Supporting information for:

Iron-Catalyzed Nitrene Transfer Reaction of Nitrosobenzenes with *N*-Acyloxyamides for Accessing *N*-Acyl Azoxy Molecules

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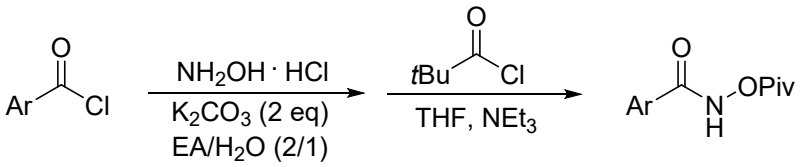
I. General Information

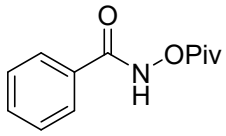
Unless otherwise noted, all the solvents and commercially available chemicals were used as received. NMR spectra were recorded on a Bruker-400 instrument or Bruker-500 instrument. ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, q = quadruplet. Melting points (M.p.) were obtained using WRS-1B melting point apparatus (Laboratory Devices, Shanghai Shenguang CO.; LTD.). High-resolution mass spectra (HRMS) were recorded on a Bruker micrTOF-Q II or an Agilent 6200 series TOF instrument. For reactions that require heating, an aluminium heating block was used as the heating source.

II. Procedures for the Synthesis of Starting Materials

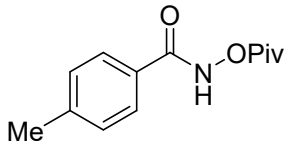


General procedures for the synthesis of *N*-Acyloxyamides: According to a previously reported method,[1] a 250 mL round bottom flask was charged with K_2CO_3 (20 mmol, 2 equiv.), ethyl acetate (EA) (40 mL) and water (20 mL), added with hydroxylamine hydrochloride (20 mmol, 2 equiv.), cooled in an ice water bath, added drop wise with acyl chloride (10 mmol). Then the resulting solution was stirred at room temperature overnight. The organic phase was separated and the aqueous phase was extracted with EA (40 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude hydroxamic acid were added with THF (40 mL) and Et_3N (26 mmol, 1.3 equiv.), cooled in an ice water bath, then stirred for a while followed by dropwise addition of PivCl (10 mmol, 1 equiv). After stirring overnight, the reaction mixture was added with EA (40 mL), water (20 mL) and HCl (1 M, 1 mL). The organic layer was separated and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA) (8:1) to give the desired product *N*-acyloxyamides **1**.

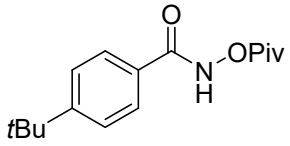
[1] X. Zhang, B. Lin, J. Chen, J. Chen, Y. Luo, Y. Xia, *Org. Lett*., 2021, **23**, 819.



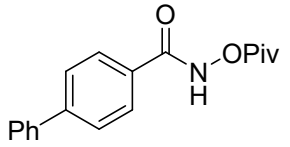
***N*-(Pivaloyloxy)benzamide** (**1a**).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 4.3800 g, 19.7 mmol, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (br, 1H), 7.83-7.83 (m, 2H), 7.60-7.55 (m, 1H), 7.50-7.45 (m, 2H), 1.39 (s, 9H).



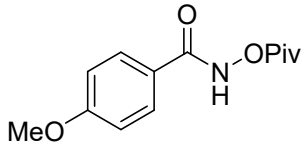
4-Methyl-*N*-(pivaloyloxy)benzamide (**1b**).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 2.3314 g, 8.9 mmol, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (br, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 2H), 2.41 (s, 3H), 1.37 (s, 9H).



4-(tert-butyl)-*N*-(pivaloyloxy)benzamide (1c).[2] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 2.6058 g, 9.4 mmol, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (br, 1H), 7.76 (d, *J* = 6.6 Hz, 2H), 7.47 (d, *J* = 6.6 Hz, 2H), 1.36 (s, 9H), 1.33 (s, 9H).



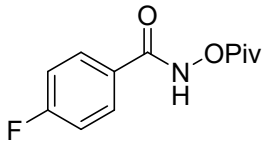
***N*-(Pivaloyloxy)-[1,1'-biphenyl]-4-carboxamide (1d)**.[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.4553 g, 4.9 mmol, 49% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (br, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.49-7.43 (m, 2H), 7.42-7.35 (m, 1H), 1.37 (s, 9H).



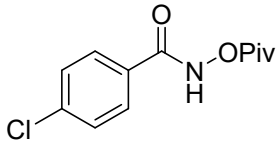
4-Methoxy-*N*-(pivaloyloxy)benzamide (1e).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.7892 g, 7.1 mmol, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ

[2] H. Wang, F. Glorius, *Angew. Chem. Int. Ed*., 2012, **51**, 7318.

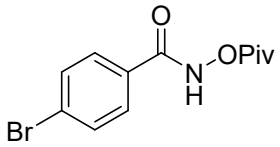
9.26 (br, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 1.36 (s, 9H).



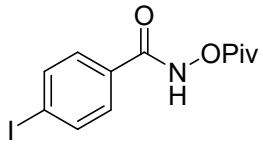
4-Fluoro-*N*-(pivaloyloxy)benzamide (1f).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 2.2601 g, 9.7 mmol, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (br, 1H), 7.85-7.82 (m, 2H), 7.16-7.12 (m, 2H), 1.39 (s, 9H).



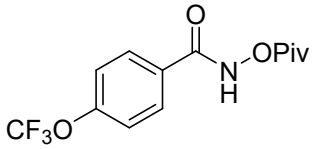
4-Chloro-*N*-(pivaloyloxy)benzamide (1g).[2] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 2.0012 g, 7.8 mmol, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (br, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 1.35 (s, 9H).



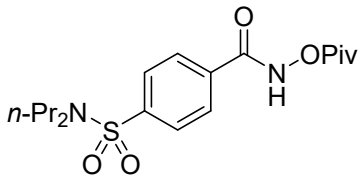
4-Bromo-*N*-(pivaloyloxy)benzamide (1h).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 2.4683 g, 8.22 mmol, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (br, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 1.36 (s, 9H).



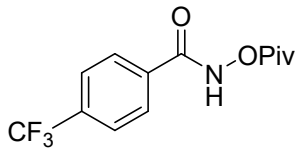
4-Iodo-*N*-(pivaloyloxy)benzamide (1i).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 3.0189 g, 8.7 mmol, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 1.36 (s, 9H).



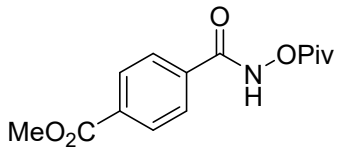
***N*-(pivaloyloxy)-4-(trifluoromethoxy)benzamide (1j).**[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.6165 g, 5.3 mmol, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 1.36 (s, 9H).



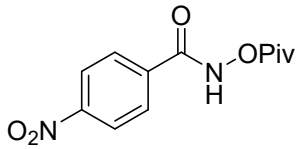
4-(*N*,*N*-dipropylsulfamoyl)-*N*-(pivaloyloxy)benzamide (1k).[3] Light yellow transparent oil was obtained by silica gel column chromatography with PE/EA (8:1). 0.4377 g, 2 mmol, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (br, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 3.27-2.85 (m, 4H), 1.74-1.43 (m, 4H), 1.36 (s, 9H), 0.86 (t, *J* = 7.4 Hz, 6H).



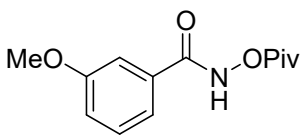
***N*-(pivaloyloxy)-4-(trifluoromethyl)benzamide (1l)**.[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 2.5653 g, 9.0 mmol, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (br, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 1.37 (s, 9H).



4-((Pivaloyloxy)carbamoyl)phenyl acetate (1m).[2] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 0.8960 g, 3.2 mmol, 32% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.12 (s, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 3.95 (s, 3H), 1.37 (s, 9H).

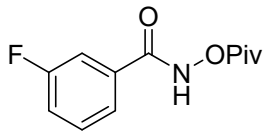


4-Nitro-*N*-(pivaloyloxy)benzamide (1n).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 2.0482 g, 7.7 mmol, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ9.38 (br, 1H), 8.32 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 1.30 (s, 9H).

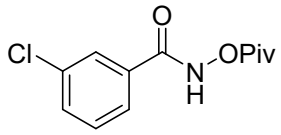


[3] R. Wang, Y. Chen, B. Fei, J. Hu, J. Chen, Y. Luo, Y. Xia, *Org. Lett.,* 2023, **25**, 2970-2974.

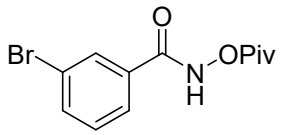
3-Methoxy-*N*-(pivaloyloxy)benzamide (1o).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.8581 g, 7.4 mmol, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (br, 1H), 7.35-7.27 (m, 3H), 7.17-6.94 (m, 1H), 3.82 (s, 3H), 1.35 (s, 9H).



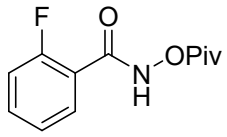
3-Fluoro-*N*-(pivaloyloxy)benzamide (1p).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.4914 g, 6.2 mmol, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (br, 1H), 7.59-7.49 (m, 2H), 7.44-7.39 (m, 1H), 7.28-7.24 (m, 1H), 1.35 (s, 9H).



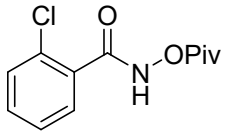
3-Chloro-*N*-(pivaloyloxy)benzamide (1q).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.2876 g, 5.1 mmol, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (br, 1H), 7.78 (s, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 1.35 (s, 9H).



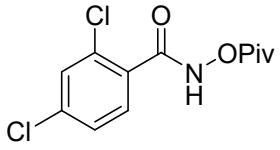
3-Bromo-*N*-(pivaloyloxy)benzamide (1r).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 2.3200 g, 10 mmol, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (br, 1H), 7.96 (s, 1H), 7.74-7.68 (m, 2H), 7.36-7.32 (m, 1H), 1.36 (s, 9H).



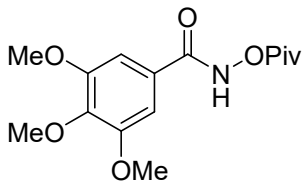
2-Fluoro-*N*-(pivaloyloxy)benzamide (1s).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.2582 g, 5.4 mmol, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (br, 1H), 8.12-8.08 (m, 1H), 7.57-7.52 (m, 1H), 7.33-7.29 (m, 1H), 7.20-7.15 (m, 1H), 1.38 (s, 9H).



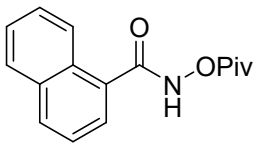
2-Chloro-*N*-(pivaloyloxy)benzamide (1t).[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.9392 g, 7.4 mmol, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ9.85 (br, 1H), 7.73 (s, 1H), 7.44 (s, 2H), 7.35 (s, 1H), 1.36 (s, 9H).



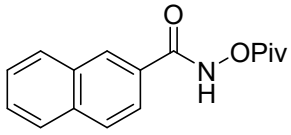
2,4-Dichloro-*N*-(pivaloyloxy)benzamide (1u).[2] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.7408 g, 6.0 mmol, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (br, 1H), 7.67 (s, 1H), 7.46 (s, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 1.34 (s, 9H).



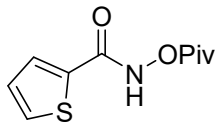
3,4,5-trimethoxy-*N*-(pivaloyloxy)benzamide (1v). White solid was obtained by silica gel column chromatography with PE/EA (8:1). 0.8547 g, 2.75 mmol, 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.55 (br, 1H), 7.05 (s, 2H), 3.89 (s, 9H), 1.37 (s, 9H).



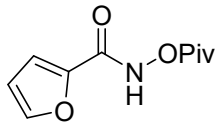
***N*-(pivaloyloxy)-1-naphthamide (1w).**[2] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.8701 g, 6.9 mmol, 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (br, 1H), 8.36 (d, *J* = 7.2 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.1 Hz, 1H), 7.76 (d, *J* = 5.8 Hz, 1H), 7.69-7.52 (m, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 1.38 (s, 9H).



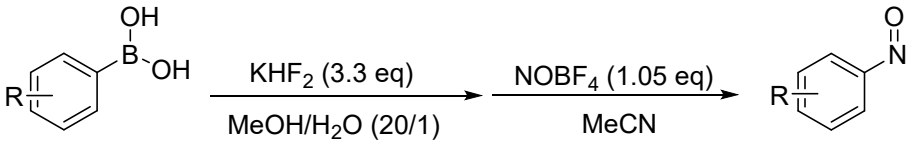
***N*-(pivaloyloxy)-2-naphthamide (1x).**[2] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.9783 g, 7.3 mmol, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (br, 1H), 8.37 (s, 1H), 8.04-7.72 (m, 4H), 7.69-7.46 (m, 2H), 1.38 (s, 9H).



***N*-(pivaloyloxy)thiophene-2-carboxamide (1y).**[2] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.1179 g, 4.9 mmol, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (br, 1H), 7.91-7.61 (m, 1H), 7.64-7.40 (m, 1H), 7.12-7.10 (m, 1H), 1.36 (s, 9H).

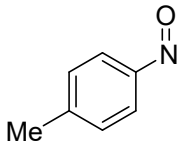


***N*-(pivaloyloxy)furan-2-carboxamide (1z).**[1] White solid was obtained by silica gel column chromatography with PE/EA (8:1). 1.3101 g, 6.2 mmol, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (br, 1H), 7.50 (s, 1H), 7.23 (d, J = 3.2 Hz, 1H), 6.55 (d, J = 1.6 Hz, 1H), 1.36 (s, 9H).

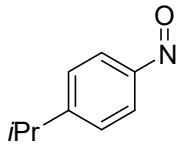


General procedures for the synthesis of nitrosobenzene. According to a previously reported method,[4] a 50 mL round bottom flask was charged with boronic acid (2 mmol, 1 eq) and MeOH (enough MeOH to give a free-flowing) under N_2, added dropwisely with KHF_2 (6.6 M in H_2O, 3.3 equiv) at 0 °C. Then the reaction was stirred at rt for 30 min, concentrated, and dissolved in a minimal amount of acetone (10 mL). The addition of Et_2O (60 mL) led to the precipitation of the white solid. After filtration, crude organotriflfluoroborates was obtained. Then a 50 mL round bottom flask was charged with crude organotriflfluoroborate (2 mmol) in CH_3CN (6 mL), added with $NOBF_4$ (2.1 mmol, 1.05 equiv.) in one portion. The reaction was stirred open to air at room temperature until the reaction mixture became homogeneous, added with H_2O (40 mL) and CH_2Cl_2 (20 mL). The resulted solution was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were combined and dried over Na_2SO_4, fifiltered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA) (20:1) to give the desired product nitrosobenzene **2**.

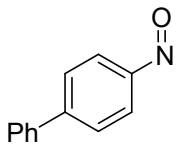
[4] G. Molander, L. Cavalcanti, *J. Org. Chem*., 2012, **77**, 4402-4413.



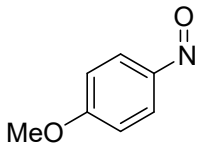
1-Methyl-4-nitrosobenzene (2b).[4] Green oil was obtained by silica gel column chromatography with PE/EA (10:1). 0.2033 g, 1.68 mmol, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H).



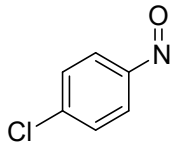
1-Isopropyl-4-nitrosobenzene (2c).[4] Green oil was obtained by silica gel column chromatography with PE/EA (10:1). 0.2525 g, 1.56 mmol, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 3.25-2.75 (m, 1H), 1.31 (d, *J* = 8.9 Hz, 6H).



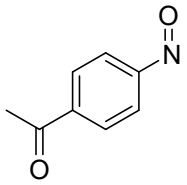
4-Nitroso-1,1'-biphenyl (2d).[4] Green solid was obtained by silica gel column chromatography with PE/EA (10:1). 0.3001 g, 1.84 mmol, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.56-7.51 (m, 2H), 7.49-7.47 (m, 1H).



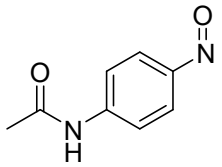
1-Methoxy-4-nitrosobenzene (2e).[4] Green oil was obtained by silica gel column chromatography with PE/EA (10:1). 0.2033 g, 1.68 mmol, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 3H).



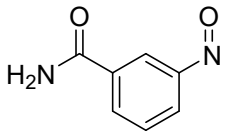
1-Chloro-4-nitrosobenzene (2f).[4] Yellow solid was obtained by silica gel column chromatography with PE/EA (10:1). 0.2452 g, 1.74 mmol, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H).



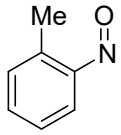
1-(4-nitrosophenyl)ethan-1-one (2g).[4] Yellow solid was obtained by silica gel column chromatography with PE/EA (10:1). 0.2712 g, 1.82 mmol, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 6.8 Hz, 2H), 7.97 (d, *J* = 6.8 Hz, 2H), 2.70 (s, 3H).



***N*-(4-nitrosophenyl)acetamide (2h).**[4] Green solid was obtained by silica gel column chromatography with PE/EA (4:1). 0.2657 g, 1.62 mmol, 81% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.66 (br, 1H), 7.95-7.89 (m, 4H), 2.15 (s, 3H).

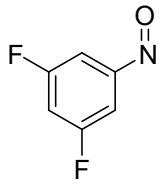


3-Nitrosobenzamide (2i).[4] Green solid was obtained by silica gel column chromatography with PE/EA (4:1). 0.2160 g, 1.44 mmol, 72% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.47 (br, 1H), 8.36 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.72 (br, 1H).



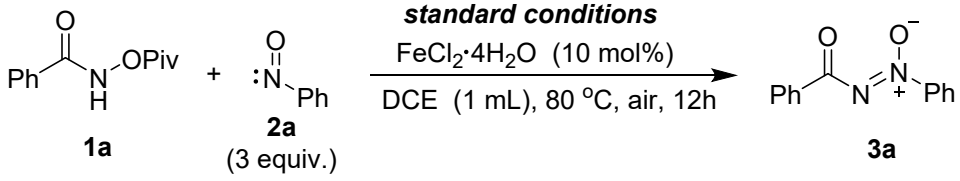
1-Methoxy-2-nitrosobenzene (2j).[4] Green oil was obtained by silica gel column chromatography with PE/EA (20:1). 0.1810 g, 1.5 mmol, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.58 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.17-7.14 (m, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 3.35 (s, 3H).

1-Bromo-2-nitrosobenzene (2k).[4] Green solid was obtained by silica gel column chromatography with PE/EA (20:1). 0.3275 g, 1.78 mmol, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.58-7.54 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H).

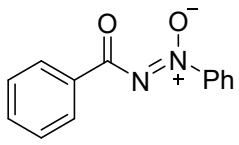


2,4-Difluoro-1-nitrosobenzene (2l).[4] Green solid was obtained by silica gel column chromatography with PE/EA (20:1). 0.2574 g, 1.8 mmol, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 4.0 Hz, 2H), 7.22-7.19 (m, 1H).

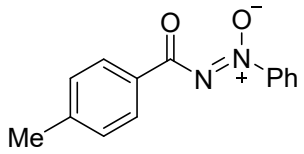
III. Iron-Catalyzed Nitrene Transfer Reaction of Nitrosobenzenes with N-Acyloxyamides for Accessing N-Acyl Azoxy Molecules



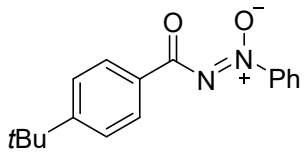
General Procedures for Iron-Catalyzed Nitrene Transfer Reaction of Nitrosobenzene with *N*-Acyloxyamides: To a 10 mL Schlenk flask under air atmosphere, **1a** (0.20 mmol), **2a** (0.60 mmol), $FeCl_2{\cdot}4H_2O$ (0.02 mmol, 10 mol%), 1,2-dichloroethane (1 mL) were added in sequence. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure and concentrated and purified by silica gel PE/EA (10:1) flash column chromatography to give the desired product **3**.



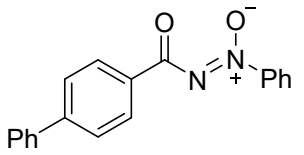
(*Z*)-2-benzoyl-1-phenyldiazene 1-oxide (3a). Prepared according to the general procedure using 0.0443 g (0.2 mmol) of **1a**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0402 g (0.18 mmol, 89% yield) of **3a** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 146.4, 134.5, 133.4, 131.2, 129.5, 129.2, 129.1, 122.6.



(*Z*)-2-(4-methylbenzoyl)-1-phenyldiazene 1-oxide (3b). Prepared according to the general procedure using 0.0470 g (0.2 mmol) of **1b**, 0.0639 g (0.60 mmol) of **2a**, 0.0039 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0307 g (0.13 mmol, 64% yield) of **3b** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.68-7.64 (m, 1H), 7.57-7.53 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 146.5, 145.7, 133.3, 129.8, 129.6, 129.2, 128.5, 122.6, 21.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}N_2O_2$ 241.0972, Found 241.0970.

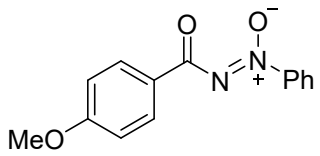


(*Z*)-2-(4-(tert-butyl)benzoyl)-1-phenyldiazene 1-oxide (3c). Prepared according to the general procedure using 0.0554 g (0.2 mmol) of **1c**, 0.0640 g (0.60 mmol) of **2a**, 0.0037 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0372 g (0.12 mmol, 66% yield) of **3c** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.57-7.53 (m, 1H), 7.53-7.51 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 158.6, 146.4, 133.3, 129.5, 129.2, 128.4, 126.1, 122.6, 35.4, 31.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}N_2O_2$ 283.1442, Found 283.1440.

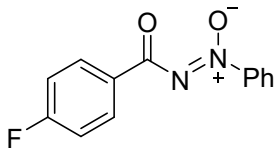


(*Z*)-2-([1,1'-biphenyl]-4-carbonyl)-1-phenyldiazene 1-oxide (3d). Prepared according to the general procedure using 0.0594 g (0.2 mmol) of **1d**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was

purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0327 g (0.11 mmol, 54% yield) of **3d** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.5 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.68-7.65 (m, 1H), 7.61 (m, 2H), 7.60-7.57 (m, 2H), 7.52-7.43 (m, 1H), 7.42-7.39 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 147.3, 146.5, 139.7, 133.4, 130.1, 129.9, 129.2, 129.1, 128.5, 127.7, 127.4, 122.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}N_2O_2$ 303.1129, Found 303.1133.

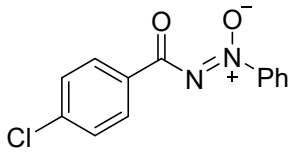


(*Z*)-2-(4-methoxybenzoyl)-1-phenyldiazene 1-oxide (3e). Prepared according to the general procedure using 0.0502 g (0.2 mmol) of **1e**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (5:1) as the eluent to give 0.0327 g (0.17 mmol, 64% yield) of **3e** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.6 Hz, 2H), 7.95 (d, *J* = 9.0 Hz, 2H), 7.82-7.60 (m, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 164.7, 146.5, 133.2, 131.9, 129.2, 123.8, 122.6, 114.4, 55.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{12}N_2NaO_3$ 279.0741, Found 279.0746.

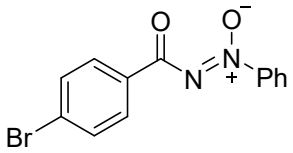


(Z)-2-(4-fluorobenzoyl)-1-phenyldiazene 1-oxide (3f). Prepared according to the general procedure using 0.0478 g (0.2 mmol) of **1f**, 0.0642 g (0.60 mmol) of **2a**, 0.0039 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0405 g (0.17 mmol, 83% yield) of **3f** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 2H), 8.03-8.01 (m, 2H), 7.69-7.66 (m, 1H), 7.58-7.55 (m, 2H), 7.15-7.18 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 167.6, 165.6, 146.4, 133.5, 132.3 (d, *J* = 9.7 Hz), 129.0, 127.7, 122.6, 116.4, (d, *J* = 22.4 Hz).

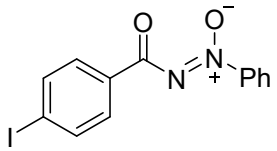
^{19}F NMR (471 MHz, $CDCl_3$) δ -102.24. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}FN_2O_2$ 245.0721, Found 245.0721.



(Z)-2-(4-chlorobenzoyl)-1-phenyldiazene 1-oxide (3g). Prepared according to the general procedure using 0.0521 g (0.2 mmol) of **1g**, 0.0643 g (0.60 mmol) of **2a**, 0.0038 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0395 g (0.15 mmol, 76% yield) of **3g** as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.69-7.66 (m, 1H), 7.57-7.54 (m, 2H), 7.46 (d, J = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 146.4, 141.1, 133.5, 130.8, 129.8, 129.3, 122.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}ClN_2O_2$ 261.0426, Found 261.0421.

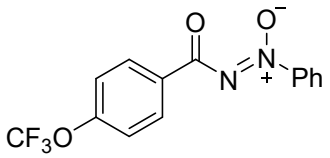


(Z)-2-(4-bromobenzoyl)-1-phenyldiazene 1-oxide (3h). Prepared according to the general procedure using 0.0600 g (0.2 mmol) of **1h**, 0.0645 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0387 g (0.128 mmol, 64% yield) of **3h** as a yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.69-7.66 (m, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.58-7.55 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 146.4, 133.6 132.4, 130.9, 130.2, 129.9, 129.3, 122.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_9BrN_2NaO_2$ 326.9740, Found 326.9741.

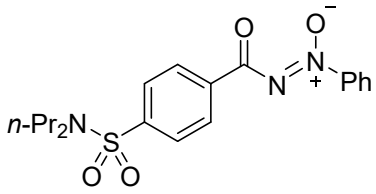


(Z)-2-(4-iodobenzoyl)-1-phenyldiazene 1-oxide (3i). Prepared according to the general procedure using 0.0769 g (0.2 mmol) of **1i**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$

and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0395 g (0.11 mmol, 56% yield) of **3i** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.74-7.71 (m, 3H), 7.62-7.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 146.4, 138.4, 133.6, 130.7, 130.4, 129.2, 124.9, 122.6, 115.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}IN_2O_2$ 352.9782, Found 352.9788.

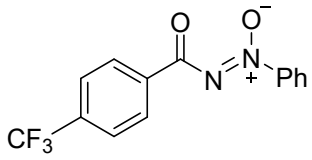


(*Z*)-1-phenyl-2-(4-(trifluoromethoxy)benzoyl)diazene 1-oxide (3j). Prepared according to the general procedure using 0.0478 g (0.2 mmol) of **1j**, 0.0641 g (0.60 mmol) of **2a**, 0.0041 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0256 g (0.08 mmol, 41% yield) of **3j** as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.6 Hz, 2H), 7.70-7.67 (m, 1H), 7.59-7.56 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 153.6, 146.4, 133.5, 131.6, 129.6, 129.3, 122.6, 120.7 (q, *J* = 46.1 Hz). HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_9F_3N_2NaO_3$ 333.00458, Found 333.0461.

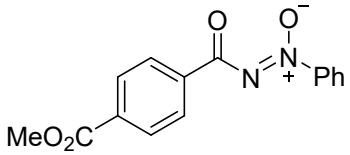


(Z)-2-(4-(*N, N*-dipropylsulfamoyl) benzoyl)-1-phenyldiazene 1-oxide (3k). Prepared according to the general procedure using 0.0769 g (0.2 mmol) of **1k**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0326 g (0.20 mmol, 42% yield) of **3k** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.0 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 8.02-7.84 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.60-7.56 (m, 2H), 3.10 (t, *J* = 6.8 Hz, 4H), 1.56 (dd, *J* = 13.6, 7.2 Hz, 4H), 0.87 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (101 MHz,

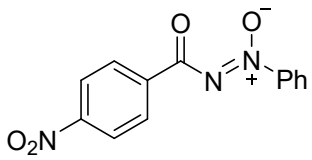
$CDCl_3$) δ 175.9, 146.4, 145.4, 134.1, 130.1, 129.4, 127.6, 122.6, 50.1, 22.0, 11.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}N_3O_4S$ 390.1483, Found 390.1484.



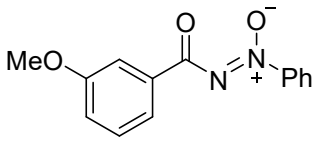
(Z)-1-phenyl-2-(4-(trifluoromethyl)benzoyl)diazene 1-oxide (3l). Prepared according to the general procedure using 0.0579 g (0.2 mmol) of **1l**, 0.0642 g (0.60 mmol) of **2a**, 0.0039 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0329 g (0.11 mmol, 56% yield) of **3l** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.71-7.68 (m, 2H), 7.59-7.55 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 146.3, 135.7, 135.6 (q, J = 32.8 Hz), 134.4, 133.7, 129.8, 129.3, 126.1 (q, J = 32.8 Hz), 124.5 (q, J = 32.8 Hz), 122.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_9F_3N_2NaO_2$ 317.0509, Found 317.0511.



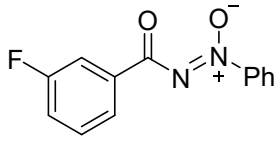
(Z)-2-(4-(methoxycarbonyl)benzoyl)-1-phenyldiazene 1-oxide (3m). Prepared according to the general procedure using 0.0533 g (0.2 mmol) of **1m**, 0.0640 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (5:1) as the eluent to give 0.0328 g (0.15mmol, 75% yield) of **3m** as a yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.18 (d, J = 7.8 Hz, 2H), 8.02-7.97 (m, 4H), 7.71-7.69 (m, 1H), 7.60-7.57 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 177.2, 165.8, 146.1, 135.3, 134.6, 134.2, 130.6, 130.3, 130.0, 122.9, 53.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}N_2NaO_4$ 307.0690, Found 307.0694.



(Z)-2-(4-nitrobenzoyl)-1-phenyldiazene 1-oxide (3n). Prepared according to the general procedure using 0.0533 g (0.2 mmol) of **1n**, 0.0643 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0238 g (0.88 mmol, 44% yield) of **3n** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.30 (m, 4H), 8.17 (d, J = 8.6 Hz, 2H), 7.73-7.70 (m, 1H), 7.61-7.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 151.1, 146.3, 136.5, 134.0, 130.5, 129.4, 124.2, 122.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}IN_3O_4$ 272.0666, Found 272.0666.

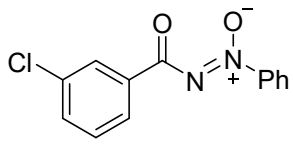


(Z)-2-(3-methoxybenzoyl)-1-phenyldiazene 1-oxide (3o). Prepared according to the general procedure using 0.0769 g (0.2 mmol) of **1o**, 0.0639 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0357 g (0.13 mmol, 64%) of **3o** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.0 Hz, 2H), 7.68-7.64 (m, 1H), 7.57-7.52 (m, 4H), 7.40-7.36 (m, 1H), 7.23-7.09 (m, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 160.1, 146.4, 133.4, 132.5, 130.1, 129.2, 122.6, 122.0, 121.2, 113.6, 55.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{12}N_2NaO_3$ 279.0741, Found 279.0744.

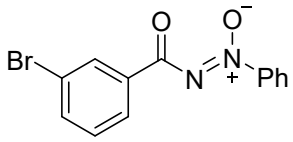


(Z)-2-(3-fluorobenzoyl)-1-phenyldiazene 1-oxide (3p). Prepared according to the general procedure using 0.0479 g (0.2 mmol) of **1p**, 0.0642 g (0.60 mmol) of **2a**, 0.0041 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0201 g (0.08 mmol, 41% yield) of **3p** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.0 Hz, 1H), 8.12 (s, 1H),

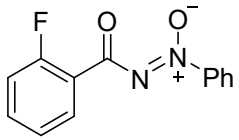
7.91 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.70-7.67 (m, 1H), 7.58-7.55 (m, 1H), 7.39-7.36 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 164.1, 161.7, 146.4, 133.6, 130.7 (d, J = 7.7 Hz), 129.3, 125.3 (d, J = 2.9 Hz), 122.6, 121.6 (d, J = 23.0 Hz), 116.2 (d, J = 23.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.12. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}FN_2O_2$ 245.0721, Found 245.0724.



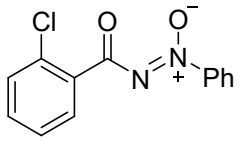
(Z)-2-(3-chlorobenzoyl)-1-phenyldiazene 1-oxide (3q). Prepared according to the general procedure using 0.0521 g (0.2 mmol) of **1q**, 0.0644 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0390 g (0.15 mmol, 75% yield) of **3q** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 7.6 Hz, 2H), 7.96 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.70-7.66 (m, 1H), 7.60-7.56 (m, 3H), 7.45-7.41 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 146.4, 135.3, 134.4, 133.6, 133.1, 130.3, 129.4, 129.3, 127.5, 122.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}ClN_2O_2$ 261.0426, Found 261.0418.



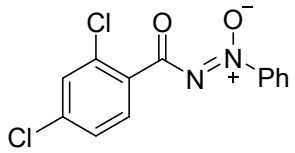
(Z)-2-(3-bromobenzoyl)-1-phenyldiazene 1-oxide (3r). Prepared according to the general procedure using 0.0600 g (0.2 mmol) of **1r**, 0.0642 g (0.60 mmol) of **2a**, 0.0038 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0390 g (0.13 mmol, 64% yield) of **3r** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.0 Hz, 2H), 8.12 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.70-7.67 (m, 1H), 7.59- 7.55 (m, 2H), 7.39-7.35 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 148.0, 134.8, 134.5, 132.0, 130.8, 129.9, 129.1, 128.4, 125.4, 114.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_9BrN_2NaO_2$ 327.9740, Found 327.9734.



(Z)-2-(2-fluorobenzoyl)-1-phenyldiazene 1-oxide (3s). Prepared according to the general procedure using 0.0480 g (0.2 mmol) of **1s**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0317 g (0.13 mmol, 65% yield) of **3s** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.74-7.64 (m, 2H), 7.60-7.56 (m, 2H), 7.53-7.43 (m, 2H), 7.34 (d, J = 8.0, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 164.1, 161.7, 146.4, 133.5 (m), 130.8, 129.3, 125.2, 122.6, 121.7 (d, J = 7.7 Hz), 116.2 (d, J = 7.7 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.04. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_9FN_2NaO_2$ 267.0541, Found 267.0549.

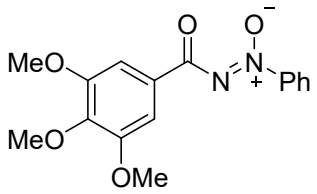


(Z)-2-(2-chlorobenzoyl)-1-phenyldiazene 1-oxide (3t). Prepared according to the general procedure using 0.0521 g (0.2 mmol) of **1t**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0369 g (0.14 mmol, 71% yield) of **3t** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 7.67-7.64 (m, 1H), 7.56-7.53 (m, 2H), 7.50-7.43 (m, 2H), 7.40-7.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 146.3, 133.9, 133.4, 132.1, 131.3, 129.2, 127.1, 122.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}ClN_2O_2$ 261.0426, Found 261.0428.

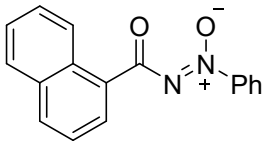


(Z)-2-(2,4-dichlorobenzoyl)-1-phenyldiazene 1-oxide (3u). Prepared according to the general procedure using 0.0578 g (0.2 mmol) of **1u**, 0.0642 g (0.60 mmol) of **2a**, 0.0039 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with

EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0417 g (0.14 mmol, 71% yield) of **3u** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.69-7.65 (m, 1H), 7.56-7.53 (m, 2H), 7.49 (s, 1H), 7.37 (d, J = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 146.2, 139.9, 134.9, 133.6, 133.0, 131.2, 129.7, 129.2, 127.6, 122.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_8Cl_2N_2NaO_2$ 316.9856, Found 316.9849.

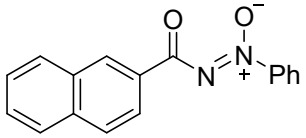


(Z)-1-phenyl-2-(3,4,5-trimethoxybenzoyl)diazene 1-oxide (3v). Prepared according to the general procedure using 0.0543 g (0.2 mmol) of **1v**, 0.0641 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0300 g (0.09 mmol, 47% yield) of **3v** as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 7.1 Hz, 2H), 7.68 (s, 1H), 7.58 (d, J = 6.7 Hz, 2H), 7.26 (s, 2H), 3.94 (s, 2H), 3.91 (s, 3H), 3.89 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.7, 153.5, 146.5, 144.0, 133.4, 129.3, 126.3, 122.6, 106.9, 61.0, 56.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_8Cl_2N_2NaO_2$ 339.0952, Found 339.0949.

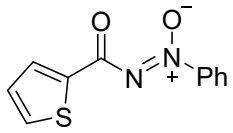


(Z)-2-(1-naphthoyl)-1-phenyldiazene 1-oxide (3w). Prepared according to the general procedure using 0.0543 g (0.2 mmol) of **1w**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0159 g (0.06 mmol, 29% yield) of **3w** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 8.4 Hz, 2H), 8.10-8.07 (m, 2H), 7.92 (d, J = 8.4 Hz, 1H), 7.73-7.70 (m, 1H), 7.68-7.64 (m, 1H), 7.63-7.58 (m, 1H), 7.57-7.53 (m, 2H), 7.49-7.46 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 146.3, 135.3,

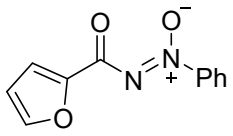
134.0, 133.3, 131.3, 130.9, 129.2, 128.9, 128.8, 127.9, 126.9, 125.8, 124.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{17}H_{13}N_2O_2$ 277.0972, Found 277.0966.



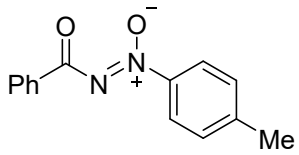
(Z)-2-(2-naphthoyl)-1-phenyldiazene 1-oxide (3x). Prepared according to the general procedure using 0.0543 g (0.2 mmol) of **1x**, 0.0639 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2.4H_2O$ and 1 mL of DCE. After stirring at 80 ^{o}C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0308 g (0.12 mmol) of **3x** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.35 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.70-7.67 (m, 1H), 7.65 -7.50 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 146.5, 136.3, 133.4, 132.5, 131.7, 129.8, 129.3, 129.2, 1291, 128.6, 128.0, 127.1, 124.4, 122.7. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{17}H_{13}N_2O_2$ 277.0972, Found 277.0978.



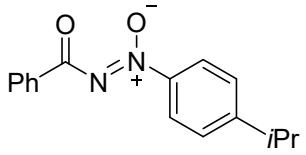
(Z)-1-phenyl-2-(thiophene-2-carbonyl)diazene 1-oxide (3y). Prepared according to the general procedure using 0.0455 g (0.2 mmol) of **1y**, 0.0644 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 ^{o}C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0343 g (0.15 mmol, 74% yield) of **3y** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69-7.65 (m, 1H), 7.57-7.53 (m, 2H), 7.5 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 146.7, 136.6, 135.4, 134.6, 133.5, 129.2, 128.6, 122.7. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{11}H_9N_2O_2S$ 233.0380, Found 233.0380.



(Z)-2-(furan-2-carbonyl)-1-phenyldiazene 1-oxide (3z). Prepared according to the general procedure using 0.0423 g (0.2 mmol) of **1z**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0341 g (0.20 mmol, 79% yield) of **3z** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 2H), 7.66 (s, 2H), 7.57-7.54 (m, 2H), 7.34 (s, 1H), 7.27 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 148.1, 146.9, 146.6, 133.5, 129.2, 122.7, 120.6, 112.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_9N_2O_3$ 217.0608, Found 217.0609.

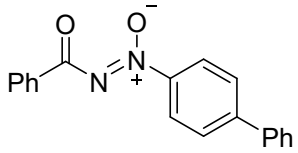


(Z)-2-benzoyl-1-(p-tolyl) diazene 1-oxide (3aa). Prepared according to the general procedure using 0.0443 g (0.2 mmol) of **1a**, 0.0727 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0333 g (0.14 mmol, 69% yield) of **3aa** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 2H), 8.10-7.88 (m, 2H), 7.64-7.61 (m, 1H), 7.50-7.47 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6, 144.4, 134.4, 131.4, 129.7, 129.5, 129.0, 122.5, 21.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{12}N_2NaO_2$ 263.0791, Found 263.0789.

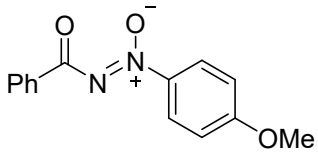


(Z)-2-benzoyl-1-(4-isopropylphenyl) diazene 1-oxide (3ab). Prepared according to the general procedure using 0.0442 g (0.2 mmol) of **1a**, 0.0896 g (0.60 mmol) of **2b**, 0.0040 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0343 g (0.13 mmol, 64% yield) of **3ab** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* =

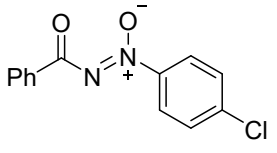
8.0 Hz, 1H), 7.64-7.61 (m, 1H), 7.50-7.47 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 3.04 (dt, *J* = 13.7, 6.8 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 155.1, 134.4, 131.4, 129.5, 128.9, 127.2, 122.7, 34.2, 23.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}N_2NaO_2$ 291.1104, Found 291.1099.



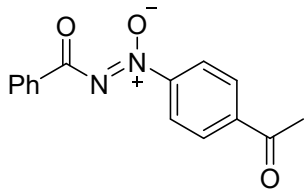
(Z)-1-([1,1'-biphenyl]-4-yl)-2-benzoyldiazene 1-oxide (3ac). Prepared according to the general procedure using 0.0442 g (0.2 mmol) of **1a**, 0.1086 g (0.60 mmol) of **2c**, 0.0040 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0336 g (0.20 mmol, 55% yield) of **3ac** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.6 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.65-7.61 (m, 3H), 7.51-7.48 (m, 4H), 7.45-7.41 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.5, 146.4, 145.4, 139.1, 134.5, 131.3, 129.5, 129.1, 129.0, 128.7, 127.7, 127.4, 123.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}N_2O_2$ 303.1129, Found 303.1136.



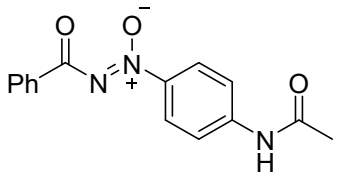
(Z)-2-benzoyl-1-(4-methoxyphenyl) diazene 1-oxide (3ad). Prepared according to the general procedure using 0.0442 g (0.2 mmol) of **1a**, 0.0822 g (0.60 mmol) of **2d**, 0.0040 g (0.02 mmol) of $FeCl_2·4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (5:1) as the eluent to give 0.0390 g (0.20 mmol, 76% yield) of **3ad** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.2 Hz, 2H), 7.99 (d, *J* = 7.4 Hz, 2H), 7.62-7.58 (m, 1H), 7.51-7.47 (m, 2H), 6.99 (d, *J* = 9.2 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 163.7, 139.6, 134.4, 131.5, 129.5, 129.0, 124.6, 114.0, 55.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2O_3$ 257.0921, Found 257.0924.



(Z)-2-benzoyl-1-(4-chlorophenyl) diazene 1-oxide (3ae). Prepared according to the general procedure using 0.0443 g (0.2 mmol) of **1a**, 0.0848 g (0.60 mmol) of **2e**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0370 g (0.20 mmol, 71% yield) of **3ae** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9.6, 2.3 Hz, 2H), 8.13-7.84 (m, 2H), 7.66-7.62 (m, 1H), 7.57-7.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 144.8, 139.9, 134.7, 131.1, 129.5, 129.4, 129.1, 124.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_9ClN_2NaO_2$ 283.0245, Found 283.0244.

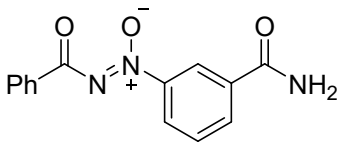


(Z)-1-(4-acetylphenyl)-2-benzoyldiazene 1-oxide (3af). Prepared according to the general procedure using 0.0444 g (0.2 mmol) of **1a**, 0.0896 g (0.60 mmol) of **2f**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (5:1) as the eluent to give 0.0407 g (0.20 mmol, 76% yield) of **3af** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.66-7.63 (m, 1H), 7.52-7.49 (m, 2H), 2.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 177.0, 149.0, 140.6, 134.7, 132.8, 129.5, 129.2, 129.1, 122.9, 26.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}N_2NaO_3$ 291.0741, Found 291.0739.

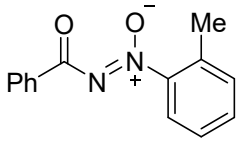


(Z)-1-(4-acetamidophenyl)-2-benzoyldiazene 1-oxide (3ag). Prepared according to the general procedure using 0.0442 g (0.2 mmol) of **1a**, 0.0984 g (0.60 mmol) of **2g**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (3:1) as the eluent to give 0.0442 g (0.20 mmol 78%

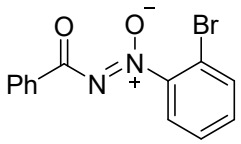
yield) of **3ag** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.1 Hz, 2H), 7.98 (d, *J* = 7.4 Hz, 2H), 7.85 (br, 1H), 7.70 (d, *J* = 9.1 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.51-7.46 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 169.4, 135.5, 133.4, 132.2, 132.0, 129.3, 128.6, 128.1, 127.4, 41.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{13}N_3NaO_3$ 306.0850, Found 306.0849.



