Supporting Information

Controllable *Z*/*E*-Selective Synthesis of *α*-Amino-Ketoximes from *N*-Nitrososulfonamides and Aryl Alkenes under Neutral Conditions

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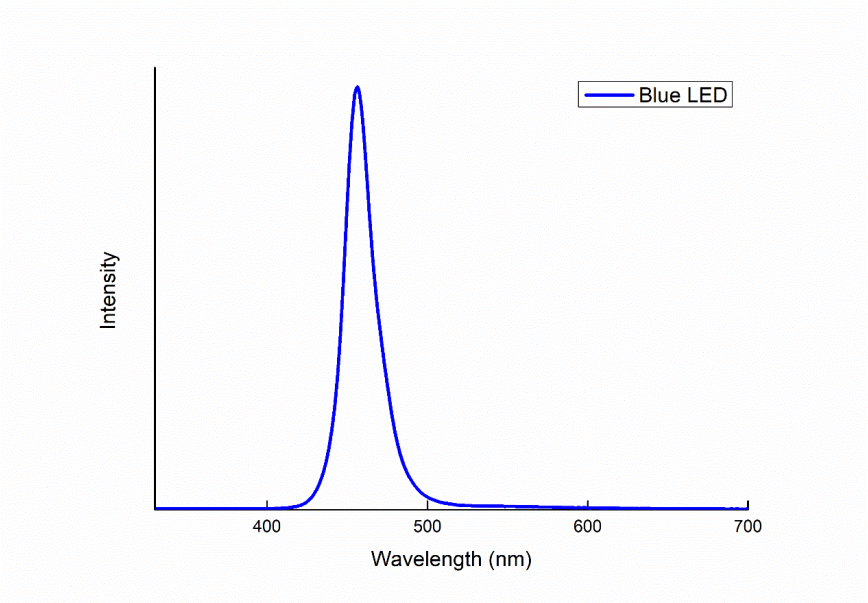
Table of Catents

1. General information

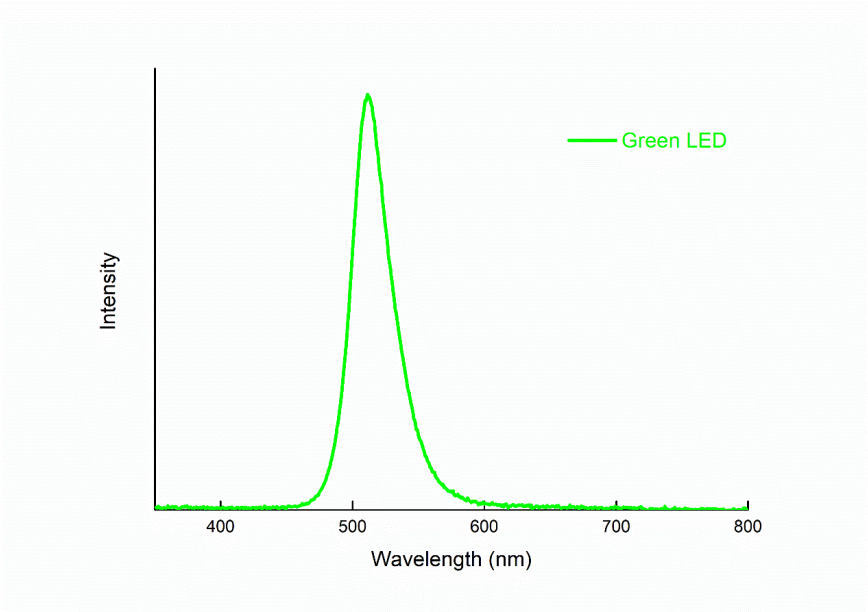
1.1. Reagents and analytical techniques

All starting materials were commercially available and used without further purification unless otherwise noted. Photocatalyst $Ru(bpy)_3Cl_2$, eosinY-Na_2, thioxanthone, Methylene Blue, $Ir(ppy)_3$ were purchased from TCI, $[Ir(dF(CF_3)ppy)_2(dtbbpy)]Cl$ ($dF(CF_3)ppy$ = 2-(2,4-difluorophenyl)-3-trifluoromethylpyridine, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) was prepared according to reported literature procedures.[1] Blue LEDs, green LEDs, yellow LEDs and UV-A LEDs (10W, λmax = 365 nm) were used as the irradiation light. Thin layer chromatography (TLC) was visualized using UV light (254 nm). Column chromatography was performed with silica gel (200-300 meshes). ^{1}H NMR spectra were recorded on Bruker 400 or 600 MHz spectrometers at ambient temperature. Chemical shift is reported in parts per million (ppm) from $CDCl_3$ (7.26 ppm), Methanol-d_4 (3.31 ppm) and DMSO-d_6 (2.50 ppm) with multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR was recorded on Bruker 400 or 600 MHz spectrometers at ambient temperature. Chemical shifts are reported in ppm from $CDCl_3$ (77 ppm), Methanol-d_4 (49 ppm) and DMSO-d_6 (39.5 ppm). High-resolution mass spectra (HRMS) was performed on Bruker Apex II FT-ICR mass instrument (ESI) and waters GCT Premier TOFMS (EI). UV-Vis absorption spectra were recorded on UV-2600. Fluorescence spectra were collected on RF-5301PC.

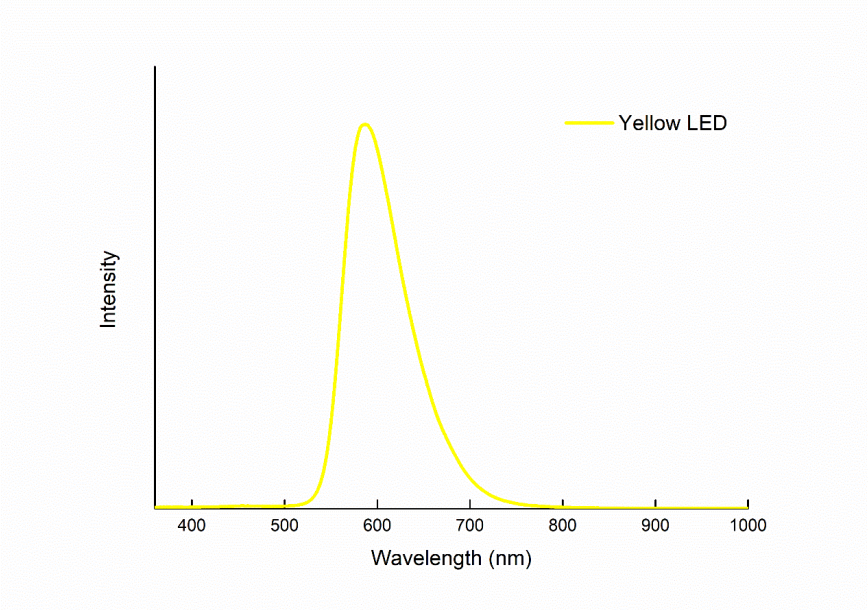
1.2. Emission spectra of the used LEDs



Supplementary Figure 1: Emission spectra of the used blue LED.



Supplementary Figure 2: Emission spectra of the used green LED.



Supplementary Figure 3: Emission spectra of the used yellow LED.

2. General preparation and characterization of starting materials

2.1. List of *N*-nitrososulfonamides, *N*-nitrosoamide and alkenes

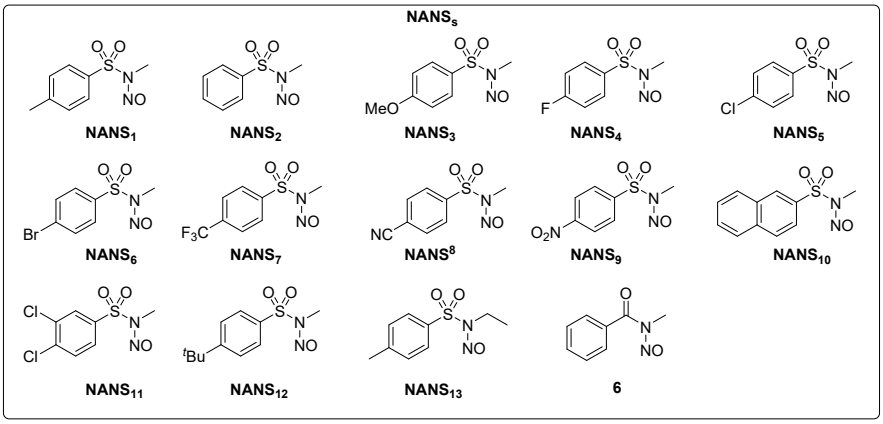
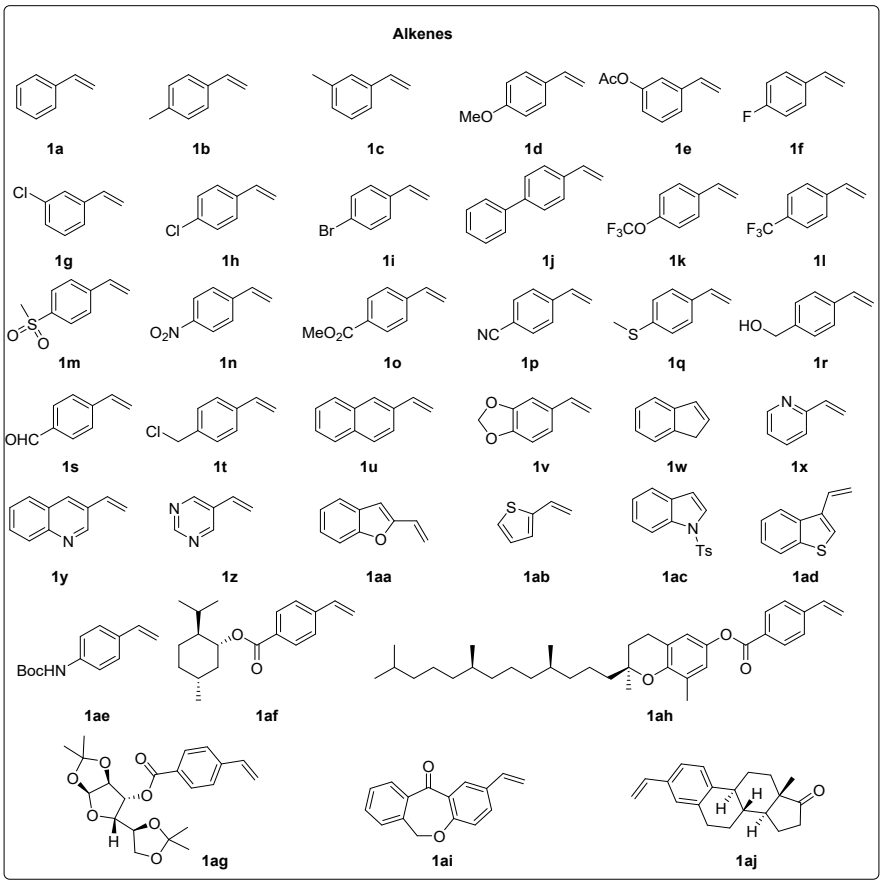


Table S1: List of *N*-nitrososulfonamides and *N*-nitrosoamide



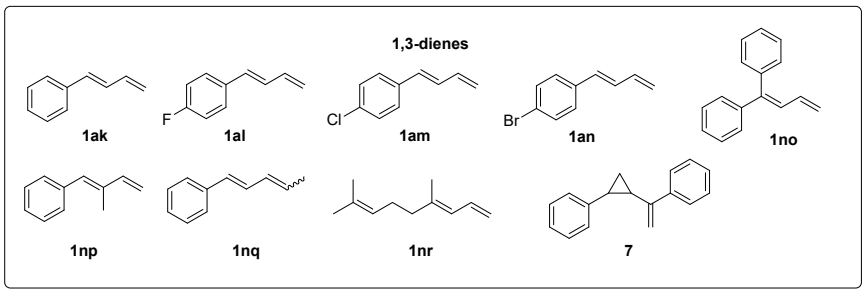
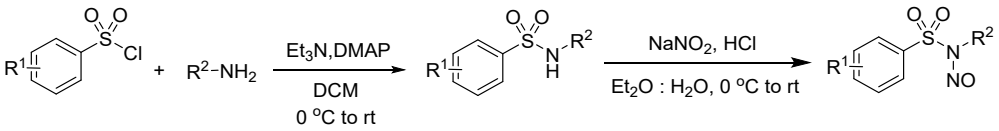


Table S2: List of alkenes

Alkenes **1a**–**1d**, **1f**–**1j**, **1u**, **1w**–**1x**, **1ab** are commercially available. Other alkenes are known compounds, and they were synthesized according to the reported literature.

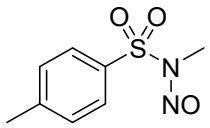
2.2. General procedure A for the synthesis of *N*-Nitrososulfonamide (NANS$_s$)



General procedure A: Step 1: Substrate primary amine (methylamine: 25–30% in water or ethylamine: 2 mol/L in THF, 2 equiv.) was dissolved in dichloromethane and cooled to 0 °C. Triethylamine (2 equiv.) and dimethylaminopyridine (0.1 equiv.) were added. Finally, the sulfonyl chloride or benzoyl chloride (20 mmol, 1 equiv.) was added portionwise. Then the solution was slowly warmed to room temperature and stirred for an additional 12 hours. Once complete, the reaction was quenched with 1 M hydrochloric acid. The aqueous layer was washed with dichloromethane, dried over magnesium sulfate, concentrated under reduced pressure. The residue was obtained as a white solid or colorless oil liquid in 90–98% yield and used directly without further purification.

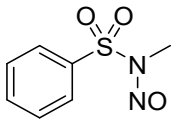
Step 2: Conc. HCl (37%, 4.0 equiv.) was added to a solution of the sulfonamides (or amide) (10 mmol, 1.0 equiv.) in diethyl ether 15 mL. The reaction mixture was stirred vigorously in a water/ice bath at 0 °C. Sodium nitrite (4.0 equiv.) in water (5.0 mL) was added over a period of 5.0 min and the reaction mixture was stirred at room temperature for 4.0 h. It was then worked up with water and extracted with diethyl ether. The combined organic layer was washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (20% EtOAc/hexanes as eluent) to provide the desired products (75 – 92% yield) as pale yellow powder.

2.3. Characterization of NANS$_s$



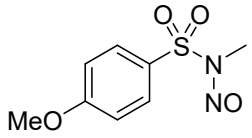
$NANS_1$

***N*-methyl-*N*-nitroso-4-methylbenzenesulfonamide ($NANS_1$) ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.10 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 146.1, 134.0, 130.3, 127.9, 28.8, 21.6. **HRMS** (ESI, m/z): (M+H) calculated for $[C_8H_{10}N_2O_3S+H]^+$: 215.0485, found: 215.0487.



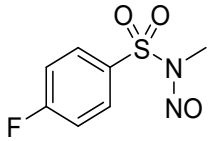
$NANS_2$

***N*-methyl-*N*-nitrosobenzenesulfonamide ($NANS_2$) ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 – 7.93 (m, 2H), 7.69 – 7.65 (m, 1H), 7.58 – 7.54 (m, 2H), 3.09 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 136.8, 134.7, 129.7, 127.7, 28.9. **HRMS** (ESI, m/z): (M+H) calculated for $[C_7H_8N_2O_3S+H]^+$: 201.0328, found: 201.0327.



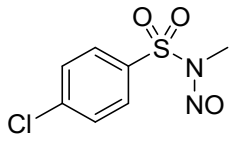
$NANS_3$

4-methoxy-*N*-methyl-*N*-nitrosobenzenesulfonamide ($NANS_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H), 3.07 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.5, 130.2, 127.8, 114.8, 55.7, 28.7. **HRMS** (ESI, m/z): (M+H) calculated for $[C_8H_{10}N_2O_4S+H]^+$: 231.0434, found: 231.0436.



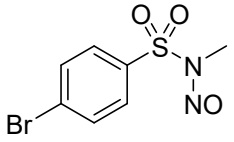
$NANS_4$

4-fluoro-*N*-methyl-*N*-nitrosobenzenesulfonamide ($NANS_4$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.03 (m, 2H), 7.33 – 7.29 (m, 2H), 3.16 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.2 (d, *J* = 257 Hz), 132.9 (d, *J* = 4 Hz), 130.8 (d, *J* = 9 Hz), 117.1 (d, *J* = 23 Hz), 28.8. **HRMS** (ESI, m/z): (M+H) calculated for $[C_7H_7FN_2O_3S+H]^+$: 219.0234, found: 219.0237.



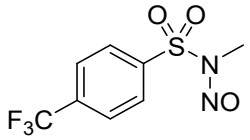
$NANS_5$

4-chloro-*N*-methyl-*N*-nitrosobenzenesulfonamide (**$NANS_5$**) **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 3.12 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 141.6, 135.4, 130.1, 129.3, 28.9. **HRMS** (ESI, m/z): (M+H) calculated for $[C_7H_7ClN_2O_3S+H]^+$: 234.9939, found: 234.9941.



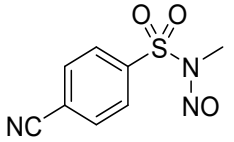
$NANS_6$

4-bromo-*N*-methyl-*N*-nitrosobenzenesulfonamide (**$NANS_6$**) **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 12.0 Hz, 2H), 3.11 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 135.9, 133.0, 130.2, 129.3, 28.9. **HRMS** (ESI, m/z): (M+H) calculated for $[C_7H_7BrN_2O_3S+H]^+$: 278.9434, found: 278.9438.



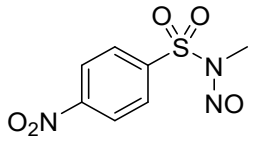
$NANS_7$

***N*-methyl-*N*-nitroso-4-(trifluoromethyl)benzenesulfonamide** (**$NANS_7$**) **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 3.14 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 140.6, 136.1 (q, *J* = 33.0 Hz), 128.5, 126.9 (q, *J* = 3.7 Hz), 122.8 (q, *J* = 272.0 Hz), 29.0. **HRMS** (ESI, m/z): (M+H) calculated for $[C_8H_7F_3N_2O_3S+H]^+$: 269.0202, found: 269.0205.



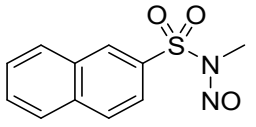
$NANS_8$

4-cyano-*N*-methyl-*N*-nitrosobenzenesulfonamide (**$NANS_8$**) **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 12.0 Hz, 2H), 7.90 (d, *J* = 12 Hz, 12H), 3.14 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 141.0, 133.4, 128.5, 118.3, 116.6, 29.1. **HRMS** (ESI, m/z): (M+H) calculated for $[C_8H_7N_3O_3S+H]^+$: 226.0281, found: 226.0280.



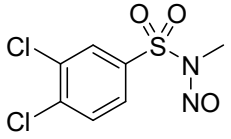
$NANS_9$

***N*-methyl-4-nitro-*N*-nitrosobenzenesulfonamide ($NANS_9$) ^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.47 (d, J = 8.0 Hz, 2H), 8.30 (d, J = 8.0 Hz, 2H), 3.19 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.2, 141.3, 129.6, 125.4, 29.9. **HRMS** (ESI, m/z): (M+H) calculated for $[C_7H_7N_3O_5S+H]^+$: 246.0179, found: 246.0182.



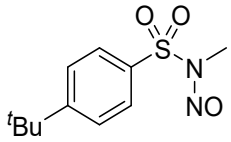
$NANS_{10}$

***N*-methyl-*N*-nitrosonaphthalene-2-sulfonamide ($NANS_{10}$) ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.87 (dd, J = 8.0, 4.0 Hz, 1H), 7.73 – 7.64 (m, 2H), 3.16 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 135.5, 133.7, 131.9, 130.2, 130.2, 130.0, 129.5, 128.2, 128.0, 121.9, 29.0. **HRMS** (ESI, m/z): (M+H) calculated for $[C_{11}H_{10}N_2O_3S+H]^+$: 251.0485, found: 251.0488.



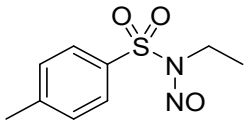
$NANS_{11}$

3,4-dichloro-*N*-methyl-*N*-nitrosobenzenesulfonamide ($NANS_{11}$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, J = 2.0 Hz, 1H), 7.80 (dd, J = 8.5, 2.2 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 3.14 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 140.0, 136.7, 134.5, 131.8, 129.6, 126.8, 29.0. **HRMS** (ESI, m/z): (M+H) calculated for $[C_7H_6Cl_2N_2O_3S+H]^+$: 268.9549, found: 268.9553.



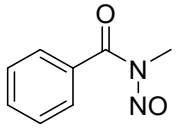
$NANS_{12}$

4-(tert-butyl)-*N*-methyl-*N*-nitrosobenzenesulfonamide ($NANS_{12}$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 3.13 (s, 3H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 158.9, 134.0, 127.8, 126.7, 35.4, 30.9, 28.9. **HRMS** (ESI, m/z): (M+H) calculated for $[C_{11}H_{16}N_2O_3S+H]^+$: 257.0954, found: 257.0955.



$NANS_{13}$

***N*-ethyl-4-methyl-*N*-nitrosobenzenesulfonamide** (**$NANS_{13}$**) **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 3.77 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 146.0, 134.9, 130.2, 127.9, 38.3, 21.6, 12.7. **HRMS** (ESI, m/z): (M+H) calculated for $[C_9H_{12}N_2O_3S+H]^+$: 229.0641, found: 229.0644.



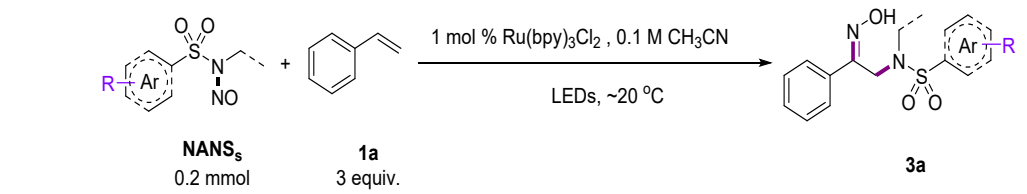
6

***N*-methyl-*N*-nitrosobenzamide** (**6**) **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.74 (m, 2H), 7.58 – 7.54 (m, 1H), 7.48 – 7.43 (m, 2H), 3.28 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.8, 132.7, 132.4, 130.6, 128.1, 26.7. **HRMS** (ESI, m/z): (M+H) calculated for $[C_9H_{10}N_2O_2+H]^+$: 179.0815, found: 179.0816.

3. Extended optimization studies

3.1. General Procedure B: $NANS_s$ and light souces screening

General Procedure B for the amidoximations of styrene with different $NANS_s$: A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, styrene (0.6 mmol, 3 equiv., unless otherwise stated), the appropriate *N*-alkyl-*N*-nitroso-sulfonamides (**$NANS_s$**) (0.2 mmol, 1.0 equiv.) and $Ru(bpy)_3Cl_2$ photosensitizer (1 mol %) were charged under air, CH_3CN (0.1 M) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with a 3 W blue LED (6 W green LED and 10 W yellow LED) at about 20 °C (the distance between the tube and the light source was about 0.5 cm), unless otherwise stated. Upon completion (as judged by TLC analysis), silica was added to the reaction and then concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel (EtOAc : petroleum ether as an eluent) to give the products. (The yields were based on the ^{1}NMR analysis using 4-nitroacetophenone as the internal standard) Note, isolated yields following purification by flash-column chromatography in parenthesis.



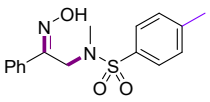
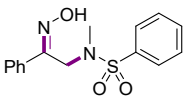
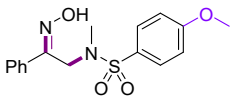
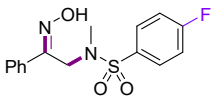
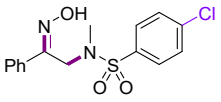
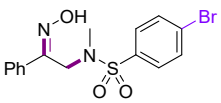
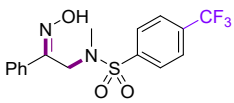
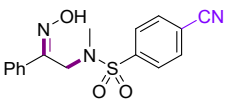
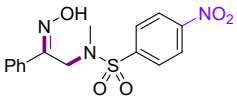
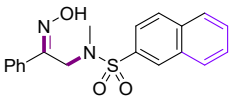
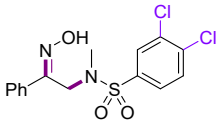
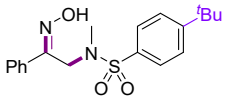
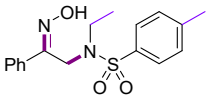
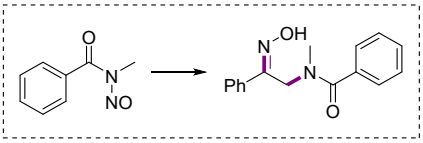
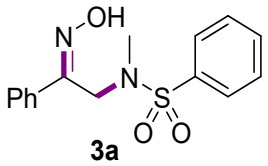
				
Blue LEDs:	**2a** 71%	**3a** 65%	**3b** 63%	**3c** 61%
Green LEds:	76%	70%	73%	75%
Yellow LEDs:	83% (80%)	76% (72%)	77% (73%)	79% (76%)
				
Blue LEDs:	**3d** 62%	**3e** 66%	**3f** 69%	**3g** 65%
Green LEds:	72%	76%	77%	71%
Yellow LEDs:	77% (72%)	79% (75%)	79% (73%)	75% (72%)
				
Blue LEDs:	**3h** 85% (80%)	**3i** 57%	**3j** 73%	**3k** 66%
Green LEds:	20%	60%	76%	81%
Yellow LEDs:	10%	79% (75%)	80% (77%)	85% (82%)
				
Blue LEDs:	**3l** 55%		**3m** 0%	
Green LEds:	60%		0%	
Yellow LEDs:	70% (68%)		0%	

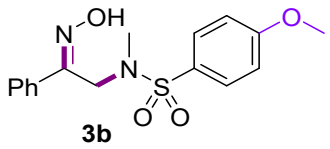
Table S3: List the product of **2a**, **3a**–**3l**

3.2. Characterization of products 3a-3l



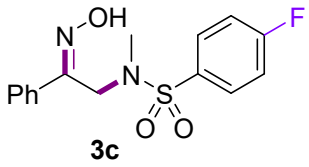
3a

(*Z*)-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*-methylbenzenesulfonamide (3a) According to the General Procedure B, afforded **3a** (44.0 mg, 72%, *Z*/*E* = 12:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.79 (brs, 1H), 7.86 – 7.84 (m, 2H), 7.79 – 7.74 (m, 3H), 7.70 – 7.66 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.40 (m, 3H), 4.27 (s, 2H), 2.44 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 150.8, 135.1, 134.3, 133.4, 129.5, 129.1, 128.4, 127.5, 126.3, 42.3, 34.9. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{15}H_{16}N_2O_3S+Na]^+$: 327.0774, found: 327.0773.



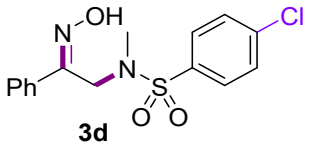
3b

(*Z*)-*N*-(2-(hydroxyimino)-2-phenylethyl)-4-methoxy-*N* methylbenzenesulfonamide (3b) According to the General Procedure B, afforded **3b** (49.0 mg, 73%, *Z*/*E* = 12:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.11 (brs, 1H), 7.79 – 7.71 (m, 4H), 7.41 – 7.38 (m, 3H), 7.02 – 6.98 (m, 2H), 4.37 (s, 2H), 3.87 (s, 3H), 2.53 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.1, 153.9, 133.2, 129.8, 128.5, 127.7, 126.8, 114.3, 55.6, 42.9, 34.8. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{18}N_2O_4S+Na]^+$: 357.0879, found: 357.0880.



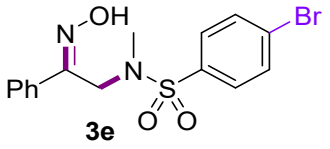
3c

(*Z*)-4-fluoro-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*-methylbenzenesulfonamide (3c) According to the General Procedure B, afforded **3c** (51.4 mg, 76%, *Z*/*E* = 11:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.87 (brs, 1H), 7.82 – 7.73 (m, 4H), 7.42 – 7.40 (m, 3H), 7.22 (t, *J* = 8.5 Hz, 2H), 4.40 (s, 2H), 2.57 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.3 (d, *J* = 254 Hz), 153.6, 133.1, 132.3 (d, *J* = 3 Hz), 130.3 (d, *J* = 9 Hz), 129.9, 128.6, 126.8, 116.5 (d, *J* = 23 Hz), 42.7, 34.8. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{15}H_{15}FN_2O_3S+Na]^+$: 345.0680, found: 345.0679.



3d

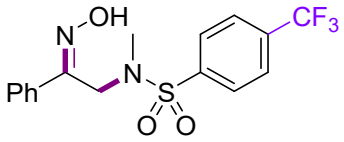
(*Z*)-4-chloro-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*-methylbenzenesulfonamide (3d) According to the General Procedure B, afforded **3d** (48.7 mg, 72%, *Z*/*E*= 10:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.11 (brs, 1H), 7.75 – 7.70 (m, 4H), 7.52 – 7.50 (m, 2H), 7.43 – 7.39 (m, 3H), 4.41 (s, 2H), 2.57 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.6, 139.526, 134.8, 133.1, 129.9, 129.5, 129.0, 128.60, 126.8, 42.8, 34.8. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{15}H_{15}ClN_2O_3S+Na]^+$: 361.0384, found: 361.0383.



3e

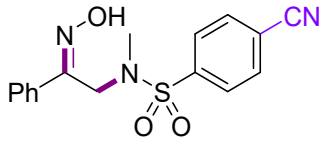
(*Z*)-4-bromo-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*-methylbenzenesulfonamide (3e) According to the General Procedure B, afforded **3e** (57.3 mg, 75%, *Z*/*E* = 13:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.80 (brs, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.78 – 7.73 (m, 4H), 7.44 – 7.39 (m, 3H), 4.29 (s, 2H), 2.46 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.7, 134.6, 134.22, 132.6, 129.5, 129.0, 128.3, 127.4, 126.3, 42.3, 34.9. **HRMS** (ESI, m/z):

(M+Na) calculated for $[C_{15}H_{15}BrN_2O_3S+Na]^+$: 404.9879, found: 404.9880.



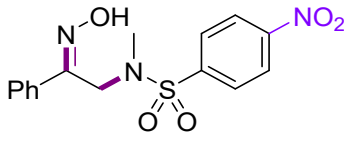
3f

(*Z*)-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*-methyl-4-(trifluoromethyl)benzenesulfonamide (**3f**) According to the General Procedure B, afforded **3f** (54.3 mg, 73%, *Z*/*E* = 9:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.03 (brs, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.73 – 7.61 (m, 2H), 7.44 – 7.37 (m, 3H), 4.45 (s, 2H), 2.61 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.5, 140.1, 134.5 (q, *J* = 33 Hz), 133.0, 130.0, 128.7, 128.0, 126.8, 126.3 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 271 Hz), 42.8, 34.8. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{15}F_3N_2O_3S+Na]^+$: 395.0648, found: 395.0646.



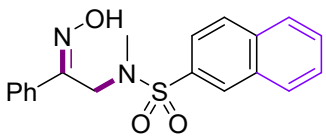
3g

(*Z*)-4-cyano-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*-methylbenzenesulfonamide (**3g**) According to the General Procedure B, afforded **3g** (47.4 mg, 72%, *Z*/*E* = 13:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.78 (brs, 1H), 8.13 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.73 – 7.70 (m, 2H), 7.41 – 7.39 (m, 3H), 4.32 (s, 2H), 2.49 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.7, 139.6, 134.2, 133.6, 129.0, 128.3, 128.2, 126.3, 117.6, 115.7, 42.4, 34.9. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{15}N_3O_3S+Na]^+$: 352.0726, found: 352.0727.



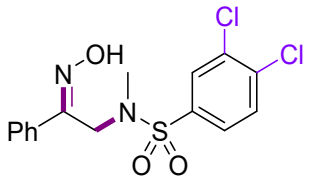
3h

(*Z*)-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*-methyl-4-nitrobenzenesulfonamide (**3h**) According to the General Procedure B, afforded **3h** (56.0 mg, 80%, *Z*/*E* = 11:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.82 (brs, 1H), 8.45 (d, *J* = 8.8 Hz, 2H), 8.09 (d, *J* = 8.9 Hz, 2H), 7.75 – 7.73 (m, 2H), 7.44 – 7.39 (m, 3H), 4.37 (s, 2H), 2.53 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.7, 150.1, 141.0, 134.2, 129.1, 129.1, 128.4, 126.3, 124.8, 42.4, 34.9. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{15}H_{15}N_3O_5S+Na]^+$: 372.0625, found: 372.0623.



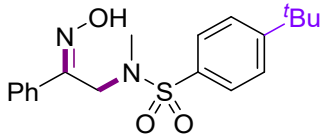
3i

(*Z*)-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*-methylnaphthalene-2-sulfonamide (3i)
According to the General Procedure B, afforded **3i** (53.0 mg, 75%, *Z*/*E* = 11:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.93 (brs, 1H), 8.38 (s, 1H), 8.00 – 7.93 (m, 3H), 7.79 – 7.76 (m, 3H), 7.69 – 7.61 (m, 2H), 7.40 – 7.37 (m, 3H), 4.48 (s, 2H), 2.61 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.8, 134.9, 133.3, 133.1, 132.2, 129.8, 129.4, 129.3, 129.1, 128.9, 128.6, 127.9, 127.6, 126.8, 122.8, 42.8, 34.9. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{19}H_{18}N_2O_3S+Na]^+$: 377.0930, found: 377.0929.



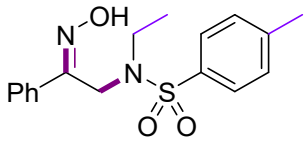
3j

(*Z*)-3,4-dichloro-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*-methylbenzenesulfonamide (3j)
According to the General Procedure B, afforded **3j** (57.5 mg, 77%, *Z*/*E* = 13:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.82 (brs, 1H), 8.04 (d, *J* = 2.2 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.79 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.74 – 7.71 (m, 2H), 7.42 – 7.40 (m, 3H), 4.36 (s, 2H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.3, 137.0, 136.4, 134.7, 133.1, 132.3, 129.7, 129.5, 128.8, 128.0, 126.8, 42.9, 35.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{15}H_{14}Cl_2N_2O_3S+Na]^+$: 394.994, found: 394.9991.



3k

(*Z*)-4-(tert-butyl)-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*-methylbenzenesulfonamide (3k)
According to the General Procedure B, afforded **3k** (59.0 mg, 82%, *Z*/*E*= 14:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.10 (brs, 1H), 7.77 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.73 – 7.71 (m, 2H), 7.55 – 7.53 (m, 2H), 7.40 – 7.38 (m, 3H), 4.42 (s, 2H), 2.56 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.7, 153.9, 133.3, 133.2, 129.8, 128.5, 127.5, 126.9, 126.2, 42.9, 35.1, 34.9, 31.1. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{19}H_{24}N_2O_3S+Na]^+$: 383.1400, found: 383.1396.



3l

(*Z*)-N-ethyl-*N*-(2-(hydroxyimino)-2-phenylethyl)-4-methylbenzenesulfonamide (3l) According to the General Procedure B, afforded **3l** (45.2 mg, 68%, *Z*/*E* = 13 : 1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.18 (brs, 1H), 7.73 – 7.70 (m, 2H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.36 (m, 3H), 7.28 – 7.26 (m, 2H), 4.60 (s, 2H), 3.04 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 0.91 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.1, 143.4, 136.0, 133.5, 129.7, 129.6, 128.5, 127.3, 127.1, 43.2, 40.6, 21.5, 13.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{20}N_2O_3S+Na]^+$: 355.1087, found: 355.1086.

4. General procedures and characterization data of products

4.1. General procedure C for the preparation of (*Z*)-*α*-amino-ketoximes

A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, the appropriate alkenes (0.6 mmol, 3 equiv.), *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ($NANS_1$) (0.2 mmol, 1.0 equiv.) and $Ru(bpy)_3Cl_2$ photosensitizer (1 mol %) were charged under air, CH_3CN (0.1 M, unless otherwise stated) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with a 10 W yellow LED at 30 °C (the distance between the tube and the light source was about 0.5 cm), unless otherwise stated. Upon completion (as judged by TLC analysis), silica was added to the reaction and then concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel (EtOAc : petroleum ether as an eluent) to give the product. (*Z*-type of *α*-amino-ketoximes were obtained as mainly products) Note: The *Z*/*E* ratios were determined by ^{1}H NMR spectroscopy.

4.2. General procedure D for the preparation of (2*E*, 3*Z*)-alkenyl-ketoximes

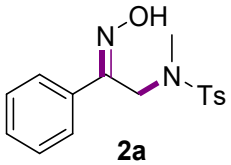
A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, the appropriate 1,3-dienes (0.6 mmol, 3 equiv.), *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ($NANS_1$) (0.2 mmol, 1.0 equiv.) and $Ru(bpy)_3Cl_2$ photosensitizer (1 mol %) were charged under air, CH_3CN (0.1 M, 2 mL) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with a 6 W Green LED at 30 °C (the distance between the tube and the light source was about 0.5 cm), unless otherwise

stated. Upon completion (as judged by TLC analysis), silica was added to the reaction and then concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel (EtOAc : petroleum ether as an eluent) to give the product. Note: The *Z*/*E* ratios were determined by ^{1}H NMR spectroscopy.

4.3. General procedure E for the preparation of (*E*)-*α*-amino-ketoximes

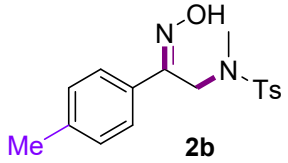
A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, the appropriate alkenes (0.6 mmol, 3 equiv.), *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ($NANS_1$) (0.2 mmol, 1.0 equiv.) and $[Ir(dF(CF_3)ppy)_2(dtbbpy)]Cl$ photosensitizer (1 mol %) were charged under air, CH_3CN (0.1 M, 2 mL) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with a 3 W blue LED at 30 °C (the distance between the tube and the light source was about 0.5 cm), unless otherwise stated. Upon completion (as judged by TLC analysis), silica was added to the reaction and then concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel (EtOAc : petroleum ether as an eluent) to give the product. (*E*-type of *α*-amino-ketoximes were obtained as mainly products) Note: The *Z*/*E* ratios were determined by ^{1}H NMR spectroscopy.

4.4. Characterization data of products



2a

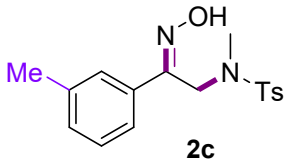
(*Z*)-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*,4-dimethylbenzenesulfonamide (2a)
According to the General Procedure C, afforded **2a** (53.0 mg, 83%, *Z*/*E* = 12:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 11.80 (brs, 1H), 7.81 – 7.73 (m, 4H), 7.48 – 7.38 (m, 5H), 4.26 (s, 2H), 2.43 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 150.8, 143.9, 134.3, 132.2, 130.0, 129.1, 128.4, 127.6, 126.3, 42.4, 34.9, 21.1. **HRMS** (ESI, m/z): (M+H) calculated for $[C_{16}H_{19}N_2O_3S]^+$: 319.1117, found: 319.1111.



2b

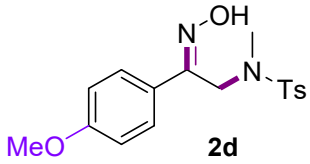
(*Z*)-*N*-(2-(hydroxyimino)-2-(*p*-tolyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2b)
According to the General Procedure C, afforded **2b** (53.0 mg, 80%, *Z*/*E* = 9:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.07 (brs, 1H), 7.69 – 7.66 (m, 4H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.37 (s, 2H), 2.53 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H). **^{13}C NMR**

(100 MHz, Chloroform-*d*) δ 153.7, 143.7, 139.9, 133.2, 130.3, 129.8, 129.3, 127.7, 126.7, 42.8, 34.8, 21.5, 21.3. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{20}N_2O_3S+Na]^+$: 355.1087, found: 355.1084.



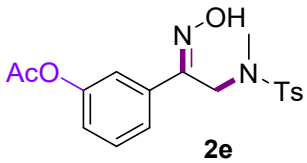
2c

(*Z*)-*N*-(2-(hydroxyimino)-2-(m-tolyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2c) According to the General Procedure C, afforded **2c** (54.0 mg, 81%, *Z*/*E* = 12:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.81 (brs, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 4.37 (s, 2H), 2.54 (s, 3H), 2.44 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.0, 143.7, 138.2, 133.3, 133.1, 130.6, 129.8, 128.5, 127.7, 127.4, 124.0, 42.8, 34.8, 21.5, 21.4. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{20}N_2O_3S+Na]^+$: 355.1087, found: 355.1085.



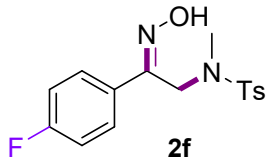
2d

(*Z*)-*N*-(2-(hydroxyimino)-2-(4-methoxyphenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2d) According to the General Procedure C, afforded **2d** (53.6 mg, 77%, *Z*/*E* = 6:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.01 (brs, 1H), 7.74 (d, *J* = 8.9 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.35 (s, 2H), 3.82 (s, 3H), 2.54 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 160.8, 153.1, 143.8, 133.1, 129.8, 128.3, 127.7, 125.6, 114.0, 55.3, 42.7, 34.8, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{20}N_2O_4S+Na]^+$: 371.1036, found: 371.1038.



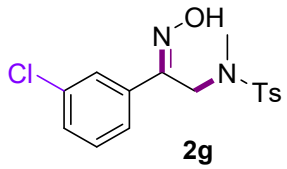
2e

(*Z*)-3-(2-((*N*,4-dimethylphenyl)sulfonamido)-1-(hydroxyimino)ethyl)phenyl acetate (2e) According to the General Procedure C, afforded **2e** (57.0 mg, 76%, *Z*/*E* = 12:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.81 (brs, 1H),7.68 – 7.66 (m, 3H), 7.53 (s, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.13 (dd, *J* = 8.0, 2.3 Hz, 1H), 4.33 (s, 2H), 2.53 (s, 3H), 2.43 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.5, 152.6, 150.7, 143.8, 134.9, 133.0, 129.8, 129.5, 127.7, 124.4, 122.9, 119.8, 42.6, 34.9, 21.5, 21.1. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{20}N_2O_5S+Na]^+$: 399.0985, found: 399.0981.



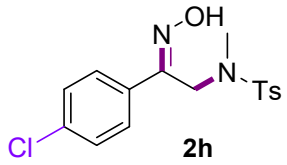
2f

(*Z*)-*N*-(2-(4-fluorophenyl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (2f) According to the General Procedure C, afforded **2f** (53.0mg, 79%, *Z*/*E* = 7:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.75 (brs, 1H), 7.78 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 8.7 Hz, 2H), 4.35 (s, 2H), 2.53 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.7 (d, *J* = 249 Hz), 152.9, 143.9, 133.0, 129.8, 129.3 (d, *J* = 4 Hz), 128.7 (d, *J* = 8 Hz), 127.6, 115.6 (d, *J* = 21 Hz), 42.9, 34.8, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{17}FN_2O_3S+Na]^+$: 359.0836, found: 359.0837.



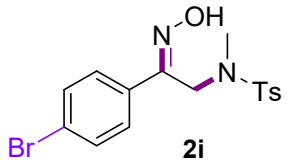
2g

(*Z*)-*N*-(2-(3-chlorophenyl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (2g) According to the General Procedure C, afforded **2g** (52.0 mg, 74%, *Z*/*E* = 8:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.97 (brs, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.73 – 7.71 (m, 3H), 7.48 – 7.45 (m, 4H), 4.23 (s, 2H), 2.43 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 149.8, 143.9, 136.4, 133.2, 132.1, 130.2, 130.0, 128.8, 127.6, 126.1, 124.8, 42.3, 35.0, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{17}ClN_2O_3S+Na]^+$: 375.0541, found: 375.0540.



2h

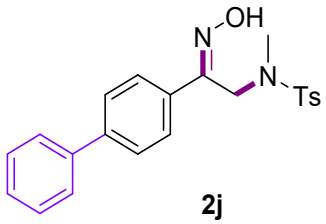
(*Z*)-*N*-(2-(4-chlorophenyl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (2h) According to the General Procedure C, afforded **2h** (53.0 mg, 75%, *Z*/*E* = 10:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.88 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.35 (dd, *J* = 8.4, 2.4 Hz, 4H), 4.34 (s, 2H), 2.53 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 152.9, 144.0, 135.8, 133.0, 131.6, 129.8, 128.8, 128.2, 127.6, 42.81, 34.9, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{17}ClN_2O_3S+Na]^+$: 375.0541, found: 375.0540.



2i

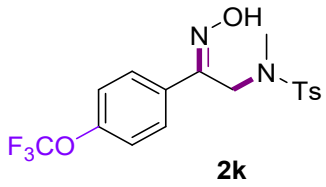
(*Z*)-*N*-(2-(4-bromophenyl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (2i) According to the General Procedure C, afforded **2i** (59.5 mg, 75%, *Z*/*E* = 8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.76 (brs, 1H), 7.67 (dd, *J* = 8.3, 6.5 Hz, 4H), 7.51 (d, *J*

= 8.5 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 4.34 (s, 2H), 2.53 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.0, 144.0, 133.0, 132.1, 131.7, 129.9, 128.4, 127.6, 124.2, 42.8, 34.9, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{17}BrN_2O_3S+Na]^+$: 419.0035, found: 419.0041.



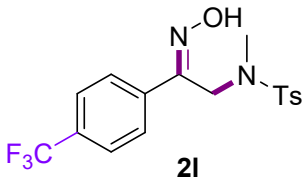
2j

(*Z*)-*N*-(2-([1,1'-biphenyl]-4-yl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (2j) According to the General Procedure C, afforded **2j** (62.5 mg, 79%, *Z*/*E* = 12:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.81 (brs, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.85 – 7.72 (m, 6H), 7.50 – 7.41 (m, 4H), 7.39 (t, *J* = 7.3 Hz, 1H), 4.26 (s, 2H), 2.44 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.4, 143.8, 140.6, 139.5, 133.3, 132.2, 130.0, 129.0, 127.7, 127.6, 126.8, 126.7, 126.6, 42.3, 34.9, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{22}H_{22}N_2O_3S+Na]^+$: 417.1243, found: 417.1246.



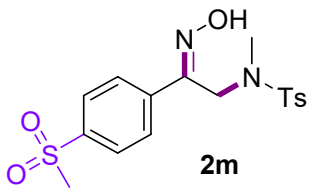
2k

(*Z*)-*N*-(2-(hydroxyimino)-2-(4-(trifluoromethoxy)phenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2k) According to the General Procedure C, afforded **2k** (57.0 mg, 71%, *Z*/*E* = 7:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.00 (brs, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.36 (s, 2H), 2.54 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 152.6, 150.2 (q, *J* = 2 Hz), 150.2, 144.0, 132.8, 131.7, 129.9, 128.5, 127.6, 120.7, 120.4 (q, *J* = 256.3 Hz), 42.8, 34.9, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{17}F_3N_2O_4S+Na]^+$: 425.0753, found: 425.0750.



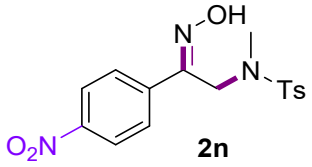
2l

(*Z*)-*N*-(2-(hydroxyimino)-2-(4-(trifluoromethyl)phenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2l) According to the General Procedure C, afforded **2l** (47.0 mg, 61%, *Z*/*E* = 6:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.81 (brs, 1H), 7.92(d, *J* = 8.1 Hz, 2H), 7.66 (dd, *J* = 15.1, 8.1 Hz, 4H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.38 (s, 2H), 2.54 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 152.8, 144.1, 136.6, 132.9, 131.4 (q, *J* = 32 Hz), 129.9, 127.6, 127.2, 125.5 (q, *J* = 4 Hz), 124.0 (q, *J* = 270 Hz), 42.8, 35.0, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{17}F_3N_2O_3S+Na]^+$: 409.0804, found: 409.0800.



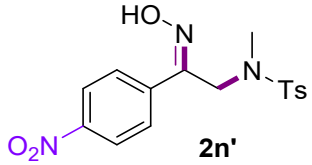
2m

(*Z*)-*N*-(2-(hydroxyimino)-2-(4-(methylsulfonyl)phenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2m) According to the General Procedure C, afforded **2m** (59.7 mg, 75%, *Z*/*E* > 20:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.19 (brs, 1H), 8.03 – 7.98 (s, 4H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 4.29 (s, 2H), 3.27 (s, 3H), 2.45 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.2, 144.0, 140.9, 139.2, 132.1, 130.0, 127.6, 127.1, 127.0, 43.4, 42.5, 35.1, 21.1. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{20}N_2O_5S_2+Na]^+$: 419.0706, found: 419.0707.



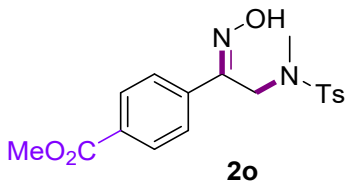
2n

(*Z*)-*N*-(2-(hydroxyimino)-2-(4-nitrophenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2n) According to the General Procedure C (3W blue LEDs was used as the light source), afforded **2n** (43.0 mg, 59%, *Z*/*E* = 2:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.31 (brs, 1H), 8.31 – 8.24 (m, 2H), 8.00 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 4.29 (s, 2H), 2.44 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.0, 147.5, 144.0, 140.7, 132.1, 130.0, 127.6, 127.4, 123.5, 42.5, 35.1, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{17}N_3O_5S+Na]^+$: 386.0781, found: 386.0783.



2n'

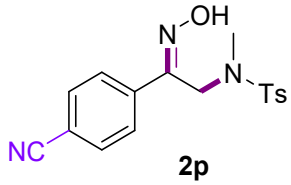
(*E*)-*N*-(2-(hydroxyimino)-2-(4-nitrophenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide
According to the General Procedure C (3W blue LEDs was used as the light source), afforded **2n′** (21.6 mg, 30%, *Z*/*E* = 2:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.67 (s, 1H), 8.26 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 4.07 (s, 2H), 2.56 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 149.6, 147.3, 143.6, 138.2, 133.4, 130.0, 129.9, 127.3, 123.1, 53.3, 34.5, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{17}N_3O_5S+Na]^+$: 386.0781, found: 386.0785.



2o

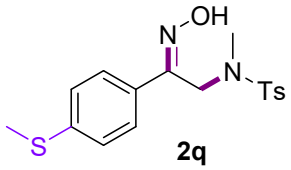
methyl (*Z*)-4-(2-((*N*,4-dimethylphenyl)sulfonamido)-1-(hydroxyimino)ethyl)benzoate (2o)

According to the General Procedure C, afforded **2o** (55.6 mg, 74%, *Z*/*E* = 12:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.05 (brs, 1H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 4.26 (s, 2H), 3.87 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 165.9, 150.4, 143.9, 138.8, 132.2, 130.0, 129.8, 129.1, 127.6, 126.5, 52.2, 42.4, 35.0, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{20}N_2O_5S+Na]^+$: 399.0985, found: 399.0986.



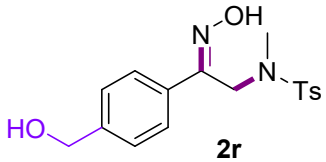
2p

(*Z*)-*N*-(2-(4-cyanophenyl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (2p) According to the General Procedure C, afforded **2p** (48.7 mg, 71%, *Z*/*E* = 12:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.22 (brs, 1H), 7.94 – 7.89 (m, 4H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 4.25 (s, 2H), 2.42 (s, 6H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.0, 144.0, 138.8, 132.3, 132.0, 130.0, 127.6, 127.0, 118.7, 111.5, 42.4, 35.1, 21.1. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{17}N_3O_3S+Na]^+$: 366.0883, found: 366.0885.



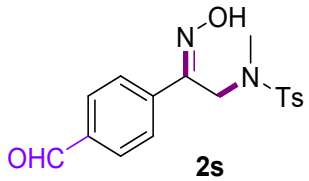
2q

(*Z*)-*N*-(2-(hydroxyimino)-2-(4-(methylthio)phenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2q) According to the General Procedure C, afforded **2q** (59.7 mg, 82%, *Z*/*E* = 5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.73 (brs, 1H), 7.72 – 7.67 (m, 4H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.35 (s, 2H), 2.54 (s, 3H), 2.49 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.2, 143.8, 141.0, 133.1, 129.8, 129.7, 129.6, 127.7, 127.2, 127.1, 125.9, 42.7, 34.8, 21.5, 15.2. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{20}N_2O_3S_2+Na]^+$: 387.0808, found: 387.0811.



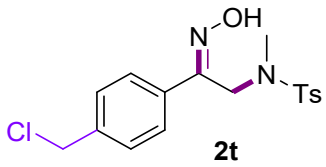
2r

(*Z*)-*N*-(2-(hydroxyimino)-2-(4-(hydroxymethyl)phenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (**2r**) According to the General Procedure C, afforded **2r** (41.1 mg, 59%, *Z*/*E* > 20:1) as a white solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.63 (s, 2H), 4.33 (s, 2H), 2.49 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Methanol-d_4) δ 153.0, 145.5, 143.8, 134.6, 134.3, 130.9, 128.9, 127.9, 127.8, 64.9, 43.7, 35.3, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{20}N_2O_4S+Na]^+$: 371.1036, found: 371.1037.



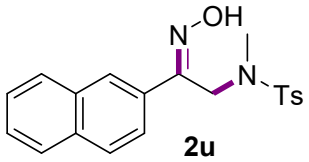
2s

(*Z*)-*N*-(2-(4-formylphenyl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (2s) According to the General Procedure C, afforded **2s** (26.5 mg, 38%, *Z*/*E* = 18:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 8.78 (brs, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 4.39 (s, 2H), 2.54 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 192.0, 152.8, 144.1, 139.0, 136.8, 132.8, 129.9, 129.8, 127.7, 127.5, 42.7, 34.9, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{18}N_2O_4S+Na]^+$: 369.0879, found: 369.0877.



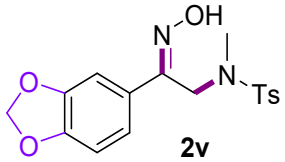
2t

(*Z*)-*N*-(2-(4-(chloromethyl)phenyl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (2t) According to the General Procedure C, afforded **2t** (46.4 mg, 63%, *Z*/*E* = 9:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.84 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.50 – 7.46 (m, 4H), 4.78 (s, 2H), 4.25 (s, 2H), 2.43 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.6, 143.9, 138.4, 134.3, 132.2, 130.0, 128.8, 127.6, 126.6, 45.8, 42.4, 34.9, 21.1. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{19}ClN_2O_3S+Na]^+$: 389.0697, found: 389.0695.



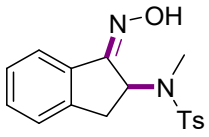
2u

(*Z*)-*N*-(2-(hydroxyimino)-2-(naphthalen-2-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2u) According to the General Procedure C, afforded **2u** (57.0 mg, 77%, *Z*/*E* = 6:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.40 (s, 1H), 8.11 (d, *J* = 1.6 Hz, 1H), 7.97 – 7.90 (m, 3H), 7.70 – 7.67 (m, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.54 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.15 (s, 2H), 2.57 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.7, 143.4, 133.5, 132.8, 132.3, 129.7, 129.2, 128.3, 128.1, 127.9, 127.5, 127.2, 126.8, 126.3, 126.1, 53.5, 34.4, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{20}H_{20}N_2O_3S+Na]^+$: 391.1087, found: 391.1086.



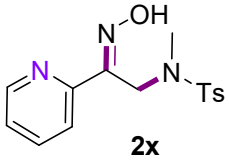
2v

(*Z*)-*N*-(2-(benzo[d][1,3]dioxol-5-yl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (2v) According to the General Procedure C, afforded **2v** (50.0 mg, 69%, *Z*/*E*= 5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.68 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 3H), 7.24 (d, *J* = 1.8 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 5.98 (s, 2H), 4.31 (s, 2H), 2.55 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.1, 149.0, 147.8, 143.8, 133.1, 129.8, 129.7, 127.7, 127.2, 121.7, 108.3, 106.7, 101.3, 42.7, 34.8, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{18}N_2O_5S+Na]^+$: 385.0829, found: 385.0832.



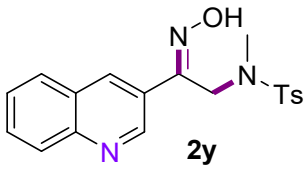
2w

(*S*,*Z*)-*N*-(1-(hydroxyimino)-2,3-dihydro-1H-inden-2-yl)-*N*,4-dimethylbenzenesulfonamide (2w) According to the General Procedure C, afforded **2w** (46.4 mg, 70%, *Z*/*E* = 1.2:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.42 (brs, 1H), 8.76 (brs, 1.2 H), 8.40 (d, *J* = 7.8 Hz, 1H), 7.82 – 7.79 (m, 4.54 H), 7.61 (d, *J* = 7.7 Hz, 1.27 H), 7.41 – 7.23 (m, 11.93 H), 5.63 (dd, *J* = 8.5, 3.0 Hz, 1.22 H), 5.42 (dd, *J* = 8.8, 5.3 Hz, 1H), 3.38 (dd, *J* = 17.9, 8.6 Hz, 1.23 H), 3.17 (dd, *J* = 17.2, 8.8 Hz, 1H), 2.89 – 2.81 (m, 2.33 H), 2.67 (s, 3H), 2.60 (s, 3.7 H), 2.43 – 2.41 (m, 6.89 H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 157.9, 155.5, 144.9, 144.5, 143.4, 143.2, 136.4, 136.3, 134.7, 132.1, 131.5, 131.1, 129.7, 129.4, 129.2, 127.6, 127.5, 127.4, 125.3, 121.4, 57.9, 55.0, 35.4, 32.4, 30.0, 29.3, 21.5, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{18}N_2O_3S+Na]^+$: 353.0930, found: 353.0928.



2x

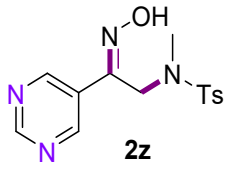
(*E*)-*N*-(2-(hydroxyimino)-2-(pyridin-2-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2x) According to the General Procedure C, afforded **2x** (22.5 mg, 35%, *E*/*Z* > 20:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 (brs, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.77 – 7.68 (m, 3H), 7.36 – 7.27 (m, 3H), 4.47 (s, 2H), 2.67 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 152.9, 152.3, 149.0, 143.6, 136.9, 133.4, 129.7, 127.7, 124.0, 122.2, 42.3, 35.7, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{15}H_{17}N_3O_3S+Na]^+$: 342.0883, found: 342.0881.



2y

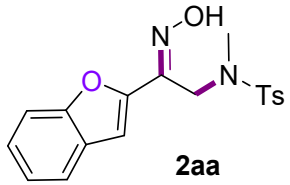
(*Z*)-*N*-(2-(hydroxyimino)-2-(quinolin-3-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (2y) According to the General Procedure C, afforded **2y** (57.0 mg, 77%, *Z*/*E* = 11:1) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.03 (brs, 1H), 9.17 (s, 1H), 8.52 (s, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.64 (d, J = 7.9 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.37 (d, J = 7.9 Hz, 2H), 4.29 (s, 2H), 2.40 (s, 4H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.1, 148.9, 147.8, 144.4, 133.9, 132.8, 130.6, 130.5, 129.2, 129.0, 128.0, 127.8, 127.7, 127.5, 43.1, 35.7, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{19}H_{19}N_3O_3S+Na]^+$: 392.1039, found: 392.1041.



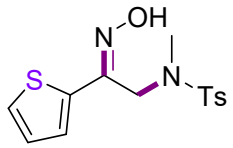
2z

(*Z*)-*N*-(2-(hydroxyimino)-2-(pyrimidin-5-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (**2z**) According to the General Procedure C, afforded **2z** (20.6 mg, 32%, *Z*/*E* = 2:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.28 (brs, 1H), 11.86 (brs, 0.5 H), 9.22 (s, 1H), 9.19 (s, 0.5 H), 9.09 (s, 2H), 9.02 (s, 1H), 7.72 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 4.28 (s, 2H), 4.08 (s, 1H), 2.56 (s, 1.5 H), 2.48 (s, 3H), 2.43 (s, 3H), 2.41 (s, 1.5 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 158.2, 158.1, 156.5, 154.5, 147.8, 146.1, 144.0, 143.7, 133.1, 132.1, 130.0, 129.9, 128.2, 127.5, 127.3, 125.5, 52.6, 42.7, 35.4, 34.6, 21.0, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{14}H_{16}N_4O_3S+Na]^+$: 343.0835, found: 343.0833.



2aa

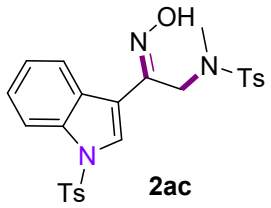
(*E*)-*N*-(2-(benzofuran-2-yl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (**2aa**) According to the General Procedure C, afforded **2aa** (55.2 mg, 77%, *E*/*Z* = 3:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.43 (brs, 1H), 12.21 (brs, 0.32H), 7.79 – 7.67 (m, 5.1H), 7.60 – 7.56 (m, 1.38 H), 7.47 – 7.34 (m, 4.73 H), 7.31 – 7.25 (m, 1.46 H), 4.23 (s, 2H), 4.20 (s, 0.80 H), 2.64 (s, 3H), 2.57 (s, 1H), 2.40 (s, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 154.2, 152.7, 150.6, 145.4, 143.9, 143.8, 143.4, 141.1, 133.8, 132.4, 130.0, 129.8, 129.6, 127.8, 127.7, 127.5, 127.3, 126.7, 126.4, 125.7, 123.4, 123.3, 122.3, 121.7, 113.1, 111.4, 111.2, 107.1, 50.5, 42.4, 35.2, 34.8, 21.02, 20.98. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{18}N_2O_4S+Na]^+$: 381.0879, found: 381.0878.



2ab

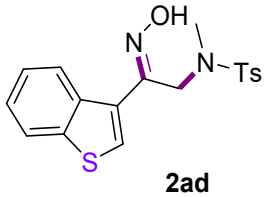
(*E*)-*N*-(2-(hydroxyimino)-2-(thiophen-2-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (**2ab**) According to the General Procedure C, afforded **2ab** (50 mg, 77%, *E*/*Z* = 10:1) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.30 (brs, 1H), 7.90 (d, J = 3.8 Hz, 1H), 7.80 (d, J = 5.1 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.48 (d, J = 7.9 Hz, 2H), 7.22 (dd, J = 5.1, 3.8 Hz, 1H), 4.08 (s, 2H), 2.49 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 143.8, 143.6, 132.5, 130.9, 130.0, 129.8, 129.4, 127.5, 125.8, 52.8, 34.2, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{14}H_{16}N_2O_3S_2+Na]^+$: 347.0495, found: 347.0497.



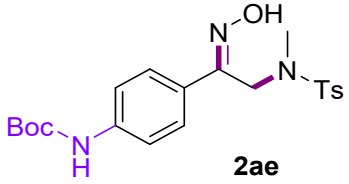
2ac

(*Z*)-*N*-(2-(hydroxyimino)-2-(1-tosyl-1H-indol-3-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (**2ac**) According to the General Procedure C, afforded **2ac** (65.5 mg, 64%, *Z*/*E* = 6:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.82 (brs, 1H), 8.35 (d, J = 1.4 Hz, 1H), 8.11 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.34 – 7.28 (m, 1H), 4.28 (s, 2H), 2.49 (s, 4H), 2.42 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 147.6, 145.8, 143.9, 134.6, 133.7, 132.6, 130.3, 130.0, 127.7, 127.5, 127.4, 126.8, 125.4, 124.1, 123.3, 116.9, 113.2, 42.9, 35.1, 21.0, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{25}H_{25}N_3O_5S_2+Na]^+$: 534.1128, found: 534.1126.



2ad

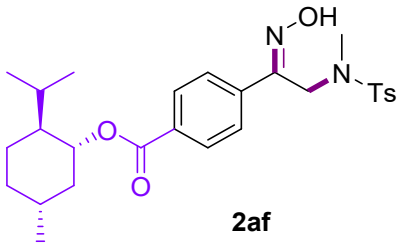
(*Z*)-*N*-(2-(benzo[b]thiophen-3-yl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (**2ad**) According to the General Procedure C, afforded **2ad** (47.0 mg, 63%, *Z*/*E* = 5:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.83 (brs, 1H), 8.53 (dd, J = 7.9, 1.6 Hz, 1H), 8.19 (s, 1H), 8.07 – 7.97 (m, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.51 – 7.40 (m, 4H), 4.33 (s, 2H), 2.53 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 148.9, 143.8, 139.6, 136.4, 132.4, 130.0, 129.9, 128.4, 127.5, 125.4, 124.8, 124.7, 122.8, 43.3, 35.1, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{18}N_2O_3S_2+Na]^+$: 397.0651, found: 397.0649.



2ae

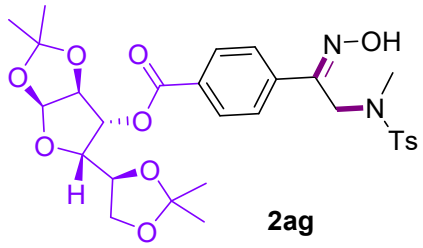
tert-butyl (*Z*)-(4-(2-((*N*,4-dimethylphenyl)sulfonamido)-1-(hydroxyimino)ethyl)phenyl)carbamate (**2ae**) According to the General Procedure C, afforded **2ae** (75.4 mg, 87%, *Z*/*E* = 10 : 1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ

11.35 (s, 1H), 9.29 (s, 1H), 7.64 (t, J = 8.0 Hz, 4H), 7.57 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 4.17 (s, 2H), 2.41 (m, 6H), 1.48 (s, 9H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 152.6, 150.0, 143.4, 140.2, 132.3, 129.6, 127.3, 126.4, 117.6, 79.0, 41.9, 34.4, 28.1, 21.1. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{21}H_{27}N_3O_5S+Na]^+$: 456.1564, found: 456.1568.



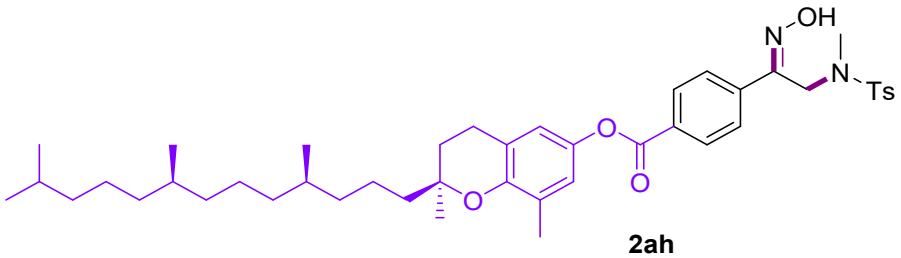
2af

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((*Z*)-2-((*N*,4-dimethylphenyl)sulfonamido)-1-(hydroxyimino)ethyl)benzoate (**2af**) According to the General Procedure C, afforded **2af** (86.0 mg, 86%, *Z*/*E* = 15:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 8.07 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.98 – 4.91 (m, 1H), 4.39 (s, 2H), 2.54 (s, 3H), 2.44 (s, 3H), 2.16 – 2.13 (m, 1H), 2.02 – 1.94 (m, 1H), 1.77 – 1.72 (m, 2H), 1.60 – 1.52 (m, 2H), 1.18 – 1.06 (m, 2H), 0.99 – 0.88 (m, 7H), 0.80 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.8, 152.9, 143.9, 137.4, 132.9, 131.6, 129.8, 129.7, 127.6, 126.8, 47.2, 42.8, 40.9, 34.9, 34.2, 31.4, 26.4, 23.5, 22.0, 21.5, 20.7, 16.4. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{27}H_{36}N_2O_5S+Na]^+$: 523.2237, found: 523.2236.



