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Supporting Information

Rhodium-catalyzed oxidative C–H/C–H cross-coupling of aniline with heteroarene: *N*-nitroso group enabled mild conditions

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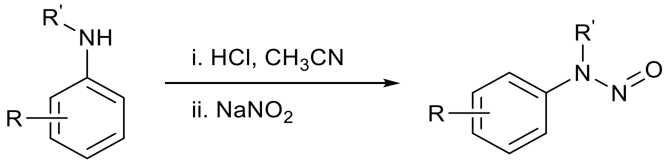
I. General remarks

NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26; DMSO-d_6: δ = 2.50). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16; DMSO-d_6: δ = 39.52). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $RhCl_3 \cdot 3H_2O$ were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. $AgSbF_6$ was purchased from Alfa Aesar. Ag salts (AgOAc and Ag_2CO_3) and Cu salts were purchased from Beijing Ou He Chemical Engineering (China) Co., Ltd. $[Cp^*RhCl_2]_2$,[1] $[Cp^*Rh(MeCN)_3][SbF_6]_2$,[2] $Rh(PPh_3)_3Cl$,[3] Substrates **1**,[4] were prepared according to the literature procedures. Dichloroethane (DCE), toluene, 1,4-dioxane, tetrahydrofuran (THF), and *N*,*N*-dimethylformamide (DMF) were dried with an innovative technology solvent purification system (model no.: PS-MD-5).

II. General procedure for the synthesis of *N*-nitrosoaniline substrates[4]

General procedure for the synthesis of *N*-nitrosoaniline substrates according to an already reported method:

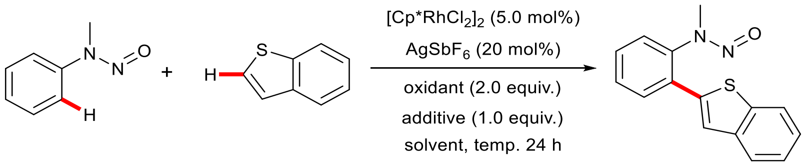


Aniline (0.05 mol, 1.0 equiv.) was dissolved in a 1:2 mixture of acetonitrile and water (30 mL) and cooled to 0 °C (ice bath). Concentrated aqueous HCl (7.3 mL, 0.24 mol) was added dropwise. The mixture was stirred vigorously for half an hour, while maintained at 0 °C. To this mixture was added an aqueous solution (13 mL) of $NaNO_2$ (3.5 g, 0.05 mol) over the course of 10 min. The reaction was allowed to proceed for 1 h. The mixture was then extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash silica gel column chromatography to give the corresponding *N*-nitrosoaniline substrates.

III. Optimization of the reaction conditions

An oven-dried Schlenk test tube with a magnetic stirring bar was charged with *N*-methyl-*N*-phenylnitrous amide **1a** (0.2 mmol, 1.0 equiv.), benzothiophene **2a** (0.6 mmol, 3.0 equiv.), [Rh] catalyst (5.0 mol%), $AgSbF_6$ (20 mol%, if required), oxidant (2.0 equiv.), additive (1.0 equiv.), base (30 mol%, if required) and solvent under an N_2 atmosphere. The mixture was stirred at the designed temperature for 24 h. After the reaction was cooled down to ambient temperature, it was diluted with 3 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 15-20 mL of CH_2Cl_2. The combined organic phase was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) to provide the desired product **3a**.

Table S1. Optimization of the heteroarylation reaction of 1a and 2a[a]



1a **2a** **3a**

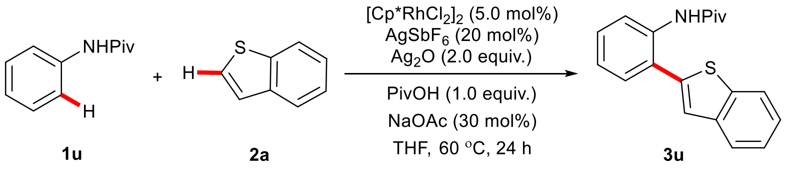
Entry	Oxidant (2.0 equiv.)	Additive (1.0 equiv.)	Solvent (mL)	Temp. (℃)	Yield[b] (%)
1	Ag_2CO_3	PivOH	toluene (1.0)	100	14
2	AgOAc	PivOH	toluene (1.0)	100	11
3	Ag_2O	PivOH	toluene (1.0)	100	23
4	$Cu(OAc)_2$	PivOH	toluene (1.0)	100	8
5	Ag_2O	PivOH	DCE (1.0)	100	43
6	Ag_2O	PivOH	DMF (1.0)	100	16
7	Ag_2O	PivOH	*t*-AmylOH (1.0)	100	nd

8	Ag_2O	PivOH	dioxane (1.0)	100	52
9	Ag_2O	PivOH	DCM (1.0)	100	39
10	Ag_2O	PivOH	MeOH (1.0)	100	43
11	Ag_2O	PivOH	THF (1.0)	100	71
12	Ag_2O	PivOH	THF (0.5)	100	75
13	Ag_2O	PivOH/NaOAc	THF (0.5)	100	84
14	**Ag_2O**	**PivOH/NaOAc**	**THF (0.5)**	**60**	**82**
15	Ag_2O	PivOH/NaOAc	THF (0.5)	40	51
16[c]	Ag_2O	PivOH/NaOAc	THF (0.5)	rt	24
17[d]	Ag_2O	PivOH	THF (0.5)	60	60
18[e]	Ag_2O	PivOH	THF (0.6)	60	nr
19	Ag_2O	—	THF (0.5)	60	45
20[f]	Ag_2O	PivOH/NaOAc	THF (0.5)	60	51
21[g]	Ag_2O	PivOH/NaOAc	THF (0.5)	60	nd

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), $[RhCp^*Cl_2]_2$ (5.0 mol%), $AgSbF_6$ (20 mol%, if required), oxidant (2.0 equiv.), additive (1.0 equiv.) and base (30 mol%, if required) under an N_2 atmosphere. [b] Isolated yield. [c] 36 h. [d] 1.5 equiv. Ag_2O. [e] Without $AgSbF_6$. [f] $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5.0 mol%). [g] $[Rh(Ph_3P)_3Cl]$ (5.0 mol%). nd: not detected. nr: no reaction.

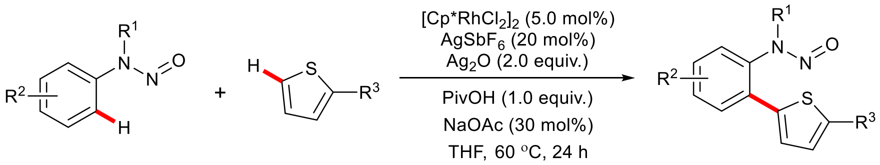
IV. General procedure for the synthesis of heteroarylated products

(i) The reaction of *N*-phenylpivalamide with benzothiophene under the standard conditions



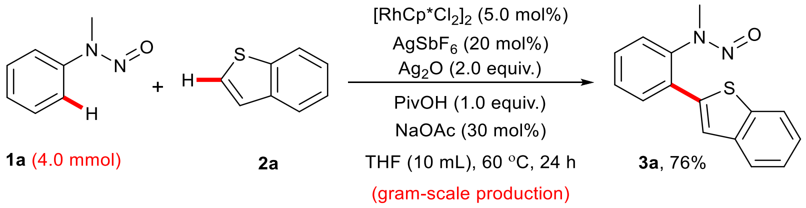
An oven-dried Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (6.2 mg, 5.0 mol%), $AgSbF_6$ (13.8 mg, 20 mol%), Ag_2O (92.0 mg, 2.0 equiv.), PivOH (20.4 mg, 1.0 equiv.), NaOAc (4.9 mg, 30 mol%), *N*-phenylpivalamide **1u** (0.2 mmol, 1.0 equiv.), benzothiophene **2a** (0.6 mmol, 3.0 equiv.), and THF (0.5 mL) under an N_2 atmosphere. The mixture was stirred at 60 ℃ for 24 h. After the reaction was cooled down to ambient temperature, it was diluted with 3 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 15-20 mL of CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) on silica gel to provide the corresponding product *N*-(2-(benzo[*b*]thiophen-2-yl)phenyl)pivalamide (**3u**) as white solid (19.8 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (s, 9H), 7.17 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.34 (d, J = 0.4 Hz, 1H), 7.37-7.46 (m, 4H), 7.81-7.84 (m, 1H), 7.88-7.90 (m, 1H), 7.96 (s, 1H), 8.41 (dd, J = 8.4 Hz, 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.6, 40.1, 121.5, 122.4, 123.8, 124.05, 124.08, 124.5, 124.9, 125.0, 129.8, 131.0, 136.0, 139.7, 140.0, 140.4, 176.7 ppm.

(ii) General procedure for the oxidative C–H/C–H cross-coupling of *N*-nitrosoanilines with heteroarenes



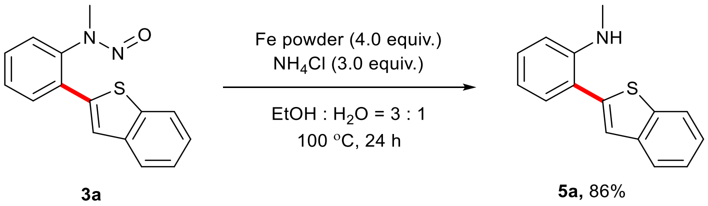
An oven-dried Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (6.2 mg, 5.0 mol%), $AgSbF_6$ (13.8 mg, 20 mol%), Ag_2O (92.0 mg, 2.0 equiv.), PivOH (20.4 mg, 1.0 equiv.), NaOAc (4.9 mg, 30 mol%), *N*-nitrosoaniline **1** (0.2 mmol, 1.0 equiv.), heteroarene **2** (0.6 mmol, 3.0 equiv.), and THF (0.5 mL) under an N_2 atmosphere. The mixture was stirred at 60 ℃ for 24 h. After the reaction was cooled down to ambient temperature, it was diluted with 3 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 15-20 mL of CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the corresponding products **3** or **4**.

V. Procedure for the synthesis of 3a on a 4 mmol scale

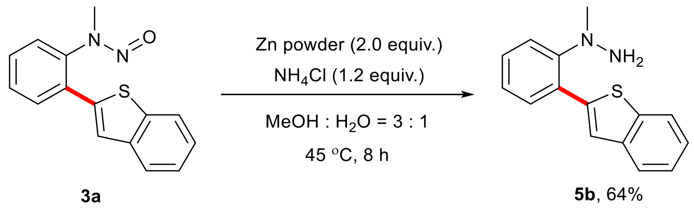


An oven-dried Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (124.0 mg, 5.0 mol%), $AgSbF_6$ (273.5 mg, 20 mol%), Ag_2O (1838.5 mg, 2.0 equiv.), PivOH (408.4 mg, 1.0 equiv.), NaOAc (98.4 mg, 30 mol%), *N*-methyl-*N*-phenylnitrous amide **1a** (4.0 mmol, 1.0 equiv.), benzothiophene **2a** (12.0 mmol, 3.0 equiv.), and THF (10 mL) under an N_2 atmosphere. The mixture was stirred at 60 ℃ for 24 h. After the reaction was cooled down to ambient temperature, it was diluted with 15 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 30-50 mL of CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) to provide the product **3a** (814.9 mg, 76% yield).

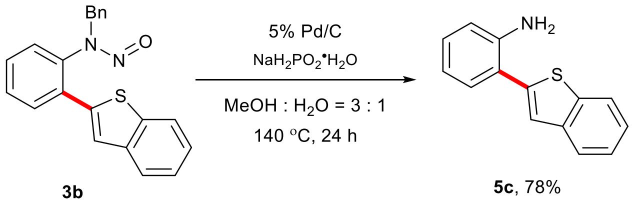
VI. General procedure for the conversion of 3a and 3b[5]



An oven-dried Schlenk tube with a magnetic stir bar was charged with *N*-(2-(benzo[*b*]thiopene-2-yl)phenyl)-*N*-methylnitrous amide (**3a**) (53.6 mg, 0.2 mmol, 1.0 equiv.), Fe powder (44.7 mg, 4.0 equiv.), NH_4Cl (31.8 mg, 3.0 equiv.), and 75% ethanol aqueous solution (2 mL). The mixture was stirred at 100 ℃ for 24 h. After being cooled to room temperature, the mixture was extracted with CH_2Cl_2 and then washed and dried. The solution was concentrated by vacuum and separated on a silica gel column using petroleum ether/CH_2Cl_2 (20:1, v/v) as eluent to give the corresponding pure denitrosation product 2-(benzo[*b*]thiophen-2-yl)-*N*-methylaniline (**5a)** as yellow solid (41.1 mg, 86%). M.p.: 47-49 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.87 (s, 3H), 4.54 (s, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.79 (t, J = 7.6 Hz, 1H), 7.31-7.41 (m, 5H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.8, 110.2. 116.8, 119.5, 122.3, 122.8, 123.5, 124.3, 124.6, 130.1, 131.1, 140.0, 140.4, 141.6, 146.9 ppm. HRMS (ESI): calcd for $C_{15}H_{14}NS$ $[M+H]^+$ 240.0847, found 240.0843.



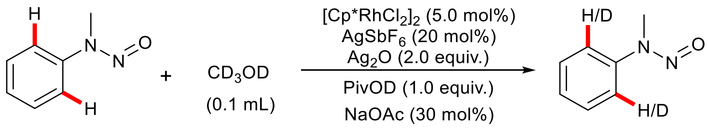
An oven-dried Schlenk tube with a magnetic stir bar was charged with *N*-(2-(benzo[*b*]thiopene-2-yl)phenyl)-*N*-methylnitrous amide (**3a**) (53.6 mg, 0.2 mmol, 1.0 equiv.), Zn powder (25.6 mg, 2.0 equiv.), NH_4Cl (12.7 mg, 1.2 equiv.), and 75% methanol aqueous solution (2 mL). The mixture was stirred at 45 ℃ for 8 h. After being cooled to room temperature, the mixture was extracted with CH_2Cl_2 and then washed and dried. The solution was concentrated by vacuum and separated on a silica gel column using petroleum ether/EtOAc (10:1, v/v) as eluent to give the corresponding pure reduced product 1-(2-(benzo[*b*]thiophen-2-yl)phenyl)-1-methylhydrazine (**5b**) as yellow oil (32.5 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.92 (s, 3H), 3.72 (s, 2H), 7.13 (t, *J* = 6.8 Hz, 1H), 7.29-7.36 (m, 4H), 7.60-7.64 (m, 2H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.6, 118.3, 122.0, 122.2, 123.5, 124.0, 124.2, 124.3, 128.1, 129.1, 130.7, 139.7, 141.0, 142.5, 152.1 ppm. HRMS (ESI): calcd for $C_{15}H_{15}N_2S$ $[M+H]^+$ 255.0956, found 255.0952.



An oven-dried Schlenk tube with a magnetic stir bar was charged with *N*-(2-(benzo[*b*]thiophen-2-yl)phenyl)-*N*-benzylnitrous amide (**3b**) (34.4 mg, 0.1 mmol, 1.0 equiv.), 5% Pd/C (40.0 mg), $NaH_2PO_2{\bullet}H_2O$ (42.4 mg, 4.0 equiv.) and 75% methanol aqueous solution (2 mL) under an N_2 atmosphere. The mixture was stirred at 140 ℃ for 24 h. After being cooled to room temperature, the solution was filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 2/1, v/v) to give 2-(benzo[*b*]thiophen-2-yl)aniline **5c** as yellow solid (17.5 mg, 78% yield). M.p.: 122-124 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 5.27 (s, 2H), 6.66 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.32-7.41 (m, 2H), 7.56 (s, 1H), 7.84 (d, J = 7.2 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 115.9, 116.7, 117.8, 121.8, 122.0, 123.5, 124.1, 124.4, 129.2, 130.3, 138.5, 140.4, 141.6, 145.8 ppm. HRMS (ESI): calcd for $C_{14}H_{12}NS$ $[M+H]^+$ 226.0690, found 226.0693.

VII. Mechanitic study

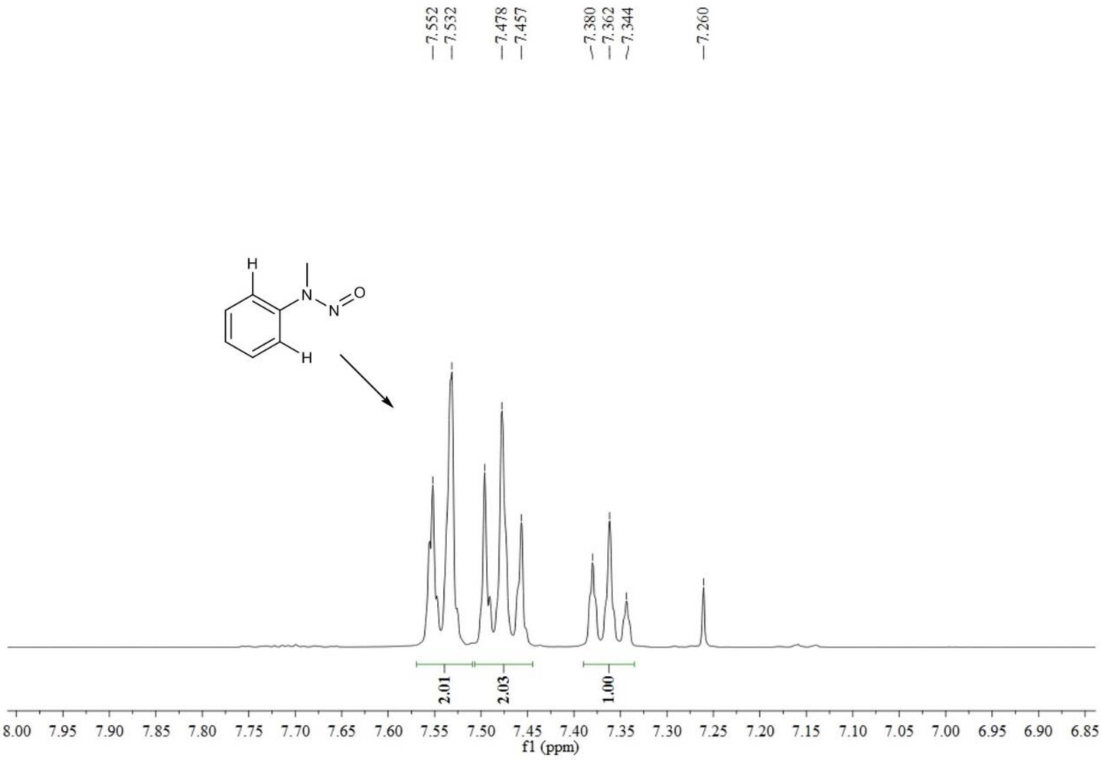
(i) H/D exchange experiments

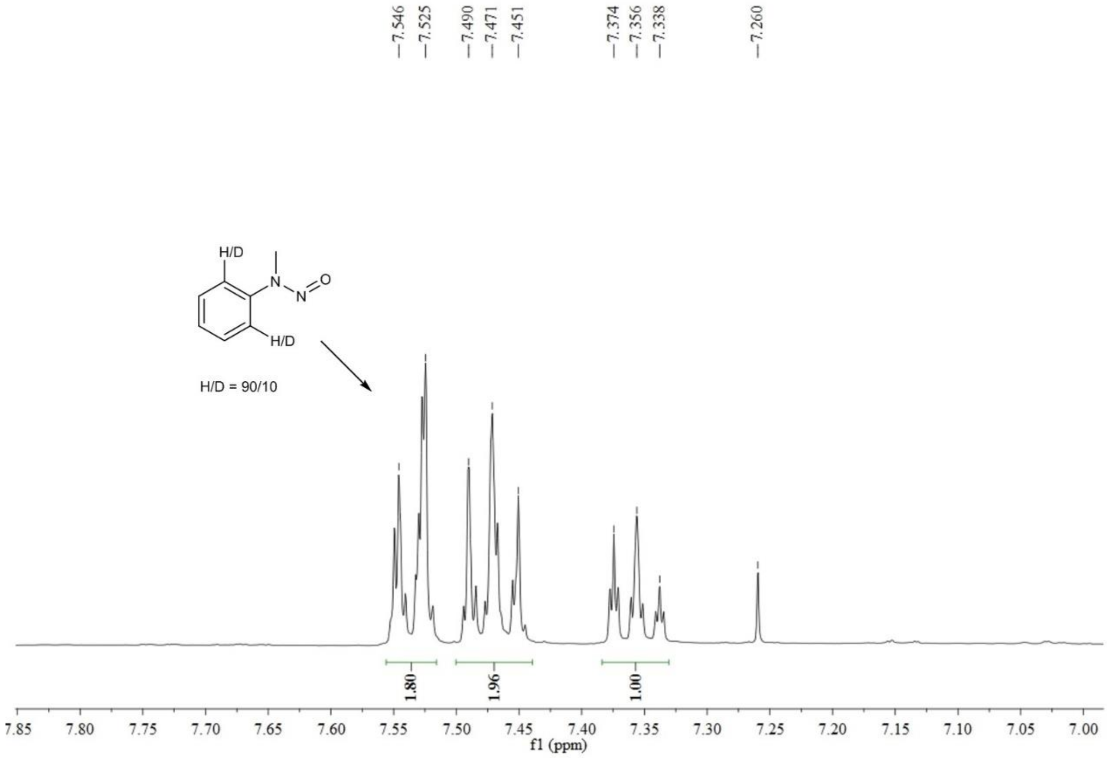


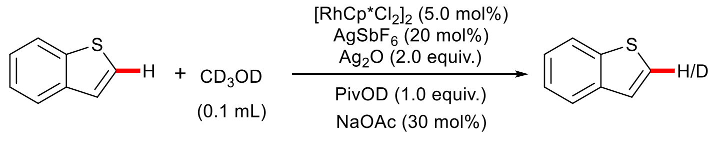
1a

10% [D_n]-**1a**

An oven-dried Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (6.2 mg, 5.0 mol%), $AgSbF_6$ (13.8mg, 20 mol%), Ag_2O (92.0 mg, 2.0 equiv.), PivOD (20.6 mg, 1.0 equiv.), NaOAc (4.9 mg, 30 mol%), *N*-methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol, 1.0 equiv.), CD_3OD (0.1 mL) and THF (0.5 mL) under an N_2 atmosphere. The mixture was stirred at 60 ℃ for 2 h and then diluted with 3 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 15-20 mL of CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 20/1, v/v) to provide [D_n]-**1a**. The deuterated ratio was calculated from ^{1}H NMR analysis.





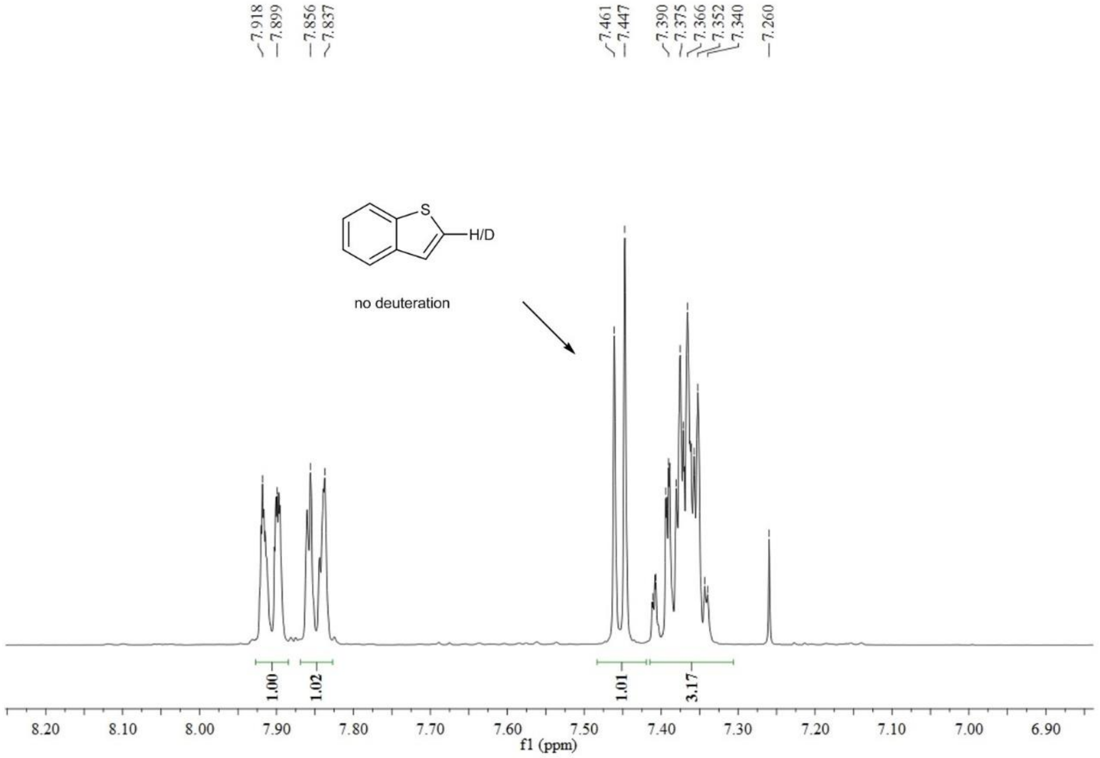


2a

[D]-**2a**

no deuteration

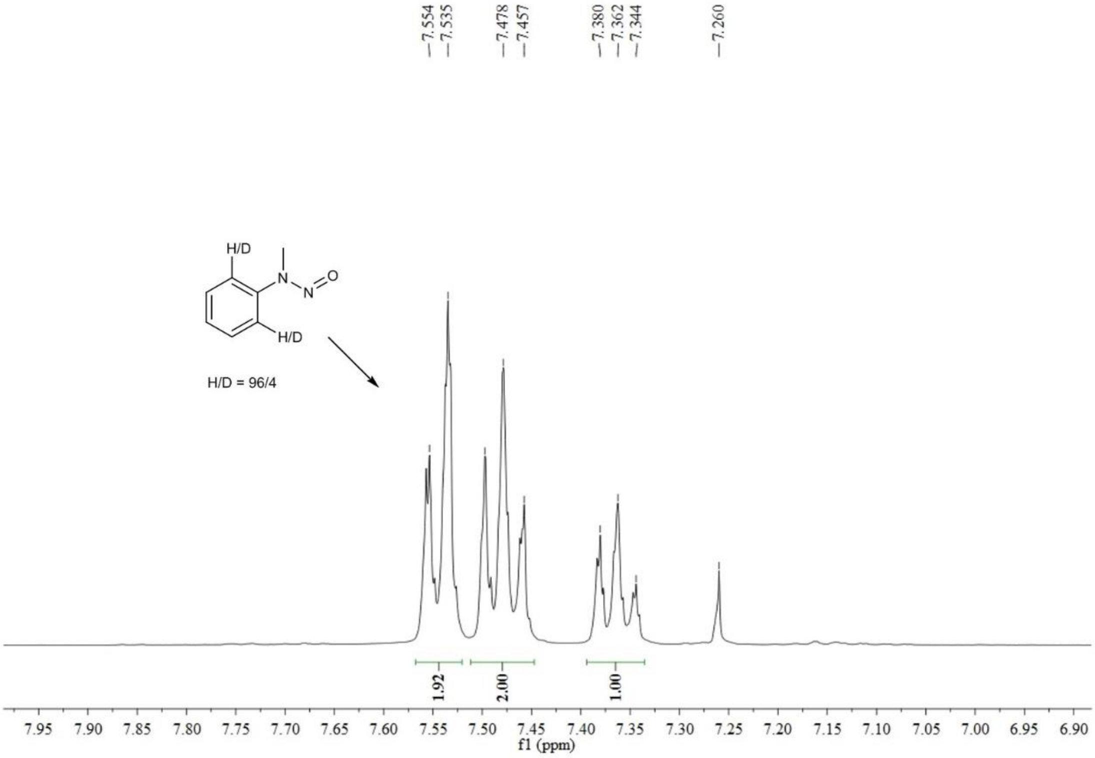
An oven-dried Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (6.2 mg, 5.0 mol%), $AgSbF_6$ (13.8 mg, 20 mol%), Ag_2O (92.0 mg, 2.0 equiv.), PivOD (20.6 mg, 1.0 equiv.), NaOAc (4.9 mg, 30 mol%), benzothiophene **2a** (26.8 mg, 0.2 mmol, 1.0 equiv.), CD_3OD (0.1 mL) and THF (0.5 mL) under an N_2 atmosphere. The mixture was stirred at 60 ℃ for 2 h and then diluted with 3 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 15-20 mL of CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 30/1, v/v) to provide [D]-**2a**. The deuterated ratio was calculated from ^{1}H NMR analysis

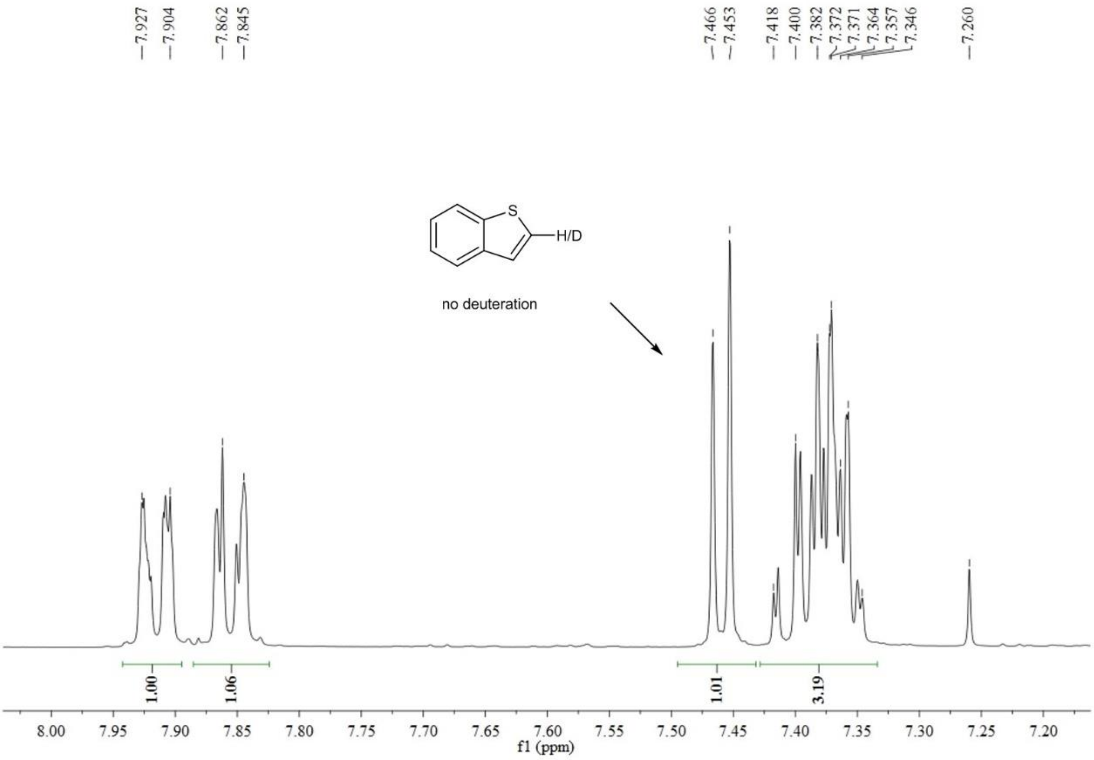


$$\mathbf{1a} + \mathbf{2a} + \underset{(0.1\text{ mL})}{CD_3OD} \xrightarrow[\substack{\text{PivOD (1.0 equiv.)} \\ \text{NaOAc (30 mol\%)} \\ \text{THF, 60 }^{o}\text{C, 2 h}}]{\substack{[Cp^*RhCl_2]_2\text{ (5.0 mol\%)} \\ AgSbF_6\text{ (20 mol\%)} \\ Ag_2O\text{ (2.0 equiv.)}}} \underset{4\%}{[D_n]\text{-}\mathbf{1a}} + \underset{\text{no deuteration}}{[D]\text{-}\mathbf{2a}} + \underset{21\%}{\mathbf{3a}}$$

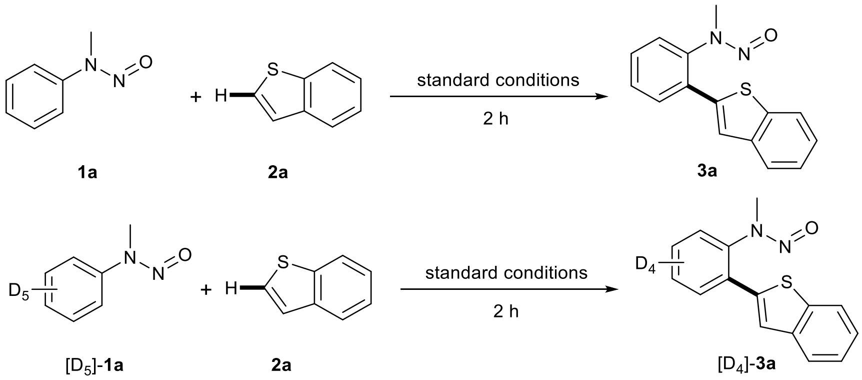
An oven-dried Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (6.2 mg, 5.0 mol%), $AgSbF_6$ (13.8 mg, 20 mol%), Ag_2O (92.0 mg, 2.0 equiv.), PivOD (20.6 mg, 1.0 equiv.), NaOAc (4.9 mg, 30 mol%), *N*-methyl-*N*-phemylnitrous amide **1a** (27.2 mg, 0.2 mmol, 1.0 equiv.), benzothiophene **2a** (80.4 mg, 0.6 mmol), CD_3OD (0.1 mL) and THF (0.5 mL) under an N_2 atmosphere. The mixture was stirred at 60 ℃

for 2 h and then diluted with 3 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 15-20 mL of CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 60/1, v/v) to provide [D_n]-**1a**, [D]-**2a**, and **3a** (11.3 mg, 21% yield). The deuterated ratio was calculated from ^{1}H NMR analysis.

