Supporting Information

# Visible-Light-Induced, Copper-Catalyzed Regiodivergent C($sp^3$)-Sulfonylation of Oxime Esters with Sodium Sulfinates

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## 1. General information

Unless otherwise noted, materials were either purchased from commercial suppliers and used as received or prepared via literature procedures. Solvents were deoxygenated and dried by thoroughly sparging with argon followed by passage through an activated column in a solvent purification system. All manipulations of air-sensitive materials were carried out in oven-dried glassware using standard Schlenk under $N_2$ atmosphere.

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian Mercury-400 Plus or Bruker (500MHz) AVANCE-NEO or Agilent Technologies DD2 (600 MHz) spectrometer in $CDCl_3$ or DMSO-$d_6$. Chemical shifts (δ) for NMR were quoted in parts per million (ppm) referenced to 0.0 pm for tetramethylsilane or 2.50 ppm for the solvent residual peak of DMSO-$d_6$. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). $^{13}$C NMR spectra were recorded on a Bruker 500 (125 MHz) or Agilent Technologies DD2 (150 MHz) spectrometer in $CDCl_3$ or DMSO-$d_6$, and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of $CDCl_3$ or 39.5 ppm of DMSO-$d_6$.

High-resolution mass spectra (HRMS) (ESI) were obtained with Bruker Daltonics APEXII 47 e FT-ICR, Agilent QTOF 700 or Agilent 1200 spectrometer. Accurate masses from high-resolution mass spectra were reported for the molecular ion $[M]^+$, $[M+H]^+$ or $[M+Na]^+$. Melting points were measured on an XT4A apparatus (uncorrected). Silicycle SiliaFlash® P60 silica gel (particle size 40–63 μm) was used for flash chromatography. Analytical thin layer chromatography was conducted with glass TLC plates (silica gel 60 F254), and spots were visualized under UV light or after treatment with standard TLC stains.

Unless otherwise noted, all photochemical reactions were carried out in dry Schlenk tube with magnetic stirring bar. The 40 W Bule LED lamps employed in this work were bought from Kessil Lighting 1689 Regatta Blvd, Richmond, CA 94804; wavelength (427 nm); The setup of photocatalytic reaction as illustrated in **Figure S1**. The distance from the light source to the irradiation vessel center is about 6.0 cm. The temperature is controlled by a fan. No filter was used in this reaction.

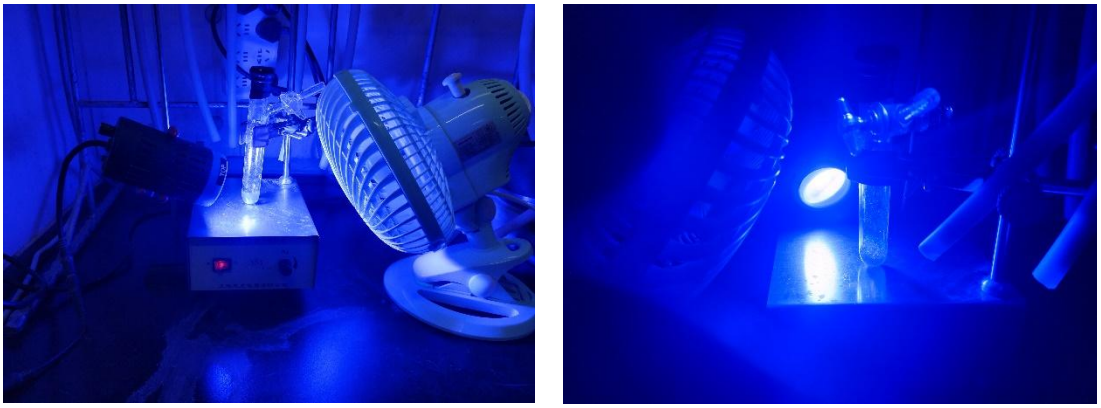
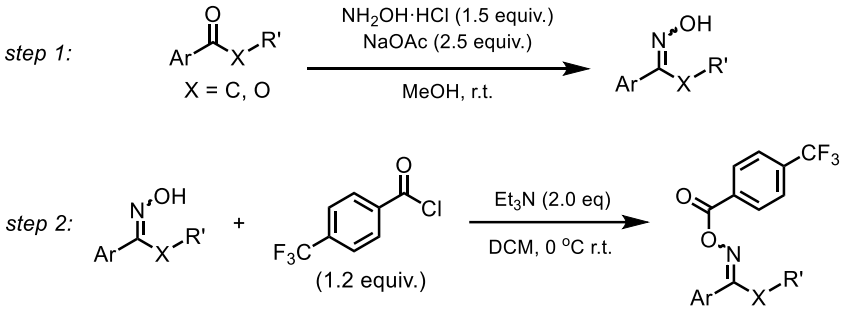


**Figure S1.** Photocatalytic Reaction Setup and Light Characteristics of 40 W Blue LED.

## 2. Experimental Procedures

### 2.1 General procedure for the preparation of *N*-acyloxy imidates.[1-5]

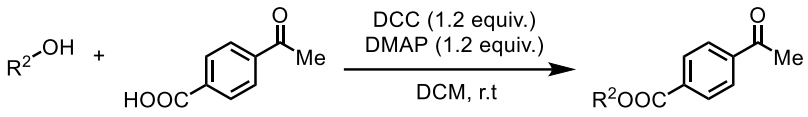
**Method A:**




**Step 1:** A solution of the corresponding ketone (5.0 mmol) in methanol (0.20 M) was subjected to the addition of sodium acetate (12.5 mmol, 2.5 equiv.) and hydroxylammonium chloride (7.5 mmol, 1.5 equiv.). This mixture was stirred at room temperature until complete consumption of the starting material was achieved. The solvent was removed by evaporation under reduced pressure, and then the residue was dissolved in ethyl acetate, followed by washing with an aqueous solution of hydrochloric acid (1.0 M), a saturated aqueous solution of sodium bicarbonate, and brine. The organic layer was dried over anhydrous sodium sulfate, and the solvents were subsequently removed by evaporation under reduced pressure. The residue obtained was utilized directly in the next step.

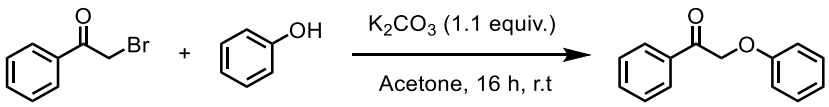
**Step 2:** To a solution of the crude oxime in anhydrous dichloromethane (0.20 M) were added 4-trifluoromethylbenzoyl chloride (1.2 equiv.) and triethylamine (2.0 equiv.) at 0 °C, and the mixture was stirred at room temperature for 20 min. The reaction was then quenched by adding a saturated aqueous solution of sodium bicarbonate and the reaction mixture was extracted three times with ethyl acetate. The

combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the pure product. Many of the *O*-acyl oxime substrates have been previously characterized.




According to the reported literature[6]. In a 100 mL clean and dry round-bottomed flask fitted with a stir bar, add the corresponding alcohols (1.3 equiv.), 4-acetylbenzoic acid (5.0 mmol, 1.0 equiv.) and DMAP (0.2 equiv.). 50 ml of dichloromethane was added to the mixture. DCC (1.2 equiv.) was slowly added to the solution at 0 °C. The mixture was then stirred at 25 °C until consumption of starting material was observed by TLC. At the end of the reaction, the residue was filtered off and dried over anhydrous sodium sulfate, the solvents were subsequently removed by evaporation under reduced pressure. The crude product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the purest product 4-acetylbenzoate as a white solid, which was used in the next step of the synthesis.

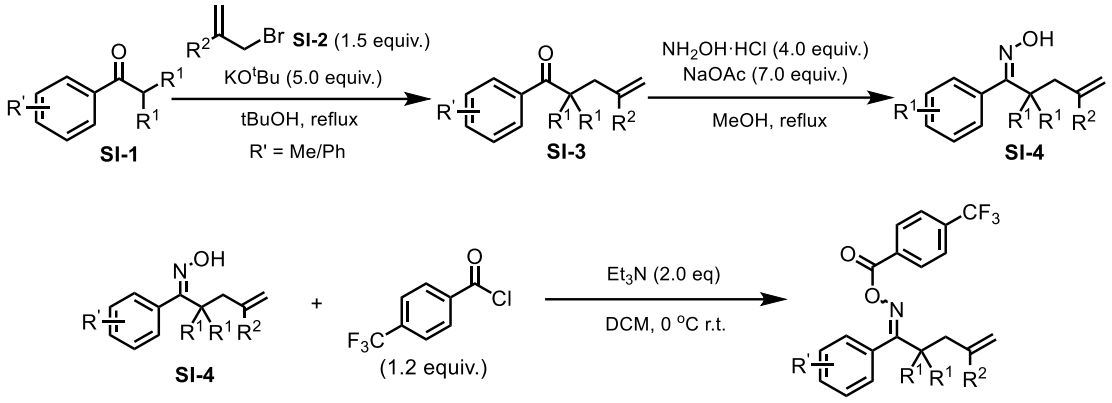
Note: For the rest of the synthesis steps, please refer to the above **method A**.




According to the reported literature[7]. Phenol (5.5 mmol, 1.1 equiv.) and $K_2CO_3$ (6.0 mmol, 1.2 equiv.) in acetone (50 mL) were added to a 250 mL pressure-resistant flask and stirred at room temperature for 20 minutes under argon. To this solution was added $\alpha$-bromoacetophenone (5.0 mmol, 1.0 equiv.), and the resulting mixture was stirred overnight at room temperature, then the suspension was filtered and concentrated under reduced pressure. The residue was dissolved in ethyl acetate and washed with aqueous KOH (5%, 20 mL) and water (20 mL). The organic phase was dried by anhydrous sodium sulfate, the solvents were subsequently removed by evaporation under reduced pressure. The crude product was recrystallized from ethanol to give the purest product 2-phenoxy-1-phenylethan-1-one as a white solid. It was then used in the next step of the synthesis.

## 2.2 General procedure for the preparation chained γ-unsaturated oxime Oxime Esters.

**Method A:**



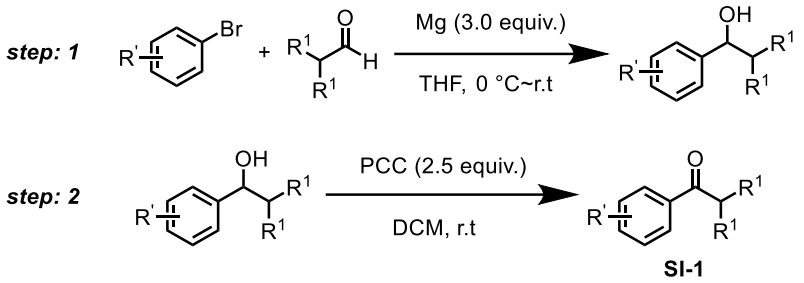

**Step 1:** According to the reported literature.[8, 9, 10] To a solution of corresponding ketone **SI-1** (1.0 equiv.) in anhydrous $^t$BuOH (3.0 mL/mmol) was added $^t$BuOK (5.0 equiv.) and the mixture was stirred at room temperature for 5 minutes. Then, corresponding alkene **SI-2** (1.5 equiv.) was added to the mixture by drop via syringe. The resulting mixture was refluxed at 90 °C and detected by TLC until the starting material was completely consumed. The resulting mixture was cooled to room temperature and $H_2O$ was added. The mixture was extracted with ethyl acetate. The organic extracts were combined, washed with brine, dried with anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by column chromatography on silica gel to give **SI-3**.

**Step 2:** $H_2NOH·HCl$ (4.0 equiv.) and NaOAc (7.0 equiv.) were added to a solution of **SI-3** (1.0 equiv.) in MeOH (2.0 mmol/mL) in a round-bottomed flask which was fitted with a reflux condenser. The mixture was refluxed at 80 °C until consumption of starting material was observed by TLC. After cooling to room temperature, the mixture was diluted with ethyl acetate, washed with brine, dried with anhydrous sodium sulfate and concentrated in vacuum to give **SI-4**, which was used for the next step without further purification.

**Step 3:** To a solution of the crude oxime in anhydrous dichloromethane (0.20 M) were added 4-trifluoromethylbenzoyl chloride (1.2 equiv.) and triethylamine (2.0 equiv.) at 0 °C, and the mixture was stirred at room temperature for 20 min. The reaction was then quenched by adding a saturated aqueous solution of sodium bicarbonate and the reaction mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the pure product. The *O*-acyl oxime substrates have been previously characterized.

## 2.3 The procedures for synthesizing ketones.

**Method A:**



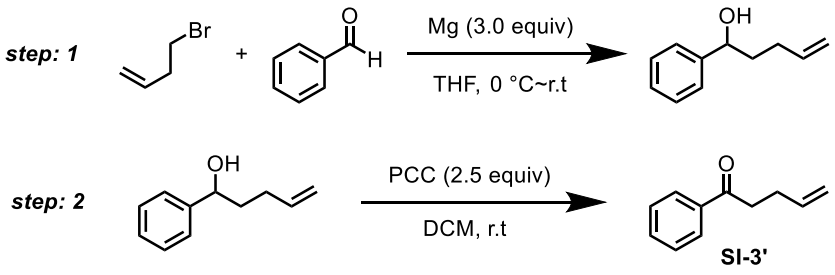

**Step 1:** To a dry 250 mL Schlenk flask with a magnetic stirrer, add magnesium shavings (3.0 equiv.), cover the tube with a rubber stopper. Then bake the bottom of the bottle with a heat gun while pumping air, so that the magnesium chips are fully dry. It was then evacuated and backfilled with argon (cycled 3 times), and 2~3 grains of iodine were added under an inert atmosphere. Dry THF (0.5 M) was added to it, after which the corresponding bromobenzene (1.0 equiv., solid dissolved in THF) was added dropwise and stirred at room temperature to make the corresponding Grignard reagent.

In a dry 250 mL Schlenk bottle equipped with a magnetic stirrer, protected by argon gas, isopropyl aldehyde (1.0 equiv.) was added, and the above Grignard reagent (1.5 equiv.) was added dropwise at 0 °C, followed by stirring of the reaction at room temperature for 36 h. At the end of the reaction, the reaction was quenched by addition of a saturated aqueous ammonium chloride solution, and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give corresponding alcohol.

**Step 2:** To the dichloromethane solution of the alcohol (1.0 equiv.) obtained above, pyridinium chlorochromate (PCC, 2.5 equiv.), diatomaceous earth (2.5 equiv.) was added sequentially. The resulting mixture to was reacted at room temperature and detected by TLC until the starting material was completely consumed. The solvent was removed under reduced pressure on a rotary evaporator and the crude product was purified by flash column chromatography on silica gel to give **SI-1**.

Note: for the rest of the synthesis steps, please refer to the above method A.

**Method B:**



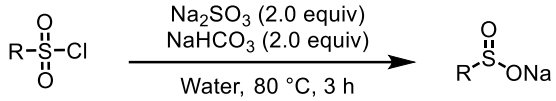
**Step 1:** To a dry 250 mL Schlenk flask with a magnetic stirrer, add magnesium shavings (3.0 equiv.), cover the tube with a rubber stopper. Then bake the bottom of the bottle with a heat gun while pumping air, so that the magnesium chips are fully dry. It was then evacuated and backfilled with argon (cycled 3 times), and 2~3 grains of iodine were added under an inert atmosphere. Dry THF (0.5 M) was added to it, after which the corresponding 4-bromo-1-butene (1.0 equiv.) was added dropwise and stirred at room temperature to make the corresponding Grignard reagent.

In a dry 250 mL Schlenk bottle equipped with a magnetic stirrer, protected by argon gas, benzaldehyde (1.0 equiv.) was added, and the above Grignard reagent (1.5 equiv.) was added dropwise at 0 °C, followed by stirring of the reaction at room temperature for 36 h. At the end of the reaction, the reaction was quenched by addition of a saturated aqueous ammonium chloride solution, and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give corresponding alcohol.

**Step 2:** To the dichloromethane solution of the alcohol (1.0 equiv.) obtained above, pyridinium chlorochromate (PCC, 2.5 equiv.), diatomaceous earth (2.5 equiv.) was added sequentially. The resulting mixture to was reacted at room temperature and detected by TLC until the starting material was completely consumed. The solvent was removed under reduced pressure on a rotary evaporator and the crude product was purified by flash column chromatography on silica gel to give **SI-3'**.

Note: for the rest of the synthesis steps, please refer to the above **method A**.

## 2.4 General experimental procedure for synthesis of sodium sulfinates[11-13].

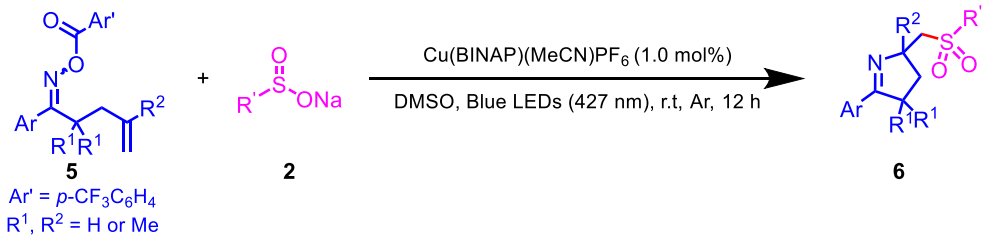



In a clean 50 mL round-bottomed flask with a magnetic stirrer, anhydrous sodium sulfite (10 mmol, 2.0 equiv.), anhydrous sodium bicarbonate (10 mmol, 2.0 equiv.), and 5.0 mL of distilled water (1.0 M). The corresponding sulfuryl chloride (5.0 mmol, 1.0 equiv.) was then added to the above mixture. The resulting mixture was stirred at 80 °C for 3 hours. After cooling to room temperature, the volatiles were removed on a rotary evaporator and the resulting solid was washed repeatedly with anhydrous ethanol. The combined ethanol washings were evaporated under reduced pressure to give the target sodium sulfite as an amorphous solid.

## 2.5 General experimental procedure for synthesis of *β*-Ketosulfones.


Corresponding Oxime Esters **1** (0.30 mmol), sodium sulfinates **2** (0.45 mmol, 1.5 equiv.) and Cu(BINAP)(MeCN)$PF_6$ (1.0 mol%) was sequentially added in a dry Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with argon (3 cycles). Dimethylsulfoxide (DMSO) (3.0 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427 nm) with fans at rt for 10 h. After irradiation, the reaction was then quenched by adding an aqueous solution of hydrochloric acid (1.0 M) and the reaction mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure, and the product was isolated by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the pure target product **3 or 4,** and directly analyzed by $^1$H NMR.

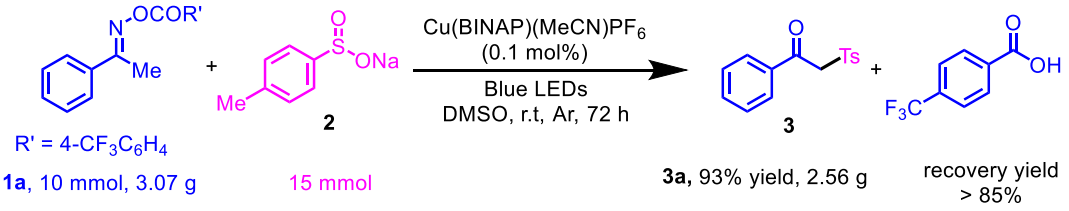
## 2.6 General experimental procedure for synthesis of Imino-Sulfonylation Products.




Corresponding γ-unsaturated oxime Oxime Esters **5** (0.30 mmol), sodium sulfinates **2** (0.60 mmol, 2.0 equiv.) and Cu(BINAP)(MeCN)$PF_6$ (1.0 mol%) was sequentially added in a dry Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with argon (3 cycles). Dimethylsulfoxide (DMSO) (3.0 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427 nm) with fan at rt for 12 h. After irradiation, the reaction was then quenched by adding a saturated salt solution and the reaction mixture was extracted three times with ethyl acetate. The combined organic layers were washed with

brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure, and the product was isolated by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the pure target product **6** or directly analyzed by $^1$H NMR.

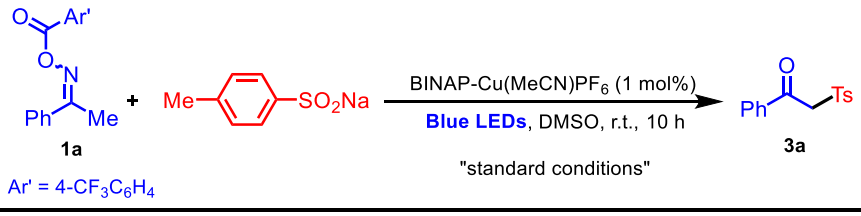
### 2.7 Procedure for the gram-scale synthesis of β-Ketosulfones.




Oxime Esters **1a** (10.0 mmol, 3.07 g), sodium 4-methylbenzoate **2a** (15.0 mmol, 2.67g) and Cu(BINAP)(MeCN)$PF_6$ (0.10 mol%) was sequentially added in a dry 100 mL Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with argon (3 cycles). Degassed dimethylsulfoxide (DMSO) (50 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427 nm) with fan at rt for 36 h. After irradiation, the reaction was then quenched by adding an aqueous solution of hydrochloric acid (1.0 M) and the reaction mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure, and the product was isolated by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product **3a** in 93% yield. Also recovered >85% of 4-trifluoromethylbenzoic acid.

## 3. Optimization of reaction conditions.

### 3.1. Optimization of reaction conditions Keto α-sulfonylation.[a]



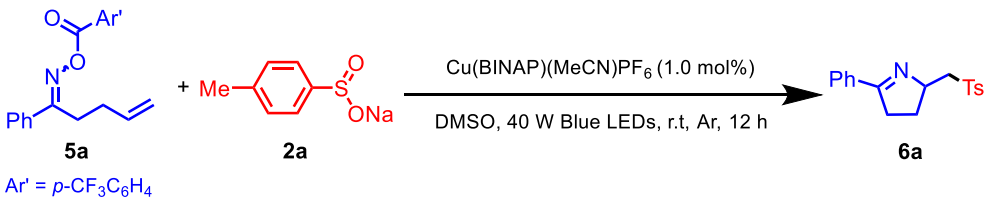

| Entry | Change from the "standard conditions" | **3a** (%)[b] | Conversion of **1a** (%)[b] |
|---|---|---|---|
| 1 | none | 92 (90) | 100 |

| | | | |
|---|---|---|---|
| 2 | no Cu(BINAP)(MeCN)$PF_6$ | 0 | 0 |
| 3 | no hν | 0 | 0 |
| 4 | no BINAP | <1 | 5 |
| 5 | no $Cu(MeCN)_4PF_6$ | 0 | 0 |
| 6 | CuCl, instead of $Cu(MeCN)_4PF_6$ | 84 | 100 |
| 7 | CuBr, instead of $Cu(MeCN)_4PF_6$ | 84 | 100 |
| 8 | CuI, instead of $Cu(MeCN)_4PF_6$ | 81 | 100 |
| 9 | CuCN, instead of $Cu(MeCN)_4PF_6$ | 87 | 100 |
| 9 | $Cu(OTf)_2$, instead of $Cu(MeCN)_4PF_6$ | 57 | 100 |
| 10 | $Cu(OAc)_2$, instead of $Cu(MeCN)_4PF_6$ | 79 | 100 |
| 11 | Dmp and Xantphos, instead of BINAP | 70 | 95 |
| 12 | Xantphos, instead of BINAP | <1 | 5 |
| 13 | DPEphos, instead of BINAP | <1 | 7 |
| 14 | dppe, instead of BINAP | <1 | 6 |
| 15 | dppp, instead of BINAP | <1 | 5 |
| 16 | BINOL, instead of BINAP | <1 | 6 |
| 17 | bpy, instead of BINAP | 5 | 10 |
| 18 | dmp, instead of BINAP | <1 | 6 |
| 19 | 1,10-phen, instead of BINAP | <1 | 8 |
| 20 | DMF, instead of DMSO | 74 | 90 |
| 21 | Acetonitrile, instead of DMSO | 13 | 25 |
| 22 | Dichloromethane, instead of DMSO | 0 | 0 |
| 23 | Toluene, instead of DMSO | trace | 10 |
| 24 | 1,4-Dioxane, instead of DMSO | trace | 15 |
| 25 | Methanol, instead of DMSO | 25 | 99 |
| 26 | $H_2O$, instead of DMSO | trace | <5 |
| 27 | 1-Butanol, instead of DMSO | trace | <5 |
| 28 | Isopropanol, instead of DMSO | trace | <5 |
| 29 | Ethanol, instead of DMSO | trace | <5 |
| 30 | Ethyl acetate, instead of DMSO | <5 | 21 |
| 31 | Anisole, instead of DMSO | 12 | 31 |
| 32 | $V_{H2O}/V_{DMSO}$ (1:1), instead of DMSO | trace | <5 |
| 33 | $V_{H2O}/V_{DMSO}$ (1:4), instead of DMSO | trace | <5 |
| 34 | green LED, instead of blue LED | <1 | 12 |

| | | | |
|---|---|---|---|
| 35 | white LED, instead of blue LED | 73 | 99 |
| 36 | CFL, instead of blue LED | 74 | 99 |
| 37 | OAc, instead of 4-$CF_3C_6H_4$ | 15 | 56 |
| 38 | OPiv, instead of 4-$CF_3C_6H_4$ | 35 | 75 |
| 39 | OBz, instead of 4-$CF_3C_6H_4$ | 75 | 89 |
| 40 | use of 2.0 mol% Cu(BINAP)(MeCN)$PF_6$ | 89 | 100 |
| 41 | 9 h | 78 | 85 |
| 42 | 4CzIPN instead of Cu(BINAP)(MeCN)$PF_6$ | 0 | 0 |
| 43 | *fac*-Ir(ppy)$_3$ instead of Cu(BINAP)(MeCN)$PF_6$ | 0 | 10 |
| 44 | Eosin Y instead of Cu(BINAP)(MeCN)$PF_6$ | <5 | 8 |
| 45 | 4CzIPN (1.0 mol%), $Cu(MeCN)_4PF_6$ (2.0 mol%) instead of Cu(BINAP)(MeCN)$PF_6$ | 10 | 10 |
| 46 | Under an atmosphere of air | <1 | 5 |

[a] Reaction condition: **1** (0.3 mmol), **2** (0.45 mmol, 1.5 equiv.), Cu(BINAP)(MeCN)$PF_6$ (1.0 mol%) and degassed DMSO (3.0 mL) at room temperature under irradiation with 40 W blue LED (427 nm) for 10 h. [b]NMR yield, determined using $^1$H NMR analysis with $CH_2Br_2$ as an internal standard. The value in parentheses is isolated yield. BINAP, racemic 2,2'-bis(dipenylphosphino)-1,1-binaphthalene; Xantphos, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; DMP, 2,9-Dimethyl-1,10-phenanthroline; DPEphos, (Oxydi-2,1-phenylene)bis(diphenylphosphine); Dppe, 1,2-Bis(diphenylphosphino)ethane; Dppp, 1,3-Bis(diphenylphosphino)propane; BINOL, 1,1'-Bi-2-naphthol; bpy, 2,2'-Bipyridine; 1,10-phen, 1,10-Phenanthroline.

### 3.2 Optimization of the reaction conditions for imino sulfonylation.[a]

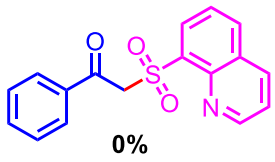



| Entry | Change from the "standard conditions" | **6a**(%)[b] | **5a** Conversion (%)[b] |
|---|---|---|---|
| 1 | none | 74(72) | 100 |
| 2 | no Cu(BINAP)(MeCN)$PF_6$ | 0 | 0 |
| 3 | no hv | 0 | 0 |
| 4 | no BINAP | 5 | 0 |

| | | | |
|---|---|---|---|
| 5 | no $Cu(MeCN)_4PF_6$ | 0 | 0 |
| 6 | DMF, instead of DMSO | trace | 90 |
| 7 | DMA, instead of DMSO | trace | 88 |
| 8 | MeCN, instead of DMSO | trace | 18 |
| 9 | DCE, instead of DMSO | 23 | 30 |
| 10 | Toluene, instead of DMSO | 9 | 35 |
| 11 | THF, instead of DMSO | trace | 30 |
| 12 | $H_2O$, instead of DMSO | trace | <5 |
| 13 | $V_{H2O}/V_{DMSO}$ (1:1), instead of DMSO | trace | <5 |
| 14 | 15 W blue LED, instead of 40 blue LED | 31 | 70 |
| 15 | 24 h, instead of 12 h | 53 | 100 |
| 16 | Use of 1.5 equiv. **2a** | 56 | 92 |

[a] Reaction condition: **5a** (0.3 mmol), **2a** (0.60 mmol, 2.0 equiv.), $Cu(BINAP)(MeCN)PF_6$ (1.0 mol%) and degassed DMSO (3.0 mL) at room temperature under irradiation with 40 W blue LED (427 nm) for 12 h. [b] NMR yield, determined using $^1H$ NMR analysis with $CH_2Br_2$ as an internal standard. The value in parentheses is isolated yield.

## 4. Unsuccessful products.



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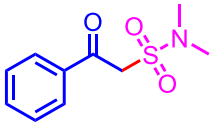

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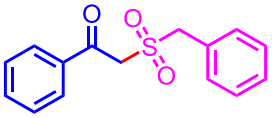

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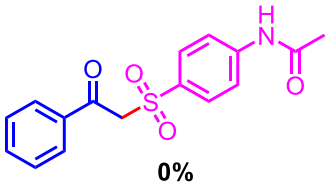

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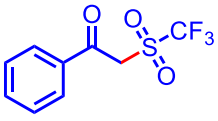

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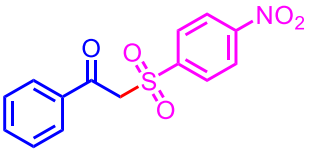

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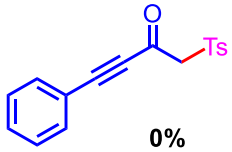

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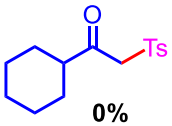

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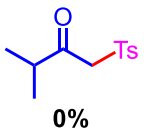

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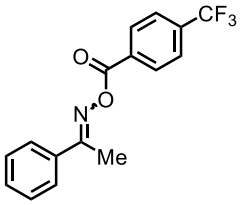
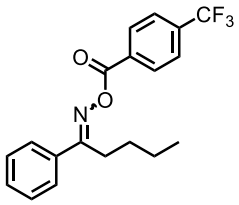
## 5. Characterization data for all compounds.

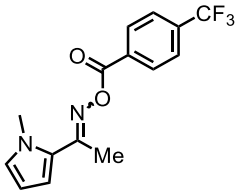
### 5.1 Characteristic data for portion materials.



**1-Phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1a):** White solid (76% yield); m.p: 127~128℃. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.47 (m, 3H), 2.54 (s, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 164.2, 162.6, 134.8 (q, *J* = 32.4 Hz), 134.5, 132.5, 130.9, 130.0, 128.7, 127.1, 125.5 (q, *J* = 3.4 Hz), 123.5 (q, *J* = 271.5 Hz), 14.7. **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.16 (s). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{13}F_3NO_2^+$: 308.0893, found: 308.0895.

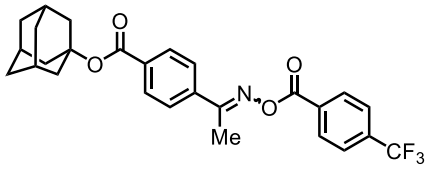


**1-Phenylpentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1y).** White solid (75% yield); m.p: 152~154℃; **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.4 Hz, 2H), 7.83–7.74 (m, 4H), 7.51–7.40 (m, 3H), 3.02–2.95 (m, 2H), 1.70–1.60 (m, 2H), 1.50–1.40 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 168.2, 162.7, 134.7 (q, *J* = 32.6 Hz), 133.8, 132.6, 130.7, 130.0, 128.7, 127.4, 125.7 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 271.2 Hz), 28.9, 28.5, 22.9, 13.8. **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.20 (s). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}F_3NO_2^+$: 350.1362, found: 350.1363.

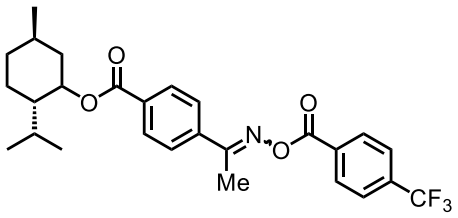


**1-(1-Methyl-1H-pyrrol-2-yl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1v).** White solid (67% yield); m.p: 108~109℃ **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 6.80 (s, 1H), 6.67 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.20–6.16 (m, 1H), 4.02 (s, 3H), 2.45 (s, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 162.7, 157.6, 134.6 (q, *J* = 32.6 Hz), 132.7, 129.9, 129.3, 126.2, 125.6 (q, *J*

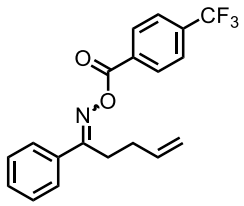
= 3.7 Hz), 123.6 (q, *J* = 271.2 Hz), 116.0, 108.1, 38.8, 14.7. **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.13 (s). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{14}F_3N_2O_2^+$: 311.1002, found: 311.1001.



**(*3S,5S,7S*)-Adamantan-1-yl 4-(1-(((4-(trifluoromethyl)benzoyl)oxy)imino)ethyl)benzoate (1ag).** White solid (42% yield); m.p: 195~196℃. **$^1$H NMR** (500 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 2.55 (s, 3H), 2.28 (s, 6H), 2.24 (s, 3H), 1.73 (dd, *J* = 20.5 Hz, 12.5Hz, 6H). **$^{13}$C NMR** (125 MHz, $CDCl_3$): δ 164.6, 163.4, 162.4, 138.0, 134.8 (q, *J* = 32.5 Hz), 132.3, 130.0, 129.6, 126.9, 125.6 (q, *J* = 3.5 Hz), 123.5 (q, *J* = 271.0 Hz), 81.6, 41.3, 36.2, 30.9, 14.7. **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.17 (s). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{14}F_3N_2O_2^+$: 486.1887, found: 486.1892.

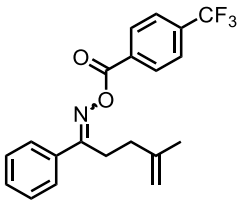


**(*2S,5R*)-2-Isopropyl-5-methylcyclohexyl 4-(1-(((4-(trifluoromethyl)benzoyl)oxy)imino)ethyl)benzoate (1ah).** White solid (47% yield); m.p: 130~131℃. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.0 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 5.02–4.90 (m, 1H), 2.57 (s, 3H), 2.14 (d, *J* = 12.0 Hz, 1H), 2.02–1.89 (m, 1H), 1.74 (d, *J* = 12.0 Hz, 2H), 1.64–1.53 (m, 2H), 1.21–1.08 (m, 2H), 0.96–0.91 (m, 6H), 0.81 (d, *J* = 6.8 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 165.4, 163.4, 162.4, 138.4, 134.9 (q, *J* = 32.7 Hz), 132.9, 132.3, 130.1, 129.8, 127.1, 125.6 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 271.2 Hz), 75.3, 47.2, 40.9, 34.3, 31.4, 26.6, 23.7, 22.0, 20.7, 16.6, 14.8. **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.18 (s). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{27}H_{31}F_3NO_4^+$: 490.2200, found: 490.2218.

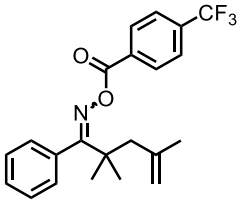


**1-Phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (5a).** Yellowish solid (54% yield); m.p: 69~70℃. **$^1$H NMR** (600 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.4 Hz, 2H), 7.83–7.74 (m, 4H), 7.52–7.41

(m, 3H), 5.91–5.83 (m, 1H), 5.13–5.04 (m, 2H), 3.12–3.04 (m, 2H), 2.42 (dd, *J* =15.0, 7.2 Hz, 2H). **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 167.3, 162.5, 136.3, 134.8 (q, *J* = 32.7 Hz), 133.5, 132.4, 130.8, 129.9, 128.7, 127.4, 125.6 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 271.2 Hz), 116.1, 30.8, 28.1. **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.20 (s). **HRMS** (ESI): m/z [M+H]+ calcd for $C_{19}H_{17}F_3NO_2^+$: 348.1206, found: 348.1207.

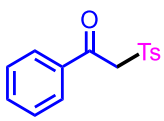



**4-Methyl-1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (5i).** Colorless oil (56% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.4 Hz, 2H), 7.80-7.75 (m, 4H), 7.51-7.43 (m, 3H), 4.80 (d, J = 18.8 Hz, 2H), 3.14-3.10 (m, 2H), 2.35 (dd, *J* = 8.8, 7.6 Hz, 2H), 1.79 (s, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 167.7, 162.6, 143.8, 134.8 (q, *J* = 32.55 Hz), 133.6, 132.5, 130.9, 130.0, 128.8, 127.4, 125.7 (q, *J* = 32.55 Hz), 123.5 (q, *J* = 271.35 Hz), 111.3, 34.6, 27.5, 22.4. **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.19 (s). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{19}F_3NO_2^+$: 362.1362, found: 362.1360.




**2,2,4-Trimethyl-1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (5j).** Colorless oil (45% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.49–7.42 (m, 3H), 7.23–7.18 (m, 2H), 5.00–4.96 (m, 1H), 4.90–4.87 (m, 1H), 2.42 (s, 2H), 1.84 (s, 3H), 1.34 (s, 6H). **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 175.8, 162.1, 141.9, 134.2 (q, *J* = 32.6 Hz), 133.1, 132.3, 129.5, 128.3, 128.0, 126.5, 125.2 (q, *J* = 2.1 Hz), 123.4 (q, *J* = 271.2 Hz), 115.0, 46.7, 41.4, 26.2, 25.1. **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.25 (s). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{23}F_3NO_2^+$: 390.1675, found: 390.1675.

## 5.2 Characteristic data for all products.

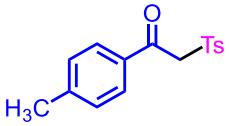



**1-Phenyl-2-tosylethan-1-one (3a)[14].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol),

sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate =5:1~3:1), product **3a** was obtained as a white solid (74.1 mg, 90% yield); mp: 105~106 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.63–7.59 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.72 (s, 2H), 2.43 (s, 3H).

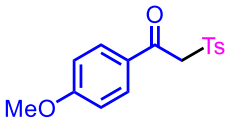
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 188.1, 145.3, 135.7, 135.7, 134.3, 129.8, 129.3, 128.8, 128.5, 63.5, 21.6.




**1-(*p*-Tolyl)-2-tosylethan-1-one (3b)[15].** The title compound was synthesized according to the General Procedure from 1-(*p*-tolyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (96.4 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate =5:1~3:1), product **3b** was obtained as a white solid (77.0 mg, 89% yield); mp: 108~109 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.76 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.69 (s, 2H), 2.42 (s, 3H), 2.41 (s, 3H).

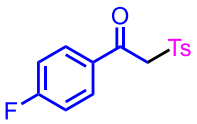
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.6, 145.5, 145.2, 135.8, 133.3, 129.7, 129.5, 129.4, 128.5, 63.5, 21.7, 21.6.




**1-(4-Methoxyphenyl)-2-tosylethan-1-one (3c)[2].** The title compound was synthesized according to the General Procedure from 1-(4-methoxyphenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (101.2 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3c** was obtained as a white solid (75.8 mg, 83% yield); mp: 128~129 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.93 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.67 (s, 2H), 3.87 (s, 3H), 2.43 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 186.3, 164.5, 145.2, 135.8, 131.8, 129.7, 128.8, 128.5, 114.0, 63.5, 55.5, 21.6.

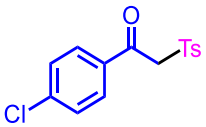



**1-(4-Fluorophenyl)-2-tosylethan-1-one (3d)[2].** The title compound was synthesized according to the General Procedure from 1-(4-fluorophenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (97.6 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate =5:1~3:1), product **3d** was obtained as a white solid (81.6 mg, 93% yield); mp: 136~137 °C.

**$^{1}$H NMR** (600 MHz, $CDCl_3$): δ 8.02–7.98 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.17–7.13 (m, 2H), 4.69 (s, 2H), 2.45 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 186.5, 166.4 (d, *J* = 256.20 Hz), 145.4, 135.6, 132.2 (d, *J* = 9.60 Hz), 132.1 (d, *J* = 2.85 Hz), 129.8, 128.5, 116.0 (d, *J* = 21.90 Hz), 63.6, 21.6.

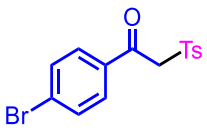
**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -102.78 – -102.85 (m).




**1-(4-Chlorophenyl)-2-tosylethan-1-one (3e)[2].** The title compound was synthesized according to the General Procedure from 1-(4-chlorophenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (102.5 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3e** was obtained as a white solid (86.2 mg, 93% yield); mp: 138~139 °C.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.69 (s, 2H), 2.44 (s, 3H).

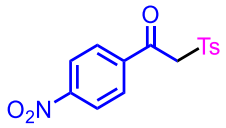
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.0, 145.5, 141.0, 135.6, 134.1, 130.7, 129.9, 129.1, 128.5, 63.7, 21.7.




**1-(4-Bromophenyl)-2-tosylethan-1-one (3f)[2].** The title compound was synthesized according to General Procedure from 1-(4-bromophenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (115.8 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1), product **3f** was obtained as a white solid (85.8 mg, 81% yield); mp: 135~136°C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 4.68 (s, 2H), 2.45 (s, 3H).

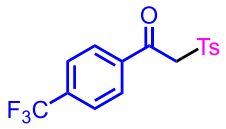
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.2, 145.5, 135.5, 134.5, 132.2, 130.8, 129.9, 129.8, 128.5, 63.7, 21.7.




**1-(4-Nitrophenyl)-2-tosylethan-1-one (3g)[2].** The title compound was synthesized according to the General Procedure from 1-(4-nitrophenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (105.7 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1), product **3g** was obtained as a yellowish solid (62.3 mg, 65% yield); mp: 148~149 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 4.78 (s, 2H), 2.46 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.0, 150.8, 145.8, 139.9, 135.4, 130.5, 130.0, 128.5, 123.9, 64.0, 21.7.



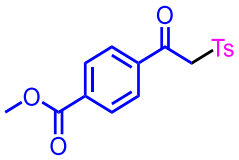

**2-Tosyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3h)[2].** The title compound was synthesized according to the General Procedure from 1-(4-(trifluoromethyl)phenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (112.6 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol,

1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3h** was obtained as a white solid (76.0 mg, 74% yield); mp: 140~141 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 4H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.74 (s, 2H), 2.45 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.5, 145.7, 138.3, 135.5, 135.3 (q, *J* = 32.70 Hz), 129.9, 129.7, 128.5, 125.8 (q, *J* = 3.13 Hz), 123.3 (q, *J* = 271.50 Hz), 63.8, 21.6.

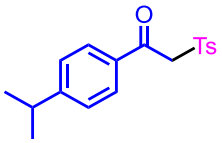
**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.69.




**Methyl 4-(2-tosylacetyl)benzoate (3i)[16].** The title compound was synthesized according to the General Procedure from methyl 4-(1-(((4-(trifluoromethyl)benzoyl)oxy)imino)ethyl)benzoate (109.6 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3i** was obtained as a white solid (91.7 mg, 92% yield); mp: 130~131 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 6.8, 1.6 Hz, 2H), 8.01 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 3.97 (s, 3H), 2.45 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 187.8, 165.9, 145.6, 138.7, 135.5, 134.8, 129.9, 129.8, 129.2, 128.6, 63.8, 52.6, 21.7.

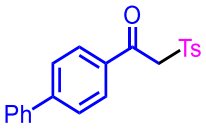



**1-(4-Isopropylphenyl)-2-tosylethan-1-one (3j)[15].** The title compound was synthesized according to the General Procedure from 1-(4-isopropylphenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (104.8 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3j** was obtained as a white solid (86.4 mg, 91% yield); mp: 134~135 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 6.6, 1.8 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 8.4, 2.4 Hz, 4H), 4.69 (s, 2H), 3.00–2.94 (m, 1H), 2.44 (s, 3H), 1.27 (d, *J* = 6.6 Hz, 6H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.6, 156.1, 145.2, 135.8, 133.7, 129.8, 129.6, 128.6, 126.9, 63.5, 34.3, 23.5, 21.7.

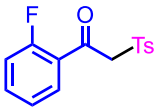
**HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{18}H_{21}O_3S^+$: 317.1206, found: 317.1207.




**1-([1,1'-Biphenyl]-4-yl)-2-tosylethan-1-one (3k)[17].** The title compound was synthesized according to the General Procedure from 1-([1,1'-biphenyl]-4-yl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (115.0 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3k** was obtained as a white solid (95.7 mg, 91% yield); mp: 120~121 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 4.74 (s, 2H), 2.42 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.6, 146.9, 145.3, 139.4, 135.7, 134.4, 129.9, 129.8, 129.0, 128.6, 128.5, 127.3, 127.2, 63.6, 21.6.

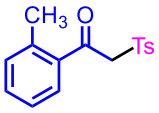



**1-(2-Fluorophenyl)-2-tosylethan-1-one (3l)[2].** The title compound was synthesized according to the General Procedure from 1-(2-fluorophenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (97.6 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3l** was obtained as a white solid (82.4 mg, 94% yield); mp: 65~66 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.58–7.54 (m, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.24–7.22 (m, 1H), 7.12–7.08 (m, 1H), 4.78 (s, 2H), 2.43 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 186.0, 161.8 (d, *J* = 253.95 Hz), 145.2, 136.1, 136.0 (d, *J* = 9.45 Hz), 131.1 (d, *J* = 1.50 Hz), 129.7, 128.5, 124.7 (d, *J* = 3.45 Hz), 124.5 (d, *J* = 11.10 Hz), 116.7 (d, *J* = 23.70 Hz), 67.1, 21.6.

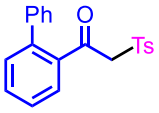
**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -109.37 – -109.44 (m).




**1-(*o*-Tolyl)-2-tosylethan-1-one (3m)[17].** The title compound was synthesized according to General Procedure from 1-(o-tolyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (96.4 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3m** was obtained as a brown oil (81.3 mg, 94% yield).

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.43–7.39 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.25 (q, *J* = 7.2 Hz, 2H), 4.69 (s, 2H), 2.43 (s, 6H).

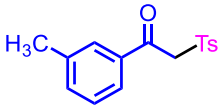
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 190.5, 145.2, 139.9, 136.0, 135.7, 132.7, 132.2, 130.3, 129.8, 128.4, 125.8, 65.5, 21.6, 21.5.




**1-([1,1'-Biphenyl]-2-yl)-2-tosylethan-1-one (3n).** The title compound was synthesized according to the General Procedure from 1-([1,1'-biphenyl]-2-yl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (115.0 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3n** was obtained as a yellow oil (71.5 mg, 68% yield).

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.57–7.47 (m, 4H), 7.45–7.37 (m, 4H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.22–7.17 (m, 2H), 3.91 (s, 2H), 2.42 (s, 3H).

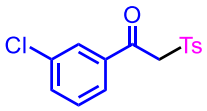
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 194.3, 145.0, 140.6, 139.6, 138.9, 135.9, 131.8, 130.0, 129.6, 129.3, 129.1, 128.9, 128.5, 128.4, 127.6, 66.4, 21.6.



**1-(*m*-Tolyl)-2-tosylethan-1-one (3o)[2].** The title compound was synthesized according to the General Procedure from 1-(m-tolyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (96.4 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3o** was obtained as a white solid (77.9 mg, 90% yield); mp: 98~99 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.71 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 4.71 (s, 2H), 2.43 (s, 3H), 2.39 (s, 3H).

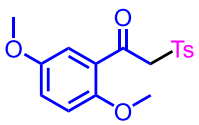
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 188.2, 145.2, 138.7, 135.8, 135.7, 135.1, 129.7, 129.6, 128.7, 128.6, 126.6, 63.5, 21.6, 21.2.




**1-(3-Chlorophenyl)-2-tosylethan-1-one (3p)[2].** The title compound was synthesized according to the General Procedure from 1-(3-chlorophenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (102.5 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3p** was obtained as a white solid (78.7 mg, 85% yield); mp: 129~130 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 9.0, 1.2 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.58–7.56 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.69 (s, 2H), 2.44 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.0, 145.6, 137.2, 135.5, 135.2, 134.1, 130.1, 129.9, 129.1, 128.5, 127.5, 63.6, 21.7.

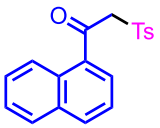



**1-(2,5-Dimethoxyphenyl)-2-tosylethan-1-one (3q).** The title compound was synthesized according to the General Procedure from 1-(2,5-dimethoxyphenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (110.2 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3q** was obtained as a white solid (93.3 mg, 93% yield); mp: 99~100 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 3.0 Hz, 1H), 7.06 (dd, *J* = 9.6, 3.6 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 4.94 (s, 2H), 3.84 (s, 3H), 3.76 (s, 3H), 2.42 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 188.7, 153.6, 153.5, 144.7, 136.7, 129.5, 128.5, 126.2, 122.3, 114.0, 113.2, 67.3, 56.0, 55.8, 21.6.

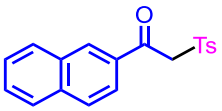
**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{19}O_5S^+$: 335.0948, found: 335.0947.




**1-(Naphthalen-1-yl)-2-tosylethan-1-one (3r)[14, 15].** The title compound was synthesized according to the General Procedure from 1-(naphthalen-1-yl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (107.2 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3r** was obtained as a pale-yellow solid (87.6 mg, 90% yield); mp: 119~120 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 8.4 Hz, 1H), 8.04–8.00 (m, 2H), 7.88–7.86 (m, 1H), 7.74–7.71 (m, 2H), 7.60–7.52 (m, 2H), 7.51–7.47 (m, 1H), 7.27–7.25 (m, 2H), 4.84 (s, 2H), 2.41 (s, 3H).

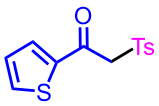
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 190.5, 145.2, 135.8, 134.6, 133.9, 133.3, 130.8, 130.3, 129.8, 128.7, 128.5, 126.8, 125.5, 124.2, 66.3, 21.6.




**1-(Naphthalen-2-yl)-2-tosylethan-1-one (3s)[15].** The title compound was synthesized according to the General Procedure from 1-(naphthalen-2-yl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (107.2 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3s** was obtained as a white solid (92.5 mg, 95% yield); mp: 149~150 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.96 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.88 (dd, *J* = 8.4, 2.8 Hz, 2H), 7.79–7.76 (m, 2H), 7.66–7.62 (m, 1H), 7.60–7.55 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.84 (s, 2H), 2.40 (s, 3H).

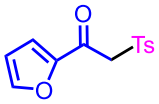
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 188.0, 145.4, 136.0, 135.7, 133.1, 132.3, 132.2, 129.9, 129.8, 129.3, 128.8, 128.6, 127.8, 127.1, 123.9, 63.8, 21.7.




**1-(Thiophen-2-yl)-2-tosylethan-1-one (3t)[14].** The title compound was synthesized according to the General Procedure from 1-(thiophen-2-yl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (94.0 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3t** was obtained as a Brown solid (79.9 mg, 95% yield); mp: 138~139 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, $J$ = 4.0 Hz, 1H), 7.77–7.75 (m, 3H), 7.34 (d, $J$ = 8.0 Hz, 2H), 7.18–7.16 (m, 1H), 4.61 (s, 2H), 2.45 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 180.3, 145.5, 143.2, 136.4, 135.5, 135.2, 129.9, 128.7, 128.6, 64.7, 21.7.

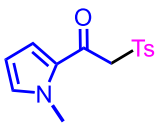



**1-(Furan-2-yl)-2-tosylethan-1-one (3u).** The title compound was synthesized according to the General Procedure from 1-(furan-2-yl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (89.2 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3u** was obtained as a white solid (74.5 mg, 94% yield); mp: 128~129 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, $J$ = 8.4 Hz, 1H), 7.61 (d, $J$ = 0.8 Hz, 1H), 7.35–7.33 (m, 3H), 6.58 (q, $J$ = 1.6 Hz, 1H), 4.57 (s, 2H), 2.44 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 175.8, 151.9, 148.0, 145.3, 135.7, 129.8, 128.5, 120.3, 113.1, 63.6, 21.6.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{13}O_4S^+$: 265.0529; found: 265.0530.



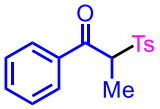

**1-(1-Methyl-1H-pyrrol-2-yl)-2-tosylethan-1-one (3v).** The title compound was synthesized according to the General Procedure from 1-(furan-2-yl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl)

oxime (89.2 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3v** was obtained as a white solid (79.0 mg, 95% yield); mp: 88~89 °C.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 3.2 Hz, 2H), 6.11 (t, *J* = 3.6 Hz, 1H), 4.85 (s, 2H), 3.75 (s, 3H), 2.38 (s, 3H).

**$^{13}$C NMR** (150 MHz, DMSO-$d_6$): δ 177.1, 144.5, 136.8, 133.9, 130.2, 129.7, 128.1, 123.1, 108.6, 63.4, 37.1, 21.2.

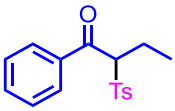
**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}NO_3S^+$: 278.0845, found: 278.0845.




**1-Phenyl-2-tosylpropan-1-one (3w)[2].** The title compound was synthesized according to the General Procedure from 1-phenylpropan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (96.4 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3w** was obtained as a white solid (79.5 mg, 92% yield); mp: 113~114 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.62–7.59 (m, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.16 (q, *J* = 6.8 Hz, 1H), 2.43 (s, 3H), 1.56 (d, *J* = 7.2 Hz, 3H).

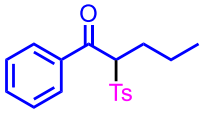
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 192.6, 145.3, 136.2, 134.0, 133.0, 129.8, 129.5, 129.1, 128.7, 64.9, 21.6, 13.2.




**1-Phenyl-2-tosylbutan-1-one (3x)[2].** The title compound was synthesized according to the General Procedure from 1-phenylbutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (100.6 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3x** was obtained as a white solid (82.6 mg, 91% yield); mp: 77~78 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.99–7.97 (m, 2H), 7.65 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.63–7.58 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.02–4.98 (m, 1H), 2.43 (s, 3H), 2.19–2.02 (m, 2H), 0.91–0.87 (m, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 192.7, 145.3, 137.4, 133.9, 133.4, 129.8, 129.4, 129.0, 128.7, 71.4, 22.0, 21.6, 11.5.

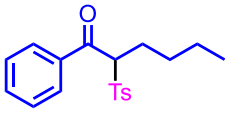



**1-Phenyl-2-tosylpentan-1-one (3y).** The title compound was synthesized according to the General Procedure from 1-phenylpentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (104.8 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3y** was obtained as a white solid (82.6 mg, 87% yield); mp: 91~92 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.0 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 5.09 (dd, *J* = 10.0, 4.4 Hz, 1H), 2.41 (s, 3H), 2.12–1.98 (m, 2H), 1.26–1.22 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 192.7, 145.2, 137.2, 133.8, 133.4, 129.7, 129.4, 128.9, 128.7, 69.7, 30.2, 21.6, 20.2, 13.7.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{20}O_3S^+$: 317.1206; found: 317.1206.

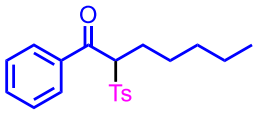



**1-Phenyl-2-tosylhexan-1-one (3z).** The title compound was synthesized according to the General Procedure from 1-phenylhexan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (109.0 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3z** was obtained as a white solid (88.2 mg, 89% yield); mp: 94~95 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.97–7.95 (m, 2H), 7.65–7.64 (m, 2H), 7.62–7.59 (m, 1H), 7.49–7.47 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 5.05 (dt, *J* = 10.9, 2.7 Hz, 1H), 2.43 (s, 3H), 2.12–2.08 (m, 1H), 2.06–1.99 (m, 1H), 1.29–1.13 (m, 4H), 0.80 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 192.8, 145.3, 137.3, 133.9, 133.4, 129.8, 129.5, 129.0, 128.7, 70.0, 29.1, 28.1, 22.4, 21.7, 13.6.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{23}O_3S^+$: 331.1362; found: 331.1364.

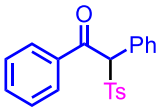



**1-Phenyl-2-tosylheptan-1-one (3aa).** The title compound was synthesized according to the General Procedure from 1-phenylheptan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (113.2 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3aa** was obtained as a colorless oil (93.0 mg, 90% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.65–7.64 (m, 2H), 7.62–7.59 (m, 1H), 7.49–7.46 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.05 (dd, *J* = 10.8, 3.6 Hz, 1H), 2.42 (s, 3H), 2.12–2.07 (m, 1H), 2.06 – 1.99 (m, 1H), 1.26–1.16 (m, 6H), 0.82–0.74 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 192.8, 145.2, 137.3, 133.9, 133.4, 129.8, 129.4, 128.9, 128.7, 70.0, 31.4, 28.3, 26.6, 22.1, 21.6, 13.8.

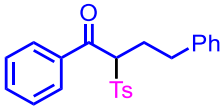
**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{25}O_3S^+$: 345.1519; found: 345.1519.




**1,2-Diphenyl-2-tosylethan-1-one (3ab)[18].** The title compound was synthesized according to the General Procedure from 1,2-diphenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (115.0 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3ab** was obtained as a white solid (55.7 mg, 53% yield); mp: 149~150 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.88–7.86 (m, 2H), 7.53–7.50 (m, 3H), 7.41–7.40 (m, 2H), 7.36–7.33 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.13 (s, 1H), 2.40 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 190.7, 145.0, 136.1, 133.9, 130.4, 130.3, 129.5, 129.0, 128.9, 128.8, 128.7, 128.6, 76.1, 21.6.

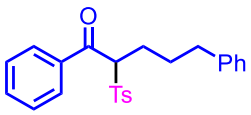


**1,4-Diphenyl-2-tosylbutan-1-one (3ac).** The title compound was synthesized according to the General Procedure from 1,4-diphenylbutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (123.4 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3ac** was obtained as a white solid (80.6 mg, 71% yield); mp: 111~112 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.6 Hz, 3H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.22–7.17 (m, 3H), 7.00 (d, *J* = 7.7 Hz, 2H), 5.02 (dd, *J* = 10.2, 3.4 Hz, 1H), 2.70–2.62 (m, 1H), 2.49–2.39 (m, 6H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 192.4, 145.3, 139.4, 137.0, 134.0, 133.3, 129.7, 129.5, 129.1, 128.7, 128.6, 128.5, 126.5, 69.0, 32.6, 29.7, 21.7.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{23}O_3S^+$: 379.1362; found: 379.1363.

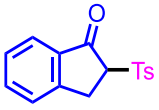



**1,5-Diphenyl-2-tosylpentan-1-one (3ad).** The title compound was synthesized according to the General Procedure from 1,5-diphenylpentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (127.6 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3ad** was obtained as a colorless oil (89.5 mg, 76% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.61 (dd, *J* = 6.6, 1.8 Hz, 2H), 7.59–7.56 (m, 1H), 7.46–7.43 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.22–7.20 (m, 2H), 7.16–7.13 (m, 1H), 7.04–7.03 (m, 2H), 5.06 (dd, *J* = 10.4, 4.0 Hz, 1H), 2.58–2.51 (m, 2H), 2.42 (s, 3H), 2.17–2.07 (m, 2H), 1.57–1.50 (m, 2H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 192.6, 145.3, 141.1, 137.1, 133.9, 133.3, 129.7, 129.5, 128.9, 128.7, 128.4, 128.2, 126.0, 69.8, 35.6, 28.8, 28.1, 21.6.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{25}O_3S^+$: 393.1519; found: 393.1519.

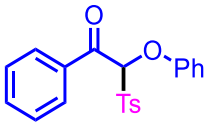



**2-Tosyl-2,3-dihydro-1H-inden-1-one (3ae)[19].** The title compound was synthesized according to the General Procedure from 2,3-dihydro-1H-inden-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (95.8 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$

(2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3ae** was obtained as a white solid (79.0 mg, 92% yield); mp: 133~134 °C.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): δ 7.77 (d, $J$ = 8.4 Hz, 2H), 7.72 (t, $J$ = 7.8 Hz, 1H), 7.64 (t, $J$ = 7.2 Hz, 2H), 7.46 (d, $J$ = 8.0 Hz, 3H), 4.91 (dd, $J$ = 6.6, 5.0 Hz, 1H), 3.52–3.50 (m, 2H), 2.42 (s, 3H).

**$^{13}$C NMR** (100 MHz, DMSO-$d_6$): δ 194.8, 152.3, 144.9, 136.0, 135.5, 135.0, 129.8, 128.7, 128.2, 126.9, 123.9, 67.8, 28.2, 21.1.

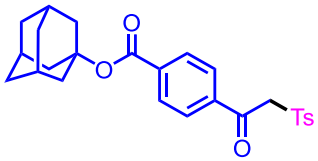



**2-Phenoxy-1-phenyl-2-tosylethan-1-one (3af).** The title compound was synthesized according to the General Procedure from 2-phenoxy-1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (119.8 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3af** was obtained as a white solid (93.4 mg, 85% yield); mp: 133~134 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.15 (d, $J$ = 7.2 Hz, 2H), 7.80 (d, $J$ = 8.0 Hz, 2H), 7.63 (t, $J$ = 7.4 Hz, 1H), 7.50 (t, $J$ = 7.8 Hz, 2H), 7.34 (d, $J$ = 8.4 Hz, 2H), 7.22 (t, $J$ = 8.0 Hz, 2H), 7.01 (t, $J$ = 7.4 Hz, 1H), 6.88 (d, $J$ = 8.0 Hz, 2H), 6.28 (s, 1H), 2.44 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 189.3, 156.9, 146.0, 134.7, 134.5, 132.6, 130.0, 129.9, 129.8, 129.7, 128.7, 123.6, 116.4, 94.4, 21.7.

**HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{21}H_{18}O_4SNa^+$: 389.0818, found: 389.0816.



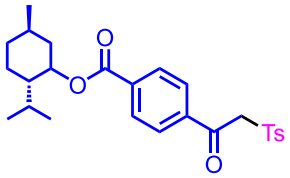

**Adamantan-1-yl 4-(2-tosylacetyl)benzoate (3ag).** The title compound was synthesized according to the General Procedure from 2,3-dihydro-1H-inden-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (95.8 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum

ether/ethyl acetate = 5:1), product **3ag** was obtained as a white solid (65.2 mg, 48% yield); mp: 160~161 °C.

**$^1$H NMR** (600 MHz, DMSO-$d_6$): δ 8.03 (d, $J$ = 5.6 Hz, 2H), 7.96 (d, $J$ = 6.0 Hz, 2H), 7.76 (d, $J$ = 5.2 Hz, 2H), 7.42 (d, $J$ = 5.6 Hz, 2H), 5.34 (s, 2H), 2.40 (s, 3H), 2.21 (s, 6H), 2.19 (s, 3H), 1.67 (s, 6H).

**$^{13}$C NMR** (150 MHz, DMSO-$d_6$): δ 189.0, 163.6, 144.7, 138.7, 136.5, 135.5, 129.6, 129.2, 129.1, 128.1, 81.3, 62.7, 40.8, 35.5, 30.3.

**HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{28}O_5SNa^+$: 475.1550, found: 475.1548.

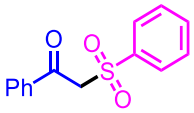



**(*2S,5R*)-2-Isopropyl-5-methylcyclohexyl 4-(2-tosylacetyl)benzoate (3ah).** The title compound was synthesized according to the General Procedure from *L*-2-isopropyl-5-methylcyclohexyl 4-(1-(((4-(trifluoromethyl)benzoyl)oxy)imino)ethyl)benzoate (146.3 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **3ah** was obtained as a white solid (121.9 mg, 89% yield); mp: 99~100 °C.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): δ 8.06 (q, $J$ = 8.4 Hz, 4H), 7.78 (d, $J$ = 8.0 Hz, 2H), 7.42 (d, $J$ = 8.0 Hz, 2H), 5.37 (s, 2H), 4.91–4.85 (m, 1H), 2.39 (s, 3H), 2.01 (d, $J$ = 12 Hz, 1H), 1.93–1.81 (m, 1H), 1.68 (d, $J$ = 11.6 Hz, 2H), 1.60–1.46 (m, 2H), 1.20–1.08 (m, 2H), 0.90 (t, $J$ = 6.8 Hz, 6H), 0.75 (d, $J$ = 7.2 Hz, 3H).

**$^{13}$C NMR** (150 MHz, DMSO-$d_6$): δ 188.9, 164.3, 144.6, 139.0, 136.4, 134.2, 129.6, 129.3, 129.2, 128.1, 74.8, 62.7, 46.5, 40.4, 33.7, 30.8, 26.2, 23.2, 21.8, 21.0, 20.4, 16.4.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{33}O_5S^+$: 457.2043, found: 457.2041.

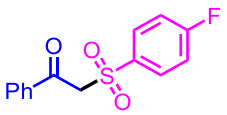



**1-Phenyl-2-(phenylsulfonyl)ethan-1-one (4a)[12].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium sodium benzenesulfinate (74.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$

(2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4a** was obtained as a white solid (74.7 mg, 95% yield); mp: 94~95 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.94–7.93 (m, 2H), 7.90–7.89 (m, 2H), 7.67–7.64 (m, 1H), 7.63–7.60 (m, 1H), 7.56–7.53 (m, 2H), 7.49–7.46 (m, 2H), 4.74 (s, 2H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.9, 138.7, 135.7, 134.3, 134.2, 129.2, 129.1, 128.8, 128.5, 63.3.

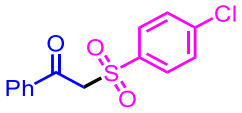



**2-((4-Fluorophenyl)sulfonyl)-1-phenylethan-1-one (4b)[2].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium 4-fluorobenzenesulfinate (82.0 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4b** was obtained as a white solid (76.1 mg, 91% yield); mp: 152~153 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.94–7.90 (m, 4H), 7.64–7.62 (m, 1H), 7.49 (t, $J$ = 8.1 Hz, 2H), 7.23–7.20 (m, 2H), 4.74 (s, 2H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 188.0, 166.1 (d, $J$ = 255.90 Hz), 135.6, 134.7 (d, $J$ = 3.0 Hz), 134.5, 131.6 (d, $J$ = 9.6 Hz), 129.2, 128.9, 116.5 (d, $J$ = 22.7 Hz), 63.4.

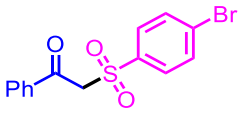
**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -102.67 – -102.81 (m).




**2-((4-Chlorophenyl)sulfonyl)-1-phenylethan-1-one (4c)[2].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium 4-chlorobenzenesulfinate (89.4 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4c** was obtained as a white solid (81.4 mg, 92% yield); mp: 134~135 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.93 (dd, $J$ = 8.4, 1.2 Hz, 2H), 7.84–7.82 (m, 2H), 7.65–7.62 (m, 1H), 7.53–7.48 (m, 4H), 4.75 (s, 2H).

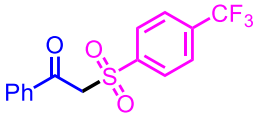
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.9, 141.0, 137.0, 135.5, 134.5, 130.1, 129.5, 129.2, 128.9, 63.2.




**2-((4-Bromophenyl)sulfonyl)-1-phenylethan-1-one (4d)[2, 14].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium 4-bromobenzenesulfinate (109.4 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **4d** was obtained as a white solid (90.6 mg, 89% yield); mp: 103~104 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.76–7.74 (m, 2H), 7.69–7.67 (m, 2H), 7.65–7.62 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 4.75 (s, 2H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.9, 137.6, 135.5, 134.5, 132.5, 130.2, 129.7, 129.2, 128.9, 63.2.

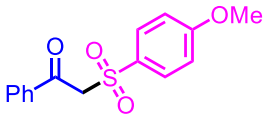



**1-Phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethan-1-one (4e)[2].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium 4-(trifluoromethyl)benzenesulfinate (104.5 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4e** was obtained as a white solid (83.7 mg, 85% yield); mp: 110~111 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.93 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.66–7.63 (m, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 4.79 (s, 2H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.7, 142.1, 135.8 (q, *J* = 32.85 Hz), 134.6, 130.5, 129.4, 129.2, 129.0, 126.3 (q, *J* = 3.45 Hz), 123.0 (q, *J* = 271.50 Hz), 63.0.

**$^{19}$F NMR** (376 MHz, CDCl3): δ -63.65.

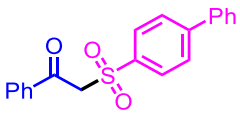



**2-((4-Methoxyphenyl)sulfonyl)-1-phenylethan-1-one (4f)[2].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium 4-methoxybenzenesulfinate (87.4 mg, 0.45 mmol, 1.5 equiv.), and

Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4f** was obtained as a white solid (82.7 mg, 95% yield); mp: 104~105 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 2H), 2.43 (s, 3H).

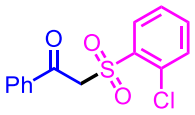
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 188.1, 145.3, 135.8, 135.7, 134.3, 129.8, 129.3, 128.8, 128.5, 63.5, 21.6.




**2-([1,1'-Biphenyl]-4-ylsulfonyl)-1-phenylethan-1-one (4g)[19].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium [1,1'-biphenyl]-4-sulfinate (108.1 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4g** was obtained as a white solid (85.8 mg, 85% yield); mp: 100~101 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.97–7.94 (m, 4H), 7.75–7.72 (m, 2H), 7.63–7.59 (m, 3H), 7.51–7.47 (m, 4H), 7.45–7.41 (m, 1H), 4.78 (s, 2H).

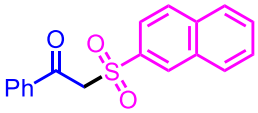
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 188.1, 147.2, 139.0, 137.2, 135.8, 134.4, 129.3, 129.1, 129.0, 128.9, 128.7, 127.8, 127.4, 63.6.




**2-((2-Chlorophenyl)sulfonyl)-1-phenylethan-1-one (4h)[2].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium 2-chlorobenzenesulfinate (89.4 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4h** was obtained as a colorless oil (77.8 mg, 88% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.06–8.04 (m, 1H), 7.95–7.83 (m, 2H), 7.63–7.56 (m, 3H), 7.50–7.42 (m, 3H), 5.06 (s, 2H).

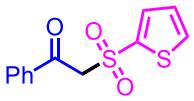
**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.8, 136.4, 135.7, 135.1, 134.4, 132.6, 132.0, 131.8, 129.1, 128.8, 127.4, 60.9.



**2-(Naphthalen-2-ylsulfonyl)-1-phenylethan-1-one (4i)[2].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium naphthalene-2-sulfinate (96.4 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4i** was obtained as a white solid (88.5 mg, 95% yield); mp: 129~130 ºC.

**$^{1}$H NMR** (500 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.98–7.90 (m, 5H), 7.88–7.86 (m, 1H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.62–7.56 (m, 2H), 7.44 (t, *J* = 7.3 Hz, 2H), 4.82 (s, 2H).

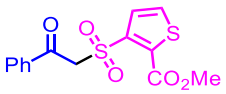
**$^{13}$C NMR** (125 MHz, $CDCl_3$): δ 188.0, 135.7, 135.6, 135.5, 134.3, 132.0, 130.6, 129.6, 129.5, 129.4, 129.2, 128.8, 128.0, 127.7, 122.9, 63.5.



**1-Phenyl-2-(thiophen-2-ylsulfonyl)ethan-1-one (4j)[14].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium thiophene-2-sulfinate (76.6 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4j** was obtained as a white solid (71.1 mg, 89% yield); mp: 137~138 ºC.

**$^{1}$H NMR** (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.74–7.73 (m, 1H), 7.70–7.69 (m, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.14–7.12 (m, 1H), 4.83 (s, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$): δ 187.8, 139.4, 135.6, 135.4, 135.0, 134.4, 129.2, 128.9, 127.9, 64.3.



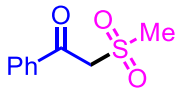
**Methyl 3-((2-oxo-2-phenylethyl)sulfonyl)thiophene-2-carboxylate (4k).** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium 2-(methoxycarbonyl)thiophene-3-

sulfinate (102.7 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4k** was obtained as a colourless oil (88.6 mg, 91% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 1H), 7.60 (d, *J* = 4.8 Hz, 1H), 7.53 (dd, *J* = 5.6, 0.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 5.36 (s, 2H), 3.96 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 188.5, 160.3, 143.2, 135.8, 134.4, 134.3, 131.7, 129.8, 129.0, 128.8, 61.9, 53.2.

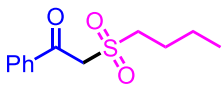
**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{17}O_3S^+$: 325.0199, found: 325.0199.




**2-(Methylsulfonyl)-1-phenylethan-1-one (4l)[2].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium methanesulfinate (46.0 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4l** was obtained as a white solid (57.7 mg, 97% yield); mp: 108~109 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 8.01–7.99 (m, 2H), 7.67–7.64 (m, 1H), 7.54–7.51 (m, 2H), 4.62 (s, 2H), 3.15 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 189.2, 135.6, 134.7, 129.2, 129.0, 61.2, 41.8.

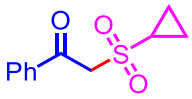



**2-(Butylsulfonyl)-1-phenylethan-1-one (4m).** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium butane-1-sulfinate (64.9 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4m** was obtained as a white solid (69.9 mg, 97% yield); mp: 81~82 °C.

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 8.02–8.01 (m, 2H), 7.67–7.64 (m, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 4.57 (s, 2H), 3.27–3.24 (m, 2H), 1.91–1.85 (m, 2H), 1.54–1.47 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$): δ 189.3, 135.7, 134.6, 129.3, 129.0, 59.5, 53.4, 23.8, 21.6, 13.5.

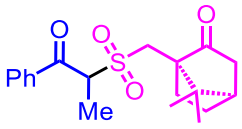
**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{17}O_3S^+$: 241.0893, found: 241.0895.



**2-(Cyclopropylsulfonyl)-1-phenylethan-1-one (4n)[2].** The title compound was synthesized according to the General Procedure from 1-phenylethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (92.2 mg, 0.3 mmol), sodium cyclopropanesulfinate (57.6 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4n** was obtained as a white solid (63.9 mg, 95% yield); mp: 65~66 °C.

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 8.02 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 4.65 (s, 2H), 2.79–2.73 (m, 1H), 1.29–1.26 (m, 2H), 1.11–1.07 (m, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$): δ 188.8, 135.7, 134.5, 129.2, 128.9, 61.0, 30.8, 5.5.

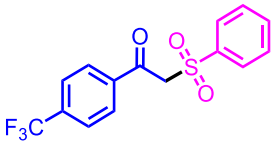


**(*1S*,*4R*)-7,7-dimethyl-1-(((1-oxo-1-phenylpropan-2-yl)sulfonyl)methyl)bicyclo[2.2.1]heptan-2-one (4o).** The title compound was synthesized according to the General Procedure from 1-phenylpropan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (96.4 mg, 0.3 mmol), sodium ((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfinate (107.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4o** was obtained as a colorless oil (63.8 mg, 61% yield, dr = 1/1.2).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.03 (t, *J* = 5.2 Hz, 4H), 7.63–7.60 (m, 2H), 7.54–7.50 (m, 4H), 5.25 (q, *J* = 4.8 Hz, 1H), 5.19 (q, *J* = 4.8 Hz, 1.2H), 3.68 (d, *J* = 10.0 Hz, 1H), 3.61 (d, *J* = 9.6 Hz, 1.2H), 3.06 (d, *J* = 9.6 Hz, 1.2H), 2.95 (d, *J* = 10.0 Hz, 1H), 2.43–2.37 (m, 2.4H), 2.36–2.31 (m, 2H), 2.11–2.09 (m, 2H), 2.03–1.98 (m, 2.4H), 1.96 (d, *J* = 12.4 Hz, 1.2H), 1.90 (d, *J* = 12.4 Hz, 1H), 1.85 (dd, *J* = 6.4, 3.2 Hz, 1.2H), 1.82 (d, *J* = 4.8 Hz, 4H), 1.75 (d, *J* = 4.8 Hz, 3H), 1.44–1.42 (m, 2.6H), 1.07 (s, 3H), 1.04 (s, 3.6H), 0.90 (s, 3.6H), 0.85 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 214.9, 214.7, 194.2, 193.8, 136.0, 135.8, 134.2, 134.0, 129.2, 129.0, 128.9, 128.8, 65.5, 65.3, 59.0, 58.5, 48.4, 48.3, 48.1, 46.1, 42.8, 42.6, 42.5, 42.4, 27.0, 26.9, 25.7, 24.9, 19.9, 19.8, 19.7, 14.1, 12.5.

**HRMS** (ESI): m/z $[M-H]^+$ calcd for $C_{19}H_{25}O_4S^+$: 349.1468; found: 349.1468.

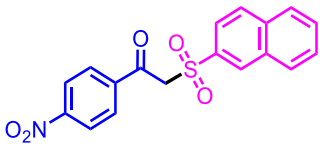


**2-(Phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (4p)[20].** The title compound was synthesized according to the General Procedure from 1-(4-(trifluoromethyl)phenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (112.6 mg, 0.3 mmol), sodium sodium benzenesulfinate (73.9 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **4p** was obtained as a white solid (76.8 mg, 78% yield); mp: 101~102 ºC.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 4.78 (s, 2H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 187.3, 138.4, 138.2 135.4 (q, *J* = 32.7 Hz), 134.4, 129.7, 129.3, 128.5, 125.9 (q, *J* = 3.75 Hz), 123.3 (q, *J* = 271.5 Hz), 63.7.

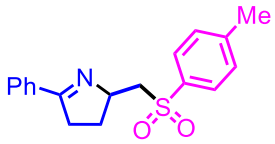
**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.32.



**2-(Naphthalen-2-ylsulfonyl)-1-(4-nitrophenyl)ethan-1-one (4q)[20].** The title compound was synthesized according to the General Procedure from 1-(4-nitrophenyl)ethan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (105.7 mg, 0.3 mmol), sodium naphthalene-2-sulfinate (96.4 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **4q** was obtained as a Yellowish solid (59.7 mg, 56% yield); mp: 197~198 ºC.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.30 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.96 (t, *J* = 7.8 Hz, 2H), 7.85 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.74–7.68 (m, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 4.85 (s, 2H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 186.9, 150.8, 140.0, 135.6, 135.2, 132.0, 130.7, 130.4, 129.9, 129.8, 129.6, 128.1, 128.0, 124.0, 122.6, 64.1.

