# Supporting Information for

## HFIP Mediated Oxime Ether Synthesis: A Metal, Base and Additive Free Approach

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## 1. General Information

All reactions were carried out in Tarsons spinot digital magnetic stirrers under standard conditions. All chemicals except oximes (excluding **1i**, **1v**, **1w** and **1x**) were purchased commercially from Sigma Aldrich, Merck, Alfa Aesar or BLDPharm and used without further purification. The oximes were synthesized according to literature procedures. Solvents used for extraction and chromatographic separations were distilled prior use. All reactions involving heating are carried out in an oil bath.

**Chromatography:** Analytical thin layer chromatography (TLC) was performed using Merck silica gel 60F254 plates using short wave (254 nm) UV light. Column chromatography purifications were performed over silica gel (60-120 mesh).

**$^1$H NMR** and **$^{13}$C NMR** spectra were recorded on a JEOL JNM ECS NMR spectrometer (400 MHz and 101 MHz respectively) using $CDCl_3$ as solvent and TMS as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) relative to the central peak of the solvent. And multiplicities are indicated as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and dd (doublet of doublet). Coupling constants (*J* values) are given in hertz (Hz).

**Melting points (MP)** were determined by JSGW Digital Melting Point Apparatus.

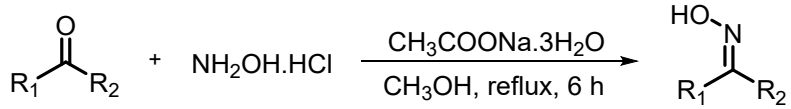
**CHN content:** The organic content (wt % C, H, N) in the synthesized compounds was determined by combustion analysis using a PERKIN ELMER 2400 SERIES 2 CHN analyzer.

**FTIR** spectra were measured on a Perkin Elmer Frontier MIR-FIR FT-IR spectrophotometer with the range 4000−400 cm−1 (resolution: 4 $cm^{-1}$) using KBr as the reference.

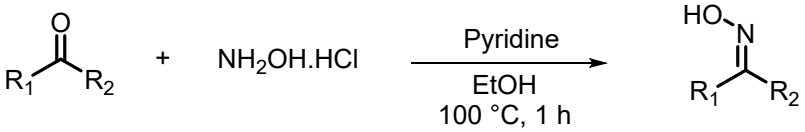
**UV-Visible** experiments were carried out in Shimadzu, UV-2550 spectrophotometer.

## 2. Preparation of Starting Materials

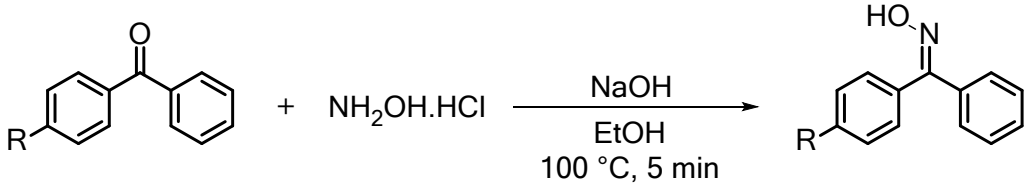
All oximes (except **1i**, **1v**, **1w**, **1x)** were prepared according to the literature procedure.[1,2]




For water soluble ketones or aldehydes, the mixture of ketones or aldehydes, hydroxylamine hydrochloride (1.6 eq.) and sodium acetate (2 eq.) in $CH_3OH$ was stirred under reflux and detected by TLC. After the reaction was completed, the mixture was poured into ice water. Precipitate is formed, filtered off and washed with little water and dried.



For water insoluble ketones or aldehydes, the mixture of ketones or aldehydes, hydroxylamine hydrochloride and pyridine in ethanol was stirred under reflux and detected by TLC. After the reaction was completed, the mixture was stirred in an ice bath until the oxime crystallizes. It is then filtered off, washed with little water and dried.




For benzophenone derivatives, the mixture of benzophenone derivative, hydroxylamine hydrochloride and sodium hydroxide in ethanol was stirred under reflux for 5 minutes and detected by TLC. After the reaction was completed, the mixture was poured into ice water. Precipitate is formed, filtered off and washed with little water and dried.

**References**

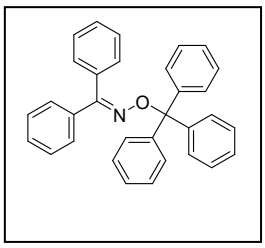

1. I. Vogel, *Practical organic chemistry*. 1974.
2. A. Lachman, Benzophenone oxime. *Organic Syntheses*. 2003, 70-70.
3. H. Zhuang, Q. Hou, F. Han, H. Lv, and C. Miao, *Green Chem*. 2023, **25**, 310-317.

### 3. General Procedure for the synthesis of oxime ether

A 50 mL round bottomed flask was charged with oxime **1** (0.25 mmol) and triphenylmethanol **2** (0.5 mmol) in presence of 1.5 mL HFIP at 30 °C for 4 h. After completion of reaction (confirmed by TLC), reaction mixture was extracted with ethyl acetate and water. The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the desired products **3a-3v**. **3w** was obtained through simple filtration after work up.

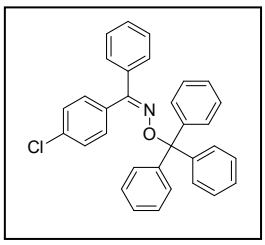
### 4. Characterization Data of Products

**Diphenylmethanone *O*-trityl oxime (3a)**



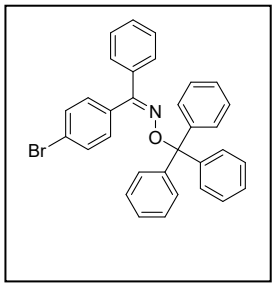
White solid, 109.6 mg, 99% yield; m.p. = 155-157 °C (lit.[3] 155.4-155.7 °C); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.49-7.38 (m, 5H), 7.34-7.17 (m, 20H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.7 (s), 144.7 (s), 136.8 (s), 133.9 (s), 129.3 (s), 129.3 (s), 129.2 (s), 128.8 (s), 128.1 (s), 128.1 (s), 128.0 (s), 127.6 (s), 127.1 (s), 91.4 (s).

**(*Z*)-(4-chlorophenyl)(phenyl)methanone *O*-trityl oxime (3b)**



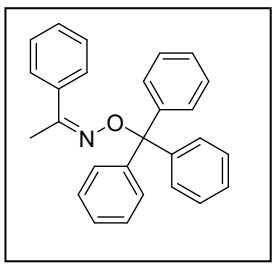
White solid, 240.5 mg, 96% yield; m.p. = 130-132 °C (lit.[3] 130.7-131.5 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 9.1 Hz, 2H), 7.44 (d, *J* = 6.6 Hz, 2H), 7.37-7.21 (m, 18H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.8 (d, *J* = 15.0 Hz), 144.6 (d, *J* = 3.3 Hz), 136.5 (s), 135.3 (d, *J* = 5.0 Hz), 134.8 (s), 133.4 (s), 132.2 (s), 131.0 (s), 129.3 (d, *J* = 1.3 Hz), 128.4 (dd, *J* = 16.5, 6.3 Hz), 128.1 (s), 127.7 (d, *J* = 3.0 Hz), 127.2 (d, *J* = 3.4 Hz), 91.7 (d, *J* = 12.6 Hz).

**(*Z*)-(4-bromophenyl)(phenyl)methanone *O*-trityl oxime (3c)**



White solid, 111.4 mg, 86% yield; m.p. = 156-158 °C (lit.[3] 155.2-156.0 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65-7.60 (m, 1H), 7.60-7.08 (m, 23H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.8 (d, *J* = 18.5 Hz), 144.5 (d, *J* = 3.2 Hz), 136.3 (s), 135.7 (s), 133.3 (s), 132.7 (s), 131.5-131.0 (m), 129.7-128.9 (m), 128.3 (d, *J* = 3.4 Hz), 128.0 (s), 127.6 (d, *J* = 3.2 Hz), 127.2 (d, *J* = 3.2 Hz), 123.3 (d, *J* = 51.8 Hz), 91.7 (d, *J* = 11.3 Hz).

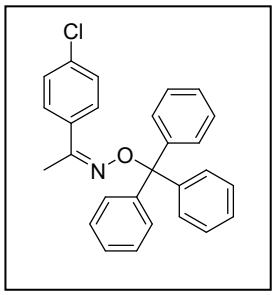
**(*Z*)-1-phenylethan-1-one *O*-trityl oxime (3d)**



White solid, 92.3 mg, 96% yield; m.p. = 139-141 °C (lit.[3] 139.8-140.7 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47-7.39 (m, 8H), 7.33-7.23 (m,

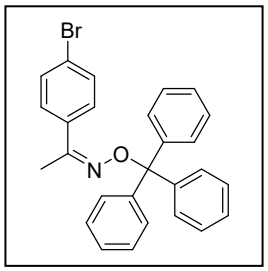
13H), 2.41 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.1(s), 144.9 (s), 137.0 (s), 129.3 (s), 128.9 (s), 128.3 (s), 127.6 (s), 127.1 (s), 126.2 (s), 91.0 (s), 13.2 (s).

**(*Z*)-1-(4-chlorophenyl)ethan-1-one *O*-trityl oxime (3e)**



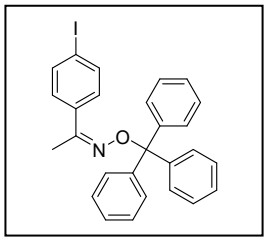

White solid, 91.6 mg, 89% yield; m.p. = 174-176 °C (lit.[3] 173.3-173.6 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 8H), 7.31-7.22 (m, 12H), 2.37 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 153.1 (s), 144.7 (s), 143.0 (s), 135.1 (d, *J* = 53.2 Hz), 129.3 (d, *J* = 12.1 Hz), 128.4 (s), 128.0 (d, *J* = 1.9 Hz), 127.5 (d, *J* = 17.1 Hz), 127.2 (s), 91.2 (s), 13.0 (s).

**(*Z*)-1-(4-bromophenyl)ethan-1-one *O*-trityl oxime (3f)**



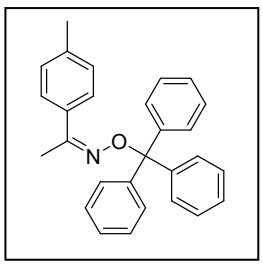

White solid, 104.0 mg, 91% yield; m.p. = 122-124 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 8H), 7.33-7.24 (m, 12H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) NMR (101 MHz, ) δ 153.2 (s), 144.7 (s), 135.9 (s), 131.4 (s), 129.3 (s), 128.0 (d, *J* = 1.4 Hz), 127.7 (d, *J* = 10.8 Hz), 127.2 (s), 123.2 (s), 91.2 (s), 13.0 (s). Anal. calcd. for $C_{27}H_{22}BrNO$: C, 71.06; H, 4.86; N, 3.07; found: C, 71.14; H, 4.62; N, 3.17.

**(*Z*)-1-(4-iodophenyl)ethan-1-one *O*-trityl oxime (3g)**



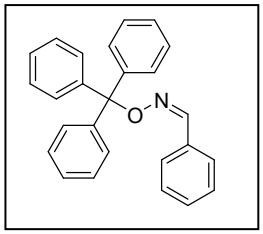

White solid, 111.3 mg, 91% yield; m.p. = 120-122 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.60-7.56 (m, 2H), 7.39-7.35 (m, 6H), 7.32-7.23 (m, 10H), 7.19-7.15 (m, 2H), 2.36 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) NMR (101 MHz) δ 153.3 (s), 144.7 (s), 137.4 (s), 136.5 (s), 129.3 (s), 127.9 (s), 127.6 (s), 127.2 (s), 95.0 (s), 91.2 (s), 12.9 (s). Anal. calcd. for $C_{27}H_{22}INO$: C, 64.42; H, 4.41; N, 2.78; found: C, 64.24; H, 4.53; N, 2.66.

**(*Z*)-1-(p-tolyl)ethan-1-one *O*-trityl oxime (3h)**



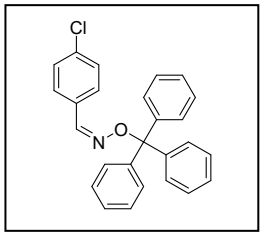

White solid, 84.5 mg, 86% yield; m.p. = 148-150 °C (lit.[3] 149.9-150.7 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (m, 6H), 7.39-7.35 (m, 2H), 7.33-7.24 (m, 10H), 7.08 (dd, *J* = 8.5, 0.6 Hz, 2H), 2.40 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.0 (s), 145.0 (s), 138.9 (s), 134.3 (s), 129.4 (s), 129.0 (s), 127.6 (s), 127.1 (s), 126.1 (s), 90.9 (s), 21.3 (s), 13.2 (s).

**(*Z*)-benzaldehyde *O*-trityl oxime (3i)**



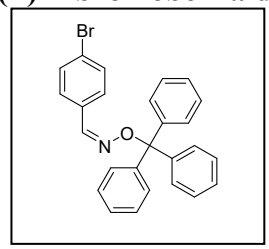
White solid, 59.9 mg, 66% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.46-7.40 (m, 8H), 7.34-7.24 (m, 13C). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.7 (s), 144.5 (s), 132.8 (s), 129.7 (s), 129.4 (s), 128.6 (s), 127.6 (s), 127.3 (s), 127.2 (s), 91.3 (s); (lit.[3]).

**(*Z*)-4-chlorobenzaldehyde *O*-trityl oxime (3j)**



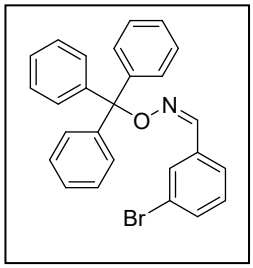
White solid, 79.5 mg, 80% yield; m.p. = 122-124 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.42-7.26 (m, 20H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.6 (s), 144.4 (s), 135.5 (s), 131.3 (s), 129.4 (s), 128.9 (s), 128.4 (s), 127.7 (s), 127.3 (s), 91.5 (s). Anal. calcd. for $C_{26}H_{20}ClNO$: C, 78.48; H, 5.07; N, 3.52; found: C, 78.35; H, 5.22; N, 3.45.

**(*Z*)-4-bromobenzaldehyde *O*-trityl oxime (3l)**



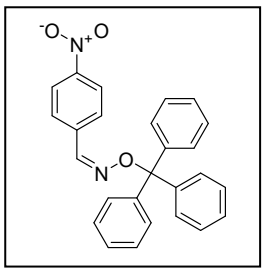
White solid, 101.3 mg, 92% yield; m.p. = 139.8-140.7 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.43-7.39 (m, 8H), 7.35-7.24 (m, 12H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.7 (s), 144.4 (s), 131.9 (s), 131.7 (s), 129.4 (s), 128.6 (s), 127.7 (s), 127.3 (s), 123.9 (s), 91.6 (s). Anal. calcd. for $C_{26}H_{20}BrNO$: C, 70.60; H, 4.56; N, 3.17; found: C, 70.78; H, 4.62; N, 3.06.

**(*Z*)-3-bromobenzaldehyde *O*-trityl oxime (3m)**



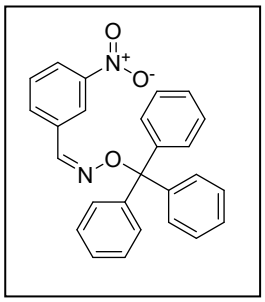
White solid, 84.0 mg, 76% yield; m.p. = 142-144 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.55 (t, *J* = 1.7 Hz, 1H), 7.43-7.40 (m, 1H), 7.39-7.36 (m, 6H), 7.33-7.24 (m, 11H), 7.14 (t, *J* = 7.9 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.4 (s), 144.3 (s), 134.8 (s), 132.6 (s), 130.1 (s), 129.9 (s), 129.4 (s), 127.7 (s), 127.3 (s), 125.9 (s), 122.8 (s), 91.6 (s). Anal. calcd. for $C_{26}H_{20}BrNO$: C, 70.60; H, 4.56; N, 3.17; found: C, 70.72; H, 4.71; N, 3.19.

**(*Z*)-4-nitrobenzaldehyde *O*-trityl oxime (3n)**



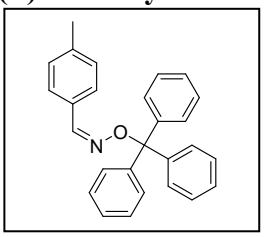
Pale yellow solid, 101.2 mg, 99% yield; m.p. = 157-159 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.13 (d, *J* = 9.1 Hz, 2H), 7.56 (d, *J* = 9.2 Hz, 2H), 7.52-7.08 (m, 16H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.3 (s), 146.7 (s), 144.0 (s), 138.8 (s), 129.3 (s), 127.7 (s), 127.7 (s), 127.5 (s), 124.0 (s), 92.3 (s). Anal. calcd. for $C_{26}H_{20}N_2O_3$: C, 76.46; H, 4.94; N, 6.86; found: C, 76.54; H, 5.04; N, 6.82.

**(*Z*)-3-nitrobenzaldehyde *O*-trityl oxime (3o)**



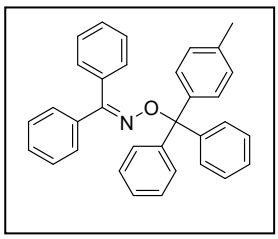
White sticky solid, 90.9 mg, 89% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.24-8.20 (m, 1H), 8.14 (m, 1H), 7.74 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.42-7.25 (m, 16H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.5 (s), 146.6 (s), 144.0 (s), 134.5 (s), 132.5 (s), 129.7 (s), 129.3 (s), 127.8 (s), 127.5 (s), 124.2 (s), 122.1 (s), 92.0 (s), 77.4 (s), 77.1 (s), 76.8 (s). Anal. calcd. for $C_{26}H_{20}N_2O_3$: C, 76.46; H, 4.94; N, 6.86; found: C, 76.68; H, 4.80; N, 6.74.

**(*Z*)-4-methylbenzaldehyde *O*-trityl oxime (3p)**



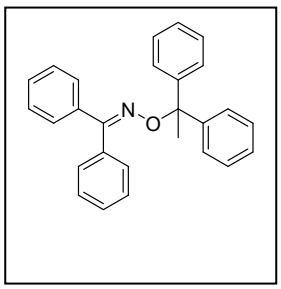
Off white solid, 73.9 mg, 78% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.76-6.77 (m, 19H), 2.31 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.6 (s), 144.6 (s), 139.8 (s), 130.0 (s), 129.4 (s), 129.3 (s), 127.6 (s), 127.2 (s), 127.1 (s), 91.1 (s), 21.5 (s). Anal. calcd. for $C_{27}H_{23}NO$: C, 85.91; H, 6.14; N, 3.71; found: C, 85.86; H, 6.32; N, 3.62.

**Diphenylmethanone *O*-(diphenyl(*p*-tolyl)methyl) oxime (3q)**



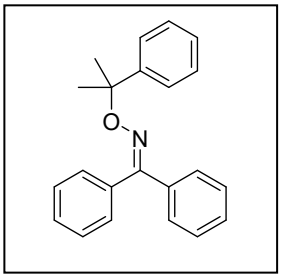
White solid, 102.9 mg, 91% yield; m.p. = 95-97 °C (lit.[3] 94.8-95.0 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.52-7.43 (m, 5H), 7.36-7.21 (m, 18H), 7.10 (dd, *J* = 8.6, 0.6 Hz, 2H), 2.34 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.7 (s), 144.9 (s), 141.8 (s), 136.8 (s), 136.7 (s), 134.0 (s), 129.4 (s), 129.30 (s), 129.26 (s), 129.1 (s), 128.8 (s), 128.3 (s), 128.2 (s), 128.13 (s), 128.06 (s), 127.6 (s), 127.0 (s), 91.3 (s), 21.2 (s).

**Diphenylmethanone *O*-(1,1-diphenylethyl) oxime (3r)**



White solid, 56.6 mg, 60% yield; m.p. = 75-77 °C (lit.[3] 74.6-75.3 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50-7.41 (m, 5H), 7.34-7.32 (m, 2H), 7.28-7.26 (m, 1H), 7.25-7.22 (m, 11H), 7.21-7.17 (m, 2H), 2.13 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.8 (s), 146.5 (s), 136.9 (s), 134.0 (s), 129.4 (s), 129.1 (s), 128.7 (s), 128.1 (s), 127.94 (s), 127. 90 (s), 126.8 (s), 126.7 (s), 85.9 (s), 27.4 (s).