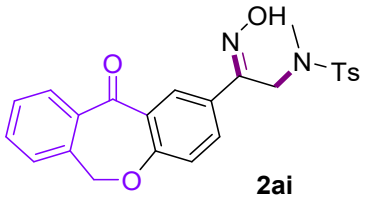
2ag

(3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-((*Z*)-2-((*N*,4-dimethylphenyl)sulfonamido)-1-(hydroxyimino)ethyl)benzoate (**2ag**) According to the General Procedure C, afforded **2ah** (58.2 mg, 48%, *Z*/*E* = 7:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.24 (brs, 1H), 8.00 (d, J = 8.3 Hz, 2H), 7.86 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.94 (d, J = 3.6 Hz, 1H), 5.49 (d, J = 2.9 Hz, 1H), 4.63 (d, J = 3.6 Hz, 1H), 4.43 – 4.38 (m, 1H), 4.33 – 4.31 (m, 3H), 4.16 – 4.08 (m, 2H), 2.50 (s, 3H), 2.44 (s, 3H), 1.54 (s, 3H), 1.41 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.8, 152.2, 143.9, 138.3, 132.9, 130.0, 129.9, 129.7, 127.6, 126.9, 112.4, 109.6, 105.1, 83.3, 79.9, 72.5, 67.2, 42.6, 34.8, 26.8, 26.7, 26.1, 25.1, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{29}H_{36}N_2O_{10}S+Na]^+$: 627.1983, found: 627.1982.



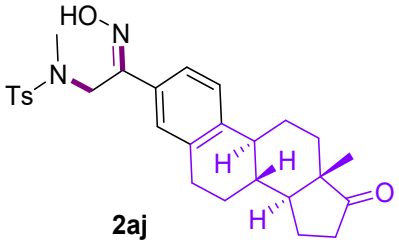
2ah

(S)-2,8-dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 4-((*Z*)-2-((*N*,4-dimethylphenyl)sulfonamido)-1-(hydroxyimino)ethyl)benzoate (**2ah**) According to the General Procedure C, afforded **2ag** (60.0 mg, 40%, *Z*/*E* = 5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.74 (brs, 1H), 8.20 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 6.79 (dd, *J* = 20.4, 2.8 Hz, 2H), 4.41 (s, 2H), 2.79 – 2.75 (m, 2H), 2.56 (s, 3H), 2.46 (s, 3H), 2.18 (s, 3H), 1.87 – 1.72 (m, 2H), 1.62 – 1.46 (m, 4H), 1.45 – 1.34 (m, 4H), 1.31 – 1.26 (m, 10H), 1.17 – 1.04 (m, 6H), 0.88 – 0.85 (m, 12H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.4, 153.1, 149.9, 143.9, 142.6, 137.9, 133.0, 130.8, 130.2, 129.9, 127.7, 127.4, 127.0, 121.1, 121.1, 119.1, 42.8, 40.1, 39.4, 37.4, 37.4, 37.3, 34.9, 32.8, 32.7, 31.0, 28.0, 24.8, 24.4, 24.2, 22.7, 22.6, 22.5, 21.5, 21.0, 19.7, 19.6, 16.1. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{44}H_{62}N_2O_6S+Na]^+$: 769.4221, found: 769.4226.



2ai

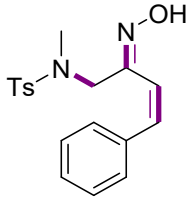
(*Z*)-*N*-(2-(hydroxyimino)-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (**2ai**) According to the General Procedure C, afforded **2ai** (64.9 mg, 72%, *Z*/*E* = 8:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.77 (brs, 1H), 8.53 (d, *J* = 2.4 Hz, 1H), 7.94 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.67 (t, *J* = 7.1 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 1H), 5.36 (s, 2H), 4.25 (s, 2H), 2.44 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 190.0, 161.3, 149.9, 143.8, 141.0, 135.7, 133.3, 133.1, 132.2, 130.0, 129.4, 129.3, 128.8, 128.4, 128.2, 127.6, 124.7, 120.8, 72.7, 42.3, 35.0, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{24}H_{22}N_2O_5S+Na]^+$: 473.1142, found: 473.1143.



2aj

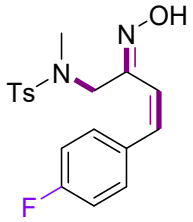
***N*-((*Z*)-2-(hydroxyimino)-2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide** (**2aj**) According to the General Procedure C, afforded **2aj** (57.5

mg, 58%, *Z*/*E* = 5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.72 (brs, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.48 (m, 2H), 7.35 – 7.30 (m, 3H), 4.35 (s, 2H), 2.97 – 2.93 (m, 2H), 2.54 – 2.41 (m, 8H), 2.33 – 2.28 (m, 1H), 2.22 – 1.96 (m, 4H), 1.69 – 1.40 (m, 6H), 0.92 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 221.1, 153.5, 143.7, 141.6, 136.7, 133.2, 130.7, 129.8, 127.7, 127.4, 125.5, 124.1, 50.5, 48.0, 44.4, 42.6, 37.9, 35.8, 34.8, 31.5, 29.3, 26.4, 25.5, 21.6, 21.5, 13.8. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{28}H_{34}N_2O_4S+Na]^+$: 517.2131, found: 517.2134.



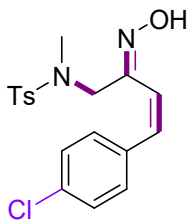
4a

***N*-((2*E*,3*Z*)-2-(hydroxyimino)-4-phenylbut-3-en-1-yl)-*N*,4-dimethylbenzenesulfonamide** (**4a**) According to the General Procedure D, afforded **4a** (58.0 mg, 84%) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.83 (brs, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.28 – 7.21 (m, 4H), 6.85 (d, *J* = 12.4 Hz, 1H), 6.17 (d, *J* = 12.4 Hz, 1H), 3.62 (s, 2H), 2.59 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.3, 143.4, 136.3, 135.8, 134.2, 129.5, 128.4, 128.4, 127.4, 119.4, 51.4, 35.1, 21.4. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{20}N_2O_3S+Na]^+$: 367.1087, found: 367.1083.



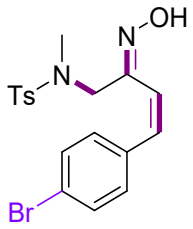
4b

***N*-((2*E*,3*Z*)-4-(4-fluorophenyl)-2-(hydroxyimino)but-3-en-1-yl)-*N*,4-dimethylbenzenesulfonamide** (**4b**) According to the General Procedure D, afforded **4b** (59 mg, 81%) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.69 (brs, 1H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.23 (m, 4H), 7.02 (t, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 12.4 Hz, 1H), 6.13 (d, *J* = 12.4 Hz, 1H), 3.62 (s, 2H), 2.60 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 162.6 (d, *J* = 247 Hz), 153.1, 143.5, 134.6, 134.2, 132.43 (d, *J* = 4 Hz), 130.2 (d, *J* = 8 Hz), 129.6, 127.4, 119.2, 115.4 (d, *J* = 22 Hz), 51.5, 35.0, 21.4. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{19}FN_2O_3S+Na]^+$: 385.0993, found: 385.0988.



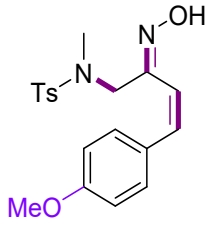
4c

***N*-((2*E*,3*Z*)-4-(4-chlorophenyl)-2-(hydroxyimino)but-3-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (4c)** According to the General Procedure D, afforded **4c** (55 mg, 73%) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.38 (brs, 1H), 7.51 (d, J = 8.1 Hz, 2H), 7.41 – 7.36 (m, 4H), 7.25 (d, J = 8.3 Hz, 2H), 6.72 (d, J = 12.5 Hz, 1H), 6.09 (d, J = 12.5 Hz, 1H), 3.60 (s, 2H), 2.52 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.2, 143.4, 135.3, 133.7, 132.7, 132.6, 129.9, 129.8, 128.4, 127.1, 121.3, 51.6, 34.9, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{19}ClN_2O_3S+Na]^+$: 401.0697, found: 401.0695.



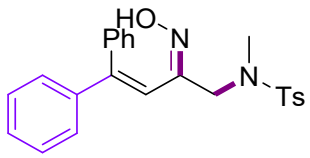
4d

***N*-((2*E*,3*Z*)-4-(4-bromophenyl)-2-(hydroxyimino)but-3-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (4d)** According to the General Procedure D, afforded **4d** (59 mg, 71 %) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.42 (brs, 1H), 7.51 (d, J = 7.9 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.27 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 12.4 Hz, 1H), 6.17 (d, J = 12.4 Hz, 1H), 3.61 (s, 2H), 2.61 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.0, 143.5, 135.3, 134.5, 134.2, 131.6, 130.0, 129.7, 127.4, 122.5, 120.0, 51.6, 35.0, 29.7, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{19}BrN_2O_3S+Na]^+$: 445.0192, found: 445.0189.



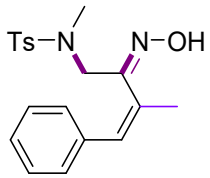
4e

***N*-((2*E*,3*Z*)-2-(hydroxyimino)-4-(4-methoxyphenyl)but-3-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (4e)** According to the General Procedure D, afforded **4d** (53.5 mg, 71%) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.94 (brs, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.25 – 7.19 (m, 4H), 6.85 (d, J = 8.3 Hz, 2H), 6.78 (d, J = 12.3 Hz, 1H), 6.03 (d, J = 12.3 Hz, 1H), 3.81 (s, 3H), 3.67 (s, 2H), 2.61 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 159.7, 153.5, 143.4, 135.4, 134.1, 129.9, 129.5, 128.8, 127.4, 117.3, 113.8, 55.2, 51.4, 35.0, 21.4. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{19}H_{22}N_2O_4S+Na]^+$: 397.1192, found: 397.1195.



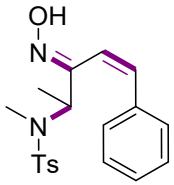
4f

(*E*)-*N*-(2-(hydroxyimino)-4,4-diphenylbut-3-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (4f) According to the General Procedure D, afforded **4f** (65.0 mg, 77%, *E*/*Z* = 20:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.24 (brs, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.36 (m, 3H), 7.32 – 7.30 (m, 3H), 7.29 – 7.21 (m, 6H), 6.60 (s, 1H), 3.29 (s, 2H), 2.56 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.3, 148.6, 143.2, 141.2, 139.3, 134.3, 130.0, 129.5, 128.7, 128.5, 128.5, 128.4, 128.2, 127.5, 117.5, 51.2, 35.3, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{24}H_{24}N_2O_3S+Na]^+$: 443.1400, found: 443.1397.



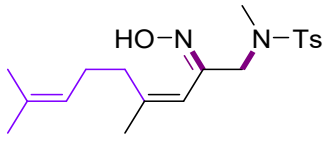
4g

***N*-((2*E*,3*Z*)-2-(hydroxyimino)-3-methyl-4-phenylbut-3-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (4g)** According to the General Procedure D, afforded **4g** (43.0 mg, 60%, *E*/*Z* = 5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.77 (brs, 1H), 7.60 – 7.52 (m, 2H), 7.54 – 7.25 (m, 6H), 7.21 – 7.18 (m, 1H), 6.63 – 6.62 (m, 1H), 3.84 (s, 2H), 2.46 (s, 3H), 2.40 (s, 3H), 2.17 (d, *J* = 1.7 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 157.5, 143.5, 136.8, 133.5, 132.4, 131.0, 129.6, 128.5, 128.3, 127.5, 127.2, 45.3, 36.5, 24.9, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{19}H_{22}N_2O_3S+Na]^+$: 381.1243, found: 381.1240.



4h

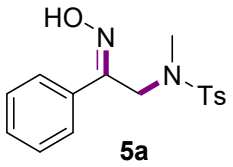
***N*-((S,3*E*,4*Z*)-3-(hydroxyimino)-5-phenylpent-4-en-2-yl)-*N*,4-dimethylbenzenesulfonamide (4h)** According to the General Procedure D, afforded **4h** (67.0 mg, 93%) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.65 (brs, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.29 – 7.20 (m, 5H), 6.73 (d, *J* = 12.4 Hz, 1H), 6.02 (d, *J* = 12.4 Hz, 1H), 4.60 (q, *J* = 7.0 Hz, 1H), 2.64 (s, 3H), 2.40 (s, 3H), 0.99 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.0, 143.1, 136.4, 136.2, 135.2, 129.5, 128.3, 127.1, 120.0, 54.0, 28.7, 21.4, 13.7. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{19}H_{22}N_2O_3S+Na]^+$: 381.1243, found: 381.1244.



4i

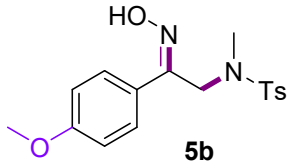
***N*-((2*E*,3*Z*)-2-(hydroxyimino)-4,8-dimethylnona-3,7-dien-1-yl)-*N*,4-dimethylbenzenesulfonamide (4i)** According to the General Procedure D, afforded **4i** (42.0

mg, 57%, *E*/*Z* = 4:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.29 (brs, 1H), 7.66 – 7.64 (m, 2H), 7.32 – 7.30 (m, 2H), 5.61 (s, 0.79H), 5.51 (s, 0.21H), 5.12 – 5.11 (m, 1H), 3.77 (s, 2H), 2.62 – 2.61 (m, 3H), 2.42 (s, 3H), 2.15 (s, 3H), 1.85 – 1.58 (m, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.4, 148.1, 143.6, 134.0, 132.2, 129.7, 127.5, 123.4, 113.5, 53.3, 39.8, 34.5, 26.4, 25.7, 21.5, 20.0, 17.8. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{19}H_{28}N_2O_3S+Na]^+$: 387.1713, found: 387.1709.



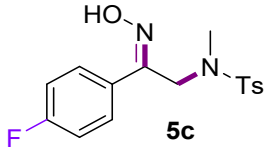
5a

(*E*)-*N*-(2-(hydroxyimino)-2-phenylethyl)-*N*,4-dimethylbenzenesulfonamide (5a) According to the General Procedure E, afforded **5a** (51.0 mg, 80%, *E*/*Z* = 20:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.33 (brs, 1H), 7.66 – 7.59 (m, 4H), 7.44 – 7.38 (m, 5H), 4.01 (s, 2H), 2.51 (d, *J* = 2.5 Hz, 3H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.5, 143.6, 133.2, 131.5, 129.9, 128.9, 128.6, 128.0, 127.4, 53.5, 34.4, 21.0. **HRMS** (ESI, m/z): (M+H) calculated for $[C_{16}H_{19}N_2O_3S]^+$: 319.1117, found: 319.1113.



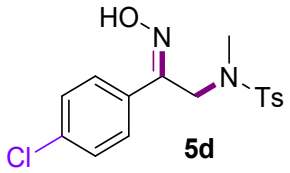
5b

(*E*)-*N*-(2-(hydroxyimino)-2-(4-methoxyphenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (5b) According to the General Procedure E, afforded **5b** (54.0 mg, 77%, *E*/*Z* = 12:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.79 (brs, 1H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.03 (s, 2H), 3.84 (s, 3H), 2.57 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 160.5, 152.2, 143.6, 133.6, 130.7, 129.7, 127.5, 122.0, 113.6, 55.2, 53.2, 34.1, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{20}N_2O_4S+Na]^+$: 371.1036, found: 371.1034.



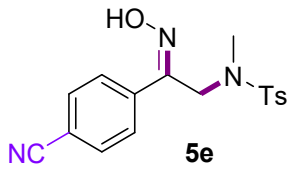
5c

(*E*)-*N*-(2-(4-fluorophenyl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (5c) According to the General Procedure E, afforded **5c** (54.0 mg, 80%, *E*/*Z* = 20:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.38 (brs, 1H), 7.67 – 7.61 (m, 4H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.18 (m, 2H), 3.98 (s, 2H), 2.49 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 162.0 (d, *J* = 245.0 Hz), 149.5, 143.6, 133.3, 131.1 (d, *J* = 8.0 Hz), 129.9, 127.7 (d, *J* = 3.0 Hz), 127.4, 114.9, 53.5, 34.3, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{17}FN_2O_3S+Na]^+$: 359.0836, found: 359.0839.



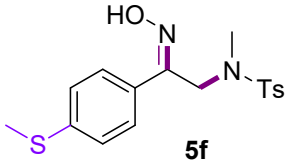
5d

(*E*)-*N*-(2-(4-chlorophenyl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (5d) According to the General Procedure E, afforded **5d** (55.0 mg, 78%, *E*/*Z* = 20:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.42 (brs, 1H), 7.60 – 7.56 (m, 4H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 3.98 (s, 2H), 2.49 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 149.5, 143.5, 133.6, 133.3, 130.5, 130.1, 129.8, 128.0, 127.3, 53.3, 34.3, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{17}ClN_2O_3S+Na]^+$: 375.0541, found: 375.0544.



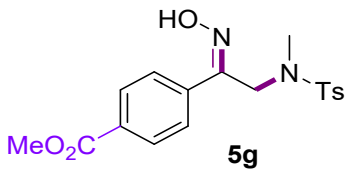
5e

(*E*)-*N*-(2-(4-cyanophenyl)-2-(hydroxyimino)ethyl)-*N*,4-dimethylbenzenesulfonamide (5e) According to the General Procedure E, afforded **5e** (55.0 mg, 76%, *E*/*Z* = 12:1) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.61 (brs, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 4.04 (s, 2H), 2.54 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 149.7, 143.6, 136.2, 133.3, 131.9, 129. 9, 129.5, 127.3, 118.6, 111.4, 53.2, 34.5, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{17}N_3O_3S+Na]^+$: 366.0883, found: 366.0887.



5f

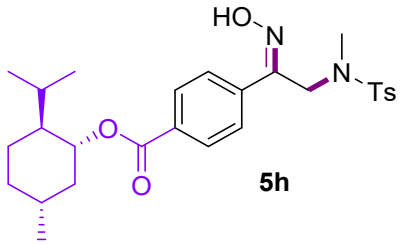
(*E*)-*N*-(2-(hydroxyimino)-2-(4-(methylthio)phenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (5f) According to the General Procedure E, afforded **5f** (51.0 mg, 70%, *E*/*Z* = 6:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.98 (brs, 1H), 7.63 – 7.55 (m, 4H), 7.28 – 7.24 (m, 4H), 4.03 (s, 2H), 2.57 (s, 3H), 2.49 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 152.3, 143.6, 141.2, 133.5, 129.7, 129.1, 127.4, 126.0, 125.3, 53.1, 34.1, 21.4, 15.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{17}H_{20}N_2O_3S_2+Na]^+$: 387.0808, found: 387.0805.



5g

methyl (*E*)-4-(2-((*N*,4-dimethylphenyl)sulfonamido)-1-(hydroxyimino)ethyl)benzoate (5g) According to the General Procedure E, afforded **5g** (52.4 mg, 70%, *E*/*Z* = 15:1) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.50 (brs, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 4.05 (s, 2H), 3.87 (s, 3H), 2.54 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 165.9, 150.1, 143.5, 136.3, 133.4, 129.8, 129.7, 128.9, 128.7, 127.3, 79.2, 53.3, 52.2, 34.4, 21.0. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{20}N_2O_5S+Na]^+$: 399.0985, found: 399.0988.

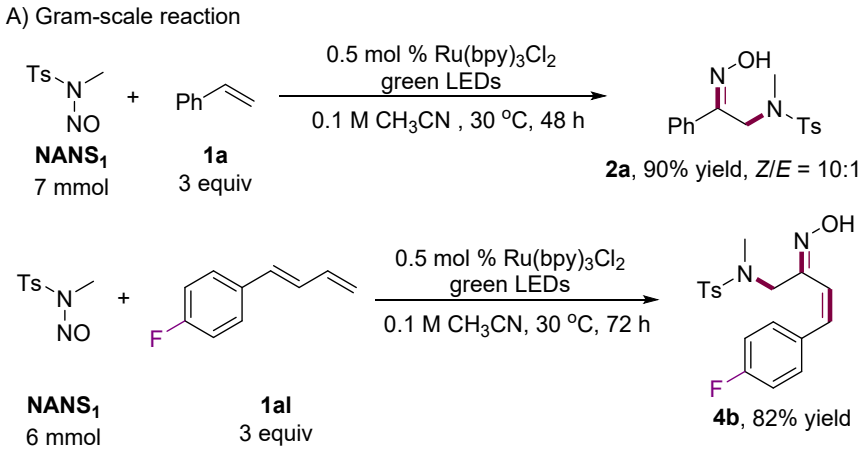


5h

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((*E*)-2-((*N*,4-dimethylphenyl)sulfonamido)-1-(hydroxyimino)ethyl)benzoate (**5h**) According to the General Procedure E, afforded **5h** (80.0 mg, 80%, *E*/*Z* = 15:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.06 (brs, 1H), 8.09 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 4.99 – 4.92 (m, 1H), 4.11 – 4.03 (m, 2H), 2.61 (s, 3H), 2.40 (s, 3H), 2.15 – 2.10 (m, 1H), 2.01 – 1.94 (m, 1H), 1.76 – 1.71 (m, 2H), 1.60 – 1.52 (m, 2H), 1.15 – 1.09 (m, 2H), 0.94 – 0.92 (m, 7H), 0.80 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.54, 152.44, 143.69, 134.48, 133.55, 131.45, 129.65, 129.39, 128.43, 127.37, 75.11, 53.13, 47.13, 40.80, 34.22, 34.16, 31.33, 26.31, 23.42, 21.94, 21.40, 20.70, 16.34. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{27}H_{36}N_2O_5S+Na]^+$: 523.2237, found: 523.2239.

5. Gram-scale reaction and synthetic applications

5.1. Gram-scale reactions

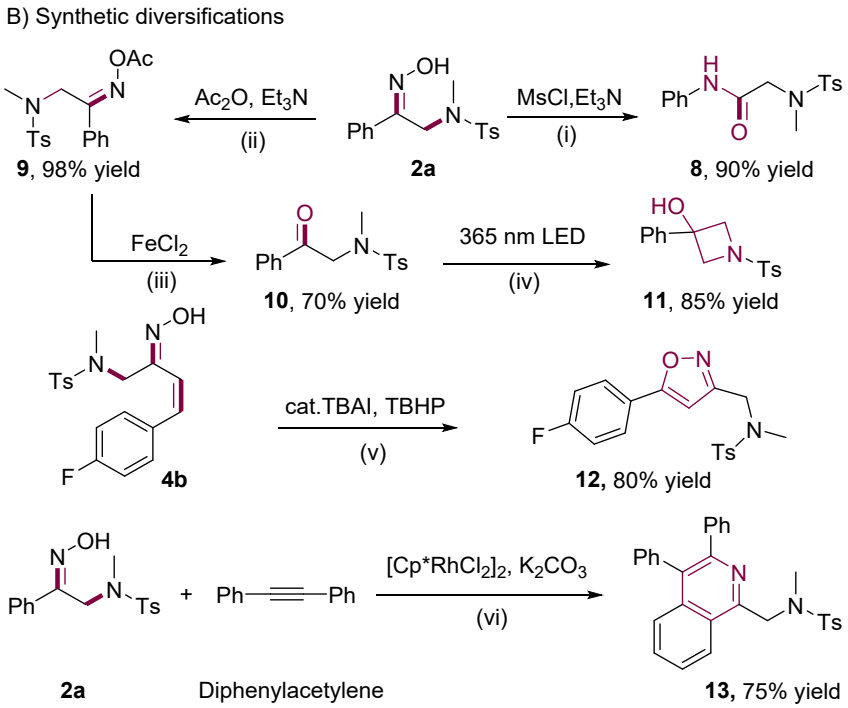


General Procedure F, A 100 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, the appropriate alkenes (21 mmol, 3 equiv., unless otherwise stated), *N*-methyl-*N*-

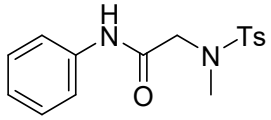
nitroso-*p*-toluenesulfonamide (**NANS$_1$**) (7 mmol, 1.0 equiv.) and Ru(bpy)$_3$Cl$_2$ photosensitizer (25 mg, 0.5 mol%) were charged under air, CH_3CN (0.1 M, 70 mL) was added, then the vessel was bubbled with a stream of argon for 40 min via a syringe needle and the tightly sealed tube was irradiated with a 20 W Green LED at 30 °C (the distance between the tube and the light source was about 2 cm), unless otherwise stated. Upon completion (as judged by TLC analysis), silica was added to the reaction and then concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel (EtOAc : petroleum ether as an eluent) to give the product **2a** as a white solid (2.1 g, 90% yield). (*Z*-type of *α*-amino-ketoximes are mainly products)

According to the General Procedure E, when **1al** (6 mmol) was used as alkene, the product **4b** obtained as a white solid (1.79 g, 82.5 % yield).

5.2. Synthetic applications



(i) Methanesulfonyl chloride (58 µL, 0.75 mmol) was slowly added to a solution of **2a** (159 mg, 0.5 mmol) and triethylamine (139 µL, 1.0 mmol) in methylene chloride (5 mL) at -25 °C. The reaction was stirred for two hours, then diluted with (3x 5 mL) of DCM and washed with ice-cold 1N HCl, followed by saturated aqueous $NaHCO_3$. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated. Chromatography through silica gel (80g, 0 to 30% EtOAc in hexanes) gave product **8** as a white solid (143.0 mg, 90%).[2]

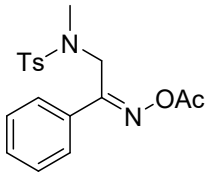


8

2-((*N*,4-dimethylphenyl)sulfonamido)-*N*-phenylacetamide (**8**) **^{1}H NMR** (400 MHz,

Chloroform-*d*) δ 8.40 (brs, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.14 (t, *J* = 7.4 Hz, 1H), 3.72 (s, 2H), 2.85 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.7, 144.6, 136.9, 132.6, 130.1, 129.0, 127.6, 124.8, 120.0, 54.9, 37.2, 21.6. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{18}N_2O_3S+Na]^+$: 341.0930, found: 341.0932.

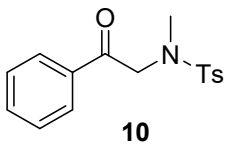
(ii) Acetic anhydride (Ac_2O, 150 uL, 1.5 mmol) was slowly added to a solution of **2a** (318 mg, 1 mmol) and triethylamine (278 μL, 2.0 mmol) in methylene chloride (5 mL) at -0 °C. The reaction was stirred for two hours, then diluted with (3 x 10 mL) of DCM and washed with saturated brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated. Chromatography through silica gel (20 to 30% EtOAc in hexanes) gave product **9** as a white solid (353 mg, 98%, *Z*/*E* = 5:1).



9

(*Z*)-*N*-(2-(acetoxyimino)-2-phenylethyl)-*N*,4-dimethylbenzenesulfonamide (9) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.86 (m, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.59 – 7.53 (m, 0.83 H), 7.50 – 7.41 (m, 3.66H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 0.44H), 4.43 (s, 2H), 4.24 (s, 0.38H), 2.62 (s, 0.62H), 2.54 (s, 3H), 2.46 (s, 3H), 2.43 (s, 0.67H), 2.23 (s, 3H), 2.07 (s, 0.61H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.6, 168.0, 160.9, 160.0, 144.0, 143.8, 133.0, 132.9, 131.6, 130.9, 130.4, 129.8, 129.6, 129.4, 128.5, 128.3, 128.3, 127.7, 127.5, 127.4, 53.0, 44.8, 35.0, 34.3, 21.4, 21.4, 19.6, 19.3. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{20}N_2O_4S+Na]^+$: 383.1036, found: 383.1038.

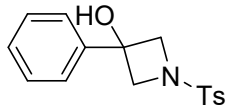
(iii) A 25 mL oven-dried reaction tube were charged with **9** (180 mg, 0.5 mmol), $FeCl_2$ (95 mg, 1.5 equiv.) and 2 mL CH_3CN. The tube was bubbled with a stream of argon for 20 min via a syringe needle and then the mixture was stirred for 12 h at room temperature. Upon completion of the reaction, hydrochloric acid KOH (HCl, 6 mol/L, 5.0 mL) was added and extracted with EtOAc (3 x 5.0 mL), the combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was further purified by chromatography on silica gel to give the product **10** as a white solid (114 mg, 70 %).



10

***N*,4-dimethyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide (10) ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 – 7.91 (m, 2H), 7.76 – 7.68 (m, 2H), 7.63 – 7.55 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.56 (s, 2H), 2.82 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 193.6, 143.6, 134.8, 134.7, 133.8, 129.6, 128.7, 128.2, 127.5, 56.0, 35.5, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{17}NO_3S+Na]^+$: 326.0821, found: 326.0824.

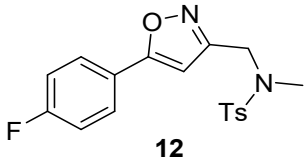
(iv) The starting materials **10** (60.6 mg, 0.2 mmol) were added into 2.0 mL of CH_3CN in an airtight quartz tube, which was bubbled with a stream of argon for 20 min via a syringe needle. Then the reaction was stirred at room temperature under UV irradiation (365 nm) for 24 h. Upon completion (as judged by TLC analysis), silica was added to the reaction and then concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel (EtOAc : petroleum ether as an eluent) to give the products **11** as a white solid (51.5 mg, 85%). [3]



11

3-phenyl-1-tosylazetidin-3-ol (**11**) **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.77 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.36 – 7.27 (m, 5H), 4.12 (d, J = 9.2 Hz, 2H), 3.97 (d, J = 8.7 Hz, 2H), 2.58 (s, 1H), 2.47 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 144.4, 141.9, 131.4, 129.9, 128.7, 128.5, 128.2, 124.5, 70.4, 65.2, 21.6. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{16}H_{17}NO_3S+Na]^+$: 326.0821, found: 326.0822.

(v) To the mixture of **4b** (181 mg, 0.5 mmol), *n*-Bu4NI (0.05 mmol, 19 mg), TBHP (1.0 mmol, 70% in water), 0.5 mL H_2O and 2 mL DMSO were successively added into the tube. Then the reaction mixture was stirred at 70 °C under air for 12 hours. The reaction was monitored by TLC until the reaction was complete. After the reaction finished, the reaction mixture was cooled to room temperature and quenched by the addition of a saturated solution of $Na_2S_2O_3$ (5 mL). The mixture was extracted with ethyl acetate (3×10 mL), the combined organic phases were washed with saturated brine (3 x 10 mL), and dried over anhydrous MgSO4. Then the solvent was evaporated under vacuum. After removing the solvents in vacuo, the residue was purified by flash column chromatography on silica gel to give the products **12** as a white solid (144 mg, 80 %).[4]

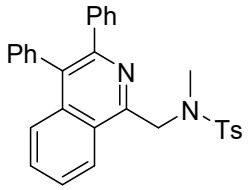


12

***N*-((5-(4-fluorophenyl)isoxazol-3-yl)methyl)-*N*,4-dimethylbenzenesulfonamide** (**12**) **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.67 (m, 4H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 6.55 (s, 1H), 4.26 (s, 2H), 2.70 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.6, 165.0, 162.5, 160.7, 143.9, 133.9, 129.8, 127.9, 127.8, 127.4, 123.4, 123.4, 116.3, 116.1, 98.9, 45.6, 34.8, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{18}H_{17}FN_2O_3S+Na]^+$: 383.0836, found: 383.0835.

(vi) **2a** (63.6 mg, 0.20 mmol, 1 equiv.), diphenylacetylene (39 mg, 0.22 mmol, 1.1 equiv.) $[Cp^*RhCl_2]_2$ (2.5 mol%, 3 mg) and K_2CO_3 (28 mg, 0.2 mmol, 1 equiv.) were weighed in a 10 mL test tube. MeOH (1 mL) was added and the reaction mixture was stirred in an oil bath at 60 °C for 16h. The reaction was cooled down and diluted with dichloromethane. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was

performed by flash column chromatography on silica gel to give the products **13** as a white solid (72 mg, 75 %).[5]



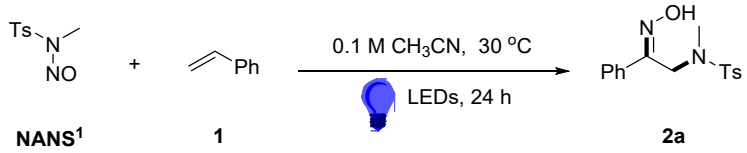
13

***N*-((3,4-diphenylisoquinolin-1-yl)methyl)-*N*,4-dimethylbenzenesulfonamide (13)** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.80 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 6.8 Hz, 2H), 7.72 – 7.61 (m, 3H), 7.38 – 7.34 (m, 5H), 7.26 – 7.20 (m, 4H), 7.15 – 7.14 (m, 3H), 4.84 (s, 2H), 2.67 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.6, 149.0, 143.7, 140.5, 137.1, 136.6, 132.9, 131.3, 131.1, 130.5, 130.0, 129.7, 128.3, 127.8, 127.6, 127.5, 127.4, 127.0, 126.1, 126.0, 125.8, 55.4, 34.7, 21.5. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{30}H_{26}N_2O_2S+Na]^+$: 501.1607, found: 501.1603.

6. Mechanistic investigations

6.1. Control experiments

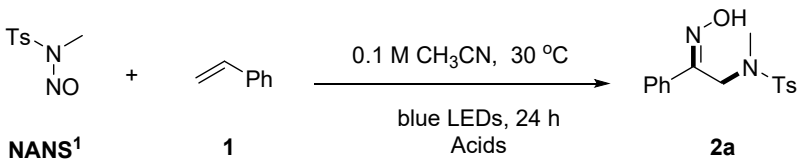
Direct sensitization



365 nm LEDs	**2a** 0%
400 nm LEDs	**2a** 0%
450 nm LEDs	**2a** 0%

A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, the **NANS$_1$** (0.2 mmol, 1.0 equiv.), styrene (3.0 equiv.) were charged under air, CH_3CN (0.1 M) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle. The reaction was direct irradiated at 365 nm (or 400nm, 450 nm light source) for 24 hours, then detected by TLC.

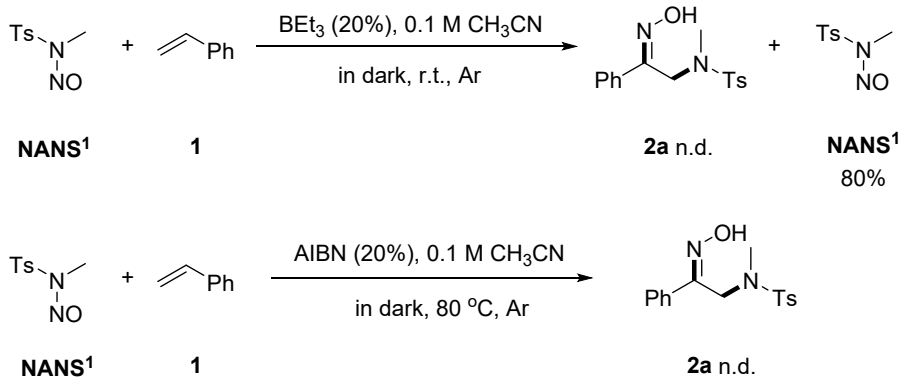
The effect of acids



2 equiv. CH_3COOH	**2a** 0%
2 equiv. CF_3COOH	**2a** 0%
2 equiv. conc. HCl	**2a** 0%

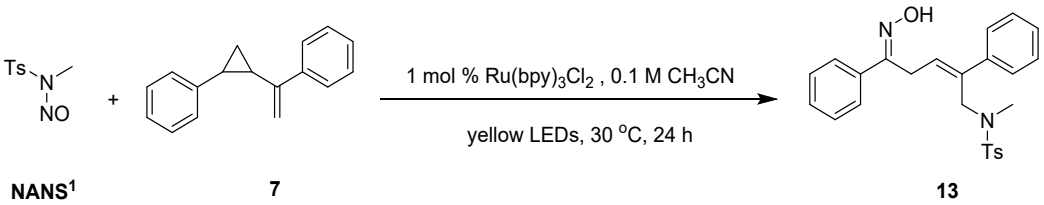
A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, the **$NANS_1$** (0.2 mmol, 1.0 equiv.), styrene (3.0 equiv.) and acid (2.0 equiv.) were charged under air, CH_3CN (0.1 M) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle. The reaction was direct irradiated at blue LED for 24 hours, then detected by TLC.

Radical initiators

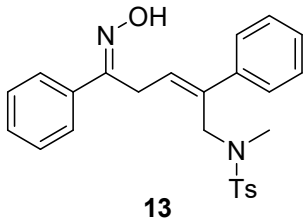


A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, the $NANS_1$ (0.2 mmol, 1.0 equiv.) and styrene (3.0 equiv.) were charged under air, CH_3CN (0.1 M) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle. Next, Et_3B 20% (or AIBN 20%) was added. The reaction was stirred for 24 h at room temperature (or 80 °C, when AIBN was used). then detected by TLC.

6.2. Radical clock experiments



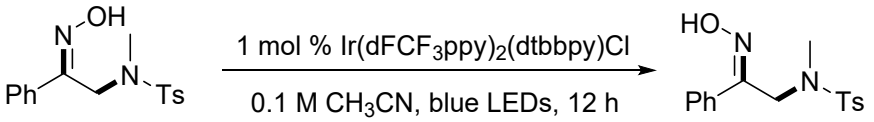
A 10 mL Schlenk tube equipped with a rubber septum and magnetic stirring bar, the **$NANS_1$** (0.2 mmol 1.0 equiv.), alkene **7** (3.0 equiv.) and $Ru(bpy)_3Cl_2$ photosensitizer (1 mol %) were charged under air, CH_3CN (0.1 M) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with a 10 W yellow LED at 30 °C. After completion of the reaction, product **13** was purified by flash column chromatography.



13

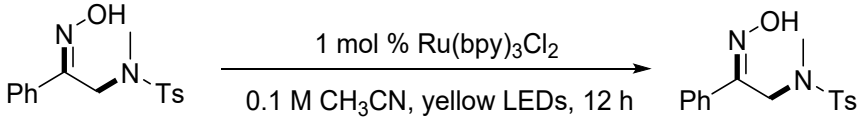
***N*-((2*Z*,5*E*)-5-(hydroxyimino)-2,5-diphenylpent-2-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (13),** afforded **13** (54.7 mg, 63%, *E*/*Z* = 10 : 1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.69 (brs, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.41 – 7.34 (m, 5H), 7.31 – 7.23 (m, 6H), 5.98 (t, *J* = 7.3 Hz, 1H), 4.22 (s, 2H), 3.76 (d, *J* = 7.4 Hz, 2H), 2.46 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 157.0, 143.6, 140.0, 136.4, 135.2, 133.6, 129.8, 129.7, 129.6, 128.8, 128.3, 127.7, 127.6, 126.7, 126.5, 47.8, 33.7, 26.3, 21.6. **HRMS** (ESI, m/z): (M+Na) calculated for $[C_{25}H_{26}N_2O_3S+Na]^+$: 457.1556, found: 457.1558.

6.3. *E*/*Z* Isomerisation Reactions



2a *Z*-type **2a**/**5a,** *Z*/*E* = 1:19

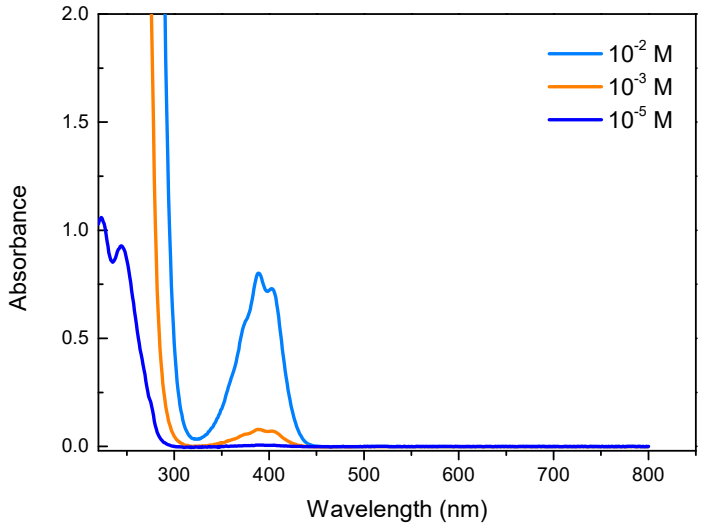
A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, the **2a** (0.2 mmol, 1.0 equiv.) and Ir[(dFCF$_3$ppy)$_2$(dtbbpy)]Cl photosensitizer (1 mol %) were charged under air, CH_3CN (0.1 M, 2 mL) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with a 3 W blue LEDs at 30 °C for 12 h (the distance between the tube and the light source was about 0.5 cm). Then the solution was concentrated in vacuo and the internal standard (4-nitroacetophenone) was added. The *Z*/*E* ratio was determined via ^{1}H NMR.



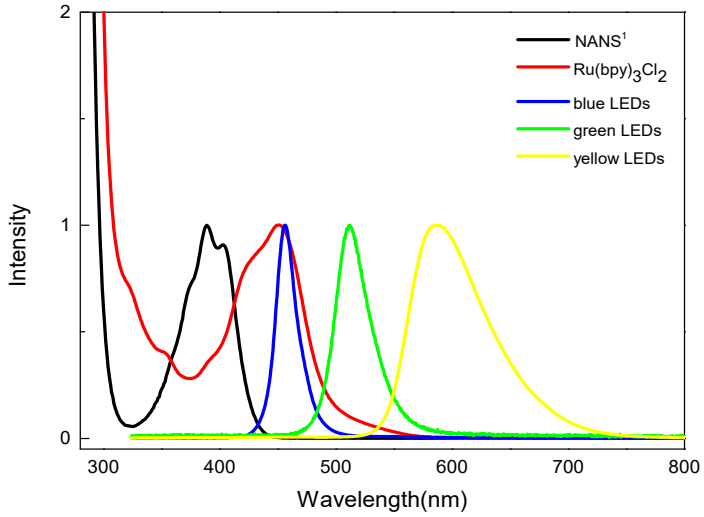
2a *Z*-type **2a**/**5a,** *Z*/*E* = 8:1

A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, the **2a** (0.2 mmol, 1.0 equiv.) and Ru(bpy)$_3$Cl$_2$ photosensitizer (1 mol %) were charged under air, CH_3CN (0.1 M, 2 mL) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with a 10 W yellow LED at 30 °C for 12 h (the distance between the tube and the light source was about 0.5 cm). Then the solution was concentrated in vacuo and the internal standard (4-nitroacetophenone) was added. The *Z*/*E* ratio was determined via ^{1}H NMR.

6.4. UV/Vis absorption spectra of $NANS_1$



Supplementary Figure 4: UV-Vis absorption spectra of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ($NANS_1$) in different concentrations. (10^{-2}, 10^{-3}, 10^{-5} mol·L^{-1} in CH_3CN)



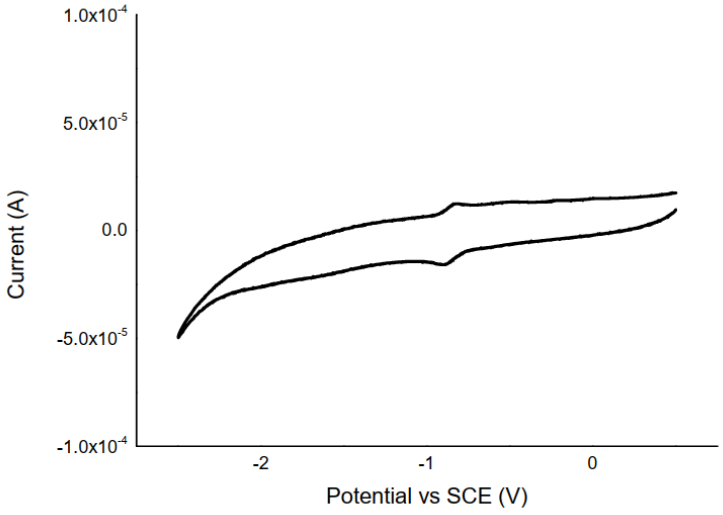
Supplementary Figure 5: Emission spectra of the used light sources, UV-Vis absorption spectra of $NANS_1$ and $Ru(bpy)Cl_2$ in CH_3CN. ($NANS_1$ = *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide)

Conclusion: The maximum absorption wavelength of the $Ru(bpy)_3Cl_2$ is 570nm and emission spectra of the used yellow LED wavelength from 525 to 750nm, so the $Ru(bpy)_3Cl_2$ could be excited by yellow LED.

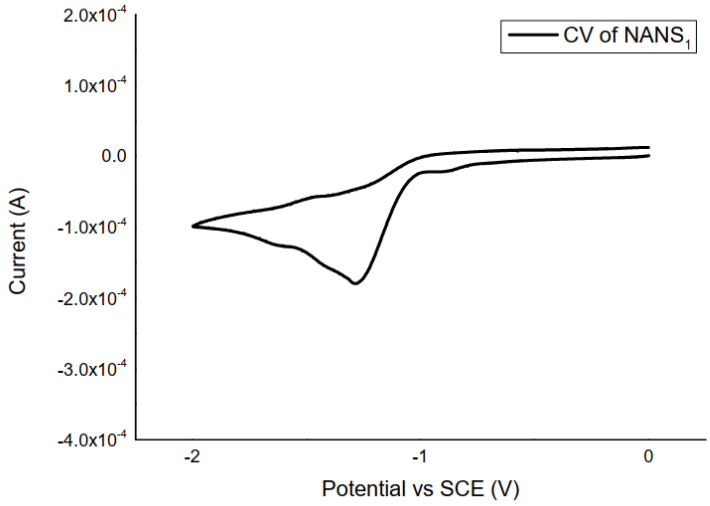
6.5. Cyclic voltammetry study

Cyclic voltammetry experiments were conducted in a Metrohm Autolab RST5200E potentiostat equipped with a glassy carbon working electrode, a platinum wire counter electrode and a SCE reference electrode. The measurements were carried out at a concentration of 0.01 M *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ($NANS_1$) in chromatographic CH_3CN with an electrolyte (tetrabutylammonium hexafluorophosphate 0.1 M in chromatographic CH_3CN), with a scan rate of 50 mV/s.

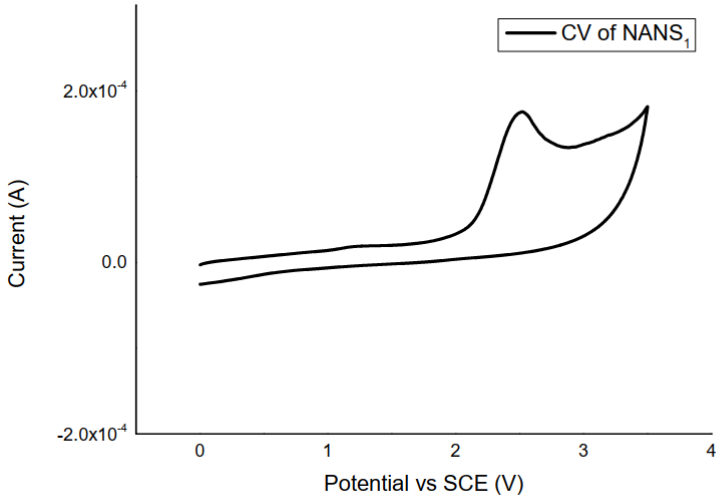
Conclusion: the reduction potential of $NANS_1$ by cyclic voltammetry (– 1.3 V vs SCE), which is lower than the oxidation potential of the photoexcited $Ru(bpy)_3Cl_2$ (– 0.81 V vs SCE). However, we noted that a more strongly reducing $Ir(ppy)_3$ (– 1.7 V vs SCE) was less efficient than a less reducing catalyst $Ru(bpy)_3Cl_2$, suggesting that energy transfer is more likely to be operative than an electron transfer pathway.



Supplementary Figure 6: Cyclic Voltammetry of nBu_4NPF_6 in CH_3CN.



Supplementary Figure 7: Cyclic Voltammetry of $NANS_1$ in CH_3CN
Right: from 0 V to -2 V.
E_{red} = -1.3 V

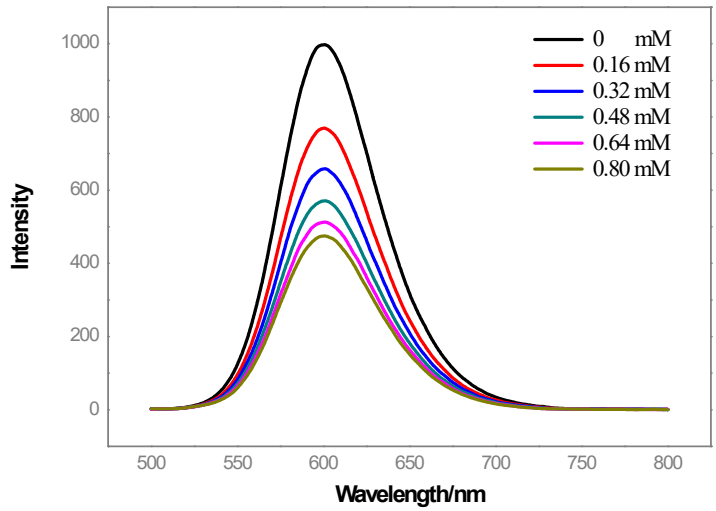


Supplementary Figure 8: Cyclic Voltammetry of $NANS_1$ in CH_3CN
Right: from 0 V to -3.5 V.
E_{ox} = 2.5 V

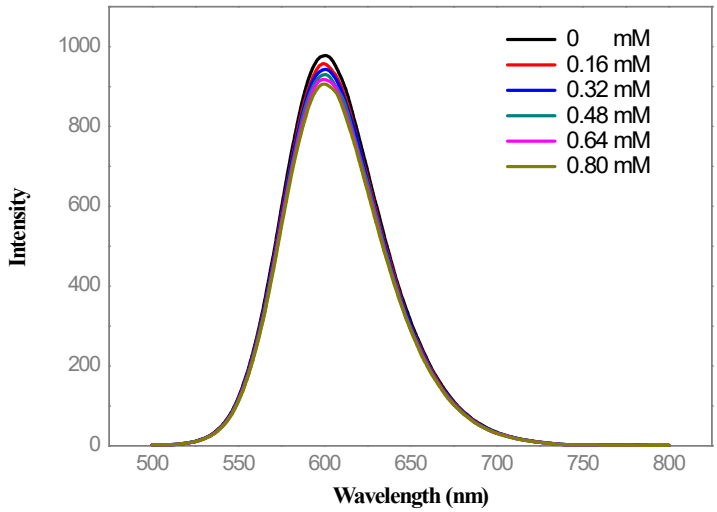
Conclusion: Probing the role of the photocatalyst in radical initiation, we examined the reduction potential of $NANS_1$ by cyclic voltammetry (-1.3 V vs SCE), which is lower than the reduction potential of the photoexcited $Ru(bpy)_3Cl_2$ (0.8 V vs SCE). However, we noted that a more strongly reducing Ir(ppy)3 (–1.7 V vs SCE) was less efficient than a less reducing catalyst $Ru(bpy)_3Cl_2$, suggesting that energy transfer is more likely to be operative than an electron transfer pathway.

6.6. Luminescence quenching experiments

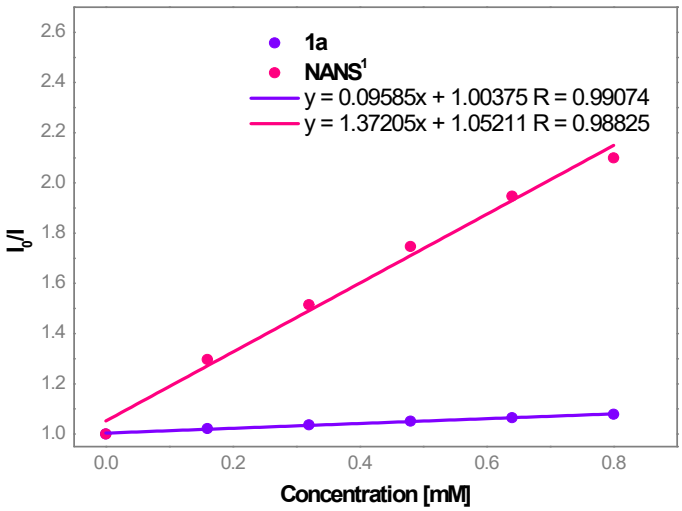
Stern-Volmer quenching experiments were carried out using a 0.05 mM solution of $Ru(bpy)_3Cl_2$ and variable concentrations (0.16, 0.32, 0.48, 0.64, 0.80 mM) of styrene in CH_3CN. The samples were prepared in 3mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside nitrogen filled glove-box. The intensity of the emission peak at 600 nm (λex = 460 nm) expressed as the ratio I_0/I, where I_0 is the emission intensity of $Ru(bpy)_3Cl_2$ at 600 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured. Fluorescence emission spectra and Stern-Volmer plots for each component are given in the Supplementary Figures below.



Supplementary Figure 9: Emission spectra of $Ru(bpy)_3Cl_2$ (0.05 mM) at different concentrations of $NANS_1$.



Supplementary Figure 10: Emission spectra of $Ru(bpy)_3Cl_2$ (0.05 mM) at different concentrations of styrene.



Supplementary Figure 11: Stern-Volmer plot of $Ru(bpy)_3Cl_2$ (0.05 mM) at different concentrations of $NANS_1$ and styrene, respectively.

6.7. Quantum yield measurement

A solution of ferrioxalate was chosen as actinometer following the procedure described by the IUPAC (subcommittee on photochemistry). The procedure is based on the decomposition under irradiation of ferric ions to ferrous ions which are complexed by 1,10-phenanthroline. This photochemical transformation has a known quantum yield and the complexation of Fe^{2+} with 1,10-phenanthroline can be monitored by UV-Visible absorption since its extinction coefficient at 510 nm is known ($\varepsilon = 11100\ M^{-1}\ cm^{-1}$). Therefore, the moles of iron-phenanthroline complex formed are related to moles of photons absorbed. 0.006 M, 0.012 M, or 0.15 M solutions of ferrioxalate can be used for actinometry. In this case we chose a concentration of 0.15 M. The solutions were prepared and stored in a dark laboratory as follows:

Potassium ferrioxalate solution 0.15 M: 1.84 g of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ and 1.75 mL of H_2SO_4 (95%−98%) were added into a 25 mL volumetric flack and filled to the mark with ultrapure water; 1,10-phenanthroline 0.01 M: 100 mg of 1,10-phenantroline monohydrate were added to 50 mL volumetric flask and filled to the mark with ultrapure water; Buffer solution: 2.5 g of NaOAc and 0.25 mL of H_2SO_4 (95%−98%) were added to 25 mL volumetric flask and filled to the mark with ultrapure water.

Model reaction solution: In a 10 mL Schlenk tube, equipped with a magnetic stir bar, charged with $Ru(bpy)_3Cl_2$ (2 mg), *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ($NANS_1$) (1 equiv, 0.2 mmol, 42.8 mg), styrene (3 equiv, 0.6 mmol, 69 µL), CH_3CN (2 mL) was added and the vessel was bubbled with a stream of argon for 20 min via a syringe needle. Then the mixture was stirred for 10 min until the reaction became a homogenous solution.

Actinometry procedure:

(1) 2 mL of potassium ferrioxalate solutions (0.15 M) were added to a quartz cuvette under

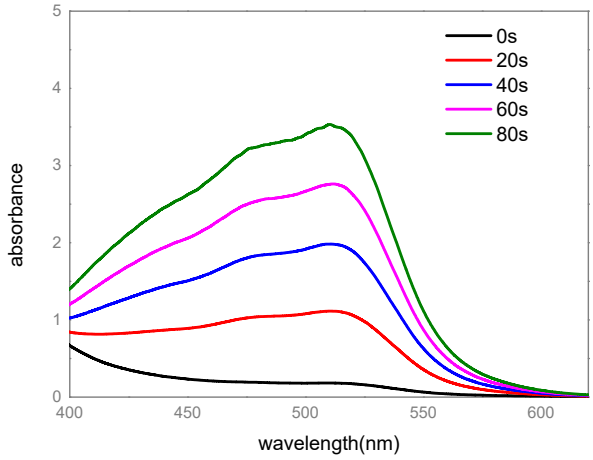
dark conditions while being stirred. Then, the actinometry solutions were irradiated with 458 nm blue LED for specified time intervals (0, 20, 40, 60, 80 s) and a 0.1 mL aliquot was taken.

(2) 4 mL of buffer solution and 1 mL of 0.01M 1,10-phenanthroline were added to each aliquot, and the final volume was raised to 10 mL with ultrapure water. All samples were stored in the dark and stirred for one hour.

(3) The absorbance spectrum of each sample was monitored at 510 nm for each time interval by the UV-2600 spectrometer. The absorbance to each time was related with the photochemically produced Fe^{2+} ions across the Lambert-Beer Law:

$$mole\ Fe^{2+} = \frac{V_1 \cdot V_3 \cdot \Delta A(510nm)}{V_2 \cdot l \cdot \varepsilon(510nm)}$$

where V_1 is the irradiated volume (0.002 L= 2 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (0.0001 L= 0.1 mL), V_3 is the final volume after complexation with phenanthroline (0.01 L= 10 mL), l is the optical path-length of the irradiation quartz cuvette (1 cm), ΔA(510 nm) the optical difference in absorbance between the irradiated solution and that taken in the dark, ε(510 nm) is the extinction coefficient of the complex $Fe(phen)_3^{2+}$ (11100 M^{-1} cm^{-1}).

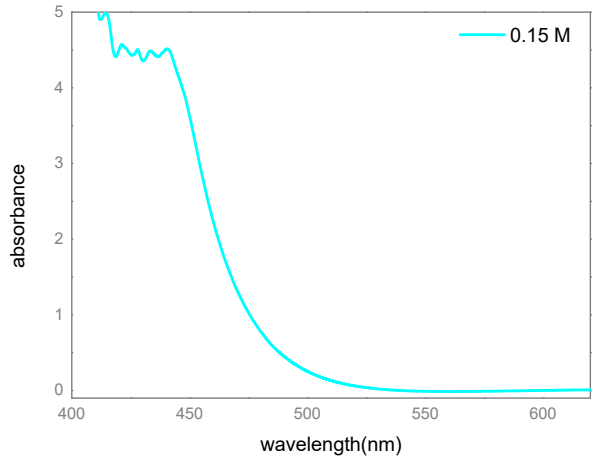


Supplementary Figure 12: The absorbance spectrum of the actinometry solution was monitored at 510 nm

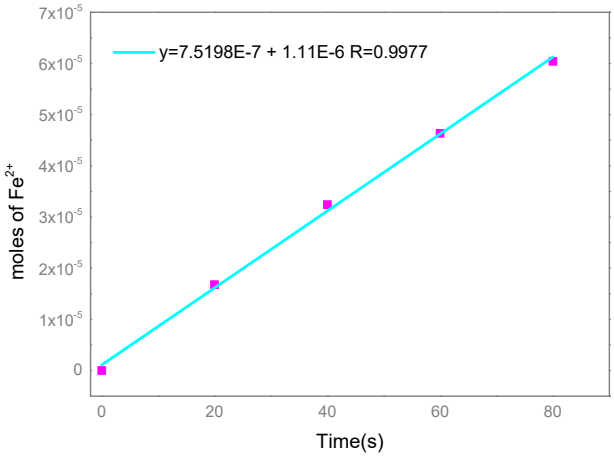
(4) The moles of Fe^{2+} formed (x) are plotted as a function of time (t). The slope of the line (*dx*/*dt*) was correlated to the moles of incident photons by unit of time ($q_{n,p}$) using the following:

$$q_{n,p} = \frac{dx/dt}{\Phi(\lambda) \cdot f}, f = [1 - 10^{-A(\lambda)}]$$

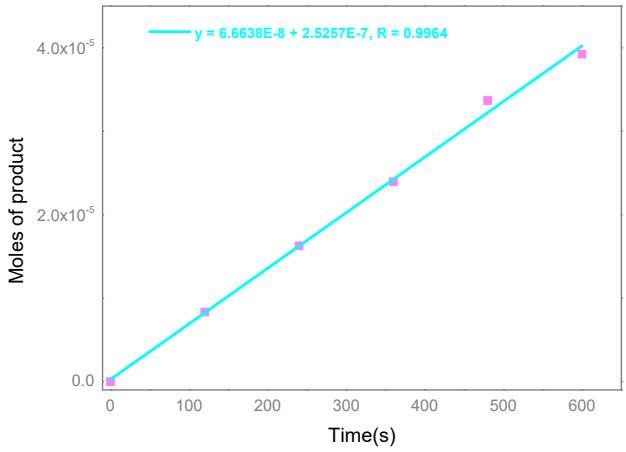
Where Φ (λ) is the quantum yield of the actinometer reaction at the irradiated wavelength, in this case being 1.12 at 458 nm. The value of the photon flux must be divided by the fraction of absorbed light f at the irradiation wavelength, and A(λ) is the absorbance of the actinometer solution (ferrioxalate) at the irradiated wavelength (405 nm) obtaining a value of 2.478, $f = 1$. Therefore, the moles of incident photons by unit of time was determined as 6.7141×10^{-7} einstein s^{-1}.



Supplementary Figure 13: Absorbance of a 0.15 M solution of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ in ultrapure water.



Supplementary Figure 14: The moles of Fe^{2+} formed (x) are plotted as a function of time (t) (5) The kinetics of the reaction under study were done as irradiating the actinometer solution described above. The model reaction solutions were irradiated using the same spectrometer with consecutive measurements every two minutes (0 min, 2 min, 4 min, 6 min, 8 min). Then, solvent was removed and product yield was determined from ^1H NMR analysis of the crude reaction mixture using 4-Nitroacetophenone as an internal standard. Plotting the moles of product versus the irradiation time.



Supplementary Figure 15: Plotting the moles of product versus the irradiation time

The reaction quantum yield (Φ) was determined with the following formula:

$$\Phi = \frac{{}^{dx}/_{dt}(mole\ of\ product\ formation\ rate)}{q_{n,p}(photon\ flux\ x\ f)}$$

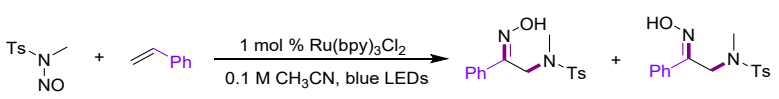
Where, *f* is the fraction of light absorbed at λ= 405 nm by the reaction mixture. the fraction of absorbed light (*f*) is approximately equal to 1.

$$\Phi = \frac{6.6638\ ^{10\ -\ 8}}{6.7141^{10\ -\ 7}}$$

The reaction quantum yield (Φ) was thus determined to be Φ = 0.099.

6.8. Reaction progress monitoring

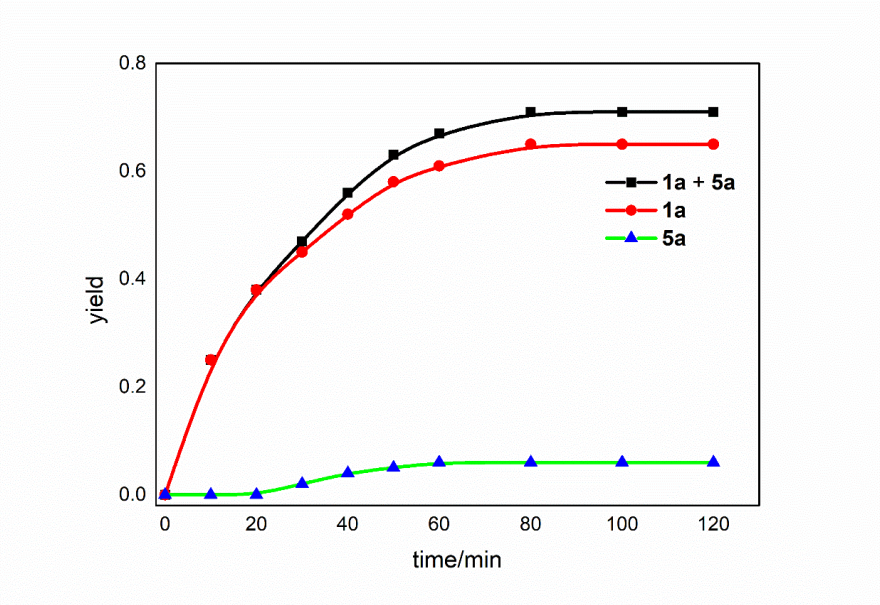
According to general procedure B, the model reaction ($Ru(bpy)_3Cl_2$ was used as photocatalyst) was conducted for 10, 20, 30, 40, 50, 60, 80, 100, 120 min and 12 h on a 0.2 mmol scale, respectively. Upon completion, the solution was concentrated in vacuo. Then internal standard (4-nitroacetophenone) was added. The total yield and *Z*/*E* ratio was determined via ^{1}H NMR.



NANS[1] **1** **2a** **5a**

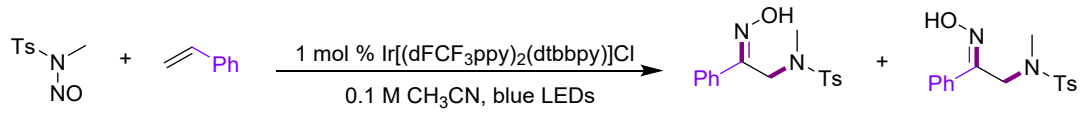
t	total yield	*Z*-type (2a)/*E*-type (5a) (Z/E)
10 min	25%	>20:1

20 min	38%	>20:1
30 min	47%	18:1
40 min	56%	15:1
50 min	63%	11:1
60 min	67%	11:1
80 min	69%	11:1
100 min	71%	11:1
120 min	71%	10:1
12 h	71%	8:1



Supplementary Figure 16: Yield–time monitoring experiment in the presence of Ru(II) photocatalyst.