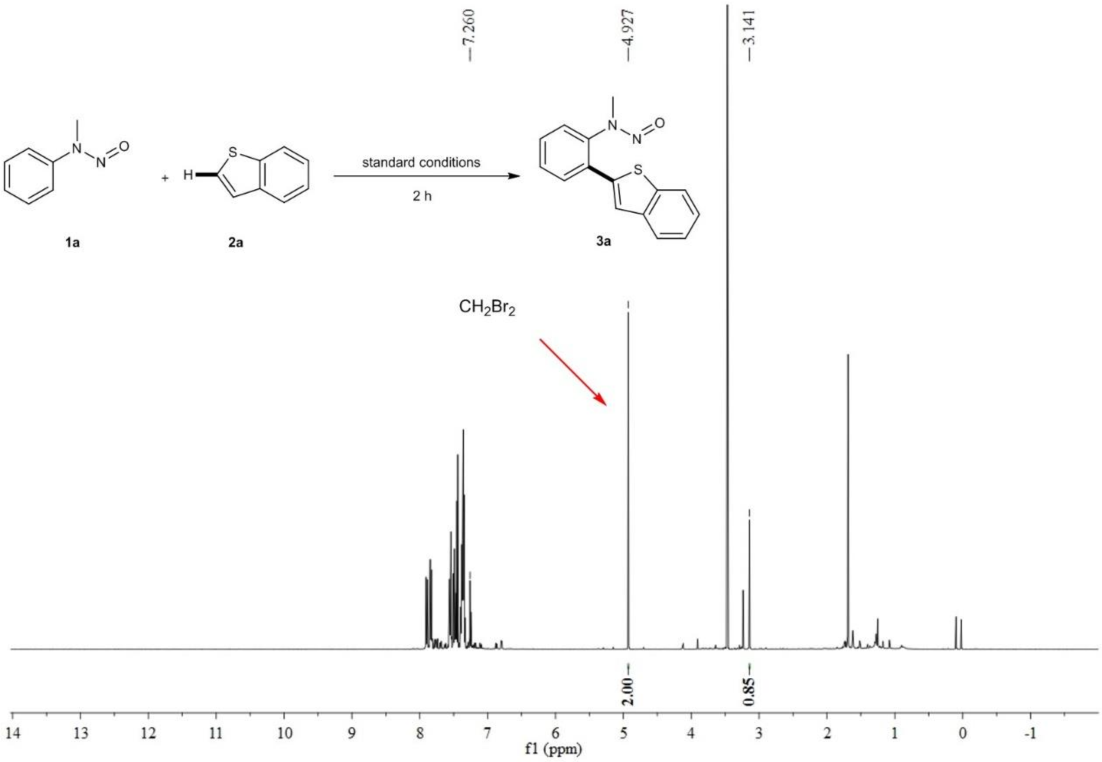


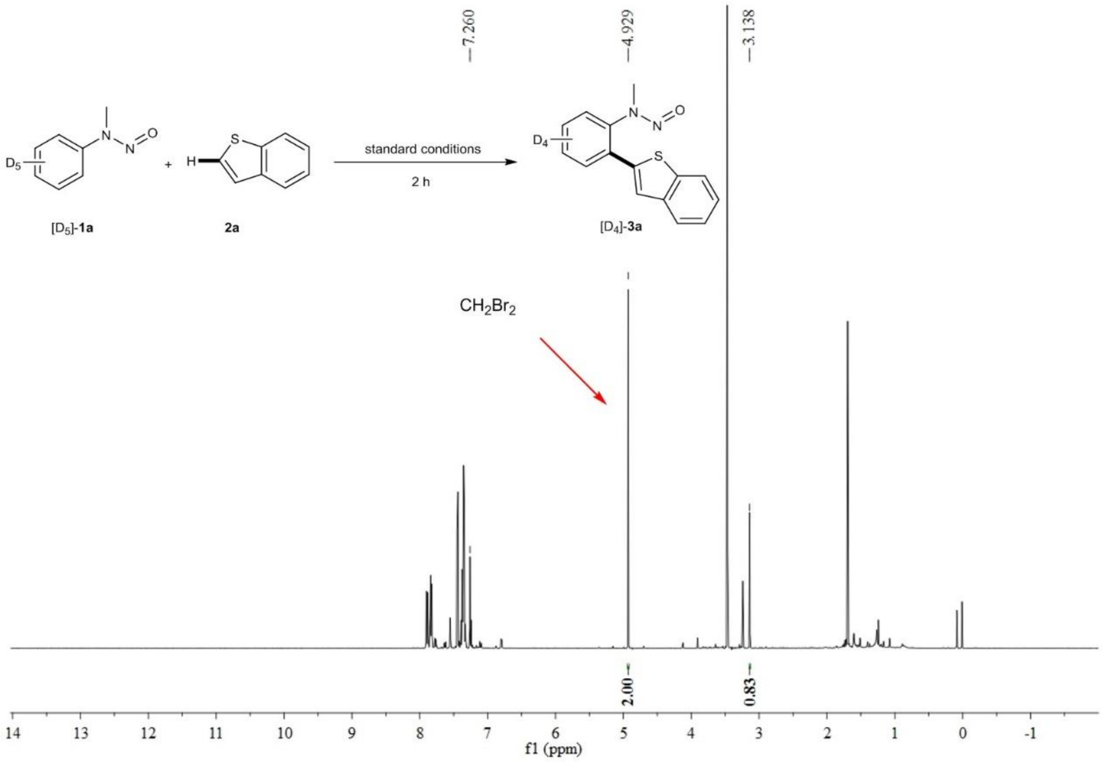


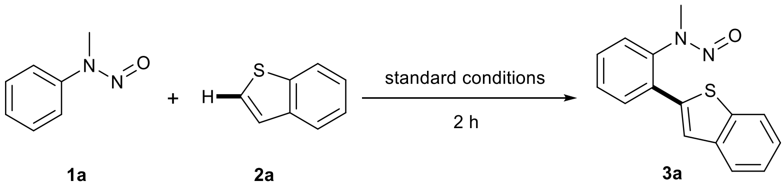
(ii) Kinetic isotope experiments

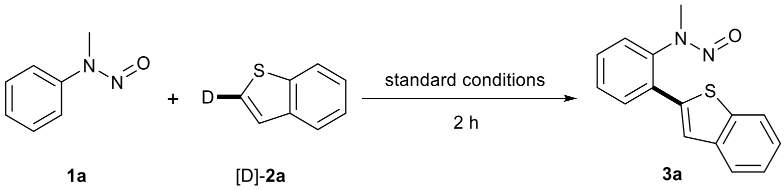


An oven-dried Schlenk tube with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (6.2 mg, 5.0 mol%), $AgSbF_6$ (13.8 mg, 20 mol%), Ag_2O (92.0 mg, 2.0 equiv.), PivOD (20.6 mg, 1.0 equiv.), NaOAc (4.9 mg, 30 mol%), *N*-methyl-*N*-phemylnitrous amide **1a** (27.2 mg, 0.2 mmol, 1.0 equiv.) or [D_5]-**1a** (28.2 mg, 0.2 mmol, 1.0 equiv.), benzothiophene **2a** (80.4 mg, 0.6 mmol) and THF (0.5 mL) under an N_2 atmosphere. The resulting mixture was stirred at 60 ℃ for 2 h and then diluted with 3 mL of CH_2Cl_2. The mixture was filtered through a celite pad and washed with 15-20 mL of CH_2Cl_2. The yield of **3a** or [D_4]-**3a** was determined by ^{1}H NMR analysis of the crude product using dibromomethane (0.1 mmol, 7 μL) as internal standard. A kinetic isotope effect (KIE) value ($k_H/k_D = 1.02$) was obtained.

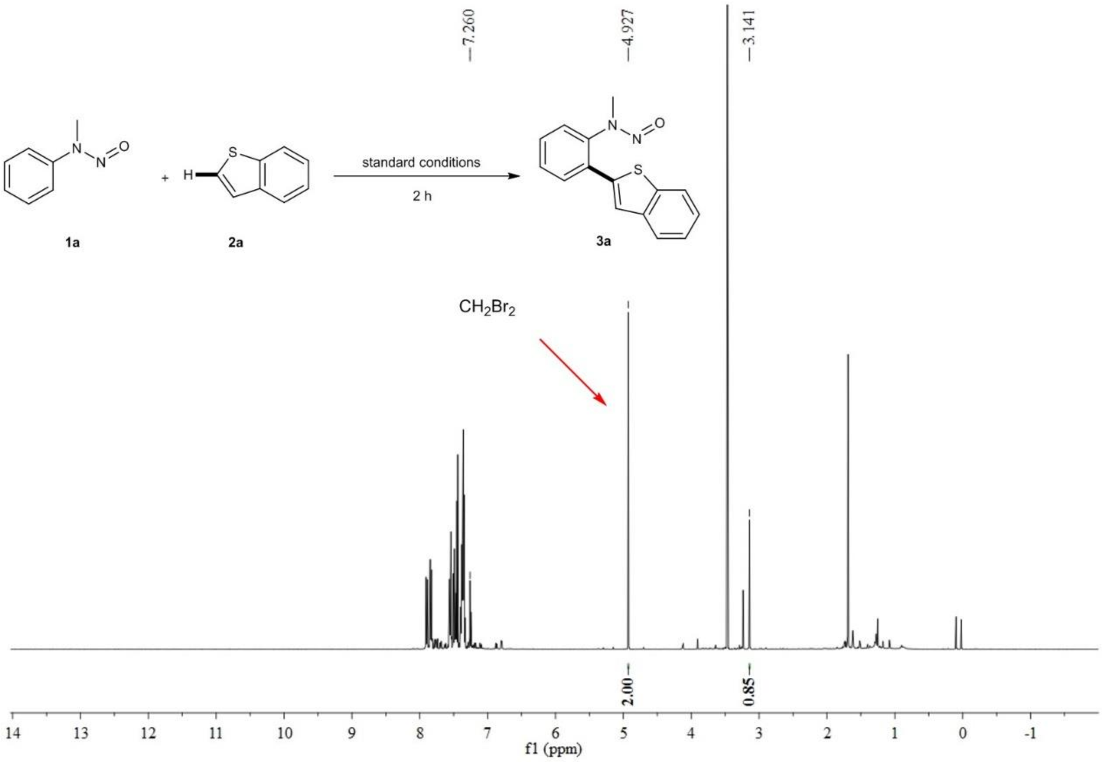


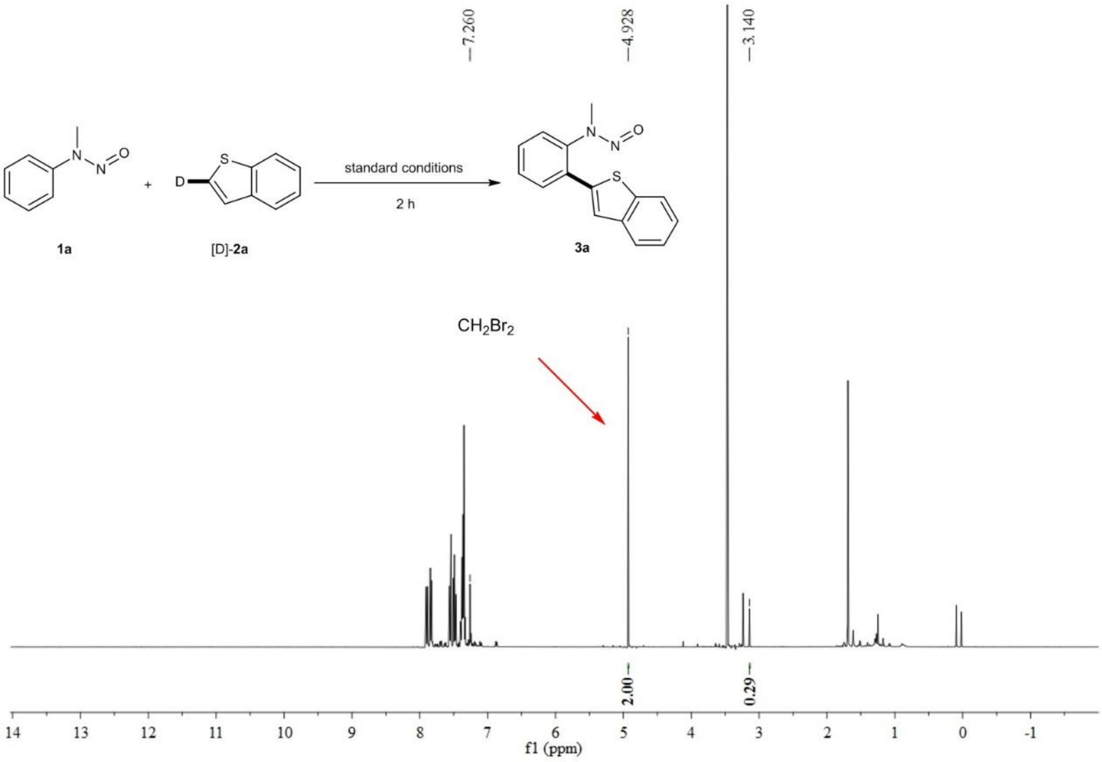




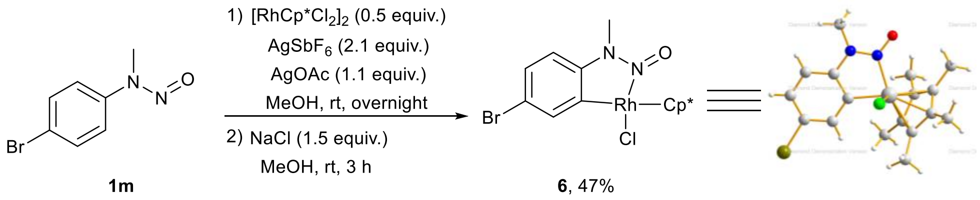


An oven-dried Schlenk tube with a magnetic stir bar was charged with [Cp*RhCl$_2$]$_2$ (6.2 mg, 5.0 mol%), AgSbF$_6$ (13.8 mg, 20 mol%), Ag$_2$O (92.0 mg, 2.0 equiv.), PivOD (20.6 mg, 1.0 equiv.), NaOAc (4.9 mg, 30 mol%), *N*-methyl-*N*-phemylnitrous amide **1a** (27.2 mg, 0.2 mmol, 1.0 equiv.), benzothiophene **2a** (80.4 mg, 0.6 mmol) or [D]-**2a** (81.0 mg, 0.6 mmol) and THF (0.5 mL) under an N$_2$ atmosphere. The resulting mixture was stirred at 60 ℃ for 2 h and then diluted with 3 mL of CH$_2$Cl$_2$. The mixture was filtered through a celite pad and washed with 15-20 mL of CH$_2$Cl$_2$. The yield of **3a** was determined by ^{1}H NMR analysis of the crude product using dibromomethane (0.1 mmol, 7 μL) as internal standard. A significant kinetic isotope effect (KIE) value (k_H/k_D = 2.93) was obtained.



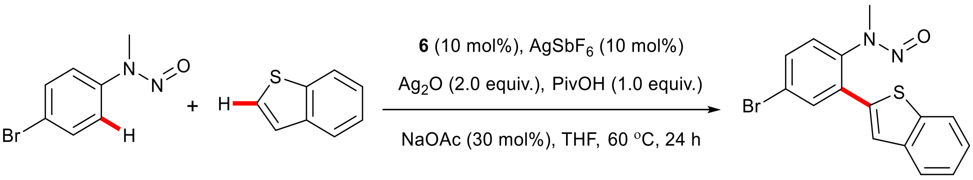


(iii) Synthesis of the cyclometalated Rh(III) complex 6[4]



A Schlenk tube with a magnetic bar was charged with **1m** (42.8 mg, 0.2 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (62.6 mg, 0.5 equiv.), $AgSbF_6$ (143.6 mg, 2.1 equiv.), AgOAc (36.5 mg, 1.1 equiv.), and MeOH (2 mL) under an N_2 atmosphere and stirred overnight at room temperature. NaCl (17.4 mg, 1.5 equiv.) was added and the resulting mixture was stirred at room temperature for another 3 h. The solution was filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was concentrated and the residue was purified by column chromatography on alumina (CH_2Cl_2/EtOAc = 20/1, v/v) to provide the complex **6** as red orange solid (45.7 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 15H), 3.57 (s, 3H), 6.88 (d, J = 8.4 Hz, 1H), 7.27 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.79 (d, J = 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.2, 31.5, 99.2, 99.3, 113.7, 120.5, 126.8, 138.1, 141.41, 141.43, 163.2, 163.5 ppm. HRMS (ESI): calcd for $C_{17}H_{21}BrN_2ORh$ $[M-Cl]^+$ 450.9887, found 450.9881.

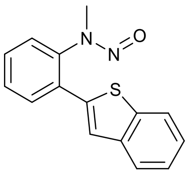
(iv) Complex 6-catalyzed heteroarylation of *N*-(4-bromophenyl)-*N*-methylnitrous amide 1m



1m **2a** (3.0 equiv.) **3m**, 63%

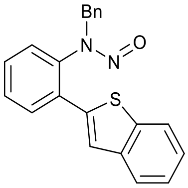
An oven-dried Schlenk tube with a magnetic bar was charged with **1m** (42.8 mg, 0.2 mmol, 1.0 equiv.), **2a** (80.4 mg, 3.0 equiv.), complex **6** (9.7 mg, 10 mol%), $AgSbF_6$ (6.8 mg, 10 mol%), Ag_2O (92.0 mg, 2.0 equiv.), PivOH (20.4 mg, 1.0 equiv.), NaOAc (4.9 mg, 30 mol%) and THF (0.5 mL) under an N_2 atmosphere. The mixture was stirred at 60 ℃ for 24 h and then diluted with 3 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 15-20 mL of CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide **3m** as inseparable yellow solid mixture of *syn* and *anti* isomers (43.6 mg, 63% yield).

VIII. Experimental data for the described compounds



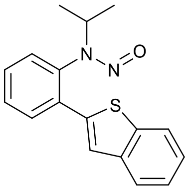
N-(2-(Benzo[*b*]thiopene-2-yl)phenyl)-*N*-methylnitrous amide (3a)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **3a** as inseparable yellow solid mixture of *syn* and *anti* isomers (44.0 mg, 82% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 13:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.13 (s, 3H), 7.24 (s, 1H), 7.33-7.39 (m, 2H), 7.47 (d, *J* = 6.4 Hz, 1H), 7.51-7. 58 (m, 2H), 7.75 (t, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.6, 122.3, 124.0, 124.1, 124.8, 125.0, 127.5, 129.6, 129.7, 130.6, 131.7, 139.2, 140.0, 140.55, 140.60 ppm. HRMS (ESI): calcd for $C_{15}H_{12}N_2NaOS$ $[M+Na]^+$ 291.0568, found 291.0562.



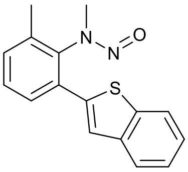
N-(2-(Benzo[*b*]thiophen-2-yl)phenyl)-*N*-benzylnitrous amide (3b)

Following the general procedure. *N*-Benzyl-*N*-phenylnitrous amide **1b** (42.4 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **3b** as inseparable yellow oily mixture of syn and *anti* isomers (58.5 mg, 85% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 1:0.37. ^{1}H NMR (400 MHz, DMSO-d_6) (*syn* and *anti* isomers): δ = 4.91 (s, 2H × 1), 6.74 (d, *J* = 8.0 Hz, 1H × 0.37), 6.98-7.00 (m, 2H × 1), 7.14-7.29 (m, 4H × 1 + 3H × 0.37), 7.36-7.43 (m, 4H × 1 + 3H × 0.37), 7.48-7.55 (m, 4H × 0.37), 7.62 (t, *J* = 7.2 Hz, 1H × 1), 7.69 (m, 1H × 0.37), 7.79-7.87 (m, 2H × 1 + 1H × 0.37), 7.97 (m, 1H × 1 + 1H × 0.37) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) (*syn* and *anti* isomers): δ = 50.2, 57.5, 122.7, 122.8, 123.4, 124.44, 124.47, 124.50, 125.1, 125.2, 125.3, 125.4, 128.1, 128.6, 128.9, 128.96, 129.02, 129.1, 129.2, 129.3, 129.8, 130.0, 130.46, 130.49, 131.1, 131.4, 131.7, 132.1, 134.1, 135.0, 135.8, 138.55, 138.64, 139.1, 139.9, 140.0, 140.1, 140.3. HRMS (ESI): calcd for $C_{21}H_{16}N_2NaOS$ $[M+Na]^+$ 367.0881, found 367.0882.



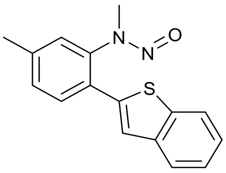
N-(2-(Benzo[*b*]thiopene-2-yl)phenyl)-*N*-isopropylnitrous amide (3c)

Following the general procedure. *N*-Isopropyl-*N*-phenylnitrous amide **1c** (32.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **3c** as inseparable yellow oily mixture of *syn* and *anti* isomers (49.2 mg, 83% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 1:0.57. ^{1}H NMR (400 MHz, $CDCl_3$) (*syn* and *anti* isomers): δ = 0.95 (d, J = 7.6 Hz, 3H × 1), 1.18 (d, J = 7.6 Hz, 3H × 1), 1.43 (d, J = 7.6 Hz, 6H × 0.57), 4.56 (m, 1H × 1), 4.96 (m, 1H × 1), 7.00 (dd, J = 7.6 Hz, 1.6 Hz, 1H × 1), 7.11 (s, 1H × 1), 7.30-7.38 (m, 2H × 1 + 4H × 0.57), 7.44-7.53 (m, 2H × 1 + 1H × 0.57), 7.59 (t, J = 7.6 Hz, 1H × 0.57), 7.67 (dd, J = 7.6 Hz, 1.2 Hz, 1H × 1), 7.74-7.77 (m, 3H × 0.57), 7.81 (t, J = 7.6 Hz, 2H × 1) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) (*syn* and *anti* isomers): δ = 19.2, 21.6, 22.5, 29.9, 48.6, 57.2, 122.23, 122.24, 123.2, 124.1, 124.2, 124.5, 124.76, 124.85, 124.9, 129.0, 129.3, 129.6, 130.0, 130.23, 130.25, 131.5, 131.9, 133.3, 134.2, 136.2, 137.0, 139.1, 134.0, 140.1, 140.2, 140.4, 140.6 ppm. HRMS (ESI): calcd for $C_{17}H_{16}N_2NaOS$ $[M+Na]^+$ 319.0881, found 319.0879.



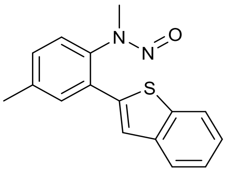
N-(2-(Benzo[*b*]thiopene-2-yl)-6-methylphenyl)-*N*-methylnitrous amide (3e)

Following the general procedure. *N*-Methyl-*N*-(*o*-tolyl)nitrous amide **1e** (30.0 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **3e** as inseparable yellow oily mixture of *syn* and *anti* isomers (45.7 mg, 81% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 10:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.18 (s, 3H), 3.18 (s, 3H), 7.34-7.43 (m, 2H), 7.46 (s, 1H), 7.54-7.61 (m, 2H), 7.73 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.84-7.89 (m, 1H), 7.93-7.98 (m, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 17.6, 35.3, 122.2, 123.9, 124.0, 124.8, 124.9, 128.6, 130.1, 131.6, 131.7, 136.7, 138.5, 138.8, 139.3, 139.7 ppm. HRMS (ESI): calcd for $C_{16}H_{14}N_2NaOS$ $[M+Na]^+$ 305.0725, found 305.0717.



N-(2-(Benzo[b]thiopene-2-yl)-5-methylphenyl)-N-methylnitrous amide (3f)

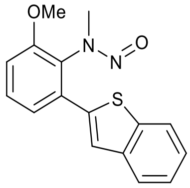
Following the general procedure. *N*-Methyl-*N*-(*m*-tolyl)nitrous amide **1f** (30.0 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **3f** as inseparable yellow solid mixture of *syn* and *anti* isomers (44.0 mg, 78% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 14:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.47 (s, 3H), 3.12 (s, 3H), 7.20 (s, 1H), 7.28 (s, 1H), 7.31-7.38 (m, 3H), 7.63 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.2 Hz, 1H), 7.82(d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.2, 35.6, 122.2, 123.6, 124.0, 124.76, 124.81, 127.6, 128.1, 130.5, 131.4, 139.4, 140.0, 140.1, 140.3 140.4 ppm. HRMS (ESI): calcd for $C_{16}H_{14}N_2NaOS$ [M+Na]$^+$ 305.0725, found 305.0721.



N-(2-(Benzo[b]thiopene-2-yl)-4-methylphenyl)-N-methylnitrous amide (3g)

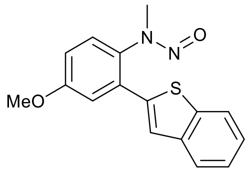
Following the general procedure. *N*-Methyl-*N*-(*p*-tolyl)nitrous amide **1g** (30.0 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **3g** as inseparable yellow solid mixture of *syn* and *anti* isomers (44.0 mg, 78% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 12:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.49 (s, 3H), 3.12 (s, 3H), 7.22 (s, 1H), 7.34-7.38 (m, 4H), 7.55 (s, 1H), 7.76 (d, J = 7.2 Hz, 1H), 7.81 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.3, 35.6, 122.2, 123.8, 124.0, 124.8, 124.9, 127.3, 130.2, 130.3, 132.1, 138.2, 139.4, 139.9, 140.0, 140.5 ppm. HRMS (ESI): calcd for $C_{16}H_{14}N_2NaOS$

$[M+Na]^+$ 305.0725, found 305.0720.



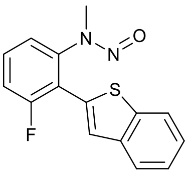
_N_-(2-(Benzo[_b_]thiopene-2-yl)-6-methoxyphenyl)-_N_-methylnitrous amide (3h)

Following the general procedure. *N*-(2-Methoxyphenyl)-*N*-methylnitrous amide **1h** (33.2 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3h** as inseparable yellow solid mixture of *syn* and *anti* isomers (48.3 mg, 81% yield). By ^1H NMR, the *syn*:*anti* ratio was determined to be approximately 10:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^1H NMR (400 MHz, DMSO-d_6): δ = 3.23 (s, 3H), 3.87 (s, 3H), 7.32-7.41 (m, 3H), 7.49 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.53 (s, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.85 (dd, J = 6.8 Hz, 2.0 Hz, 1H), 7.92-7.98 (m, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 35.3, 56.4, 112.8, 121.8, 122.2, 123.9, 124.0, 124.7, 124.9, 128.0, 131.2, 132.8, 138.5, 139.3, 139.7, 155.6 ppm. HRMS (ESI): calcd for $C_{16}H_{14}N_2NaO_2S$ $[M+Na]^+$ 321.0674, found 321.0669.



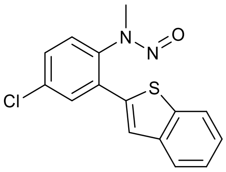
_N_-(2-(Benzo[_b_]thiopene-2-yl)-4-methoxyphenyl)-_N_-methylnitrous amide (3i)

Following the general procedure. *N*-(4-Methoxyphenyl)-*N*-methylnitrous amide **1i** (33.2 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3i** as inseparable brown oily mixture of *syn* and *anti* isomers (45.9 mg, 77% yield). By ^1H NMR, the *syn*:*anti* ratio was determined to be approximately 10:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.12 (s, 3H), 3.92 (s, 3H), 7.03 (dd, J = 8.4 Hz, 2.8 Hz, 1H), 7.23-7.24 (m, 2H), 7.32-7.39 (m, 3H), 7.75-7.77 (m, 1H), 7.81-7.83 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.9, 56.0, 114.7, 116.6, 122.4, 124.1, 124.2, 124.9, 125.1, 129.0, 132.1, 133.9, 139.2, 140.0, 140.6, 160.3 ppm. HRMS (ESI): calcd for $C_{16}H_{14}N_2NaO_2S$ $[M+Na]^+$ 321.0674, found 321.0669.



N-(2-(Benzo[*b*]thiopene-2-yl)-5-fluorophenyl)-*N*-methylnitrous amide (3j)

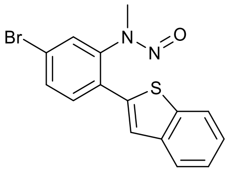
Following the general procedure. *N*-(3-Fluorophenyl)-*N*-methylnitrous amide **1j** (30.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc =60/1, v/v) afforded **3j** as inseparable yellow oily mixture of *syn* and *anti* isomers (43.5 mg, 76% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 10:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.21 (s, 3H), 7.37-7.44 (m, 2H), 7.48-7.53 (m, 1H), 7.65-7.71 (m, 2H), 7.80 (dd, J = 9.2 Hz, 2.8 Hz, 1H), 7.86-7.90 (m, 1H), 7.95-8.00 (m, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 35.2, 116.8 (d, J = 23 Hz), 118.7 (d, J = 17 Hz), 122.2, 123.0 (d, J = 3 Hz), 124.1, 124.7, 125.1, 126.8 (d, J = 3 Hz), 130.7, 131.2 (d, J = 10 Hz), 139.1, 140.0, 142.0 (d, J = 4 Hz), 159.6 (d, J = 247 Hz) ppm. HRMS (ESI): calcd for $C_{15}H_{11}FN_2NaOS$ $[M+Na]^+$ 309.0474, found 309.0468.



N-(2-(Benzo[*b*]thiopene-2-yl)-4-chlorophenyl)-*N*-methylnitrous amide (3k)

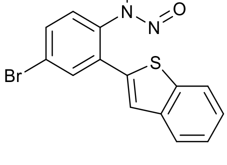
Following the general procedure. *N*-(4-Chlorophenyl)-*N*-methylnitrous amide **1k** (34.0 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 4/1, v/v) afforded **3k** as inseparable yellow oily mixture of *syn* and *anti* isomers (50.7 mg, 84% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 13:1. The NMR data listed here represent peak information only for the major *syn* isomer.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.10 (s, 3H), 7.26 (s, 1H), 7.36-7.38 (m, 2H), 7.41 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.73 (s, 1H), 7.78 (d, *J* = 6.8 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.5, 122.4, 124.3, 124.7, 125.1, 125.4, 128.8, 129.5, 131.4, 132.3, 135.5, 137.8, 139.2, 139.8, 140.7 ppm. HRMS (ESI): calcd for $C_{15}H_{11}ClN_2NaOS$ [M+Na]$^+$ 325.0178, found 325.0175.



N-(2-(Benzo[*b*]thiopene-2-yl)-5-bromophenyl)-*N*-methylnitrous amide (3l)

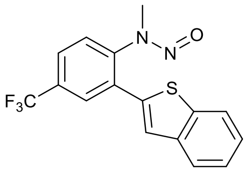
Following the general procedure. *N*-(3-Bromophenyl)-*N*-methylnitrous amide **1l** (42.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/CH$_2$Cl$_2$ = 4/1, v/v) afforded **3l** as inseparable yellow solid mixture of *syn* and *anti* isomers (56.7 mg, 82% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 10:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.22 (s, 3H), 7.36-7.43 (m, 2H), 7.57 (d, *J* = 0.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.85-7.90 (m, 2H), 7.93 (d, *J* = 1.6 Hz, 1H), 7.96-8.00 (m, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 35.3, 122.0, 122.3, 124.1, 124.3, 124.8, 125.1, 129.7, 130.2, 132.6, 132.7, 137.6, 139.3, 139.8, 140.6 ppm. HRMS (ESI): calcd for $C_{15}H_{11}BrN_2NaOS$ [M+Na]$^+$ 368.9673, found 368.9665.



N-(2-(Benzo[*b*]thiopene-2-yl)-4-bromophenyl)-*N*-methylnitrous amide (3m)

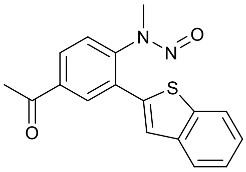
Following the general procedure. *N*-(4-Bromophenyl)-*N*-methylnitrous amide **1m** (42.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/CH$_2$Cl$_2$ = 4/1, v/v) afforded **3m** as inseparable yellow solid mixture of *syn* and *anti* isomers (59.5 mg, 86% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately

13:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.10 (s, 3H), 7.27 (s, 1H), 7.33-7.41 (m, 3H), 7.65 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.77-7.83 (m, 2H), 7.89 (d, *J* = 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.5, 122.4, 123.4, 124.3, 124.7, 125.0, 125.4, 128.9, 132.42, 132.43, 134.3, 137.6, 139.6, 139.8, 140.7 ppm. HRMS (ESI): calcd for $C_{15}H_{11}BrN_2NaOS$ [M+Na]$^+$ 368.9673, found 368.9667.



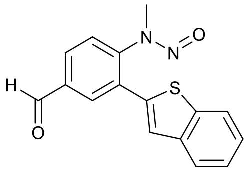
N-(2-(Benzo[*b*]thiopene-2-yl)-4-(trifluoromethyl)phenyl)-*N*-methylnitrous amide (3n)

Following the general procedure. *N*-Methyl-*N*-(4-(trifluoromethyl)phenyl)nitrous amide **1n** (40.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 4/1, v/v) afforded **3n** as inseparable yellow solid mixture of *syn* and *anti* isomers (48.4 mg, 72% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 14:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.13 (s, 3H), 7.32 (s, 1H), 7.36-7.42 (m, 3H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 8.00 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.3, 122.4, 124.3, 125.0, 125.1, 125.5, 126.3 (q, *J* = 4 Hz), 127.9, 128.8 (q, *J* = 4 Hz), 131.3, 131.6, 131.9, 137.7, 139.8, 140.7, 143.4 ppm. HRMS (ESI): calcd for $C_{16}H_{12}F_3N_2NaOS$ [M+H]$^+$ 337.0622, found 337.0619.



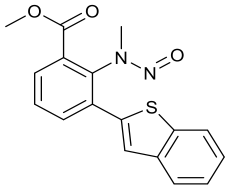
N-(4-Acetyl-2-(benzo[*b*]thiophen-2-yl)phenyl)-*N*-methylnitrous amide (3o)

Following the general procedure. *N*-(4-Acetylphenyl)-*N*-methylnitrous amide **1o** (35.6 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3o** as inseparable yellow oily mixture of *syn* and *anti* isomers (45.9 mg, 74% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 15:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.69 (s, 3H), 3.11 (s, 3H), 7.30 (s, 1H), 7.34-7.40 (m, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.77-7.83 (m, 2H), 8.06-8.09 (m, 1H) 8.28 (d, J = 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.9, 35.3, 122.3, 124.2, 124.6, 125.0, 125.2, 127.4, 129.2, 130.5, 131.8, 137.5, 138.3, 139.8, 140.6, 144.0, 196.6 ppm. HRMS (ESI): calcd for $C_{17}H_{14}N_2NaO_2S$ $[M+Na]^+$ 333.0674, found 333.0671.



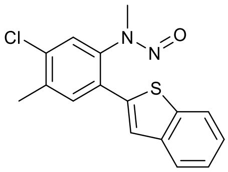
***N*-(2-(Benzo[*b*]thiophen-2-yl)-4-formylphenyl)-*N*-methylnitrous amide (3p)**

Following the general procedure. *N*-(4-Formylphenyl)-*N*-methylnitrous amide **1p** (32.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3p** as inseparable yellow oily mixture of *syn* and *anti* isomers (30.2 mg, 51% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 15:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.12 (s, 3H), 7.32 (s, 1H), 7.36-7.42 (m, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 8.22 (s, 1H), 10.13 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.3, 122.4, 124.3, 124.8, 125.1, 125.4, 127.9, 130.2, 131.1, 133.1, 136.6, 137.9, 139.8, 140.6, 145.1, 190.7 ppm. HRMS (ESI): calcd for $C_{16}H_{12}N_2NaO_2S$ $[M+Na]^+$ 319.0517, found 319.0515.



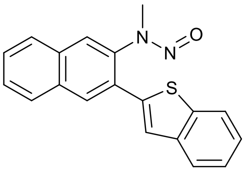
Methyl 3-(benzo[*b*]thiophen-2-yl)-2-(methyl(nitroso)amino)benzoate (3q)

Following the general procedure. Methyl 2-(methyl(nitroso)amino)benzoate **1q** (38.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc/CH_2Cl_2 = 20/1/1, v/v/v) afforded **3q** as inseparable yellow oily mixture of *syn* and *anti* isomers (49.6 mg, 76% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 1:0.13. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.13 (s, 3H), 3.83 (s, 3H), 7.25 (s, 1H), 7.33-7.40 (m, 2H), 7.64 (t, J = 8.0 Hz, 1H), 7.74-7.84 (m, 2H), 7.90 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 8.02-8.06 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.7, 52.9, 122.2, 124.2, 124.7, 124.9, 125.2, 129.8, 130.6, 131.2, 133.2, 135.0, 137.9, 139.2, 139.8, 140.7, 165.9 ppm. HRMS (ESI): calcd for $C_{17}H_{14}N_2NaO_3S$ $[M+Na]^+$ 349.0623, found 349.0623.



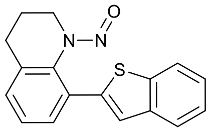
N-(2-(Benzo[b]thiophen-2-yl)-5-chloro-4-methylphenyl)-N-methylnitrous amide (3r)

Following the general procedure. *N*-(3-Chloro-4-methylphenyl)-*N*-methylnitrous amide **1r** (36.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 4/1, v/v) afforded **3r** as inseparable yellow solid mixture of *syn* and *anti* isomers (52.5 mg, 83% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 12:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 3H), 3.10 (s, 3H), 7.21 (s, 1H), 7.33-7.39 (m, 2H), 7.48 (s, 1H), 7.60 (s, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0, 35.5, 122.4, 124.17, 124.18, 125.0, 125.2, 128.0, 129.0, 133.5, 135.2, 138.0, 138.3, 139.1, 140.0, 140.6 ppm. HRMS (ESI): calcd for $C_{16}H_{13}ClN_2NaOS$ $[M+Na]^+$ 339.0335, found 339.0343.



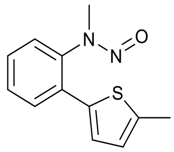
N-(3-(Benzo[b]thiopene-2-yl)naphthalene-2-yl)-N-methylnitrous amide (3s)

Following the general procedure. *N*-Methyl-*N*-(naphthalen-2-yl)nitrous amide **1s** (37.2 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **3s** as inseparable yellow oily mixture of *syn* and *anti* isomers (49.6 mg, 78% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 15:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.17 (s, 3H), 7.29 (s, 1H), 7.37-7.41 (m, 2H), 7.58-7.62 (m, 2H), 7.78 (d, J = 6.8 Hz, 1H), 7.84 (d, J = 7.2 Hz, 1H), 7.92-7.94 (m, 3H), 8.19 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.8, 122.3, 124.0, 124.1, 124.8, 125.0, 126.4, 127.9, 128.0, 128.2, 128.4, 131.4, 133.0, 133.3, 138.3, 139.5, 140.2, 140.5 ppm. HRMS (ESI): calcd for $C_{19}H_{15}N_2OS$ [M+H]$^+$ 319.0905, found 319.0897.