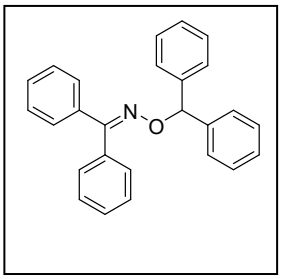
**Diphenylmethanone *O*-(2-phenylpropan-2-yl) oxime (3s)**



Colourless oily liquid, 42.5 mg, 54% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47-7.39 (m, 7H), 7.36-7.18 (m, 9H), 1.69 (s, 6H).$^{13}$C NMR

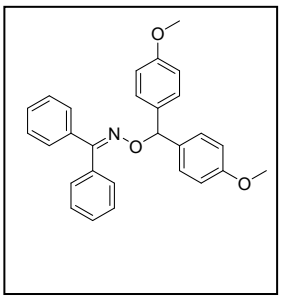
(101 MHz, $CDCl_3$) δ 155.7 (s), 147.5 (s), 137.3 (s), 133.9 (s), 129.6 (s), 129.0 (s), 128.6 (s), 128.1 (s), 128.02 (s), 128.01 (s), 128.00 (s), 126.5 (s), 125.4 (s), 82.4 (s), 28.3 (s); (lit.[3]).

**Diphenylmethanone *O*-benzhydryl oxime (3t)**



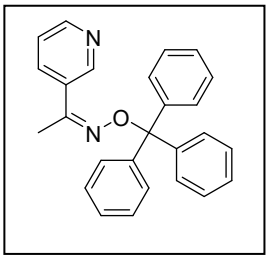
White solid, 53.9 mg, 59% yield; m.p. = 102-104 °C (lit.[3] 101.8-102.5 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 7H), 7.32-7.24 (m, 14H), 6.38 (s, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.5 (s), 141.8 (s), 136.6 (s), 133.6 (s), 129.4 (s), 128.8 (s), 128.5 (s), 128.3 (s), 128.2 (s), 128.1 (s), 128.0 (s), 127.4 (s), 127.3 (s), 87.3 (s).

**Diphenylmethanone *O*-(bis(4-methoxyphenyl)methyl) oxime (3u)**



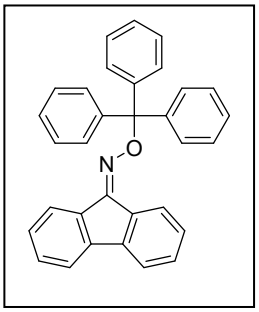
White solid, 56.3 mg, 53% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43-7.36 (m, 7H), 7.31-7.24 (m, 4H), 7.19-7.15 (m, 4H), 6.83-6.79 (m, 4H), 6.29 (s, 1H), 3.76 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.9 (s), 157.2 (s), 136.7 (s), 134.3 (s), 133.6 (s), 129.5 (s), 129.3 (s), 128.8 (s), 128.6 (s), 128.2 (s), 128.1 (s), 128.0 (s), 113.6 (s), 86.5 (s), 55.3 (s). Anal. calcd. for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31; found: C, 79.53; H, 6.04; N, 3.25.

**(*Z*)-1-(pyridin-3-yl)ethan-1-one *O*-trityl oxime (3v)**



Off white solid, 76.8 mg, 81% yield; m.p. = 160-162 °C (lit.[3] 160.8-161.2 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 2.3, 0.8 Hz, 1H), 8.50 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.73-7.70 (m, 1H), 7.42-7.39 (m, 6H), 7.34-7.24 (m, 9H), 7.19-7.15 (m, 1H), 2.43 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.0 (s), 149.8 (s), 147.6 (s), 144.6 (s), 133.4 (s), 132.7 (s), 129.3 (s), 127.7 (s), 127.3 (s), 123.2 (s), 91.5 (s), 12.9 (s).

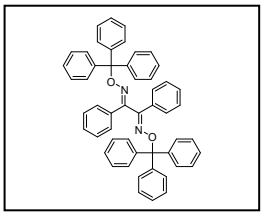
**9*H*-Fluoren-9-one *O*-trityl oxime (3w)**



Yellow solid, 55.7 mg, 51% yield; m.p. = 152-154 °C (lit.[3] 152.5-153.0 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.55-8.52 (m, 1H), 7.68-7.64 (m, 1H), 7.58 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.52-7.50 (m, 1H), 7.48-7.45 (m, 6H), 7.43 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.37-7.28 (m, 12H), 7.17 (td, *J* = 7.5, 1.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.0 (s), 144.3 (s), 141.8 (s), 140.0 (s), 136.2 (s), 131.0 (s), 130.4 (s), 129.7 (s), 129.6 (s),

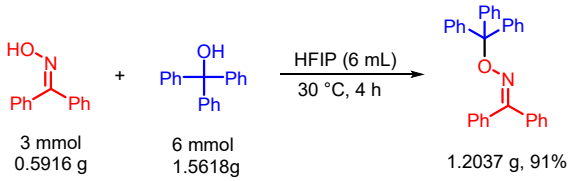
129.0 (s), 128.4 (s), 127.8 (s), 127.7 (s), 127.4 (s), 122.0 (s), 120.0 (s), 119.8 (s), 93.4 (s).

**(1*E*,2*E*)-1,2-diphenylethane-1,2-dione *O*,*O*-dityrityl dioxime (3x)**



White solid, 127.6 mg, 70% yield; m.p. > 200 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.30-6.99 (m, 40H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.2 (s), 144.0 (s), 131.6 (s), 129.5 (s), 129.3 (s), 128.2 (s), 127.4 (s), 127.2 (s), 127.0 (s), 91.8 (s). Anal. calcd. for $C_{52}H_{40}N_2O_2$: C, 86.16; H, 5.56; N, 3.86; found: C, 86.25; H, 5.68; N, 3.74.

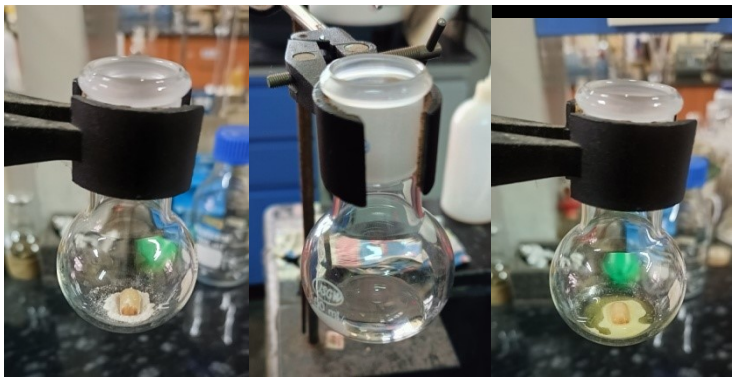
## 5. Scaled-up Reaction




To a 100 mL round bottomed flask, diphenylmethanone oxime (0.5916 g, 3 mmol, 1.0 equiv.), triphenylmethanol (1.5618 g, 6 mmol, 2.0 equiv.) and HFIP (6 mL) was added. The resulting mixture was stirred at 30 °C for 4 hours. The reaction mixture was extracted with ethyl acetate and water. The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the desired product in 91% yield.

## 6. The Experiments for Mechanism Investigation

### (1) The Reaction Phenomenon of Triphenylmethanol and HFIP



(a) (b) (c)

**Figure S1.** (a) 0.5 mmol **2a**, (b) 1.5 mL HFIP, colorless and transparent; (c) **2a** was slowly added to (b), the color was changed into transparent yellow.

**(2) UV-Vis Spectra Analysis**

**Preparation of diphenylmethanone oxime solution:**

Diphenylmethanone oxime (0.0197 g, 0.1 mmol) was dissolved in 3 mL $CH_3CN$, and the UV-Vis absorption spectra was measured in a 4 mL quartz cuvette as shown in Figure S2, (a).

**Preparation of triphenylmethanol solution:**

Triphenylmethanol (0.0260 g, 0.1 mmol) was dissolved in 3 mL $CH_3CN$, and the UV-Vis absorption spectra was measured in a 4 mL quartz cuvette as shown in Figure S2, (b).

**Preparation of HFIP solution:**

HFIP (10.5 μL, 0.1 mmol) was dissolved in 3 mL $CH_3CN$, and the UV-Vis absorption spectra was measured in a 4 mL quartz cuvette as shown in Figure S2, (c).

**Preparation of 3a (oxime ether) solution:**

Oxime ether **3a** (0.0439 g, 0.1 mmol) was dissolved in 3 mL $CH_3CN$, and the UV-Vis absorption spectra was measured in a 4 mL quartz cuvette as shown in Figure S2, (d).

**The procedure of drawing the UV-Vis absorption spectra of reaction:**

Triphenylmethanol (0.5 mmol, 0.1302 g) and HFIP (1.5 mL) were added to a round bottom bottomed flask and stirred. Then, diphenylmethanone oxime was added into the system batch by batch and measured after reacting for 5 min and standing.

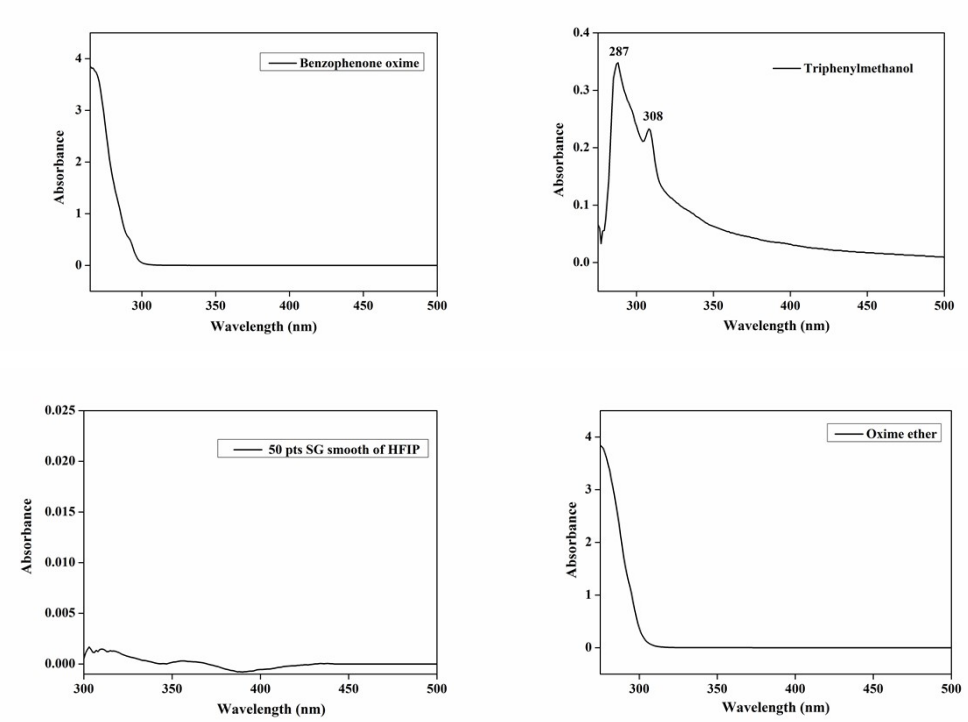



**Figure S2.** The UV-Vis absorption spectra of (a) diphenylmethanone oxime; (b) triphenylmethanol; (c) HFIP; (d) Oxime ether **3a**.

## FT-IR Analysis

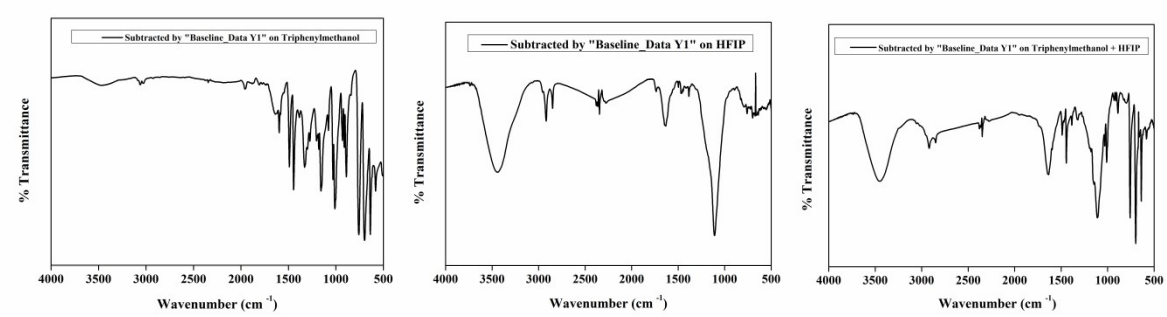
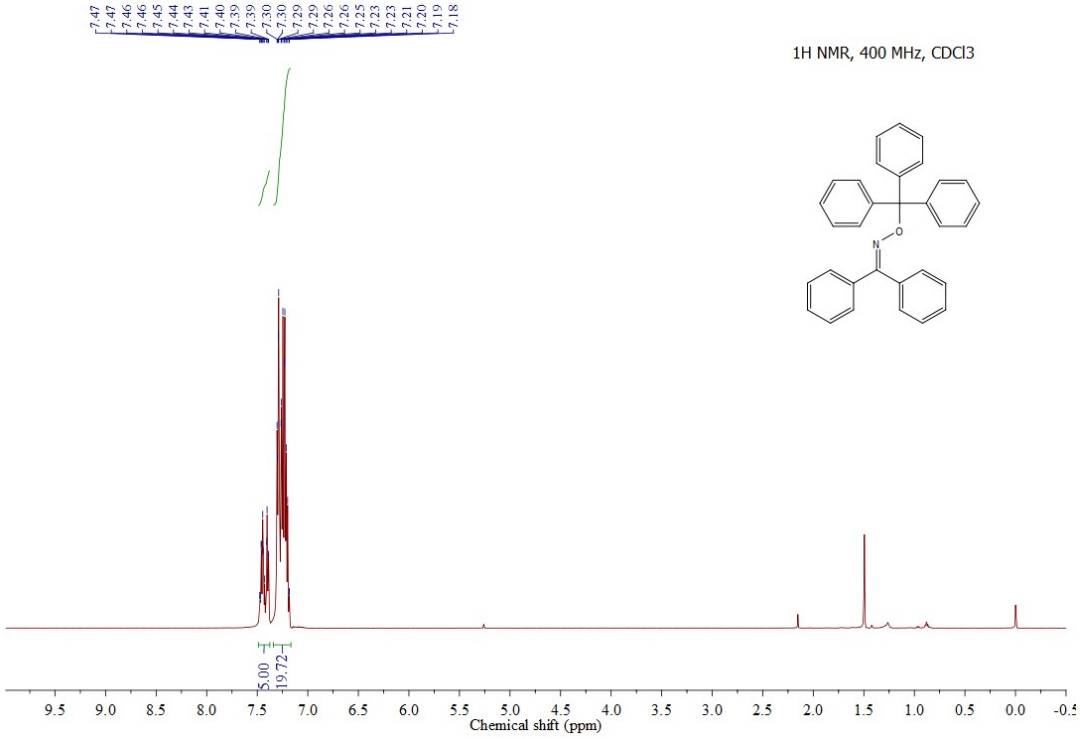


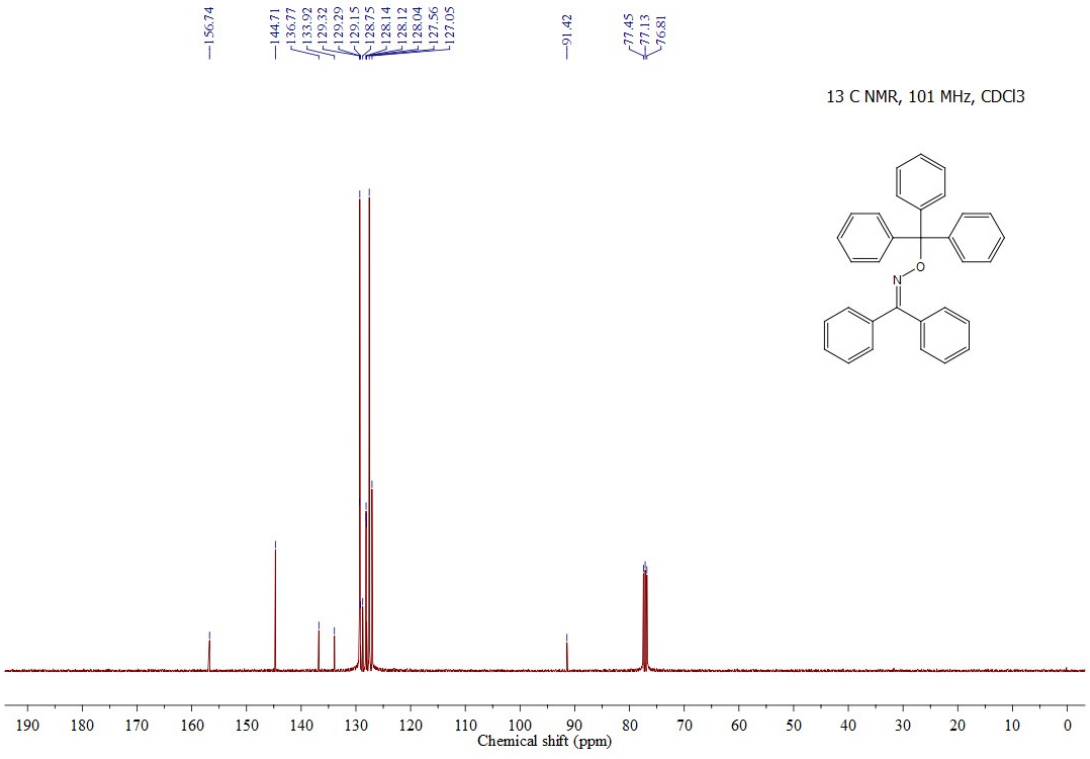

**Figure S3.** The FT-IR absorption spectra of (a) triphenylmethanol in $CH_3CN$; (b) HFIP in $CH_3CN$; (c) triphenylmethanol + HFIP in $CH_3CN$.