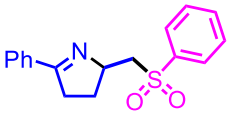



**5-Phenyl-2-(tosylmethyl)-3,4-dihydro-2H-pyrrole (6a)**. The title compound was synthesized according to the General Procedure from 1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (104.2 mg, 0.3 mmol), sodium 4-methylbenzoate (106.9 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6a** was obtained as a white solid (67.7 mg, 72% yield); m.p: 121~122 °C.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 6.8 Hz, 2H), 7.45–7.41 (m, 1H), 7.37 (t, *J* = 7.2 Hz, 4H), 4.55–4.52 (m, 1H), 3.79 (dd, *J* = 14.4, 4.0 Hz, 1H), 3.18 (dd, *J* = 14.0, 9.6 Hz, 1H), 3.08–3.04 (m, 1H), 2.98–2.91 (m, 1H), 2.45 (s, 3H), 2.45–2.39 (m, 1H), 1.97–1.91 (m, 1H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 174.1, 144.6, 136.9, 133.8, 130.8, 129.8, 128.4, 128.2, 127.7, 67.5, 61.6, 35.4, 28.8, 21.6.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{20}NO_2S^+$: 314.1209; found: 314.1208.

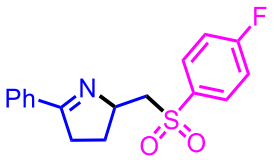



**5-Phenyl-2-((phenylsulfonyl)methyl)-3,4-dihydro-2H-pyrrole (6b)**. The title compound was synthesized according to the General Procedure from 1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (104.2 mg, 0.3 mmol), sodium benzoate (98.5 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6b** was obtained as a orange solid (62.0 mg, 69% yield); m.p: 89~90 °C.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.71–7.65 (m, 3H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.44–7.35 (m, 3H), 4.59–4.53 (m, 1H), 3.83–3.78 (m, 1H), 3.24–3.18 (m, 1H), 3.12–3.04 (m, 1H), 2.98–2.89 (m, 1H), 2.47–2.38 (m, 1H), 1.99–1.89 (m, 1H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 173.5, 139.9, 133.7, 133.6, 130.8, 129.2, 128.4, 128.2, 127.7, 67.5, 61.6, 35.4, 28.8.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{18}NO_2S^+$: 300.1053; found: 300.1053.



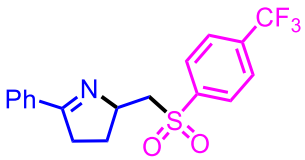

**5-Phenyl-2-((phenylsulfonyl)methyl)-3,4-dihydro-2H-pyrrole (6c)**. The title compound was synthesized according to the General Procedure from 1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (104.2 mg, 0.3 mmol), sodium 4-fluorobenzenesulfinate (109.3 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6c** was obtained as a yellowish solid (53.3 mg, 56% yield); m.p: 118~119 °C.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 8.02–7.98 (m, 2H), 7.69–7.67 (d, *J* = 2H), 7.45–7.36 (m, 3H), 7.26–7.22 (m, 2H), 4.59–4.55 (m, 1H), 3.75 (dd, *J* = 14.0, 4.8 Hz, 1H), 3.27–3.21 (m, 1H), 3.11–3.04 (m, 1H), 2.98–2.89 (m, 1H), 2.47–2.48 (m, 1H), 1.97–1.87 (m, 1H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 174.2, 165.8 (d, *J* = 254.7 Hz), 136.1 (d, *J* = 3.3 Hz), 133.7, 131.1 (d, *J* = 9.6 Hz), 130.9, 128.5, 127.7, 116.4 (d, *J* = 22.5 Hz), 67.5, 62.7, 35.3, 30.6.

**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -102.38 (s).

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{17}FNO_2S^+$: 318.0959; found: 318.0959.



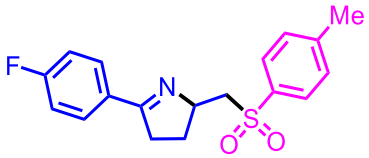

**5-Phenyl-2-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)-3,4-dihydro-2H-pyrrole (6d)**. The title compound was synthesized according to the General Procedure from 1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (104.2 mg, 0.3 mmol), sodium 4-(trifluoromethyl)benzenesulfinate (139.3 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6d** was obtained as a yellowish solid (71.6 mg, 65% yield); m.p: 172~173 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.44–7.40 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 4.63–4.57 (m, 1H), 3.69 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.38–3.72 (m, 1H), 3.10-3.03 (m, 1H), 2.96–2.87 (m, 1H), 2.47-2.38 (m, 1H), 1.93–1.84 (m, 1H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 173.6, 142.5, 135.3, 135.1, 133.5, 131.0, 129.0, 128.4, 127.7, 126.2 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 271.4 Hz), 66.6, 63.1, 37.4, 29.2.

**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -63.21 (s).

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{17}F_3NO_2S^+$: 368.0927; found: 368.0927.



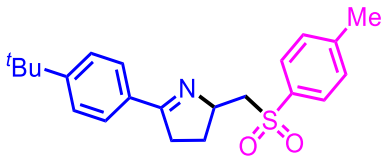

**5-(4-Fluorophenyl)-2-(tosylmethyl)-3,4-dihydro-2H-pyrrole (6e)**. The title compound was synthesized according to the General Procedure from 1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (109.6 mg, 0.3 mmol), sodium 4-methylbenzoate (106.9 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6e** was obtained as a brown solid (68.6 mg, 69% yield); m.p: 126~127 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.70 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.07–7.03 (m, 2H), 4.54–4.52 (m, 1H), 3.76 (dd, *J* = 14.0, 4.0 Hz, 1H), 3.21–3.15 (m, 1H), 3.09–3.01 (m, 1H), 2.95–2.86 (m, 1H), 2.46 (s, 3H), 2.43–2.37 (m, 1H), 1.99–1.89 (m, 1H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 172.2, 164.4 (d, *J* = 249.9 Hz), 142.2, 137.6. 130.1 (d, *J* = 3.0 Hz), 130.0 (d, *J* = 9.0 Hz), 129.8, 128.2, 115.5 (d, *J* = 21.5 Hz), 67.0, 62.3, 35.4, 29.3, 21.6.

**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -110.819.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{18}FNO_2S^+$: 332.1115; found: 332.1115.



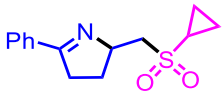

**5-(4-(*tert*-Butyl)phenyl)-2-(tosylmethyl)-3,4-dihydro-2H-pyrrole (6f)**. The title compound was synthesized according to the General Procedure from 1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (121.0 mg, 0.3 mmol), sodium 4-methylbenzoate (106.9 mg, 0.60 mmol,

2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6f** was obtained as a yellow oil (68.7 mg, 62% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.40–7.35 (m, 4H), 4.55–4.48 (m, 1H), 3.78 (dd, *J* = 14.0, 3.6 Hz, 1H), 3.16 (dd, *J* = 14.0, 9.6 Hz, 1H), 3.10–3.02 (m, 1H), 2.95–2.85 (m, 1H), 2.45 (s, 3H), 2.40–2.34 (m, 1H), 1.98–1.86 (m, 1H), 1.32 (s, 9H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 173.9, 154.2, 145.6, 136.9, 131.0, 129.8, 128.1, 127.5, 125.3, 67.4, 62.7, 35.3, 34.4, 31.1, 28.7, 21.6.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{18}FNO_2S^+$: 370.1835; found: 370.1834.

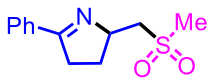



**2-((Cyclopropylsulfonyl)methyl)-5-phenyl-3,4-dihydro-2H-pyrrole (6g)**. The title compound was synthesized according to the General Procedure from 1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (121.0 mg, 0.3 mmol), sodium cyclopropanesulfinate (76.9 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6g** was obtained as a yellow oil (41.9 mg, 53% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.43 (m, 3H), 4.75 (t, *J* = 7.2 Hz, 1H), 3.62–3.56 (m, 1H), 3.20–3.10 (m, 2H), 3.02–2.93 (m, *J* = 17.7, 9.2 Hz, 1H), 2.86–2.76 (m, 1H), 2.52–2.43 (m, 1H), 1.96–1.86 (m, 1H), 1.42–1.35 (m, 1H), 1.24–1.17 (m, 1H), 1.15–1.02 (m, 2H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 174.1, 133.9, 130.9, 128.5, 127.8, 67.5, 59.5, 35.3, 30.9, 29.0, 5.2, 4.9.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{18}NO_2S^+$: 264.1053; found: 264.1053.



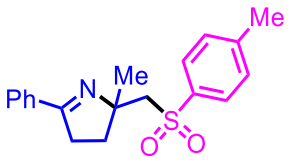

**2-((Methylsulfonyl)methyl)-5-phenyl-3,4-dihydro-2H-pyrrole (6h)**. The title compound was synthesized according to the General Procedure from 1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (121.0 mg, 0.3 mmol), sodium methanesulfinate (61.3mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column

chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6h** was obtained as a yellow solid (50.5 mg, 71% yield); m.p: 93~94°C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.84–7.81 (m, 2H), 7.49–7.40 (m, 3H), 4.73–4.65 (m, 1H), 3.38–3.33 (m, 1H), 3.24–3.22 (m, 1H), 3.20 (s, 3H), 3.17–3.08 (m, 1H), 2.99–2.89 (m, 1H), 2.49–2.40 (m, 1H), 1.83–1.74 (m, 1H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 173.4, 133.7, 131.0, 128.5, 127.8, 67.6, 60.7, 42.8, 34.9, 28.5.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{16}NO_2S^+$: 238.0896; found: 238.0897.

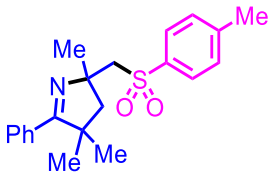



**2-Methyl-5-phenyl-2-(tosylmethyl)-3,4-dihydro-2H-pyrrole (6i)**. The title compound was synthesized according to the General Procedure from 1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (121.0 mg, 0.3 mmol), sodium 4-methylbenzoate (106.9 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6i** was obtained as a white solid (73.7 mg, 75% yield); m.p: 96~97 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.74–7.71 (m, 2H), 7.65–7.62 (m, 2H), 7.44–7.33 (m, 3H), 7.24–7.22 (m, 1H), 3.54 (dd, *J* = 38.8, 14.4 Hz, 2H), 3.17–3.02 (m, 2H), 2.68–2.60 (m, 1H), 2.37 (s, 3H), 2.02–1.95 (m, 1H), 1.45 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 171.3, 144.9, 139.6, 134.9, 131.6, 129.6, 128.2, 127.8, 127.7, 74.5, 66.4, 35.6, 33.0, 27.9, 21.5.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{22}NO_2S^+$: 328.1366; found: 328.1366.

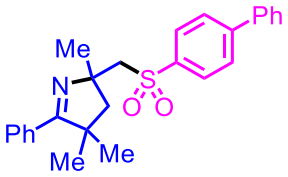



**2,4,4-Trimethyl-5-phenyl-2-(tosylmethyl)-3,4-dihydro-2H-pyrrole (6j)**[10]. The title compound was synthesized according to the General Procedure from 2,2,4-trimethyl-1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (116.8 mg, 0.3 mmol), sodium 4-methylbenzoate (106.9 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column

chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~2:1), product **6j** was obtained as a colorless oil (69.3 mg, 65% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.80 (d, *J* = 5.6 Hz, 2H), 7.58–7.57 (m, 2H), 7.39–7.37 (m, 1H), 7.34 (d, *J* = 4.8 Hz, 2H), 7.31 (d, *J* = 5.6 Hz, 2H), 3.60 (d, *J* = 9.6 Hz, 1H), 3.34 (d, *J* = 9.2 Hz, 1H), 2.68 (d, *J* = 9.2 Hz, 1H), 2.43 (s, 3H), 2.01 (d, *J* = 9.2 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 178.4, 144.3, 138.7, 134.1, 129.7, 129.6, 128.1, 128.0, 127.7, 70.6, 66.4, 52.1, 50.9, 28.9, 28.8, 28.3, 21.5.

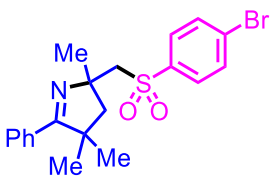



**2-(([1,1'-Biphenyl]-4-ylsulfonyl)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrole (6k)**. The title compound was synthesized according to the General Procedure from 2,2,4-trimethyl-1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (116.8 mg, 0.3 mmol), sodium [1,1'-biphenyl]-4-sulfinate (144.2 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~2:1), product **6k** was obtained as a colorless oil (86.4 mg, 69% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.60–7.55 (m, 4H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.45–7.41 (m, 1H), 7.38–7.34 (m, 1H), 7.33–7.29 (m, 2H), 3.65 (d, *J* = 14.4 Hz, 1H), 3.44 (d, *J* = 14.4 Hz, 1H), 2.71 (d, *J* = 13.6 Hz, 1H), 2.04 (d, *J* = 13.6 Hz, 1H), 1.57 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 178.5, 146.3, 140.1, 139.2, 134.1, 129.6, 129.0, 128.6, 128.3, 128.1, 128.0, 127.8, 127.4, 70.7, 66.5, 52.1, 51.1, 29.1, 29.0, 28.3.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{28}NO_2S^+$: 418.1835; found: 418.1835.



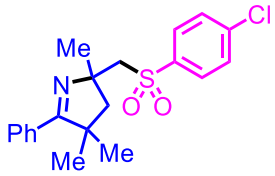

**2-(((4-Bromophenyl)sulfonyl)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrole (6l)**. The title compound was synthesized according to the General Procedure from 2,2,4-trimethyl-1-

phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (116.8 mg, 0.3 mmol), sodium 4-bromobenzenesulfinate (145.8 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~2:1), product **6l** was obtained as a pale-yellow oil (70.6 mg, 56% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.40–7.33 (m, 3H), 3.57 (d, *J* = 14.4 Hz, 1H), 3.41 (d, *J* = 14.4 Hz, 1H), 2.64 (d, *J* = 13.6 Hz, 1H), 2.01 (d, *J* = 13.6 Hz, 1H), 1.53 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 178.5, 140.6, 133.9, 132.4, 129.8, 129.4, 128.6, 128.2, 128.0, 70.5, 66.5, 52.0, 51.2, 29.1, 29.0, 28.3.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{23}BrNO_2S^+$: 420.0627; found: 420.0629.

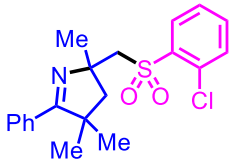



**2-(((4-Chlorophenyl)sulfonyl)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrole (6m).** The title compound was synthesized according to the General Procedure from 2,2,4-trimethyl-1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (116.8 mg, 0.3 mmol), sodium 4-chlorobenzenesulfinate (119.2 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~2:1), product **6m** was obtained as a white solid (86.8 mg, 77% yield); mp: 110~111 ºC.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.8 Hz, 2H), 7.55–7.53 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.41–7.32 (m, 3H), 3.58 (d, *J* = 14.4 Hz, 1H), 3.41 (d, *J* = 14.4 Hz, 1H), 2.64 (d, *J* = 13.6 Hz, 1H), 2.01 (d, *J* = 13.6 Hz, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 178.5, 140.1, 140.0, 133.9, 129.7, 129.4, 129.3, 128.1, 128.0, 70.5, 66.5, 52.0, 51.2, 29.1, 29.0, 28.3.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{23}ClNO_2S^+$: 376.1133; found: 376.1133.

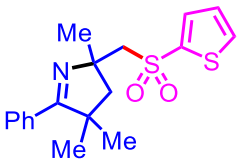


**2-(((2-Chlorophenyl)sulfonyl)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrole (6n)**. The title compound was synthesized according to the General Procedure from 2,2,4-trimethyl-1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (116.8 mg, 0.3 mmol), sodium 2-chlorobenzenesulfinate (119.2 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~2:1), product **6n** was obtained as a white solid (78.9 mg, 70% yield); mp: > 300 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.56–7.52 (m, 4H), 7.43–7.36 (m, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 3.92 (d, *J* = 14.4 Hz, 1H), 3.65 (d, *J* = 14.4 Hz, 1H), 2.67 (d, *J* = 13.6 Hz, 1H), 2.02 (d, *J* = 13.6 Hz, 1H), 1.57 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$): δ 178.5, 138.9, 134.4, 134.0, 132.6, 131.8, 131.2, 129.7, 128.1, 128.0, 127.4, 70.6, 64.4, 52.1, 51.5, 29.0, 28.9, 28.4.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{23}ClNO_2S^+$: 376.1133; found: 376.1132.

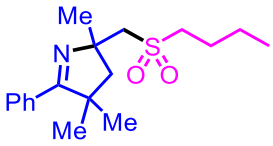



**2,4,4-Trimethyl-5-phenyl-2-((thiophen-2-ylsulfonyl)methyl)-3,4-dihydro-2H-pyrrole (6o)**. The title compound was synthesized according to the General Procedure from 2,2,4-trimethyl-1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (116.8 mg, 0.3 mmol), sodium thiophene-2-sulfinate (102.1 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~2:1), product **6o** was obtained as a white solid (74.0 mg, 71% yield); mp: 72~73 °C.

**$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.69 (d, *J* = 2.4 Hz, 1H), 7.67 (d, *J* = 3.6 Hz, 1H), 7.63 (d, *J* = 4.4 Hz, 2H), 7.39 (t, *J* = 4.8 Hz, 1H), 7.35 (t, *J* = 10.0 Hz, 2H), 7.11 (t, *J* = 3.2 Hz, 1H), 3.75 (d, *J* = 9.2 Hz, 1H), 3.48 (d, *J* = 9.6 Hz, 1H), 2.65 (d, *J* = 9.2 Hz, 1H), 2.02 (d, *J* = 9.2 Hz, 1H), 1.58 (s, 3H), 1.45 (s, 3H), 1.39 (s, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 178.6, 143.0, 134.1, 133.6, 133.5, 129.6, 128.1, 128.0, 127.7, 70.7, 68.1, 52.2, 50.9, 28.9, 28.8, 28.3.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{22}NO_2S_2^+$: 348.1086; found: 348.1087.




**2-((Butylsulfonyl)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrolen (6p)**. The title compound was synthesized according to the General Procedure from 2,2,4-trimethyl-1-phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (116.8 mg, 0.3 mmol), sodium butane-1-sulfinate (86.5 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~1.5:1), product **6p** was obtained as a colorless oil (62.7 mg, 65% yield).

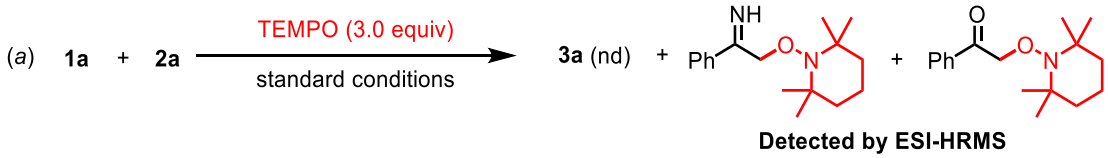
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.70–7.68 (m, 2H), 7.44–7.37 (m, 3H), 3.33 (s, 2H), 3.18–3.06 (m, 2H), 2.61 (d, *J* = 13.6 Hz, 1H), 1.98 (d, *J* = 13.6 Hz, 1H), 1.88–1.75 (m, 2H), 1.55 (s, 3H), 1.45 (s, 3H), 1.43 (br, 1H), 1.42 (br, 1H), 1.40 (s, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 179.3, 134.1, 129.7, 128.3, 127.9, 70.1, 62.7, 55.6, 52.0, 51.2, 29.4, 29.0, 28.1, 23.9, 21.7, 13.5.

**HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{28}NO_2S^+$: 322.1835; found: 322.1835.

## 6. Mechanistic Studies.

### 6.1 Radical Inhibition Experiment.




**Detected by ESI-HRMS**

Oxime Esters **1a** (0.30 mmol), sodium 4-methylbenzoate **2a** (0.45 mmol, 1.5 equiv.), TEMPO (140.6 mg, 0.9 mmol, 3.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%) was sequentially added in a dry Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with argon (3 cycles). Dimethylsulfoxide (DMSO) (3.0 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427nm) with fan at rt for 10 h. After irradiation, the reaction mixture was rapidly extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The mixture was analyzed by $^1$H NMR and ESI-HRMS. The

reaction was inhibited to varying degrees, with the target product obtained in yields of 0%. Trapping product (**Figure S2**, **a** and **b**) were detected by HRMS.

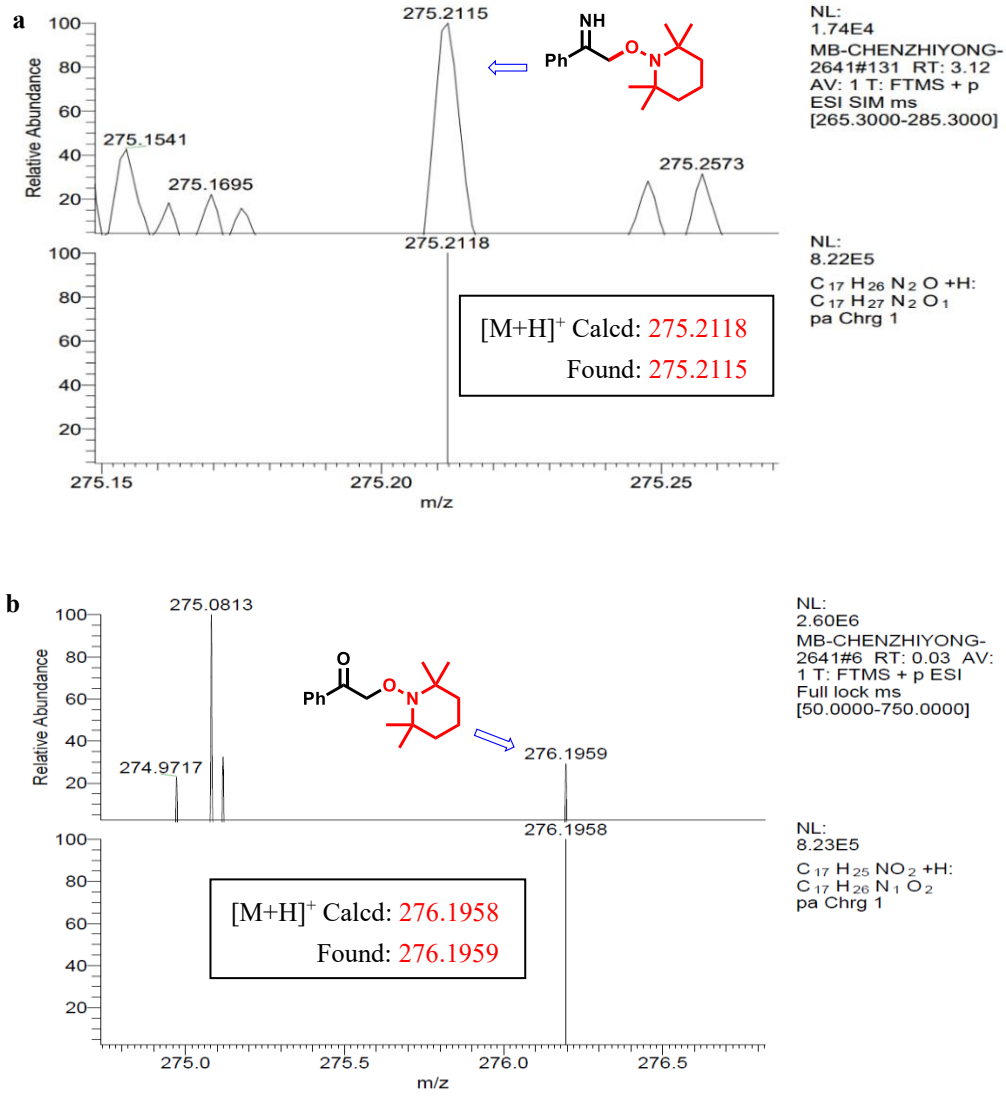
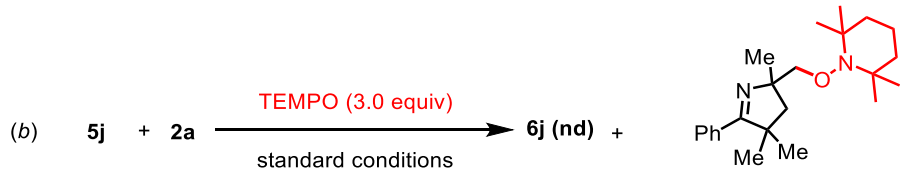



**Figure S2**

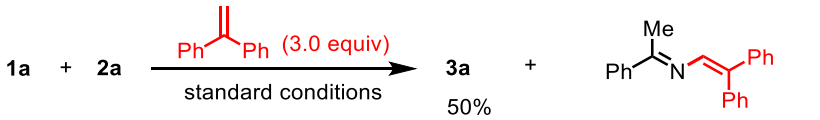



**7**, 78%

*γ*-Unsaturated oxime esters **5j** (0.30 mmol), sodium 4-methylbenzoate **2a** (0.45 mmol, 2.0 equiv.), TEMPO (140.6 mg, 0.9 mmol, 3.0 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (1.0 mol%) was sequentially added in a dry Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with argon (3 cycles). Dimethylsulfoxide (DMSO) (3.0 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles.

Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427nm) with fan at rt for 12 h. After irradiation, the reaction was then quenched by adding a saturated salt solution and the reaction mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The mixture was analyzed by $^1$H NMR and ESI-HRMS. The reaction was inhibited to varying degrees, trace amounts of target product **6j** detected by TLC, with the radical trapping product obtained in yields of **7** (78%, 83.5 mg). ***2,2,6,6-Tetramethyl-1-((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methoxy)piperidine*** **(7).** Column chromatography eluent (petroleum ether/ethyl acetate = 5:1), Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.69–7.63 (m, 2H), 7.38–7.33 (m, 3H), 3.91 (d, *J* = 8.4 Hz, 1H), 3.80 (d, *J* = 8.4 Hz, 1H), 2.36 (d, *J* = 12.6 Hz, 1H), 1.69 (d, *J* = 12.6 Hz, 1H), 1.44 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.25 (s, 3H), 1.21 (s, 3H), 1.14 (s, 3H), 1.09 (s, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 177.8, 135.4, 128.9, 128.0, 127.97, 82.7, 72.5, 60.0, 51.9, 48.9, 39.7, 33.3, 33.1, 29.6, 27.9, 26.7, 20.6, 20.3, 17.0. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{37}N_2O^+$: 357.2900, found: 357.2903.

## 6.2 Radical capture experiment.




**Detected by ESI-HRMS**

Oxime Esters **1a** (0.30 mmol), sodium 4-methylbenzoate **2a** (0.45 mmol, 1.5 equiv.), 1,1-diphenylethylene (162.2 mg, 0.9 mmol, 3.0 equiv.), and Cu(BINAP)(MeCN)PF6 (2.62 mg, 1.0 mol%) was sequentially added in a dry Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with argon (3 cycles). Dimethylsulfoxide (DMSO) (3.0 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427nm) with fan at rt for 10 h. After irradiation, the reaction mixture was rapidly extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The mixture was analyzed by $^1$H NMR and ESI-HRMS. The reaction was inhibited to varying degrees, with the target product obtained in yields of 50%. Trapping product (**Figure S3**) were detected by HRMS.

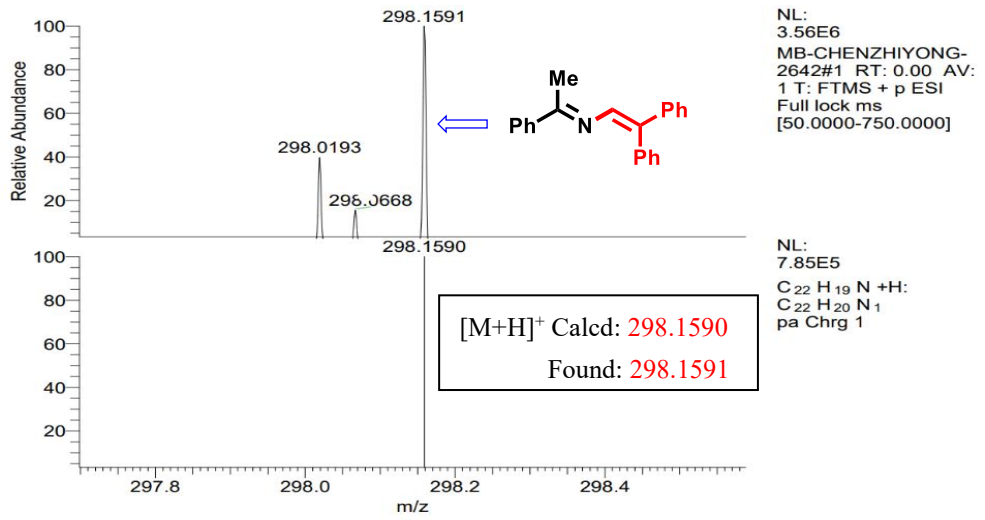
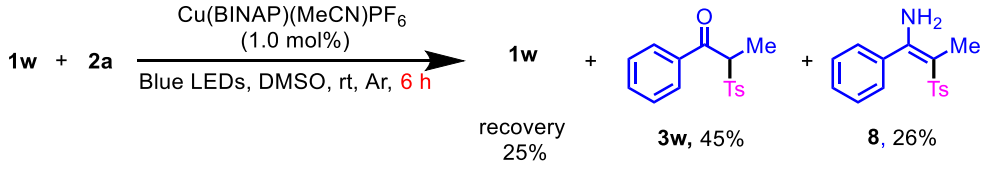


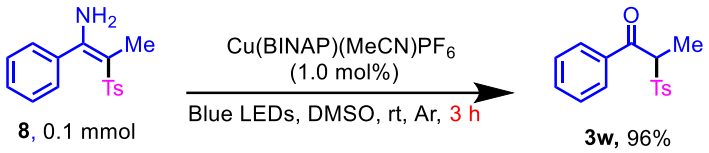

**Figure S3**

### 6.3 Intermediate monitoring experiment.




Corresponding Oxime Esters **1w** (0.30 mmol), sodium 4-methylbenzoate **2a** (0.45 mmol, 1.5 equiv.) and Cu(BINAP)(MeCN)$PF_6$ (1.0 mol%) was sequentially added in a dry Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with argon (3 cycles), DMSO (3.0 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427 nm) with fan at rt for 6 h. After irradiation, the reaction mixture was rapidly extracted three times with ethyl acetate. the solvent was removed under vacuum, dried over anhydrous sodium sulfate and the crude product was isolated by flash column chromatography on silica gel using petroleum ether/ethyl acetate/appropriate amount of triethylamine as eluent to provide the pure target product **8** or directly analyzed by $^1$H NMR. **1-Phenyl-2-tosylprop-1-en-1-amine (8).** The title compound was synthesized according to the General Procedure from 1-phenylpropan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (96.4 mg, 0.3 mmol), sodium 4-methylbenzoate (80.2 mg, 0.45 mmol, 1.5 equiv.), and Cu(BINAP)(MeCN)$PF_6$ (2.62 mg, 1.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **8** was obtained as a white solid (22.4 mg, 26% yield); mp: 95~96 °C. **$^1$H NMR** (400 MHz, DMSO-$d_6$): δ 7.79 (d, $J$ = 8.0 Hz, 2H),

7.49–7.38 (m, 5H), 7.32–7.24 (m, 2H), 6.83 (s, 2H), 2.40 (s, 3H), 1.49 (s, 3H). **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): δ 154.8, 142.8, 139.8, 137.5, 129.7, 129.0, 128.4, 127.7, 126.0, 92.8, 21.0, 14.4. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{18}NO_2S^+$: 288.1053; found: 288.1052




**8**, 0.1 mmol **3w**, 96%

1-Phenyl-2-tosylprop-1-en-1-amine **8** (0.10 mmol, 28 mg) and Cu(BINAP)(MeCN)$PF_6$ (1.0 mol%) was sequentially added in a dry Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with argon (3 cycles), DMSO (3.0 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427 nm) with fan at rt for 3 h. The crude product was isolated by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the pure target product **3w** (27 mg, 96% yield).

## 6.4 UV-Vis absorption spectra.

### 6.4.1 UV-Vis absorption spectra of catalysts.

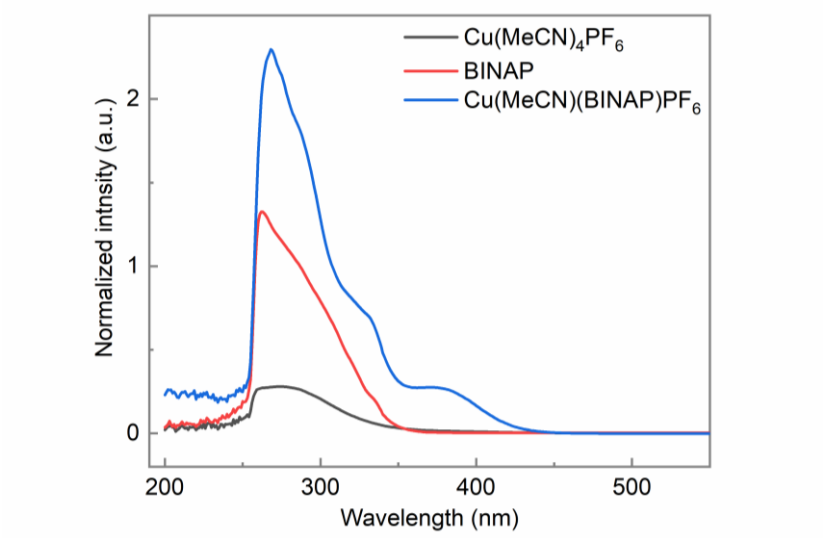



**Figure S4.** UV-Vis Absorption Spectra of catalysts and ligand in DMSO.

The UV-visible absorption spectra of catalyst Cu(MeCN)$_4$$PF_6$, ligand BINAP, and catalyst Cu(MeCN)(BINAP)$PF_6$ was measured directly in DMSO ($1\times10^{-4}$ M) (**Figure S4**). The results show that only when the catalyst Cu(MeCN)$_4$$PF_6$ is coordinated with the ligand BINAP to form the complex Cu(MeCN)(BINAP)$PF_6$, there is a significant absorption in the UV-visible region (in the range of 380~460 nm), and good optical properties are exhibited.

### 6.4.2 UV-Vis absorption spectra of substrates and rection mixture.

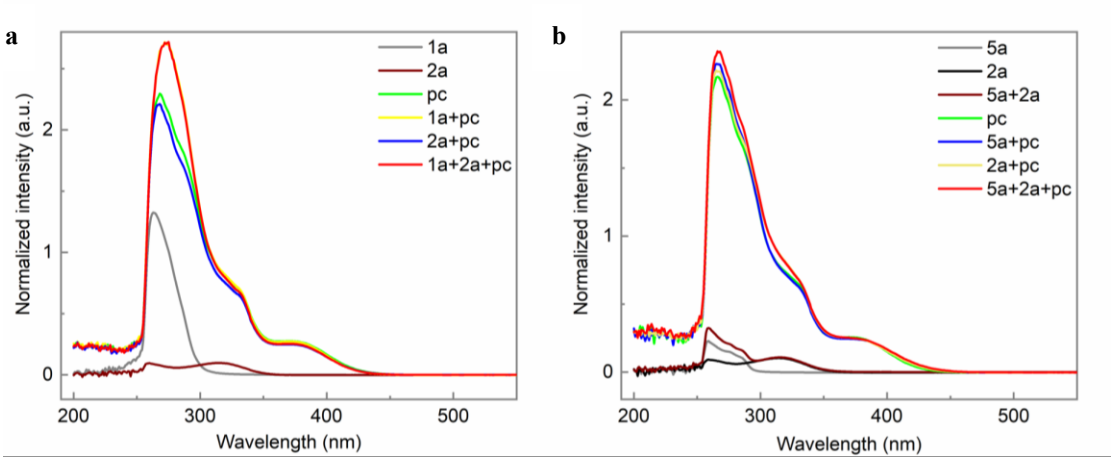



**Figure S5.** UV-Vis absorption spectra of substrates, catalysts and mixtures in DMSO.

The below reactants were added sequentially in graduated test tube and the added DMSO solution was fixed to the graduated line to obtain a series of mixtures at a concentration of $1\times10^{-4}$ M. The UV-visible absorption spectra were determined using a 1 cm cuvette in a UV-2800A spectrophotometer and the spectral data were recorded from 200~800 nm (**Figure S5** a, b).

The results show that only solutions of the complex Cu(MeCN)(BINAP)$PF_6$ and solutions containing the complex show significant absorption in the blue range in the visible region, whereas the other substrates and their mixtures show no absorption in the visible region.

Note**: 1a**: Oxime Esters, **2a**: sodium 4-methylbenzoate, **5a**: $\gamma$-unsaturated oxime esters, **pc**: catalyst Cu(MeCN)(BINAP)$PF_6$.

## 6.5 Fluorescence Quenching Experiments.

Luminescence quenching experiments have been carried out in order to clarify the interaction between the excited state complex Cu(MeCN)(BINAP)$PF_6$ and substrates **1a**, **2a** and **5a**[11].

**Experimental methods**: 0.3 mL of Cu(MeCN)(BINAP)$PF_6$ solution at a concentration of $10^{-4}$ mol/L was taken in a cuvette, followed by the addition of a gradient volume of substrate **1a** or **2a** or **5a** ($10^{-3}$ mol/L), and then the volume of the solution was allowed to Constant volume to 3.0 mL to obtain samples to be tested at different concentration gradients. **Note**: No filters were used in any of the tests.

Fluorescence emission spectra were collected using HORIBA FluroMax-4 for all experiments. All solutions were excited at $\lambda$ = 268 nm, the slit width was set to 6 nm, and the sampling (scanning) interval was set to 2 nm. The emission spectra were recorded at wavelengths ranging from 520 to 575 nm, with

the maximum emission peak at λ = 546 nm. (**Figure S6**, **Figure S7 and Figure S8**).

The results showed that the fluorescence intensity of the catalysts tends to decrease with increasing concentrations of substrates **1a** and **5a**, with Stern-Volmer constants[27] of 3.653 $uM^{-1}$ (**Figure S6**. b) and 7.677 $uM^{-1}$ (**Figure S8**. b), respectively, whereas the fluorescence of the catalysts was almost unaffected by the concentration of sodium 4-methylbenzoate (**2a**), with a Stern-Volmer constant of -0.096 uM-1 (**Figure S7**. b). According to the Stern-Volmer constant, the fluorescence of the excited state catalyst could not be burst by sodium 4-methylbenzoate (**2a**), but could be burst by oxime esters (**1a**) and *γ,δ*-unsaturated oxime esters (**5a**).

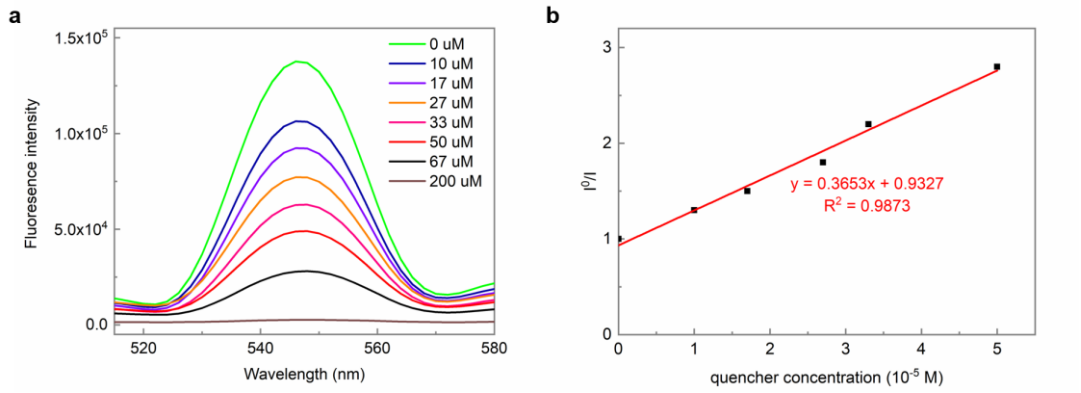



**Figure S6.** (a) complex Cu(MeCN)(BINAP)$PF_6$ emission quenching by **1a**；(b) Stern-Volmer plots.

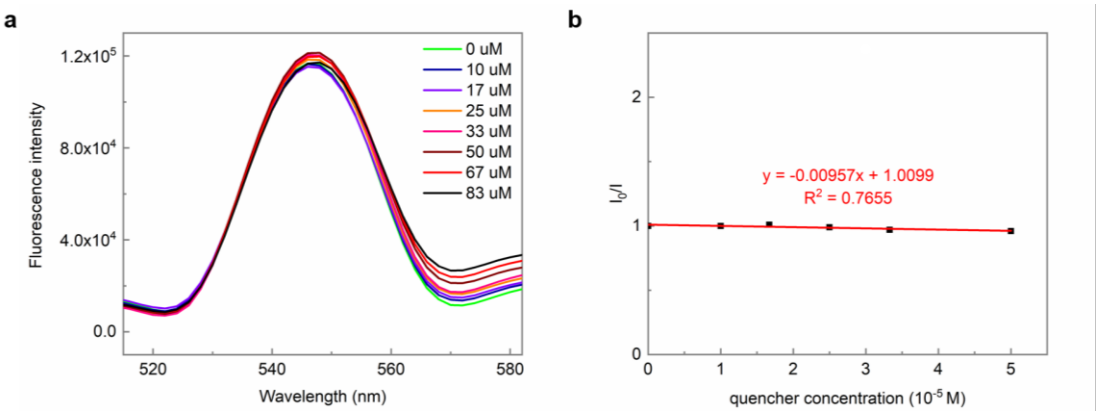



**Figure S7.** (a) complex Cu(MeCN)(BINAP)$PF_6$ emission quenching by **2a**；(b) Stern-Volmer plots.

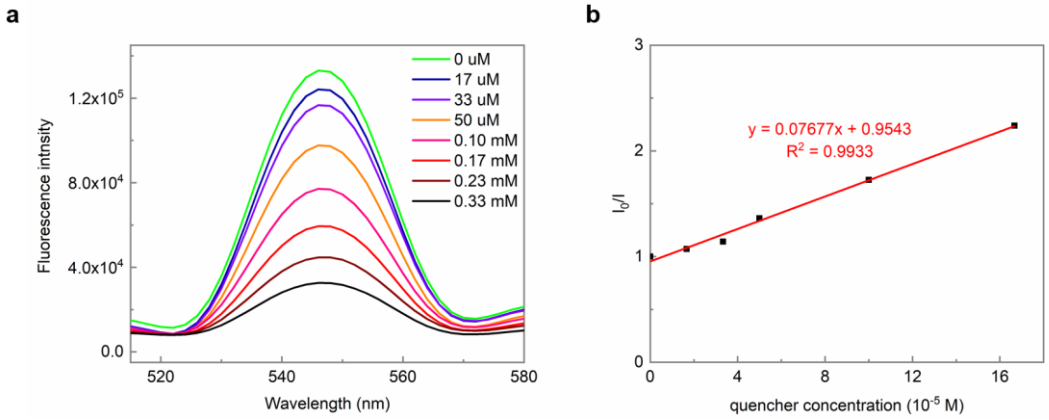



**Figure S8.** (a) complex Cu(MeCN)(BINAP)$PF_6$ emission quenching by **5a**； (b) Stern-Volmer plots.

## 6.6 Cyclic Voltammetry Experiments.

Cyclic voltammograms (CVs) were performed on a CHI660E electrochemistry workstation. Regular 3-electrode systems were used. Measurements were recorded in a DMSO solution of $Bu_4NPF_6$ (0.1 M) at a scan rate of 100 mV/s under the protection of $N_2$ at room temperature using a glassy carbon disk (*d* = 0.5 cm) as a working electrode and a platinum wire as a counter electrode. An Ag/AgCl (3 M KCl) electrode was used as a reference electrode in all the experiments, and its potential (0.59 V vs. $Fc^+$/Fc) was calibrated with the ferrocenium/ferrocene ($Fc^+$/Fc) redox couple (**Figure S9**).

According to the emission spectrum of the catalyst, the triplet state energy corresponding to the maximum emission wavelength of 546 nm is 2.27 eV[11, 28], and combined with the redox potential of its ground state, $E^0_{1/2}(Cu^{II}/Cu^{I})$ = -0.73 V (vs Ag/AgCl in DMSO), the estimated redox potential of the catalyst in the excited state is $E_{ox}(Cu^{II}/Cu^{I*}) = E^0_{1/2}(Cu^{II}/Cu^{I}) - ET$ = -0.73－2.27 = -3.0 V (vs. Ag/AgCl in DMSO)[4, 11, 27, 28]. The above estimates indicate that the catalyst in the excited state exhibits good reducing power and has the ability to reduce the oxime ester to imine radicals (**Figure S10~S13**).

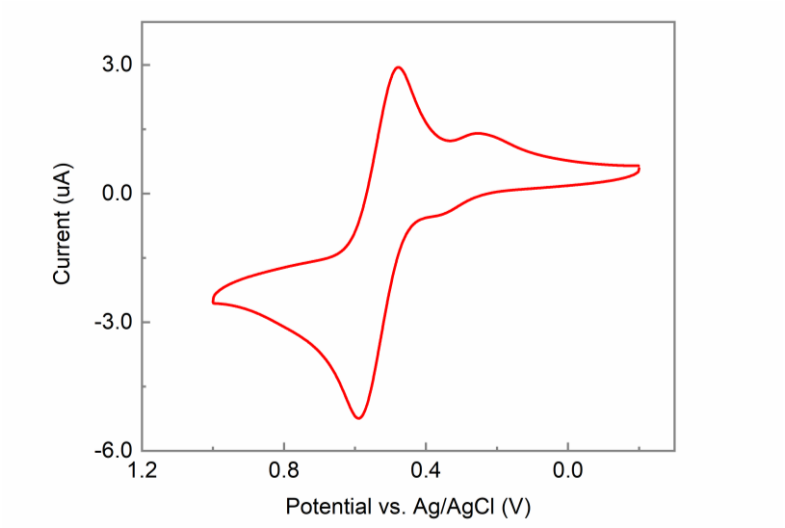



**Figure S9**. CV of ferrocenium [peak potential $E_p$ (Fc+/Fc) = 0.59 V] in DMSO.

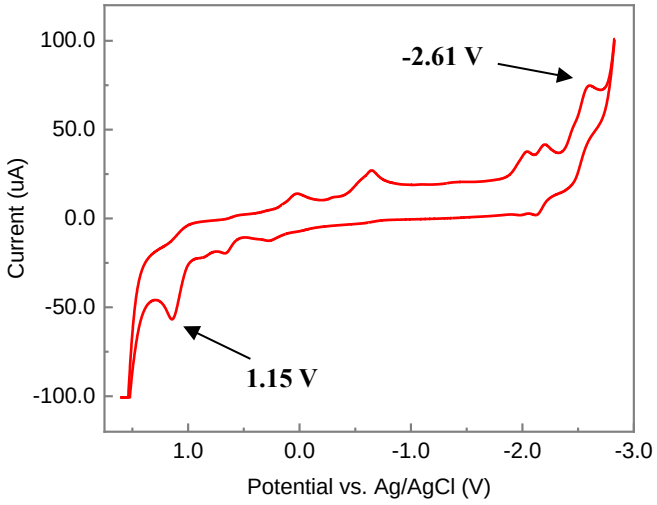



**Figure S10**. CV of [(BINAP)Cu(MeCN)][$PF_6$] $E^0_{1/2}(Cu^{II}/Cu^{I})$ = (1.15-2.61)/2 = -0.73 V (vs Ag/AgCl in DMSO).

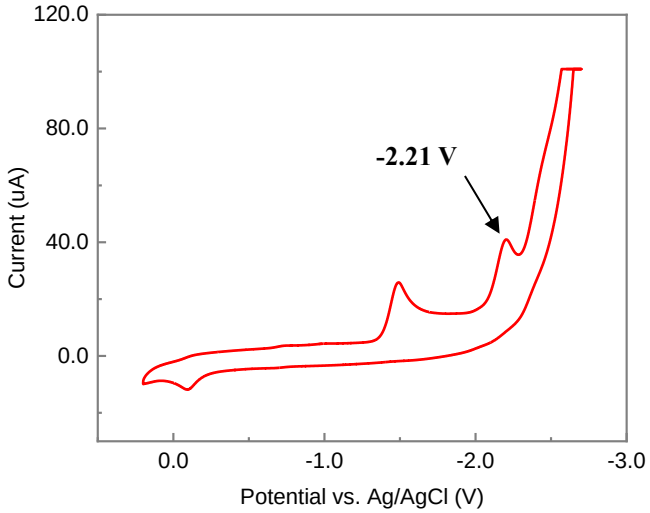


**Figure S11**. CV of oxime esters (**1a**) $E_p^{0/-1}$(**1a**) = -2.21 V (vs Ag/AgCl in DMSO).

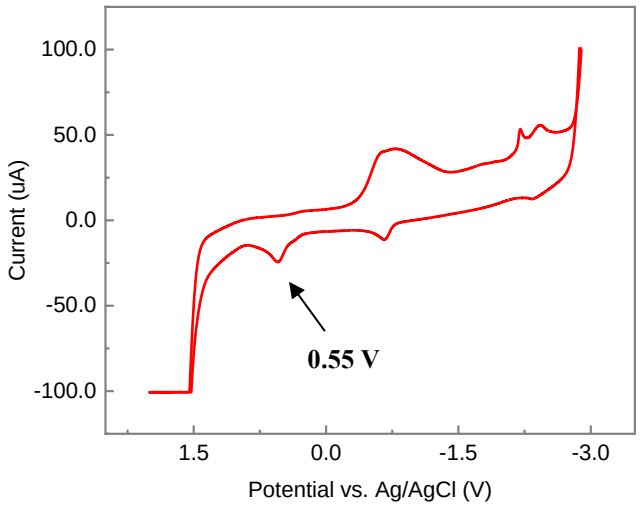



**Figure S12**. CV of sodium 4-methylbenzoate (**2a**) $E_p^{ox}$ (**2a**) = 0.55 V (vs Ag/AgCl in DMSO).

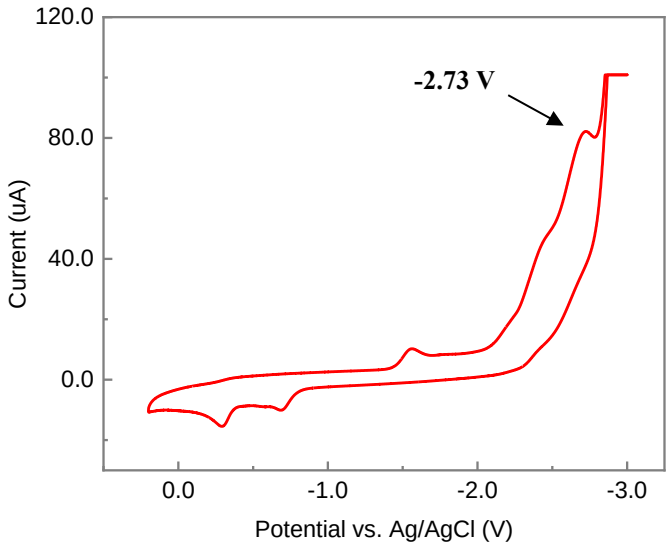



**Figure S13**. CV of $\gamma,\delta$-unsaturated oxime esters (**5a**) $E_p^{0/-1}$(**5a**) = -2.73 V (vs Ag/AgCl in DMSO).

## 7. DFT Computational Study

### 7.1 Computational Methods

All of the structures were fully optimized with the B3LYP method and 6-31+G(d) basis set. Grimmes's DFT-D3 dispersion correction was used to describe the van der waals interaction. The solvation energy corrections calculated at the M052x/6-31G(d) level with the SMD solvation model for DMSO minus electronic energy in gas phase. The thermal correction to Gibbs free energy calculated by B3LYP/6-31+G(d) at 273.15K in gas phase. The B3LYP/6-31+G(d) calculated imaginary frequencies for the transition states in gas phase. The Single point energy calculated by DLPNO-CCSD(T)/aug-cc-

pvTZ level of theory. Vibrational frequency calculations were performed to ensure that a transition state has only one imaginary frequency and a local minimum has no imaginary frequency. Transition states connecting relevant minima were further examined by running intrinsic reaction coordinate (IRC) calculations [22].

## 7.2 B3LYP absolute calculation energies (Hartree), energy corrections (Hartree), and imaginary frequency ($cm^{-1}$)

| Geometry | E(DLPNOCCSD(T)/ aug-cc-pvTZ[a] | G(corr-solv)[b] | G(corrthe)[c] | IF[d] |
|---|---|---|---|---|
| Radical A | -480.1712613 | -0.008965896 | 0.159963 | |
| TS-II | -480.1024744 | -0.009201796 | 0.153955 | -2166.59 |
| Radical B | -480.1705472 | -0.011777596 | 0.159771 | |
| TS-I | -480.150399 | -0.010231196 | 0.161037 | -488.21 |
| Radical B’ | -480.1838797 | -0.009091096 | 0.162178 | |
| TS-III | -480.1454848 | -0.010556496 | 0.162732 | -485.75 |
| Radical P2 | -480.1828231 | -0.009862396 | 0.163244 | |

[a]The single point energy calculated at the DLPNO-CCSD(T)/aug-cc-pvTZ level. [b]The solvation energy corrections calculated at the M052x/6-31G(d) level with the SMD solvation model for DMSO minus electronic energy in gas phase. [c]The thermal correction to Gibbs free energy calculated by B3LYP/6-31+G(d) at 273.15K in gas phase. [d]The B3LYP/6-31+G(d) calculated imaginary frequencies for the transition states in gas phase.

## 7.3 Free energy profiles for the reaction pathways

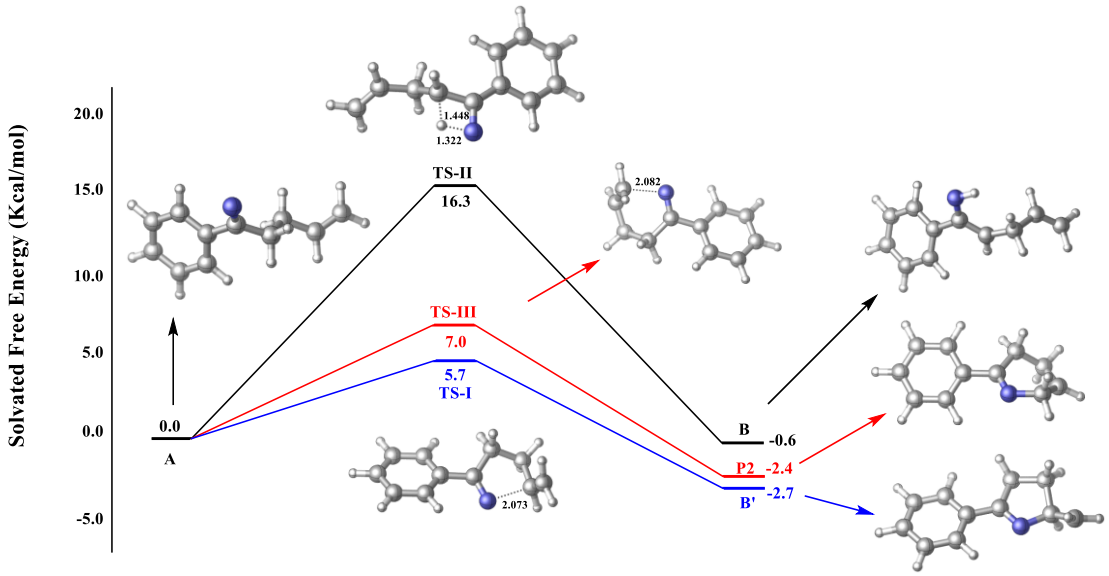



**Figure S14.** Computed free energy profiles for the three tentative reaction pathways at the DLPNO-CCSD(T)/aug-cc-pvTZ//SMD(DMSO)-M052x/631G(d)//B3LYP/6-31+G(d) level. The relative free

energies are given in kcal/mol. The preferred pathway is shown in blue.

Density functional theory (DFT) calculations were used to study the reaction mechanisms. The detailed information for the reaction mechanism is shown in Figure 1. At beginning, radical **A** generated radicals **B**, **B'** and **P2** via the transition states **TS-II**, **TS-I** and **TS-III** with an energy barrier of only 16.3/7.0/5.7 kcal/mol, respectively. The 5-member ring formation barrier is 5.7 kcal/mol from **TS-I** to **B'** releasing 2.7 kcal/mol, which confirmed that the reaction for produced 5-member ring radical **B'** is more favorable.

## 7.4 Cartesian coordinates

B3LYP/6-31+G(d) geometries for all the optimized compounds and transition states

**Radical A**

| | | | |
|---|---|---|---|
| C | 2.37937700 | -1.57409300 | -0.55794000 |
| C | 1.21442800 | -0.84020500 | -0.79836700 |
| C | 1.02964800 | 0.41213000 | -0.18965500 |
| C | 2.02603200 | 0.91117200 | 0.66897200 |
| C | 3.18489000 | 0.17231200 | 0.91061700 |
| C | 3.36610700 | -1.07198600 | 0.29610100 |
| H | 2.51287800 | -2.53990900 | -1.03864900 |
| H | 0.46150400 | -1.24422600 | -1.46814100 |
| H | 1.88208900 | 1.87093900 | 1.15722300 |
| H | 3.94375900 | 0.56572700 | 1.58228200 |
| H | 4.26842600 | -1.64793300 | 0.48560600 |
| C | -0.19554100 | 1.23535400 | -0.46100400 |
| C | -1.53704500 | 0.56679400 | -0.76845600 |
| H | -1.40790700 | -0.09232200 | -1.63583600 |
| C | -2.09230800 | -0.23415800 | 0.43086700 |
| H | -2.24298900 | 0.43864200 | 1.28397300 |
| H | -1.35225400 | -0.98739100 | 0.73311300 |
| C | -3.38446200 | -0.92172800 | 0.08121300 |
| H | -3.33208800 | -1.64518000 | -0.73538600 |

| | | | |
|---|---|---|---|
| C | -4.55729700 | -0.70717500 | 0.68918600 |
| H | -5.45850700 | -1.24114300 | 0.39350000 |
| H | -4.65634900 | 0.00665700 | 1.50671400 |
| N | -0.13886900 | 2.49702300 | -0.43110400 |
| H | -2.24945100 | 1.34648000 | -1.05586900 |

**TS-II**

| | | | |
|---|---|---|---|
| C | 2.55808400 | -1.63126900 | -0.20310400 |
| C | 1.30631300 | -1.03976900 | -0.39016900 |
| C | 1.12325000 | 0.32956300 | -0.13114200 |
| C | 2.21267600 | 1.09763700 | 0.32247400 |
| C | 3.45963600 | 0.50434900 | 0.50977900 |
| C | 3.63505300 | -0.86130400 | 0.24679400 |
| H | 2.69148600 | -2.69036500 | -0.40790100 |
| H | 0.47024900 | -1.63830200 | -0.74179200 |
| H | 2.07395100 | 2.15580800 | 0.52811100 |
| H | 4.29615400 | 1.10286500 | 0.86137800 |
| H | 4.60875900 | -1.32182000 | 0.39435900 |
| C | -0.19192800 | 0.94385900 | -0.34666300 |
| C | -1.51178000 | 0.34415700 | -0.70306700 |
| H | -1.63653000 | 0.09583200 | -1.76039200 |
| C | -2.27247800 | -0.50094000 | 0.30068300 |
| H | -2.21434200 | -0.04537800 | 1.29766700 |
| H | -1.76868200 | -1.48095700 | 0.37442400 |
| C | -3.70976900 | -0.71986600 | -0.09151600 |
| H | -3.87009500 | -1.17583300 | -1.07073200 |
| C | -4.76722400 | -0.40254400 | 0.66403600 |
| H | -5.78484500 | -0.59286600 | 0.32813100 |
| H | -4.65256600 | 0.05580700 | 1.64609000 |
| N | -0.50665200 | 2.19693100 | -0.27495100 |
| H | -1.71797500 | 1.77345100 | -0.59331300 |

**Radical B**

| | | | |
|---|---|---|---|
| C | 2.84216900 | -1.48294100 | -0.31355400 |
| C | 1.53107900 | -1.06491500 | -0.55992100 |
| C | 1.09280600 | 0.20395600 | -0.14379200 |
| C | 2.00025200 | 1.04296500 | 0.52596000 |
| C | 3.30746600 | 0.62238000 | 0.78000700 |
| C | 3.73423000 | -0.64248600 | 0.35971300 |
| H | 3.16616900 | -2.46383300 | -0.65285400 |
| H | 0.85548500 | -1.72479500 | -1.09770500 |
| H | 1.67169200 | 2.02419700 | 0.85574000 |
| H | 3.99226000 | 1.28128700 | 1.30858900 |
| H | 4.75277200 | -0.96922200 | 0.55465400 |
| C | -0.30409200 | 0.67890400 | -0.41650200 |
| C | -1.36085000 | -0.27581400 | -0.38403500 |
| H | -1.12337100 | -1.28856200 | -0.06843600 |
| C | -2.80591400 | -0.00964600 | -0.68154200 |
| H | -3.17517700 | -0.79575600 | -1.35481300 |
| H | -2.93975700 | 0.94937900 | -1.19863400 |
| C | -3.63539800 | -0.01952100 | 0.58758600 |
| H | -3.40506100 | 0.76777400 | 1.30671900 |
| C | -4.58973400 | -0.91452700 | 0.86642500 |
| H | -5.15412600 | -0.87122200 | 1.79594100 |
| H | -4.84273900 | -1.71708900 | 0.17426200 |
| N | -0.46010500 | 1.97000200 | -0.64917900 |
| H | -1.44949500 | 2.18770200 | -0.80128800 |

**TS-I**

| | | | |
|---|---|---|---|
| C | -3.07654200 | 1.10058700 | 0.00609800 |
| C | -1.68177100 | 1.17032300 | -0.06289300 |
| C | -0.90811700 | -0.00331300 | -0.05685100 |
| C | -1.56317400 | -1.24620200 | 0.02990200 |

| | | | |
|---|---|---|---|
| C | -2.95474800 | -1.31285800 | 0.10594900 |
| C | -3.71733800 | -0.13882400 | 0.09191100 |
| H | -3.66060000 | 2.01751700 | -0.00650100 |
| H | -1.20414900 | 2.14239700 | -0.13672100 |
| H | -0.97286200 | -2.15767700 | 0.05101900 |
| H | -3.44433400 | -2.28070200 | 0.18193200 |
| H | -4.80164700 | -0.19055900 | 0.15189500 |
| C | 0.58649800 | 0.04571400 | -0.15334800 |
| C | 1.37070900 | 1.20932700 | 0.43919200 |
| H | 1.40425500 | 1.06752800 | 1.52919400 |
| C | 2.76935000 | 1.15283800 | -0.18945200 |
| H | 3.49497300 | 1.67871800 | 0.44222500 |
| H | 2.74864100 | 1.66006300 | -1.16041600 |
| C | 3.17784900 | -0.29688300 | -0.39164600 |
| H | 3.47320400 | -0.58876100 | -1.39719400 |
| C | 3.65077300 | -1.07048000 | 0.65420700 |
| H | 4.05161900 | -2.06656000 | 0.48163900 |
| H | 3.54898500 | -0.74950300 | 1.68967200 |
| N | 1.22238000 | -0.90964400 | -0.70407200 |
| H | 0.88432800 | 2.17367300 | 0.26334600 |

**Radical B’**

| | | | |
|---|---|---|---|
| C | 3.10579900 | 1.01657100 | -0.06033200 |
| C | 1.71572100 | 1.15744600 | -0.00532800 |
| C | 0.88104900 | 0.02664900 | 0.03897800 |
| C | 1.47449500 | -1.25089200 | 0.02220400 |
| C | 2.86002000 | -1.39035800 | -0.03787200 |
| C | 3.68228500 | -0.25617900 | -0.07808400 |
| H | 3.73549700 | 1.90232900 | -0.09008600 |
| H | 1.28378800 | 2.15368300 | 0.00847800 |
| H | 0.83960200 | -2.13117800 | 0.05254800 |

| | | | |
|---|---|---|---|
| H | 3.30164000 | -2.38383500 | -0.05402600 |
| H | 4.76292900 | -0.36663400 | -0.12407700 |
| C | -0.59084500 | 0.17945400 | 0.10600300 |
| C | -1.29202200 | 1.52664300 | 0.01047900 |
| H | -0.89620300 | 2.15503100 | -0.79400800 |
| C | -2.75354600 | 1.10312300 | -0.20652700 |
| H | -2.98772800 | 1.08556200 | -1.27760800 |
| H | -3.47944900 | 1.75201900 | 0.29173700 |
| C | -2.78069500 | -0.35444500 | 0.36091100 |
| H | -3.04654800 | -0.31252200 | 1.42968900 |
| C | -3.72367200 | -1.27178200 | -0.33357100 |
| H | -3.41040300 | -1.80352300 | -1.22919200 |
| N | -1.37746000 | -0.82380800 | 0.28583400 |
| H | -1.15512500 | 2.07813200 | 0.95190500 |
| H | -4.77732000 | -1.27979000 | -0.06737600 |

**TS-III**

| | | | |
|---|---|---|---|
| C | 2.99328500 | 1.09557300 | -0.32765700 |
| C | 1.59991600 | 1.09642500 | -0.44230300 |
| C | 0.85573300 | -0.04579600 | -0.09974200 |
| C | 1.53661200 | -1.18332700 | 0.36947400 |
| C | 2.92706400 | -1.17750300 | 0.49607300 |
| C | 3.66111000 | -0.03868800 | 0.14477200 |
| H | 3.55540700 | 1.98367300 | -0.60624600 |
| H | 1.09801400 | 1.98483300 | -0.81524900 |
| H | 0.96864600 | -2.06652700 | 0.64771600 |
| H | 3.43713300 | -2.06066900 | 0.87322200 |
| H | 4.74392600 | -0.03440700 | 0.24240400 |
| C | -0.64024600 | -0.07330600 | -0.26134500 |
| C | -1.42981000 | 1.21869000 | -0.00003500 |
| H | -1.74633800 | 1.61621500 | -0.97373700 |

| | | | |
|---|---|---|---|
| C | -2.66302900 | 0.98117700 | 0.89644000 |
| H | -3.29370200 | 1.88464900 | 0.87410300 |
| H | -2.33961000 | 0.87080300 | 1.94051100 |
| C | -3.42046300 | -0.25187900 | 0.49354300 |
| H | -3.89799200 | -0.83699600 | 1.27798600 |
| C | -3.22752200 | -0.81433800 | -0.74677700 |
| H | -3.64609200 | -1.79177500 | -0.97488200 |
| H | -3.00206500 | -0.20152000 | -1.61600900 |
| N | -1.17815400 | -1.16645800 | -0.63721700 |
| H | -0.78615100 | 1.97477500 | 0.45605200 |

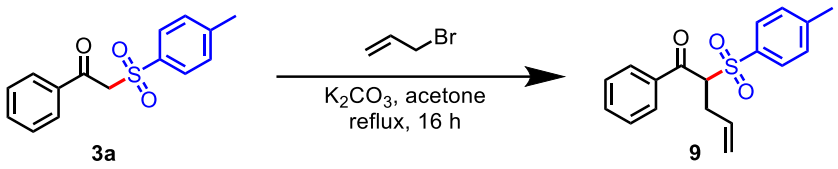
**Radical P2**

| | | | |
|---|---|---|---|
| C | 2.96264800 | 1.11661000 | -0.28501800 |
| C | 1.56747600 | 1.13202100 | -0.37949700 |
| C | 0.81374000 | -0.01543000 | -0.07461000 |
| C | 1.49603800 | -1.17473600 | 0.34033600 |
| C | 2.88700300 | -1.18623000 | 0.44685400 |
| C | 3.62748300 | -0.04010600 | 0.13153900 |
| H | 3.52773900 | 2.01070400 | -0.53707800 |
| H | 1.07257800 | 2.03965000 | -0.71237100 |
| H | 0.92417200 | -2.06365600 | 0.58892900 |
| H | 3.39462000 | -2.08822800 | 0.78047300 |
| H | 4.71161200 | -0.04906800 | 0.21368400 |
| C | -0.67468400 | -0.02194500 | -0.20618400 |
| C | -1.45065000 | 1.27805200 | -0.08337200 |
| H | -1.73062300 | 1.60897000 | -1.09473900 |
| C | -2.73116600 | 1.06484300 | 0.75053900 |
| H | -3.38346400 | 1.94691100 | 0.65993400 |
| H | -2.45636700 | 1.01475800 | 1.81975700 |
| C | -3.43188800 | -0.17920100 | 0.32506800 |
| H | -4.42799100 | -0.41609100 | 0.69048100 |

| | | | |
|---|---|---|---|
| C | -2.72438400 | -1.13760500 | -0.57844400 |
| H | -3.08648200 | -2.16174800 | -0.42550900 |
| H | -2.93442300 | -0.91147700 | -1.64360500 |
| N | -1.26018800 | -1.14538700 | -0.43142000 |
| H | -0.83975300 | 2.06934200 | 0.35671700 |

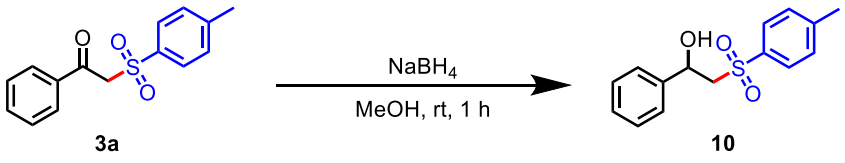
## 8. Late-stage modification

### 8.1 Experimental procedure for synthesis of 9.



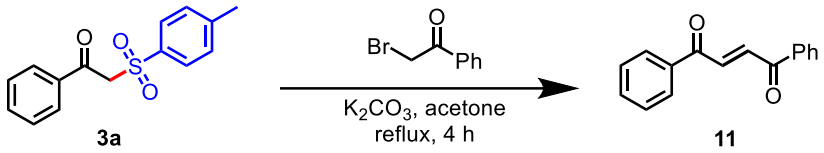

According to the literature method[23], Anhydrous potassium carbonate (280 mg, 2.0 mmol) was added to acetone (10 mL) solution containing **3a** (1.0 mmol), and the resulting reaction mixture was stirred at room temperature for 10 min. Subsequently, the allyl halide (1.2 mmol) was added to the reaction mixture at room temperature. The reaction mixture was stirred by reflux for 16 h. The reaction was detected with a TLC plate until **3a** was completely consumed. The reaction mixture was cooled to room temperature, concentrated under reduced pressure and extracted with ethyl acetate (3×60 mL). The combined organic layer was washed with salt water, dried with anhydrous sodium sulfate, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 7:1~3:1) to afford the pure product. **1-Phenyl-2-tosylpent-4-en-1-one (9)**. White solid (254.7 mg, 81% yield), m.p. 112~113°C. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.65–5.50 (m, 1H), 5.13 (dd, *J* = 10.6, 3.4 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 4.96 (d, *J* = 10.0 Hz, 1H), 2.90–2.72 (m, 2H), 2.43 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 192.0, 145.4, 137.1, 133.9, 133.2, 131.9, 129.8, 129.5, 129.0, 128.7, 118.9, 69.2, 32.4, 21.6.

### 8.2 Experimental procedure for synthesis of 10.



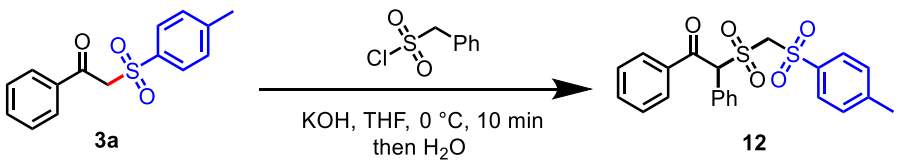
According to the literature method[20], sodium borohydride (0.75 mmol, 1.5 eq.) was gradually added to a solution of **3a** (137 mg, 0.5 mmol, 1.0 eq.) in anhydrous methanol (5.0 mL) and stirred for 1 h at room temperature. Thin layer chromatography analysis was used to detect the reaction process. At the end of the reaction, the solvent was removed under reduced pressure and the crude oil was treated with ice water. The aqueous layer was acidified (pH = 2) and extracted with ethyl acetate (3×10 mL). The combined organic layers were dried with anhydrous sodium sulfate, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to afford the pure product. **1-Phenyl-2-tosylethan-1-ol (10).** White solid (128.6 mg, 93% yield), m.p. 106~107°C. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.34–7.23 (m, 5H), 5.24 (d, *J* = 10.0 Hz, 1H), 3.77 (s, 1H), 3.47 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.31 (dd, *J* = 14.4, 1.6 Hz, 1H), 2.46 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 145.2, 140.7, 136.1, 130.0, 128.7, 128.2, 128.0, 125.6, 68.4, 63.9, 21.6.

## 8.3 Experimental procedure for synthesis of 11.




According to the literature method[24], anhydrous potassium carbonate (0.75 mmol, 1.5 eq.) was added to a solution of **3a** (0.5 mmol) in acetone (16 mL) and the reaction mixture was stirred at room temperature for 5 min. A solution of acetone (4.0 mL) containing *α*-bromoacetophenone (0.6 mmol) was added to the resulting reaction mixture at room temperature, refluxed for 4 h. The solution was cooled to room temperature and the solvent was concentrated. The residue was diluted with water (10 mL) and extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 20:1~10:1) to afford the pure product. **(E)-1,4-Diphenylbut-2-ene-1,4-dione (11)**. Yellow solid (96.9 mg, 82% yield), m.p. 121~123°C. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.11–8.04 (m, 4H), 8.02 (s, 2H), 7.69–7.60 (m, 2H), 7.59–7.50 (m, 4H); **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 189.8, 136.9, 135.1, 133.8, 128.9, 128.8.

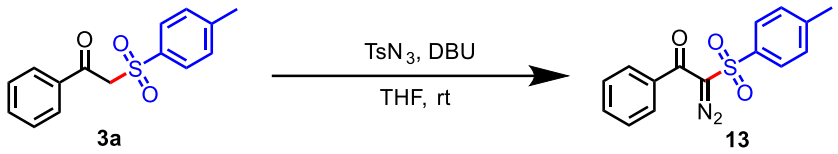
## 8.4 Experimental procedure for synthesis of 12.




According to the literature method[25], potassium hydroxide (4.0 mmol, 8.0 equiv.) in THF (8 mL)

was stirred well followed by the addition of **3a** (300 mg, 0.5 mmol). The above resulting mixture was stirred at 0°C for 10 min, and then a solution of benzylsulfonyl chloride (1.0 mmol, 2.0 equiv.) in THF (2 mL) was added dropwise to the mixture. The yellow solution immediately turned colorless. The insoluble potassium hydroxide was filtered off and the filtrate was subjected to removal of solvent in vacuum. Afterwards 60 mL of water was added to the residue and extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 3:1) to afford the pure product. **1,2-Diphenyl-2-((tosylmethyl)sulfonyl)ethan-1-one (12)**. White solid (171.7 mg, 80% yield), m.p. 192~193°C. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.68–7.60 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49–7.41 (m, 5H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 1H), 4.91 (d, *J* = 15.2 Hz, 1H), 4.58 (d, *J* = 15.2 Hz, 1H), 2.44 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 190.5, 146.3, 135.2, 135.0, 134.3, 131.1, 130.3, 130.0, 129.6, 129.1, 128.9, 128.8, 126.5, 74.4, 70.2, 21.7.

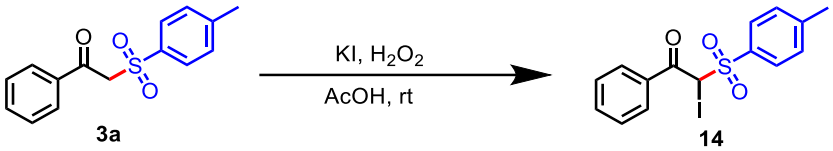
## 8.5 Experimental procedure for synthesis of 13.



**3a** **13**

According to literature method[26], DBU (182 mg, 1.2 mmol) was added to a solution of compounds **3a** (1.0 mmol) in THF (10 mL) and stirred at room temperature for 10 min, followed by the addition of *p*-toluenesulphonyl azide (217 mg, 1.1 mmol) to the reaction mixture, and the resulting system was stirred at room temperature for 20 h. At the end of the reaction, it was concentrated under reduced pressure and the mixture was water (10 mL) was diluted, and the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to afford the pure product. **2-Diazo-1-phenyl-2-tosylethan-1-one (13).** Yellow solid (237.3 mg, 79% yield), m.p. 109~110°C. **$^1$H NMR** (400 MHz, DMSO-$d_6$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53–7.44 (m, 4H), 2.41 (s, 3H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): δ 182.1, 145.1, 138.3, 135.8, 133.0, 129.7, 128.9, 127.9, 127.3, 83.0 21.1.

### 8.6 Experimental procedure for synthesis of 14.




According to literature method[27], add KI (1.1 mmol) and 30% hydrogen peroxide (8 mmol) to a **3a** (1.0 mmol) solution of acetic acid (1.0 ml). Stir for 4 hours at room temperature. Upon completion of the reaction (monitored by TLC plate), the acetic acid was removed under reduced pressure, water (10 mL) was added and extracted with ethyl acetate (3×20 mL). The combined organic phases were dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1~3:1) to afford the pure product. **2-Iodo-1-phenyl-2-tosylethan-1-one (14).** White solid (360.2 mg, 90% yield), m.p. 110~111°C. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.90 (t, *J* = 7.8 Hz, 4H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.54 (s, 1H), 2.45 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 188.2, 146.1, 134.5, 133.6, 132.1, 130.9, 129.5, 129.1, 129.0, 37.8, 21.7.