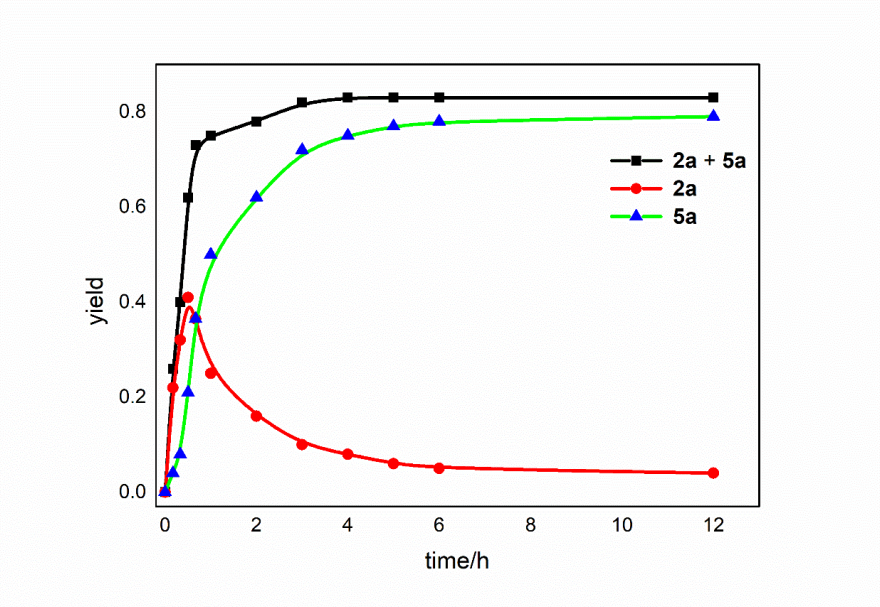
According to general procedure E, the model reaction (Ir[(dFCF$_3$ppy)$_2$(dtbbpy)]Cl was used as photocatalyst) was conducted for 10, 20, 30, 40 min and 1, 2, 3, 4, 5, 6, 12 h on a 0.2 mmol scale, respectively. Upon completion, the solution was concentrated in vacuo. Then internal standard (4-Nitroacetophenone) was added. The total yield and *Z*/*E* ratio was determined via ^{1}H NMR.



NANS[1] **1** **2a** **5a**

t	total yield	Z-type/E-type (Z/E)
10 min	26%	5:1
20 min	40%	4:1
30 min	62%	2:1
40 min	73%	1:1
1 h	75%	1:2

2 h	79%	1:4
3 h	82%	1:7
4 h	83%	1:10
5 h	83%	1:13
6 h	83%	1:15
12 h	83%	1:20



Supplementary Figure 17: Yield–time monitoring experiment in the presence of Ir(III) photocatalyst.

6.9. Computational studies

Computational Details

All calculations were performed using density functional theory as implemented within the Gaussian 16 (revision A.03) suite of programs.[6] Geometry optimizations and vibrational frequency calculations were performed using the ωB97X-D functional[7] with the 6-311++G(d,p) basis set[8] to calculate triplet energies, and the UB3LYP functional[9] and the 6-311++G(d,p) basis set to calculate homolytic bond dissociation energies (BDEs). All stationary points were confirmed to have no imaginary frequencies. Reported Gibbs free energies and enthalpies include thermal corrections computed at 298.15 K and 1 atm, and are reported in kcal/mol using the conversion of 1 hartree = 627.5095kcal/mol.

Calculation of Triplet Energies

The gas phase triplet energies were calculated as follows:

$$E_T = \Delta G°(\text{triplet}) - \Delta G°(\text{singlet})$$

Table S4 The triplet energy of **NANS$_s$** were computed using the ωB97X-D functional with the 6-311++G(d,p) basis set

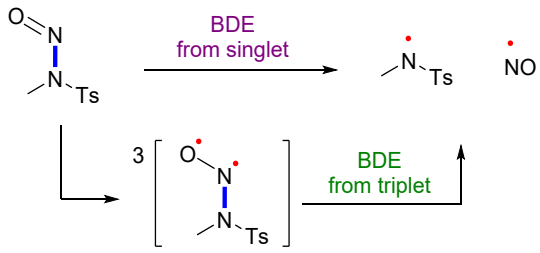
Subsstrate	$NANS_1$	$NANS_2$	$NANS_7$	$NANS_9$	$NANS_{12}$	$NANS_{13}$
E_T (calc.)	36.8	39.7	39.2	38.8	39.7	38.7

Calculation of Homolytic Bond Dissociation Energies (BDE)

The gas phase BDEs were calculated as follows:

$$\text{N-N BDE} = \Sigma\Delta H°(\text{products}) - \Sigma\Delta H°(\text{starting materials})$$

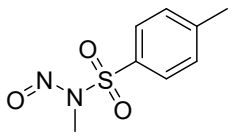
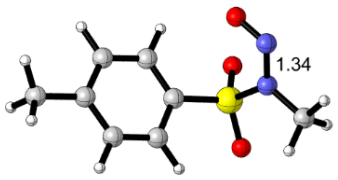
Table S5 The N-N BDEs of $NANS_1$ from the singlet and triplet state were computed using the UB3LYP functional and 6-311++G(d,p) basis set

Homolytic Cleavage	N-N BDE	
	From Singlet	From Triplet
	33.2	-7.8

Optimized Cartesian Coordinates

Geometry optimizations and frequency calculations for the determination of triplet energies were carried out using the ωB97X-D functional with the 6-311++G(d,p) basis set. Visualization carried out with CYL view[10]. EE = Electronic Energy

E_T: $NANS_1$ (singlet state)

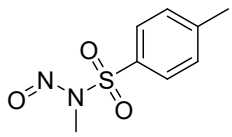
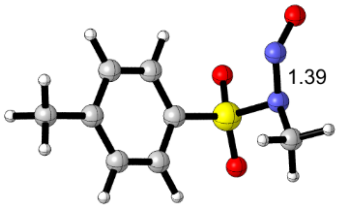
Total EE (hartree)	-1044.075666
EE + Zero-Point Energy Correction (hartree)	-1043.895196
EE + Thermal Enthalpy Correction (hartree)	-1043.880263
EE + Thermal Free Energy Correction (hartree)	-1043.937108
Imaginary Frequencies (cm^{-1})	None

Cartesian Coordinates

C	2.51720100	0.97797500	0.46667100
C	1.16430800	0.96721900	0.77190300
C	0.41272500	-0.14622000	0.41896400
C	0.97711400	-1.23628600	-0.23781700
C	2.32780600	-1.19881500	-0.54299300

C	3.11651500	-0.09800700	-0.19269800
H	3.11545500	1.84083200	0.73866000
H	0.69961300	1.80892500	1.26931000
H	0.37723200	-2.09776800	-0.50726200
H	2.77942100	-2.03961000	-1.05834900
C	-2.94963100	-1.01099900	-1.28675000
H	-2.37460100	-1.92025900	-1.45922000
H	-3.78440100	-1.21184900	-0.61679700
H	-3.32633000	-0.62953900	-2.23472400
C	4.58667200	-0.08798400	-0.49845300
H	5.13843000	-0.59654400	0.29915400
H	4.79905600	-0.61274000	-1.43233400
H	4.96959200	0.93177000	-0.57026800
O	-1.68725800	-1.55541600	1.15398500
O	-1.67182700	0.89335800	1.68279800
O	-1.18126500	1.97763700	-1.00832800
S	-1.30785700	-0.19970700	0.81010800
N	-2.09240500	0.03843800	-0.73397300
N	-1.91634100	1.13244200	-1.46752600

E_T: $NANS_1$ (triplet state)

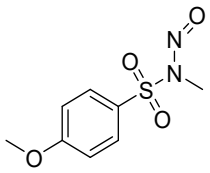
Total EE (hartree)	-1044.014658
EE + Zero-Point Energy Correction (hartree)	-1043.835145
EE + Thermal Enthalpy Correction (hartree)	-1043.820105
EE + Thermal Free Energy Correction (hartree)	-1043.878500
Imaginary Frequencies (cm^{-1})	None
$<S^2>$	2.0099

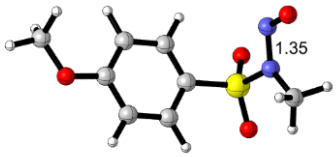
Cartesian Coordinates

C	2.31224400	1.20671600	0.50290400
C	0.97949600	0.93382000	0.76697900
C	0.46533300	-0.30539200	0.39416700
C	1.25240700	-1.26268800	-0.23740500
C	2.58425100	-0.96811800	-0.48965400
C	3.13261300	0.26367600	-0.12431700
H	2.72416700	2.16791900	0.79112700
H	0.35421000	1.66887600	1.25958100
H	0.83571800	-2.22102000	-0.52290000

H	3.20778100	-1.70884900	-0.97856800
C	-1.73737900	-0.56901000	-2.01135200
H	-0.73417900	-0.27249000	-2.32930200
H	-1.80160700	-1.65265400	-1.92634000
H	-2.47730600	-0.22295800	-2.73203400
C	4.58355800	0.56093600	-0.37299800
H	5.17497000	0.30764100	0.51315900
H	4.97021600	-0.02437200	-1.20949100
H	4.73913300	1.62165400	-0.58096600
O	-1.48865800	-2.06800900	0.59014800
O	-1.72468000	0.13320800	1.79636700
O	-2.95480900	2.13800800	-0.33888500
S	-1.24732600	-0.64171800	0.67137200
N	-2.09404000	0.00900400	-0.70631800
N	-2.06679600	1.39363200	-0.71899500

E_T: $NANS_2$ (singlet state)





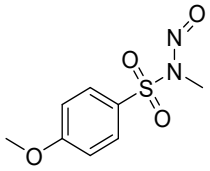
Total EE (hartree)	-1019.286833
EE + Zero-Point Energy Correction (hartree)	-1119.100877
EE + Thermal Enthalpy Correction (hartree)	-1119.085230
EE + Thermal Free Energy Correction (hartree)	-1119.144154
Imaginary Frequencies (cm^{-1})	None

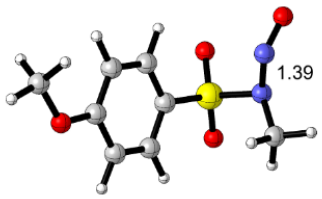
Cartesian Coordinates

C	-2.17655500	0.53118700	-0.83325900
C	-0.83469900	0.29057100	-1.08432500
C	-0.12617200	-0.57217600	-0.25666600
C	-0.73581800	-1.20062900	0.83078300
C	-2.07000600	-0.95943200	1.08111200
C	-2.79878600	-0.09242100	0.25418400
H	-2.72210900	1.19836500	-1.48660000
H	-0.35066700	0.77241000	-1.92552300
H	-0.17549100	-1.87426300	1.46779500
H	-2.57092400	-1.43749400	1.91428200
C	2.51137600	0.34149600	1.81234400
H	1.75245700	0.94457600	2.31597300
H	2.42090200	-0.70290600	2.10021800

H	3.50533600	0.70341900	2.07576500
O	2.02439300	-2.04132900	0.09936300
O	1.90949500	-0.56079200	-1.93034100
O	2.80774700	2.52823000	0.41466300
S	1.59007700	-0.82273900	-0.54733400
N	2.34587800	0.43777400	0.36466700
N	2.44081800	1.60464700	-0.27663100
C	-4.88858200	0.95013900	-0.21203800
H	-4.95108100	0.59410800	-1.24413100
H	-5.87886800	0.93257800	0.23914400
H	-4.49553100	1.97052800	-0.19129100
O	-4.08746900	0.07803400	0.58164500

E_T: $NANS_2$ (triplet state)





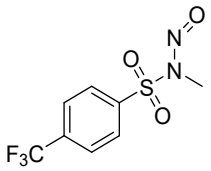
Total EE (hartree)	-1019.221966
EE + Zero-Point Energy Correction (hartree)	-1119.036902
EE + Thermal Enthalpy Correction (hartree)	-1119.021182
EE + Thermal Free Energy Correction (hartree)	-1119.080943
Imaginary Frequencies (cm^{-1})	None
$\langle S^2 \rangle$	2.0099

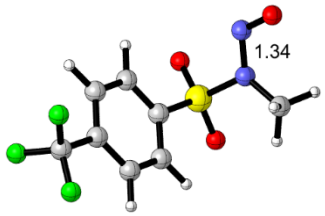
Cartesian Coordinates

C	-2.10591100	0.86449400	-0.51638200
C	-0.75117500	0.72880600	-0.77811300
C	-0.09113000	-0.43496100	-0.40003100
C	-0.76553600	-1.47233700	0.24782300
C	-2.11281700	-1.33756900	0.50744600
C	-2.79172600	-0.17050900	0.12866300
H	-2.61288100	1.77006700	-0.82051500
H	-0.21948900	1.52636600	-1.28310700
H	-0.24202600	-2.37508100	0.53831800
H	-2.66234800	-2.12942300	1.00203800
C	2.14195500	-0.48898600	1.99649800
H	1.11231200	-0.31962400	2.32305700
H	2.33346900	-1.55569200	1.89107600
H	2.83925400	-0.07110600	2.72165300
O	2.04373000	-1.96089800	-0.62355200

O	2.02495000	0.27120400	-1.79650300
O	3.01156600	2.37646700	0.37147400
S	1.64031100	-0.57013300	-0.68337800
N	2.42055800	0.15099800	0.70167900
N	2.22490600	1.52162400	0.74276100
C	-4.85278500	1.01988400	0.06434800
H	-4.84556800	1.17156200	-1.01874000
H	-5.87026600	0.82309600	0.39695900
H	-4.46901700	1.91068900	0.56952200
O	-4.09923400	-0.13552500	0.42372900

E_T: $NANS_7$ (singlet state)





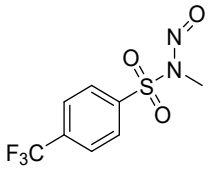
Total EE (hartree)	-1341.817122
EE + Zero-Point Energy Correction (hartree)	-1341.659392
EE + Thermal Enthalpy Correction (hartree)	-1341.642768
EE + Thermal Free Energy Correction (hartree)	-1341.704766
Imaginary Frequencies (cm^{-1})	None

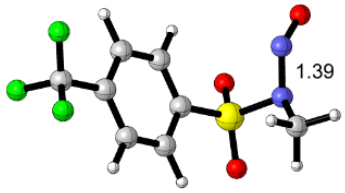
Cartesian Coordinates

C	-1.53927600	0.36630400	-1.14344600
C	-0.18762000	0.09102900	-1.26454000
C	0.44202000	-0.60181300	-0.23648000
C	-0.23086600	-1.02303800	0.90145100
C	-1.58597600	-0.74095900	1.01382500
C	-2.22699200	-0.04770000	-0.00455500
H	-2.05126000	0.89948600	-1.93543800
H	0.36086700	0.40674700	-2.14325000
H	0.28160600	-1.56554500	1.68589000
H	-2.12844900	-1.06484700	1.89241700
C	2.95490800	0.63577300	1.81585500
H	2.17376500	1.31768700	2.15883900
H	2.83478300	-0.34272600	2.27397300
H	3.93600000	1.03564800	2.07223800
C	-3.70106000	0.24525800	0.08558700
O	2.54426300	-2.00828600	0.50956200
O	2.58668800	-0.90020300	-1.74901500

O	3.36686300	2.54600900	0.07922600
S	2.18702000	-0.91502100	-0.36412200
N	2.87870300	0.48045100	0.36492300
N	3.03237100	1.52155400	-0.46566400
F	-3.97437200	1.53184200	-0.20058400
F	-4.40769500	-0.49884600	-0.78951100
F	-4.20798700	-0.00071000	1.30144100

E_T: $NANS_7$ (triplet state)





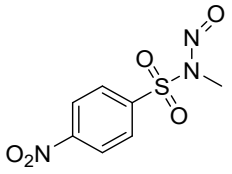
Total EE (hartree)	-1341.752371
EE + Zero-Point Energy Correction (hartree)	-1341.595648
EE + Thermal Enthalpy Correction (hartree)	-1341.578872
EE + Thermal Free Energy Correction (hartree)	-1341.642242
Imaginary Frequencies (cm^{-1})	None
<S^2>	2.0099

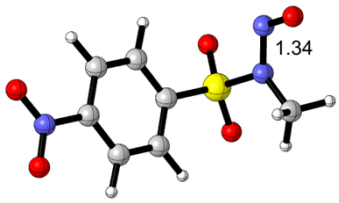
Cartesian Coordinates

C	-1.46531500	0.95201400	-0.70677200
C	-0.10821900	0.75703300	-0.90482100
C	0.46972700	-0.41840900	-0.43652700
C	-0.26345100	-1.39718700	0.22064100
C	-1.62307700	-1.19350500	0.41293900
C	-2.21088700	-0.02115600	-0.04570600
H	-1.93535400	1.85845500	-1.06841900
H	0.48275700	1.50389600	-1.41996500
H	0.20939200	-2.30492700	0.57368100
H	-2.21068000	-1.94841200	0.91919200
C	2.56330100	-0.40743600	2.06819000
H	1.52995000	-0.16550000	2.33017600
H	2.70382700	-1.48681600	2.03735800
H	3.24732900	0.02093900	2.79964600
C	-3.69053900	0.19807700	0.12455100
O	2.55401900	-2.04144300	-0.46415500
O	2.68553500	0.11347500	-1.76879100
O	3.66348800	2.30180800	0.32305700
S	2.22372200	-0.64195000	-0.62633600

N	2.93709300	0.13537200	0.75227200
N	2.80986100	1.51382400	0.69171500
F	-3.97392900	1.45989100	0.49417000
F	-4.35885800	-0.02251700	-1.02669000
F	-4.23266100	-0.61049800	1.04651500

E_T: $NANS_9$ (singlet state)





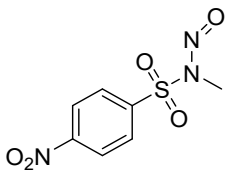
Total EE (hartree)	-1209.254687
EE + Zero-Point Energy Correction (hartree)	-1209.098843
EE + Thermal Enthalpy Correction (hartree)	-1209.083238
EE + Thermal Free Energy Correction (hartree)	-1209.142913
Imaginary Frequencies (cm^{-1})	None

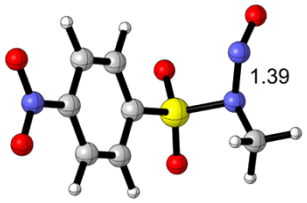
Cartesian Coordinates

C	-1.87344500	0.69448400	-1.01061300
C	-0.52419000	0.43652500	-1.19357400
C	0.09341100	-0.49547300	-0.36833600
C	-0.58396200	-1.17533800	0.63609000
C	-1.93321700	-0.91433000	0.82065800
C	-2.54541000	0.01346100	-0.00692400
H	-2.38877600	1.40955600	-1.63697100
H	0.02916600	0.95085900	-1.96917900
H	-0.07981500	-1.90054200	1.26214200
H	-2.49388100	-1.42639700	1.59029000
C	2.65781200	0.13956200	1.91023700
H	1.87980400	0.69995400	2.43329800
H	2.55625300	-0.92537000	2.10315000
H	3.64168700	0.47302400	2.23996800
O	2.17330100	-2.07861800	-0.01210400
O	2.22841600	-0.43900400	-1.92072800
O	3.03816600	2.43385300	0.71104400
S	1.83647900	-0.79492100	-0.58051500
N	2.54974300	0.36177200	0.46975500
N	2.68911900	1.58314800	-0.07017700
N	-3.98318100	0.28743100	0.18774200
O	-4.52504200	1.05364700	-0.58447500

O	-4.54782500	-0.26764700	1.10989700

E_T: $NANS_9$ (triplet state)



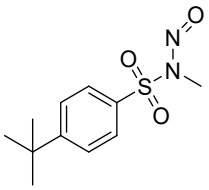


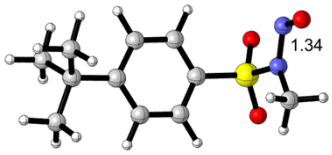
Total EE (hartree)	-1209.189916
EE + Zero-Point Energy Correction (hartree)	-1209.035393
EE + Thermal Enthalpy Correction (hartree)	-1209.019540
EE + Thermal Free Energy Correction (hartree)	-1209.081130
Imaginary Frequencies (cm^{-1})	None
$\langle S^2 \rangle$	2.0099

Cartesian Coordinates

C	-1.79064200	1.11177200	-0.52437800
C	-0.43511800	0.92722300	-0.74584000
C	0.12084100	-0.31946600	-0.48094000
C	-0.62765000	-1.38577100	0.00223900
C	-1.98276800	-1.19950500	0.22936100
C	-2.53098400	0.04442500	-0.03949600
H	-2.25833600	2.06597400	-0.72486800
H	0.16935200	1.74082400	-1.12638200
H	-0.17026000	-2.34776500	0.19477700
H	-2.59659700	-2.00817700	0.60152800
C	2.23574500	-0.74692000	1.97565300
H	1.20834100	-0.53894600	2.28514900
H	2.36285000	-1.80863500	1.76989500
H	2.93204800	-0.44932700	2.75847500
O	2.17606100	-1.95102000	-0.78416900
O	2.33654100	0.38255800	-1.72963400
O	3.36318400	2.19309200	0.68005800
S	1.87317300	-0.53825000	-0.71742500
N	2.60380900	-0.00265500	0.76002400
N	2.49805400	1.36986300	0.92236600
N	-3.97365900	0.24248100	0.20101500
O	-4.48324400	1.26549500	-0.21249300
O	-4.57405900	-0.62766400	0.80083800

E_T: $NANS_{12}$ (singlet state)





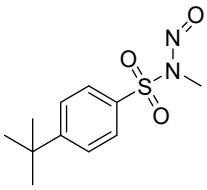
Total EE (hartree)	-1162.019900
EE + Zero-Point Energy Correction (hartree)	-1161.754219
EE + Thermal Enthalpy Correction (hartree)	-1161.735705
EE + Thermal Free Energy Correction (hartree)	-1161.800488
Imaginary Frequencies (cm-1)	None

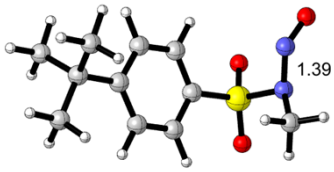
Cartesian Coordinates

C	-1.51140100	0.34994400	-1.12476200
C	-0.15893800	0.08782500	-1.24964800
C	0.47926700	-0.61870200	-0.23389900
C	-0.20734400	-1.05330600	0.89026900
C	-1.56565600	-0.77747500	0.99282500
C	-2.24284800	-0.07420300	-0.00534600
H	-2.00420300	0.89526100	-1.92118100
H	0.38837000	0.42167300	-2.12315200
H	0.29968200	-1.60464300	1.67293800
H	-2.08938700	-1.12723300	1.87254200
C	2.97131900	0.65580400	1.81320800
H	2.19212500	1.34785300	2.14022900
H	2.83586200	-0.31724900	2.27869600
H	3.95210200	1.04990700	2.07998700
C	-3.73747300	0.24416600	0.08072800
O	2.58839300	-2.00205400	0.52594000
O	2.62722500	-0.91126500	-1.73949900
O	3.40834900	2.54846200	0.06671000
S	2.21483900	-0.91938900	-0.35671100
N	2.91210300	0.48687900	0.36376000
N	3.07650300	1.51680900	-0.47145300
C	-4.37688000	-0.30350600	1.36104100
H	-4.29581000	-1.39287900	1.42272700
H	-3.92591600	0.12884000	2.25921000
H	-5.44029300	-0.04866000	1.36795100
C	-4.45527900	-0.38210200	-1.12820800
H	-4.32440900	-1.46858000	-1.13976000
H	-5.52712000	-0.16832800	-1.07298100
H	-4.08245100	0.01718000	-2.07497800
C	-3.92548300	1.77159900	0.05610000

H	-3.41613800	2.24140000	0.90321800
H	-3.53688300	2.21431600	-0.86478600
H	-4.99063700	2.01413700	0.12152100

E_T: $NANS_{12}$ (triplet state)





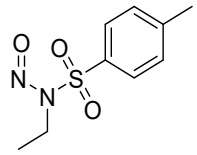
Total EE (hartree)	-1161.954999
EE + Zero-Point Energy Correction (hartree)	-1161.690306
EE + Thermal Enthalpy Correction (hartree)	-1161.671693
EE + Thermal Free Energy Correction (hartree)	-1161.737295
Imaginary Frequencies (cm^{-1})	None
$<S^2>$	2.0099

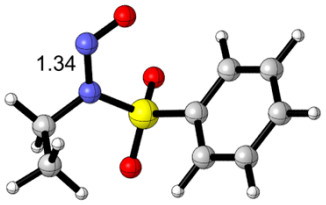
Cartesian Coordinates

C	-1.44316800	0.89712200	-0.73296700
C	-0.08465100	0.71730800	-0.92306700
C	0.51001300	-0.44448700	-0.43641800
C	-0.22969600	-1.40960400	0.23225100
C	-1.59316000	-1.20723400	0.40950200
C	-2.22530600	-0.05574500	-0.06404200
H	-1.90066400	1.80029000	-1.11928000
H	0.50009000	1.46300300	-1.44819100
H	0.24327800	-2.30990800	0.60559400
H	-2.15677300	-1.97162300	0.92775600
C	2.58986900	-0.35551200	2.07845100
H	1.55085900	-0.12073400	2.32482500
H	2.74268800	-1.43363500	2.07446100
H	3.26076700	0.09780400	2.80720800
C	-3.72411000	0.19601500	0.11810100
O	2.60709300	-2.04719600	-0.41254700
O	2.72735300	0.07615100	-1.76634200
O	3.67042900	2.32470500	0.27422100
S	2.25543300	-0.65578800	-0.61069600
N	2.97037100	0.15937700	0.75401900
N	2.82770300	1.53410300	0.66388800
C	-4.41846400	-0.94360700	0.87112000
H	-4.33601400	-1.89468000	0.33661200
H	-4.00978000	-1.07539000	1.87744600

H	-5.48212900	-0.71077500	0.97250600
C	-4.38122800	0.33701200	-1.26658900
H	-4.24660500	-0.57458300	-1.85698300
H	-5.45511800	0.51248900	-1.15001400
H	-3.96375900	1.17484100	-1.83111600
C	-3.92060400	1.49833100	0.91486000
H	-3.45072200	1.42731400	1.90073400
H	-3.49644700	2.36139500	0.39499200
H	-4.98909300	1.68557500	1.05937300

E_T: $NANS_{13}$ (singlet state)





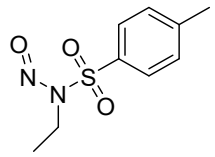
Total EE (hartree)	-1044.055791
EE + Zero-Point Energy Correction (hartree)	-1043.873219
EE + Thermal Enthalpy Correction (hartree)	-1043.859058
EE + Thermal Free Energy Correction (hartree)	-1043.913664
Imaginary Frequencies (cm^{-1})	None

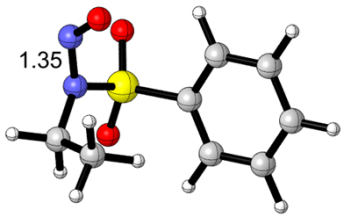
Cartesian Coordinates

C	-1.36666100	1.32507800	-0.33828200
C	-2.63744000	1.64681100	0.11664400
C	-3.50836900	0.63861300	0.51766200
C	-3.11750400	-0.69483700	0.46591600
C	-1.84696100	-1.03256100	0.01995100
C	-0.98965500	-0.01254700	-0.37116800
H	-0.68346100	2.09265400	-0.67978100
H	-2.95089400	2.68344400	0.14759600
H	-4.50110100	0.89487700	0.86988600
H	-3.80146500	-1.47607200	0.77480700
H	-1.51519600	-2.06135500	-0.02199300
C	2.73623900	0.73453900	0.47025700
H	3.44698200	0.34681600	1.20125800
H	3.22025300	0.73704800	-0.50571500
C	2.25817300	2.12629900	0.85319500
H	1.74145400	2.10620400	1.81545100
H	3.11515400	2.79892700	0.93534400
H	1.58622700	2.52926300	0.09387000
O	0.59719000	-1.79147800	1.54553800

O	0.66984500	-1.79235400	-1.40218000
O	1.09590800	0.65203100	-1.82359900
N	1.65214500	-0.25769200	0.44011900
N	1.50934700	-1.00789400	1.54578800
S	0.63382000	-0.42041600	-0.96844900

E_T: $NANS_{13}$ (triplet state)





Total EE (hartree)	-1043.991027
EE + Zero-Point Energy Correction (hartree)	-1043.809599
EE + Thermal Enthalpy Correction (hartree)	-1043.795169
EE + Thermal Free Energy Correction (hartree)	-1043.851989
Imaginary Frequencies (cm^{-1})	None
$<S^2>$	2.0086

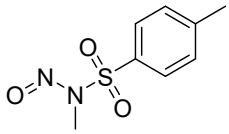
Cartesian Coordinates

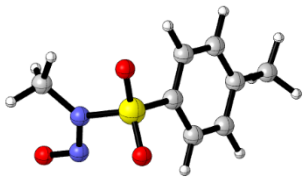
C	1.64482100	-0.54835700	1.10156400
C	2.90640100	0.03175500	1.10245800
C	3.40241200	0.62223400	-0.05518000
C	2.64766900	0.62723300	-1.22369900
C	1.38709500	0.04654300	-1.24215000
C	0.90205000	-0.52797600	-0.07277900
H	1.23942500	-1.02013300	1.98829900
H	3.50326700	0.01836900	2.00671200
H	4.38686000	1.07603800	-0.04867500
H	3.04154100	1.08090000	-2.12525100
H	0.79003800	0.03491600	-2.14554800
C	-1.93201300	0.87436900	1.34622500
H	-2.97761100	1.18640900	1.39750000
H	-1.77953200	0.13152600	2.13008600
C	-0.99520300	2.06554100	1.49893300
H	-1.16635100	2.80925900	0.71870600
H	-1.17806200	2.54024500	2.46611900
H	0.05225700	1.76069000	1.45920100
O	-1.42103400	1.70603600	-1.62135500
O	-1.01939800	-1.77539600	-1.36217600
O	-0.92217500	-1.94324200	1.16705400

N	-1.78382300	0.14634200	0.07308400
N	-2.06047900	0.81494900	-1.07104200
S	-0.74251600	-1.21215600	-0.06636600

Geometry optimizations and frequency calculations for the determination of BDEs were carried out using the UB3LYP functional, and the 6-311++G(d,p) basis set

BDE: NANS$_1$ (singlet state)





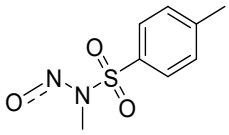
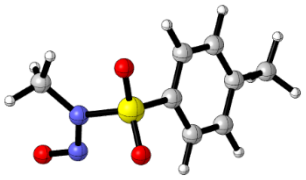
Total EE (hartree)	-1044.296156
EE + Zero-Point Energy Correction (hartree)	-1044.117877
EE + Thermal Enthalpy Correction (hartree)	-1044.102570
EE + Thermal Free Energy Correction (hartree)	-1044.162002
Imaginary Frequencies (cm^{-1})	None

Cartesian Coordinates

C	-3.20740100	-0.25548100	0.18032800
C	-2.48788400	-0.77834300	-0.90338200
C	-1.15718400	-0.44136000	-1.11550800
C	-0.53856700	0.43340800	-0.22303400
C	-1.22463800	0.97770100	0.85918400
C	-2.55820400	0.62736900	1.05028000
H	-2.97815300	-1.45516400	-1.59487700
H	-0.60593300	-0.84048800	-1.95691400
H	-0.73058600	1.67600200	1.52277500
H	-3.10331600	1.05514100	1.88448600
C	-4.64587800	-0.64803800	0.40351200
H	-5.21231100	-0.62380200	-0.53076200
H	-4.71185900	-1.66762500	0.79735600
H	-5.13568000	0.01635100	1.11735500
S	1.16808300	0.88991500	-0.48876500
O	1.47350900	0.79081500	-1.90327100
O	1.47524100	2.07947900	0.29447400
N	2.07738800	-0.37770800	0.32367000
N	1.93008100	-1.60047700	-0.22442800

O	2.55080400	-2.47854100	0.33917600
C	2.89515300	-0.14855300	1.51959800
H	2.52115300	-0.76155400	2.34197100
H	3.92737300	-0.43202800	1.30760600
H	2.83888900	0.90757200	1.76765100

BDE: **$NANS_1$** (triplet state)

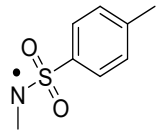
Total EE (hartree)	-1044.229782
EE + Zero-Point Energy Correction (hartree)	-1044.052703
EE + Thermal Enthalpy Correction (hartree)	-1044.037216
EE + Thermal Free Energy Correction (hartree)	-1044.098038
Imaginary Frequencies (cm^{-1})	None
$<S^2>$	2.0080

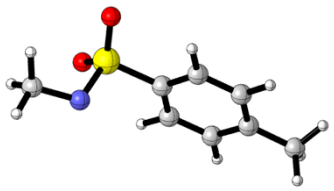
Cartesian Coordinates

C	-3.08974600	0.09761500	-0.10695700
C	-2.35904700	0.77616500	0.87822500
C	-1.01135300	0.51262700	1.08638200
C	-0.38420300	-0.45010100	0.29440700
C	-1.08375100	-1.14805400	-0.68809400
C	-2.43373800	-0.86803200	-0.87871800
H	-2.85355000	1.51832800	1.49575300
H	-0.45527800	1.02997000	1.85743300
H	-0.58617200	-1.91378100	-1.26966700
H	-2.98696200	-1.41753500	-1.63256100
C	-4.54698500	0.41248800	-0.33096400
H	-5.08379200	0.49874600	0.61702600
H	-4.66012600	1.36659700	-0.85636000
H	-5.03503500	-0.35725100	-0.93121000
S	1.35625700	-0.79120000	0.54291600
O	1.71519100	-0.43717300	1.90457400
O	1.67170200	-2.08240900	-0.05582100
N	2.24092400	0.36814500	-0.47103400
N	2.22534400	1.65289800	-0.03748300
O	1.40139000	2.54228200	-0.28198200
C	2.20171700	0.19322300	-1.93410700
H	1.27836600	0.59940400	-2.36070600

H	3.05979700	0.71926300	-2.35327700
H	2.29513500	-0.86902800	-2.14868800

BDE: Sulfamidyl radicals





Total EE (hartree)	-914.307218
EE + Zero-Point Energy Correction (hartree)	-914.139467
EE + Thermal Enthalpy Correction (hartree)	-914.125852
EE + Thermal Free Energy Correction (hartree)	-914.181238
Imaginary Frequencies (cm^{-1})	None
$<S^2>$	0.7548

Cartesian Coordinates

C	-2.97300400	0.00131800	0.15213900
C	-2.26359100	-1.20252100	0.05567000
C	-0.88393800	-1.21343500	-0.11821600
C	-0.20624700	0.00039800	-0.20034700
C	-0.88281700	1.21405800	-0.11837100
C	-2.26321000	1.20402100	0.05586200
H	-2.79826100	-2.14480500	0.11123000
H	-0.34032700	-2.14551400	-0.20735300
H	-0.33884200	2.14591900	-0.20757700
H	-2.79718800	2.14654700	0.11158900
C	-4.46529700	-0.00061400	0.37013500
H	-4.94127500	-0.84146300	-0.13928300
H	-4.70011700	-0.08876600	1.43646900
H	-4.92287600	0.92220400	0.00817000
S	1.56851700	-0.00019500	-0.40691900
O	1.97466500	-1.27301600	-1.01064500
O	1.97561600	1.27269700	-1.00982200
N	2.10273600	-0.00132100	1.21319300
C	3.54701200	0.00008400	1.31335800
H	3.81877400	0.00048800	2.36832900
H	3.97515600	-0.88298200	0.81985600
H	3.97382900	0.88343700	0.81928200

BDE: NO radical

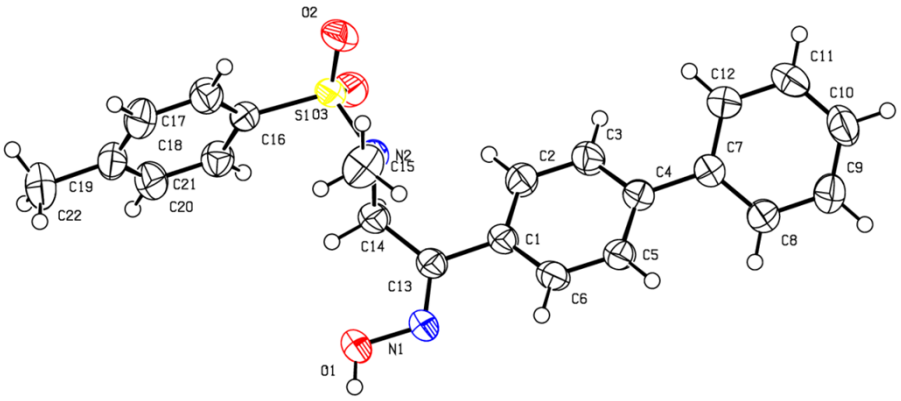
N=O	

Total EE (hartree)	-129.931657
EE + Zero-Point Energy Correction (hartree)	-129.927145
EE + Thermal Enthalpy Correction (hartree)	-129.923840
EE + Thermal Free Energy Correction (hartree)	-129.947133
Imaginary Frequencies (cm^{-1})	None
$<S^2>$	0.7529

Cartesian Coordinates

N	0.00000000	0.00000000	-0.61224900
O	0.00000000	0.00000000	0.53571800

7. X-ray crystal structure analysis of 2j and 4c

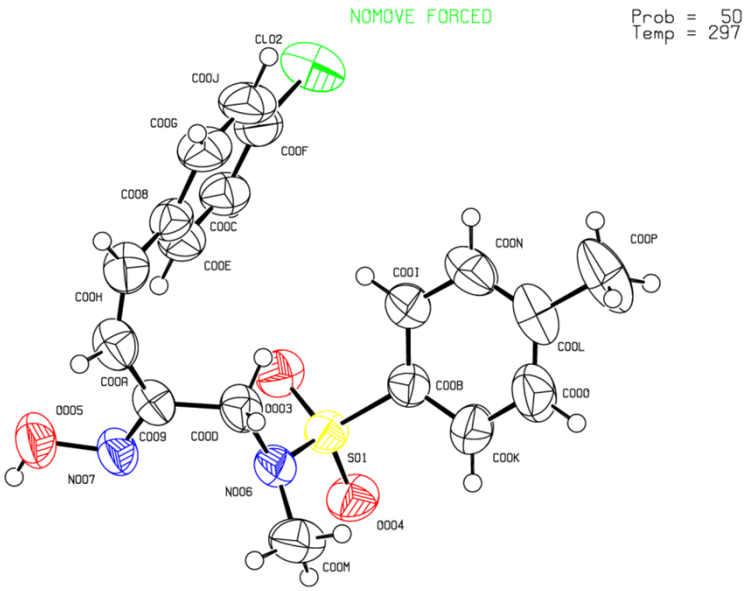


X-ray crystal structure of **2j** (**CCDC** 2070573)

Table S6 Crystal data and structure refinement for 2j

Identification code	yuanpf_YP765
Empirical formula	$C_{22}H_{22}N_2O_3S$
Formula weight	394.47
Temperature/K	293.75(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.8908(7)
b/Å	11.0797(6)

c/Å	11.2738(6)
α/°	65.070(6)
β/°	88.314(5)
γ/°	66.204(6)
Volume/Å^3	1010.27(12)
Z	2
ρ_{calc}g/cm^3	1.297
μ/mm^{-1}	1.627
F(000)	416.0
Crystal size/mm^3	0.11 × 0.07 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.758 to 133.174
Index ranges	-11 ≤ h ≤ 9, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected	6288
Independent reflections	3567 [R_{int} = 0.0170, R_{sigma} = 0.0211]
Data/restraints/parameters	3567/0/257
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0393, wR_2 = 0.1094
Final R indexes [all data]	R_1 = 0.0423, wR_2 = 0.1127
Largest diff. peak/hole / e Å^{-3}	0.23/-0.33



X-ray crystal structure of **4c** (**CCDC** 2075040)

Table S7 Crystal data and structure refinement for 4c.

Identification code	yuanpanfeng_0323-2
Empirical formula	$C_{18}H_{19}ClN_2O_3S$
Formula weight	378.86

Temperature/K	297.36(10)
Crystal system	triclinic
Space group	P-1
a/Å	5.31790(10)
b/Å	10.4579(3)
c/Å	16.7990(4)
α/°	89.360(2)
β/°	87.747(2)
γ/°	79.838(2)
Volume/Å^3	918.89(4)
Z	2
ρ_{calc}g/cm^3	1.369
μ/mm^{-1}	3.069
F(000)	396.0
Crystal size/mm^3	0.15 × 0.04 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.264 to 151.22
Index ranges	-6 ≤ h ≤ 5, -13 ≤ k ≤ 13, -19 ≤ l ≤ 20
Reflections collected	8516
Independent reflections	3467 [R_{int} = 0.0604, R_{sigma} = 0.0595]
Data/restraints/parameters	3467/0/229
Goodness-of-fit on F^2	1.185
Final R indexes [I>=2σ (I)]	R_1 = 0.0525, wR_2 = 0.1432
Final R indexes [all data]	R_1 = 0.0721, wR_2 = 0.1784
Largest diff. peak/hole / e Å^{-3}	0.33/-0.51

8. References

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3 Ishida N.; Shimamoto Y.; Murakami M. Solar-Driven Incorporation of Carbon Dioxide into α-Amino Ketones. *Angew. Chem. Int. Ed.* **2012**, *51*, 11750 –11752.

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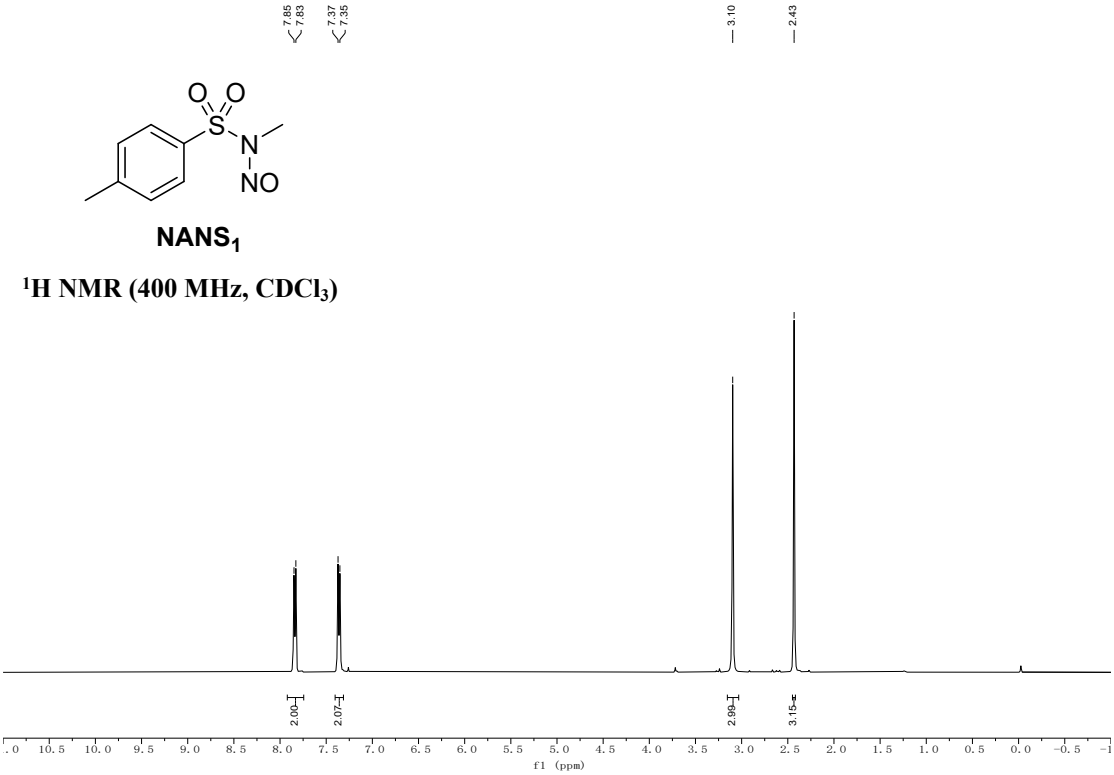
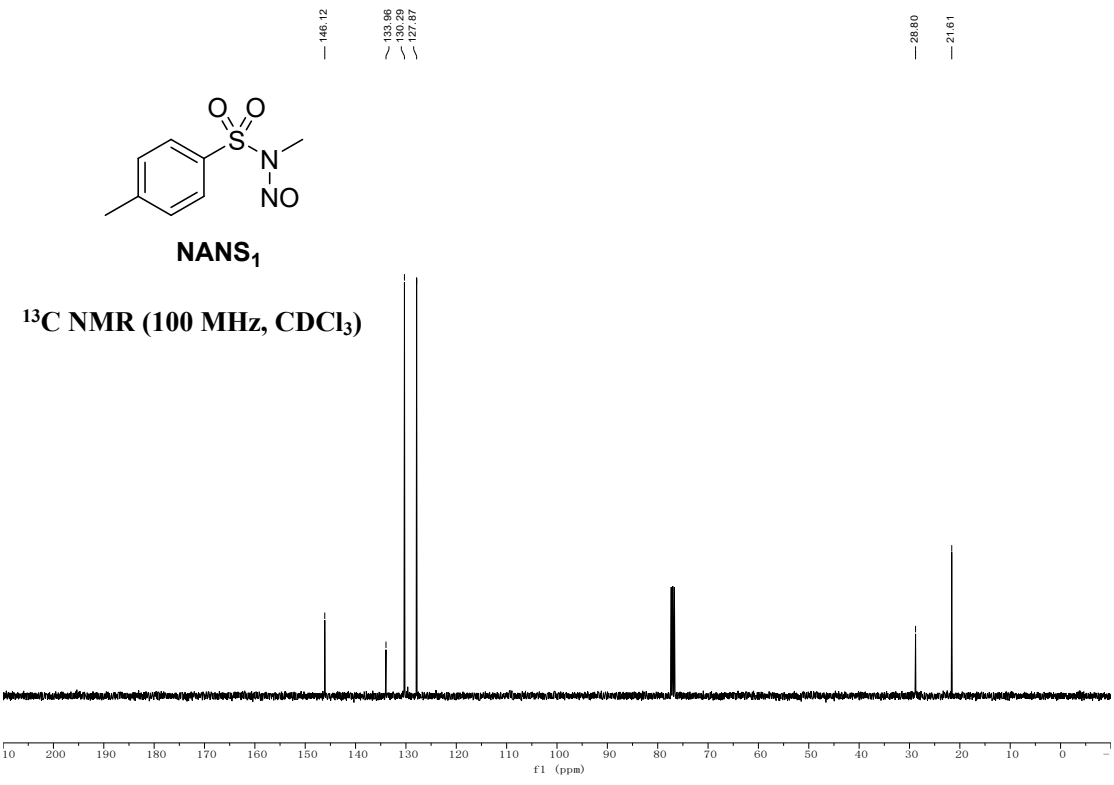
9. NMR spectra for all compounds



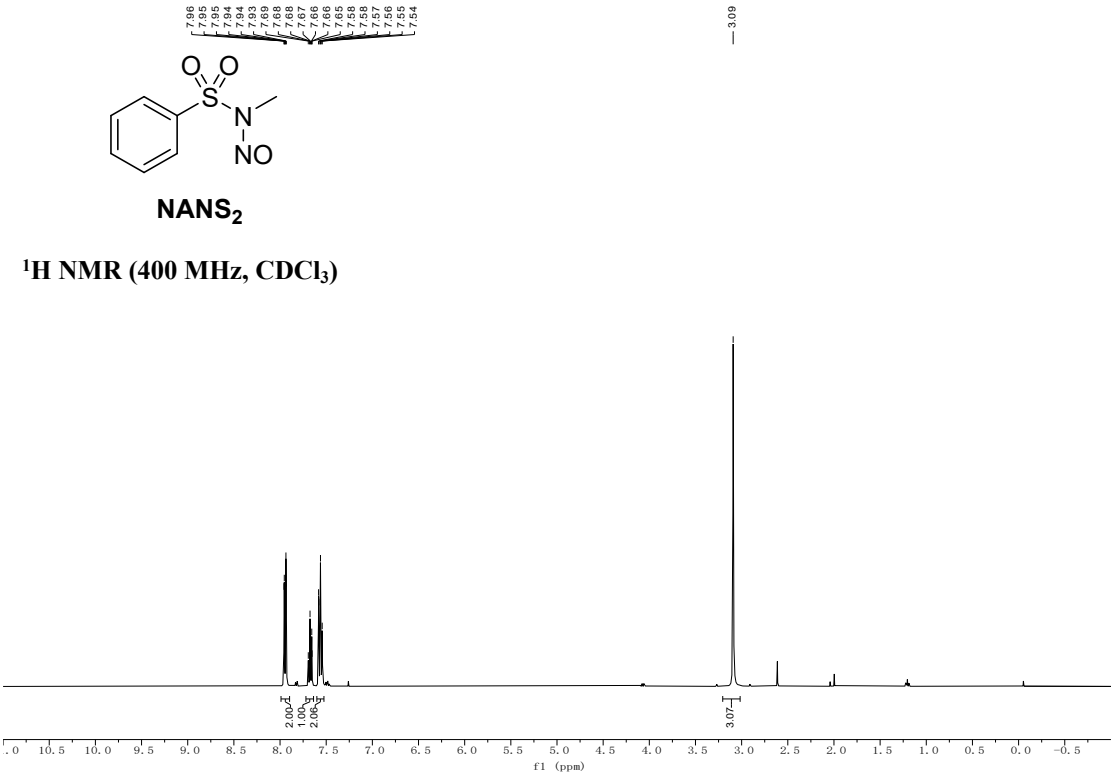
NANS$_1$

^{1}H NMR (400 MHz, $CDCl_3$)



NANS$_1$

^{13}C NMR (100 MHz, $CDCl_3$)



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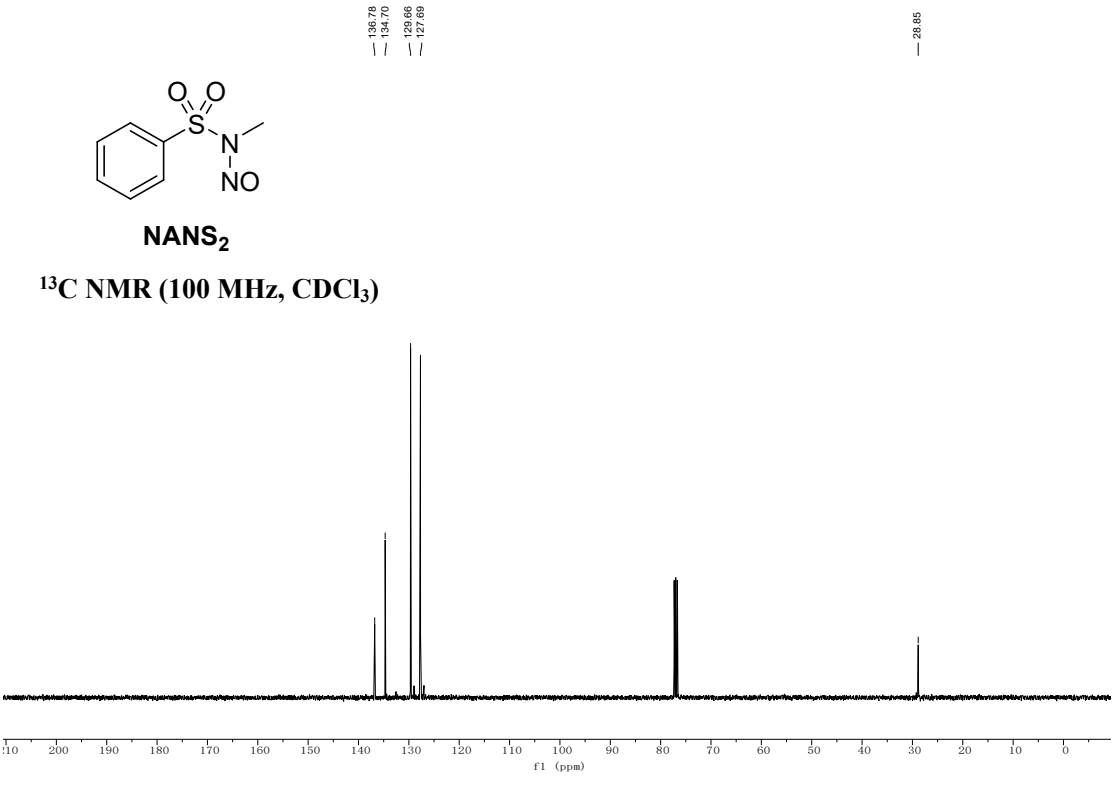

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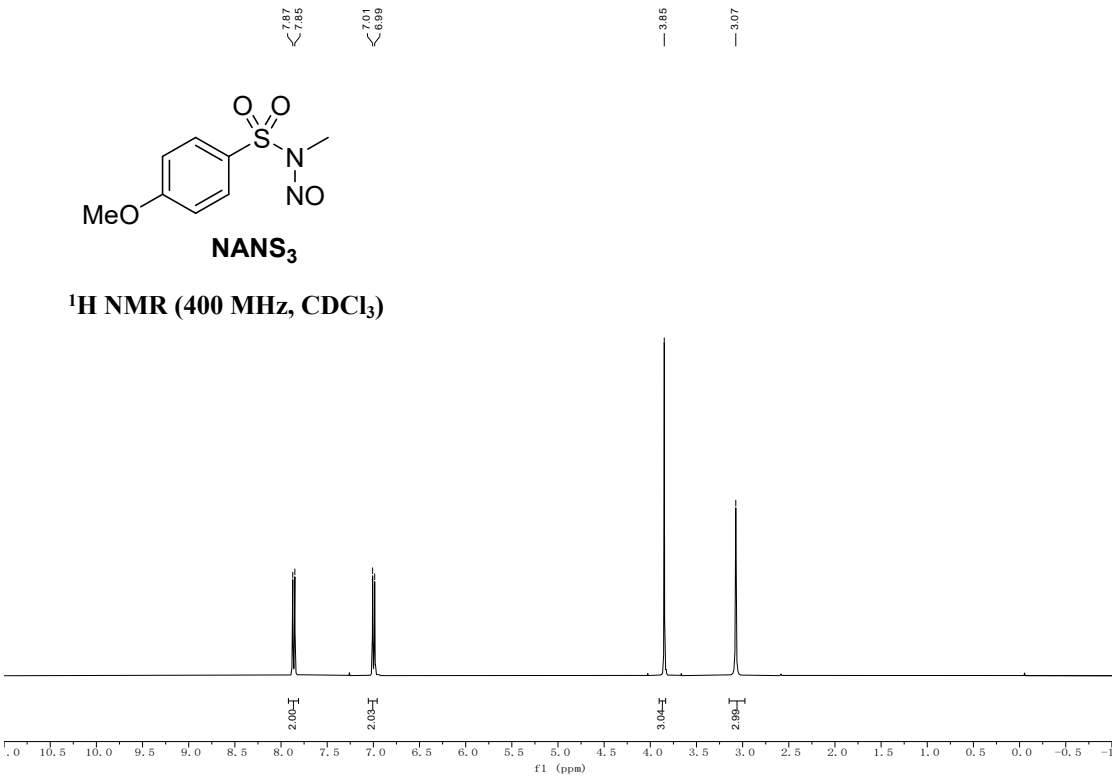

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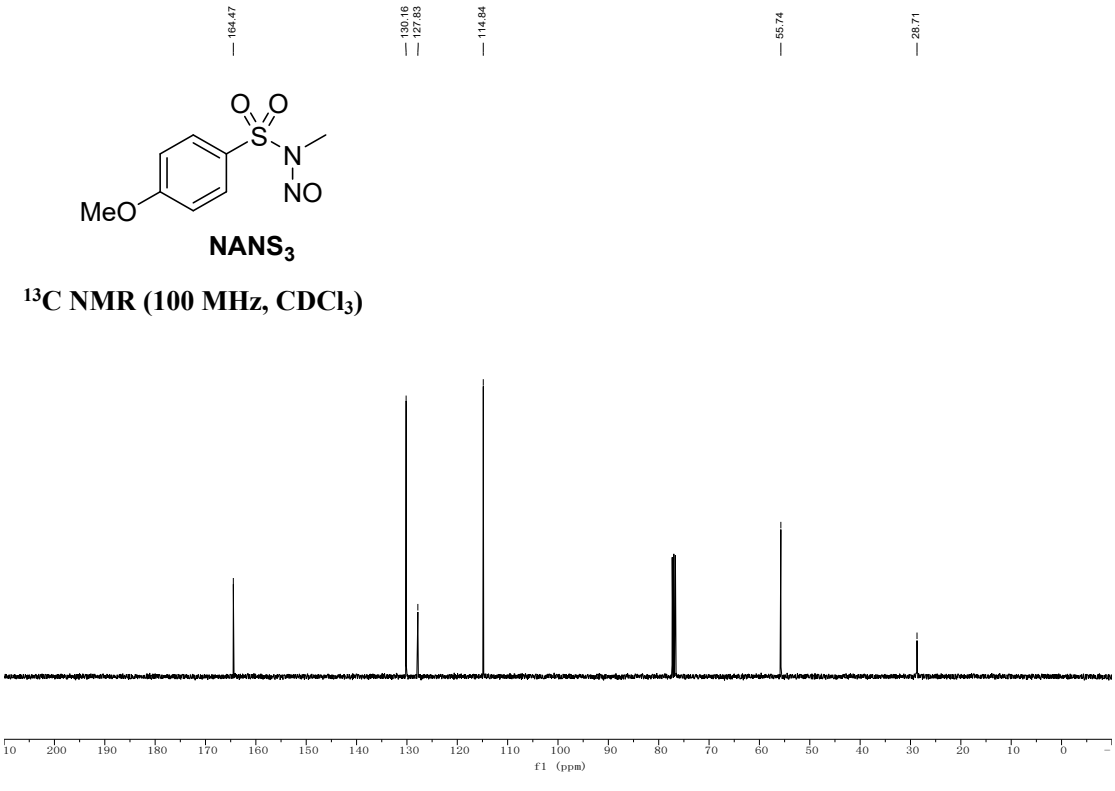

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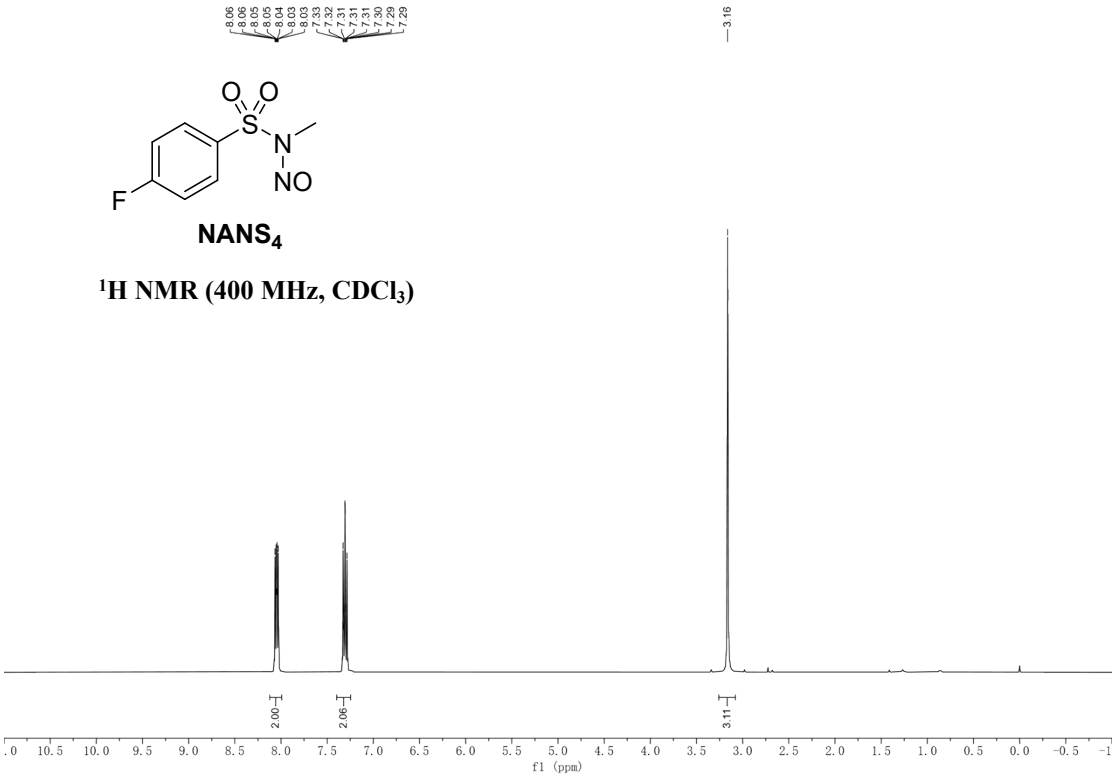

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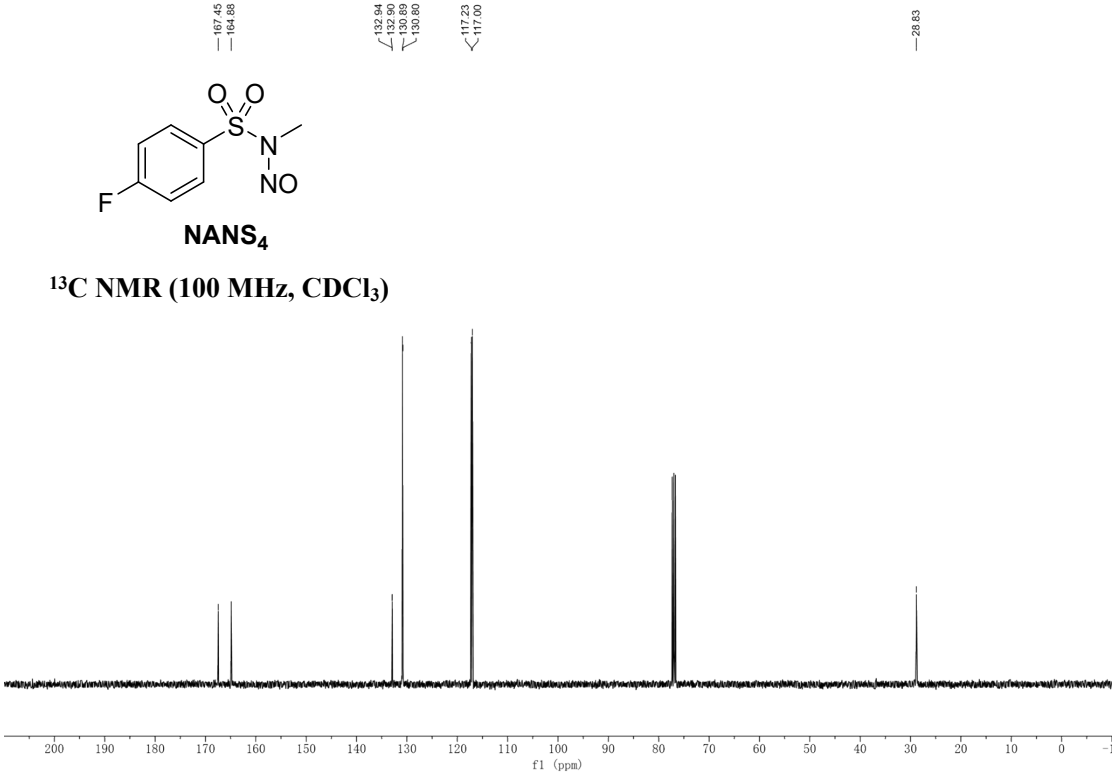

NANS$_4$

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$NANS_5$

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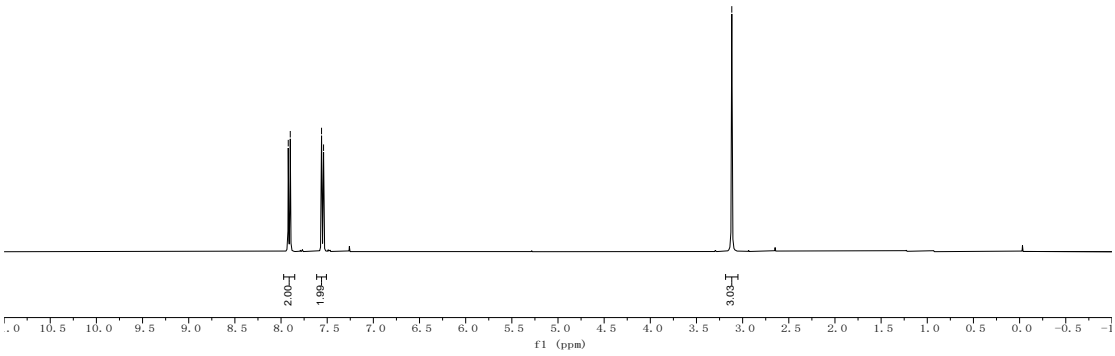

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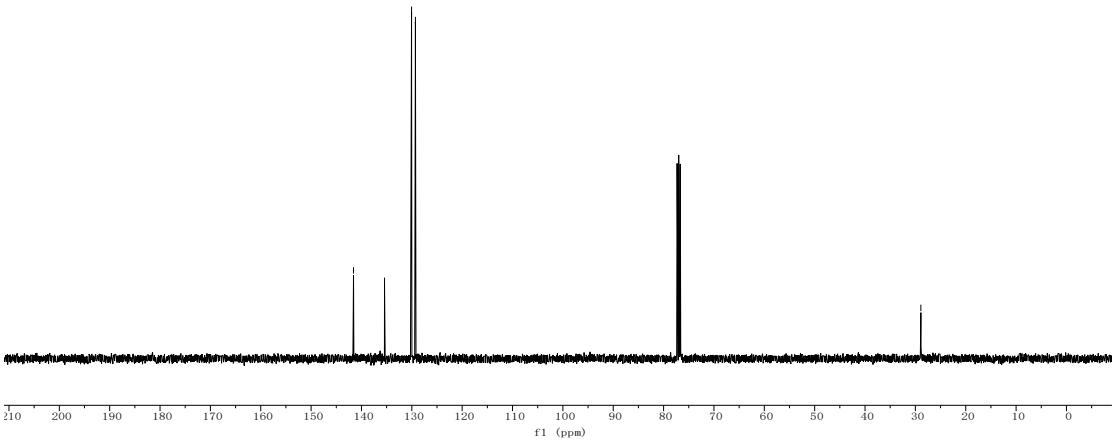

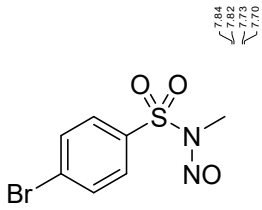

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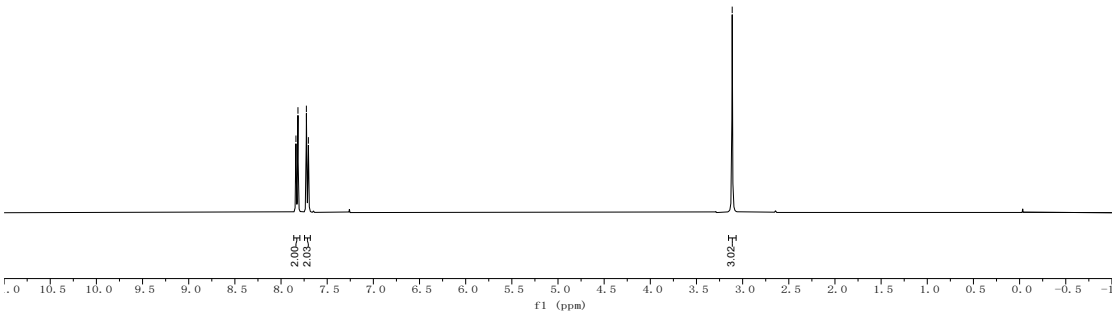

