Supporting information

Regioselective *ortho* C–H Insertion of *N*-Nitrosoanilines with Naphthoquinone Carbenes

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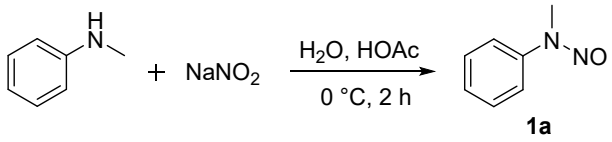
1. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 MHz or 500 MHz spectrometer. Chemical shifts of protons are reported in parts per million downfield from tetramethylsilane. Chemical shifts of carbon are referenced to the center line of a triplet at 77.0 ppm of chloroform-d_3, a heptet at 39.5 ppm of dimethyl sulfoxide-d_6 or a heptet at 29.8 ppm of acetone-d_6. Peaks are labeled as single (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), double doublet (dd), triple doublet (td), multiplet (m). Melting points were determined with a commercially available melting point apparatus. High-resolution mass spectra (HRMS) were acquired using an electron spray ionization time of flight (ESI-TOF) mass spectrometer in positive mode. All reagents were used without further purification as received from commercial suppliers unless otherwise noted. All solvents were dried and distilled prior to use according to the standard protocols.

2. General procedure for the preparation of substrates

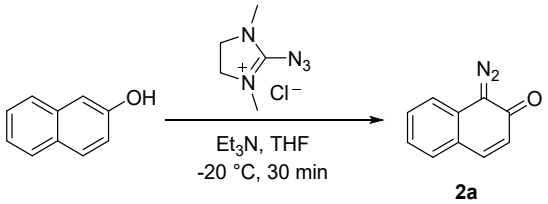
2.1 Preparation of *N*-nitrosoaniline 1 (taking 1a as an example)[1]



Scheme S1. Preparation of **1a**

To a solution of *N*-CH_3 aniline (1.1 g, 10 mmol) in a mixture of acetic acid (5 mL) and water (1 mL), an aqueous solution of $NaNO_2$ (1.0 g, 15 mmol) in water (3 mL) was added at 0 °C (in an ice-water bath). The reaction mixture was stirred for 2 h, then extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over sodium sulfate. The solvent was evaporated to give a residue, which was purified by flash chromatography to give yellow oil **1a** (1.3 g, 92%).

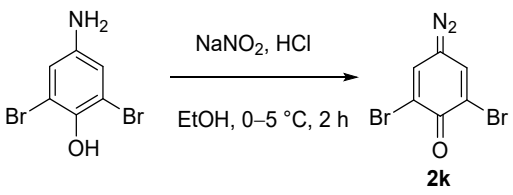
2.2 Preparation of diazonaphthoquinones 2a–2j (taking 2a as an example)[2]



Scheme S2. Preparation of **2a**

To a solution of 2-chloro-1,3-dimethylimidazoliniumchloride (253.6 mg, 1.5 mmol) in acetonitrile (2.0 mL), sodium azide (108.6 mg, 1.7 mmol) was added at -20 °C and the mixture was stirred for 30 min. A mixture of 2-naphthol (144.7 mg, 1.0 mmol) and triethylamine (202.4 mg, 2.0 mmol) in dry THF (4.0 mL) was added to the reaction mixture and was stirred for 20 min. The reaction was quenched with ice water and organic parts were extracted with CH_2Cl_2 (3 x 15 mL). The combined extracts were washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to afford crude compounds. The crude materials were purified by flash chromatography to give brown solid **2a** (127.6 mg, 75%).

2.3 Preparation of 2,6-dibromo-4-diazocyclohexa-2,5-dien-1-one 2k[3]



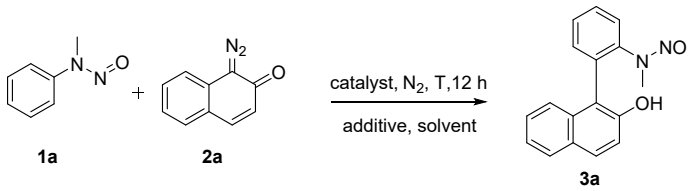
Scheme S3. Preparation of **2k**

To a solution of 4-amino-2,6-dibromophenol (266.9 mg, 1 mmol) in ethanol (5 mL), concentrated HCl (12 N, 0.5 mL) was added drop wise at 0–5 °C. The mixture was allowed to stir at the same temperature for another 10 min, then an ice-cold solution of $NaNO_2$ (207 mg, 3 mmol) was added to the mixture drop wise. The resulting mixture was allowed to stir at 0–5 °C for 2 h. It was diluted with 10 mL cold dichloromethane followed by the addition of ice. Then, the mixture was stirred vigorously with a cold solution of K_2CO_3 (7 mmol). The organic layer was separated with dichloromethane, and the aqueous layer was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, concentrated in vacuo at low temperature, and directly used in the next reaction without further purification.

3. General experimental procedure

3.1 Optimization of reaction conditions

Table S1. Screening of additive and optimization of reaction conditions[a]

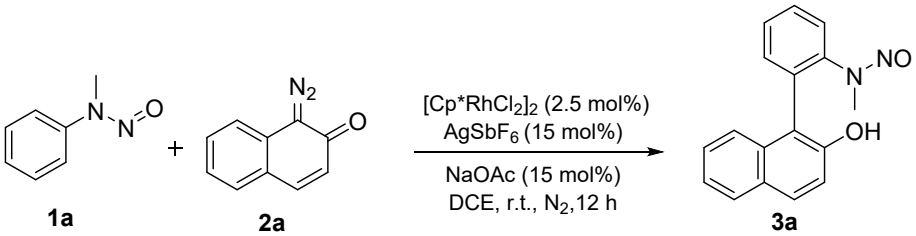


1a 2a 3a

Entry	Catalyst (mol%)	Additive 1 (mol%)	Additive 2 (mol%)	solvent	T (°C)	Yield[b] (%)
1	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)		DCE	r.t.	68
2	$Cp^*Co(CO)I_2$ (2.5)	$AgSbF_6$ (15)		DCE	r.t.	0
3	$[RuCl_2(p\text{-cymene})]_2$ (2.5)	$AgSbF_6$ (15)		DCE	r.t.	0
4	$[Cp^*IrCl_2]_2$ (2.5)	$AgSbF_6$ (15)		DCE	r.t.	0
5	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)	AgOAc (15)	DCE	r.t.	72
6	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)	NaOAc (15)	DCE	r.t.	86 (85[c])
7	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)	NaOAc (15)	MeOH	r.t.	23
8	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)	NaOAc (15)	THF	r.t.	32
9	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)	NaOAc (15)	1,4-Dioxane	r.t.	0
10	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)	NaOAc (15)	DMSO	r.t.	0
11	$[Cp^*RhCl_2]_2$ (2.5)	AgOAc (15)	NaOAc (15)	DCE	60	73

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), solvent (2.0 mL) under N_2 for 12 h; [b]Yield determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard; [c]Isolated yield after column chromatography.

3.2 General procedure for the synthesis of compound 3 (taking 3a as an example)



1a 2a 3a

Scheme S4. Preparation of compound **3a**

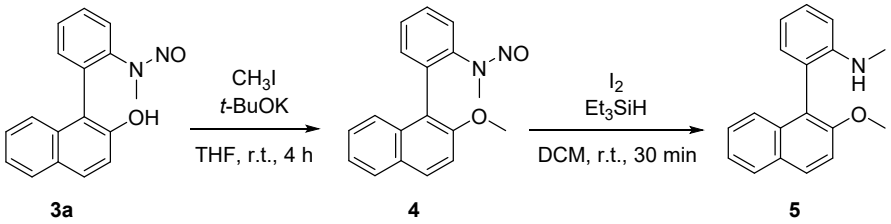
A 25 mL reaction tube equipped with a magnetic stirrer bar were charged with $[Cp^*RhCl_2]_2$ (4.6 mg, 2.5 mol%), $AgSbF_6$ (15.5 mg, 15 mol%), NaOAc (7.5 mg, 15 mol%), **1a** (40.8 mg, 0.3 mmol), and DCE (1.5 mL). To the mixture was then added 1-diazonaphthalen-2(1H)-one **2a** (51.0 mg, 0.3 mmol) in DCE (1.5 mL). The reaction mixture was stirred at r.t. under N_2 atmosphere for 12 h. The crude mixture was filtered through celite and concentrated under reduced pressure. The residue was then purified by flash chromatography (petroleum ether (PE): ethyl acetate (EA) = 20:1–4:1) to give the desired product **3a** (71.7 mg, 85%) as a yellow solid.

3.3 Gram Scale Experiment of compound 3a

A 50 mL flask equipped with a magnetic stirrer bar were charged with $[Cp^*RhCl_2]_2$ (61.8 mg, 2.5 mol%), $AgSbF_6$ (206.1 mg, 15 mol%), NaOAc (49.3 mg, 15 mol%), **1a** (544.2 mg, 4 mmol), and DCE (10 mL). To the mixture was then added 1-diazonaphthalen-2(1H)-one **2a** (680.7 mg, 3 mmol) in DCE (10 mL). The reaction mixture was stirred at r.t. under N_2 atmosphere for 12 h. The crude mixture was filtered through celite and concentrated under reduced pressure. The residue was then purified by flash chromatography to give the desired product **3a** (924.1 mg, 83%) as a yellow solid.

4. Transformations of product 3a

4.1 Preparation of compound 4 and 5



3a **4** **5**

Preparation of compound **4** and **5** (see the article **Scheme 4a**)

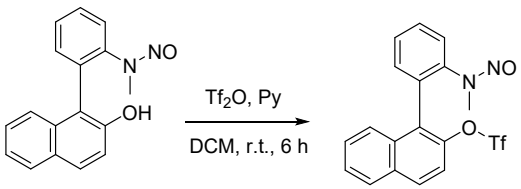
(1) Preparation of compound 4

In a 50 mL round bottom flask, **3a** (139.0 mg, 0.5 mmol), potassium *tert*-butoxide (67.4 mg, 0.6 mmol) and dry THF (5 mL) were added at r.t. under N_2 atmosphere. Then, CH_3I (85.2 mg, 0.6 mmol) was added drop wise by a syringe. The mixture was stirred at r.t. for 4 h. After completion of the reaction, mixture was quenched with saturated NH_4Cl solution and extracted with DCM (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography to obtain product **4** (143.2 mg, 98% yield) as a white solid.

(2) Preparation of compound 5[4]

In a 25 mL round bottom flask, **4** (87.6 mg, 0.3 mmol) was allowed to stir in DCM (3 mL) approximately for 2 min at r.t. to which iodine (22.9 mg, 0.3 mmol) and triethylsilane (52.3 mg, 0.45 mmol) was added. The reaction was further allowed to stir for 30 min and the progress of the reaction was monitored by TLC. After completion, the reaction mixture was quenched with saturated solution of sodium thiosulfate (20 mL) extracted with ethyl acetate (2 x 25 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography to obtain product **5** (65.0 mg, 82% yield) as a yellow oil.

4.2 Preparation of compound 6

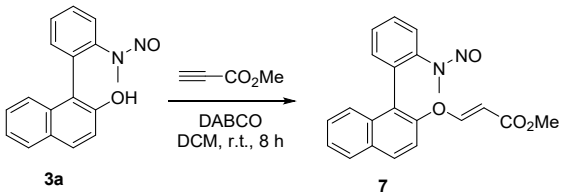


3a **6**

Preparation of **compound 6** (see the article **Scheme 4b**)

To a solution of **3a** (139.0 mg, 0.5 mmol) in dry CH_2Cl_2, pyridine (79.1 mg, 1.0 mmol) was added and the solution was cooled to 0 ºC. Next, trifluoromethanesulfonic anhydride (169.3 mg, 0.6 mmol) was added dropwise and stirred for 6 h at r.t.. After completion of the reaction time, the reaction mixture was concentrated under reduced pressure. The crude product was purified by column chromatography to obtain product **6** (170.2 mg, 83%) as a yellow oil.

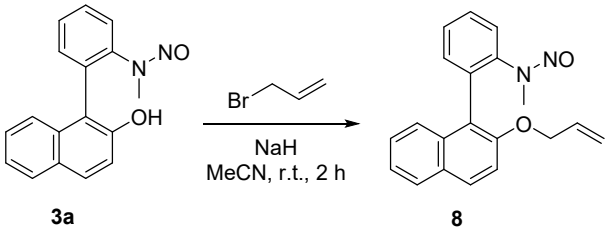
4.3 Preparation of compound 7



Preparation of **7** (see the article **Scheme 4c**)

In an oven dried 25 mL round bottom flask, **3a** (83.5 mg, 0.3 mmol) was dissolved in dry DCM (5 mL). Then DABCO (3.36 mg, 0.03 mmol) and methyl propiolate (30.6 mg, 0.36 mmol) were added. The reaction mixture was allowed to stir at r.t. for 7 h under N_2 atmosphere. The solvent was evaporated under reduced pressure. The residue was purified by flash chromatography to obtain product **7** (98.5 mg, 91%) as a yellow oil.

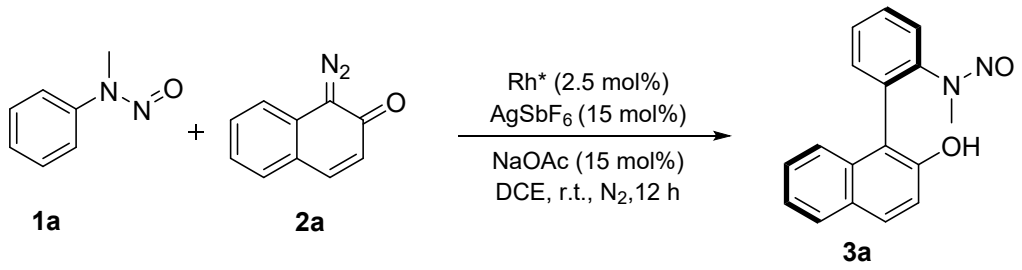
4.4 Preparation of compound 8

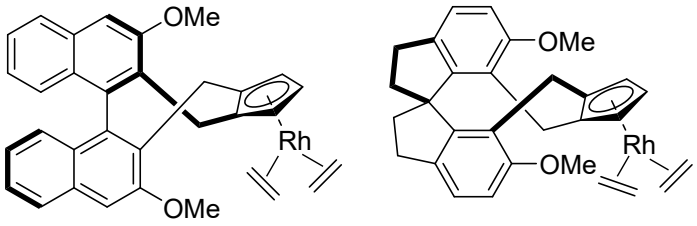


Preparation of compound **8** (see the article **Scheme 4d**)

To a dry three-neck flask was charged with **3a** (55.7 mg, 0.2 mmol), NaH (49.9 mg, 1.0 mmol) and MeCN (3 mL) under N_2 atmosphere. The reaction mixture was stirred vigorously at r.t. for 0.5 h and allylbromide (242.0 mg, 2.0 mmol) dissolved in MeCN (2 mL) was added. The reaction mixture was stirred vigorously at r.t. for 2 h until the substrate **3a** disappeared (monitored by TLC). At this time, the reaction was quenched by H_2O (10 mL) and extracted with DCM (3 x 10 mL). Then, the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography to obtain product **8** (60.0 mg, 94%) as a yellow oil.

4.5 Preparation of axially chiral biaryl product



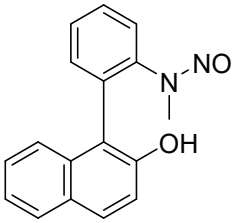


Rh*-1 Rh*-2

(+)-**3a**, 83% yield, 46% ee (-)-**3a,** 58% yield, 23% ee

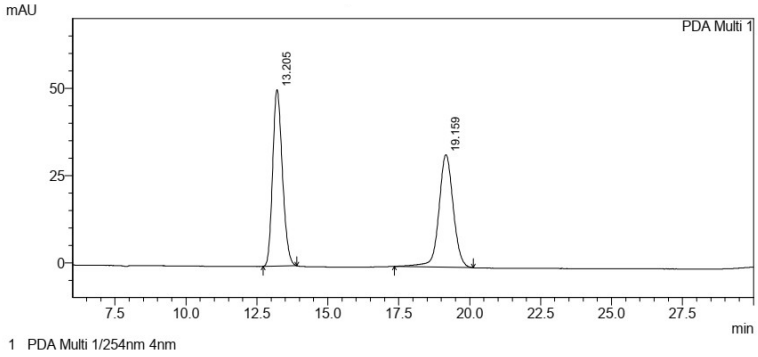
A 25 mL reaction tube equipped with a magnetic stirrer bar were charged with Cat. [Rh] (0.00125mmol, 2.5 mol%), $AgSbF_6$ (2.6 mg, 15 mol%), NaOAc (0.7 mg, 15 mol%), **1a** (6.8 mg, 0.05 mmol), and DCE (0.25 mL). To the mixture was then added 1-diazonaphthalen-2(1H)-one **2a** (8.5 mg, 0.05 mmol) in DCE (0.25 mL). The reaction mixture was stirred at r.t. under N_2 atmosphere for 12 h. The crude mixture was filtered through celite and concentrated under reduced pressure. The residue was then purified by flash chromatography) to give the product **3a.**

Racemic Product 3a



3a

HPLC condition: Chiralpak AS-H (Hex/$_i$PrOH = 90/10, 1.0 mL/min, t_R (major) = 13.205 min, t_R (minor) = 19.159 min).



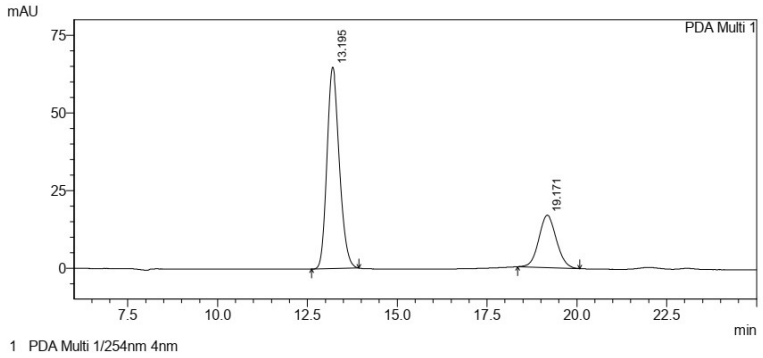
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.205	1207648	50633	51.507	61.045
2	19.159	1136995	32311	48.493	38.955
Total		2344643	82944	100.000	100.000

(+)-3a, 83% yield, 46% ee; $[\alpha]_D^{20}$ = 5.0 (c=1.0 in MeCN).

HPLC condition: Chiralpak AS-H (Hex/$_i$PrOH = 90/10, 1.0 mL/min, t_R (major) = 13.195 min, t_R (minor) = 19.171 min).



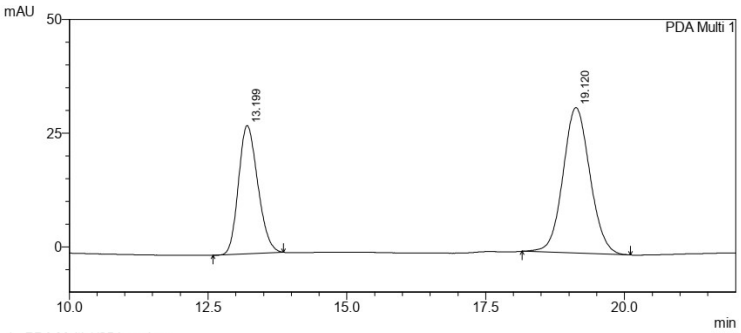
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.195	1566468	65007	73.099	79.383
2	19.171	576479	16883	26.901	20.617
Total		2142947	81891	100.000	100.000

(-)-3a, 58% yield, 23% ee; $[\alpha]_D^{25}$ = -3.0 (c=1.0 in MeCN).

HPLC condition: Chiralpak AS-H (Hex/$_i$PrOH = 90/10, 1.0 mL/min, t_R (minor) = 13.199 min), t_R (major) = 19.120 min.



1 PDA Multi 1/254nm 4nm

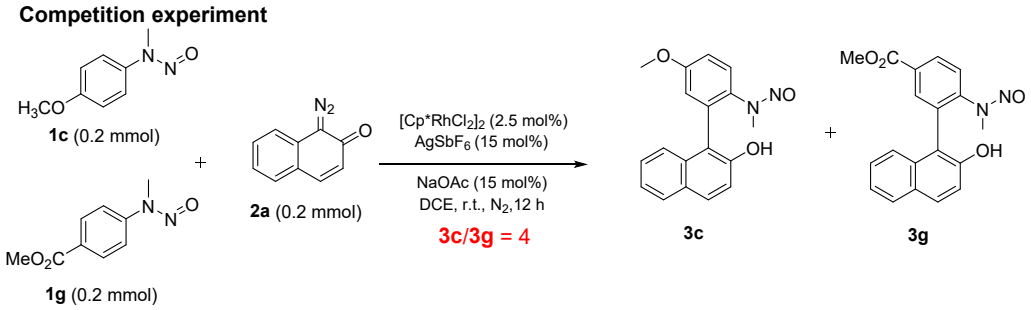
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.199	681892	28249	38.637	46.849
2	19.120	1082959	32049	61.363	53.151
Total		1764850	60298	100.000	100.000

5. Control experiments

5.1 Electronic effect



Competition experiment of **1c**, **1g** with **2a** (see the article **Scheme 5a**)

A 25 mL reaction tube equipped with a magnetic stirrer bar were charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol%), $AgSbF_6$ (10.3 mg, 15 mol%), AgOAc (5.0 mg, 15 mol%), **1c** (33.2 mg, 0.2 mmol), **1g** (38.8 mg, 0.2 mmol) and DCE (1 mL). To the mixture was added **2a** (34.1 mg, 0.2 mmol) in DCE (1 mL). The reaction mixture was stirred at r.t. under N_2 atmosphere for 12 h. The crude mixture was filtered through celite and concentrated in vacuo. The residue was then purified by flash column chromatography. The ratio of **3c** and **3h** was determined to be 4:1 by ^{1}H NMR analysis.

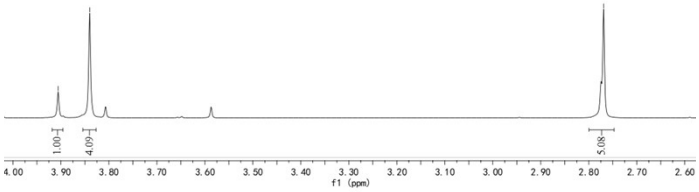
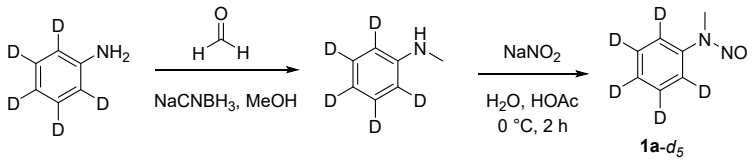


Figure S1 ^{1}H NMR spectra of the mixture of **3c** and **3h**

5.2 Kinetic isotopic effects

a) Preparation of compound 1a-d_5[1,4]



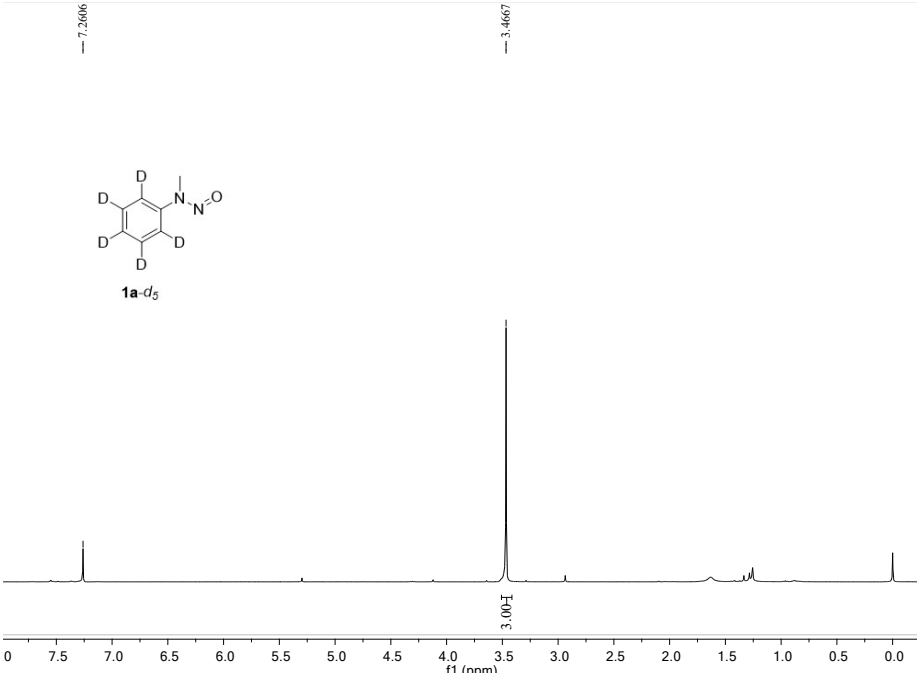
Scheme S5. Preparation of compound **1a-d_5**

To a solution of d_5-aniline (490.8 mg, 5 mmol) in methanol (10 mL) was added formaldehyde (243.2 mg, 3 mmol, 37% w/w in H_2O), and $NaCNBH_3$ (282.8 mg, 4.5 mmol). The solution was stirred at 25 ℃ for 12 h, then extracted with CH_2Cl_2, and the organic layer was washed with brine, and dried

over sodium sulfate. The solvent was evaporated to give a residue, which was purified by flash chromatography to give d_5-*N*-methylaniline (60.1 mg, 18%) as a yellow oil.

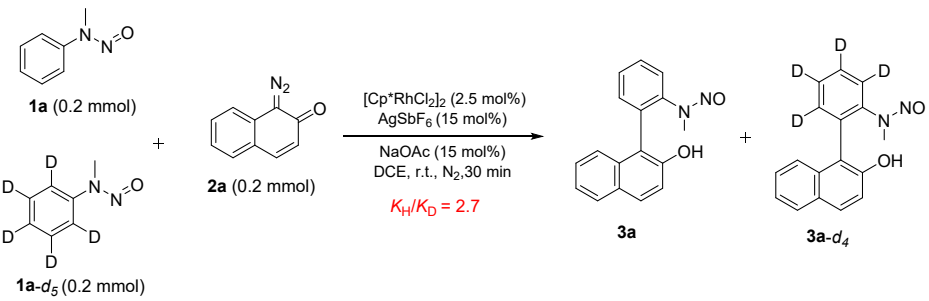
To a solution of d_5-*N*-methylaniline (44.9 mg, 0.4 mmol) in a mixture of acetic acid (3 mL) and water (0.5 mL), an aqueous solution of $NaNO_2$ (41.4 mg, 0.6 mmol) in water (1 mL) was added at 0 °C (in an ice-water bath). The reaction mixture was stirred for 2 h, then extracted with CH_2Cl_2. Then the organic layer was washed with brine, and dried over sodium sulfate. The solvent was evaporated to give a residue, which was purified by flash-chromatography to give a yellow oil **1a**-d_5 (53.5 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.47 (s, 3H).