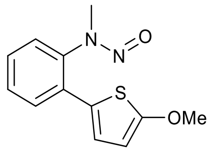
8-(Benzo[b]thiopene-2-yl)-1-nitroso-1,2,3,4-tetrahydroquiline (3t)

Following the general procedure. 1-Nitroso-1,2,3,4-tetrahydroquinoline **1t** (32.4 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **3t** as yellow solid (38.8 mg, 66% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.06-2.12 (m, 2H), 2.74 (t, J = 5.6 Hz, 2H), 3.95 (t, J = 6.4 Hz, 2H), 7.26-7.35 (m, 5H), 7.56 (d, J = 7.4 Hz, 1H), 7.73 (t, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 22.8, 27.8, 43.4, 122.2, 123.0, 123.7, 124.3, 124.4, 127.0, 128.5, 128.7, 131.2, 133.6, 135.6, 140.1, 140.4, 142.1 ppm. HRMS (ESI): calcd for $C_{17}H_{14}N_2NaOS$ [M+Na]$^+$ 317.0725, found 317.0721.



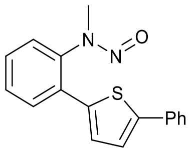
N-(2-(5-Methylthiopene-2-yl)phenyl)-N-methylnitrous amide (4a)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 2-methylthiophene **2b** (58.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **4a** as inseparable yellow oily mixture of *syn* and *anti* isomers (41.3 mg, 89% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 15:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.48 (s, 3H), 3.12 (s, 3H), 6.70 (d, J = 3.2 Hz, 1H), 6.80 (d, J = 3.2 Hz, 1H), 7.38-7.45 (m, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 15.4, 35.4, 126.1, 127.2, 127.5, 128.5, 129.7, 130.9, 131.0, 136.4, 139.9, 142.0 ppm. HRMS (ESI): calcd for $C_{12}H_{13}N_2OS$ [M+H]$^+$ 233.0749, found 233.0748.



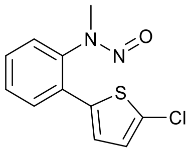
N-(2-(5-Methoxythiopene-2-yl)phenyl)-N-methylnitrous amide (4b)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 2-methoxythiophene **2c** (68.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 40/1, v/v) afforded **4b** as inseparable yellow oily mixture of *syn* and *anti* isomers (44.6 mg, 90% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 13:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.15 (s, 3H), 3.89 (s, 3H), 6.14 (d, J = 3.6 Hz, 1H), 6.63 (d, J = 4.0 Hz, 1H), 7.36-7.42 (m, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.4, 60.3, 104.6, 124.5, 125.2, 127.6, 128.2, 129.7, 130.7, 130.9, 139.8, 168.0 ppm. HRMS (ESI): calcd for $C_{12}H_{12}N_2NaO_2S$ [M+Na]$^+$ 271.0517, found 271.0515.



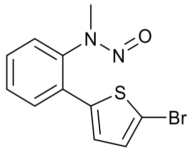
N-Methyl-N-(2-(5-phenylthiophen-2-yl)phenyl)nitrous amide (4c)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 2-phenylthiophene **2d** (96.0 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) afforded **4c** as inseparable yellow solid mixture of *syn* and *anti* isomers (54.7 mg, 93% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 15:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.16 (s, 3H), 6.97 (d, J = 3.6 Hz, 1H), 7.26 (d, J = 3.2 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.44 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.59 (d, J = 7.2 Hz, 2H), 7.68 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.5, 123.8, 125.9, 127.7, 128.1, 128.3, 128.9, 129.08, 129.09, 129.12, 129.8, 130.6, 131.0, 133.8, 138.1, 140.1, 146.1 ppm. HRMS (ESI): calcd for $C_{17}H_{14}N_2NaOS$ [M+Na]$^+$ 317.0725, found 317.0718.



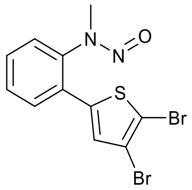
N-(2-(5-Chlorolthiopene-2-yl)phenyl)-N-methylnitrous amide (4d)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 2-chlorothiophene **2e** (70.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **4d** as inseparable yellow oily mixture of *syn* and *anti* isomers (43.8 mg, 87% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 12:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.14 (s, 3H), 6.79 (d, J = 2.8 Hz, 1H), 6.86 (d, J = 2.8 Hz, 1H), 7.39 (d, J = 7.2 Hz, 1H), 7.46-7.53 (m, 2H), 7.58 (d, J = 7.2 Hz 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.4, 126.6, 127.0, 127.6, 129.3, 129.8, 130.0, 131.0, 131.7, 137.5, 140.1 ppm. HRMS (ESI): calcd for $C_{11}H_9ClN_2NaOS$ [M+Na]$^+$ 275.0022, found 275.0026.



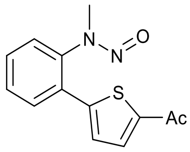
N-(2-(5-Bromolthiopene-2-yl)phenyl)-N-methylnitrous amide (4e)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 2-bromothiophene **2f** (97.2 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **4e** as inseparable brown oily mixture of *syn* and *anti* isomers (52.1 mg, 88% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 12:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.13 (s, 3H), 6.76 (d, *J* = 2.8 Hz, 1H), 7.01 (d, *J* = 3.2 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.46-7.53 (m, 2H), 7.57 (d, *J* = 7.6 Hz 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.4, 114.0, 127.5, 127.6, 129.4, 129.8, 129.9, 130.7, 131.0, 140.0, 140.4 ppm. HRMS (ESI): calcd for $C_{11}H_9BrN_2NaOS$ [M+Na]$^+$ 318.9517, found 318.9515.



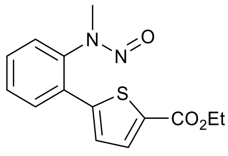
N-(2-(4,5-Dibromolthiopene-2-yl)phenyl)-N-methylnitrous amide (4f)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 2,3-dibromolthiophene **2g** (143.9 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **4f** as inseparable brown oil mixture of *syn* and *anti* isomers (63.6 mg, 85% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 10:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.17 (s, 3H), 6.87 (s, 1H), 7.40-7.42 (m, 1H), 7.52-7.54 (m, 2H), 7.57-7.59 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.6, 112.9, 114.6, 127.7, 129.1, 129.5, 129.99, 130.02, 130.8, 140.1, 140.4 ppm. HRMS (ESI): calcd for $C_{11}H_8Br_2N_2NaOS$ [M+Na]$^+$ 396.8622, found 396.8629.



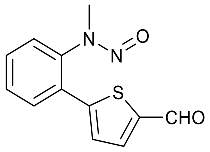
N-(2-(5-Acetylthiopene-2-yl)phenyl)-N-methylnitrous amide (4g)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 2-acetylthiophene **2h** (75.6 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4g** as inseparable yellow solid mixture of *syn* and *anti* isomers (28.1 mg, 54% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 12:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.56 (s, 3H), 3.12 (s, 3H), 6.97 (d, J = 4.0 Hz, 1H), 7.44-7.46 (m, 1H), 7.53-7.57 (m, 2H), 7.61 (d, J = 3.6 Hz, 1H), 7.64-7.67 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 26.8, 35.5, 127.5, 128.2, 129.8, 129.9, 130.2, 131.4, 133.0, 140.4, 145.2, 147.4, 190.6 ppm. HRMS (ESI): calcd for $C_{13}H_{12}N_2NaO_2S$ [M+Na]$^+$ 283.0517, found 283.0509.



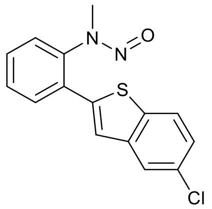
Ethyl 5-(2-(methyl(nitroso)amino)phenyl)thiophene-2-carboxylate (4h)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and ethyl thiophene-2-carboxylate **2i** (93.6 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) afforded **4h** as inseparable yellow solid mixture of *syn* and *anti* isomers (30.7 mg, 53% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 12:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.37 (t, J = 7.2 Hz, 3H), 3.11 (s, 3H), 4.33-4.38 (m, 2H), 6.96 (d, J = 4.0 Hz, 1H), 7.43-7.45 (m, 1H), 7.52-7.57 (m, 2H), 7.64-7.66 (m, 1H), 7.72 (d, J = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.5, 35.4, 61.5, 127.6, 127.8, 129.75, 129.84, 130.0, 131.4, 133.8, 135.0, 140.4, 145.7, 162.0 ppm. HRMS (ESI): calcd for $C_{14}H_{14}N_2NaO_3S$ [M+Na]$^+$ 313.0623, found 313.0620.



N-(2-(5-Formylthiopene-2-yl)phenyl)-N-methylnitrous amide (4i)

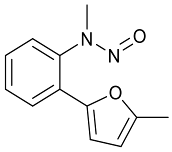
Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 2-thiophencarboxaldehyde **2j** (67.2 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4i** as inseparable brown oily mixture of *syn* and *anti* isomers (25.1 mg, 51% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 12:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.13 (s, 3H), 7.07 (d, J = 3.6 Hz, 1H), 7.44-7.46 (m, 1H), 7.56-7.58 (m, 2H), 7.66-7.71 (m, 2H), 9.88 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.5, 127.5, 128.3, 129.5, 129.9, 130.5, 131.4, 136.8, 140.4, 144.4, 148.8, 182.9 ppm. HRMS (ESI): calcd for $C_{12}H_{10}N_2NaO_2S$ [M+Na]$^+$ 269.0361, found 269.0356.



N-(2-(5-Chlorobenzo[*b*]thiophen-2-yl)phenyl)-N-methylnitrous amide (4j)

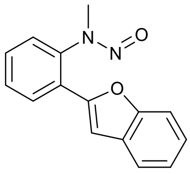
Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 5-chlorobenzothiophene **2k** (100.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **4j** as inseparable yellow solid mixture of *syn* and *anti* isomers (51.3 mg, 85% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 12:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.13 (s, 3H), 7.18 (s, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 6.8 Hz, 1H), 7.53-7.59 (m, 2H), 7.71-7.74 (m, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.5, 123.2, 123.3, 123.5, 125.4, 127.5, 129.8, 129.9, 130.2, 131.1, 131.6, 138.6, 140.6, 141.0, 141.4 ppm. HRMS (ESI): calcd for $C_{15}H_{11}ClN_2NaOS$ [M+Na]$^+$

325.0178, found 325.0184.



_N_-(2-(5-Methylfuran-2-yl)phenyl)-_N_-methylnitrous amide (4k)

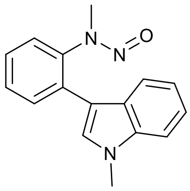
Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 2-methylfuran **2l** (49.2 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **4k** as inseparable yellow oily mixture of *syn* and *anti* isomers (37.2 mg, 86% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 12:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.32 (s, 3H), 3.26 (s, 3H), 6.03 (s, 1H), 6.17 (s, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 13.7, 35.1, 108.2, 110.8, 127.58, 127.61, 127.8, 128.0, 129.7, 137.9, 148.1, 153.2 ppm. HRMS (ESI): calcd for $C_{12}H_{13}N_2O_2$ $[M+H]^+$ 217.0977, found 217.0979.



_N_-(2-(Benzofuran-2-yl)phenyl)-_N_-methylnitrous amide (4l)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and benzofuran **2m** (70.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 60/1, v/v) afforded **4l** as inseparable yellow oily mixture of *syn* and *anti* isomers (35.8 mg, 71% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 12:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.31 (s, 3H), 6.66 (s, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.48-7.61 (m, 4H), 8.03 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 35.2, 106.2, 111.4, 121.5, 123.4, 125.2, 127.0, 127.9, 128.8, 129.2, 129.7, 129.8, 139.4, 151.8, 154.9 ppm. HRMS (ESI): calcd for

$C_{15}H_{12}N_2NaO_2$ [M+Na]$^+$ 275.0796, found 275.0789.



N-Methyl-N-(2-(1-methyl-1H-indol-3-yl)phenyl)nitrous amide (4m)

Following the general procedure. *N*-Methyl-*N*-phenylnitrous amide **1a** (27.2 mg, 0.2 mmol) and 1-methyl-1*H*-indole **2n** (78.6 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 40/1, v/v) afforded **4m** as inseparable burgundy solid mixture of *syn* and *anti* isomers (23.9 mg, 45% yield). By ^{1}H NMR, the *syn*:*anti* ratio was determined to be approximately 11:1. The NMR data listed here represent peak information only for the major *syn* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.93 (s, 3H), 3.80 (s, 3H), 6.93 (s, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.1, 35.3, 109.7, 112.1, 119.6. 120.4, 122.5, 126.7, 127.2, 127.3, 128.2, 129.4, 130.9, 131.8, 137.0, 140.8 ppm. HRMS (ESI): calcd for $C_{16}H_{15}N_3NaO$ [M+Na]$^+$ 288.1113, found 288.1108.

IX. References

(1) J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.

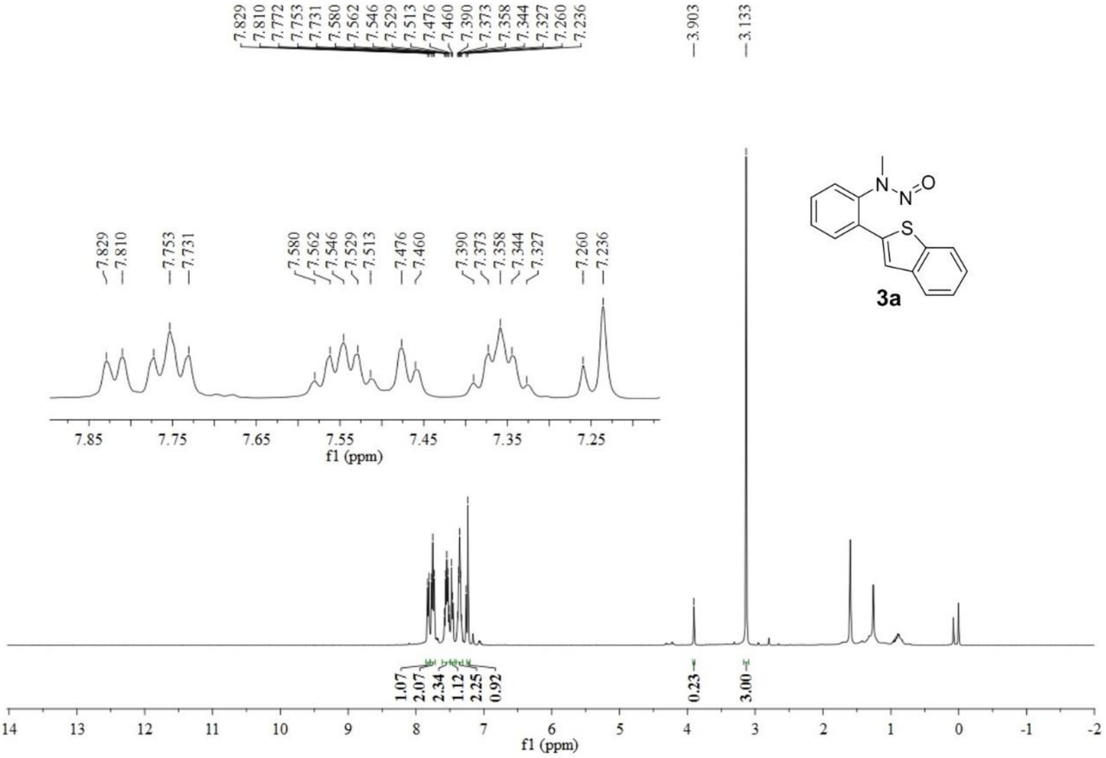
(2) Y. Li, B.-J. Li, W.-H. Wang, W.-P. Huang, X.-S. Zhang, K. Chen and Z.-J. Shi, *Angew. Chem., Int. Ed.,* 2011, **50**, 2115.

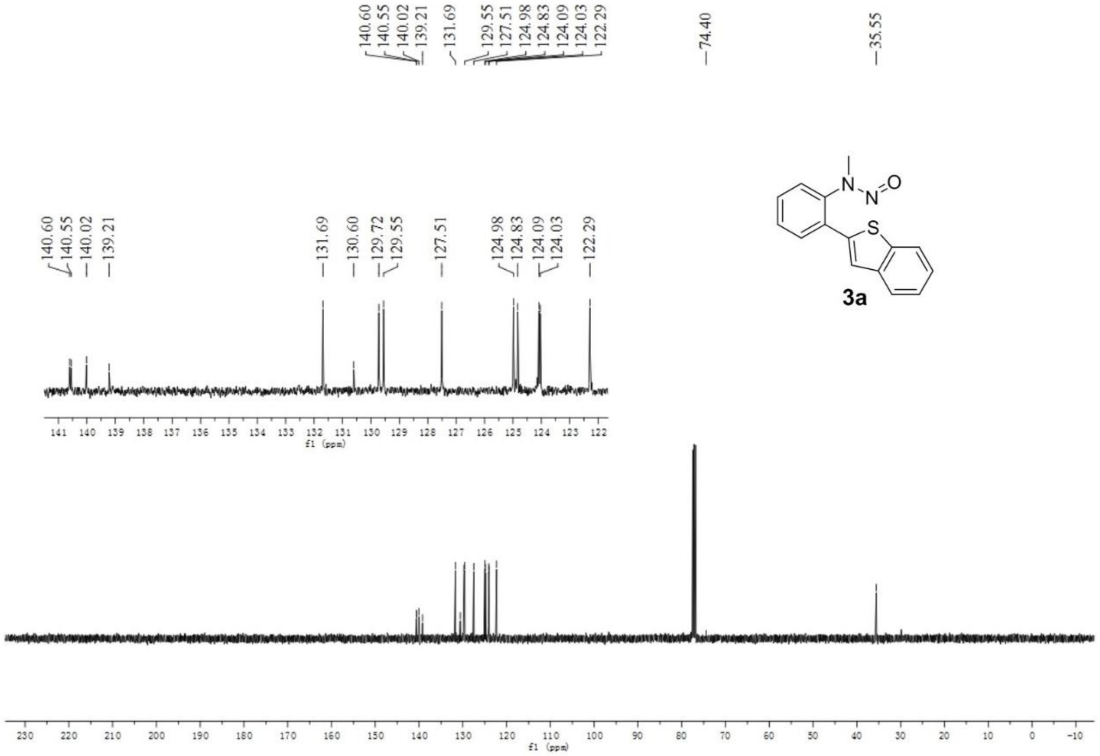
(3) (*a*) J. A. Osborn and G. Wolkinson, *Inorg. Syn.,* 1967, **10**, 67; (*b*) J. Wang, X. Tong, X. Xie and Z. Zhang, *Org. Lett.,* 2010, **12**, 5370.

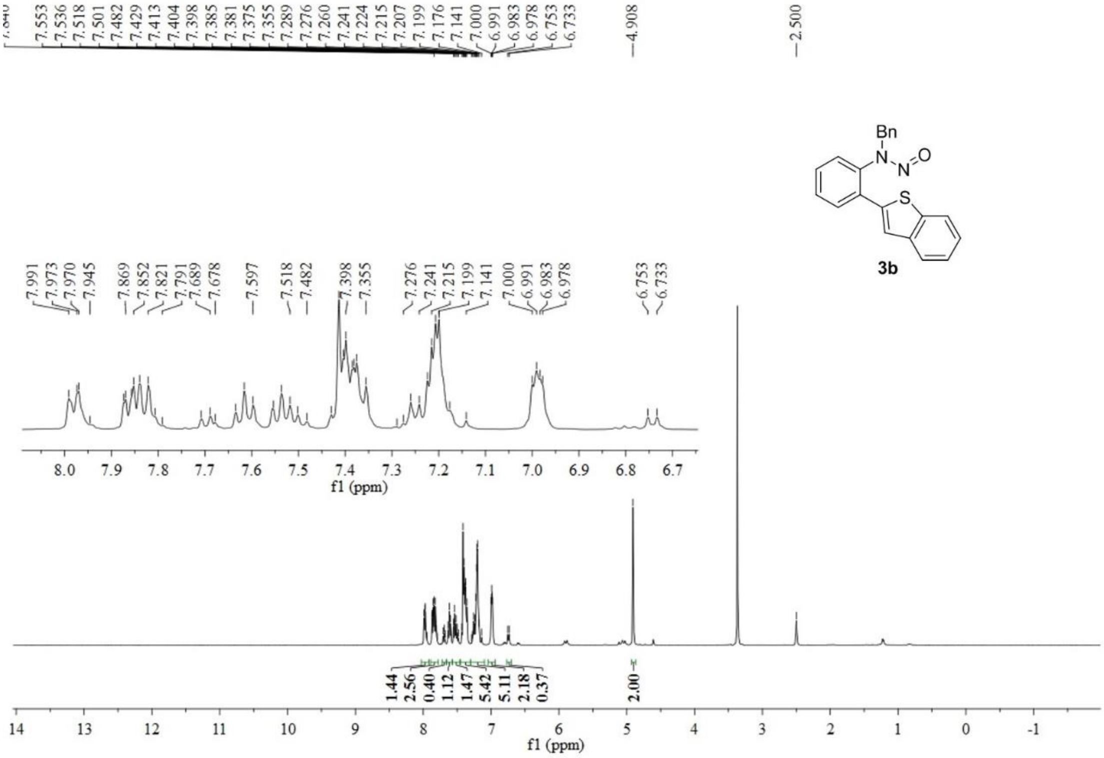
(4) B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu and J. Zhu, *J. Am. Chem. Soc.,* 2013, **135**, 468.

(5) (*a*) T. Gao and P. Sun, *J. Org. Chem.,* 2014, **79**, 9888; (*b*) C. Song, C. Yang, F. Zhang, J. Wang and J. Zhu, *Org. Lett.,* 2016, **18**, 4510; (*c*) X. Huang, J. Huang, C. Du, X. Zhang, F. Song and J. You, *Angew. Chem., Int. Ed.,* 2013, **52**, 12970.

X. ^{1}H NMR and ^{13}C NMR spectra of compounds



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Bn
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7.141
7.000
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6.978
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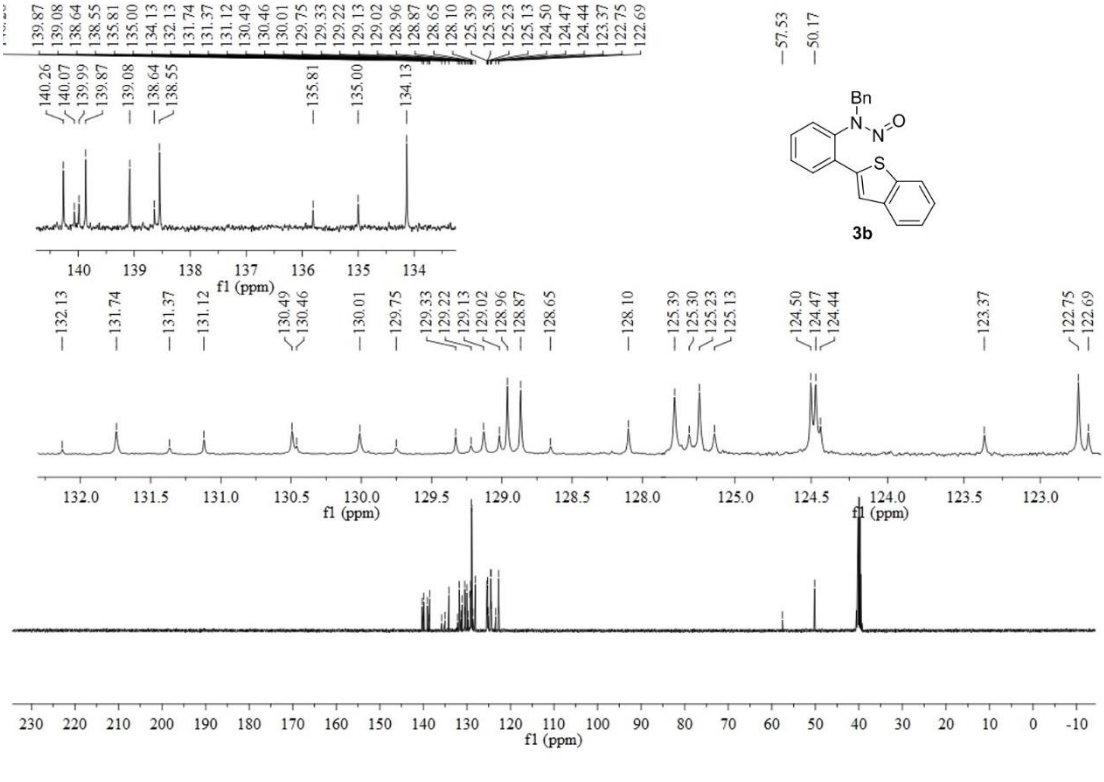
f1 (ppm)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135.00
134.13
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f1 (ppm)
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N
O
S
3b
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122.69
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f1 (ppm)
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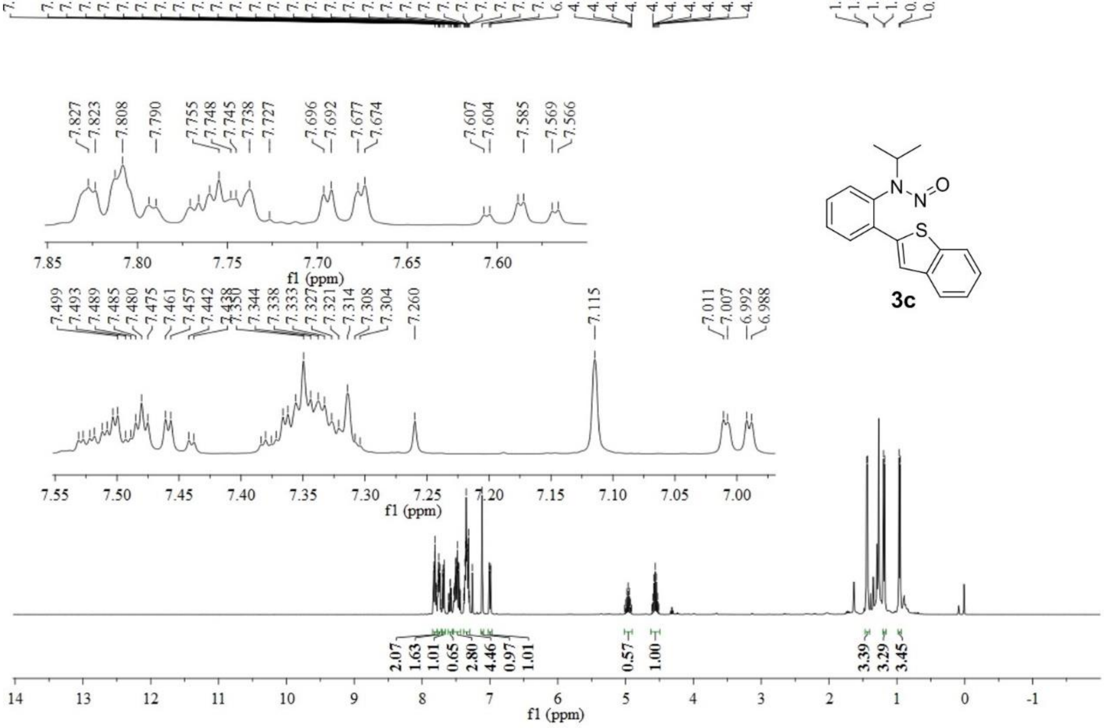
f1 (ppm)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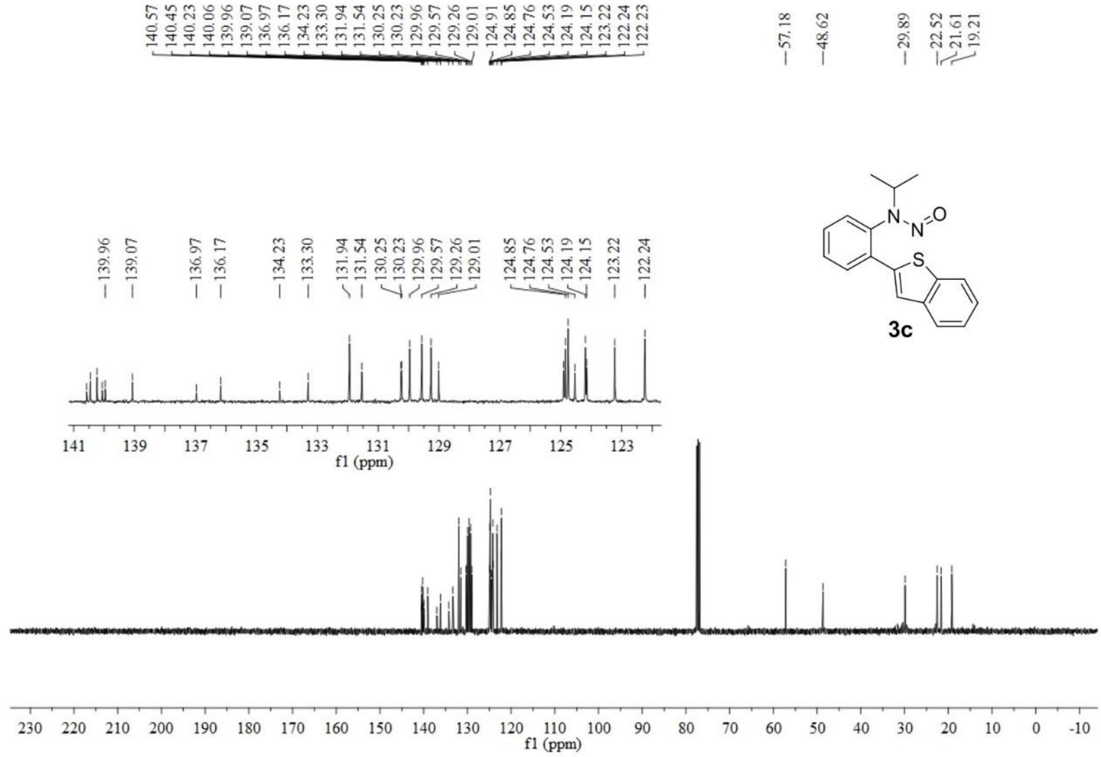
f1 (ppm)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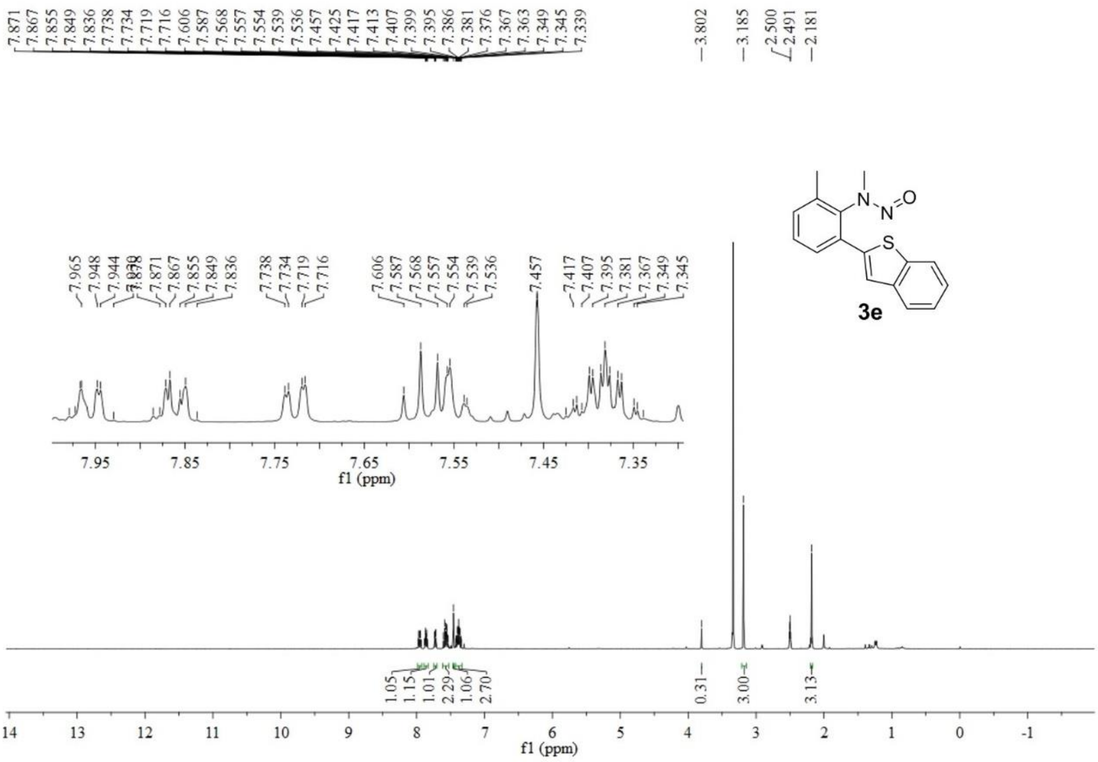
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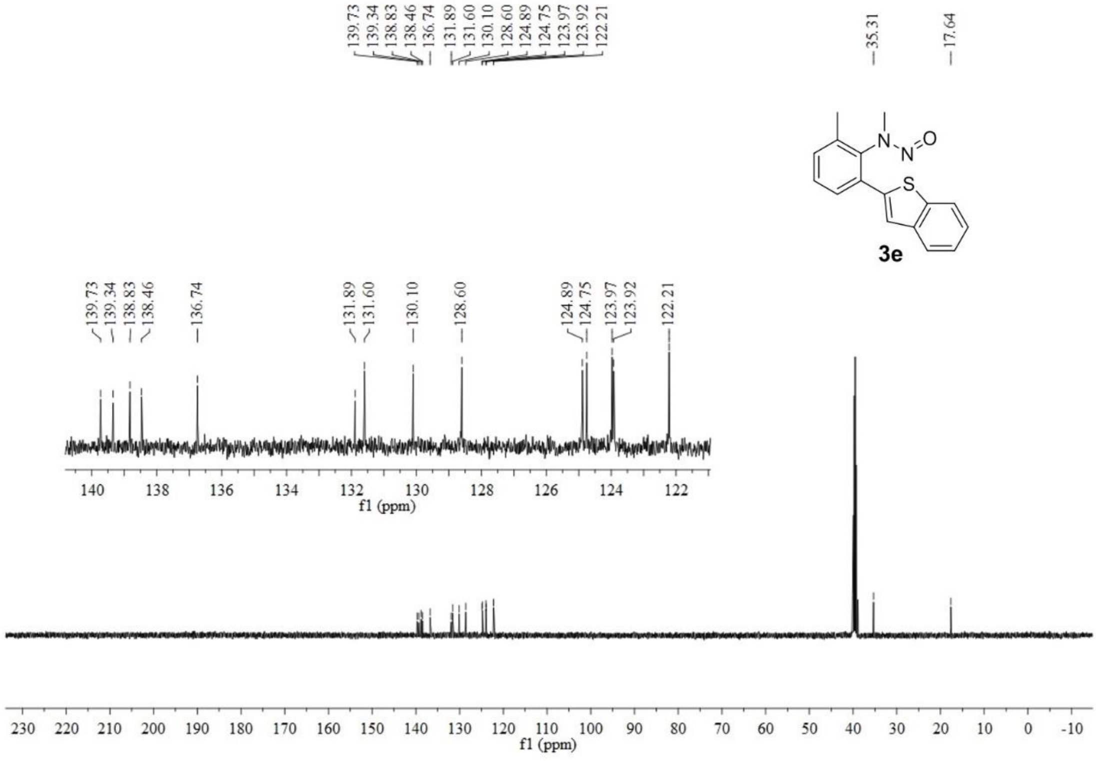
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124
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f1 (ppm)
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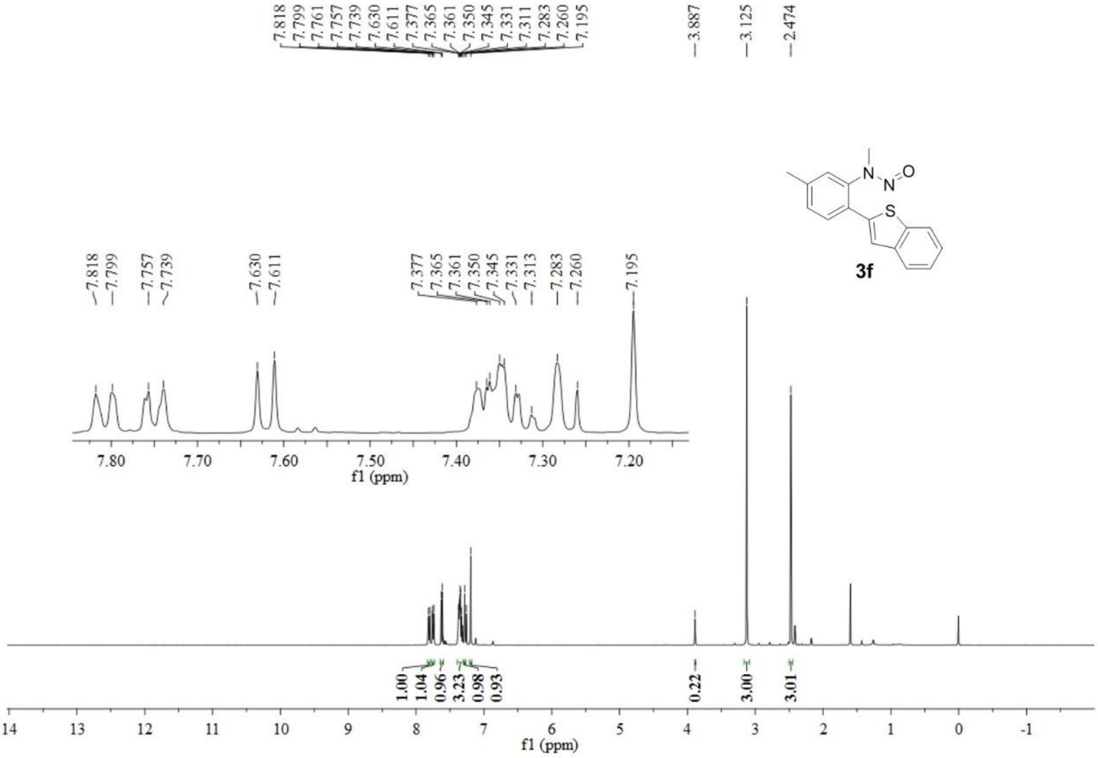
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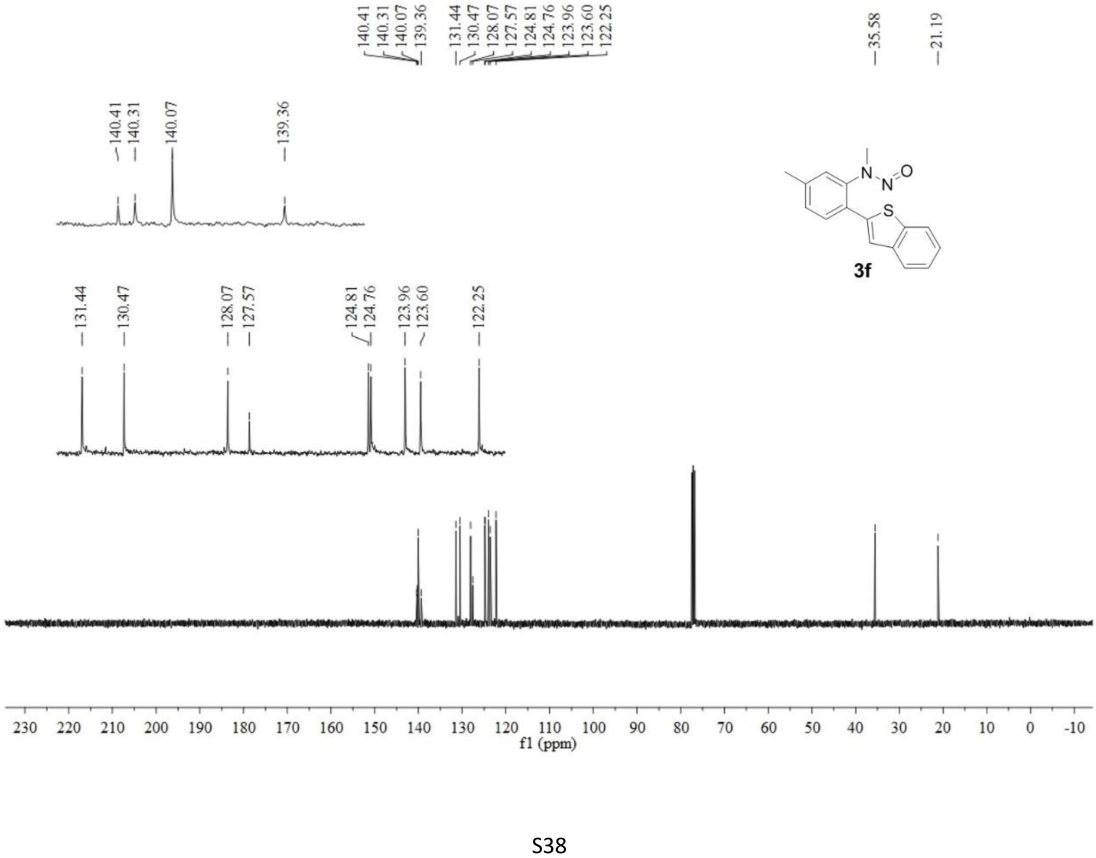
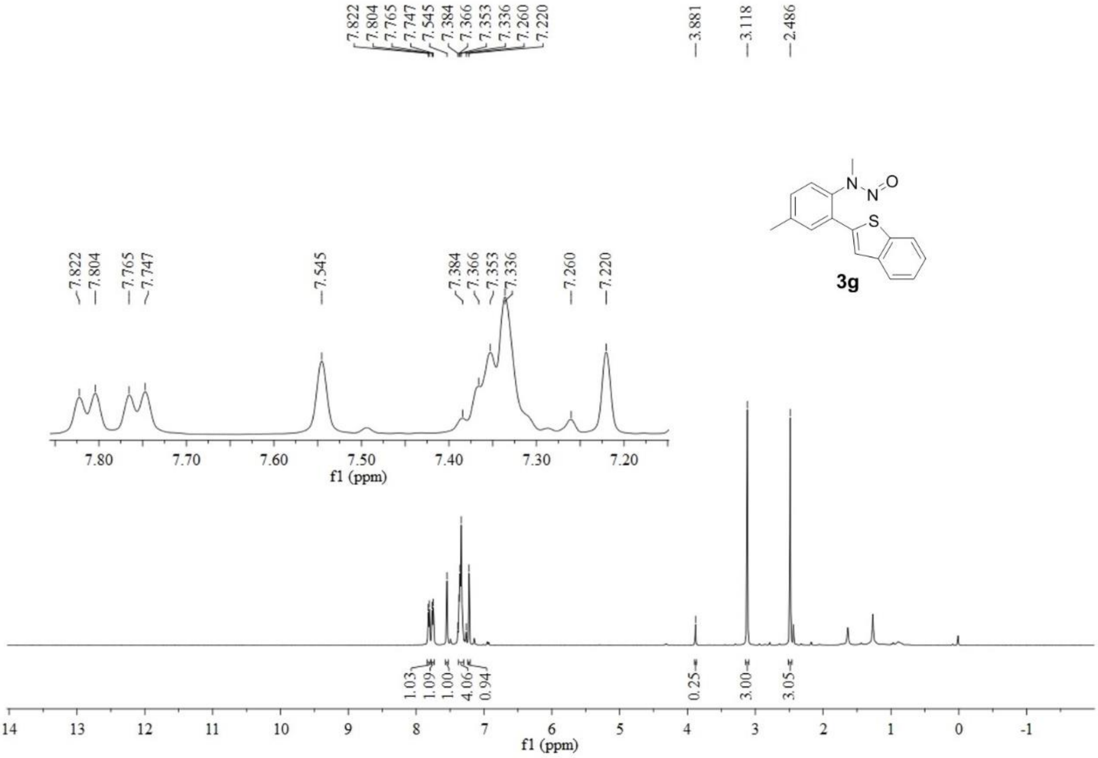
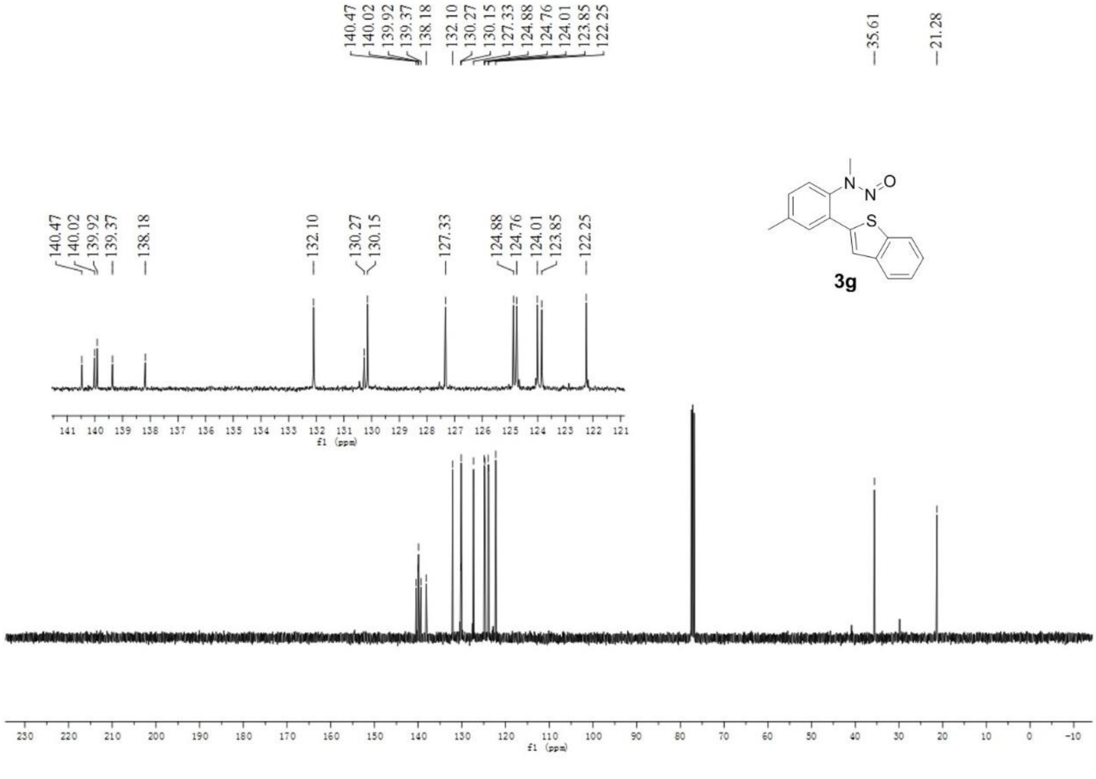
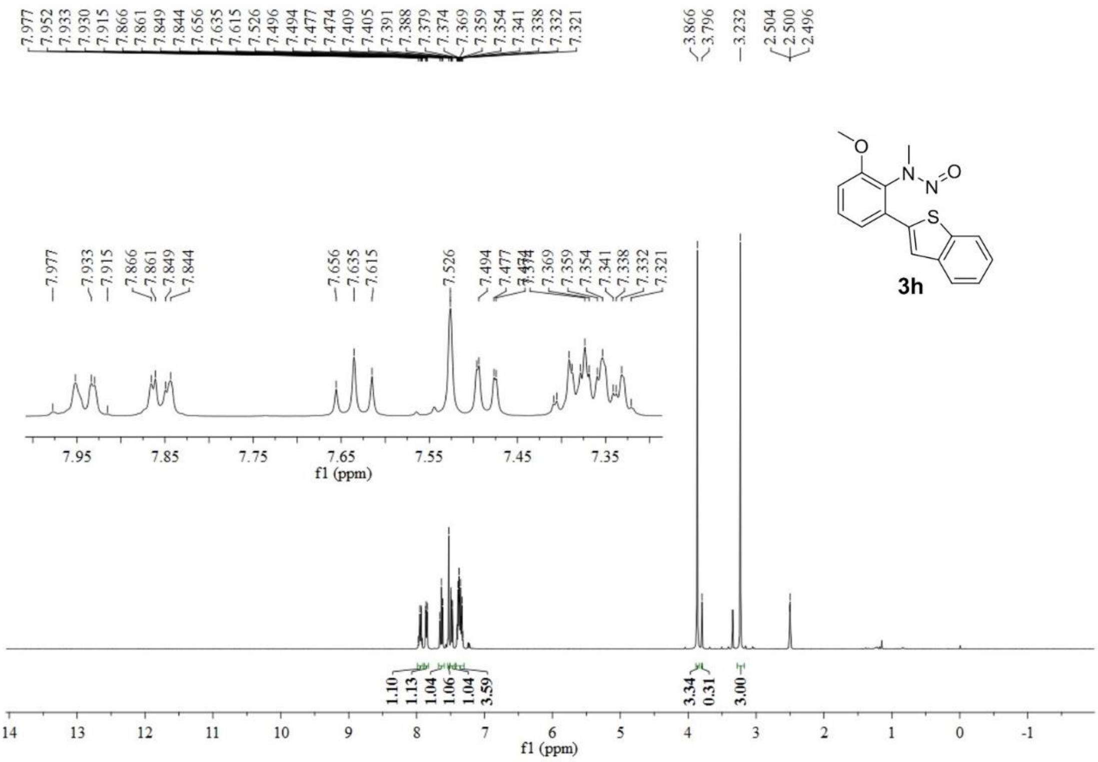
5
4
3
2
1
0
-1
f1 (ppm)


