Supporting Information

Iminyl Radical-Promoted Imino Sulfonylation, Imino Cyanogenation and Imino Thiocyanation of γ, δ-Unsaturated Oxime Esters: Synthesis of Versatile Functionalized Pyrrolines

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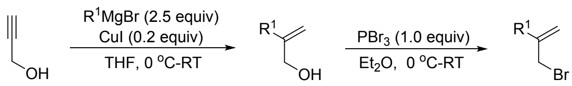
General Information:

The ^{1}H NMR, ^{19}F NMR and ^{13}C NMR were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR and ^{13}C NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.00), as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource.

Preparation of Starting Materials:

General Procedure 1:



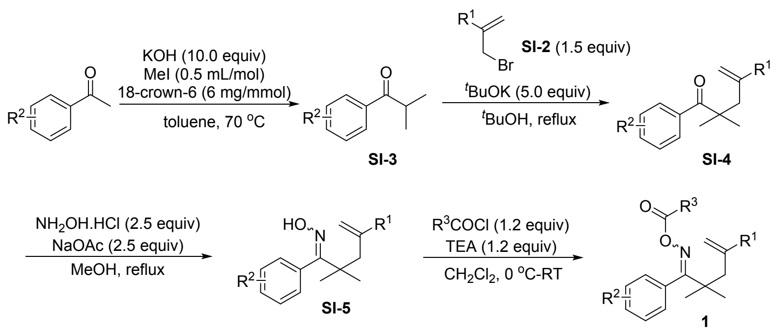
SI-1 **SI-2**

To a stirred solution of propargyl alcohol (1.0 equiv) in anhydrous THF under N_2, was added CuI (0.2 equiv). The resulting suspension was cooled to 0 °C. R^1MgBr (2.5 equiv) in anhydrous THF, which was freshly prepared from Mg and R^1Br, was added via cannula, at such a rate as to maintain the temperature below 10 °C. The reaction was allowed to warm slowly to room temperature overnight. The reaction was again cooled to 0 °C, and then was treated with H_2O to give a light green suspension. Then it was treated with EtOAc. After treatment with 1 M hydrochloric acid, a green gelatinous precipitate was formed, which was thoroughly extracted with EtOAc. The combined organic layers were dried on Na_2SO_4. After removing the solvent, the residue was purified by column chromatography to give **SI-1**. (*Angew. Chem., Int. Ed.* **2015**, *54*, 3092.)

To a solution of the appropriate alcohol (1.0 equiv) in anhydrous Et_2O at 0 °C was added PBr_3 (1.0 equiv). The solution was warmed to room temperature and stirred for

7 hours. The reaction was cooled to 0 ^{o}C and water was added. The organic portion was isolated, washed with brine, dried and concentrated in vacuum to afford **SI-2**, which was used in the next step without further purification. (*Angew. Chem., Int. Ed.* **2015**, *54*, 3092.)

General Procedure 2:



To a stirred suspension of KOH (10.0 equiv) in toluene (1 mL/mol) containing of acetophenone (1.0 equiv) and 18-crown-6 (6 mg/mmol) was added CH_3I (0.5 mL/mol) dropwise. The mixture was stirred at 70 ^{o}C for 24 h. After cooling to room temperature, separation of the solid phase by filtration and evaporation of the toluene. The remainder was purified by column chromatography on silica gel to afford corresponding products **SI-3**. (*Org. Lett*. **2017**, *19*, 5940.)

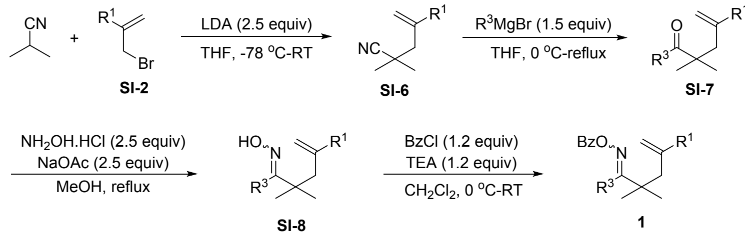
To a solution of **SI-3** (1.0 equiv) in anhydrous ^{t}BuOH (3.0 mL/mmol) was added KO^{t}Bu (5.0 equiv) and the mixture was stirred at room temperature for 5 minutes. Then, **SI-2** (1.5 equiv) was added via syringe and the mixture was heated at 90 ^{o}C for 16 hours. The mixture was cooled to room temperature and H_2O was added. The mixture was extracted with EtOAc. The organic extracts were combined, washed with brine, dried with Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatography to give **SI-4**. (*Angew. Chem., Int. Ed*. **2015**, *54*, 3092.)

H_2NOH-HCl (2.5 equiv) and NaOAc (2.5 equiv) were added to a solution of **SI-4** (1.0 equiv) in MeOH (4.0 mL/mmol) in a round-bottomed flask which was fitted with a reflux condenser. The mixture was heated at 80 ^{o}C until consumption of starting material was observed by TLC. After cooling to room temperature, the mixture was diluted with EtOAc, washed with brine, dried with Na_2SO_4 and concentrated in vacuum to give **SI-5**, which was used for the next step without further purification.

(*Angew. Chem., Int. Ed.* **2015**, *54*, 3092.)

To a solution of **SI-5** (1.0 equiv) in anhydrous DCM (4 mL/mmol) at 0 °C was added Et_3N (1.2 equiv) followed by R^3COCl (1.2 equiv) dropwise via syringe. The mixture was then warmed to room temperature and stirred until the reaction was complete as observed by TLC. MeOH (1.0 mL/mmol) was then added and the mixture stirred for further 10 minutes. The mixture was diluted with DCM, washed with brine, dried with Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatograph to afford **1**. (*Angew. Chem., Int. Ed.* **2015**, *54*, 3092.)

General Procedure 3:

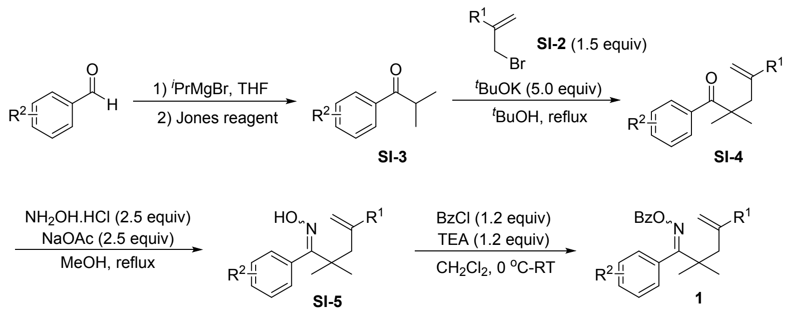


To a 100 mL flame-dried round-bottomed flask equipped with a stirring bar was added diisopropylamine (2.5 equiv) and n-BuLi (2.5 equiv) in THF, and the reaction mixture was stirred at 0 °C for 30 min. Then nitriles (1.0 equiv) was slowly added at -78 °C. After stirring for 1 h, **SI-2** (1.2 equiv) was added dropwise and the reaction mixture was allowed to warm up to room temperature while stirring overnight. The reaction was quenched with saturated aqueous NH_4Cl solution. Organic materials were then extracted three times with EtOAc. The organic phase was washed with water and brine, and dried over Na_2SO_4. After filtration, the solvent was evaporated to give a crude mixture, which was purified by flash column chromatography to afford **SI-6**. (*ACS Catal.* **2016**, *6*, 5571.)

To a 100 mL flame-dried round-bottomed flask equipped with a stirring bar was added **SI-6** (1.0 equiv). It was solubilized in anhydrous THF (0.25 M). The solution was cooled to 0 °C and R^3MgBr (1.5 equiv) was slowly added to the reaction flask. Then, the mixture was stirred overnight in a sealed tube at 60 °C. After cooling down to 0 °C, reaction was quenched with 3 N HCl (aq.) and warmed up for 4 h to finish the hydrolysis. The crude mixture was then extracted with EtOAc, washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography to give **SI-7**. (*ACS Catal*. **2016**, *6*, 5571.)

(Note: The remaining procedure follows the **General Procedure 2**, step 3 and step 4.)

General Procedure 4:

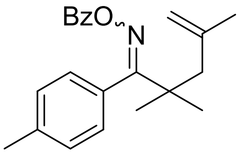


To a magnetically stirred aldehyde (1.0 equiv), was added isopropylmagnesium bromide (1.5 equiv), which was prepared from magnesium (1.5 equiv) and isopropyl bromide (1.5 equiv). The reaction mixture was stirred at RT for 36 h. Then, it was poured into saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc. The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. The crude secondary alcohol was purified by column chromatography on silica using petroleum ether/ethyl acetate as eluent.

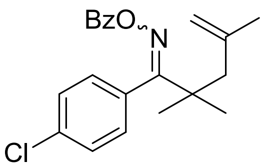
A solution of secondary alcohol (1.0 equiv) in ^{t}BuOMe was stirred at 0 °C while Jones reagent (4.0 equiv) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred overnight. The ^{t}BuOMe layer was then separated from the aqueous layer, which was extracted with EtOAc for 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated in vacuo. The crude ketone product **SI-3** was directly used in the next step without further purification.

(Note: The remaining procedure follows the **General Procedure 2**, step 2, step 3 and step 4.)

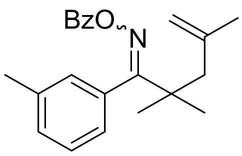
Characterization of Starting Materials (New Compounds):



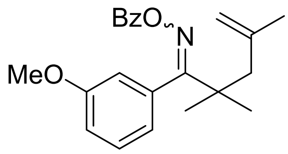
2,2,4-trimethyl-1-(p-tolyl)pent-4-en-1-one O-benzoyl oxime (**1b**) was Synthesized by **General Procedure 3**, appearance: yellow oil; R_f: 0.3 (PE:EA, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.26 – 7.19 (m, 4H), 7.03 (d, *J* = 8.1 Hz, 2H), 4.94 – 4.91 (m, 1H), 4.82 (d, *J* = 0.9 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 2H), 1.79 (s, 3H), 1.28 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.11, 163.48, 142.01, 137.78, 132.68, 130.33, 130.15, 129.14, 128.45, 128.07, 126.46, 114.87, 46.68, 41.32, 26.16, 25.15, 21.10. ESI-MS: Calcd for $C_{22}H_{25}NO_2$: [$M+H^+$] 336.1958, found 336.1959.



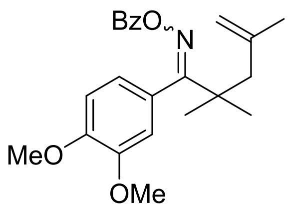
1-(4-chlorophenyl)-2,2,4-trimethylpent-4-en-1-one O-benzoyl oxime (**1c**) was Synthesized by **General Procedure 2**, appearance: yellow oil; R_f: 0.6 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 1H), 7.52 – 7.49 (m, 2H), 7.44 – 7.41 (m, 2H), 7.29 (dd, *J* = 11.0, 4.5 Hz, 2H), 7.16 – 7.09 (m, 2H), 4.99 – 4.93 (m, 1H), 4.86 (d, *J* = 0.9 Hz, 1H), 2.35 (s, 2H), 1.81 (s, 3H), 1.31 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.89, 163.27, 141.85, 134.37, 134.27, 132.91, 131.65, 130.38, 129.15, 128.23, 128.11, 115.06, 46.77, 41.40, 26.24, 25.17. ESI-MS: Calcd for $C_{21}H_{22}ClNO_2$: [$M+H^+$] 356.1412, found 356.1413.



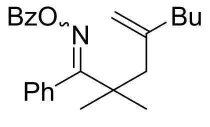
2,2,4-trimethyl-1-(m-tolyl)pent-4-en-1-one O-benzoyl oxime (**1d**) was Synthesized by **General Procedure 2**, appearance: yellow oil; R_f: 0.5 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.24 – 7.16 (m, 3H), 6.95 – 6.91 (m, 2H), 4.93 – 4.91 (m, 1H), 4.82 (d, J = 0.9 Hz, 1H), 2.36 (s, 2H), 2.34 (s, 3H), 1.79 (s, 3H), 1.28 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.92, 163.33, 141.94, 137.33, 133.06, 132.64, 130.26, 129.06, 128.64, 128.01, 127.65, 126.92, 123.62, 114.90, 46.63, 41.19, 26.13, 25.11, 21.25. ESI-MS: Calcd for $C_{22}H_{25}NO_2$: [M+H$^+$] 336.1958, found 336.1960.



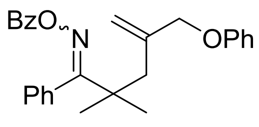
1-(3-methoxyphenyl)-2,2,4-trimethylpent-4-en-1-one O-benzoyl oxime (**1e**) was Synthesized by **General Procedure 3**, appearance: yellow oil; R_f: 0.2 (PE:EA, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.4 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.9 Hz, 1H), 7.29 (t, J = 7.7 Hz, 2H), 6.94 (dd, J = 8.3, 2.5 Hz, 1H), 6.75 (d, J = 7.6 Hz, 1H), 6.71 (s, 1H), 4.96 (s, 1H), 4.86 (s, 1H), 3.81 (s, 3H), 2.39 (s, 2H), 1.83 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.83, 163.64, 159.11, 142.22, 134.60, 132.89, 129.37, 129.11, 129.04, 128.27, 119.26, 115.09, 113.59, 112.47, 55.31, 46.90, 41.48, 26.36, 25.36. ESI-MS: Calcd for $C_{22}H_{25}NO_3$: [M+H$^+$] 352.1907, found 352.1911.



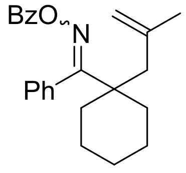
1-(3,4-dimethoxyphenyl)-2,2,4-trimethylpent-4-en-1-one O-benzoyl oxime (**1f**) was Synthesized by **General Procedure 4**, appearance: while soild; M.p.: 85-88 ºC. R_f: 0.8 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.45 – 7.40 (m, 1H), 7.26 (t, J = 7.8 Hz, 2H), 6.90 (d, J = 8.2 Hz, 1H), 6.73 – 6.67 (m, 2H), 4.95 – 4.92 (m, 1H), 4.85 (s, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 2.34 (s, 2H), 1.79 (s, 3H), 1.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.63, 163.54, 148.59, 148.23, 142.11, 132.77, 129.13, 128.85, 128.16, 125.43, 119.20, 114.74, 110.35, 110.09, 55.78, 55.66, 46.82, 41.51, 26.32, 25.16. ESI-MS: Calcd for $C_{23}H_{27}NO_4$: [M+H$^+$] 382.2013, found 382.2014.



2,2-dimethyl-4-methylene-1-phenyloctan-1-one O-benzoyl oxime (**1d**) was Synthesized by **General Procedures 1 and 2**, appearance: yellow oil; R_f: 0.5 (PE:EA, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.45 – 7.38 (m, 4H), 7.27 – 7.22 (m, 2H), 7.18 – 7.13 (m, 2H), 4.96 (d, *J* = 1.5 Hz, 1H), 4.92 (s, 1H), 2.34 (s, 2H), 2.05 – 2.00 (m, 2H), 1.43 – 1.37 (m, 2H), 1.31 (s, 6H), 1.28 – 1.24 (m, 2H), 0.88 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.28, 163.54, 146.12, 133.38, 132.83, 129.27, 129.00, 128.20, 127.92, 126.66, 113.46, 44.92, 41.53, 38.17, 30.29, 26.19, 22.39, 13.96. ESI-MS: Calcd for $C_{24}H_{29}NO_2$: [M+H$^+$] 364.2271, found 364.2272.



2,2-dimethyl-4-(phenoxymethyl)-1-phenylpent-4-en-1-one O-benzoyl oxime (**1f**) was Synthesized by **General Procedure 2**, appearance: yellow oil; R_f: 0.6 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.43 – 7.38 (m, 4H), 7.23 (ddd, *J* = 7.3, 6.8, 4.2 Hz, 4H), 7.19 – 7.14 (m, 2H), 6.94 – 6.86 (m, 3H), 5.42 (d, *J* = 1.3 Hz, 1H), 5.25 (s, 1H), 4.54 (s, 2H), 2.55 (s, 2H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.61, 163.48, 158.43, 141.21, 133.07, 132.86, 129.29, 129.23, 128.79, 128.27, 128.17, 127.96, 126.59, 120.66, 116.78, 114.67, 71.68, 42.19, 41.30, 26.52. ESI-MS: Calcd for $C_{27}H_{27}NO_3$: [M+H$^+$] 414.2064, found 414.2066.



(1-(2-methylallyl)cyclohexyl)(phenyl)methanone O-benzoyl oxime (**1g**) was Synthesized by **General Procedure 2**, appearance: yellow oil; R_f: 0.4 (PE:EA, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.46 – 7.38 (m, 4H), 7.28 – 7.22 (m, 4H), 4.97 (d, *J* = 1.5 Hz, 1H), 4.95 (s, 1H), 2.38 (s, 2H), 2.05 – 1.98 (m, 2H), 1.84 (s, 3H), 1.73 – 1.63 (m, 3H), 1.59 – 1.53 (m, 5H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 173.43, 163.60, 141.90, 133.27, 132.82, 129.31, 129.09, 128.25, 128.22, 127.91, 126.82, 114.92, 45.14, 34.25, 31.91, 29.35, 25.95, 25.47, 22.68, 22.46. ESI-MS: Calcd for $C_{24}H_{27}NO_2$: [M+H$^+$] 362.2115, found 362.2116.

General Procedures for the Synthesis of Imino-Functionalization Products:

General Procedure for Iminosulfonylation:

In a 38 mL sealed tube, the mixture of γ, δ-unsaturated oxime **1** (0.2 mmol), sodium sulfinate **2** (0.4 mmol), $Cu(OAc)_2$ (36.3 mg, 0.2 mmol) were dissolved in anhydrous MeCN (2.0 mL). Then, the reaction mixture was thoroughly degassed by vacuum purge-and-refill with N_2. The reaction mixture was heated to 90 ^oC for 2 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum Ether) to give the iminosulfonylation products **3**.

General Procedure for Iminocyanogenation:

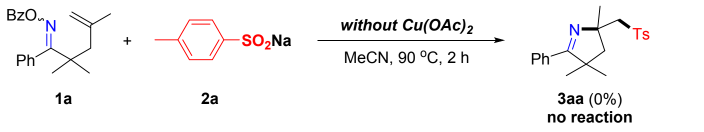
In a 38 mL sealed tube, the mixture of γ, δ-unsaturated oxime **1** (0.2 mmol), CuCN (44.8 mg, 0.5 mmol) were dissolved in anhydrous MeCN (2.0 mL). Then, the reaction mixture was thoroughly degassed by vacuum purge-and-refill with N_2. The reaction mixture was heated to 90 ^oC for 2.5 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum Ether) to give the iminocyanogenation products **4**.

General Procedure for Iminothiocyanation:

In a 38 mL sealed tube, the mixture of γ, δ-unsaturated oxime **1** (0.2 mmol), CuSCN (60.8 mg, 0.5 mmol) were dissolved in anhydrous MeCN (2.0 mL). Then, the reaction mixture was thoroughly degassed by vacuum purge-and-refill with N_2. The reaction mixture was heated to 90 ^oC for 2.5 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum Ether) to give the iminothiocyanation products **5**.

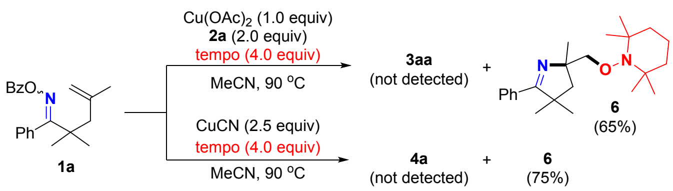
Mechanistic studies:

a)



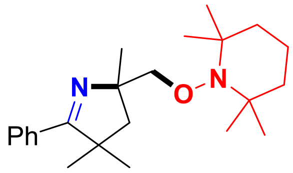
In a 38 mL sealed tube, the mixture of **1a** (64.2 mg, 0.2 mmol) and **2a** (71.2 mg, 0.4 mmol) were dissolved in anhydrous MeCN (2.0 mL). Then, the reaction mixture was thoroughly degassed by vacuum purge-and-refill with N_2. The reaction mixture was heated to 90 ^{o}C for 2 h. Thin-layer chromatography (TLC) analysis indicated that no reaction.

b)



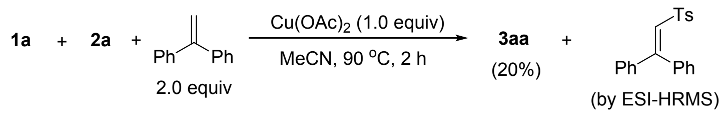
In a 38 mL sealed tube, the mixture of **1a** (64.2 mg, 0.2 mmol), **2a** (71.2 mg, 0.4 mmol), $Cu(OAc)_2$ (36.3 mg, 0.2 mmol) and TEMPO (125.0 mg, 0.8 mmol) were dissolved in anhydrous MeCN (2.0 mL). Then, the reaction mixture was thoroughly degassed by vacuum purge-and-refill with N_2. The reaction mixture was heated to 90 ^{o}C for 2.0 h. Thin-layer chromatography (TLC) analysis indicated that **3aa** was not detected and radical trapping product **6** was obtained in 65% yield. (46.3 mg, yellow oil)

In a 38 mL sealed tube, the mixture of **1a** (64.2 mg, 0.2 mmol), CuCN (44.8 mg, 0.5 mmol), TEMPO (125.0 mg, 0.8 mmol) were dissolved in anhydrous MeCN (2.0 mL). Then, the reaction mixture was thoroughly degassed by vacuum purge-and-refill with N_2. The reaction mixture was heated to 90 ^{o}C for 2.5 h. Thin-layer chromatography (TLC) analysis indicated that **4a** was not detected and radical trapping product **6** was obtained in 75% yield. (53.4 mg, yellow oil)

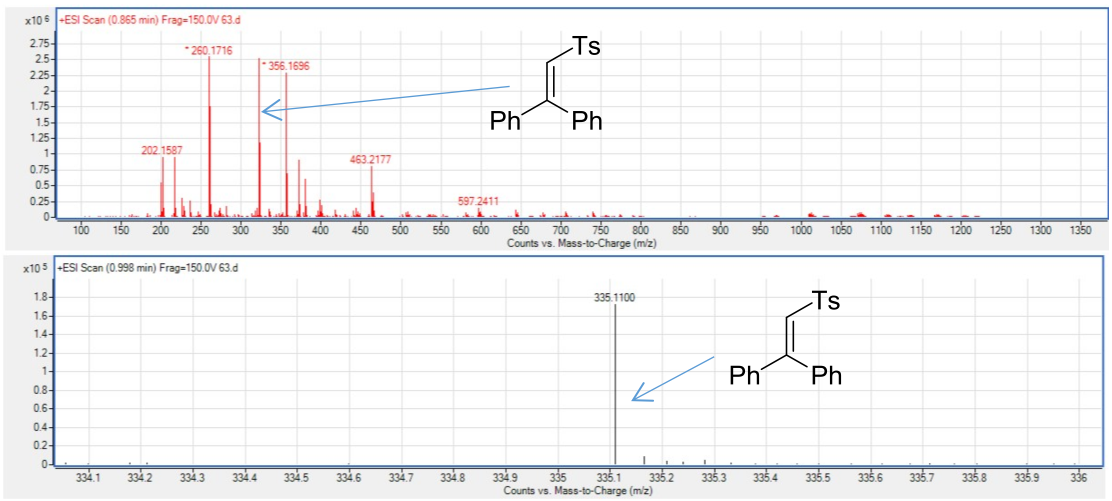


6: appearance: yellow oil; R_f: 0.5 (PE:EA, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.36 (dd, J = 5.1, 1.9 Hz, 3H), 3.92 (d, J = 8.4 Hz, 1H), 3.80 (d, J = 8.4 Hz, 1H), 2.36 (d, J = 13.0 Hz, 1H), 1.70 (d, J = 13.0 Hz, 1H), 1.44 (s, 6H), 1.35 (s, 3H), 1.34 (s, 3H), 1.25 (s, 3H), 1.20 (s, 3H), 1.14 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.01, 135.37, 128.97, 128.07, 128.01, 82.70, 72.54, 60.08, 51.93, 48.98, 39.78, 33.28, 33.12, 29.61, 27.95, 26.70, 20.64, 20.35, 17.07. ESI-MS: Calcd for $C_{23}H_{36}N_2O$: [M+H$^+$] 357.2900, found 357.2905.

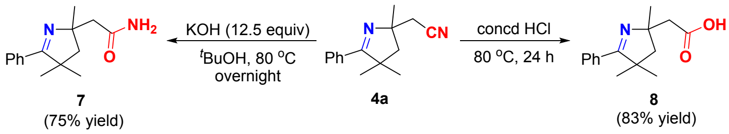
c)



In a 38 mL sealed tube, the mixture of **1a** (64.2 mg, 0.2 mmol), **2a** (71.2 mg, 0.4 mmol), $Cu(OAc)_2$ (36.3 mg, 0.2 mmol) and 1,1-diphenylethylene (72.1 mg, 0.4 mmol) were dissolved in anhydrous MeCN (2.0 mL). Then, the reaction mixture was thoroughly degassed by vacuum purge-and-refill with N_2. The reaction mixture was heated to 90 °C for 2 h. **3aa** was obtained in 20% isolated yield and the sulfonyl radical coupling product could be detected by ESI-HRMS.

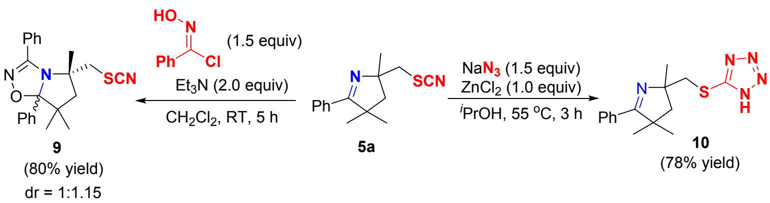


Derivatization:



The mixture of **4a** (45.2 mg, 0.2 mmol), solid KOH (140.3 mg, 2.5 mmol) and ^{t}BuOH (1 mL) was stirred at 80 °C overnight. The reaction was cooled to room temperature and extracted with EtOAc. The combined organic layers were dried with Na_2SO_4, filtered, concentrated under reduced pressure. The residue was purified by column chromatography with pure EA to give the product **7** (36.6 mg, 75%) as a yellow oil. (Reference: *Org. Lett.* **2017**, *19*, 3255.)

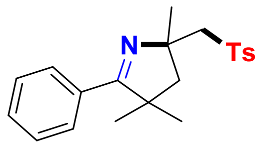
The mixture of **4a** (45.2 mg, 0.2 mmol) and concentrated HCl (1 mL) was stirred at 80 °C for 24 h. The reaction was quenched by NaOH (2 M) and aqueous layer was washed with EtOAc, then the aqueous layer was acidified by HCl (2 M), and extracted with EtOAc. Collected organic layers were dried over anhydrous Na_2SO_4, and solvent was evaporated under reduced pressure. The residue was purified by column chromatography with petroleum ether/EA (2:1) to give the product **8** (40.7 mg, 83%) as a slight yellow oil. (Reference: *Org. Lett.* **2017**, *19*, 3255.)



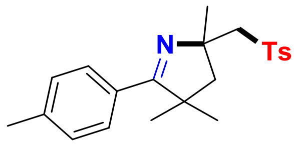
To a 50 mL round-bottom flask equipped with a magnetic stirring bar were added **5a** (64.5 mg, 0.25 mmol), N-hydroxybenzimidoyl chloride (59 mg, 0.38 mmol), Et_3N (51 mg, 0.5 mmol) and CH_2Cl_2 (4.0 mL). The mixture was stirred at RT for 5 h. The solvent was removed in vacuo, and the crude product was purified by column chromatography using Petroleum Ether/EA (30:1) to give the product **9** (75.4 mg, 80%) as a white solid. (Reference: *ACS Catal.* **2017**, *7*, 8441)

To a 38 mL oven-dried Sealed tube was charged with **5a** (51.6 mg, 0.2 mmol), $ZnCl_2$ (27.3 mg, 0.2 mmol), and NaN_3 (19.5 mg, 0.3 mmol). ^{i}PrOH (1 mL) was then injected into the tube by syringe. The resulting mixture was then heated to 55 °C and stirred vigorously for 3 h. Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed under reduced pressure. The crude product was isolated by column chromatography with pure EA to give the product **10** (47.0 mg, 78%) as a white solid. (Reference: A*sian J. Org. Chem.* **2017**, *6*, 682)

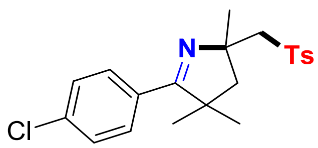
Characterization of Catalytic Products:



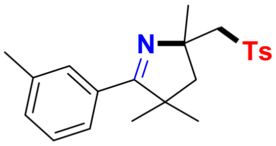
3aa: yield: 72%, 51.1 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.41 – 7.29 (m, 5H), 3.60 (d, *J* = 14.2 Hz, 1H), 3.34 (d, *J* = 14.2 Hz, 1H), 2.68 (d, *J* = 13.6 Hz, 1H), 2.43 (s, 3H), 2.01 (d, *J* = 13.6 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.48, 144.30, 138.82, 134.24, 129.78, 129.59, 128.11, 128.06, 127.77, 70.67, 66.53, 52.14, 51.02, 28.98, 28.32, 21.57, 21.54. ESI-MS: Calcd for $C_{21}H_{25}NO_2S$: [M+H$^+$] 356.1679, found 356.1677.



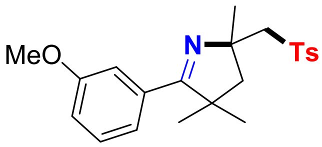
3ba: yield: 88%, 65.0 mg; appearance: yellow solid; M.p.:117-121ºC. R_f: 0.4 (PE:EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.60 (d, *J* = 14.2 Hz, 1H), 3.32 (d, *J* = 14.2 Hz, 1H), 2.65 (d, *J* = 13.6 Hz, 1H), 2.42 (s, 3H), 2.35 (s, 3H), 1.99 (d, *J* = 13.6 Hz, 1H), 1.53 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.02, 144.21, 139.72, 138.70, 131.12, 129.71, 128.75, 128.02, 127.70, 70.37, 66.50, 51.89, 51.16, 28.99, 28.87, 28.36, 21.51, 21.24. ESI-MS: Calcd for $C_{22}H_{27}NO_2S$: [M+H$^+$] 370.1835, found 370.1834.



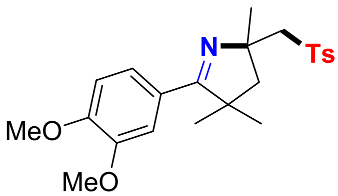
3ca: yield: 50%, 38.9 mg; appearance: yellow solid; M.p.:130-135ºC. R_f: 0.5 (PE:EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 4H), 3.56 (d, *J* = 14.2 Hz, 1H), 3.34 (d, *J* = 14.2 Hz, 1H), 2.68 (d, *J* = 13.6 Hz, 1H), 2.42 (s, 3H), 1.99 (d, *J* = 13.6 Hz, 1H), 1.51 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.13, 144.30, 138.73, 135.80, 132.52, 129.75, 129.50, 128.33, 127.72, 70.69, 66.32, 51.95, 51.00, 29.03, 28.95, 28.19, 21.55. ESI-MS: Calcd for $C_{21}H_{24}ClNO_2S$: [$M+H^+$] 390.1289, found 390.1288.



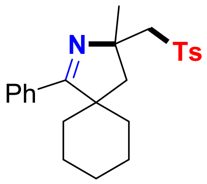
3da: yield: 45%, 33.2 mg; appearance: yellow oil; R_f: 0.5 (PE:EA, 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.20 (dd, J = 11.1, 7.5 Hz, 2H), 3.61 (d, J = 14.2 Hz, 1H), 3.33 (d, J = 14.2 Hz, 1H), 2.67 (d, J = 13.6 Hz, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 2.00 (d, J = 13.6 Hz, 1H), 1.54 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.60, 144.22, 138.74, 137.77, 134.12, 130.33, 129.71, 128.76, 127.88, 127.70, 124.87, 70.53, 66.47, 52.09, 50.93, 28.97, 28.90, 28.32, 21.53, 21.36. ESI-MS: Calcd for $C_{22}H_{27}NO_2S$: [$M+H^+$] 370.1835, found 370.1836.



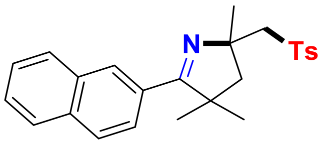
3ea: yield: 57%, 43.9 mg; appearance: yellow oil; R_f: 0.1 (PE:EA, 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 5.3 Hz, 1H), 7.15 (dd, J = 8.0, 5.0 Hz, 2H), 6.93 (dd, J = 8.1, 2.3 Hz, 1H), 3.81 (s, 3H), 3.61 (d, J = 14.2 Hz, 1H), 3.33 (d, J = 14.2 Hz, 1H), 2.67 (d, J = 13.6 Hz, 1H), 2.43 (s, 3H), 2.01 (d, J = 13.6 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.25, 159.28, 144.29, 138.71, 135.52, 129.74, 129.06, 127.70, 120.35, 115.20, 113.73, 70.60, 66.46, 55.21, 52.12, 50.96, 28.95, 28.90, 28.32, 21.53. ESI-MS: Calcd for $C_{22}H_{27}NO_3S$: [$M+H^+$] 386.1784, found 386.1788.



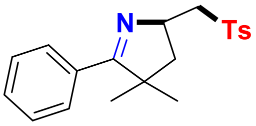
3fa: yield: 85%, 70.6 mg; appearance: yellow oil; R_f: 0.4 (PE:EA, 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2H), 7.20 (dd, J = 5.0, 3.0 Hz, 3H), 7.16 (dd, J = 8.4, 1.9 Hz, 1H), 6.72 (d, J = 8.4 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.51 (d, J = 14.2 Hz, 1H), 3.22 (d, J = 14.2 Hz, 1H), 2.57 (d, J = 13.6 Hz, 1H), 2.31 (s, 3H), 1.90 (d, J = 13.6 Hz, 1H), 1.44 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.94, 150.44, 148.51, 144.08, 138.68, 129.58, 127.57, 126.52, 120.97, 111.63, 110.11, 70.03, 66.46, 55.77, 55.73, 51.63, 51.41, 29.12, 28.85, 28.49, 21.38. ESI-MS: Calcd for $C_{23}H_{29}NO_4S$: [M+H$^+$] 416.1890, found 416.1891.



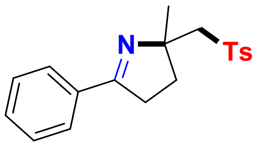
3ga: yield: 73%, 57.7 mg; appearance: yellow oil; R_f: 0.3 (PE:EA, 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.42 (m, 2H), 7.32 (dd, *J* = 11.9, 7.8 Hz, 5H), 3.60 (d, *J* = 14.2 Hz, 1H), 3.32 (d, *J* = 14.2 Hz, 1H), 2.63 (d, *J* = 13.8 Hz, 1H), 2.42 (s, 3H), 2.07 (d, *J* = 13.8 Hz, 1H), 1.70 (m, 6H), 1.58 (d, *J* = 8.7 Hz, 2H), 1.53 (s, 3H), 1.43 – 1.35 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.48, 144.27, 138.81, 135.26, 129.74, 128.98, 128.03, 127.93, 127.71, 71.42, 66.64, 58.25, 44.26, 35.43, 35.25, 29.70, 25.31, 23.08, 22.87, 21.53. ESI-MS: Calcd for $C_{24}H_{29}NO_2S$: [M+H$^+$] 396.1992, found 396.1998.



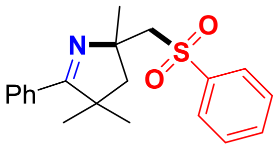
3ha: yield: 71%, 57.5 mg; appearance: brown oil; R_f: 0.3 (PE:EA, 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.85 – 7.78 (m, 5H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.65 (d, *J* = 14.2 Hz, 1H), 3.42 (d, *J* = 14.2 Hz, 1H), 2.75 (d, *J* = 13.6 Hz, 1H), 2.41 (s, 3H), 2.06 (d, *J* = 13.6 Hz, 1H), 1.59 (s, 3H), 1.54 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.30, 138.74, 133.82, 132.73, 129.78, 128.65, 127.93, 127.78, 127.76, 127.58, 126.95, 126.30, 125.64, 70.67, 66.43, 52.16, 51.20, 29.22, 29.05, 28.52, 21.54. ESI-MS: Calcd for $C_{25}H_{27}NO_2S$: [M+H$^+$] 406.1835, found 406.1836.



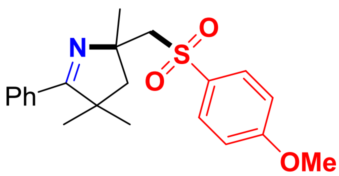
3ia: yield: 75%, 51.2 mg; appearance: yellow solid; M.p.:132-138ºC. R_f: 0.3 (PE:EA, 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.59 (dd, J = 8.2, 1.4 Hz, 2H), 7.39 – 7.31 (m, 5H), 4.43 – 4.33 (m, 1H), 3.87 (dd, J = 14.0, 4.0 Hz, 1H), 3.17 (dd, J = 14.0, 9.8 Hz, 1H), 2.45 (s, 3H), 2.34 (dd, J = 13.0, 6.8 Hz, 1H), 1.82 (dd, J = 13.0, 8.8 Hz, 1H), 1.35 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.90, 144.59, 137.12, 133.92, 129.81, 128.16, 128.07, 127.84, 62.65, 62.19, 51.09, 48.27, 27.16, 25.68, 21.57. ESI-MS: Calcd for $C_{20}H_{23}NO_2S$: [M+H$^+$] 342.1522, found 342.1521.



3ja: yield: 22%, 14.4 mg; appearance: yellow oil; R_f: 0.5 (PE:EA, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 7.7 Hz, 2H), 7.38 (dd, J = 18.7, 7.2 Hz, 3H), 7.23 (d, J = 7.9 Hz, 2H), 3.58 (d, J = 14.4 Hz, 1H), 3.49 (d, J = 14.4 Hz, 1H), 3.13 – 3.04 (m, 2H), 2.68 – 2.60 (m, 1H), 2.37 (s, 3H), 2.01 – 1.95 (m, 1H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.89, 144.17, 138.39, 133.88, 130.68, 129.64, 128.25, 127.84, 127.82, 74.55, 65.31, 35.63, 33.08, 27.89, 21.52. ESI-MS: Calcd for $C_{19}H_{21}NO_2S$: [M+H$^+$] 328.1366, found 328.1368.

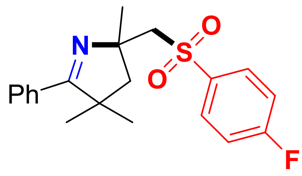


3ab: yield: 73%, 49.8 mg; appearance: yellow oil; R_f: 0.5 (PE:EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8 Hz, 2H), 7.61 – 7.56 (m, 3H), 7.51 (t, J = 7.6 Hz, 2H), 7.38 – 7.30 (m, 3H), 3.62 (d, J = 14.2 Hz, 1H), 3.36 (d, J = 14.2 Hz, 1H), 2.66 (d, J = 13.6 Hz, 1H), 2.01 (d, J = 13.6 Hz, 1H), 1.55 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.43, 141.63, 134.11, 133.29, 129.57, 129.11, 128.06, 128.00, 127.65, 70.59, 66.41, 52.07, 51.06, 29.59, 28.91, 28.26. ESI-MS: Calcd for $C_{20}H_{23}NO_2S$: [M+H$^+$] 342.1522, found 342.1523.

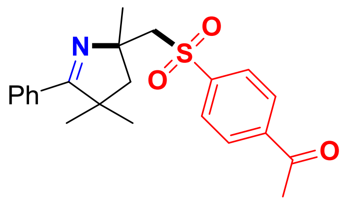


3ac: yield: 63%, 46.9 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.57 (dd, J = 8.1, 1.4 Hz, 2H), 7.38 – 7.31 (m, 3H), 6.95 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H), 3.58 (d, J = 14.2 Hz, 1H), 3.33 (d, J = 14.2 Hz, 1H), 2.66 (d, J = 13.6 Hz, 1H), 1.98 (d, J = 13.6

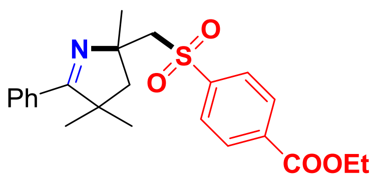
Hz, 1H), 1.53 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.32, 163.41, 134.13, 133.20, 129.86, 129.53, 128.04, 127.98, 114.25, 70.55, 66.62, 55.58, 55.54, 52.01, 50.89, 28.89, 28.25. ESI-MS: Calcd for $C_{21}H_{25}NO_3S$: [M+H$^+$] 372.1628, found 372.1627.



3ad: yield: 66%, 47.4 mg; appearance: yellow oil; R_f: 0.3 (PE:EA, 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.56 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.14 (t, *J* = 8.6 Hz, 2H), 3.61 (d, *J* = 14.3 Hz, 1H), 3.44 (d, *J* = 14.3 Hz, 1H), 2.68 (d, *J* = 13.6 Hz, 1H), 2.00 (d, *J* = 13.6 Hz, 1H), 1.54 (s, 3H), 1.42 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.90, 165.44 (d, *J* = 255.8 Hz), 137.52 (d, *J* = 3.3 Hz), 133.72, 130.57 (d, *J* = 9.7 Hz), 129.68, 127.98 (d, *J* = 12.6 Hz), 116.38, 116.15, 70.51, 66.21, 51.95, 50.78, 28.96, 28.85, 28.08. ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.06. ESI-MS: Calcd for $C_{20}H_{22}FNO_2S$: [M+H$^+$] 360.1428, found 360.1429.

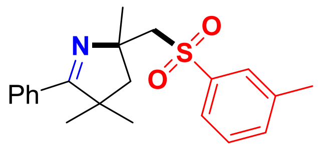


3ae: yield: 36%, 27.6 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (q, *J* = 8.5 Hz, 4H), 7.54 – 7.50 (m, 2H), 7.38 – 7.28 (m, 3H), 3.60 (d, *J* = 14.4 Hz, 1H), 3.45 (d, *J* = 14.4 Hz, 1H), 2.65 (d, *J* = 13.6 Hz, 1H), 2.62 (s, 3H), 2.01 (d, *J* = 13.6 Hz, 1H), 1.53 (s, 3H), 1.43 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.61, 178.51, 145.25, 140.47, 133.89, 129.74, 128.85, 128.22, 128.09, 128.04, 70.52, 66.31, 52.05, 51.22, 29.18, 28.99, 28.27, 26.83. ESI-MS: Calcd for $C_{22}H_{25}NO_3S$: [M+H$^+$] 384.1628, found 384.1630.

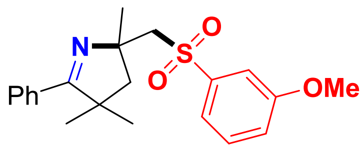


3af: yield: 52%, 43.0 mg; appearance: yellow oil; R_f: 0.3 (PE:EA, 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.2 Hz, 2H), 7.97 (d, J =

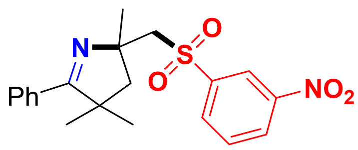
8.2 Hz, 2H), 7.53 (d, J = 7.7 Hz, 2H), 7.37 – 7.29 (m, 3H), 4.43 (d, *J* = 7.1 Hz, 1H), 4.39 (d, *J* = 7.1 Hz, 1H), 3.61 (d, J = 14.3 Hz, 1H), 3.42 (d, J = 14.3 Hz, 1H), 2.64 (d, J = 13.6 Hz, 1H), 2.01 (d, J = 13.6 Hz, 1H), 1.53 (s, 3H), 1.43 (s, 3H), 1.40 (d, J = 5.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.47, 164.97, 145.19, 134.80, 133.88, 130.23, 129.69, 128.08, 128.02, 127.82, 70.52, 66.34, 61.65, 52.04, 51.21, 29.63, 29.08, 28.26, 14.19. ESI-MS: Calcd for $C_{23}H_{27}NO_4S$: [M+H$^+$] 414.1734, found 414.1736.



3ag: yield: 57%, 40.5 mg; appearance: yellow oil; R_f: 0.3 (PE:EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.60 – 7.55 (m, 2H), 7.41 – 7.32 (m, 5H), 3.61 (d, *J* = 14.2 Hz, 1H), 3.36 (d, *J* = 14.2 Hz, 1H), 2.69 (d, *J* = 13.6 Hz, 1H), 2.37 (s, 3H), 2.01 (d, *J* = 13.6 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.37, 141.51, 139.36, 134.16, 134.06, 129.56, 128.99, 128.07, 128.01, 124.75, 70.61, 66.36, 52.09, 50.99, 29.01, 28.96, 28.24, 21.20. ESI-MS: Calcd for $C_{21}H_{25}NO_2S$: [M+H$^+$] 356.1679, found 356.1680.

