Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


**Supplementary Information**

# Photoinduced Amination of Iodoalkanes Enabled by Bifunctional *O*-Benzoyl Oxime

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# 1. Experimental section

## a) General information

All chemicals, unless otherwise noted, were purchased from commercial sources and were used without further purification. All organic solvents applied in the reactions were pre-dried by over appropriate drying reagents unless otherwise noted. Unless stated otherwise, all reactions were carried out under nitrogen atmosphere. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates, and visualized using UV fluorescence ($\lambda_{max}$ = 254 nm), and/or developed using standard $KMnO_4$ stain. The photoreaction instrument (WPTEC-1020L) was purchased from WATTCAS, China.

**SPECTROPHOTOCOLORMETER ANALYSIS REPORT**

**Color Parameters：**

| | |
|---|---|
| CIE(1931:) | x =0.1776 y =0.0296 |
| CIE(1960:) | u =0.2367 v =0.0592 |
| CIE(1976:) | u' =0.2367 v' =0.0888 |

Color Temperature：Tc=25000K Dominant Wave: WL.D=435.20nm Purity: PUR=93.54

Peak Wave: WL.P=392.5nm Delta Wave: WL.H=18.0nm

Color Tolerance: SDCM=186.7 Ra:Ra=15.0

CRI1=56.1 CRI2=16.3 CRI3=0.0 CRI4=0.0 CRI5=47.6

CRI6=0.0 CRI7=0.0 CRI8=0.0 CRI9=0.0 CRI10=0.0

CRI11=0.0 CRI12=0.0 CRI13=42.0 CRI14=6.3 CRI15=66.7

**Photology Parameters:**

Lum Flux: Φ(lm)=4.75lm Optical Power: Φe(mW)=2769.6mW η(lm/W)=0.4lm/W

**Eletric Parameters:**

Forward Voltage: VF = 22.68 V Forward Current: IF = 498.9 mA Power = 11.32 W

***Status:***

Wavelength Range：380nm---780nm Intergration Time ： 1000 ms

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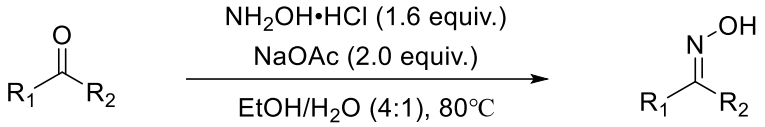
| | |
|---|---|
| Test Project：LED COB TESTING | Test Equipment：ZP OPTO SYSTEM |
| Product Model: HIGH POWER COB | Manufacturer: LEARNEW OPTO |
| Temperature:25 | Humidity:40% |
| Tester:MESSI LAN | Time: 2019-02-20 15:01 |
| Test Mechanism: ZP OPTO LAB | |

$^{1}$H NMR (400 MHz), $^{13}$C NMR (101 MHz) and $^{19}$F NMR (376 MHz) spectra were recorded on a Bruker AV-400 spectrometer or a Quantum-I Plus 400 in Chloroform-d. For $^{1}$H NMR, Chloroform-d ($\delta$ = 7.26 ppm) or tetramethylsilane (TMS, $\delta$ = 0 ppm) serves as the internal standard; for $^{13}$C NMR, Chloroform-*d* ($\delta$ = 77.16 ppm) serves as the internal standard. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, hept = heptet, m = multiplet, br = broad), coupling constant (in Hz), and integration. HR-MS spectra were recorded on a Waters Xevo G2QTOF/UPLC mass spectrometer using electrospray ionization.

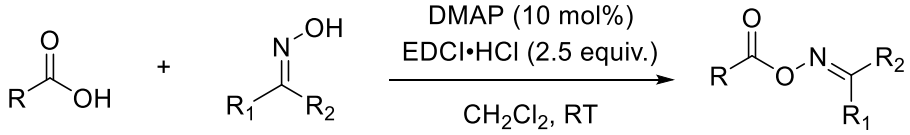
**b) Methods for the synthesis of substrates**

**General procedure for the synthesis of oxime (General Procedure 1)**




All oximes were prepared following reported literature procedure[1]. In a 250 mL round bottom flask equipped with a condenser, aromatic ketones (50.0 mmol, 1.0 equiv.) were dissolved in the mixture of EtOH/$H_2O$ (v/v, 4:1, 125 mL). Then, hydroxylamine hydrochloride (80.0 mmol, 1.6 equiv.) and NaOAc (100.0 mmol, 2.0 equiv.) were added in one portion. The reaction mixture was refluxed overnight and the consumption of the starting material was observed by TLC. After that, the reaction was cooled to room temperature and concentrated under reduced pressure to remove the ethanol as much as possible. Then the white solid was diluted with water (55.0 mL), extracted with ethyl acetate (80 mL × 3) and dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded the product in quantitative yield. This product was sufficiently pure as determined from NMR and was used without further purification.

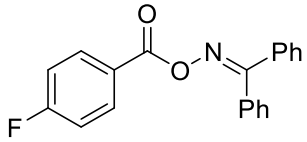
**General procedure for the synthesis of oxime esters (General Procedure 2)**




According to a related literature[1]， to a solution of ketoxime from previous step (5.0 mmol) and aromatic carboxylic acid (5.0 mmol) in $CH_2Cl_2$ (50 mL), DMAP (20 mol%, 1 mmol) and EDCI (12.5 mmol) was added. The mixture was stirred at room temperature under inert atmosphere until the reaction was complete as observed from TLC monitoring. The mixture was diluted with distilled water (50 mL) and the $CH_2Cl_2$ layer was separated, dried over anhydrous $Na_2SO_4$ and concentrated. The solvent was

removed and the residue was purified by silica gel column chromatography (petroleum ether / ethylacetate as eluent) to give the corresponding compound.

**diphenylmethanone *O*-(4-fluorobenzoyl) oxime (2b)**




Synthesized by following General Procedure 2 using benzophenone oxime (986 mg, 5.0 mmol) and 4-Fluorobenzoic acid (700 mg, 5.0 mmol). Purified by flash column chromatography (petroleum ether: ethyl acetate, 5:1, v:v) as white solid (yield 73%).

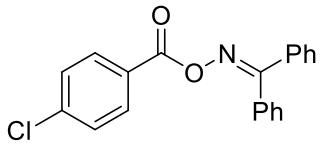
**$^{1}$H NMR** (400 MHz, Chloroform-d) δ 7.81 (dd, J = 8.9, 5.4 Hz, 2H), 7.67 (d, J = 7.3 Hz, 2H), 7.55 – 7.49 (m, 3H), 7.47 (d, J = 6.4 Hz, 1H), 7.39 (t, J = 7.4 Hz, 4H), 7.03 (t, J = 8.7 Hz, 2H).

**$^{19}$F NMR** (376 MHz, Chloroform-d) δ -104.77.

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 165.7, 164.6, 162.9, 134.6, 132.8, 132.3, 132.2, 131.2, 129.8, 129.2, 128.8, 128.5, 128.4, 125.1, 115.7.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{20}H_{15}FNO_2$: 320.1081, found: 320.1081.

**diphenylmethanone *O*-(4-chlorobenzoyl) oxime (2c)**



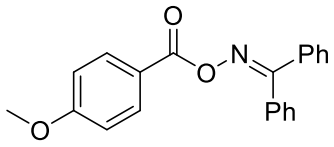

Synthesized by following General Procedure 2 using benzophenone oxime (986 mg, 5.0 mmol) and 4-Chlorobenzoic acid (780 mg, 5.0 mmol). Purified by flash column chromatography (petroleum ether: ethyl acetate, 3:1, v:v) as white solid (yield 68%).

**$^{1}$H NMR** (400 MHz, Chloroform-d) δ 7.72 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 3.4 Hz, 3H), 7.47 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 7.5 Hz, 4H), 7.34 (d, J = 8.4 Hz, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 134.5, 132.8, 131.2, 129.8, 129.2, 128.9, 128.8, 128.5, 128.4, 127.3.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{20}H_{15}ClNO_2$: 336.0786, found: 336.0788.

**diphenylmethanone *O*-(4-methoxybenzoyl) oxime (2d)**



Synthesized by following General Procedure 2 using benzophenone oxime (986 mg, 5.0 mmol) and 4-Methoxybenzoic acid (760 mg, 5.0 mmol). Purified by flash column chromatography (petroleum ether: ethyl acetate, 3:1, v:v) as white solid (yield 80%).

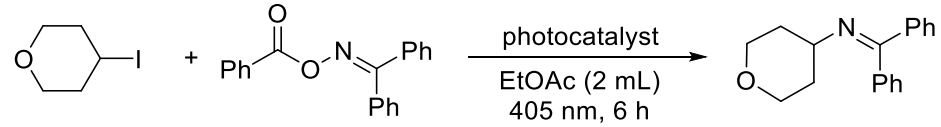
**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.76 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 7.3 Hz, 2H), 7.53 – 7.48 (m, 3H), 7.46 (d, J = 7.3 Hz, 1H), 7.43 – 7.36 (m, 4H), 6.85 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 165.1, 163.6, 134.8, 133.0, 131.8, 131.0, 129.7, 129.2, 128.9, 128.5, 128.3, 121.1, 113.8, 55.5.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{21}H_{18}NO_3$: 332.1281, found: 332.1277.

## c) Optimization of the reaction conditions

**Table S1.** Photocatalyst

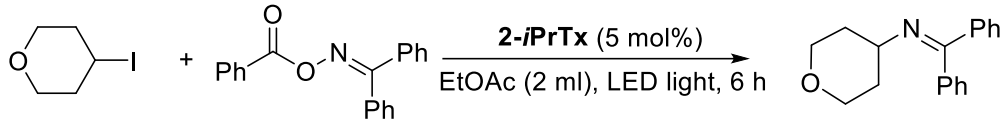



**1u,** 2.0 equiv. **2,** 0.2 mmol **3u**

| Entry | Photocatalyst | Yield (%)[α] |
|---|---|---|
| 1 | Thioxanthone | 66 |
| 2 | 2,4-diethyl-9H-thioxanthen-9-one | 57 |
| 3 | 4-CzIPN | 35 |
| 4 | 2-*i*Pr-thioxanthone | 70 |
| 5 | $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ | 66 |

[α] Yields of isolated products.

**Table S2.** LED light

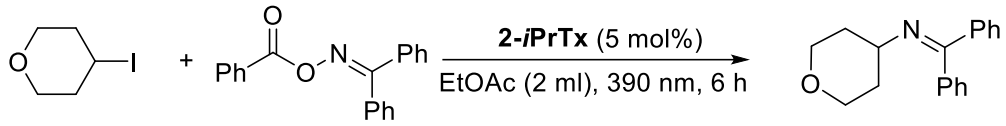



**1u**, 2.0 equiv. **2**, 0.2 mmol **3u**

| Entry | LED light | Yield (%)[α] |
|---|---|---|
| 1 | 10W 365 nm | 35 |
| 2 | 10W 390 nm | 73 |
| 3 | 10W 370 nm | 67 |

[α] Yields of isolated products.

**Table S3.** Solvent

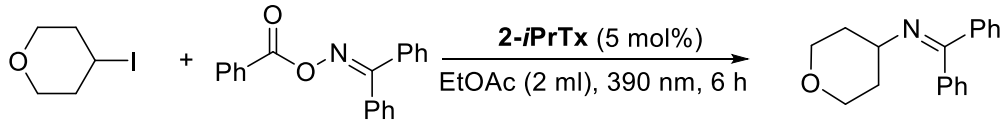



**1u**, 2.0 equiv. **2**, 0.2 mmol **3u**

| Entry | Solvent | Yield (%)[α] |
|---|---|---|
| 1 | EA | 73 |
| 2 | DMSO | 12 |
| 3 | DCM | 16 |
| 4 | DMF | 8 |
| 5 | Acetone | 68 |
| 6 | Isopropyl acetate | 48 |

[α] Yields of isolated products.

**Table S4.** Substrate ratio

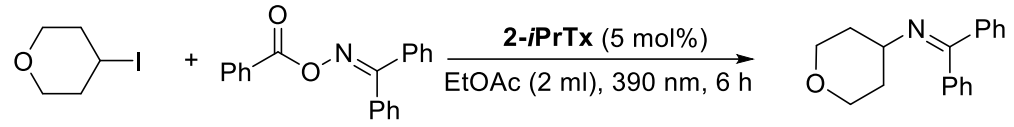



**1u**, *x* equiv. **2**, 0.2 mmol **3u**

| Entry | **2** / **1u** (equiv.) | Yield (%)[α] |
|---|---|---|
| 1 | 2/3 | 62 |
| 2 | 1/2 | 73 |
| 3 | 2/5 | 58 |
| 4 | 3/2 | 53 |

[α] Yields of isolated products.

**Table S5.** Control experiments.

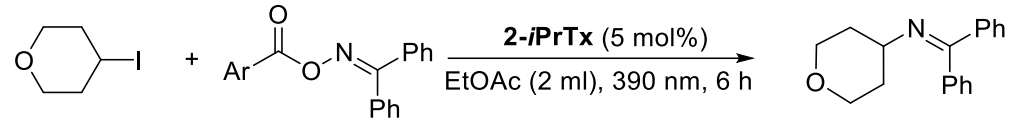



**1u**, 2.0 equiv. **2**, 0.2 mmol **3u**

| Entry | **2** / **1u** (equiv.) | 2-*i*PrTX (mol %) | Solvent (2 mL) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | 0/2 | 5 | EtOAc | - |
| 2 | 1/0 | 5 | EtOAc | - |
| 3 | 1/2 | - | EtOAc | - |
| 4[b] | 1/2 | 5 | EtOAc | - |

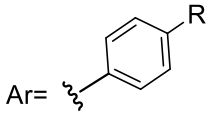
[a] Yields of isolated products. [b] Without light.

**Table S6.** oxime esters with different substituents.




**1u**, 2.0 equiv. **2b-2c**, 0.2 mmol **3u**

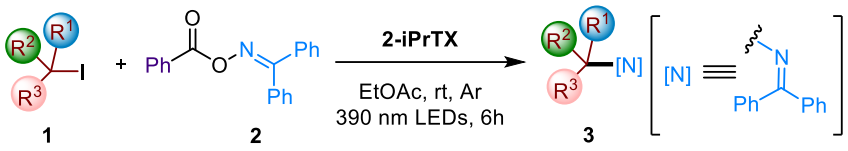
| Entry | oxime esters | 2-*i*PrTX (mol %) | Solvent (2 mL) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | **2b** | 5 | EtOAc | 28 |
| 2 | **2c** | 5 | EtOAc | 21 |
| 3 | **2d** | 5 | EtOAc | 32 |



**2b**, R=F
**2c**, R=Cl
**2d**, R=OMe

[a] Yields of isolated products.

## d) General procedure for the photoreactions




An oven dried 8 mL reaction vial was charged with a stir bar, **2** (0.2 mmol, 1.0 equiv.), and **2-*i*PrTX** photosensitizer (2.5 mg, 5 mol %) were charged under air, then addition of EtOAc (2.0 mL, 0.1 M) and **1u** (0.4 mmol, 2.0 equiv., if liquid). The reaction vial was sealed, evacuated and backfilled three times with 1 atm of $N_2$. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WPTEC-1020LC) for 6 hours until the reaction was complete. After irradiation, the resulting homogenous solution was transferred to a 25 mL round bottom flask with aid of DCM (2 x 3 mL). $NEt_3$ (approx. 0.5 mL) and $SiO_2$ were added to this solution and the volatiles were removed under reduced pressure, affording a powder which was loaded on column. Purification by flash column chromatography on $SiO_2$, pre-basified with $NEt_3$ using pentane: EtOAc mixtures afforded the corresponding amines products.

***Note**: $Et_3N$ was used as the product can be partially hydrolyzed by acidic silica, causing a slight decrease in the yield (approx. 10-15%). The amount of $Et_3N$ added to the eluent was approximately 1 ml for 300 ml of solvent. When $Et_3N$ was used for TLC analysis, one Pasteur pipette drop was used for 10 ml of eluent. "Pre-basified" silica refers to silica gel, which have been soaked with 2-3% triethylamine in hexanes prior to use.*

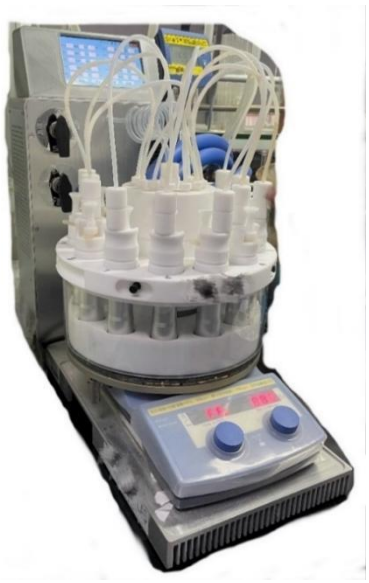
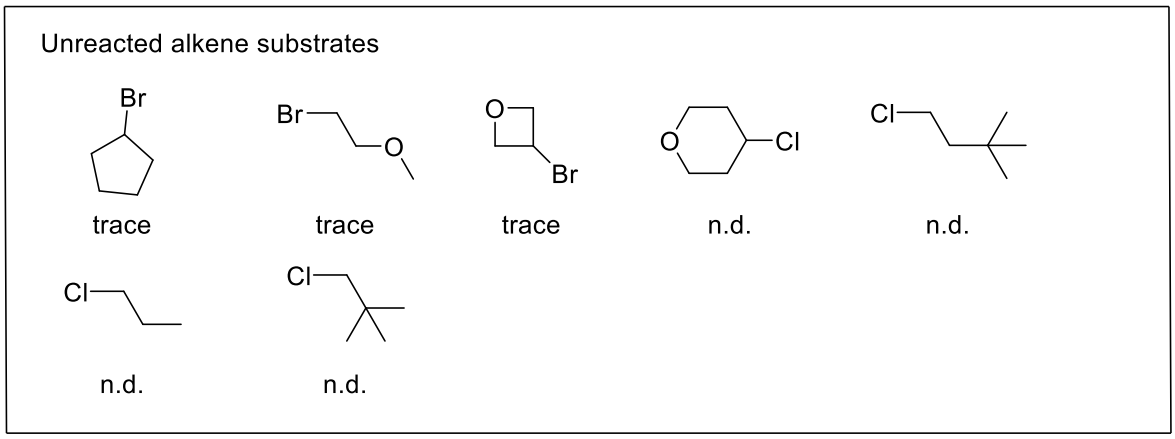
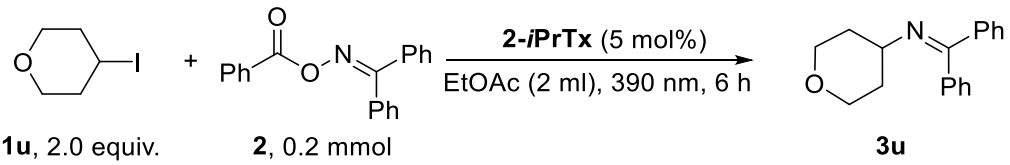


**Figure S1.** Reaction setup for general photoreactions.




## e) Mechanistic experiments

### 1) Radical-trapping experiments




An oven dried 8 mL reaction vial was charged with a stir bar, **2** (60.2mg, 0.2 mmol, 1.0 equiv.), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 93.6 mg, 0.6 mmol, 3 equiv.) and 2-*i*Pr-thioxanthone photosensitizer (2.5 mg, 5 mol %) were charged under air, then addition of EtOAc (2.0 mL, 0.1 M) and **1u** (46.0 μL, 0.4 mmol, 2 equiv.). The reaction

vial was sealed, evacuated and backfilled three times with 1 atm of $N_2$. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WPTEC-1020LC) for 6 hours. After irradiation, the resulting homogenous solution was checked by TLC, GC-MS, and HRMS analysis, and only a trace amount of the desired product **3u** was observed. The major byproducts **1d** and **1f** were observed by GC-MS measurement.

**HRMS** (ESI) for **1d**: m/z calculated for $[C_{14}H_{27}NO_2]$ $[M+H]^+$ : 242.3750, found: 242.3757.

**HRMS** (ESI) for **1f**: m/z calculated for $[C_{15}H_{23}NO]$ $[M+H]^+$ : 234.3550, found: 234.3553.

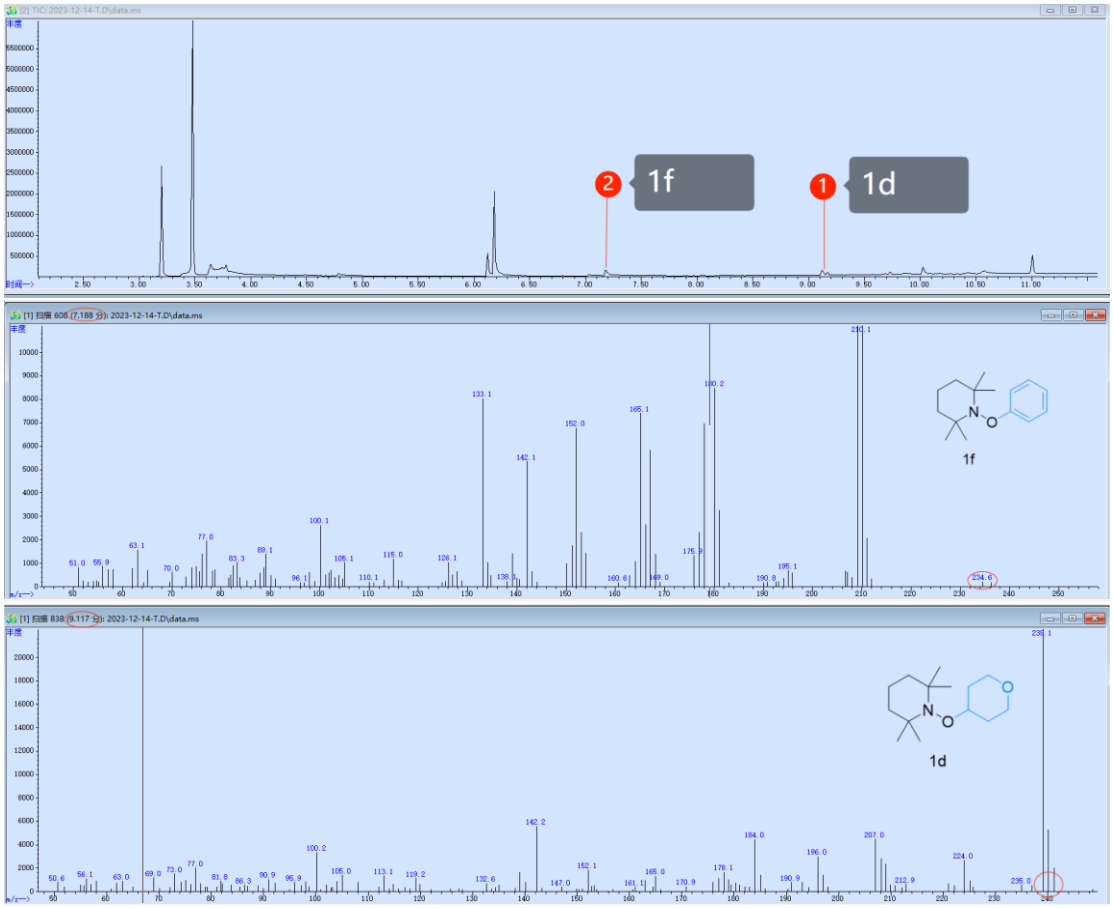



**Figure S2**. GCMS data for radical-trapping experiments

**2) Radical crossover experiments**

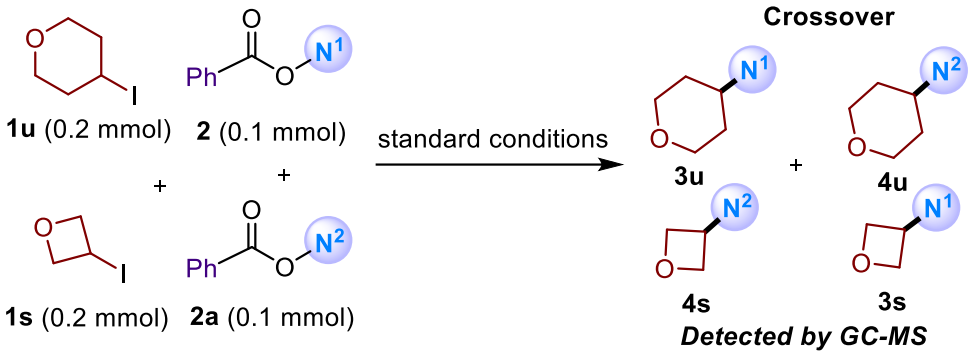



**Figure S3**. Radical crossover experiment.

An oven dried 8 mL reaction vial was charged with a stir bar, **2** (30.1mg, 0.1 mmol, 1.0 equiv.), **2a** (36.1 mg, 0.1 mmol, 1 equiv.) and **2-*i*PrTX** photosensitizer (2.5 mg, 5 mol %) were charged under air, then addition of EtOAc (2.0 mL, 0.07 M), **1u** (23.0 μL, 0.2 mmol, 2 equiv.) and **1s** (19.0 μL, 0.2 mmol, 2 equiv.). The reaction vial was sealed, evacuated and backfilled three times with 1 atm of $N_2$. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WPTEC-1020LC) for 6 hours. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WPTEC-1020LC) for 6 hours, then the analysis was performed by GCMS (Figure S4), and desired products **3u**, **3s**, **4u** and **4s** was observed by GC-MS measurement.

**HRMS** (ESI) for **3u**: m/z calculated for $[C_{18}H_{19}NO]$ $[M+H]^+$ : 266.3560, found: 266.3565.

**HRMS** (ESI) for **3s**: m/z calculated for $[C_{16}H_{15}NO]$ $[M+H]^+$ : 238.3020, found: 238.3017.

**HRMS** (ESI) for **4u**: m/z calculated for $[C_{20}H_{23}NO_3]$ $[M+H]^+$ : 326.4080, found: 326.4076.

**HRMS** (ESI) for **4s**: m/z calculated for $[C_{18}H_{19}NO_3]$ $[M+H]^+$ : 298.3540, found: 298.3538.

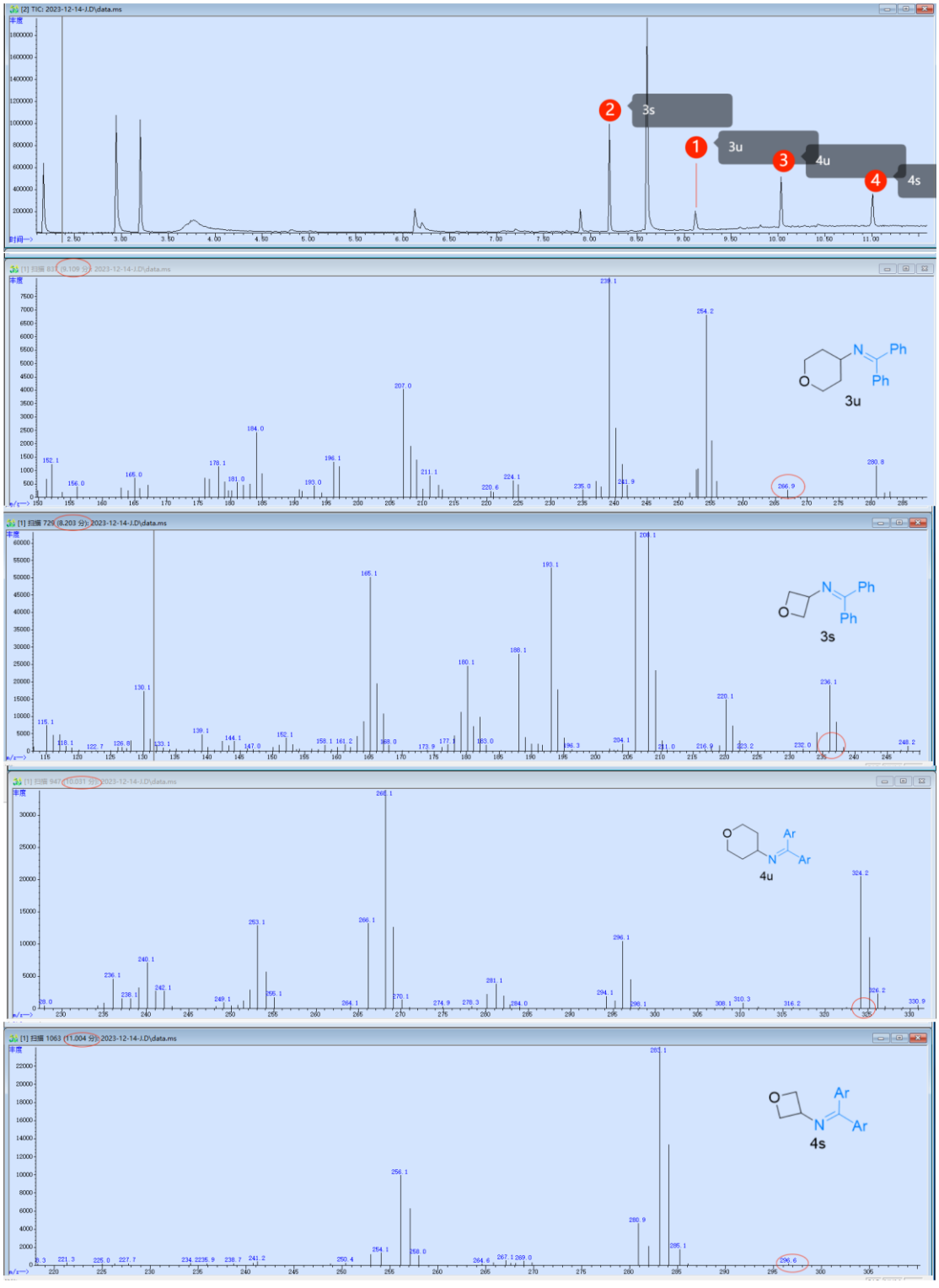



**Figure S4**. GCMS data for crossover study

**3) Quantum yield measurement**

**Determination of the light intensity at 390 nm:**

The photon flux was determined by ferrioxalate actinometry similar to a procedure by Yoon,[9] the photon flux of the LED ($\lambda_{max}$= 390 nm) was first determined by standard ferrioxalate actinometry. For this, a 10 mL 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in $H_2SO_4$ (10 mL of a 0.05 M solution). A 20 mL buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (20 mg) and sodium acetate (4.5 g) in $H_2SO_4$ (20 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 4.00 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90 seconds at 390 nm with excitation and emission slit width of 10 nm on the benchtop under air. After irradiation, 1.00 mL of this irradiated ferrioxalate solution, 0.20 mL of phenanthroline buffer solution and 2.00 mL of water were added to an 8 mL scintillation vial with a stir bar. stirred for 1 h to allow the ferrous ions to completely coordinate with the phenanthroline. The absorption of the solution was measured at 510 nm. A non-irradiated sample was also prepared identically and the absorption at 510 nm was also measured. Each sample preparation and measurements were repeated two more times. The average of the absorption of the irradiated and non-irradiated samples were determined and used for the calculation of photon flux.