^{1}H NMR (400 MHz) Spectrum of 1a-d_5 in $CDCl_3$



b) Determination of KIE

Competitive experiment



Intermolecular competition experiment of **1a**, **1a**-d_5 with **2a** (see the article **Scheme 5b**)

A 25 mL reaction tube equipped with a magnetic stirrer bar were charged with $[Cp^*RhCl_2]_2$ (3.1mg,

2.5 mol%), $AgSbF_6$ (10.3 mg, 15 mol%), AgOAc (5.0 mg, 15 mol%), **1a** (27.2 mg, 0.2 mmol), **1a**-d_5 (38.2 mg, 0.2 mmol), and DCE (1 mL). To the mixture was added **2a** (34.1 mg, 0.2 mmol) in DCE (1 mL). The reaction mixture was stirred at r.t. under N_2 atmosphere for 30 min. The crude mixture was filtered through celite and concentrated under reduced pressure. The residue was then purified by flash column chromatography to afford the mixture of **3a and 3a**-d_4. The ratio of **3a** and **3a**-d_4 was determined to be 0.73: 0.27 by ^{1}H NMR analysis (DMSO-d_6). The KIE value is equal to 2.7.

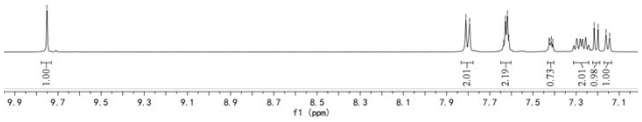
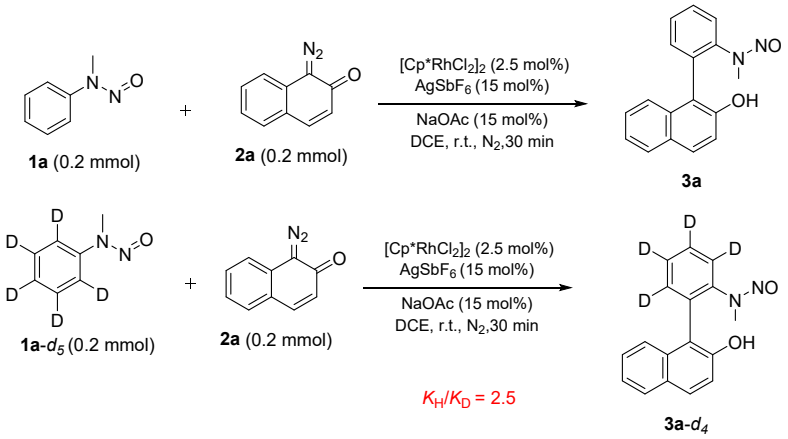


Figure S2 ^{1}H NMR spectra of the mixture of **3a** and **3a**-d_4

Parallel experiment



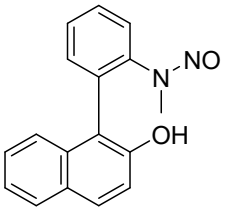
parallel experiment of **1a**, **1a**-d_5 with **2a** (see the article **Scheme 5c**)

A 25 mL reaction tube equipped with a magnetic stirrer bar were charged with $[Cp^*RhCl_2]_2$ (3.1mg, 2.5 mol%), $AgSbF_6$ (10.3 mg, 15 mol%), AgOAc (5.0 mg, 15 mol%), **1a** (27.2 mg, 0.2 mmol) and DCE (1 mL). To the mixture was added **2a** (34.1 mg, 0.2 mmol) in DCE (1 mL). The reaction mixture was stirred at r.t. under N_2 atmosphere for 30 min. The crude mixture was filtered through celite and concentrated under reduced pressure. The residue was then purified by flash column chromatography to afford the mixture of **3a** (37mg, 66.47%yield).

In another reaction tube, **1a**-d_5 (28.2 mg, 0.2 mmol) was used instead of **1a**. The product **3a**-d_4 was obtained in a (15mg, 26.56%yield). The kinetic isotope effect (KIE) is determined as 2.5.

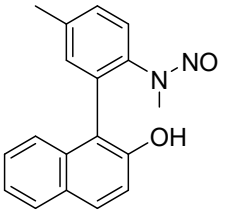
6. Characterization data for products

***N*-(2-(2-hydroxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3a)**



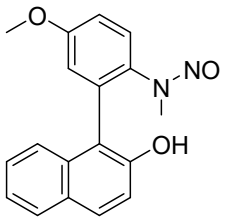
Yellow solid (71.1 mg, 85% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 161.3–161.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83–7.74 (m, 2H), 7.68–7.60 (m, 3H), 7.55–7.48 (m, 1H), 7.34–7.29 (m, 2H), 7.27–7.22 (m, 1H), 7.17 (d, *J* = 8.9 Hz, 1H), 5.43 (s, 1H), 2.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.7, 142.9, 133.4, 132.8, 130.5, 130.2(1), 130.1(6), 129.8, 128.8, 128.2, 127.1, 126.5, 123.9, 123.7, 117.8, 117.2, 34.5; **HRMS (ESI)**: calculated for $C_{17}H_{13}N_2O_2$ $[M-H]^-$: 277.0983, found: 277.0980.

***N*-(2-(2-hydroxynaphthalen-1-yl)-4-methylphenyl)-*N*-methylnitrous amide (3b)**



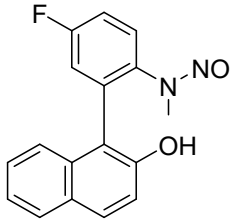
Yellow solid (79.5 mg, 91% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 133.1–133.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36–7.27 (m, 3H), 7.26–7.22 (m, 1H), 7.17 (d, *J* = 8.9 Hz, 1H), 5.46 (s, 1H), 2.78 (s, 3H), 2.49 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.7, 140.4, 140.1, 133.7, 132.8, 130.4(3), 130.3(8), 129.9, 128.8, 128.2, 127.0, 126.4, 124.0, 123.6, 117.8, 117.3, 34.5, 21.1; **HRMS (ESI)**: calculated for $C_{18}H_{15}N_2O_2$ $[M-H]^-$: 291.1139, found: 291.1141.

***N*-(2-(2-hydroxynaphthalen-1-yl)-4-methoxyphenyl)-*N*-methylnitrous amide (3c)**



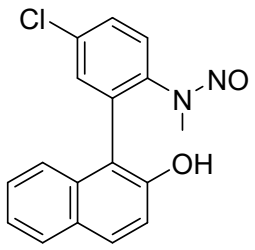
Yellow solid (87.4 mg, 95% yield), *syn*:*anti* = 8:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 173.0–173.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.38–7.27 (m, 3H), 7.21–7.10 (m, 2H), 7.02–6.99 (m, 1H), 5.61 (s, 1H), 3.87 (s, 3H), 2.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.4, 150.7, 135.9, 132.7, 131.9, 130.5, 128.8, 128.2, 128.0, 127.1, 123.9, 123.6, 117.9, 117.8, 117.1, 115.3, 55.7, 34.8; **HRMS (ESI)**: calculated for $C_{18}H_{15}N_2O_3$ $[M-H]^-$: 307.1088, found: 307.1089.

***N*-(4-fluoro-2-(2-hydroxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3d)**



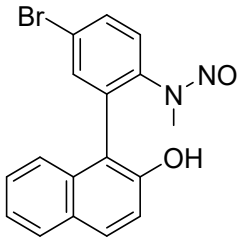
Yellow solid (61.1 mg, 69% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 147.6–148.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.58 (dd, *J* = 8.8, 5.1 Hz, 1H), 7.40–7.30 (m, 3H), 7.29–7.21 (m, 2H), 7.14 (d, *J* = 8.9 Hz, 1H), 5.76 (s, 1H), 2.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.7 (*J* = 251.3 Hz), 150. 7, 139.0, 133.2 (*J* = 8.7 Hz), 132.5, 130.9, 128.8, 128.31 (*J* = 4.4 Hz), 128.29 (*J* = 9.0 Hz), 127.3, 123.8, 123.6, 120.1 (*J* = 22.4 Hz), 117.9, 116.5 (*J* = 22.6 Hz), 116.2, 34.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -110.97; **HRMS (ESI)**: calculated for $C_{17}H_{12}N_2O_2F$ $[M-H]^-$: 295.0888, found: 295.0886.

***N*-(4-bromo-2-(2-hydroxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3e)**



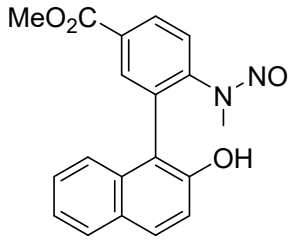
Yellow solid (70.1 mg, 75% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 152.9–153.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81–7.76 (m, 2H), 7.61 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.57–7.54 (m, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 7.40–7.29 (m, 2H), 7.26 (dd, *J* = 6.7, 2.0 Hz, 1H), 7.14 (d, *J* = 8.9 Hz, 1H), 5.52 (s, 1H), 2.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.7, 141.4, 135.3, 133.2, 132.5, 132.2, 131.0, 129.7, 128.8, 128.3, 127.5, 127.4, 123.9, 123.6, 117.8, 116.1, 34.5; **HRMS (ESI)**: calculated for $C_{17}H_{12}N_2O_2Cl$ $[M-H]^-$: 311.0593, found: 311.0586.

***N*-(4-chloro-2-(2-hydroxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3f)**



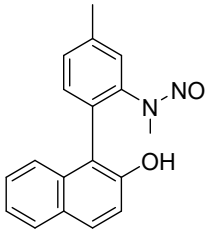
Yellow solid (77.8 mg, 73% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 145.1–145.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85–7.72 (m, 3H), 7.69–7.65 (m, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.41–7.30 (m, 2H), 7.28–7.23 (m, 1H), 7.14 (d, *J* = 8.9 Hz, 1H), 5.51 (s, 1H), 2.76 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.7, 142.0, 136.2, 132.7, 132.6, 132.5, 131.0, 128.9, 128.3, 127.7, 127.4, 123.9, 123.6, 123.2, 117.8, 116.2, 34.3; **HRMS (ESI)**: calculated for $C_{17}H_{12}N_2O_2Br$ $[M-H]^-$: 355.0088, found: 355.0092.

Methyl 3-(2-hydroxynaphthalen-1-yl)-4-(methyl(nitroso)amino)benzoate (3g)



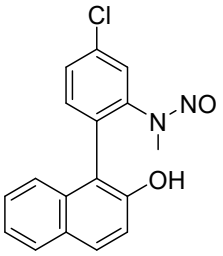
Yellow solid (79.2 mg, 79% yield), *syn*:*anti* = 13:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 113.2–113.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.0 Hz, 1H), 8.21–8.17 (m, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.36–7.28 (m, 2H), 7.23–7.19 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 5.61 (s, 1H), 3.93 (s, 3H), 2.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.0, 150.8, 146.5, 135.0, 132.7, 131.0, 130.8, 130.7, 130.3, 128.9, 128.3, 127.4, 126.0, 123.8, 123.6, 117.8, 116.7, 52.5, 34.1; **HRMS (ESI)**: calculated for $C_{19}H_{15}N_2O_4$ $[M-H]^-$: 335.1037, found: 335.1045.

***N*-(2-(2-hydroxynaphthalen-1-yl)-5-methylphenyl)-*N*-methylnitrous amide (3h)**



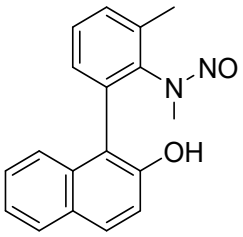
Yellow solid (80.5 mg, 92% yield), *syn*:*anti* = 12:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 152.3–152.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.48–7.42 (m, 2H), 7.41–7.35 (m, 1H), 7.34–7.28 (m, 2H), 7.28–7.23 (m, 1H), 7.16 (d, *J* = 8.9 Hz, 1H), 5.50 (s, 1H), 2.77 (s, 3H), 2.53 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.8, 142.6, 140.1, 133.1, 132.9, 130.6, 130.3, 128.8, 128.2, 127.1, 127.0, 126.8, 123.9, 123.6, 117.7, 117.1, 34.5, 21.2; **HRMS (ESI)**: calculated for $C_{18}H_{15}N_2O_2$ $[M-H]^-$: 291.1139, found: 291.1134.

***N*-(5-chloro-2-(2-hydroxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3i)**



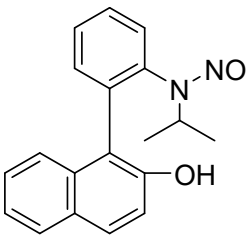
Yellow solid (77.7 mg, 83% yield), *syn*:*anti* = 12:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 126.1–126.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.66–7.60 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.38–7.29 (m, 2H), 7.26–7.21 (m, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 5.44 (s, 1H), 2.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.7, 143.7, 135.3, 134.5, 132.7, 130.8, 129.7, 128.9, 128.7, 128.3, 127.3, 126.6, 123.8, 123.6, 117.8, 116.3, 34.2; **HRMS (ESI)**: calculated for $C_{17}H_{12}N_2O_2Cl$ $[M-H]^-$: 311.0593, found: 311.0590.

***N*-(2-(2-hydroxynaphthalen-1-yl)-6-methylphenyl)-*N*-methylnitrous amide (3j)**



Yellow solid (78.1 mg, 89% yield), *syn*:*anti* > 20:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 147.2–147.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.61–7.50 (m, 2H), 7.36–7.27 (m, 3H), 7.23–7.18 (m, 1H), 7.15 (d, *J* = 8.9 Hz, 1H), 5.38 (s, 1H), 2.80 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.7, 141.6, 136.9, 133.0, 132.9, 131.8, 130.8, 130.3, 128.7, 128.1, 126.7, 124.1, 123.5, 117.9, 117.3, 34.5, 18.3; **HRMS (ESI)**: calculated for $C_{18}H_{17}N_2O_2$ $[M+H]^-$: 293.1285, found: 293.1285

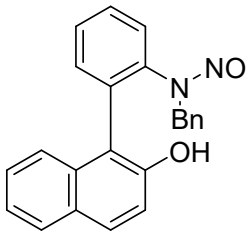
***N*-(2-(2-hydroxynaphthalen-1-yl)phenyl)-*N*-isopropylnitrous amide (3k)**



Yellow solid (83.9 mg, 91% yield), *syn*:*anti* = 3:1 (by ^{1}H NMR). **Mp**: 132.6–132.9 °C; **^{1}H NMR**

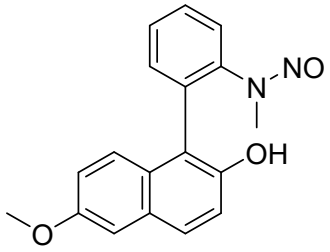
(400 MHz, $CDCl_3$) (*syn* and *anti* isomers): δ 7.83–7.74 (m, 3H), 7.67–7.57 (m, 3H), 7.53–7.46 (m, 3H), 7.37–7.28 (m, 2H), 7.22–7.18 (m, 1H), 7.17–7.11 (m, 2H), 5.68 (s, 0.34H), 5.48 (s, 1H), 4.46 (dt, *J* = 13.6, 6.8 Hz, 0.34H), 3.84 (dt, *J* = 12.9, 6.2 Hz, 1H), 1.31 (d, *J* = 5.9 Hz, 3H), 0.94 (d, *J* = 6.2 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 1H), 0.63 (d, *J* = 6.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) (*syn* and *anti* isomers): δ 152.5, 151.2, 140.7, 140.4, 134.2, 134.1, 133.4, 133.3, 133.2, 132.8, 130.4, 130.1, 129.8, 129.4, 129.2, 129.0, 128.7, 128.6, 128.3, 128.1, 126.7, 126.6, 124.5, 123.7, 123.5, 123.4, 118.9, 118.7, 118.3, 116.7, 57.9, 50.1, 22.9, 21.2, 19.2, 18.5; **HRMS (ESI)**: calculated for $C_{19}H_{17}N_2O_2$ $[M-H]^-$: 305.1296, found: 305.1292.

***N*-benzyl-*N*-(2-(2-hydroxynaphthalen-1-yl)phenyl)nitrous amide (3l)**



Yellow solid (86.6 mg, 82% yield), *syn*:*anti* = 12:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 144.5–145.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81–7.76 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.56–7.48 (m, 2H), 7.37–7.30 (m, 3H), 7.28–7.25 (m, 1H), 7.21–7.17 (m, 1H), 7.14–7.09 (m, 3H), 6.83 (d, *J* = 6.3 Hz, 2H), 5.37 (s, 1H), 4.71 (d, *J* = 14.7 Hz, 1H), 4.30 (d, *J* = 14.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.8, 141.5, 134.1, 133.6, 132.9, 131.1, 130.6, 130.0, 129.6, 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 127.5, 127.0, 124.1, 123.7, 118.0, 117.2, 48.7; **HRMS (ESI)**: calculated for $C_{23}H_{17}N_2O_2$ $[M-H]^-$: 353.1296, found: 353.1295.

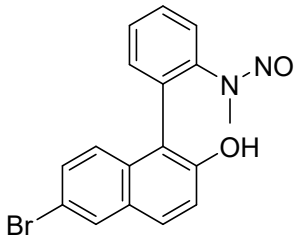
***N*-(2-(2-hydroxy-6-methoxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3ab)**



Yellow solid (77.7 mg, 84% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 139.5–139.8 °C; **^{1}H NMR** (400

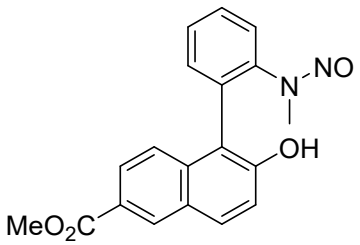
MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.9 Hz, 1H), 7.64–7.59 (m, 3H), 7.52–7.48 (m, 1H), 7.16–7.11 (m, 2H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.03–6.97 (m, 1H), 5.35 (s, 1H), 3.87 (s, 3H), 2.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.0, 149.1, 142.8, 133.3, 130.4, 129.8, 129.6(8), 129.6(6), 129.1, 128.0, 126.5, 125.4, 119.5, 118.2, 117.5, 106.6, 55.3, 34.5; **HRMS (ESI)**: calculated for $C_{18}H_{15}N_2O_3$ $[M-H]^-$: 307.1088, found: 307.1089.

***N*-(2-(6-bromo-2-hydroxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3ac)**



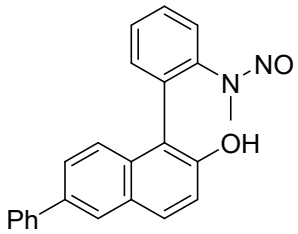
Yellow solid (101.1 mg, 94% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 161.7–162.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94–7.91 (m, 1H), 7.71–7.63 (m, 3H), 7.63–7.59 (m, 1H), 7.51–7.46 (m, 1H), 7.38 (dd, *J* = 9.0, 1.9 Hz, 1H), 7.18 (d, *J* = 8.9 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 1H), 5.57 (s, 1H), 2.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.1, 142.8, 133.3, 131.4, 130.3, 130.2, 130.0, 129.9(3), 129.8(7), 129.7, 129.5, 126.6, 125.7, 119.0, 117.5, 117.4, 34.5; **HRMS (ESI)**: calculated for $C_{17}H_{12}N_2O_2Br$ $[M-H]^-$: 355.0088, found: 355.0090

Methyl 6-hydroxy-5-(2-(methyl(nitroso)amino)phenyl)-2-naphthoate (3ad)



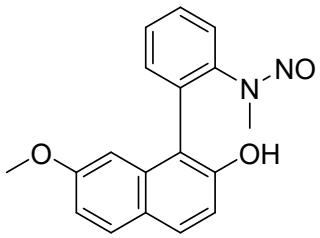
Yellow solid (96.5 mg, 96% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 154.1–154.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 1.4 Hz, 1H), 7.91–7.85 (m, 2H), 7.67–7.63 (m, 2H), 7.63–7.58 (m, 1H), 7.53–7.47 (m, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 6.14 (s, 1H), 3.94 (s, 3H), 2.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.2, 153.0, 142.8, 135.3, 133.3, 131.9, 131.4, 129.9(3), 129.8(9), 129.8(1), 127.7(6), 126.5, 126.4, 125.1, 124.1, 118.7, 117.5, 52.2, 34.5; **HRMS (ESI)**: calculated for $C_{19}H_{15}N_2O_4$ $[M-H]^-$: 335.1037, found: 335.1028.

***N*-(2-(2-hydroxy-6-phenylnaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3ae)**



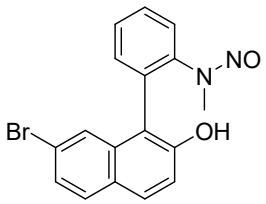
Yellow solid (96.1 mg, 90% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 159.1–160.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99–7.94 (m, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.68–7.63 (m, 5H), 7.61–7.57 (m, 1H), 7.55–7.51 (m, 1H), 7.47–7.42 (m, 2H), 7.37–7.29 (m, 2H), 7.18 (d, *J* = 8.9 Hz, 1H), 5.52 (s, 1H), 2.84 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.8, 142.9, 140.7, 136.4, 133.4, 132.0, 130.8, 130.1, 129.8(0), 129.7(8), 129.1, 128.8, 127.2(1), 127.1(6), 126.7, 126.5, 126.1, 124.5, 118.2, 117.2, 34.6; **HRMS (ESI)**: calculated for $C_{23}H_{17}N_2O_2$ $[M-H]^-$: 353.1296, found: 353.1290.

***N*-(2-(2-hydroxy-7-methoxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3af)**



Yellow solid (80.5 mg, 87% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 159.1–159.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73–7.65 (m, 2H), 7.66–7.62 (m, 3H), 7.54–7.49 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.50 (s, 1H), 5.44 (s, 1H), 3.65 (s, 3H), 2.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.7, 151.2, 142.9, 134.0, 133.3, 130.3, 130.2, 129.8, 129.7, 129.7, 126.7, 124.2, 116.4, 115.8, 115.1, 103.1, 55.1, 34.4; **HRMS (ESI)**: calculated for $C_{18}H_{15}N_2O_3$ $[M-H]^-$: 307.1088, found: 307.1085.

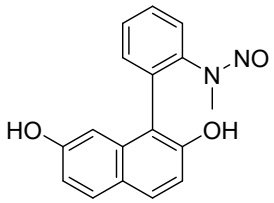
***N*-(2-(7-bromo-2-hydroxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3ag)**



Yellow solid (99.9 mg, 93% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here

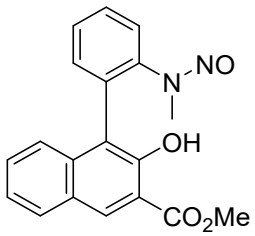
represent peak information only for the major *syn* isomer. **Mp**: 151.9–152.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.9 Hz, 1H), 7.69–7.59 (m, 4H), 7.52–7.46 (m, 1H), 7.43–7.36 (m, 2H), 7.15 (d, *J* = 8.9 Hz, 1H), 5.76 (s, 1H), 2.86 (s, 3H); **^{13}C NMR (**101 MHz, $CDCl_3$**)**: δ 151.7, 142.7, 134.1, 133.4, 130.4, 130.0, 129.9, 129.7, 127.2, 127.0, 126.5, 125.9, 121.6, 118.3, 116.5, 34.6; **HRMS (ESI)**: calculated for $C_{17}H_{12}N_2O_2Br$ $[M-H]^-$: 355.0088, found: 355.0088.

***N*-(2-(2,7-dihydroxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3ah)**



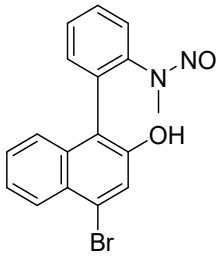
Yellow solid (75.3 mg, 85% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 111.2–111.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74–7.66 (m, 2H), 7.66–7.61 (m, 3H), 7.53–7.48 (m, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 5.31 (s, 1H), 5.22 (s, 1H), 2.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.9, 151.3, 142.8, 134.3, 133.4, 130.4, 130.3, 130.2, 129.9, 129.7, 126.6, 124.2, 115.9, 115.5, 115.1, 106.3, 34.6; **HRMS (ESI)**: calculated for $C_{17}H_{13}N_2O_3$ $[M-H]^-$: 293.0932, found: 293.0926.

Methyl 3-hydroxy-4-(2-(methyl(nitroso)amino)phenyl)-2-naphthoate (3ai)



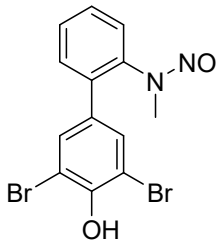
Yellow solid (92.2 mg, 91% yield), *syn*:*anti* > 20:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 126.3–126.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.76 (s, 1H), 8.55 (s, 1H), 7.84–7.79 (m, 1H), 7.64–7.55 (m, 3H), 7.50–7.45 (m, 1H), 7.44–7.38 (m, 1H), 7.35–7.29 (m, 2H), 4.03 (s, 3H), 2.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 170.3, 152.9, 142.5, 136.3, 133.1, 133.0, 131.0, 129.9, 129.6, 129.0(3), 128.9(5), 126.8, 125.7, 124.3, 124.2, 119.7, 113.6, 52.8, 34.4; **HRMS (ESI)**: calculated for $C_{19}H_{15}N_2O_4$ $[M-H]^-$: 335.1037, found: 335.1034.

***N*-(2-(4-bromo-2-hydroxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (3aj)**



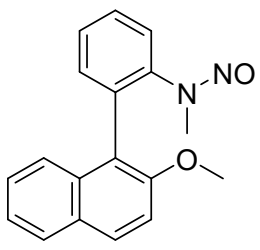
Yellow solid (98.4 mg, 92% yield), *syn*:*anti* = 8:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 142.7–143.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.70–7.61 (m, 3H), 7.56 (s, 1H), 7.48 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.44–7.34 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 5.37 (s, 1H), 2.84 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.6, 142.7, 133.5, 133.3, 129.9, 129.8, 127.8, 127.5, 127.4(4), 127.4(1), 126.4, 124.9, 124.4, 124.3, 122.0, 117.5, 34.7; **HRMS (ESI)**: calculated for $C_{17}H_{12}N_2O_2Br$ $[M-H]^-$: 355.0088, found: 355.0086.