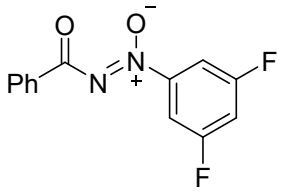
(Z)-2-benzoyl-1-(3-carbamoylphenyl)diazene 1-oxide (3ah). Prepared according to the general procedure using 0.0442 g (0.2 mmol) of **1a**, 0.0902 g (0.60 mmol) of **2h**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (2:1) as the eluent to give 0.0420 g (0.20 mmol, 78% yield) of **3ah** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.66-7.62 (m, 2H), 7.51-7.45 (m, 2H), 6.65 (br, 1H), 6.36 (br, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179, 167.6, 146.5, 134.8, 132.4, 130.9, 130.1, 129.8, 129.5, 129.1, 128.4, 125.8, 121.4, 121.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{11}N_3NaO_3$ 292.0693, Found 292.0699.



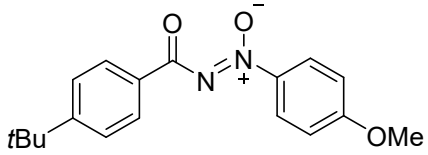
(Z)-2-benzoyl-1-(2-methoxyphenyl)diazene 1-oxide (3ai). Prepared according to the general procedure using 0.0442 g (0.2 mmol) of **1a**, 0.0902 g (0.60 mmol) of **2i**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0389 g (0.16 mmol, 81% yield) of **3ai** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-7.97 (m, 2H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.72-7.60 (m, 1H), 7.53-7.50 (m, 2H), 7.48-7.45 (m, 1H), 7.37-7.35 (m, 2H), 2.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.0, 147.6, 134.5, 132.3, 131.4, 129.5, 129.0, 126.8, 123.8, 19.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2O_2$ 241.0972, Found 241.0974.



(Z)-2-benzoyl-1-(2-bromophenyl)diazene 1-oxide (3aj). Prepared according to the general procedure using 0.0443 g (0.2 mmol) of **1a**, 0.1122 g (0.60 mmol) of **2j**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0515 g (0.20 mmol, 85% yield) of **3aj** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.68-7.66 (m, 1H), 7.51-7.47 (m, 3H), 7.43-7.39 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 148.0, 134.8, 134.5, 132.0, 130.8, 129.9, 129.1, 128.4, 125.4, 114.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_9BrN_2NaO_2$ 326.9740, Found 326.9739.



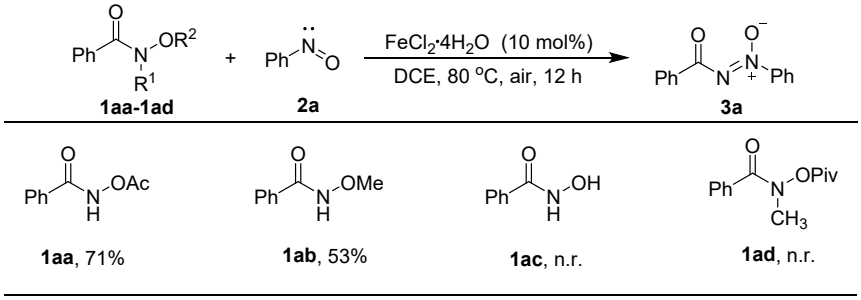
(Z)-2-benzoyl-1-(2,4-difluorophenyl)diazene 1-oxide (3ak). Prepared according to the general procedure using 0.0443 g (0.2 mmol) of **1a**, 0.0858 g (0.60 mmol) of **2k**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0221 g (0.20 mmol, 42% yield) of **3ak** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.57-7.54 (m, 1H), 7.49-7.46 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.61-6.57 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 161.2, 159.5 (d, *J* = 14.5 Hz), 157.5(d, *J* = 14.5 Hz), 135.4 (t, *J* = 13.4 Hz), 129.5, 127.6, 124.2, 122.3, 98.5(d, *J* = 8.0 Hz), 98.4 (d, *J* = 8.0 Hz), 95.0 (t, *J* = 25.6 Hz). HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_8F_2N_2NaO_2$ 285.0447, Found 285.0450.



(Z)-2-(4-(tert-butyl)benzoyl)-1-(4-methoxyphenyl)diazene 1-oxide (3al). Prepared according to the general procedure using 0.0594 g (0.2 mmol) of **1d**, 0.0822 g (0.60 mmol) of **2d**, 0.0040 g (0.02

mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA filtered and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (5:1) as the eluent to give 0.0518 g (0.20 mmol, 83% yield) of **3al** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 158.3, 129.4, 126.0, 124.6, 114.0, 55.8, 35.3, 31.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}N_2O_3$ 313.1547, Found 313.1547.

Substrate scope of *N*-OR amides.



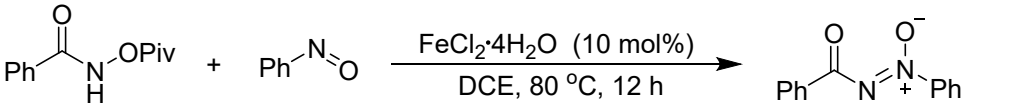
Prepared according to the general procedure using 0.0358 g (0.2 mmol) of **1aa**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, the reaction mixture was diluted with EA, filtered, and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (10:1) as the eluent to give 0.0321 g (0.14 mmol, 71% yield) of **3a** as a yellow oil.

Prepared according to the general procedure using 0.0302 g (0.2 mmol) of **1ab**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h, added with EA (5 mL) to dilute, the reaction mixture was diluted with EA, filtered, and concentrated under reduced pressure. The resulted residue was purified by flash column chromatography on silica gel PE/EA (1:10) as the eluent to give 0.0240 g (0.14 mmol, 53% yield) of **3a** as a yellow oil.

Prepared according to the general procedure using 0.0275 g (0.2 mmol) of **1ac**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h. the reaction was monitored by ^{1}H NMR and no desired product was observed.

Prepared according to the general procedure using 0.0471 g (0.2 mmol) of **1ad**, 0.0642 g (0.60 mmol) of **2a**, 0.0040 g (0.02 mmol) of $FeCl_2{\cdot}4H_2O$ and 1 mL of DCE. After stirring at 80 °C for 12 h. the reaction was monitored by ^1H NMR and no desired product was observed.

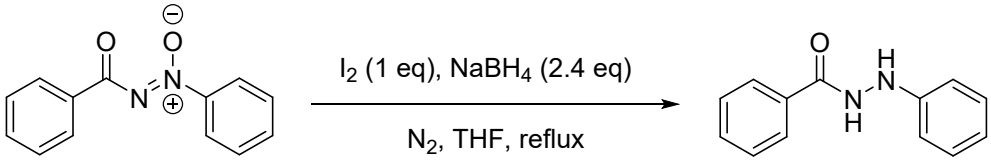
IV. Gram-Scale Reaction.



1a **2a** **3a**, 1.07 g, 79% yield

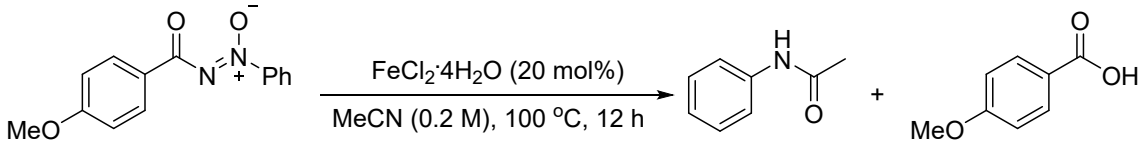
A 25 mL Schlenk flask was charged with 1.33 g (6 mmol) of **1a,** 1.93 g (18 mmol), 0.0120 g $FeCl_2{\cdot}4H_2O$. The reaction mixture was stirred at 80 °C for 12 h, added with EA to dilute, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography using solution PE/EA (10:1) as the eluent to give 1.07 g (4.74 mmol, 79% yield) of **3a** as a yellow oil.

V. Further Derivatizations.



3a **4**

A 10 mL Schlenk flask was charged with 0.0452 (0.20 mmol) of **3a**, 0.0508 g (0.20 mmol) of I_2, 0.0183 g (0.48 mmol) of $NaBH_4$ and (1 mL) THF under nitrogen atmosphere. The reaction mixture was stirred at reflux for 12 h, added with EA to dilute, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography using solution PE/EA (4:1) as the eluent to give 0.0349 g (0.20 mmol, 82% yield) of **4** as a white solid.[5] ^1H NMR (400 MHz, DMSO-d_6) δ 10.36 (s, 1H), 7.93-7.90 (m, 3H), 7.58-7.50 (m, 1H), 7.50 (m, 2H), 7.15-7.13 (m, 2H), 6.80 (d, J = 7.7 Hz, 2H), 6.74-6.70 (m, 1H).

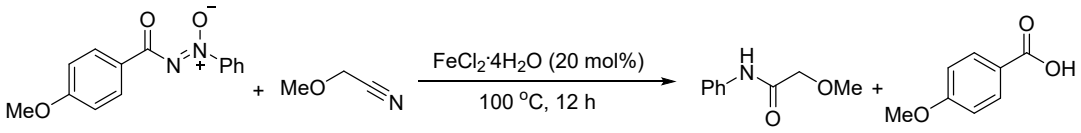


3e **5** **7**

Prepared according to a previously reported procedure,[6] a 10 mL Schlenk flask was charged with

[5] R. Liu, Z. Li, S. Liu, J. Zheng, B. Cheng, R. Yu, H. Geng, *J. Agric. Food Chem*., 2023, **71**, 6803-6817.
[6] Y. Yan, Z. Zhang, Y. Wan, G. Zhang, M. Ma, Q. Liu, *J. Org. Chem*., 2017, **82**, 7957-7963.

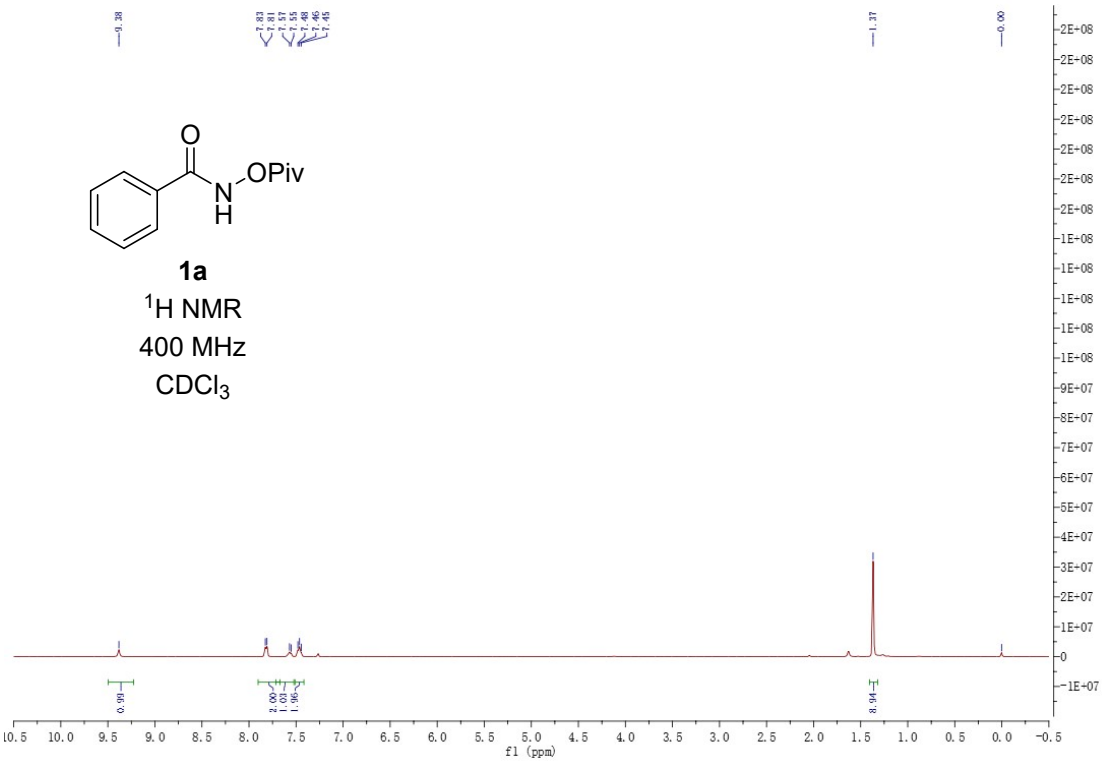
0.0512 g (0.20 mmol) of **3e**, 0.0080 g (0.04 mmol) of $FeCl_2{\cdot}4H_2O$, 1 mL (0.2 M) of MeCN. The reaction mixture was stirred at 100 °C for 12 h, added with EA to dilute, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography using solution PE/EA (2:1) as the eluent to give 0.0154 g (0.20 mmol, 57% yield) of **5** as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.90 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.30-7.26 (m, 2H), 7.04-7.00 (m, 1H), 2.04 (s, 3H).



3e 0.2 M **6** **7**

Prepared according to a previously reported procedure,[6] a 10 mL Schlenk flask was charged with 0.0512 g (0.20 mmol) of **3e**, 0.0080 g (0.04 mmol) of $FeCl_2{\cdot}4H_2O$, 1 mL (0.2 M) of 2-methoxyacetonitrile. The reaction mixture was stirred at 100 °C for 12 h, added with EA (5 mL) to dilute, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography using solution PE/EA (2:1) as the eluent to give 0.0168 g (0.20 mmol, 51% yield) of **6** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (br, 1H), 7.57 (d, *J* = 6.5 Hz, 2H), 7.34 (s, 2H), 7.13 (s, 1H), 4.02 (s, 2H), 3.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 137.1, 129.1, 124.5, 119.8, 72.1, 59.3.