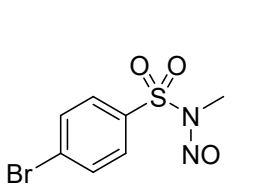

$NANS_6$

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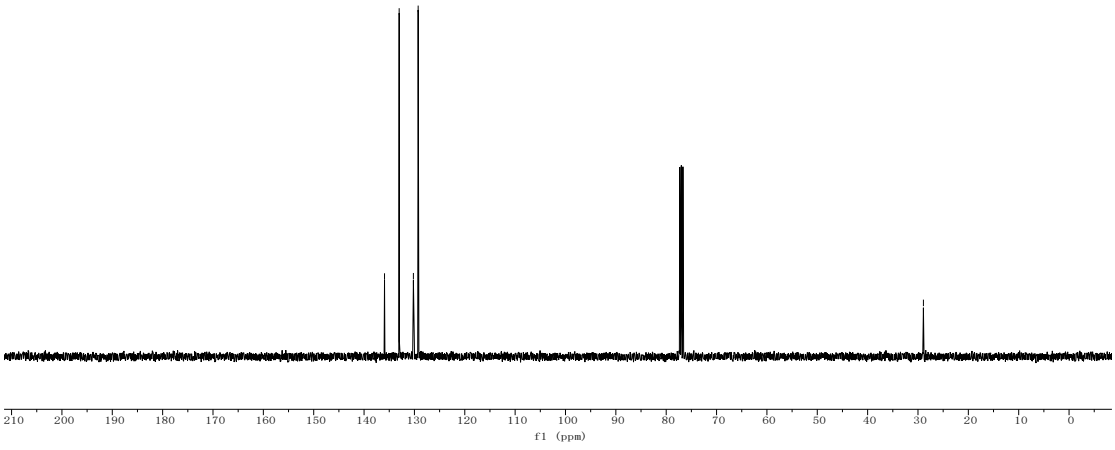

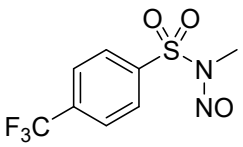

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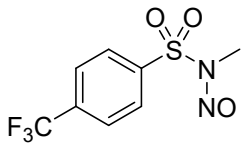

$NANS_7$

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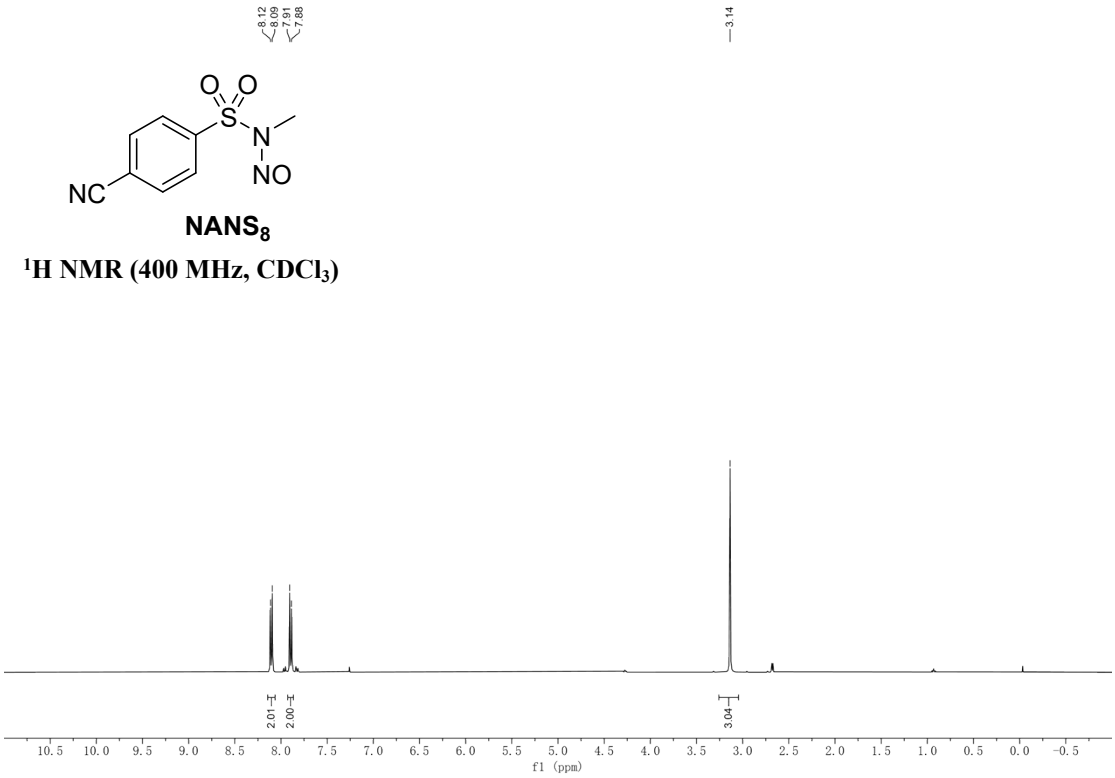

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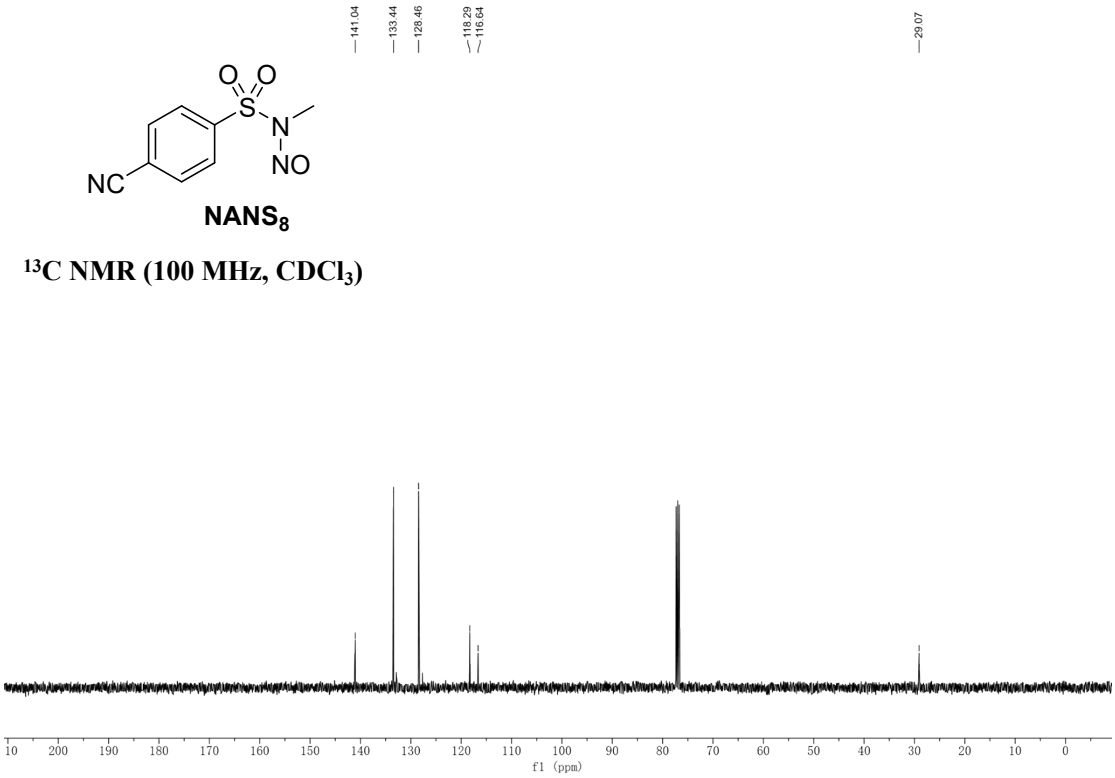

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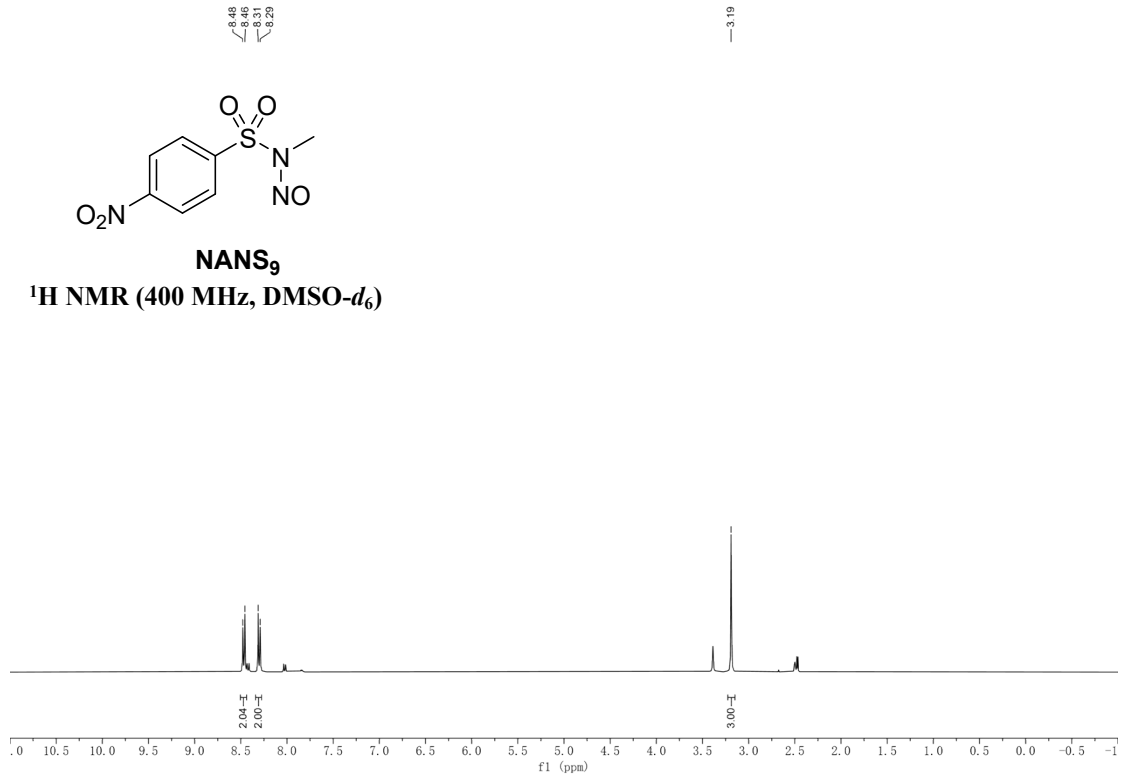

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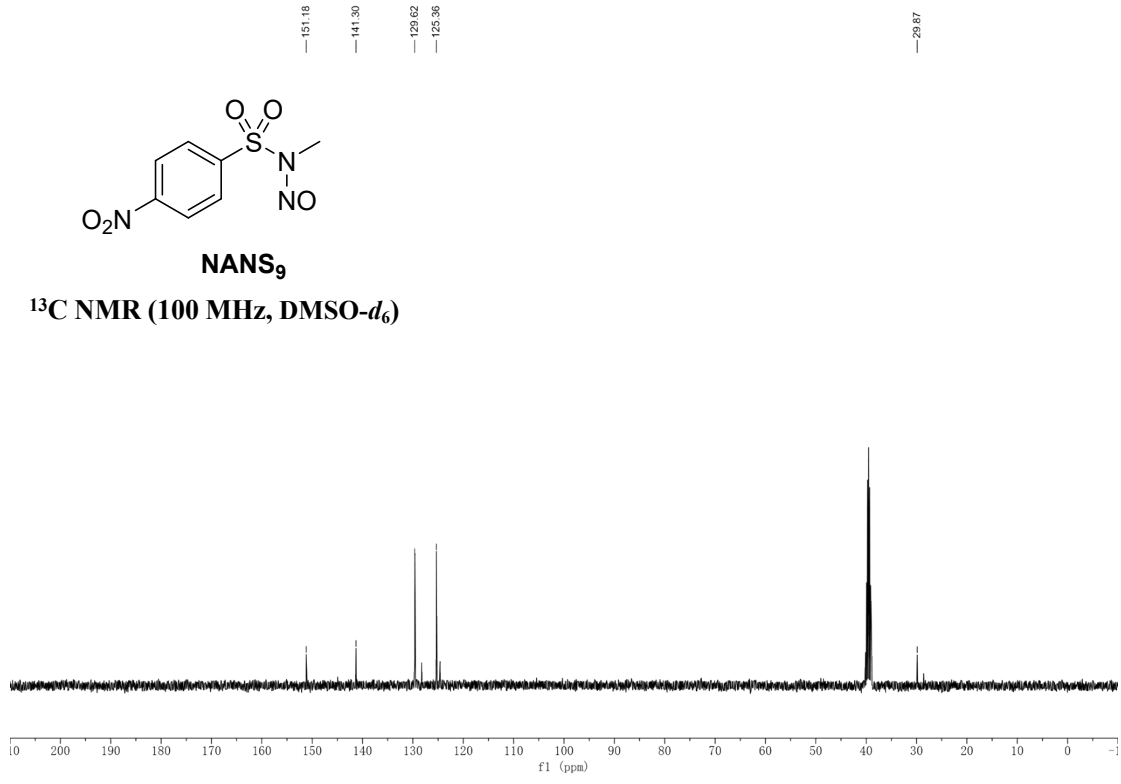

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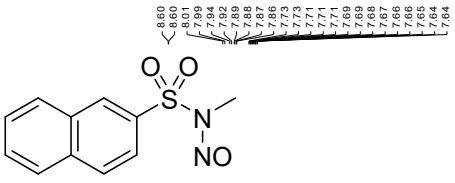

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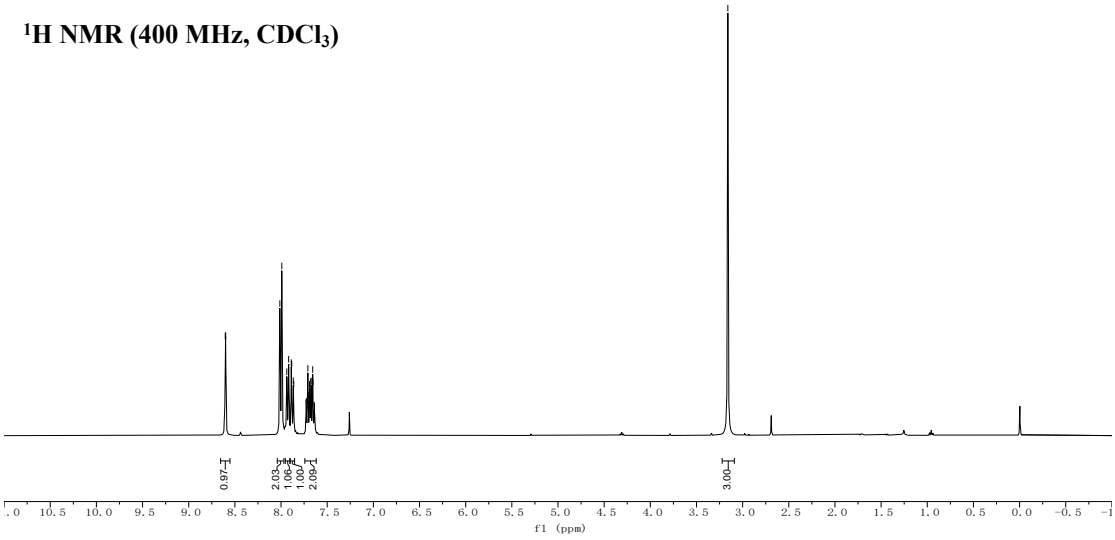

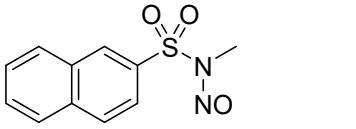

$NANS_{10}$

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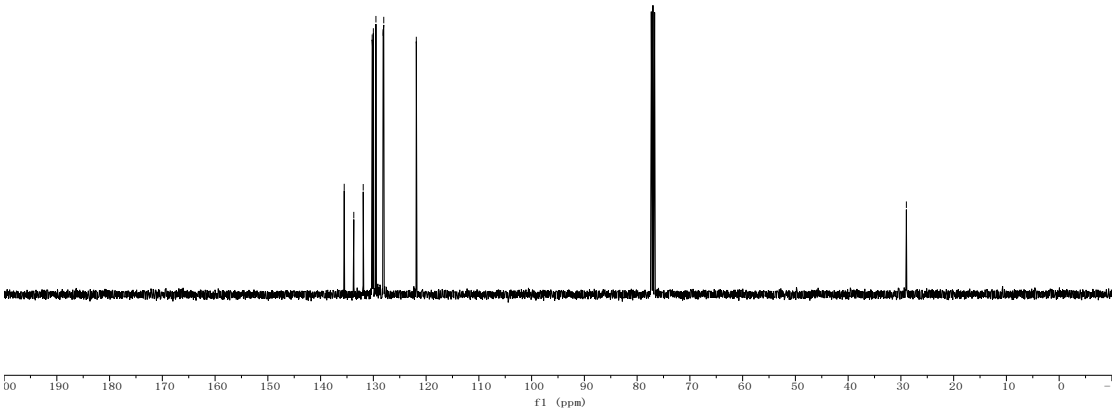

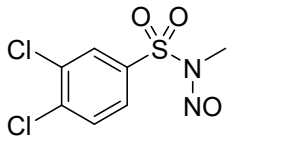

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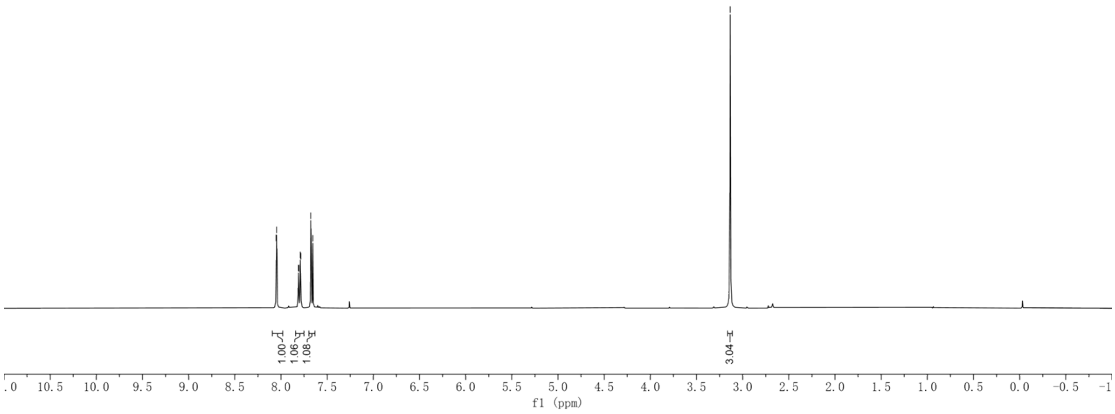

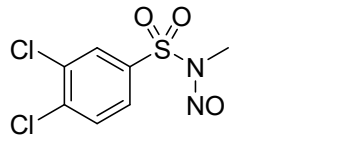

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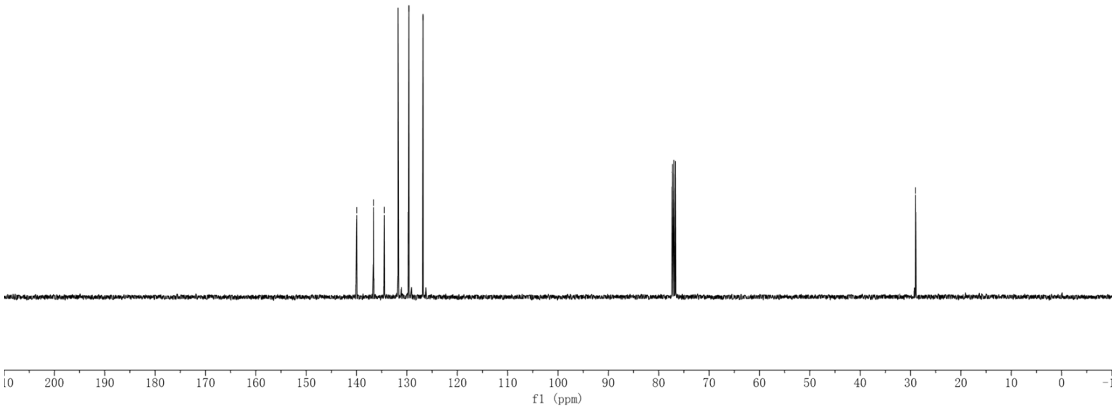

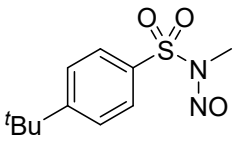

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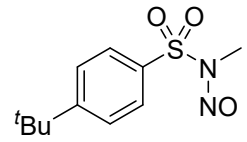

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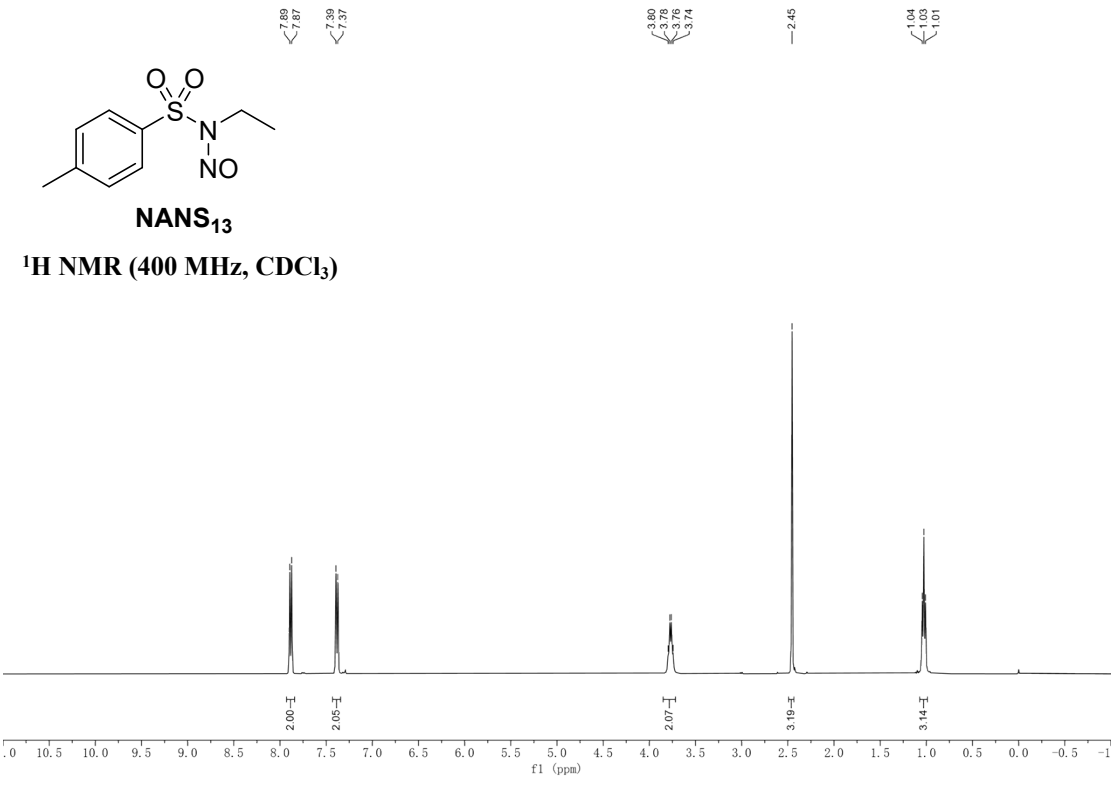

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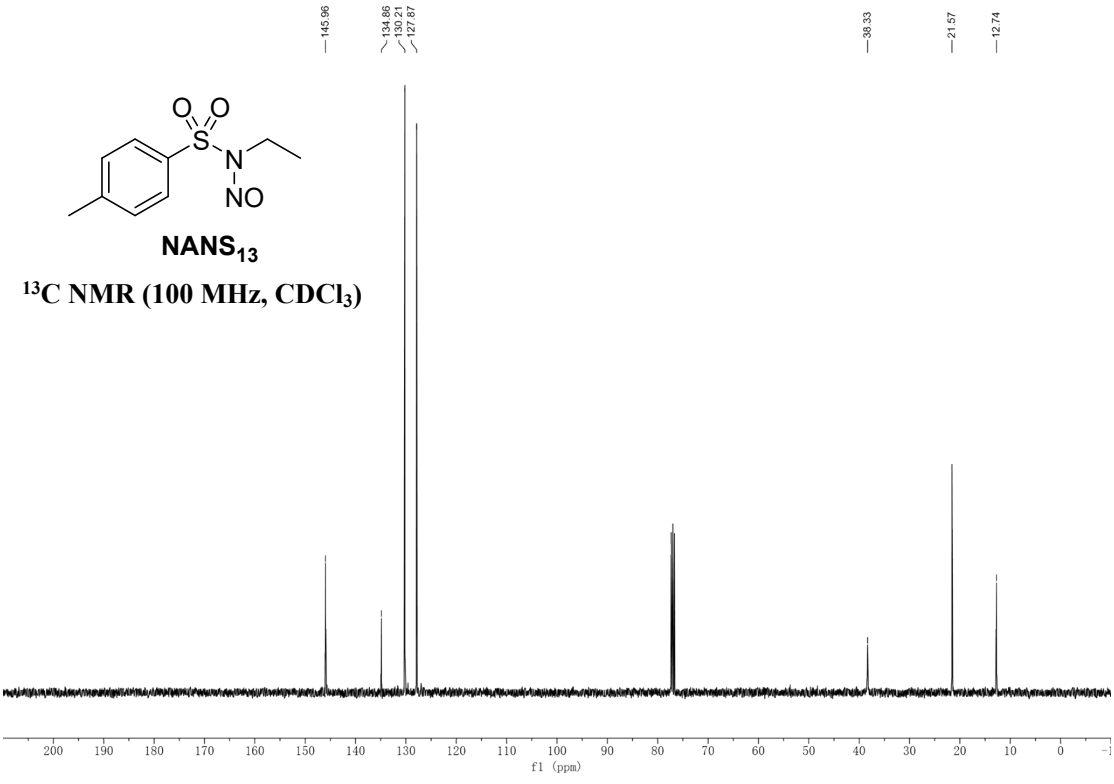

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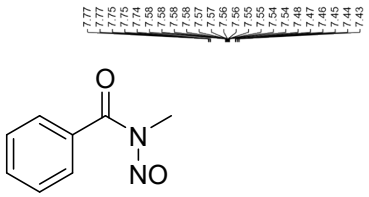

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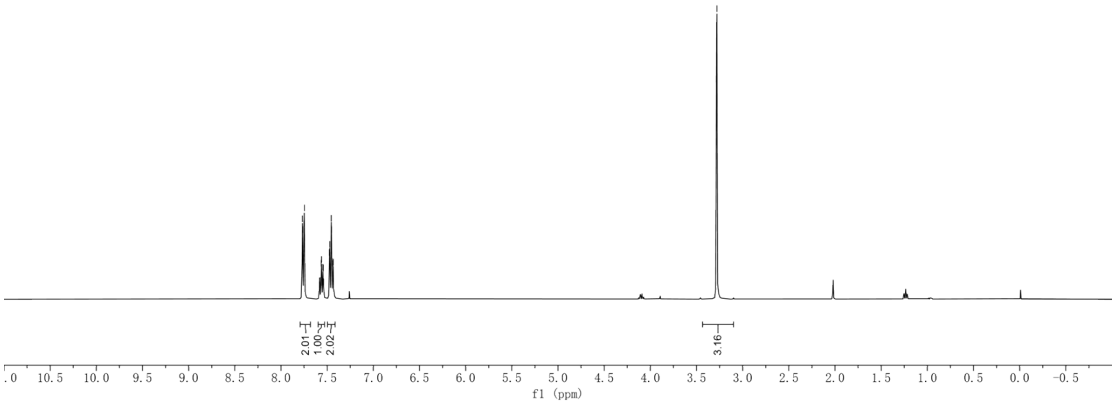

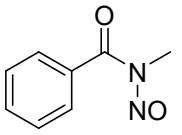

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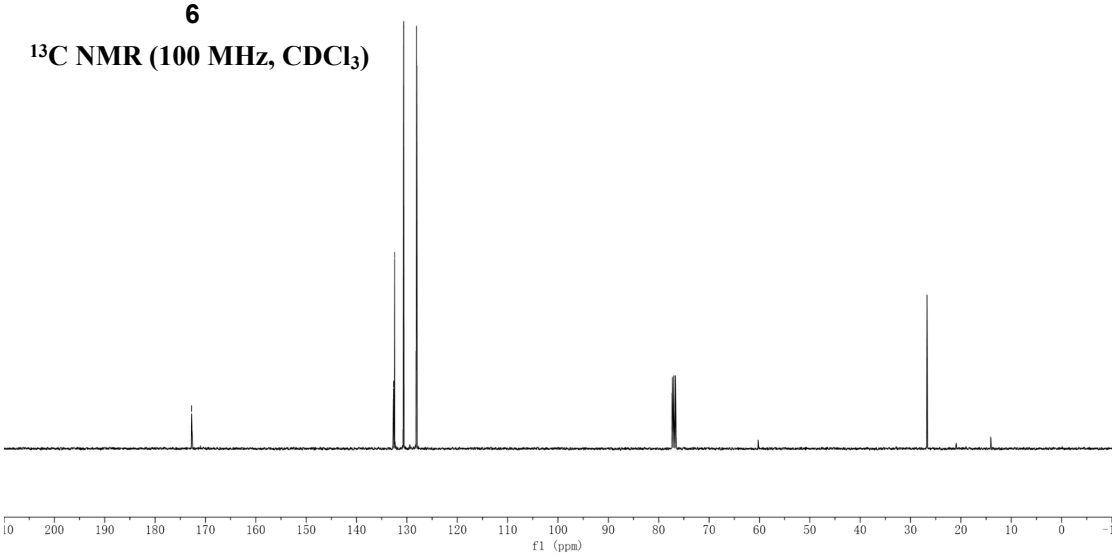

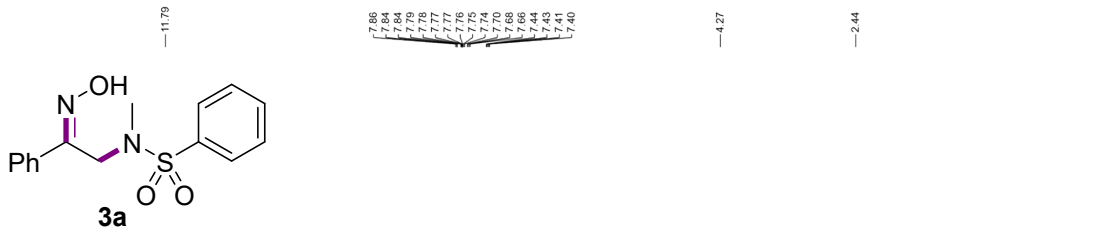

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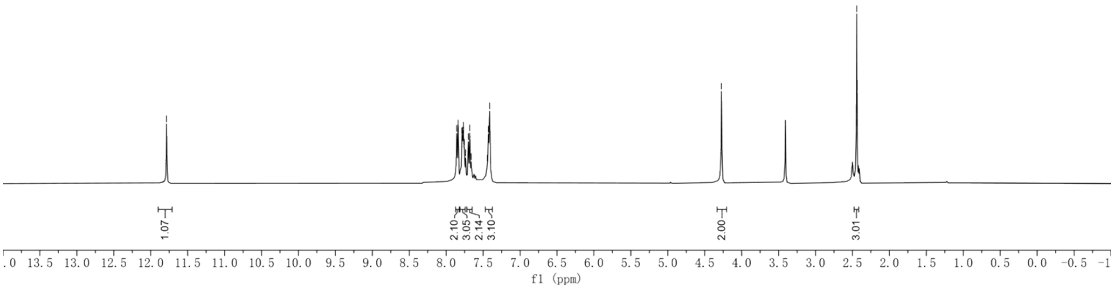

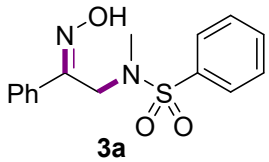

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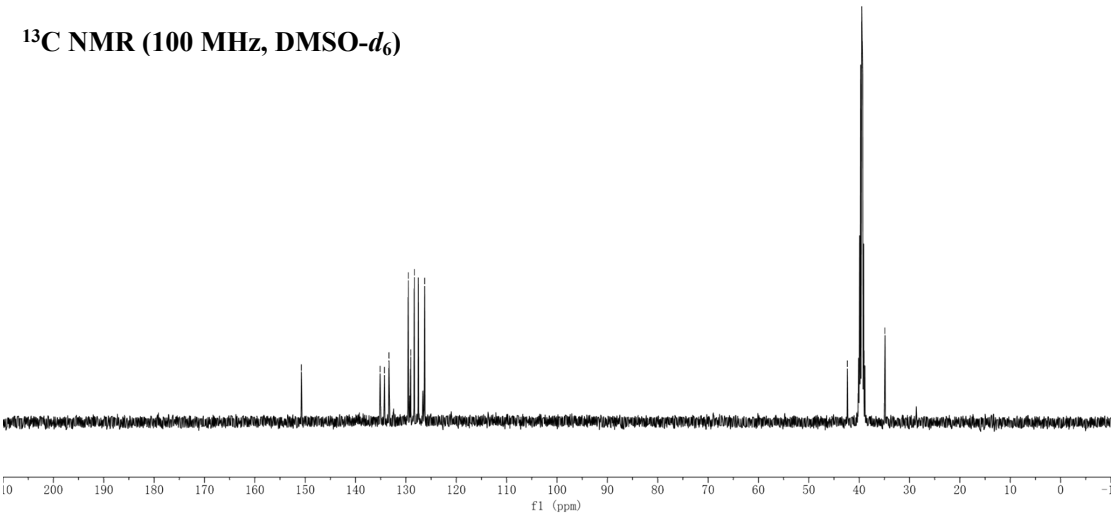

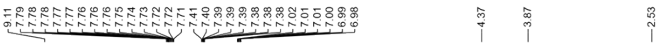

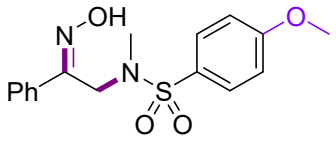

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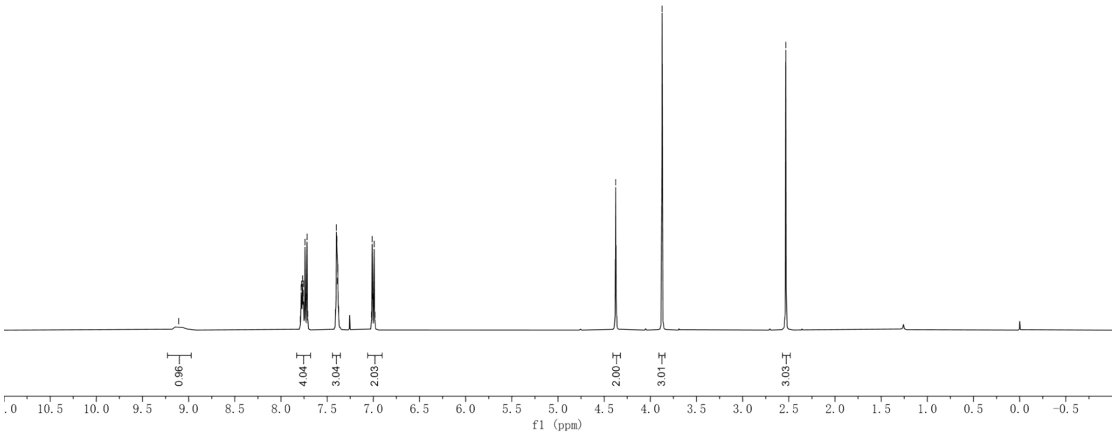

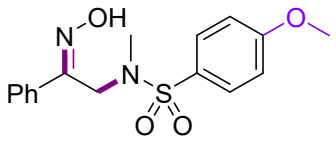

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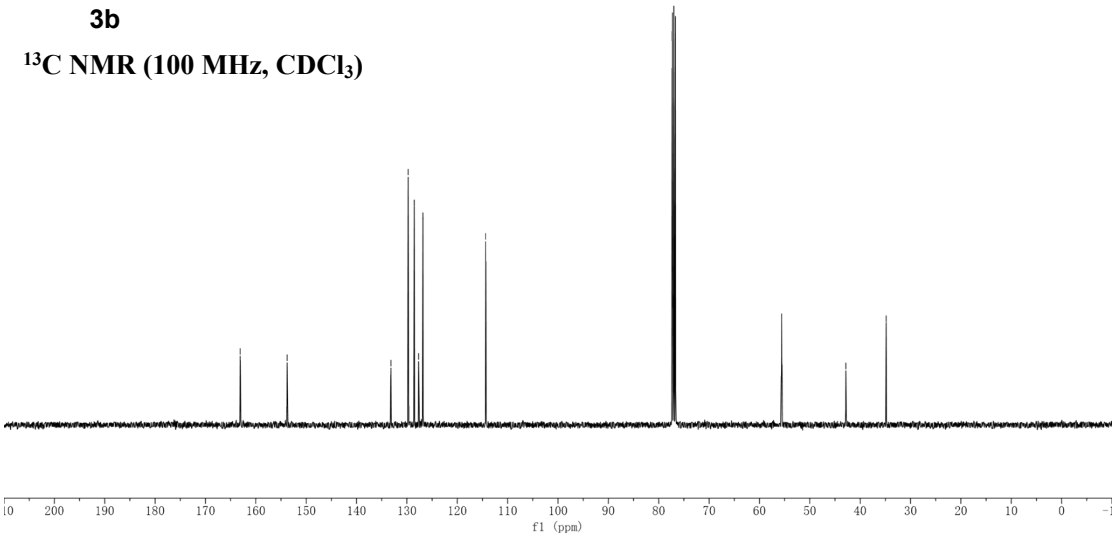

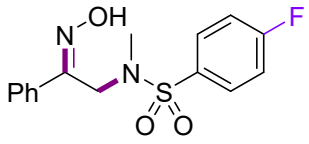

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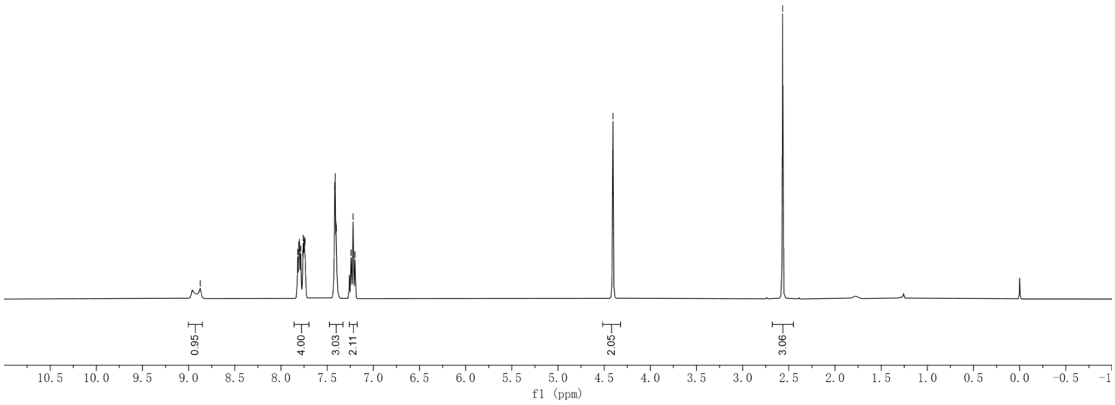
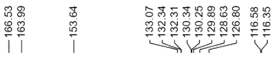
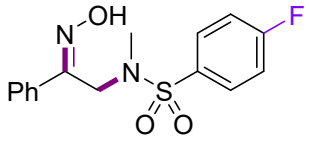
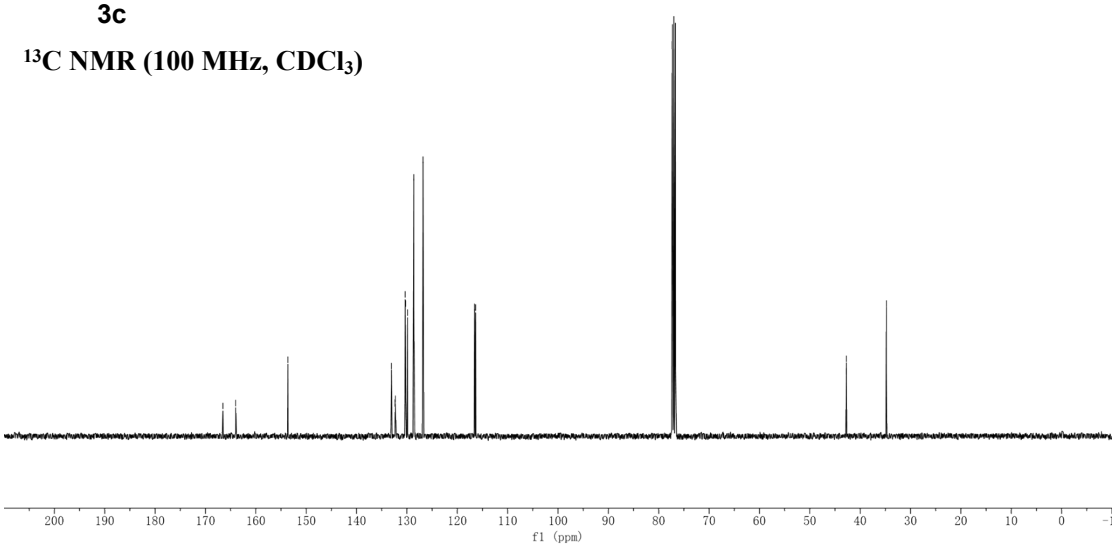


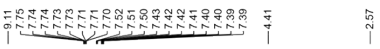


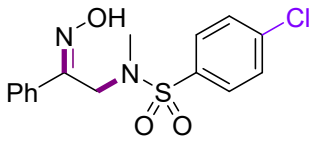


3c

^{13}C NMR (100 MHz, $CDCl_3$)

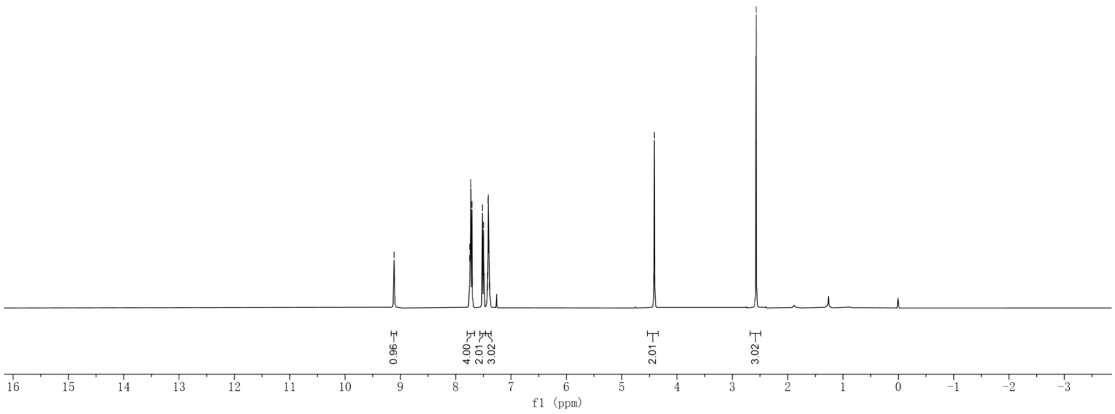


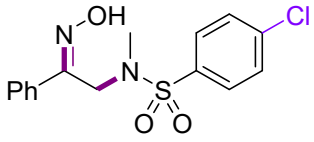




3d

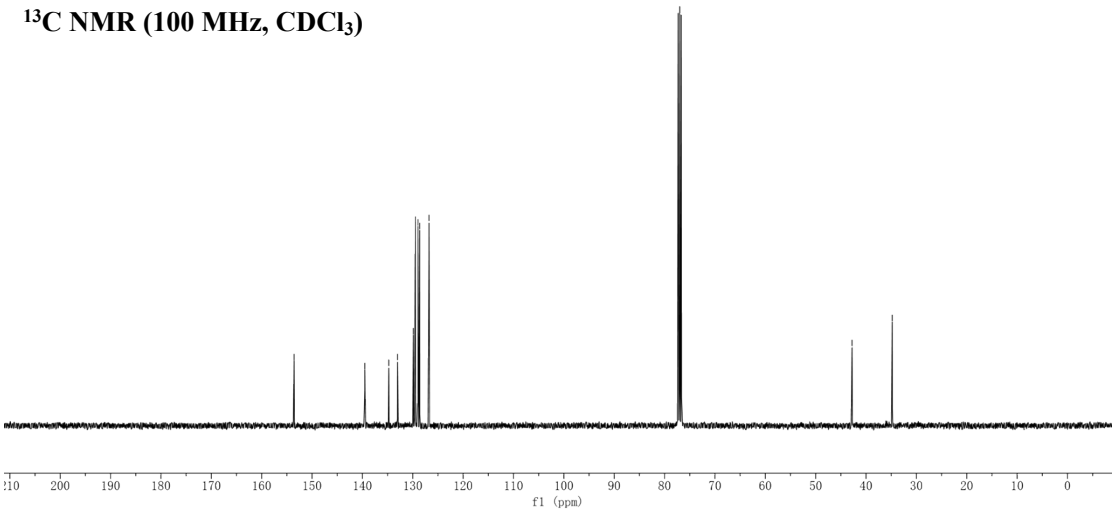
^{1}H NMR (400 MHz, $CDCl_3$)

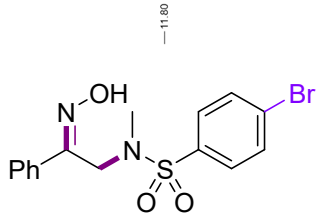




3d

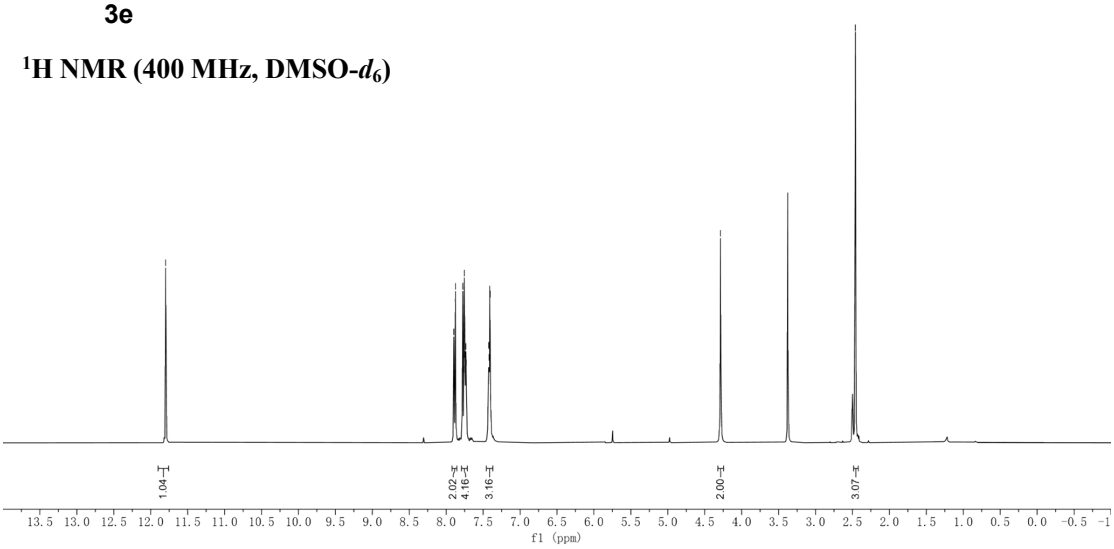
^{13}C NMR (100 MHz, $CDCl_3$)

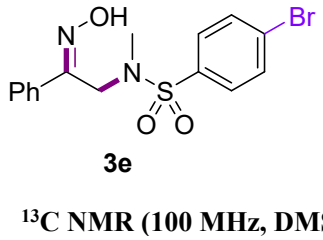




3e

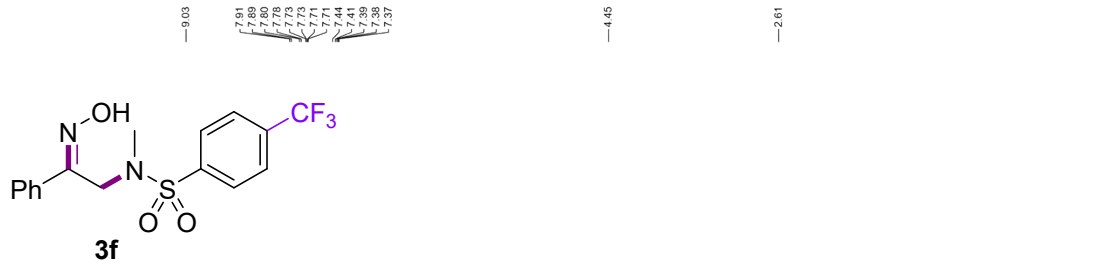
^{1}H NMR (400 MHz, DMSO-d_6)





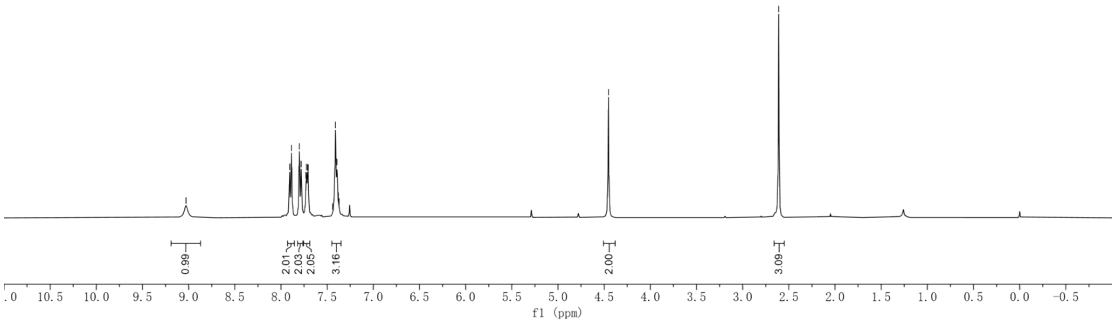
3e

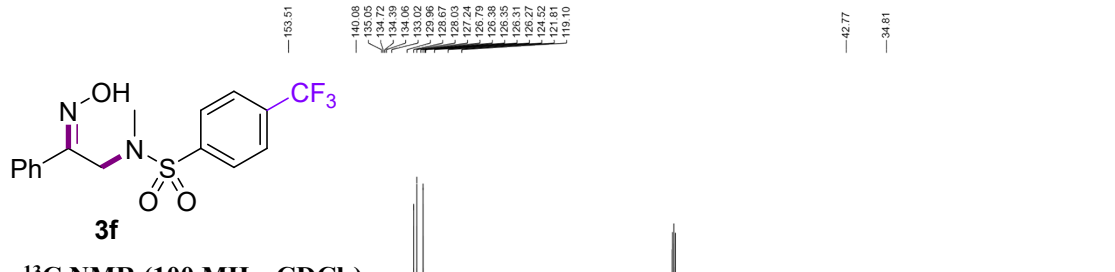
^{13}C NMR (100 MHz, DMSO-d_6)



3f

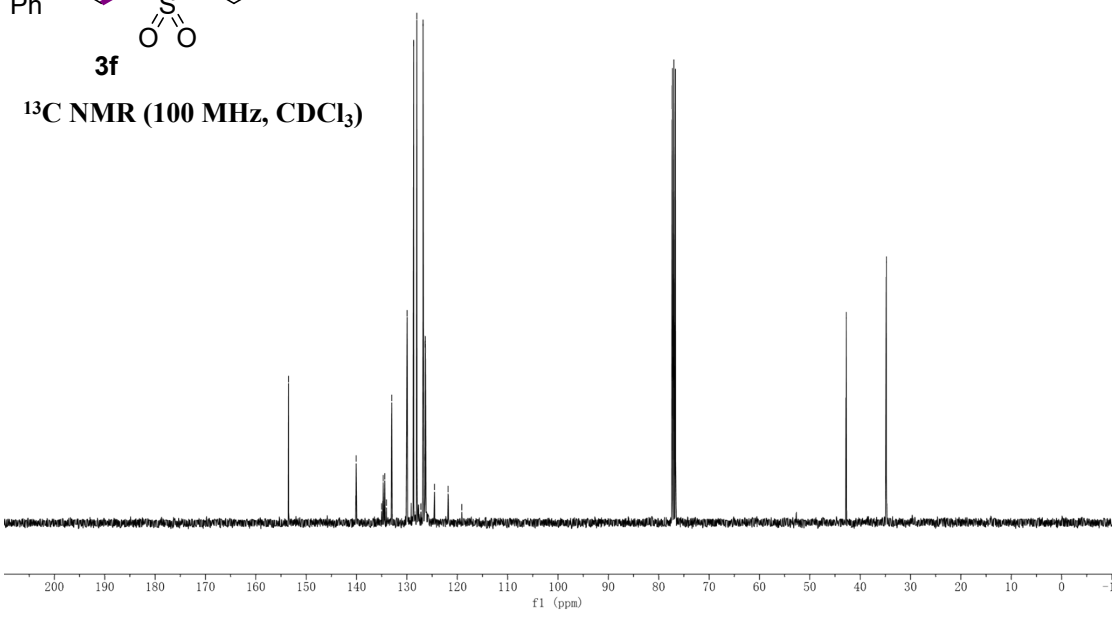
^{1}H NMR (400 MHz, $CDCl_3$)

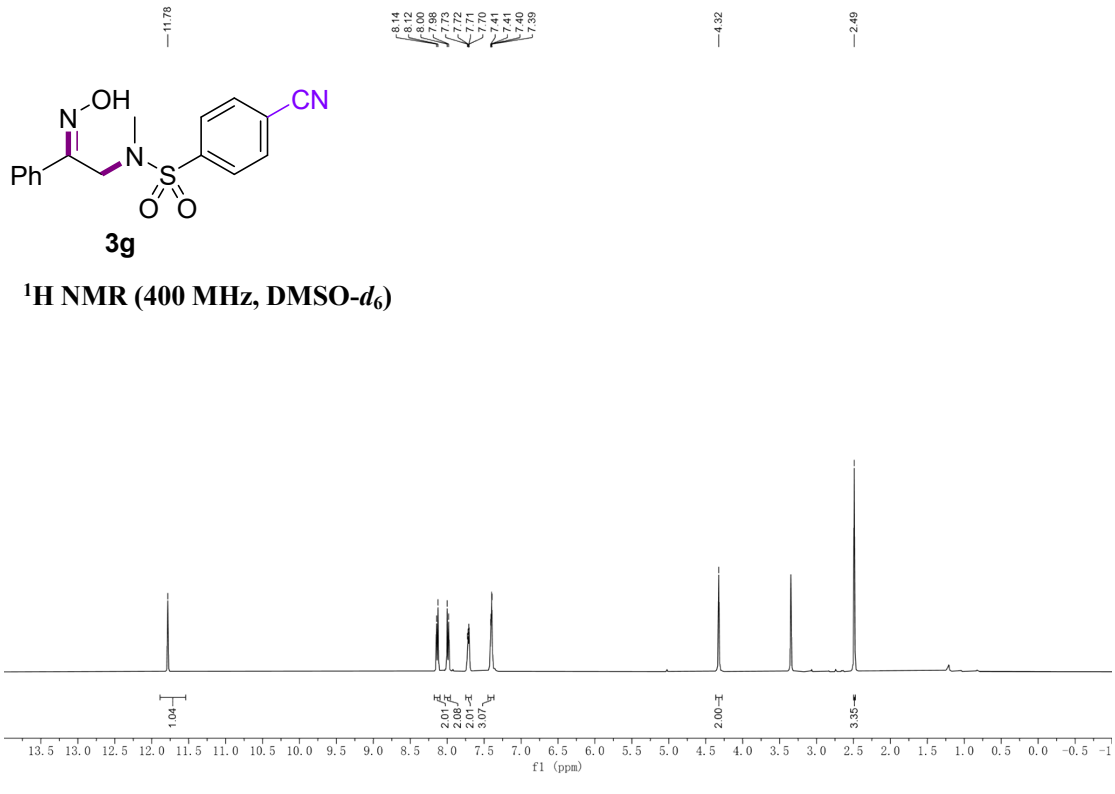




3f

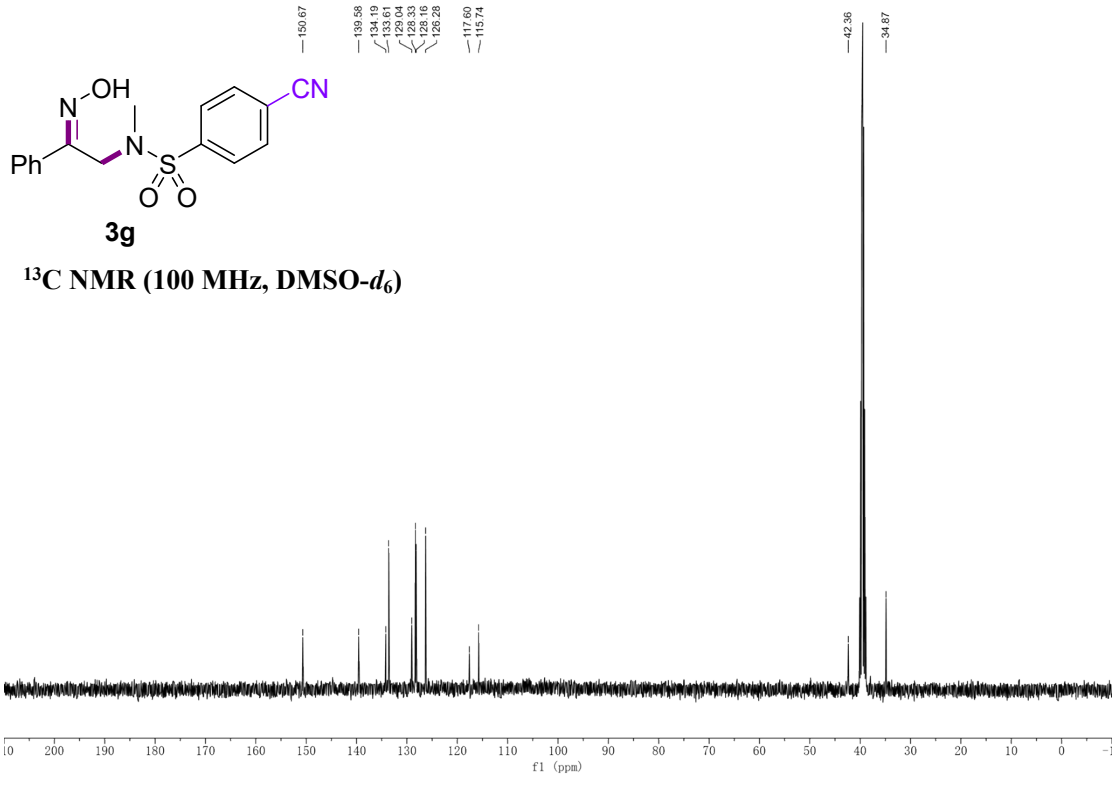
^{13}C NMR (100 MHz, $CDCl_3$)





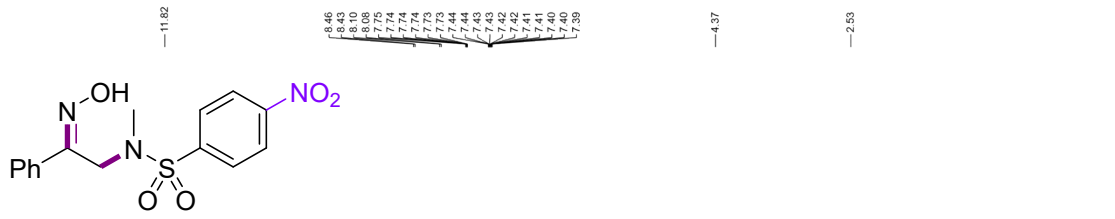
3g

^{1}H NMR (400 MHz, DMSO-d_6)



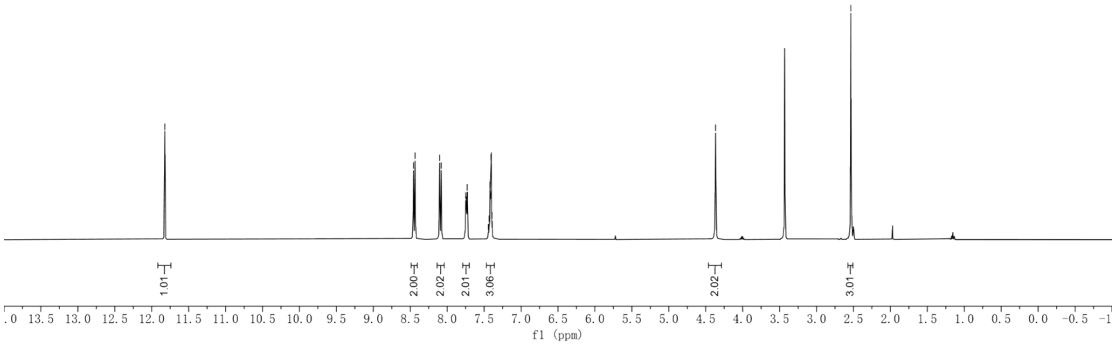
3g

^{13}C NMR (100 MHz, DMSO-d_6)



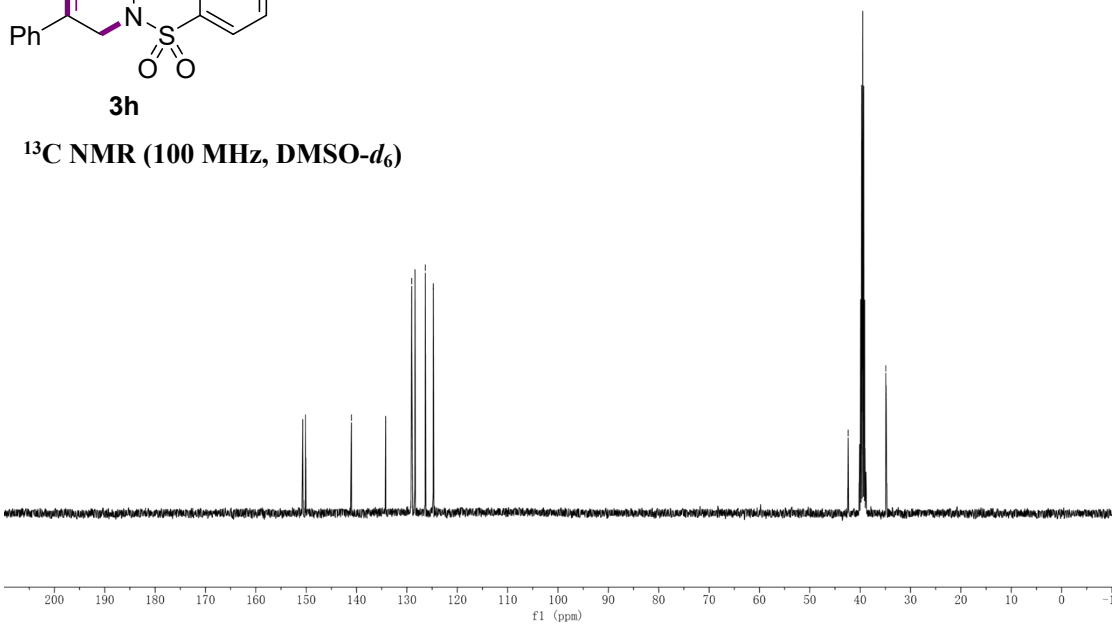
3h

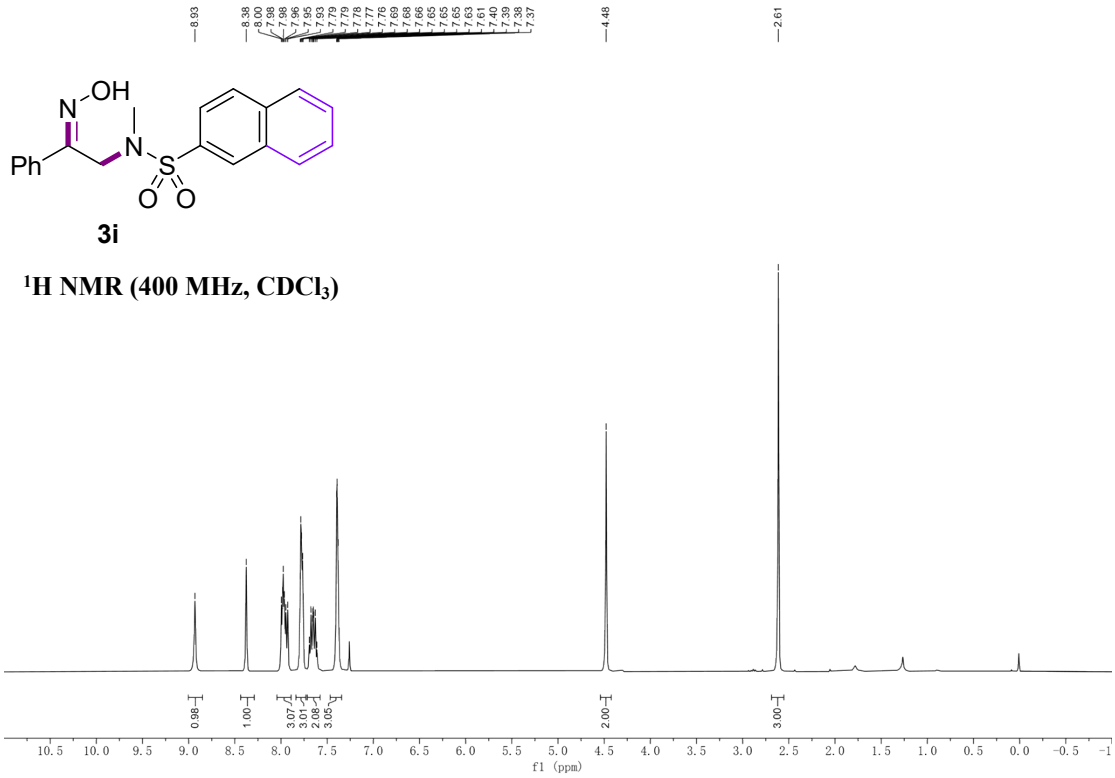
^{1}H NMR (400 MHz, DMSO-d_6)