***N*-(3',5'-dibromo-4'-hydroxy-[1,1'-biphenyl]-2-yl)-*N*-methylnitrous amide (3ak)**



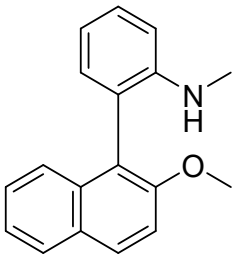
Yellow solid (98.4 mg, 42% yield), *syn*:*anti* = 10:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 149.2–149.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56–7.49 (m, 2H), 7.47–7.43 (m, 2H), 7.41–7.36 (m, 2H), 6.02 (s, 1H), 3.01 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.2, 140.3, 134.2, 132.9, 132.1, 131.5, 131.2, 129.5, 129.2, 127.3, 126.7, 110.2, 35.6; **HRMS (ESI)**: calculated for $C_{13}H_{10}N_2O_2Br_2Na$ $[M+Na]^+$: 406.9001, found: 406.8999.

***N*-(2-(2-methoxynaphthalen-1-yl)phenyl)-*N*-methylnitrous amide (4)**



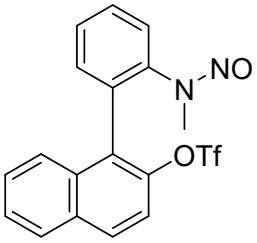
Yellow solid (143.2 mg, 98% yield), *syn*:*anti* > 20:1 (by ^{1}H NMR). The NMR data listed here represent peak information only for the major *syn* isomer. **Mp**: 150.1–150.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 9.1 Hz, 1H), 7.79 (dd, *J* = 6.5, 2.8 Hz, 1H), 7.60–7.55 (m, *J* = 2.9 Hz, 3H), 7.46–7.41 (m, 1H), 7.40–7.36 (m, 1H), 7.35–7.30 (m, 2H), 7.28 (d, *J* = 9.1 Hz, 1H), 3.77 (s, 3H), 2.74 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.7, 142.6, 133.0, 132.9, 131.7, 130.3, 128.8, 128.7, 128.6, 128.1, 127.1, 125.7, 124.3, 123.8, 120.4, 112.7, 56.2, 34.4; **HRMS (ESI)**: calculated for $C_{18}H_{16}N_2O_2K$ $[M+K]^+$: 331.0843, found: 331.0832.

2-(2-Methoxynaphthalen-1-yl)-*N*-methylaniline (5)



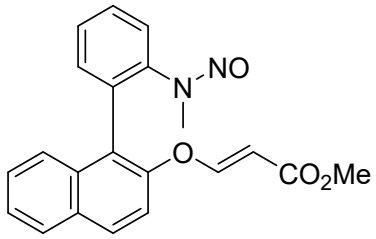
Yellow oil (65.0 mg, 82% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 9.0 Hz, 1H), 7.84–7.79 (m, 1H), 7.42–7.30 (m, 5H), 7.05 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.84 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 3.83 (s, 3H), 2.71 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.7, 147.4, 133.6, 131.3, 129.6, 129.3, 128.8, 127.9, 126.6, 125.1, 123.8, 121.5, 121.4, 116.8, 114.1, 109.9, 56.9, 30.9; **HRMS (ESI)**: calculated for $C_{18}H_{18}NO$ $[M+H]^+$: 264.1383, found: 264.1391.

1-(2-(Methyl(nitroso)amino)phenyl)naphthalen-2-yl trifluoromethanesulfonate (6)



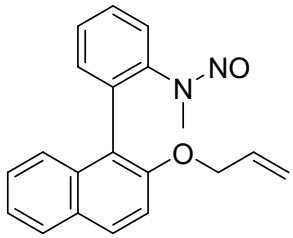
Yellow oil (170.2 mg, 83% yield), *syn*:*anti* > 20:1 (by ^{1}H NMR). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 9.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.71–7.65 (m, *J* = 7.6, 1.6 Hz, 1H), 7.65–7.58 (m, 2H), 7.58–7.52 (m, 3H), 7.52–7.47 (m, 1H), 7.40 (d, *J* = 9.1 Hz, 1H), 2.98 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.8, 142.1, 133.3, 132.9, 132.6, 131.0, 130.2, 128.6, 128.5, 128.4, 128.3, 128.0, 127.2, 126.2, 125.2, 119.0, 118.3(*J* =320.3 Hz), 34.1; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -74.32. **HRMS (ESI)**: calculated for $C_{18}H_{13}F_3N_2O_4SNa$ $[M+Na]^+$: 433.0440, found: 433.0436.

Methyl (E)-3-((1-(2-(methyl(nitroso)amino)phenyl)naphthalen-2-yl)oxy)acrylate (7)



Yellow oil (98.5 mg, 91% yield), *syn*:*anti* > 20:1 (by ^{1}H NMR). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 9.0 Hz, 1H), 7.87–7.83 (m, 1H), 7.65 (d, *J* = 12.3 Hz, 1H), 7.62–7.58 (m, 1H), 7.58–7.53 (m, 2H), 7.48–7.39 (m, 4H), 7.29–7.25 (m, 1H), 5.32 (d, *J* = 12.3 Hz, 1H), 3.67 (s, 3H), 2.84 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.3, 159.4, 149.5, 142.3, 132.7, 132.6, 131.2, 130.8, 129.9, 129.4, 128.7, 128.2, 127.6, 125.9, 125.5, 125.4, 125.0, 118.1, 101.8, 51.3, 34.5; **HRMS (ESI)**: calculated for $C_{21}H_{18}N_2O_4Na$ $[M+Na]^+$: 385.1159, found: 385.1155.

***N*-(2-(2-(allyloxy)naphthalen-1-yl)phenyl)-*N*-methylnitrous amide (8)**



Yellow oil (60.0 mg, 94% yield), *syn*:*anti* > 20:1 (by ^{1}H NMR). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 9.1 Hz, 1H), 7.80–7.75 (m, 1H), 7.60–7.52 (m, 3H), 7.46–7.41 (m, 1H), 7.41–7.35 (m, 1H), 7.35–7.29 (m, 2H), 7.25 (d, *J* = 9.0 Hz, 1H), 5.92–5.79 (m, 1H), 5.22–5.09 (m, 2H), 4.60–4.47 (m, 2H), 2.76 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 152.8, 142.6, 133.1, 133.0, 131.7, 130.1, 128.9, 128.6, 128.5, 128.0, 127.0, 125.5, 124.5, 123.9, 121.1, 117.0, 114.2, 69.6, 34.4; **HRMS (ESI)**: calculated for $C_{20}H_{18}N_2O_2Na$ $[M+Na]^+$: 341.1261, found: 341.1265.

7. X-ray structure of 3a

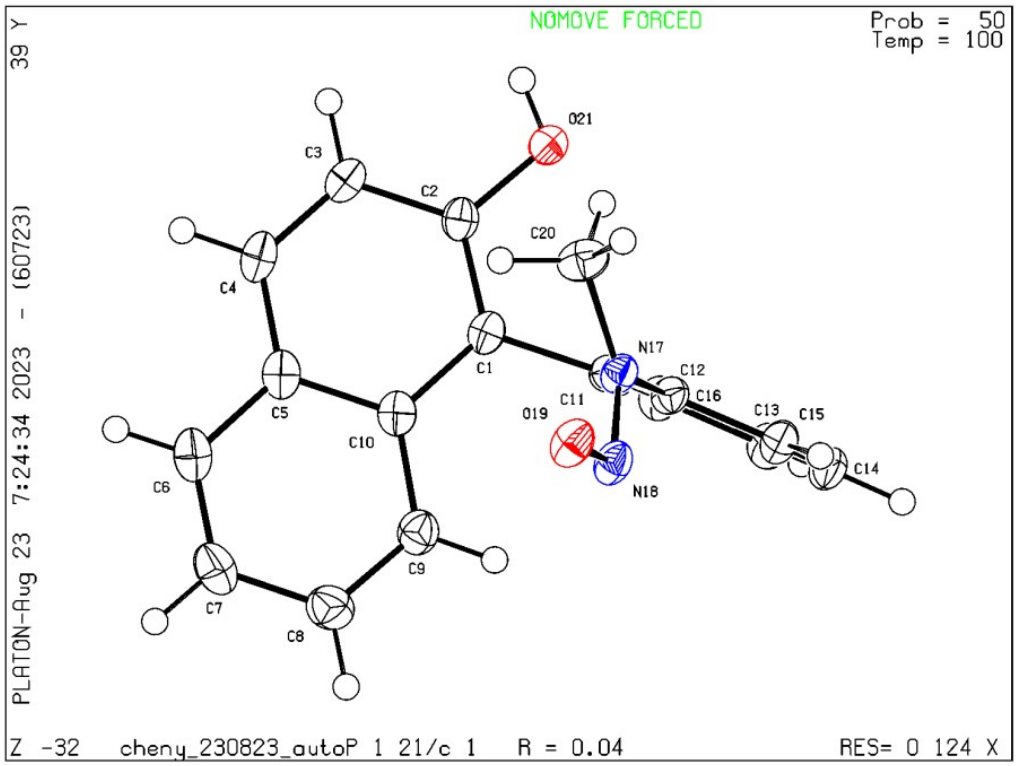
The structure of **3a** was determined by single crystal X-ray analysis (ellipsoid contour at 50% probability). **CCDC 2290351** contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Experimental

Single crystals of **3a** ($C_{17}H_{14}N_2O_2$) were grown by slow evaporation in petroleum ether/CH_2Cl_2 = 1/1 under an air atmosphere. A suitable crystal was selected and mounted on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation.

Crystal structure determination of 3a

Crystal Data for $C_{17}H_{14}N_2O_2$ (M =278.30 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 11.3559(4) Å, b = 8.1137(2) Å, c = 16.0334(4) Å, β = 101.324(3)°, V = 1448.52(7) Å^3, Z = 4, T = 100.00(10) K, μ(Cu Kα) = 0.688 mm^{-1}, *Dcalc* = 1.276 g/cm^3, 8568 reflections measured (7.94° ≤ 2Θ ≤ 151.188°), 2857 unique (R_{int} = 0.0272, R_{sigma} = 0.0291) which were used in all calculations. The final R_1 was 0.0429 (I > 2σ(I)) and wR_2 was 0.1226 (all data).



8. References

[1] T. Ohwada, M. Miura, H. Tanaka, S. Sakamoto, K. Yamaguchi, H. Ikeda and S. Inagaki, *J. Am. Chem. Soc.,* **2001**, *123*, 10164–10172.

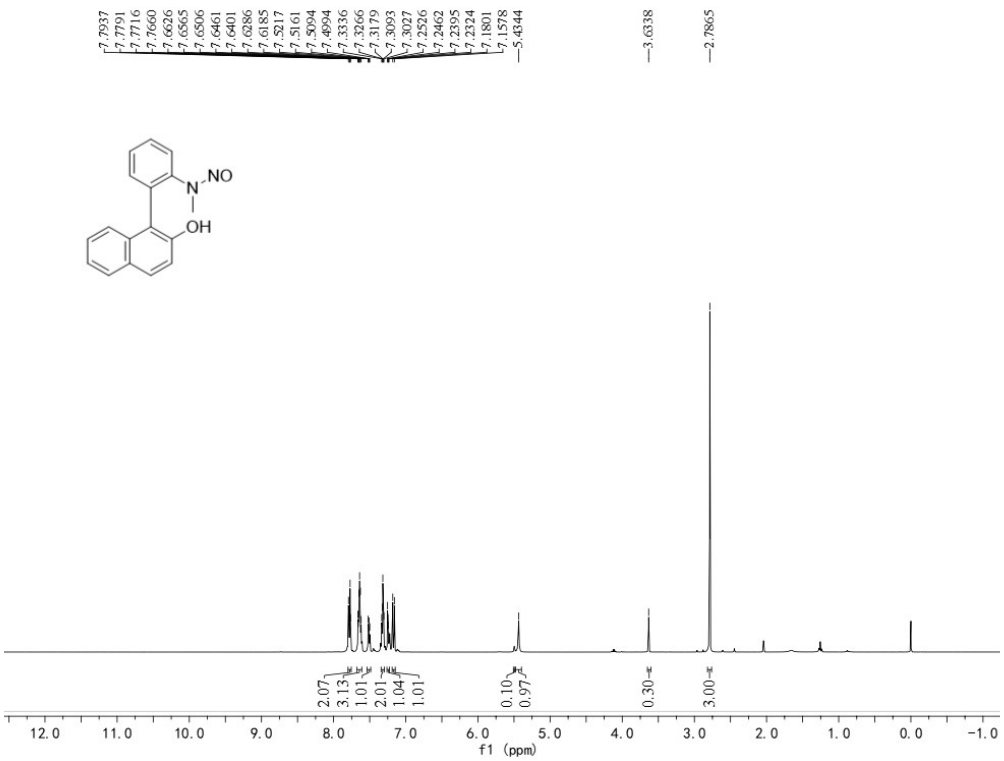
[2] S. Pan, S. Kundu and R. Samanta, *Org. Lett.,* **2023**, *25*, 2873–2877.

[3] K. Wu, B. Cao, C. Y. Zhou and C. M. Che, *Chem. Asian J.,* **2018**, *24*, 4815–4819.

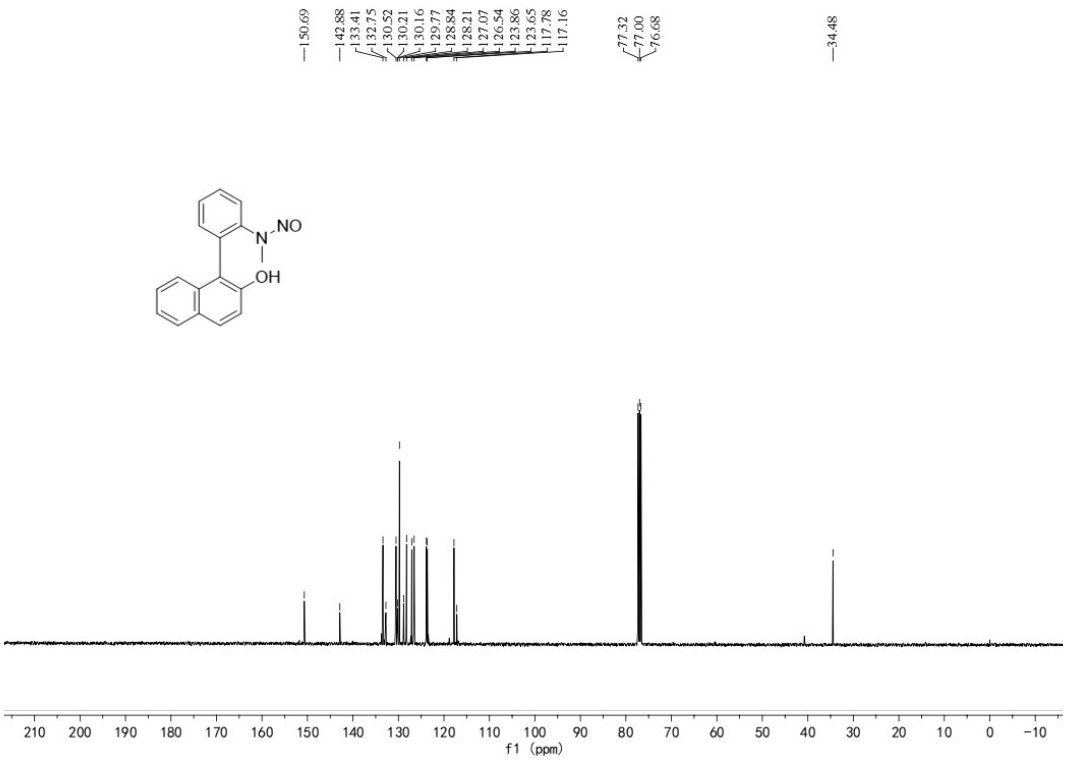
[4] P. Chaudhary, R. Korde, S. Gupta, P. Sureshbabu, S. Sabiah and J. Kandasamy, *Adv. Synth. Catal.,* **2018**, *360*, 556–561.

9. NMR spectra of products

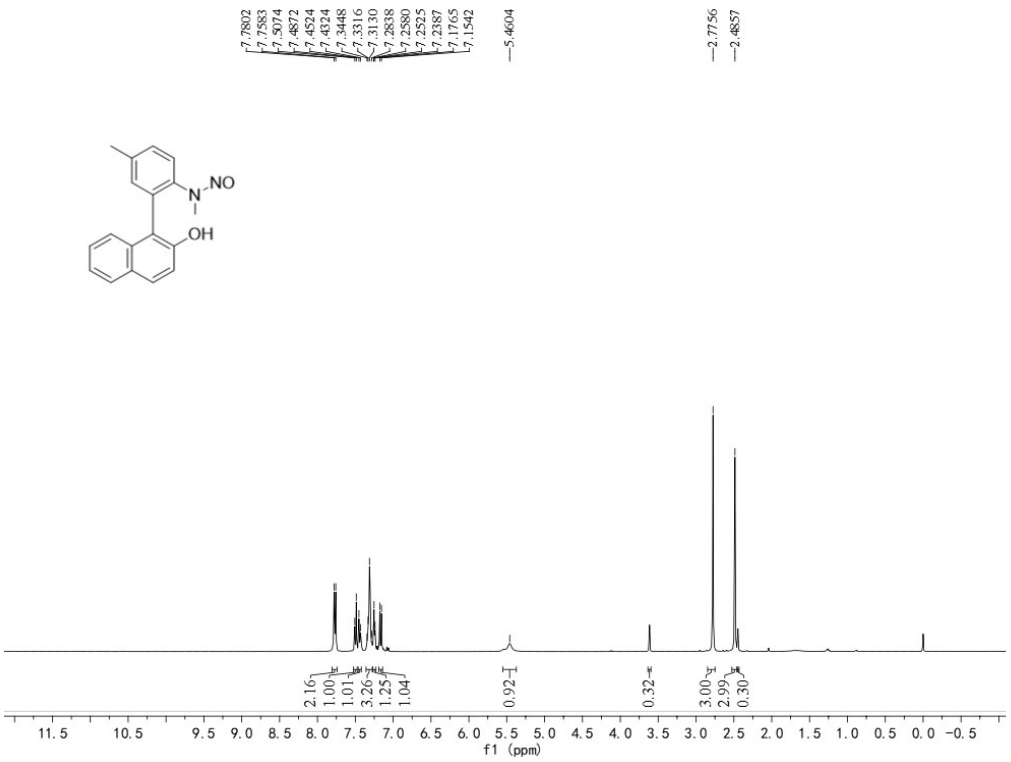
^{1}H NMR (400 MHz) Spectrum of 3a in $CDCl_3$



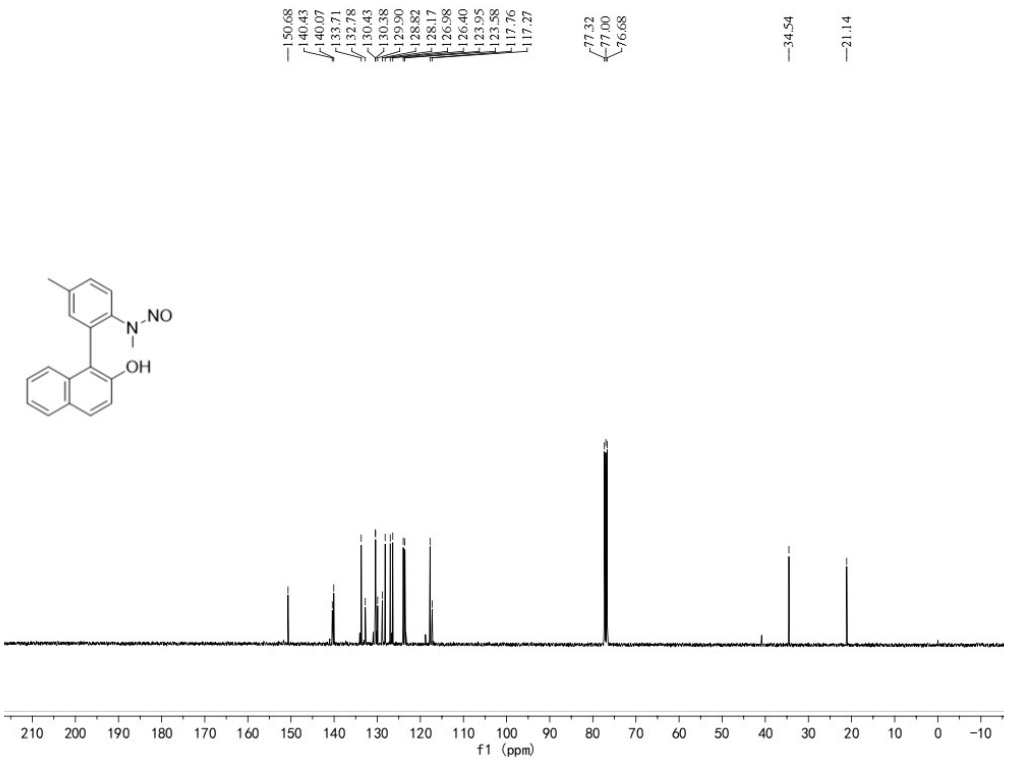
^{13}C NMR (101 MHz) Spectrum of 3a in $CDCl_3$



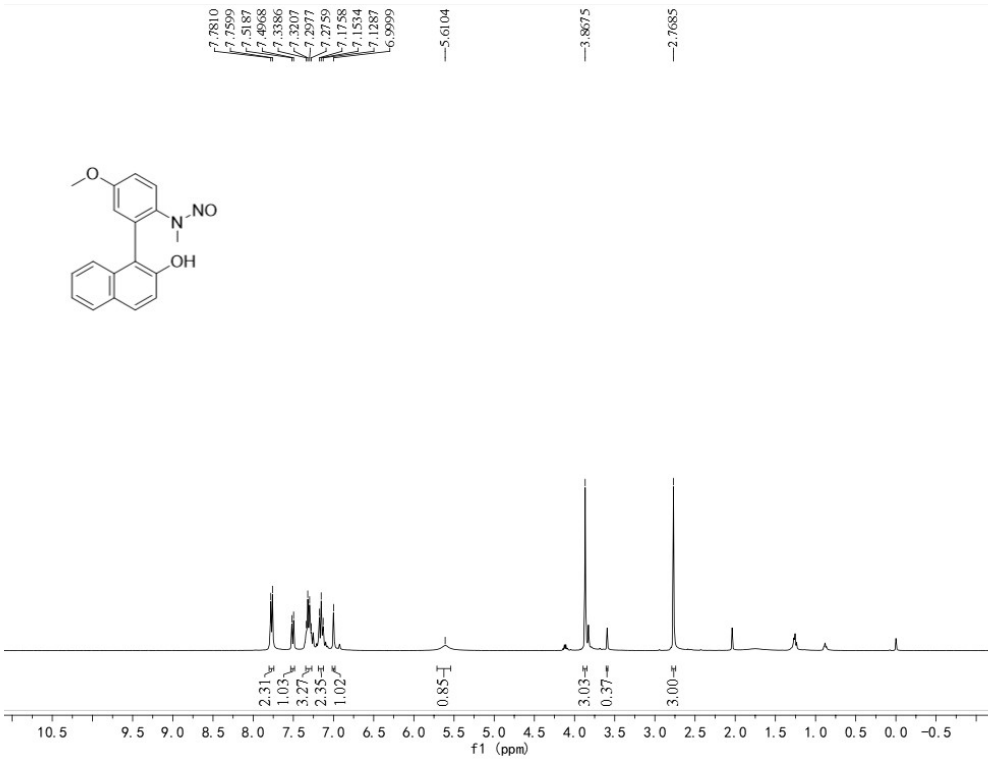
^{1}H NMR (400 MHz) Spectrum of 3b in $CDCl_3$



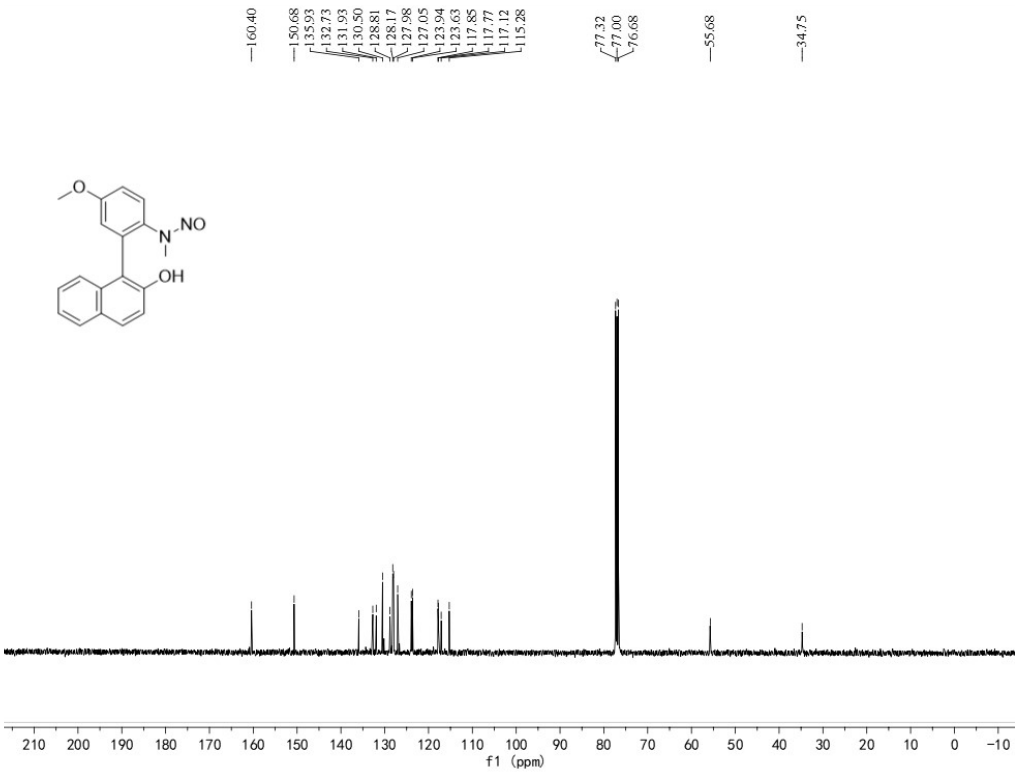
^{13}C NMR (101 MHz) Spectrum of 3b in $CDCl_3$