Conversion was calculated using equation 1.

$$\text{mol } Fe^{2+} = \frac{V \times \Delta A(510 \text{ nm})}{l \times \mathcal{E}} \quad (1)$$

Where V is the total volume (0.0128 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11100 L $mol^{-1}cm^{-1}$).[12]

The average value of the experiment was $9.35\times10^{-7}$ mol of $Fe^{2+}$.

The photon flux can be calculated using equation 2.

$$\text{Photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \times t \times f} \quad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.13 at 392 nm)[12,13], t is the irradiation time, and f is the fraction of light absorbed at $\lambda_{max}$ = 390 nm by the ferrioxalate actinometer. This value is calculated using equation 3 where A is the absorbance of the ferrioxalte solution at 390 nm. An absorption spectrum gave an A value of > 3, indicating that the fraction of absorbed light (f) is > 0.999.

$$f = 1 - 10^{-A(390\ nm)} \quad (3)$$

The average photon flux was calculated to be $9.19\times10^{-9}$ einsteins $s^{-1}$

**Determination of the amination reaction quantum yield**

An oven dried 8 mL reaction vial was charged with a stir bar, **2** (60.2mg, 0.2 mmol, 1.0 equiv.) and 2-*i*Pr-thioxanthone photosensitizer (2.5 mg, 5 mol %) were charged under air, then addition of EtOAc (2.0 mL, 0.1 M) and **1u** (46.0 μL, 0.4 mmol, 2 equiv.). The reaction vial was sealed, evacuated and backfilled three times with 1 atm of $N_2$, then irradiated at 390 nm at ambient temperature for 20 minutes using the same setup as for the photon flux determination. Then, the NMR yield of **3u** was determined (40%) using $CH_2Br_2$ as internal standard. The reaction quantum yield was determined using equation 4, where photon flux was determined as above described, *t* is the reaction time, f is the fraction of incident light absorbed by the reaction mixture.

$$\Phi = \frac{mol\ of\ product\ formed}{photon\ flux \times t \times f} \quad (4)$$

This value is calculated using equation 3 where A is the absorbance of the reaction mixture at 390 nm. An absorption spectrum gave an A (390 nm) value of > 3, indicating that the fraction of absorbed light (f) is > 0.999.

$$\Phi = \frac{0.0002\ \text{mol} \times 0.40\ (yield)}{9.19\times10^{-9} \times 20 \times 60 \times 1.0} = 7.3$$

The amination reaction quantum yield (Φ) was determined to be 7.3, which is above unity, indicating that a radical chain propagation might be operative in this reaction.

**4) UV-Vis absorption spectrum**

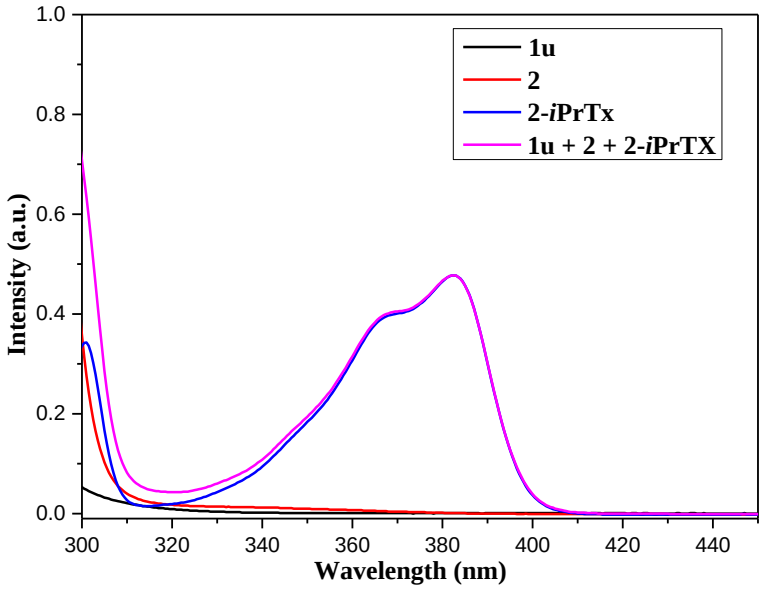
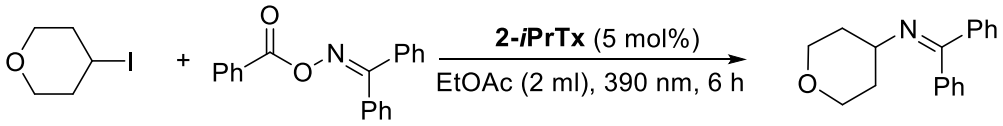



**Figure S5**. UV-Vis absorption spectrum

UV-visible absorption spectra were collected on a SPECORD 200 PLUS. 2-iPrthioxanthone photosensitizer (2-*i*PrTX), **1u**, **2** and mixed sample were prepared in EtOAc (Fig. S5), a broad absorption peak in the 360-410 nm wavelength range was observed only for 2-*i*PrTX, indicating that it is the only photochemically active compound under violet LED light irradiation (> 380 nm).

**f) Synthetic applications**

**Procedure for the gram-scale reaction**




**1u**, 12 mmol **2** (1.81 g, 6 mmol) **3u**, 1.13g, 71%

An oven dried 250 mL reaction vial was charged with a stir bar, **2** (1.81 g, 6mol, 1.0 equiv.), and **2-*i*PrTX** (75 mg, 5 mol %). To this was added EtOAc (90 mL, 0.07 M) followed by addition of iodide alkane **1u** (2.54 g, 12 mmol, 2.0 equiv.) via pipettor. The reaction vial was sealed, evacuated and backfilled three times with 1 atm of $N_2$. The reaction mixture was stirred and irradiated with commercially available 50 W 390 nm LED lamp and flow pump for 6 hours until the reaction was complete (monitored by TLC). After reaction, $NEt_3$ (approx. 5 mL) and $SiO_2$ were added to this solution and the

volatiles were removed under reduced pressure, affording a powder which was loaded on column. Purification by flash column chromatography on $SiO_2$, pre-basified with $NEt_3$ using pentane: EtOAc (100:1 to 2:1, v/v) mixtures afforded the target product **3u** as a yellow solid (1.13 g, 71% yield).

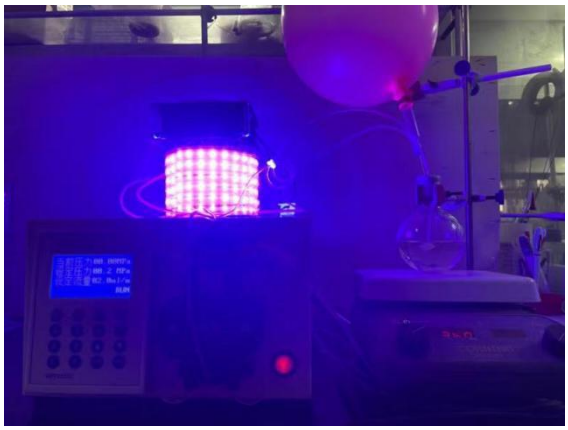
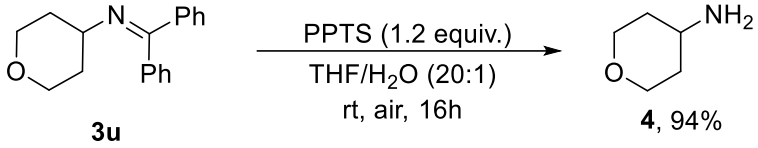


**Figure S6.** Gram scale reaction setup

**Products derivatization**




**3u** **4**, 94%

A 25 mL vial was charged with compound **3u** (53.0 mg, 0.2 mmol), THF (3.7 mL) and $H_2O$ (0.3 mL) were added. Pyridinium p-toluene sulfonate (0.24 mmol, 60 mg, 1.2 equiv) was added to the vial. The reaction was stirred at room temperature for 16 hrs. The reaction was then diluted with EtOAc (5.0 mL) and $H_2O$ (2.0 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (10.0 mL x 2). The combined organic phases were dried ($Na_2SO_4$), filtered, and evaporated. Crude mixture was purified using column chromatography to give **4** as a colorless oil (19.0 mg, 94%).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 4.01 – 3.90 (m, 2H), 3.39 (td, *J* = 11.7, 2.1 Hz, 2H), 2.86 (tt, *J* = 10.6, 4.2 Hz, 1H), 1.77 (ddd, *J* = 12.7, 4.0, 2.0 Hz, 2H), 1.62 (s, 2H), 1.46 – 1.32 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 66.8, 47.7, 36.7.

**HRMS** (ESI) for **4**: m/z calculated for $[C_5H_{12}NO]$ $[M+H]^+$ : 102.0913, found: 102.0920.

## g) References


1. T. Patra, P. Bellotti, F. Strieth-Kalthoff, F. Glorius. *Angew. Chem. Int. Ed*. **2020**, *59*, 3172–3177.

2. V. K. Soni, S. Lee, J. Kang, Y. K. Moon, H. S. Hwang, Y. You, E. J. Cho. *ACS Catal.* **2019**, *9*, 10454−10463.

3. S. S. Li, Y. S. Jiang, L. N. Chen, D. N. Chen, X. L. Luo, C. X. Pan, P. J. Xia. *Org. Lett.* **2023**, *25*, 7009−7013.

4. G. Tan, F. Paulus, A. Petti, M. A. Wiethoff, A. Lauer, C. Daniliuc, F. Glorius. *Chem. Sci.,* **2023***, 14,* 2447–2454.

5. Y. S. Jiang, S. S. Li, X. L. Luo, L. N. Chen, D. N. Chen, P. J. Xia. *Org. Lett.* **2023***, 25,* 6671−6676.

6. Y. Zhao, W. J. Xia. *Chem. Soc. Rev.*, **2018**, *47*, 2591.

7. X. K. Qi, M. J. Zheng, C. Yang, Y. Zhao, L. Guo, W. J. Xia. *J. Am. Chem. Soc.* **2023**, *145*, 16630–16641.

8. W. Zhao, R. P. Wurz, J. C. Peters, G. C. Fu. *J. Am. Chem. Soc.* **2017**, *139*, 12153-12156.

9. M. A. Cismesia, T. P. Yoon, *Chem. Sci*. **2015**, *6*, 5426–5434.

10. F. Juliá, T. Constantin, D. Leonori. *Chem. Rev.* **2022**, *122*, 2292–2352.

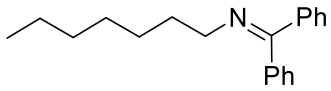
11. J. Zhang, M. Jiang, C. S. Wang, K. Guo, Q. X. Li, C. Ma, S. F. Ni, G. Q. Chen, Y. Zong, H. Lu, L. W. Xu, X. X. Shao. *Nat. Commun.*, **2022**, *13*, 7961.

12. H. Heath, *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.* **1956**, *235*, 518–536.

13. E. E. Wegner, A. W. Adamson, *J. Am. Chem. Soc.* **1966**, *88*, 394–404.

# 2. Characterization data of the products

**N-heptyl-1,1-diphenylmethanimine (3a)**



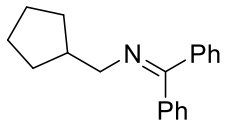

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1a** (90.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (200:1 to 100:1, v/v) as eluent afforded **3a** (29.6 mg, 53% yield) as a colorless oil.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.37 (s, 1H), 7.32 (dd, *J* = 10.5, 4.1 Hz, 2H), 7.16 (d, *J* = 7.3 Hz, 2H), 3.37 (t, *J* = 7.0 Hz, 2H), 1.67 (d, *J* = 7.5 Hz, 3H), 1.27 (d, *J* = 13.1 Hz, 9H), 0.87 (t, *J* = 6.0 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.8, 140.1, 137.1, 129.8, 128.5, 128.4, 128.3, 128.08, 127.9, 54.0, 31.9, 31.3, 29.2, 27.5, 22.7, 14.2.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{20}H_{26}N$: 280.2060, found: 280.2069.

**N-(cyclopentylmethyl)-1,1-diphenylmethanimine (3b)**



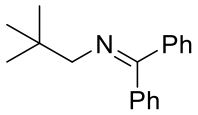

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1b** (83.6 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (200:1 to 100:1, v/v) as eluent afforded **3b** (23.7 mg, 45% yield) as a colorless oil.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 6.7 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.36 (d, *J* = 6.9 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.16 (d, *J* = 6.4 Hz, 2H), 3.35 (d, *J* = 6.9 Hz, 2H), 2.28 (dt, *J* = 14.4, 7.2 Hz, 1H), 1.78 (dt, *J* = 10.5, 4.9 Hz, 2H), 1.55 (dt, *J* = 8.8, 4.5 Hz, 4H), 1.22 (td, *J* = 7.7, 4.3 Hz, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.5, 140.2, 137.2, 132.5, 129.8, 128.5, 128.4, 128.24, 128.1, 59.1, 41.6, 30.7, 25.3.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{19}H_{22}N$: 264.1747, found: 264.1744.

**N-neopentyl-1,1-diphenylmethanimine (3c)**



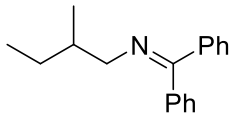

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1c** (79.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (200:1 to 100:1, v/v) as eluent afforded **3c** (32.6 mg, 65% yield) as a colorless oil.

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 6.9 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.37 – 7.31 (m, 3H), 7.14 (d, *J* = 6.4 Hz, 2H), 3.13 (s, 2H), 0.97 (s, 9H), 0.90 (s, 1H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 167.4, 140.4, 137.2, 129.8, 128.4, 128.4, 128.2, 128.1, 128.1, 65.6, 33.0, 28.1.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{18}H_{22}N$: 252.3805, found: 252.3804.

**N-(2-methylbutyl)-1,1-diphenylmethanimine (3d)**

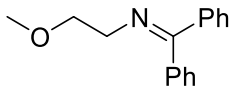



Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1d** (77.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (200:1 to 100:1, v/v) as eluent afforded **3d** (90.4 mg, 36% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.45 (h, *J* = 8.0, 7.4 Hz, 3H), 7.37 – 7.29 (m, 3H), 7.15 (d, *J* = 6.5 Hz, 2H), 3.31 (dd, *J* = 13.2, 6.0 Hz, 1H), 3.18 (dd, *J* = 13.2, 6.9 Hz, 1H), 1.82 (dq, *J* = 13.7, 6.9 Hz, 1H), 1.44 (dq, *J* = 13.2, 6.9 Hz, 1H), 1.14 (dt, *J* = 13.9, 7.4 Hz, 1H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H).

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{18}H_{22}N$: 252.1747, found: 252.1740.

**N-(2-methoxyethyl)-1,1-diphenylmethanimine (3e)**



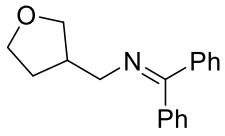

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1e** (74.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (200:1 to 100:1, v/v) as eluent afforded **3e** (19.6 mg, 41% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.0 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.36 (d, *J* = 7.0 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.19 (d, *J* = 6.4 Hz, 2H), 3.71 (t, *J* = 6.0 Hz, 2H), 3.56 (t, *J* = 6.0 Hz, 2H), 3.36 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 169.6, 139.9, 136.9, 130.0, 128.6, 128.5, 128.4, 128.1, 127.9, 53.8.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{16}H_{18}NO$: 240.1383, found: 240.1382.

**1,1-diphenyl-N-((tetrahydrofuran-3-yl)methyl)methanimine (3f)**



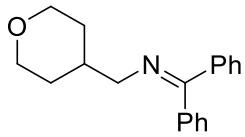
Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1f** (84.8 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3f** (30.8 mg, 58% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 6.9 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.41 – 7.33 (m, 2H), 7.35 – 7.30 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 3.96 – 3.91 (m, 1H), 3.85 – 3.70 (m, 2H), 3.57 (dd, *J* = 8.5, 6.2 Hz, 1H), 3.45 – 3.34 (m, 2H), 2.65 (hept, *J* = 7.1 Hz, 1H), 2.05 (dtd, *J* = 13.3, 7.8, 5.6 Hz, 1H), 1.72 – 1.58 (m, 1H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 168.6, 139.8, 136.9, 130.1, 128.6, 128.5, 128.4, 128.14, 127.8, 71.9, 56.6, 41.0, 30.5.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{18}H_{20}NO$: 266.1539, found: 266.1530.

**1,1-diphenyl-N-((tetrahydro-2H-pyran-4-yl)methyl)methanimine (3g)**



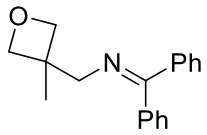

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1g** (90.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3g** (30.1 mg, 54% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.45 (q, *J* = 8.5, 7.5 Hz, 3H), 7.36 (d, *J* = 6.7 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 3.96 (dd, *J* = 11.2, 3.9 Hz, 2H), 3.48 – 3.36 (m, 2H), 3.27 (d, *J* = 6.6 Hz, 2H), 2.00 (dddt, *J* = 14.3, 11.3, 6.8, 3.9 Hz, 1H), 1.68 (d, *J* = 12.9 Hz, 2H), 1.32 (qd, *J* = 11.3, 10.3, 3.0 Hz, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 168.4, 140.0, 137.0, 130.0, 128.6, 128.4, 128.4, 128.12, 127.9, 68.1, 59.8, 37.0, 31.4.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{19}H_{22}NO$: 280.1696 found: 280.1691.

**N-((3-methyloxetan-3-yl)methyl)-1,1-diphenylmethanimine(3h)**



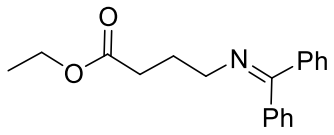

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1h** (84.8 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 2:1, v/v) as eluent afforded **3h** (26.0 mg, 49% yield) as a colorless oil.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.0 Hz, 2H), 7.51 – 7.44 (m, 3H), 7.37 (t, *J* = 1.4 Hz, 1H), 7.33 (dd, *J* = 8.0, 6.5 Hz, 2H), 7.16 (d, *J* = 6.3 Hz, 2H), 4.62 (d, *J* = 5.7 Hz, 2H), 4.41 (d, *J* = 5.7 Hz, 2H), 3.53 (s, 2H), 1.33 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 169.1, 139.8, 136.9, 132.5, 130.1, 128.7, 128.5, 128.1, 127.9, 60.8, 40.6, 22.7.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{18}H_{20}NO$: 266.1539, found: 266.1529.

**ethyl 4-((diphenylmethylene)amino)butanoate (3i)**




Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1i** (96.8 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with

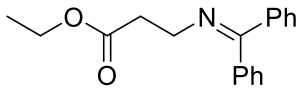
pentane/EtOAc (10:1 to 1:1, v/v) as eluent afforded **3i** (34.9 mg, 59% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 6.9 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.40 – 7.35 (m, 1H), 7.35 – 7.28 (m, 2H), 7.15 (d, *J* = 6.2 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.40 (t, *J* = 6.6 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.01 (p, *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 173.8, 168.5, 139.8, 136.9, 130.0, 128.6, 128.4, 128.1, 127.8, 60.3, 52.8, 32.4, 26.6, 14.3.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{19}H_{22}NO$: 296.1645, found: 296.1654.

**ethyl 3-((diphenylmethylene)amino)propanoate (3j)**



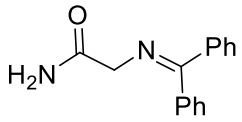

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1j** (91.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 1:1, v/v) as eluent afforded **3j** (28.8 mg, 51% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.0 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.36 (t, *J* = 1.4 Hz, 1H), 7.32 (dd, *J* = 8.0, 6.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.64 (t, *J* = 7.0 Hz, 2H), 2.70 (t, *J* = 7.0 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 172.6, 169.1, 136.7, 130.1, 128.6, 128.6, 128.5, 128.1, 127.8, 60.4, 49.5, 36.2, 14.3.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{18}H_{20}NO_2$: 282.1489, found: 282.1489.

**2-((diphenylmethylene)amino)acetamide (3k)**



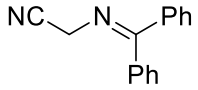
Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1k** (74.0 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 1:2, v/v) as eluent afforded **3k** (34.9 mg, 73% yield) as a white solid.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.6 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.36 (t, *J* = 1.4 Hz, 1H), 7.33 (dd, *J* = 8.0, 6.5 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.13 (s, 1H), 3.98 (s, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 173.9, 170.4, 138.8, 136.0, 130.8, 129.1, 129.0, 128.5, 128.3, 127.3, 56.6.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{15}H_{15}N_2O$: 239.1179, found: 239.1187.

**2-((diphenylmethylene)amino)acetonitrile (3l)**



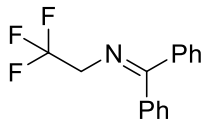
Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1l** (66.8 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3l** (33.4 mg, 76% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.49 (m, 3H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 4.23 (s, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 174.4, 138.3, 134.9, 131.3, 129.6, 129.2, 128.9, 128.4, 127.3, 117.7, 41.4.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{15}H_{13}N_2$: 221.1073, found: 221.1064.

**1,1-diphenyl-N-(2,2,2-trifluoroethyl)methanimine (3m)**



Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1m** (84.0 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (20:1 to 10:1, v/v) as eluent afforded **3m** (21.6 mg, 41% yield) as a colorless oil.

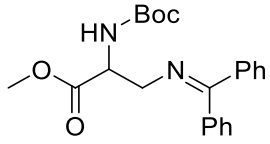
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.51 (q, *J* = 5.4 Hz, 3H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 3.87 (q, *J* = 9.5 Hz, 2H).

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -70.92 (t, *J* = 9.5 Hz).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 173.1, 135.7, 131.0, 129.20, 129.02, 128.9, 128.3, 127.4, 125.2 (q, *J* = 276.7 Hz), 55.14 (q, *J* = 31.0 Hz).

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{15}H_{13}F_3N$: 264.0995, found: 264.1004.

**methyl 2-((tert-butoxycarbonyl)amino)-3-((diphenylmethylene)amino)propanoate (3n)**



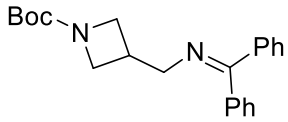
Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1n** (131.7 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 2:1, v/v) as eluent afforded **3n** (30.6 mg, 40% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.42 (m, 3H), 7.40 – 7.36 (m, 1H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 5.59 (d, *J* = 8.6 Hz, 1H), 4.55 (dt, *J* = 7.8, 3.8 Hz, 1H), 3.82 (dd, *J* = 14.4, 3.7 Hz, 1H), 3.75 (s, 3H), 3.66 (dd, *J* = 14.4, 3.8 Hz, 1H), 1.45 (s, 9H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 170.7, 155.5, 139.2, 136.3, 130.5, 128.7, 128.6, 128.1, 127.7, 55.3, 52.4.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{22}H_{27}N_2O_4$: 383.1965, found: 383.1974.

**tert-butyl 3-(((diphenylmethylene)amino)methyl)azetidine-1-carboxylate (3o)**



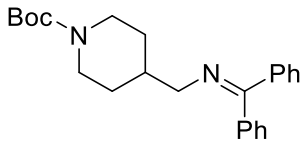

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1o** (118.9 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3o** (24.6 mg, 35% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.1 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.37 (dd, *J* = 6.1, 3.8 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.16 (d, *J* = 6.2 Hz, 2H), 4.01 (t, *J* = 8.4 Hz, 2H), 3.78 – 3.66 (m, 2H), 3.52 (d, *J* = 6.8 Hz, 2H), 2.87 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.43 (s, 9H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 169.5, 156.6, 139.7, 136.8, 130.2, 128.7, 128.7, 128.46, 128.1, 127.8, 79.2, 56.5, 29.9, 28.5.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{22}H_{27}N_2O_2$: 351.2067, found: 351.2066.

**tert-butyl 4-(((diphenylmethylene)amino)methyl)piperidine-1-carboxylate (3p)**



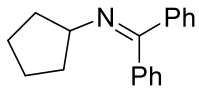

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1p** (130.1 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3p** (44.0 mg, 58% yield) as a colorless oil.

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 6.9 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.38 – 7.29 (m, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 4.08 (s, 2H), 3.26 (d, *J* = 6.6 Hz, 2H), 2.77 – 2.64 (m, 2H), 1.89 (dtd, *J* = 14.6, 7.6, 6.8, 3.3 Hz, 1H), 1.73 (d, *J* = 13.0 Hz, 2H), 1.44 (s, 9H), 1.12 (td, *J* = 12.0, 7.0 Hz, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 168.4, 155.1, 140.0, 137.1, 130.1, 128.7, 128.5, 128.45, 128.2, 128.0, 79.4, 59.6, 38.2, 28.6.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{24}H_{31}N_2O_2$: 379.2380, found: 379.2378.

**N-cyclopentyl-1,1-diphenylmethanimine (3q)**



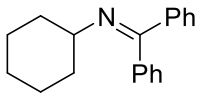

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1q** (78.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (200:1 to 100:1, v/v) as eluent afforded **3q** (25.5 mg, 51% yield) as a colorless oil.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 6.5 Hz, 2H), 7.45 (q, *J* = 7.6, 6.9 Hz, 3H), 7.39 – 7.34 (m, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 3.72 (p, *J* = 6.8 Hz, 1H), 1.87 (td, *J* = 6.4, 3.3 Hz, 2H), 1.77 – 1.70 (m, 4H), 1.54 (tt, *J* = 9.8, 6.0 Hz, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.8, 140.4, 137.7, 129.6, 128.5, 128.4, 128.2, 128.1, 128.0, 63.4, 35.0, 25.1.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{18}H_{20}N$: 250.1590, found: 250.1585.

**N-cyclohexyl-1,1-diphenylmethanimine (3r)**



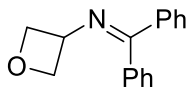

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1r** (84.0 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (200:1 to 100:1, v/v) as eluent afforded **3r** (22.2 mg, 42% yield) as a colorless oil.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 6.5 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.38 – 7.33 (m, 1H), 7.33 – 7.28 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 3.22 (p, *J* = 6.8 Hz, 1H), 1.80 – 1.67 (m, 3H), 1.63 (d, *J* = 5.7 Hz, 2H), 1.59 – 1.55 (m, 1H), 1.35 – 1.22 (m, 2H), 1.20 – 1.10 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 140.5, 137.5, 129.7, 128.4, 128.1, 128.1, 127.75, 61.5, 34.0, 25.8.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{19}H_{22}N$: 264.1747, found: 264.1740.

**N-(oxetan-3-yl)-1,1-diphenylmethanimine (3s)**



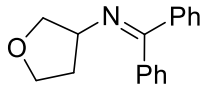

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1s** (73.6 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3s** (22.4 mg, 47% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.45 (p, *J* = 3.5 Hz, 3H), 7.43 – 7.39 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 3.6 Hz, 2H), 4.84 (d, *J* = 3.5 Hz, 2H), 4.75 – 4.63 (m, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 169.6 139.2, 136.8, 130.5, 128.9, 128.7, 128.7, 128.23, 127.5, 79.2, 56.4.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{16}H_{16}NO$: 238.1226, found: 238.1224.

**1,1-diphenyl-N-(tetrahydrofuran-3-yl)methanimine (3t)**



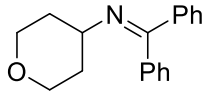

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1t** (79.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3t** (31.2 mg, 62% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.1 Hz, 2H), 7.46 (q, *J* = 6.3 Hz, 3H), 7.38 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 4.11 (q, *J* = 7.3 Hz, 1H), 4.03 (p, *J* = 6.0 Hz, 1H), 3.85 (q, *J* = 6.5 Hz, 2H), 3.79 (dd, *J* = 8.5, 4.9 Hz, 1H), 2.04 (q, *J* = 6.7 Hz, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.8, 139.7, 137.0, 130.1, 128.6, 128.6, 128.5, 128.13, 127.9, 74.4, 68.2, 62.0, 35.2.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{17}H_{18}NO$: 252.1383, found: 252.1379.

**1,1-diphenyl-N-(tetrahydro-2H-pyran-4-yl)methanimine(3u)**




Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1u** (84.8 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with

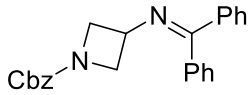
pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3u** (40.0 mg, 75% yield) as a yellow oil.

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.46 (q, *J* = 4.7, 3.9 Hz, 3H), 7.34 (dt, *J* = 14.3, 6.6 Hz, 3H), 7.16 (d, *J* = 7.1 Hz, 2H), 4.01 (dt, *J* = 11.4, 3.7 Hz, 2H), 3.48 (td, *J* = 9.4, 4.6 Hz, 1H), 3.36 (t, *J* = 10.3 Hz, 2H), 1.91 (ddt, *J* = 13.9, 10.3, 5.2 Hz, 2H), 1.58 (d, *J* = 11.1 Hz, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 166.7, 140.0, 130.0, 128.6, 128.5, 128.4, 128.1, 127.6, 66.1, 58.0, 33.8.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{18}H_{20}NO$: 266.1539, found: 266.1548.