140.41
140.31
140.07
139.36
131.44
130.47
128.07
127.57
124.81
124.76
123.96
123.60
122.25
35.58
21.19
140.41
140.31
140.07
139.36
N
N
O
S
3f
131.44
130.47
128.07
127.57
124.81
124.76
123.96
123.60
122.25
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.822
7.804
7.765
7.747
7.545
7.384
7.366
7.353
7.336
7.260
7.220
3.881
3.118
2.486
N
N
O
S
3g
7.80
7.70
7.60
7.50
7.40
7.30
7.20
f1 (ppm)
1.03
1.09
1.00
4.06
0.94
0.25
3.00
3.05
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


140.47
140.02
139.92
139.37
138.18
132.10
130.27
130.15
127.33
124.88
124.76
124.01
123.85
122.25
35.61
21.28
N
N
O
S
3g
141
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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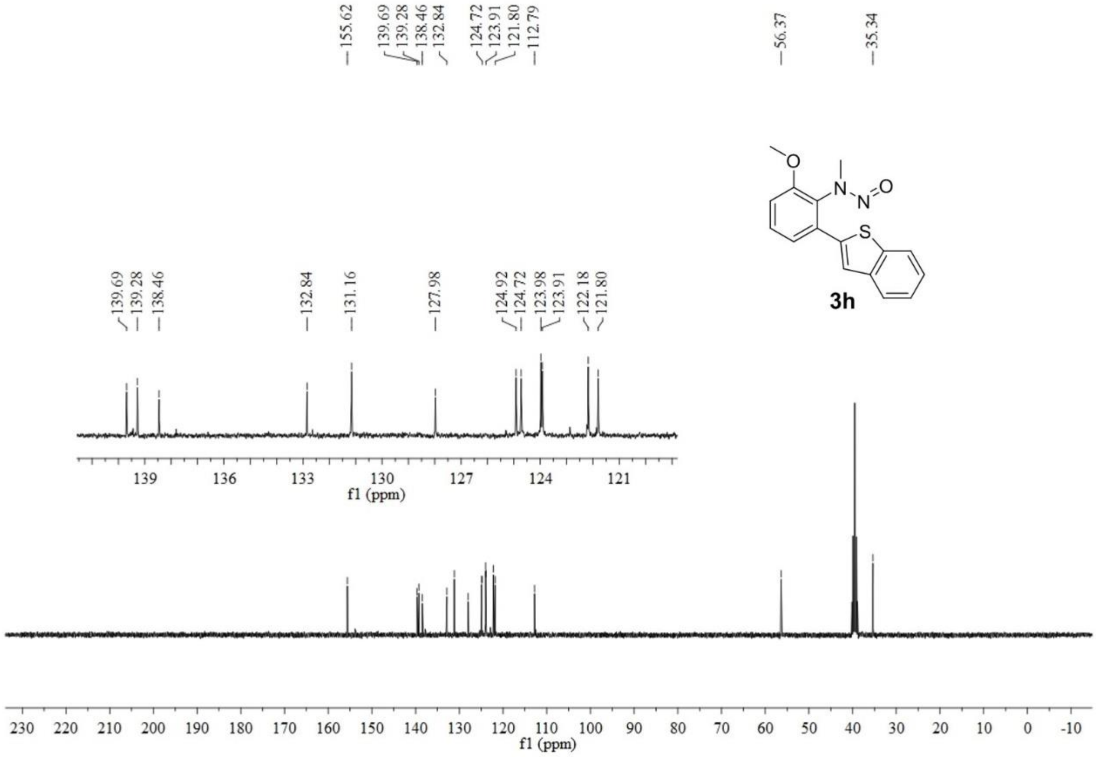
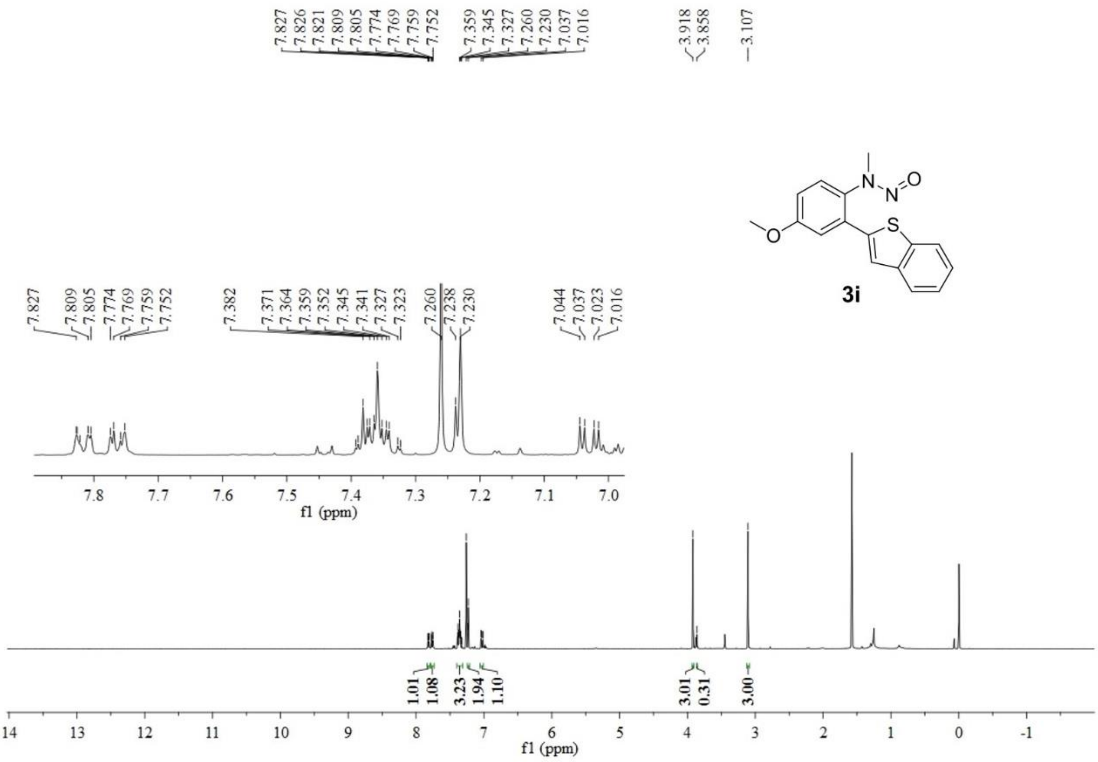
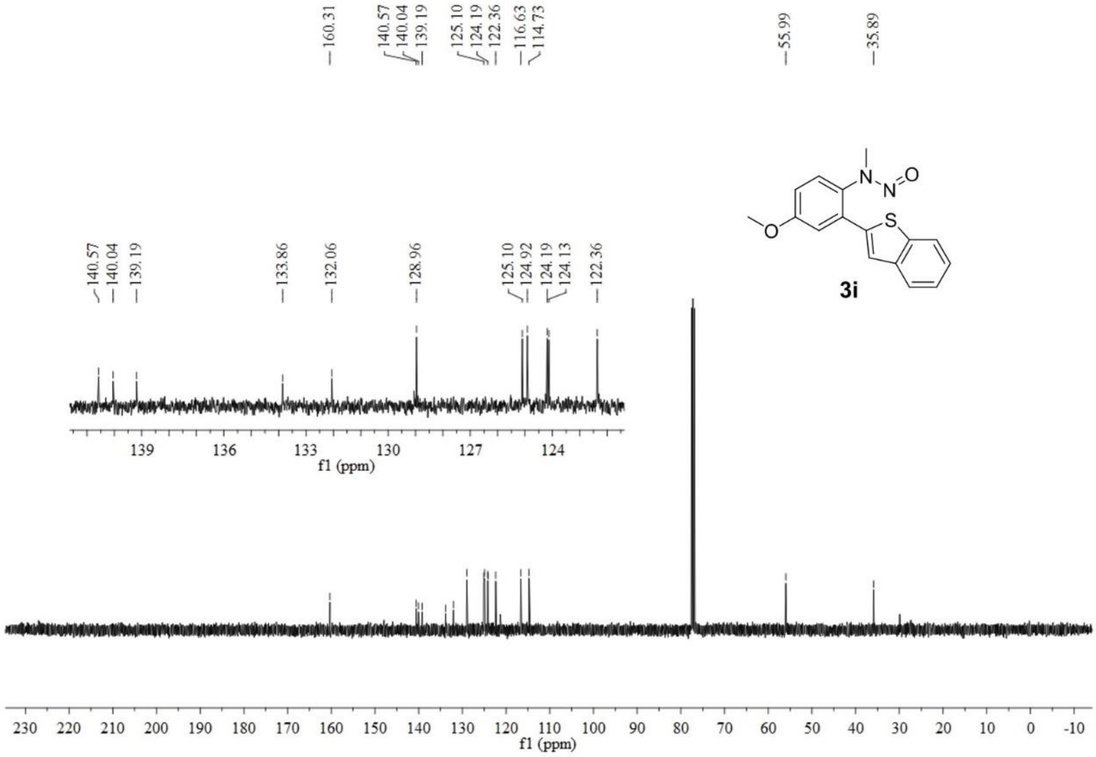
7.952
7.933
7.930
7.915
7.866
7.861
7.849
7.844
7.656
7.635
7.615
7.526
7.496
7.494
7.477
7.474
7.409
7.405
7.391
7.388
7.379
7.374
7.369
7.359
7.354
7.341
7.338
7.332
7.321
3.866
3.796
3.232
2.504
2.500
2.496
O
N
N
O
S
3h
1.10
1.13
1.04
1.06
1.04
3.59
3.34
0.31
3.00
f1 (ppm)
f1 (ppm)


155.62
139.69
139.28
138.46
132.84
124.72
123.91
121.80
112.79
56.37
35.34
139.69
139.28
138.46
132.84
131.16
127.98
124.92
124.72
123.98
123.91
122.18
121.80
O
N
N
O
S
3h
f1 (ppm)
f1 (ppm)



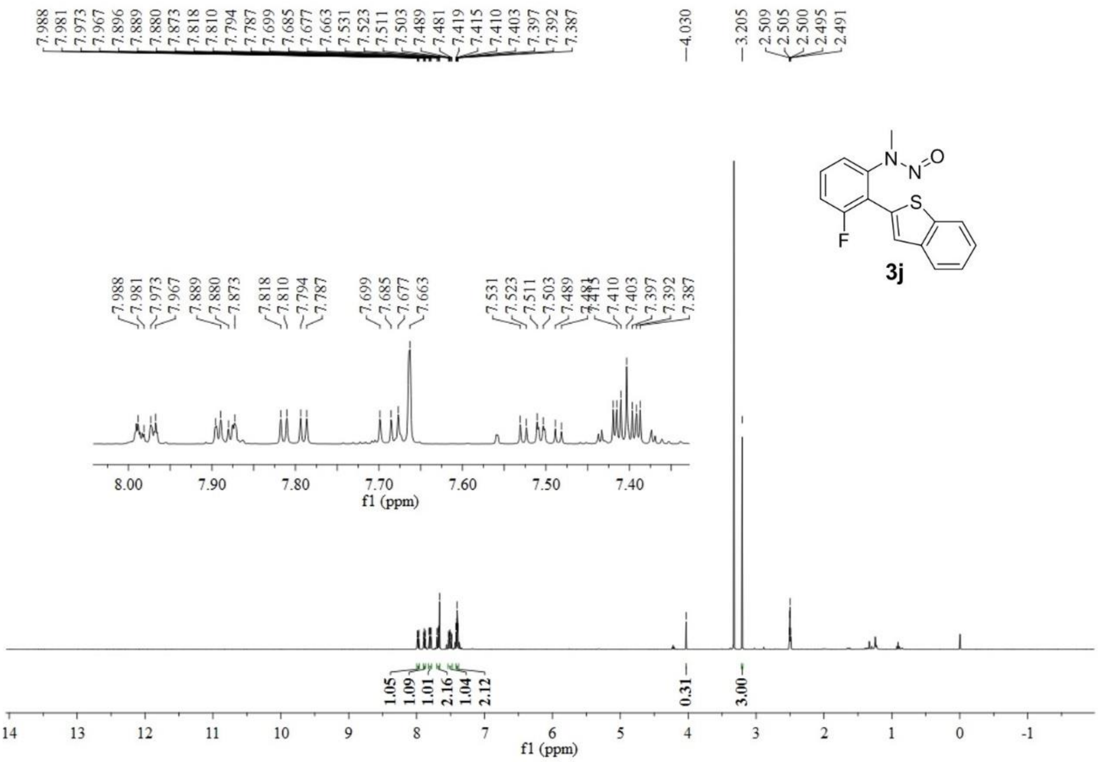
7.827
7.826
7.821
7.809
7.805
7.774
7.769
7.759
7.752
7.359
7.345
7.327
7.260
7.230
7.037
7.016
3.918
3.858
3.107
7.827
7.809
7.805
7.774
7.769
7.759
7.752
7.382
7.371
7.364
7.359
7.352
7.345
7.341
7.327
7.323
7.260
7.238
7.230
7.044
7.037
7.023
7.016
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.01
1.08
3.23
1.94
1.10
3.01
0.31
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)
S
N
O

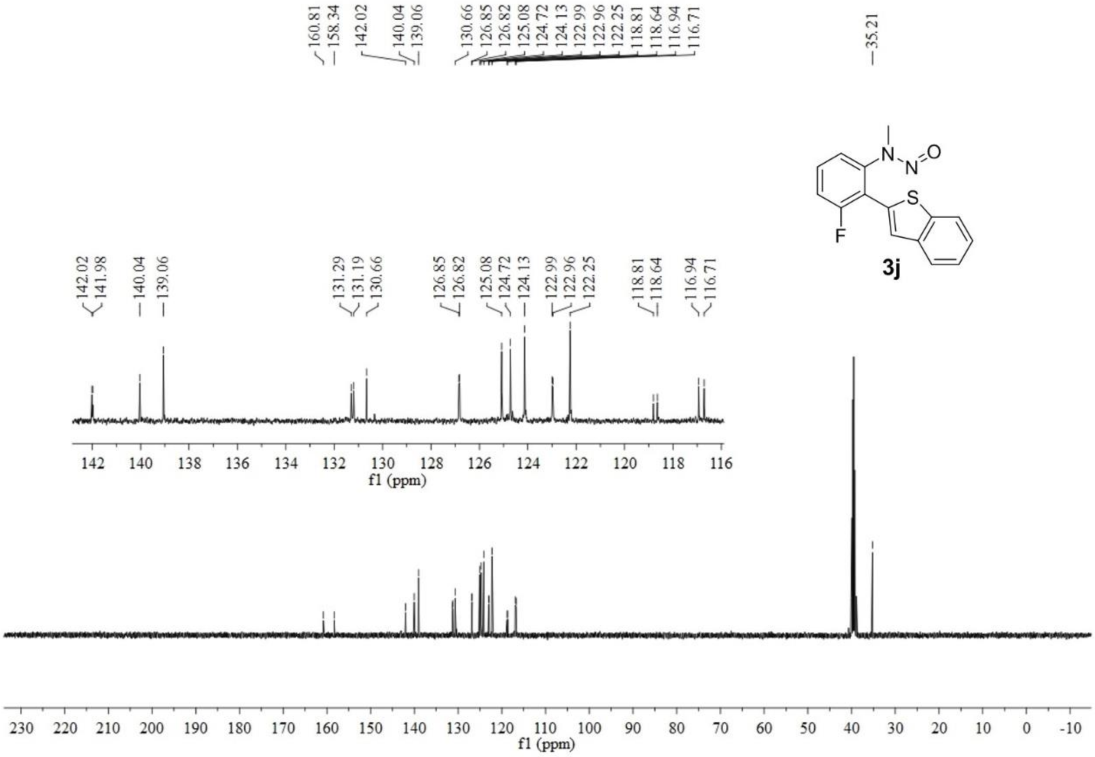
3i

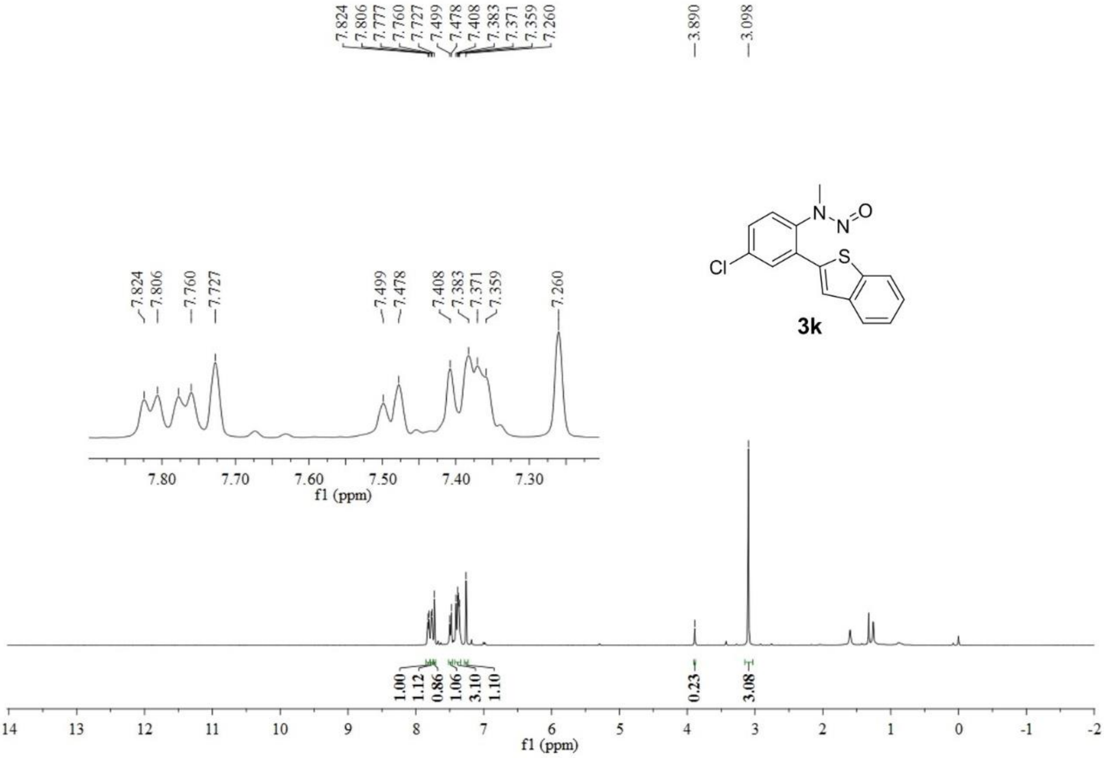


160.31
140.57
140.04
139.19
125.10
124.19
122.36
116.63
114.73
55.99
35.89
140.57
140.04
139.19
133.86
132.06
128.96
125.10
124.92
124.19
124.13
122.36
139 136 133 130 127 124
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
S
N
O

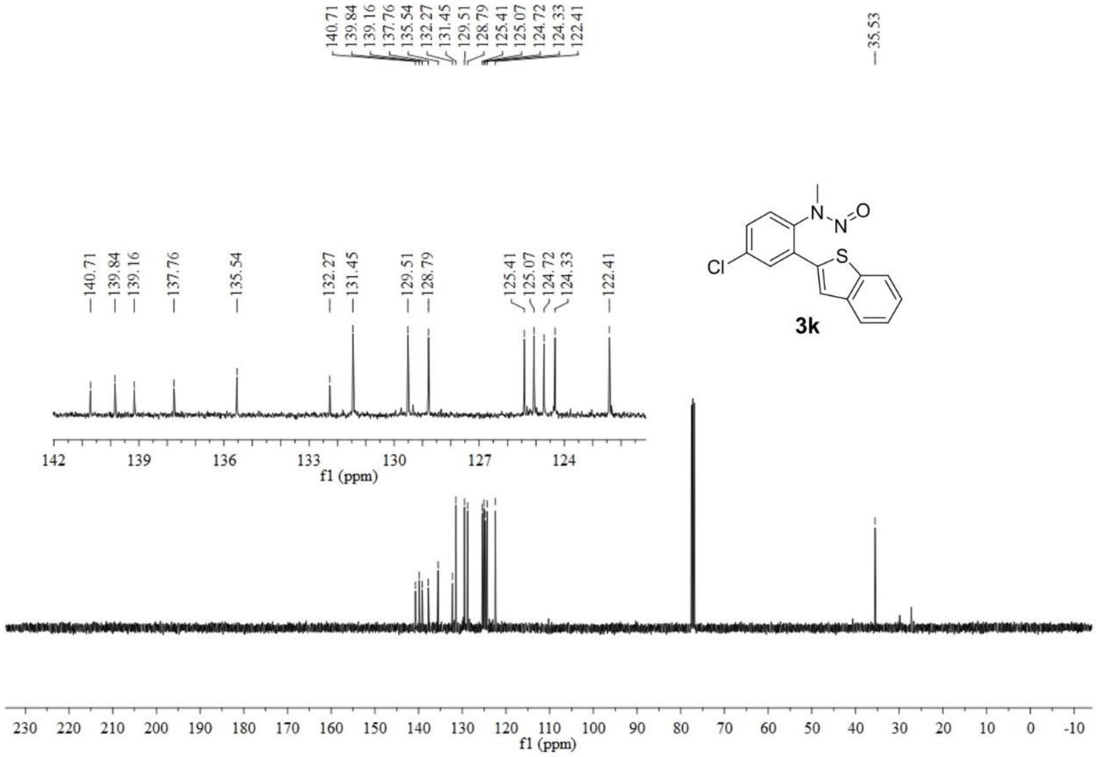
3i


7.988
7.981
7.973
7.967
7.896
7.889
7.880
7.873
7.818
7.810
7.794
7.787
7.699
7.685
7.677
7.663
7.531
7.523
7.511
7.503
7.489
7.481
7.419
7.415
7.410
7.403
7.397
7.392
7.387
4.030
3.205
2.509
2.505
2.500
2.495
2.491
S
N
N
O
F
3j
8.00
7.90
7.80
7.70
7.60
7.50
7.40
f1 (ppm)
1.05
1.09
1.01
2.16
1.04
2.12
0.31
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