## 7. Copies of $^{1}H$ NMR and $^{13}C$ NMR Spectra

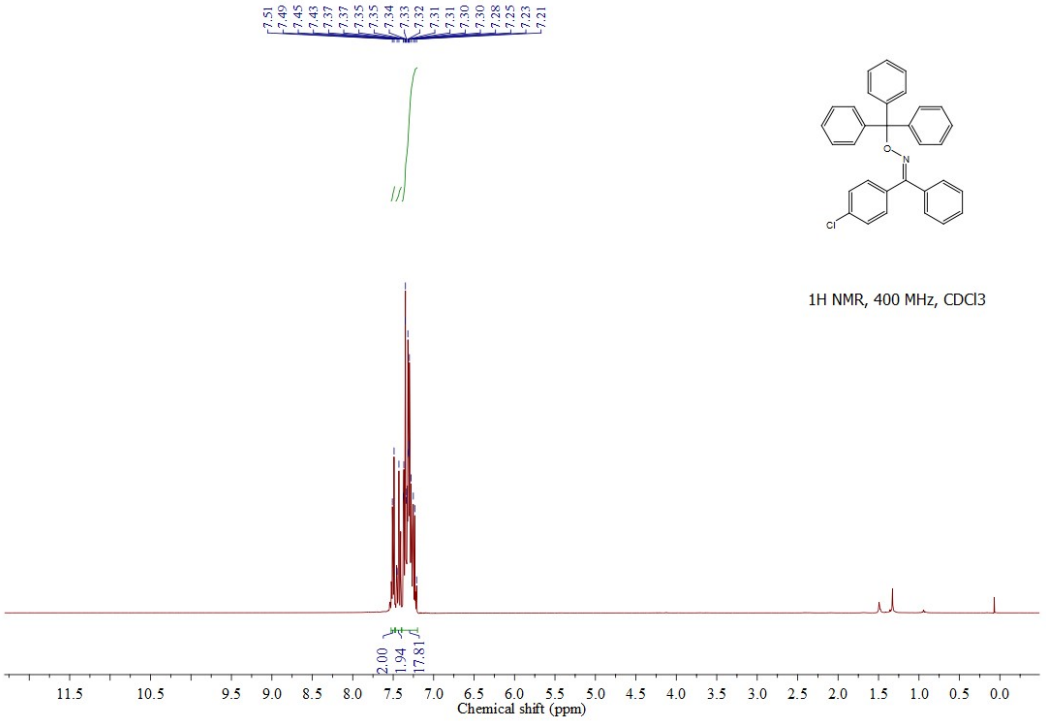
### $^{1}H$ NMR (500 MHz) Spectrum of 3a in $CDCl_3$



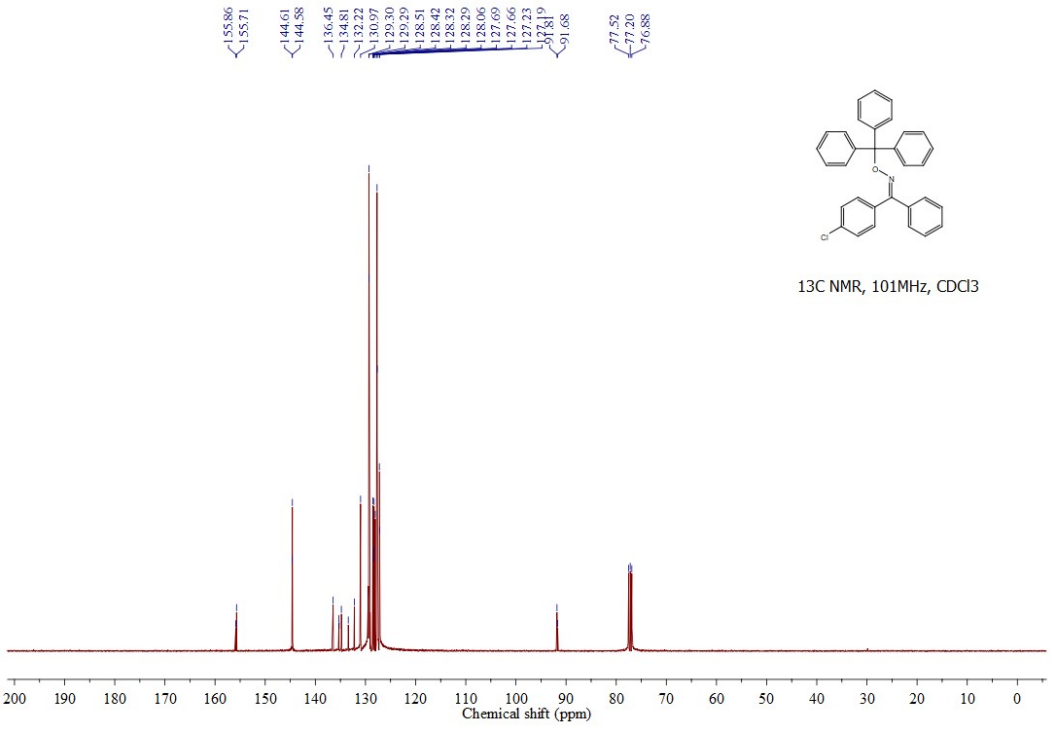

### $^{13}C$ NMR (101 MHz) Spectrum of 3a in $CDCl_3$



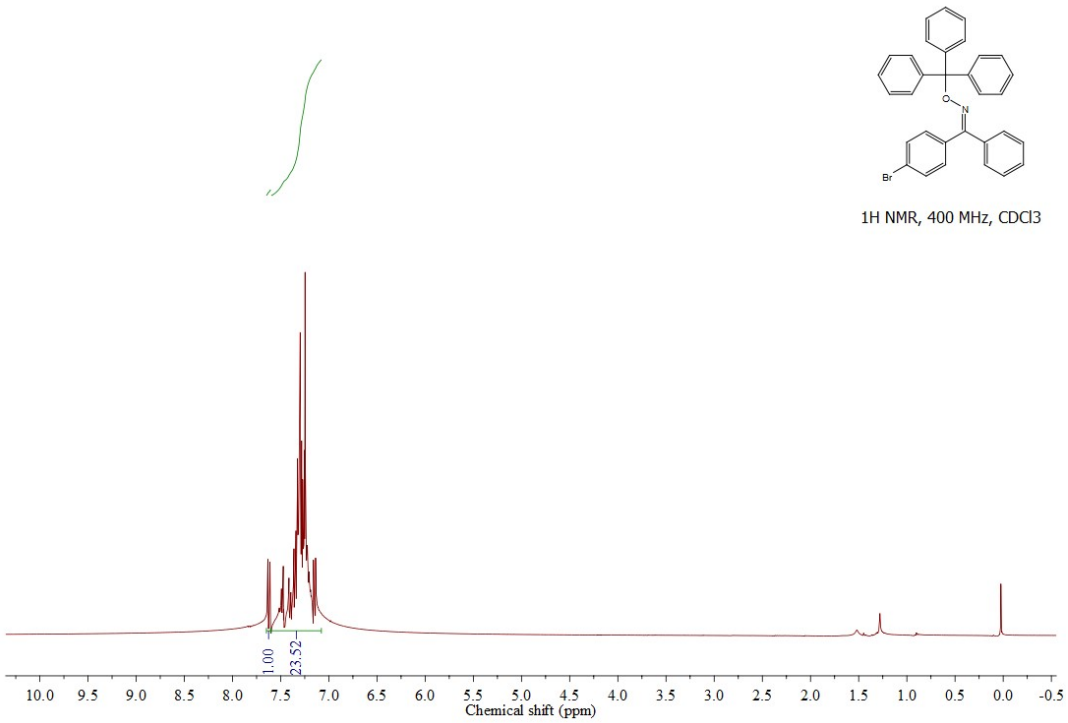
## $^{1}$H NMR (400 MHz) Spectrum of 3b in $CDCl_3$



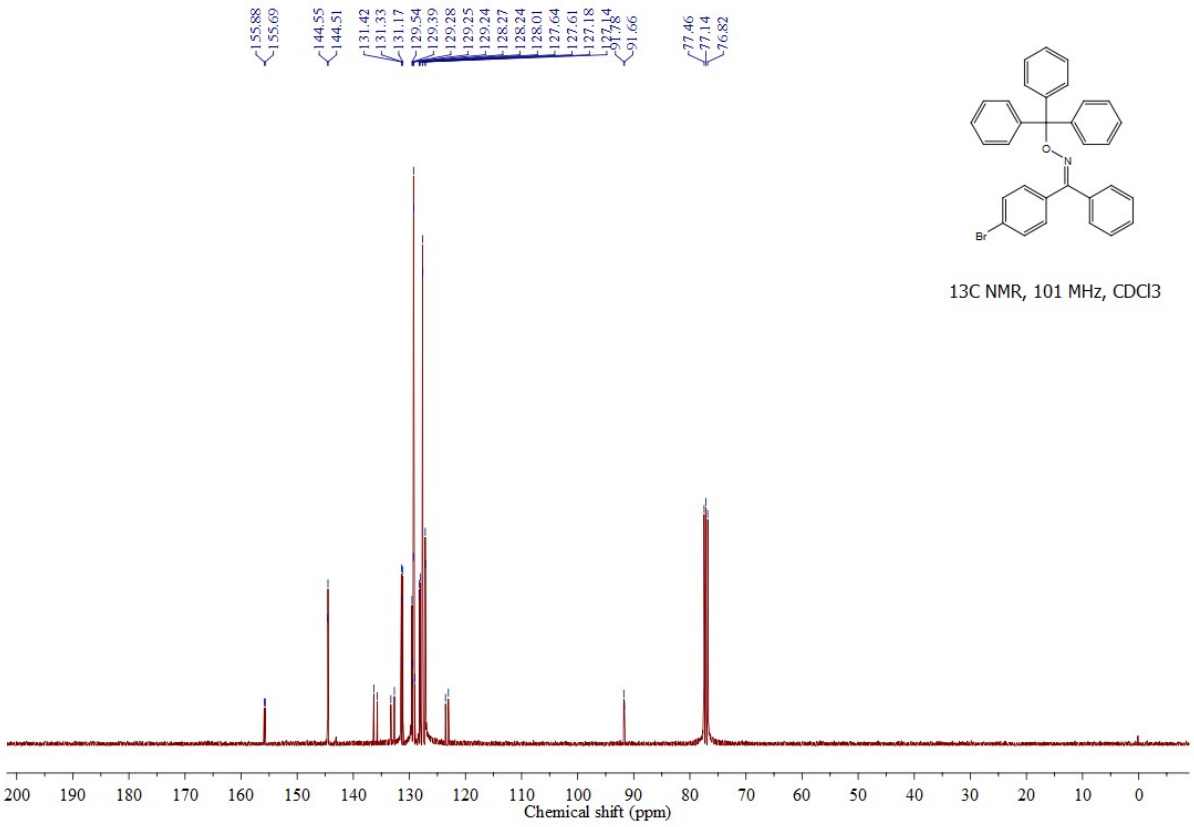

## $^{13}$C NMR (101 MHz) Spectrum of 3b in $CDCl_3$



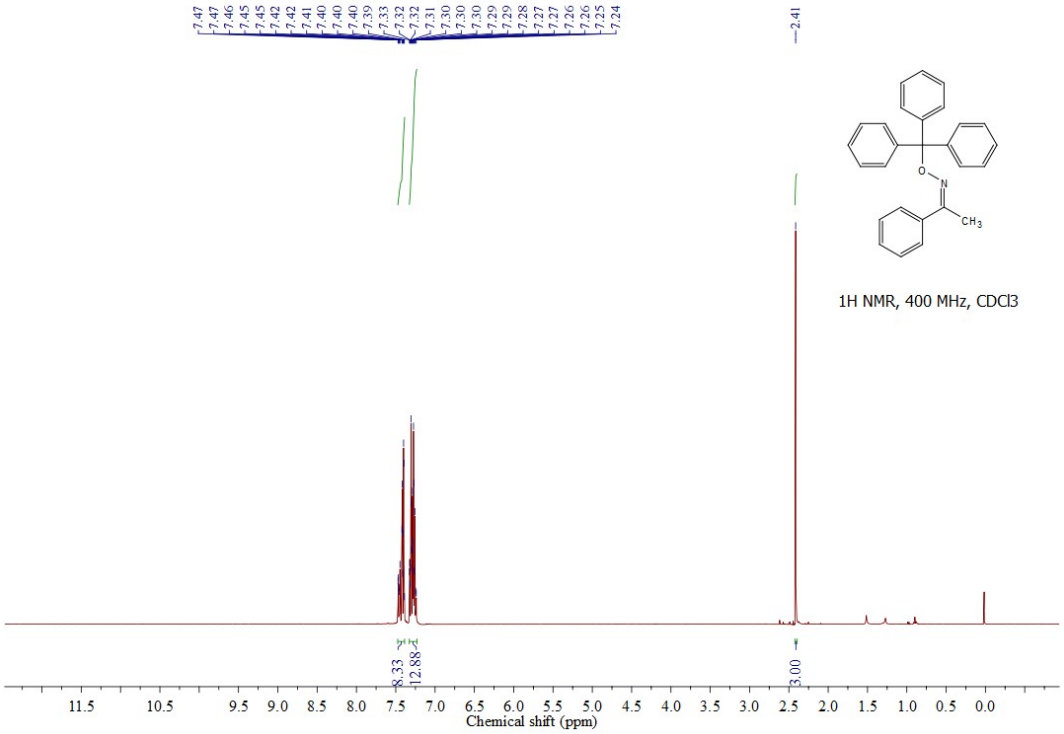
## $^{1}$H NMR (400 MHz) Spectrum of 3c in $CDCl_3$



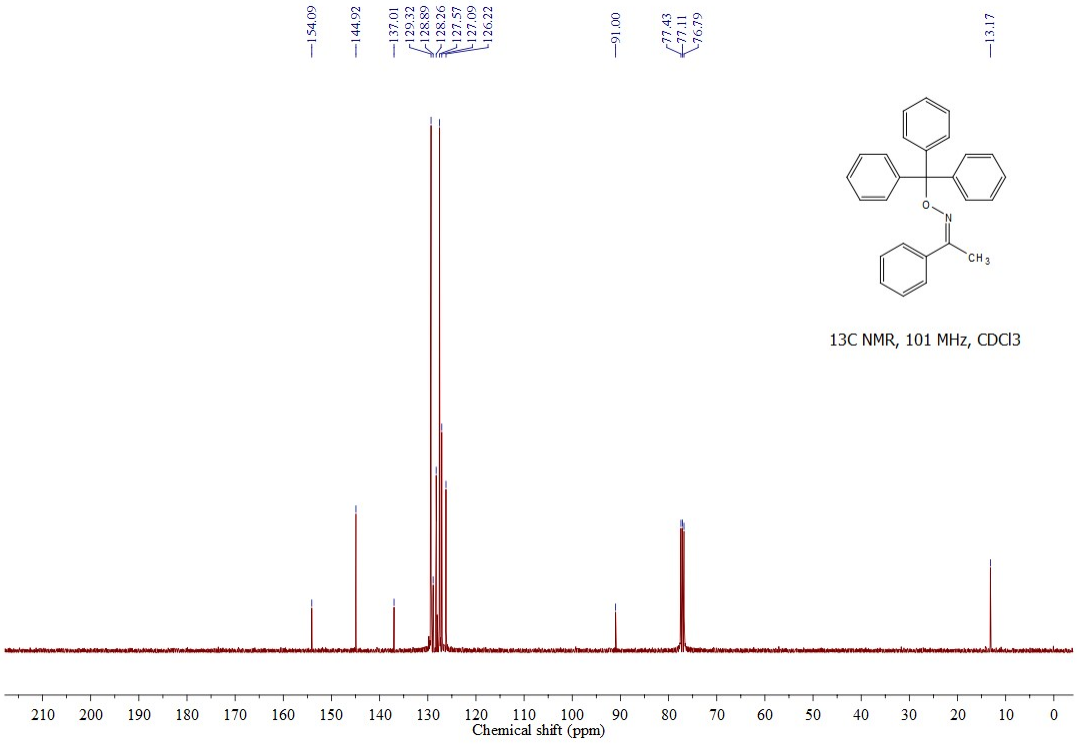

## $^{13}$C NMR (101 MHz) Spectrum of 3c in $CDCl_3$



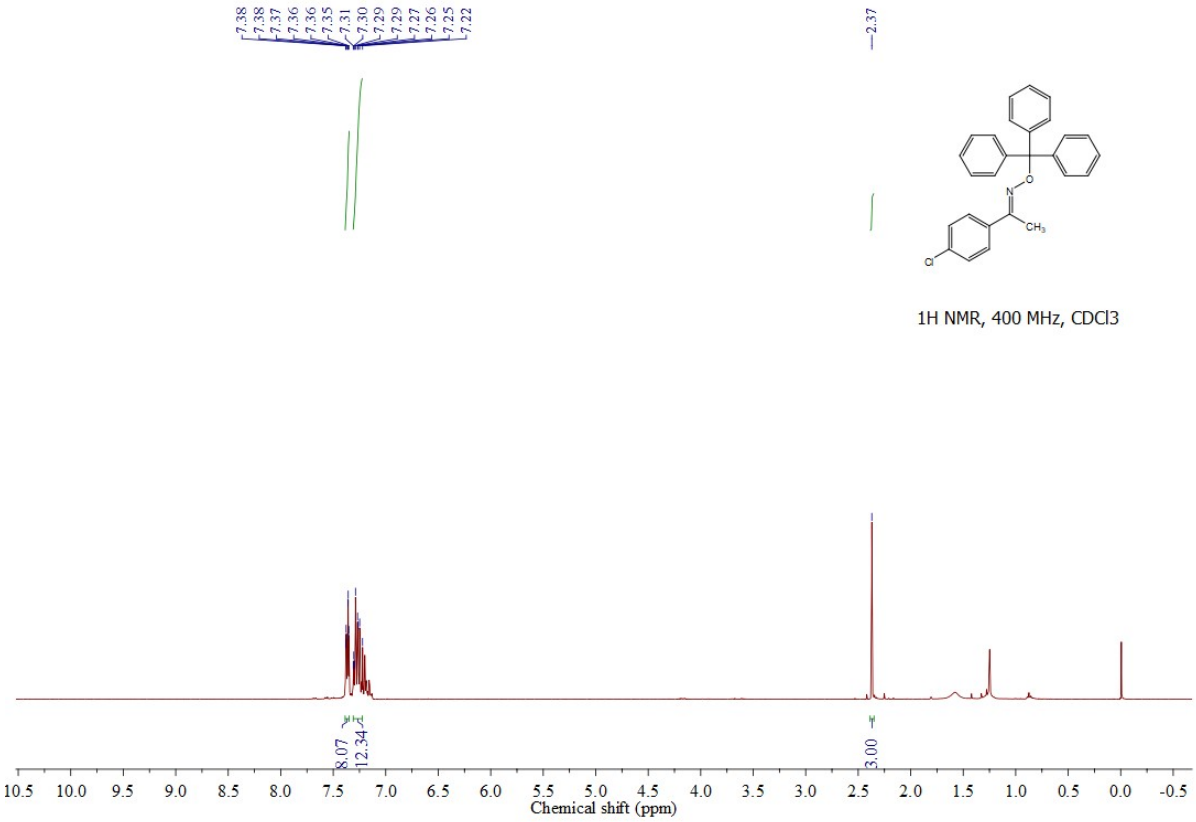
## $^{1}$H NMR (400 MHz) Spectrum of 3d in $CDCl_3$