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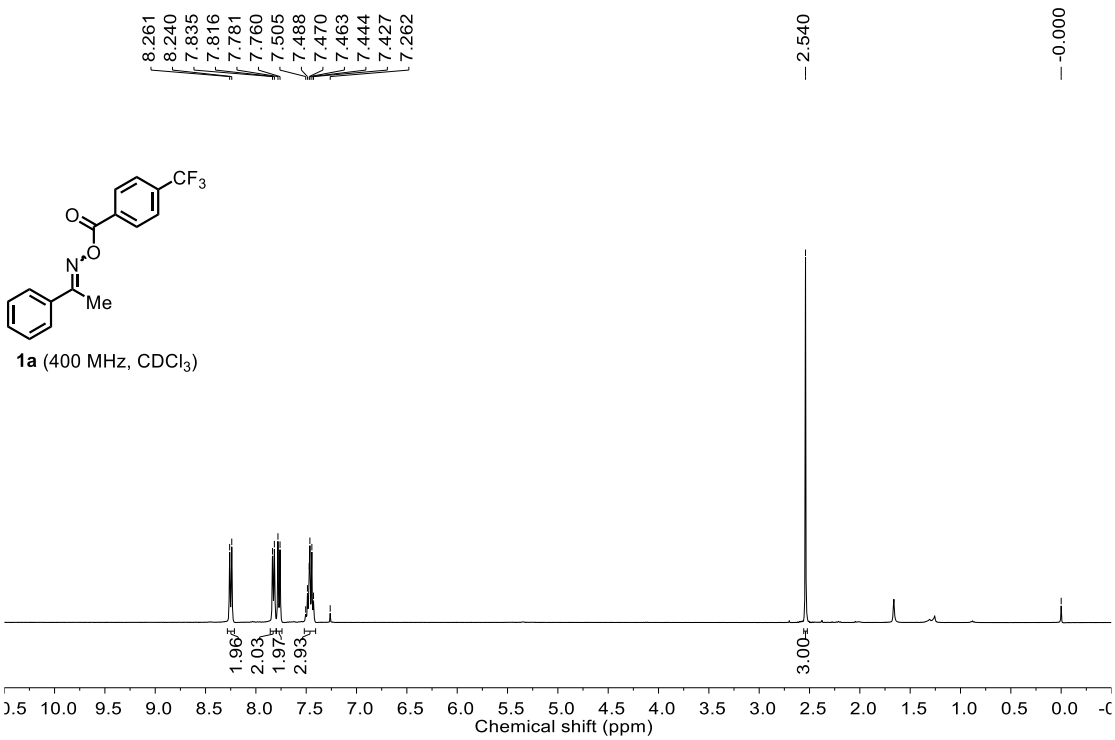
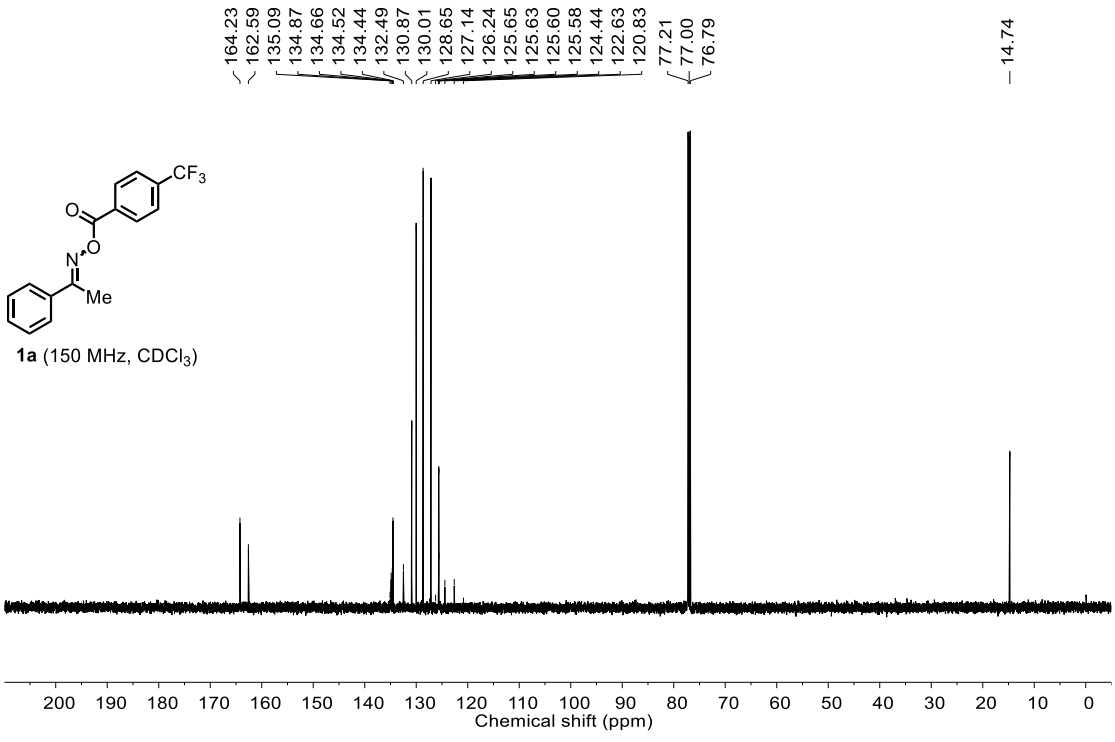
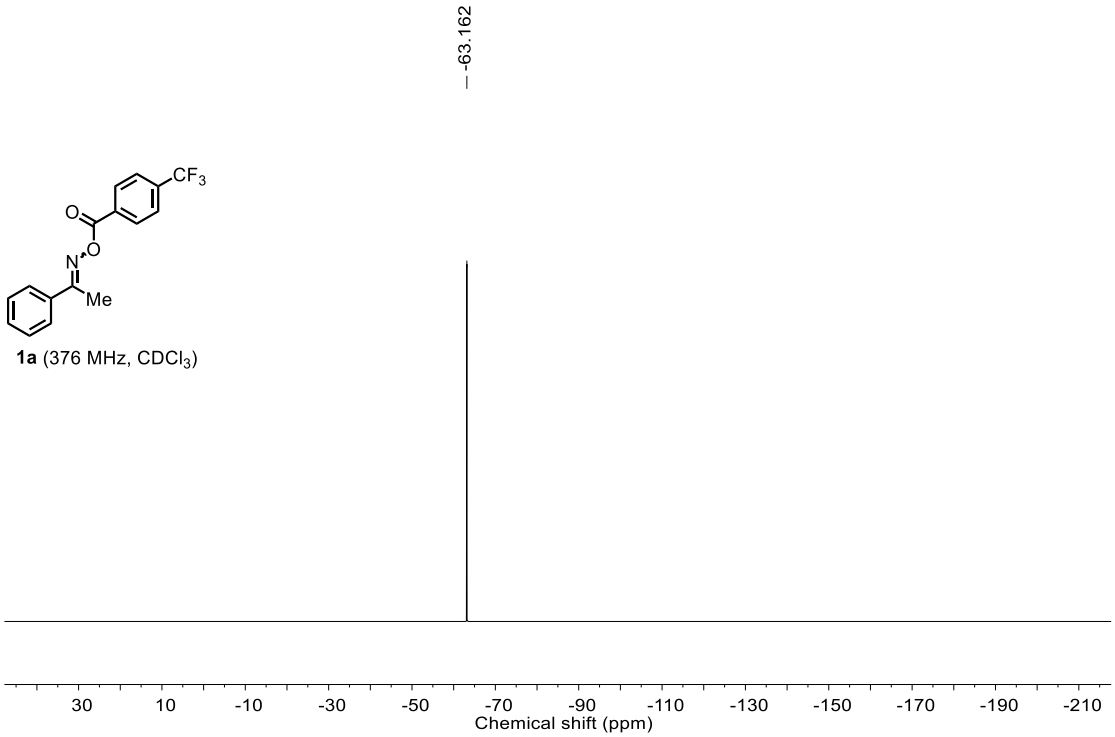
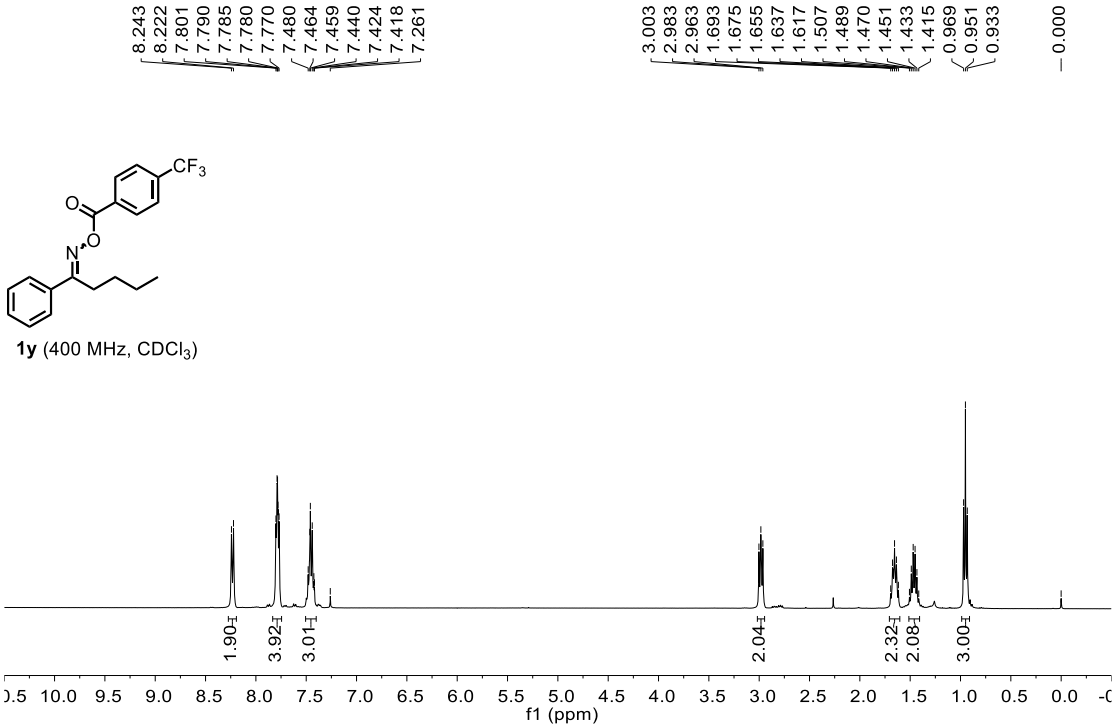
## 10. Cope of NMR Spectra






**1a** (376 MHz, $CDCl_3$)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8.222
7.801
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7.785
7.780
7.770
7.480
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7.459
7.440
7.424
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7.261
3.003
2.983
2.963
1.693
1.675
1.655
1.637
1.617
1.507
1.489
1.470
1.451
1.433
1.415
0.969
0.951
0.933
0.000
CF3
O
N
O
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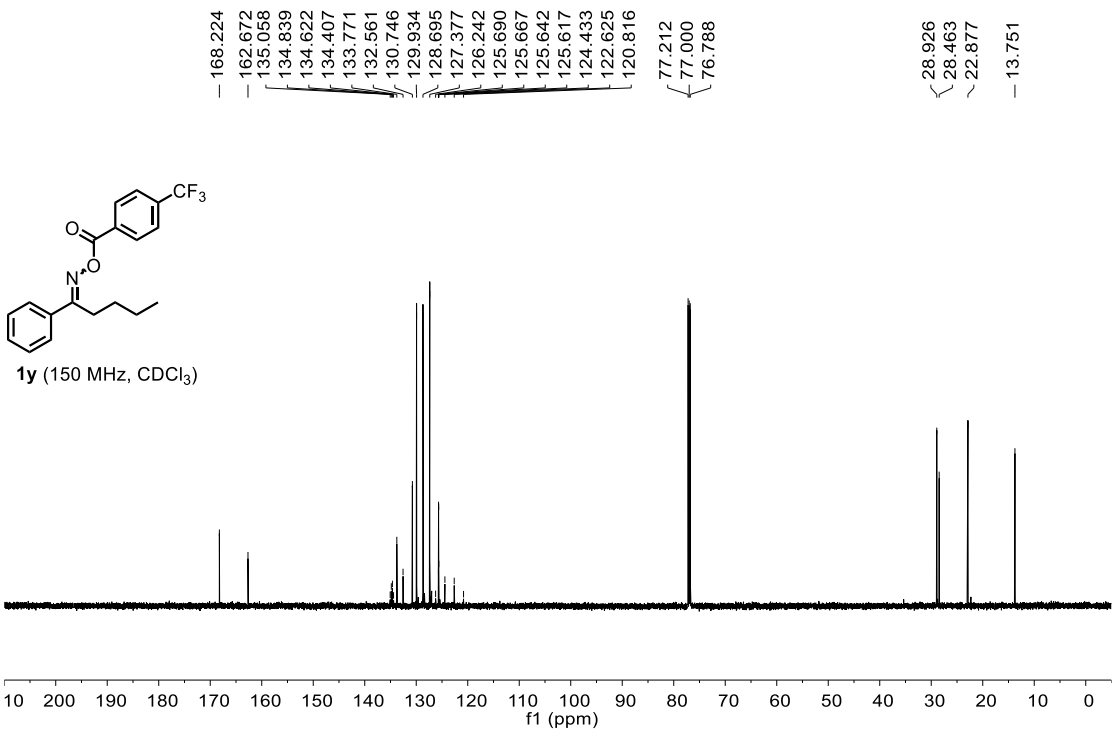
1.90
3.92
3.01
2.04
2.32
2.08
3.00
f1 (ppm)


168.224
162.672
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134.622
134.407
133.771
132.561
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129.934
128.695
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126.242
125.690
125.667
125.642
125.617
124.433
122.625
120.816
77.212
77.000
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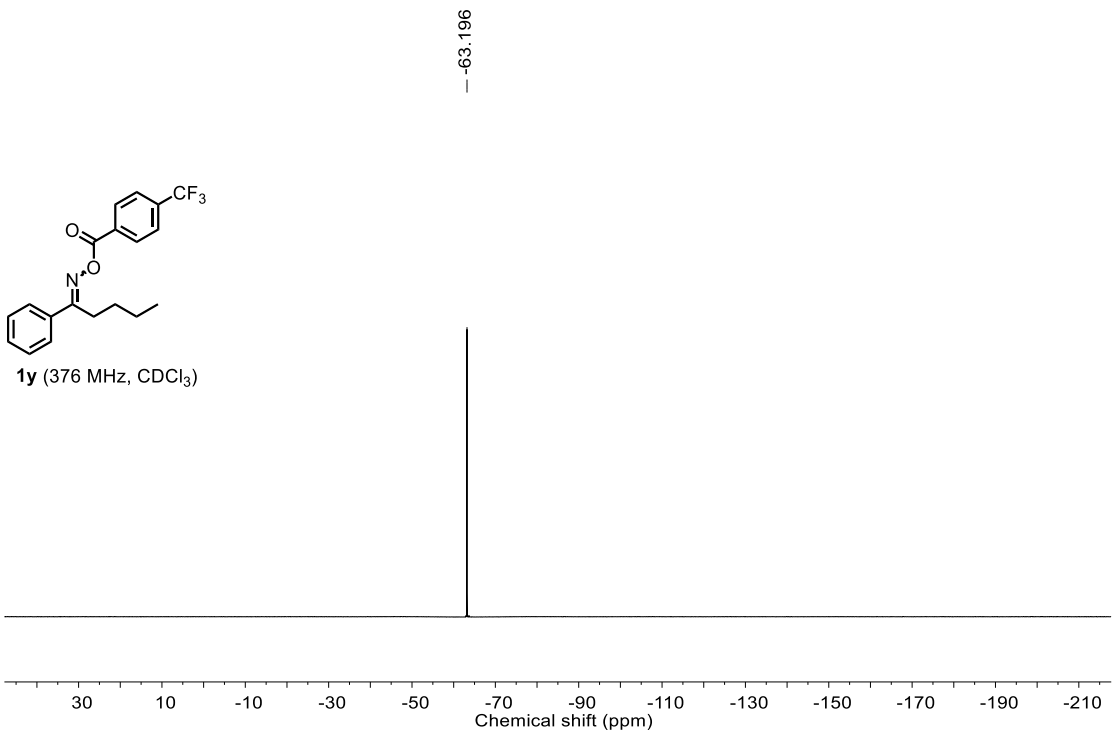
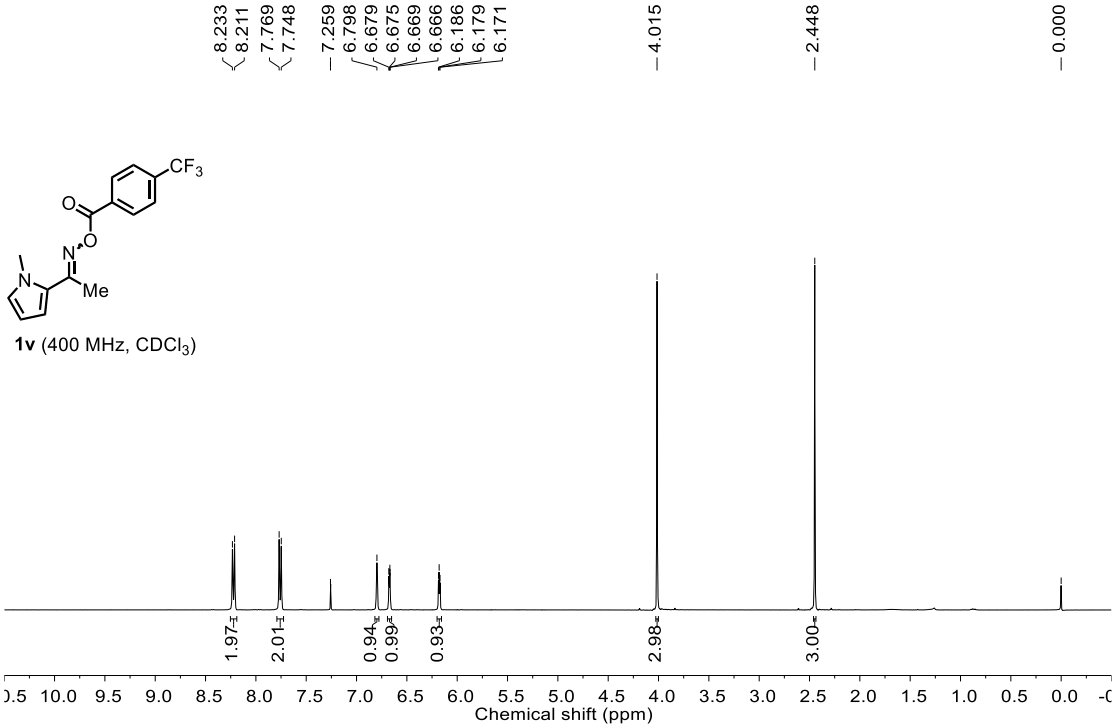
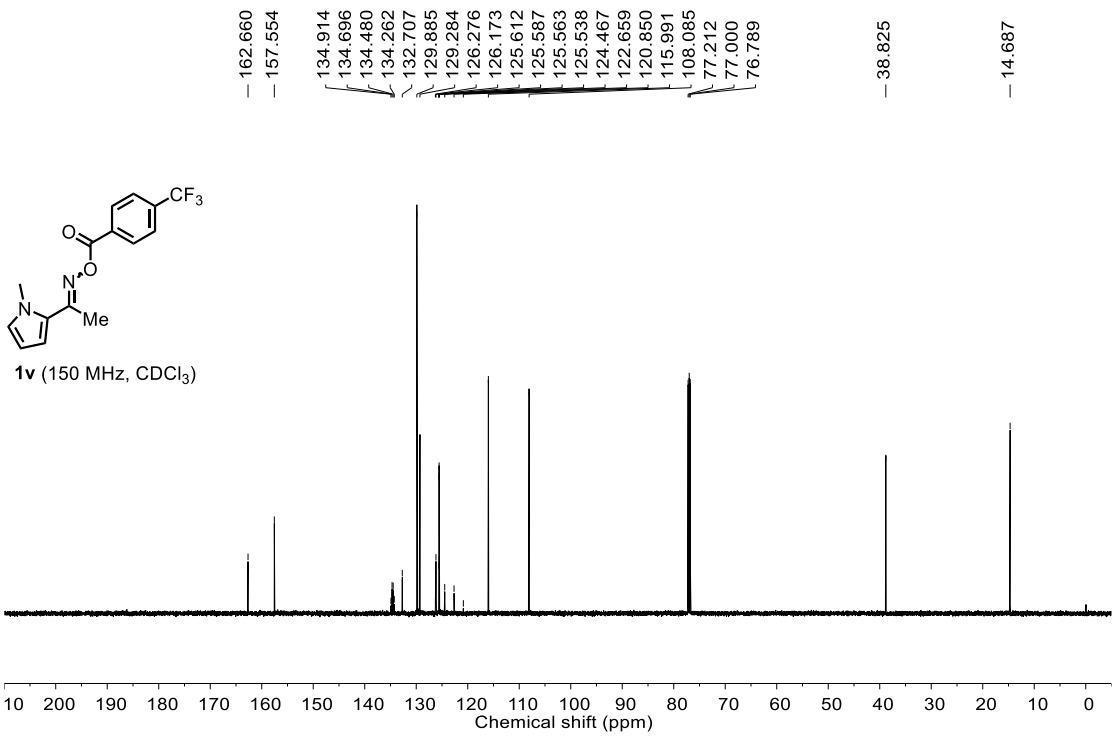
N
O
1y (150 MHz, CDCl3)
f1 (ppm)



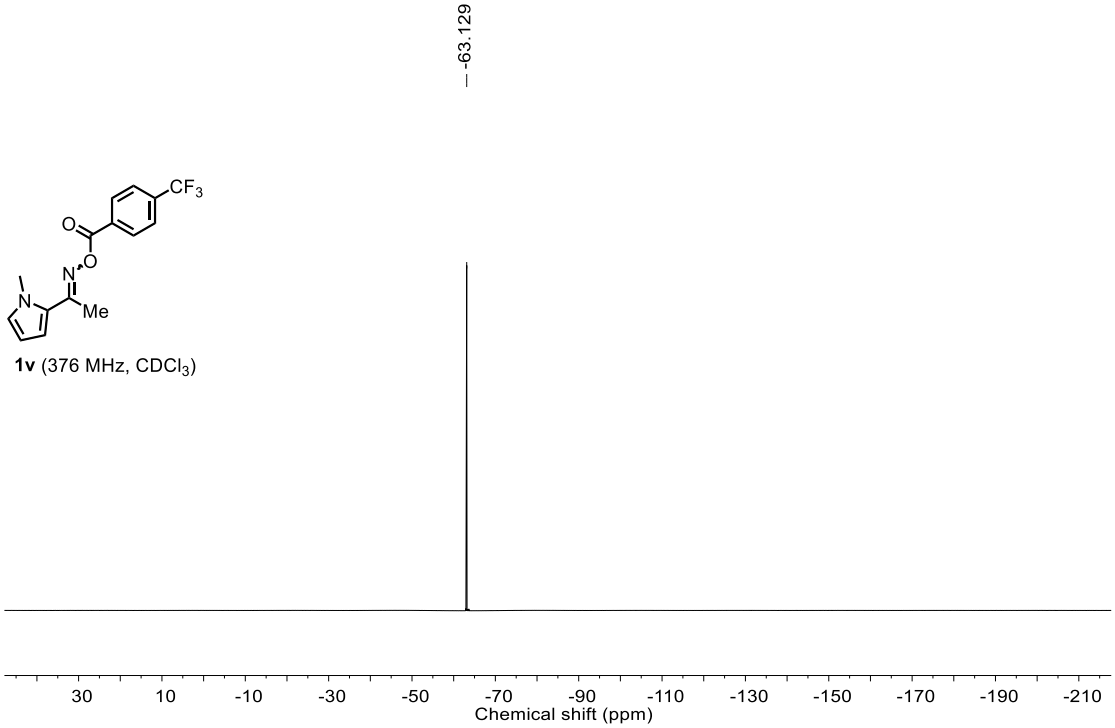

**1y** (376 MHz, $CDCl_3$)



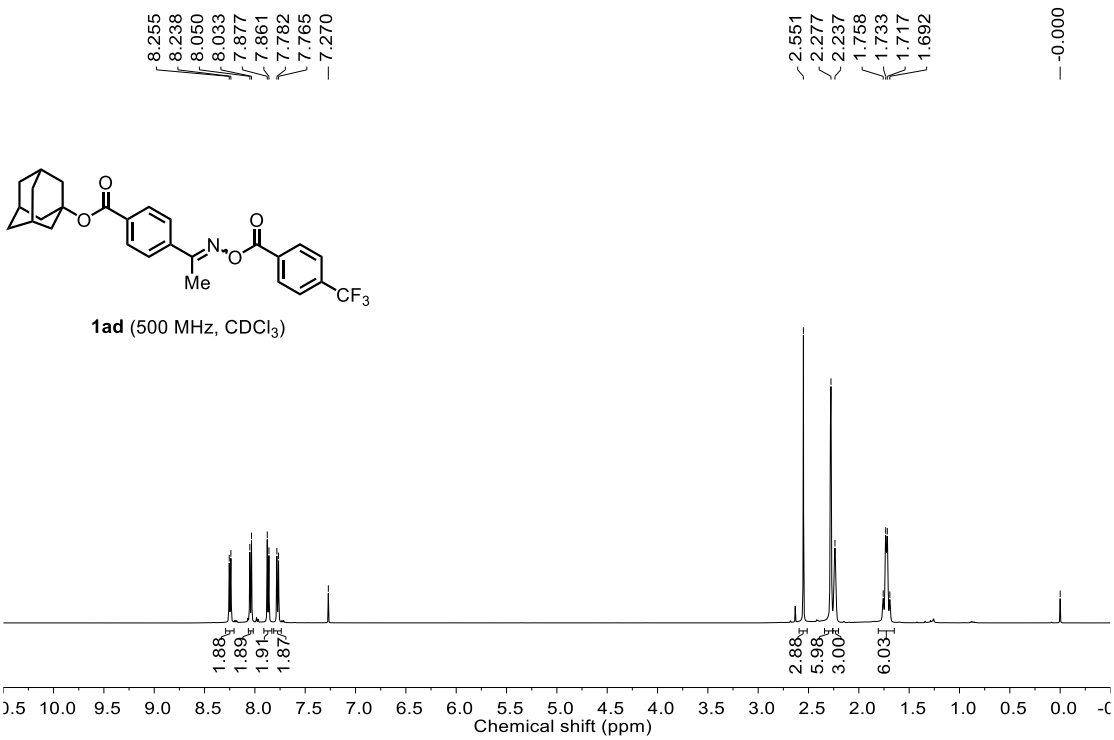

**1v** (400 MHz, $CDCl_3$)



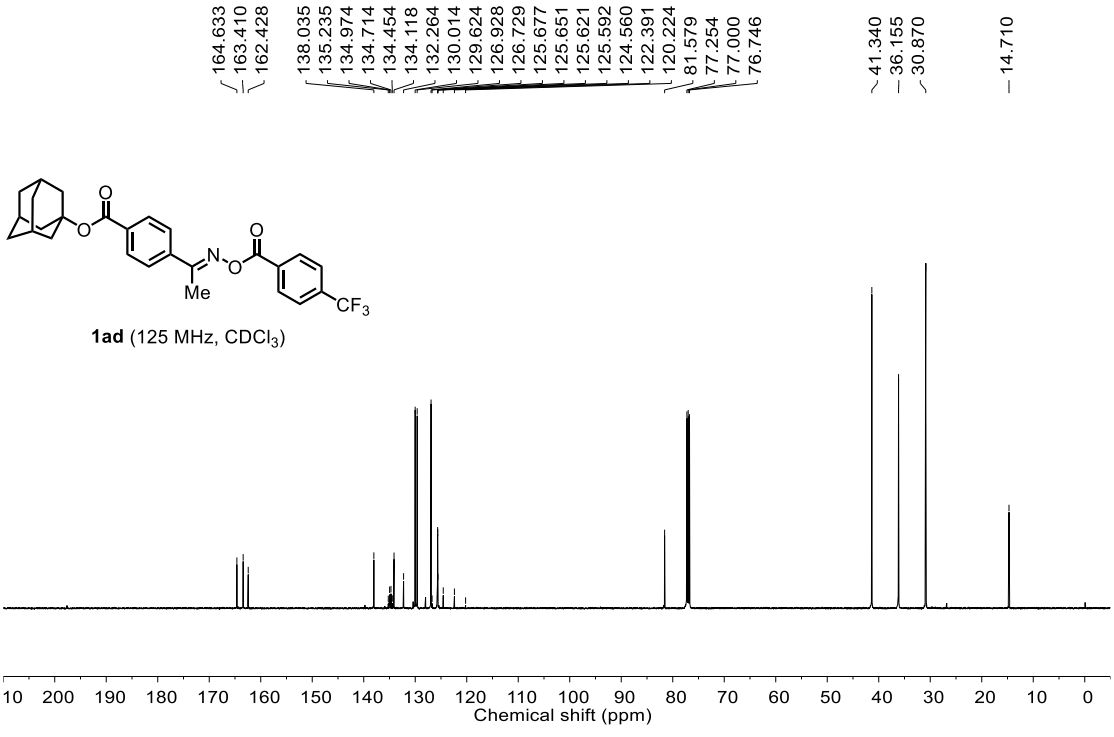

**1v** (150 MHz, $CDCl_3$)



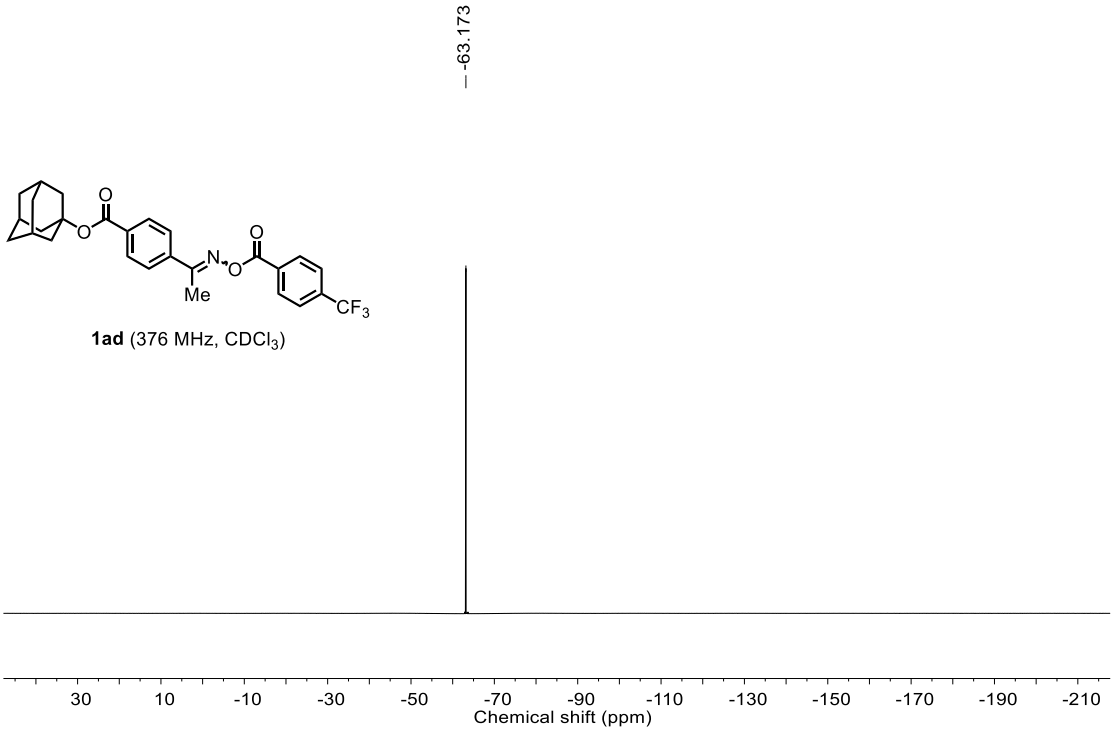

**1v** (376 MHz, $CDCl_3$)



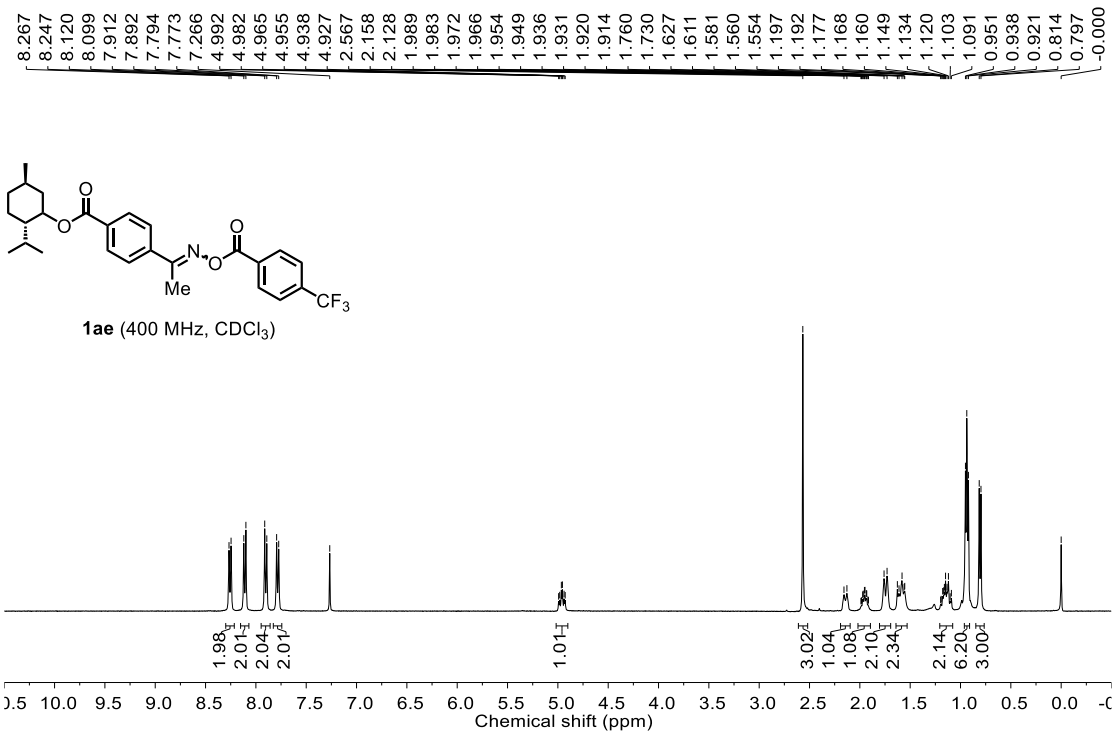

**1ad** (500 MHz, $CDCl_3$)




**1ad** (125 MHz, $CDCl_3$)




**1ad** (376 MHz, $CDCl_3$)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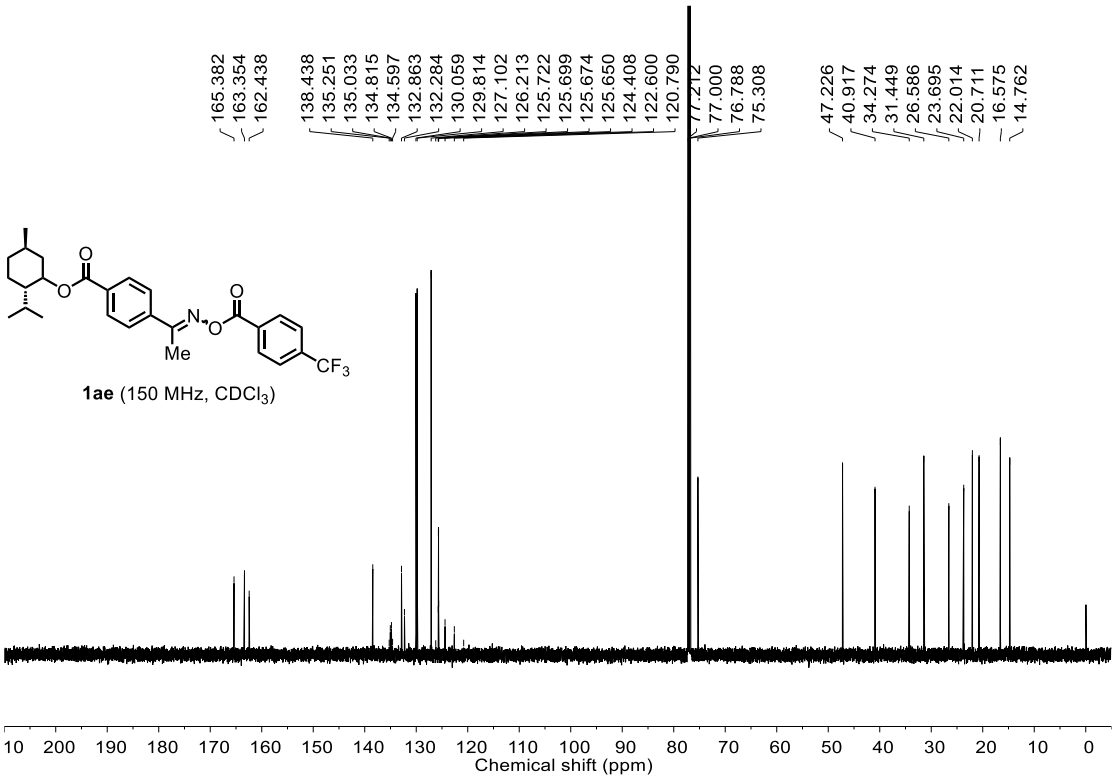
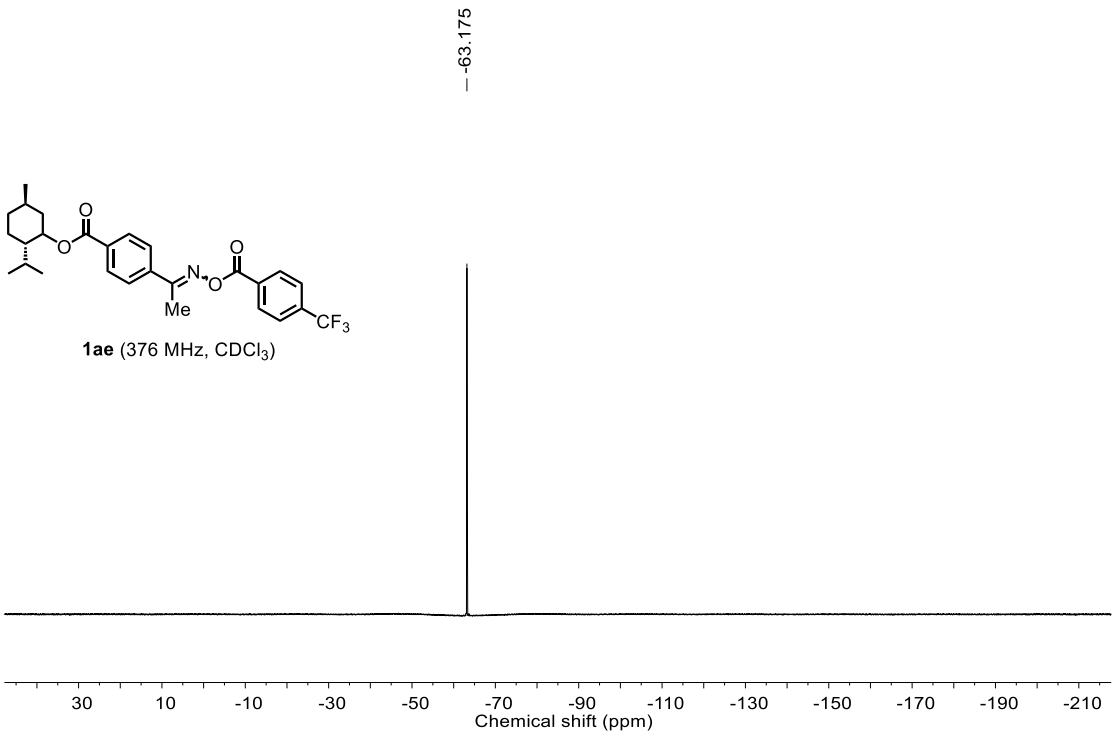
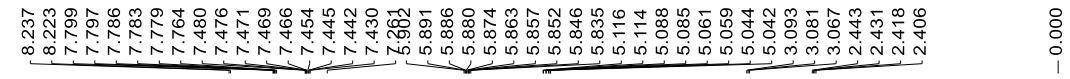
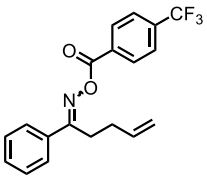
4.938
4.927
2.567
2.158
2.128
1.989
1.983
1.972
1.966
1.954
1.949
1.936
1.931
1.920
1.914
1.760
1.730
1.627
1.611
1.581
1.560
1.554
1.197
1.192
1.177
1.168
1.160
1.149
1.134
1.120
1.103
1.091
0.951
0.938
0.921
0.814
0.797
-0.000
Me
CF3
1ae (400 MHz, CDCl3)
1.98
2.01
2.04
2.01
1.01
3.02
1.04
1.08
2.10
2.34
2.14
6.20
3.00
Chemical shift (ppm)


165.382
163.354
162.438
138.438
135.251
135.033
134.815
134.597
132.863
132.284
130.059
129.814
127.102
126.213
125.722
125.699
125.674
125.650
124.408
122.600
120.790
77.212
77.000
76.788
75.308
47.226
40.917
34.274
31.449
26.586
23.695
22.014
20.711
16.575
14.762
Me
CF3
1ae (150 MHz, CDCl3)
Chemical shift (ppm)

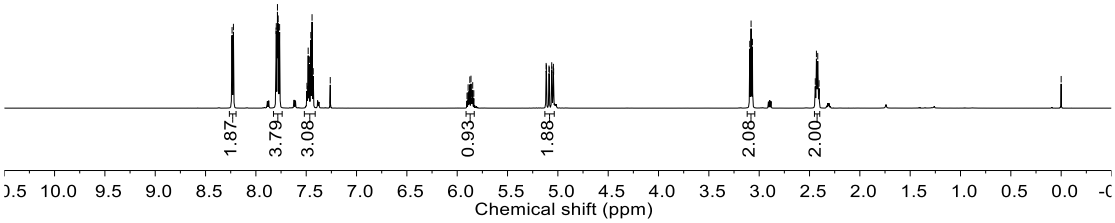


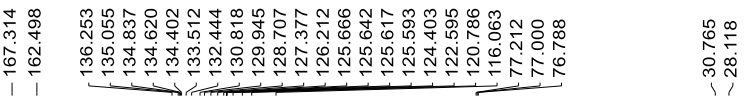

**1ae** (376 MHz, $CDCl_3$)

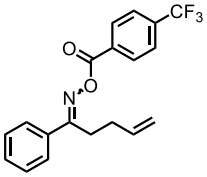


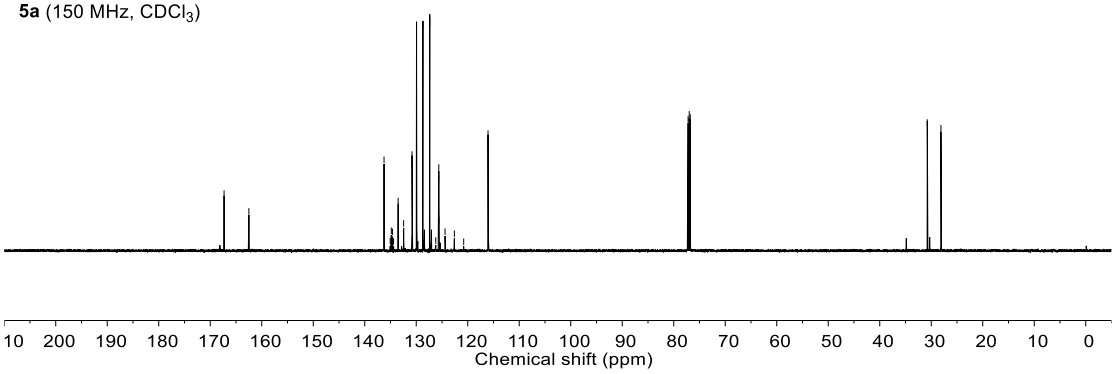

**5a** (600 MHz, $CDCl_3$)

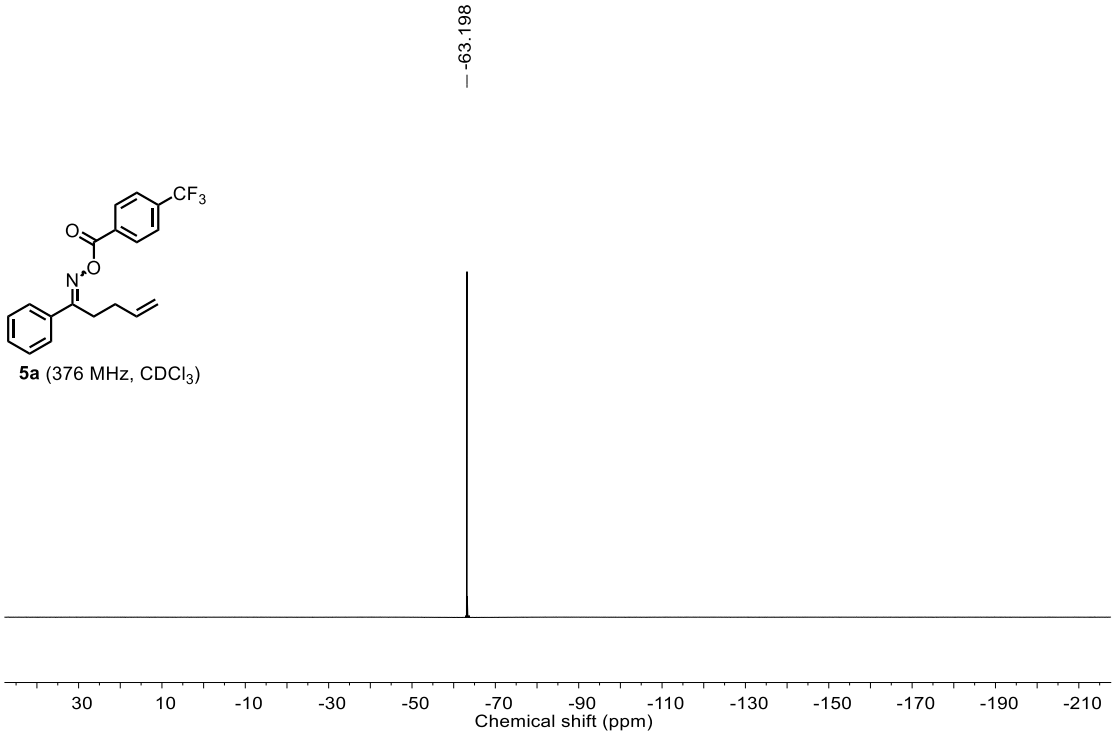


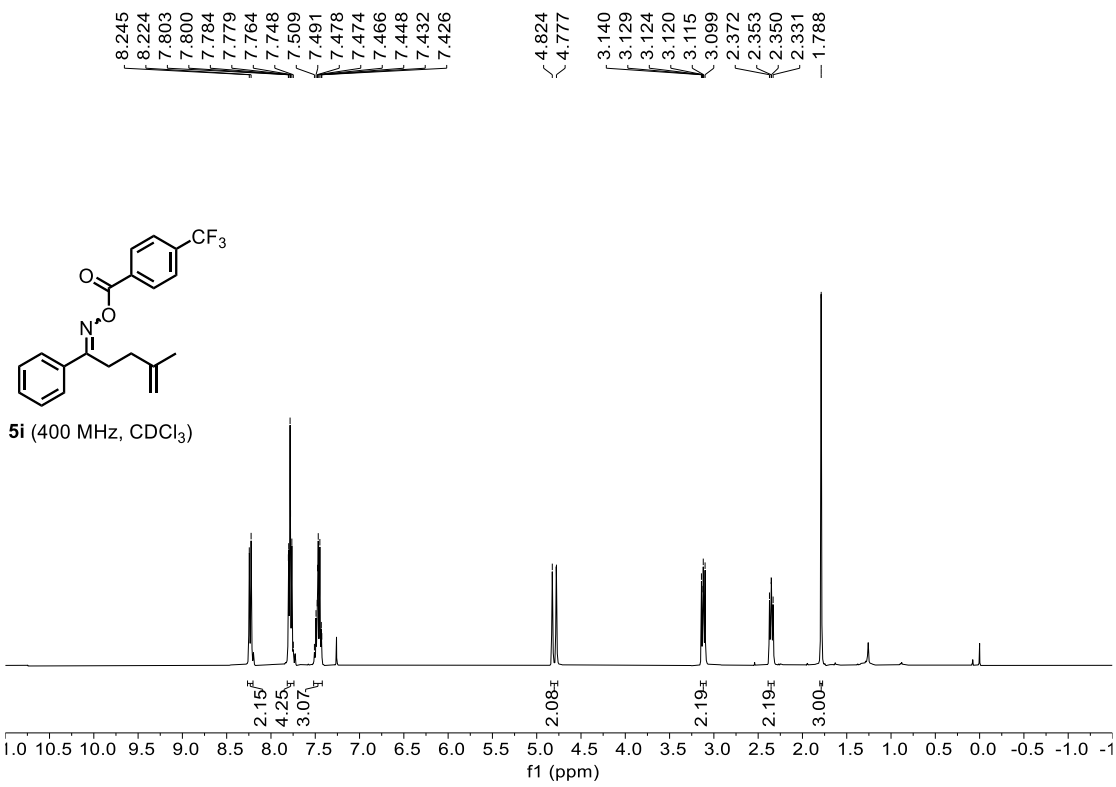



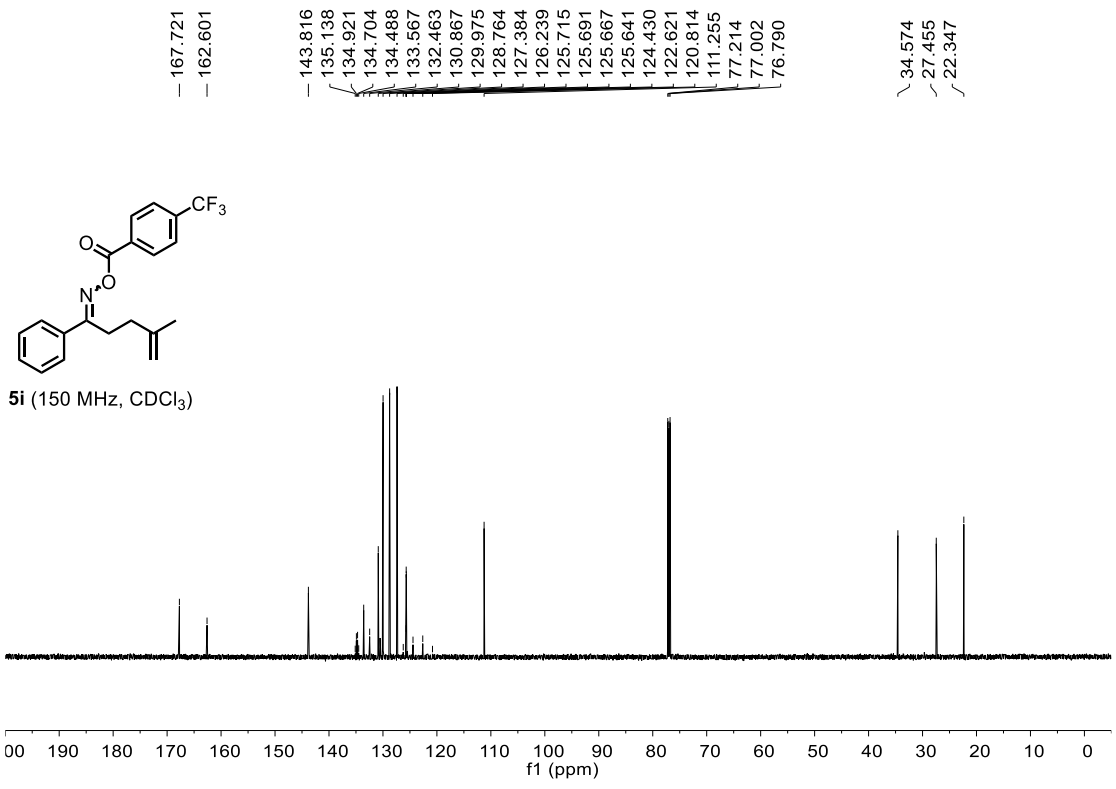

**5a** (150 MHz, $CDCl_3$)

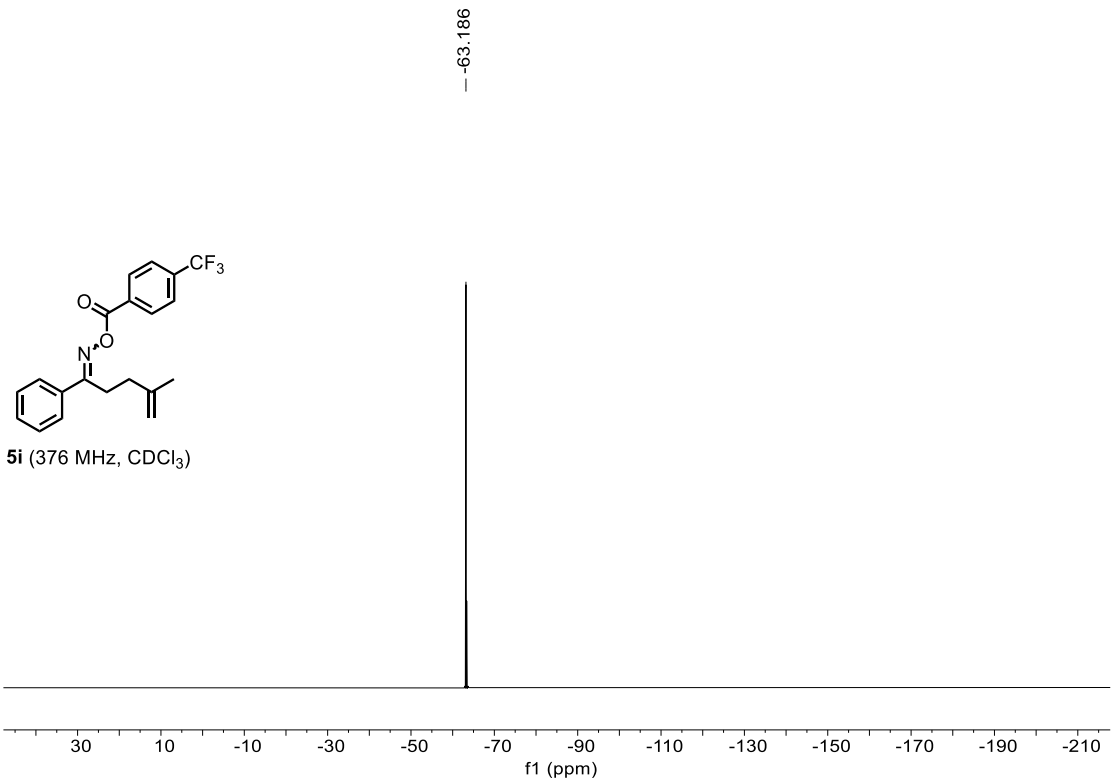




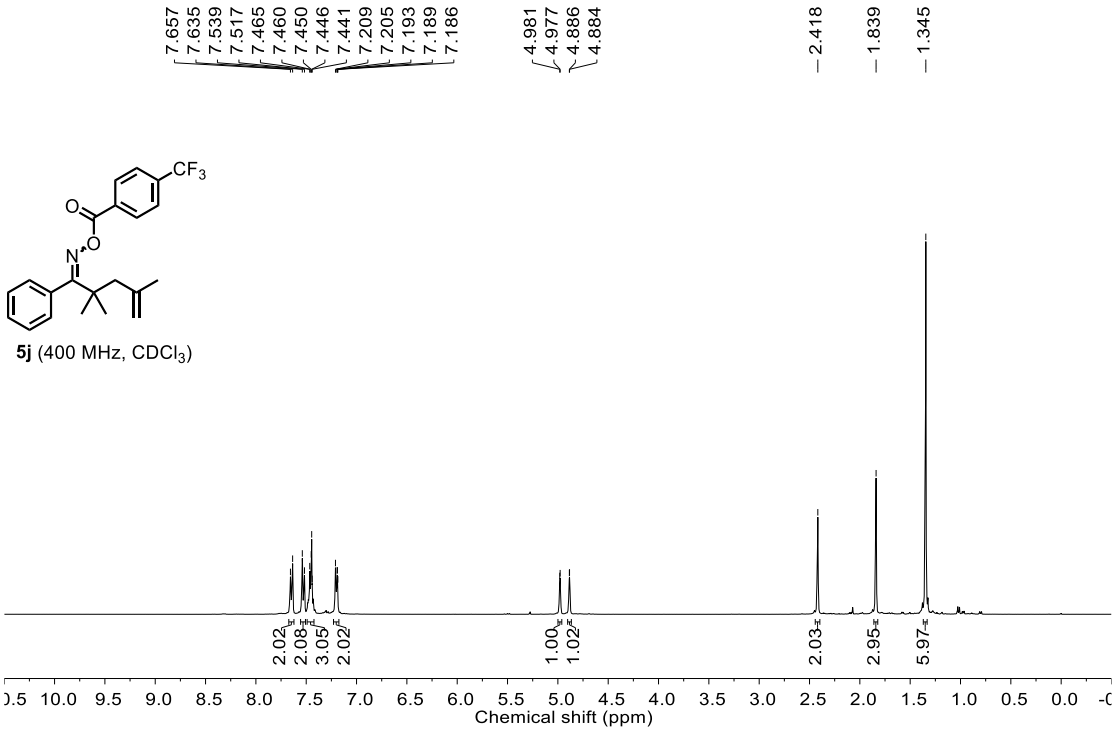

**5a** (376 MHz, $CDCl_3$)


8.245
8.224
7.803
7.800
7.784
7.779
7.764
7.748
7.509
7.491
7.478
7.474
7.466
7.448
7.432
7.426
4.824
4.777
3.140
3.129
3.124
3.120
3.115
3.099
2.372
2.353
2.350
2.331
1.788
CF3
O
O
N
5i (400 MHz, CDCl3)
2.15
4.25
3.07
2.08
2.19
2.19
3.00
f1 (ppm)

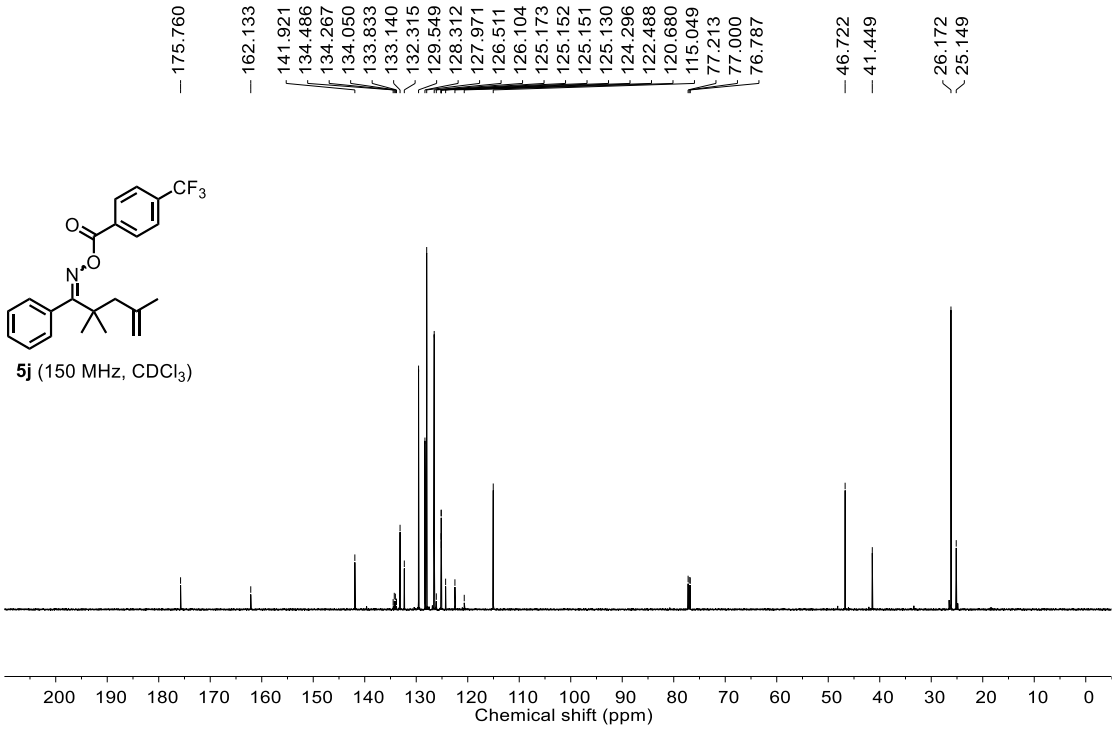

167.721
162.601
143.816
135.138
134.921
134.704
134.488
133.567
132.463
130.867
129.975
128.764
127.384
126.239
125.715
125.691
125.667
125.641
124.430
122.621
120.814
111.255
77.214
77.002
76.790
34.574
27.455
22.347
CF3
O
O
N
5i (150 MHz, CDCl3)
f1 (ppm)