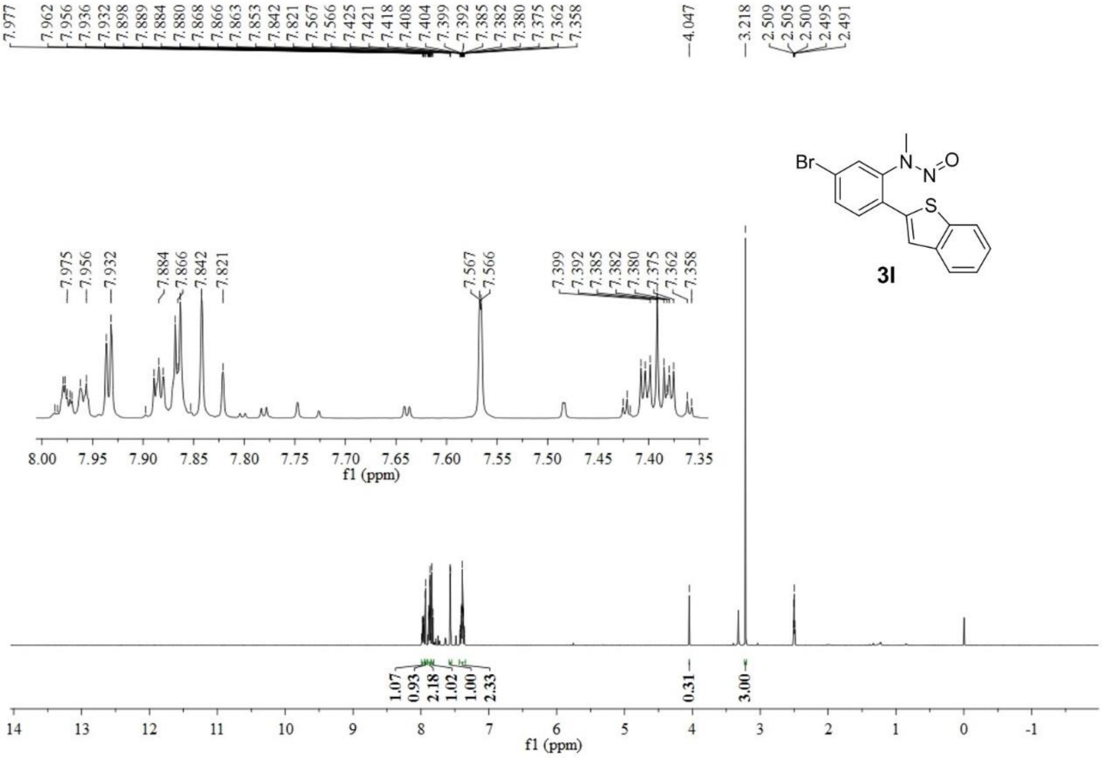

160.81
158.34
142.02
140.04
139.06
130.66
126.85
126.82
125.08
124.72
124.13
122.99
122.96
122.25
118.81
118.64
116.94
116.71
35.21
S
N
N
O
F
3j
142.02
141.98
140.04
139.06
131.29
131.19
130.66
126.85
126.82
125.08
124.72
124.13
122.99
122.96
122.25
118.81
118.64
116.94
116.71
142
140
138
136
134
132
130
128
126
124
122
120
118
116
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

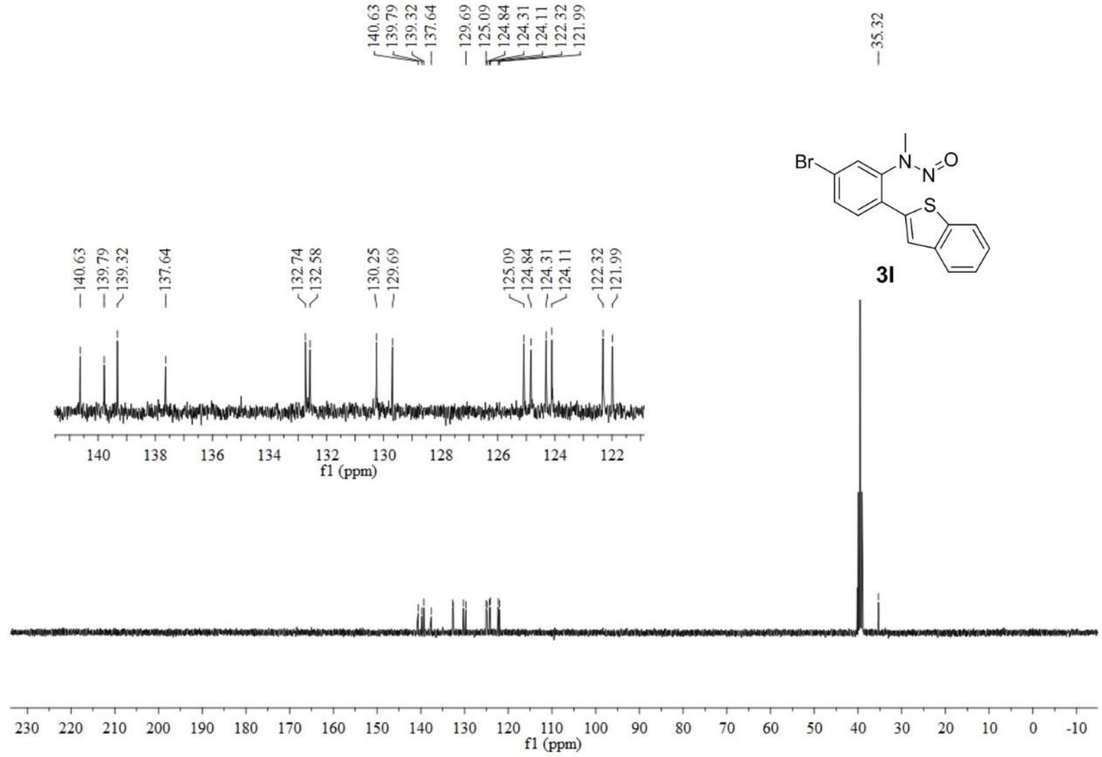

7.824
7.806
7.777
7.760
7.727
7.499
7.478
7.408
7.383
7.371
7.359
7.260
3.890
3.098
Cl
N
N
O
S
7.80
7.70
7.60
7.50
7.40
7.30
f1 (ppm)
1.00
1.12
0.86
1.06
3.10
1.10
0.23
3.08
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

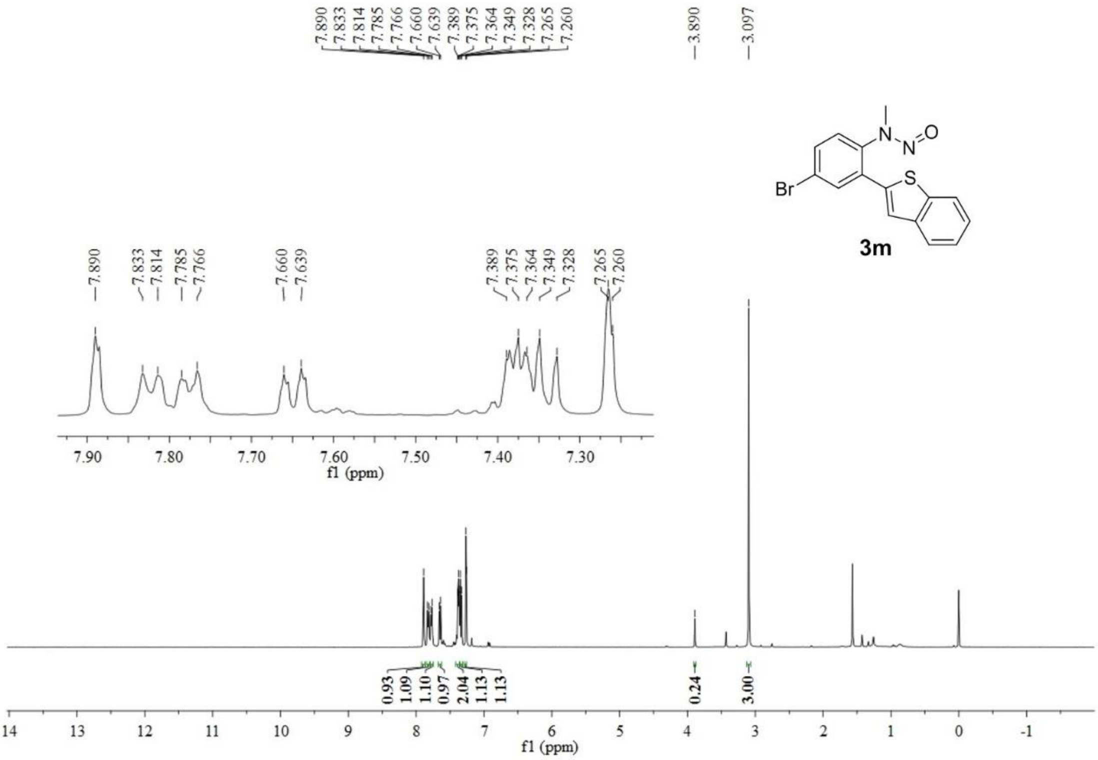
3k

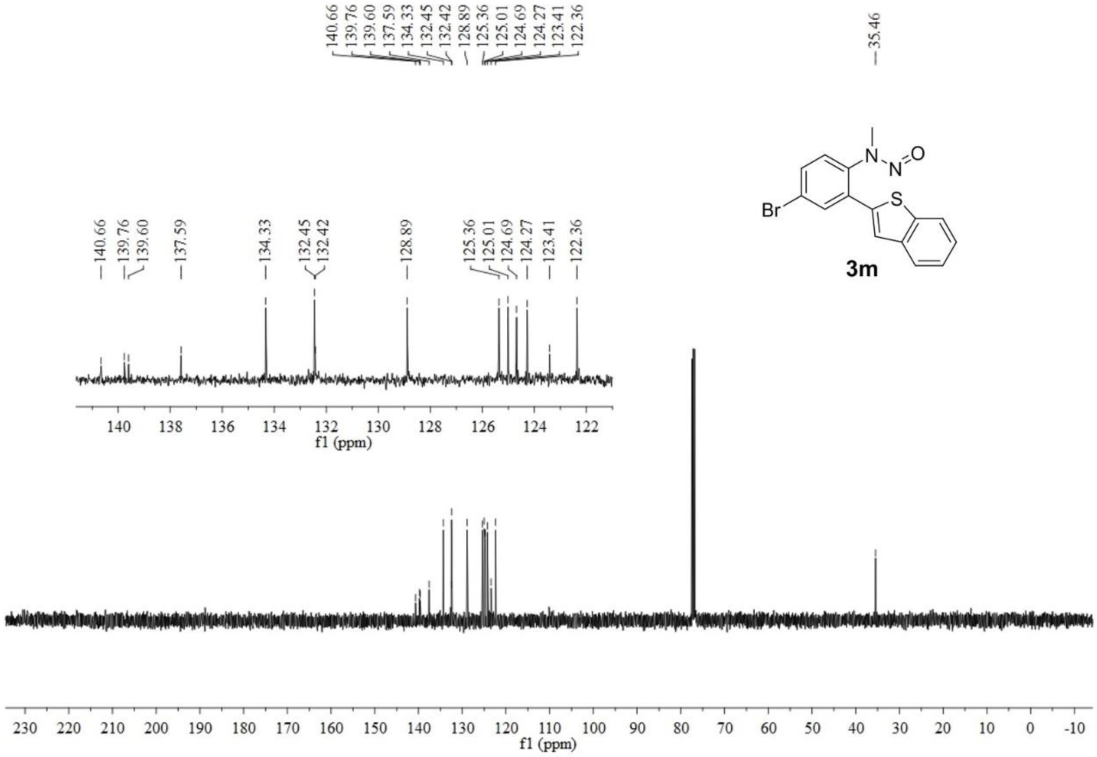

140.71
139.84
139.16
137.76
135.54
132.27
131.45
129.51
128.79
125.41
125.07
124.72
124.33
122.41
35.53
Cl
N
N
O
S
142
139
136
133
130
127
124
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

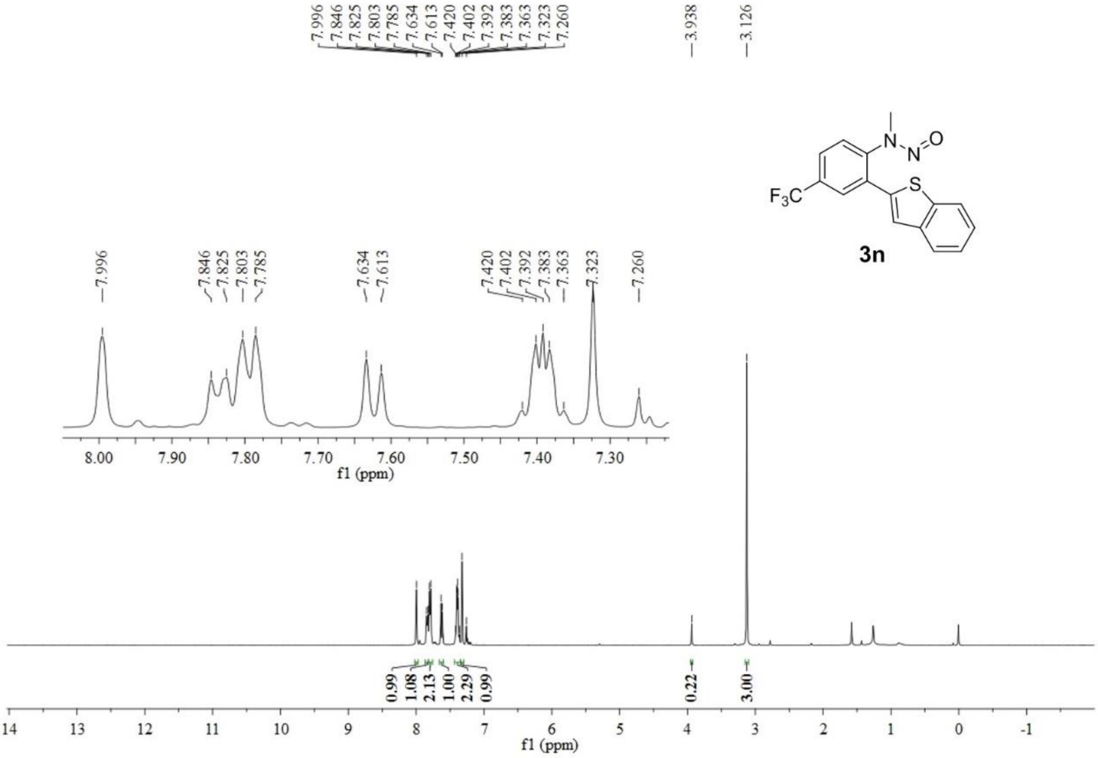
3k

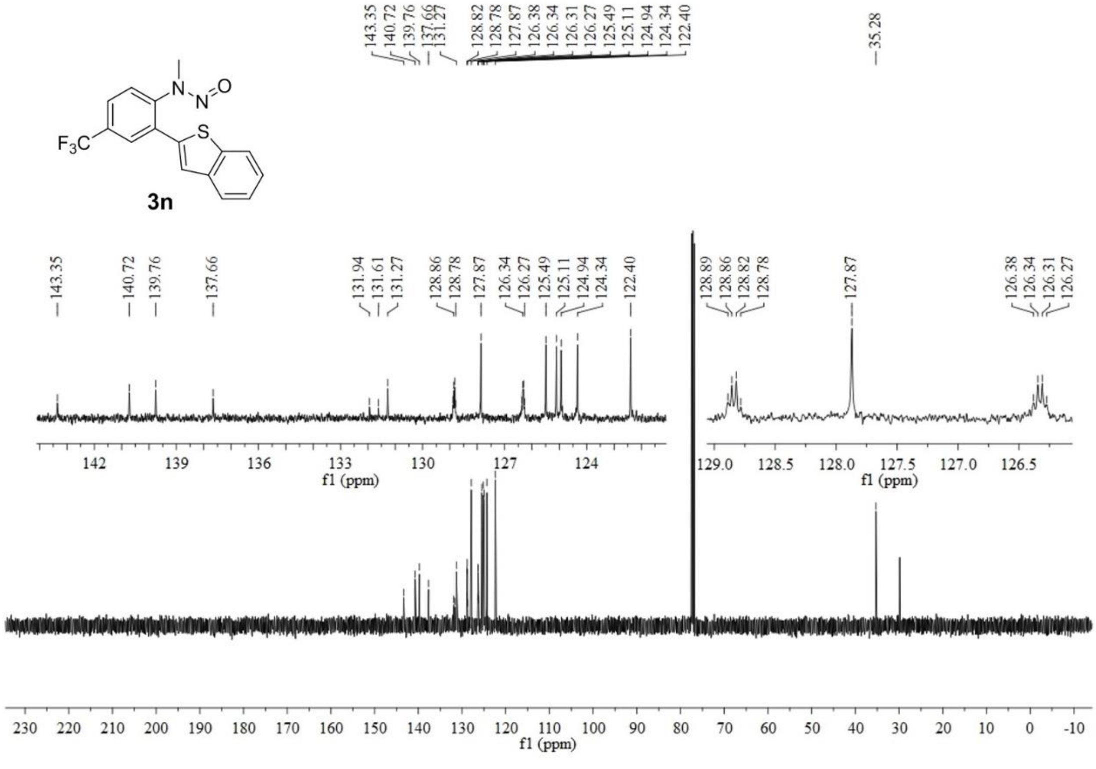

7.977
7.962
7.956
7.936
7.932
7.898
7.889
7.884
7.880
7.868
7.866
7.863
7.853
7.842
7.821
7.567
7.566
7.425
7.421
7.418
7.408
7.404
7.399
7.392
7.385
7.382
7.380
7.375
7.362
7.358
4.047
3.218
2.509
2.505
2.500
2.495
2.491
Br
N
N
O
S
3l
7.975
7.956
7.932
7.884
7.866
7.842
7.821
7.567
7.566
7.399
7.392
7.385
7.382
7.380
7.375
7.362
7.358
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
f1 (ppm)
1.07
0.93
2.18
1.02
1.00
2.33
0.31
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

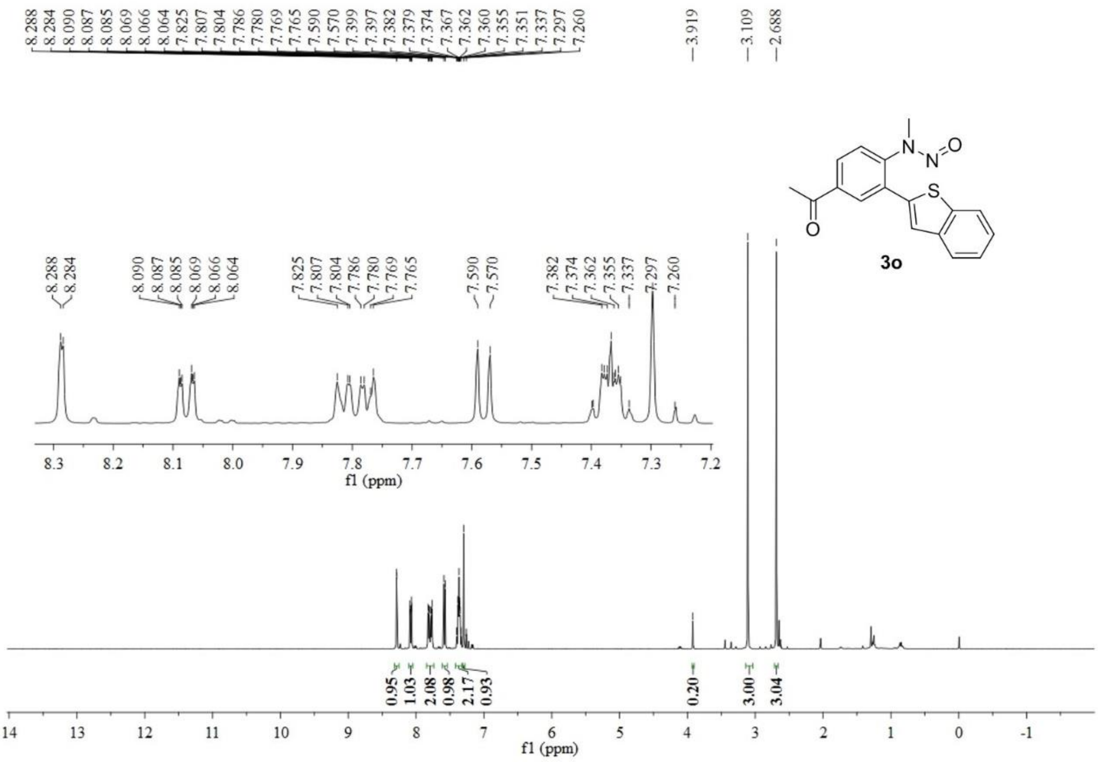

140.63
139.79
139.32
137.64
129.69
125.09
124.84
124.31
124.11
122.32
121.99
35.32
Br
N
N
O
S
3l
140.63
139.79
139.32
137.64
132.74
132.58
130.25
129.69
125.09
124.84
124.31
124.11
122.32
121.99
140
138
136
134
132
130
128
126
124
122
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

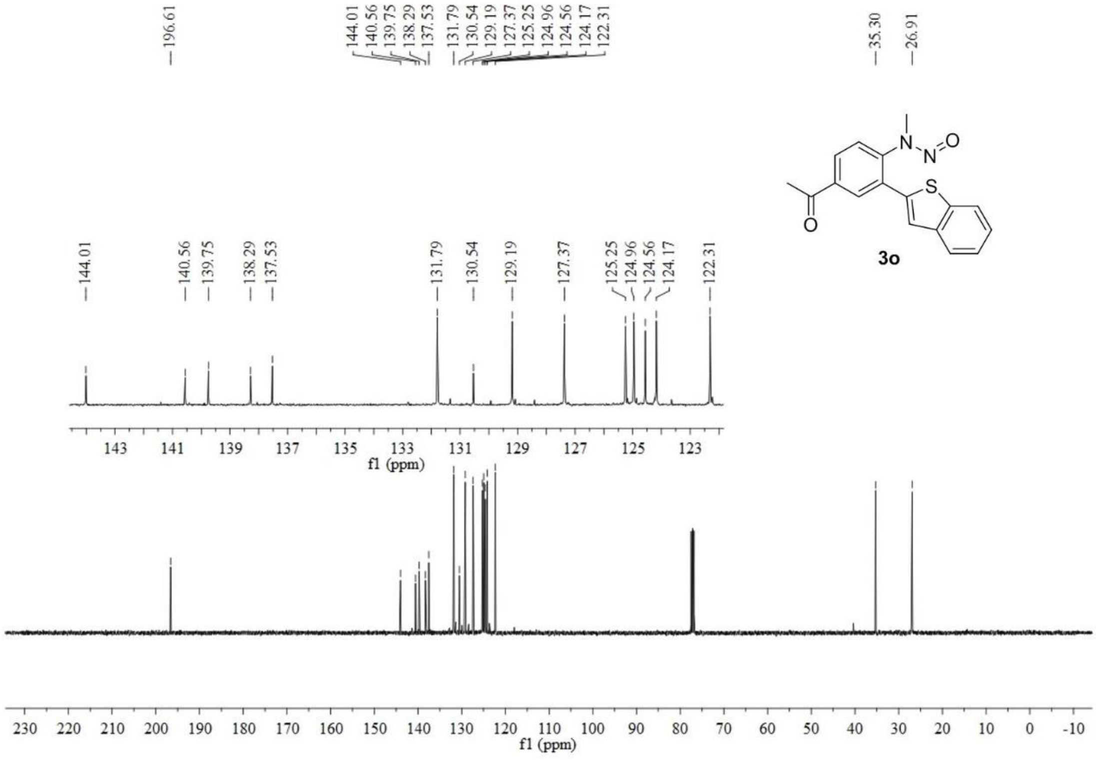

7.890
7.833
7.814
7.785
7.766
7.660
7.639
7.389
7.375
7.364
7.349
7.328
7.265
7.260
3.890
3.097
Br
N
N
O
S
3m
7.90 7.80 7.70 7.60 7.50 7.40 7.30
f1 (ppm)
0.93
1.09
1.10
0.97
2.04
1.13
1.13
0.24
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

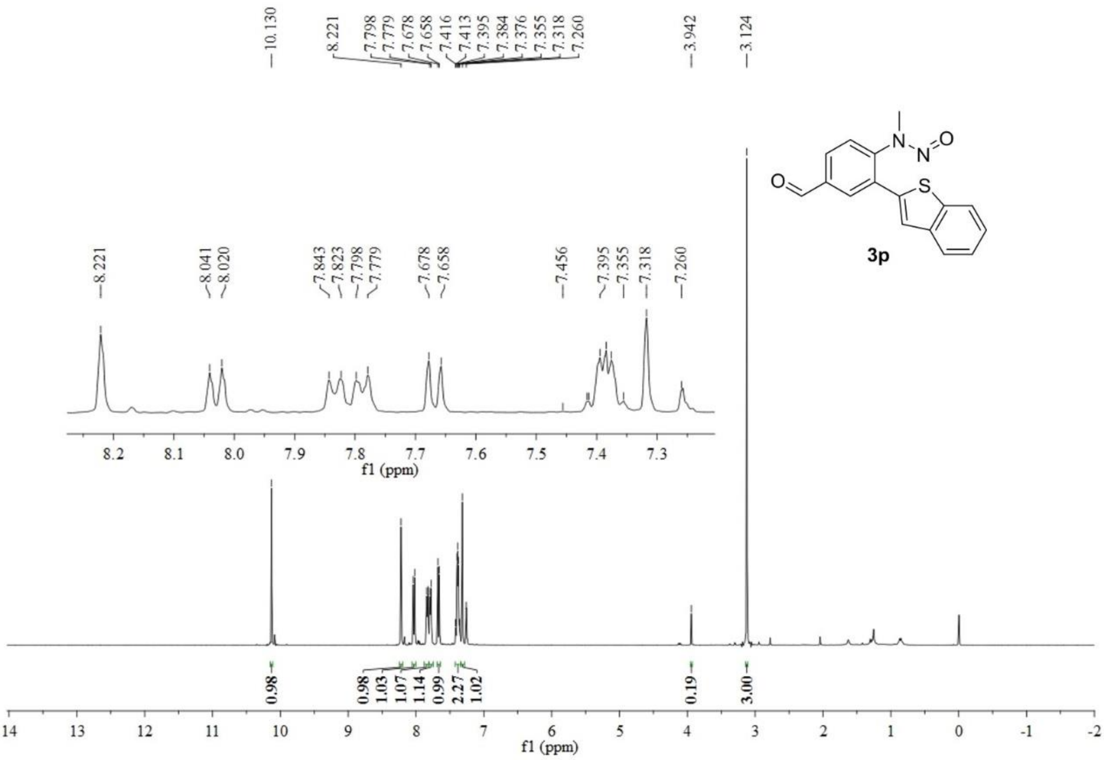

140.66
139.76
139.60
137.59
134.33
132.45
132.42
128.89
125.36
125.01
124.69
124.27
123.41
122.36
35.46
Br
N
N
O
S
3m
140 138 136 134 132 130 128 126 124 122
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

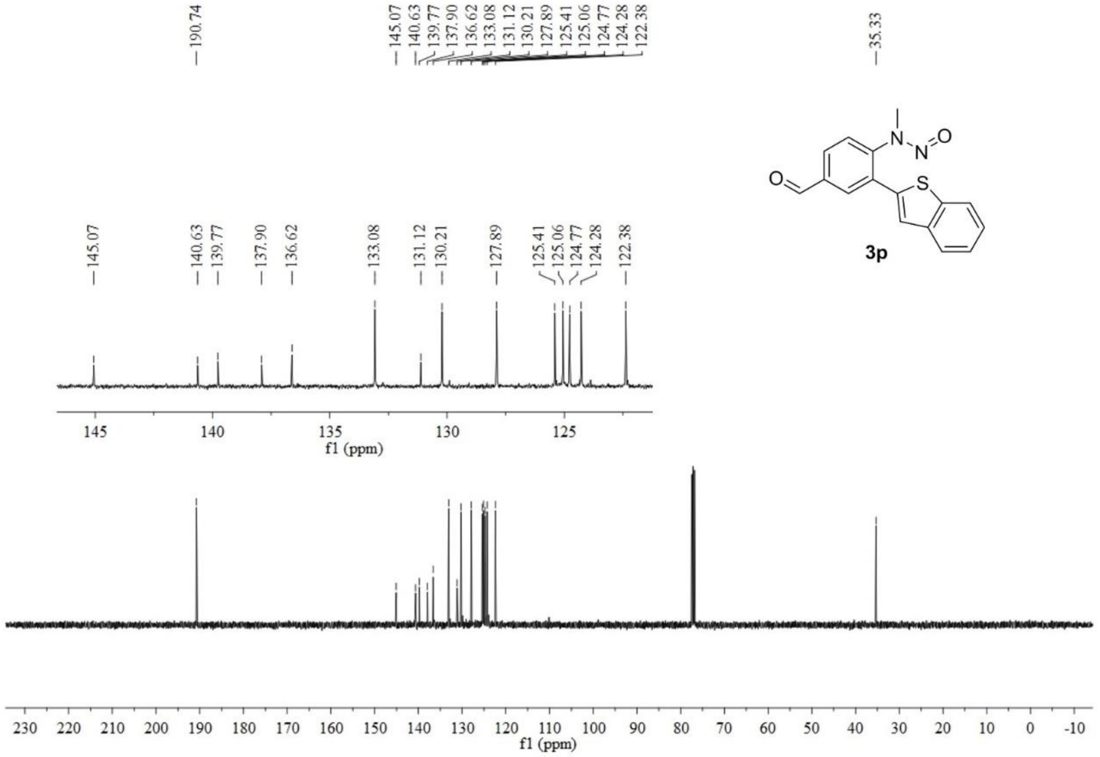

7.996
7.846
7.825
7.803
7.785
7.634
7.613
7.420
7.402
7.392
7.383
7.363
7.323
7.260
3.938
3.126
F3C
N
N
O
S
3n
8.00 7.90 7.80 7.70 7.60 7.50 7.40 7.30
f1 (ppm)
0.99
1.08
2.13
1.00
2.29
0.99
0.22
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

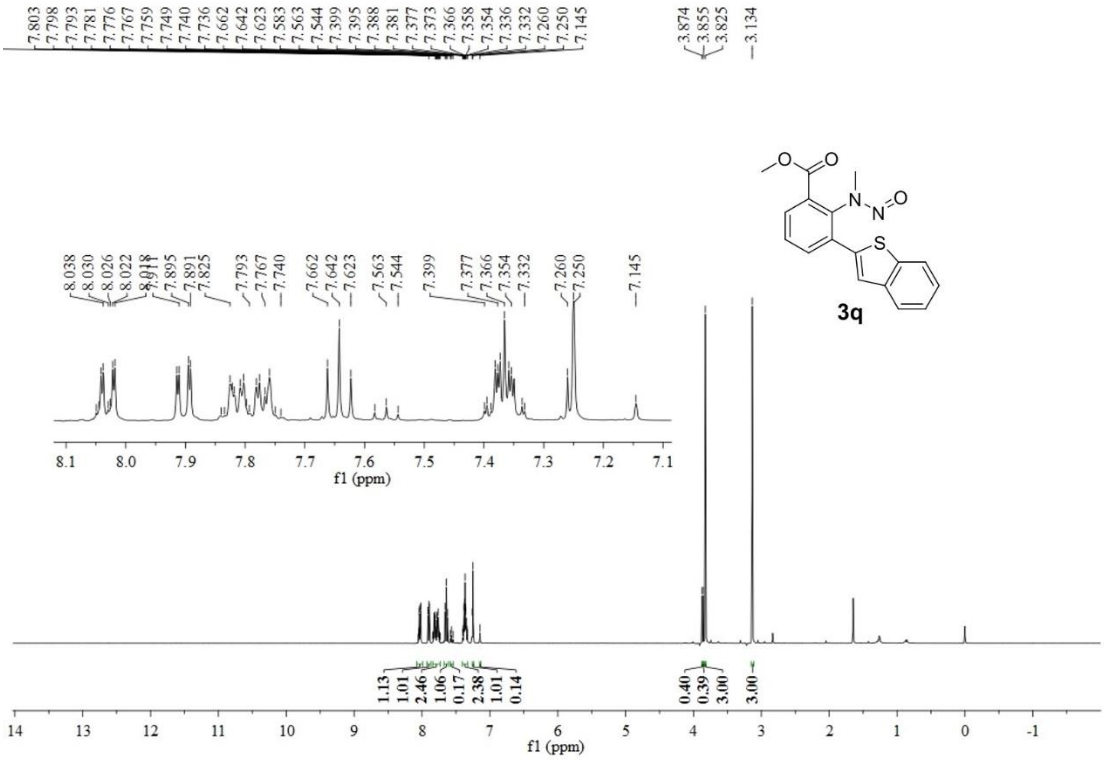

143.35
140.72
139.76
137.66
131.94
131.61
131.27
128.89
128.86
128.82
128.78
127.87
126.38
126.34
126.31
126.27
125.49
125.11
124.94
124.34
122.40
35.28
F3C
N
N
O
S
3n
142 139 136 133 130 127 124
f1 (ppm)
129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.288
8.284
8.090
8.087
8.085
8.069
8.066
8.064
7.825
7.807
7.804
7.786
7.780
7.769
7.765
7.590
7.570
7.399
7.397
7.382
7.379
7.374
7.367
7.362
7.360
7.355
7.351
7.337
7.297
7.260
3.919
3.109
2.688
3o
0.95
1.03
2.08
0.98
2.17
0.93
0.20
3.00
3.04
f1 (ppm)

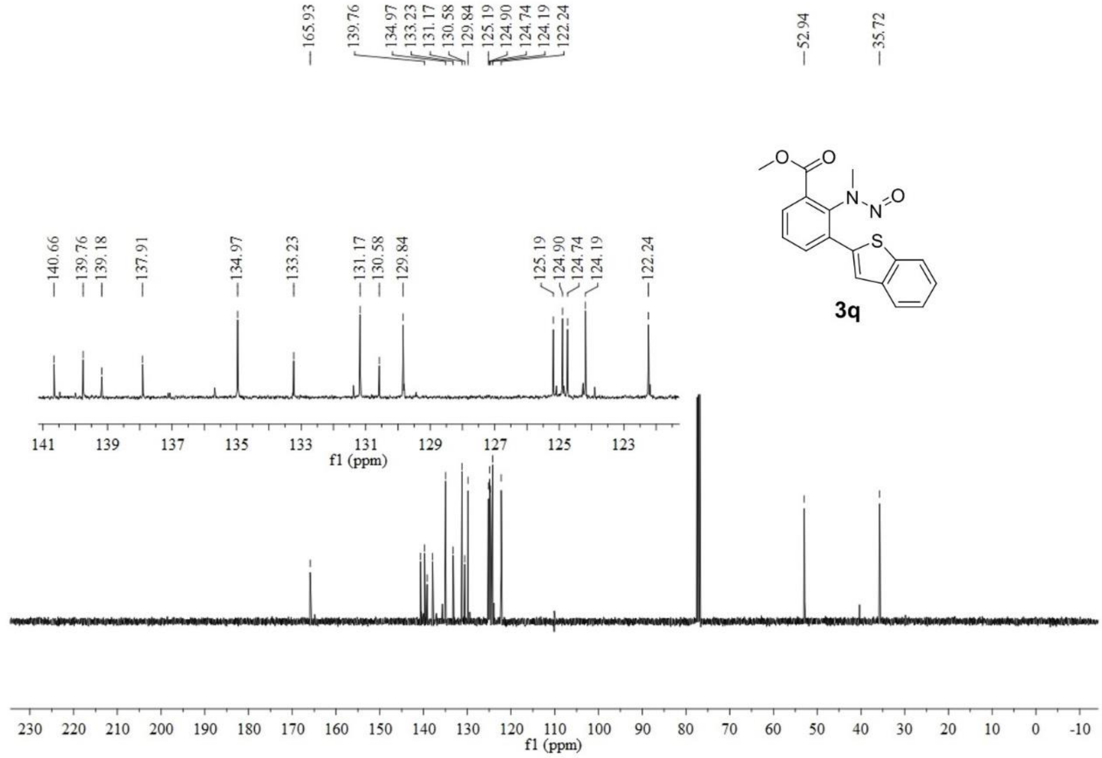

196.61
144.01
140.56
139.75
138.29
137.53
131.79
130.54
129.19
127.37
125.25
124.96
124.56
124.17
122.31
35.30
26.91
3o
f1 (ppm)


10.130
8.221
7.798
7.779
7.678
7.658
7.416
7.413
7.395
7.384
7.376
7.355
7.318
7.260
3.942
3.124
8.221
8.041
8.020
7.843
7.823
7.798
7.779
7.678
7.658
7.456
7.395
7.355
7.318
7.260
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
0.98
0.98
1.03
1.07
1.14
0.99
2.27
1.02
0.19
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
O
N
N
O
S
3p