## $^{13}$C NMR (101 MHz) Spectrum of 3d in $CDCl_3$

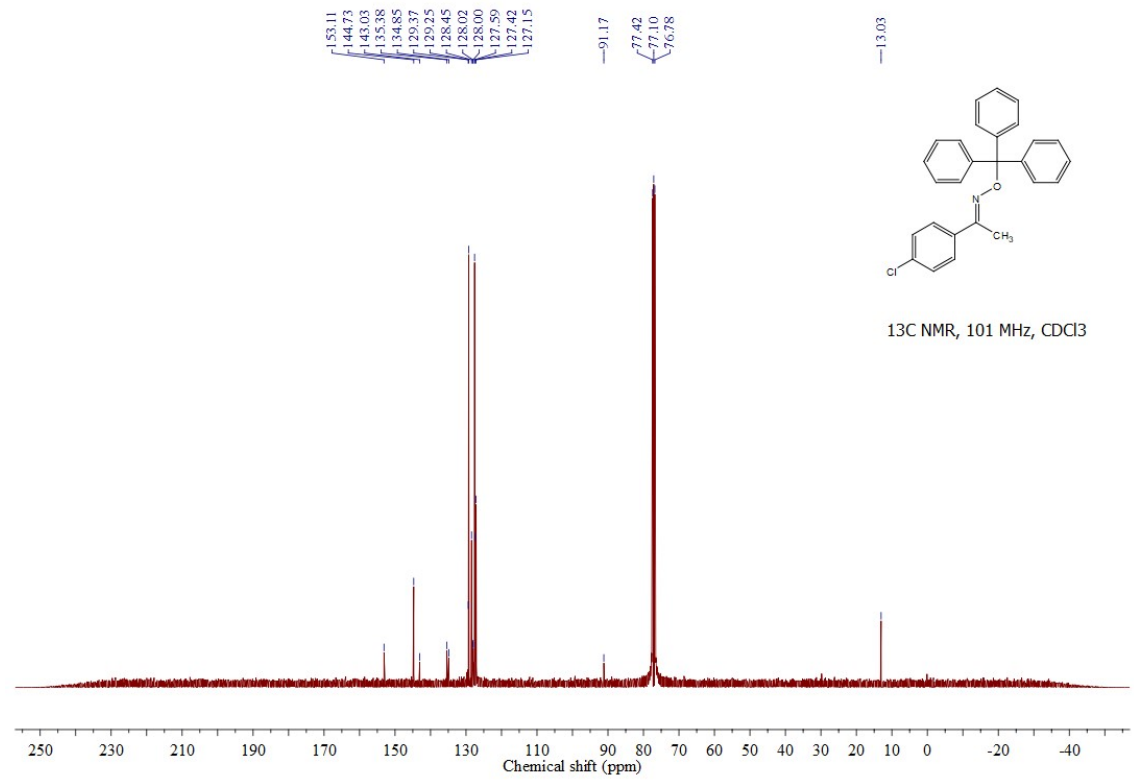


## $^{1}$H NMR (400 MHz) Spectrum of 3e in $CDCl_3$



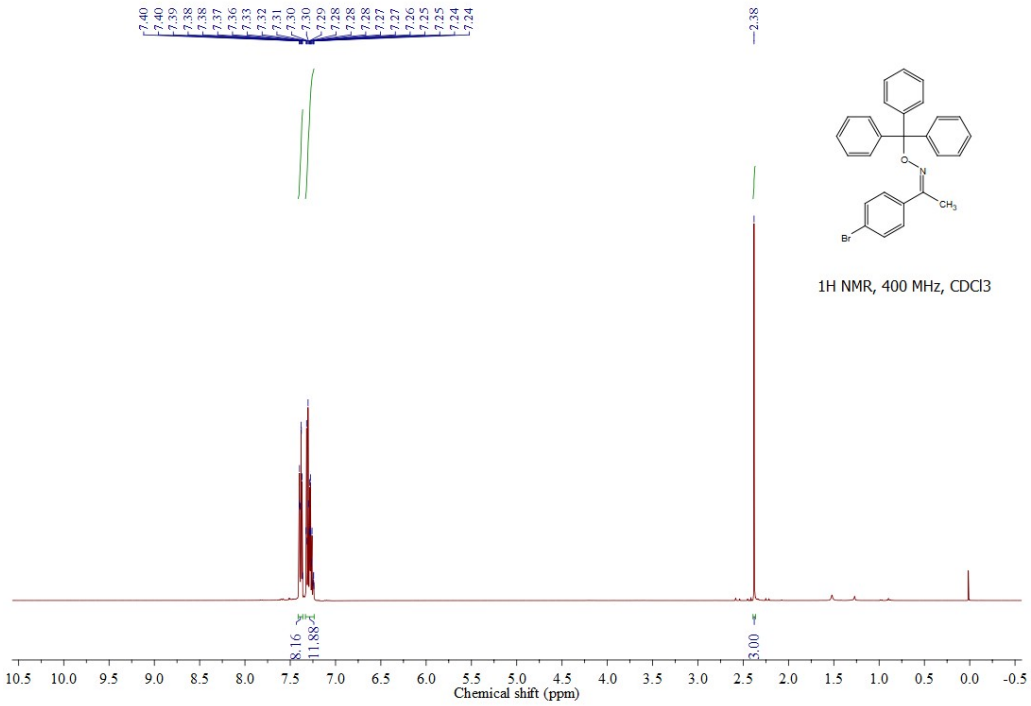

1H NMR, 400 MHz, CDCl3

## $^{13}$C NMR (101 MHz) Spectrum of 3e in $CDCl_3$

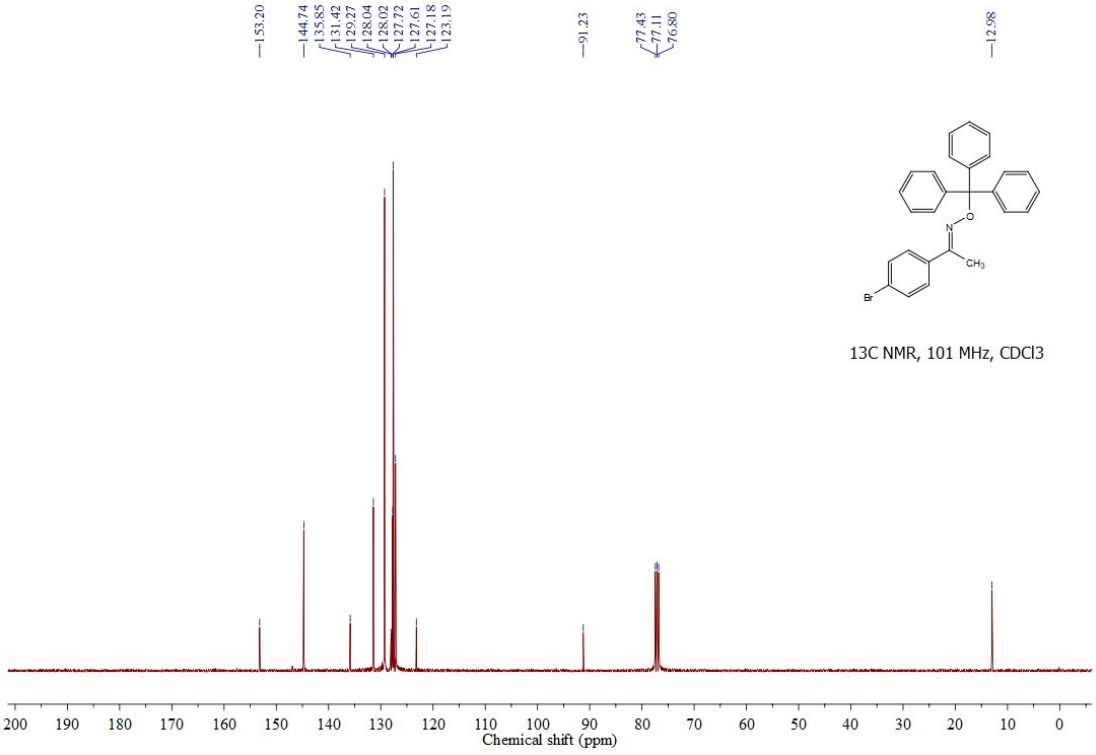



13C NMR, 101 MHz, CDCl3

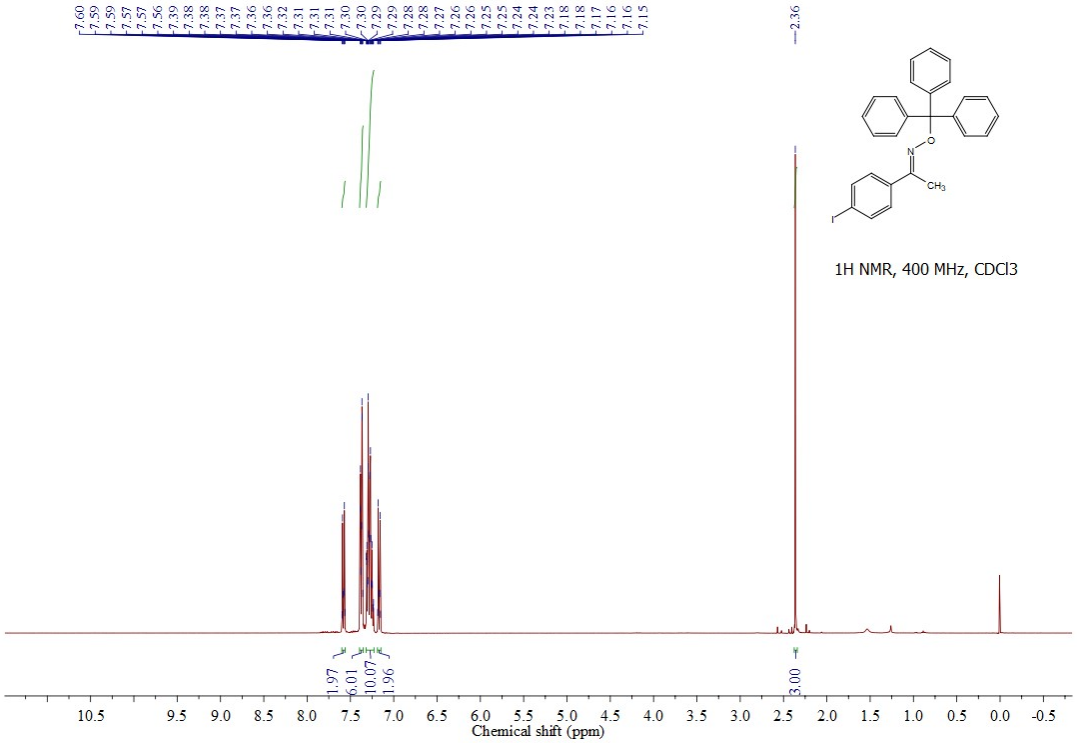
## $^{1}$H NMR (400 MHz) Spectrum of 3f in $CDCl_3$



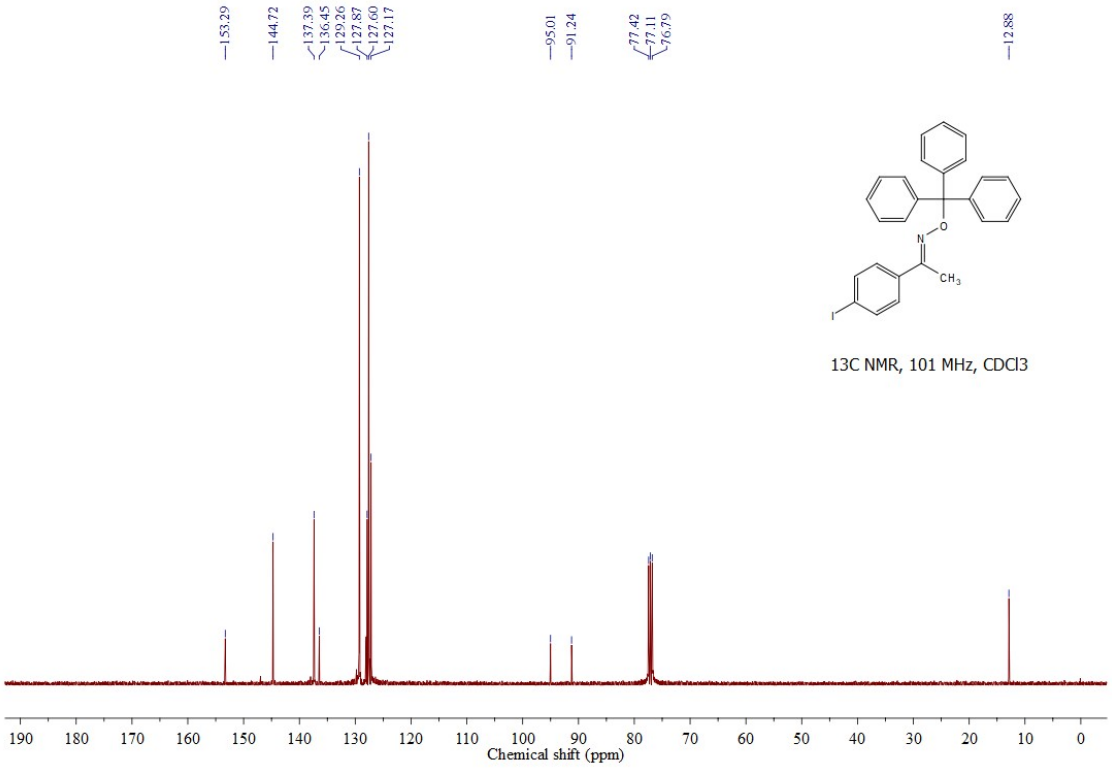

## $^{13}$C NMR (101 MHz) Spectrum of 3f in $CDCl_3$



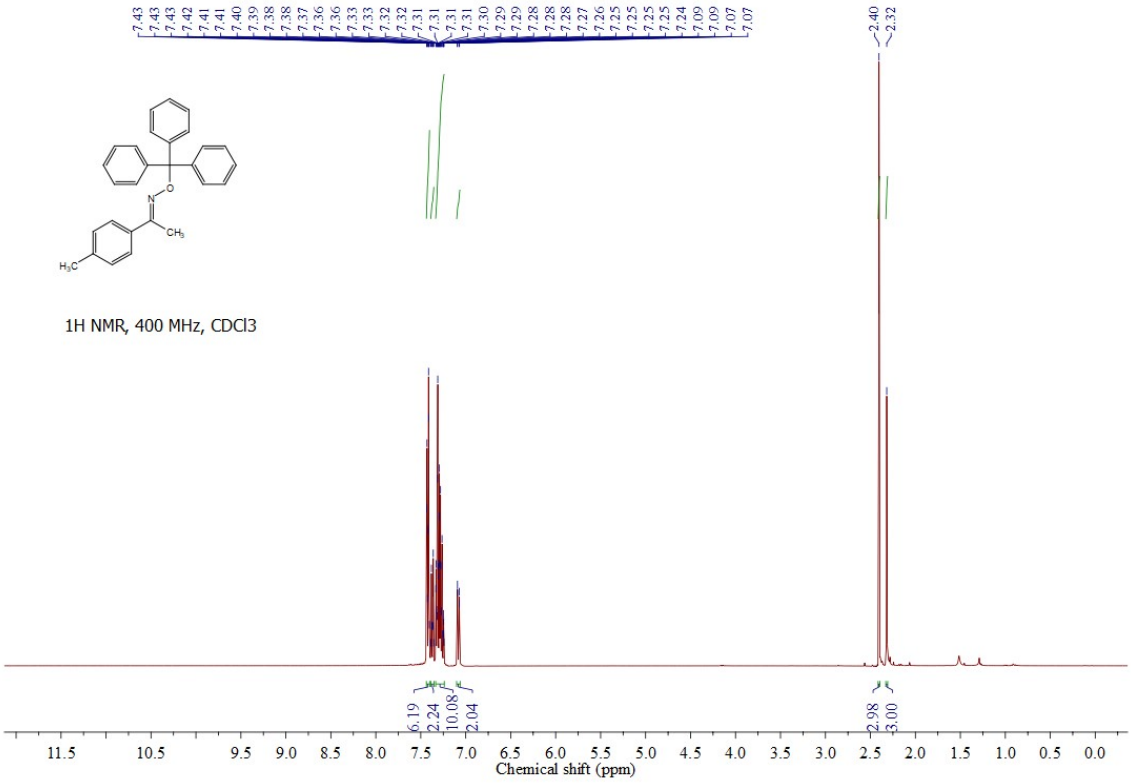
## $^{1}$H NMR (400 MHz) Spectrum of 3g in $CDCl_3$



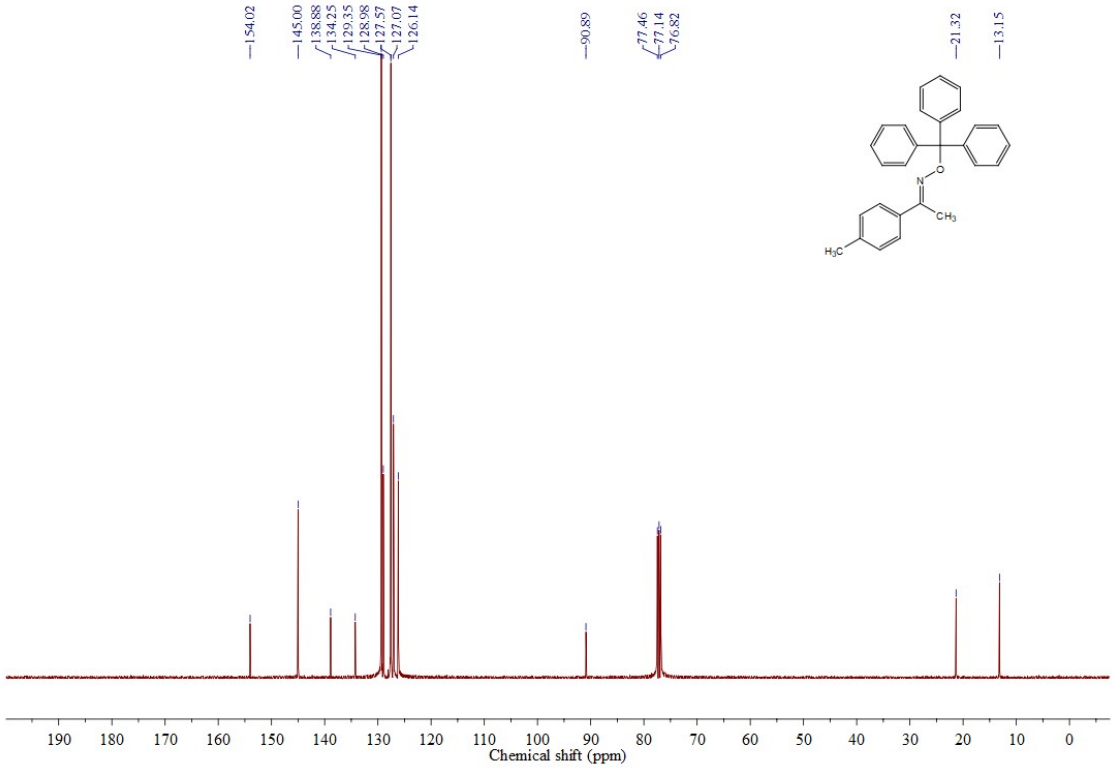

## $^{13}$C NMR (101 MHz) Spectrum of 3g in $CDCl_3$



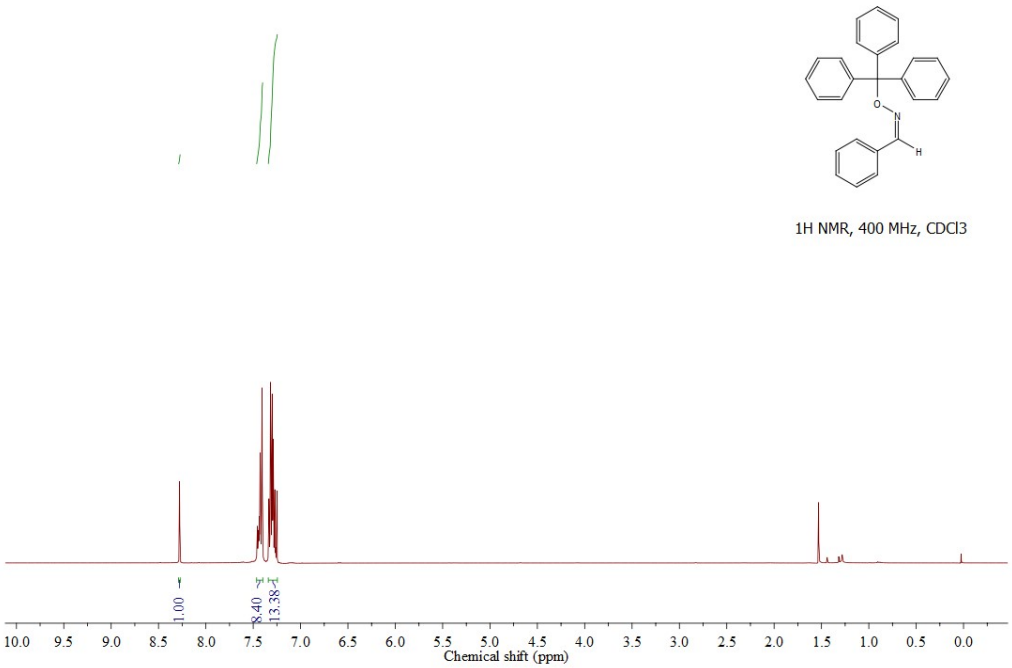
## $^{1}$H NMR (400 MHz) Spectrum of 3h in $CDCl_3$