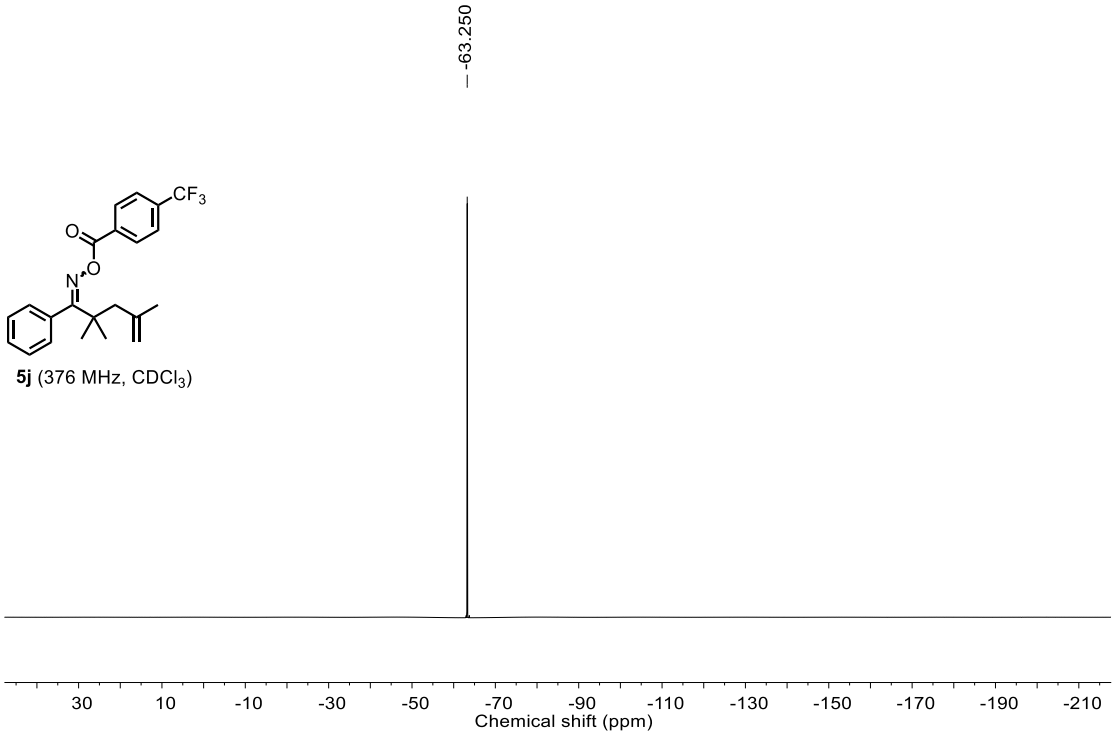

**5i** (376 MHz, $CDCl_3$)



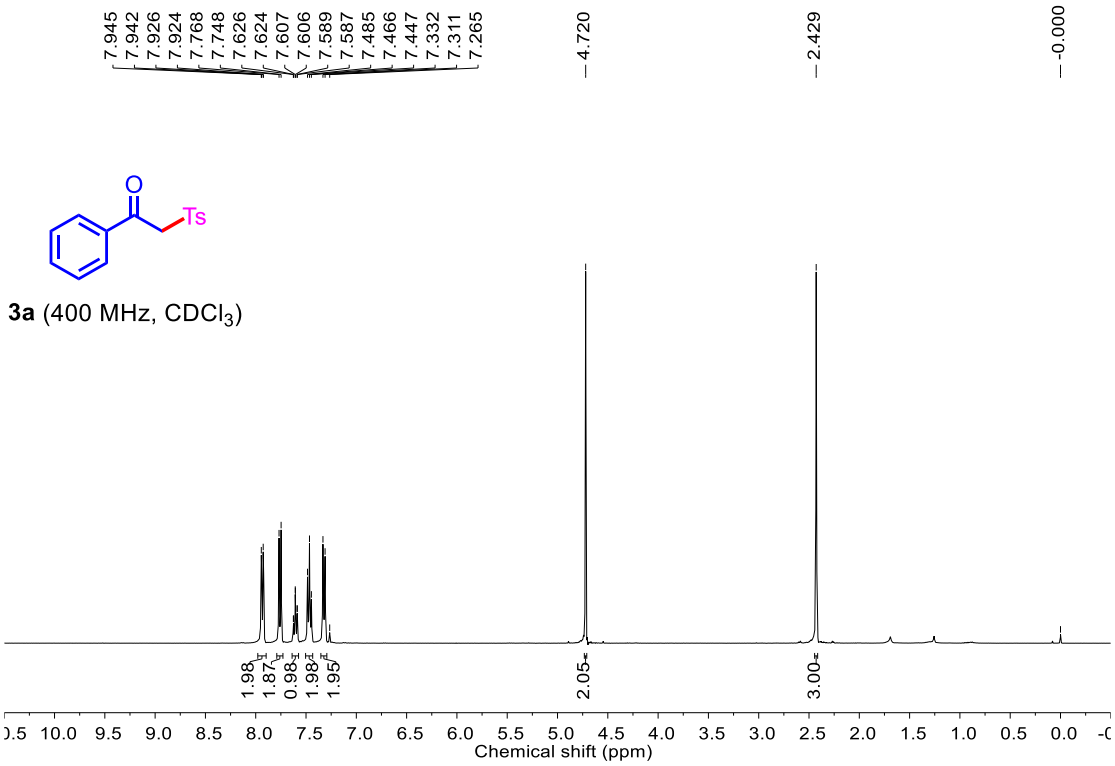

**5j** (400 MHz, $CDCl_3$)



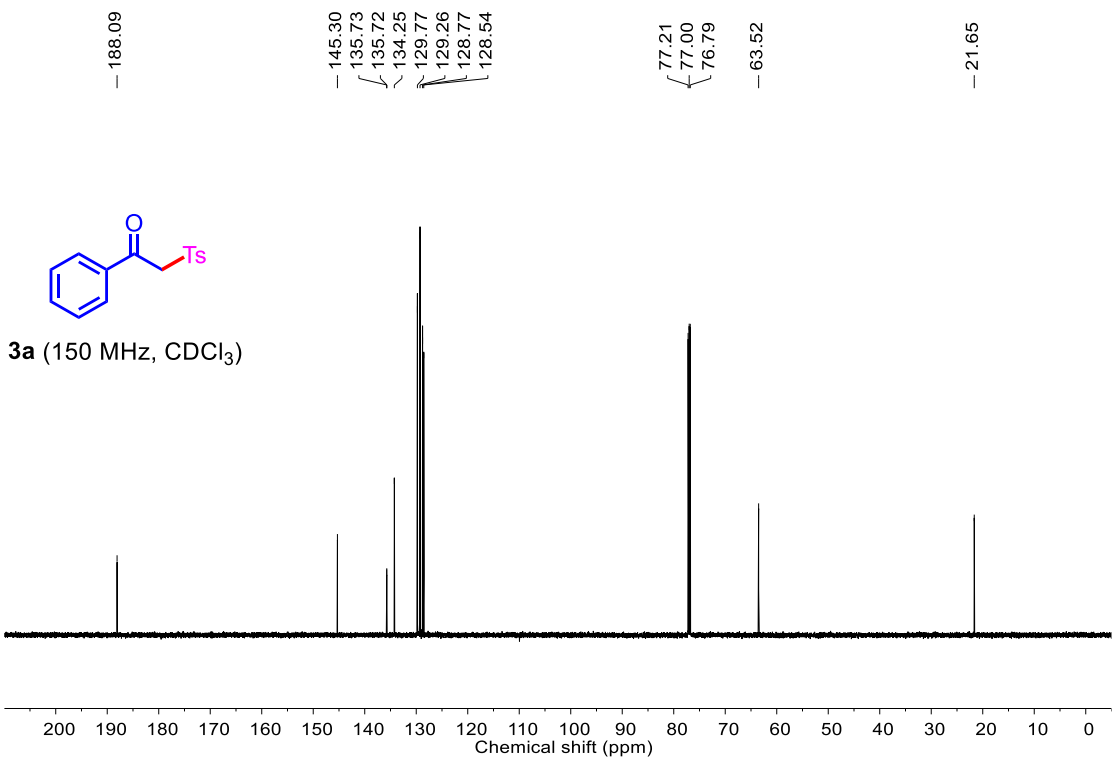

**5j** (150 MHz, $CDCl_3$)



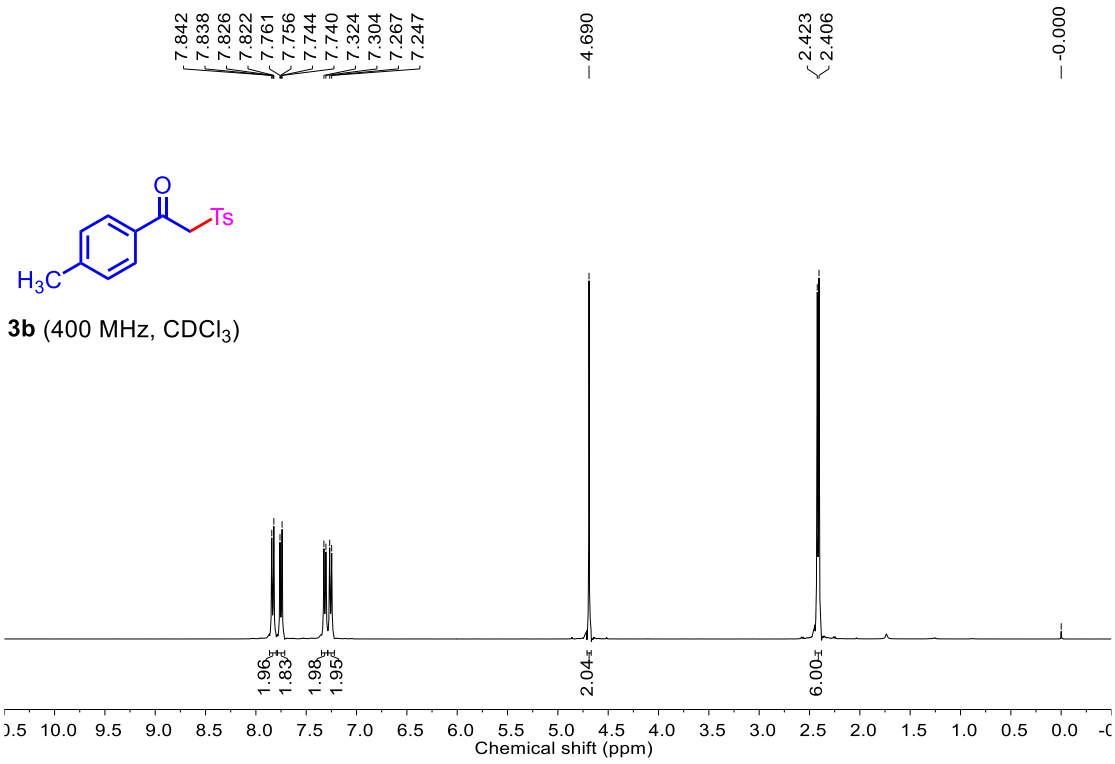

**5j** (376 MHz, $CDCl_3$)



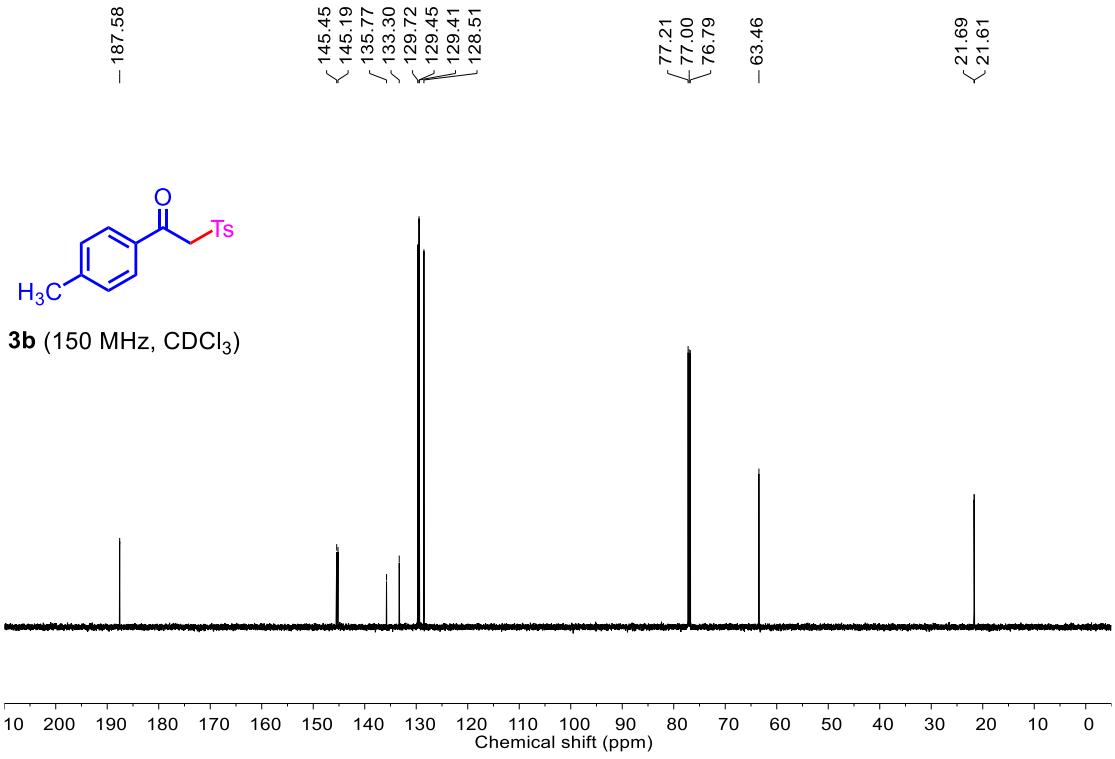

**3a** (400 MHz, $CDCl_3$)



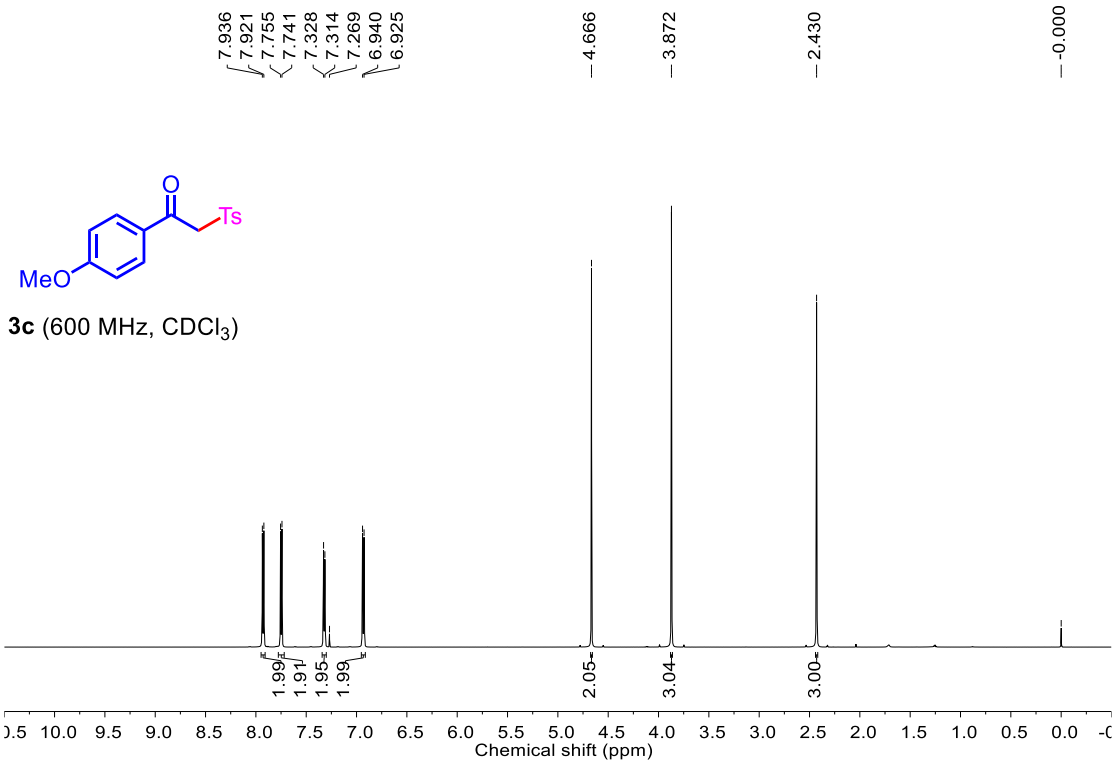

**3a** (150 MHz, $CDCl_3$)



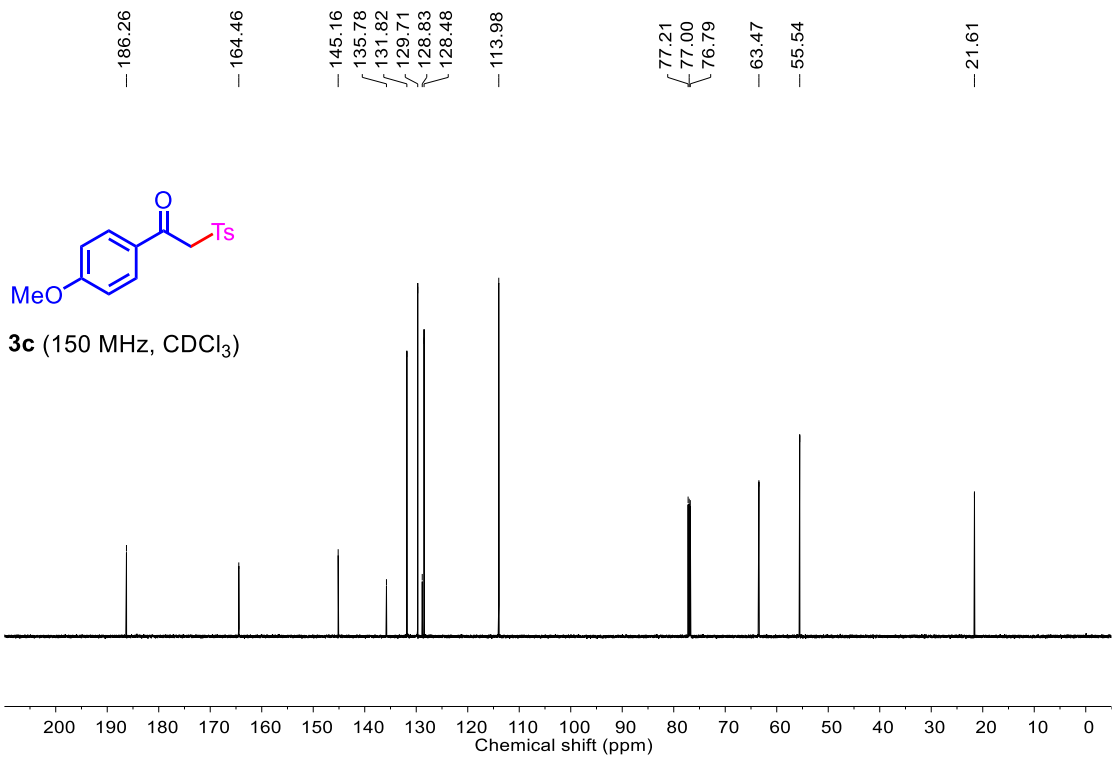

**3b** (400 MHz, $CDCl_3$)



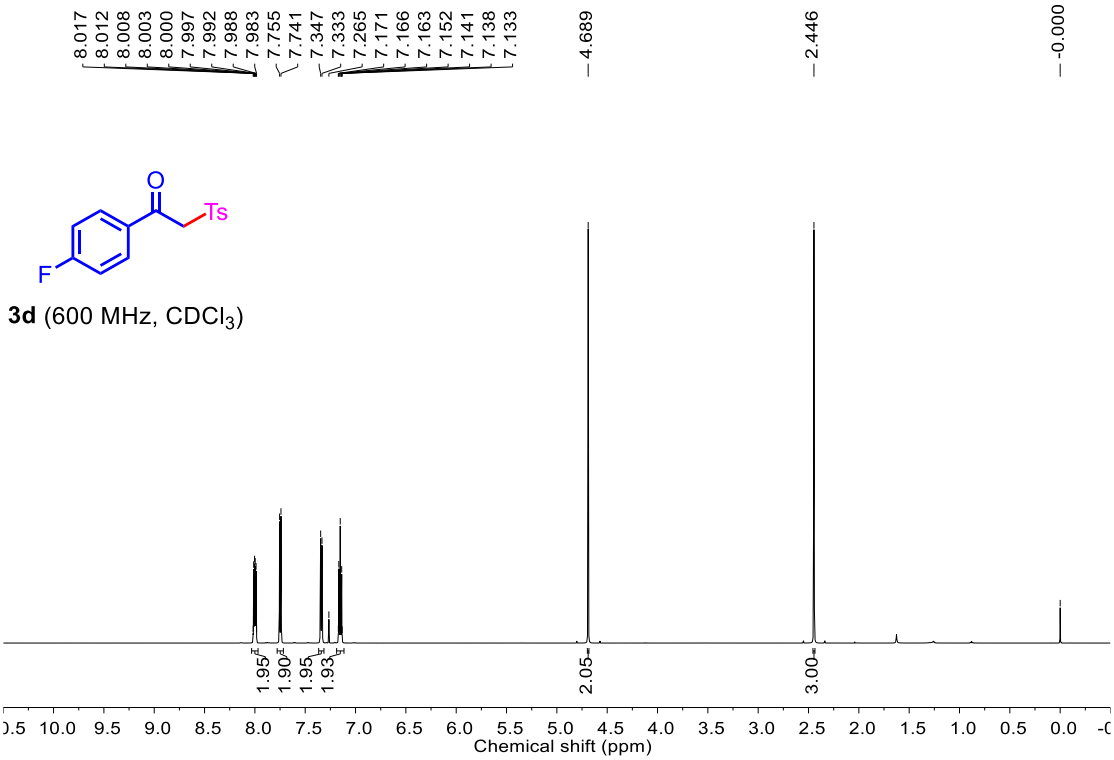

**3b** (150 MHz, $CDCl_3$)



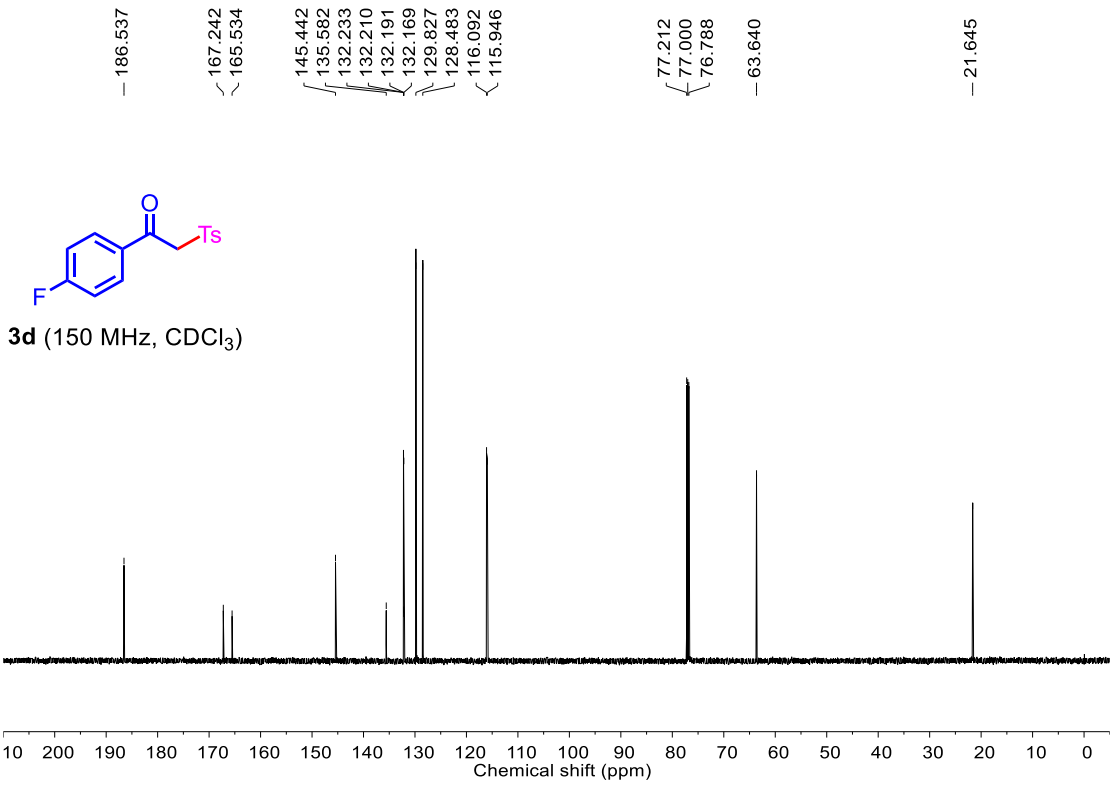

**3c** (600 MHz, $CDCl_3$)



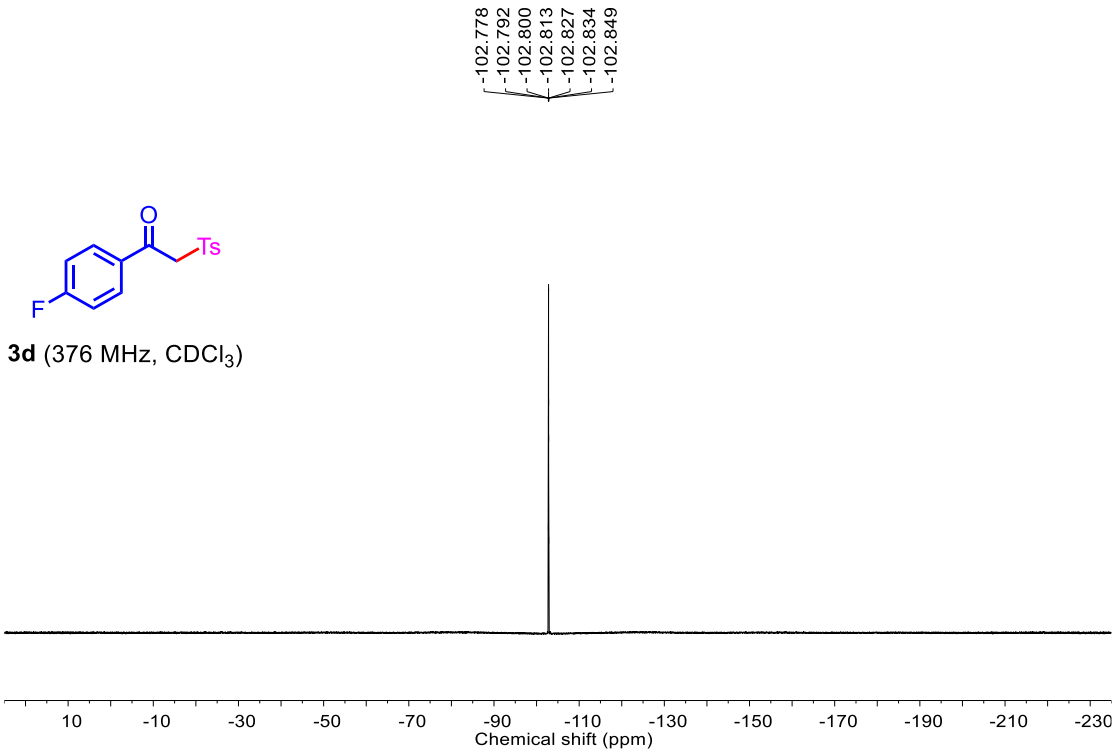

**3c** (150 MHz, $CDCl_3$)



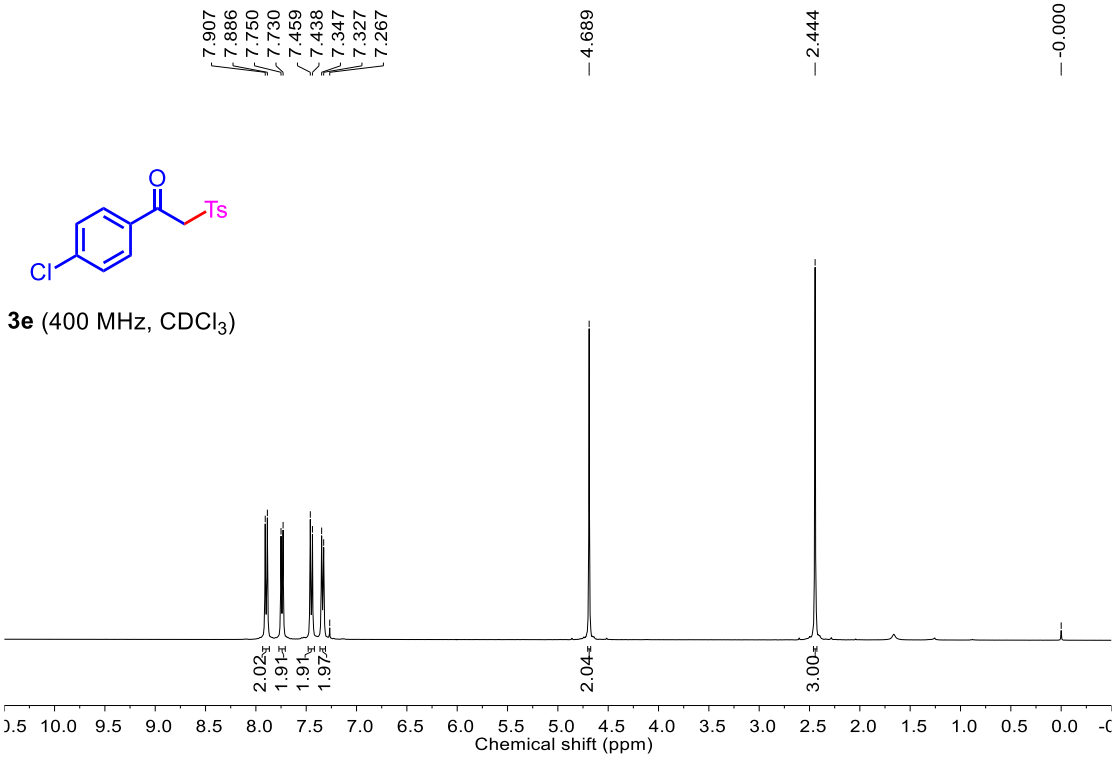

**3d** (600 MHz, $CDCl_3$)



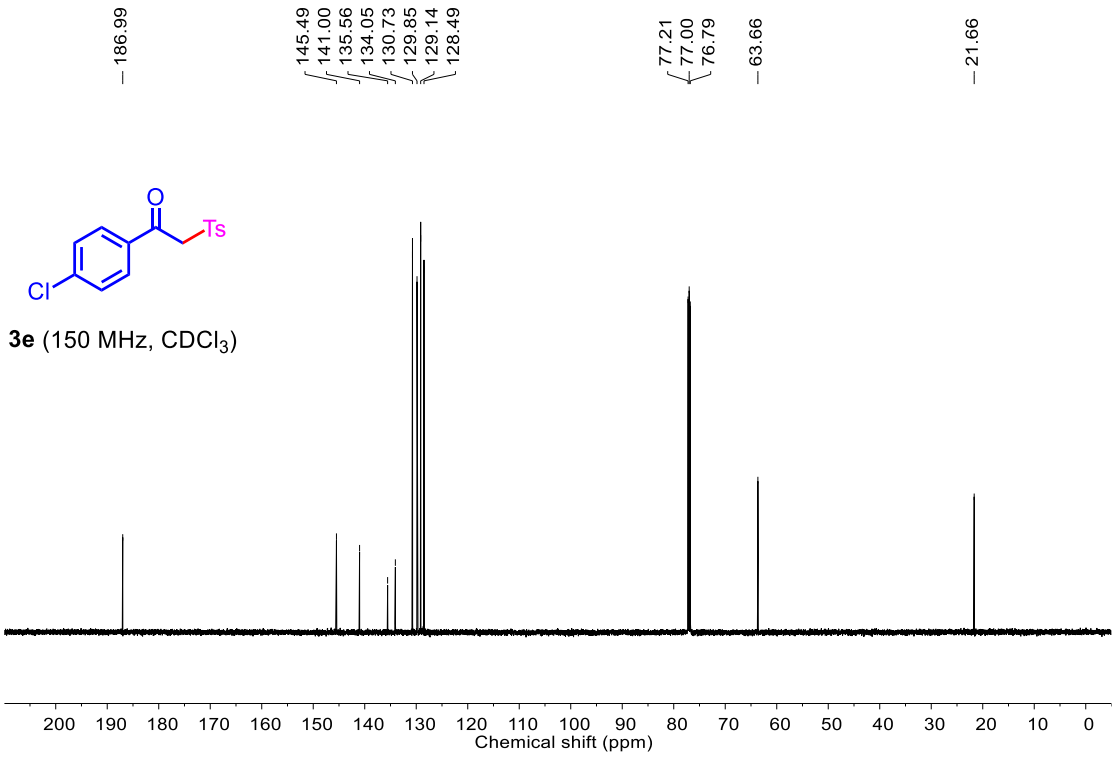

**3d** (150 MHz, $CDCl_3$)



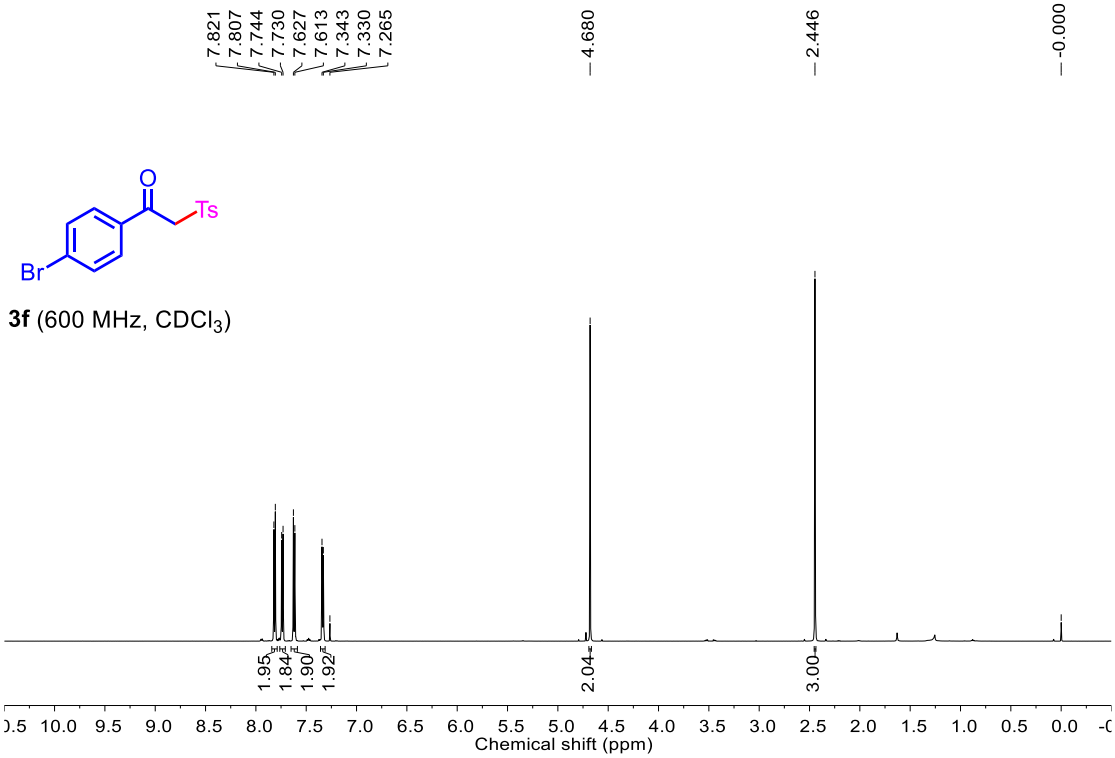

**3d** (376 MHz, $CDCl_3$)



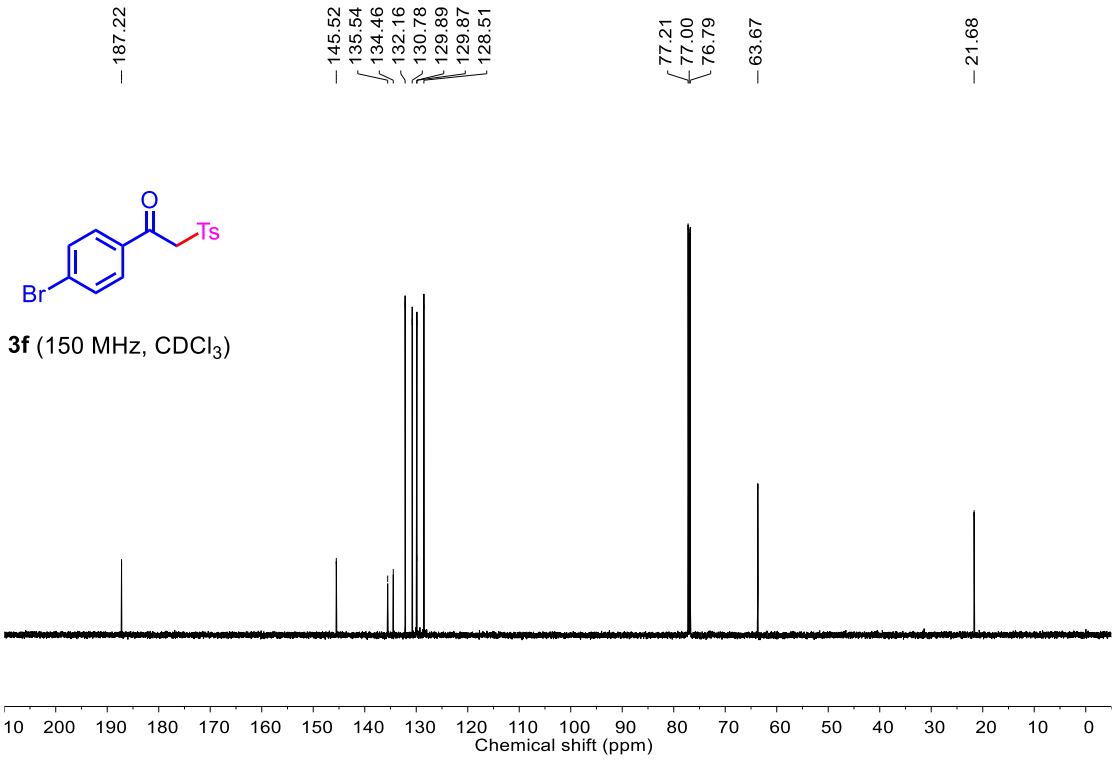

**3e** (400 MHz, $CDCl_3$)



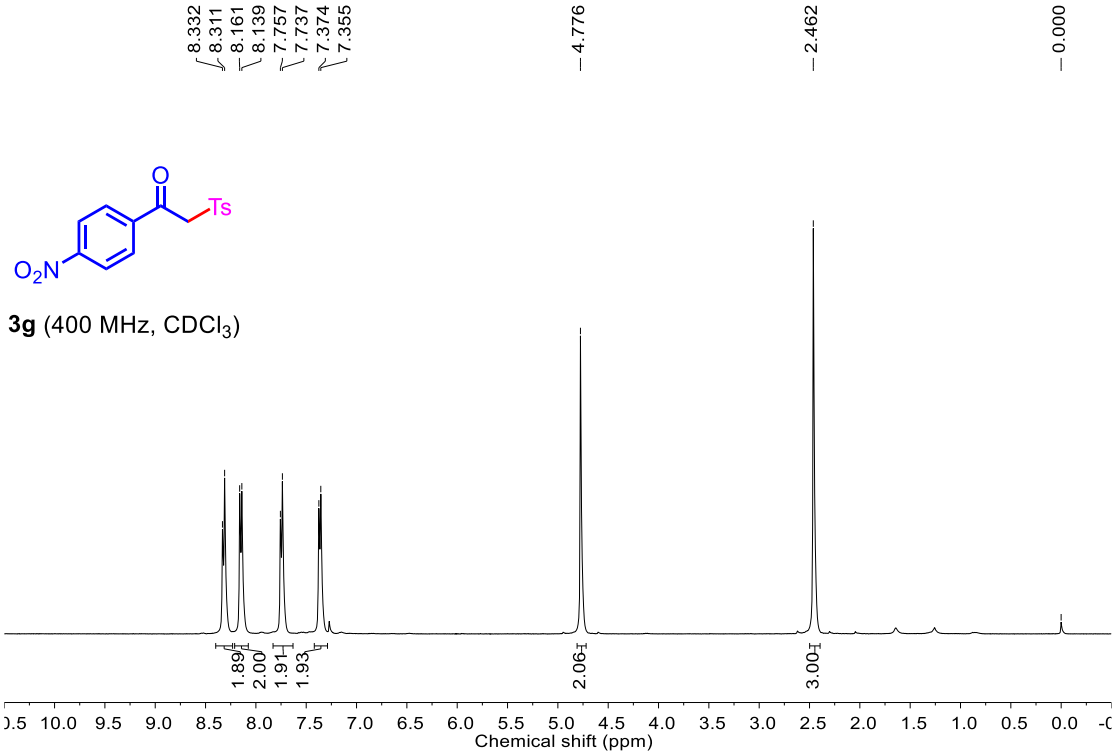

**3e** (150 MHz, $CDCl_3$)

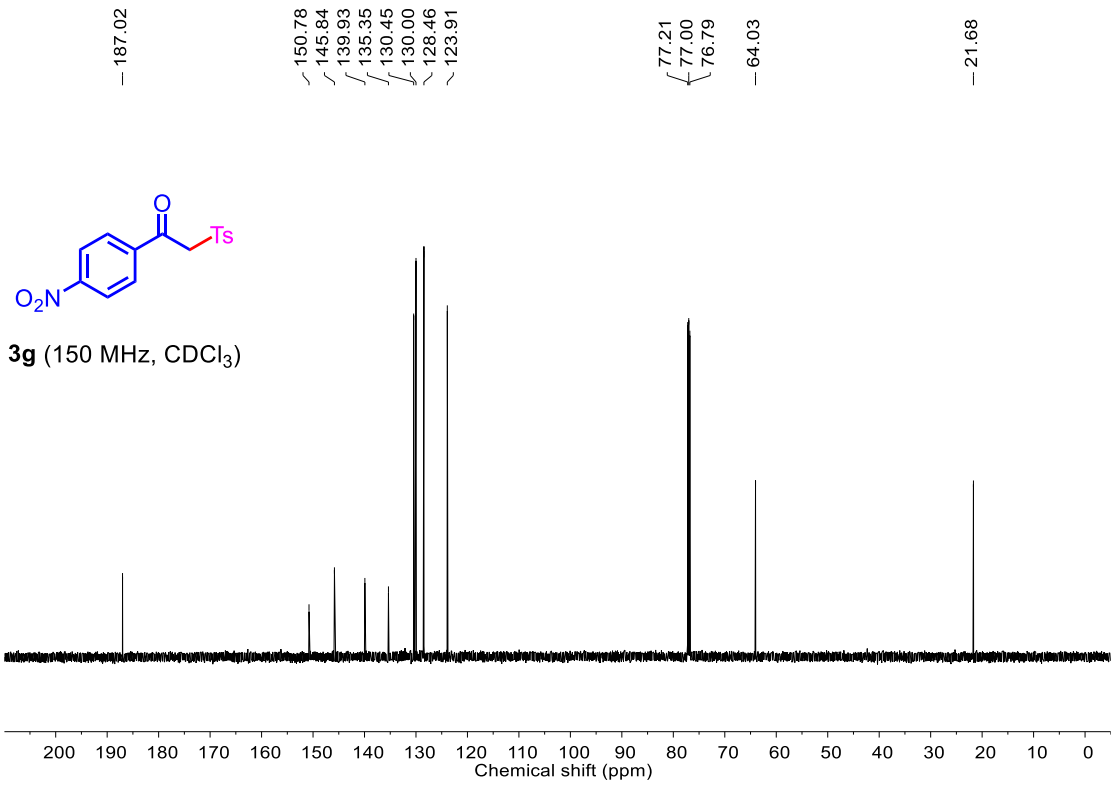


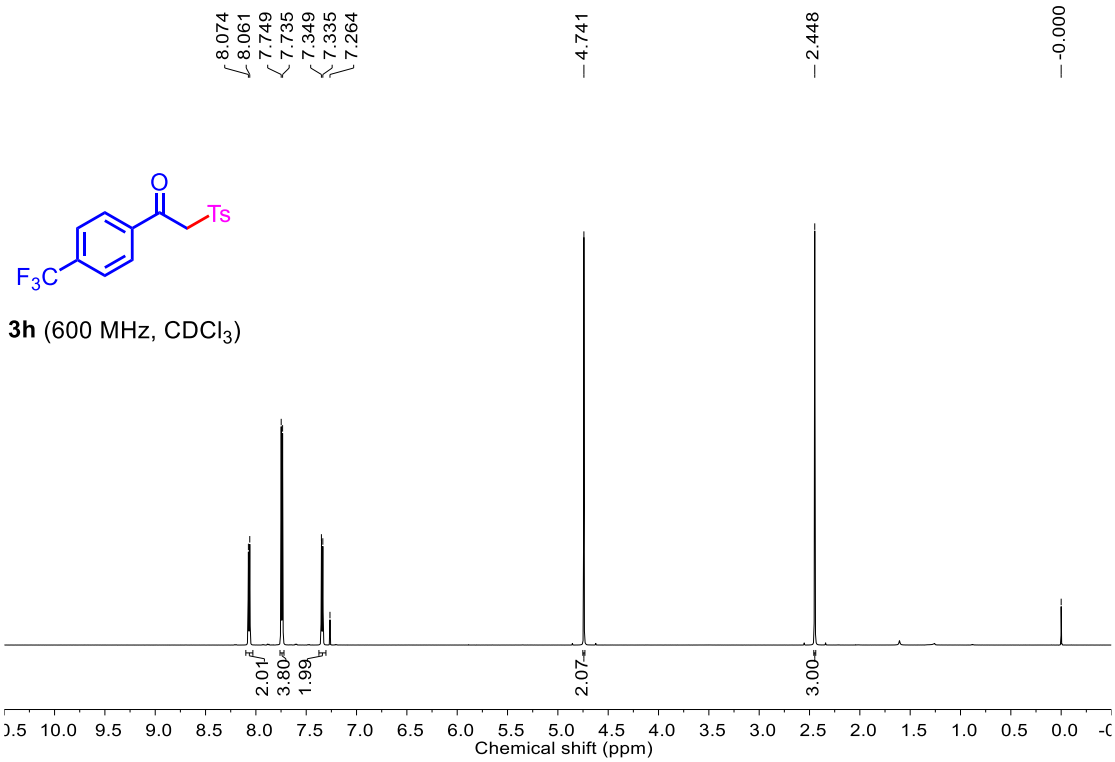

**3f** (600 MHz, $CDCl_3$)



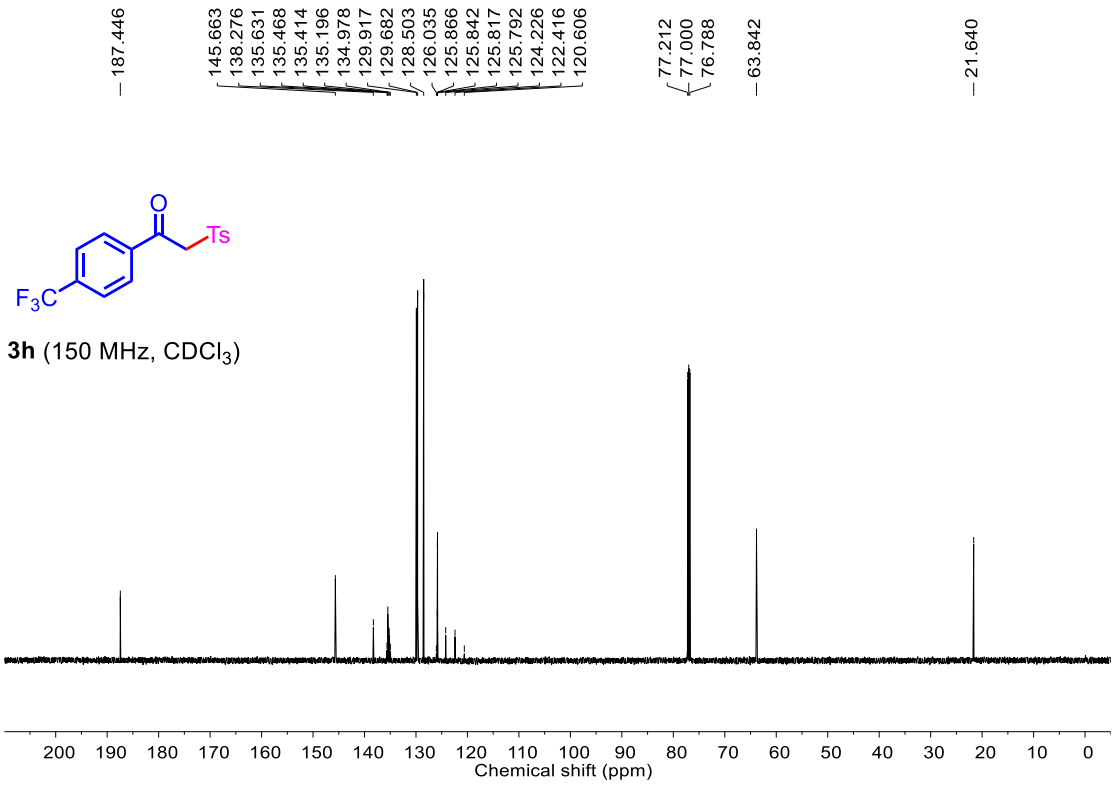

**3f** (150 MHz, $CDCl_3$)


8.332
8.311
8.161
8.139
7.757
7.737
7.374
7.355
4.776
2.462
0.000
O
Ts
O2N
3g (400 MHz, CDCl3)
1.89
2.00
1.91
1.93
2.06
3.00
Chemical shift (ppm)

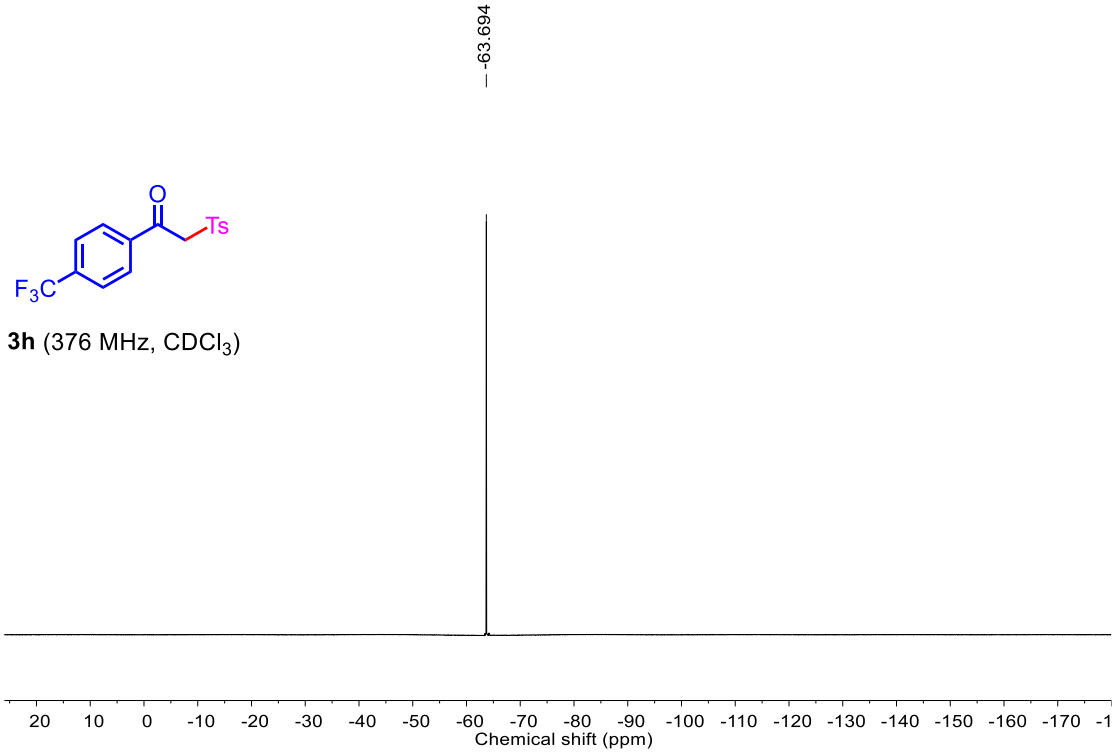

187.02
150.78
145.84
139.93
135.35
130.45
130.00
128.46
123.91
77.21
77.00
76.79
64.03
21.68
O
Ts
O2N
3g (150 MHz, CDCl3)
Chemical shift (ppm)



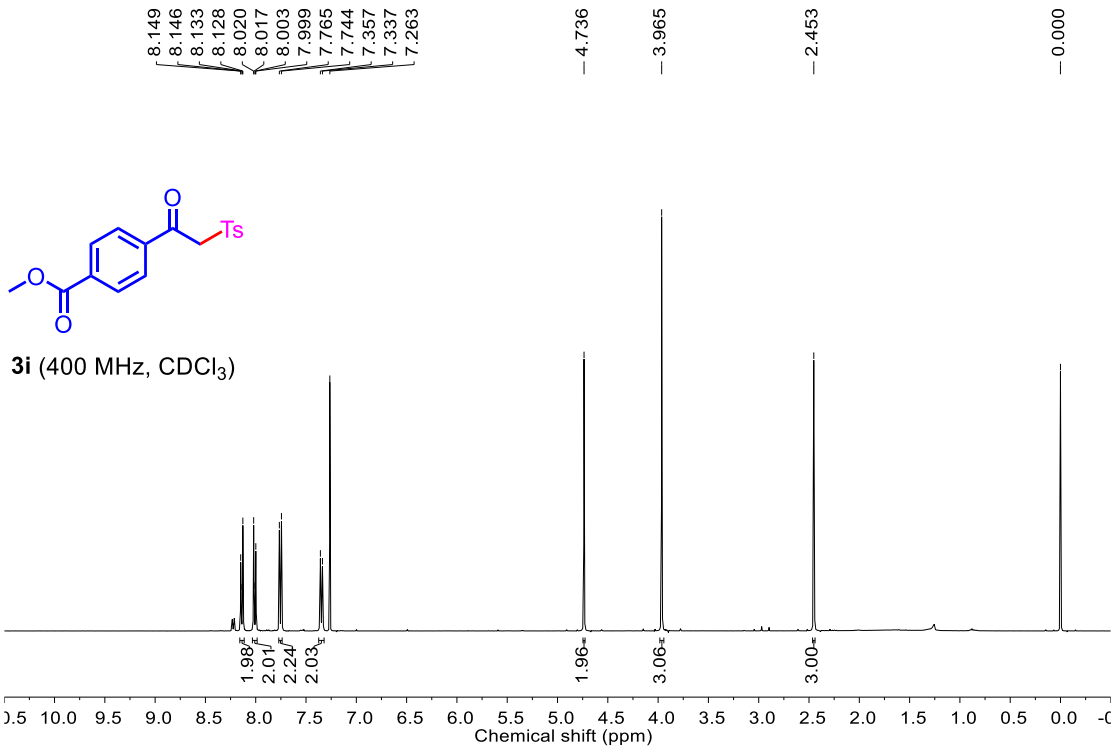

**3h** (600 MHz, $CDCl_3$)



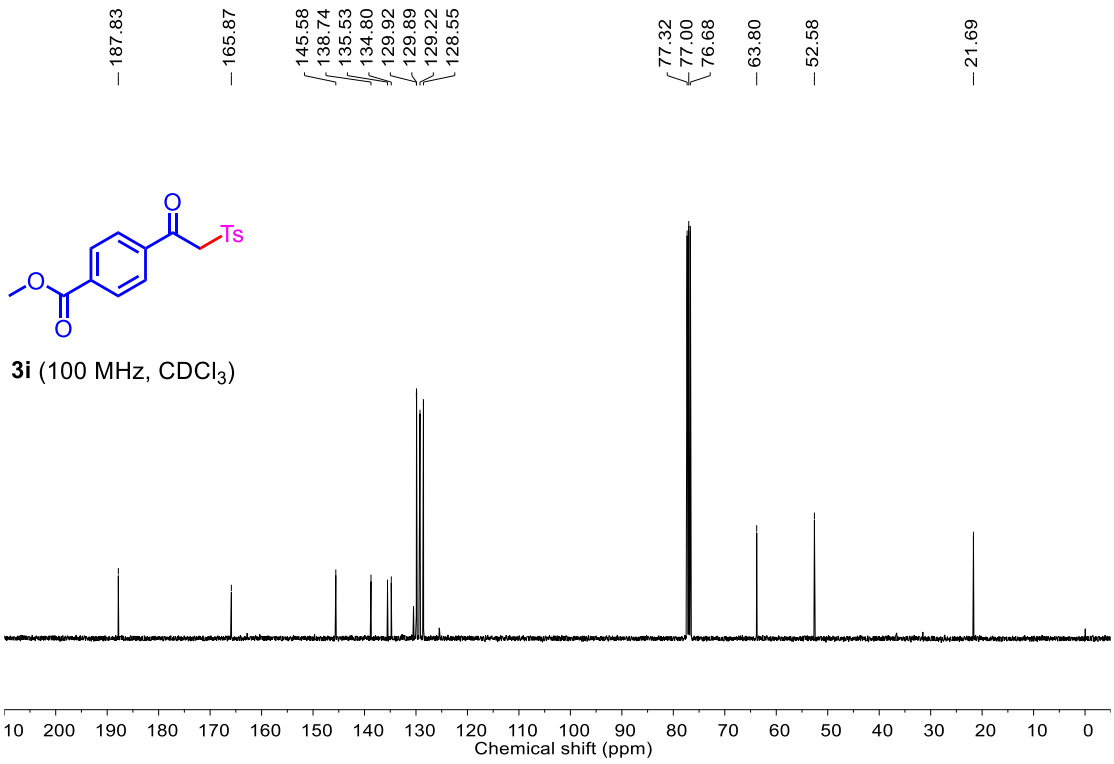

**3h** (150 MHz, $CDCl_3$)



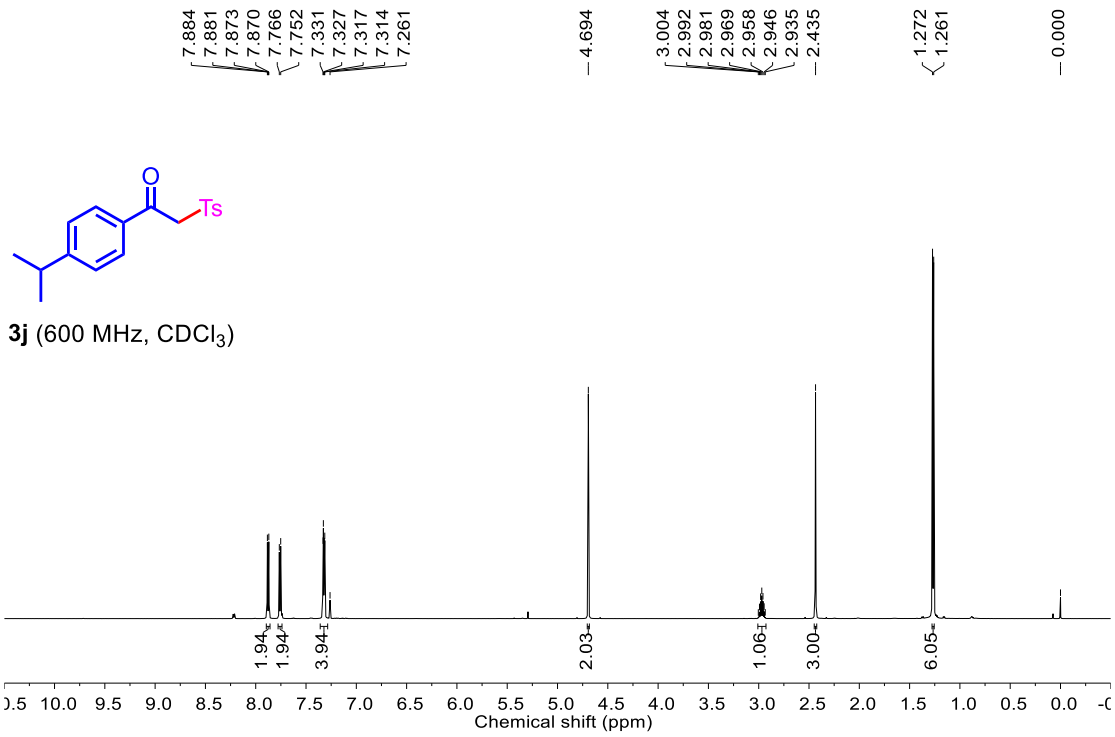

**3h** (376 MHz, $CDCl_3$)



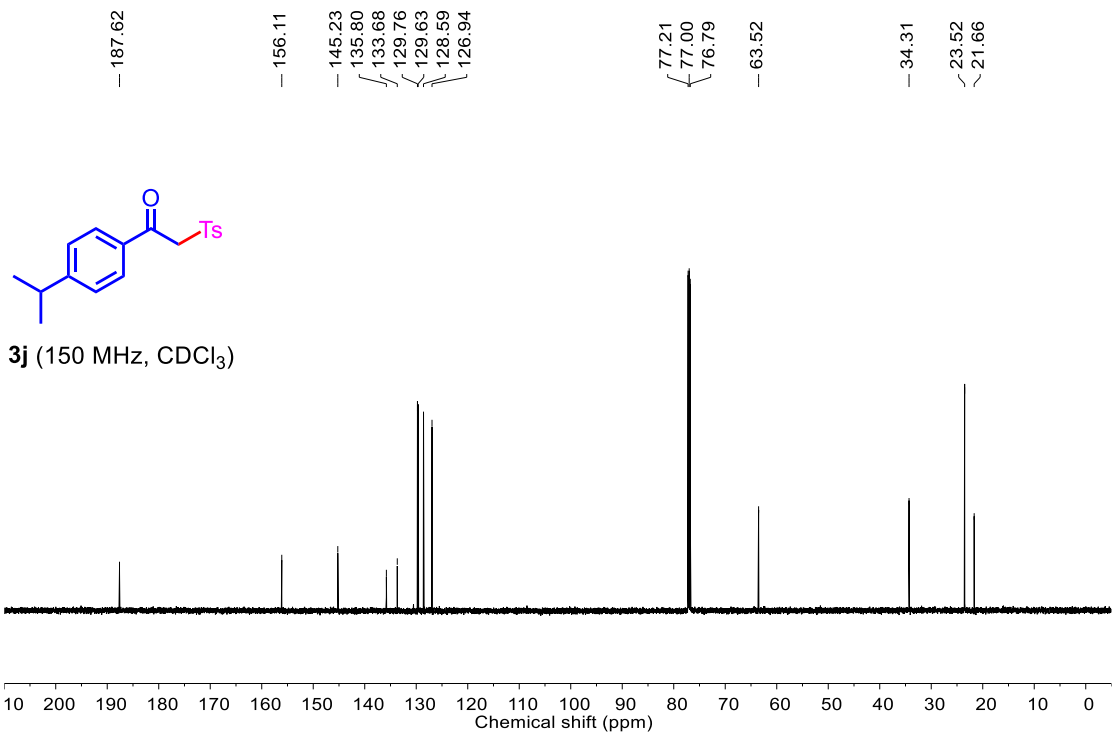

**3i** (400 MHz, $CDCl_3$)



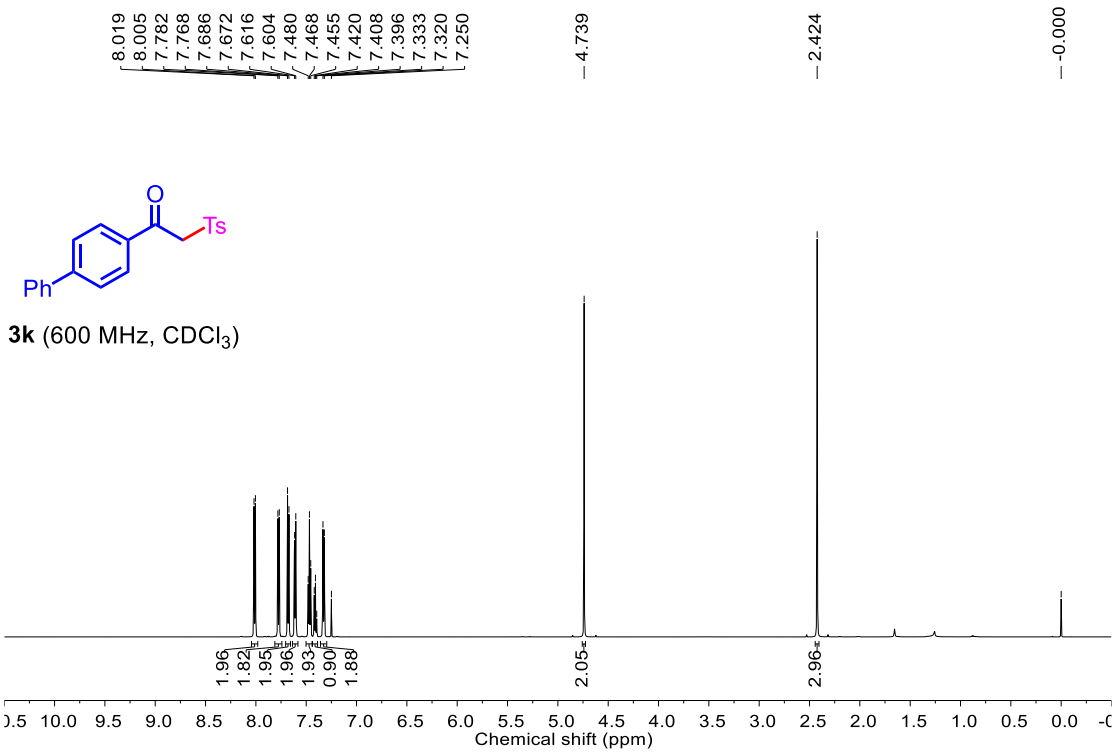

**3i** (100 MHz, $CDCl_3$)

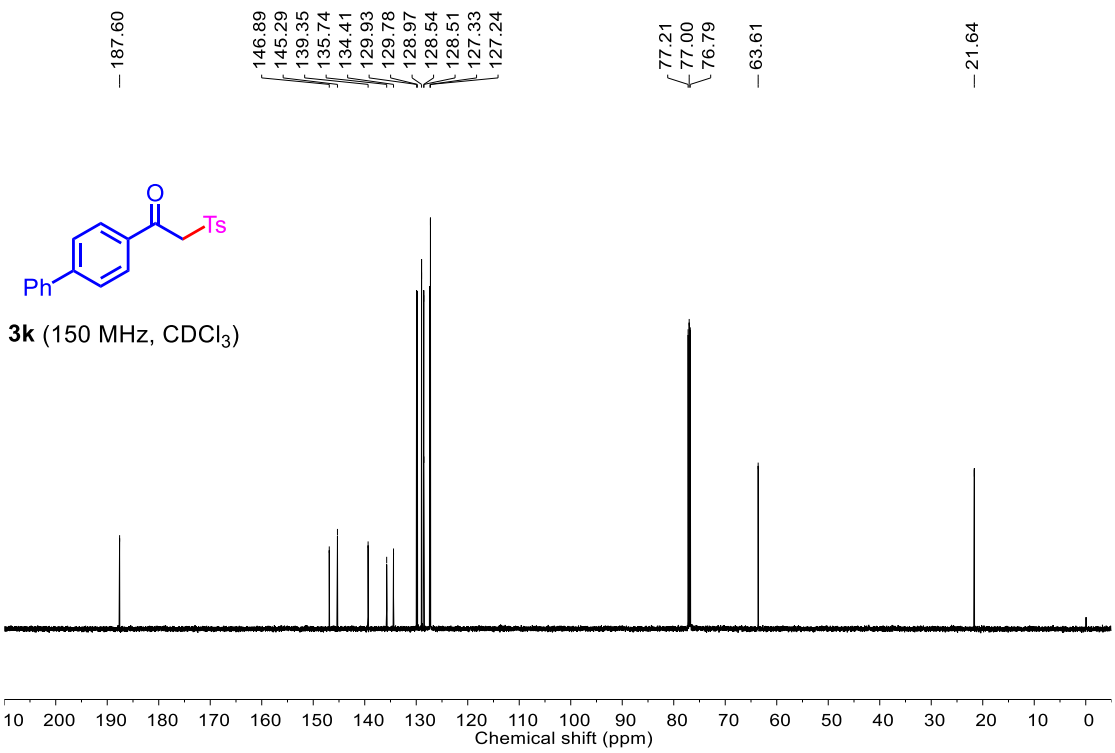


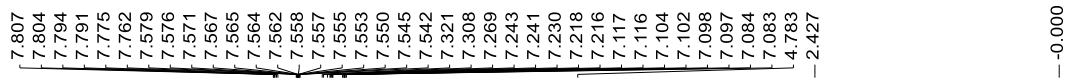

**3j** (600 MHz, $CDCl_3$)

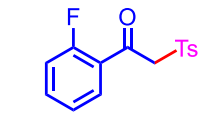



**3j** (150 MHz, $CDCl_3$)


8.019
8.005
7.782
7.768
7.686
7.672
7.616
7.604
7.480
7.468
7.455
7.420
7.408
7.396
7.333
7.320
7.250
4.739
2.424
-0.000
O
Ts
Ph
3k (600 MHz, CDCl3)
1.96
1.82
1.95
1.96
1.93
0.90
1.88
2.05
2.96
Chemical shift (ppm)


187.60
146.89
145.29
139.35
135.74
134.41
129.93
129.78
128.97
128.54
128.51
127.33
127.24
77.21
77.00
76.79
63.61
21.64
O
Ts
Ph
3k (150 MHz, CDCl3)
Chemical shift (ppm)