VI. NMR Spectra

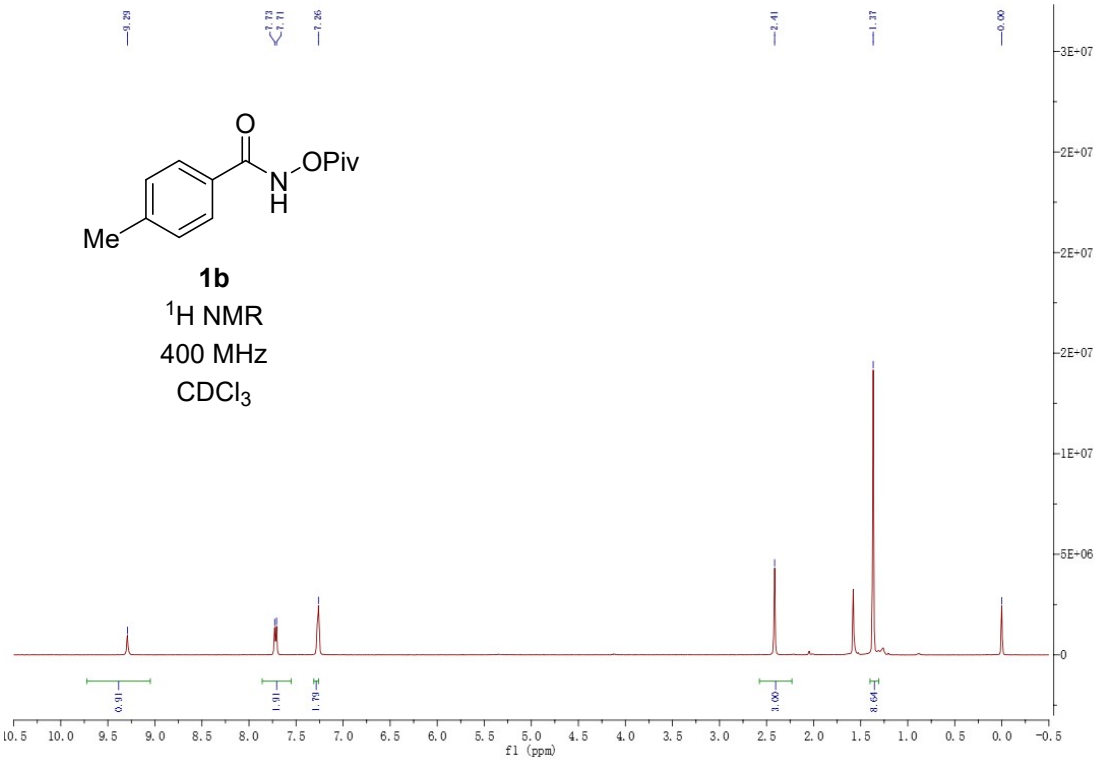


1a

^{1}H NMR

400 MHz

$CDCl_3$

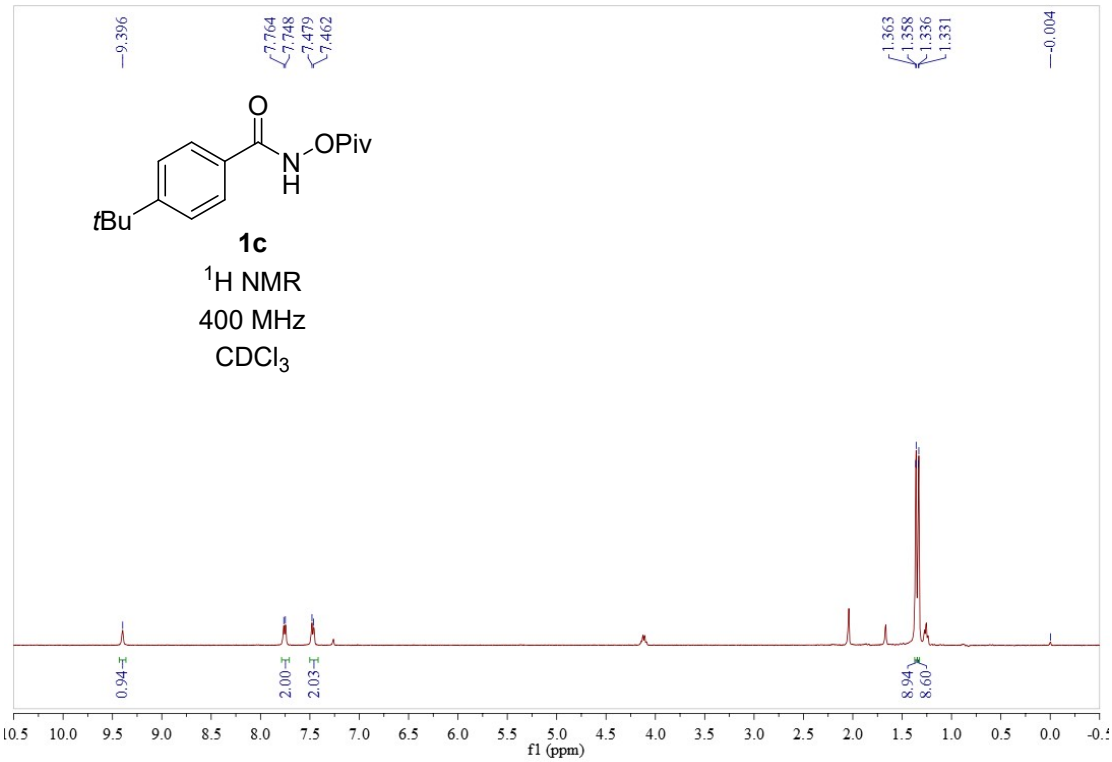


1b

^{1}H NMR

400 MHz

$CDCl_3$

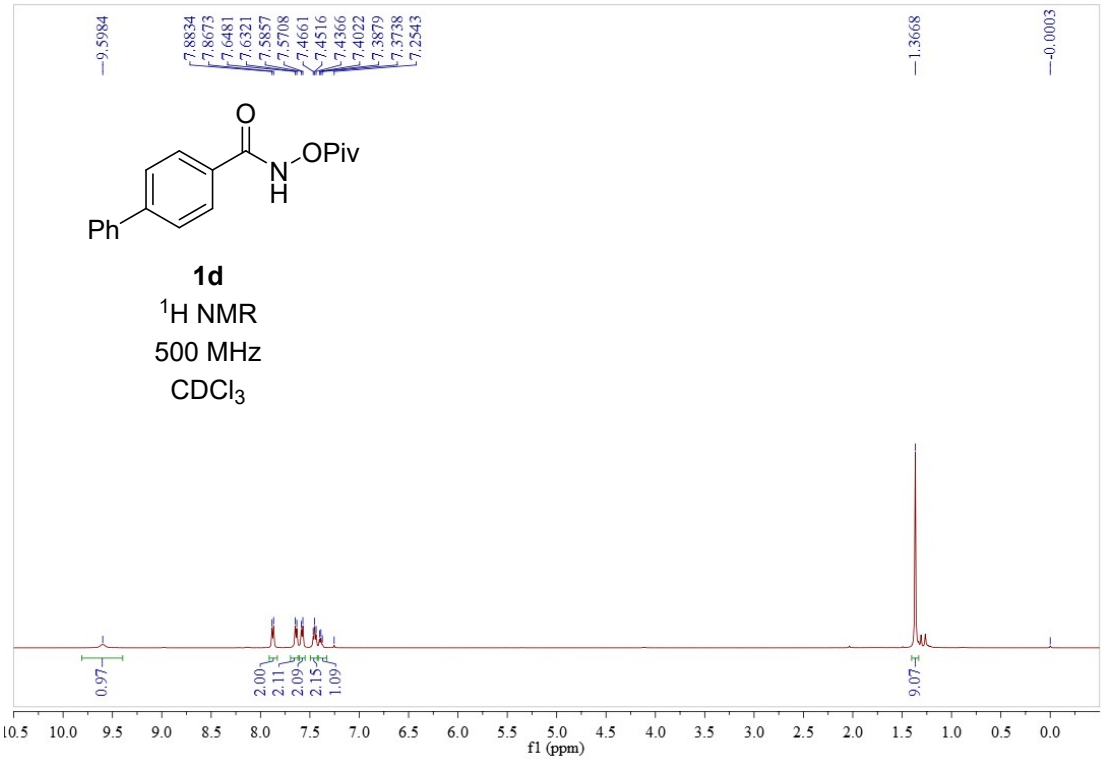


1c

^{1}H NMR

400 MHz

$CDCl_3$

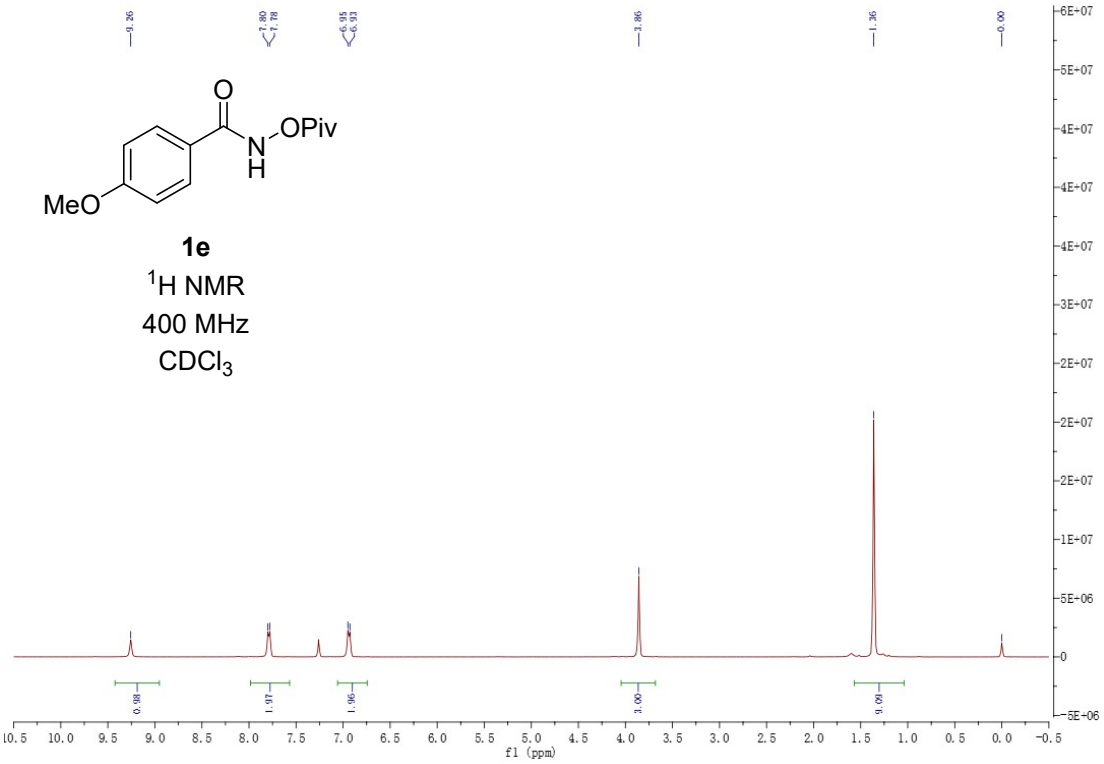


1d

^{1}H NMR

500 MHz

$CDCl_3$

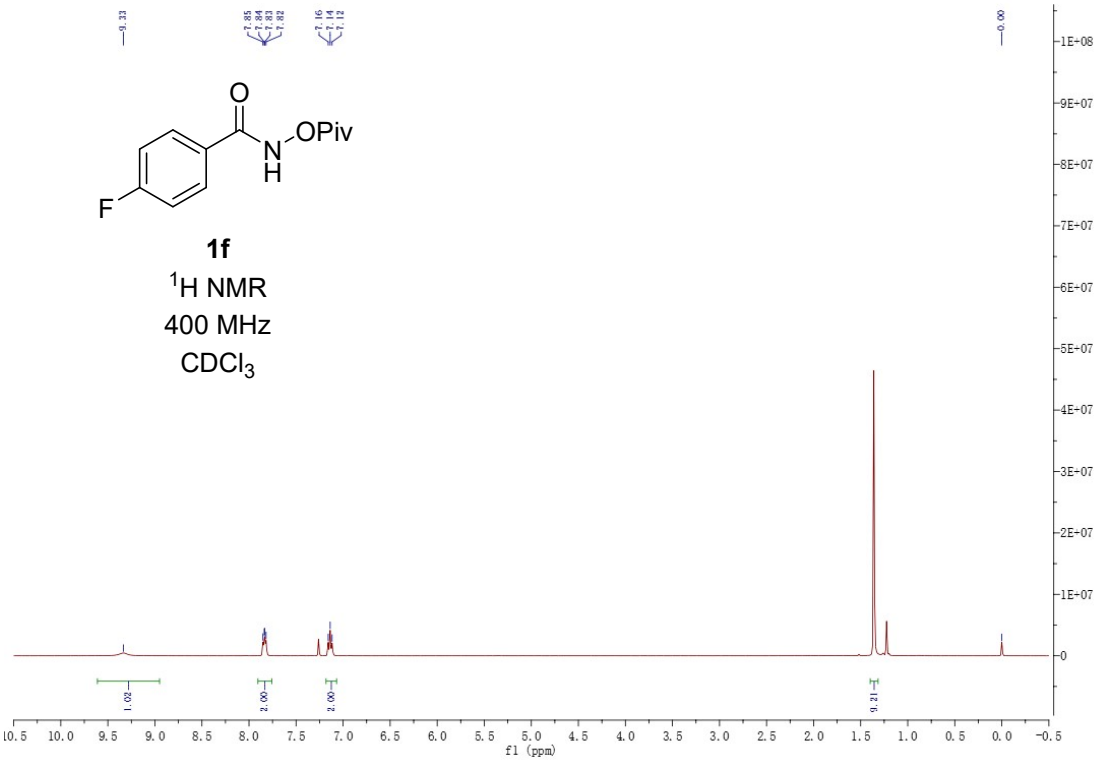


1e

^{1}H NMR

400 MHz

$CDCl_3$

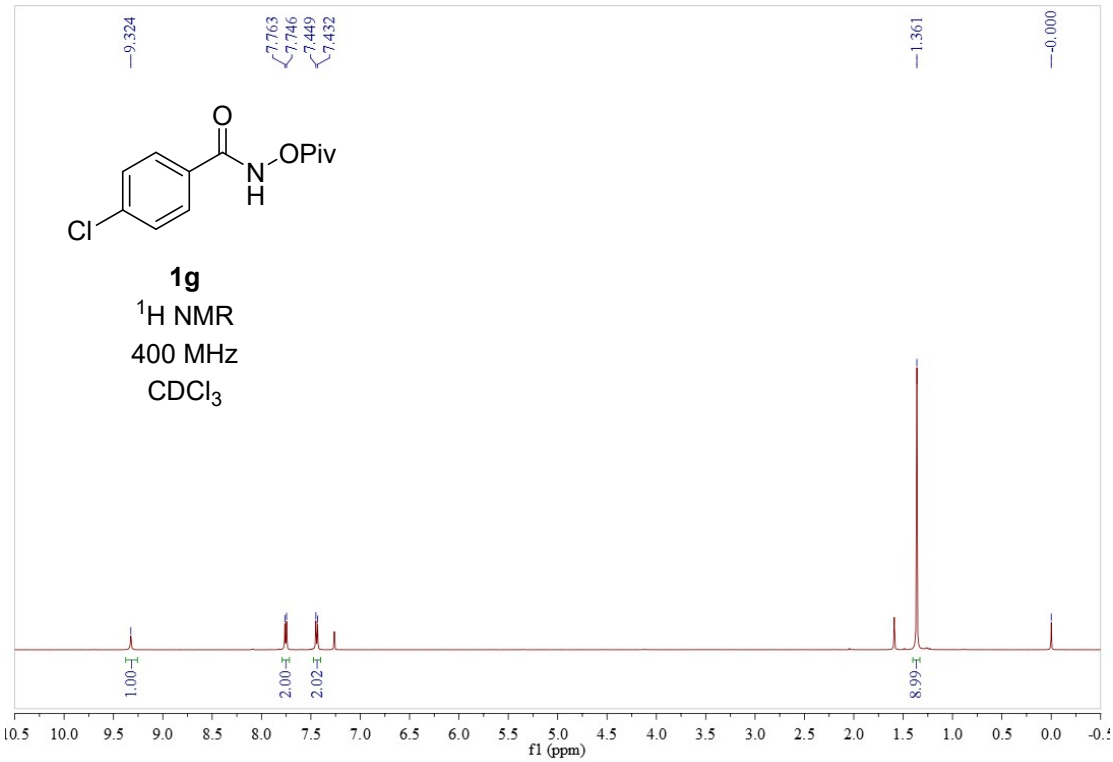


1f

^{1}H NMR

400 MHz

$CDCl_3$

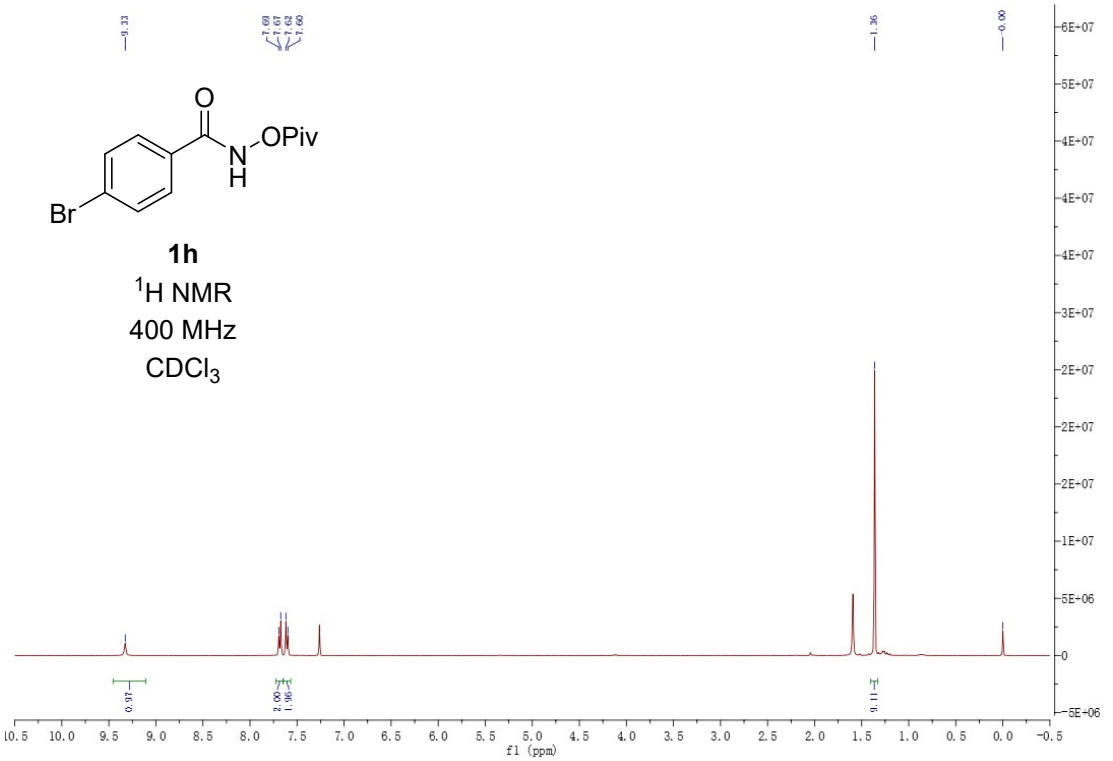


1g

^{1}H NMR

400 MHz

$CDCl_3$

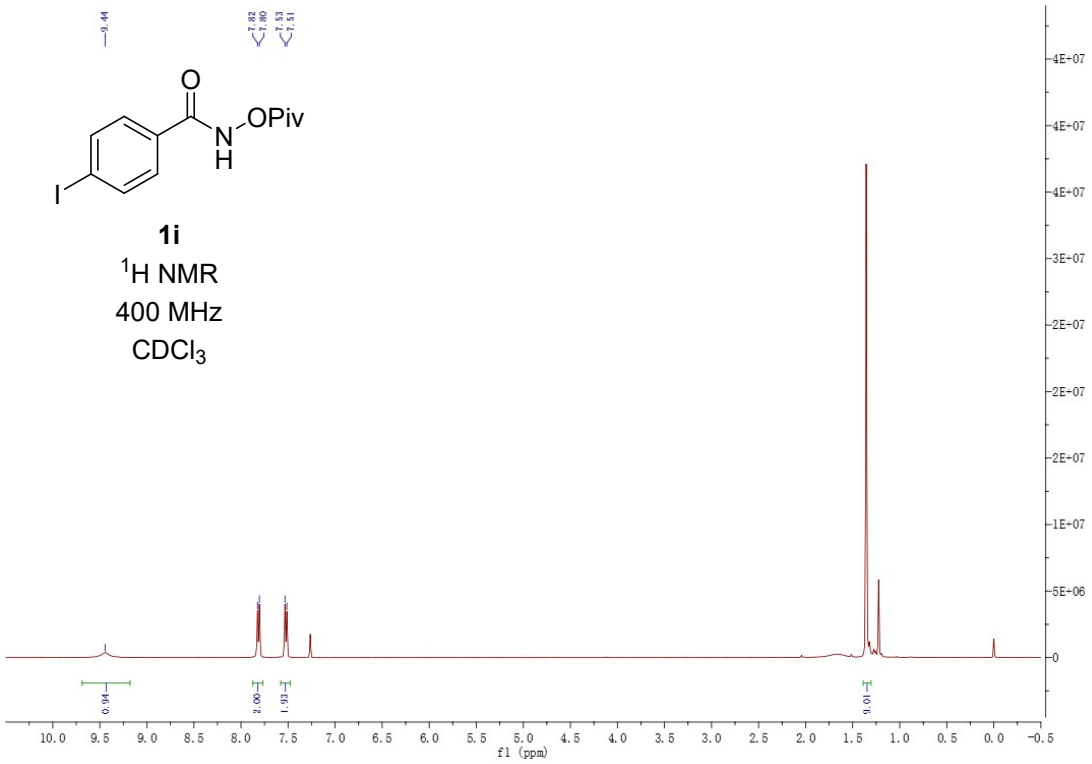


1h

^{1}H NMR

400 MHz

$CDCl_3$

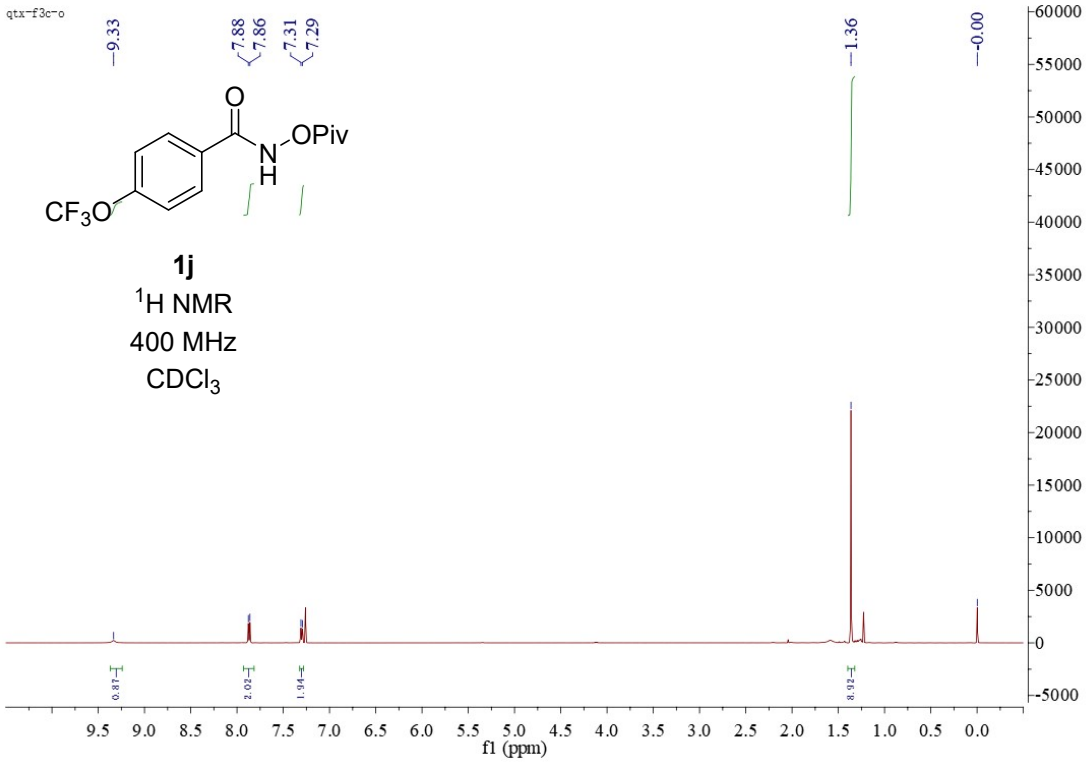


1i

^{1}H NMR

400 MHz

$CDCl_3$

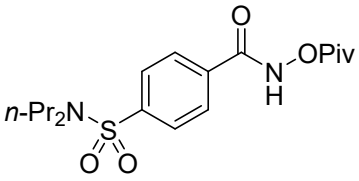


1j

^{1}H NMR

400 MHz

$CDCl_3$

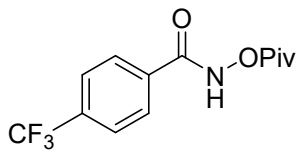


1k

^{1}H NMR

400 MHz

$CDCl_3$

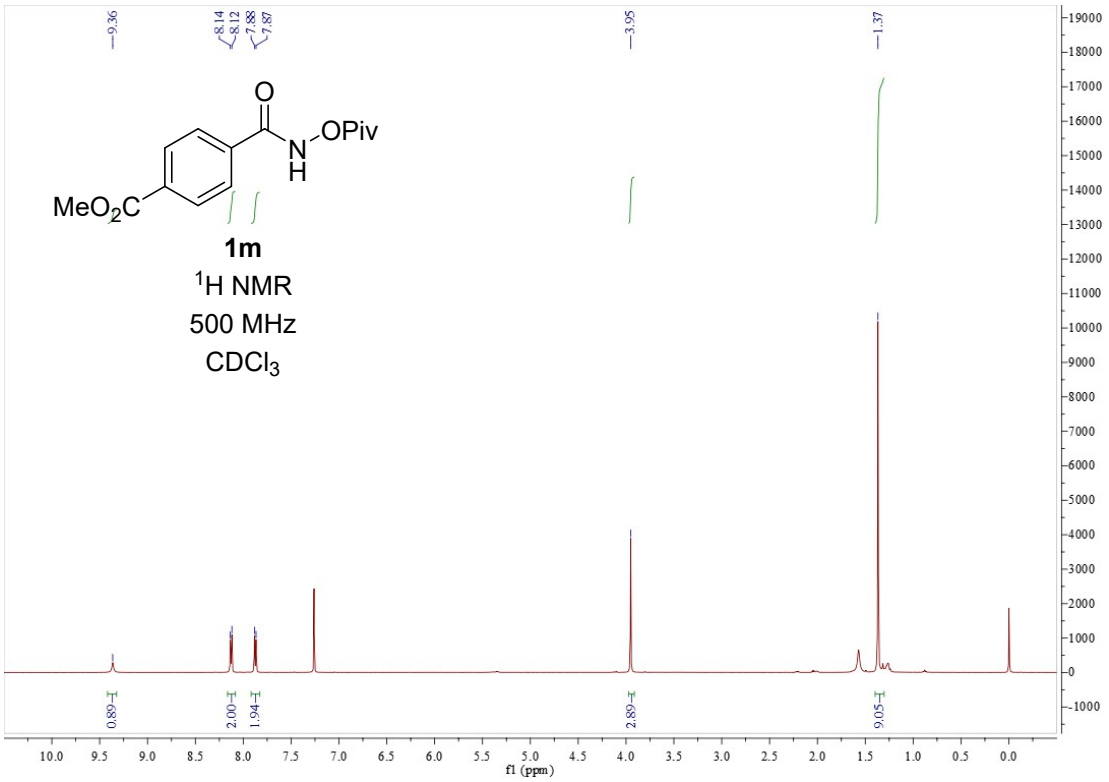


1l

^{1}H NMR

400 MHz

$CDCl_3$

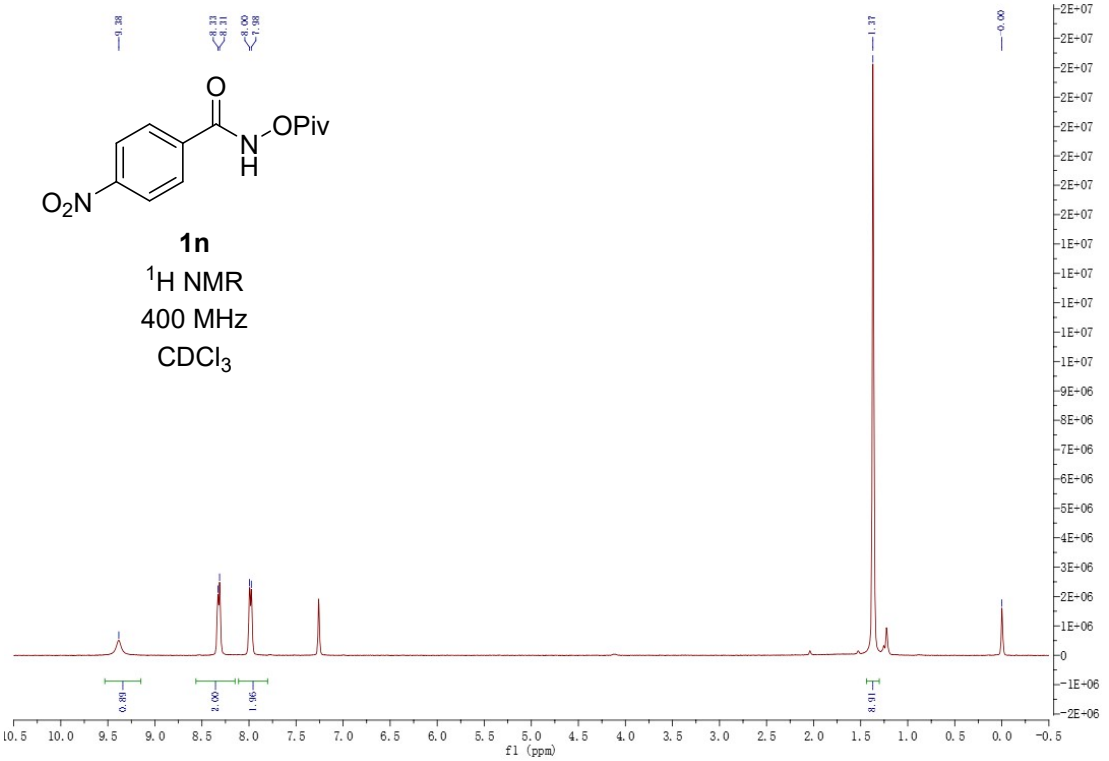


1m

^{1}H NMR

500 MHz

$CDCl_3$

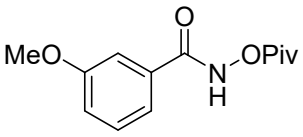


1n

^{1}H NMR

400 MHz

$CDCl_3$

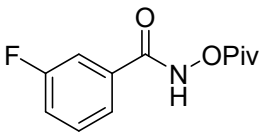


1o

^{1}H NMR

400 MHz

$CDCl_3$

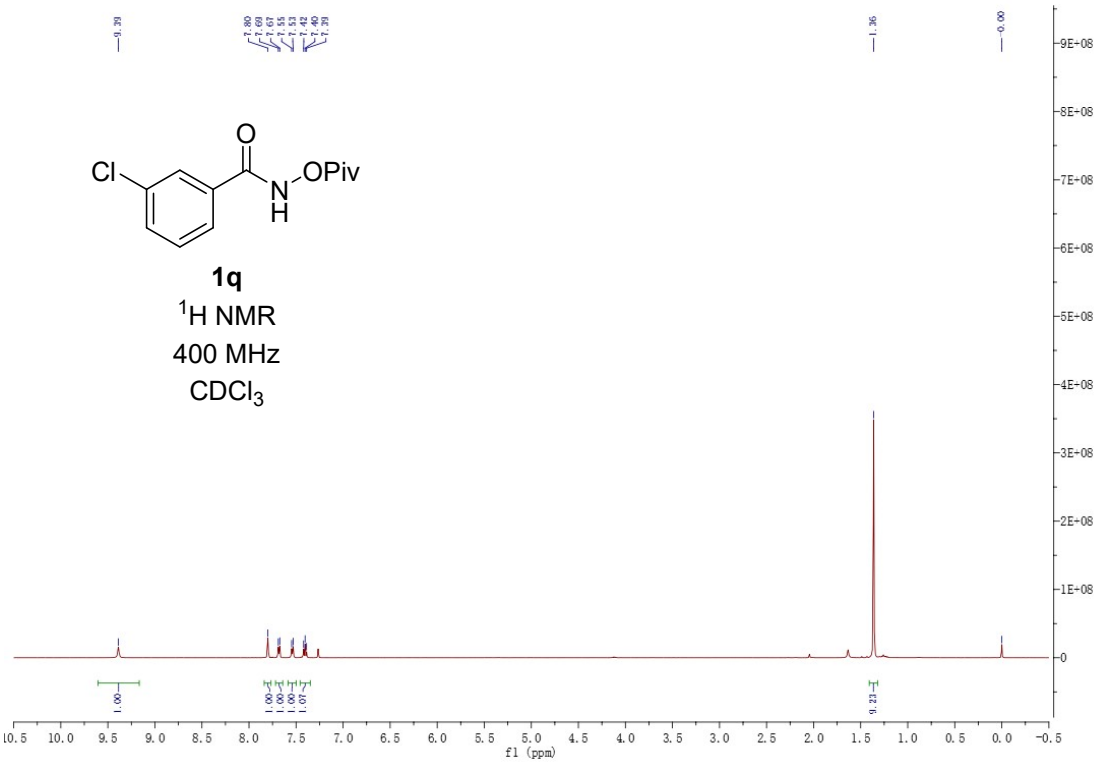


1p

^{1}H NMR

400 MHz

$CDCl_3$

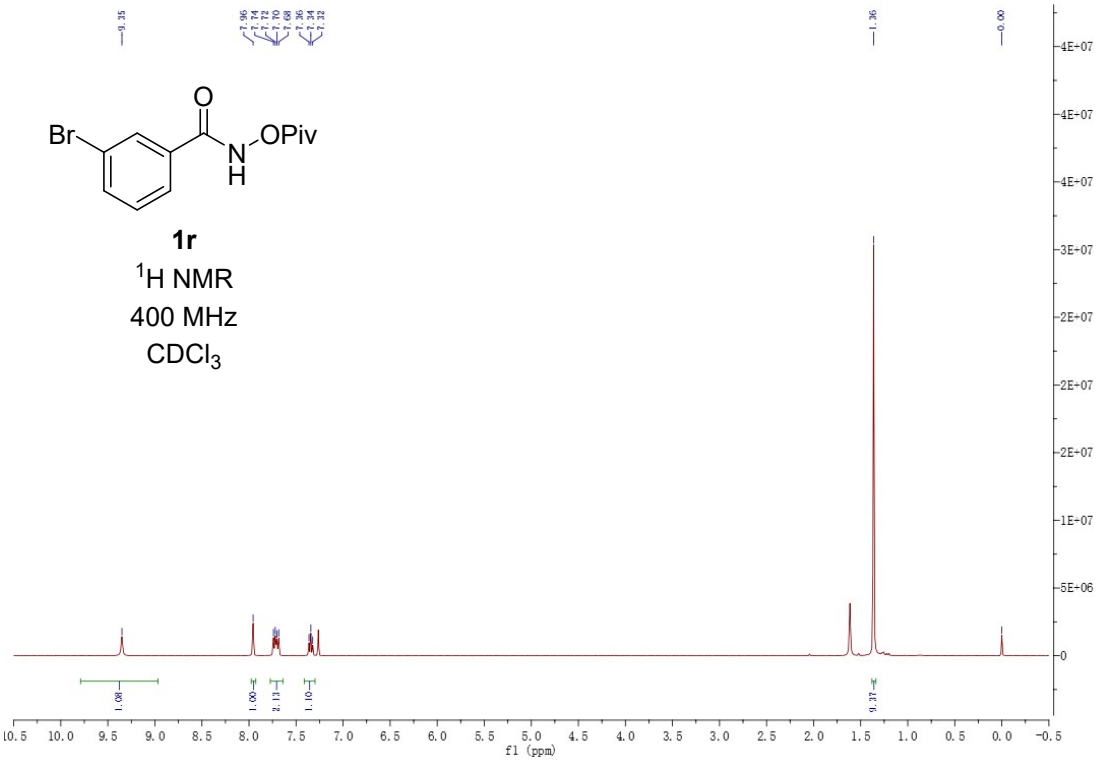


1q

^{1}H NMR

400 MHz

$CDCl_3$

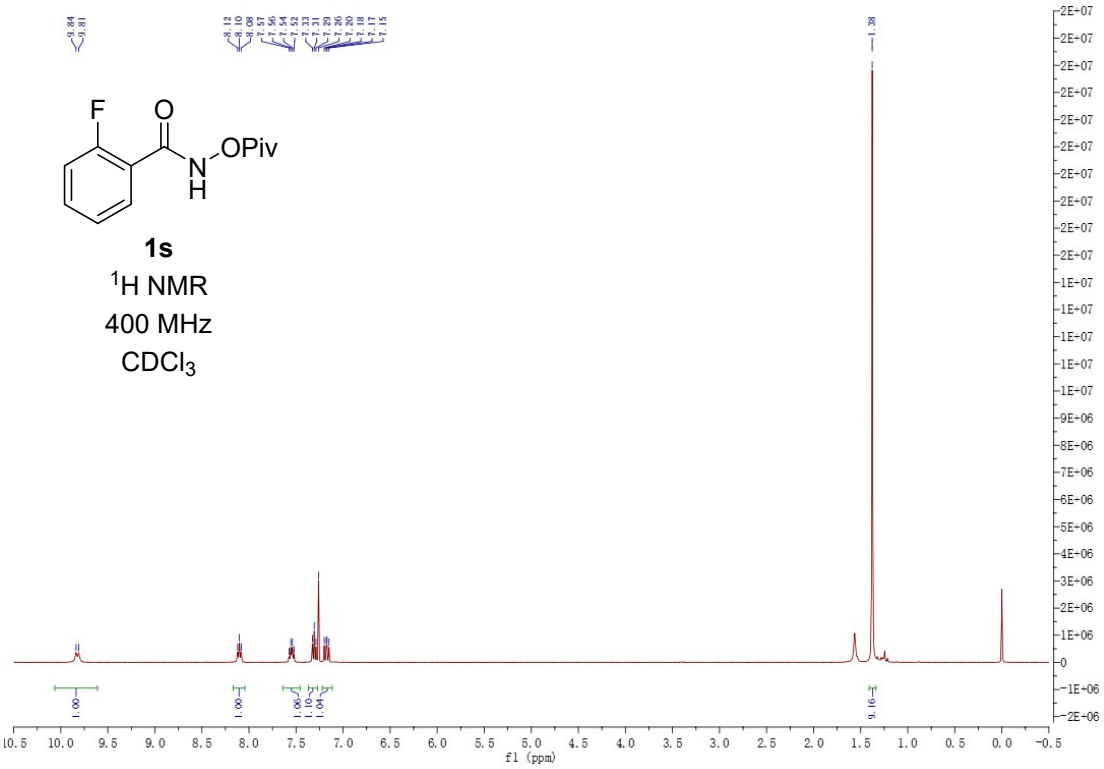


1r

^{1}H NMR

400 MHz

$CDCl_3$

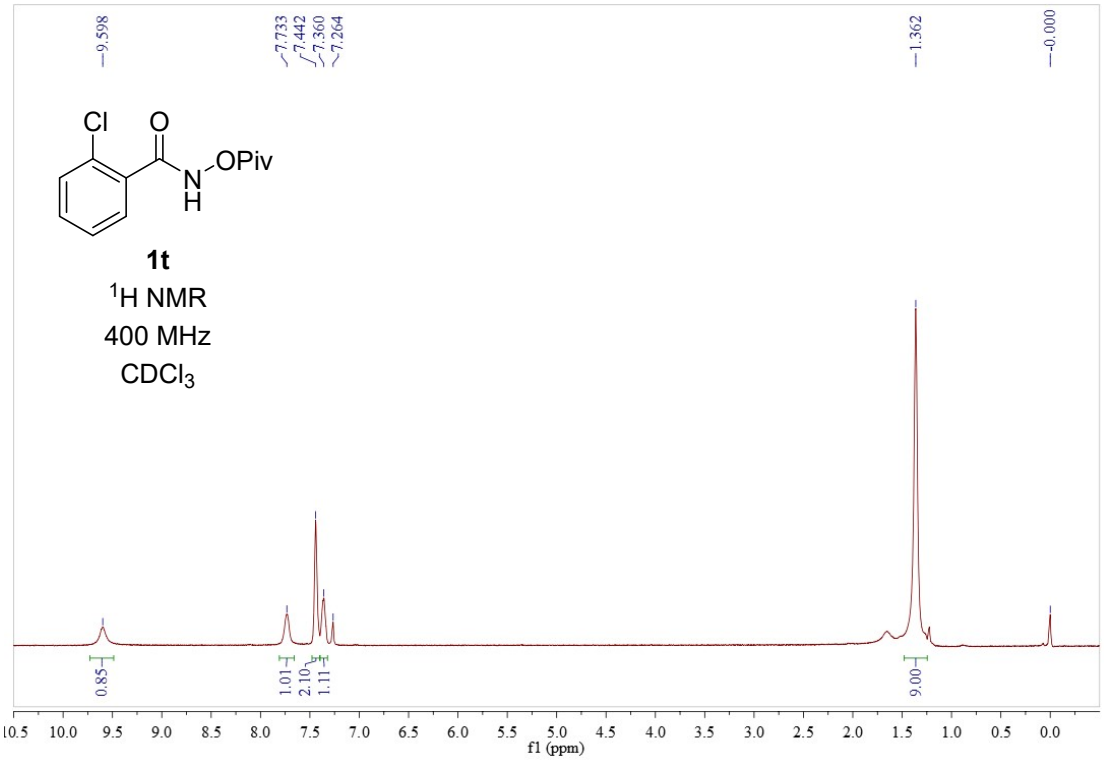


1s

^{1}H NMR

400 MHz

$CDCl_3$

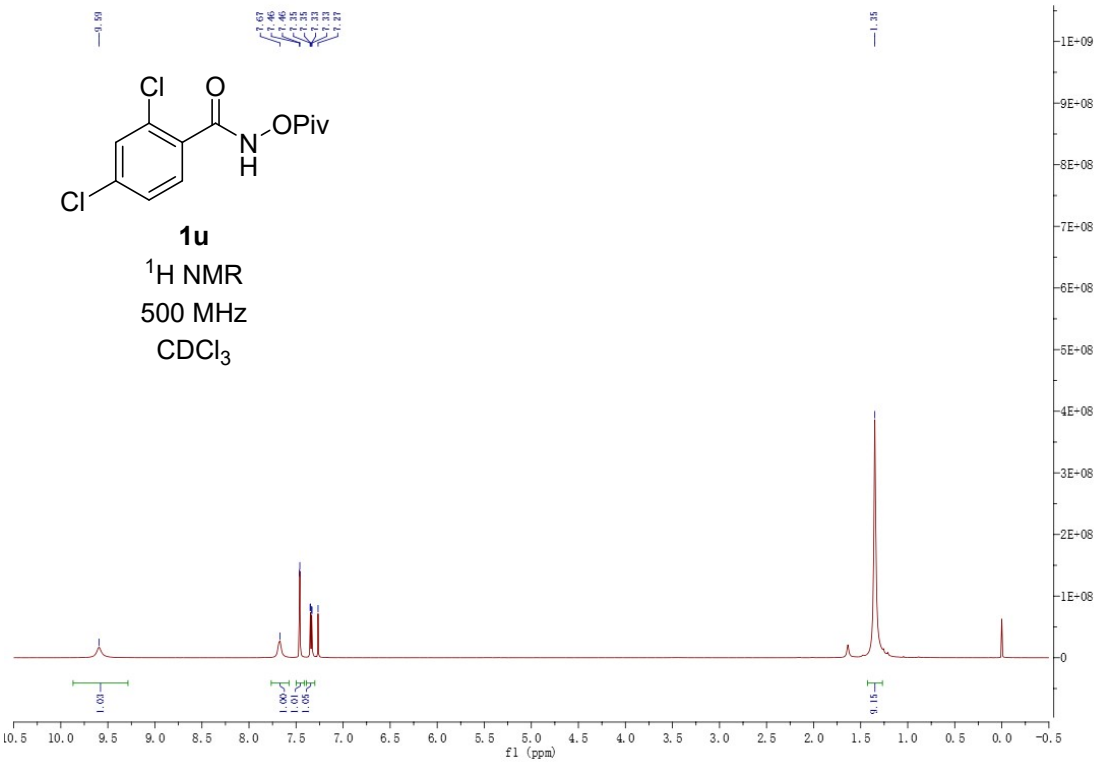


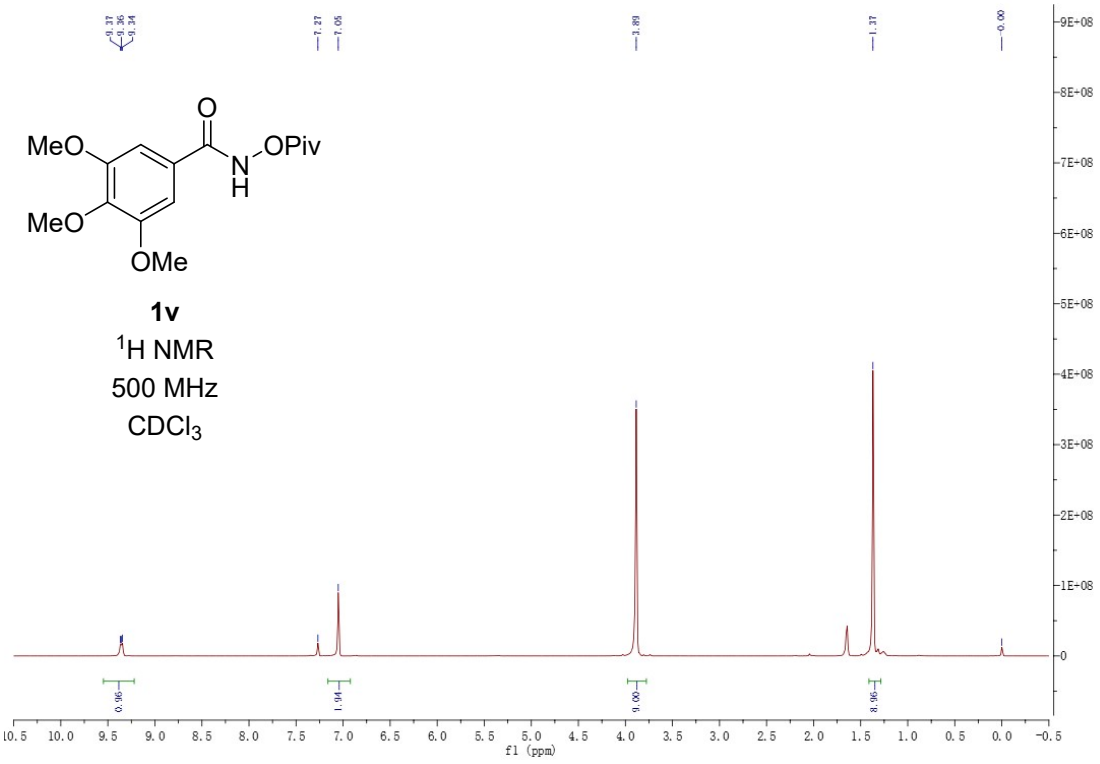
1t

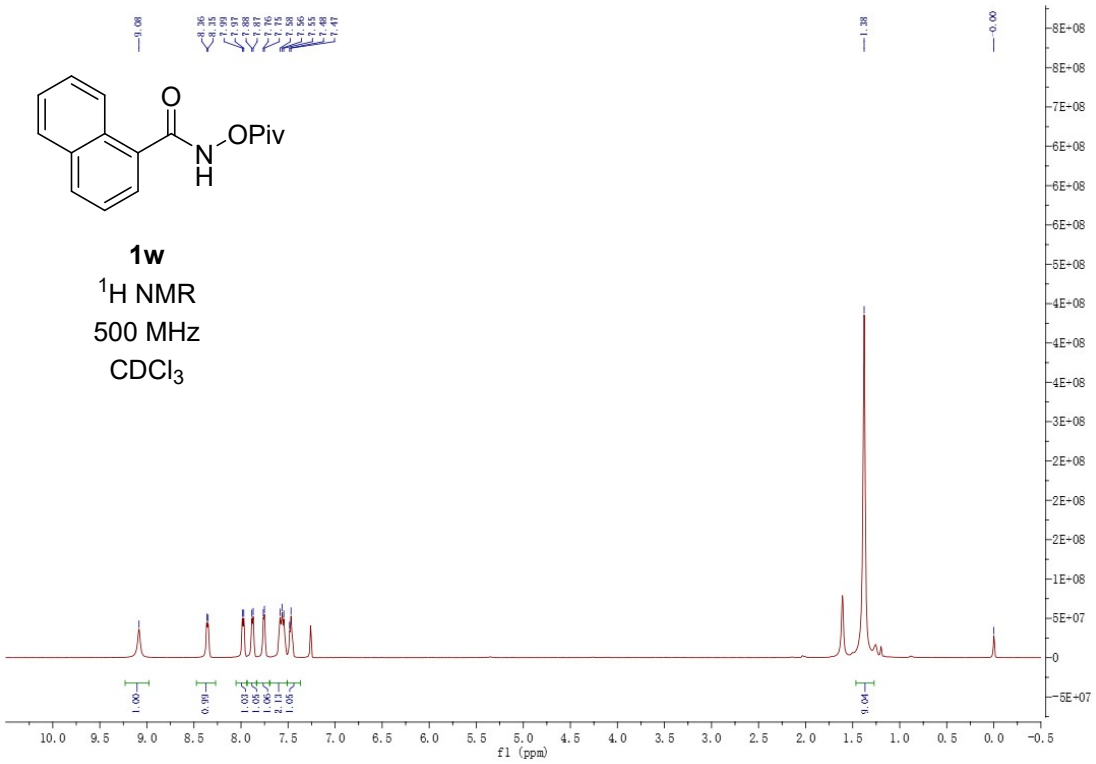
^{1}H NMR

400 MHz

$CDCl_3$


Cl
O
N
H
OPiv
Cl
1u
1H NMR
500 MHz
CDCl3
f1 (ppm)


O
MeO
N
H
OPiv
MeO
OMe
1v
1H NMR
500 MHz
CDCl3
f1 (ppm)

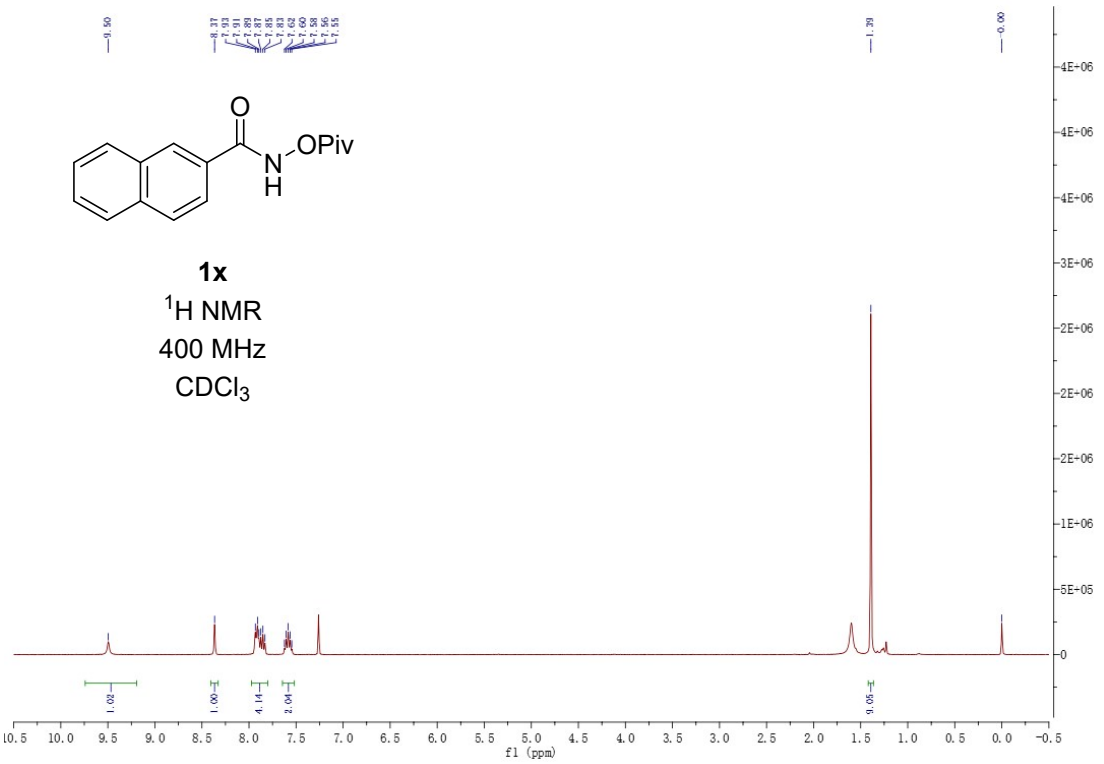


1w

^{1}H NMR

500 MHz

$CDCl_3$

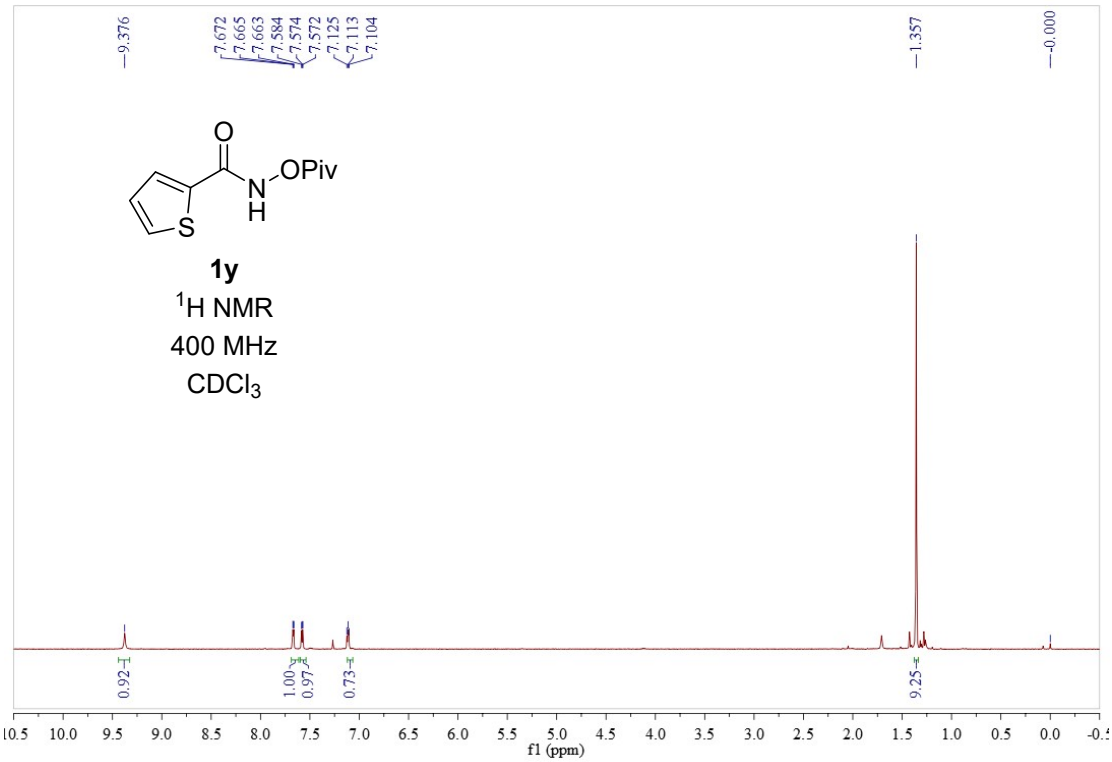


1x

^{1}H NMR

400 MHz

$CDCl_3$

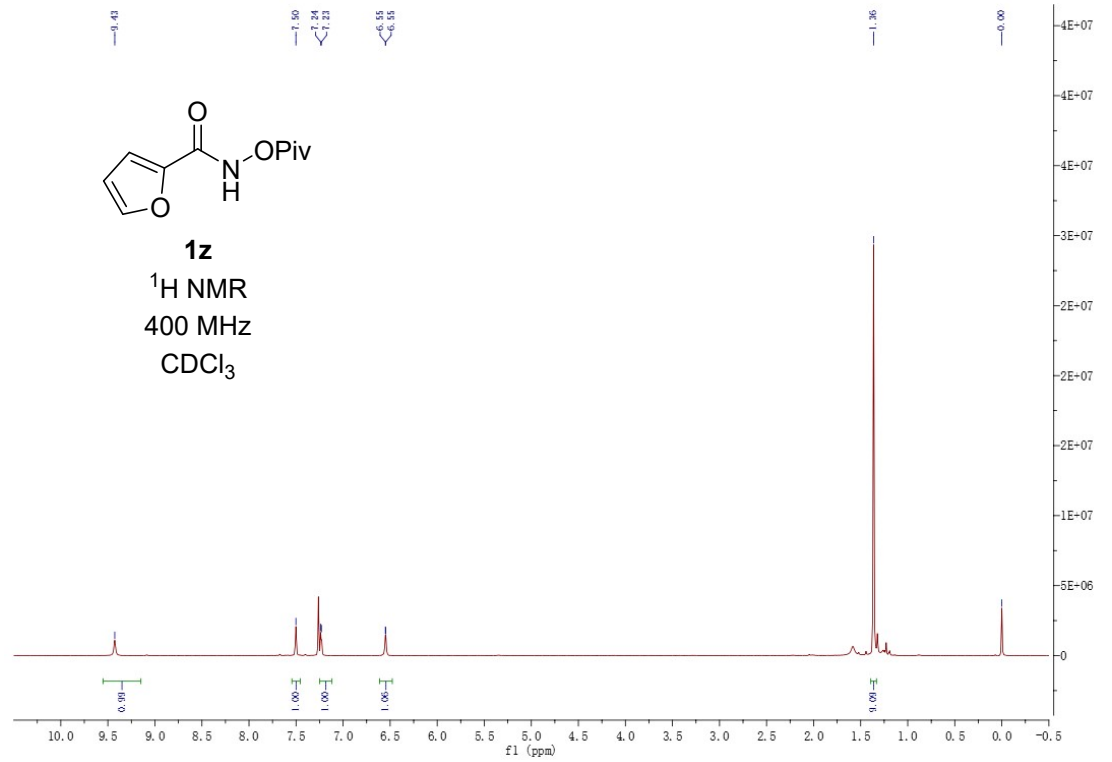


1y

^{1}H NMR

400 MHz

$CDCl_3$

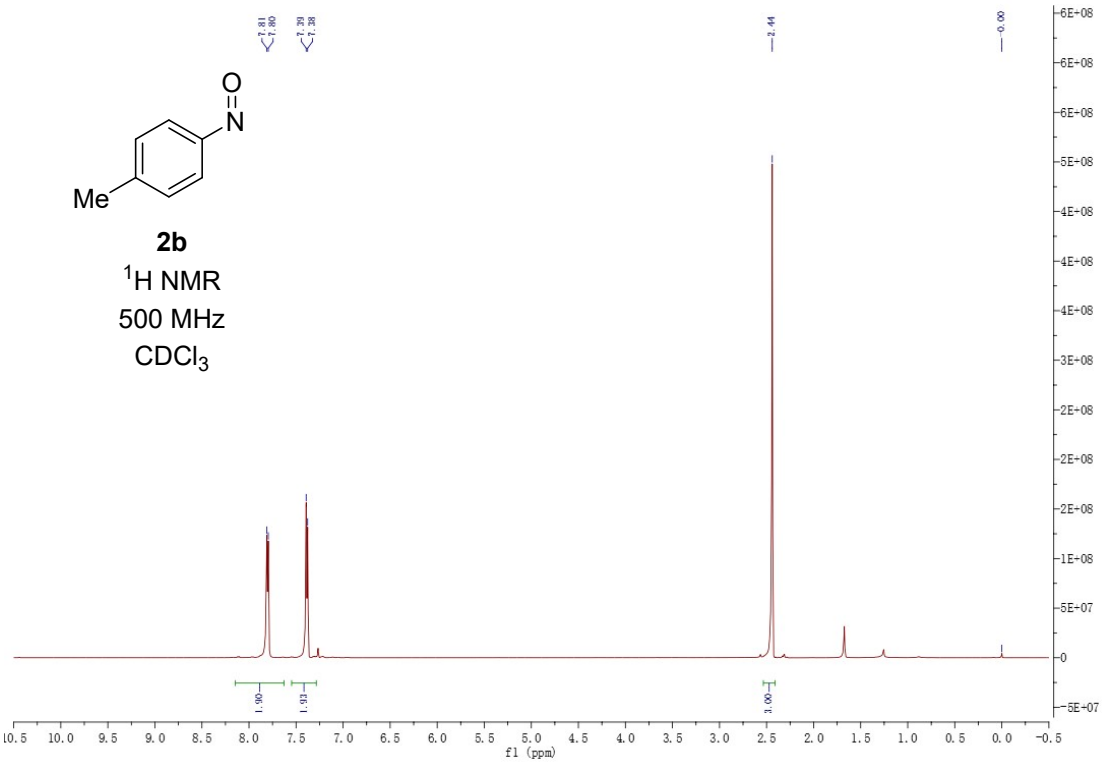


1z

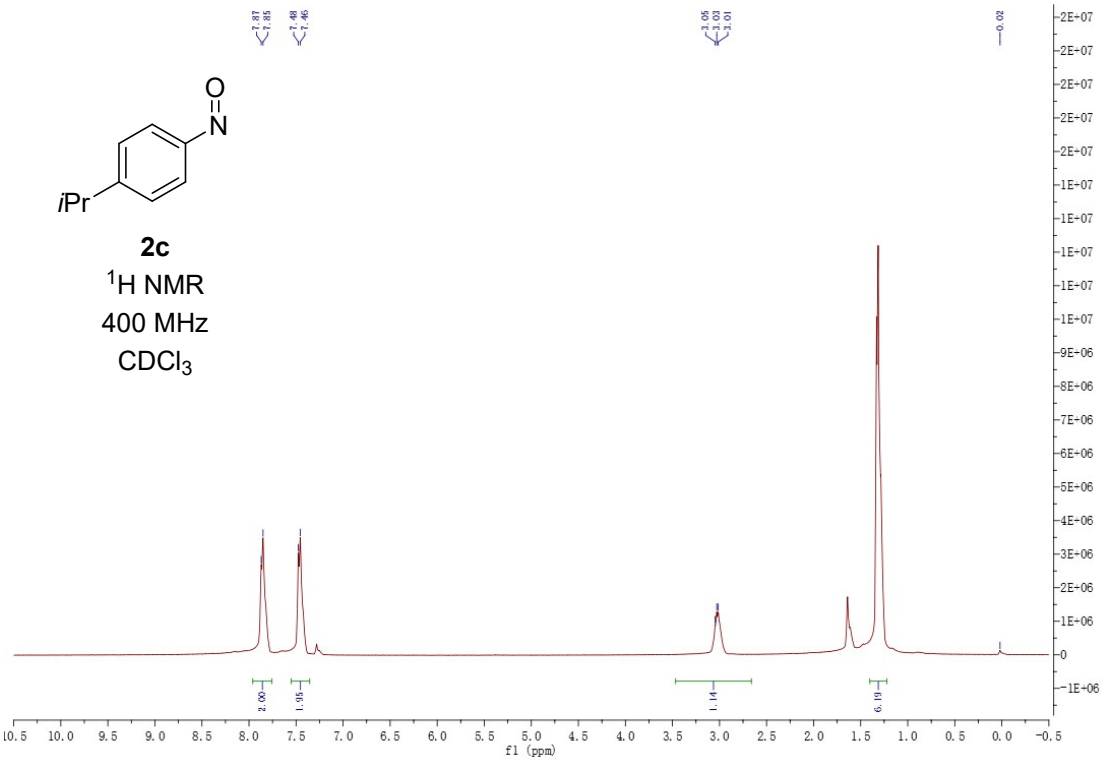
^{1}H NMR

400 MHz

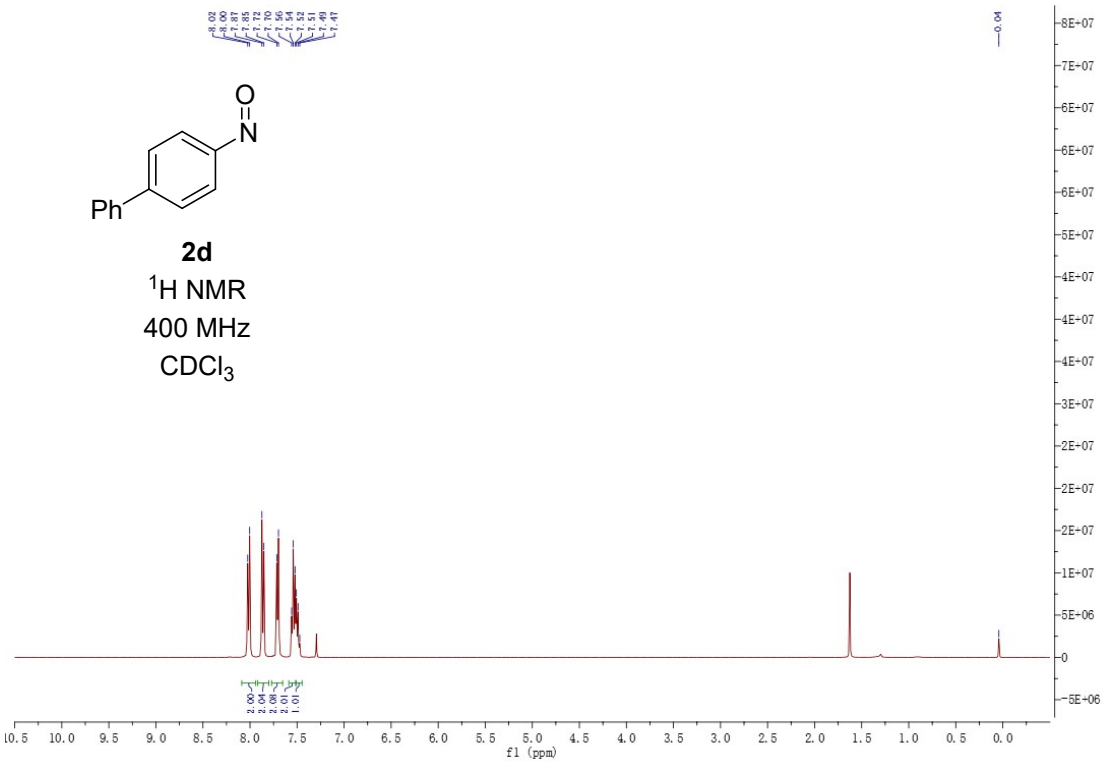
$CDCl_3$

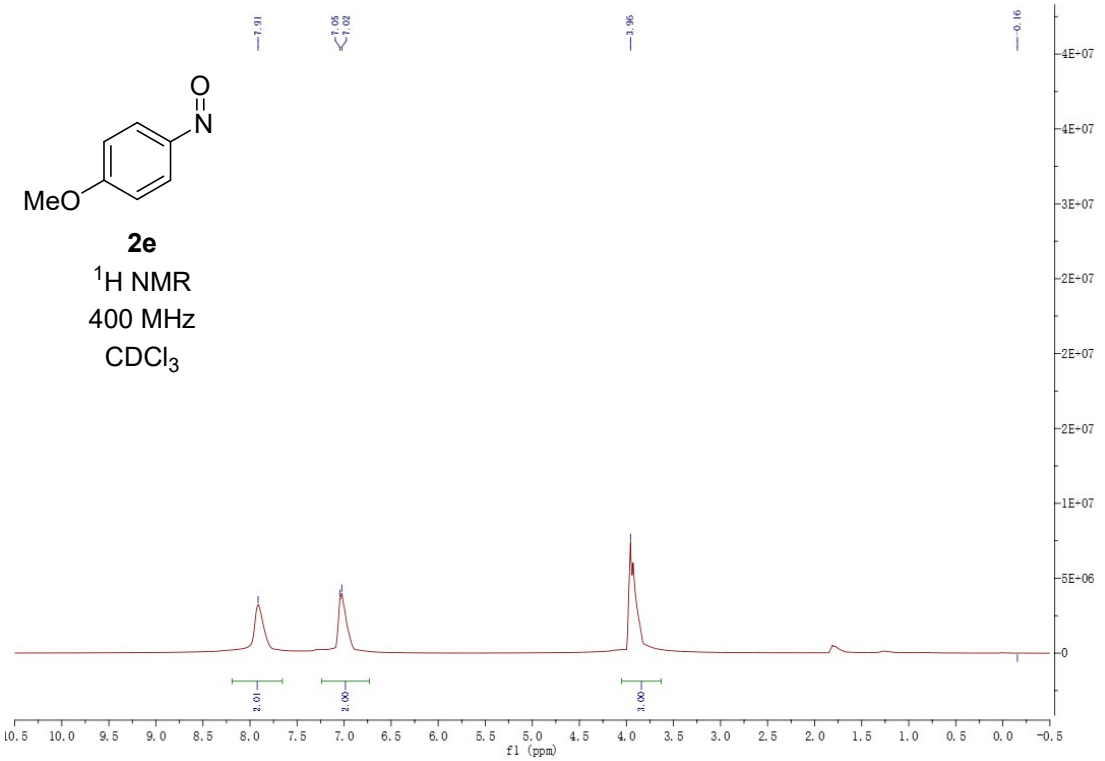


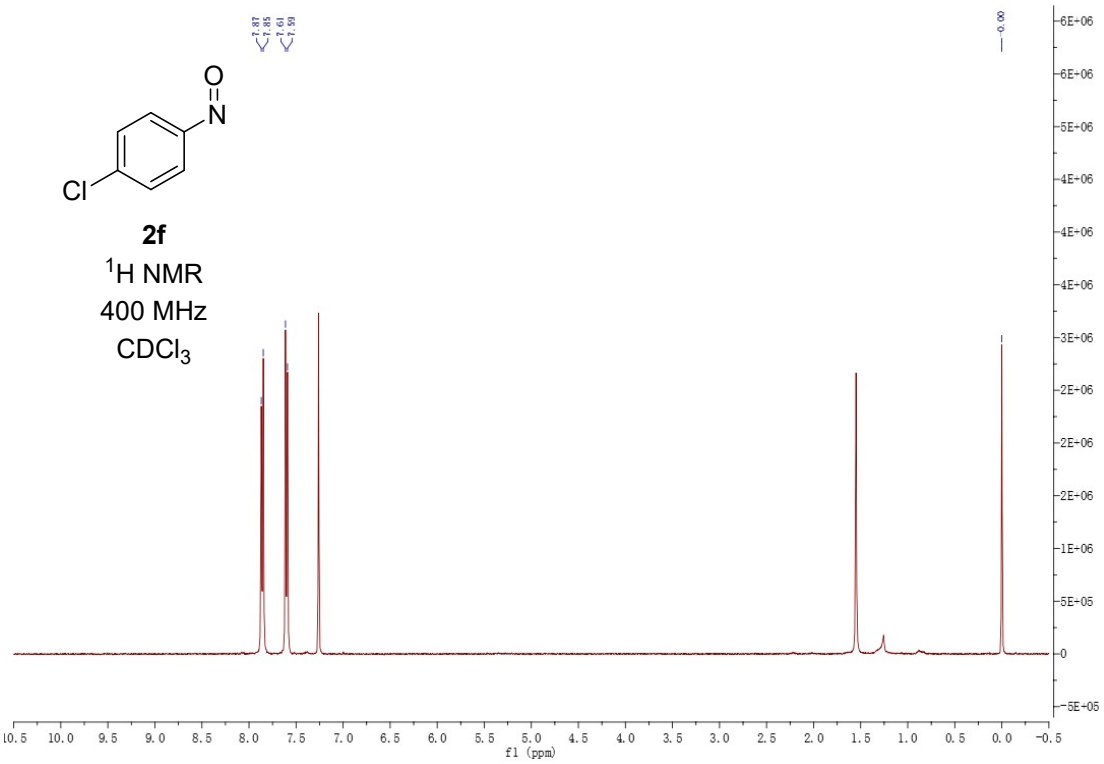
2b
^{1}H NMR
500 MHz
$CDCl_3$

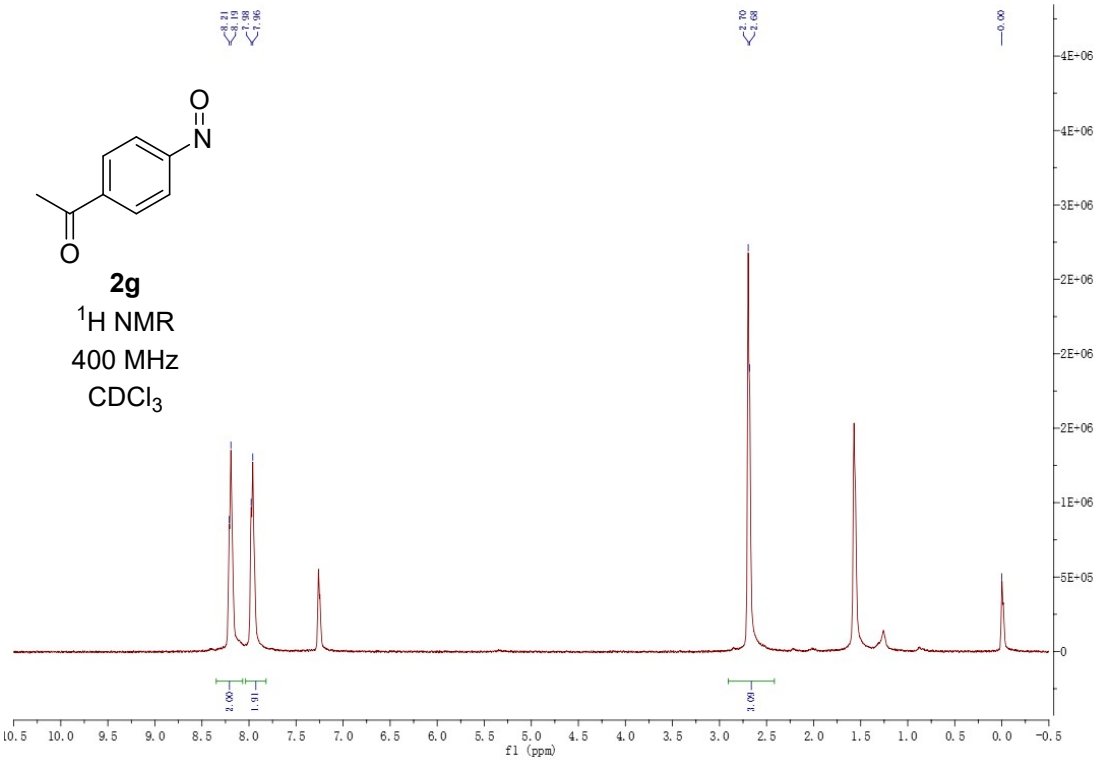


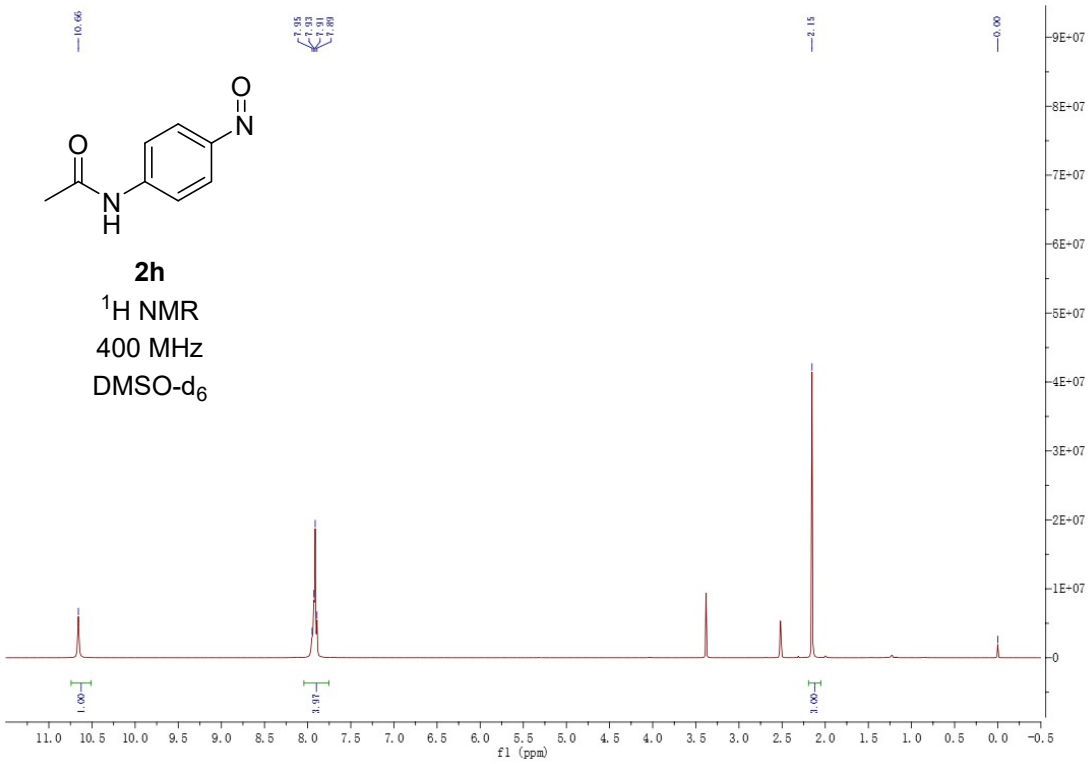
2c
^{1}H NMR
400 MHz
$CDCl_3$


Ph
2d
1H NMR
400 MHz
CDCl3
f1 (ppm)