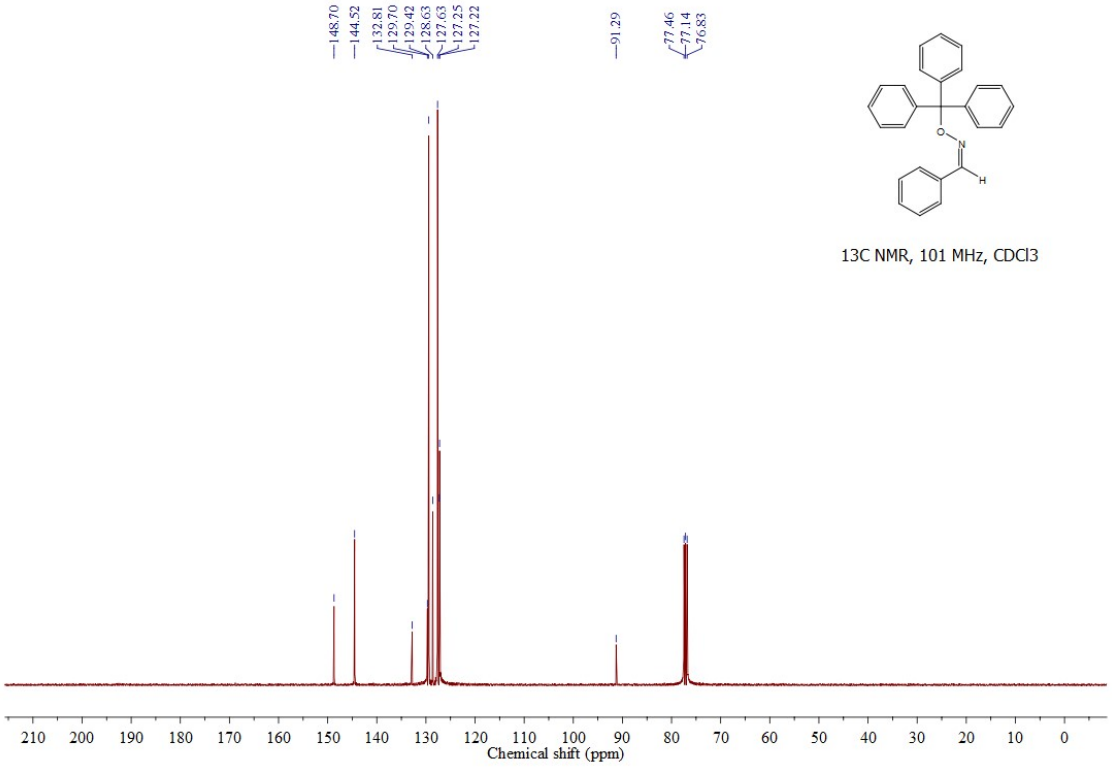

## $^{13}$C NMR (101 MHz) Spectrum of 3h in $CDCl_3$



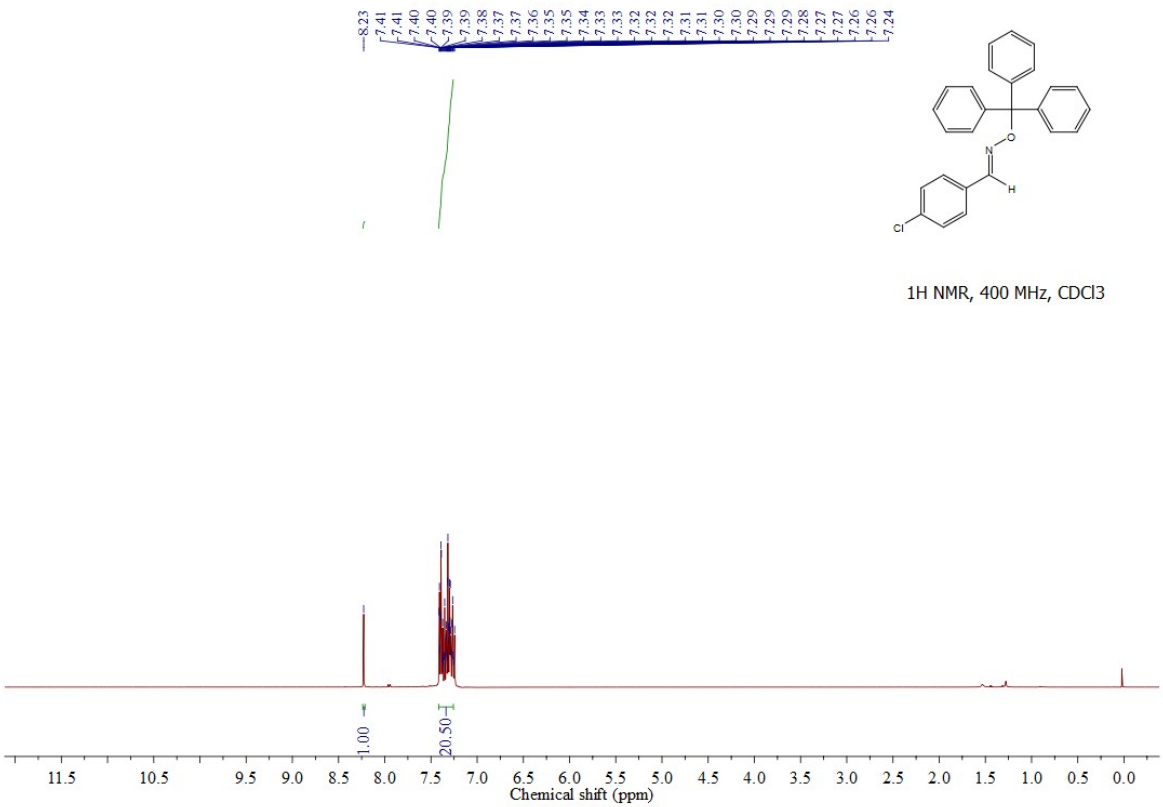
## $^{1}$H NMR (400 MHz) Spectrum of 3i in $CDCl_3$




## $^{13}$C NMR (101 MHz) Spectrum of 3i in $CDCl_3$

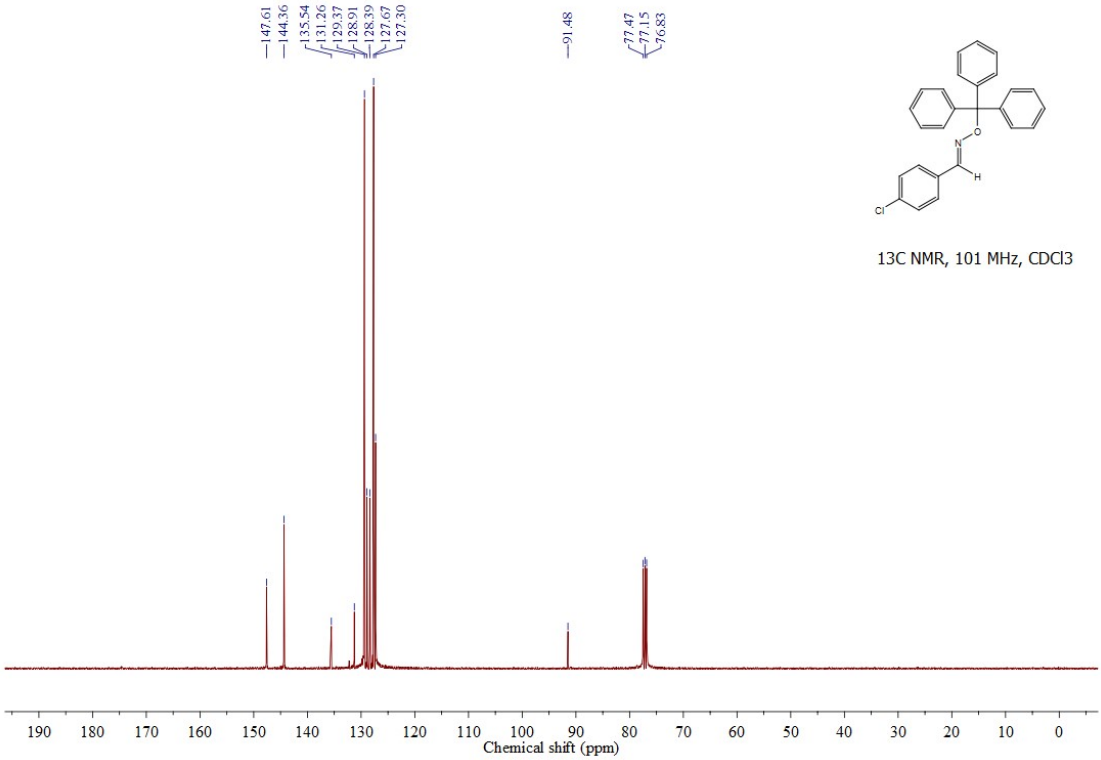


## $^{1}$H NMR (400 MHz) Spectrum of 3j in $CDCl_3$



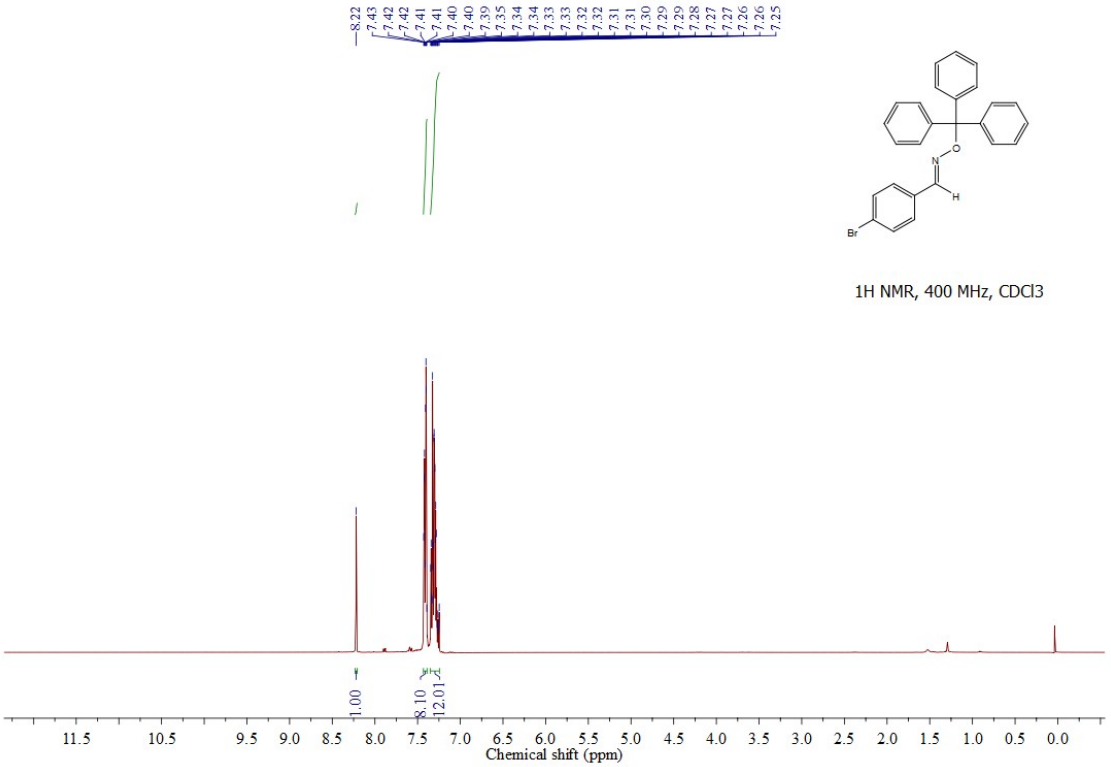

1H NMR, 400 MHz, CDCl3

## $^{13}$C NMR (101 MHz) Spectrum of 3j in $CDCl_3$

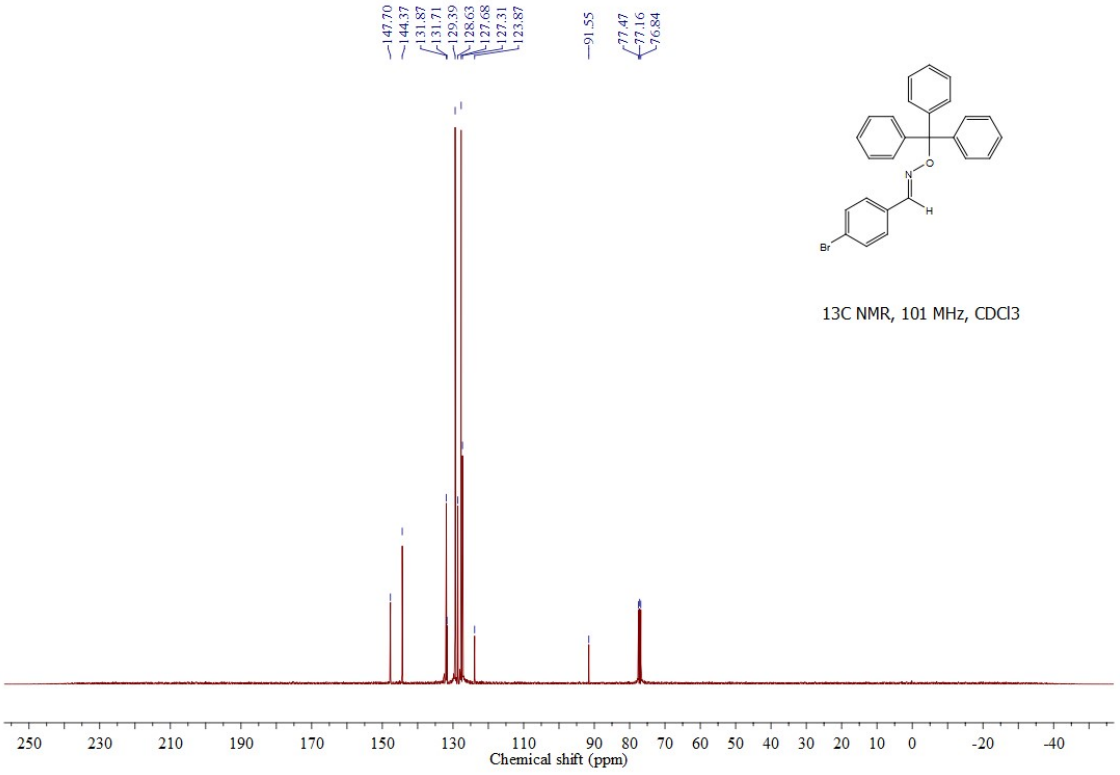



13C NMR, 101 MHz, CDCl3

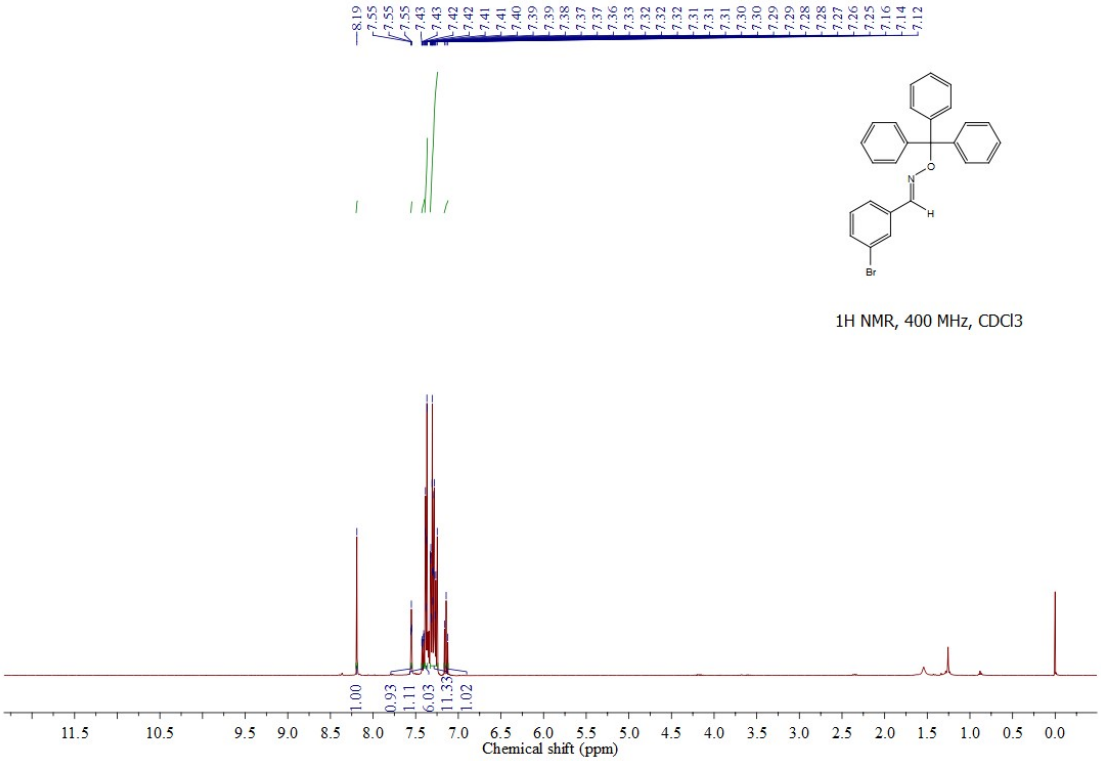
## $^{1}$H NMR (400 MHz) Spectrum of 3l in $CDCl_3$



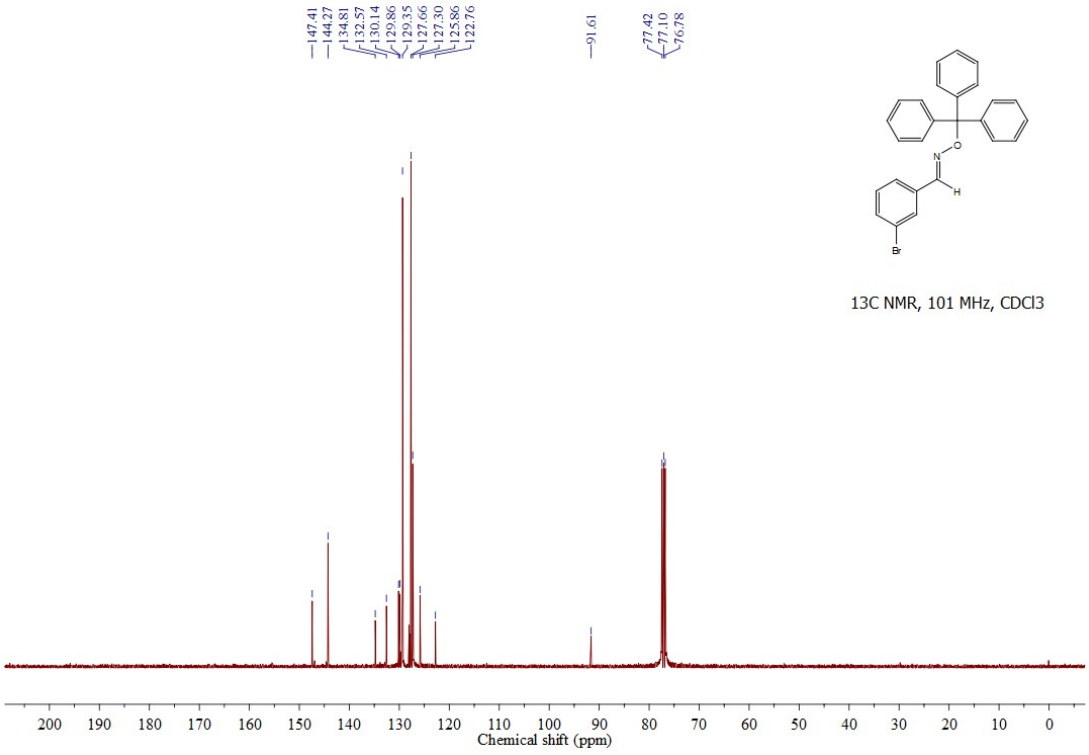

## $^{13}$C NMR (101 MHz) Spectrum of 3l in $CDCl_3$



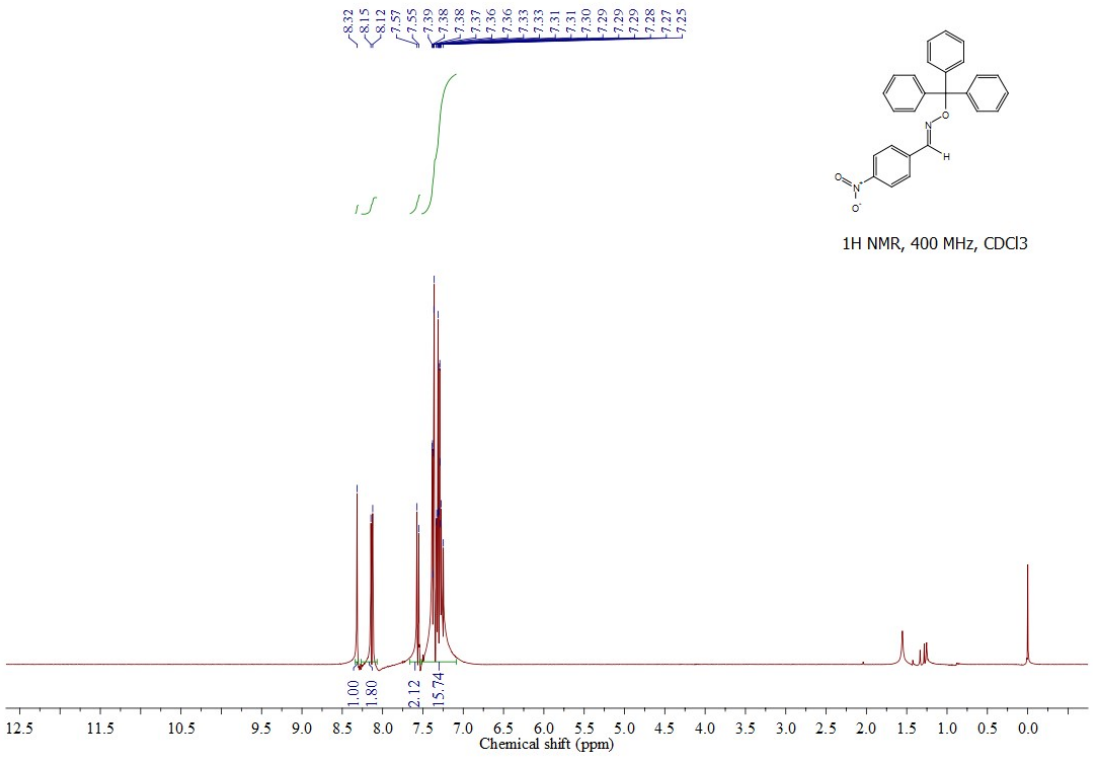
## $^{1}$H NMR (400 MHz) Spectrum of 3m in $CDCl_3$