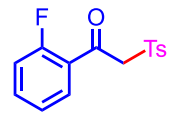


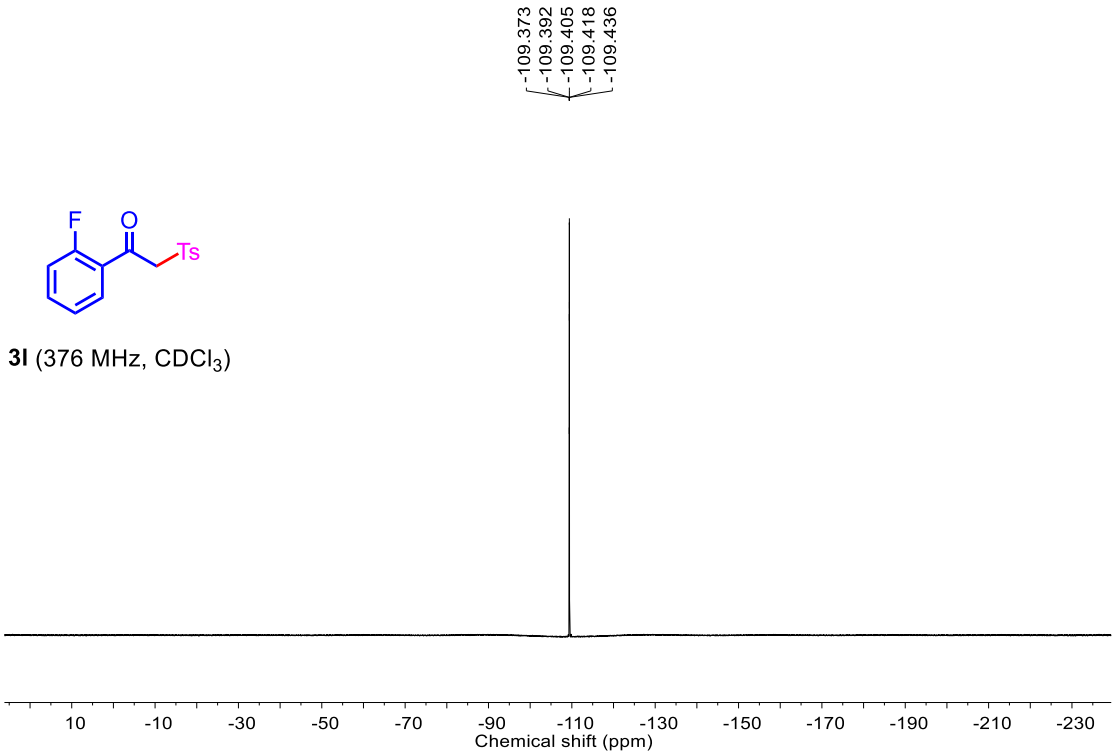

**3l** (600 MHz, $CDCl_3$)



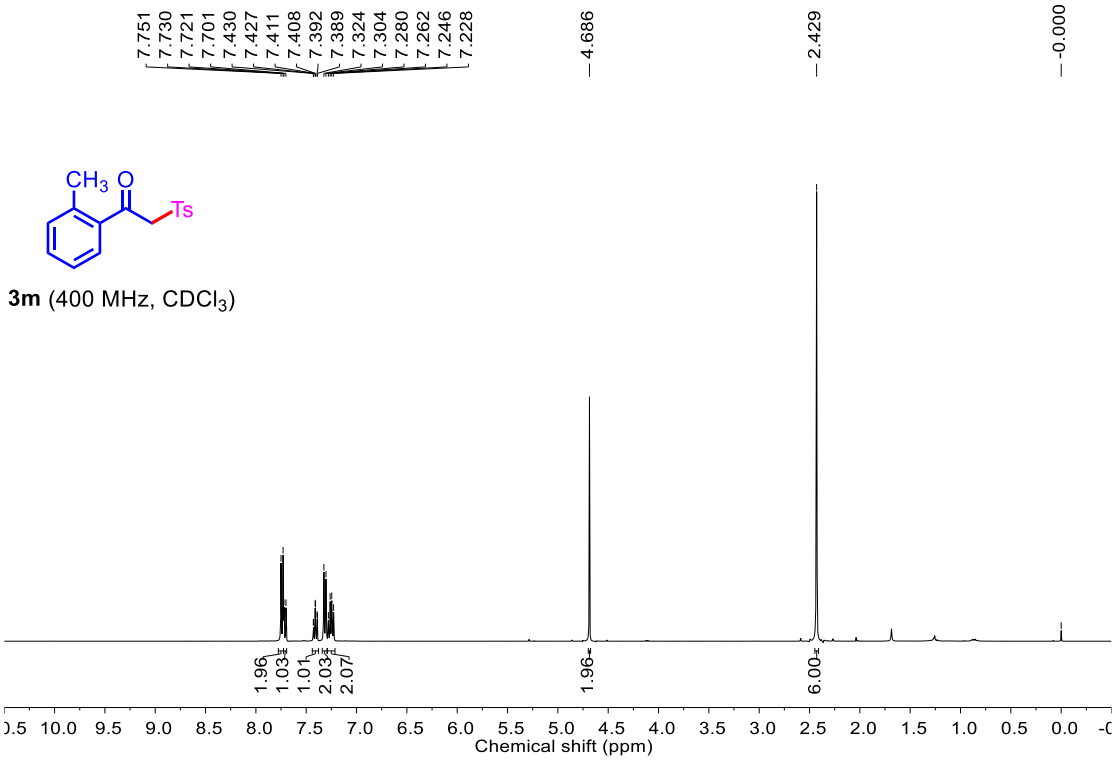




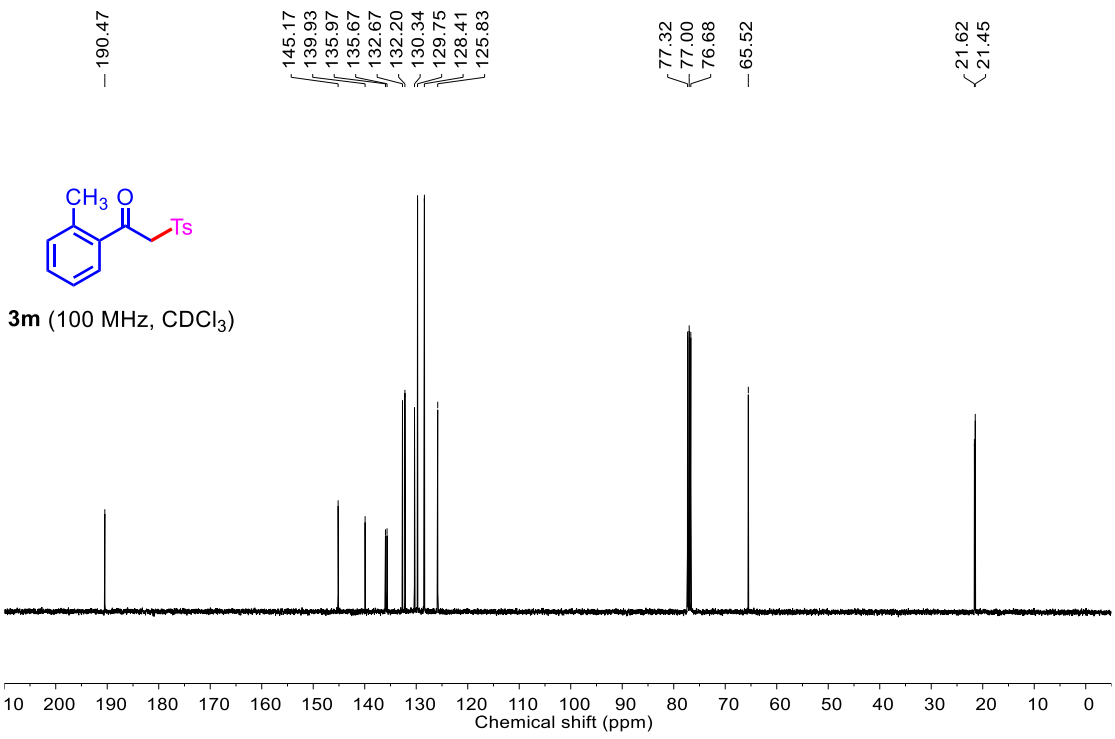

**3l** (150 MHz, $CDCl_3$)



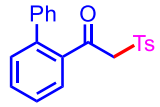

**3l** (376 MHz, $CDCl_3$)



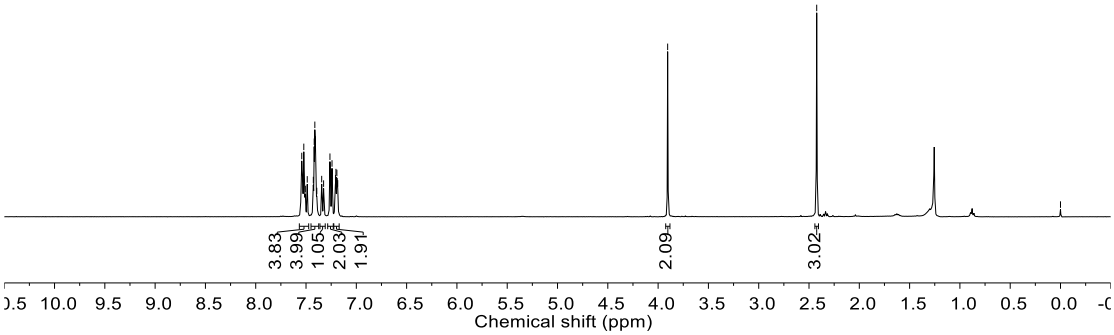

**3m** (400 MHz, $CDCl_3$)

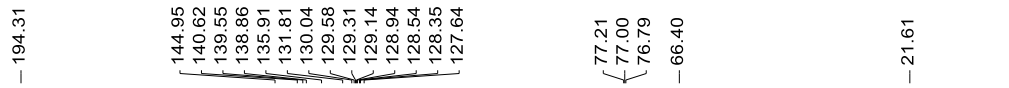


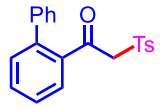

**3m** (100 MHz, $CDCl_3$)

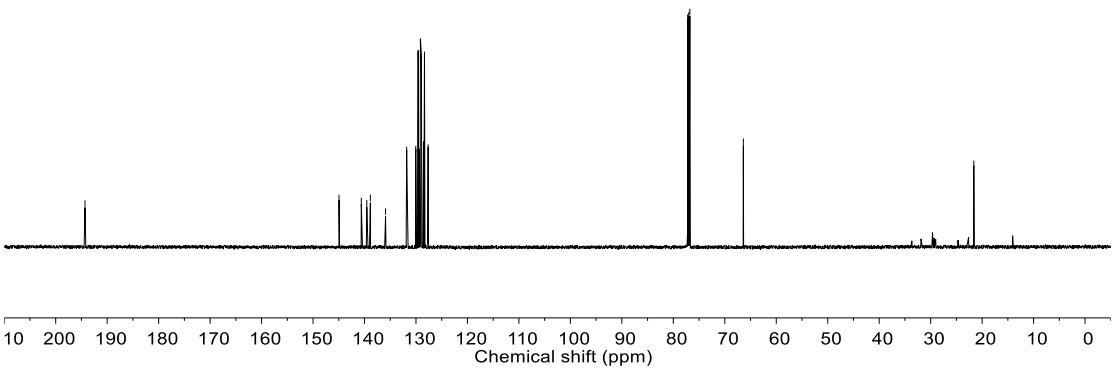

**3n** (400 MHz, $CDCl_3$)

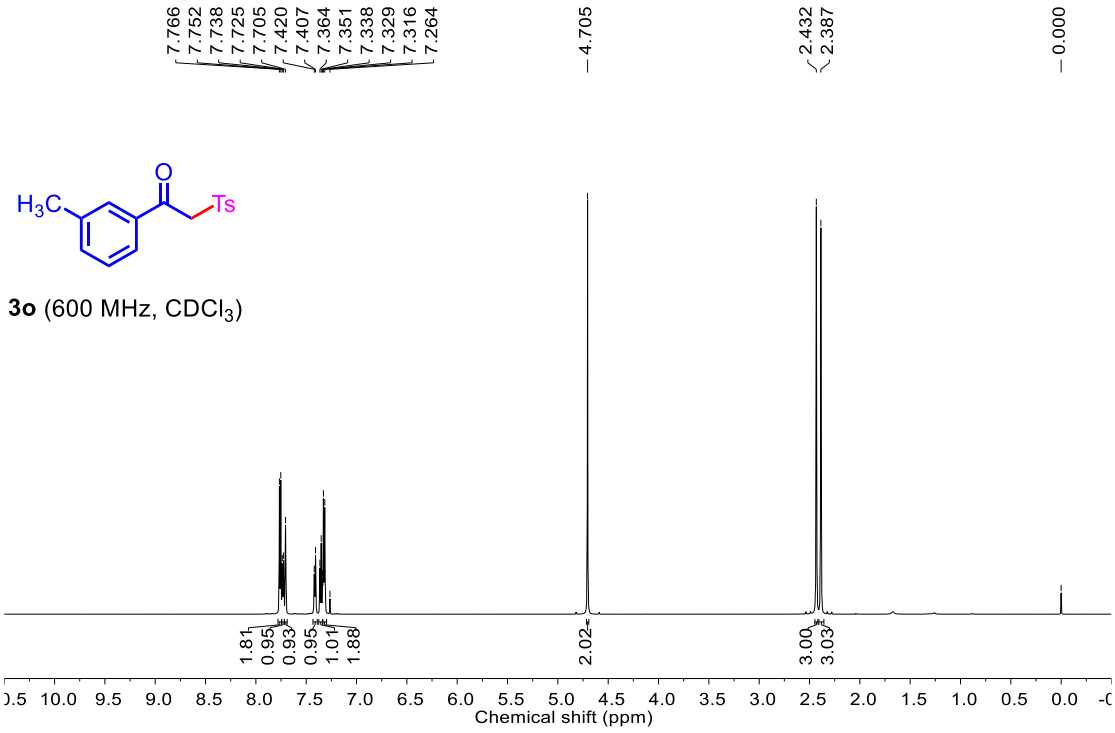


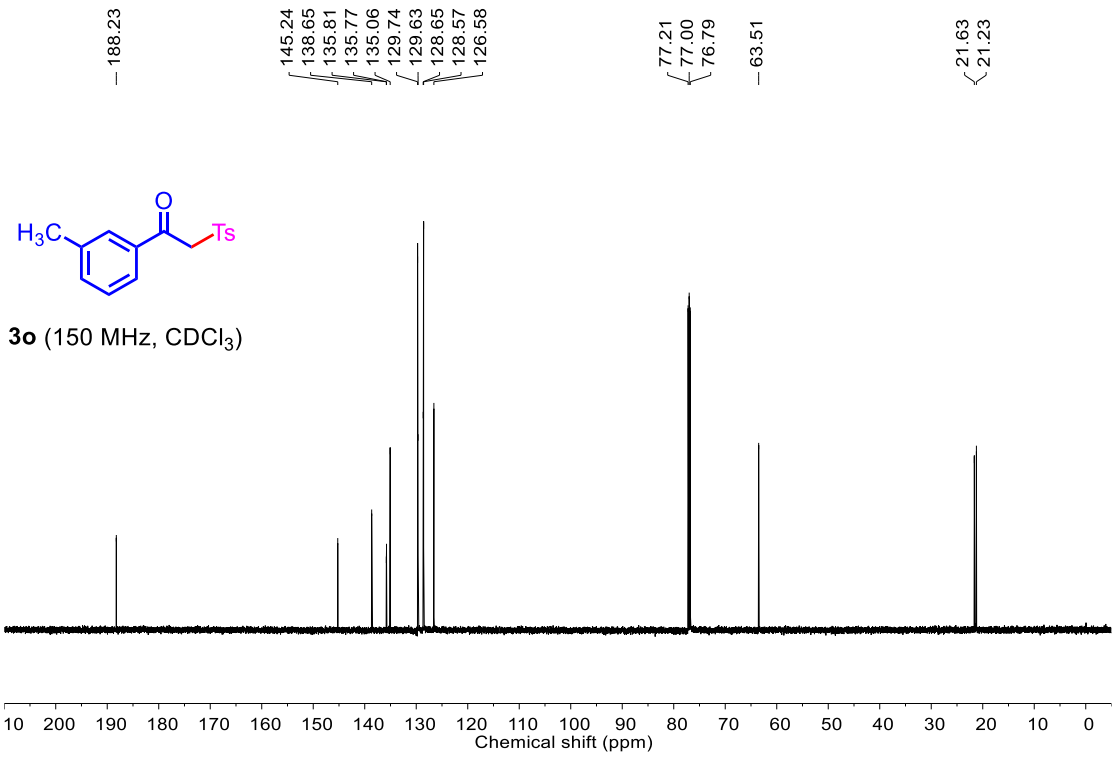




**3n** (150 MHz, $CDCl_3$)

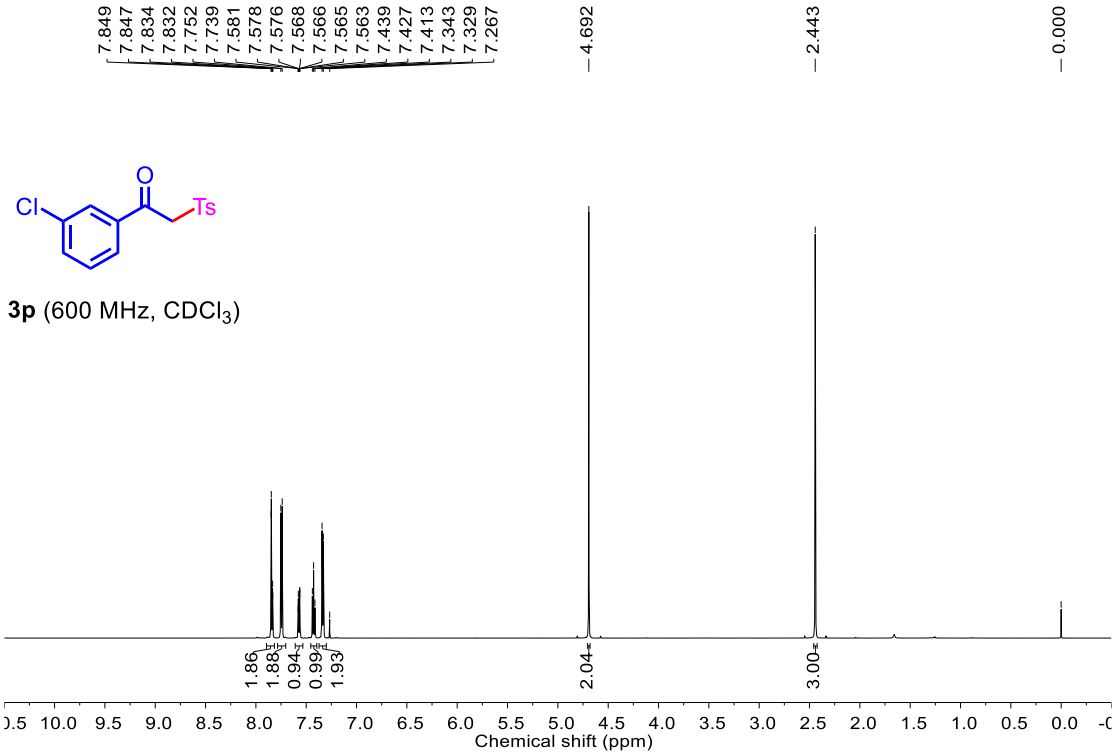




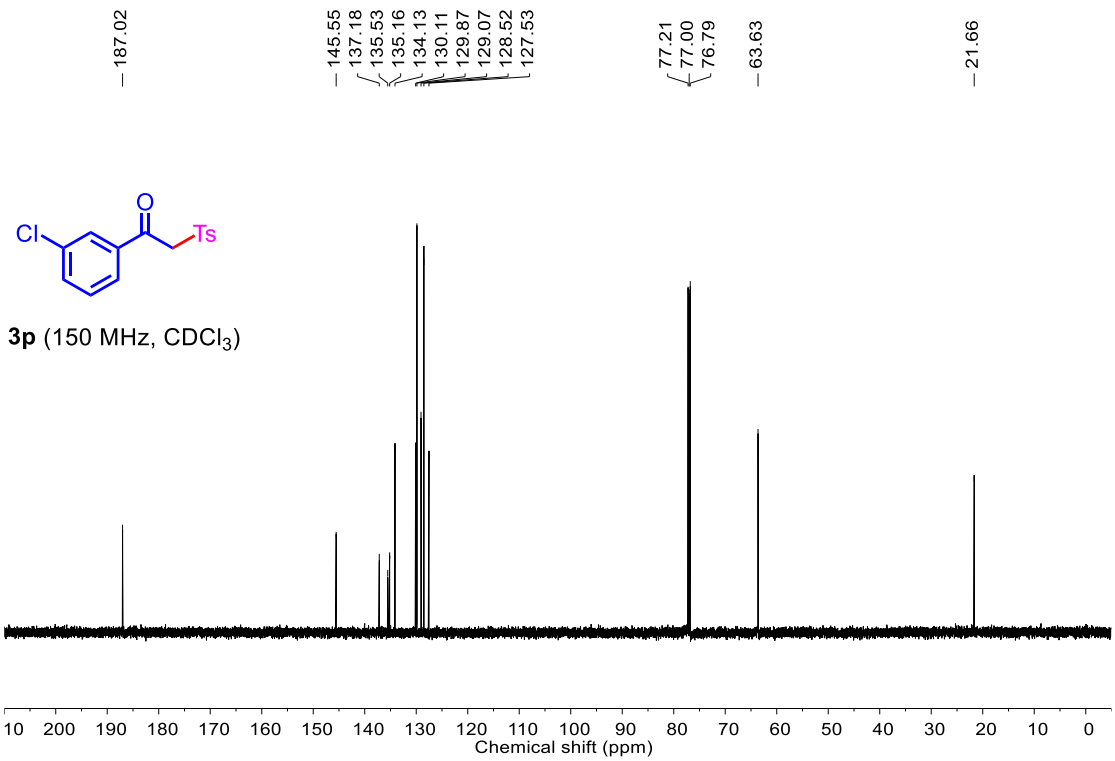

**3o** (600 MHz, $CDCl_3$)



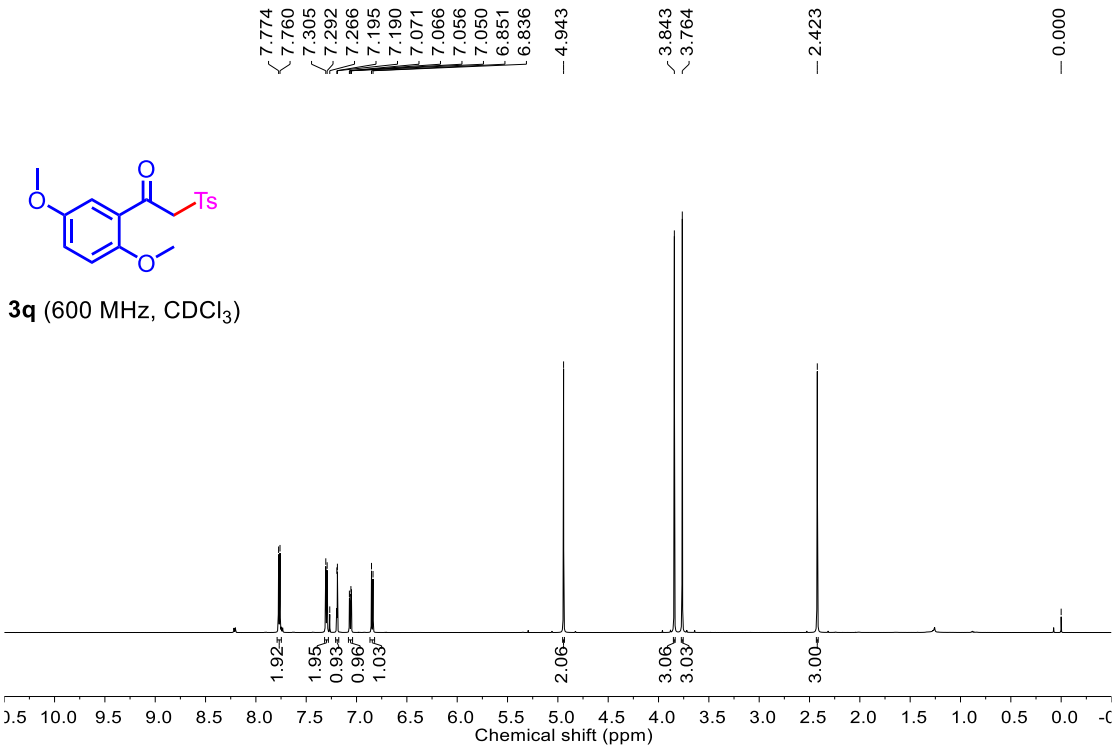

**3o** (150 MHz, $CDCl_3$)



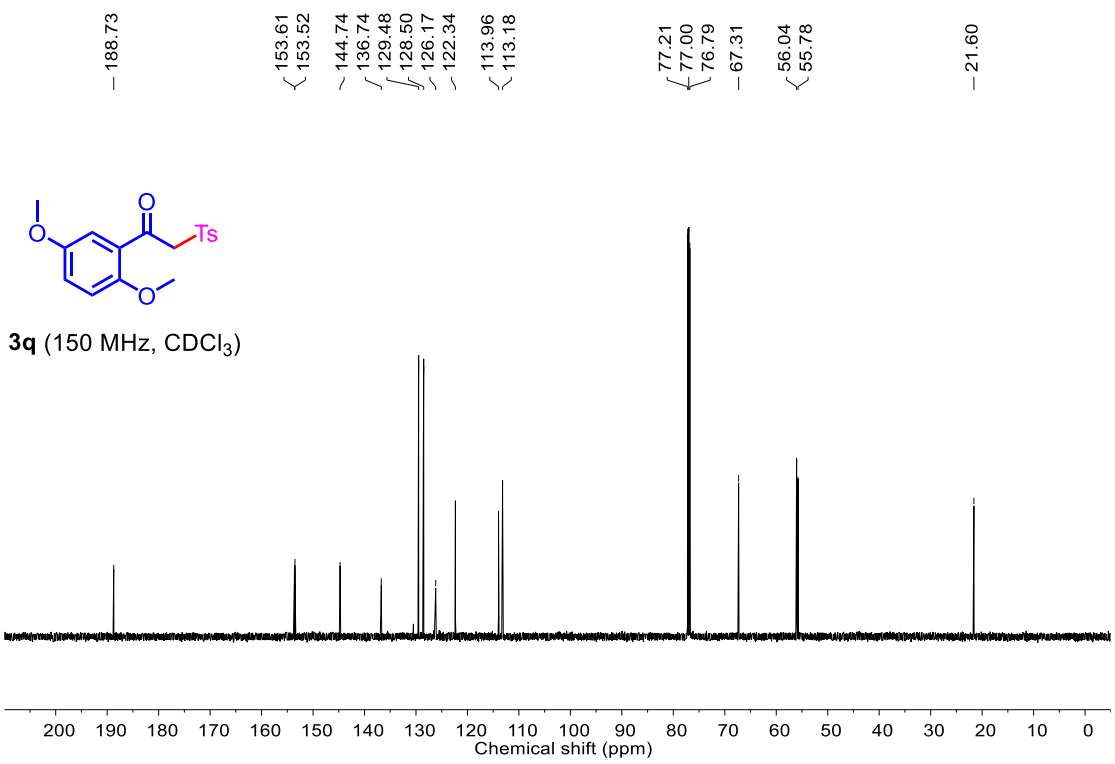

**3p** (600 MHz, $CDCl_3$)



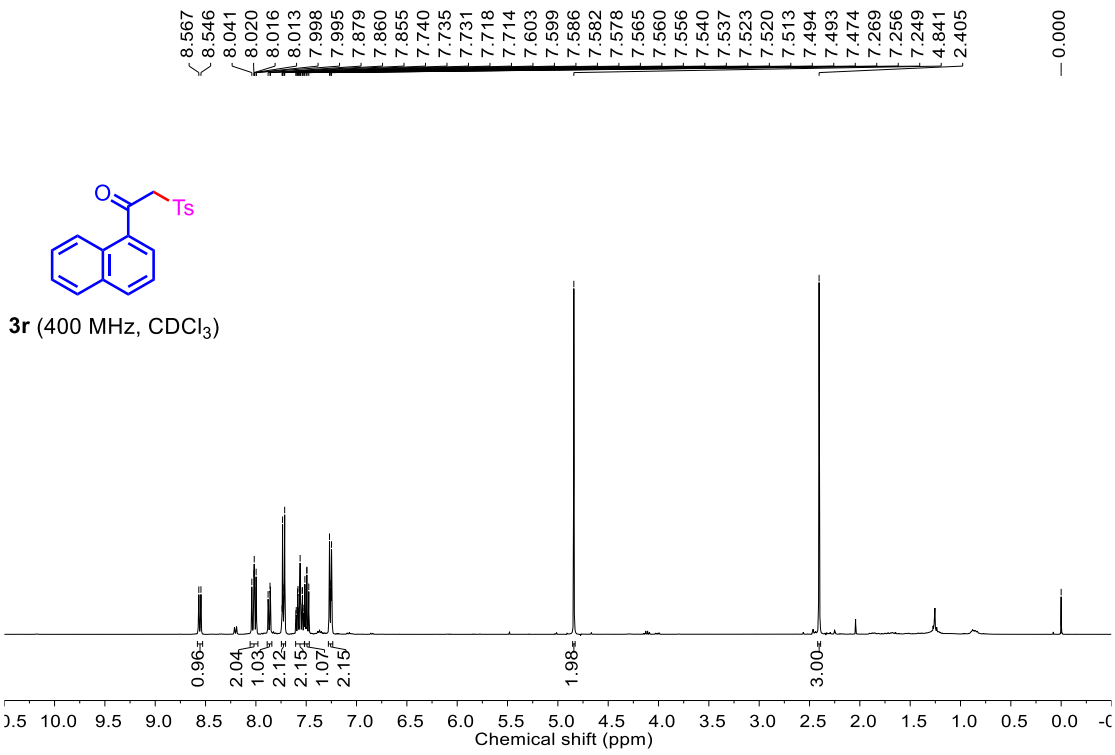

**3p** (150 MHz, $CDCl_3$)



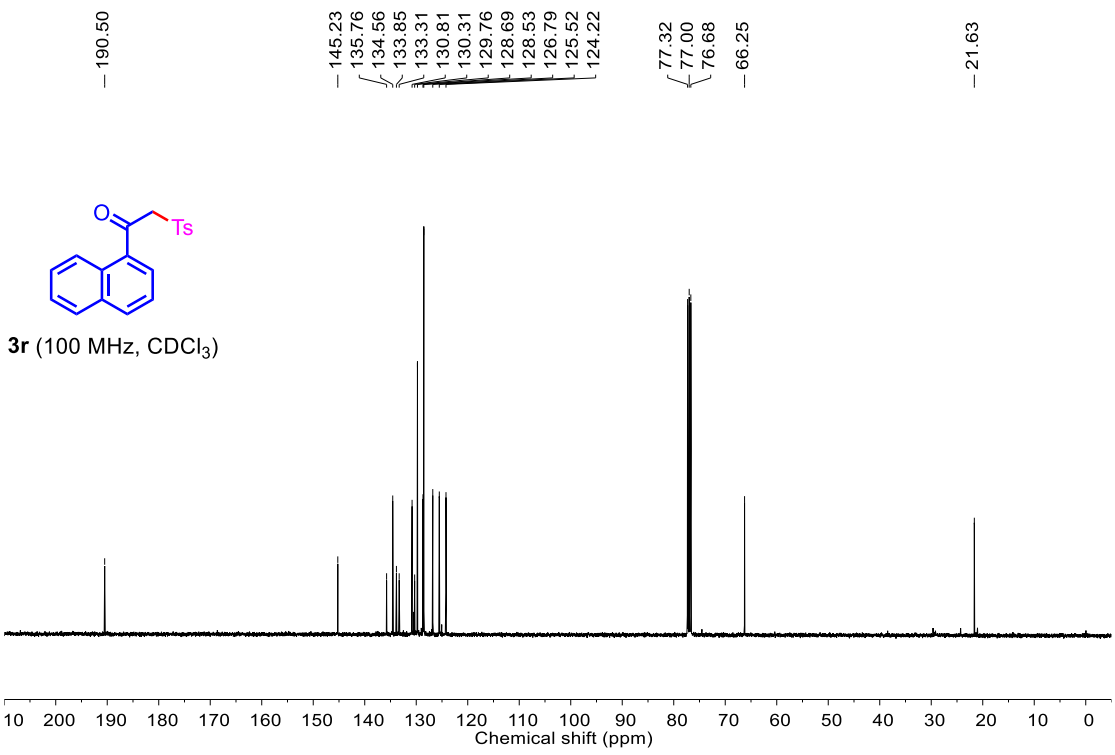

**3q** (600 MHz, $CDCl_3$)



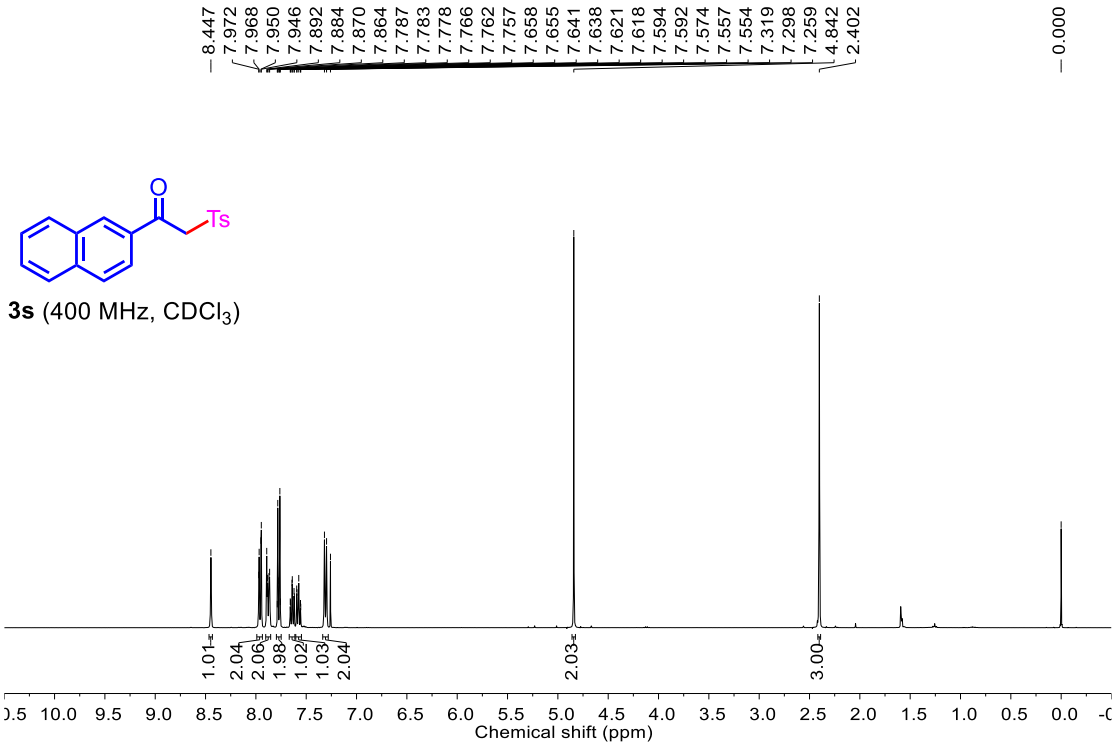

**3q** (150 MHz, $CDCl_3$)



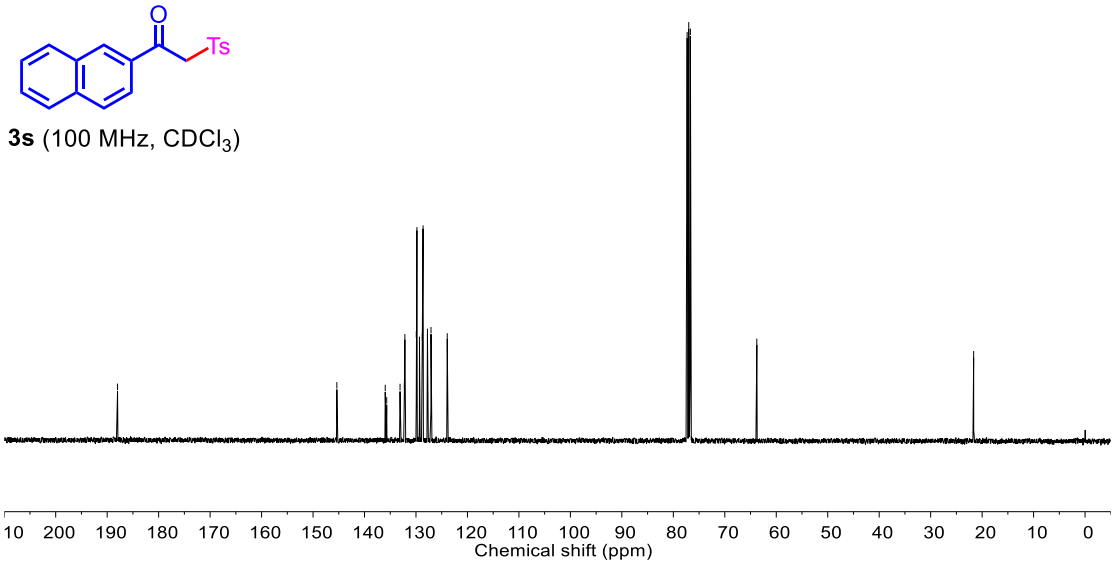

**3r** (400 MHz, $CDCl_3$)



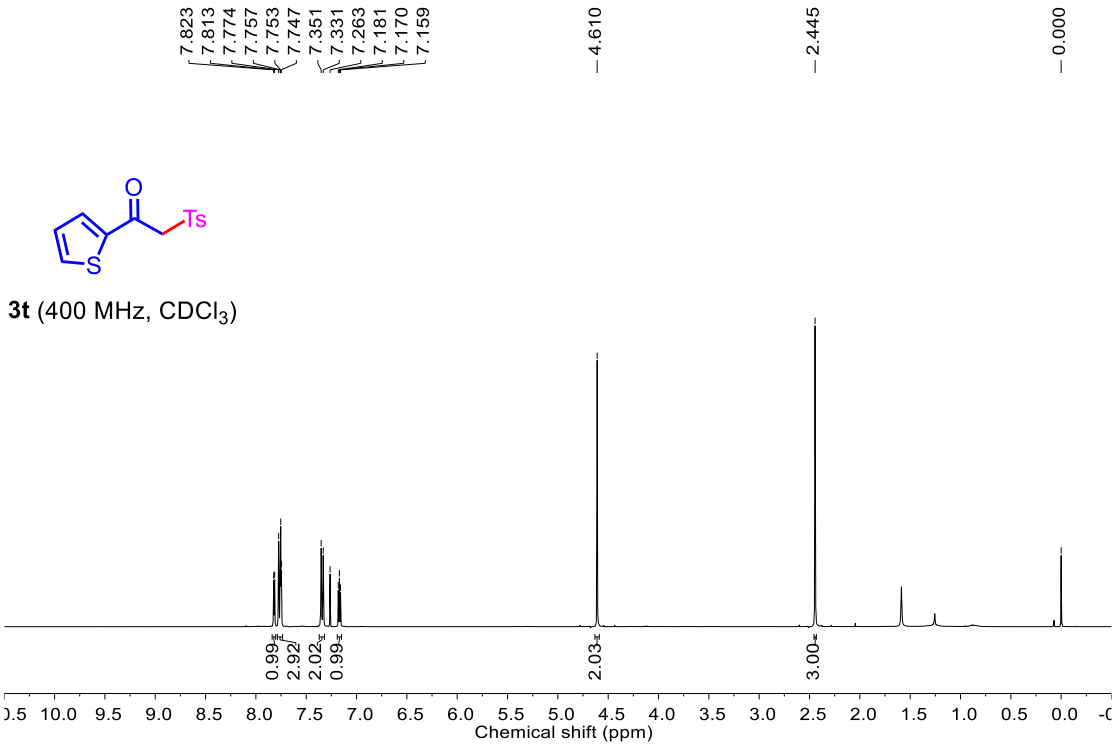

**3r** (100 MHz, $CDCl_3$)

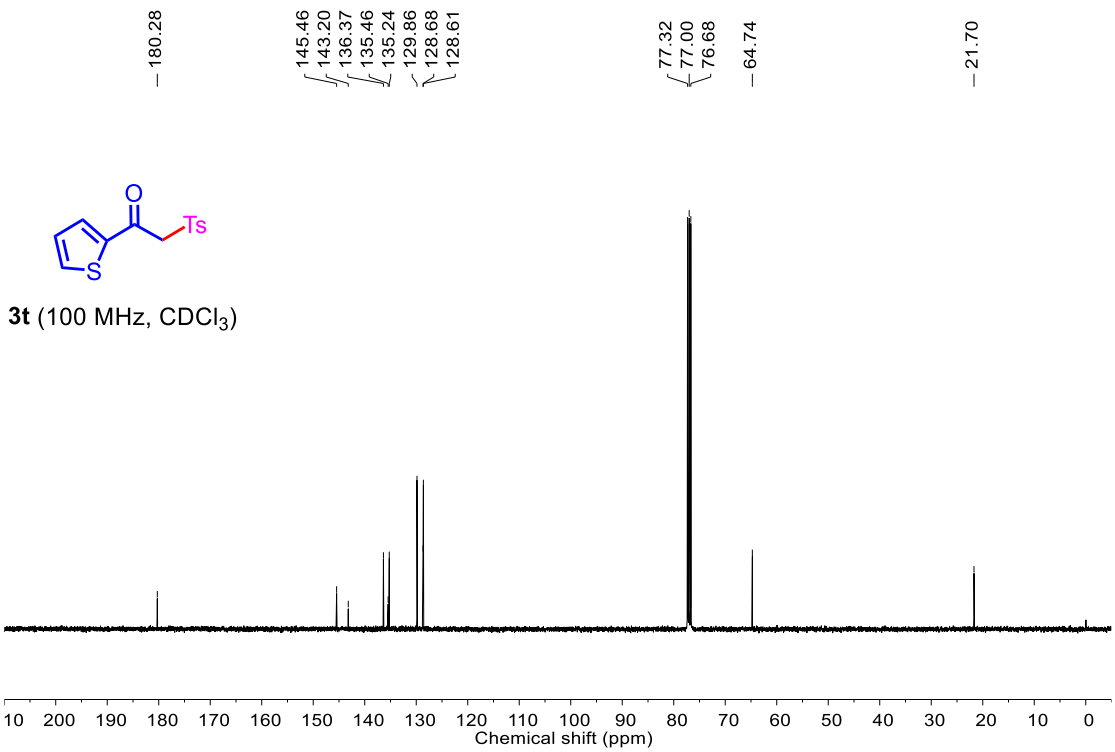


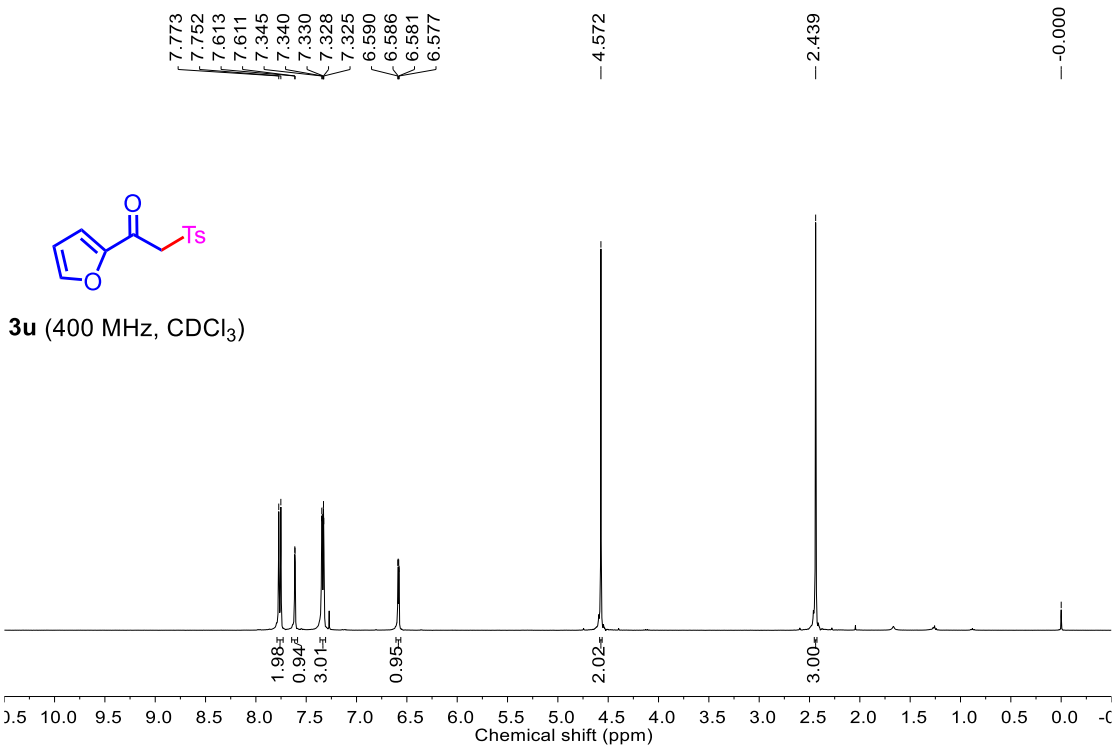

**3s** (400 MHz, $CDCl_3$)



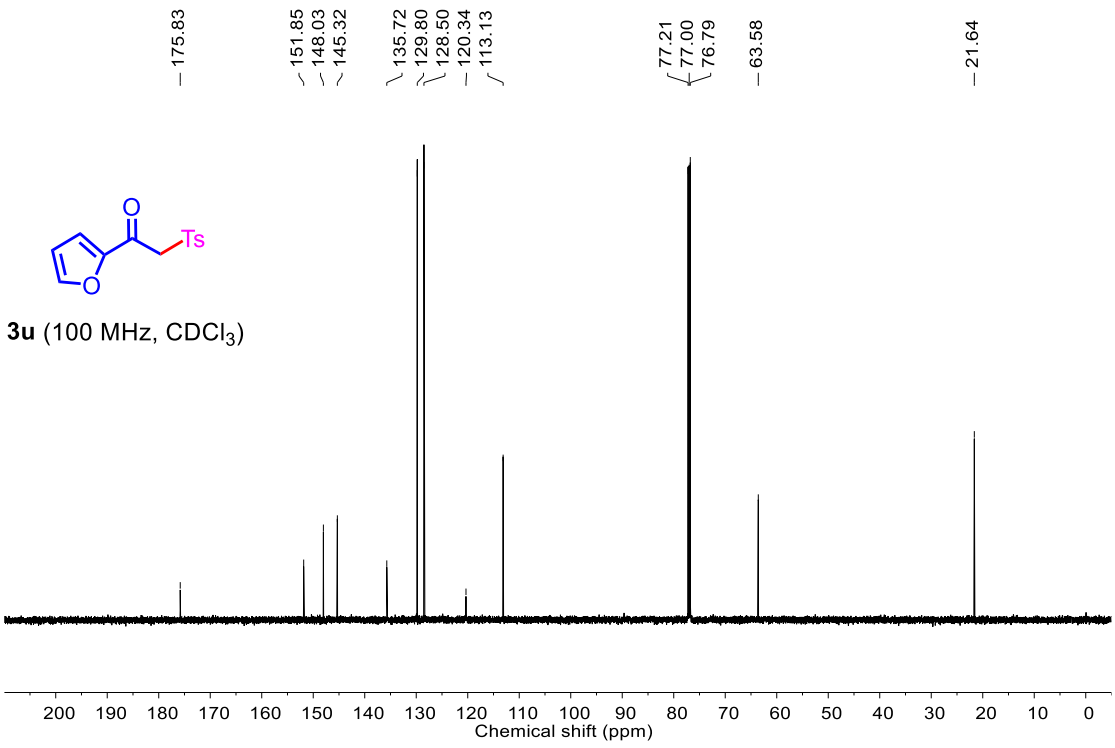

**3s** (100 MHz, $CDCl_3$)


7.823
7.813
7.774
7.757
7.753
7.747
7.351
7.331
7.263
7.181
7.170
7.159
4.610
2.445
0.000
O
Ts
S
3t (400 MHz, CDCl3)
0.99
2.92
2.02
0.99
2.03
3.00
Chemical shift (ppm)

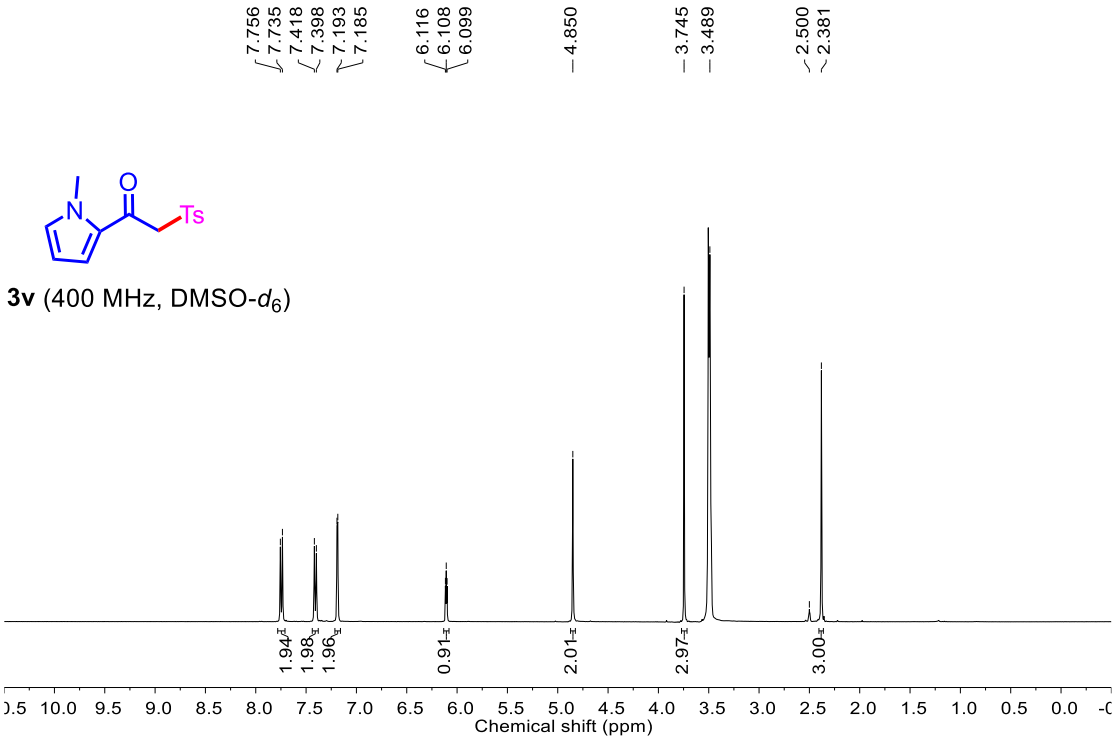

180.28
145.46
143.20
136.37
135.46
135.24
129.86
128.68
128.61
77.32
77.00
76.68
64.74
21.70
O
Ts
S
3t (100 MHz, CDCl3)
Chemical shift (ppm)



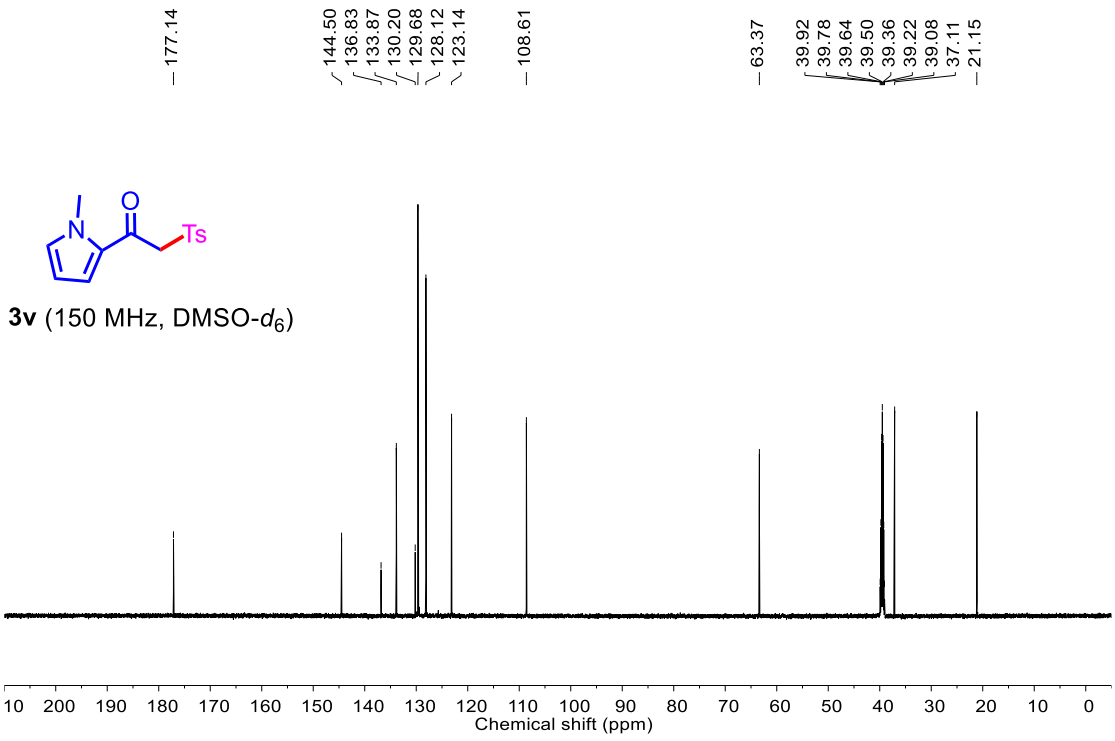

**3u** (400 MHz, $CDCl_3$)



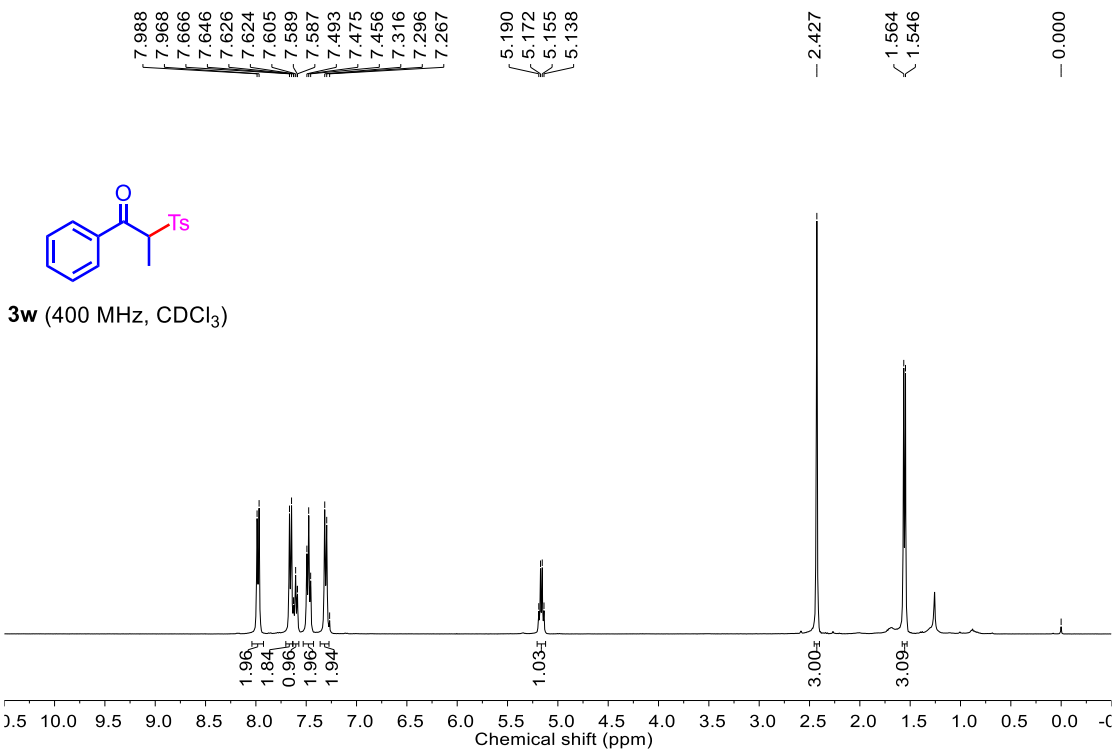

**3u** (100 MHz, $CDCl_3$)



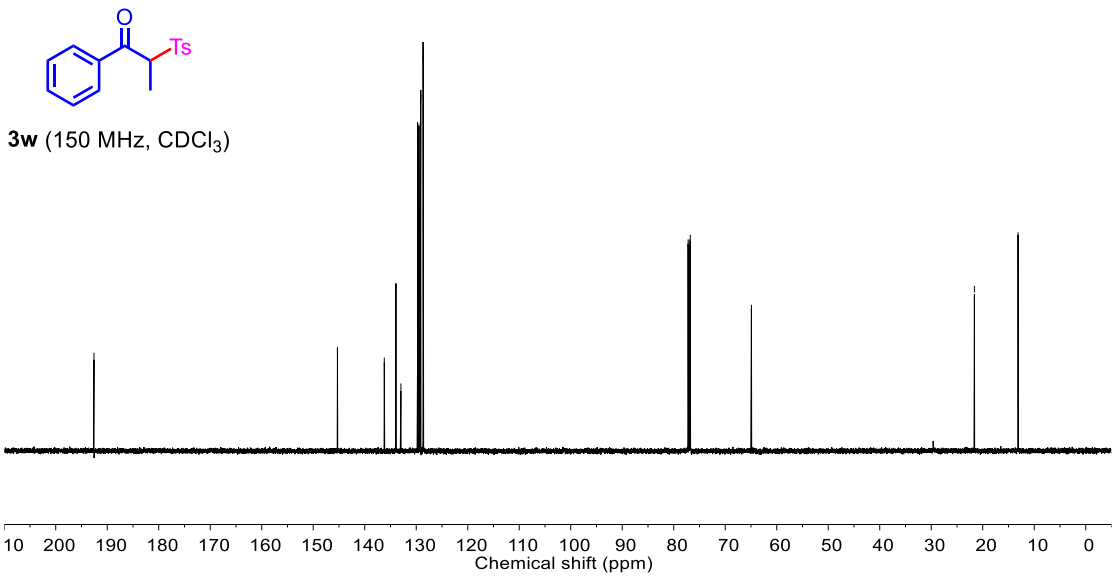

**3v** (400 MHz, DMSO-$d_6$)



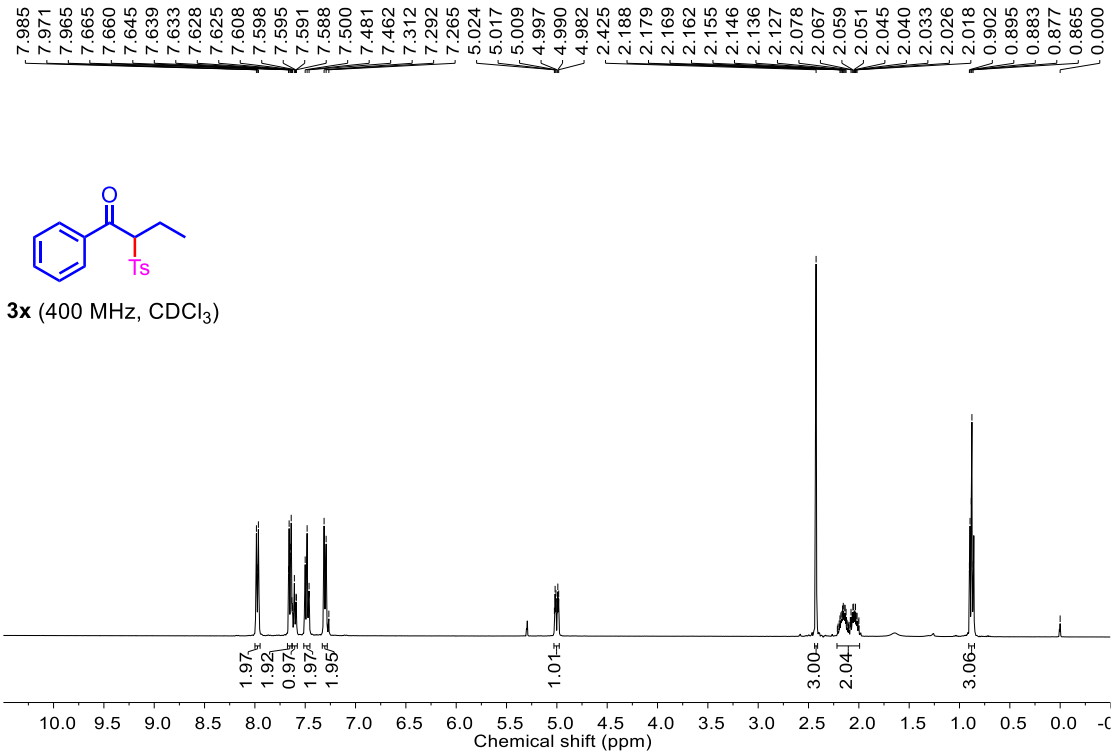

**3v** (150 MHz, DMSO-$d_6$)

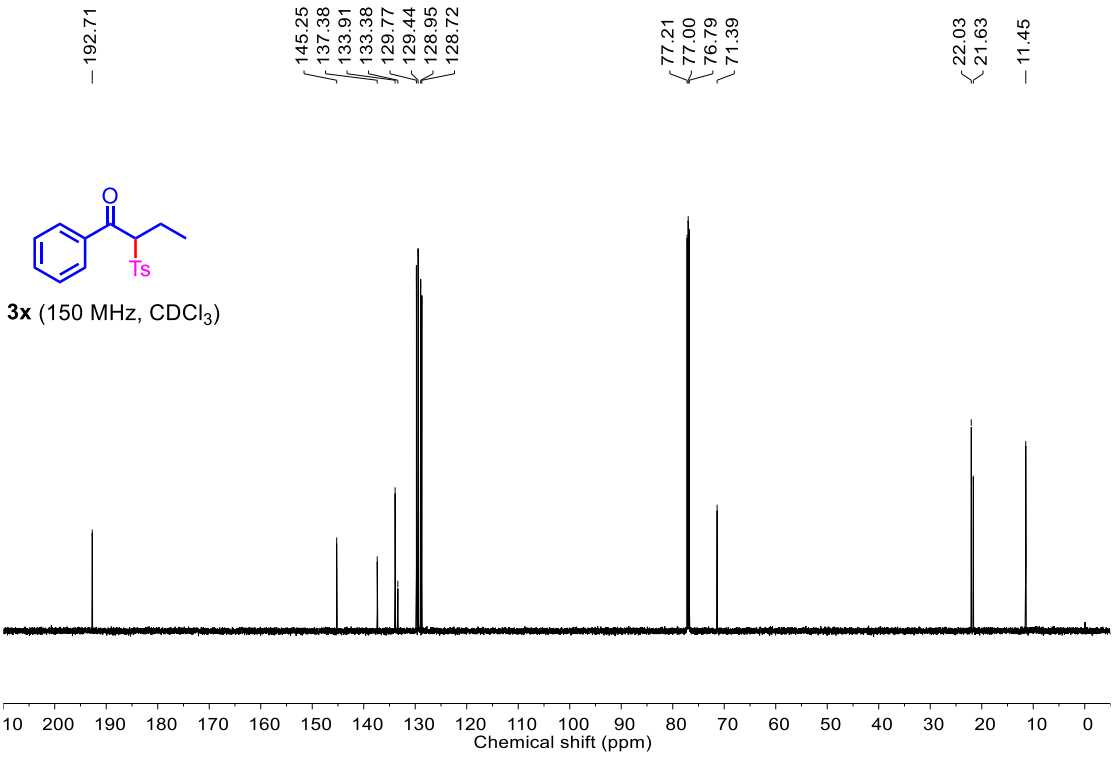


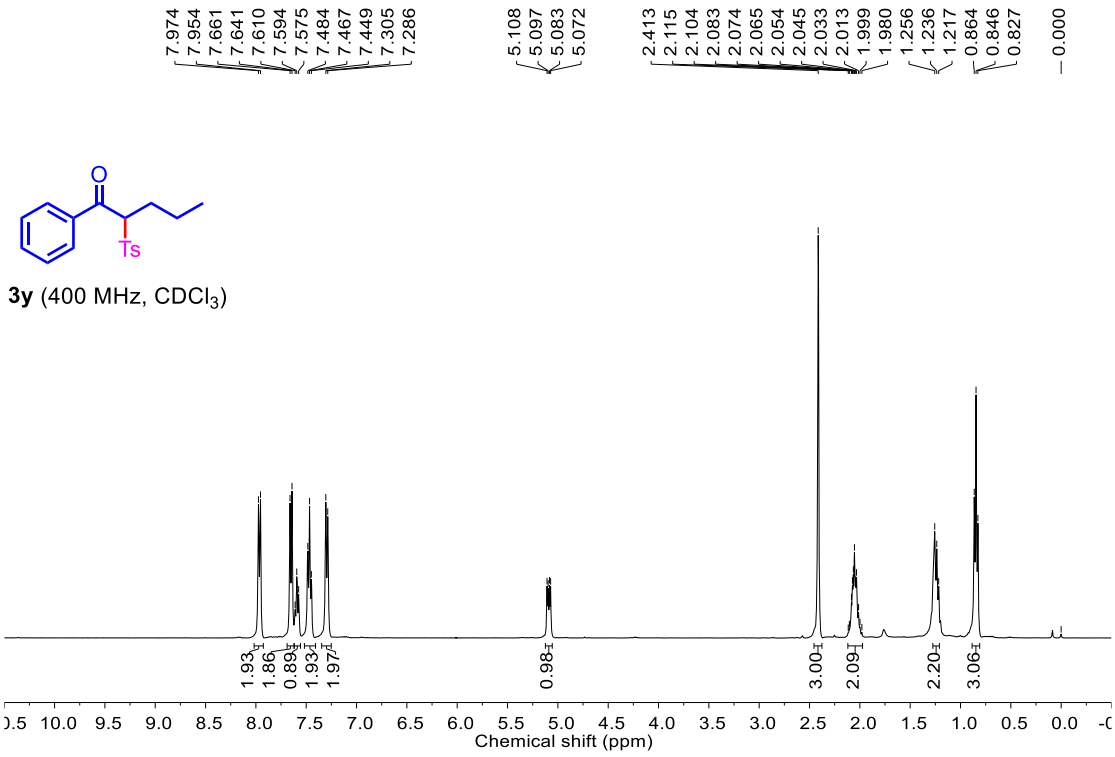

**3w** (400 MHz, $CDCl_3$)

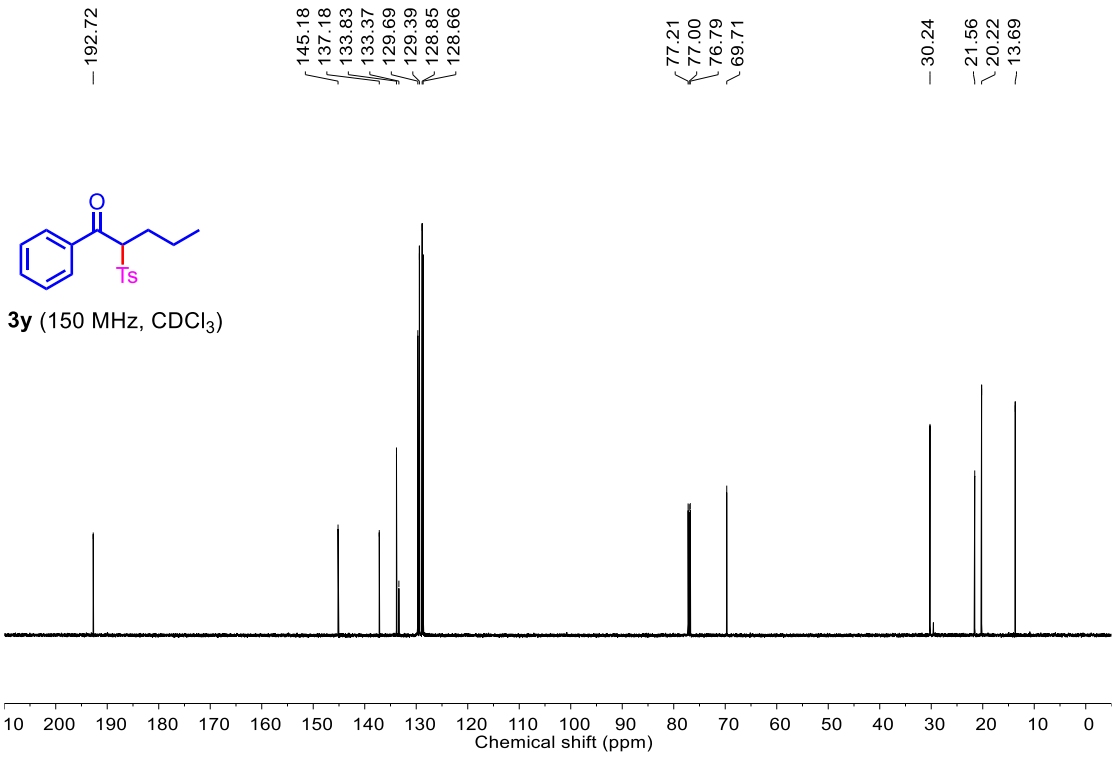


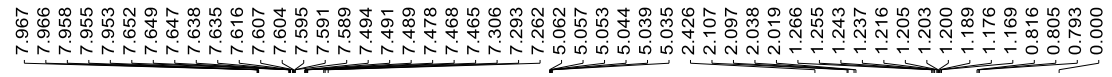

**3w** (150 MHz, $CDCl_3$)

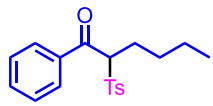

7.985
7.971
7.965
7.665
7.660
7.645
7.639
7.633
7.628
7.625
7.608
7.598
7.595
7.591
7.588
7.500
7.481
7.462
7.312
7.292
7.265
5.024
5.017
5.009
4.997
4.990
4.982
2.425
2.188
2.179
2.169
2.162
2.155
2.146
2.136
2.127
2.078
2.067
2.059
2.051
2.045
2.040
2.033
2.026
2.018
0.902
0.895
0.883
0.877
0.865
0.000
O
Ts
3x (400 MHz, CDCl3)
1.97
1.92
0.97
1.97
1.95
1.01
3.00
2.04
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)


192.71
145.25
137.38
133.91
133.38
129.77
129.44
128.95
128.72
77.21
77.00
76.79
71.39
22.03
21.63
11.45
O
Ts
3x (150 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

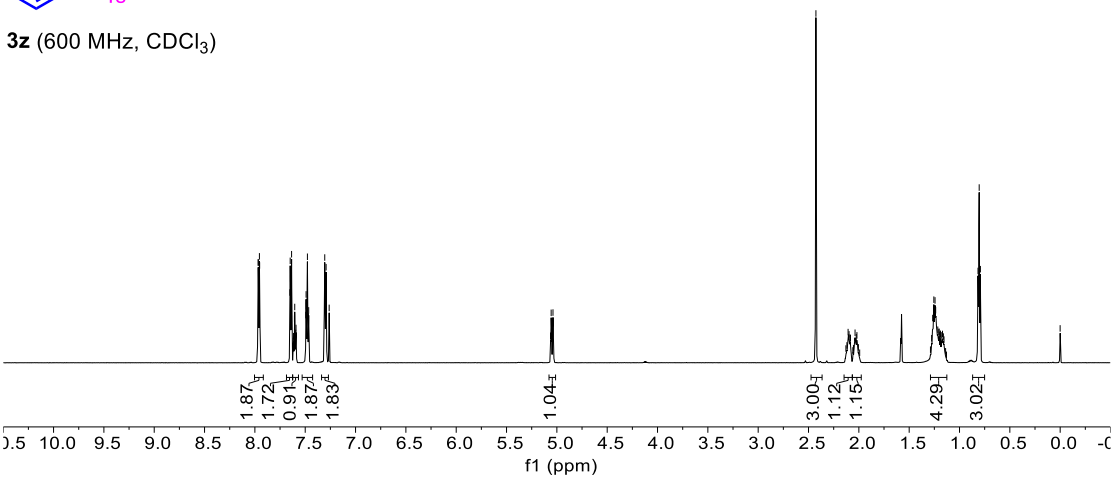

7.974
7.954
7.661
7.641
7.610
7.594
7.575
7.484
7.467
7.449
7.305
7.286
5.108
5.097
5.083
5.072
2.413
2.115
2.104
2.083
2.074
2.065
2.054
2.045
2.033
2.013
1.999
1.980
1.256
1.236
1.217
0.864
0.846
0.827
0.000
O
Ts
3y (400 MHz, CDCl3)
1.93
1.86
0.89
1.93
1.97
0.98
3.00
2.09
2.20
3.06
Chemical shift (ppm)

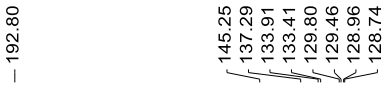

192.72
145.18
137.18
133.83
133.37
129.69
129.39
128.85
128.66
77.21
77.00
76.79
69.71
30.24
21.56
20.22
13.69
O
Ts
3y (150 MHz, CDCl3)
Chemical shift (ppm)

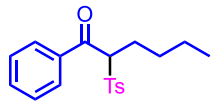


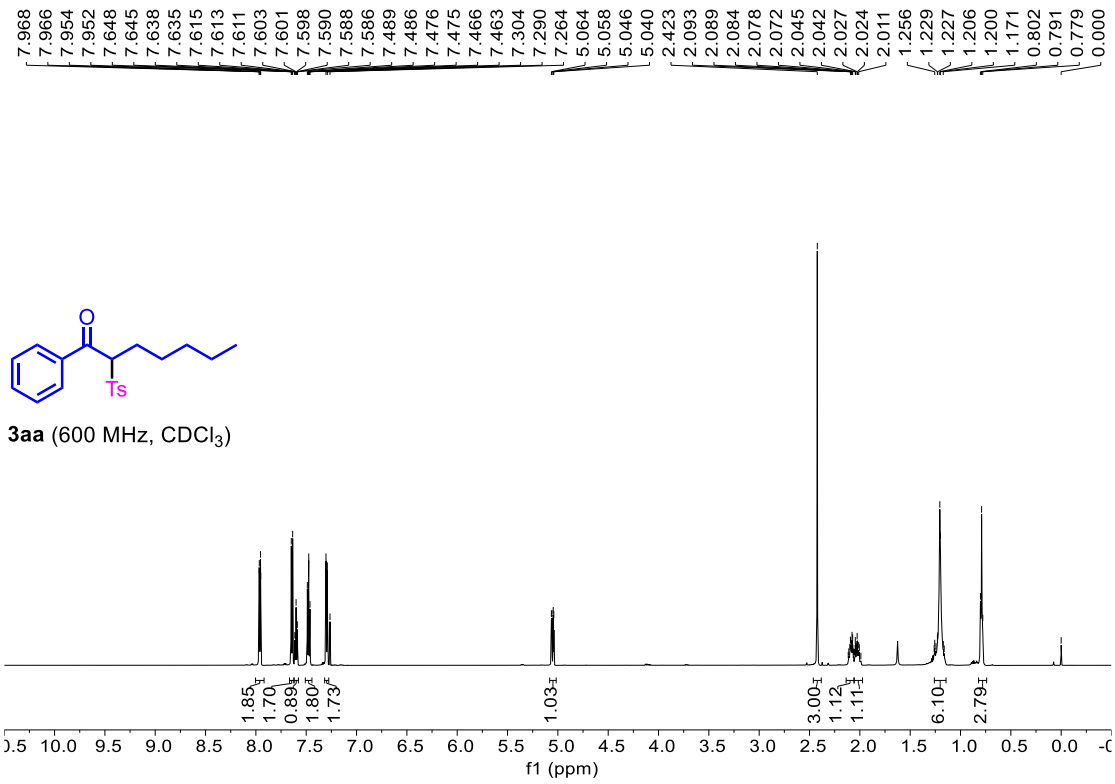

**3z** (600 MHz, $CDCl_3$)

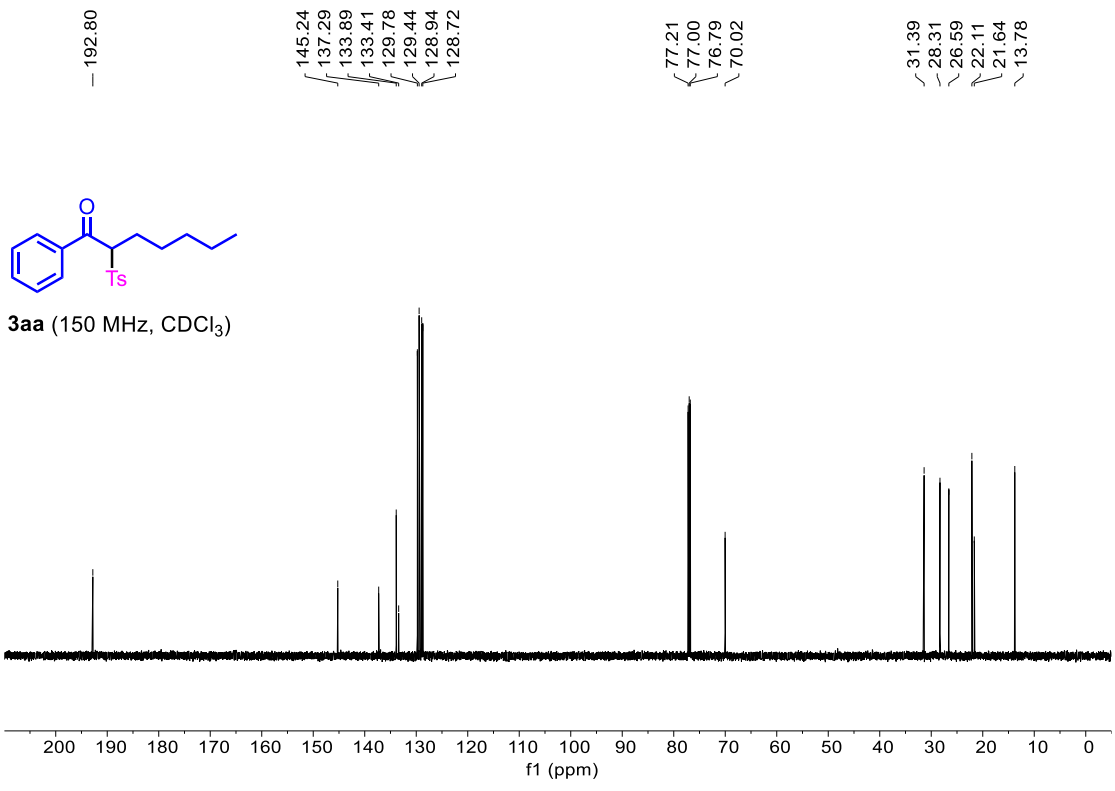


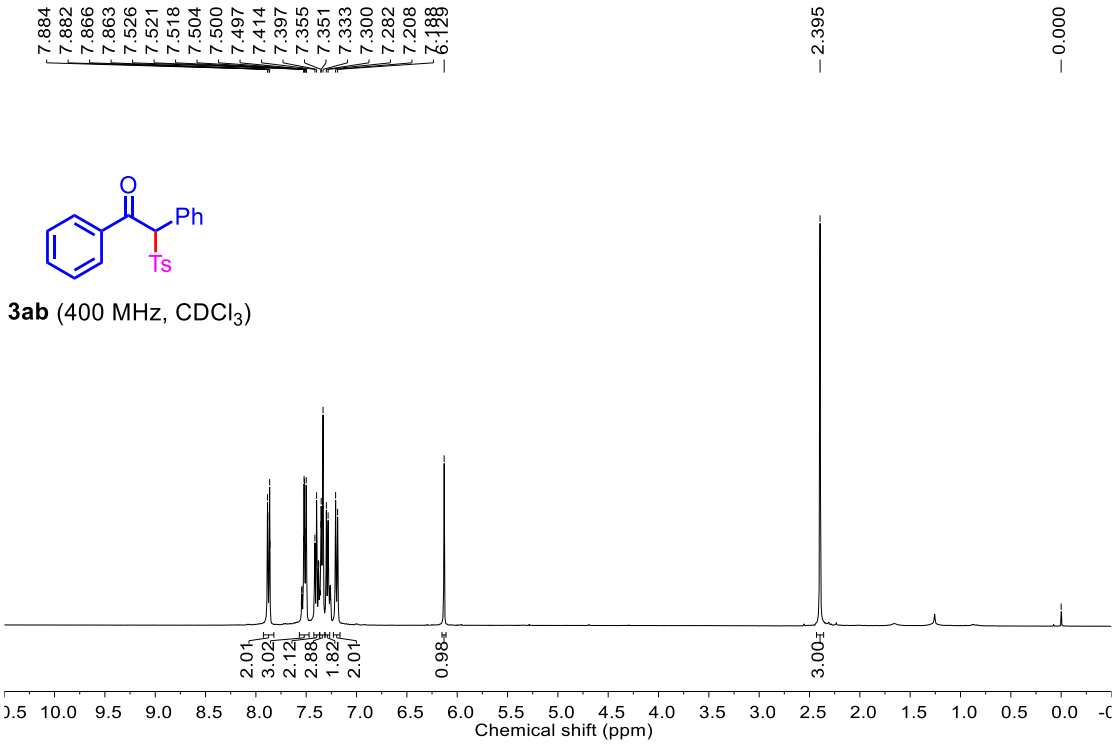



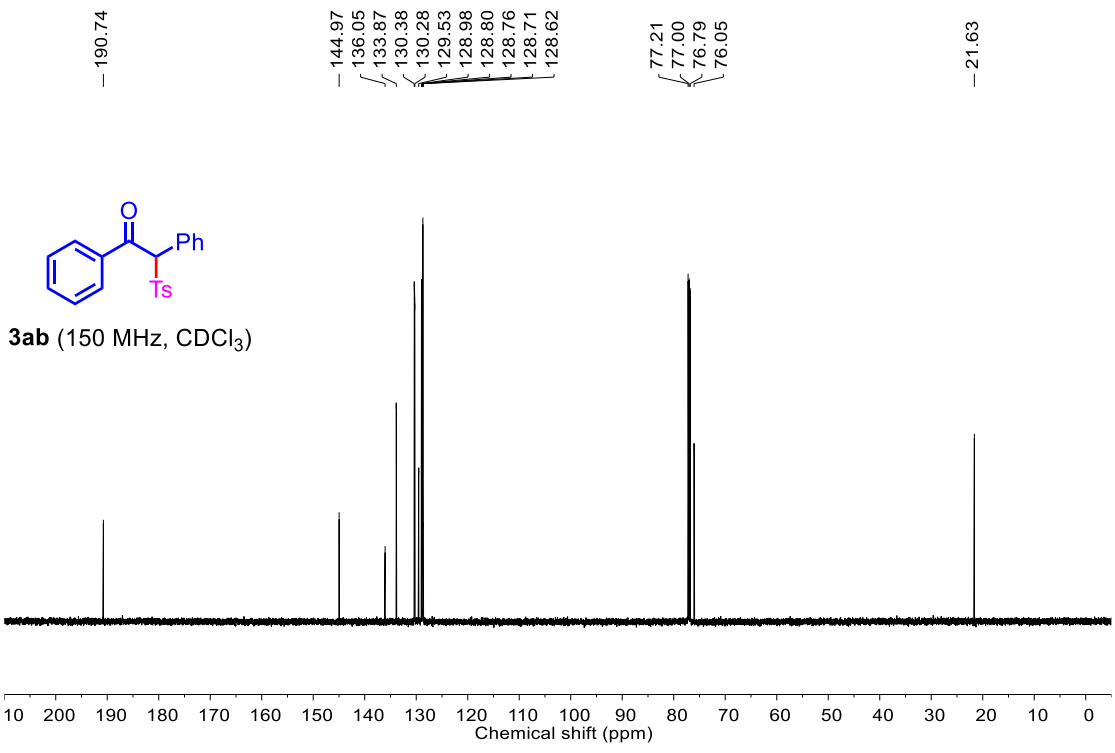

**3z** (150 MHz, $CDCl_3$)


7.968
7.966
7.954
7.952
7.648
7.645
7.638
7.635
7.615
7.613
7.611
7.603
7.601
7.598
7.590
7.588
7.586
7.489
7.486
7.476
7.475
7.466
7.463
7.304
7.290
7.264
5.064
5.058
5.046
5.040
2.423
2.093
2.089
2.084
2.078
2.072
2.045
2.042
2.027
2.024
2.011
1.256
1.229
1.227
1.206
1.200
1.171
0.802
0.791
0.779
0.000
O
Ts
3aa (600 MHz, CDCl3)
1.85
1.70
0.89
1.80
1.73
1.03
3.00
1.12
1.11
6.10
2.79
f1 (ppm)

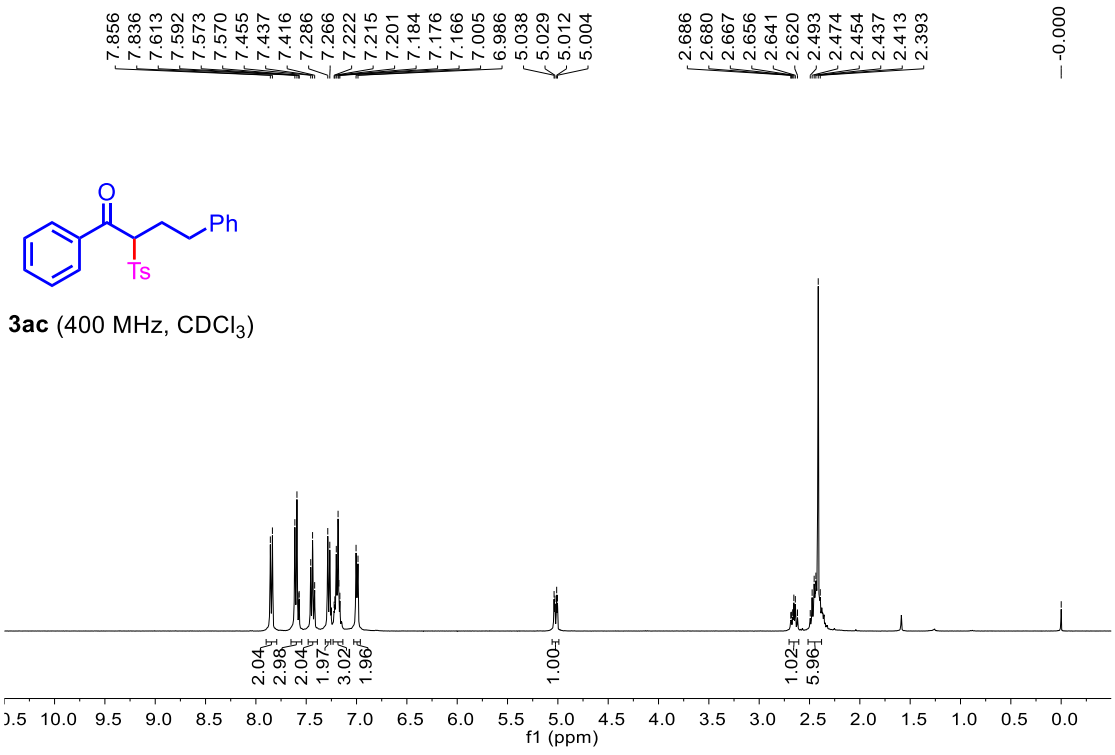

192.80
145.24
137.29
133.89
133.41
129.78
129.44
128.94
128.72
77.21
77.00
76.79
70.02
31.39
28.31
26.59
22.11
21.64
13.78
O
Ts
3aa (150 MHz, CDCl3)
f1 (ppm)