**benzyl 3-((diphenylmethylene)amino)azetidine-1-carboxylate (3v)**



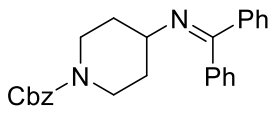

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1v** (126.9 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3v** (32.0 mg, 43% yield) as a colorless oil.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.1 Hz, 2H), 7.45 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.42 – 7.39 (m, 1H), 7.35 (d, *J* = 3.2 Hz, 7H), 7.05 (dd, *J* = 6.4, 3.1 Hz, 2H), 5.09 (s, 2H), 4.73 (dd, *J* = 10.2, 8.3 Hz, 1H), 4.37 (dd, *J* = 10.8, 5.3 Hz, 1H), 4.32 – 4.24 (m, 1H), 4.13 (s, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 170.3, 156.4, 139.1, 136.8, 136.7, 130.6, 129.0, 128.75, 128.7, 128.6, 128.5, 128.3, 128.1, 128.0, 67.1, 66.7, 50.9, 2.3.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{24}H_{23}N_2O_2$: 371.1754, found: 371.1751.

**benzyl 4-((diphenylmethylene)amino)piperidine-1-carboxylate (3w)**



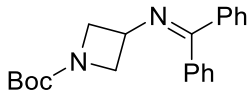

Following the General procedure, **2** (60.2 mg, 0.2 mmol) and **1w** (138.1 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3w** (37.5 mg, 47% yield) as a colorless oil.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 6.9 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.37 (t, *J* = 3.6 Hz, 5H), 7.35 – 7.31 (m, 3H), 7.16 (d, *J* = 7.7 Hz, 2H), 5.15 (s, 2H), 4.07 (s, 2H), 3.47 (tt, *J* = 8.3, 3.9 Hz, 1H), 3.01 (t, *J* = 10.7 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.64 (s, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.8, 155.4, 139.9, 137.0, 130.1, 128.7, 128.6, 128.54, 128.5, 128.4, 128.1, 128.0, 127.9, 127.6, 67.3, 67.1, 58.3, 44.0, 42.0, 27.2.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{26}H_{27}N_2O_2$: 399.2067, found: 399.2076.

**tert-butyl 3-((diphenylmethylene)amino)azetidine-1-carboxylate (3x)**



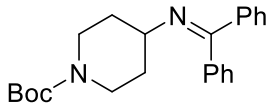

Following the **General procedure**, **2** (60.2 mg, 0.2 mmol) and **1x** (113.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3x** (23.7 mg, 50% yield) as a colorless oil.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.40 (d, *J* = 6.9 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.05 (d, *J* = 5.1 Hz, 2H), 4.23 (p, *J* = 6.1, 5.3 Hz, 1H), 4.04 (p, *J* = 8.3 Hz, 4H), 1.73 (s, 1H), 1.43 (s, 9H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 170.1, 156.4, 139.2, 136.7, 132.5, 130.5, 128.9, 128.7, 128.2, 127.6, 79.40, 50.6, 28.5.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{21}H_{25}N_2O_2$: 337.1911, found: 237.1903.

**tert-butyl 4-((diphenylmethylene)amino)piperidine-1-carboxylate (3y)**



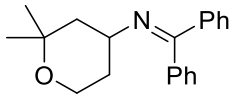

Following the **General procedure**, **2** (60.2 mg, 0.2 mmol) and **1y** (124.5 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3y** (30.0 mg, 41% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 6.4 Hz, 2H), 7.47 (d, *J* = 12.7 Hz, 3H), 7.40 – 7.34 (m, 1H), 7.32 (dt, *J* = 6.5, 3.2 Hz, 2H), 7.15 (d, *J* = 6.0 Hz, 2H), 3.99 (s, 2H), 3.42 (dq, *J* = 8.5, 4.7 Hz, 1H), 2.97 – 2.73 (m, 2H), 1.77 – 1.67 (m, 2H), 1.58 (d, *J* = 12.0 Hz, 2H), 1.46 (d, *J* = 3.2 Hz, 9H), 1.35 – 1.19 (m, 1H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.8, 155.0, 140.1, 137.1, 128.6, 128.5, 128.4, 128.1, 127.6, 79.4, 58.7, 42.4, 42.3, 42.2, 41.6, 41.6, 41.4, 32.9, 28.6.

**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{23}H_{29}N_2O_2$: 365.2224, found: 365.2226.

**N-(2,2-dimethyltetrahydro-2H-pyran-4-yl)-1,1-diphenylmethanimine (3z)**




Following the **General procedure**, **2** (60.2 mg, 0.2 mmol) and **1z** (96.0 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 3:1, v/v) as eluent afforded **3z**(31.2 mg, 53% yield) as a colorless oil.

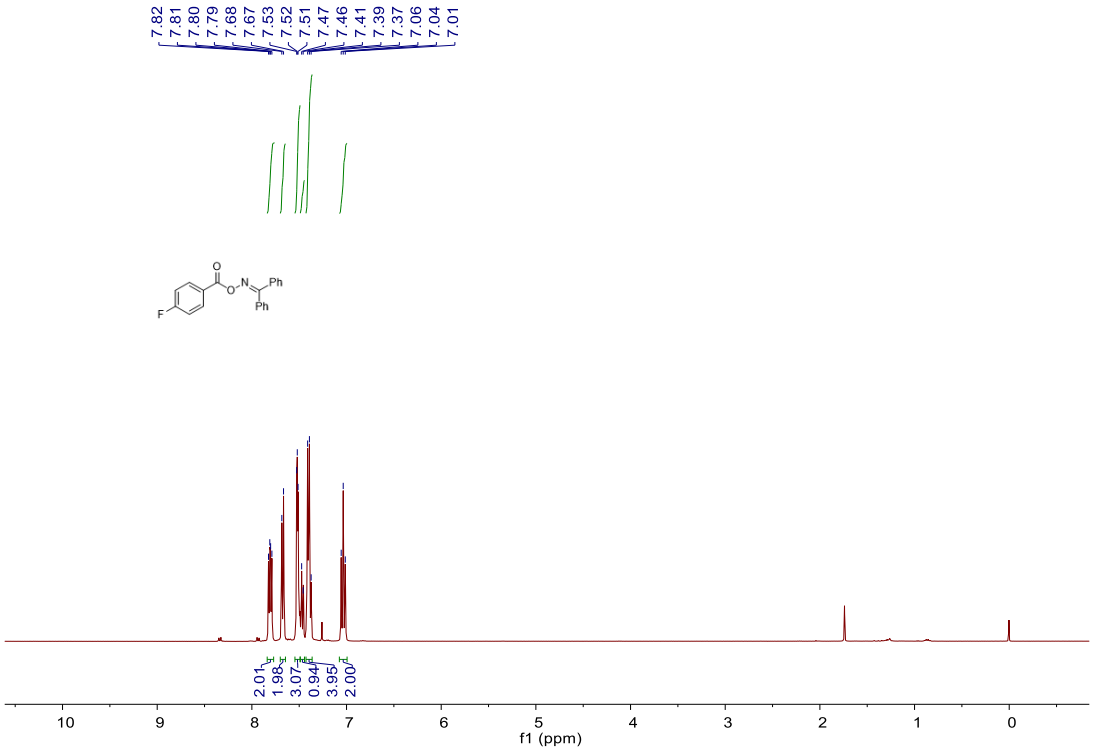
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 6.9 Hz, 2H), 7.45 (q, *J* = 5.9 Hz, 3H), 7.37 – 7.34 (m, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 2H), 3.79 (ddd, *J* = 11.9, 4.8, 2.0 Hz, 1H), 3.70 – 3.56 (m, 1H), 3.57 – 3.42 (m, 1H), 1.87 (qd, *J* = 12.5, 4.9 Hz, 1H), 1.70 (s, 2H), 1.53 – 1.42 (m, 2H), 1.24 (s, 3H), 0.97 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.1, 140.0, 137.2, 130.0, 128.5, 128.5, 128.4, 128.13, 127.5, 71.6, 60.2, 55.7, 43.7, 33.5, 31.4, 22.8

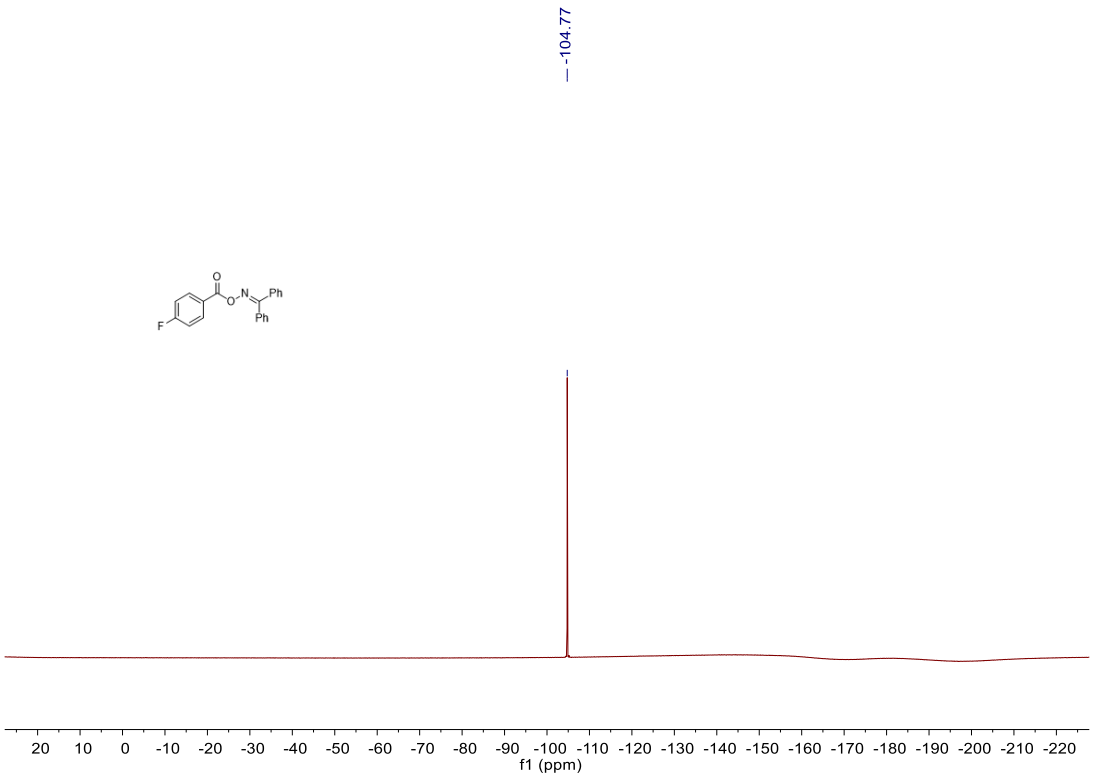
**HRMS** (ESI) (m/z): $[M+H]^+$ called. for $C_{20}H_{24}NO$: 294.1852, found: 294.1849.

# 3. NMR spectra for the products

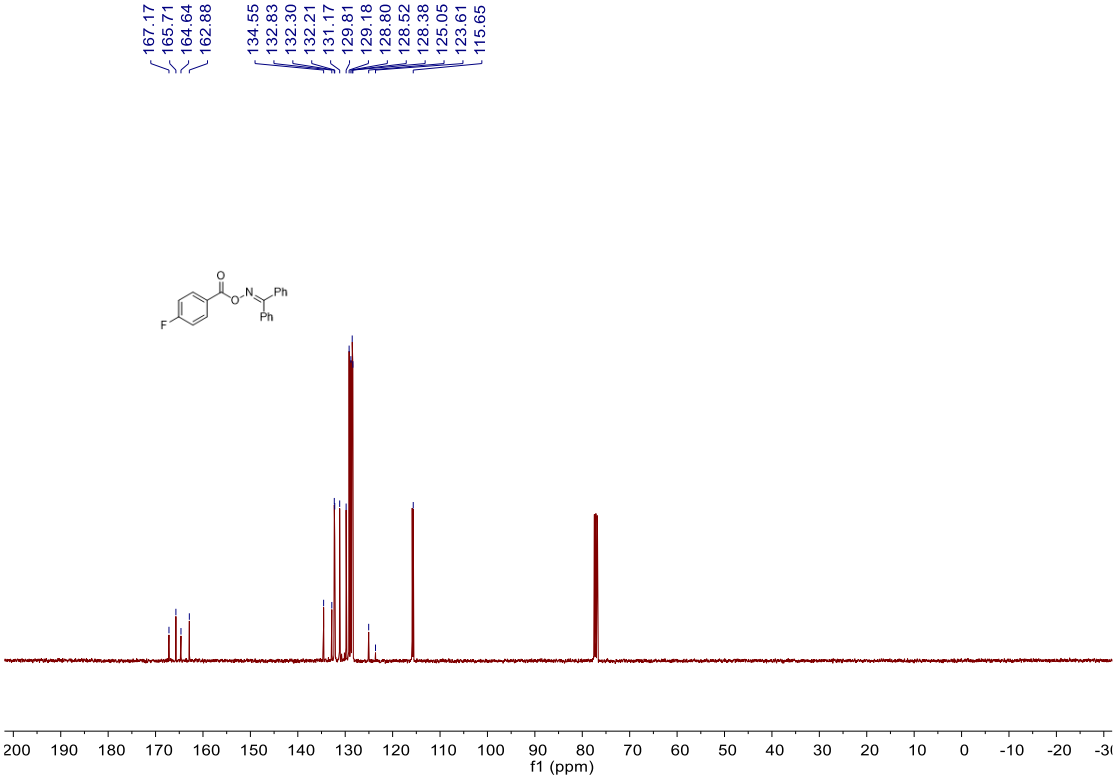
$^{1}$H NMR spectra of compound **2b** in $CDCl_3$ (400 MHz):



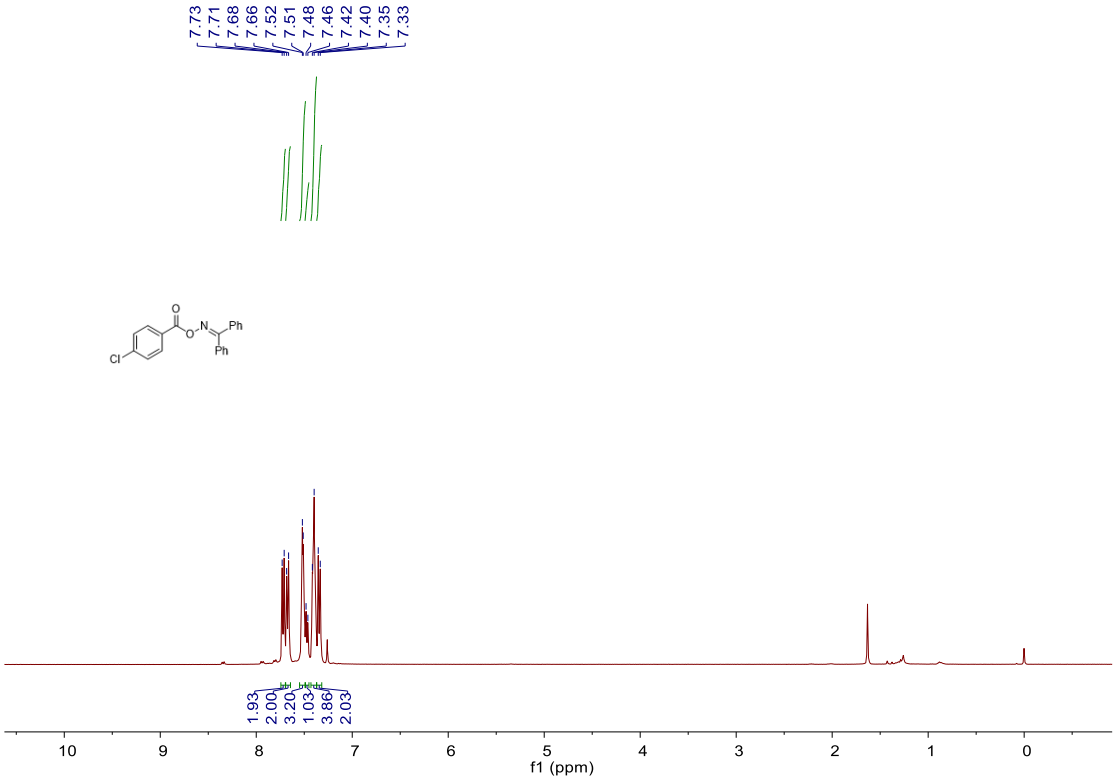

$^{19}$F NMR spectra of compound **2b** in $CDCl_3$ (101 MHz):



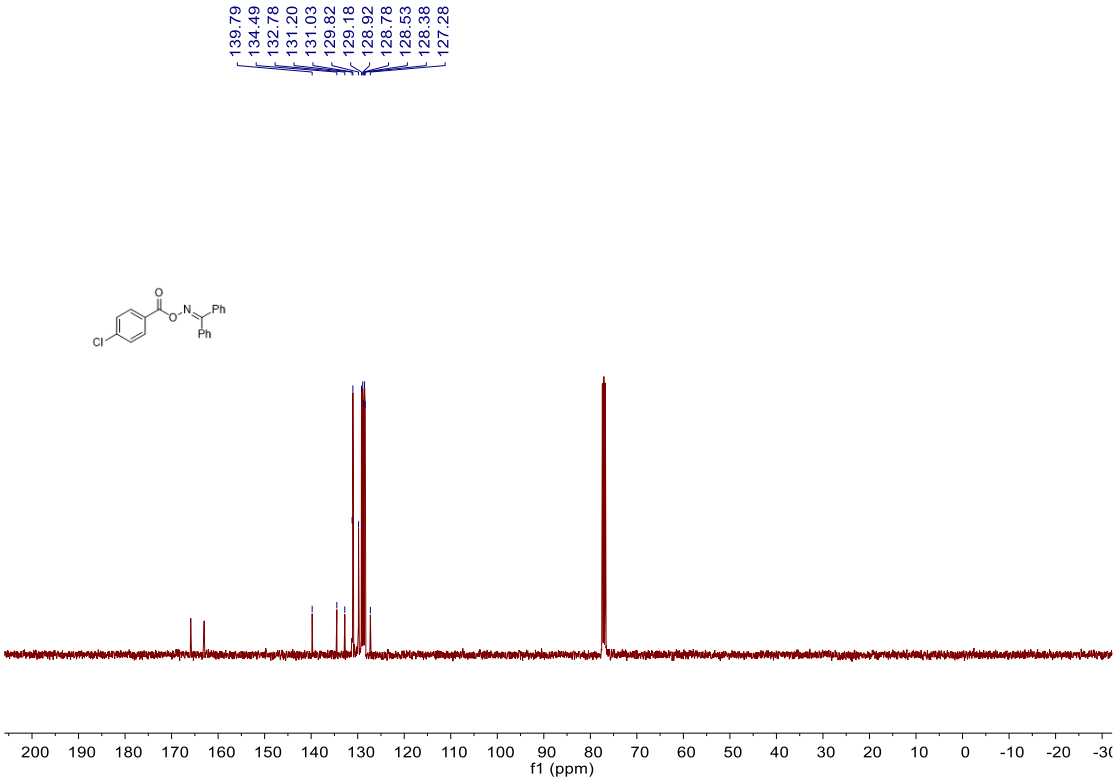
$^{13}C$ NMR spectra of compound **2b** in $CDCl_3$ (101 MHz):



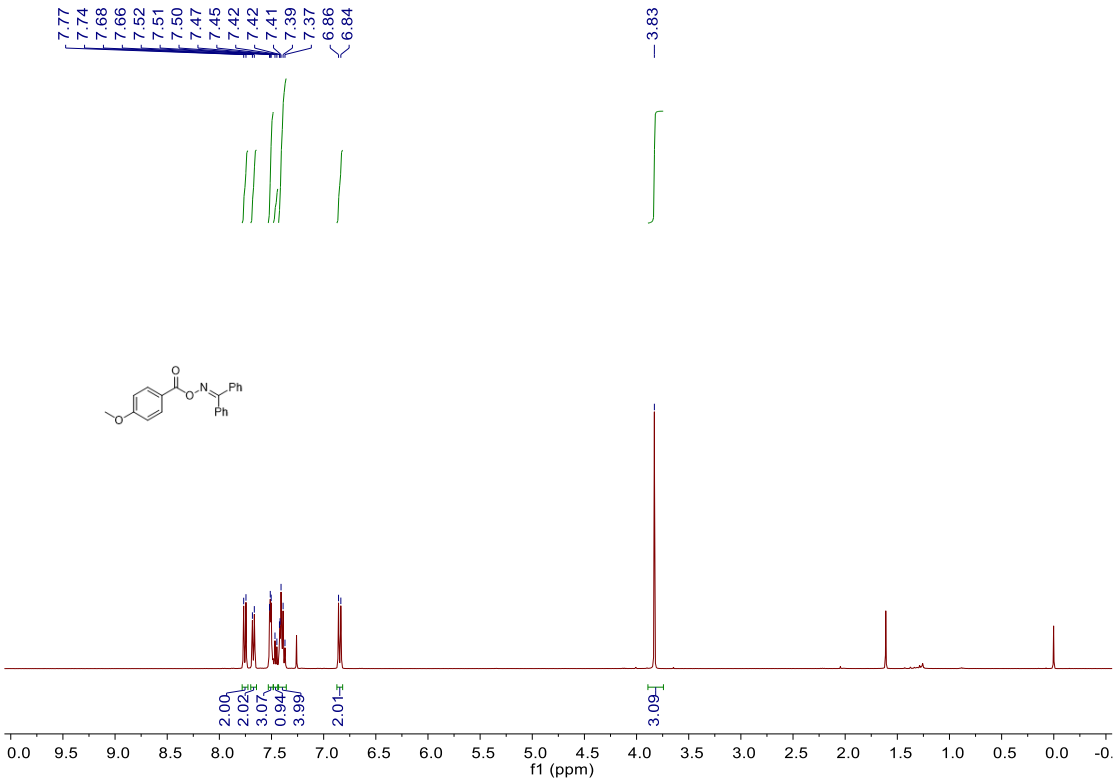

$^{1}H$ NMR spectra of compound **2c** in $CDCl_3$ (400 MHz):



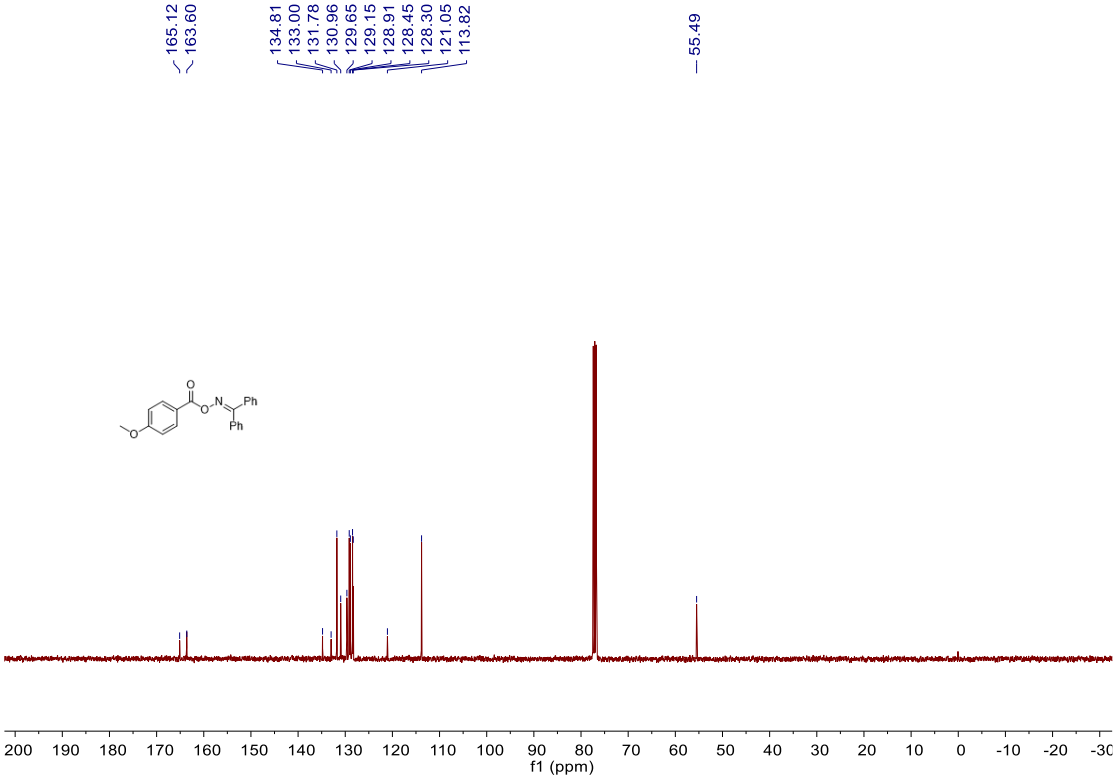
$^{13}$C NMR spectra of compound **2c** in $CDCl_3$ (101 MHz):



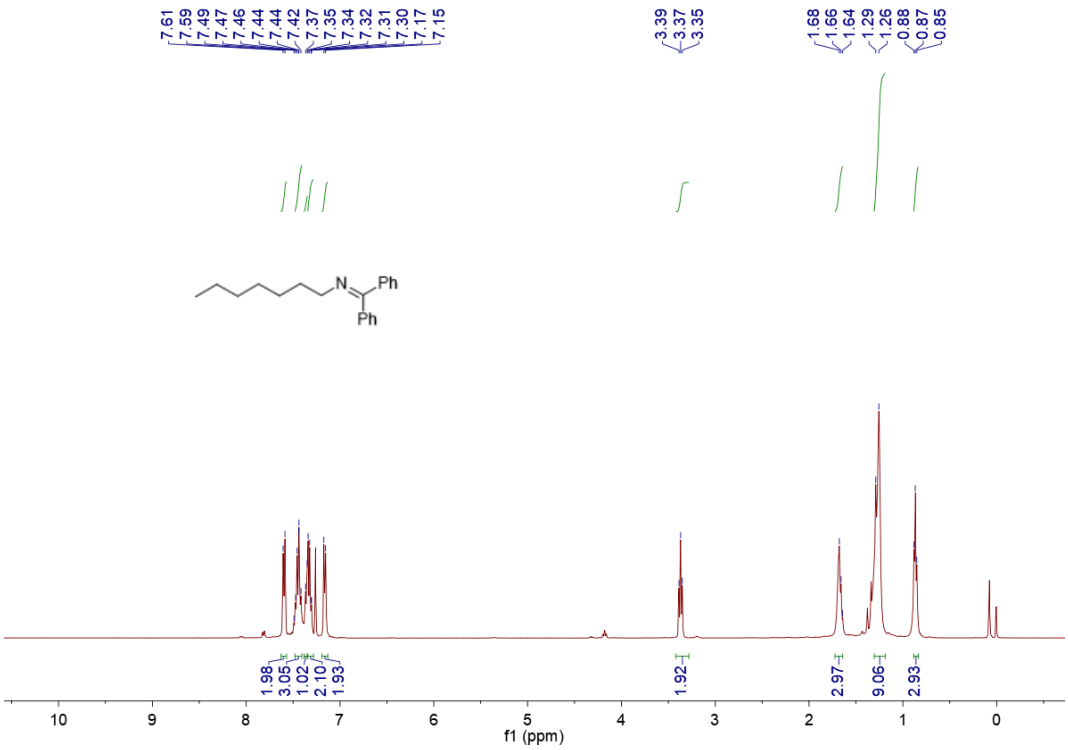

$^{1}$H NMR spectra of compound **2d** in $CDCl_3$ (400 MHz):



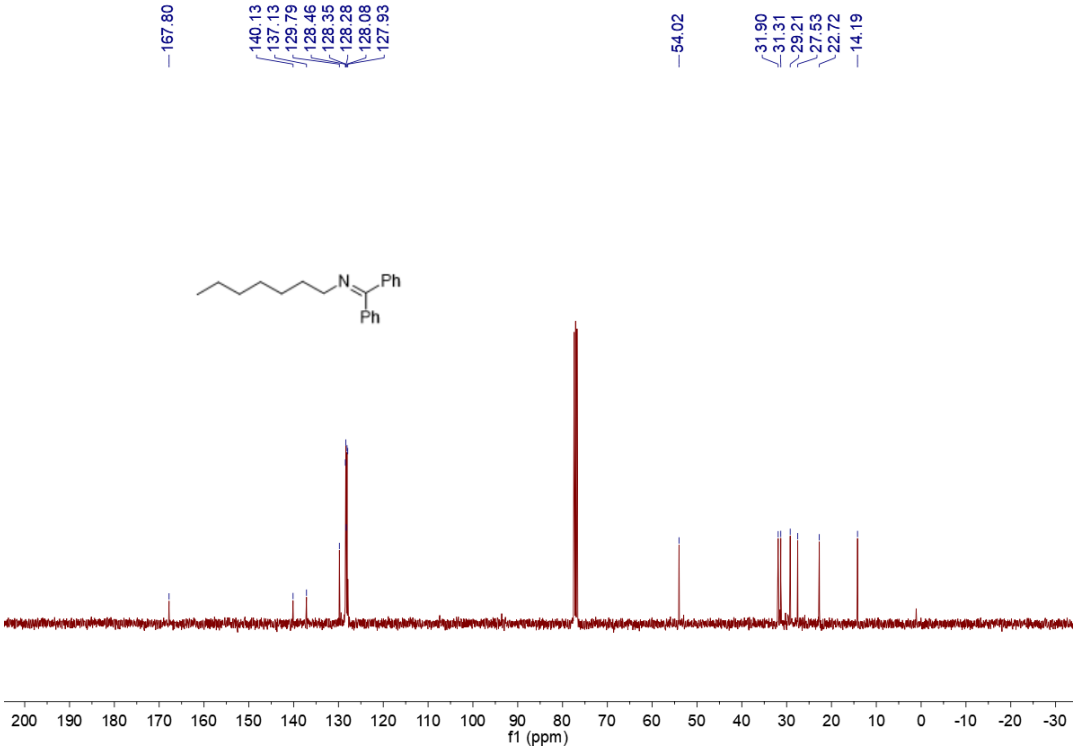
$^{13}$C NMR spectra of compound **2d** in $CDCl_3$ (101 MHz):



