

Supporting Information

Metal-Free N-Arylation of Sulfoximines using Diaryliodonium Salts at Room Temperature

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Table of contents:

Sr. No.	Content	Page No.
1	S1. General Considerations	1-2
2	S2. Experimental Procedures, Analytical data, Gram Scale reaction and Control experiments	2-13
3	S3. References	14
4	S4. Copies of ^1H , ^{13}C NMR Spectra	16-38

S1 General Considerations:

S1.1 Solvents and Reagents: All the reactions were carried out in flame or oven-dried glassware using anhydrous solvents unless otherwise indicated. All the reagents were commercially procured from Aldrich, TCI and Alfa Aesar and used without further purification. Solvents like THF were freshly dried and distilled over Na/benzophenone, and kept under an inert atmosphere, and were freshly distilled before use.

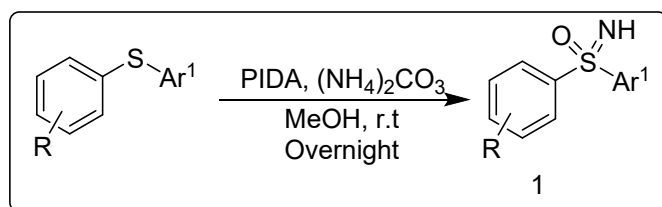
S1.2 NMR and Mass Spectrometry & Chromatography: ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 (400 MHz) and Jeol 500 (500 MHz) spectrophotometer operating at 400 MHz and 500 MHz for ^1H and 126 MHz for ^{13}C experiments as solutions in CDCl_3 ; Spectra were recorded at 295 K in CDCl_3 and $\text{DMSO}-d_6$. Chemical shifts were calibrated to the residual proton and carbon resonance of the solvent, CDCl_3 (^1H δ 7.269; ^{13}C δ 77.0) and $\text{DMSO}-d_6$ (^1H δ 2.5; ^{13}C δ 39.5). Spin multiplicities are described as s (singlet), bs (broad singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), sept (septet) and m (multiplet). Peaks at 1.26 ppm and 1.56 ppm in ^1H NMR spectra correspond to grease and moisture, respectively, whereas peak at 29.67 ppm in ^{13}C NMR spectra corresponds to grease. Coupling constant (J) values are reported in hertz (Hz). Analytical TLC was performed using 2 x 4 cm plate coated with a 0.25 mm thickness of silica gel (60_{F-254} Merck), and visualization was accomplished with UV light or staining the plates with ethanolic *p*-anisaldehyde solution/ phosphomolybdic acid solution/ ninhydrin solution and heating to 120 °C. The abbreviations used:

singlet = s, doublet = d, triplet = t, quartet = q, double doublet = dd, multiplet = m, broad singlet = brs.
Mass spectra were recorded on Water Q-ToF-Micro Micromass.

S2. Experimental Procedures, Analytical data, Gram Scale reaction and Control experiments

S2.1 General procedure for the synthesis of NH Sulfoximines (1)

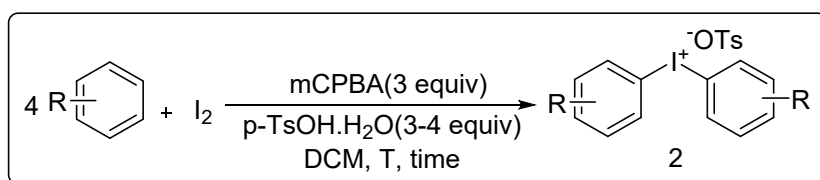
To a stirred solution of sulfide (186 mg, 1 mmol, 1 equiv.) in MeOH (10 mL) was added the $(\text{NH}_4)_2\text{CO}_3$ (144 mg, 1.5 mmol, 1.5 equiv.). Subsequently, $\text{PhI}(\text{OAc})_2$ (740 mg, 2.3 mmol, 2.3 equiv.) was added and the solution was stirred at rt. After the disappearance of the sulfide (checked by TLC), the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography. (10 mmol sulfide and 100 mL MeOH were used for the Gram-Scale Reaction)¹



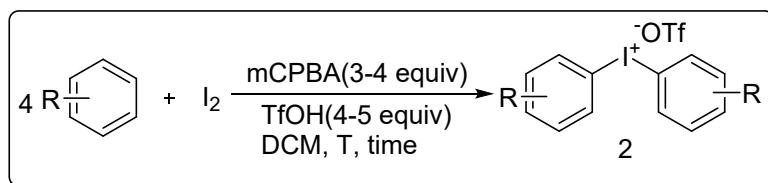
S2.2 General Procedure for the synthesis of iodonium salts (2)

Diaryliodonium salts (2) were synthesized according to the reported literature procedure and were directly used in the reaction.

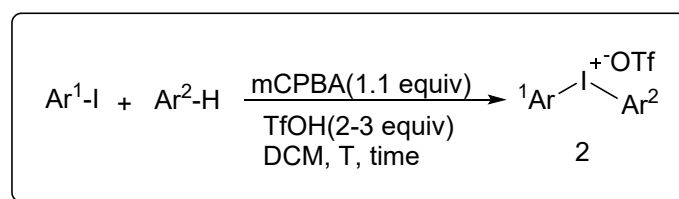
Method 1²



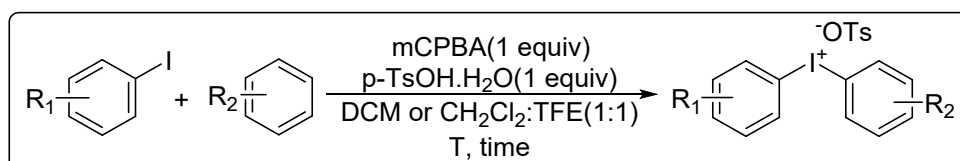
Method 2³



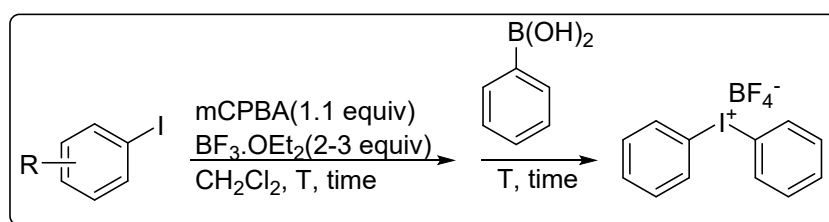
Method 3³



Method 4²

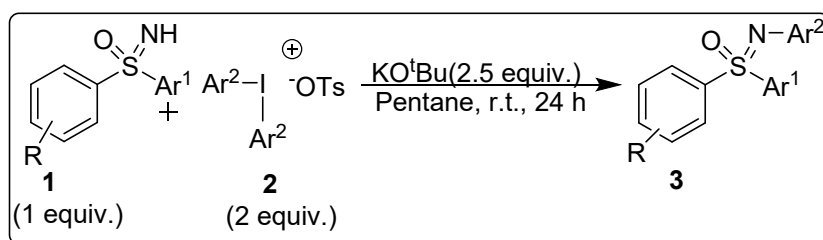


Method 5³



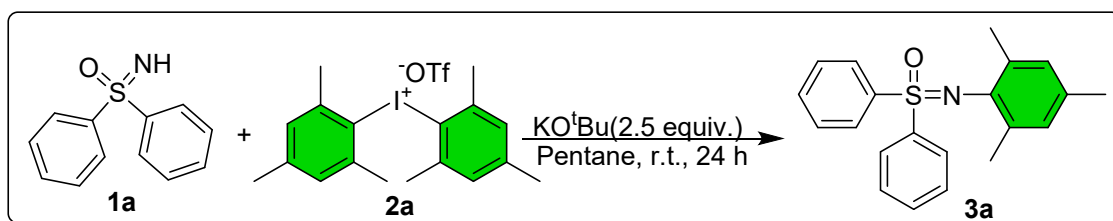
S2.3 General procedure for the synthesis of N-arylated sulfoximine (3)

The sulfoximine **1** (50 mg, 0.23 mmol), diaryliodonium salt **2** (208 mg, 0.46 mmol), *t*-BuOK (64 mg, 0.57 mmol) and 5 mL anhydrous pentane were added to a dry 10 mL microwave vial, which was capped. The vial was evacuated and backfilled with nitrogen three times. The stirring was started. The solution was stirred at ambient temperature for 24 h. The crude reaction mixture was then transferred to a round-bottom flask using ethyl acetate. The solvent was evaporated and then the crude reaction was loaded onto silica without any work-up. The crude was purified using flash column chromatography to get the desired product (**3**).



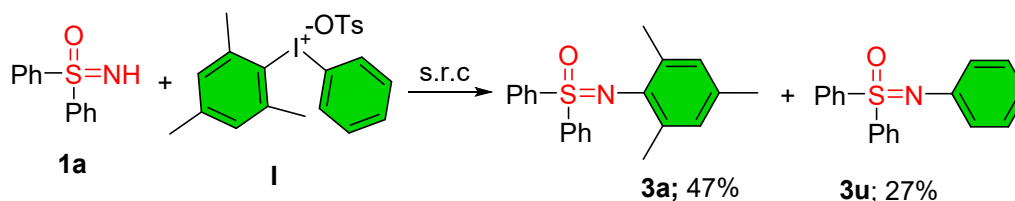
S2.4 Gram scale reaction for the synthesis of N-arylated sulfoximine (3a)

The sulfoximine **1a** (500 mg, 2.3 mmol), dimesityleneiodonium salt **2a** (2.36 g, 4.6 mmol), *t*-BuOK (644 mg, 5.75 mmol) and 20 mL anhydrous pentane were added to a dry 50 mL round-bottom flask, which was capped. The round-bottom flask was evacuated and backfilled with nitrogen three times. The stirring was started. The solution was stirred at ambient temperature for 24 h. The crude reaction mixture was then transferred to a round flask using ethyl acetate. The solvent was evaporated, and then the crude reaction was loaded onto silica without any work-up. The crude was purified using manual flash column chromatography to get the desired product (**3a**).

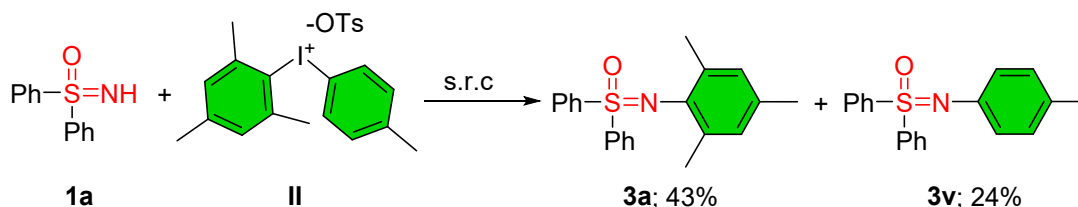


S2.5 Chemoselectivity Trends

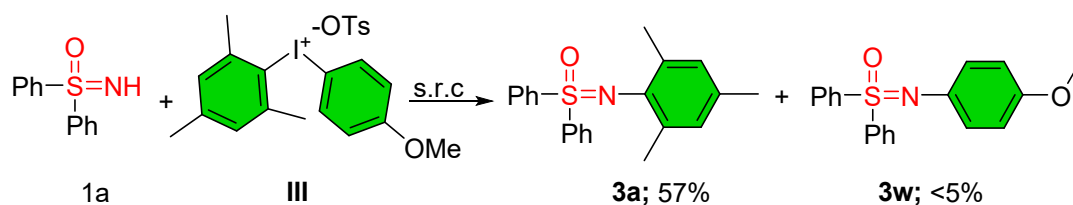
The chemoselectivity was investigated in the following reactions.



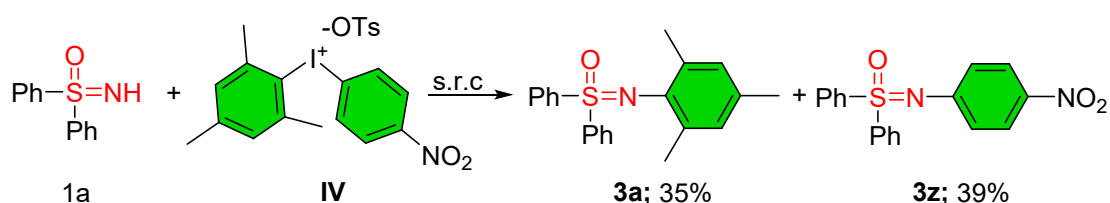
Following the general procedure S2.3. Sulfoximine **1a** (50 mg, 0.23 mmol), unsymmetrical salt **I** (227 mg, 0.46 mmol) and *t*-BuOK (65 mg, 0.57 mmol) were combined, and the resulting reaction mixture was stirred at rt for 24 h. After the completion of the reaction, the crude was purified by column chromatography to yield **3a** in 47% (36 mg) and product **3u** was obtained 27% (18 mg).



Following the general procedure S2.3. Sulfoximine **1a** (50 mg, 0.23 mmol), salt **II** (233 mg, 0.46 mmol) and *t*-BuOK (65 mg, 0.57 mmol) were combined, and the resulting reaction mixture was stirred at rt for 24 h. After the completion of the reaction, the solvent was evaporated under vacuum. The crude obtained was purified by column chromatography to yield **3a** in 43% (33 mg) and **3v** was obtained 24% (17 mg).



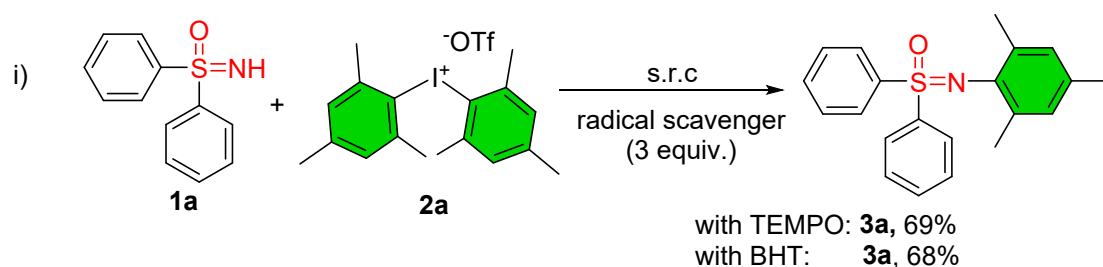
Following the general procedure S2.3. Sulfoximine **1a** (50 mg, 0.23 mmol), salt **III** (241 mg, 0.46 mmol) and *t*-BuOK (65 mg, 0.57 mmol) were combined, and the resulting reaction mixture was stirred at rt for 24 h. After the completion of the reaction, the crude was purified by column chromatography to yield **3a** in 57% (43 mg) and **3w** was obtained <5%.



Following the general procedure S2.3. Sulfoximine **1a** (50 mg, 0.23 mmol), salt **IV** (248 mg, 0.46 mmol) and *t*-BuOK (65 mg, 0.57 mmol) were combined, and the resulting reaction mixture was stirred at rt for 24 h. After the completion of the reaction, the crude was purified by column chromatography to yield **3a** in 35% (27 mg) and product **3z** was obtained 39% (30 mg).

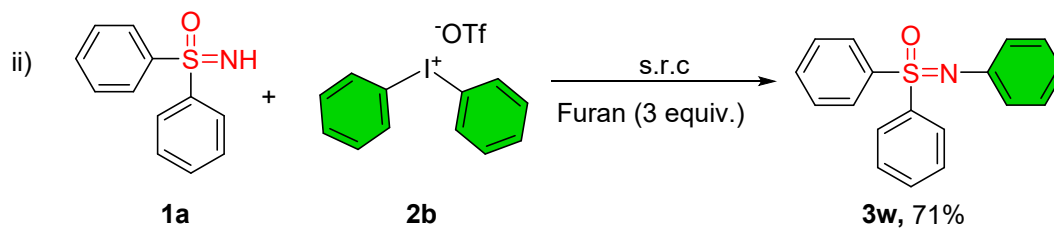
S2.6 Radical Trapping Method

i) Radical-trapping Experiment

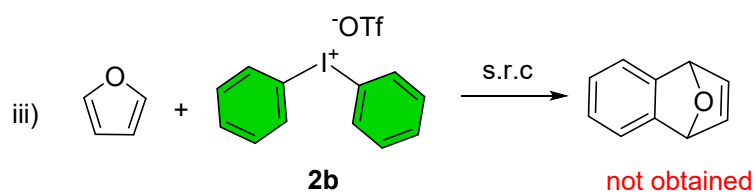


Following the general procedure S2.3. Sulfoximine **1a** (50 mg, 0.23 mmol), **2a** (236 mg, 0.46 mmol), *t*-BuOK (65 mg, 0.57 mmol) and TEMPO (107 mg, 0.69 mmol) or BHT (152 mg, 0.69 mmol) were added in pentane. The mixture was stirred at rt for 24 h. The crude obtained after solvent evaporation under vacuum was purified by column chromatography, yielding **3a** in 69% (53 mg) with TEMPO and 68% (52 mg) with BHT.

ii) Benzyne-trapping experiment



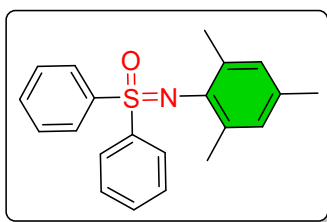
Following the general procedure S2.3. Sulfoximine **1a** (50 mg, 0.23 mmol), **2b** (198 mg, 0.46 mmol), *t*-BuOK (65 mg, 0.57 mmol) and furan (65 mg, 0.69 mmol) dissolve in pentane. The mixture was stirred at rt for 24 h. The reaction mixture was purified by column chromatography; the yield of **3w** was 71% (47 mg).



Furan (1 mmol, 68 mg), **2b** (2 mmol, 860 mg), and *t*-BuOK (2.5 mmol, 280 mg) were taken in pentane. The mixture was stirred at rt for 24 h. We didn't observe any desired cycloadduct in the reaction mixture.

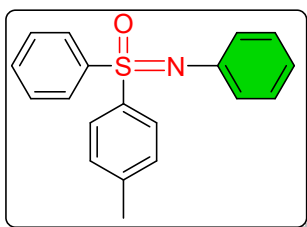
Analytical Data of Compound 3

(Mesitylimino)diphenyl- λ^6 -sulfanone (3a)^{4,5}



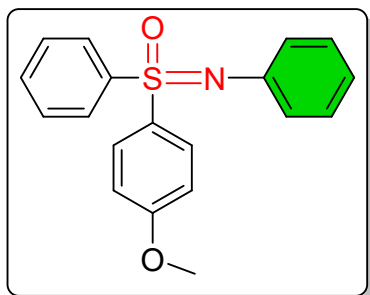
The General procedure S2.3 was followed. Transparent oil (55 mg, 72%); $R_f = 0.31$ (10:90 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.06 – 7.86 (m, 4H), 7.61 – 7.50 (m, 2H), 7.51 – 7.42 (m, 4H), 6.77 (s, 2H), 2.26 (s, 6H), 2.21 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 142.32, 137.80, 133.52, 132.25, 131.90, 128.95, 128.89, 127.96, 20.62, 20.37. Spectral data are consistent with previous reports.

Phenyl(phenylimino)(p-tolyl)- λ^6 -sulfanone (3b)^{6,7}



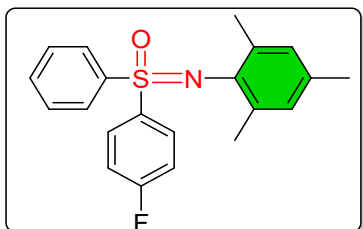
The General procedure S2.3 was followed. Colorless solid (51 mg, 73%); $R_f = 0.3$ (15:85 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.07 (dd, $J = 8.1, 1.4$ Hz, 2H), 7.95 (d, $J = 8.3$ Hz, 2H), 7.56 – 7.44 (m, 3H), 7.28 (d, $J = 6.8$ Hz, 3H), 7.16 (d, $J = 3.9$ Hz, 4H), 6.90 (m, $J = 8.5, 4.9, 3.7$ Hz, 1H), 2.39 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 144.82, 143.51, 141.35, 137.91, 132.45, 129.95, 129.19, 128.92, 128.62, 128.40, 123.76, 121.58, 21.45. Spectral data are consistent with previous reports.

4-Methoxyphenyl(phenyl)(phenylimino)- λ^6 -sulfanone (3c)⁷



The General procedure S2.3 was followed. Colorless solid (56 mg, 76%); $R_f = 0.3$ (25:75 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (dd, $J = 8.0, 1.5$ Hz, 2H), 8.03 – 7.97 (m, 2H), 7.53 – 7.42 (m, 3H), 7.16 (d, $J = 4.2$ Hz, 4H), 6.95 (d, $J = 9.0$ Hz, 2H), 6.90 (p, $J = 4.3$ Hz, 1H), 3.83 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 163.04, 144.88, 141.69, 132.33, 132.15, 130.73, 129.17, 128.92, 128.23, 123.76, 121.55, 114.56, 55.57. Spectral data are consistent with previous reports.