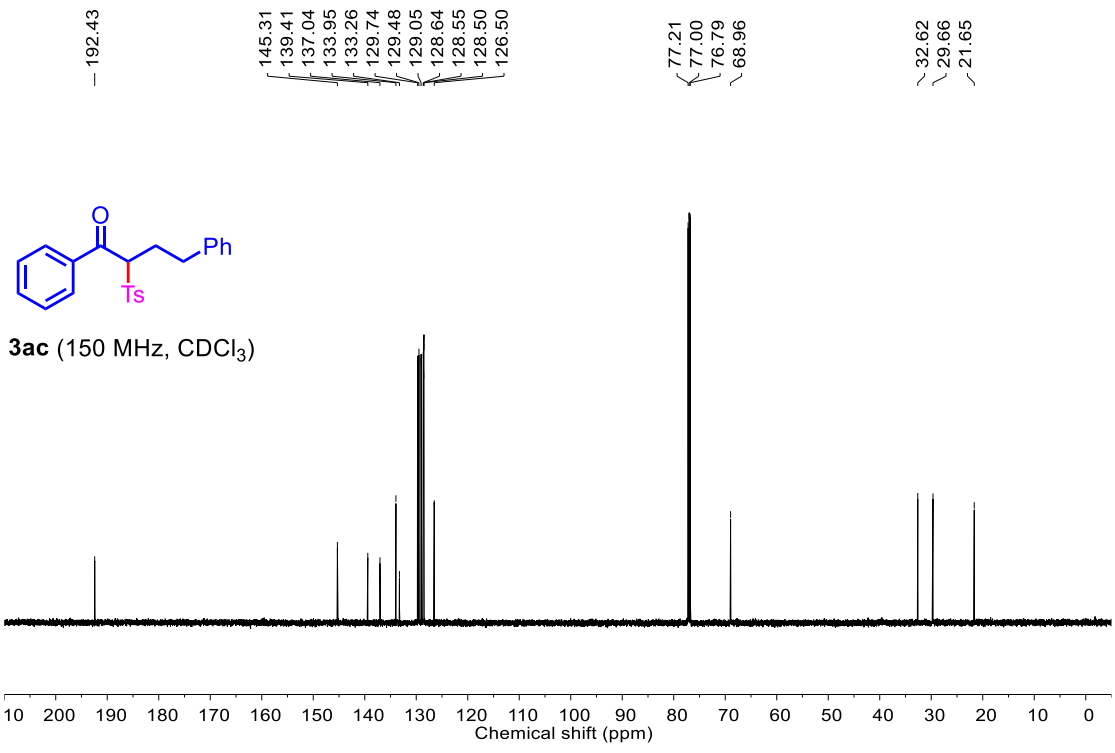

**3ab** (400 MHz, $CDCl_3$)



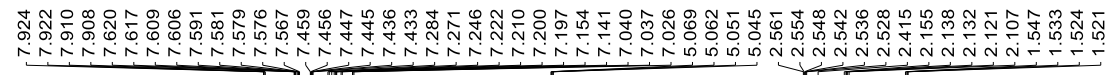

**3ab** (150 MHz, $CDCl_3$)

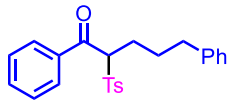



**3ac** (400 MHz, $CDCl_3$)




**3ac** (150 MHz, $CDCl_3$)

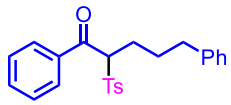


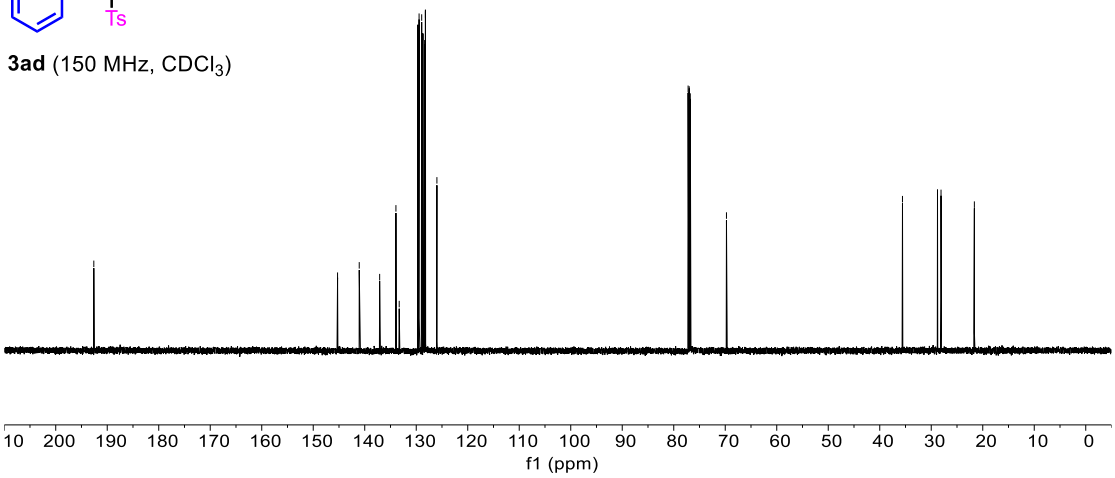

**3ad** (600 MHz, $CDCl_3$)

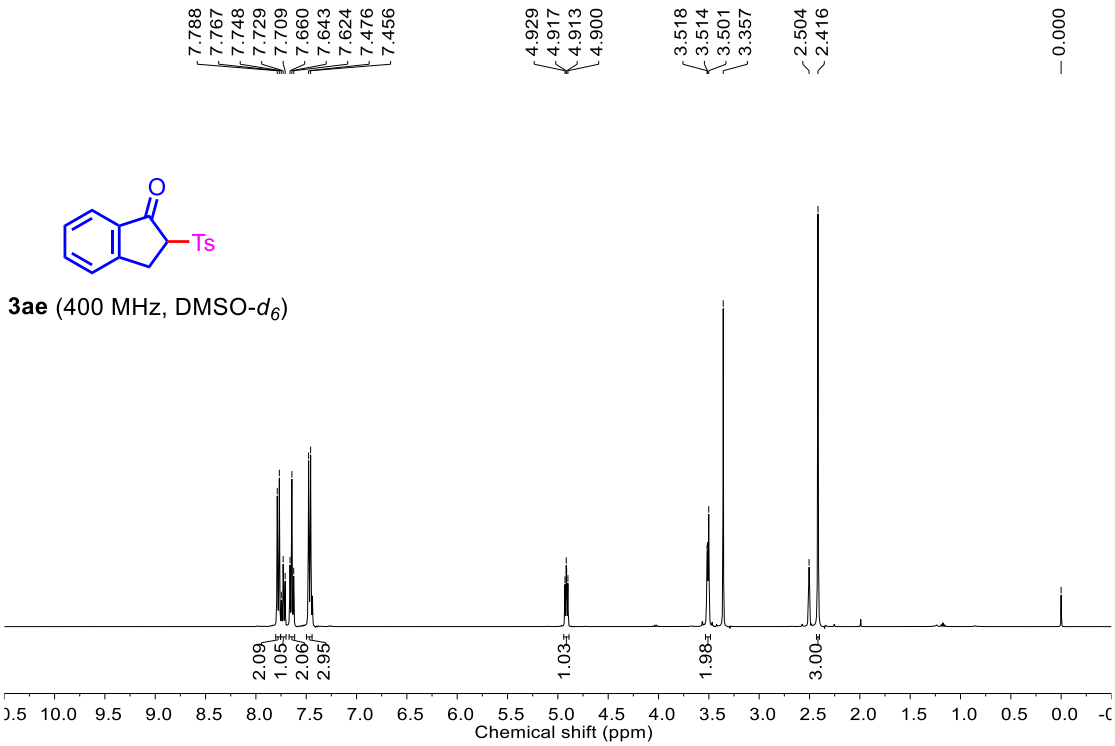




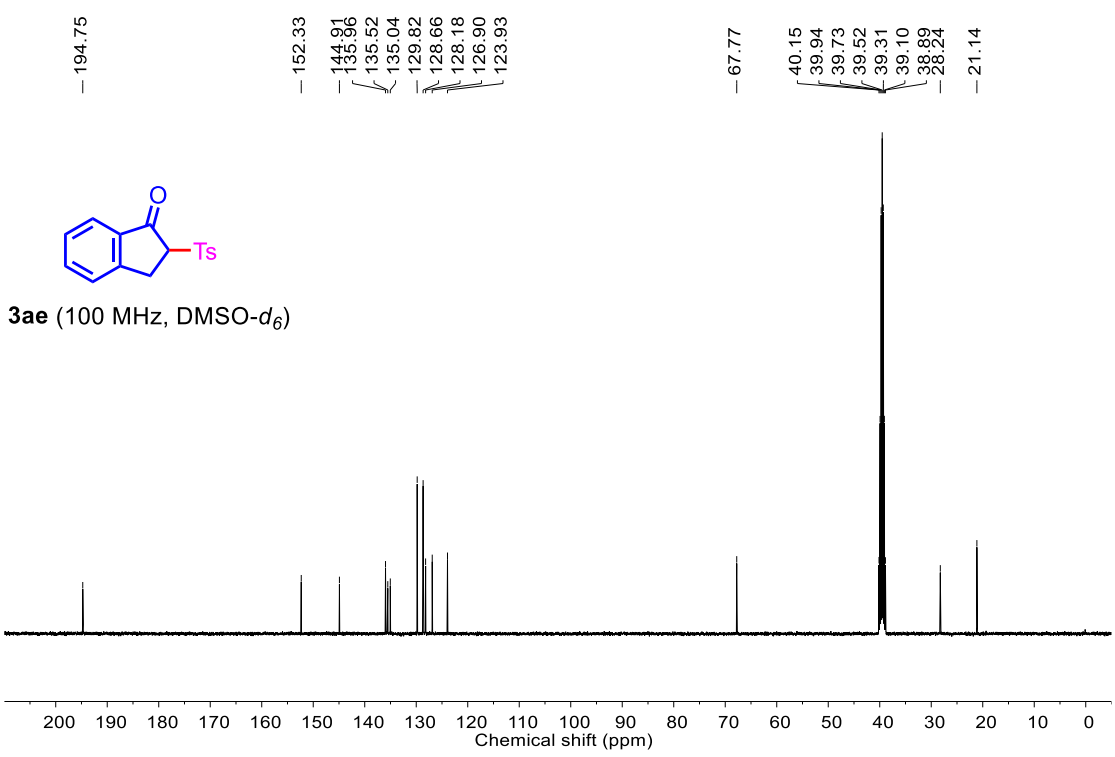



**3ad** (150 MHz, $CDCl_3$)

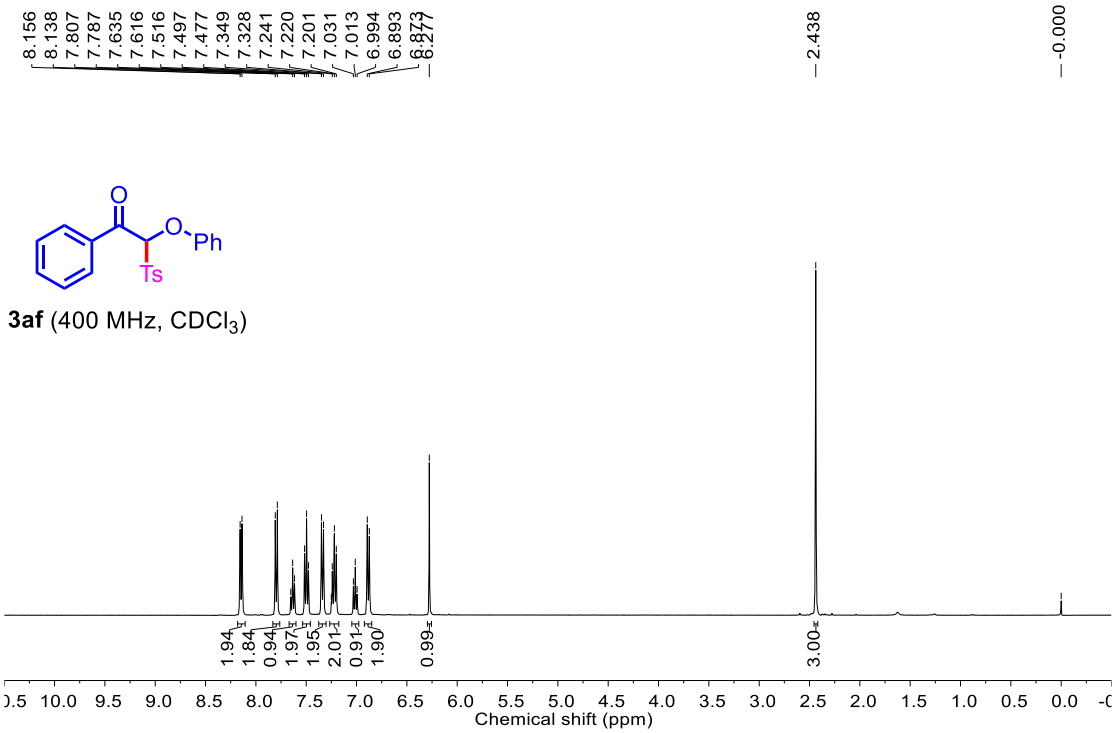




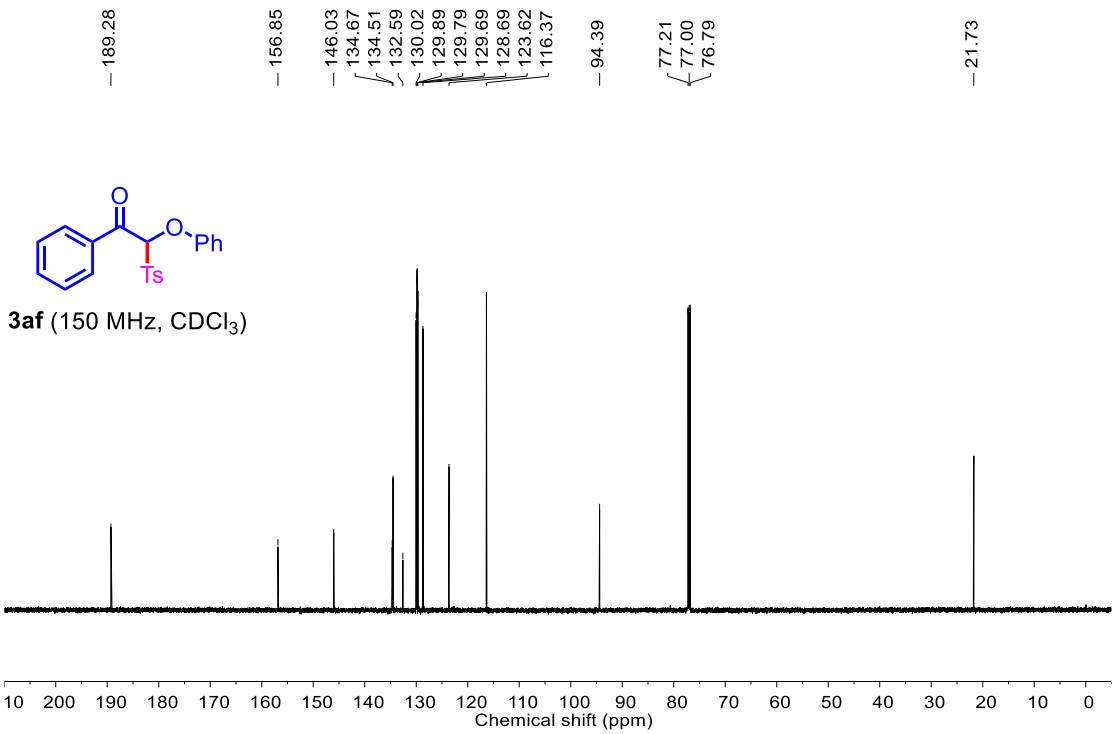

**3ae** (400 MHz, DMSO-$d_6$)



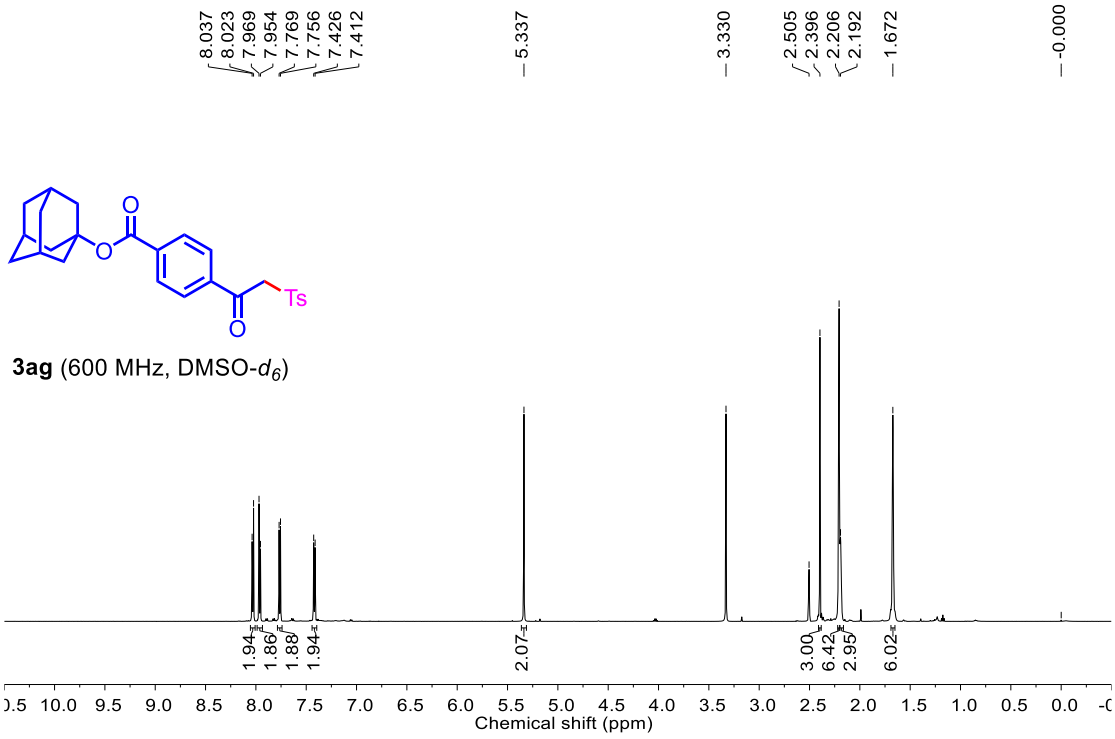

**3ae** (100 MHz, DMSO-$d_6$)



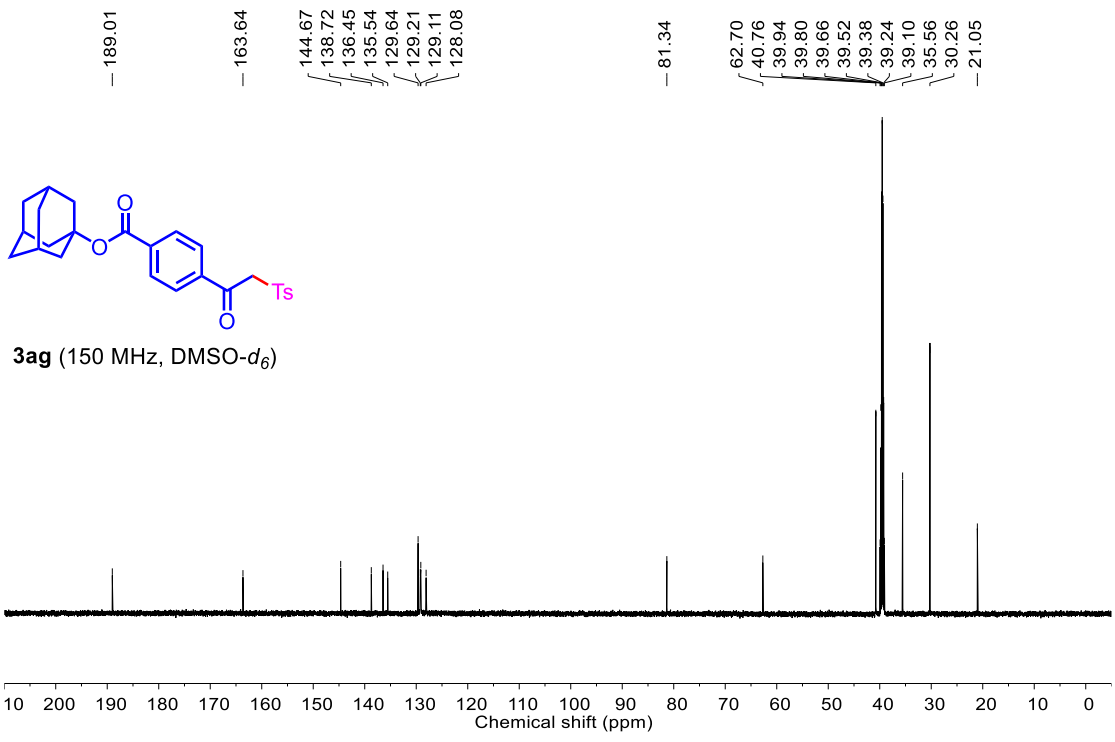

**3af** (400 MHz, $CDCl_3$)



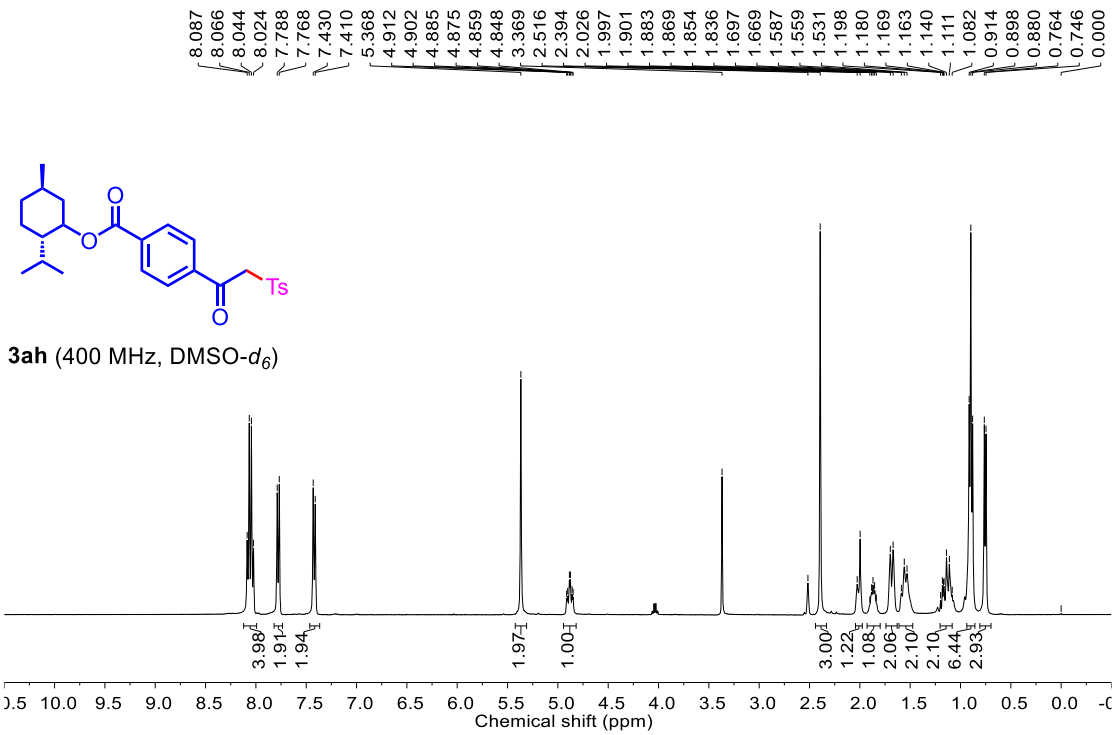

**3af** (150 MHz, $CDCl_3$)



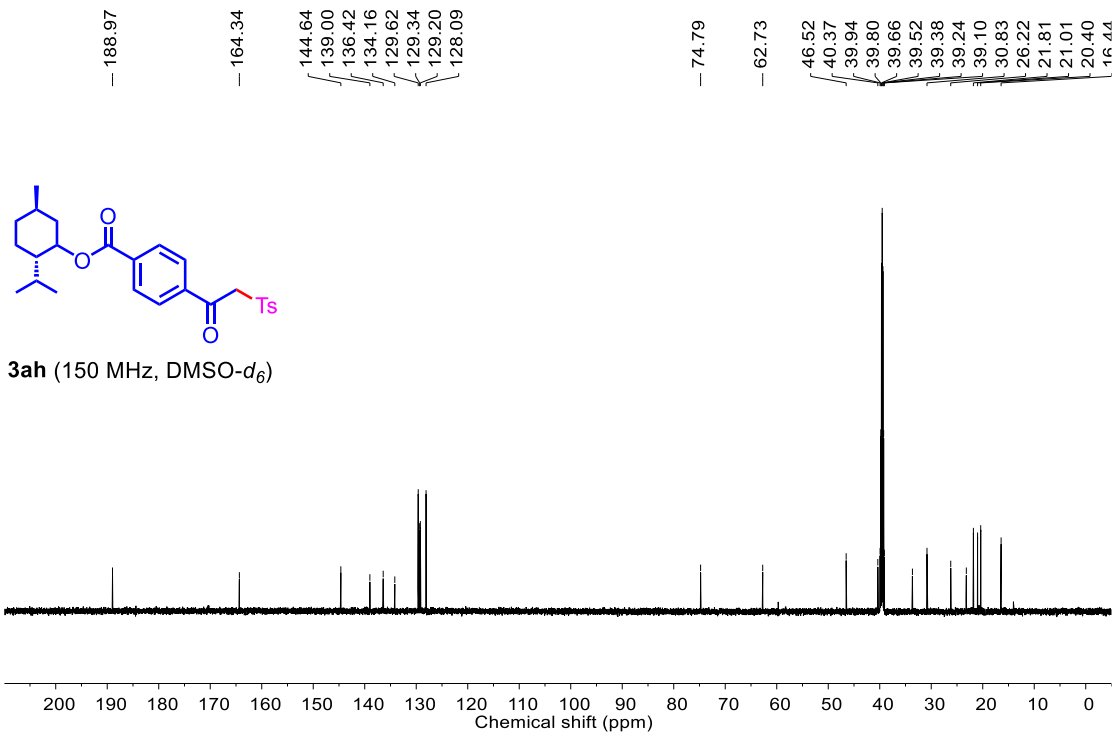

**3ag** (600 MHz, DMSO-$d_6$)



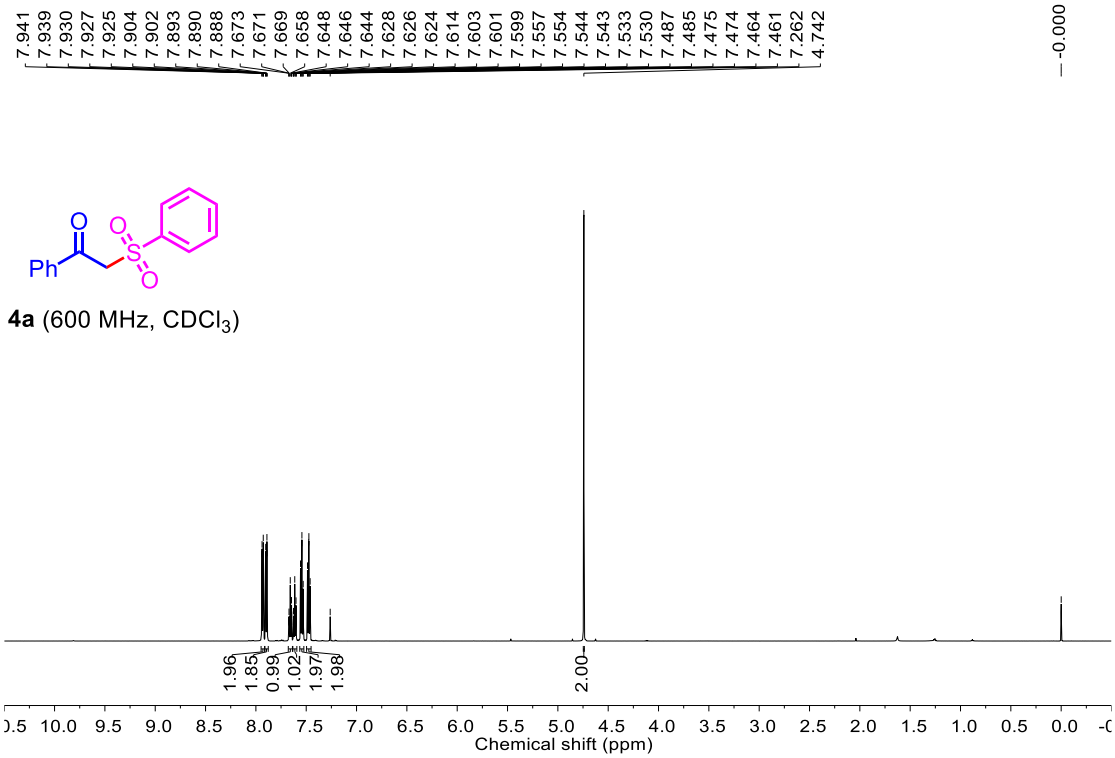

**3ag** (150 MHz, DMSO-$d_6$)



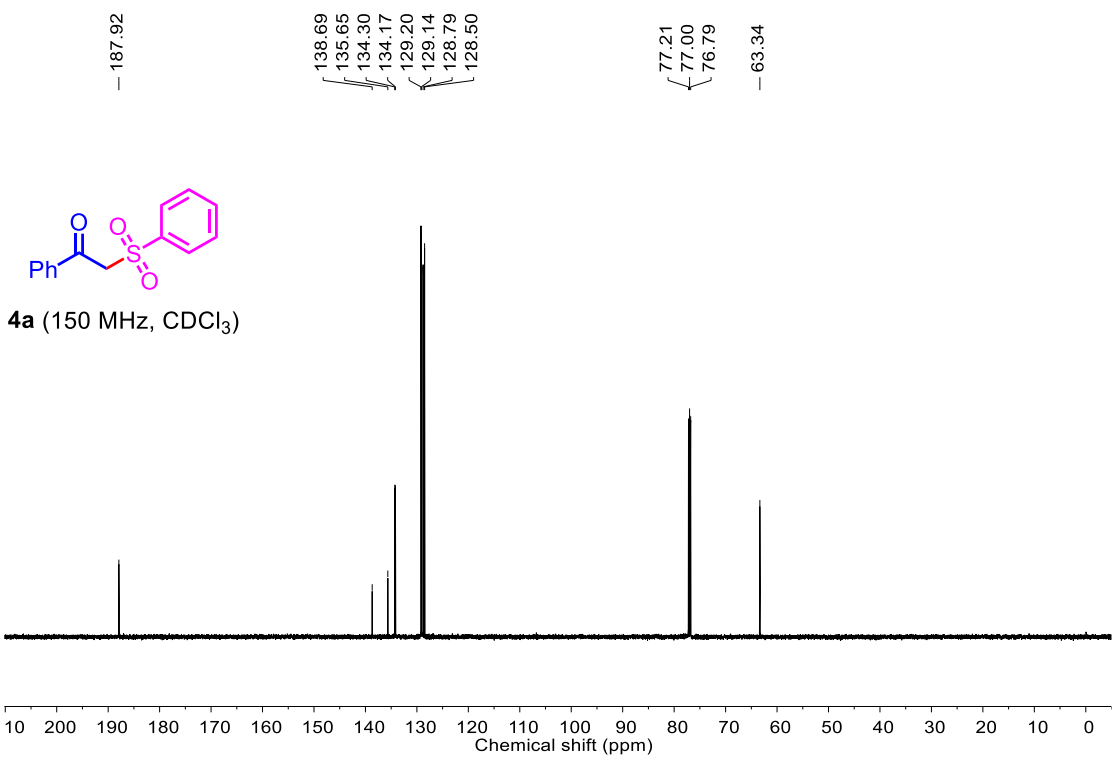

**3ah** (400 MHz, DMSO-$d_6$)



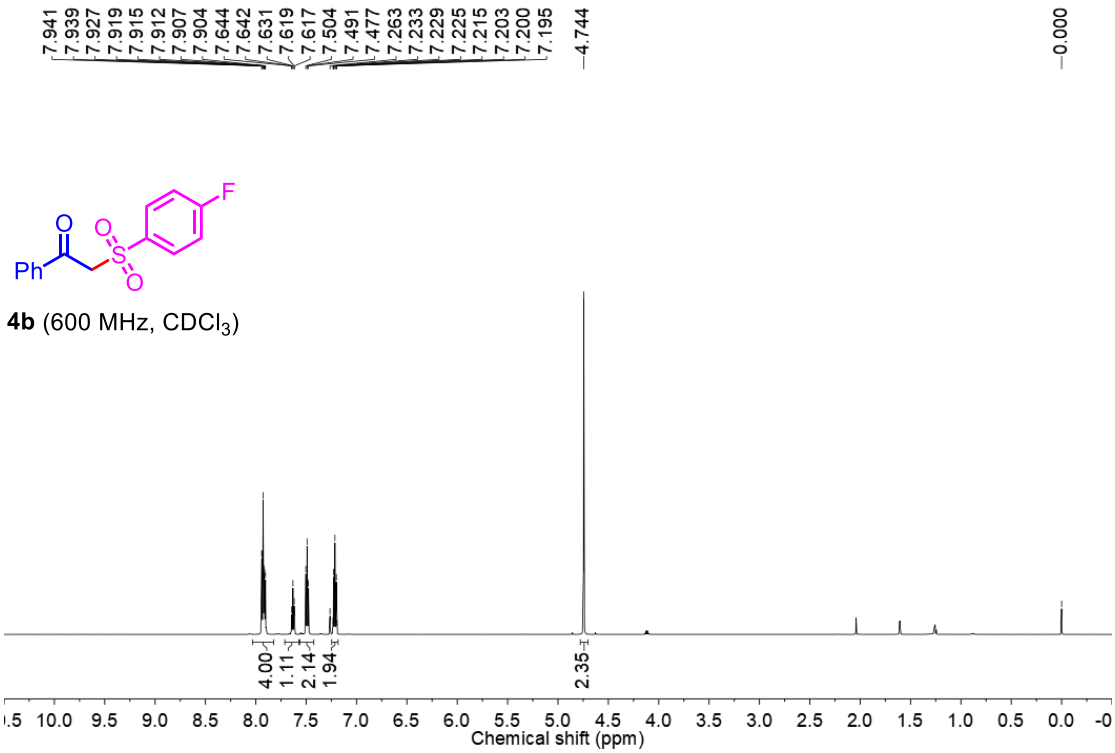

**3ah** (150 MHz, DMSO-$d_6$)



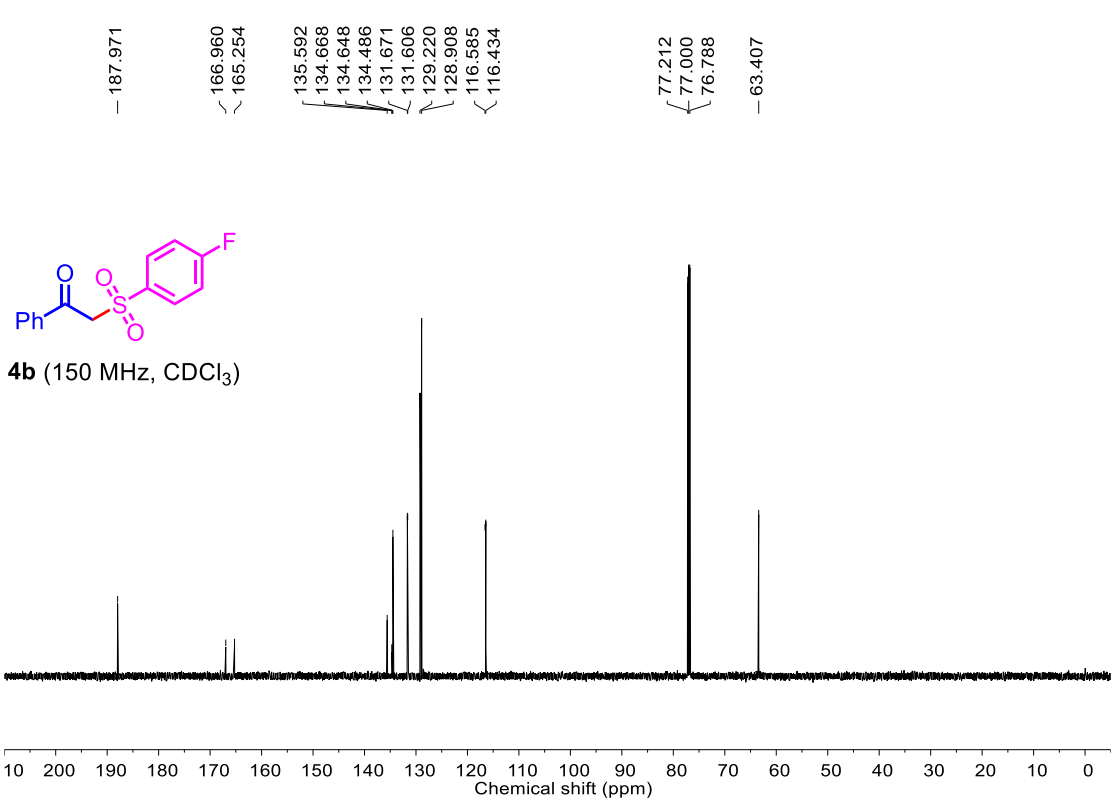

**4a** (600 MHz, $CDCl_3$)



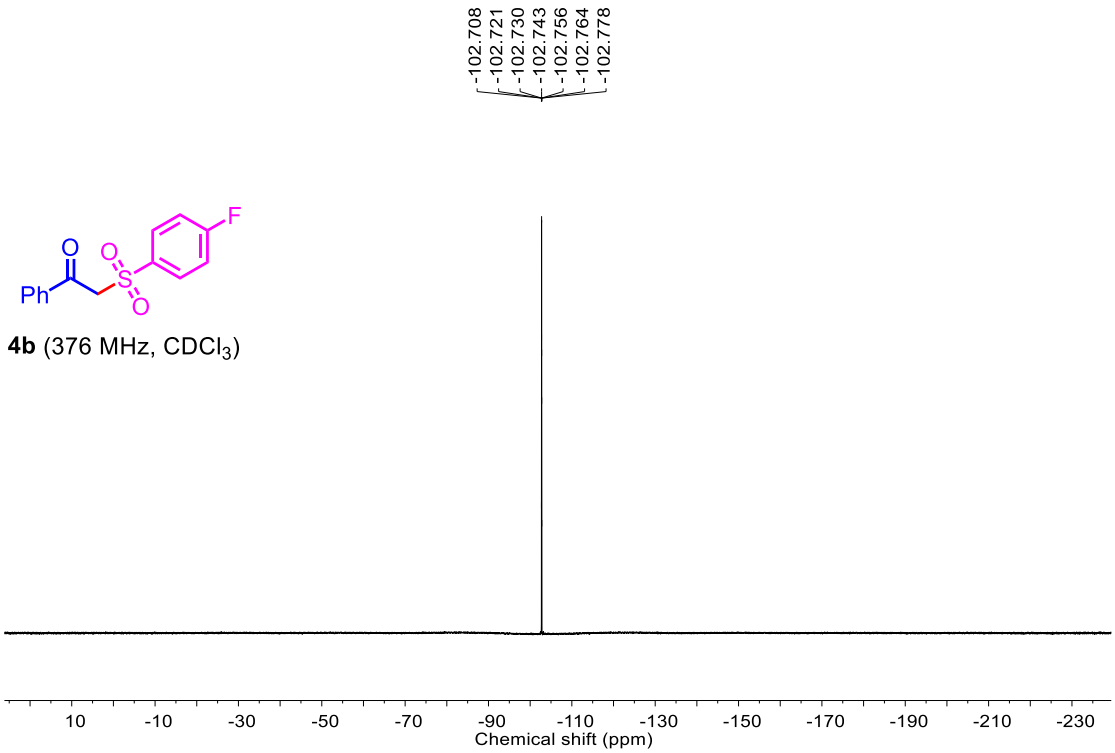

**4a** (150 MHz, $CDCl_3$)



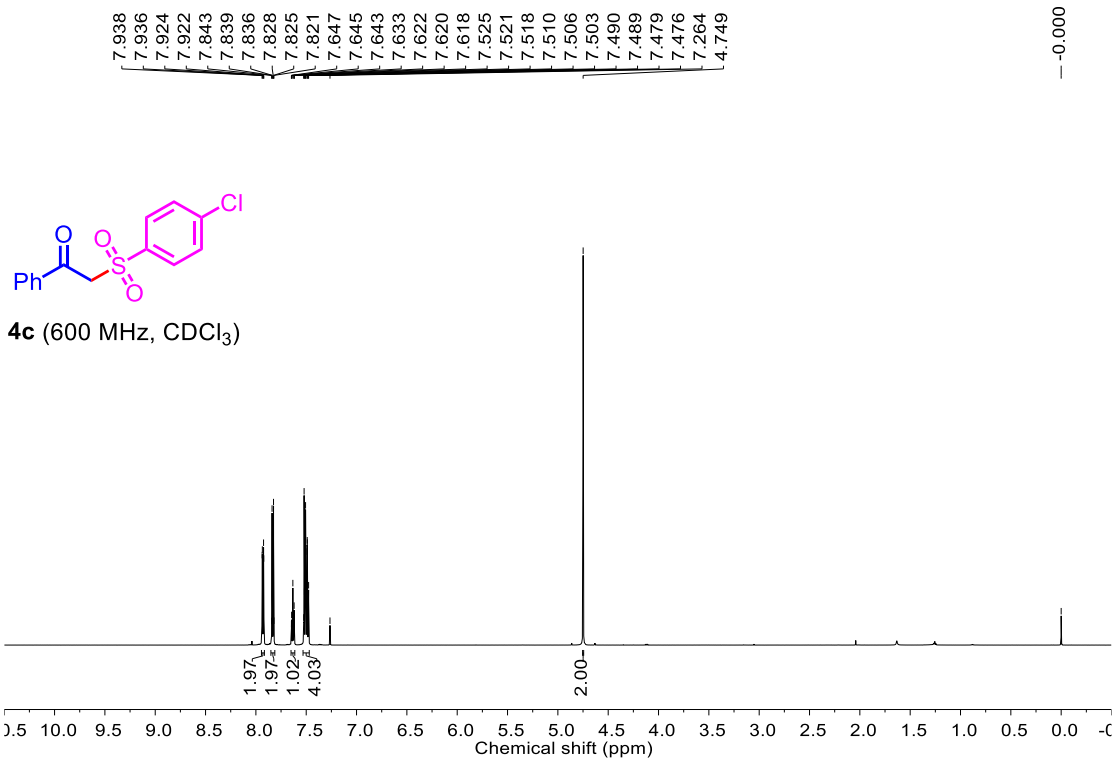

**4b** (600 MHz, $CDCl_3$)



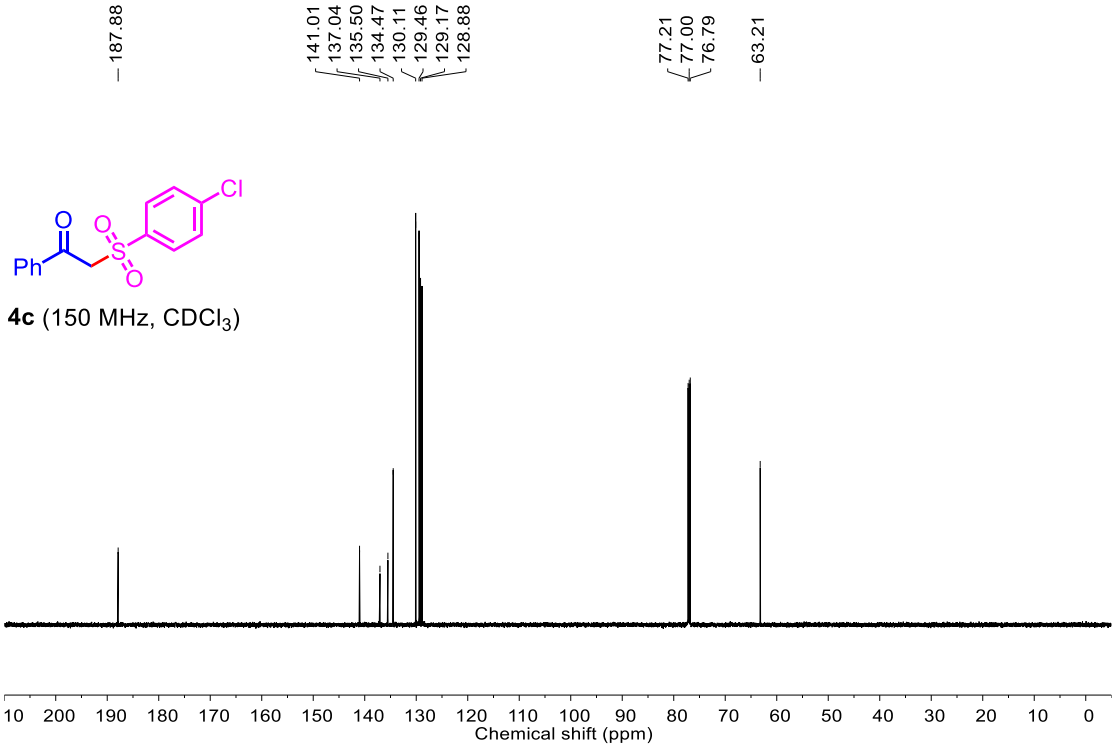

**4b** (150 MHz, $CDCl_3$)



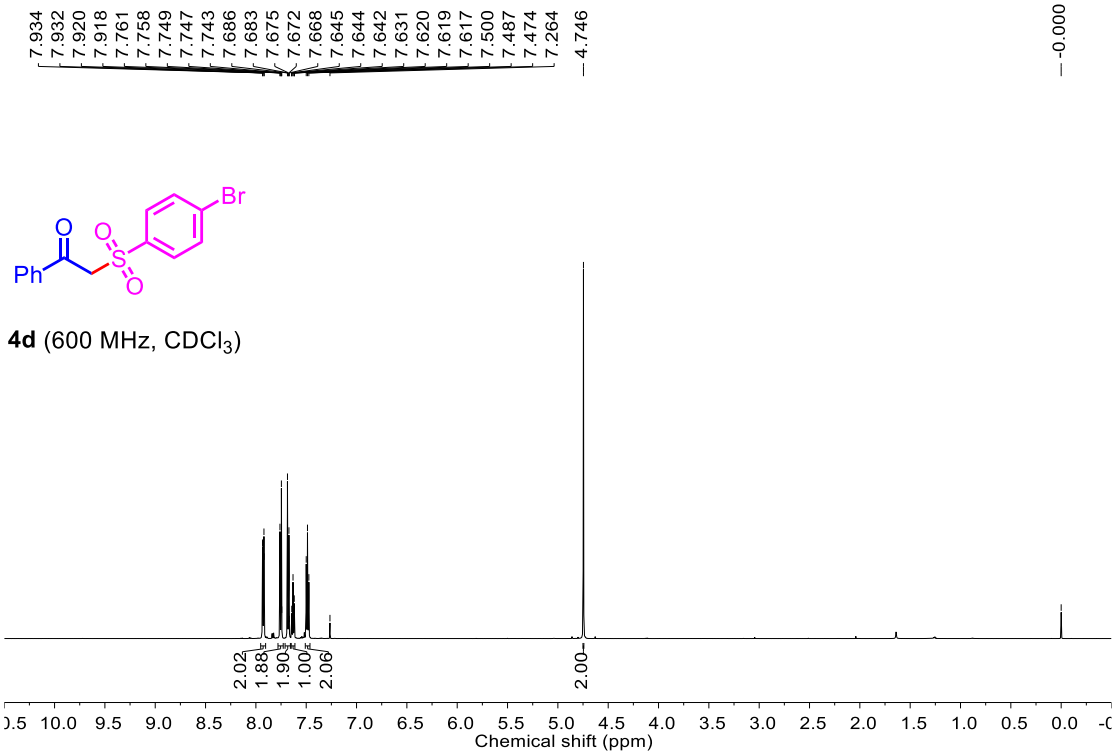

**4b** (376 MHz, $CDCl_3$)



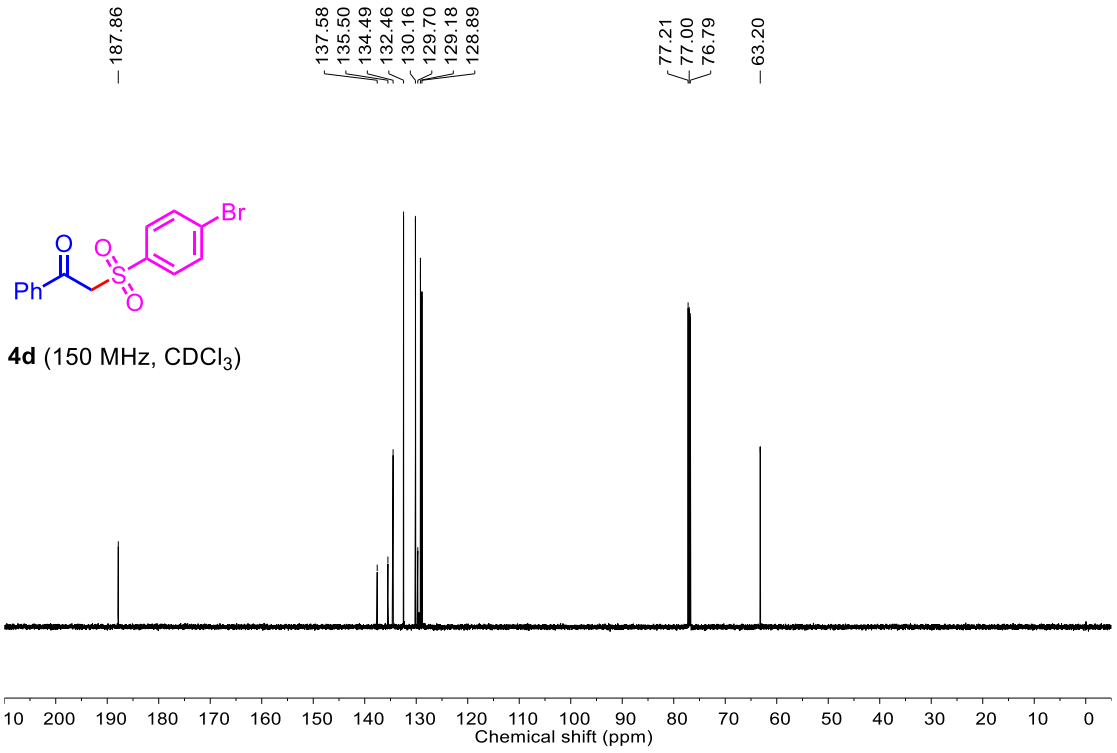

**4c** (600 MHz, $CDCl_3$)



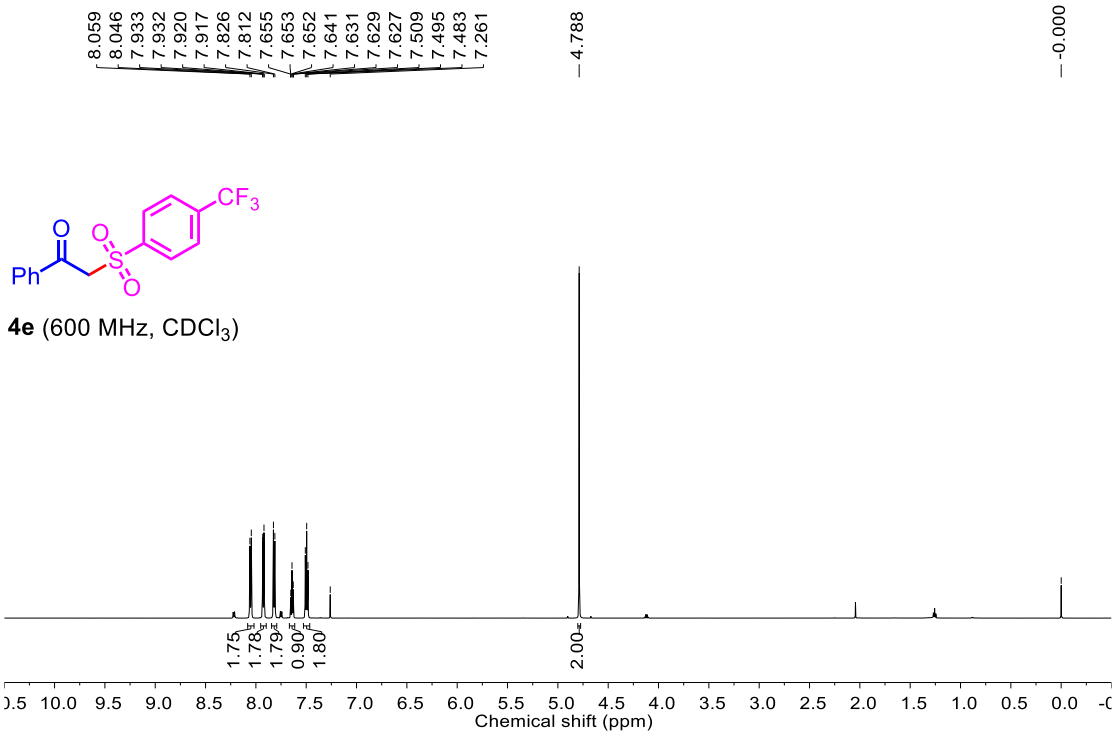

**4c** (150 MHz, $CDCl_3$)



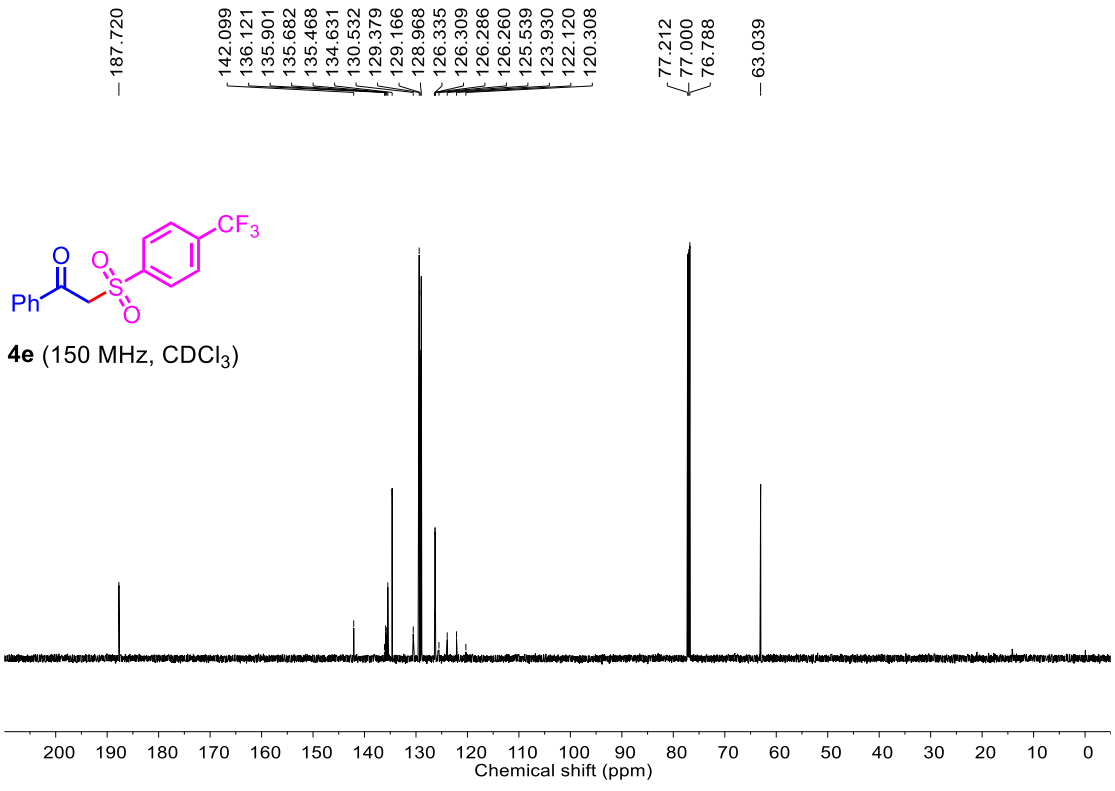

**4d** (600 MHz, $CDCl_3$)



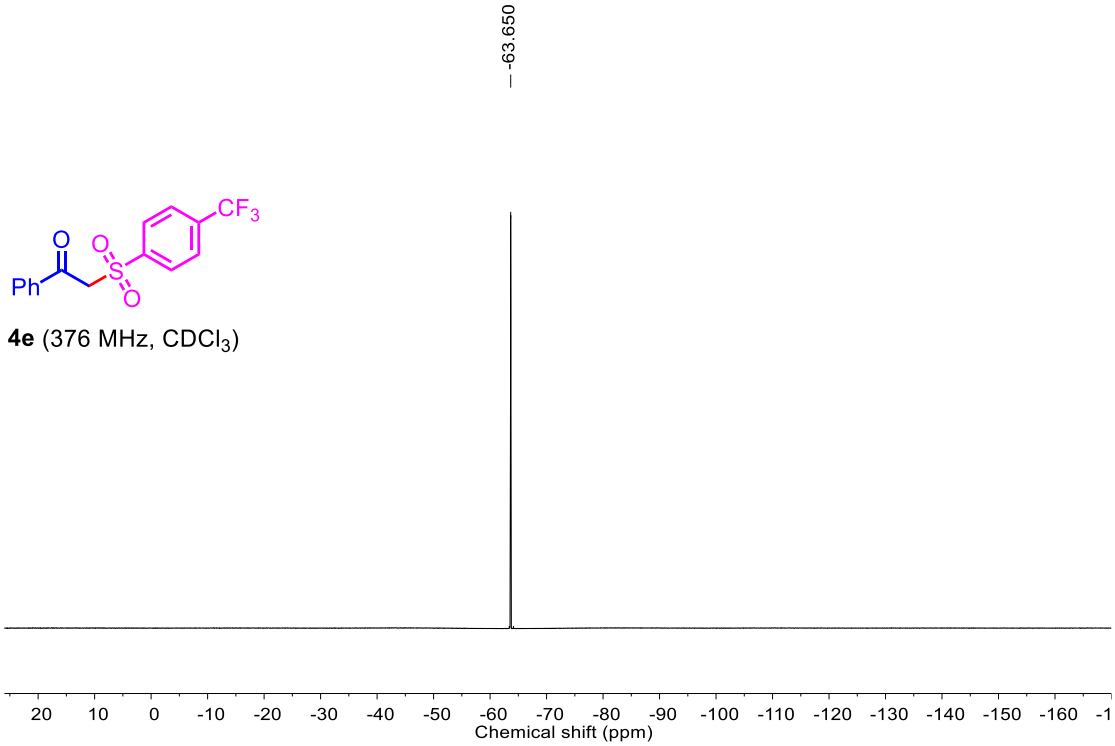

**4d** (150 MHz, $CDCl_3$)



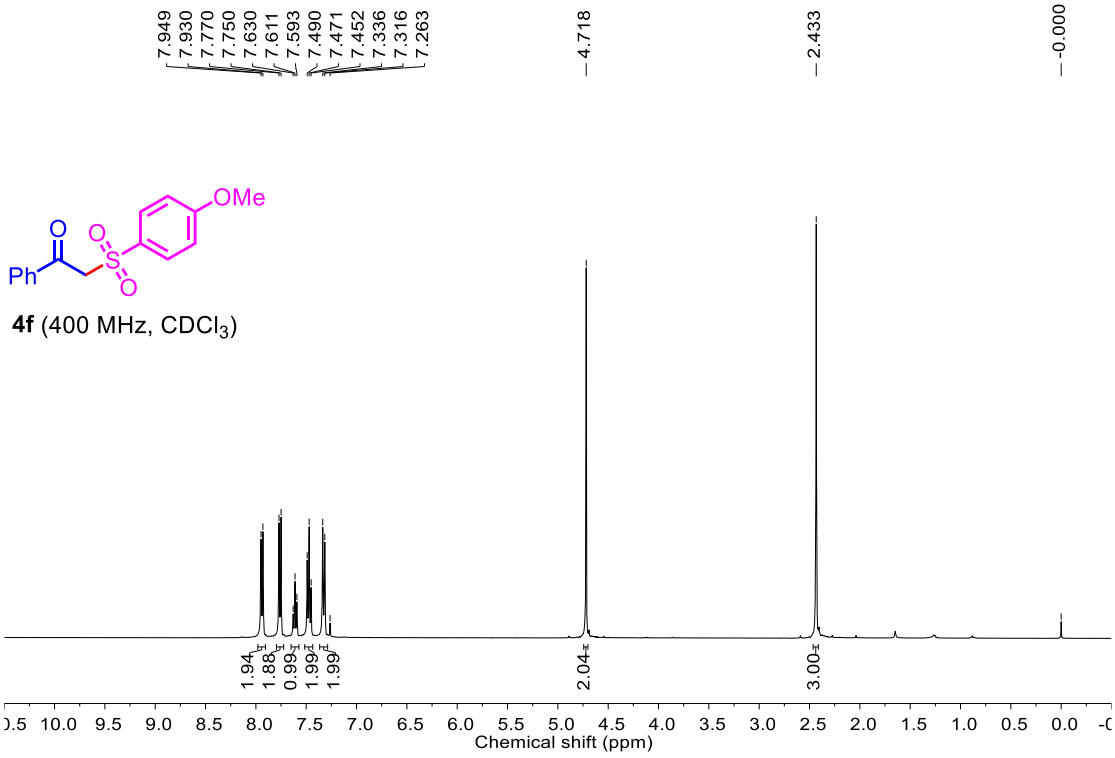

**4e** (600 MHz, $CDCl_3$)

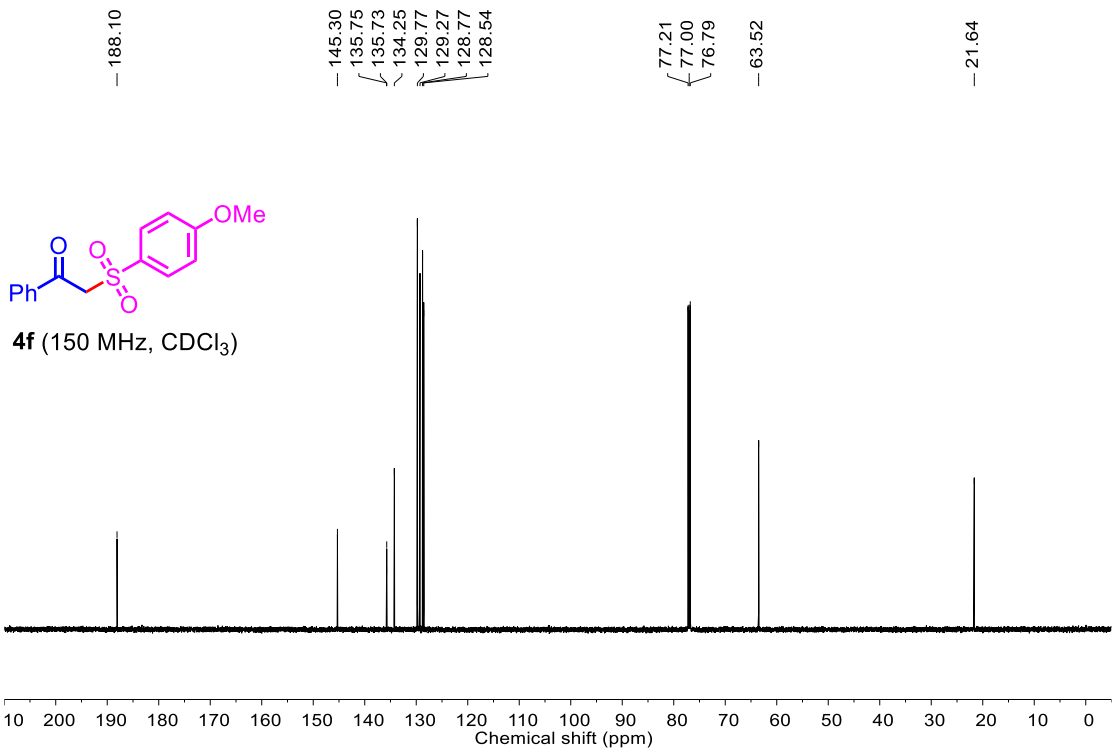


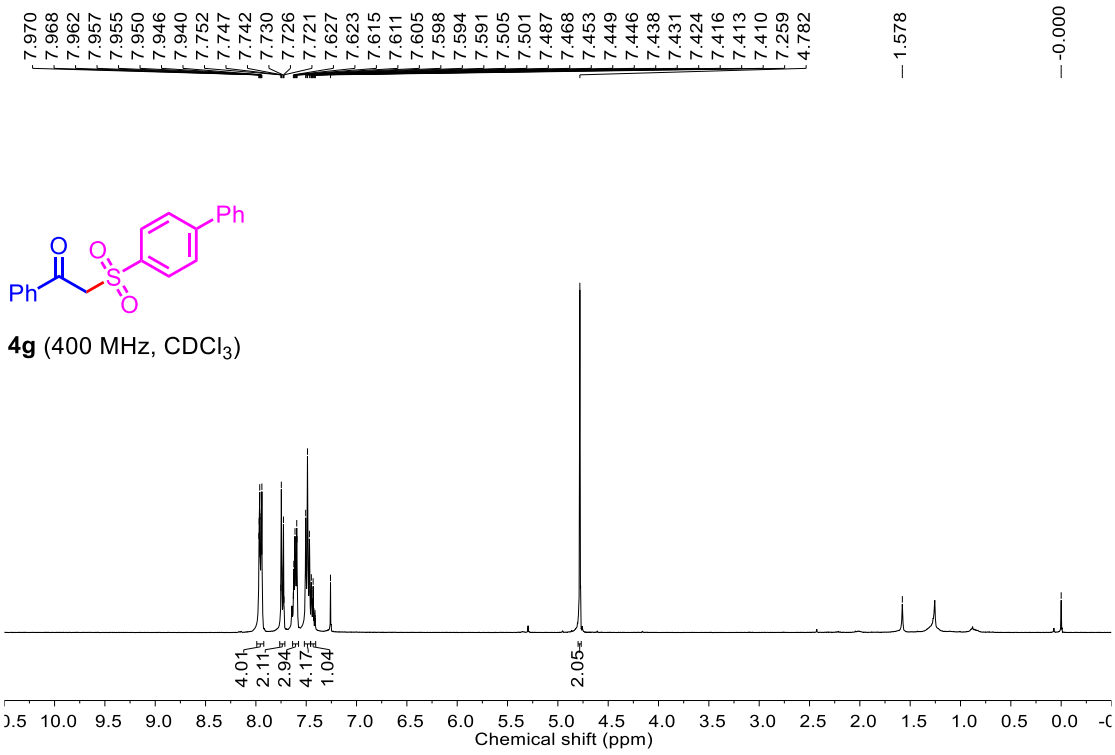

**4e** (150 MHz, $CDCl_3$)



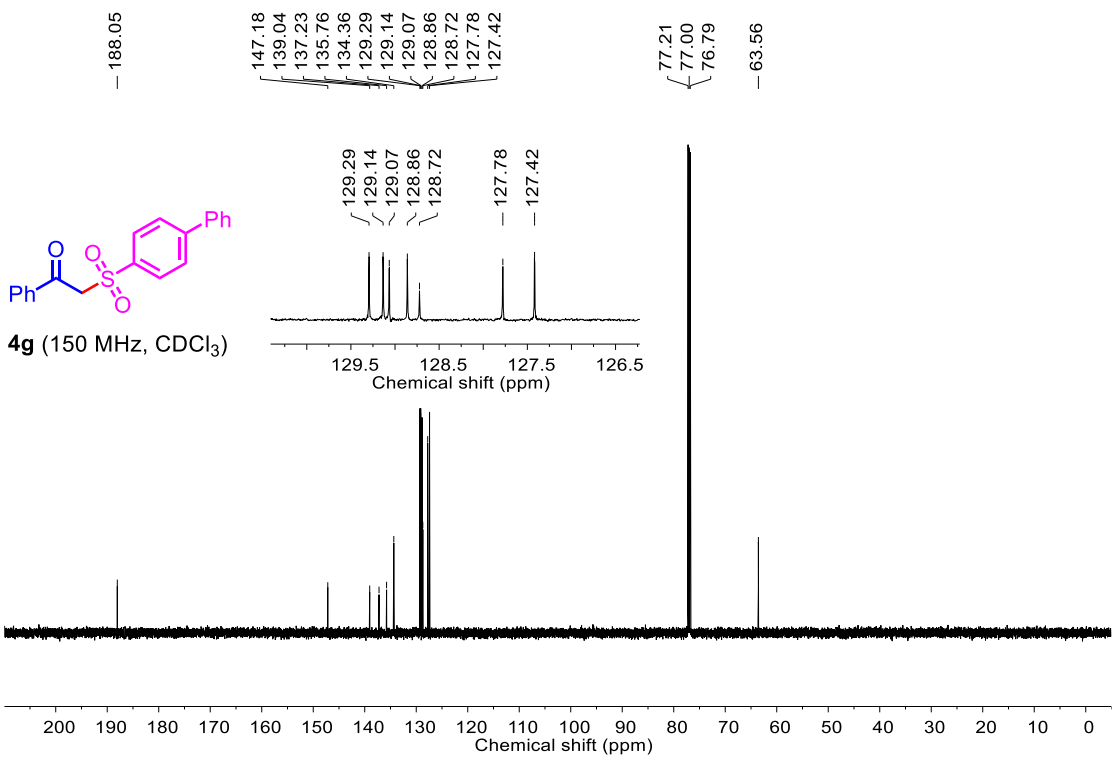

**4e** (376 MHz, $CDCl_3$)


7.949
7.930
7.770
7.750
7.630
7.611
7.593
7.490
7.471
7.452
7.336
7.316
7.263
4.718
2.433
-0.000
OMe
O
O
S
O
Ph
4f (400 MHz, CDCl3)
1.94
1.88
0.99
1.99
1.99
2.04
3.00
Chemical shift (ppm)

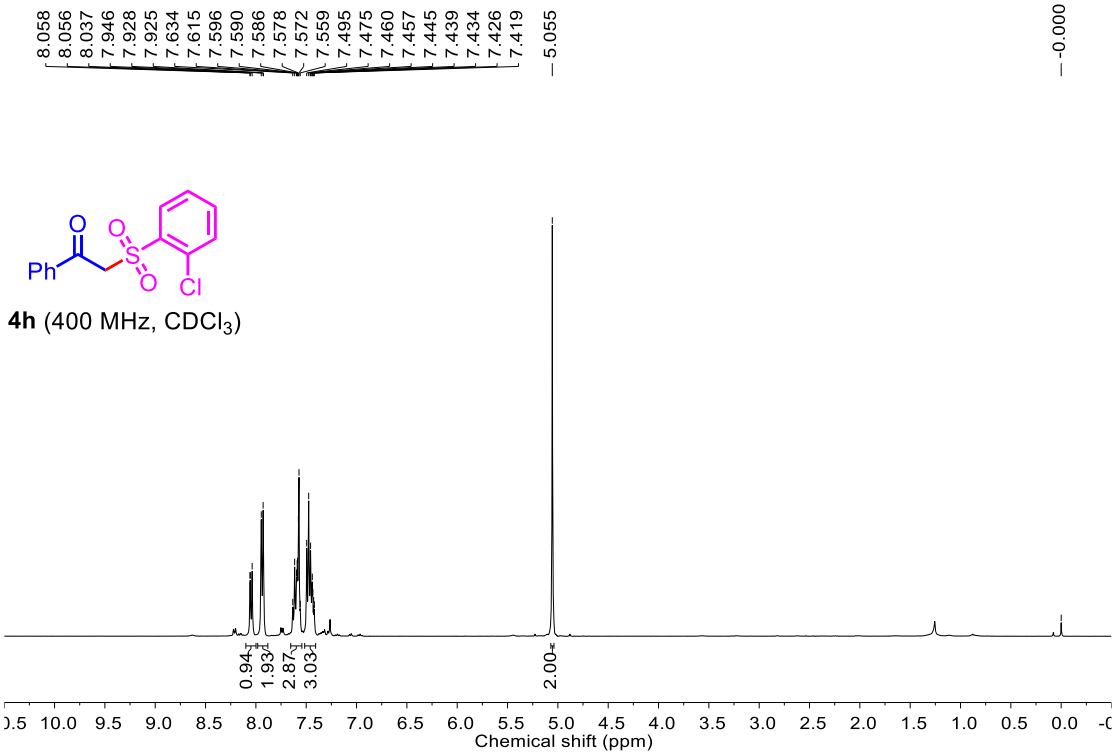

188.10
145.30
135.75
135.73
134.25
129.77
129.27
128.77
128.54
77.21
77.00
76.79
63.52
21.64
OMe
O
O
S
O
Ph
4f (150 MHz, CDCl3)
Chemical shift (ppm)

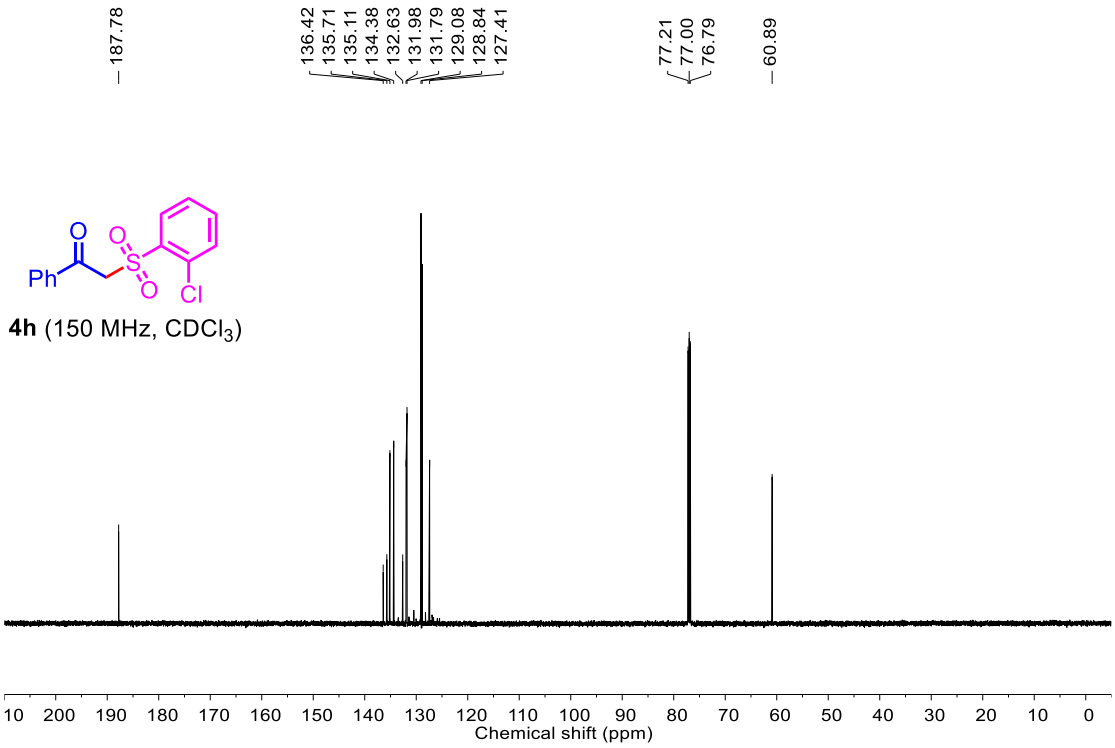


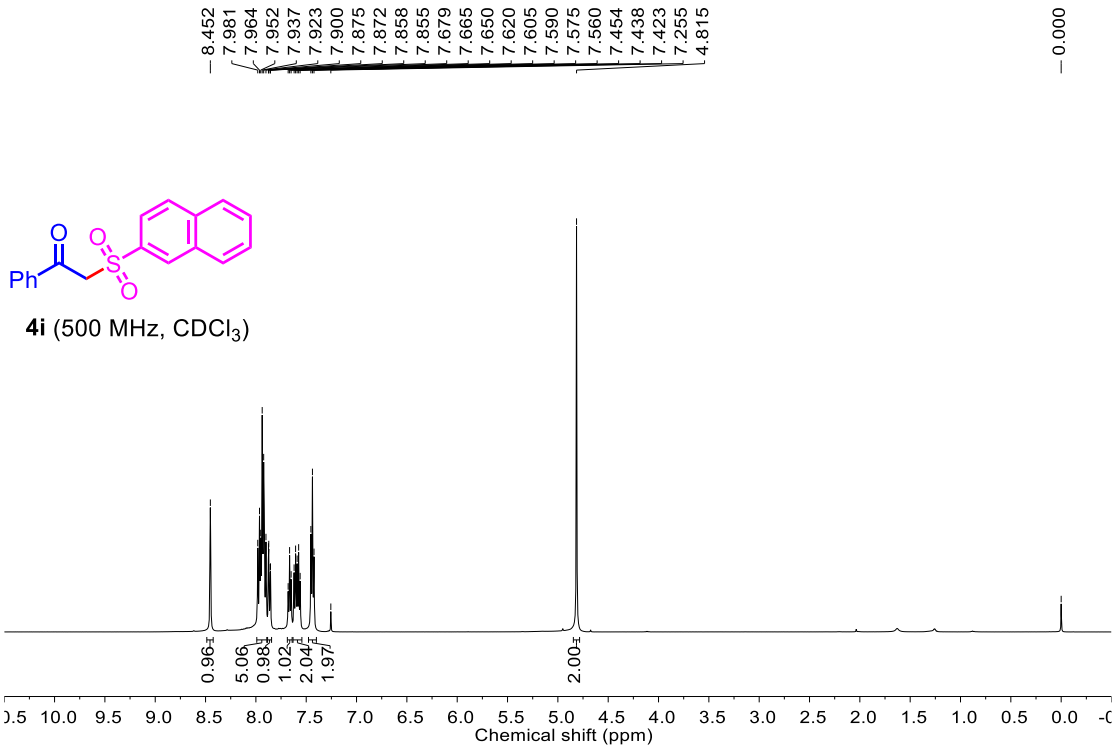

**4g** (400 MHz, $CDCl_3$)

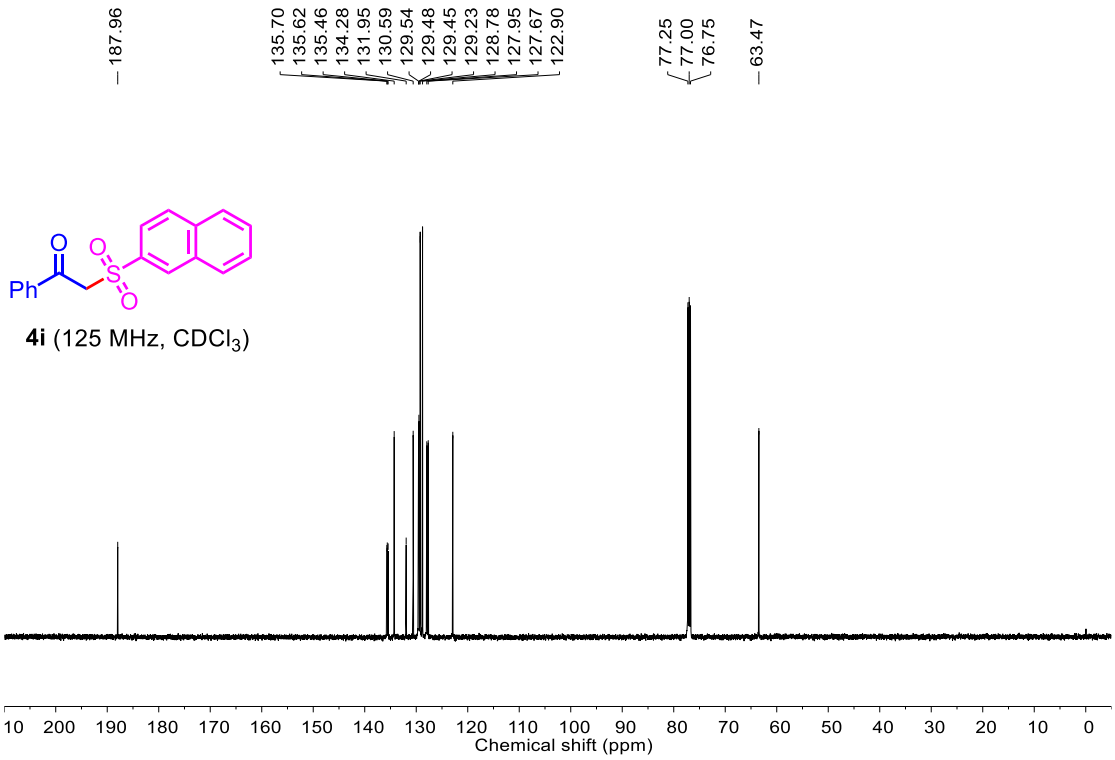


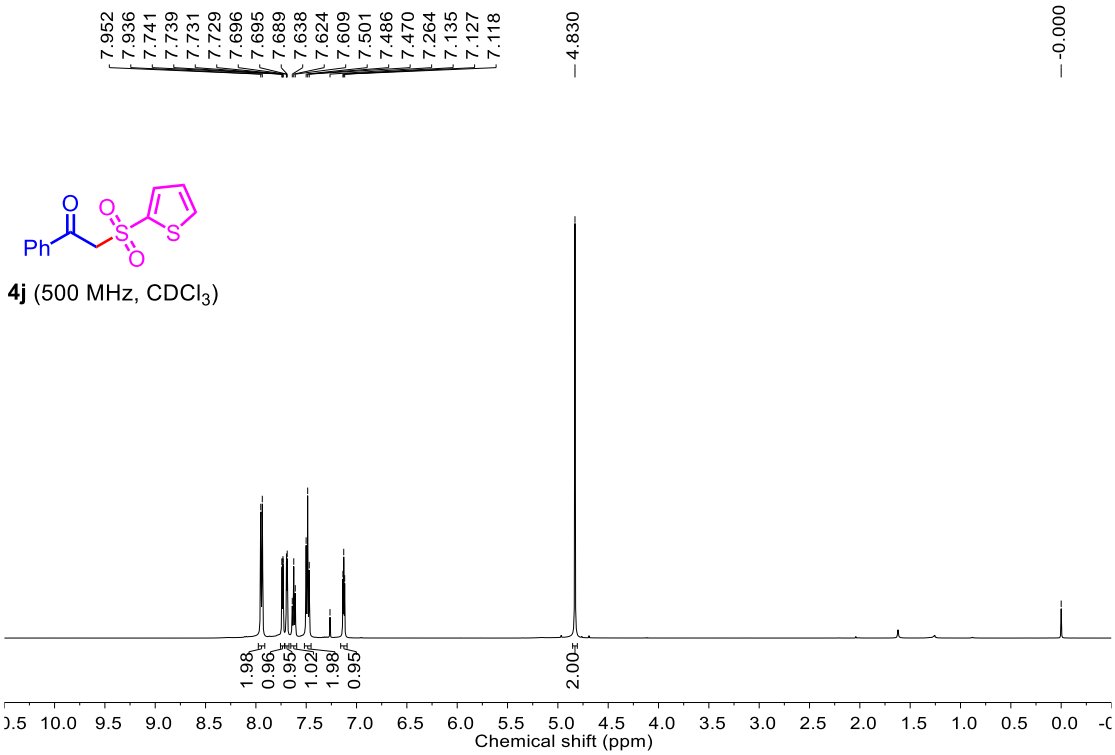

**4g** (150 MHz, $CDCl_3$)


8.058
8.056
8.037
7.946
7.928
7.925
7.634
7.615
7.596
7.590
7.586
7.578
7.572
7.559
7.495
7.475
7.460
7.457
7.445
7.439
7.434
7.426
7.419
5.055
-0.000
Ph
O
O
S
O
Cl
4h (400 MHz, CDCl3)
0.94
1.93
2.87
3.03
2.00
Chemical shift (ppm)

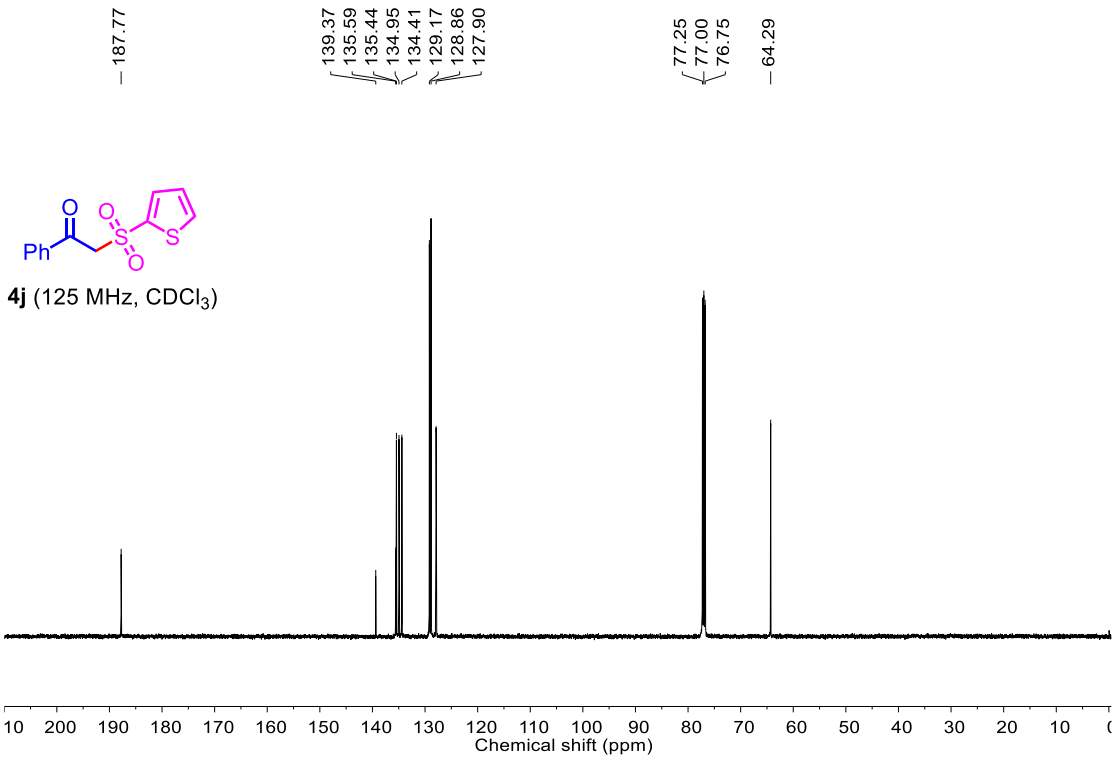

187.78
136.42
135.71
135.11
134.38
132.63
131.98
131.79
129.08
128.84
127.41
77.21
77.00
76.79
60.89
Ph
O
O
S
O
Cl
4h (150 MHz, CDCl3)
Chemical shift (ppm)


8.452
7.981
7.964
7.952
7.937
7.923
7.900
7.875
7.872
7.858
7.855
7.679
7.665
7.650
7.620
7.605
7.590
7.575
7.560
7.454
7.438
7.423
7.255
4.815
0.000
Ph
O
O
S
O
4i (500 MHz, CDCl3)
0.96
5.06
0.98
1.02
2.04
1.97
2.00
Chemical shift (ppm)

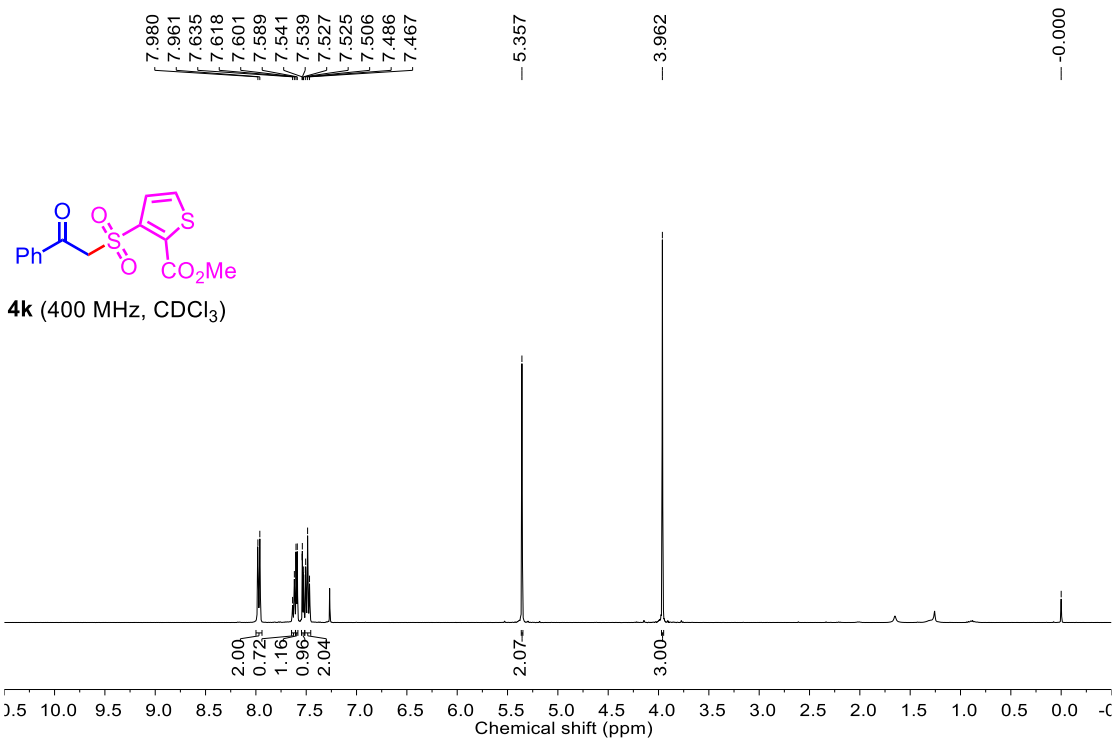

187.96
135.70
135.62
135.46
134.28
131.95
130.59
129.54
129.48
129.45
129.23
128.78
127.95
127.67
122.90
77.25
77.00
76.75
63.47
Ph
O
O
S
O
4i (125 MHz, CDCl3)
Chemical shift (ppm)

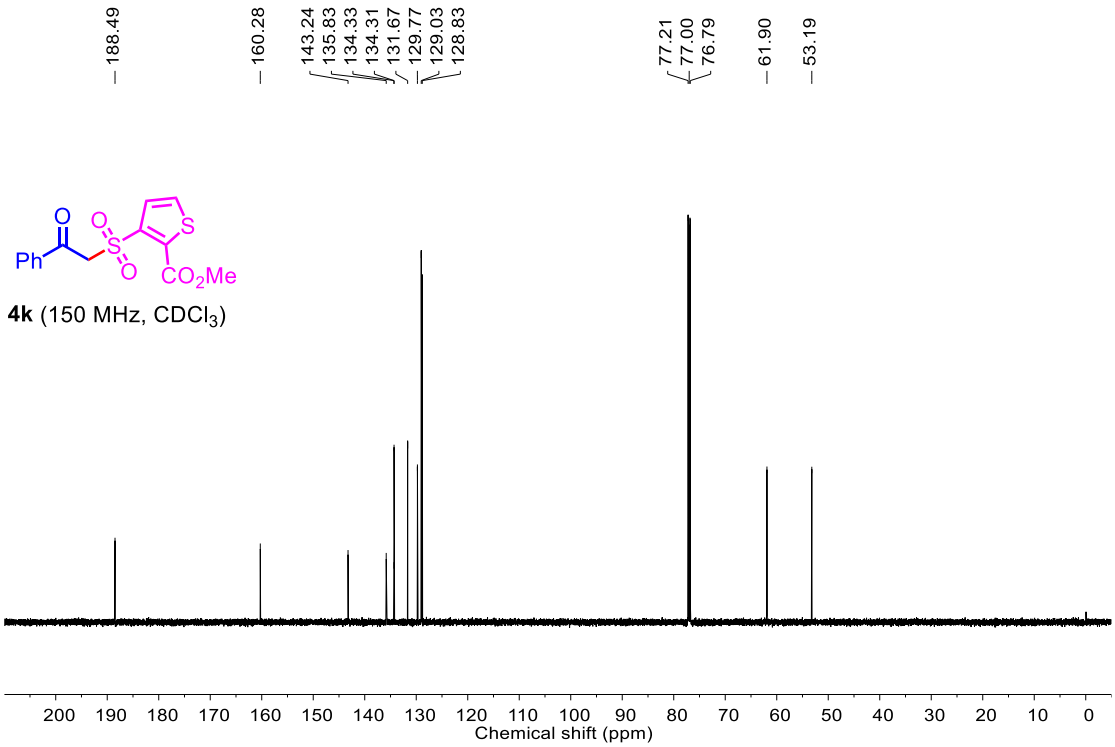


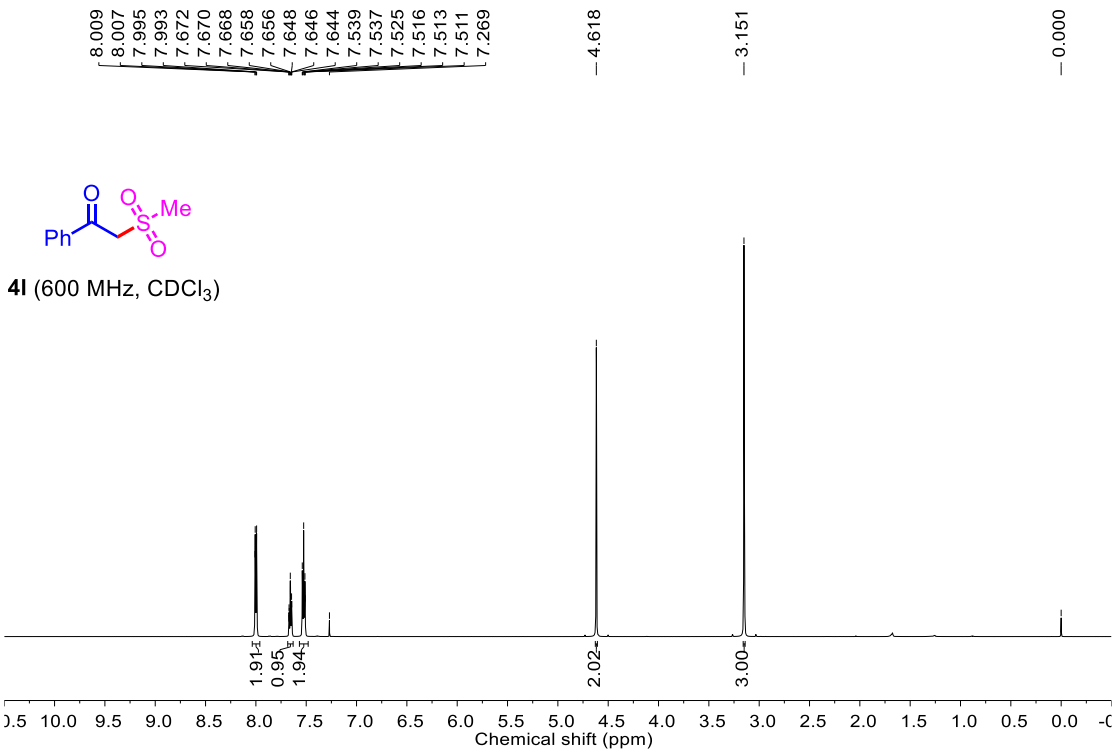

**4j** (500 MHz, $CDCl_3$)



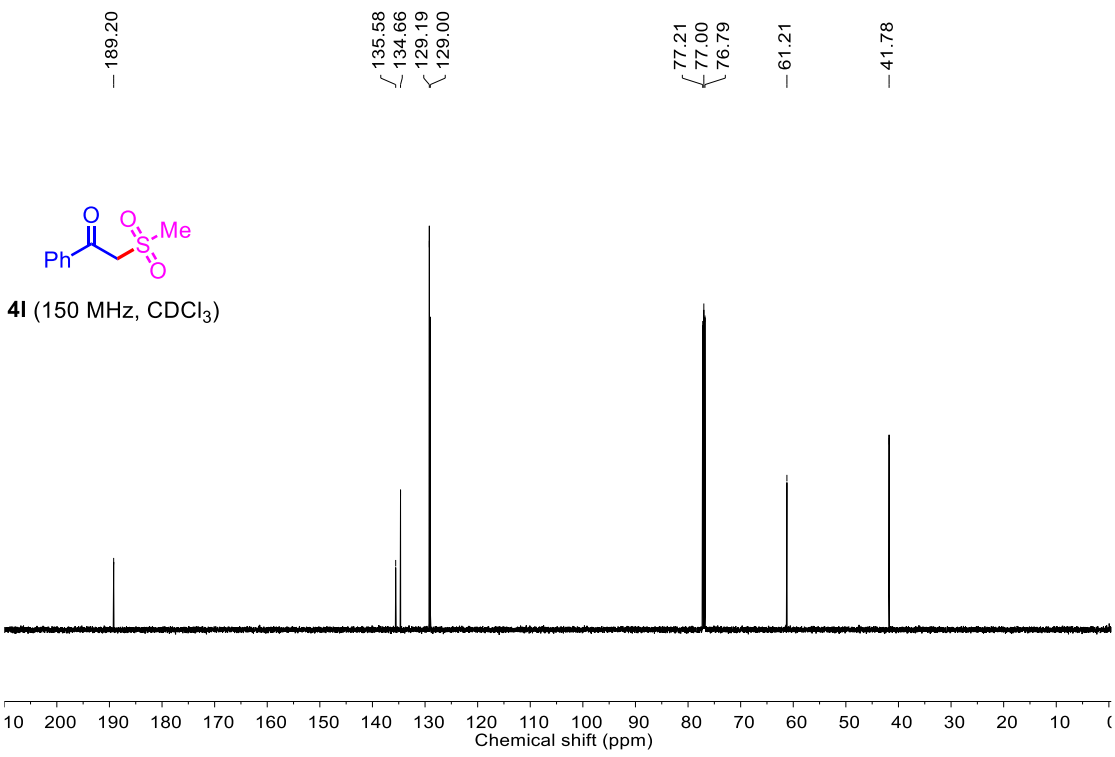

**4j** (125 MHz, $CDCl_3$)


7.980
7.961
7.635
7.618
7.601
7.589
7.541
7.539
7.527
7.525
7.506
7.486
7.467
5.357
3.962
-0.000
Ph
O
O
S
O
S
CO2Me
4k (400 MHz, CDCl3)
2.00
0.72
1.16
0.96
2.04
2.07
3.00
Chemical shift (ppm)