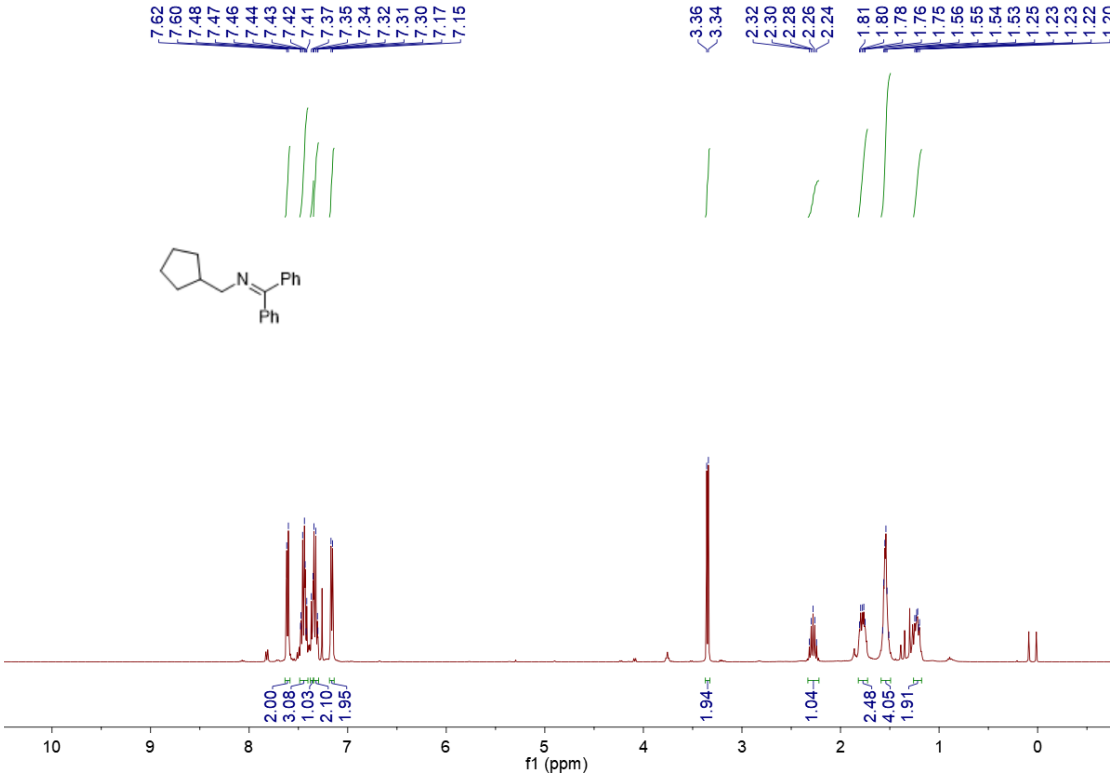

$^{1}$H NMR spectra of compound **3a** in $CDCl_3$ (400 MHz):



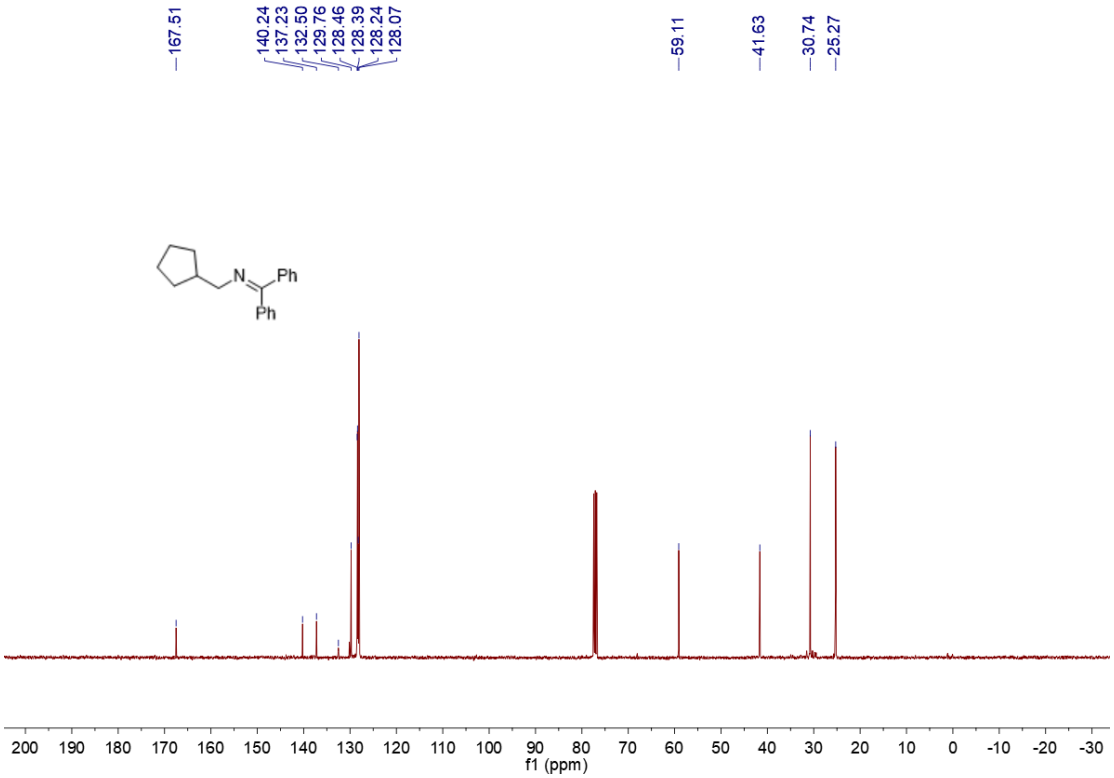
$^{13}C$ NMR spectra of compound **3a** in $CDCl_3$ (101 MHz):



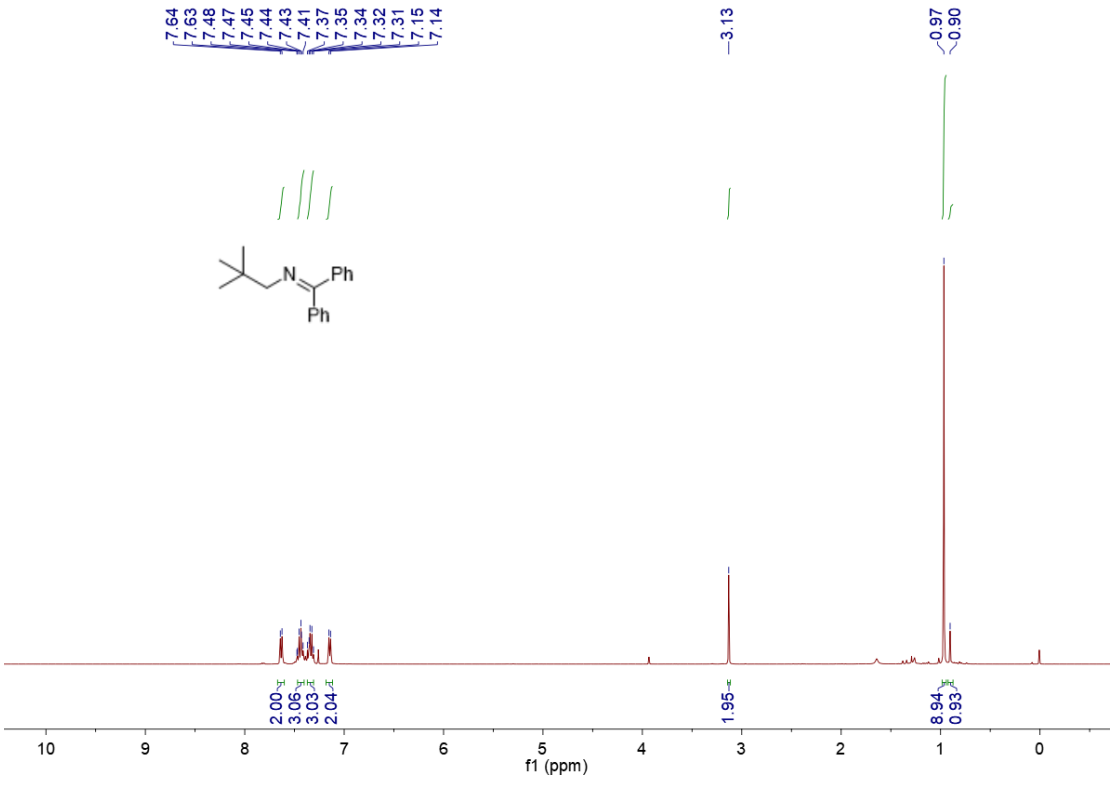

$^{1}H$ NMR spectra of compound **3b** in $CDCl_3$ (400 MHz):



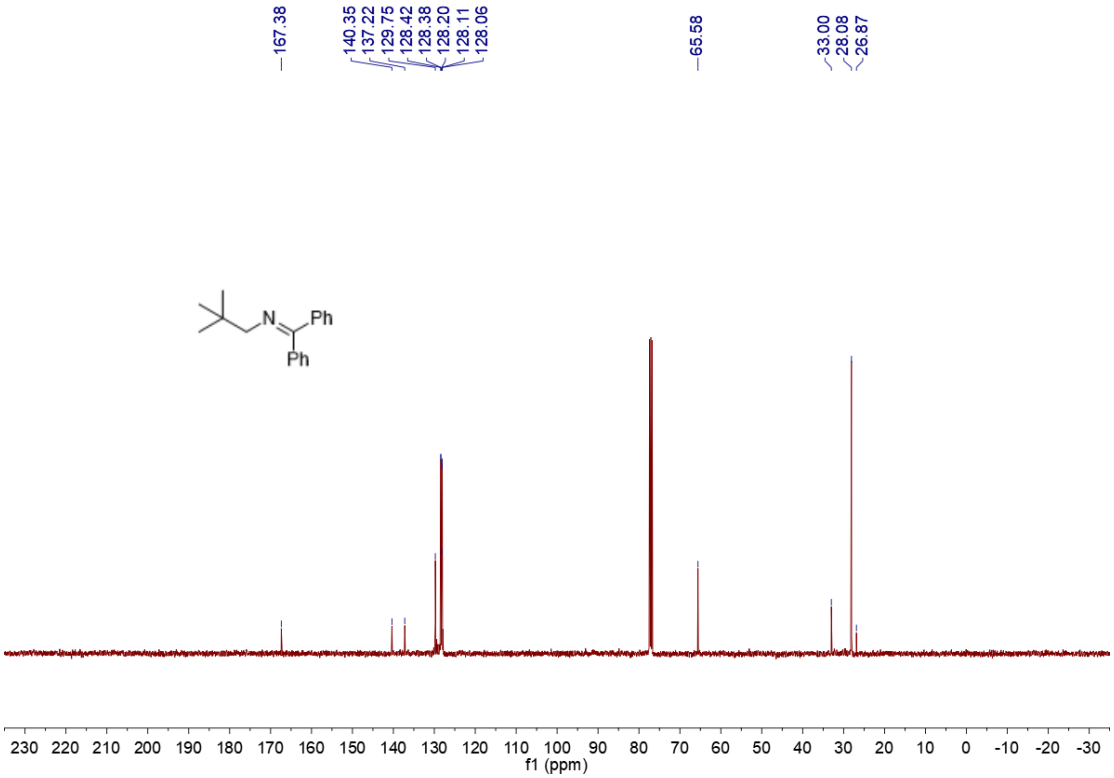
$^{13}$C NMR spectra of compound **3b** in $CDCl_3$ (101 MHz):



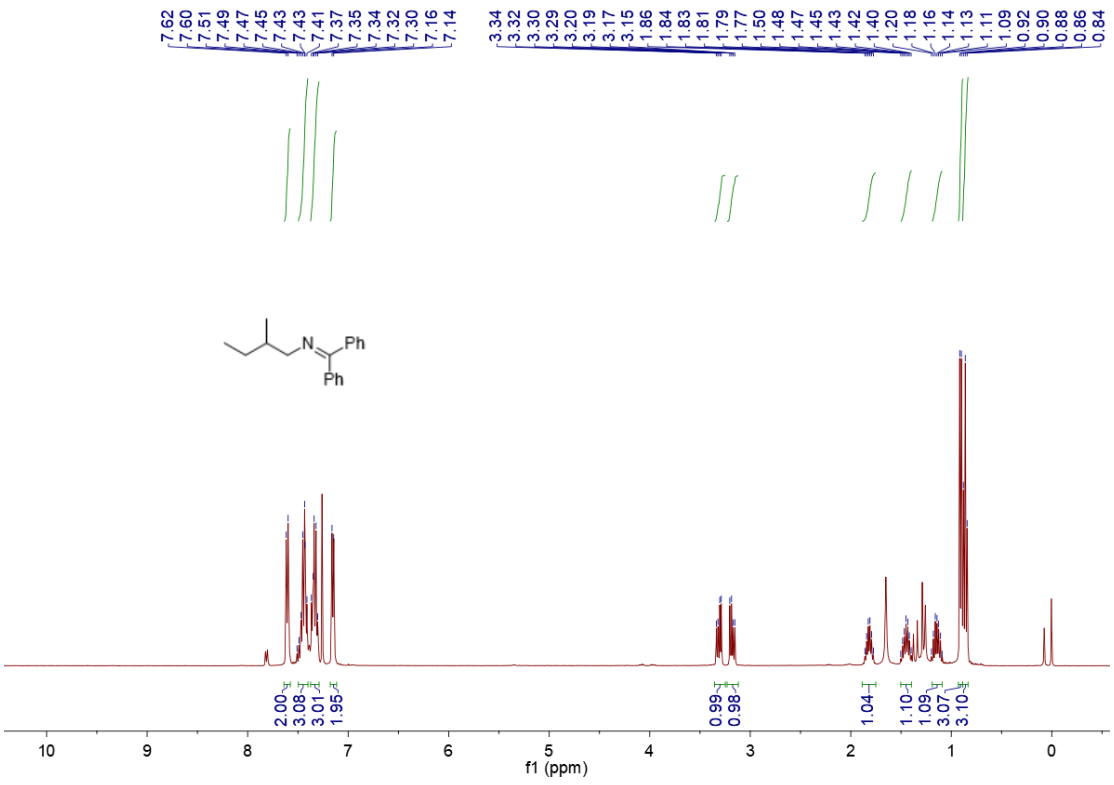

$^{1}$H NMR spectra of compound **3c** in $CDCl_3$ (400 MHz):



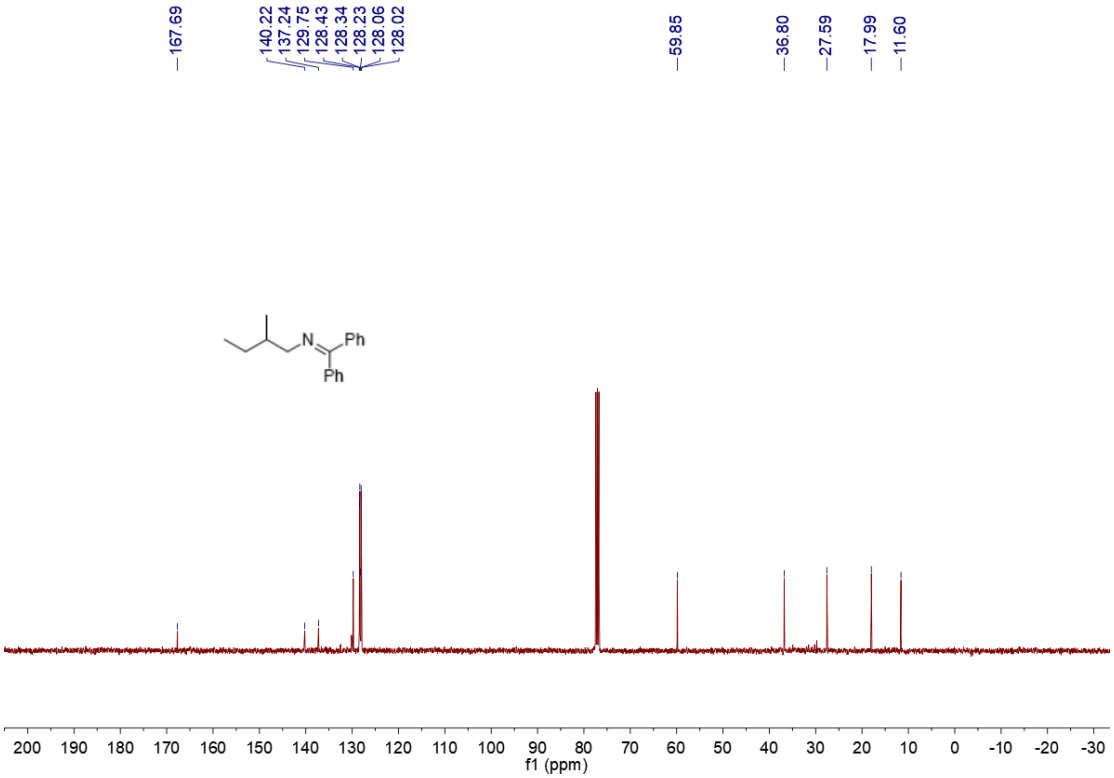
$^{13}$C NMR spectra of compound **3c** in $CDCl_3$ (101 MHz):



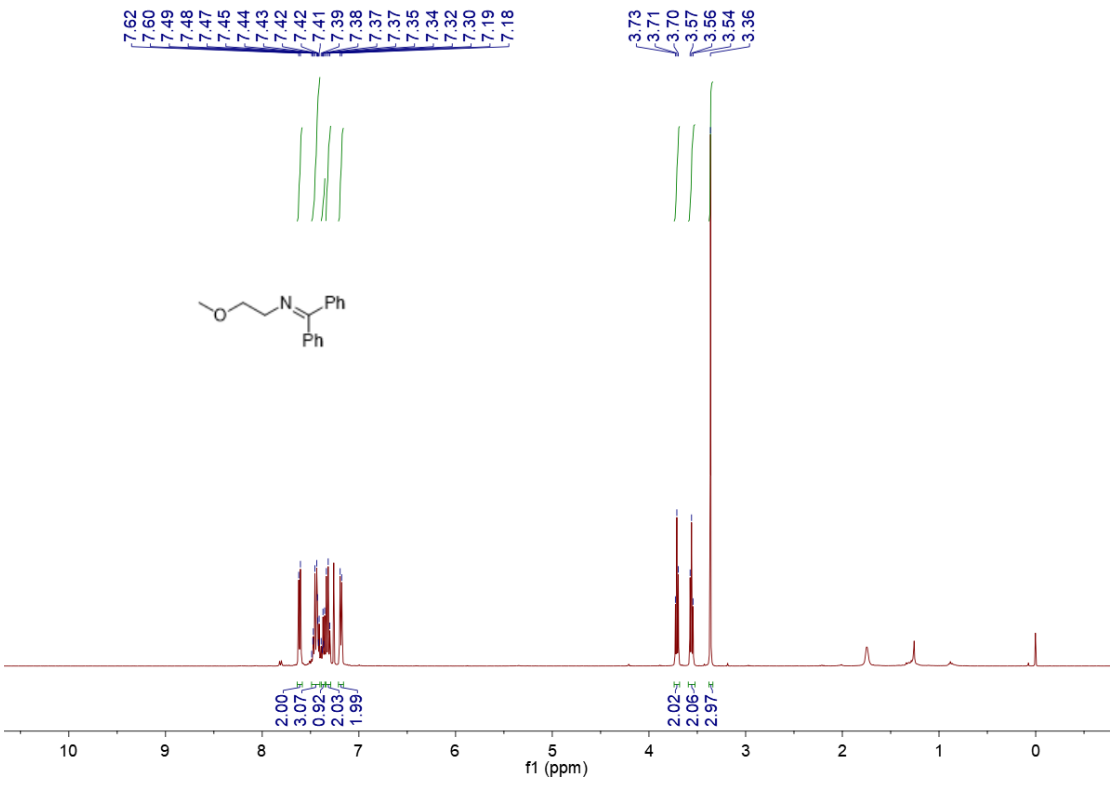

$^{1}$H NMR spectra of compound **3d** in $CDCl_3$ (400 MHz):



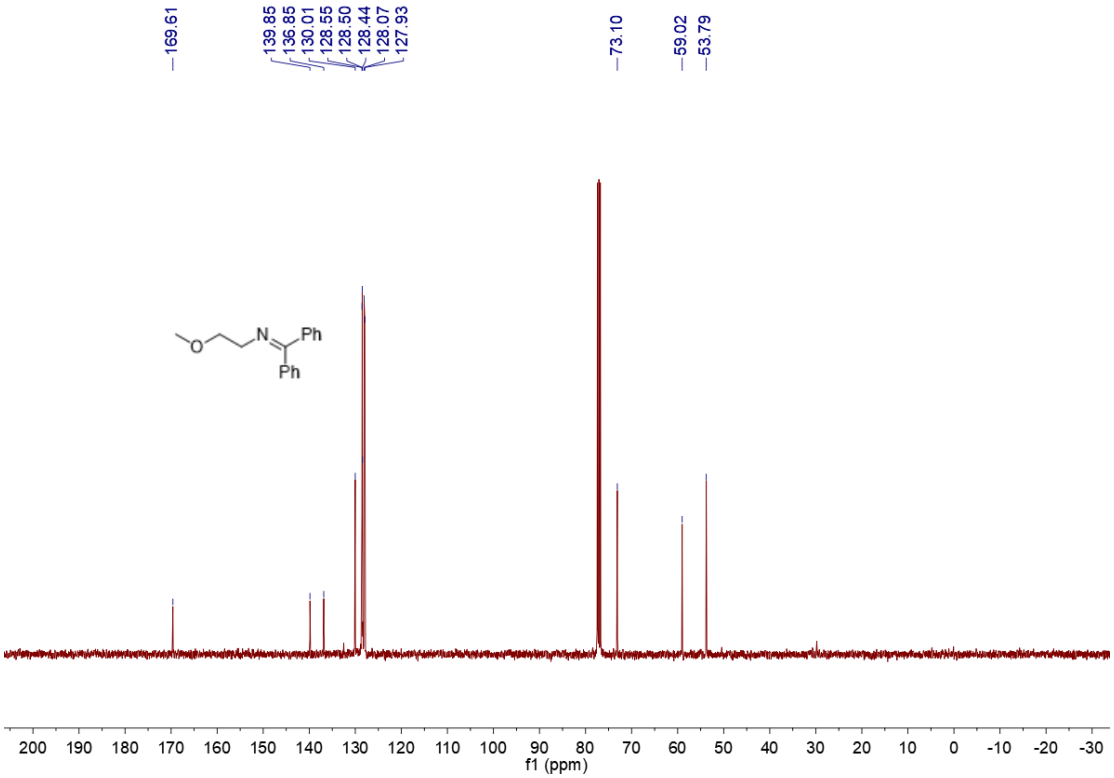
$^{13}$C NMR spectra of compound **3d** in $CDCl_3$ (101 MHz):



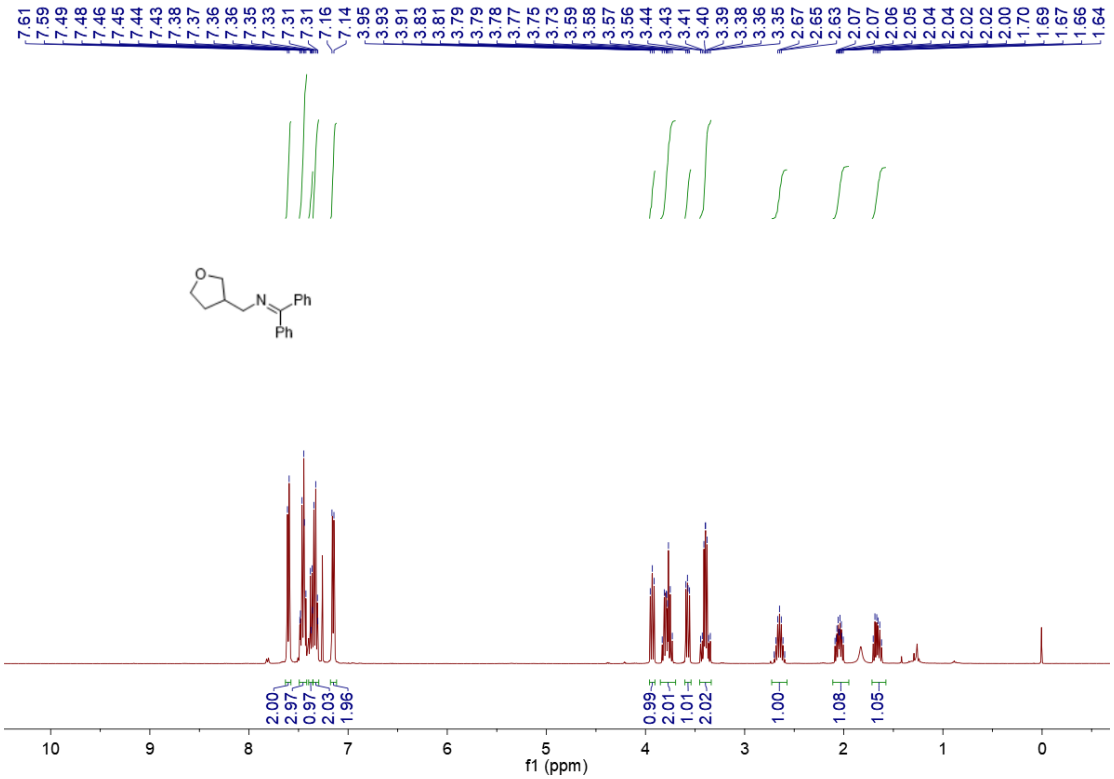

$^{1}$H NMR spectra of compound **3e** in $CDCl_3$ (400 MHz):



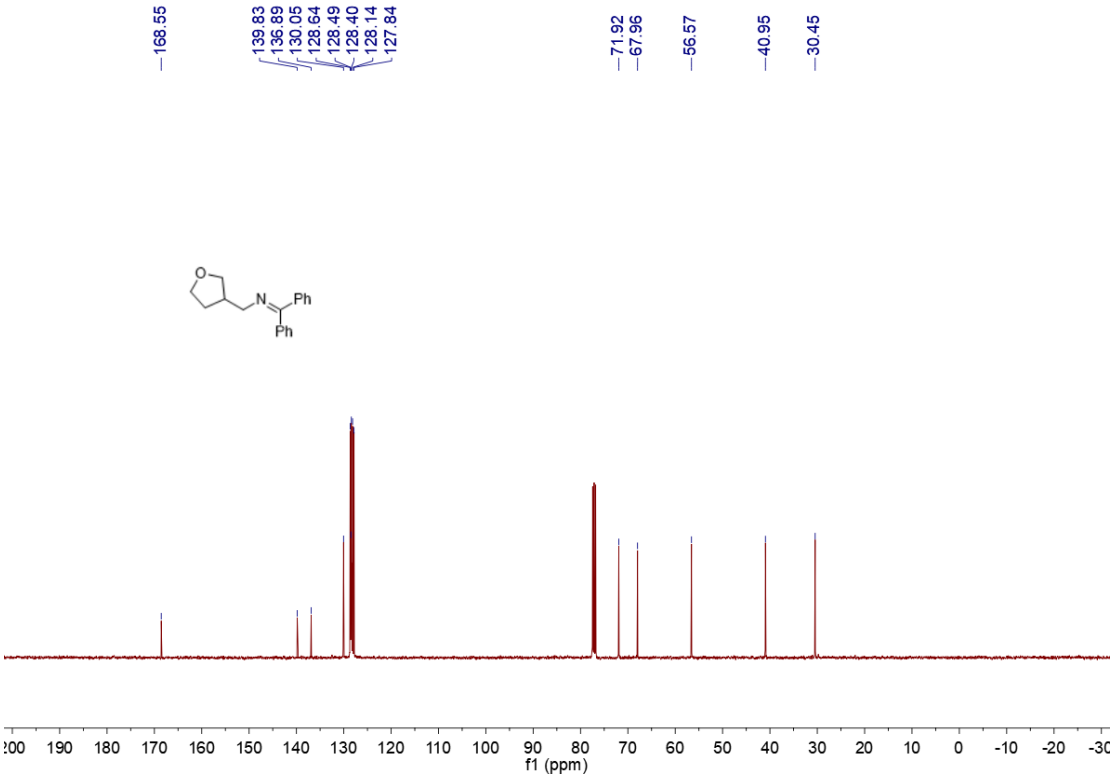
$^{13}C$ NMR spectra of compound **3e** in $CDCl_3$ (101 MHz):



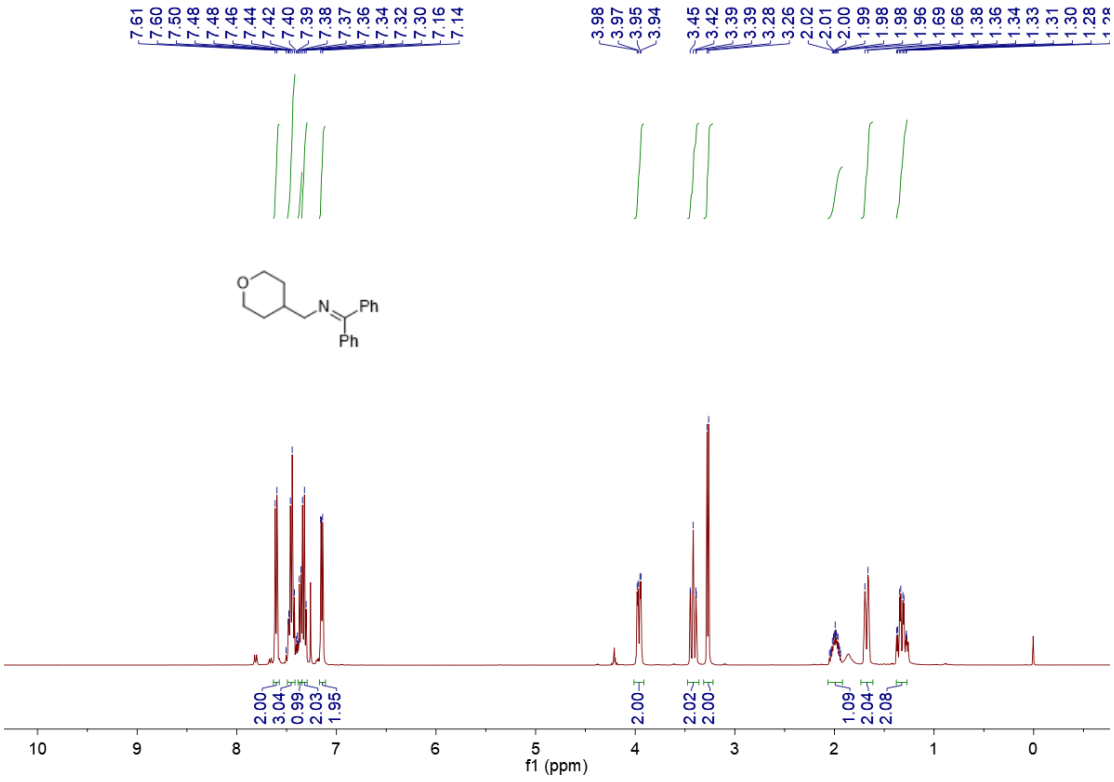

$^{1}H$ NMR spectra of compound **3f** in $CDCl_3$ (400 MHz):



