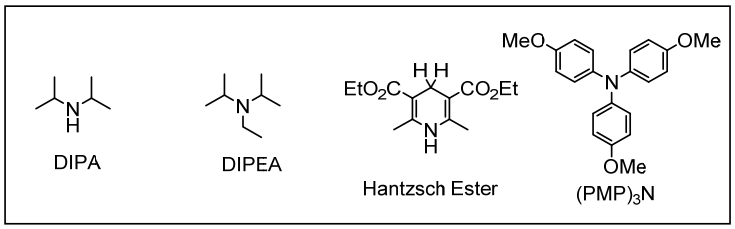

**Figure S2.** UPLC-MS analysis of a coupling reaction with 1:2.5 stoichiometry of **3a**:**4a**

### 2.3 The Effect of the Stoichiometric Reductant

In a glovebox under an atmosphere of nitrogen, solid reagents were added to a 4-mL vial: model oxime substrate (**3a**) (72 mg, 0.3 mmol, 1.0 equiv.); benzoic acid (37 mg, 0.1 mmol, 1.0 equiv.); photocatalyst Ir[dF(Me)ppy]$_2$dtbbpyPF$_6$ (6 mg, 2E-3 mmol, 2 mol%); 4-cyanopyridine (**4a**) (69 mg, 0.66 mmol, 2.2 equiv.). The reactants were then dissolved by the addition of DMSO (3 mL) and stirred for 10 minutes until the solution was homogeneous. The bases were then added to their respective reactions: DIPA (153 µL, 1.1 mmol), DIPEA (191 µL, 1.1 mmol), Hantzsch ester (279 mg, 1.1 mmol); or tris-4-methoxyphenyl amine (369 mg, 1.1 mmol). The reaction was stirred for 10 minutes before being removed from the glovebox and having its cap sealed by parafilm. The reaction was placed into the photoreactor and irradiated with blue light (455 nm, 5W per reaction). At 2.5 hours the reaction was considered complete. The reaction is quenched by opening the vial and exposing the vial contents to oxygen. Triethylamine was added to each reaction to quench any hydrogen cyanide that was evolved in the reaction. The reaction is then added to a 25 mL volumetric flask along with a solution of biphenyl in MeCN (5 mL, 12.5 mM biphenyl). The contents of the flask were then diluted until the volume reached 25 mL. Aliquots (20 µL, 50 µL, and 100 µL) of the diluted reaction were then taken to measure by UPLC-MS. The reaction yield was determined by UPLC-MS calibration relative to a pure sample of model substrate **5**.

**Table S3.** Testing the Effect of Alternative Stoichiometric Reductants



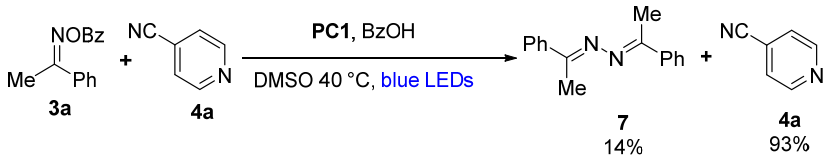




| **Base / Reductant** | Yield |
|---|---|
| Diisopropylamine (DIPA) | 86% |
| Diisopropylethylamine (DIPEA) | 27% |
| Hantzsch Ester | 26% |
| Tris-para-methoxyphenylamine (PMP)$_3$N | 0% |

## 2.4 Evidence for Iminyl Radicals

**Scheme S1.** Evidence of the dimerization of Iminyl Radicals

*Reaction run without stoichiometric reductant*




Reaction without DIPA

In a glovebox under an atmosphere of nitrogen, solid reagents were added to a 4-mL vial: model oxime substrate **3a** (72 mg, 0.3 mmol, 1.0 equiv.); benzoic acid (37 mg, 0.1 mmol, 1.0 equiv.); photocatalyst Ir[dF(Me)ppy]$_2$dtbbpyPF$_6$ (6 mg, 2E-3 mmol, 2 mol%); 4-cyanopyridine **4a** (69 mg, 0.66 mmol, 2.2 equiv.). The reactants were then dissolved by the addition of DMSO (3 mL) and stirred for 10 minutes until the solution was homogeneous. The reaction was then irradiated for 2.5 h in the TAK 120 photoreactor (455 nm, 5W, 40 °C). The reaction is quenched by opening the vial and exposing the vial contents to oxygen.

The reaction was then added to a 25 mL volumetric flask along with a solution of biphenyl in MeCN (5 mL, 12.5 mM biphenyl). The contents of the flask were then diluted until the volume reached 25 mL. Aliquots (20 µL, 50 µL, and 100 µL) of the diluted reaction were then taken to measure by UPLC-MS. The remainder of the diluted reaction was then concentrated under reduced pressure to remove the MeCN. The remaining crude oil is dissolved in methylene chloride (50 mL). Isopropyl amine (2 mL) was then added to the reaction to raise the pH, deprotonate the desired product, and prevent the formation of hydrogen cyanide. The methylene chloride solution was washed with water (3 x 50 mL) followed by a wash with brine (50 mL). The remaining organic fraction was then dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to afford a crude product.

The crude product was purified by FLASH chromatography using a Teledyne-Isco Combiflash, [12 g column, $CH_2Cl_2$ (Solvent A), MeOH (Solvent B)]. The column utilized a gradient elution: 5 min (100% A), 5 min (100% A to 97.5% A: 2.5% B), 10 min (97.5% A: 2.5% B to 95% A: 5% B), 10 min (95% A: 5% B), 10 (Hold 95% A: 5% B), 5 min (95% A: 5% B to 90% A: 10% B), 5 min (Hold 90% A: 10% B). The product fractions were collected and concentrated under reduced pressure to afford the pure product **7** (10 mg, 14%). $^1$H NMR (500 MHz, $CD_3CN$) δ 7.93 (dd, $J$ = 6.8, 3.0 Hz, 4H), 7.50 – 7.40 (m, 6H), 2.28 (s, 6H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 158.35, 139.49, 130.64, 129.37, 127.56, 15.18. MS (ESI) m/z calcd. for $C_{16}H_{17}N_2$ ($[M + H]^+$) 237.1, found 237.7.

**Observation of Azine (Dimer of Iminyl Radicals) via UPLC-MS**

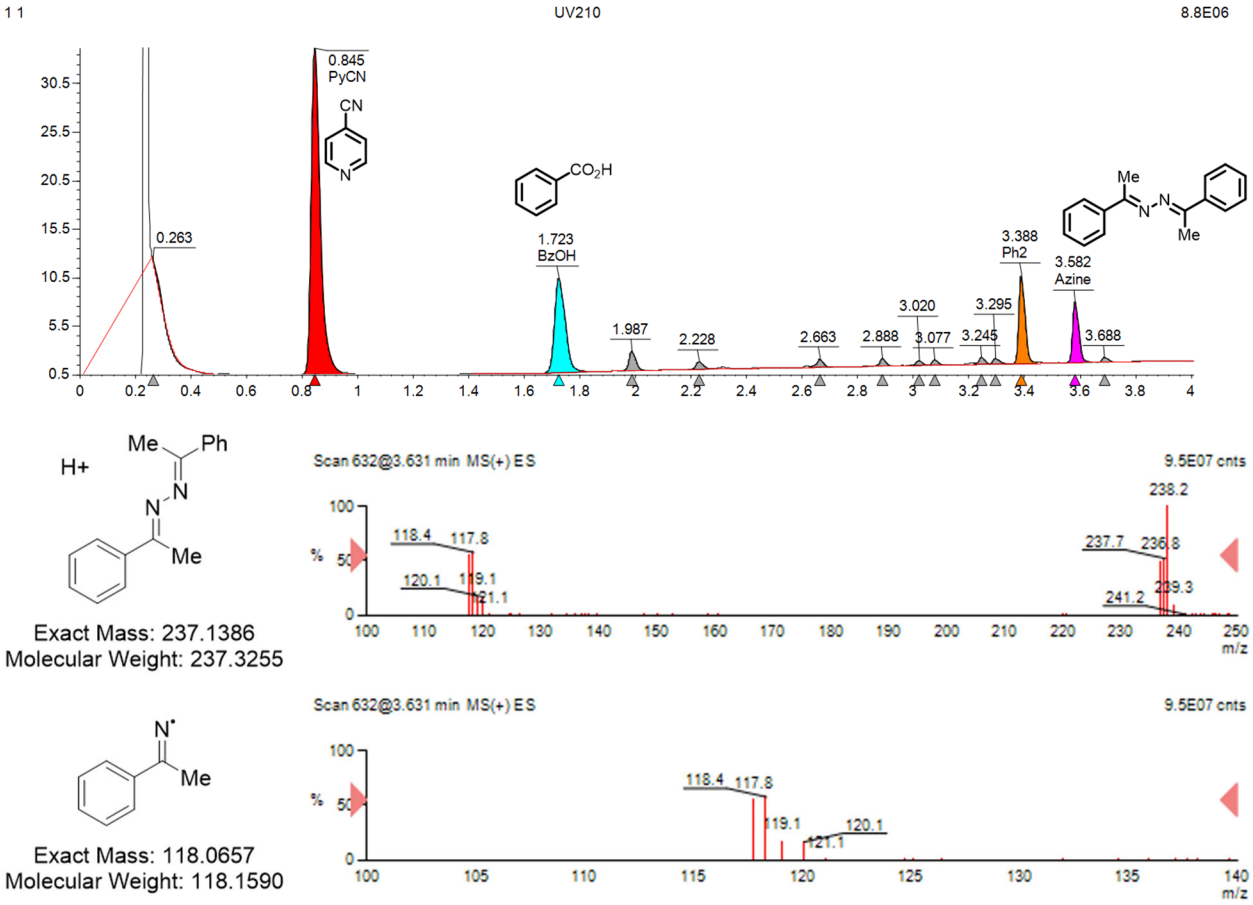



**Figure S3.** UPLC chromatograph with compound assignments for key UV signals. Low resolution mass spectrum (ESI +) for the retention time identified as the azine and identification of a fragmentation pattern for N-N bond cleavage of the dimeric structure.

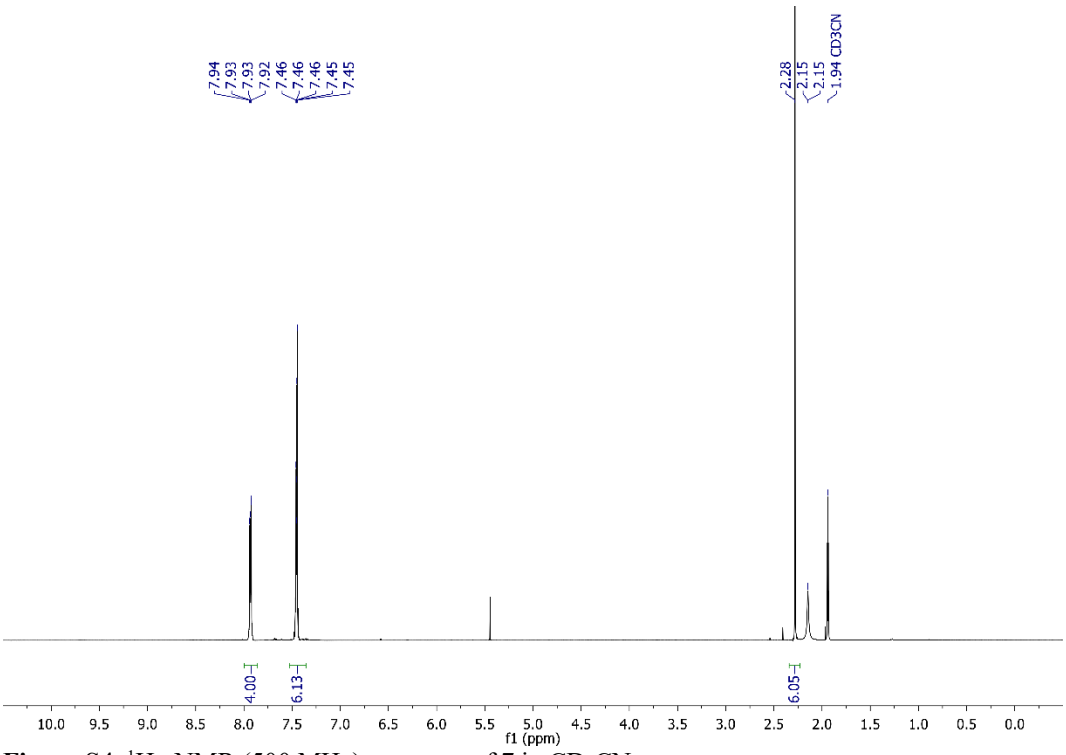



**Figure S4.** $^{1}$H qNMR (500 MHz) spectrum of **7** in $CD_3CN$.

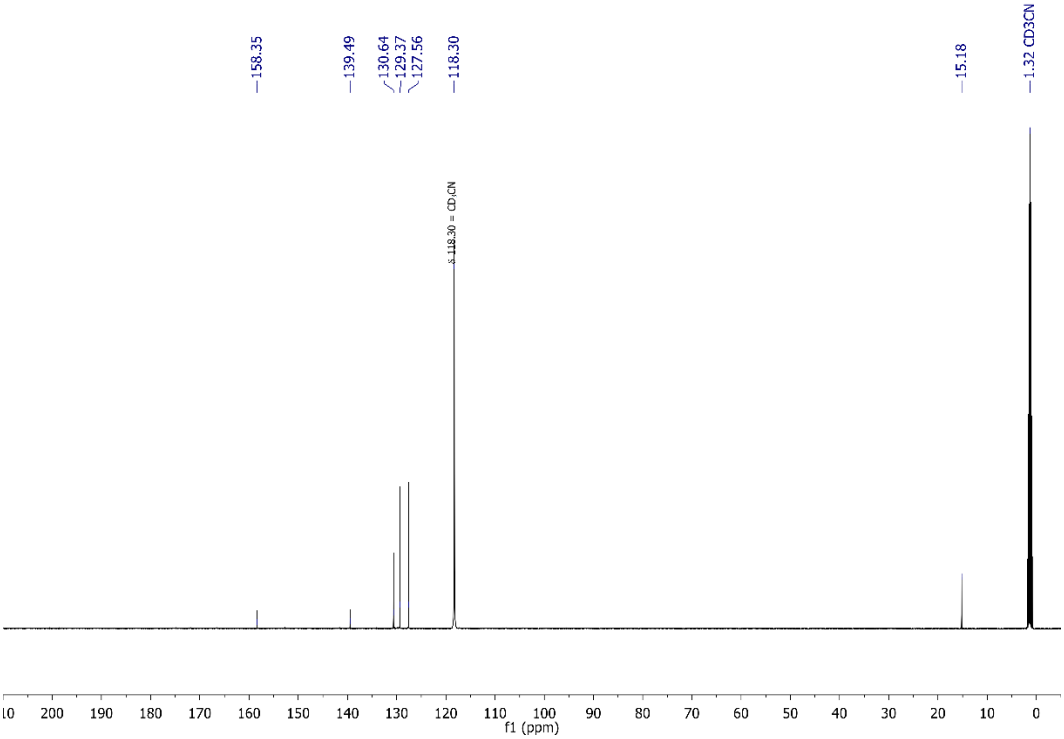



**Figure S5.** $^{13}$C NMR (126 MHz) spectrum of **7** in $CD_3CN$.

2.5 Comparison of Oxime Consumption Without DIPA Reductant

In a glovebox under an atmosphere of nitrogen, solid reagents were added to a 4-mL vial: model oxime substrate **3a** (72 mg, 0.3 mmol, 1.0 equiv.); benzoic acid (37 mg, 0.1 mmol, 1.0 equiv.); photocatalyst (2E-3 mmol, 2 mol%) (Table 4); 4-cyanopyridine **4a** (69 mg, 0.66 mmol, 2.2 equiv.). The reactants were then dissolved by the addition of DMSO (3 mL) and stirred for 10 minutes until the solution was homogeneous. The reaction was then irradiated for 2.5 h in the TAK 120 photoreactor (455 nm, 5W, 40 °C). The reaction was quenched by opening the vial and exposing the vial contents to oxygen.

The reaction was then added to a 25 mL volumetric flask along with a solution of biphenyl in MeCN (5 mL, 12.5 mM biphenyl). The contents of the flask were then diluted until the volume reached 25 mL. Aliquots (20 μL, 50 μL, and 100 μL) of the diluted reaction were then taken to measure by UPLC-MS. For each reaction, the ratio of absorbance of the starting oxime was compared to the constant biphenyl internal standard was calculated. The amount of oxime remaining in each reaction was determined by comparing the product to internal standard for each reaction to the product to internal standard ratio of a reaction without photocatalyst added.

**Table S4.** Comparison of Photocatalysts Triplet Energies in the Coupling Reaction

| Entry | Photocatalyst | Amount of Photocatalyst | Triplet Energy ($E^T$) [kcal $mol^{-1}$] | $E_{red}$ (V) vs. SCE | $E^*_{ox}$ (V) vs. SCE | Oxime Remaining (%) |
|---|---|---|---|---|---|---|
| 1 | **PC1** | 6 mg | 55.8 | –1.42 | 0.97 | 0 |
| 2 | **PC3** | 6 mg | 61.8 | –1.37 | 1.21 | 51 |
| 3 | **PC4** | 4 mg | 58.1 | –2.2 | 0.31 | 0 |
| 4 | **PC5** | 5 mg | 46 | –1.33 | 0.77 | 98 |
| 5 | **PC6** | 4 mg | 43.6 | –1.06 | 0.83 | 98 |

## 3. *O*-Benzoyl Oxime & Iminium Hydrochloride Substrate Scope

3.1 General Reaction Procedure A:

Reactions were conducted in a 4 mL vial (Chemglass), with a PTFE stir bar, and a vial cap containing a septum. All reaction contents were measured inside of a glovebox where the atmosphere contained <0.1 ppm oxygen. *O*-benzoyl oxime substrate (**3a-3r**) (0.3 mmol, 1.0 equiv.); benzoic acid (37 mg, 0.1 mmol, 1.0 equiv.); photocatalyst (**PC1**) $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); and cyanoarene (**4a-4ai)** (0.66 mmol, 2.2 equiv.) were added to a 4 mL vial. The reactants were then dissolved by the addition of DMSO (3 mL) and stirred for 10 minutes until the solution was homogeneous. DIPA (153 μL, 1.1 mmol, 3.6 equiv.) was then added to the reaction. The reaction was capped and stirred for ten minutes until the DIPA was miscible with the reaction. The reaction vessel was then removed from the glovebox and sealed with parafilm to further protect the reaction from oxygen. The reaction was then placed into the photoreactor and irradiated with blue light (455 nm, 5W per reaction) for 2.5 hours.

***Caution!*** *Cyanide may be produced as a byproduct in these reactions. Cyanide is toxic and could lead to the release of HCN gas (extremely toxic). Reactions and their aqueous work-up should be conducted in well-ventilated enclosures (e.g. fumehood) and aqueous cyanide-containing waste should be kept basic and disposed of in accordance with local guidelines.*

At 2.5 hours the reaction is considered complete, and the reaction was quenched by opening the vial and exposing the vial contents to oxygen. The reaction was then added to a 25 mL volumetric flask along with a solution of biphenyl in MeCN (5 mL, 12.5 mM biphenyl). The contents of the flask were then diluted until the volume reached 25 mL. Aliquots (20 μL, 50 μL, and 100 μL) of the diluted reaction were then taken to measure by UPLC-MS. The remainder of the diluted reaction was then concentrated under reduced pressure to remove the MeCN. The remaining crude oil is dissolved in methylene chloride (50 mL). Isopropyl amine (2 mL) was then added to the reaction to raise the pH, deprotonate the desired product, and prevent the formation of hydrogen cyanide. The methylene chloride solution was washed with water (3 x 50 mL) followed by a wash with brine (50 mL). The remaining organic fraction was then dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to afford a crude product.

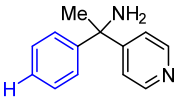
The crude product was purified by FLASH chromatography using a Teledyne-Isco Combiflash, [12 g column, $CH_2Cl_2$ (Solvent A), MeOH (Solvent B)]. The column utilized a gradient elution: 5 min (100% A), 5 min (100% A to 97.5% A: 2.5% B), 10 min (97.5% A: 2.5% B to 95% A: 5% B), 10 min (95% A: 5% B), 10 (Hold 95% A: 5% B), 5 min (95% A: 5% B to 90% A: 10% B), 5 min (Hold 90% A: 10% B). The product fractions were collected and concentrated under reduced pressure to afford the pure product. After characterization, the pure product is used to produce a calibration curve according to the general UPLC calibration procedure.

3.2 General Iminium Salt Reaction Procedure:

Reactions were conducted in a 4 mL vial (Chemglass), with a PTFE stir bar, and a vial cap containing a septum. All reaction contents were measured inside of a glovebox where the atmosphere contained <0.1 ppm oxygen. Iminium HCl salt (0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.) were added to a 4 mL vial. The reactants were then dissolved by the addition of DMSO (3 mL) and stirred for 10 minutes until the solution was homogeneous. DIPA (153 µL, 1.1 mmol, 3.6 equiv.) was then added to the reaction. The reaction was capped and stirred for ten minutes until the DIPA was miscible with the reaction. The reaction vessel was then removed from the glovebox and sealed with parafilm to further protect the reaction from oxygen. The reaction was then placed into the photoreactor and irradiated with blue light (455 nm, 5W per reaction).

***Caution!*** *Cyanide may be produced as a byproduct in these reactions. Cyanide is toxic and could lead to the release of HCN gas (extremely toxic). Reactions and their aqueous work-up should be conducted in well-ventilated enclosures (e.g. fumehood) and aqueous cyanide-containing waste should be kept basic and disposed of in accordance with local guidelines.*

At 2.5 hours the reaction as considered complete, and the reaction was quenched by opening the vial and exposing the vial contents to oxygen. The reaction was then added to a 25 mL volumetric flask along with a solution of biphenyl in MeCN (5 mL, 12.5 mM biphenyl). Isopropyl amine (2 mL) was then added to the reaction to raise the pH, deprotonate the desired product, and prevent the formation of hydrogen cyanide. The contents of the flask were then diluted until the volume reached 25 mL. Aliquots (20 µL, 50 µL, and 100 µL) of the diluted reaction were then taken to measure by UPLC-MS. The yield of the reaction was determined via UPLC-MS calibration.




Compound **5a** was synthesized following General Procedure A using 4-pyridinecarbonitrile (733 mg, 7.04 mmol), **PC1** (72 mg, 7.2E-2 mmol), benzoic acid (444 mg, 3.2 mmol), DIPA (1.836 mL, 1.1 mmol) and *O*-benzoyl oxime (**3a**) (765 mg, 3.2 mmol) in DMSO (36 mL). The product was obtained as a viscous brown oil (513 mg, 70%). The yield of product **5a** was determined to be 80% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.45 (d, $J$ = 5.9 Hz, 2H), 7.40 (d, $J$ = 7.7 Hz, 2H), 7.35 (d, $J$ = 6.0 Hz, 2H), 7.31 (t, $J$ = 7.7 Hz, 2H), 7.22 (t, $J$ = 7.3 Hz, 1H), 2.07 (s, 2H), 1.79 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 160.09, 150.51, 149.96, 129.16, 127.49, 127.06, 122.30, 58.73, 31.31. MS (ESI) m/z calcd. for $C_{13}H_{15}N_2$ ($[M + H]^+$) 199.1, found 199.2.

Compound **5a** was also synthesized from the corresponding iminium HCl salt **6a** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6a** (156 mg. 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 μL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.). The yield of product **5a** was determined to be 81% by a calibrated UPLC-MS.

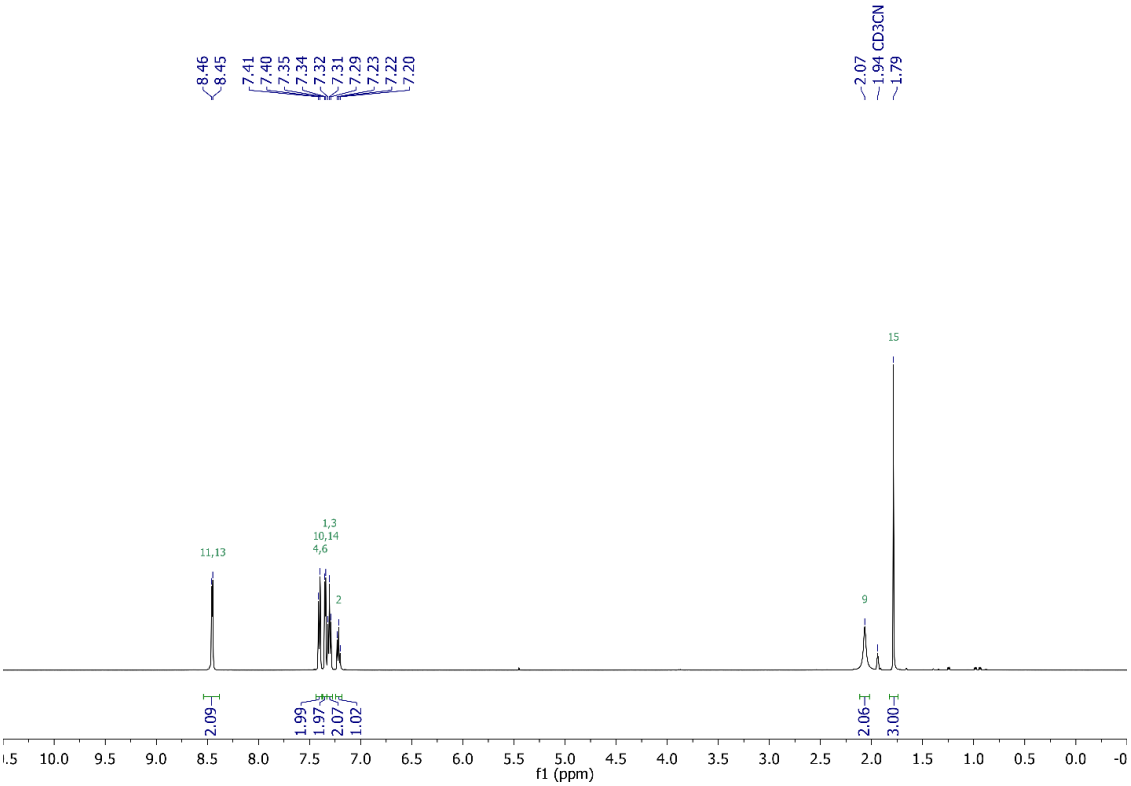



**Figure S6.** $^{1}$H qNMR (500 MHz) spectrum of **5a** in $CD_3CN$.

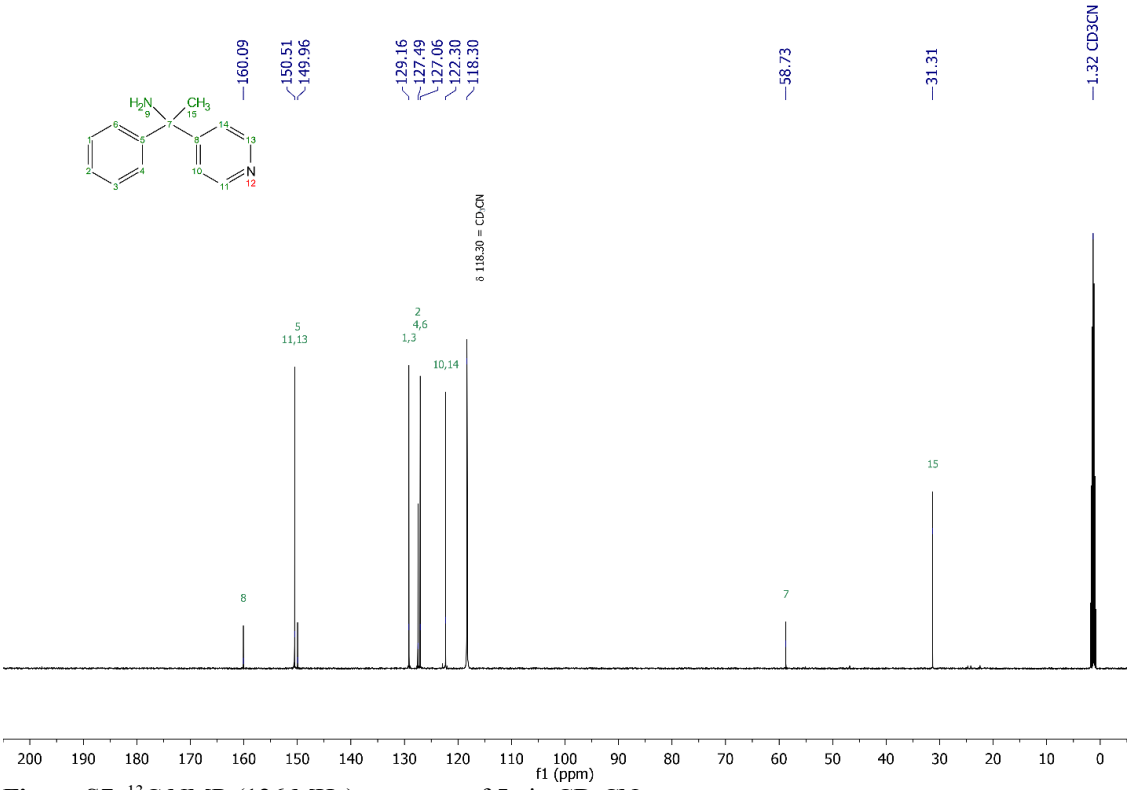



**Figure S7.** $^{13}$C NMR (126 MHz) spectrum of **5a** in $CD_3CN$.

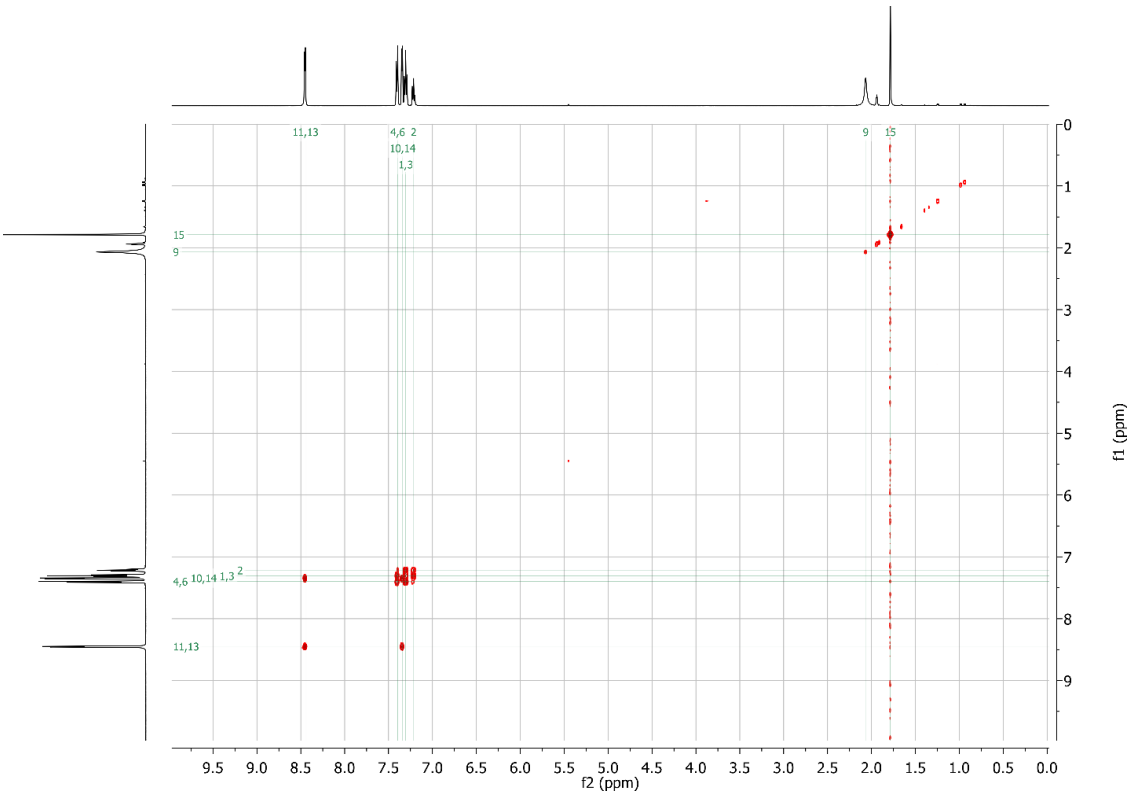



**Figure S8.** COSY NMR (126 MHz) spectrum of **5a** in $CD_3CN$.

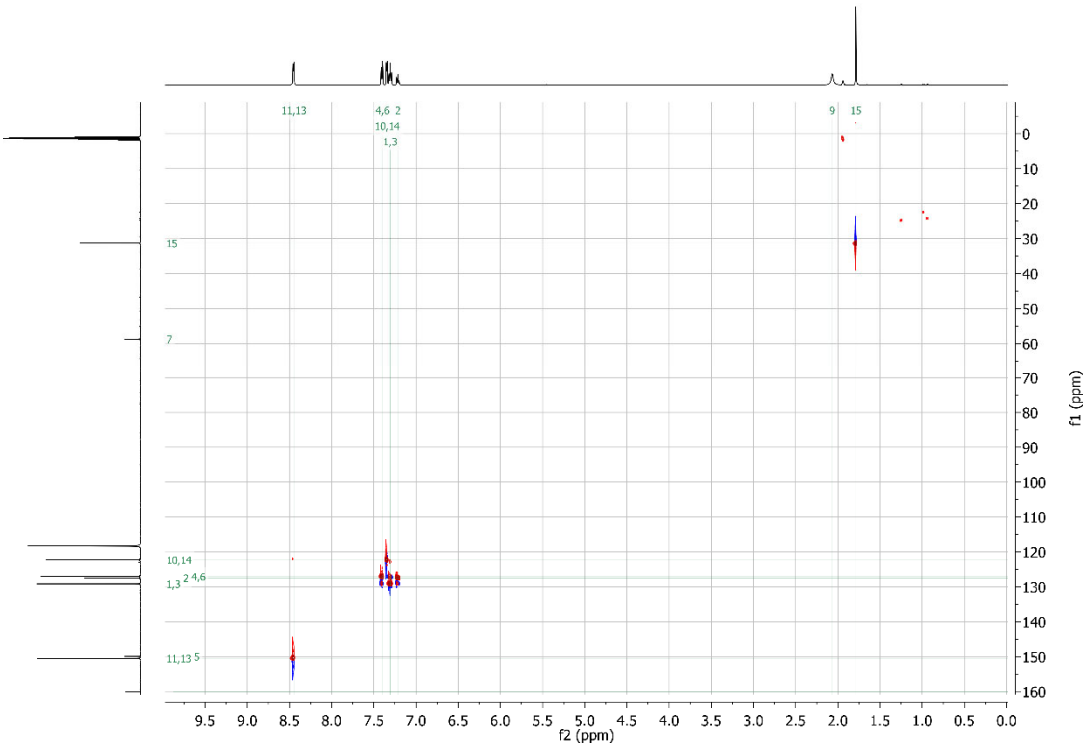



**Figure S9.** HSQC NMR (126 MHz) spectrum of **5a** in $CD_3CN$.

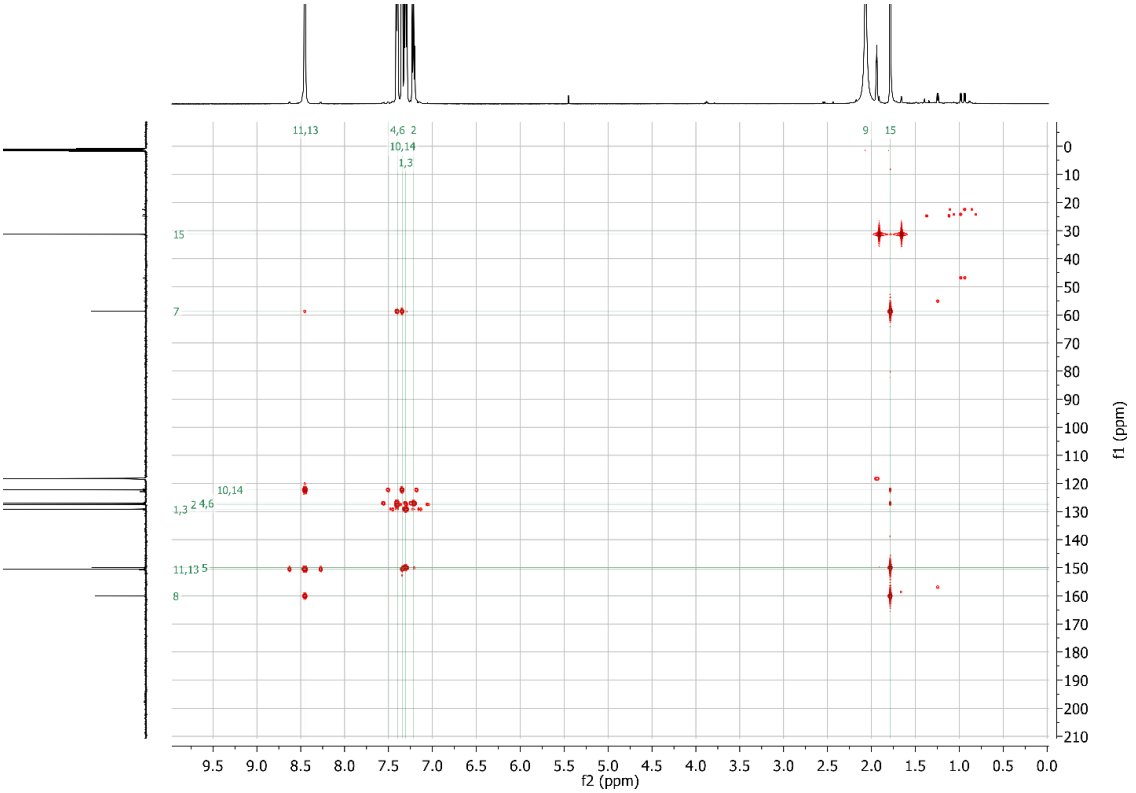
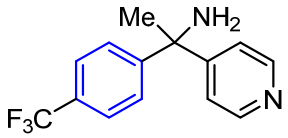



**Figure S10.** HMBC NMR (126 MHz) spectrum of **5a** in $CD_3CN$.




Compound **5b** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3b**) (88 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (50 mg, 64%). The yield of product **5b** was determined to be 91% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.47 (d, $J$ = 5.4 Hz, 2H), 7.67 – 7.55 (m, 4H), 7.34 (d, $J$ = 5.6 Hz, 2H), 2.14 (s, 2H), 1.81 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 159.14, 154.45, 150.71, 129.03 (q, $J$ = 32.2 Hz), 126.57 (q, $J$ = 271.6, 270.8, 254.6 Hz), 126.00 (q, $J$ = 3.7 Hz), 122.27, 118.30, 58.88, 31.09. $^{19}$F NMR (471 MHz, $CD_3CN$) δ -62.89. MS (ESI) m/z calcd. for $C_{14}H_{13}F_3N_2$ ($[M + H]^+$) 267.1, found 267.2.

Compound **5b** was also synthesized from the corresponding iminium HCl salt **6b** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt (**6b**) (211 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 μL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.). The yield of product **5b** was determined to be 14% by a calibrated UPLC-MS.

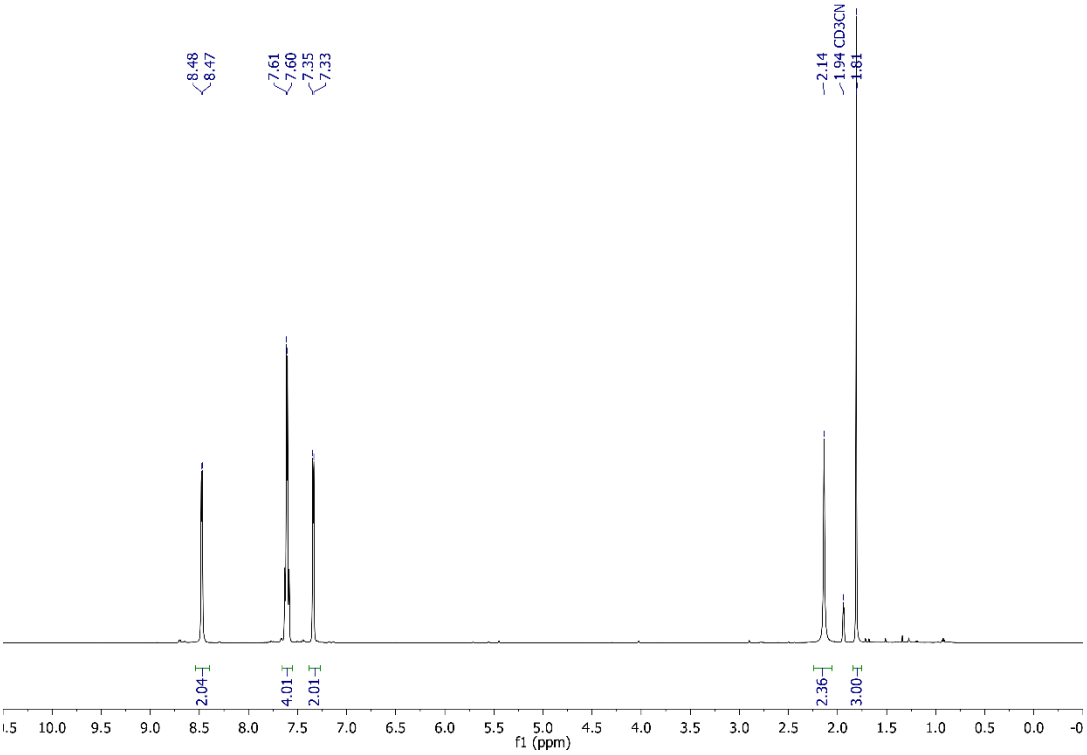



**Figure S11.** $^{1}$H qNMR (500 MHz) spectrum of **5b** in $CD_3CN$.

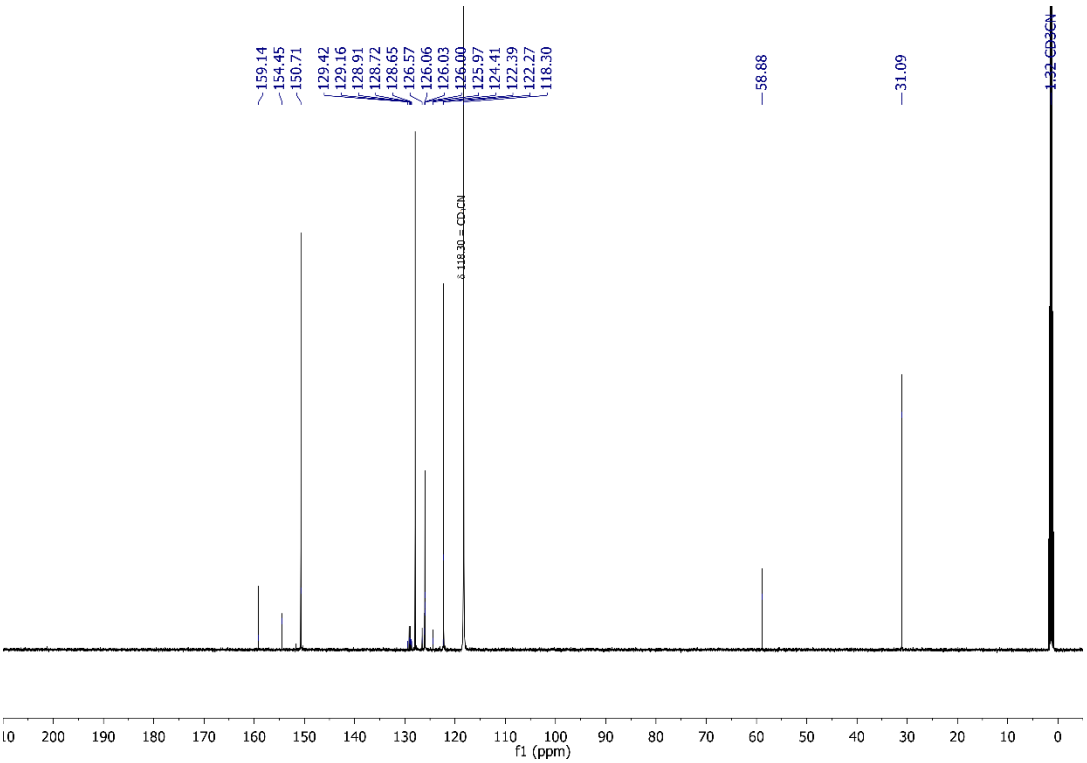



**Figure S12.** $^{13}$C NMR (126 MHz) spectrum of **5b** in $CD_3CN$.

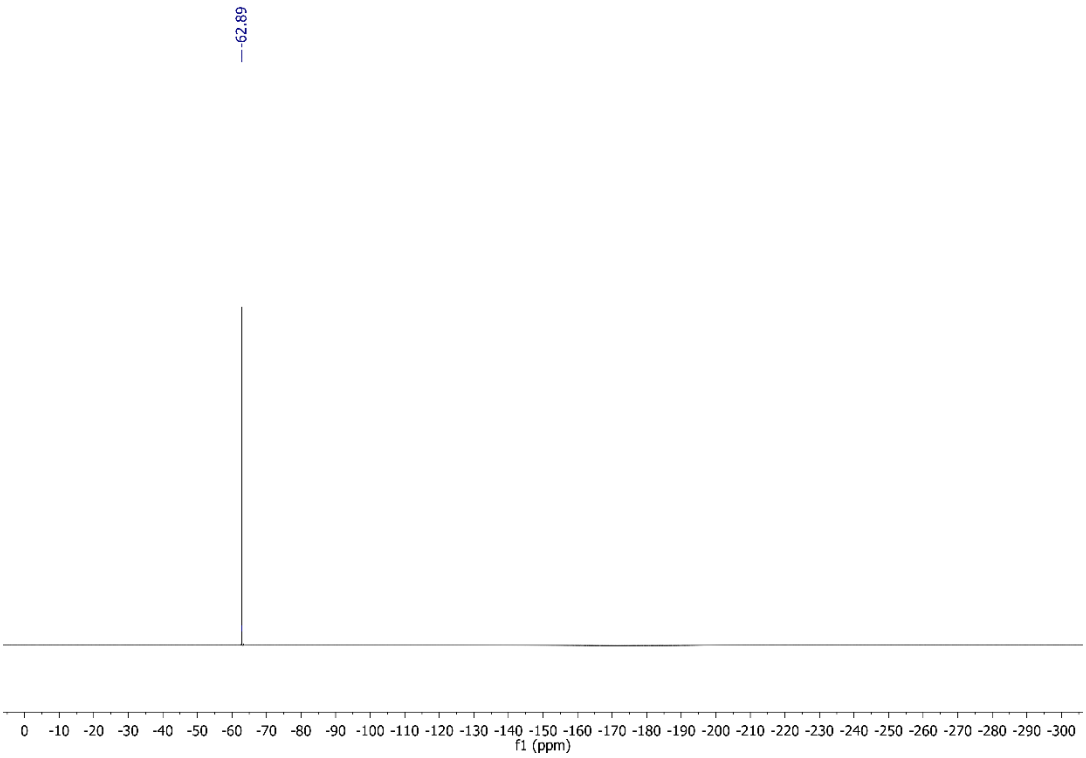
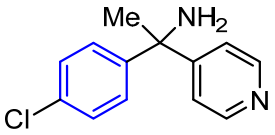



**Figure S13.** $^{19}F$ NMR (471 MHz) spectrum of compound **5b** in $CD_3CN$.




Compound **5c** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3c**) (82 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (51 mg, 73%). The yield of product **5f** was determined to be 98% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, Acetonitrile-$d_3$) δ 8.46 (d, $J$ = 6.2 Hz, 2H), 7.38 (d, $J$ = 8.8 Hz, 2H), 7.33 (d, $J$ = 6.2 Hz, 2H), 7.31 – 7.28 (m, 2H), 2.18 (s, 3H), 1.76 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 159.54, 150.59, 148.86, 132.78, 129.02, 128.99, 122.23, 118.30, 58.51, 41.38, 31.24. MS (ESI) m/z calcd. for $C_{13}H_{14}ClN_2$ ([M + H]$^+$) 233.1, found 233.2.

Compound **5c** was also synthesized from the corresponding iminium HCl salt **6c** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt (**6c**) (125 mg,0.66 mmol, 2.2 equiv.); photocatalyst Ir[dF(Me)ppy]$_2$dtbbpyPF$_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 μL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.). The yield of product **5c** was determined to be 66% by a calibrated UPLC-MS.

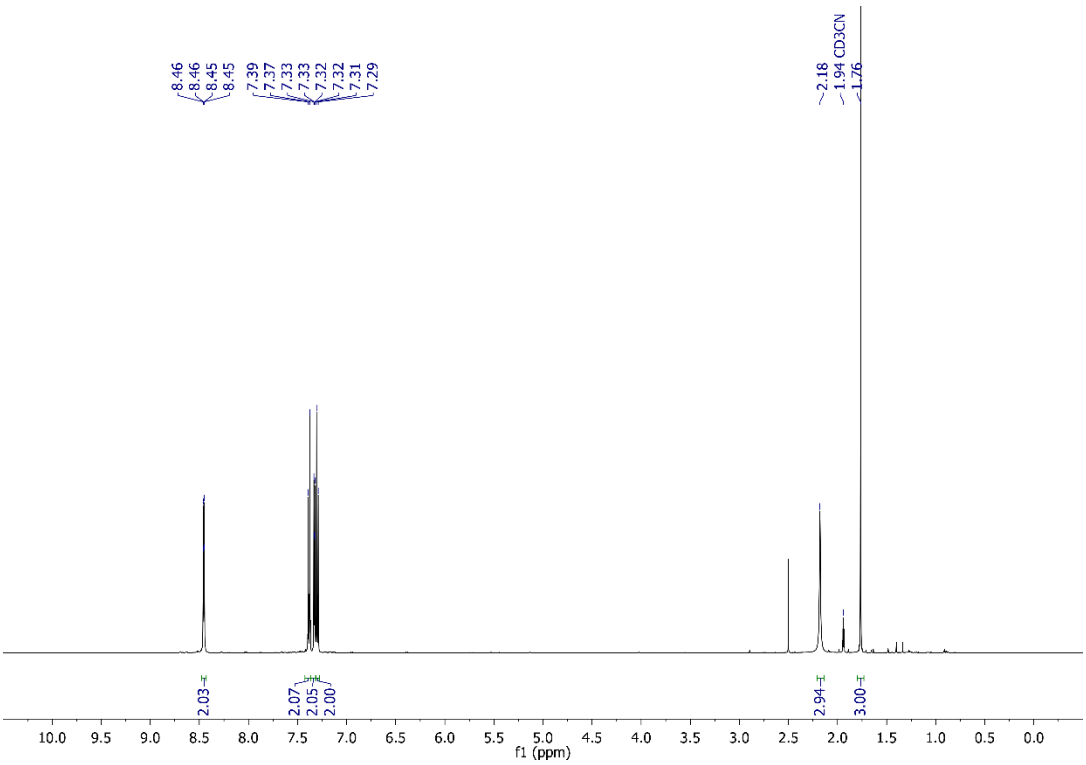



**Figure S14.** $^{1}$H qNMR (500 MHz) spectrum of **5c** in $CD_3CN$.

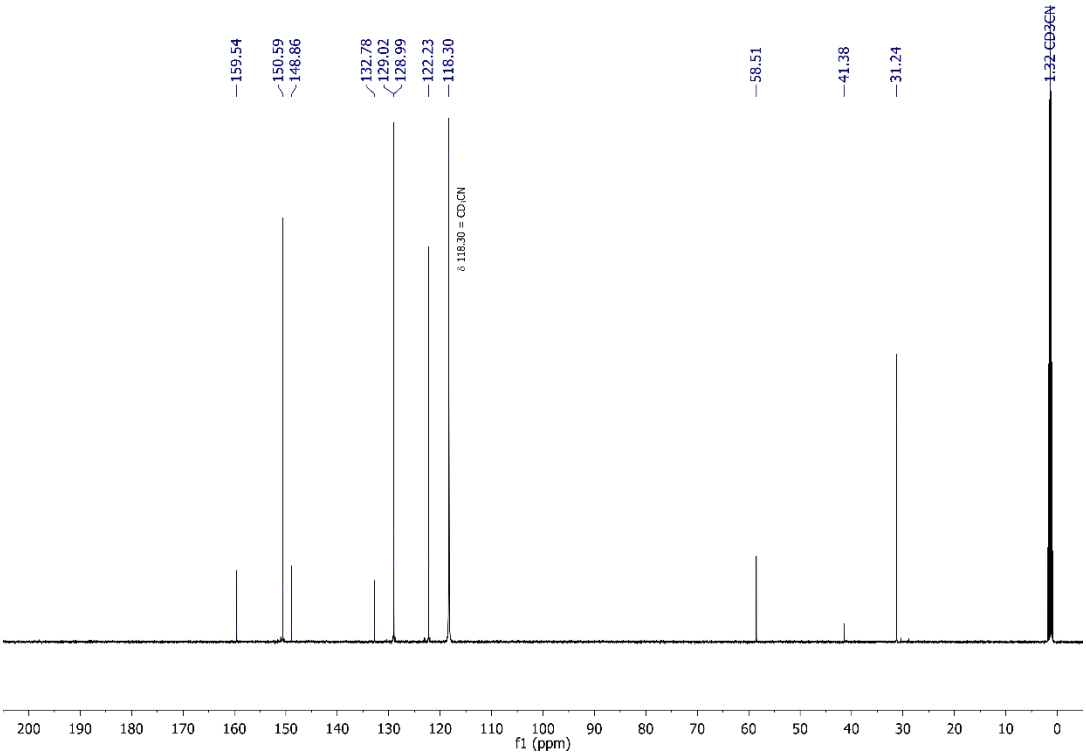
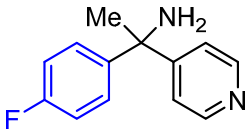



**Figure S15.** $^{13}$C NMR (126 MHz) spectrum of **5c** in $CD_3CN$.




Synthesis of **5d** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3d**) (77 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (50 mg, 77%). The yield of product **5f** was determined to be 94% by a calibrated UPLC-MS. $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.46 (dd, *J* = 4.6, 1.5 Hz, 2H), 7.41 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.34 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.03 (t, *J* = 8.9 Hz, 2H), 2.09 (s, 3H), 1.78 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 163.32, 161.39, 159.85, 150.58, 146.07, 146.05, 129.16, 129.09, 122.23, 118.31, 115.66, 115.49, 58.43, 31.49. $^{19}$F NMR (471 MHz, $CD_3CN$) δ -118.40. MS (ESI) m/z calcd. for $C_{13}H_{14}FN_2$ ($[M + H]^+$) 217.1, found 217.2

Compound **5d** was also synthesized from the corresponding iminium HCl salt **6d** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt (**6d**)(174 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 μL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.). The yield of product **5d** was determined to be 87% by a calibrated UPLC-MS.

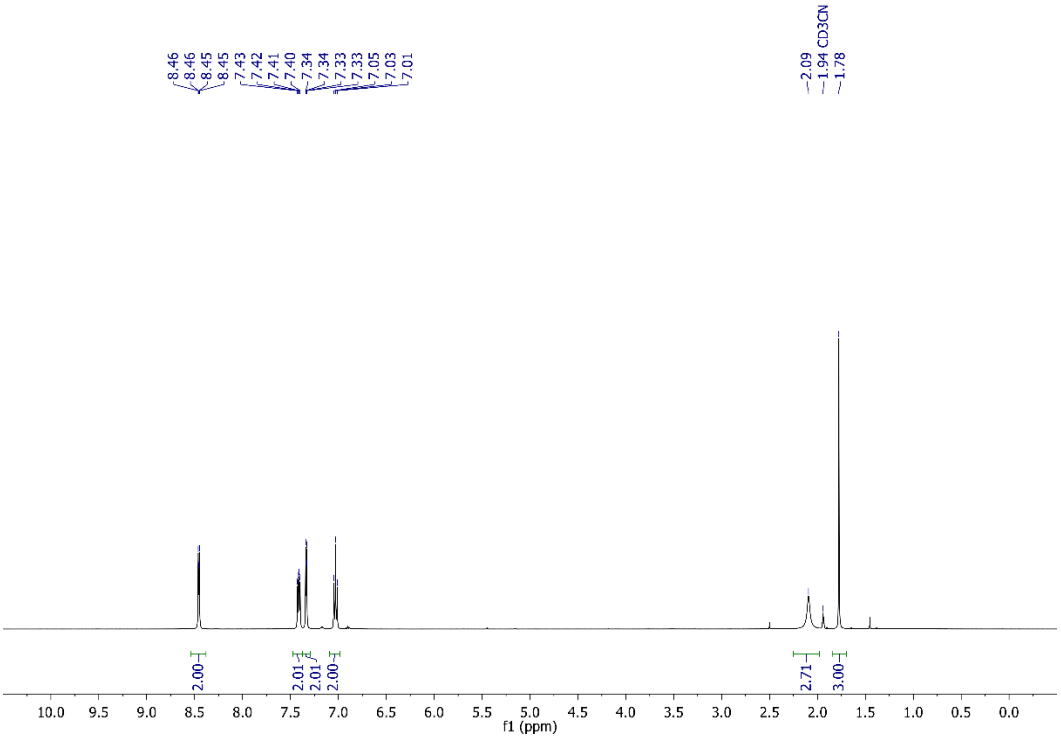



**Figure S16.** $^{1}$H qNMR (500 MHz) spectrum of **5d** in $CD_3CN$.

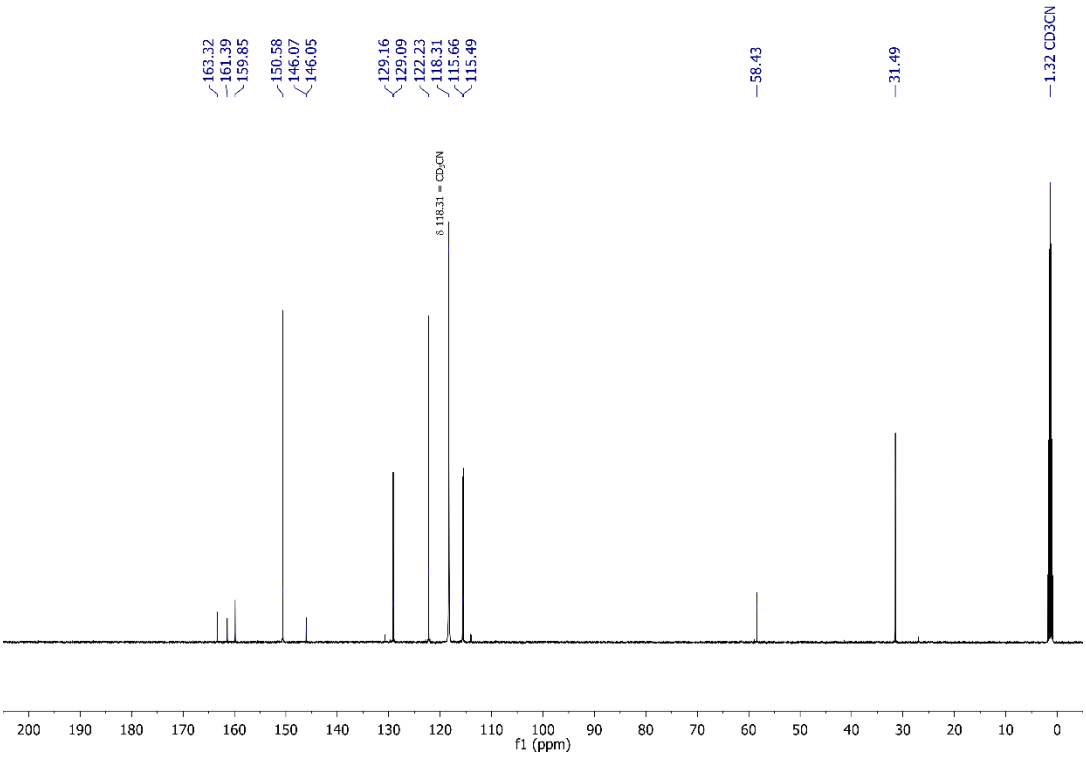



**Figure S17.** $^{13}$C NMR (126 MHz) spectrum of **5d** in $CD_3CN$.

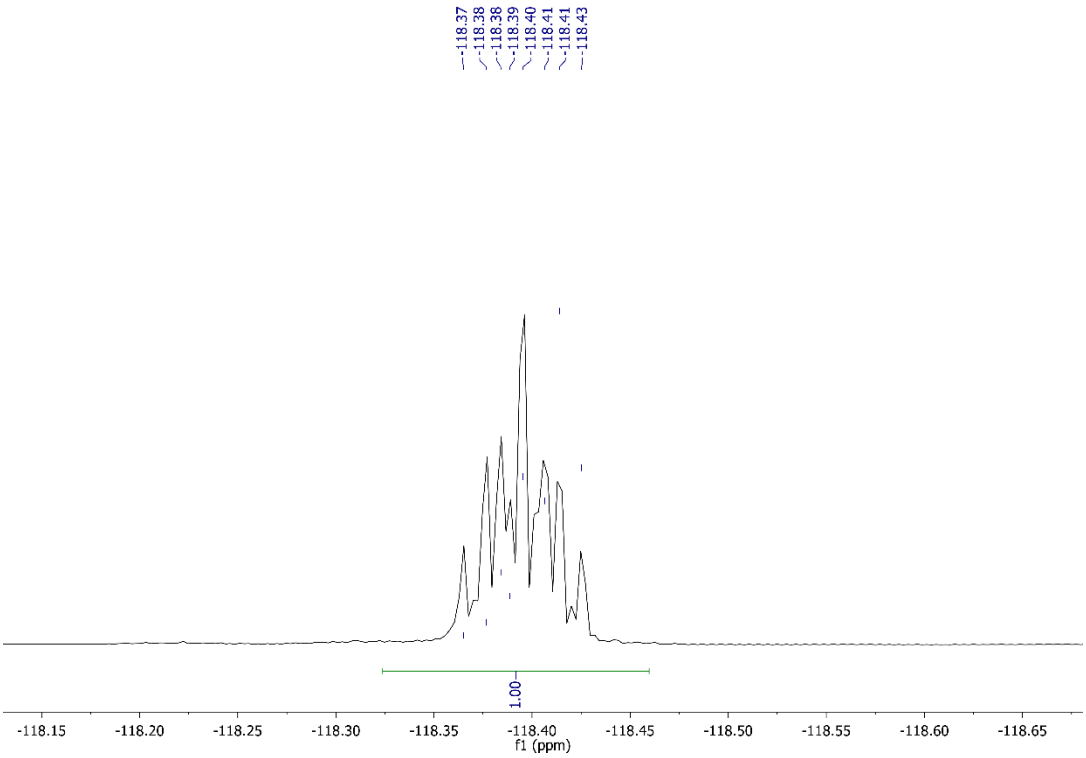
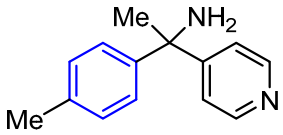



**Figure S18.** $^{19}F$ NMR (471 MHz) spectrum of compound **5d** in $CD_3CN$.




Synthesis of **5e** was synthesized following General Procedure A using 4-pyridinecarbonitrile (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3e**) (76 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (50 mg, 79%). The yield of product **5e** was determined to be 98% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.44 (d, $J$ = 6.2 Hz, 2H), 7.34 (d, $J$ = 6.2 Hz, 2H), 7.27 (d, $J$ = 8.3 Hz, 2H), 7.12 (d, $J$ = 8.0 Hz, 2H), 2.29 (s, 3H), 1.76 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 160.26, 150.47, 147.05, 137.09, 129.74, 126.99, 122.27, 58.46, 31.37, 20.94. MS (ESI) m/z calcd. for $C_{14}H_{17}N_2$ ($[M + H]^+$) 213.1, found 213.2

Compound **5e** was also synthesized from the corresponding iminium HCl salt **6e** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt (**6e**) (112 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 μL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.). The yield of product **5e** was determined to be 93% by a calibrated UPLC-MS.