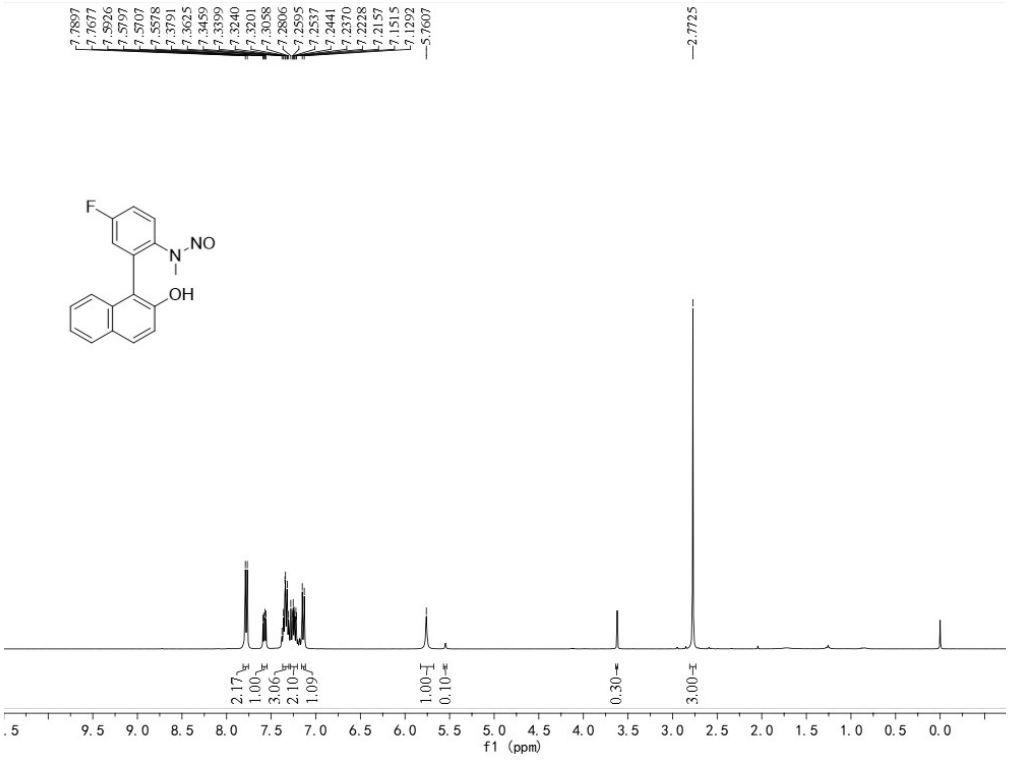
^{1}H NMR (400 MHz) Spectrum of 3c in $CDCl_3$



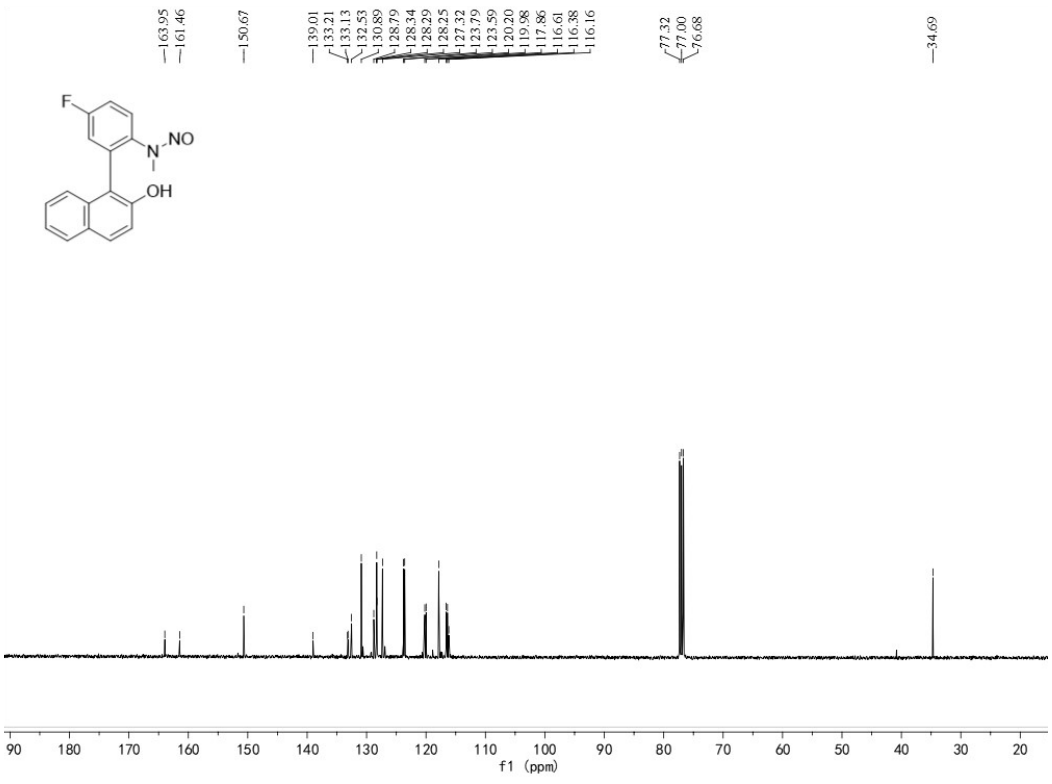
^{13}C NMR (101 MHz) Spectrum of 3c in $CDCl_3$



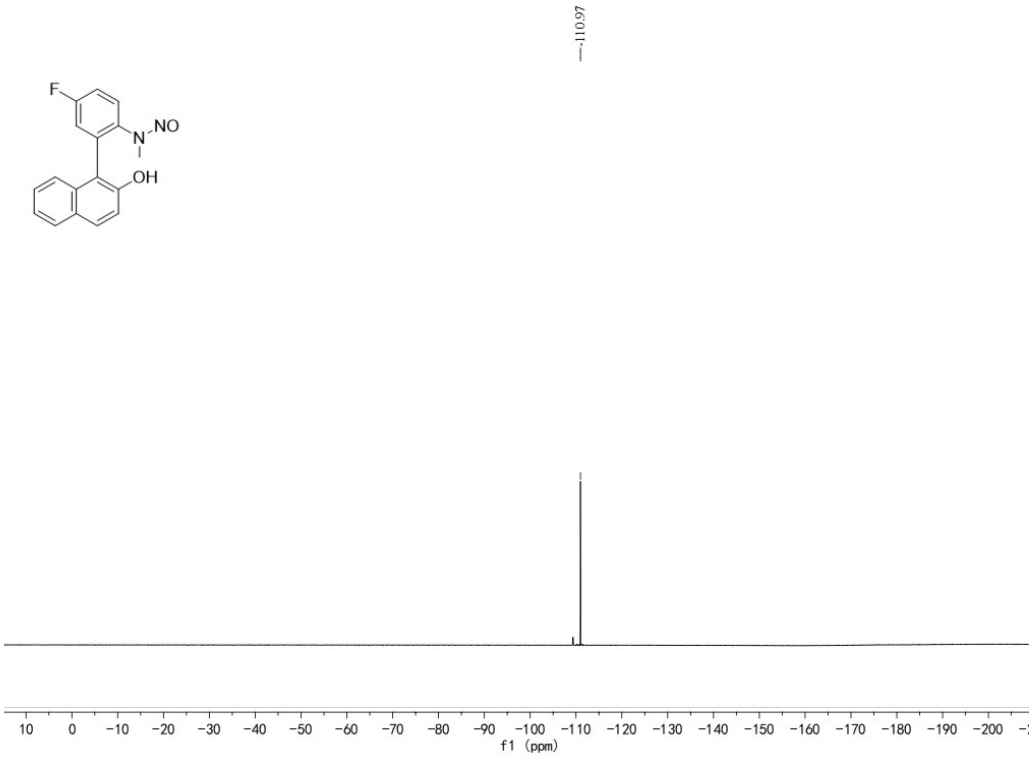
^{1}H NMR (400 MHz) Spectrum of 3d in $CDCl_3$



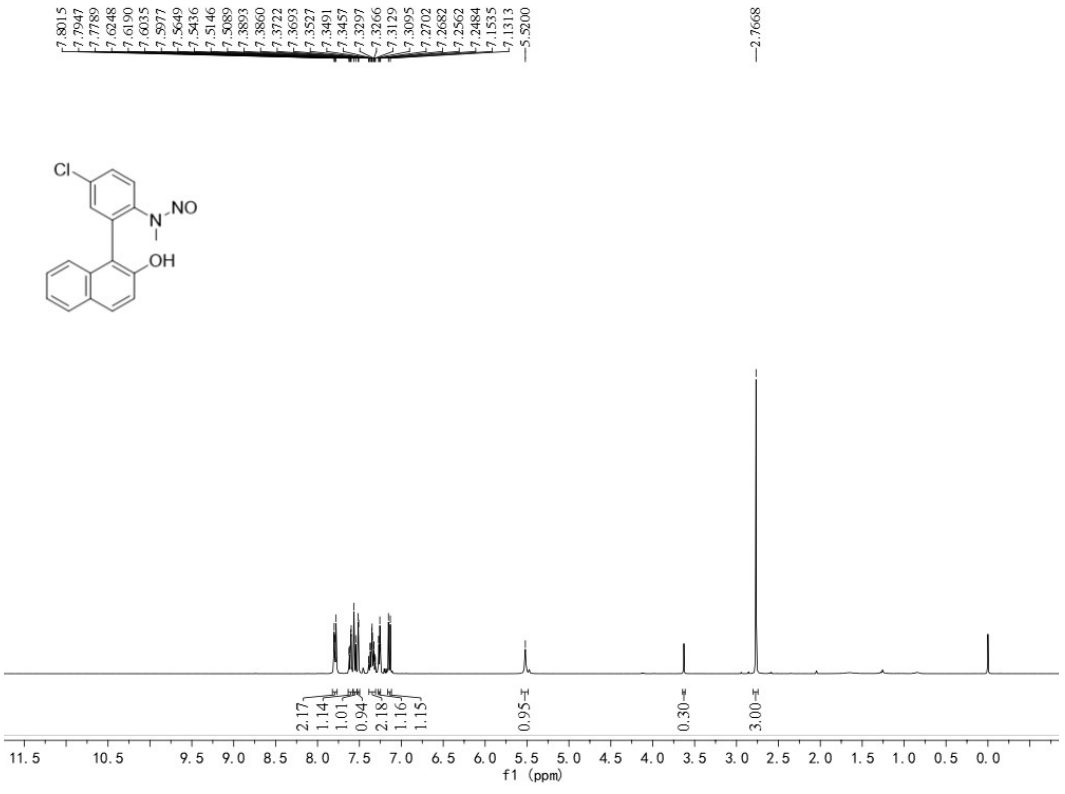
^{13}C NMR (101 MHz) Spectrum of 3d in $CDCl_3$



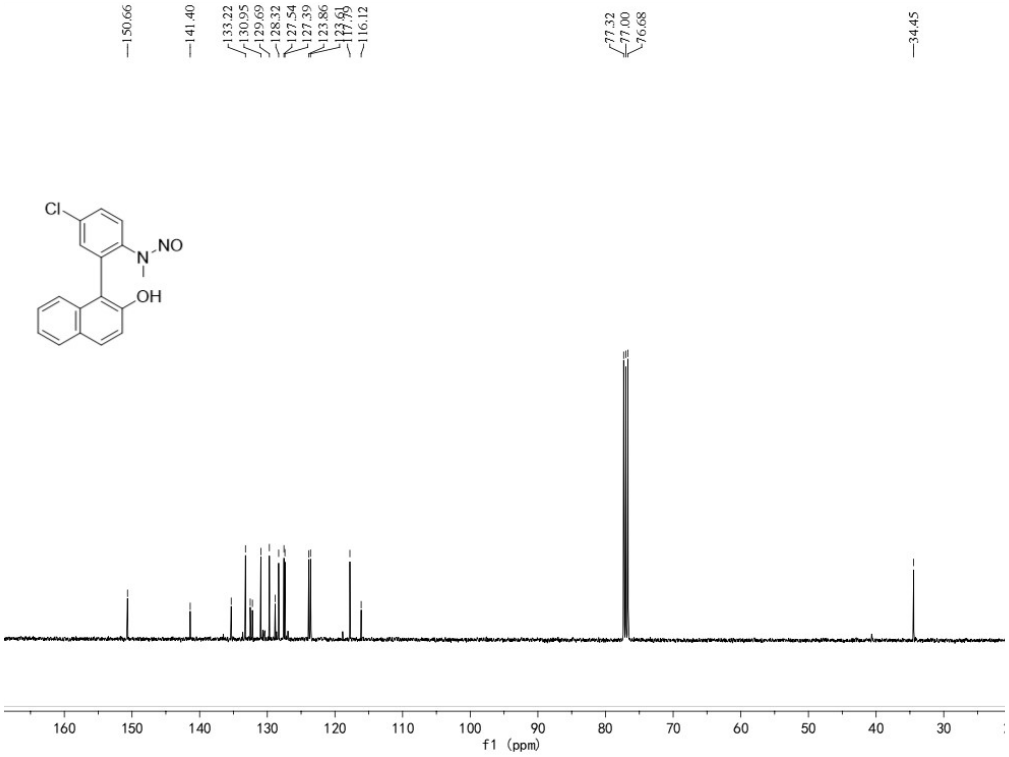
^{19}F NMR (376 MHz) Spectrum of 3d in $CDCl_3$



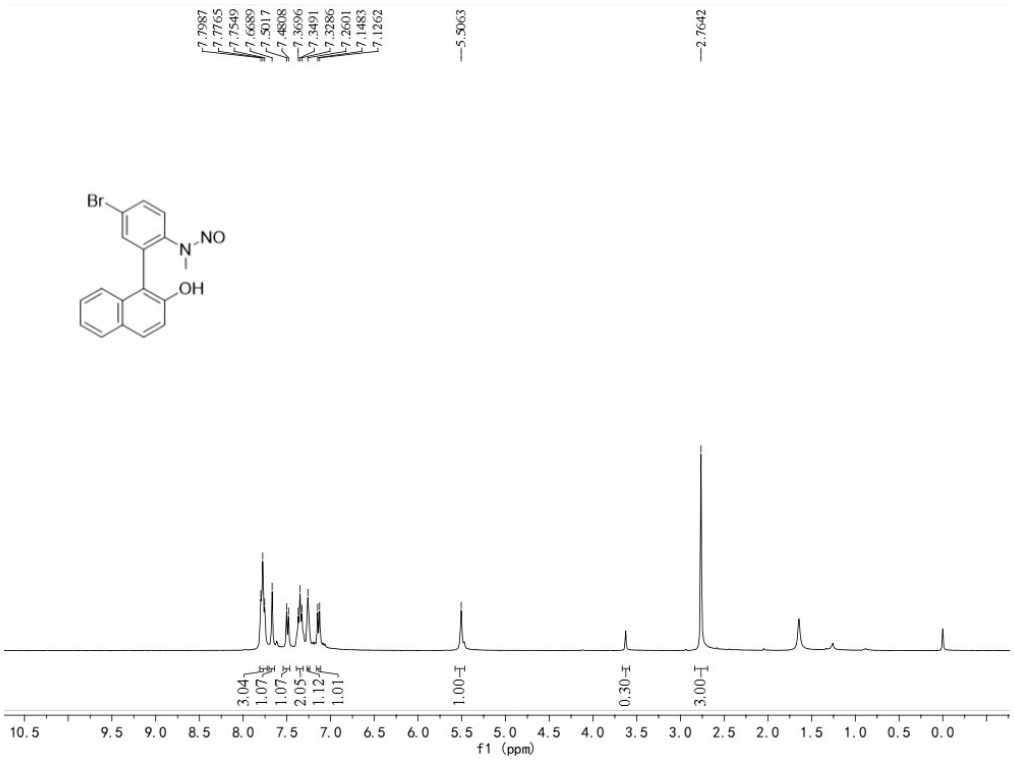
^{1}H NMR (400 MHz) Spectrum of 3e in $CDCl_3$



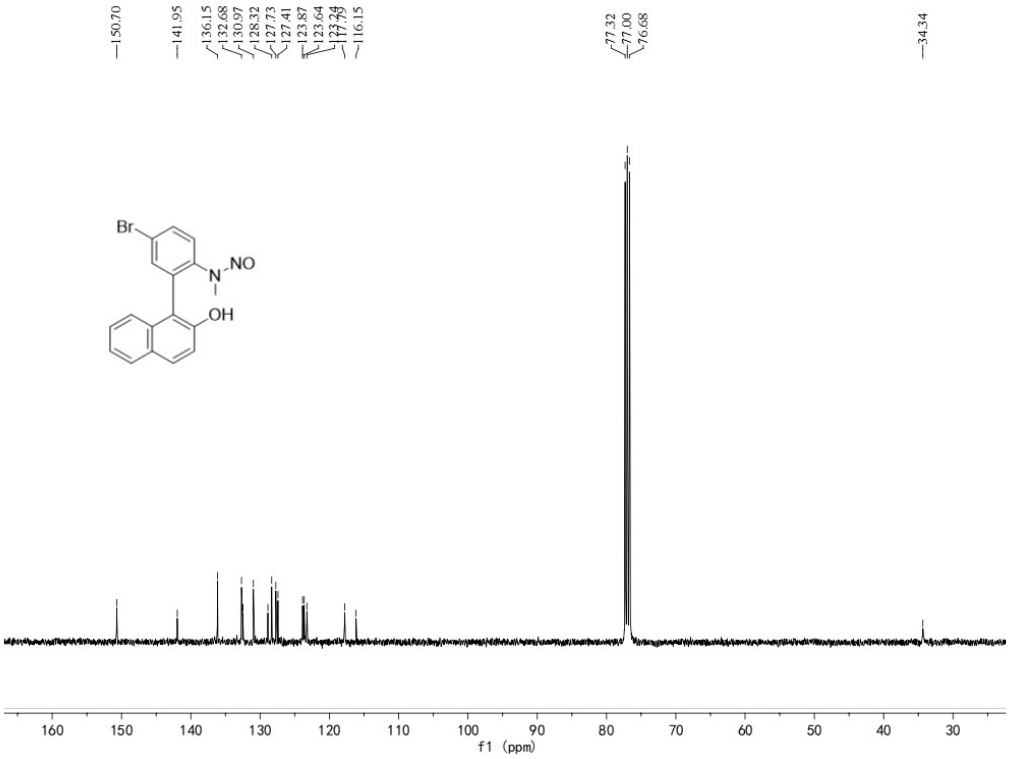
^{13}C NMR (101 MHz) Spectrum of 3e in $CDCl_3$



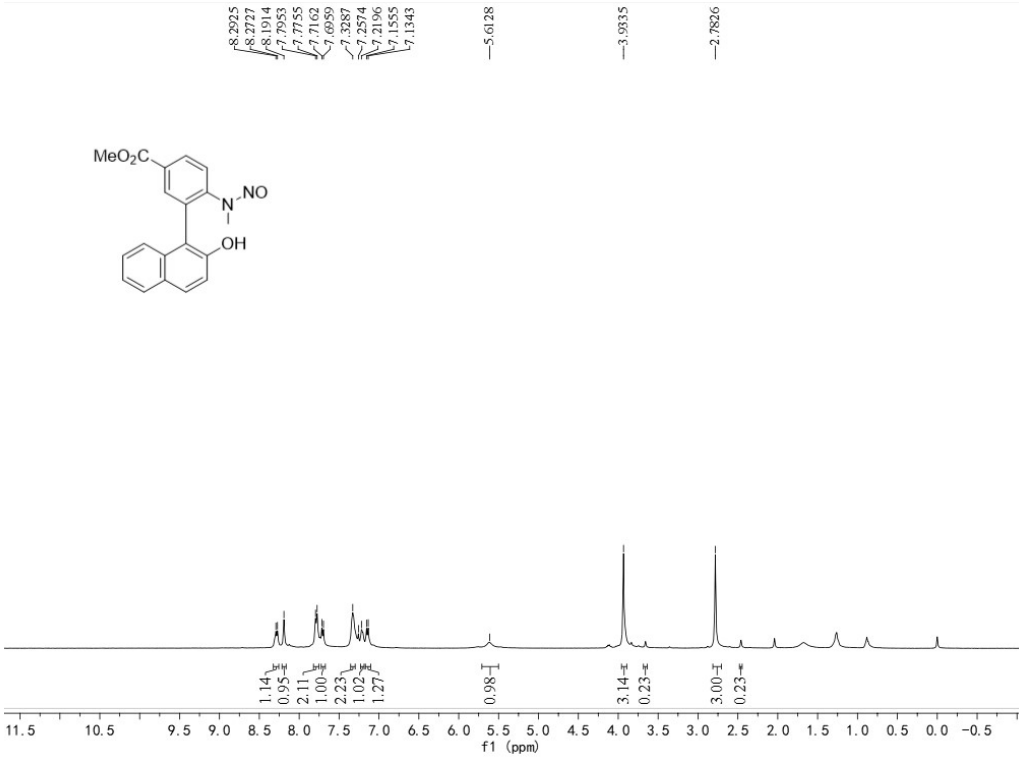
^{1}H NMR (400 MHz) Spectrum of 3f in $CDCl_3$



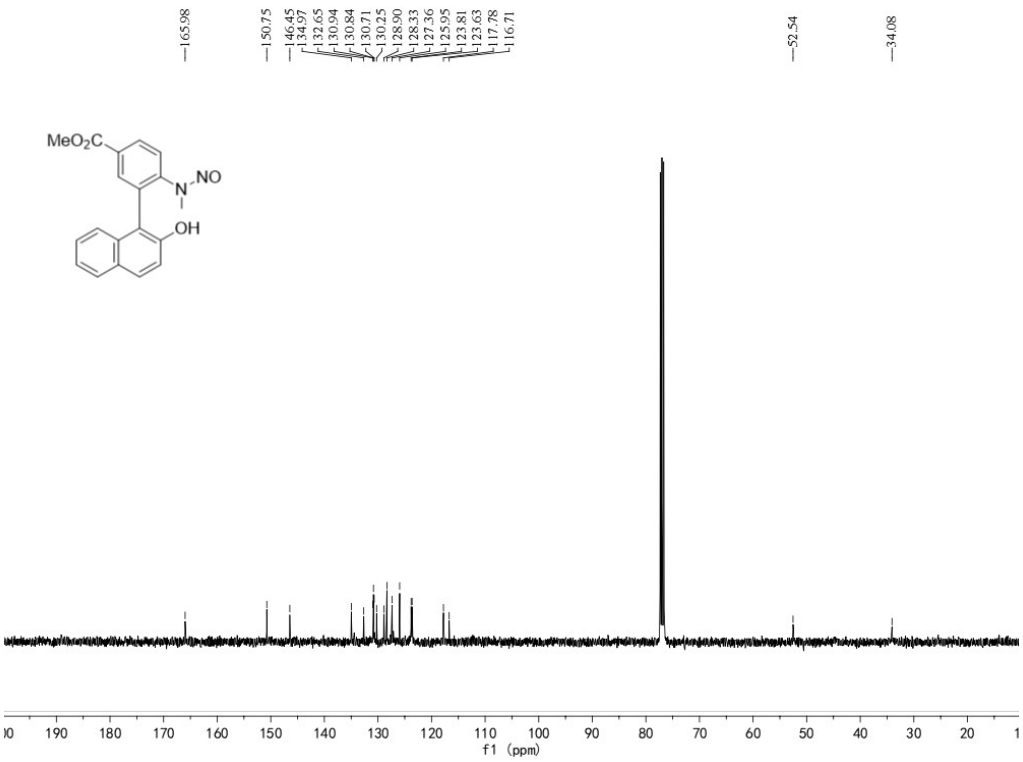
^{13}C NMR (101 MHz) Spectrum of 3f in $CDCl_3$



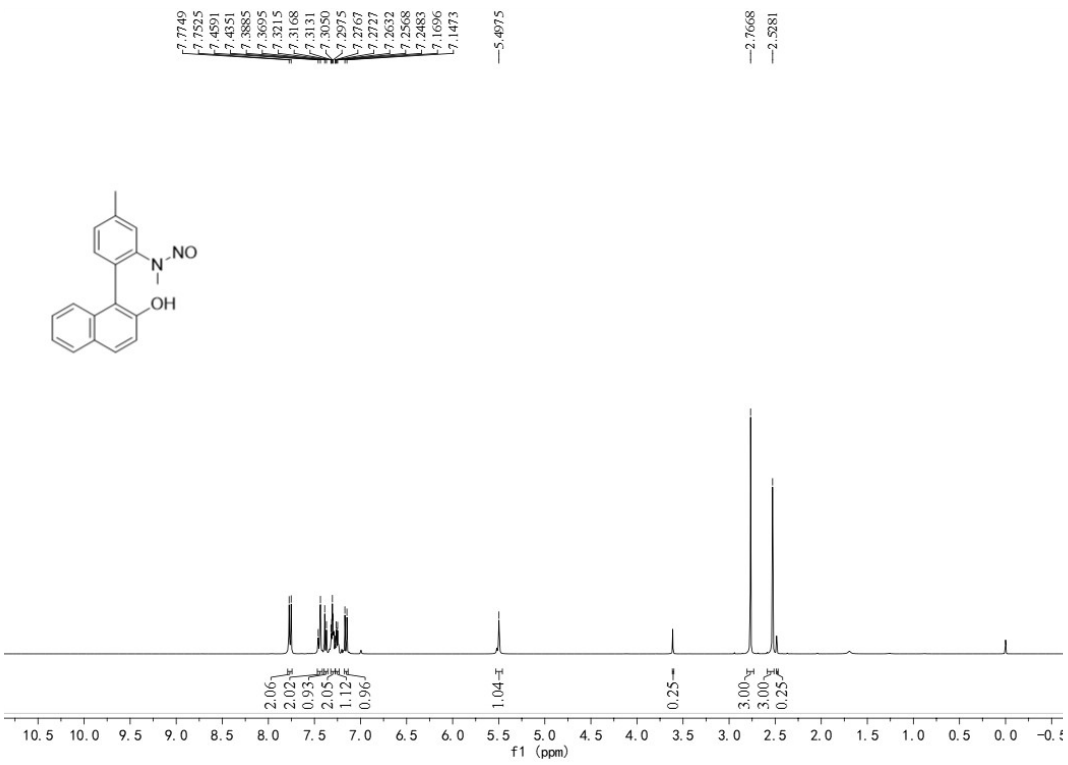
^{1}H NMR (400 MHz) Spectrum of 3g in $CDCl_3$