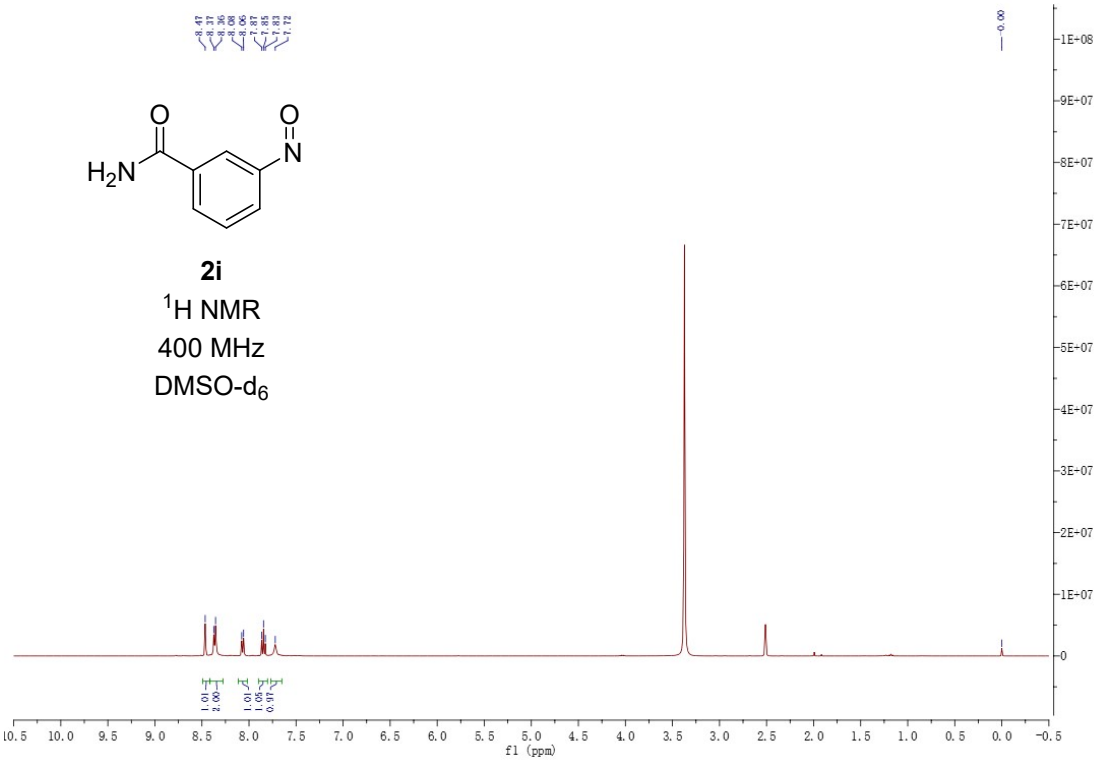

MeO
2e
1H NMR
400 MHz
CDCl3
f1 (ppm)


Cl
O
N
2f
1H NMR
400 MHz
CDCl3
f1 (ppm)

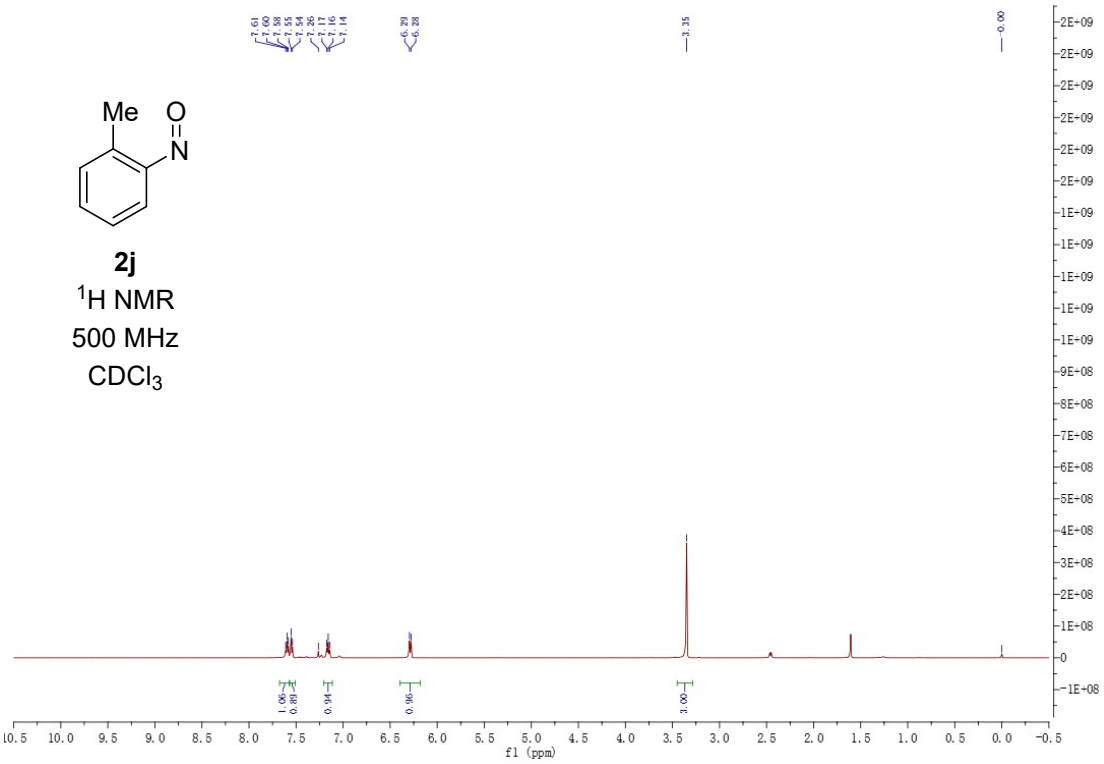

O
N
O
2g
1H NMR
400 MHz
CDCl3
f1 (ppm)

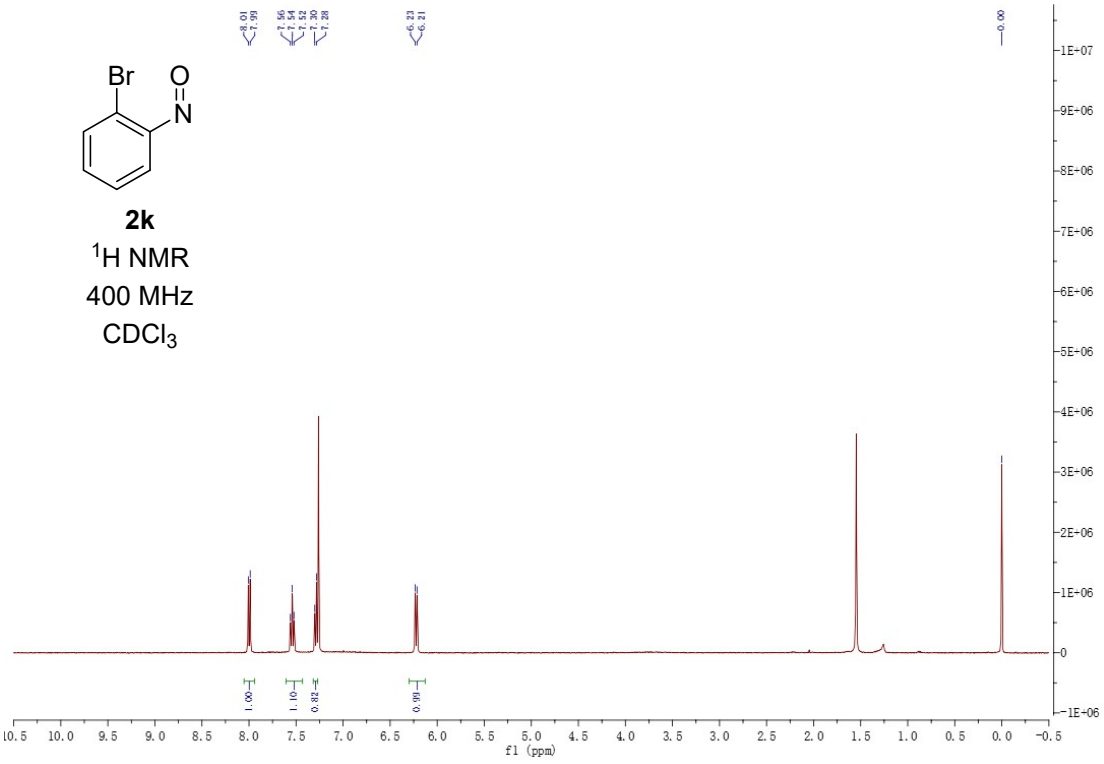


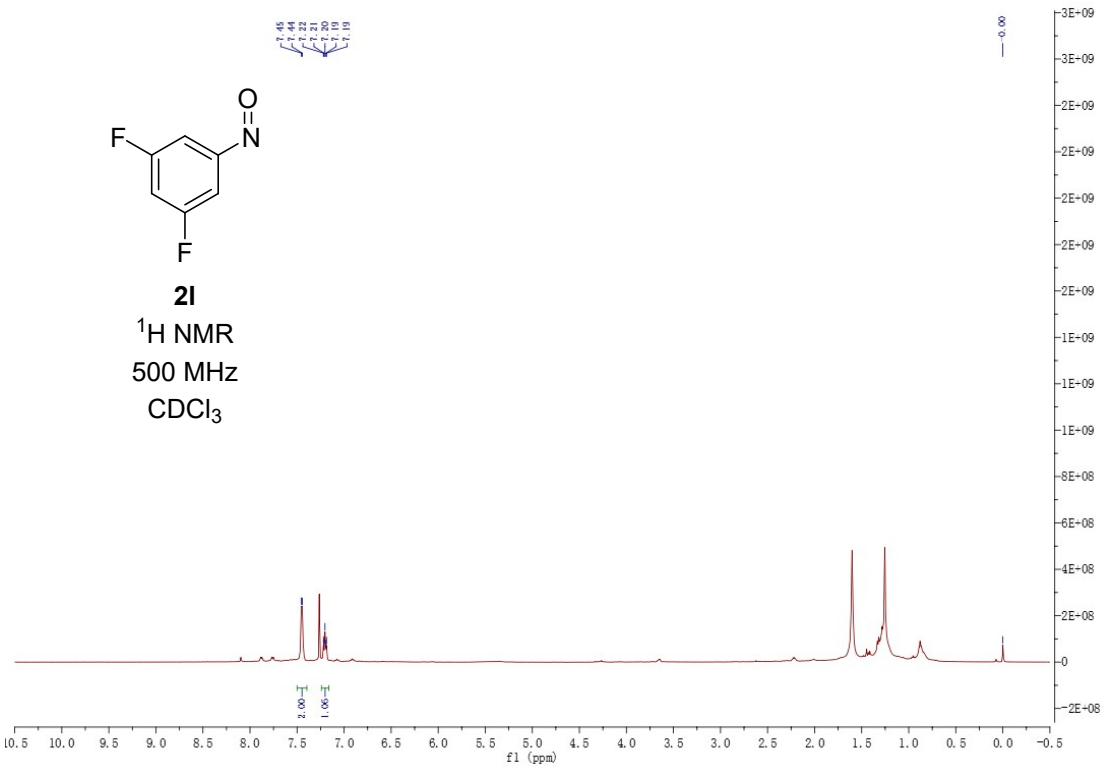
2h
^{1}H NMR
400 MHz
DMSO-d_6



2i
^{1}H NMR
400 MHz
DMSO-d_6


Me
O
N
2j
1H NMR
500 MHz
CDCl3
f1 (ppm)


Br
O
N
2k
1H NMR
400 MHz
CDCl3
f1 (ppm)

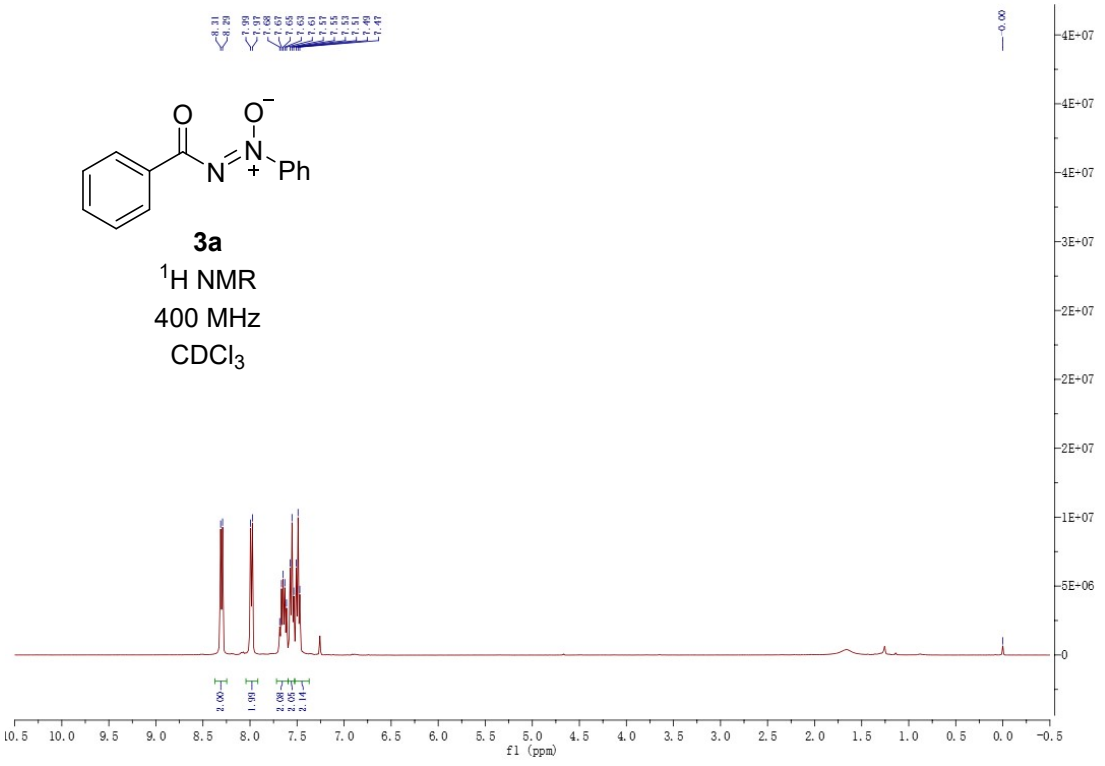


2l

^{1}H NMR

500 MHz

$CDCl_3$

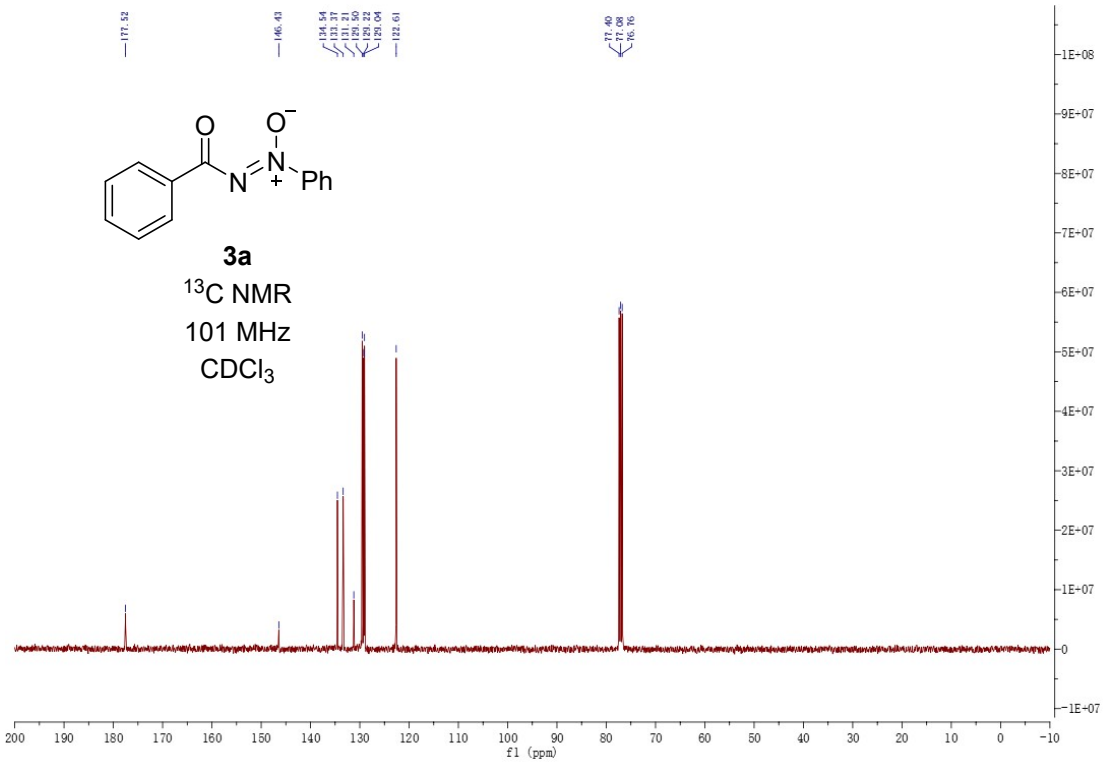


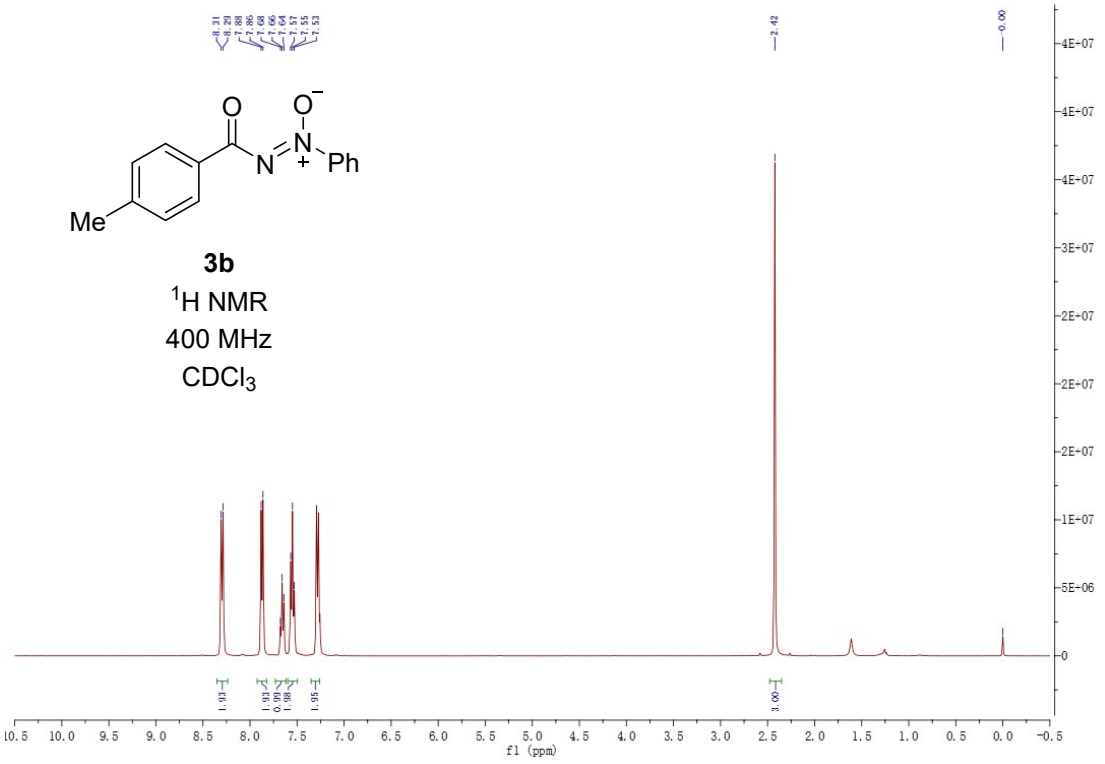
3a

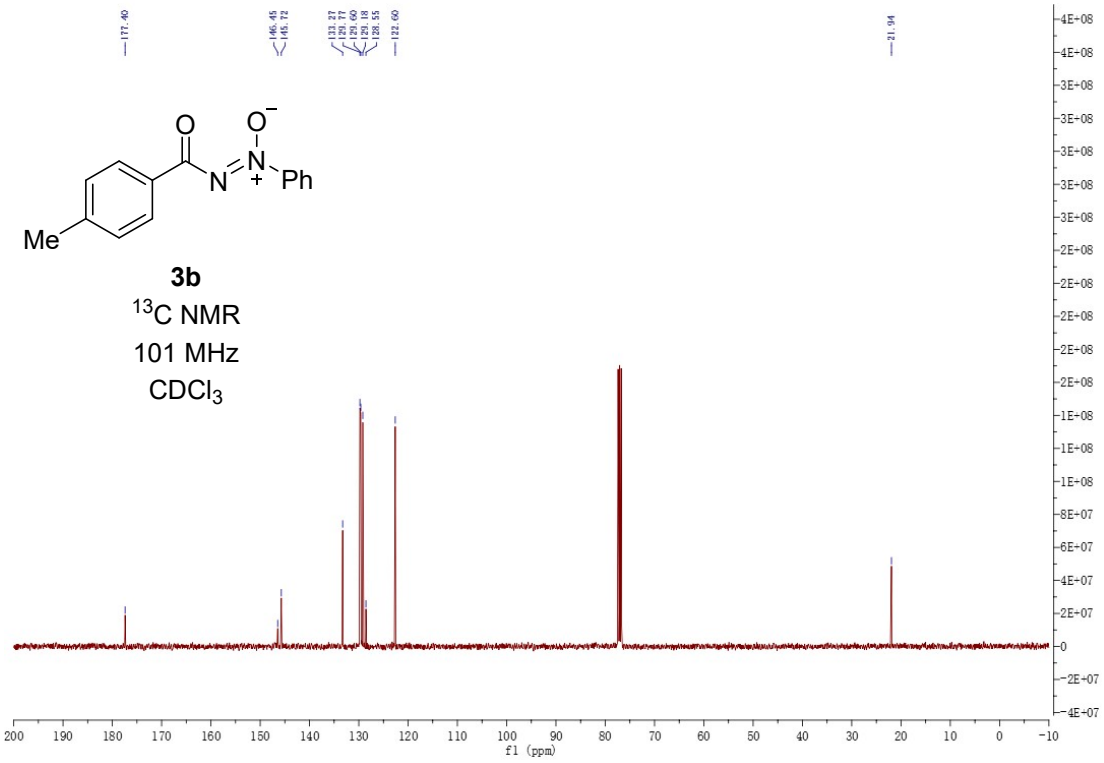
^{1}H NMR

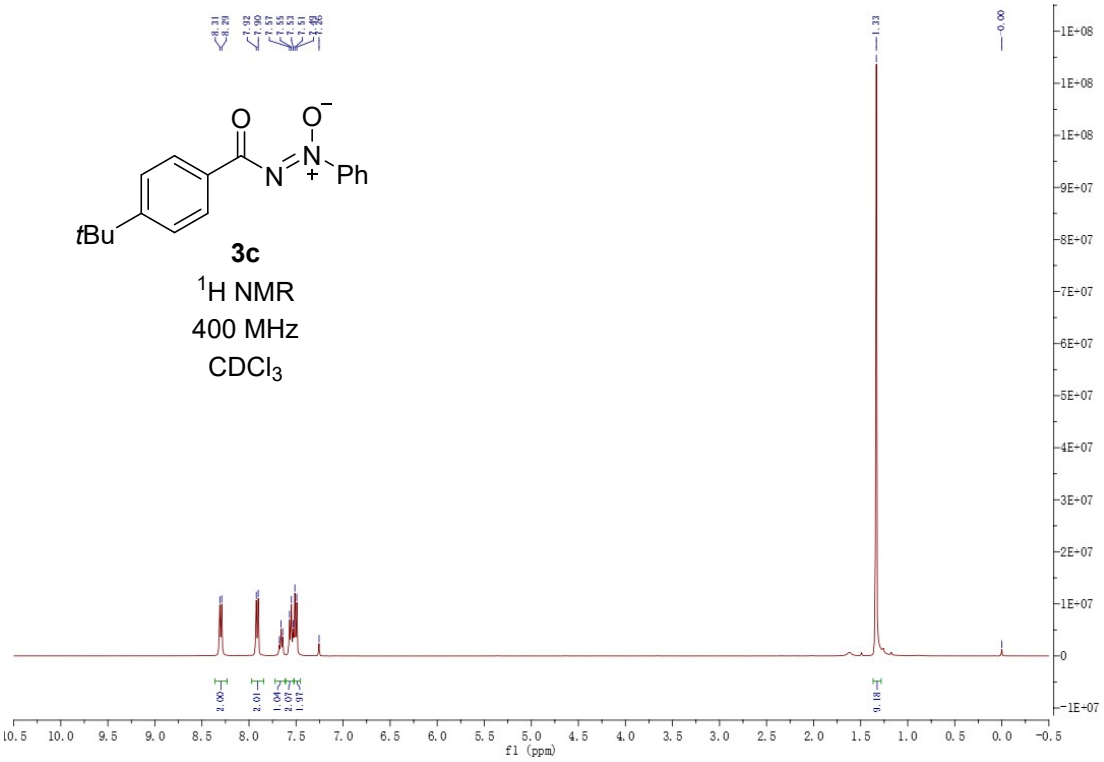
400 MHz

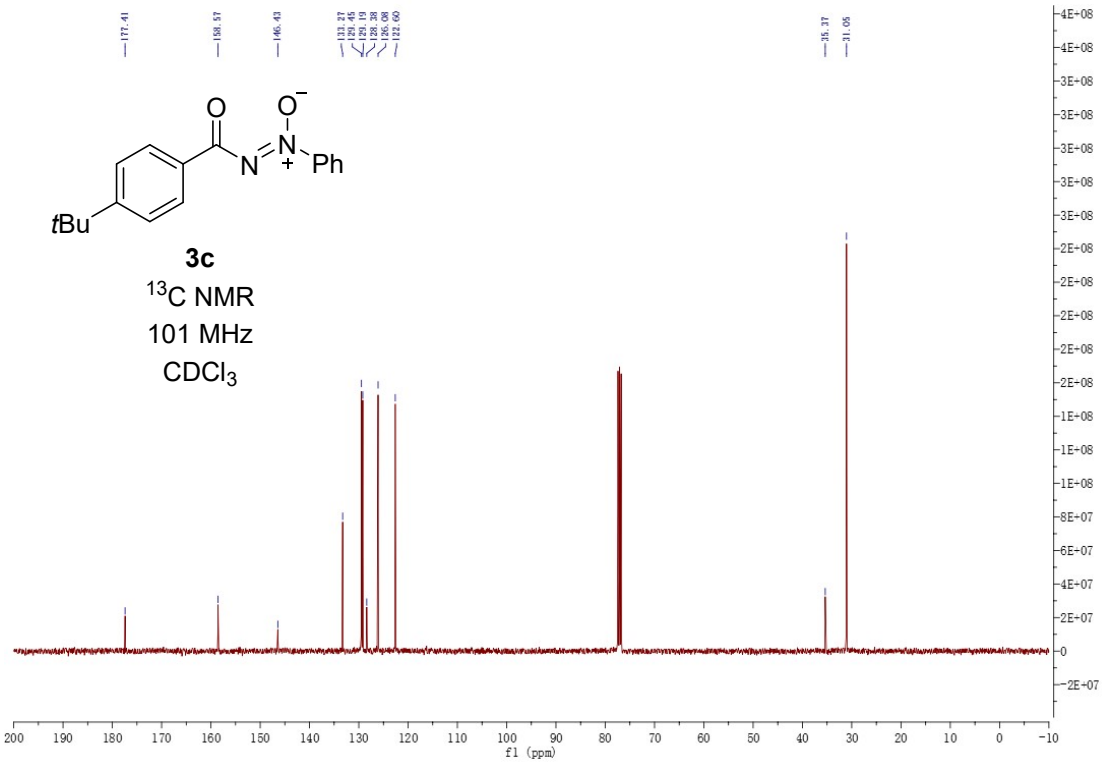
$CDCl_3$


177.52
166.43
134.54
133.37
131.21
129.90
129.23
128.04
122.61
77.40
77.08
76.76
O
O
N
N
Ph
3a
13C NMR
101 MHz
CDCl3
f1 (ppm)


8.31
8.29
7.88
7.86
7.68
7.66
7.64
7.57
7.55
7.53
2.42
0.00
O
O
N
N
Ph
Me
3b
1H NMR
400 MHz
CDCl3
1.93
1.93
0.99
1.08
1.95
3.00
f1 (ppm)


Me
Ph
3b
13C NMR
101 MHz
CDCl3
f1 (ppm)


tBu
Ph
3c
1H NMR
400 MHz
CDCl3
f1 (ppm)

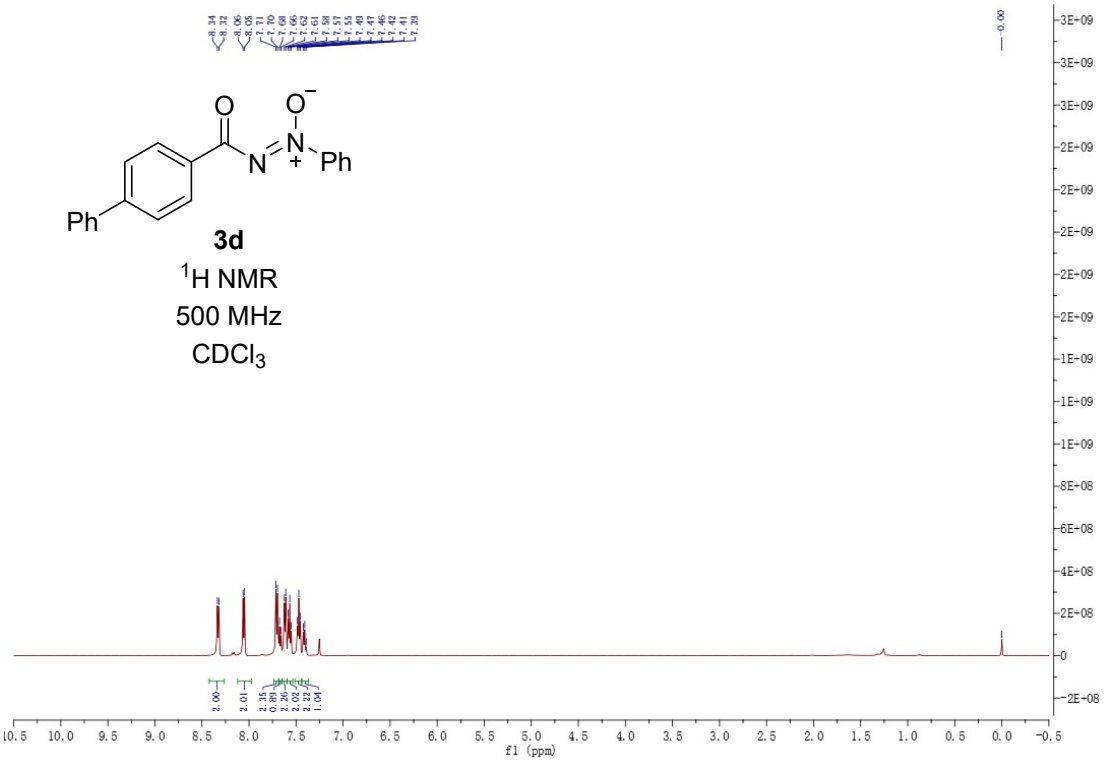


3c

^{13}C NMR

101 MHz

$CDCl_3$

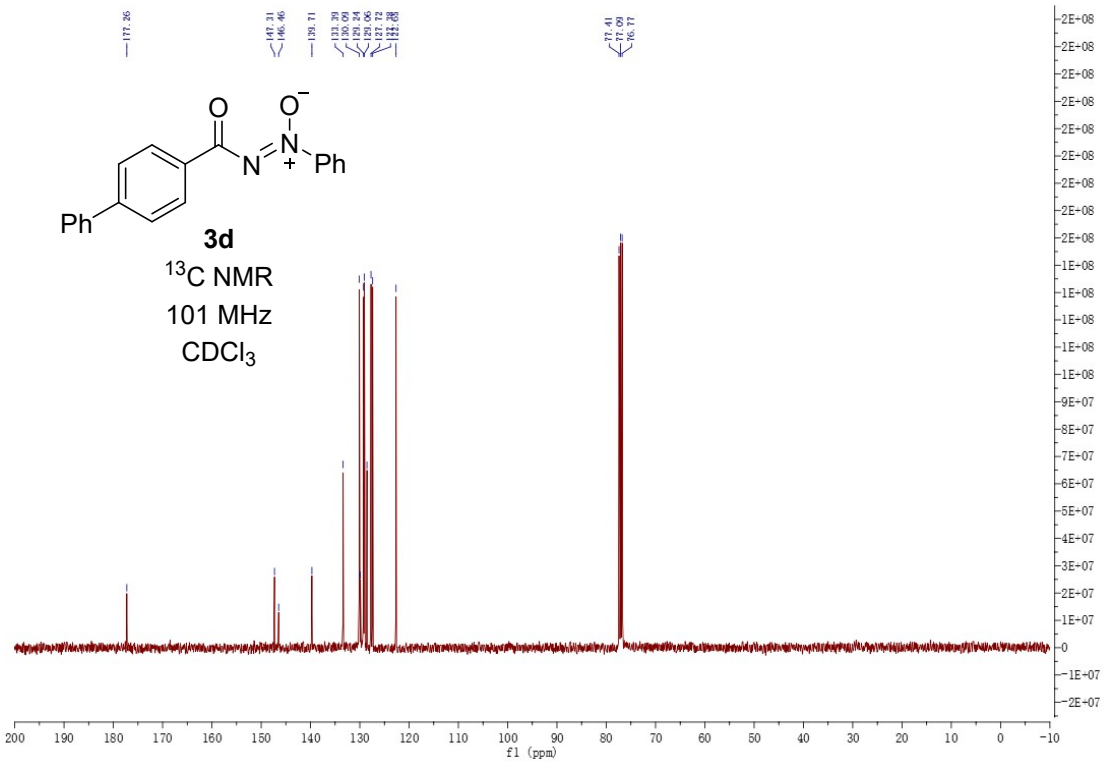


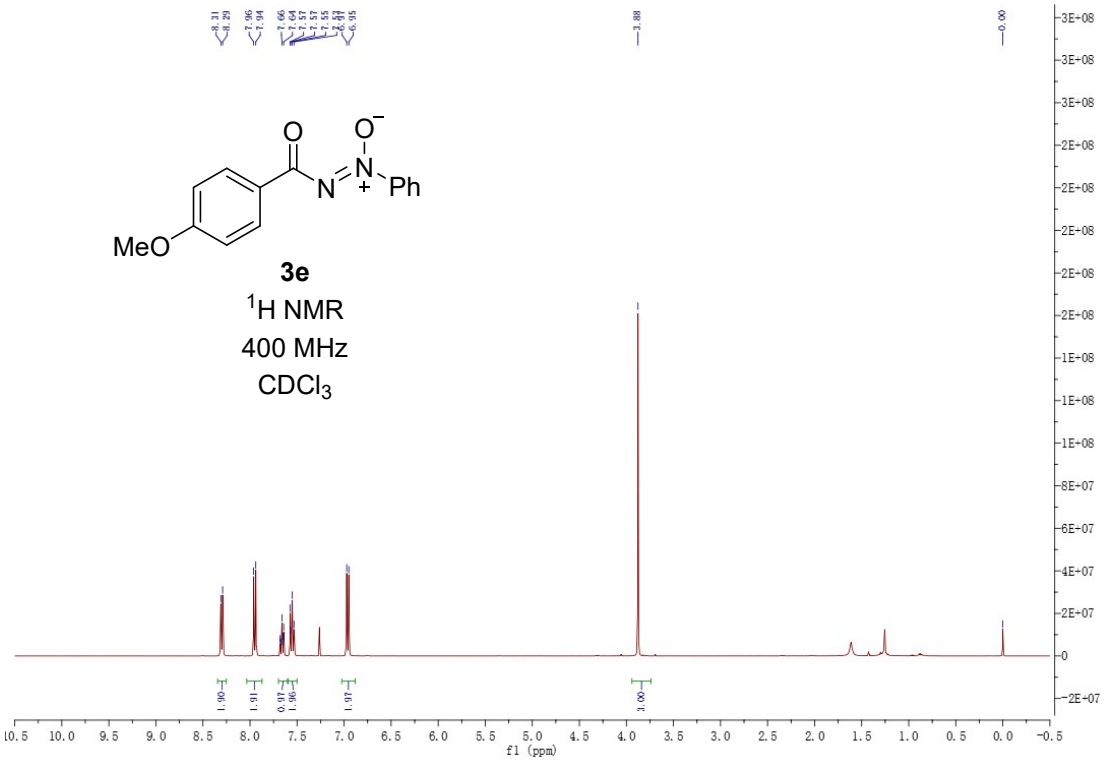
3d

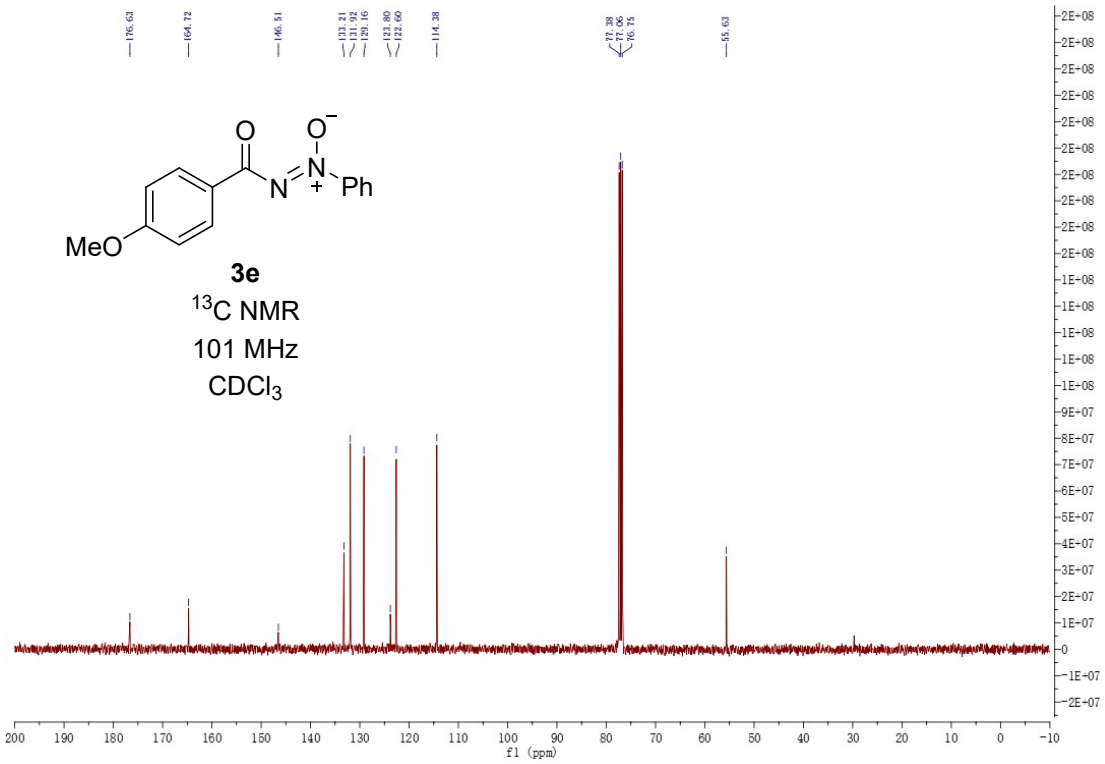
^{1}H NMR

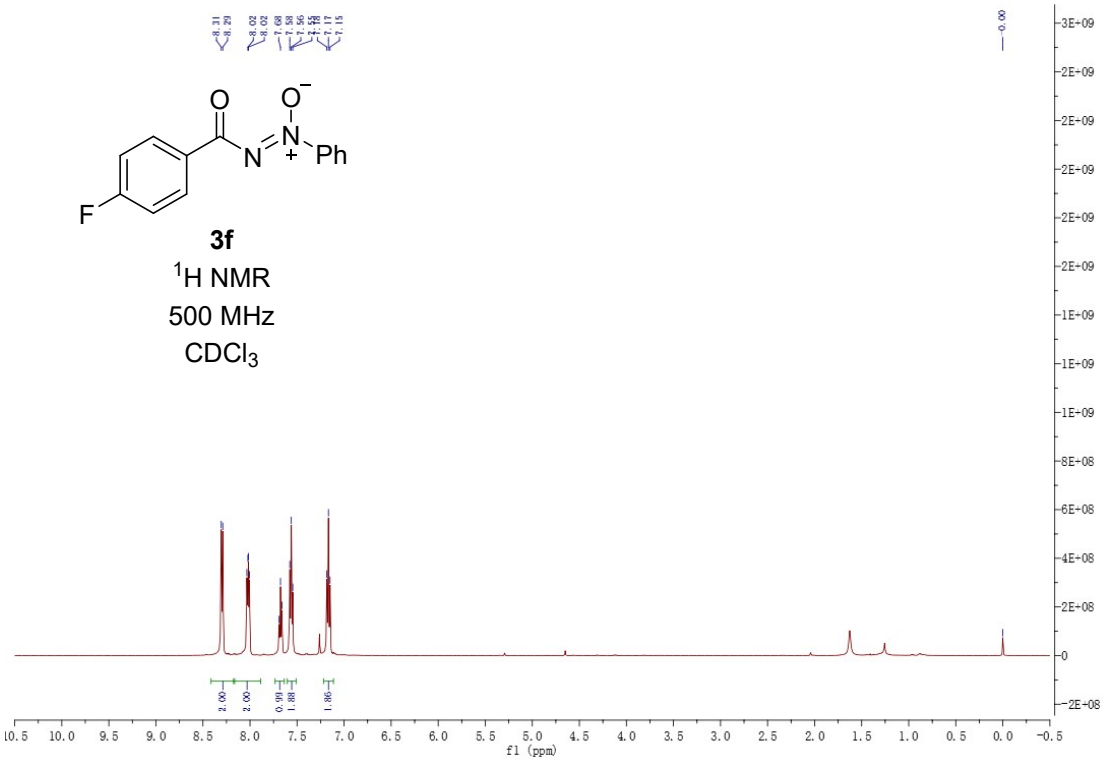
500 MHz

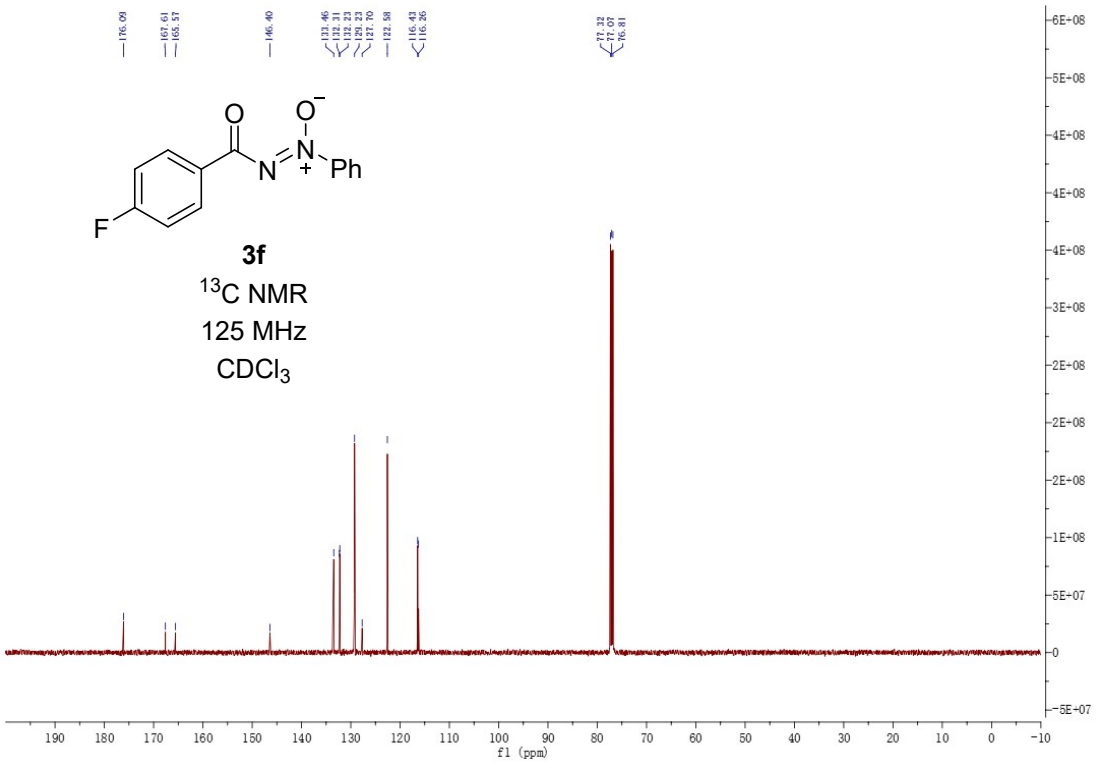
$CDCl_3$

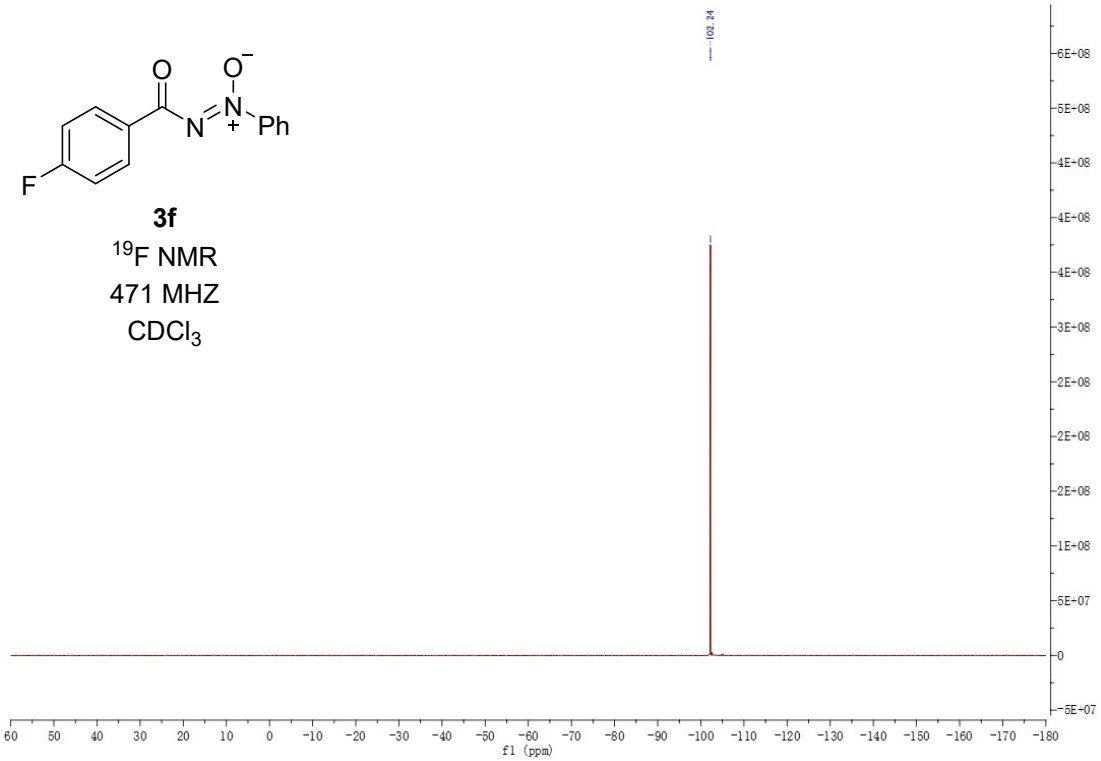

Ph
3d
13C NMR
101 MHz
CDCl3
f1 (ppm)