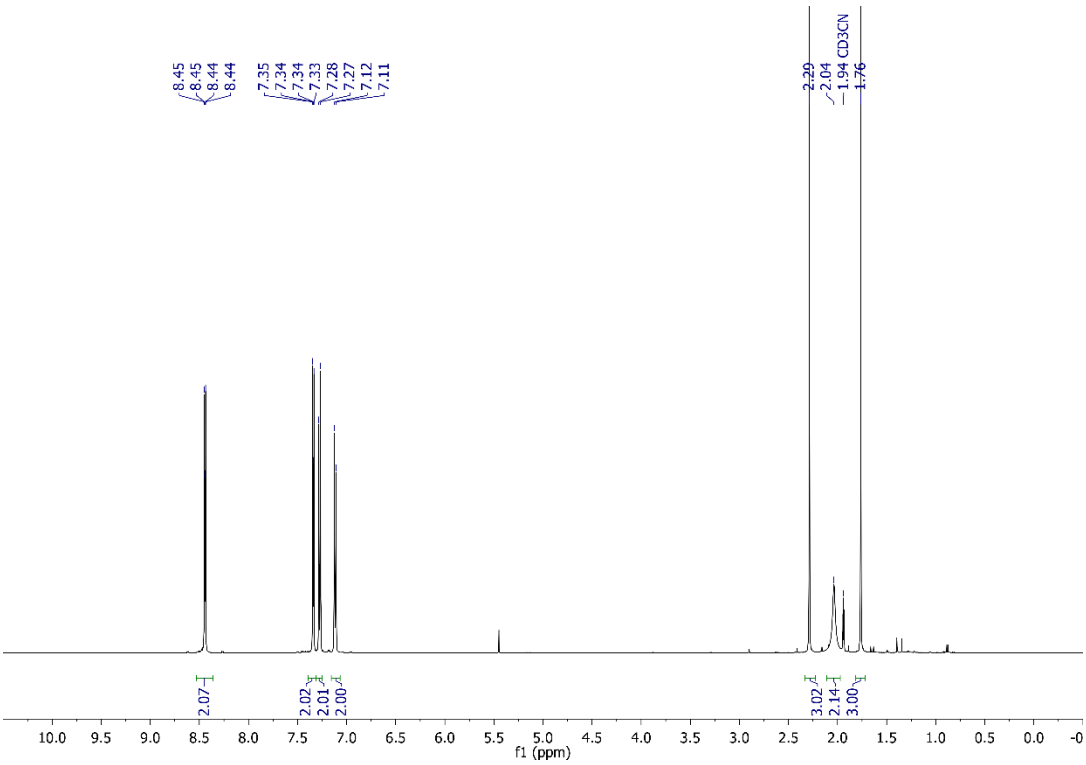



**Figure S19.** $^{1}$H qNMR (500 MHz) spectrum of **5e** in $CD_3CN$.

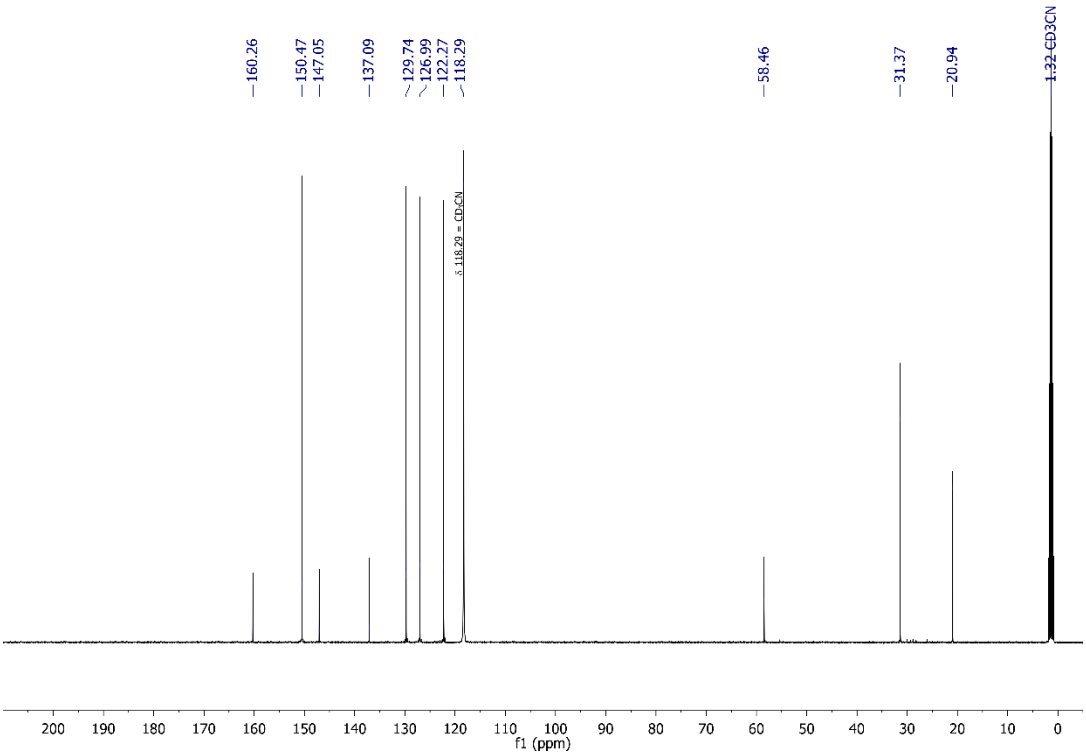
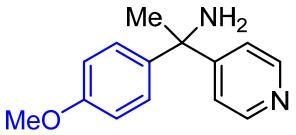



**Figure S20.** $^{13}$C NMR (126 MHz) spectrum of **5e** in $CD_3CN$.




Synthesis of **5f** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3f**) (81 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (44 mg, 64%). The yield of product **5f** was determined to be 79% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.44 (d, J = 6.0 Hz, 2H), 7.34 (d, J = 6.1 Hz, 2H), 7.31 (d, J = 8.9 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 2.06 (s, 2H), 1.76 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) 160.37, 159.23, 150.47, 142.05, 128.26, 122.24, 118.30, 114.34, 58.25, 55.85, 31.54. MS (ESI) m/z calcd. for $C_{14}H_{16}N_2O$ ($[M + H]^+$) 229.1, found 229.2.

Compound **5f** was also synthesized from the corresponding iminium HCl salt **6f** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt (**6f**) (186 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 μL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine **4a** (31 mg, 0.3 mmol, 1.0 equiv.). The yield of product **5f** was determined to be 94% by a calibrated UPLC-MS.

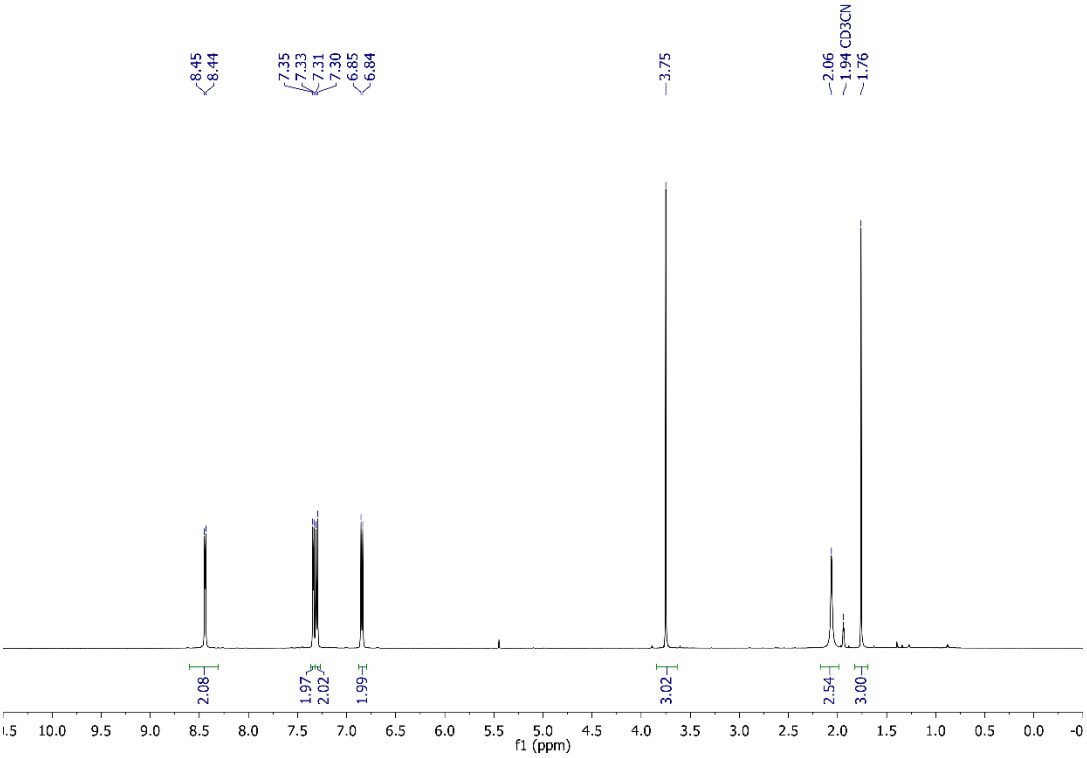



**Figure S21.** $^{1}$H qNMR (500 MHz) spectrum of **5f** in $CD_3CN$.

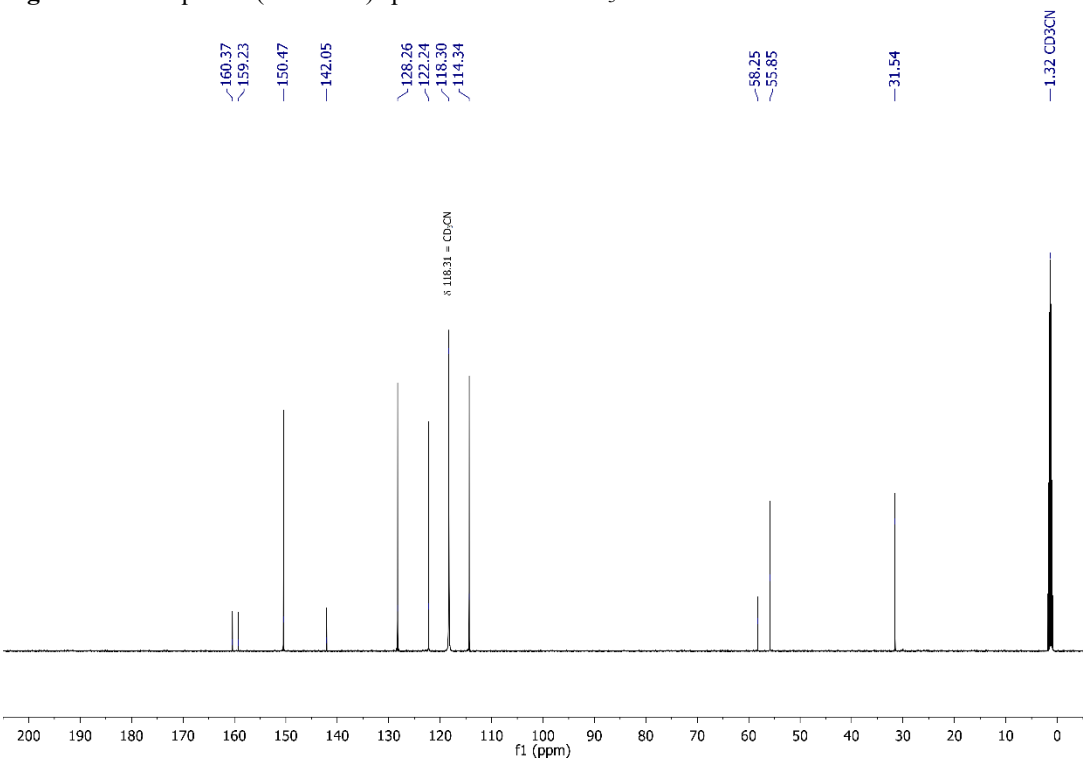
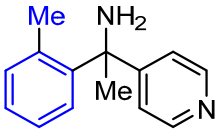



**Figure S22.** $^{13}$C NMR (126 MHz) spectrum of **5f** in $CD_3CN$.




Synthesis of **5g** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3g**) (76 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (21 mg, 30%). The yield of product **5g** was determined to be 32% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.43 (d, *J* = 5.5 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 5.1 Hz, 3H), 7.09 (d, *J* = 7.4 Hz, 1H), 2.08 (s, 3H), 1.86 (s, 3H), 1.73 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 160.67, 150.57, 146.52, 137.35, 133.32, 128.25, 126.94, 126.59, 121.74, 118.30, 59.31, 32.93, 21.80. MS (ESI) M/Z CALCD. FOR $C_{14}H_{17}N_2$ ($[M + H]^+$) 213.1, found 213.2

Compound **5g** was also synthesized from the corresponding iminium HCl salt **6g** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt (**6g**) (112 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 μL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.). The yield of product **5g** was determined to be 82% by a calibrated UPLC-MS.

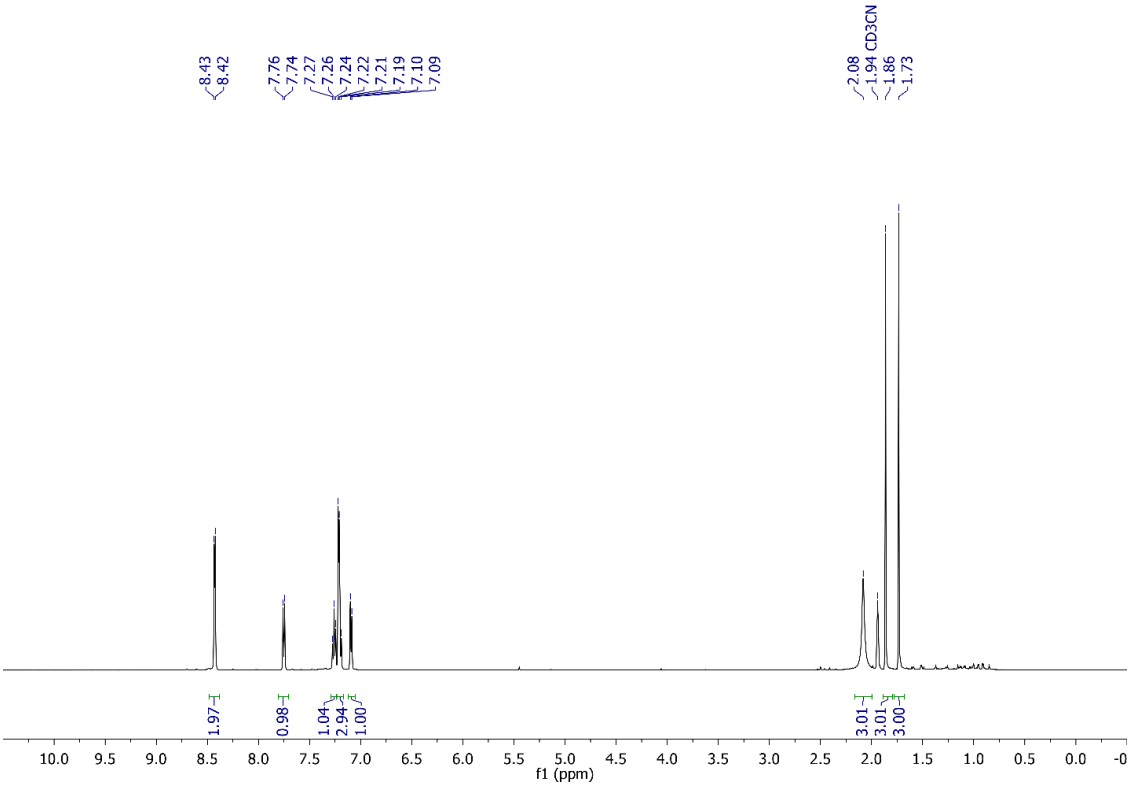



**Figure S23.** $^{1}$H qNMR (500 MHz) spectrum of **5g** in $CD_3CN$.

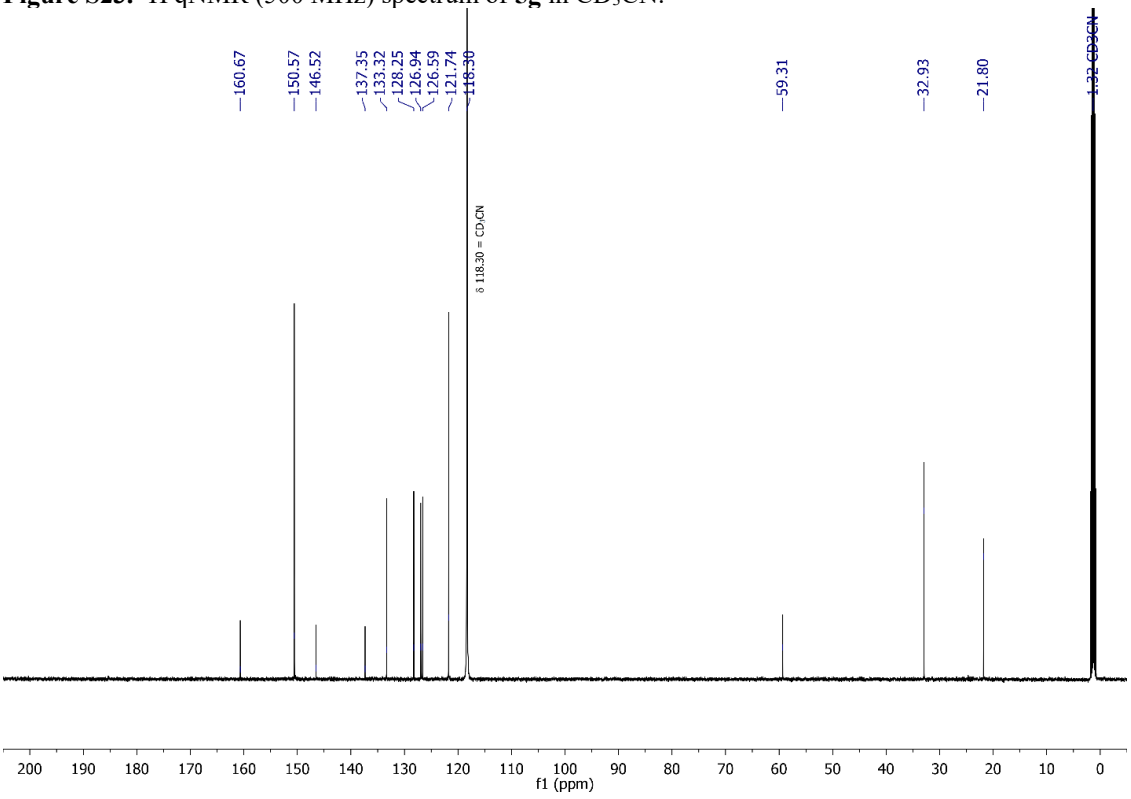
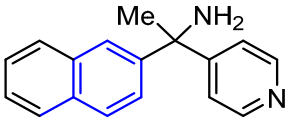



**Figure S24.** $^{13}$C NMR (126 MHz) spectrum of **5g** in $CD_3CN$.




Compound **5h** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3h**) (87 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (37 mg, 50%). The yield of product **5h**was determined to be 50% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.45 (d, *J* = 6.2 Hz, 2H), 8.02 (d, *J* = 1.5 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.84 – 7.81 (m, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.48 (pd, *J* = 6.9, 1.5 Hz, 2H), 7.39 – 7.35 (m, 3H), 2.18 (s, 3H), 1.87 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 159.81, 150.56, 147.31, 134.11, 133.09, 129.03, 128.75, 128.33, 127.22, 126.93, 126.48, 124.77, 122.41, 58.93, 31.19. MS (ESI) m/z calcd. for $C_{17}H_{17}N_2$ ($[M + H]^+$) 249.1, found 249.2.

Compound **5h** was also synthesized from the corresponding iminium HCl salt **6h** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt (**6h**) (136 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.). The yield of product **5h** was determined to be 98% by a calibrated UPLC-MS.

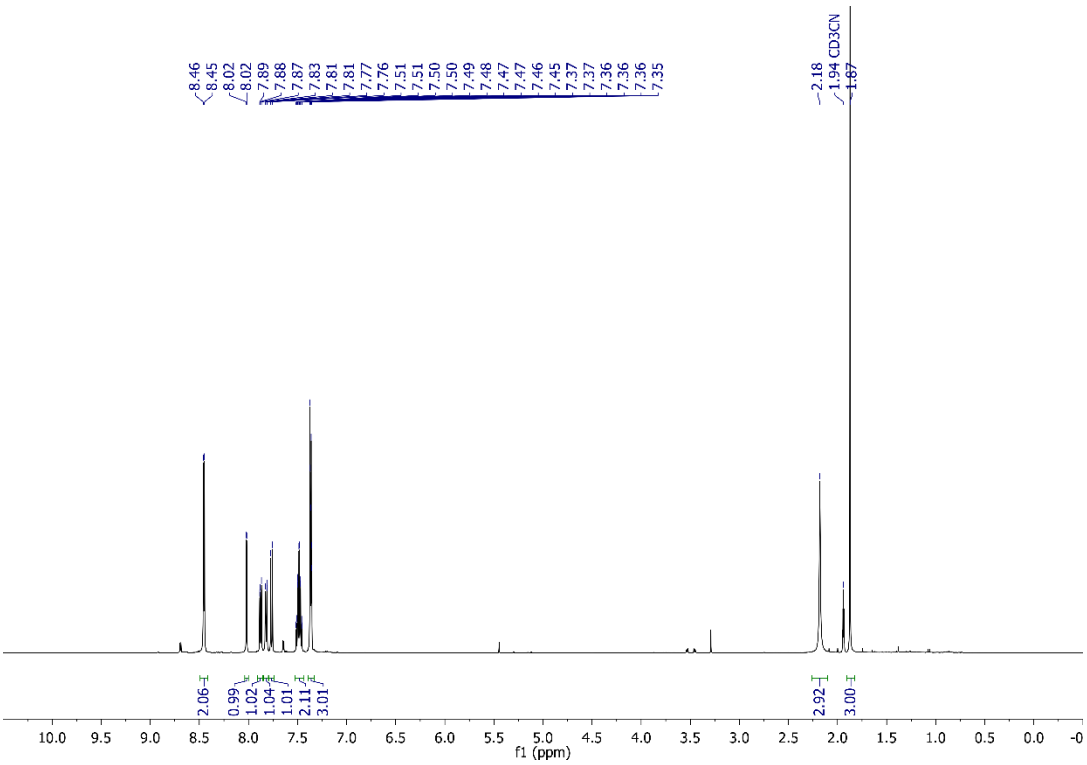



**Figure S25.** $^{1}$H qNMR (500 MHz) spectrum of **5h** in $CD_3CN$.

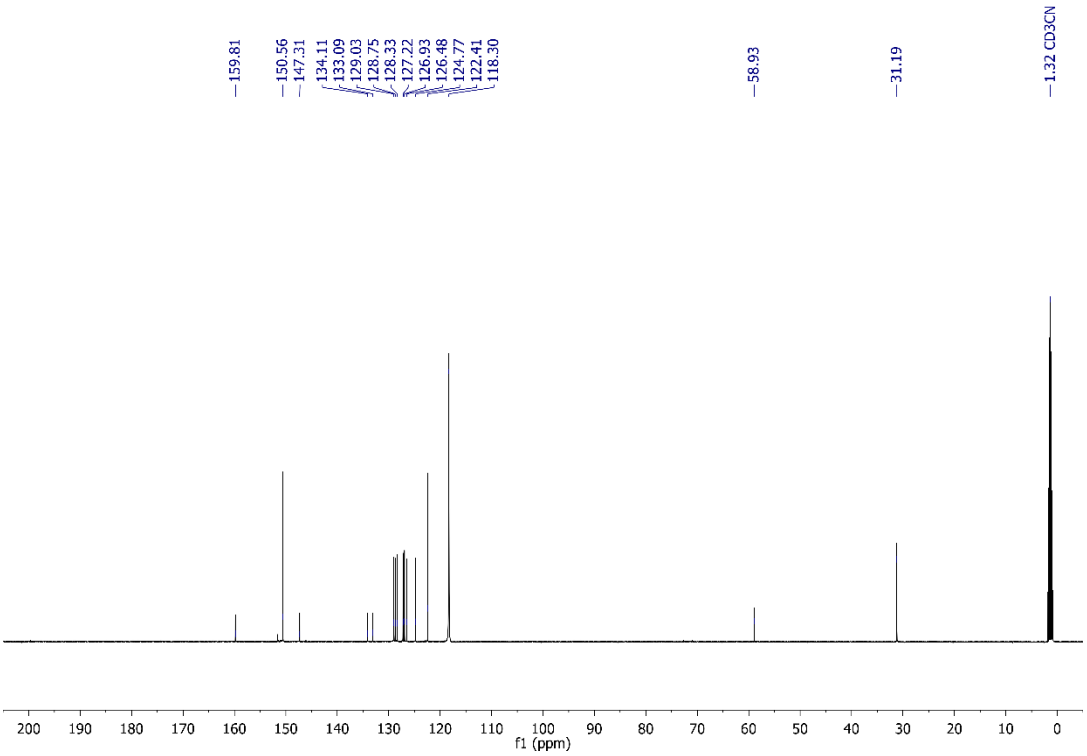
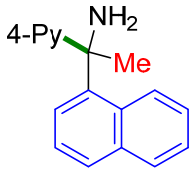



**Figure S26.** $^{13}$C NMR (126 MHz) spectrum of **5h** in $CD_3CN$.




Compound **5i** was also synthesized from the corresponding iminium HCl salt **6i** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt (**6i**) (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.). The yield of product **5i** was determined to be 76% by a calibrated UPLC-MS. Product characterization matched as described.[5] $^1$H NMR (500 MHz, $CD_3CN$) δ 8.38 (d, $J$ = 5.9 Hz, 2H), 7.93 (d, $J$ = 7.3 Hz, 1H), 7.86 (d, $J$ = 8.2 Hz, 2H), 7.71 (d, $J$ = 8.7 Hz, 1H), 7.55 (t, $J$ = 7.8 Hz, 1H), 7.35 (t, $J$ = 7.4 Hz, 1H), 7.27 (d, $J$ = 6.0 Hz, 2H), 7.18 (t, $J$ = 7.8 Hz, 1H), 2.19 (br s, 2H), 1.87 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 161.08, 150.66, 143.96, 136.00, 131.30, 129.96, 129.47, 127.97, 126.07, 125.02, 121.62, 59.44, 33.86. MS (ESI) m/z calcd. for $C_{17}H_{17}N_2$ ($[M + H]^+$) 249.1, found 249.2.

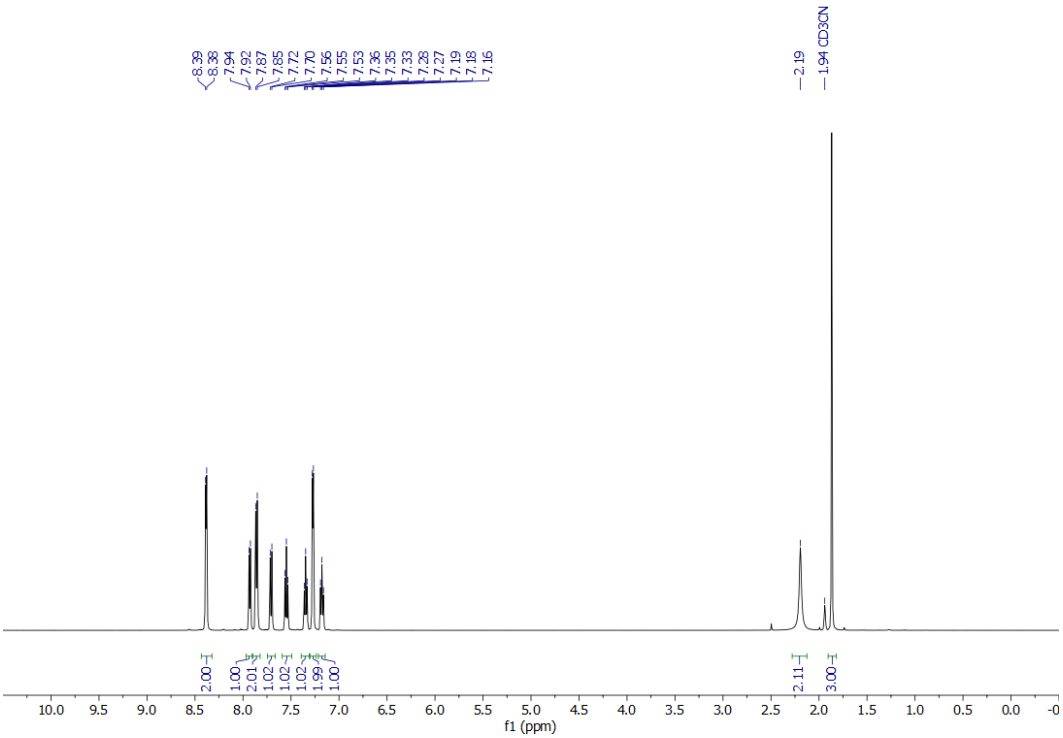



**Figure S27.** $^{1}$H qNMR (500 MHz) spectrum of **5i** in $CD_3CN$.

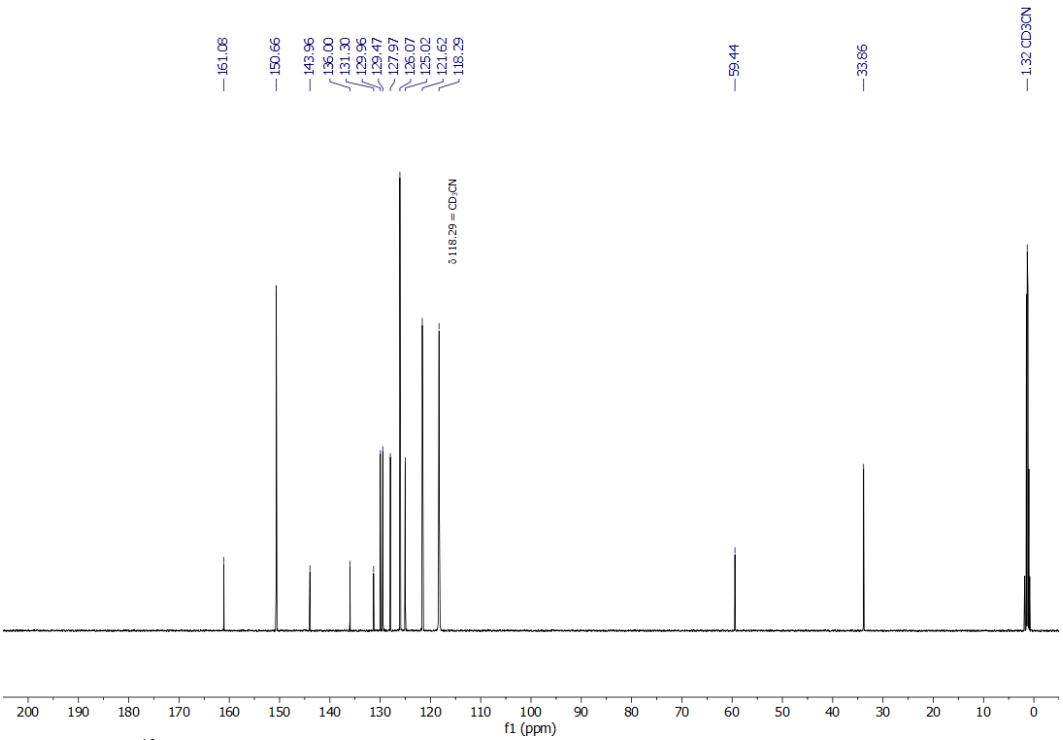
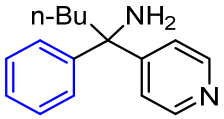



**Figure S28.** $^{13}$C NMR (126 MHz) spectrum of **5i** in $CD_3CN$.




Compound **5l** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), PC1 (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (51 mg, 71%). The yield of product **5l** was determined to be 94% by a calibrated UPLC-MS. $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.45–8.43 (m, 2H), 7.43–7.40 (m, 2H), 7.36–7.34 (m, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.22–7.18 (m, 1H), 2.25–2.16 (m, 2H), 1.37–1.27 (m, 2H), 1.23–1.08 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).$^{13}$C NMR (126 MHz, $CD_3CN$) δ 159.27, 150.41, 149.04, 129.11, 127.39, 127.38, 122.67, 61.37, 42.23, 26.92, 23.80, 14.35. MS (ESI) m/z calcd. for $C_{16}H_{17}N_2$ ($[M + H]^+$) 241.2, found 241.2.

Compound **5l** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt (**6l**) (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.). The yield of product **5l** was determined to be 76% by a calibrated UPLC-MS.

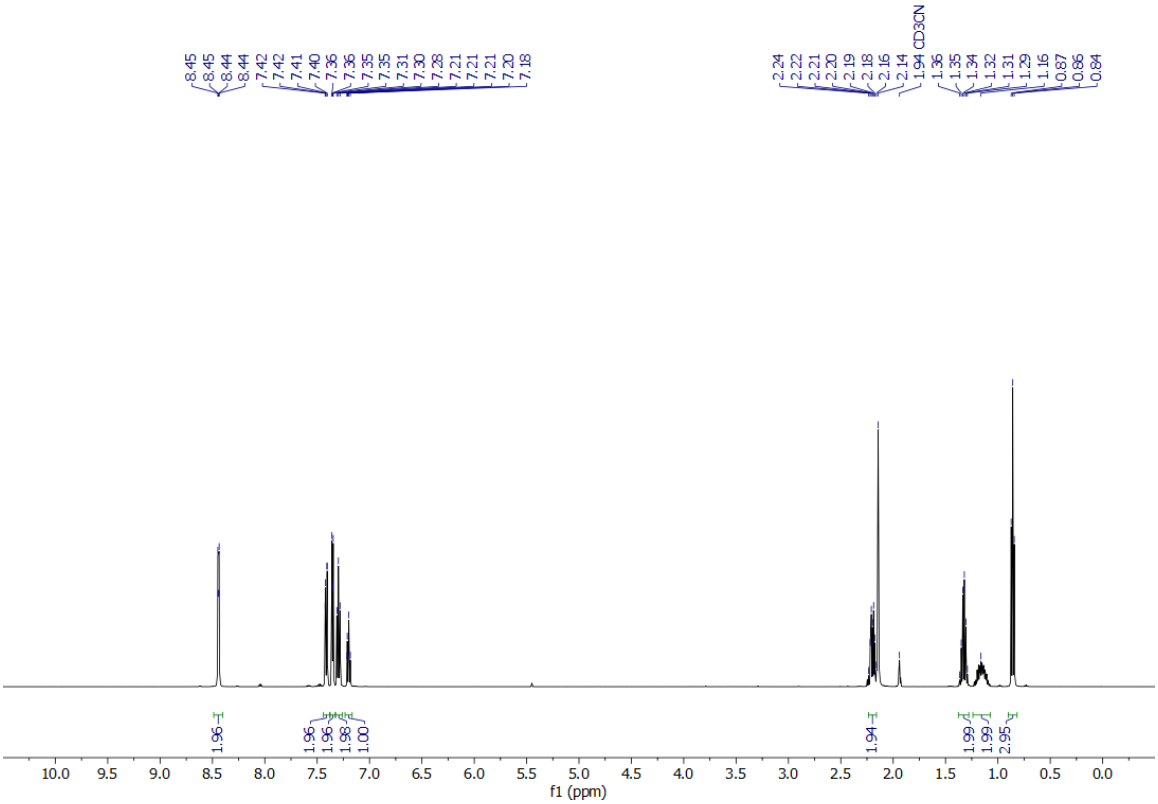



**Figure S29.** $^{1}$H qNMR (500 MHz) spectrum of **5l** in $CD_3CN$.

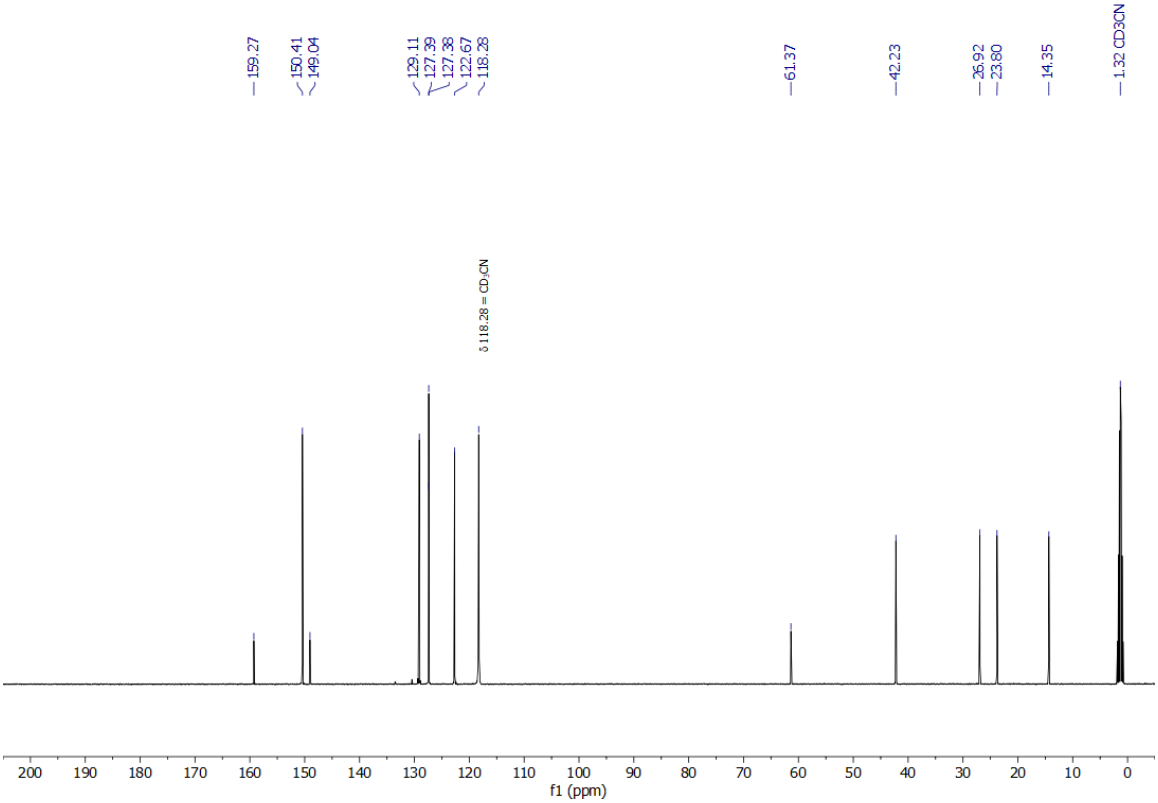
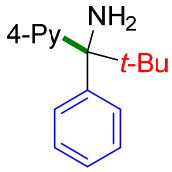



**Figure S30.** $^{13}$C NMR (126 MHz) spectrum of **5l** in $CD_3CN$.




Compound **5m** was also synthesized from the corresponding iminium HCl salt **6m** and cyanoarene **4a**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt (**6m**)(130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and 4-cyanopyridine (31 mg, 0.3 mmol, 1.0 equiv.). MS (ESI) *m/z* calcd. for $C_{16}H_{21}N_2$ ($[M + H]^+$) 241.2, found 242.3. The product **5m** was synthesized in 84% yield (retention time t = 2.310, m/z = 242.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.[5] $^1H$ NMR (500 MHz, $CD_3CN$) δ 8.41 (dd, *J* = 1.6, 4.6 Hz, 2H), 7.43–7.39 (m, 2H), 7.39–7.36 (dd, *J* = 1.7, 4.6 Hz, 2H), 7.28–7.23 (m, 2H), 7.22–7.18 (m, 1H), 2.09 (br s, 2H), 1.15 (s, 9H). $^{13}C$ NMR (126 MHz, $CD_3CN$) δ 158.48, 149.63, 147.96, 130.22, 128.04, 127.16, 125.42, 67.85, 38.68, 28.17. MS (ESI) m/z calcd. for $C_{16}H_{21}N_2$ ($[M + H]^+$) 241.2, found 241.3.

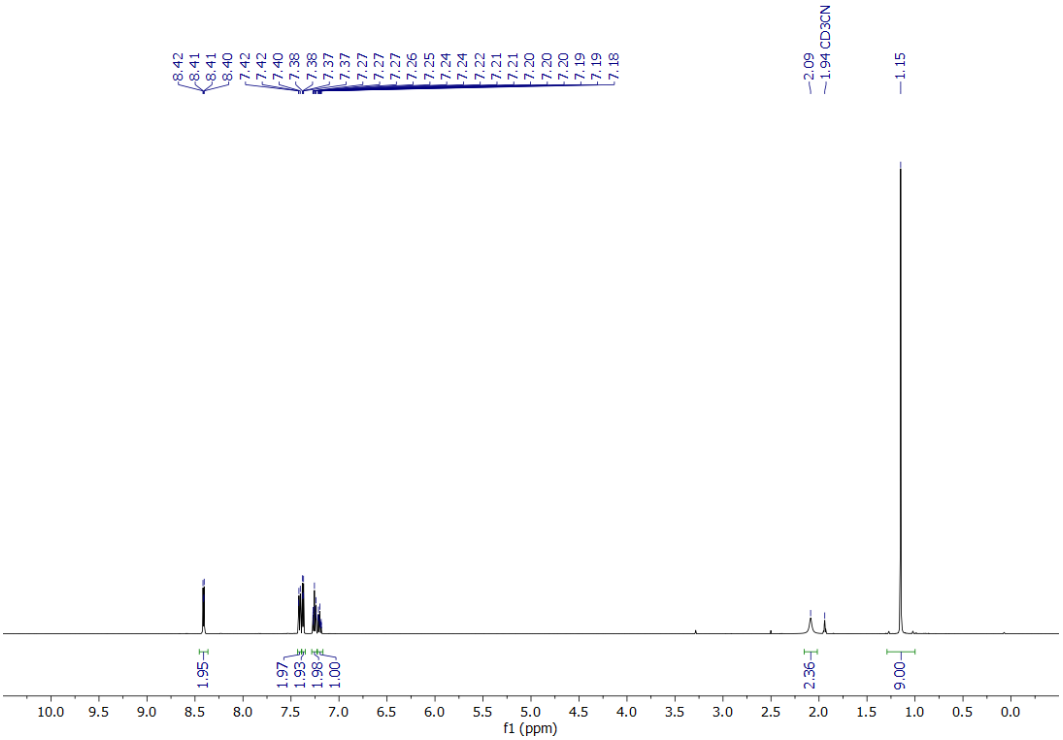



**Figure S31.** $^{1}$H qNMR (500 MHz) spectrum of **5m** in $CD_3CN$.

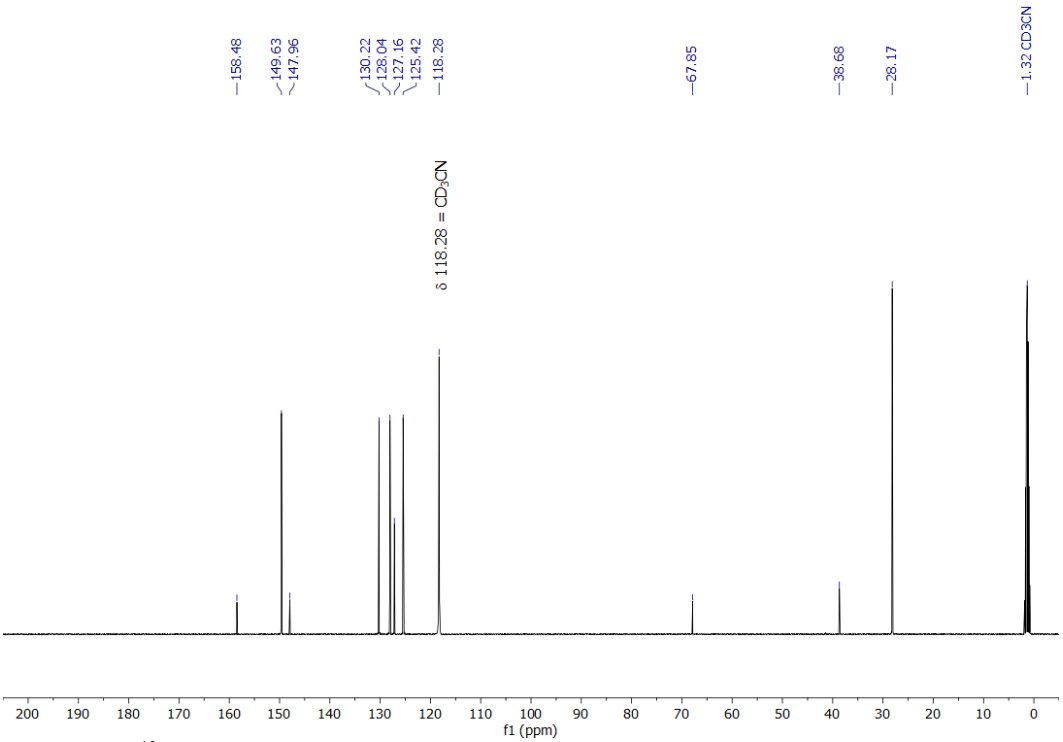
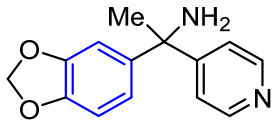



**Figure S32.** $^{13}$C NMR (126 MHz) spectrum of **5m** in $CD_3CN$.




Compound **5j** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3j**) (73 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (25 mg, 34%). The yield of product **5j** was determined to be 42% by a calibrated UPLC-MS 1H NMR: $^{1}$H NMR (500 MHz, $CD_3CN$ δ 8.44 (d, $J$ = 6.2 Hz, 2H), 7.34 (d, $J$ = 6.2 Hz, 2H), 6.92 – 6.86 (m, 2H), 6.75 (d, $J$ = 8.1 Hz, 1H), 5.91 (q, $J$ = 1.0 Hz, 2H), 2.04 (s, 2H), 1.74 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 160.09, 150.51, 148.54, 147.06, 144.20, 122.18, 120.15, 108.42, 108.00, 102.27, 58.60, 31.55. MS (ESI) m/z calcd. for $C_{14}H_{15}N_2O_2$ ($[M + H]^+$) 243.1, found 243.2.

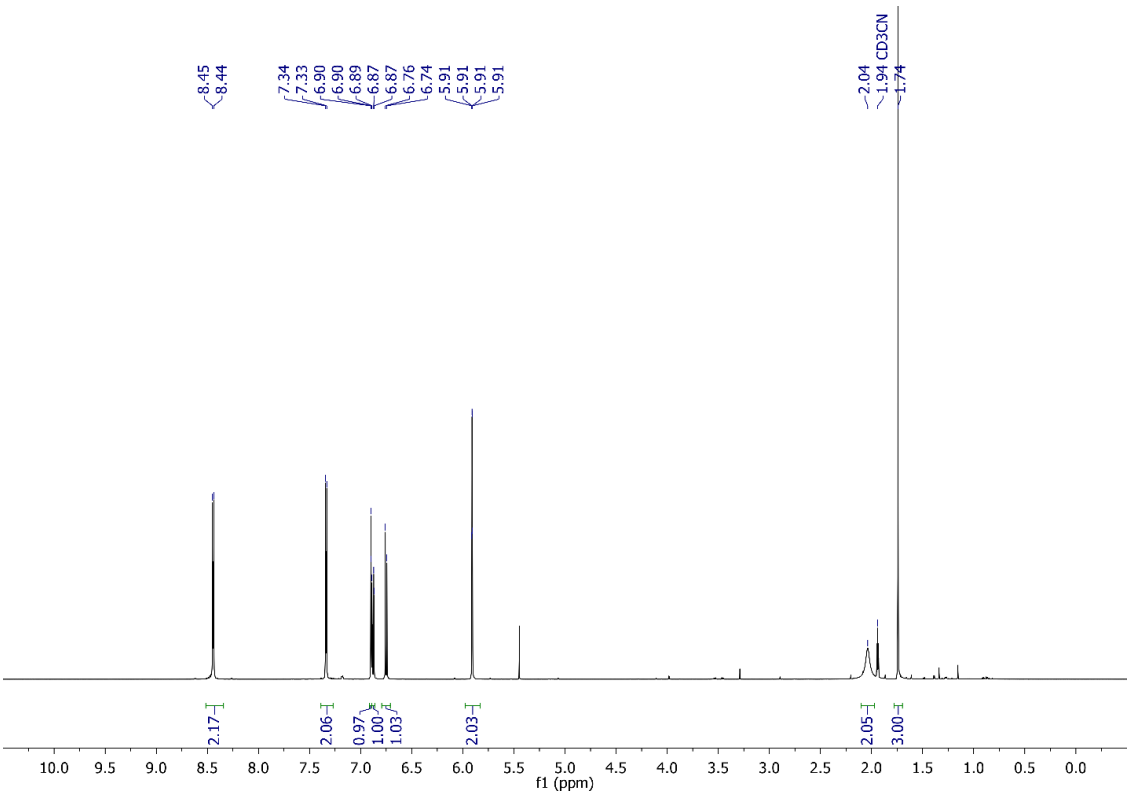



**Figure S33.** $^{1}$H qNMR (500 MHz) spectrum of **5j** in $CD_3CN$.

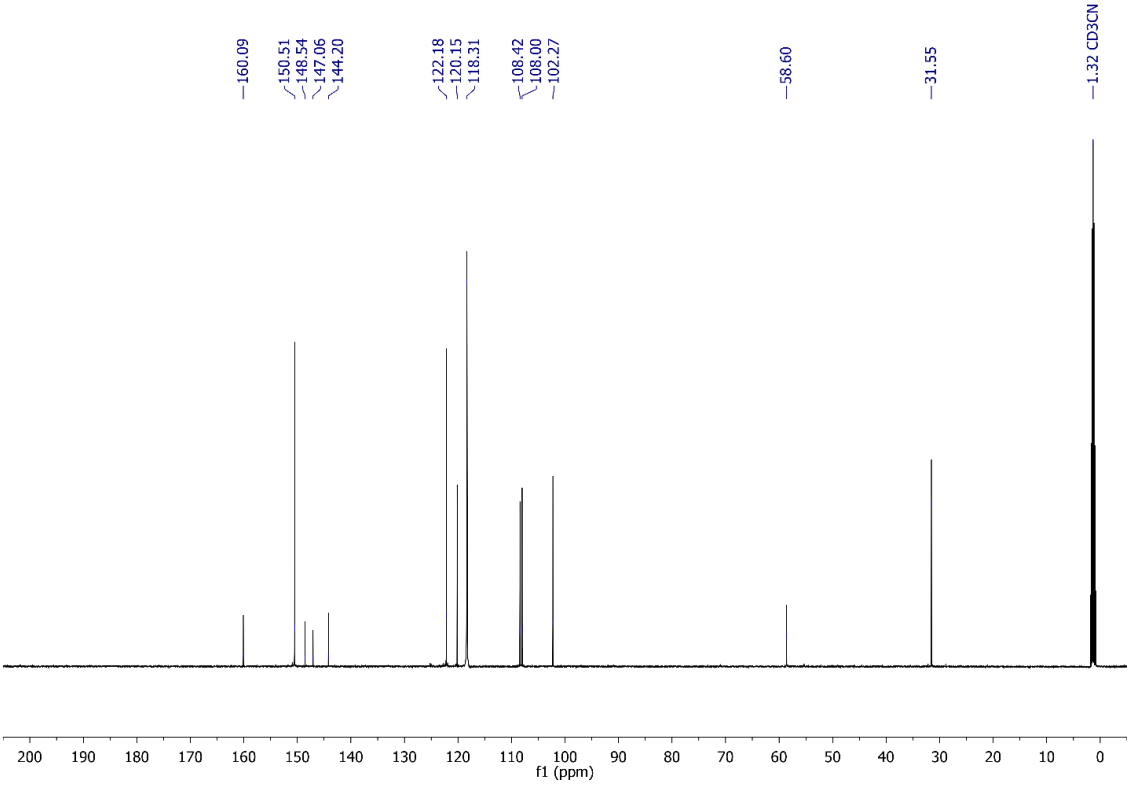
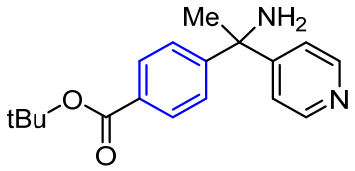



**Figure S34.** $^{13}$C NMR (126 MHz) spectrum of **5j** in $CD_3CN$.




Compound **5o** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL L, 1.1 mmol) and *O*-benzoyl oxime (**3o**) (90 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (29 mg, 32%). The yield of product **5o** was determined to be 32% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.46 (d, *J* = 6.0 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 6.0 Hz, 2H), 2.11 (s, 3H), 1.79 (s, 3H), 1.55 (s, 9H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 166.24, 159.42, 154.67, 150.63, 131.35, 130.02, 127.24, 122.27, 118.29 (MeCN residual solvent), 81.69, 58.90, 31.09, 28.33. MS (ESI) m/z calcd. for $C_{18}H_{23}N_2O_2$ ($[M + H]^+$) 299.2, found 299.2.

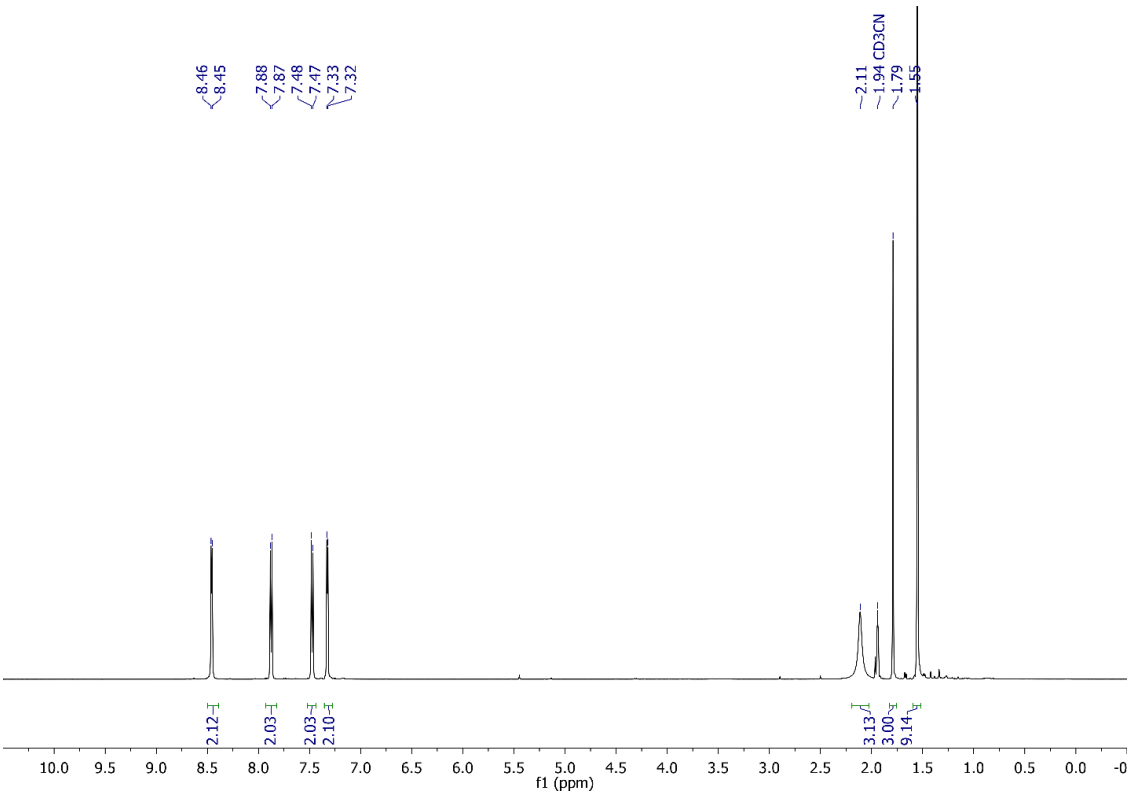



**Figure S35** $^{1}$H qNMR (500 MHz) spectrum of **5o** in $CD_3CN$.

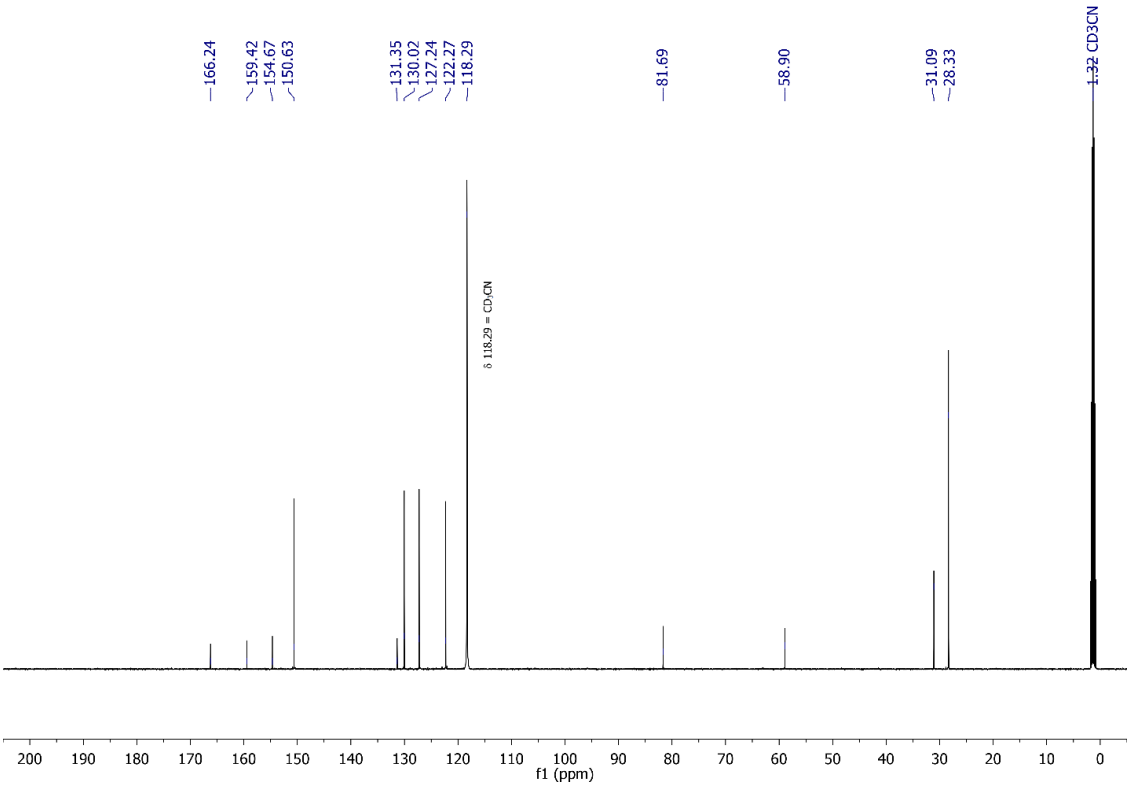
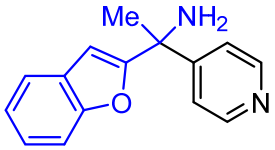



**Figure S36.** $^{13}$C NMR (126 MHz) spectrum of **5o** in $CD_3CN$.




Compound **5k** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL L, 1.1 mmol) and *O*-benzoyl oxime (**3k**) (84 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (16 mg, 31%). The yield of product **5k** was determined to be 39% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.50 (d, $J$ = 5.9 Hz, 2H), 7.60 (d, $J$ = 7.1 Hz, 1H), 7.43 (d, $J$ = 6.0 Hz, 2H), 7.38 (d, $J$ = 7.9 Hz, 1H), 7.29 – 7.19 (m, 2H), 6.77 (s, 1H), 1.79 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 150.67, 125.17, 123.92, 122.14, 121.94, 118.31, 111.78, 102.91, 56.43, 29.44. MS (ESI) M/Z CALCD. FOR $C_{15}H_{15}N_2O$ ($[M + H]^+$) 239.1, found 239.2.

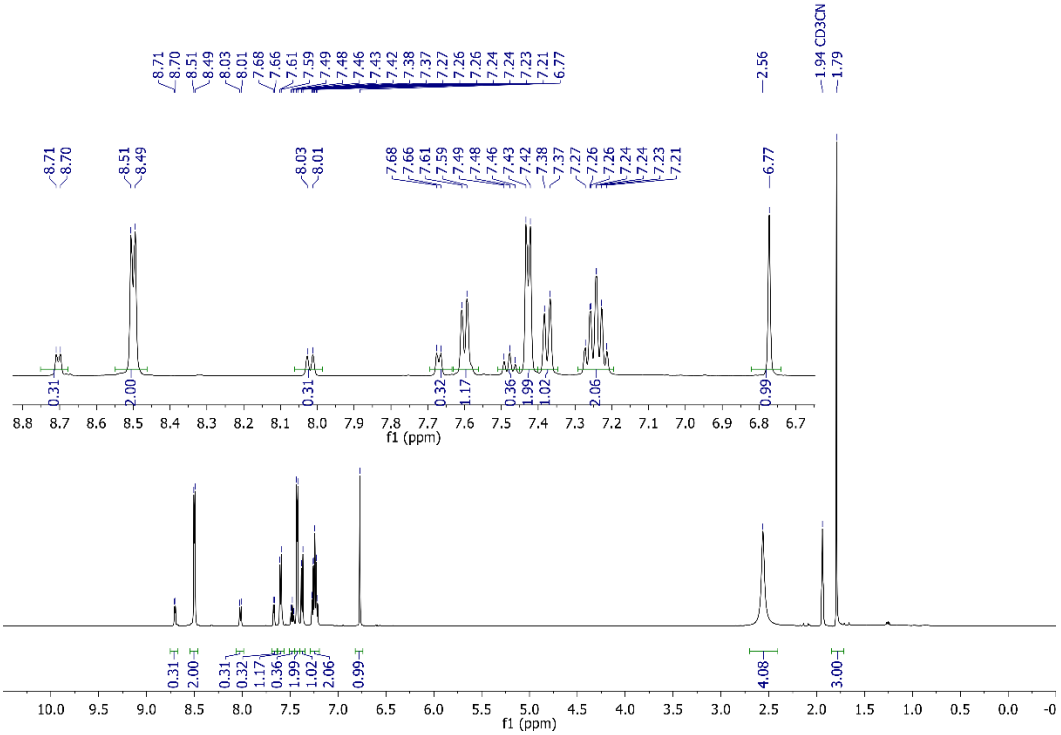


**Figure S37.** $^{1}$H qNMR (500 MHz) spectrum of **5k** in $CD_3CN$.

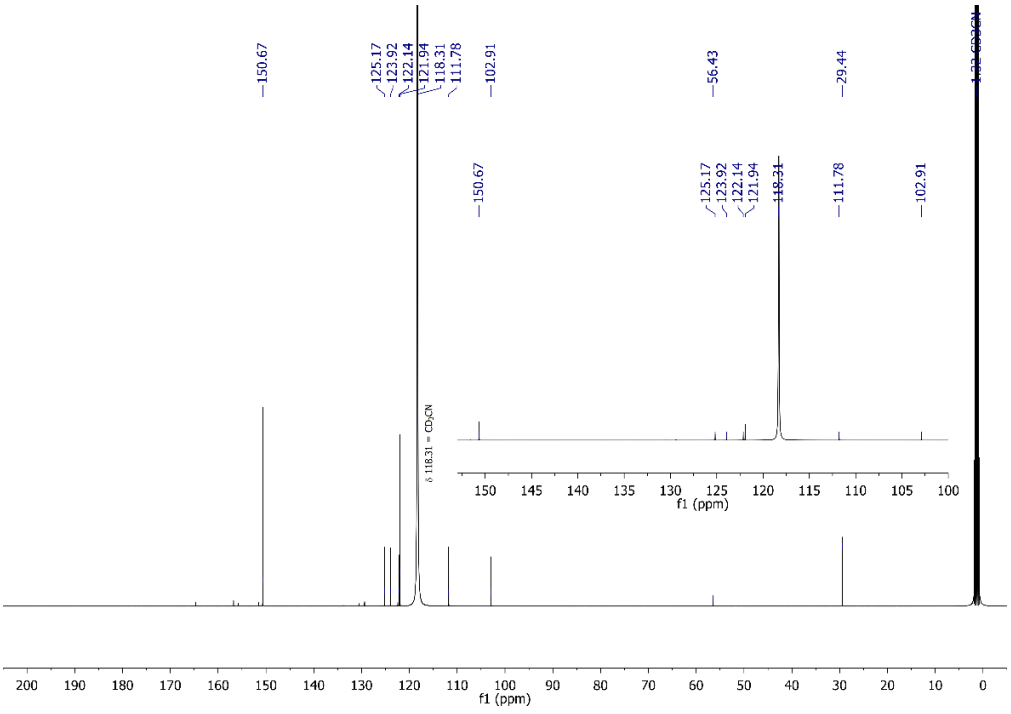
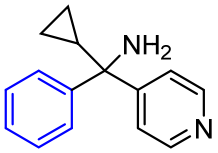


**Figure S38.** $^{13}$C NMR (126 MHz) spectrum of **5k** in $CD_3CN$.




Compound **5n** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL L, 1.1 mmol) and *O*-benzoyl oxime (**3n**) (80 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (38 mg, 56%). The yield of product **5n** was determined to be 56% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.46 (d, $J$ = 6.2 Hz, 2H), 7.45 – 7.41 (m, 2H), 7.36 (d, $J$ = 6.2 Hz, 2H), 7.31 (t, $J$ = 7.6 Hz, 2H), 7.26 – 7.20 (m, 1H), 1.88 (s, 2H), 1.63 (tt, $J$ = 8.3, 5.5 Hz, 1H), 0.59 – 0.33 (m, 4H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 159.52, 150.32, 149.40, 128.96, 127.97, 127.59, 123.09, 60.69, 22.42, 2.08, 1.71. MS (ESI) m/z calcd. for $C_{15}H_{17}N_2$ ($[M + H]^+$) 225.1, found 225.2

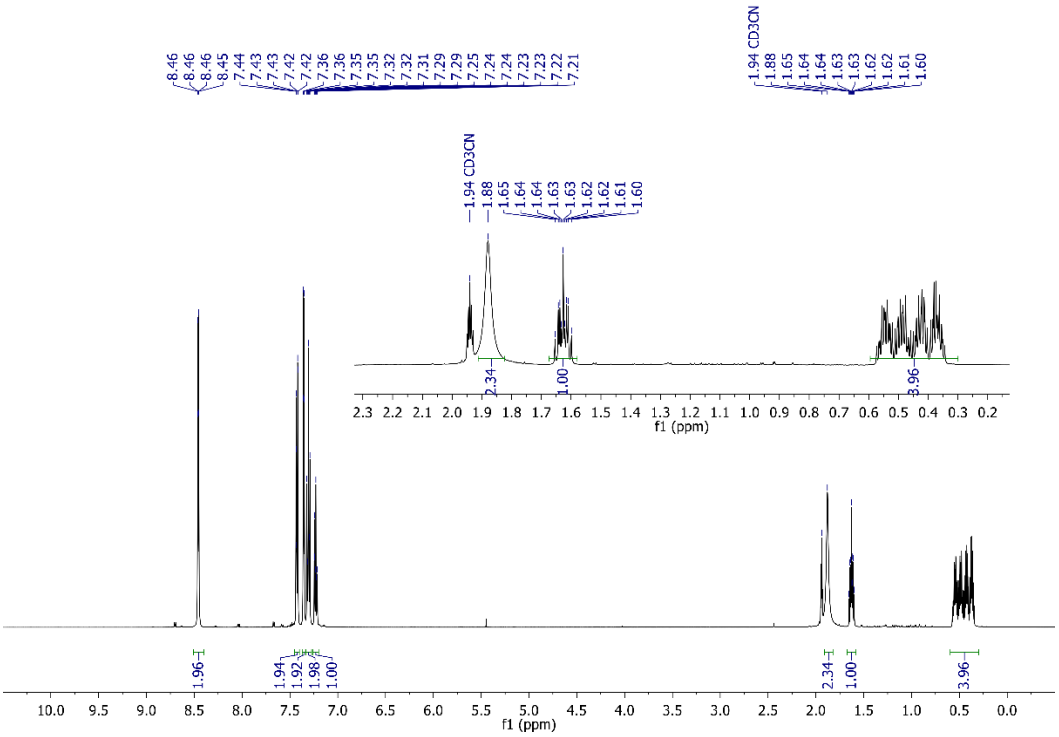



**Figure S39.** $^{1}$H qNMR (500 MHz) spectrum of **5n** in $CD_3CN$.

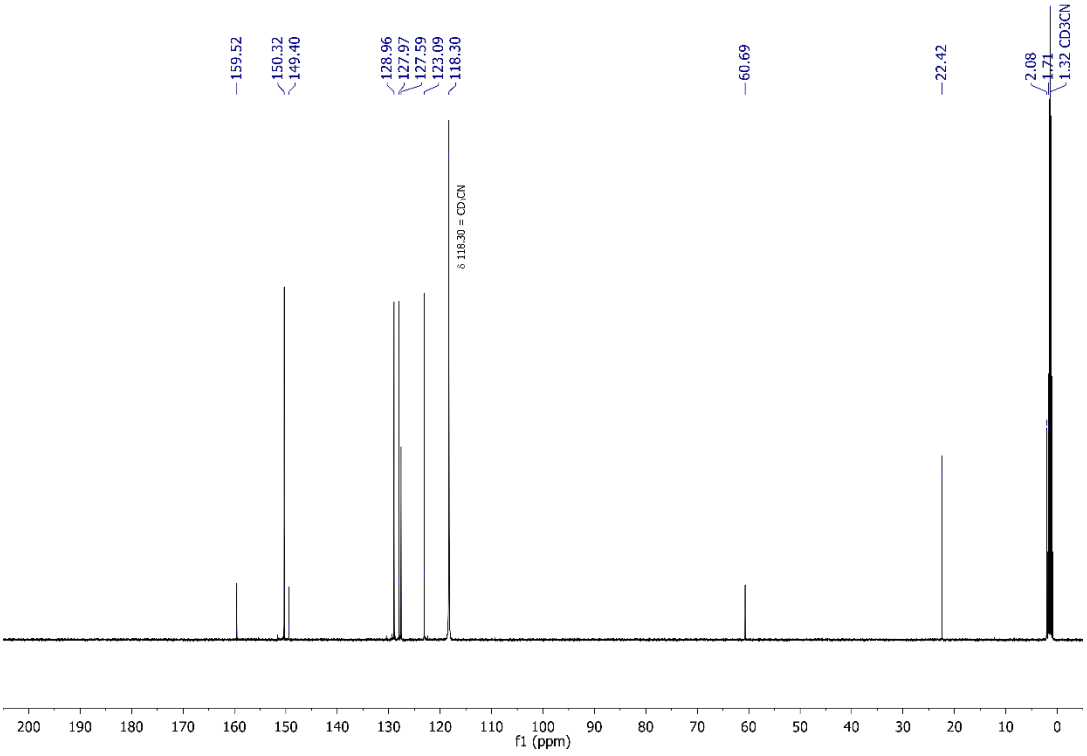
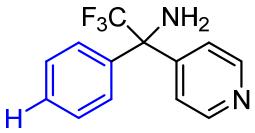



**Figure S40.** $^{13}$C NMR (126 MHz) spectrum of **5n** in $CD_3CN$.




Compound **5p** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL L, 1.1 mmol) and *O*-benzoyl oxime (**3p**) (89 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (44 mg, 58%). The yield of product **5p** was determined to be 65% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, Acetonitrile-$d_3$) δ 8.57 (d, $J$ = 6.1 Hz, 2H), 7.46 (d, $J$ = 7.1 Hz, 2H), 7.43 (d, $J$ = 5.3 Hz, 2H), 7.41 – 7.33 (m, 3H), 2.76 (s, 2H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 179.34, 168.90, 162.33, 159.04, 157.95, 157.88, 157.11, 156.23 (q, $J$ = 285.5 Hz), 151.92, 146.83, 94.93 (q, $J$ = 26.6 Hz). $^{19}$F NMR (471 MHz, $CD_3CN$) δ -73.24. MS (ESI) m/z calcd. for $C_{13}H_{12}F_3N_2$ ($[M + H]^+$) 253.1, found 253.2.