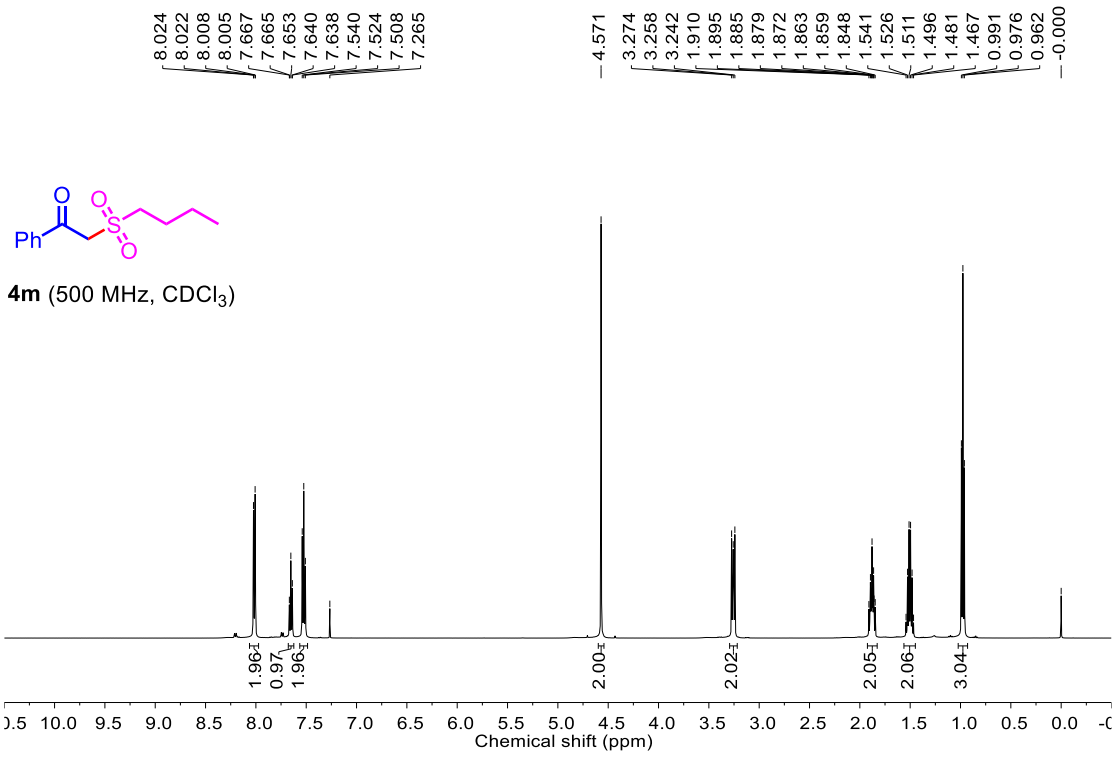

188.49
160.28
143.24
135.83
134.33
134.31
131.67
129.77
129.03
128.83
77.21
77.00
76.79
61.90
53.19
Ph
O
O
S
O
S
CO2Me
4k (150 MHz, CDCl3)
Chemical shift (ppm)



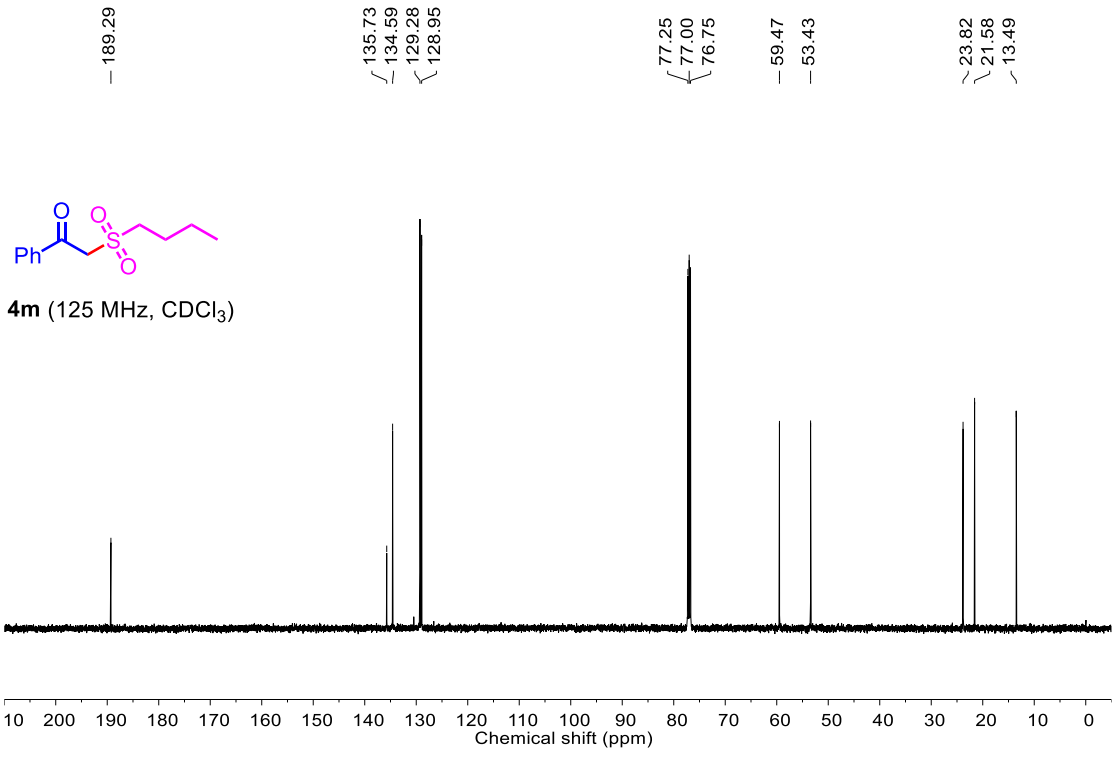

**4l** (600 MHz, $CDCl_3$)



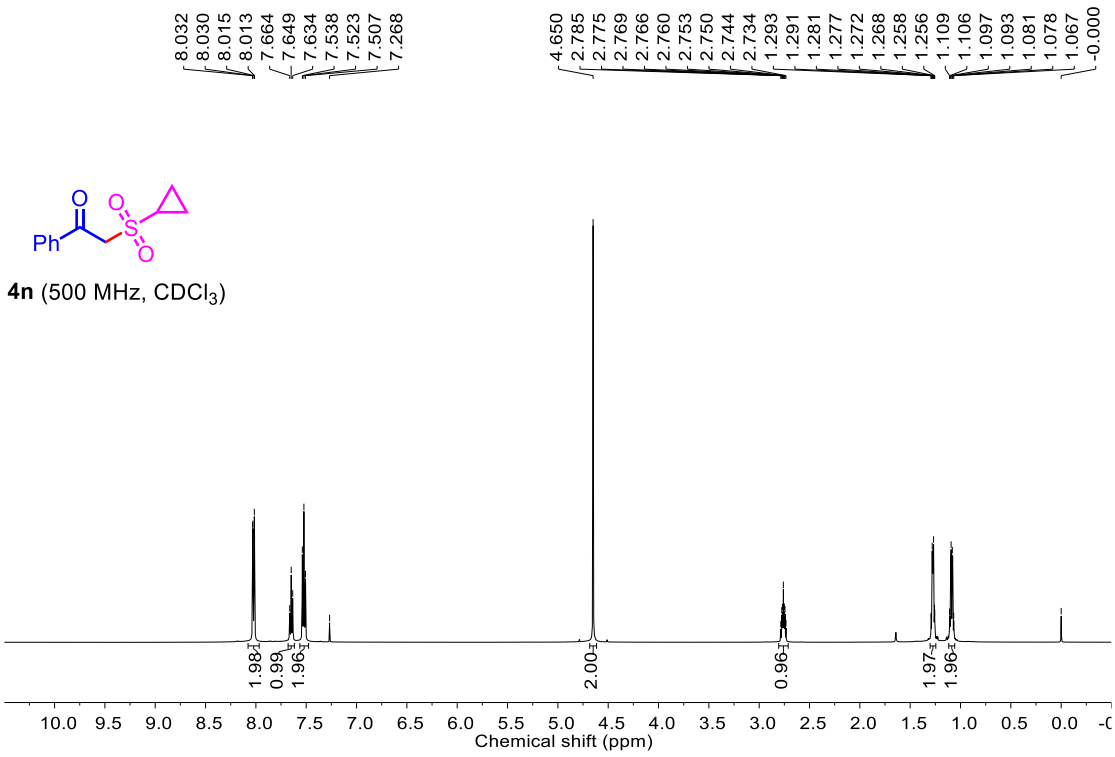

**4l** (150 MHz, $CDCl_3$)



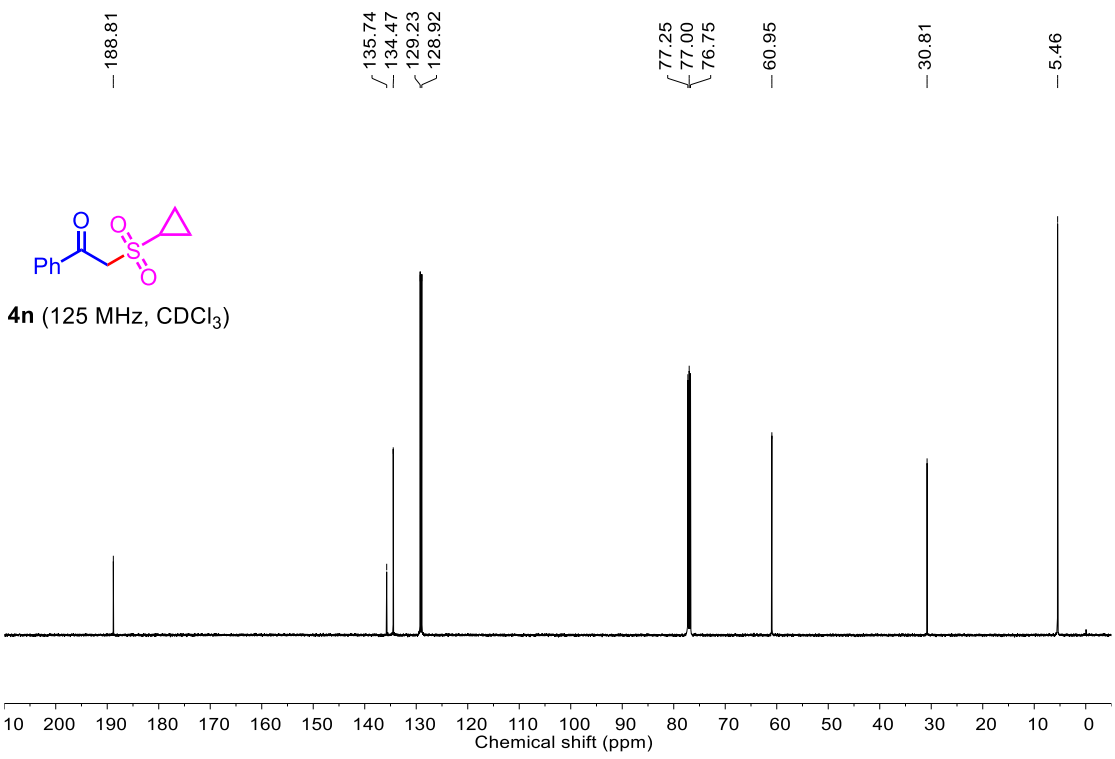

**4m** (500 MHz, $CDCl_3$)



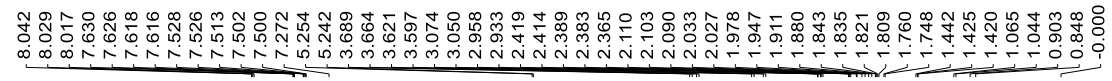

**4m** (125 MHz, $CDCl_3$)

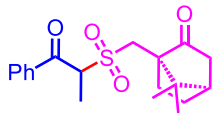



**4n** (500 MHz, $CDCl_3$)

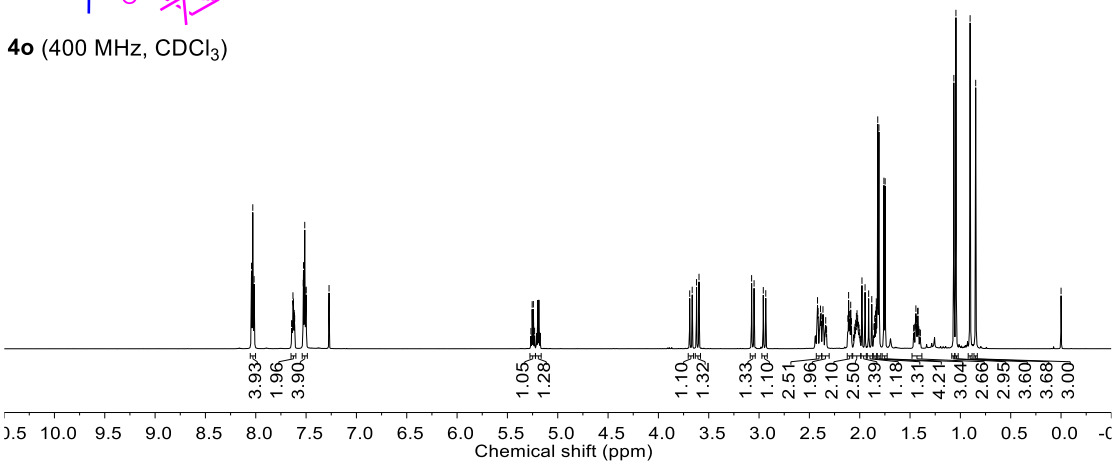


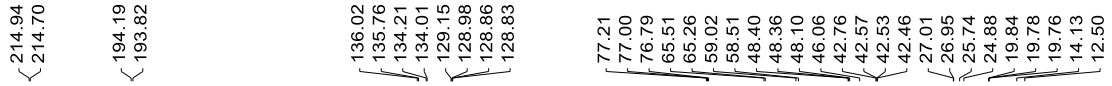

**4n** (125 MHz, $CDCl_3$)

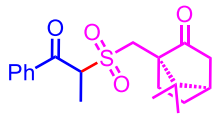




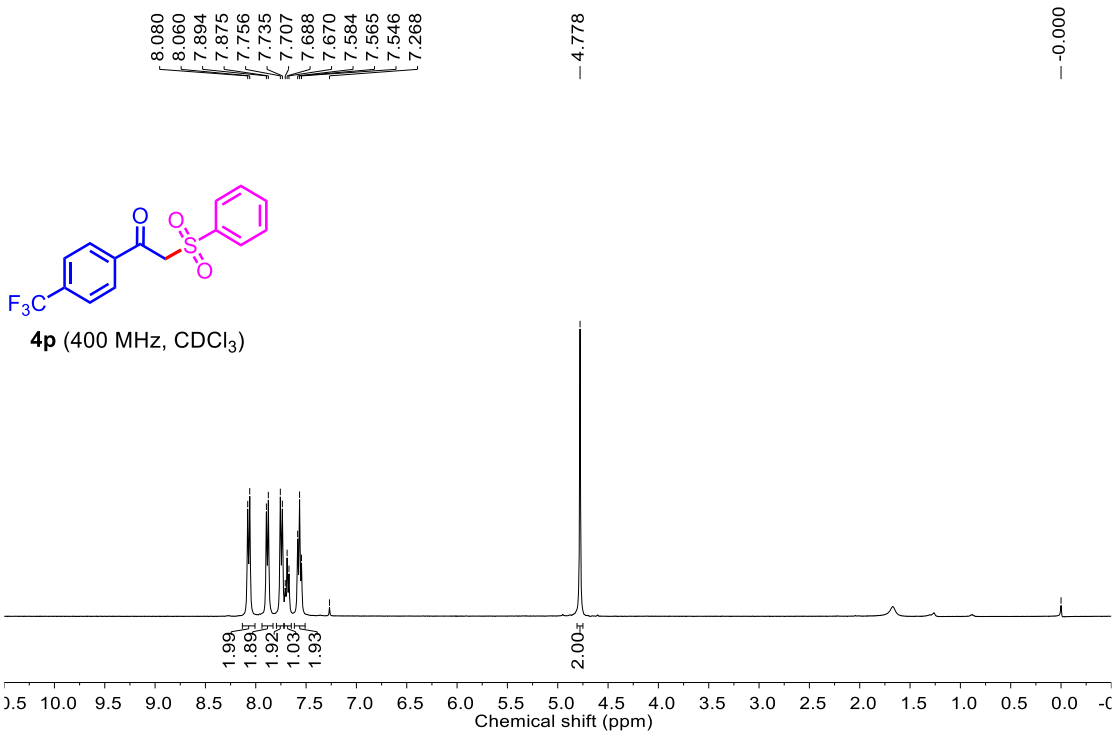
**4o** (400 MHz, $CDCl_3$)

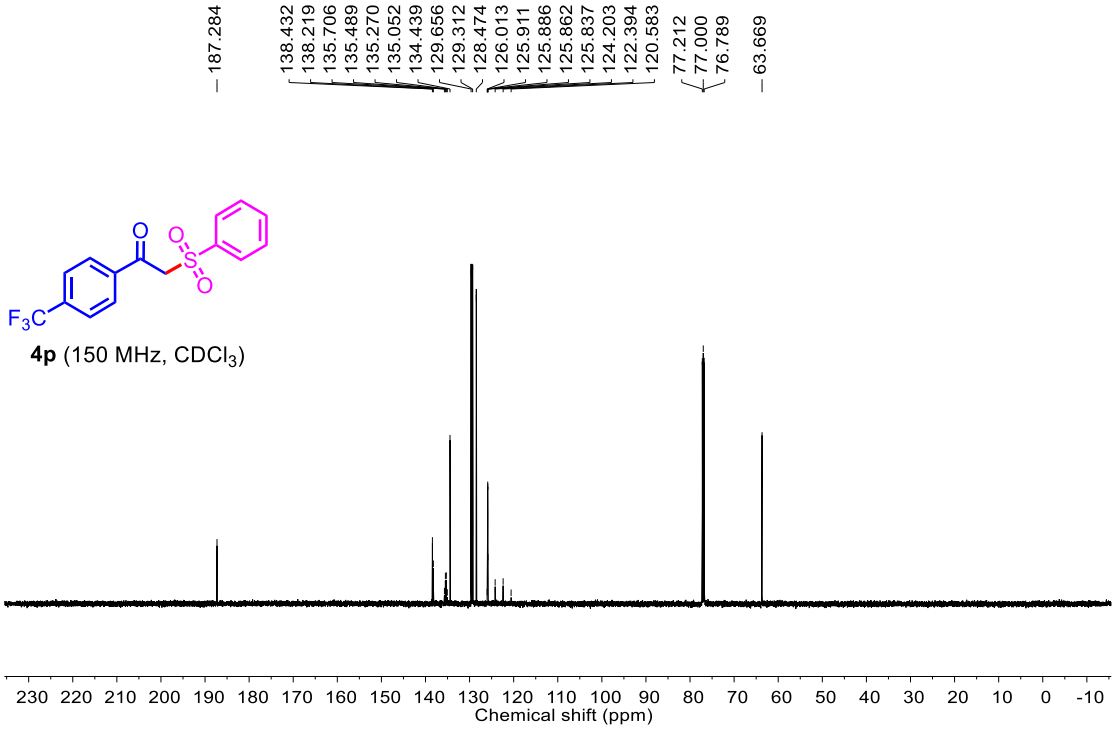


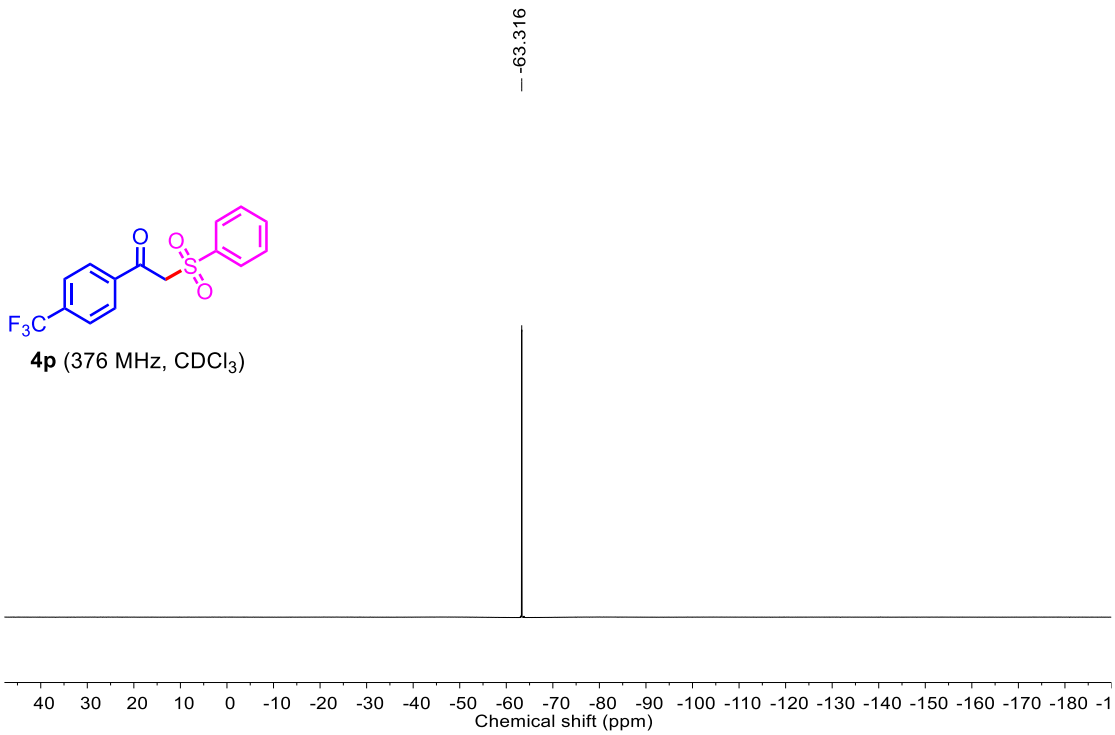



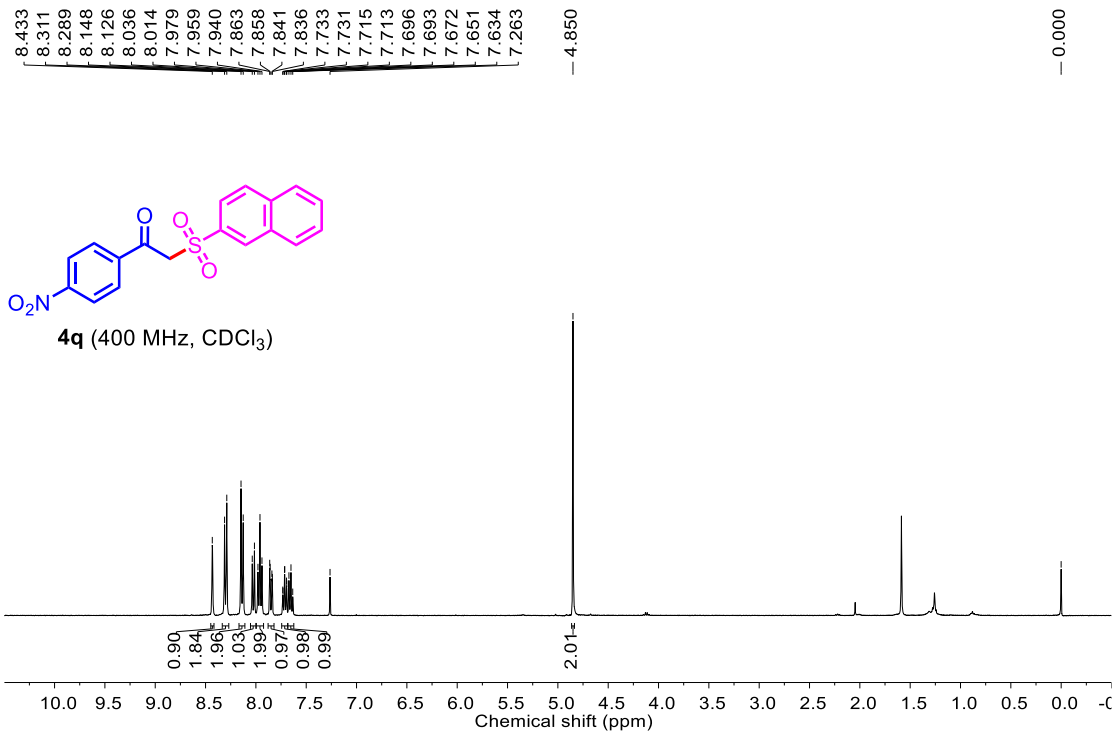


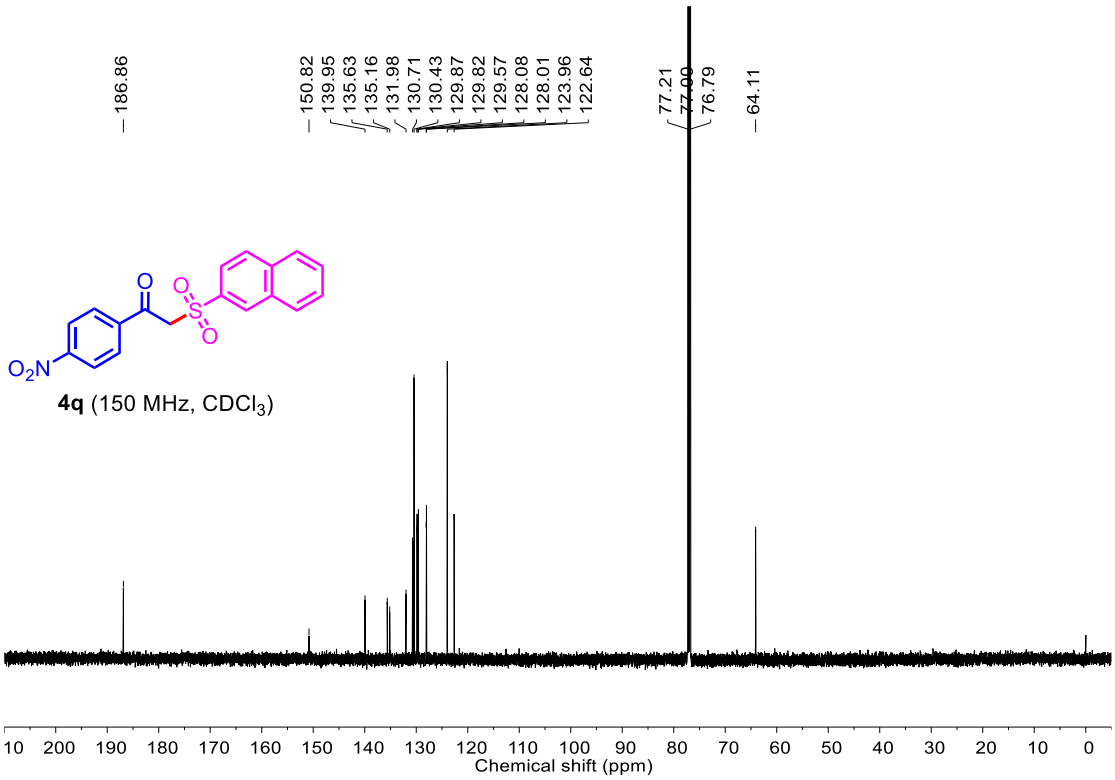
**4o** (150 MHz, $CDCl_3$)

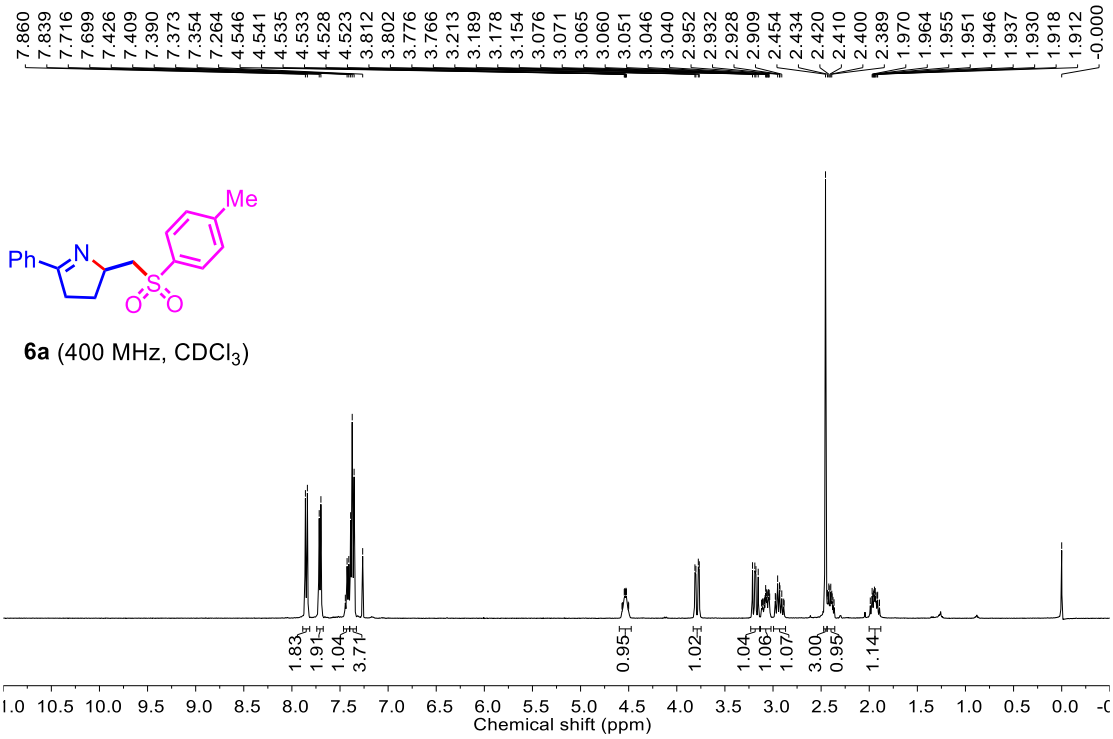

8.080
8.060
7.894
7.875
7.756
7.735
7.707
7.688
7.670
7.584
7.565
7.546
7.268
4.778
-0.000
F3C
4p (400 MHz, CDCl3)
1.99
1.89
1.92
1.03
1.93
2.00
Chemical shift (ppm)


187.284
138.432
138.219
135.706
135.489
135.270
135.052
134.439
129.656
129.312
128.474
126.013
125.911
125.886
125.862
125.837
124.203
122.394
120.583
77.212
77.000
76.789
63.669
F3C
4p (150 MHz, CDCl3)
Chemical shift (ppm)

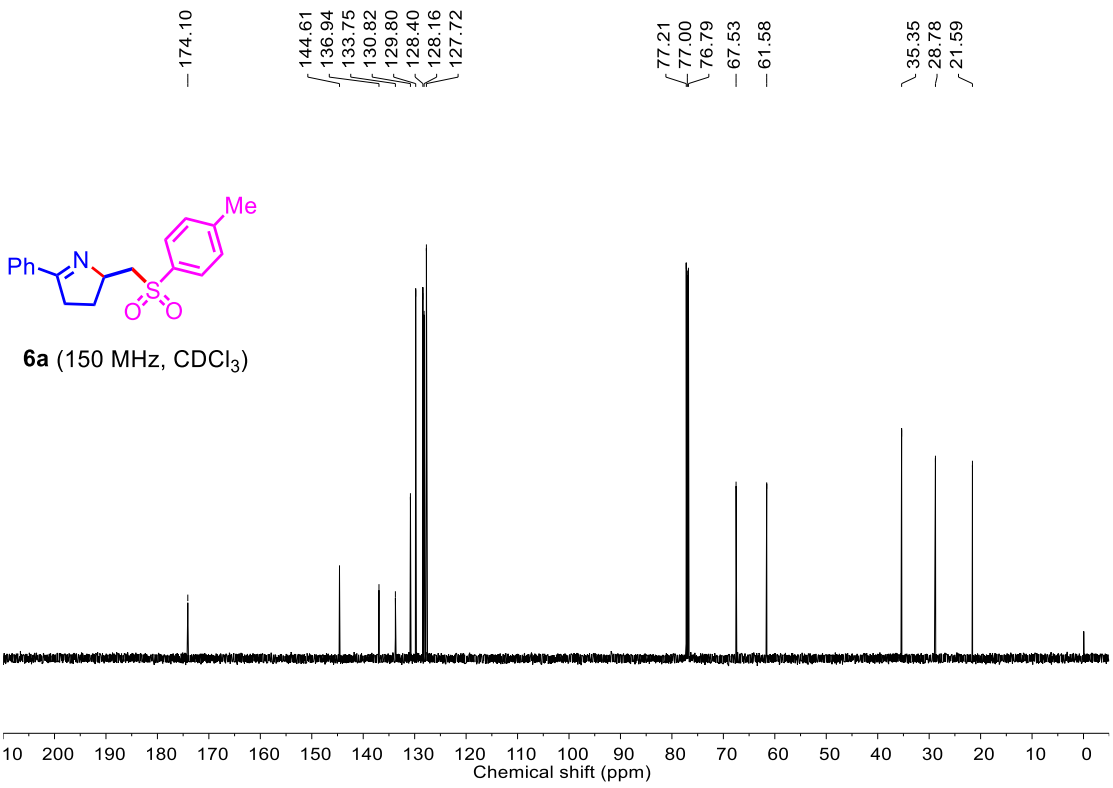

-63.316
O
O
S
O
F3C
4p (376 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -1
Chemical shift (ppm)


8.433
8.311
8.289
8.148
8.126
8.036
8.014
7.979
7.959
7.940
7.863
7.858
7.841
7.836
7.733
7.731
7.715
7.713
7.696
7.693
7.672
7.651
7.634
7.263
4.850
0.000
O2N
4q (400 MHz, CDCl3)
0.90
1.84
1.96
1.03
1.99
0.97
0.98
0.99
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)

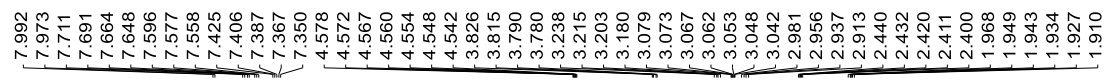

186.86
150.82
139.95
135.63
135.16
131.98
130.71
130.43
129.87
129.82
129.57
128.08
128.01
123.96
122.64
77.21
77.00
76.79
64.11
O2N
4q (150 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

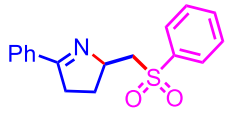



**6a** (400 MHz, $CDCl_3$)

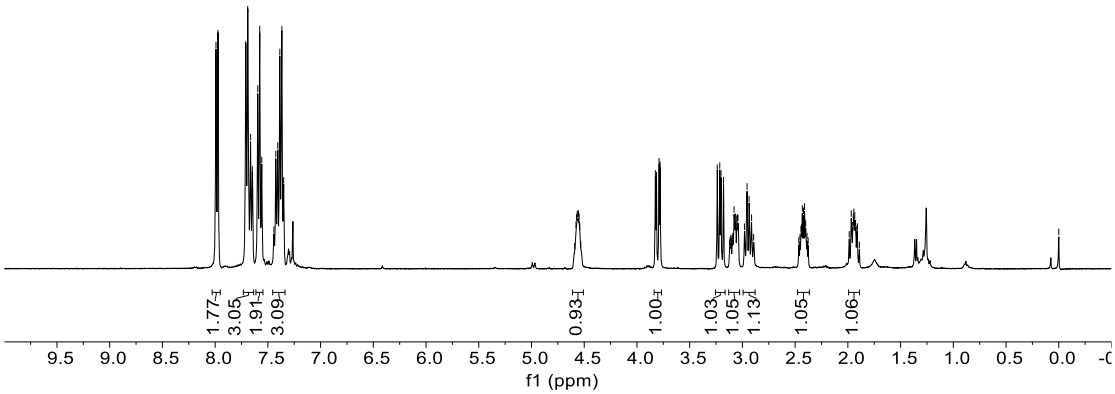


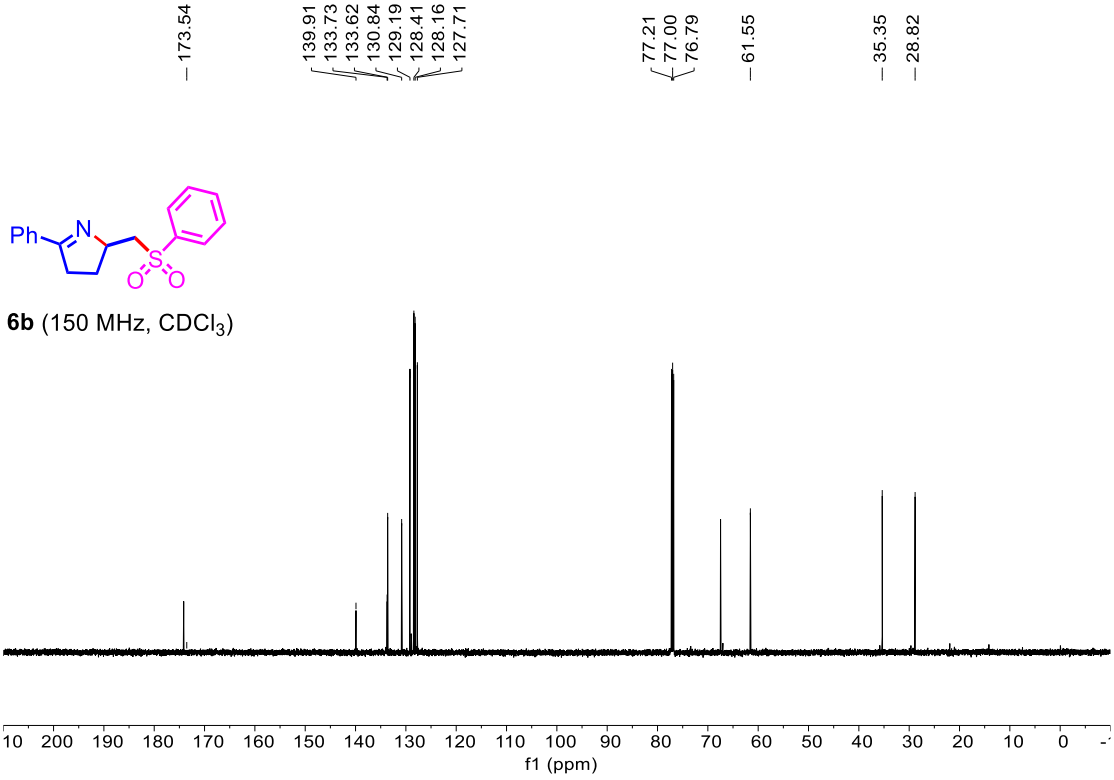

**6a** (150 MHz, $CDCl_3$)



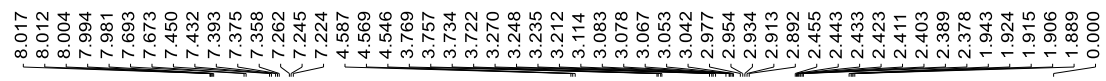



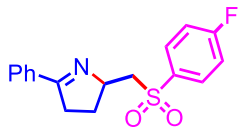

**6b** (400 MHz, $CDCl_3$)



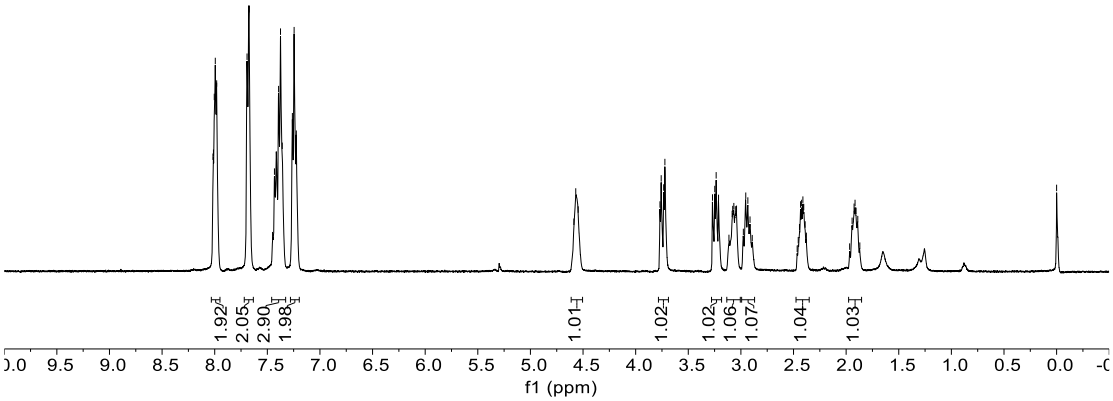



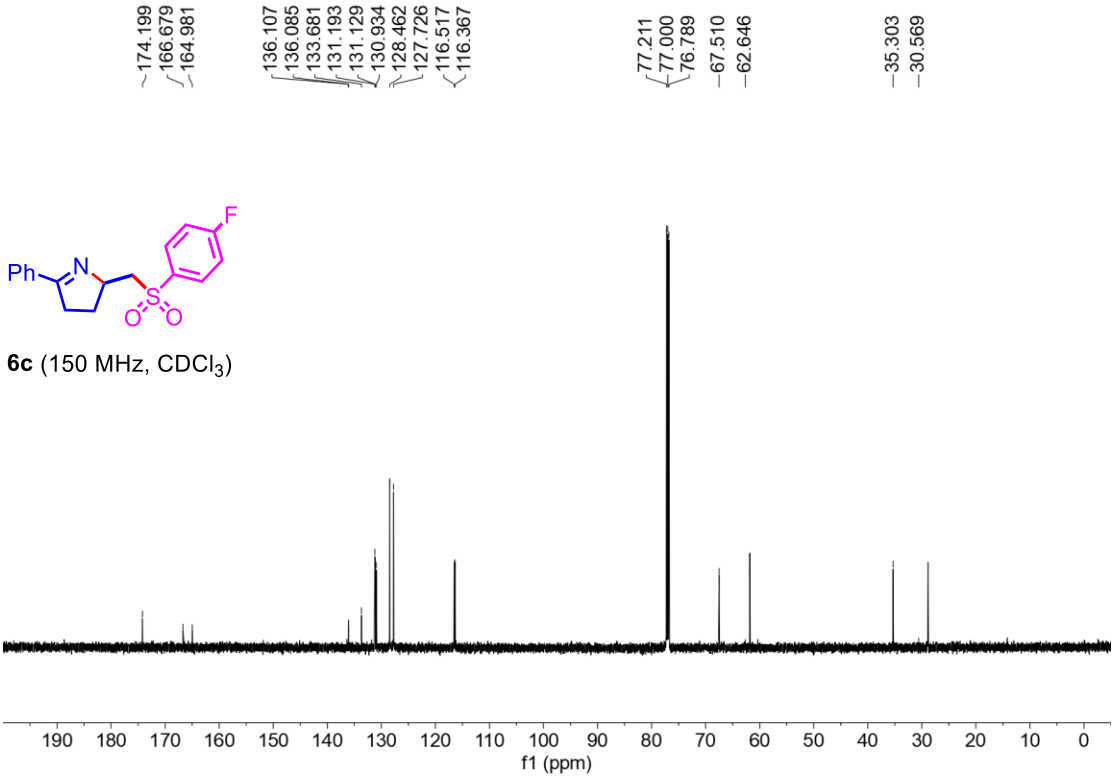

**6b** (150 MHz, $CDCl_3$)




**6c** (400 MHz, $CDCl_3$)

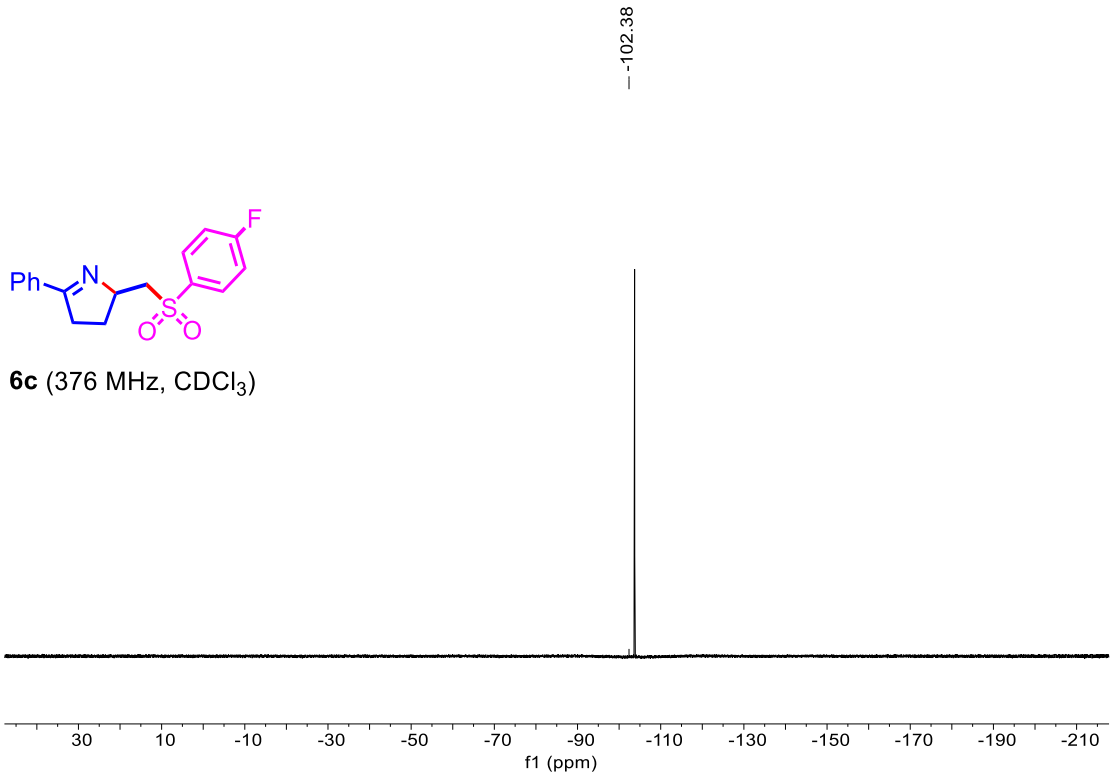


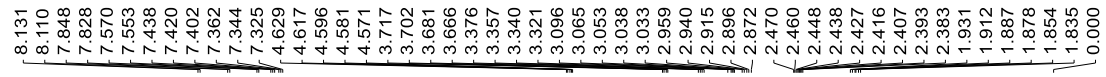


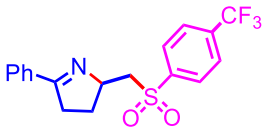


**6c** (150 MHz, $CDCl_3$)

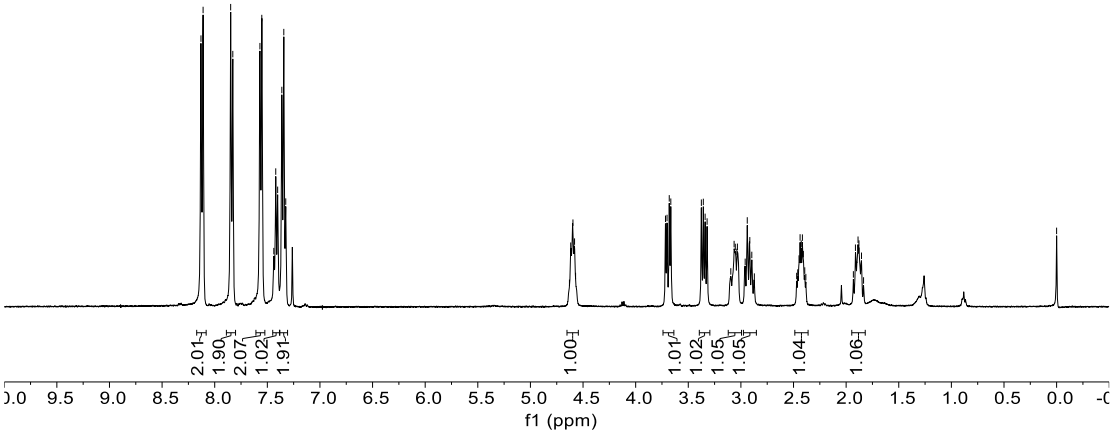


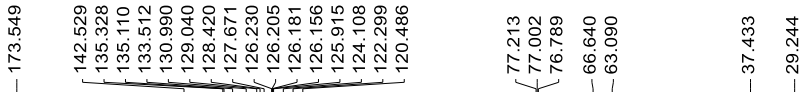

**6c** (376 MHz, $CDCl_3$)

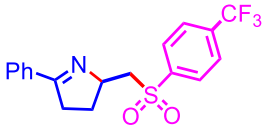


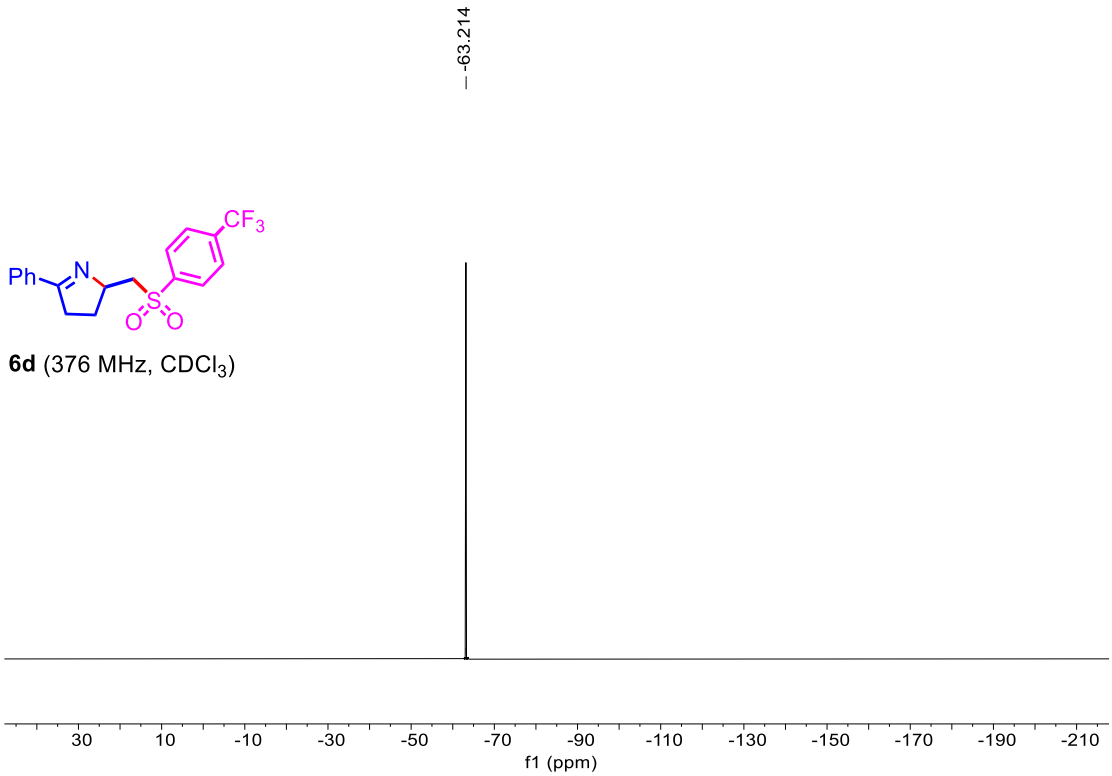

**6d** (400 MHz, $CDCl_3$)



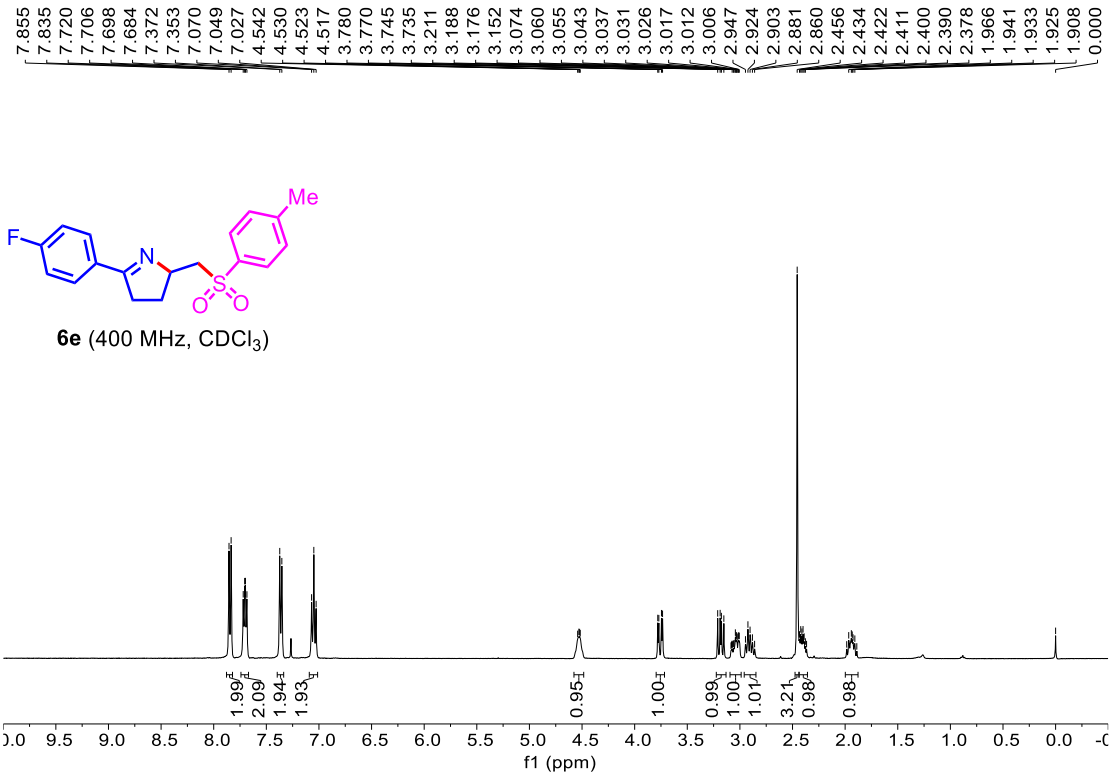



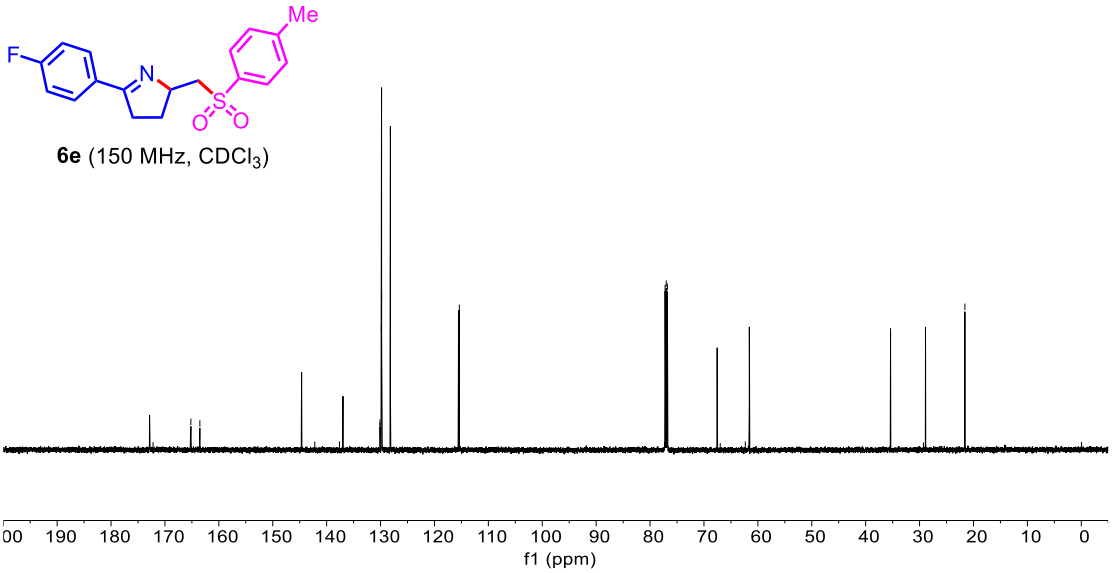

**6d** (150 MHz, $CDCl_3$)



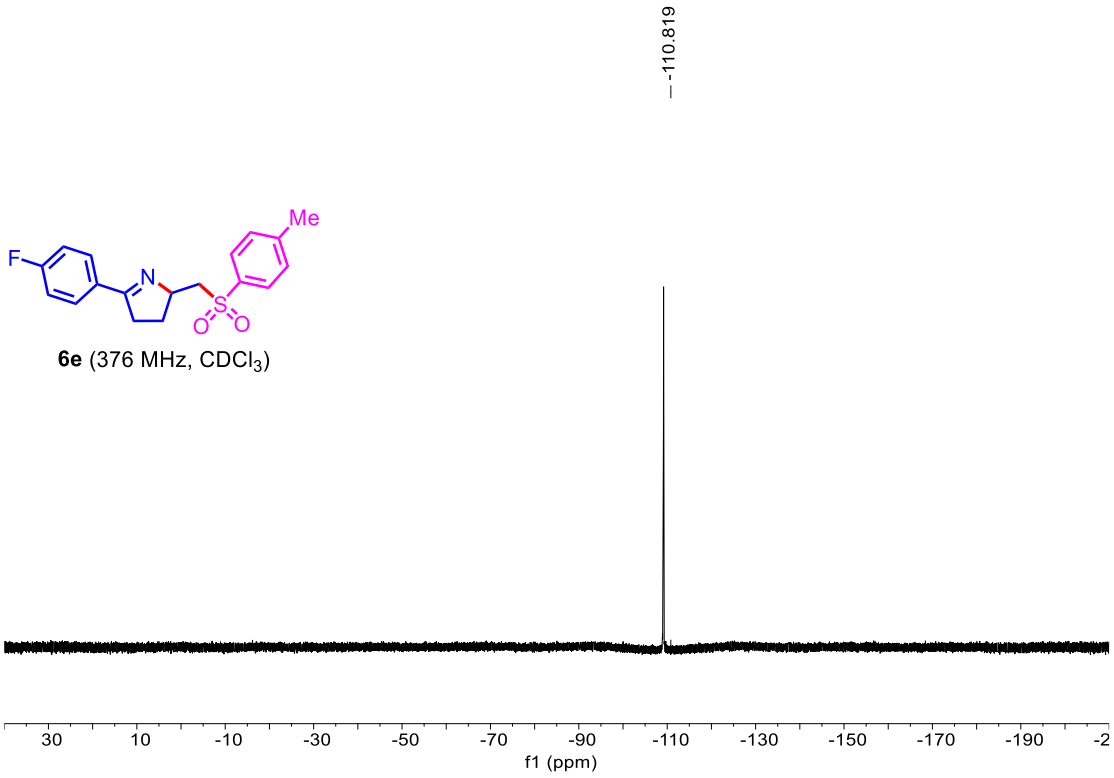

**6d** (376 MHz, $CDCl_3$)



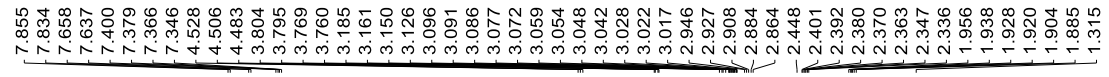

**6e** (400 MHz, $CDCl_3$)

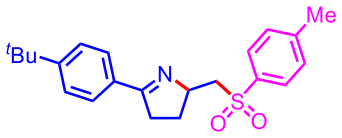



**6e** (150 MHz, $CDCl_3$)

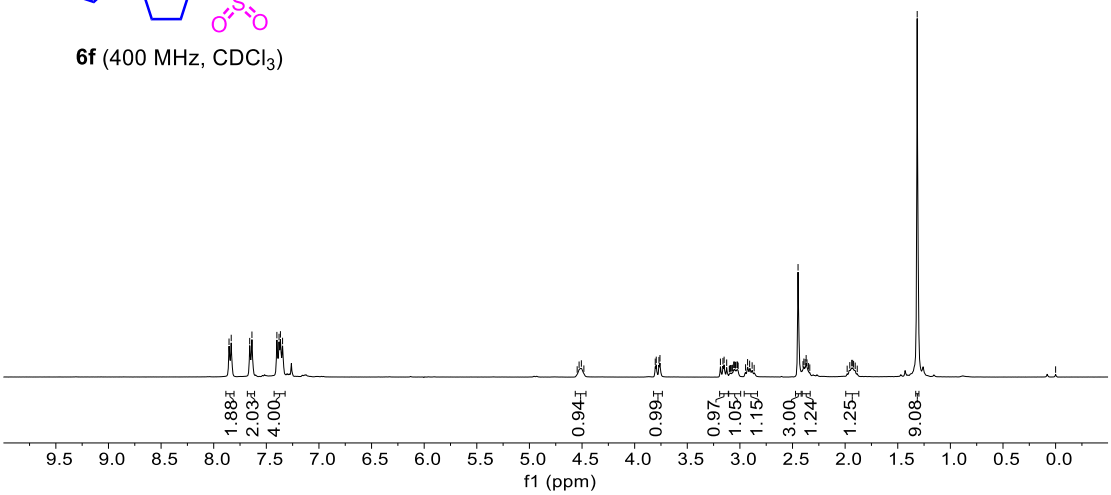



**6e** (376 MHz, $CDCl_3$)

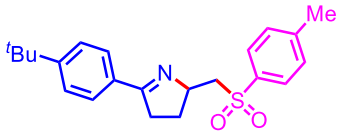


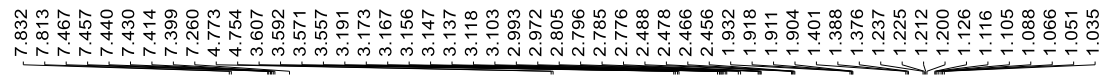

**6f** (400 MHz, $CDCl_3$)

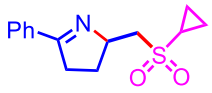




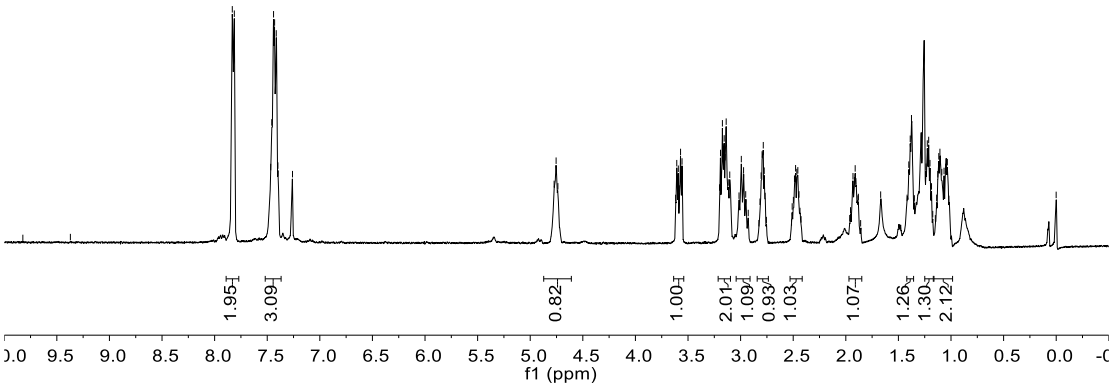


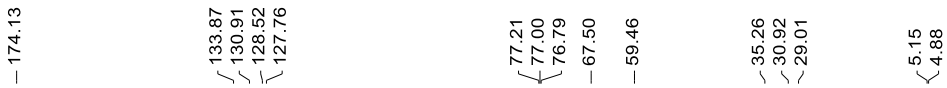

**6f** (150 MHz, $CDCl_3$)

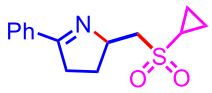


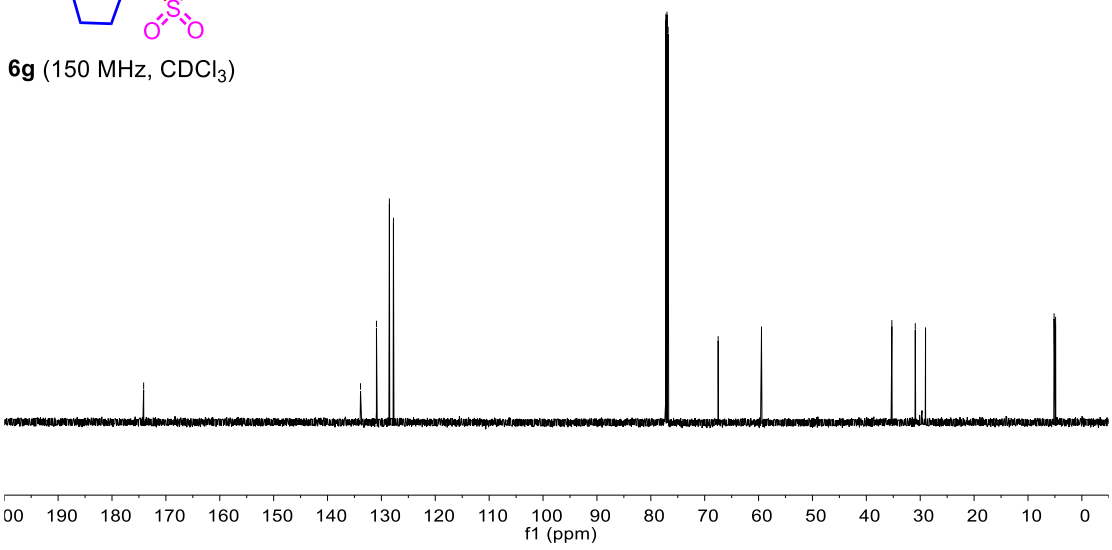

**6g** (400 MHz, $CDCl_3$)

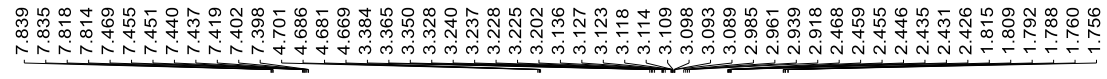


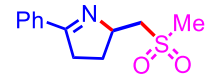




**6g** (150 MHz, $CDCl_3$)



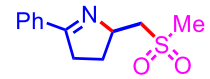


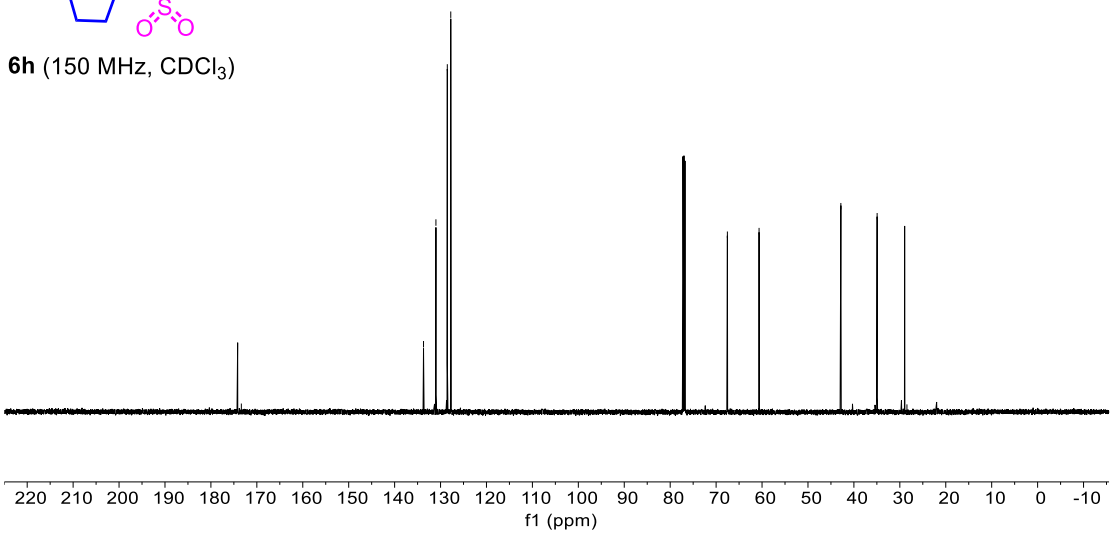

**6h** (400 MHz, $CDCl_3$)

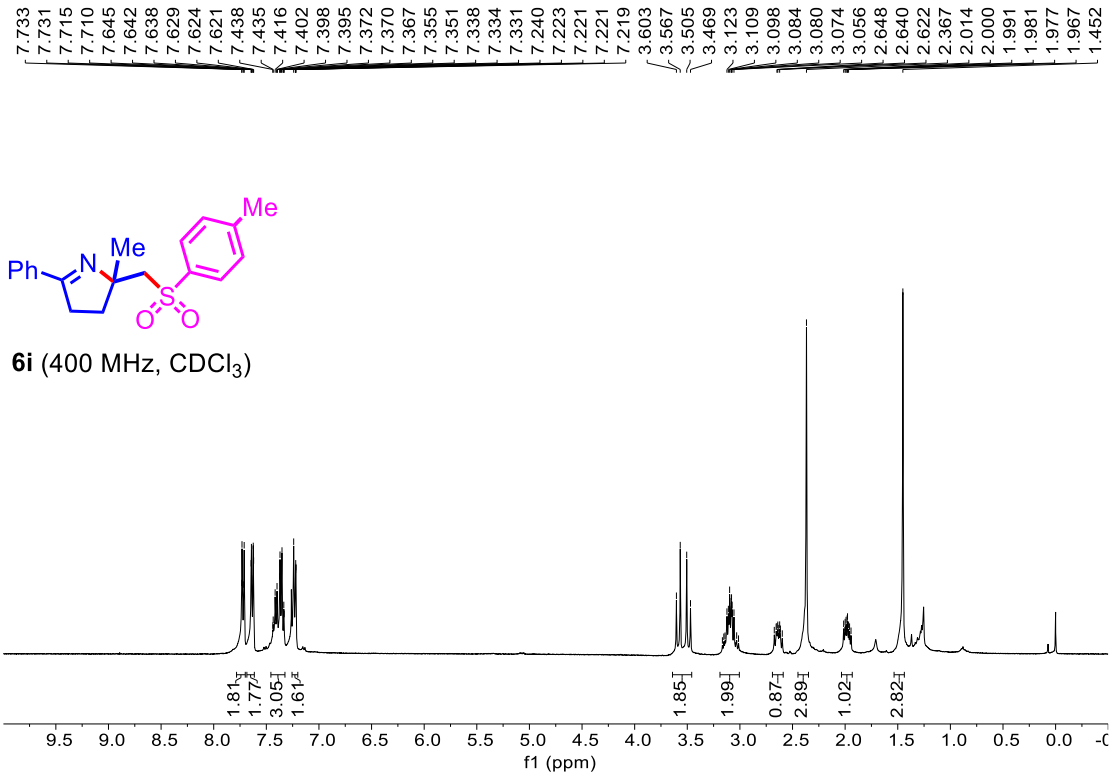


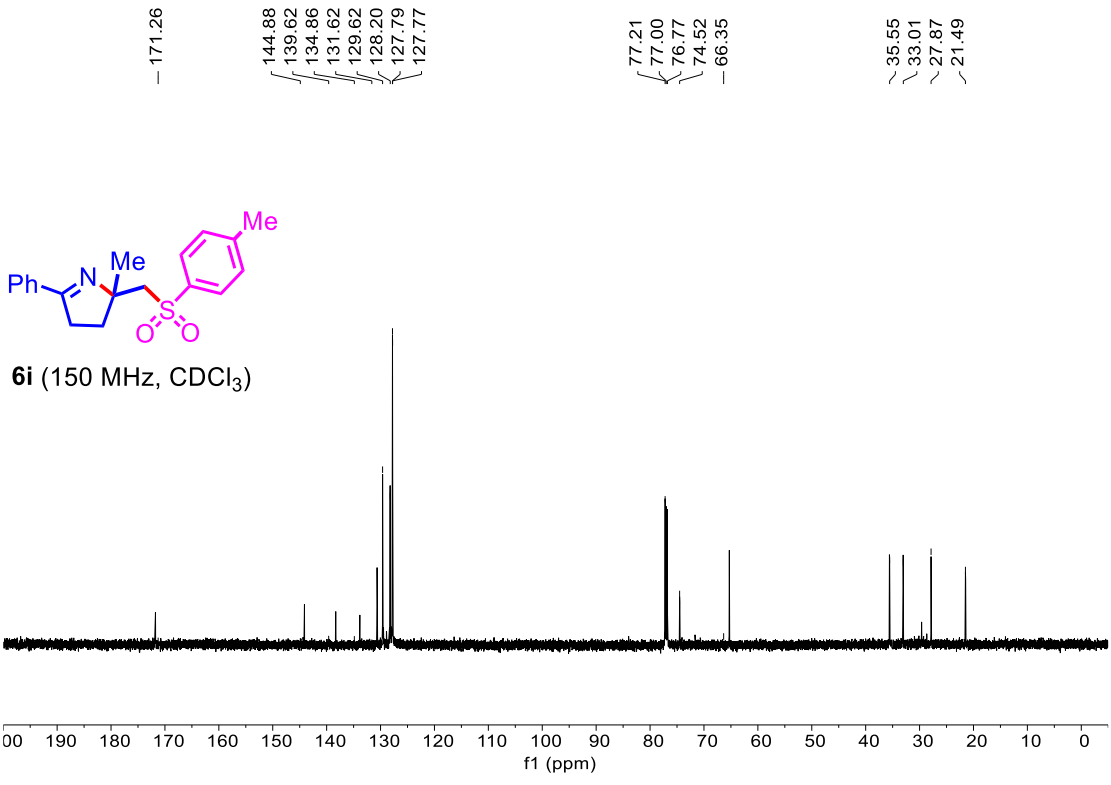


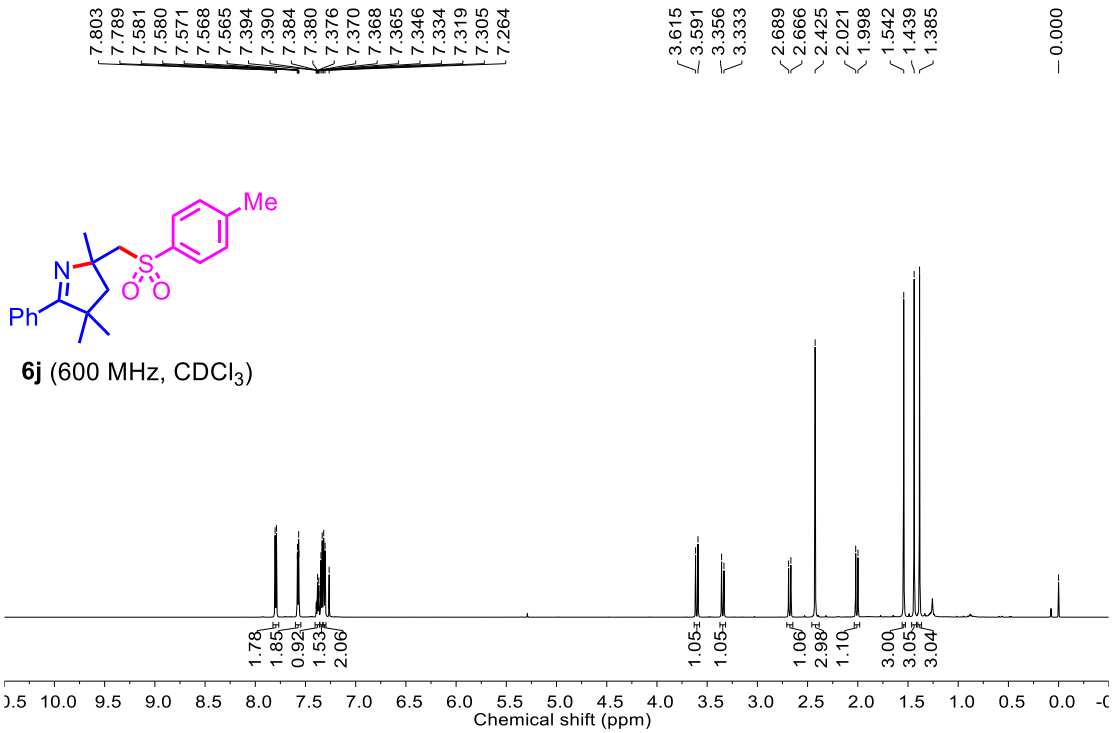



**6h** (150 MHz, $CDCl_3$)

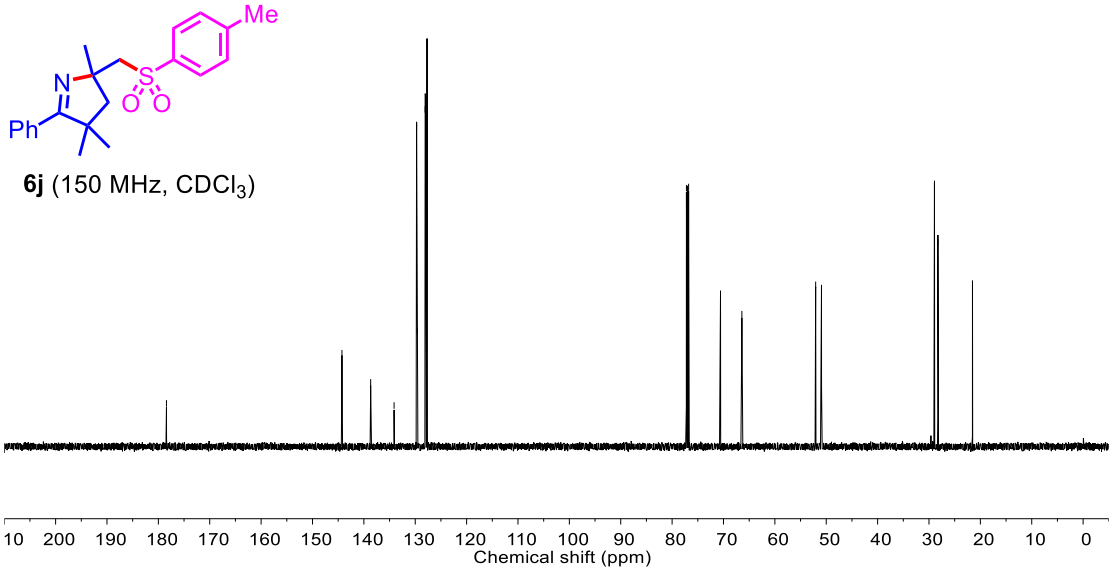



7.733
7.731
7.715
7.710
7.645
7.642
7.638
7.629
7.624
7.621
7.438
7.435
7.416
7.402
7.398
7.395
7.372
7.370
7.367
7.355
7.351
7.338
7.334
7.331
7.240
7.223
7.221
7.221
7.219
3.603
3.567
3.505
3.469
3.123
3.109
3.098
3.084
3.080
3.074
3.056
2.648
2.640
2.622
2.367
2.014
2.000
1.991
1.981
1.977
1.967
1.452
Me
Ph
N
Me
S
O
O
6i (400 MHz, CDCl3)
1.81
1.77
3.05
1.61
1.85
1.99
0.87
2.89
1.02
2.82
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