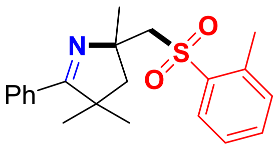


3ah: yield: 64%, 47.5 mg; appearance: yellow oil; R_f: 0.3 (PE:EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.49 (dd, *J* = 6.5, 1.2 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.33 (m, 4H), 7.13 – 7.11 (m, 1H), 3.80 (s, 3H), 3.62 (d, *J* = 14.2 Hz, 1H), 3.37 (d, *J* = 14.2 Hz, 1H), 2.68 (d, *J* = 13.5 Hz, 1H), 2.02 (d, *J* = 13.5 Hz, 1H), 1.55 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.47, 159.96, 142.81, 134.16, 130.24, 129.59, 128.11, 128.02, 119.91, 119.81, 112.12, 70.64, 66.34, 55.60, 52.13, 50.98, 29.01, 28.95, 28.28. ESI-MS: Calcd for $C_{21}H_{25}NO_3S$: [M+H$^+$] 372.1628, found 372.1629.

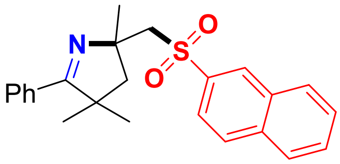


3ai: yield: 36%, 27.8 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (t, *J* = 1.9 Hz, 1H), 8.38 – 8.39 (m, 1H), 8.22 – 8.17 (m, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.38

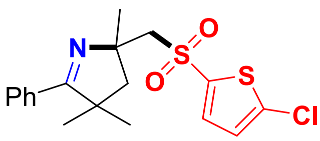
(t, J = 7.3 Hz, 1H), 7.30 (t, J = 7.4 Hz, 2H), 3.61 (d, J = 14.5 Hz, 1H), 3.55 (d, J = 14.5 Hz, 1H), 2.64 (d, J = 13.5 Hz, 1H), 2.00 (d, J = 13.5 Hz, 1H), 1.52 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.56, 148.17, 143.69, 133.60, 133.51, 130.33, 129.87, 128.11, 127.93, 127.58, 123.41, 70.42, 66.40, 51.98, 51.36, 29.37, 28.99, 28.23. ESI-MS: Calcd for $C_{20}H_{22}N_2O_4S$: [M+H$^+$] 387.1373, found 387.1374.



3aj: yield: 47%, 33.4 mg; appearance: yellow oil; R_f: 0.4 (PE:EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.60 – 7.55 (m, 2H), 7.41 – 7.33 (m, 5H), 3.61 (d, J = 14.2 Hz, 1H), 3.36 (d, J = 14.2 Hz, 1H), 2.70 (d, J = 13.6 Hz, 1H), 2.38 (s, 3H), 2.02 (d, J = 13.6 Hz, 1H), 1.55 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.51, 141.51, 139.42, 134.18, 134.11, 129.61, 129.03, 128.12, 128.04, 124.79, 70.65, 66.36, 52.14, 50.98, 29.04, 28.99, 28.27, 21.25. ESI-MS: Calcd for $C_{21}H_{25}NO_2S$: [M+H$^+$] 356.1679, found 356.1680.

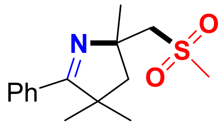


3ak: yield: 42%, 32.9 mg; appearance: yellow oil; R_f: 0.3 (PE:EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 1.5 Hz, 1H), 7.97 – 7.88 (m, 4H), 7.67 – 7.57 (m, 2H), 7.52 – 7.45 (m, 2H), 7.36 – 7.31 (m, 1H), 7.27 – 7.21 (m, 2H), 3.71 (d, J = 14.3 Hz, 1H), 3.52 (d, J = 14.3 Hz, 1H), 2.75 (d, J = 13.6 Hz, 1H), 2.04 (d, J = 13.6 Hz, 1H), 1.57 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.72, 138.50, 135.15, 133.96, 132.16, 129.58, 129.45, 129.41, 129.37, 129.04, 128.04, 127.99, 127.88, 127.51, 122.60, 70.69, 66.28, 52.06, 51.03, 29.09, 28.98, 28.23. ESI-MS: Calcd for $C_{24}H_{25}NO_2S$: [M+H$^+$] 392.1679, found 392.1673.

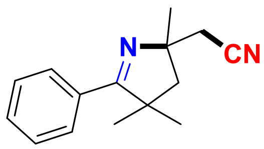


3al: yield: 60%, 45.7 mg; appearance: brown oil; R_f: 0.2 (PE:EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 8.0, 1.6 Hz, 2H), 7.46 (d, J

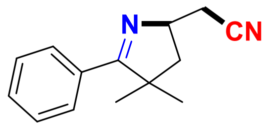
= 4.0 Hz, 1H), 7.40 – 7.34 (m, 3H), 6.92 (d, *J* = 4.0 Hz, 1H), 3.68 (d, *J* = 14.3 Hz, 1H), 3.51 (d, *J* = 14.3 Hz, 1H), 2.63 (d, *J* = 13.6 Hz, 1H), 2.01 (d, *J* = 13.6 Hz, 1H), 1.56 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.79, 140.86, 139.15, 134.01, 133.12, 129.75, 128.19, 128.06, 127.09, 70.66, 68.03, 52.14, 51.03, 29.67, 29.03, 28.31. ESI-MS: Calcd for $C_{18}H_{20}ClNO_2S_2$: [M+H$^+$] 382.0697, found 382.0699.



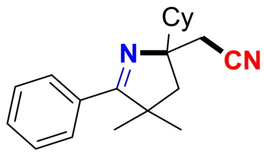
3am: yield: 45%, 25.1 mg; appearance: yellow oil; R_f: 0.3 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.45 – 7.32 (m, 3H), 3.40 (d, *J* = 14.7 Hz, 1H), 3.31 (d, *J* = 14.7 Hz, 1H), 2.98 (s, 3H), 2.57 (d, *J* = 13.4 Hz, 1H), 1.94 (d, *J* = 13.4 Hz, 1H), 1.52 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.24, 134.11, 129.65, 128.24, 127.86, 69.93, 64.95, 51.88, 51.13, 44.08, 29.41, 28.98, 27.98. ESI-MS: Calcd for $C_{15}H_{21}NO_2S$: [M+H$^+$] 280.1366, found 280.1367.



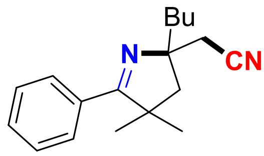
4a: yield: 75%, 33.9 mg; appearance: yellow oil; R_f: 0.1 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.8, 1.7 Hz, 2H), 7.40 (t, J = 7.4 Hz, 3H), 2.74 (d, J = 16.6 Hz, 1H), 2.69 (d, J = 16.6 Hz, 1H), 2.14 (d, J = 13.5 Hz, 1H), 2.00 (d, J = 13.5 Hz, 1H), 1.51 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.04, 133.99, 129.75, 128.23, 128.03, 117.99, 70.00, 52.30, 51.30, 32.01, 28.92, 28.56, 28.20. ESI-MS: Calcd for $C_{15}H_{18}N_2$: [M+H$^+$] 227.1543, found 227.1544.



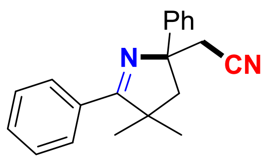
4b: yield: 70%, 29.7 mg; appearance: brown oil; R_f: 0.1 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 8.0, 1.6 Hz, 2H), 7.44 – 7.39 (m, 3H), 4.39 – 4.24 (m, 1H), 2.86 (dd, J = 16.7, 5.1 Hz, 1H), 2.80 (dd, J = 16.7, 6.8 Hz, 1H), 2.24 (dd, J = 12.7, 6.8 Hz, 1H), 1.78 (dd, J = 12.7, 9.0 Hz, 1H), 1.40 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.09, 133.84, 129.98, 128.28, 127.93, 117.75, 63.62, 51.44, 46.87, 26.99, 25.97, 24.56. ESI-MS: Calcd for $C_{14}H_{16}N_2$: [M+H$^+$] 213.1386, found 213.1387.



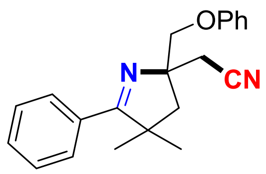
4c: yield: 46%, 27.1 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.38 (d, *J* = 6.8 Hz, 3H), 2.72 (d, *J* = 16.4 Hz, 1H), 2.67 (d, *J* = 16.4 Hz, 1H), 2.09 (d, *J* = 14.0 Hz, 1H), 1.87 (d, *J* = 14.0 Hz, 1H), 1.83 – 1.68 (m, 6H), 1.46 (s, 3H), 1.37 (s, 3H), 1.27 – 1.01 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.57, 134.56, 129.43, 128.18, 128.08, 118.64, 76.11, 51.96, 46.82, 46.27, 29.66, 28.98, 28.64, 28.27, 28.04, 27.65, 26.46, 26.35. ESI-MS: Calcd for $C_{20}H_{26}N_2$: [M+H$^+$] 295.2169, found 295.2172.



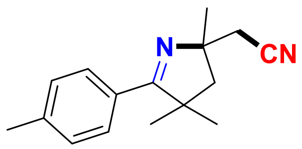
4d: yield: 65%, 34.9 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 2H), 7.42 – 7.35 (m, 3H), 2.67 (s, 2H), 2.05 (d, *J* = 13.9 Hz, 1H), 2.01 (d, *J* = 13.9 Hz, 1H), 1.81 – 1.69 (m, 2H), 1.43 (s, 3H), 1.41 (s, 3H), 1.37 – 1.25 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.89, 134.33, 129.58, 128.21, 128.04, 118.22, 73.09, 52.12, 48.84, 40.94, 30.42, 28.62, 28.58, 26.57, 22.99, 13.92. ESI-MS: Calcd for $C_{18}H_{24}N_2$: [M+H$^+$] 269.2012, found 269.2015.



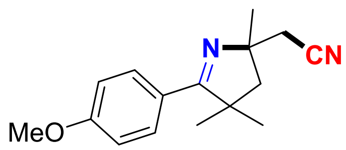
4e: yield: 39%, 22.5 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.27 (m, 1H), 3.01 (d, *J* = 16.5 Hz, 1H), 2.94 (d, *J* = 16.5 Hz, 1H), 2.53 (d, *J* = 13.2 Hz, 1H), 2.47 (d, *J* = 13.2 Hz, 1H), 1.45 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.82, 145.73, 134.11, 129.96, 128.60, 128.32, 128.23, 127.37, 125.52, 117.71, 74.23, 52.47, 52.08, 34.11, 27.44, 27.26. ESI-MS: Calcd for $C_{20}H_{20}N_2$: [M+H$^+$] 289.1699, found 289.1700.



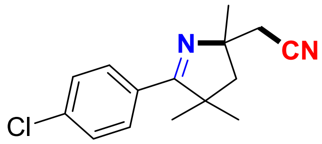
4f: yield: 60%, 38.2 mg; appearance: yellow oil; R_f: 0.1 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 2H), 7.32 (dd, J = 9.2, 6.1 Hz, 3H), 7.20 (dd, J = 8.4, 7.6 Hz, 2H), 6.92 – 6.80 (m, 3H), 4.03 (d, J = 9.0 Hz, 1H), 3.86 (d, J = 9.0 Hz, 1H), 2.84 (d, J = 16.6 Hz, 1H), 2.79 (d, J = 16.6 Hz, 1H), 2.25 (d, J = 13.9 Hz, 1H), 2.02 (d, J = 13.9 Hz, 1H), 1.40 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.64, 158.40, 133.91, 129.87, 129.48, 128.21, 128.11, 121.33, 117.61, 114.52, 73.26, 73.11, 52.43, 47.16, 28.77, 28.44, 28.11. ESI-MS: Calcd for $C_{21}H_{22}N_2O$: [M+H$^+$] 319.1805, found 319.1811.



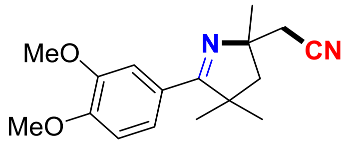
4g: yield: 72%, 34.6 mg; appearance: yellow oil; R_f: 0.1 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 2.68 (d, J = 16.5 Hz, 1H), 2.64 (d, J = 16.5 Hz, 1H), 2.37 (s, 3H), 2.11 (d, J = 13.4 Hz, 1H), 1.98 (d, J = 13.4 Hz, 1H), 1.48 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.27, 139.91, 131.20, 128.94, 128.08, 118.08, 69.79, 52.21, 51.63, 32.16, 29.05, 28.65, 28.40, 21.30. ESI-MS: Calcd for $C_{16}H_{20}N_2$: [M+H$^+$] 241.1699, found 241.1700.



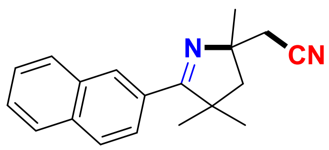
4h: yield: 62%, 31.8 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 2.68 (d, *J* = 16.7 Hz, 1H), 2.61 (d, *J* = 16.7 Hz, 1H), 2.11 (d, *J* = 13.4 Hz, 1H), 1.97 (d, *J* = 13.4 Hz, 1H), 1.48 (s, 3H), 1.47 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.40, 160.96, 129.80, 126.30, 118.10, 113.62, 69.51, 55.29, 51.97, 51.88, 32.18, 29.15, 28.65, 28.50. ESI-MS: Calcd for $C_{16}H_{20}N_2O$: [M+H$^+$] 257.1648, found 257.1650.



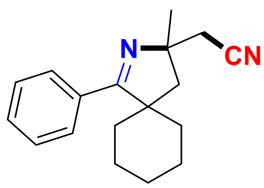
4i: yield: 75%, 39.0 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.38 – 7.32 (m, 2H), 2.68 (d, J = 16.5 Hz, 1H), 2.64 (d, J = 16.5 Hz, 1H), 2.12 (d, J = 13.5 Hz, 1H), 1.99 (d, J = 13.5 Hz, 1H), 1.47 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.42, 135.99, 132.46, 129.49, 128.50, 117.91, 70.05, 52.25, 51.44, 32.08, 28.92, 28.58, 28.20. ESI-MS: Calcd for $C_{15}H_{17}ClN_2$: [M+H$^+$] 261.1153, found 261.1152.



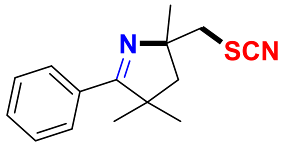
4j: yield: 83%, 47.5 mg; appearance: light green oil; R_f: 0.2 (PE:EA, 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 2.0 Hz, 1H), 7.31 (dd, J = 8.4, 2.0 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 2.67 (s, 2H), 2.12 (d, J = 13.4 Hz, 1H), 1.99 (d, J = 13.4 Hz, 1H), 1.49 (s, 3H), 1.48 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.45, 150.68, 148.77, 126.50, 121.06, 118.14, 111.64, 110.27, 69.51, 55.95, 55.91, 51.99, 32.18, 29.29, 28.64. ESI-MS: Calcd for $C_{17}H_{22}N_2O_2$: [M+H$^+$] 287.1754, found 287.1753.



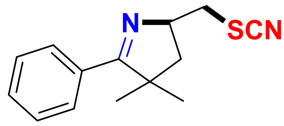
4k: yield: 67%, 37.0 mg; appearance: brown oil; R_f: 0.2 (PE:EA, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.90 – 7.83 (m, 4H), 7.52 – 7.50 (m, 2H), 2.72 (s, 2H), 2.18 (d, J = 13.4 Hz, 1H), 2.04 (d, J = 13.4 Hz, 1H), 1.55 (s, 3H), 1.53 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.30, 133.82, 132.74, 131.43, 128.61, 127.92, 127.83, 127.58, 126.92, 126.32, 125.57, 118.03, 70.01, 52.40, 51.65, 32.13, 29.15, 28.64, 28.47. ESI-MS: Calcd for $C_{19}H_{20}N_2$: [M+H$^+$] 277.1699, found 277.1701.



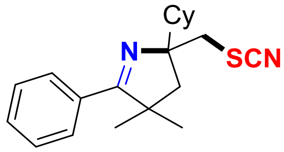
4l: yield: 75%, 39.9 mg; appearance: green oil; R_f: 0.2 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.38 (dt, *J* = 2.7, 2.2 Hz, 3H), 2.68 (s, 2H), 2.09 (d, *J* = 13.7 Hz, 1H), 2.03 (d, *J* = 13.7 Hz, 1H), 1.83 – 1.54 (m, 8H), 1.48 (s, 3H), 1.43 – 1.31 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.74, 135.19, 129.11, 128.09, 128.02, 118.12, 70.79, 58.38, 44.95, 35.42, 35.11, 32.39, 29.34, 25.23, 23.07, 22.97. ESI-MS: Calcd for $C_{18}H_{22}N_2$: [M+H$^+$] 267.1856, found 267.1857.



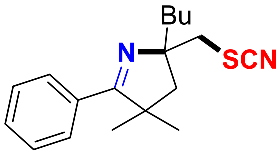
5a: yield: 80%, 41.3 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.42 – 7.36 (m, 3H), 3.43 (d, *J* = 12.7 Hz, 1H), 3.19 (d, *J* = 12.7 Hz, 1H), 2.16 (d, *J* = 13.5 Hz, 1H), 1.94 (d, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.49 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.88, 133.97, 129.84, 128.28, 128.06, 113.49, 71.74, 52.38, 50.61, 46.97, 29.64, 29.11, 28.01. ESI-MS: Calcd for $C_{15}H_{18}N_2S$: [M+H$^+$] 259.1263, found 259.1264.



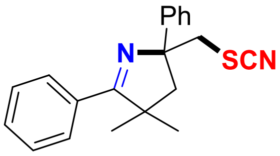
5b: yield: 65%, 31.7 mg; appearance: green oil; R_f: 0.2 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.44 – 7.36 (m, 3H), 4.39 (m, 1H), 3.33 (s, 1H), 3.31 (s, 1H), 2.23 (dd, *J* = 12.7, 6.8 Hz, 1H), 1.75 (dd, *J* = 12.7, 9.1 Hz, 1H), 1.41 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.77, 133.86, 129.99, 128.28, 127.92, 112.82, 67.14, 51.39, 46.63, 39.85, 26.99, 25.94. ESI-MS: Calcd for $C_{14}H_{16}N_2S$: [M+H$^+$] 245.1107, found 245.1108.



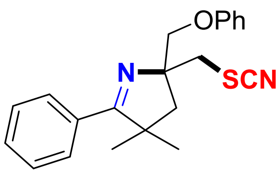
5c: yield: 75%, 48.9 mg; appearance: light yellow oil; R_f: 0.4 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.43 – 7.35 (m, 3H), 3.60 (d, *J* = 12.2 Hz, 1H), 3.23 (d, *J* = 12.2 Hz, 1H), 2.08 (d, *J* = 14.1 Hz, 1H), 1.89 (d, *J* = 14.1 Hz, 1H), 1.85 – 1.60 (m, 7H), 1.44 (s, 3H), 1.40 (s, 3H), 1.33 – 1.14 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.64, 134.19, 129.69, 128.26, 128.12, 113.90, 77.46, 52.05, 45.66, 45.57, 45.22, 28.54, 28.40, 27.98, 27.58, 26.42, 26.38, 26.35. ESI-MS: Calcd for $C_{20}H_{26}N_2S$: [M+H$^+$] 327.1889, found 327.1888.



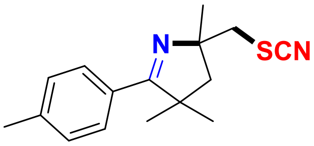
5d: yield: 54%, 32.4 mg; appearance: yellow oil; R_f: 0.3 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.39 (d, J = 7.2 Hz, 3H), 3.46 (d, J = 12.5 Hz, 1H), 3.22 (d, J = 12.5 Hz, 1H), 2.01 (s, 2H), 1.80 (dd, J = 12.3, 3.3 Hz, 1H), 1.71 (dd, J = 12.3, 3.3 Hz, 1H), 1.45 (s, 3H), 1.41 (s, 3H), 1.37 – 1.29 (m, 4H), 0.93 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.76, 134.06, 129.70, 128.21, 128.06, 113.59, 74.63, 52.12, 48.16, 45.61, 40.04, 28.79, 28.32, 26.54, 23.01, 13.88. ESI-MS: Calcd for $C_{18}H_{24}N_2S$: [M+H$^+$] 301.1733, found 301.1733.



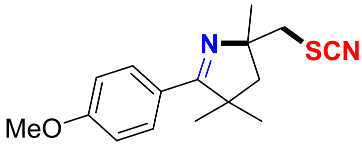
5e: yield: 35%, 22.4 mg; appearance: yellow oil; R_f: 0.3 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 6.0 Hz, 2H), 7.47 – 7.42 (m, 5H), 7.36 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 7.2 Hz, 1H), 3.72 (d, J = 12.5 Hz, 1H), 3.45 (d, J = 12.5 Hz, 1H), 2.50 (d, J = 13.2 Hz, 1H), 2.45 (d, J = 13.2 Hz, 1H), 1.45 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.86, 145.31, 133.84, 130.13, 128.61, 128.36, 128.31, 127.47, 125.89, 113.54, 76.05, 52.11, 52.06, 48.38, 27.41, 27.35. ESI-MS: Calcd for $C_{20}H_{20}N_2S$: [M+H$^+$] 321.1420, found 321.1421.



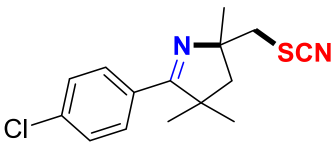
5f: yield: 73%, 51.1 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.45 – 7.40 (m, 3H), 7.33 – 7.29 (m, 2H), 7.02 – 6.92 (m, 3H), 4.25 (d, J = 9.1 Hz, 1H), 3.94 (d, J = 9.1 Hz, 1H), 3.65 (d, J = 12.9 Hz, 1H), 3.44 (d, J = 12.9 Hz, 1H), 2.35 (d, J = 14.0 Hz, 1H), 2.14 (d, J = 14.0 Hz, 1H), 1.54 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.61, 158.37, 133.66, 130.14, 129.54, 128.33, 128.24, 121.38, 114.51, 113.31, 74.91, 72.48, 52.41, 47.12, 43.21, 29.07, 28.37. ESI-MS: Calcd for $C_{21}H_{22}N_2OS$: [M+H$^+$] 351.1526, found 351.1527.



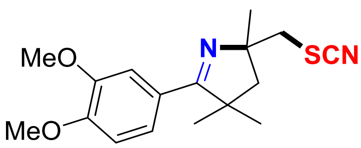
5g: yield: 67%, 36.5 mg; appearance: green oil; R_f: 0.3 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.43 (d, *J* = 12.6 Hz, 1H), 3.19 (d, *J* = 12.6 Hz, 1H), 2.37 (s, 3H), 2.14 (d, *J* = 13.4 Hz, 1H), 1.93 (d, *J* = 13.4 Hz, 1H), 1.50 (s, 3H), 1.48 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.46, 140.08, 130.99, 128.98, 128.12, 113.57, 71.47, 52.25, 50.87, 47.12, 29.22, 28.15, 28.01, 21.30. ESI-MS: Calcd for $C_{16}H_{20}N_2S$: [M+H$^+$] 273.1420, found 273.1419.



5h: yield: 55%, 31.7 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 3.43 (d, *J* = 12.6 Hz, 1H), 3.17 (d, *J* = 12.6 Hz, 1H), 2.13 (d, *J* = 13.4 Hz, 1H), 1.92 (d, *J* = 13.4 Hz, 1H), 1.51 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.53, 161.02, 129.86, 126.12, 113.64, 71.17, 55.28, 52.02, 51.12, 47.19, 29.33, 28.23, 28.00. ESI-MS: Calcd for $C_{16}H_{20}N_2OS$: [M+H$^+$] 289.1369, found 289.1370.

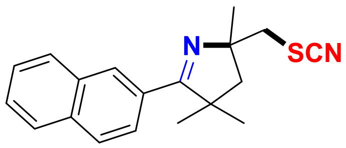


5i: yield: 68%, 39.7 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 3.43 (d, *J* = 12.8 Hz, 1H), 3.17 (d, *J* = 12.8 Hz, 1H), 2.15 (d, *J* = 13.5 Hz, 1H), 1.94 (d, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.48 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.48, 136.16, 132.28, 129.57, 128.57, 113.37, 71.83, 52.28, 50.80, 46.87, 29.11, 28.00. ESI-MS: Calcd for $C_{15}H_{17}ClN_2S$: [M+H$^+$] 293.0874, found 293.0875.

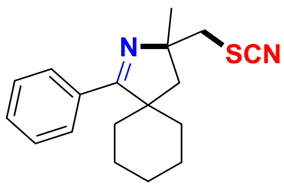


5j: yield: 81%, 51.5 mg; appearance: green oil; R_f: 0.2 (PE:EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 2.0 Hz, 1H), 7.32 (dd, *J* =

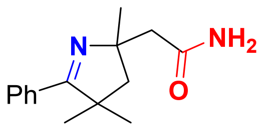
8.4, 2.0 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.44 (d, *J* = 12.8 Hz, 1H), 3.15 (d, *J* = 12.8 Hz, 1H), 2.12 (d, *J* = 13.4 Hz, 1H), 1.93 (d, *J* = 13.4 Hz, 1H), 1.54 (s, 3H), 1.49 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.47, 150.82, 148.92, 126.42, 121.03, 113.56, 111.96, 110.24, 71.23, 56.01, 55.91, 52.00, 51.36, 47.12, 29.54, 28.36, 28.02. ESI-MS: Calcd for $C_{17}H_{22}N_2O_2S$: [M+H$^+$] 319.1475, found 319.1477.



5k: yield: 50%, 32.4 mg; appearance: brown oil; R_f: 0.3 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.90 – 7.83 (m, 4H), 7.55 – 7.50 (m, 2H), 3.48 (d, *J* = 12.7 Hz, 1H), 3.24 (d, *J* = 12.7 Hz, 1H), 2.21 (d, *J* = 13.4 Hz, 1H), 2.00 (d, *J* = 13.4 Hz, 1H), 1.60 (s, 3H), 1.54 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.51, 133.95, 132.81, 131.30, 128.71, 128.03, 128.00, 127.64, 127.05, 126.38, 125.63, 113.55, 71.79, 52.51, 51.02, 47.10, 29.39, 28.33, 28.07. ESI-MS: Calcd for $C_{19}H_{20}N_2S$: [M+H$^+$] 309.1420, found 309.1421.

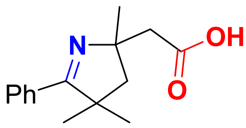


5l: yield: 80%, 47.7 mg; appearance: yellow oil; R_f: 0.2 (PE:EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.39 (dt, *J* = 5.7, 2.8 Hz, 3H), 3.45 (d, *J* = 12.7 Hz, 1H), 3.21 (d, *J* = 12.7 Hz, 1H), 2.08 (d, *J* = 13.6 Hz, 1H), 2.03 (d, *J* = 13.6 Hz, 1H), 1.85 – 1.55 (m, 9H), 1.49 (s, 3H), 1.32 – 1.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.92, 135.04, 129.26, 128.14, 128.06, 113.54, 72.53, 58.44, 47.08, 44.11, 35.28, 35.19, 28.83, 25.26, 23.09, 22.99. ESI-MS: Calcd for $C_{18}H_{22}N_2S$: [M+H$^+$] 299.1576, found 299.1577.

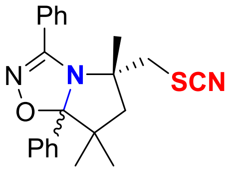


7: yield: 75%, 36.6 mg; appearance: yellow oil; R_f: 0.5 (pure EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.60 (s, 1H), 7.43 – 7.37 (m, 3H), 5.58 (s, 1H), 2.57 (d, *J* = 14.8 Hz, 1H), 2.51 (d, *J* = 14.8 Hz, 1H), 2.00 (d, *J* = 13.3 Hz, 1H), 1.95 (d, *J* = 13.3 Hz, 1H), 1.45 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H).

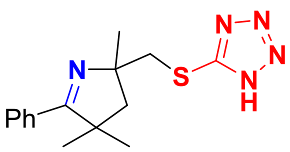
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.04, 173.86, 134.29, 129.76, 128.28, 127.97, 69.83, 53.45, 51.07, 50.28, 28.84, 28.68, 28.00. ESI-MS: Calcd for $C_{15}H_{20}N_2O$: [M+H$^+$] 245.1648, found 245.1649.



8: yield: 83%, 40.7 mg; appearance: slight yellow oil; R_f: 0.5 (PE:EA, 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.72 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.49 – 7.38 (m, 3H), 2.75 (d, *J* = 15.5 Hz, 1H), 2.56 (d, *J* = 15.5 Hz, 1H), 2.03 (d, *J* = 13.3 Hz, 1H), 1.97 (d, *J* = 13.3 Hz, 1H), 1.51 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.91, 172.47, 132.64, 130.64, 128.48, 128.14, 69.05, 53.35, 51.30, 48.99, 28.80, 28.76, 27.67. ESI-MS: Calcd for $C_{15}H_{19}NO_2$: [M+H$^+$] 246.1489, found 246.1487.

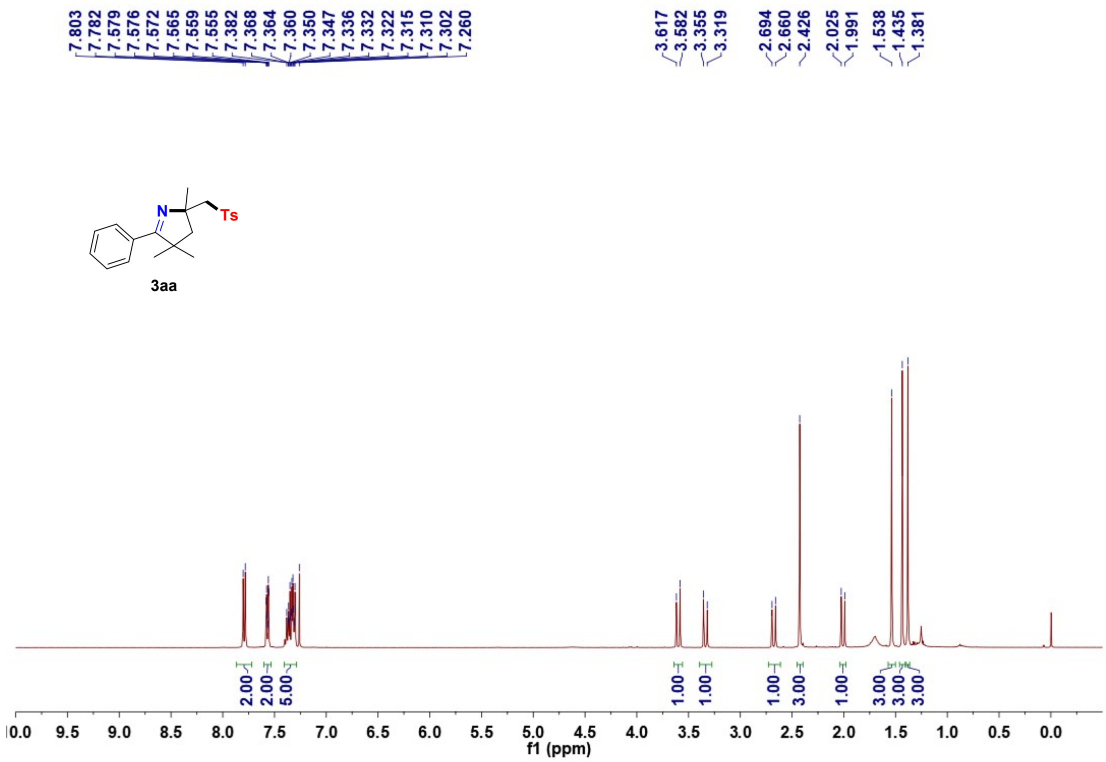


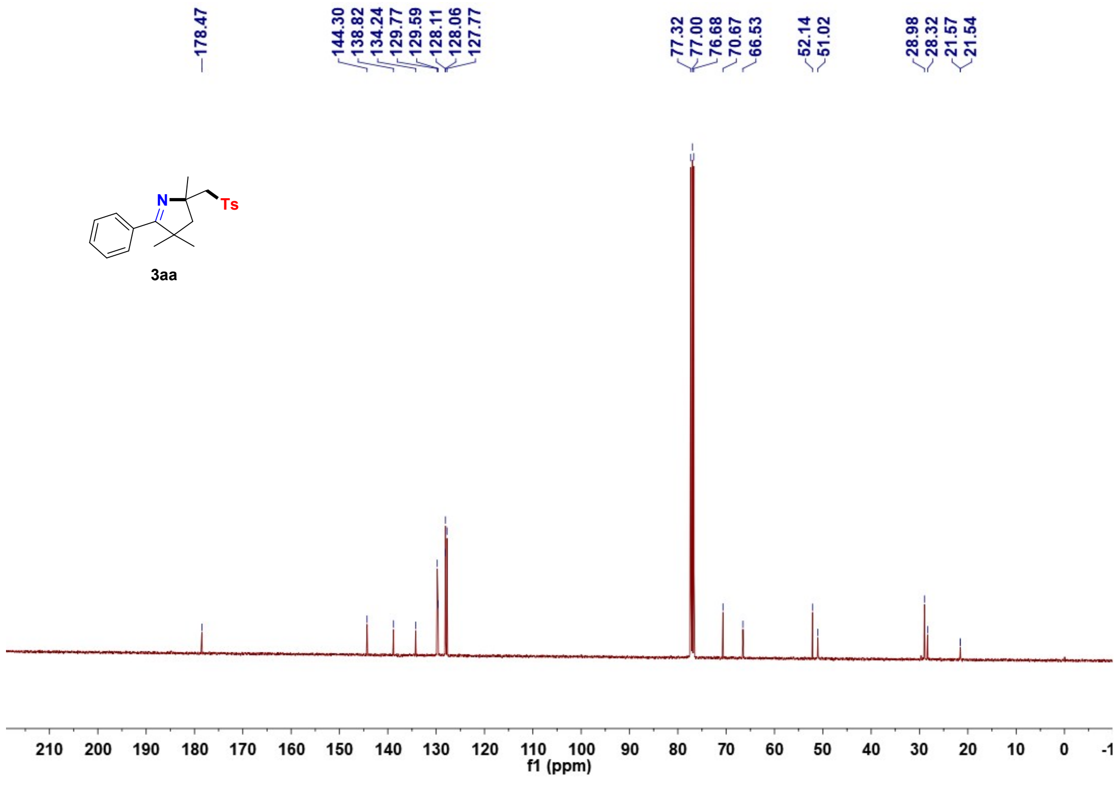
9: yield: 80%, 75.4 mg; appearance: white solid; M.p.:151-155ºC. R_f: 0.4 (PE:EA, 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.77 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.70 (dd, *J* = 8.0, 1.5 Hz, 4H), 7.43 (dt, *J* = 7.2, 3.8 Hz, 7H), 7.36 – 7.28 (m, 7H), 3.62 (d, *J* = 13.3 Hz, 1H), 3.38 (d, *J* = 13.3 Hz, 1H), 3.08 (d, *J* = 12.9 Hz, 1H), 2.78 (d, *J* = 12.9 Hz, 1H), 2.42 (t, *J* = 12.9 Hz, 2H), 2.19 (d, *J* = 13.7 Hz, 1H), 2.09 (d, *J* = 12.9 Hz, 1H), 1.78 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.21 (s, 3H), 0.88 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.73, 159.31, 139.61, 139.45, 131.40, 131.01, 129.22, 129.02, 128.52, 128.47, 128.42, 128.01, 127.68, 127.61, 127.53, 125.93, 125.91, 114.38, 114.16, 112.58, 112.34, 66.74, 66.41, 53.71, 52.00, 46.15, 45.32, 43.53, 43.46, 28.86, 28.63, 28.48, 26.01, 24.84, 24.53. ESI-MS: Calcd for $C_{22}H_{23}N_3OS$: [M+H$^+$] 378.1635, found 378.1632.

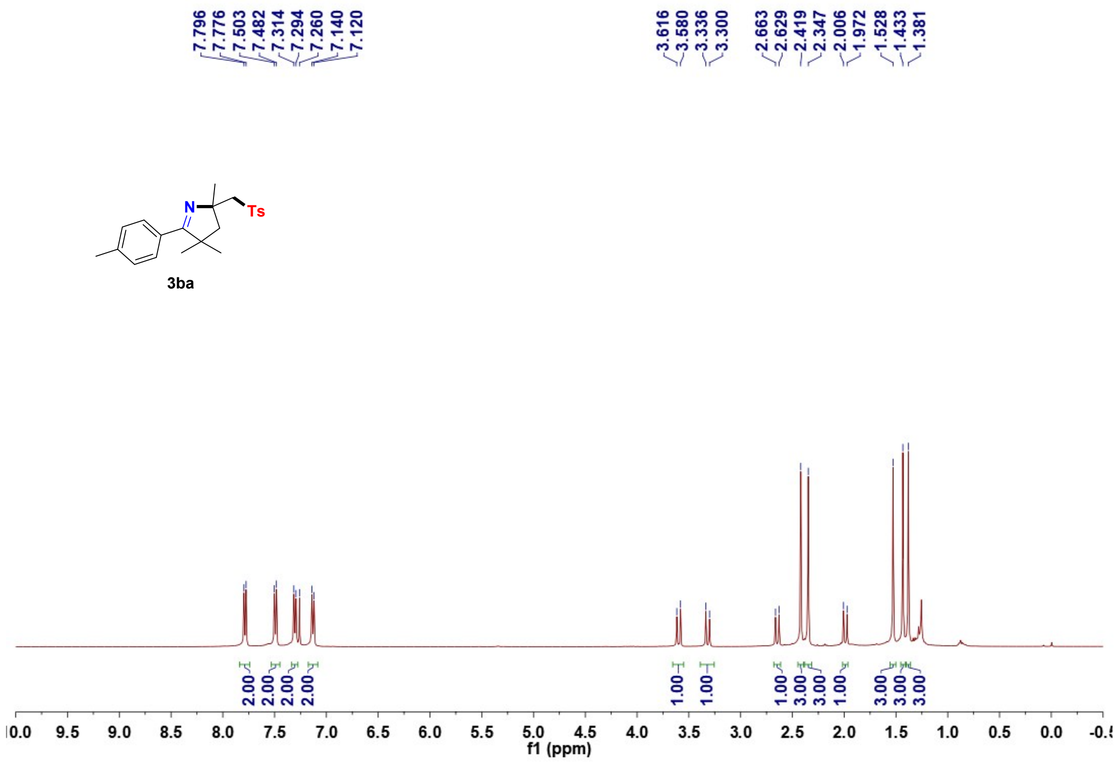


10: yield: 78%, 47.0 mg; appearance: white solid; M.p.:201-206 ºC. R_f: 0.9 (pure EA). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.52 – 7.43 (m, 3H), 7.00 (s, 1H), 3.29 (d, *J* = 15.0 Hz, 1H), 3.21 (d, *J* = 15.0 Hz, 1H), 2.13 (d, *J* = 13.3 Hz, 1H), 2.07 (d, *J* = 13.3 Hz, 1H), 1.57 (s, 3H), 1.52 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.05, 154.27, 132.69, 130.87, 128.89, 127.85, 71.50, 52.37, 51.60, 45.36, 28.59, 28.37, 27.43. ESI-MS: Calcd for $C_{15}H_{19}N_5S$: [$M+H^+$] 302.1434, found 302.1438.