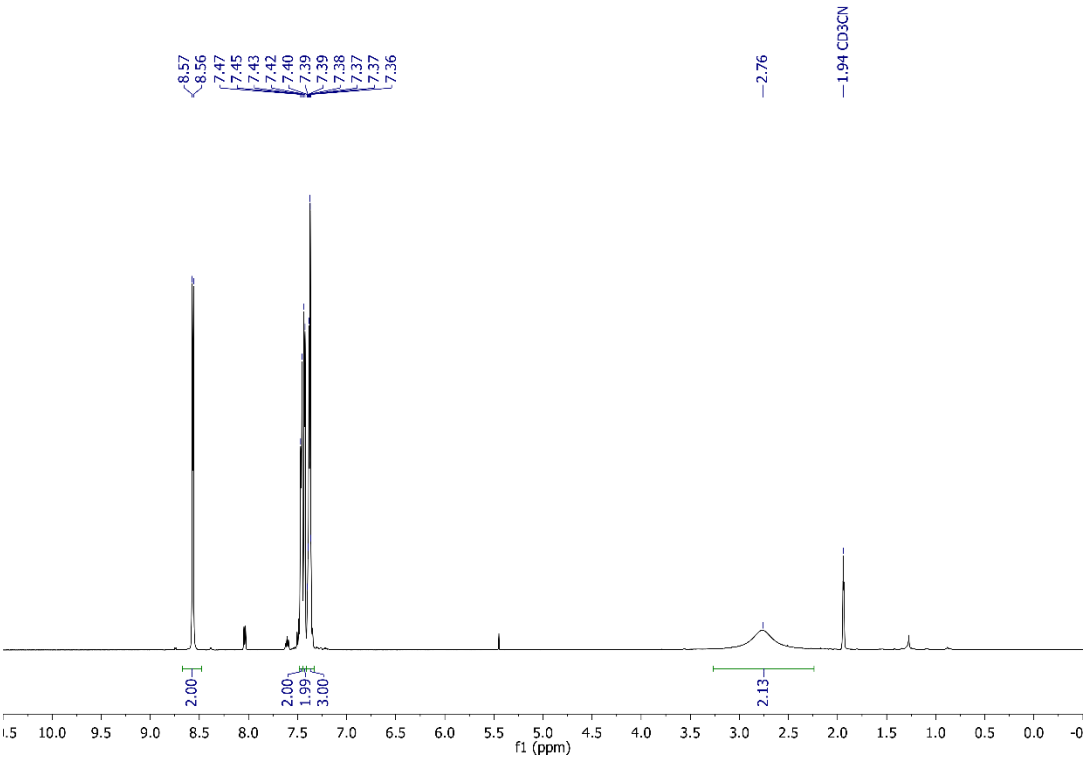



**Figure S41.** $^{1}$H qNMR (500 MHz) spectrum of **5p** in $CD_3CN$.

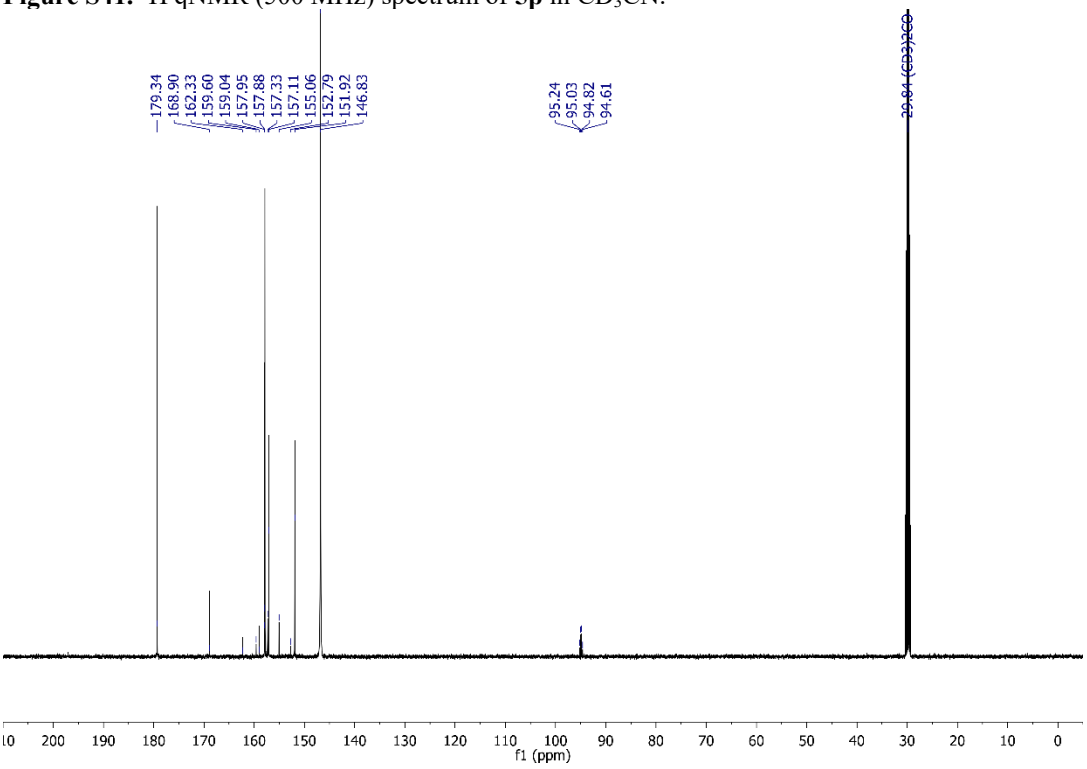



**Figure S42.** $^{13}$C NMR (126 MHz) spectrum of **5p** in $CD_3CN$.

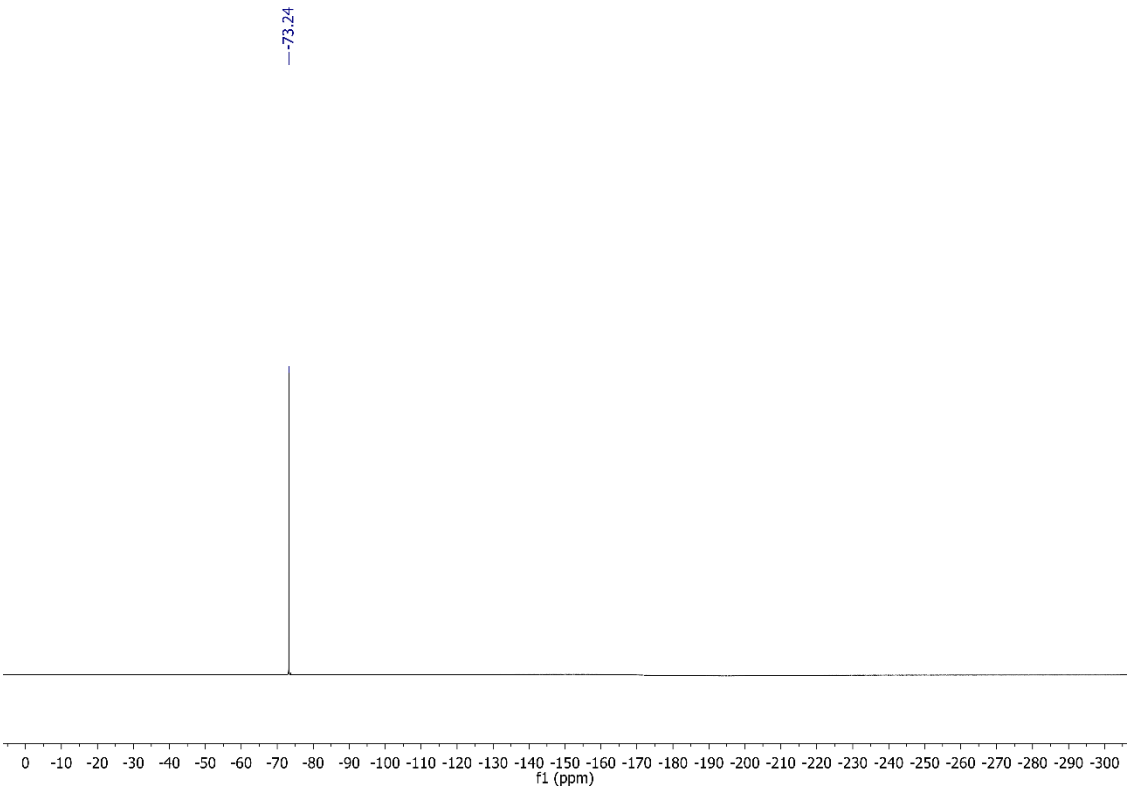
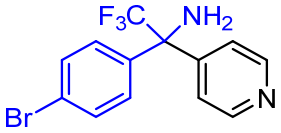



**Figure S43.** $^{19}F$ NMR (471 MHz) spectrum of compound **5p** in $CD_3CN$.




Compound **5q** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL L, 1.1 mmol) and *O*-benzoyl oxime (**3q**) (99 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (25 mg, 25%). The yield of product **5q** was determined to be 29% by a calibrated UPLC-MS. $^{1}$H NMR (500 MHz, Acetonitrile-$d_3$) δ 8.57 (d, $J$ = 6.3 Hz, 2H), 7.54 (d, $J$ = 8.8 Hz, 2H), 7.43 – 7.32 (m, 4H), 2.60 (s, 2H), 2.16 (s, 1H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 150.97, 150.11, 139.80, 132.37, 126.29 (q, $J$ = 285.5 Hz), 123.29, 123.27, 123.18, 66.23 (q, $J$ = 27.0 Hz). $^{19}$F NMR (471 MHz, $CD_3CN$) δ -73.40. MS (ESI) m/z calcd. for $C_{13}H_{11}BrF_3N_2$ ($[M + H]^+$) 331.0, found 331.0.

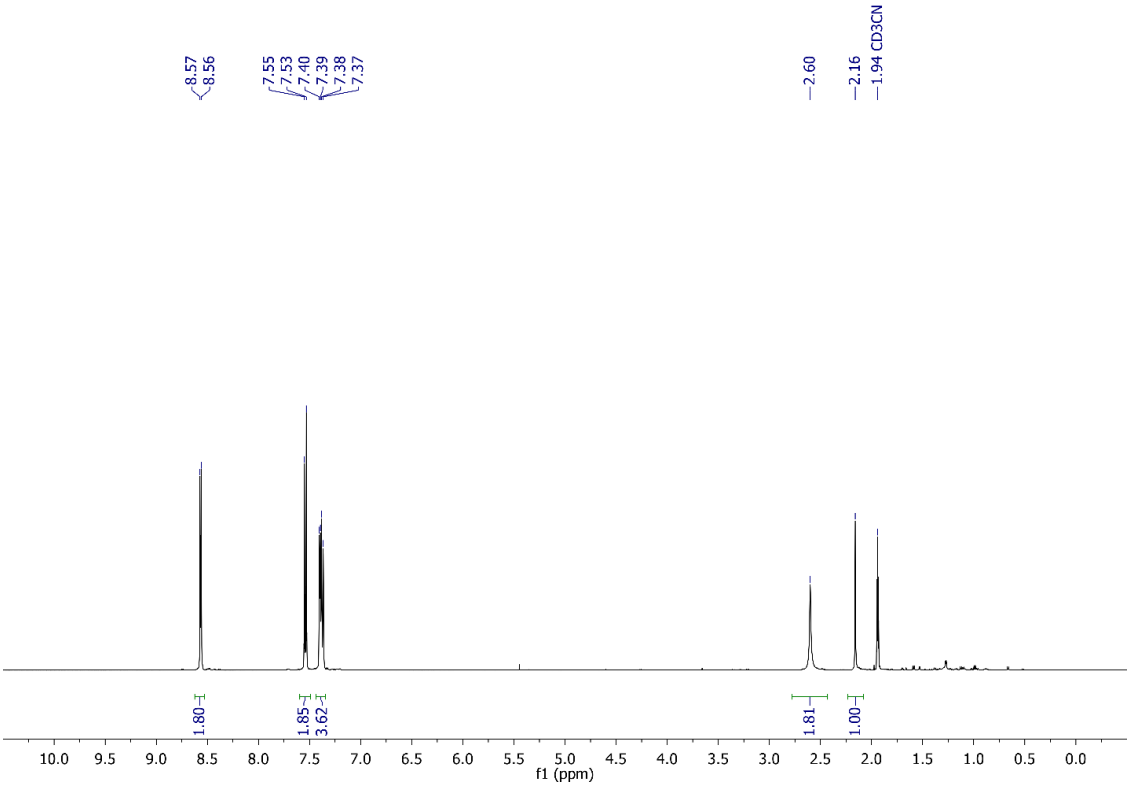



**Figure S44.** $^{1}$H qNMR (500 MHz) spectrum of **5q** in $CD_3CN$.

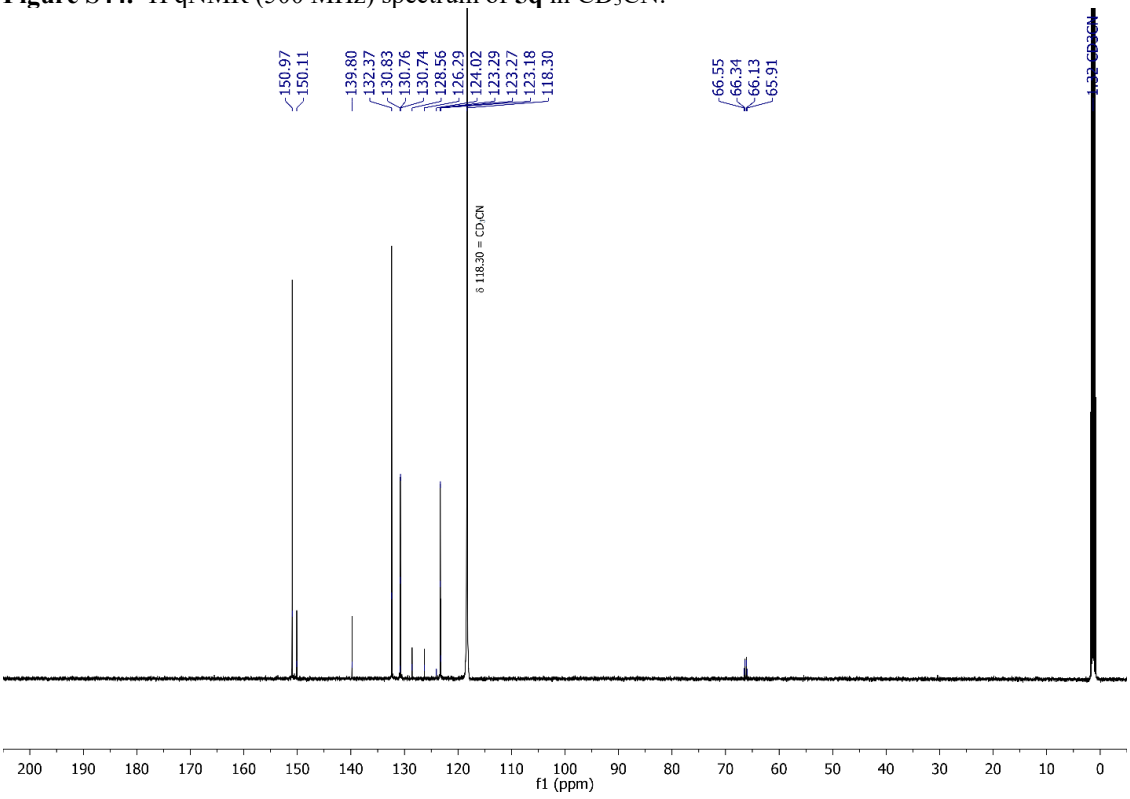



**Figure S45.** $^{13}$C NMR (126 MHz) spectrum of **5q** in $CD_3CN$.

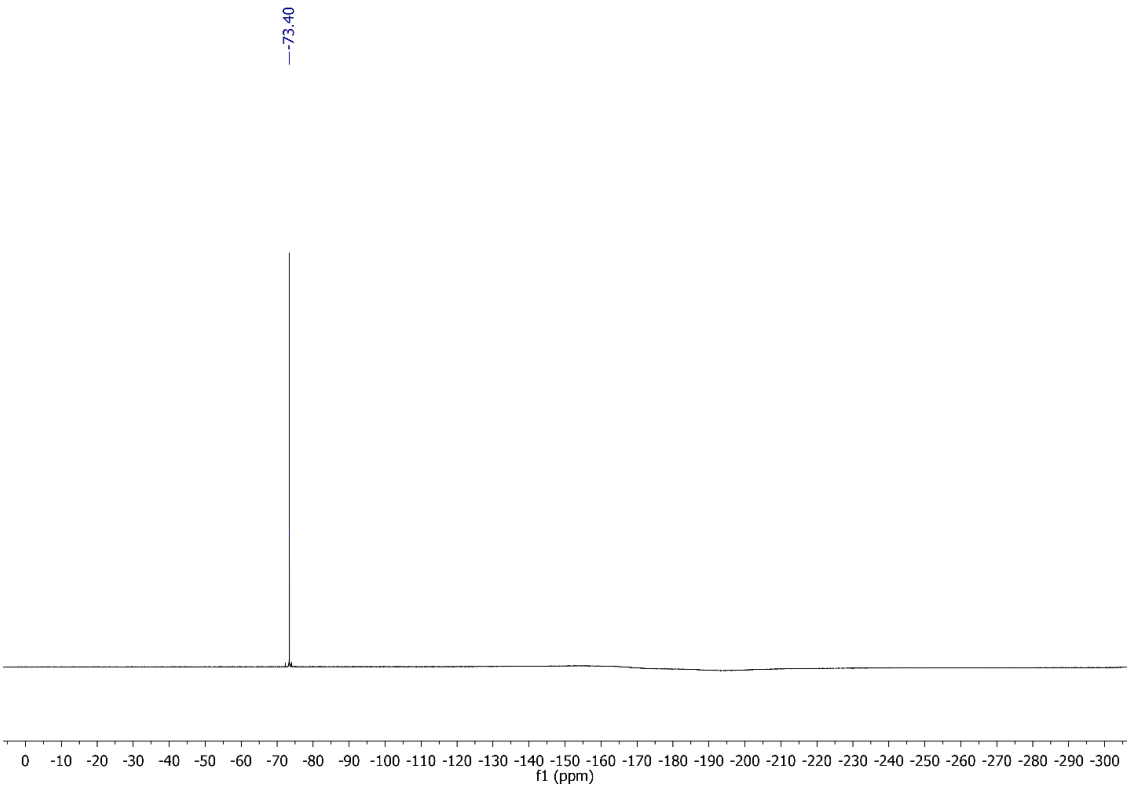
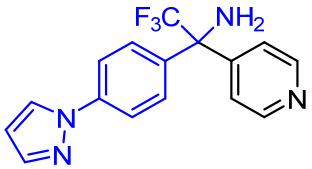



**Figure S46.** $^{19}F$ NMR (471 MHz) spectrum of compound **5q** in $CD_3CN$.




Compound **5r** was synthesized following General Procedure A using 4-pyridinecarbonitrile **4a** (69 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL L, 1.1 mmol) and *O*-benzoyl oxime (**3r**) (108 mg, 0.3 mmol) in DMSO (3 mL). The product was purified according to the general chromatography method for oximes. The product was obtained as a film on a vial (46 mg, 48%). The yield of product **5r** was determined to be 57% by a calibrated UPLC-MS $^{1}$H NMR (500 MHz, $CD_3CN$, 1.7:1 mixture of rotamers) δ 8.58 (d, *J* = 5.3 Hz, 2H), 8.14 (d, *J* = 1.6 Hz,1H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.70 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 4.7 Hz, 2H), 6.50 (s, 1H), 2.63 (br s, 1.3H), 2.14 (br s, 0.8H). $^{13}$C NMR (126 MHz, $CD_3CN$, 1.7:1 mixture of rotamers) δ 150.96, 150.43, 150.40, 142.25, 140.96, 138.21, 138.18, 129.92 (q, *J* = 1.7 Hz), 128.32, 127.64 (q, *J* = 285.8 Hz), 123.35 (q, *J* = 1.7 Hz), 119.36, 108.87, 66.21 (q, *J* = 26.8 Hz), 66.13 (q, *J* =26.7 Hz). $^{19}$F{$^{1}$H} NMR (471 MHz, $CD_3CN$) δ –73.55 (s, 3F).MS (ESI) m/z calcd. for $C_{16}H_{14}F_3N_4$ ($[M + H]^+$) 319.1, found 318.8

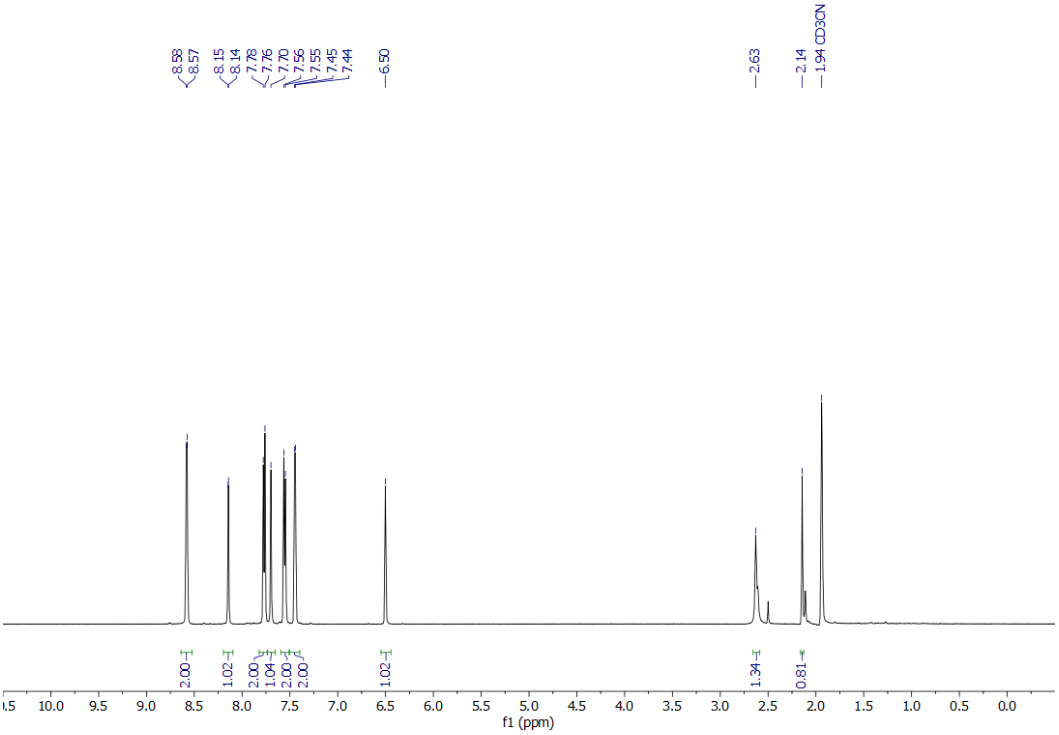



**Figure S47.** $^{1}$H qNMR (500 MHz) spectrum of **5r** in $CD_3CN$.

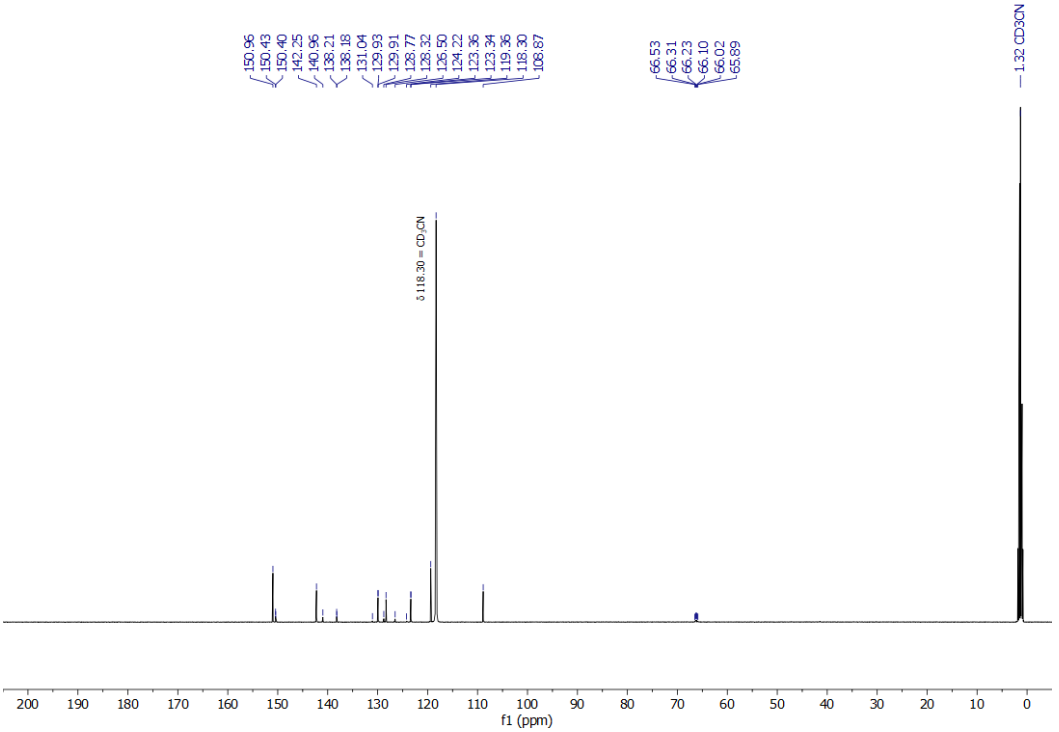



**Figure S48.** $^{13}$C NMR (126 MHz) spectrum of **5r** in $CD_3CN$.

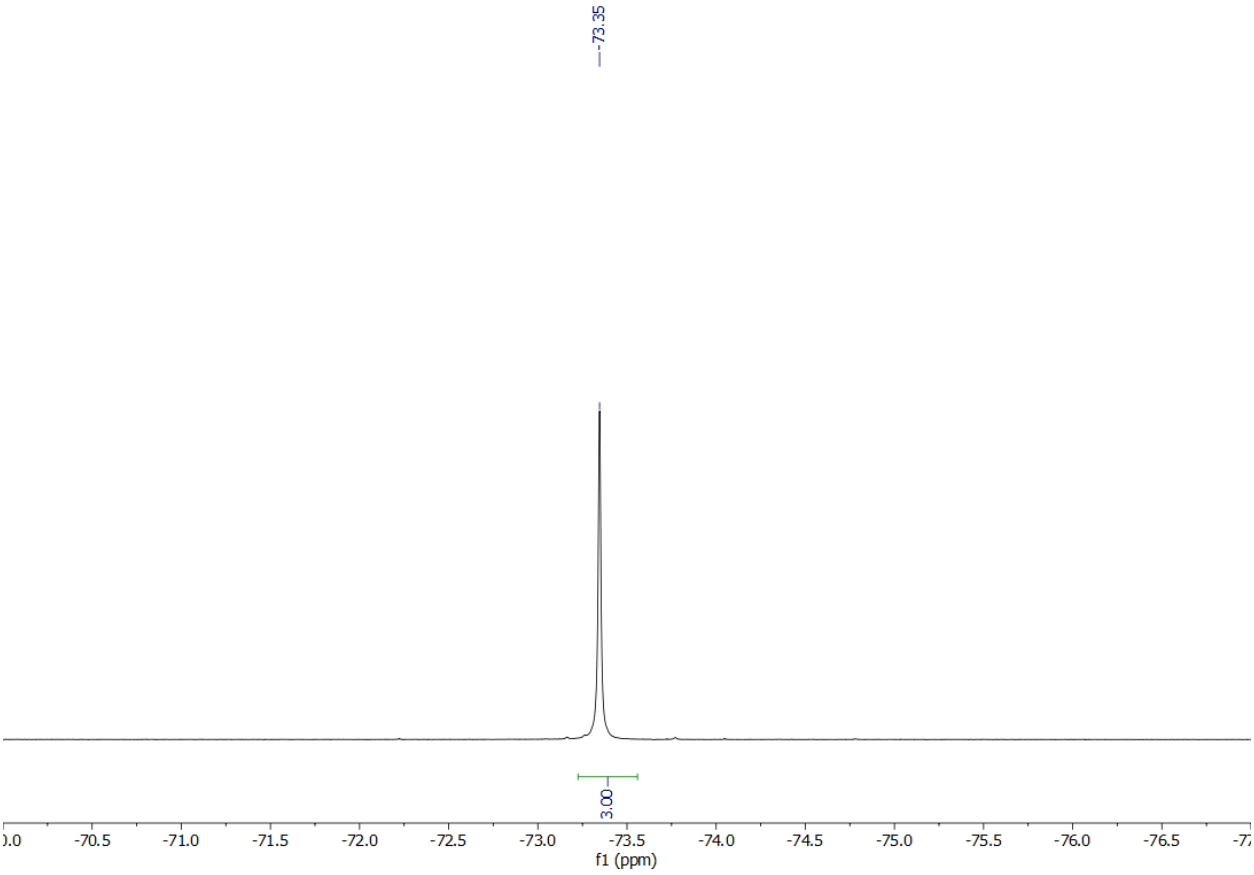
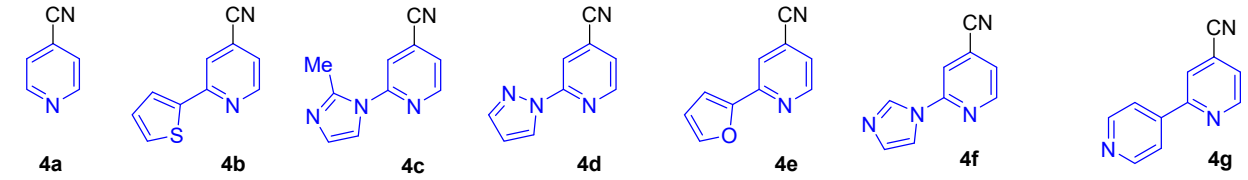


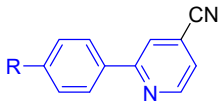

**Figure S49.** $^{19}F$ NMR (471 MHz) spectrum of compound **5r** in $CD_3CN$

## 4. Cyanoarene Scope

**Table S5.** Table of Purchased Cyanoarenes Starting Materials

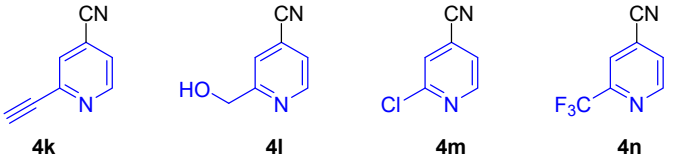
**4-pyridyl**

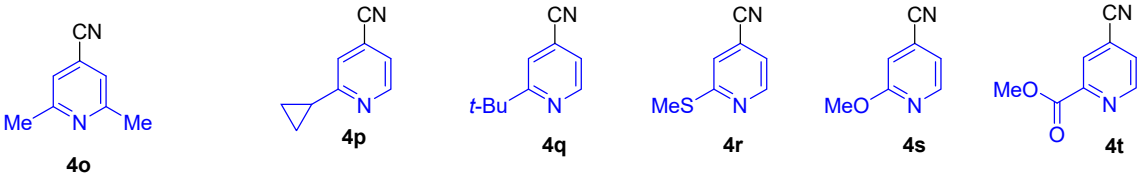


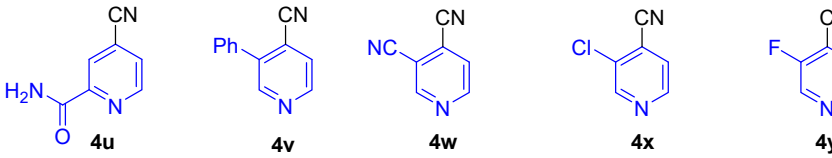




**4i**
R = OMe

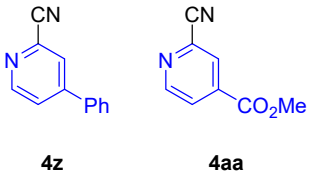
**4j**
R=$CO_2$Me



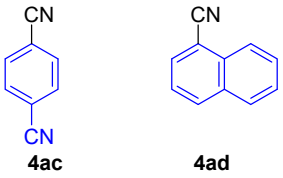



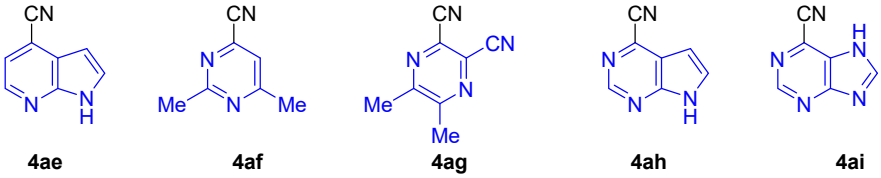

**2-pyridyl**



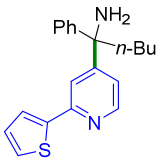

**non-heterocyclic arenes**




**non-pyridyl heterocycles**



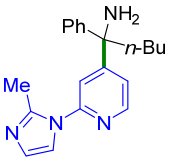
Authentic samples of compound **5s – 5ad, 5ag**, **5ai – 5az** were synthesized and characterized as described previously.[5] NMR characterization of the authentic samples included as line listing for each compound.




Compound **5s** was synthesized following General Procedure A using cyanoarene **4b** (123 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) M/Z CALCD. FOR $C_{20}H_{23}N_2S$ ($[M + H]^+$) 323.2, found 323.2. The product was synthesized in 42% yield (retention time t = 2.783, m/z = 323.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

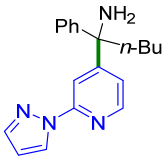
Compound **5s** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4c**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4s** (41 mg, 0.3 mmol, 1.0 equiv.). The product was synthesized in 54% yield (retention time t = 2.783, m/z = 323.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

$^1$H NMR (500 MHz, $CD_3CN$) δ 8.36 (d, *J* = 5.2 Hz, 1H), 7.85 (s, 1H), 7.62 (d, *J* = 3.4 Hz, 1H), 7.46–7.41 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22–7.15 (m, 2H), 7.10 (t, *J* = 4.3 Hz, 1H), 2.27 – 2.17 (m, 2H), 1.99 (br s, 2H), 1.38–1.28 (m, 2H), 1.26–1.09 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 160.38, 153.17, 150.07, 148.94, 146.28, 129.14, 128.61, 127.43, 127.41, 125.57, 121.52, 117.38, 61.56, 42.14, 26.95, 23.81, 14.38. ESI LRMS *m/z* calcd. for $C_{20}H_{23}N_2S$ ($[M + H]^+$) 323.2, found 323.2.




Compound **5t** was synthesized following General Procedure A using cyanoarene **4c** (122 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{20}H_{25}N_4$ ($[M + H]^+$) 321.2, found 321.3. The product was synthesized in 73% yield (retention time t = 1.930, m/z = 321.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

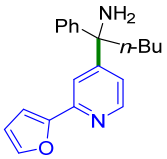
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.37 (d, *J* = 5.4 Hz, 1H), 7.48 (s, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.35–7.28 (m, 4H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.89 (s, 1H), 2.41 (s, 3H), 2.29–2.18 (m, 2H), 2.01 (s, 2H), 1.38–1.29 (m, 2H), 1.27–1.10 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 163.04, 151.75, 149.57, 148.60, 145.45, 129.23, 128.33, 127.60, 127.42, 121.76, 120.26, 116.45, 61.73, 42.12, 26.91, 23.78, 15.40, 14.33.




Compound **5u** was synthesized following General Procedure A using cyanoarene **4d** (123 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (X) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) M/Z CALCD. FOR $C_{19}H_{23}N_4$ ($[M + H]^+$) 307.2, found 307.2. The product **5u** was synthesized in 82% yield (retention time t = 2.662, m/z = 307.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

Compound **5u** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4d**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **3l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4d** (41 mg, 0.3 mmol, 1.0 equiv.). The product **5u** was synthesized in 69% yield (retention time t = 2.662, m/z = 307.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

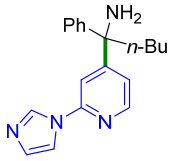
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.53 (d, *J* = 1.0 Hz, 1H), 8.28 (d, *J* = 5.2 Hz, 1H), 8.00 (s, 1H), 7.70 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 5.2 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.47 (s, 1H), 2.28–2.18 (m, 2H), 2.05 (br s, 2H), 1.37–1.28 (m, 2H), 1.24–1.09 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 163.05, 152.61, 148.86, 148.78, 142.77, 129.20, 127.95, 127.55, 127.45, 120.97, 110.94, 108.63, 61.75, 42.17, 26.90, 23.78, 14.34.




Compound **5v** was synthesized following General Procedure A using cyanoarene **4e** (112 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) M/Z CALCD. FOR $C_{20}H_{23}N_2O$ ($[M + H]^+$) 307.2, found 307.2. The product was synthesized in 35% yield (retention time t = 2.558, m/z = 307.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

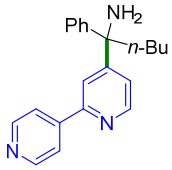
Compound **5v** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4e**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4e** (37 mg, 0.3 mmol, 1.0 equiv.). The product was synthesized in 69% yield (retention time t = 2.558, m/z = 307.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

$^1$H NMR (500 MHz, $CD_3CN$) δ 8.42 (dd, *J* = 0.4, 5.2 Hz, 1H), 7.75 (d, *J* = 1.1 Hz, 1H), 7.59 (dd, *J* = 0.6, 1.6 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 8.1 Hz, 2H), 7.23–7.18 (m, 2H), 7.02 (dd, *J* = 0.4, 3.4 Hz, 1H), 6.56 (dd, *J* = 1.8, 3.4 Hz, 1H), 2.28–2.17 (m, 2H), 1.84 (br s, 2H), 1.38–1.28 (m, 2H), 1.24–1.08 (m, 2H), 0.86 (t, *J* = 7.30 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 160.37, 155.04, 150.42, 150.00, 149.03, 144.50, 129.17, 127.46, 127.45, 121.35, 117.17, 113.05, 109.42, 61.56, 42.17, 26.94, 23.81, 14.35.




Compound **5w** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4f**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst Ir[dF(Me)ppy]$_2$dtbbpyPF$_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **6l** (41 mg, 0.3 mmol, 1.0 equiv.). MS (ESI) *m/z* calcd. for $C_{19}H_{23}N_4$ ([M + H]+) 308.2, 308.2. The product **5w** was synthesized in 25% yield (retention time t = 2.245, m/z = 321.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

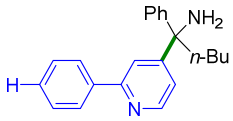
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.33–8.29 (m, 2H), 7.73 (s, 1H), 7.64 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* =7.7 Hz, 2H), 7.24 (d, *J* = 5.3 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.09 s, (1H), 2.30–2.20 (m, 2H), 2.10 (br s, 2H), 1.39–1.29 (m, 2H), 1.26–1.09 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 163.43, 150.41, 149.48, 148.63, 136.07, 131.04, 129.23, 127.60, 127.41, 121.61, 117.54, 111.50, 61.79, 42.09, 26.89, 23.79, 14.33.




Compound **5x** was synthesized following General Procedure A using cyanoarene **4g** (120 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{21}H_{24}N_3$ ([M + H]+) 318.2, found 318.3. The product was synthesized in 32% yield (retention time t = 2.342, m/z = 318.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5x** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4g**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst Ir[dF(Me)ppy]$_2$dtbbpyPF$_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4g** (40 mg, 0.3 mmol, 1.0 equiv.). The product **5x**was synthesized in 18% yield (retention time t = 2.342, m/z = 318.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

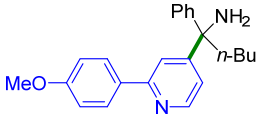
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.65 (dd, *J* = 1.7, 4.5 Hz, 2H), 8.57 (d, *J* = 5.2 Hz, 1H), 8.00 (dd, *J* = 0.5, 1.6 Hz, 1H), 7.93 (dd, *J* =1.7, 4.5 Hz, 2H), 7.48–7.44 (m, 2H), 7.39 (dd, *J* = 1.7, 5.2, Hz, 1H), 7.28–7.33 (m, 2H), 7.21 (tt, *J* = 1.1, 6.9 Hz, 1H), 2.31–2.22 (m, 2H), 2.00 (br s, 2H), 1.39–1.30 (m, 2H), 1.27–1.10 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 160.91, 155.12, 151.35, 150.75, 148.91, 147.43, 129.20, 127.51, 127.45, 123.20, 121.90, 119.84, 61.69, 42.19, 26.96, 23.81, 14.34.




Compound **5y** was synthesized following General Procedure A using cyanoarene **4h** (119 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{22}H_{25}N_2$ ([M + H]$^+$) 317.2, found 317.2. The product **5y** was synthesized in 89% yield (retention time t = 2.342, m/z = 317.2 (M+H]$^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5y** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4h**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst Ir[dF(Me)ppy]$_2$dtbbpyPF$_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 μL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4h** (40 mg, 0.3 mmol, 1.0 equiv.). The product **5y** was synthesized in 66% yield (retention time t = 2.342, m/z = 317.2 (M+H]$^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

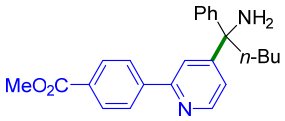
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.51 (d, *J* = 5.2 Hz, 1H), 8.03–7.99 (m, 2H), 7.89 (d, 1.0 Hz, 1H), 7.49–7.43 (m, 4H), 7.43–7.38 (m, 1H), 7.32–7.25 (m, 3H), 7.22–7.17 (m, 1H), 2.26 (t, *J* = 8.4 Hz, 2H), 2.05 (br s, 2H), 1.34 (sextet, *J* = 7.3 Hz, 2H), 1.27–1.11 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 160.38, 157.73, 150.34, 149.09, 140.60, 129.66, 129.13, 127.74, 127.44, 127.41, 121.56, 119.19, 61.64, 42.22, 26.99, 23.82, 14.38. ESI LRMS *m/z* calcd. for $C_{22}H_{25}N_2$ ([M + H]$^+$) 317.2, found 317.2.




Compound **5z** was synthesized following General Procedure A using cyanoarene **4i** (139 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{23}H_{27}N_2O$ ([M + H]$^+$) 347.2, found 347.3. The product **5z** was synthesized in 97% yield (retention time t = 2.790, m/z = 347.3 (M+H]$^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5z** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4i**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst Ir[dF(Me)ppy]$_2$dtbbpyPF$_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 μL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4i** (46 mg, 0.3 mmol, 1.0 equiv.). The product **5z** was synthesized in 95% yield (retention time t = 2.790, m/z = 347.3 (M+H]$^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

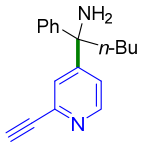
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.46 (d, *J* = 5.1 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.82 (s, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 6.0 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 2.25 (t, *J* = 8.2 Hz, 2H), 2.04 (s, 2H), 1.39–1.29 (m, 2H), 1.26–1.09 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 161.50, 160.24, 157.46, 150.19, 149.18, 133.10, 129.12, 129.05, 127.45, 127.38, 120.85, 118.29, 114.98, 61.63, 56.02, 42.21, 27.01, 23.83, 14.37.




Compound **5aa** was synthesized following General Procedure A using cyanoarene **4j** (157 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{24}H_{27}N_2O_2$ ([M + H]$^+$) 375.2, found 375.3. The product **5aa** was synthesized in 25% yield (retention time t = 2.905, m/z = 375.3 (M+H]$^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5aa** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4j**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst Ir[dF(Me)ppy]$_2$dtbbpyPF$_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4j** (52 mg, 0.3 mmol, 1.0 equiv.). The product **5aa** was synthesized in 46% yield (retention time t = 2.905, m/z = 375.3 (M+H]$^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

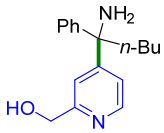
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.54 (d, *J* = 5.1 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.96 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 3.89 (s, 3H), 2.31–2.21 (m, 2H), 1.99 (br s, 2H), 1.39–1.29 (m, 2H), 1.26 – 1.10 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 4H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 13C NMR (126 MHz, CD3CN) δ 167.49, 160.68, 156.46, 150.57, 149.00, 144.76, 131.34, 130.65, 129.17, 127.85, 127.46, 127.44, 122.34, 119.81, 61.67, 52.77, 42.20, 26.98, 23.82, 14.36.




Compound **5ab** was synthesized following General Procedure A using cyanoarene **4k** (85 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{18}H_{22}N_2$ ([M + H]$^+$) 265.2, found 265.2. The product **5ab** was synthesized in 9% yield (retention time t = 2.362, m/z = 265.2 (M+H]$^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5ab** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4k**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst Ir[dF(Me)ppy]$_2$dtbbpyPF$_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4k** (28 mg, 0.3 mmol, 1.0 equiv.). The product **5ab** was synthesized in 45% yield (retention time t = 2.362, m/z = 265.2 (M+H]$^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

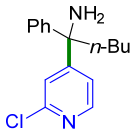
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.44 (d, *J* = 5.2 Hz, 1H), 7.58 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.40–7.36 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 3.42 (s, 3H), 2.27–2.15 (m, 2H), 1.95 (br s, 2H), 1.39–1.30 (m, 2H), 1.25–1.08 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H) (s, 6H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 160.08, 150.80, 148.58, 142.82, 129.19, 127.53, 127.39, 126.54, 122.78, 84.09, 77.90, 61.33, 42.01, 26.84, 23.74, 14.32.




Compound **5ac** was synthesized following General Procedure A using cyanoarene **4l** (89 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{17}H_{23}N_2O$ ($[M + H]^+$) 271.2, found 271.3. The product **5ac** was synthesized in 89% yield (retention time t = 1.968, m/z = 265.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5ac** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4l**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4l** (30 mg, 0.3 mmol, 1.0 equiv.). The product **5ac** was synthesized in 90% yield (retention time t = 1.968, m/z = 265.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

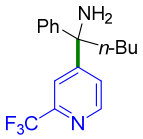
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.36 (d, *J* = 5.2 Hz, 1H), 7.44 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 5.1, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 4.59 (s, 2H), 2.30–2.05 (m, 3H), 1.37–1.27 (m, 2H), 1.22–1.07 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 161.63, 160.09, 149.37, 149.08, 129.12, 127.40, 121.16, 119.10, 65.41, 61.52, 42.28, 26.93, 23.81, 14.35.




Compound **5ai** was synthesized following General Procedure A using cyanoarene **4m** (91 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C16H_{20}ClN2$ ($[M + H]^+$) 275.1, found 275.2. The product **5ai** was synthesized in 0% yield (retention time t = 2.568, m/z = 275.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5ai** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4m**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4m** (30 mg, 0.3 mmol, 1.0 equiv.). The product **5ai** was synthesized in 39% yield (retention time t = 2.568, m/z = 275.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

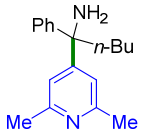
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.22 (d, *J* = 5.3 Hz, 1H), 7.46 (d, *J* = 1.0 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 2H). 7.31 (t, *J* = 7.4 Hz, 2H), 7.28 (dd, *J* =1.5, 5.3 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 163.47, 152.16, 150.36, 148.37, 129.25, 127.65, 127.37, 123.01, 122.12, 61.60, 42.03, 26.82, 23.73, 14.30.




Compound **5aj** was synthesized following General Procedure A using cyanoarene **4n** (114 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C17H_{19}F_3N_2$ ($[M + H]^+$) 309.2, found 309.3. The product **5aj** was synthesized in 0% yield (retention time t = 2.91, m/z = 309.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5aj** was also synthesized from the corresponding iminium HCl salt **3l** and cyanoarene **4n**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4n** (38 mg, 0.3 mmol, 1.0 equiv.). The product **5aj** was synthesized in 65% yield (retention time t = 2.91, m/z = 309.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

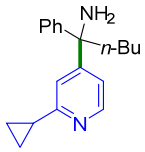
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.59 (d, *J* = 5.2 Hz, 1H), 7.84 (d, *J* = 1.3 Hz, 1H), 7.60 (dd, *J* = 1.5, 5.2 Hz, 1H), 7.44–7.39 (m, 2H), 7.34–7.30 (m, 2H), 7.24–7.20 (m, 1H), 2.31–2.16 (m, 2H), 2.00 (br s, 1H), 1.38–1.29 (m, 2H), 1.25–1.06 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 161.97, 150.90, 148.32 (q, *J* = 33.6 Hz), 148.28, 129.32, 127.73, 127.42, 125.89, 123.07 (q, *J* = 273.4 Hz), 119.55 (q, *J* = 2.9 Hz), 61.71, 42.08, 26.83, 23.73, 14.30. $^{19}$F{$^1$H} NMR (471 MHz, $CD_3CN$) δ –68.29 (s, 3F). $^{19}$F NMR (471 MHz, $CD_3CN$) δ –68.29 (s, 3F).




Compound **5ad** was synthesized following General Procedure A using cyanoarene **4o** (87 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{18}H_2N_2$ ($[M + H]^+$) 269.2, found 269.0. The product **5ad** was synthesized in 94% yield (retention time t = 2.922, m/z = 269.0 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5ad** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4o**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4o** (29 mg, 0.3 mmol, 1.0 equiv.). The product **5ad** was synthesized in 56% yield (retention time t = 2.922, m/z = 269.0 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

$^1$H NMR (500 MHz, $CD_3CN$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.04 (s, 2H), 2.38 (s, 6H), 2.22–2.10 (m, 2H), 1.95 (br s, 2H), 1.32 (sextet, 7.4 Hz, 2H), 1.20–1.08 (m, 2H), 0.86 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 159.87, 158.25, 149.33, 129.02, 127.34, 127.24, 118.92, 61.25, 42.28, 26.93, 24.62, 23.84, 14.37.




Compound **5ae** was synthesized following General Procedure A using cyanoarene **4p** (95 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.27 (d, *J* = 5.3 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.09 (dd, *J* = 5.3, 1.8 Hz, 1H), 2.25 – 2.18 (m, 2H), 2.04 – 1.93 (m, 4H), 1.36 (h, *J* = 7.3 Hz, 2H), 1.18 (dd, *J* = 16.9, 11.6 Hz, 2H), 0.98 – 0.91 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 163.28, 159.20, 149.89, 149.25, 129.06, 127.36, 127.30, 120.30, 119.60, 118.27, 61.31, 42.20, 26.96, 23.83, 17.68, 14.37, 10.11, 10.09. MS (ESI) m/z calcd. for $C_{19}H_{25}N_2$ ($[M + H]^+$) 281.2, found 280.9. The product **5ae** was synthesized in 89% yield (retention time t = 2.478, m/z = 280.9 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

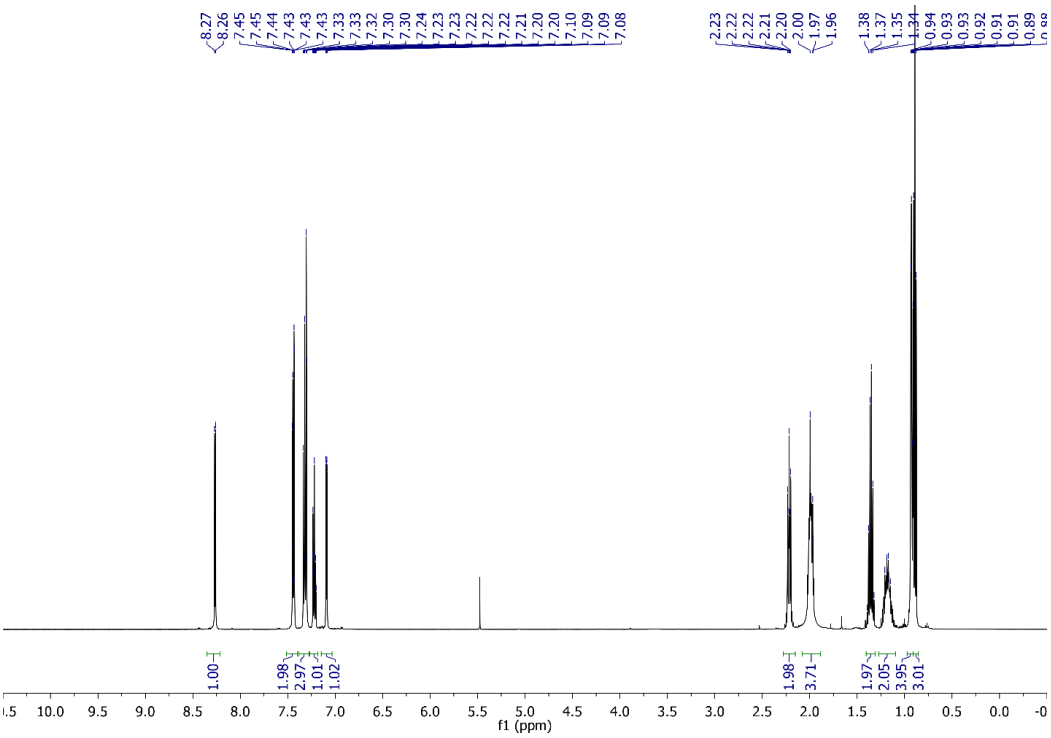



**Figure S50.** $^{1}$H qNMR (500 MHz) spectrum of **5ae** in $CD_3CN$.

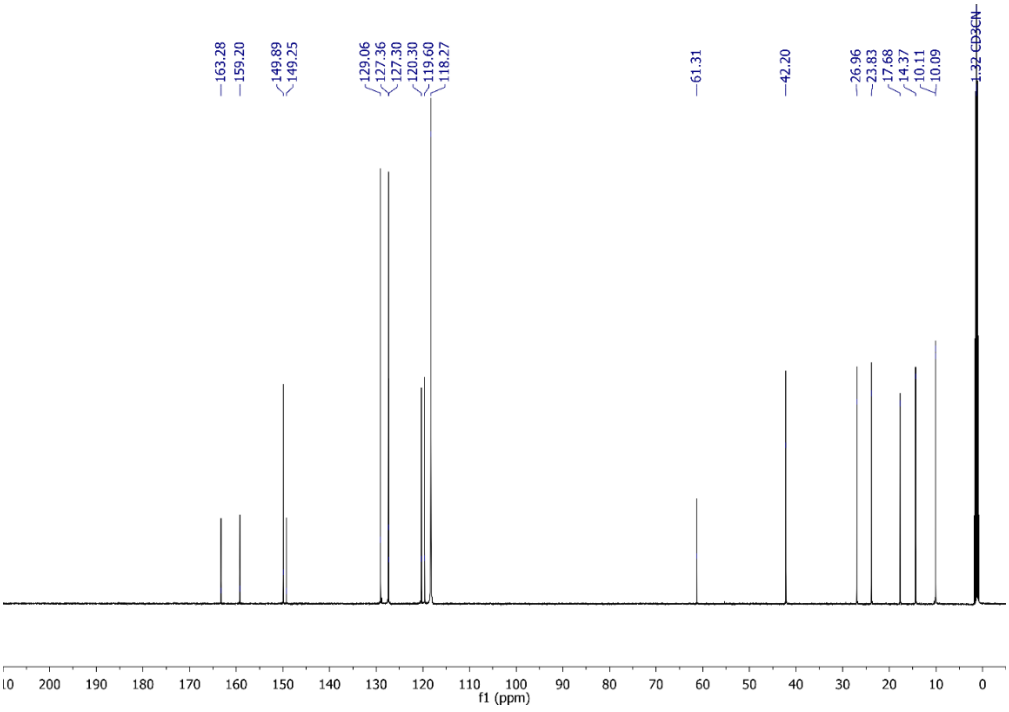
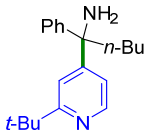



**Figure S51.** $^{13}$C NMR (126 MHz) spectrum of **5ae** in $CD_3CN$.




Compound **5af** was synthesized following General Procedure A using cyanoarene **4q** (106 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). $^{1}$H NMR (500 MHz, $CD_3CN$) δ 8.35 (d, $J$ = 5.2 Hz, 1H), 7.48 (s, 1H), 7.42 (d, $J$ = 7.9 Hz, 2H), 7.29 (t, $J$ = 7.6 Hz, 2H), 7.19 (t, $J$ = 7.2 Hz, 1H), 7.11 (d, $J$ = 5.1 Hz, 1H), 2.20 (t, $J$ = 8.0 Hz, 2H), 1.98 (s, 2H), 1.30 (s, 12H), 1.16 (ddq, $J$ = 21.2, 14.1, 7.5 Hz, 2H), 0.86 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 169.83, 159.34, 149.26, 149.04, 129.04, 127.36, 127.28, 119.94, 117.71, 61.62, 42.37, 38.19, 30.54, 27.00, 23.80, 14.38. MS (ESI) m/z calcd. for $C_{20}H_{29}N_2$ ($[M + H]^+$) 297.2, found 296.9. The product **5af** was synthesized in 97% yield (retention time t = 2.718, m/z = 296.9 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

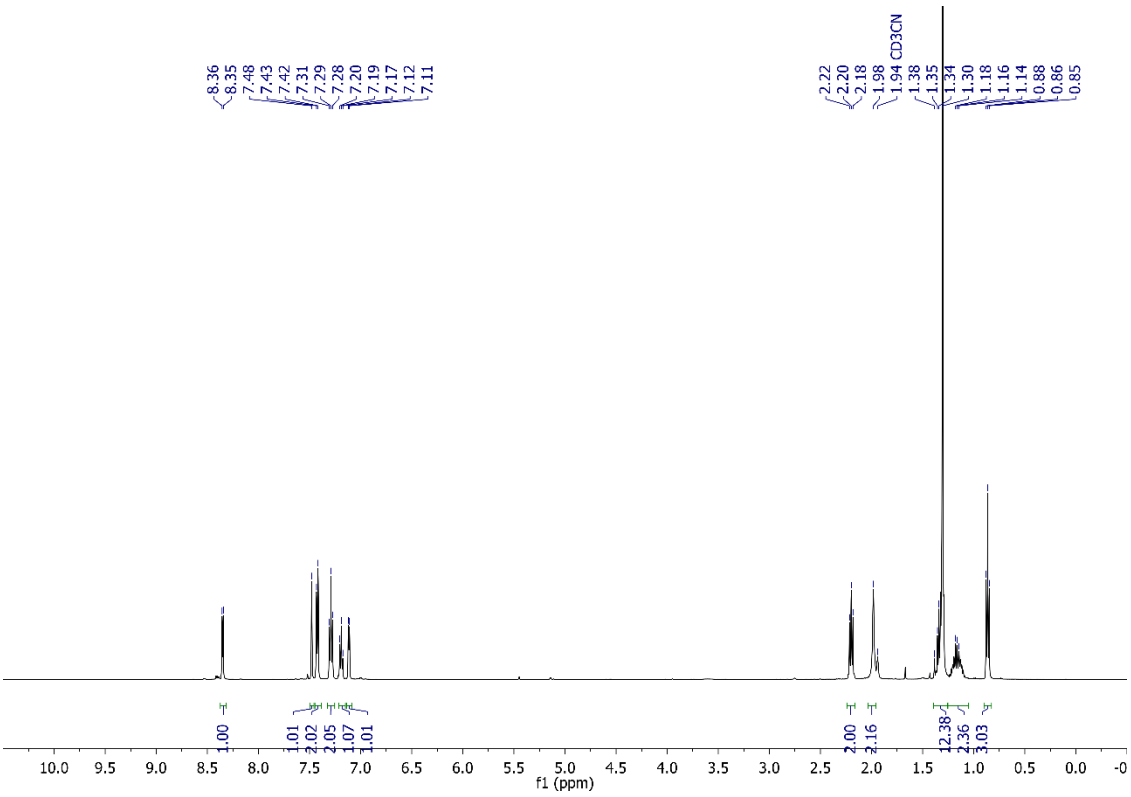



**Figure S52.** $^{1}$H qNMR (500 MHz) spectrum of **5af** in $CD_3CN$.

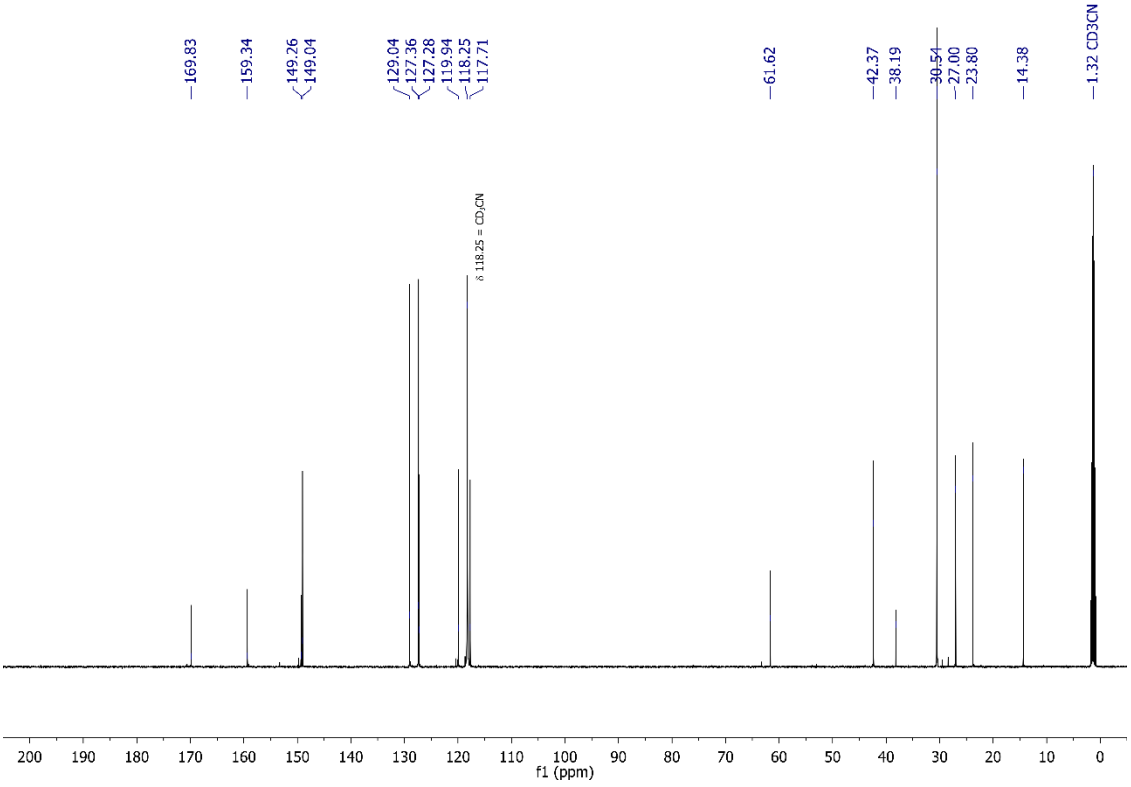
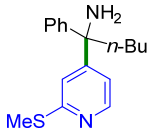


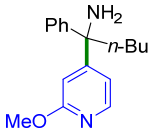

**Figure S53.** $^{13}$C NMR (126 MHz) spectrum of **5af** in $CD_3CN$.




Compound **5ag** was synthesized following General Procedure A using cyanoarene **4q** (99 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{17}H_{22}N_2S$ ($[M + H]^+$) 287.2, found 287.2. The product **40** was synthesized in 79% yield (retention time t = 2.55, m/z = 287.0 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5ag** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4q**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4q** (33 mg, 0.3 mmol, 1.0 equiv.). The product **5ag** was synthesized in 60% yield (retention time t = 2.55, m/z = 287.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

$^1$H NMR (500 MHz, $CD_3CN$) δ 8.26 (d, *J* = 5.4 Hz, 1H), 7.42–7.38 (m, 2H) 7.32–7.27 (m, 3H), 7.20 (t , *J* = 7.3 Hz, 1H), 2.49 (s, 3H), 2.22–2.12 (m, 2H), 2.07 (br s, 2H), 1.37–1.27 (m, 2H), 1.22–1.06 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 160.61, 159.66, 149.96, 148.84, 129.14, 127.46, 127.37, 119.70, 118.92, 61.45, 49.90, 42.02, 26.92, 23.79, 14.34, 13.43.