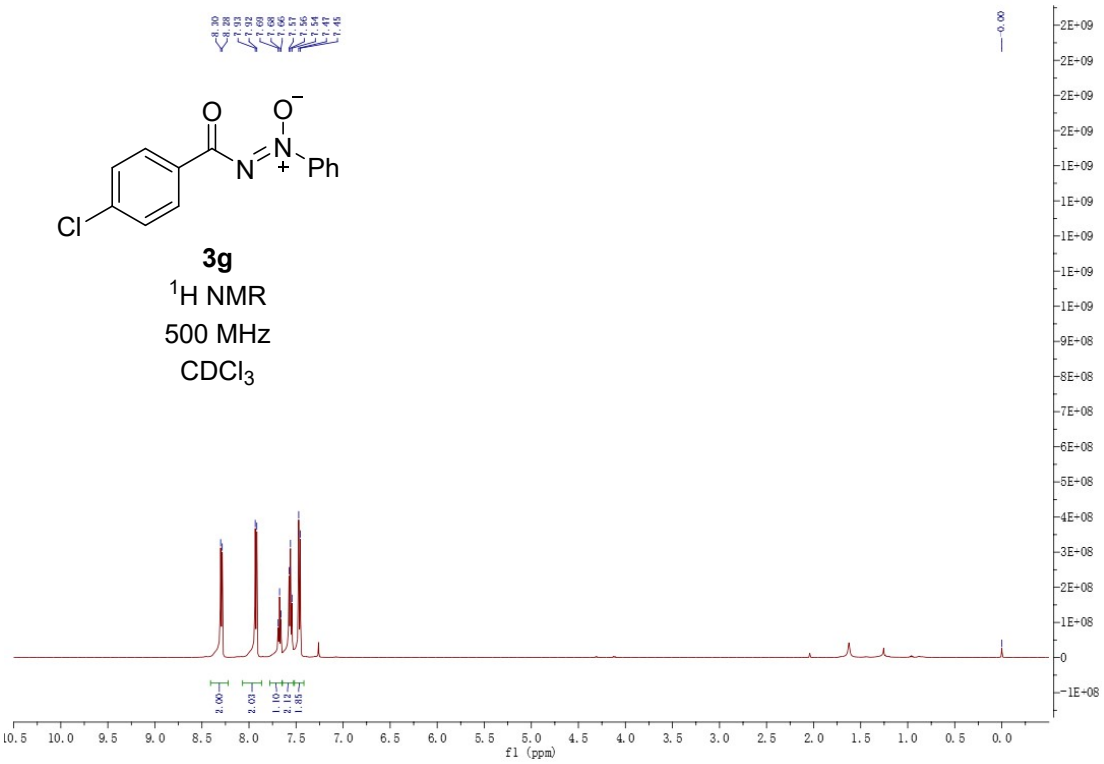

MeO
3e
1H NMR
400 MHz
CDCl3
f1 (ppm)

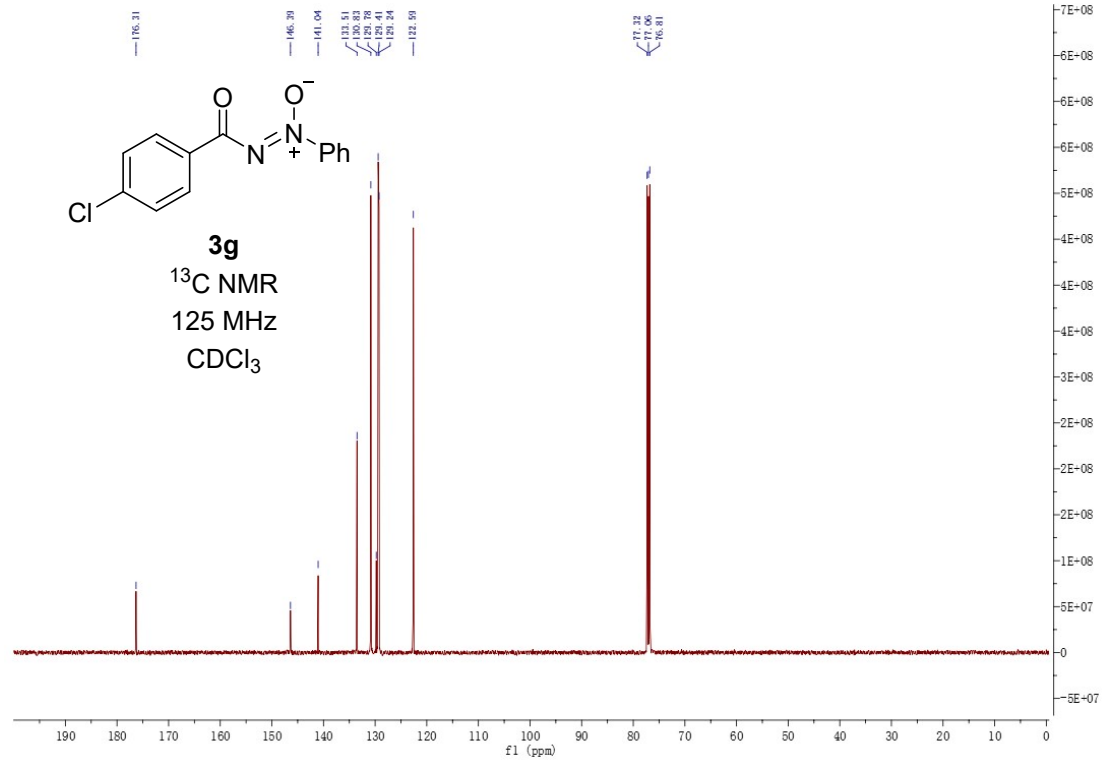

MeO
Ph
3e
13C NMR
101 MHz
CDCl3
f1 (ppm)

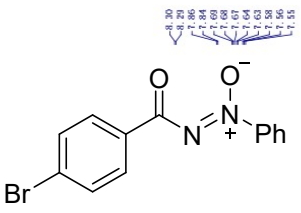

F
Ph
3f
1H NMR
500 MHz
CDCl3
f1 (ppm)


O
O
N
N
Ph
F
3f
13C NMR
125 MHz
CDCl3
f1 (ppm)


O
O
N
N
Ph
F
3f
19F NMR
471 MHZ
CDCl3
f1 (ppm)


Cl
O
O
N
N
Ph
3g
1H NMR
500 MHz
CDCl3
f1 (ppm)


Cl
O
O
N
N
Ph
3g
13C NMR
125 MHz
CDCl3
f1 (ppm)

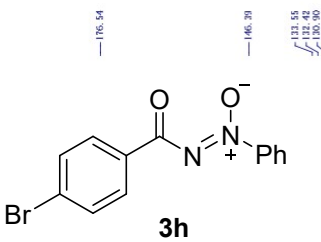


3h

^{1}H NMR

500 MHZ

$CDCl_3$

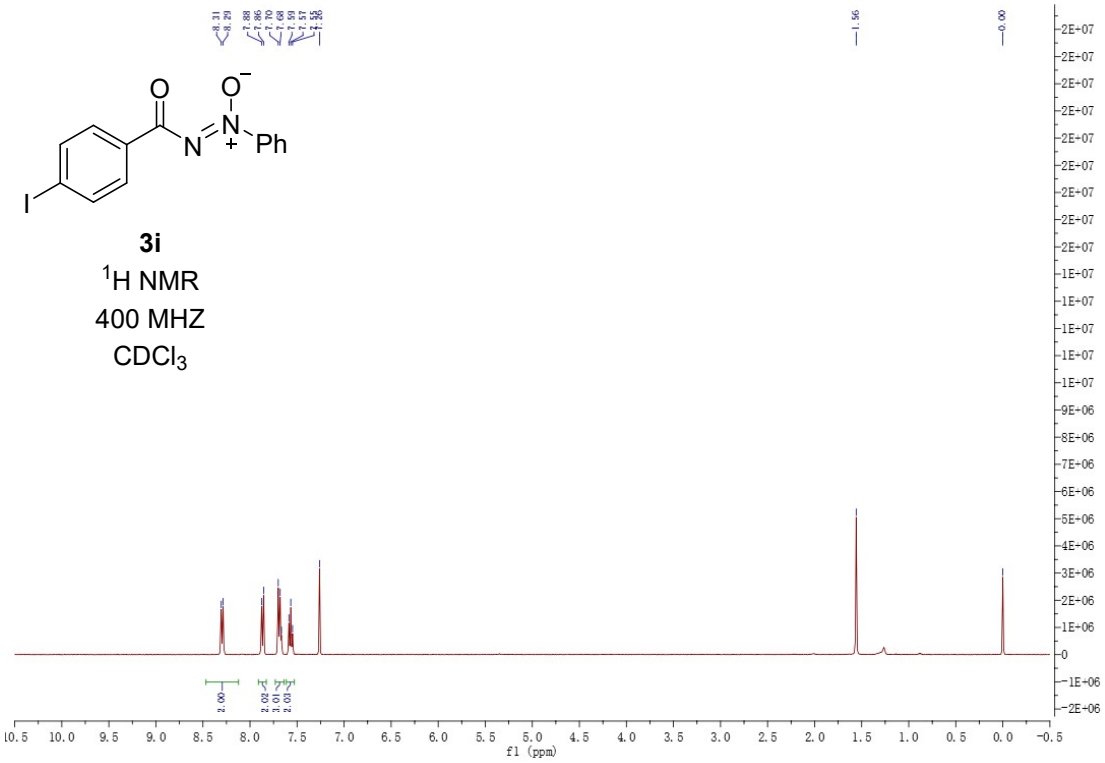


3h

^{13}C NMR

101 MHz

$CDCl_3$

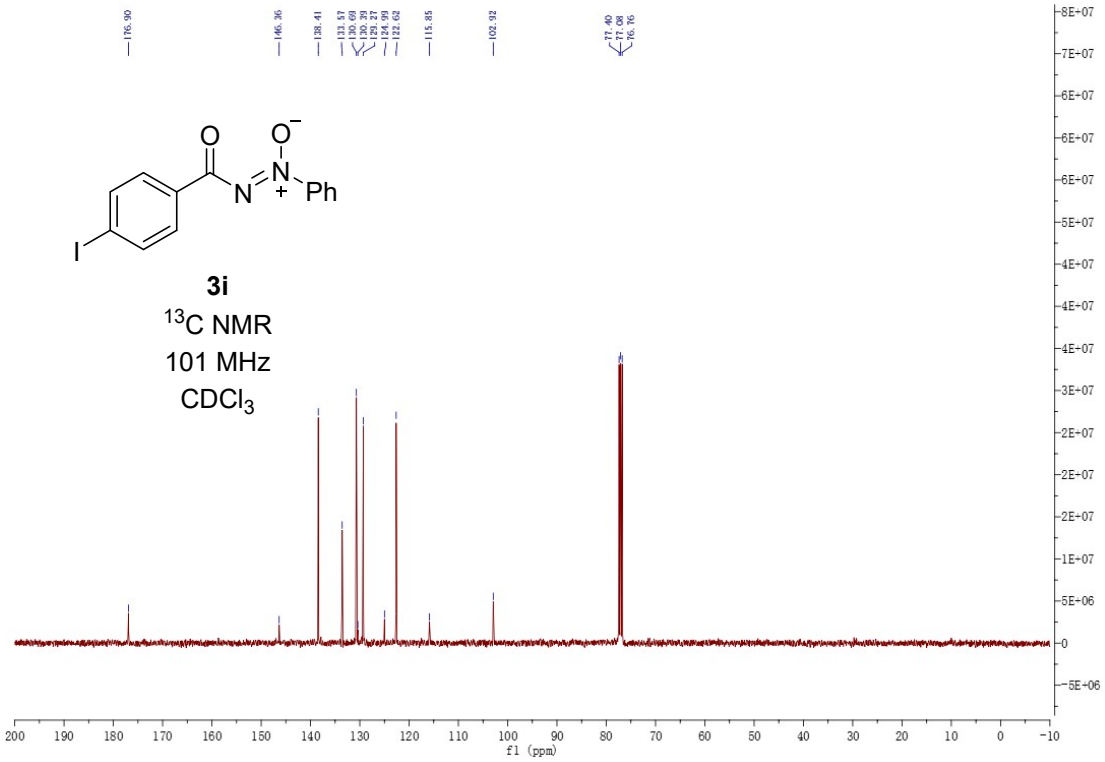


3i

^{1}H NMR

400 MHZ

$CDCl_3$

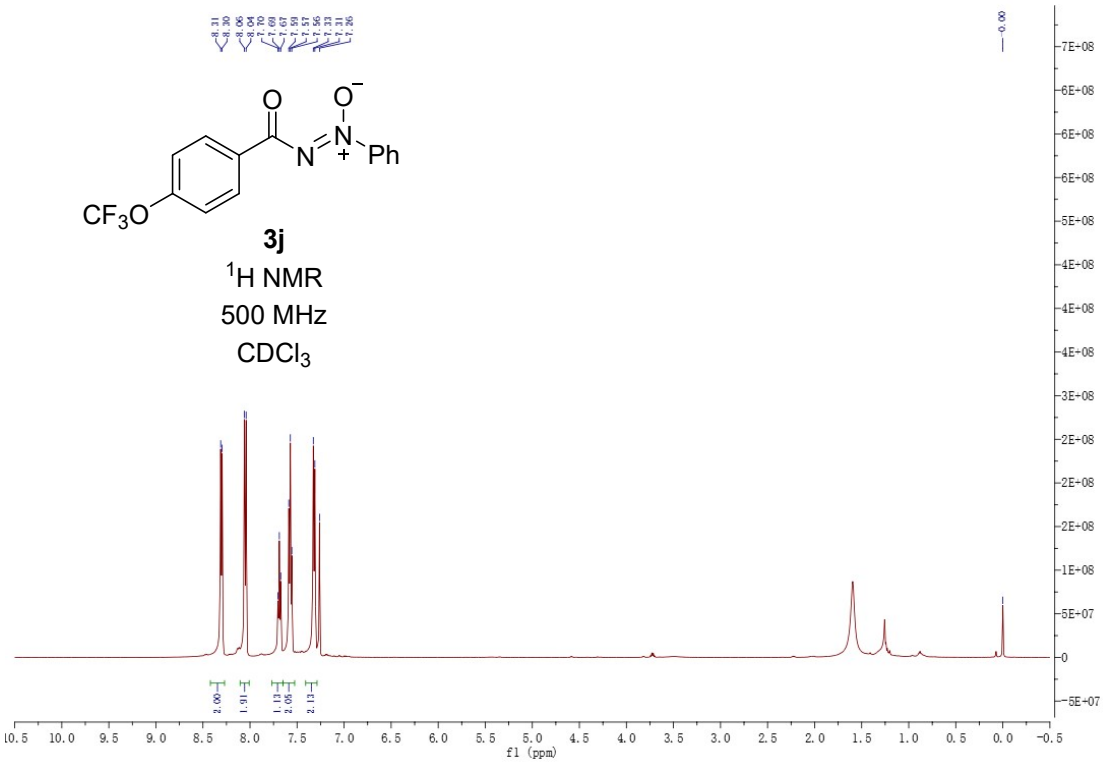


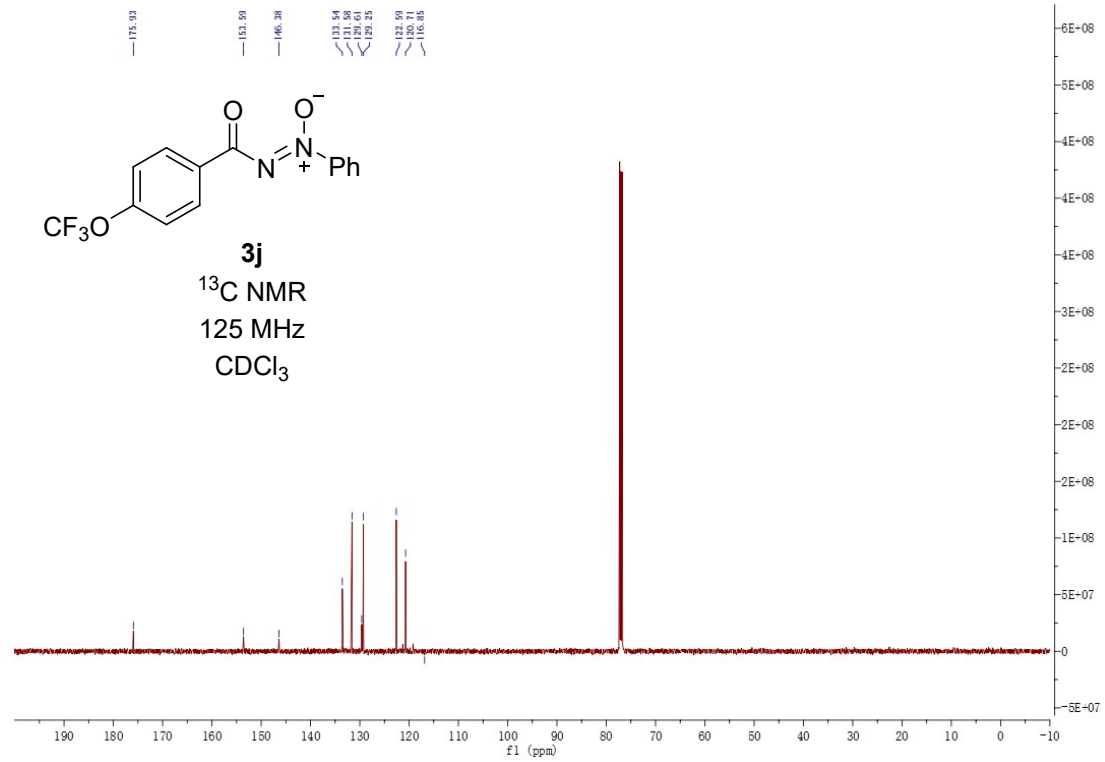
3i

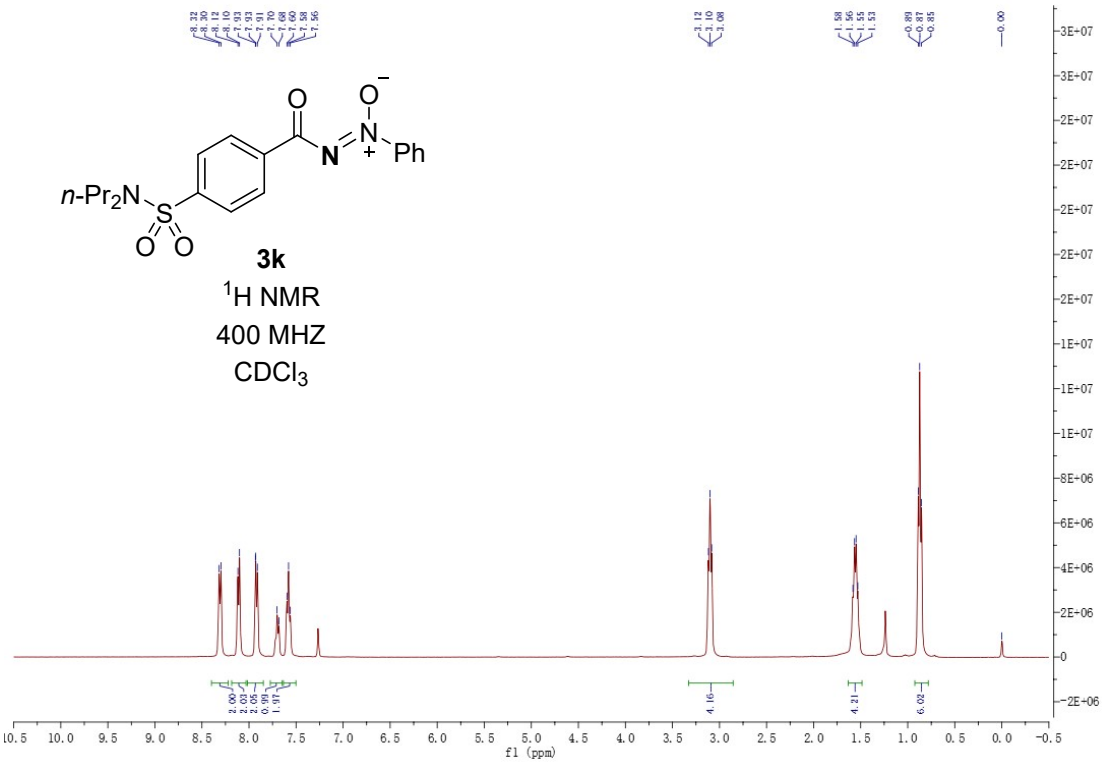
^{13}C NMR

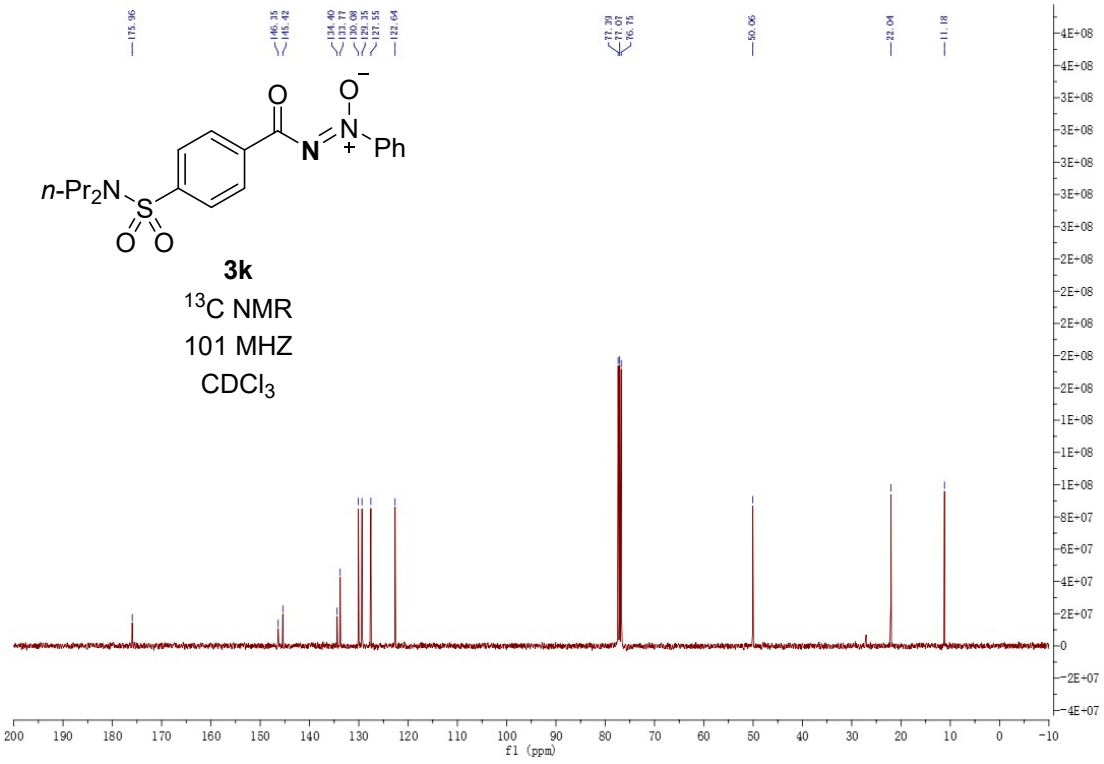
101 MHz

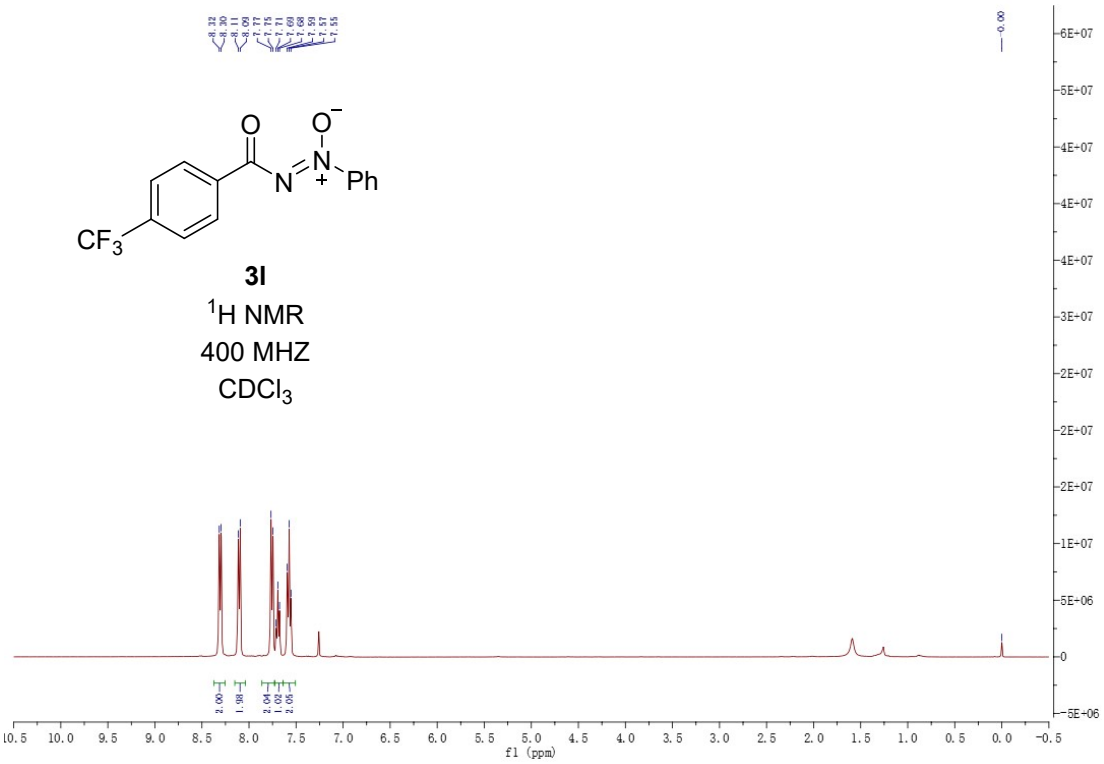
$CDCl_3$

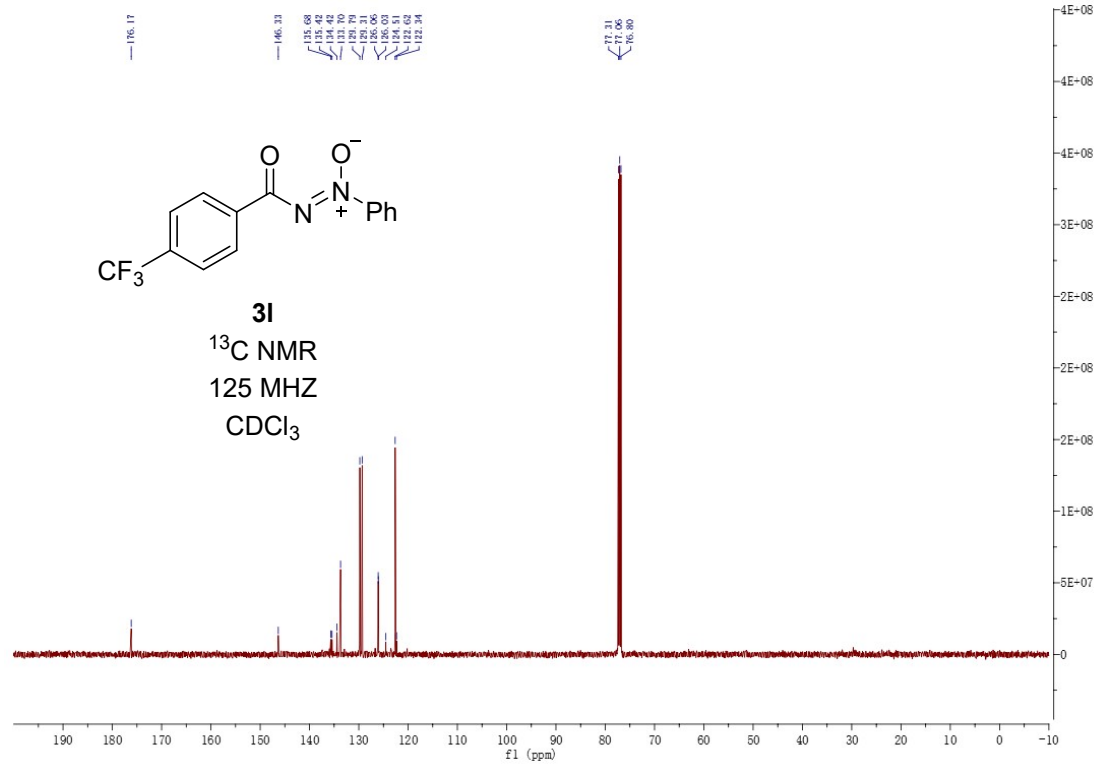

O
O
N
N
Ph
CF3O
3j
1H NMR
500 MHz
CDCl3
f1 (ppm)

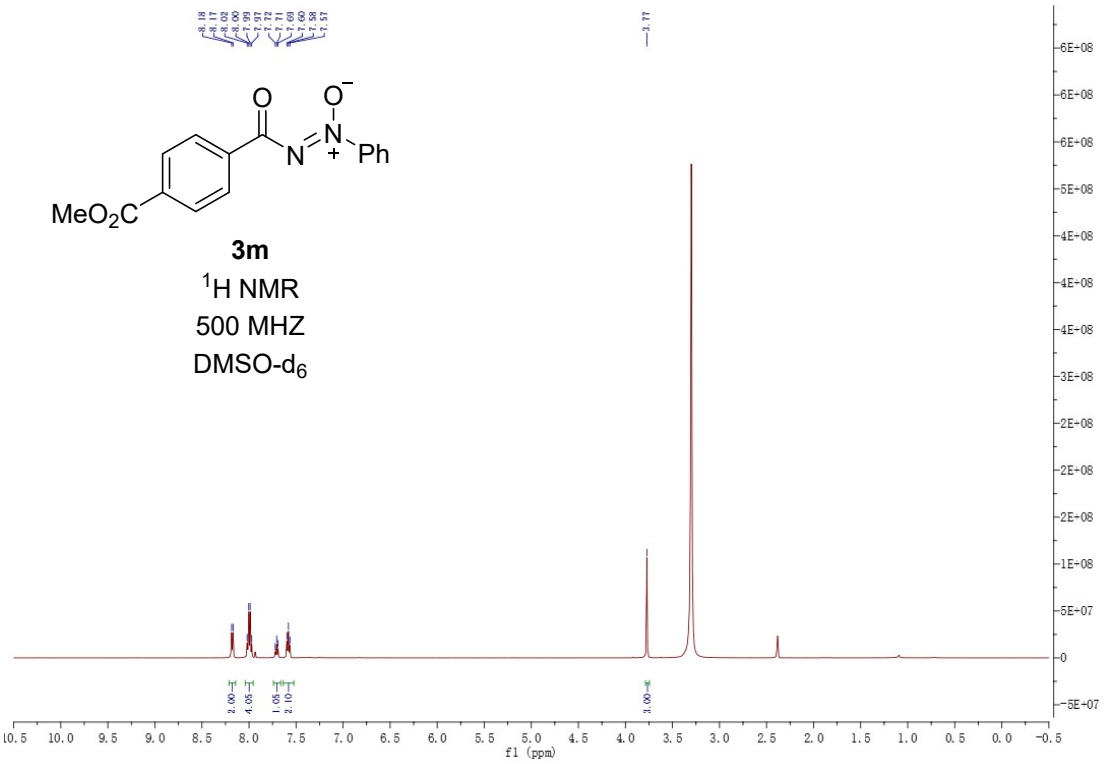

O
O
N
N
Ph
CF3O
3j
13C NMR
125 MHz
CDCl3
f1 (ppm)

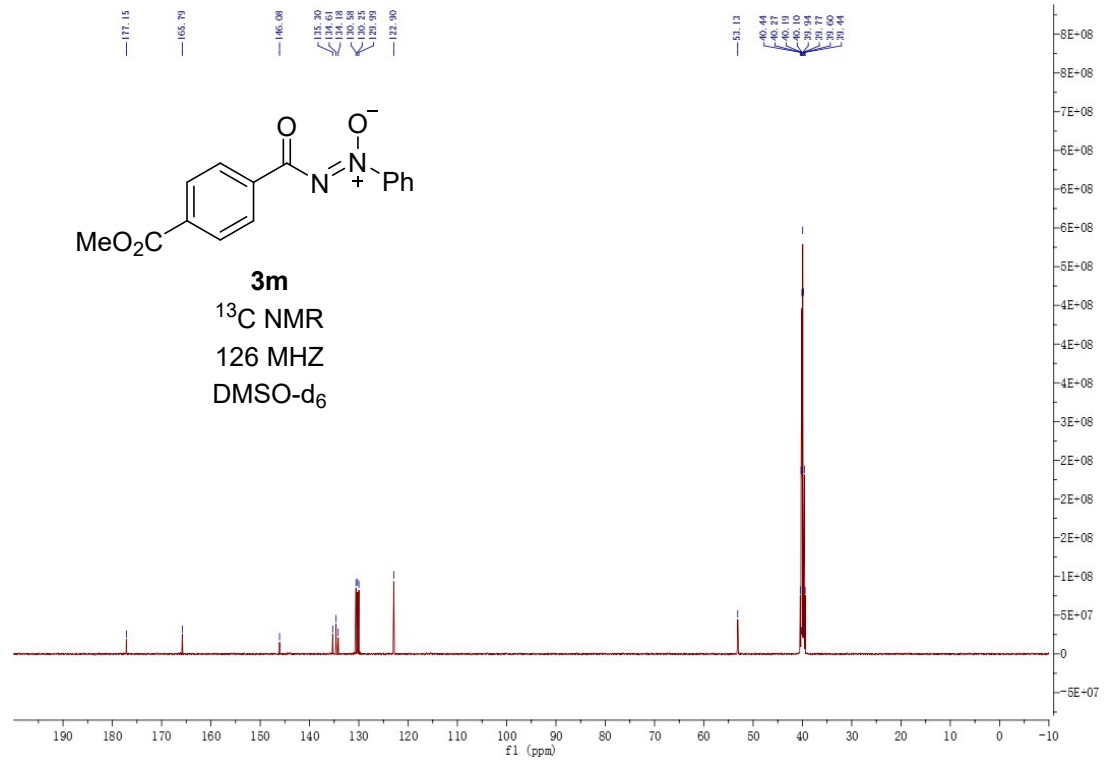

n-Pr2N
S
O
O
O
N
O
Ph
3k
1H NMR
400 MHZ
CDCl3
f1 (ppm)

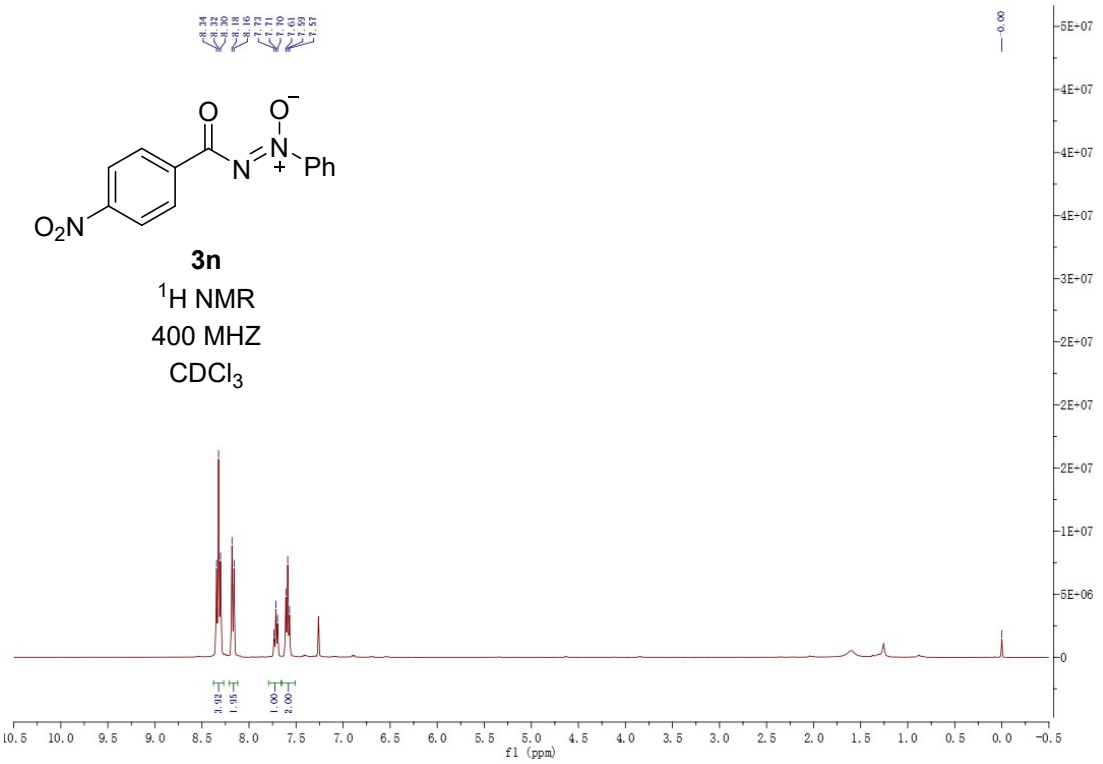

n-Pr2N
S
O
O
O
N
O
Ph
3k
13C NMR
101 MHZ
CDCl3
f1 (ppm)

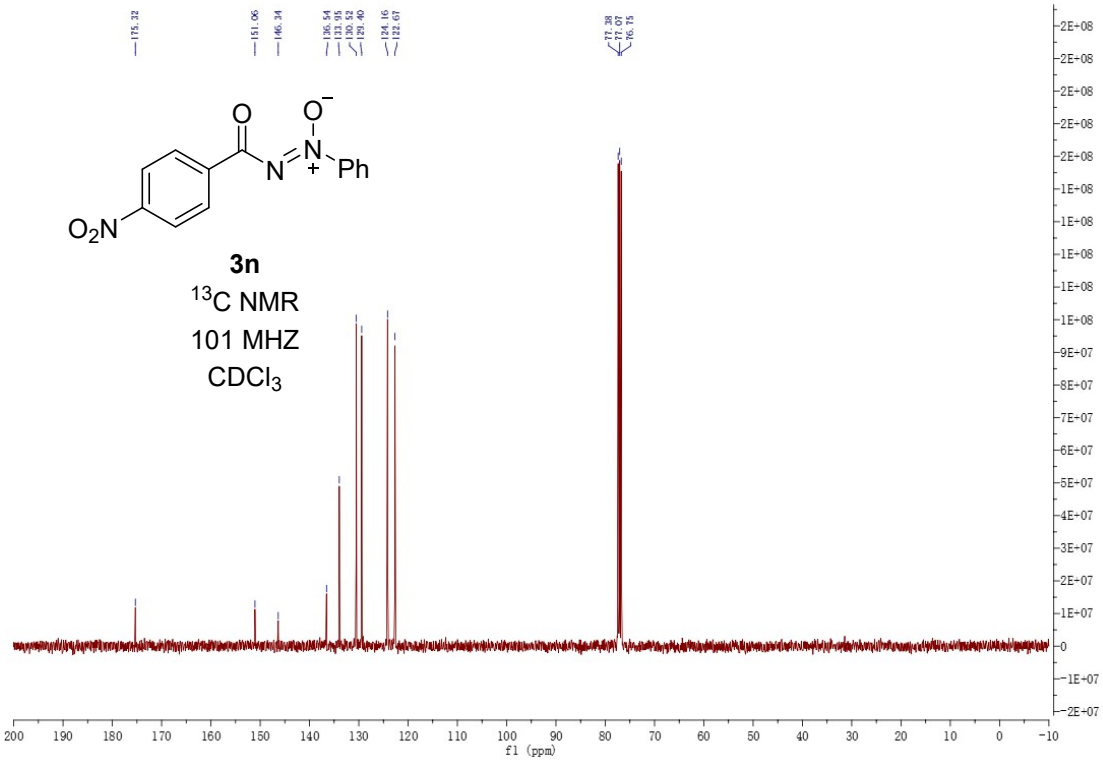

O
O
N
N
Ph
CF3
3I
1H NMR
400 MHZ
CDCl3
f1 (ppm)

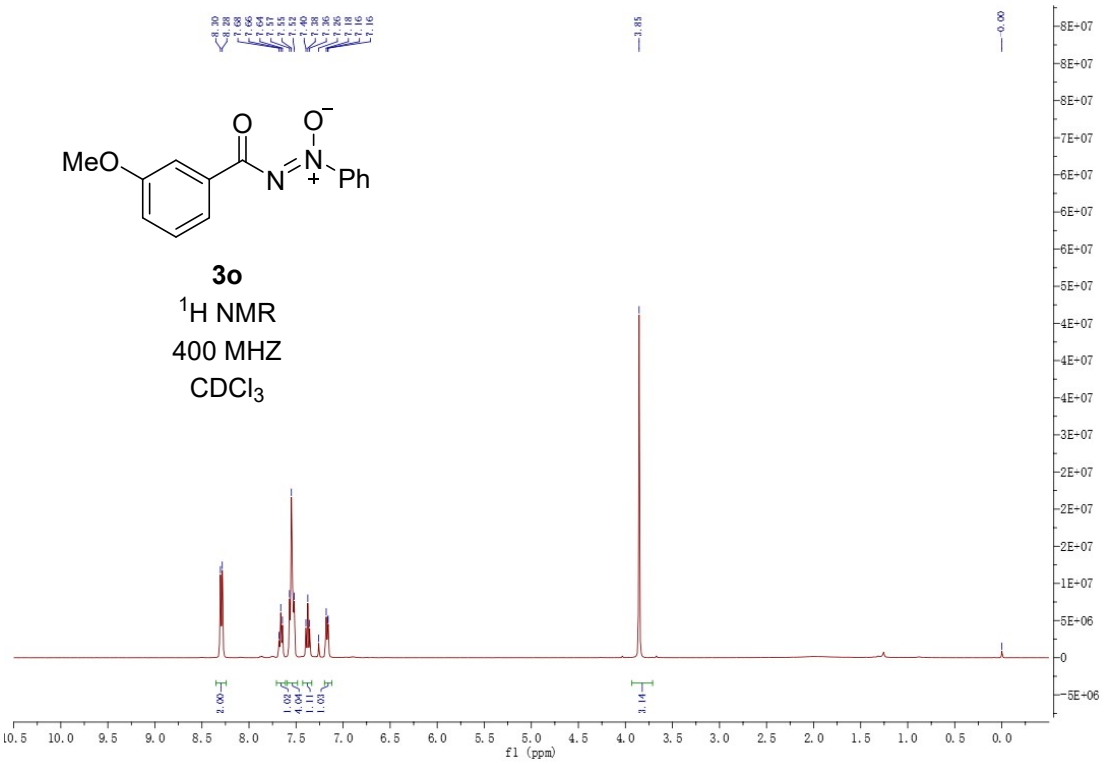

O
O
N
N
Ph
CF3
3I
13C NMR
125 MHZ
CDCl3
f1 (ppm)