3h

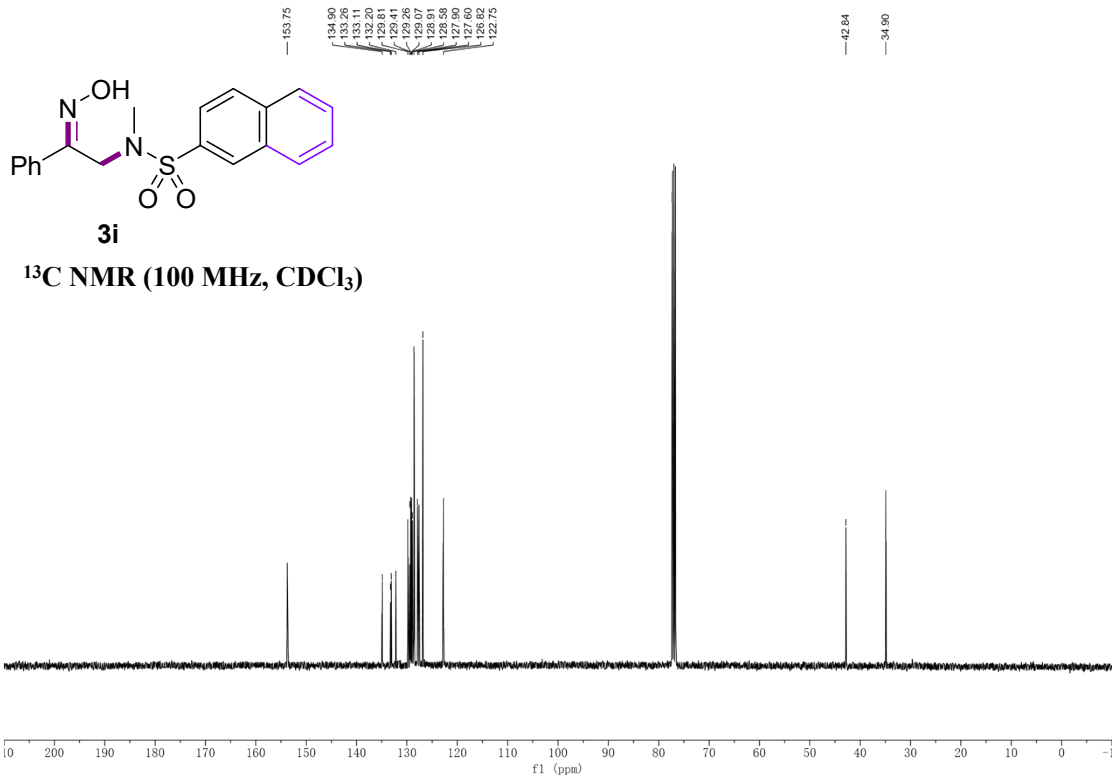
^{13}C NMR (100 MHz, DMSO-d_6)





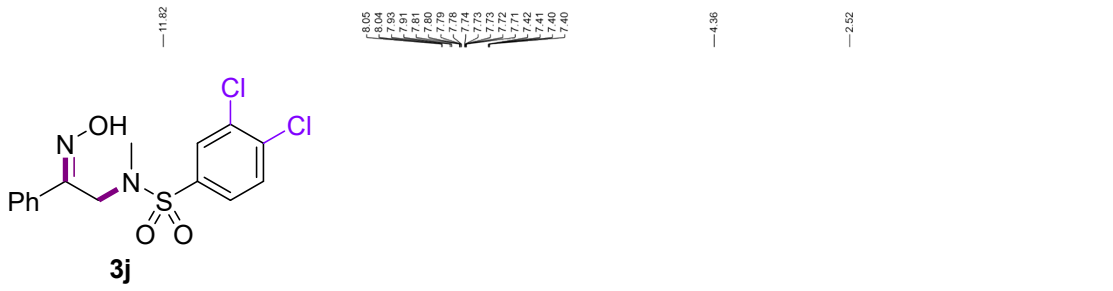
3i

^{1}H NMR (400 MHz, $CDCl_3$)



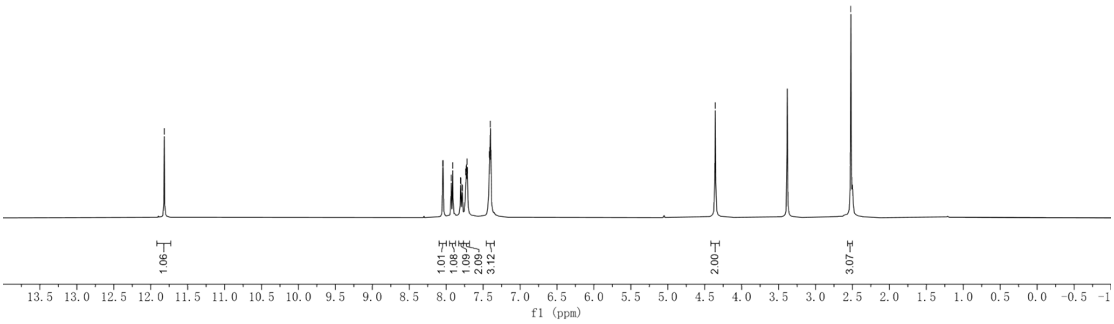
3i

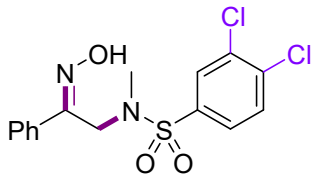
^{13}C NMR (100 MHz, $CDCl_3$)



3j

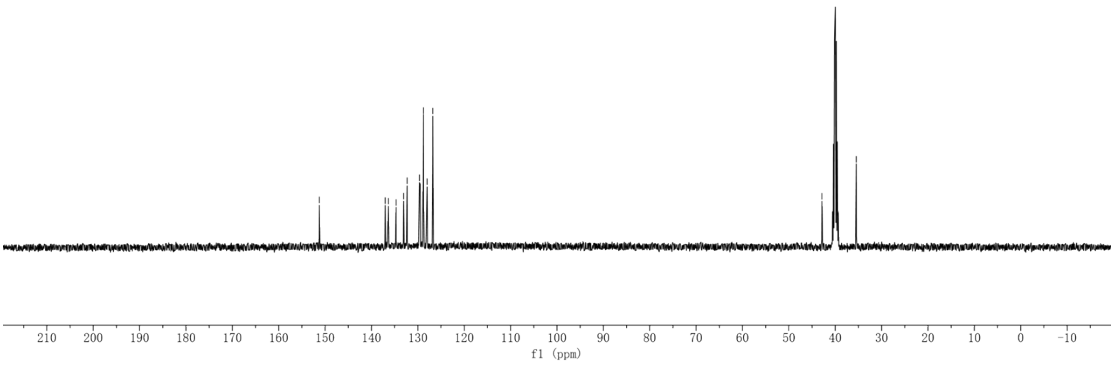
^{1}H NMR (400 MHz, DMSO-d_6)

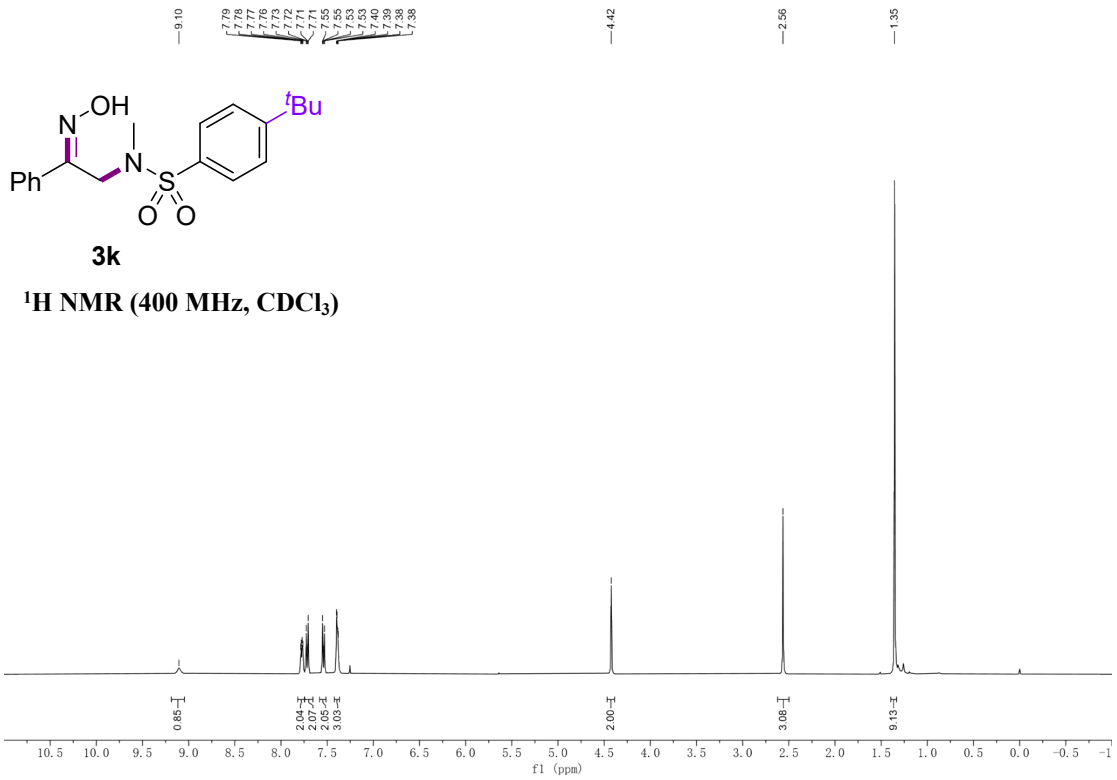




3j

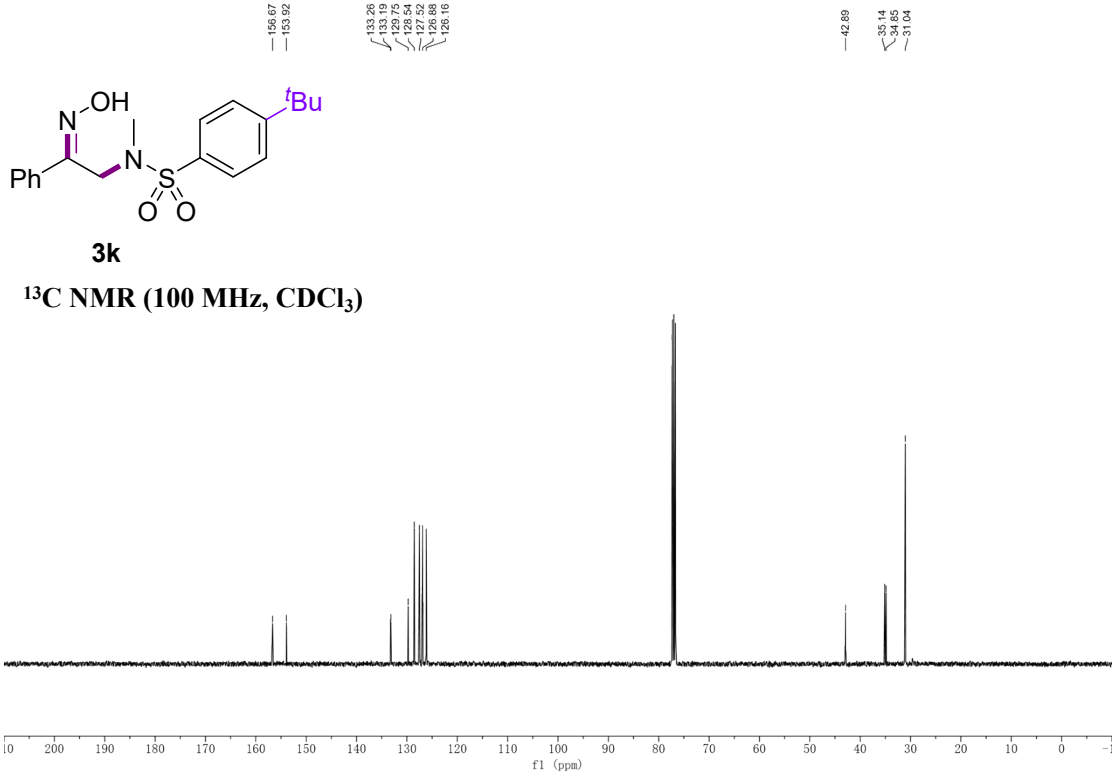
^{13}C NMR (100 MHz, DMSO-d_6)





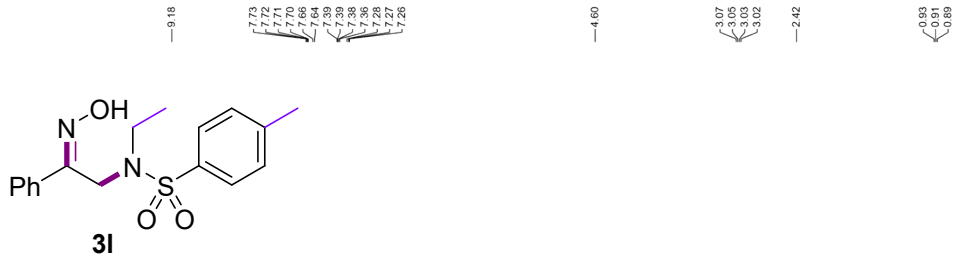
3k

^{1}H NMR (400 MHz, $CDCl_3$)



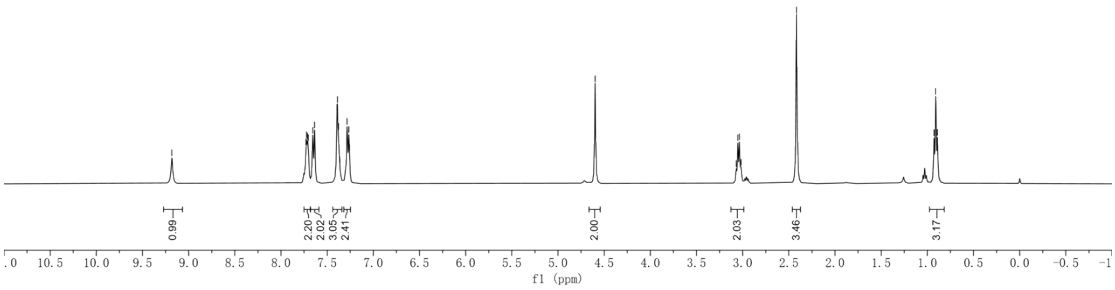
3k

^{13}C NMR (100 MHz, $CDCl_3$)



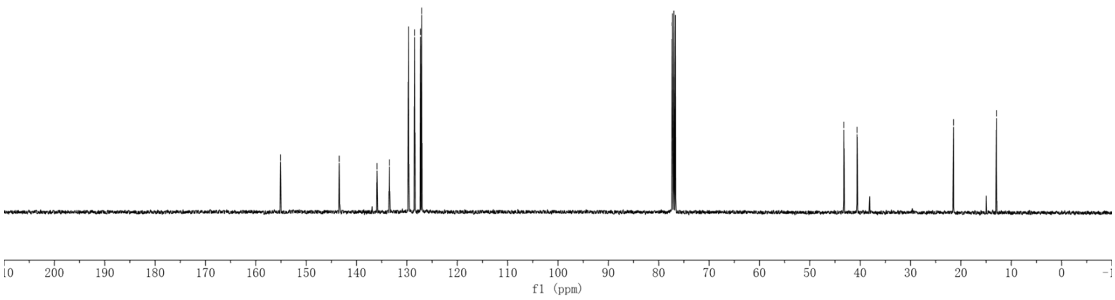
3l

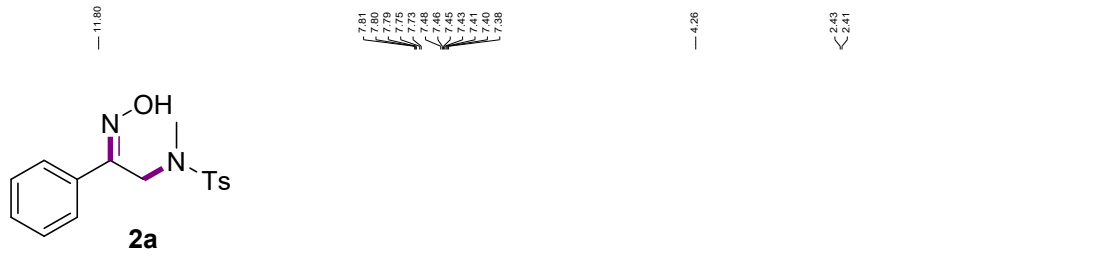
^{1}H NMR (400 MHz, $CDCl_3$)



3l

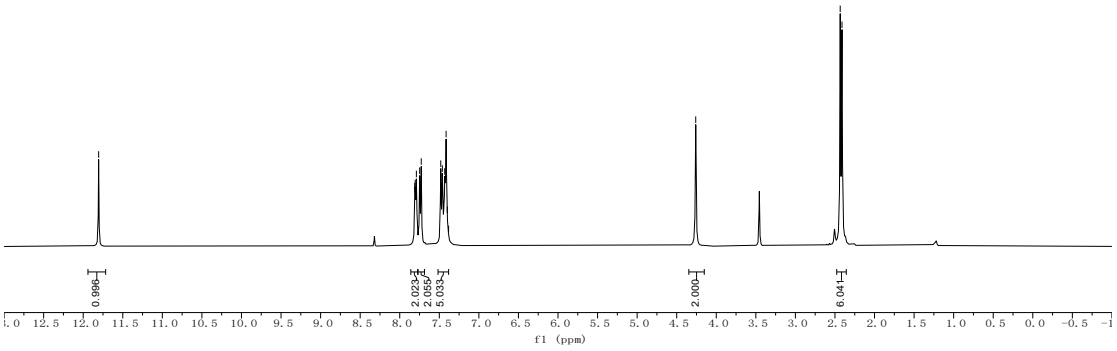
^{13}C NMR (100 MHz, $CDCl_3$)

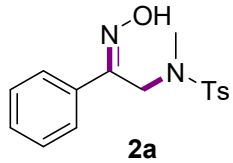




2a

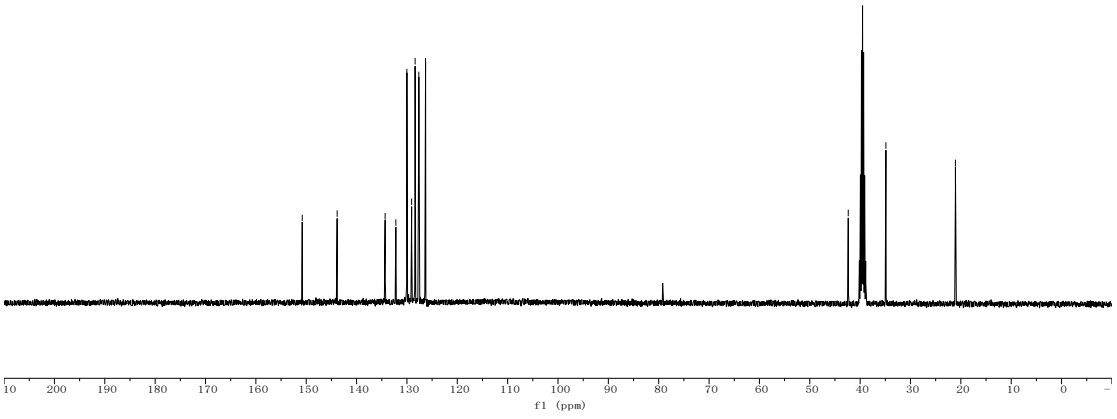
^{1}H NMR (400 MHz, DMSO-d_6)

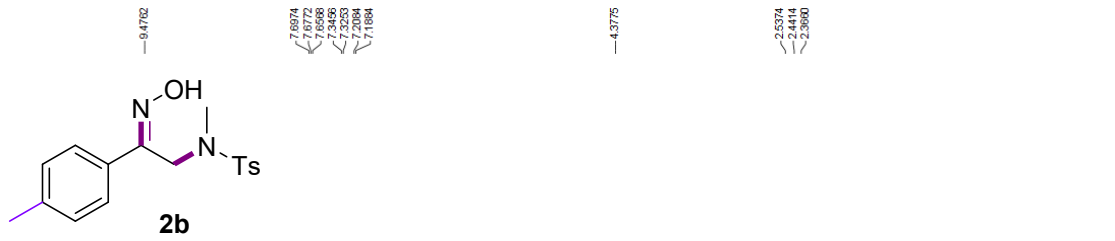




2a

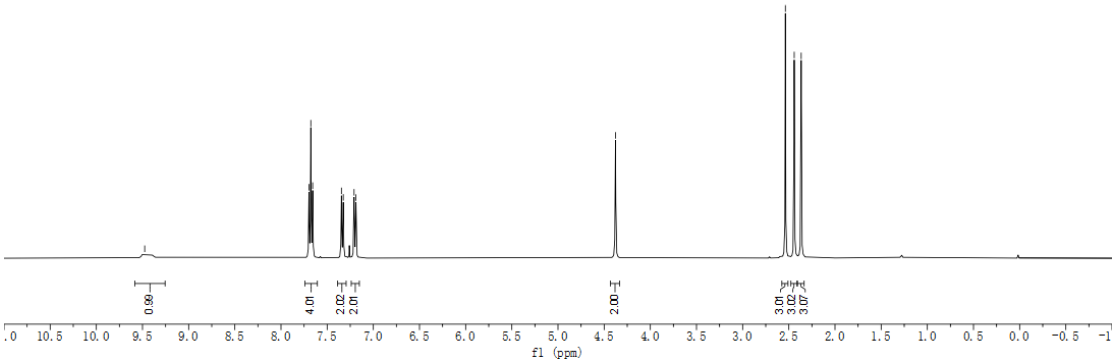
^{13}C NMR (100 MHz, DMSO-d_6)

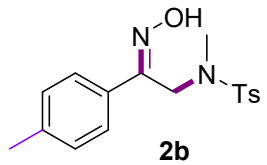




2b

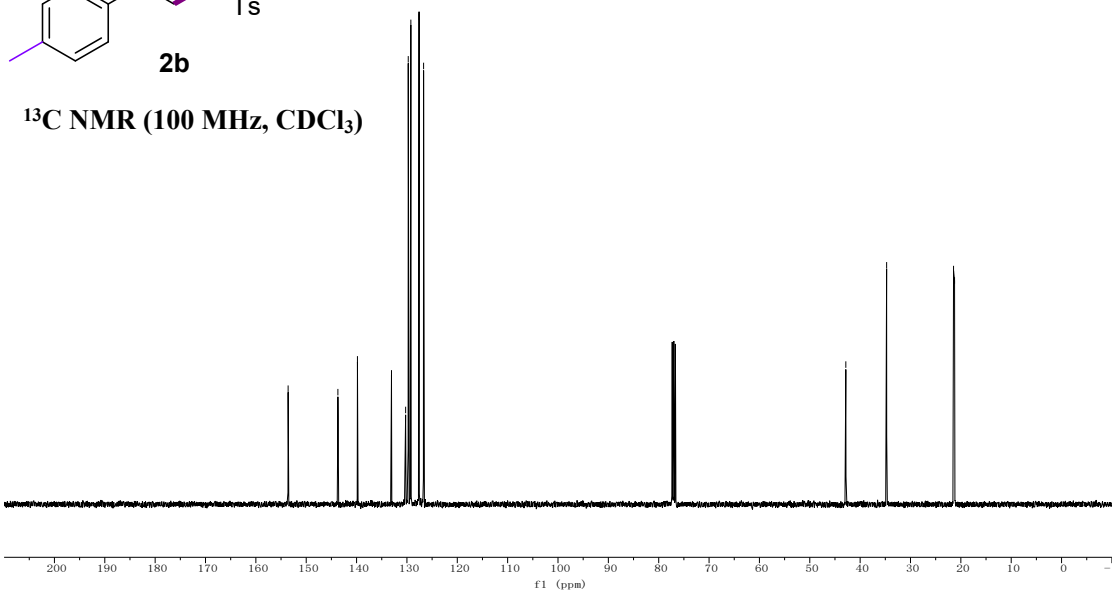
^{1}H NMR (400 MHz, $CDCl_3$)

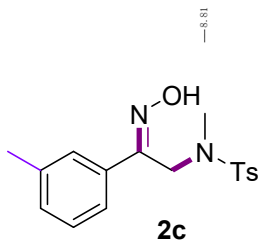




2b

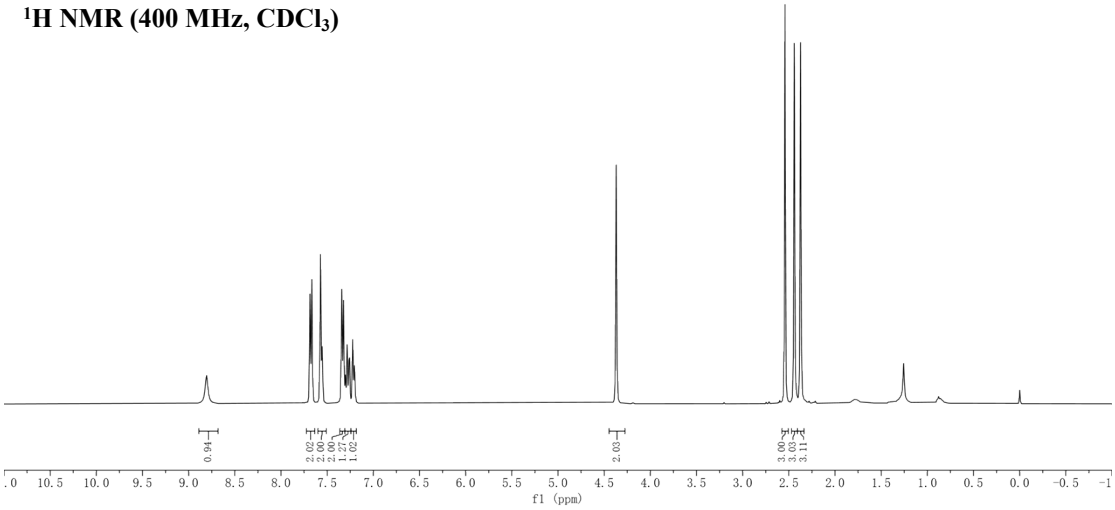
^{13}C NMR (100 MHz, $CDCl_3$)

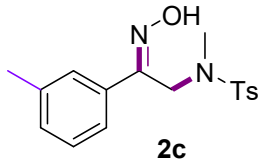




2c

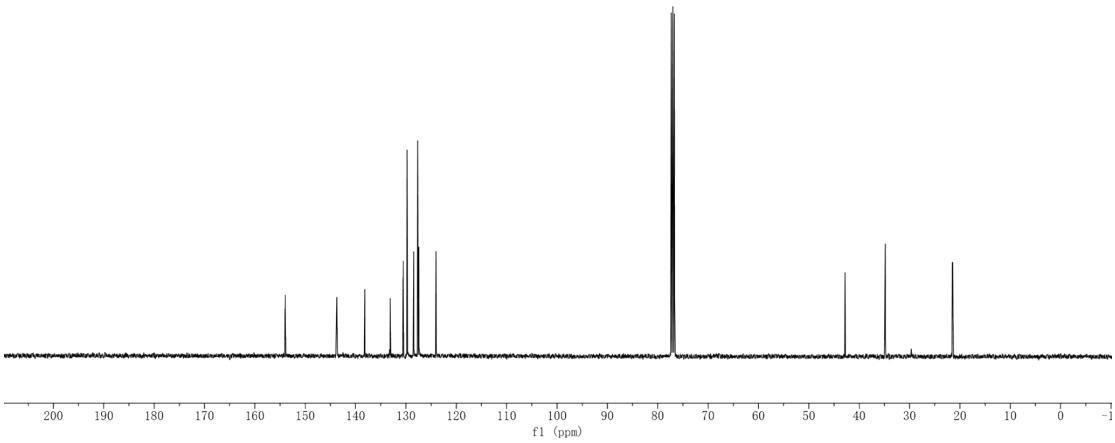
^{1}H NMR (400 MHz, $CDCl_3$)

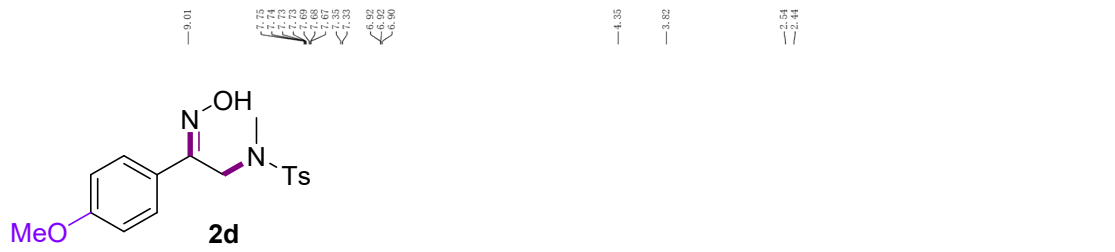




2c

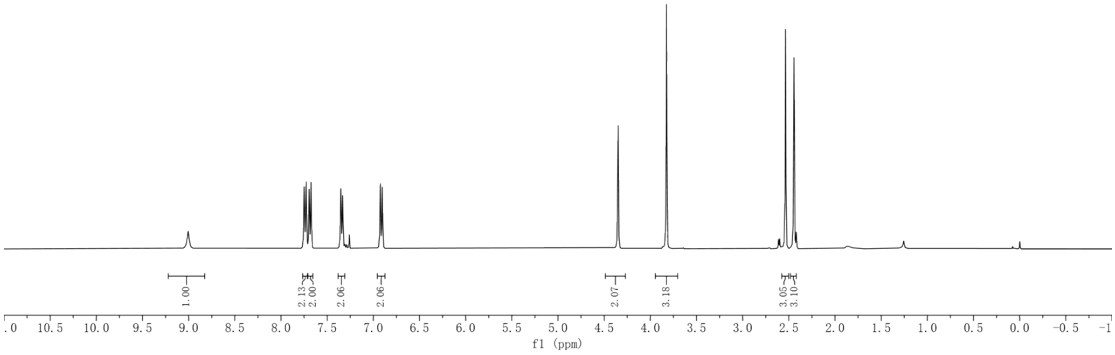
^{13}C NMR (100 MHz, $CDCl_3$)

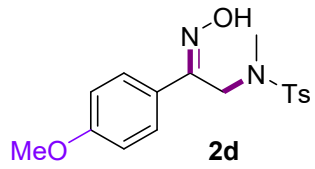




2d

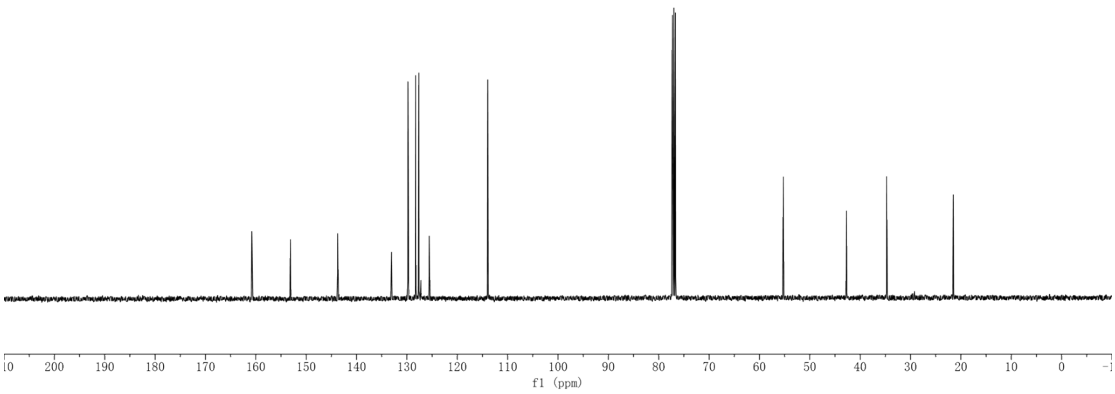
^{1}H NMR (400 MHz, $CDCl_3$)





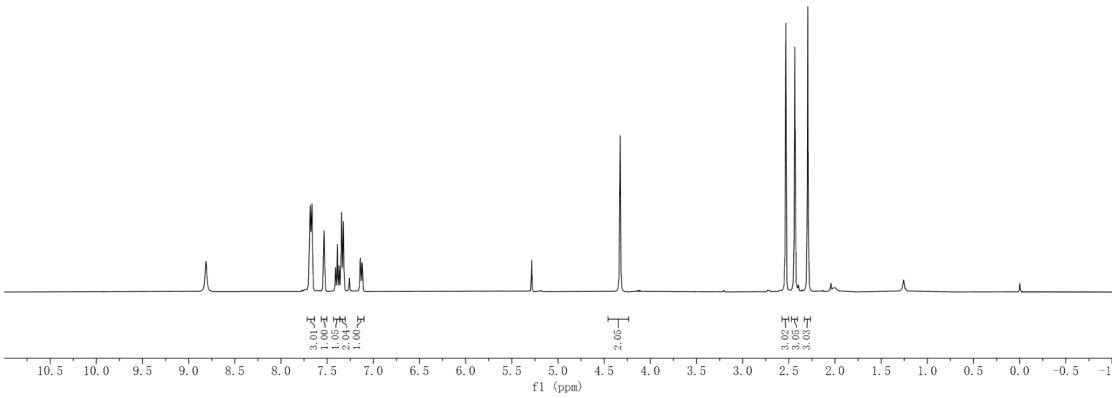
2d

^{13}C NMR (100 MHz, $CDCl_3$)



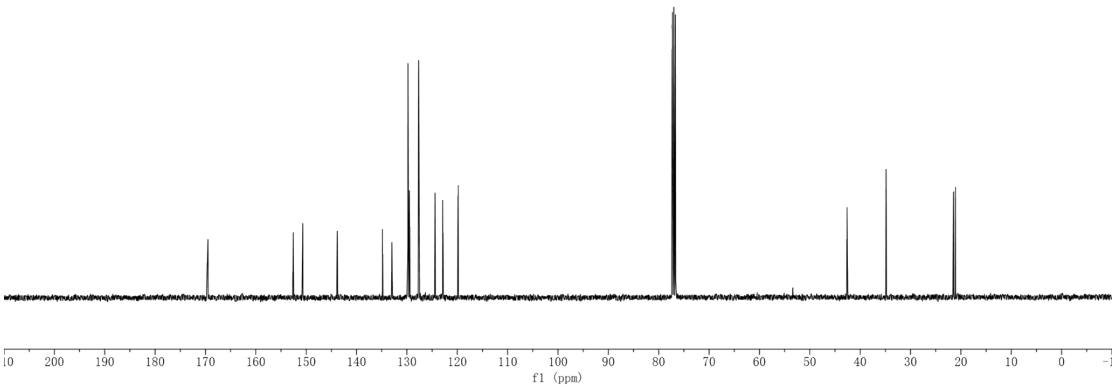
2e

^{1}H NMR (400 MHz, $CDCl_3$)



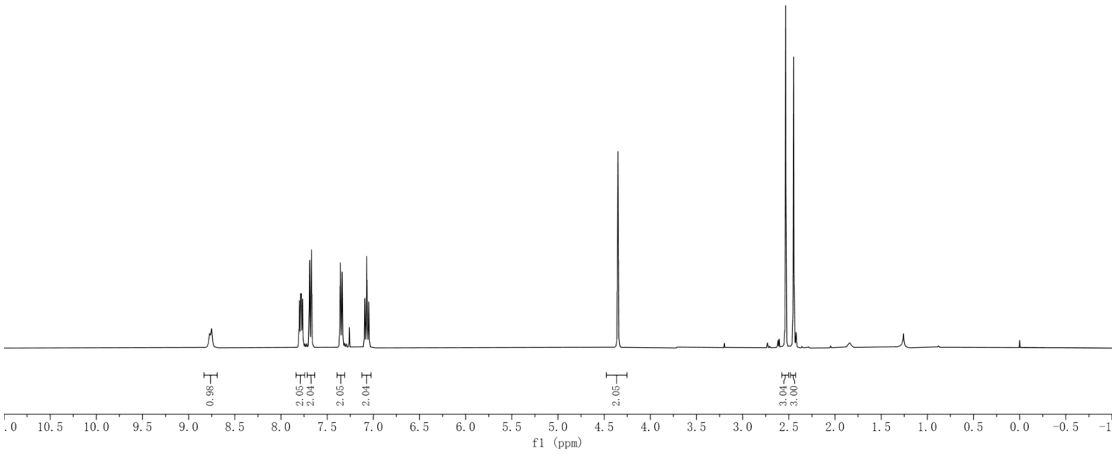
2e

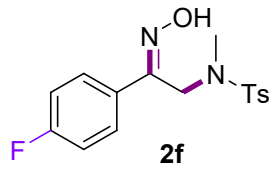
^{13}C NMR (100 MHz, $CDCl_3$)



2f

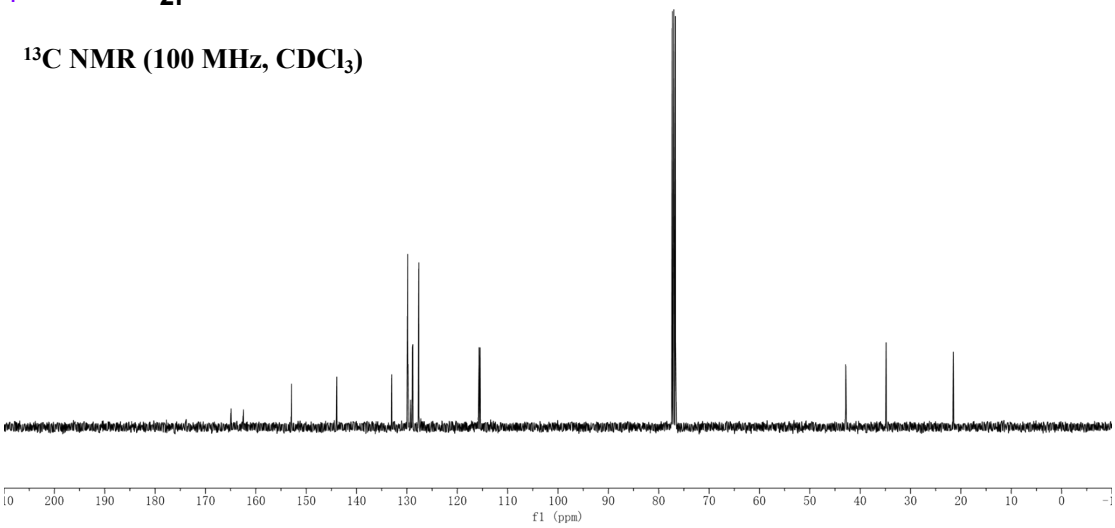
^{1}H NMR (400 MHz, $CDCl_3$)

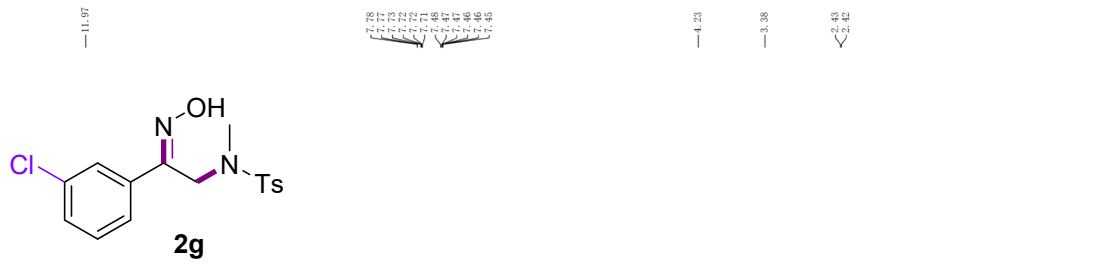




2f

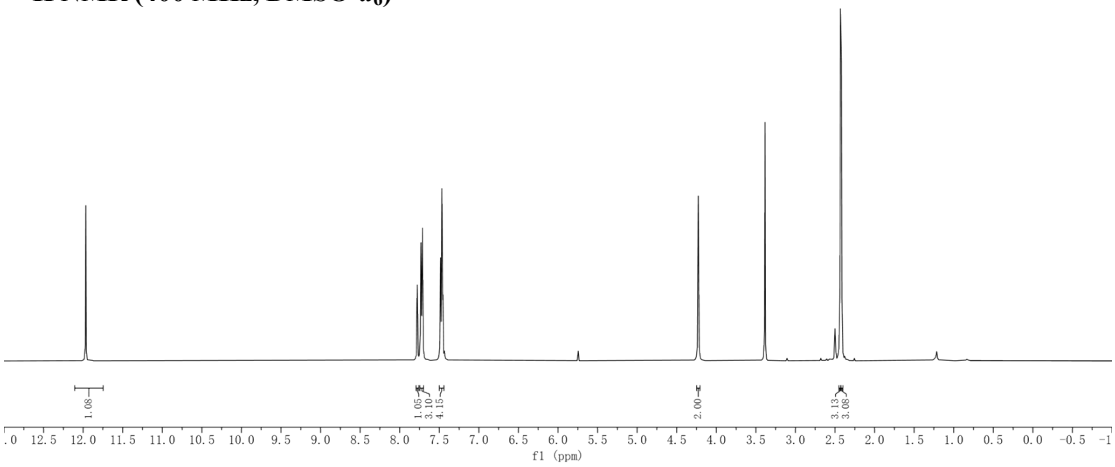
^{13}C NMR (100 MHz, $CDCl_3$)

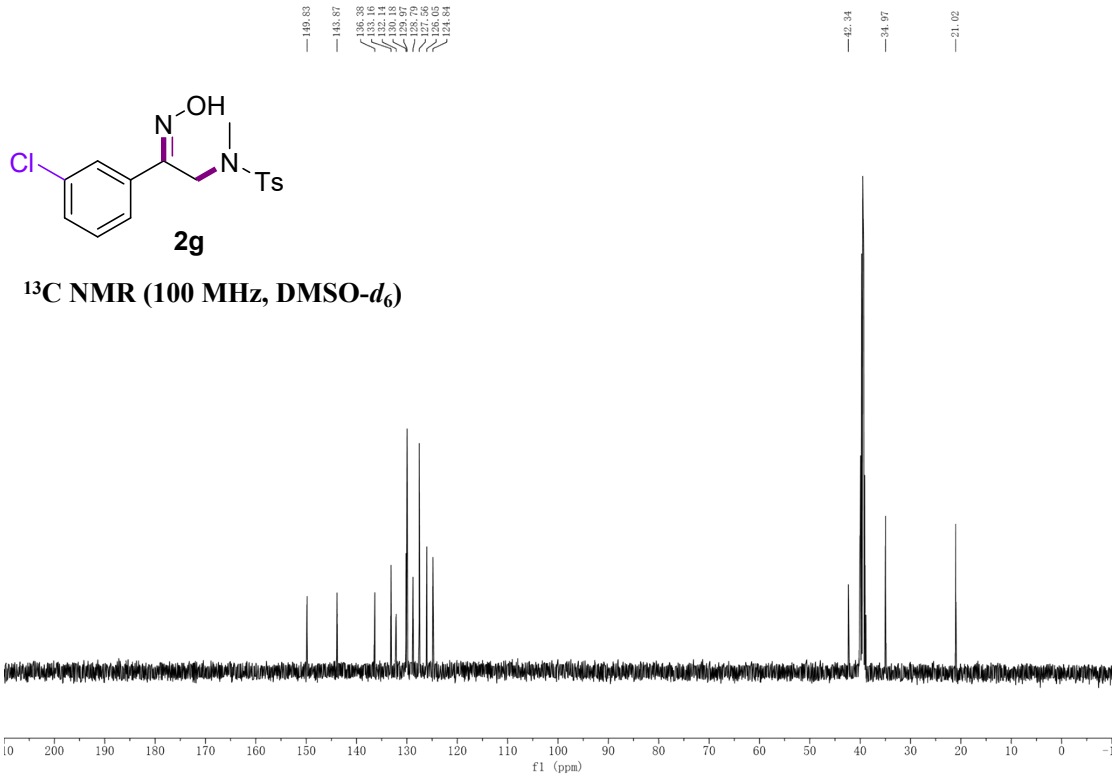




2g

^{1}H NMR (400 MHz, DMSO-d_6)



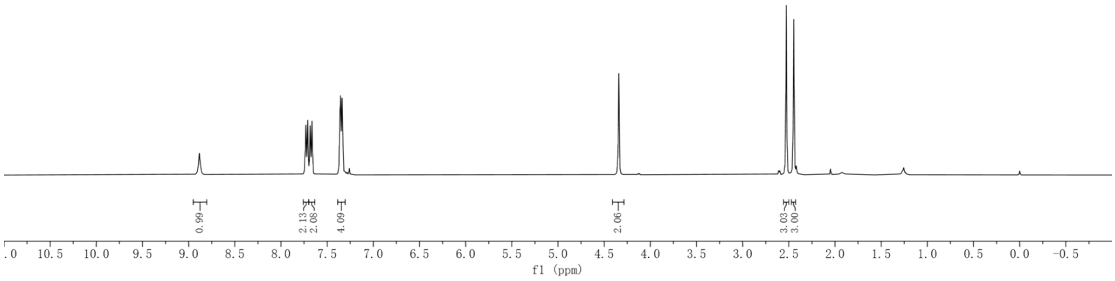


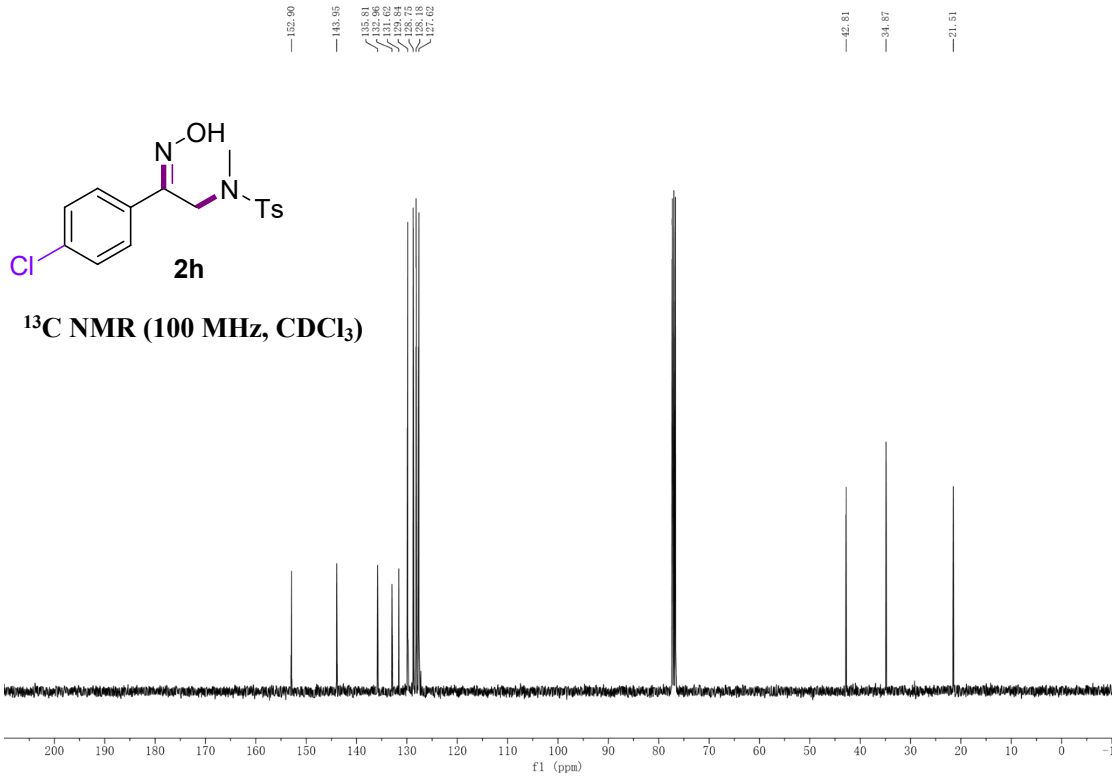
2g

^{13}C NMR (100 MHz, DMSO-d_6)

2h

^{1}H NMR (400 MHz, $CDCl_3$)



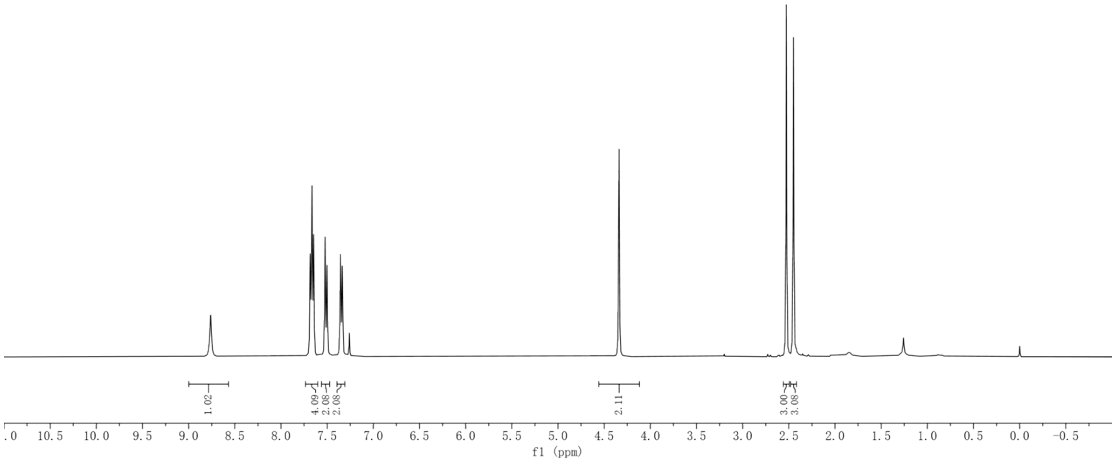


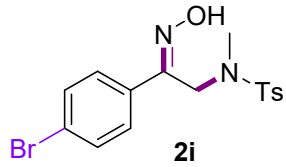
2h

^{13}C NMR (100 MHz, $CDCl_3$)

2i

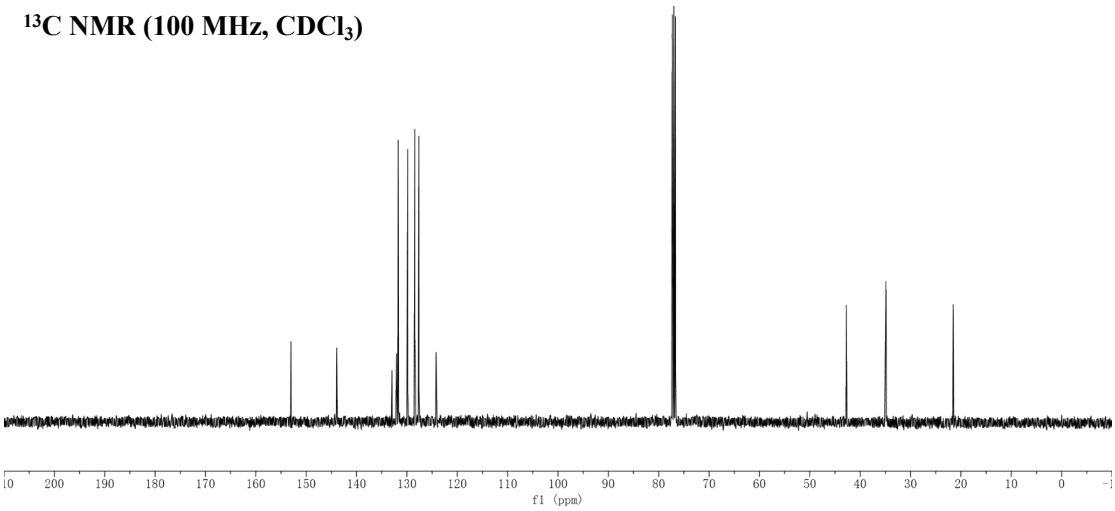
^{1}H NMR (400 MHz, $CDCl_3$)

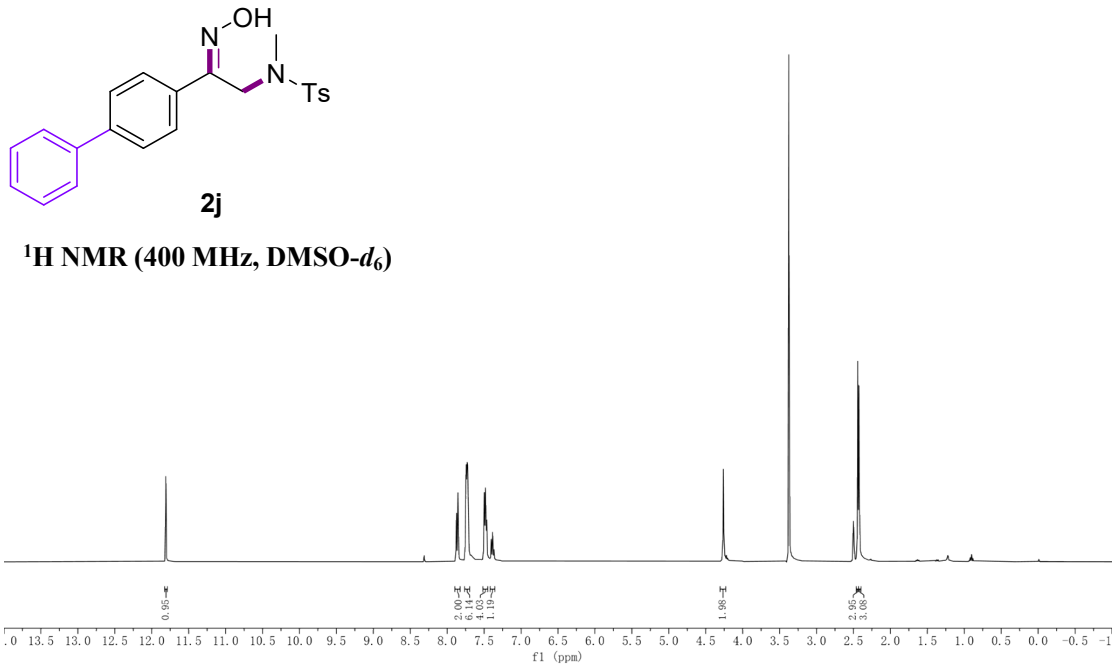




2i

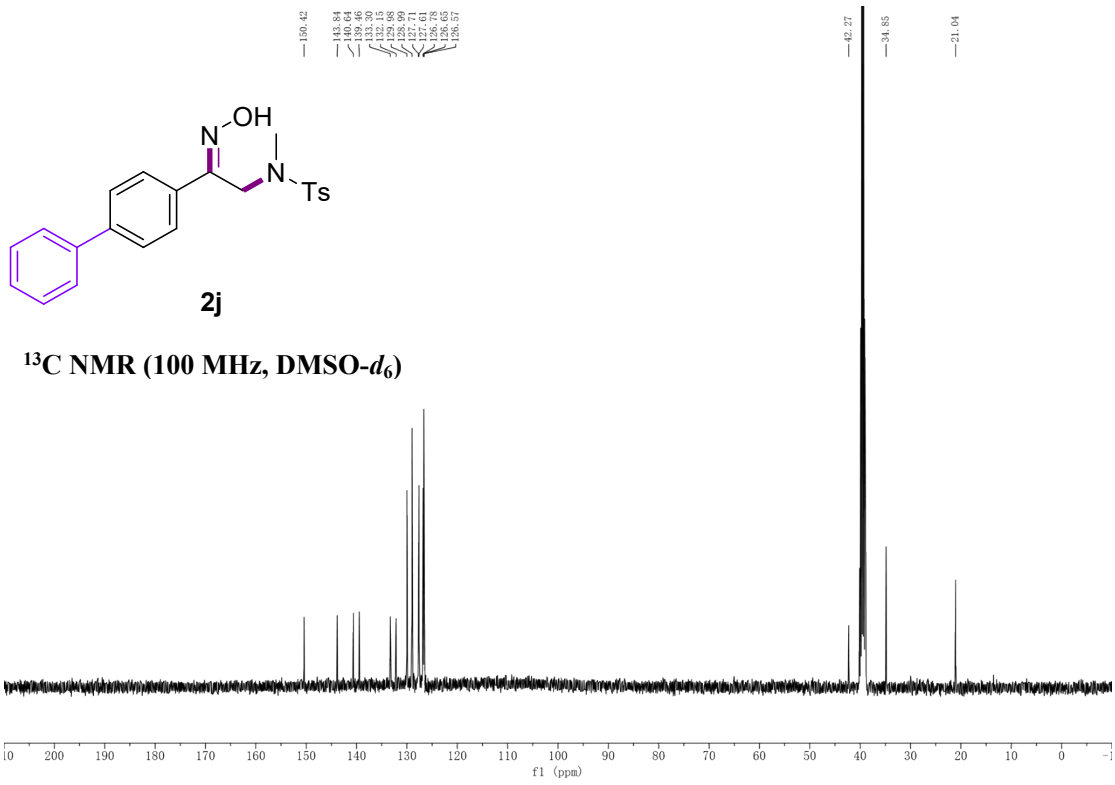
^{13}C NMR (100 MHz, $CDCl_3$)





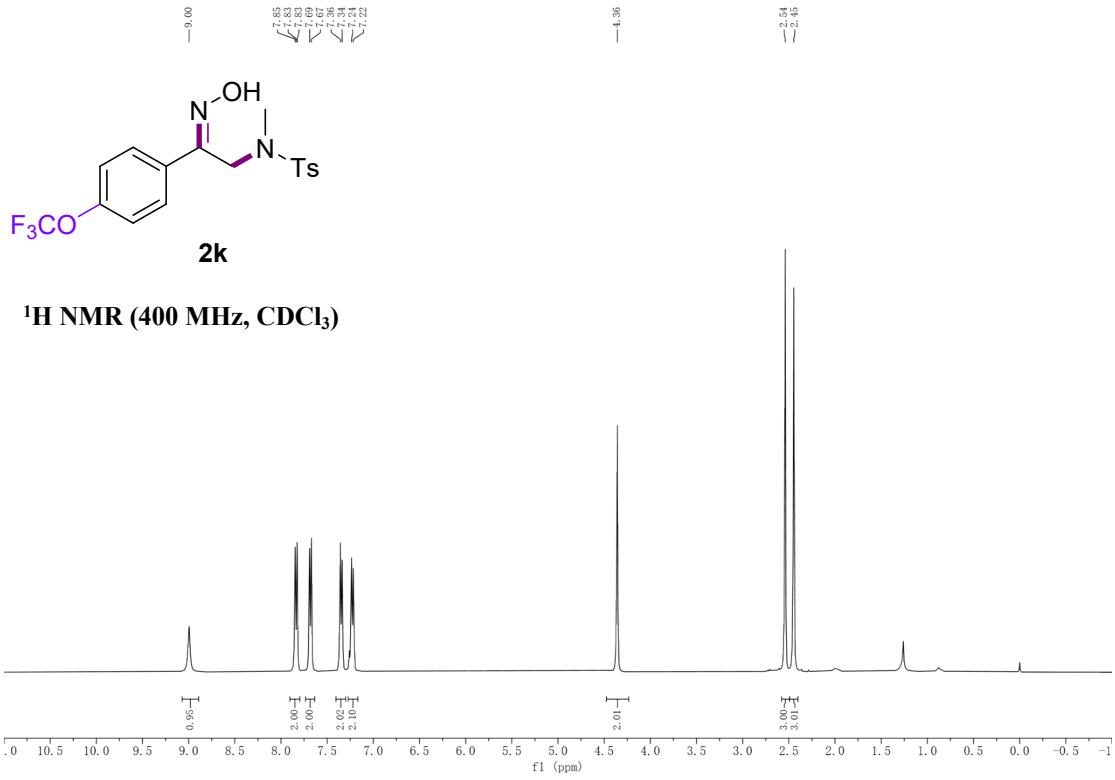
2j

^{1}H NMR (400 MHz, DMSO-d_6)



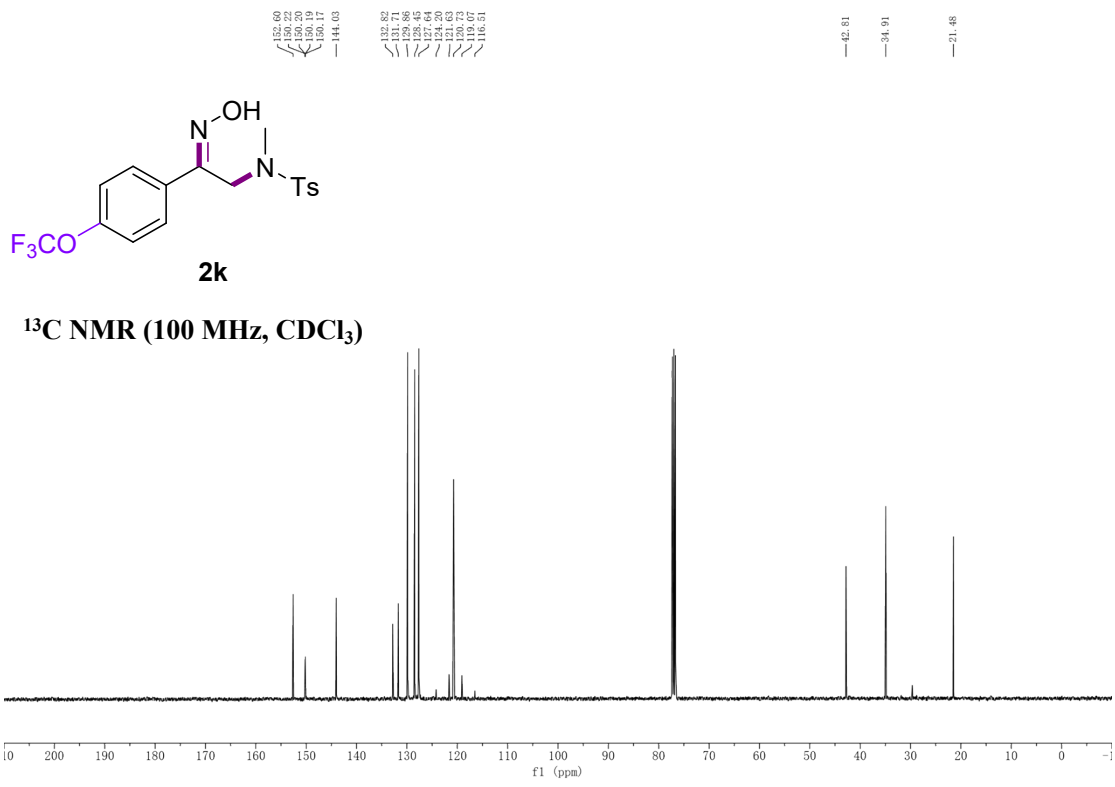
2j

^{13}C NMR (100 MHz, DMSO-d_6)



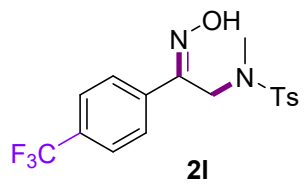
2k

^{1}H NMR (400 MHz, $CDCl_3$)



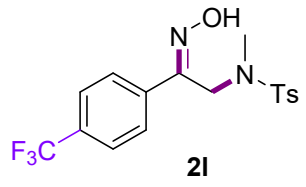
2k

^{13}C NMR (100 MHz, $CDCl_3$)



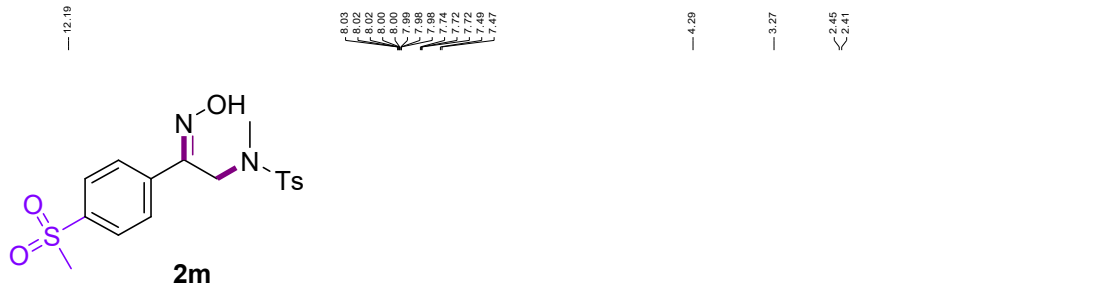
2l

^{1}H NMR (400 MHz, $CDCl_3$)



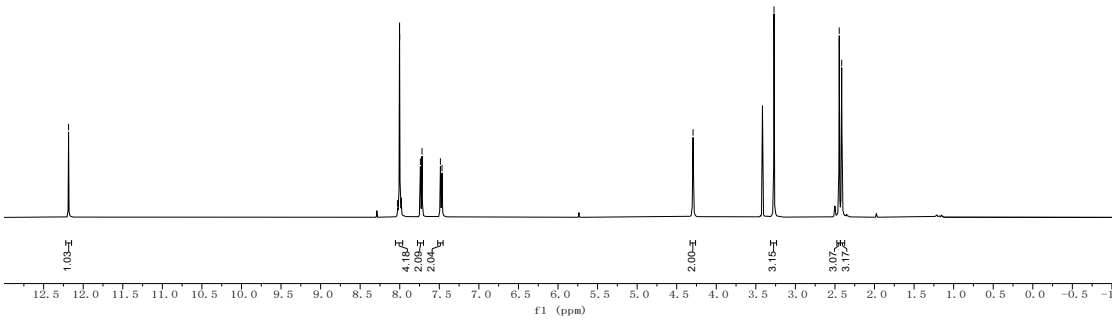
2l

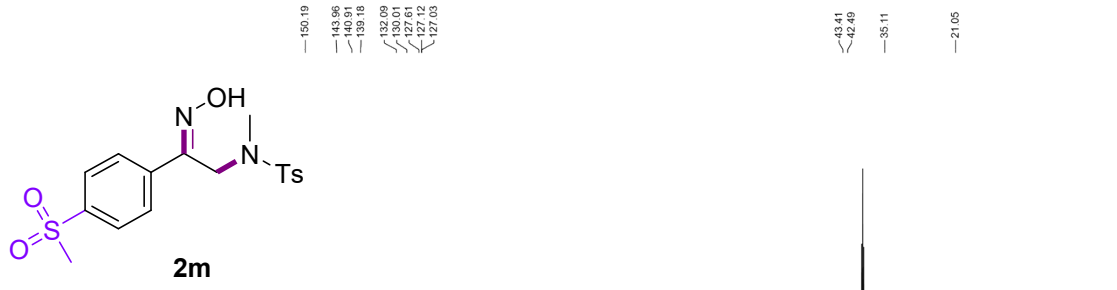
^{13}C NMR (100 MHz, $CDCl_3$)



2m

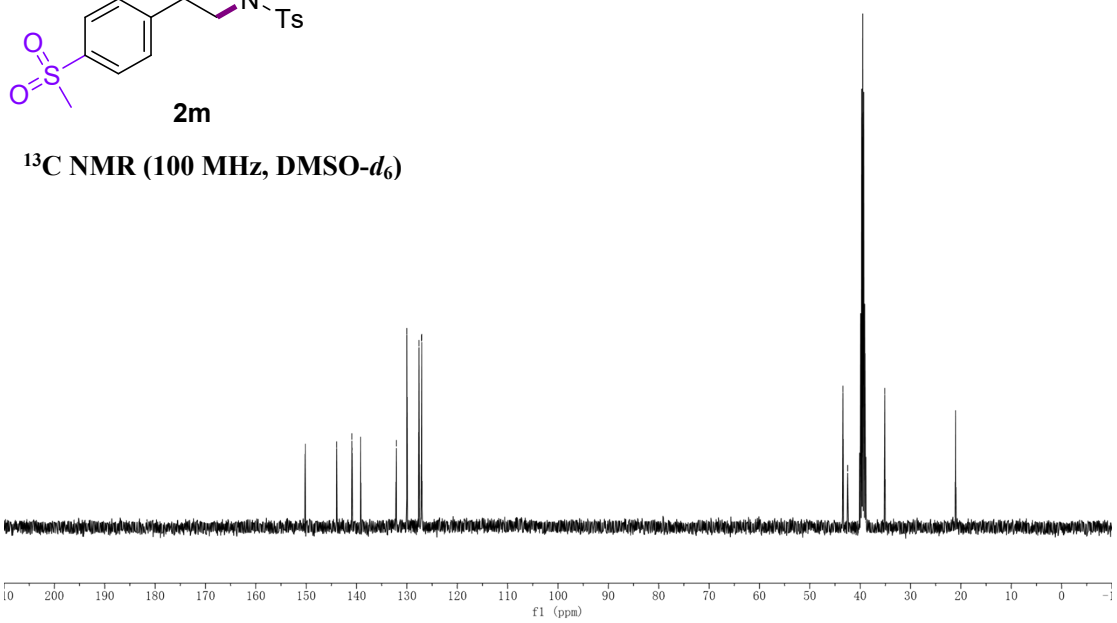
^{1}H NMR (400 MHz, DMSO-d_6)