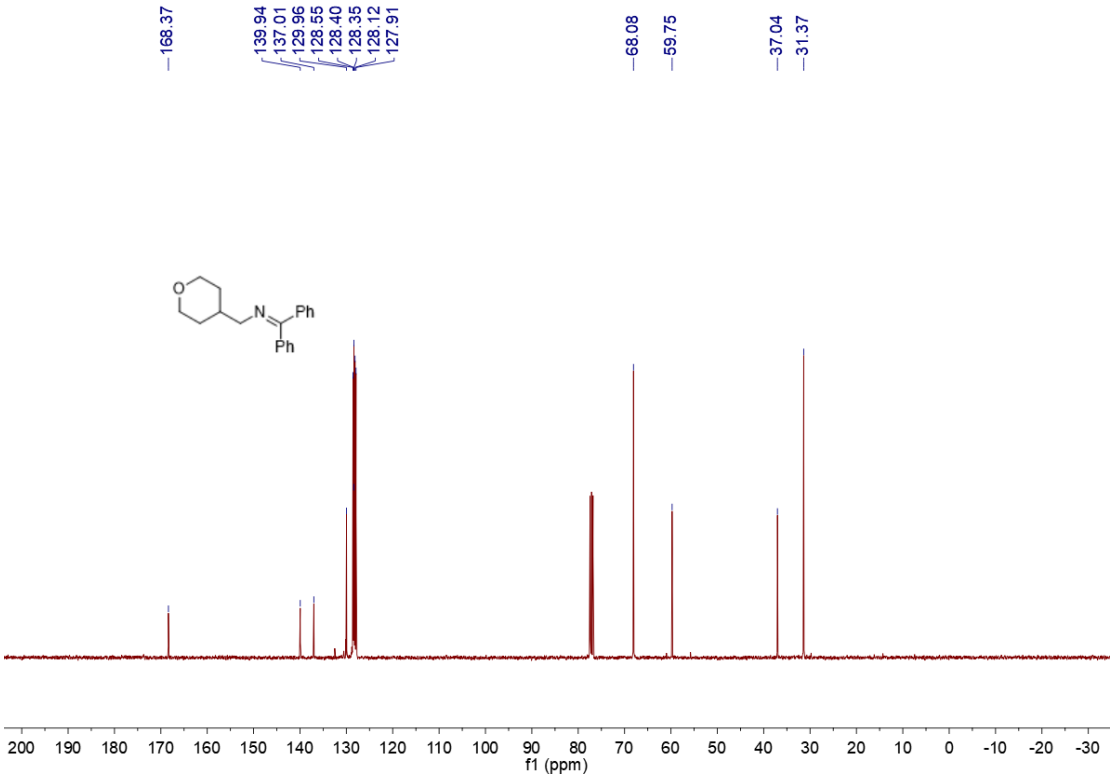

$^{13}C$ NMR spectra of compound **3f** in $CDCl_3$ (101 MHz):



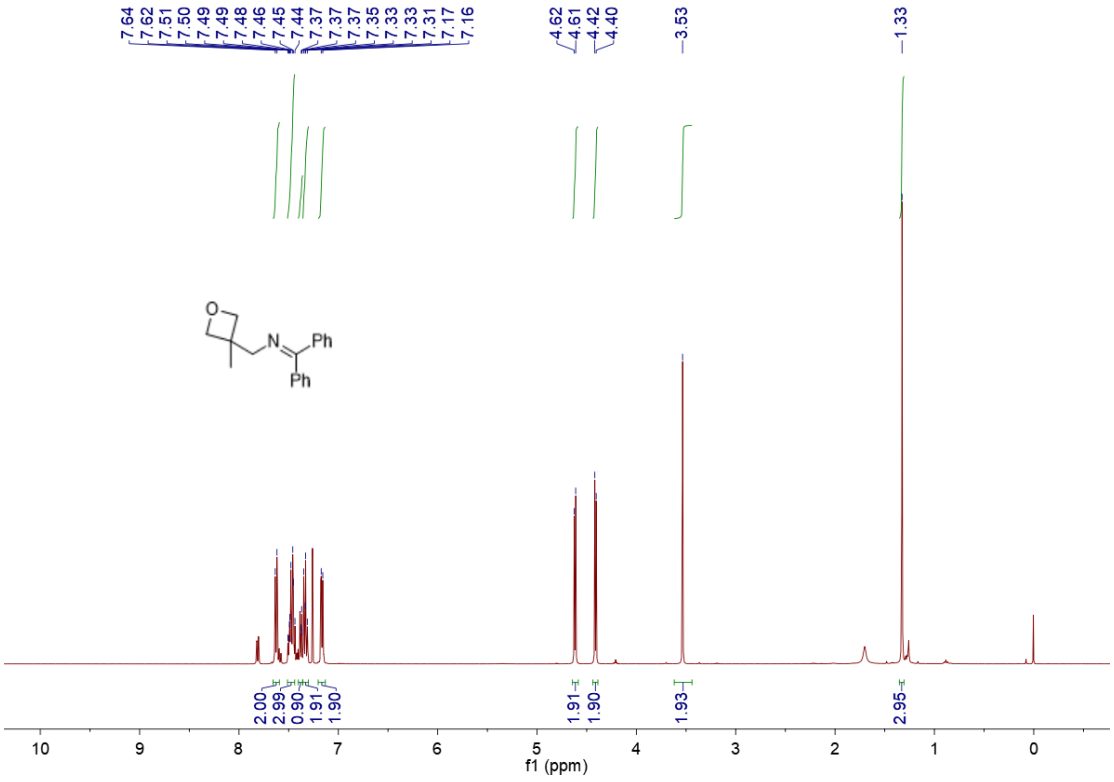

$^1$H NMR spectra of compound **3g** in $CDCl_3$ (400 MHz):



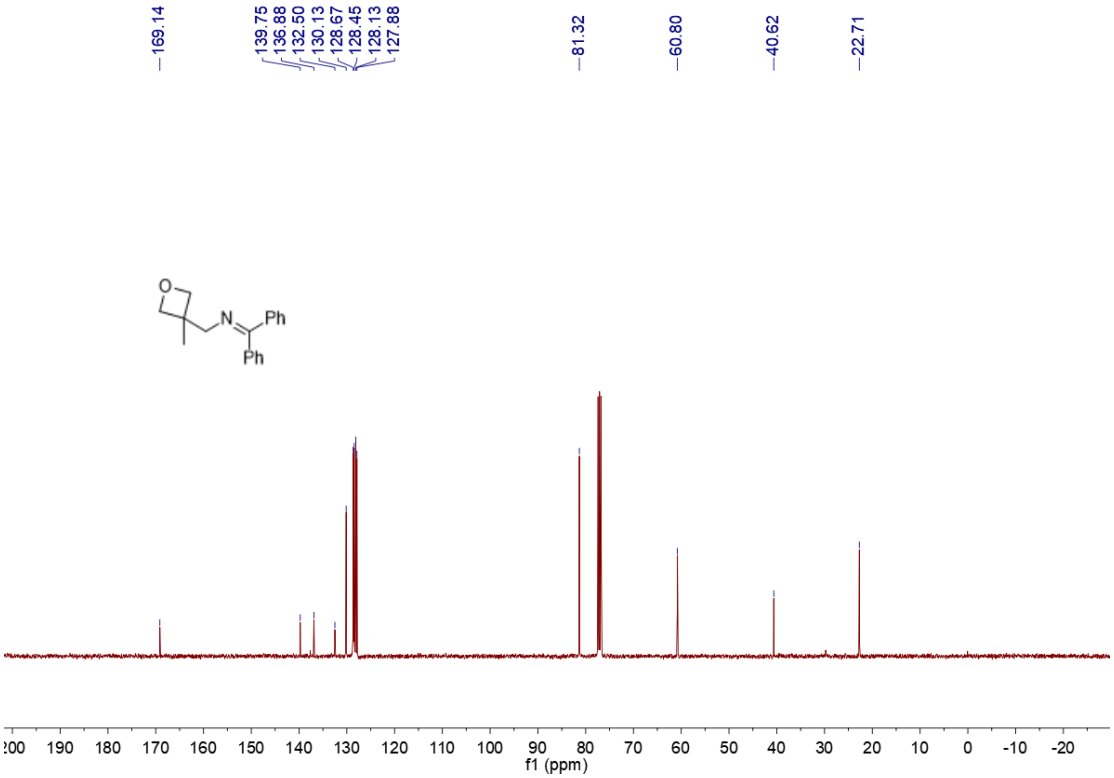
$^{13}$C NMR spectra of compound **3g** in $CDCl_3$ (101 MHz):



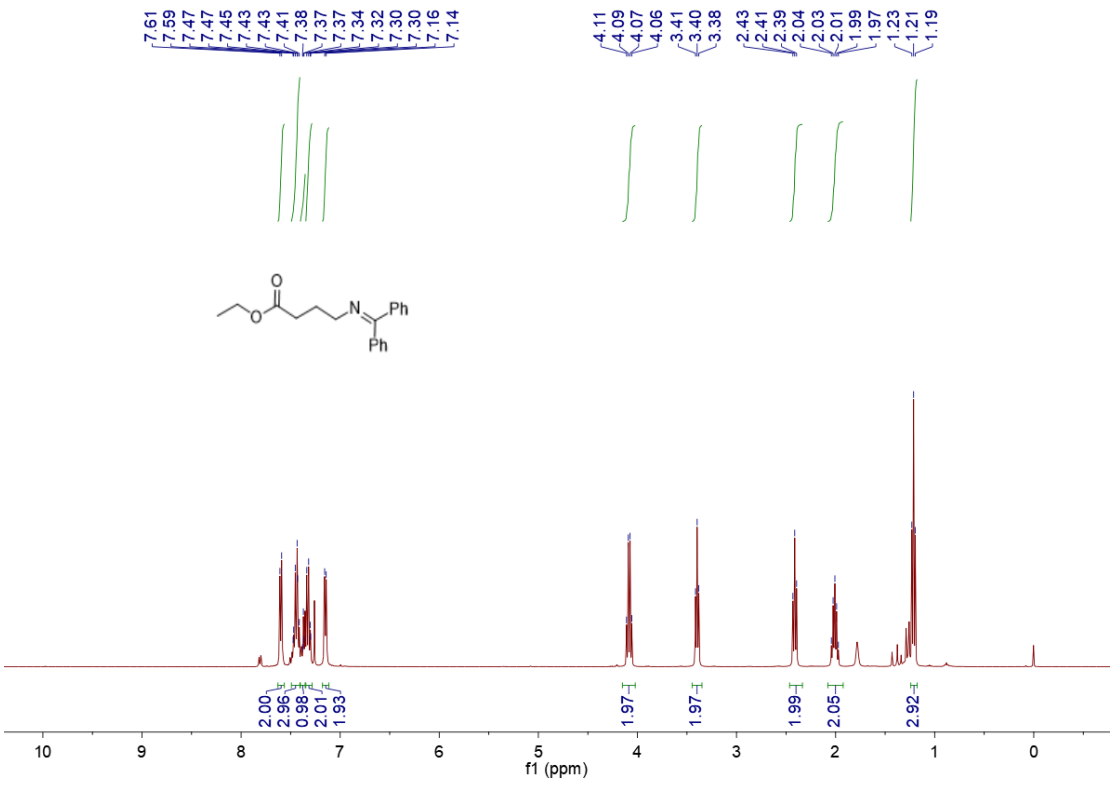

$^{1}$H NMR spectra of compound **3h** in $CDCl_3$ (400 MHz):



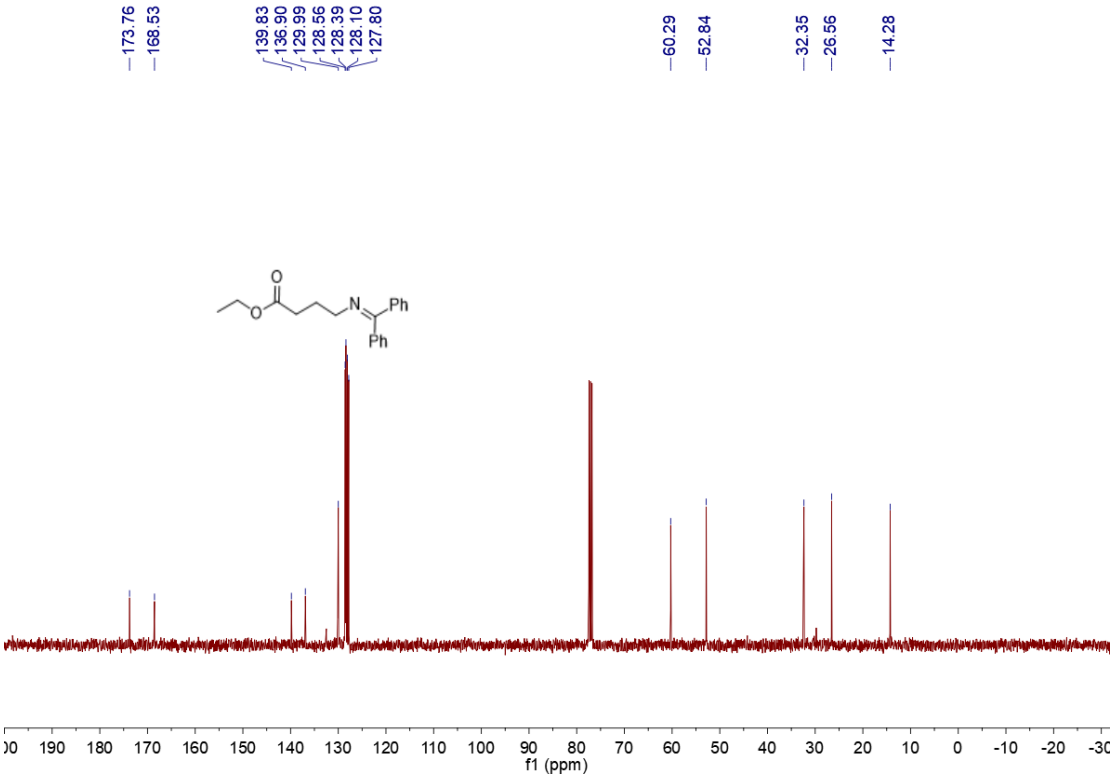
$^{13}$C NMR spectra of compound **3h** in $CDCl_3$ (101 MHz):



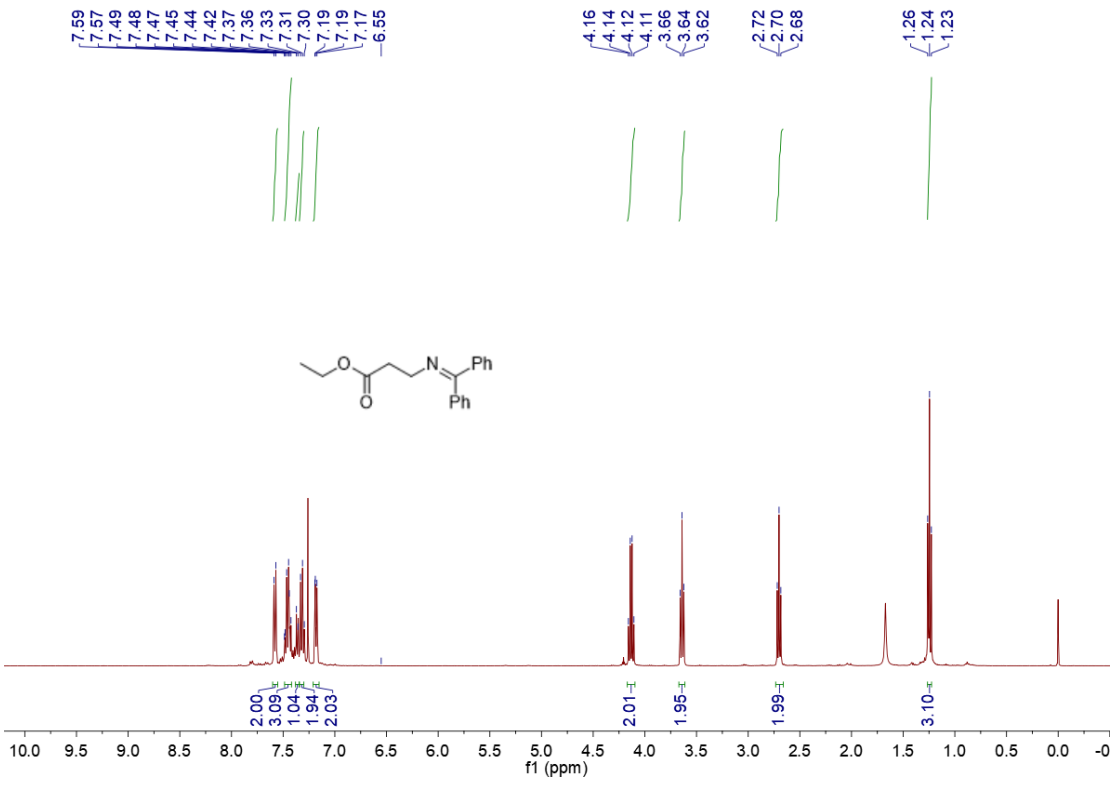

$^{1}$H NMR spectra of compound **3i** in $CDCl_3$ (400 MHz):



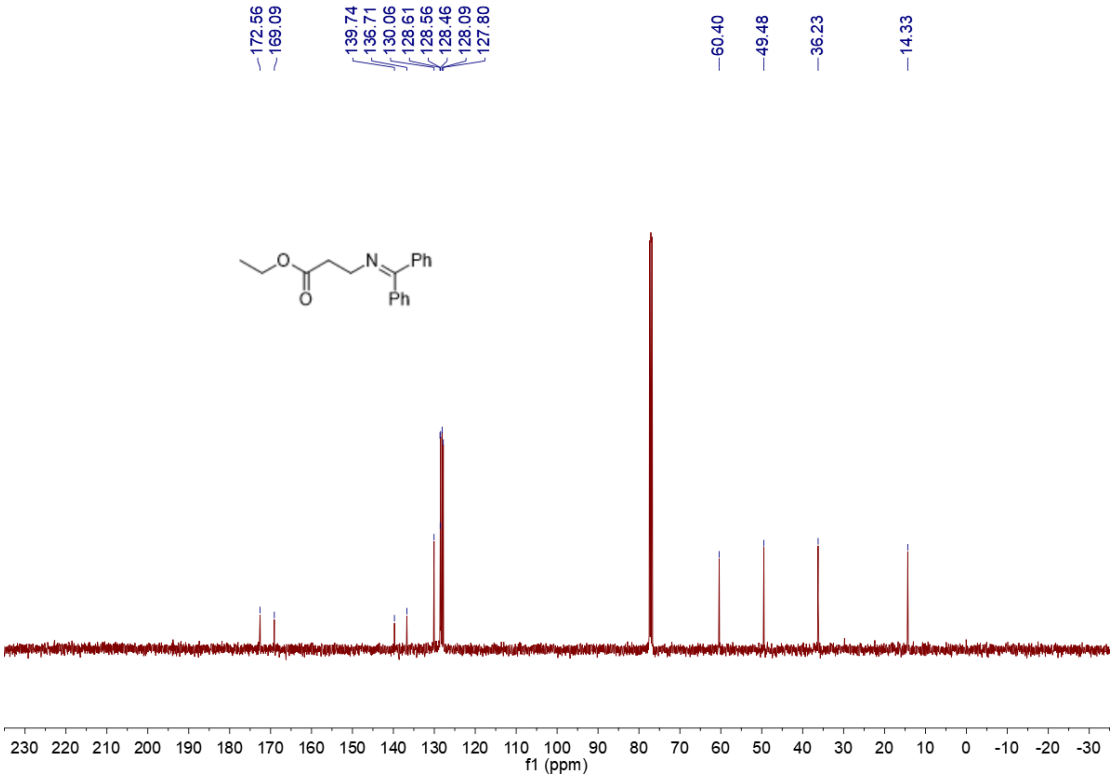

$^{13}$C NMR spectra of compound **3i** in $CDCl_3$ (101 MHz):



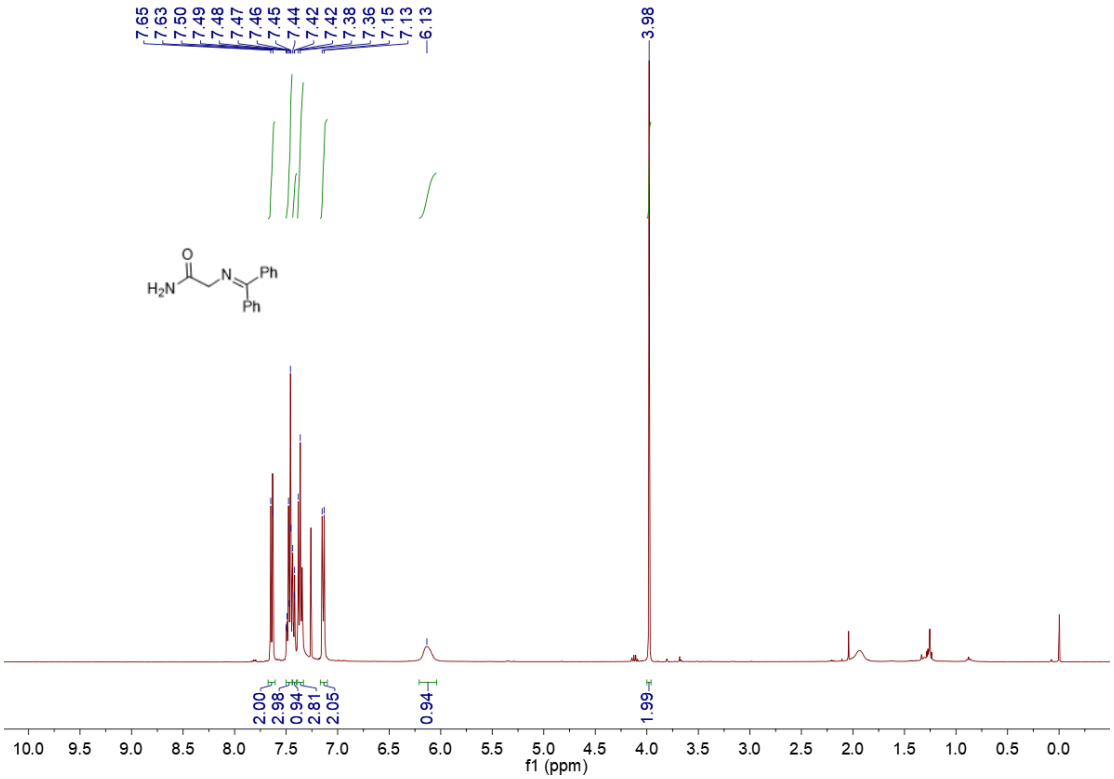

$^1$H NMR spectra of compound **3j** in $CDCl_3$ (400 MHz):



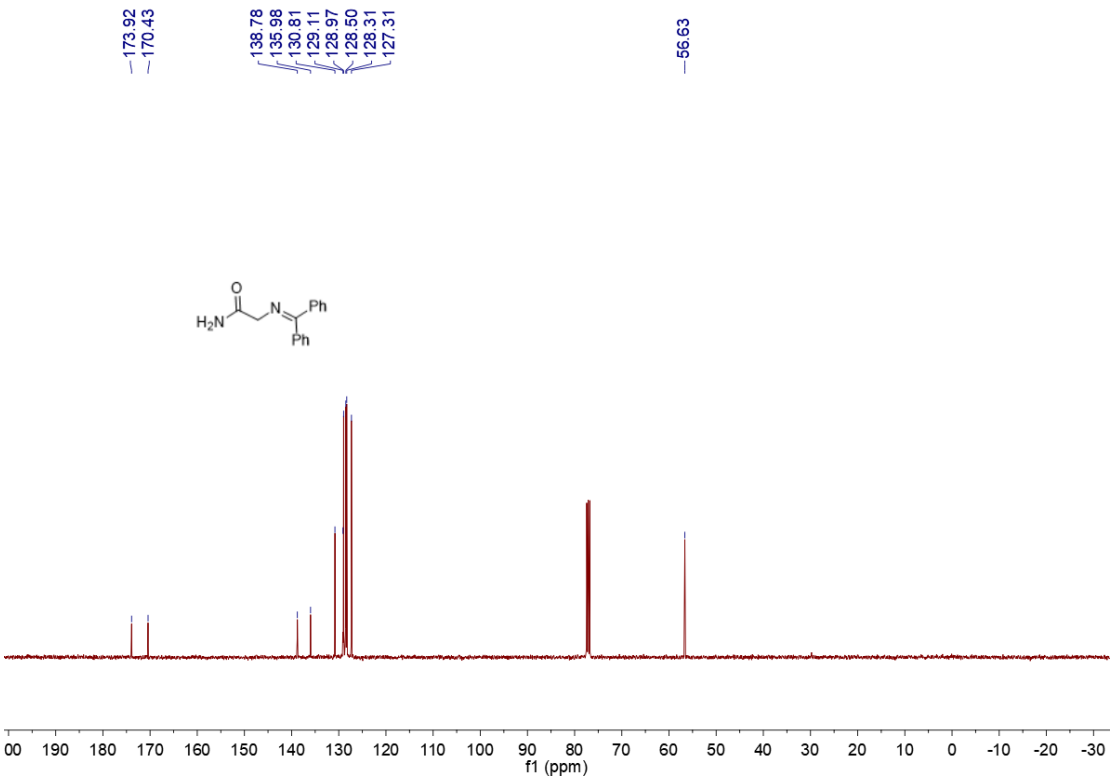
$^{13}$C NMR spectra of compound **3j** in $CDCl_3$ (101 MHz):



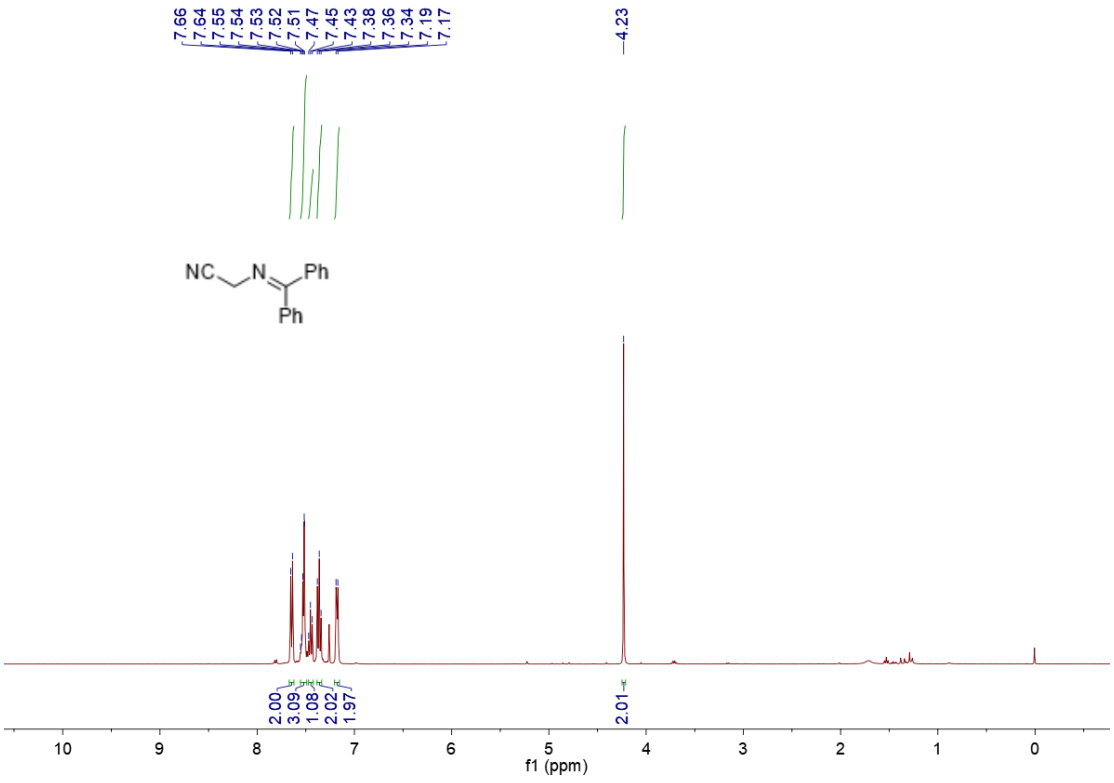

$^{1}$H NMR spectra of compound **3k** in $CDCl_3$ (400 MHz):