NMR Spectra:



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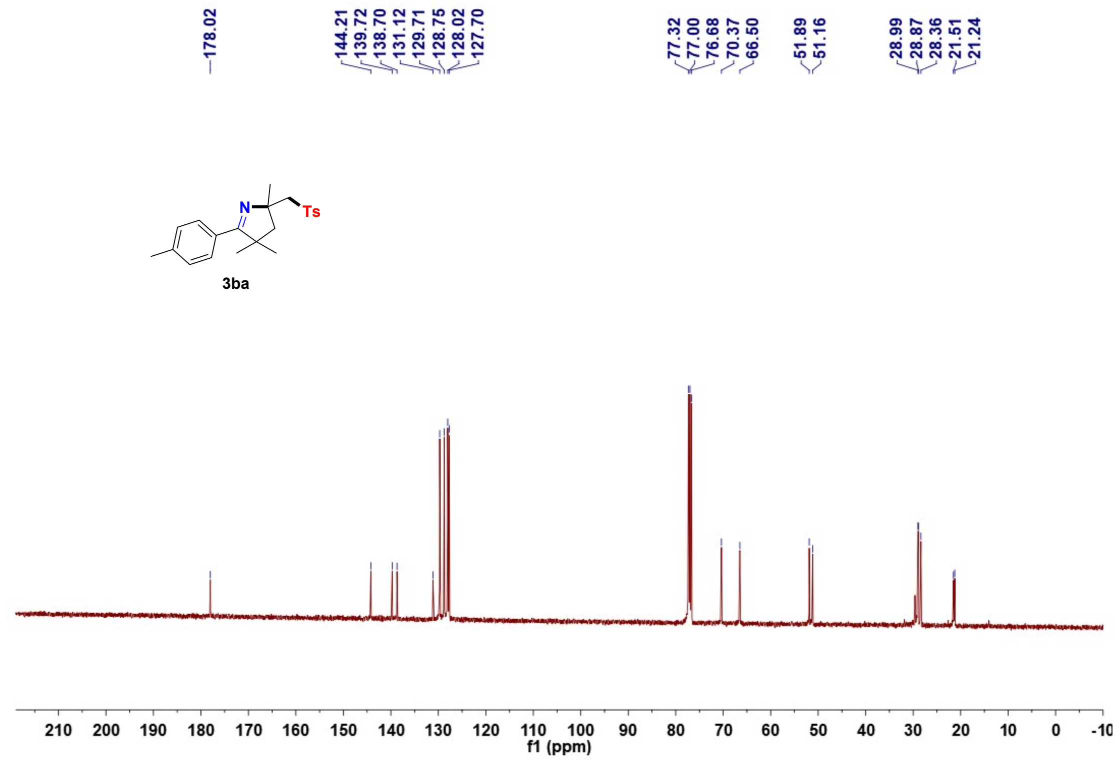
f1 (ppm)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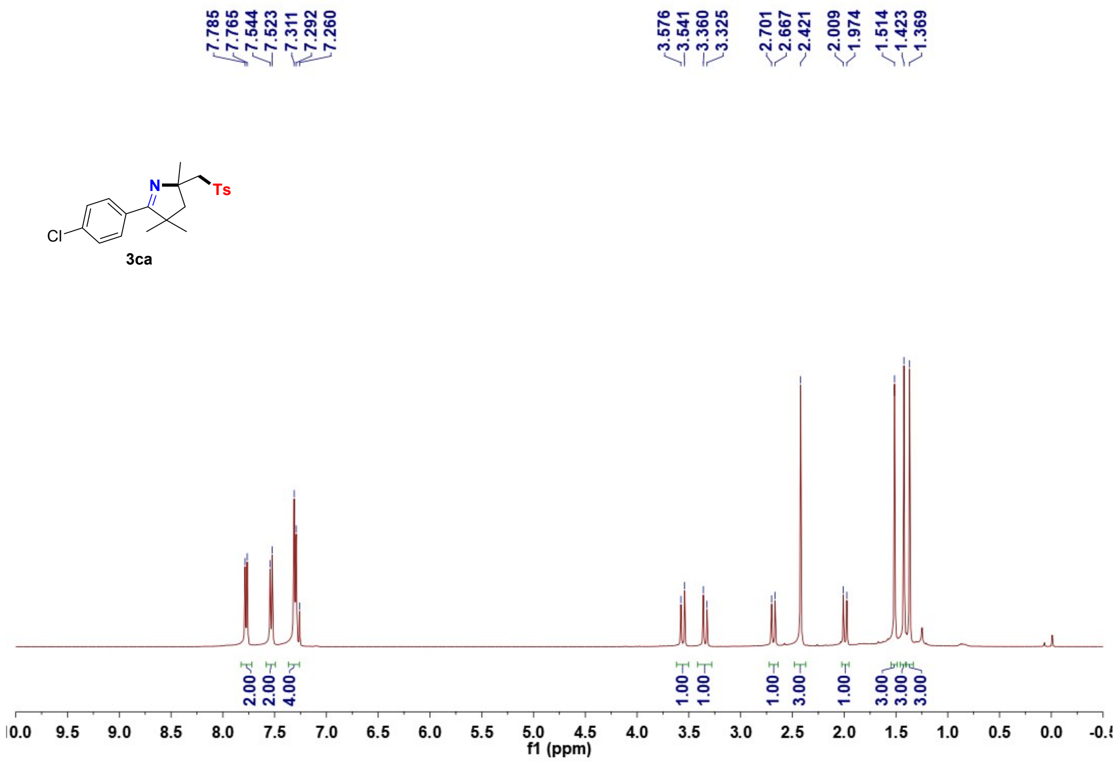

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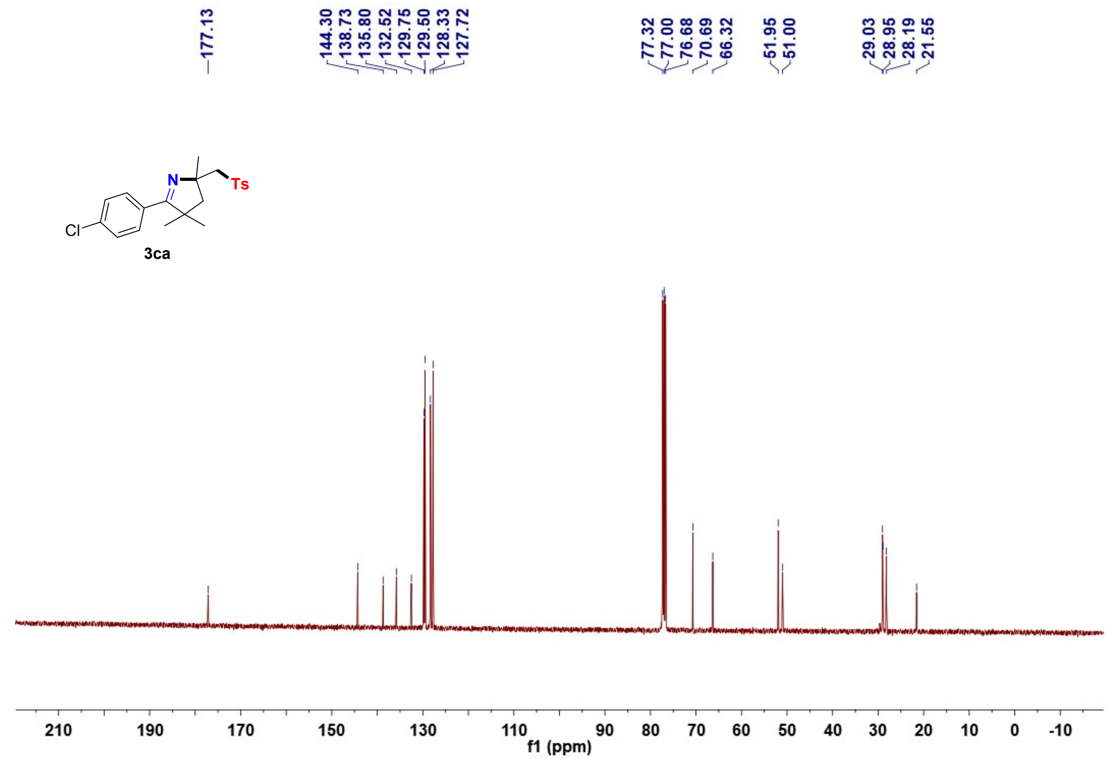

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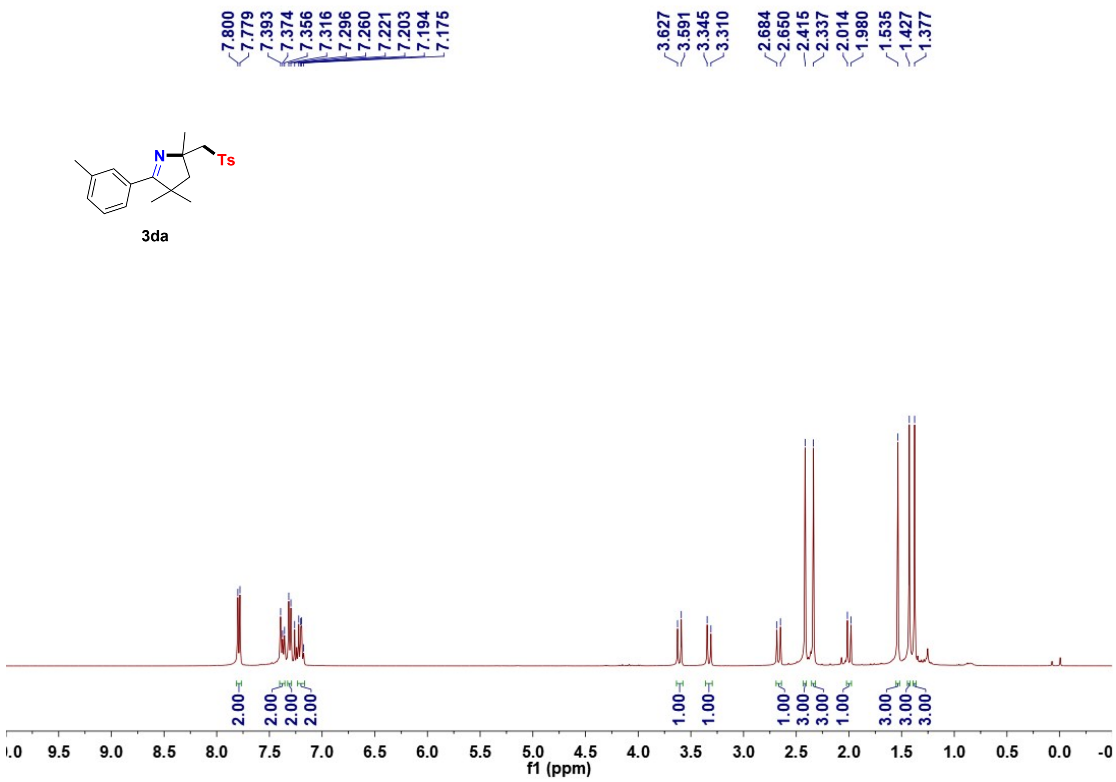
f1 (ppm)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2.415
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1.535
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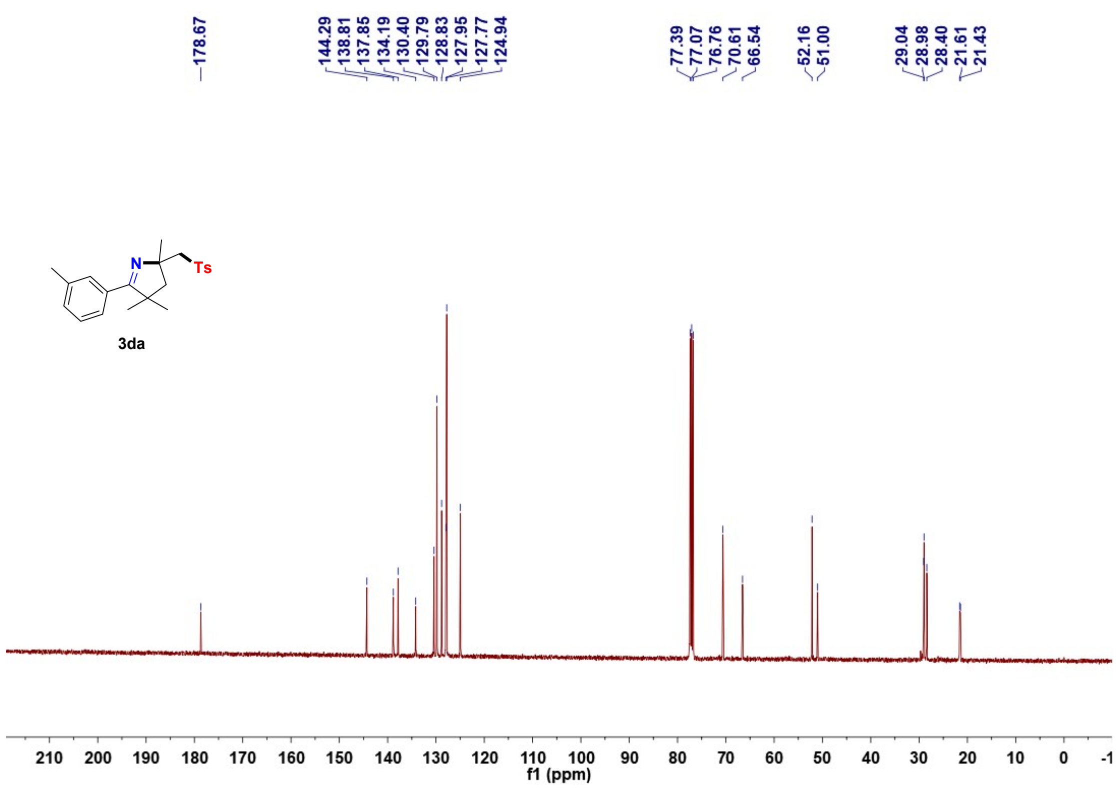
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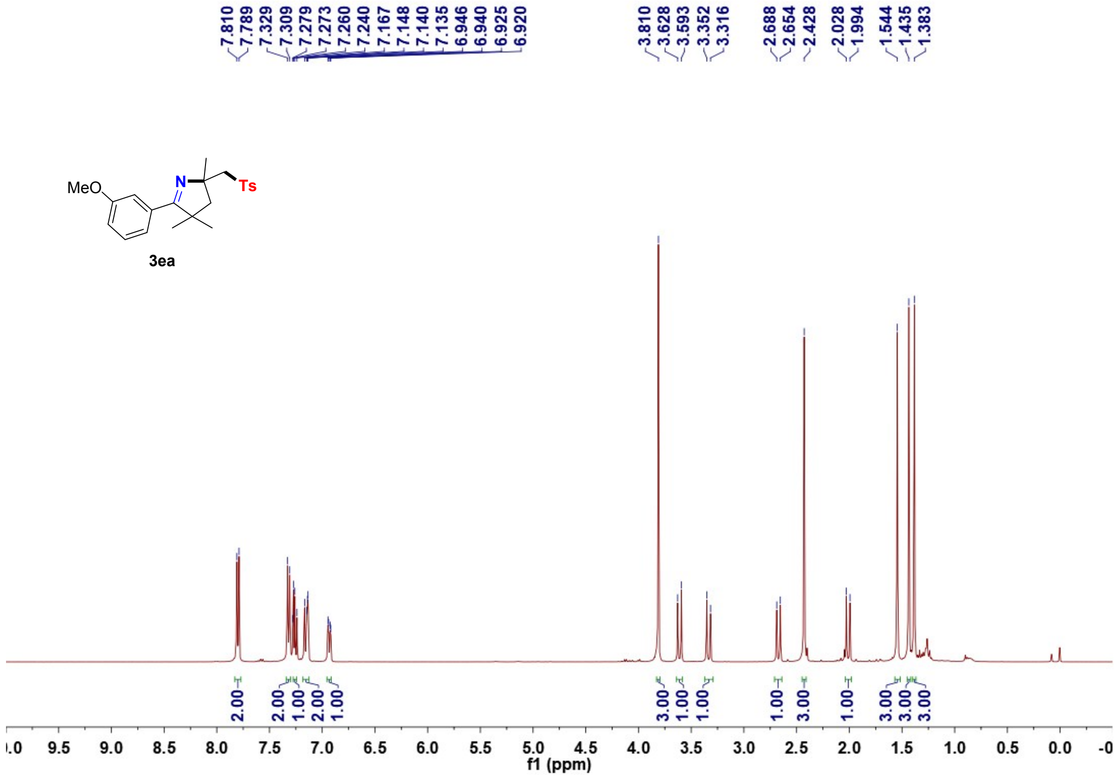

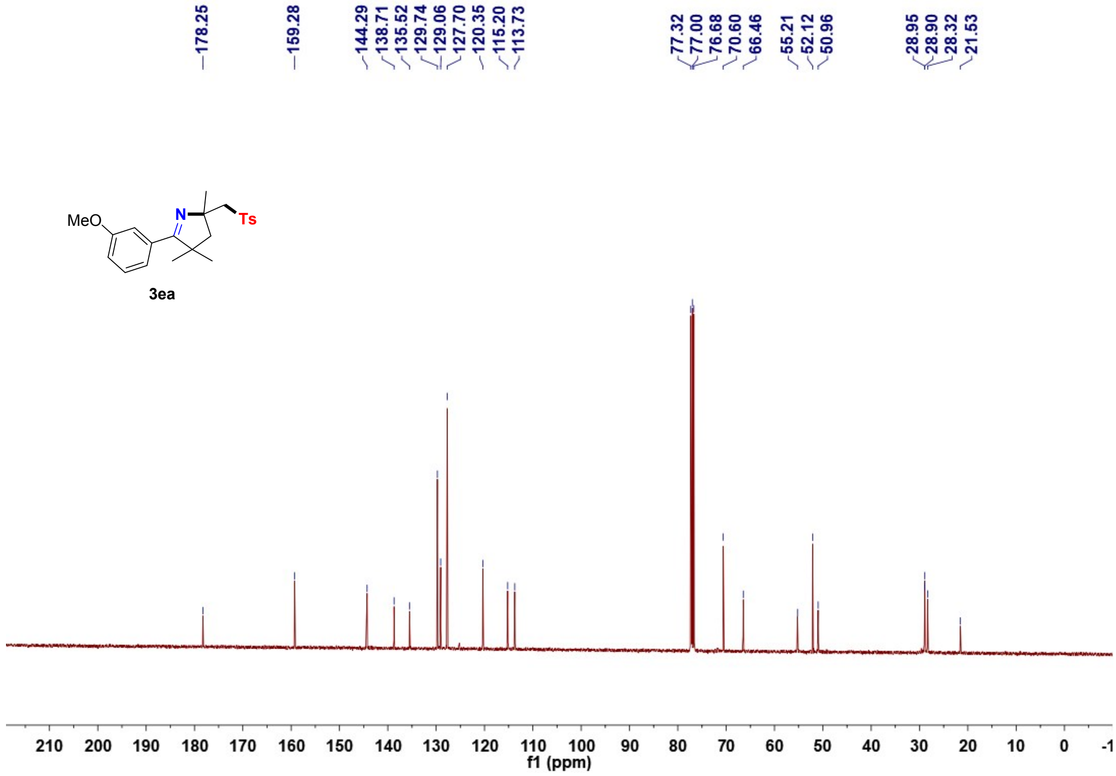

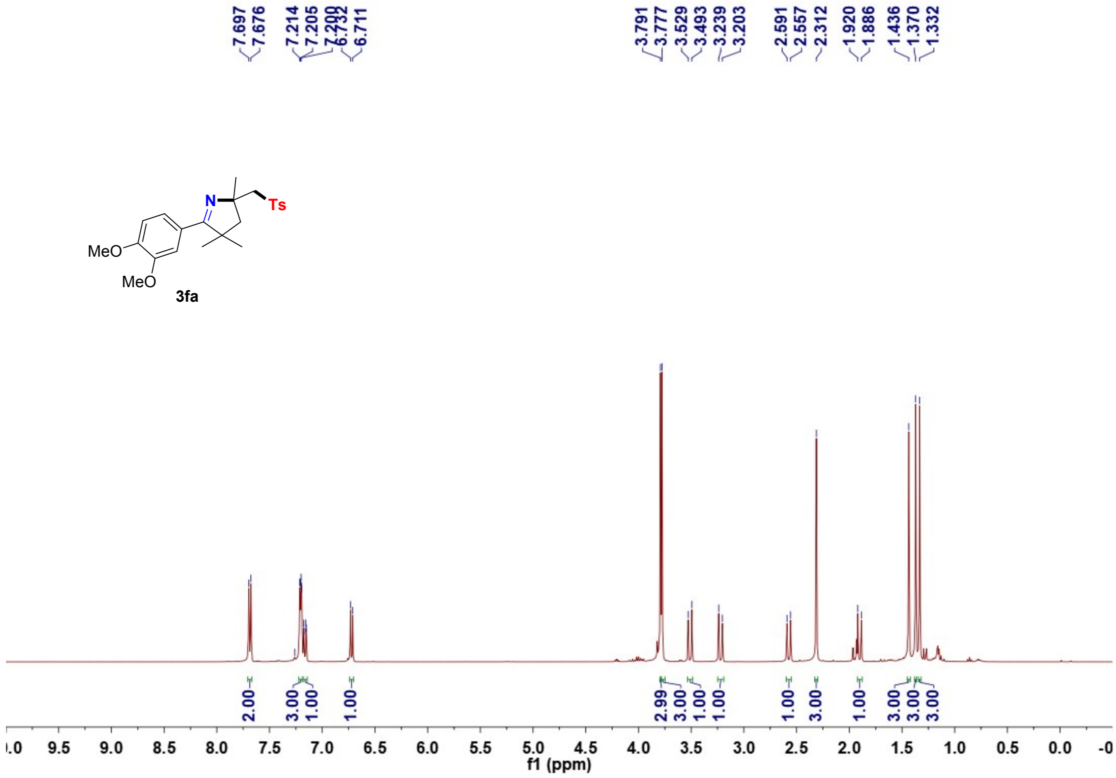
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1.332
N
Ts
MeO
MeO
3fa
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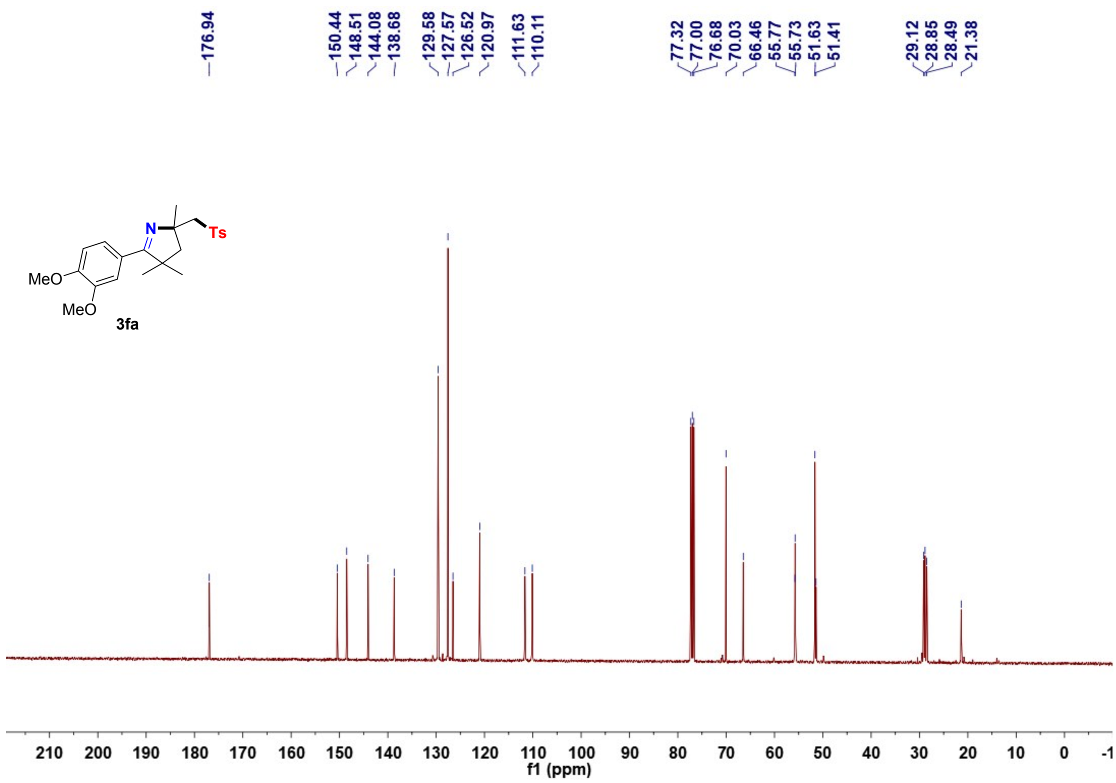
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Ts
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MeO
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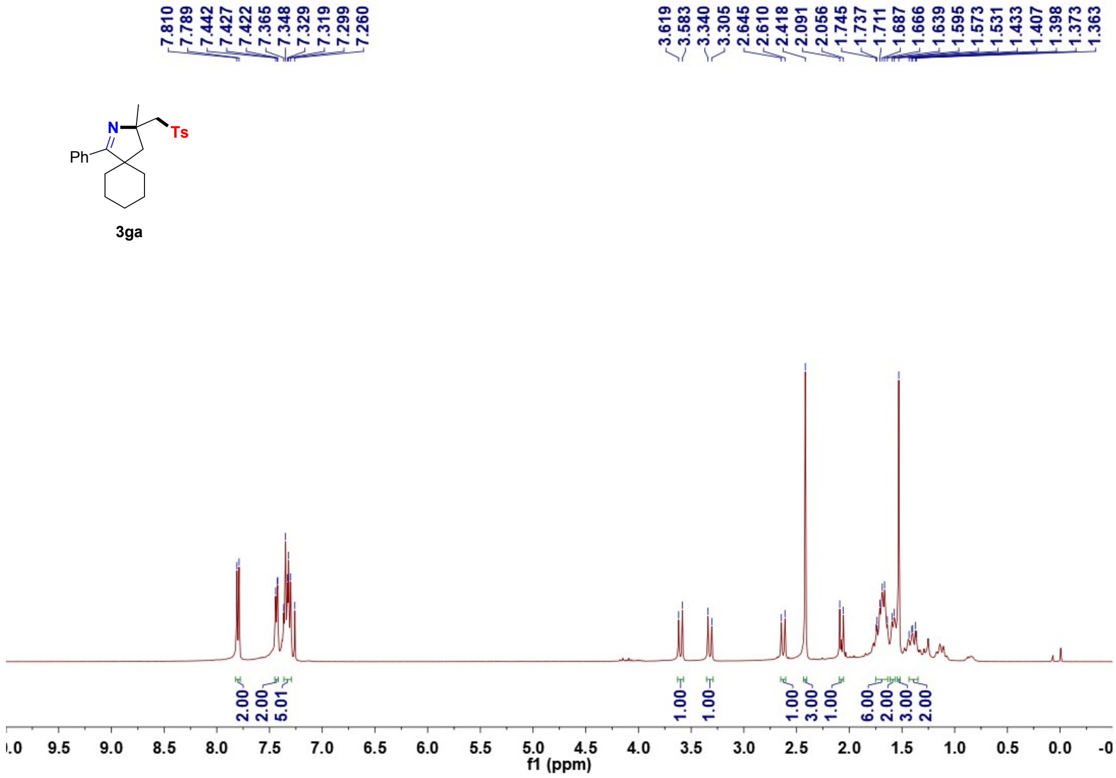
f1 (ppm)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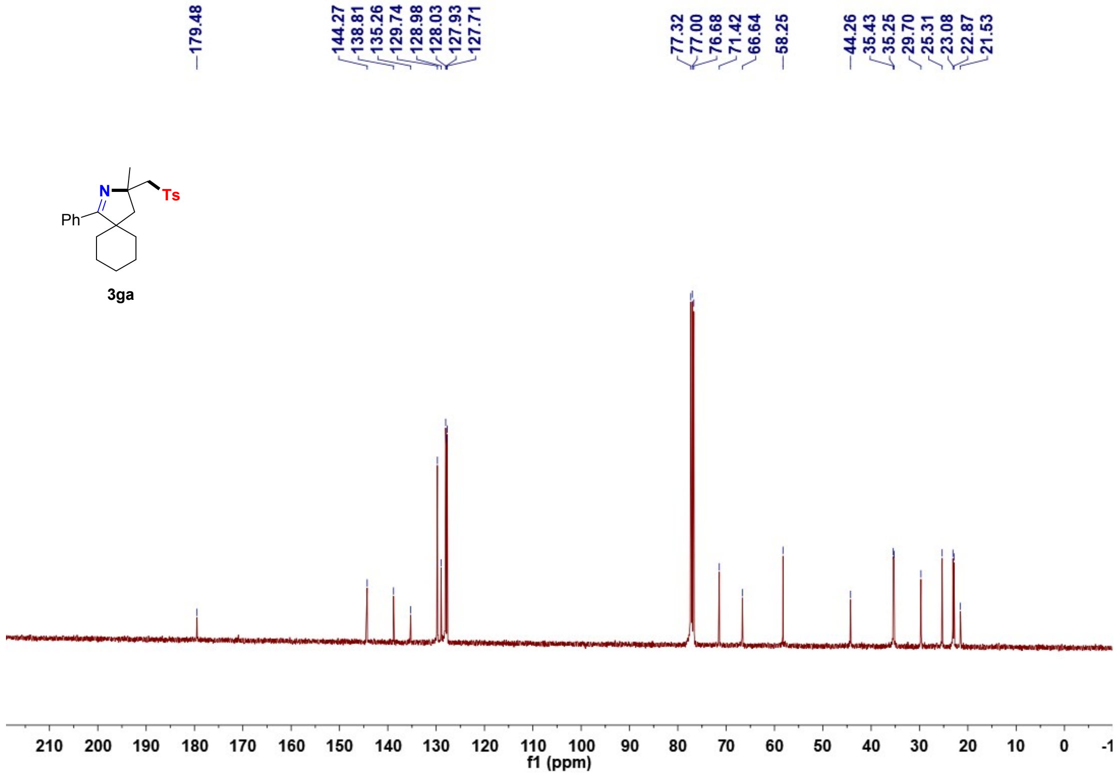
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77.00
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71.42
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58.25
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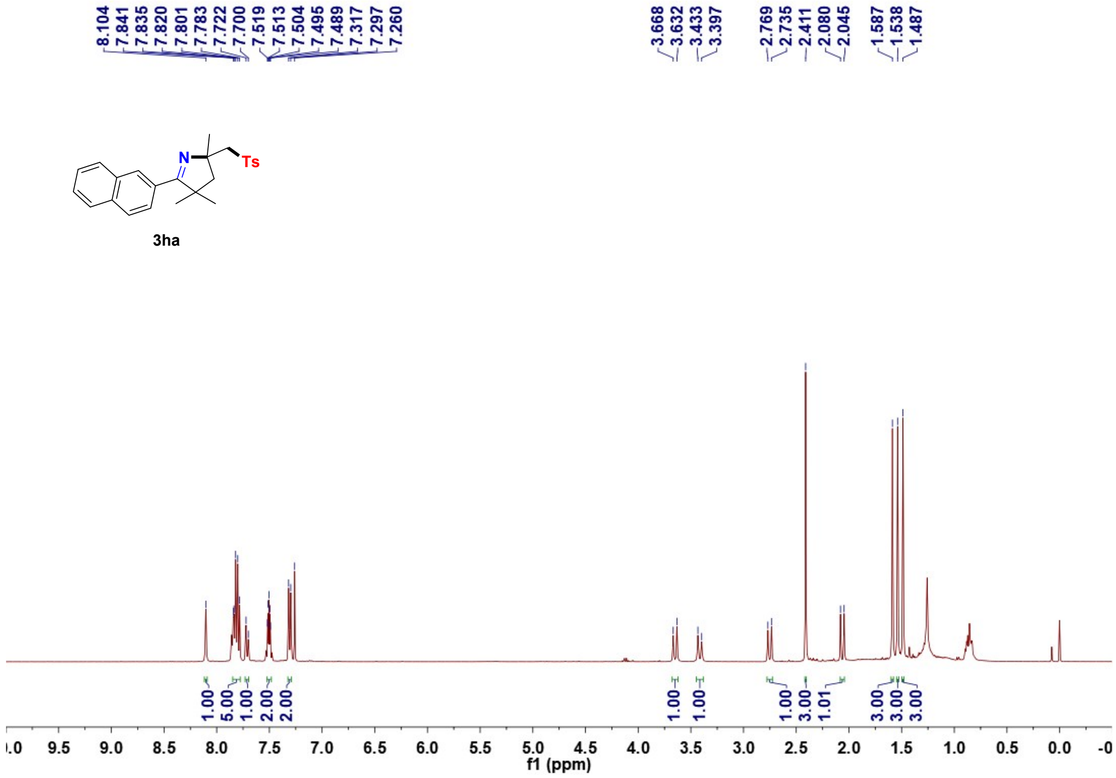
21.53
N
Ts
Ph
3ga
f1 (ppm)



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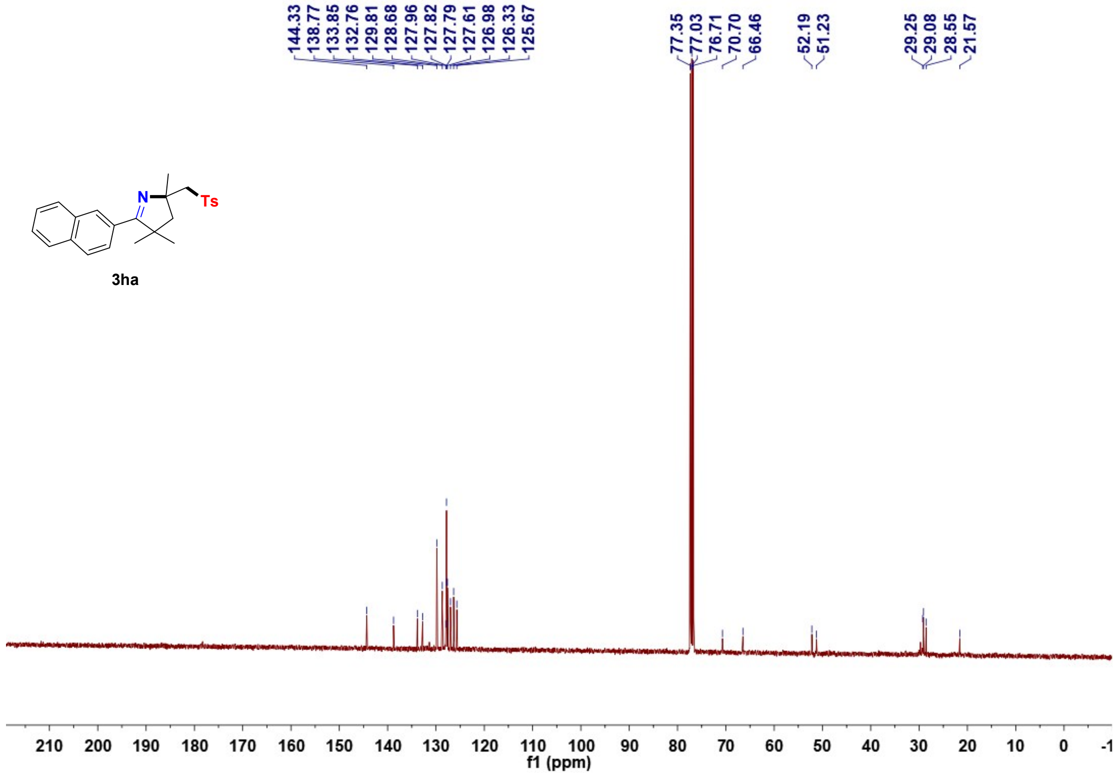

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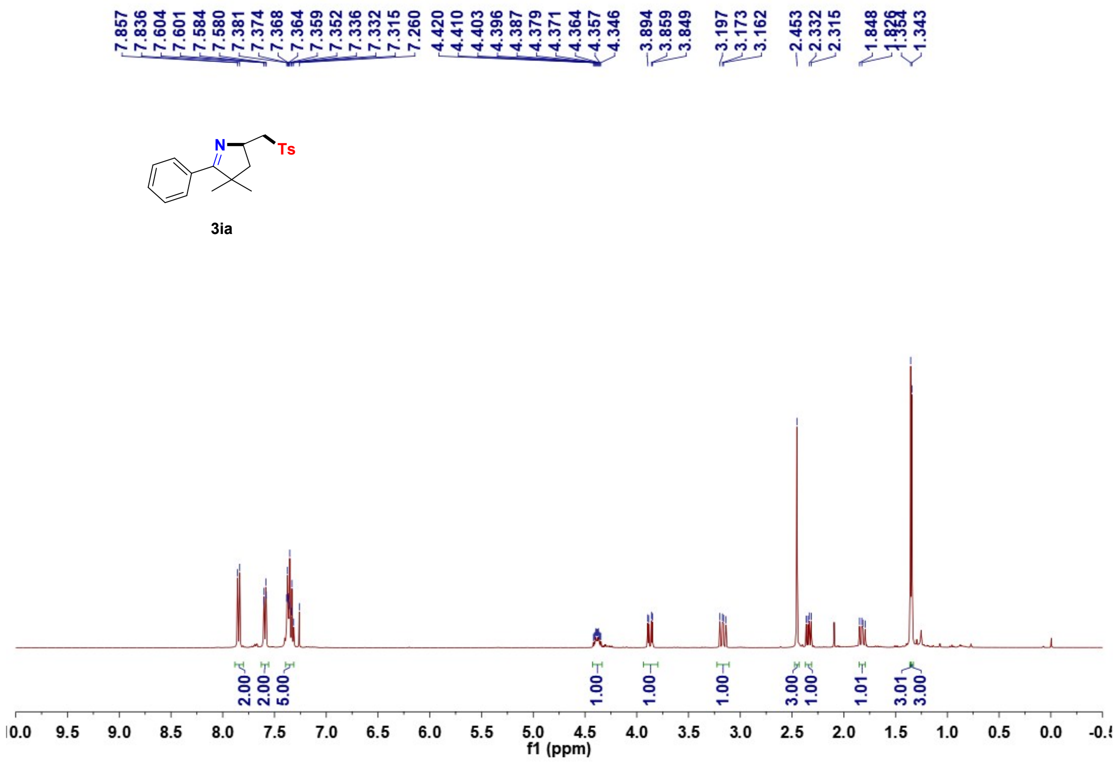
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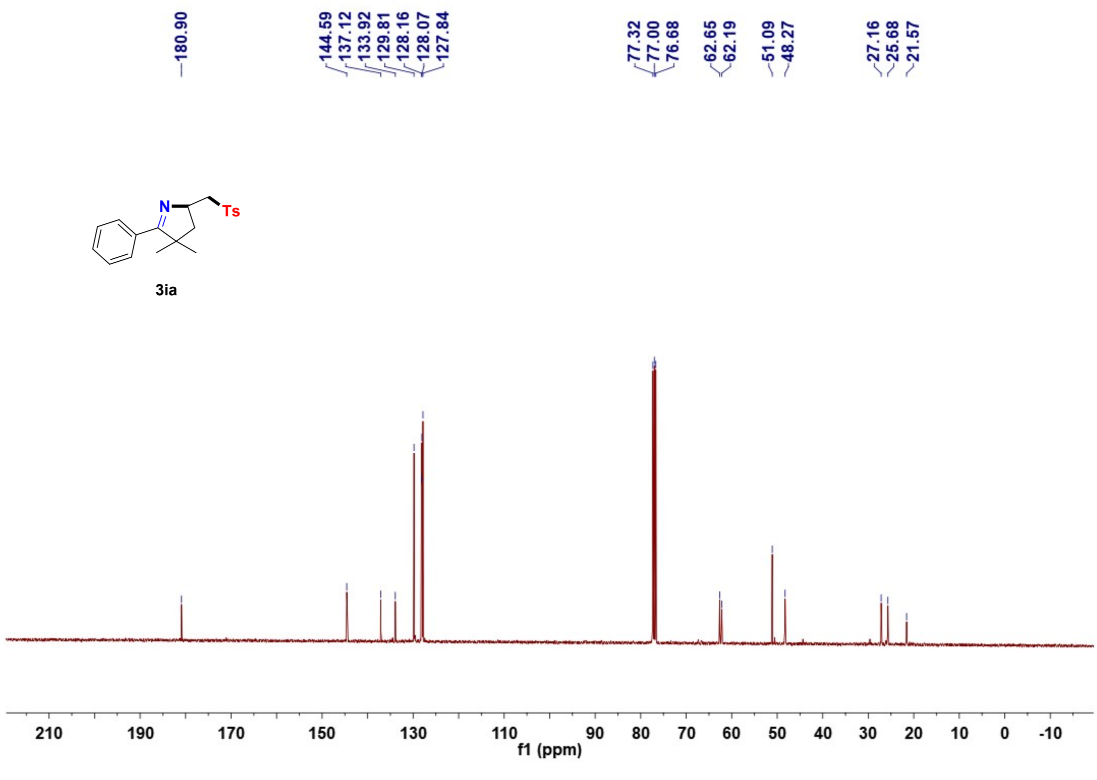
3.894 3.859 3.849
3.197 3.173 3.162
2.453 2.332 2.315
1.848 1.826 1.354 1.343
N
Ts
3ia
2.00 2.00 5.00 1.00 1.00 1.00 3.00 1.00 1.01 3.01 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.32 77.00 76.68
62.65 62.19
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27.16 25.68 21.57
N
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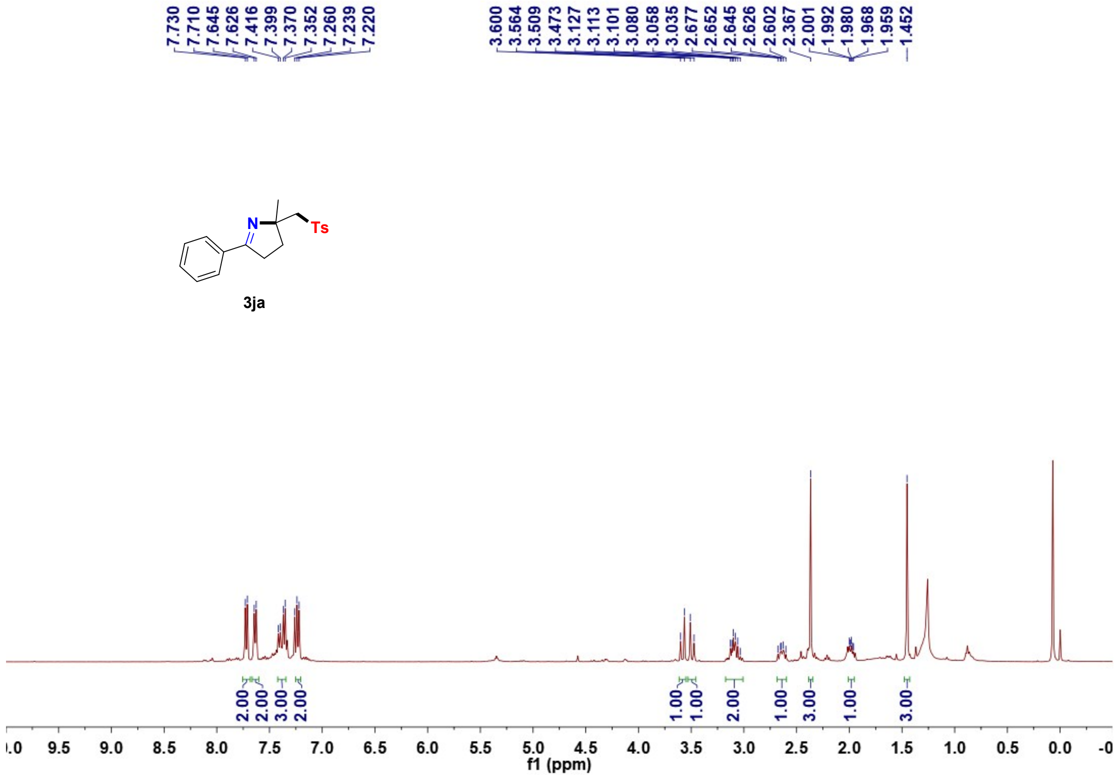
f1 (ppm)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3.600 3.564 3.509 3.473 3.127 3.113 3.101 3.080 3.058 3.035 2.677 2.652 2.645 2.626 2.602 2.367 2.001 1.992 1.980 1.968 1.959 1.452
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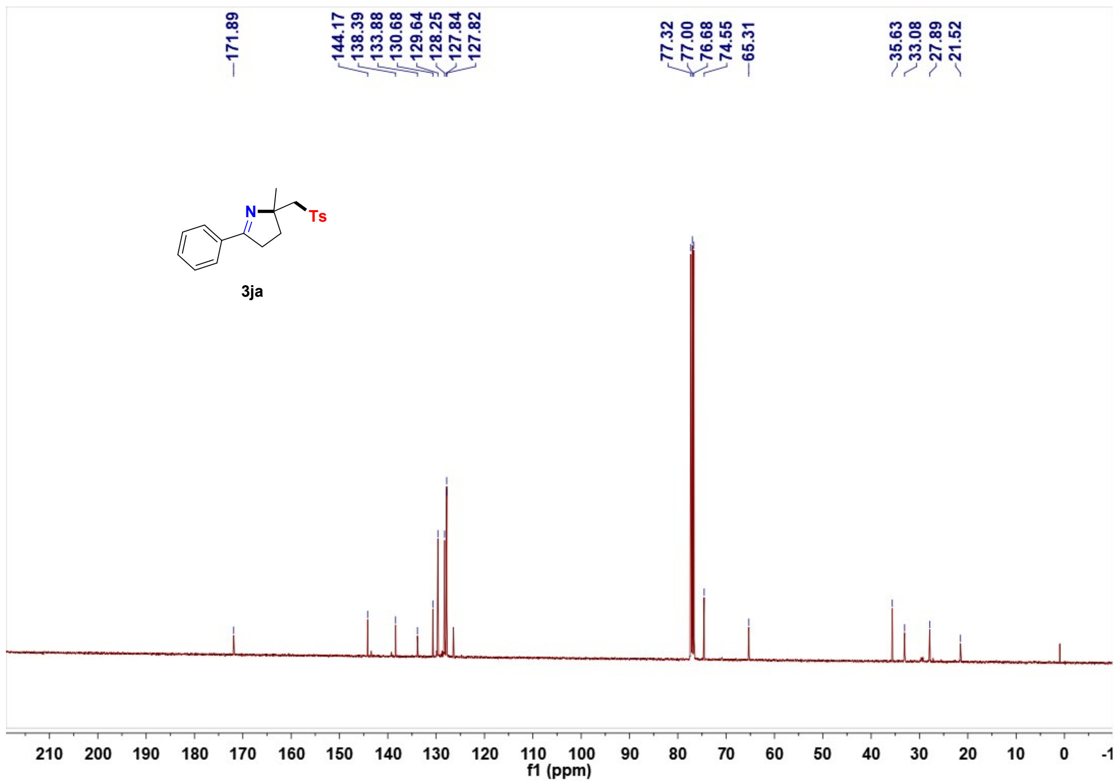
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35.63 33.08 27.89 21.52
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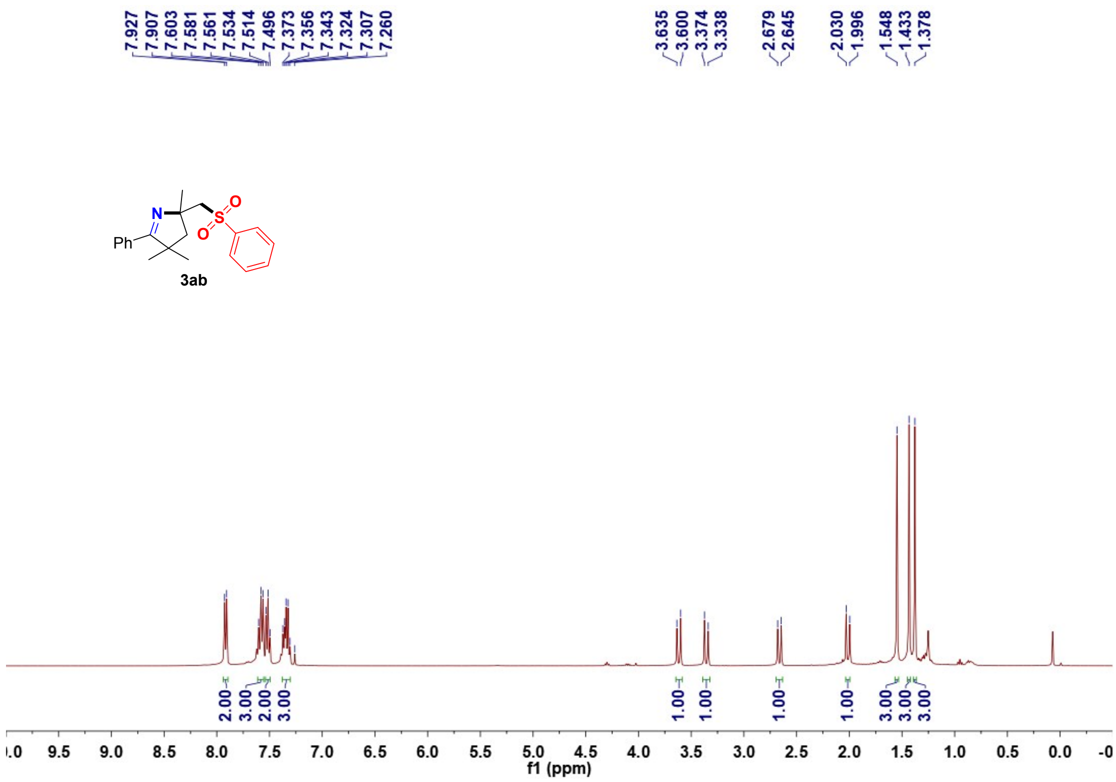
f1 (ppm)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2.00
3.00
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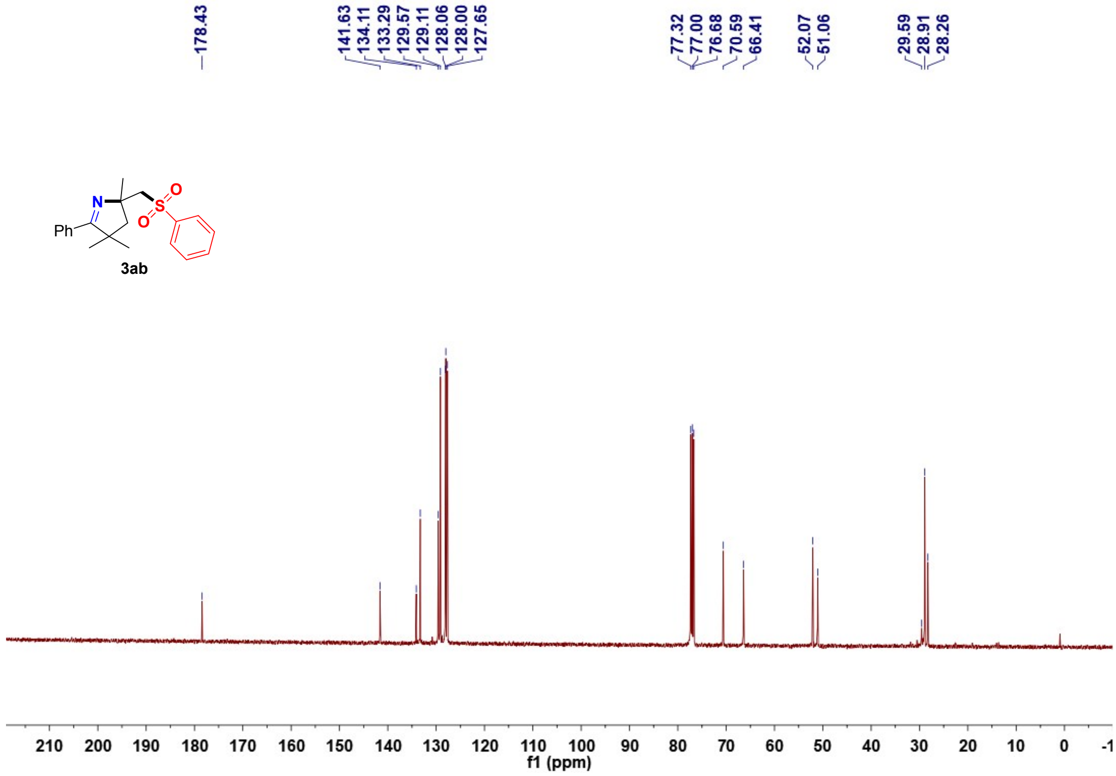
1.00
3.00
3.00
3.00
f1 (ppm)
N
Ph
S
O
O