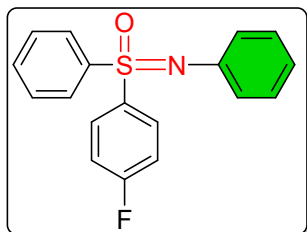
(4-Fluorophenyl)(mesitylimino)(phenyl)- λ^6 -sulfanone (3d)



The General procedure S2.3 was followed. Pale yellow solid (60 mg, 75%); $R_f = 0.32$ (20:80 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.03 – 7.89 (m, 4H), 7.54 (d, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.15 (t, $J = 8.6$ Hz, 2H), 6.78 (s, 2H), 2.27 (s, 6H), 2.21 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 164.93 (d, $J = 254.5$ Hz), 142.26, 138.22, 137.61, 133.40, 132.40, 132.07, 130.72 (d, $J = 9.3$ Hz),

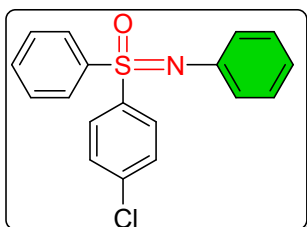
129.04, 129.00, 127.86, 116.13 (d, $J = 22.5$ Hz), 20.42. ^{19}F NMR (471 MHz, CDCl_3) δ -106.03. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{20}\text{FNOS}$ ($\text{M}+\text{Na}^+$) 376.1142; found 376.1146

(4-Fluorophenyl)(phenyl)(phenylimino)- λ^6 -sulfanone (3e)^{7, 8}



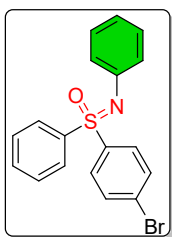
The general procedure S2.3 was followed. White solid (50 mg, 71%); $R_f = 0.56$ (20:80 EtOAc: hexanes, visualized by 254 nm UV light). ^1H NMR (500 MHz, CDCl_3) δ 8.29 – 7.83 (m, 4H), 7.79 – 7.43 (m, 3H), 7.26 – 7.07 (m, 6H), 6.92 (ddt, $J = 6.4, 4.6, 2.4$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.21(d, $J = 255.3$ Hz), 144.39, 140.90, 136.90, 136.87, 132.75, 131.32 (d, $J = 9.5$ Hz), 129.34, 129.02, 128.46, 123.75, 121.90, 116.52 (d, $J = 22.6$ Hz). Spectral data are consistent with previous reports.

(4-Chlorophenyl)(phenyl)(phenylimino)- λ^6 -sulfanone (3f)⁷



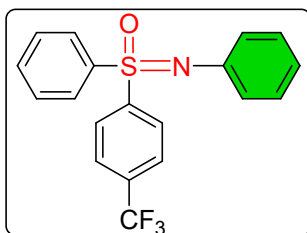
The General procedure S2.3 was followed. Colorless solid (54 mg, 72%); $R_f = 0.3$ (15:85 EtOAc: hexanes, visualized by 254 nm UV light). ^1H NMR (500 MHz, CDCl_3) δ 8.12 – 8.04 (m, 2H), 8.04 – 7.97 (m, 2H), 7.63 – 7.48 (m, 3H), 7.48 – 7.38 (m, 2H), 7.23 – 7.11 (m, 4H), 6.93 (ddd, $J = 8.5, 4.5, 1.9$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.28, 140.66, 139.56, 139.35, 132.86, 130.05, 129.57, 129.38, 129.04, 128.51, 123.74, 121.96. Spectral data are consistent with previous reports.

(4-Bromophenyl)(phenyl)(phenylimino)- λ^6 -sulfanone (3g)⁶



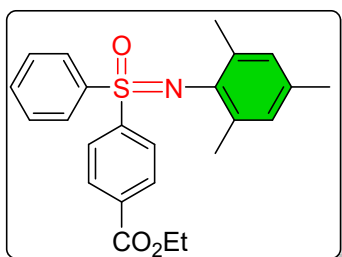
The General procedure S2.3 was followed. Yellow solid (63 mg, 74%); $R_f = 0.3$ (20:80 EtOAc: hexanes, visualized by 254 nm UV light). ^1H NMR (500 MHz, CDCl_3) δ 8.12 – 8.05 (m, 2H), 7.92 (d, $J = 8.7$ Hz, 2H), 7.62 (d, $J = 8.7$ Hz, 2H), 7.52 (dt, $J = 14.7, 7.1$ Hz, 3H), 7.22 – 7.11 (m, 4H), 6.98 – 6.88 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.25, 140.60, 140.14, 132.87, 132.56, 130.16, 129.38, 129.04, 128.51, 127.90, 123.74, 121.97. Spectral data are consistent with previous reports.

Phenyl(phenylimino)(4-(trifluoromethyl)phenyl)- λ^6 -sulfanone (3h)⁸



The General procedure S2.3 was followed. Colorless solid (57 mg, 69%); $R_f = 0.3$ (15:85 EtOAc: hexanes, visualized by 254 nm UV light). ^1H NMR (500 MHz, CDCl_3) δ 8.19 (d, $J = 8.2$ Hz, 2H), 8.10 (d, $J = 7.5$ Hz, 2H), 7.74 (d, $J = 8.3$ Hz, 2H), 7.55 (dd, $J = 16.8, 7.4$ Hz, 3H), 7.18 (q, $J = 8.2$ Hz, 4H), 6.94 (t, $J = 6.6$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.88, 143.99, 140.10, 134.32 (q, $J = 33$ Hz), 134.19, 133.15, 129.49, 129.11, 129.09, 128.71, 126.37 (q, $J = 3.7$ Hz), 126.36, 123.74 (q, $J = 274$ Hz), 122.15. Spectral data are consistent with previous reports.

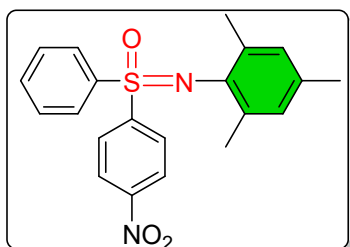
Ethyl 4-(N-mesitylphenylsulfonimidoyl)benzoate (3i)



The General procedure S2.3 was followed. Pale yellow solid (66 mg, 71%); $R_f = 0.3$ (25:75 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.11 – 8.08 (m, 2H), 8.05 – 8.03 (m, 2H), 7.92 – 7.90 (m, 2H), 7.61 – 7.57 (m, 1H), 7.54–7.51 (m, 2H), 6.76 (s, 2H), 4.40 (q, $J = 7.1$ Hz, 2H), 2.24 (s, 6H), 2.20 (s, 3H), 1.40 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 165.26, 146.72, 141.26,

137.35, 133.63, 133.38, 132.77, 132.17, 130.00, 129.09, 129.03, 128.37, 127.56, 61.59, 29.71, 20.61, 20.35, 14.25. **HRMS** (ESI) calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_3\text{S}$ ($\text{M}+\text{H}^+$) 408.1628; found 408.1638.

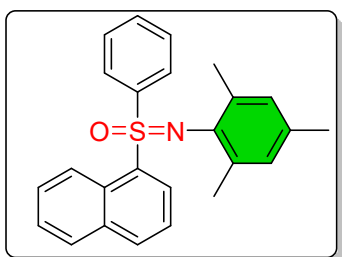
(Mesitylimino)(4-nitrophenyl)(phenyl)- λ^6 -sulfanone (3j)



The General procedure S2.3 was followed. Yellow solid (59 mg, 68%); $R_f = 0.3$ (25:75 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.25 (d, $J = 8.9$ Hz, 2H), 8.14 – 8.08 (m, 2H), 7.98 (d, $J = 8.9$ Hz, 2H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.58 (t, $J = 7.7$ Hz, 2H), 6.79 (s, 2H), 2.25 (s, 6H), 2.21 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.56, 149.06, 140.20, 136.89, 133.41, 133.24,

132.58, 129.43, 129.21, 128.72, 128.55, 124.09, 20.65, 20.40. **HRMS** (ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_3\text{S}$ ($\text{M}+\text{H}^+$) 381.1267; found 381.1271.

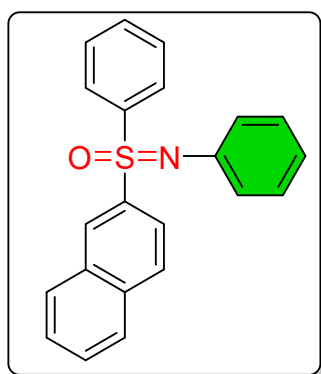
(Mesitylimino)(naphthalen-1-yl)(phenyl)- λ^6 -sulfanone (3k)



The General procedure S2.3 was followed. Yellow solid (69 mg, 78%); $R_f = 0.5$ (15:85 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.65 (s, 1H), 8.02 – 7.88 (m, 6H), 7.64 – 7.60 (m, 2H), 7.53 – 7.46 (m, 3H), 6.78 (s, 2H), 2.31 (s, 6H), 2.21 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 142.54, 139.14, 137.75, 134.70, 133.61, 132.30, 132.01, 129.40, 129.33, 129.09, 129.02, 128.95,

128.77, 127.93, 127.88, 127.38, 123.55, 20.65, 20.51. **HRMS** (ESI) calcd for $\text{C}_{25}\text{H}_{23}\text{NOS}$ ($\text{M}+\text{H}^+$) 386.1573; found 386.1575.

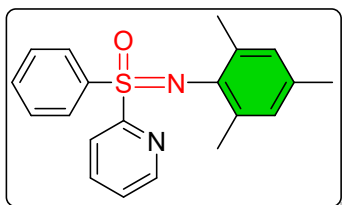
Naphthalen-1-yl(phenyl)(phenylimino)- λ^6 -sulfanone (3l)^{7,8}



The General procedure S2.3 was followed. Yellow solid (59 mg, 72%); $R_f = 0.55$ (15:85 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.71 (s, 1H), 8.15 (d, $J = 7.2$ Hz, 2H), 7.99 (t, $J = 6.6$ Hz, 2H), 7.89 (dd, $J = 20.3, 8.2$ Hz, 2H), 7.68 – 7.57 (m, 2H),

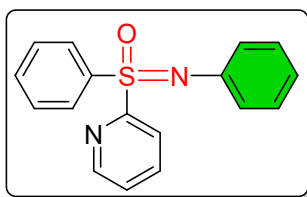
7.51 (q, $J = 7.2$ Hz, 3H), 7.24 – 7.15 (m, 4H), 6.91 (t, $J = 7.2$ Hz, 1H). Spectral data are consistent with previous reports.

(Mesitylimino)(phenyl)(pyridin-2-yl)- λ^6 -sulfanone (3m)



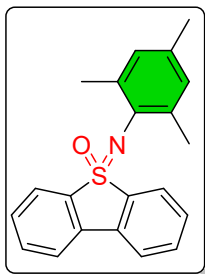
The General procedure S2.3 was followed. Yellow solid (56 mg, 73%); $R_f = 0.55$ (25:75 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.58 – 8.53 (m, 1H), 8.30 – 8.21 (m, 2H), 8.08 (d, $J = 7.9$ Hz, 1H), 7.83 – 7.75 (m, 1H), 7.63 (d, $J = 7.4$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 2H), 7.37 – 7.30 (m, 1H), 6.75 (s, 2H), 2.29 (s, 6H), 2.19 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.16, 149.75, 139.20, 137.53, 137.46, 133.94, 133.00, 132.16, 129.71, 128.80, 128.77, 125.92, 122.68, 20.67, 20.09. **HRMS** (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{NOS}$ ($\text{M}+\text{H}^+$) 337.1369; found 337.1390.

Phenyl(phenylimino)(pyridin-2-yl)- λ^6 -sulfanone (3n)⁸



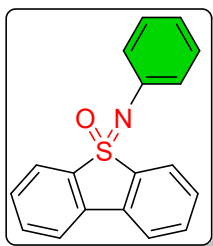
The General procedure S2.3 was followed. Colorless solid (48 mg, 71%); $R_f = 0.3$ (25:75 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$) δ 8.79 – 8.60 (m, 1H), 8.40 (d, $J = 7.9$ Hz, 1H), 8.31 – 7.97 (m, 3H), 7.73 – 7.66 (m, 1H), 7.65 – 7.59 (m, 3H), 7.27 – 7.09 (m, 2H), 7.09 – 6.95 (m, 2H), 6.95 – 6.75 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, $\text{DMSO}-d_6$) δ 157.88, 150.93, 144.94, 139.43, 138.28, 134.07, 129.93, 129.70, 129.48, 127.73, 124.08, 123.70, 122.14. Spectral data are consistent with previous reports.

5-(Mesitylimino)-5H-5 λ^4 -dibenzo[b,d]thiophene 5-oxide (3o)



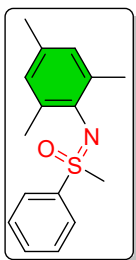
The General procedure S2.3 was followed. Yellow solid (50 mg, 65%); $R_f = 0.3$ (20:80 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.86 (d, $J = 7.7$ Hz, 2H), 7.63 (td, $J = 7.6, 5.9$ Hz, 4H), 7.47 (t, $J = 7.5$ Hz, 2H), 6.84 (s, 2H), 2.27 (s, 3H), 2.11 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 139.57, 137.29, 133.95, 132.79, 132.65, 131.38, 129.98, 128.87, 122.22, 121.61, 20.81, 19.16. **HRMS** (ESI) calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_3$ ($\text{M}+\text{H}^+$) 334.1260; found 334.1268.

5-(phenylimino)-5H-5 λ^4 -dibenzo[b,d]thiophene 5-oxide (3p)⁸



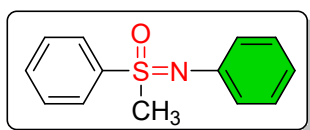
The General procedure S2.3 was followed Pale Yellow solid (47 mg, 77%); $R_f = 0.5$ (20:80 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.86 (d, $J = 7.7$ Hz, 2H), 7.79 (d, $J = 7.7$ Hz, 2H), 7.64 (t, $J = 7.6$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.31 – 7.25 (m, 4H), 7.08 (t, $J = 6.9$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 143.88, 138.92, 133.13, 131.99, 130.20, 129.13, 124.55, 123.06, 122.46, 121.63. Spectral data are consistent with previous reports.

(Mesitylimino)(methyl)(phenyl)- λ^6 -sulfanone (3q)⁹



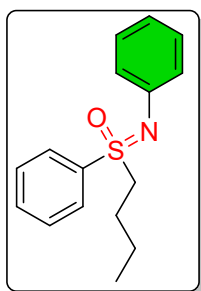
The General procedure S2.3 was followed. Brown Solid (45 mg, 72%); $R_f = 0.5$ (20:80 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.22 – 8.16 (m, 2H), 7.66 (d, $J = 7.3$ Hz, 1H), 7.61 (t, $J = 7.5$ Hz, 2H), 6.88 (s, 2H), 3.07 (s, 3H), 2.37 (s, 6H), 2.27 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 141.47, 138.02, 133.80, 132.97, 132.36, 129.21, 129.07, 127.94, 43.33, 20.67, 19.94. Spectral data are consistent with previous reports.

(E)-1-methyl-N,1-diphenyl- λ^4 -sulfanimine (3r)^{6, 10}



The General procedure S2.3 was followed. White solid (40 mg, 75%); $R_f = 0.3$ (15:75 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.00 – 7.98 (m, 2H), 7.60-7.58 (m, 1H), 7.55-7.51 (m, 2H), 7.15-7.11 (m, 2H), 7.04 – 7.01 (m, 2H), 6.90-6.86 (m, 1H), 3.25 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 144.97, 139.58, 133.17, 129.50, 128.98, 128.62, 123.33, 121.70, 46.01. Spectral data are consistent with previous reports.

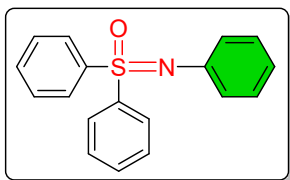
Butyl(phenyl)(phenylimino)- λ^6 -sulfanone(3s)¹¹



The General procedure S2.3 was followed. Brown Solid (46 mg, 74%); $R_f = 0.3$ (15:75 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.94 – 7.92 (m, 2H), 7.61-7.55 (m, 1H), 7.54-7.51 (m, 2H), 7.14-7.10 (m, 2H), 7.03 – 7.01 (m, 2H), 6.88-6.84 (m, 1H), 3.37 (ddd, $J = 13.9, 11.4, 5.1$ Hz, 1H), 3.27 (ddd, $J = 13.9, 11.3, 5.1$ Hz, 1H), 1.89 – 1.78 (m, 1H), 1.76 – 1.66 (m, 1H), 1.40 (dt, $J = 14.8, 7.4$ Hz, 2H), 0.90 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 145.23, 138.21, 137.78, 133.04, 129.38, 129.30, 128.91, 123.30, 121.38, 57.43, 24.67, 21.42, 13.52. Spectral data are consistent with previous reports.

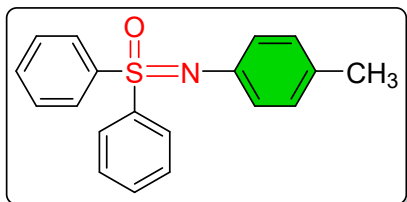
Diphenyl(phenylimino)- λ^6 -sulfanone (3u)^{6, 8, 10}

The General procedure S2.3 was followed. Colorless solid (49 mg, 73%); $R_f = 0.5$ (15:85 EtOAc: hexanes, visualized by 254 nm UV light). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.26 – 7.93 (m, 4H), 7.65 –



7.41 (m, 6H), 7.28 – 7.08 (m, 4H), 7.03 – 6.82 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 144.66, 141.00, 132.62, 129.26, 128.96, 128.56, 123.77, 121.70. Spectral data are consistent with previous reports.

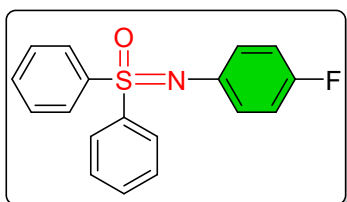
Diphenyl(*p*-tolylimino)-λ⁶-sulfanone (**3v**)⁷



The General procedure S2.3 was followed. Colorless solid (48 mg, 68%); *R_f* = 0.3 (15:75 EtOAc: hexanes, visualized by 254 nm UV light). ¹H NMR (500 MHz, CDCl₃) δ 8.05 – 7.82 (m, 4H), 7.49 – 7.30 (m, 6H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 2.14 (s, 1H). Spectral data are consistent with previous

reports.

((4-((4-Fluorophenyl)imino)diphenyl)-λ⁶-sulfanone (**3x**)⁷

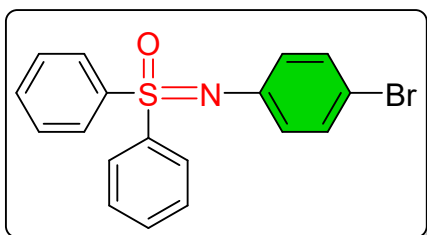


The General procedure S2.3 was followed. Colorless solid (53 mg, 74%); *R_f* = 0.3 (15:75 EtOAc: hexanes, visualized by 254 nm UV light). ¹H NMR (500 MHz, CDCl₃) δ 8.08-8.06 (m, 4H), 7.52 (m, 6H), 7.12 (dd, *J* = 8.4, 4.9 Hz, 2H), 6.86 (t, *J* = 8.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 158.37 (d, *J* = 239.8 Hz), 157.42, 140.67, 132.76, 129.38,

129.31, 128.57, 128.49, 124.79 (d, *J* = 7.8 Hz), 115.54 (d, *J* = 22.2 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -122.22. Spectral data are consistent with previous reports.

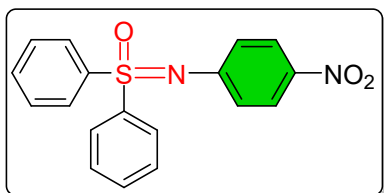
((4-bromophenyl)imino)diphenyl-λ⁶-sulfanone (**3y**)¹²

The General procedure S2.3 was followed. Pale solid (54 mg, 72%); *R_f* = 0.3 (15:75 EtOAc: hexanes, visualized by 254 nm UV light). ¹H NMR (500 MHz, CDCl₃) δ



7.97–7.94 (m, 4H), 7.47–7.38 (m, 6H), 7.17-7.14 (m, 2H), 6.96-6.92 (m, 2H). Spectra data are consistent with previous reports

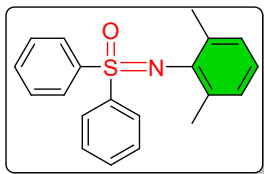
((4-Nitrophenyl)imino)diphenyl-λ⁶-sulfanone (**3z**)^{7, 8}



The General procedure S2.3 was followed. Colorless solid (58 mg, 75%); *R_f* = 0.5 (25:75 EtOAc: hexanes, visualized by 254 nm UV light). ¹H NMR (500 MHz, CDCl₃) δ 8.09-8.04 (m, 4H), 7.61-7.56

(m, 8H), 7.25-7.16 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.39, 142.23, 139.23, 133.65, 129.72, 128.37, 125.16, 123.08. Spectral data are consistent with previous reports.

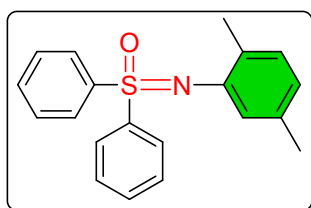
((2,6-Dimethylphenyl)imino)diphenyl- λ^6 -sulfanone (3aa)⁸



reports.

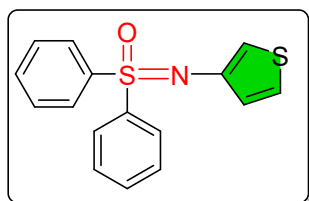
The General procedure S2.3 was followed. White solid (54 mg, 73%); $R_f = 0.7$ (20:80 EtOAc: hexanes, visualized by 254 nm UV light). ^1H NMR (400 MHz, CDCl_3) δ 7.90 – 7.76 (m, 4H), 7.55 – 7.32 (m, 6H), 6.85 (d, $J = 7.4$ Hz, 2H), 6.72 (t, $J = 7.4$ Hz, 1H), 2.19 (s, 6H). Spectral data are consistent with previous

((2,5-Dimethylphenyl)imino)diphenyl- λ^6 -sulfanone (3ab)⁵



The General procedure S2.3 was followed. Yellow solid (51 mg, 70%); $R_f = 0.7$ (20:80 EtOAc: hexanes, visualized by 254 nm UV light). ^1H NMR (500 MHz, CDCl_3) δ 8.07 – 8.04 (m, 4H), 7.54 – 7.46 (m, 6H), 7.01 – 6.96 (m, 2H), 6.72 (dd, $J = 8.1, 2.2$ Hz, 1H), 2.51 (s, 3H), 2.21 (s, 3H). Spectral data are consistent with previous reports.