Compound **5ah** was synthesized following General Procedure A using cyanoarene **4s** (89 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). The product was isolated as a film on a vial (54 mg, 67%). The product **5ah** was synthesized in 81% yield (retention time t = 2.420, m/z = 254.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

$^1$H NMR (500 MHz, $CD_3CN$) δ 7.98 (d, *J* = 6.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.87 – 6.83 (m, 2H), 3.85 (s, 3H), 2.20 – 2.13 (m, 2H), 2.03 (s, 2H), 1.37 – 1.25 (m, 3H), 1.23 – 1.07 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 165.46, 162.57, 149.02, 147.35, 129.07, 127.37, 127.34, 118.28, 116.63, 108.93, 61.39, 53.81, 42.06, 26.93, 23.81, 14.36. MS (ESI) *m/z* calcd. for $C_{17}H_{23}N_2O$ ($[M + H – NH_2]^+$) 254.2, found 254.2.

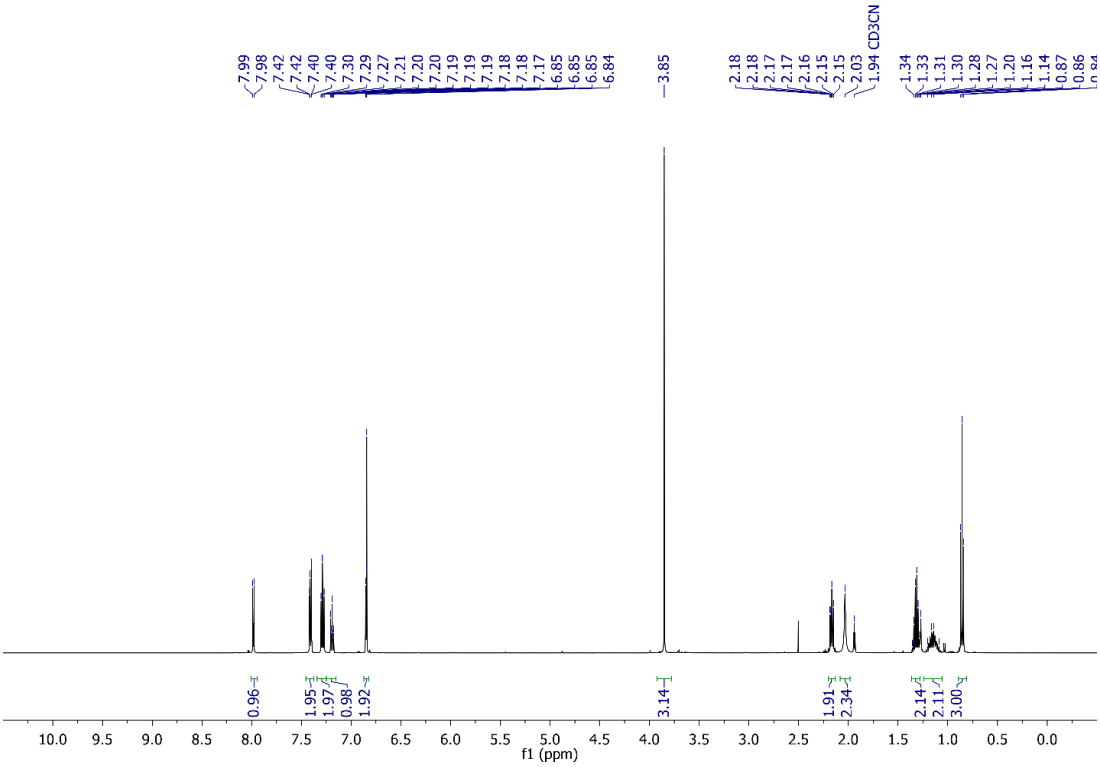



**Figure S54.** $^{1}$H qNMR (500 MHz) spectrum of **5ah** in $CD_3CN$.

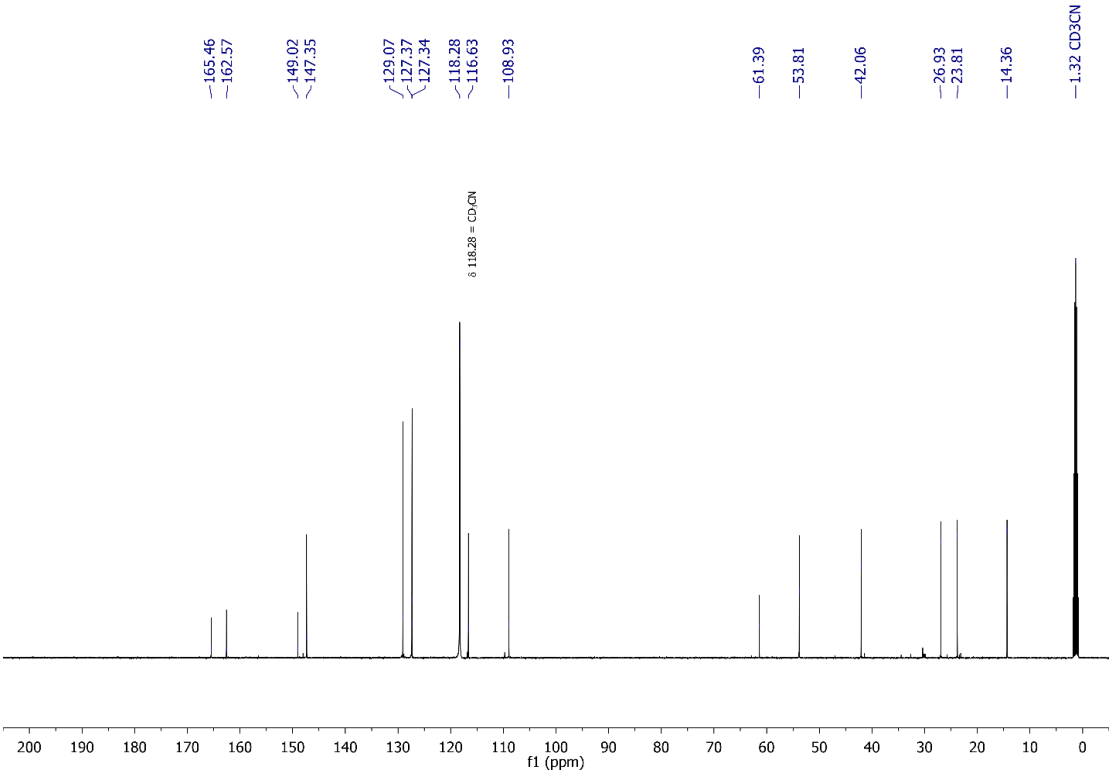
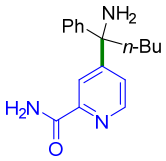


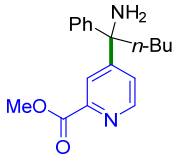

**Figure S55.** $^{13}$C NMR (126 MHz) spectrum of **5ah** in $CD_3CN$.




Compound **5al** was synthesized following General Procedure A using cyanoarene **4u** (97 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{17}H_{22}N_3O$ ($[M + H]^+$) 284.2, found 284.3. The product **5al** was synthesized in 22% yield (retention time t = 2.110, m/z = 284.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

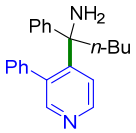
Compound **5al** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4u**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4u** (32 mg, 0.3 mmol, 1.0 equiv.). The product **5al** was synthesized in 64% yield (retention time t = 2.110, m/z = 284.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

$^1$H NMR (500 MHz, $CD_3CN$) δ 8.45 (d, *J* = 5.1 Hz, 1H), 8.12 (s, 1H), 7.82 (br s, 1H), 7.55 (d, *J* = 5.0 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.47 (br s, 1H), 2.22 (d of quintet, *J* = 5.2, 13.5 Hz, 2H), 1.99 (br s, 2H), 1.35–1.25 (m, 2H), 1.22–1.04 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 167.66, 161.27, 150.84, 149.37, 148.64, 129.20, 127.53, 127.44, 125.33, 120.93, 61.61, 42.15, 26.85, 23.74, 14.34.




Synthesis of **5ak** was synthesized following General Procedure A using cyanoarene **4t** (107 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). The reaction was unsuccessful.

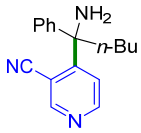
Compound **5ak** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4t**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4t** (36 mg, 0.3 mmol, 1.0 equiv.). The reaction was unsuccessful.




Compound **5am** was synthesized following General Procedure A using cyanoarene **4v** (119 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{22}H_{25}N_2$ ($[M + H]^+$) 317.2, found 317.3. The product **5am**was synthesized in 10% yield (retention time t = 2.68, m/z = 317.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

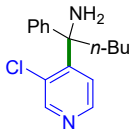
Compound **5am** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4v**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4v** (40 mg, 0.3 mmol, 1.0 equiv.). The product **5am** was synthesized in 42% yield (retention time t = 2.68, m/z = 317.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

$^1$H NMR (500 MHz, $CD_3CN$) δ 8.58 (d, *J* = 5.3 Hz, 1H), 8.08 (s, 1H), 7.86 (d, *J* = 5.3 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.17–7.11 (m, 3H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.98–6.94 (m, 2H), 6.51 (d, *J* = 7.4 Hz, 2H), 2.02 (td, *J* = 4.9, 12.2 Hz, 1H), 1.89 (td, *J* = 12.6, 4.7 Hz, 1H), 1.71 (br s, 2H), 1.29–1.17 (m, 2H), 1.14–0.98 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 1H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 155.75, 152.92, 150.43, 149.58, 140.30, 137.98, 130.50, 128.86, 128.19, 127.92, 127.24, 127.12, 122.51, 61.85, 41.60, 26.93, 23.80, 14.34.




Compound **5an** was synthesized following General Procedure A using cyanoarene **4w** (85 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{22}H_{25}N_2$ ($[M + H]^+$) 266.2, found 265.9. The product **5an** was synthesized in 0% yield (retention time t = 2.24, m/z = 265.9 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

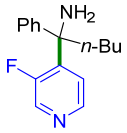
Compound **5an** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4w**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4w** (28 mg, 0.3 mmol, 1.0 equiv.). The product **5an** was synthesized in 0% yield (retention time t = 2.24, m/z = 265.9 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.




Compound **5ao** was synthesized following General Procedure A using cyanoarene **4x** (91 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{16}H_{20}ClN_2$ ($[M + H]^+$) 275.1, found 275.2. The product **5ao** was synthesized in 17% yield (retention time t = 2.587, m/z = 275.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5ao** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4x**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4x** (30 mg, 0.3 mmol, 1.0 equiv.). The product **5ao** was not synthesized by this method. However, des-halogenated product **5l** was synthesized in 23% yield (retention time t = 2.587, m/z = 275.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

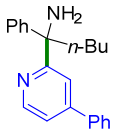
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.51 (d, *J* = 5.2 Hz, 1H), 8.38 (s, 1H), 7.86 (d, *J* = 5.2 Hz, 1H), 7.28–7.17 (m, 5H), 2.49 (ddd, *J* = 4.7, 12.3, 13.0 Hz, 1H), 2.15–2.19 (m, 1H), 2.07 (br s, 2H), 1.29 (sextet, 7.4 Hz, 2H), 1.18–0.97 (m, 2H), 0.83 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 155.08, 151.65, 148.97, 148.26, 131.74, 128.94, 127.28, 127.06, 124.23, 61.98, 40.14, 26.98, 23.78, 14.30.




Compound **5ap** was synthesized following General Procedure A using cyanoarene **4y** (81 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{16}H_{20}FN_2$ ($[M + H]^+$) 259.2, found 259.3. The product **5ap** was synthesized in 44% yield (retention time t = 2.310, m/z = 259.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

Compound **5ap** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4y**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4y** (28 mg, 0.3 mmol, 1.0 equiv.). The product **5ap** was synthesized in 76% yield (retention time t = 2.310, m/z = 259.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

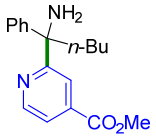
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.42 (d, *J* = 4.9 Hz, 1H), 8.25 (d, *J* = 3.4 Hz, 1H), 7.71 (dd, *J* = 5.3, 7.0 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 2.32 (dt, *J* = 4.3, 12.6 Hz, 1H), 2.17 (dt, *J* = 4.4 12.8 Hz, 1H), 2.07 (br s, 2H), 1.37–1.26 (m, 2H), 1.25–1.14 (m, 1H) , 1.14–1.04 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 13C NMR (126 MHz, CD3CN) δ 159.57, 157.55, 148.43, 146.86, 146.82, 145.47, 145.40, 139.28, 139.07, 129.05, 127.54, 126.76, 126.75, 123.51, 123.49, 60.33, 60.32, 40.68, 40.66, 26.91, 23.77, 14.33. $^{19}$F{$^1$H} NMR (471 MHz, $CD_3CN$) δ –126.87 (s, 1F). $^{19}$F NMR (471 MHz, $CD_3CN$) δ –126.87 (dd, *J* = 3.5, 7.2 Hz, 1F).




Compound **5aq** was synthesized following General Procedure A using cyanoarene **4z** (120 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{22}H_{25}N_2$ ($[M + H]^+$) 317.2, found 317.2. The product **5aq** was synthesized in 95% yield (retention time t = 2.832, m/z = 317.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

Compound **5aq** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4z**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4z** (40 mg, 0.3 mmol, 1.0 equiv.). The product **5aq** was synthesized in 22% yield (retention time t = 2.832, m/z = 317.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

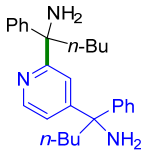
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.52 (d, *J* = 5.0 Hz, 1H), 7.79 (s, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.53–7.41 (m, 5H), 7.39 (dd, *J* = 1.3, 5.0 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 2.43–2.28 (m, 2H), 2.20 (br s, 2H), 1.39–1.29 (m, 2H), 1.29–1.12 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 1H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 169.02, 149.95, 149.48, 149.27, 139.40, 130.10, 130.00, 128.84, 127.99, 127.48, 127.00, 120.09, 119.22, 63.45, 42.25, 27.12, 23.98, 14.46.




Compound **5ar** was synthesized following General Procedure A using cyanoarene **4aa** (107 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{18}H_{23}N_2O_2$ ($[M + H]^+$) 299.2 found 299.2. The product **5ar** was synthesized in 16% yield (retention time t = 2.393, m/z = 299.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

Compound **5ar** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4aa**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4aa** (36 mg, 0.3 mmol, 1.0 equiv.). The product **5ar** was synthesized in 0% yield (retention time t = 2.393, m/z = 299.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

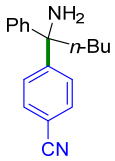
$^1$H NMR (500 MHz, $CD_3CN$) δ 8.65 (d, *J* = 4.9 Hz, 1H), 8.01 (s, 1H), 7.62 (dd, *J* = 1.1, 4.9 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 3.88 (s, 3H), 2.38–2.27 (m, 2H), 2.22–2.10 (m, 2H), 1.36–1.28 (m, 2H), 1.19–1.11 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 169.73, 166.75, 150.32, 148.90, 138.84, 128.96, 127.43, 127.21, 121.17, 120.63, 63.47, 53.28, 42.28, 26.97, 23.91, 14.41.




Compound **5as** was synthesized following General Procedure A using cyanoarene **4ab** (85 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{27}H_{36}N_3$ ($[M + H]^+$) 402.3 found 402.4. The product **5as** was synthesized in 0% yield (retention time t = 2.435, m/z = 402.4 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

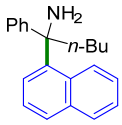
Compound **5as** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4ab**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4ab** (28 mg, 0.3 mmol, 1.0 equiv.). The product **5as** was synthesized in 14% yield (retention time t = 2.435, m/z = 402.4 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination

$^1$H NMR (500 MHz, $CD_3OD$) δ 8.66–8.61 (m, 1H), 7.44–7.30 (m, 8H), 7.29–7.23 (m, 3H), 7.17–7.10 (m, 1H), 2.58–2.47 (m, 1H), 2.47–2.39 (m, 2H), 2.32–2.19 (m, 2H) 1.44–1.13 (m, 6H), 1.13–0.94 (m, 2H), 0.90–0.81 (m, 6H). $^{13}$C NMR (126 MHz, $CD_3OD$) δ 169.93, 160.68, 157.98, 157.87, 149.81, 149.79, 145.81, 145.73, 141.27, 130.16, 130.12, 129.95, 129.88, 129.69, 129.66, 128.67, 128.62, 127.98, 127.91, 127.63, 127.60, 122.38, 122.35, 121.48, 66.32, 66.31, 63.29, 63.26, 27.21, 26.83, 26.82, 23.94, 23.90, 23.78, 23.75, 14.29, 14.27, 14.19, 14.18.



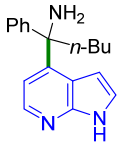

Compound **5at** was synthesized following General Procedure A using cyanoarene **4ac** (85 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). Reaction was unsuccessful.

Compound **5at** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4ac**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4ac** (28 mg, 0.3 mmol, 1.0 equiv.). Reaction was unsuccessful




Compound **5au** was synthesized following General Procedure A using cyanoarene **4ad** (101 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). Reaction was unsuccessful.

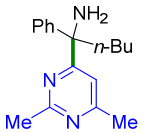
Compound **5au** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4ad**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4ad** (34 mg, 0.3 mmol, 1.0 equiv.). Reaction was unsuccessful.




Compound **5av** was synthesized following General Procedure A using cyanoarene **4ae** (94 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{27}H_{36}N_3$ ($[M + H]^+$) 280.2 found 280.2. The product **5av** was synthesized in 39% yield (retention time t = 2.18, m/z = 280.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5av** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4ae**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4ae** (31 mg, 0.3 mmol, 1.0 equiv.). The product **5av** was synthesized in 27% yield (retention time t = 2.18, m/z = 280.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

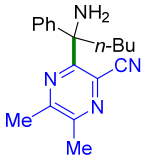
$^1$H NMR (500 MHz, $CD_3CN$) δ 10.49 (s, 1H), 8.29 (d, *J* = 5.0 Hz, 1H), 7.39 (t, *J* = 6.5 Hz, 3H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.19–7.13 (m, 2H), 6.01 (d, *J* = 3.1 Hz, 1H), 2.45 (td, *J* = 12.6, 4.3 Hz, 1H), 2.26 (td, *J* = 12.6, 3.8 Hz, 1H), 2.06 (s, 2H), 1.35 – 1.13 (m, 3H), 1.08–0.96 (m, 1H), 0.81 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 151.36, 150.27, 149.92, 143.72, 128.87, 127.44, 127.15, 125.11, 118.57, 113.91, 101.96, 61.92, 41.53, 27.01, 23.88, 14.36. ESI LRMS *m/z* calcd. for $C_{18}H_{22}N_2$ ($[M – NH_2]^+$) 280.2, found 280.3.




Compound **5aw** was synthesized following General Procedure A using cyanoarene **4af** (88 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{27}H_{36}N_3$ ($[M + H]^+$) 270.2 found 270.2. The product **5aw** was not successfully synthesized.

Compound **5w** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4af**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4af** (29 mg, 0.3 mmol, 1.0 equiv.). The product **5aw** was synthesized in 8% yield (retention time t = 2.37, m/z = 270.2 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

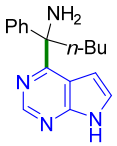
$^1$H NMR (500 MHz, $CD_3CN$) δ 7.46 (dd, *J* = 1.2, 8.4, 2H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.23 (s, 1H), 7.20–7.15 (m, 1H), 2.52 (s, 3H), 2.38 (s, 3H), 2.28–2.18 (m, 2H), 2.12 (br s, 2H), 1.38–1.24 (m, 2H), 1.23–1.05 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 176.07, 168.20, 167.58, 148.22, 128.93, 127.42, 127.32, 114.97, 62.90, 41.62, 26.84, 26.18, 24.34, 23.88, 14.36



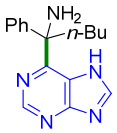

Compound **5ax** was synthesized following General Procedure A using cyanoarene **4ag** (81 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 µL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{18}H_{23}N_4$ ($[M + H]^+$) 295.2 found 295.3. The product **5ax** was synthesized in 0% yield (retention time t = 2.565, m/z = 295.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

Compound **5ax** was also synthesized from the corresponding iminium HCl salt **6l** and cyanoarene **4ag**. The reaction was conducted by following the General Iminium Salt Reaction Procedure using iminium HCl salt **6l** (130 mg, 0.66 mmol, 2.2 equiv.); photocatalyst $Ir[dF(Me)ppy]_2dtbbpyPF_6$ (6 mg, 2E-3 mmol, 2 mol%); DIPA (153 µL, 1.1 mmol, 3.6 equiv.); and cyanoarene **4ag** (29 mg, 0.3 mmol, 1.0 equiv.). The product **5ax** was synthesized in 10% yield (retention time t = 2.565, m/z = 295.3 $(M+H]^+$) as determined by a calibrated UPLC generated from an authentic sample using the UPLC-MS Method for Yield Determination.

$^1$H NMR (500 MHz, $CD_3CN$) δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 5.27 (very br s, 2H), 2.57 (s, 3H), 2.53 (s, 3H), 2.25 (dt, *J* = 4.2, 13.0 Hz, 1H), 2.06 (dt, *J* = 4.2, 13.0 Hz, 1H), 1.24–1.14 (m, 2H), 1.14–1.04 (m, 1H), 0.92–0.81 (m, 1H), 0.76 (t, *J* = 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, $CD_3CN$) δ 165.67, 162.07, 152.92, 152.60, 144.02, 143.03, 128.84, 127.58, 118.28, 74.75, 40.82, 27.26, 23.58, 22.95, 22.48, 14.27.



Compound **5ay** was synthesized following General Procedure A using cyanoarene **4ah** (95 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{18}H_{23}N_4$ ($[M + H]^+$) 295.2 found 295.3. The product **5ay** was not successfully synthesized.



Compound **5az** was synthesized following General Procedure A using cyanoarene **4ai** (96 mg, 0.66 mmol), **PC1** (6 mg, 6E-3 mmol), benzoic acid (37 mg, 0.3 mmol), DIPA (153 μL, 1.1 mmol) and *O*-benzoyl oxime (**3l**) (84 mg, 0.3 mmol) in DMSO (3 mL). MS (ESI) *m/z* calcd. for $C_{18}H_{23}N_4$ ($[M + H]^+$) 295.2 found 295.3. The product **5az** was not successfully synthesized.

## 5. Synthesis of *O*-Benzoyl Oximes Starting Materials

### 5.1 Oxime Synthesis:

Hydroxyl amine was suspended in EtOH (0.5 M), and pyridine (2.5 equivalents) was added. The suspension was heated to 75 °C to generate a homogeneous solution. The ketone was then added in one portion. The reaction was considered complete when the starting ketone was no longer detected via UPLC-MS. The crude reaction was cooled to room temperature and concentrated under reduced pressure. The concentrate was dissolved in EtOAc and washed with saturated $NH_4Cl$ (1 equal volume). The reaction was washed twice with water (2 x 1 equal volume), and once with brine. The organic layer was then collected, dried over sodium sulfate and concentrated to a crude solid. The identity of the crude product was confirmed via UPLC-MS analysis, and the isolated material was utilized in the following benzoylation reaction without further purification.

### 5.2 Benzoylation of Oximes:

General Method A:

Oxime (1 equivalent) was added to a round bottom flask containing a stir bar and placed under an atmosphere of nitrogen. The oxime was dissolved in methylene chloride to afford a 1.65 M solution. The solution was then diluted with hexanes until the total concentration of oxime was 0.33 M. Pyridine (1.1 equivalent) was then added to the reaction flask via syringe. Benzoyl chloride (1.1 equivalent) was then added to the reaction dropwise via a syringe. If a substantial increase in reaction temperature was observed, addition of benzoyl chloride was halted for two minutes. During addition of benzoyl chloride, a white precipitate was formed. The reaction was stirred at 23 °C, until the oxime is observed to be consumed by LC-MS. Upon completion of the reaction, the reaction was diluted 1:1 with deionized water and contents of the reaction were placed into a separatory funnel. The two immiscible layers were mixed, and then upon separation, the aqueous layer was removed, and the organic layer was washed with water (3 x 50 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure to afford a mostly pure crude product. The products were then recrystallized to afford pure product.

General Method B:

*Note: Used when starting materials were insoluble in high concentrations of hexanes.*

Oxime (1 equivalent) was added to a round bottom flask containing a stir bar and placed under an atmosphere of nitrogen. The oxime was dissolved in methylene chloride to afford a 0.33 M solution. Pyridine (1.1 equivalent) was then added to the reaction flask via syringe. Benzoyl chloride (1.1 equivalent) was then added to the reaction dropwise via a syringe. If a substantial increase in reaction temperature was observed, addition of benzoyl chloride was halted for two minutes. During addition of benzoyl chloride, a white precipitate was formed. The reaction is stirred at 23 °C, until the oxime is observed to be consumed by LC-MS. Upon completion of the reaction, the reaction was diluted 1:1 with deionized water and contents of the reaction were placed into a separatory funnel. The two immiscible layers were mixed, and then upon separation, the aqueous layer was removed, and the organic layer was washed with water (3 x 50 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure to afford a mostly pure crude product. The products were then recrystallized to afford pure product.

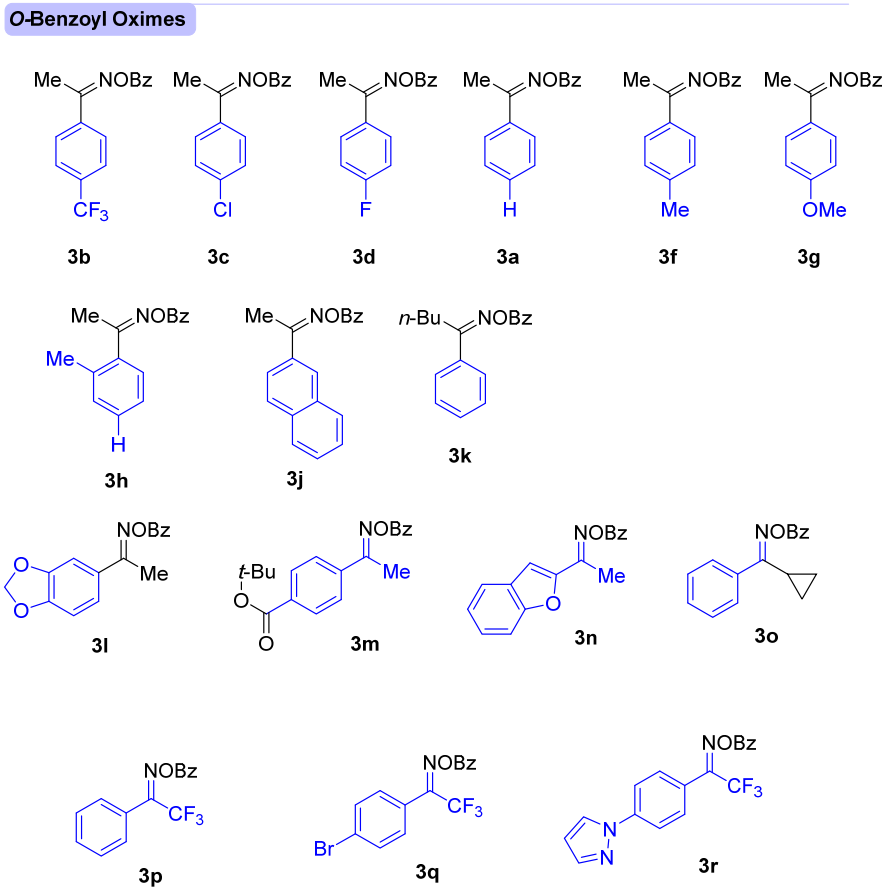
General Method C:

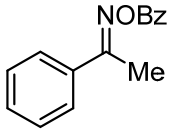
*Note: Used for heterocyclic ketones.*

Oxime (1 equivalent) was added to a round bottom flask containing a stir bar and placed under an atmosphere of nitrogen. The oxime was dissolved in methylene chloride to afford a 0.33 M solution. Triethylamine (1.1 equivalent) was then added to the reaction flask via syringe. Benzoyl chloride (1.1 equivalent) was then added to the reaction dropwise via a syringe. If a substantial increase in reaction temperature was observed, addition of benzoyl chloride was halted for two minutes. During addition of benzoyl chloride, a white precipitate was formed. The reaction is stirred at 23 °C, until the oxime is observed to be consumed by LC-MS. Upon completion of the reaction, the reaction was diluted 1:1 with deionized water and contents of the reaction were placed into a separatory funnel. The two immiscible layers were mixed, and then upon separation, the aqueous layer was removed, and the organic layer was

washed with water (3 x 50 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure to afford a mostly pure crude product. The products were then recrystallized to afford pure product.

**Table S6.** Table of *O*-Benzoylated Oximes Synthesized






Compound **3a** was synthesized according to general method A using acetophenone (9.33 mL, 80 mmol), pyridine (16.11 mL, 200 mmol), hydroxylamine hydrochloride (8.339 g, 120 mmol), and ethanol (160 mL). Then the crude material of the first step was reacted with pyridine (6450 mL, 80 mmol), benzoyl chloride (9.286 mL, 80 mmol), in methylene chloride (48 mL) and hexanes (194 mL) according to the General Method A. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (15.636 g, 80%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.09 (d, $J$ = 7.1 Hz, 2H), 7.83 (d, $J$ = 6.8 Hz, 2H), 7.71 (t, $J$ = 7.5 Hz, 1H), 7.59 (t, $J$ = 7.7 Hz, 2H), 7.56 – 7.48 (m, 3H), 2.52 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 164.01, 162.89, 134.48, 133.71, 130.77, 129.24, 128.97, 128.68, 128.55, 126.94, 14.34. MS (ESI) *m/z* calcd. for $C_{15}H_{14}NO_2$ ($[M + H]^+$) 240.1, found 240.2

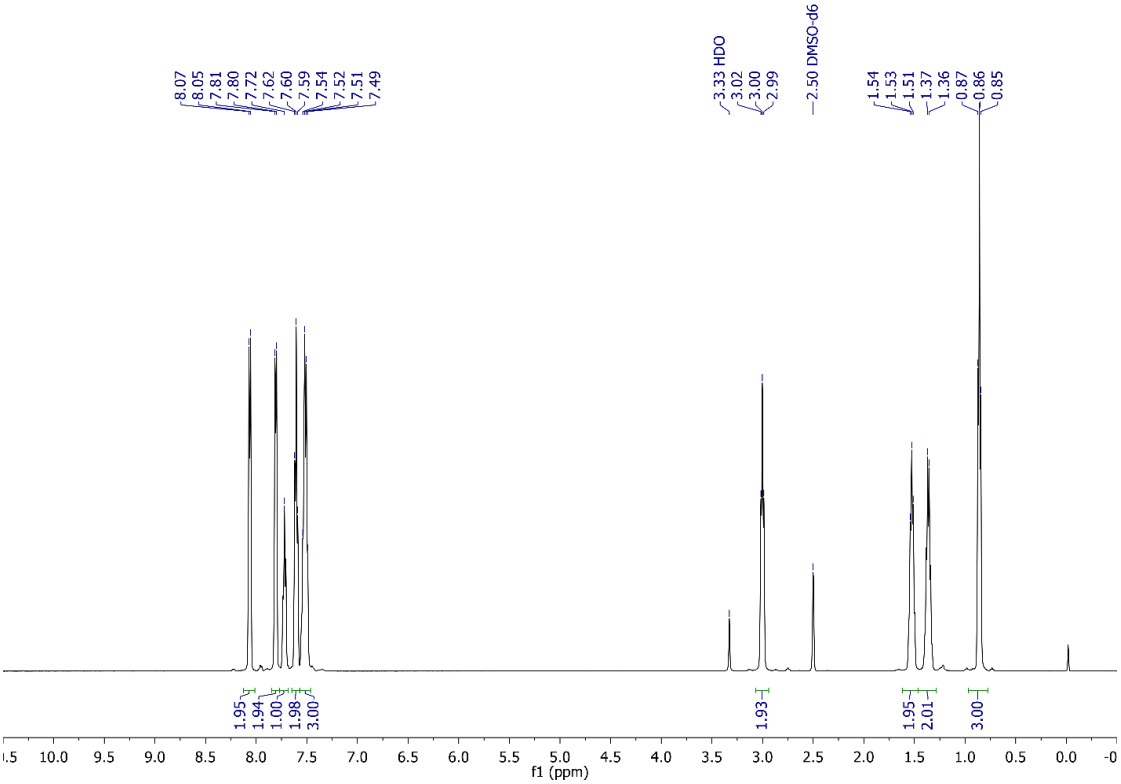



**Figure S56.** $^{1}$H qNMR (500 MHz) spectrum of **3a** in DMSO-$d_6$.

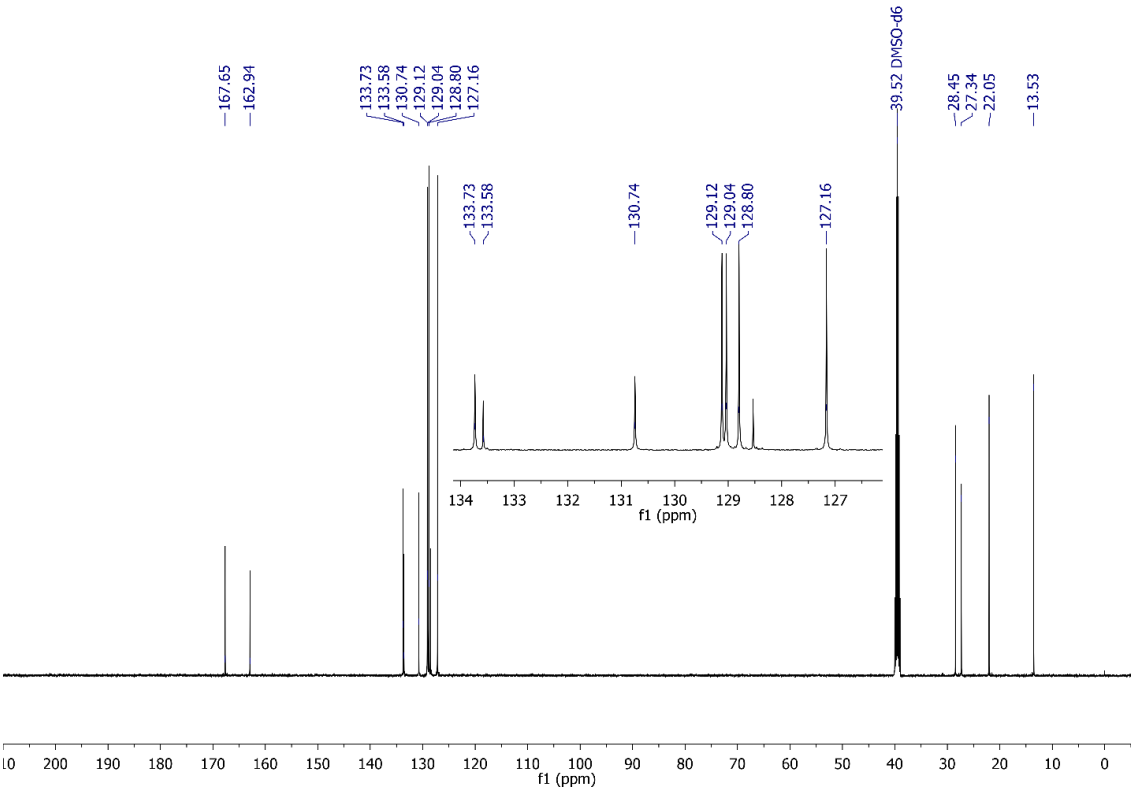
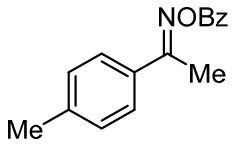



**Figure S57.** $^{13}$C NMR (126 MHz) spectrum of **3a** in DMSO-$d_6$.




Compound **3f** was synthesized according to general method A using 4-methylacetophenone (3.73 mL, 28 mmol), pyridine (5.537 mL, 70 mmol), hydroxylamine hydrochloride (2.918 g, 42 mmol), and ethanol (80 mL). Then the crude material of the first step was reacted with pyridine (2.258 mL, 28 mmol), benzoyl chloride (3.250 mL, 28 mmol), in methylene chloride (17 mL) and hexanes (68 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (4.449 g, 63%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.08 (d, $J$ = 7.3 Hz, 2H), 7.75 – 7.69 (m, 3H), 7.59 (t, $J$ = 7.7 Hz, 2H), 7.30 (d, $J$ = 8.0 Hz, 2H), 2.49 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 163.78, 162.91, 140.68, 133.67, 131.59, 129.25, 129.22, 128.97, 128.61, 126.87, 20.89, 14.19. MS (ESI) *m/z* calcd. for $C_{16}H_{15}NO_2$ ($[M + H]^+$) 254.1, found ($[M+H]^+$) 254.2.

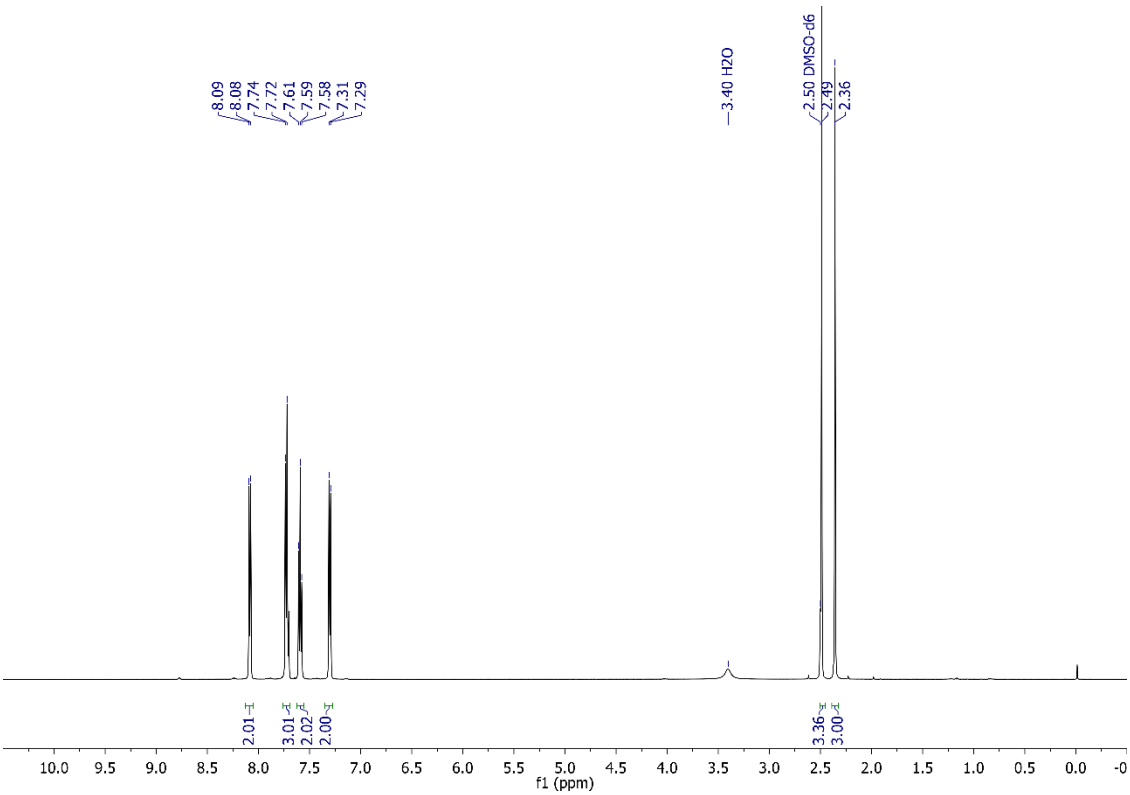



**Figure S58.** $^{1}$H qNMR (500 MHz) spectrum of **3f** in DMSO-$d_6$.

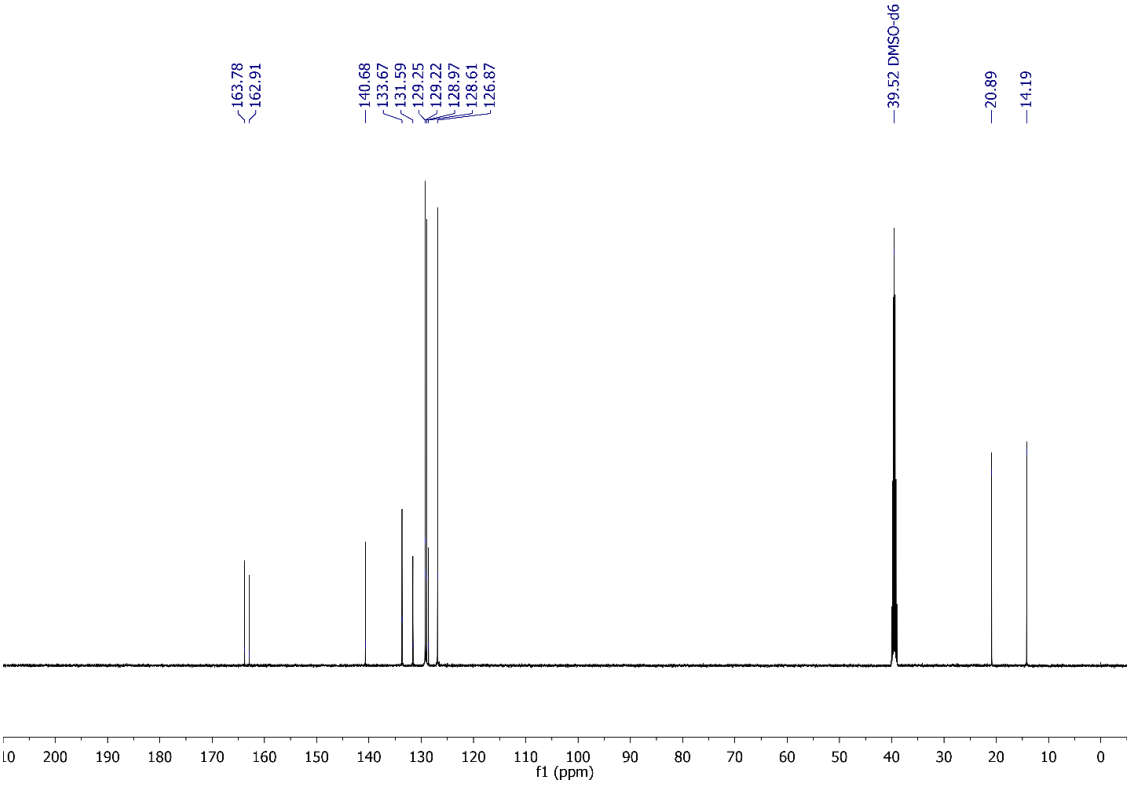
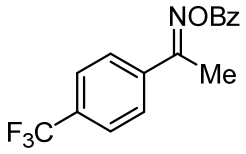



**Figure S59.** $^{13}$C NMR (126 MHz) spectrum of **3f** in DMSO-$d_6$.




Compound **3b** was synthesized according to general method A using 4-trifluoromethyl acetophenone (2.822 g, 15 mmol), pyridine (3.0 mL, 37.5 mmol), hydroxylamine hydrochloride (1.564 g, 22.5 mmol), and ethanol (30 mL). Then the crude material of the first step was reacted with pyridine (1.33 mL, 16.5 mmol), benzoyl chloride (1.741 mL, 15 mmol), in methylene chloride (9 mL) and hexanes (24 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (1.41 g, 31%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.10 (d, $J$ = 7.3 Hz, 2H), 8.05 (d, $J$ = 8.1 Hz, 2H), 7.87 (d, $J$ = 8.2 Hz, 2H), 7.73 (t, $J$ = 7.4 Hz, 1H), 7.60 (t, $J$ = 7.7 Hz, 2H), 2.57 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 163.10, 162.75, 138.47, 133.88, 130.80 (q, $J$ = 31.9 Hz), 129.33, 129.03, 128.29, 127.87, 125.60 (q, $J$ = 3.8 Hz), 125.26 (q, $J$ = 272.7, 271.6 Hz), 14.41. $^{19}$F NMR (471 MHz, DMSO-$d_6$) δ -61.41. MS (ESI) *m/z* calcd. for $C_{16}H_{12}F_3NO_2$ ($[M + H]^+$) 308.1, found 308.1

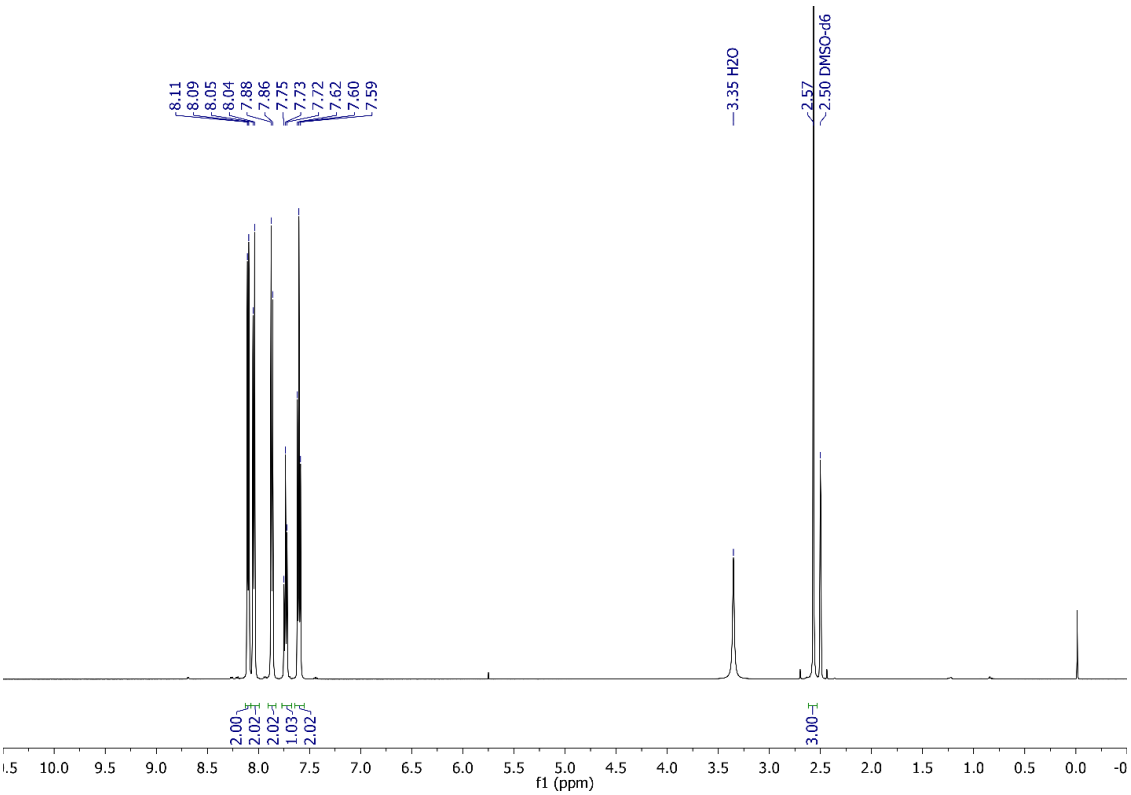



**Figure S60.** $^{1}$H qNMR (500 MHz) spectrum of compound **3b** in DMSO-$d_6$

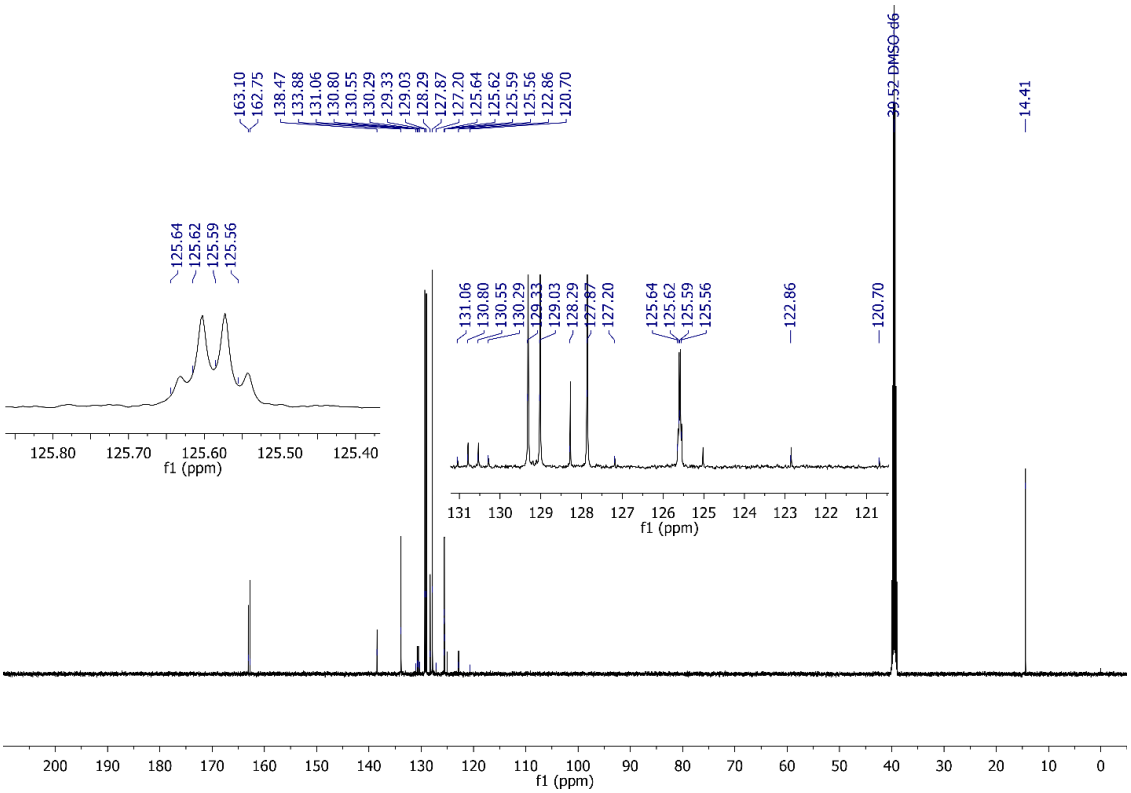



**Figure S61.** $^{13}$C NMR (126 MHz) spectrum of **3b** in DMSO-$d_6$.

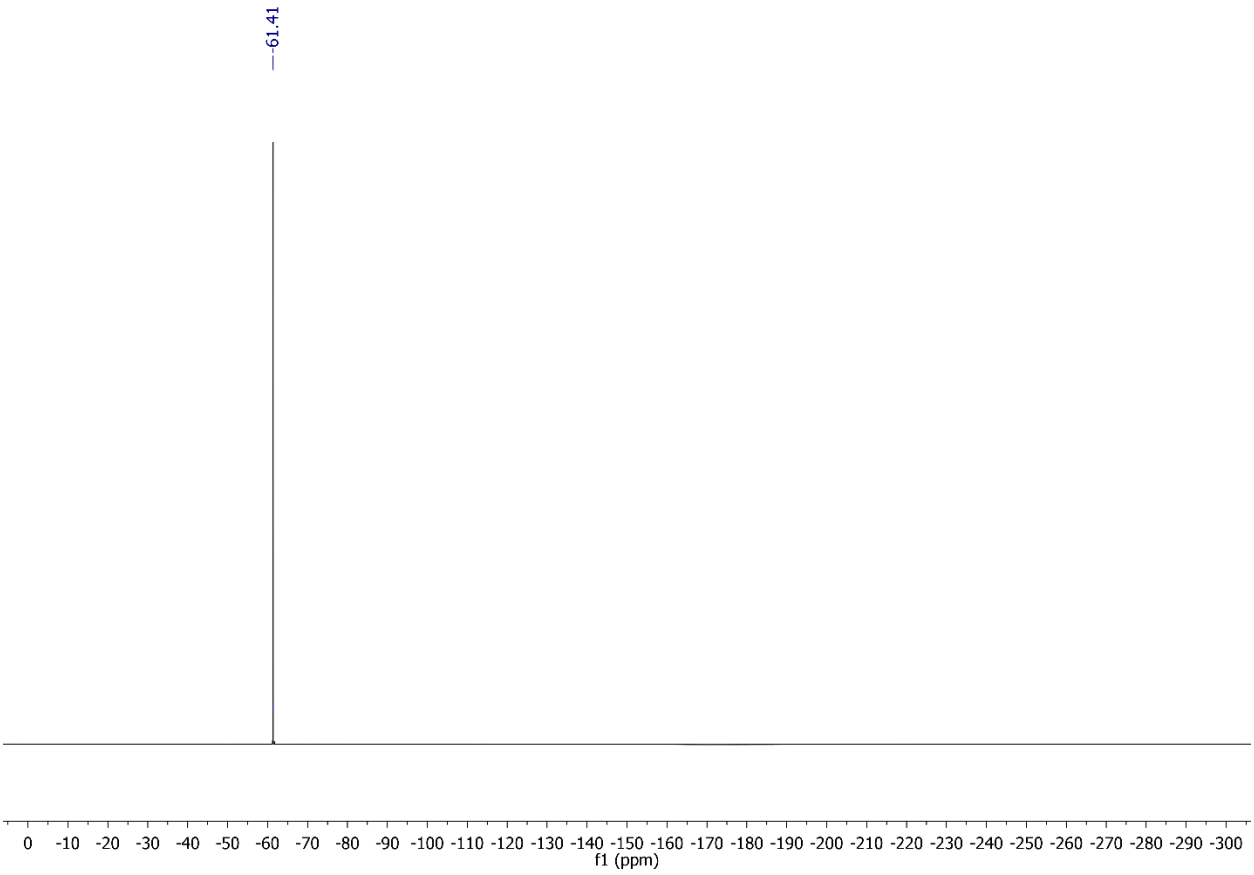
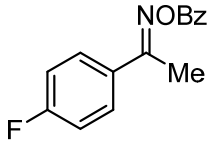



**Figure S62.** $^{19}F$ NMR (471 MHz) spectrum of compound **3b** in DMSO-$d_6$




Compound **3d** was synthesized according to general method A using 4-fluoroacetophenone (1.381 g, 10 mmol), pyridine (2.013 mL, 25 mmol), hydroxylamine hydrochloride (1.042 g, 15 mmol), and ethanol (20 mL). Then the crude material of the first step was reacted with pyridine (0.806 mL, 10 mmol), benzoyl chloride (1.16 mL, 10 mmol), in methylene chloride (6 mL) hexanes (24 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (1.311 g, 51%).

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.09 (d, $J$ = 7.6 Hz, 2H), 7.94 – 7.87 (m, 2H), 7.73 (t, $J$ = 6.8 Hz, 1H), 7.60 (t, $J$ = 7.6 Hz, 2H), 7.34 (t, $J$ = 8.8 Hz, 2H), 2.52 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 164.61, 163.07, 162.84, 162.63, 133.73, 130.93, 130.90, 129.44, 129.37, 129.24, 128.97, 128.46, 115.77, 115.60, 14.33. MS (ESI) m/z calcd. for $C_{15}H_{12}FNO_2$ ($[M + H]^+$) 258.1, found 258.3

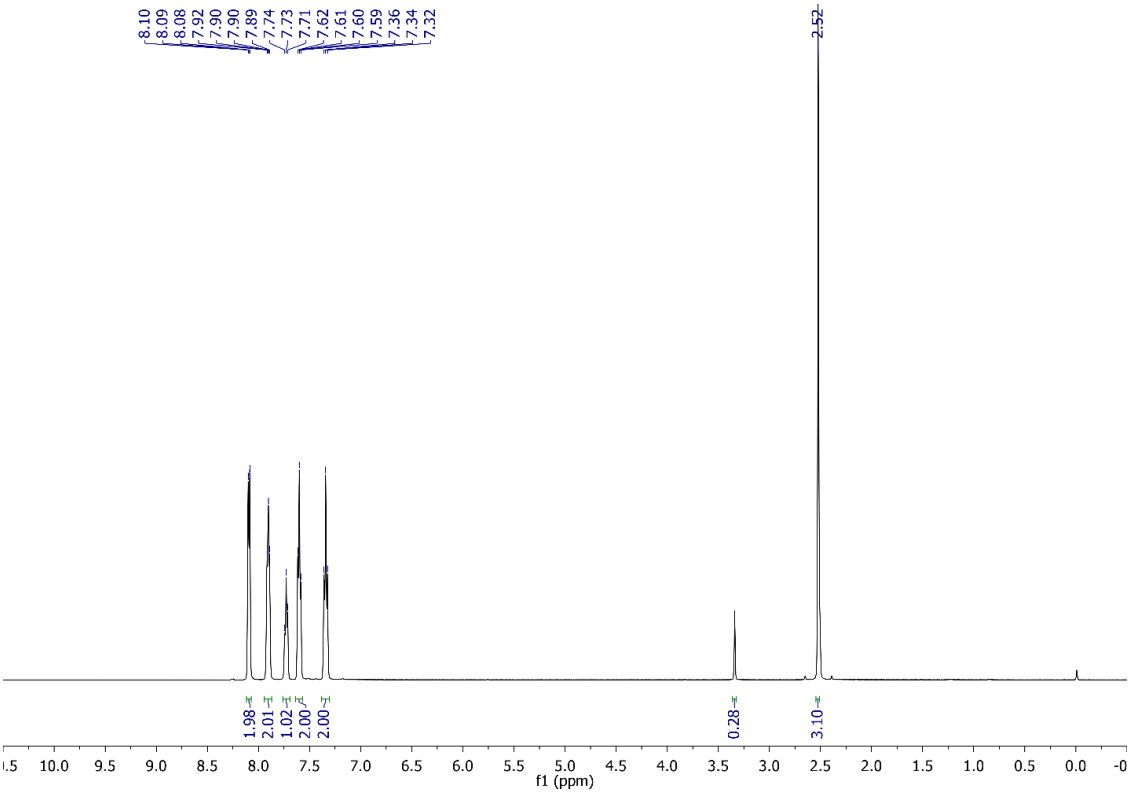



**Figure S63.** [1]H qNMR (500 MHz) spectrum of compound **3d** in DMSO-$d_6$

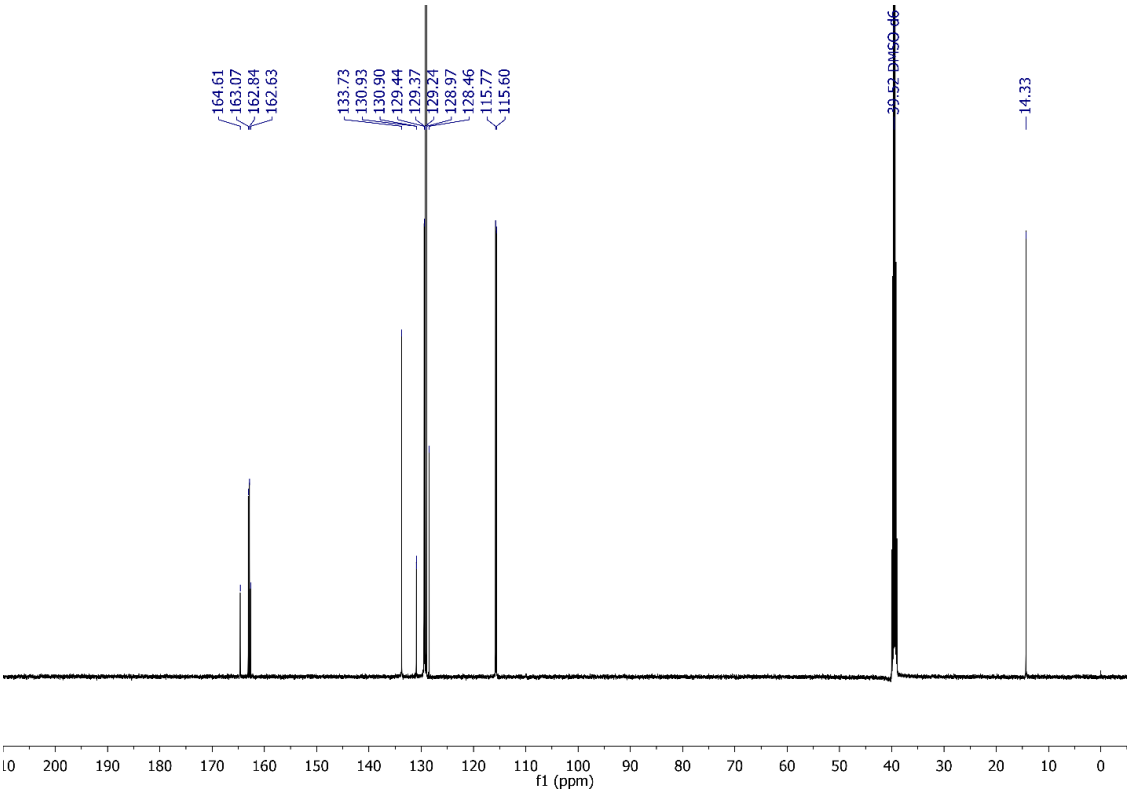
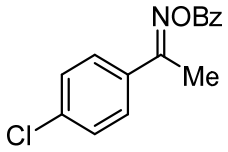



**Figure S64.** [13]C NMR (126 MHz) spectrum of **3d** in DMSO-$d_6$.




Compound **3c** was synthesized according to general method A using 4-chloroacetophenone (3.242 mL, 25 mmol), pyridine (5.03 mL, 62.5 mmol), hydroxylamine hydrochloride (2.61 g, 37.5 mmol), and ethanol (50 mL). Then the crude material of the first step was reacted with pyridine (1.582 mL, 20 mmol), benzoyl chloride (2.321 mL, 20 mmol), in methylene chloride (12 mL) and hexanes (48 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (2.556 g, 47%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.09 (d, $J$ = 9.9 Hz, 2H), 7.86 (d, $J$ = 8.5 Hz, 2H), 7.73 (t, $J$ = 6.8 Hz, 1H), 7.64 – 7.53 (m, 4H), 2.52 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 163.06, 162.78, 135.61, 133.78, 133.27, 129.26, 128.99, 128.77 (2C), 128.39, 14.23. MS (ESI) *m/z* calcd for $C_{15}H_{14}NO_2$ ($[M + H]^+$) 274.1, found 274.1.