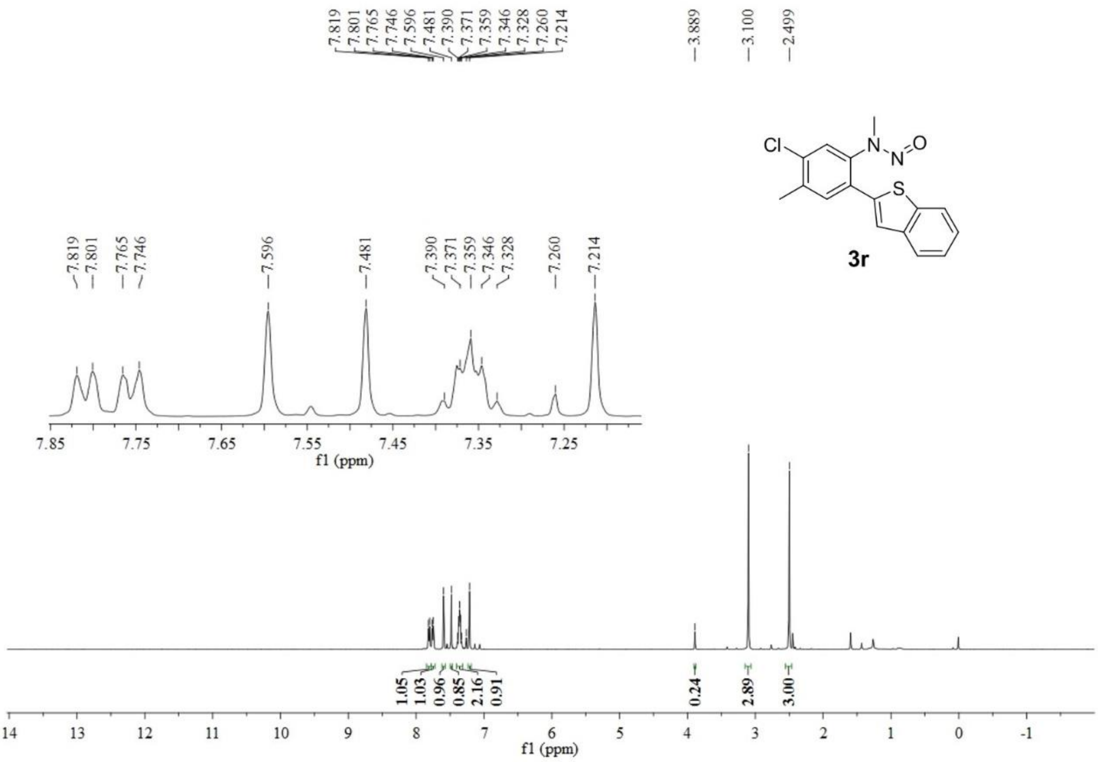

190.74
145.07
140.63
139.77
137.90
136.62
133.08
131.12
130.21
127.89
125.41
125.06
124.77
124.28
122.38
35.33
145.07
140.63
139.77
137.90
136.62
133.08
131.12
130.21
127.89
125.41
125.06
124.77
124.28
122.38
145
140
135
130
125
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
O
N
N
O
S
3p

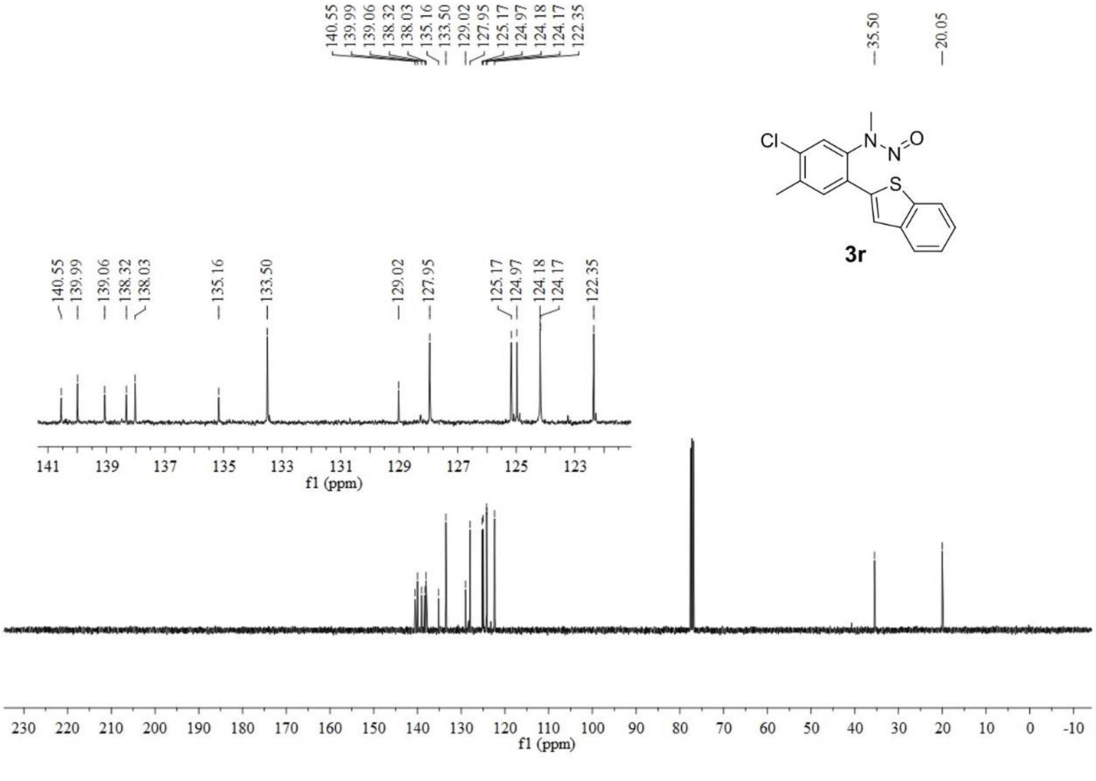

7.803
7.798
7.793
7.781
7.776
7.767
7.759
7.749
7.740
7.736
7.662
7.642
7.623
7.583
7.563
7.544
7.399
7.395
7.388
7.381
7.377
7.373
7.366
7.358
7.354
7.336
7.332
7.260
7.250
7.145
3.874
3.855
3.825
3.134
O
N
N
O
S
8.038
8.030
8.026
8.022
8.018
7.911
7.895
7.891
7.825
7.793
7.767
7.740
7.662
7.642
7.623
7.563
7.544
7.399
7.377
7.366
7.354
7.332
7.260
7.250
7.145
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
1.13
1.01
2.46
1.06
0.17
2.38
1.01
0.14
0.40
0.39
3.00
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

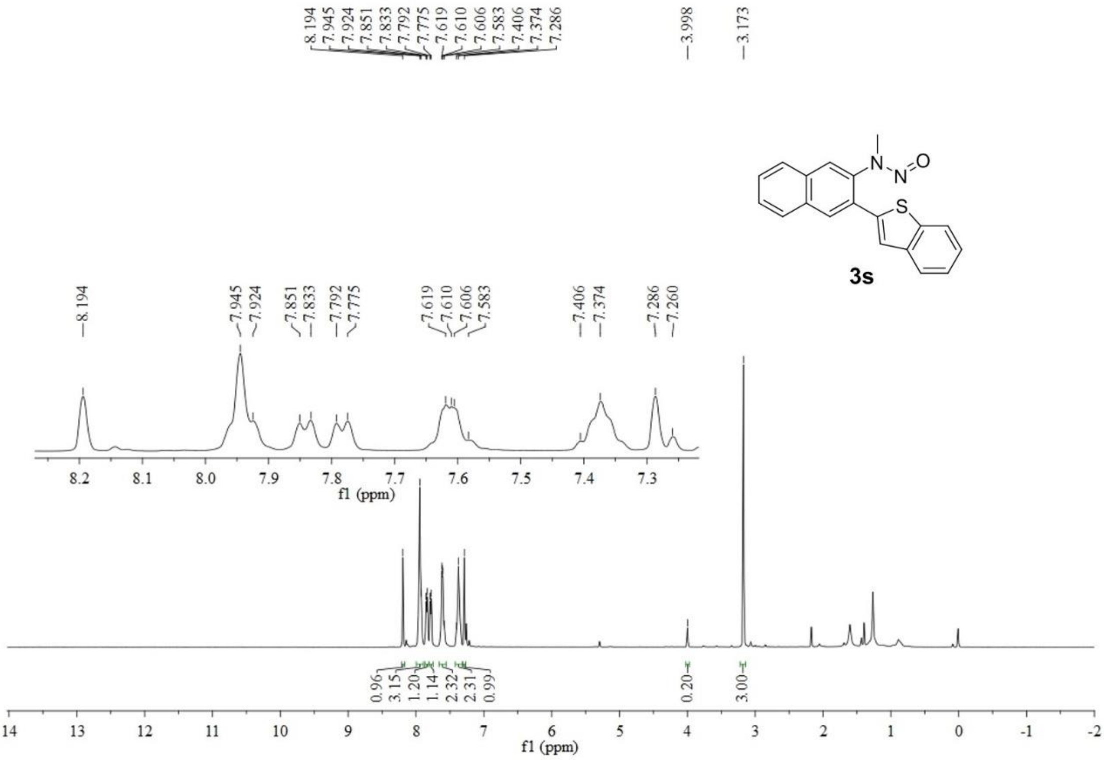
3q

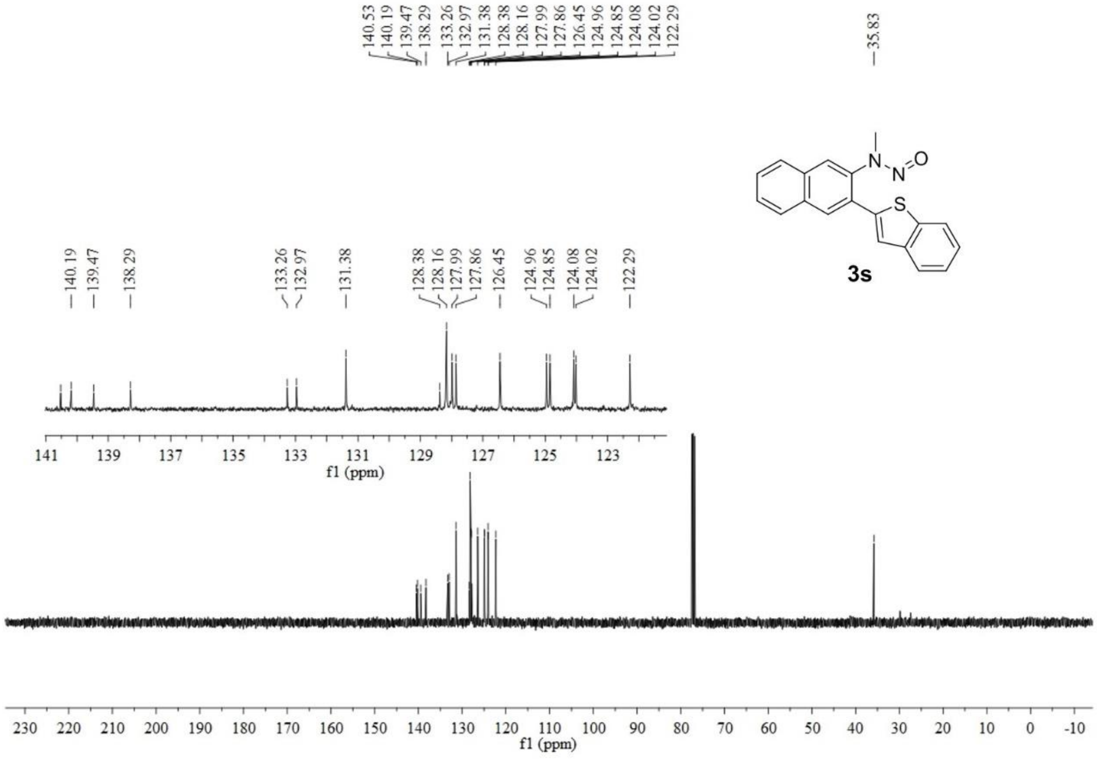

165.93
139.76
134.97
133.23
131.17
130.58
129.84
125.19
124.90
124.74
124.19
122.24
52.94
35.72
O
N
N
O
S
140.66
139.76
139.18
137.91
134.97
133.23
131.17
130.58
129.84
125.19
124.90
124.74
124.19
122.24
141 139 137 135 133 131 129 127 125 123
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

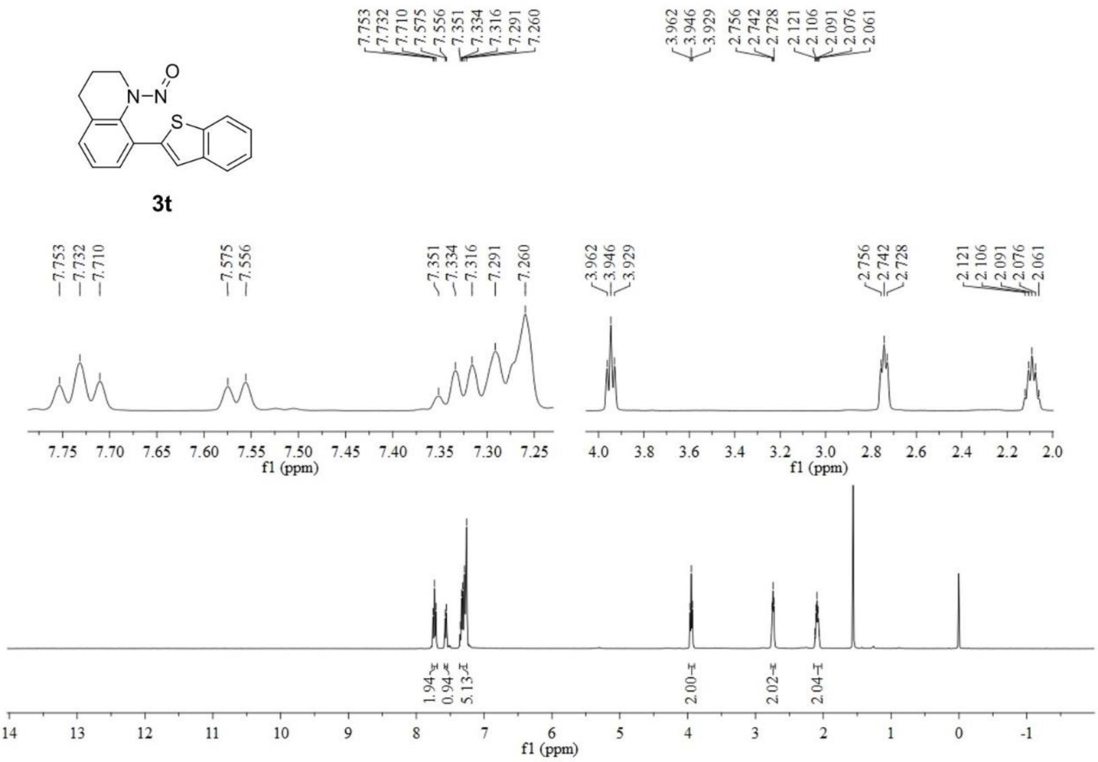
3q


7.819
7.801
7.765
7.746
7.596
7.481
7.390
7.371
7.359
7.346
7.328
7.260
7.214
3.889
3.100
2.499
Cl
N
N
O
S
3r
7.85 7.75 7.65 7.55 7.45 7.35 7.25
f1 (ppm)
1.05
1.03
0.96
0.85
2.16
0.91
0.24
2.89
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

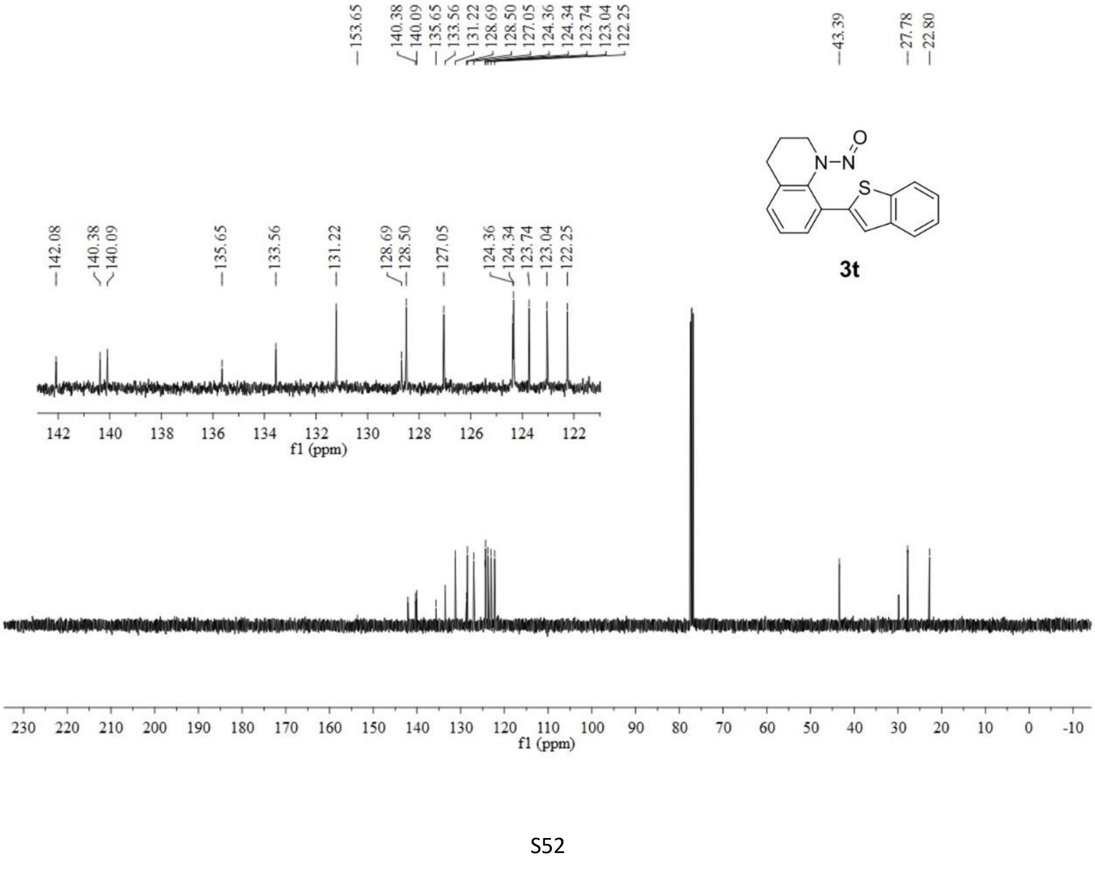

140.55
139.99
139.06
138.32
138.03
135.16
133.50
129.02
127.95
125.17
124.97
124.18
124.17
122.35
35.50
20.05
Cl
N
N
O
S
3r
141 139 137 135 133 131 129 127 125 123
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3s
8.194
7.945
7.924
7.851
7.833
7.792
7.775
7.619
7.610
7.606
7.583
7.406
7.374
7.286
3.998
3.173
N
N
O
S
8.194
7.945
7.924
7.851
7.833
7.792
7.775
7.619
7.610
7.606
7.583
7.406
7.374
7.286
7.260
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
0.96
3.15
1.20
1.14
2.32
2.31
0.99
0.20
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

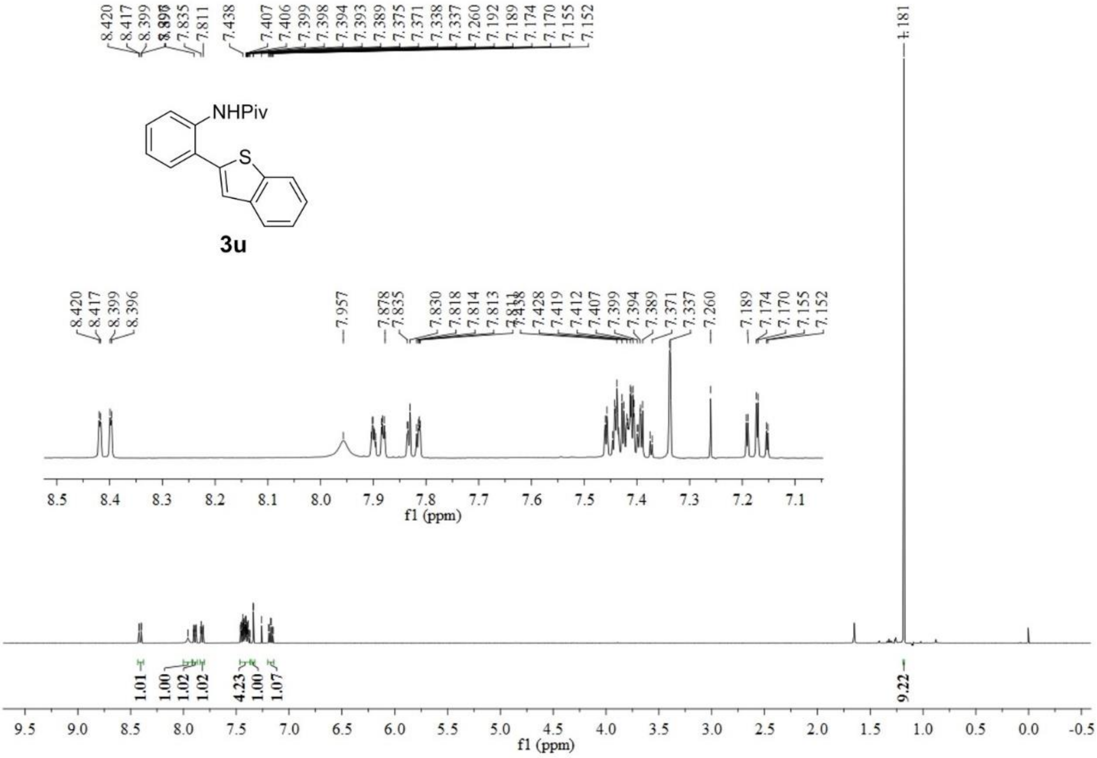

3s
140.53
140.19
139.47
138.29
133.26
132.97
131.38
128.38
128.16
127.99
127.86
126.45
124.96
124.85
124.08
124.02
122.29
35.83
N
N
O
S
140.19
139.47
138.29
133.26
132.97
131.38
128.38
128.16
127.99
127.86
126.45
124.96
124.85
124.08
124.02
122.29
141
139
137
135
133
131
129
127
125
123
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

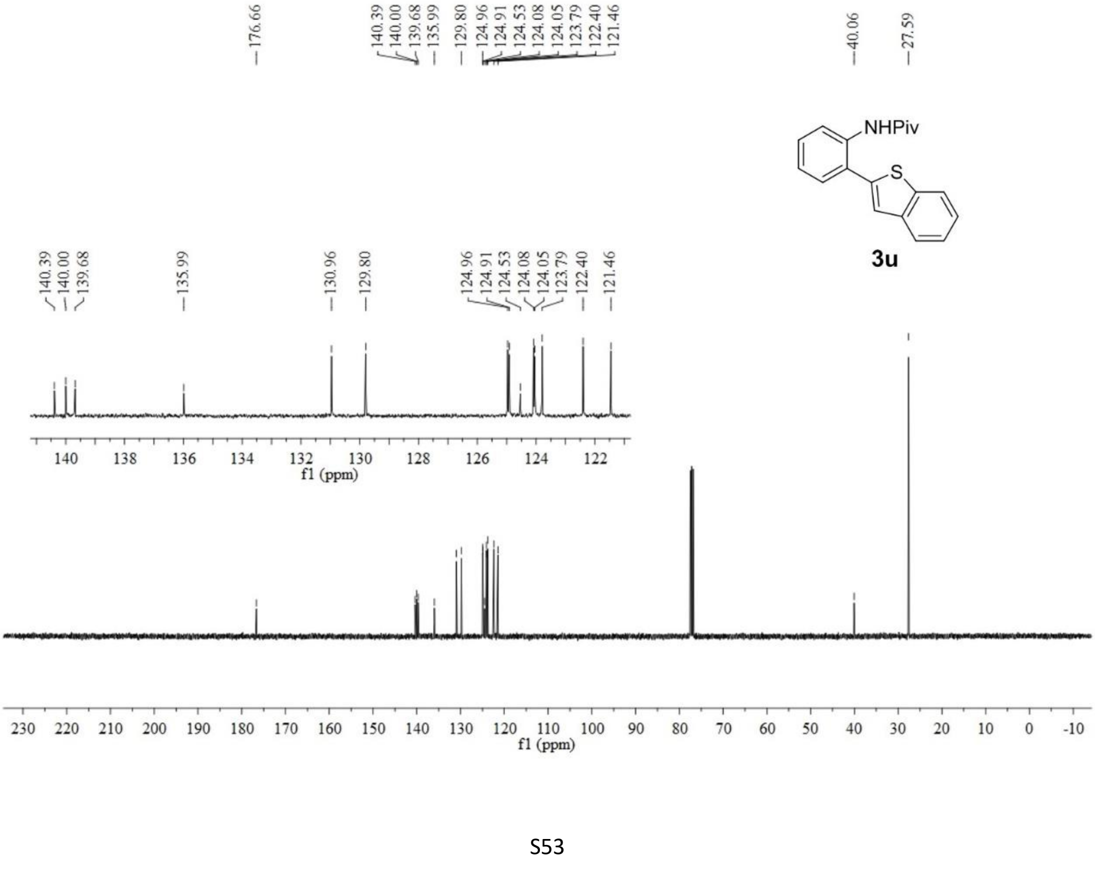


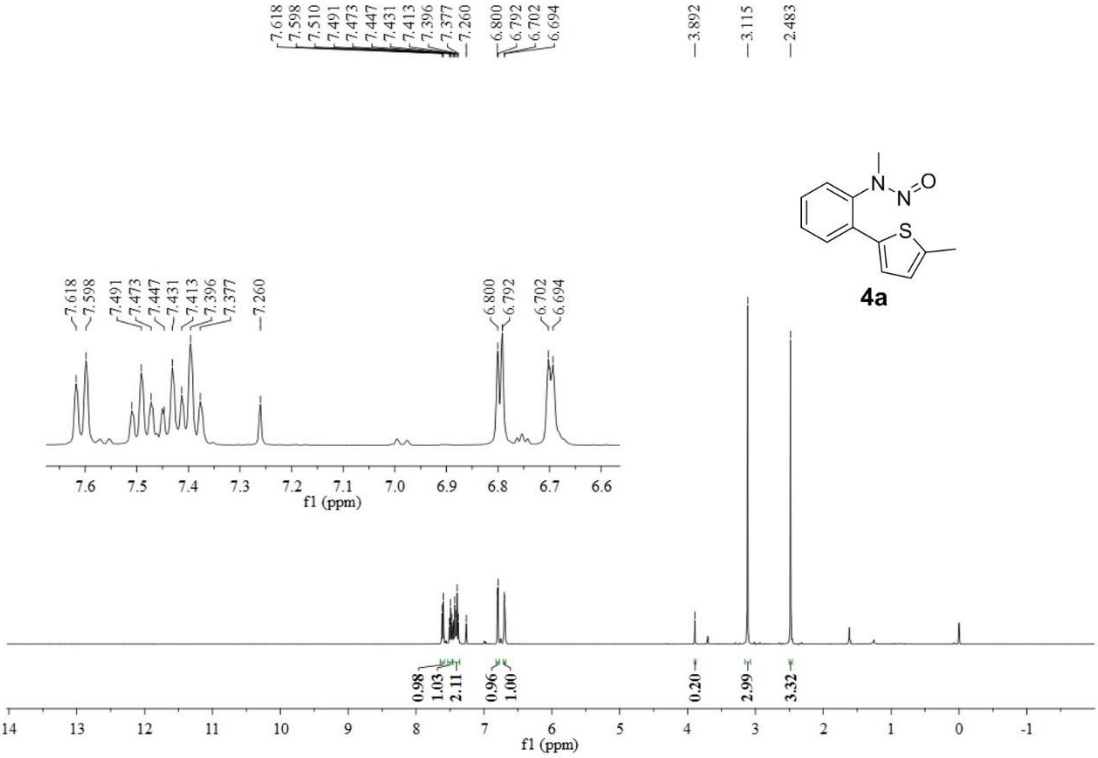
7.753
7.732
7.710
7.575
7.556
7.351
7.334
7.316
7.291
7.260
3.962
3.946
3.929
2.756
2.742
2.728
2.121
2.106
2.091
2.076
2.061
S
N
N
O
3t
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)
1.94
0.94
5.13
2.00
2.02
2.04
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)



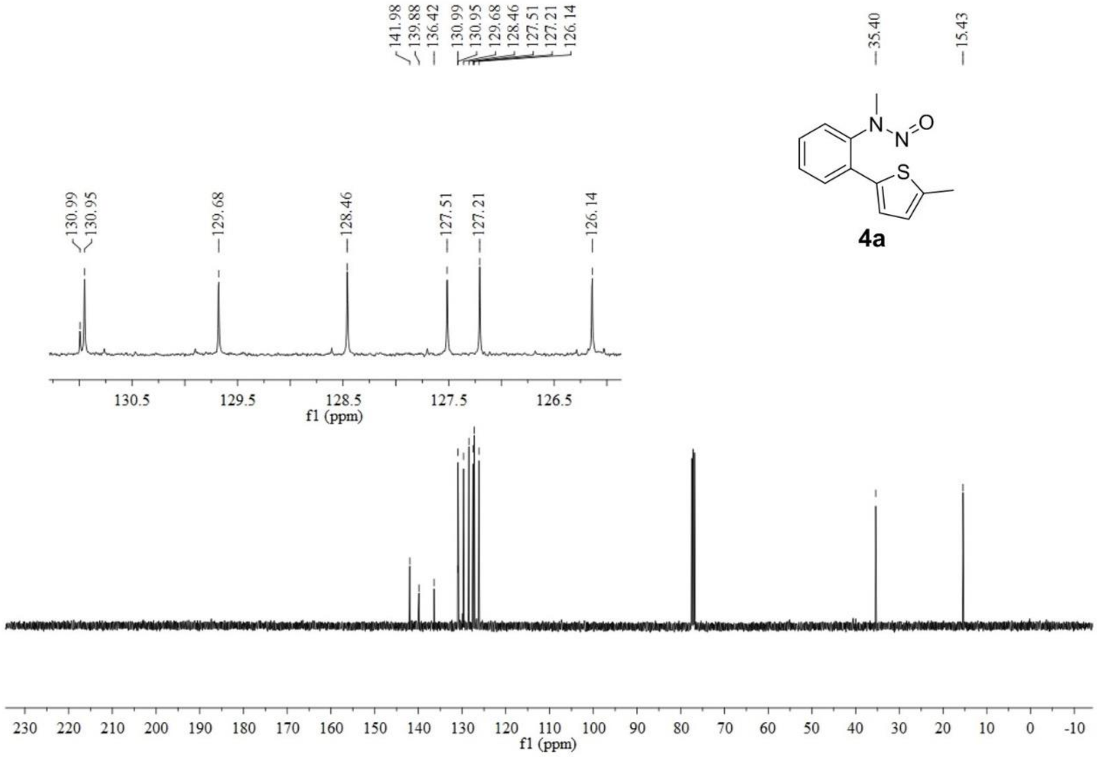
153.65
140.38
140.09
135.65
133.56
131.22
128.69
128.50
127.05
124.36
124.34
123.74
123.04
122.25
43.39
27.78
22.80
142.08
S
N
N
O
3t
142 140 138 136 134 132 130 128 126 124 122
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.420
8.417
8.399
8.396
7.835
7.811
7.438
7.407
7.406
7.399
7.398
7.394
7.393
7.389
7.375
7.371
7.338
7.337
7.260
7.192
7.189
7.174
7.170
7.155
7.152
1.181
NHPiv
S
3u
8.420
8.417
8.399
8.396
7.957
7.878
7.835
7.830
7.818
7.814
7.813
7.811
7.438
7.428
7.419
7.412
7.407
7.399
7.394
7.389
7.371
7.337
7.260
7.189
7.174
7.170
7.155
7.152
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
1.01
1.00
1.02
1.02
4.23
1.00
1.07
9.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

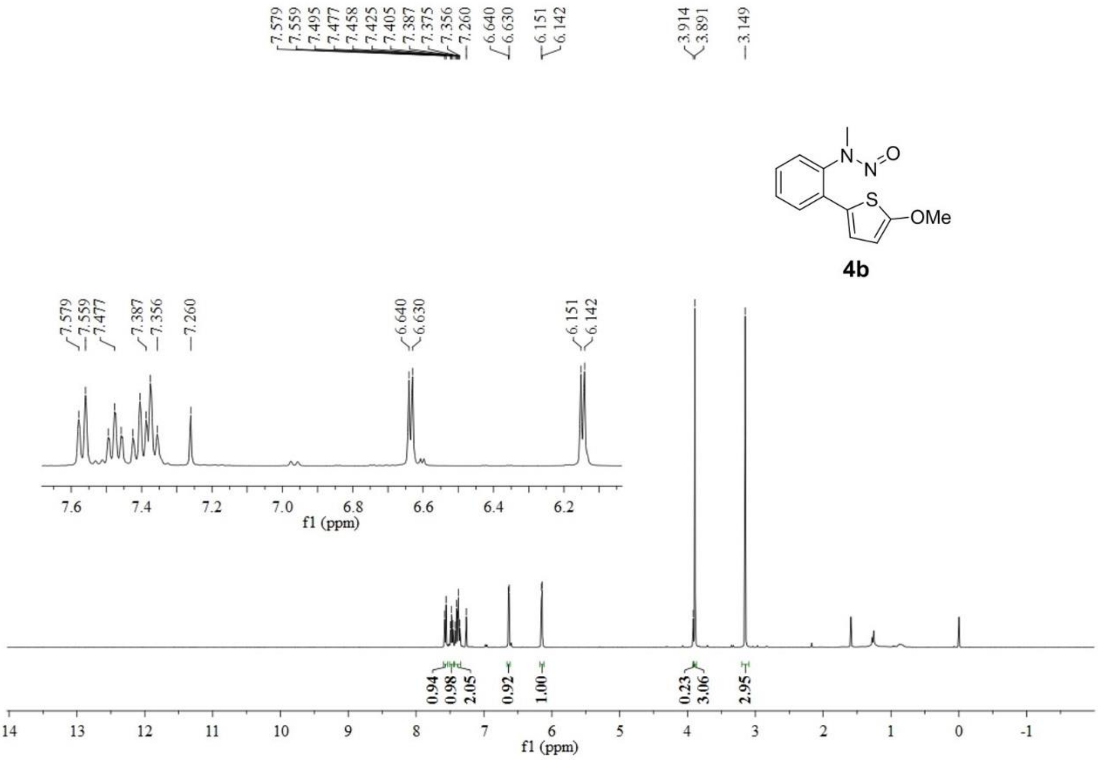

176.66
140.39
140.00
139.68
135.99
129.80
124.96
124.91
124.53
124.08
124.05
123.79
122.40
121.46
40.06
27.59
NHPiv
S
3u
140.39
140.00
139.68
135.99
130.96
129.80
124.96
124.91
124.53
124.08
124.05
123.79
122.40
121.46
140
138
136
134
132
130
128
126
124
122
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

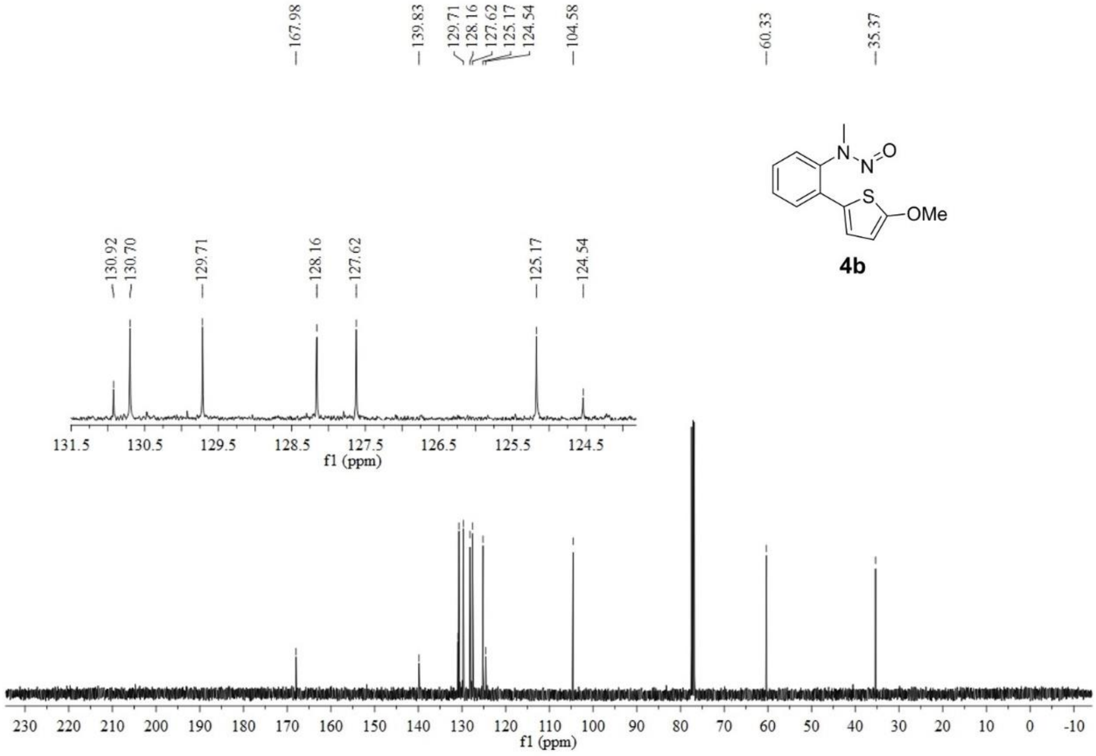

7.618
7.598
7.510
7.491
7.473
7.447
7.431
7.413
7.396
7.377
7.260
6.800
6.792
6.702
6.694
3.892
3.115
2.483
0.98
1.03
2.11
0.96
1.00
0.20
2.99
3.32
f1 (ppm)
N
N
O
S