Diphenyl(thiophen-3-ylimino)- λ^6 -sulfanone (3ac)⁷



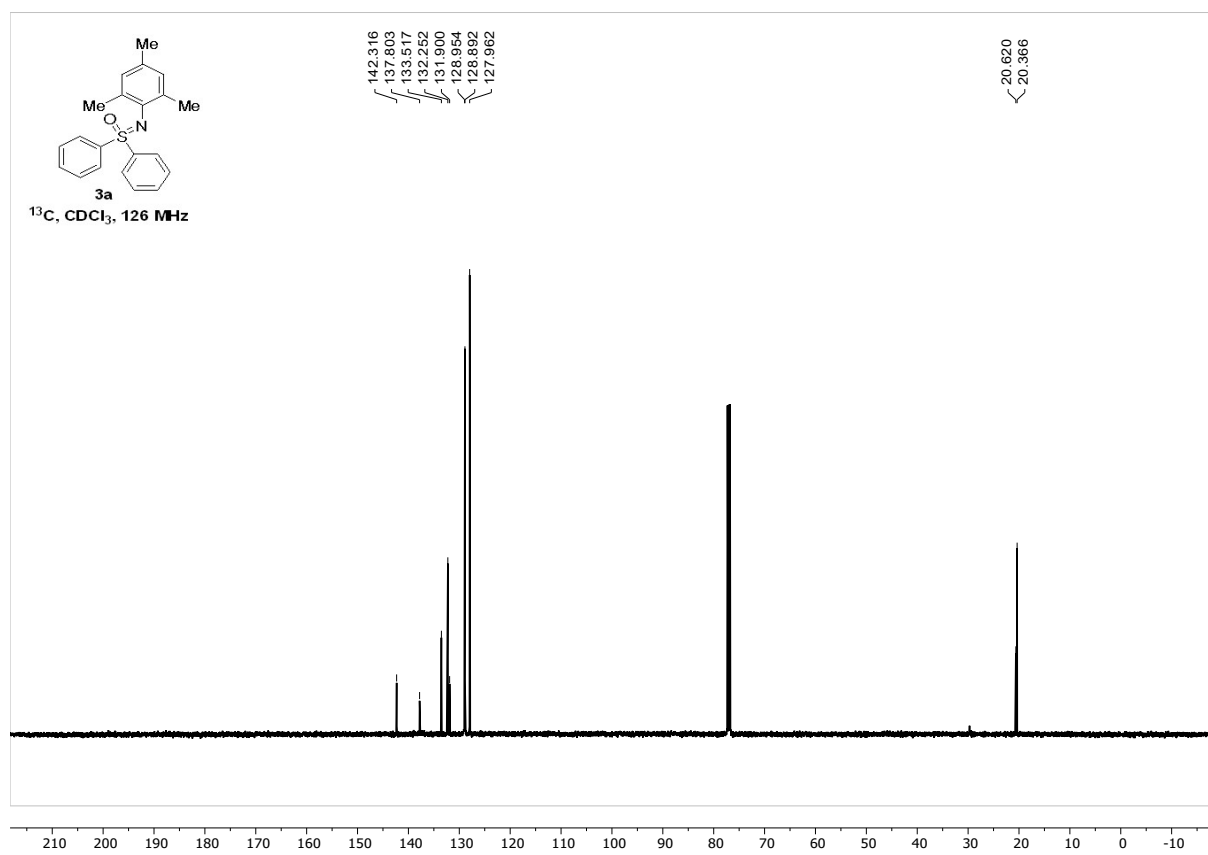
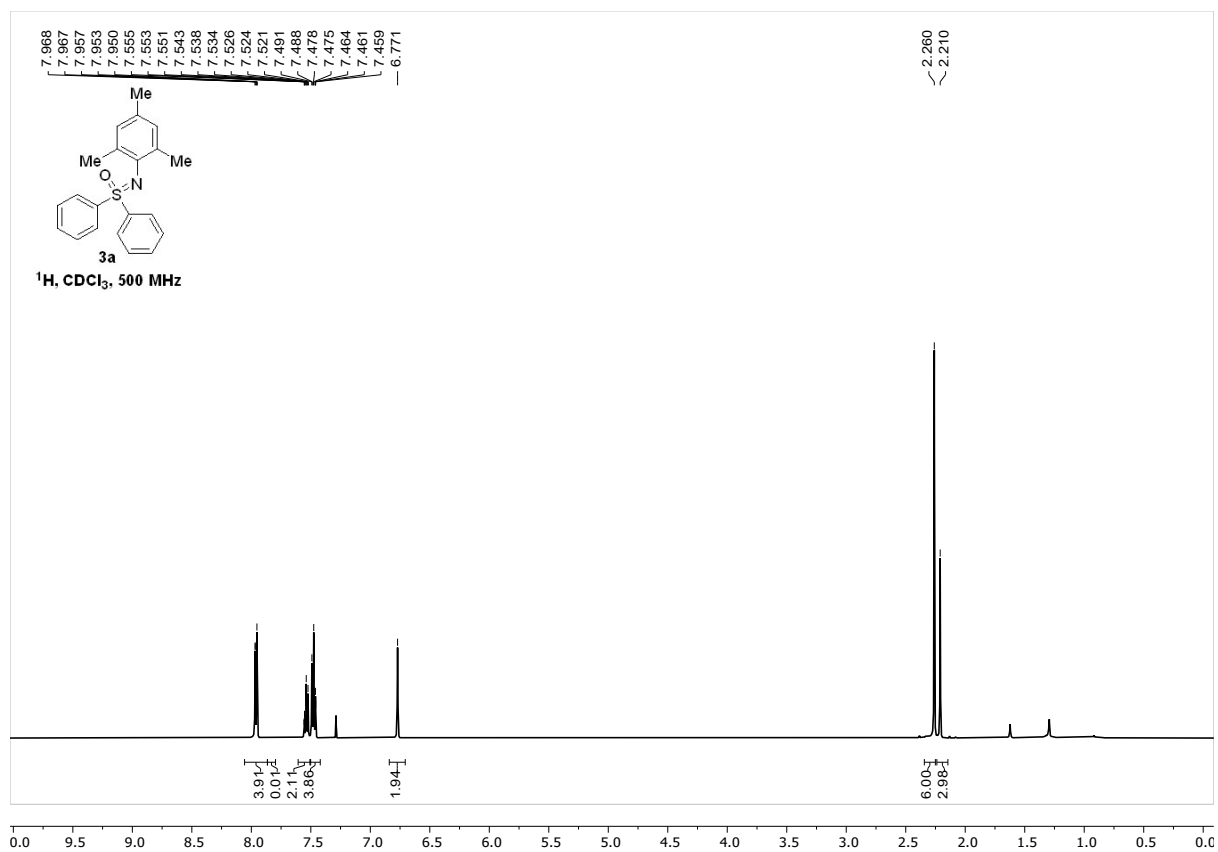
The General procedure S2.3 was followed. White solid (31 mg, 45%); $R_f = 0.5$ (20:80 EtOAc: hexanes, visualized by 254 nm UV light). ^1H NMR (500 MHz, CDCl_3) δ 8.09 – 8.07 (m, 4H), 7.58 – 7.50 (m, 6H), 6.70 (dd, $J = 5.6, 3.6$ Hz, 1H), 6.65 (dd, $J = 5.6, 1.4$ Hz, 1H), 6.48 (dd, $J = 3.6, 1.4$ Hz, 1H). Spectral data are consistent with previous reports.

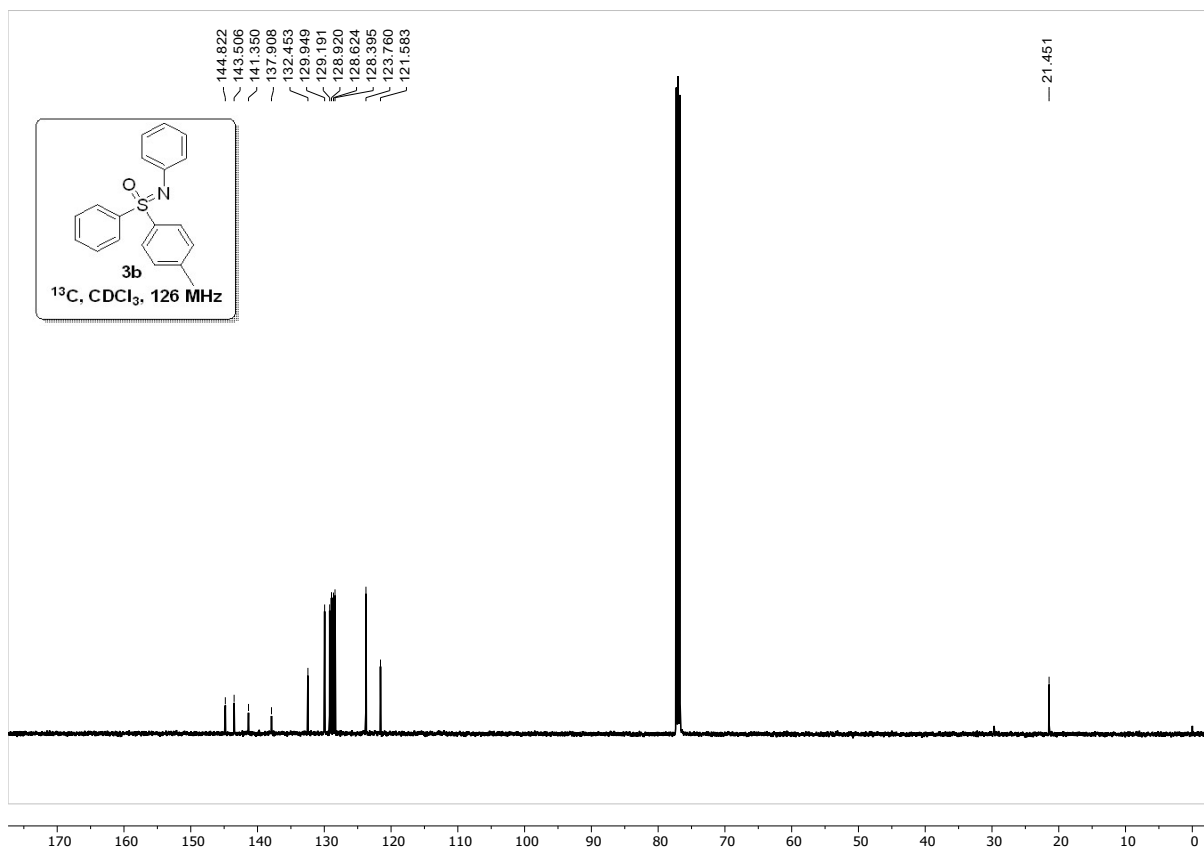
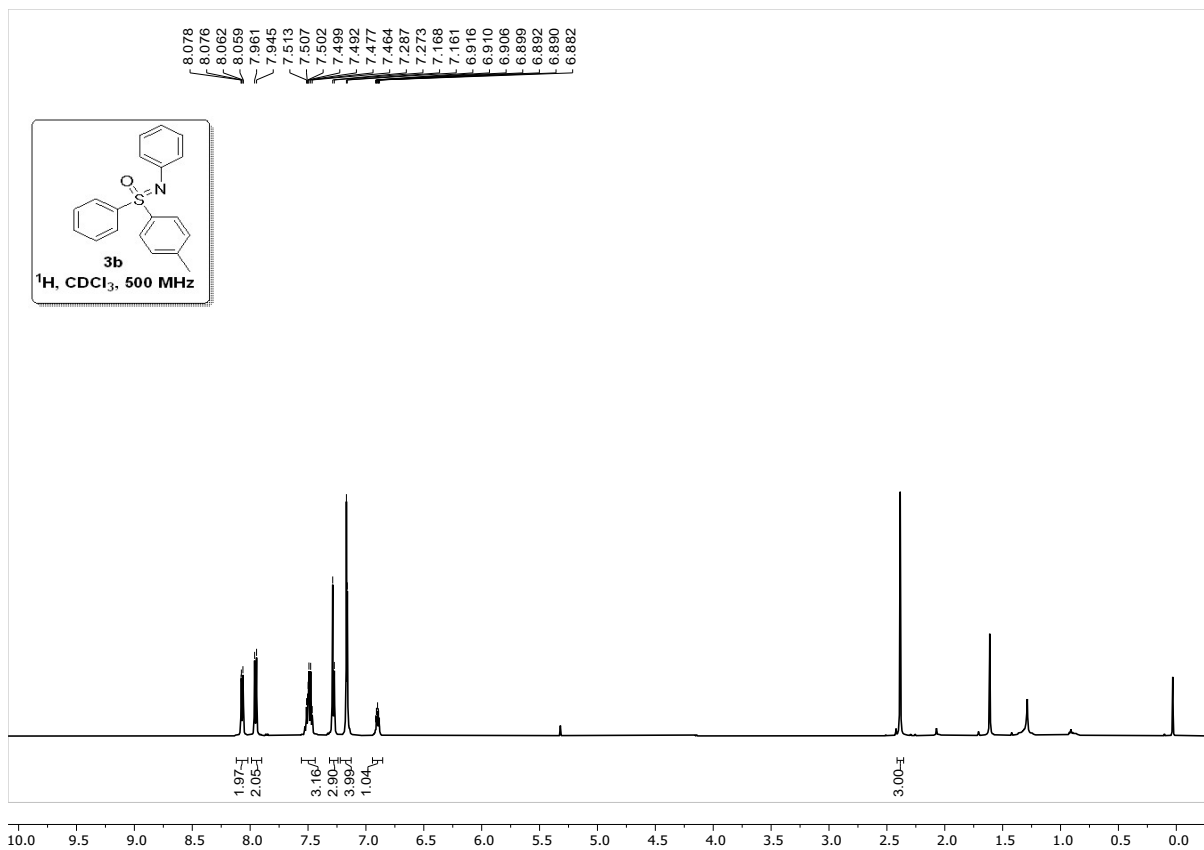
S.3 References

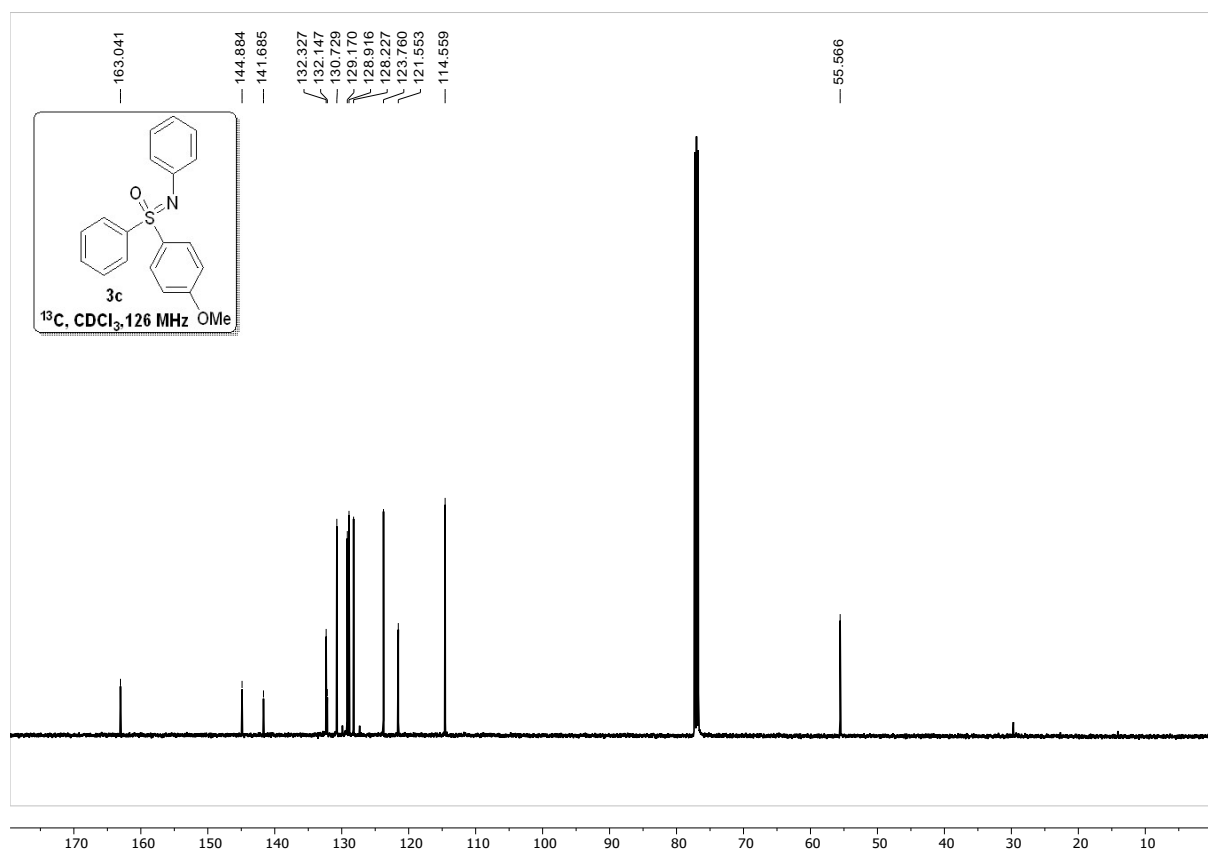
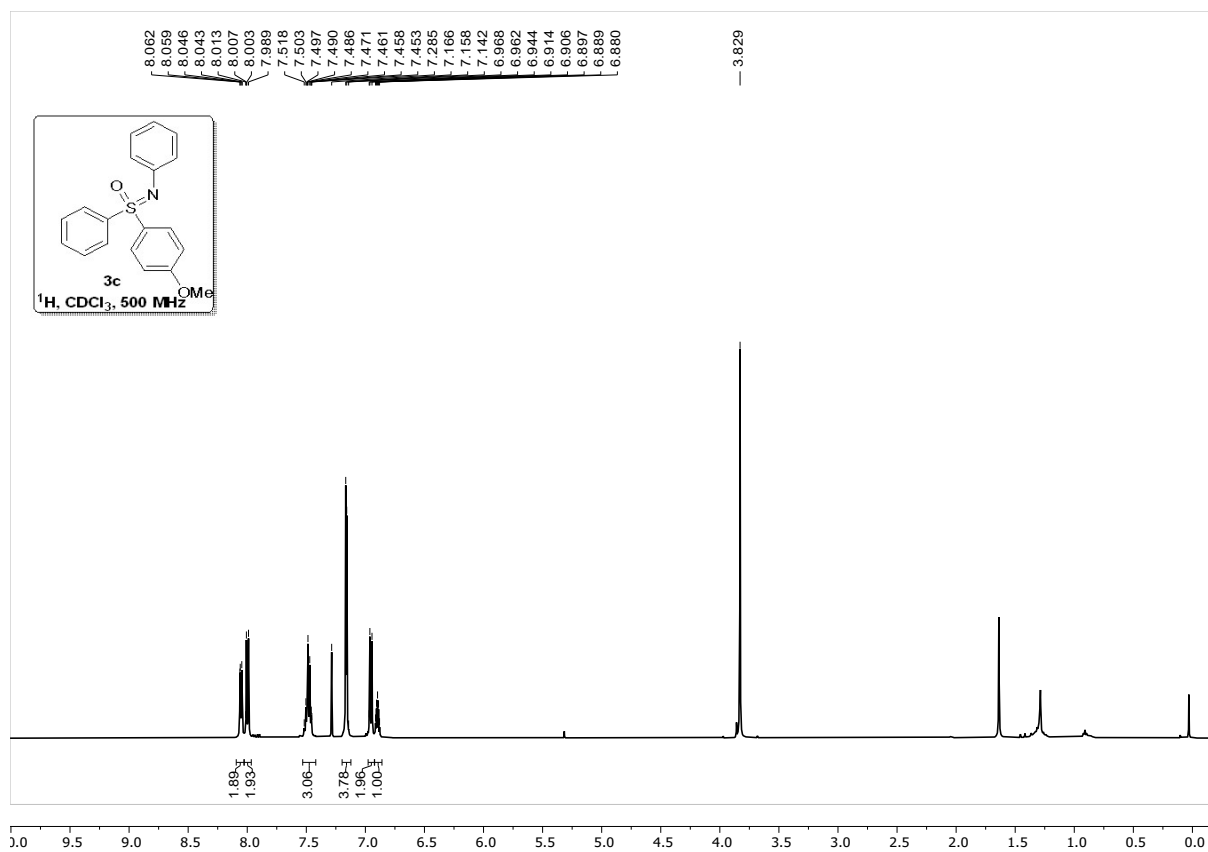
(1) Xie, Y.; Zhou, B.; Zhou, S.; Zhou, S.; Wei, W.; Liu, J.; Zhan, Y.; Cheng, D.; Chen, M.; Li, Y.; et al. Sulfimine-Promoted Fast O Transfer: One-step Synthesis of Sulfoximine from Sulfide. *ChemistrySelect* **2017**, 2 (4), 1620-1624.