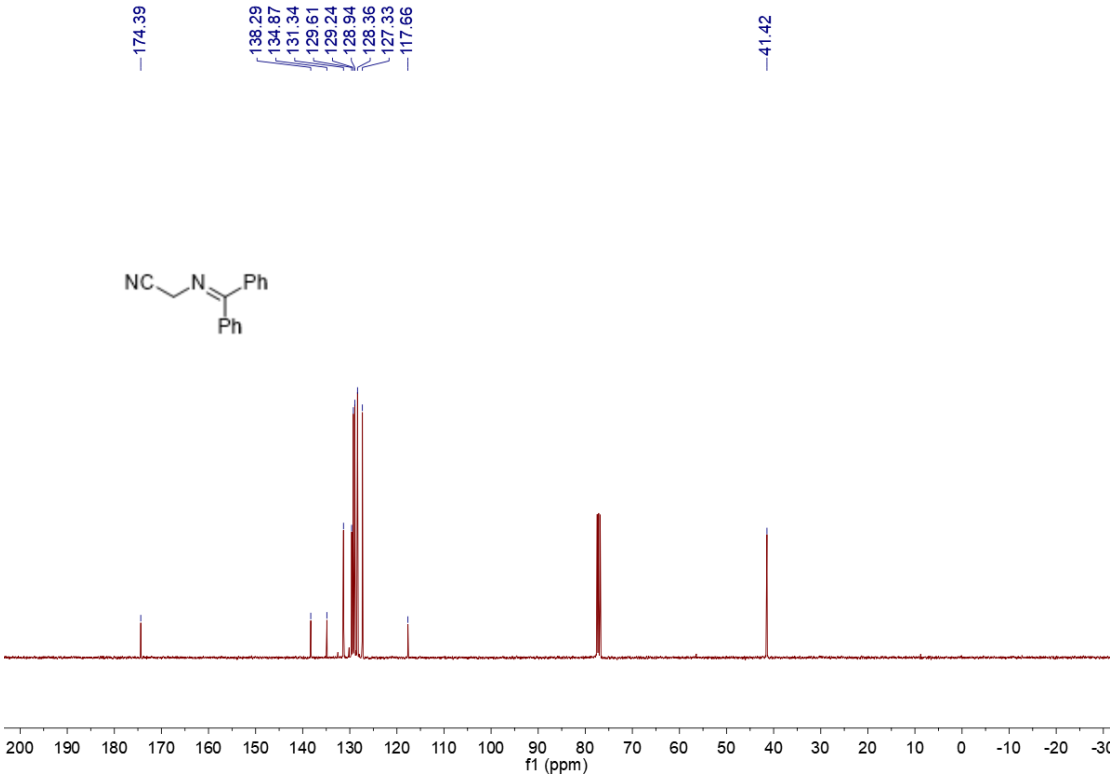

$^{13}$C NMR spectra of compound **3k** in $CDCl_3$ (101 MHz):



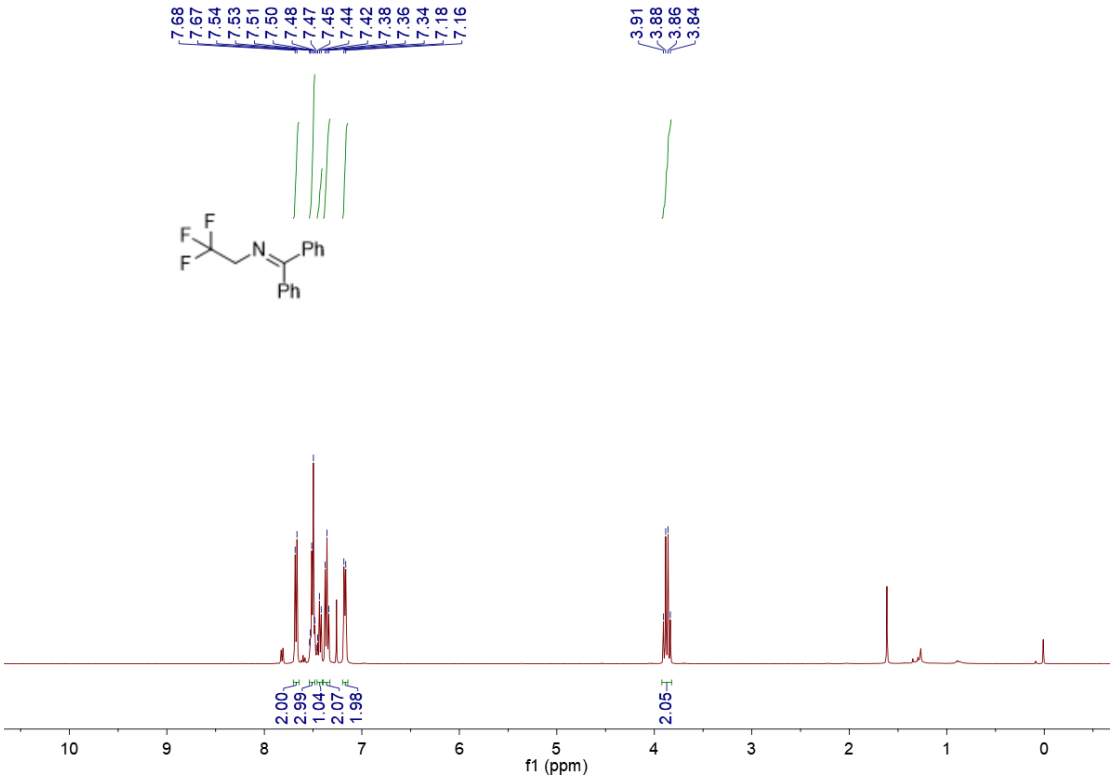

$^1$H NMR spectra of compound **3l** in $CDCl_3$ (400 MHz):



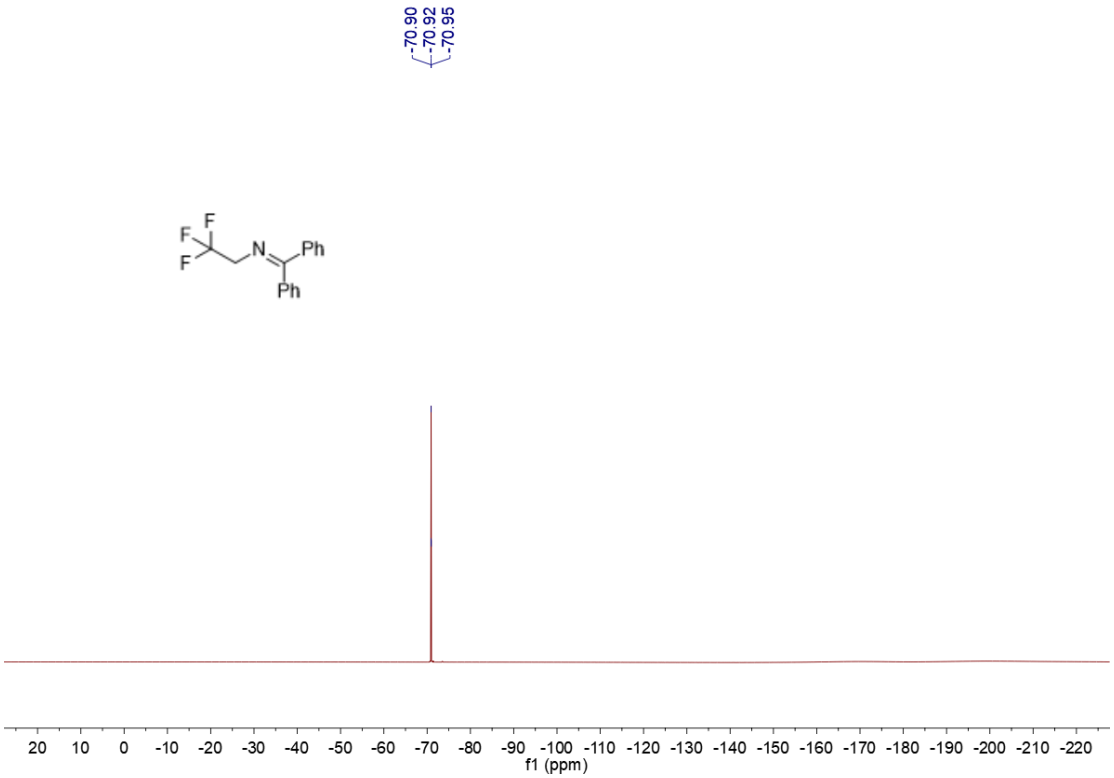
$^{13}$C NMR spectra of compound **3l** in $CDCl_3$ (101 MHz):



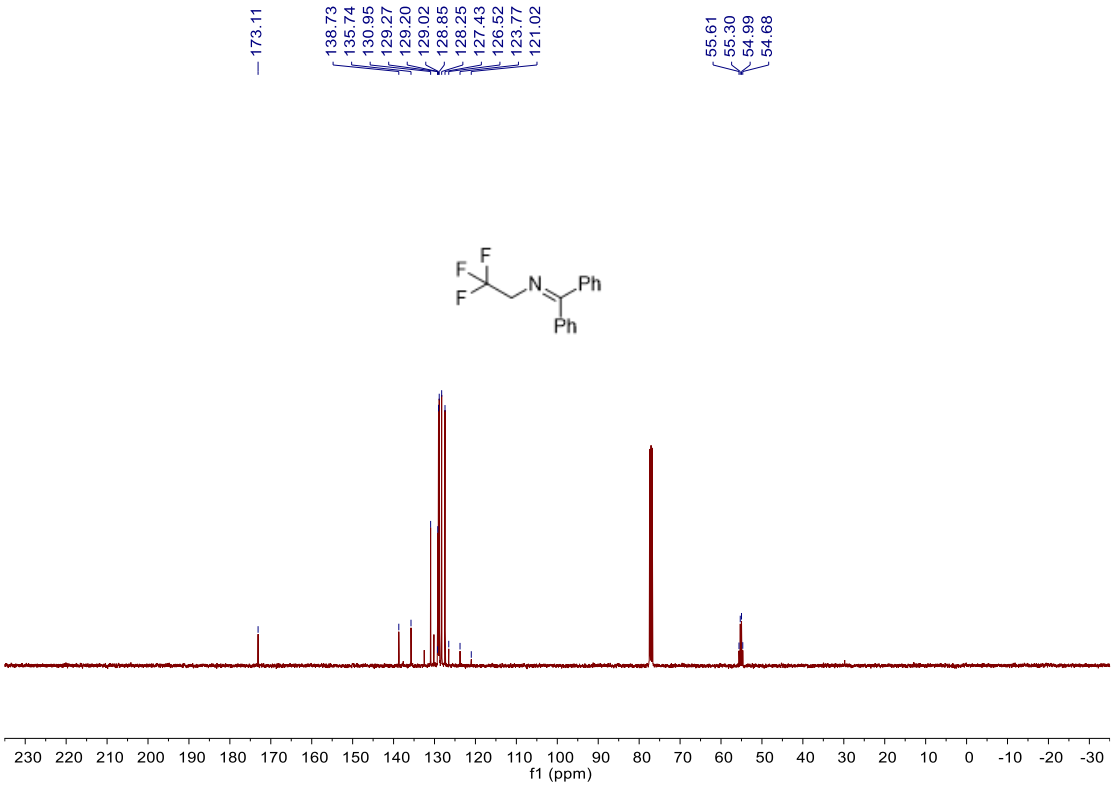

$^{1}$H NMR spectra of compound **3m** in $CDCl_3$ (400 MHz):



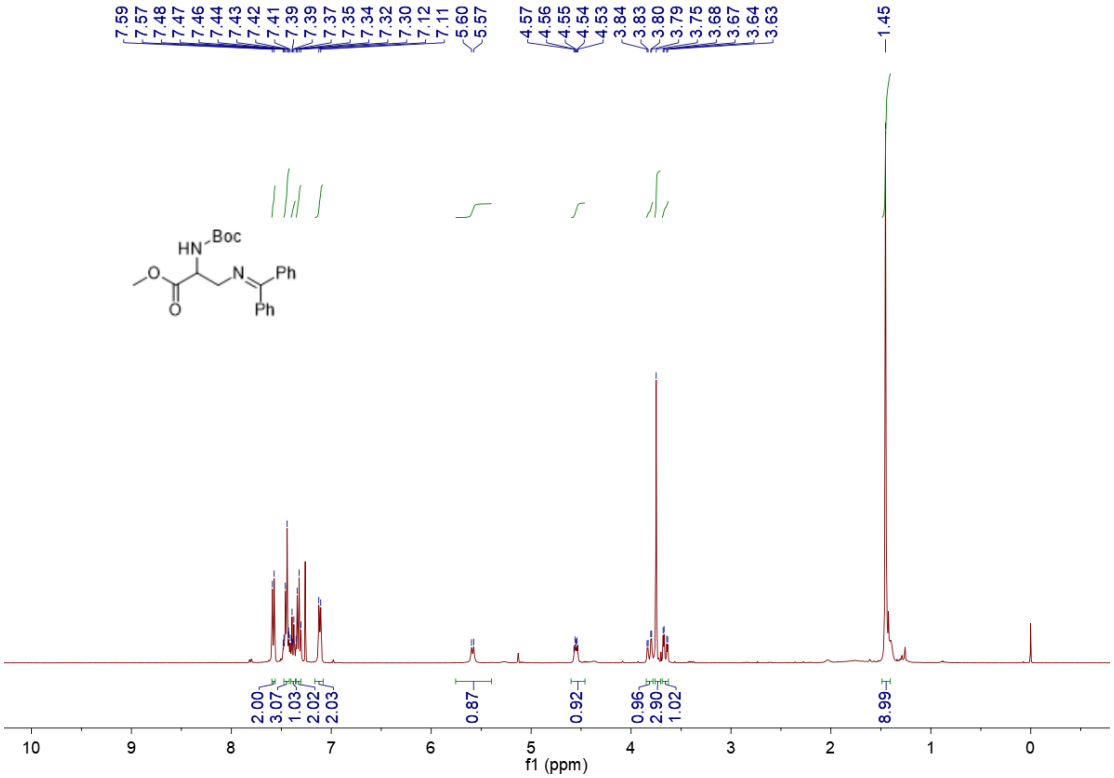

$^{19}$F NMR spectra of compound **3m** in $CDCl_3$ (101 MHz):



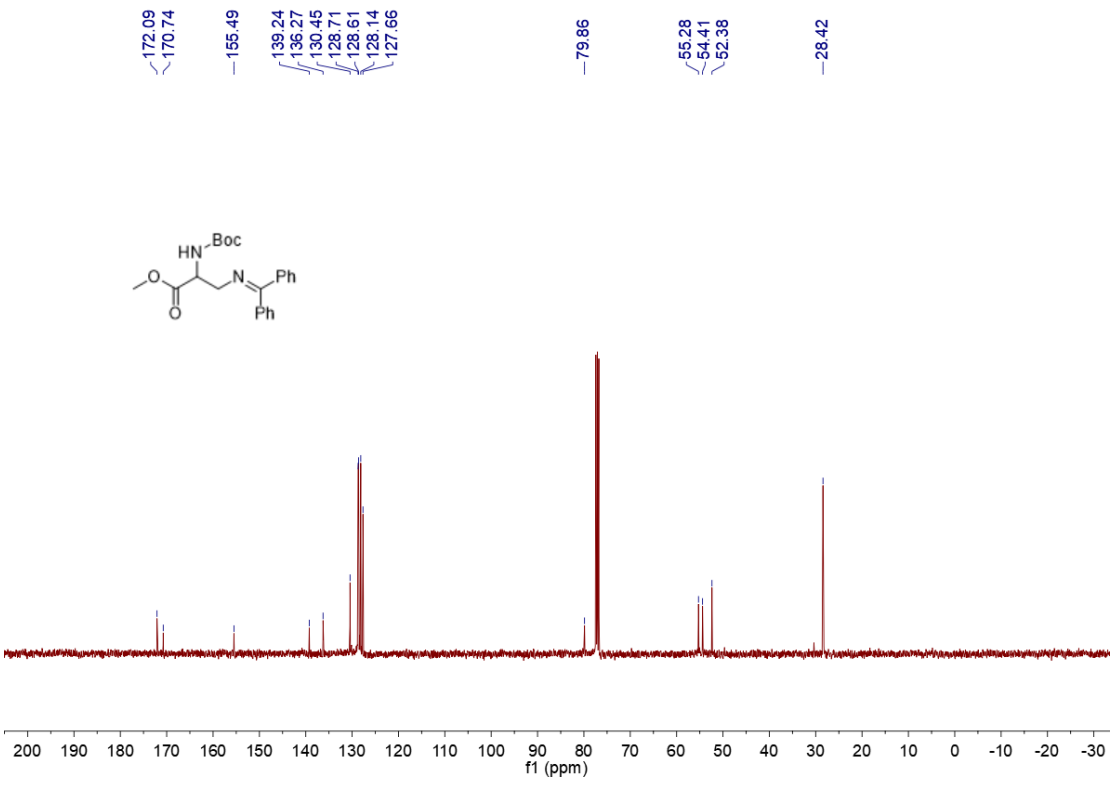

$^{13}C$ NMR spectra of compound **3m** in $CDCl_3$ (101 MHz):



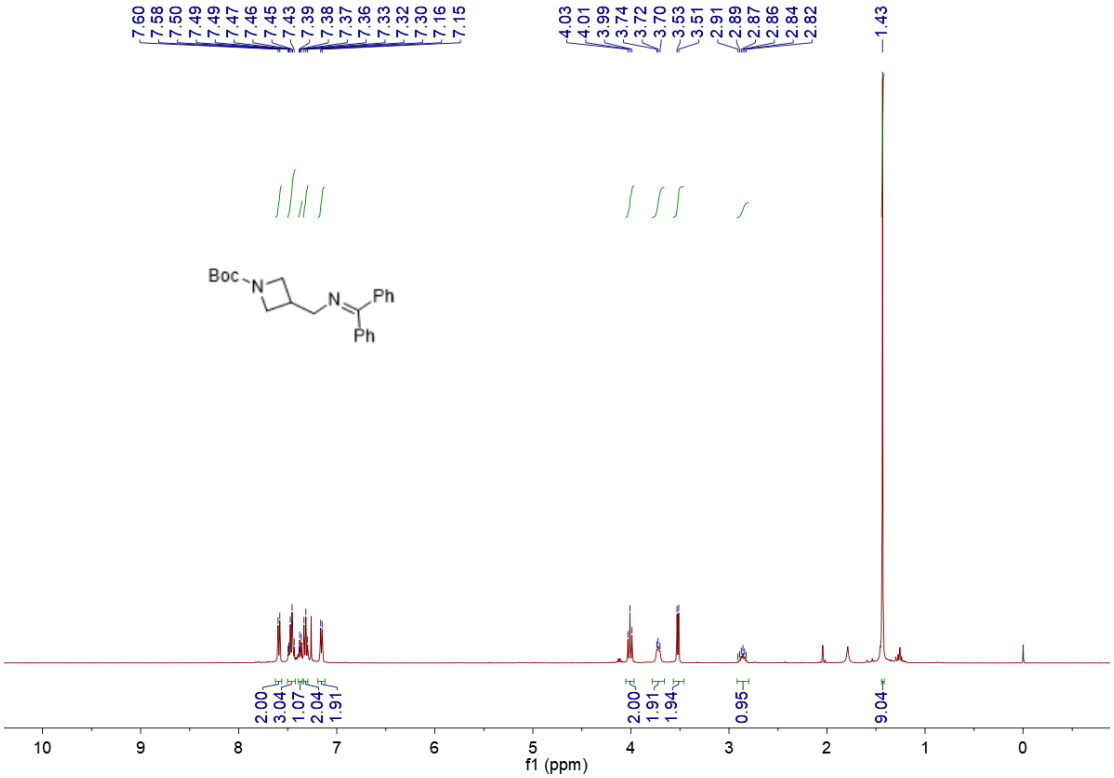

$^{1}H$ NMR spectra of compound **3n** in $CDCl_3$ (400 MHz):



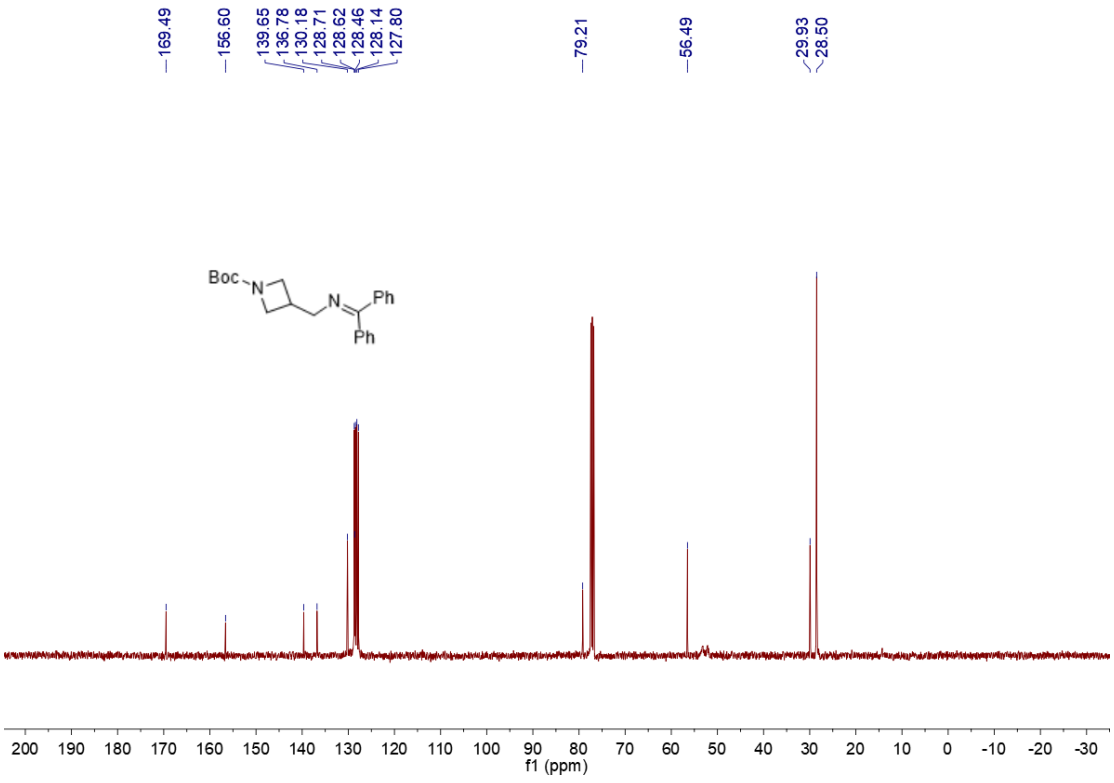

$^{13}C$ NMR spectra of compound **3n** in $CDCl_3$ (101 MHz):



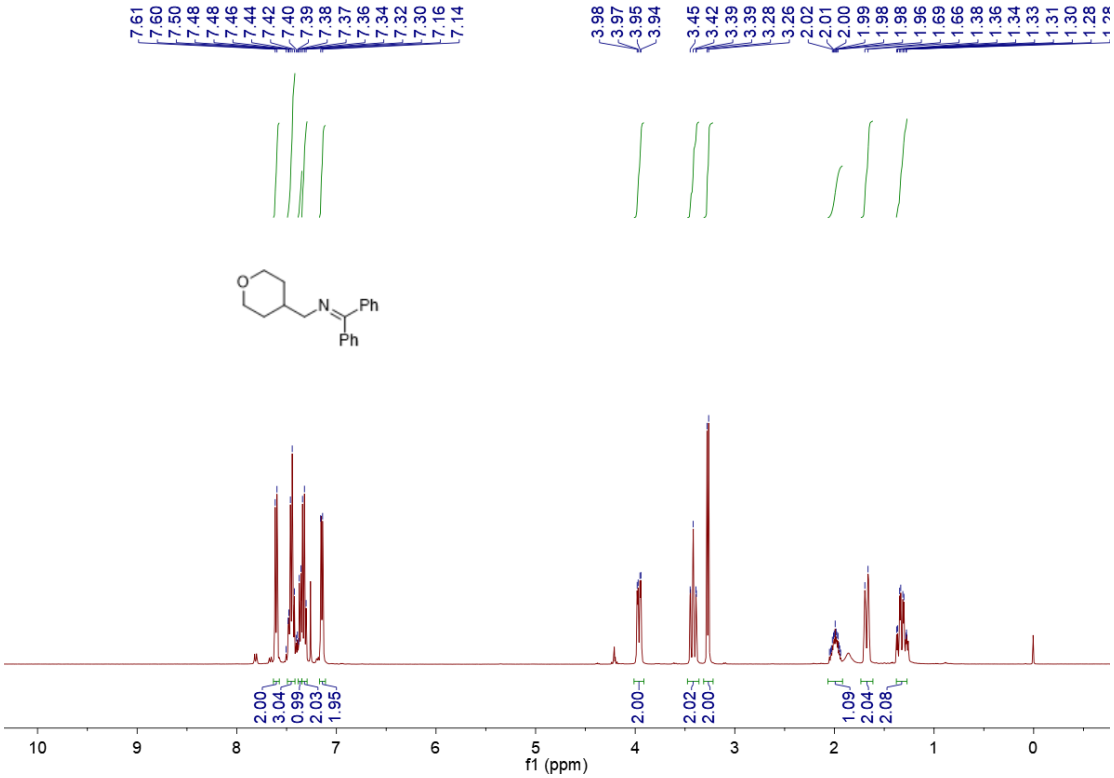
$^{1}$H NMR spectra of compound **3o** in $CDCl_3$ (400 MHz):



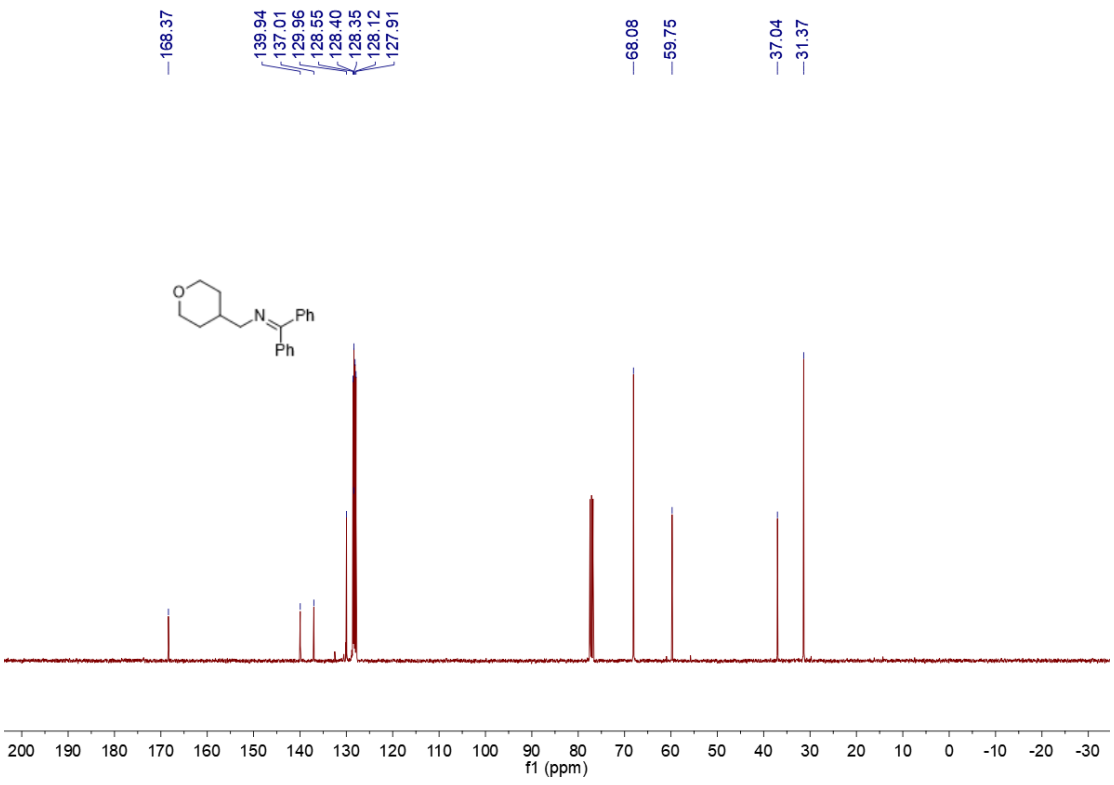

$^{13}$C NMR spectra of compound **3o** in $CDCl_3$ (101 MHz):



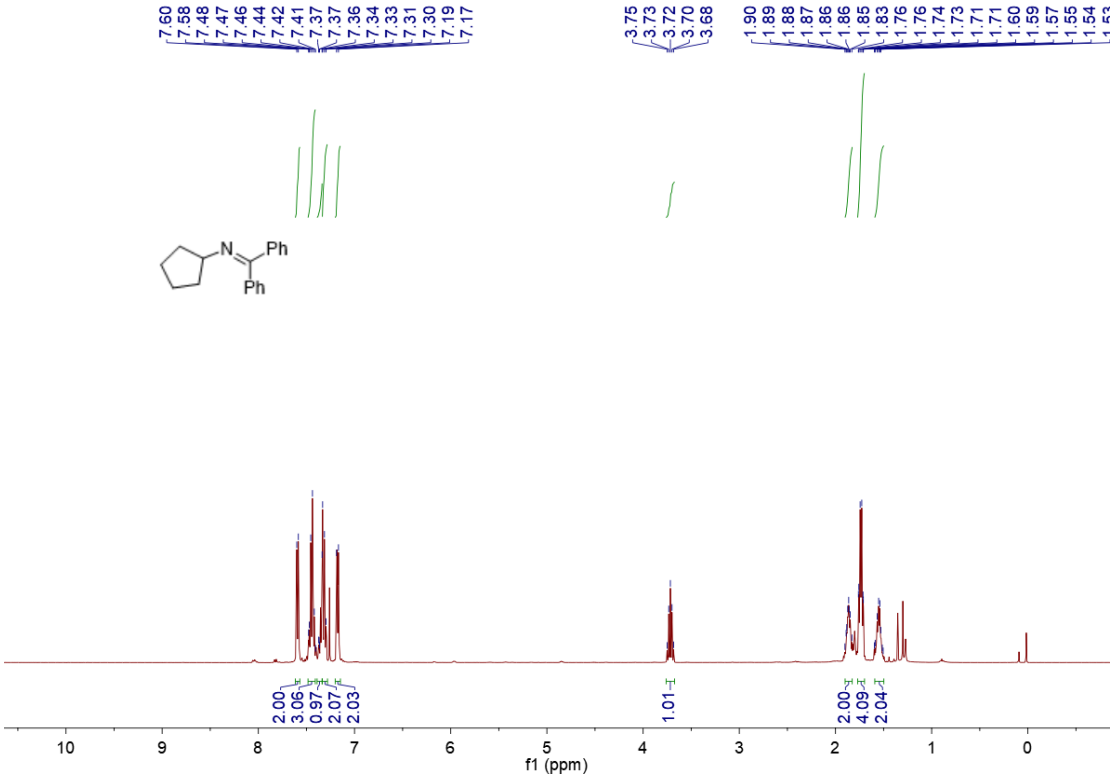
$^{1}$H NMR spectra of compound **3p** in $CDCl_3$ (400 MHz):