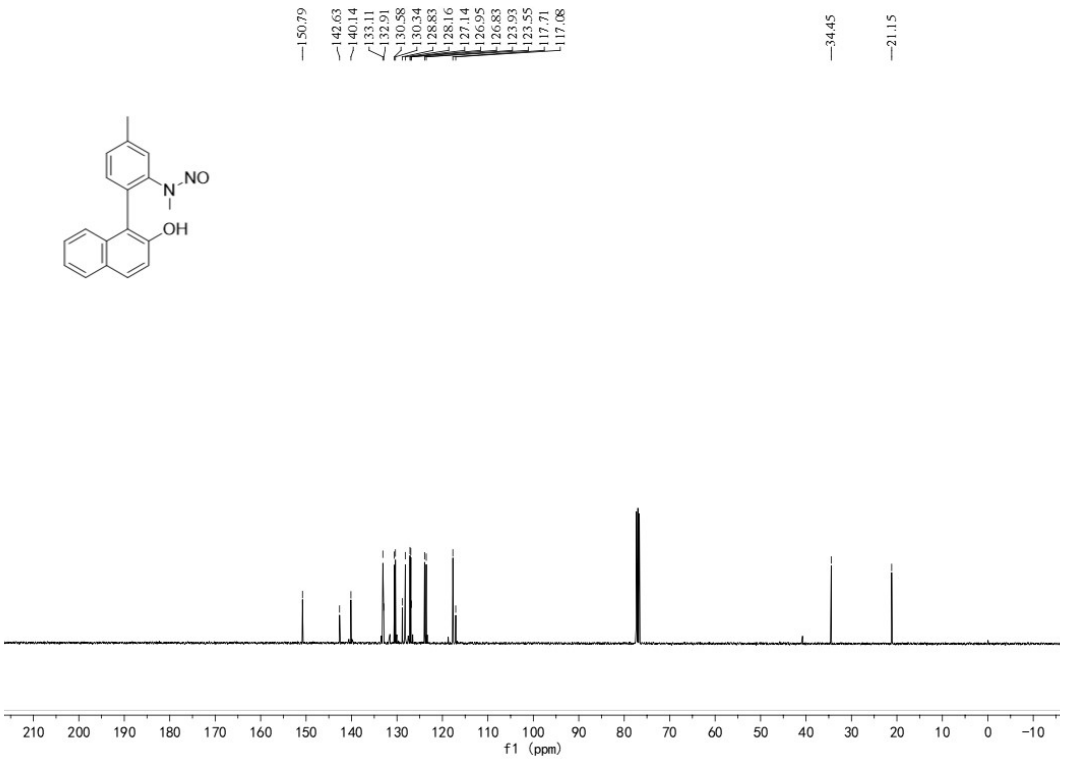
^{13}C NMR (101 MHz) Spectrum of 3g in $CDCl_3$



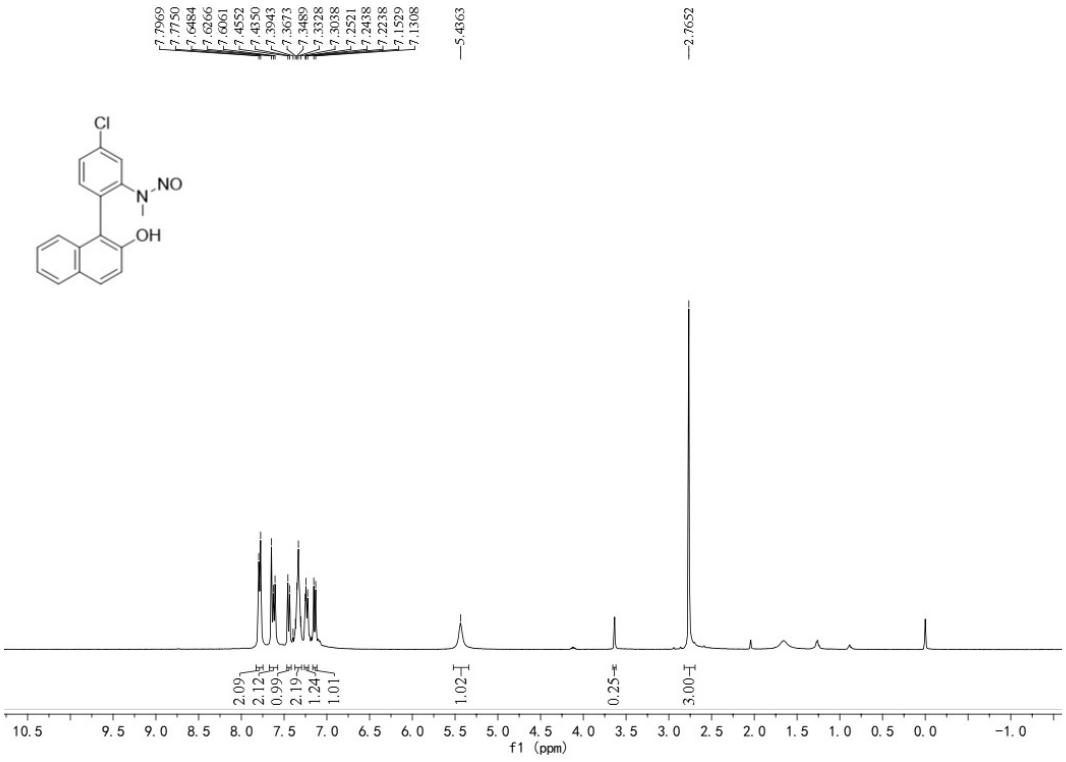
^{1}H NMR (400 MHz) Spectrum of 3h in $CDCl_3$



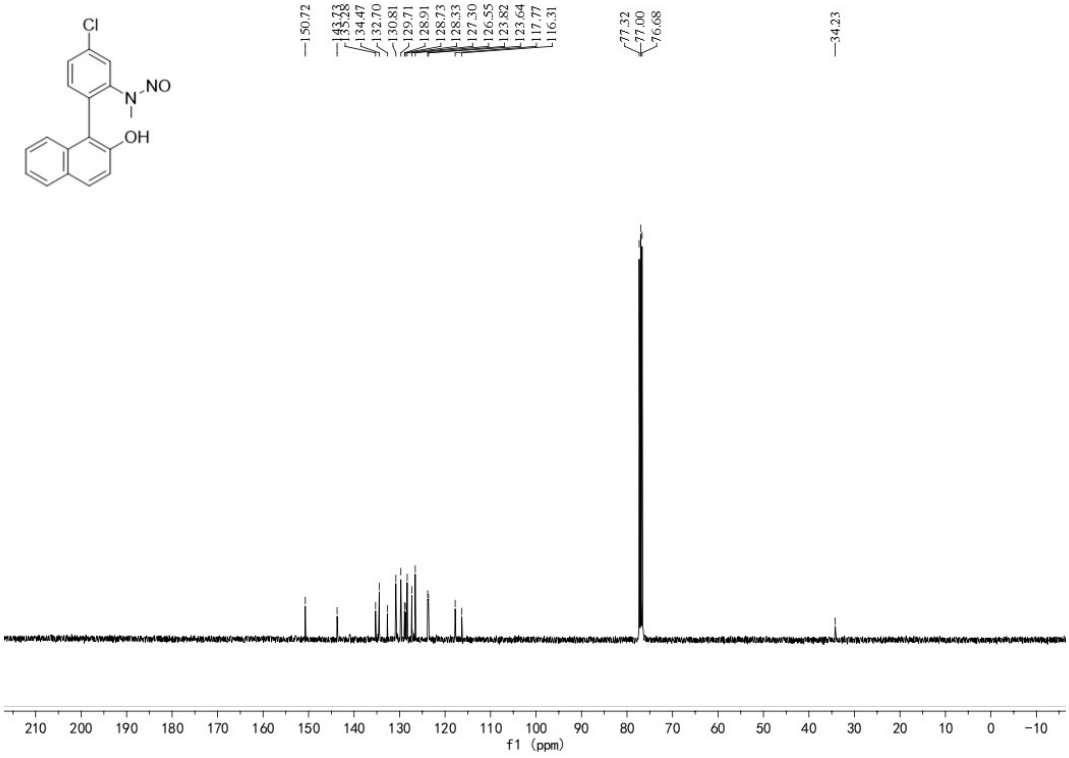
^{13}C NMR (101 MHz) Spectrum of 3h in $CDCl_3$



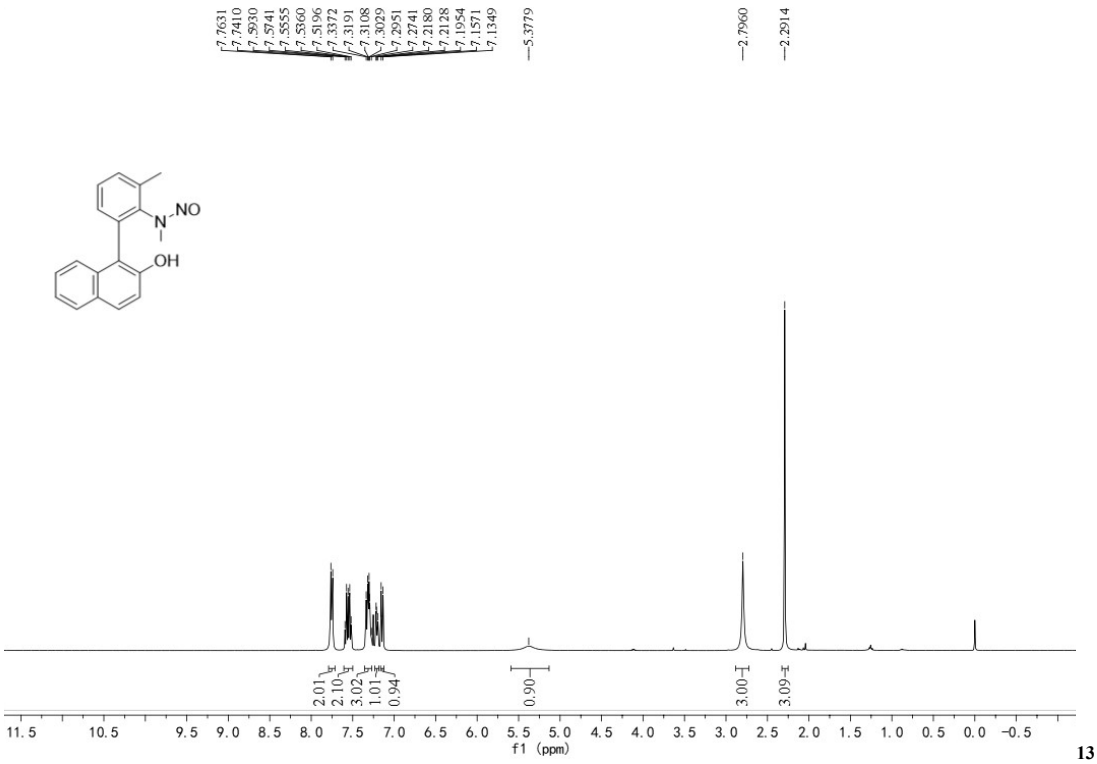
^{1}H NMR (400 MHz) Spectrum of 3i in $CDCl_3$



^{13}C NMR (101 MHz) Spectrum of 3i in $CDCl_3$



^{1}H NMR (400 MHz) Spectrum of 3j in $CDCl_3$



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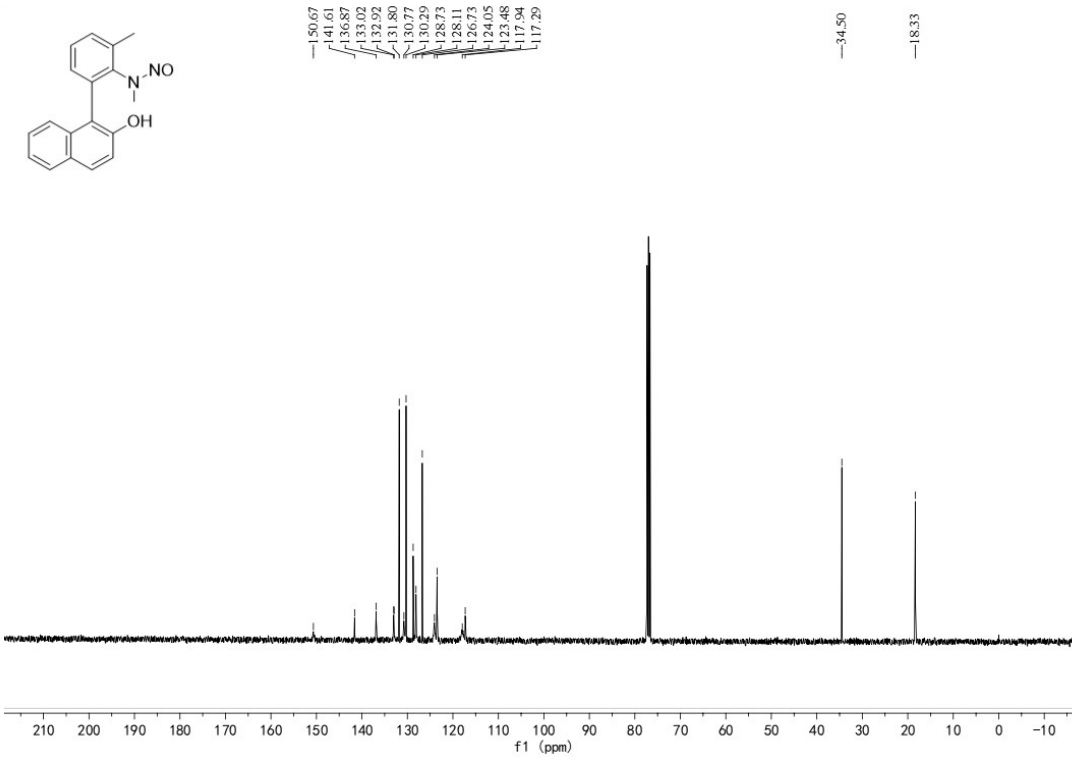
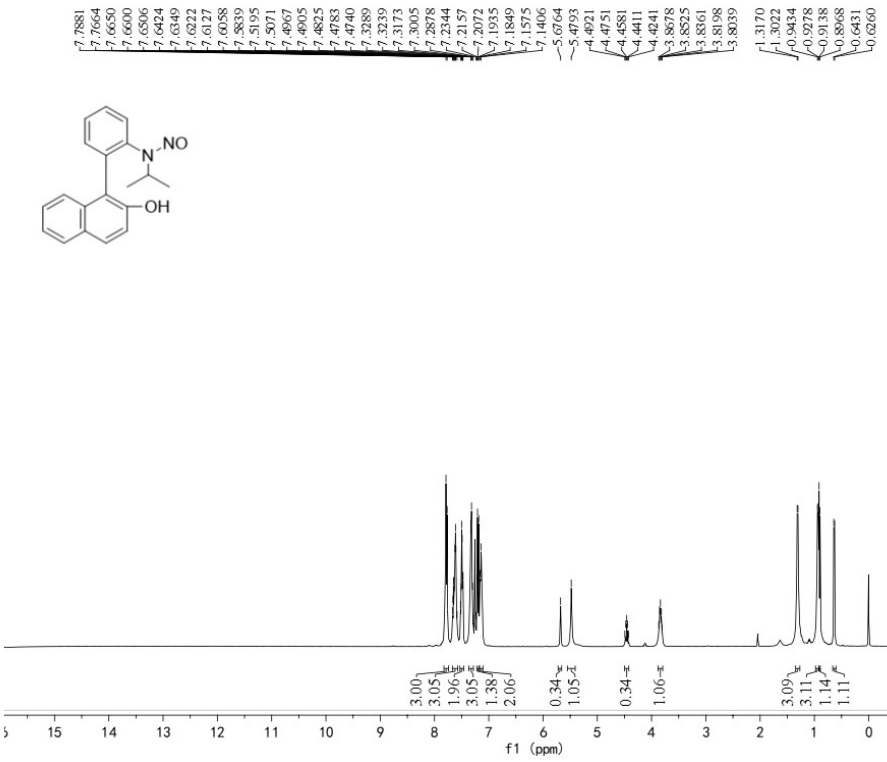
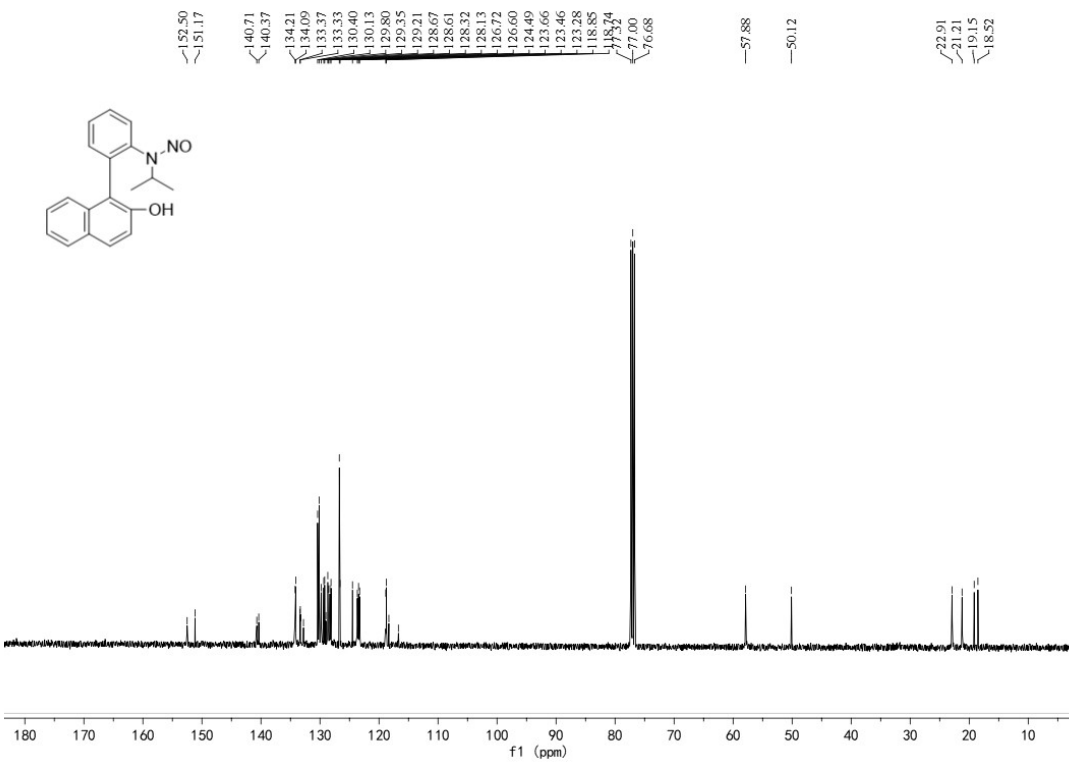
C NMR (101 MHz) Spectrum of 3j in $CDCl_3$



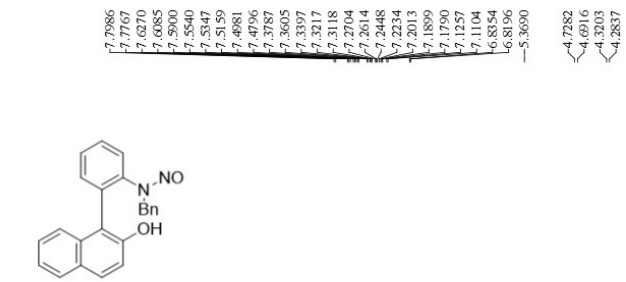
^{1}H NMR (400 MHz) Spectrum of 3k in $CDCl_3$

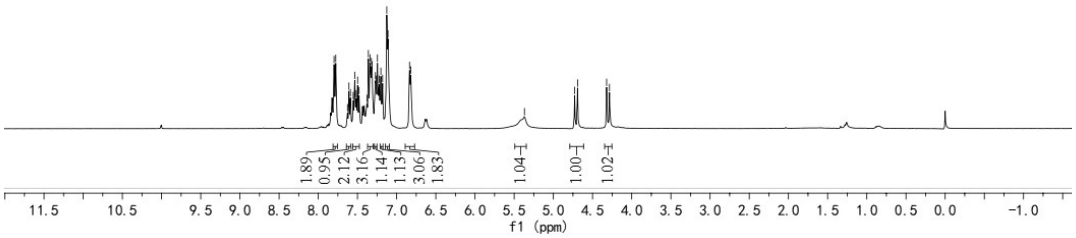


^{13}C NMR (101 MHz) Spectrum of 3k in $CDCl_3$

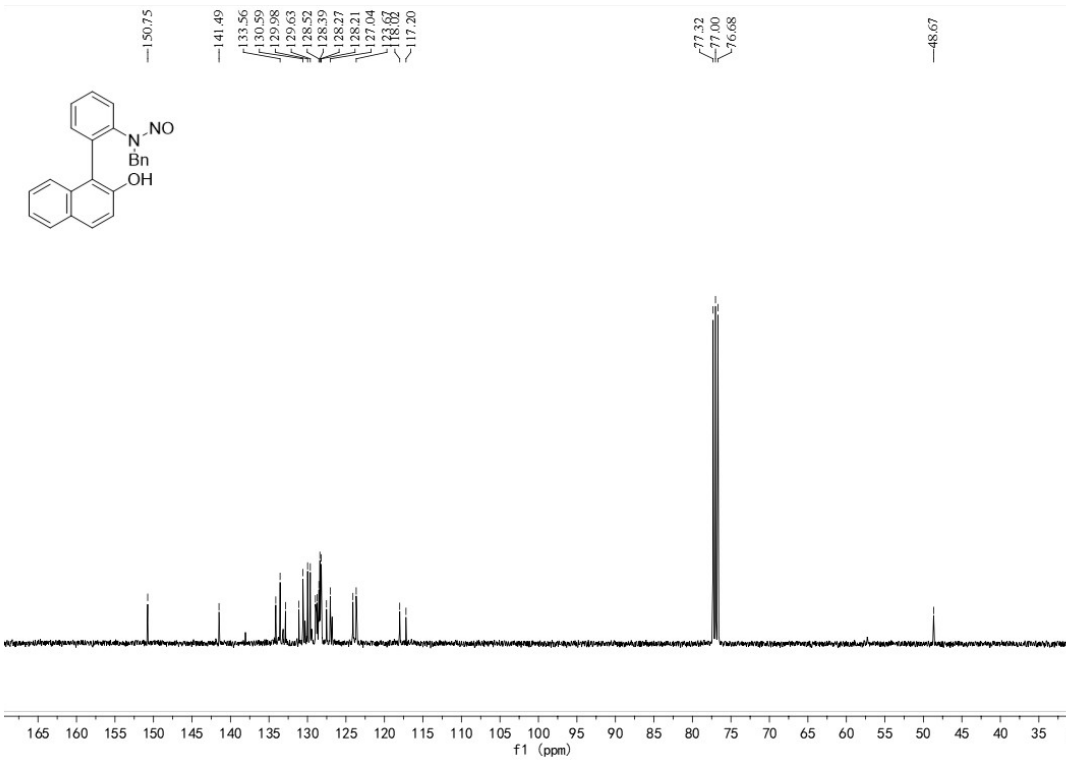


^{1}H NMR (400 MHz) Spectrum of 3l in $CDCl_3$

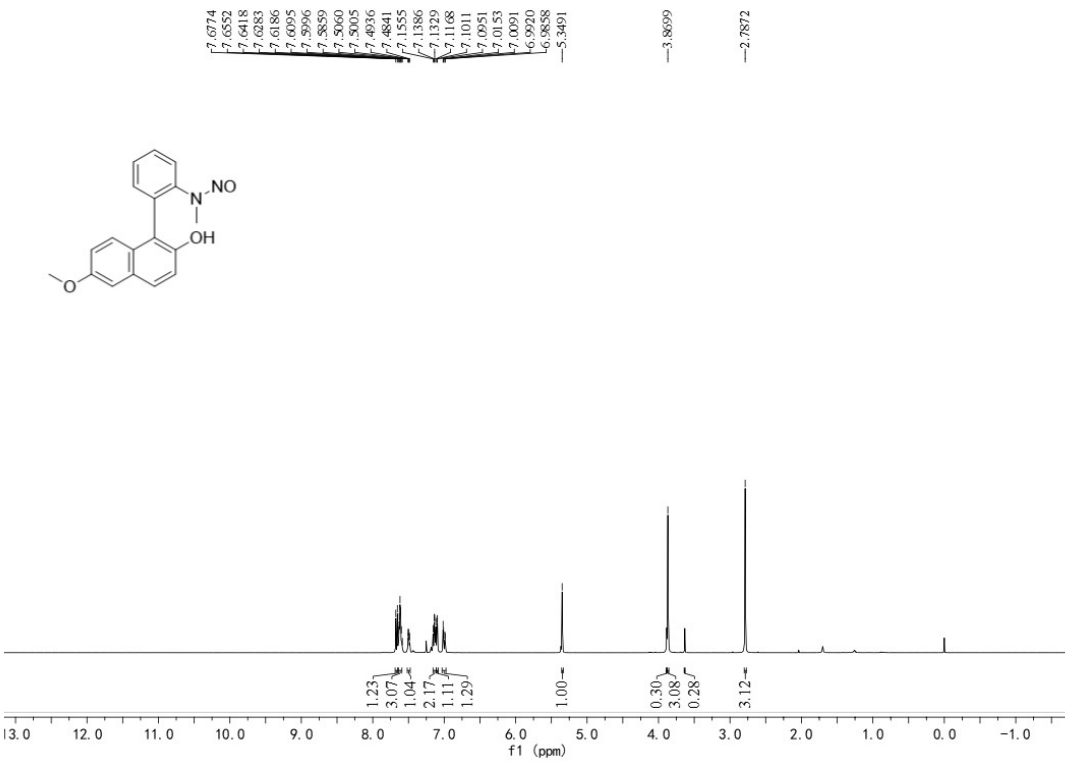




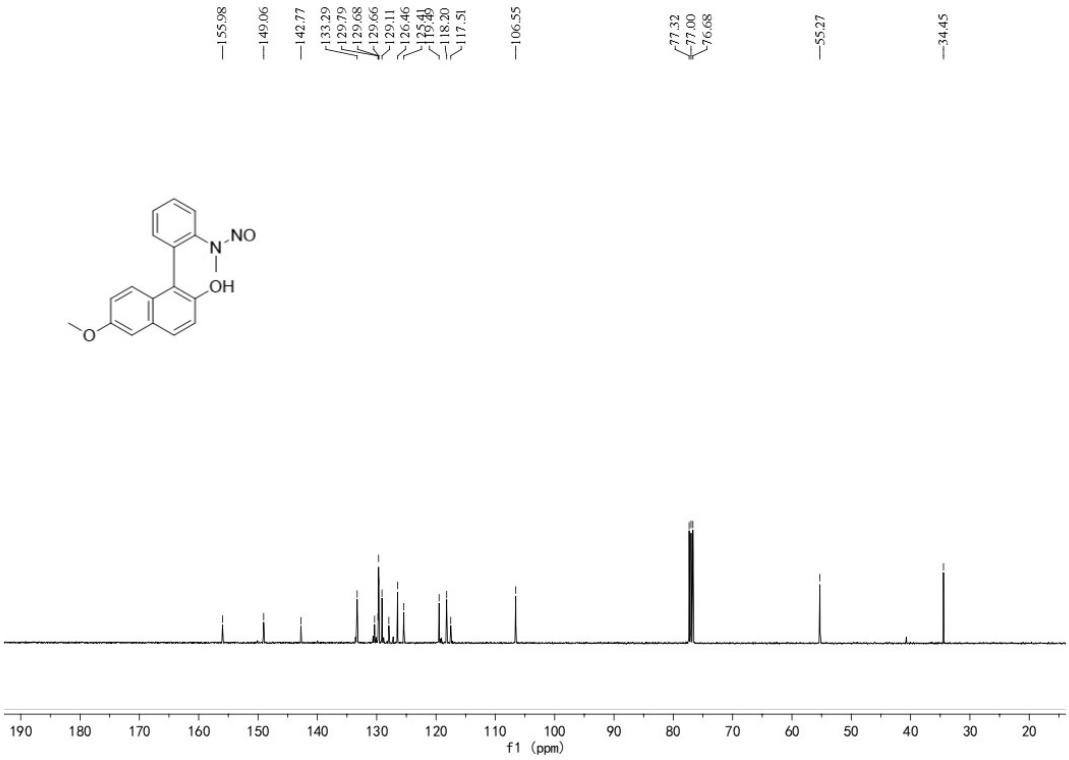
^{13}C NMR (101 MHz) Spectrum of 3l in $CDCl_3$