3ab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f1 (ppm)
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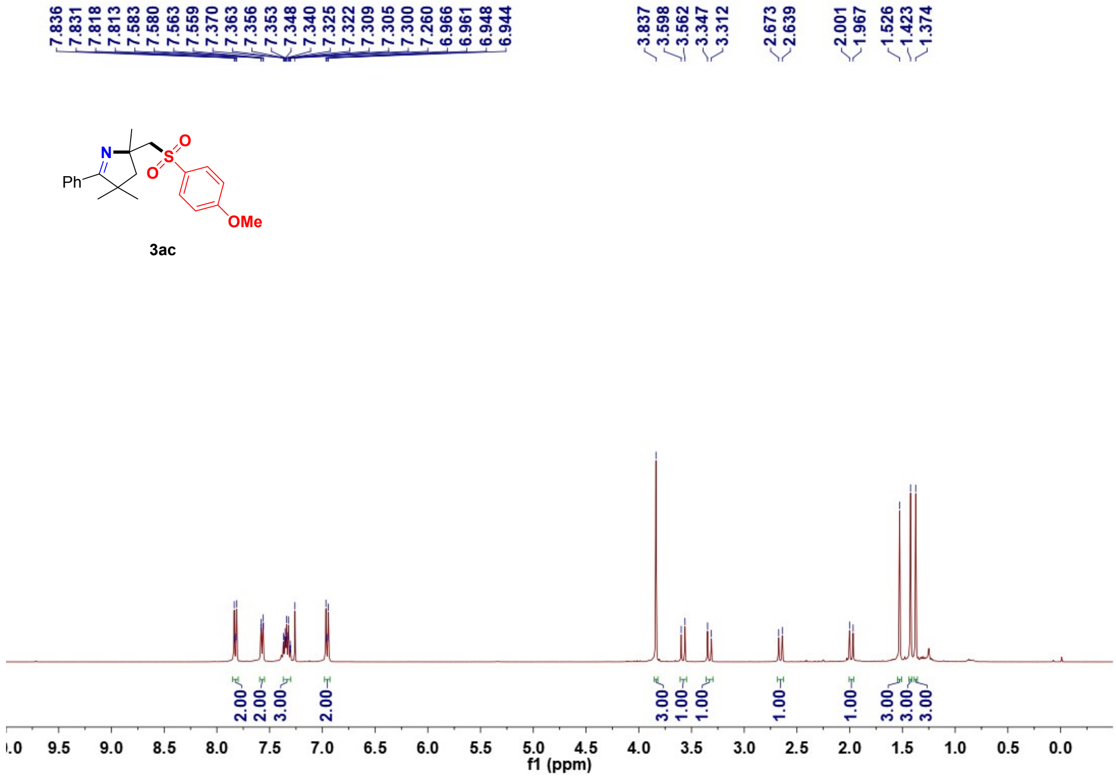
Ph
S
O
O

3ab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1.526
1.423
1.374
Ph
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S
O
O
OMe
3ac
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2.00
3.00
2.00
3.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
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
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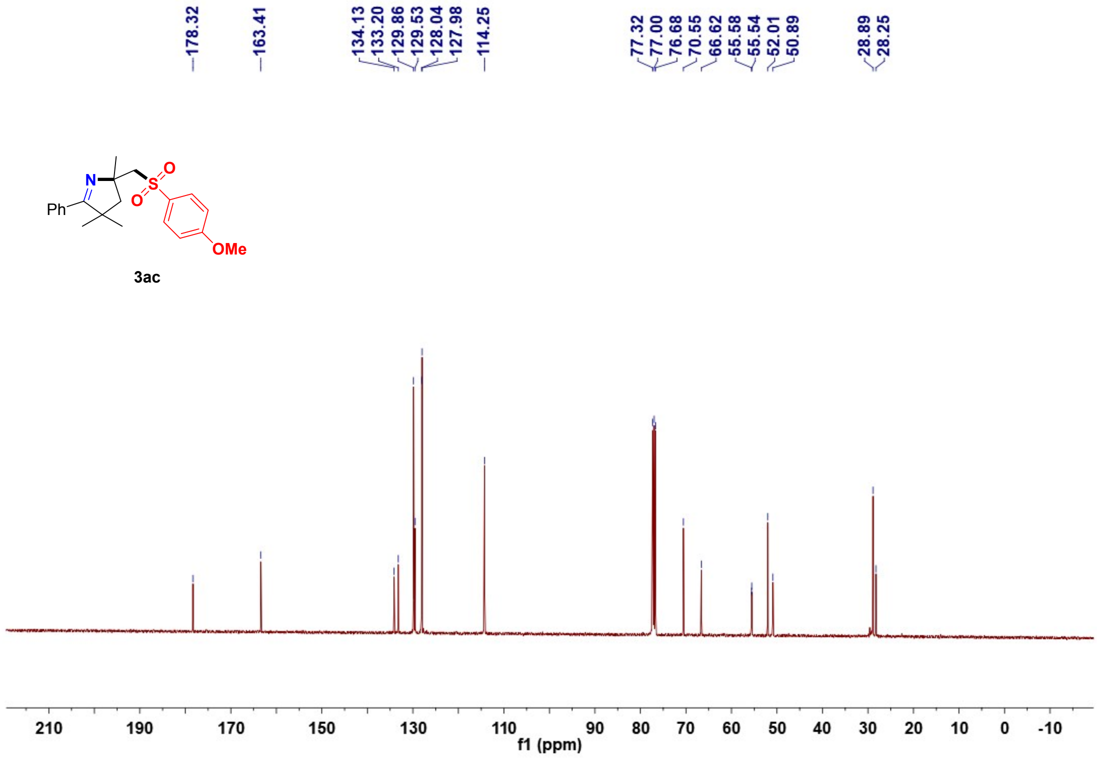
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66.62
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55.54
52.01
50.89
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Ph
N
S
O
O
OMe
3ac
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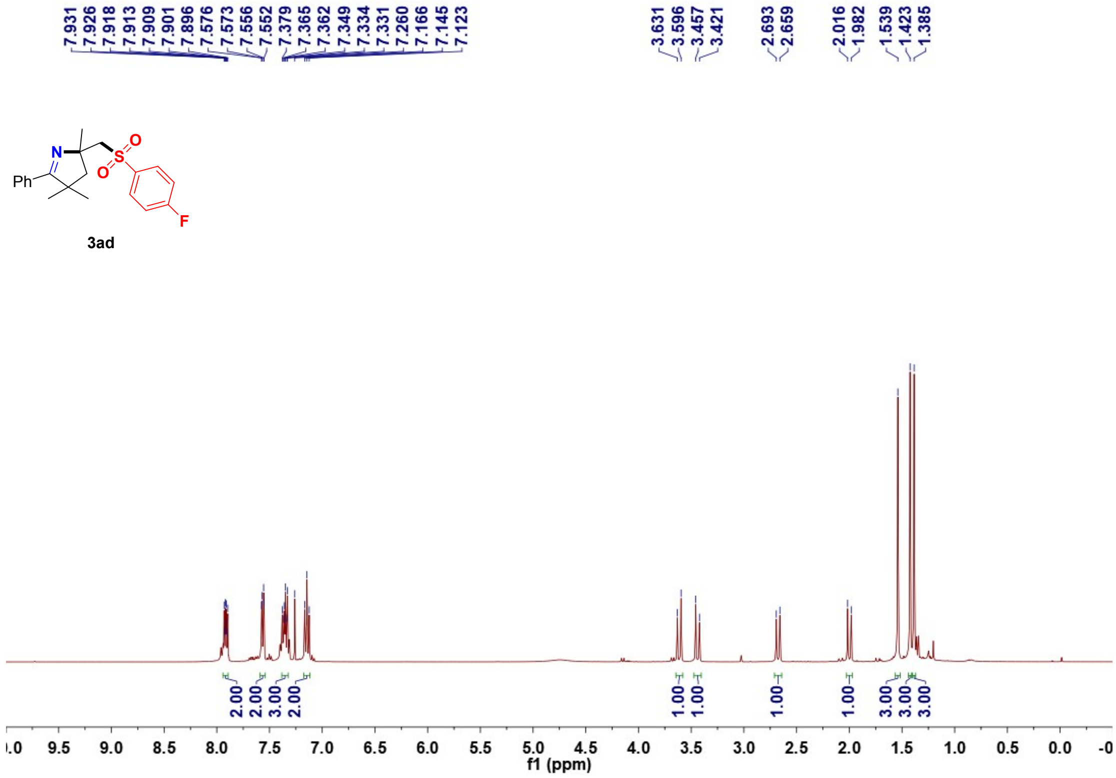

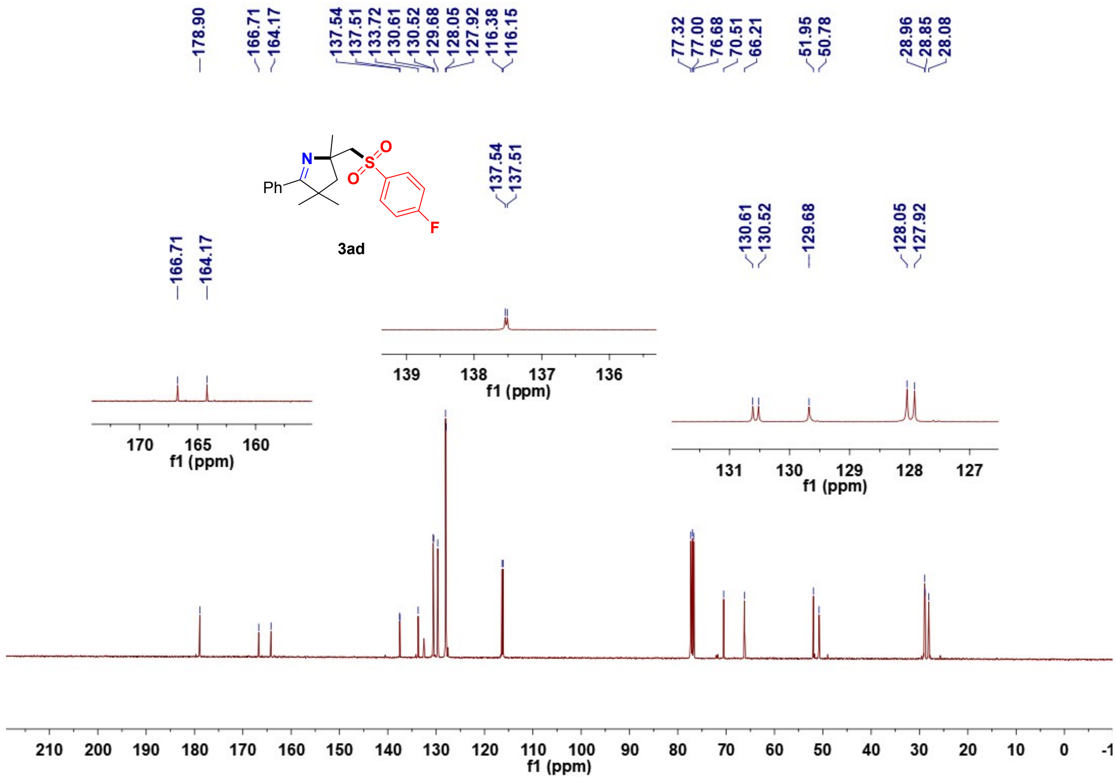

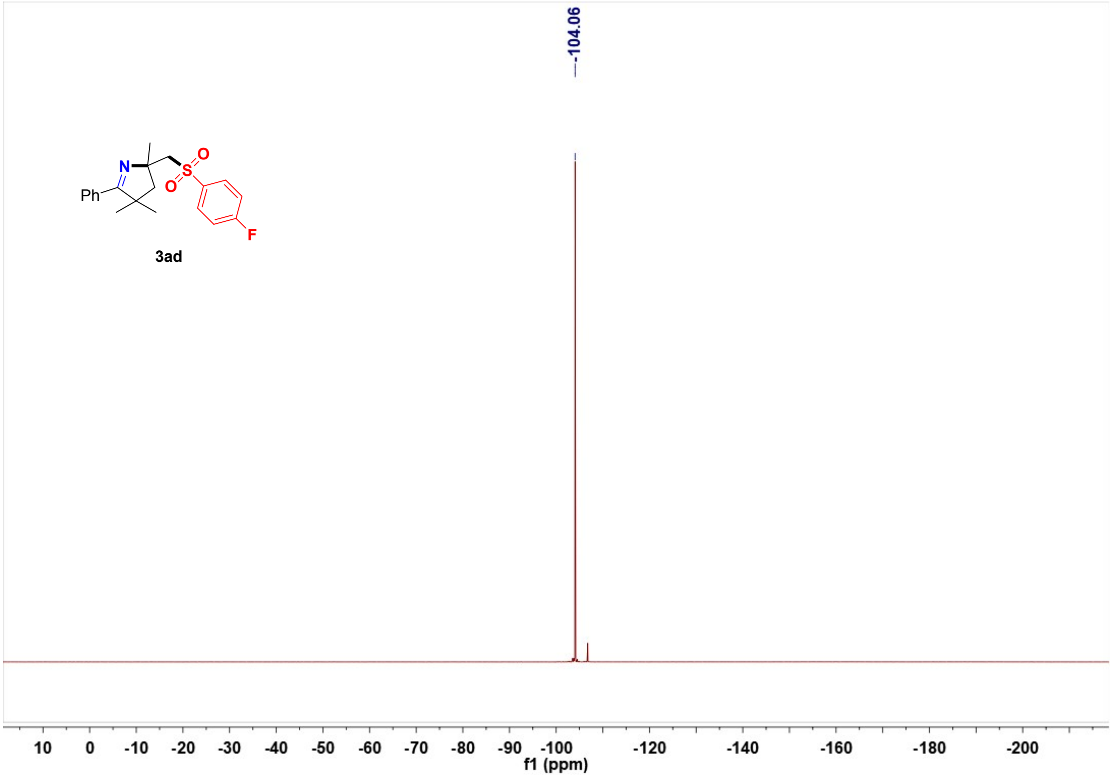
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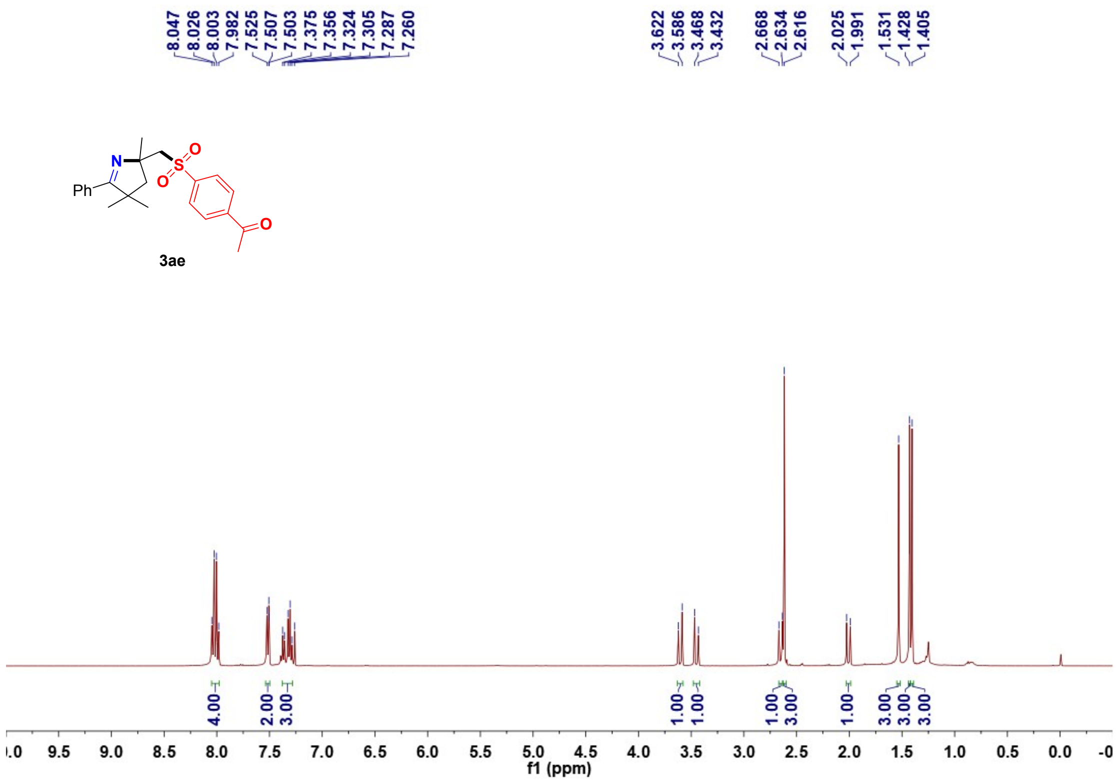

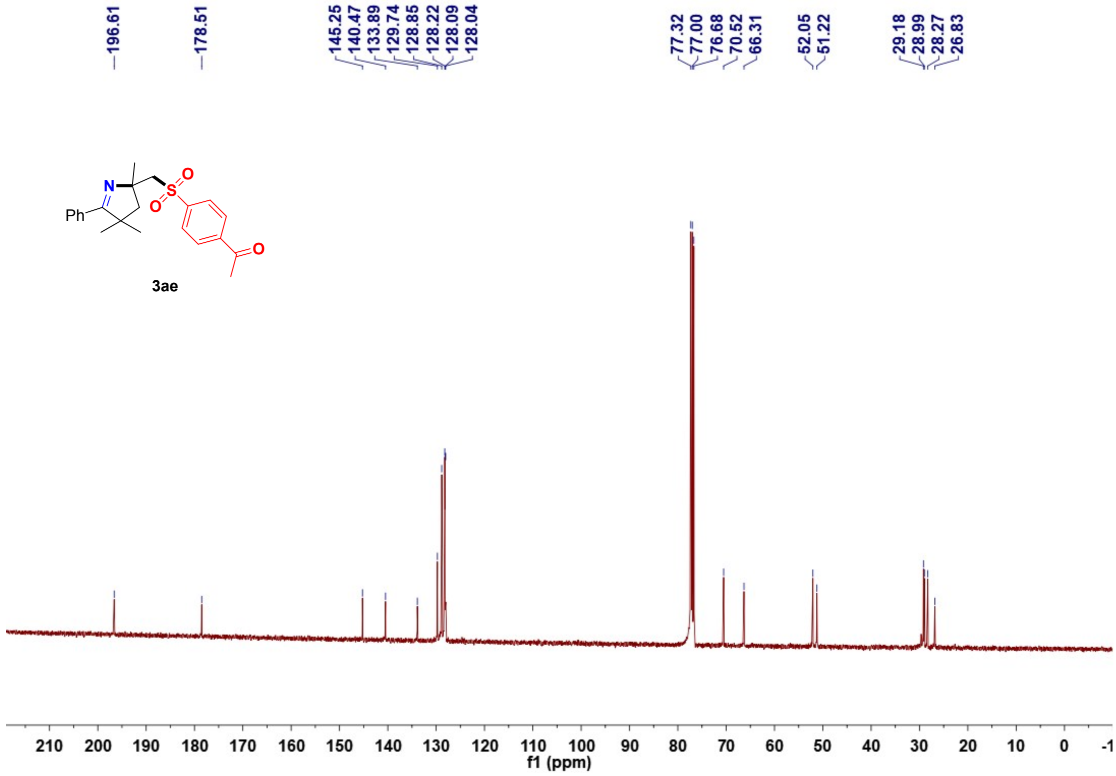

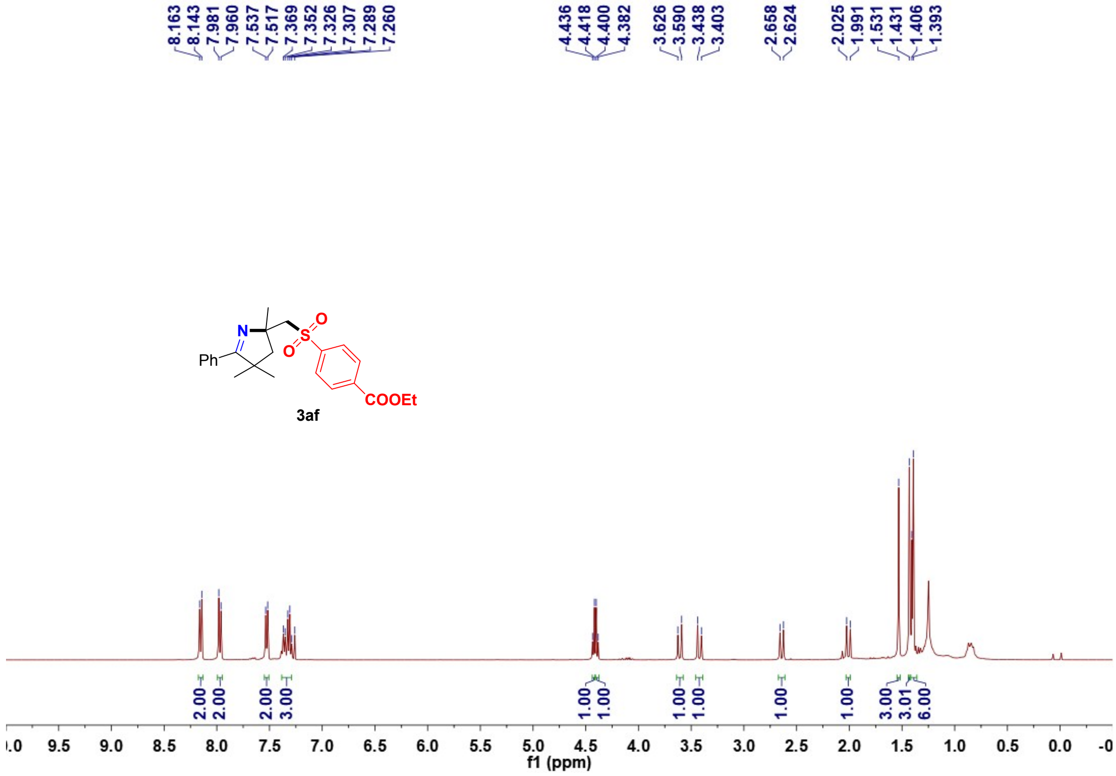
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N
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O
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3af
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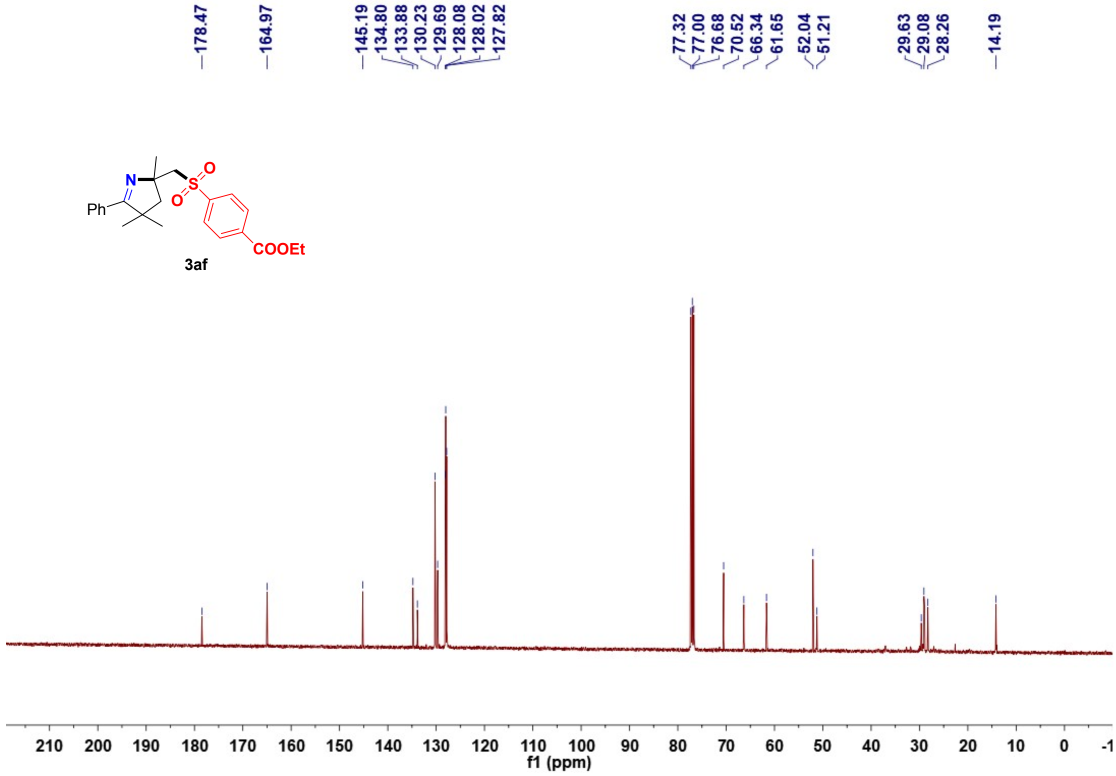
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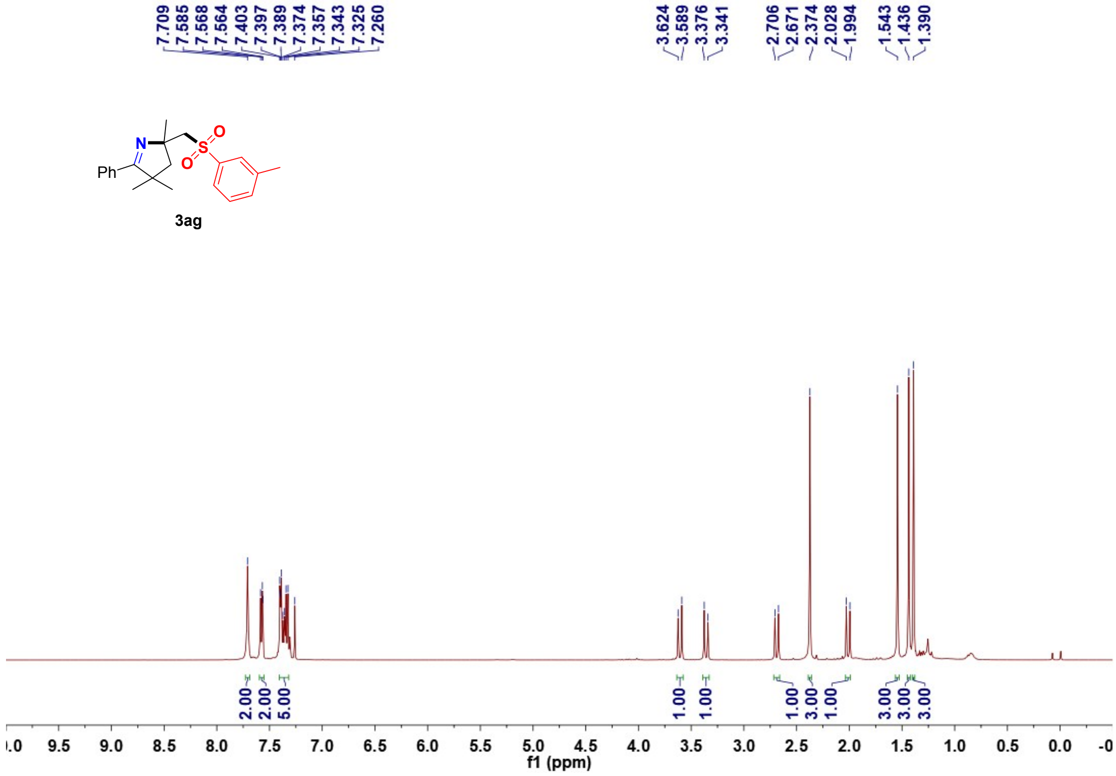
f1 (ppm)



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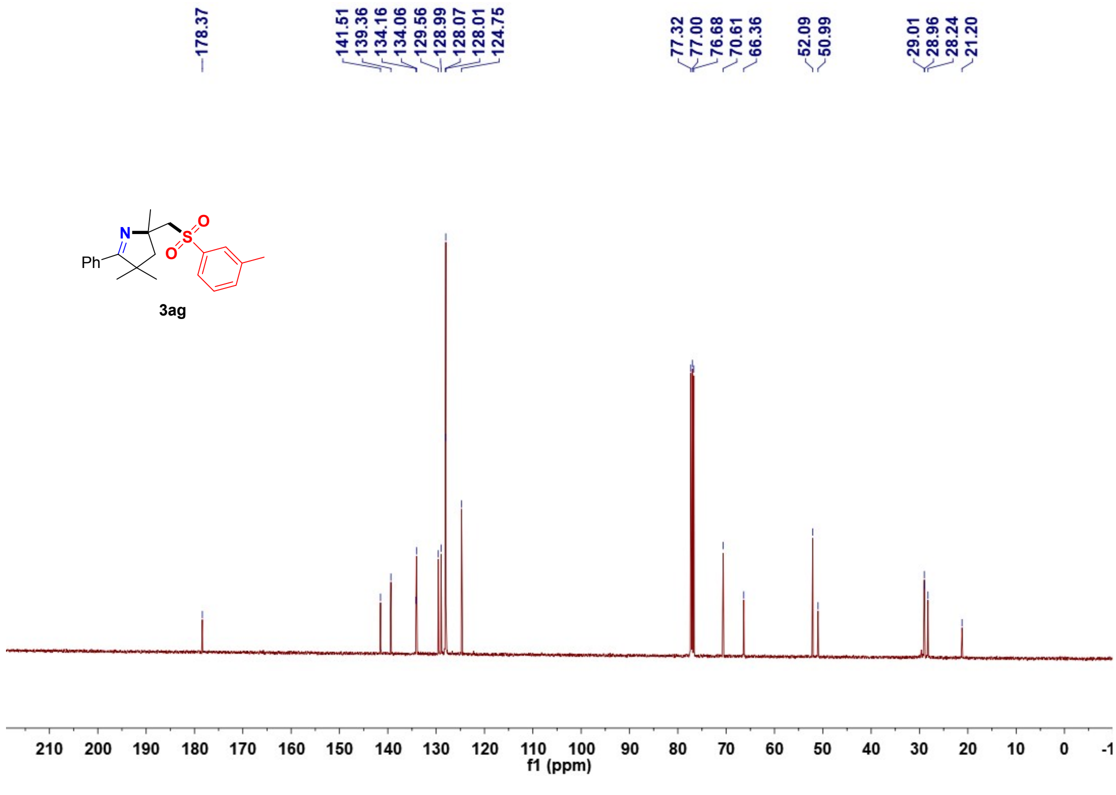

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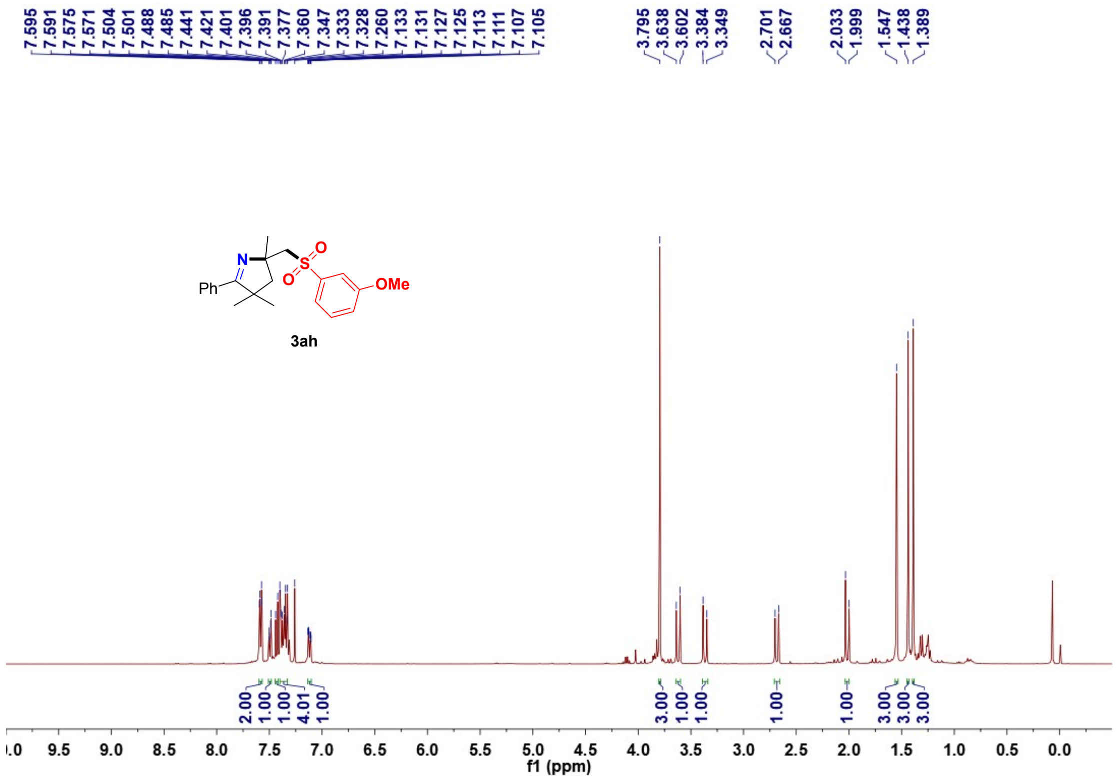