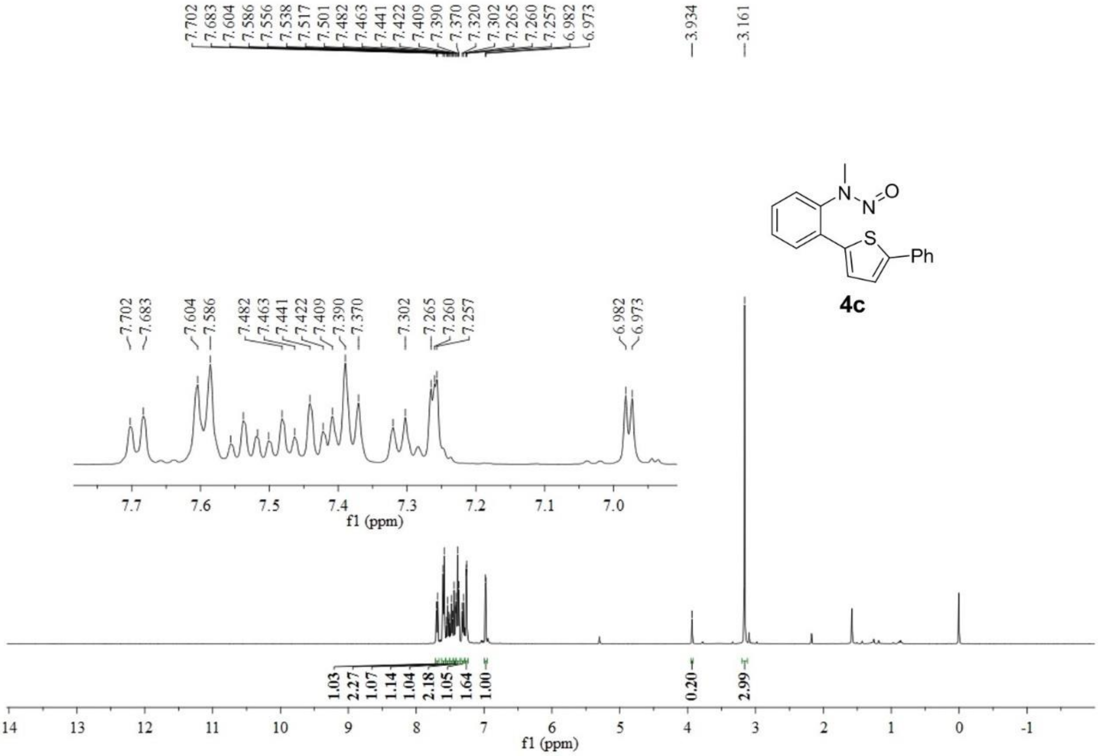
4a

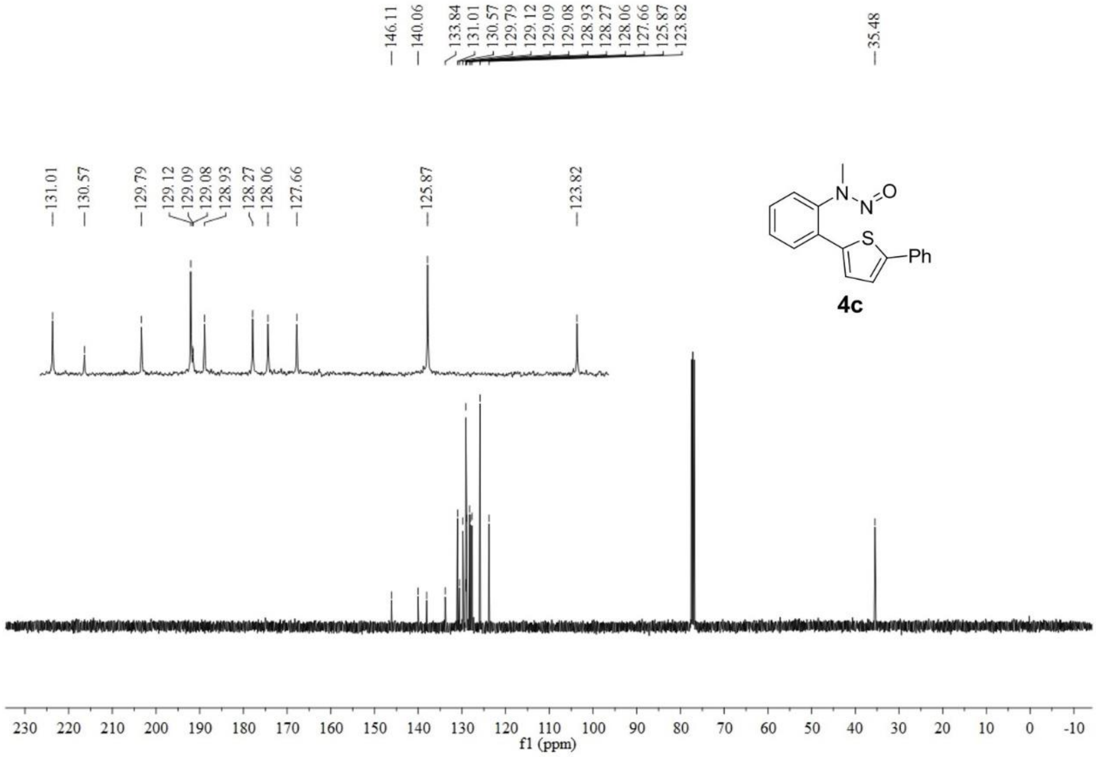

141.98
139.88
136.42
130.99
130.95
129.68
128.46
127.51
127.21
126.14
35.40
15.43
f1 (ppm)
N
N
O
S

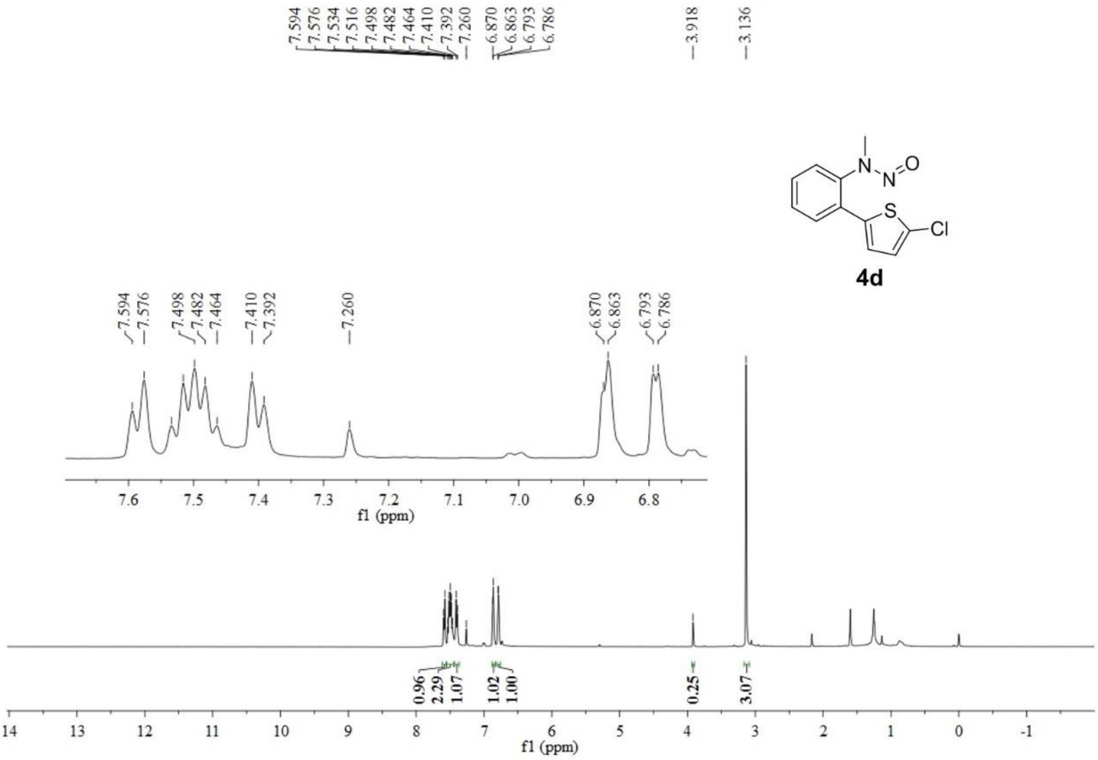
4a

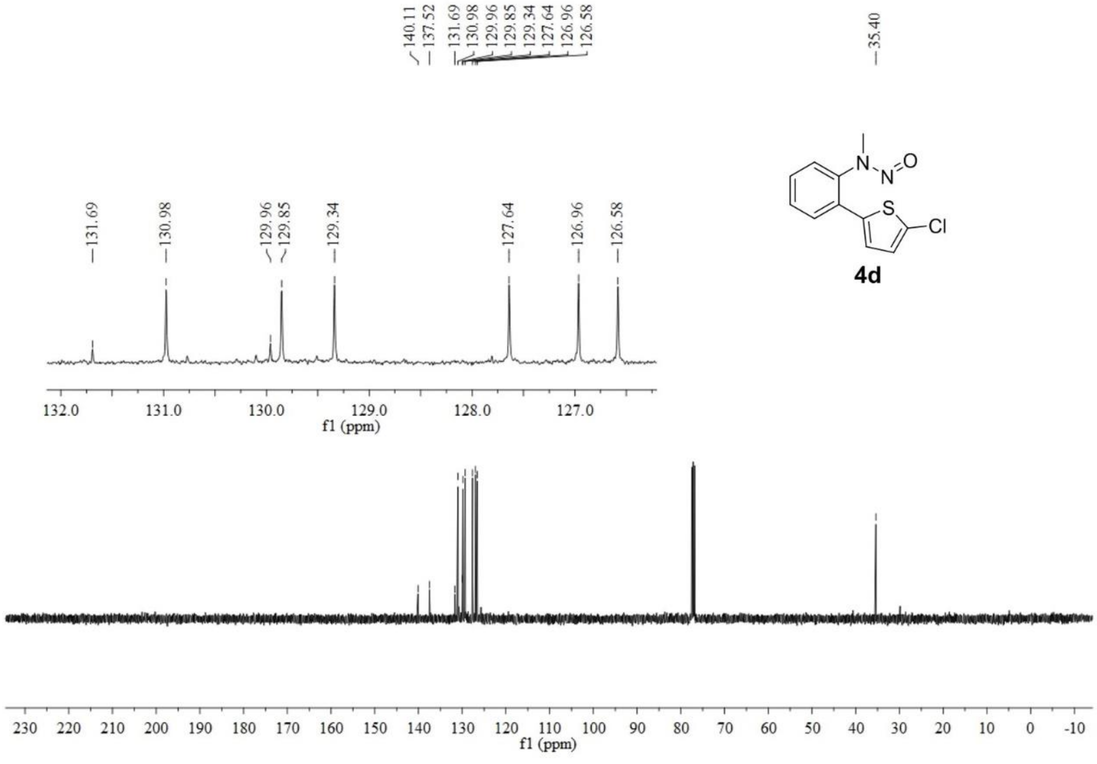

7.579
7.559
7.495
7.477
7.458
7.425
7.405
7.387
7.375
7.356
7.260
6.640
6.630
6.151
6.142
3.914
3.891
3.149
N
N
O
S
OMe
4b
0.94
0.98
2.05
0.92
1.00
0.23
3.06
2.95
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2
f1 (ppm)

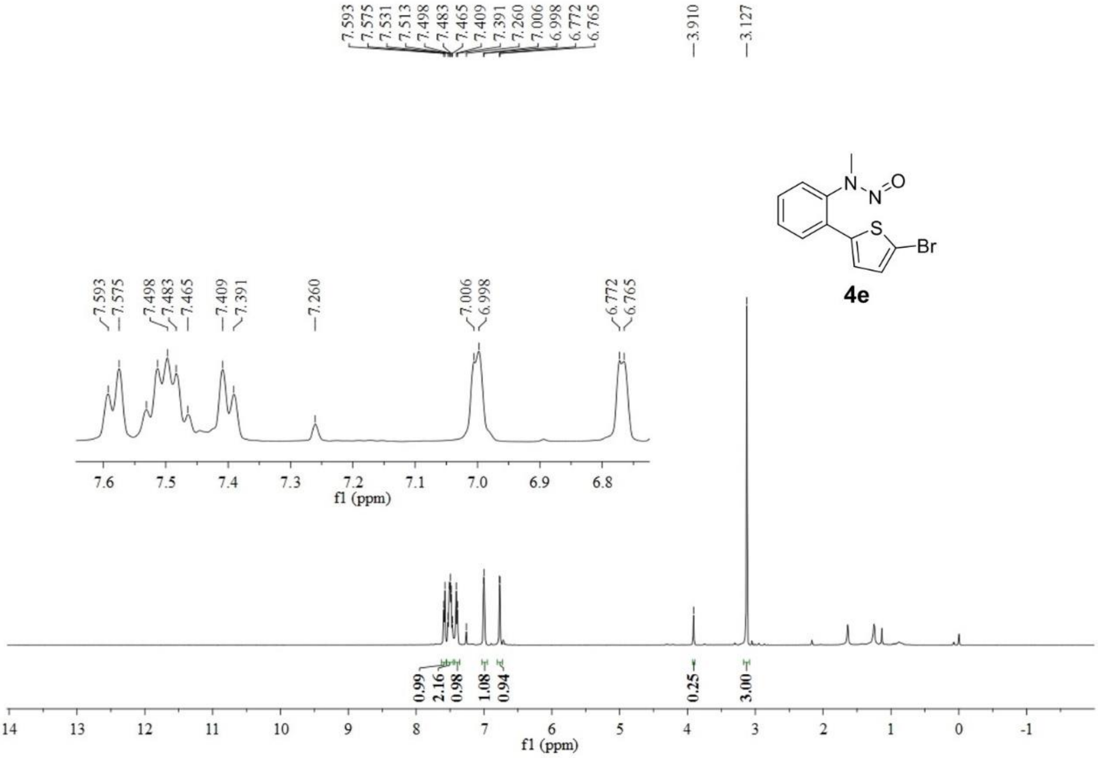

167.98
139.83
129.71
128.16
127.62
125.17
124.54
104.58
60.33
35.37
N
N
O
S
OMe
4b
130.92
130.70
129.71
128.16
127.62
125.17
124.54
131.5 130.5 129.5 128.5 127.5 126.5 125.5 124.5
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.702
7.683
7.604
7.586
7.556
7.538
7.517
7.501
7.482
7.463
7.441
7.422
7.409
7.390
7.370
7.320
7.302
7.265
7.260
7.257
6.982
6.973
3.934
3.161
N
N
O
S
Ph
4c
1.03
2.27
1.07
1.14
1.04
2.18
1.05
1.64
1.00
0.20
2.99
f1 (ppm)

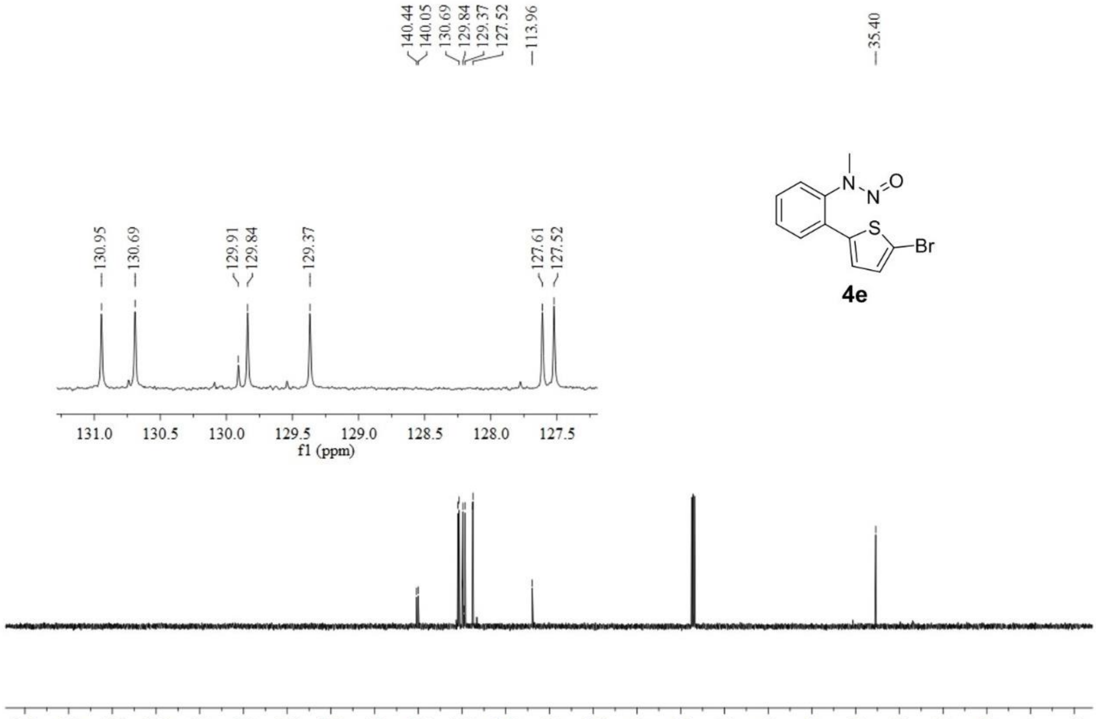

146.11
140.06
133.84
131.01
130.57
129.79
129.12
129.09
129.08
128.93
128.27
128.06
127.66
125.87
123.82
35.48
N
N
O
S
Ph
4c
f1 (ppm)


7.594
7.576
7.534
7.516
7.498
7.482
7.464
7.410
7.392
7.260
6.870
6.863
6.793
6.786
3.918
3.136
4d
0.96
2.29
1.07
1.02
1.00
0.25
3.07
f1 (ppm)

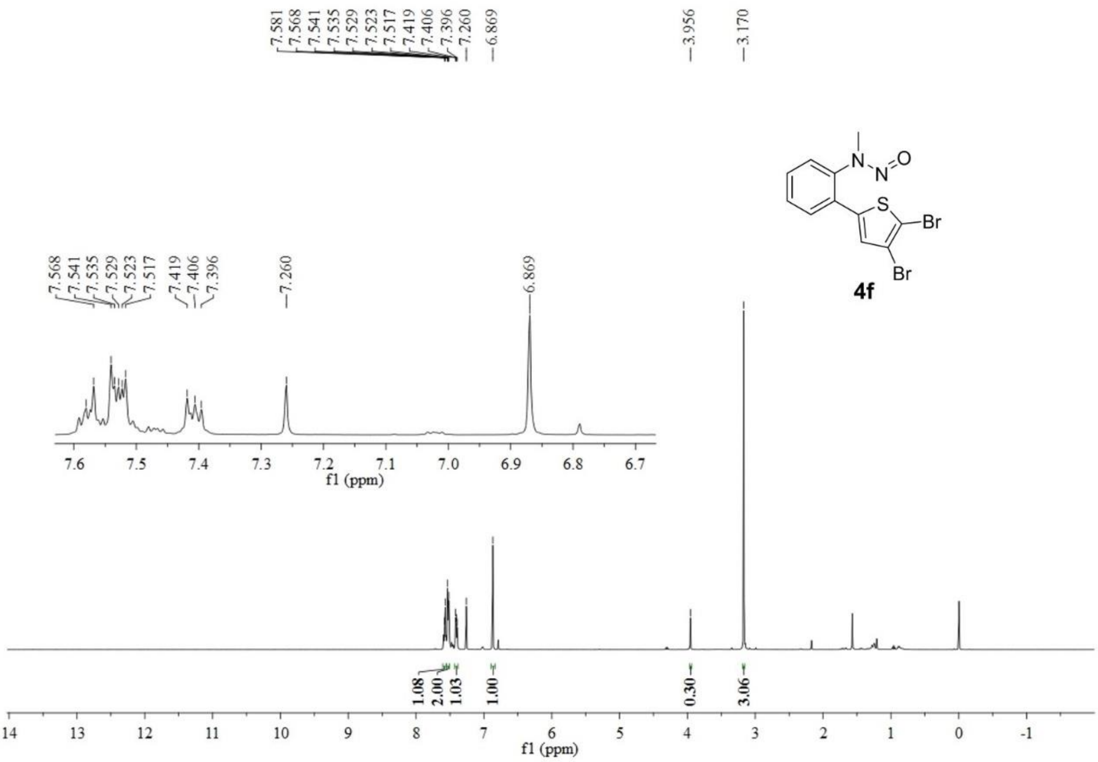

140.11
137.52
131.69
130.98
129.96
129.85
129.34
127.64
126.96
126.58
35.40
4d
f1 (ppm)


7.593
7.575
7.531
7.513
7.498
7.483
7.465
7.409
7.391
7.260
7.006
6.998
6.772
6.765
3.910
3.127
N
N
O
S
Br
0.99
2.16
0.98
1.08
0.94
0.25
3.00
f1 (ppm)

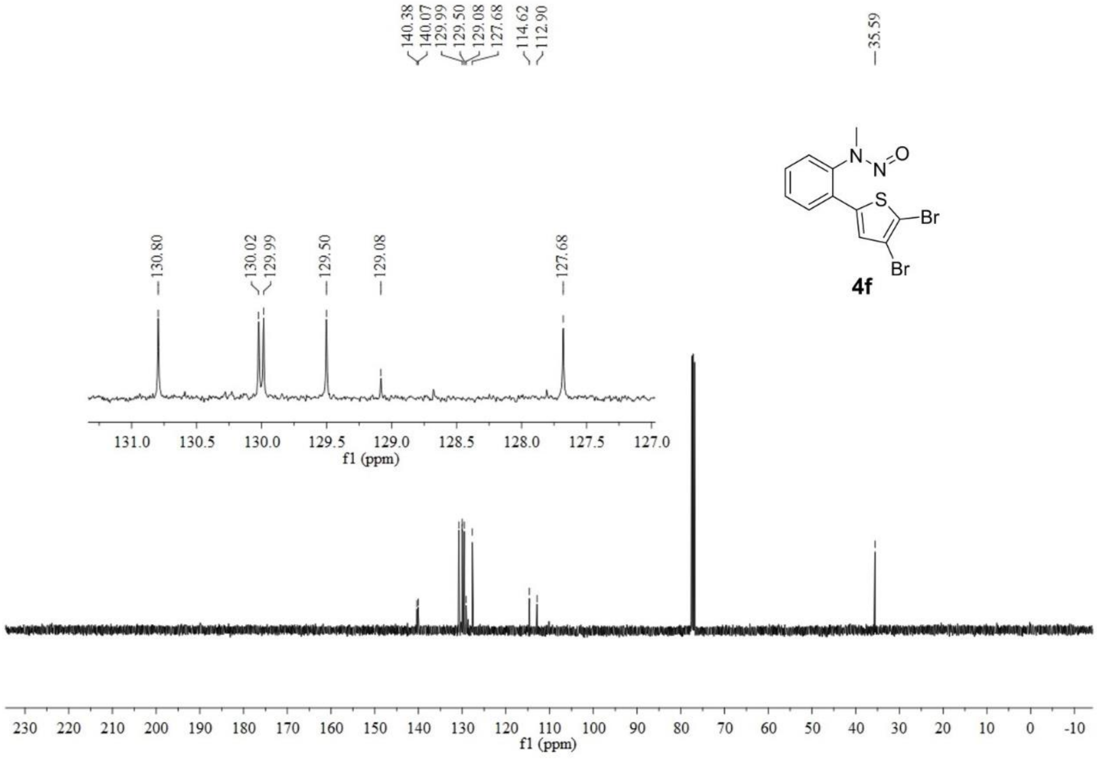
4e


140.44
140.05
130.69
129.84
129.37
127.52
113.96
35.40
130.95
130.69
129.91
129.84
129.37
127.61
127.52
N
N
O
S
Br
f1 (ppm)

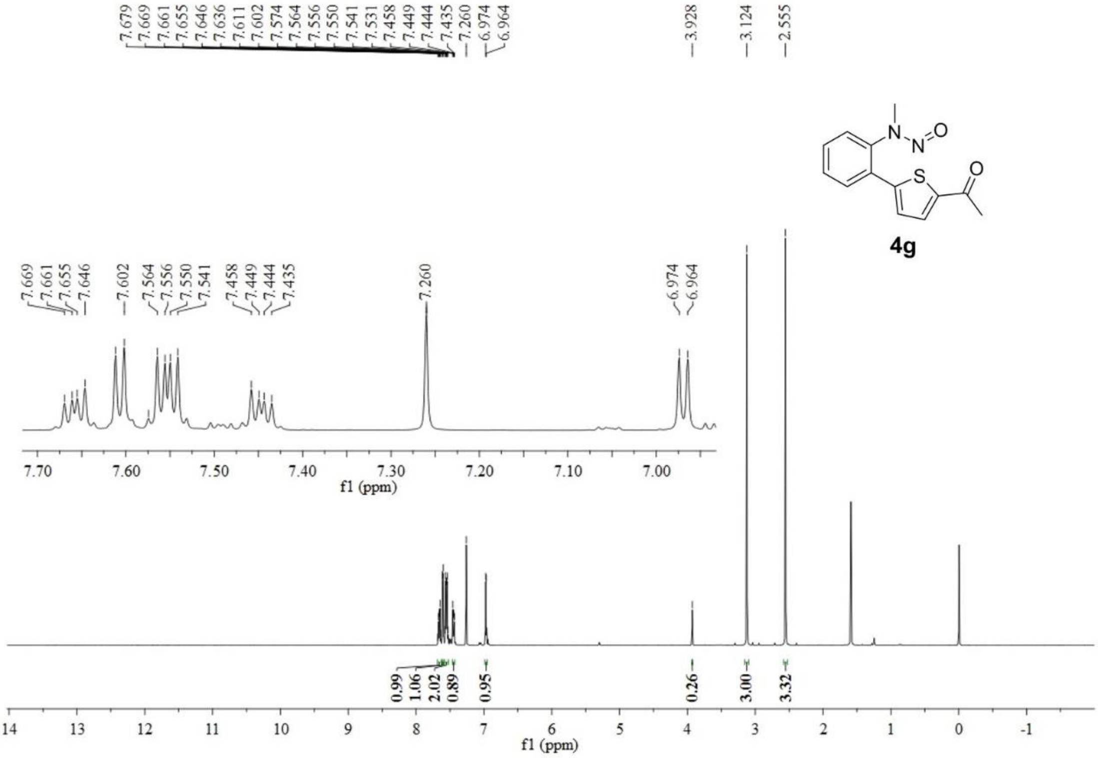
4e


7.581
7.568
7.541
7.535
7.529
7.523
7.517
7.419
7.406
7.396
7.260
6.869
3.956
3.170
N
N
O
S
Br
Br
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
1.08
2.00
1.03
1.00
0.30
3.06
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

4f

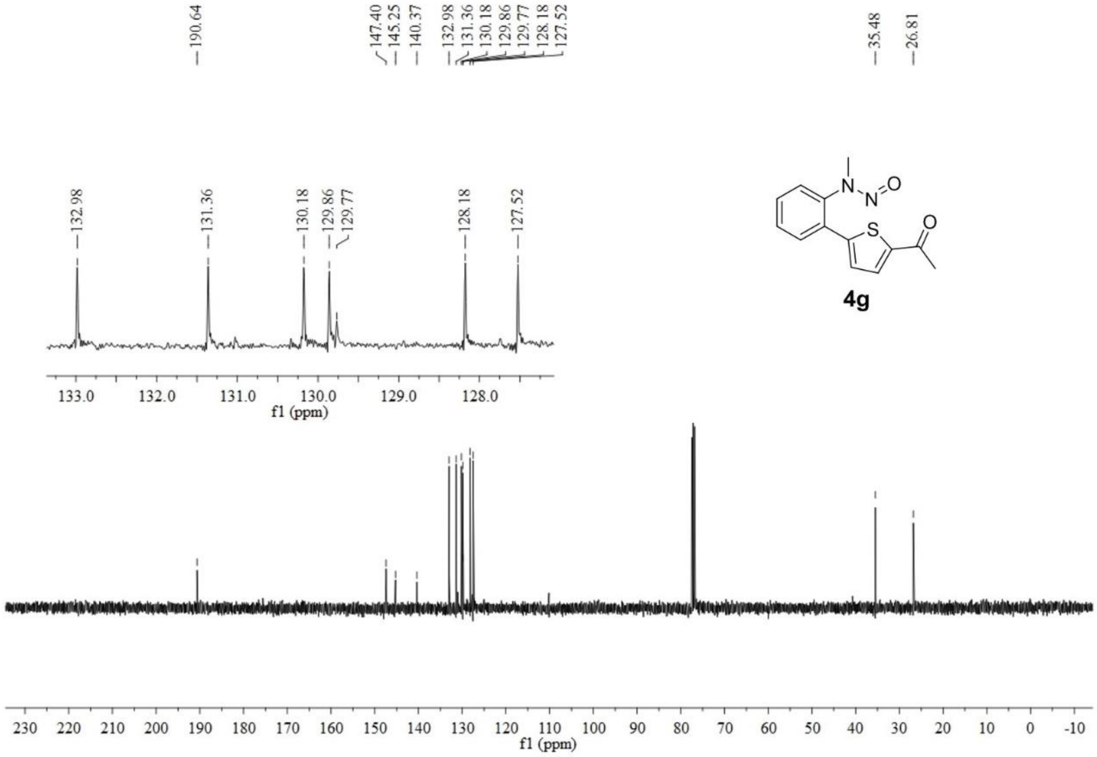

140.38
140.07
129.99
129.50
129.08
127.68
114.62
112.90
35.59
N
N
O
S
Br
Br
130.80
130.02
129.99
129.50
129.08
127.68
131.0
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4f



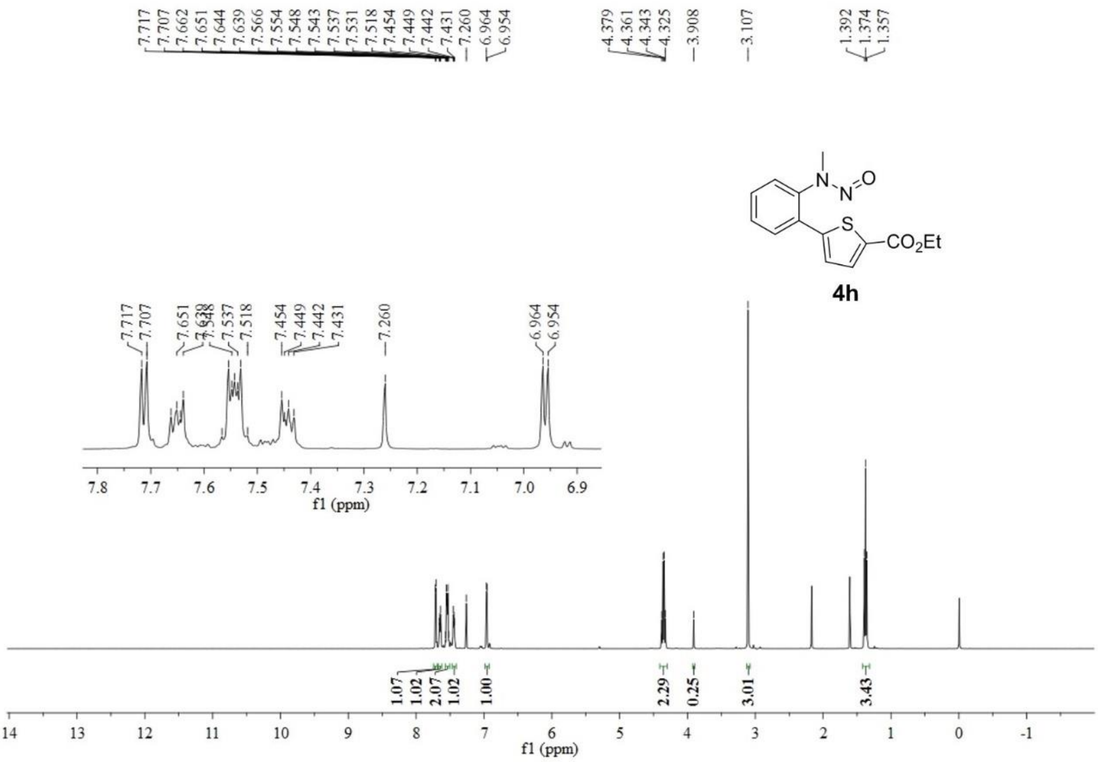
7.679
7.669
7.661
7.655
7.646
7.636
7.611
7.602
7.574
7.564
7.556
7.550
7.541
7.531
7.458
7.449
7.444
7.435
7.260
6.974
6.964
3.928
3.124
2.555
N
N
O
S
O
7.669
7.661
7.655
7.646
7.602
7.564
7.556
7.550
7.541
7.458
7.449
7.444
7.435
7.260
6.974
6.964
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
f1 (ppm)
0.99
1.06
2.02
0.89
0.95
0.26
3.00
3.32
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