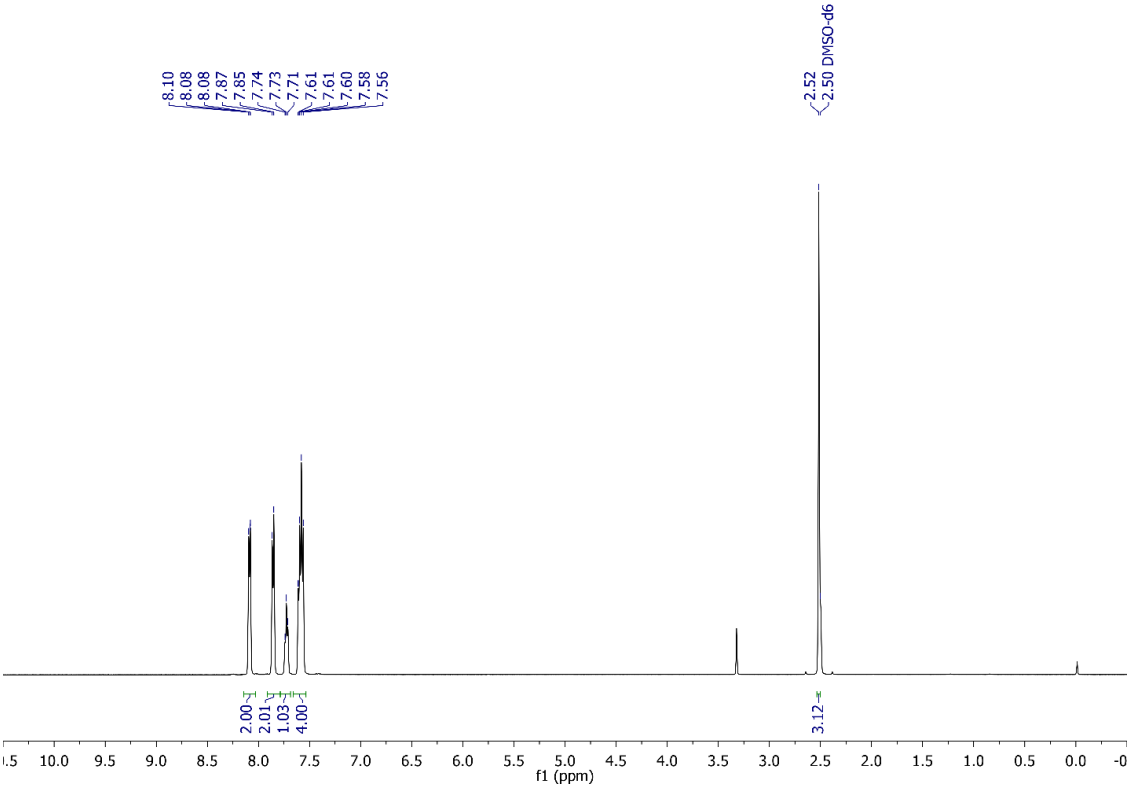



**Figure S65.** $^{1}$H qNMR (500 MHz) spectrum of compound **3c** in DMSO-$d_6$

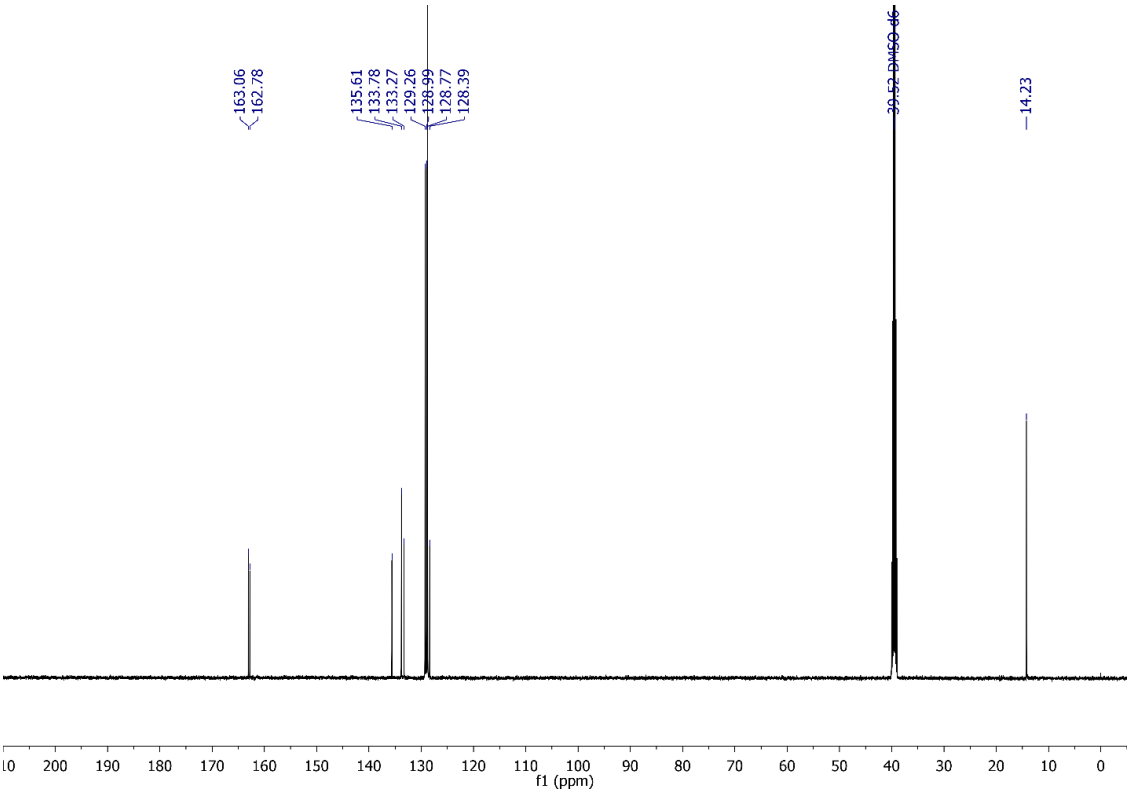
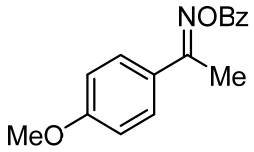



**Figure S66.** $^{13}$C NMR (126 MHz) spectrum of **3c** in DMSO-$d_6$.




Compound **3g** was synthesized according to general method A using 4-methoxyacetophenone(4.505 g, 18 mmol), pyridine (6 mL, 27 mmol), hydroxylamine hydrochloride (3.12 g, 45 mmol), and ethanol (60 mL). Then the crude material of the first step (3.3 g) was reacted with pyridine (1.61 mL, 20 mmol), benzoyl chloride (2.32 mL, 20 mmol), in methylene chloride (12 mL) and hexanes (49 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (3.35 g, 62%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.08 (d, $J$ = 7.9 Hz, 2H), 7.94 – 7.77 (m, 2H), 7.71 (t, $J$ = 6.8 Hz, 1H), 7.59 (t, $J$ = 7.1 Hz, 2H), 7.04 (d, $J$ = 8.6 Hz, 2H), 3.82 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 163.31, 162.94, 161.32, 133.62, 129.18, 128.95, 128.67, 128.54, 126.51, 114.06, 55.31, 14.04. MS (ESI) *m/z* calcd for $C_{16}H_{16}NO_3$ ($[M + H]^+$) 270.1, found 270.2

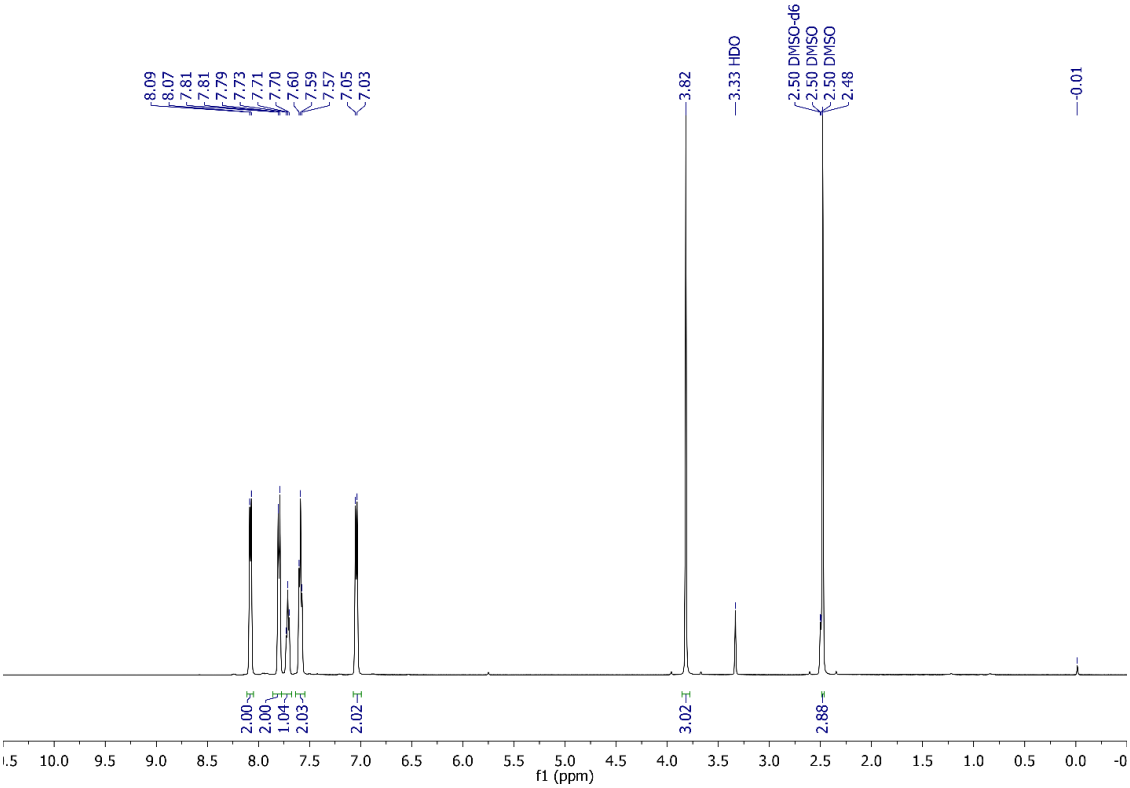



**Figure S67.** [1]H qNMR (500 MHz) spectrum of compound **3g** in DMSO-$d_6$

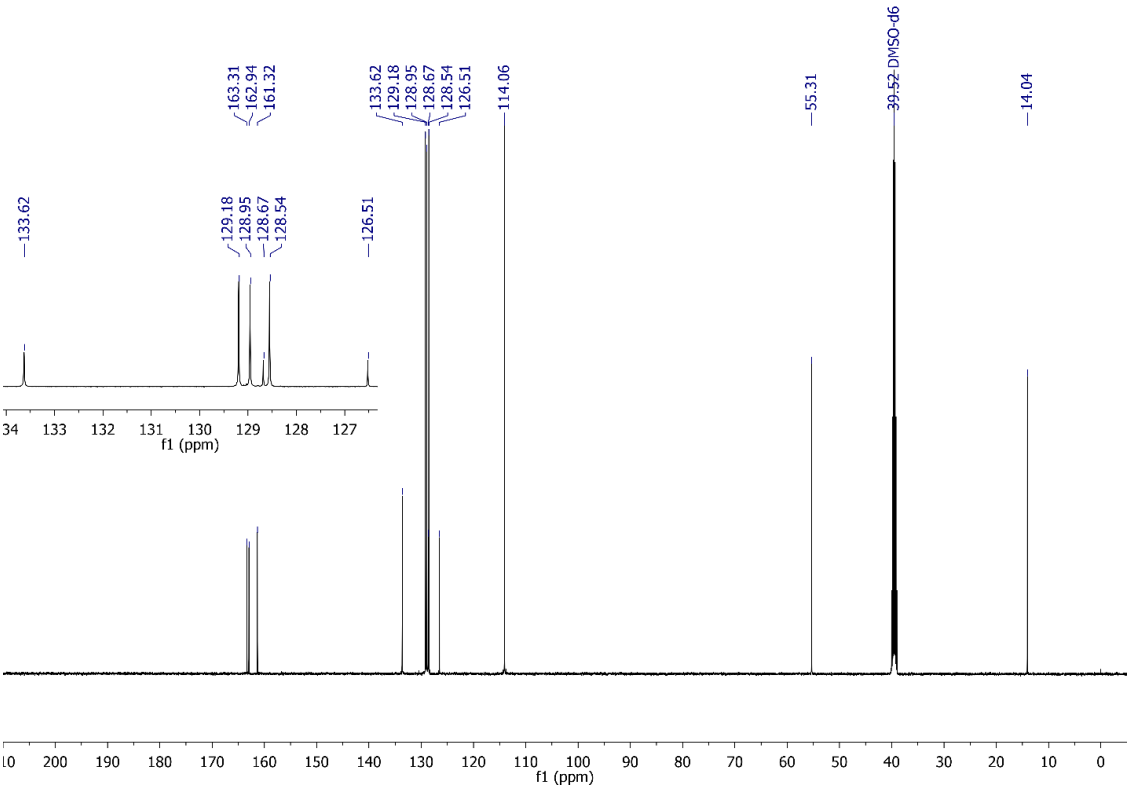
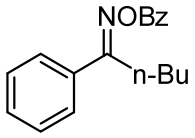



**Figure S68.** [13]C NMR (126 MHz) spectrum of **3g** in DMSO-$d_6$.




Compound **3l** was synthesized according to general method A using valerophenone (4.597 g, 28 mmol), pyridine (5.64 mL, 70 mmol), hydroxylamine hydrochloride (2.92 g, 42 mmol), and ethanol (56 mL). Then the crude material of the first step was reacted with pyridine (2.258 mL, 28 mmol), benzoyl chloride (3.25 mL, 28 mmol), in methylene chloride (17 mL) and hexanes (68 mL) according to the General Method A. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (6.09 g, 77%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.06 (d, $J$ = 7.9 Hz, 2H), 7.81 (d, $J$ = 7.7 Hz, 2H), 7.72 (t, $J$ = 6.8 Hz, 1H), 7.60 (t, $J$ = 7.4 Hz, 2H), 7.51 (q, $J$ = 8.1, 6.1 Hz, 3H), 3.00 (t, $J$ = 7.4 Hz, 2H), 1.60 – 1.48 (m, 2H), 1.36 (q, $J$ = 7.1 Hz, 2H), 0.86 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 167.65, 162.94, 133.73, 133.58, 130.74, 129.12, 129.04, 128.80, 127.16, 28.45, 27.34, 22.05, 13.53. MS (ESI) *m/z* calcd. for $C_{18}H_{20}NO_2$ ($[M + H]^+$) 280.1, found 280.2

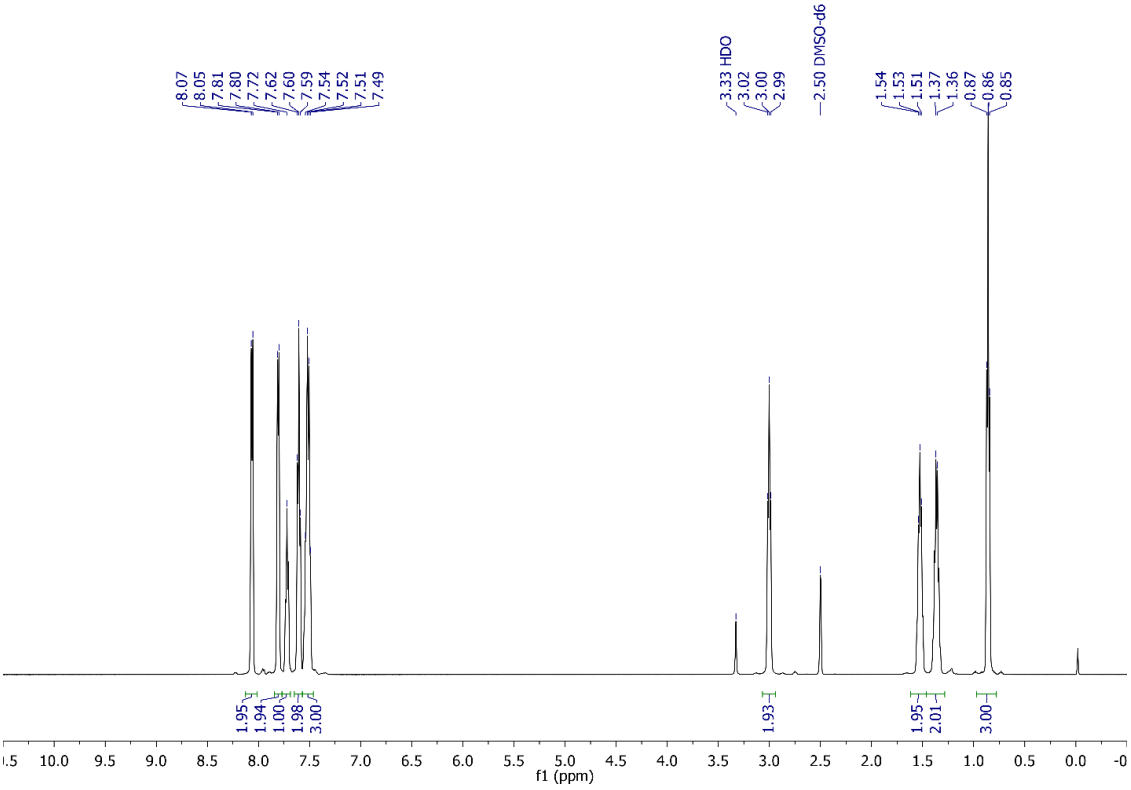



**Figure S69.** [1]H qNMR (500 MHz) spectrum of compound **3l** in DMSO-$d_6$

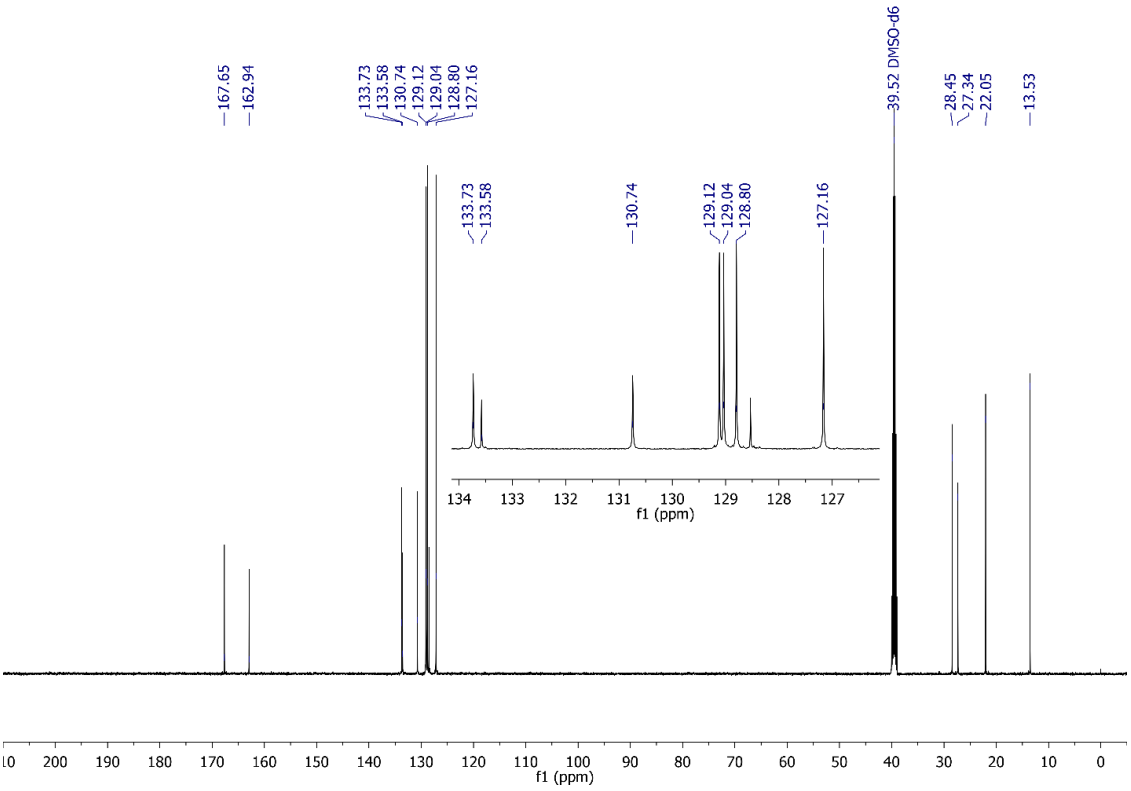
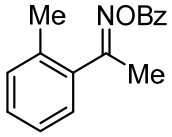



**Figure S70.** [13]C NMR (126 MHz) spectrum of **3l** in DMSO-$d_6$.




Compound **3h** was synthesized according to general method A using 2-methylacetophenone (3.9 mL, 30 mmol), pyridine (6.0 mL, 75 mmol), hydroxylamine hydrochloride (3.13 g, 45 mmol), and ethanol (60 mL). Then the crude material of the first step was reacted with pyridine (2.39 mL, 29.6 mmol), benzoyl chloride (3.44 mL, 29.6 mmol), in methylene chloride (18 mL) and hexanes (72 mL) according to the General Method A. The crude product was recrystallized from $CH_2Cl_2$/Hexanes, filtered cold (-20 °C) to afford the product as a beige solid (5.74 g, 76%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.09 (d, $J$ = 8.5 Hz, 2H), 7.72 (t, $J$ = 6.8 Hz, 1H), 7.60 (t, $J$ = 7.5 Hz, 2H), 7.38 (dt, $J$ = 7.8, 1.6, 1.1 Hz, 2H), 7.34 – 7.27 (m, 2H), 2.45 (s, 3H), 2.39 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 166.53, 162.90, 135.42, 135.39, 133.67, 130.67, 129.37, 129.22, 128.95, 128.58, 128.15, 125.87, 19.68, 17.84. MS (ESI) *m/z* calcd. for $C_{16}H_{16}NO_2$ ($[M + H]^+$) 254.1, found ($[M+H]^+$) 254.2

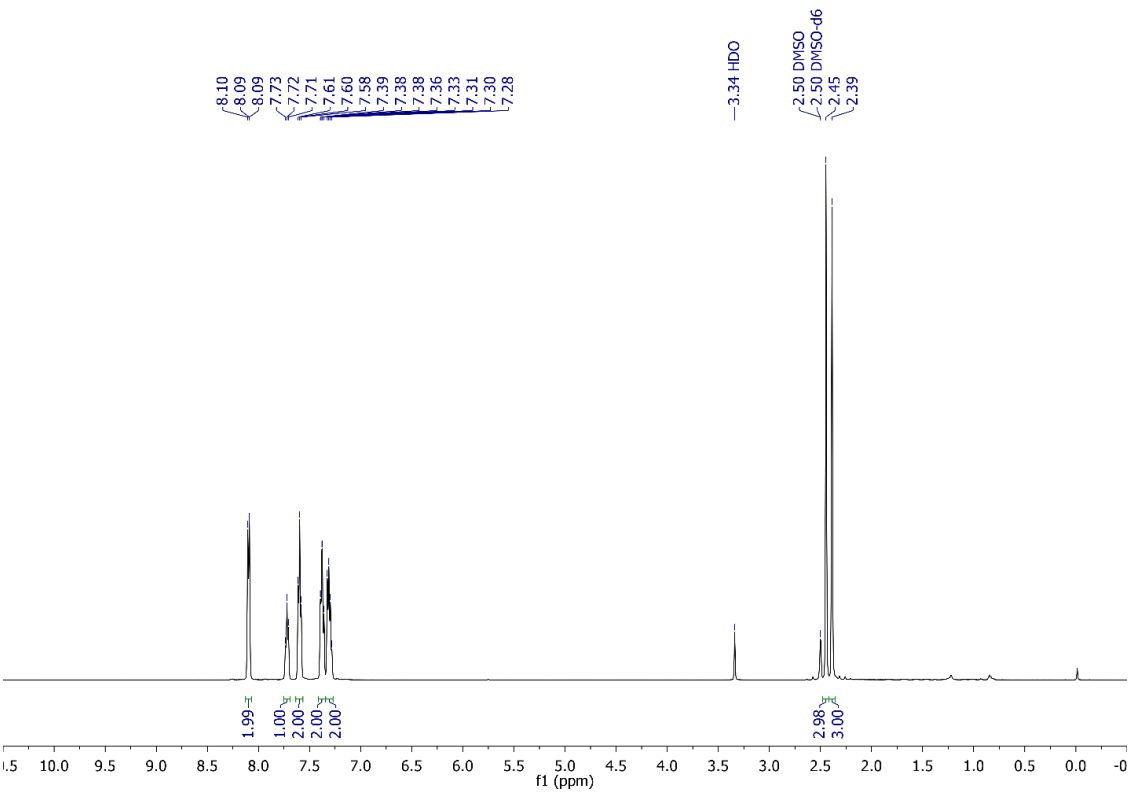



**Figure S71.** [1]H qNMR (500 MHz) spectrum of compound **3h** in DMSO-$d_6$

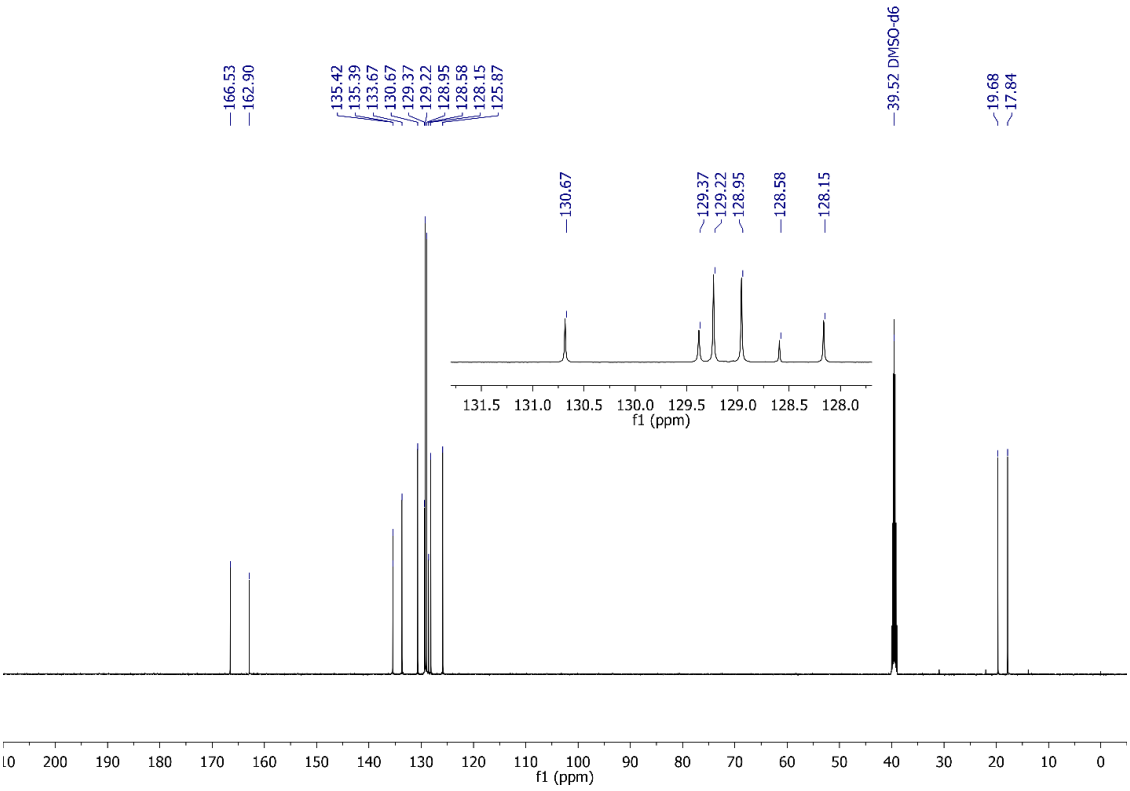
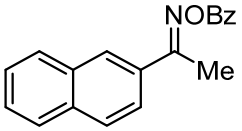



**Figure S72.** [13]C NMR (126 MHz) spectrum of **3h** in DMSO-$d_6$.




Compound **3j** was synthesized according to general method A using acetonapthophenone (4.26 g, 25 mmol), pyridine (5.03 mL, mmol), hydroxylamine hydrochloride (2.61 g, 37.5 mmol), and ethanol (50 mL). Then the crude material of the first step (ca. 20 mmol recovered) was reacted with pyridine (1.61 mL, 20 mmol), benzoyl chloride (2.32 mL, 20 mmol), in methylene chloride (12 mL) and hexanes (48 mL) according to the General Method A. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (5.04 g, 68%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.41 (s, 1H), 8.12 (d, $J$ = 7.6 Hz, 2H), 8.07 (d, $J$ = 7.1 Hz, 1H), 8.02 (s, 2H), 7.98 (d, $J$ = 6.9 Hz, 1H), 7.74 (t, $J$ = 6.8 Hz, 1H), 7.60 (d, $J$ = 6.5 Hz, 4H), 2.65 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 163.74, 162.93, 133.87, 133.78, 132.56, 131.74, 129.30, 129.03, 128.76, 128.54, 128.20, 127.81, 127.59, 127.57, 126.78, 123.39, 14.14. MS (ESI) *m/z* calcd. for $C_{19}H_{16}NO_2$ ($[M + H]^+$) 290.1, found 290.1.

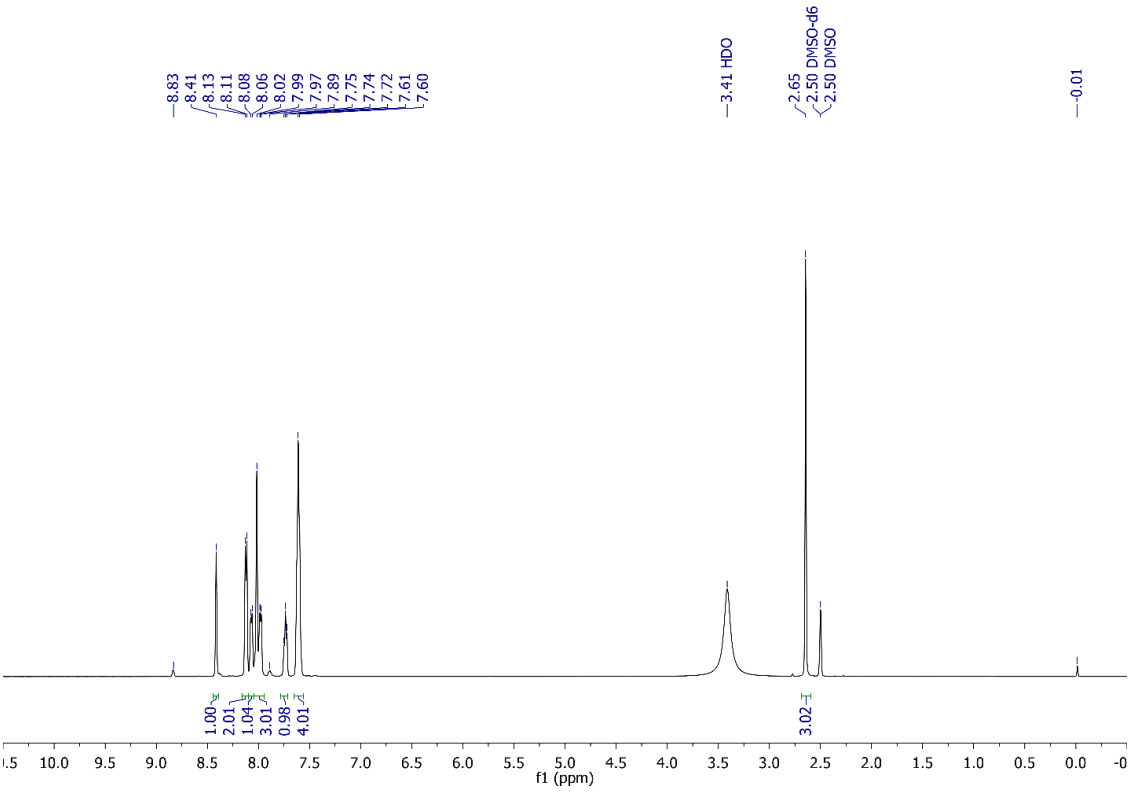



**Figure S73.** [1]H qNMR (500 MHz) spectrum of compound **3j** in DMSO-$d_6$

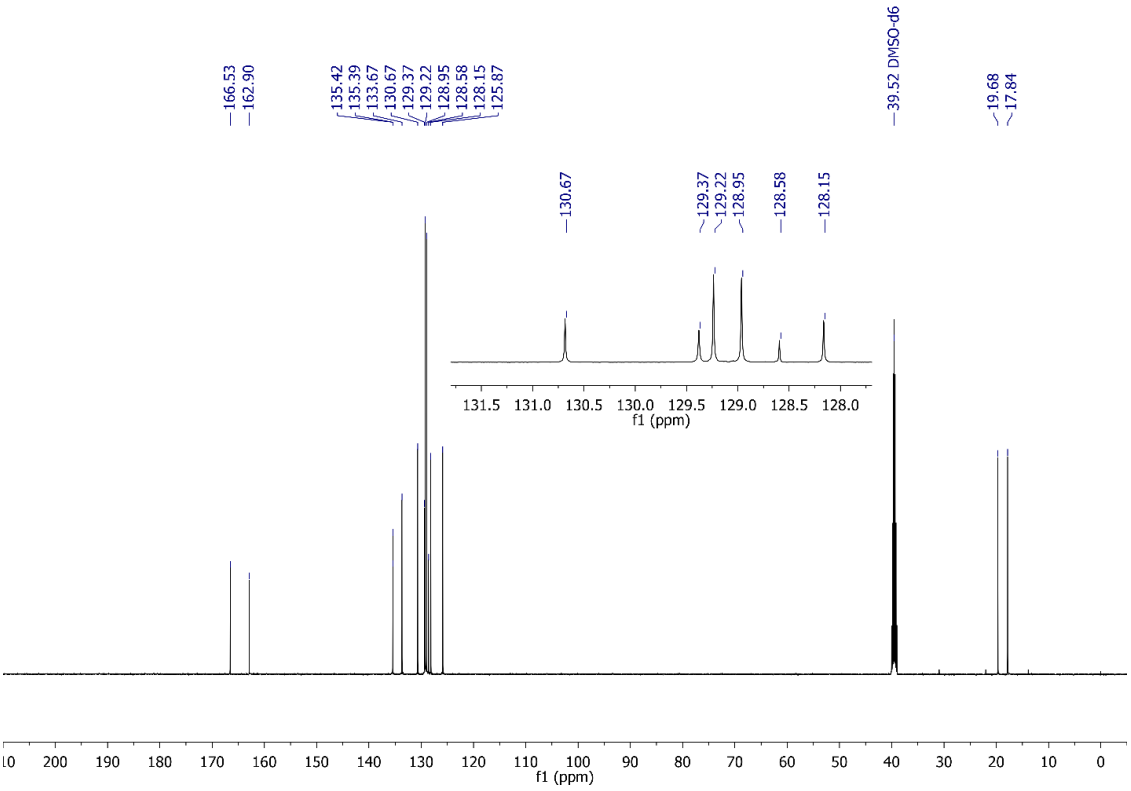
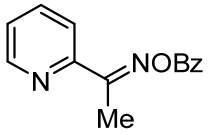



**Figure S74.** [13]C NMR (126 MHz) spectrum of **3j** in DMSO-$d_6$.




Compound **3s** was synthesized according to general method C using 2-acetylpyridine (3.028 g, 25 mmol), triethylamine (5.03 mL, 62.5 mmol), hydroxylamine hydrochloride (2.61 g, 37.5 mmol), and ethanol (50 mL). Then the crude material of the first step was reacted with pyridine (1.451 mL, 18 mmol), benzoyl chloride (2.09 mL, 18 mmol), in methylene chloride (55 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$ to afford the product as a white crystalline solid (3.792 g, 63%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.74 – 8.68 (m, 1H), 8.11 (d, $J$ = 8.0 Hz, 2H), 8.04 (d, $J$ = 7.5 Hz, 1H), 7.95 (dt, $J$ = 15.4, 7.6 Hz, 1H), 7.73 (d, $J$ = 7.3 Hz, 1H), 7.61 (t, $J$ = 7.2 Hz, 2H), 7.58 – 7.52 (m, 1H), 2.58 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 164.41, 162.70, 151.85, 149.34, 137.16, 133.87, 129.32, 129.02, 128.28, 125.56, 121.39, 12.83. MS (ESI) m/z calcd. for $C_{14}H_{13}N_2O_2$ ([M + H]$^+$) 241.1, found 241.2

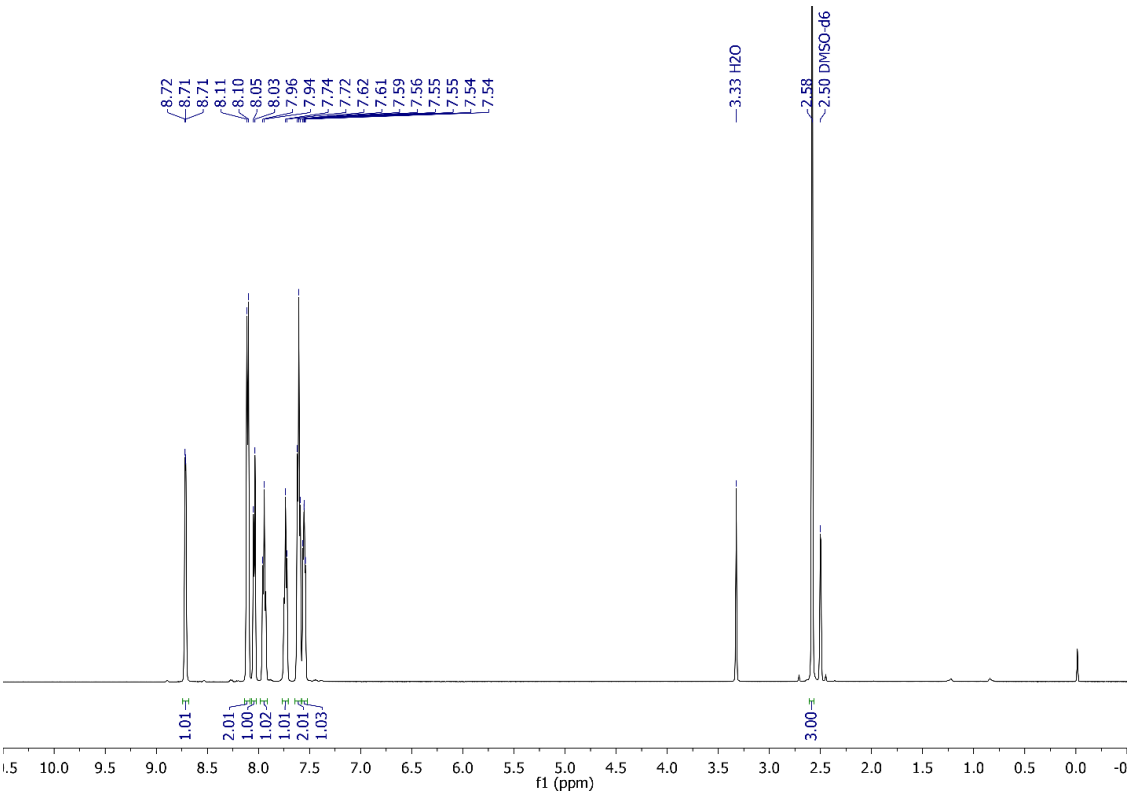



**Figure S75.** [1]H qNMR (500 MHz) spectrum of compound **3s** in DMSO-$d_6$

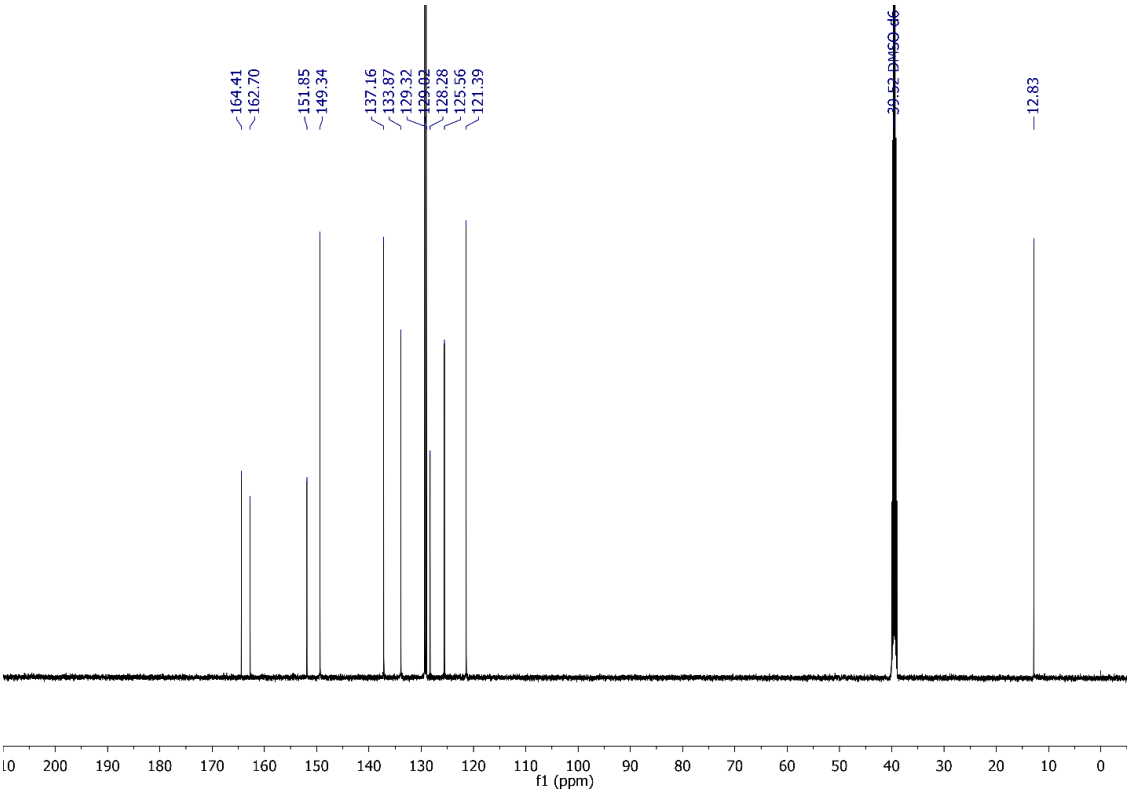
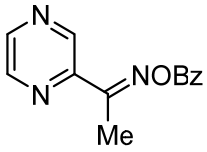



**Figure S76.** [13]C NMR (126 MHz) spectrum of **3s** in DMSO-$d_6$.




Compound **3t** was synthesized according to general method C using 2-acetylpyrazine (2.422 g, 20 mmol), $Et_3N$ (6.97 mL, 50 mmol), hydroxylamine hydrochloride (2.08 g, 30 mmol), and ethanol (40 mL). Then the crude material of the first step was reacted with pyridine (1.45 mL, 18 mmol), benzoyl chloride (2.1 mL, 18 mmol), in methylene chloride (55 mL) and according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (2.35 g, 54%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 9.20 (s, 1H), 8.80 (s, 2H), 8.12 (d, $J$ = 7.9 Hz, 2H), 7.75 (t, $J$ = 6.8 Hz, 1H), 7.62 (t, $J$ = 7.2 Hz, 2H), 2.59 (s, 3H). $^{13}$C NMR (126 MHz, DMSO) δ 163.08, 162.56, 147.69, 146.04, 144.19, 142.61, 134.04, 129.41, 129.08, 128.03, 12.75. MS (ESI) m/z calcd. for $C_{13}H_{12}N_3O_2$ ($[M + H]^+$) 242.1, found 242.2

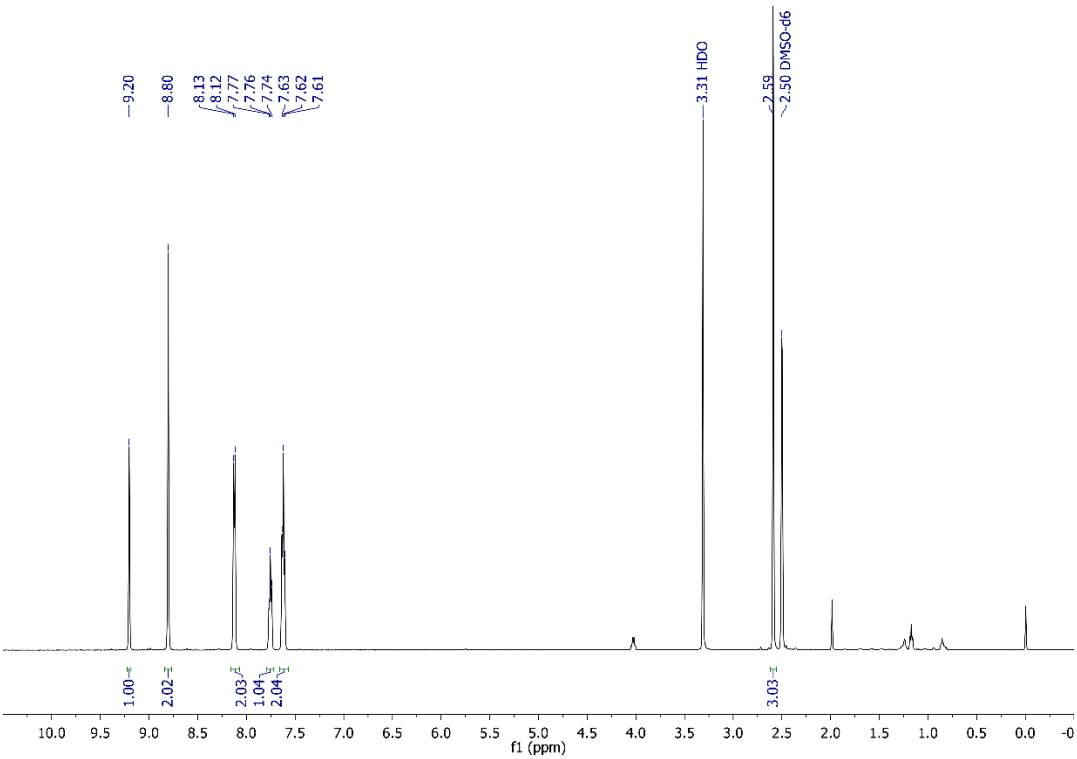



**Figure S77.** [1]H qNMR (500 MHz) spectrum of compound **3t** in DMSO-$d_6$

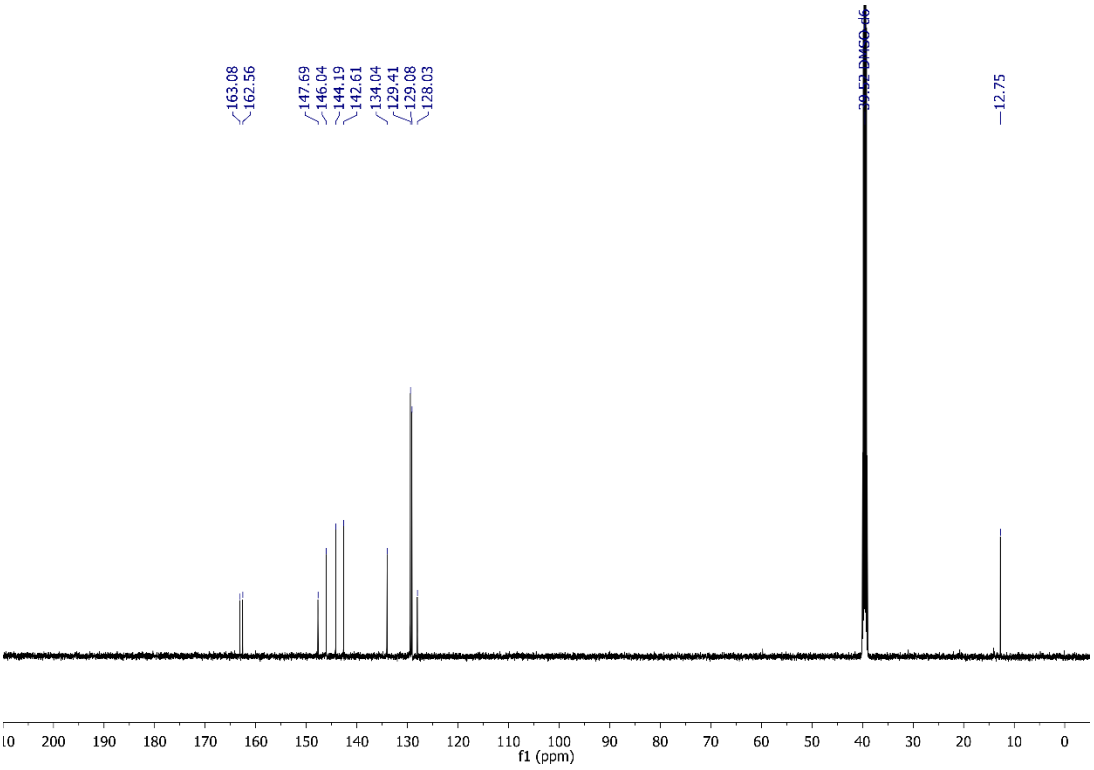
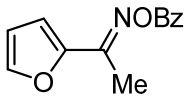



**Figure S78.** [13]C NMR (126 MHz) spectrum of **3t** in DMSO-$d_6$.




Compound **3u** a was synthesized according to general method A using 1-(furan-2-yl)ethan-1-one (5.0 mL, 50 mmol), pyridine (10 mL, 125 mmol), hydroxylamine hydrochloride (5.212 g, 75 mmol), and ethanol (100 mL). Then the crude material (5.8 g) of the first step was reacted with pyridine (3.73 mL, 46.4 mmol), benzoyl chloride (5.38 mL, 46.4 mmol), in methylene chloride (28 mL) and hexanes (112 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a dark brown solid. The product required further purification and was dissolved in hot $CH_2Cl_2$/Hexanes, filtered, and recrystallized to afford the product as a brown solid (4.212 g, 39%). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.07 (d, $J$ = 7.3 Hz, 2H), 7.93 (s, 1H), 7.71 (t, $J$ = 7.4 Hz, 1H), 7.58 (t, $J$ = 7.7 Hz, 2H), 7.22 (d, $J$ = 3.4 Hz, 1H), 6.68 (dd, $J$ = 3.3, 1.6 Hz, 1H), 2.43 (s, 3H). $^{13}$C NMR (126 MHz, DMSO) δ 162.68, 154.93, 147.61, 146.12, 133.72, 129.25, 128.94, 128.42, 115.10, 112.13, 13.16. MS (ESI) M/Z CALCD. FOR C13H11NO3 ($[M + H]^+$) 230.1, found 230.1

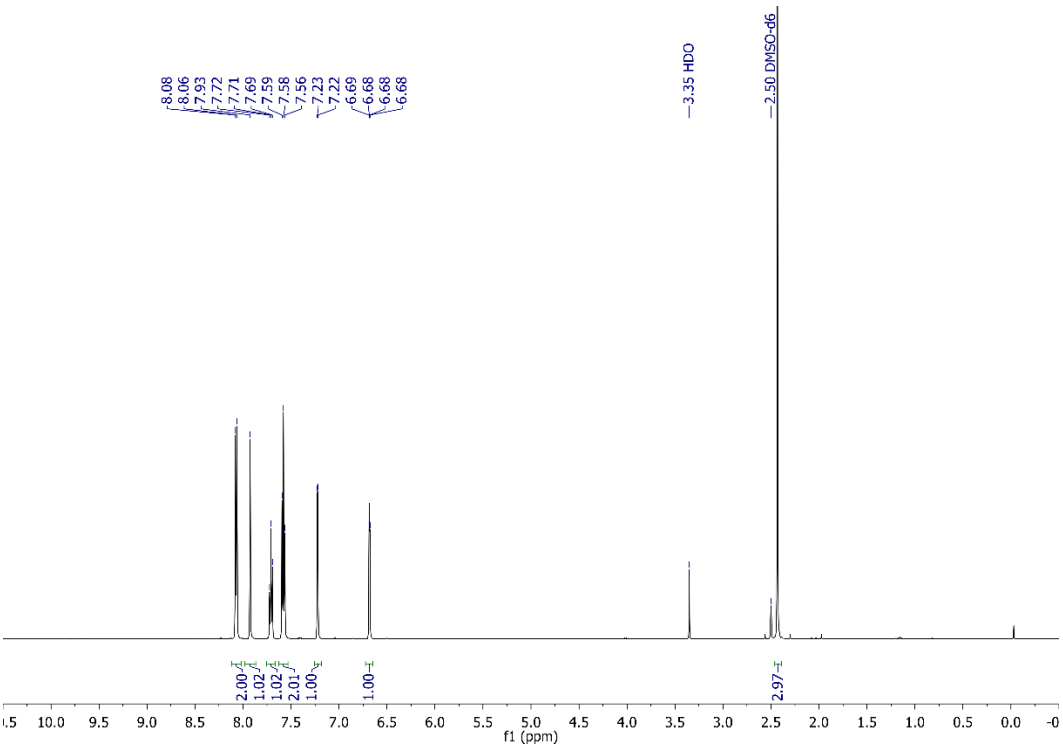



**Figure S79.** $^{1}$H qNMR (500 MHz) spectrum of compound **3u** in DMSO-$d_6$

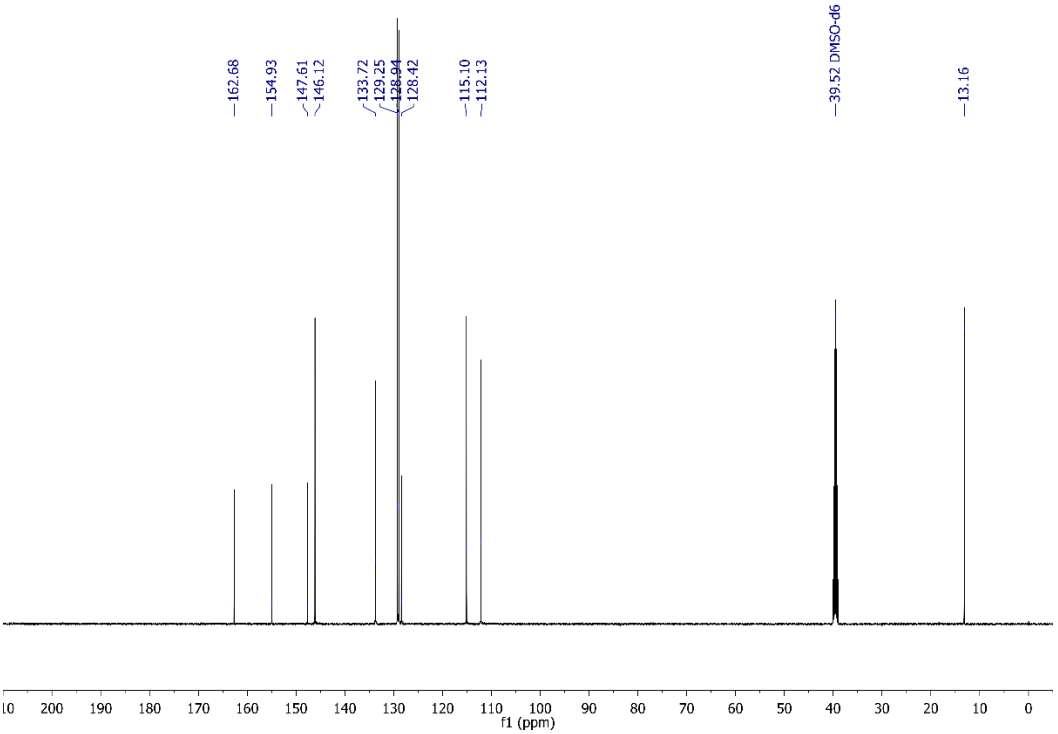
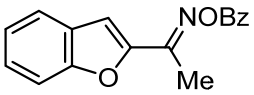



**Figure S80.** $^{13}$C NMR (126 MHz) spectrum of **3u** in DMSO-$d_6$.




Compound **3n** was synthesized according to general method B using 1-(benzofuran-2-yl)ethan-1-one (4.00 g, 25 mmol), pyridine (5.03 mL, 62.5 mmol), hydroxylamine hydrochloride (2.61 g, 37.5 mmol), and ethanol (50 mL). Then the crude material of the first step was reacted with pyridine (1.61 mL, 20 mmol), benzoyl chloride (2.32 mL, 20 mmol), in methylene chloride (60 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (2.645 g, 47%).

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.10 (d, $J$ = 7.1 Hz, 2H), 7.78 – 7.67 (m, 4H), 7.59 (t, $J$ = 6.9 Hz, 2H), 7.45 (t, $J$ = 7.3 Hz, 1H), 7.32 (t, $J$ = 7.1 Hz, 1H), 2.54 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 162.59, 155.35, 154.94, 149.57, 133.89, 129.37, 129.02, 128.23, 127.26, 126.97, 123.63, 122.22, 111.65, 111.62, 13.35. MS (ESI) m/z calcd. for $C_{17}H_{15}NO_3$ ($[M + H]^+$) 280.1, found 280.1

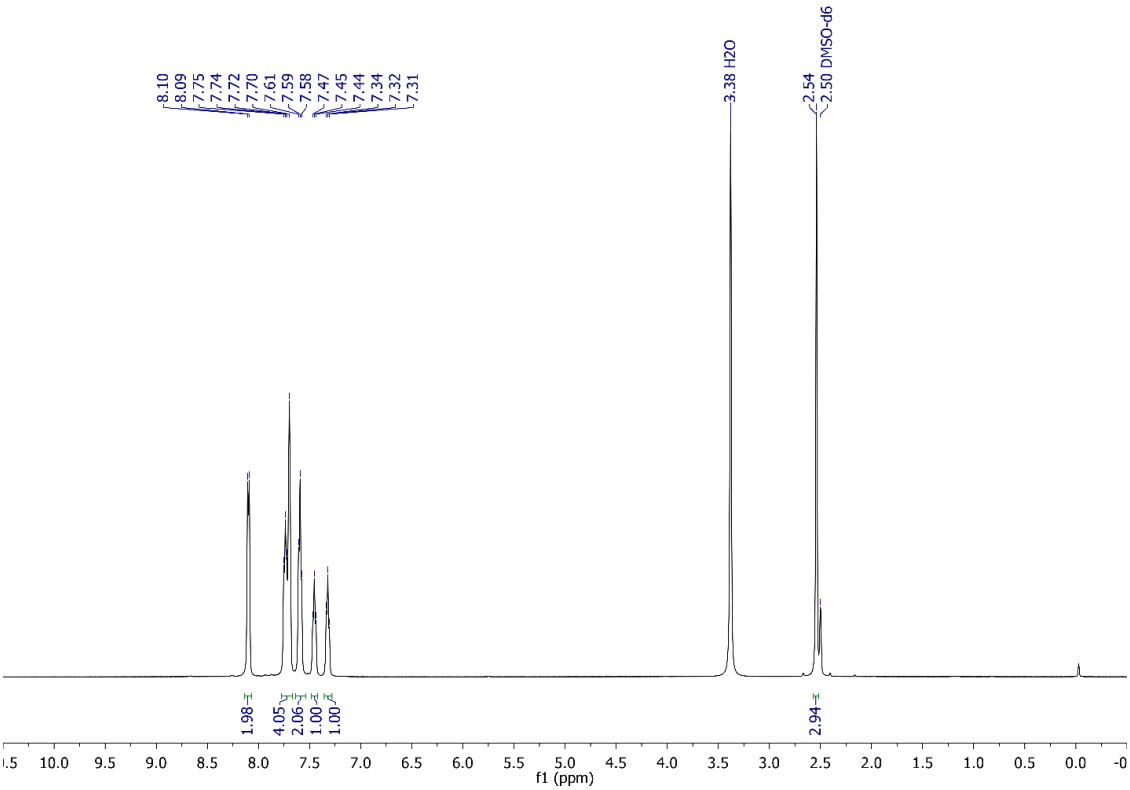



**Figure S81.** [1]H qNMR (500 MHz) spectrum of compound **3n** in DMSO-$d_6$

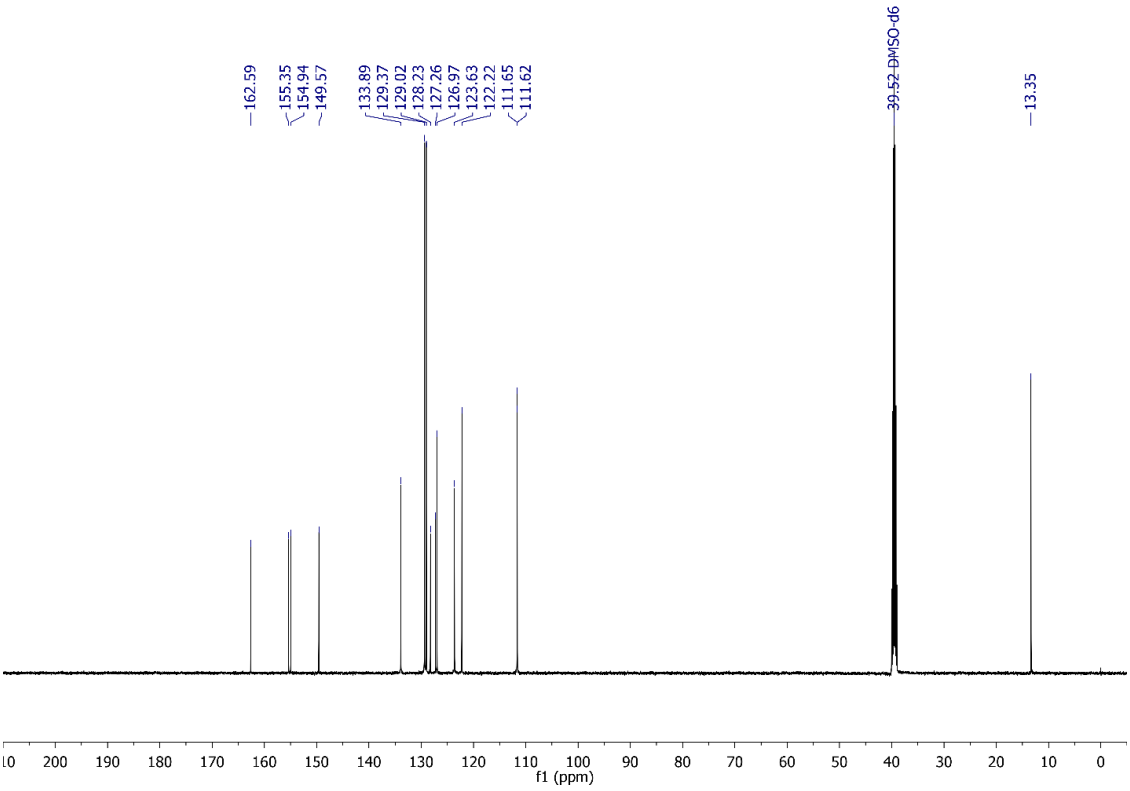
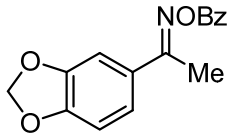



**Figure S82.** [13]C NMR (126 MHz) spectrum of **3n** in DMSO-$d_6$.




Compound **3k** was synthesized according to general method A using 3′,4′-(Methylenedioxy)acetophenone (1.970 g, 12.0 mmol), pyridine (2.42 mL, 30 mmol), hydroxylamine hydrochloride (1.250 g, 18.0 mmol), and ethanol (24 mL). Then the crude material of the first step was reacted with pyridine (0.90 mL, 11.16 mmol), benzoyl chloride (1.30 mL, 11.16 mmol), in methylene chloride (7 mL) and hexanes (27 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (2.134g, 63%).