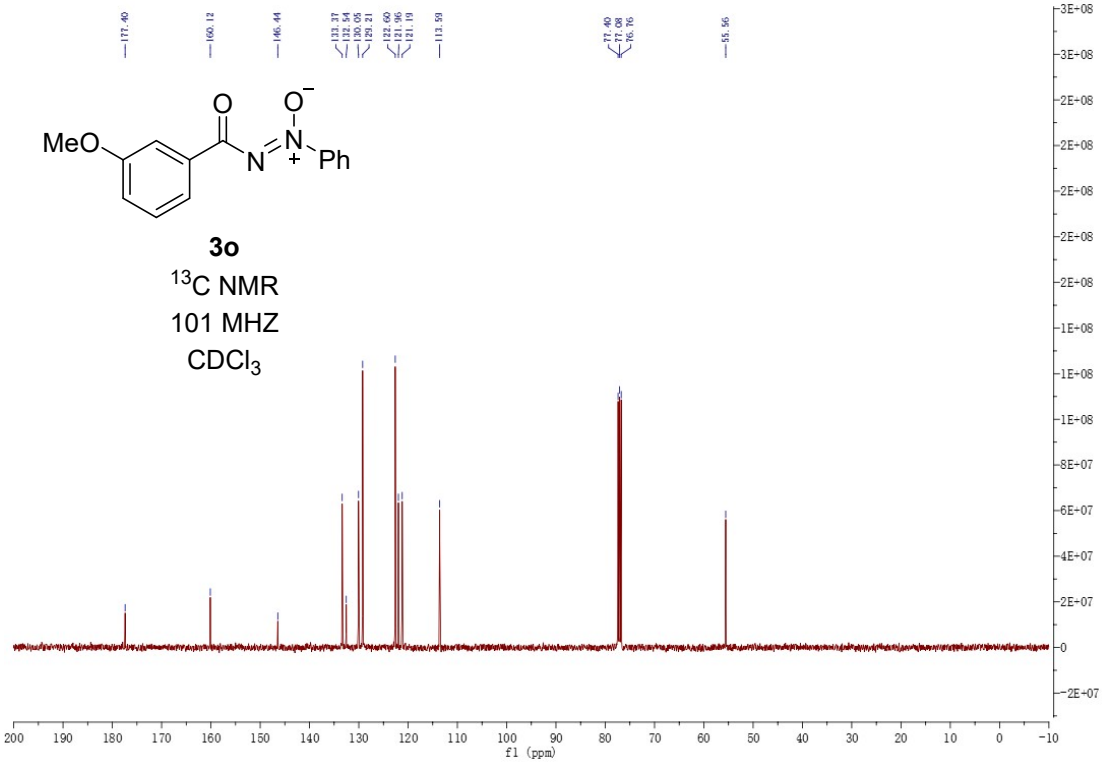

MeO2C
N
O
O
Ph
3m
1H NMR
500 MHZ
DMSO-d6
f1 (ppm)

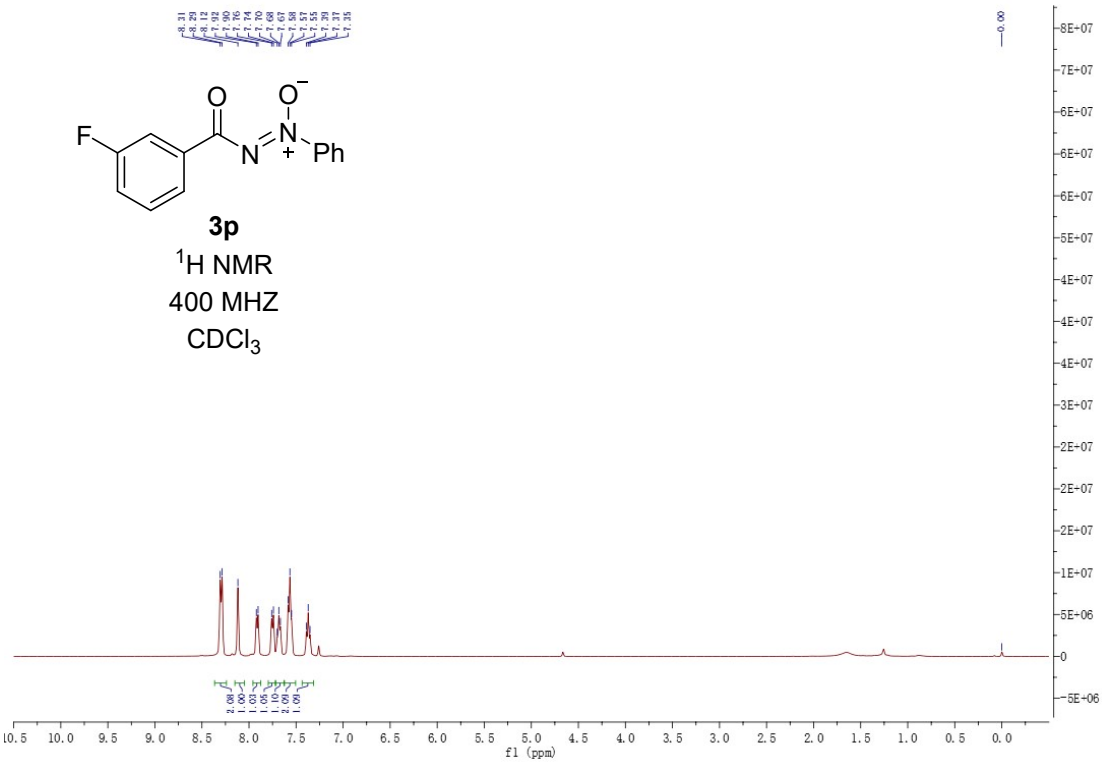

MeO2C
N
O
O
Ph
3m
13C NMR
126 MHZ
DMSO-d6
f1 (ppm)

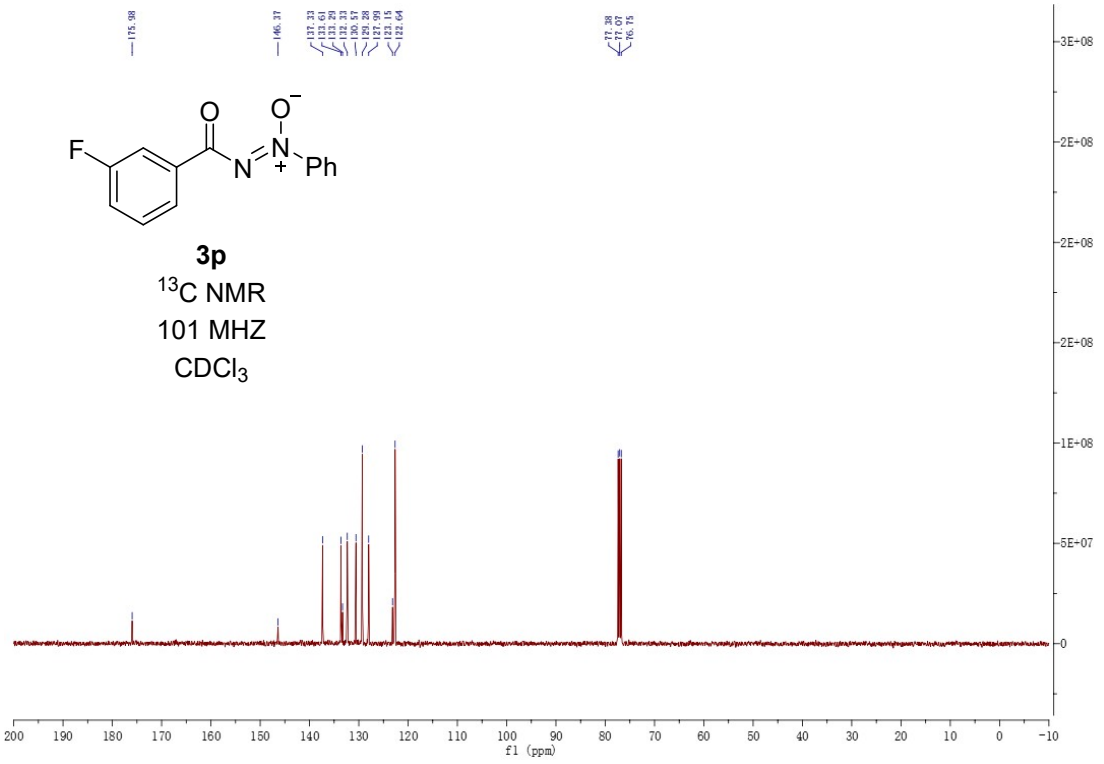

O
O
N
N
Ph
O_2N
3n
^{1}H NMR
400 MHZ
$CDCl_3$
f1 (ppm)

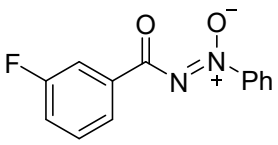

O
O
N
N
Ph
O_2N
3n
^{13}C NMR
101 MHZ
$CDCl_3$
f1 (ppm)


MeO
O
O
N
N
Ph
3o
1H NMR
400 MHZ
CDCl3
f1 (ppm)


MeO
O
O
N
N
Ph
3o
13C NMR
101 MHZ
CDCl3
f1 (ppm)


F
O
O
N
N
Ph
3p
1H NMR
400 MHZ
CDCl3
f1 (ppm)


F
O
O
N
N
Ph
3p
13C NMR
101 MHZ
CDCl3
f1 (ppm)

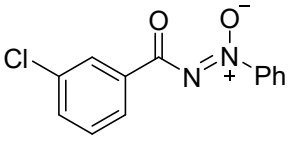


3p

^{19}F NMR

471 MHZ

$CDCl_3$

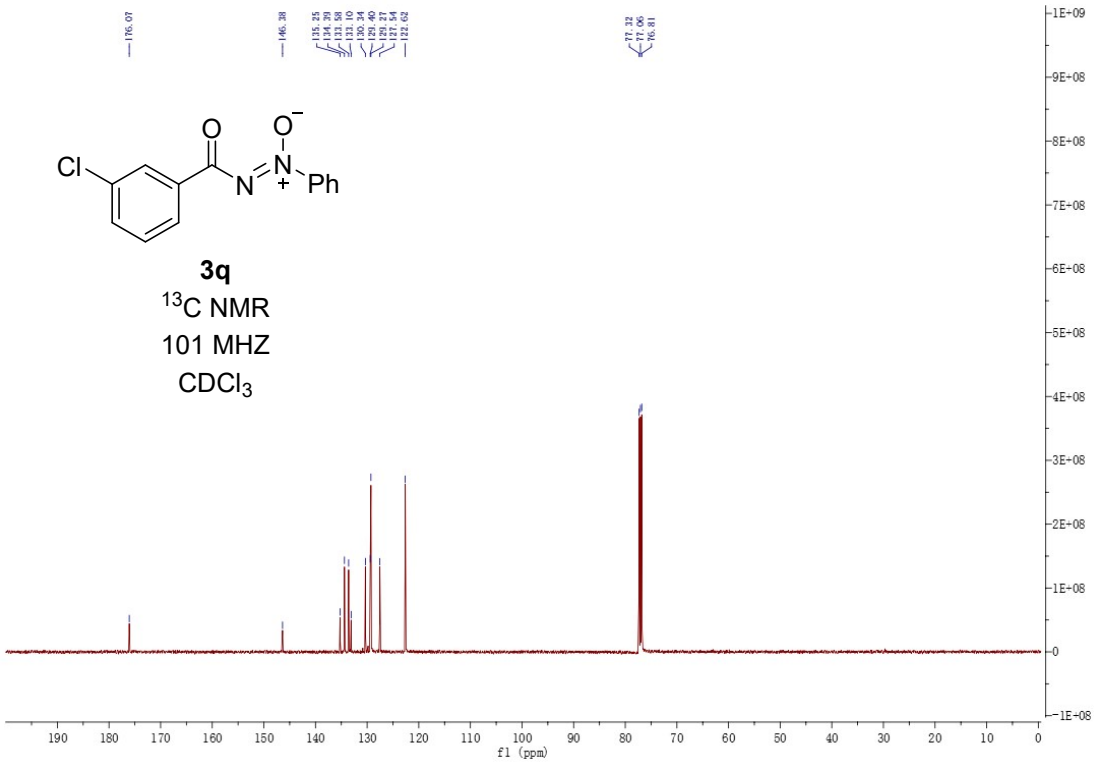


3q

^{1}H NMR

400 MHZ

$CDCl_3$

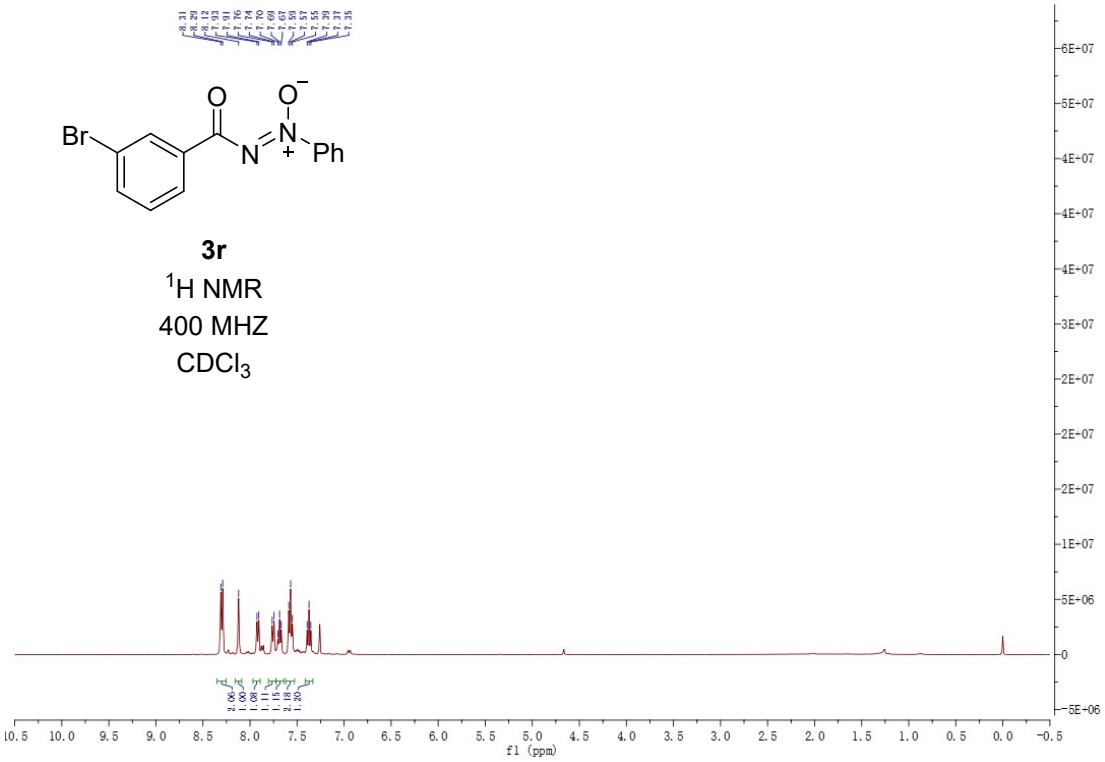


3q

^{13}C NMR

101 MHZ

$CDCl_3$

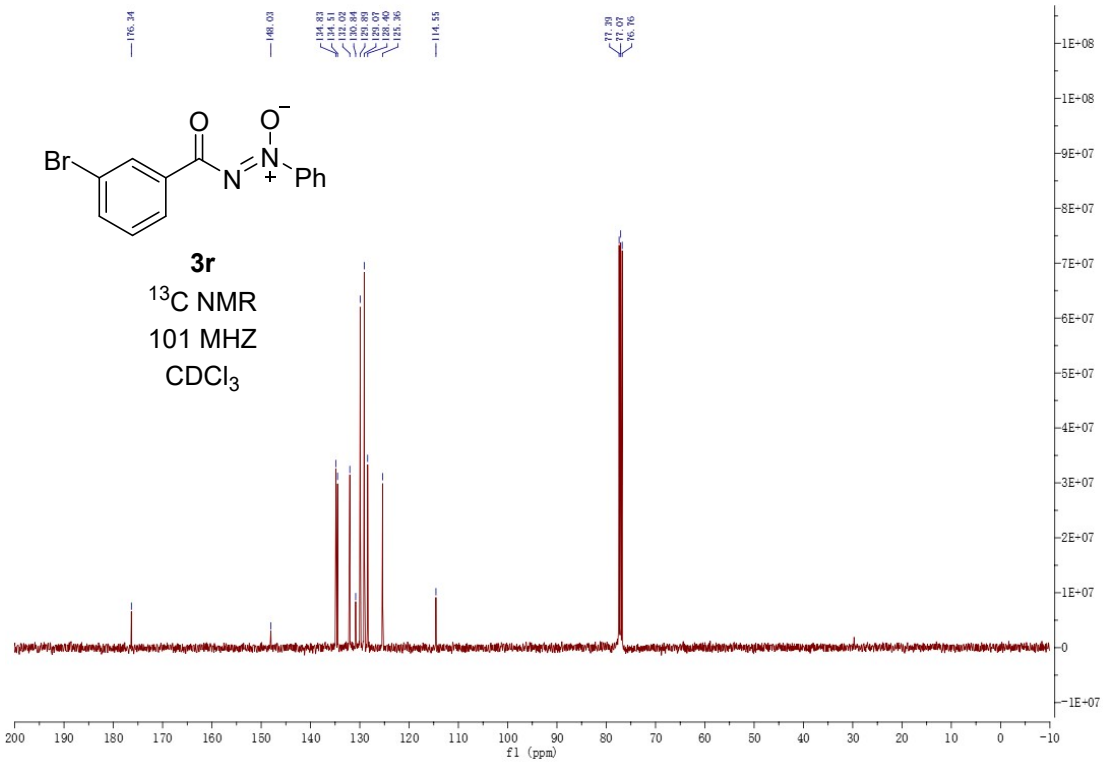


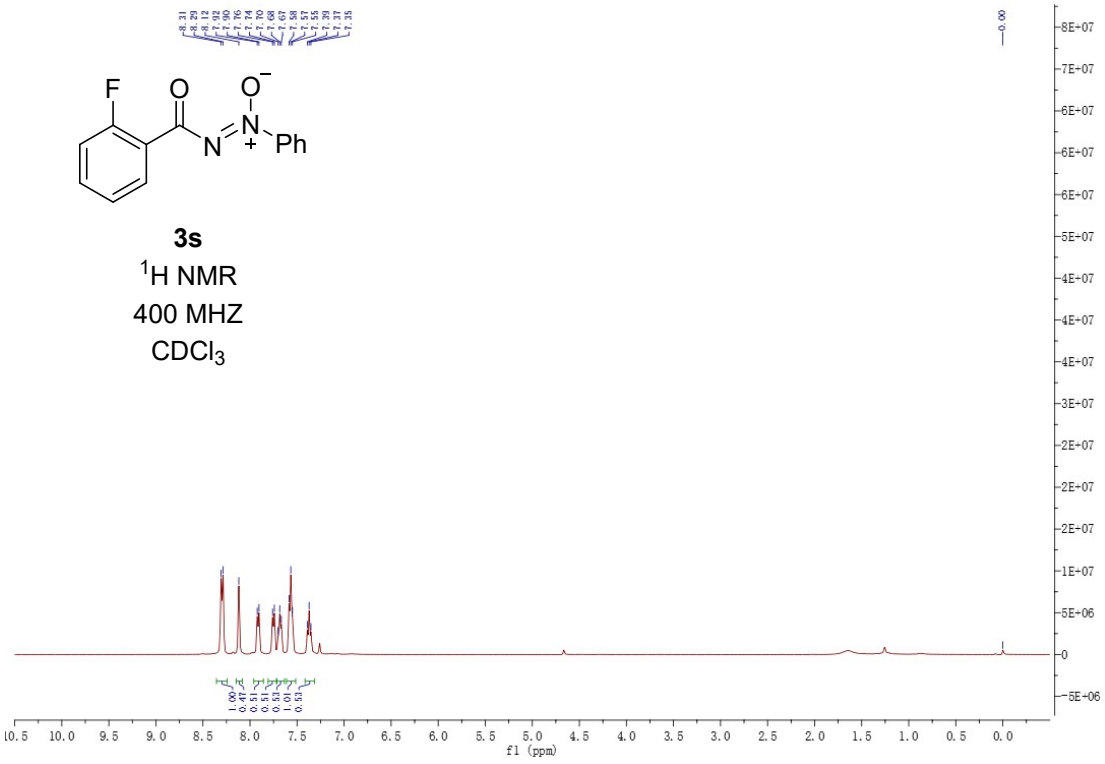
3r

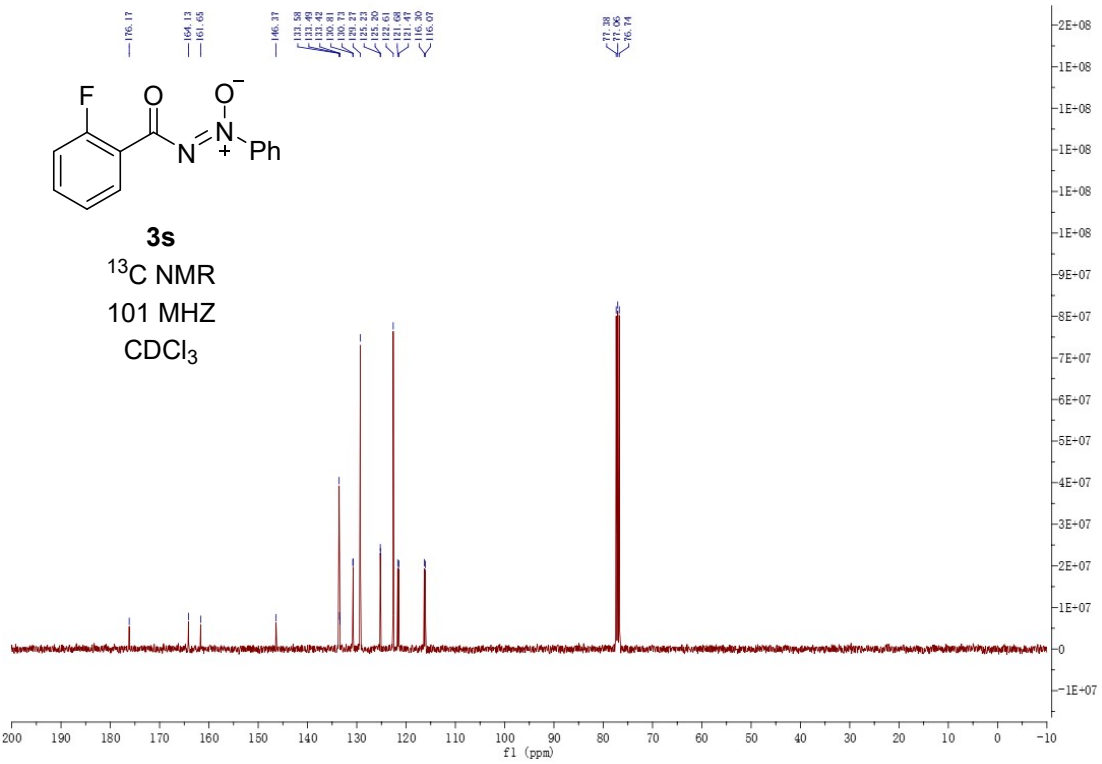
^{1}H NMR

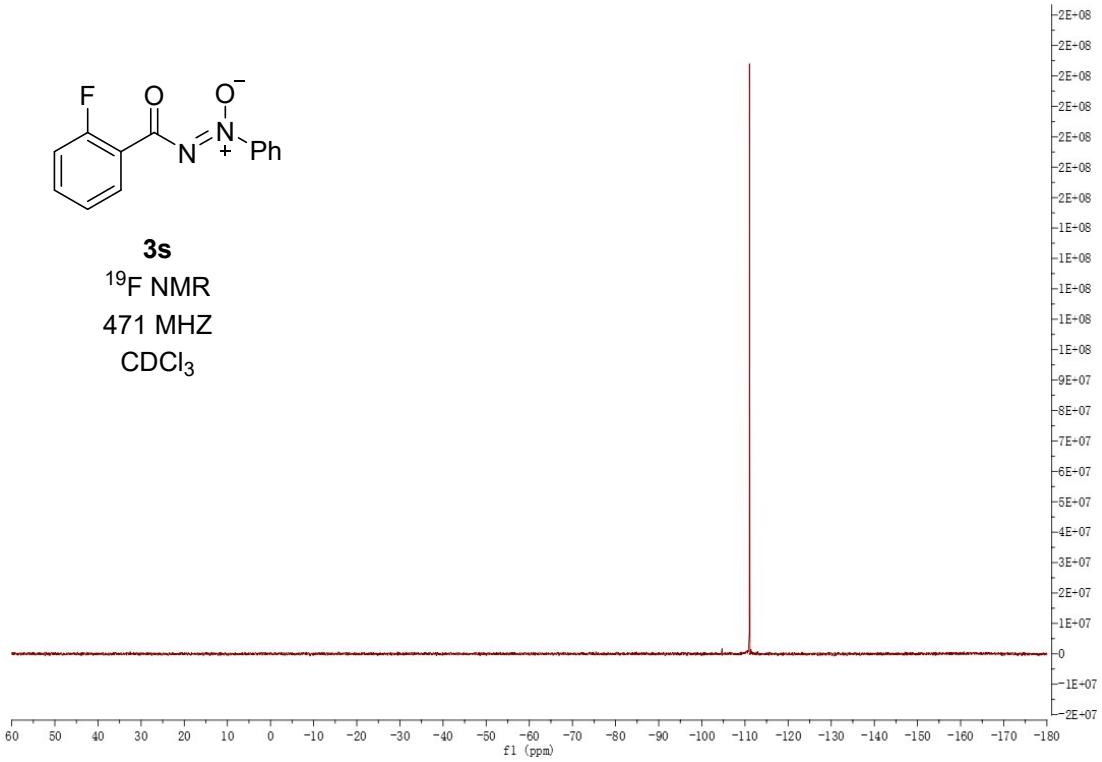
400 MHZ

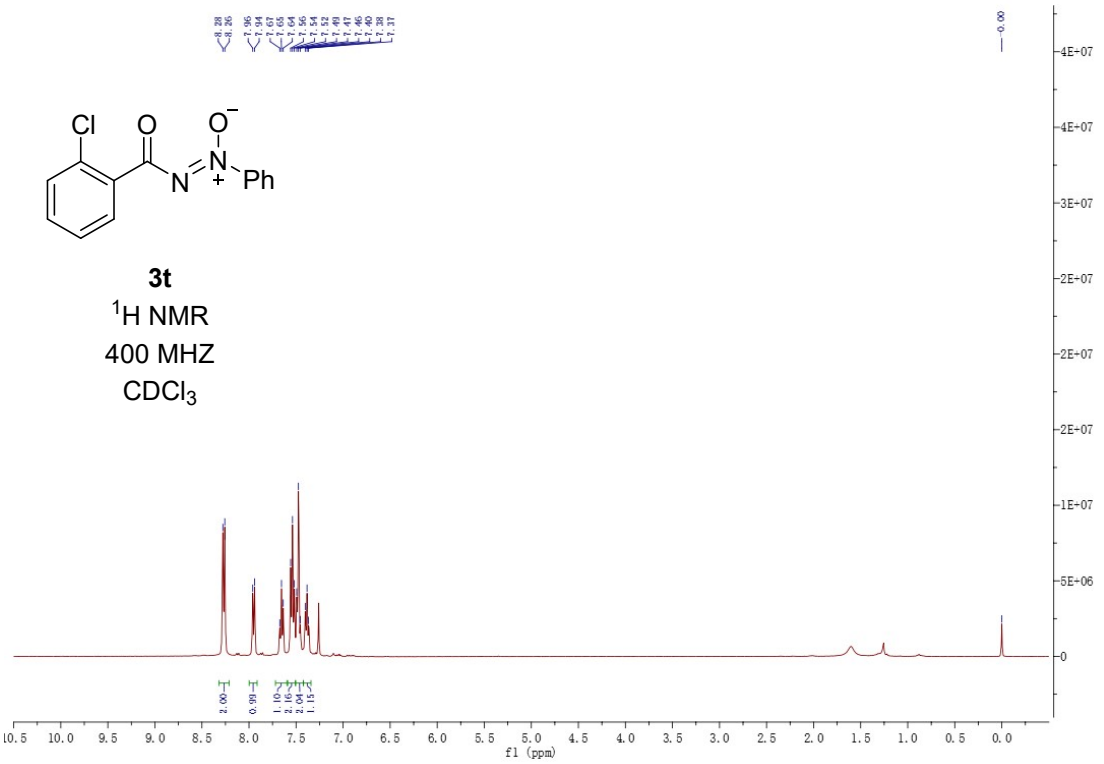
$CDCl_3$

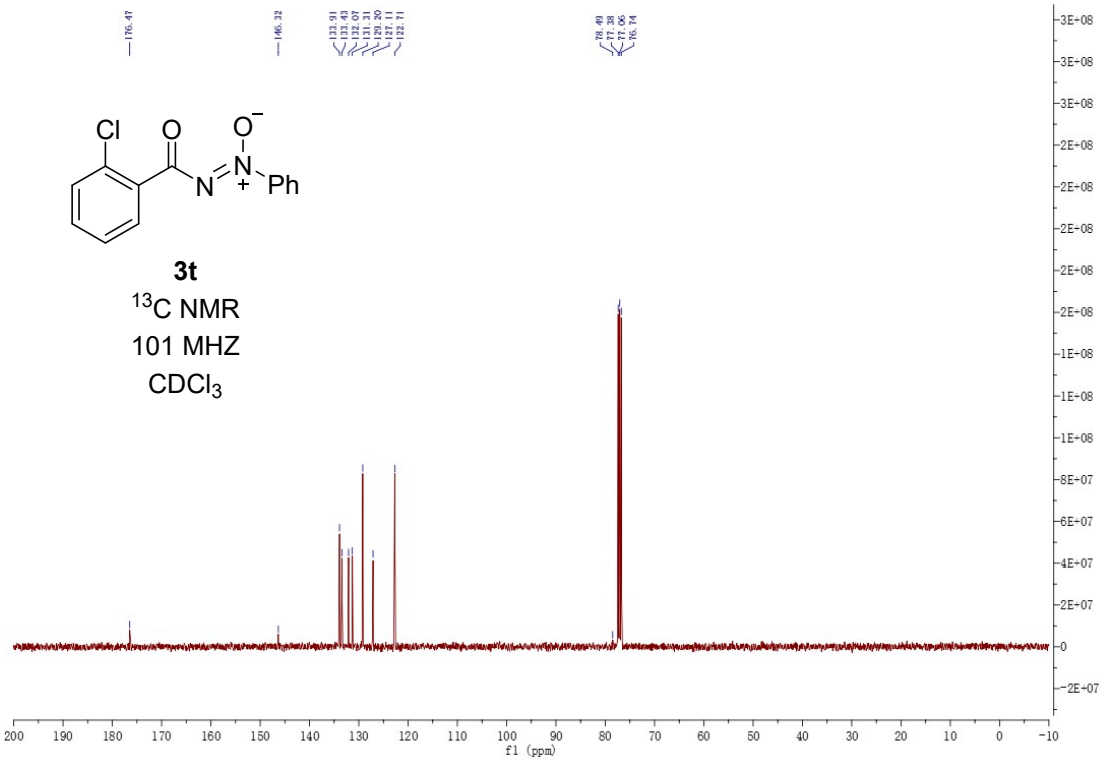

Br
O
O
N
N
Ph
3r
13C NMR
101 MHZ
CDCl3
f1 (ppm)

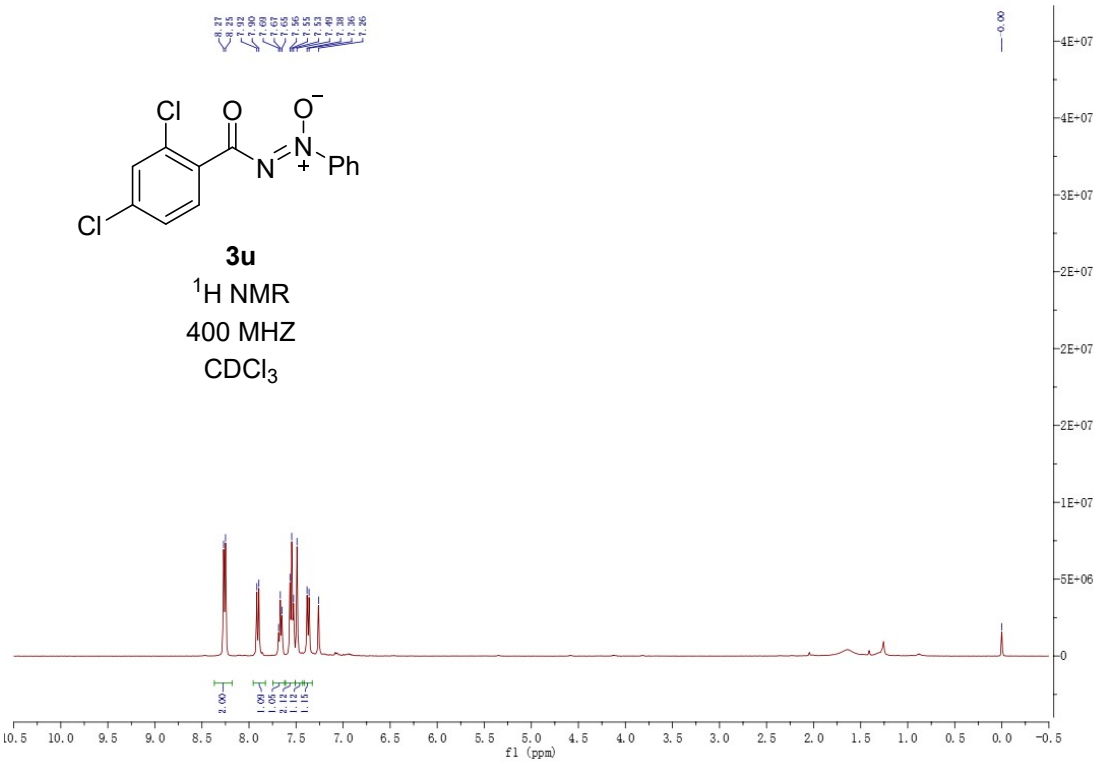

F
O
O
N
N
Ph
3s
1H NMR
400 MHZ
CDCl3
f1 (ppm)


F
O
O
N
N
Ph
3s
13C NMR
101 MHZ
CDCl3
f1 (ppm)


F
O
O
N
N
Ph
3s
19F NMR
471 MHZ
CDCl3
f1 (ppm)


Cl
O
O
N
N
Ph
3t
1H NMR
400 MHZ
CDCl3
f1 (ppm)


Cl
O
O
N
N
Ph
3t
13C NMR
101 MHZ
CDCl3
f1 (ppm)

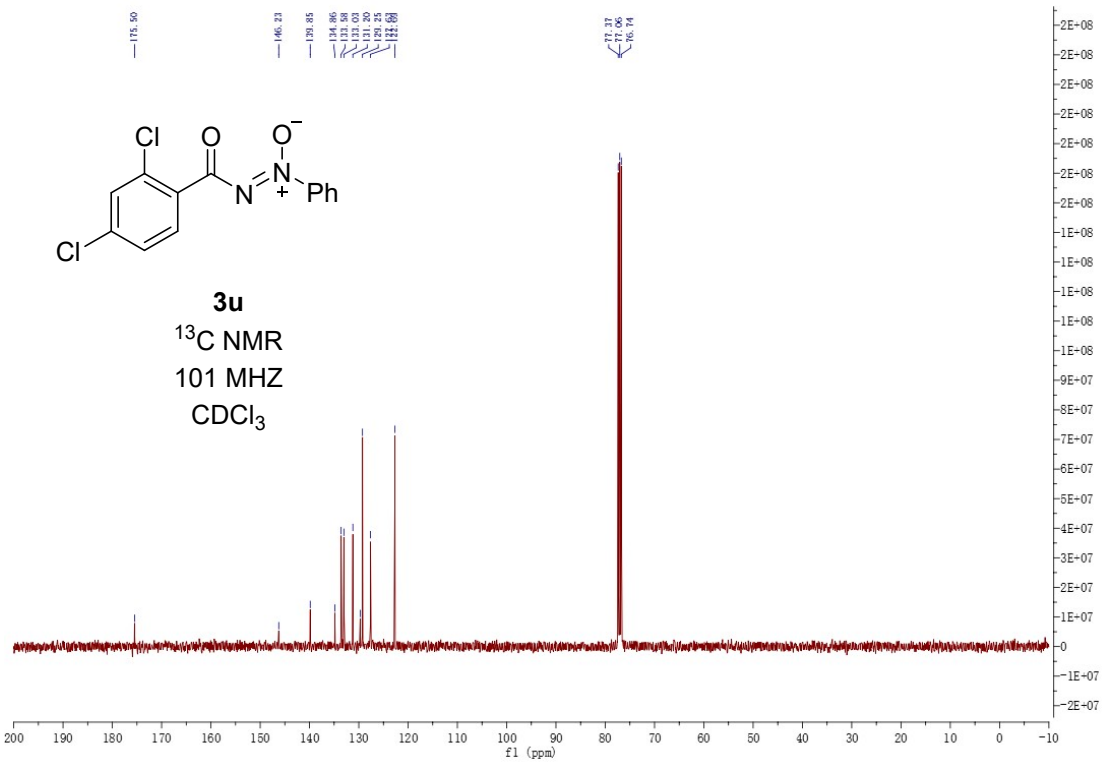


3u

^{1}H NMR

400 MHZ

$CDCl_3$

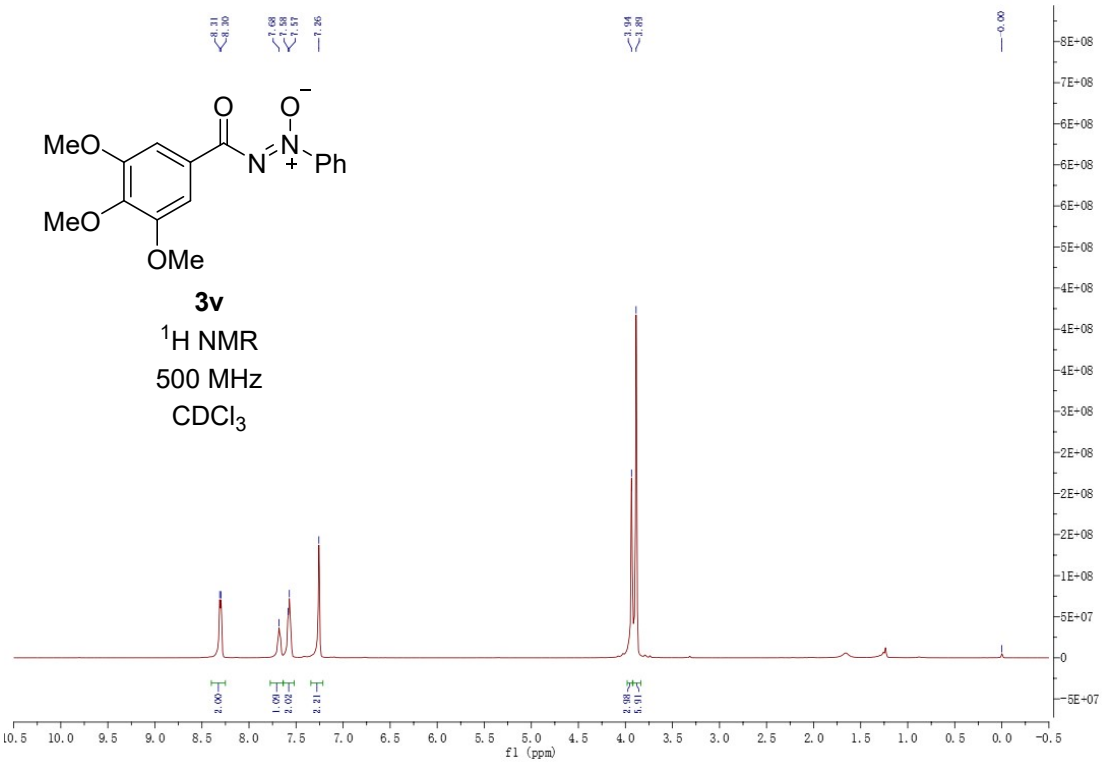


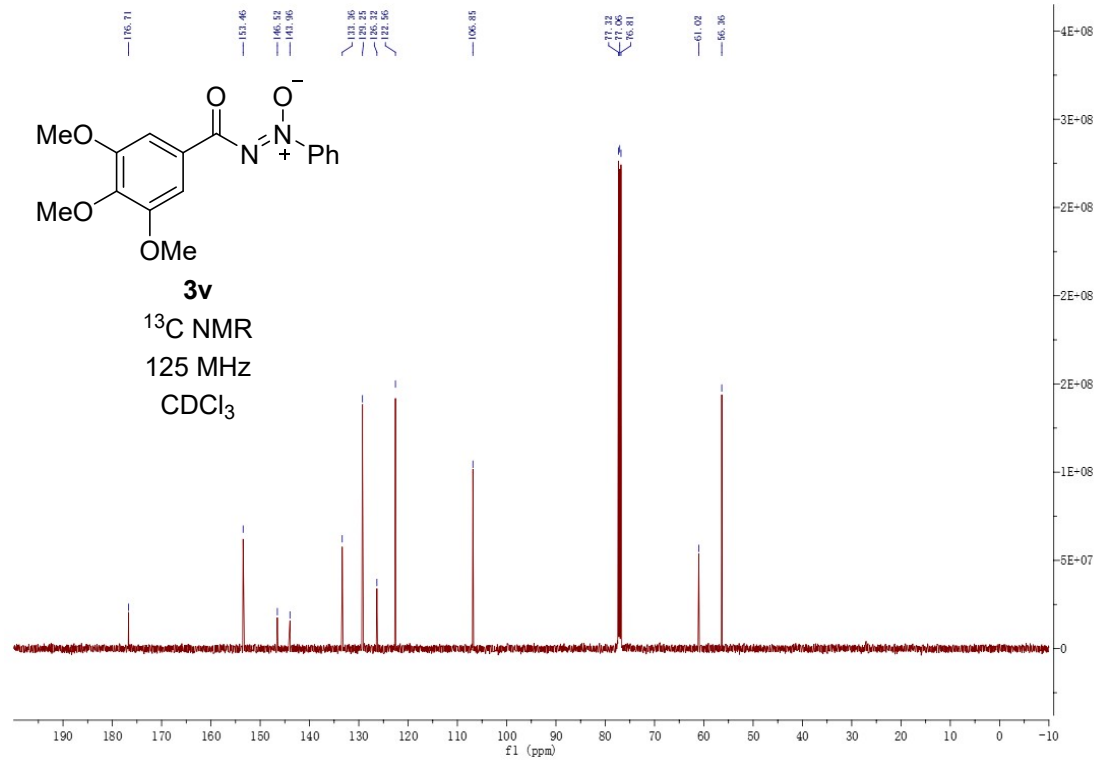
3u

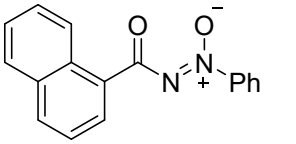
^{13}C NMR

101 MHZ

$CDCl_3$


MeO
MeO
OMe
O
O
N
N
Ph
3v
1H NMR
500 MHz
CDCl3
f1 (ppm)


MeO
MeO
OMe
O
O
N
N
Ph
3v
13C NMR
125 MHz
CDCl3
f1 (ppm)