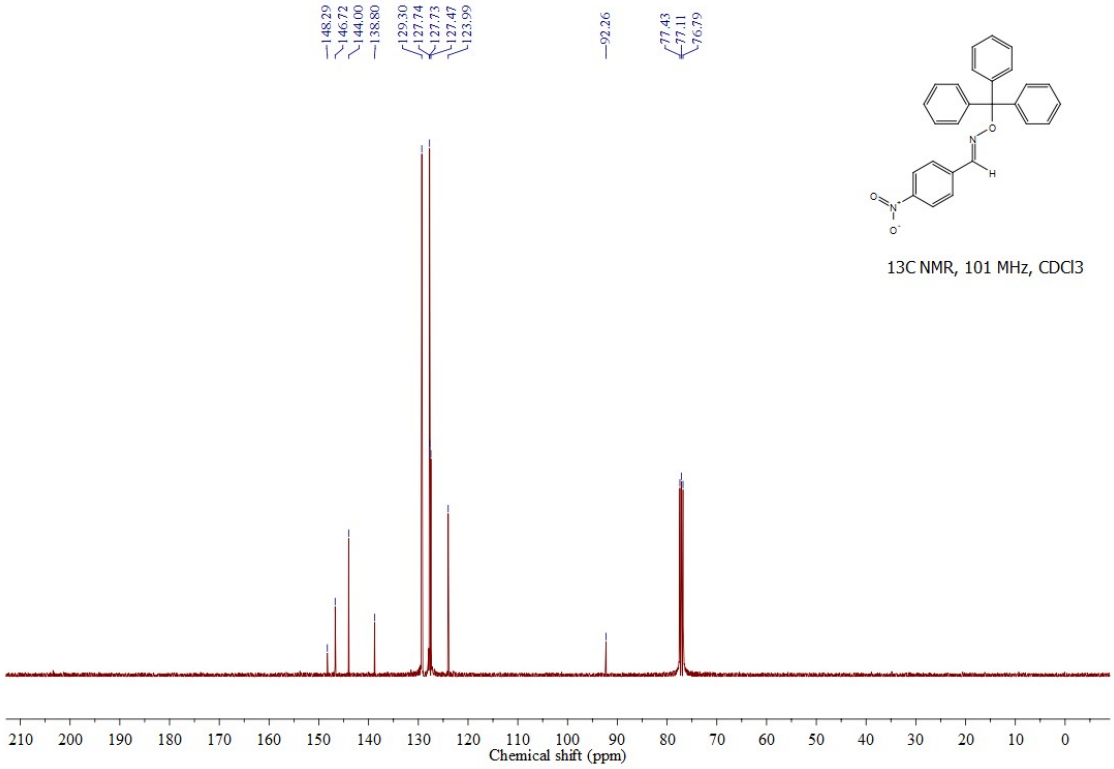

## $^{13}$C NMR (101 MHz) Spectrum of 3m in $CDCl_3$



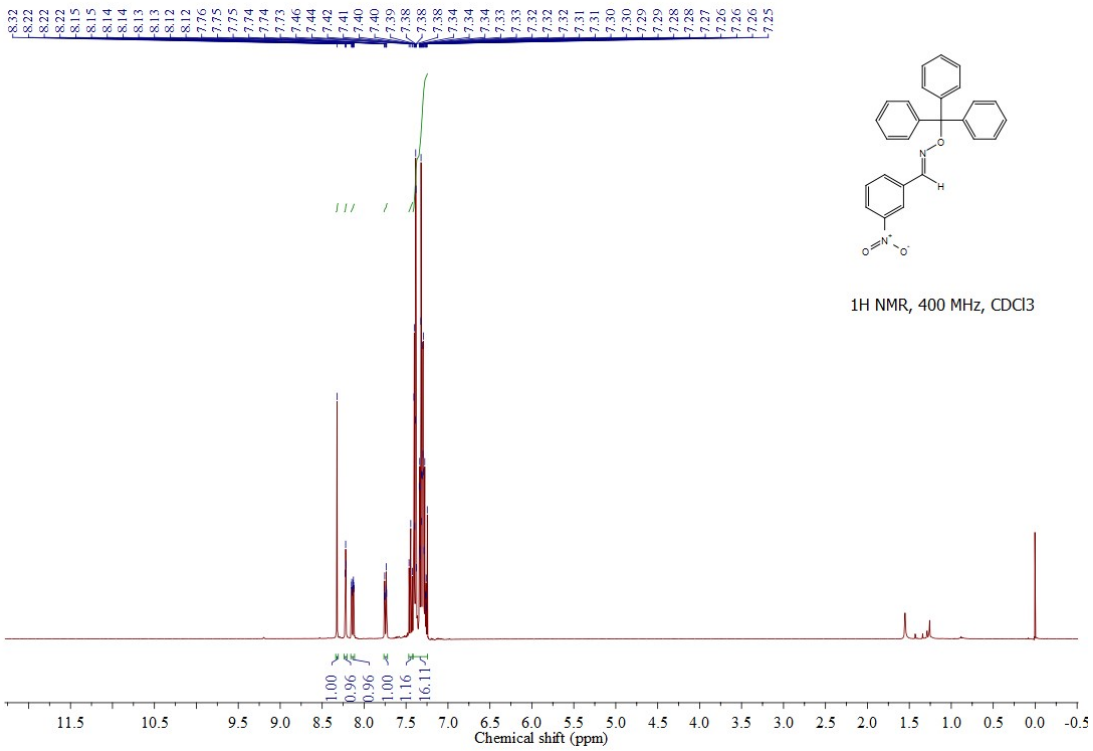
## $^{1}$H NMR (400 MHz) Spectrum of 3n in $CDCl_3$



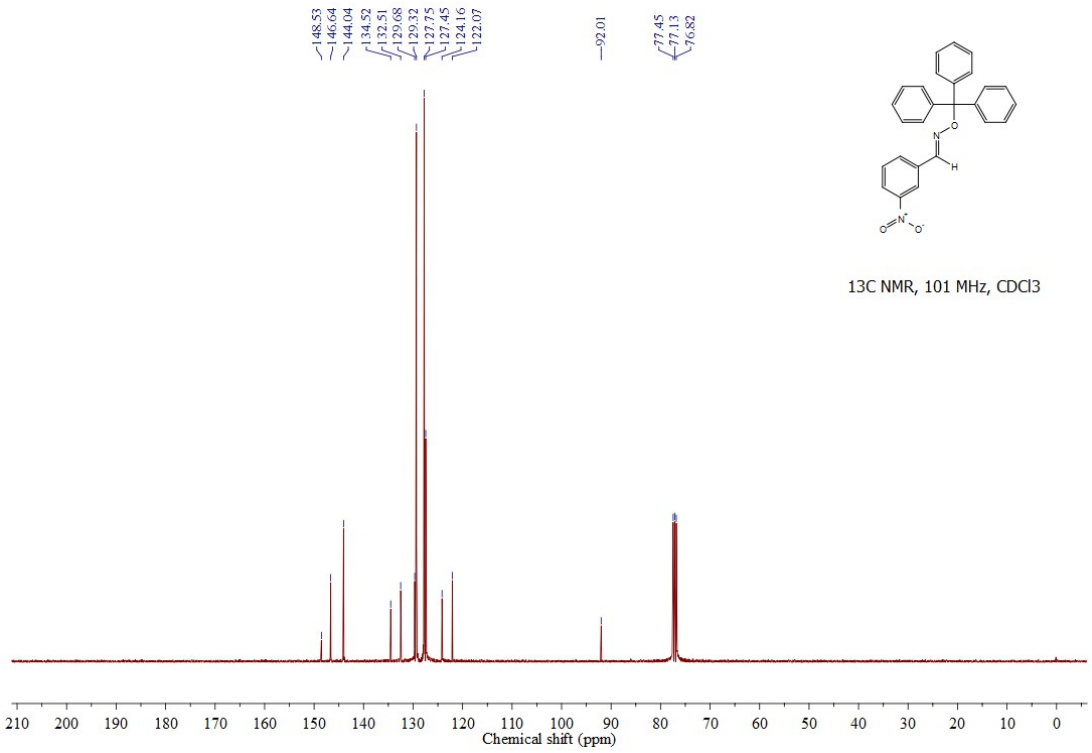

## $^{13}$C NMR (101 MHz) Spectrum of 3n in $CDCl_3$



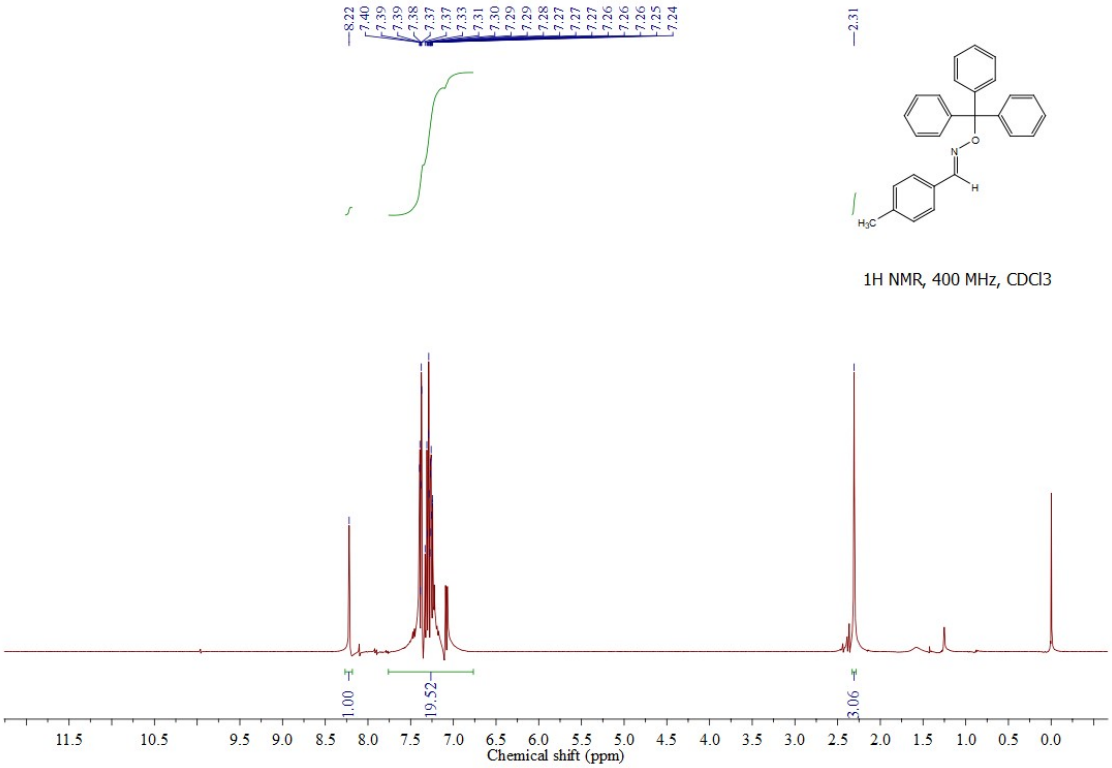
## $^{1}$H NMR (400 MHz) Spectrum of 3o in $CDCl_3$



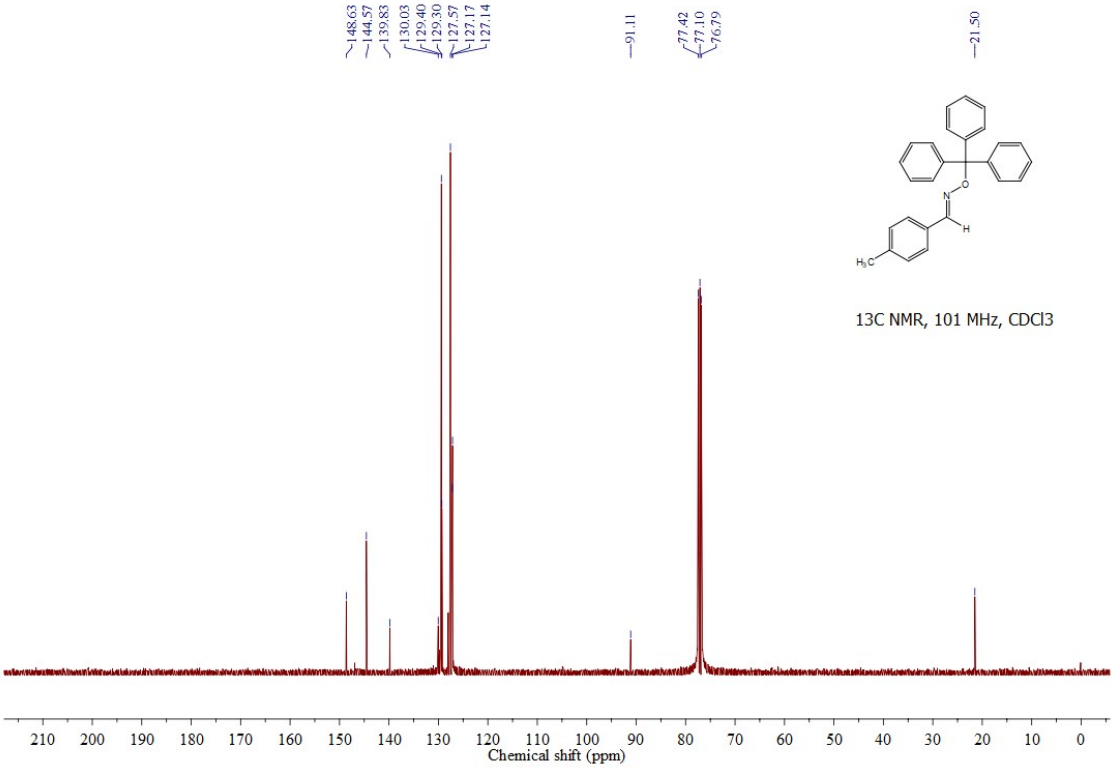

## $^{13}$C NMR (101 MHz) Spectrum of 3o in $CDCl_3$



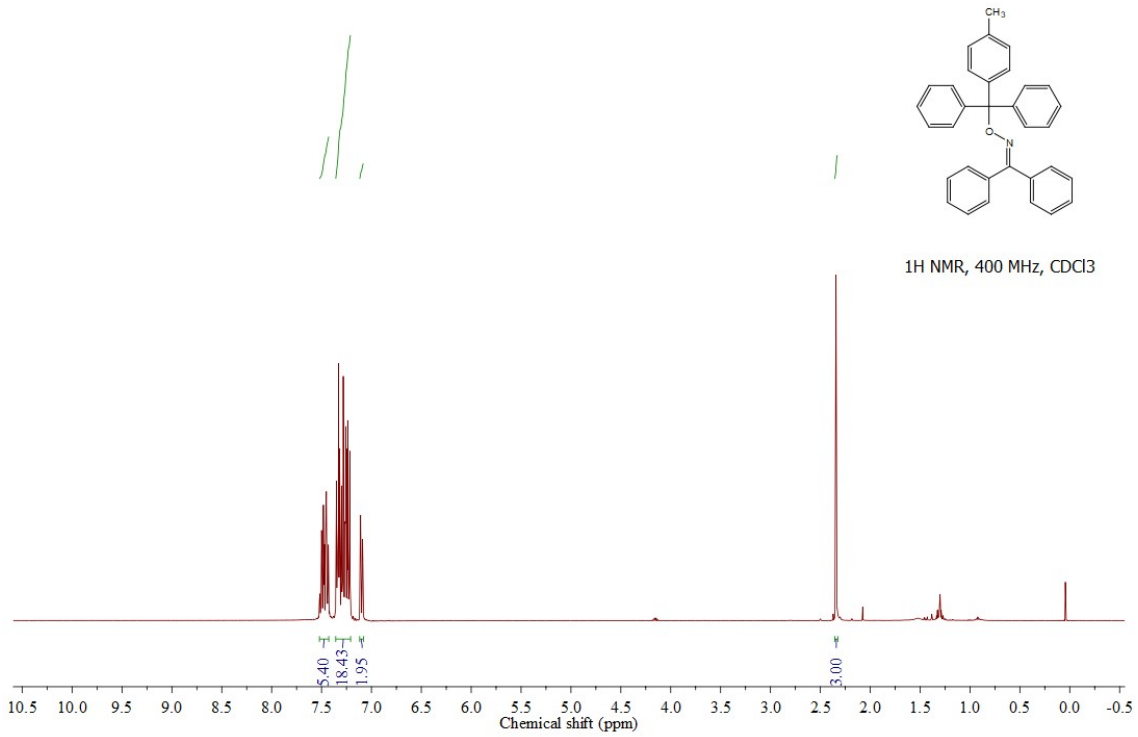
## $^{1}$H NMR (400 MHz) Spectrum of 3p in $CDCl_3$



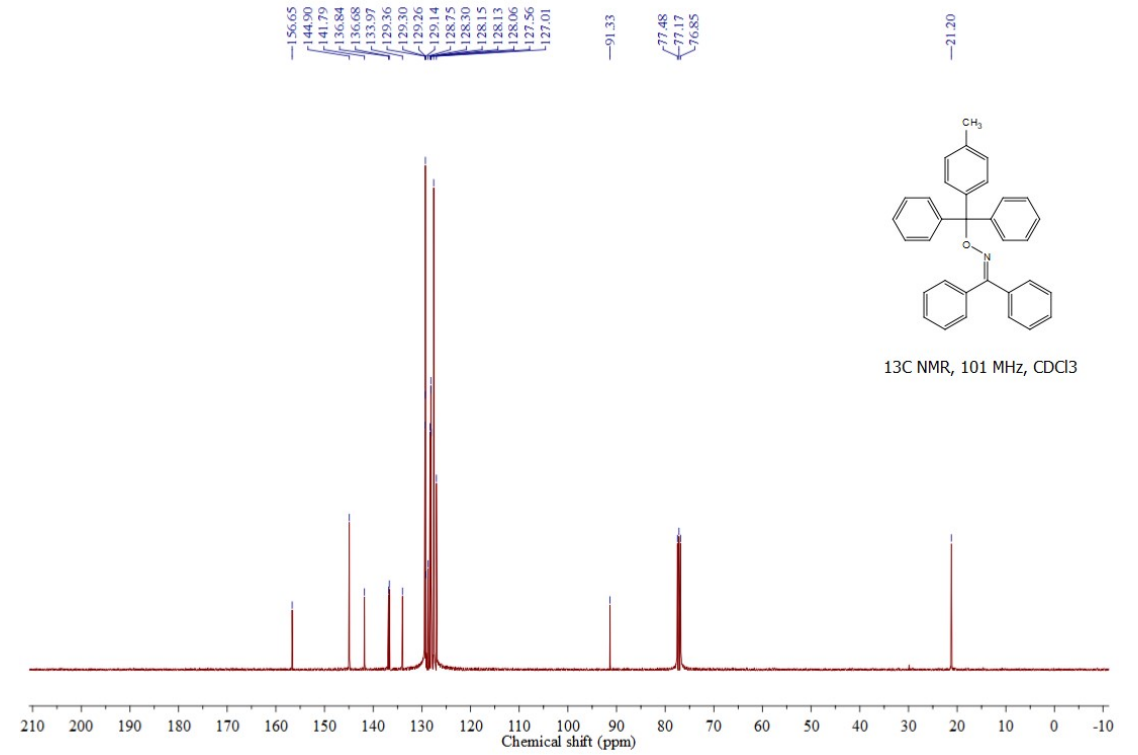

## $^{13}$C NMR (101 MHz) Spectrum of 3p in $CDCl_3$



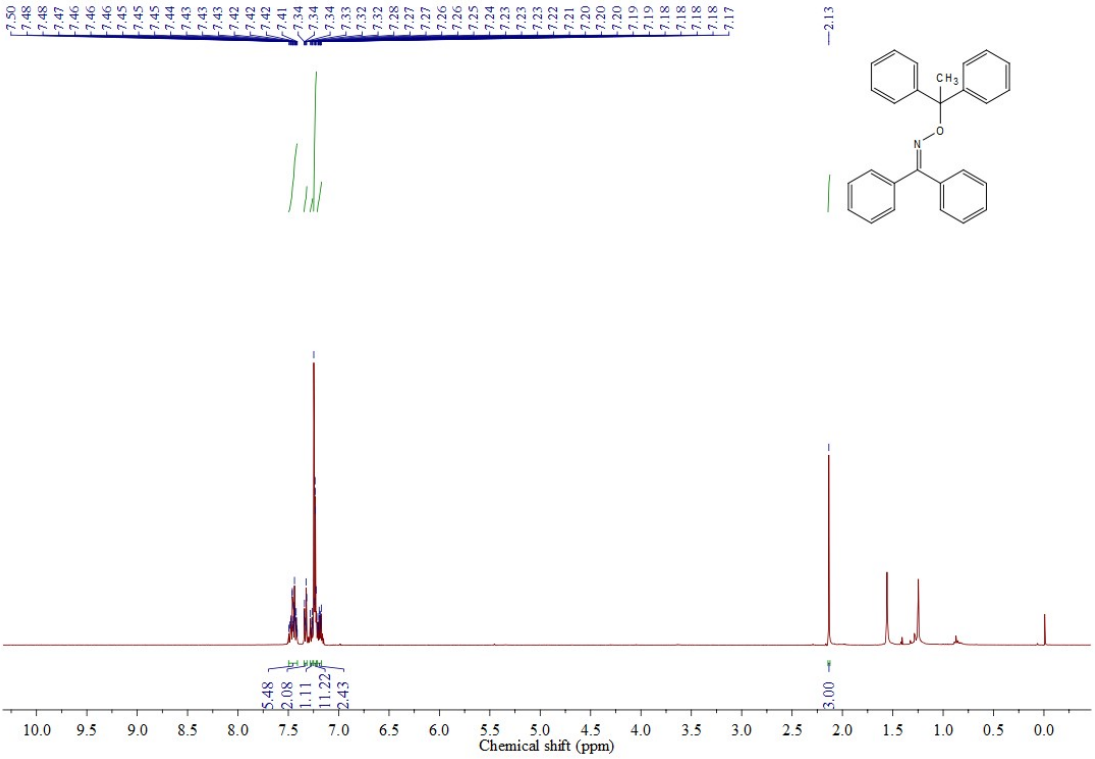
## $^{1}$H NMR (400 MHz) Spectrum of 3q in $CDCl_3$