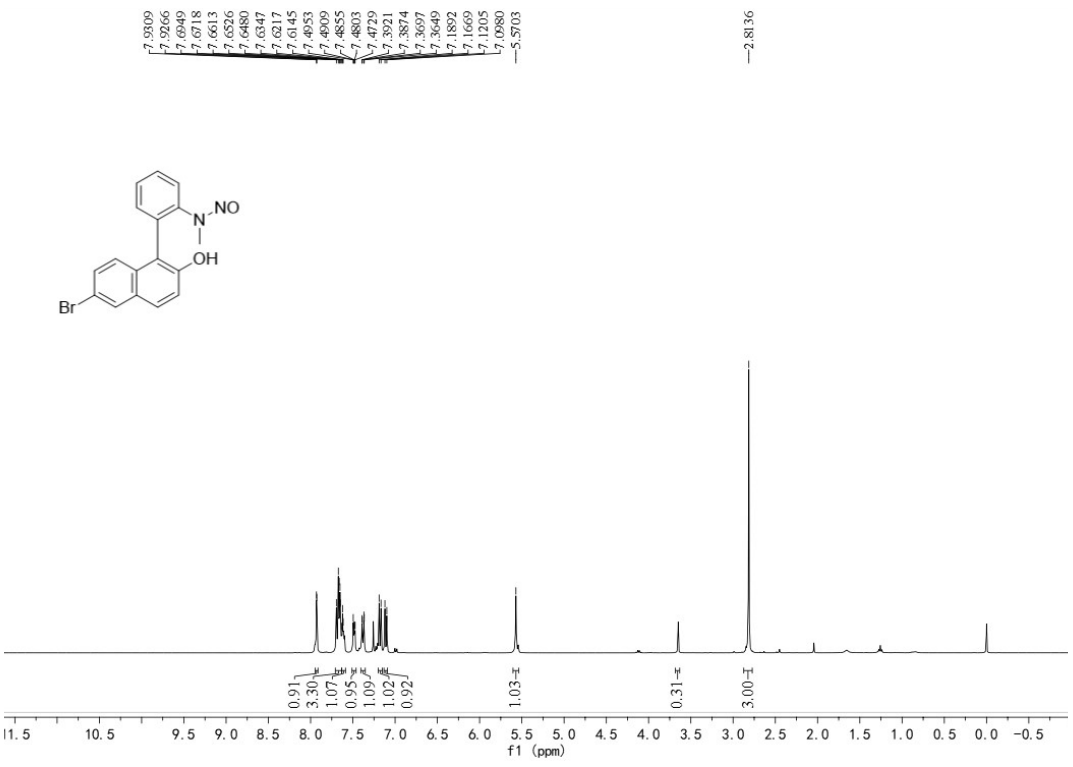
^{1}H NMR (400 MHz) Spectrum of 3ab in $CDCl_3$



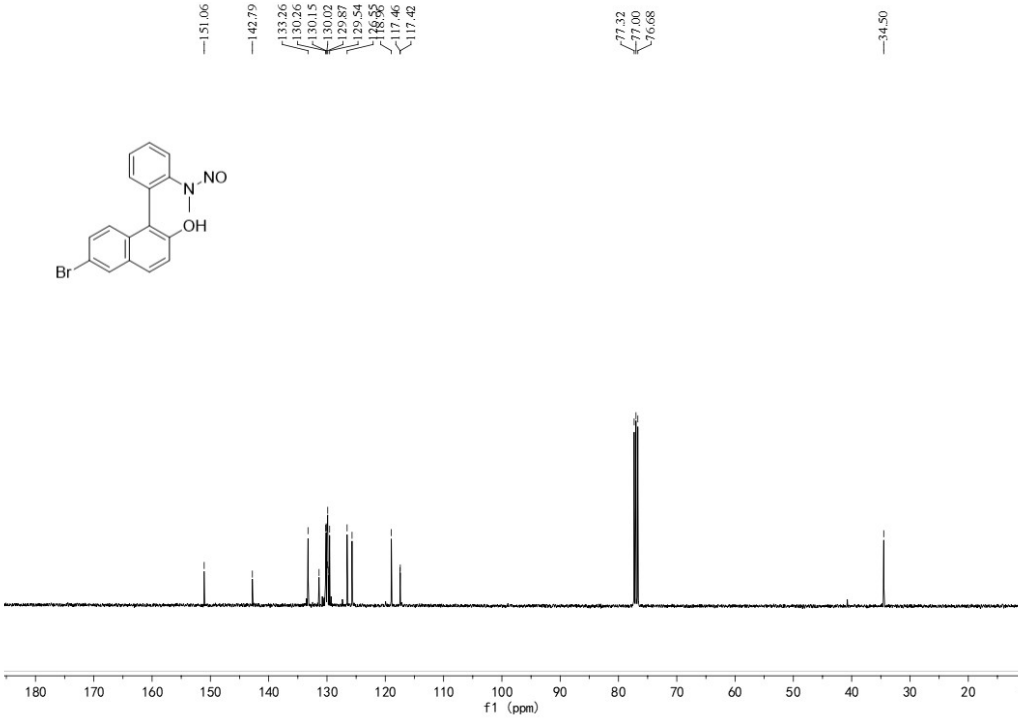
^{13}C NMR (101 MHz) Spectrum of 3ab in $CDCl_3$



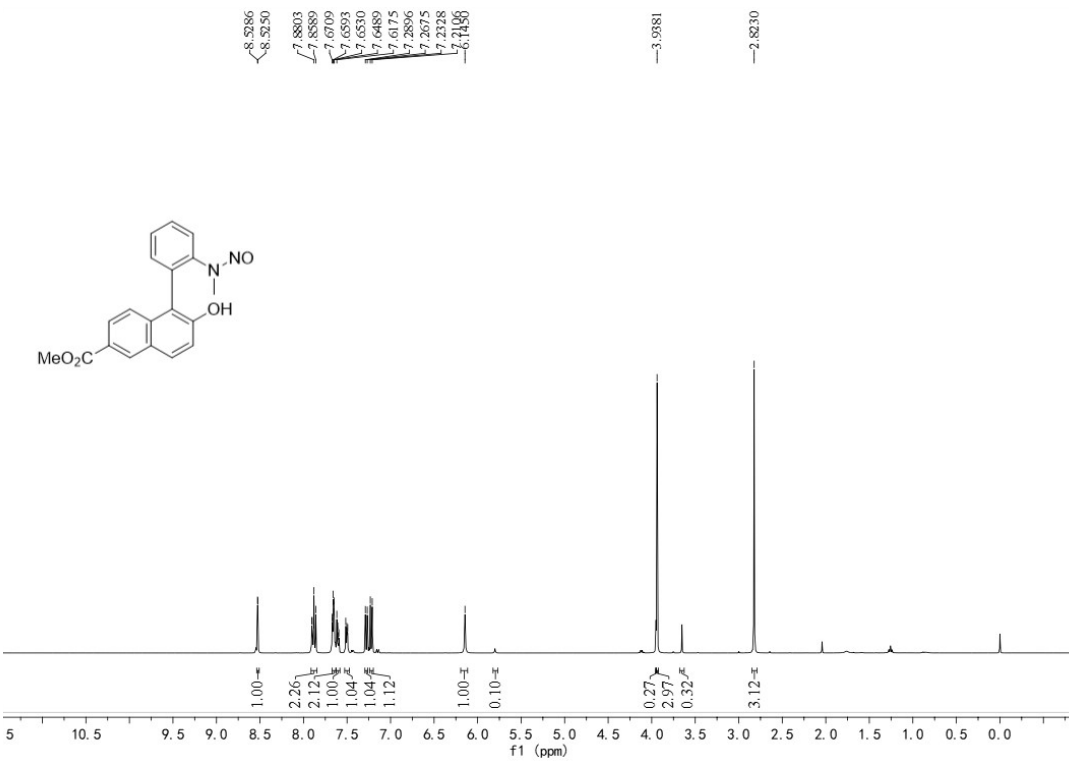
^{1}H NMR (400 MHz) Spectrum of 3ac in $CDCl_3$



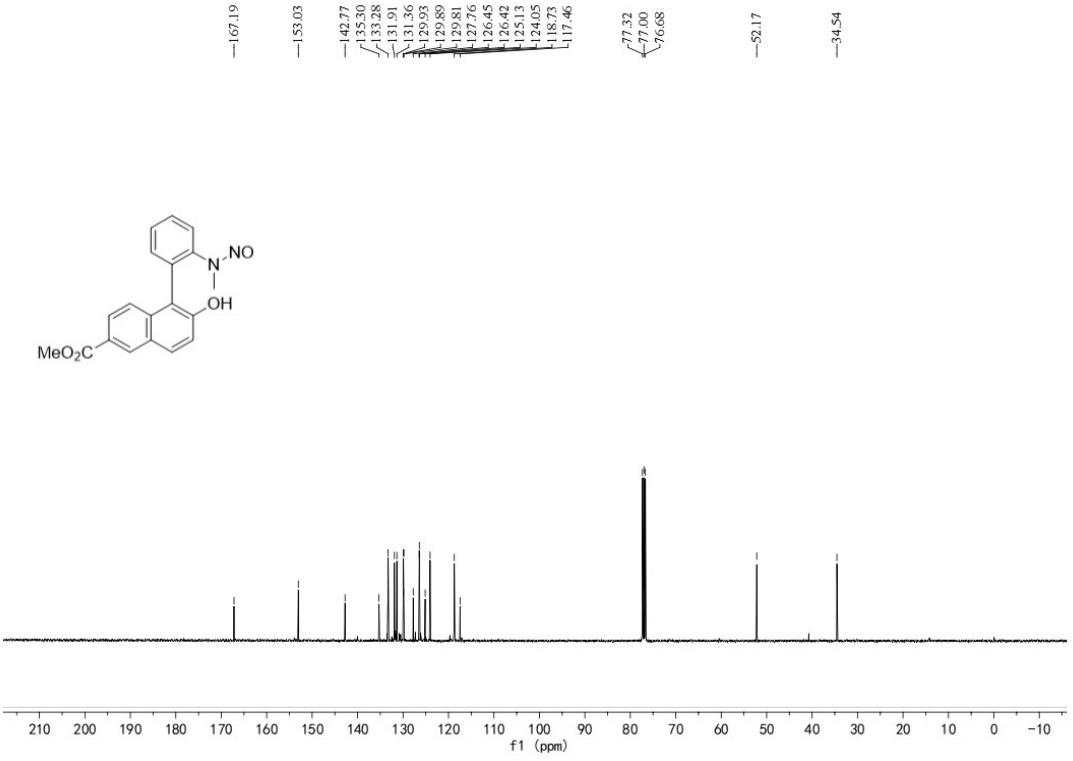
^{13}C NMR (101 MHz) Spectrum of 3ac in $CDCl_3$



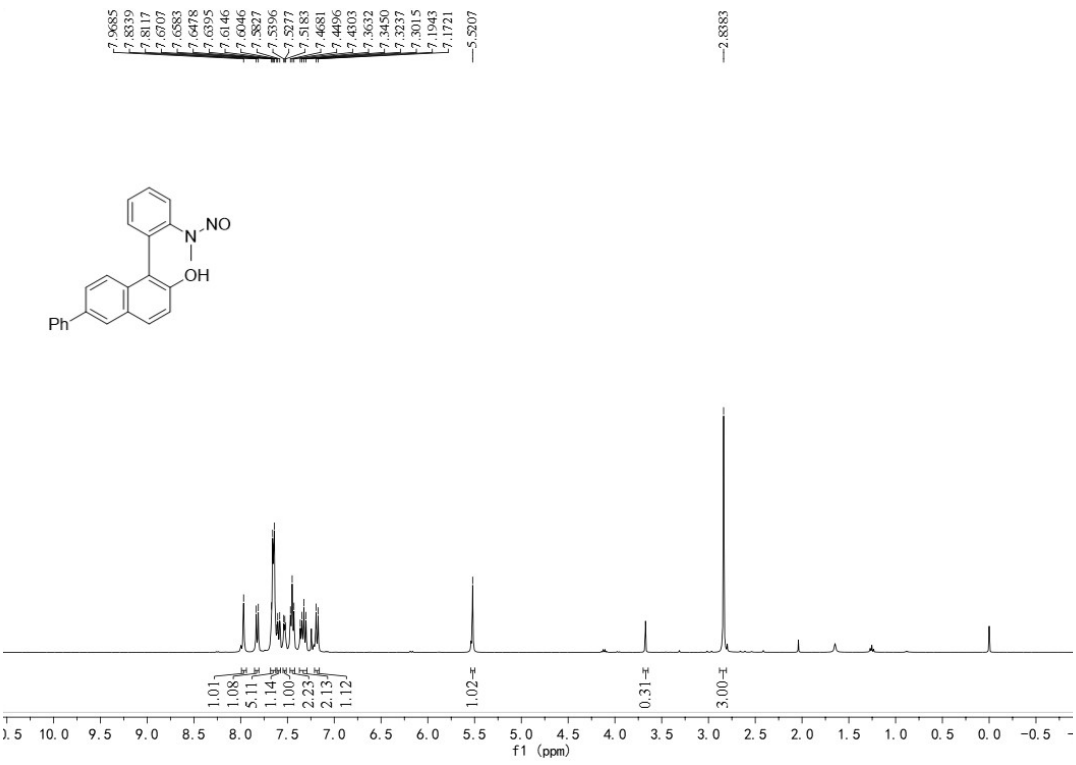
^{1}H NMR (400 MHz) Spectrum of 3ad in $CDCl_3$



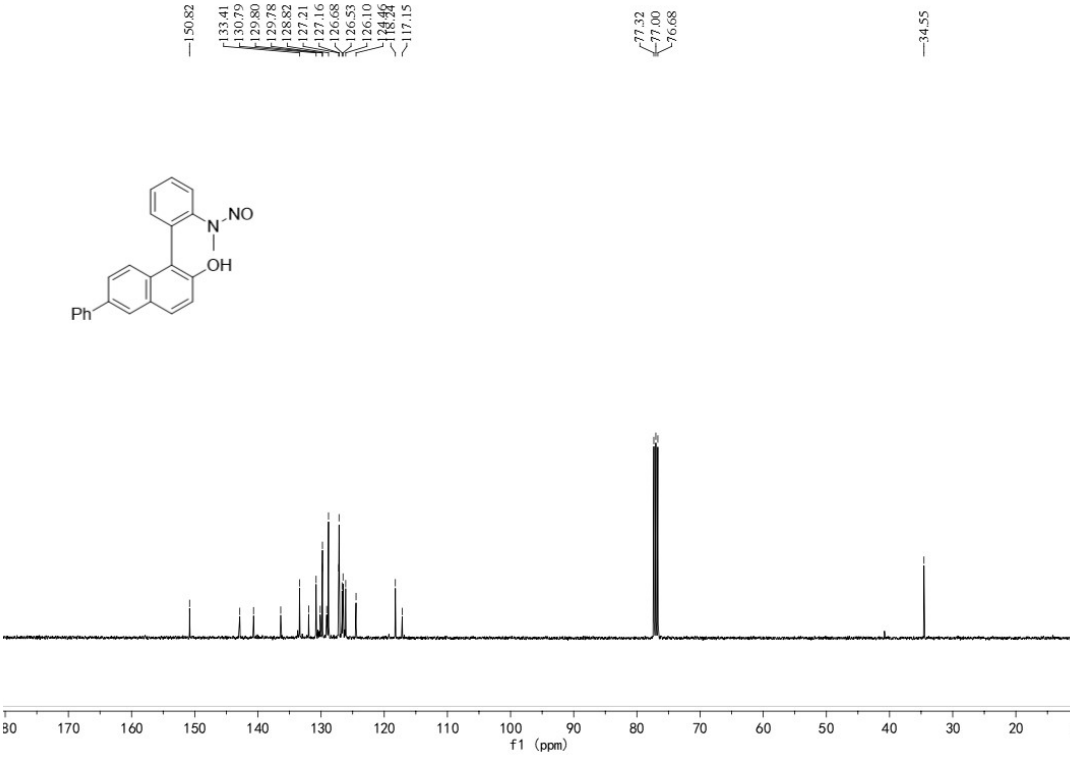
^{13}C NMR (101 MHz) Spectrum of 3ad in $CDCl_3$



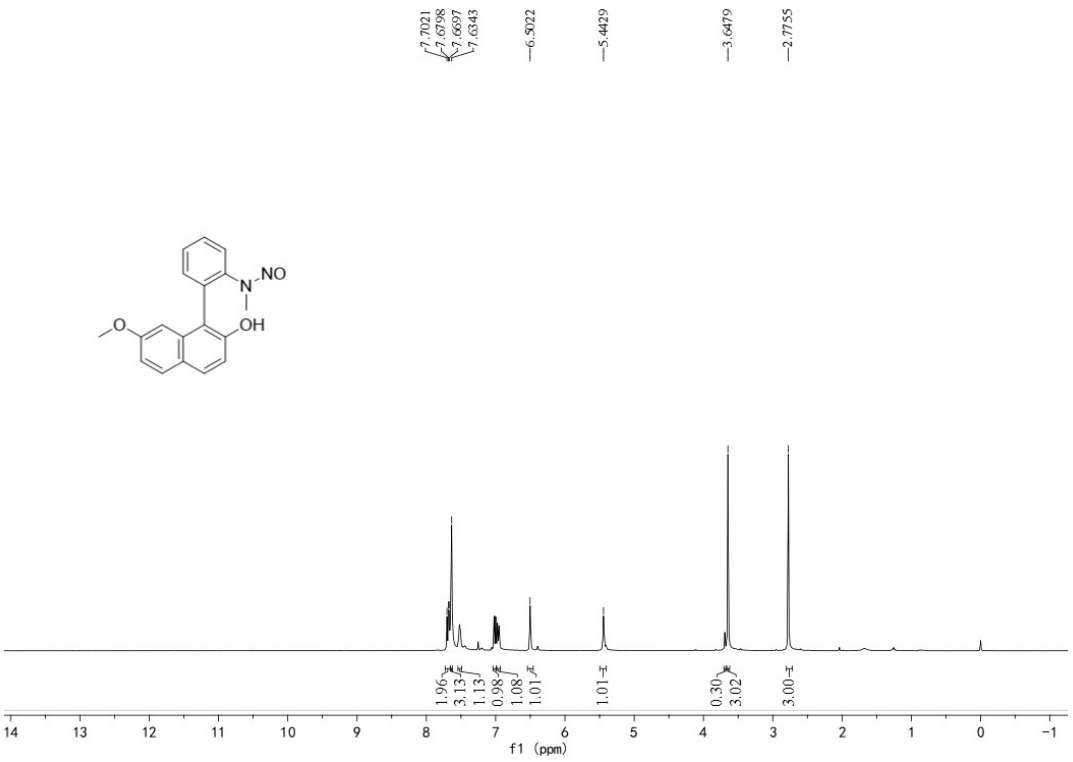
^{1}H NMR (400 MHz) Spectrum of 3ae in $CDCl_3$



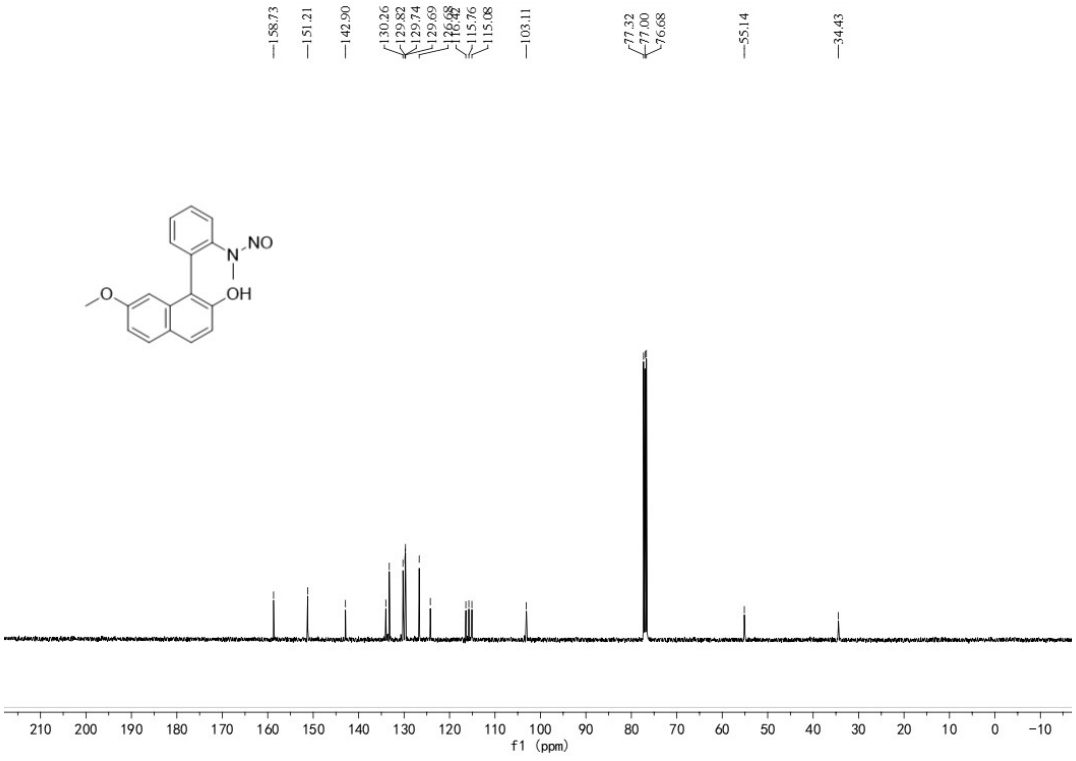
^{13}C NMR (101 MHz) Spectrum of 3ae in $CDCl_3$



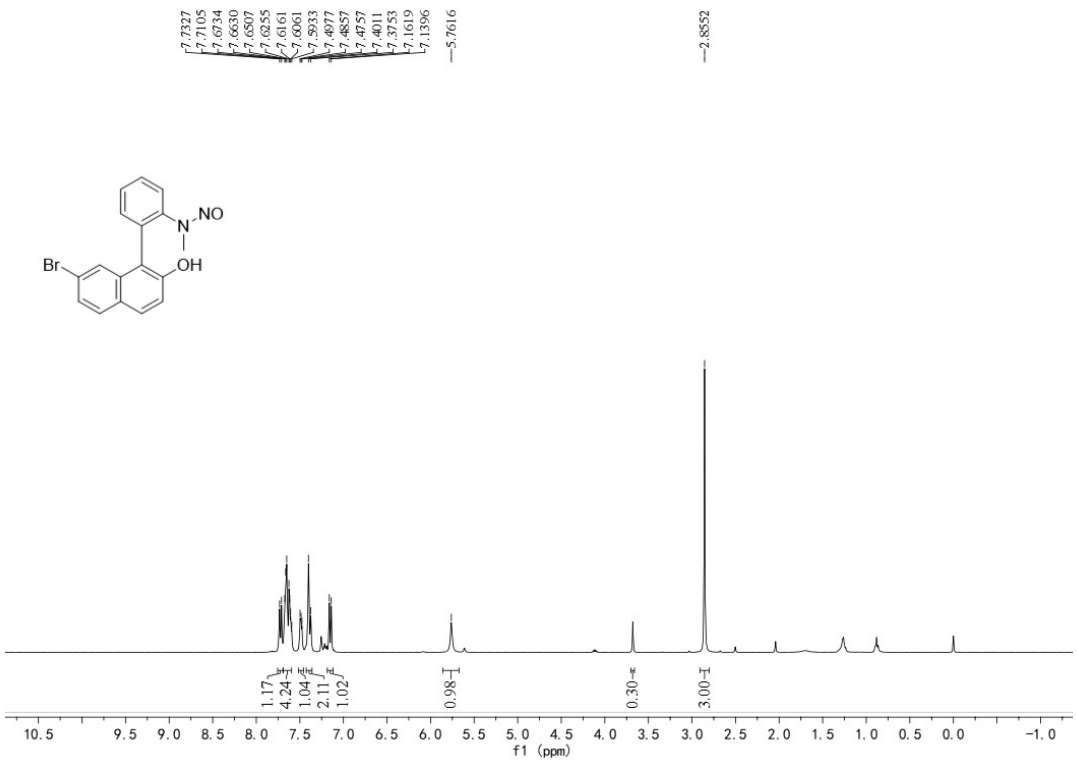
^{1}H NMR (400 MHz) Spectrum of 3af in $CDCl_3$