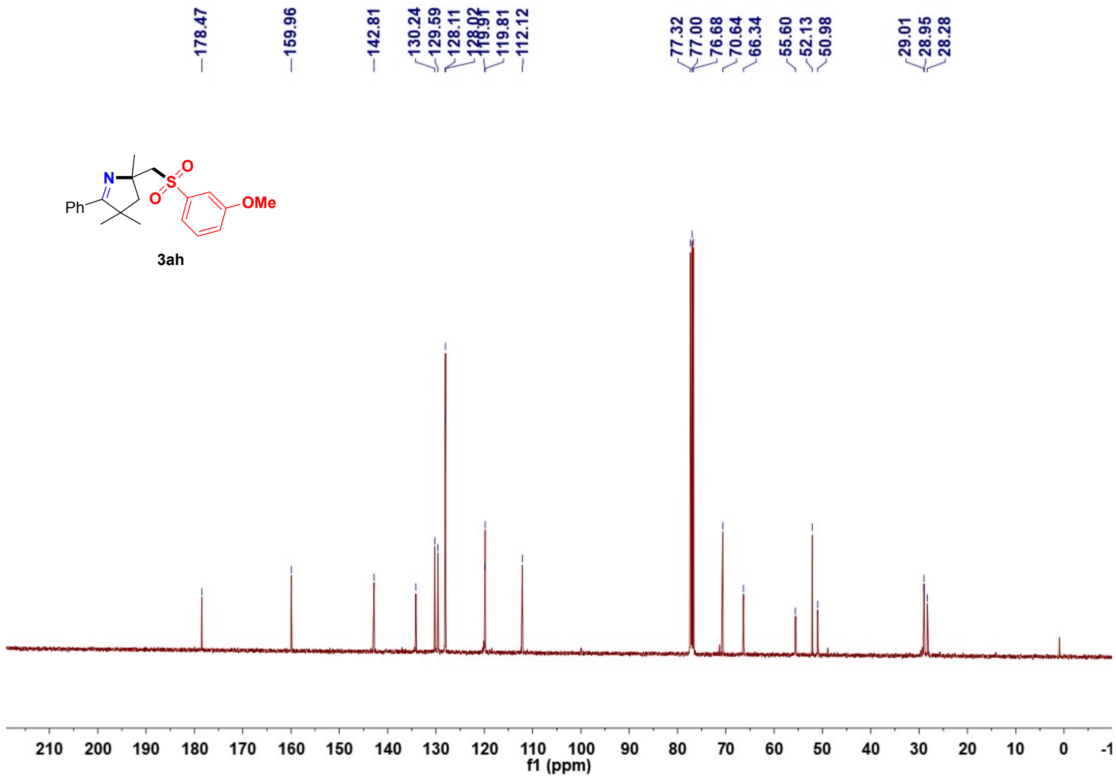

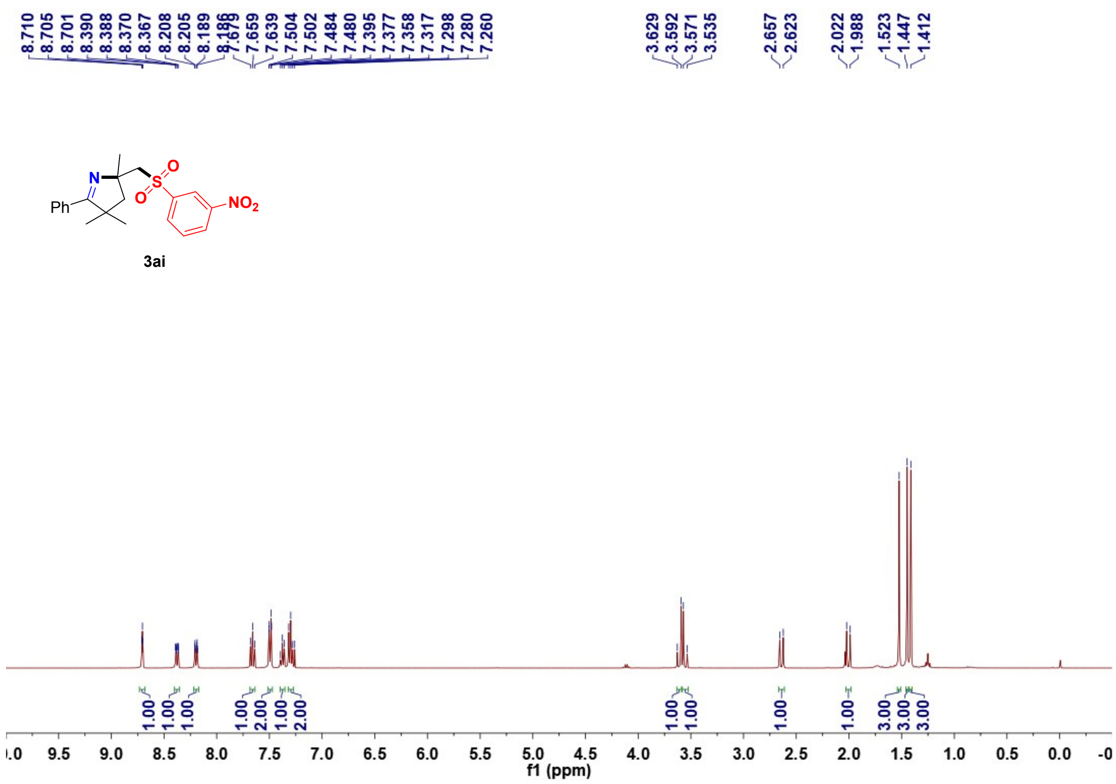

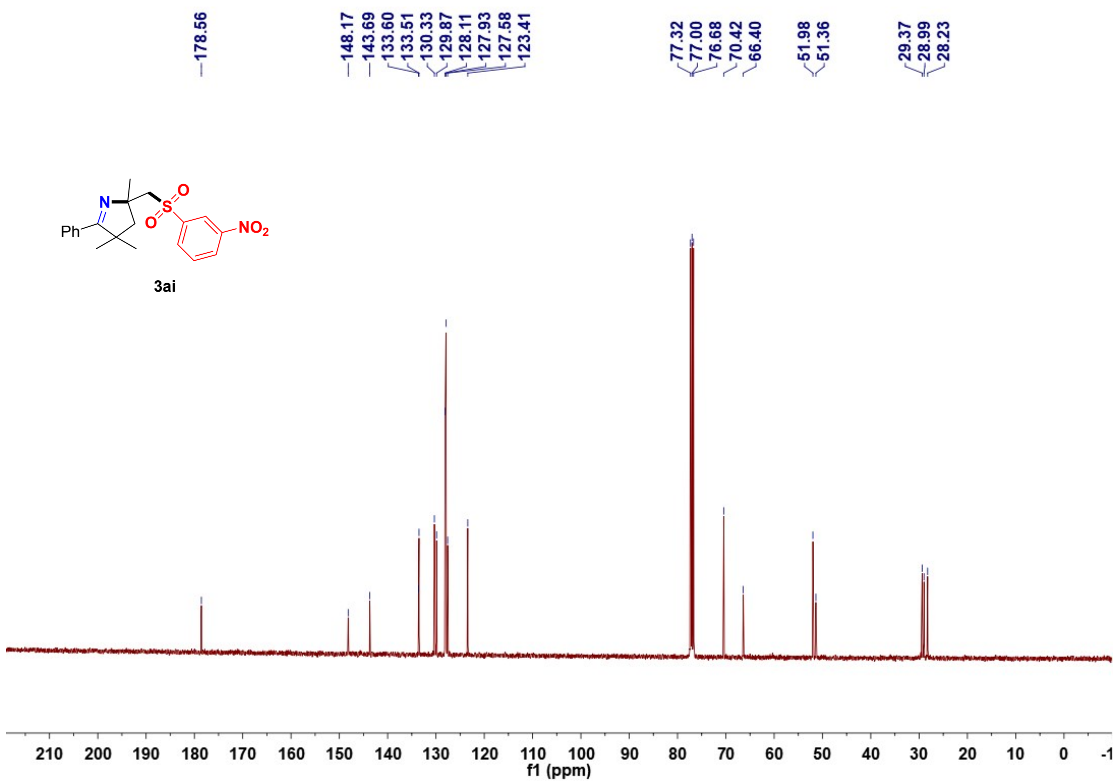

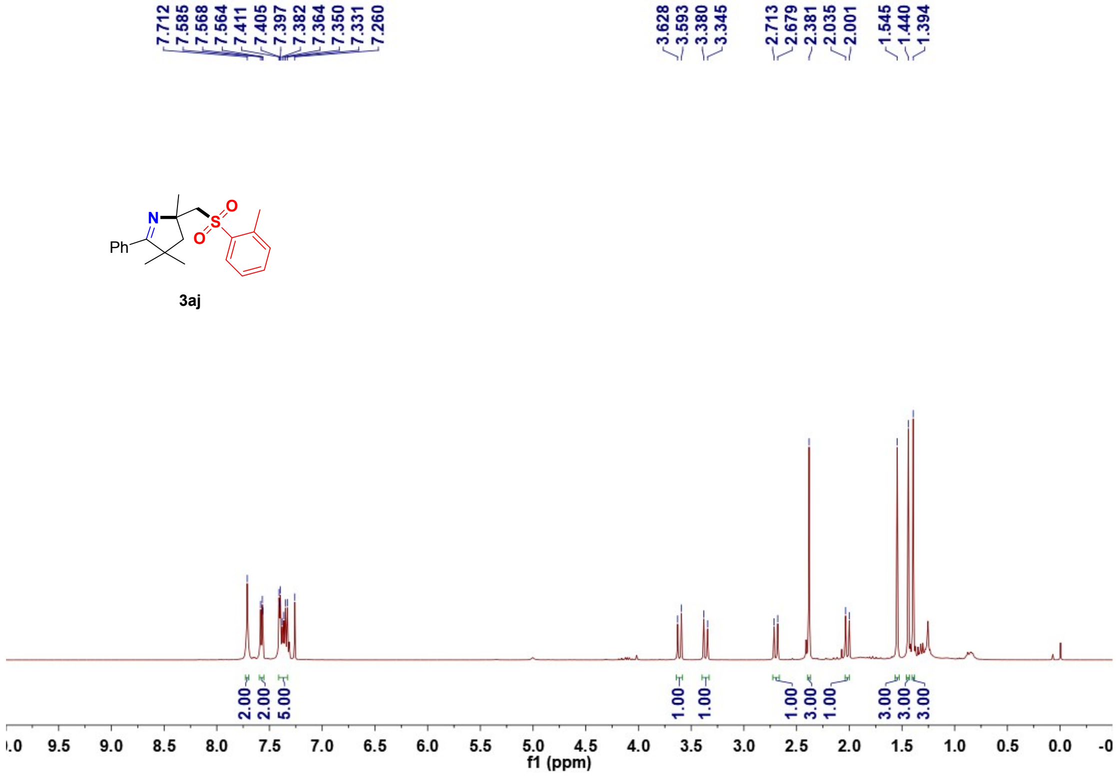
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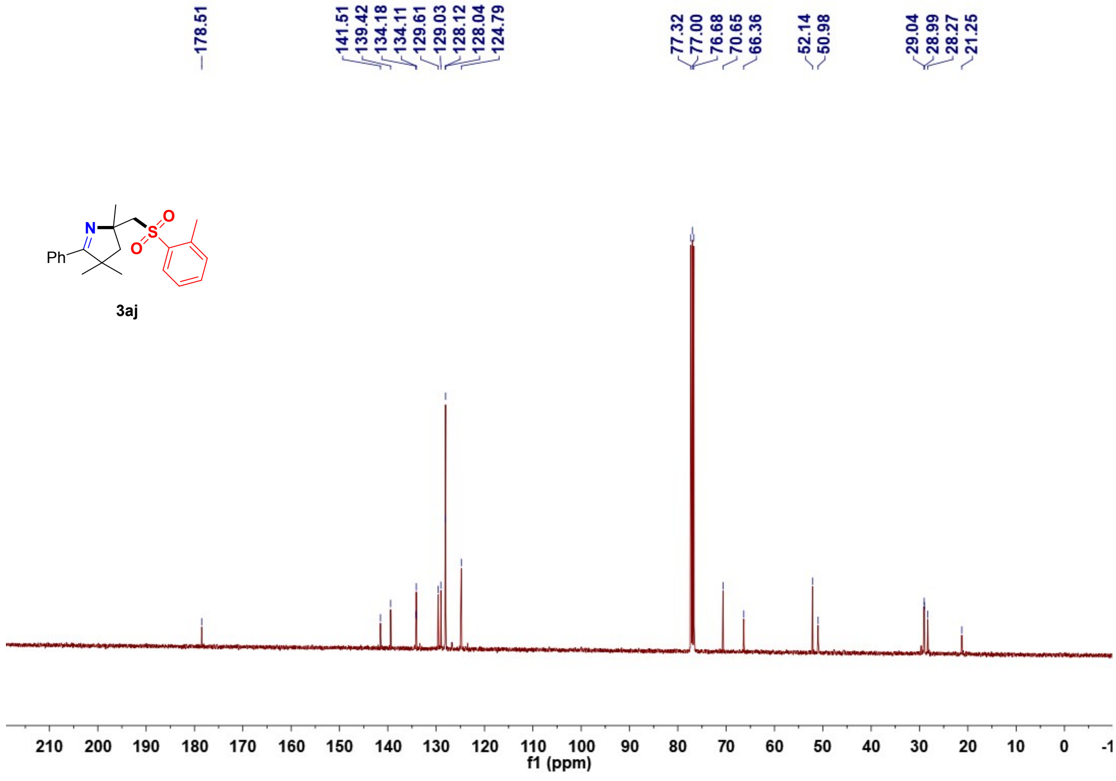
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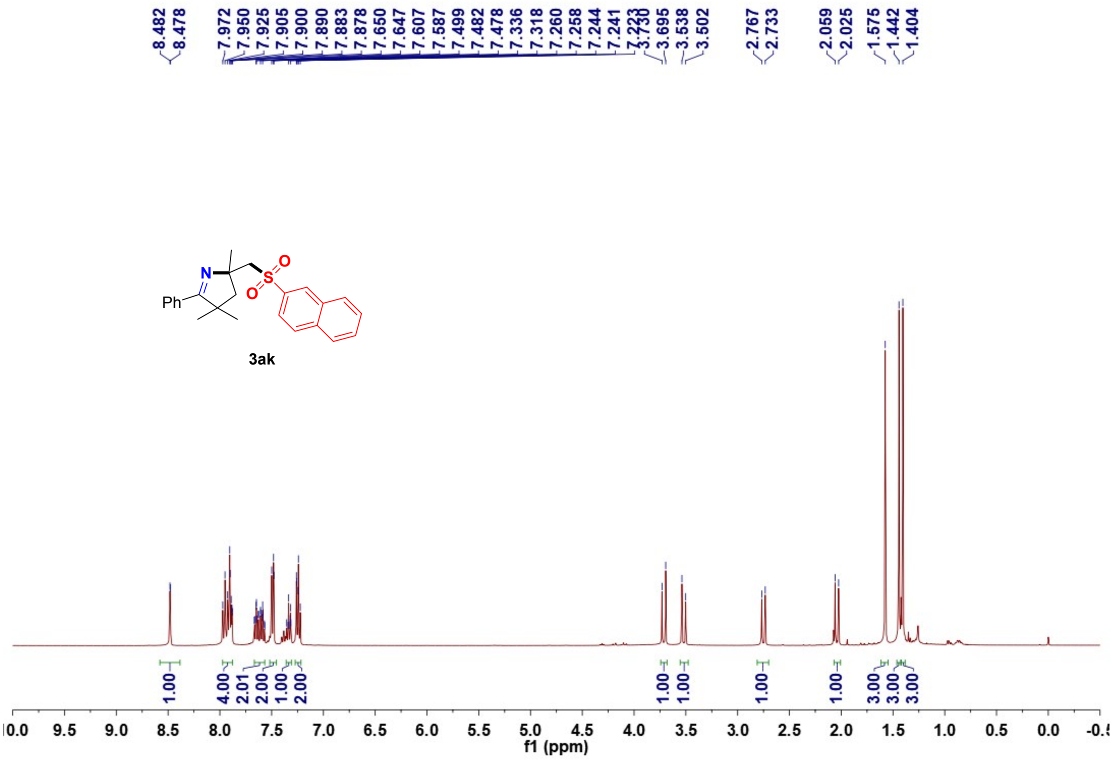
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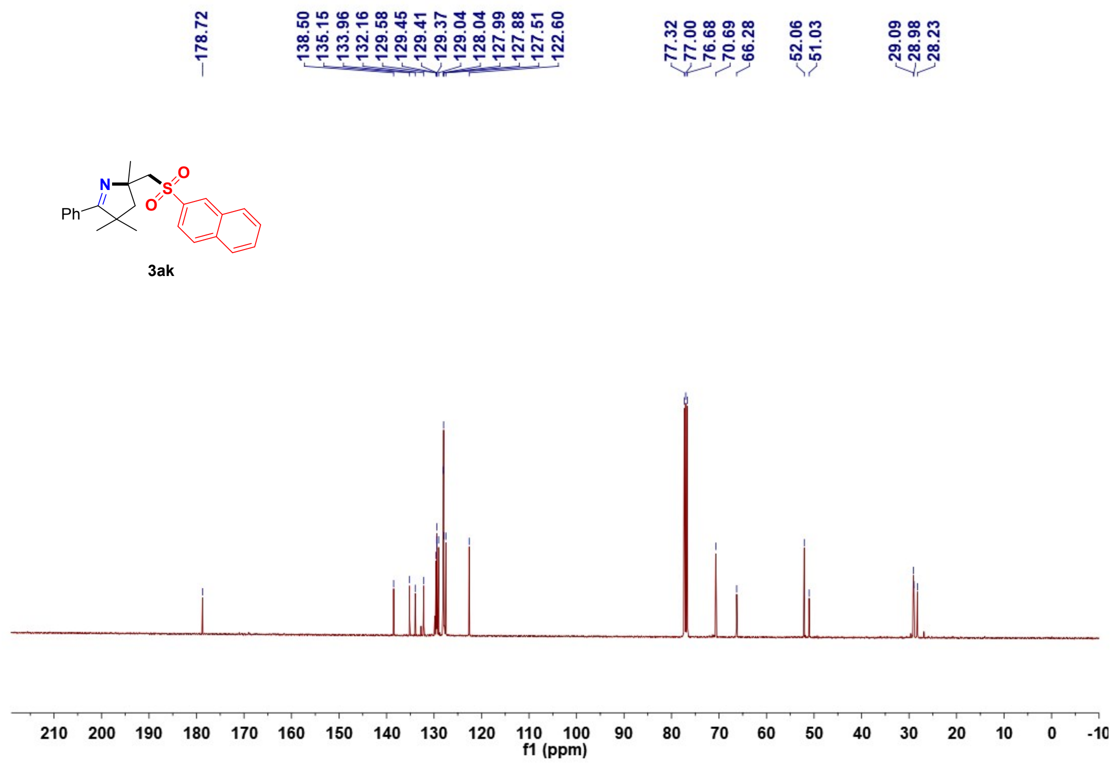
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122.60
77.32
77.00
76.68
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28.98
28.23
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O
O
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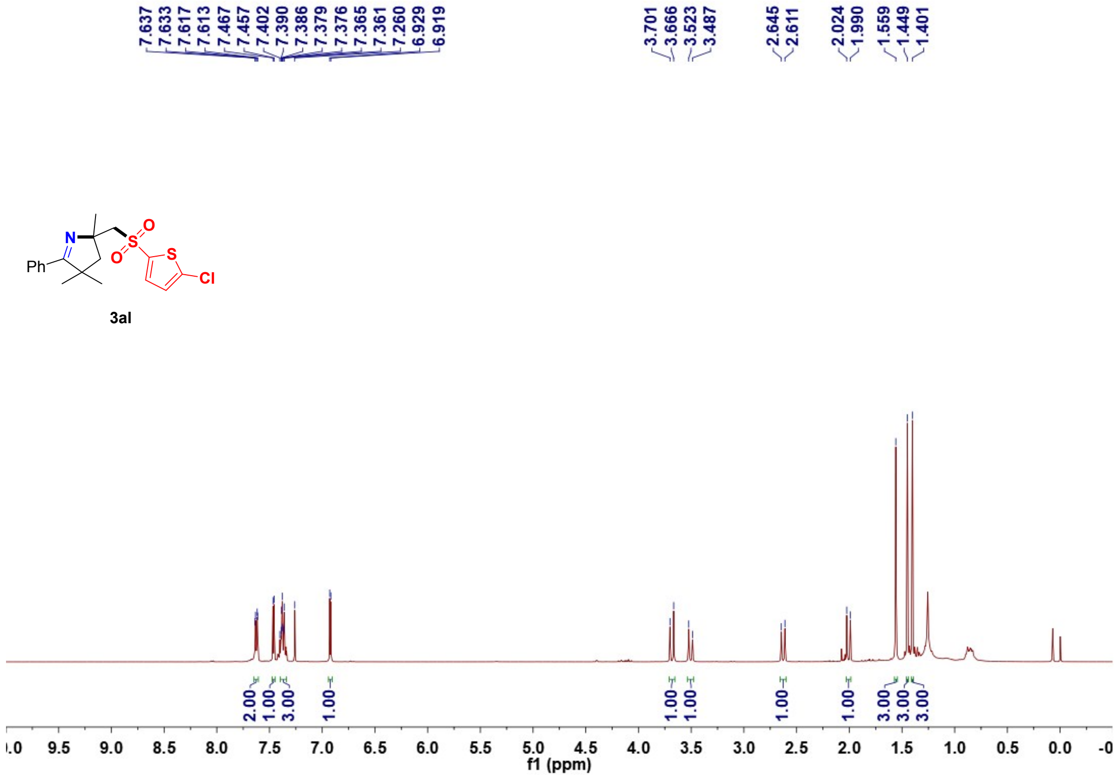
f1 (ppm)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6.929
6.919
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3.666
3.523
3.487
2.645
2.611
2.024
1.990
1.559
1.449
1.401
Ph
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S
O
O
S
Cl
3al
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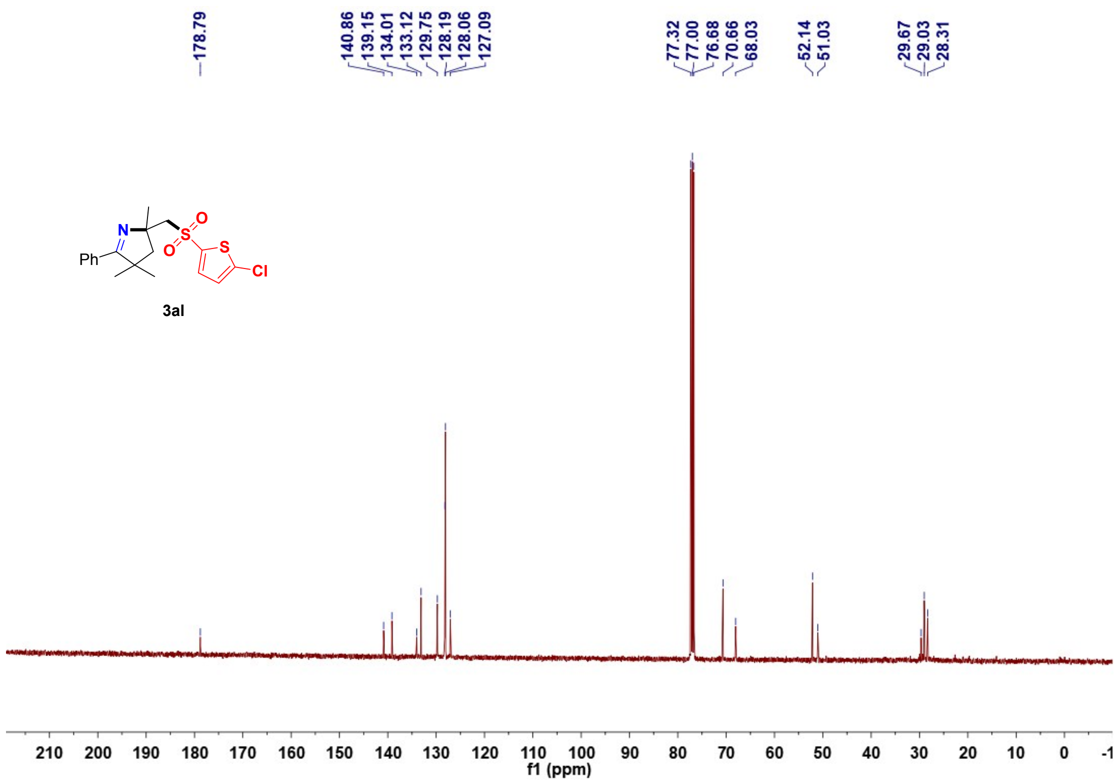
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70.66
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28.31
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S
O
O
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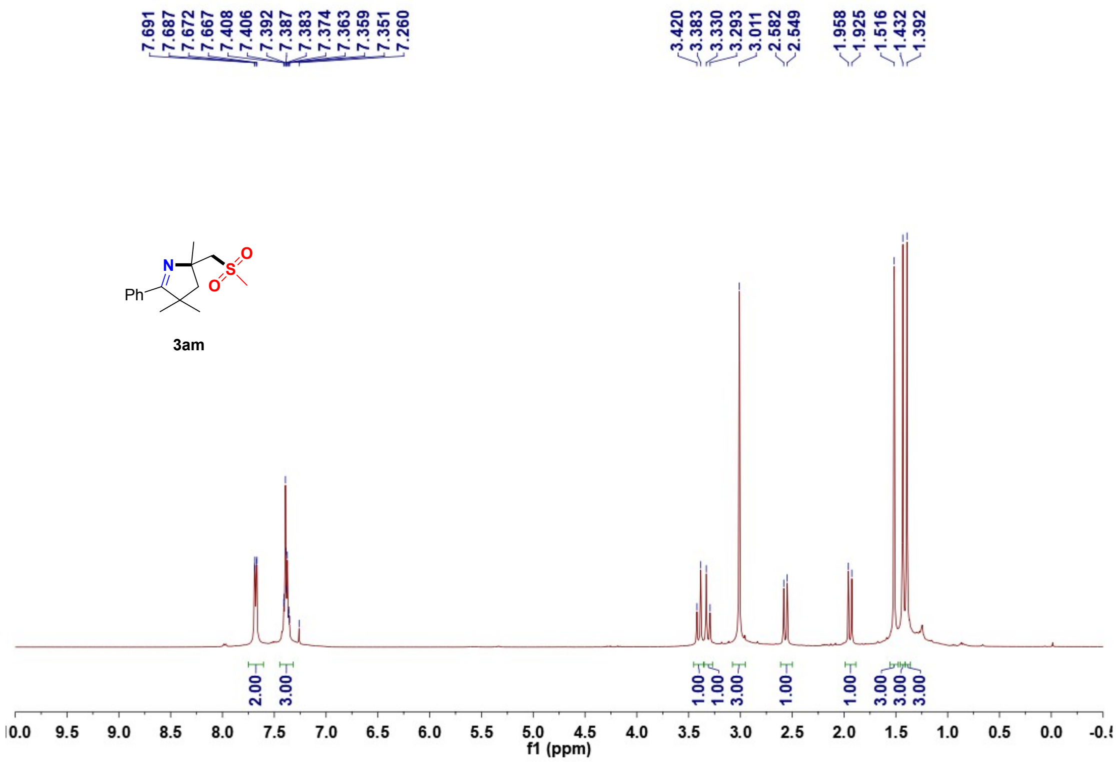
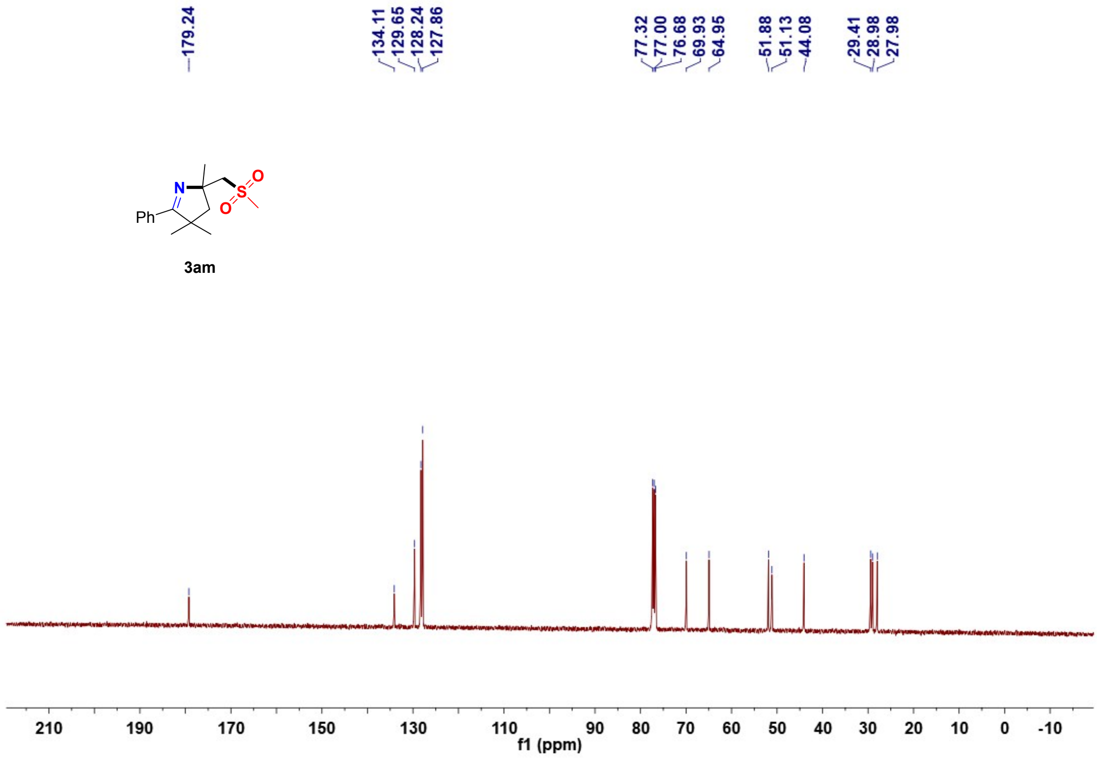
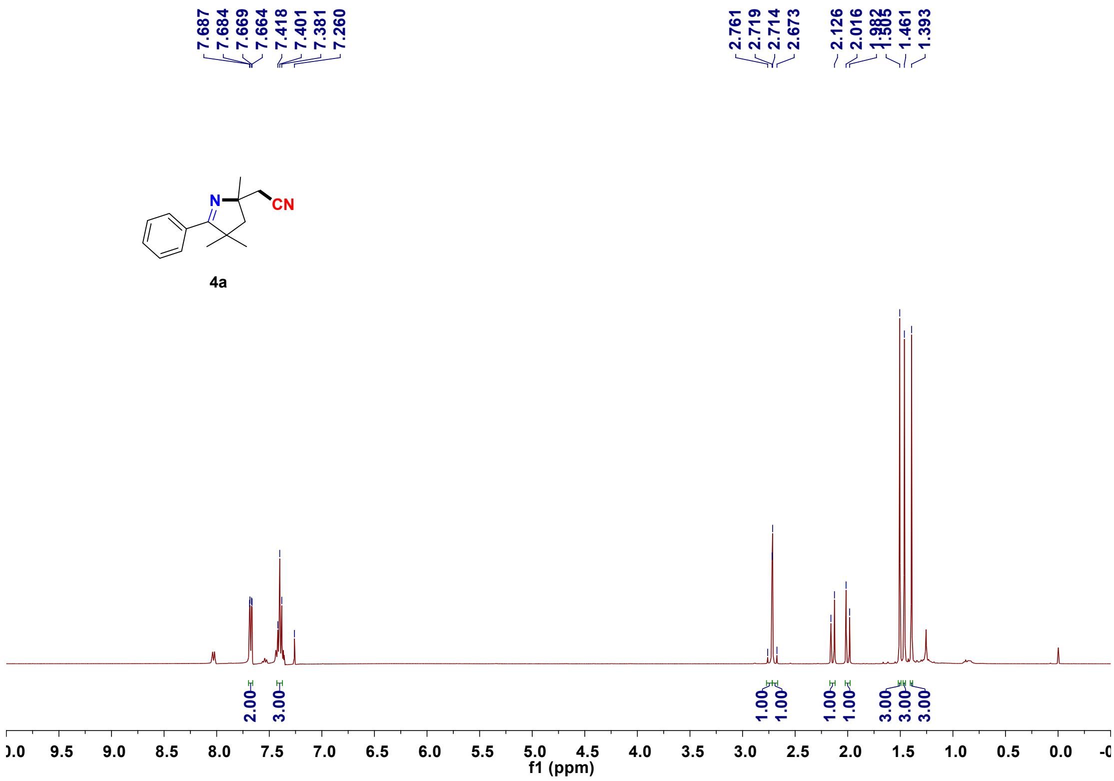
Cl
3al
f1 (ppm)



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2.673
2.126
2.016
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1.505
1.461
1.393
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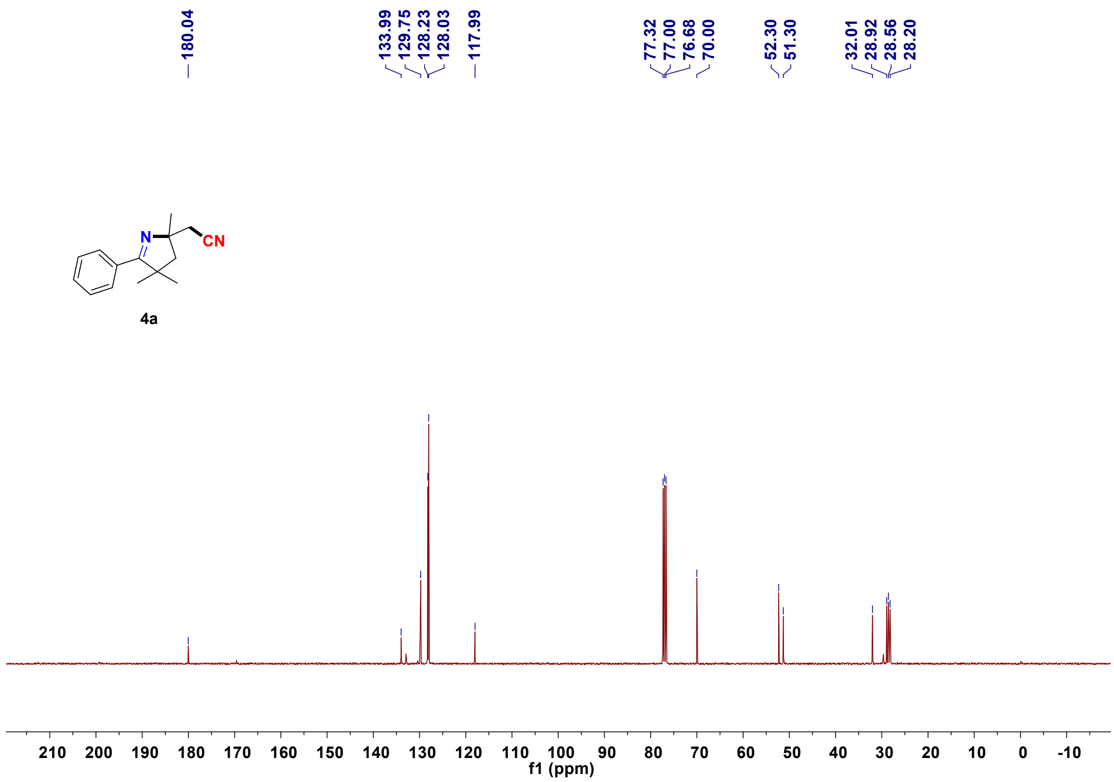
3.00
3.00
3.00
f1 (ppm)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4a
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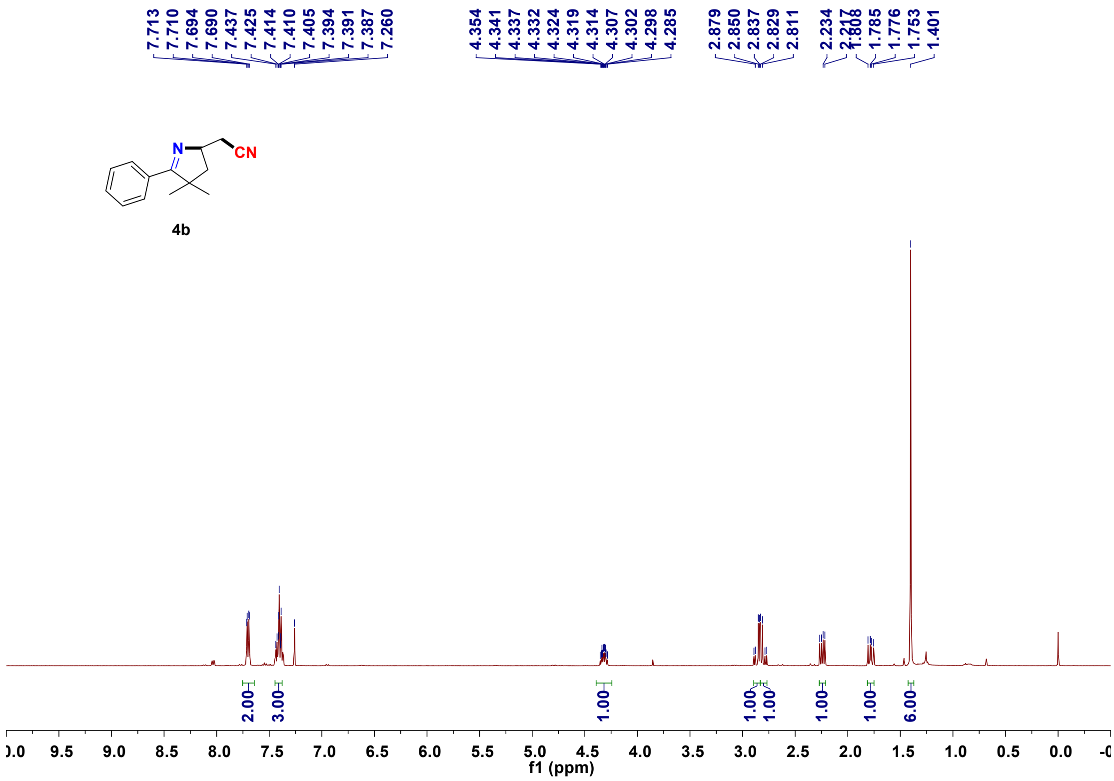
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7.391
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7.260
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4.341
4.337
4.332
4.324
4.319
4.314
4.307
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4.298
4.285
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2.829
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2.217
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1.785
1.776
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1.00
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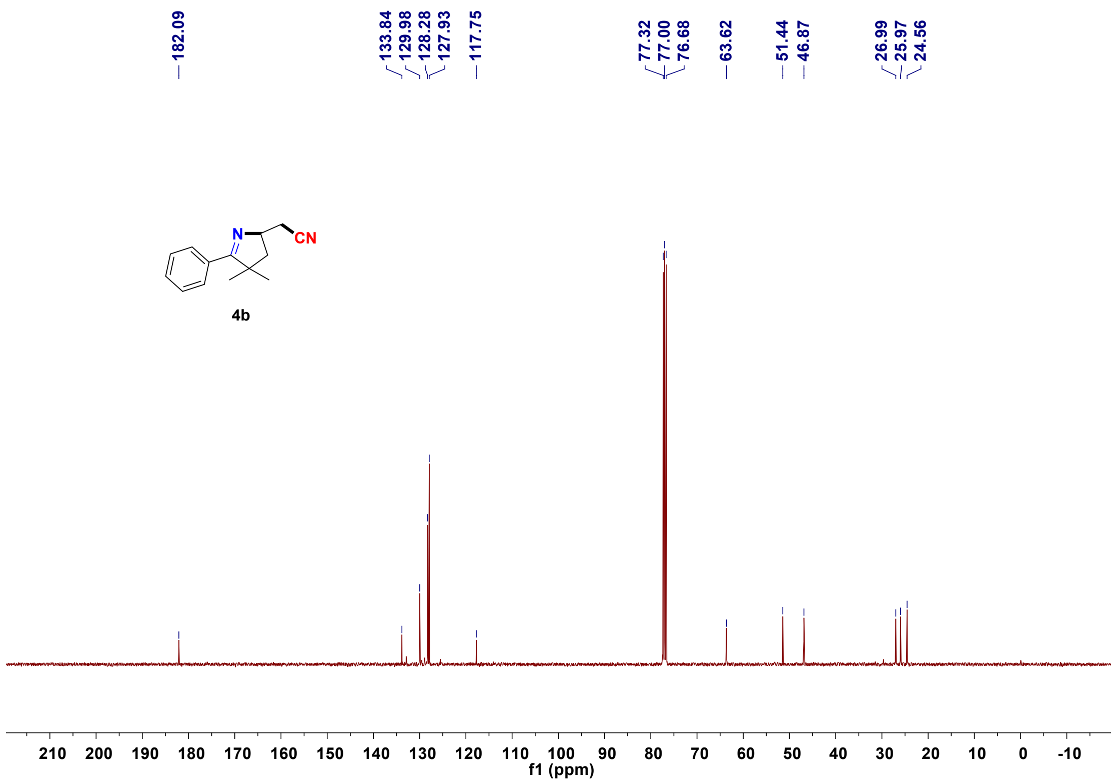
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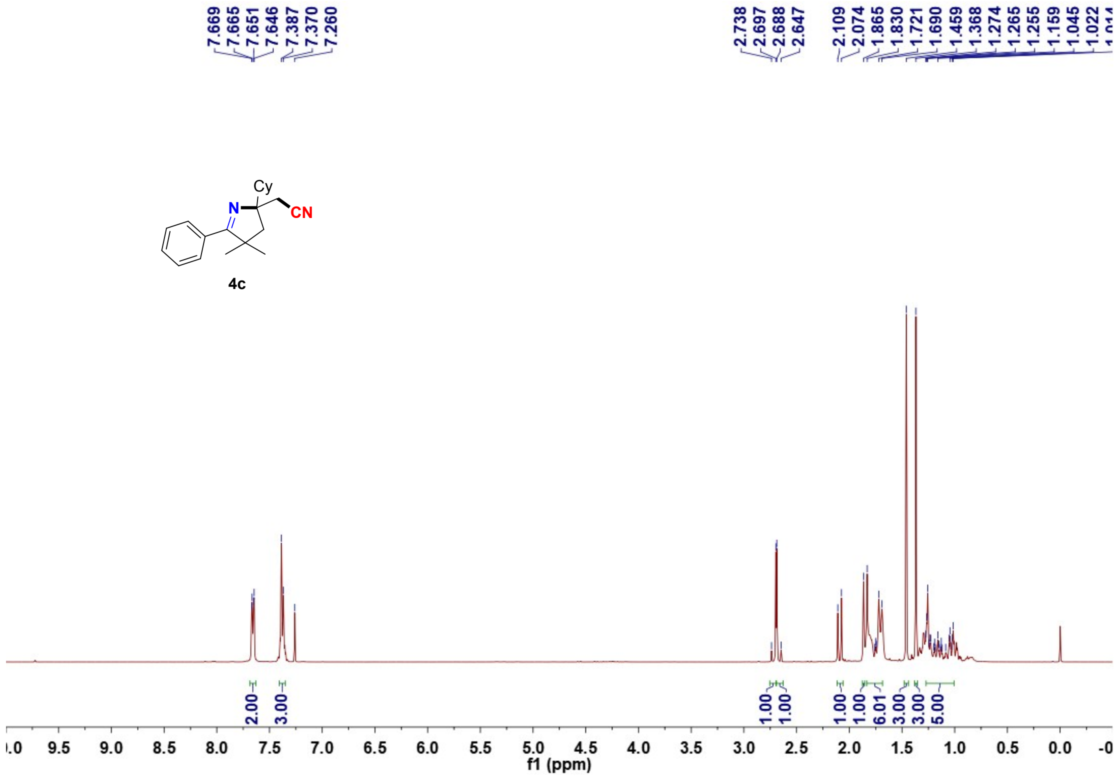
4b
f1 (ppm)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1.830
1.721
1.690
1.459
1.368
1.274
1.265
1.255
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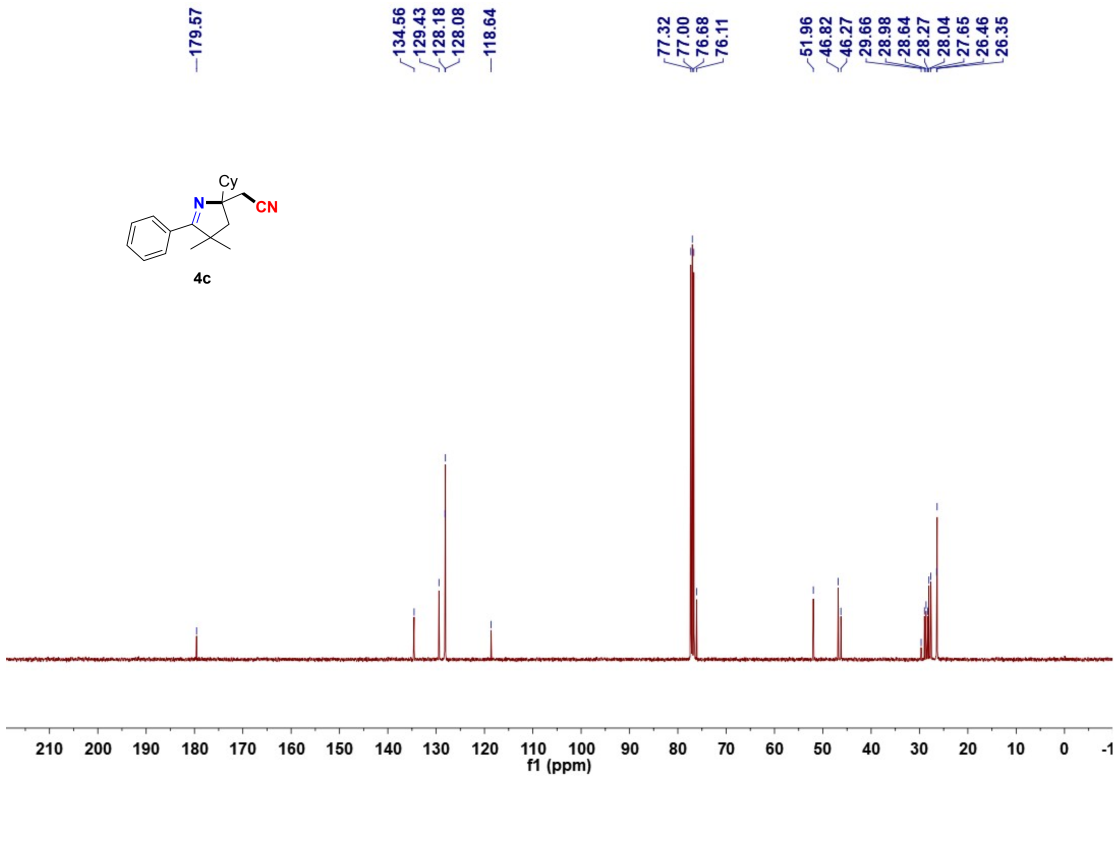
1.045
1.022
Cy
N
CN
4c
2.00
3.00
1.00
1.00
1.00
1.00
6.01
3.00
3.00
5.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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46.27
29.66
28.98
28.64
28.27
28.04
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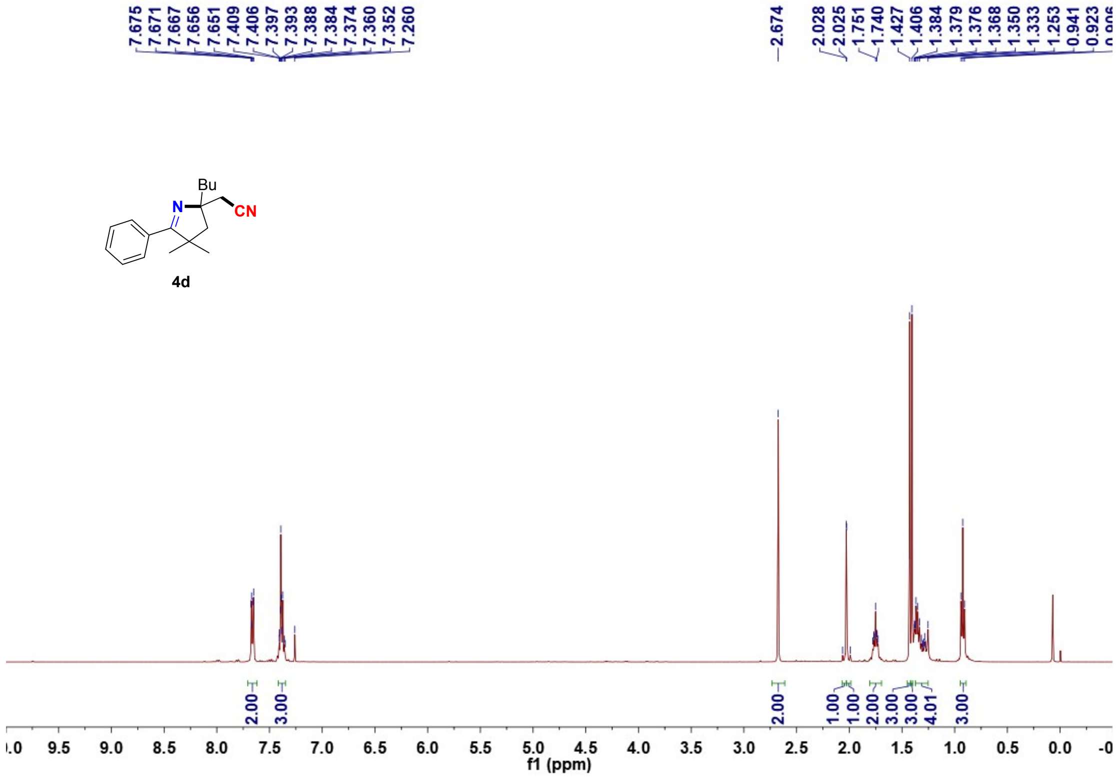
Cy
N
CN
4c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.360
7.352
7.260
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2.028
2.025
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1.740
1.427
1.406
1.384
1.379
1.376
1.368
1.350
1.333
1.253
0.941
0.923
Bu
N
CN
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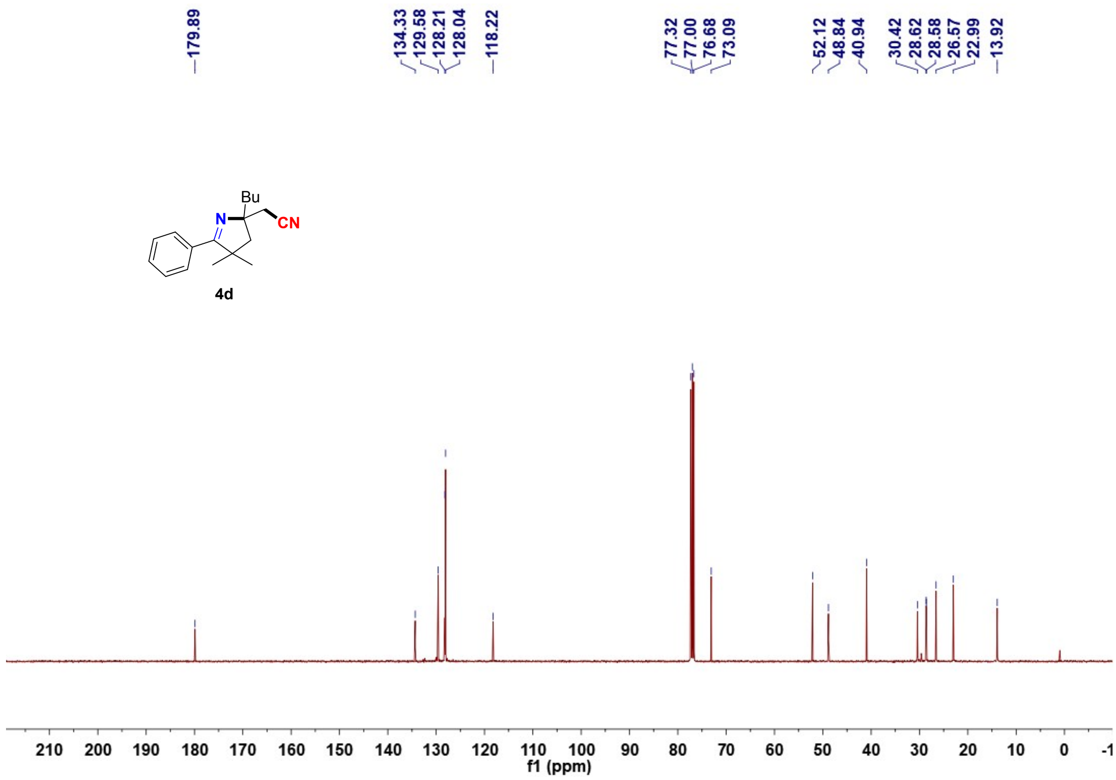
2.00
1.00
1.00
2.00
3.00
3.00
4.01
3.00
f1 (ppm)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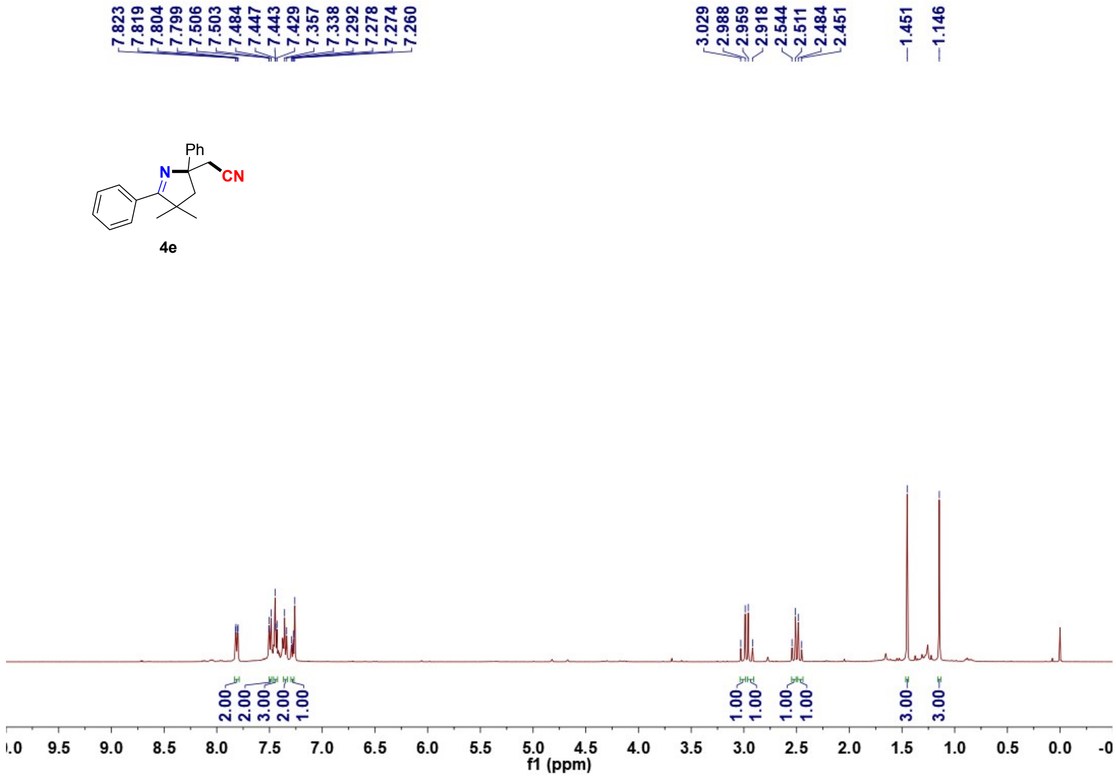
13.92
Bu
N
CN
4d
f1 (ppm)