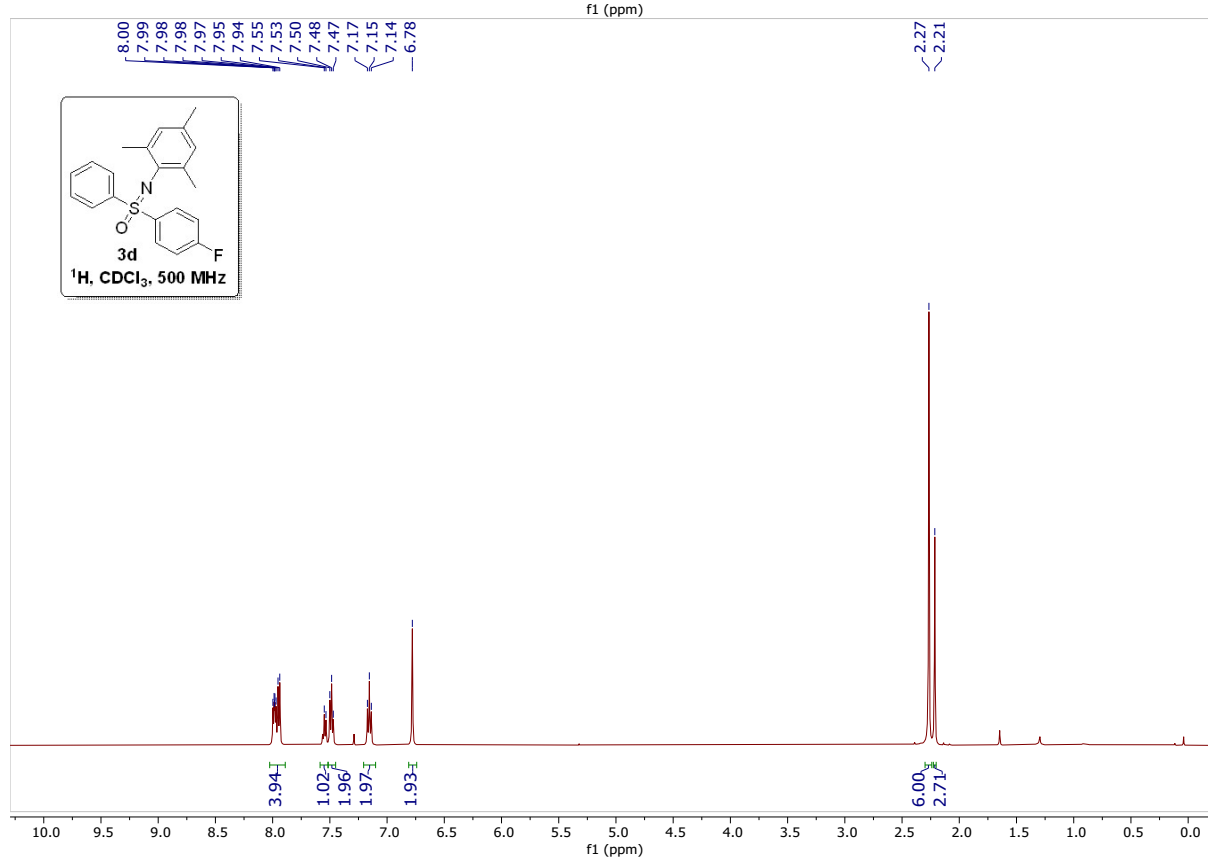
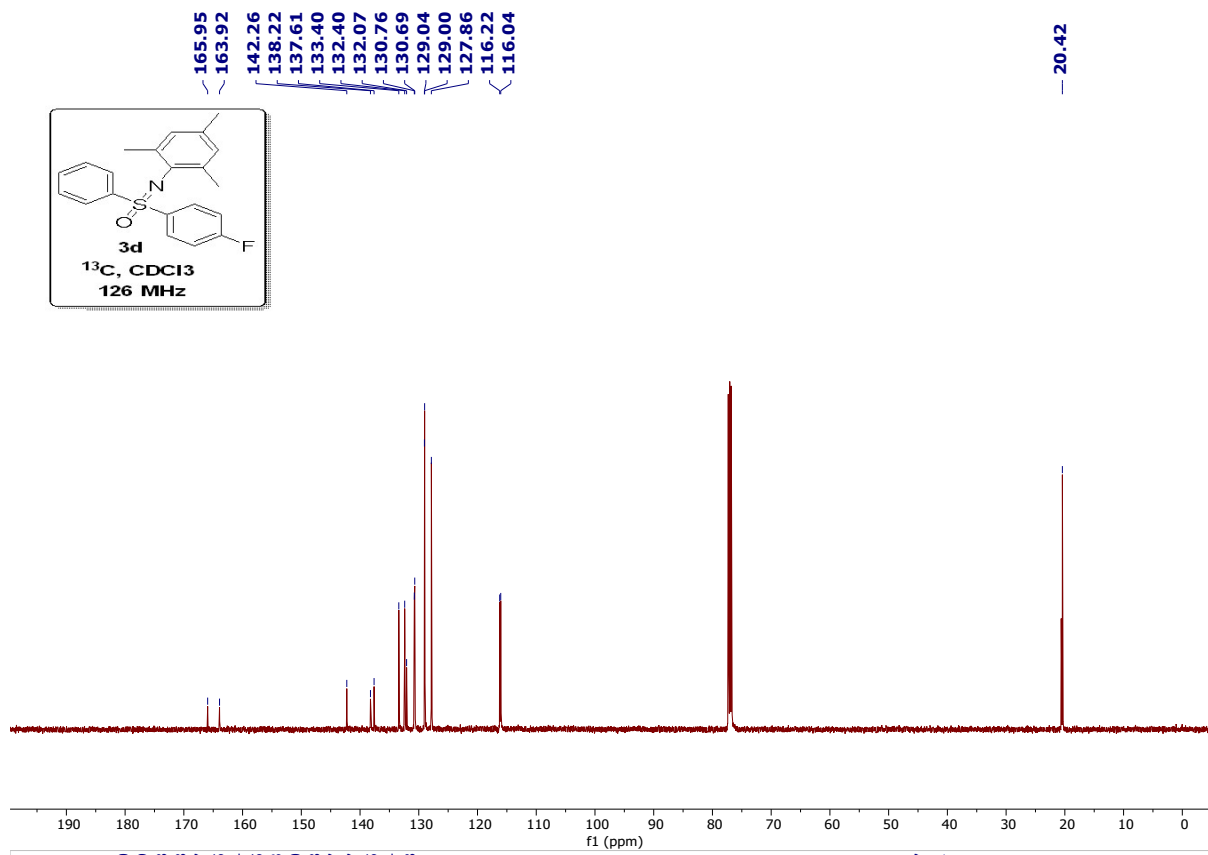
- (2) Zhu, M.; Jalalian, N.; Olofsson, B. One-Pot Synthesis of Diaryliodonium Salts Using Toluenesulfonic Acid: A Fast Entry to Electron-Rich Diaryliodonium Tosylates and Triflates. *Synlett* **2008**, 2008 (04), 592-596.
- (3) Bielawski, M.; Aili, D.; Olofsson, B. Regiospecific One-Pot Synthesis of Diaryliodonium Tetrafluoroborates from Arylboronic Acids and Aryl Iodides. *The Journal of Organic Chemistry* **2008**, 73 (12), 4602-4607.
- (4) Gupta, S.; Baranwal, S.; Muniyappan, N.; Sabiah, S.; Kandasamy, J. Copper-Catalyzed N-Arylation of Sulfoximines with Arylboronic Acids under Mild Conditions. *Synthesis* **2019**, 51 (10), 2171-2182.
- (5) Wimmer, A.; König, B. Visible-Light-Mediated Photoredox-Catalyzed N-Arylation of NH-Sulfoximines with Electron-Rich Arenes. *Advanced Synthesis & Catalysis* **2018**, 360 (17), 3277-3285.
- (6) Zhu, H.; Teng, F.; Pan, C.; Cheng, J.; Yu, J.-T. Radical N-arylation/alkylation of sulfoximines. *Tetrahedron Letters* **2016**, 57 (22), 2372-2374.
- (7) Wang, C.; Zhang, H.; Wells, L. A.; Liu, T.; Meng, T.; Liu, Q.; Walsh, P. J.; Kozłowski, M. C.; Jia, T. Autocatalytic photoredox Chan-Lam coupling of free diaryl sulfoximines with arylboronic acids. *Nature Communications* **2021**, 12 (1), 932.
- (8) Yang, L.; Zhong, Y.; Chen, W. Palladium-Catalyzed N-Arylation of NH-Sulfoximines with (Hetero)aryl Chlorides in an Aqueous Micellar Environment. *Organic Letters* **2025**, 27 (10), 2532-2536.
- (9) Virolleaud, M.-A.; Sridharan, V.; Mailhol, D.; Bonne, D.; Bressy, C.; Chouraqui, G.; Commeiras, L.; Coquerel, Y.; Rodriguez, J. Consecutive reactions with sulfoximines: a direct access to 2-sulfonimidoylylidene tetrahydrofurans and 6-sulfonimidoylmethyl-3,4-dihydro-2H-pyrans. *Tetrahedron* **2009**, 65 (47), 9756-9764.
- (10) Vaddula, B.; Leazer, J.; Varma, R. S. Copper-Catalyzed Ultrasound-Expedited N-Arylation of Sulfoximines using Diaryliodonium Salts. *Advanced Synthesis & Catalysis* **2012**, 354 (6), 986-990.
- (11) Aithagani, S. K.; Dara, S.; Munagala, G.; Aruri, H.; Yadav, M.; Sharma, S.; Vishwakarma, R. A.; Singh, P. P. Metal-Free Approach for the Synthesis of N-Aryl Sulfoximines via Aryne Intermediate. *Organic Letters* **2015**, 17 (22), 5547-5549.
- (12) Bachon, A.-K.; Steinkamp, A.-D.; Bolm, C. N-Arylated Sulfoximines as Cross-Coupling Building Blocks. *Adv Synth Catal* **2018**, 360 (6), 1088-1093.

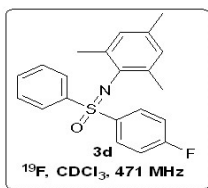
Copies of ^1H , ^{13}C , ^{19}F NMR Spectra of Compounds



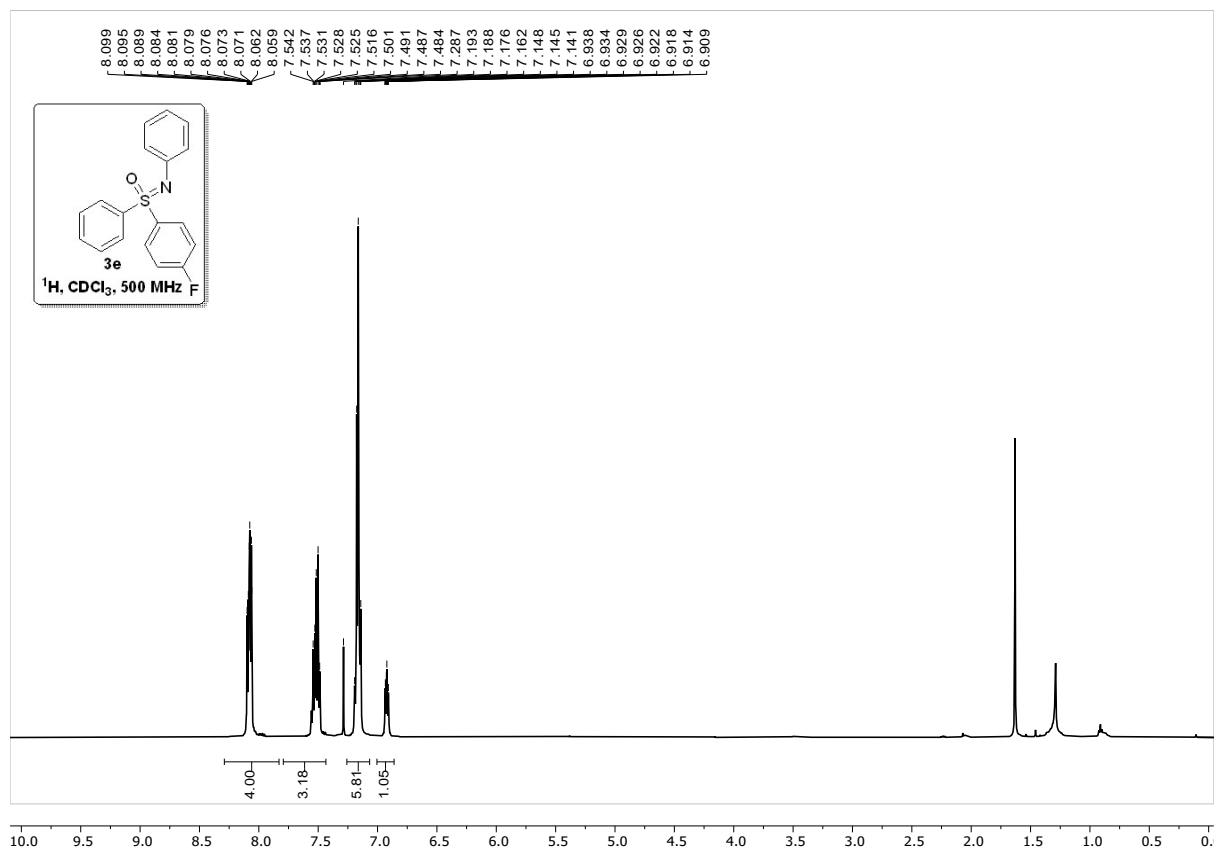
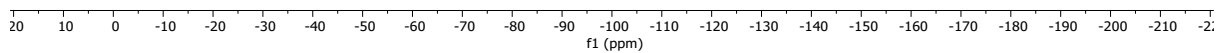


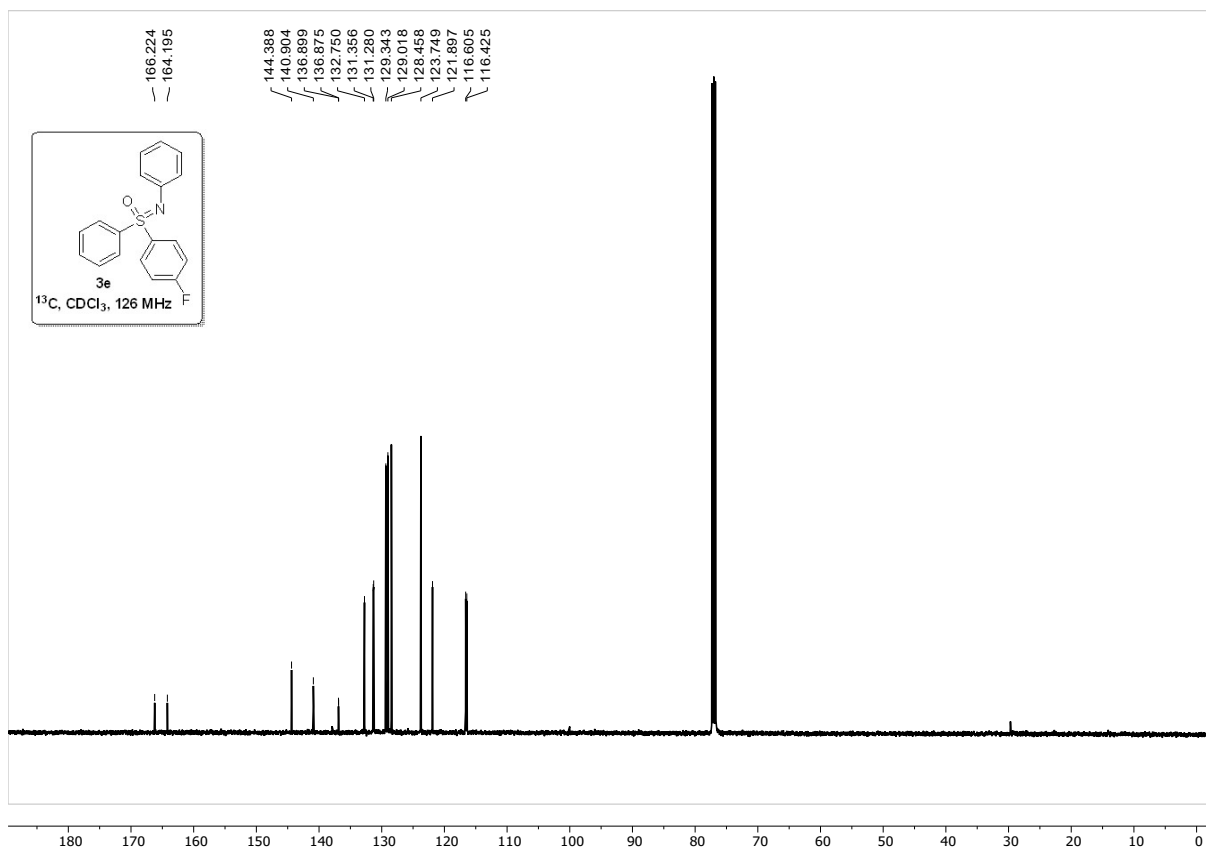


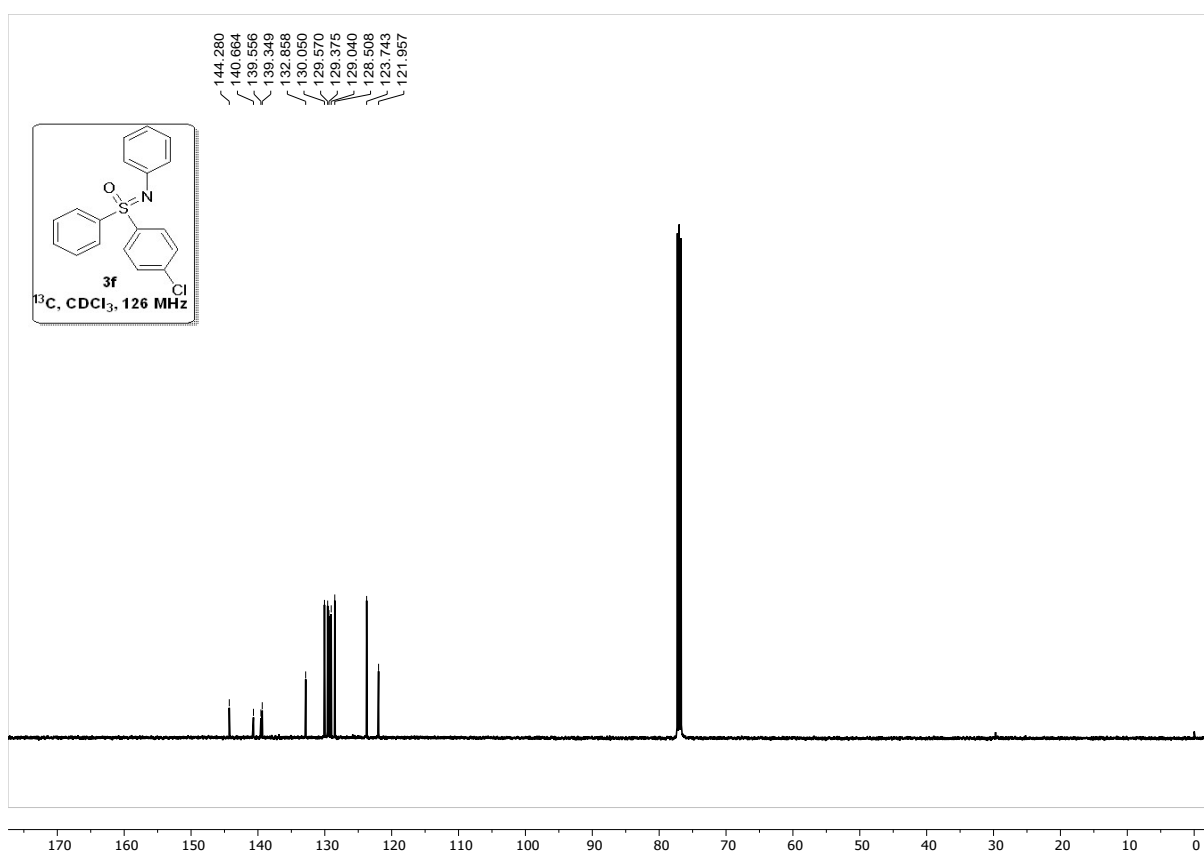
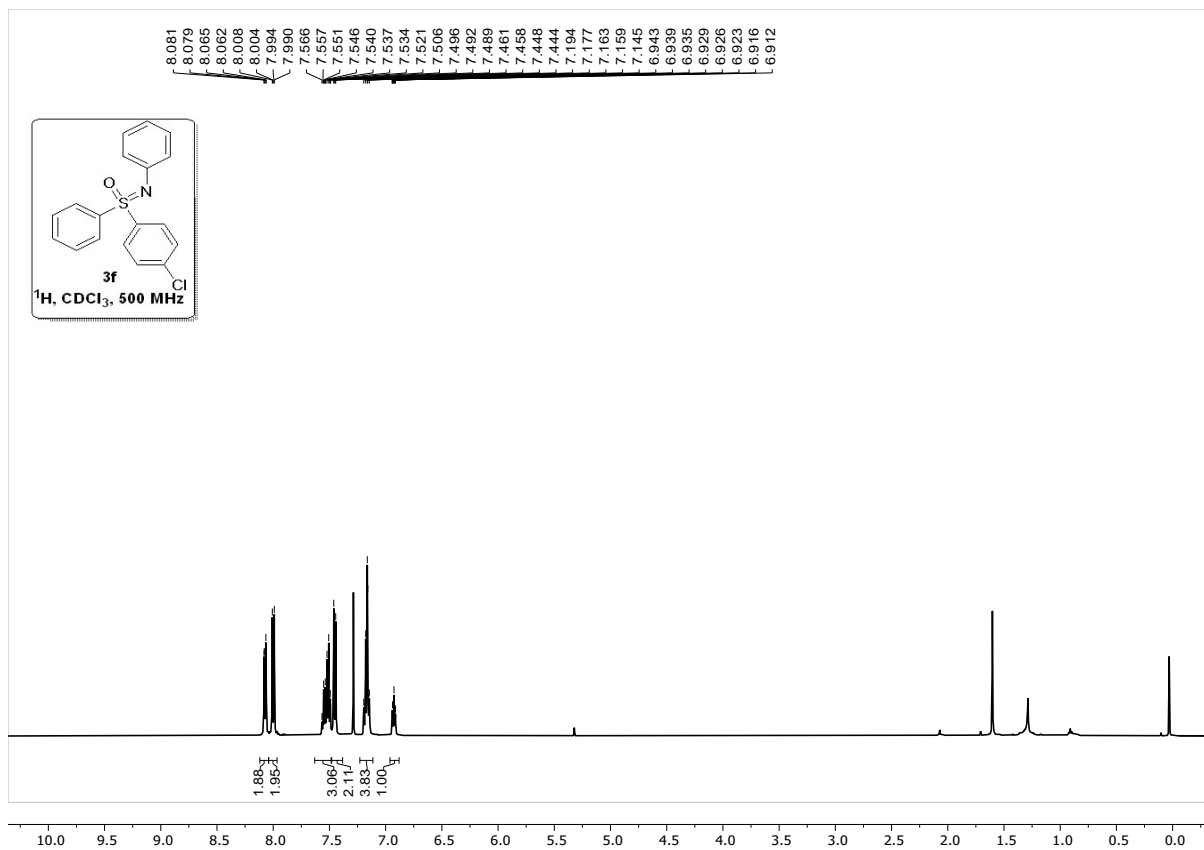