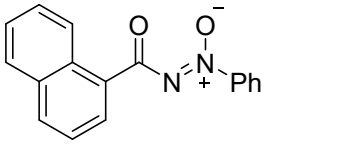


3w

^{1}H NMR

400 MHz

$CDCl_3$

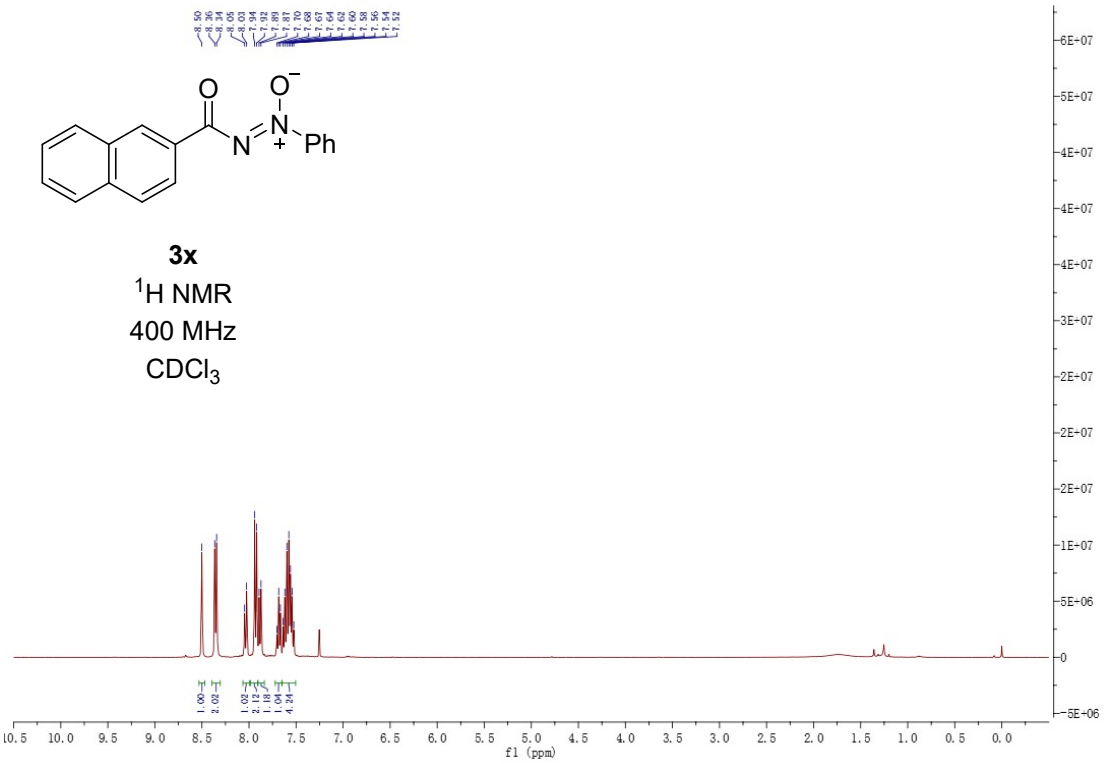


3w

^{13}C NMR

125 MHz

$CDCl_3$

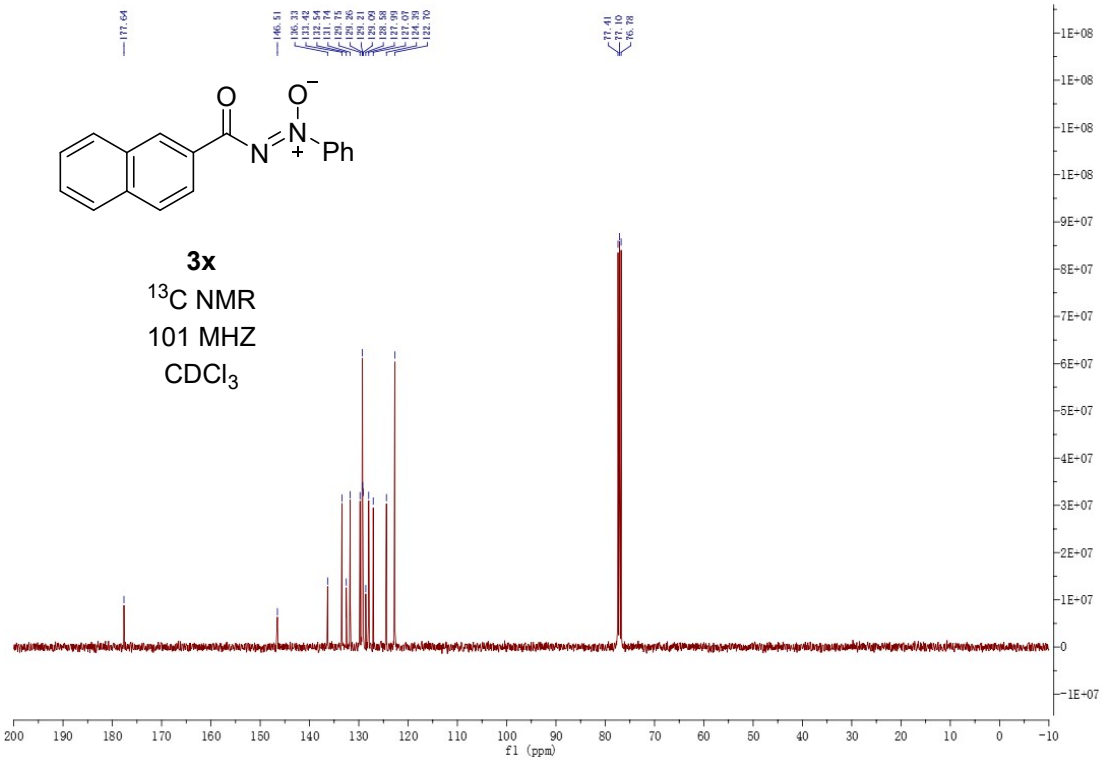


3x

^{1}H NMR

400 MHz

$CDCl_3$

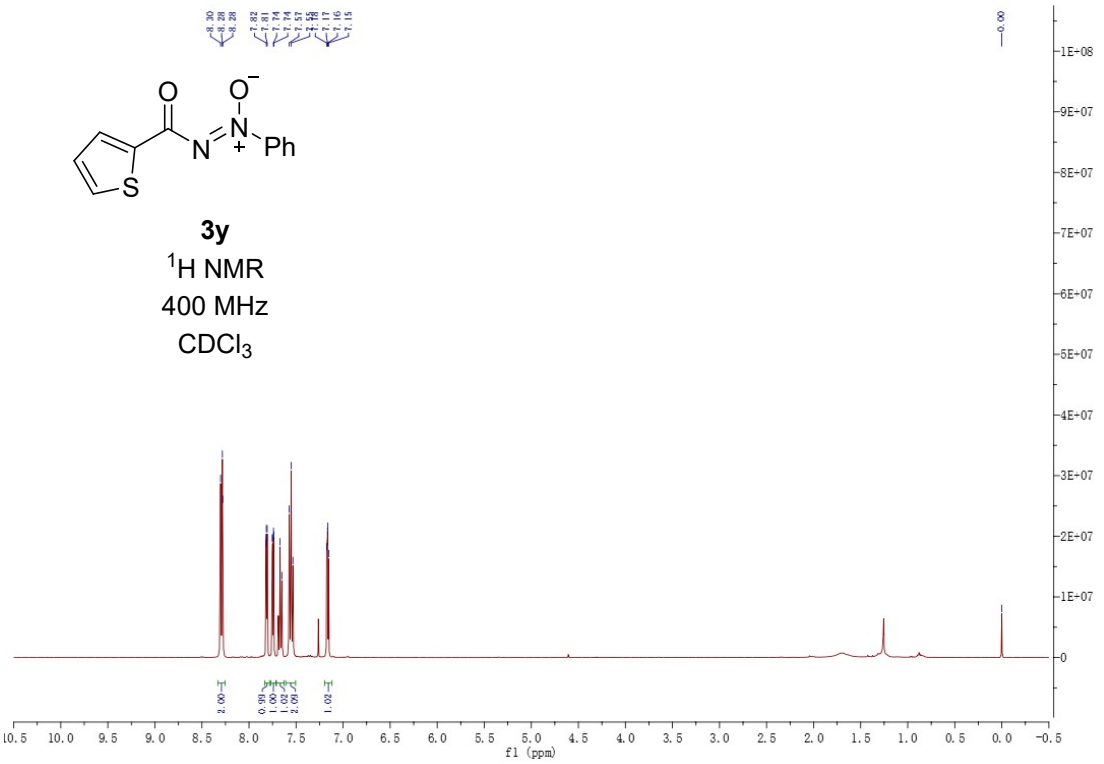


3x

^{13}C NMR

101 MHZ

$CDCl_3$

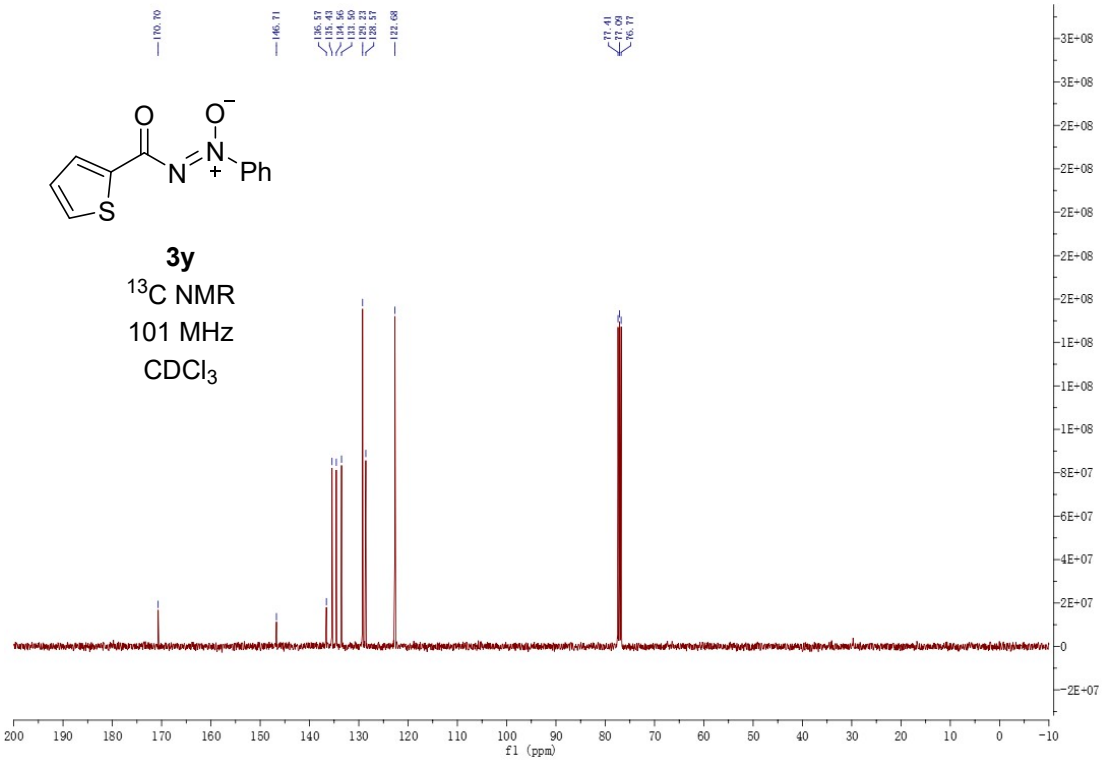


3y

^{1}H NMR

400 MHz

$CDCl_3$

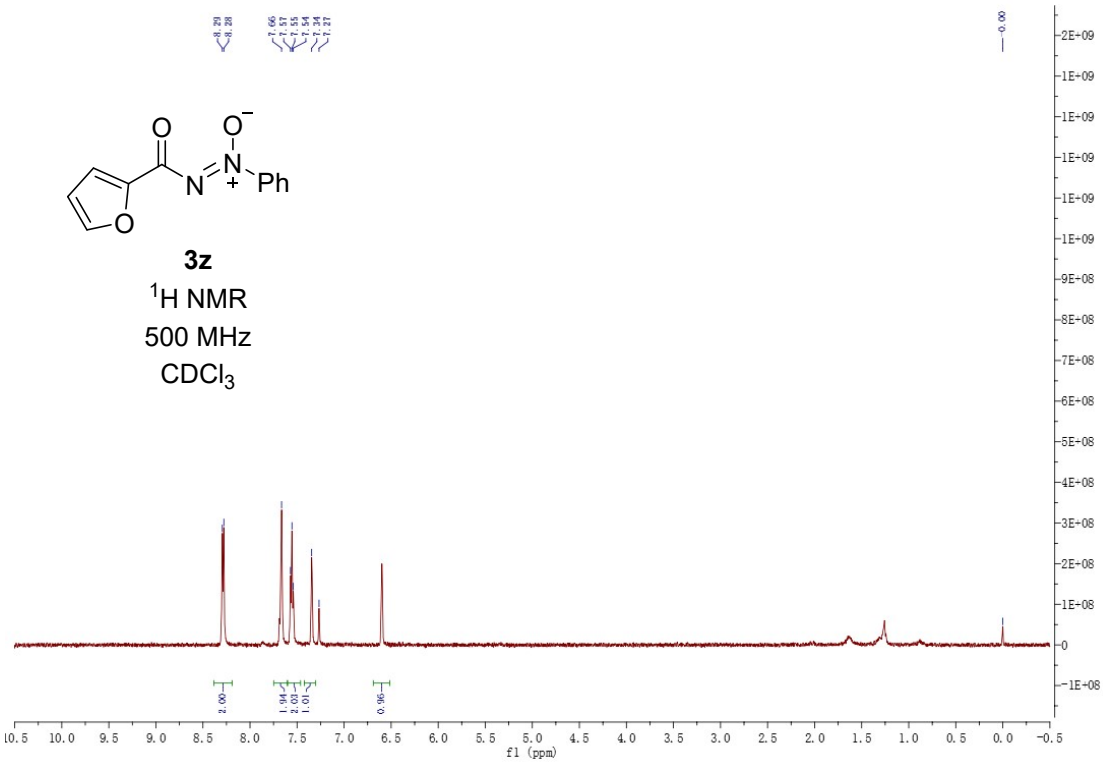


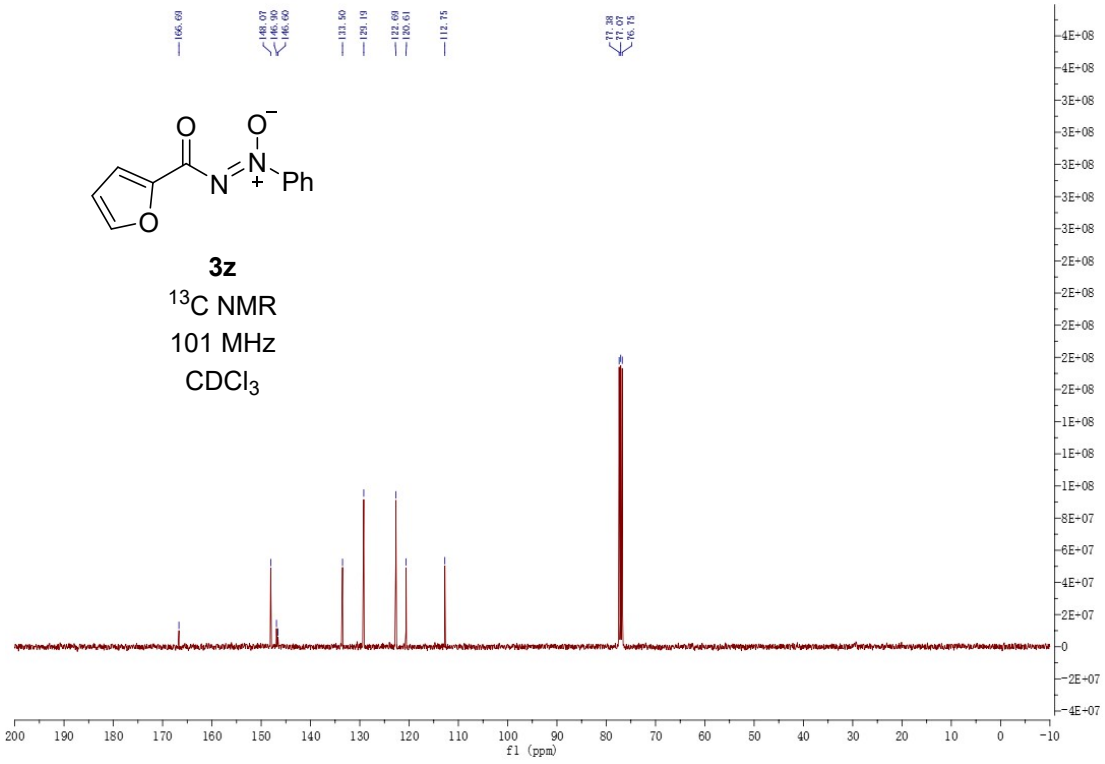
3y

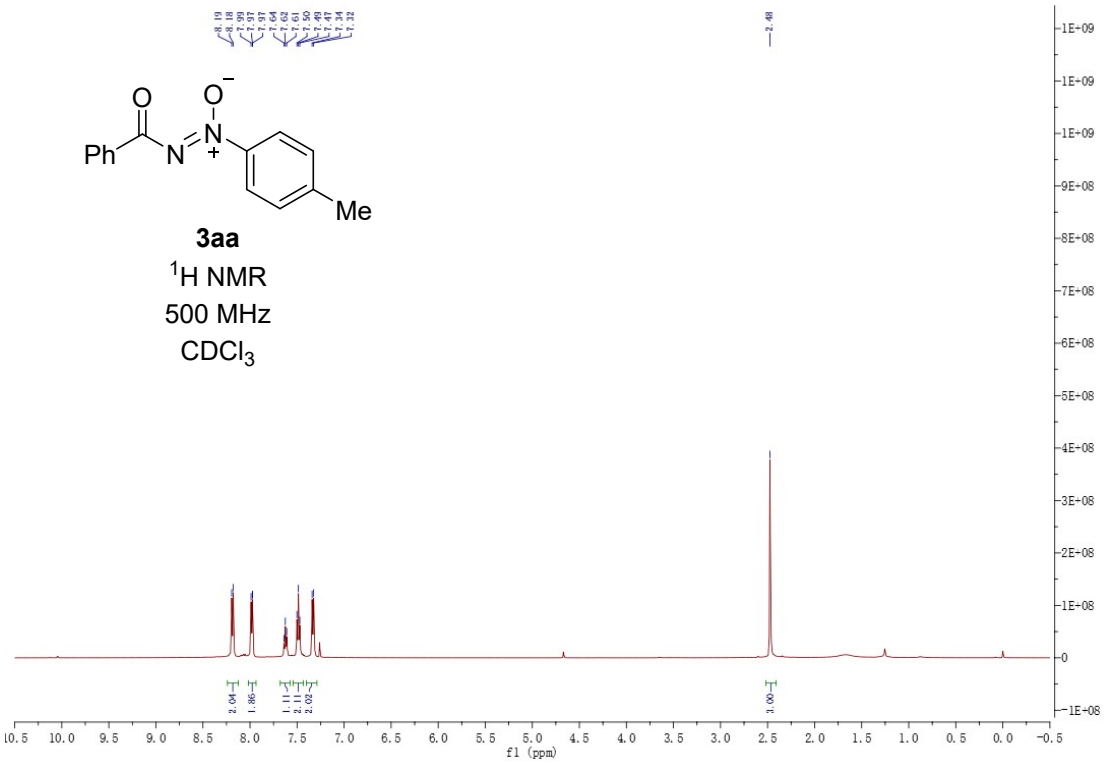
^{13}C NMR

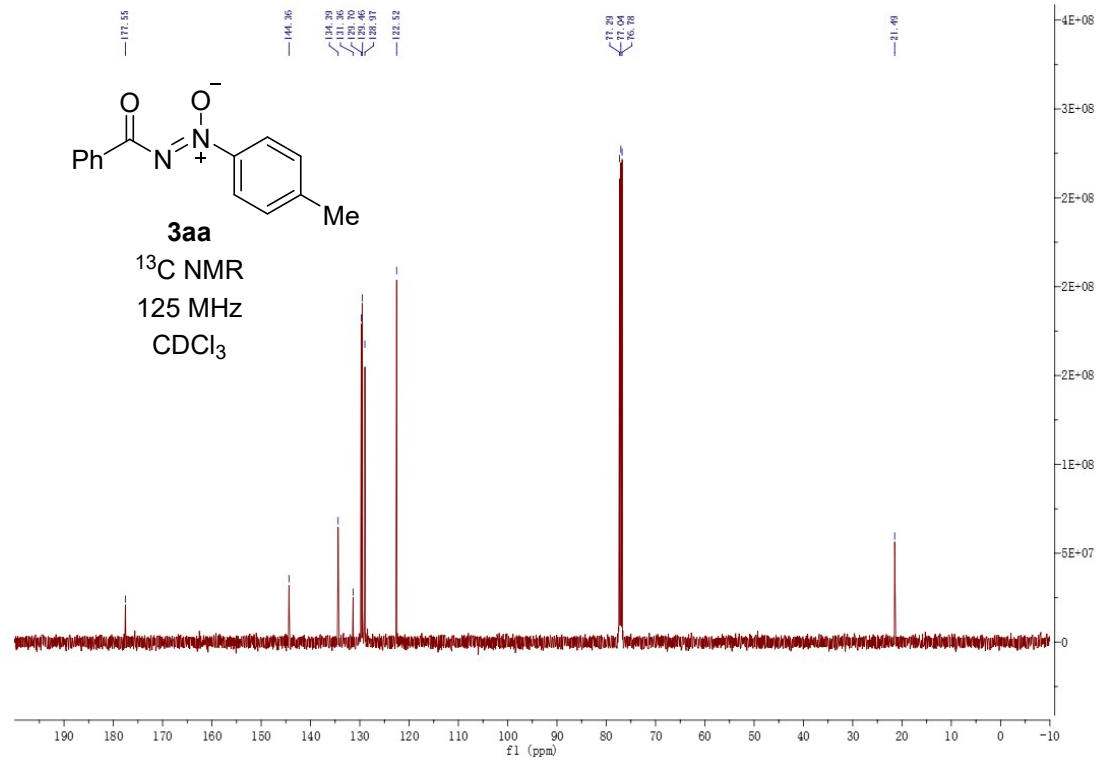
101 MHz

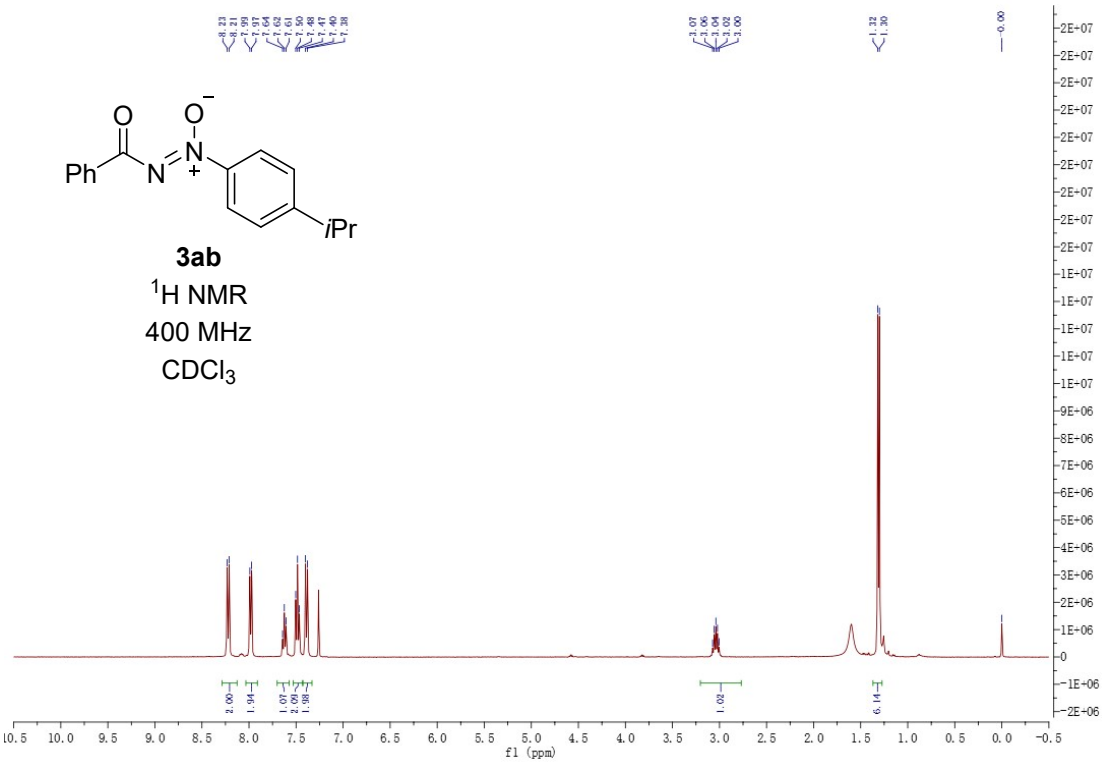
$CDCl_3$

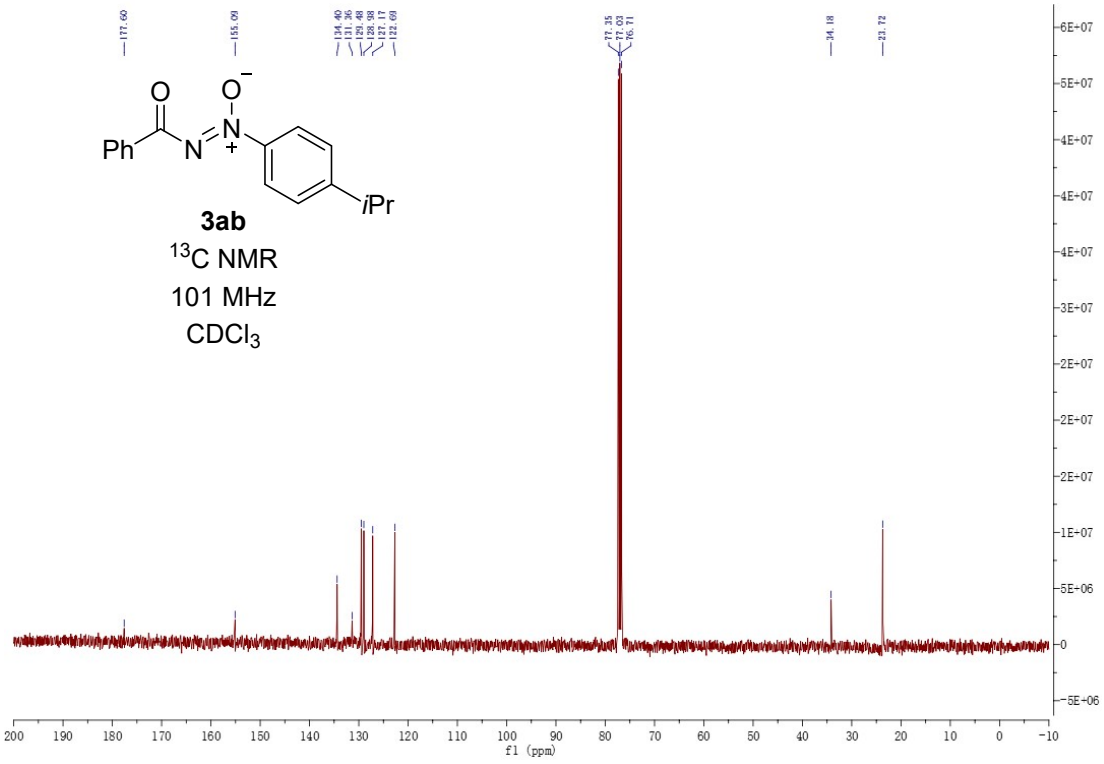

3z
1H NMR
500 MHz
CDCl3
f1 (ppm)

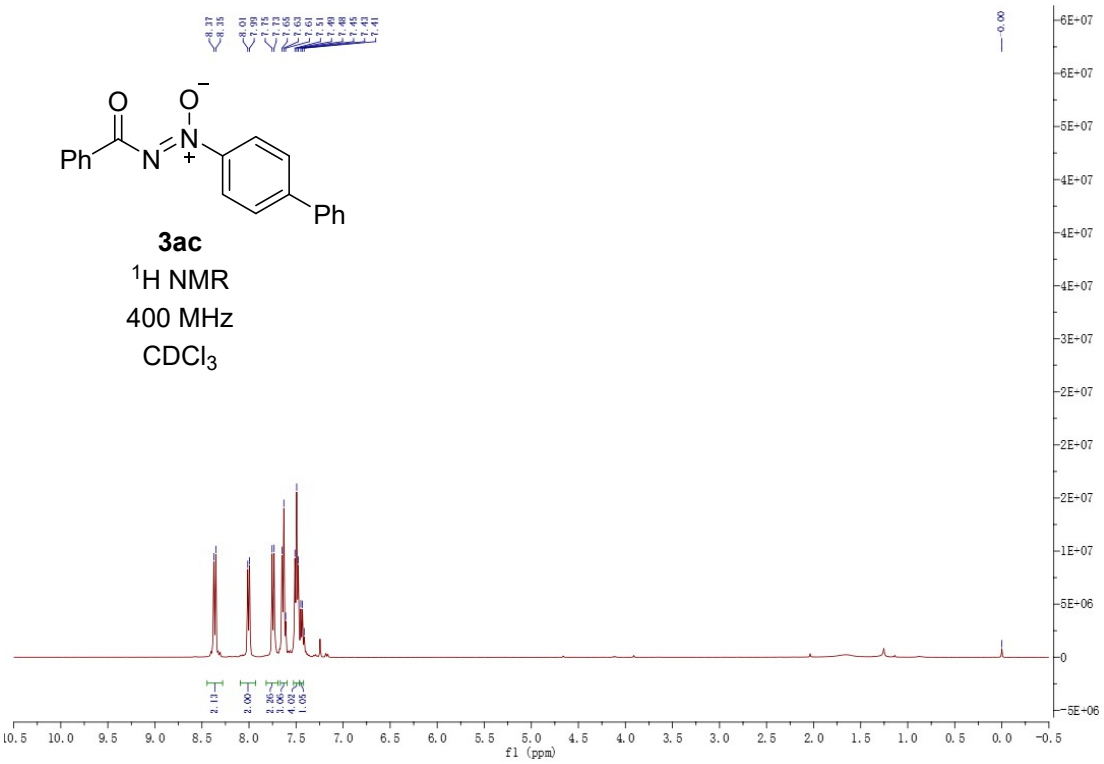

3z
13C NMR
101 MHz
CDCl3
f1 (ppm)

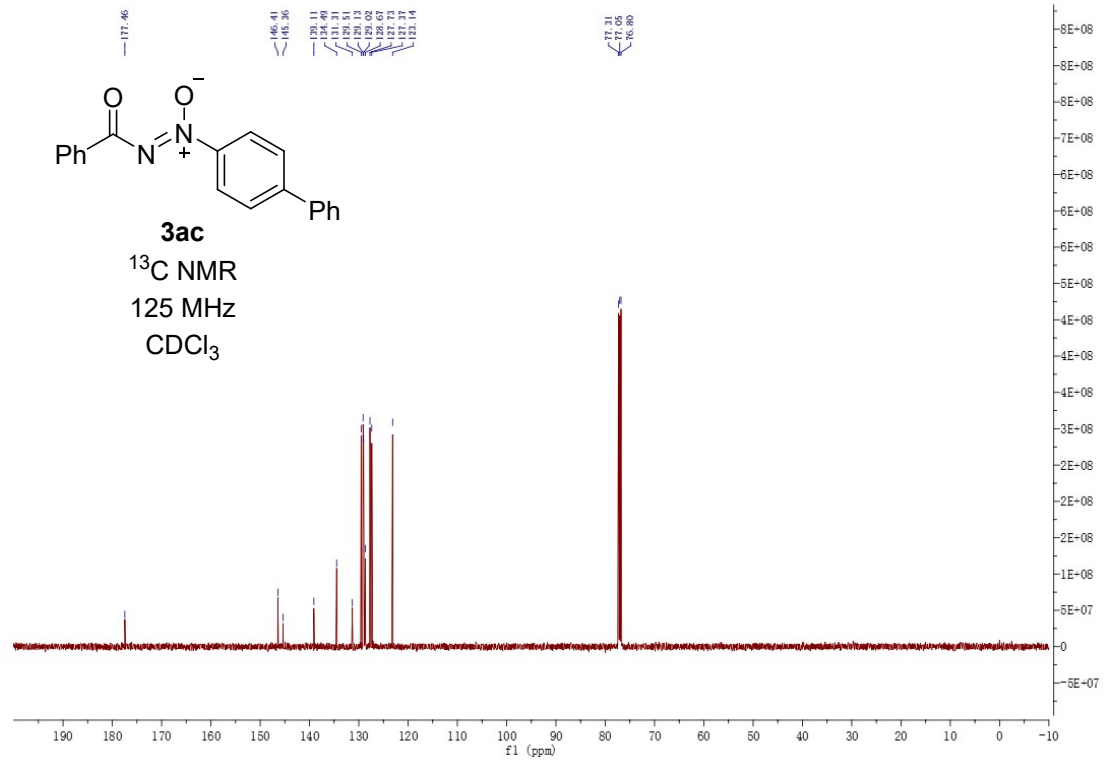

Ph
N
O
O
Me
3aa
1H NMR
500 MHz
CDCl3
f1 (ppm)

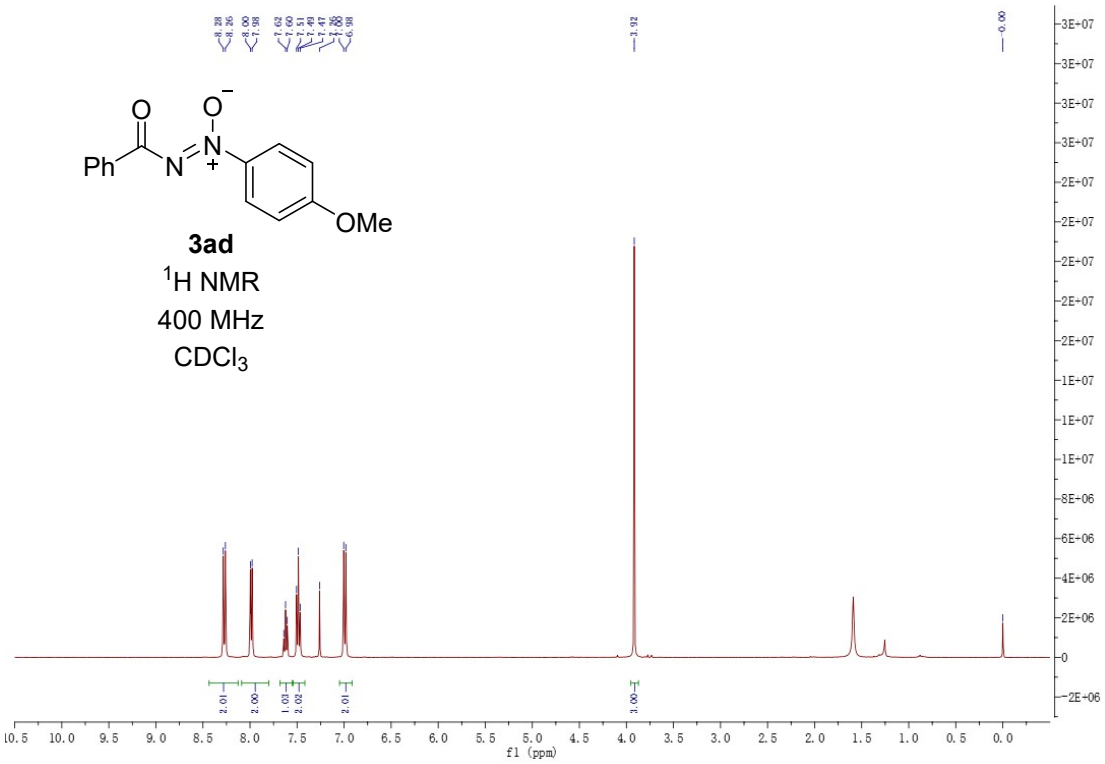

Ph
N
O
O
Me
3aa
13C NMR
125 MHz
CDCl3
f1 (ppm)

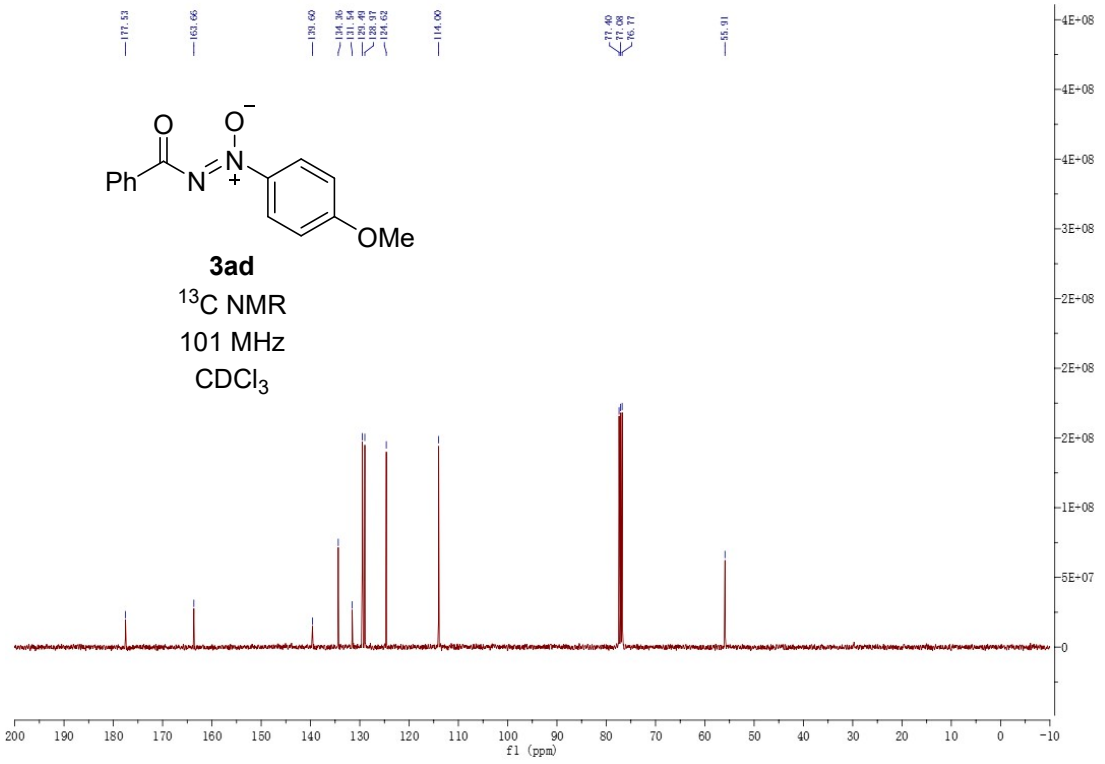

Ph
N
O
N
O
iPr
3ab
1H NMR
400 MHz
CDCl3
f1 (ppm)

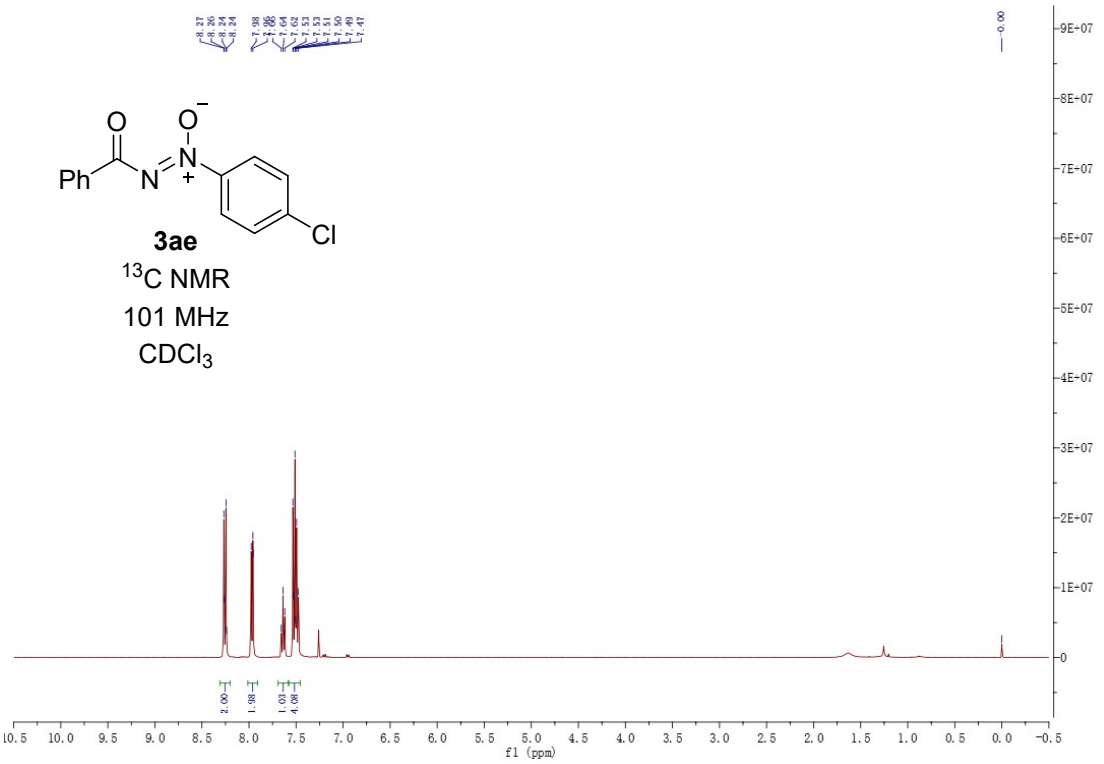

Ph
N
O
N
O
iPr
3ab
13C NMR
101 MHz
CDCl3
f1 (ppm)

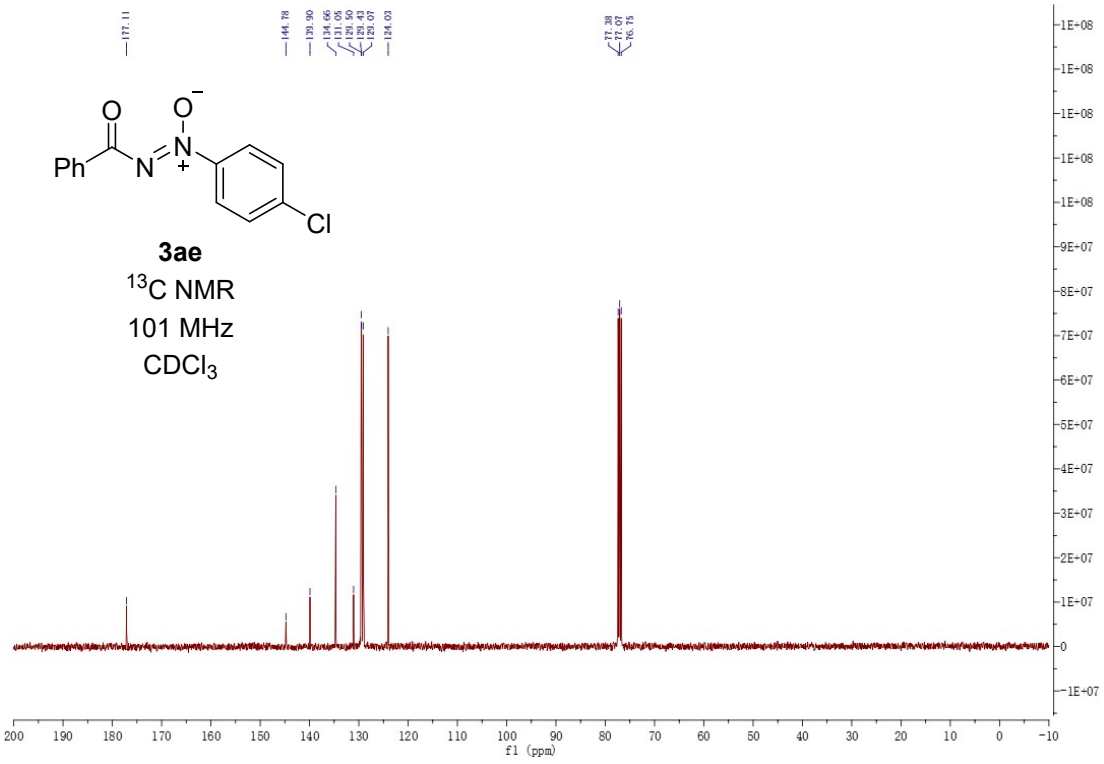

Ph
N
O
O
N
Ph
3ac
1H NMR
400 MHz
CDCl3
f1 (ppm)

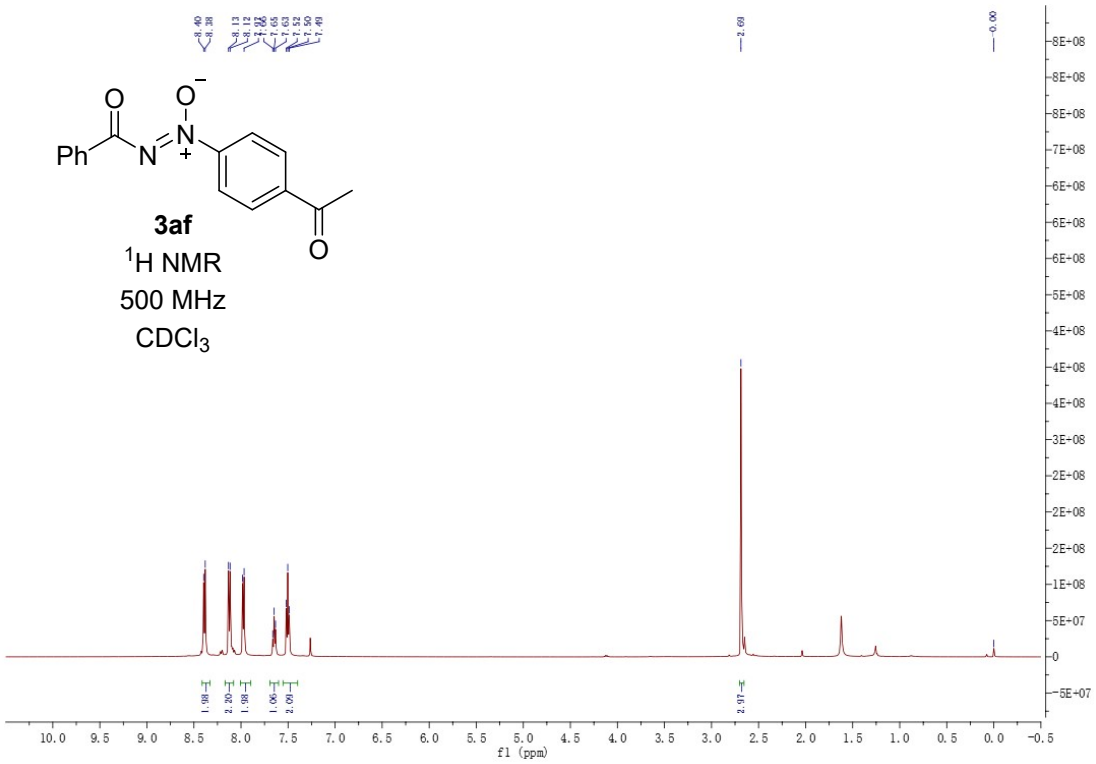

Ph
N
O
O
N
Ph
3ac
13C NMR
125 MHz
CDCl3
f1 (ppm)