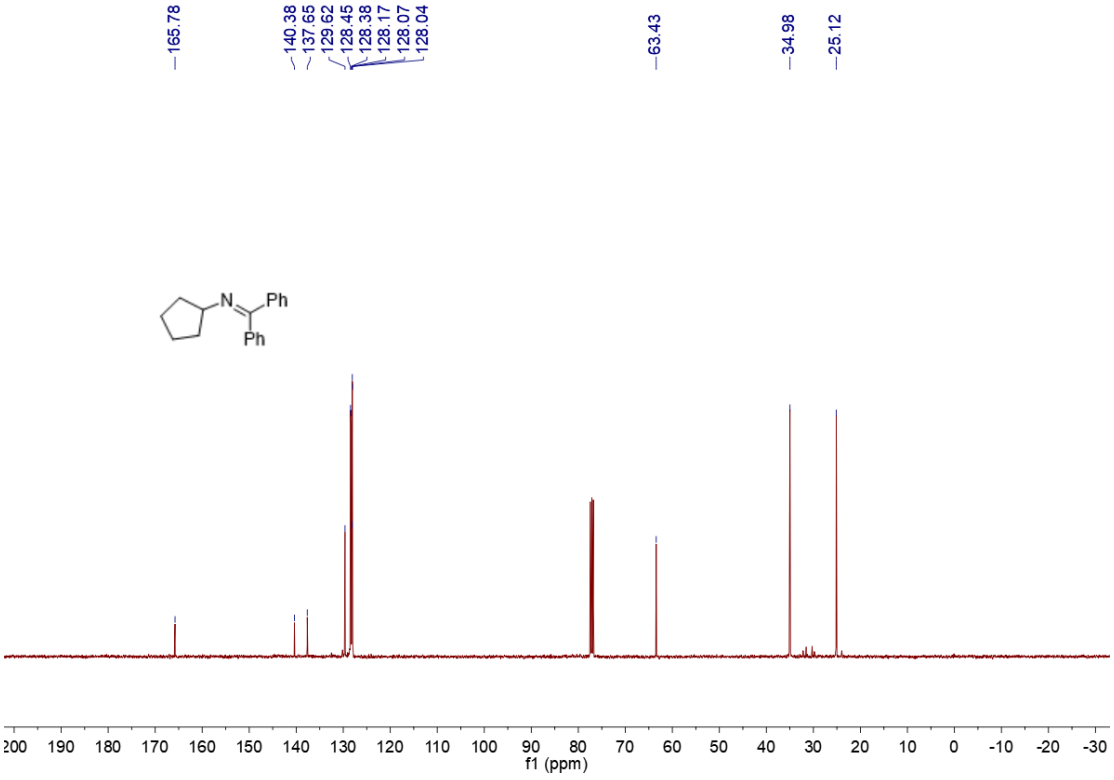

$^{13}$C NMR spectra of compound **3p** in $CDCl_3$ (101 MHz):



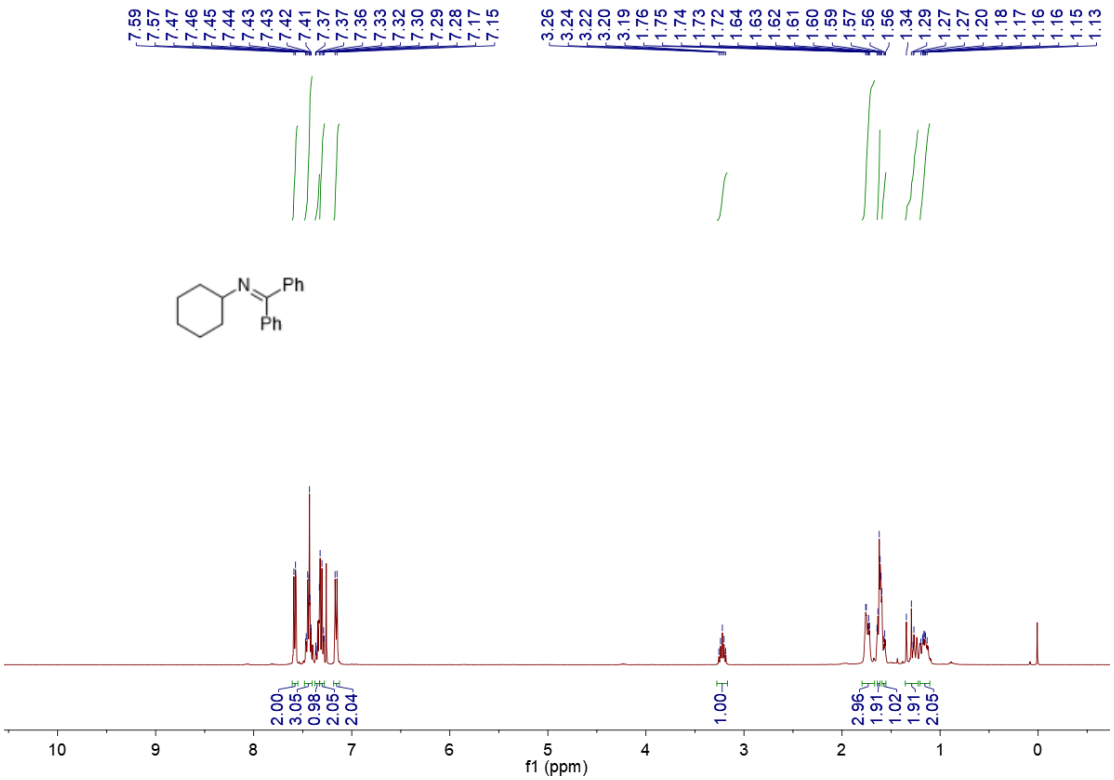
$^{1}$H NMR spectra of compound **3q** in $CDCl_3$ (400 MHz):



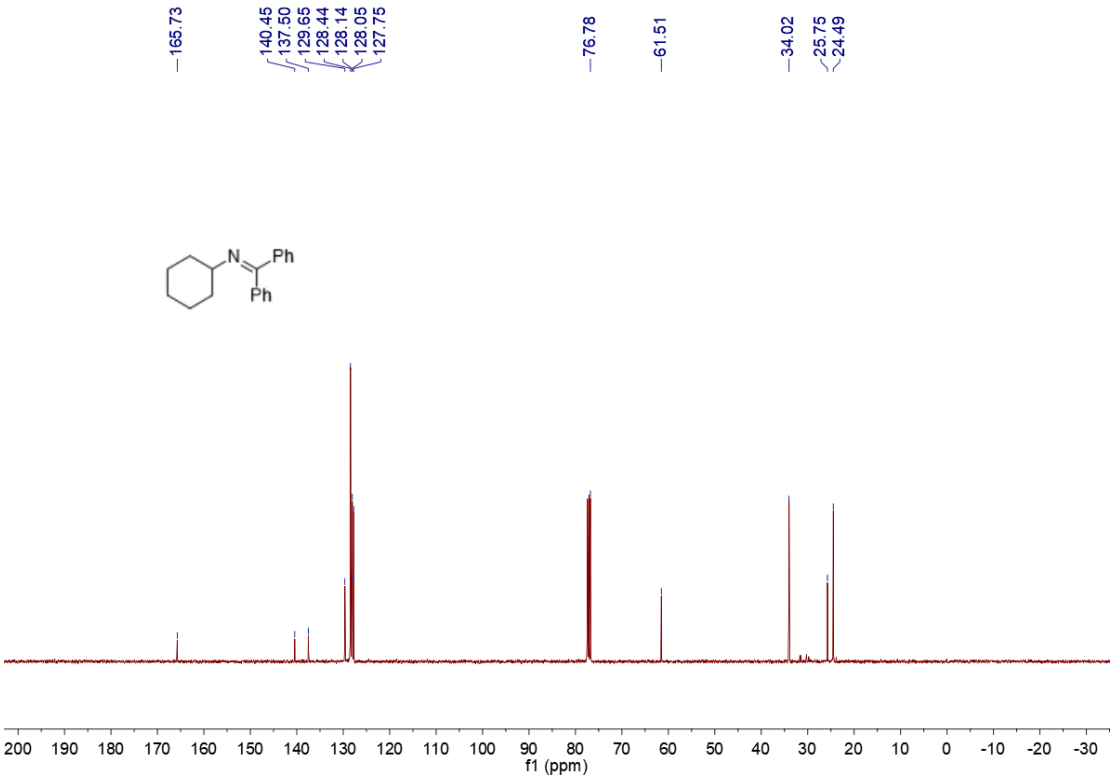

$^{13}$C NMR spectra of compound **3q** in $CDCl_3$ (101 MHz):



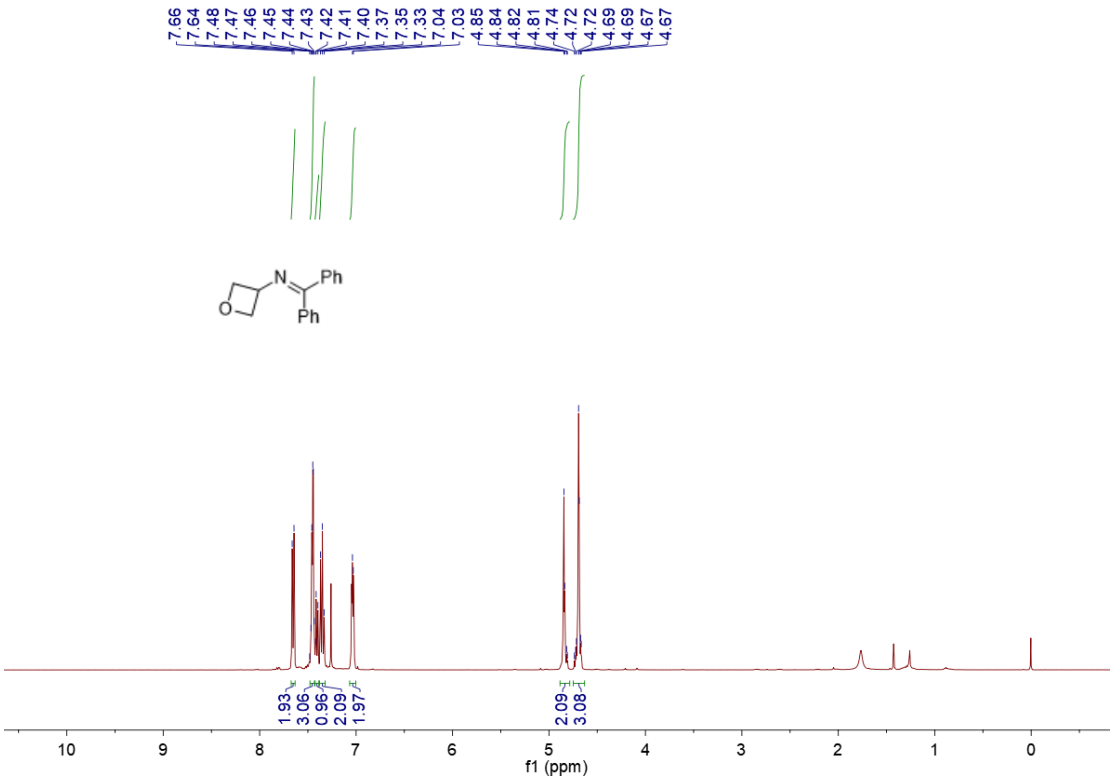

$^{1}$H NMR spectra of compound **3r** in $CDCl_3$ (400 MHz):



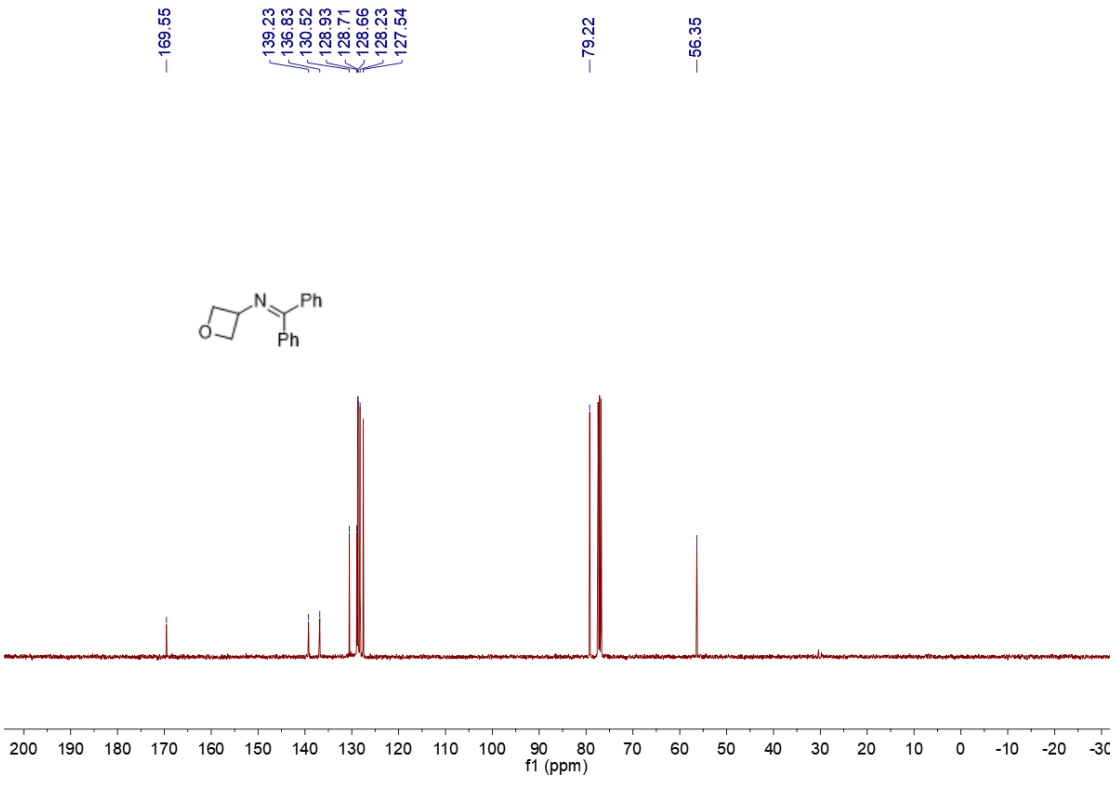

$^{13}C$ NMR spectra of compound **3r** in $CDCl_3$ (101 MHz):



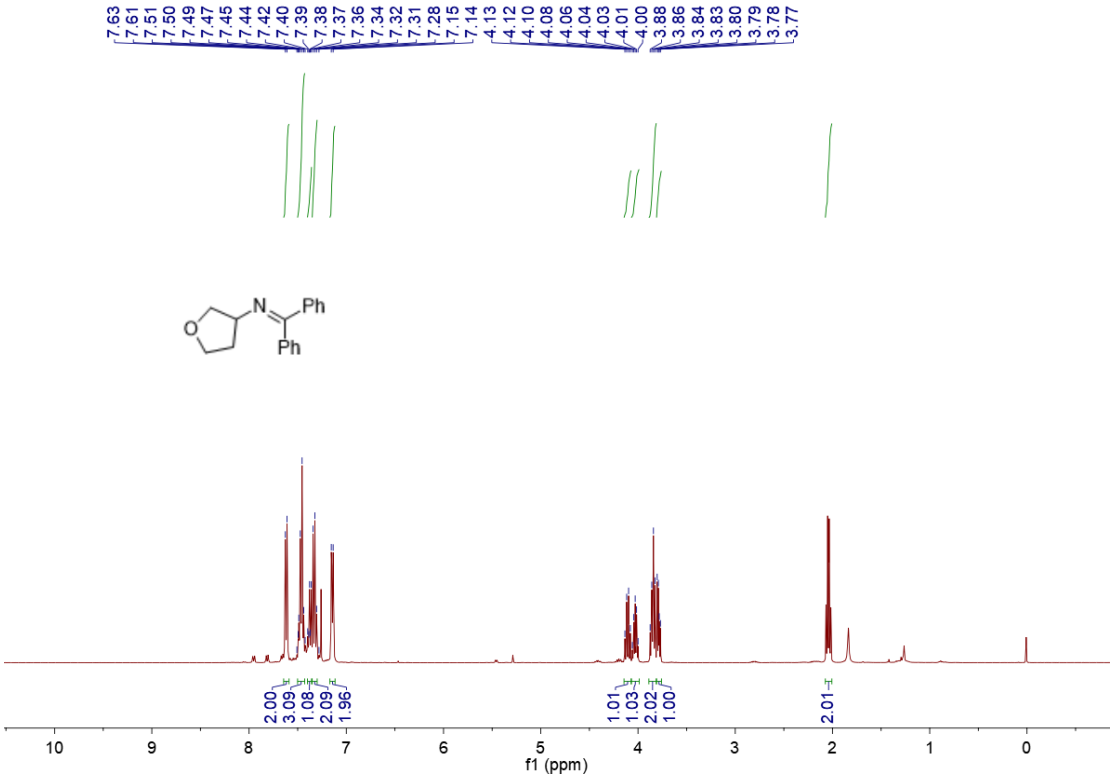

$^{1}H$ NMR spectra of compound **3s** in $CDCl_3$ (400 MHz):



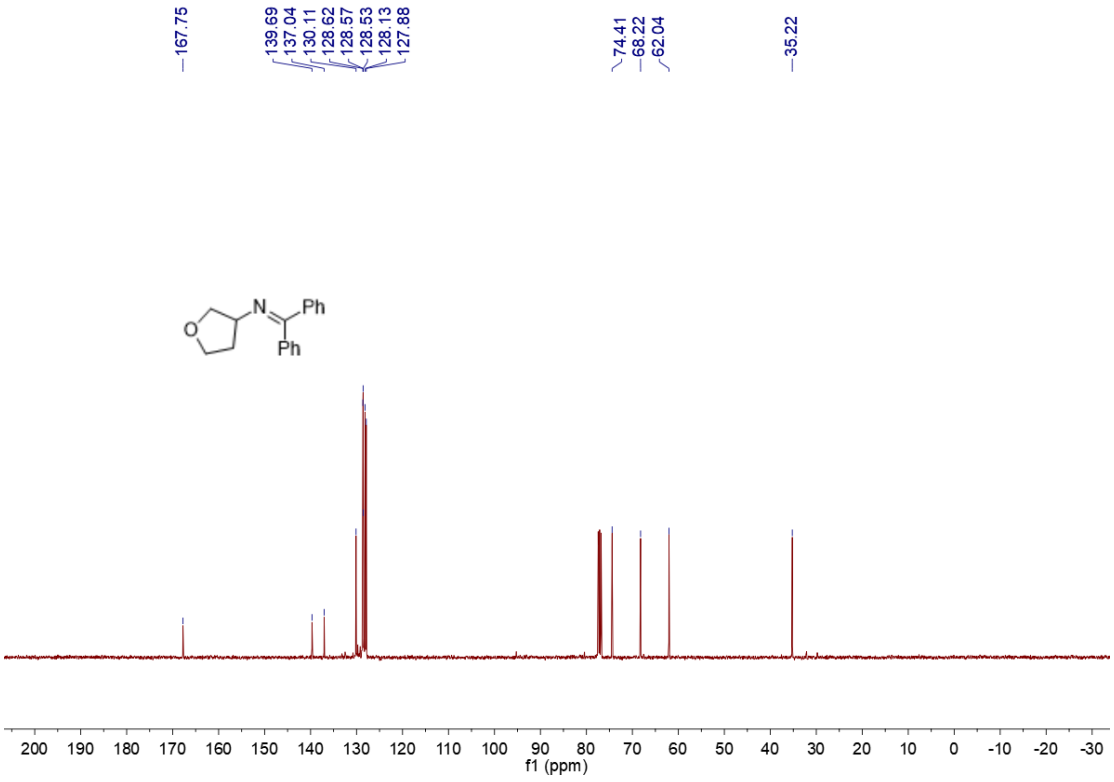

$^{13}C$ NMR spectra of compound **3s** in $CDCl_3$ (101 MHz):



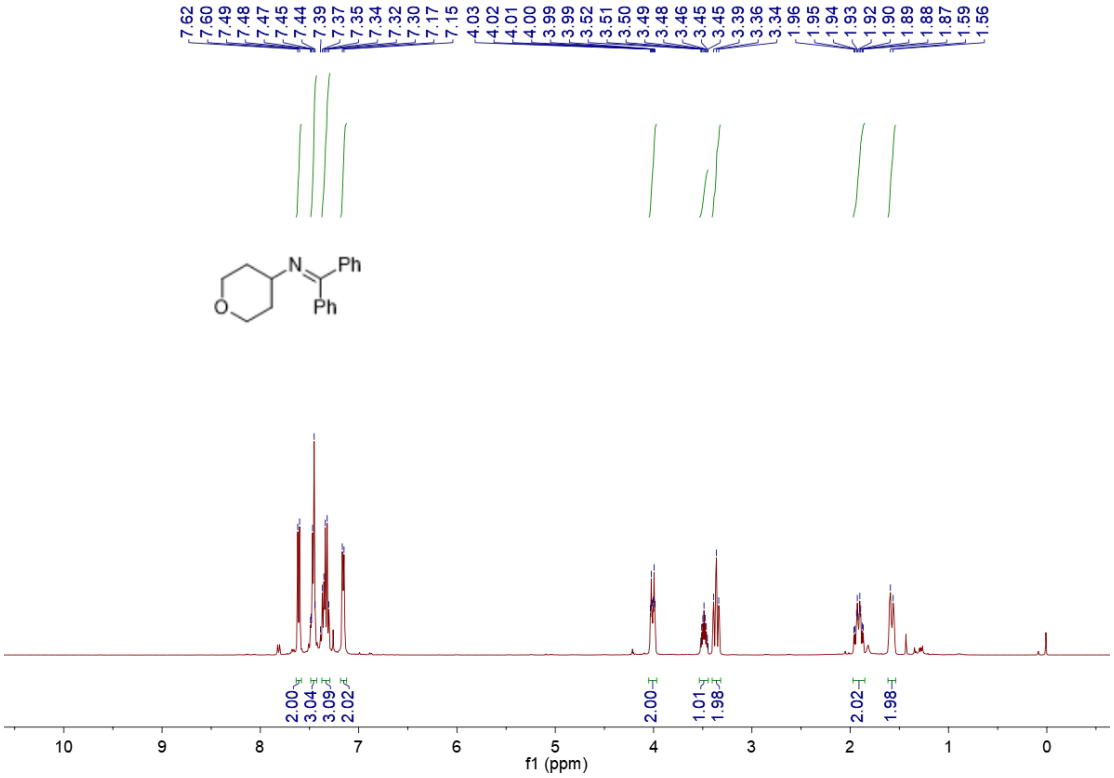
$^{1}$H NMR spectra of compound **3t** in $CDCl_3$ (400 MHz):



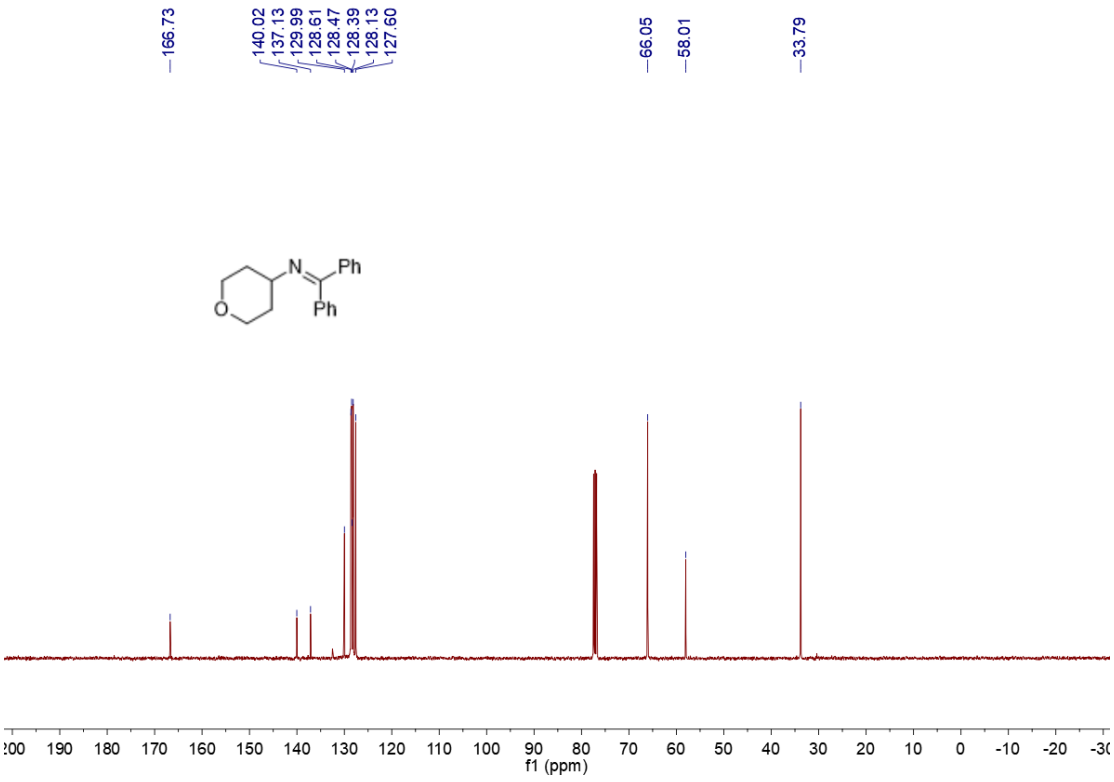

$^{13}$C NMR spectra of compound **3t** in $CDCl_3$ (101 MHz):



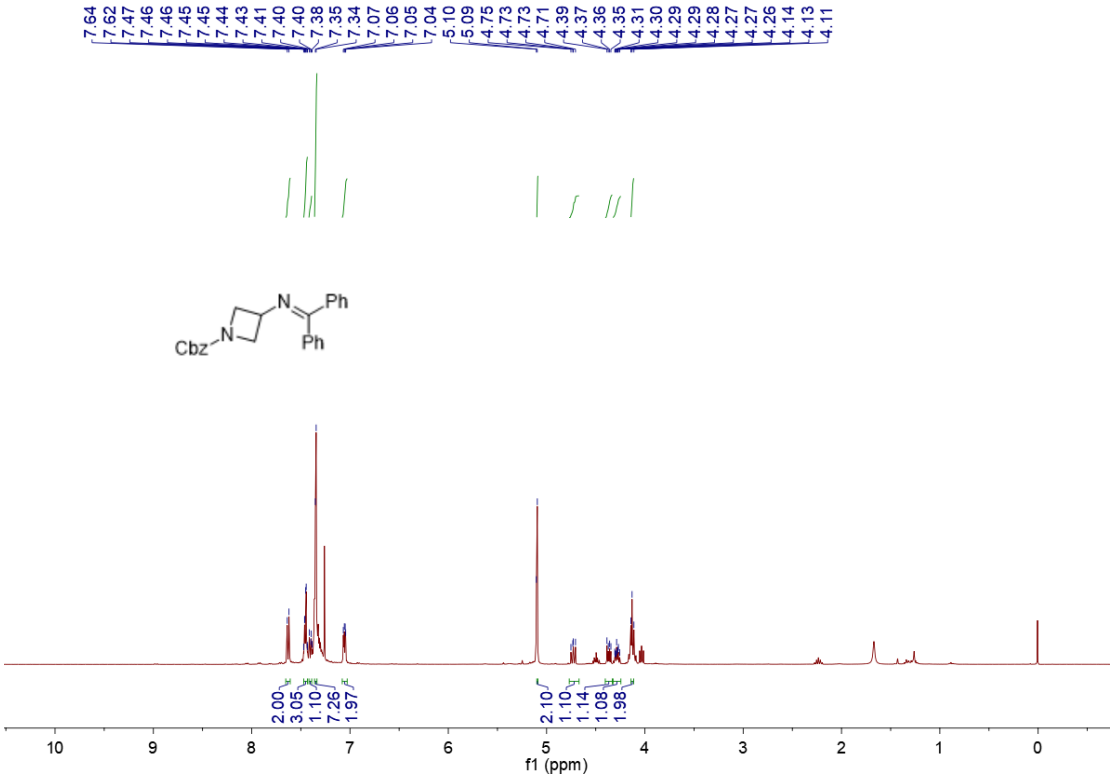
$^{1}$H NMR spectra of compound **3u** in $CDCl_3$ (400 MHz):