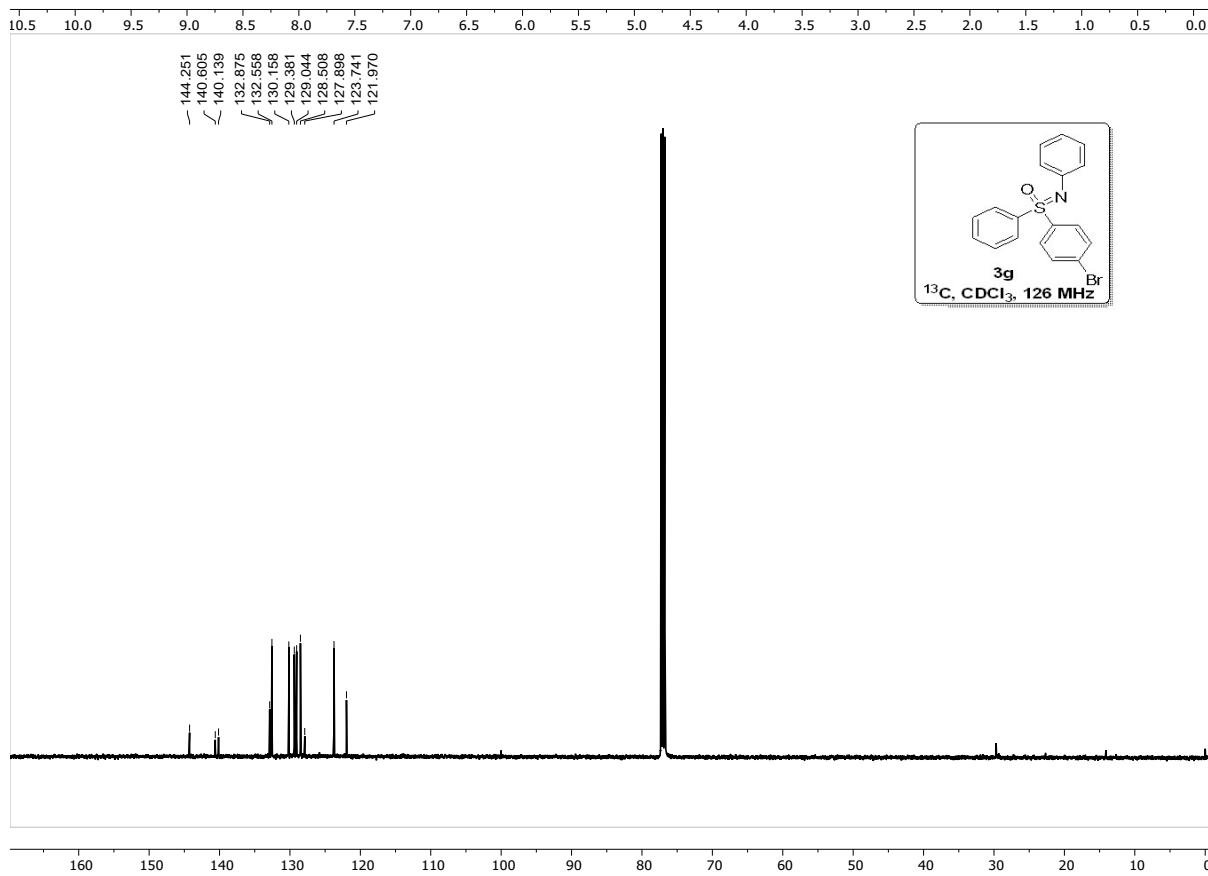
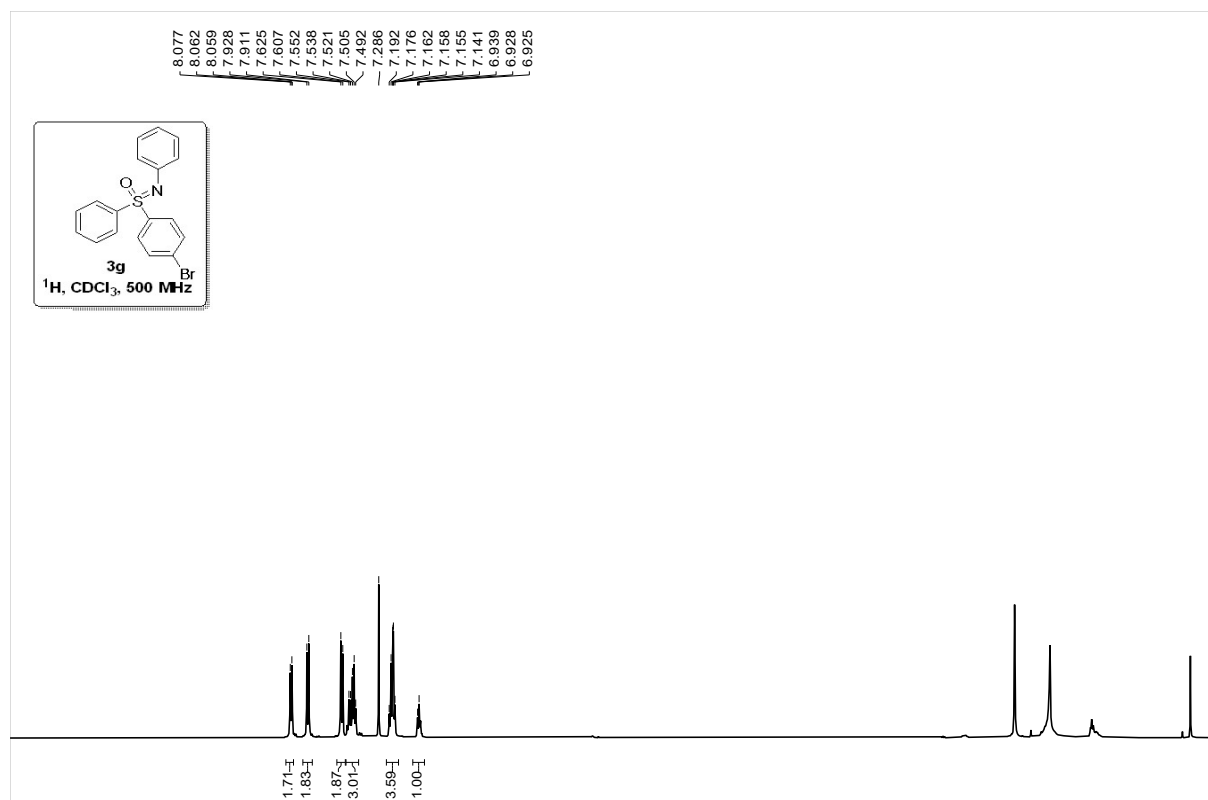


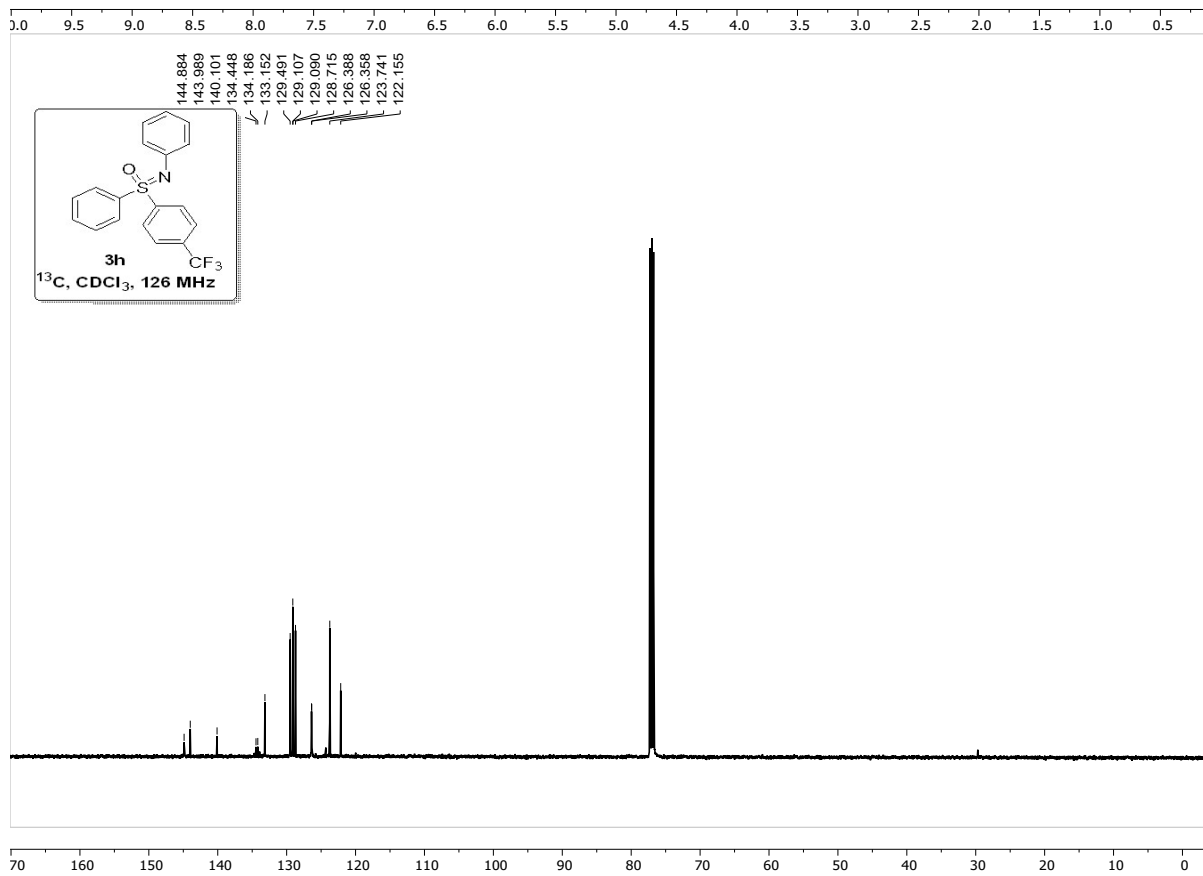
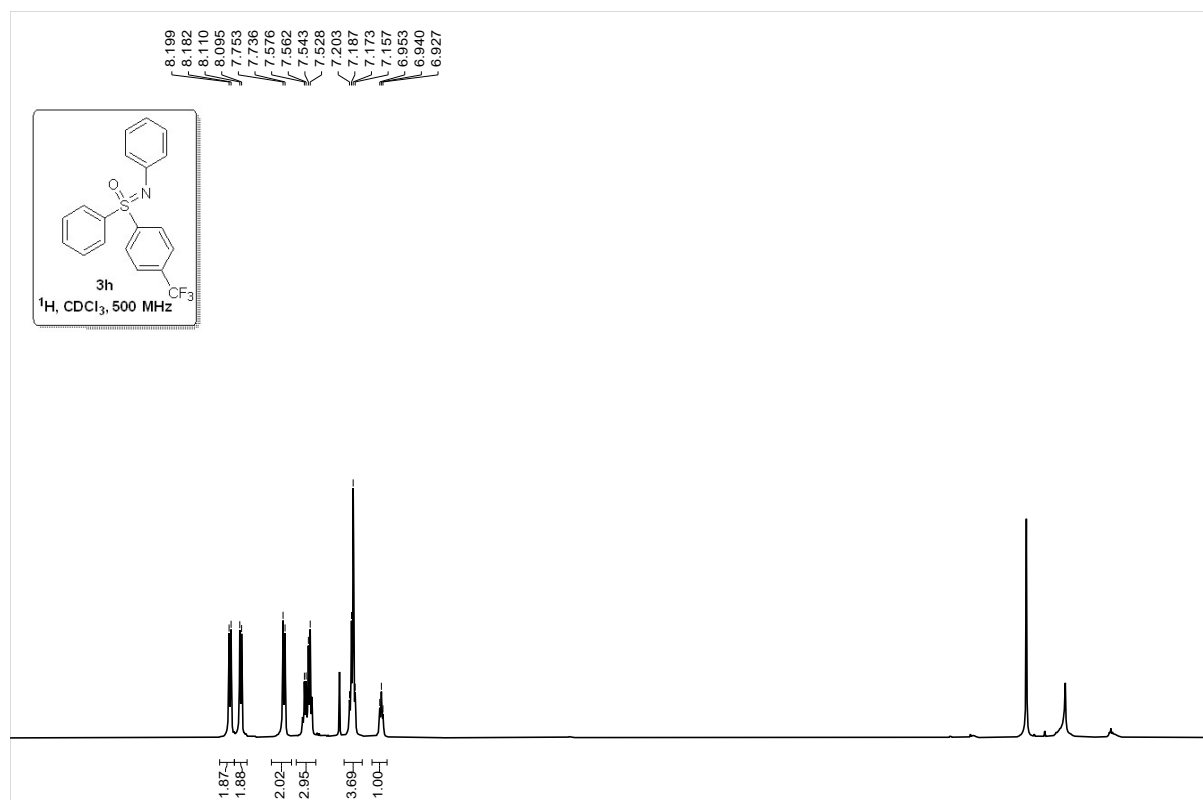
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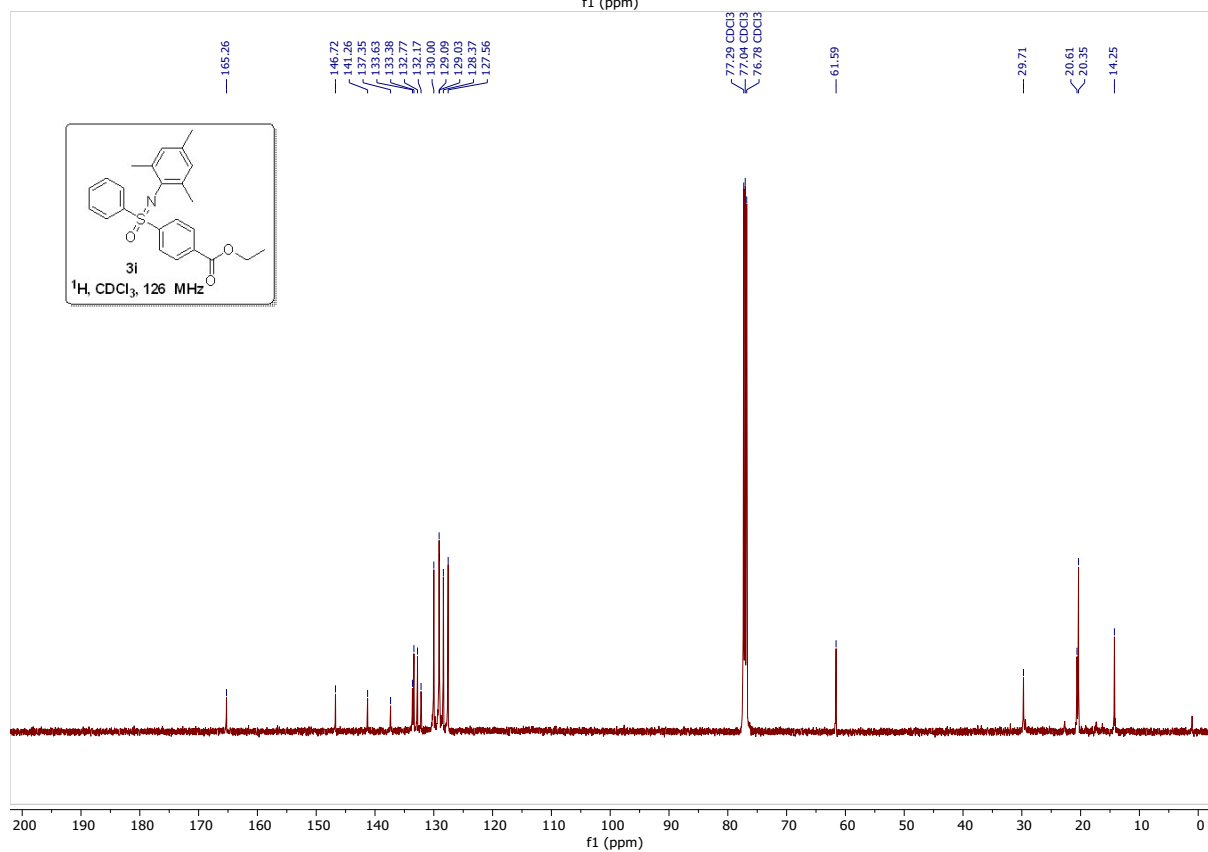
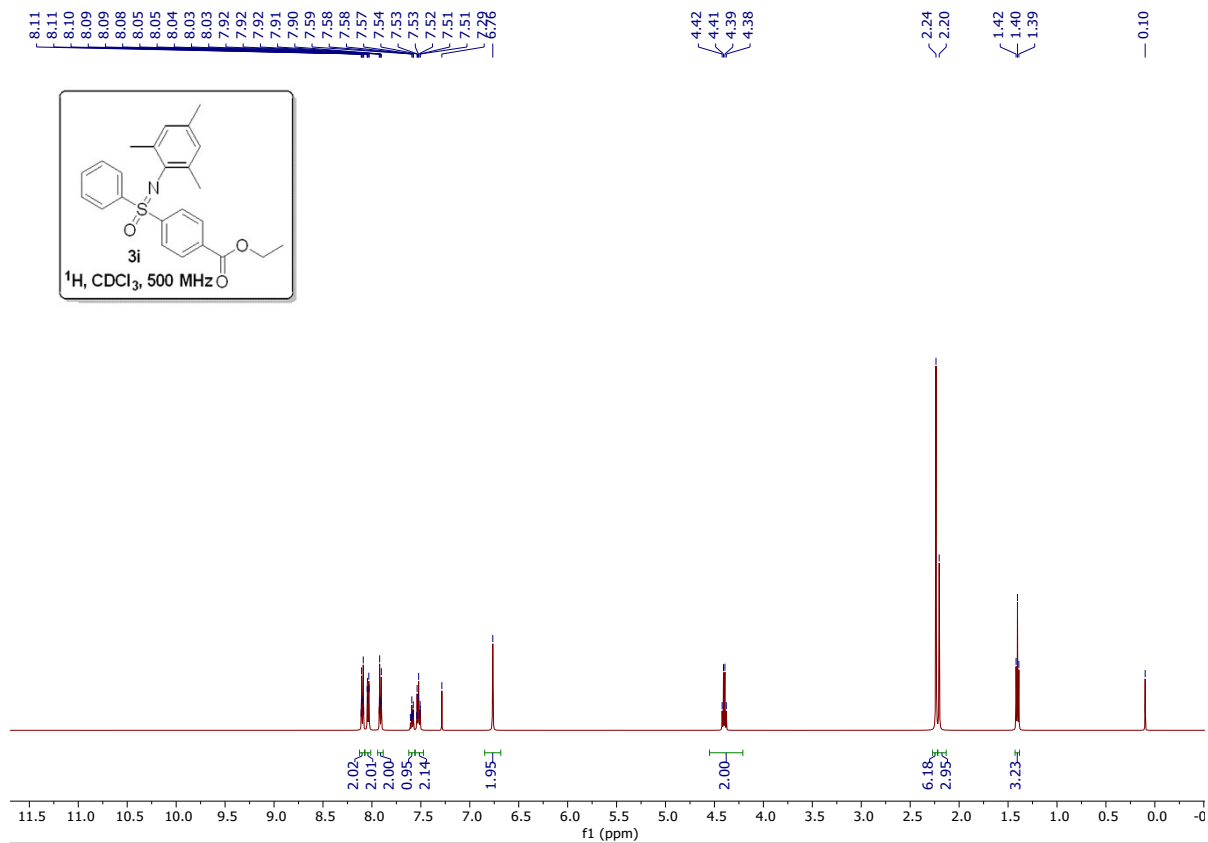