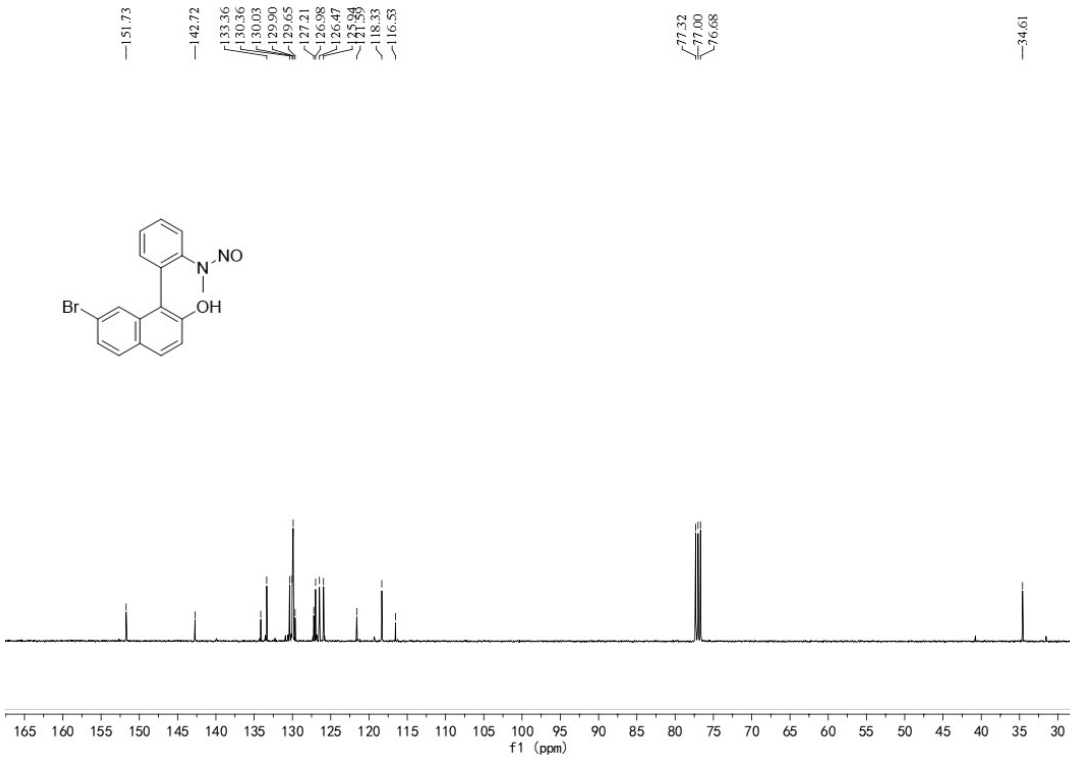
^{13}C NMR (101 MHz) Spectrum of 3af in $CDCl_3$



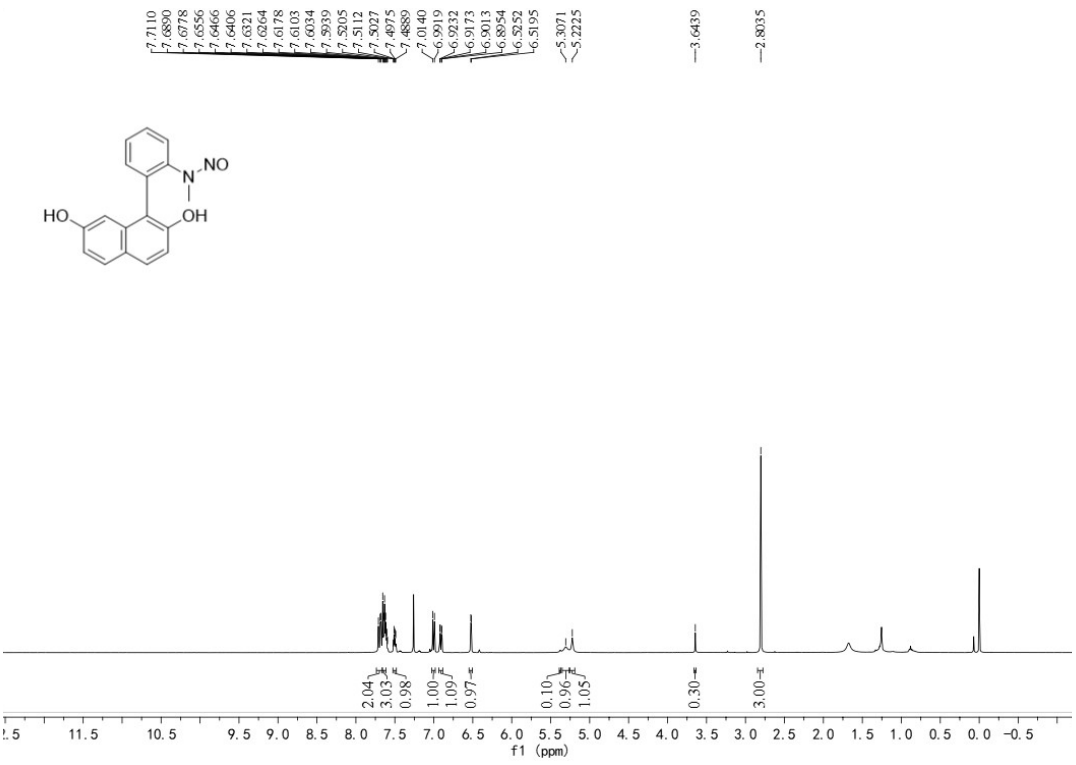
^{1}H NMR (400 MHz) Spectrum of 3ag in $CDCl_3$



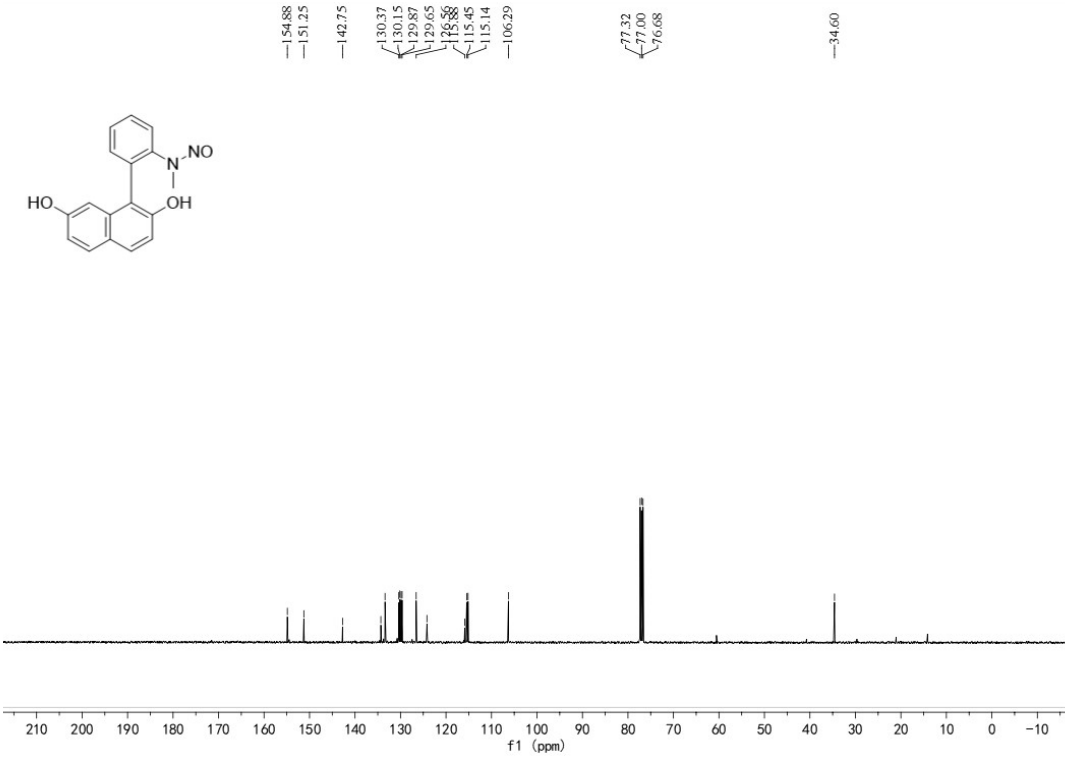
^{13}C NMR (101 MHz) Spectrum of 3ag in $CDCl_3$



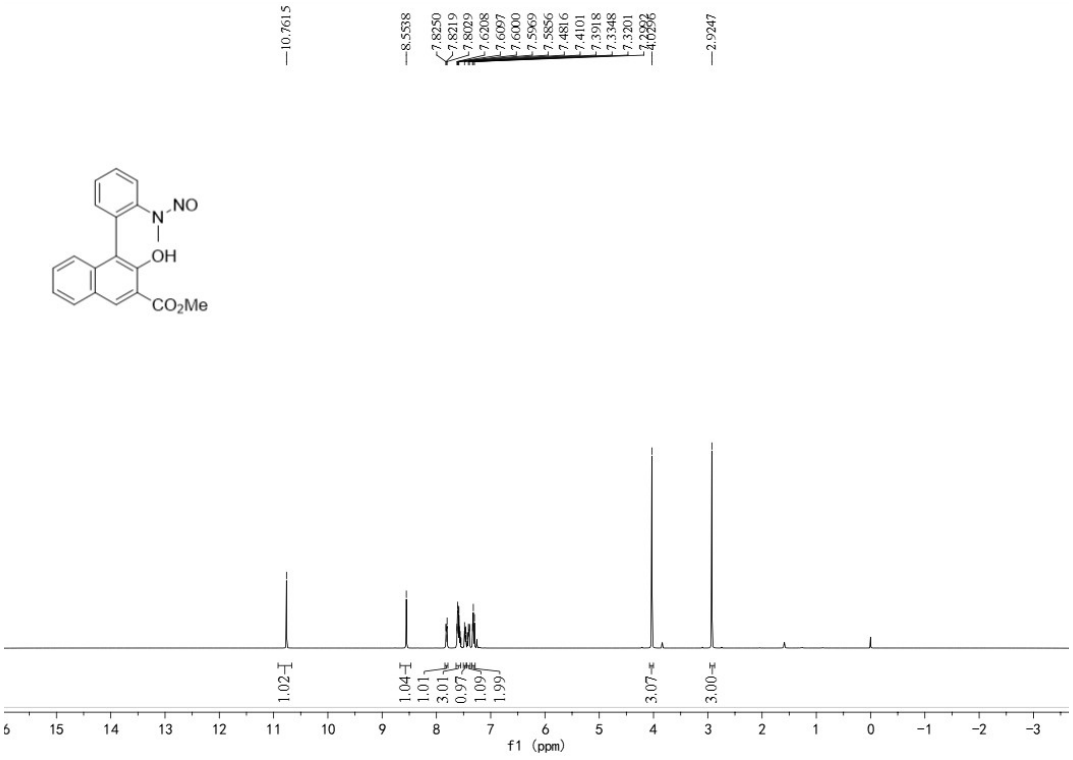
^{1}H NMR (400 MHz) Spectrum of 3ah in $CDCl_3$



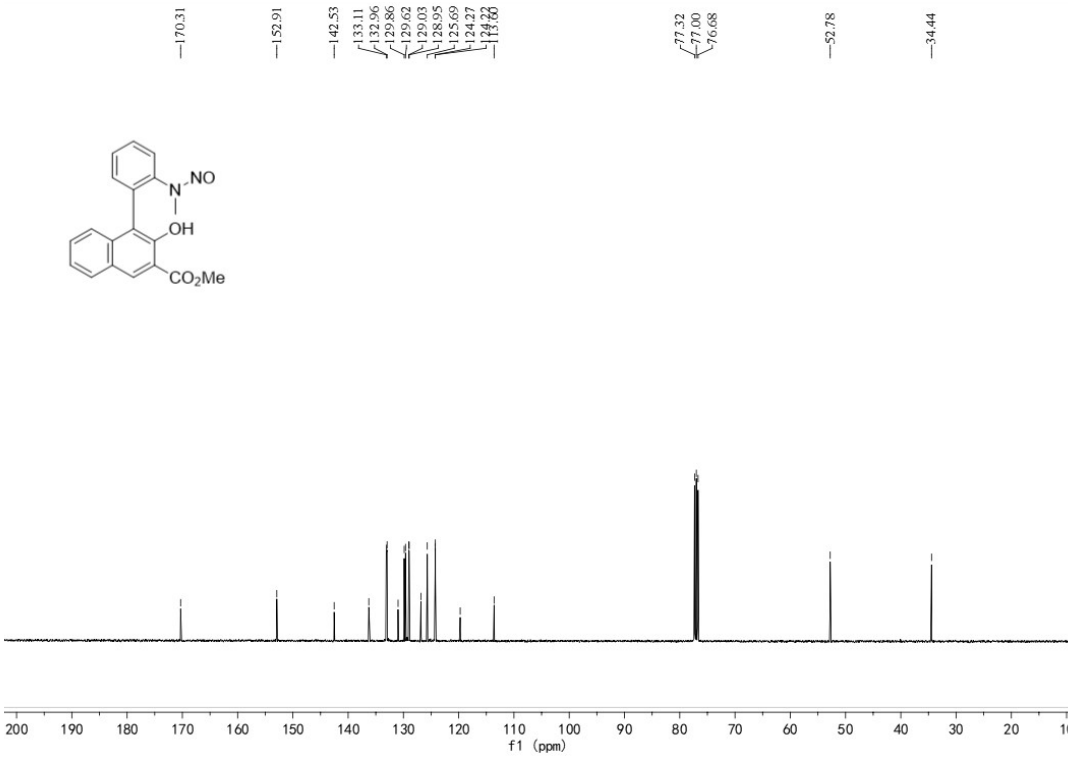
^{13}C NMR (101 MHz) Spectrum of 3ah in $CDCl_3$



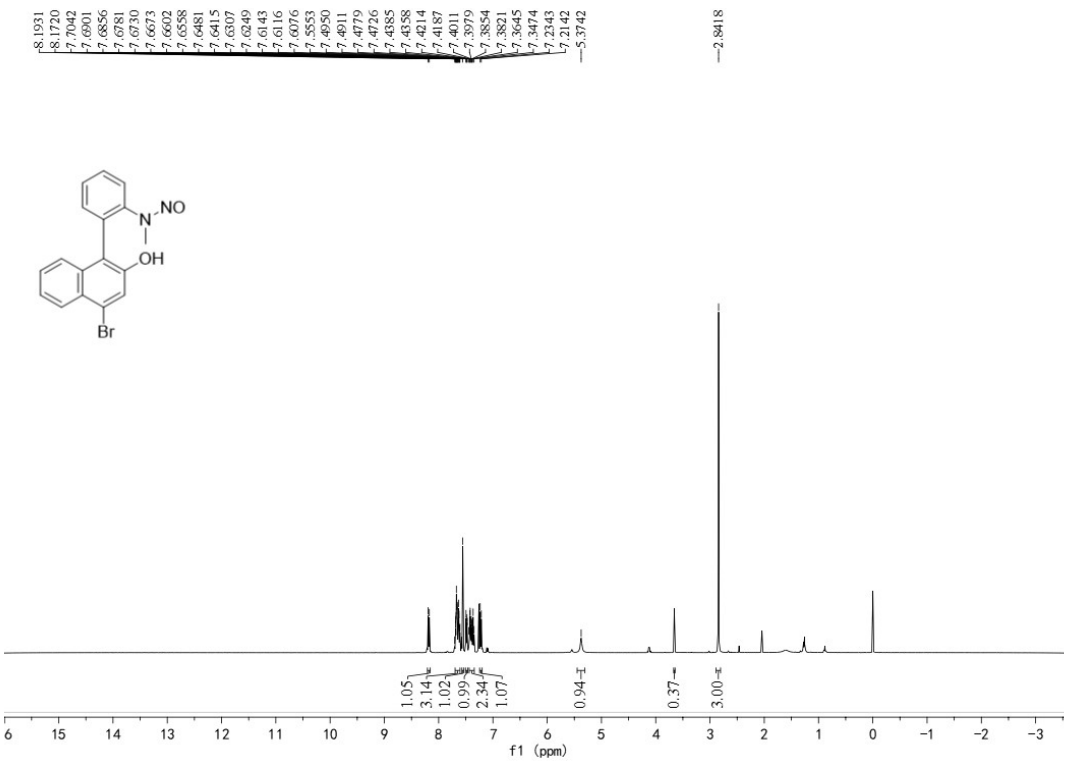
^{1}H NMR (400 MHz) Spectrum of 3ai in $CDCl_3$



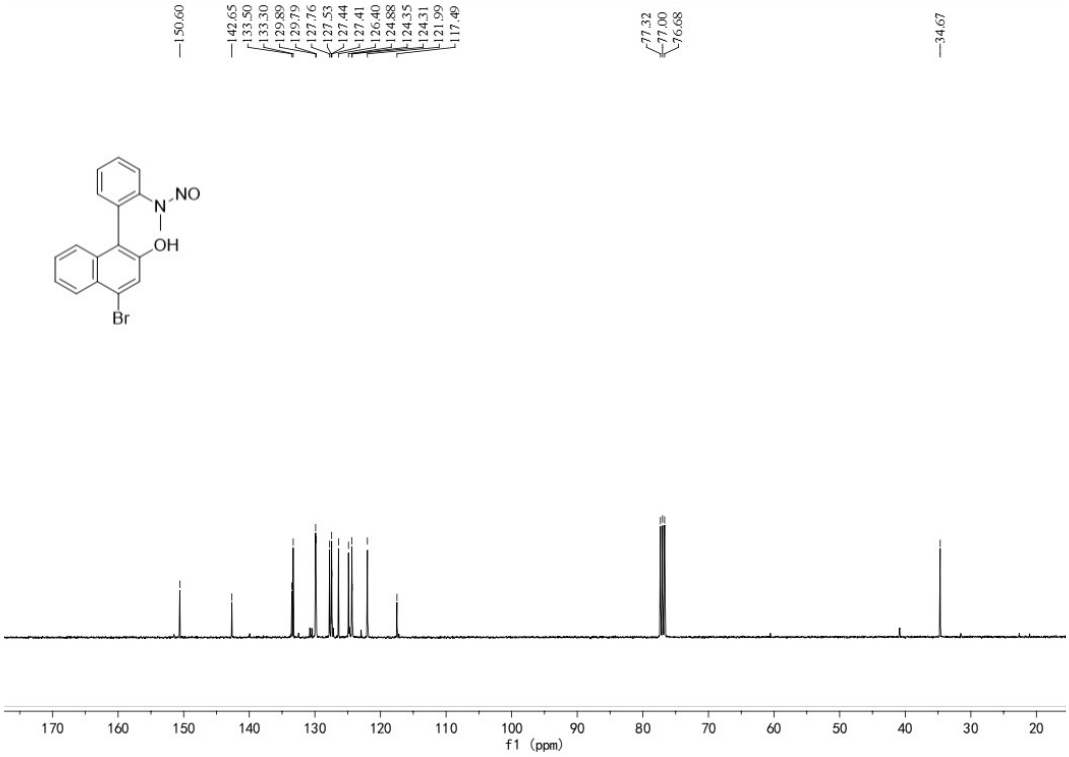
^{13}C NMR (101 MHz) Spectrum of 3ai in $CDCl_3$



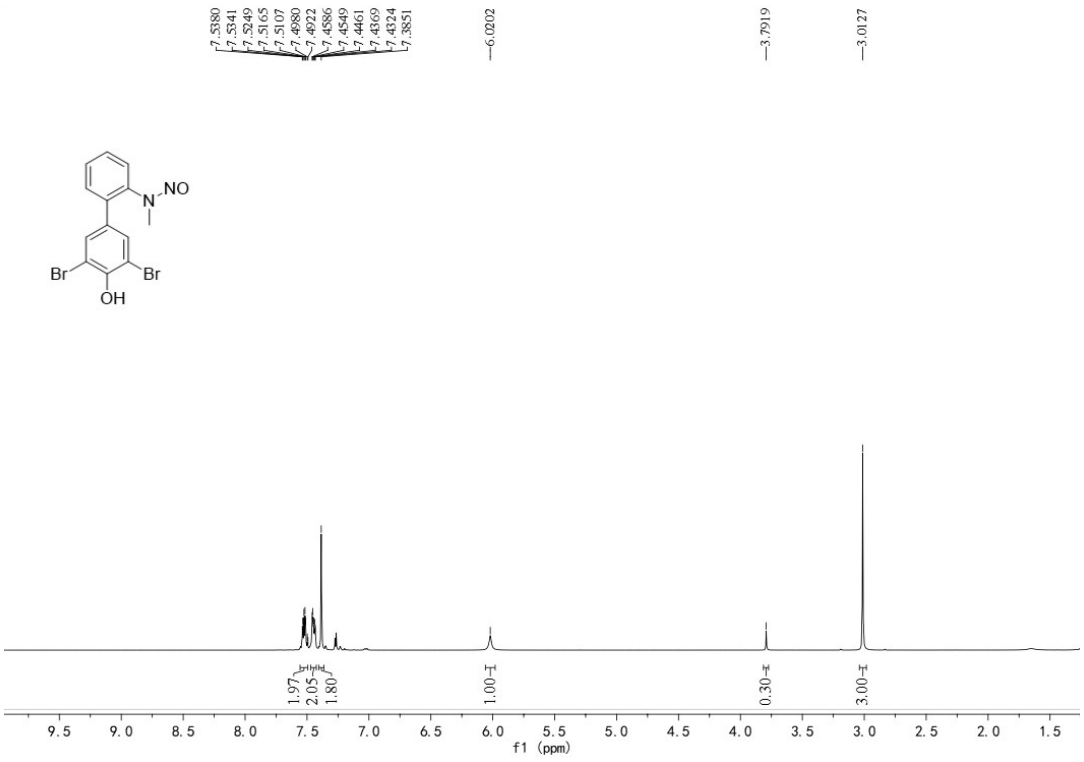
^{1}H NMR (400 MHz) Spectrum of 3aj in $CDCl_3$



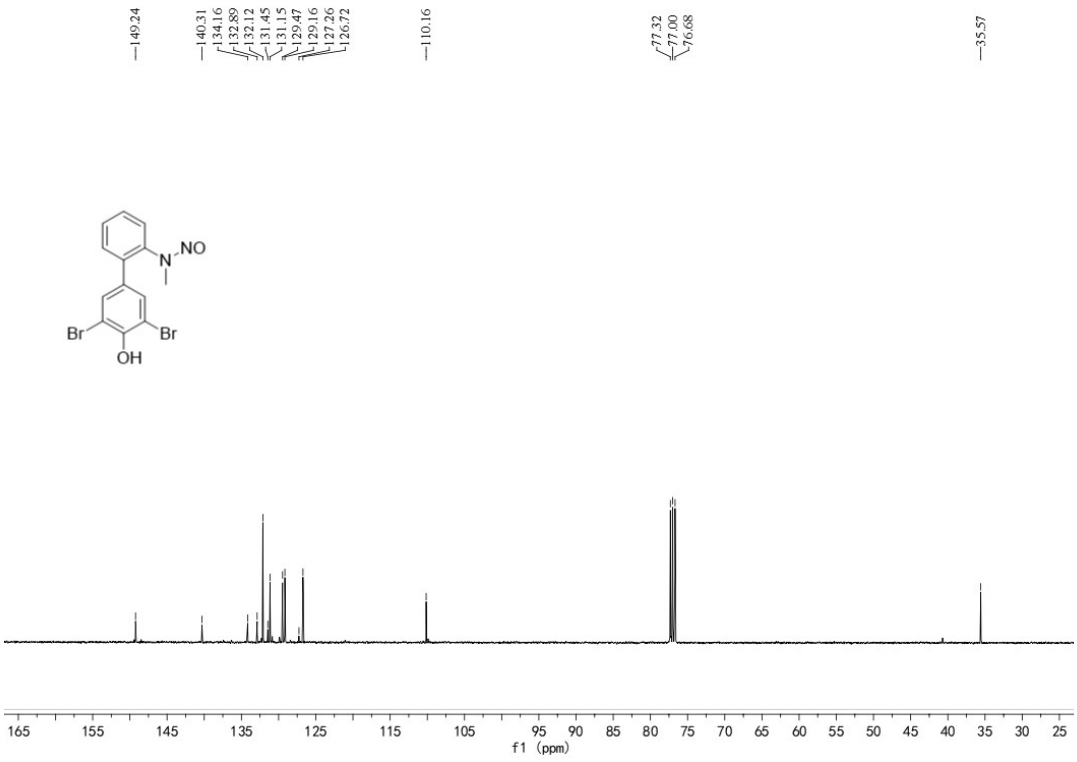
^{13}C NMR (101 MHz) Spectrum of 3aj in $CDCl_3$