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.11 – 8.05 (m, 2H), 7.72 (t, $J$ = 6.8 Hz, 1H), 7.59 (t, $J$ = 7.5 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.06 – 7.01 (m, 1H), 6.12 (s, 2H), 2.47 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 163.37, 162.89, 149.53, 147.70, 133.68, 129.20, 128.97, 128.58, 128.23, 121.99, 108.28, 106.54, 101.69, 14.28. MS (ESI) m/z calcd. for $C_{16}H_{14}NO_4$ ([M + H]+) 284.1, found 284.1

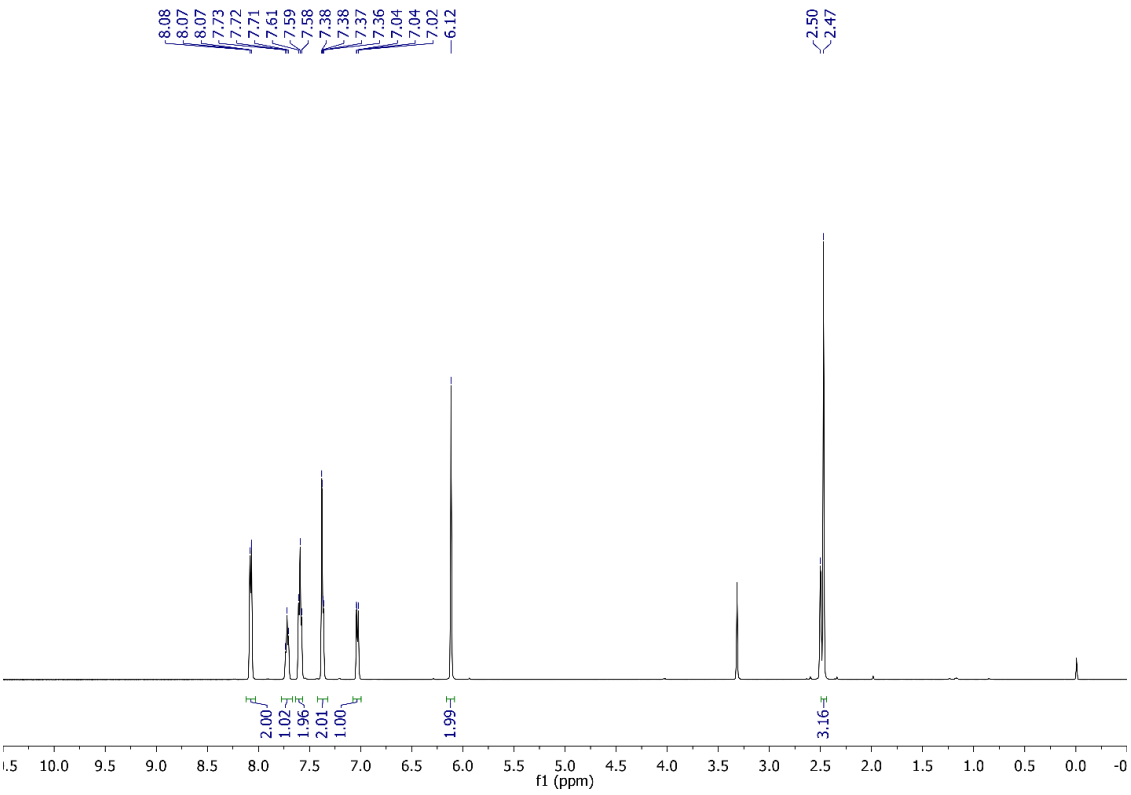



**Figure S83.** [1]H qNMR (500 MHz) spectrum of compound **3k** in DMSO-$d_6$

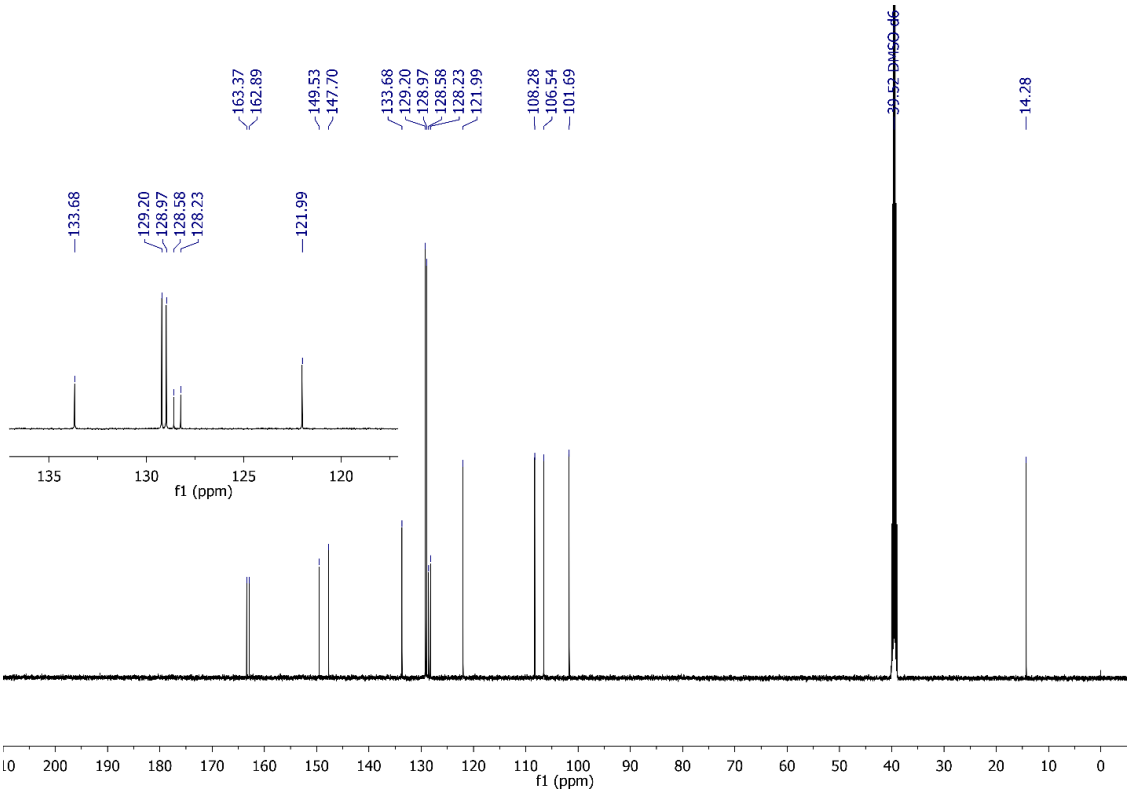
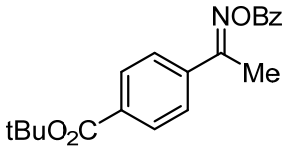



**Figure S84.** [13]C NMR (126 MHz) spectrum of **3k** in DMSO-$d_6$.




Compound **3m** was synthesized according to general method A using tert-butyl 4-acetylbenzoate (1.652 g, 7.5 mmol), pyridine (1.51 mL, 18.75 mmol), hydroxylamine hydrochloride (782 mg, 11.25 mmol), and ethanol (15.0 mL). Then the crude material of the first step was reacted with pyridine (0.610 mL, 7.5 mmol), benzoyl chloride (0. 870 mL, 7.5 mmol), in methylene chloride (23 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$ to afford the product as a white crystalline solid (1.02 g, 40%).

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.10 (d, $J$ = 8.0 Hz, 2H), 8.00 (d, $J$ = 8.3 Hz, 2H), 7.94 (d, $J$ = 8.0 Hz, 2H), 7.73 (t, $J$ = 7.4 Hz, 1H), 7.60 (t, $J$ = 7.6 Hz, 2H), 2.55 (s, 3H), 1.56 (s, 9H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 164.37, 163.38, 162.78, 138.41, 133.85, 133.07, 129.31, 129.27, 129.02, 128.35, 127.19, 81.17, 27.73, 14.41. MS (ESI) m/z calcd. for $C_{20}H_{22}NO_4$ ($[M + H]^+$) 340.1, found 340.2

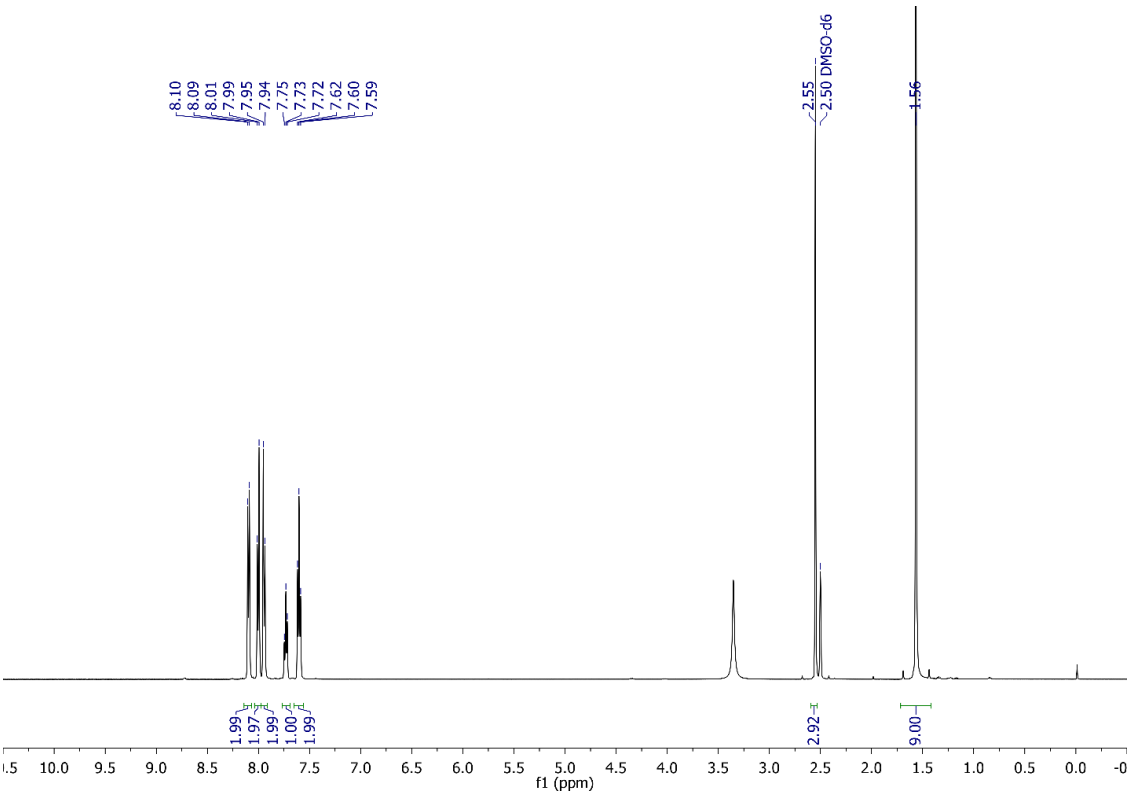



**Figure S85.** [1]H qNMR (500 MHz) spectrum of compound **3m** in DMSO-$d_6$

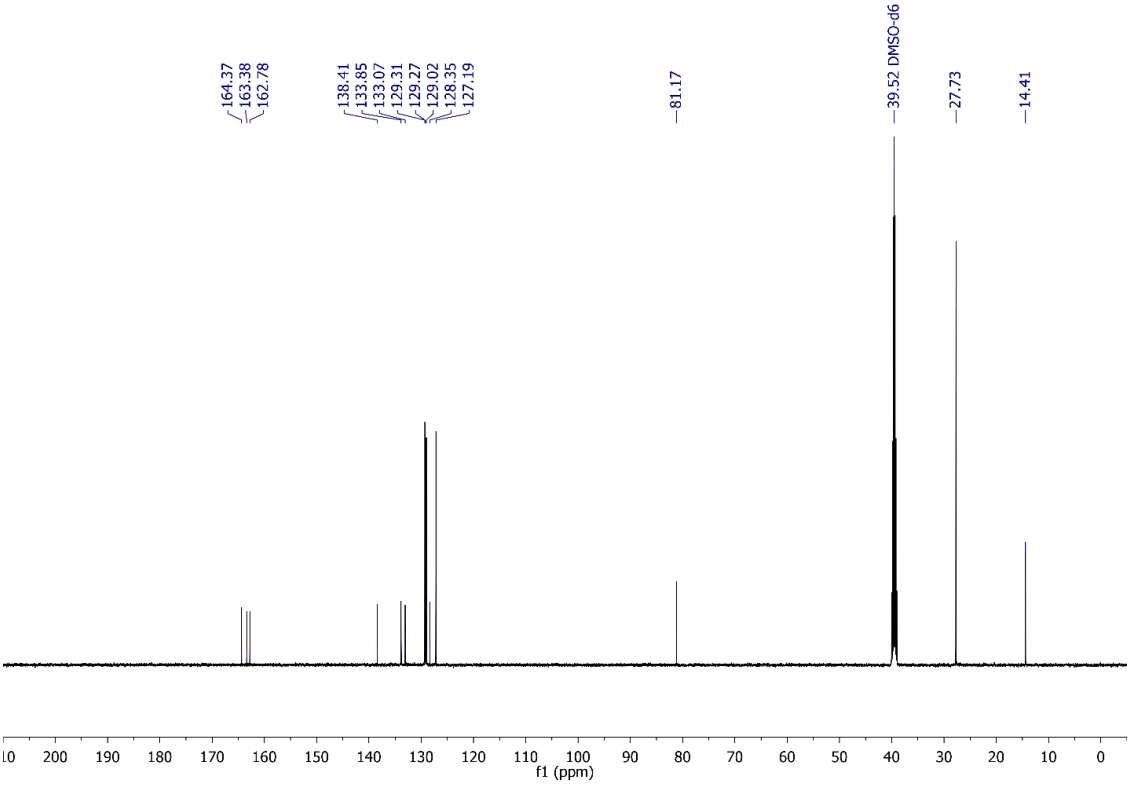
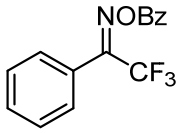



**Figure S86.** [13]C NMR (126 MHz) spectrum of **3m** in DMSO-$d_6$.




Compound **3p** was synthesized according to general method A using 2,2,2-trifluoro-1-phenylethan-1-one (1.80 g, 10.0 mmol), pyridine (2.01 mL, 25.0 mmol), hydroxylamine hydrochloride (1.042 g, 15.0 mmol), and ethanol (20 mL). Then the crude material of the first step was reacted with pyridine (0.81 mL, 10.0 mmol), benzoyl chloride (1.15 mL, 10.0 mmol), in methylene chloride (6 mL) and hexanes (24 ml) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (1.299 g, 44%). The remaining mother liquor contained product which could not be purified by further recrystallization.$^1$H NMR (500 MHz, DMSO-$d_6$) δ 7.74 (d, $J$ = 7.8 Hz, 1H), 7.72 – 7.60 (m, 3H), 7.50 (t, $J$ = 7.1 Hz, 1H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 161.57, 153.93 (q, $J$ = 32.7 Hz), 134.44, 131.63, 129.35, 129.05, 128.92, 128.23, 125.30, 120.01 (q, $J$ = 276.7 Hz). $^{19}$F NMR (471 MHz, DMSO) δ -65.93. MS (ESI) m/z calcd. for $C_{15}H_{10}F_3NO_2$ ([M + H]$^+$) 294.1, found 294.2.

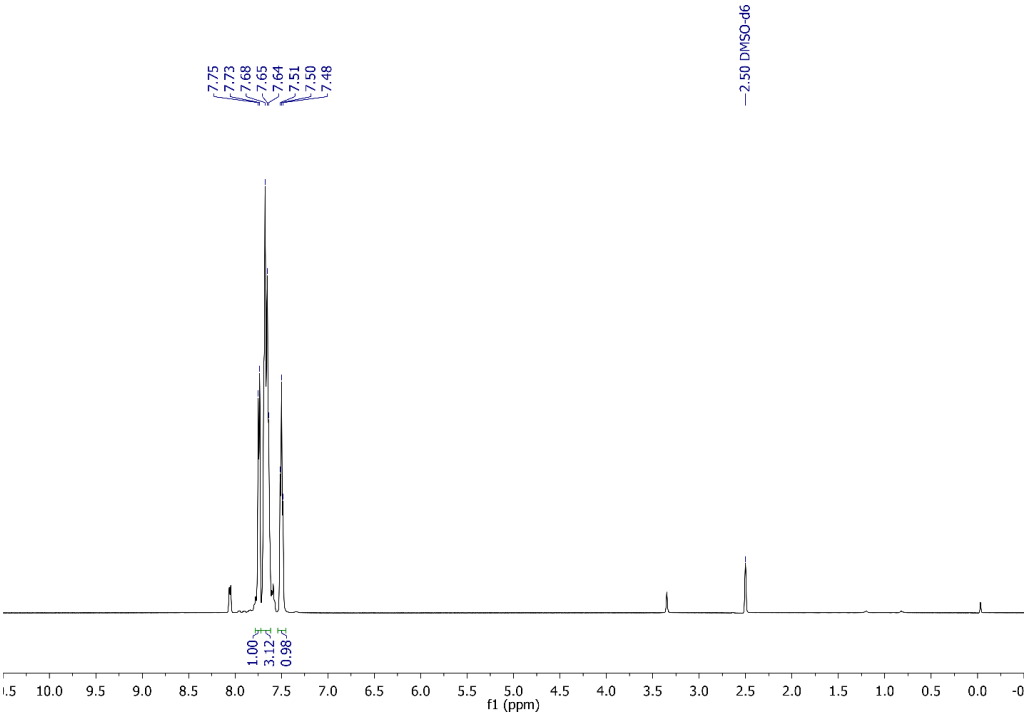



**Figure S87.** [1]H qNMR (500 MHz) spectrum of compound **3p** in DMSO-$d_6$

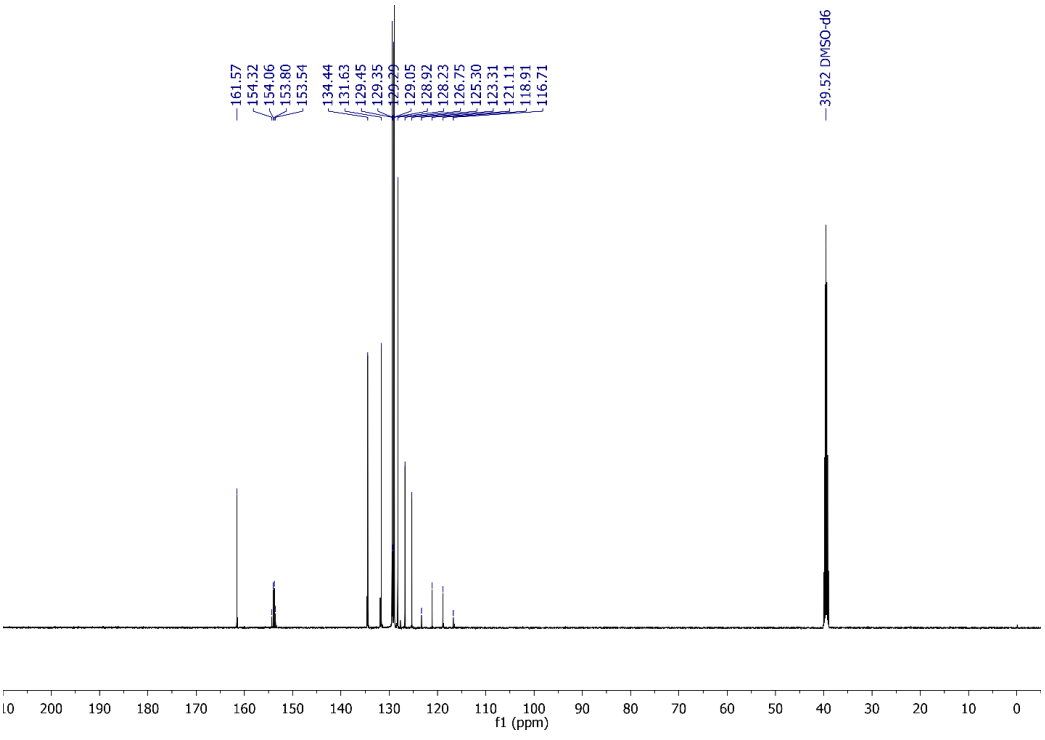



**Figure S88.** [13]C NMR (126 MHz) spectrum of **3p** in DMSO-$d_6$.

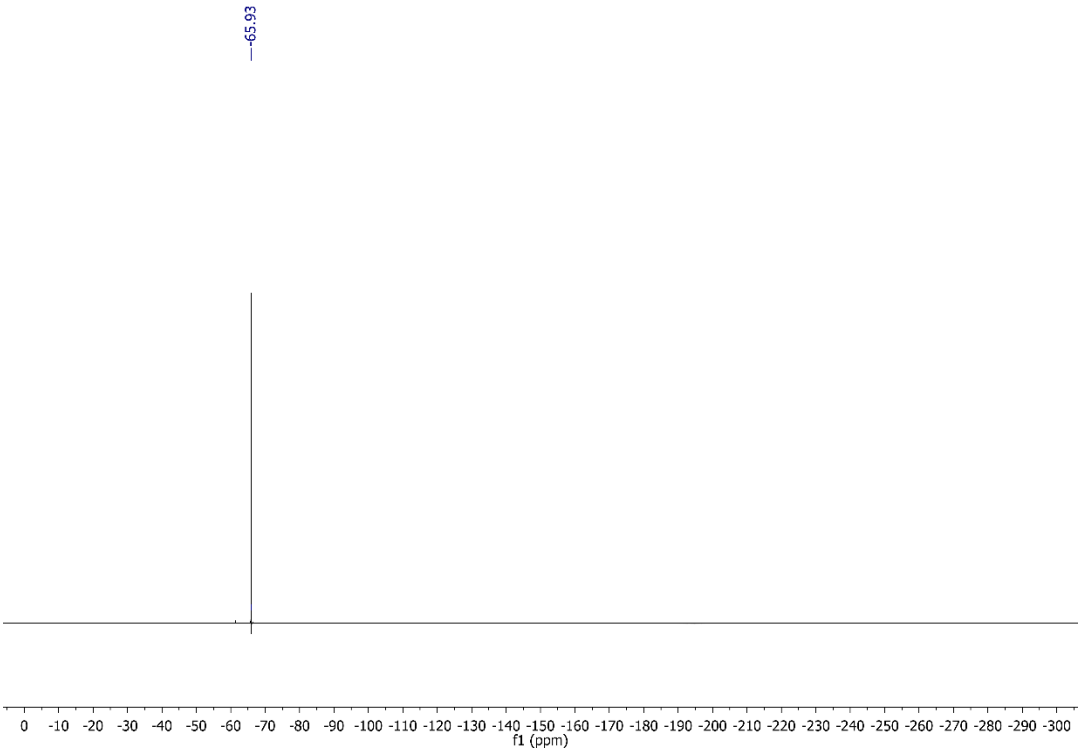
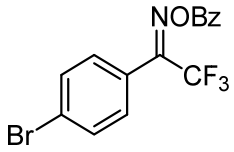



**Figure S89.** $^{19}$F NMR (471 MHz) spectrum of compound **3p** in DMSO-$d_6$.




Compound **3q** was synthesized according to general method A using 1-(4-bromophenyl)-2,2,2-trifluoroethan-1-one (2.532 g, 10 mmol), pyridine (2.01 mL, 25.0 mmol), hydroxylamine hydrochloride (1.042 g, 15 mmol), and ethanol (20 mL). Then the crude material of the first step was reacted with pyridine ( 0.887 mL, 11 mmol), benzoyl chloride (1.16 mL, 10 mmol), in methylene chloride (6 mL) and hexanes (24 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes (-20 °C and rapid filtration required) to afford the product as a white crystalline solid (1.1 g, 30%).$^1$H NMR (500 MHz, DMSO-$d_6$) δ 7.88 (d, $J$ = 8.6 Hz, 2H), 7.78 (d, $J$ = 7.3 Hz, 2H), 7.74 – 7.66 (m, 3H), 7.55 (t, $J$ = 7.8 Hz, 2H). $^{13}$C NMR (126 MHz, DMSO) δ 161.55, 153.24, 152.97, 152.71, 152.45, 134.57, 130.53, 129.44, 129.19, 126.67, 125.54, 124.35, 123.14, 120.94, 118.74, 116.54. $^{19}$F NMR (471 MHz, DMSO) δ -65.84.MS (ESI) m/z calcd. For $C_{14}H_{10}F_3BrNO_2$ ([M + H]+) 372.0, found 372.1

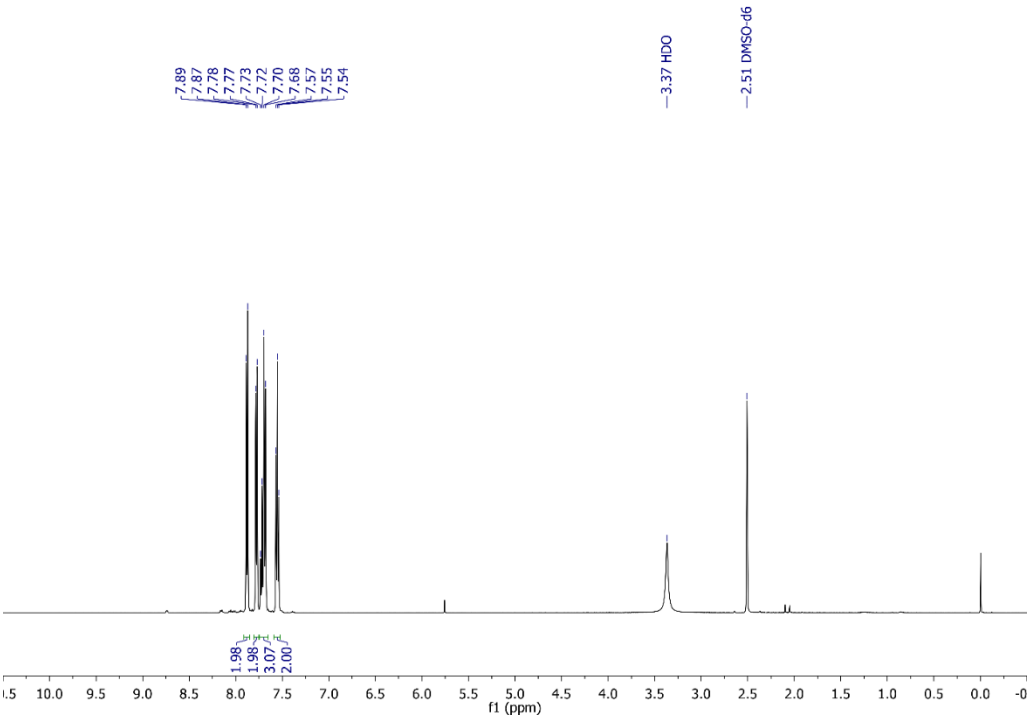



**Figure S90.** [1]H qNMR (500 MHz) spectrum of compound **3q** in DMSO-$d_6$

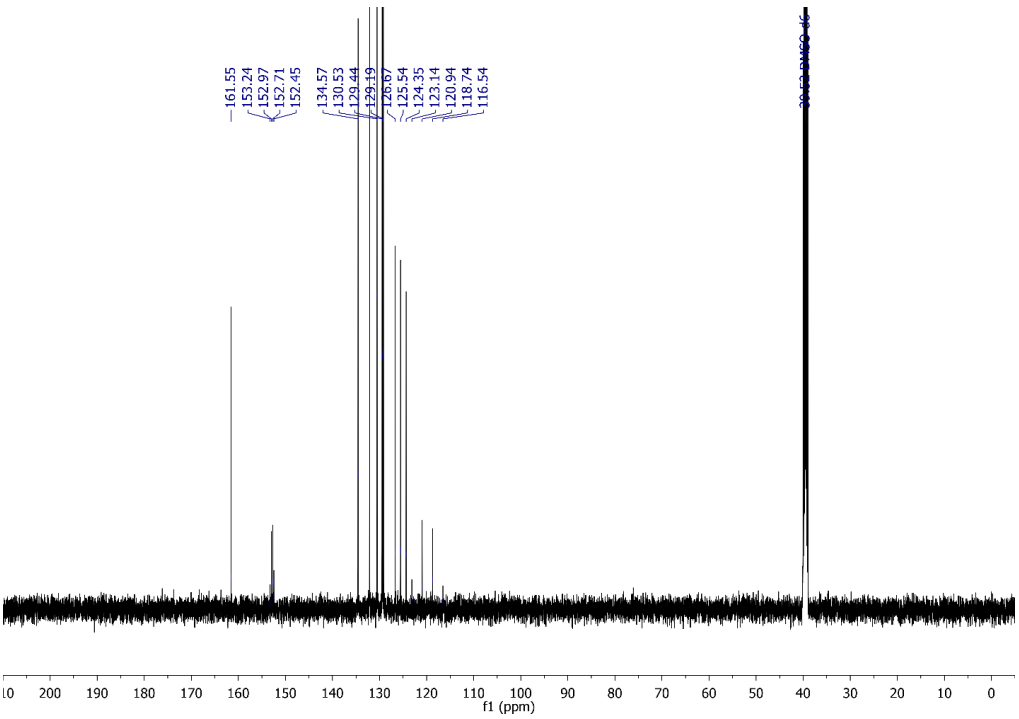



**Figure S91.** [13]C NMR (126 MHz) spectrum of **3q** in DMSO-$d_6$.

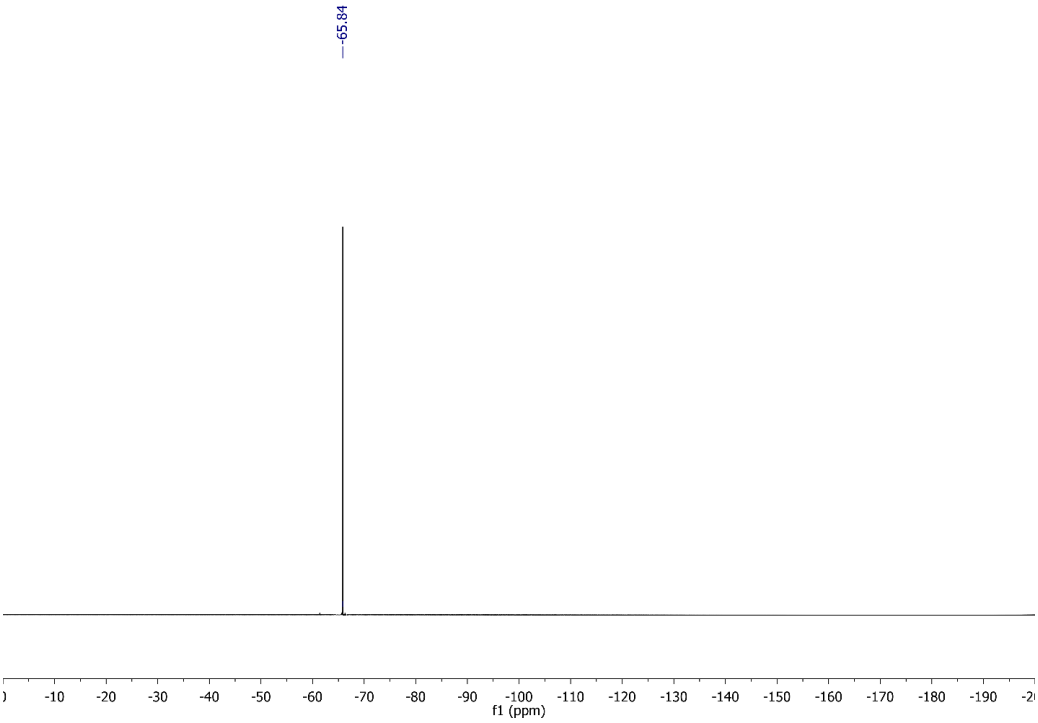
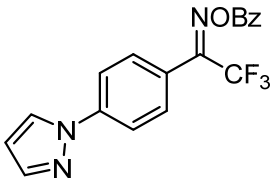



**Figure S92.** $^{19}$F NMR (471 MHz) spectrum of compound **3q** in DMSO-$d_6$.




Compound **3r** was synthesized according to general method A using 1-(4-(1H-pyrazol-1-yl)phenyl)-2,2,2-trifluoroethan-1-one[6] (2.40 g, 10.0 mmol), pyridine (2.0 mL, 25.0 mmol), hydroxylamine hydrochloride (1.042 g, 15.0 mmol), and ethanol (20 mL). Then the crude material of the first step was reacted with triethylamine (1.35 mL, 9.68 mmol), benzoyl chloride (1.06 mL, 9.68 mmol), in methylene chloride (6 mL) and hexanes (24 mL) according to the general method. The crude product was recrystallized from $CH_2Cl_2$/Hexanes to afford the product as a white crystalline solid (3.233 g, 90%). The crystalline solid is observed to be a mixture of isomers the oxime. $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.66 (dd, $J$ = 9.3, 2.5 Hz, 1H), 8.16 – 8.12 (m, 1H), 8.08 (ddd, $J$ = 11.5, 7.7, 1.6 Hz, 2H), 7.89 – 7.76 (m, 5H), 7.71 – 7.62 (m, 1H), 7.56 – 7.50 (m, 1H), 6.62 (dt, $J$ = 2.8, 1.5 Hz, 1H). $^{13}$C NMR (126 MHz, DMSO) δ 161.65, 161.42, 153.39, 153.35, 153.14, 153.10, 152.88, 152.86, 152.62, 142.04, 141.95, 141.66, 134.68, 134.45, 130.61, 130.17, 129.47, 129.44, 129.32, 129.13, 128.28, 128.24, 126.78, 126.68, 124.92, 123.37, 122.37, 121.17, 121.03, 118.97, 118.77, 118.28, 118.26, 116.77, 116.51, 114.26, 108.68, 108.66. MS (ESI) m/z calcd. for $C_{18}H_{12}F_3N_3O_2$ ([M + H]$^+$) 360.1, found 360.1

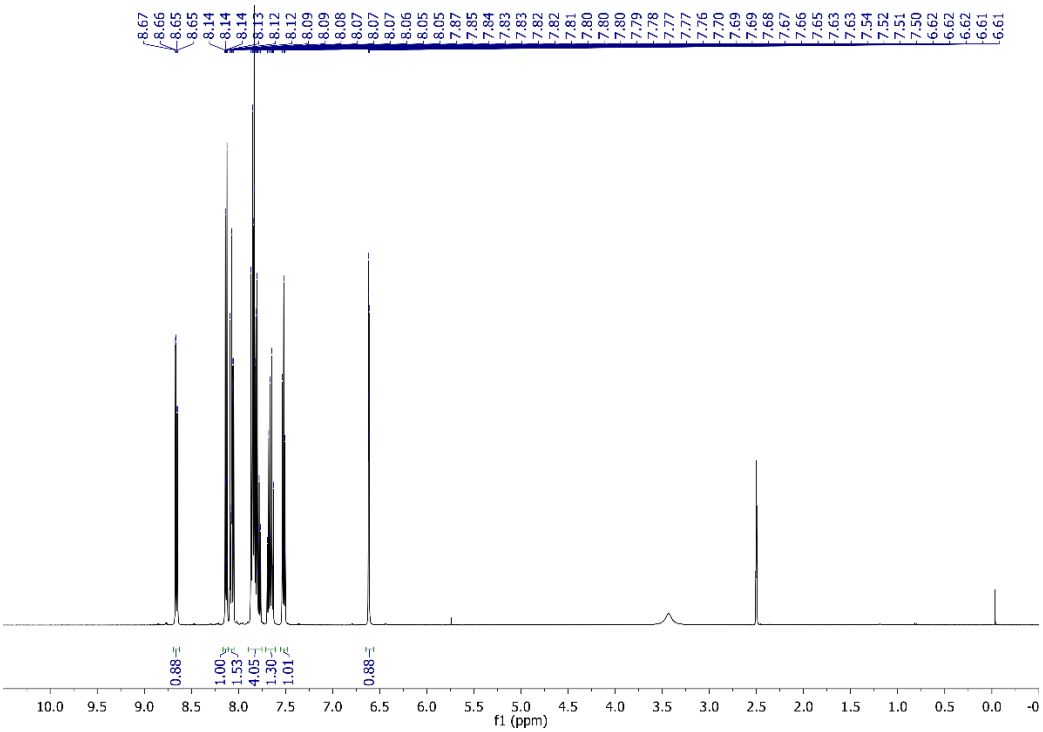


**Figure S93.** $^{1}$H qNMR (500 MHz) spectrum of **3r** in $CD_3CN$.

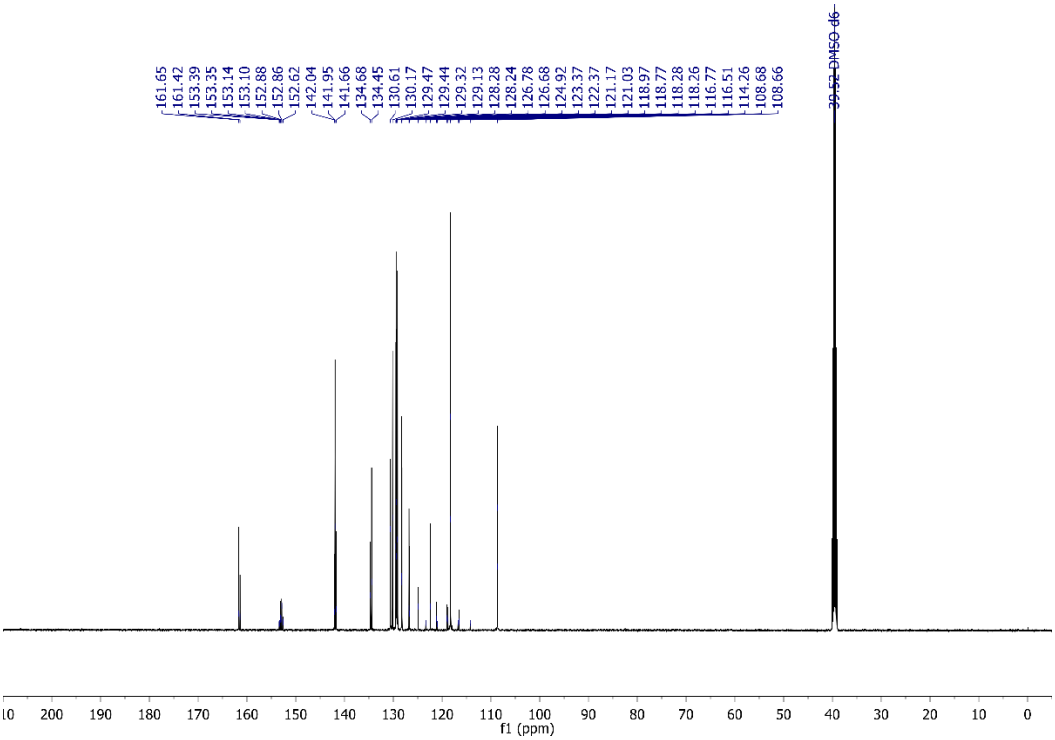


**Figure S94.** $^{13}$C NMR (126 MHz) spectrum of **3r** in DMSO-$d_6$.

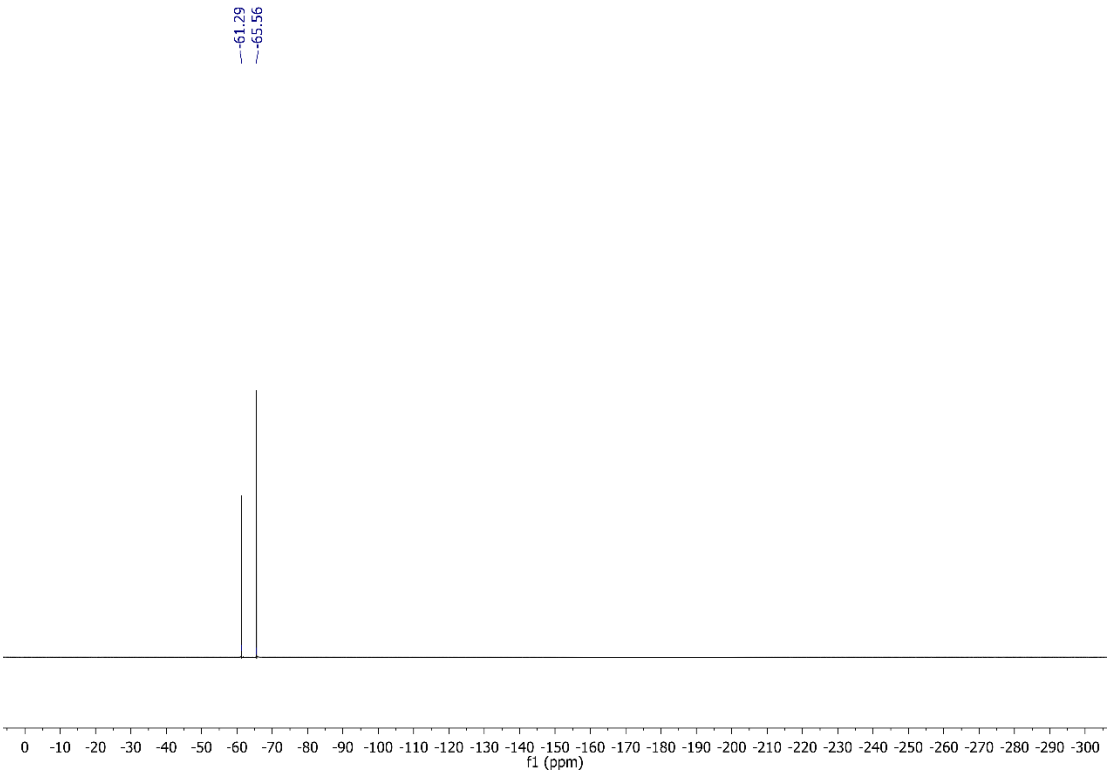
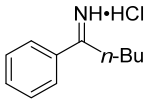


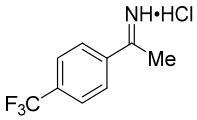

**Figure S95.** $^{19}F$ NMR (471 MHz) spectrum of compound **3r** in DMSO-$d_6$.

**6. Synthesis of Iminium Hydrochlorides**

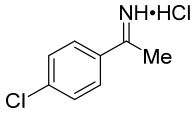
**3. Synthesis of Substrates**



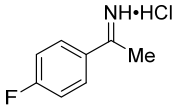

**Synthesis of 6l•HCl** was prepared following a literature procedure.[7]



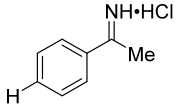

**Synthesis of 6b•HCl** was prepared following a literature procedure.[7]



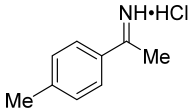

**Synthesis of 6c•HCl** was prepared following a literature procedure.[7]



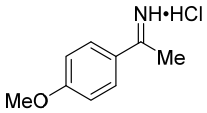

**Synthesis of 6d•HCl** was prepared following a literature procedure.[7]



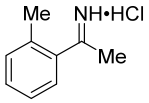

**Synthesis of 6a•HCl** was prepared following a literature procedure.[7]



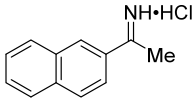

**Synthesis of 6e•HCl** was prepared following a literature procedure.[7]



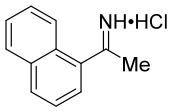

**Synthesis of 6f•HCl** was prepared following a literature procedure.[7]



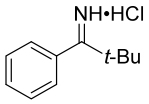

**Synthesis of 6g•HCl** was prepared following a literature procedure.[7]




**Synthesis of 6h•HCl** was prepared following a literature procedure.[7]




**Synthesis of 6i•HCl** was prepared following a literature procedure.[7]




**Synthesis of 6m•HCl** was prepared following a literature procedure.[7]

## 7. UV-Vis Absorption/Emission Spectra and Stern-Volmer Plot

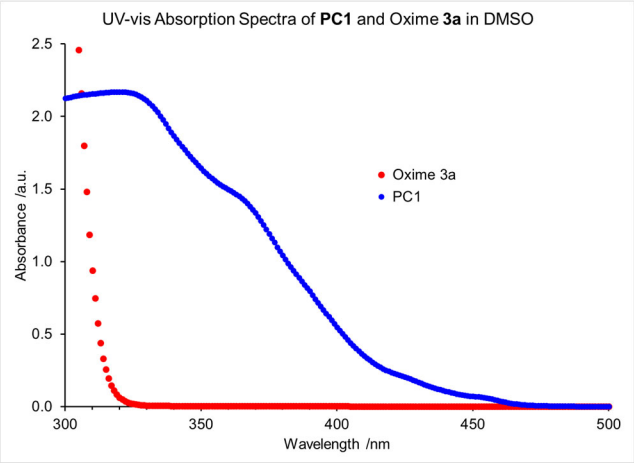



**Figure S96.** (A) UV-vis absorption spectra of **PC1** and oxime **3a** in DMSO illustrating the absorbance edge for PC1 (ca. 470 nm) and **3a** (ca. 330 nm).

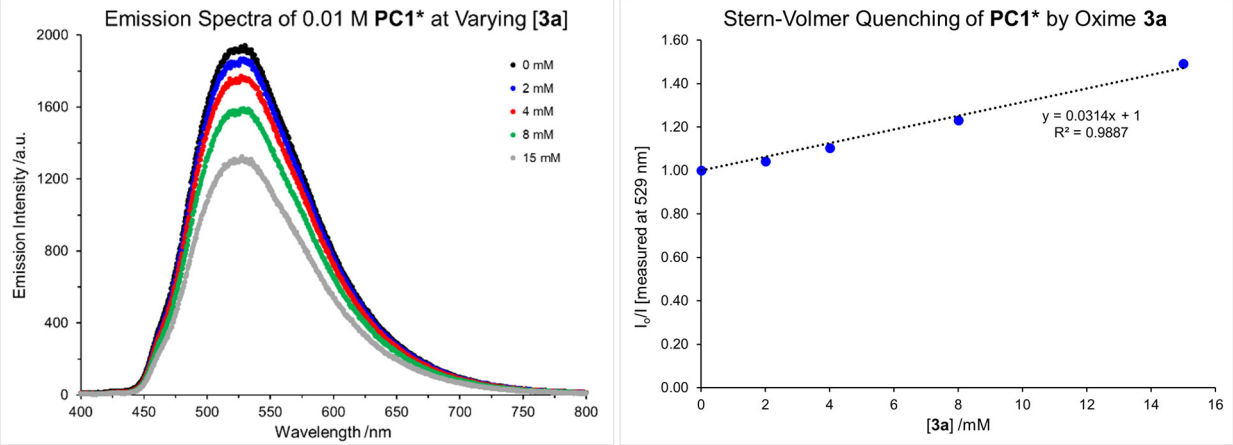



**Figure S97.** (Left) Emission spectra of **PC1*** ([**PC1**] = 0.01 M in DMSO) as a function of concentration of oxime **3a** (0, 2, 4, 8, 15 mM) in DMSO using $\lambda_{exc}$ = 380 nm. (Right) Stern-Volmer plot for the quenching of **PC1*** ([**PC1**] = 0.01 M in DMSO) by oxime **3a** ($\lambda_{ex}$ = 380 nm, $\lambda_{em}$ = 529 nm).

If one wants to estimate the rate constant for the quenching event ($k_q$), the data from the Stern-Volmer plot in **Figure S93B** can be fit to the following Stern-Volmer equation:[8]

$$I_o/I = 1 + K_{SV}[\mathbf{3a}]$$

where $I_o$ is the emission intensity of **PC1*** ([**PC1**] = 0.01 M) at 529 nm with no oxime present ([**3a**] = 0 mM), $I$ is the emission intensity of **PC1*** ([**PC1**] = 0.01 M) at 529 nm with oxime present ([**3a**] = 2 , 4, 8, 15 mM) and the $K_{SV}$ is the Stern-Volmer constant. Since $K_{SV} = k_q \bullet \tau_o$ where $\tau_o$ is the lifetime of the excited state (**PC1***), if one estimates this lifetime to be between 0.5 and 2.5 μs,[9] typical values for Ir-based photocatalysts containing two phenyl-pyridyl ligands and one bipyridyl ligand (e.g. $Ir(ppy)_2dtbbpy]PF_6$, $\tau_o$ = 0.54 μs), one arrives at an estimated $k_q$ value between $1.3 \times 10^7$ $M^{-1} \bullet s^{-1}$ and $6.3 \times 10^7$ $M^{-1} \bullet s^{-1}$.

## 8. DFT Computational Study

### 8.1 Computational Method

All of the quantum chemical calculations were performed using the *Gaussian 16* program.[10] Geometry optimizations and frequency calculations were performed at the M06-2X/6-31+G(d,p) level of theory[11,12] with SMD[13] solvation in DMSO. A "tight" geometry convergence (opt=tight), an "ultrafine" integration grid, and a 2-electron integral accuracy of $10^{-14}$ (int=(Acc2E=14,ultrafine)) were used. The stationary points were characterized by the presence of only positive eigenvalues of the Hessian for minima. All Gibbs energies were calculated for a temperature of 298.15 K and a pressure of 1 atm using the quasiharmonic approximation proposed by Cramer and Truhlar, in which all of the real vibrational frequencies lower than 100 $cm^{-1}$ were set to 100 $cm^{-1}$.[14] All molecular structures were rendered in CYLView[15] in combination with POV-Ray 3.6.[16] All CYLView generated images have the following color-coding for labeling elements: C = silver, H = white, O = light red, N = blue.

The DFT-calculated reduction potentials against SCE were obtained using the following equation:

$$\begin{aligned} E^{\circ,calc} &= -[(\text{energy of reduced species} - \text{energy of oxidized species})/(n_e \bullet F)] - 3.96\ \text{V} - 0.244\ \text{V} \\ &= [EA/(n_e \bullet F)] - 3.96\ \text{V} - 0.244\ \text{V} \end{aligned}$$

where $n_e = 1$, and $n_e \bullet F = 23.061\ \text{kcal} \bullet \text{mol}^{-1} \bullet \text{V}^{-1}$. The adoption of the SHE reference potential is explained below. In the second equality, *EA* refers to the electron affinity and follows the conventional definition, namely, energy of the oxidized species minus energy of the reduced species. More positive values of *EA* correspond to more favorable single-electron reductions. To convert *EA* and $E^{\circ,calc}$ to reduction potential values that are comparable to experiment, appropriate values of SHE and conversion factors between different electrodes needed to be identified. The value of SHE in DMSO of 3.96 V was adopted from the review of Marenich et al.,[17] while the conversion factor from SHE to SCE (–0.244 V) was taken from Pavlishchuk et al.[18]

## 8.2 DFT Calculations Regarding the PCET Reduction of 4-Cyanopyridine

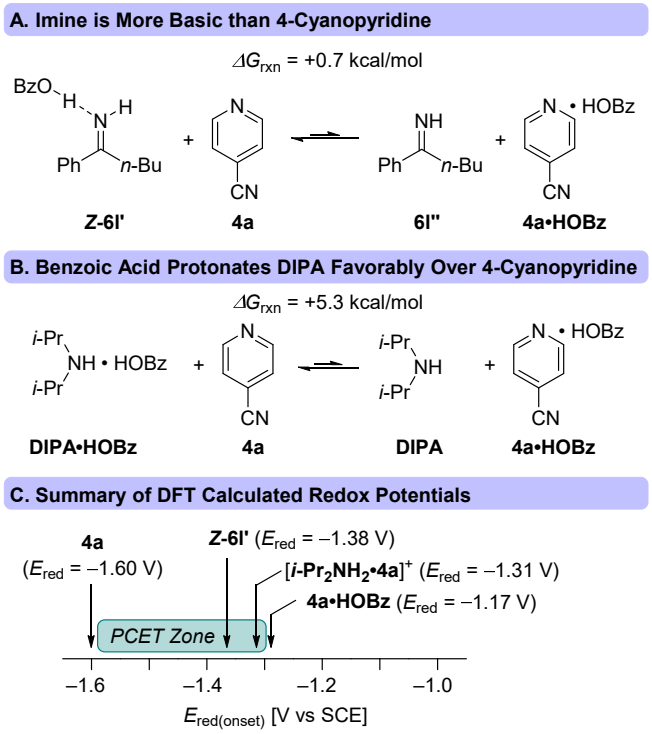
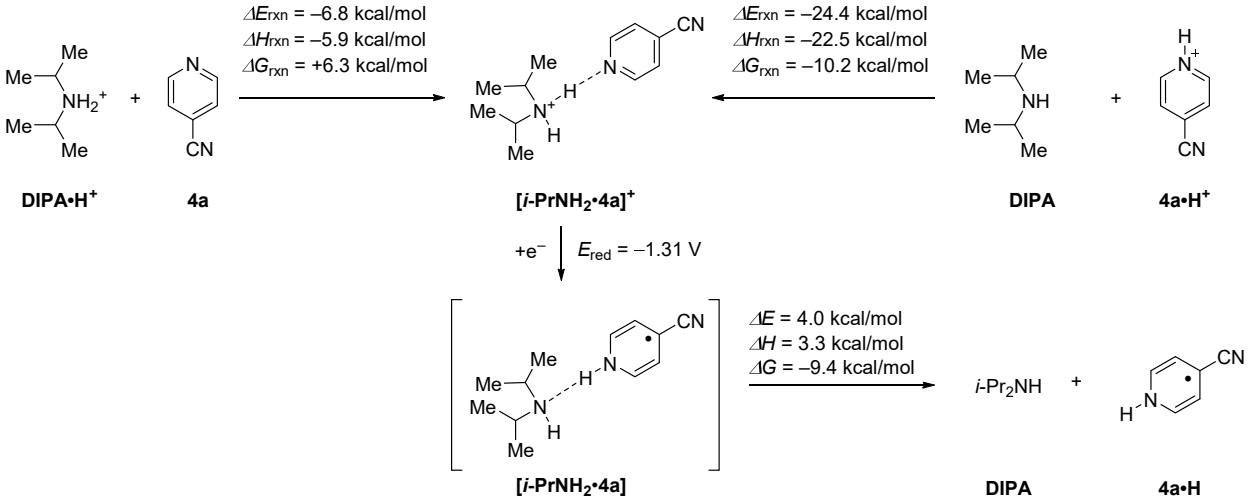
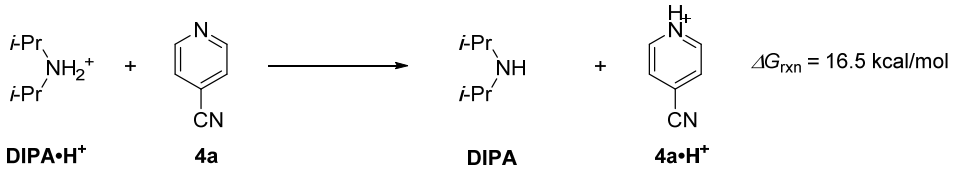



**Figure S98.** DFT calculated energies and redox potentials using M06-2X/6-31+G(d,p) SMD=DMSO.




**Scheme S99.** DFT analysis (using M06-2X/6-31+G(d,p) SMD=DMSO) of hydrogen bonded complex [***i*-PrNH₂•4a**]$^+$ and its reduction potential (vs SCE).




**Scheme S100.** DFT calculated energies (M06-2X/6-31+G(d,p) SMD=DMSO) for the proton exchange equilibrium between diisopropylammonium **DIPA•H**$^+$ and 4-cyanopyridine (**4a**).

To characterize the hydrogen bonded complex [***i*-PrNH$_2$•4a]$^+$**, the DFT data in Scheme S99 (top left) were obtained and the hydrogen-bonding interaction contributes −5.9 kcal/mol by enthalpy but is disfavored by entropy, resulting in a net +6.3 kcal/mol in Gibbs energy relative to infinitely separated **DIPA**•H$^+$ + **4a**. Thus, the hydrogen-bonding is enthalpically favorable but not strong enough to overcome the entropy loss due to complex formation. The Gibbs energy change suggests that complex formation between **DIPA**•H$^+$ and **4a** is slightly endergonic but not prohibitive.

We also calculated the energy of [***i*-PrNH$_2$•4a]$^+$** relative to the pyridinium ion **4a**•H$^+$ and neutral **DIPA**. [***i*-PrNH$_2$•4a]$^+$** is lower in energy than infinitely separated **DIPA** and **4a**•H$^+$ by 22.5 kcal/mol by enthalpy and 10.2 kcal/mol by Gibbs energy (Scheme S99, top right). The more favorable energies in this equation compared with the energy changes discussed in the preceding paragraph are a consequence of the lower stability of pyridinium **4a**•H$^+$ relative to **DIPA•H$^+$**. This is further supported by the computed equilibrium in Scheme S100.

To characterize the association of the diisoproylammonium (DIPA•H$^+$) and 4-cyanopyridine (**4a**), we used DFT calculations to evaluate the energies of two tautomerically related hydrogen-bonded complexes: the diisopropylammonium•pyridine complex **DIPA**•H$^+$…**4a** and the diisopropylamine•pyridinium complex **DIPA**…**4a**•H$^+$ (Scheme S101). The **DIPA**•H$^+$…**4a** complex could be located as a minimum. However, the "pyridinium complex" (**DIPA**…**4a**•H$^+$) could not be located as a stationary point. All attempts of full optimization of the "pyridinium complex" (**DIPA**…**4a**•H$^+$) led back to **DIPA**•H$^+$…**4a** in which the proton in the N-H$^+$…N hydrogen bond resides on the diisopropylammonium. Constraining the N$^+$–H bond of the pyridinium moiety of the complex **DIPA**…**4a**•H$^+$ at 1.02 Å (that is, the bond length found in 4-cyanopyridinium ion) led to a structure that is 12.5 kcal/mol less stable than **DIPA**•H$^+$…**4a**. These calculations suggest that the hydrogen-bonded complex associating the proton donor and acceptor is best described by the diisopropylammonium–pyridine form **DIPA**•H$^+$…**4a.** Thus, the proton in the PCET step to generated **4a•H** is best understood as coming from diisopropylammonium at early stages of the reaction. At later stages of the reaction, the iminium benzoate (**6l'**) may be the source of the proton for the PCET to generated **4a•H**.

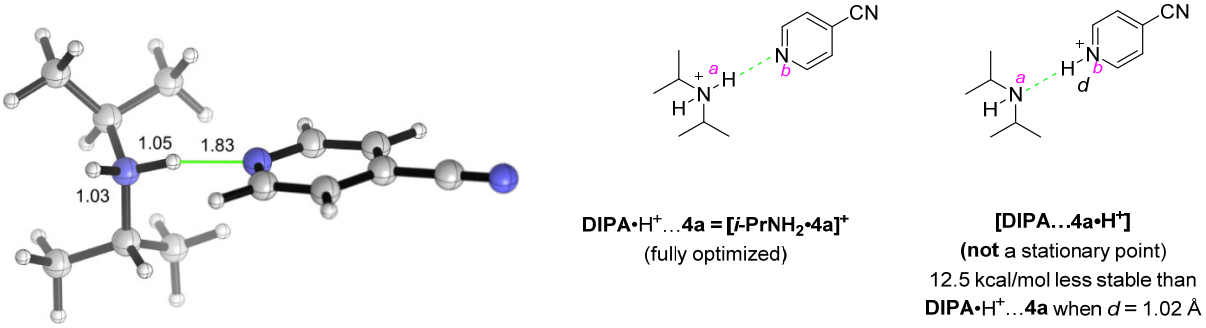



**Figure S101.** DFT computed structure of **DIPA**•H$^+$…**4a** = [***i*-PrNH$_2$•4a]$^+$**.

**8.3 DFT Illustrations of Alpha-Amino Radical Without and With *ortho*-Methyl Substituent**

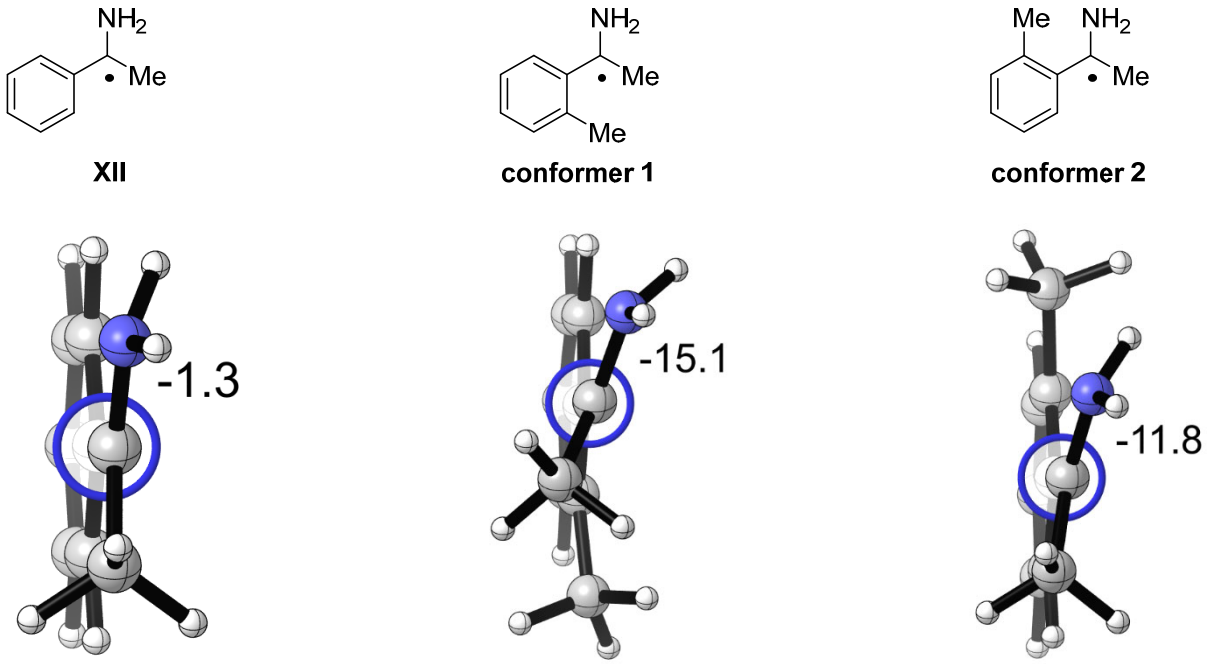



**Figure S103.** Newman projection (blue circle) illustrating the dihedral angle between the arene and the imine derived π-systems for alpha-amino radicals derived from iminium chloride **6a** (left) and **6g** (middle = **conformer 1**; right = **conformer 2**), **conformer 2** is +0.25 kcal/mol relative to **conformer 1**. SOMO energies of alpha-amino radicals (left) –4.74 eV vs vacuum, (middle) –4.74 eV vs vacuum, and (right) –4.64 eV vs vacuum.

**8.4 Illustration of Data Against Cyclopropane Ring Opening**

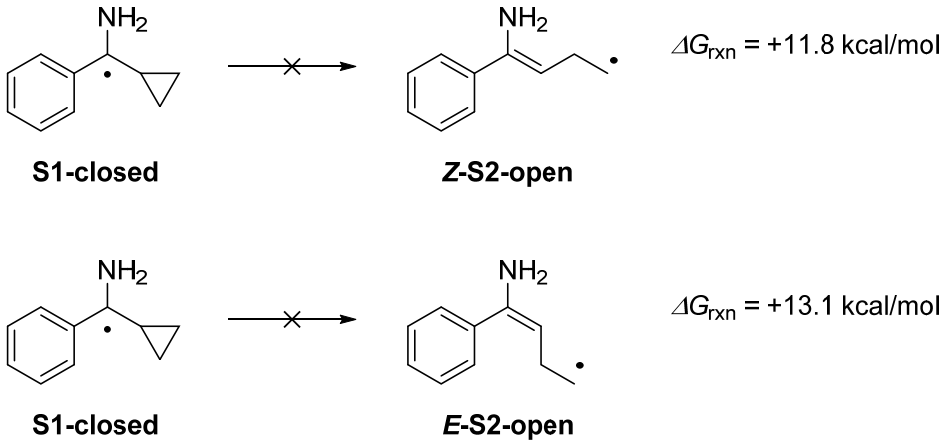
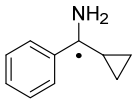



**Figure S104.** DFT calculated Gibbs free energy for ring opening of methylcyclopropyl radical illustrating the process is unfavored. **S1-closed** is the preferred form of the radical due to the radical being benzylic and α- to a heteroatom.