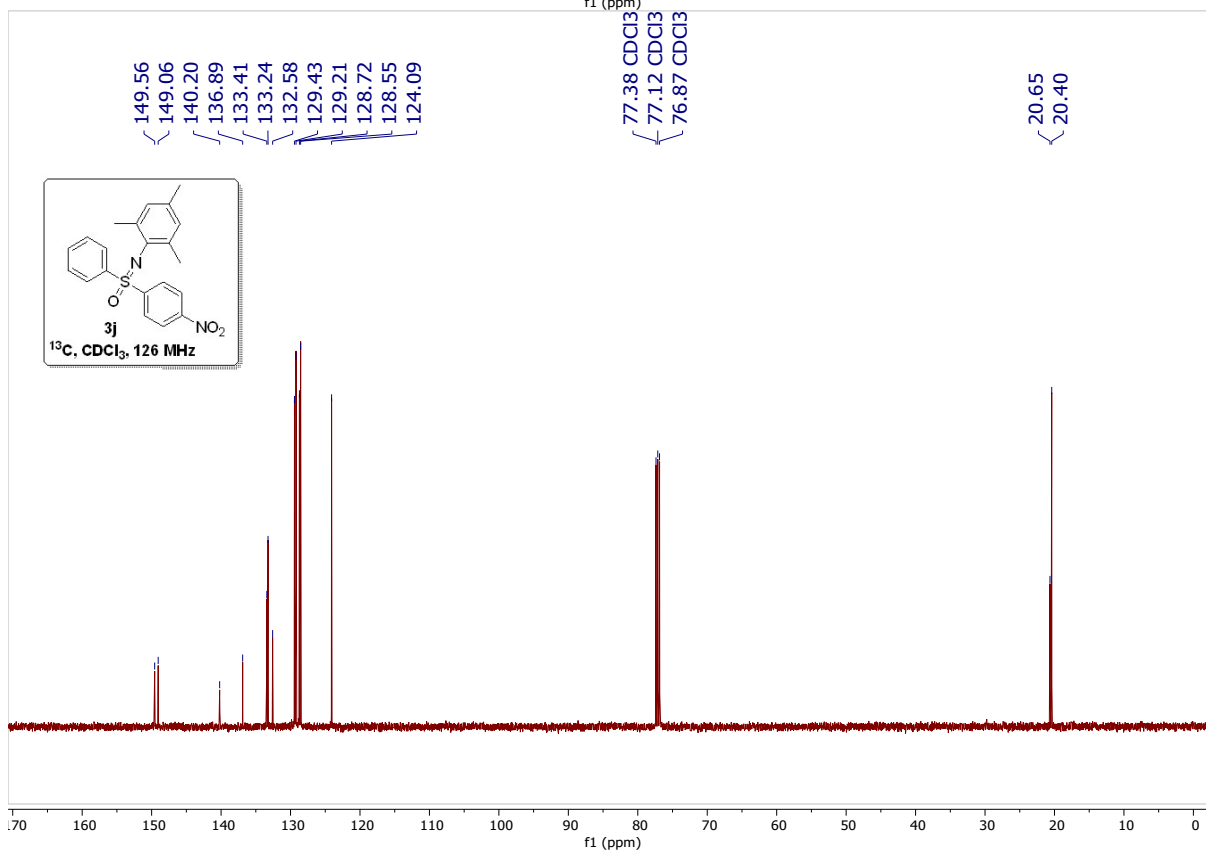
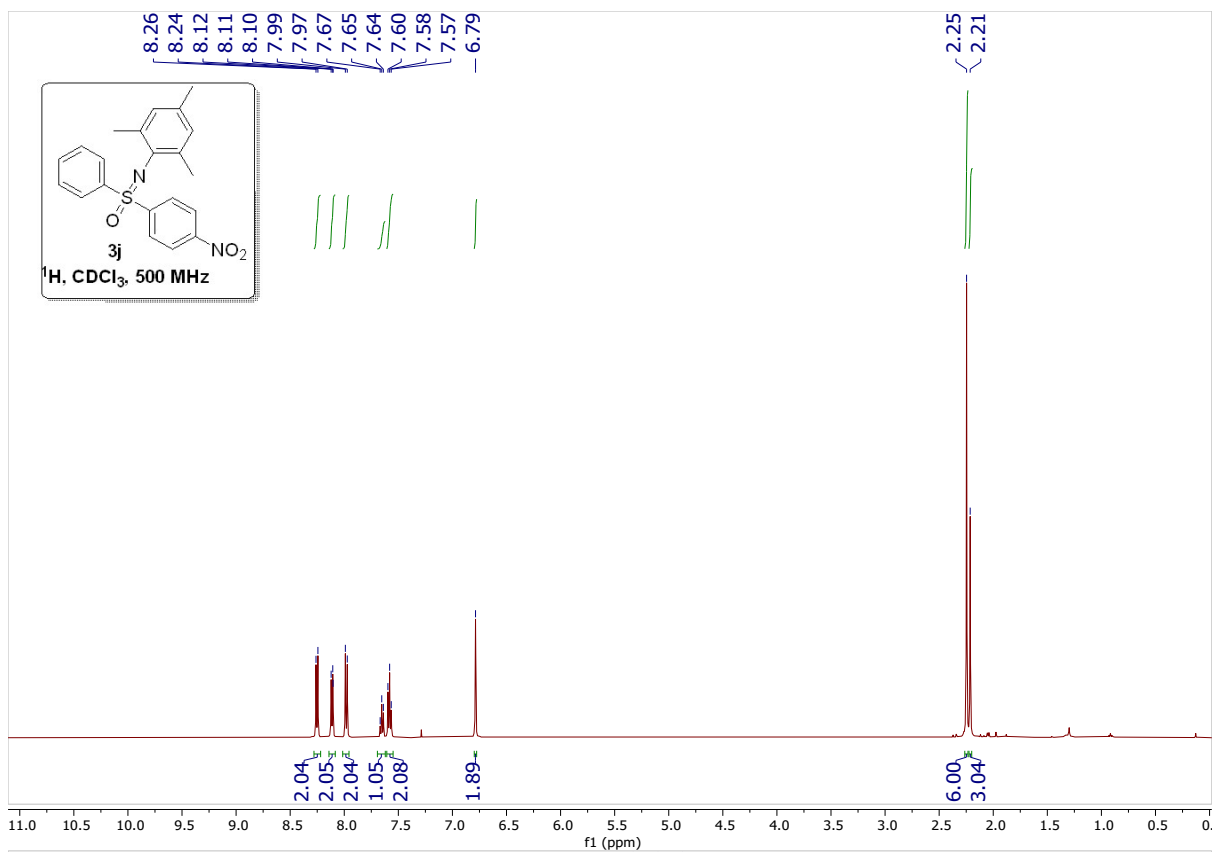


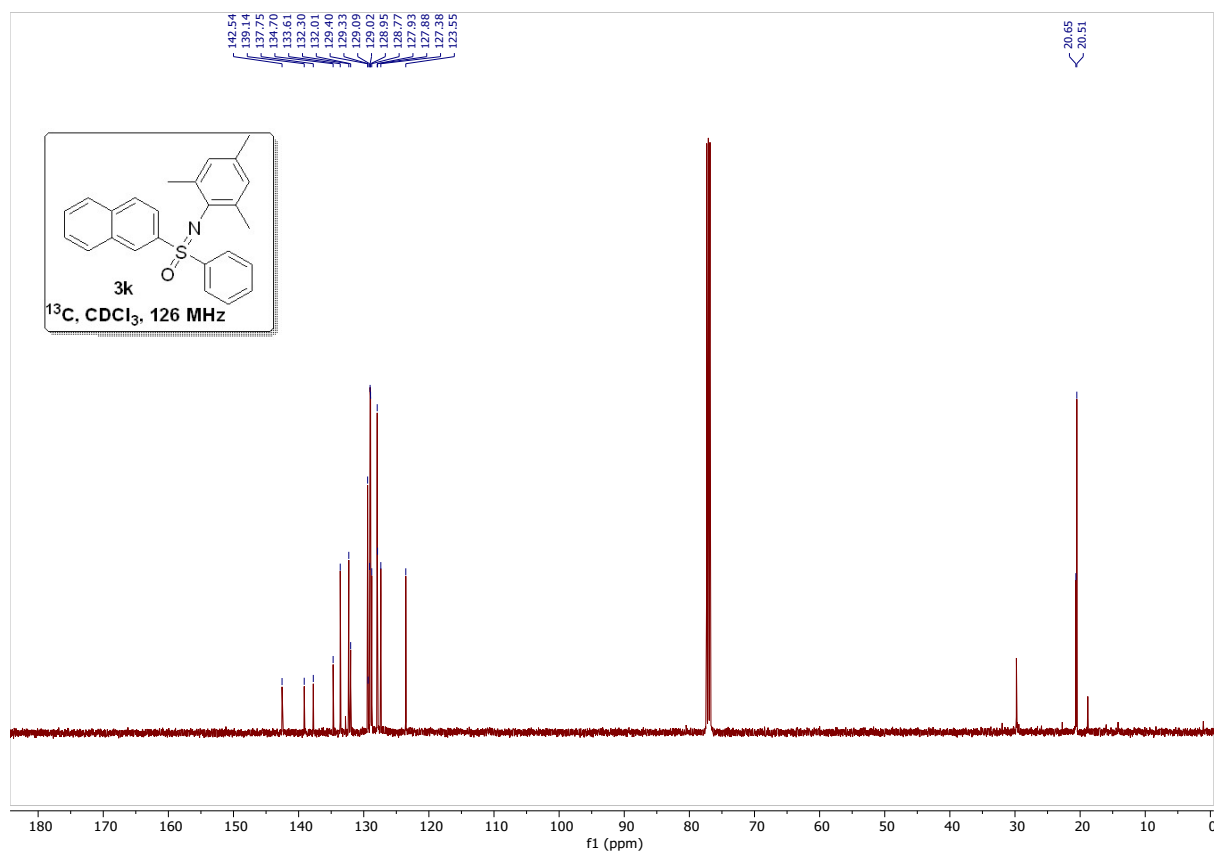
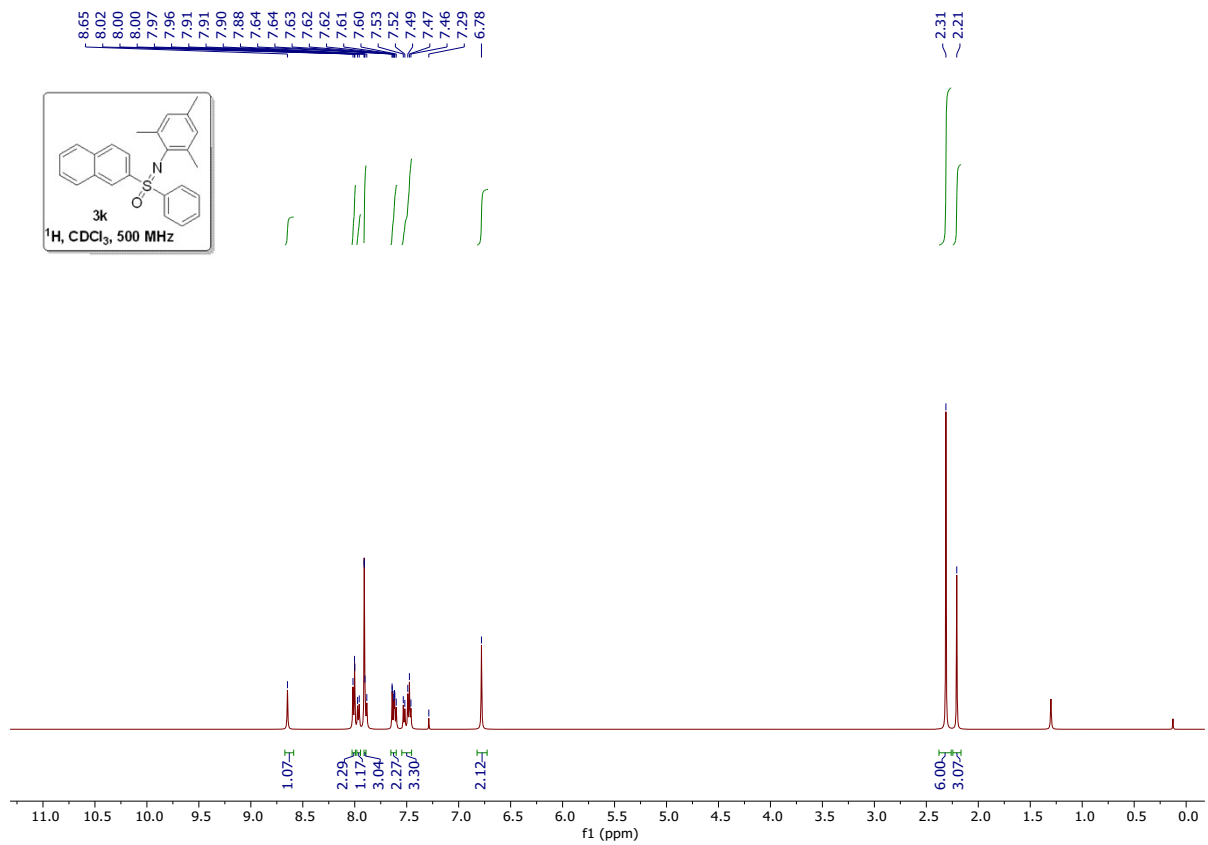


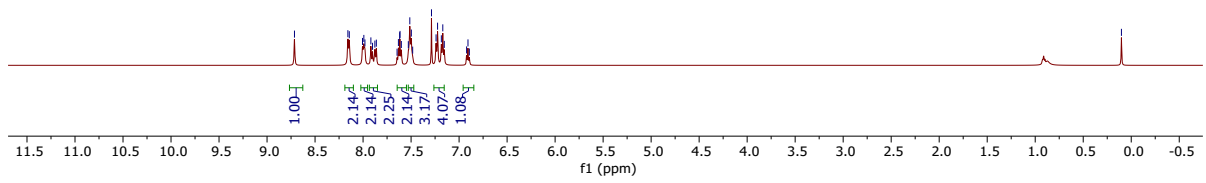
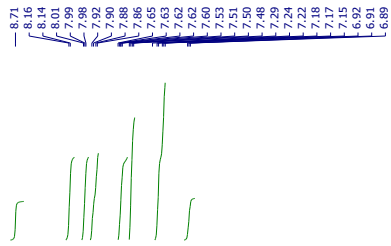
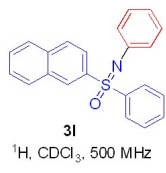


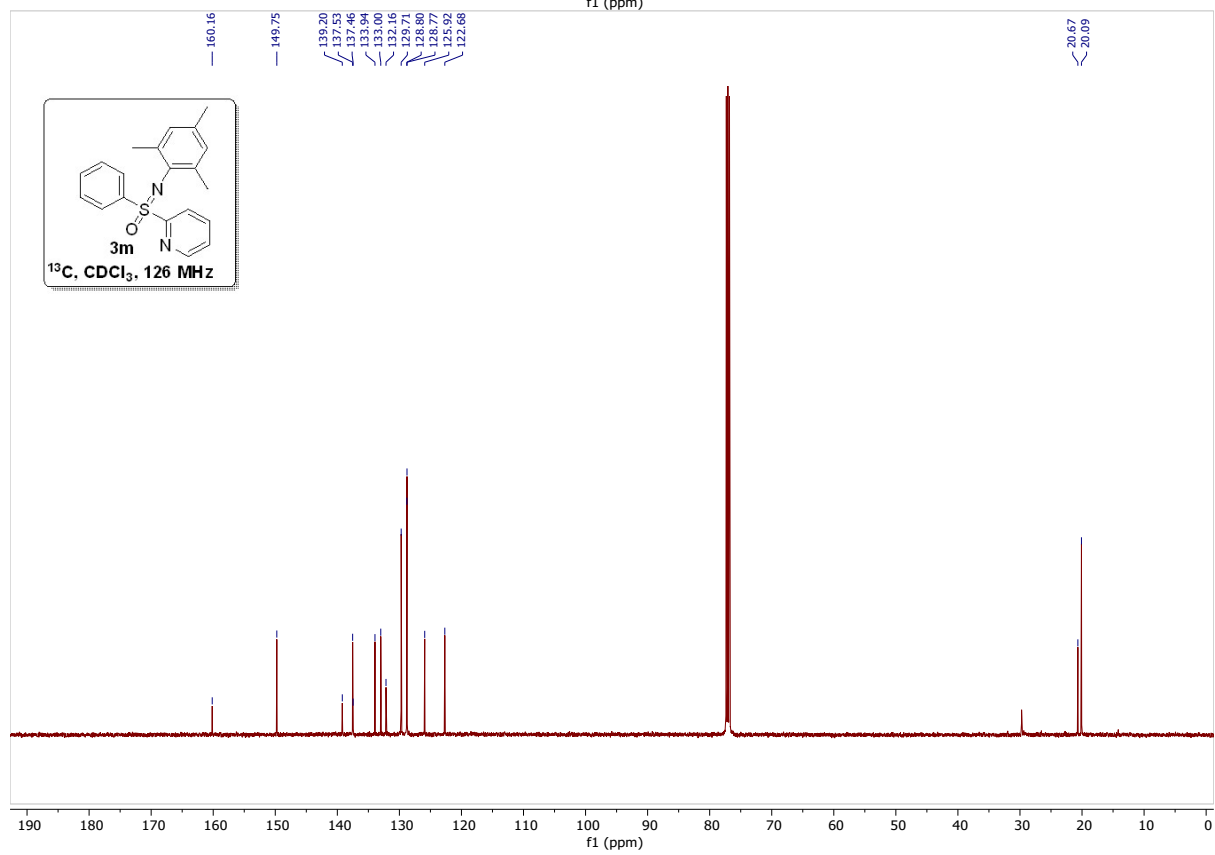
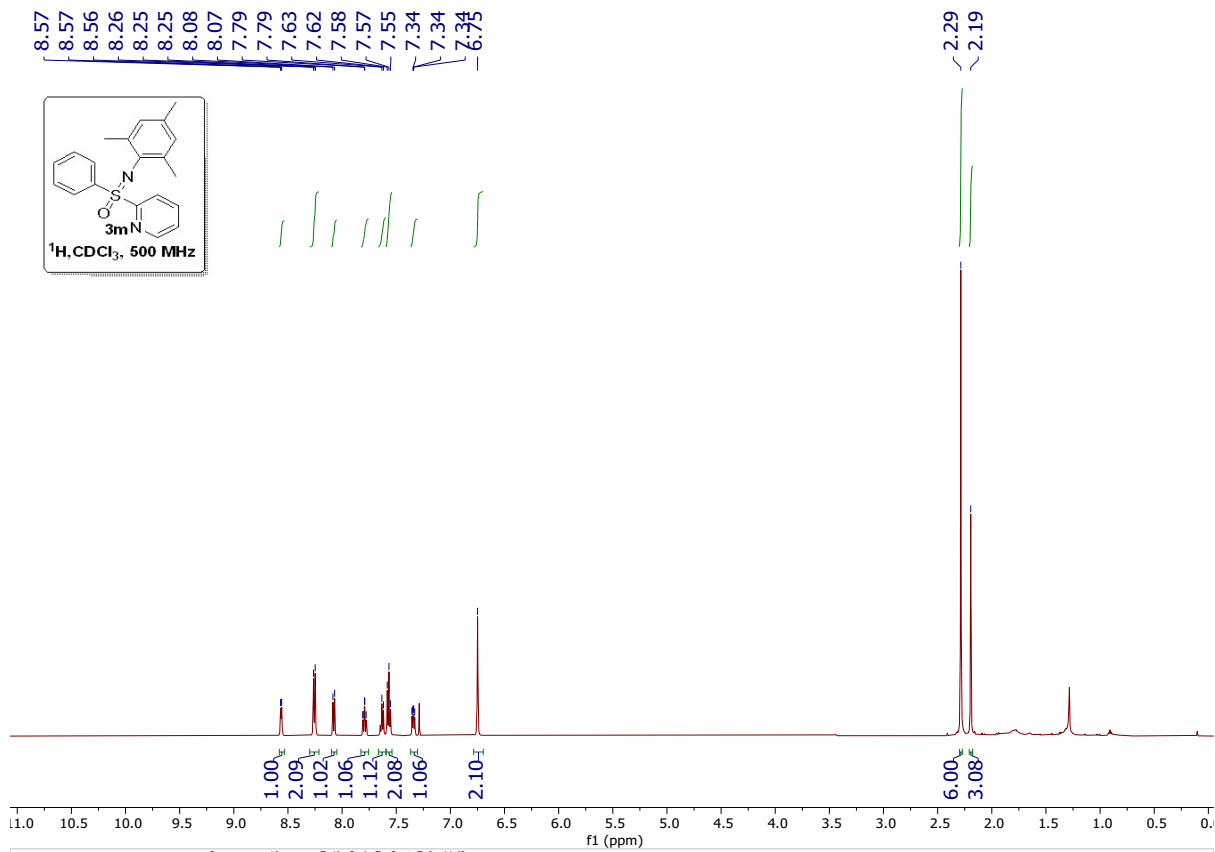