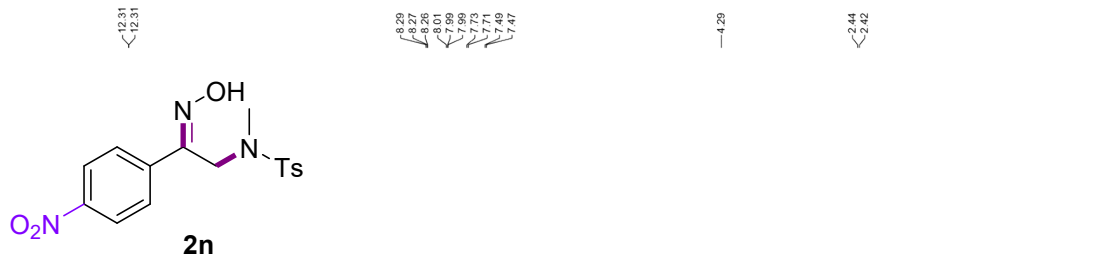




2m

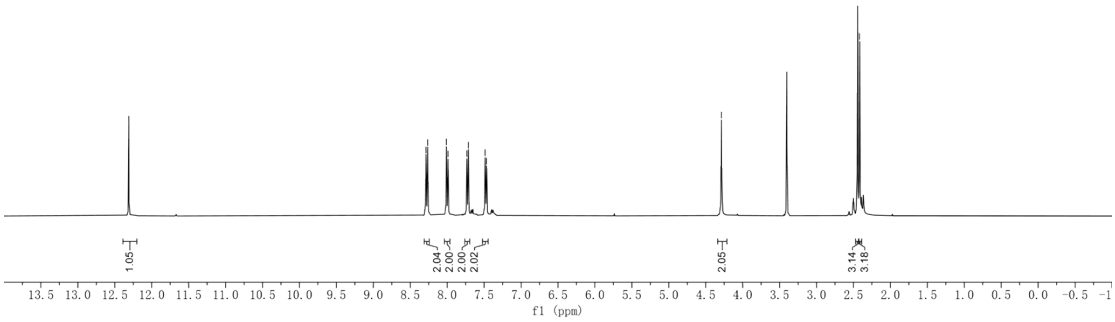
^{13}C NMR (100 MHz, DMSO-d_6)

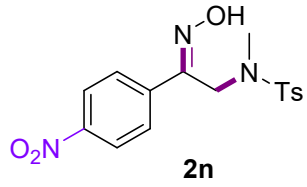




2n

^{1}H NMR (400 MHz, DMSO-d_6)

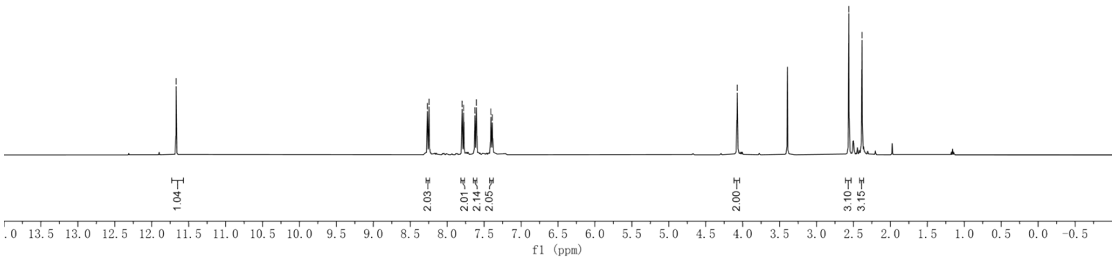


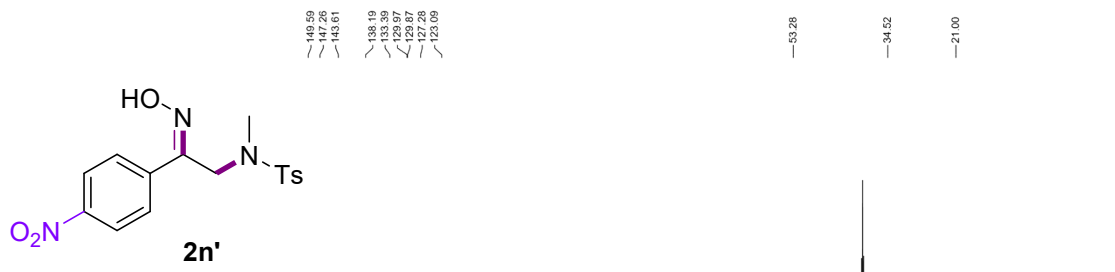


2n

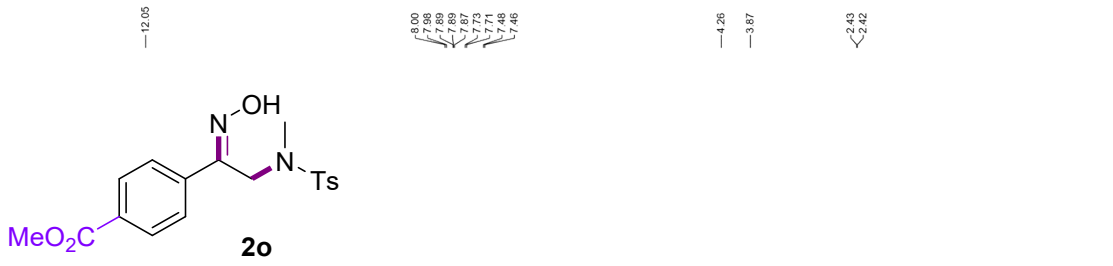
^{13}C NMR (100 MHz, DMSO-d_6)

^{1}H NMR (400 MHz, DMSO-d_6)



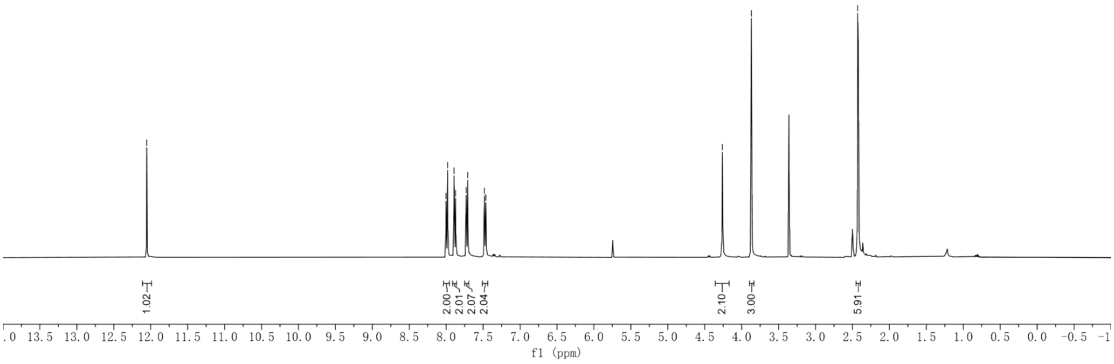


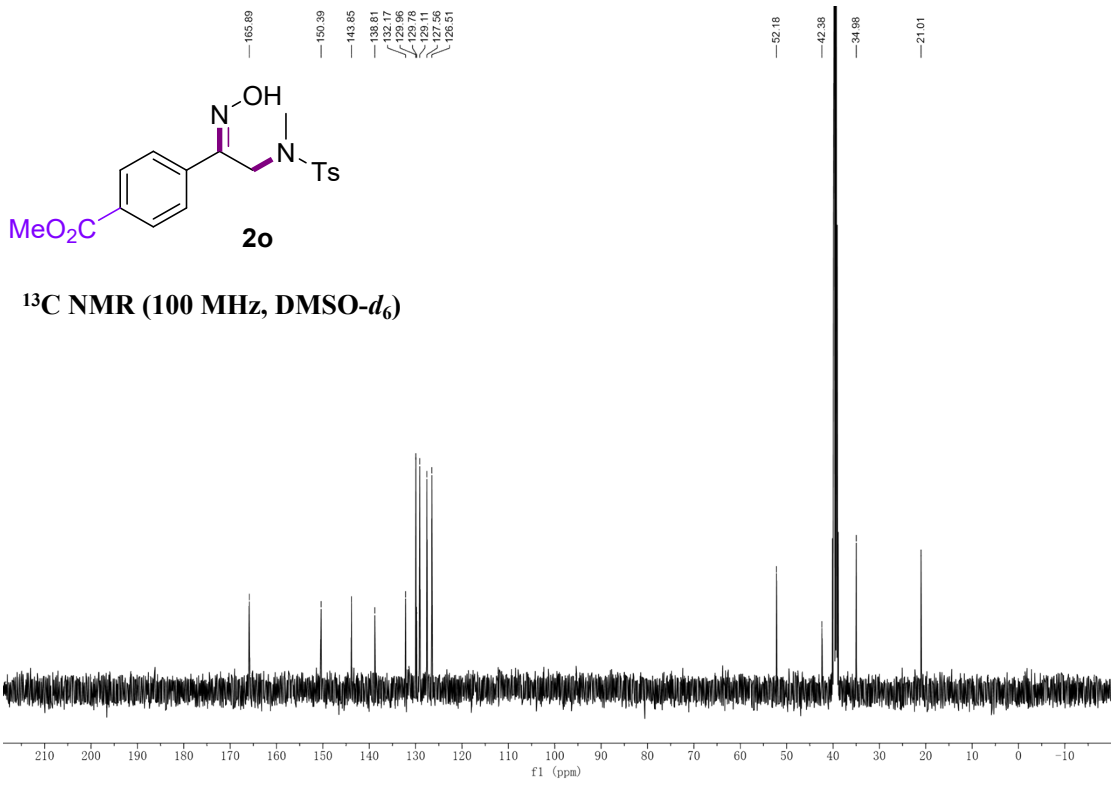
^{13}C NMR (100 MHz, DMSO-d_6)



2o

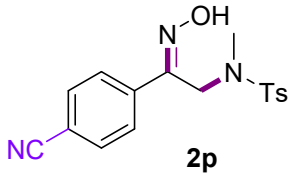
^{1}H NMR (400 MHz, DMSO-d_6)





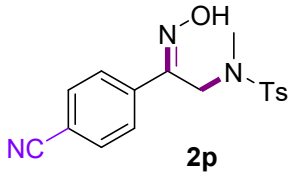
2o

^{13}C NMR (100 MHz, DMSO-d_6)



2p

^{1}H NMR (400 MHz, DMSO-d_6)

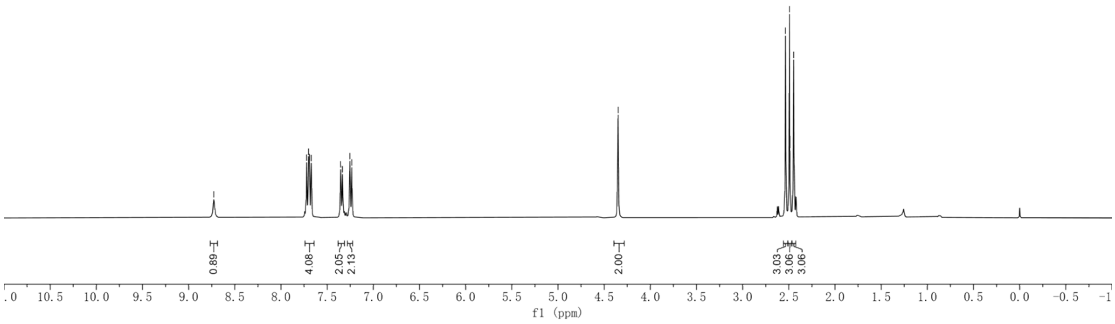


2p

^{13}C NMR (100 MHz, DMSO-d_6)

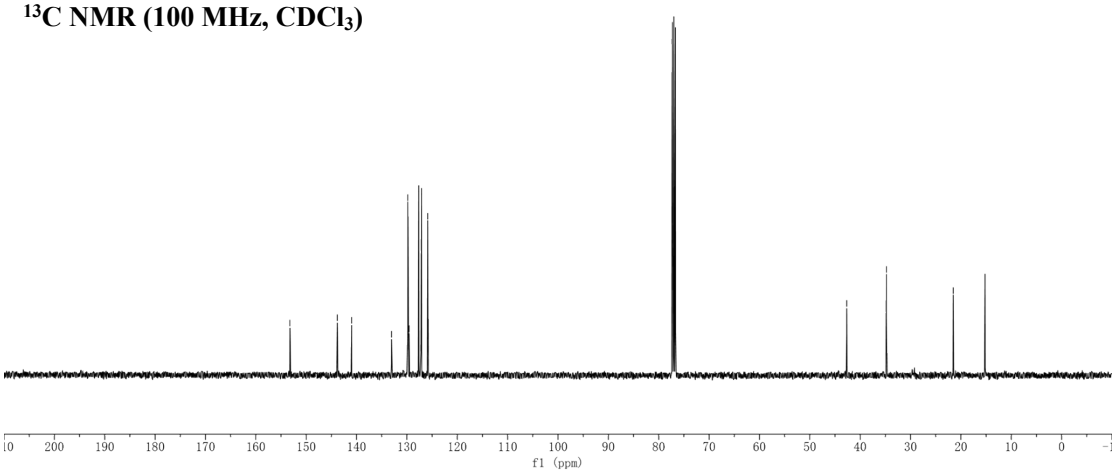
2q

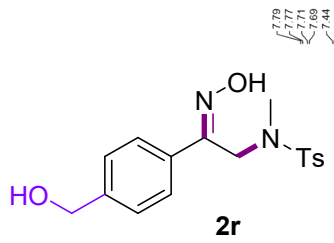
^{1}H NMR (400 MHz, $CDCl_3$)



2q

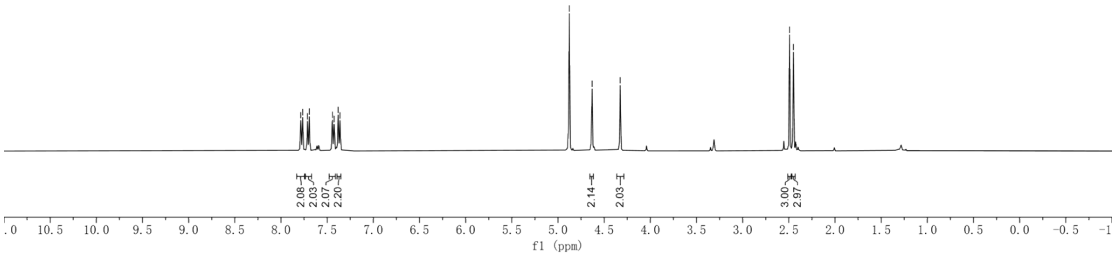
^{13}C NMR (100 MHz, $CDCl_3$)





2r

^{1}H NMR (400 MHz, Methanol-d_4)

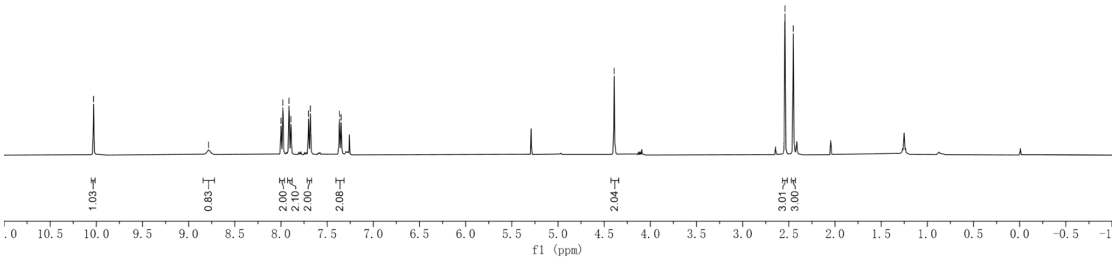


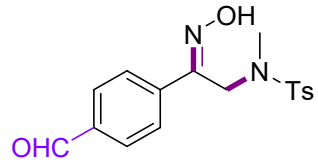
2r

^{13}C NMR (100 MHz, Methanol-d_4)

2s

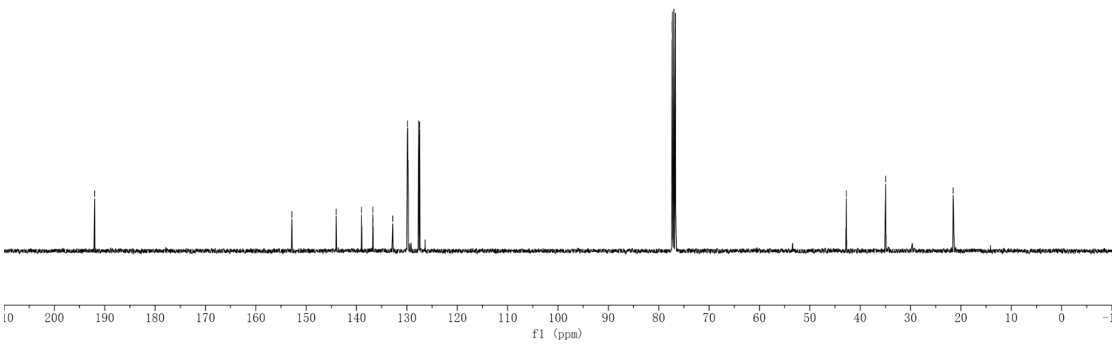
^{1}H NMR (400 MHz, $CDCl_3$)

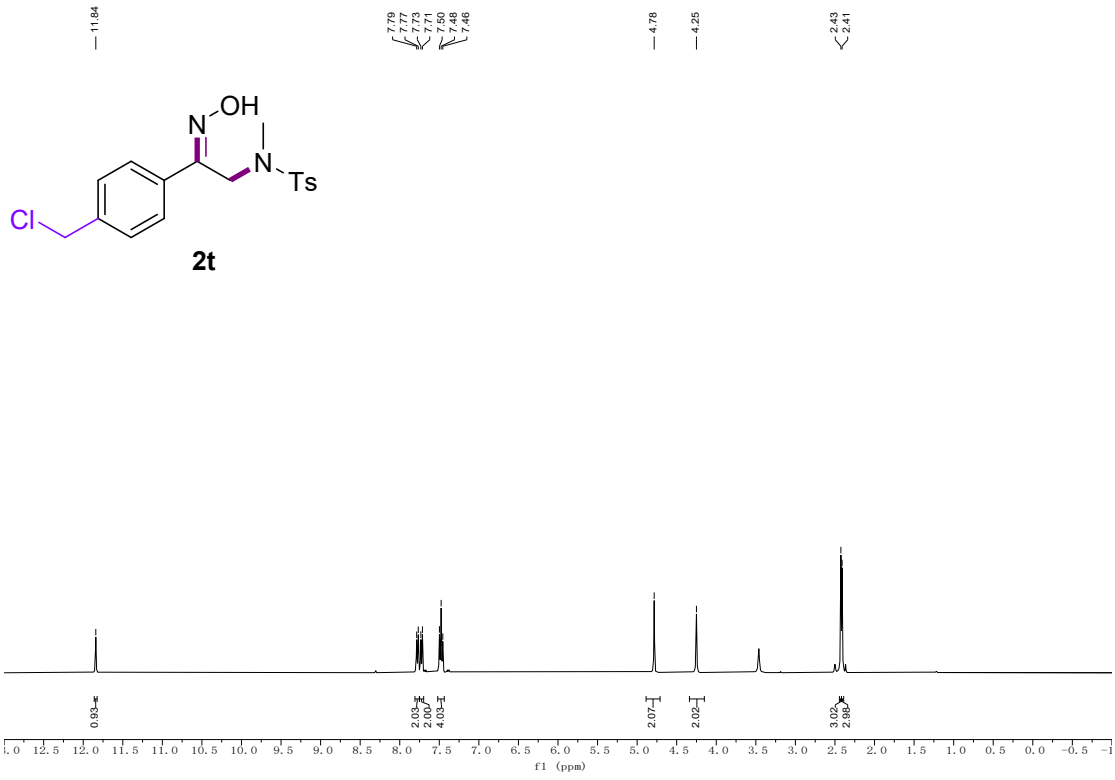




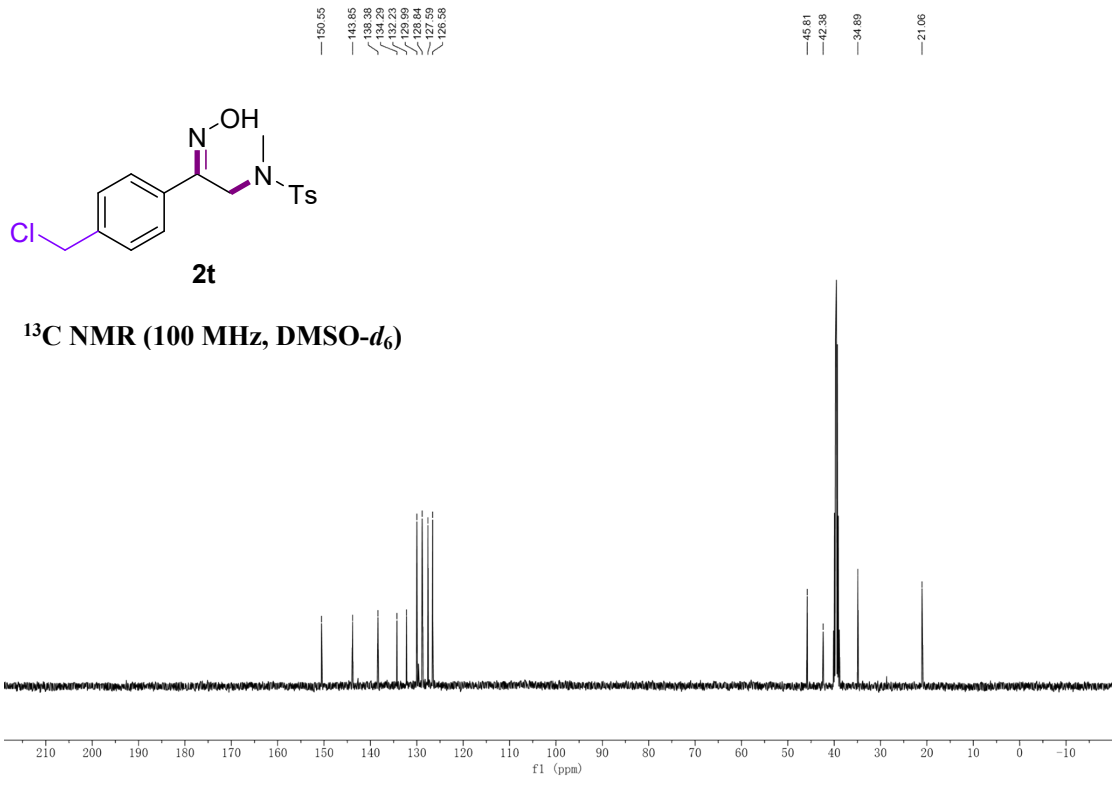
2s

^{13}C NMR (100 MHz, $CDCl_3$)



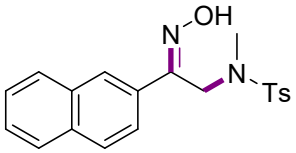


2t



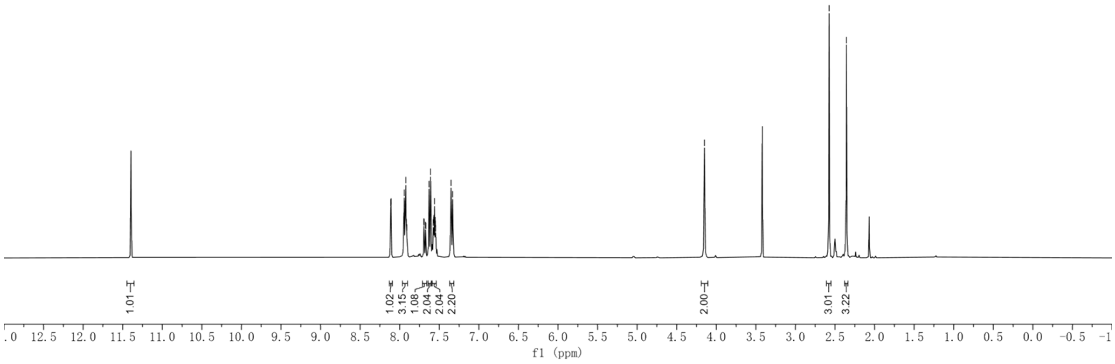
2t

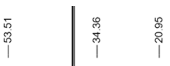
^{13}C NMR (100 MHz, DMSO-d_6)

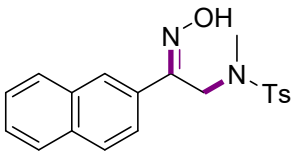


2u

^{1}H NMR (400 MHz, DMSO-d_6)

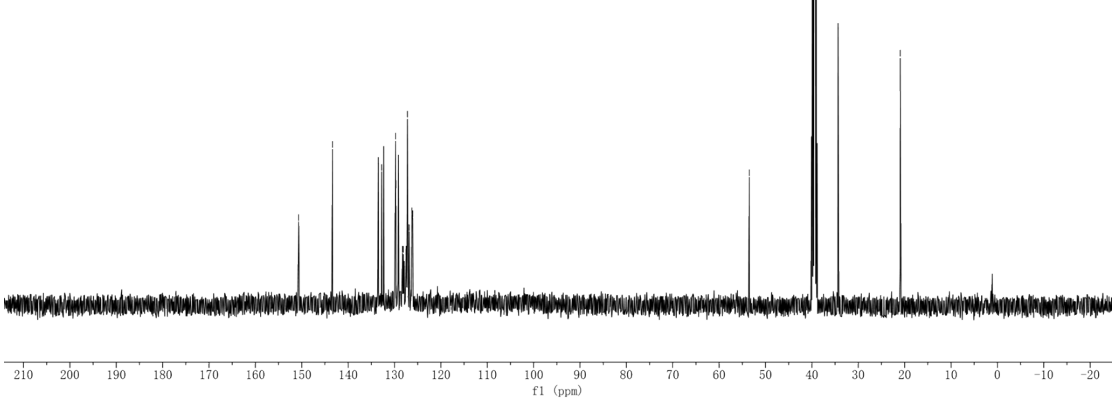






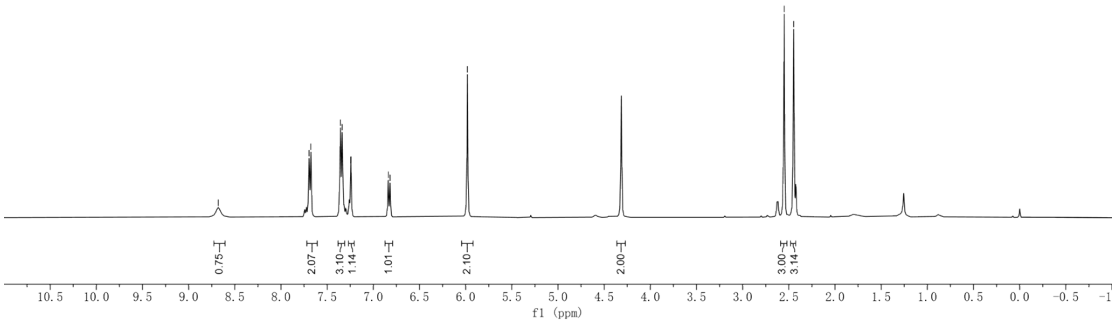
2u

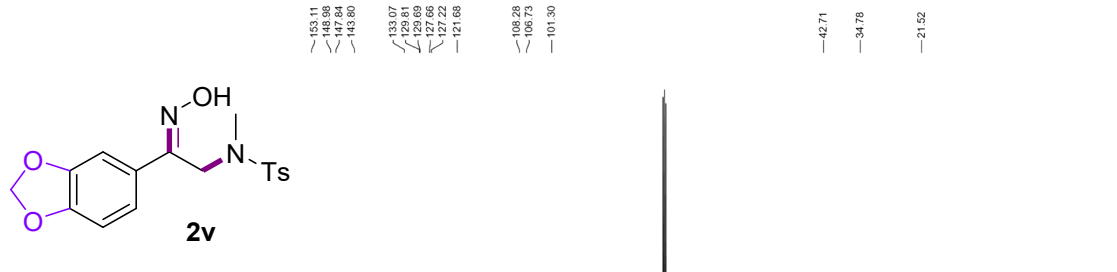
^{13}C NMR (100 MHz, DMSO-d_6)



2v

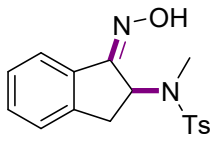
^{1}H NMR (400 MHz, $CDCl_3$)





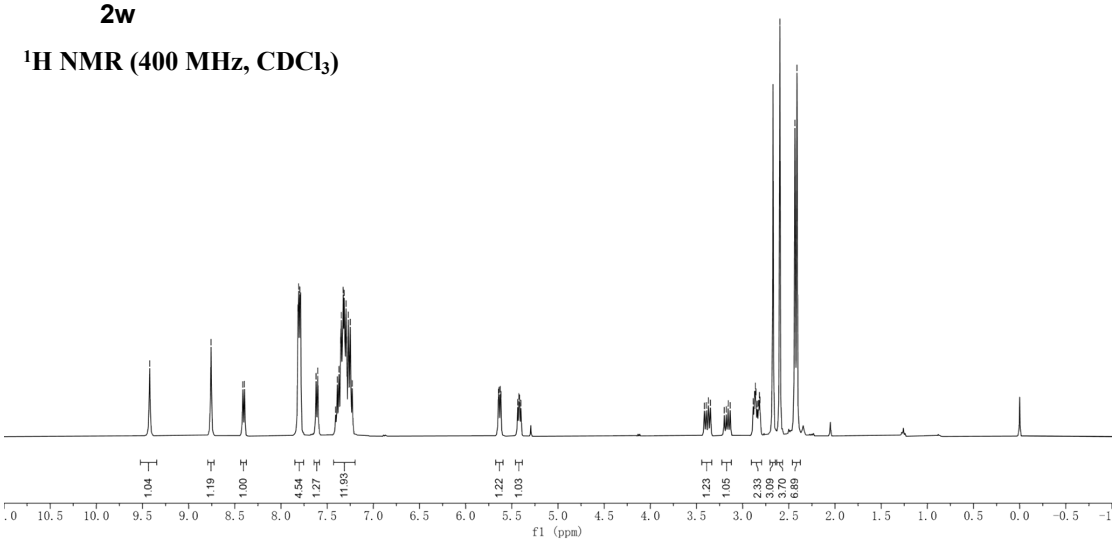
2v

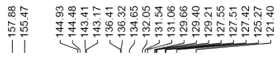
^{13}C NMR (100 MHz, $CDCl_3$)

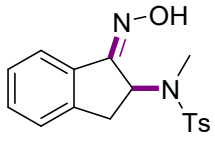


2w

^{1}H NMR (400 MHz, $CDCl_3$)





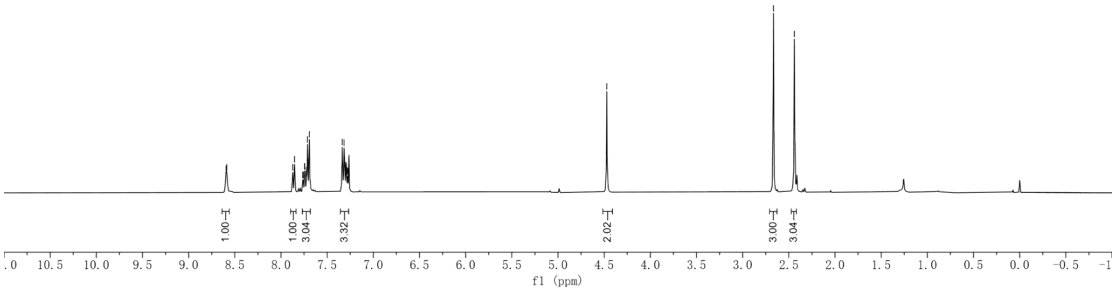


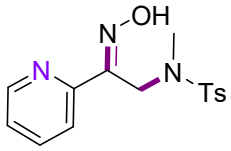
2w

^{13}C NMR (100 MHz, $CDCl_3$)

2x

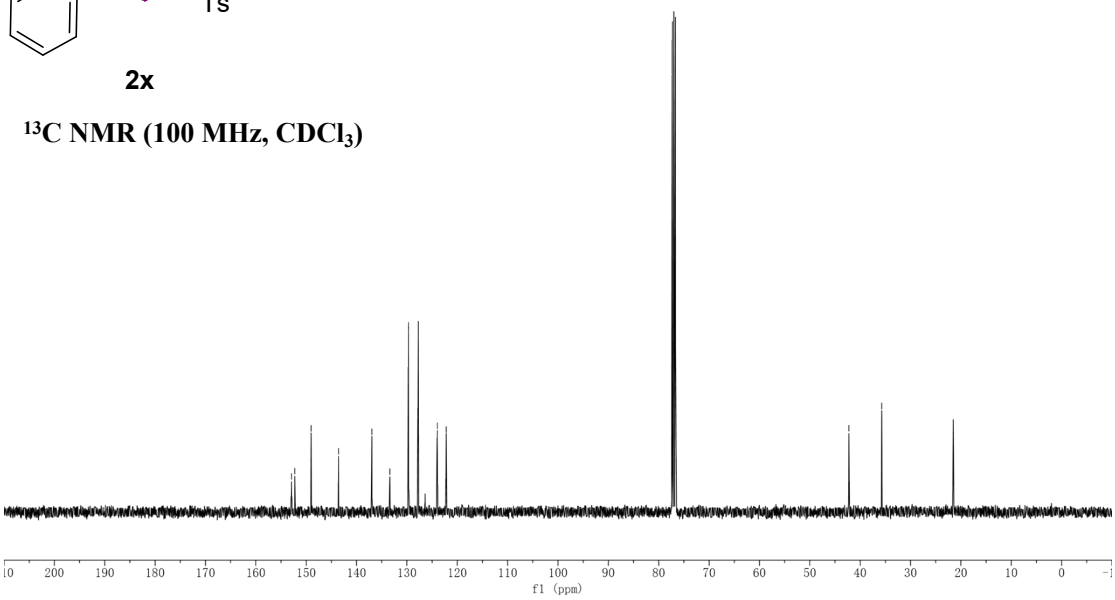
^{1}H NMR (400 MHz, $CDCl_3$)

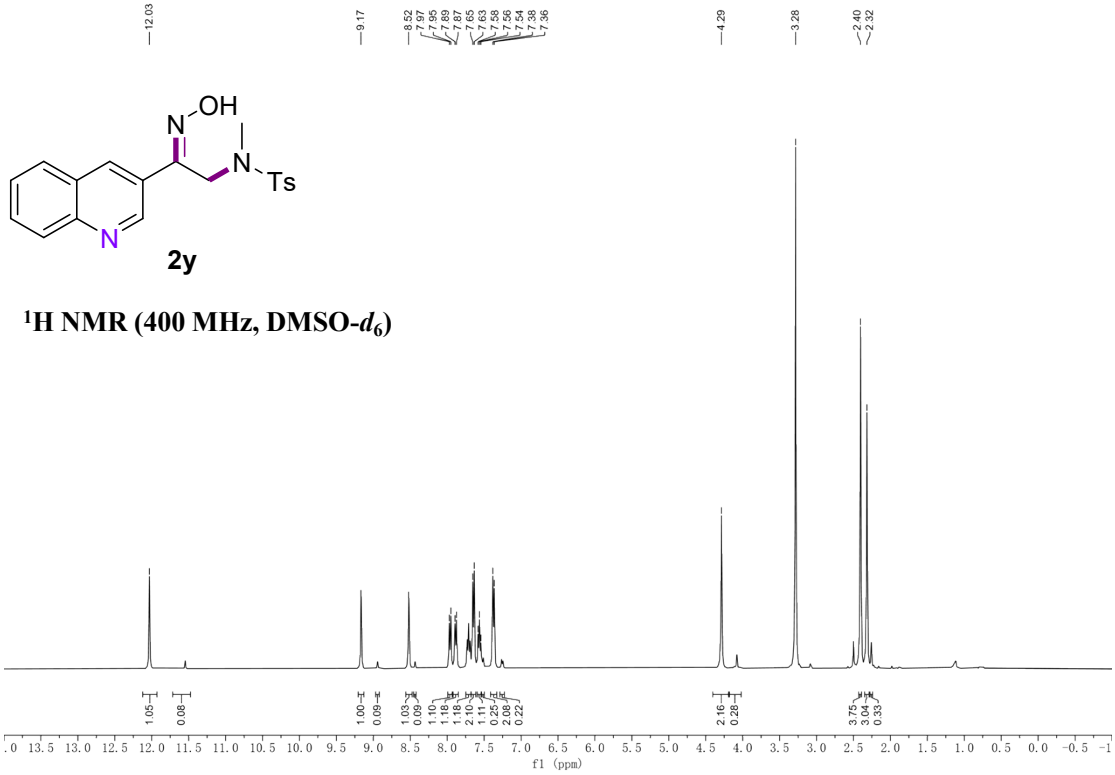




2x

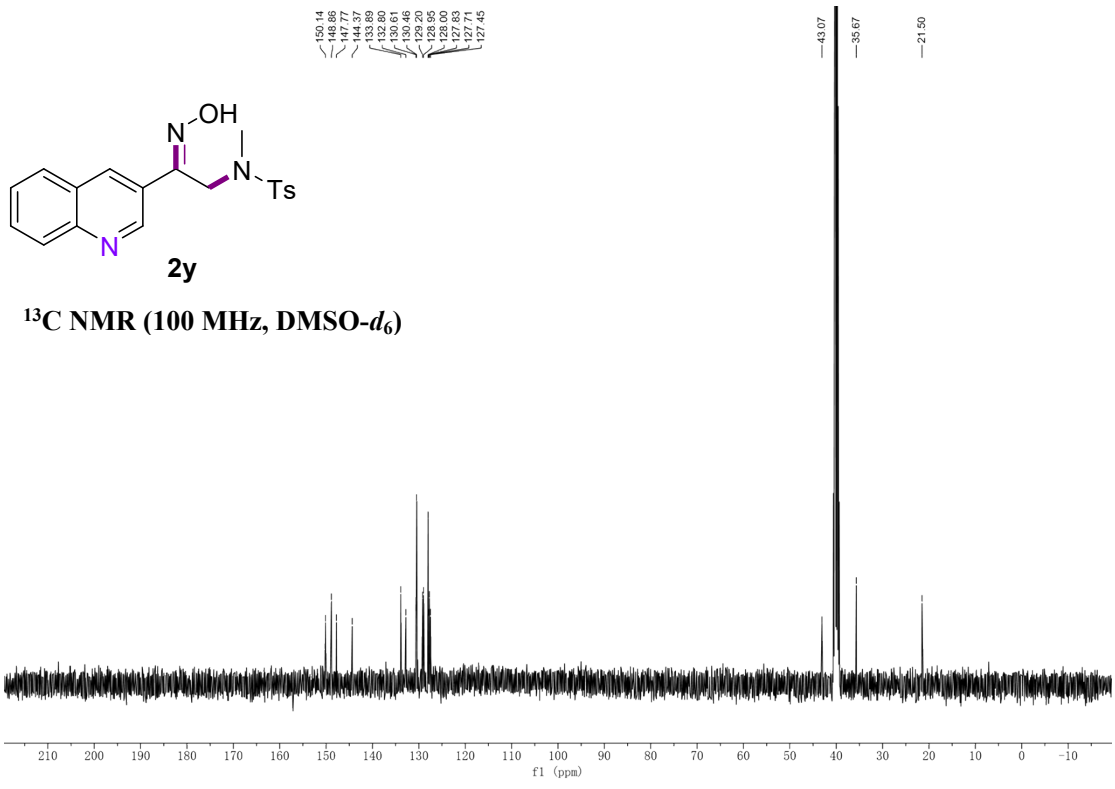
^{13}C NMR (100 MHz, $CDCl_3$)





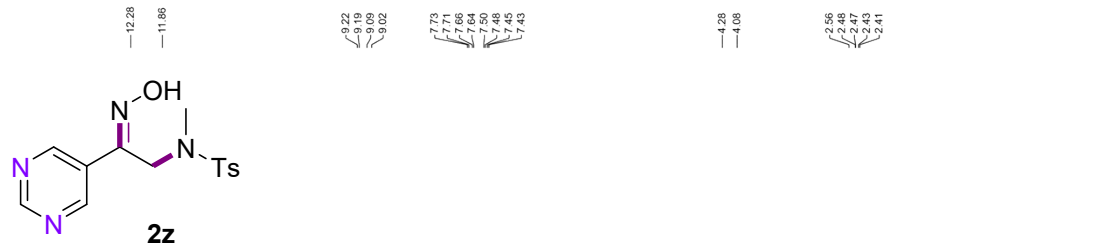
2y

^{1}H NMR (400 MHz, DMSO-d_6)



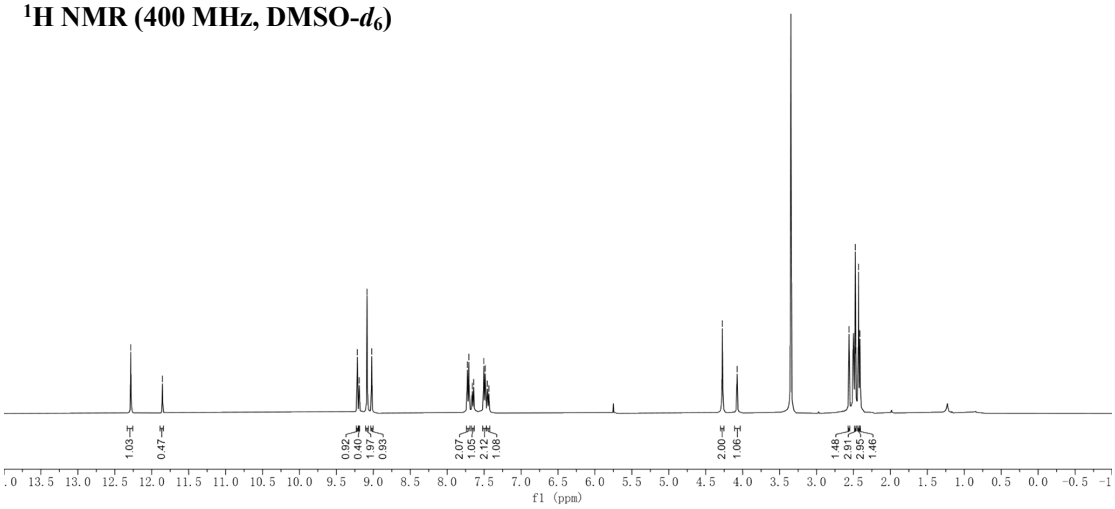
2y

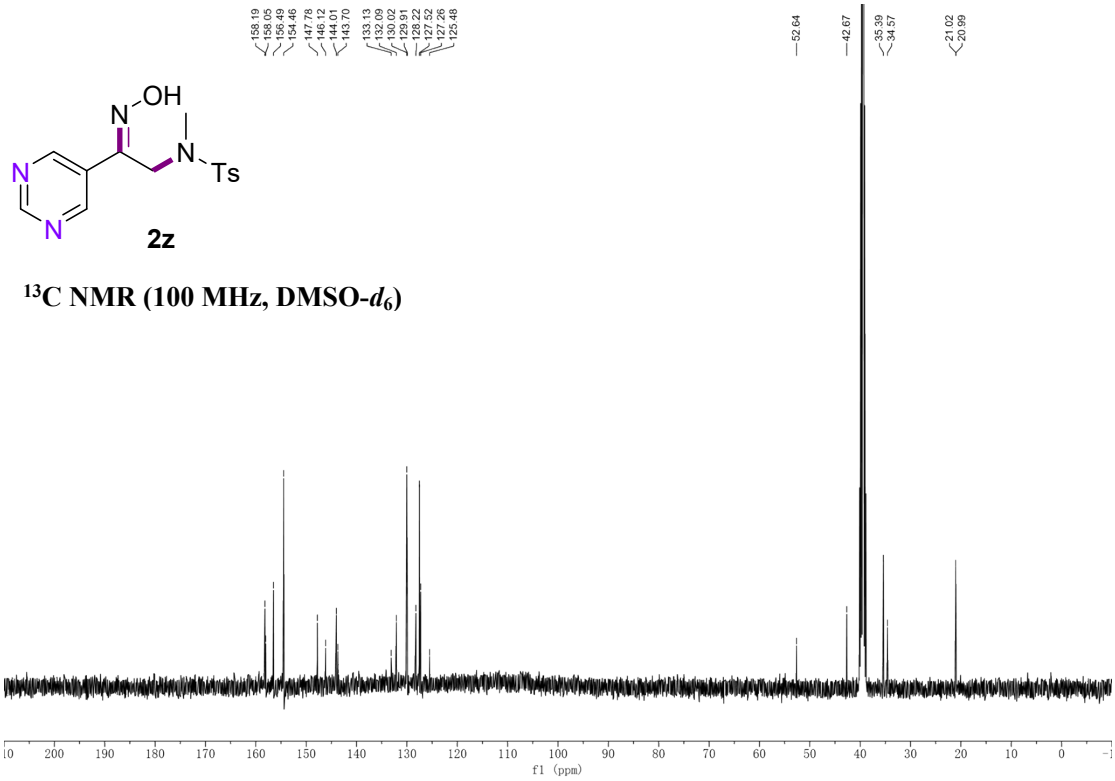
^{13}C NMR (100 MHz, DMSO-d_6)



2z

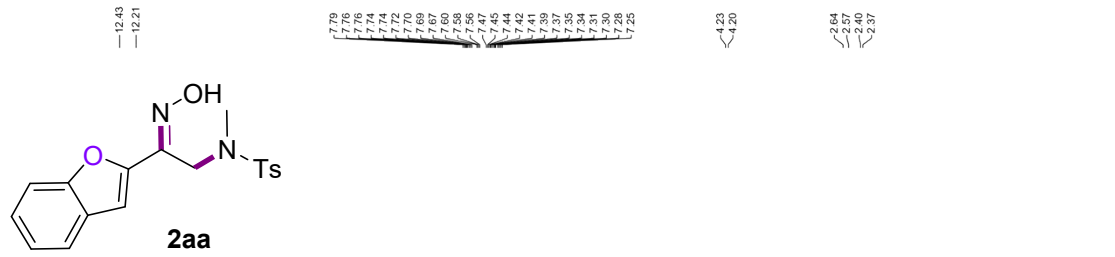
^{1}H NMR (400 MHz, DMSO-d_6)





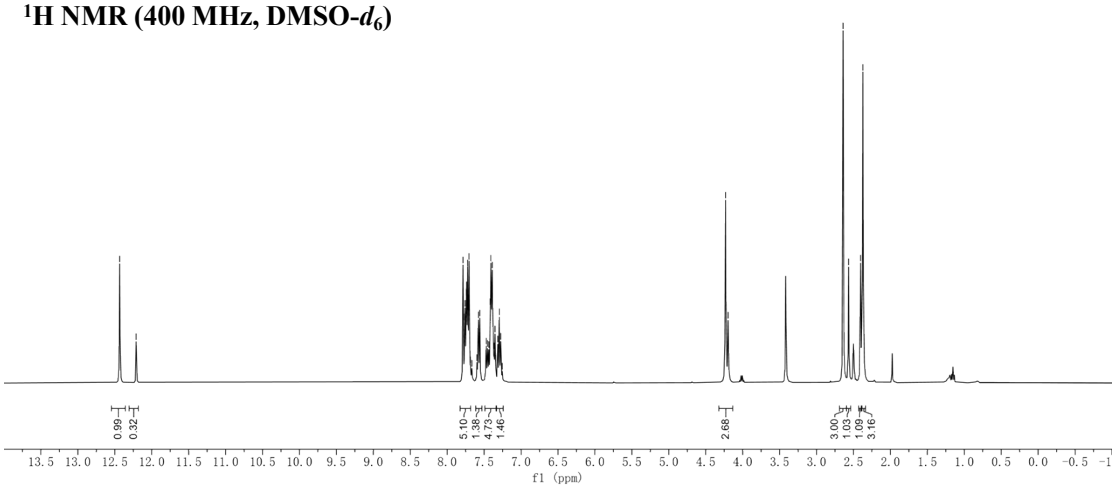
2z

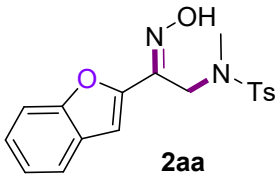
^{13}C NMR (100 MHz, DMSO-d_6)



2aa

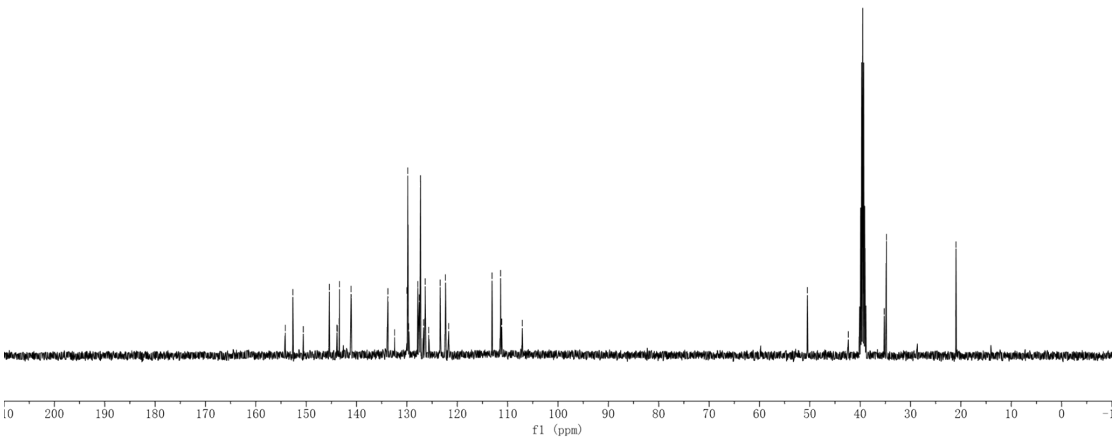
^{1}H NMR (400 MHz, DMSO-d_6)

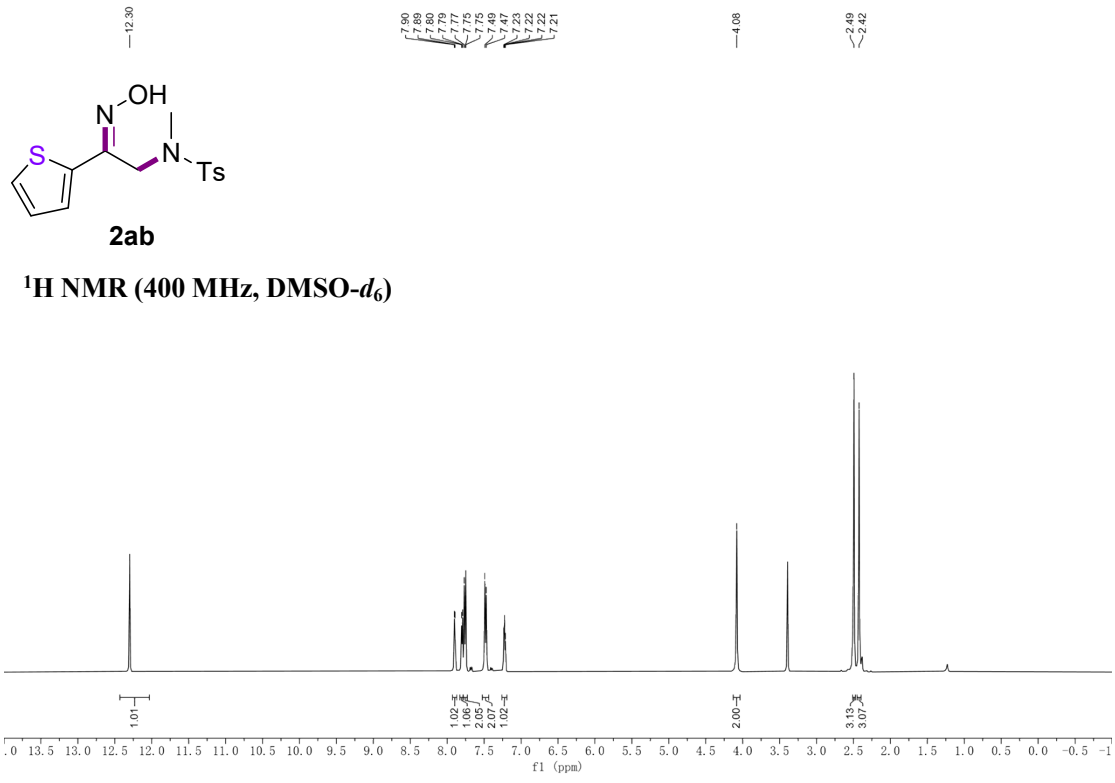




2aa

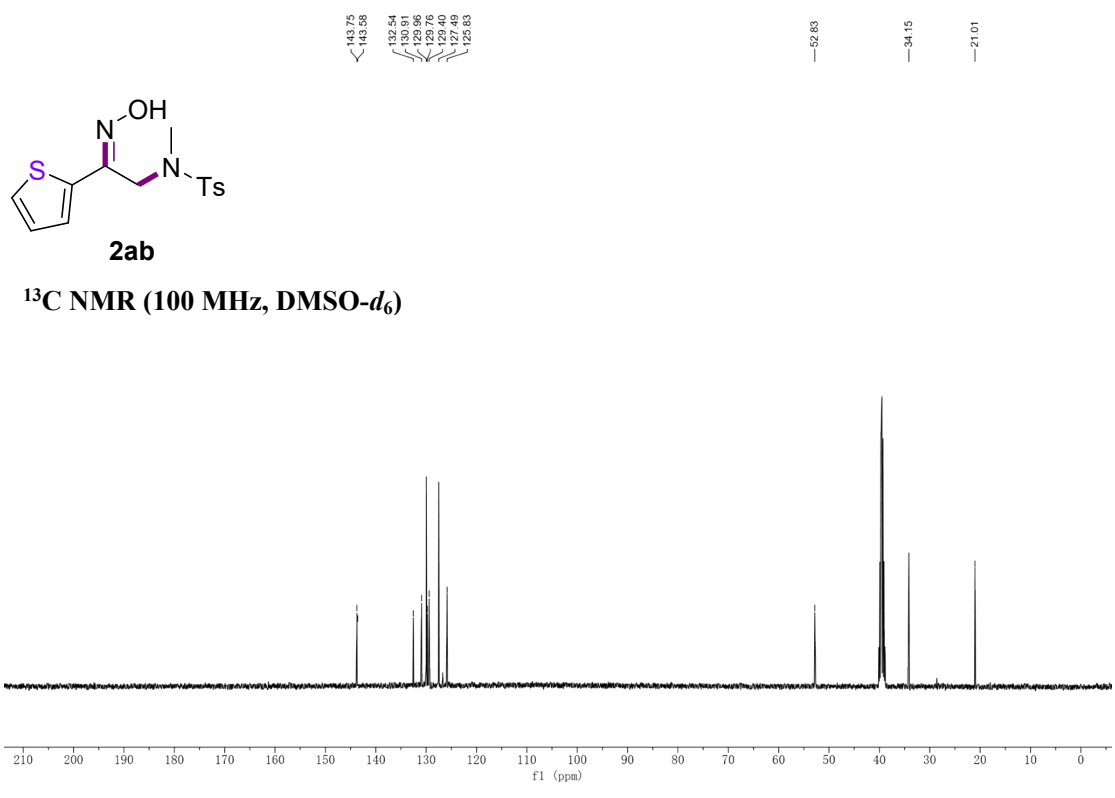
^{13}C NMR (100 MHz, DMSO-d_6)





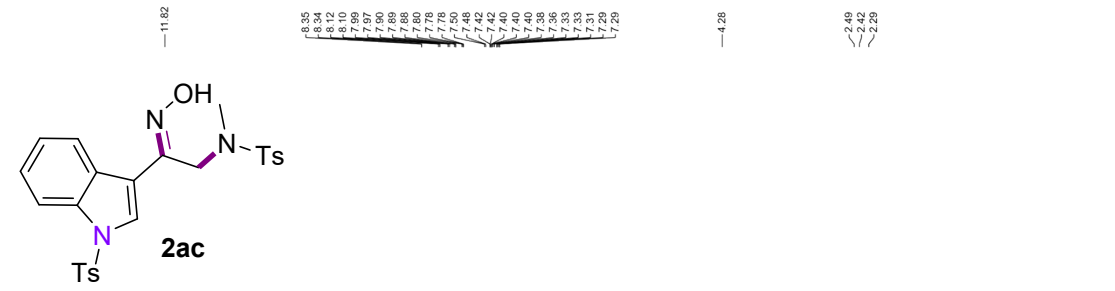
2ab

^{1}H NMR (400 MHz, DMSO-d_6)



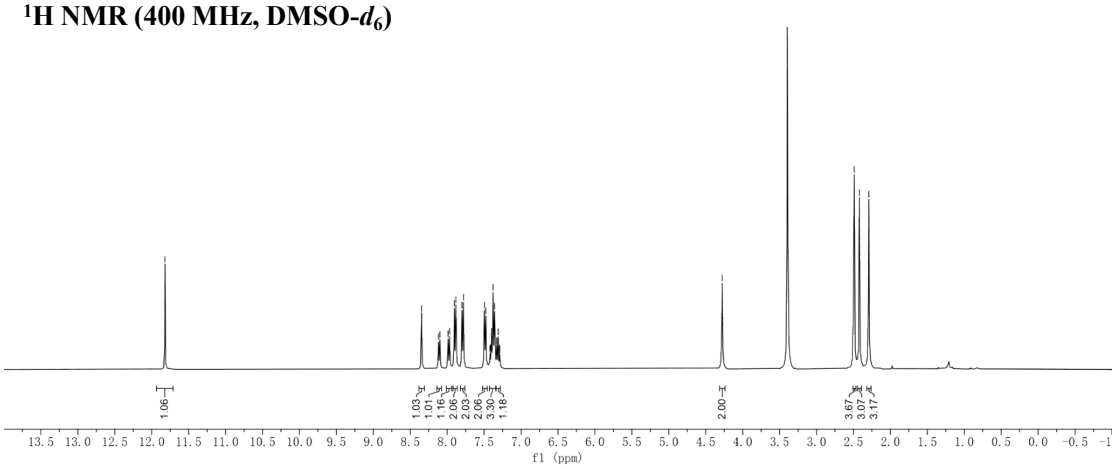
2ab

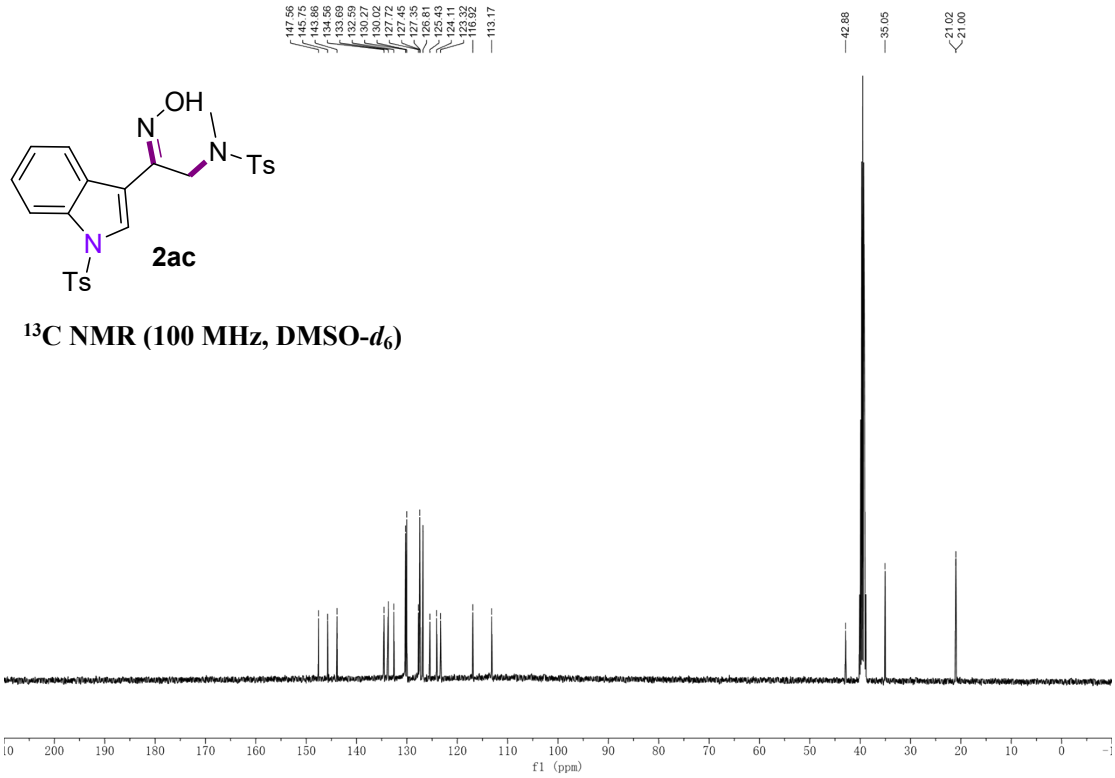
^{13}C NMR (100 MHz, DMSO-d_6)



2ac

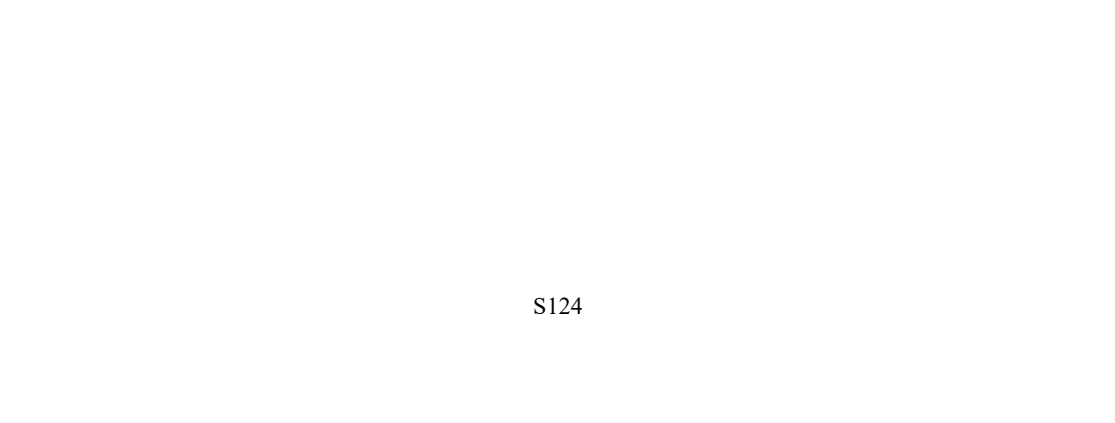
^{1}H NMR (400 MHz, DMSO-d_6)

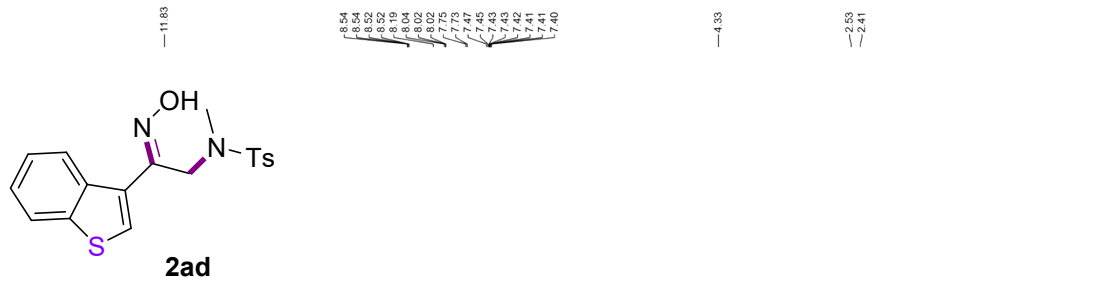




2ac

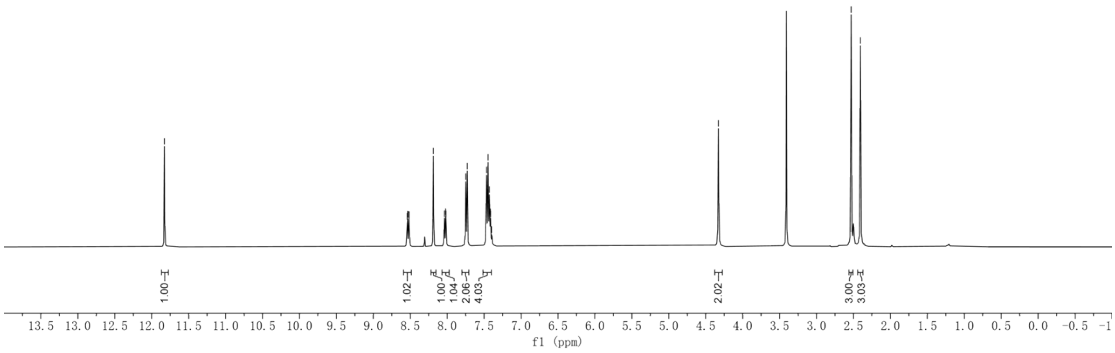
^{13}C NMR (100 MHz, DMSO-d_6)

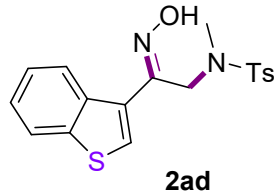




2ad

^{1}H NMR (400 MHz, DMSO-d_6)