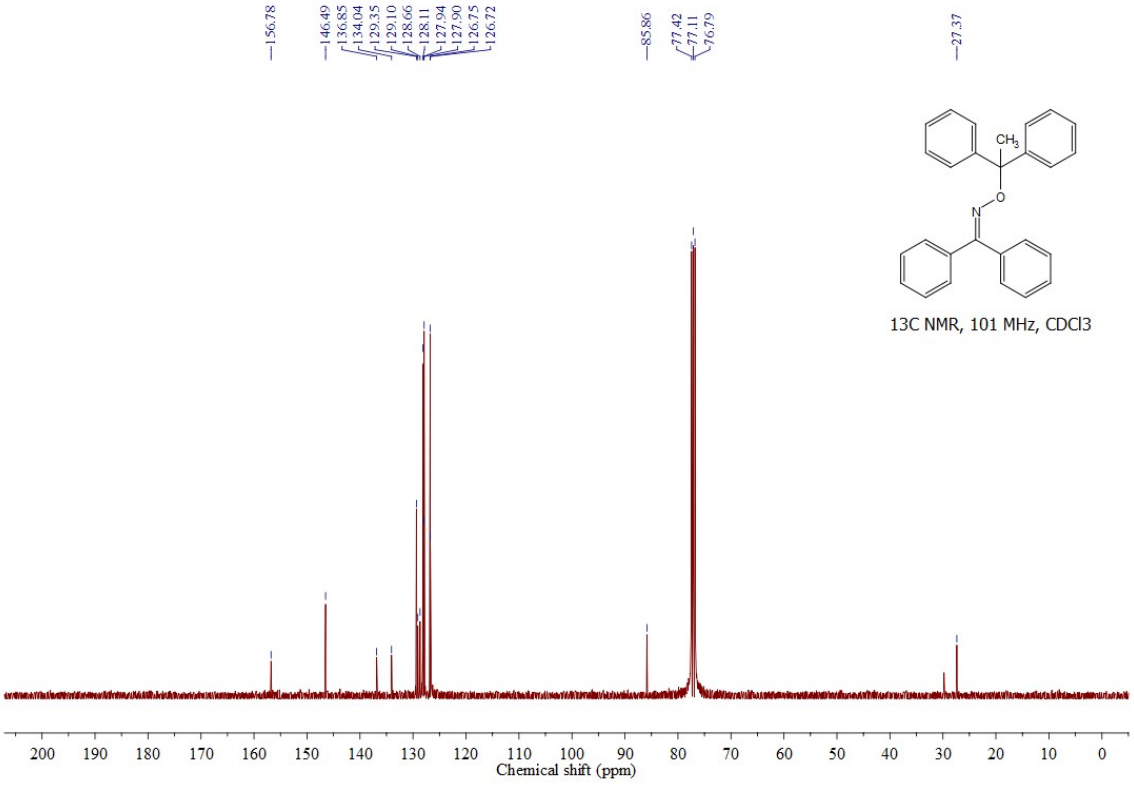

## $^{13}$C NMR (101 MHz) Spectrum of 3q in $CDCl_3$



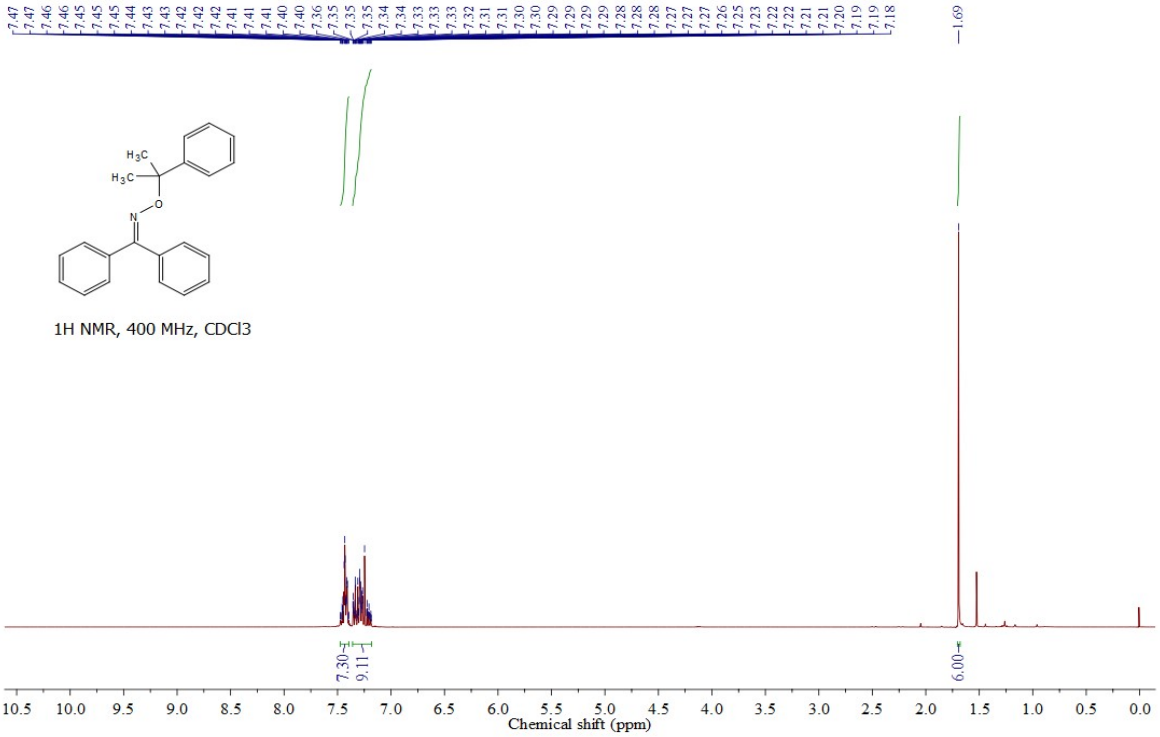
## $^{1}$H NMR (400 MHz) Spectrum of 3r in $CDCl_3$



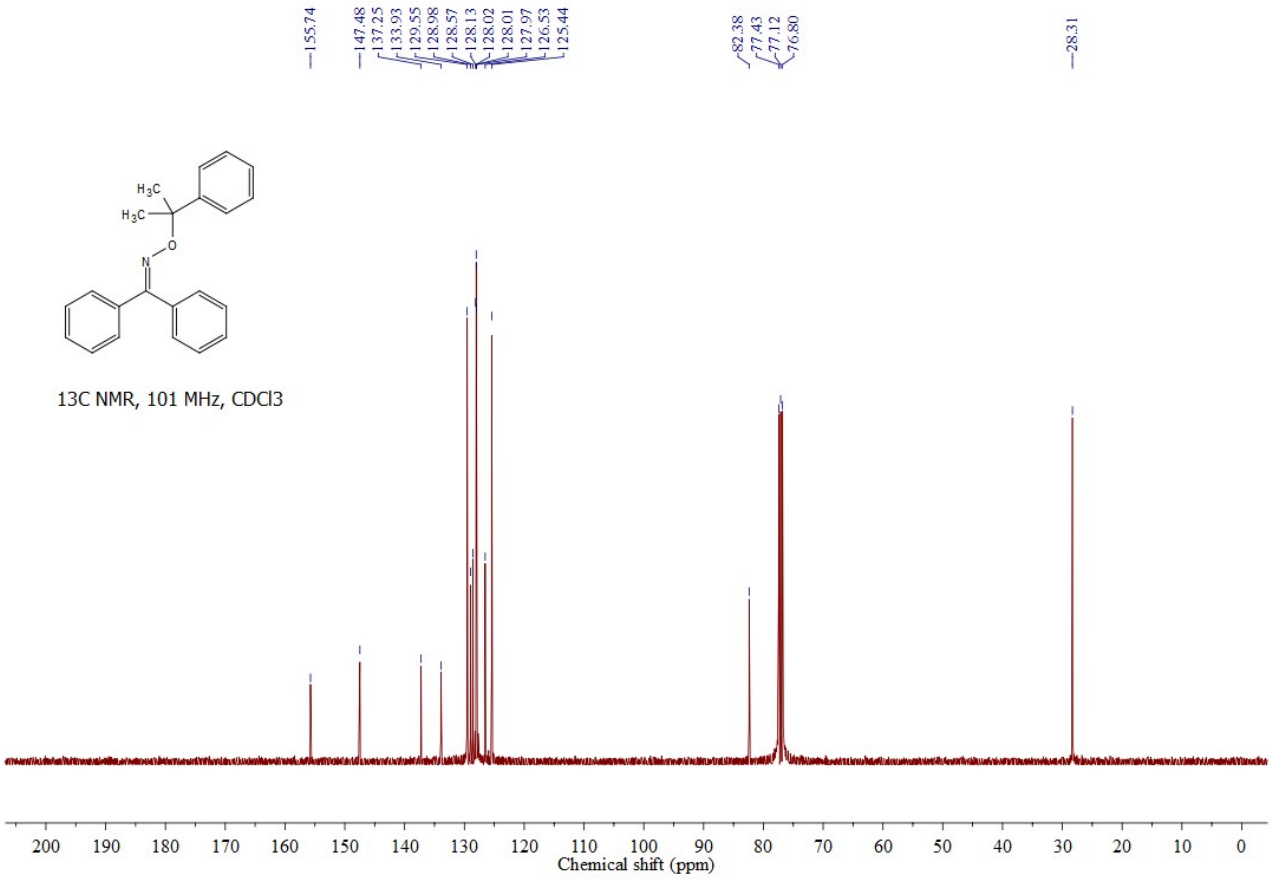

## $^{13}$C NMR (101 MHz) Spectrum of 3r in $CDCl_3$



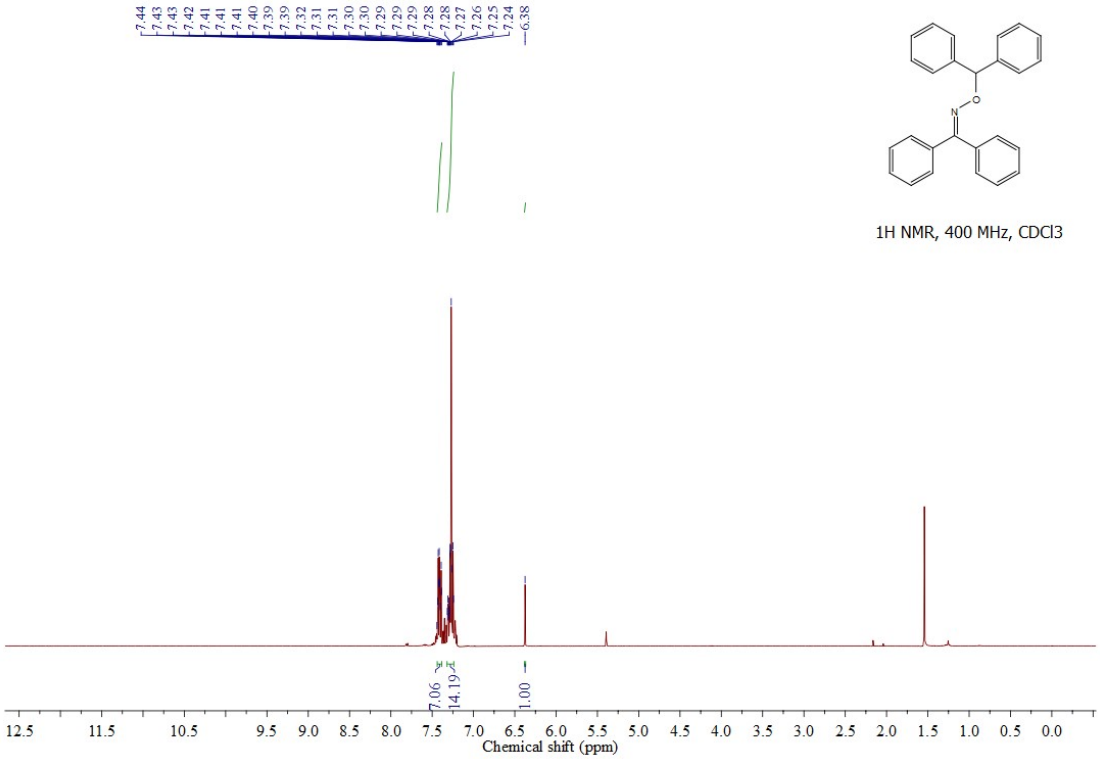
## $^{1}$H NMR (400 MHz) Spectrum of 3s in $CDCl_3$



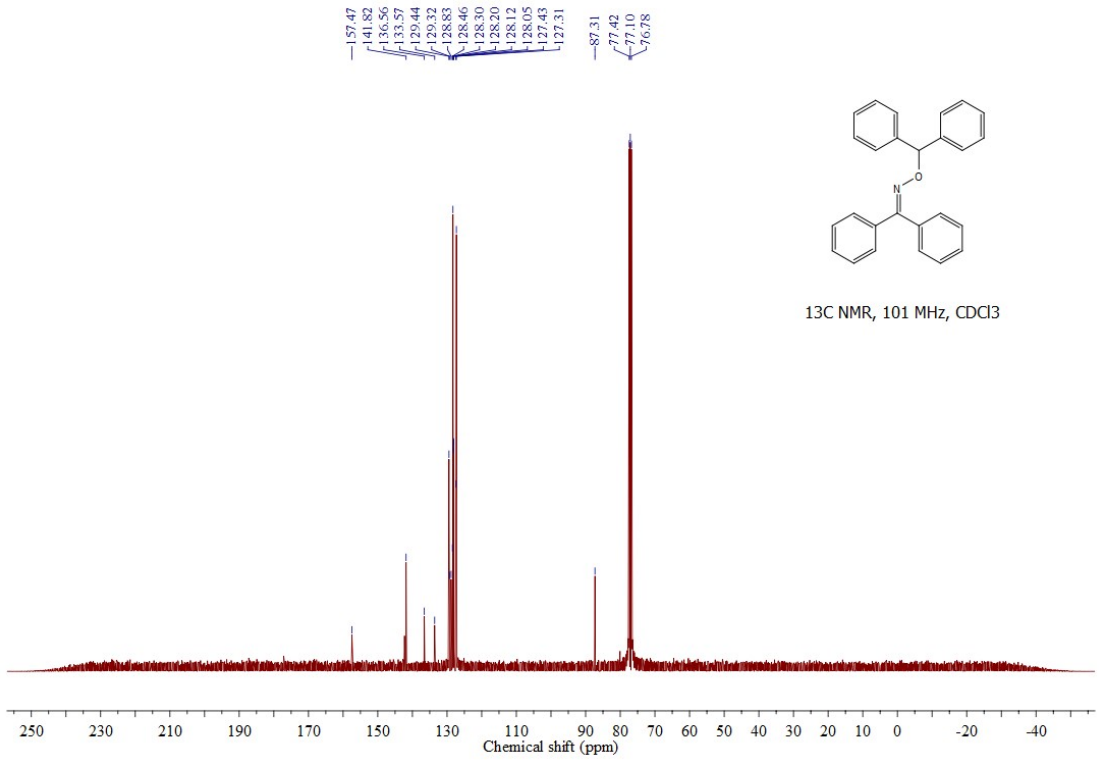

## $^{13}$C NMR (101 MHz) Spectrum of 3s in $CDCl_3$



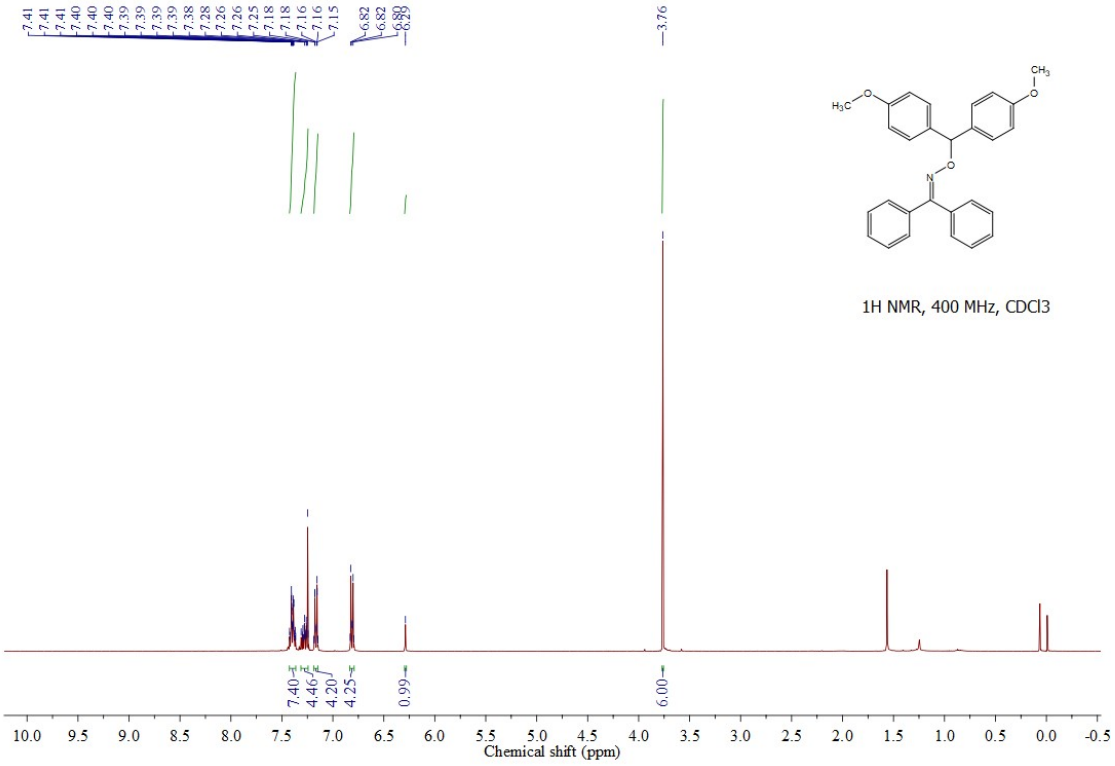
## $^{1}$H NMR (400 MHz) Spectrum of 3t in $CDCl_3$