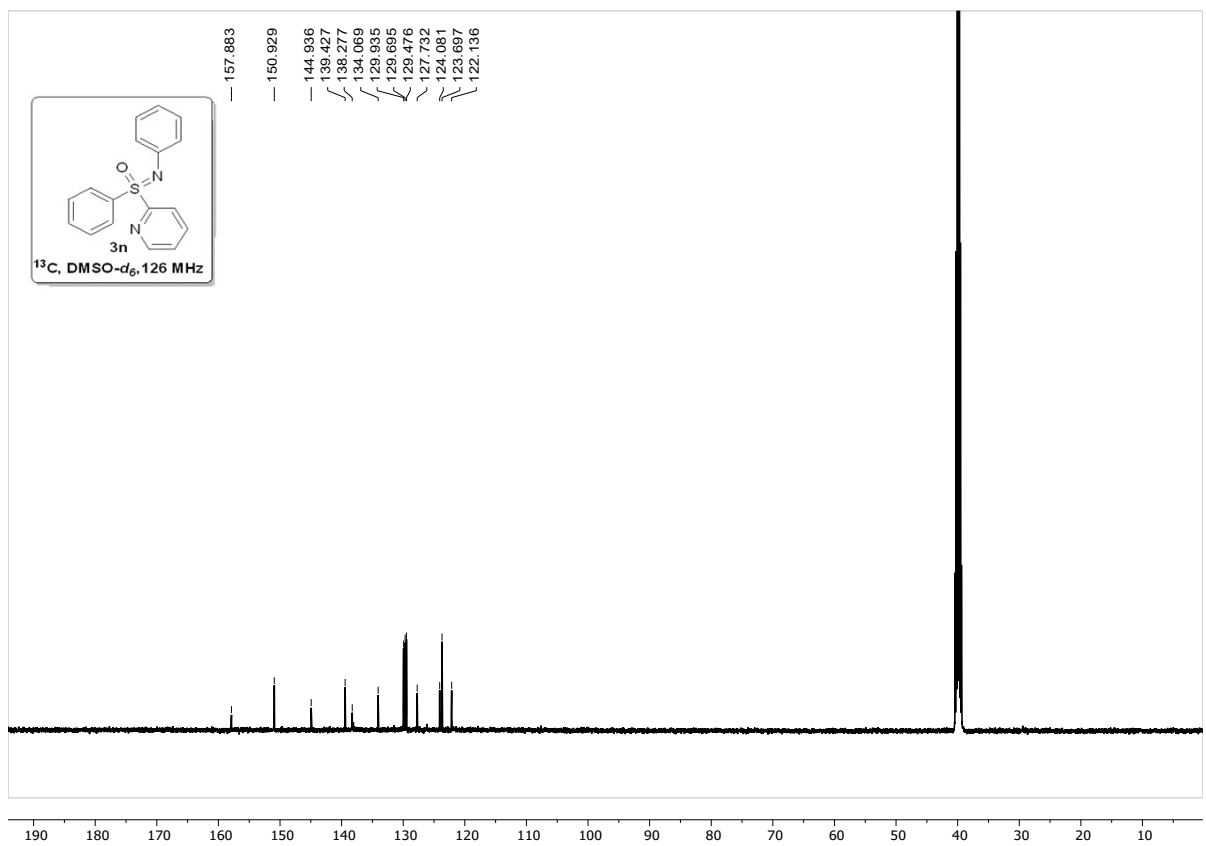
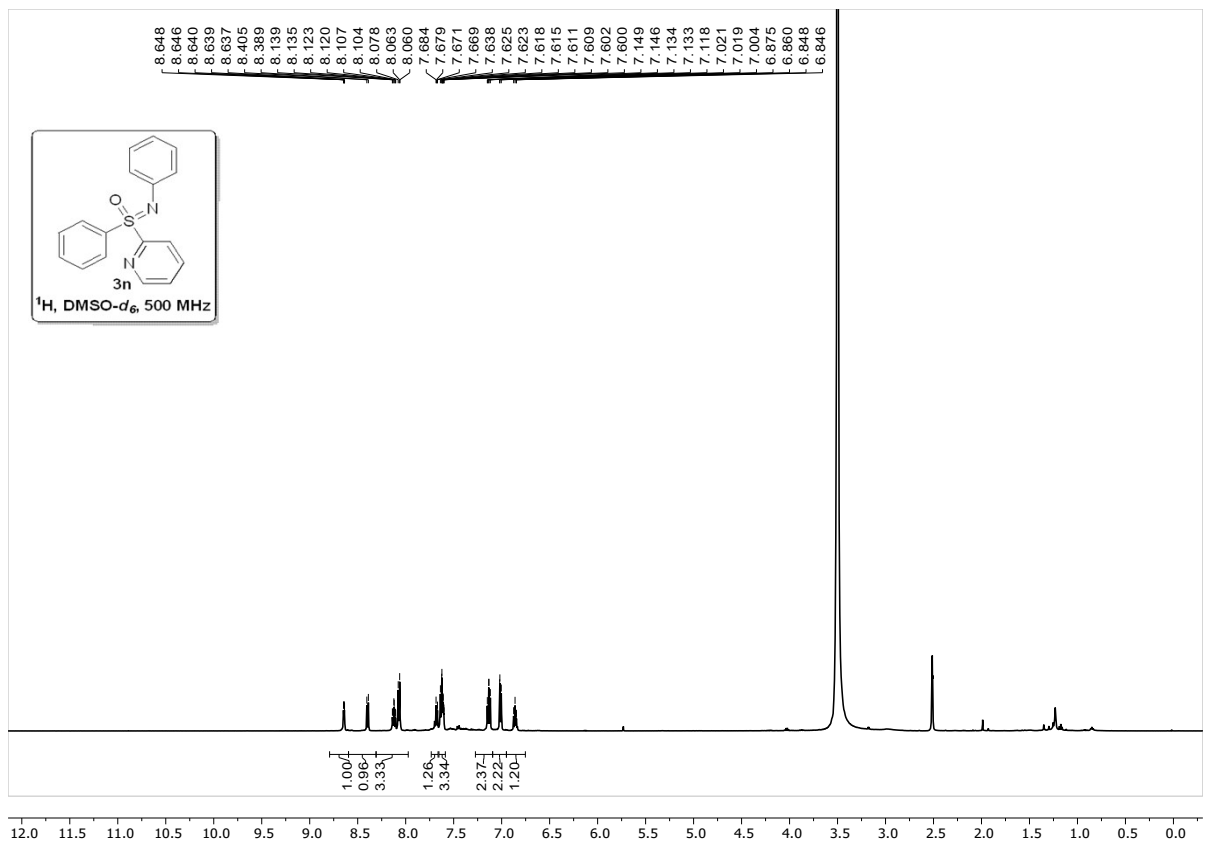


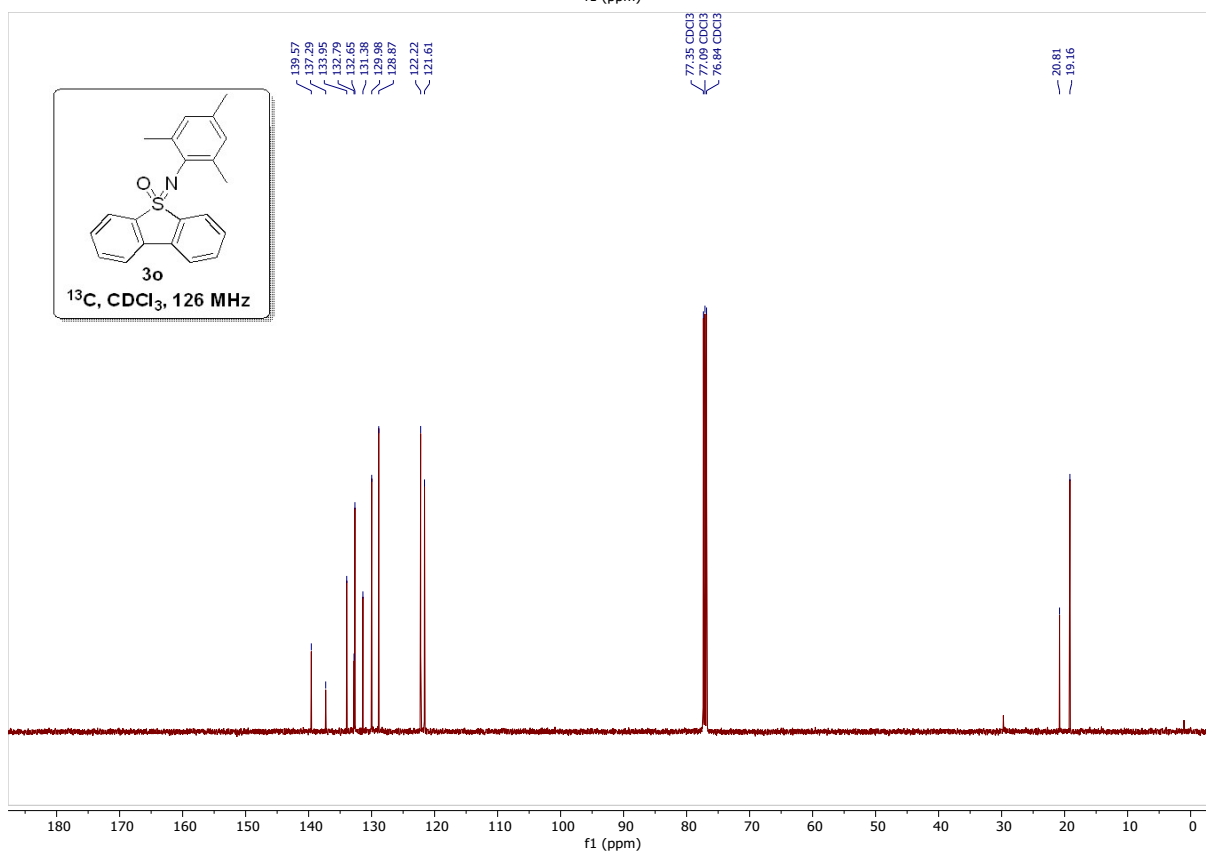
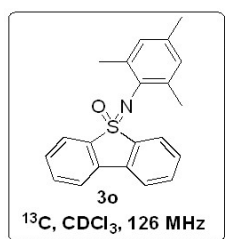
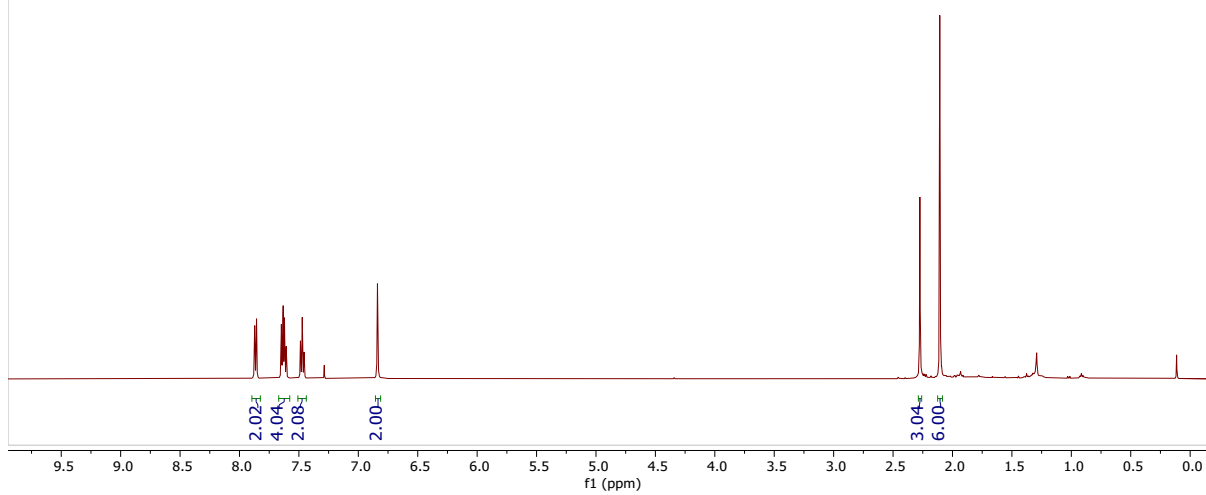
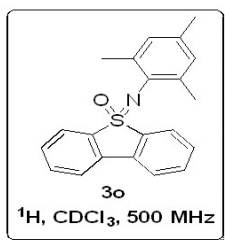


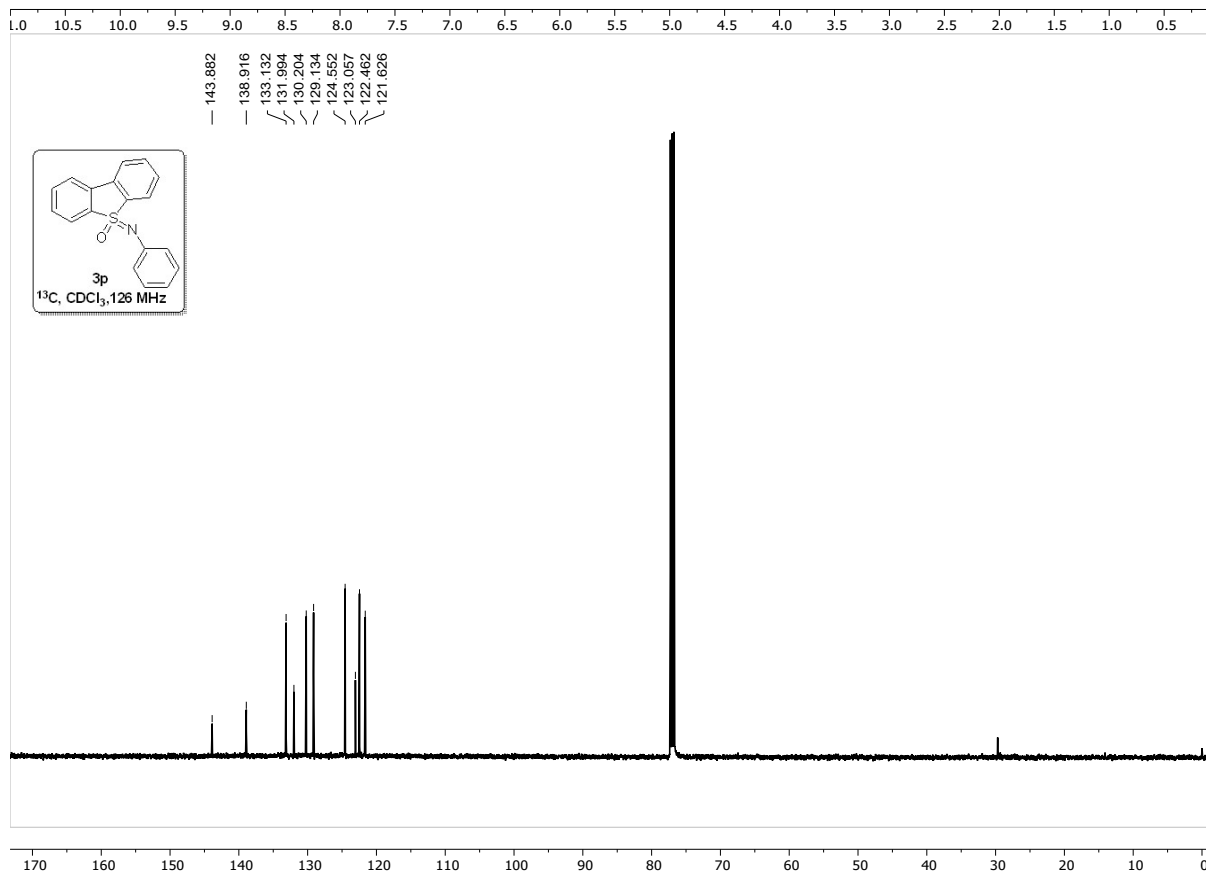
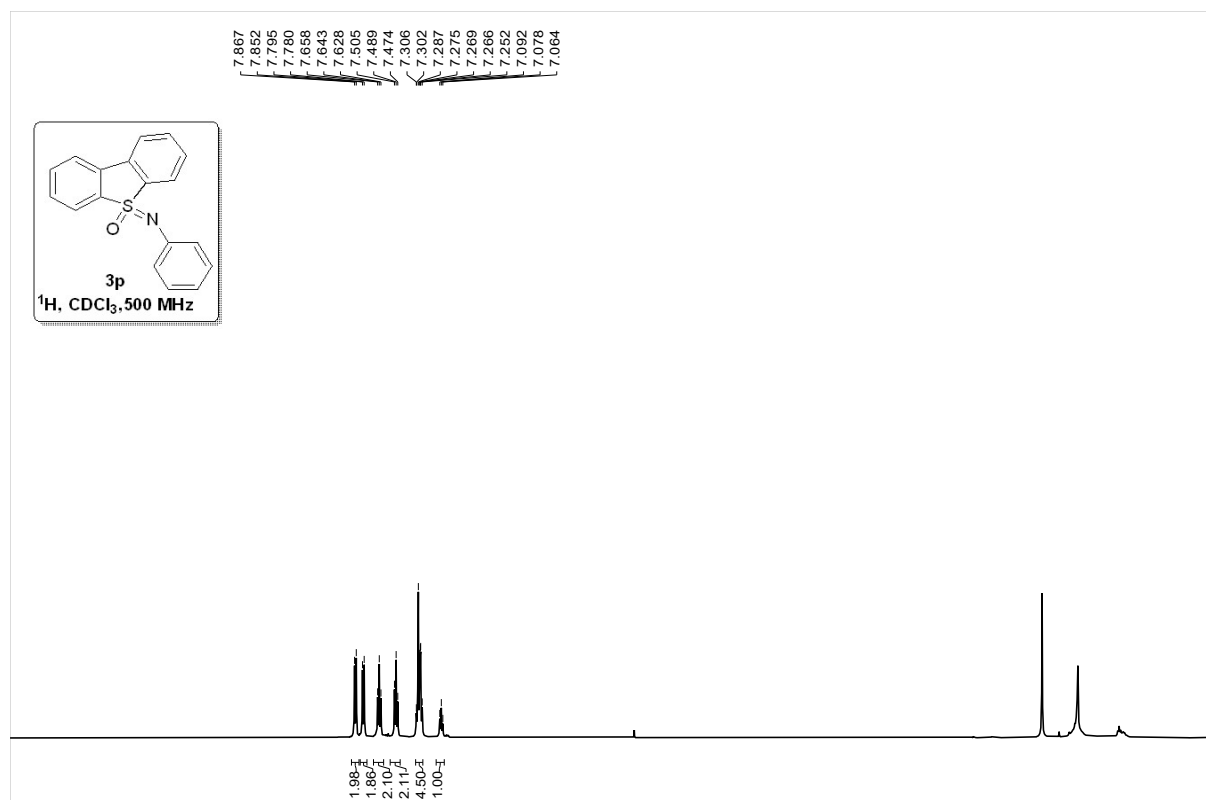


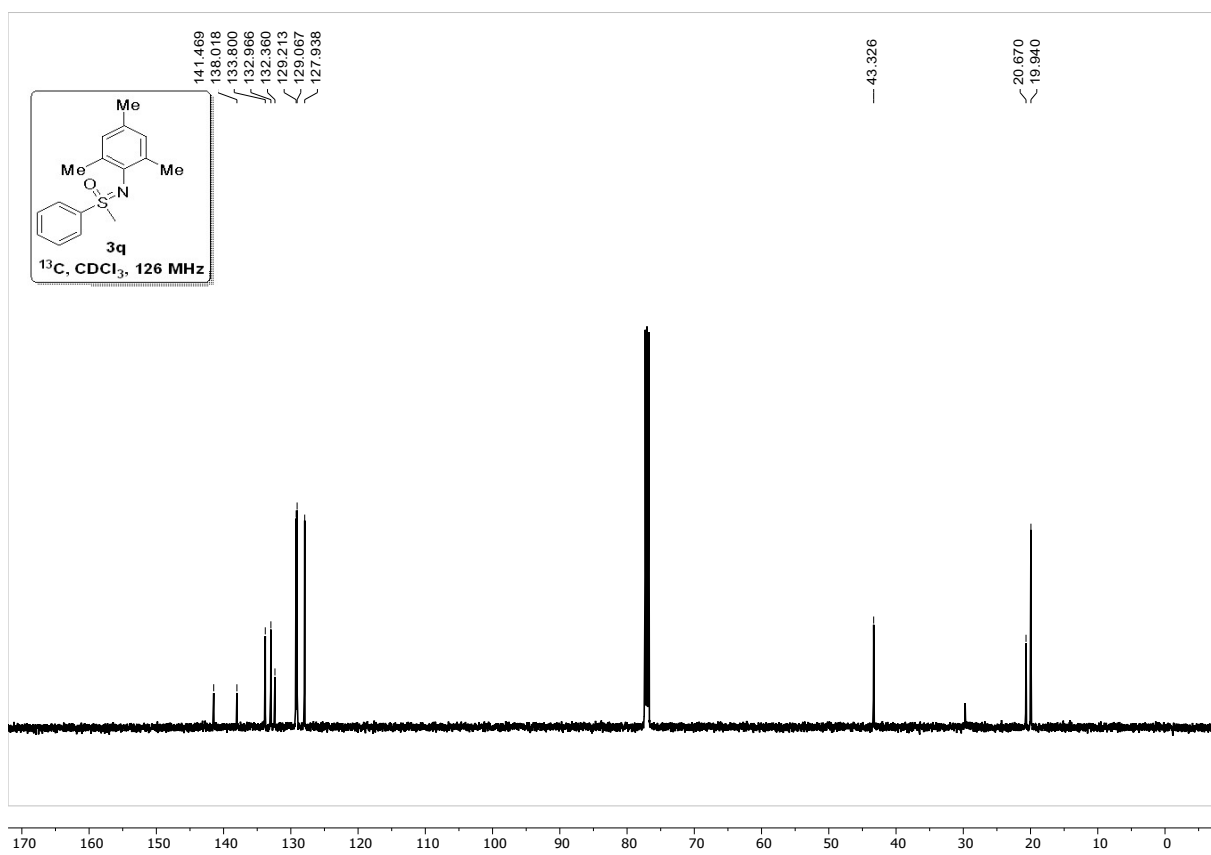
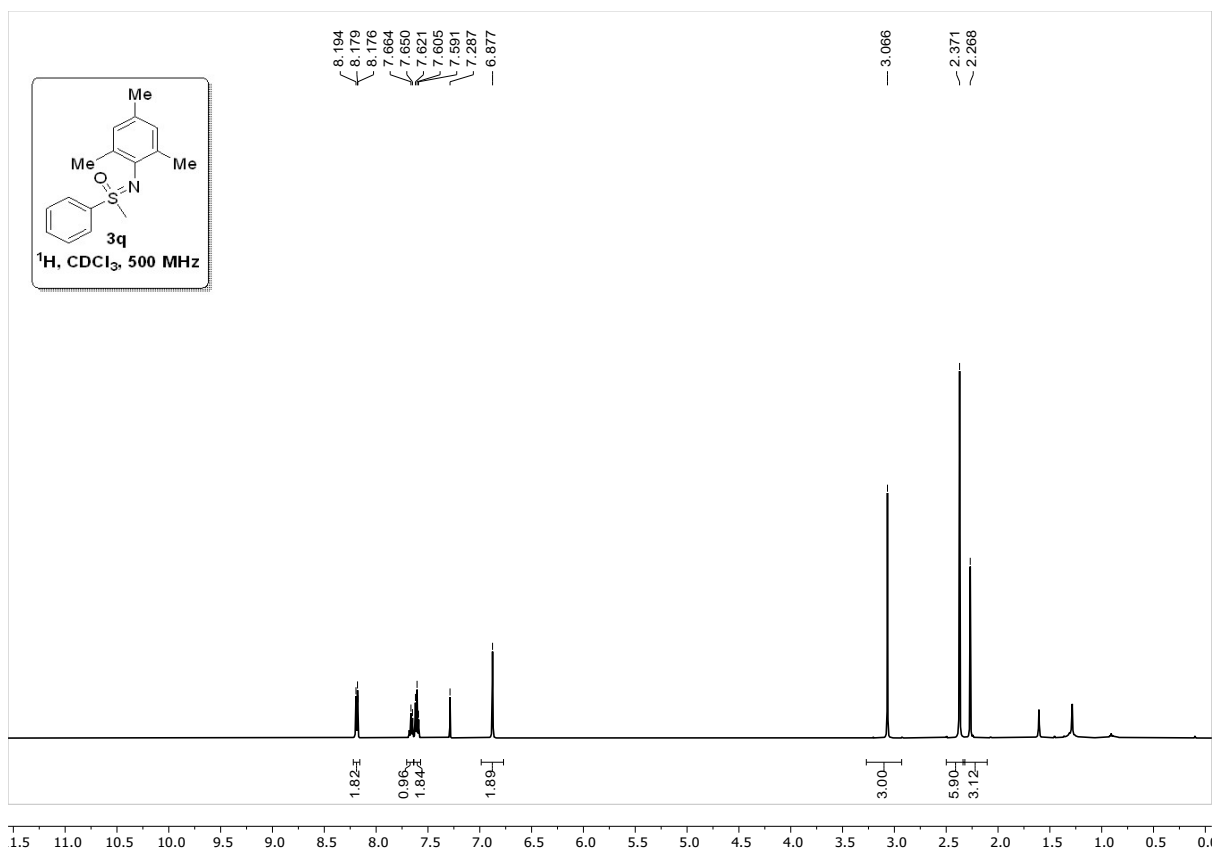