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7.274
7.260
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2.988
2.959
2.918
2.544
2.511
2.484
2.451
1.451
1.146
Ph
N
CN
4e
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1.00
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1.00
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3.00
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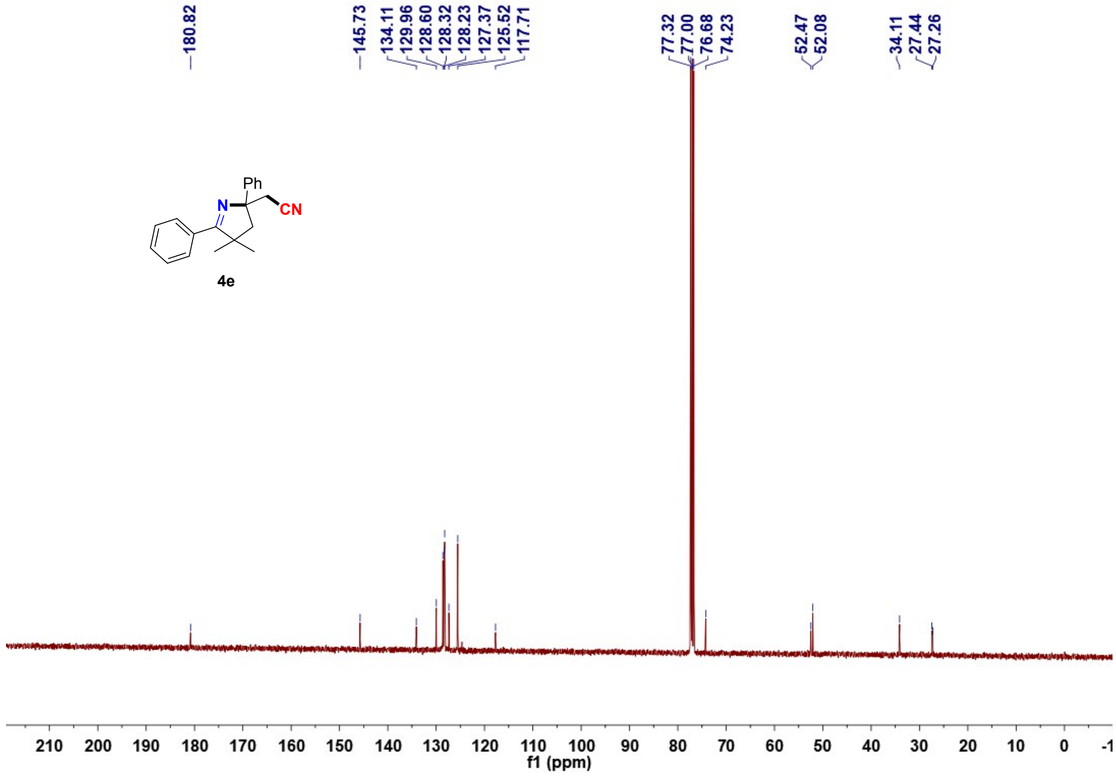

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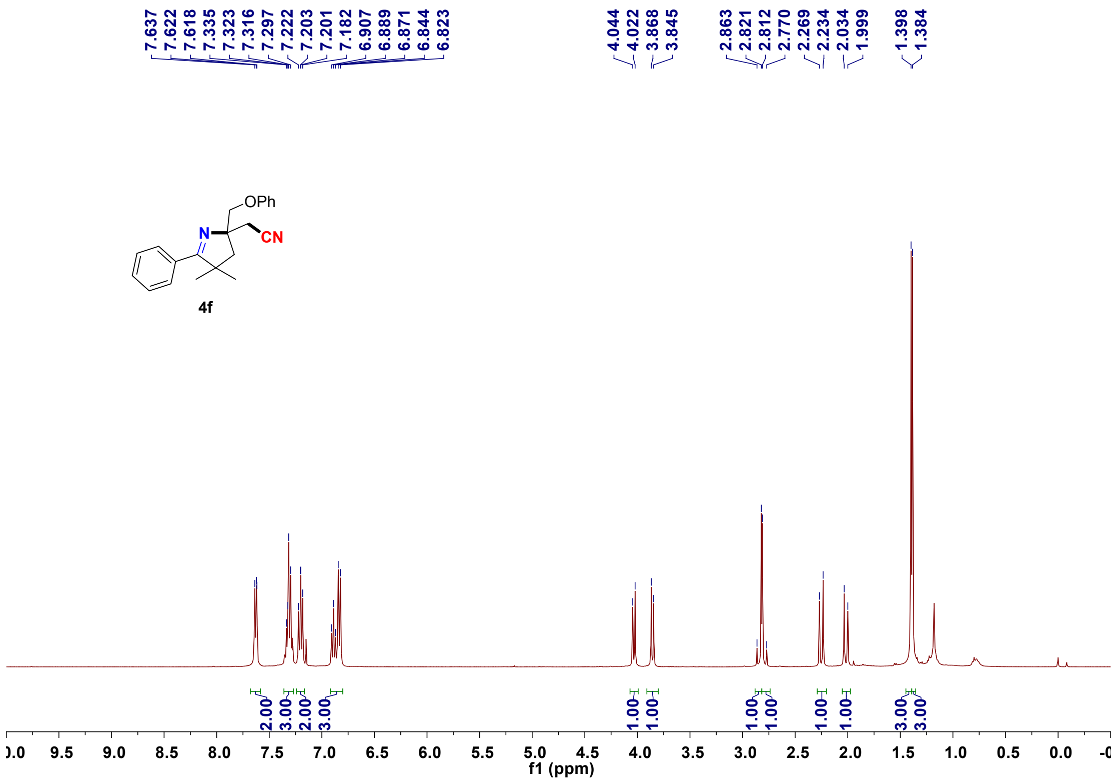
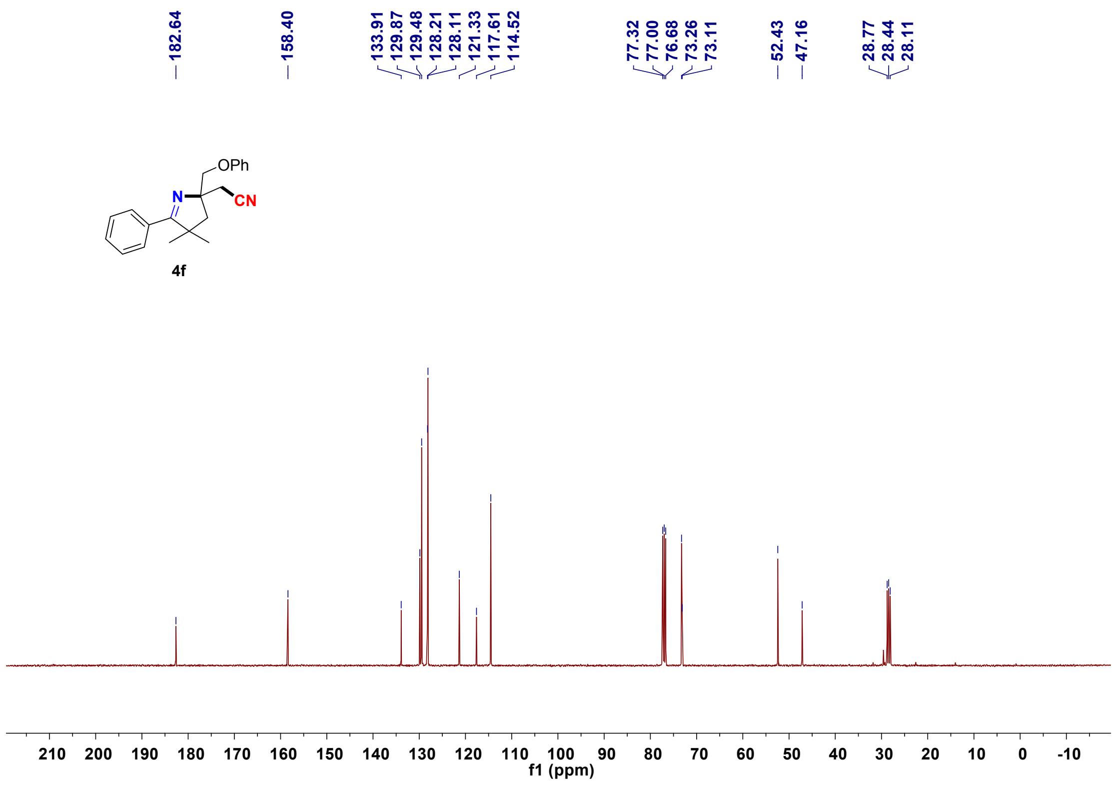
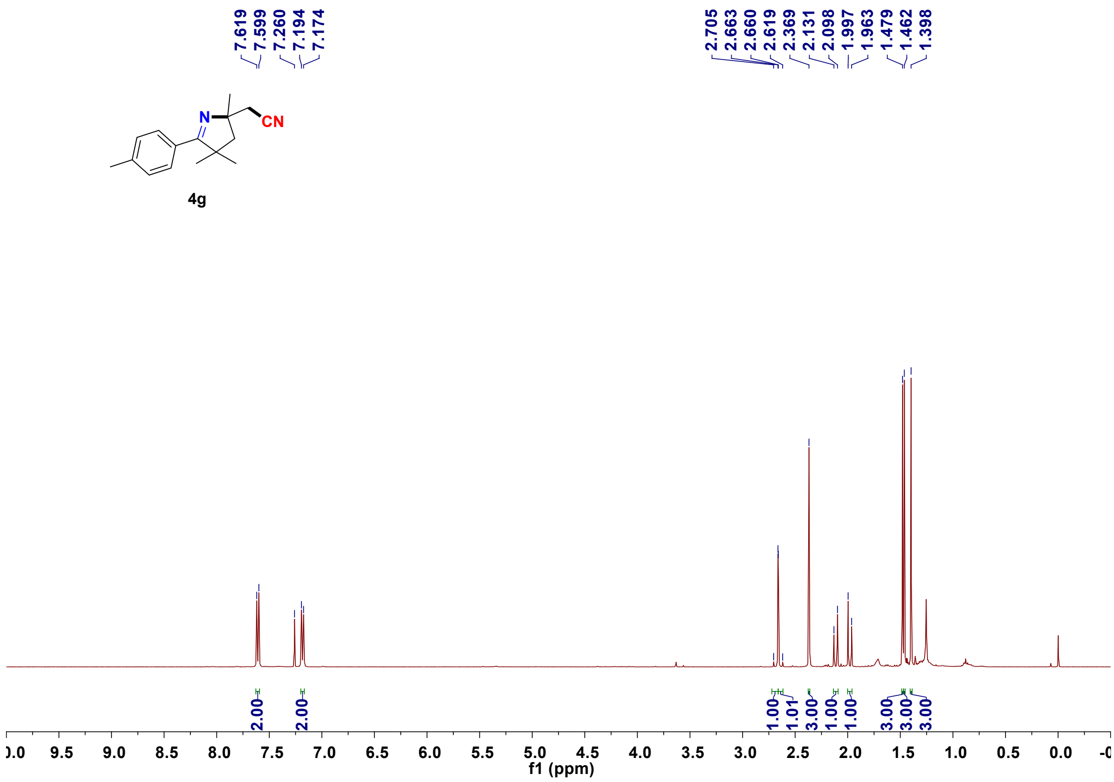
27.26
Ph
N
CN
4e
f1 (ppm)



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1.963
1.479
1.462
1.398
N
CN
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1.00
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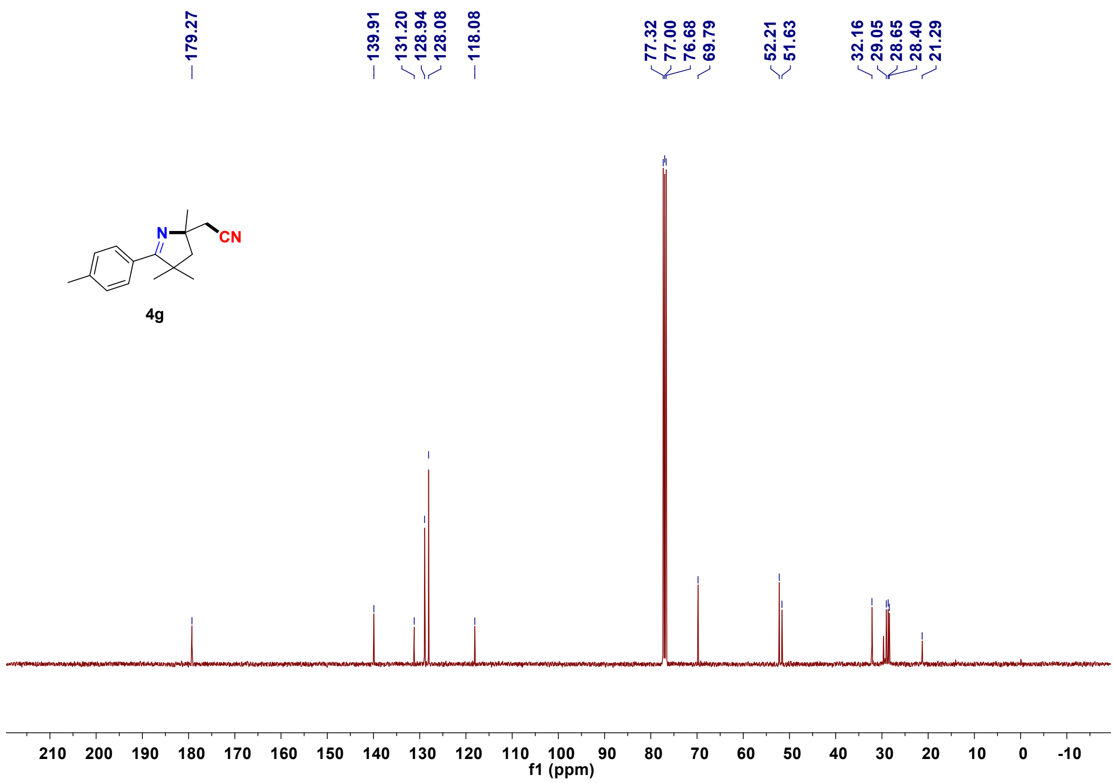
3.00
3.00
3.00
f1 (ppm)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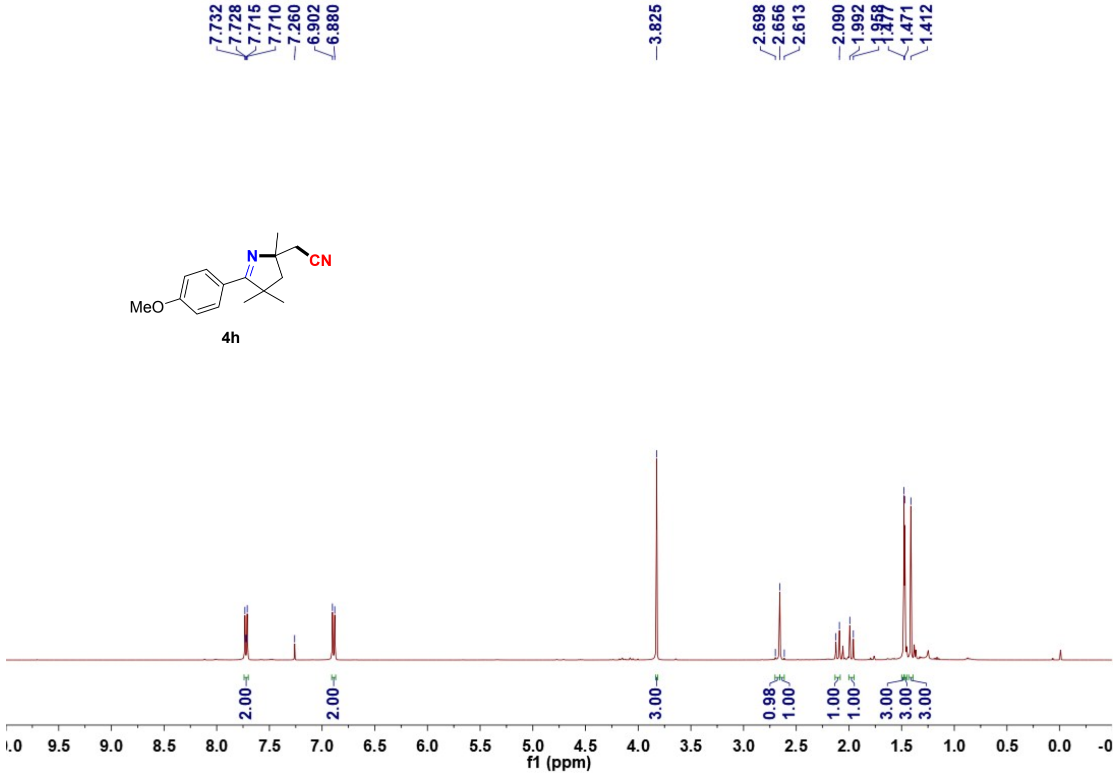
CN
4g
f1 (ppm)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1.992
1.477
1.471
1.412
MeO
N
CN
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1.00
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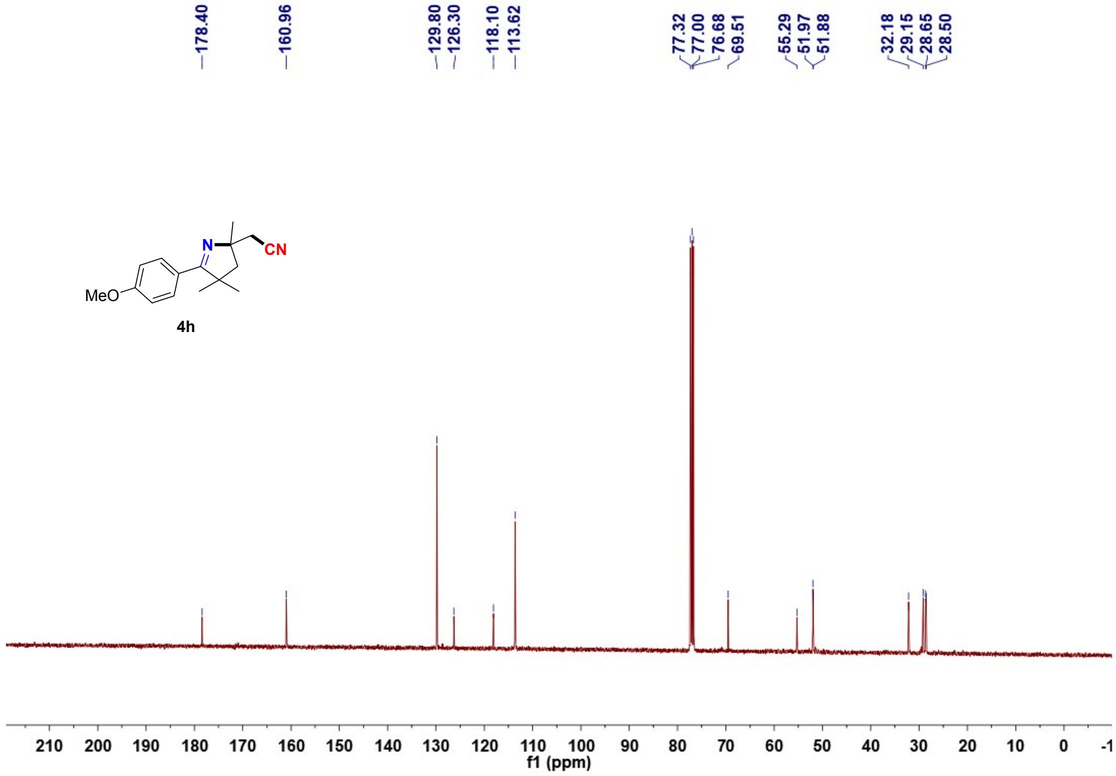
3.00
3.00
3.00
f1 (ppm)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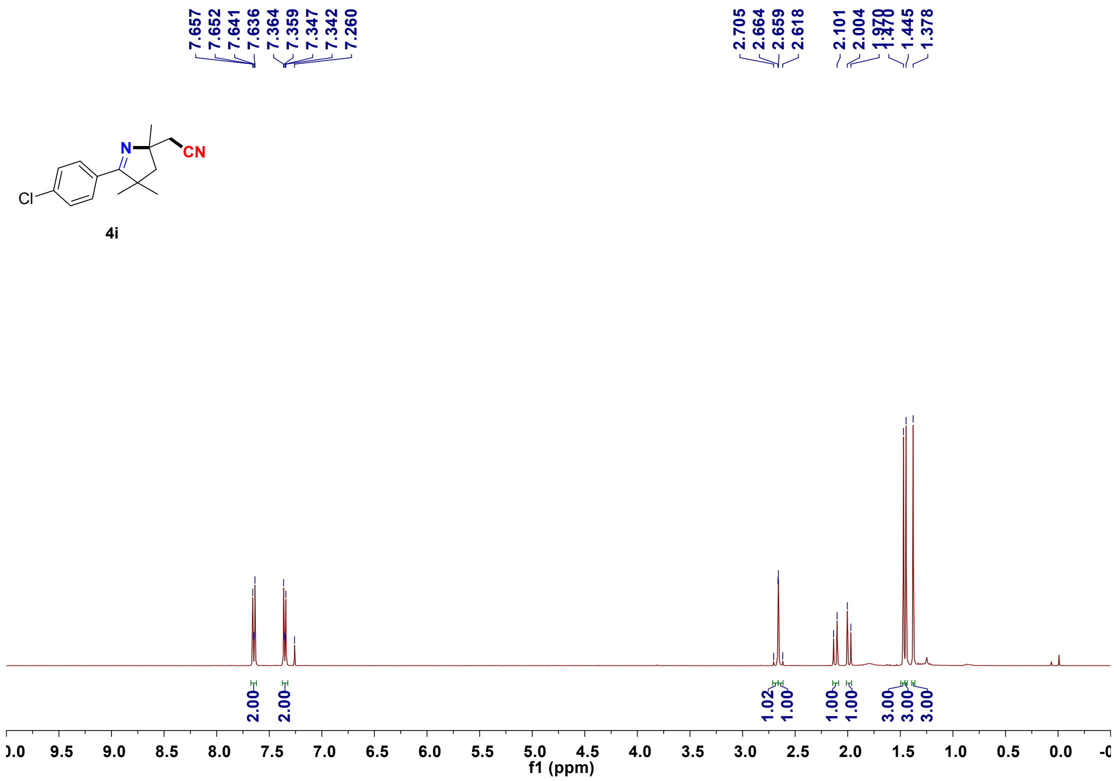
4h
f1 (ppm)



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Cl
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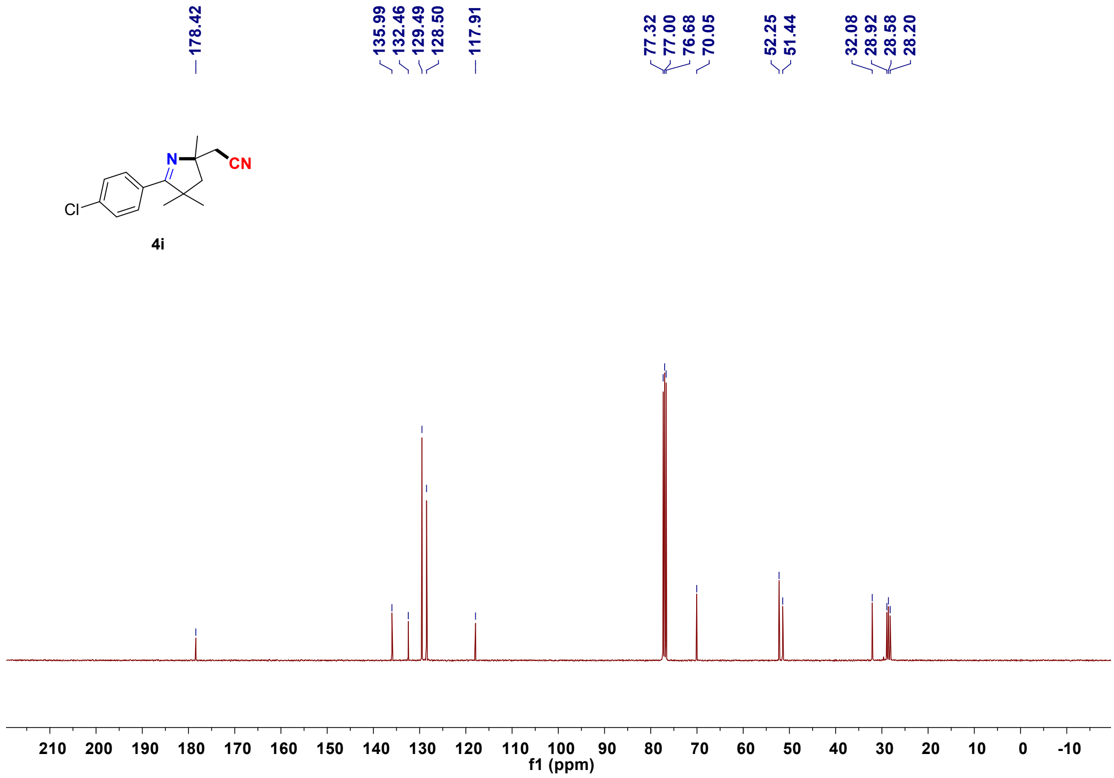

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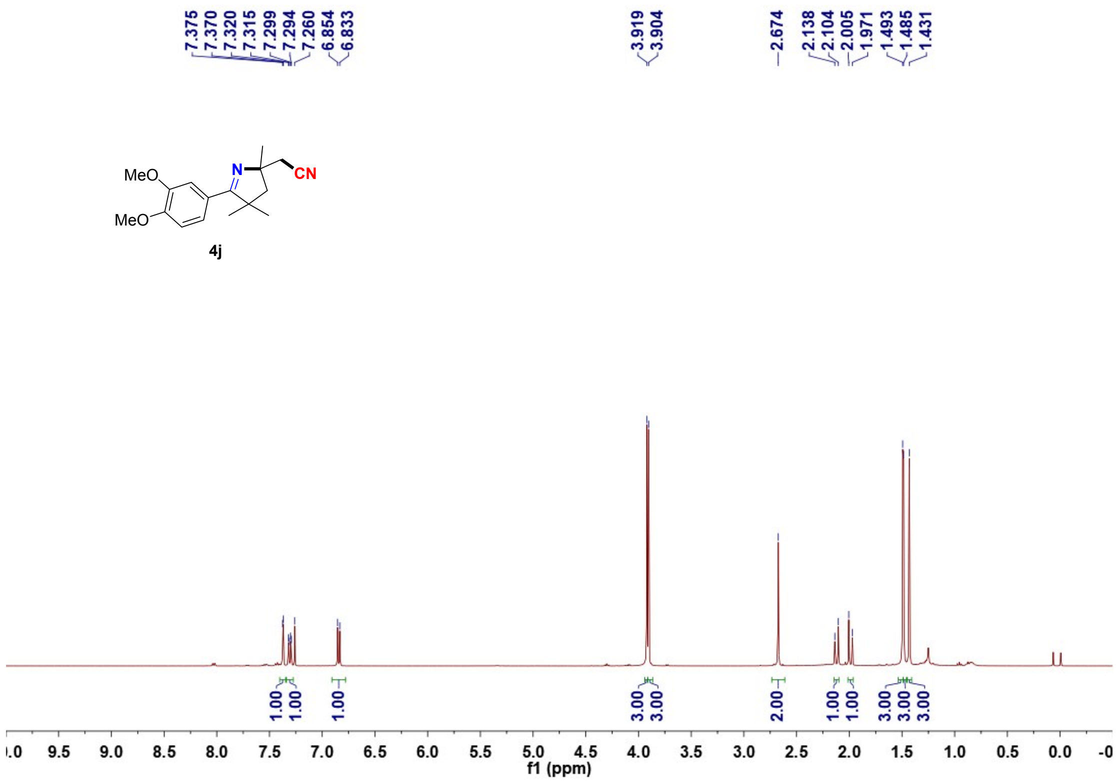
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1.493
1.485
1.431
MeO
MeO
N
CN
4j
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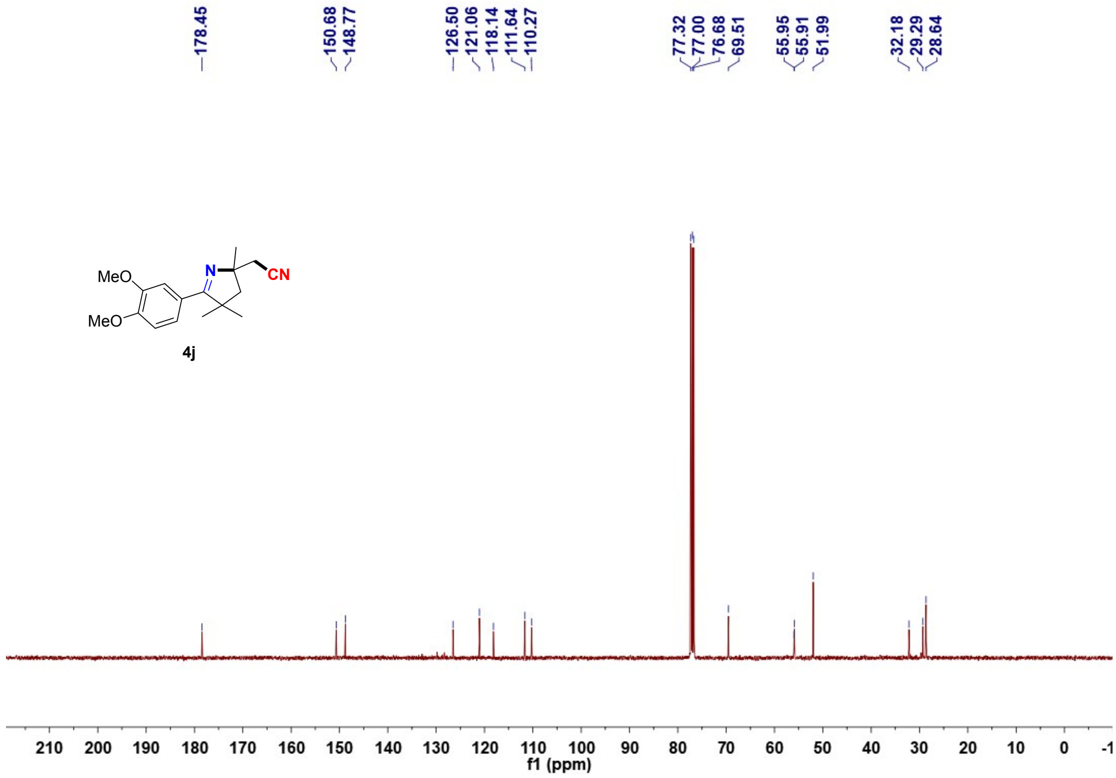
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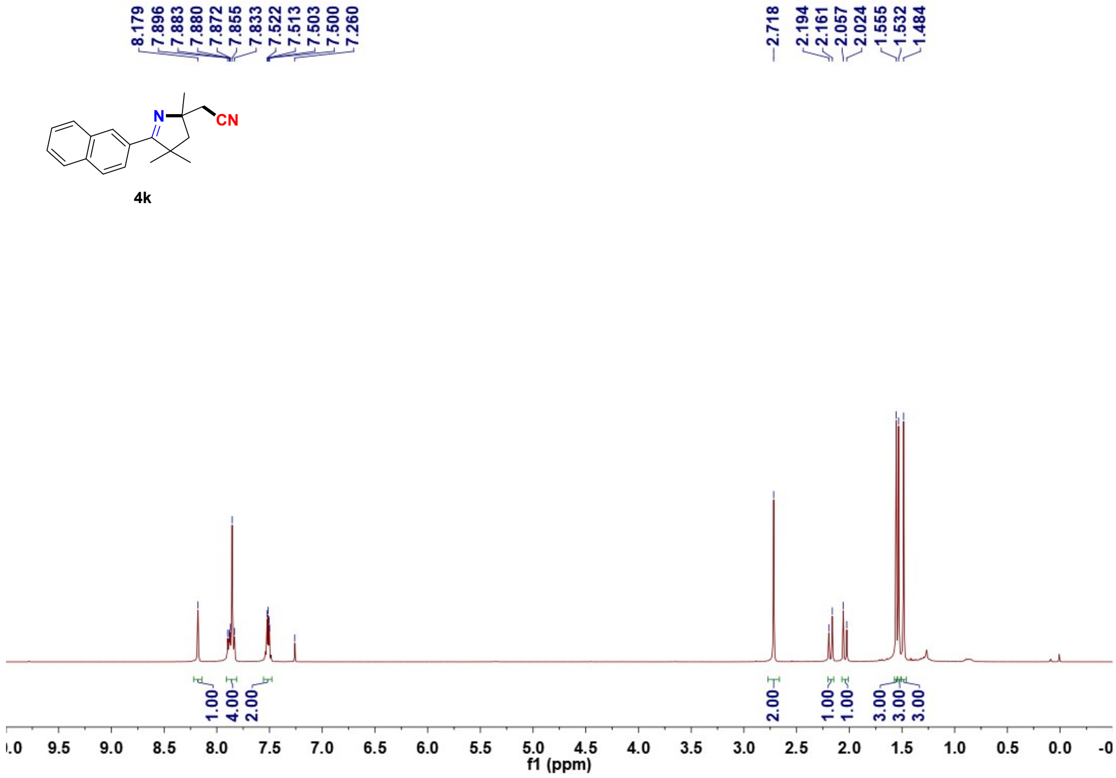
CN
4j
f1 (ppm)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2.057
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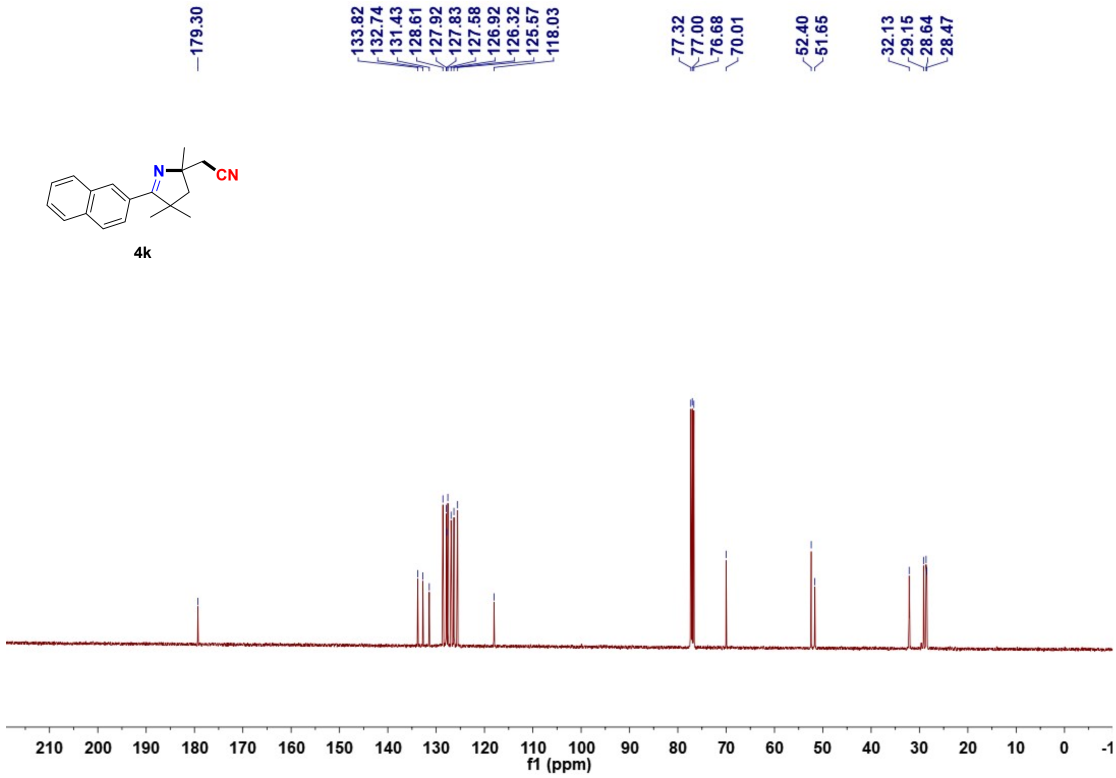
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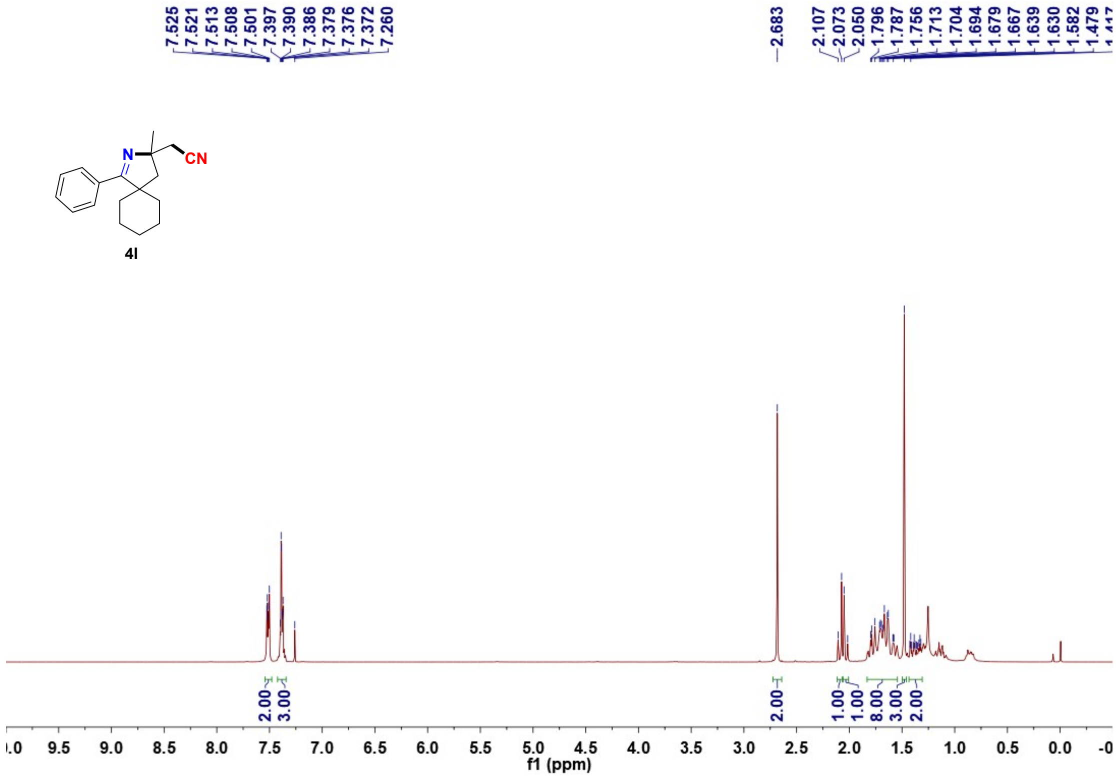
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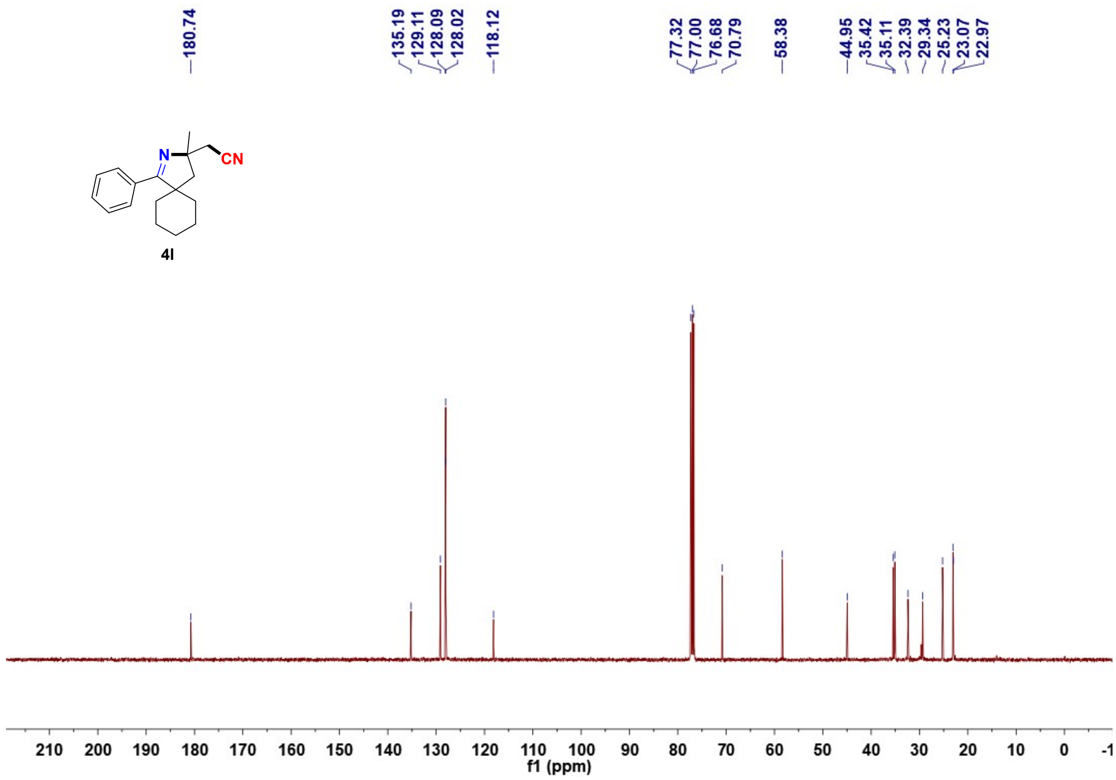
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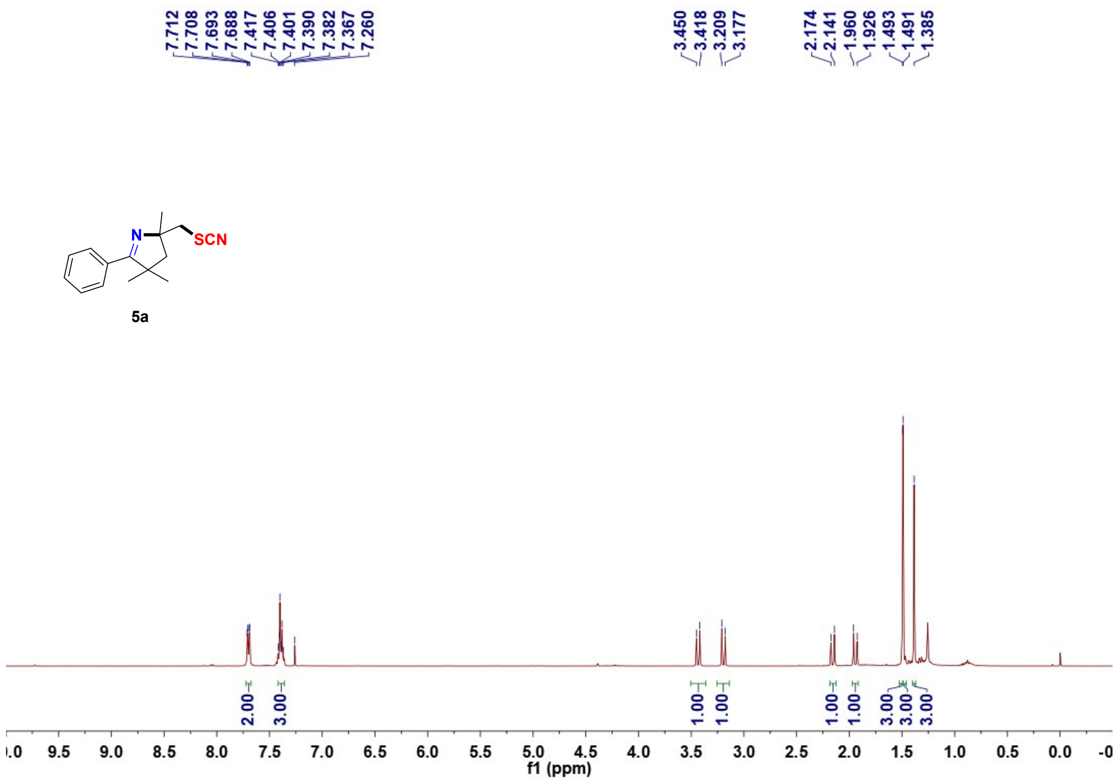
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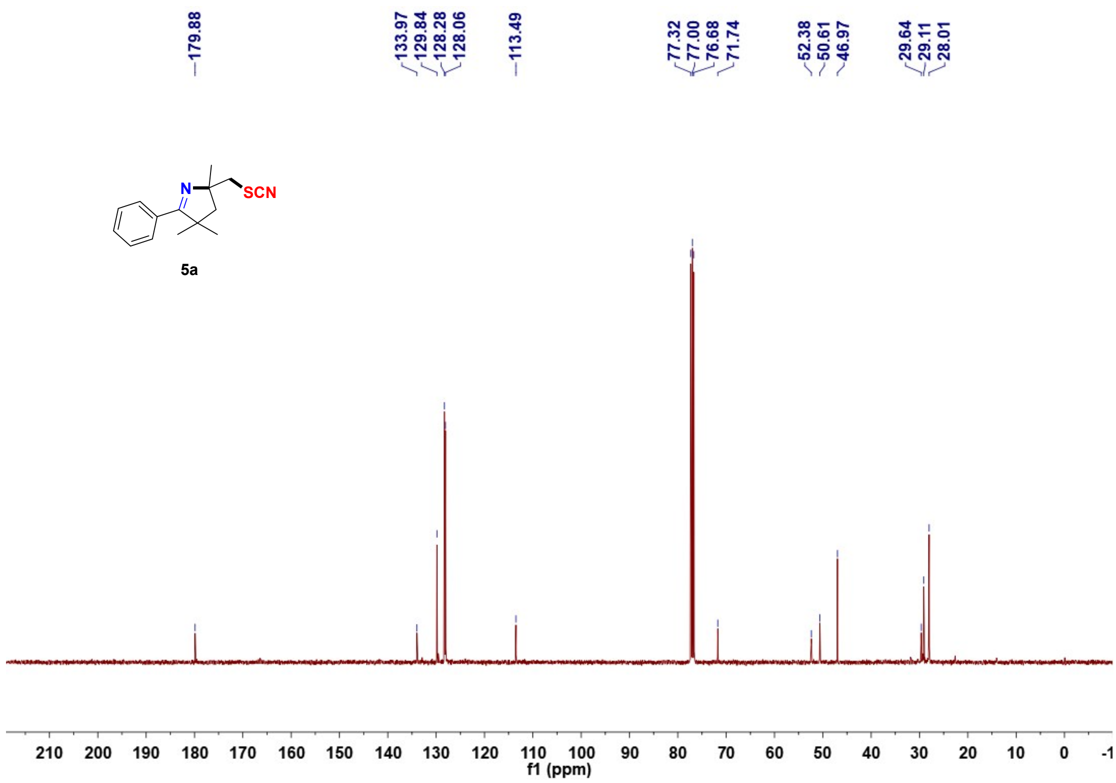
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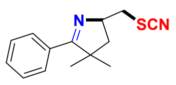
f1 (ppm)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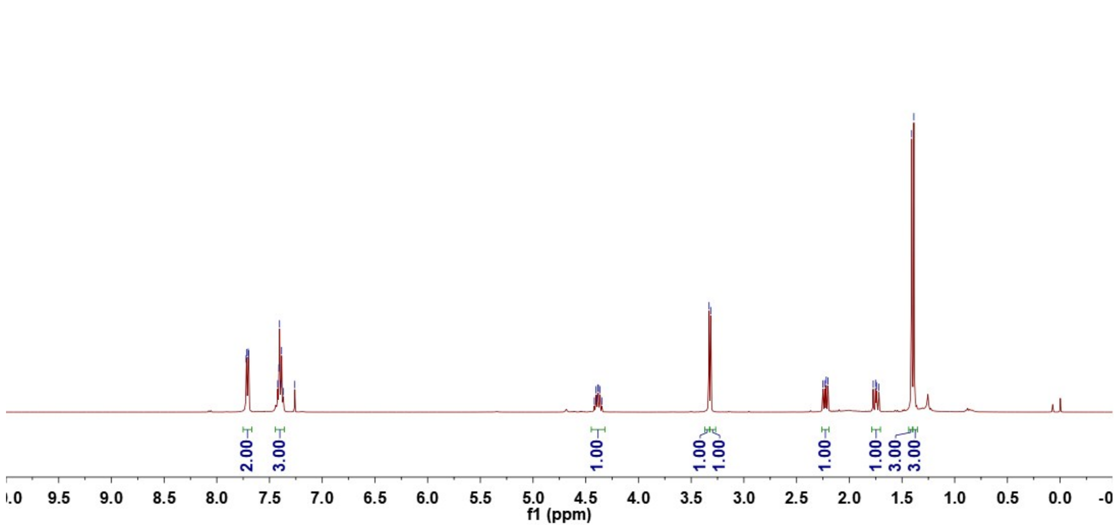
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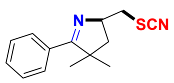
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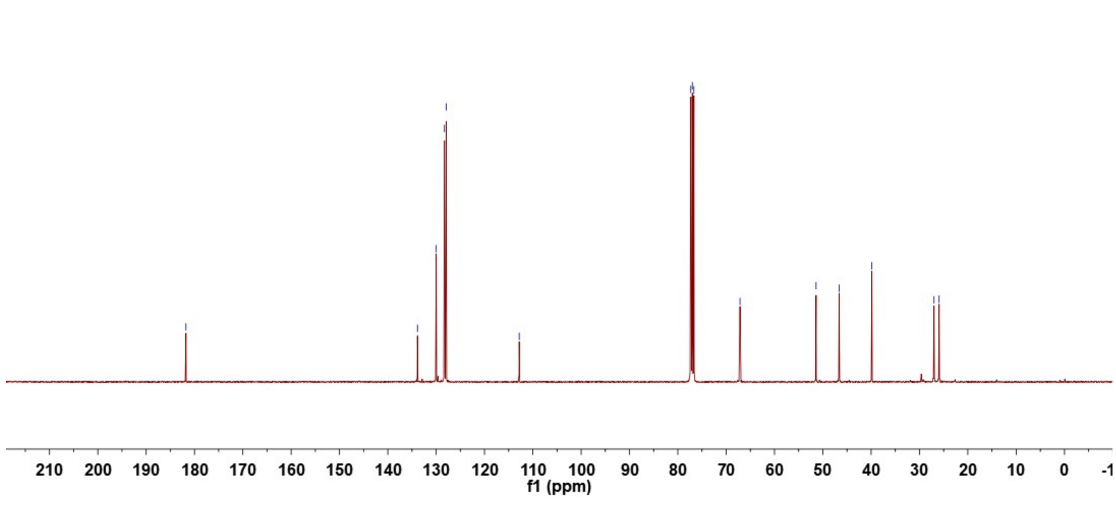
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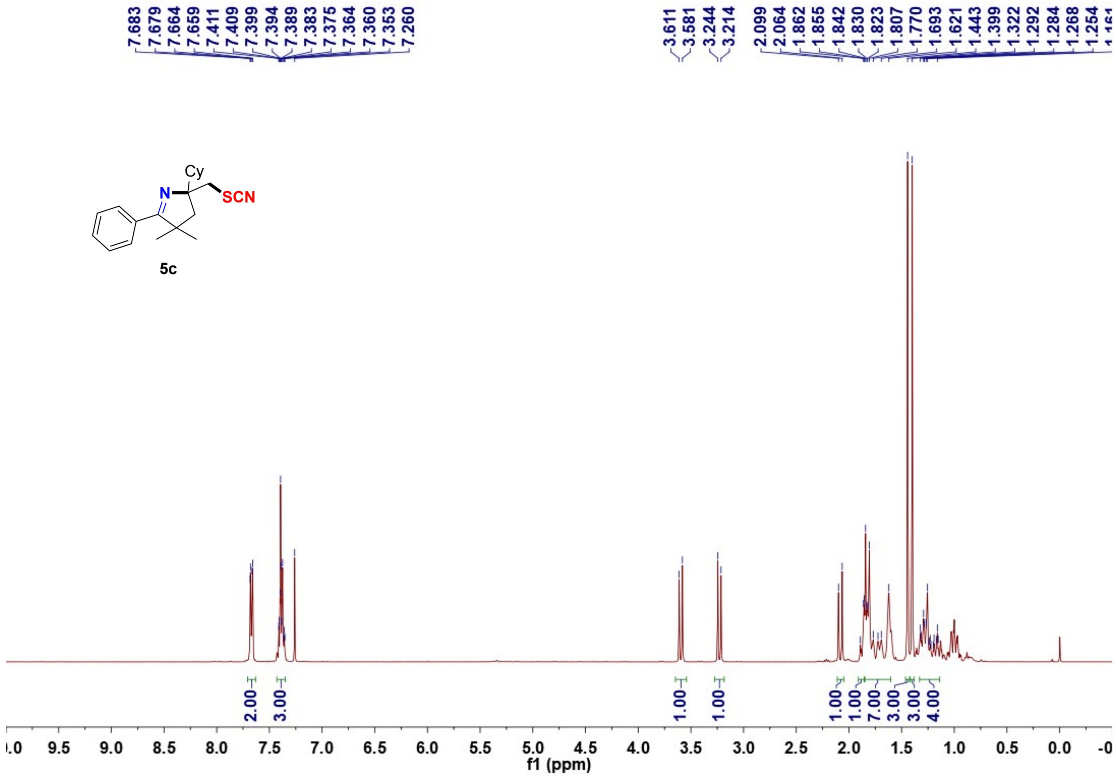