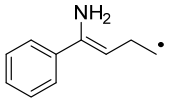
**8.5 Cartesian Coordinates and Energies of DFT Optimized Structures**



**S1-closed**

Structure: **S1-closed**
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -442.819949 hartree
SCF Energy + ZPVE: -442.623246 hartree
Enthalpy: -442.612292 hartree
Free Energy: -442.659624 hartree
Free Energy with quasiharmonic correction: -442.658537 hartree

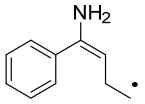
```
6 1.502068 1.189465 -0.055328
6 2.862346 0.913815 -0.042011
6 3.332723 -0.403069 0.003444
6 2.397525 -1.447618 0.032901
6 1.035872 -1.191582 0.020050
1 1.186109 2.225818 -0.121266
1 3.568117 1.739845 -0.075182
1 2.739525 -2.478443 0.073637
1 0.350406 -2.030796 0.066585
1 4.397593 -0.611968 0.014655
6 0.531422 0.142672 -0.023622
6 -0.864517 0.428250 -0.017092
6 -1.893913 -0.618299 -0.188000
6 -3.093520 -0.692656 0.742006
6 -3.284634 -0.291827 -0.687070
1 -1.516237 -1.576660 -0.521253
1 -3.174835 0.083210 1.498006
1 -3.420371 -1.678815 1.053828
1 -3.735431 -1.009944 -1.363519
1 -3.527848 0.744284 -0.902198
7 -1.292005 1.737250 0.093276
1 -0.702066 2.373121 0.616757
1 -2.273159 1.884695 0.295347
```



***Z*-S2-open**

Structure: ***Z*-S2-open**
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -442.797087 hartree
SCF Energy + ZPVE: -442.603118 hartree
Enthalpy: -442.591141 hartree
Free Energy: -442.640989 hartree
Free Energy with quasiharmonic correction: -442.639757 hartree

```
6 -1.655945 1.113847 -0.206183
6 -2.998070 0.736000 -0.230890
6 -3.357306 -0.596818 -0.033522
6 -2.362328 -1.549050 0.195026
6 -1.021868 -1.172017 0.224225
1 -1.386835 2.152437 -0.373704
1 -3.763420 1.486044 -0.407998
1 -2.631170 -2.587430 0.365710
1 -0.259322 -1.916940 0.431943
1 -4.402509 -0.890720 -0.050237
6 -0.647871 0.163020 0.010466
7 1.004762 1.891723 0.437985
1 0.425212 2.184719 1.217662
1 1.974969 2.134633 0.597146
6 0.785401 0.571324 0.023882
6 1.752029 -0.256348 -0.425177
1 1.447063 -1.212321 -0.842471
6 3.240938 0.013560 -0.417451
1 3.599843 0.132410 -1.447973
1 3.461196 0.951501 0.104356
6 3.971692 -1.109955 0.247384
1 4.258770 -1.990615 -0.317311
1 4.002837 -1.167151 1.330420
```

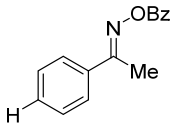



***E*-S2-open**

Structure: ***E*-S2-open**
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -442.794540 hartree
SCF Energy + ZPVE: -442.600941 hartree
Enthalpy: -442.588890 hartree
Free Energy: -442.638817 hartree
Free Energy with quasiharmonic correction: -442.637674 hartree

```
6 1.367039 0.894038 0.771167
6 2.625698 0.318292 0.934805
6 2.989525 -0.798916 0.181642
6 2.088004 -1.334251 -0.738863
6 0.827521 -0.760614 -0.900281
1 1.086255 1.763239 1.358968
1 3.323009 0.742418 1.651395
1 2.368301 -2.194742 -1.339259
1 0.136491 -1.167878 -1.633373
1 3.971598 -1.245308 0.306525
6 0.447718 0.352407 -0.138544
7 -0.842948 2.390877 -0.352861
1 -0.085667 2.761910 -0.918161
1 -1.727074 2.817398 -0.610500
6 -0.888753 0.985026 -0.315440
```

```
6 -2.052547 0.305611 -0.365554
1 -2.958271 0.886568 -0.545443
6 -2.273727 -1.165825 -0.080272
1 -2.619820 -1.675630 -0.988542
1 -1.329506 -1.634416 0.214667
6 -3.284678 -1.334975 1.009743
1 -4.343960 -1.385979 0.780936
1 -2.995524 -1.168473 2.042405
```

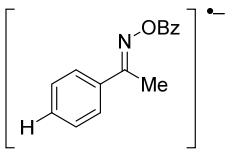



***E*-3a**

Structure: ***E*-3a**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -784.309711 hartree
SCF Energy + ZPVE: -784.063000 hartree
Enthalpy: -784.046606 hartree
Free Energy: -784.108172 hartree
Free Energy with quasiharmonic correction: -784.104475 hartree

```
6 1.687461 2.522671 0.829926
6 1.336856 1.204200 0.206520
6 2.378408 0.160440 0.009200
6 3.719934 0.530430 -0.141905
6 4.697335 -0.442003 -0.349896
6 4.345757 -1.790370 -0.395577
6 3.010019 -2.165281 -0.235531
6 2.030400 -1.197203 -0.035916
7 0.167459 0.881938 -0.209455
8 -0.746949 1.935786 -0.015996
6 -2.050976 1.606203 -0.228217
6 -2.486523 0.191958 -0.047652
6 -1.981840 -0.611878 0.980797
6 -2.494343 -1.892892 1.166667
6 -3.490909 -2.379460 0.318302
6 -3.993043 -1.576485 -0.706100
6 -3.502188 -0.284535 -0.880678
8 -2.808172 2.506219 -0.503039
1 2.570011 2.426848 1.462611
1 1.898740 3.259221 0.046513
1 0.853998 2.897650 1.425090
1 4.003712 1.578350 -0.112107
1 5.733790 -0.143685 -0.474558
1 5.108932 -2.547302 -0.549576
1 2.732196 -3.214636 -0.260049
1 0.992809 -1.488837 0.098293
1 -1.206440 -0.236765 1.641279
1 -2.113370 -2.512888 1.972180
1 -3.878589 -3.383955 0.459163
```

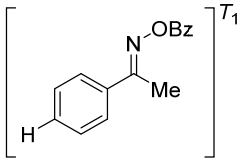
```
1 -4.769670 -1.952808 -1.364479
1 -3.895451 0.354423 -1.665526
```




***E*-3a$^{\bullet-}$**

Structure: ***E*-3a$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -784.385248 hartree
SCF Energy + ZPVE: -784.141864 hartree
Enthalpy: -784.125164 hartree
Free Energy: -784.187921 hartree
Free Energy with quasiharmonic correction: -784.184134 hartree

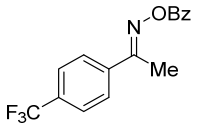
```
6 1.086306 2.272483 1.171533
6 1.119836 1.204291 0.110997
6 2.234482 0.326179 -0.055276
6 3.462517 0.460337 0.673036
6 4.518419 -0.416748 0.489994
6 4.442889 -1.479783 -0.430218
6 3.258803 -1.620492 -1.172320
6 2.190679 -0.753477 -1.007264
7 0.085863 1.027403 -0.736860
8 -0.946609 1.993432 -0.436337
6 -2.187912 1.504598 -0.402721
6 -2.395553 0.065686 -0.042808
6 -1.682900 -0.534879 1.002256
6 -1.981381 -1.839968 1.382722
6 -2.975348 -2.557801 0.711384
6 -3.686480 -1.958839 -0.327534
6 -3.408355 -0.641889 -0.693554
8 -3.124051 2.254168 -0.617386
1 1.881663 2.141415 1.905056
1 1.184111 3.278431 0.742257
1 0.131620 2.253497 1.707680
1 3.587269 1.270601 1.384374
1 5.427069 -0.270024 1.070110
1 5.275841 -2.161614 -0.568081
1 3.171931 -2.427737 -1.897169
1 1.291231 -0.898091 -1.596781
1 -0.902084 0.018354 1.516344
1 -1.434591 -2.301203 2.199523
1 -3.195924 -3.580553 1.002406
1 -4.461826 -2.512290 -0.848576
1 -3.968080 -0.161604 -1.490701
```




***E*-3a($T_1$)**

Structure: ***E*-3a($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -784.218448 hartree
SCF Energy + ZPVE: -783.975083 hartree
Enthalpy: -783.958257 hartree
Free Energy: -784.021835 hartree
Free Energy with quasiharmonic correction: -784.018044 hartree

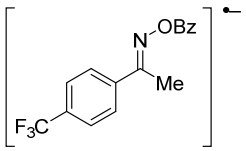
```
6 1.254270 2.461851 -0.650418
6 1.319436 1.050463 -0.157735
6 2.530580 0.349773 0.134881
6 3.786766 0.986099 -0.023920
6 4.964281 0.305428 0.256433
6 4.931745 -1.019564 0.702199
6 3.698927 -1.661243 0.865622
6 2.514478 -0.994551 0.588067
7 0.091063 0.399234 0.045567
8 -0.251123 -0.234752 -1.141878
6 -1.465006 -0.904153 -1.115385
6 -2.561999 -0.358115 -0.276528
6 -2.739365 1.017176 -0.085379
6 -3.840788 1.472436 0.633590
6 -4.749400 0.561760 1.175914
6 -4.570116 -0.808817 0.984740
6 -3.484121 -1.270320 0.246265
8 -1.559213 -1.869049 -1.826871
1 1.813023 3.139476 0.004817
1 1.685648 2.545215 -1.656569
1 0.216959 2.801450 -0.694881
1 3.830681 2.013404 -0.372178
1 5.917029 0.810236 0.125717
1 5.855524 -1.546291 0.920160
1 3.664677 -2.689811 1.212556
1 1.565406 -1.505398 0.723013
1 -2.035792 1.727727 -0.507077
1 -3.988593 2.538611 0.772726
1 -5.600598 0.921989 1.745817
1 -5.277062 -1.516517 1.405803
1 -3.339782 -2.333642 0.081063
```




***E*-3b**

Structure: ***E*-3b**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1121.270489 hartree
SCF Energy + ZPVE: -1121.018920 hartree
Enthalpy: -1120.998874 hartree
Free Energy: -1121.070562 hartree
Free Energy with quasiharmonic correction: -1121.064238 hartree

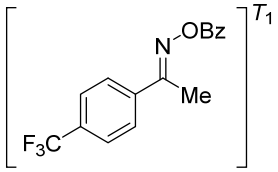
```
6 3.244790 -1.006756 0.524240
6 4.113940 -0.051294 0.003231
6 3.638234 1.177677 -0.454598
6 2.277492 1.452486 -0.387705
6 1.389205 0.496719 0.122072
6 1.882406 -0.730161 0.580675
6 -0.070553 0.783341 0.155302
7 -0.821243 -0.245164 -0.000454
8 -2.168101 0.135290 0.045078
6 -3.039800 -0.898007 -0.100376
6 -4.447121 -0.408627 -0.064798
8 -2.710435 -2.049185 -0.237447
6 -4.763045 0.948528 0.067466
6 -6.098041 1.344961 0.089571
6 -7.113643 0.393954 -0.018814
6 -6.796770 -0.959355 -0.149744
6 -5.464905 -1.361558 -0.173191
6 -0.579079 2.182666 0.341128
6 5.589481 -0.311134 -0.066122
9 6.291860 0.543471 0.709246
9 5.922760 -1.551185 0.327332
9 6.071154 -0.156483 -1.317524
1 3.622570 -1.956136 0.888193
1 4.324198 1.915322 -0.861016
1 1.908368 2.406227 -0.751180
1 1.198414 -1.463995 0.993432
1 -3.974284 1.688906 0.151520
1 -6.345382 2.396979 0.190939
1 -8.153039 0.707700 -0.001121
1 -7.586709 -1.699066 -0.233900
1 -5.203108 -2.409979 -0.275026
1 -1.353588 2.194860 1.111991
1 0.223588 2.857765 0.634462
1 -1.031549 2.545856 -0.587681
```




***E*-3b$^{\bullet-}$**

Structure: ***E*-3b$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -1121.356768 hartree
SCF Energy + ZPVE: -1121.108423 hartree
Enthalpy: -1121.088097 hartree
Free Energy: -1121.161452 hartree
Free Energy with quasiharmonic correction: -1121.154437 hartree

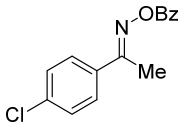
```
6 -3.303220 -1.150084 -0.236288
6 -4.120184 -0.011257 -0.051611
6 -3.510432 1.208610 0.324316
6 -2.145420 1.292037 0.490831
6 -1.288870 0.154598 0.304312
6 -1.938811 -1.075020 -0.073653
6 0.125330 0.235525 0.471687
7 0.826008 -0.877726 0.219874
8 2.228362 -0.689601 0.455612
6 2.930237 -0.156979 -0.549875
6 4.396984 -0.137506 -0.247246
8 2.450768 0.271200 -1.578757
6 4.918047 -0.663911 0.939756
6 6.290795 -0.616343 1.174072
6 7.143720 -0.044213 0.229169
6 6.623695 0.481712 -0.954762
6 5.252540 0.435957 -1.192564
6 0.745524 1.542689 0.896605
6 -5.584735 -0.118657 -0.149061
9 -6.205496 -0.463134 1.026862
9 -6.184313 1.040482 -0.516814
9 -5.995975 -1.061233 -1.032833
1 -3.757237 -2.097614 -0.516447
1 -4.121872 2.094560 0.475160
1 -1.717897 2.252536 0.760193
1 -1.336838 -1.963249 -0.231896
1 4.253887 -1.108197 1.673201
1 6.694679 -1.025851 2.094810
1 8.213014 -0.008159 0.415419
1 7.286000 0.927427 -1.690524
1 4.833337 0.841624 -2.107882
1 0.207840 1.966810 1.750045
1 1.788519 1.423954 1.189763
1 0.702336 2.279464 0.085134
```




***E*-3b($T_1$)**

Structure: ***E*-3b($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -1121.180623 hartree
SCF Energy + ZPVE: -1120.932202 hartree
Enthalpy: -1120.911795 hartree
Free Energy: -1120.985396 hartree
Free Energy with quasiharmonic correction: -1120.978951 hartree

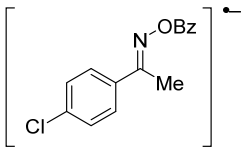
```
6 2.451490 -0.525248 0.942240
6 3.512995 -0.305913 0.061089
6 3.434384 0.697378 -0.912851
6 2.299132 1.481678 -1.006464
6 1.205688 1.278392 -0.124702
6 1.310463 0.255738 0.852112
6 0.034217 2.084285 -0.230433
7 -1.017497 1.876987 0.680370
8 -1.886696 0.977171 0.104240
6 -3.004850 0.705526 0.876024
6 -3.884582 -0.282088 0.204093
8 -3.199035 1.222988 1.941456
6 -3.561008 -0.854246 -1.032100
6 -4.429819 -1.777480 -1.608130
6 -5.613118 -2.127902 -0.956967
6 -5.933697 -1.556067 0.275968
6 -5.070911 -0.633773 0.858071
6 -0.155258 3.183031 -1.226473
6 4.754586 -1.136514 0.127405
9 5.865613 -0.384475 0.295134
9 4.737753 -2.027711 1.133490
9 4.960783 -1.841791 -1.008486
1 2.516265 -1.301985 1.696970
1 4.263858 0.859625 -1.595906
1 2.246324 2.254578 -1.766074
1 0.492344 0.083272 1.544527
1 -2.641587 -0.584618 -1.540052
1 -4.182038 -2.223754 -2.565891
1 -6.287146 -2.848115 -1.410948
1 -6.854292 -1.829218 0.781790
1 -5.306723 -0.181216 1.815945
1 -1.084193 3.720280 -1.024044
1 0.675215 3.896822 -1.193069
1 -0.205299 2.779167 -2.245936
```




***E*-3c**

Structure: ***E*-3c**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1243.885638 hartree
SCF Energy + ZPVE: -1243.648406 hartree
Enthalpy: -1243.630784 hartree
Free Energy: -1243.696147 hartree
Free Energy with quasiharmonic correction: -1243.691383 hartree

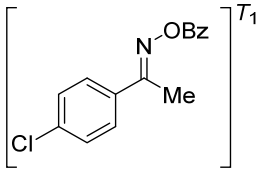
```
6 3.930814 -1.108366 0.502753
6 4.807598 -0.162883 -0.022603
6 4.359434 1.068381 -0.488424
6 2.998902 1.358099 -0.421534
6 2.094146 0.422023 0.091241
6 2.573765 -0.810121 0.554658
6 0.639977 0.727791 0.122746
7 -0.128181 -0.291231 -0.014658
8 -1.469500 0.112407 0.038698
17 6.516276 -0.531007 -0.091254
6 -2.359548 -0.902020 -0.116594
6 -3.758103 -0.388522 -0.060440
8 -2.052815 -2.056697 -0.277524
6 -4.048427 0.970729 0.104710
6 -5.375726 1.390839 0.146122
6 -6.409391 0.461219 0.024058
6 -6.118209 -0.894171 -0.140220
6 -4.794038 -1.319896 -0.182905
6 0.149105 2.136136 0.291037
1 4.301506 -2.058852 0.871836
1 5.057462 1.791417 -0.896973
1 2.648205 2.316487 -0.791829
1 1.881932 -1.534807 0.971333
1 -3.245815 1.694696 0.199431
1 -5.602920 2.444594 0.273389
1 -7.442713 0.793310 0.057060
1 -6.922080 -1.617391 -0.235087
1 -4.552331 -2.370304 -0.310565
1 0.962815 2.808776 0.557890
1 -0.317911 2.486549 -0.635367
1 -0.610835 2.170147 1.075794
```




***E*-3c$^{\bullet-}$**

Structure: ***E*-3c$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -1243.958380 hartree
SCF Energy + ZPVE: -1243.724631 hartree
Enthalpy: -1243.706621 hartree
Free Energy: -1243.773059 hartree
Free Energy with quasiharmonic correction: -1243.768575 hartree

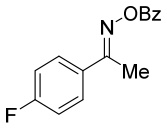
```
6 2.868148 -0.864633 -0.948771
6 3.952674 -0.446719 -0.170566
6 3.812445 0.643081 0.702774
6 2.598841 1.298331 0.803813
6 1.451306 0.900157 0.042009
6 1.651759 -0.211453 -0.852855
6 0.184969 1.553702 0.122750
7 -0.764307 1.125312 -0.730137
8 -1.963002 1.905112 -0.534675
17 5.499847 -1.275514 -0.296408
6 -3.101312 1.207398 -0.518615
6 -3.075006 -0.226728 -0.088498
8 -4.141239 1.772065 -0.806417
6 -2.305849 -0.649406 1.002520
6 -2.398794 -1.965371 1.446224
6 -3.240329 -2.869539 0.792308
6 -4.006448 -2.448591 -0.293920
6 -3.936402 -1.123590 -0.723941
6 -0.092506 2.659870 1.105397
1 2.980026 -1.704789 -1.629252
1 4.658444 0.976712 1.297217
1 2.541841 2.144084 1.480762
1 0.823451 -0.556519 -1.462067
1 -1.644285 0.050068 1.505173
1 -1.810457 -2.288472 2.299654
1 -3.300456 -3.898720 1.133635
1 -4.664064 -3.147585 -0.801714
1 -4.542658 -0.781898 -1.557698
1 0.699603 2.755337 1.847273
1 -0.205380 3.628819 0.602698
1 -1.030375 2.473037 1.639170
```




***E*-3c($T_1$)**

Structure: ***E*-3c($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -1243.794686 hartree
SCF Energy + ZPVE: -1243.560851 hartree
Enthalpy: -1243.542786 hartree
Free Energy: -1243.610674 hartree
Free Energy with quasiharmonic correction: -1243.605375 hartree

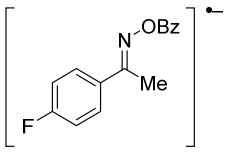
```
6 2.939841 -0.935680 0.983988
6 4.019807 -0.825482 0.106714
6 4.058247 0.163399 -0.876031
6 3.001136 1.054282 -0.984812
6 1.884954 0.972227 -0.115408
6 1.883560 -0.046292 0.872444
6 0.796456 1.885553 -0.240582
7 -0.277056 1.787934 0.663466
8 -1.213686 0.947753 0.095814
17 5.350623 -1.951771 0.240636
6 -2.346752 0.763293 0.868473
6 -3.298177 -0.159603 0.200645
8 -2.502764 1.295402 1.933467
6 -3.020488 -0.753165 -1.036641
6 -3.954513 -1.612113 -1.610038
6 -5.157521 -1.877663 -0.955099
6 -5.432558 -1.284578 0.278857
6 -4.504332 -0.426208 0.858328
6 0.714018 2.975592 -1.261374
1 2.928020 -1.709678 1.744643
1 4.906102 0.233130 -1.549747
1 3.035623 1.819230 -1.753922
1 1.047014 -0.133495 1.559339
1 -2.086049 -0.549110 -1.547629
1 -3.742070 -2.074726 -2.568561
1 -5.882487 -2.548264 -1.406595
1 -6.368576 -1.491849 0.787648
1 -4.704411 0.041849 1.816927
1 1.603040 3.615588 -1.233966
1 0.637630 2.557923 -2.273780
1 -0.165511 3.597368 -1.080459
```




***E*-3d**

Structure: ***E*-3d**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -883.527583 hartree
SCF Energy + ZPVE: -883.289015 hartree
Enthalpy: -883.271775 hartree
Free Energy: -883.335964 hartree
Free Energy with quasiharmonic correction: -883.331397 hartree

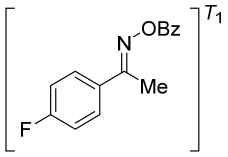
```
6 4.329488 -1.236996 0.470638
6 5.204289 -0.293705 -0.046817
6 4.793543 0.948603 -0.500910
6 3.437647 1.258441 -0.428151
6 2.518860 0.330641 0.077752
6 2.977710 -0.915448 0.527991
6 1.070673 0.660678 0.115089
7 0.281955 -0.341581 -0.031954
8 -1.051542 0.089392 0.031142
9 6.521923 -0.598877 -0.103439
6 -1.963610 -0.904649 -0.120660
6 -3.350560 -0.360190 -0.058789
8 -1.683740 -2.066231 -0.282303
6 -3.609480 1.005538 0.105226
6 -4.926690 1.455658 0.153046
6 -5.981729 0.549443 0.038487
6 -5.722002 -0.812417 -0.124816
6 -4.407946 -1.268045 -0.173849
6 0.605457 2.075955 0.300870
1 4.704669 -2.191255 0.824880
1 5.518144 1.650709 -0.899213
1 3.099627 2.225486 -0.787364
1 2.272682 -1.630859 0.938363
1 -2.790504 1.711640 0.194076
1 -5.129311 2.514525 0.279486
1 -7.007132 0.904759 0.076552
1 -6.542419 -1.517581 -0.213719
1 -4.190843 -2.323909 -0.300739
1 -0.154446 2.114221 1.085445
1 1.431189 2.730041 0.576692
1 0.145705 2.446853 -0.621186
```




***E*-3d$^{\bullet-}$**

Structure: ***E*-3d$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -883.604701 hartree
SCF Energy + ZPVE: -883.369685 hartree
Enthalpy: -883.352195 hartree
Free Energy: -883.416815 hartree
Free Energy with quasiharmonic correction: -883.412918 hartree

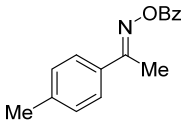
```
6 4.325546 -1.266492 0.373489
6 5.210152 -0.300452 -0.081664
6 4.807623 0.970410 -0.454708
6 3.452680 1.284518 -0.364607
6 2.520805 0.338147 0.082997
6 2.976624 -0.936871 0.453706
6 1.076187 0.675510 0.146445
7 0.264212 -0.311942 -0.003995
8 -1.040851 0.105909 0.069977
9 6.527784 -0.613093 -0.158079
6 -2.001691 -0.924004 -0.064423
6 -3.317836 -0.387562 -0.052918
8 -1.659520 -2.111938 -0.163622
6 -3.615397 1.016033 0.056709
6 -4.923252 1.464183 0.063658
6 -6.012632 0.571977 -0.035113
6 -5.734979 -0.808299 -0.142899
6 -4.437745 -1.283193 -0.152204
6 0.619282 2.090270 0.362056
1 4.691517 -2.245272 0.665755
1 5.536968 1.691696 -0.808059
1 3.124983 2.274711 -0.665721
1 2.266675 -1.671862 0.818444
1 -2.800668 1.729717 0.133507
1 -5.112262 2.532655 0.147151
1 -7.034578 0.936844 -0.028384
1 -6.557752 -1.516432 -0.220040
1 -4.241987 -2.348441 -0.235351
1 -0.153033 2.111391 1.136173
1 1.442910 2.736391 0.665228
1 0.168466 2.493204 -0.552016
```




***E*-3d($T_1$)**

Structure: ***E*-3d($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -883.435774 hartree
SCF Energy + ZPVE: -883.200541 hartree
Enthalpy: -883.182924 hartree
Free Energy: -883.248728 hartree
Free Energy with quasiharmonic correction: -883.244417 hartree

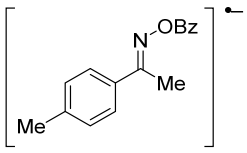
```
6 3.174802 -1.290526 1.111466
6 4.261882 -1.300473 0.246190
6 4.406961 -0.388115 -0.789904
6 3.423073 0.574297 -0.967081
6 2.292616 0.628831 -0.113704
6 2.193529 -0.328211 0.929463
6 1.286122 1.622865 -0.309658
7 0.196916 1.674249 0.578404
8 -0.804369 0.883564 0.045978
9 5.221034 -2.242249 0.421065
6 -1.968783 0.874742 0.791696
6 -2.982730 -0.022502 0.183236
8 -2.106563 1.522461 1.793572
6 -2.718503 -0.782577 -0.962360
6 -3.711686 -1.610031 -1.480174
6 -4.960452 -1.678343 -0.861431
6 -5.222163 -0.918590 0.280587
6 -4.234779 -0.091300 0.804674
6 1.313364 2.653404 -1.393863
1 3.108228 -2.025374 1.907165
1 5.274617 -0.438398 -1.439632
1 3.525450 1.290459 -1.775796
1 1.340974 -0.309095 1.601774
1 -1.748531 -0.731741 -1.444605
1 -3.509558 -2.201875 -2.367166
1 -5.731533 -2.324913 -1.269509
1 -6.193858 -0.972092 0.760993
1 -4.423653 0.504525 1.692030
1 0.486909 3.356520 -1.268295
1 2.252549 3.218163 -1.384167
1 1.218610 2.185286 -2.382431
```




***E*-3e**

Structure: ***E*-3e**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -823.615733 hartree
SCF Energy + ZPVE: -823.341478 hartree
Enthalpy: -823.323202 hartree
Free Energy: -823.390032 hartree
Free Energy with quasiharmonic correction: -823.384736 hartree

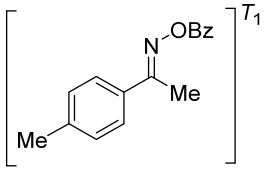
```
6 4.314425 -1.203012 0.457287
6 5.243983 -0.279522 -0.042645
6 4.771275 0.960170 -0.481415
6 3.414660 1.277210 -0.418491
6 2.492609 0.347806 0.073199
6 2.960204 -0.899593 0.514310
6 1.043246 0.670320 0.104509
7 0.257503 -0.336087 -0.035635
8 -1.078566 0.091436 0.024092
6 -1.986909 -0.905603 -0.121660
6 -3.376106 -0.366293 -0.057485
8 -1.704446 -2.067237 -0.280484
6 -3.639980 0.998346 0.107428
6 -4.958803 1.443505 0.157918
6 -6.010670 0.533353 0.045246
6 -5.746042 -0.827457 -0.118855
6 -4.430325 -1.278034 -0.170608
6 0.568655 2.084266 0.279099
6 6.709656 -0.619721 -0.083954
1 4.662245 -2.170237 0.812503
1 5.472416 1.690119 -0.877655
1 3.078470 2.246737 -0.774526
1 2.256738 -1.623224 0.914398
1 -2.823333 1.707325 0.194996
1 -5.165185 2.501562 0.285102
1 -7.037339 0.884758 0.085477
1 -6.563944 -1.535738 -0.206283
1 -4.209390 -2.333027 -0.298109
1 0.095844 2.441426 -0.641715
1 -0.183405 2.125470 1.071223
1 1.391835 2.747787 0.539081
1 7.280314 0.154205 -0.602712
1 7.112237 -0.718884 0.929835
1 6.874822 -1.573703 -0.594328
```




***E*-3e$^{\bullet-}$**

Structure: ***E*-3e$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -823.692363 hartree
SCF Energy + ZPVE: -823.421632 hartree
Enthalpy: -823.403121 hartree
Free Energy: -823.470164 hartree
Free Energy with quasiharmonic correction: -823.465776 hartree

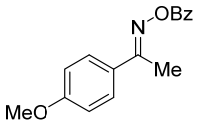
```
6 -5.250416 -0.286697 0.076402
6 -4.784180 0.978888 0.440202
6 -3.428742 1.300536 0.358942
6 -2.494834 0.355331 -0.080907
6 -2.960546 -0.918001 -0.448557
6 -4.312225 -1.229223 -0.369412
6 -1.048448 0.685276 -0.137185
6 -0.582521 2.099443 -0.339386
7 -0.239870 -0.306346 0.006706
8 1.067921 0.108464 -0.061216
6 2.024727 -0.924496 0.069098
8 1.679464 -2.111532 0.170059
6 3.343259 -0.393685 0.052924
6 4.459887 -1.293938 0.149313
6 5.759026 -0.824595 0.135493
6 6.042286 0.554569 0.025940
6 4.956171 1.451284 -0.070115
6 3.646509 1.008670 -0.058774
1 -3.101690 2.291238 0.661447
6 -6.714512 -0.633432 0.138131
1 -5.489317 1.726521 0.795114
1 -2.253090 -1.659397 -0.807069
1 -4.651539 -2.219211 -0.666266
1 -0.121964 2.488108 0.575962
1 -1.403553 2.754944 -0.628774
1 0.184643 2.124578 -1.118619
1 4.259881 -2.358302 0.233744
1 6.579034 -1.536192 0.210440
1 7.065735 0.915107 0.015684
1 5.149437 2.518900 -0.155016
1 2.834384 1.725557 -0.133665
1 -6.872572 -1.576009 0.671441
1 -7.284364 0.149737 0.644292
1 -7.127673 -0.756177 -0.869053
```




***E*-3e($T_1$)**

Structure: ***E*-3e($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -823.523970 hartree
SCF Energy + ZPVE: -823.253063 hartree
Enthalpy: -823.234397 hartree
Free Energy: -823.302932 hartree
Free Energy with quasiharmonic correction: -823.297904 hartree

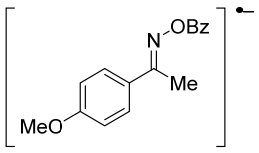
```
6 3.175950 -1.243582 1.065355
6 4.299932 -1.274144 0.221189
6 4.386379 -0.308897 -0.790470
6 3.398131 0.652300 -0.962903
6 2.264736 0.684869 -0.115433
6 2.179830 -0.295007 0.908988
6 1.246579 1.668368 -0.295056
7 0.157696 1.694096 0.594909
8 -0.834784 0.895736 0.053963
6 -1.996148 0.859686 0.801428
6 -2.997071 -0.047773 0.185532
8 -2.143766 1.493786 1.810954
6 -2.722326 -0.792887 -0.967369
6 -3.703065 -1.630709 -1.492241
6 -4.949990 -1.724342 -0.873117
6 -5.222202 -0.979694 0.276356
6 -4.247232 -0.142070 0.807343
6 1.258883 2.717532 -1.362280
6 5.368582 -2.316339 0.408857
1 3.088226 -1.982683 1.858731
1 5.246107 -0.313050 -1.456224
1 3.497345 1.383083 -1.759883
1 1.325667 -0.298179 1.580713
1 -1.753702 -0.722396 -1.449849
1 -3.492669 -2.210903 -2.385002
1 -5.711333 -2.378916 -1.286685
1 -6.192383 -1.053049 0.757238
1 -4.444394 0.442351 1.700471
1 1.168152 2.265642 -2.358770
1 0.424437 3.408928 -1.224082
1 2.191141 3.293511 -1.345005
1 6.175230 -2.189431 -0.317328
1 5.799636 -2.258892 1.414126
1 4.957260 -3.324722 0.290772
```




***E*-3f**

Structure: ***E*-3f**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -898.801821 hartree
SCF Energy + ZPVE: -898.521756 hartree
Enthalpy: -898.502892 hartree
Free Energy: -898.570307 hartree
Free Energy with quasiharmonic correction: -898.565703 hartree

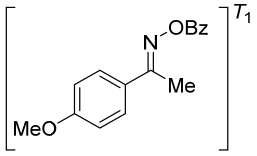
```
6 3.977506 -0.945961 0.398136
6 4.844295 0.038214 -0.091849
6 4.329767 1.273985 -0.508548
6 2.968344 1.522754 -0.433883
6 2.084009 0.542340 0.043681
6 2.610528 -0.685371 0.458046
6 0.624335 0.797843 0.083403
7 -0.118955 -0.239689 -0.068297
8 -1.472515 0.129304 0.014809
6 -2.338484 -0.900818 -0.148376
6 -3.749141 -0.424574 -0.055780
8 -2.009366 -2.045074 -0.341813
6 -4.070517 0.920990 0.156389
6 -5.406997 1.306153 0.231734
6 -6.419363 0.355052 0.096979
6 -6.097303 -0.986756 -0.114232
6 -4.763734 -1.377349 -0.190748
6 0.087732 2.186440 0.283049
8 6.185006 -0.111584 -0.192184
6 6.745511 -1.355331 0.213100
1 4.350595 -1.904024 0.740185
1 5.014096 2.026136 -0.888333
1 2.591005 2.483437 -0.771395
1 1.943687 -1.447850 0.848546
1 -3.284166 1.661297 0.261100
1 -5.657942 2.349401 0.395698
1 -7.459960 0.659709 0.156589
1 -6.884456 -1.726827 -0.219131
1 -4.498079 -2.416862 -0.354768
1 -0.429212 2.527028 -0.619968
1 -0.641667 2.184982 1.097395
1 0.884254 2.887813 0.526173
1 6.344903 -2.180168 -0.385646
1 7.818317 -1.269372 0.043093
1 6.557375 -1.543704 1.275436
```




***E*-3f$^{\bullet-}$**

Structure: ***E*-3f$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -898.877977 hartree
SCF Energy + ZPVE: -898.601541 hartree
Enthalpy: -898.582437 hartree
Free Energy: -898.650079 hartree
Free Energy with quasiharmonic correction: -898.646341 hartree

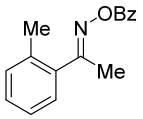
```
6 3.983930 -0.956342 0.346870
6 4.850564 0.040072 -0.116065
6 4.335146 1.290570 -0.480885
6 2.973886 1.540094 -0.384068
6 2.086362 0.550297 0.069318
6 2.618101 -0.691585 0.434220
6 0.627540 0.810206 0.136683
7 -0.136584 -0.214873 -0.015161
8 -1.462415 0.141564 0.075835
6 -2.375141 -0.925982 -0.080153
6 -3.714984 -0.452102 -0.051823
8 -1.982130 -2.095322 -0.210602
6 -4.078377 0.933279 0.090837
6 -5.405871 1.318866 0.109921
6 -6.452693 0.378749 -0.007673
6 -6.110242 -0.984588 -0.146498
6 -4.792296 -1.397051 -0.168952
6 0.098184 2.198746 0.361749
8 6.192640 -0.111741 -0.237660
6 6.748839 -1.370912 0.118458
1 4.355872 -1.928407 0.649038
1 5.017294 2.054538 -0.841162
1 2.598141 2.513626 -0.685168
1 1.953419 -1.465784 0.804989
1 -3.297631 1.682415 0.182419
1 -5.644845 2.375106 0.217938
1 -7.490678 0.694726 0.008890
1 -6.898887 -1.728988 -0.238116
1 -4.546637 -2.449631 -0.276910
1 -0.411988 2.566407 -0.535612
1 -0.643220 2.181990 1.166001
1 0.893732 2.894076 0.628551
1 6.336980 -2.173592 -0.502800
1 7.820594 -1.286821 -0.059999
1 6.571494 -1.595457 1.175851
```




***E*-3f($T_1$)**

Structure: ***E*-3f($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -898.709600 hartree
SCF Energy + ZPVE: -898.433106 hartree
Enthalpy: -898.413720 hartree
Free Energy: -898.483978 hartree
Free Energy with quasiharmonic correction: -898.478632 hartree

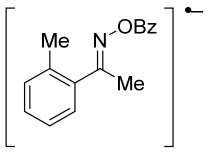
```
6 3.018587 -0.962467 0.731800
6 4.091310 -0.728063 -0.139709
6 4.065701 0.394693 -0.985110
6 2.994322 1.265323 -0.963708
6 1.892911 1.051970 -0.091362
6 1.941326 -0.085706 0.750486
6 0.787448 1.951275 -0.074780
7 -0.260995 1.724262 0.835297
8 -1.202510 0.936993 0.190433
6 -2.307884 0.639401 0.961500
6 -3.274384 -0.198704 0.206846
8 -2.439453 1.022240 2.092854
6 -3.043497 -0.602677 -1.113449
6 -3.990488 -1.387964 -1.766042
6 -5.159902 -1.768924 -1.106970
6 -5.387974 -1.365498 0.210253
6 -4.446849 -0.581006 0.868287
6 0.656603 3.156562 -0.953327
8 5.185274 -1.520632 -0.236482
6 5.245682 -2.670375 0.598700
1 3.013332 -1.819889 1.394843
1 4.903553 0.561727 -1.655426
1 2.998218 2.123249 -1.629166
1 1.120907 -0.283032 1.434891
1 -2.135150 -0.308138 -1.627496
1 -3.814839 -1.702511 -2.789822
1 -5.895154 -2.381260 -1.620378
1 -6.297697 -1.662263 0.722496
1 -4.610228 -0.259749 1.892054
1 0.544561 2.867741 -2.006882
1 -0.221231 3.740077 -0.665937
1 1.538781 3.802723 -0.880984
1 4.415891 -3.353715 0.387824
1 6.189866 -3.161697 0.364871
1 5.232209 -2.388953 1.657122
```




***E*-3g**

Structure: ***E*-3g**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -823.613519 hartree
SCF Energy + ZPVE: -823.338914 hartree
Enthalpy: -823.321006 hartree
Free Energy: -823.385867 hartree
Free Energy with quasiharmonic correction: -823.381690 hartree

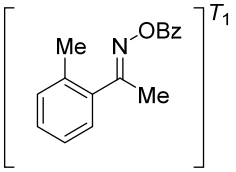
```
6 -4.468487 -1.615178 0.809986
6 -5.409241 -0.837868 0.136933
6 -5.012677 0.336434 -0.501867
6 -3.683771 0.771603 -0.475836
6 -2.742534 -0.017854 0.212430
6 -3.137986 -1.204512 0.840816
6 -1.310405 0.388490 0.287310
7 -0.478820 -0.511538 -0.090196
8 0.835862 -0.038421 0.072330
6 1.792873 -0.912675 -0.329539
6 3.153388 -0.337643 -0.122795
8 1.568064 -2.003966 -0.790555
6 3.349157 0.943287 0.406159
6 4.644007 1.427431 0.576560
6 5.739384 0.638978 0.221817
6 5.542629 -0.638511 -0.305691
6 4.251194 -1.127405 -0.478579
6 -0.915679 1.736129 0.820599
6 -3.296541 2.036397 -1.200624
1 -4.765099 -2.533580 1.307098
1 -6.449844 -1.146581 0.101572
1 -5.745872 0.928520 -1.043949
1 -2.393697 -1.796609 1.365357
1 2.498020 1.556962 0.681915
1 4.797587 2.420783 0.986316
1 6.747262 1.020145 0.356402
1 6.394618 -1.251910 -0.581514
1 4.083192 -2.118664 -0.887581
1 -0.399411 2.320023 0.051880
1 -0.222692 1.605998 1.657331
1 -1.789571 2.286905 1.166853
1 -3.249310 2.890297 -0.516210
1 -2.319867 1.944907 -1.684854
1 -4.036841 2.270032 -1.969516
```




***E*-3g$^{\bullet-}$**

Structure: ***E*-3g$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -823.689560 hartree
SCF Energy + ZPVE: -823.418403 hartree
Enthalpy: -823.400243 hartree
Free Energy: -823.465797 hartree
Free Energy with quasiharmonic correction: -823.461975 hartree

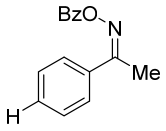
```
6 4.950752 -1.207134 -0.736419
6 5.528355 0.018576 -0.408939
6 4.737348 1.027683 0.135901
6 3.364102 0.859466 0.355654
6 2.782741 -0.381522 0.013897
6 3.590847 -1.400215 -0.514938
6 1.334129 -0.676514 0.186298
7 0.512503 0.257891 -0.138079
8 -0.789185 -0.152710 0.030712
6 -1.760693 0.836911 -0.245358
6 -3.072156 0.299914 -0.136996
8 -1.431252 1.999786 -0.524416
6 -3.356470 -1.073112 0.187498
6 -4.660310 -1.523866 0.278160
6 -5.758615 -0.664134 0.058957
6 -5.493931 0.686063 -0.259657
6 -4.201043 1.162779 -0.356476
6 0.887400 -2.026443 0.678358
6 2.587271 1.997670 0.969263
1 5.551886 -2.007108 -1.157833
1 6.589748 0.186577 -0.566476
1 5.193998 1.975821 0.409505
1 3.139030 -2.355042 -0.770823
1 -2.534414 -1.760783 0.362009
1 -4.839424 -2.568662 0.524548
1 -6.777250 -1.030863 0.132872
1 -6.323600 1.368722 -0.433039
1 -4.015059 2.204496 -0.601969
1 1.729624 -2.615105 1.042461
1 0.161568 -1.900327 1.487278
1 0.381998 -2.581142 -0.120361
1 2.021088 2.548965 0.212691
1 1.864753 1.640573 1.707789
1 3.273667 2.695308 1.456320
```




***E*-3g($T_1$)**

Structure: ***E*-3g($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -823.517432 hartree
SCF Energy + ZPVE: -823.245648 hartree
Enthalpy: -823.227426 hartree
Free Energy: -823.295414 hartree
Free Energy with quasiharmonic correction: -823.289394 hartree

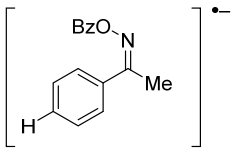
```
6 -2.817413 -2.180901 1.012903
6 -3.978358 -2.270585 0.242432
6 -4.354260 -1.182690 -0.546917
6 -3.617629 0.001200 -0.601769
6 -2.423714 0.100173 0.182659
6 -2.059481 -1.022570 0.980827
6 -1.565312 1.248235 0.219761
7 -0.442597 1.186228 1.076123
8 0.611723 0.690832 0.328933
6 1.794134 0.576621 1.033090
6 2.880391 0.051759 0.167127
8 1.894602 0.868459 2.194183
6 2.677054 -0.257268 -1.183039
6 3.737597 -0.745028 -1.942428
6 4.992634 -0.924779 -1.359846
6 5.193199 -0.616698 -0.012720
6 4.138847 -0.128859 0.751963
6 -1.657850 2.548967 -0.522958
6 -4.133627 1.107228 -1.488164
1 -2.503075 -3.012123 1.636906
1 -4.583699 -3.171596 0.253203
1 -5.256811 -1.251763 -1.148797
1 -1.162365 -0.968855 1.590045
1 1.702380 -0.118741 -1.637734
1 3.583361 -0.985019 -2.989579
1 5.816252 -1.305616 -1.956336
1 6.169622 -0.757194 0.439886
1 4.280140 0.114731 1.800148
1 -1.465712 2.414625 -1.594407
1 -0.900146 3.234323 -0.133675
1 -2.633090 3.027481 -0.411278
1 -4.436887 1.983956 -0.907638
1 -3.389521 1.434080 -2.219019
1 -5.010143 0.754959 -2.037033
```




***Z*-3a**

Structure: ***Z*-3a**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -784.313665 hartree
SCF Energy + ZPVE: -784.066908 hartree
Enthalpy: -784.050533 hartree
Free Energy: -784.112326 hartree
Free Energy with quasiharmonic correction: -784.108060 hartree

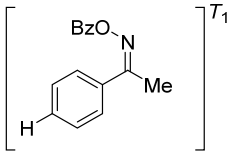
```
6 -3.154865 2.530655 0.050003
6 -2.031313 1.537659 0.038426
6 -2.367219 0.085919 0.048924
6 -1.803594 -0.775114 0.999971
6 -2.165082 -2.119472 1.026830
6 -3.079304 -2.619309 0.097635
6 -3.642114 -1.766012 -0.850441
6 -3.298413 -0.414494 -0.867878
7 -0.849156 2.034784 0.031574
8 0.122583 1.019571 -0.029565
6 1.399766 1.469070 0.021588
6 2.357655 0.327890 -0.053807
6 1.926829 -1.001695 -0.132162
6 2.867460 -2.027154 -0.195077
6 4.230858 -1.729738 -0.180955
6 4.658738 -0.403179 -0.102727
6 3.723737 0.625624 -0.038068
8 1.713605 2.629700 0.119430
1 -2.765957 3.549588 0.086477
1 -3.798781 2.349791 0.915911
1 -3.768412 2.414608 -0.848728
1 -1.091452 -0.389742 1.723233
1 -1.730148 -2.777842 1.772760
1 -3.354147 -3.669626 0.116046
1 -4.354192 -2.148766 -1.575143
1 -3.744076 0.245037 -1.606894
1 0.866339 -1.233119 -0.143168
1 2.535425 -3.058850 -0.255421
1 4.960529 -2.532478 -0.231180
1 5.719199 -0.171778 -0.091671
1 4.041430 1.661618 0.024256
```




***Z*-3a$^{\bullet-}$**

Structure: ***Z*-3a$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -784.389331 hartree
SCF Energy + ZPVE: -784.145927 hartree
Enthalpy: -784.129353 hartree
Free Energy: -784.191302 hartree
Free Energy with quasiharmonic correction: -784.187945 hartree

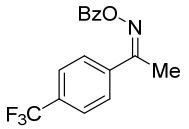
```
6 -3.087075 2.567880 0.208567
6 -2.003463 1.527814 0.135997
6 -2.408282 0.095476 0.059503
6 -1.794268 -0.883046 0.854943
6 -2.224245 -2.206722 0.802700
6 -3.264168 -2.576222 -0.052466
6 -3.882118 -1.609561 -0.844639
6 -3.465230 -0.280194 -0.780255
7 -0.797713 1.973711 0.147666
8 0.144915 0.977673 0.037866
6 1.481248 1.440621 -0.031240
6 2.390453 0.348991 -0.052845
6 1.993771 -1.033247 0.018902
6 2.936574 -2.043514 -0.009789
6 4.317906 -1.766247 -0.109598
6 4.720974 -0.414456 -0.185088
6 3.800195 0.614733 -0.159166
8 1.740580 2.652591 -0.076622
1 -2.648046 3.557786 0.347408
1 -3.768696 2.354227 1.038048
1 -3.680771 2.577138 -0.711333
1 -0.983955 -0.602895 1.519474
1 -1.743835 -2.951850 1.430194
1 -3.592424 -3.610375 -0.097457
1 -4.693321 -1.886759 -1.511227
1 -3.958223 0.464607 -1.398158
1 0.939276 -1.281968 0.093886
1 2.600637 -3.077213 0.046344
1 5.048085 -2.568743 -0.129352
1 5.779526 -0.174491 -0.265428
1 4.128146 1.648619 -0.219177
```




***Z*-3a($T_1$)**

Structure: ***Z*-3a($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -784.224593 hartree
SCF Energy + ZPVE: -783.981171 hartree
Enthalpy: -783.964320 hartree
Free Energy: -784.028637 hartree
Free Energy with quasiharmonic correction: -784.024079 hartree

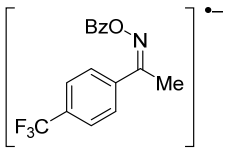
```
6 -1.880166 2.179925 -1.599787
6 -1.752600 1.289135 -0.404792
6 -2.659645 0.235423 -0.075982
6 -2.462746 -0.576589 1.070913
6 -3.350449 -1.598639 1.374158
6 -4.455676 -1.848474 0.552729
6 -4.663310 -1.056898 -0.581337
6 -3.784597 -0.028945 -0.896577
7 -0.661502 1.538649 0.447117
8 0.401278 0.787175 -0.018408
6 1.564053 0.945189 0.712397
6 2.654028 0.098518 0.165654
6 2.463220 -0.749829 -0.931526
6 3.525901 -1.521575 -1.394505
6 4.770744 -1.447885 -0.768567
6 4.959020 -0.600814 0.325497
6 3.902202 0.172289 0.794196
8 1.644815 1.678967 1.659698
1 -1.140612 2.982538 -1.553909
1 -2.877573 2.629552 -1.656668
1 -1.717633 1.616497 -2.528203
1 -1.611615 -0.392569 1.720582
1 -3.182483 -2.207692 2.257561
1 -5.146174 -2.650448 0.794024
1 -5.517815 -1.245385 -1.224728
1 -3.959100 0.574029 -1.782444
1 1.496385 -0.808939 -1.418985
1 3.381215 -2.181183 -2.244099
1 5.596100 -2.051825 -1.133569
1 5.927654 -0.544059 0.811707
1 4.033544 0.834840 1.643763
```




***Z*-3b**

Structure: ***Z*-3b**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1121.267979 hartree
SCF Energy + ZPVE: -1121.016619 hartree
Enthalpy: -1120.996597 hartree
Free Energy: -1121.068824 hartree
Free Energy with quasiharmonic correction: -1121.061604 hartree

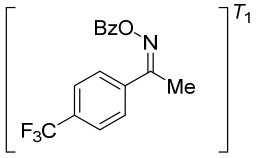
```
6 1.884413 -0.293337 1.009880
6 2.889624 -0.256850 0.042322
6 2.922508 0.749656 -0.918972
6 1.942052 1.738802 -0.905485
6 0.920198 1.704584 0.047371
6 0.897818 0.684998 1.007436
6 -0.104945 2.787670 0.062941
7 -1.373647 2.608687 0.062259
8 -1.688193 1.241071 -0.007914
6 -3.019467 0.977864 0.015163
6 -3.262452 -0.491755 -0.052743
8 -3.879376 1.820162 0.084130
6 -2.214341 -1.418766 -0.095205
6 -2.502101 -2.780408 -0.152118
6 -3.827461 -3.216823 -0.167479
6 -4.871482 -2.290963 -0.124960
6 -4.590500 -0.929228 -0.066827
6 0.363351 4.210784 0.091139
6 3.919775 -1.347656 0.018988
9 5.055449 -0.974493 -0.596944
9 4.261210 -1.756801 1.255696
9 3.478052 -2.447616 -0.631520
1 1.869636 -1.078512 1.759656
1 3.706901 0.772722 -1.668367
1 1.970731 2.529427 -1.648954
1 0.115448 0.662373 1.759127
1 -1.183060 -1.080424 -0.082885
1 -1.690574 -3.500639 -0.184779
1 -4.047209 -4.279333 -0.212595
1 -5.902401 -2.630319 -0.136837
1 -5.392370 -0.198446 -0.032330
1 1.014078 4.368642 0.956480
1 0.947887 4.430216 -0.807816
1 -0.487323 4.892368 0.139966
```




***Z*-3b$^{\bullet-}$**

Structure: ***Z*-3b$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -1121.355564 hartree
SCF Energy + ZPVE: -1121.106654 hartree
Enthalpy: -1121.086605 hartree
Free Energy: -1121.158741 hartree
Free Energy with quasiharmonic correction: -1121.152297 hartree

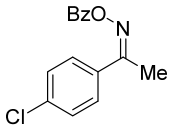
```
6 1.785467 -0.685094 0.459615
6 3.110680 -0.332911 0.109858
6 3.363001 0.992275 -0.307959
6 2.345953 1.918323 -0.363619
6 0.979107 1.594203 -0.029050
6 0.760444 0.230380 0.394750
6 -0.011076 2.622125 -0.086049
7 -1.343921 2.568225 -0.019723
8 -1.792185 1.217472 -0.064344
6 -3.096954 1.049261 0.164298
6 -3.493220 -0.383977 -0.009104
8 -3.873474 1.926371 0.481504
6 -2.626806 -1.337831 -0.555977
6 -3.050499 -2.657441 -0.699405
6 -4.333727 -3.030264 -0.296476
6 -5.198584 -2.079052 0.247390
6 -4.780608 -0.758322 0.388326
6 0.437003 4.059590 -0.244066
6 4.168435 -1.355275 0.109540
9 5.417056 -0.834925 0.109430
9 4.104590 -2.197409 1.175532
9 4.138650 -2.195741 -0.975516
1 1.569498 -1.695823 0.798877
1 4.370134 1.290542 -0.586603
1 2.593745 2.922930 -0.688611
1 -0.224565 -0.087027 0.705729
1 -1.630244 -1.048464 -0.873830
1 -2.378324 -3.394691 -1.127660
1 -4.659865 -4.060104 -0.407892
1 -6.197432 -2.366546 0.561149
1 -5.443514 -0.008040 0.807752
1 1.209687 4.326191 0.484045
1 0.847023 4.244322 -1.244054
1 -0.417771 4.725105 -0.105560
```




***Z*-3b($T_1$)**

Structure: ***Z*-3b($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -1121.180600 hartree
SCF Energy + ZPVE: -1120.932215 hartree
Enthalpy: -1120.911792 hartree
Free Energy: -1120.985562 hartree
Free Energy with quasiharmonic correction: -1120.978943 hartree

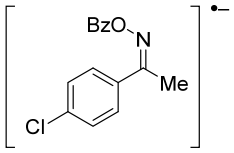
```
6 2.457037 -0.528712 0.889338
6 3.520538 -0.286097 0.009631
6 3.439675 0.737580 -0.936114
6 2.298327 1.522270 -1.006422
6 1.208600 1.296599 -0.129948
6 1.316496 0.248685 0.823297
6 0.035474 2.102955 -0.211559
7 -1.010699 1.874686 0.700479
8 -1.881475 0.984395 0.111912
6 -2.993227 0.694063 0.886242
6 -3.872173 -0.287302 0.204283
8 -3.183017 1.192712 1.961367
6 -3.555597 -0.835694 -1.044424
6 -4.423295 -1.754715 -1.628879
6 -5.598493 -2.124447 -0.973702
6 -5.912181 -1.576109 0.271621
6 -5.050477 -0.658208 0.862183
6 -0.159553 3.223471 -1.181784
6 4.739108 -1.146391 0.114549
9 5.684757 -0.830263 -0.786816
9 5.322826 -1.062176 1.331741
9 4.457633 -2.457102 -0.063535
1 2.527981 -1.326368 1.623684
1 4.264466 0.922275 -1.616321
1 2.243281 2.313562 -1.746687
1 0.499682 0.057580 1.512384
1 -2.642492 -0.551011 -1.555570
1 -4.180936 -2.182578 -2.596379
1 -6.271584 -2.841363 -1.434246
1 -6.826481 -1.864216 0.780548
1 -5.280897 -0.223940 1.829795
1 0.669167 3.938522 -1.133927
1 -0.210415 2.842558 -2.209968
1 -1.089446 3.753493 -0.965283
```




***Z*-3c**

Structure: ***Z*-3c**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1243.883202 hartree
SCF Energy + ZPVE: -1243.645809 hartree
Enthalpy: -1243.628343 hartree
Free Energy: -1243.692615 hartree
Free Energy with quasiharmonic correction: -1243.688536 hartree

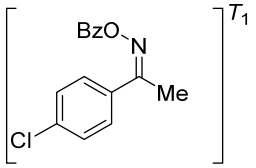
```
6 3.235980 -1.101729 -0.034727
6 3.491390 -0.103005 0.897861
6 2.710517 1.050483 0.877615
6 1.670750 1.191141 -0.046801
6 1.435369 0.170186 -0.975855
6 2.220885 -0.977934 -0.979500
6 0.869679 2.447229 -0.065123
6 1.598910 3.756970 -0.087589
7 -0.410301 2.519913 -0.072307
8 -0.989298 1.240934 -0.003703
6 -2.345810 1.247417 -0.017320
8 -3.022769 2.243332 -0.080631
6 -2.876360 -0.144550 0.052677
6 -4.264882 -0.308860 0.068923
6 -4.811268 -1.587379 0.128803
6 -3.972394 -2.702574 0.170777
6 -2.586662 -2.538722 0.153557
6 -2.033891 -1.261589 0.095164
17 4.219879 -2.547841 -0.026344
1 4.288270 -0.217667 1.625020
1 2.910608 1.834477 1.601516
1 0.643102 0.273321 -1.710354
1 2.044219 -1.764619 -1.705487
1 2.207063 3.864213 0.815932
1 2.274686 3.789174 -0.947508
1 0.892844 4.587068 -0.142327
1 -4.904367 0.567514 0.034612
1 -5.889124 -1.714926 0.142209
1 -4.398965 -3.700135 0.216851
1 -1.934876 -3.406176 0.185484
1 -0.956034 -1.134968 0.081937
```




***Z*-3c$^{\bullet-}$**

Structure: ***Z*-3c$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -1243.959502 hartree
SCF Energy + ZPVE: -1243.725598 hartree
Enthalpy: -1243.707868 hartree
Free Energy: -1243.772724 hartree
Free Energy with quasiharmonic correction: -1243.769202 hartree

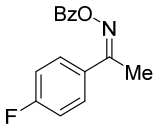
```
6 -3.655500 -0.003742 -0.788937
6 -3.332379 -1.091711 0.013245
6 -2.217568 -1.075886 0.846754
6 -1.403138 0.052146 0.861500
6 -1.699764 1.165233 0.062023
6 -2.840045 1.125421 -0.749996
6 -0.871177 2.402669 0.105870
7 0.413672 2.451175 0.107518
8 0.998223 1.210589 0.016413
17 -4.355019 -2.512369 -0.020109
6 2.414614 1.229853 -0.021295
6 2.933833 -0.092080 -0.057399
8 3.042460 2.299029 -0.025367
6 2.120595 -1.279875 -0.042773
6 2.699013 -2.534766 -0.075769
6 4.100063 -2.704577 -0.125793
6 4.909966 -1.547534 -0.146002
6 4.358322 -0.281607 -0.115447
6 -1.579276 3.728104 0.155154
1 -4.529710 -0.031831 -1.430903
1 -1.986116 -1.930608 1.474151
1 -0.533376 0.067307 1.508751
1 -3.097288 1.975412 -1.374434
1 1.039271 -1.185873 -0.006729
1 2.053633 -3.411033 -0.063482
1 4.541395 -3.695644 -0.149311
1 5.992541 -1.651469 -0.187574
1 4.996245 0.597469 -0.133211
1 -2.142954 3.904760 -0.766681
1 -2.290923 3.751935 0.986556
1 -0.853900 4.534789 0.276908
```




***Z*-3c($T_1$)**

Structure: ***Z*-3c($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -1243.794686 hartree
SCF Energy + ZPVE: -1243.560851 hartree
Enthalpy: -1243.542786 hartree
Free Energy: -1243.610674 hartree
Free Energy with quasiharmonic correction: -1243.605375 hartree

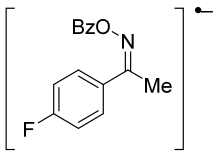
```
6 -4.019776 -0.825490 0.106728
6 -4.058229 0.163384 -0.876024
6 -3.001129 1.054276 -0.984814
6 -1.884944 0.972238 -0.115412
6 -1.883536 -0.046274 0.872445
6 -2.939806 -0.935671 0.984000
6 -0.796459 1.885578 -0.240592
6 -0.714031 2.975598 -1.261405
7 0.277060 1.787975 0.663452
8 1.213683 0.947782 0.095805
6 2.346755 0.763330 0.868455
8 2.502788 1.295467 1.933431
6 3.298158 -0.159599 0.200640
6 4.504325 -0.426192 0.858308
6 5.432530 -1.284592 0.278848
6 5.157461 -1.877720 -0.955080
6 3.954441 -1.612182 -1.610003
6 3.020437 -0.753203 -1.036618
17 -5.350580 -1.951794 0.240661
1 -4.906087 0.233102 -1.549737
1 -3.035625 1.819220 -1.753927
1 -1.046986 -0.133465 1.559338
1 -2.927975 -1.709664 1.744661
1 -0.637678 2.557908 -2.273806
1 -1.603041 3.615608 -1.233985
1 0.165513 3.597363 -1.080525
1 4.704428 0.041898 1.816886
1 6.368556 -1.491854 0.787628
1 5.882410 -2.548345 -1.406567
1 3.741973 -2.074829 -2.568504
1 2.085989 -0.549159 -1.547594
```




***Z*-3d**

Structure: ***Z*-3d**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -883.517194 hartree
SCF Energy + ZPVE: -883.278816 hartree
Enthalpy: -883.261609 hartree
Free Energy: -883.325461 hartree
Free Energy with quasiharmonic correction: -883.320947 hartree

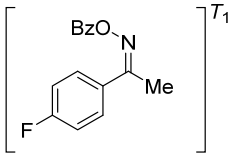
```
6 -3.685544 -1.172264 0.398763
6 -4.430616 -0.409829 -0.487639
6 -4.013103 0.822662 -0.960749
6 -2.788396 1.314759 -0.514771
6 -1.996660 0.567292 0.364537
6 -2.455213 -0.676528 0.818140
6 -0.708725 1.135082 0.850412
7 0.424907 0.538191 0.851404
8 0.334158 -0.763973 0.312956
9 -5.624427 -0.891918 -0.906235
6 1.528331 -1.382778 0.105879
6 2.751386 -0.563360 -0.127962
8 1.521226 -2.590183 0.064526
6 2.722172 0.603304 -0.899610
6 3.910689 1.272278 -1.179181
6 5.120794 0.793064 -0.673515
6 5.147496 -0.369479 0.097242
6 3.964820 -1.057664 0.357845
6 -0.706168 2.527791 1.407983
1 -4.062520 -2.128420 0.745765
1 -4.633689 1.380546 -1.653788
1 -2.447086 2.281254 -0.872316
1 -1.854529 -1.257576 1.509387
1 1.782012 0.977992 -1.291498
1 3.892315 2.169625 -1.789639
1 6.043794 1.324763 -0.884685
1 6.088053 -0.743880 0.488856
1 3.975061 -1.972230 0.942939
1 -1.407986 2.590962 2.245124
1 0.294130 2.803239 1.746118
1 -1.034718 3.240913 0.645930
```




***Z*-3d$^{\bullet-}$**

Structure: ***Z*-3d$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -883.601181 hartree
SCF Energy + ZPVE: -883.366041 hartree
Enthalpy: -883.348651 hartree
Free Energy: -883.412579 hartree
Free Energy with quasiharmonic correction: -883.409054 hartree

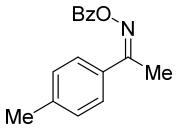
```
6 -2.256579 1.653986 -0.814823
6 -3.358971 1.817795 0.009421
6 -3.873762 0.796360 0.789139
6 -3.248835 -0.448210 0.735263
6 -2.117619 -0.654930 -0.065794
6 -1.634954 0.409163 -0.842642
6 -1.495385 -2.007361 -0.122638
7 -0.235167 -2.262253 -0.122580
8 0.543644 -1.133456 -0.017845
9 -3.962603 3.030947 0.049148
6 1.936409 -1.387552 0.034001
6 2.669791 -0.171065 0.058674
8 2.376795 -2.546394 0.060280
6 2.068713 1.136546 0.017673
6 2.850182 2.276501 0.042276
6 4.259135 2.209061 0.110395
6 4.862088 0.932422 0.156487
6 4.105340 -0.222736 0.134460
6 -2.403519 -3.204232 -0.186828
1 -1.897323 2.482885 -1.415980
1 -4.741370 0.972295 1.416256
1 -3.646138 -1.258692 1.338392
1 -0.771134 0.262460 -1.481012
1 0.987568 1.226136 -0.031293
1 2.361794 3.248602 0.009779
1 4.860833 3.111931 0.127862
1 5.946118 0.853014 0.211963
1 4.585923 -1.196235 0.171485
1 -3.112236 -3.104814 -1.015056
1 -1.814632 -4.113492 -0.321867
1 -2.985535 -3.302534 0.735336
```




***Z*-3d($T_1$)**

Structure: ***Z*-3d($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -883.428977 hartree
SCF Energy + ZPVE: -883.194126 hartree
Enthalpy: -883.176410 hartree
Free Energy: -883.242397 hartree
Free Energy with quasiharmonic correction: -883.238052 hartree

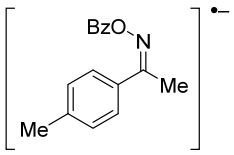
```
6 -3.041283 1.550857 -0.550134
6 -4.306844 1.055922 -0.262156
6 -4.513061 -0.183670 0.327752
6 -3.406638 -0.959076 0.643754
6 -2.092226 -0.502062 0.372477
6 -1.939426 0.771382 -0.233511
6 -0.963782 -1.314505 0.699902
7 0.335384 -0.821118 0.486398
8 0.725951 -1.214888 -0.786376
9 -5.385955 1.814741 -0.572365
6 2.053997 -0.995161 -1.109127
6 2.848502 0.005032 -0.347065
8 2.482744 -1.643619 -2.027238
6 2.332530 1.244136 0.048630
6 3.167921 2.166944 0.671851
6 4.504768 1.850267 0.919054
6 5.017214 0.614268 0.524425
6 4.194277 -0.303435 -0.122628
6 -1.055967 -2.685899 1.292123
1 -2.932300 2.525558 -1.014275
1 -5.522500 -0.526268 0.530555
1 -3.558488 -1.929663 1.104458
1 -0.947068 1.148623 -0.458496
1 1.295568 1.498929 -0.140765
1 2.773014 3.133739 0.967293
1 5.148177 2.570005 1.416118
1 6.056928 0.367258 0.713939
1 4.585440 -1.262977 -0.446567
1 -1.545615 -3.380010 0.596910
1 -0.057876 -3.070029 1.513757
1 -1.638811 -2.681962 2.220386
```




***Z*-3e**

Structure: ***Z*-3e**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -823.613371 hartree
SCF Energy + ZPVE: -823.338985 hartree
Enthalpy: -823.320846 hartree
Free Energy: -823.386694 hartree
Free Energy with quasiharmonic correction: -823.381973 hartree

```
6 2.260092 -1.497114 0.960509
6 3.283833 -1.807387 0.054192
6 3.691196 -0.818229 -0.844784
6 3.098483 0.444347 -0.842769
6 2.060125 0.736969 0.046449
6 1.648816 -0.248918 0.955358
6 1.455601 2.097233 0.054138
7 0.200985 2.366938 0.058284
8 -0.567670 1.190391 -0.010101
6 -1.905663 1.399035 0.020483
6 -2.638352 0.101570 -0.054699
8 -2.428032 2.483380 0.102039
6 -1.970724 -1.126476 -0.129932
6 -2.706722 -2.307422 -0.191826
6 -4.101534 -2.265634 -0.179045
6 -4.765864 -1.040016 -0.104126
6 -4.035914 0.143273 -0.041558
6 2.369976 3.286273 0.068102
6 3.913260 -3.174823 0.052577
1 1.937275 -2.247262 1.678630
1 4.487379 -1.033246 -1.552789
1 3.439649 1.194917 -1.549846
1 0.858691 -0.033050 1.667850
1 -0.885791 -1.159425 -0.139381
1 -2.190578 -3.260541 -0.250377
1 -4.671573 -3.188621 -0.227510
1 -5.850826 -1.007344 -0.094048
1 -4.538844 1.103286 0.018039
1 3.046445 3.224142 0.925706
1 2.984154 3.299537 -0.837536
1 1.794196 4.211803 0.119584
1 4.808000 -3.197523 -0.574132
1 4.190413 -3.479628 1.066194
1 3.210470 -3.921866 -0.332285
```




***Z*-3e$^{\bullet-}$**

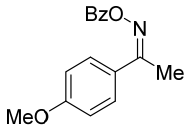
Structure: ***Z*-3e$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -823.688813 hartree
SCF Energy + ZPVE: -823.418020 hartree
Enthalpy: -823.399567 hartree
Free Energy: -823.466507 hartree
Free Energy with quasiharmonic correction: -823.461941 hartree

```
6 2.302524 -1.577921 0.794770
6 3.431296 -1.765313 -0.015044
6 3.884030 -0.680209 -0.769852
6 3.232612 0.552362 -0.721489
6 2.090317 0.728424 0.068379
6 1.637122 -0.357753 0.833668
6 1.432466 2.062945 0.130189
7 0.166257 2.288689 0.130635
8 -0.585917 1.141189 0.020740
6 -1.982124 1.363544 -0.044318
6 -2.688765 0.130901 -0.059883
8 -2.448608 2.511739 -0.089508
6 -2.058282 -1.162045 0.003381
6 -2.813028 -2.319861 -0.014069
6 -4.222567 -2.285830 -0.096718
6 -4.854109 -1.023871 -0.164801
6 -4.124323 0.148611 -0.150106
6 2.309065 3.283453 0.199526
6 4.121569 -3.102289 -0.070650
1 1.939849 -2.403366 1.403500
1 4.761635 -0.796211 -1.400977
1 3.615585 1.376668 -1.316267
1 0.765883 -0.240670 1.469021
1 -0.975855 -1.225141 0.064144
1 -2.302825 -3.279964 0.035830
1 -4.803341 -3.202392 -0.108336
1 -5.939094 -0.970271 -0.231704
1 -4.626642 1.110295 -0.204139
1 3.016725 3.201638 1.030626
1 2.892705 3.396495 -0.719919
1 1.697106 4.177725 0.332466
1 5.084366 -3.028880 -0.582448
1 4.292063 -3.498459 0.934999
1 3.507432 -3.832609 -0.608989
```