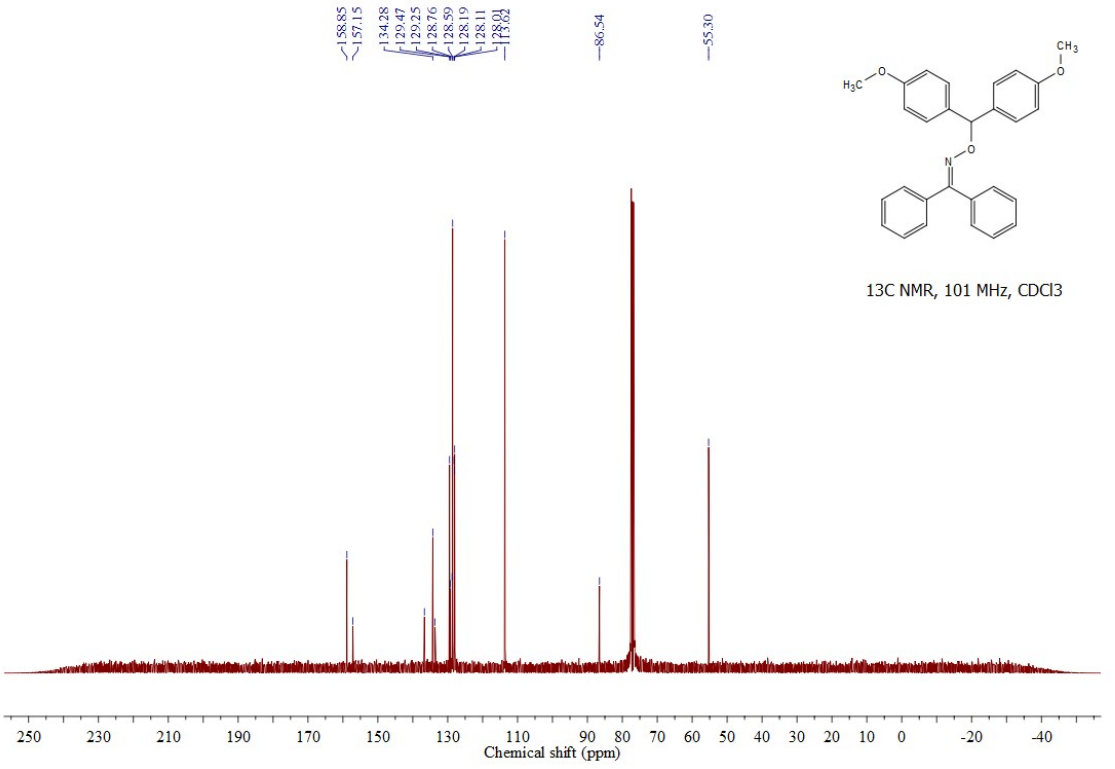

## $^{13}$C NMR (101 MHz) Spectrum of 3t in $CDCl_3$



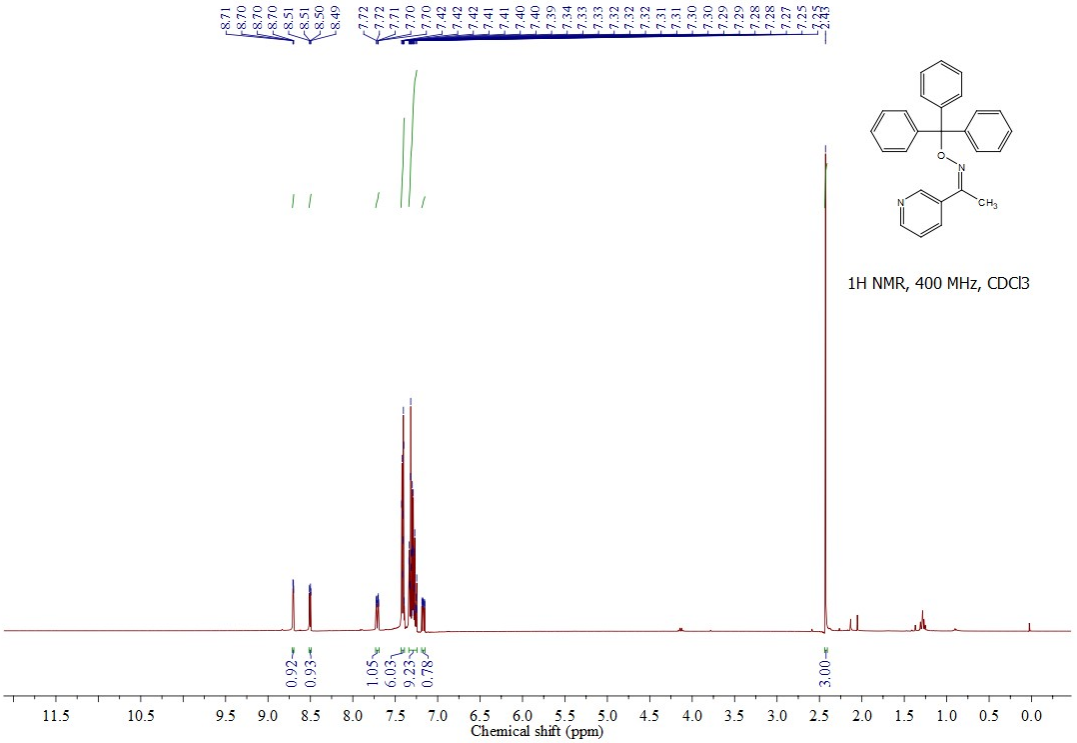
## $^{1}$H NMR (400 MHz) Spectrum of 3u in $CDCl_3$



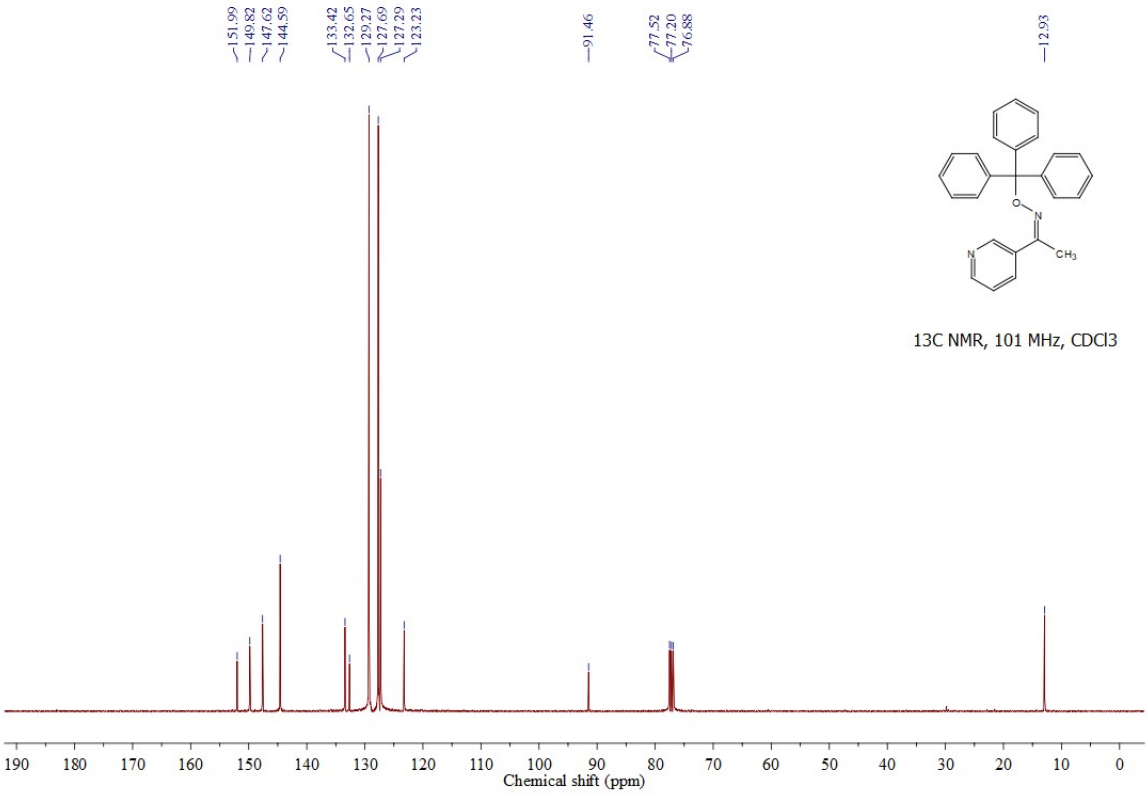

## $^{13}$C NMR (101 MHz) Spectrum of 3u in $CDCl_3$



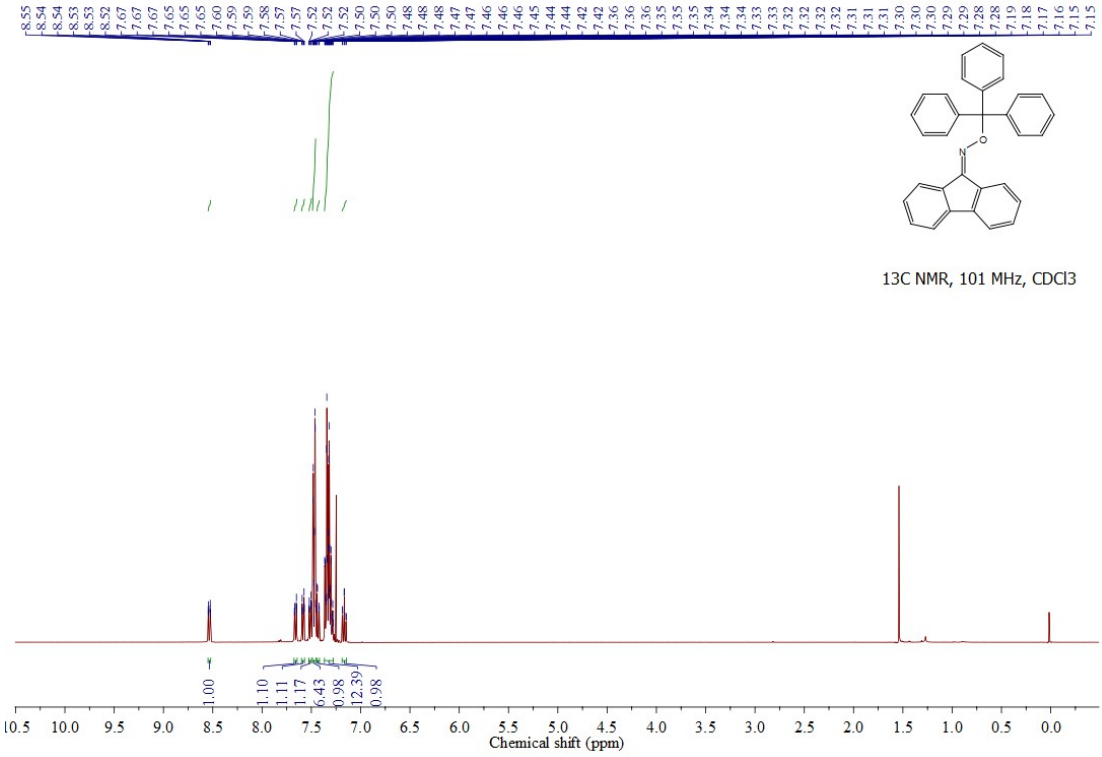
## $^{1}$H NMR (400 MHz) Spectrum of 3v in $CDCl_3$



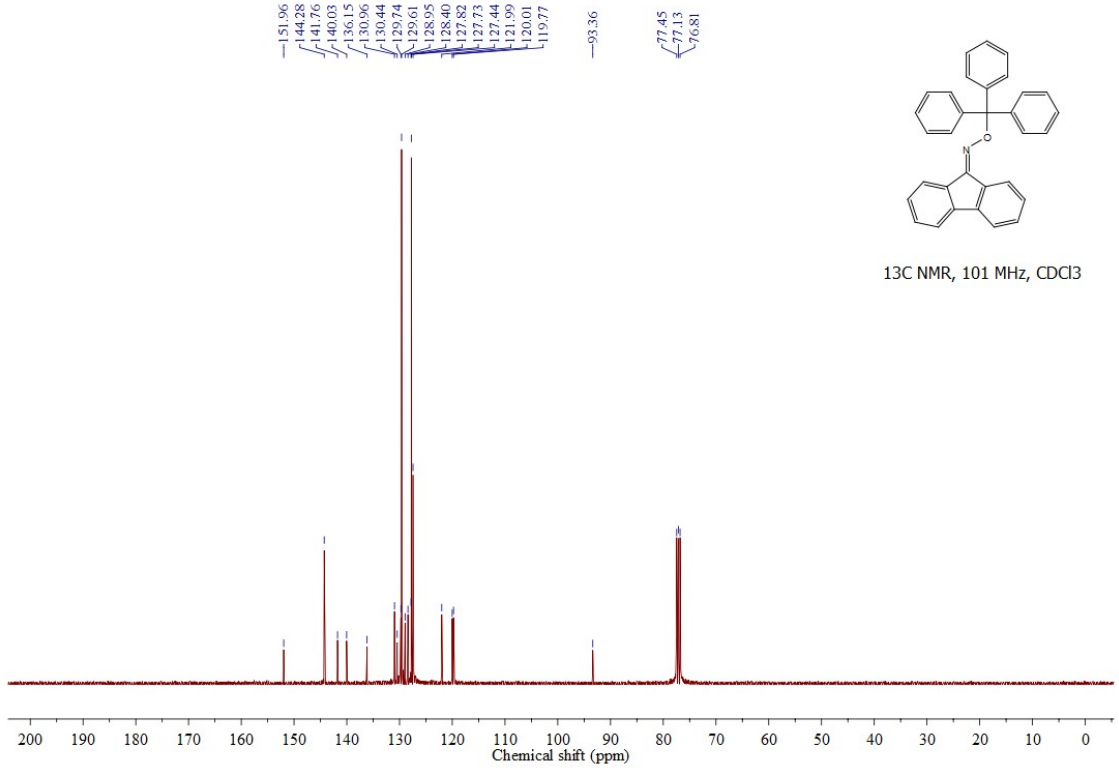

## $^{13}$C NMR (101 MHz) Spectrum of 3v in $CDCl_3$



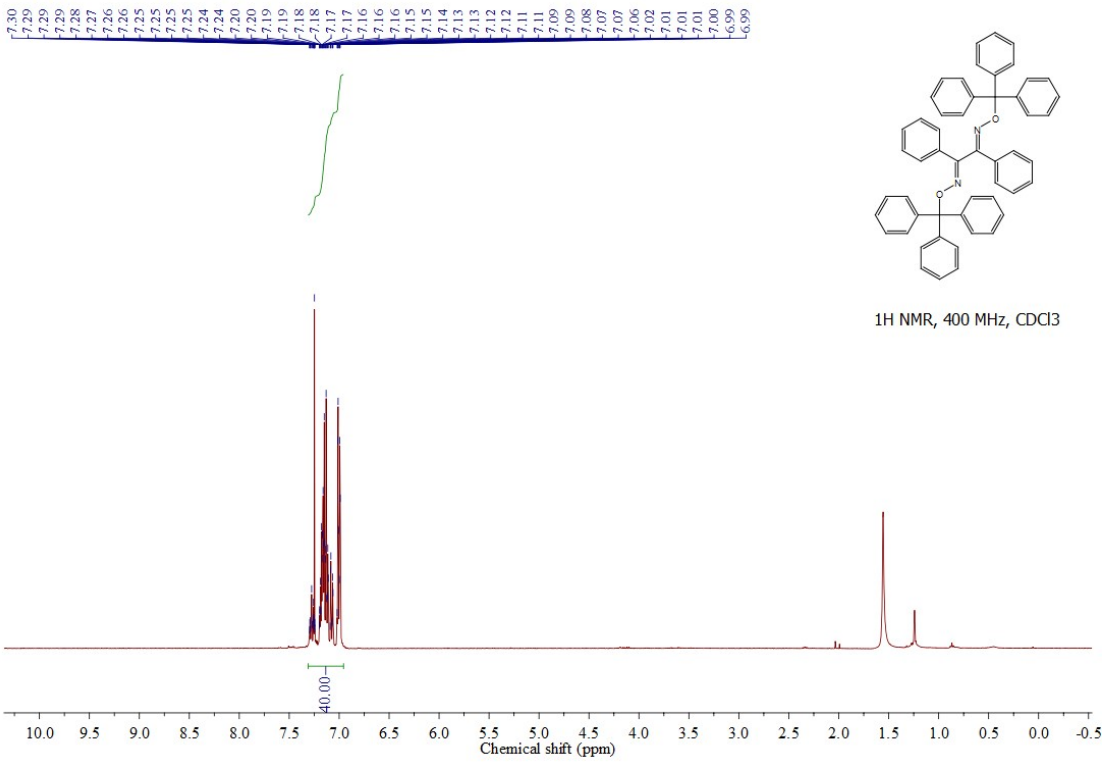
## $^{1}$H NMR (400 MHz) Spectrum of 3w in $CDCl_3$




## $^{13}$C NMR (101 MHz) Spectrum of 3w in $CDCl_3$

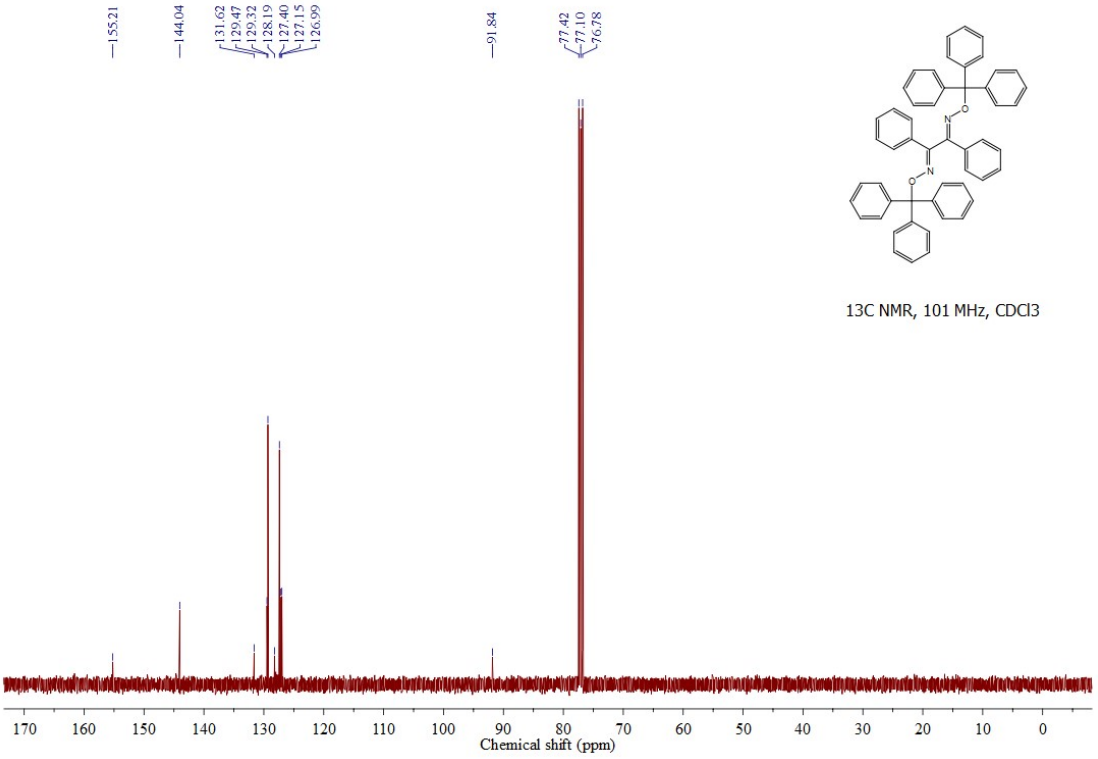


## $^{1}$H NMR (400 MHz) Spectrum of 3x in $CDCl_3$




1H NMR, 400 MHz, CDCl3

## $^{13}$C NMR (101 MHz) Spectrum of 3x in $CDCl_3$




13C NMR, 101 MHz, CDCl3