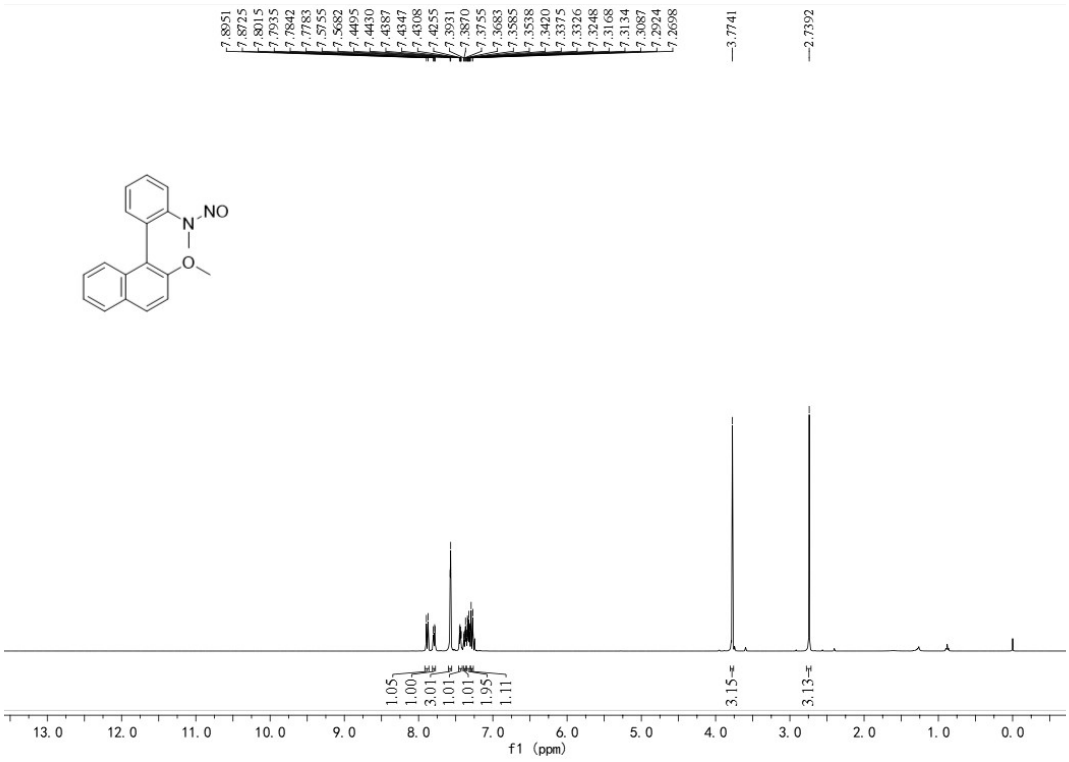
^{1}H NMR (400 MHz) Spectrum of 3ak in $CDCl_3$



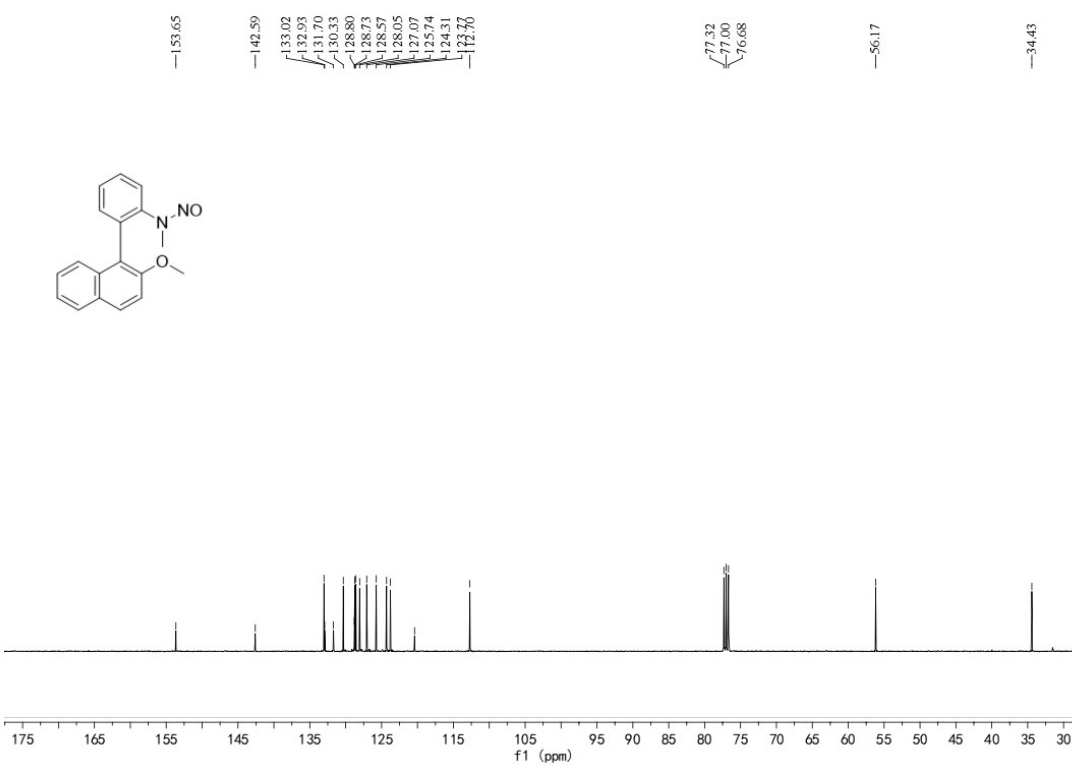
^{13}C NMR (101 MHz) Spectrum of 3ak in $CDCl_3$



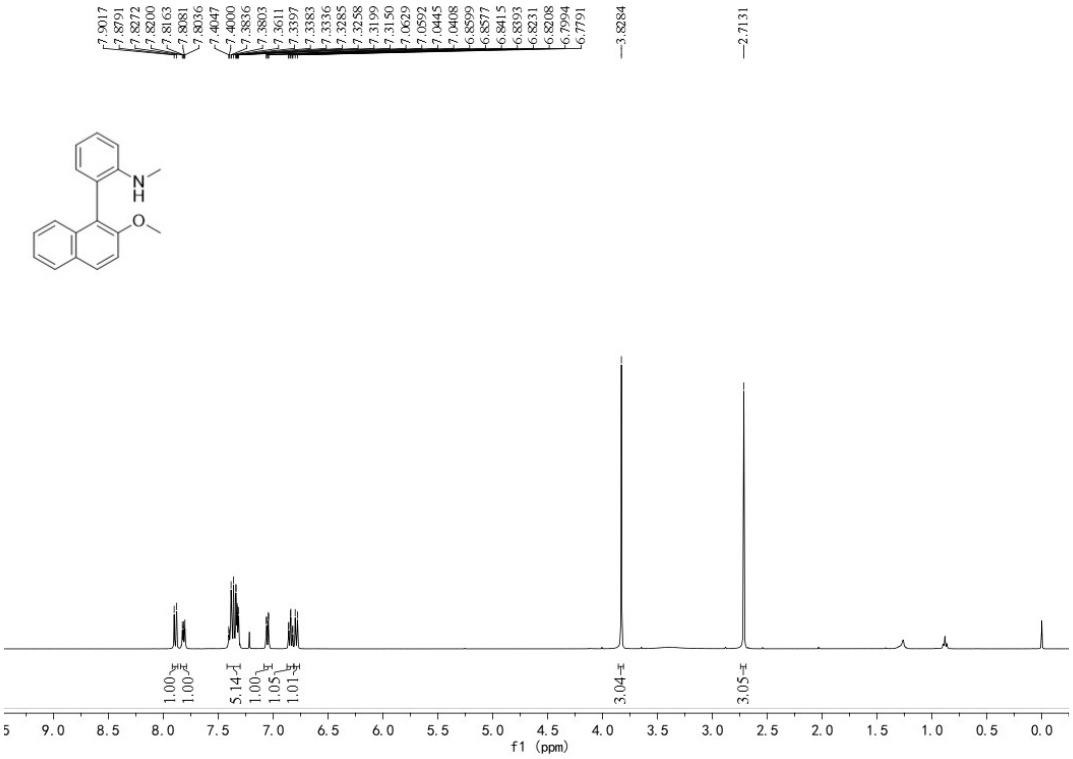
^{1}H NMR (400 MHz) Spectrum of 4 in $CDCl_3$



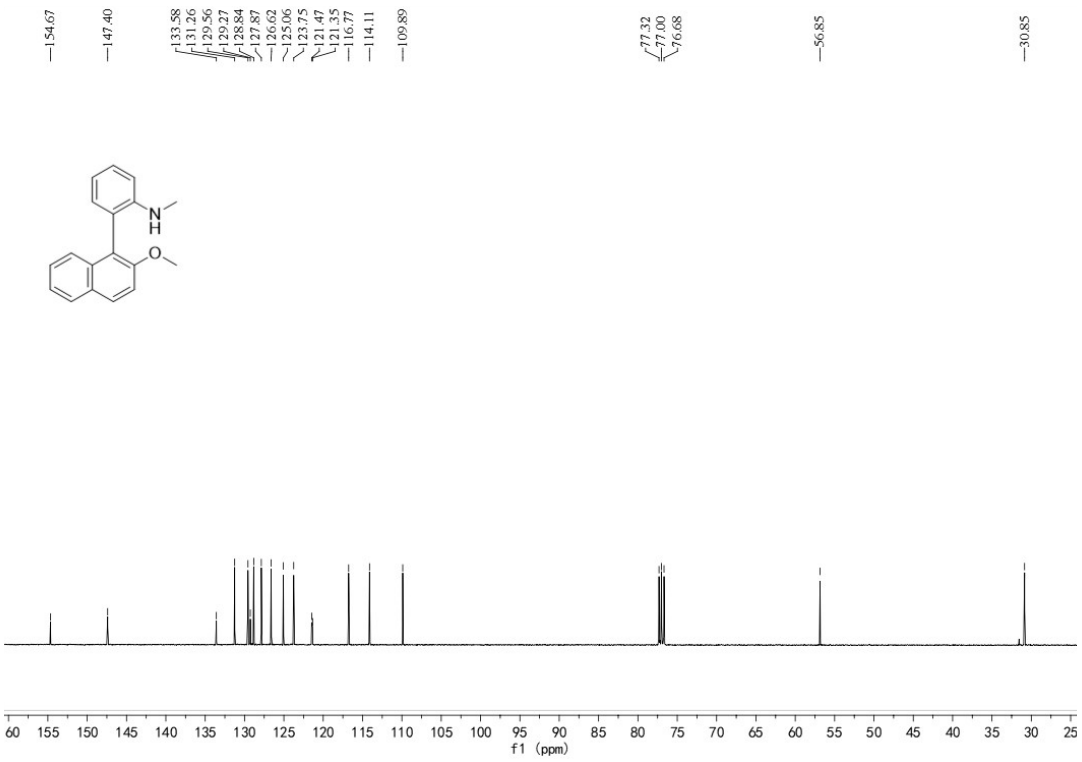
^{13}C NMR (101 MHz) Spectrum of 4 in $CDCl_3$



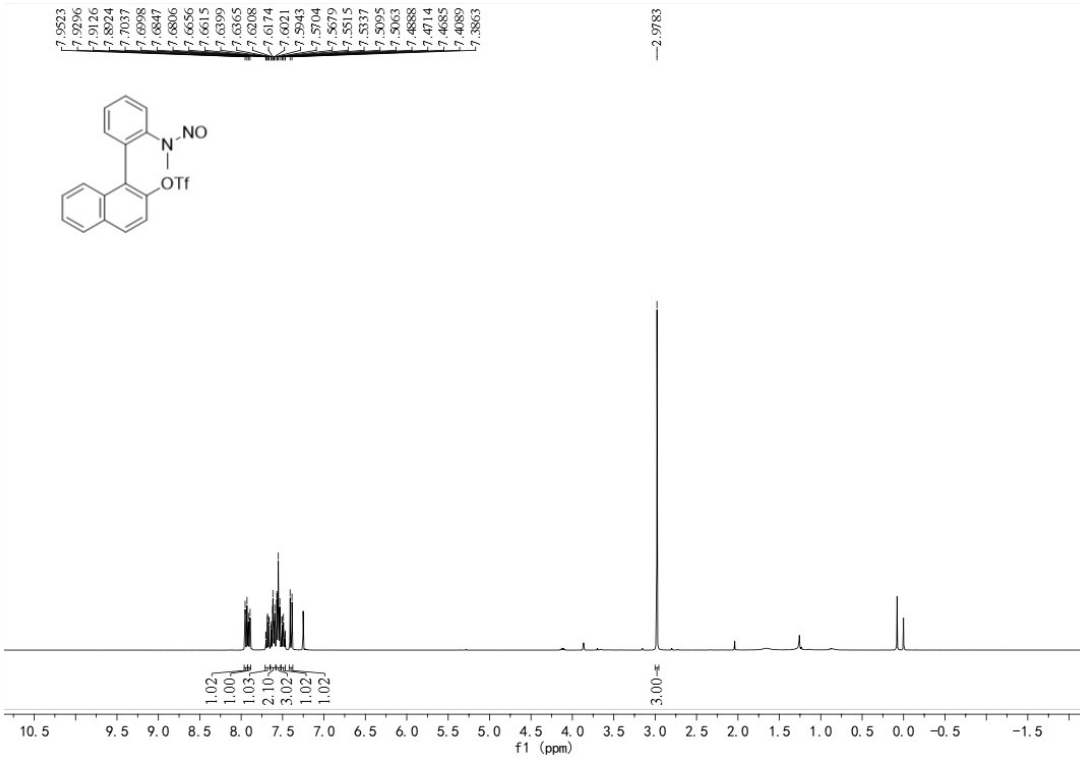
^{1}H NMR (400 MHz) Spectrum of 5 in $CDCl_3$



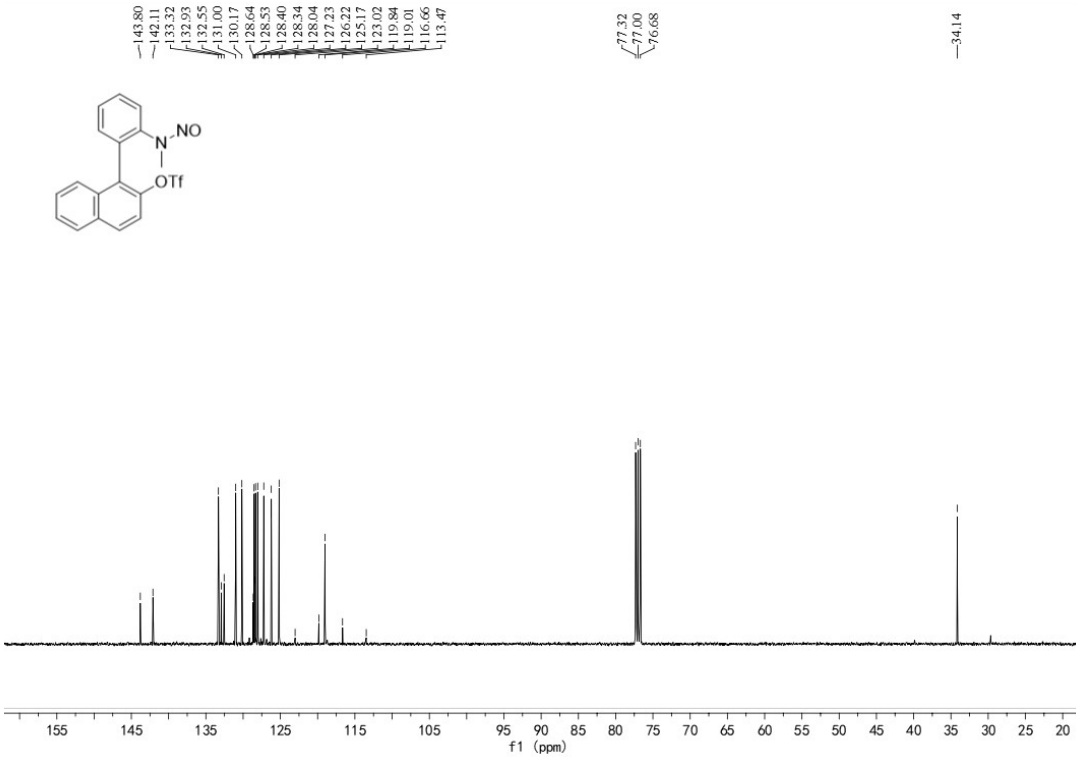
^{13}C NMR (101 MHz) Spectrum of 5 in $CDCl_3$



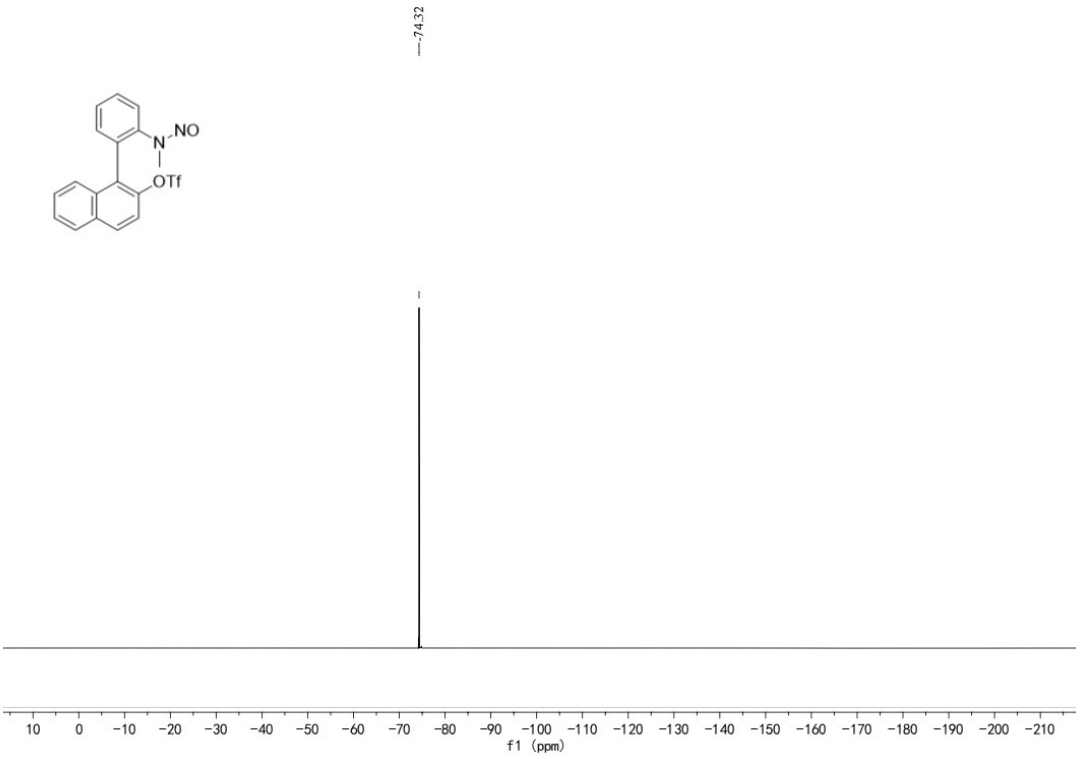
^{1}H NMR (400 MHz) Spectrum of 6 in $CDCl_3$



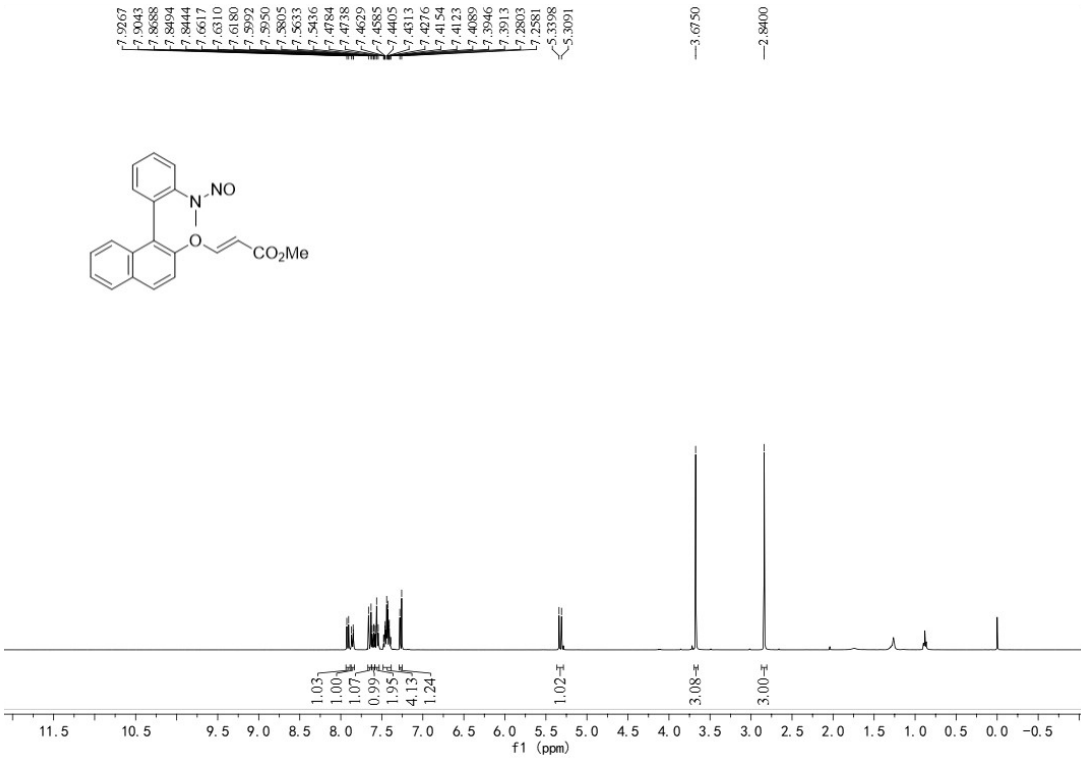
^{13}C NMR (101 MHz) Spectrum of 6 in $CDCl_3$



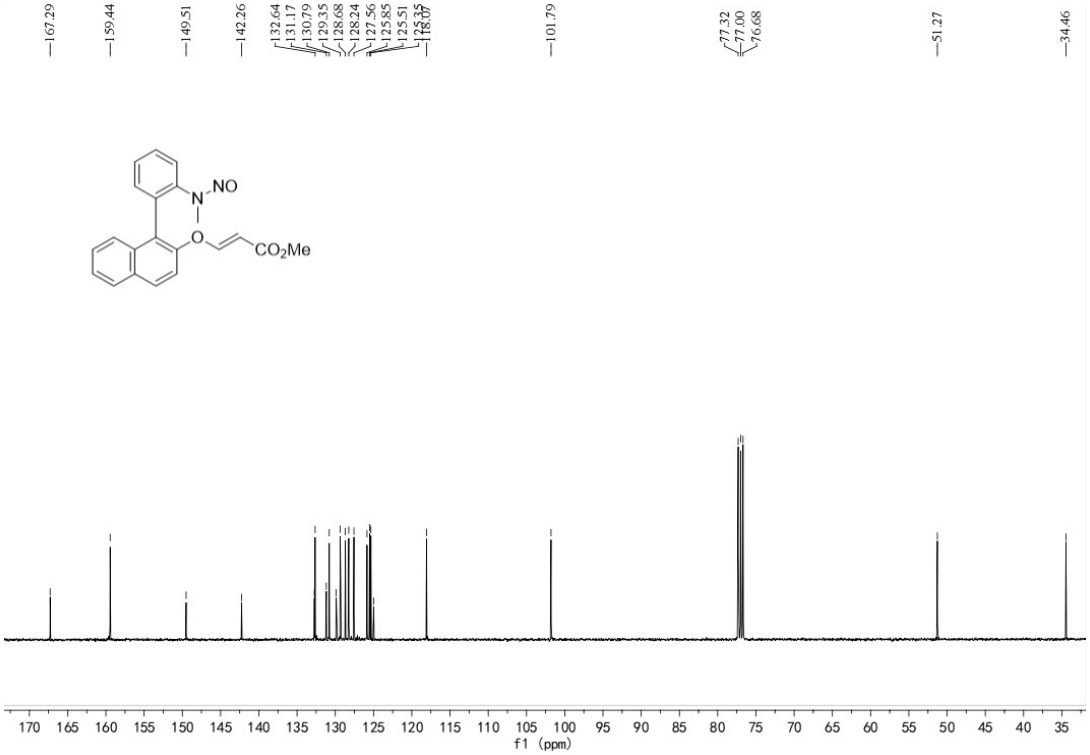
^{19}F NMR (376 MHz) Spectrum of 6 in $CDCl_3$



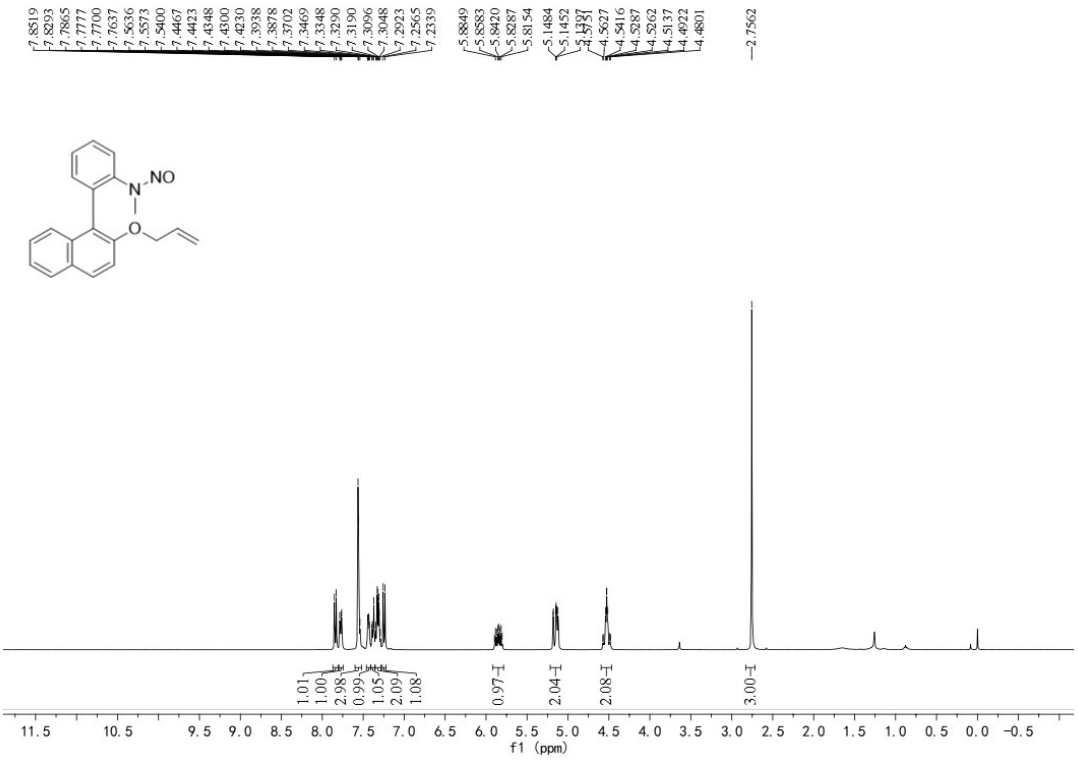
^{1}H NMR (400 MHz) Spectrum of 7 in $CDCl_3$



^{13}C NMR (101 MHz) Spectrum of 7 in $CDCl_3$



^{1}H NMR (400 MHz) Spectrum of 8 in $CDCl_3$



^{13}C NMR (101 MHz) Spectrum of 8 in $CDCl_3$