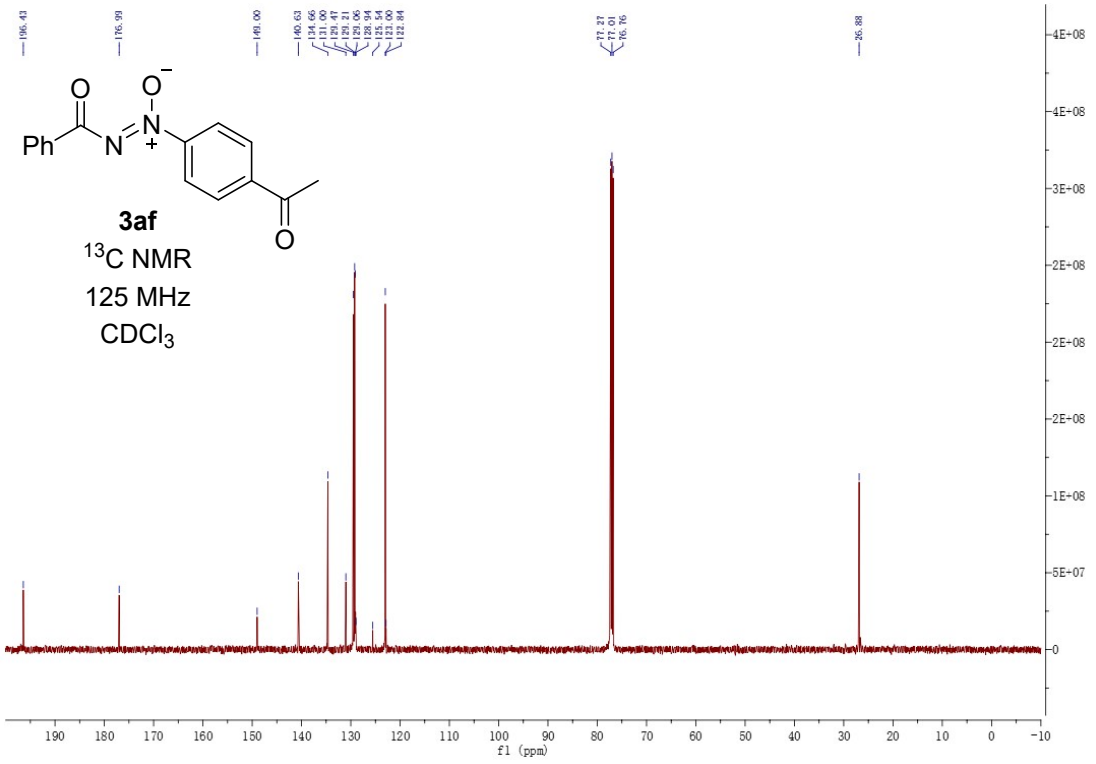

Ph
N
O
O
OMe
3ad
1H NMR
400 MHz
CDCl3
f1 (ppm)

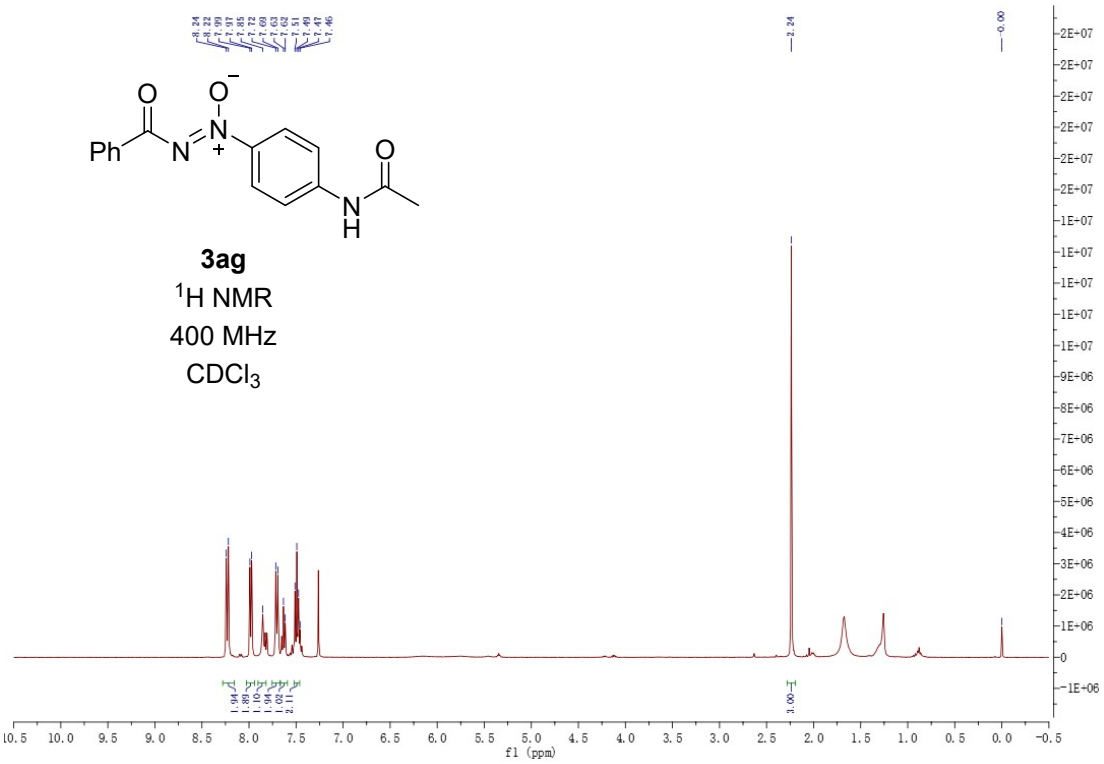

Ph
N
O
O
OMe
3ad
13C NMR
101 MHz
CDCl3
f1 (ppm)

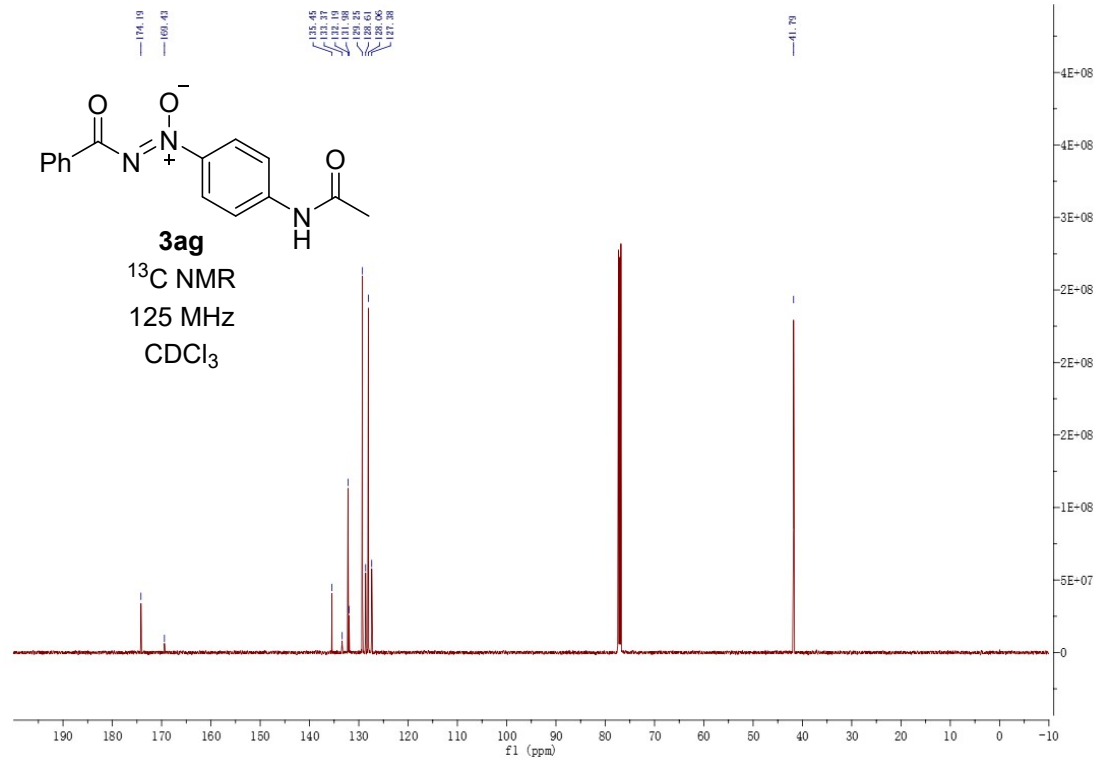

Ph
N
O
O
Cl
3ae
13C NMR
101 MHz
CDCl3
f1 (ppm)

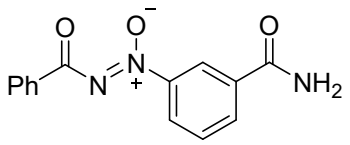

Ph
N
O
O
Cl
3ae
13C NMR
101 MHz
CDCl3
f1 (ppm)


3af
1H NMR
500 MHz
CDCl3
f1 (ppm)


3af
13C NMR
125 MHz
CDCl3
f1 (ppm)


Ph
O
O
N
N
O
N
H
3ag
1H NMR
400 MHz
CDCl3
f1 (ppm)


Ph
O
O
N
N
O
N
H
3ag
13C NMR
125 MHz
CDCl3
f1 (ppm)

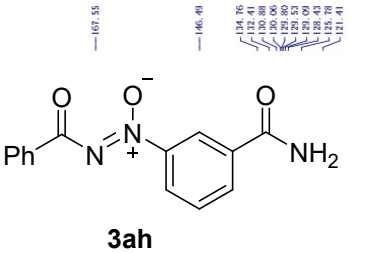


3ah

^{1}H NMR

400 MHz

$CDCl_3$

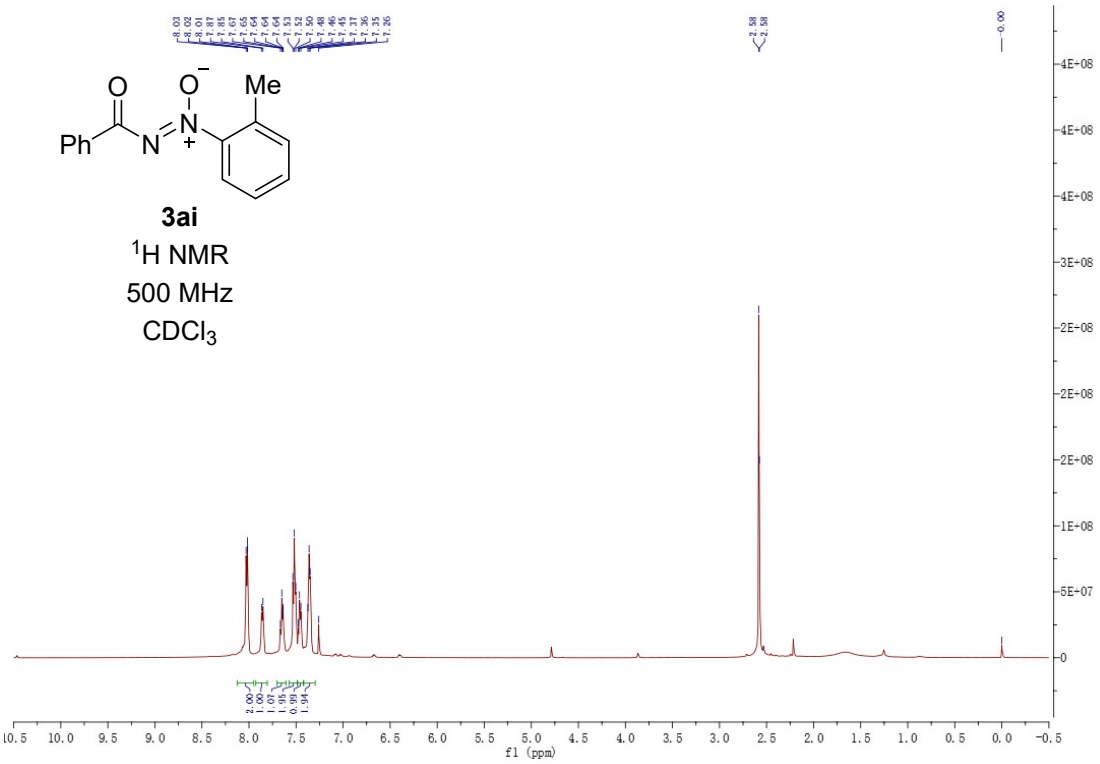


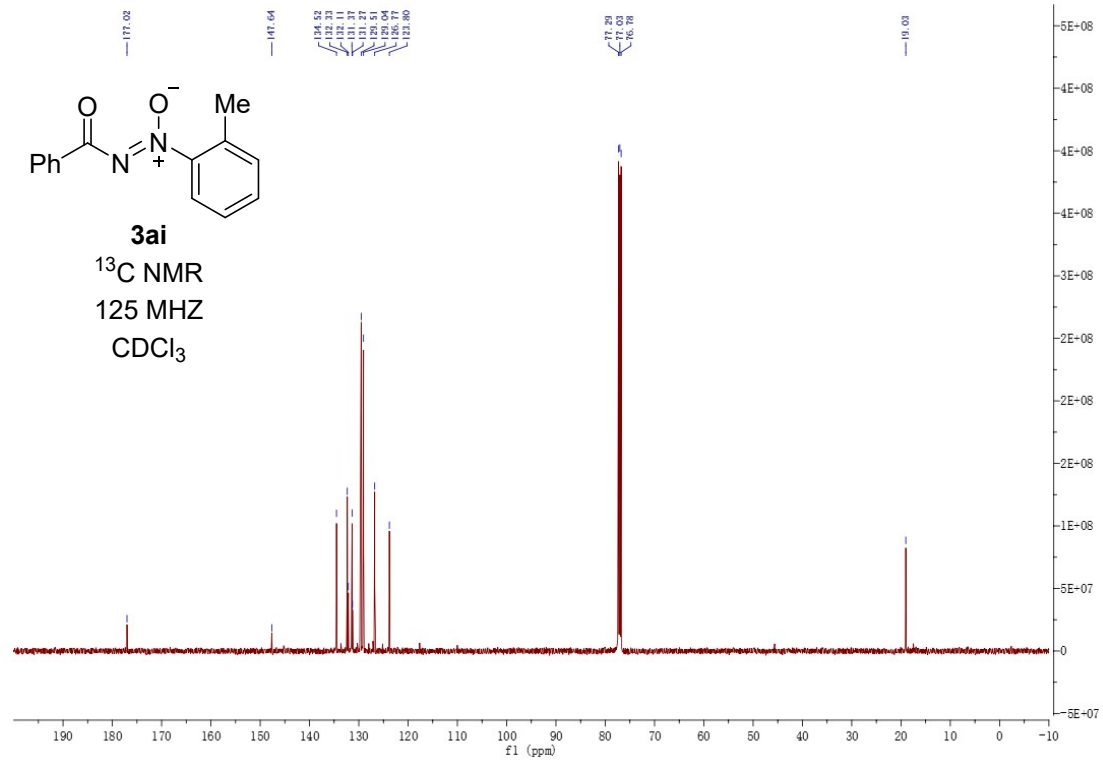
3ah

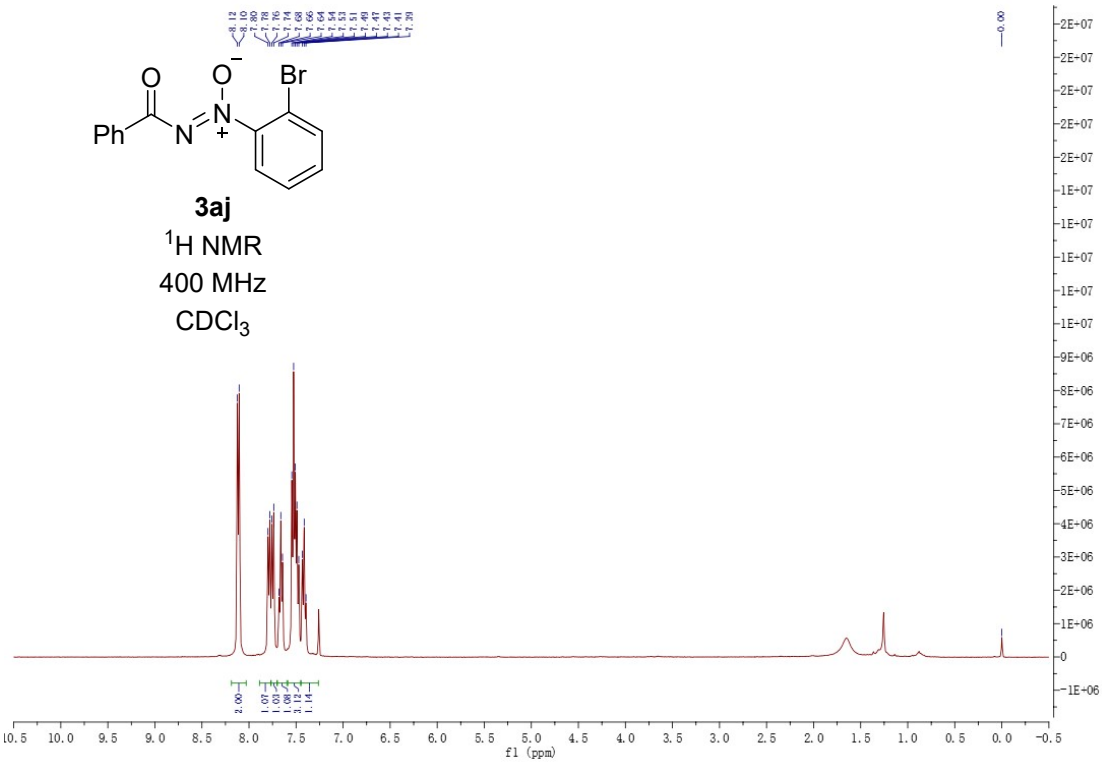
^{13}C NMR

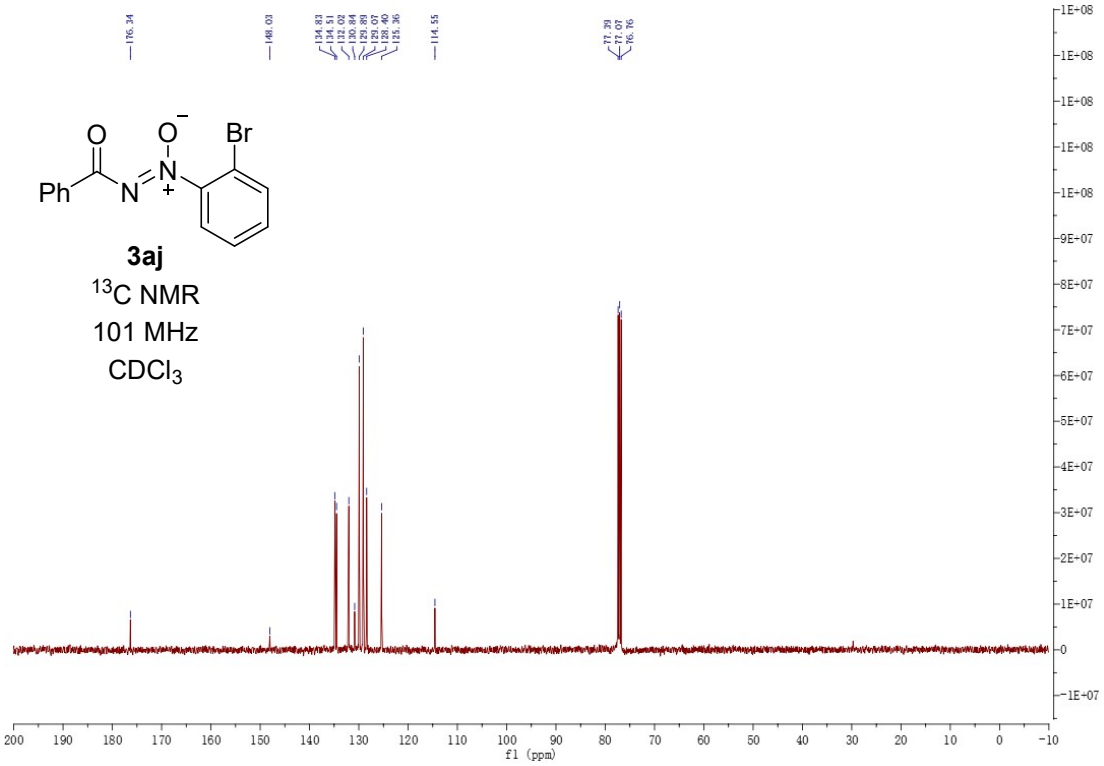
126 MHz

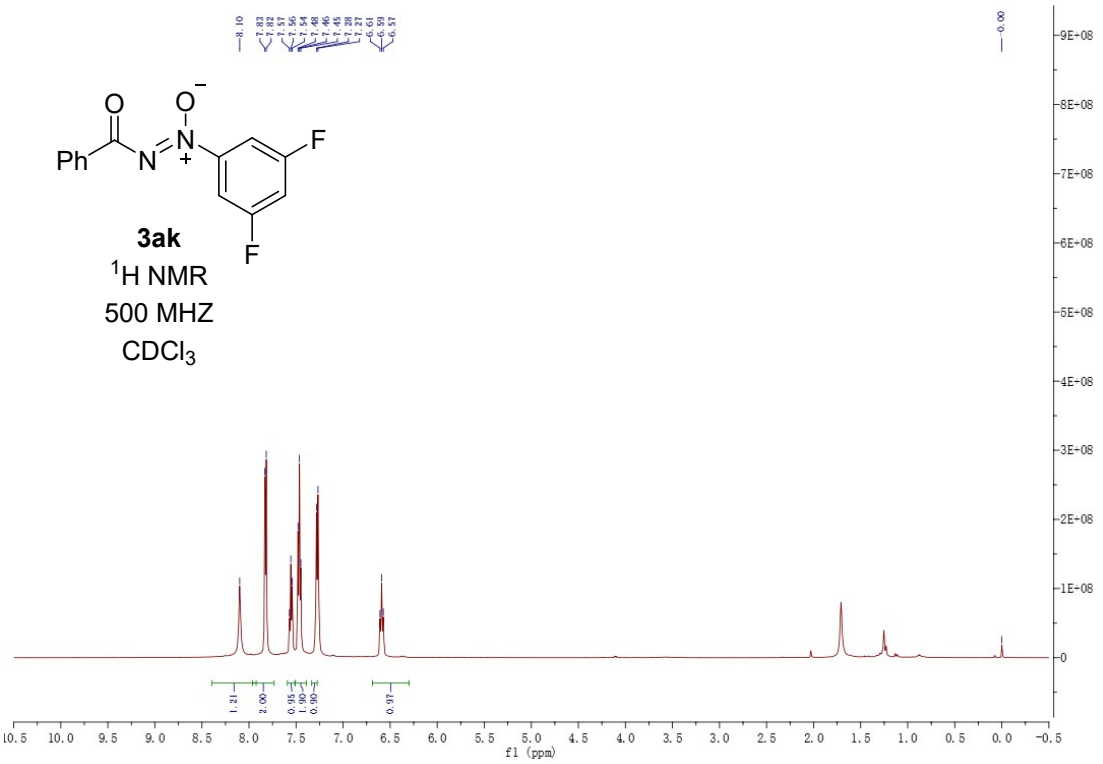
$CDCl_3$

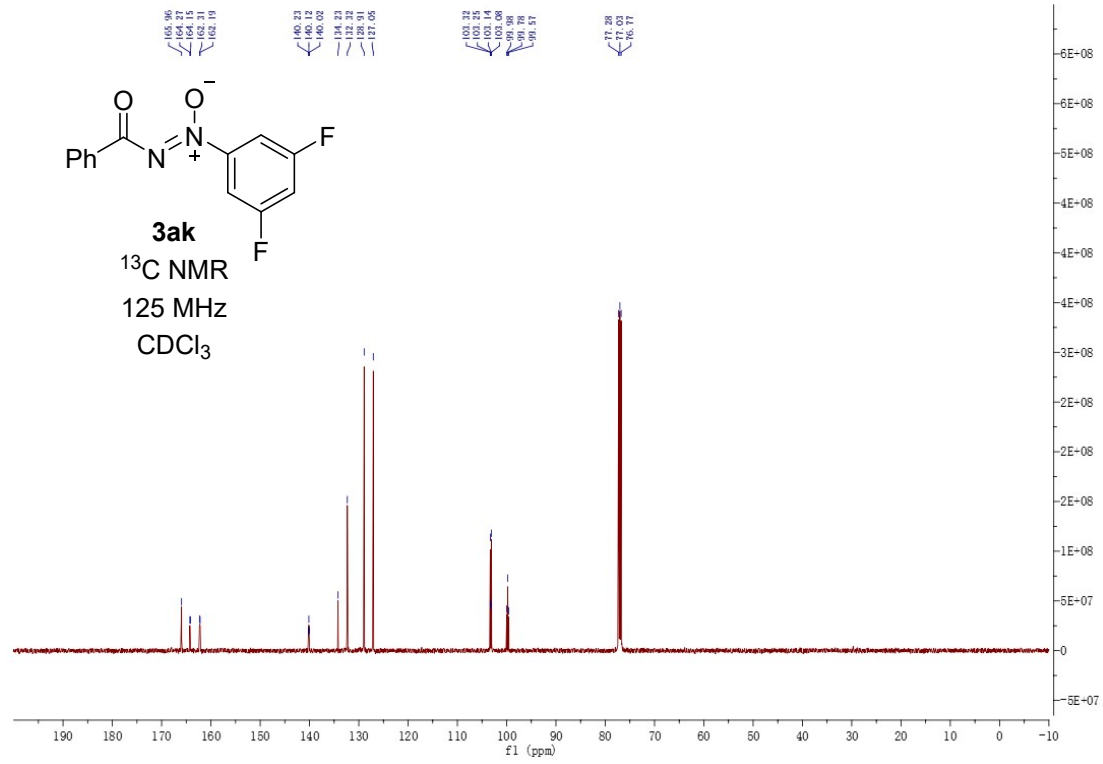

Ph
N
O
O
Me
3ai
1H NMR
500 MHz
CDCl3
f1 (ppm)

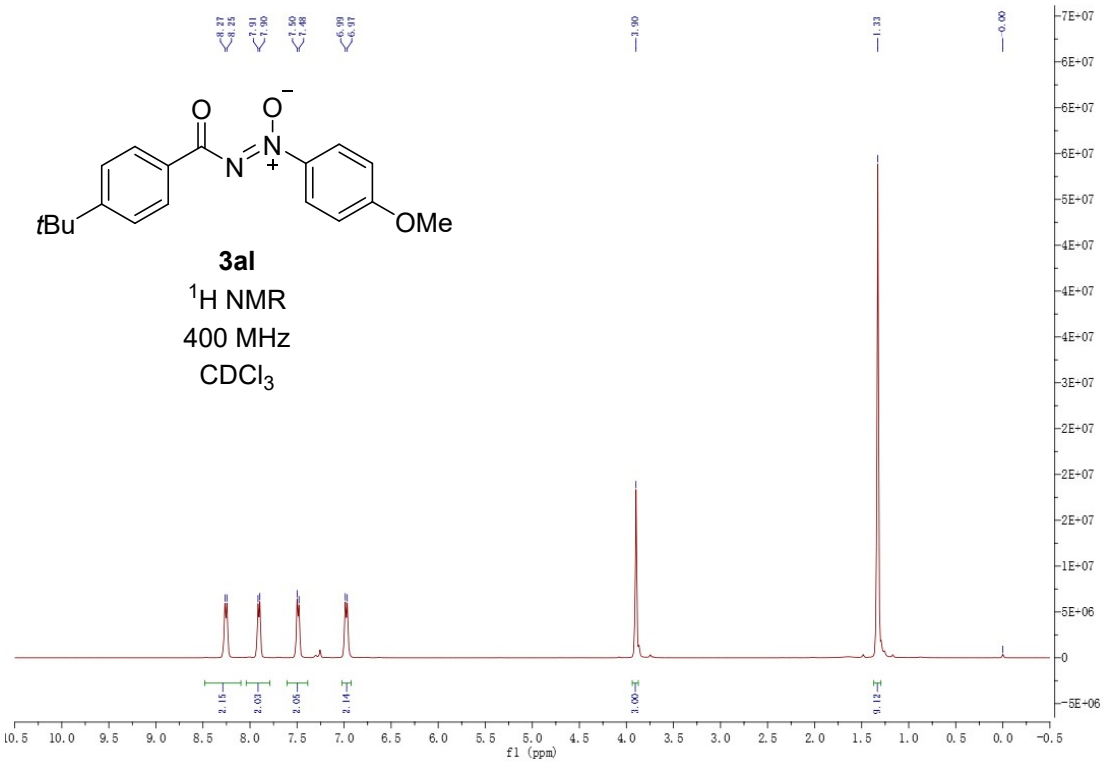

Ph
N
O
O
Me
3ai
13C NMR
125 MHZ
CDCl3
f1 (ppm)

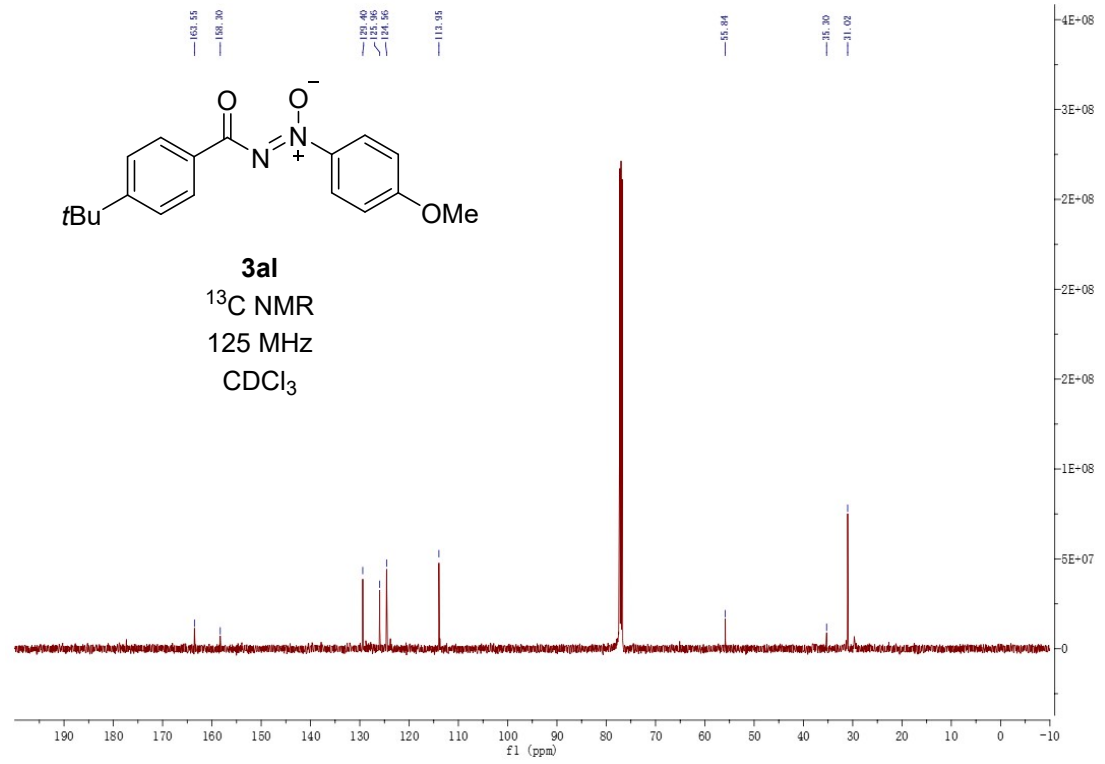

Ph
O
N
O
Br
3aj
1H NMR
400 MHz
CDCl3
f1 (ppm)

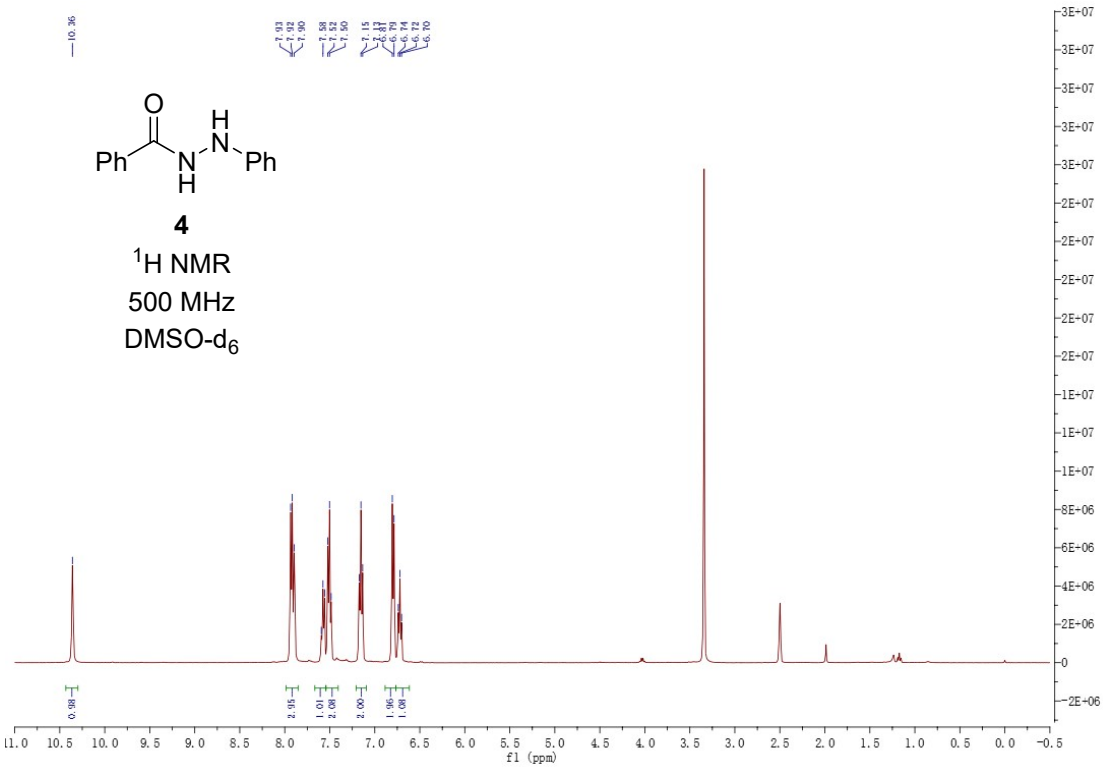

Ph
O
N
O
Br
3aj
13C NMR
101 MHz
CDCl3
f1 (ppm)


Ph
N
O
O
F
F
3ak
1H NMR
500 MHZ
CDCl3
f1 (ppm)


Ph
N
O
O
F
F
3ak
13C NMR
125 MHz
CDCl3
f1 (ppm)


tBu
OMe
3al
1H NMR
400 MHz
CDCl3
f1 (ppm)


tBu
OMe
3al
13C NMR
125 MHz
CDCl3
f1 (ppm)

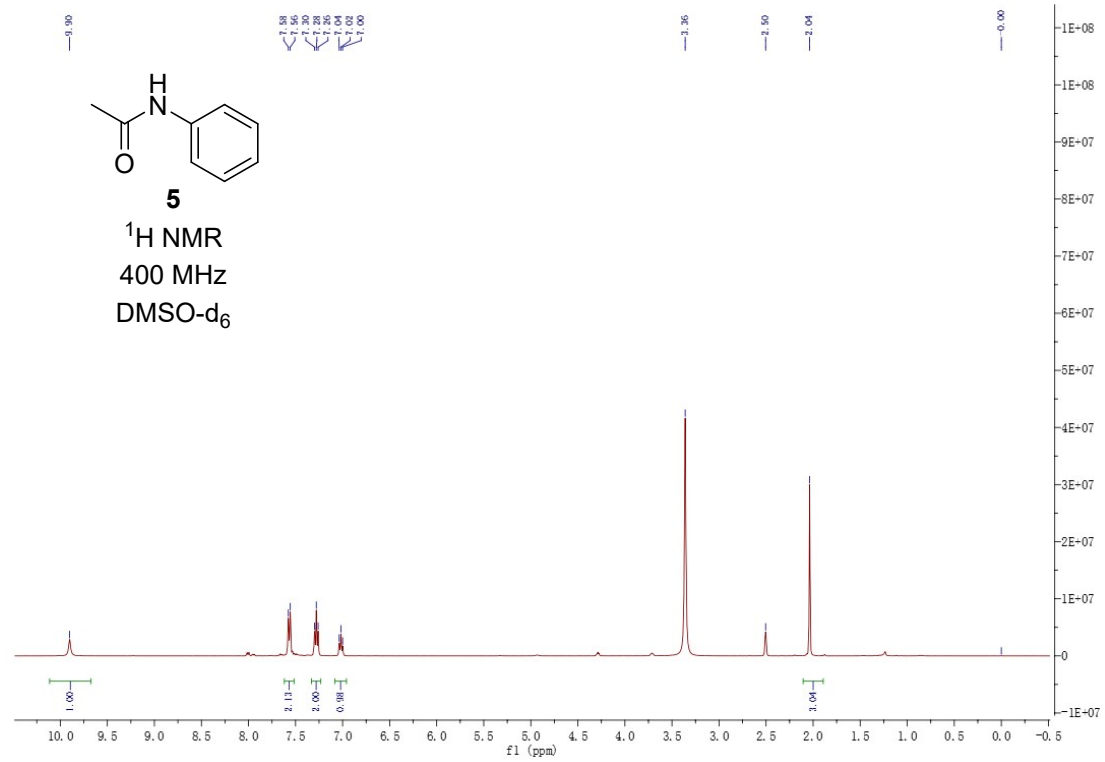


4

^{1}H NMR

500 MHz

DMSO-d_6

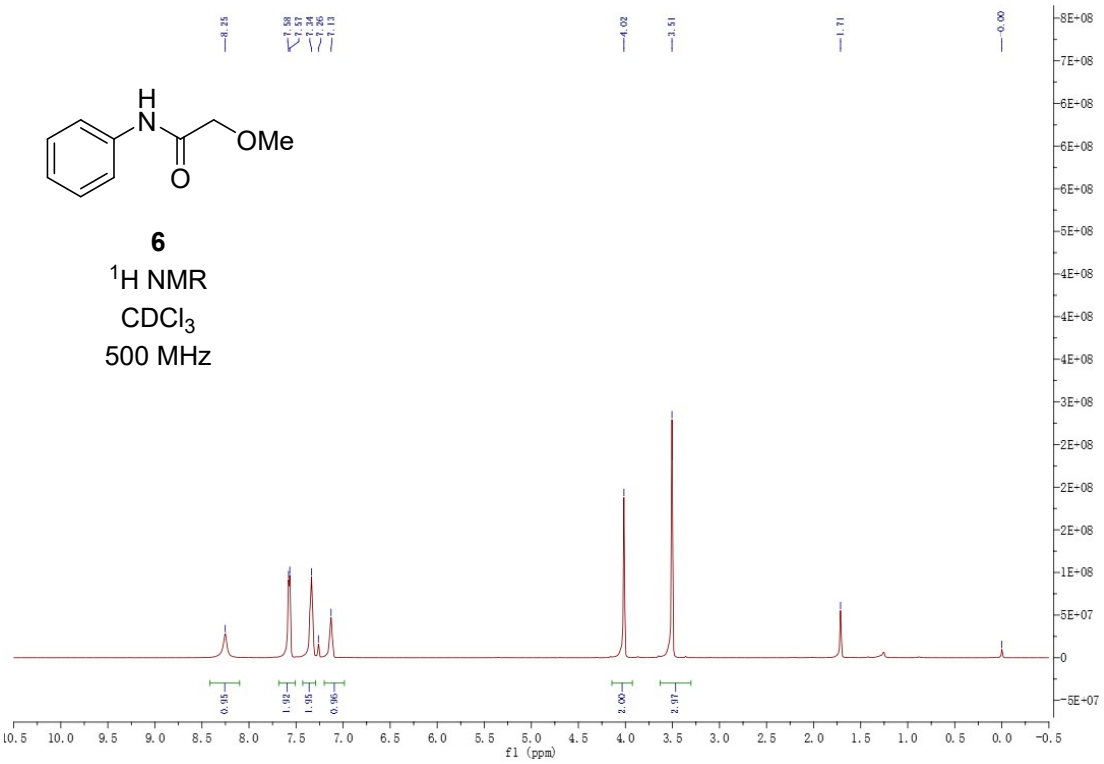


5

^{1}H NMR

400 MHz

DMSO-d_6

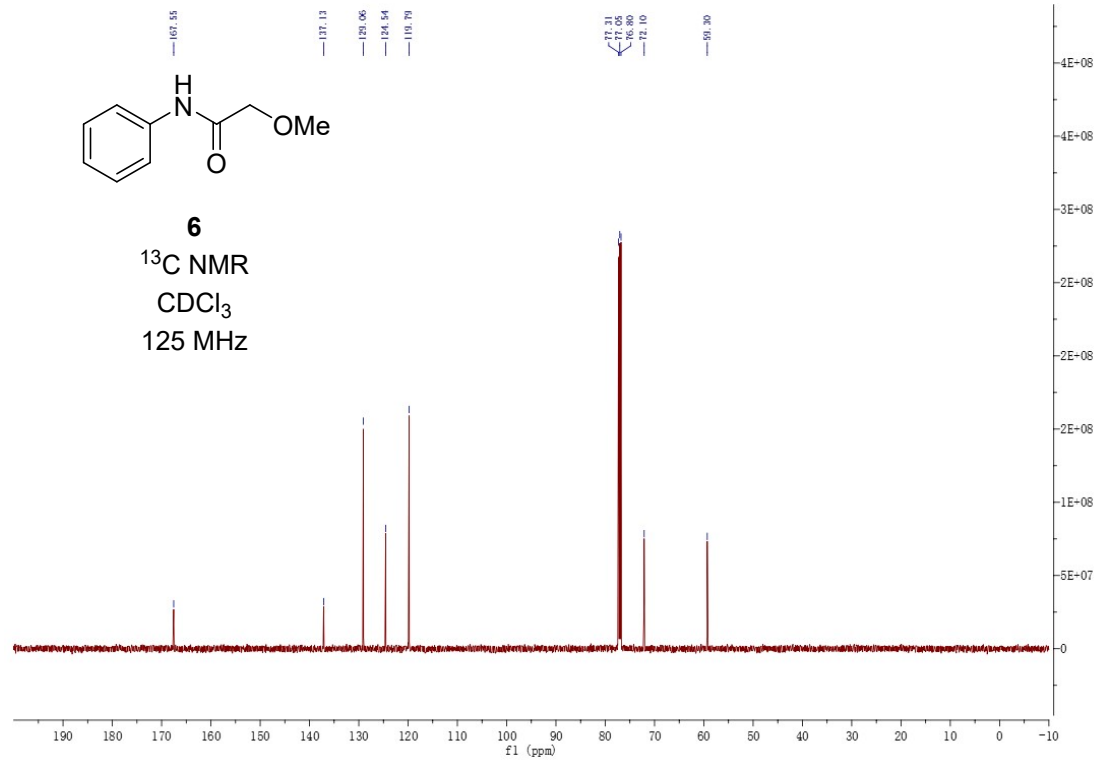


6

^{1}H NMR

$CDCl_3$

500 MHz

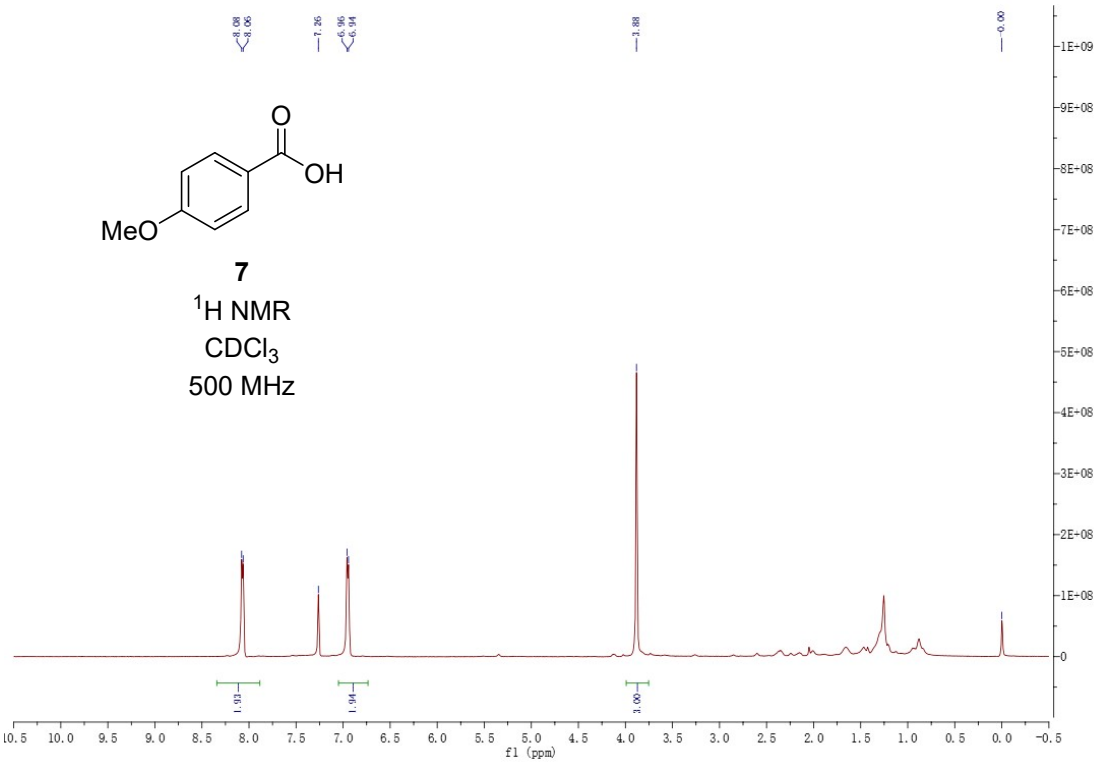


6

^{13}C NMR

$CDCl_3$

125 MHz


8.08
8.06
7.26
6.96
6.94
3.88
0.00
O
OH
MeO
7
1H NMR
CDCl3
500 MHz
1.93
1.94
3.00
f1 (ppm)