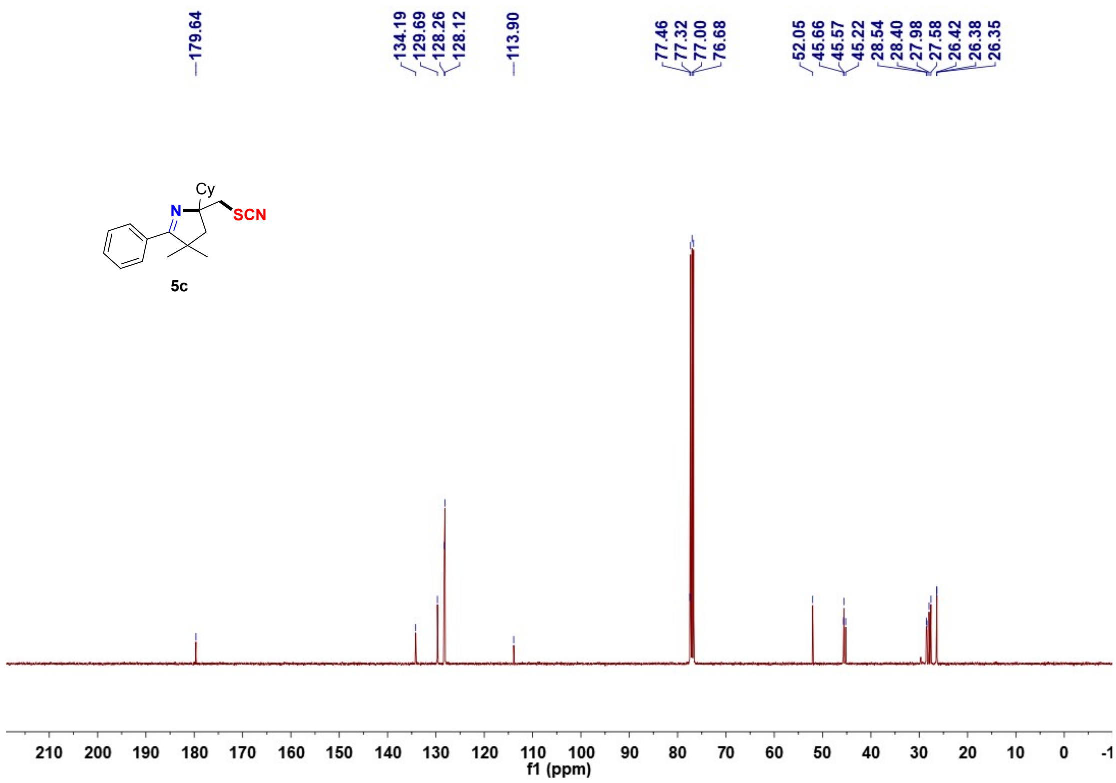

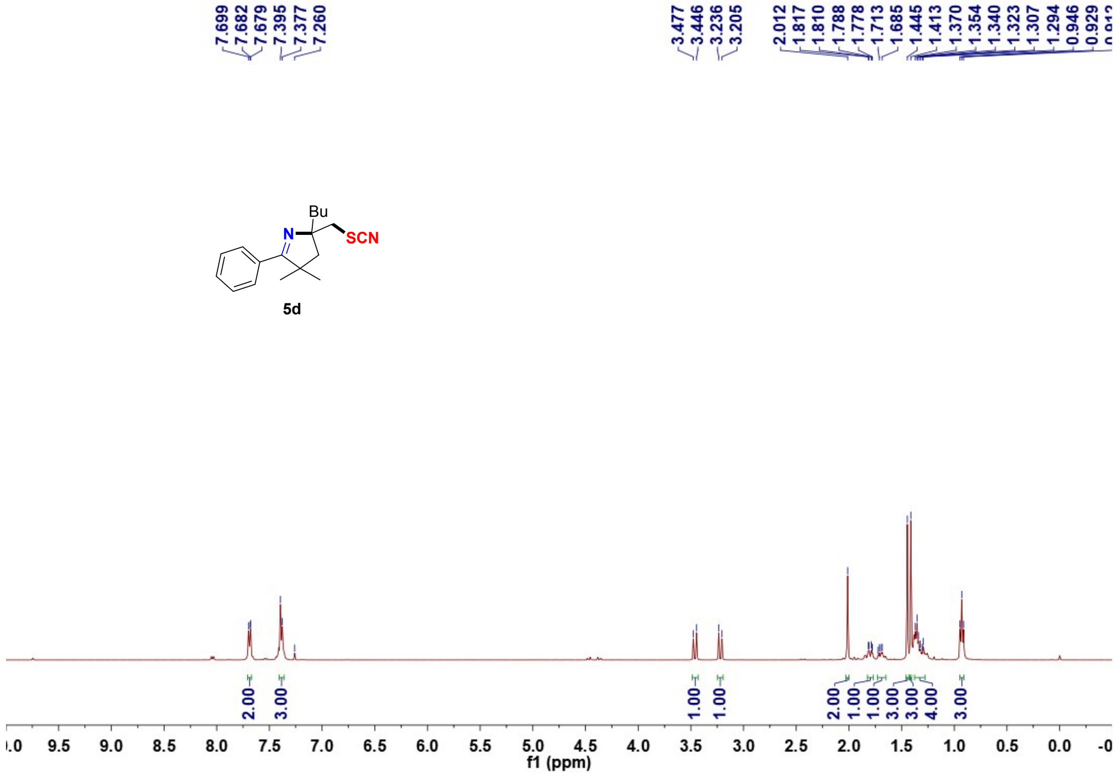
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7.260
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3.446
3.236
3.205
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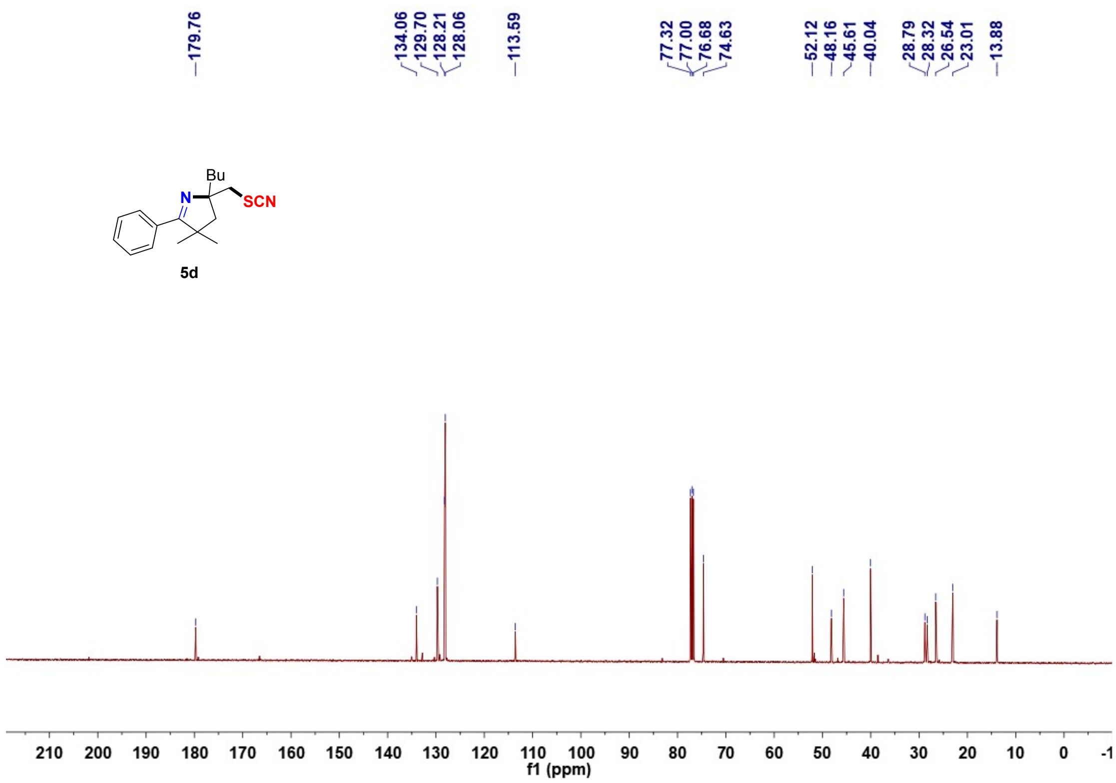
1.810
1.788
1.778
1.713
1.685
1.445
1.413
1.370
1.354
1.340
1.323
1.307
1.294
0.946
0.929
Bu
N
SCN
5d
2.00
3.00
1.00
1.00
2.00
1.00
1.00
3.00
3.00
4.00
3.00
f1 (ppm)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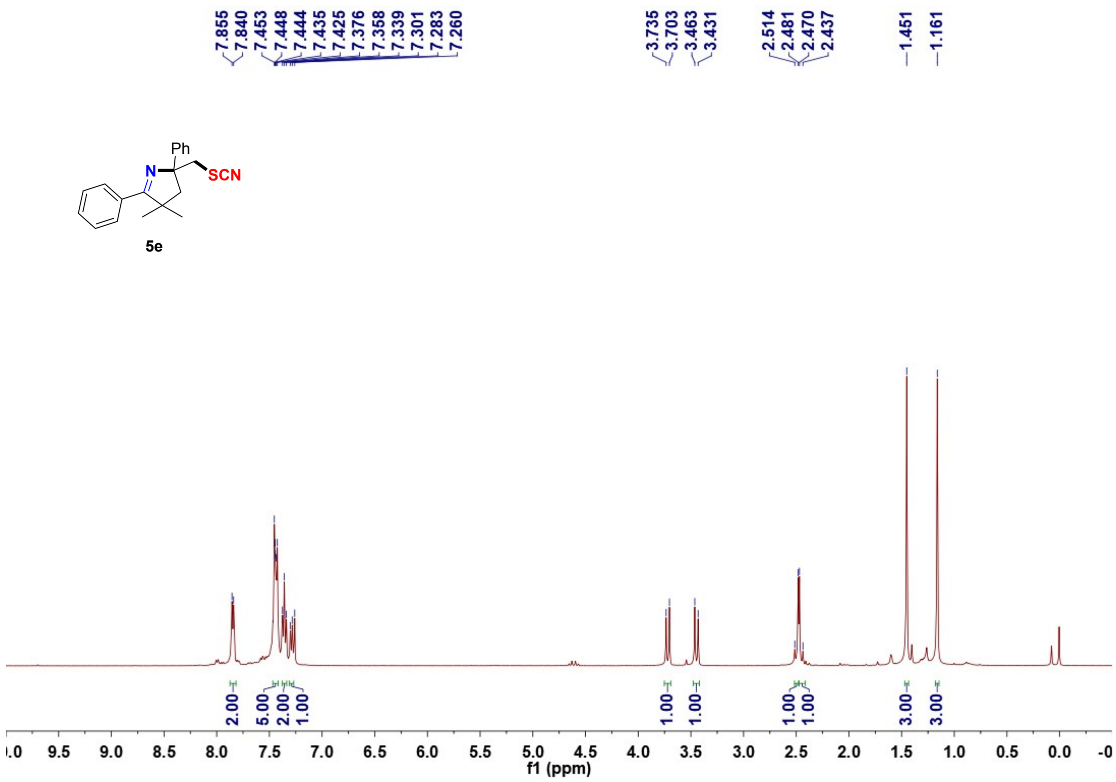
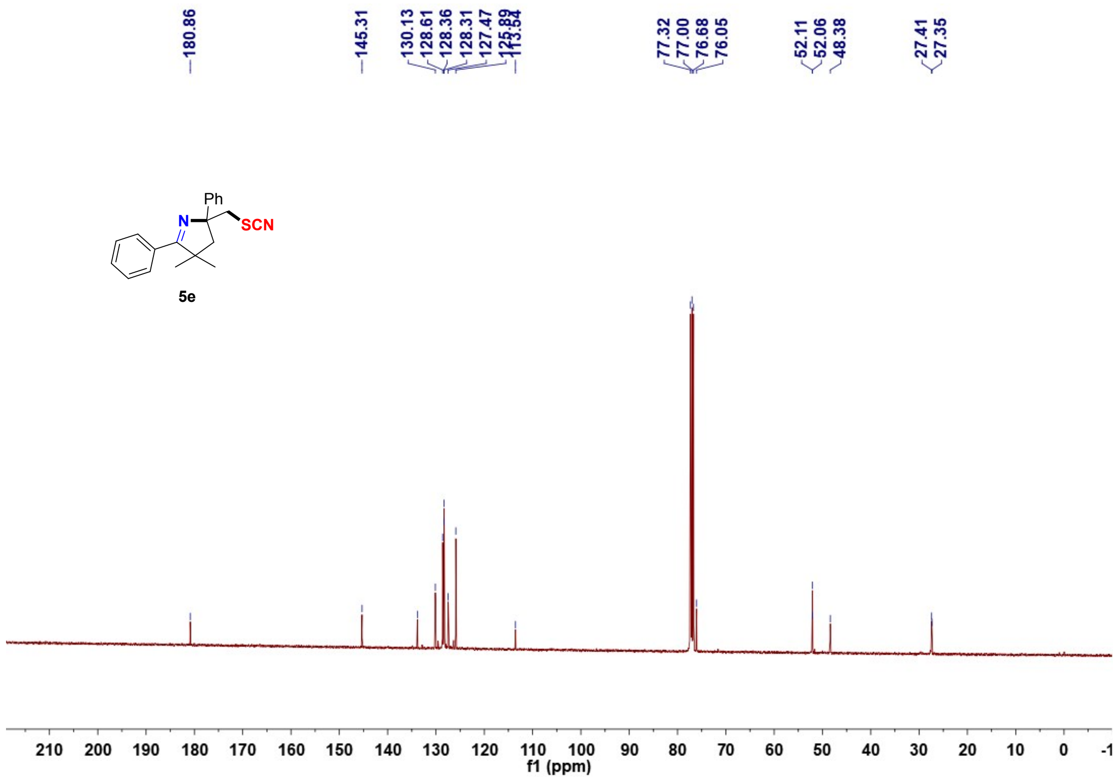
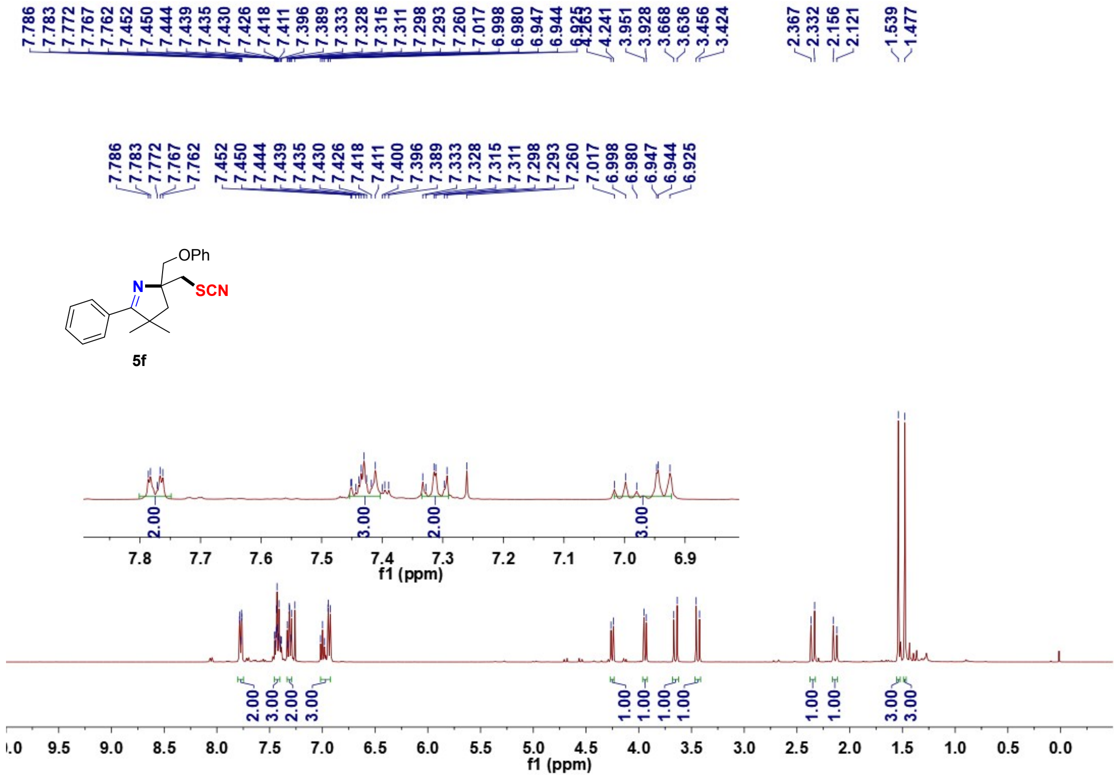
134.06
129.70
128.21
128.06
113.59
77.32
77.00
76.68
74.63
52.12
48.16
45.61
40.04
28.79
28.32
26.54
23.01
13.88
Bu
N
SCN
5d
f1 (ppm)


Ph
N
SCN
5e
f1 (ppm)


Ph
N
SCN
5e
f1 (ppm)



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7.767
7.762
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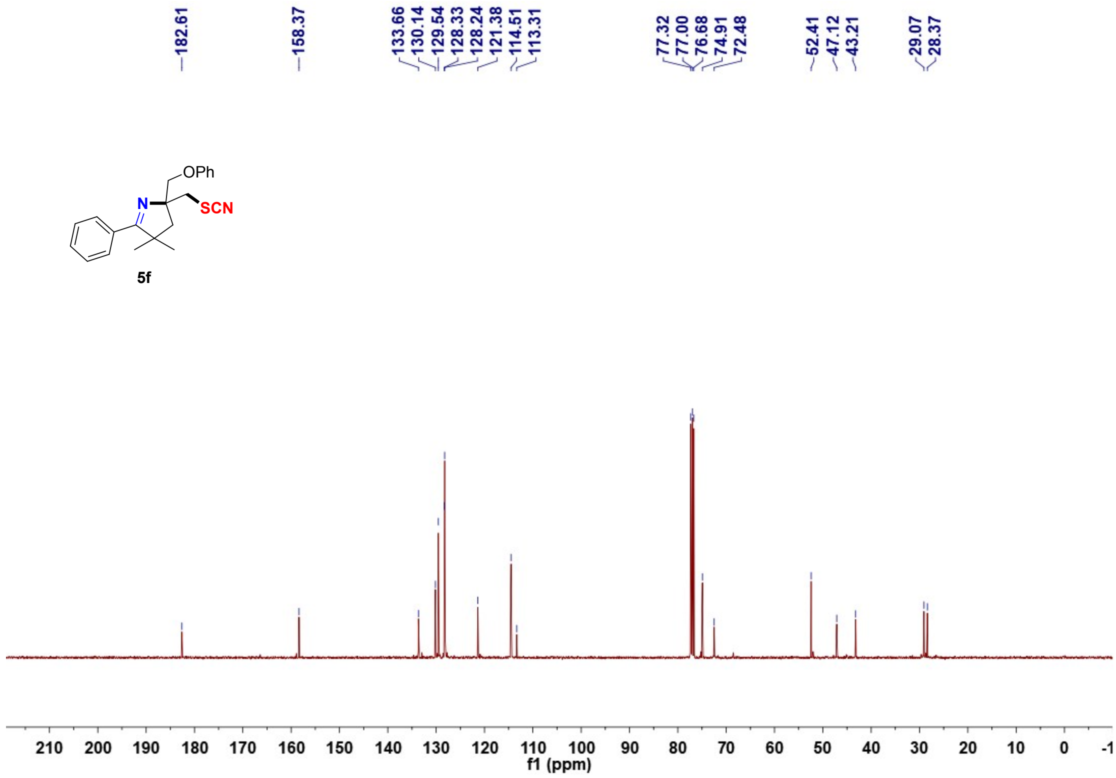
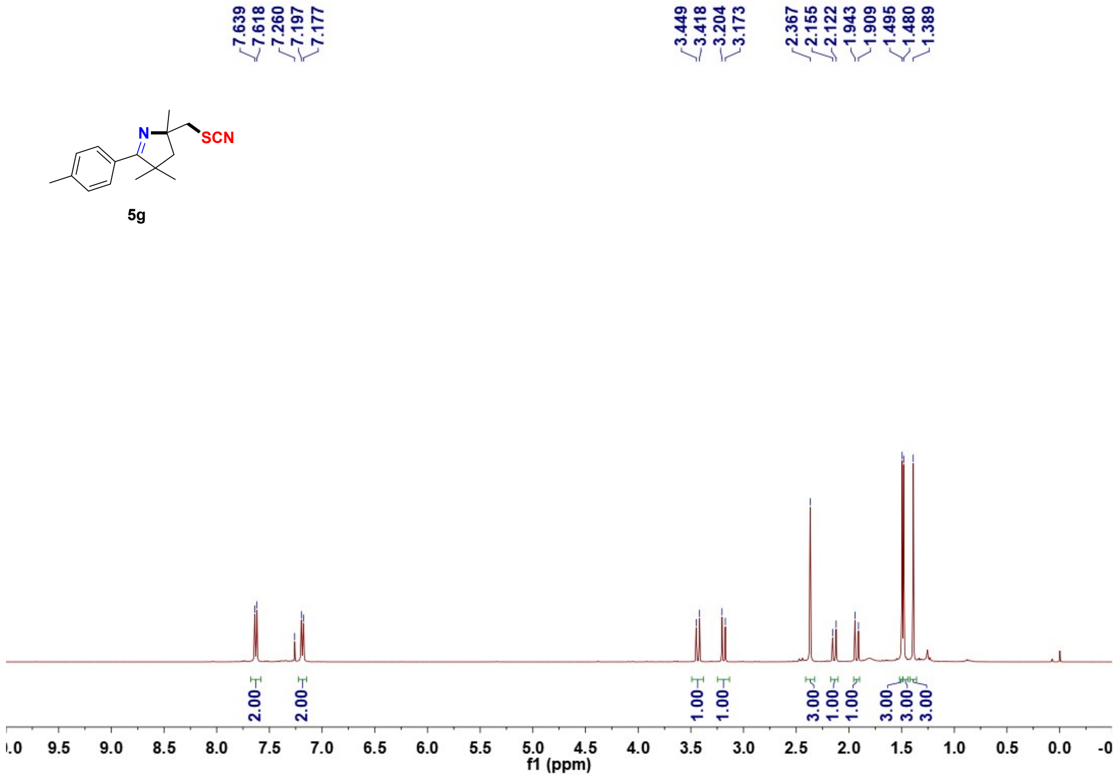
7.450
7.444
7.439
7.435
7.430
7.426
7.418
7.411
7.396
7.389
7.333
7.328
7.315
7.311
7.298
7.293
7.260
7.017
6.998
6.980
6.947
6.944
6.925
4.263
4.241
3.951
3.928
3.668
3.636
3.456
3.424
2.367
2.332
2.156
2.121
1.539
1.477
2.00
3.00
2.00
3.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)
OPh
N
SCN

5f



182.61
158.37
133.66
130.14
129.54
128.33
128.24
121.38
114.51
113.31
77.32
77.00
76.68
74.91
72.48
52.41
47.12
43.21
29.07
28.37
f1 (ppm)
OPh
N
SCN

5f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7.260
7.197
7.177
3.449
3.418
3.204
3.173
2.367
2.155
2.122
1.943
1.909
1.495
1.480
1.389
N
SCN
5g
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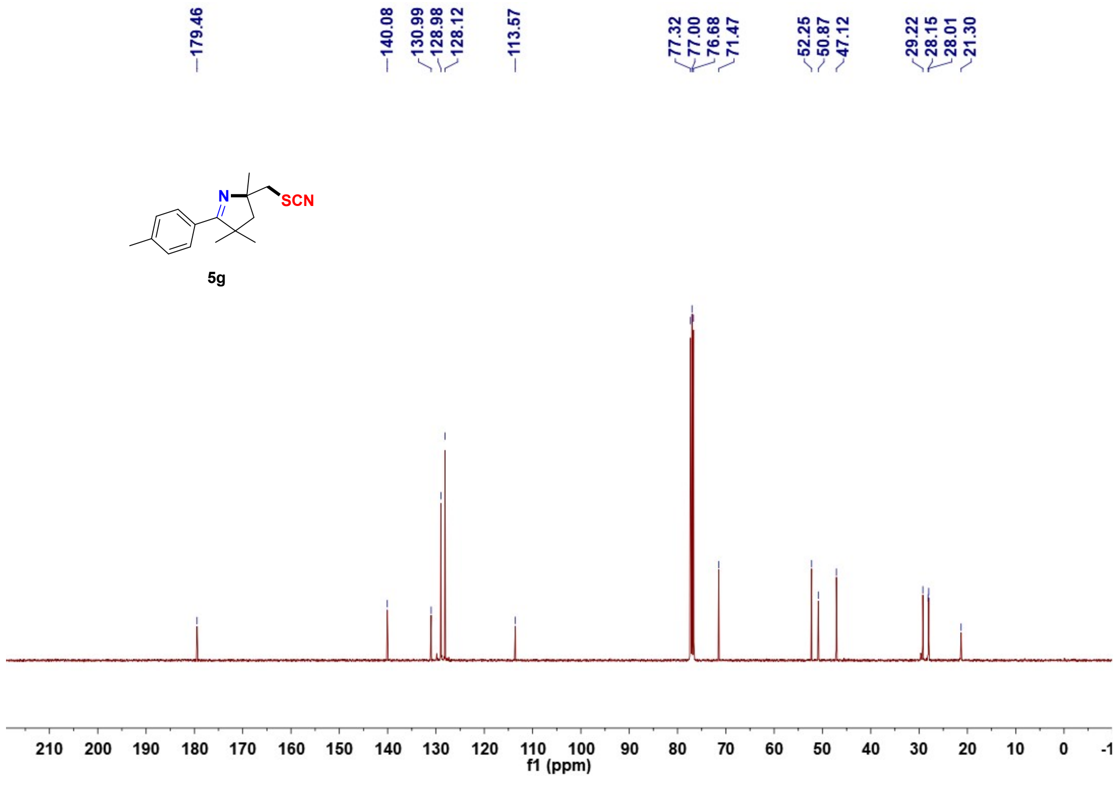
2.00
1.00
1.00
3.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)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128.12
113.57
77.32
77.00
76.68
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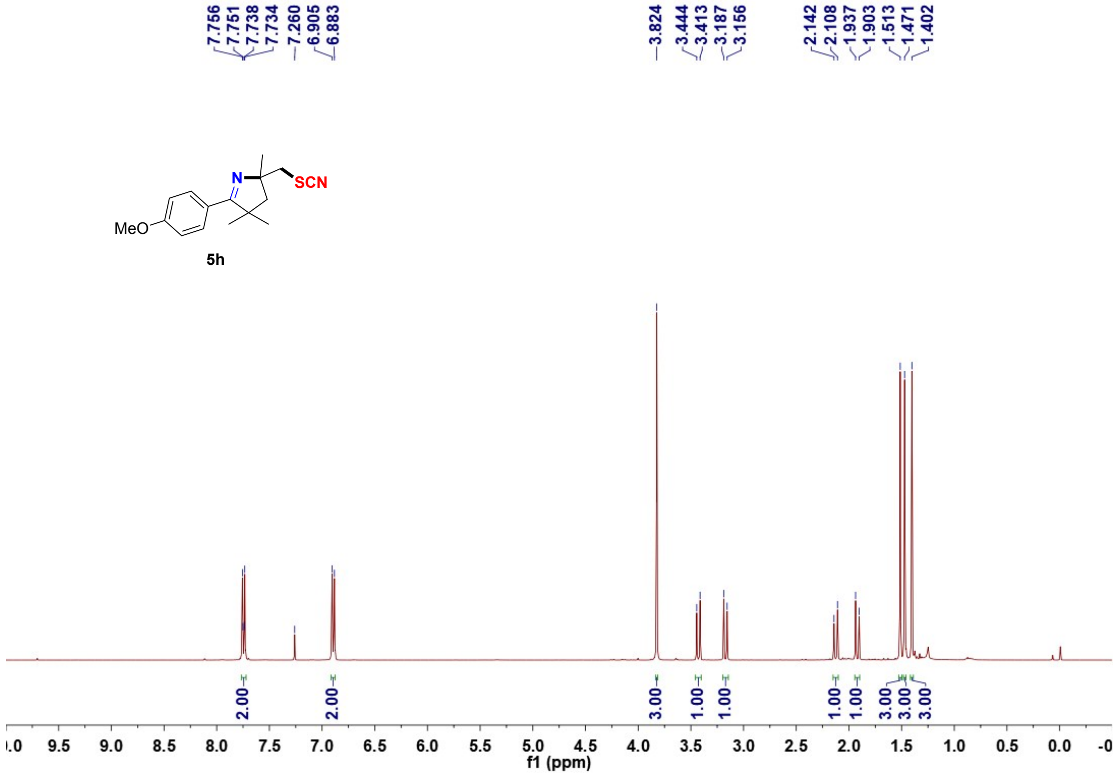
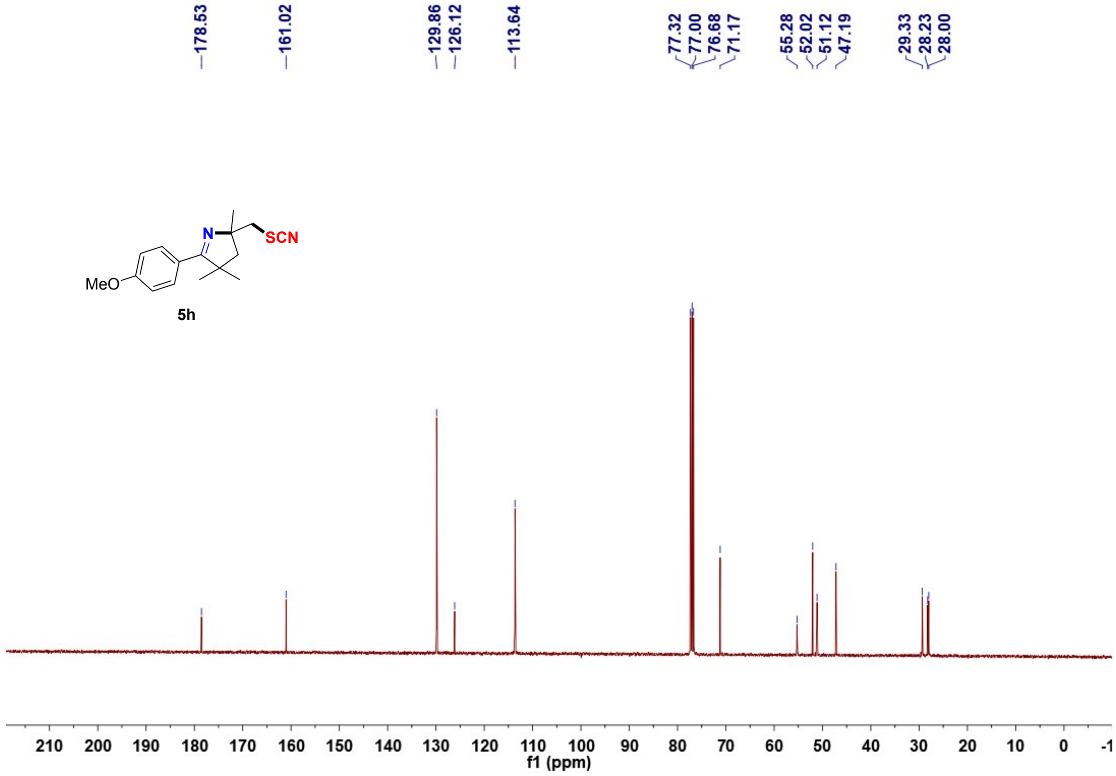
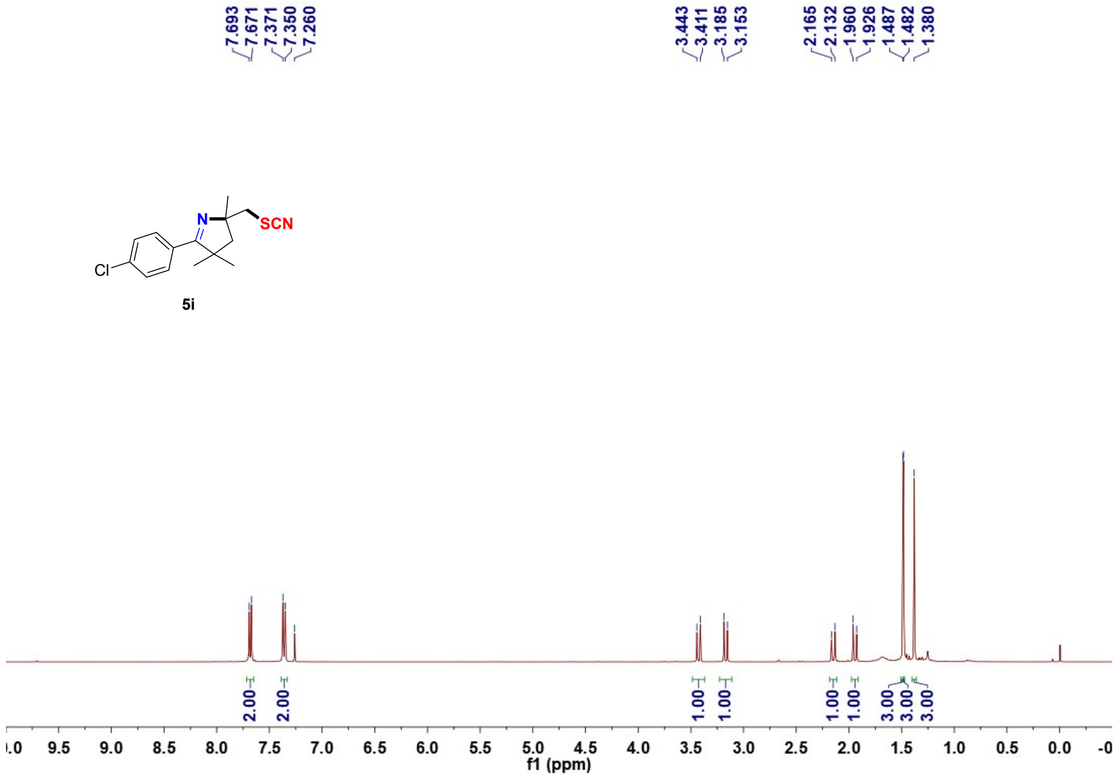
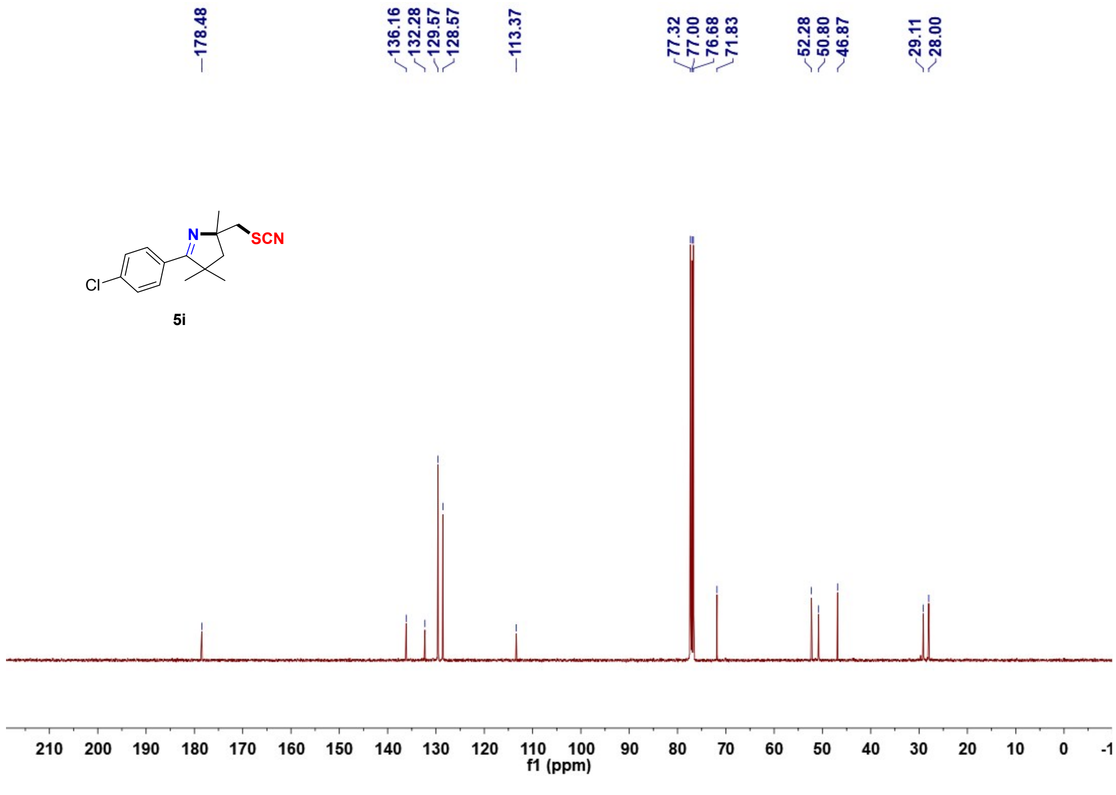
50.87
47.12
29.22
28.15
28.01
21.30
N
SCN
5g
f1 (ppm)