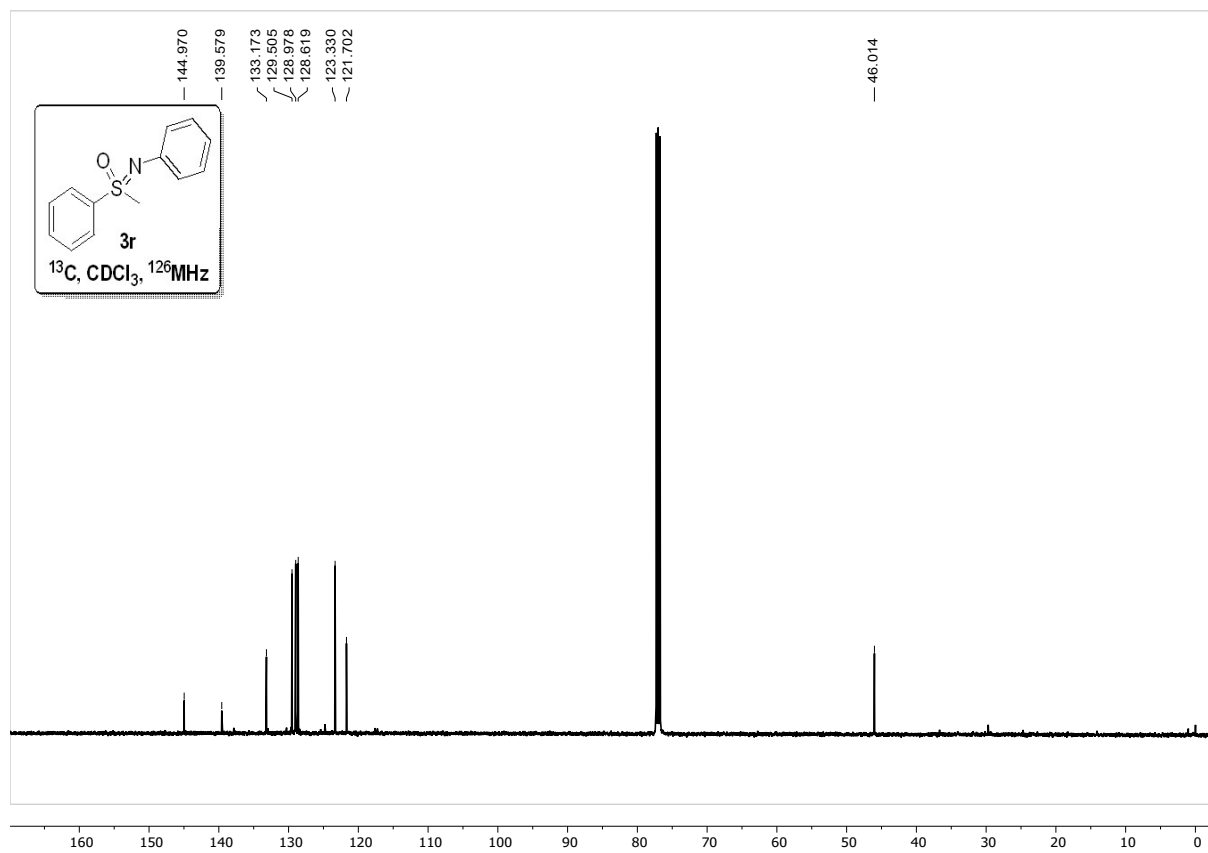
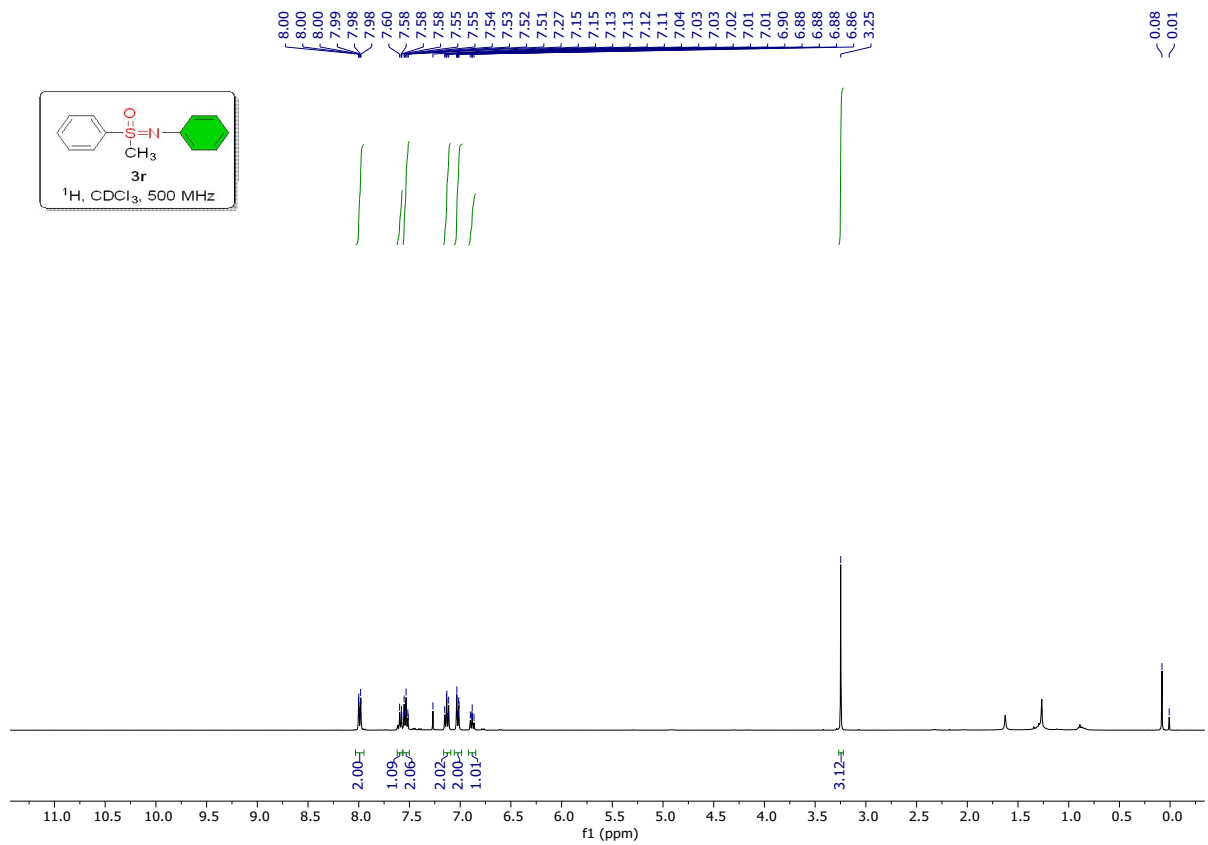




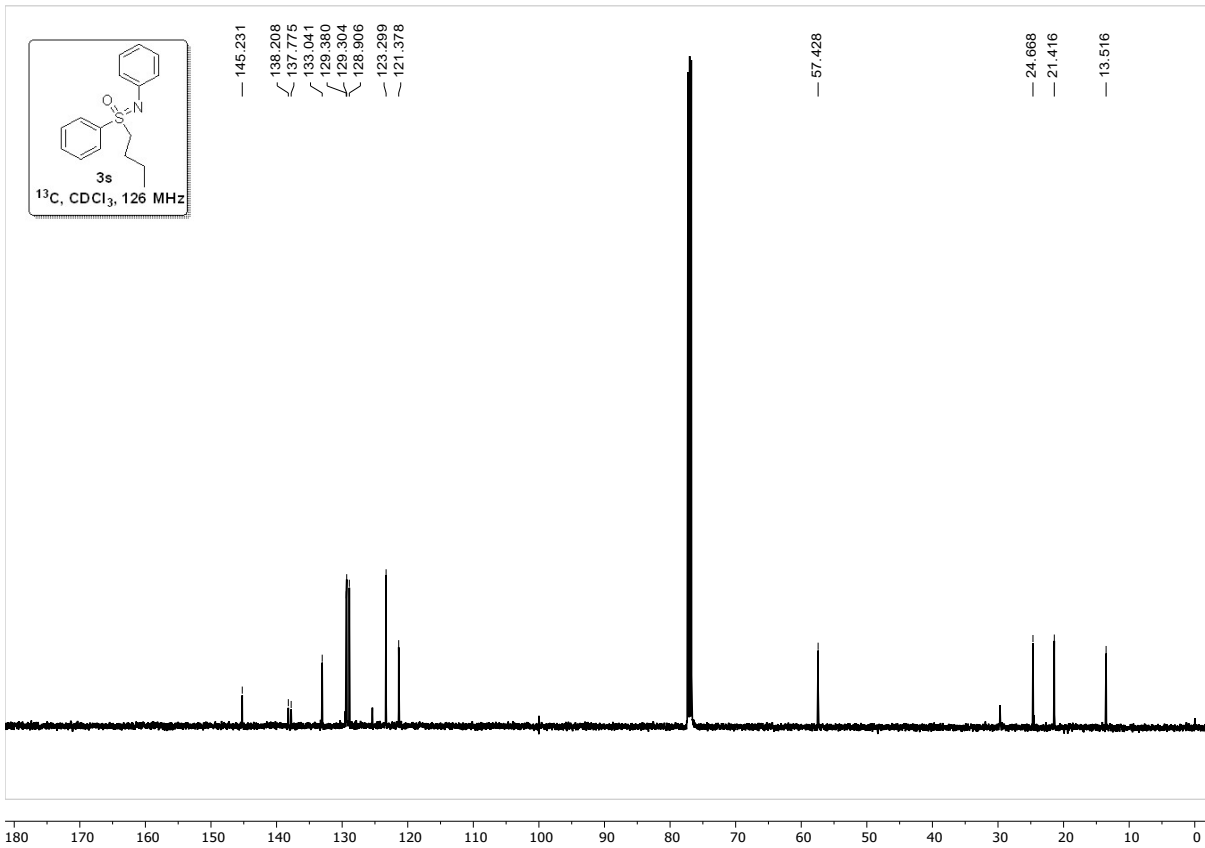
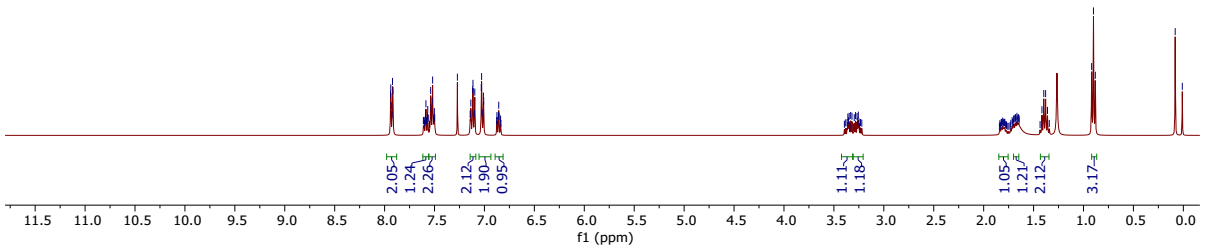
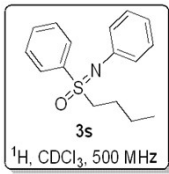


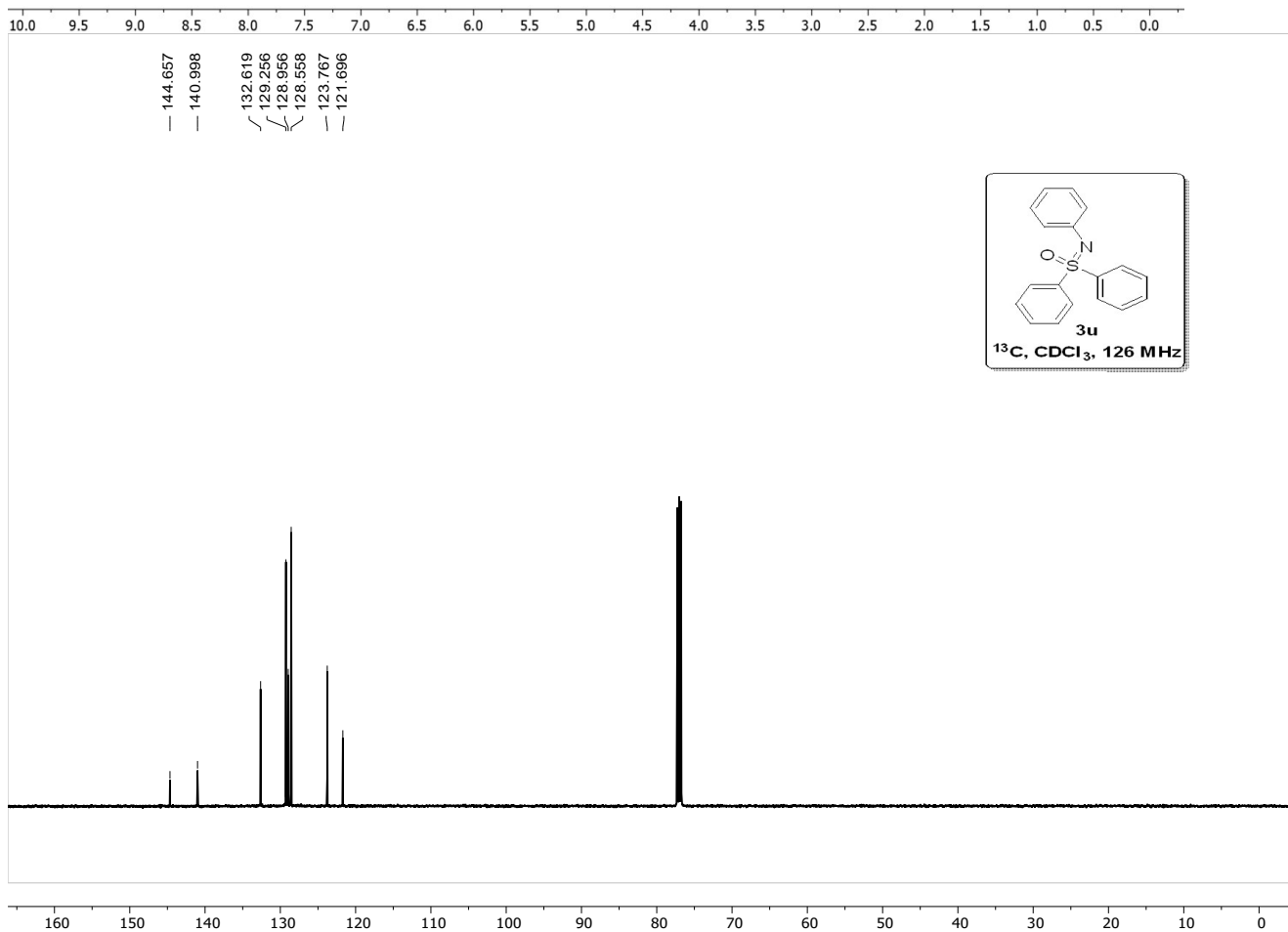
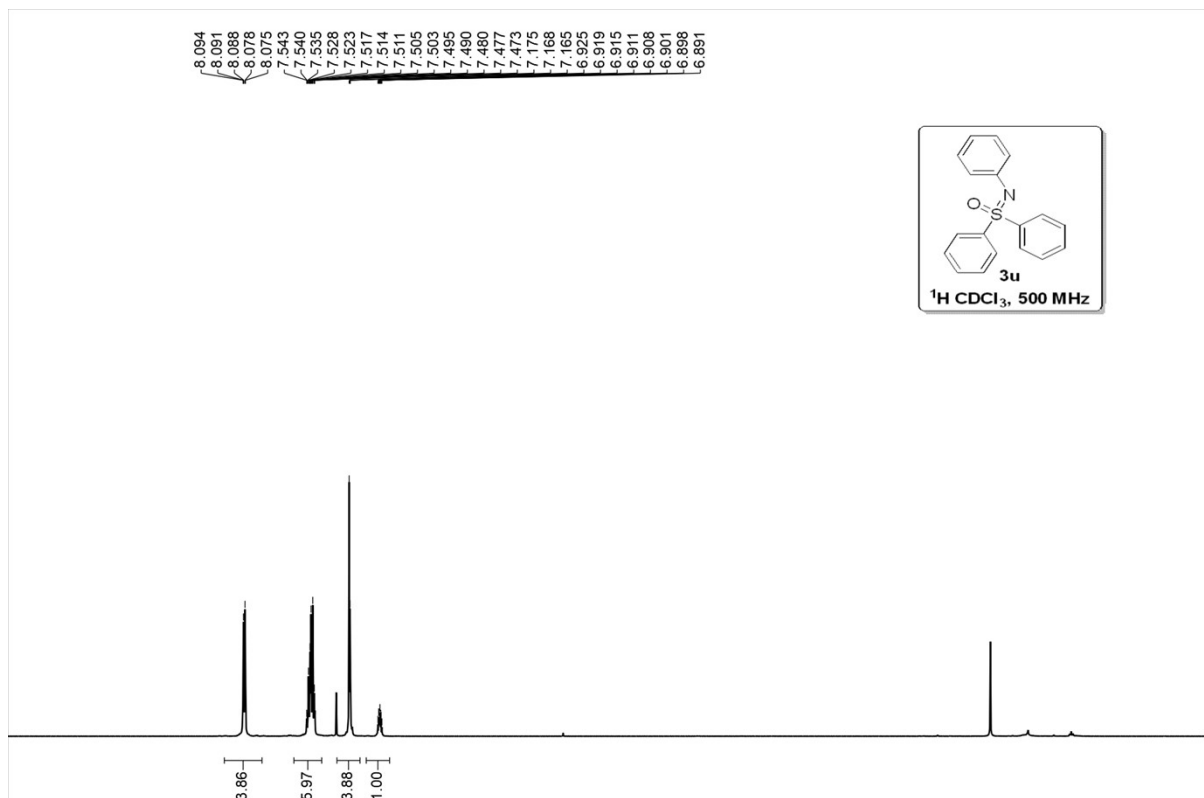


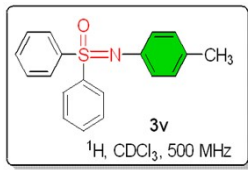




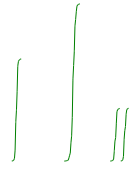
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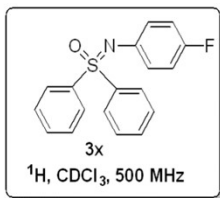
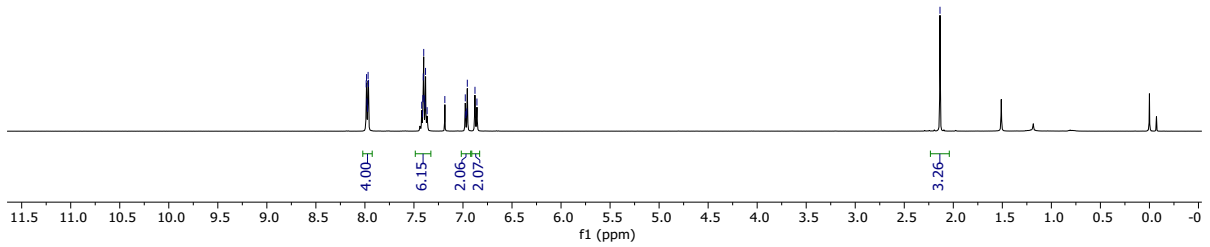




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