2ad

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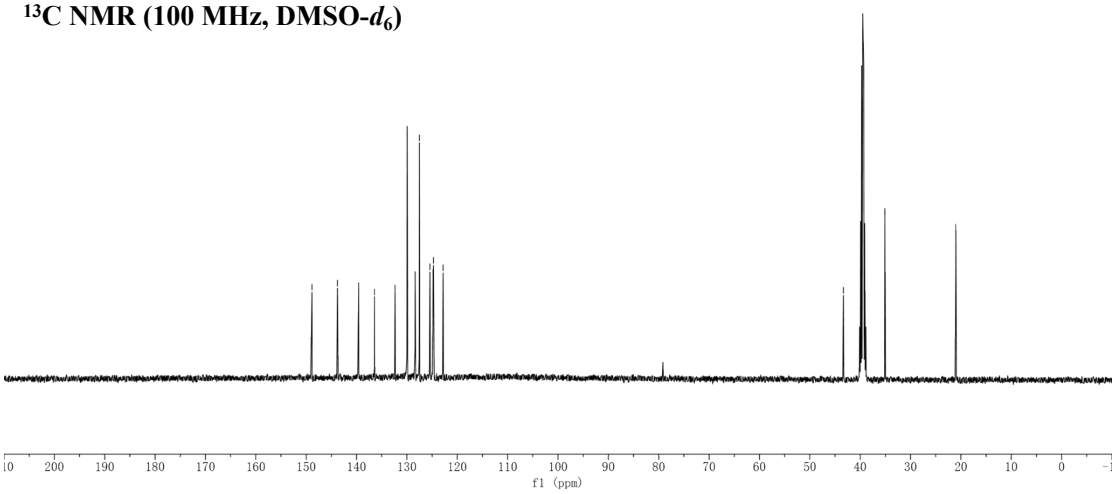
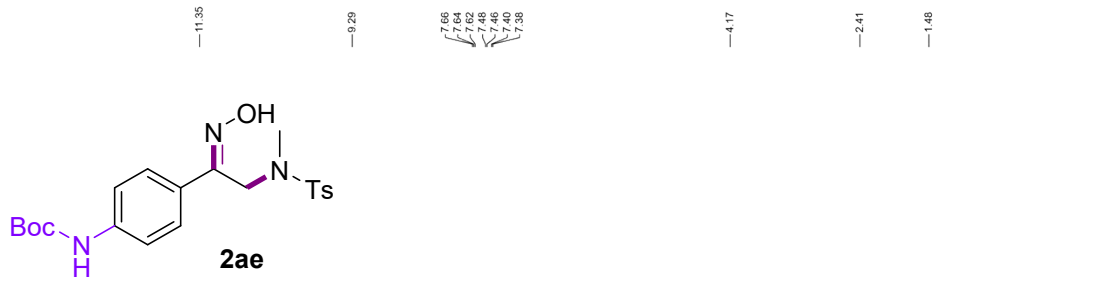
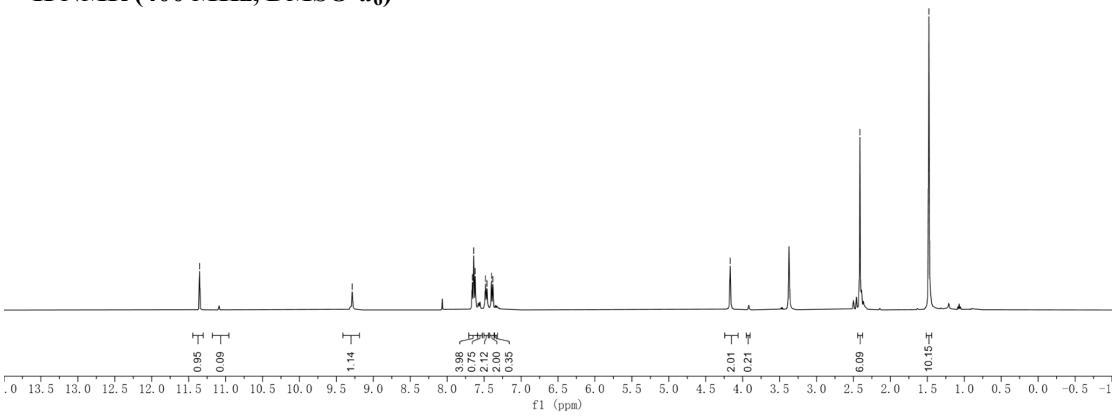
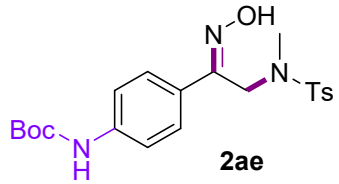




2ae

^{1}H NMR (400 MHz, DMSO-d_6)





2ae

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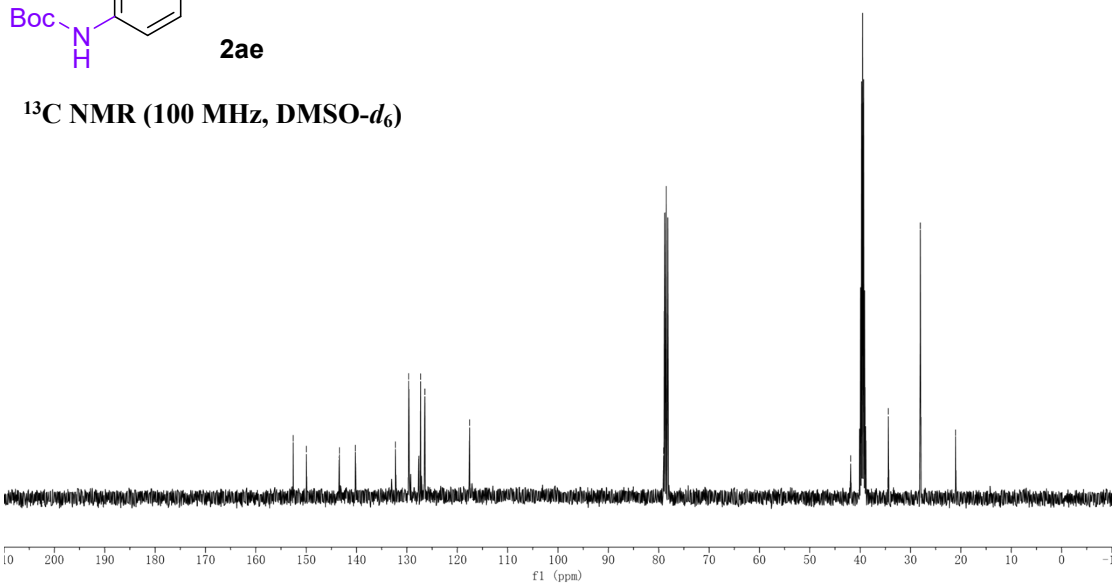
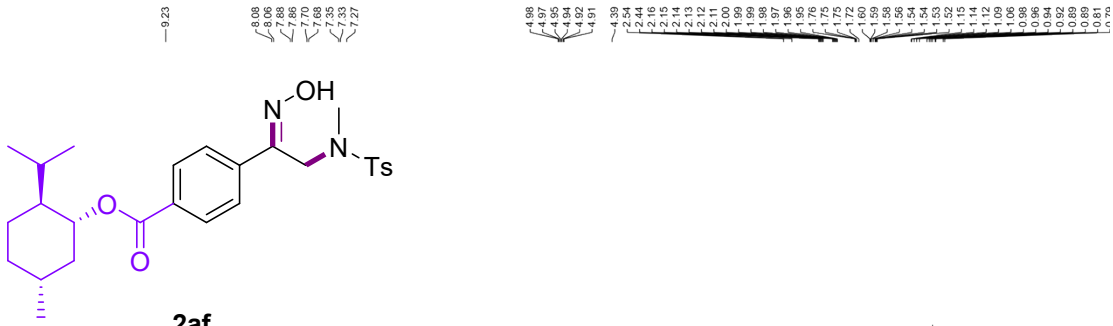
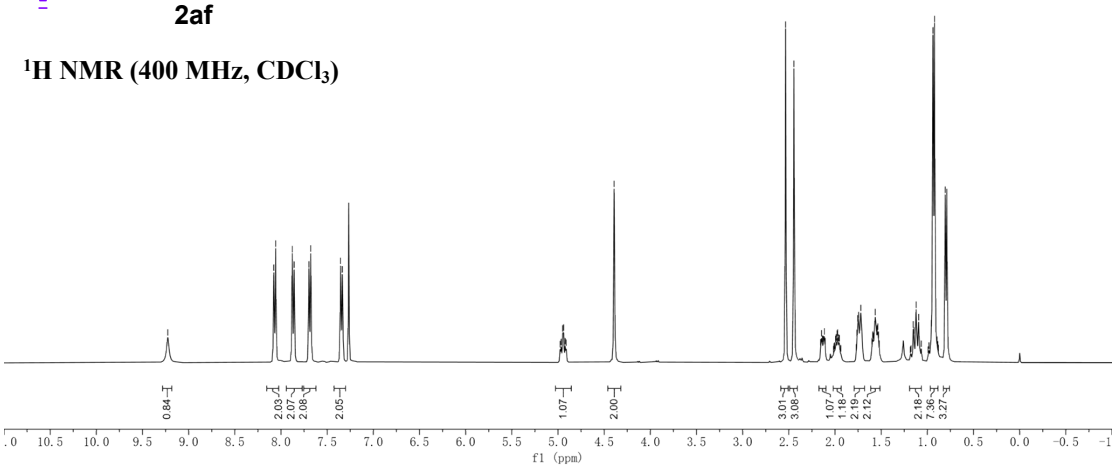




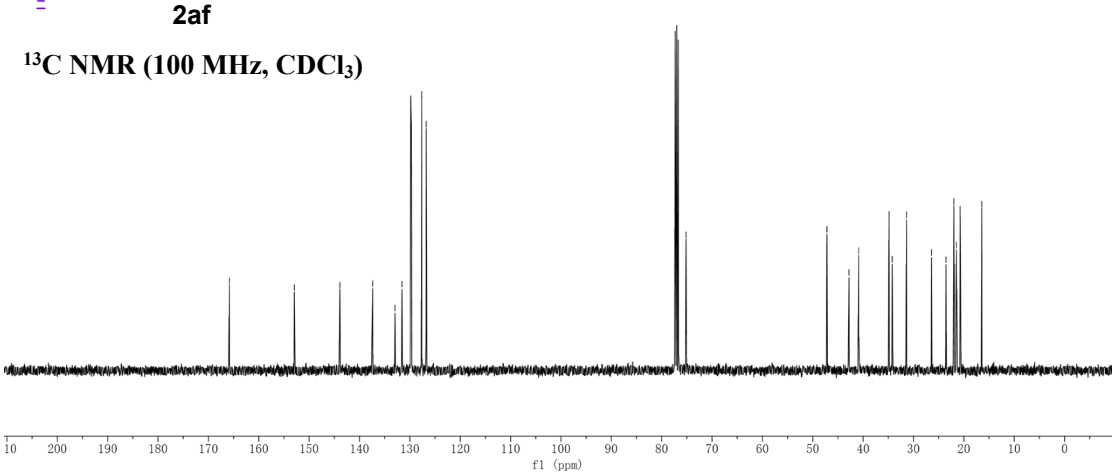
2af

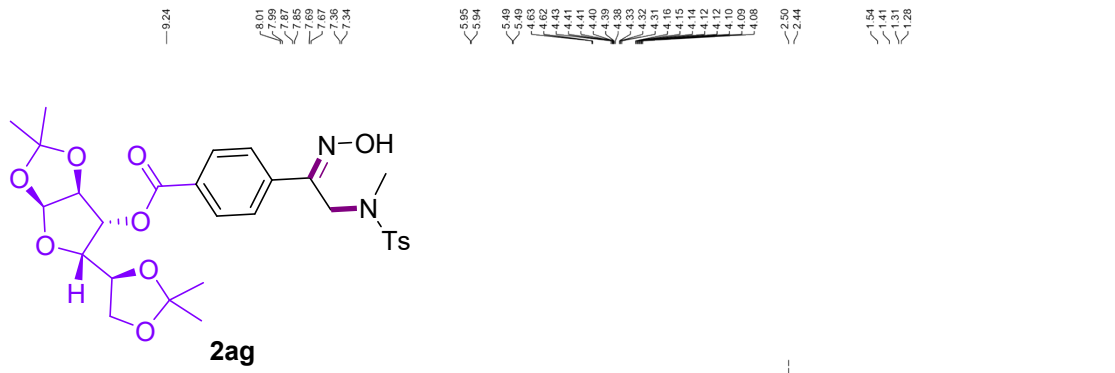
^{1}H NMR (400 MHz, $CDCl_3$)



2af

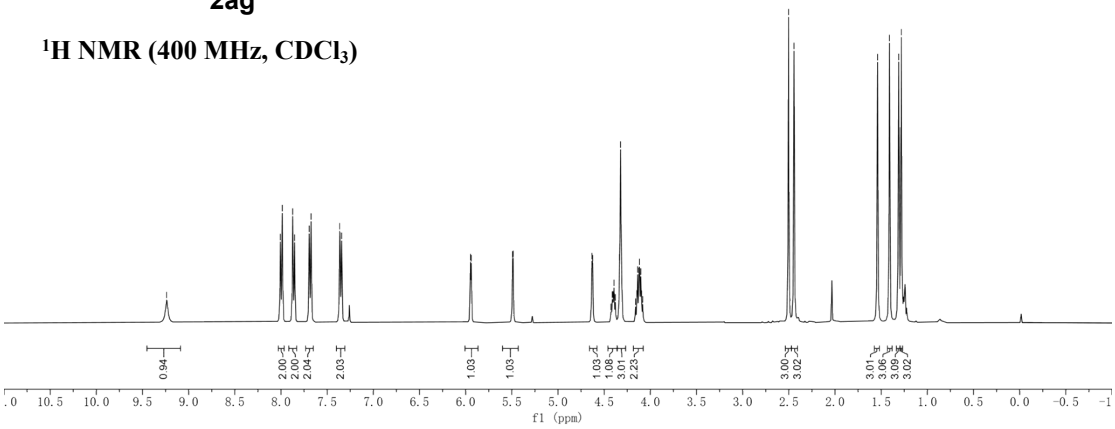
^{13}C NMR (100 MHz, $CDCl_3$)

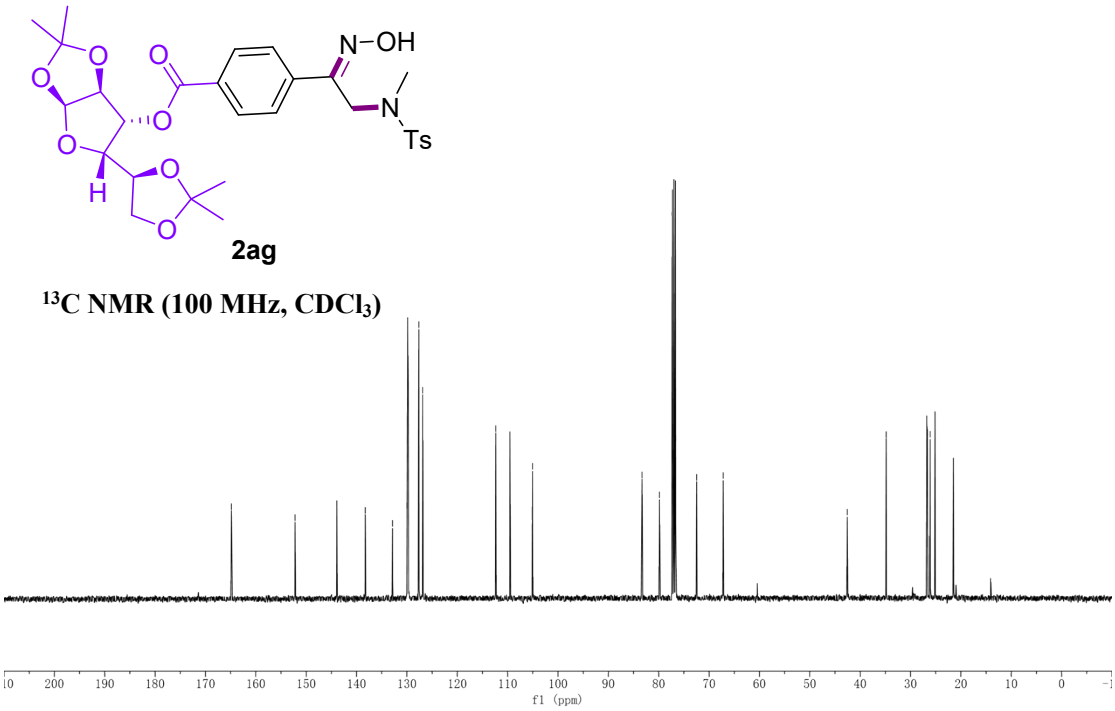




2ag

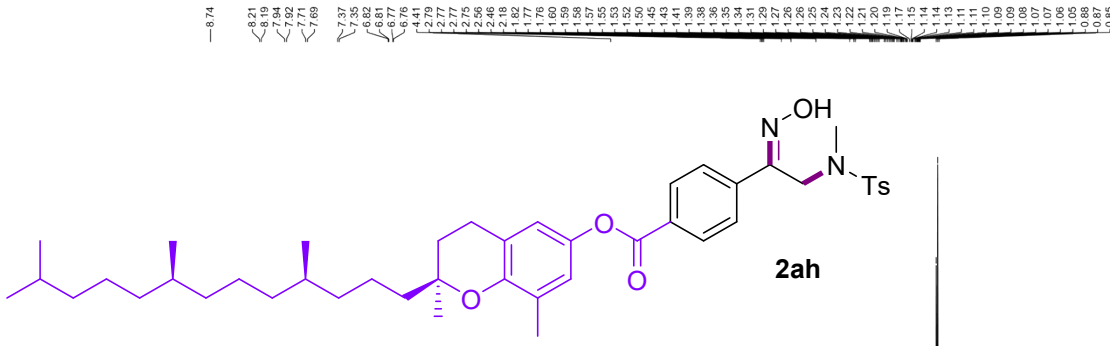
^{1}H NMR (400 MHz, $CDCl_3$)



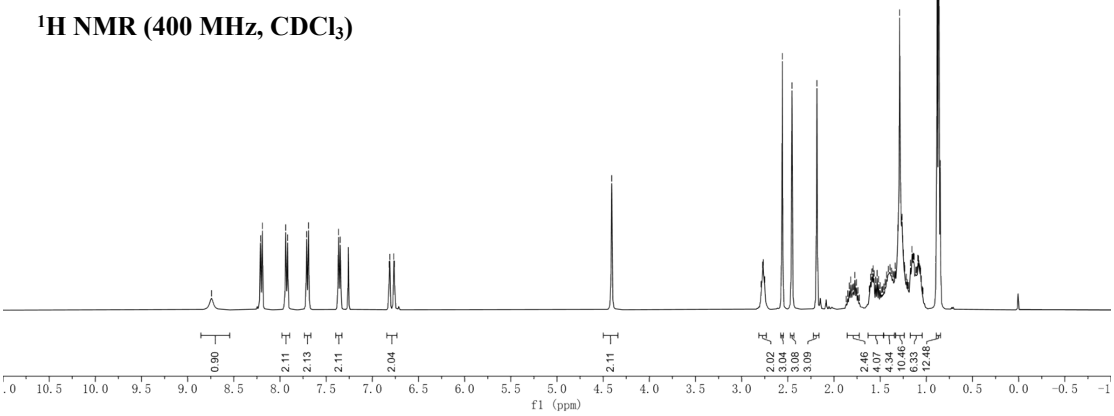


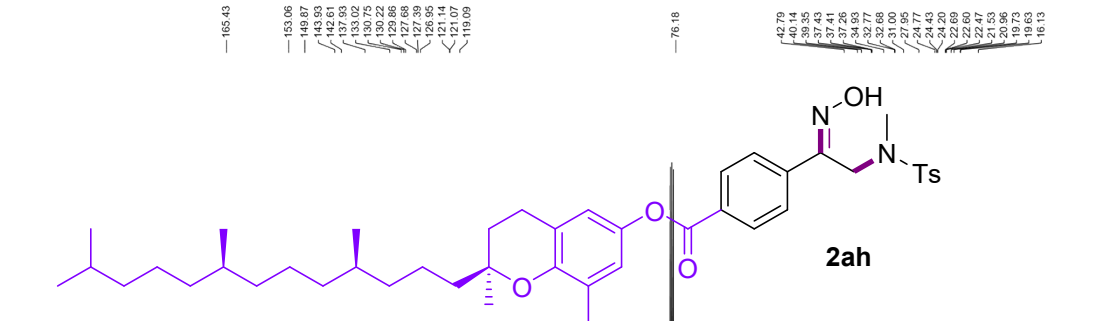
2ag

^{13}C NMR (100 MHz, $CDCl_3$)

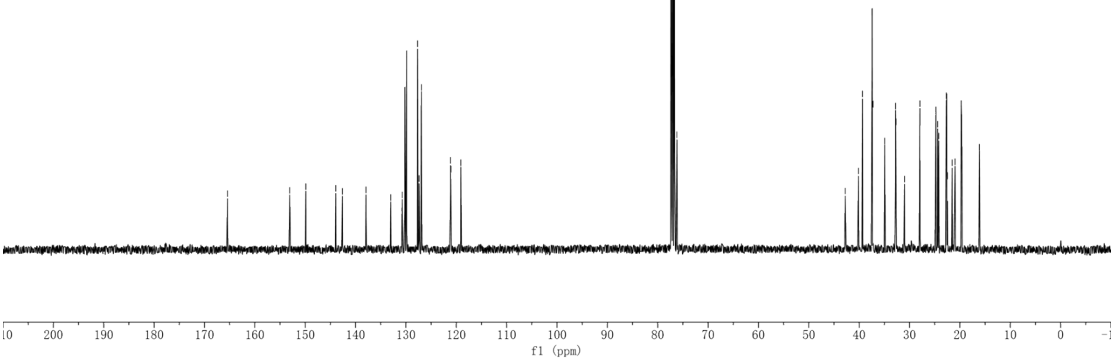


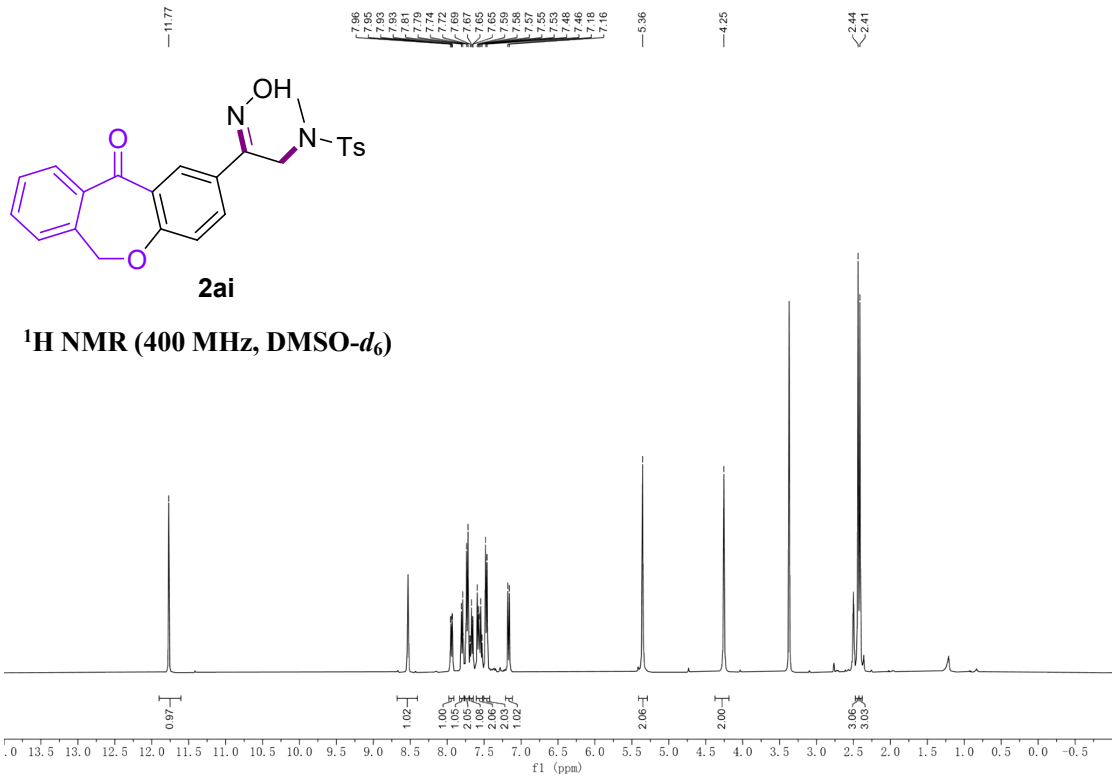
^{1}H NMR (400 MHz, $CDCl_3$)





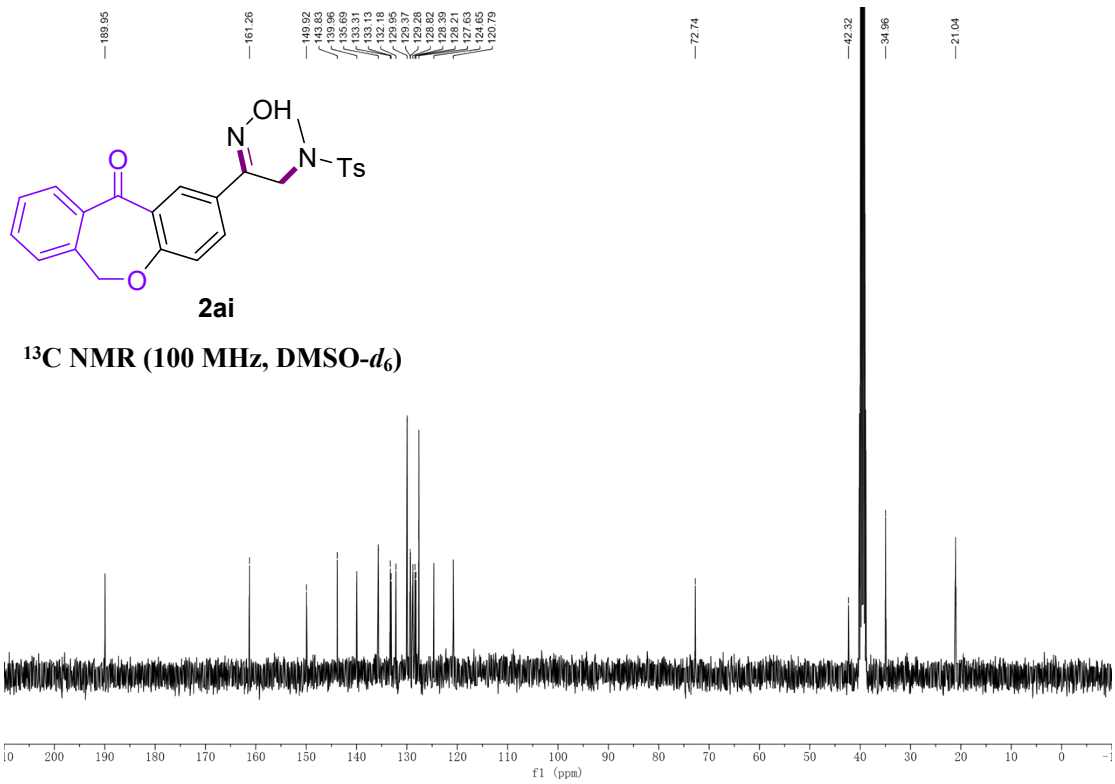
^{13}C NMR (100 MHz, $CDCl_3$)





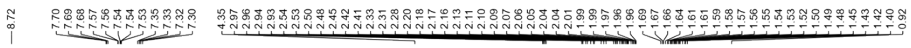
2ai

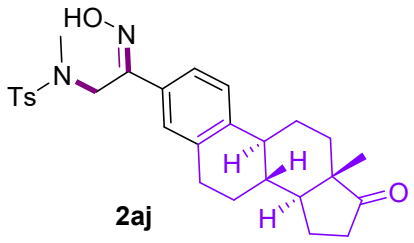
^{1}H NMR (400 MHz, DMSO-d_6)



2ai

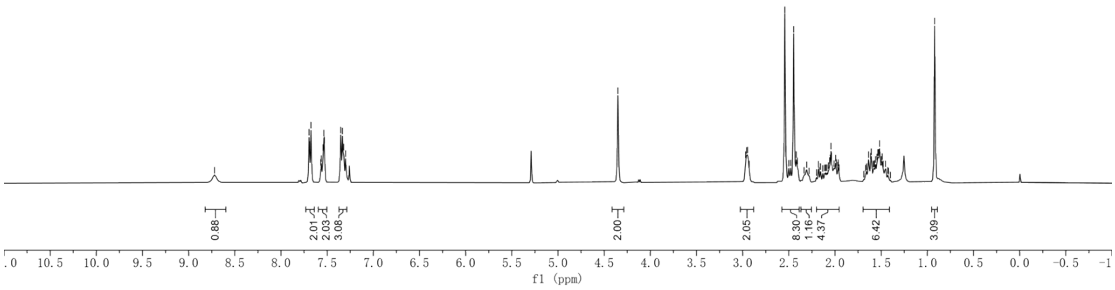
^{13}C NMR (100 MHz, DMSO-d_6)

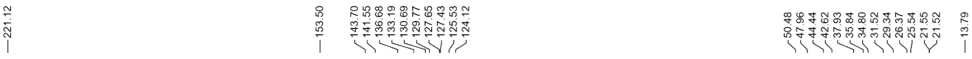


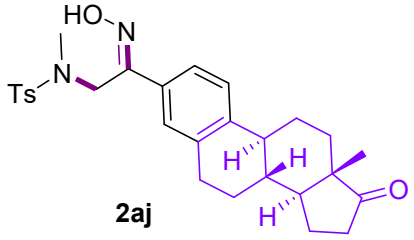


2aj

^{1}H NMR (400 MHz, $CDCl_3$)

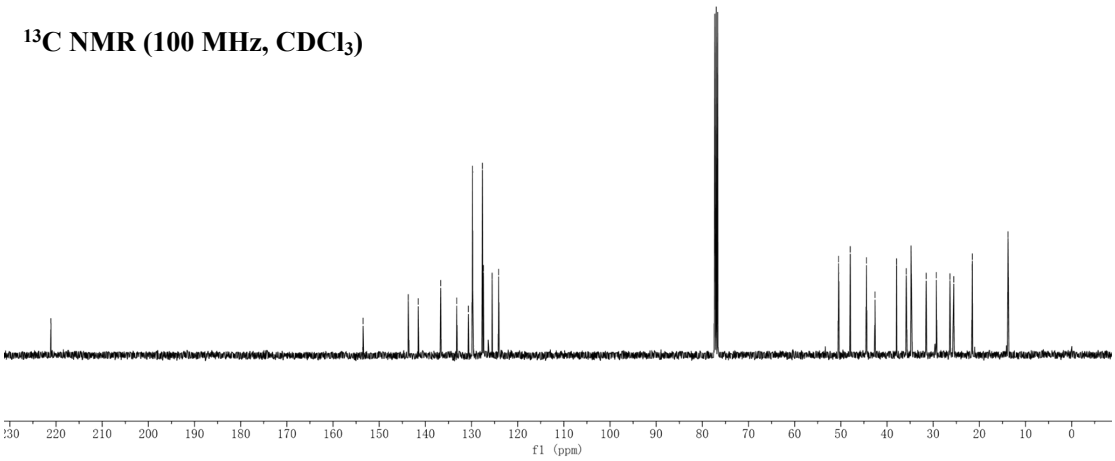


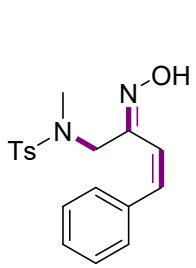




2aj

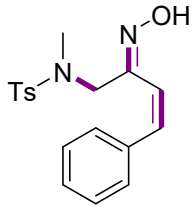
^{13}C NMR (100 MHz, $CDCl_3$)





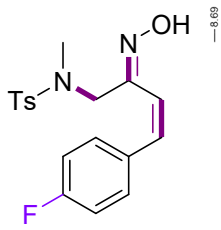
4a

^{1}H NMR (400 MHz, $CDCl_3$)



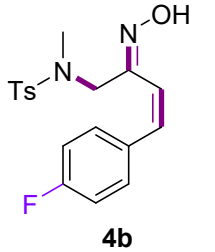
4a

^{13}C NMR (100 MHz, $CDCl_3$)



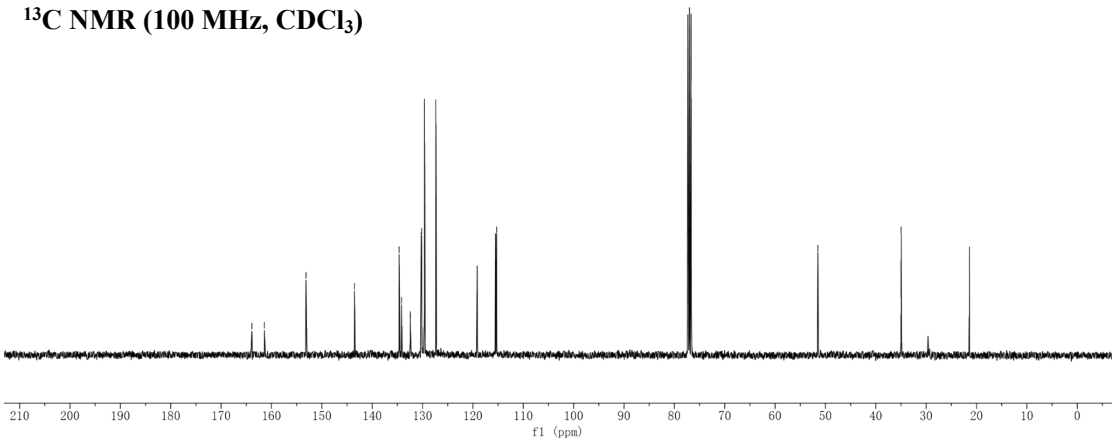
4b

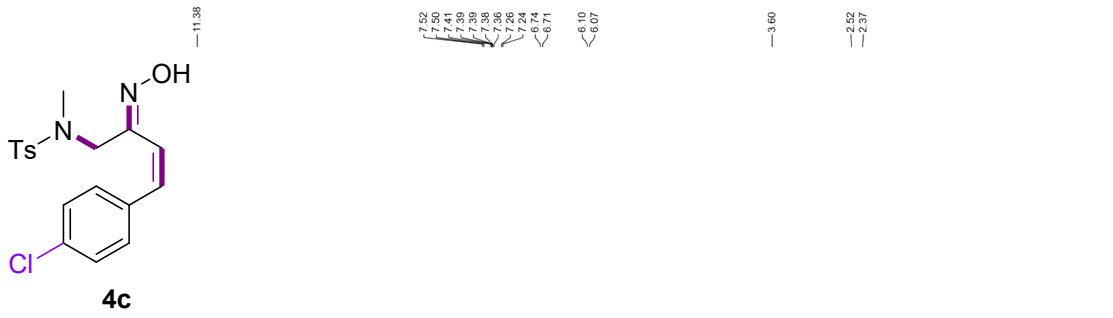
^{1}H NMR (400 MHz, $CDCl_3$)



4b

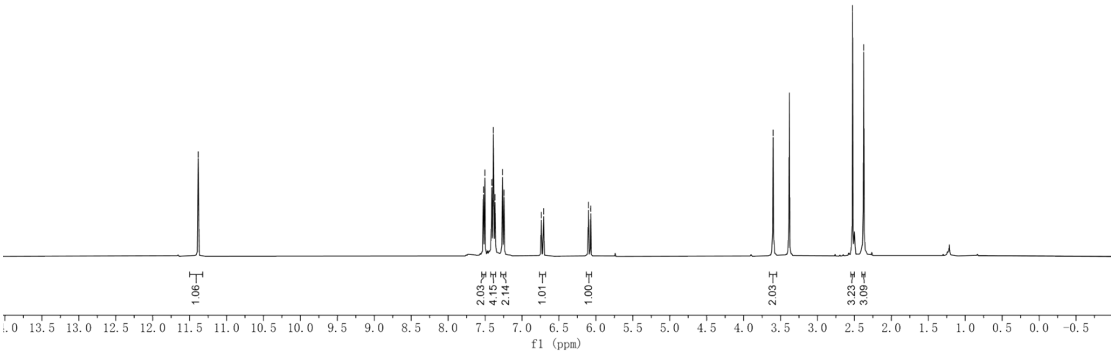
^{13}C NMR (100 MHz, $CDCl_3$)

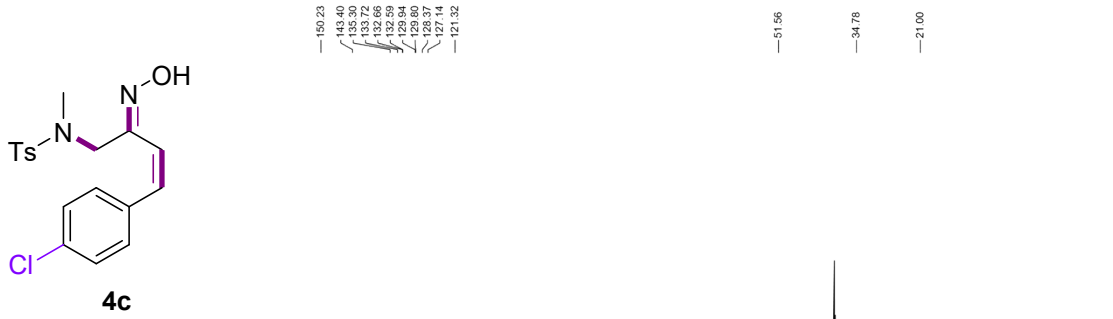




4c

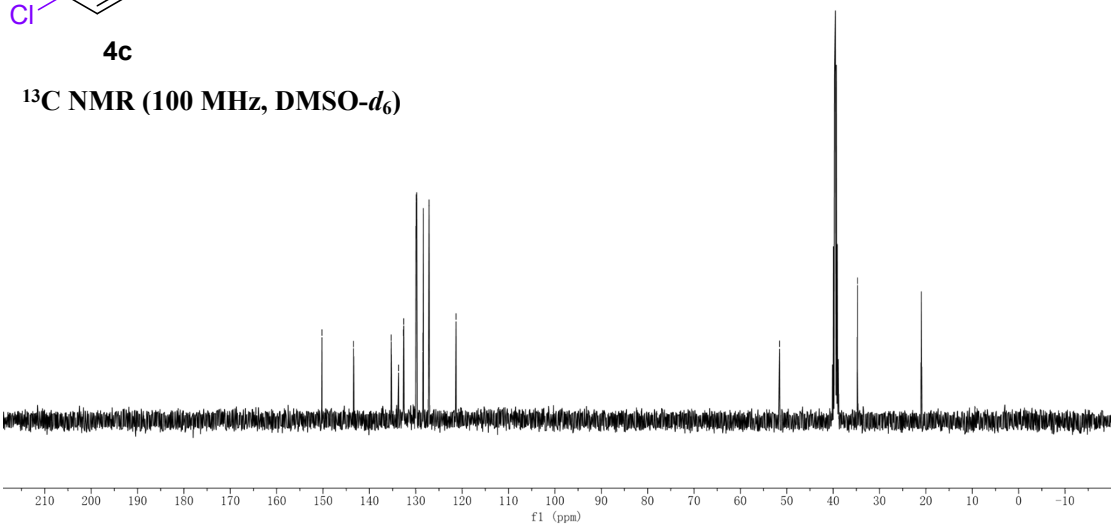
^{1}H NMR (400 MHz, DMSO-d_6)

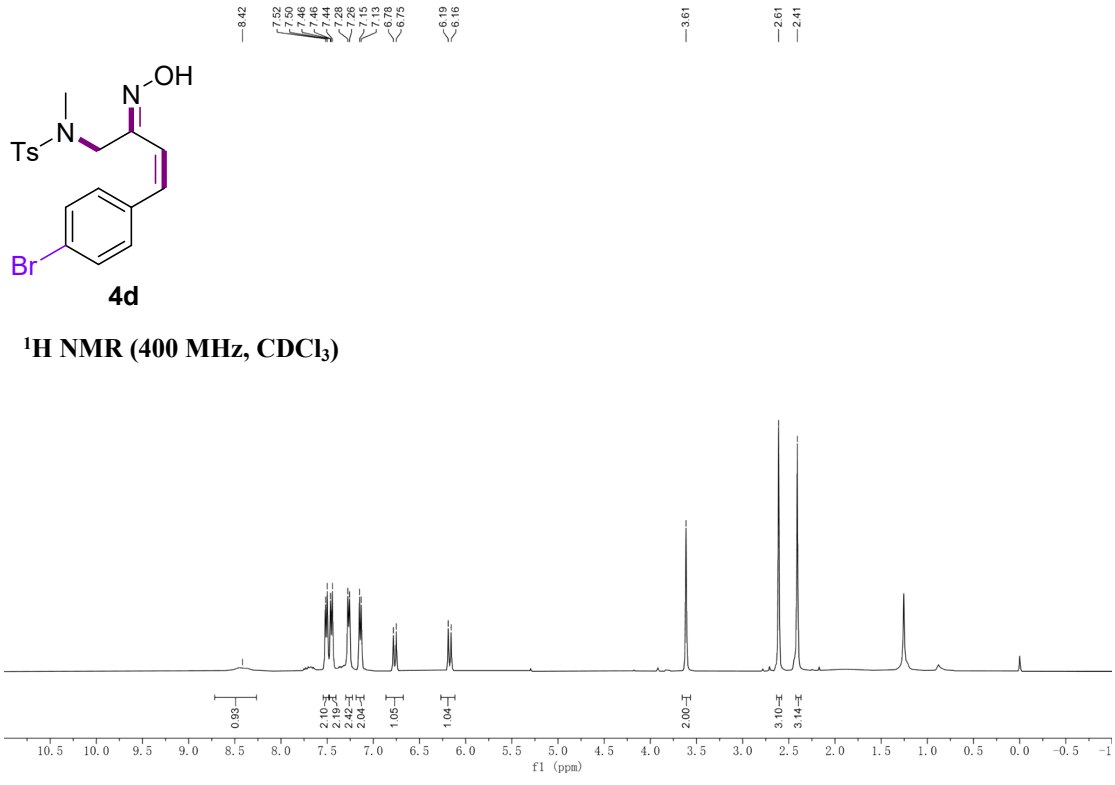




4c

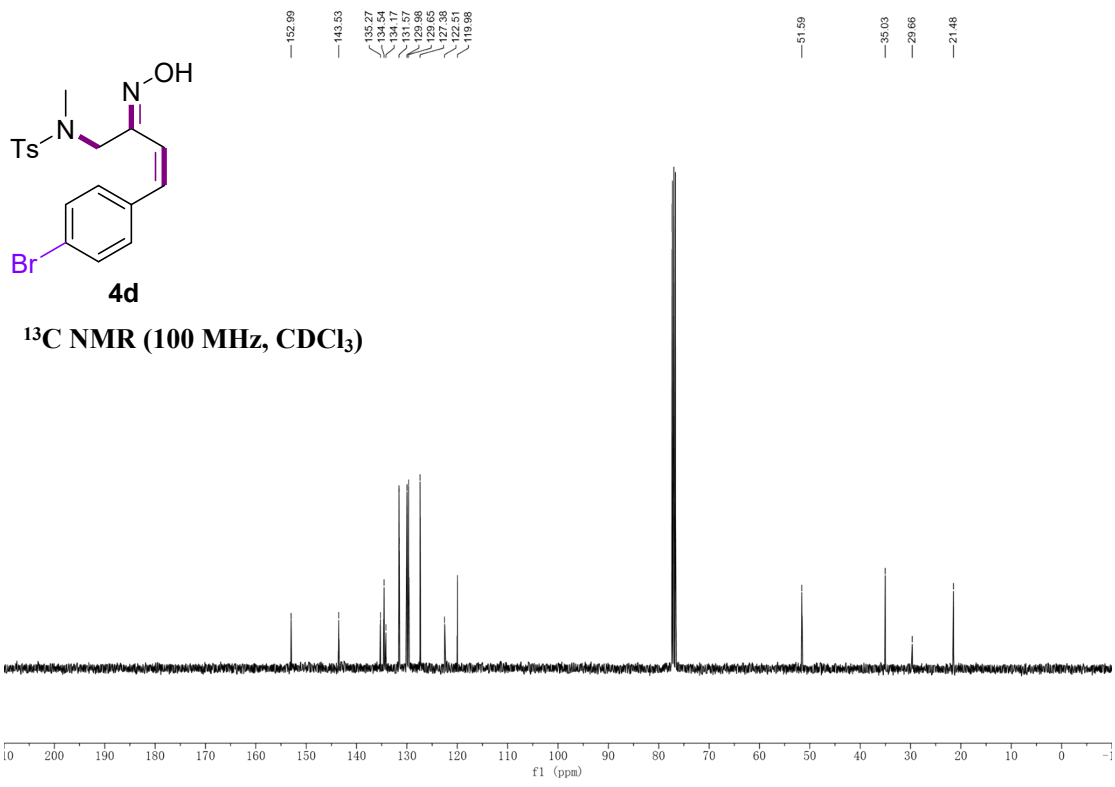
^{13}C NMR (100 MHz, DMSO-d_6)





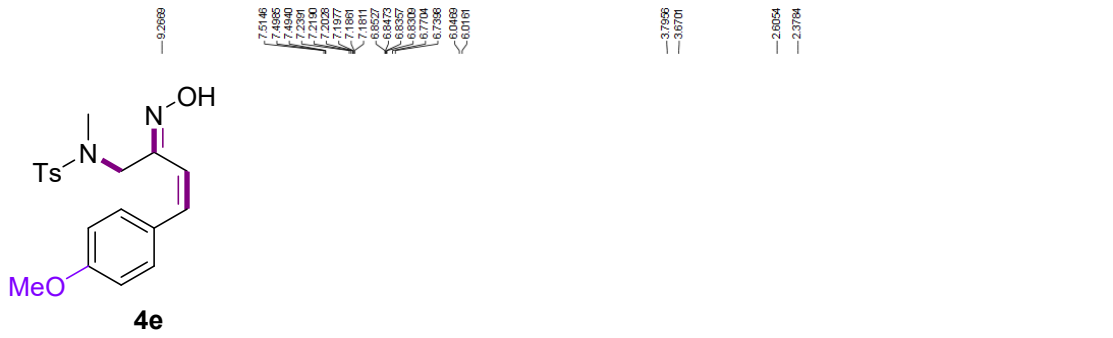
4d

^{1}H NMR (400 MHz, $CDCl_3$)



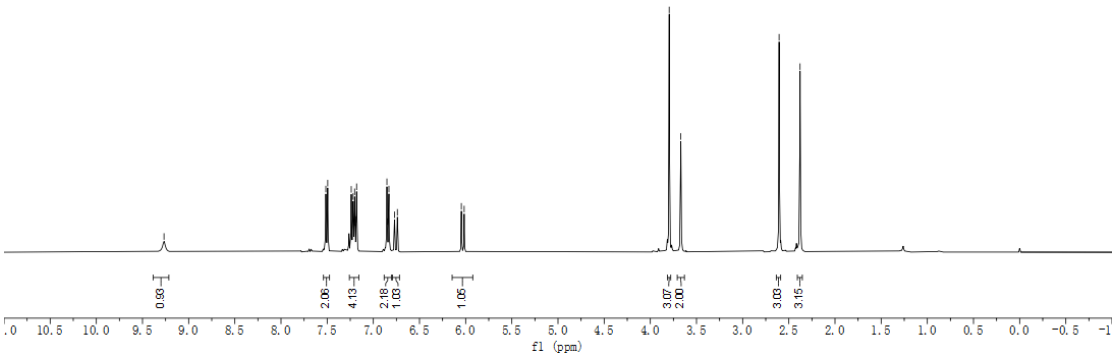
4d

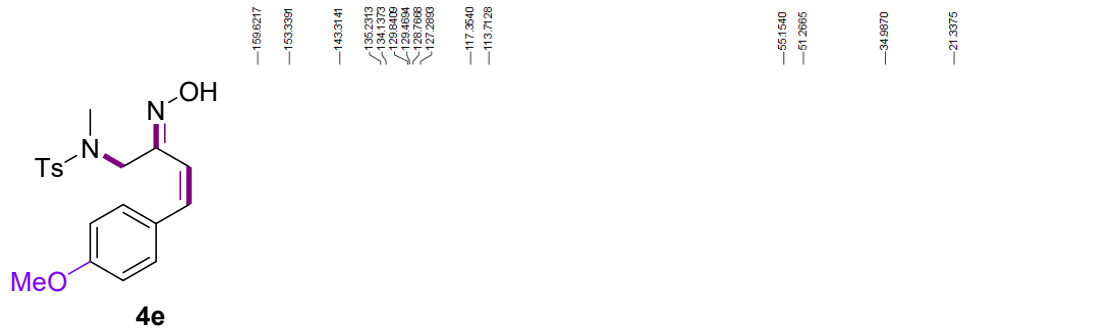
^{13}C NMR (100 MHz, $CDCl_3$)



4e

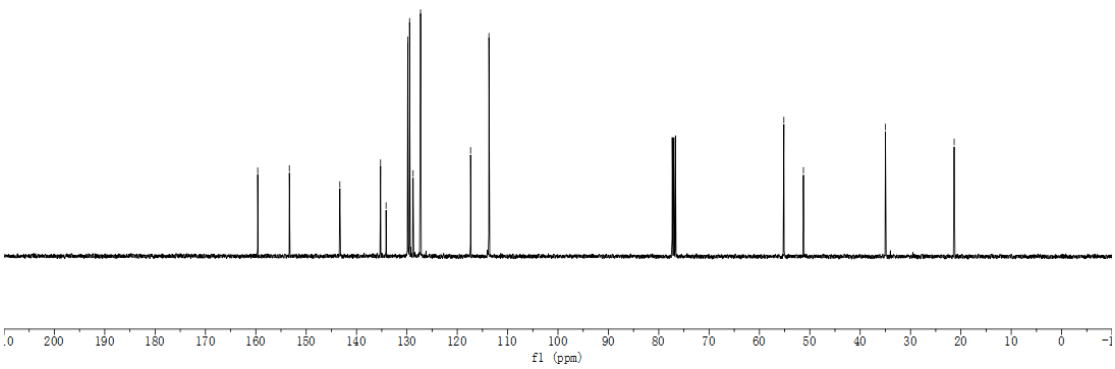
^{1}H NMR (400 MHz, $CDCl_3$)

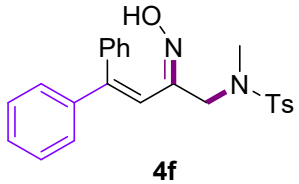




4e

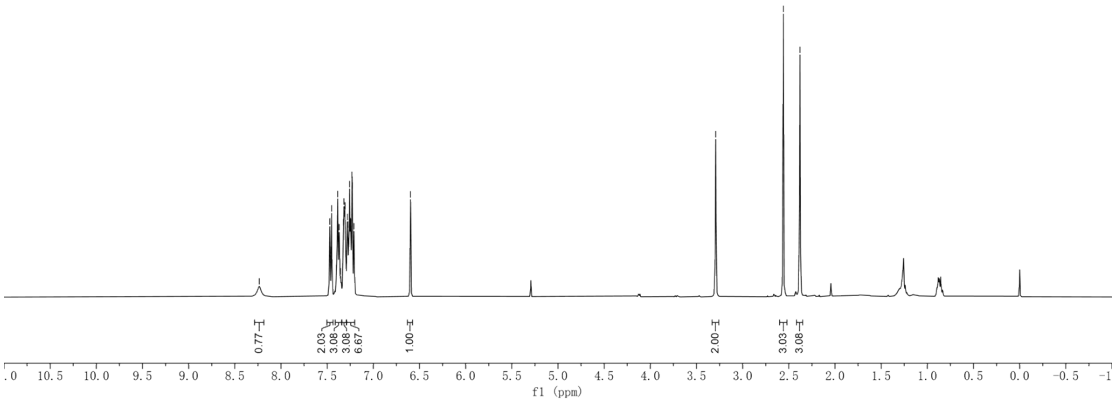
^{13}C NMR (100 MHz, $CDCl_3$)

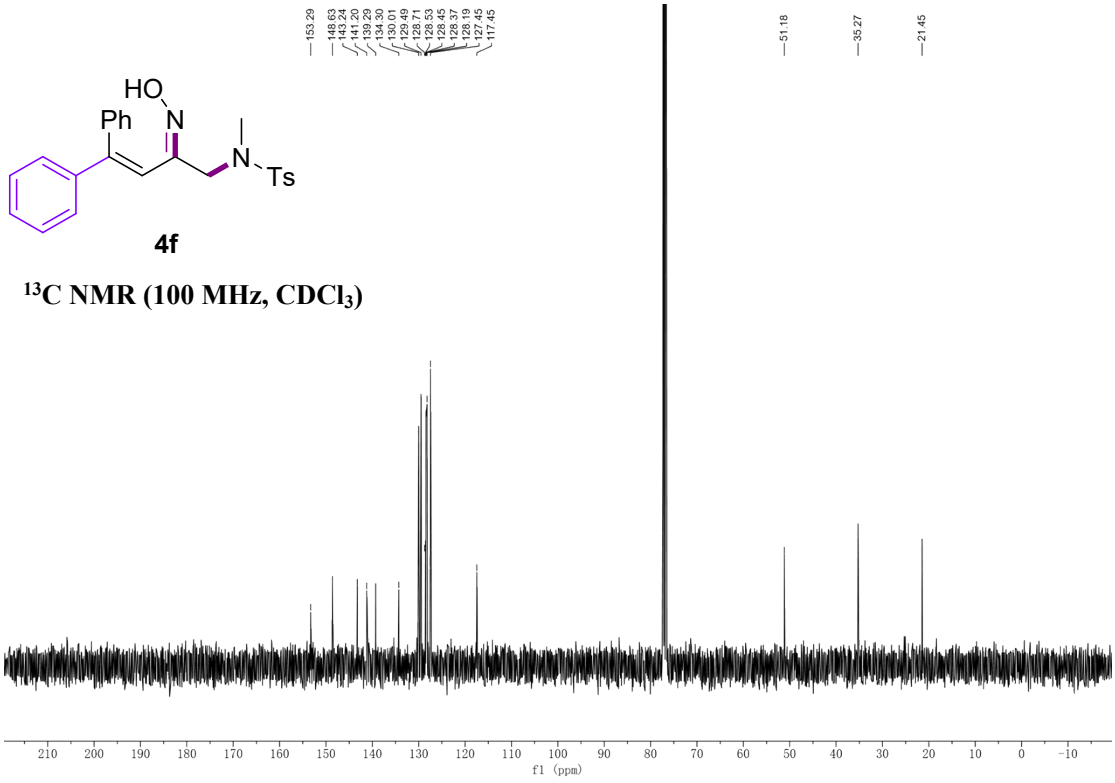




4f

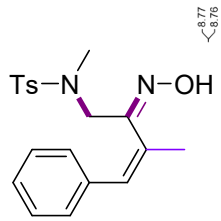
^{1}H NMR (400 MHz, $CDCl_3$)





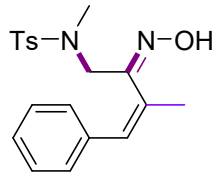
4f

^{13}C NMR (100 MHz, $CDCl_3$)



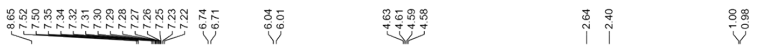
4g

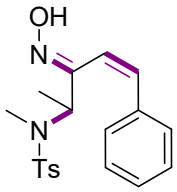
^{1}H NMR (400 MHz, $CDCl_3$)



4g

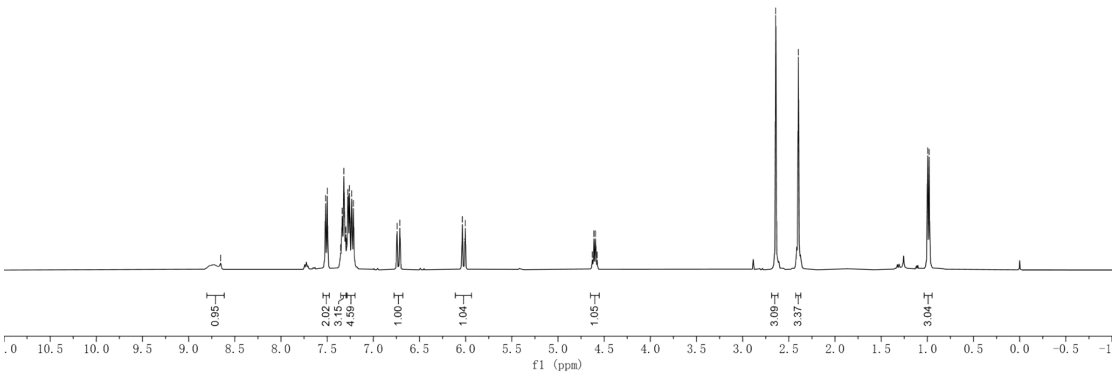
^{13}C NMR (100 MHz, $CDCl_3$)

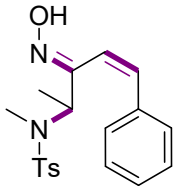




4h

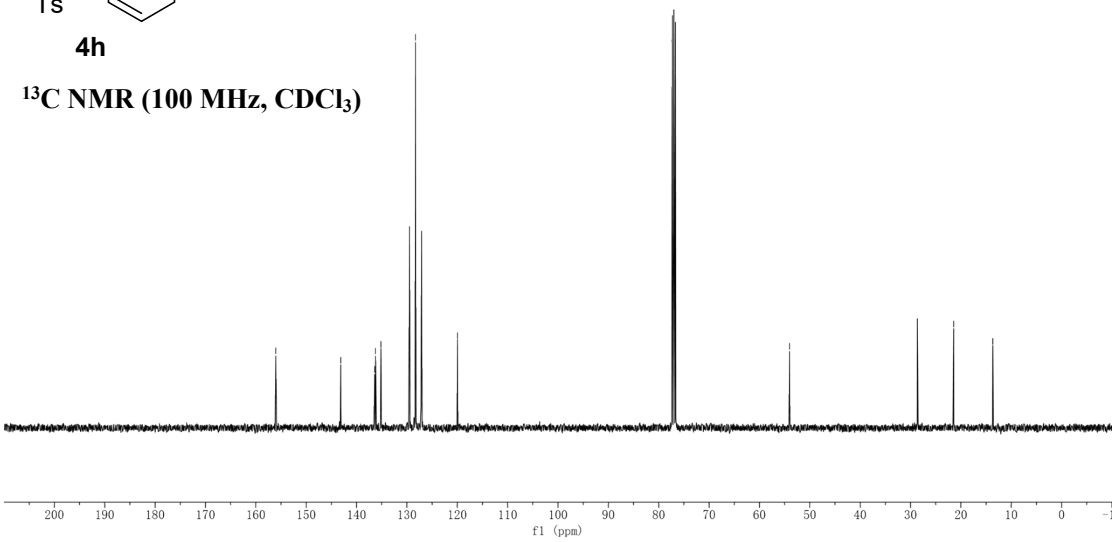
^{1}H NMR (400 MHz, $CDCl_3$)

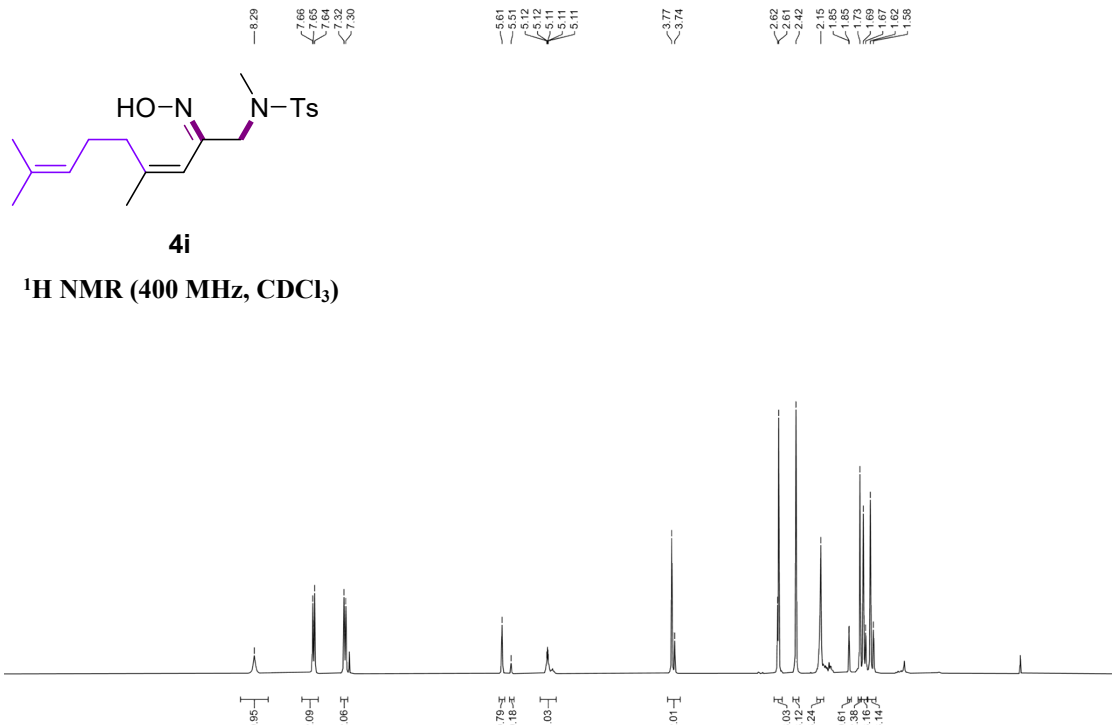




4h

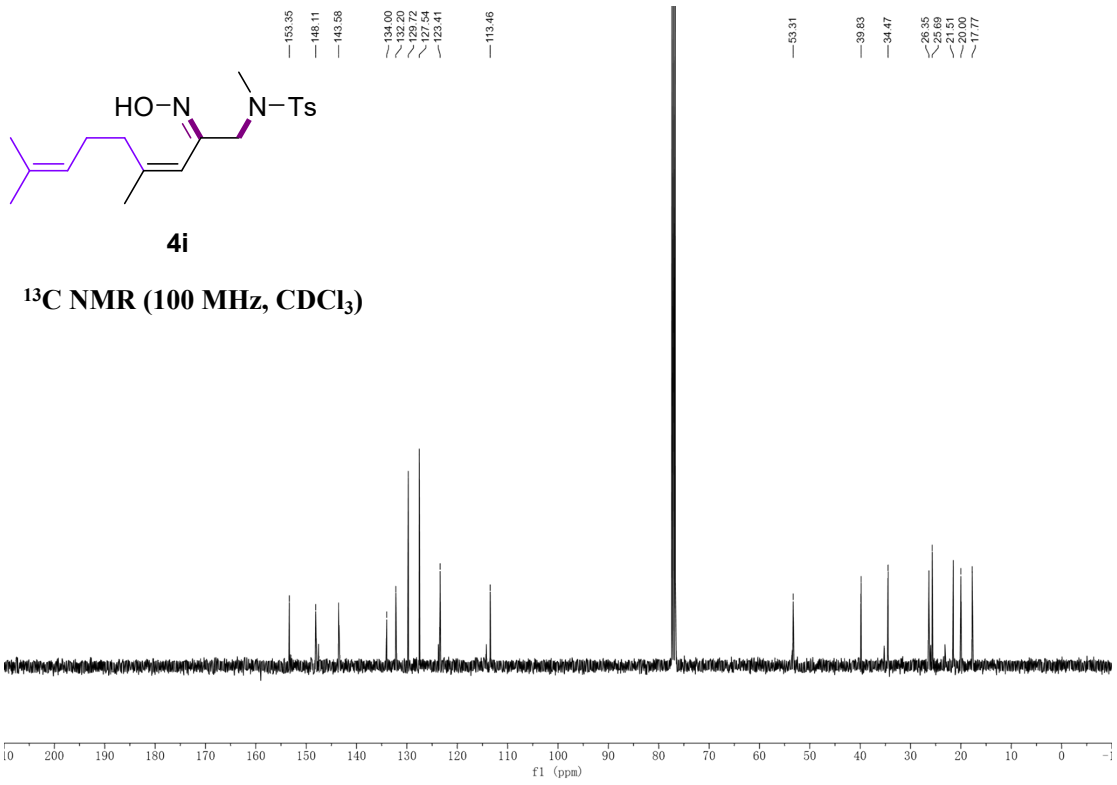
^{13}C NMR (100 MHz, $CDCl_3$)





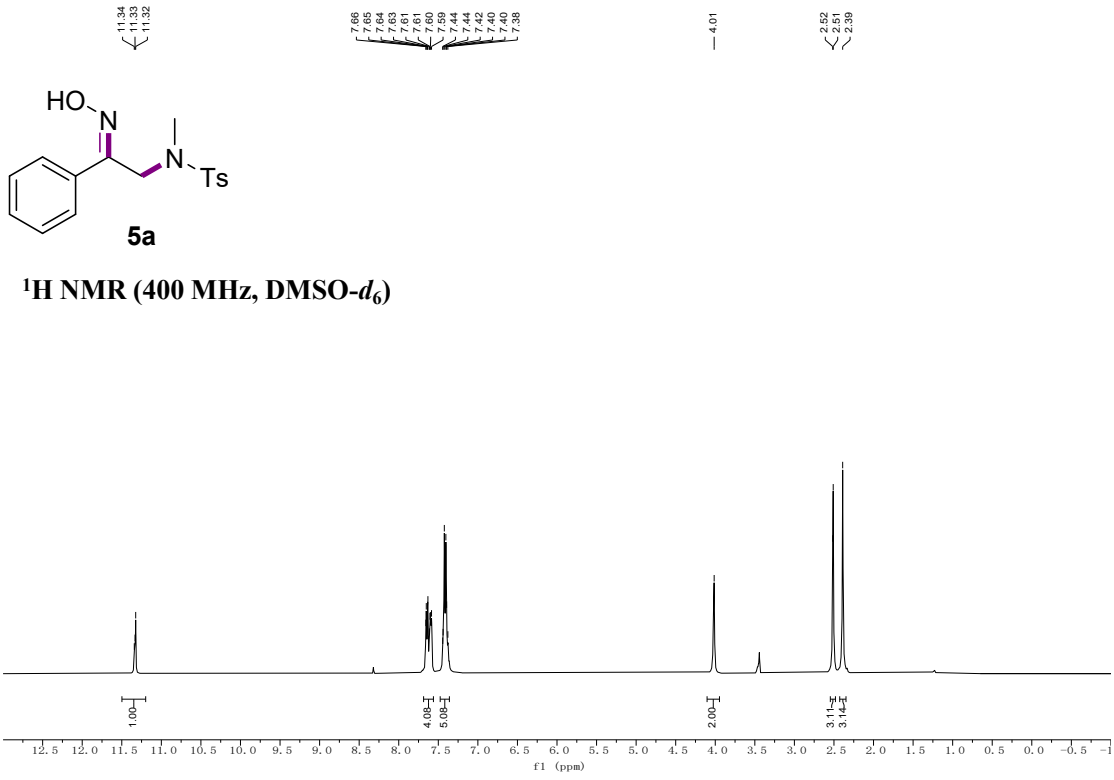
4i

^{1}H NMR (400 MHz, $CDCl_3$)