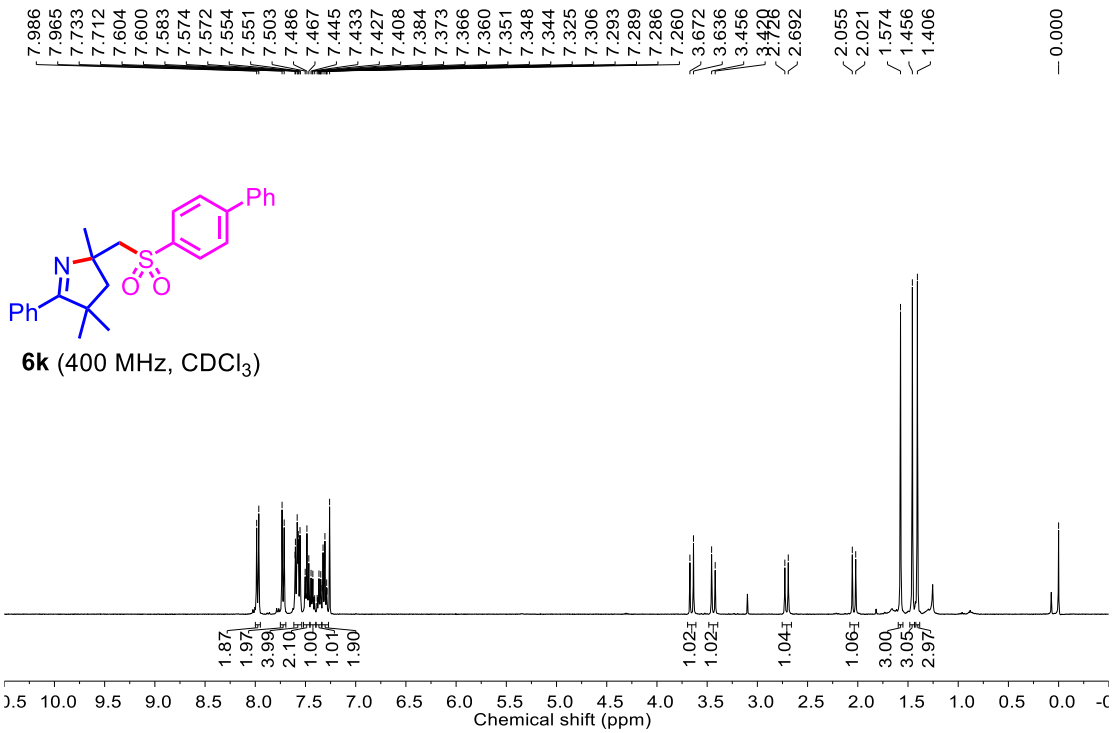

171.26
144.88
139.62
134.86
131.62
129.62
128.20
127.79
127.77
77.21
77.00
76.77
74.52
66.35
35.55
33.01
27.87
21.49
Me
Ph
N
Me
S
O
O
6i (150 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



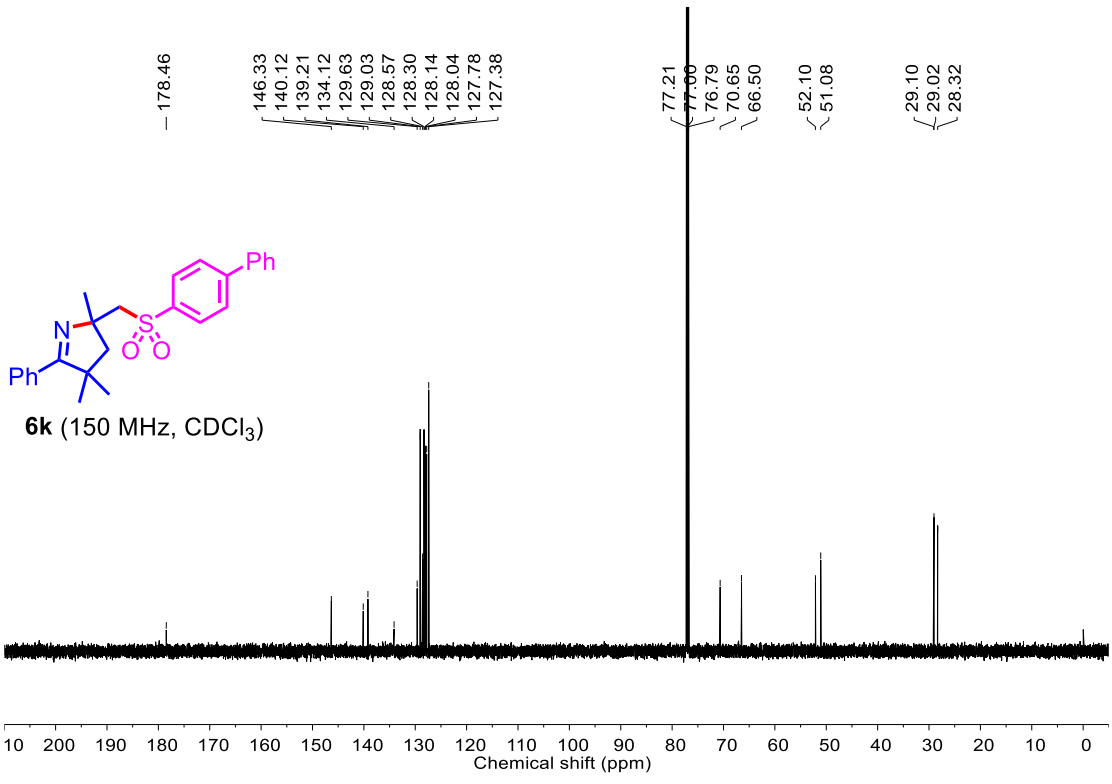

**6j** (600 MHz, $CDCl_3$)



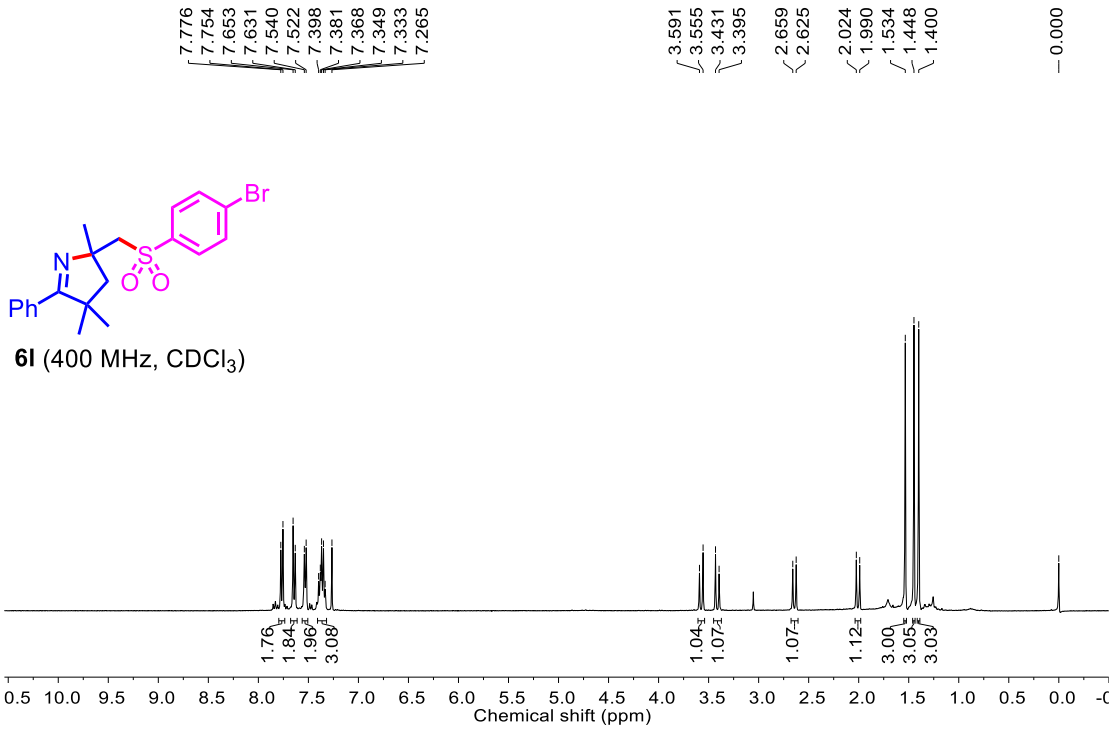

**6j** (150 MHz, $CDCl_3$)



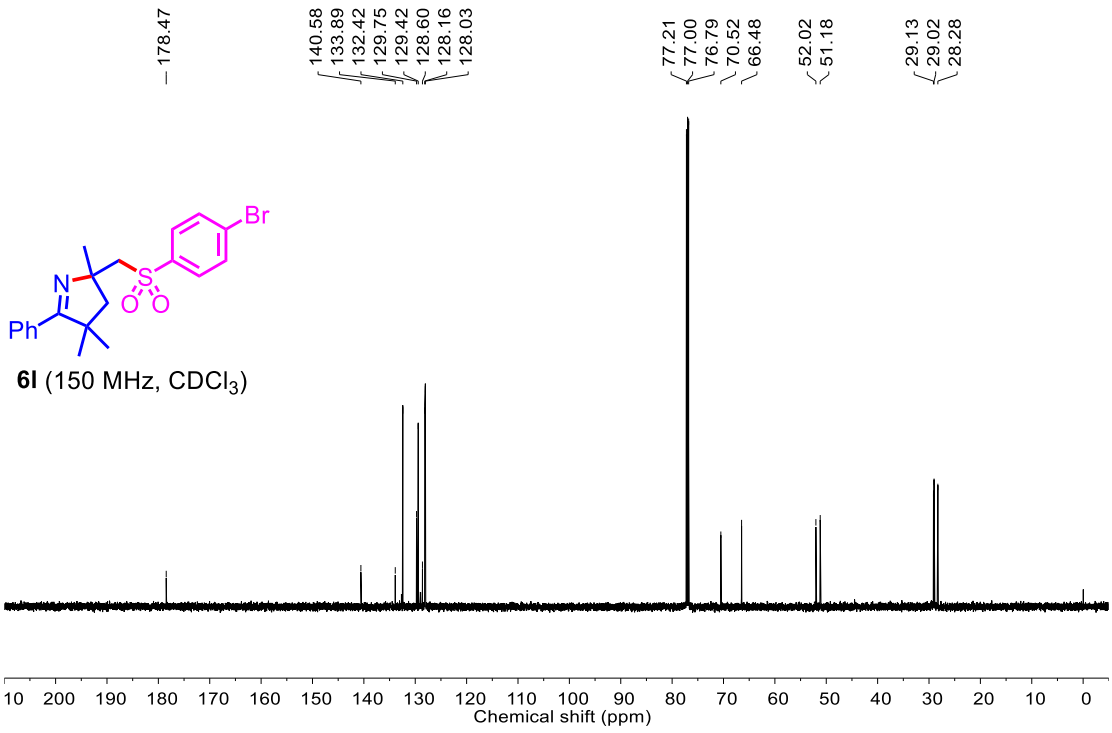

**6k** (400 MHz, $CDCl_3$)



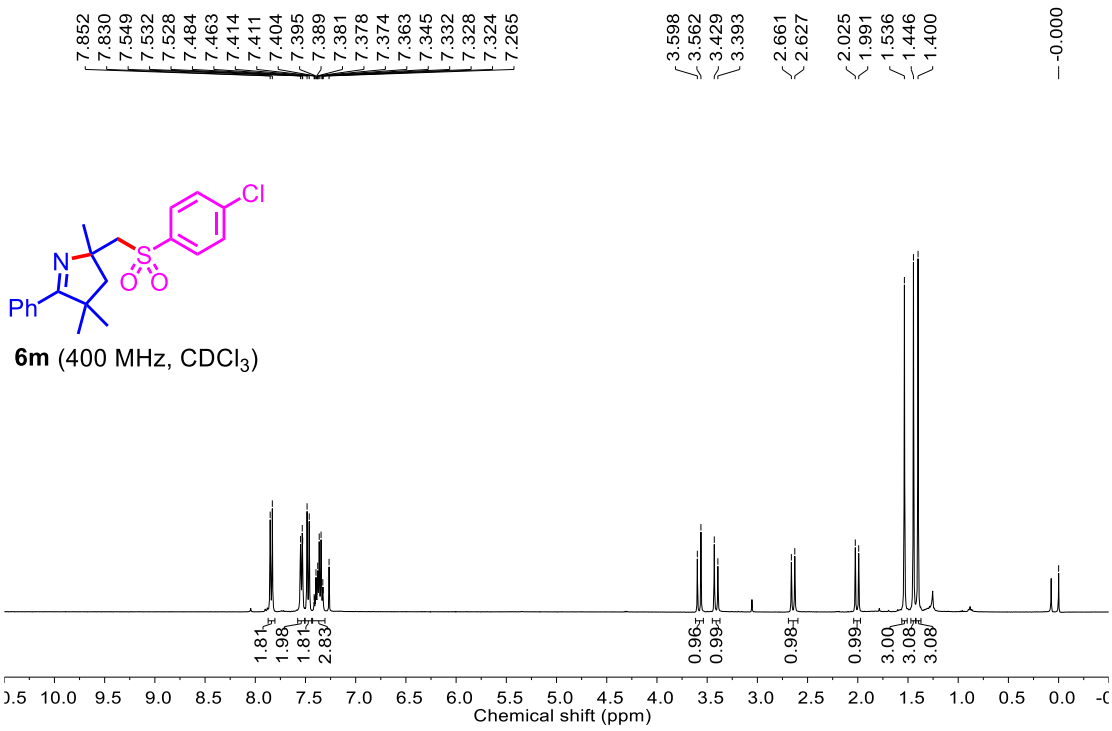

**6k** (150 MHz, $CDCl_3$)



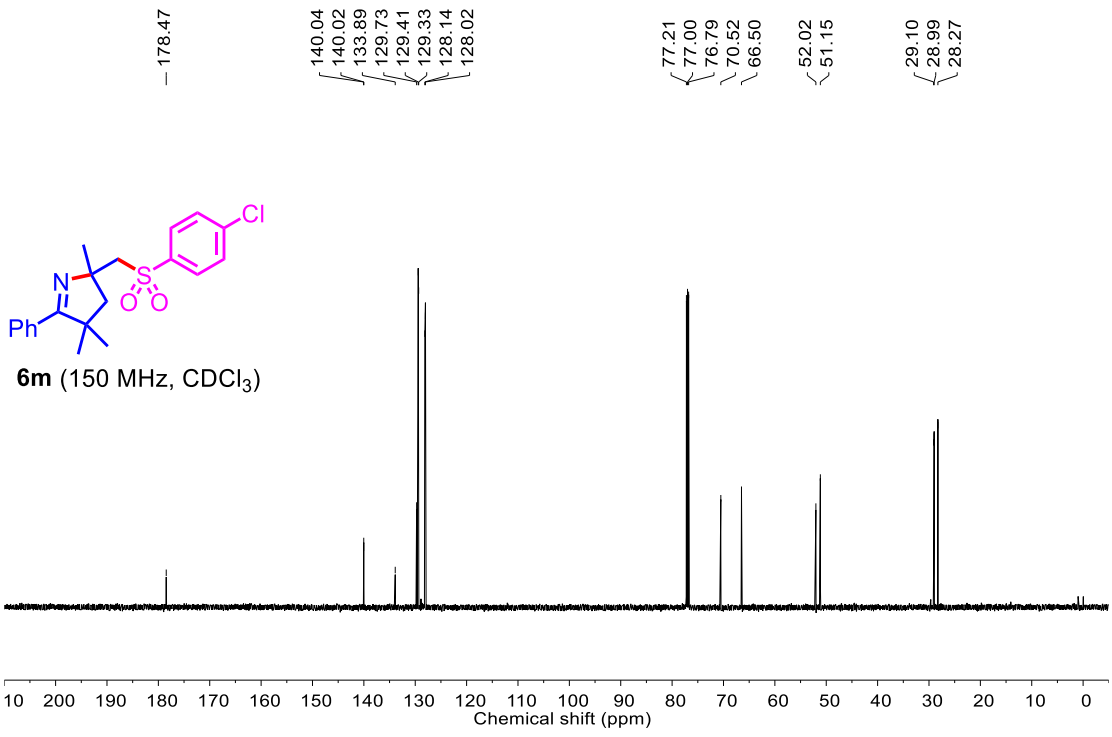

**6l** (400 MHz, $CDCl_3$)



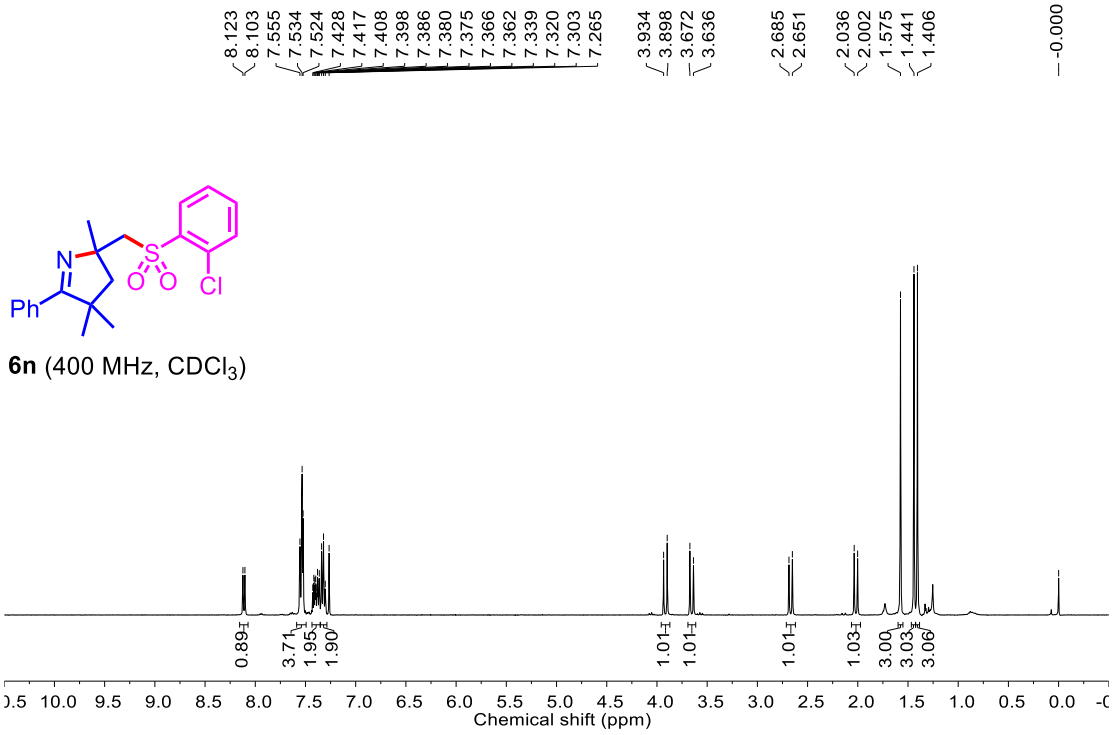

**6l** (150 MHz, $CDCl_3$)



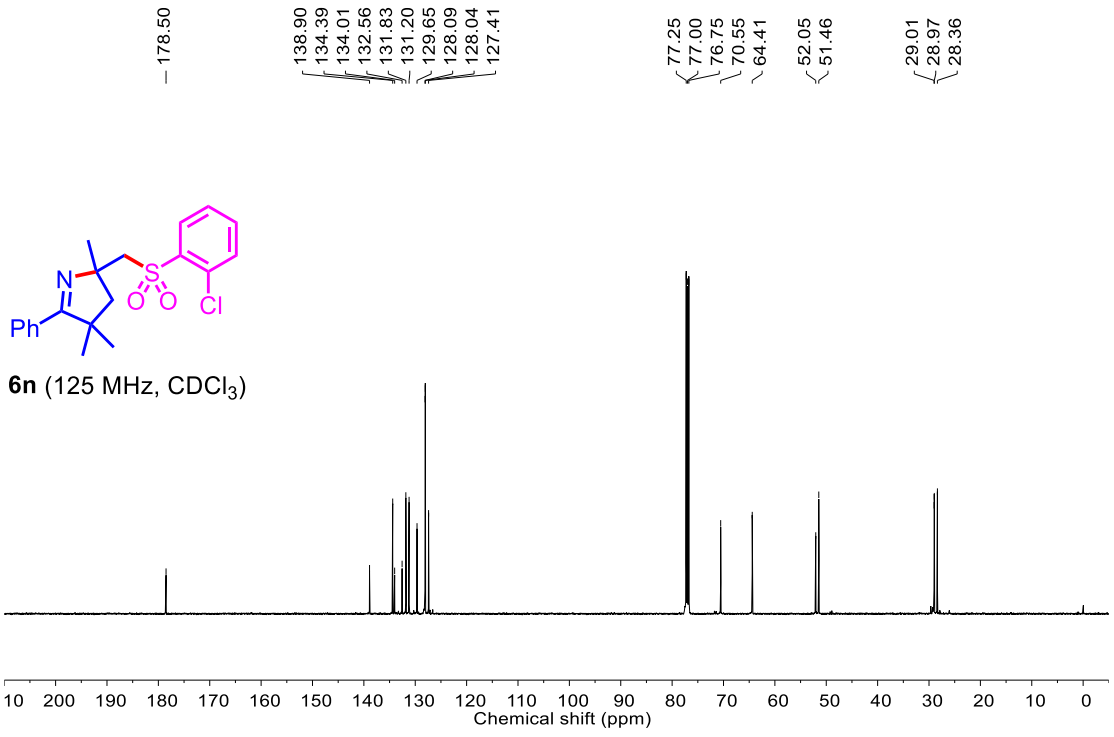

**6m** (400 MHz, $CDCl_3$)



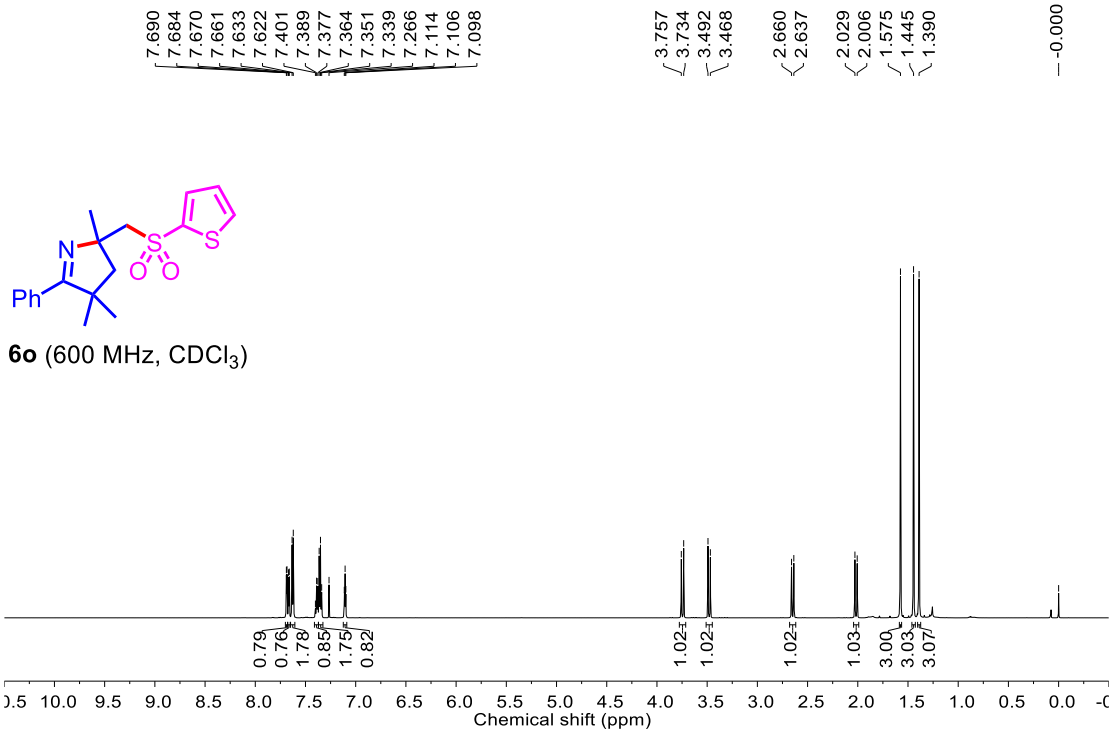

**6m** (150 MHz, $CDCl_3$)



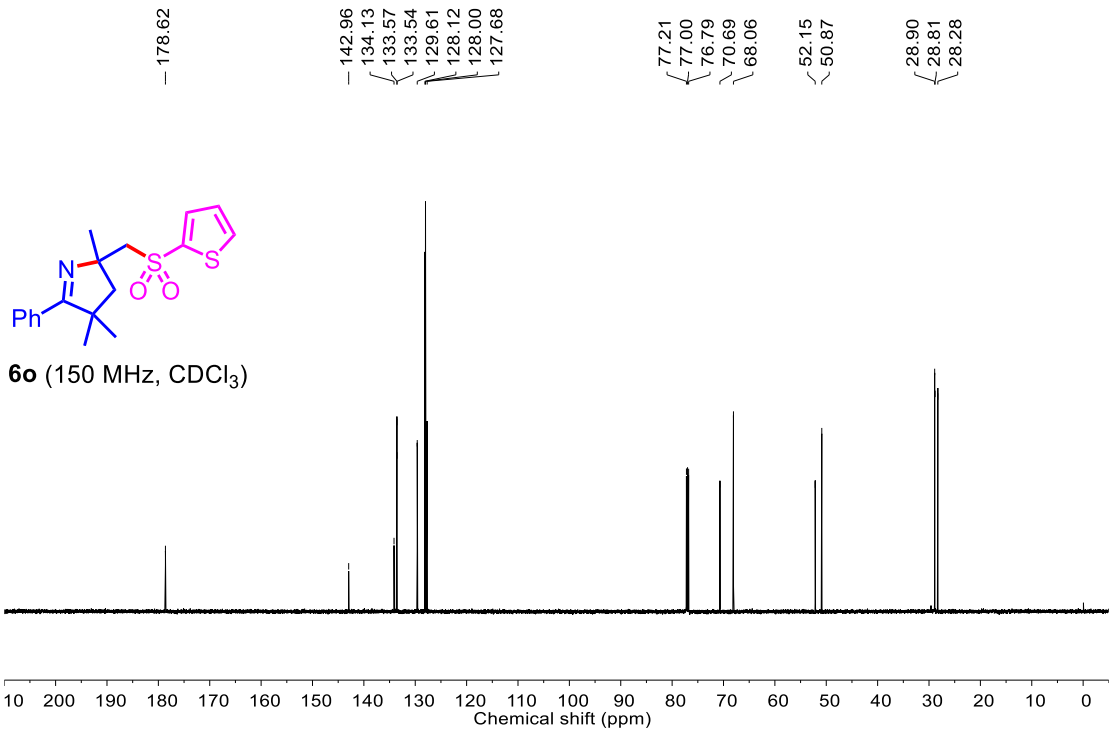

**6n** (400 MHz, $CDCl_3$)



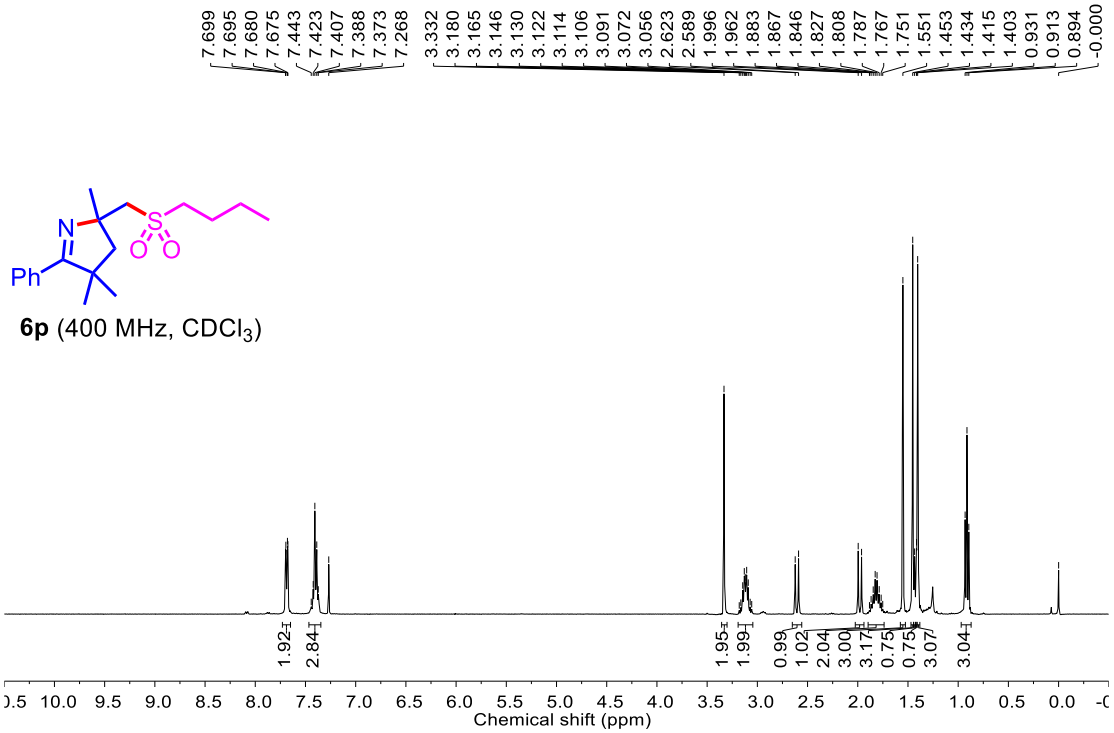

**6n** (125 MHz, $CDCl_3$)

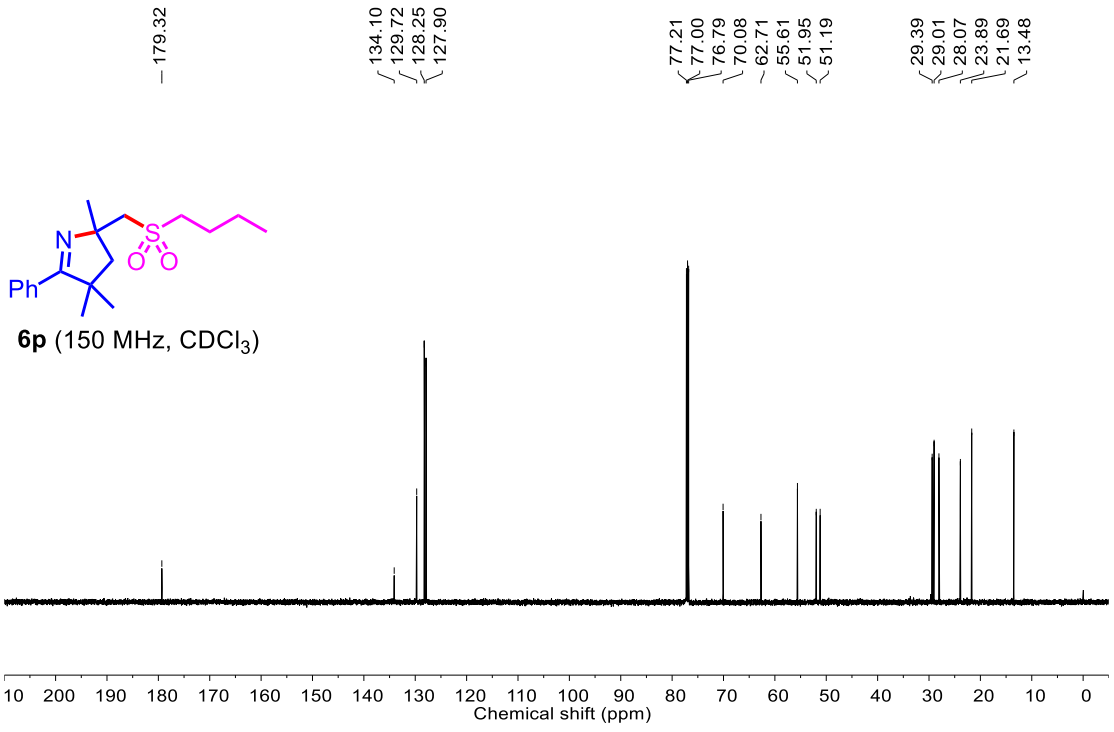


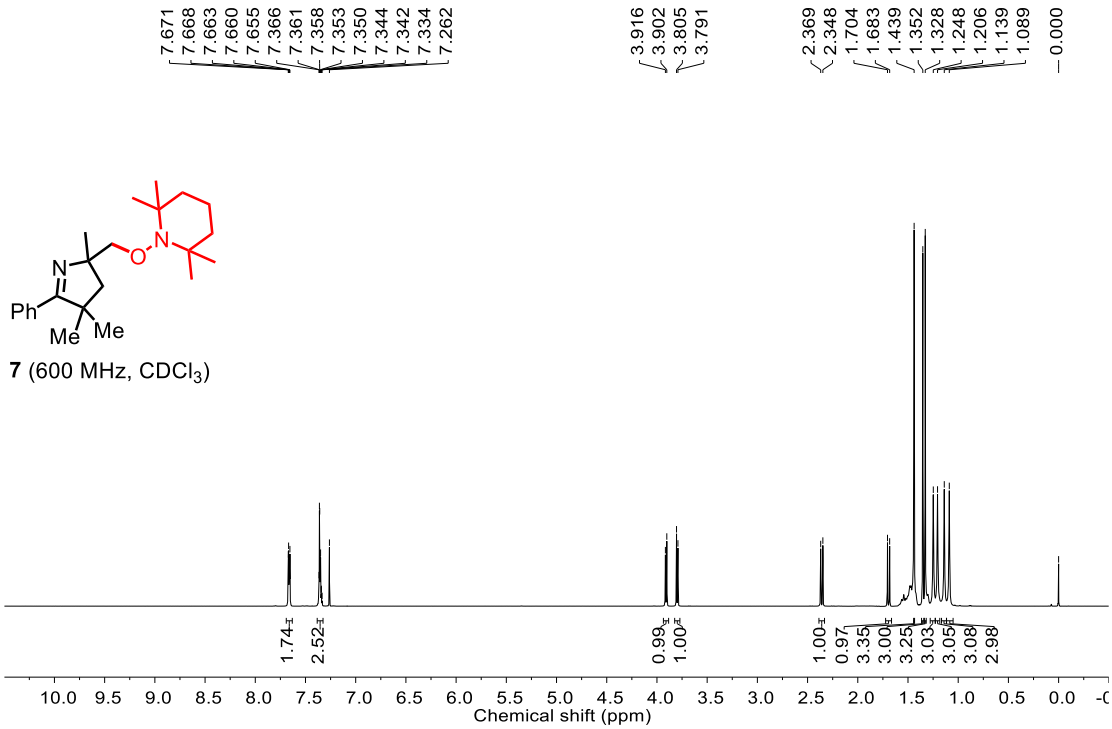

**6o** (600 MHz, $CDCl_3$)



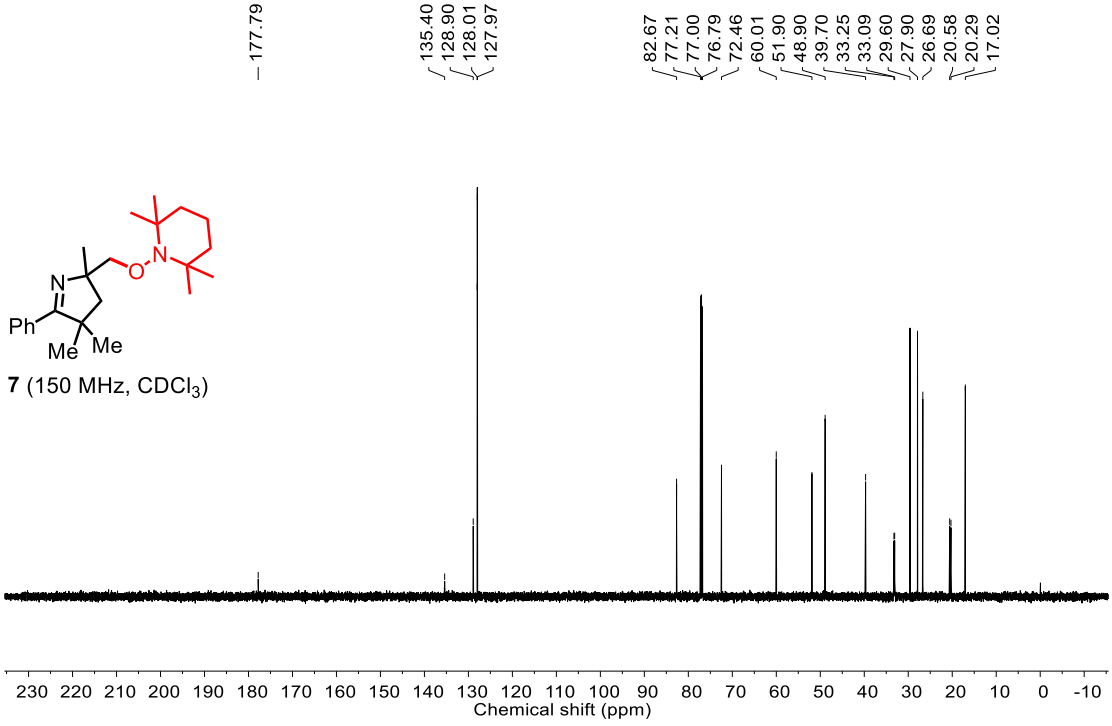

**6o** (150 MHz, $CDCl_3$)


7.699
7.695
7.680
7.675
7.443
7.423
7.407
7.388
7.373
7.268
3.332
3.180
3.165
3.146
3.130
3.122
3.114
3.106
3.091
3.072
3.056
2.623
2.589
1.996
1.962
1.883
1.867
1.846
1.827
1.808
1.787
1.767
1.751
1.551
1.453
1.434
1.415
1.403
0.931
0.913
0.894
-0.000
N
S
O
O
Ph
6p (400 MHz, CDCl3)
1.92
2.84
1.95
1.99
0.99
1.02
2.04
3.00
3.17
0.75
0.75
3.07
3.04
Chemical shift (ppm)

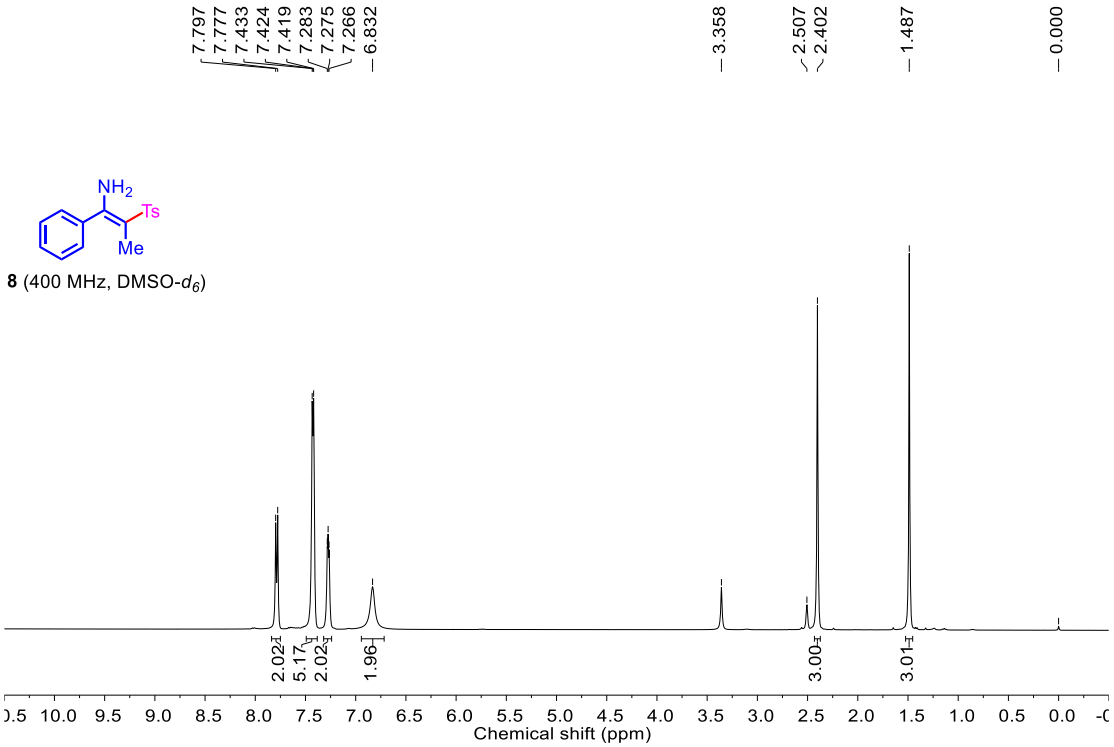

179.32
134.10
129.72
128.25
127.90
77.21
77.00
76.79
70.08
62.71
55.61
51.95
51.19
29.39
29.01
28.07
23.89
21.69
13.48
N
S
O
O
Ph
6p (150 MHz, CDCl3)
Chemical shift (ppm)



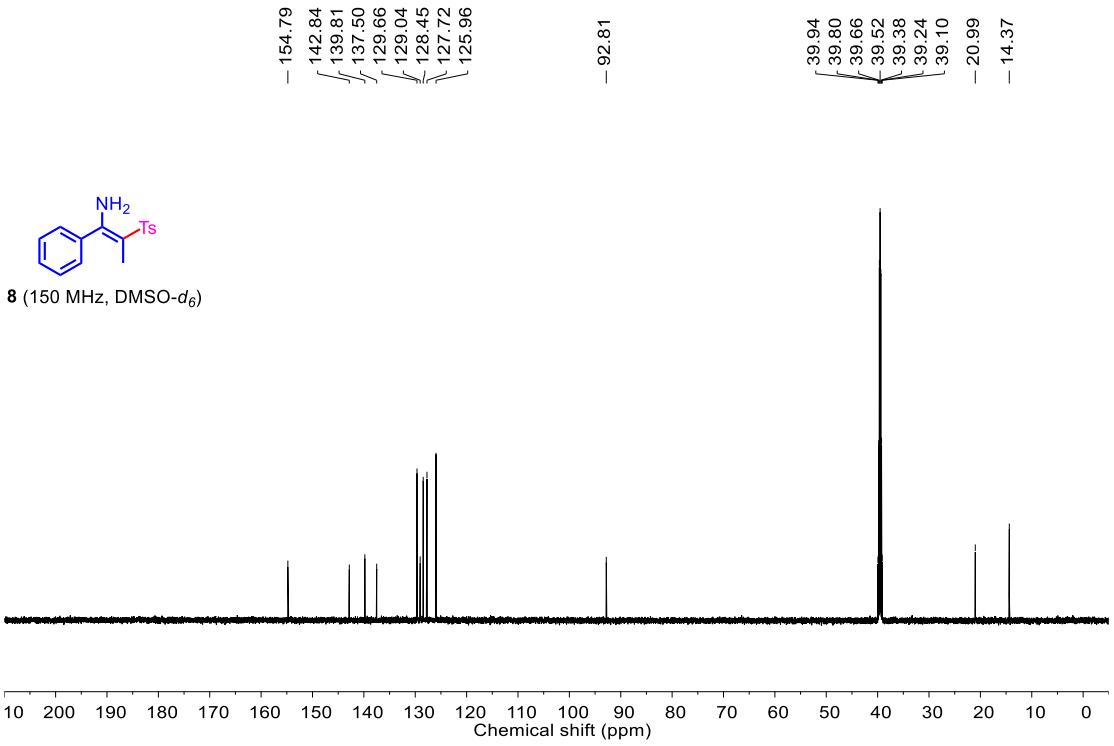

**7** (600 MHz, $CDCl_3$)



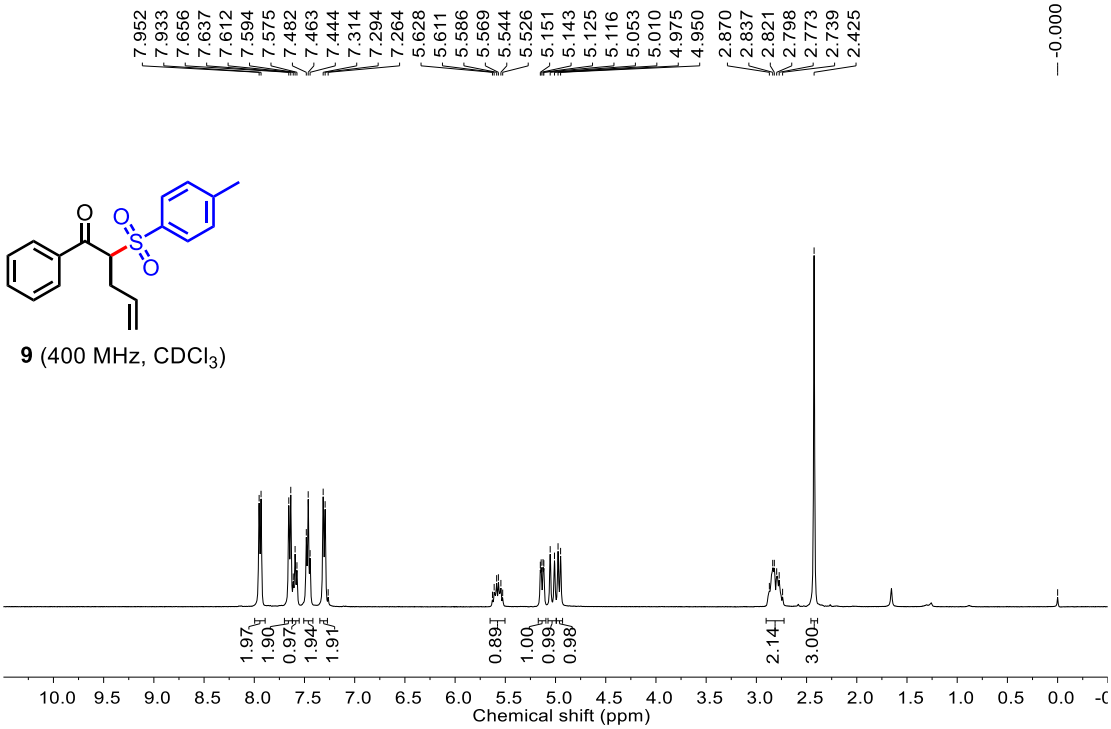

**7** (150 MHz, $CDCl_3$)

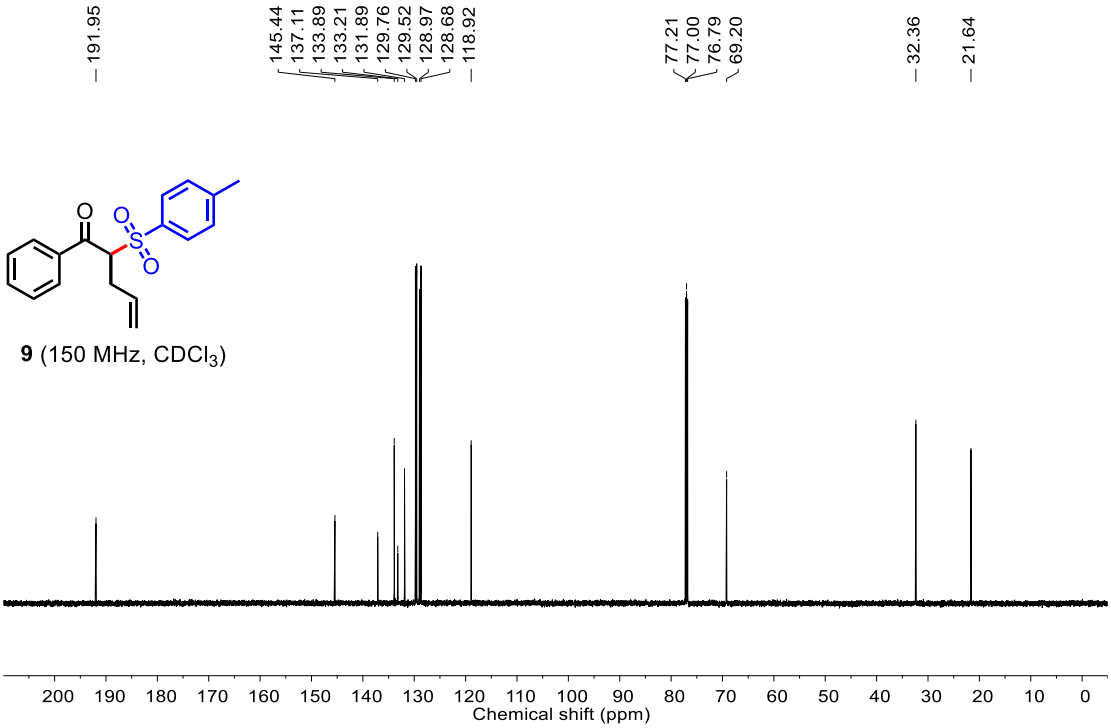


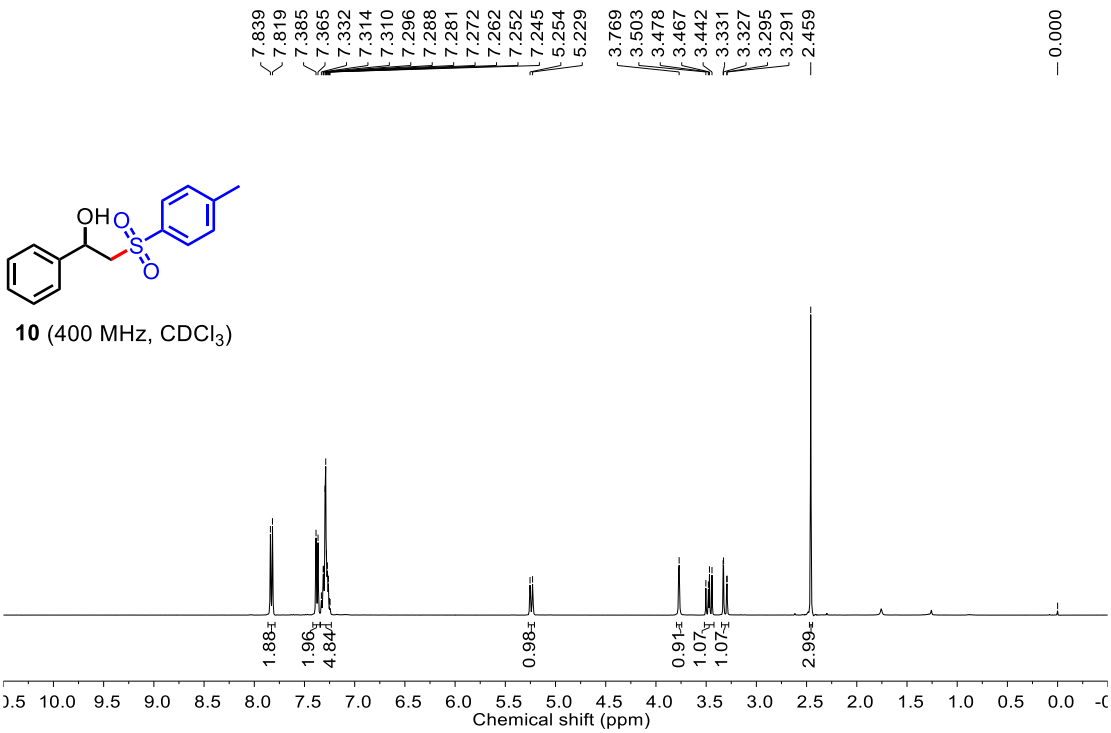

**8** (400 MHz, DMSO-$d_6$)



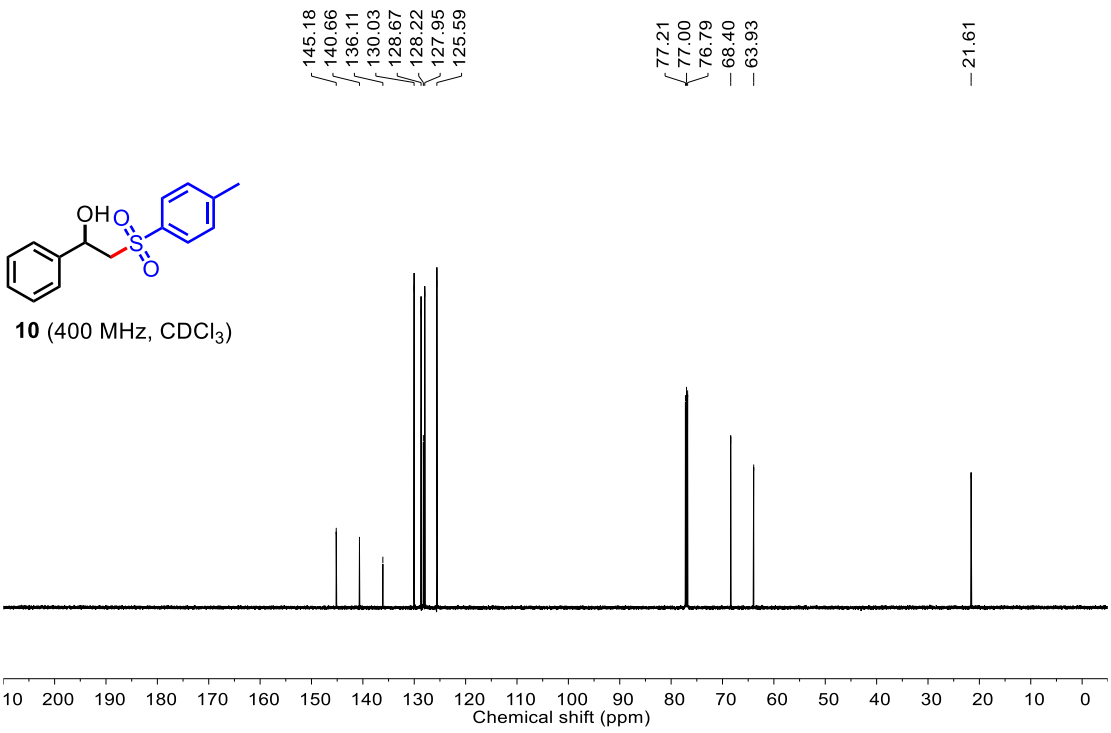

**8** (150 MHz, DMSO-$d_6$)


7.952
7.933
7.656
7.637
7.612
7.594
7.575
7.482
7.463
7.444
7.314
7.294
7.264
5.628
5.611
5.586
5.569
5.544
5.526
5.151
5.143
5.125
5.116
5.053
5.010
4.975
4.950
2.870
2.837
2.821
2.798
2.773
2.739
2.425
-0.000
9 (400 MHz, CDCl3)
1.97
1.90
0.97
1.94
1.91
0.89
1.00
0.99
0.98
2.14
3.00
Chemical shift (ppm)

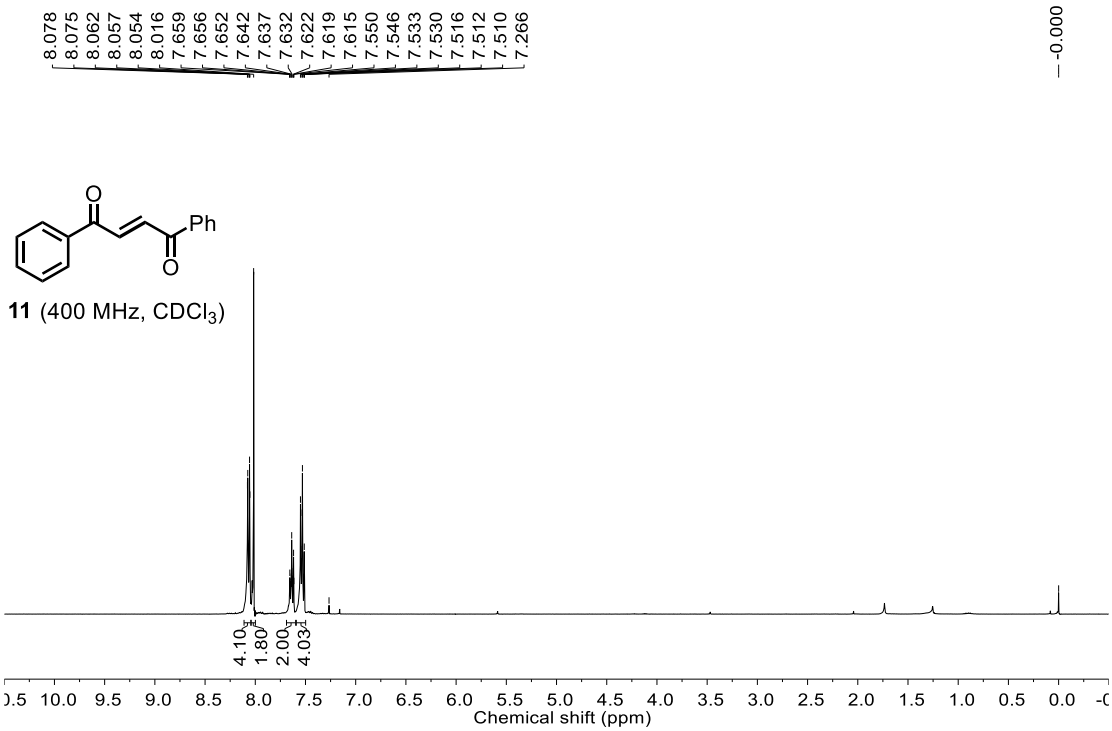

191.95
145.44
137.11
133.89
133.21
131.89
129.76
129.52
128.97
128.68
118.92
77.21
77.00
76.79
69.20
32.36
21.64
9 (150 MHz, CDCl3)
Chemical shift (ppm)

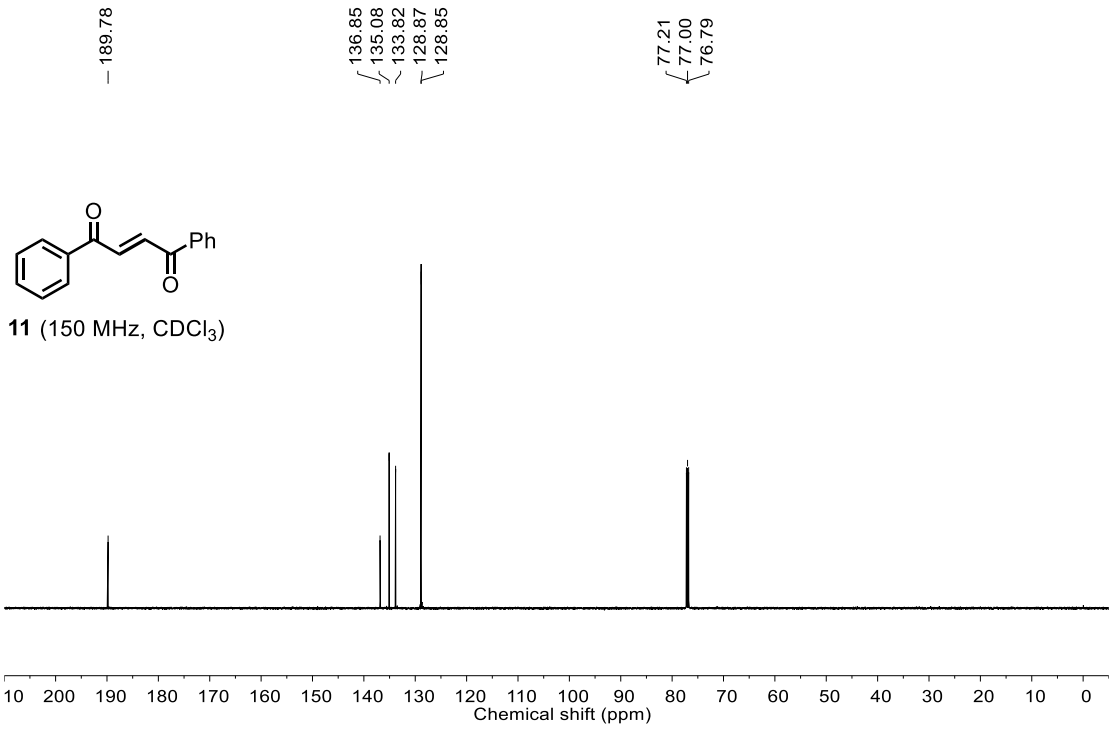


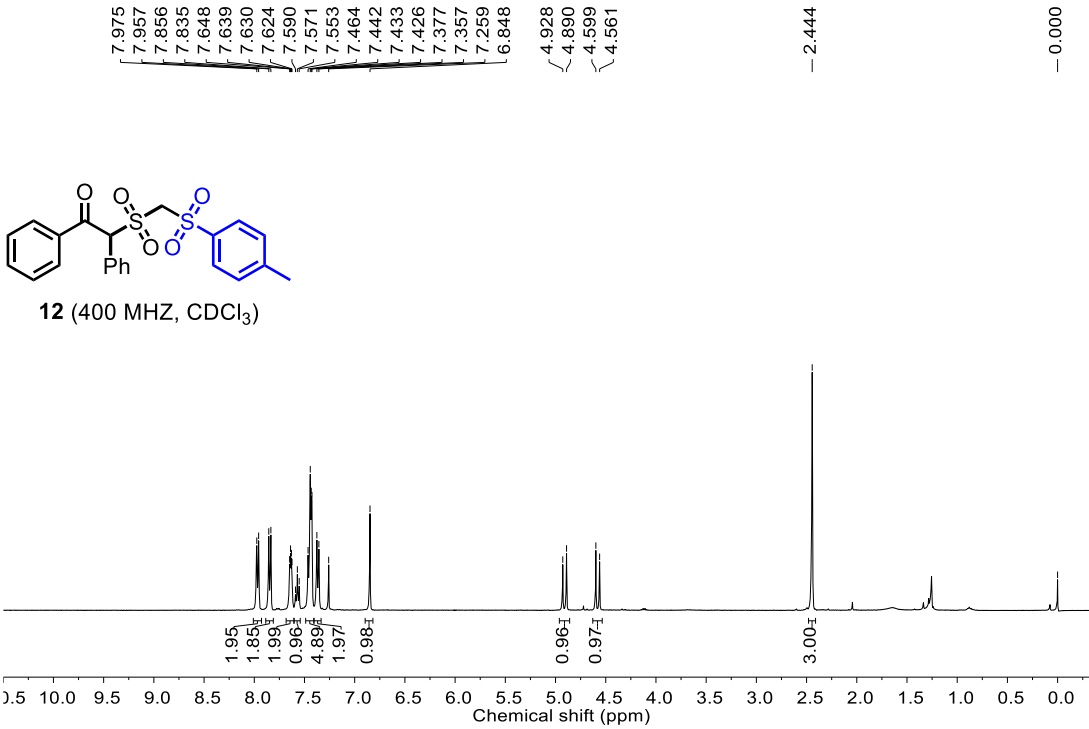

**10** (400 MHz, $CDCl_3$)



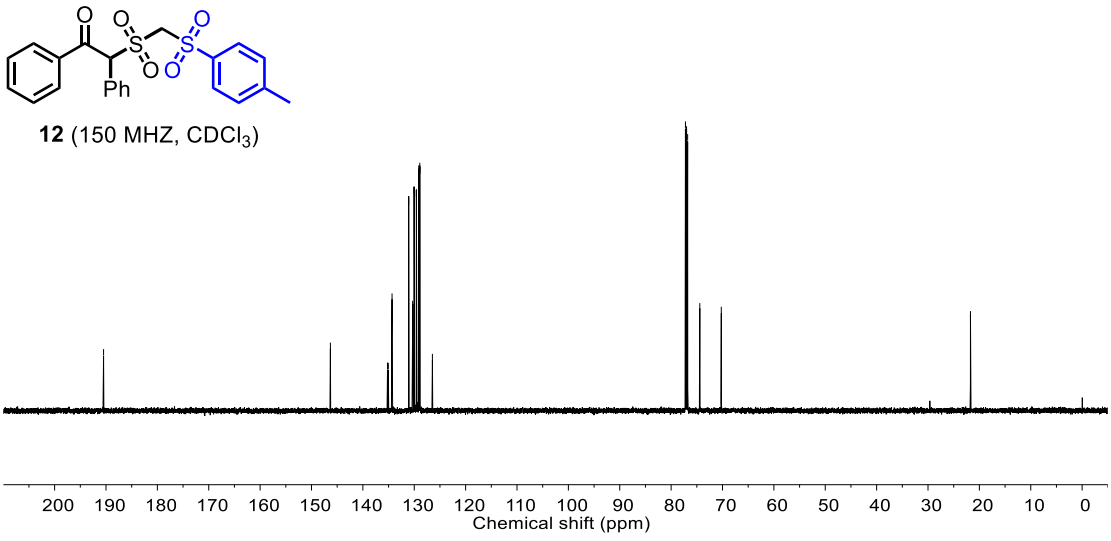

**10** (400 MHz, $CDCl_3$)


8.078
8.075
8.062
8.057
8.054
8.016
7.659
7.656
7.652
7.642
7.637
7.632
7.622
7.619
7.615
7.550
7.546
7.533
7.530
7.516
7.512
7.510
7.266
-0.000
O
Ph
O
11 (400 MHz, CDCl3)
4.10
1.80
2.00
4.03
Chemical shift (ppm)

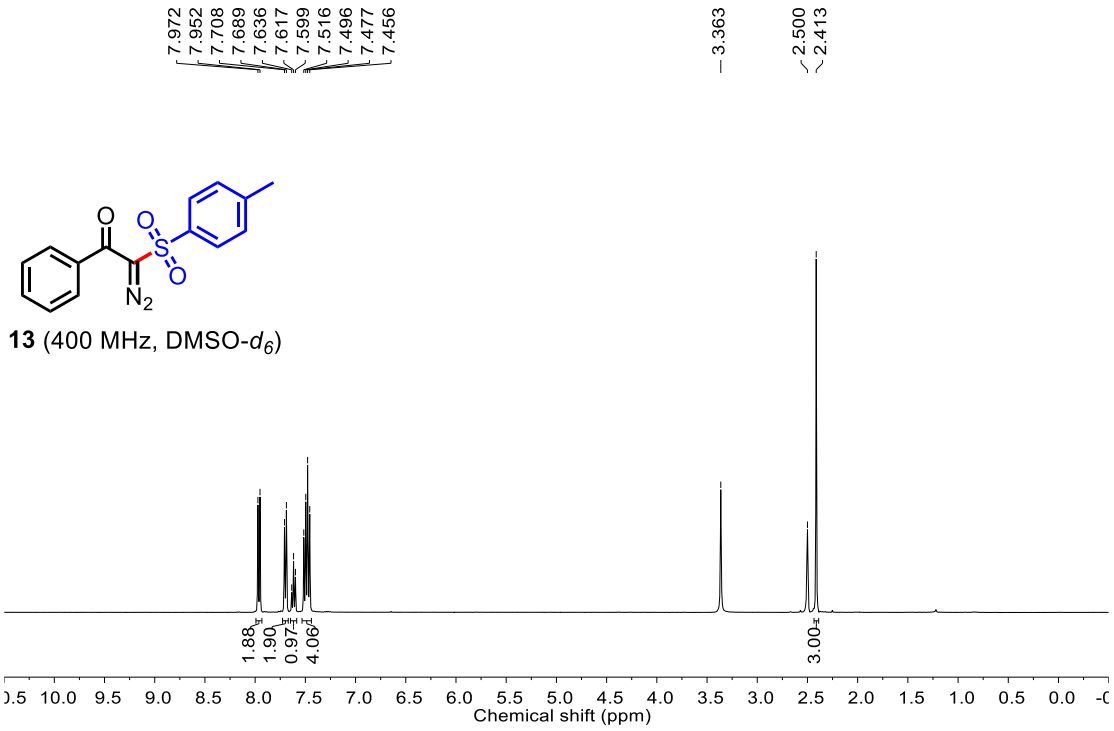

189.78
136.85
135.08
133.82
128.87
128.85
77.21
77.00
76.79
O
Ph
O
11 (150 MHz, CDCl3)
Chemical shift (ppm)



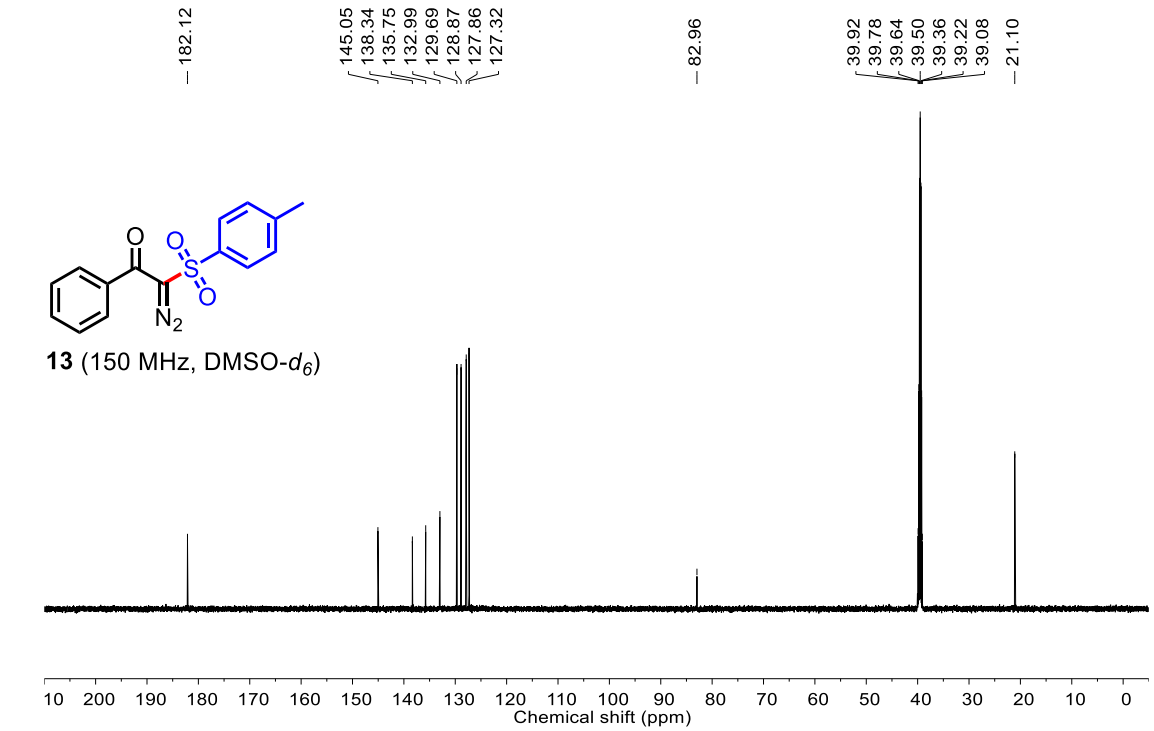

**12** (400 MHZ, $CDCl_3$)



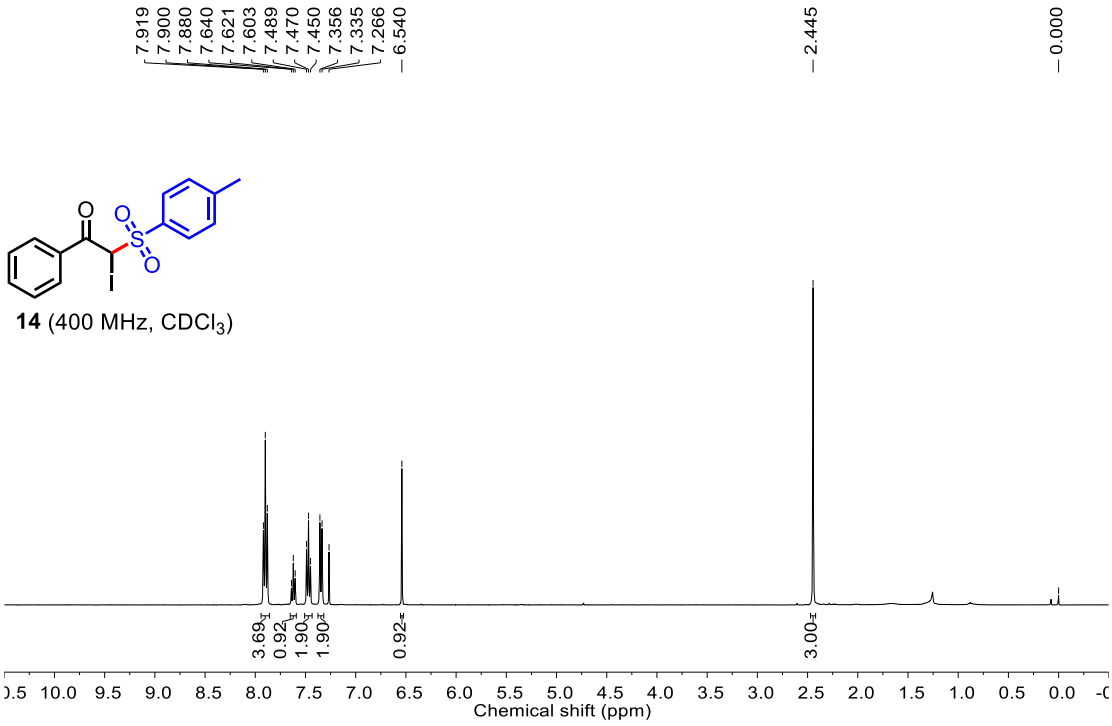

**12** (150 MHZ, $CDCl_3$)

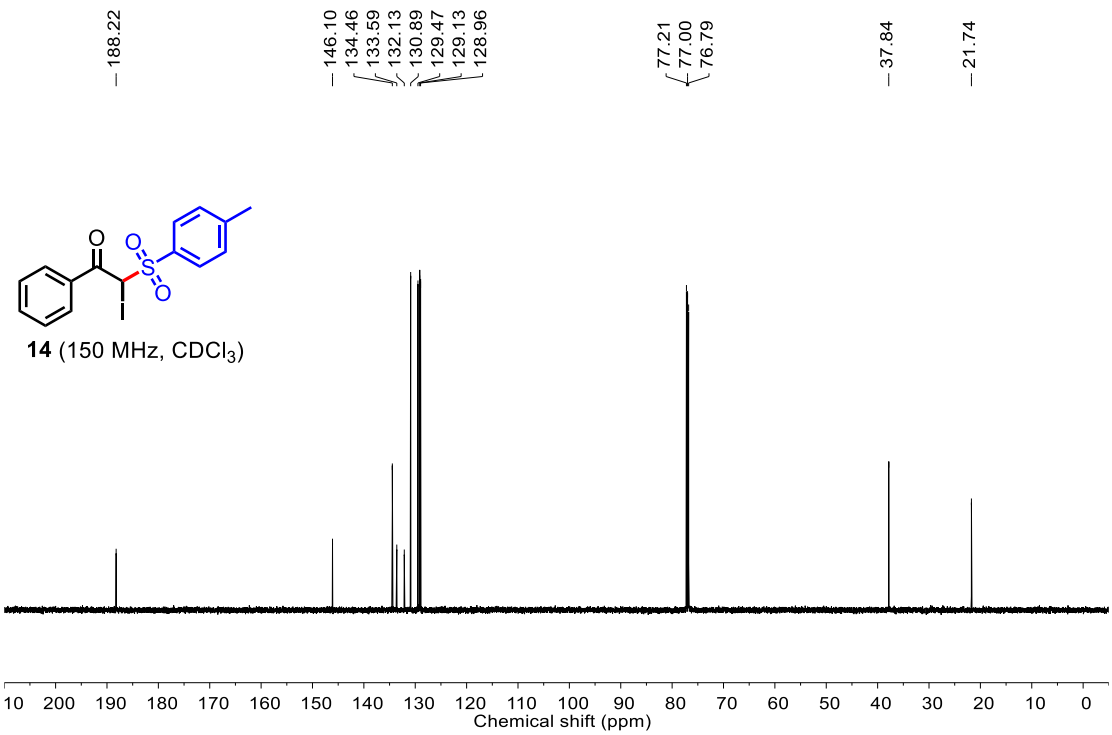



**13** (400 MHz, DMSO-$d_6$)




**13** (150 MHz, DMSO-$d_6$)


7.919
7.900
7.880
7.640
7.621
7.603
7.489
7.470
7.450
7.356
7.335
7.266
6.540
2.445
0.000
O
O
S
O
I
14 (400 MHz, CDCl3)
3.69
0.92
1.90
1.90
0.92
3.00
Chemical shift (ppm)


188.22
146.10
134.46
133.59
132.13
130.89
129.47
129.13
128.96
77.21
77.00
76.79
37.84
21.74
O
O
S
O
I
14 (150 MHz, CDCl3)
Chemical shift (ppm)