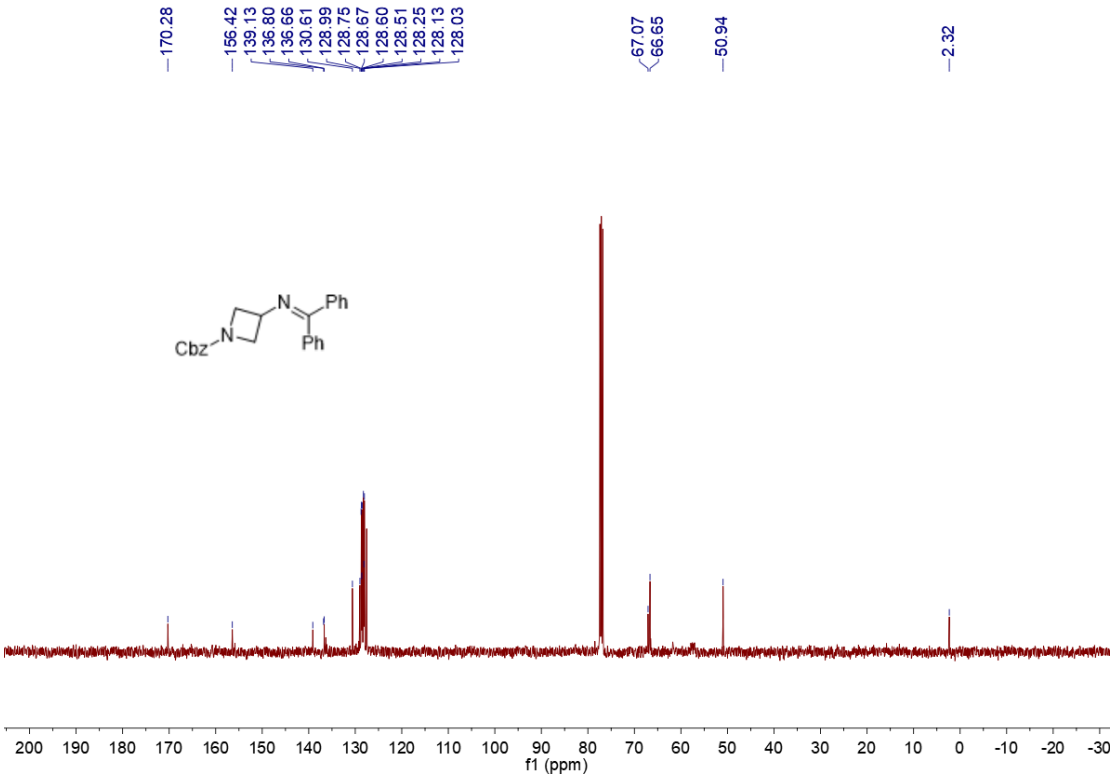

$^{13}$C NMR spectra of compound **3u** in $CDCl_3$ (101 MHz):



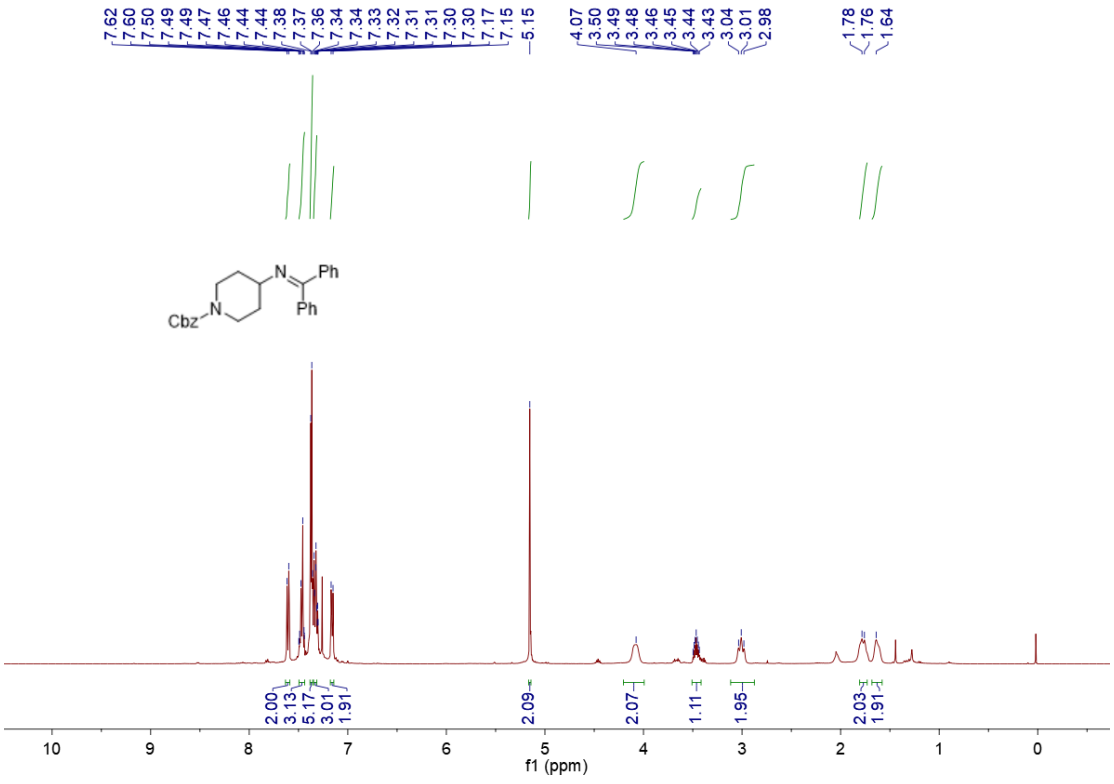
$^{1}$H NMR spectra of compound **3v** in $CDCl_3$ (400 MHz):



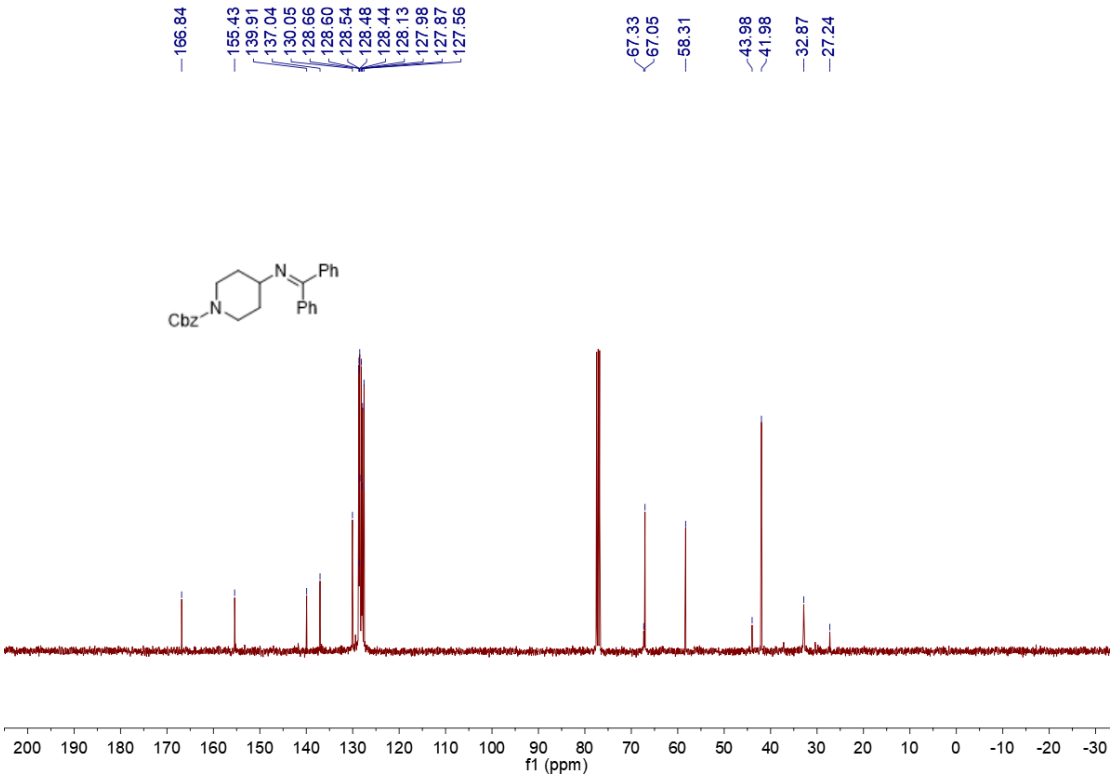

$^{13}$C NMR spectra of compound **3v** in $CDCl_3$ (101 MHz):



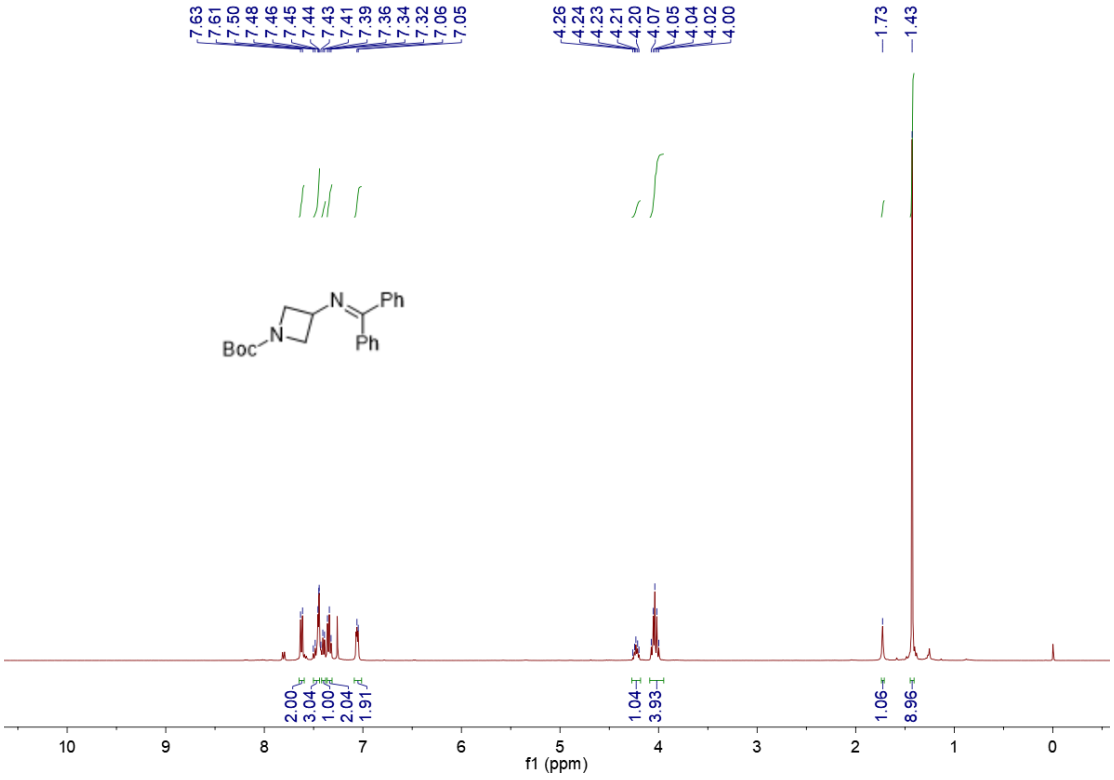

$^{1}$H NMR spectra of compound **3w** in $CDCl_3$ (400 MHz):



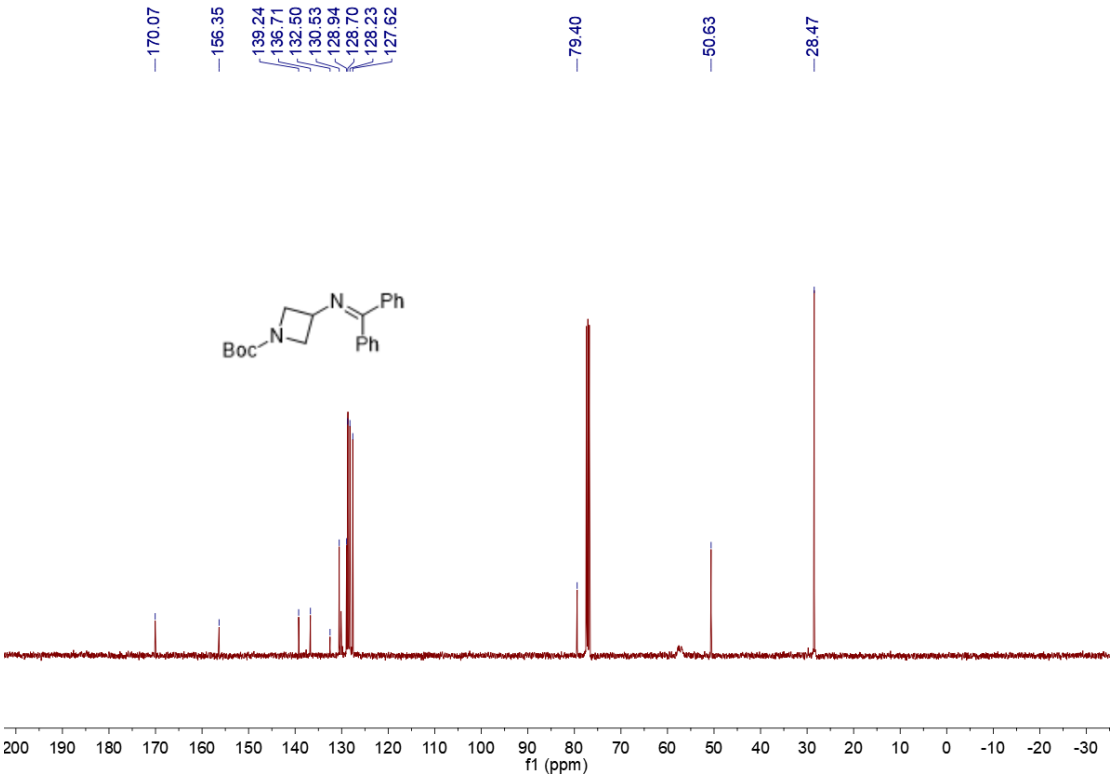

$^{13}$C NMR spectra of compound **3w** in $CDCl_3$ (101 MHz):



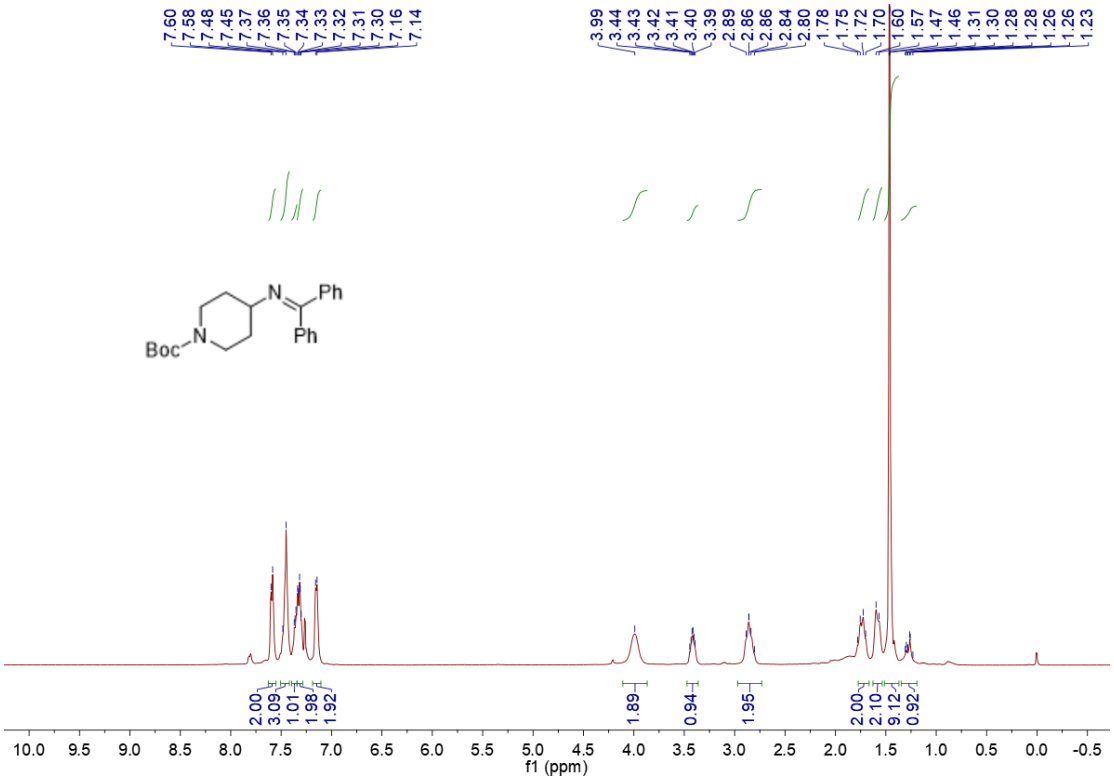

$^{1}$H NMR spectra of compound **3x** in $CDCl_3$ (400 MHz):



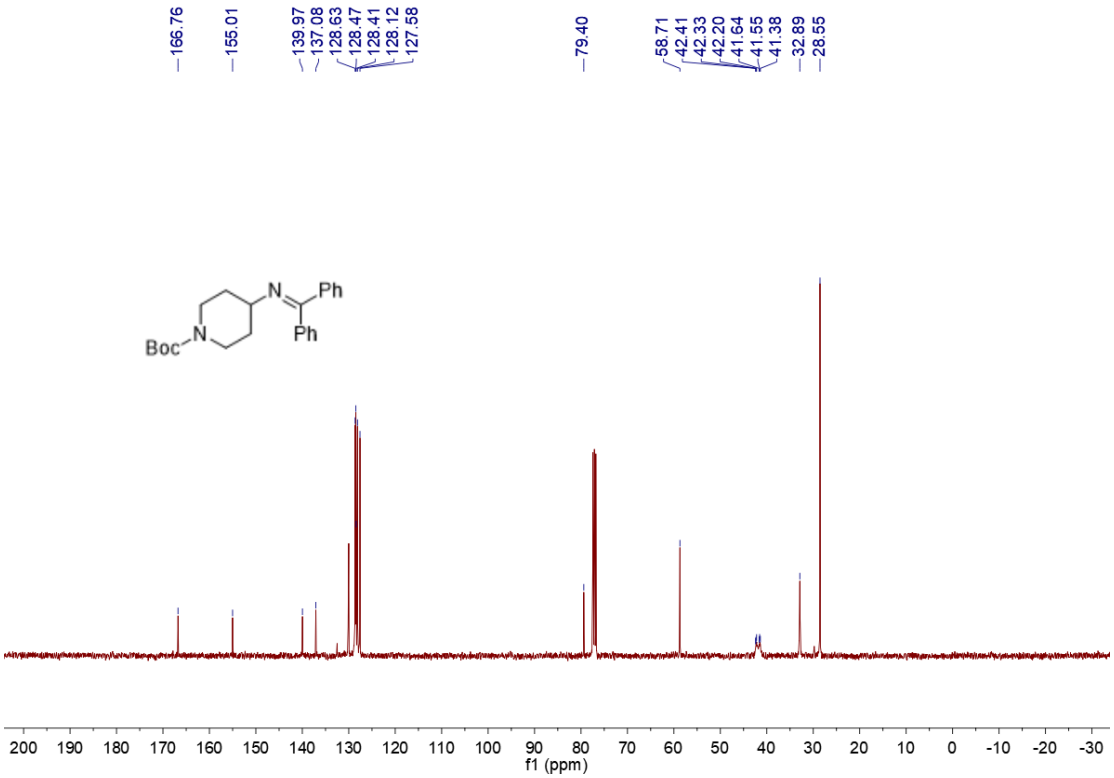

$^{13}$C NMR spectra of compound **3x** in $CDCl_3$ (101 MHz):



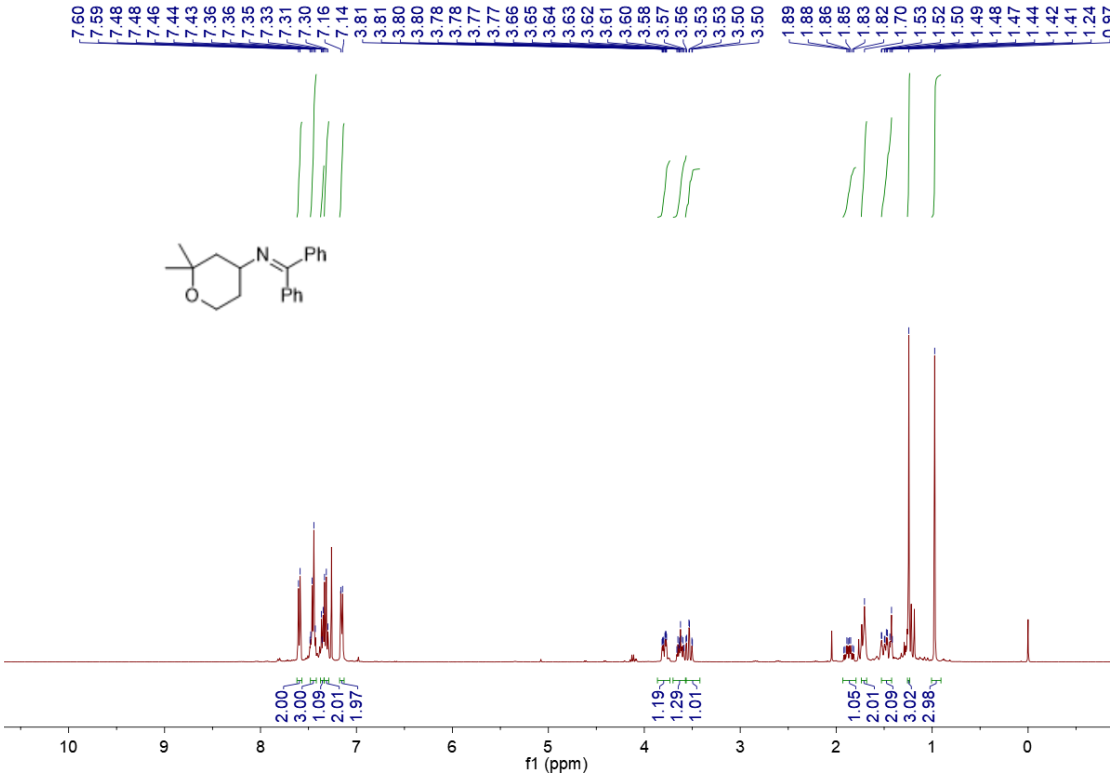

$^{1}$H NMR spectra of compound **3y** in $CDCl_3$ (400 MHz):



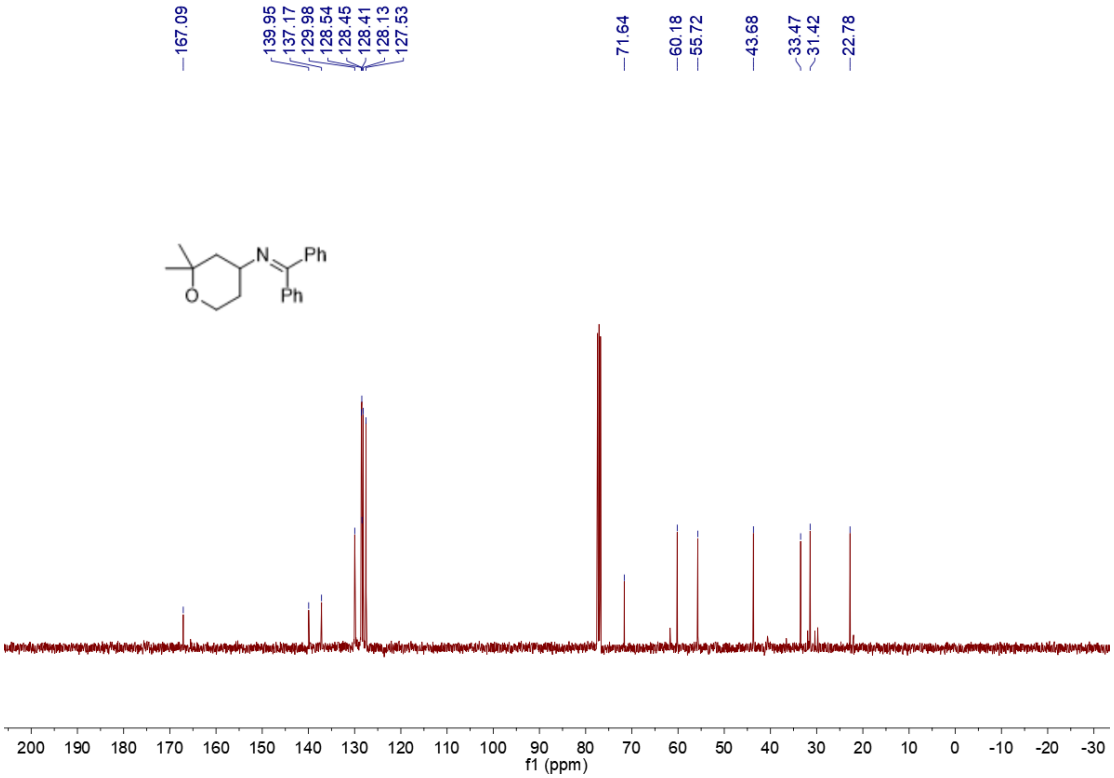

$^{13}$C NMR spectra of compound **3y** in $CDCl_3$ (101 MHz):



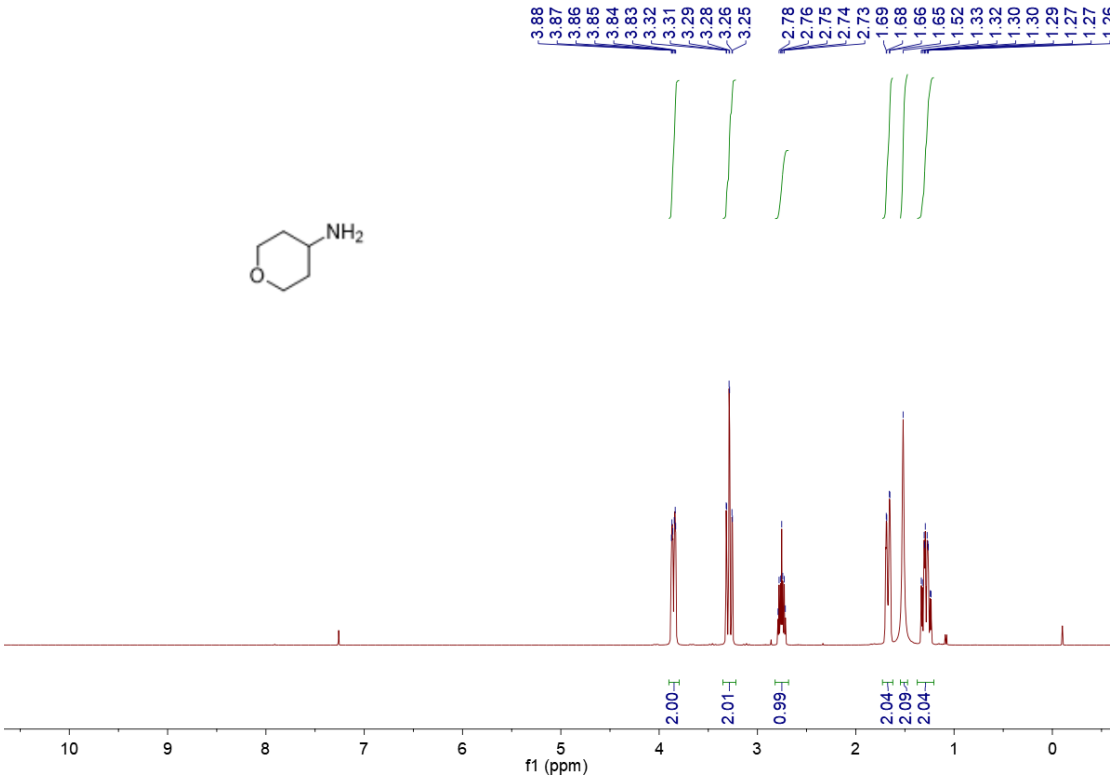

$^{1}$H NMR spectra of compound **3z** in $CDCl_3$ (400 MHz):



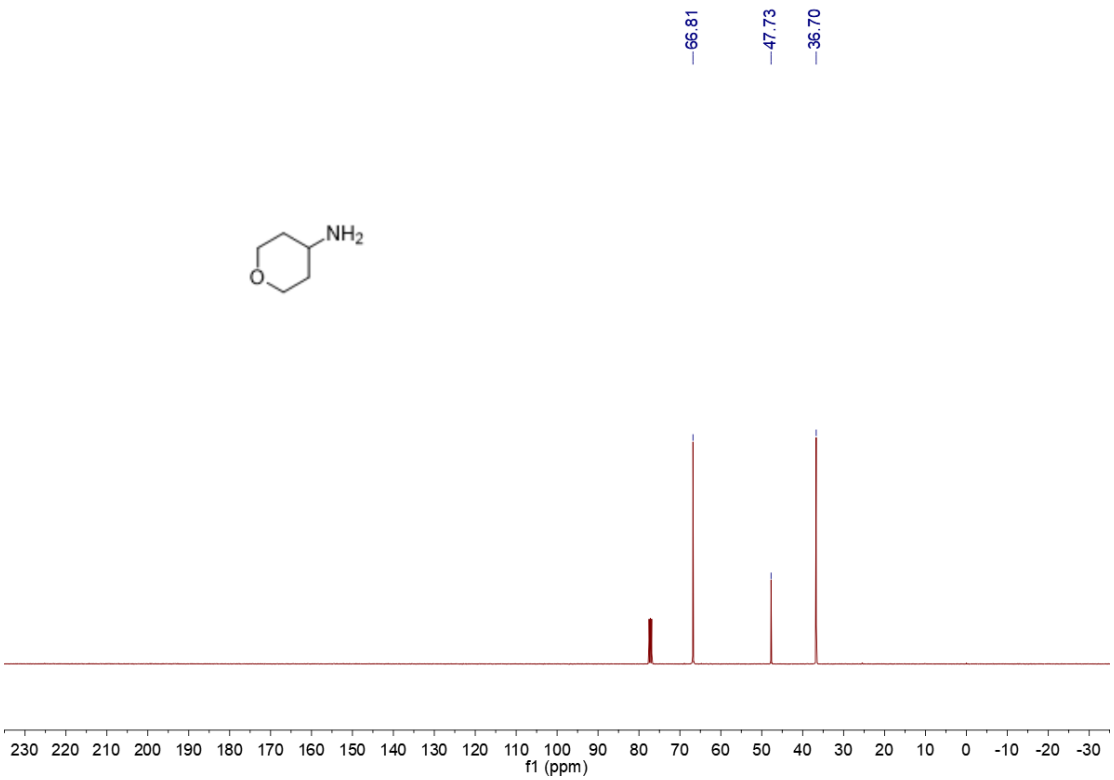

$^{13}$C NMR spectra of compound **3z** in $CDCl_3$ (101 MHz):




$^{1}$H NMR spectra of compound **4** in $CDCl_3$ (400 MHz):




$^{13}$C NMR spectra of compound **4** in $CDCl_3$ (101 MHz):


66.81
47.73
36.70
NH2
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)