7.693
7.671
7.371
7.350
7.260
3.443
3.411
3.185
3.153
2.165
2.132
1.960
1.926
1.487
1.482
1.380
Cl
N
SCN
5i
2.00
2.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)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136.16
132.28
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128.57
113.37
77.32
77.00
76.68
71.83
52.28
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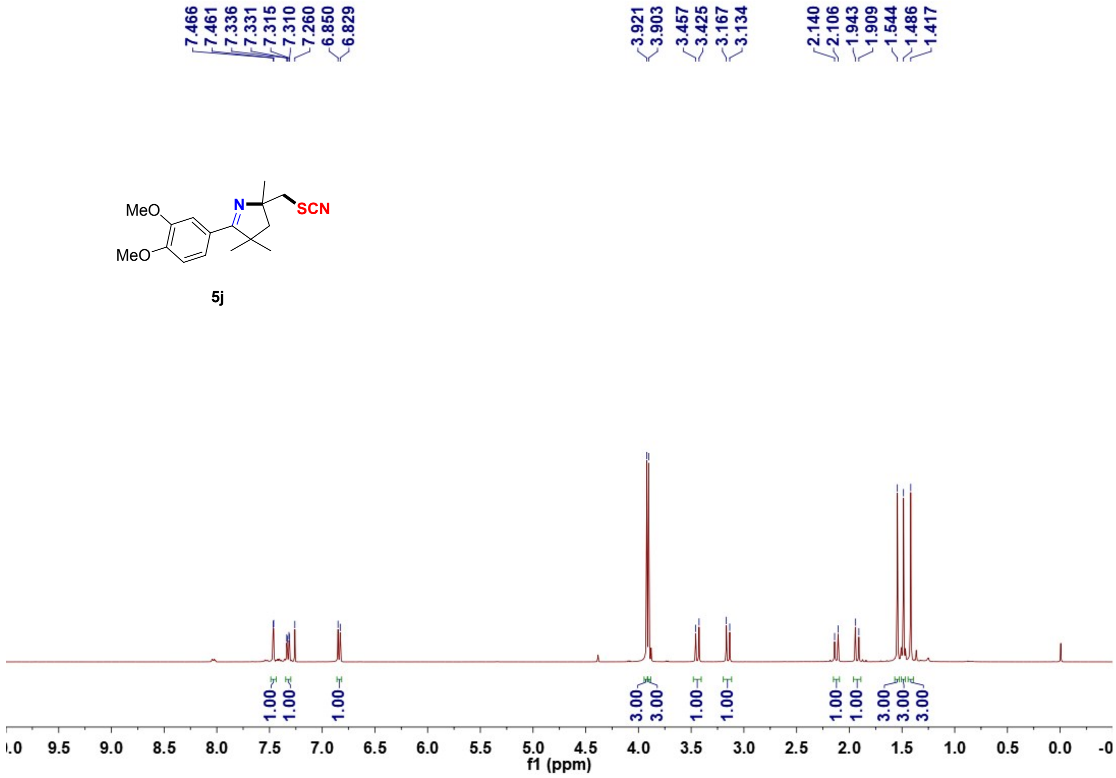
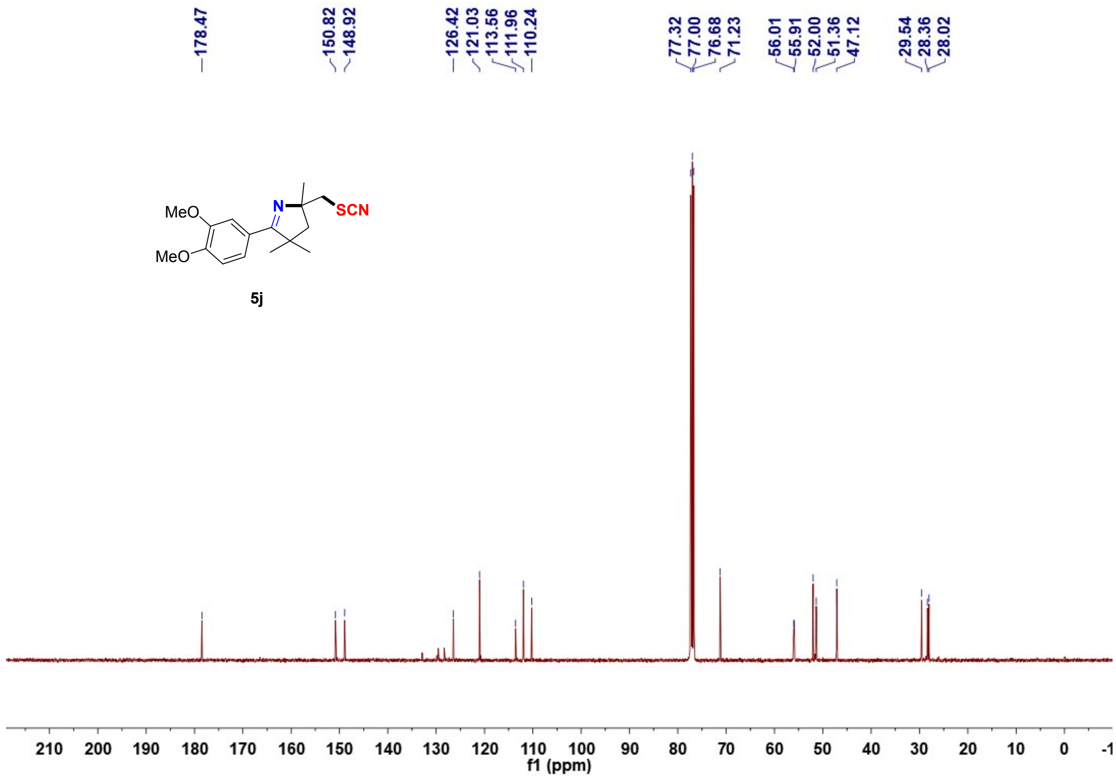
46.87
29.11
28.00
Cl
N
SCN
5i
f1 (ppm)



7.466
7.461
7.336
7.331
7.315
7.310
7.260
6.850
6.829
3.921
3.903
3.457
3.425
3.167
3.134
2.140
2.106
1.943
1.909
1.544
1.486
1.417
MeO
MeO
N
SCN
5j
1.00
1.00
1.00
3.00
3.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)



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148.92
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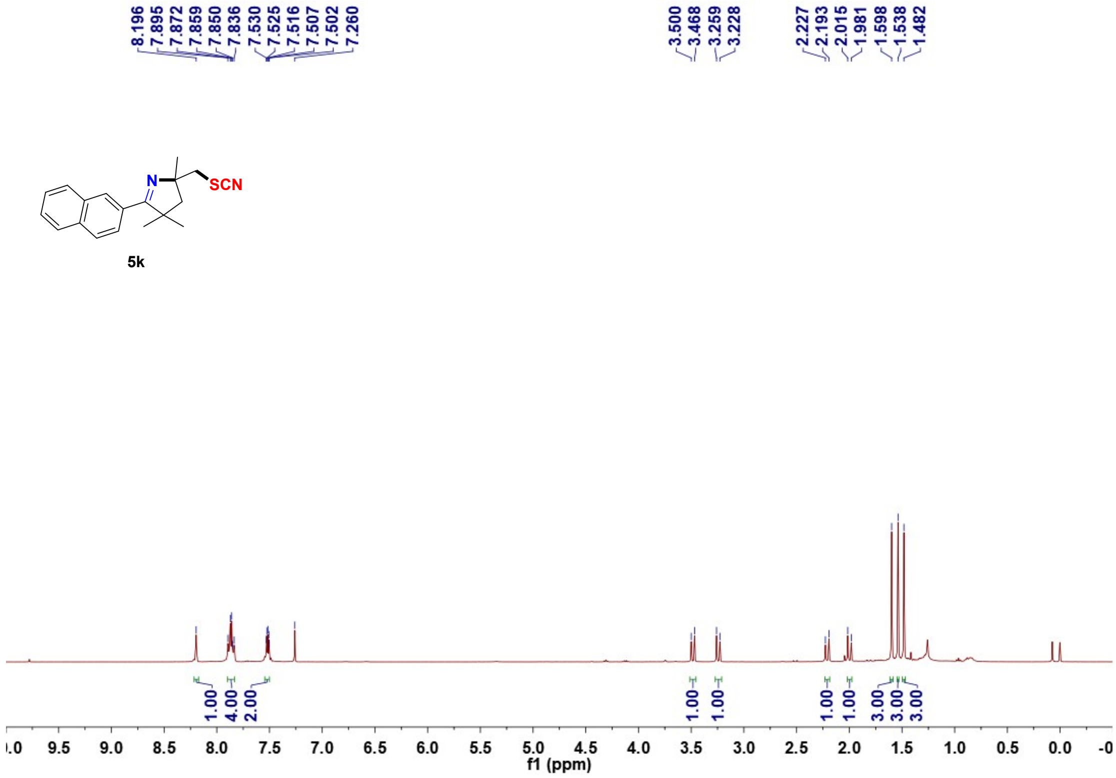
121.03
113.56
111.96
110.24
77.32
77.00
76.68
71.23
56.01
55.91
52.00
51.36
47.12
29.54
28.36
28.02
MeO
MeO
N
SCN
5j
f1 (ppm)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7.850
7.836
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7.525
7.516
7.507
7.502
7.260
3.500
3.468
3.259
3.228
2.227
2.193
2.015
1.981
1.598
1.538
1.482
N
SCN
5k
1.00
4.00
2.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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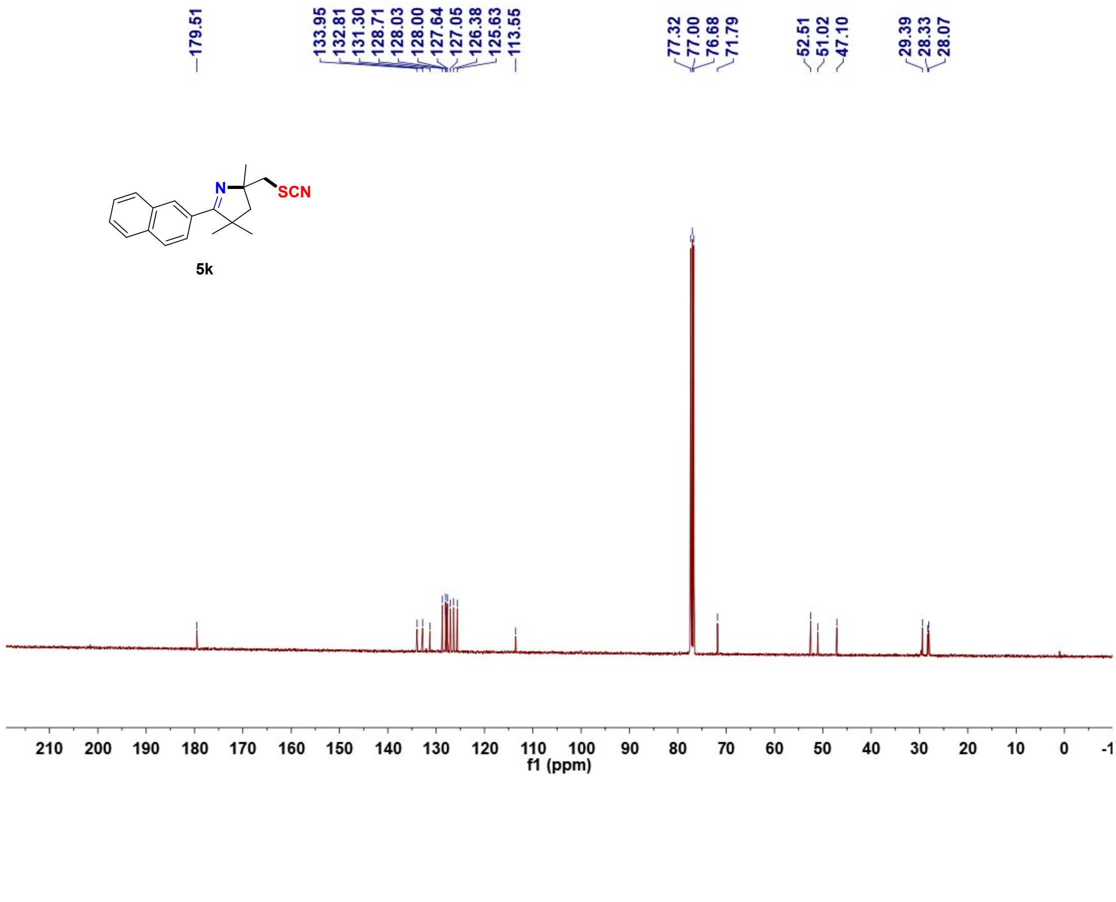
0.0
f1 (ppm)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128.00
127.64
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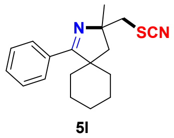
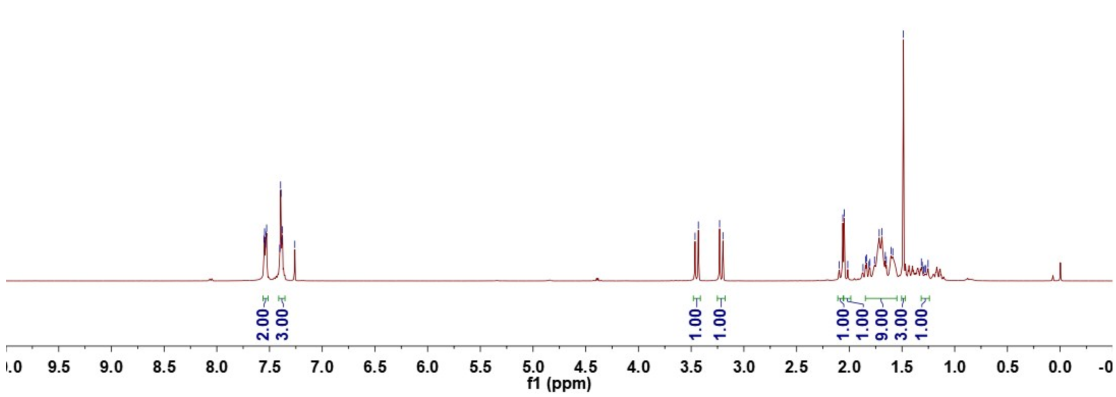
126.38
125.63
113.55
77.32
77.00
76.68
71.79
52.51
51.02
47.10
29.39
28.33
28.07
N
SCN
5k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



N
SCN

5l



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7.534
7.527
7.402
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7.392
7.384
7.377
7.260
3.463
3.432
3.231
3.199
2.096
2.062
2.049
2.015
1.846
1.837
1.814
1.804
1.760
1.716
1.690
1.659
1.649
1.604
1.587
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3.00
1.00
1.00
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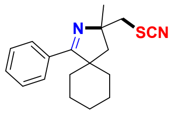
3.00
1.00
f1 (ppm)



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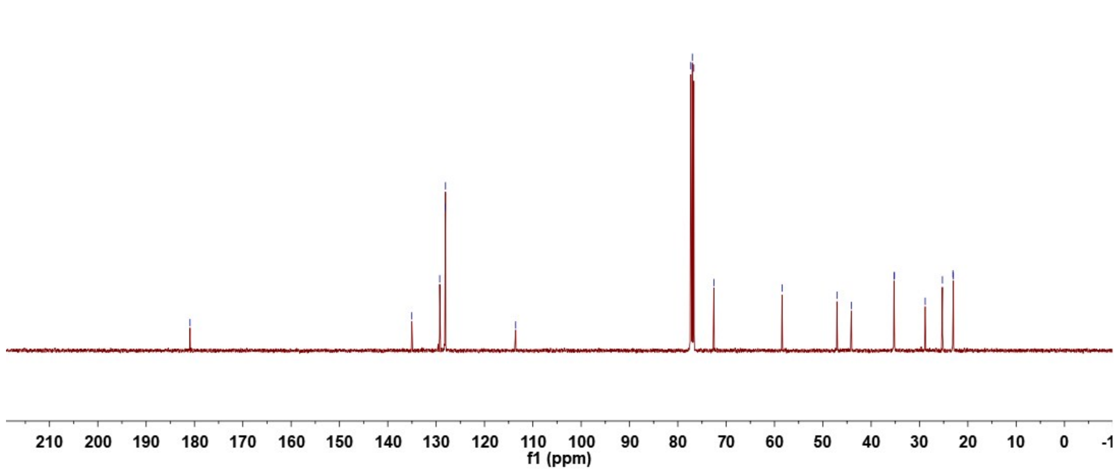
SCN

5l



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128.06
113.54
77.32
77.00
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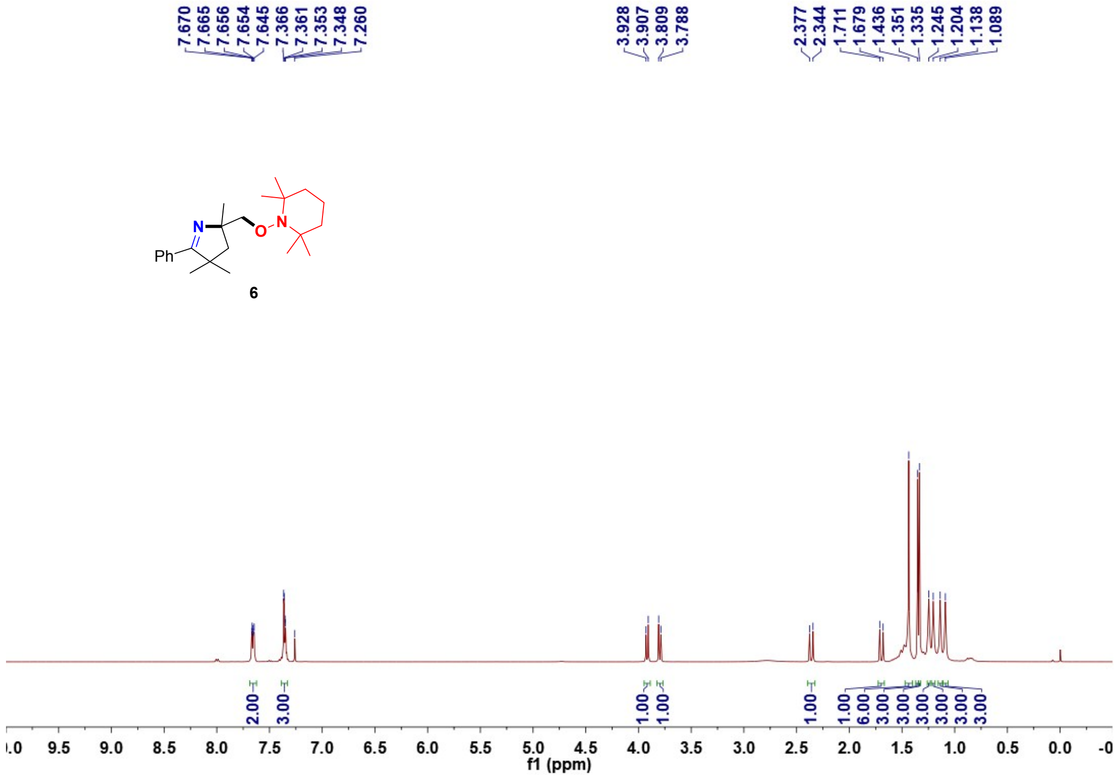
25.26
23.09
22.99
f1 (ppm)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7.260
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3.809
3.788
2.377
2.344
1.711
1.679
1.436
1.351
1.335
1.245
1.204
1.138
1.089
N
O
N
Ph
6
2.00
3.00
1.00
1.00
1.00
1.00
6.00
3.00
3.00
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
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1.0
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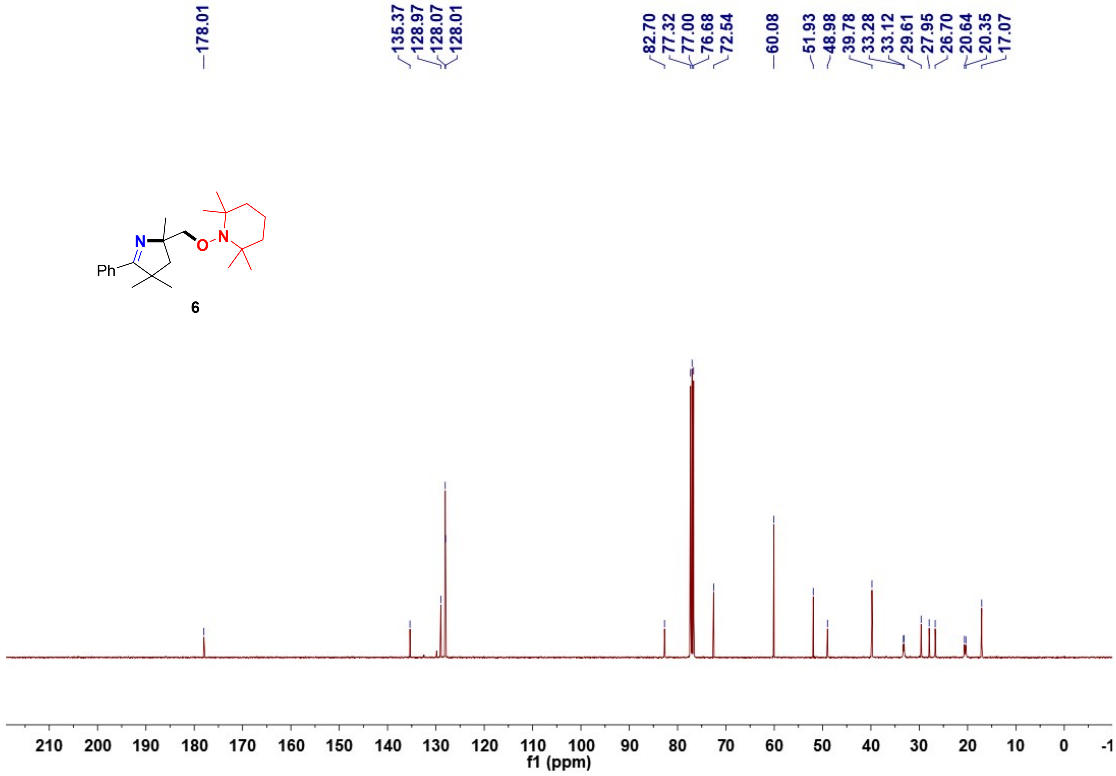
0.0
f1 (ppm)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128.07
128.01
82.70
77.32
77.00
76.68
72.54
60.08
51.93
48.98
39.78
33.28
33.12
29.61
27.95
26.70
20.64
20.35
17.07
N
O
N
Ph
6
210
200
190
180
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80
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50
40
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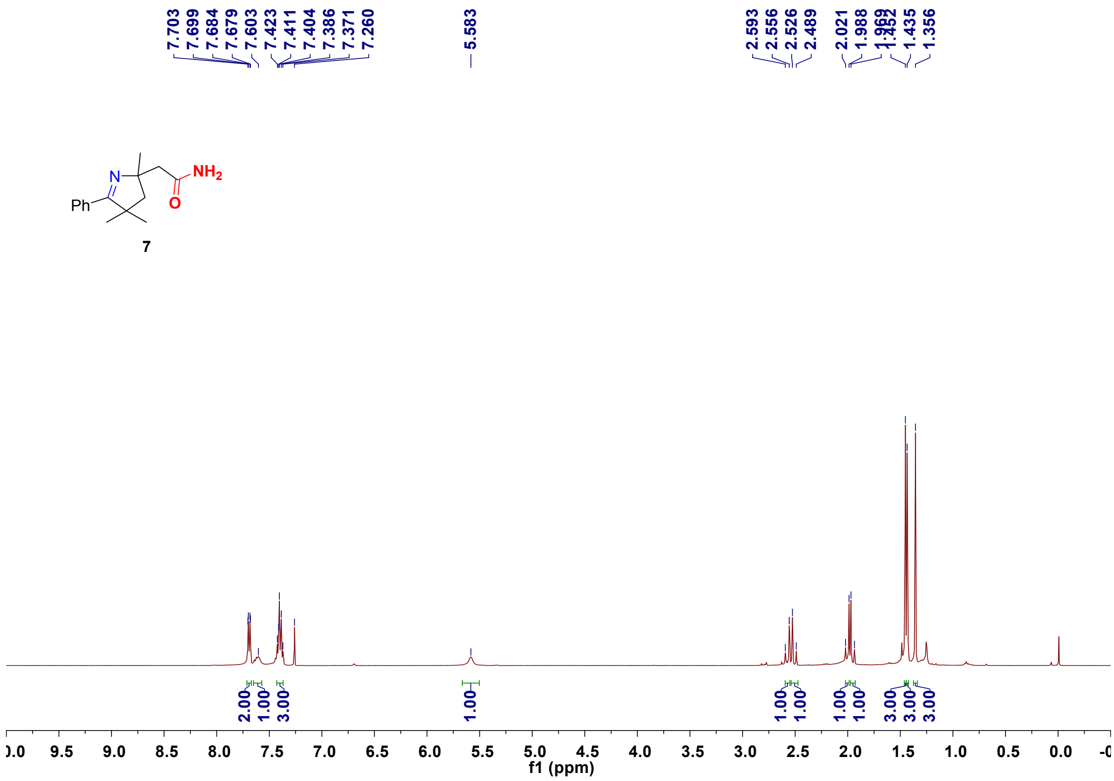
f1 (ppm)



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7.699
7.684
7.679
7.603
7.423
7.411
7.404
7.386
7.371
7.260
5.583
2.593
2.556
2.526
2.489
2.021
1.988
1.969
1.452
1.435
1.356
NH2
N
Ph
O
7
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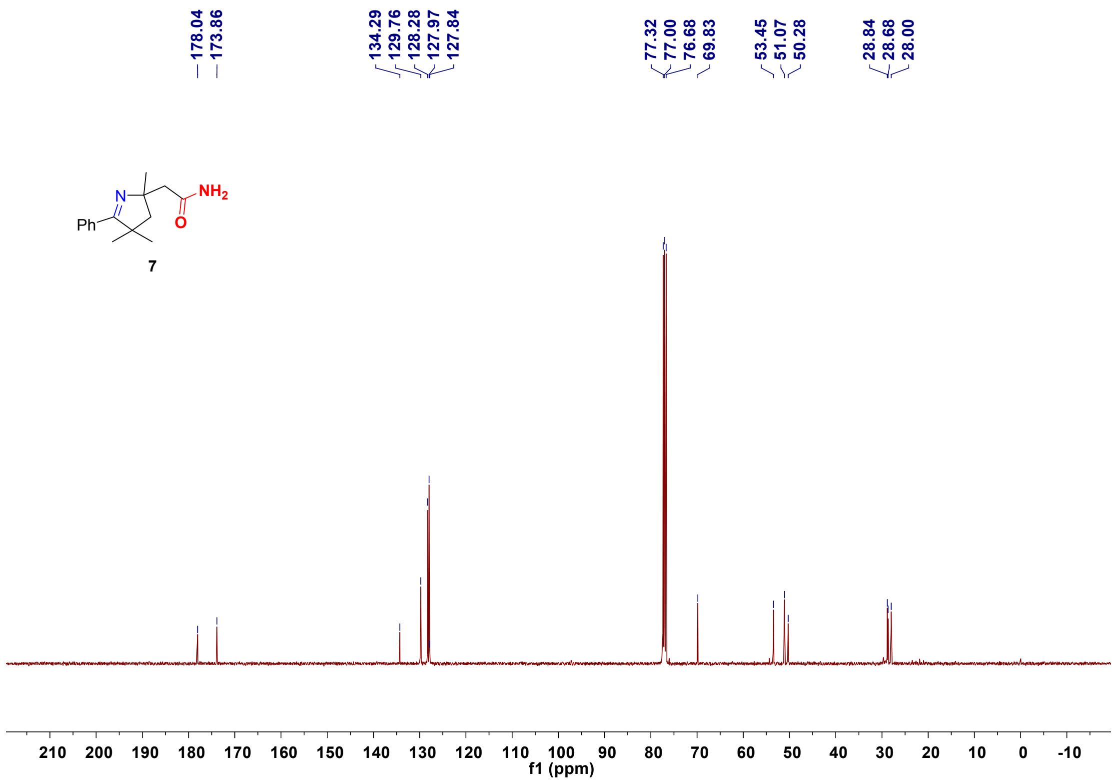
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)



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173.86
134.29
129.76
128.28
127.97
127.84
77.32
77.00
76.68
69.83
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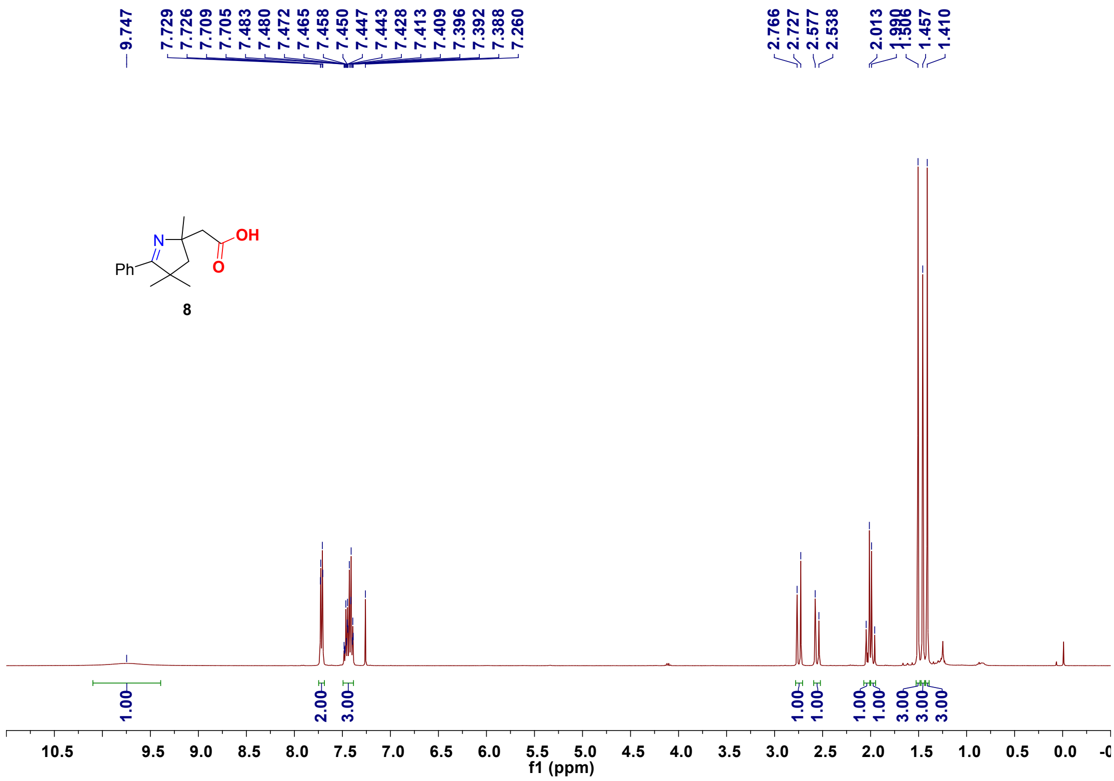
51.07
50.28
28.84
28.68
28.00
NH2
N
Ph
O
7
f1 (ppm)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7.705
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7.480
7.472
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7.458
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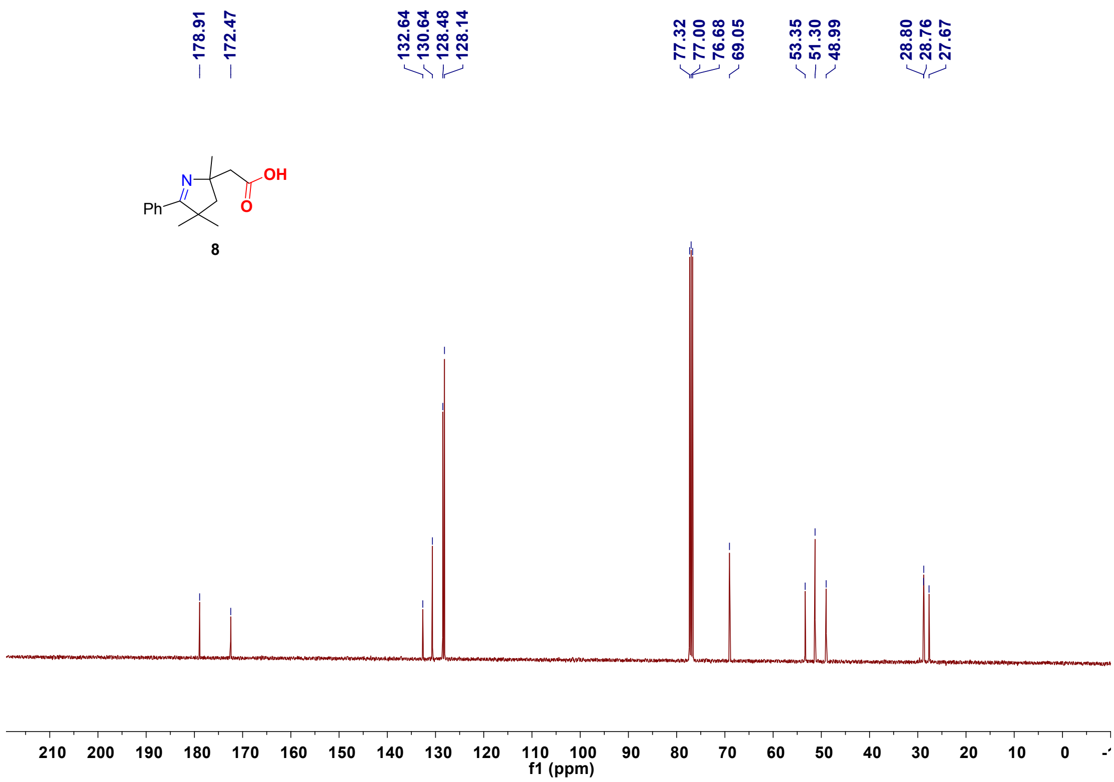
7.447
7.443
7.428
7.413
7.409
7.396
7.392
7.388
7.260
2.766
2.727
2.577
2.538
2.013
1.990
1.506
1.457
1.410
N
OH
O
Ph
8
1.00
2.00
3.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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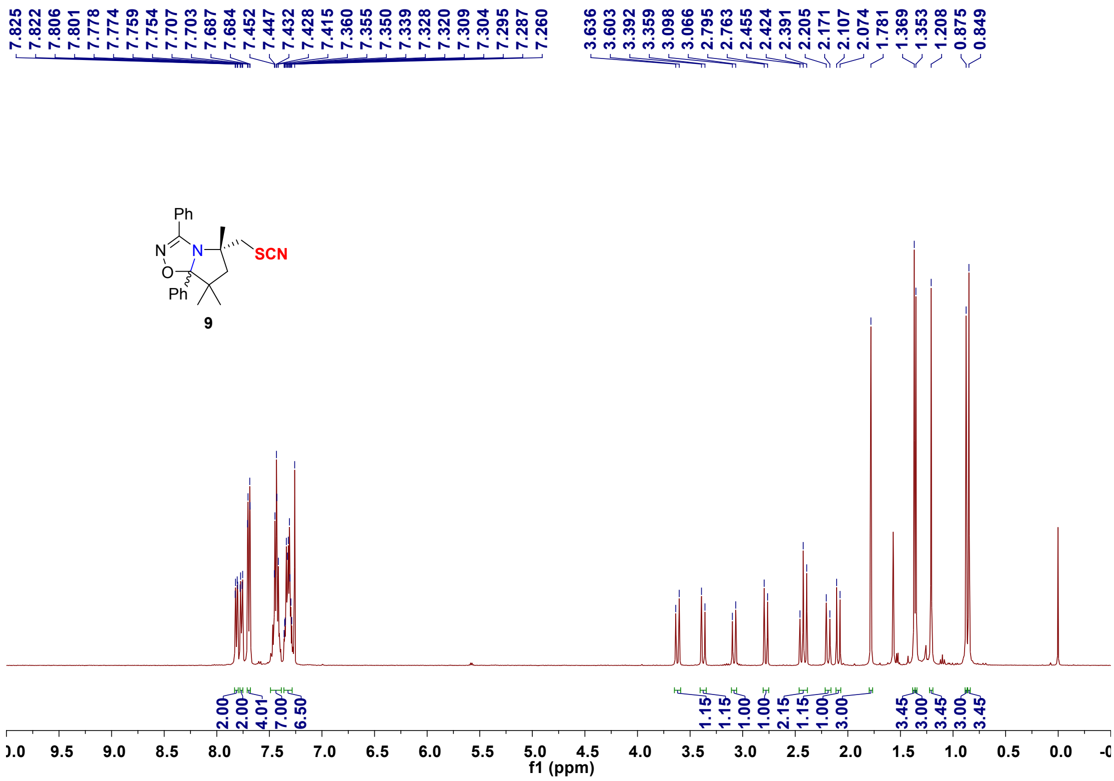
130.64
128.48
128.14
77.32
77.00
76.68
69.05
53.35
51.30
48.99
28.80
28.76
27.67
N
OH
O
Ph
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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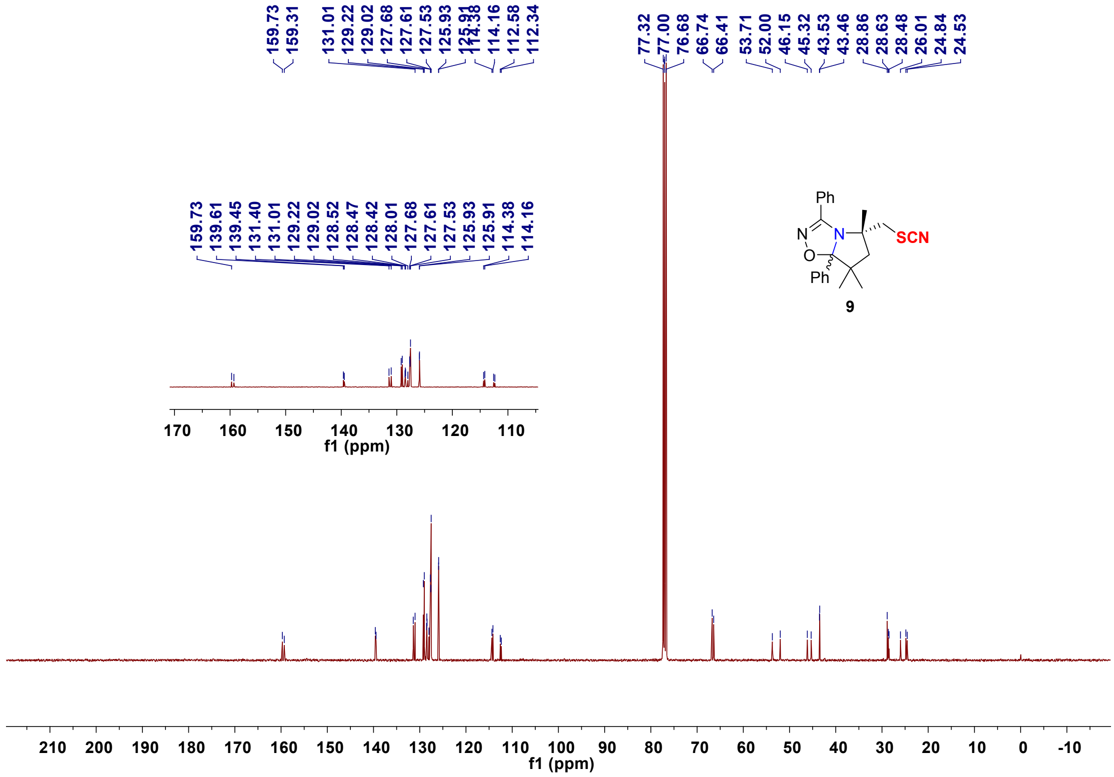
3.636 3.603 3.392 3.359 3.098 3.066 2.795 2.763 2.455 2.424 2.391 2.205 2.171 2.107 2.074 1.781 1.369 1.353 1.208 0.875 0.849
Ph
N
O
N
SCN
Ph
9
2.00 2.00 4.01 7.00 6.50
1.15 1.15 1.00 1.00 2.15 1.15 1.00 3.00
3.45 3.00 3.45 3.00 3.45
f1 (ppm)


159.73 159.31
131.01 129.22 129.02 127.68 127.61 127.53 125.93 125.91 114.38 114.16 112.58 112.34
77.32 77.00 76.68 66.74 66.41
53.71 52.00 46.15 45.32 43.53 43.46 28.86 28.63 28.48 26.01 24.84 24.53
159.73 159.61 139.45 131.40 131.01 129.22 129.02 128.52 128.47 128.42 128.01 127.68 127.61 127.53 125.93 125.91 114.38 114.16
f1 (ppm)
Ph
N
O
N
SCN
Ph
9
f1 (ppm)