***Z*-3e($T_1$)**

Structure: ***Z*-3e($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -823.516414 hartree
SCF Energy + ZPVE: -823.245601 hartree
Enthalpy: -823.227129 hartree
Free Energy: -823.294729 hartree
Free Energy with quasiharmonic correction: -823.289914 hartree

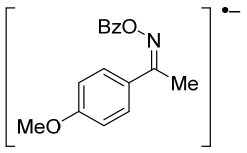
```
6 3.661487 0.646269 0.880098
6 3.316913 1.777852 0.128082
6 2.272442 1.654523 -0.803115
6 1.593932 0.458966 -0.976123
6 1.940293 -0.688963 -0.214925
6 2.996586 -0.562247 0.719593
6 1.235330 -1.923588 -0.354510
7 0.292439 -2.039760 -1.390029
8 -0.944592 -1.447544 -1.165829
6 -1.395115 -1.177037 0.110133
6 -2.438770 -0.123205 0.101498
8 -0.994176 -1.768888 1.078505
6 -2.722084 0.631943 -1.042592
6 -3.699621 1.622019 -0.985390
6 -4.392292 1.854290 0.203449
6 -4.108876 1.098447 1.343148
6 -3.131665 0.110314 1.294938
6 1.542119 -3.161324 0.426540
6 4.032619 3.089097 0.306698
1 4.468512 0.716809 1.605451
1 1.989528 2.518327 -1.400702
1 0.793320 0.402744 -1.708594
1 3.291279 -1.418084 1.319307
1 -2.181657 0.451978 -1.965677
1 -3.920073 2.212235 -1.869073
1 -5.154776 2.626501 0.242861
1 -4.649018 1.280529 2.266745
1 -2.899494 -0.484285 2.172790
1 2.558253 -3.518295 0.217907
1 1.465084 -2.970107 1.502490
1 0.838115 -3.955386 0.169243
1 3.348332 3.860917 0.675957
1 4.855510 2.995056 1.019599
1 4.440371 3.446707 -0.644645
```




***Z*-3f**

Structure: ***Z*-3f**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -898.799554 hartree
SCF Energy + ZPVE: -898.519495 hartree
Enthalpy: -898.500735 hartree
Free Energy: -898.567379 hartree
Free Energy with quasiharmonic correction: -898.563224 hartree

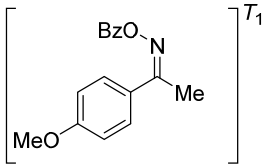
```
6 3.552120 -0.094413 -0.667714
6 3.234931 -1.120508 0.227018
6 2.117612 -0.992170 1.066672
6 1.319061 0.136423 0.997004
6 1.620867 1.175556 0.099322
6 2.750883 1.047327 -0.711203
6 0.808742 2.418298 0.040843
7 -0.473097 2.491511 0.011606
8 -1.053466 1.209996 -0.028978
6 -2.407781 1.215889 -0.027854
6 -2.937788 -0.177990 -0.079146
8 -3.088262 2.211297 0.014434
6 -2.094542 -1.294783 -0.111570
6 -2.646011 -2.573253 -0.152122
6 -4.031584 -2.738985 -0.161243
6 -4.871388 -1.624146 -0.129577
6 -4.326102 -0.344309 -0.087889
6 1.521202 3.739316 0.022932
8 3.945436 -2.264065 0.357506
6 5.090426 -2.431521 -0.470904
1 4.410689 -0.164552 -1.324942
1 1.892559 -1.790992 1.766522
1 0.461506 0.220069 1.656664
1 3.012947 1.837144 -1.408976
1 -1.016841 -1.166729 -0.104931
1 -1.993226 -3.440241 -0.176451
1 -4.457224 -3.737522 -0.193009
1 -5.949167 -1.753013 -0.136702
1 -4.966374 0.531786 -0.061663
1 2.175170 3.820351 0.896224
1 2.149652 3.817239 -0.869433
1 0.803706 4.561456 0.022609
1 5.508396 -3.403510 -0.210653
1 4.813392 -2.424102 -1.530436
1 5.832937 -1.650173 -0.277181
```




***Z*-3f**$^{\bullet-}$

Structure: ***Z*-3f**$^{\bullet-}$
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -898.874815 hartree
SCF Energy + ZPVE: -898.598222 hartree
Enthalpy: -898.579176 hartree
Free Energy: -898.646594 hartree
Free Energy with quasiharmonic correction: -898.642856 hartree

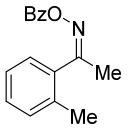
```
6 3.682913 -0.022653 -0.590403
6 3.324307 -1.128902 0.184215
6 2.136804 -1.096357 0.930154
6 1.312360 0.015816 0.885333
6 1.650136 1.137803 0.105752
6 2.850712 1.098423 -0.609685
6 0.814302 2.367603 0.076497
7 -0.471568 2.421828 0.058863
8 -1.062218 1.178651 0.015212
6 -2.475714 1.200786 -0.038228
6 -2.998658 -0.120173 -0.073524
8 -3.103962 2.270054 -0.050144
6 -2.188200 -1.310342 -0.060122
6 -2.769473 -2.563843 -0.091805
6 -4.171265 -2.730822 -0.139163
6 -4.978521 -1.571466 -0.158615
6 -4.423926 -0.306922 -0.129642
6 1.511141 3.701644 0.059233
8 4.057221 -2.264316 0.281194
6 5.271638 -2.331435 -0.455900
1 4.596132 -0.014990 -1.173694
1 1.876582 -1.956695 1.539514
1 0.399760 0.020853 1.470280
1 3.151989 1.949861 -1.212598
1 -1.106600 -1.218759 -0.027254
1 -2.125897 -3.441514 -0.081021
1 -4.614912 -3.720887 -0.161600
1 -6.061454 -1.672856 -0.198298
1 -5.059967 0.573560 -0.146676
1 2.235731 3.769967 0.876626
1 2.056919 3.845181 -0.879117
1 0.779560 4.506129 0.156249
1 5.699068 -3.310672 -0.241441
1 5.084666 -2.241819 -1.531467
1 5.969749 -1.550239 -0.136224
```




***Z*-3f($T_1$)**

Structure: ***Z*-3f($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -898.702943 hartree
SCF Energy + ZPVE: -898.426423 hartree
Enthalpy: -898.407123 hartree
Free Energy: -898.475758 hartree
Free Energy with quasiharmonic correction: -898.472077 hartree

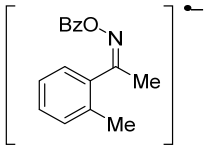
```
6 -4.107039 -0.483990 0.015188
6 -2.879981 -1.112595 0.268157
6 -1.694480 -0.420397 0.056137
6 -1.684956 0.914643 -0.413950
6 -2.943696 1.527160 -0.660087
6 -4.123763 0.842671 -0.449400
6 -0.473122 1.632440 -0.632682
6 -0.407864 3.061454 -1.077272
7 0.763848 0.991190 -0.443686
8 1.144526 1.200240 0.879854
6 2.429614 0.814225 1.209933
8 2.890487 1.315121 2.202804
6 3.147338 -0.179705 0.367352
6 4.527390 -0.002602 0.224053
6 5.274725 -0.932443 -0.493656
6 4.649921 -2.053320 -1.041016
6 3.276698 -2.241937 -0.875867
6 2.519057 -1.302880 -0.181557
8 -5.315893 -1.068467 0.188890
6 -5.341250 -2.411313 0.657470
1 -2.838127 -2.133578 0.629674
1 -0.755799 -0.925696 0.262390
1 -2.984597 2.551325 -1.017726
1 -5.082237 1.316918 -0.638282
1 0.629847 3.358040 -1.246277
1 -0.965939 3.217519 -2.007743
1 -0.836147 3.730433 -0.319441
1 5.005055 0.866117 0.666573
1 6.342645 -0.785127 -0.619701
1 5.233426 -2.783444 -1.593780
1 2.793222 -3.120525 -1.290947
1 1.452798 -1.454978 -0.056379
1 -4.879943 -2.491243 1.647640
1 -4.831937 -3.081856 -0.042991
1 -6.393705 -2.685860 0.723581
```




***Z*-3g**

Structure: ***Z*-3g**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -823.614467 hartree
SCF Energy + ZPVE: -823.339645 hartree
Enthalpy: -823.321903 hartree
Free Energy: -823.385823 hartree
Free Energy with quasiharmonic correction: -823.381965 hartree

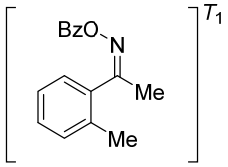
```
6 3.375940 -1.915190 -0.983483
6 2.867744 -2.659332 0.081246
6 2.079433 -2.039697 1.047607
6 1.761092 -0.677894 0.974365
6 2.273344 0.060974 -0.108042
6 3.088062 -0.556271 -1.066211
6 2.009776 1.521908 -0.254824
7 0.850549 2.055057 -0.373703
8 -0.141063 1.055525 -0.426251
6 -1.372627 1.470772 -0.051530
6 -2.356560 0.354649 -0.160560
8 -1.630887 2.587187 0.328147
6 -1.961716 -0.954763 -0.460171
6 -2.920546 -1.962363 -0.534519
6 -4.266437 -1.666551 -0.313372
6 -4.657927 -0.360740 -0.012695
6 -3.703870 0.649523 0.067612
6 3.176116 2.462046 -0.263618
6 0.899791 -0.068551 2.050670
1 3.996242 -2.386154 -1.739630
1 3.091709 -3.718790 0.163887
1 1.698065 -2.619157 1.885102
1 3.483596 0.031901 -1.890078
1 -0.913959 -1.184614 -0.628613
1 -2.616764 -2.978831 -0.764207
1 -5.010897 -2.454830 -0.374400
1 -5.704677 -0.131199 0.160107
1 -3.992580 1.668848 0.303801
1 3.852535 2.210947 -1.086680
1 2.841206 3.494853 -0.373908
1 3.738098 2.353323 0.669414
1 -0.157470 -0.300242 1.874885
1 1.166468 -0.482956 3.026747
1 1.000503 1.018687 2.099479
```




***Z*-3g$^{\bullet-}$**

Structure: ***Z*-3g$^{\bullet-}$**
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -823.689881 hartree
SCF Energy + ZPVE: -823.418668 hartree
Enthalpy: -823.400588 hartree
Free Energy: -823.465541 hartree
Free Energy with quasiharmonic correction: -823.462018 hartree

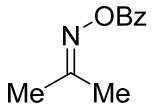
```
6 3.494501 -1.857945 -0.971678
6 3.035339 -2.609529 0.109073
6 2.226526 -2.011723 1.073563
6 1.841782 -0.668620 0.982419
6 2.305503 0.082513 -0.115725
6 3.137758 -0.515319 -1.071190
6 1.980243 1.531483 -0.270640
7 0.793410 2.013245 -0.350070
8 -0.158895 1.014706 -0.358817
6 -1.464836 1.441669 -0.036988
6 -2.387910 0.367100 -0.149260
8 -1.691016 2.611730 0.310020
6 -2.022204 -0.969267 -0.543973
6 -2.974718 -1.966957 -0.632362
6 -4.334555 -1.722889 -0.337754
6 -4.705655 -0.418219 0.058469
6 -3.774953 0.597507 0.155133
6 3.116473 2.510329 -0.336607
6 0.956526 -0.085459 2.052663
1 4.129585 -2.309339 -1.727832
1 3.311534 -3.655467 0.206263
1 1.881227 -2.595957 1.923490
1 3.497214 0.076443 -1.909109
1 -0.984531 -1.191242 -0.775982
1 -2.663591 -2.964898 -0.935435
1 -5.072226 -2.515344 -0.411194
1 -5.746719 -0.205290 0.293901
1 -4.078120 1.594833 0.461036
1 3.761322 2.294984 -1.195138
1 2.737391 3.530458 -0.426420
1 3.734085 2.430083 0.564252
1 -0.097351 -0.279591 1.822463
1 1.181231 -0.539953 3.021500
1 1.075449 0.998022 2.138211
```




***Z*-3g($T_1$)**

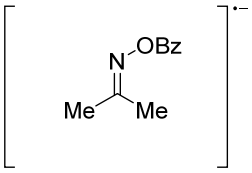
Structure: ***Z*-3g($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -823.487101 hartree
SCF Energy + ZPVE: -823.217451 hartree
Enthalpy: -823.199139 hartree
Free Energy: -823.264414 hartree
Free Energy with quasiharmonic correction: -823.261251 hartree

```
6 -0.968646 2.686947 -0.267545
6 -0.368388 1.881730 0.704306
6 -0.999765 0.726049 1.137335
6 -2.134229 0.225031 0.302557
6 -2.964368 1.263850 -0.313701
6 -2.340602 2.413022 -0.670380
6 -2.344310 -1.133198 -0.018126
6 -3.686091 -1.593978 -0.528797
7 -1.456299 -2.123105 0.085970
8 -0.137633 -1.655486 0.267604
6 0.443994 -1.011979 -0.776511
8 -0.095604 -0.830155 -1.841952
6 1.824896 -0.569715 -0.430565
6 2.387412 -0.804716 0.829012
6 3.670313 -0.339173 1.107282
6 4.388839 0.358958 0.135106
6 3.825422 0.592868 -1.120499
6 2.543403 0.130394 -1.404164
1 -0.493421 3.604411 -0.595473
6 -0.742336 0.114316 2.476621
1 0.530117 2.222607 1.215332
1 -3.985253 1.055417 -0.616279
1 -2.869852 3.160325 -1.255071
1 -3.747385 -2.681888 -0.458003
1 -4.509249 -1.151224 0.036070
1 -3.800877 -1.315223 -1.582070
1 1.825968 -1.343478 1.585151
1 4.108855 -0.520209 2.083657
1 5.388363 0.721170 0.356522
1 4.383460 1.136850 -1.876183
1 2.089545 0.310164 -2.373718
1 -1.534108 0.424666 3.173171
1 -0.752970 -0.978860 2.447866
1 0.213526 0.459692 2.880436
```



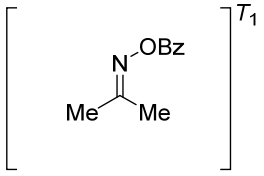

Structure: **acetone *O*-benzoyl oxime**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -592.643006 hartree
SCF Energy + ZPVE: -592.449797 hartree
Enthalpy: -592.436514 hartree
Free Energy: -592.489651 hartree
Free Energy with quasiharmonic correction: -592.487633 hartree

```
6 3.134898 0.266235 -0.000000
7 2.255580 -0.665154 -0.000003
8 0.963613 -0.091663 -0.000002
6 -0.043761 -0.994455 0.000001
6 -1.370290 -0.309614 0.000000
8 0.109104 -2.191667 0.000002
6 -1.490915 1.084723 -0.000000
6 -2.756498 1.666774 -0.000001
6 -3.897716 0.863475 -0.000001
6 -3.776011 -0.527171 -0.000000
6 -2.514035 -1.114041 0.000000
6 2.822925 1.733468 0.000003
6 4.564597 -0.173423 -0.000001
1 -0.604195 1.710070 -0.000000
1 -2.851728 2.748082 -0.000001
1 -4.882412 1.321332 -0.000001
1 -4.663279 -1.152528 -0.000000
1 -2.404044 -2.193852 0.000001
1 2.231350 1.996016 -0.882313
1 2.231345 1.996011 0.882317
1 3.744517 2.316605 0.000008
1 5.070137 0.233319 0.882070
1 4.648214 -1.261482 -0.000004
1 5.070136 0.233322 -0.882072
```



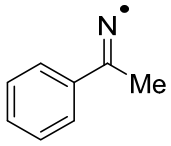

Structure: **acetone *O*-benzoyl oxime**$^{\bullet-}$
Charge = -1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -592.717432 hartree
SCF Energy + ZPVE: -592.527922 hartree
Enthalpy: -592.514296 hartree
Free Energy: -592.568669 hartree
Free Energy with quasiharmonic correction: -592.566650 hartree

```
6 3.145231 0.268784 0.000000
7 2.244415 -0.643854 0.000001
8 0.979008 -0.077789 -0.000001
6 -0.083488 -1.005517 -0.000000
6 -1.339174 -0.339532 -0.000000
8 0.126579 -2.228467 -0.000001
6 -1.492836 1.092785 -0.000000
6 -2.748364 1.670726 0.000000
6 -3.925377 0.889248 0.000001
6 -3.789196 -0.517730 0.000000
6 -2.547385 -1.121191 0.000000
6 2.844572 1.739838 -0.000001
6 4.574267 -0.181431 0.000001
1 -0.608311 1.722804 -0.000000
1 -2.827316 2.756315 0.000000
1 -4.905184 1.355689 0.000001
1 -4.680429 -1.142566 0.000001
1 -2.461772 -2.204204 0.000000
1 2.250851 2.008103 -0.880133
1 2.250852 2.008104 0.880131
1 3.768030 2.321714 -0.000002
1 5.091513 0.213173 0.881627
1 4.645143 -1.271155 0.000002
1 5.091513 0.213172 -0.881625
```




Structure: **acetone *O*-benzoyl oxime ($T_1$)**
Charge = 0, Multiplicity = 3
Number of imaginary frequencies: 0
SCF Energy: -592.510127 hartree
SCF Energy + ZPVE: -592.321912 hartree
Enthalpy: -592.307628 hartree
Free Energy: -592.364485 hartree
Free Energy with quasiharmonic correction: -592.361554 hartree

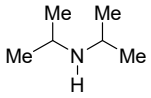
```
6 3.138673 0.254642 0.000005
7 2.243507 -0.662453 -0.000001
8 0.966528 -0.078637 -0.000014
6 -0.063703 -0.984716 -0.000024
6 -1.338694 -0.319672 -0.000011
8 0.089969 -2.199813 -0.000003
6 -1.481161 1.152759 -0.000014
6 -2.710199 1.705988 -0.000002
6 -3.911169 0.881923 0.000014
6 -3.776949 -0.565704 0.000017
6 -2.563116 -1.150656 0.000005
6 2.843538 1.725397 0.000000
6 4.563233 -0.202681 0.000018
1 -0.586745 1.764853 -0.000025
1 -2.822158 2.785965 -0.000004
1 -4.890248 1.342617 0.000023
1 -4.677109 -1.172757 0.000029
1 -2.444988 -2.228107 0.000007
1 2.253641 1.994636 -0.881783
1 2.253627 1.994640 0.881774
1 3.770809 2.299785 0.000006
1 5.075932 0.195706 0.881960
1 4.632038 -1.291951 0.000020
1 5.075947 0.195703 -0.881917
```




**VII**

Structure: **VII**
Charge = 0, Multiplicity = 1 Number of imaginary frequencies: 0
SCF Energy: -364.226956 hartree
SCF Energy + ZPVE: -364.088768 hartree
Free Energy: -364.122983 hartree
Free Energy with quasiharmonic correction: -364.121473 hartree

```
6 0.585379 1.241645 0.000002
6 1.969686 1.111680 0.000004
6 2.555109 -0.157227 0.000002
6 1.748237 -1.293036 -0.000003
6 0.358510 -1.166823 -0.000004
1 2.594116 1.999902 0.000008
1 2.196808 -2.281714 -0.000006
1 -0.256865 -2.060752 -0.000007
1 3.636332 -0.257397 0.000004
6 -0.231001 0.101150 -0.000002
7 -2.267590 1.382556 -0.000007
6 -1.722202 0.247425 -0.000002
6 -2.597779 -0.988744 0.000007
1 -2.387106 -1.590696 0.888384
1 -2.387112 -1.590704 -0.888365
1 -3.649932 -0.701377 0.000009
1 0.131261 2.228431 0.000004
```

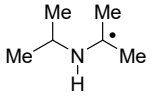



**DIPA**

Structure: **DIPA**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -292.293965 hartree
SCF Energy + ZPVE: -292.087399 hartree
Free Energy: -292.120483 hartree
Free Energy with quasiharmonic correction: -292.120121 hartree

```
6 -1.036557 -0.025665 -0.219511
1 -0.553051 -0.132901 -1.201427
6 1.379268 -0.073536 0.455640
1 1.951242 -0.164283 1.387666
6 -1.698140 1.350783 -0.160609
1 -0.956100 2.152298 -0.216644
1 -2.405120 1.479636 -0.987926
1 -2.245738 1.460357 0.783026
6 -2.083914 -1.127461 -0.090061
```

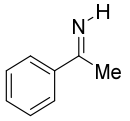
```
1 -2.871739 -1.009398 -0.840241
1 -1.631179 -2.116844 -0.218599
1 -2.551447 -1.088837 0.901724
6 1.694252 1.289639 -0.152509
1 2.768107 1.372668 -0.347165
1 1.172340 1.430598 -1.105924
1 1.402819 2.099364 0.523942
6 1.827623 -1.206959 -0.474231
1 1.611350 -2.182865 -0.025583
1 1.321780 -1.155472 -1.444795
1 2.906014 -1.149441 -0.658040
7 -0.035934 -0.166283 0.856326
1 -0.162934 -1.071705 1.303389
```




**VIII**

Structure: **VII**
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -291.647225 hartree
SCF Energy + ZPVE: -291.454572 hartree
Free Energy: -291.488651 hartree
Free Energy with quasiharmonic correction: -291.488589 hartree

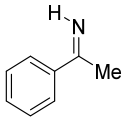
```
6 1.207181 0.136252 0.234945
1 1.071087 0.804982 1.092836
6 -1.252814 0.015976 -0.132048
6 1.524579 0.976935 -1.003147
1 0.709526 1.672485 -1.227507
1 2.441424 1.556557 -0.853387
1 1.667225 0.324348 -1.873124
6 2.343644 -0.829197 0.549299
1 3.280691 -0.284526 0.696386
1 2.129945 -1.405229 1.454684
1 2.487039 -1.531469 -0.281162
6 -1.543214 1.207628 0.728100
1 -2.506558 1.644066 0.449304
1 -1.604028 0.929618 1.796483
1 -0.783605 1.992170 0.642956
6 -2.393218 -0.904086 -0.442648
1 -2.109834 -1.661367 -1.182728
1 -2.737317 -1.442248 0.459160
1 -3.249898 -0.348078 -0.834904
7 -0.030693 -0.635262 0.085255
1 0.102201 -1.425520 -0.542790
```




***E*-IX**

Structure: ***E*-IX**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -364.881258 hartree
SCF Energy + ZPVE: -364.729494 hartree
Free Energy: -364.762756 hartree
Free Energy with quasiharmonic correction: -364.761480 hartree

```
6 -0.586895 -1.231667 -0.000001
6 -1.975183 -1.148384 -0.000001
6 -2.603806 0.099703 -0.000000
6 -1.832784 1.259959 0.000001
6 -0.439651 1.176160 0.000001
1 -2.570210 -2.056843 -0.000002
1 -2.312163 2.234235 0.000002
1 0.142200 2.092051 0.000004
1 -3.687868 0.164563 0.000000
6 0.199338 -0.069850 -0.000000
7 2.224080 -1.338784 0.000002
6 1.693286 -0.175127 0.000001
6 2.488134 1.105254 -0.000002
1 2.250247 1.707141 0.882803
1 2.250245 1.707130 -0.882815
1 3.557850 0.886558 0.000000
1 3.243091 -1.260033 0.000002
1 -0.096589 -2.199612 -0.000001
```

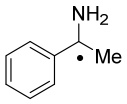



***Z*-IX**

Structure: ***Z*-IX**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -364.879818 hartree
SCF Energy + ZPVE: -364.727918 hartree
Free Energy: -364.760470 hartree
Free Energy with quasiharmonic correction: -364.760068 hartree

```
6 0.573945 1.212247 -0.178404
6 1.963360 1.123662 -0.190972
6 2.588743 -0.110481 -0.006269
6 1.815641 -1.255780 0.179066
6 0.424030 -1.169427 0.179257
1 2.557958 2.017659 -0.352753
1 2.294424 -2.220009 0.320590
1 -0.163335 -2.071059 0.321431
```

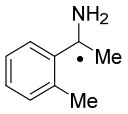
```
1 3.672421 -0.179119 -0.014674
6 -0.212427 0.067774 0.014802
7 -2.344680 1.226627 0.362711
6 -1.708036 0.165808 0.038340
6 -2.492339 -1.061150 -0.339028
1 -2.384380 -1.834747 0.428754
1 -2.134195 -1.483094 -1.282877
1 -3.549240 -0.805388 -0.427170
1 -1.701666 1.975577 0.630779
1 0.103275 2.177873 -0.343810
```




**XII**

Structure: **XII**
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -365.457969 hartree
SCF Energy + ZPVE: -365.296556 hartree
Free Energy: -365.330292 hartree
Free Energy with quasiharmonic correction: -365.330194 hartree

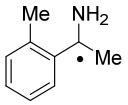
```
6 0.592860 1.226386 -0.042749
6 1.979068 1.170347 -0.034586
6 2.654689 -0.055898 0.008158
6 1.901219 -1.238414 0.037306
6 0.515905 -1.203183 0.029252
1 2.545407 2.097574 -0.067611
1 2.406246 -2.200404 0.068334
1 -0.036763 -2.137152 0.058472
1 3.739390 -0.090116 0.014503
6 -0.194053 0.035152 -0.004688
7 -2.306689 1.244078 0.000155
6 -1.612495 0.055952 0.003235
6 -2.427696 -1.199136 -0.055130
1 -2.296004 -1.807040 0.849047
1 -2.145809 -1.826146 -0.908792
1 -3.490667 -0.963000 -0.147207
1 -3.292195 1.194597 0.224531
1 0.115243 2.200234 -0.096504
1 -1.855012 2.075677 0.359357
```




**conformer 1**

Structure: **conformer 1**
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -404.749598 hartree
SCF Energy + ZPVE: -404.559996 hartree
Enthalpy: -404.549084 hartree
Free Energy: -404.595247 hartree
Free Energy with quasiharmonic correction: -404.594976 hartree

```
6 0.599998 -1.464713 0.070297
6 1.986123 -1.463176 0.113364
6 2.688654 -0.256373 0.086236
6 1.963613 0.937123 -0.007080
6 0.571946 0.975448 -0.054261
1 2.519332 -2.407892 0.179148
1 2.503093 1.879759 -0.073079
1 3.773549 -0.239706 0.117792
6 -0.161900 -0.258280 0.010955
7 -2.179068 -1.565891 -0.289054
6 -1.589503 -0.345345 -0.009282
6 -2.554404 0.711502 0.439751
1 -3.004000 1.257369 -0.400317
1 -2.094793 1.435115 1.111366
1 -3.375788 0.231930 0.985636
1 -3.181844 -1.546617 -0.428560
1 0.081589 -2.416517 0.133356
1 -1.705378 -2.181132 -0.940279
6 -0.088419 2.317797 -0.264426
1 -0.912245 2.253305 -0.981197
1 -0.490417 2.742227 0.661398
1 0.643724 3.029501 -0.655219
```

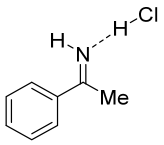



**conformer 2**

Structure: **conformer 2**
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -404.749874 hartree
SCF Energy + ZPVE: -404.559818 hartree
Enthalpy: -404.549060 hartree
Free Energy: -404.594753 hartree
Free Energy with quasiharmonic correction: -404.594584 hartree

```
6 -0.484738 -1.476702 -0.032480
6 -1.864874 -1.580689 -0.064827
6 -2.659112 -0.429655 -0.059150
```

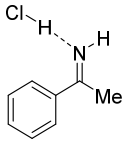
```
6 -2.023505 0.815559 -0.000257
6 -0.638833 0.963585 0.033836
1 -2.324038 -2.565141 -0.099595
1 -2.631838 1.716872 0.038434
1 -3.742192 -0.494957 -0.083938
6 0.191654 -0.215183 -0.001176
7 2.389995 0.894911 -0.220562
6 1.615541 -0.227548 -0.009835
6 2.391518 -1.495193 0.202497
1 2.376331 -2.136807 -0.689456
1 1.995230 -2.084375 1.034845
1 3.437655 -1.264464 0.422667
1 3.362475 0.724070 -0.442564
1 0.101501 -2.388922 -0.057092
1 1.997534 1.672709 -0.731176
6 -0.095225 2.366936 0.179862
1 0.673429 2.429638 0.955643
1 0.336144 2.755554 -0.750863
1 -0.906758 3.044783 0.456215
```




***E*-IX•HCl**

Structure: ***E*-IX•HCl**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -825.693063 hartree
SCF Energy + ZPVE: -825.527686 hartree
Free Energy: -825.565009 hartree
Free Energy with quasiharmonic correction: -825.563459 hartree

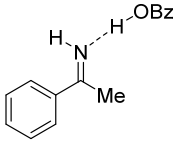
```
6 -1.517376 -1.221950 -0.186491
6 -2.895375 -1.402116 -0.162564
6 -3.740801 -0.309828 0.040758
6 -3.206978 0.967933 0.206546
6 -1.829040 1.157562 0.170147
1 -3.309992 -2.393819 -0.311236
1 -3.862875 1.818487 0.360759
1 -1.422592 2.155231 0.299816
1 -4.816593 -0.454977 0.060908
6 -0.974376 0.060579 -0.011237
7 1.296443 -0.689309 0.233737
6 0.482320 0.276258 -0.030552
6 1.052295 1.615673 -0.347111
1 0.827984 2.298444 0.479486
1 0.586253 2.018143 -1.249362
1 2.134446 1.555392 -0.470664
1 2.332062 -0.553308 0.183363
1 -0.877388 -2.078176 -0.378917
1 0.959948 -1.609076 0.510018
17 4.361743 -0.282109 0.047217
```




***Z*-IX•HCl**

Structure: ***Z*-IX•HCl**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -825.692971 hartree
SCF Energy + ZPVE: -825.527489 hartree
Free Energy: -825.564852 hartree
Free Energy with quasiharmonic correction: -825.563305 hartree

```
6 0.272585 -0.902898 0.381308
6 1.136256 -1.991215 0.345015
6 2.473494 -1.813825 -0.015336
6 2.950849 -0.542282 -0.332494
6 2.094712 0.553412 -0.289671
1 0.766773 -2.978132 0.604148
1 3.990385 -0.401964 -0.610241
1 2.476201 1.538028 -0.538164
1 3.144621 -2.667001 -0.042496
6 0.746267 0.378628 0.056434
7 -1.429306 1.395725 0.078792
6 -0.146642 1.547382 0.088027
6 0.409315 2.929263 0.127317
1 0.912797 3.138981 -0.822129
1 1.151833 3.011312 0.924690
1 -0.382664 3.663387 0.276788
1 -1.928492 0.485385 -0.005692
1 -0.761731 -1.057978 0.674862
1 -2.025631 2.219617 0.126552
17 -3.350586 -1.039559 -0.194321
```

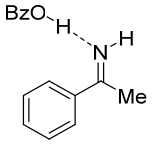



***E*-IX•HOBz**

Structure: ***E*-IX•HOBz**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -785.583353 hartree
SCF Energy + ZPVE: -785.314716 hartree
Free Energy: -785.363686 hartree
Free Energy with quasiharmonic correction: -785.357477 hartree

```
6 -3.827251 -1.163774 -0.323316
6 -5.125855 -1.663809 -0.305289
6 -6.195069 -0.824421 0.012107
6 -5.959804 0.519467 0.299283
6 -4.661064 1.024564 0.270501
```

```
1 -5.303989 -2.707281 -0.546128
1 -6.787436 1.178223 0.543485
1 -4.493506 2.073340 0.493729
1 -7.207873 -1.215598 0.027564
6 -3.580484 0.184095 -0.027071
7 -1.155884 -0.017620 0.140645
6 -2.187161 0.720596 -0.036070
6 -1.992376 2.192205 -0.257727
1 -2.360164 2.753016 0.607903
1 -2.553641 2.530484 -1.133177
1 -0.932969 2.415540 -0.390894
1 0.360045 0.356279 0.089077
1 -3.008507 -1.824661 -0.594064
6 4.467019 -1.297511 0.081352
6 3.587875 -0.211387 0.041051
6 4.089692 1.089949 -0.057948
6 5.466197 1.300924 -0.116044
6 6.342236 0.215287 -0.076216
6 5.841829 -1.084542 0.022523
1 4.062726 -2.301966 0.158262
1 3.403158 1.929400 -0.088434
1 5.855027 2.311746 -0.192586
1 7.414462 0.381855 -0.122045
1 6.522874 -1.929587 0.053168
1 -1.375375 -0.998553 0.321022
6 2.114190 -0.476859 0.105085
8 1.657674 -1.606431 0.202218
8 1.369391 0.609230 0.047192
```

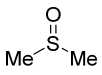



***Z*-IX•HOBz**

Structure: ***Z*-IX•HOBz**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -785.584112 hartree
SCF Energy + ZPVE: -785.315453 hartree
Free Energy: -785.364560 hartree
Free Energy with quasiharmonic correction: -785.358157 hartree

```
6 -2.434677 0.898157 0.742710
6 -2.865453 2.217927 0.646141
6 -3.973500 2.536807 -0.141428
6 -4.654358 1.528170 -0.822121
6 -4.229955 0.204238 -0.718961
1 -2.341114 2.997342 1.190638
1 -5.518934 1.769720 -1.432723
1 -4.769674 -0.570916 -1.254083
1 -4.308937 3.566821 -0.217198
6 -3.107798 -0.120540 0.053690
7 -1.409207 -1.746550 0.463188
```

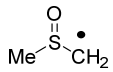
```
6 -2.633454 -1.529657 0.154314
6 -3.613592 -2.634537 -0.118472
1 -3.886258 -2.636878 -1.178907
1 -4.531412 -2.488479 0.457905
1 -3.174681 -3.602838 0.128527
1 -0.136185 -0.816552 0.426054
1 -1.584821 0.650537 1.371107
6 4.232145 -0.870844 -0.272412
6 3.044567 -0.181758 -0.009716
6 3.060741 1.209096 0.133323
6 4.262084 1.905492 0.013468
6 5.446611 1.216015 -0.249069
6 5.431203 -0.172941 -0.391828
1 4.204036 -1.950549 -0.380903
1 2.136449 1.739068 0.337296
1 4.273936 2.985415 0.124828
1 6.381724 1.760381 -0.342475
1 6.352541 -0.709747 -0.596272
1 -1.195363 -2.743485 0.521860
6 1.771775 -0.962607 0.111940
8 1.732958 -2.177041 -0.014272
8 0.710181 -0.220721 0.365842
```




**DMSO**

Structure: **DMSO**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -553.097263 hartree
SCF Energy + ZPVE: -553.017022 hartree
Free Energy: -553.045180 hartree
Free Energy with quasiharmonic correction: -553.045180 hartree

```
6 -1.352098 -0.795160 0.189660
1 -1.326178 -1.776815 -0.290295
1 -2.285956 -0.286855 -0.058080
1 -1.244702 -0.887067 1.273701
16 -0.000000 0.215521 -0.447472
8 -0.000009 1.499366 0.379121
6 1.352106 -0.795146 0.189661
1 1.244722 -0.887047 1.273704
1 1.326176 -1.776807 -0.290283
1 2.285962 -0.286848 -0.058098
```



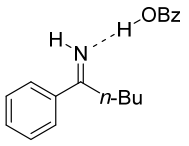

**[DMSO – H•]**

Structure: [**DMSO – H•**]
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -552.422394 hartree
SCF Energy + ZPVE: -552.356643 hartree
Free Energy: -552.385654 hartree
Free Energy with quasiharmonic correction: -552.385654 hartree

```
6 -1.549713 -0.202832 0.199899
1 -1.897861 -1.144824 -0.230830
1 -2.187164 0.618901 -0.131246
1 -1.517652 -0.255313 1.290302
16 0.119548 0.139090 -0.414815
8 0.640146 1.358191 0.333464
6 0.906741 -1.277999 0.224670
1 0.472501 -2.248279 0.006401
1 1.954073 -1.176470 0.487288
```


Structure: **H•**
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -0.495776 hartree
SCF Energy + ZPVE: -0.495776 hartree
Free Energy: -0.506430 hartree
Free Energy with quasiharmonic correction: -0.506430 hartree

```
1 0.000000 0.000000 0.000000
```

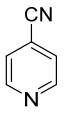



***E*-6l'**

Structure: ***E*-6l'**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -903.470003 hartree
SCF Energy + ZPVE: -903.115298 hartree
Enthalpy: -903.093692 hartree
Free Energy: -903.170461 hartree
Free Energy with quasiharmonic correction: -903.162211 hartree

```
6 3.571313 -2.130876 0.170310
6 4.860593 -2.627858 0.003574
6 5.933870 -1.750561 -0.159245
6 5.712734 -0.374013 -0.140343
6 4.424495 0.125332 0.041347
1 5.028385 -3.700413 0.007979
1 6.543225 0.314353 -0.262588
1 4.269589 1.199686 0.058517
1 6.939220 -2.138949 -0.291373
6 3.338014 -0.748343 0.183243
7 0.907068 -0.879729 0.025610
6 1.953931 -0.214126 0.345585
6 1.757339 1.188230 0.866288
1 2.602437 1.489574 1.491826
1 0.860415 1.192894 1.494555
1 -0.585015 -0.436522 0.166047
1 2.750579 -2.827721 0.316928
6 -4.824629 -1.565176 -0.455296
6 -3.851640 -0.652362 -0.037830
6 -4.234665 0.592721 0.470289
6 -5.586429 0.920550 0.559401
6 -6.556235 0.007946 0.142019
6 -6.174591 -1.235631 -0.365443
1 -4.511931 -2.527776 -0.847643
1 -3.475822 1.297596 0.793059
1 -5.883135 1.887584 0.953909
1 -7.609033 0.265308 0.212138
1 -6.928630 -1.945959 -0.690472
1 1.099031 -1.795977 -0.381922
6 -2.407653 -1.039223 -0.149135
8 -2.054150 -2.121916 -0.592417
8 -1.569870 -0.112309 0.270389
6 1.566311 2.191608 -0.282833
1 2.424042 2.149130 -0.966878
1 0.683446 1.896978 -0.864559
6 1.392866 3.619633 0.228066
1 0.543615 3.651406 0.922714
1 2.281807 3.906064 0.804442
6 1.169873 4.615947 -0.906199
```

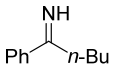
```
1 1.048361 5.634512 -0.525003
1 2.018400 4.615700 -1.599329
1 0.270731 4.361653 -1.478170
```




**4a**

Structure: **4a**
Charge, Spin Multiplicity: 0, 1
Number of imaginary frequencies: 0
SCF Energy: -340.410271 hartree
SCF Energy + ZPVE: -340.322040 hartree
Free Energy: -340.352278 hartree
Free Energy with quasiharmonic correction: -340.352278 hartree

```
6 -0.110915 1.207593 -0.000091
6 -1.501701 1.146473 0.000060
7 -2.189659 -0.000100 0.000084
6 -1.501557 -1.146552 -0.000001
6 -0.110736 -1.207499 -0.000058
6 0.588790 0.000103 -0.000101
1 0.406997 2.159805 -0.000256
1 -2.084434 2.063171 0.000090
1 -2.084214 -2.063304 0.000098
1 0.407300 -2.159636 -0.000177
6 2.030810 -0.000097 -0.000011
7 3.187688 0.000076 0.000125
```

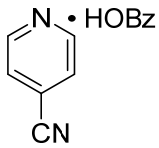



**6l''**

Structure: **6l''**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -482.767340 hartree
SCF Energy + ZPVE: -482.529939 hartree
Enthalpy: -482.517093 hartree
Free Energy: -482.568993 hartree
Free Energy with quasiharmonic correction: -482.567357 hartree

```
6 1.644928 -1.116826 -0.376437
6 1.296765 0.211409 -0.097759
6 2.292978 1.092741 0.344846
6 3.608638 0.660737 0.492496
6 3.949547 -0.659468 0.195001
6 2.964781 -1.545518 -0.240403
1 0.892263 -1.820849 -0.716753
1 2.037238 2.118524 0.597896
1 4.366051 1.353246 0.847157
1 4.975582 -0.996511 0.308074
```

```
1 3.221691 -2.574371 -0.473934
6 -0.114708 0.694200 -0.258191
7 -0.410336 1.896965 -0.575033
6 -1.215790 -0.310568 -0.013323
1 0.435475 2.450199 -0.732486
6 -2.627020 0.262804 -0.028727
1 -1.133561 -1.097481 -0.775548
1 -1.016181 -0.808269 0.945392
6 -3.683192 -0.806945 0.243283
1 -2.708626 1.058981 0.722271
1 -2.823300 0.731592 -1.000658
6 -5.100242 -0.240298 0.227393
1 -3.595522 -1.601851 -0.508852
1 -3.484083 -1.274752 1.216226
1 -5.846030 -1.017400 0.421785
1 -5.218740 0.537017 0.990550
1 -5.330015 0.209553 -0.744962
```

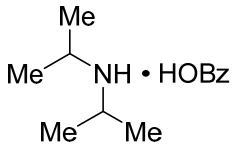



**4a•HOBz**

Structure: **4a•HOBz**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -761.111988 hartree
SCF Energy + ZPVE: -760.906352 hartree
Enthalpy: -760.890660 hartree
Free Energy: -760.951720 hartree
Free Energy with quasiharmonic correction: -760.947475 hartree

```
6 3.539637 -1.099109 -0.000001
6 2.181519 -0.801044 -0.000012
7 1.721236 0.454599 -0.000016
6 2.589152 1.472327 -0.000010
6 3.965985 1.282612 0.000000
6 4.438220 -0.031132 0.000006
1 3.883134 -2.126853 0.000002
1 1.429533 -1.584590 -0.000017
1 2.167839 2.473076 -0.000016
1 4.644412 2.127773 0.000004
6 5.858199 -0.284796 0.000013
7 6.996753 -0.488068 0.000020
1 0.110882 0.708034 -0.000008
8 -0.895622 0.892638 -0.000008
6 -1.554614 -0.253054 -0.000007
8 -1.001403 -1.342199 -0.000013
6 -3.042231 -0.100735 -0.000001
6 -3.643665 1.161729 0.000004
6 -3.833560 -1.253321 0.000001
6 -5.033150 1.267569 0.000010
```

```
1 -3.025293 2.053002 0.000002
6 -5.221556 -1.144373 0.000007
1 -3.352526 -2.226383 -0.000003
6 -5.821899 0.116302 0.000012
1 -5.500093 2.247671 0.000014
1 -5.835227 -2.039944 0.000008
1 -6.904604 0.201134 0.000017
```

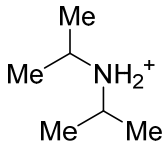



**DIPA•HOBz**

Structure: **DIPA•HOBz**
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -713.003123 hartree
SCF Energy + ZPVE: -712.680401 hartree
Enthalpy: -712.661543 hartree
Free Energy: -712.729307 hartree
Free Energy with quasiharmonic correction: -712.723736 hartree

```
6 -3.216242 0.994656 -0.301426
1 -4.122775 0.637401 0.201505
6 -2.461883 -1.258458 0.574630
1 -1.579734 -1.898150 0.449077
6 -3.576313 1.379594 -1.731060
1 -4.032651 0.536771 -2.261259
1 -4.283112 2.214334 -1.736943
1 -2.677957 1.689247 -2.278549
6 -2.666387 2.193111 0.467493
1 -3.433311 2.969634 0.551523
1 -2.349998 1.914383 1.476623
1 -1.803530 2.618299 -0.057357
6 -3.698439 -2.056583 0.168334
1 -3.789430 -2.950538 0.793268
1 -4.614725 -1.468843 0.289909
1 -3.627952 -2.376877 -0.876653
6 -2.527361 -0.810752 2.029854
1 -1.630067 -0.253326 2.316080
1 -3.404350 -0.181643 2.217283
1 -2.603703 -1.689854 2.676430
7 -2.213436 -0.105218 -0.330131
1 -0.854285 0.304264 -0.078393
1 -2.173125 -0.484276 -1.277435
8 0.196561 0.550516 0.136525
6 0.990690 -0.341707 -0.399796
8 0.598826 -1.306096 -1.049518
6 2.454174 -0.098495 -0.160113
6 3.384958 -0.995782 -0.691696
6 2.893892 1.002130 0.581528
```

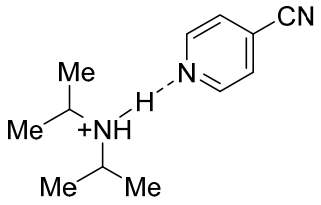
```
6 4.747439 -0.794629 -0.483964
1 3.029390 -1.845841 -1.265557
6 4.257770 1.202519 0.788765
1 2.166828 1.694842 0.992152
6 5.184897 0.305133 0.256947
1 5.467902 -1.493401 -0.898304
1 4.597143 2.057978 1.365006
1 6.247213 0.462329 0.419477
```




**DIPA•H$^+$**

Structure: **DIPA•H$^+$**
Charge = 1, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -292.767070 hartree
SCF Energy + ZPVE: -292.545052 hartree
Enthalpy: -292.534812 hartree
Free Energy: -292.578317 hartree
Free Energy with quasiharmonic correction: -292.577862 hartree

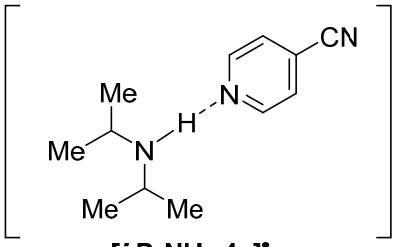
```
6 -1.068164 -0.027757 -0.265583
1 -0.537098 -0.144499 -1.212104
6 1.433178 -0.063246 0.421973
1 1.970494 -0.134380 1.371230
6 -1.696172 1.353825 -0.180787
1 -0.951364 2.148460 -0.271049
1 -2.417718 1.466353 -0.993858
1 -2.228277 1.472331 0.769535
6 -2.088663 -1.142841 -0.108653
1 -2.837391 -1.061133 -0.900355
1 -1.612815 -2.125650 -0.183908
1 -2.598538 -1.066115 0.857654
6 1.706127 1.285664 -0.218838
1 2.780776 1.367535 -0.401119
1 1.193077 1.388039 -1.179993
1 1.407132 2.108355 0.437259
6 1.808549 -1.241955 -0.460814
1 1.552170 -2.192476 0.017229
1 1.321763 -1.191213 -1.439032
1 2.889176 -1.222790 -0.623230
7 -0.022022 -0.174993 0.826567
1 -0.138619 -1.088220 1.280322
1 -0.207747 0.518211 1.561650
```




**[*i*-PrNH$_2$•4a]$^+$**

Structure: **[*i*-PrNH$_2$•4a]$^+$**
Charge = 1, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -633.188236 hartree
SCF Energy + ZPVE: -632.877512 hartree
Enthalpy: -632.859391 hartree
Free Energy: -632.924526 hartree
Free Energy with quasiharmonic correction: -632.920133 hartree

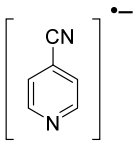
```
6 2.917961 1.044649 -0.010644
1 3.724450 0.621115 0.591757
6 2.326530 -1.467821 0.120892
1 1.576245 -2.109968 -0.351075
6 2.037254 1.936261 0.852524
1 1.593600 1.383211 1.685312
1 2.642681 2.747844 1.264401
1 1.232849 2.376594 0.252698
6 3.510074 1.786130 -1.198804
1 4.113414 2.624218 -0.841083
1 4.151570 1.127422 -1.792845
1 2.715603 2.182099 -1.840845
6 2.058410 -1.399419 1.615396
1 2.125916 -2.410415 2.025524
1 2.796444 -0.777201 2.131120
1 1.056081 -1.012242 1.824058
6 3.716531 -1.980072 -0.219467
1 3.879971 -1.990012 -1.301474
1 4.497200 -1.375300 0.251728
1 3.816061 -3.003686 0.150702
7 2.097954 -0.121541 -0.521057
1 2.262983 -0.234782 -1.527026
1 1.074044 0.096027 -0.417917
7 -0.738643 0.129301 -0.199972
6 -1.398226 0.665250 0.832091
6 -1.434062 -0.475533 -1.168815
6 -2.783821 0.623630 0.945236
1 -0.797175 1.147285 1.598261
6 -2.821247 -0.573795 -1.155744
1 -0.860066 -0.898891 -1.988588
6 -3.498193 -0.009343 -0.073507
1 -3.287209 1.068768 1.795590
1 -3.353218 -1.070810 -1.958567
6 -4.937364 -0.080430 -0.007926
7 -6.091387 -0.137519 0.044012
```




**[*i*-PrNH$_2$•4a]$^{\bullet}$**

Structure: **[*i*-PrNH$_2$•4a]$^{\bullet}$**
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -633.289051 hartree
SCF Energy + ZPVE: -632.983122 hartree
Enthalpy: -632.964847 hartree
Free Energy: -633.031051 hartree
Free Energy with quasiharmonic correction: -633.026422 hartree

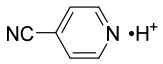
```
6 2.849962 1.025988 0.004607
1 3.691292 0.584051 0.544900
6 2.243108 -1.466904 0.084041
1 1.466133 -2.091944 -0.369455
6 2.035850 1.896416 0.953569
1 1.626740 1.315428 1.784905
1 2.678760 2.678632 1.366623
1 1.207301 2.375789 0.420977
6 3.378914 1.816679 -1.183150
1 3.996977 2.646292 -0.830057
1 3.989790 1.184023 -1.835428
1 2.549702 2.230185 -1.768243
6 2.038413 -1.445615 1.591324
1 2.110104 -2.468804 1.969884
1 2.804966 -0.847272 2.094188
1 1.051180 -1.052101 1.853558
6 3.610327 -1.996445 -0.322481
1 3.729888 -1.983141 -1.410511
1 4.419897 -1.413264 0.127462
1 3.712006 -3.029958 0.019794
7 1.998885 -0.107179 -0.503036
1 2.128164 -0.191232 -1.515519
1 0.908134 0.106982 -0.349294
7 -0.621815 0.176173 -0.197237
6 -1.323588 0.585879 0.904146
6 -1.360239 -0.331174 -1.232109
6 -2.686422 0.521316 1.016682
1 -0.728151 0.984053 1.723329
6 -2.724607 -0.442320 -1.227269
1 -0.789660 -0.657937 -2.099870
6 -3.464612 -0.008138 -0.071875
1 -3.172599 0.867153 1.923349
1 -3.239398 -0.855792 -2.088601
6 -4.858461 -0.097501 -0.009814
7 -6.030368 -0.173311 0.041985
```




**4a**$^{\bullet-}$

Structure: **4a**$^{\bullet-}$
Charge = −1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -340.502002 hartree
SCF Energy + ZPVE: -340.416655 hartree
Free Energy: -340.447861 hartree
Free Energy with quasiharmonic correction: -340.447861 hartree

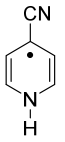
```
6 0.127648 -1.217892 -0.000010
6 1.498802 -1.150153 0.000019
7 2.237013 0.000133 0.000042
6 1.498610 1.150298 0.000033
6 0.127443 1.217794 0.000007
6 -0.642122 -0.000115 -0.000014
1 -0.369277 -2.183477 -0.000029
1 2.071777 -2.076167 0.000021
1 2.071429 2.076409 0.000050
1 -0.369646 2.183293 0.000002
6 -2.036739 -0.000260 -0.000033
7 -3.215033 0.000140 -0.000050
```




**4a•H**$^{+}$

Structure: **4a•H**$^{+}$
Charge = 1, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -340.855358 hartree
SCF Energy + ZPVE: -340.753396 hartree
Free Energy: -340.783778 hartree
Free Energy with quasiharmonic correction: -340.783778 hartree

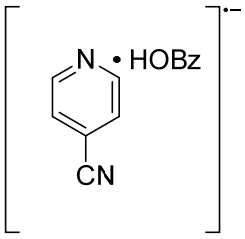
```
6 0.058975 1.216434 0.000010
6 1.440590 1.184402 -0.000027
7 2.070626 -0.000003 -0.000054
6 1.440586 -1.184405 -0.000044
6 0.058970 -1.216432 -0.000006
6 -0.628046 0.000003 0.000018
1 -0.464048 2.164534 0.000030
1 2.062800 2.070229 -0.000037
1 2.062793 -2.070235 -0.000065
1 -0.464056 -2.164530 0.000001
6 -2.070991 0.000006 0.000051
7 -3.226357 -0.000004 0.000074
1 3.092125 -0.000005 -0.000084
```




**4a•H**

Structure: **4a•H**
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -340.988685 hartree
SCF Energy + ZPVE: -340.889906 hartree
Free Energy: -340.921302 hartree
Free Energy with quasiharmonic correction: -340.921302 hartree

```
6 -0.073509 1.228177 -0.000009
6 -1.433039 1.199967 0.000027
7 -2.109009 -0.000000 0.000053
6 -1.433038 -1.199967 0.000043
6 -0.073509 -1.228177 0.000008
6 0.669250 0.000000 -0.000018
1 0.439316 2.183111 -0.000029
1 -2.045513 2.092517 0.000036
1 -2.045513 -2.092517 0.000064
1 0.439316 -2.183110 0.000001
6 2.074739 0.000000 -0.000050
7 3.244431 0.000000 -0.000076
1 -3.120924 -0.000000 0.000082
```

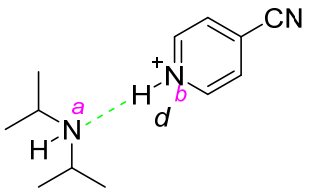



**[4a•HOBz]•−**

Structure: **[4a-HOBz]•−**
Charge = −1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -761.219615 hartree
SCF Energy + ZPVE: -761.016945 hartree
Enthalpy: -761.000778 hartree
Free Energy: -761.064441 hartree
Free Energy with quasiharmonic correction: -761.058957 hartree

```
6 3.505073 -1.128019 -0.000008
6 2.171414 -0.848969 0.000001
7 1.712359 0.444286 0.000012
6 2.598606 1.492491 0.000005
6 3.945101 1.286522 -0.000003
6 4.461295 -0.054378 -0.000006
1 3.836846 -2.160309 -0.000017
```

```
1 1.395022 -1.605538 0.000000
1 2.161021 2.484378 0.000006
1 4.618004 2.136771 -0.000009
6 5.841557 -0.304915 -0.000005
7 6.994363 -0.514831 -0.000005
1 0.671426 0.634362 0.000015
8 -0.914328 0.996751 0.000022
6 -1.517093 -0.119849 0.000009
8 -0.969892 -1.243250 -0.000001
6 -3.039629 -0.067027 0.000003
6 -3.710462 1.159602 -0.000008
6 -3.782458 -1.251263 0.000007
6 -5.104669 1.202897 -0.000015
1 -3.125450 2.073923 -0.000011
6 -5.176426 -1.211984 0.000001
1 -3.252007 -2.198494 0.000015
6 -5.840312 0.016372 -0.000010
1 -5.618067 2.160268 -0.000025
1 -5.745927 -2.137068 0.000006
1 -6.926145 0.048634 -0.000015
```




**[DIPA…4a•H$^+$]**

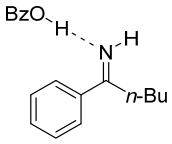
(optimized with constraint *d* = 1.02 Å)

The complex **[DIPA…4a•H$^+$]** was obtained by a constrained optimization with the N$^b$–H distance fixed at 1.02 Å, the bond length found in the optimized structure of 4-cyanopyridinium ion (**4a•H$^+$**). Submitting the resultant geometry of **[DIPA…4a•H$^+$]** to another optimization without any distance constraint led back to **[*i*-PrNH$_2$•4a]$^+$.**

Structure: **[DIPA…4a•H$^+$]**
Charge = 1, Multiplicity = 1
SCF Energy: -633.168238 hartree

```
6 2.844214 1.029460 -0.044055
1 3.729095 0.635986 0.472549
6 2.281226 -1.426083 0.100561
1 1.517071 -2.096079 -0.315391
6 2.072641 1.922347 0.925032
1 1.696622 1.352598 1.780447
1 2.715380 2.723153 1.305166
1 1.217989 2.383528 0.414162
6 3.313520 1.824072 -1.257313
1 3.906135 2.689450 -0.946623
1 3.928686 1.204027 -1.918337
1 2.451091 2.189514 -1.828124
6 2.108638 -1.399827 1.615517
```

```
1 2.228279 -2.411026 2.015571
1 2.860540 -0.761510 2.092176
1 1.115159 -1.036602 1.900583
6 3.653353 -1.970297 -0.298190
1 3.761752 -1.987732 -1.387944
1 4.462916 -1.362545 0.120078
1 3.777582 -2.992575 0.073243
7 1.992402 -0.099484 -0.494929
1 2.103890 -0.201269 -1.503710
7 -0.707474 0.090625 -0.171437
6 -1.323588 0.590489 0.908046
6 -1.364992 -0.461794 -1.199576
6 -2.703984 0.553644 0.994202
1 -0.690322 1.010397 1.681044
6 -2.746198 -0.534667 -1.180502
1 -0.758699 -0.834137 -2.017659
6 -3.412060 -0.015361 -0.067391
1 -3.210418 0.956791 1.862475
1 -3.284716 -0.979949 -2.007827
6 -4.853197 -0.069550 -0.012979
7 -6.007174 -0.112842 0.029661
1 0.310242 0.115283 -0.235037
```

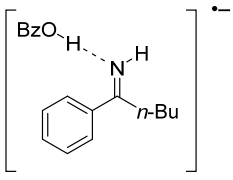



***Z*-6l'**

Structure: ***Z*-6l'**
Charge = 0, Multiplicity = 1
SCF Energy: -903.471306 hartree
SCF Energy + ZPVE: -903.116823 hartree
Enthalpy: -903.095176 hartree
Free Energy: -903.171887 hartree
Free Energy with quasiharmonic correction: -903.163717 hartree

```
6 1.190243 1.641796 0.674165
6 1.284471 3.025288 0.797981
6 2.207373 3.735069 0.028086
6 3.042859 3.053550 -0.856718
6 2.957728 1.667397 -0.973521
1 0.642027 3.548567 1.499663
1 3.765319 3.599976 -1.455183
1 3.616592 1.150443 -1.664778
1 2.280385 4.814290 0.123641
6 2.019956 0.950511 -0.219045
7 0.756911 -1.068969 -0.122197
6 1.895987 -0.529298 -0.353357
6 3.118616 -1.329620 -0.721539
1 3.500611 -0.979785 -1.688306
1 2.819689 -2.375156 -0.849633
1 -0.689778 -0.461492 0.026145
1 0.483847 1.088960 1.285859
```

```
6 -4.989692 -1.488594 -0.162887
6 -3.962511 -0.555039 0.003450
6 -4.270768 0.787178 0.245583
6 -5.602685 1.191049 0.320173
6 -6.626773 0.257618 0.154151
6 -6.319585 -1.082869 -0.087543
1 -4.734726 -2.527011 -0.349943
1 -3.470102 1.507883 0.373952
1 -5.841325 2.233432 0.507961
1 -7.663940 0.574302 0.213054
1 -7.115941 -1.809495 -0.216523
1 0.784233 -2.085503 -0.220497
6 -2.542830 -1.026372 -0.082839
8 -2.252500 -2.192997 -0.300558
8 -1.649297 -0.072798 0.098111
6 4.229737 -1.230702 0.332520
1 4.544813 -0.186108 0.446118
1 3.833772 -1.552165 1.304905
6 5.439864 -2.086964 -0.034460
1 5.121933 -3.130798 -0.150756
1 5.823986 -1.764442 -1.010815
6 6.547814 -1.998922 1.011137
1 7.407158 -2.618038 0.735810
1 6.899106 -0.967206 1.122832
1 6.189517 -2.337962 1.989437
```




[*Z*-6l']•–

Structure: [***Z*-6l'**]•–
Charge = -1, Multiplicity = 2
SCF Energy: -903.570946 hartree
SCF Energy + ZPVE: -903.219410 hartree
Enthalpy: -903.197009 hartree
Free Energy: -903.276338 hartree
Free Energy with quasiharmonic correction: -903.267578 hartree

```
6 1.172807 2.055873 0.002198
6 1.401574 3.396694 0.274135
6 2.694949 3.937387 0.249093
6 3.769008 3.086214 -0.057169
6 3.564643 1.743869 -0.331354
1 0.555204 4.037360 0.511081
1 4.781953 3.480839 -0.077947
1 4.423866 1.118825 -0.555441
1 2.862845 4.987783 0.464398
6 2.253268 1.172238 -0.318813
7 0.794903 -0.751729 -0.531043
6 2.036738 -0.201069 -0.606901
6 3.160265 -1.149320 -0.918634
```

1 3.905966 -0.664286 -1.559214
1 2.758203 -1.994406 -1.492066
1 -0.071126 -0.243468 -0.316675
1 0.153170 1.680549 0.032060
6 -4.850898 -1.509990 -0.219871
6 -3.984426 -0.436551 0.007279
6 -4.516579 0.794106 0.403584
6 -5.892606 0.950789 0.571403
6 -6.751454 -0.125846 0.341881
6 -6.227621 -1.357908 -0.054750
1 -4.428287 -2.461747 -0.527055
1 -3.836369 1.622065 0.577571
1 -6.296094 1.910989 0.880648
1 -7.823272 -0.005361 0.471682
1 -6.892532 -2.198098 -0.234734
1 0.661451 -1.714679 -0.804675
6 -2.476485 -0.609499 -0.176630
8 -2.064491 -1.742341 -0.513605
8 -1.765549 0.416000 0.028768
6 3.854212 -1.692353 0.341097
1 4.252160 -0.853789 0.928280
1 3.107137 -2.193628 0.971304
6 4.984802 -2.665301 0.015293
1 4.584846 -3.496213 -0.580466
1 5.725636 -2.156593 -0.615538
6 5.664292 -3.211371 1.268224
1 6.472869 -3.905026 1.017058
1 6.092793 -2.399027 1.865796
1 4.946637 -3.747047 1.899535

**9. References**


(1) (a) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities. *J.* Org. *Chem.* **1997**, *62*, 7512–7515. (b) Fulmer, G. R.; Miller, A. J. M. Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M. Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176–2179.

(2) DiRocco, D. A.; Dykstra, K.; Krska, S.; Vachal, P.; Conway, D. V.; Tudge, M. Late-Stage Functionalization of Biologically Active Heterocycles Through Photoredox Catalysis. *Angew. Chem. int. Ed.* **2014**, *53*, 4802–4806.

(3) The Photoreactor TAK120. http://wppr.photoreactor.de/tak120 (accessed August 28, 2019).

(4) Le, C.; Wismer, M. K.; Shi, Z.-C.; Zhang, R.; Conway, D. V.; Li, G.; Vachal, P.; Davies, I. W.; MacMillan, D. W. C. A General Small Scale Reactor To Enable Standardization and Acceleration of Photocatalytic Reactions. *ACS Cent. Sci.* **2017**, *3*, 647−653.

(5) Lehnherr, D.; Nicastri, M. C.; Lam, Y.-h.; Liu, J.; Newman, J. A.; Regalado, E. L.; DiRocco, D. A.; Rovis, T. Electrochemical Synthesis of Hindered Primary- and Secondary-Amines via Proton-Coupled Electron Transfer. *J. Am. Chem. Soc.*, *accepted*.

(6) Sebhat, I. K.; Franklin, C.; Lo, M. M. C.; Chen, D.; Jewell, J. P.; Miller, R.; Pang, J.; Palyha, O.; Kan, Y.; Kelly, T. M.; Guan, X.M; Marsh, D.J.; Kosinski, J.A.; Metzger, J.M.; Lyons, K.; Dragovic, J.; Guzzo, P.R.; Henderson, A.J.; Reitman, M.L; Nargund, R.P.; Wyvratt, M.J.; Lin, L.S. Discovery of MK-5046, a Potent, Selective Bombesin Receptor Subtype-3 Agonist for the Treatment of Obesity. *ACS Med. Chem. Lett.* **2011**, *2*, 43–47.

(7) G. Hou, F. Gosselin, W. Li, J. C. McWilliams, Y. Sun, M. Weisel, P. D. O'Shea, C.-y. Chen, I. W. Davies, X. Zhang, Enantioselective Hydrogenation of N-H Imines. *J. Am. Chem. Soc.* **2009**, *131*, 9882–9883.

(8) Arias-Rotondo D. M.; McCusker, J. K. The photophysics of photoredox catalysis: a roadmap for catalyst design. *Chem. Soc. Rev.* **2016**, *45*, 5803–5820.

(9) Ochola, J. R.; Wolf, M. O. The effect of photocatalyst excited state lifetime on the rate of photoredox catalysis. *Org. Biomol. Chem.* **2016**, *14*, 9088–9092.

(10) Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

(11) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(12) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L.A. *J. Comp. Chem.* **2001**, *22*, 976–984.

(13) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions *J. Phys. Chem. B*, **2009**, *113*, 6378–6396.

(14) Ribeiro, R. F.; Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Use of Solution-Phase Vibrational Frequencies in Continuum Models. *J. Phys. Chem. B* **2011**, *115*, 14556–14562.

(15) CYLview, 1.0.561 BETA; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org).

(16) Persistence of Vision Pty. Ltd. (2004), Persistence of Vision Raytracer (Version 3.6), [Computer software]. Retrieved from http://www.povray.org/download/

(17) Marenich, A. V.; Ho, J.; Coote, M. L.; Cramer, C. J.; Truhlar, D. G. Computational electrochemistry: prediction of liquid-phase reduction potentials. *Phys. Chem. Chem. Phys.* **2014**, *16*, 15068–15106.

(18) Pavlishchuk, V. V.; Addison, A. W. Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C. *Inorg. Chim. Acta* **2000**, *298*, 97–101.