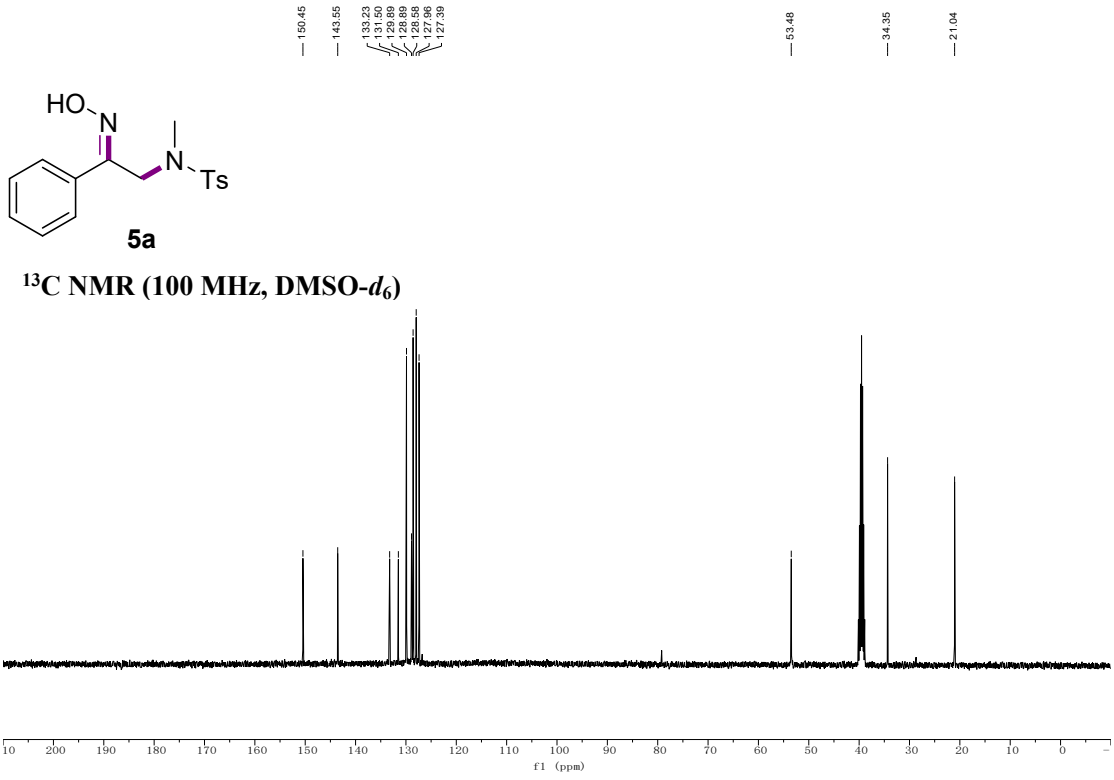
4i

^{13}C NMR (100 MHz, $CDCl_3$)



5a

^{1}H NMR (400 MHz, DMSO-d_6)

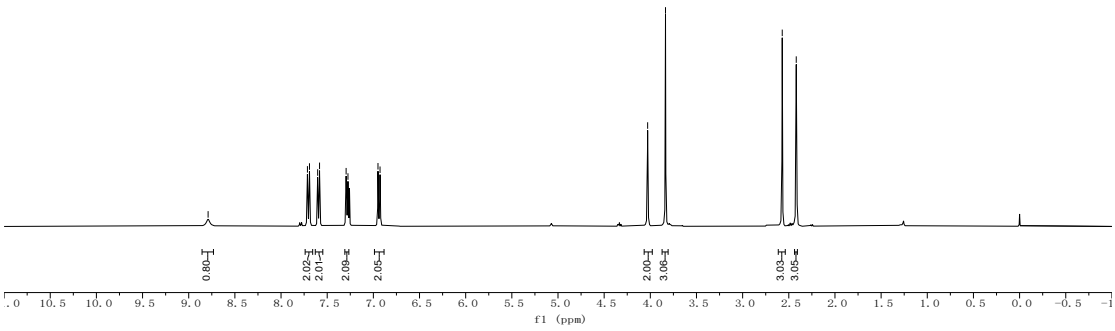


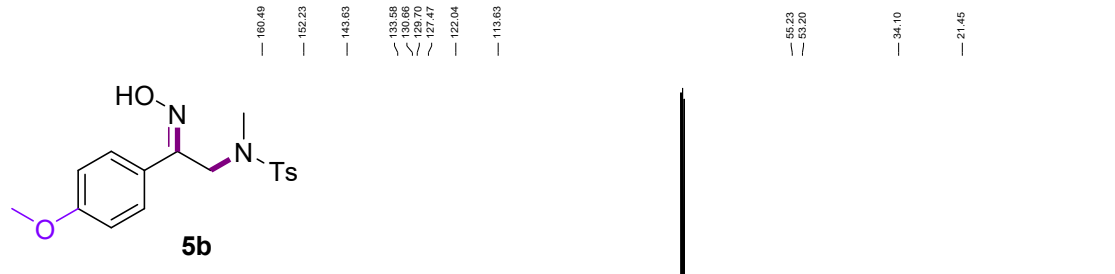
5a

^{13}C NMR (100 MHz, DMSO-d_6)

5b

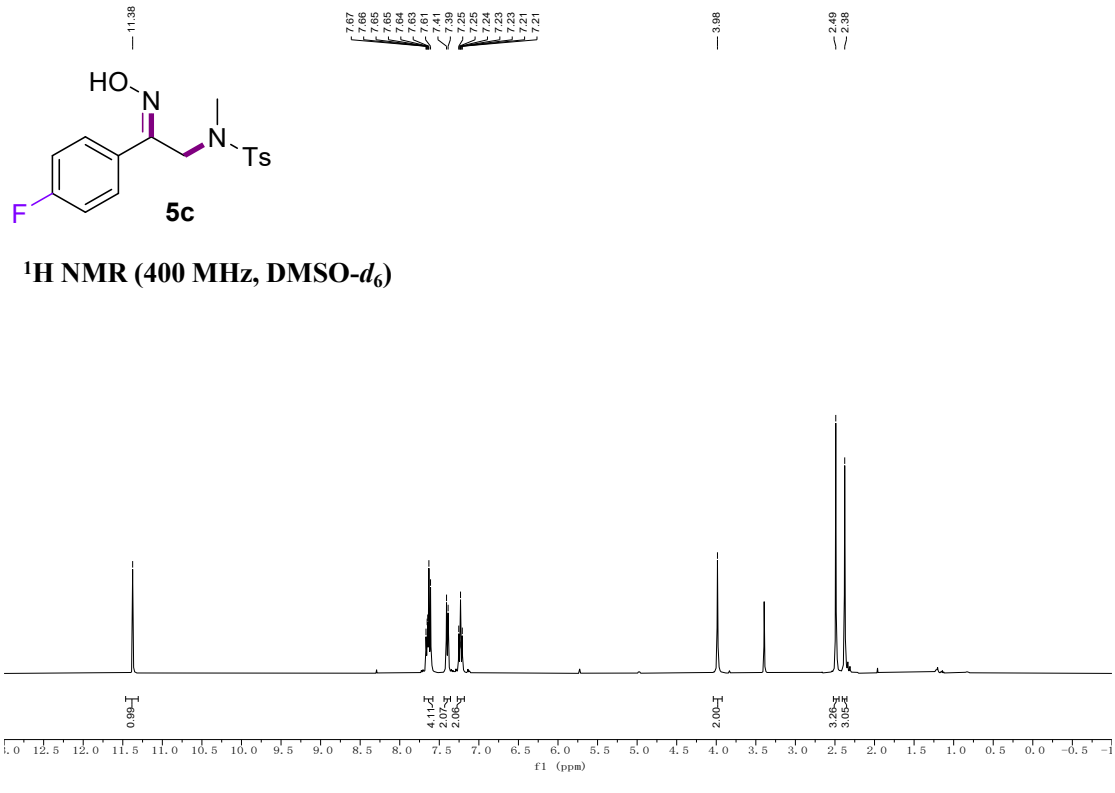
^{1}H NMR (400 MHz, $CDCl_3$)



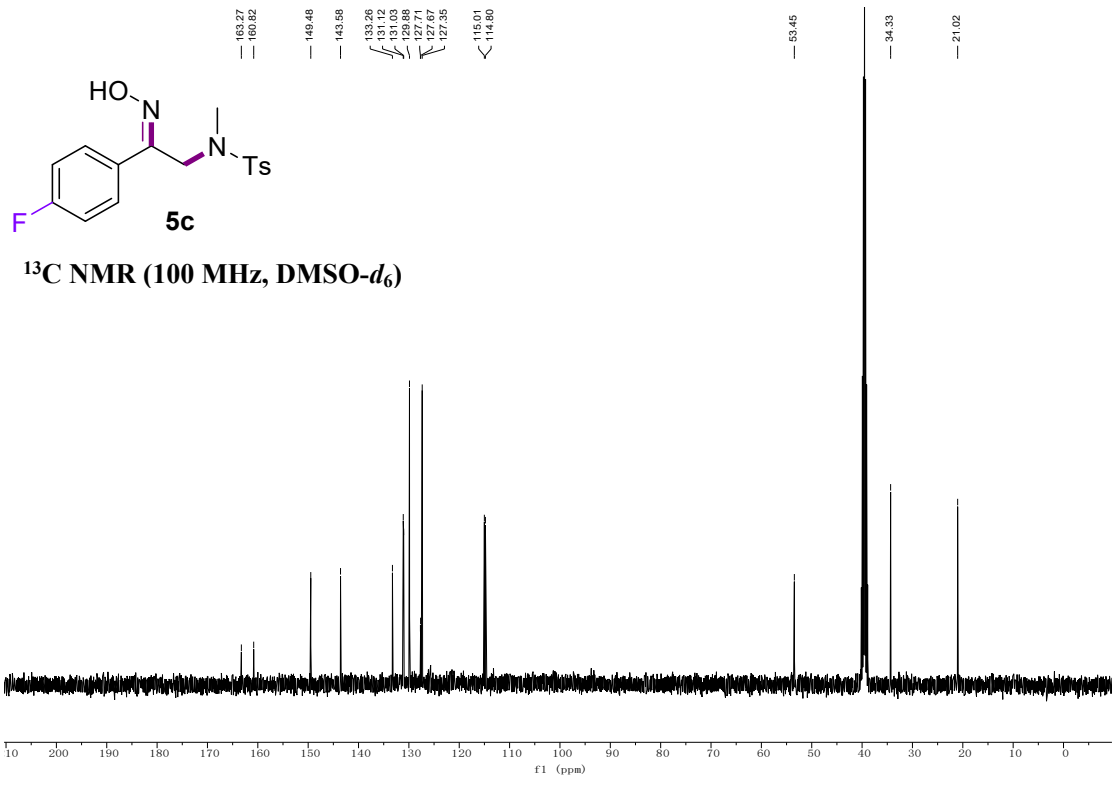


5b

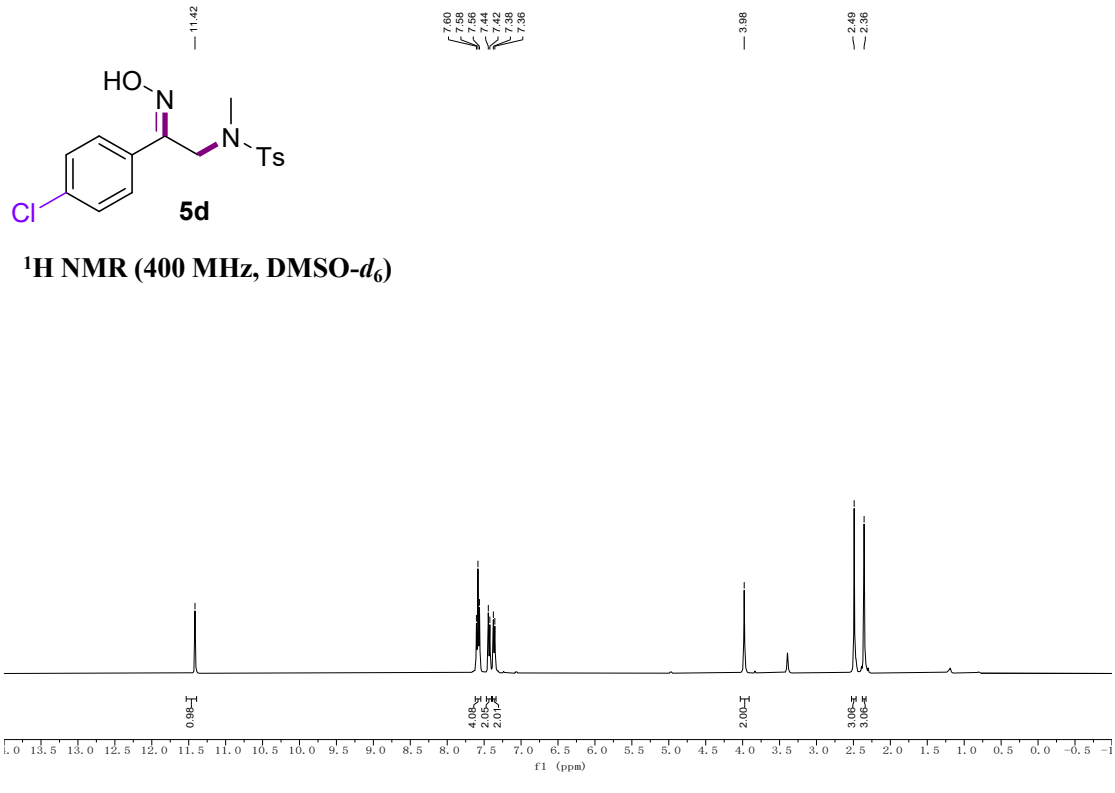
^{13}C NMR (100 MHz, $CDCl_3$)



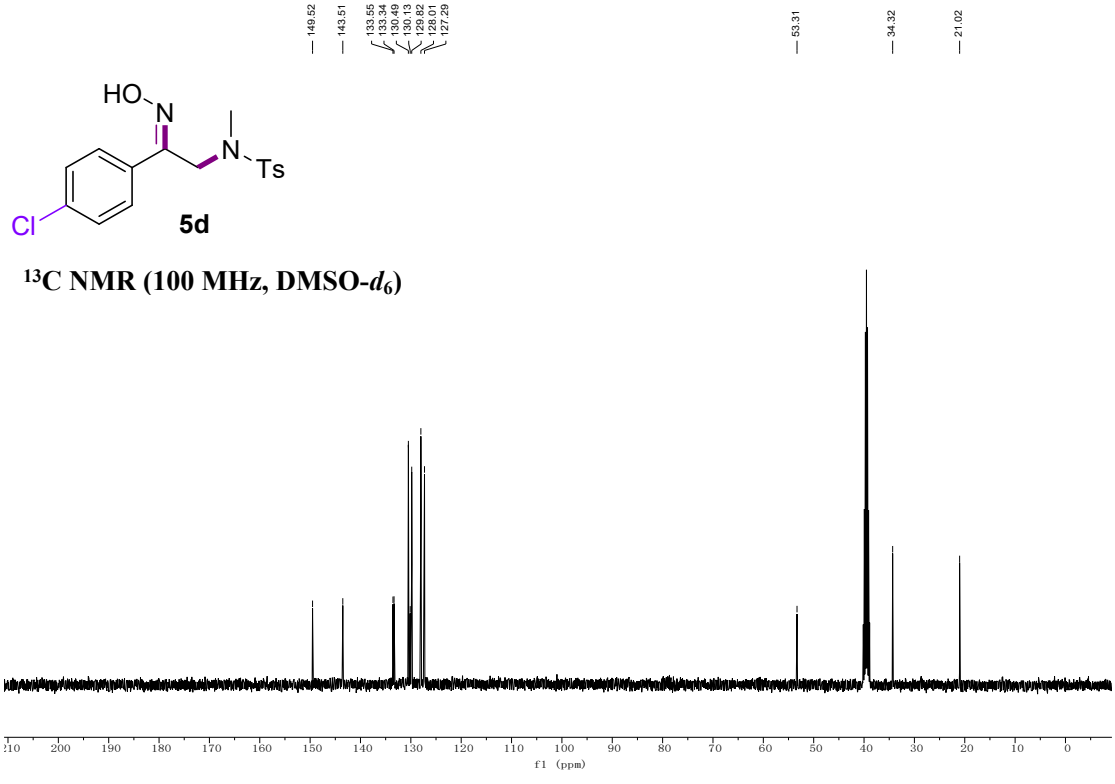
^{1}H NMR (400 MHz, DMSO-d_6)



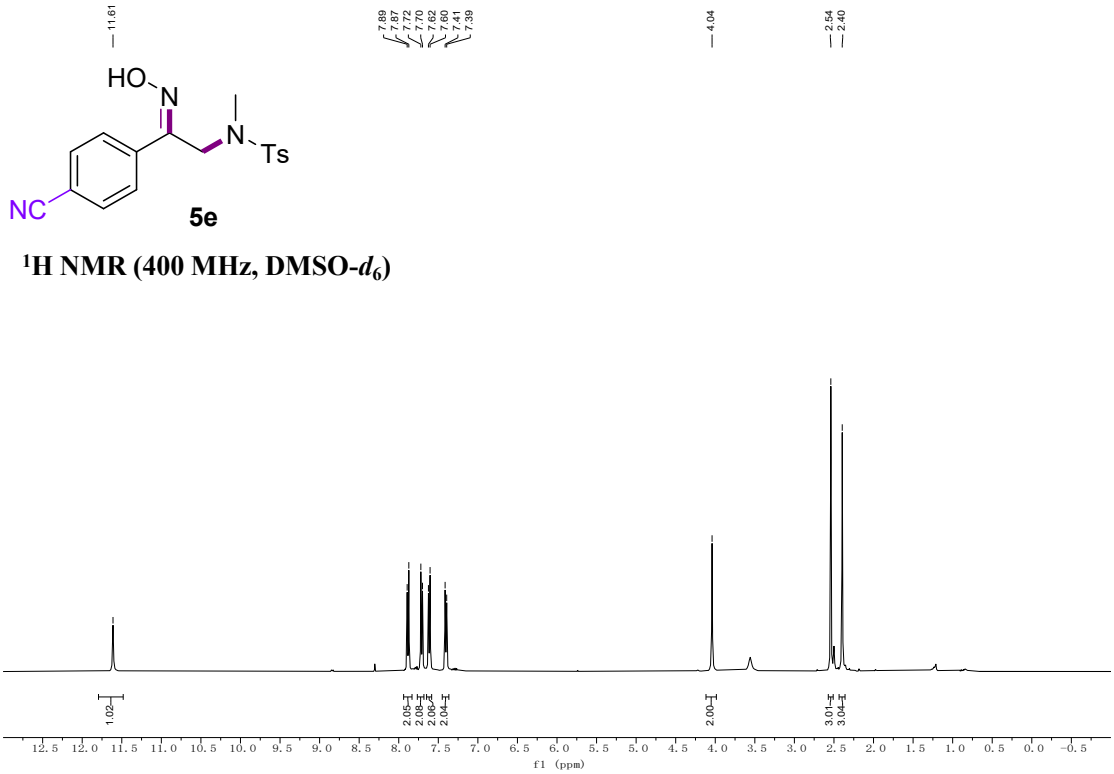
^{13}C NMR (100 MHz, DMSO-d_6)



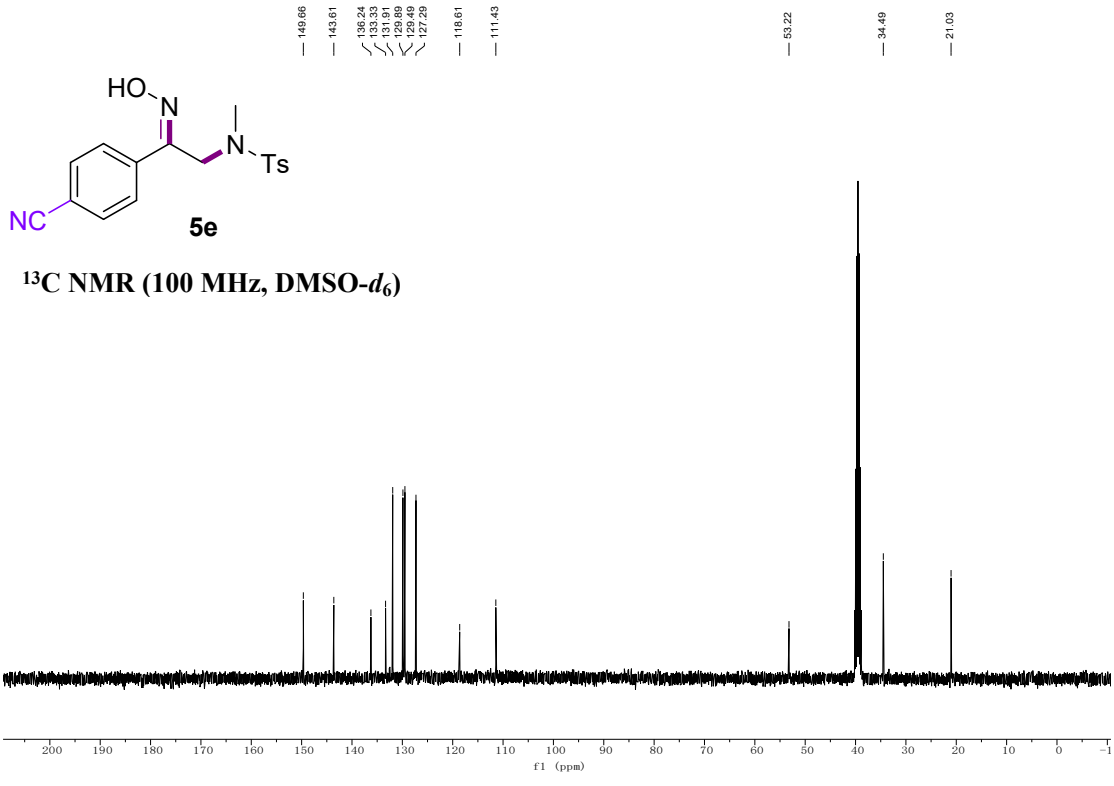
^{1}H NMR (400 MHz, DMSO-d_6)



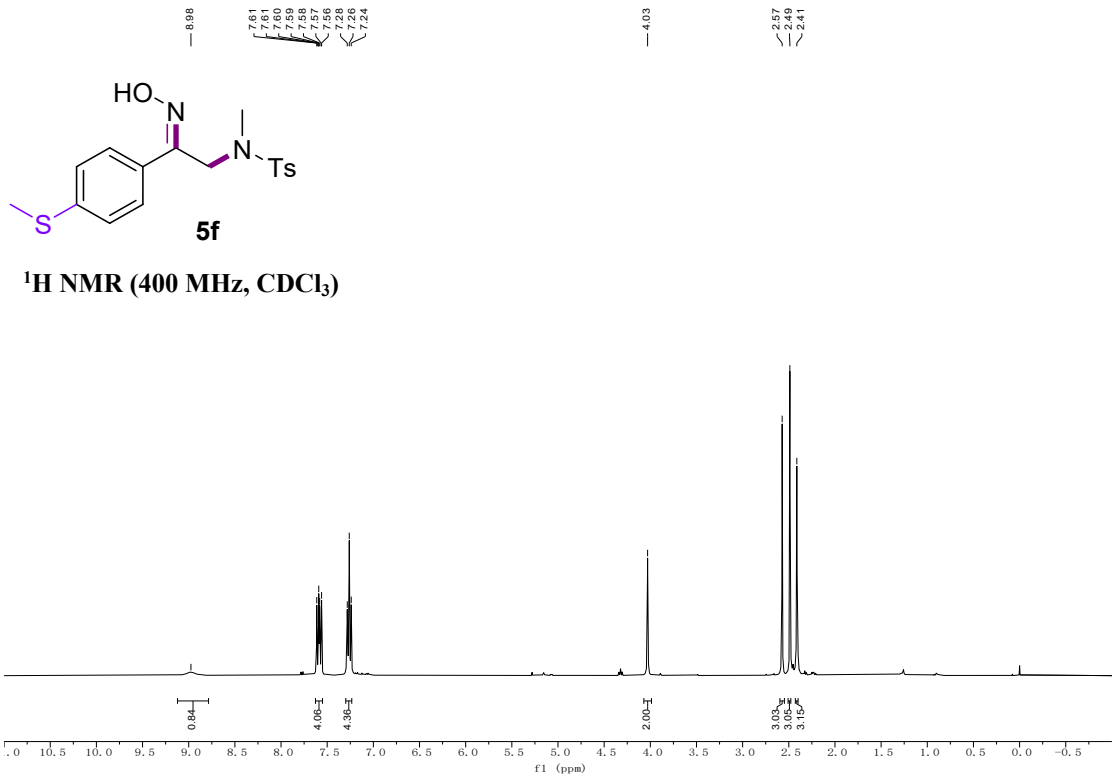
^{13}C NMR (100 MHz, DMSO-d_6)



^{1}H NMR (400 MHz, DMSO-d_6)

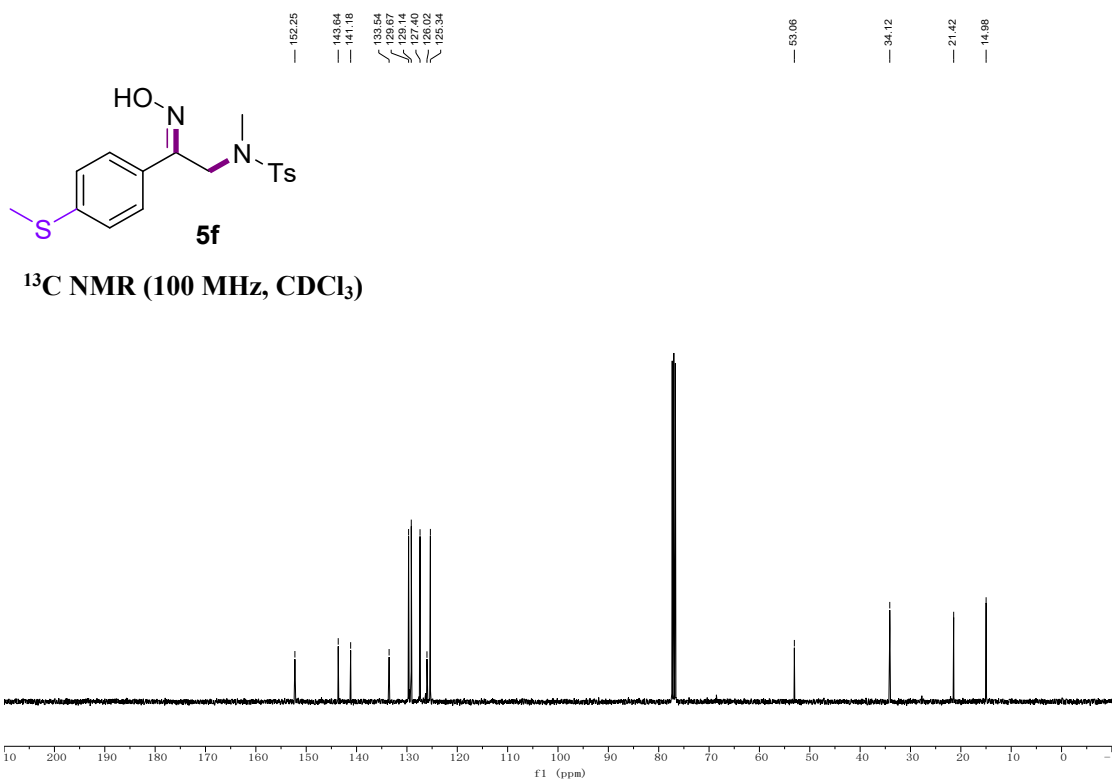


^{13}C NMR (100 MHz, DMSO-d_6)



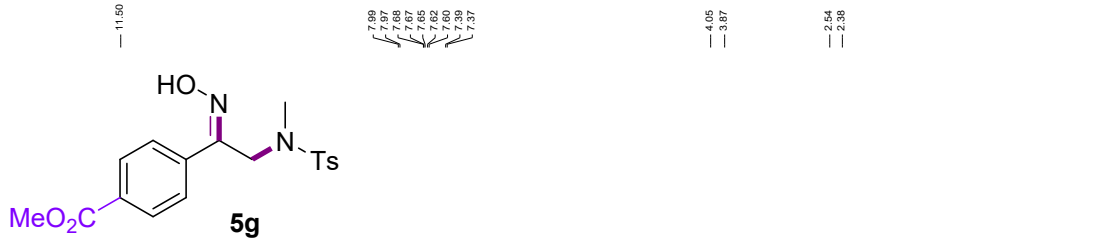
5f

^{1}H NMR (400 MHz, $CDCl_3$)



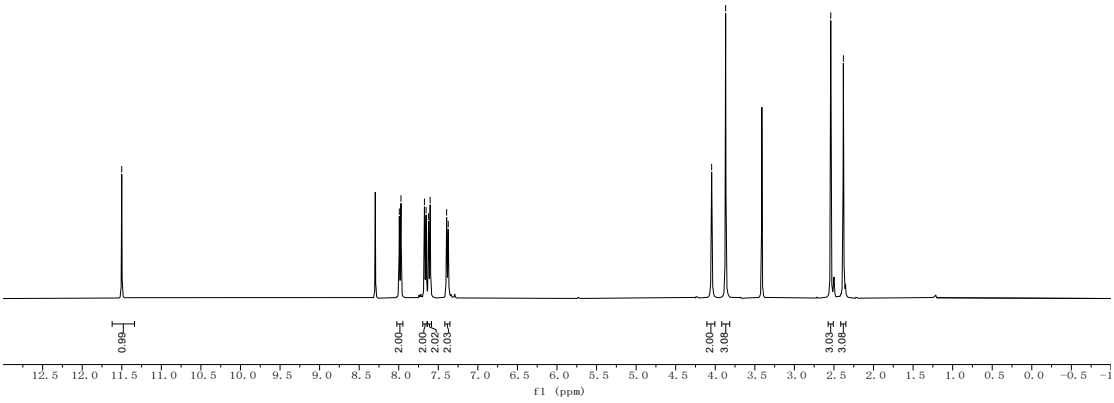
5f

^{13}C NMR (100 MHz, $CDCl_3$)



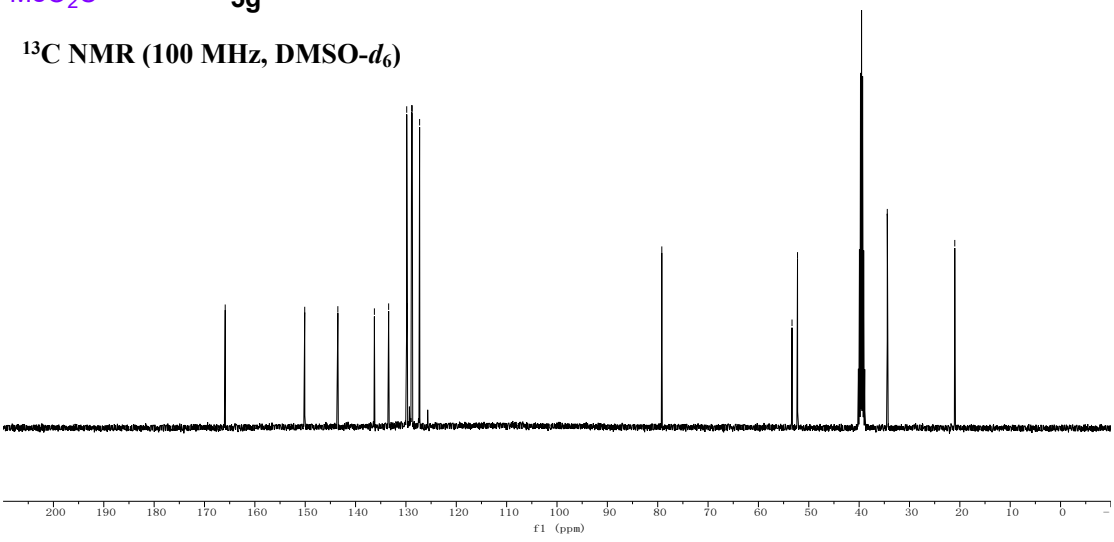
5g

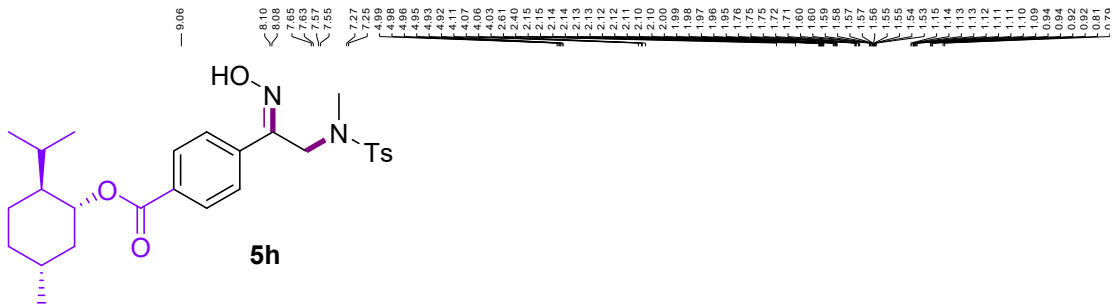
^{1}H NMR (400 MHz, DMSO-d_6)



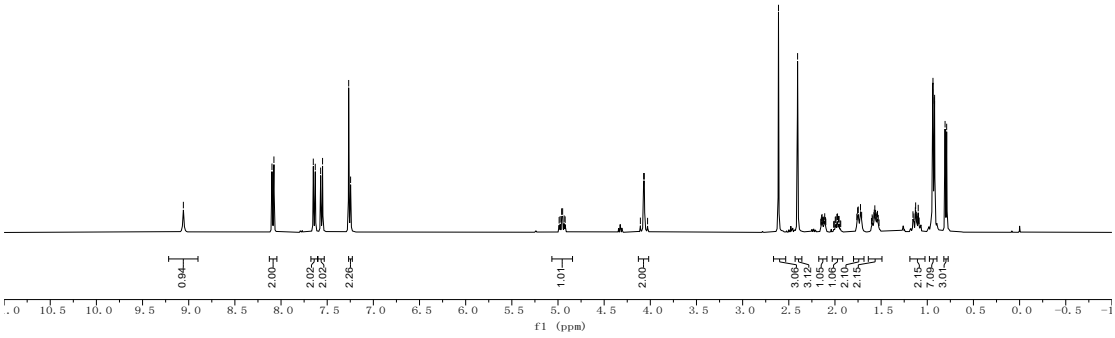
5g

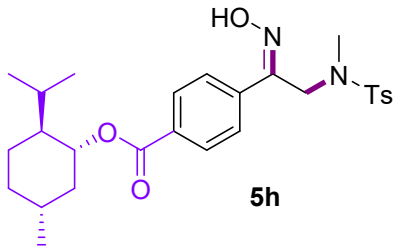
^{13}C NMR (100 MHz, DMSO-d_6)



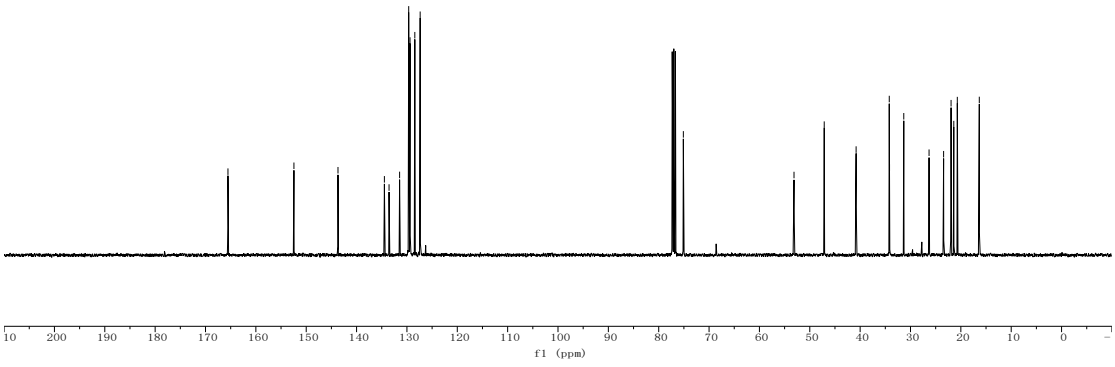


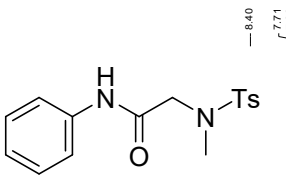
^{1}H NMR (400 MHz, $CDCl_3$)





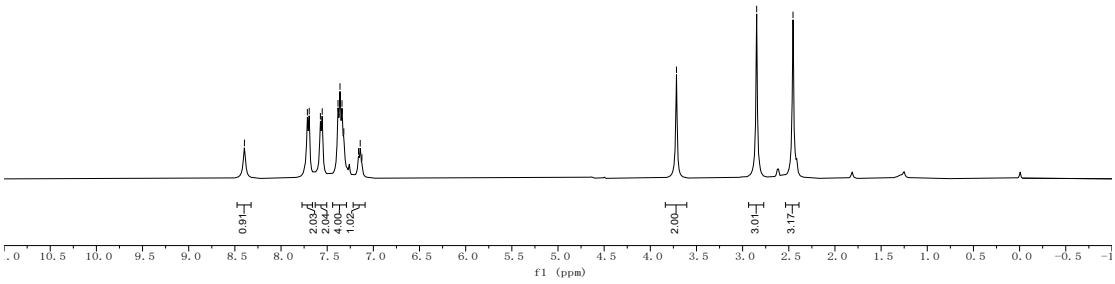
^{13}C NMR (100 MHz, $CDCl_3$)

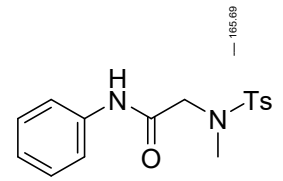




8

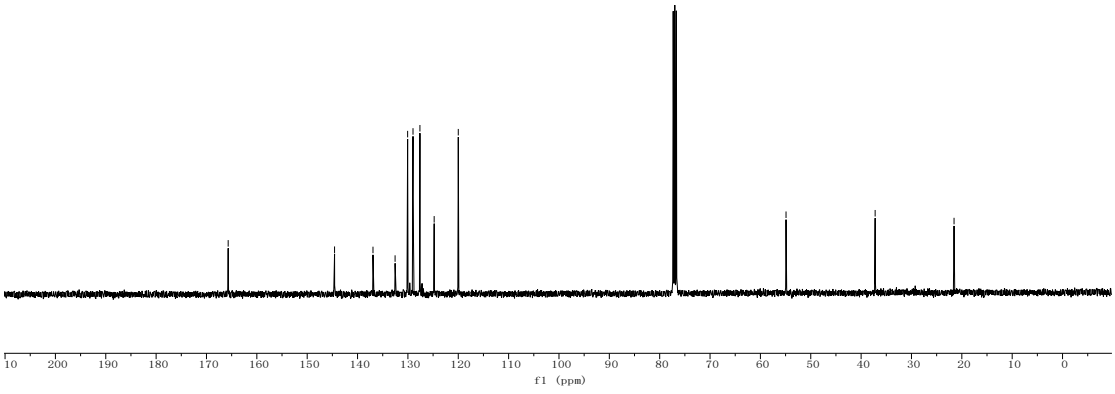
^{1}H NMR (400 MHz, $CDCl_3$)

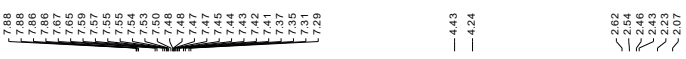


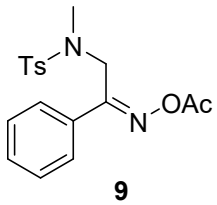


8

^{13}C NMR (100 MHz, $CDCl_3$)

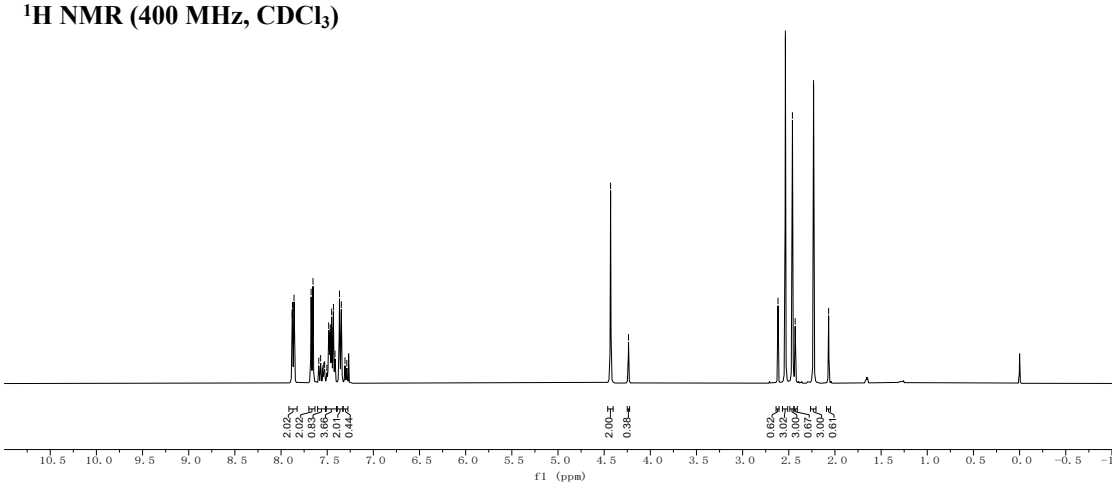


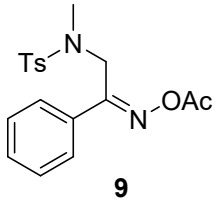




9

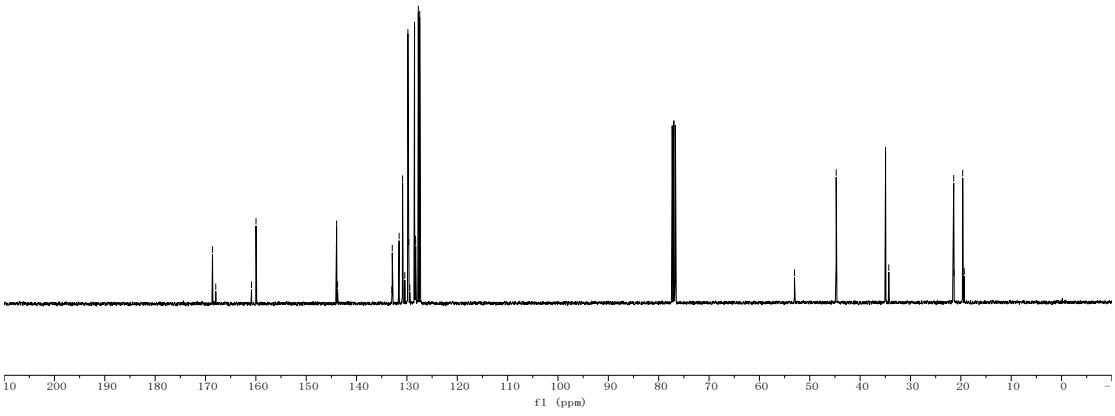
^{1}H NMR (400 MHz, $CDCl_3$)

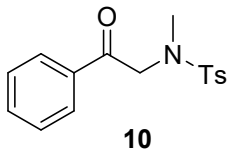




9

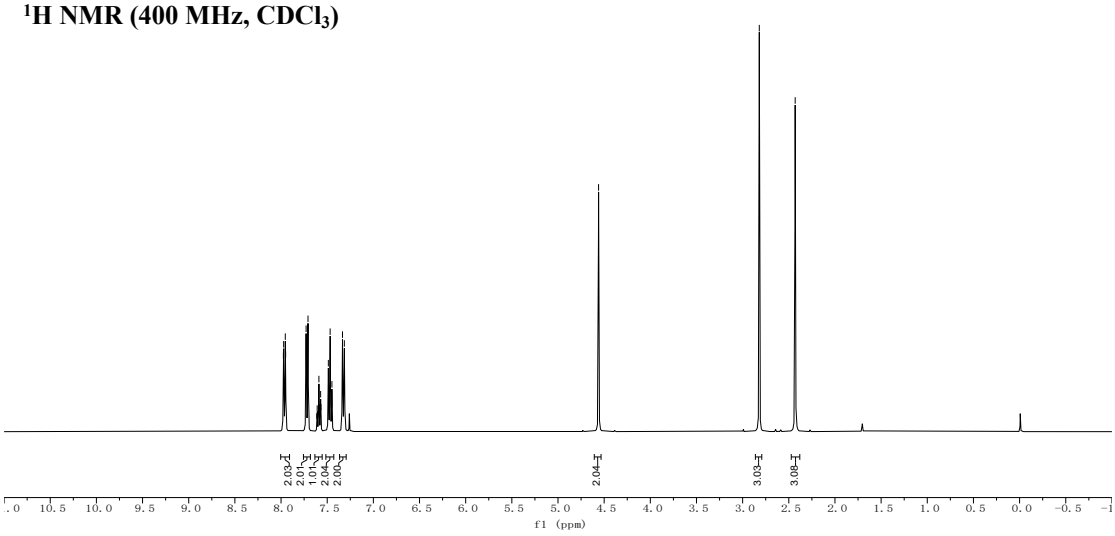
^{13}C NMR (100 MHz, $CDCl_3$)

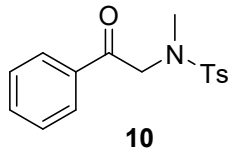




10

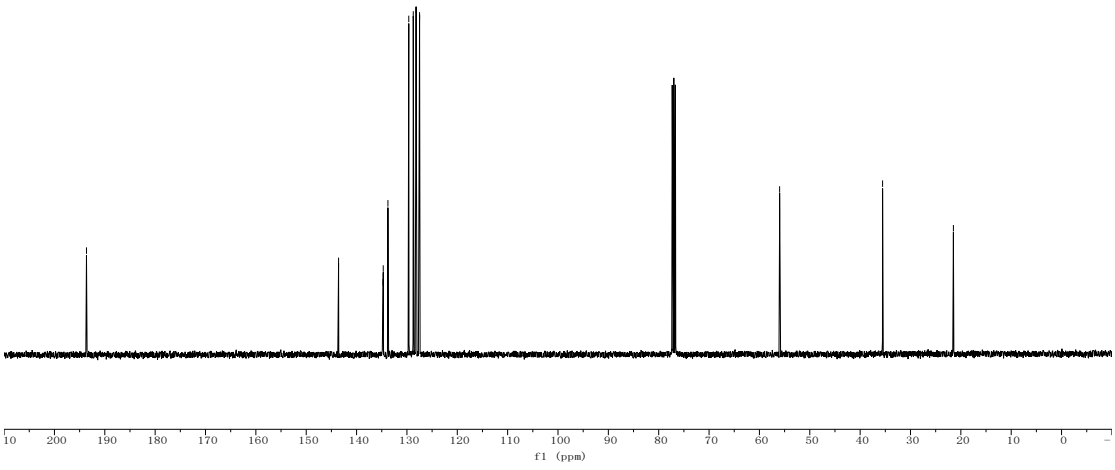
^{1}H NMR (400 MHz, $CDCl_3$)

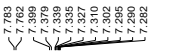


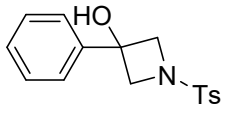


10

^{13}C NMR (100 MHz, $CDCl_3$)

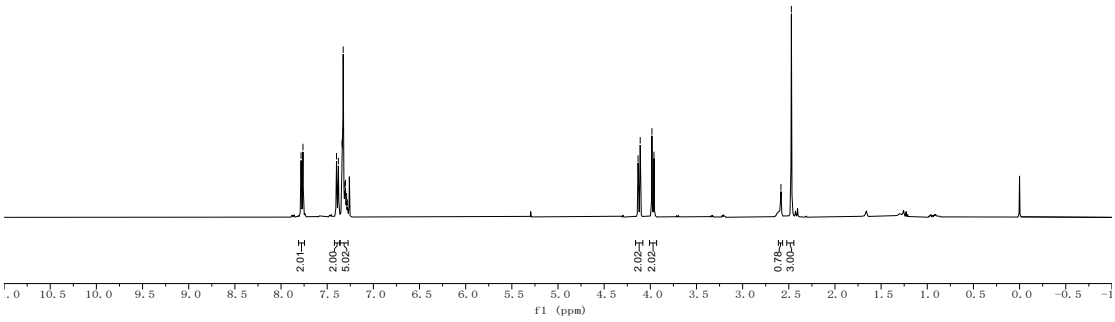


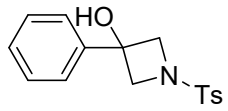




11

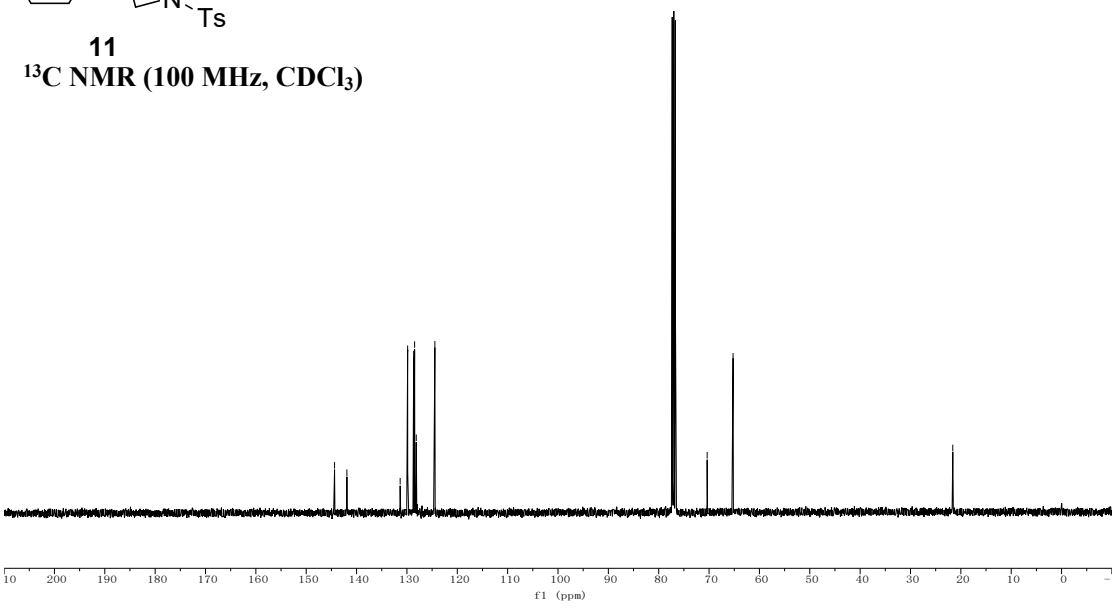
^{1}H NMR (400 MHz, $CDCl_3$)

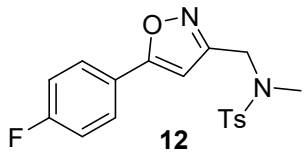




11

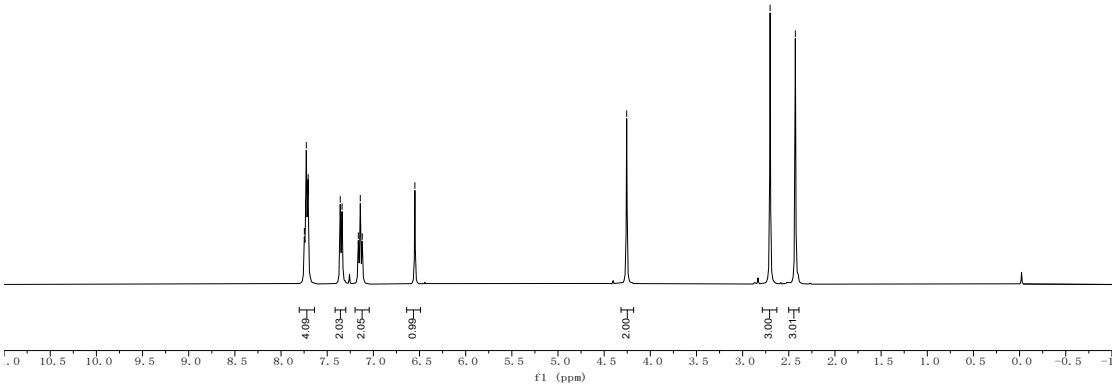
^{13}C NMR (100 MHz, $CDCl_3$)

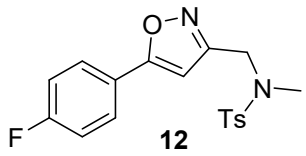




12

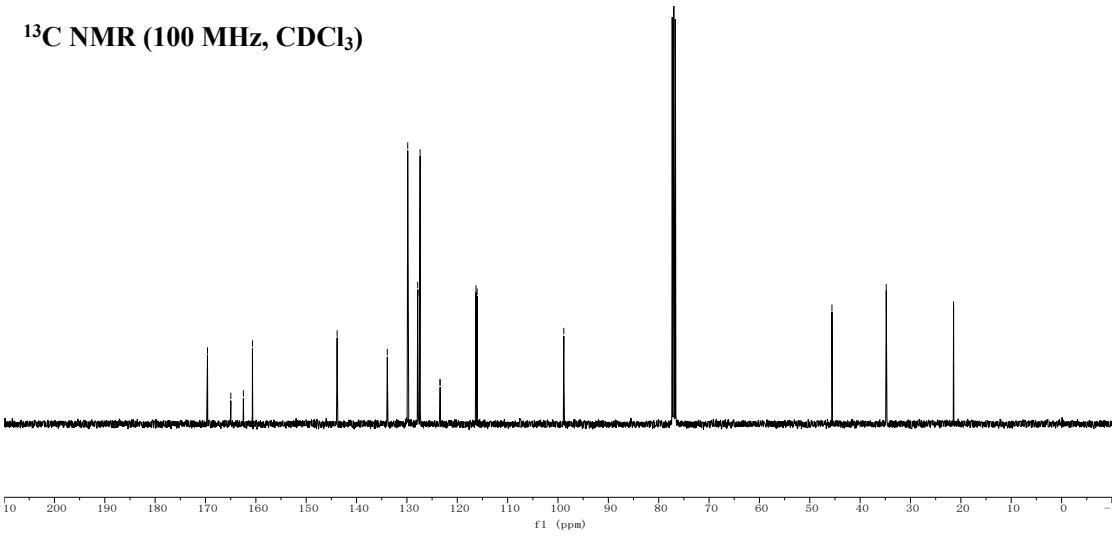
^{1}H NMR (400 MHz, $CDCl_3$)

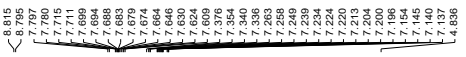


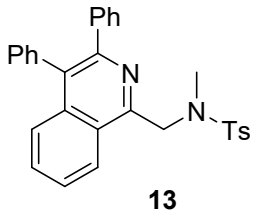


12

^{13}C NMR (100 MHz, $CDCl_3$)

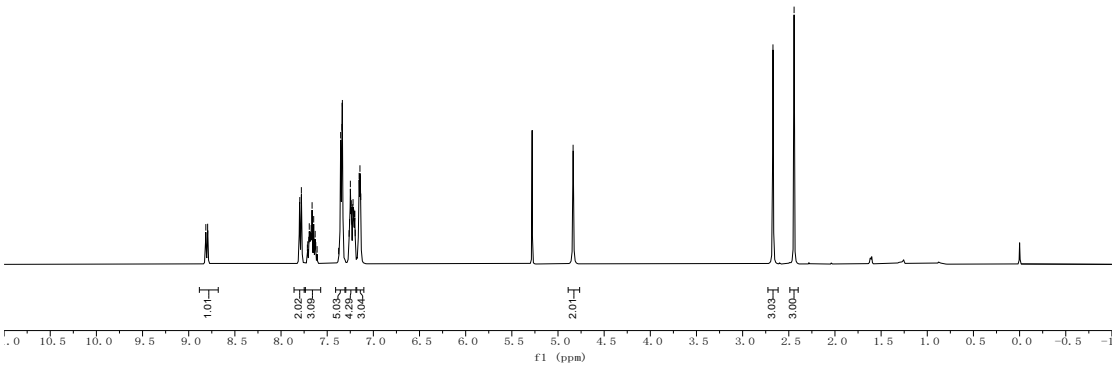


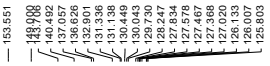


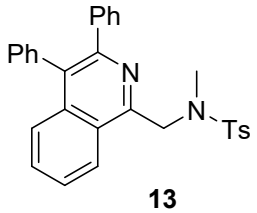


13

^{1}H NMR (400 MHz, $CDCl_3$)

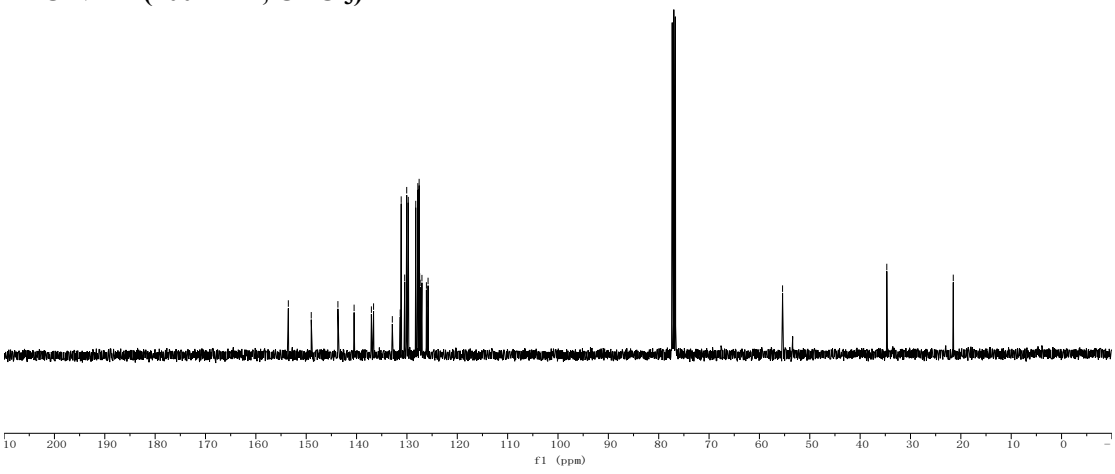


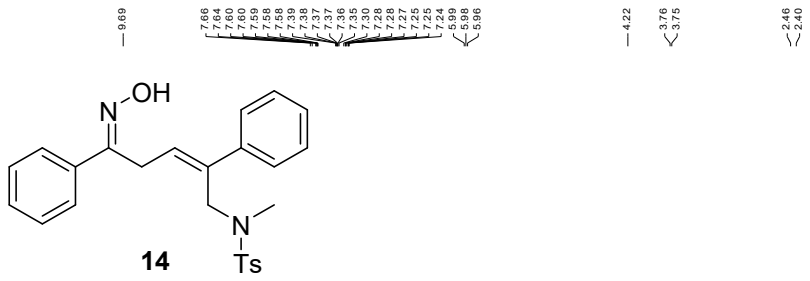




13

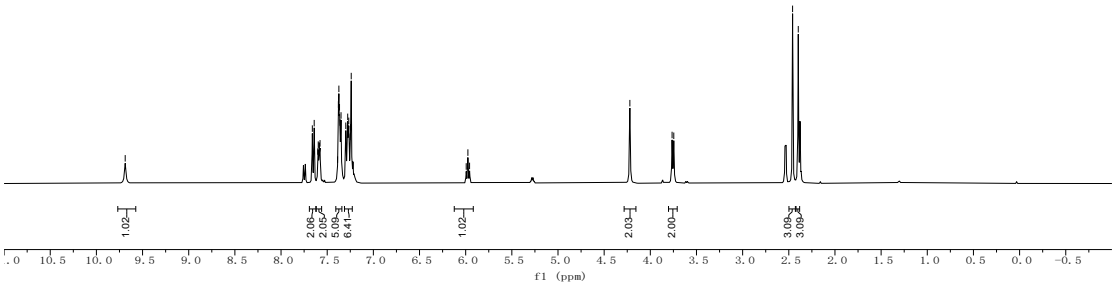
^{13}C NMR (100 MHz, $CDCl_3$)

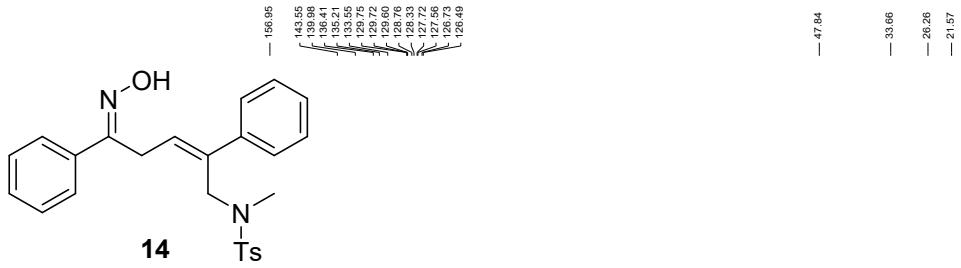




14

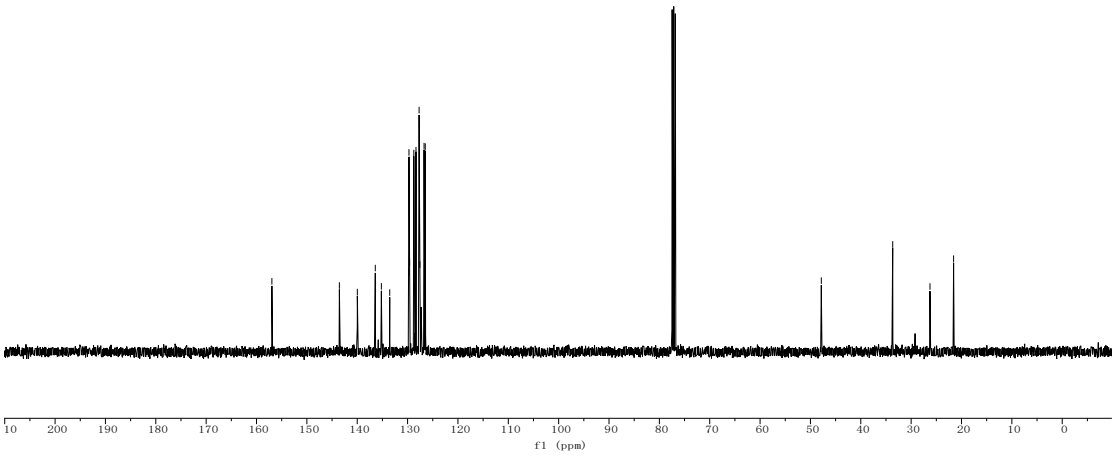
^{1}H NMR (400 MHz, $CDCl_3$)

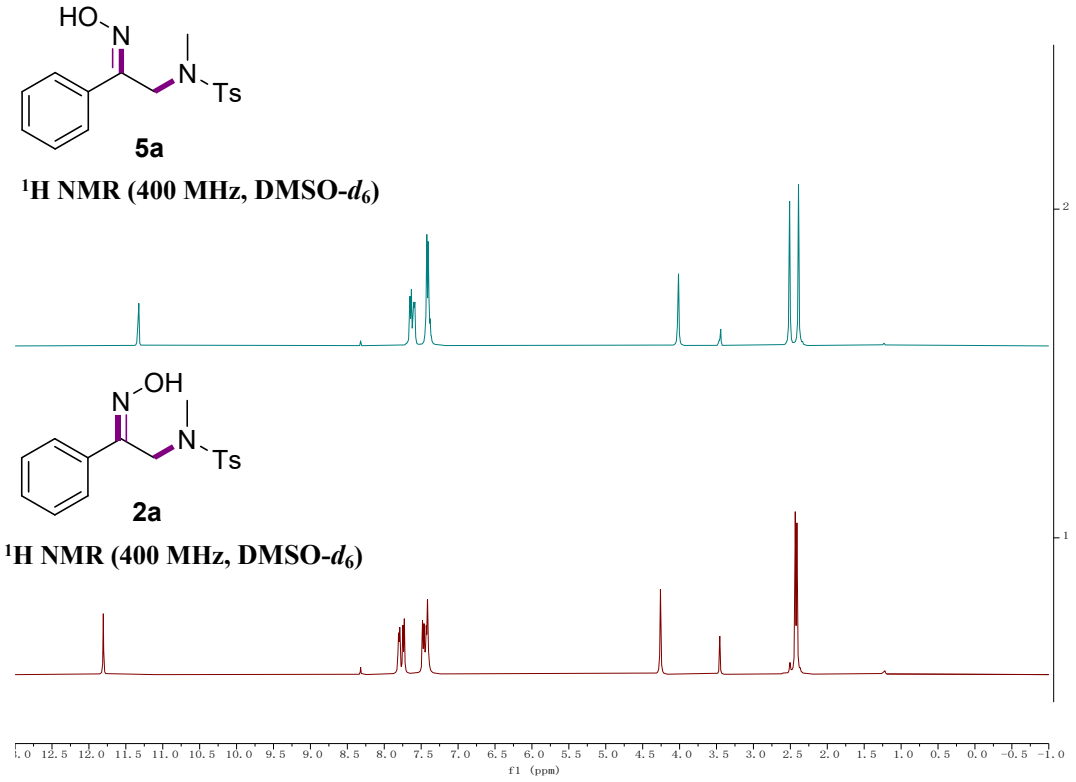


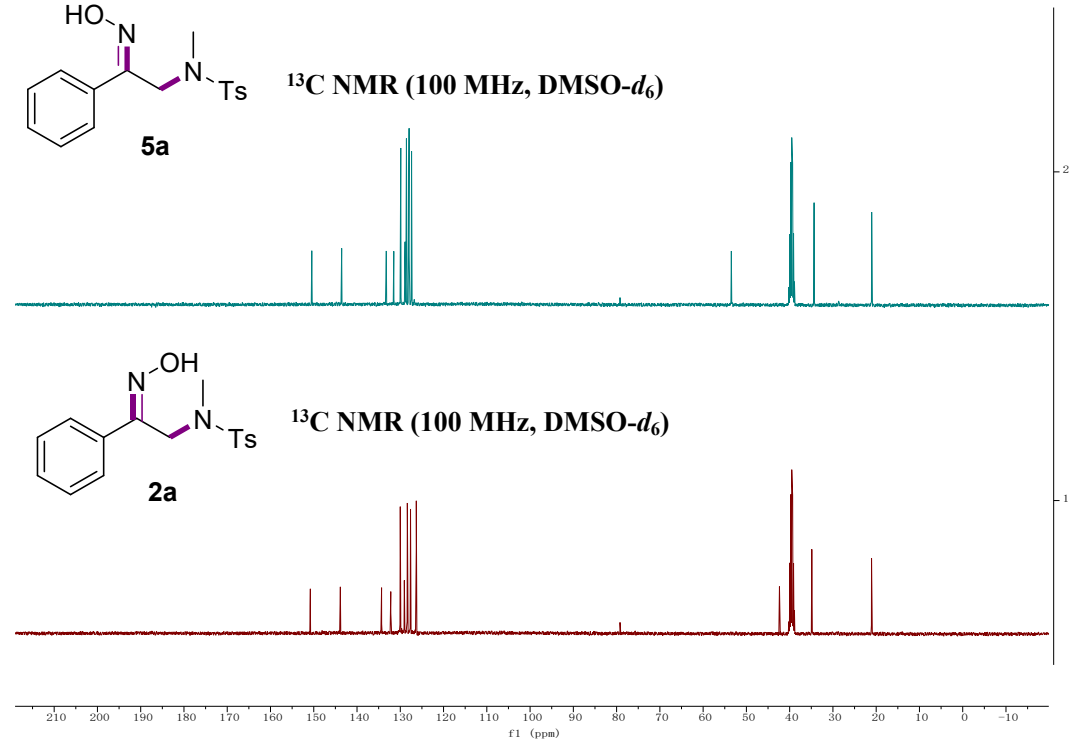


14

^{13}C NMR (100 MHz, $CDCl_3$)




HO
N
N
Ts
5a
1H NMR (400 MHz, DMSO-d6)
OH
N
N
Ts
2a
1H NMR (400 MHz, DMSO-d6)
f1 (ppm)


HO
N
N
Ts
5a
13C NMR (100 MHz, DMSO-d6)
OH
N
N
Ts
2a
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)