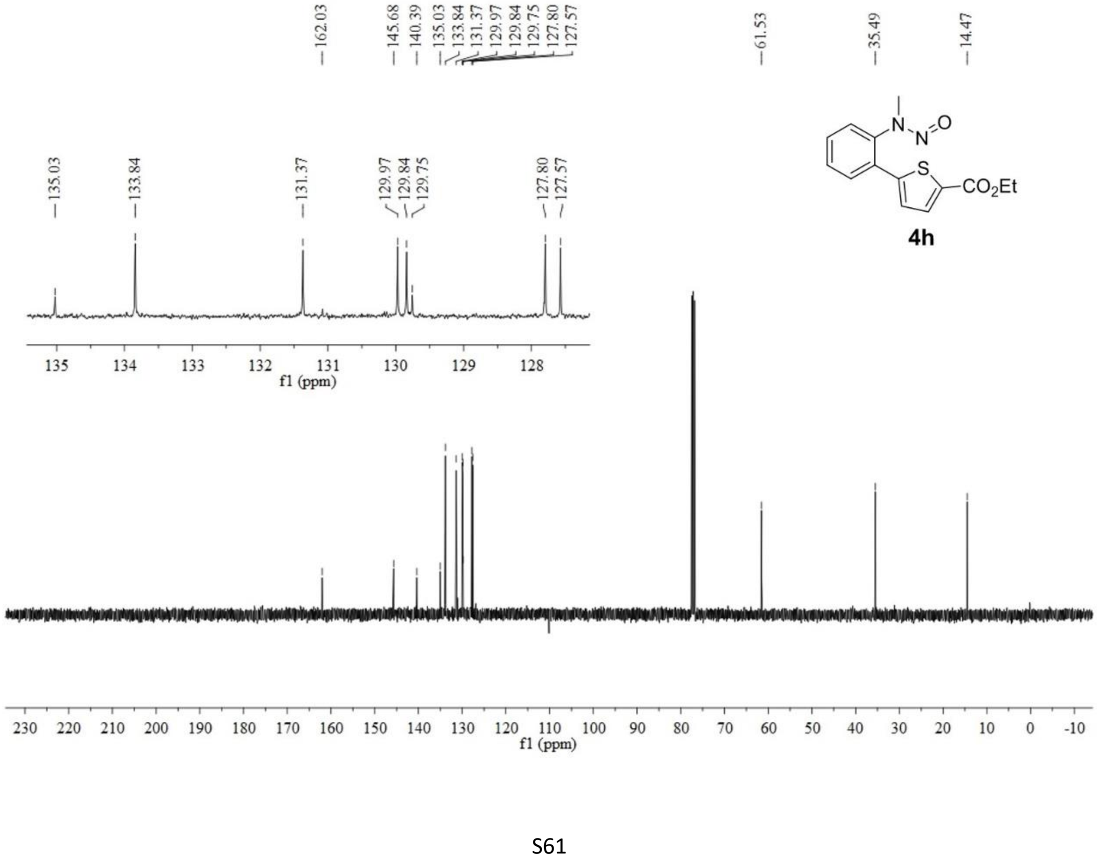
4g

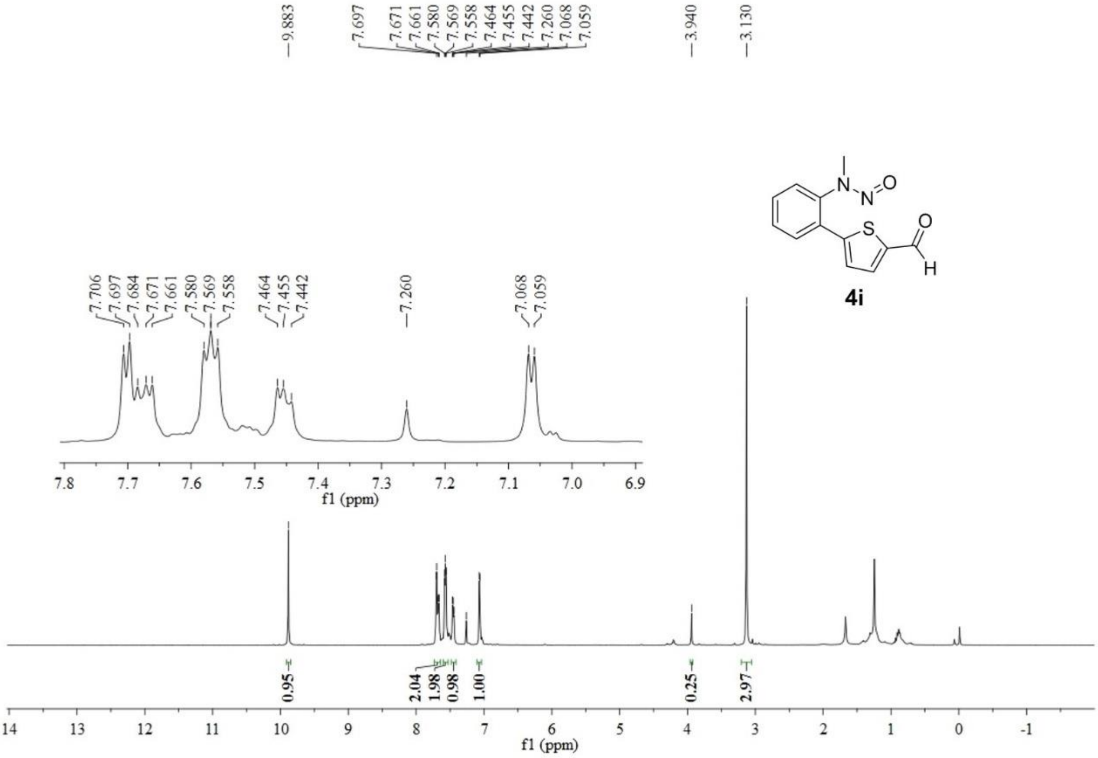


190.64
147.40
145.25
140.37
132.98
131.36
130.18
129.86
129.77
128.18
127.52
35.48
26.81
N
N
O
S
O
132.98
131.36
130.18
129.86
129.77
128.18
127.52
133.0
132.0
131.0
130.0
129.0
128.0
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4g

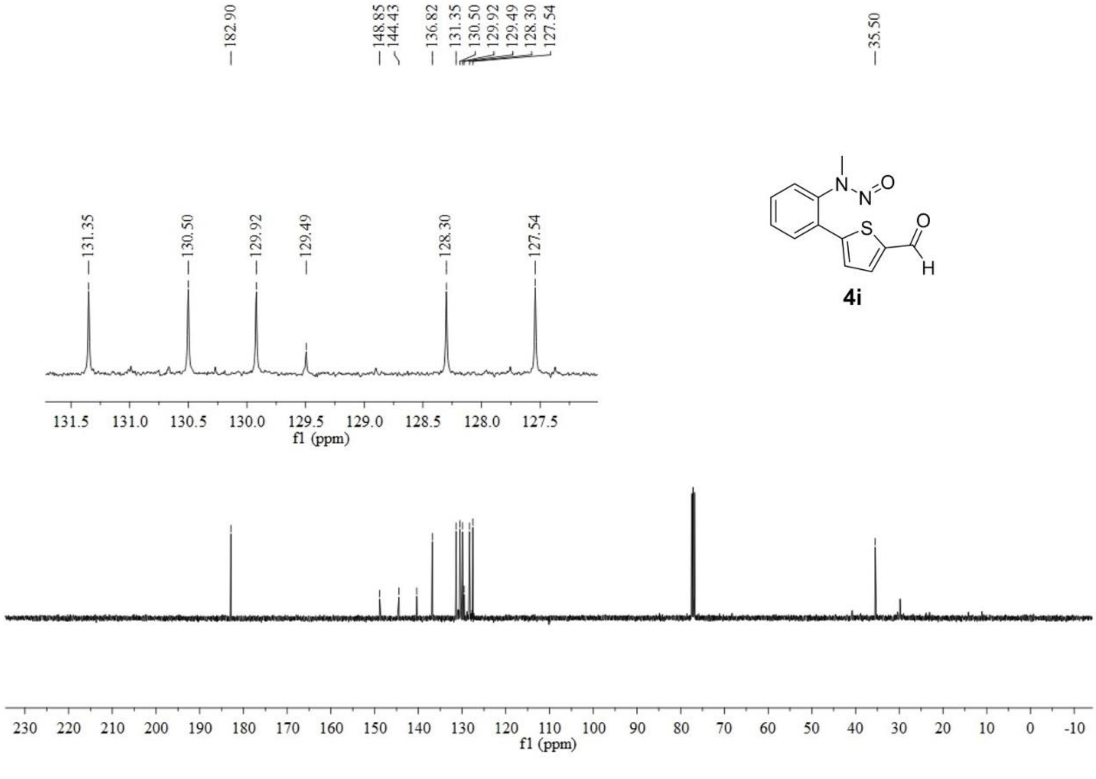

7.717
7.707
7.662
7.651
7.644
7.639
7.566
7.554
7.548
7.543
7.537
7.531
7.518
7.454
7.449
7.442
7.431
7.260
6.964
6.954
4.379
4.361
4.343
4.325
3.908
3.107
1.392
1.374
1.357
N
N
O
S
CO2Et
4h
1.07
1.02
2.07
1.02
1.00
2.29
0.25
3.01
3.43
f1 (ppm)


162.03
145.68
140.39
135.03
133.84
131.37
129.97
129.84
129.75
127.80
127.57
61.53
35.49
14.47
N
N
O
S
CO2Et
4h
f1 (ppm)



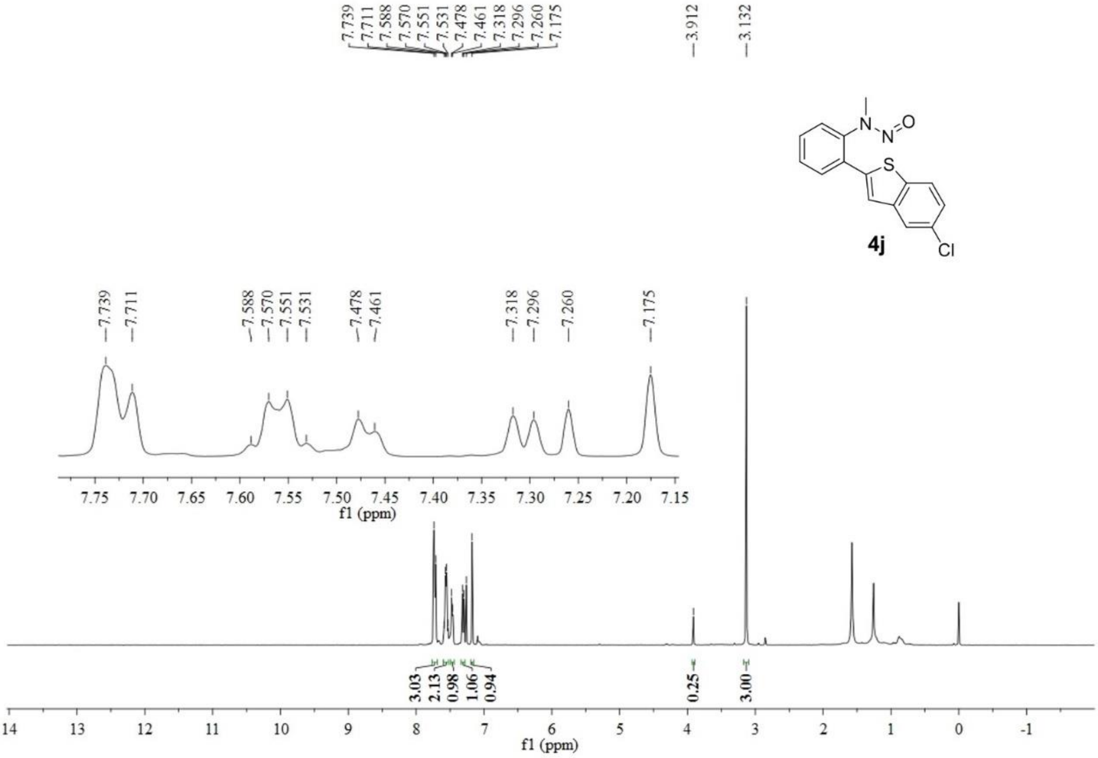
9.883
7.697
7.671
7.661
7.580
7.569
7.558
7.464
7.455
7.442
7.260
7.068
7.059
3.940
3.130
7.706
7.697
7.684
7.671
7.661
7.580
7.569
7.558
7.464
7.455
7.442
7.260
7.068
7.059
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
0.95
2.04
1.98
0.98
1.00
0.25
2.97
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)
N
N
O
S
O
H

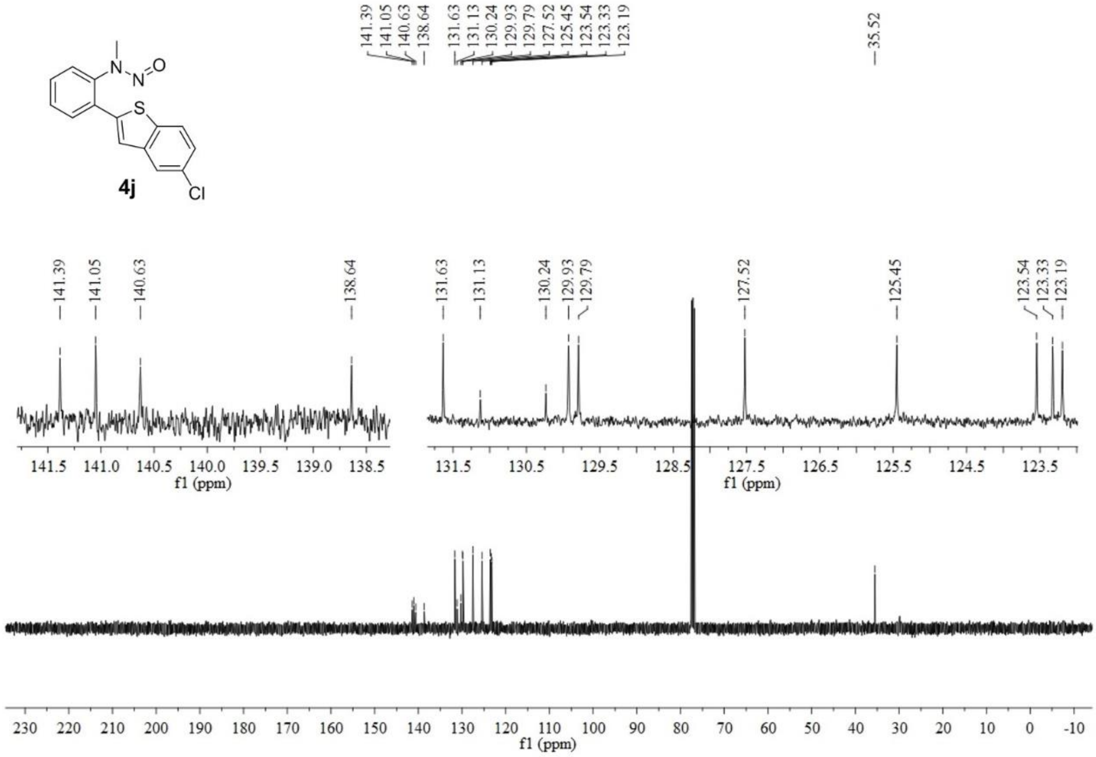
4i

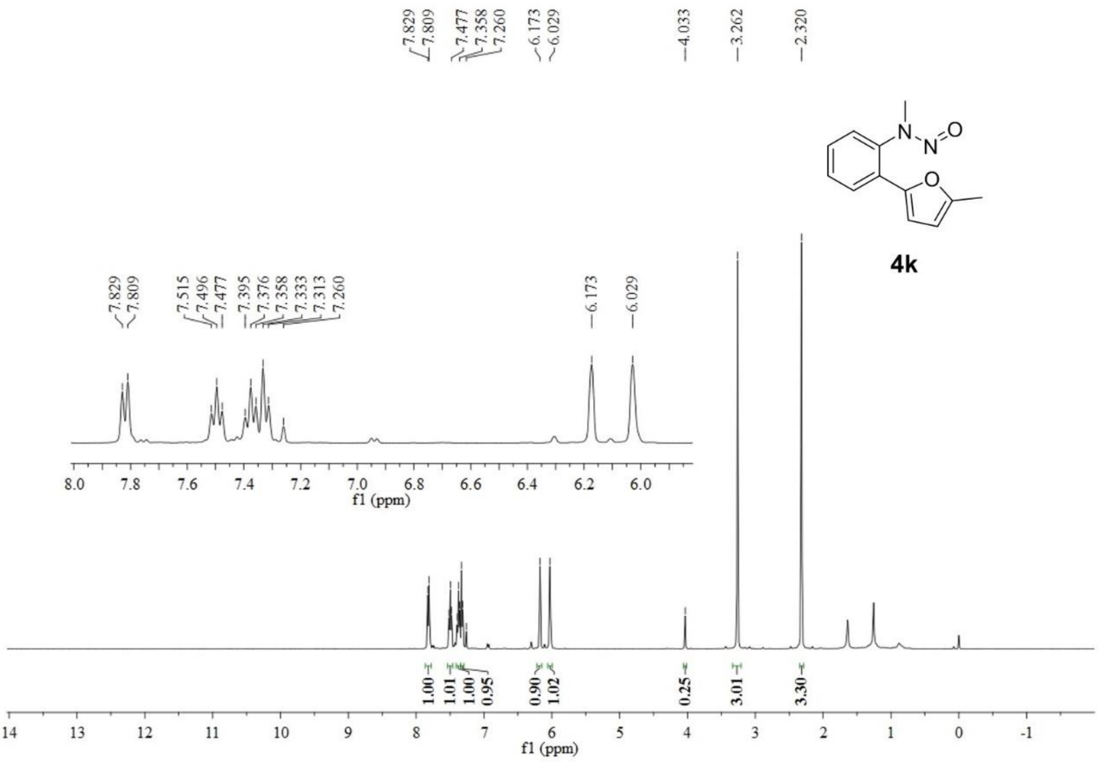


182.90
148.85
144.43
136.82
131.35
130.50
129.92
129.49
128.30
127.54
35.50
131.35
130.50
129.92
129.49
128.30
127.54
131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
N
N
O
S
O
H

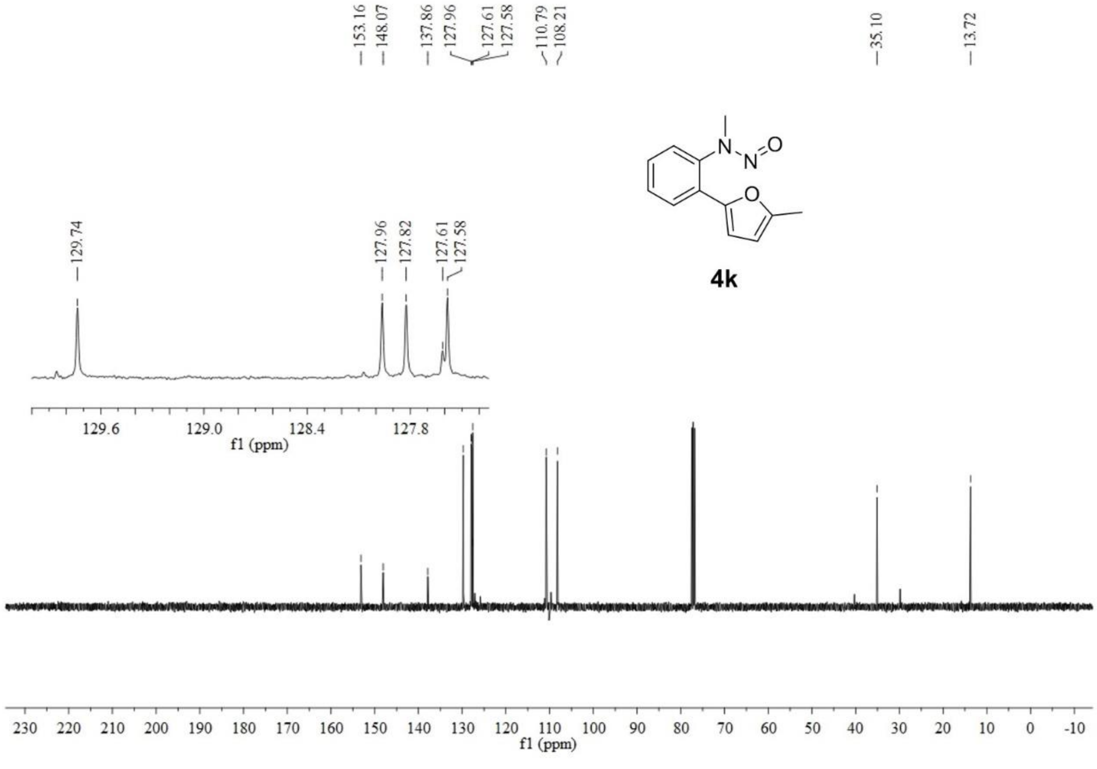
4i


7.739
7.711
7.588
7.570
7.551
7.531
7.478
7.461
7.318
7.296
7.260
7.175
3.912
3.132
4j
Cl
3.03
2.13
0.98
1.06
0.94
0.25
3.00
f1 (ppm)
f1 (ppm)

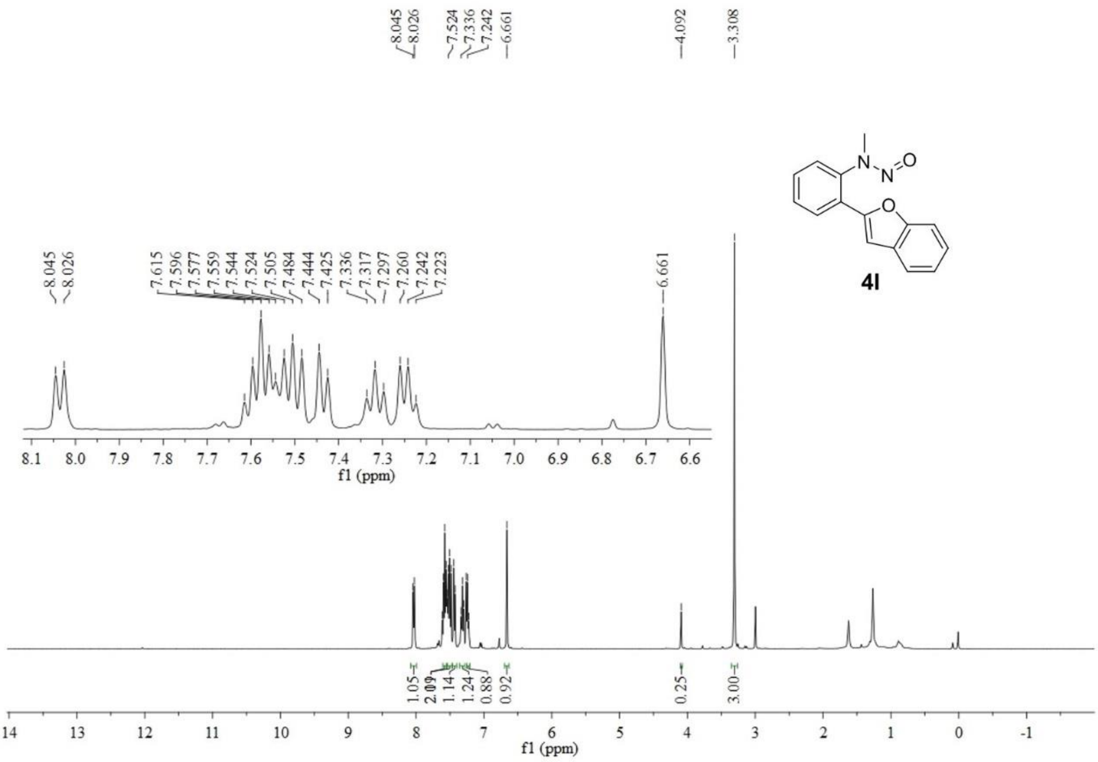

141.39
141.05
140.63
138.64
131.63
131.13
130.24
129.93
129.79
127.52
125.45
123.54
123.33
123.19
35.52
4j
Cl
f1 (ppm)
f1 (ppm)
f1 (ppm)

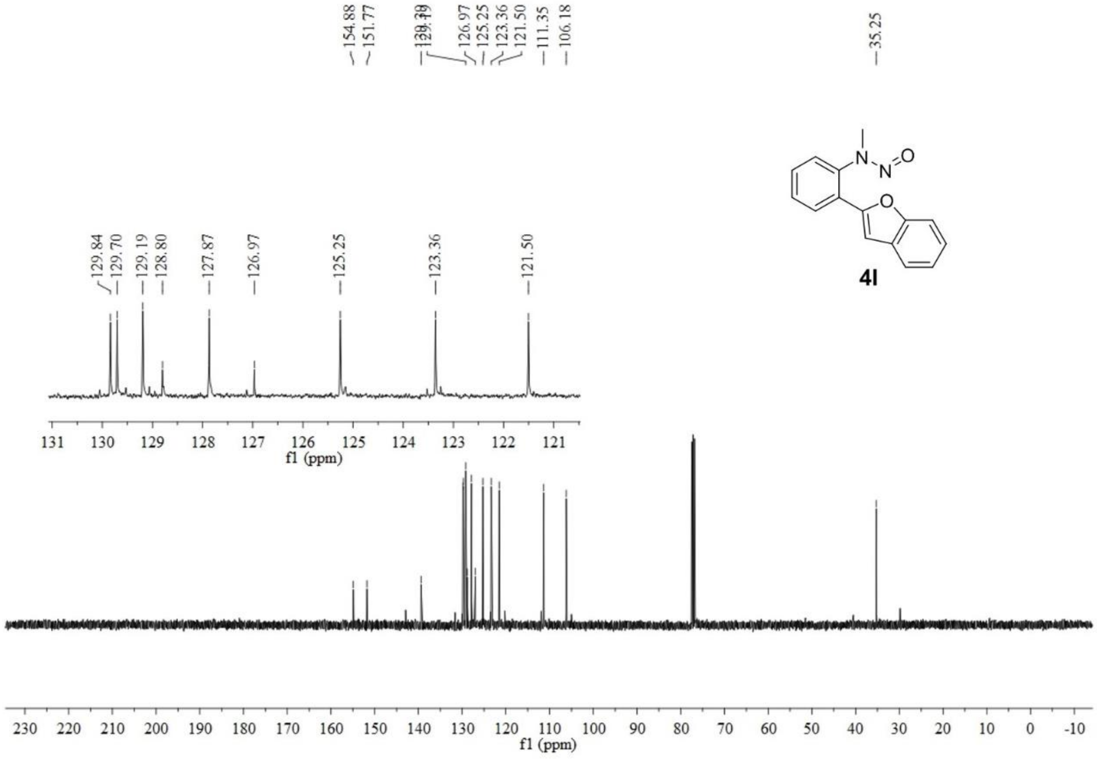

7.829
7.809
7.477
7.358
7.260
6.173
6.029
4.033
3.262
2.320
7.829
7.809
7.515
7.496
7.477
7.395
7.376
7.358
7.333
7.313
7.260
6.173
6.029
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0
f1 (ppm)
1.00
1.01
1.00
0.95
0.90
1.02
0.25
3.01
3.30
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)
N
N
O
O

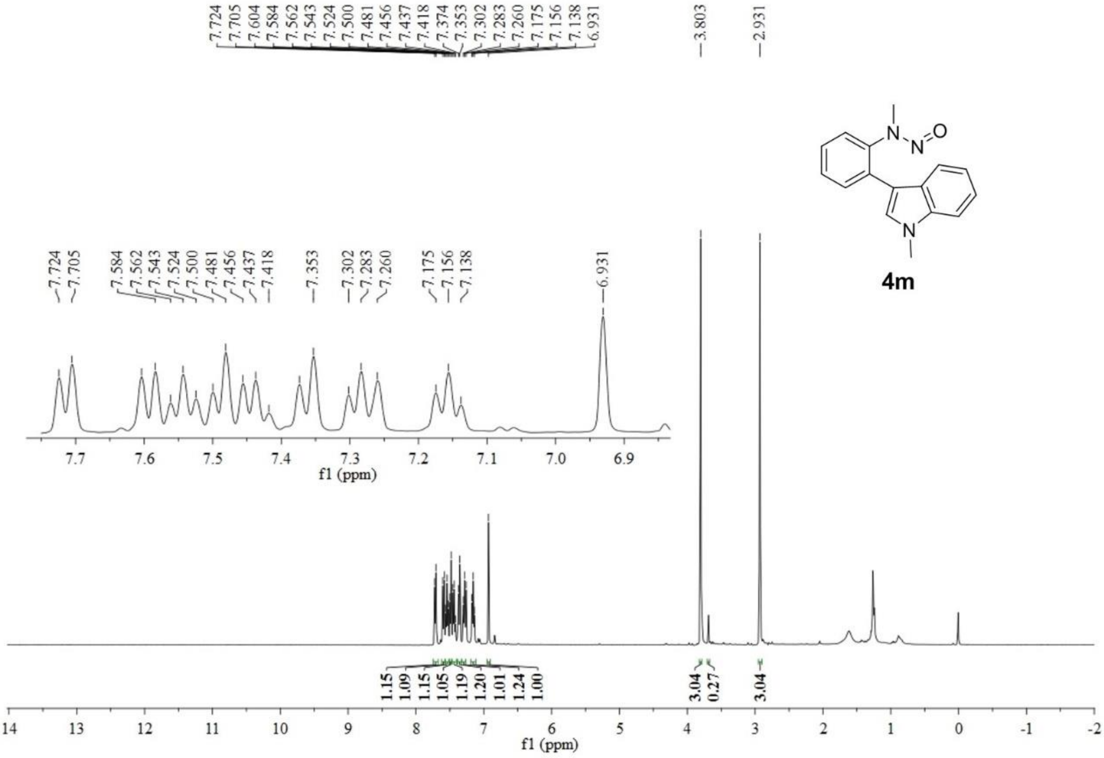
4k


153.16
148.07
137.86
127.96
127.61
127.58
110.79
108.21
35.10
13.72
129.74
127.96
127.82
127.61
127.58
129.6 129.0 128.4 127.8
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
N
N
O
O

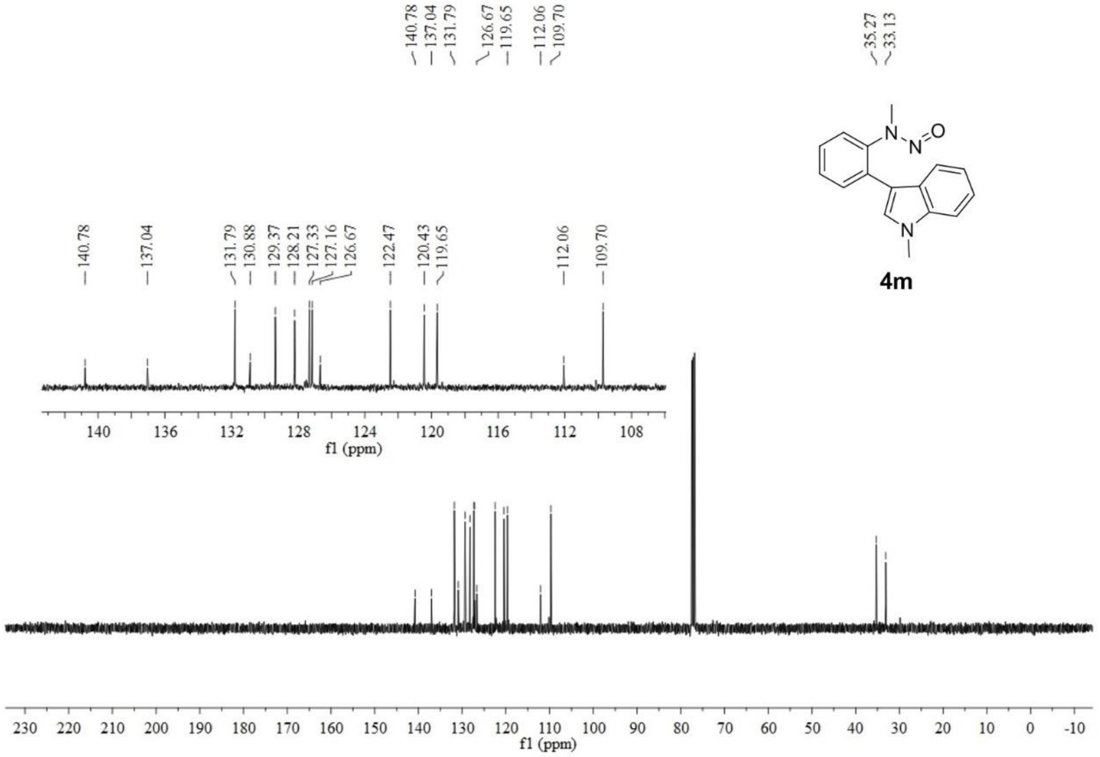
4k


8.045
8.026
7.524
7.336
7.242
6.661
4.092
3.308
4l
8.045
8.026
7.615
7.596
7.577
7.559
7.544
7.524
7.505
7.484
7.444
7.425
7.336
7.317
7.297
7.260
7.242
7.223
6.661
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
1.05
2.09
1.14
1.24
0.88
0.92
0.25
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

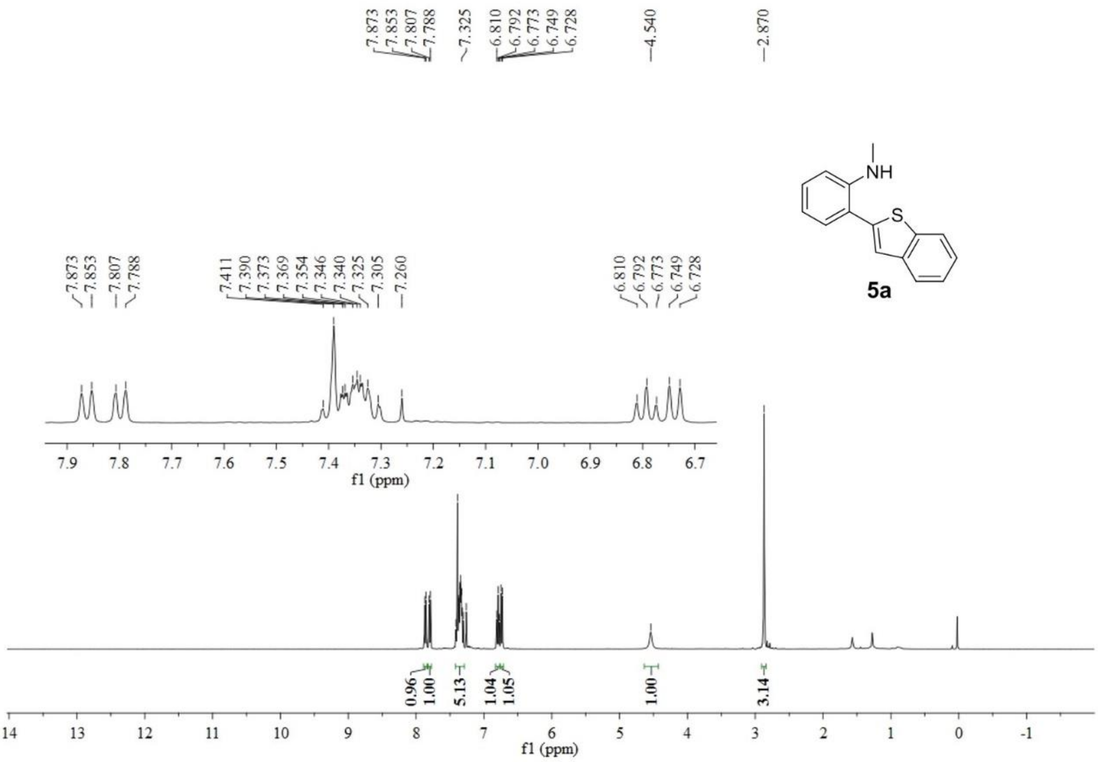

154.88
151.77
129.70
129.19
126.97
125.25
123.36
121.50
111.35
106.18
35.25
4l
129.84
129.70
129.19
128.80
127.87
126.97
125.25
123.36
121.50
131 130 129 128 127 126 125 124 123 122 121
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

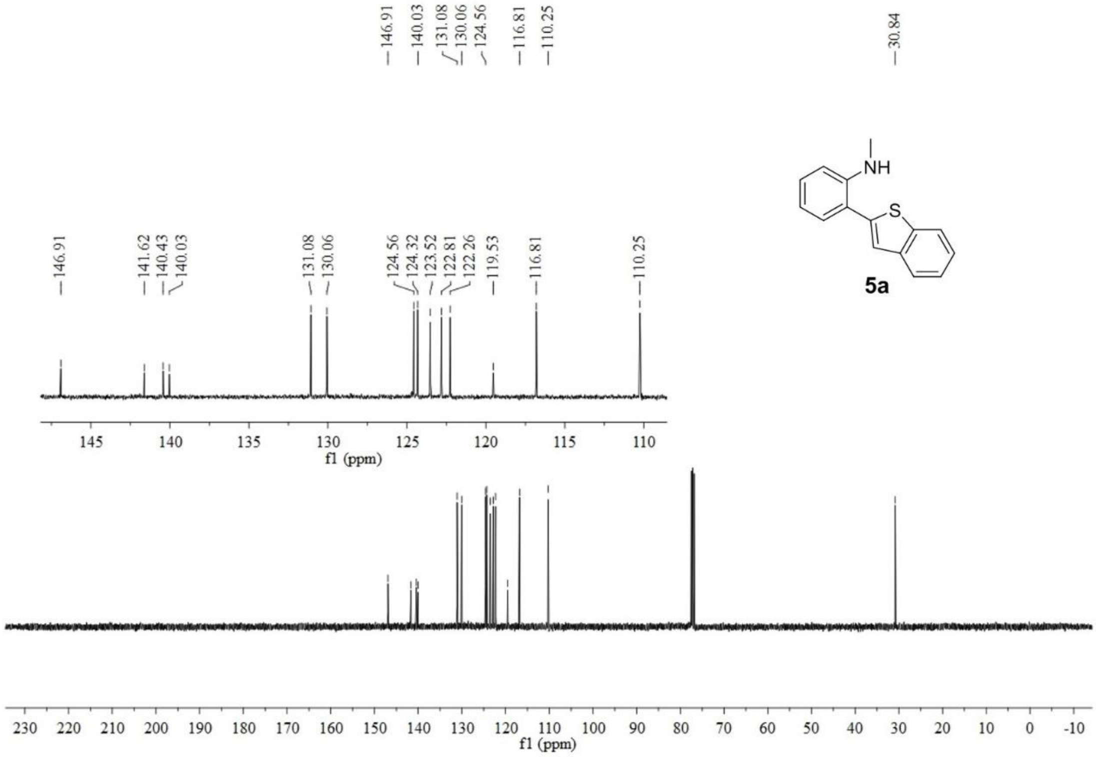

7.724
7.705
7.604
7.584
7.562
7.543
7.524
7.500
7.481
7.456
7.437
7.418
7.374
7.353
7.302
7.283
7.260
7.175
7.156
7.138
6.931
3.803
2.931
N
N
O
N
1.15
1.09
1.15
1.05
1.19
1.20
1.01
1.24
1.00
3.04
0.27
3.04
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

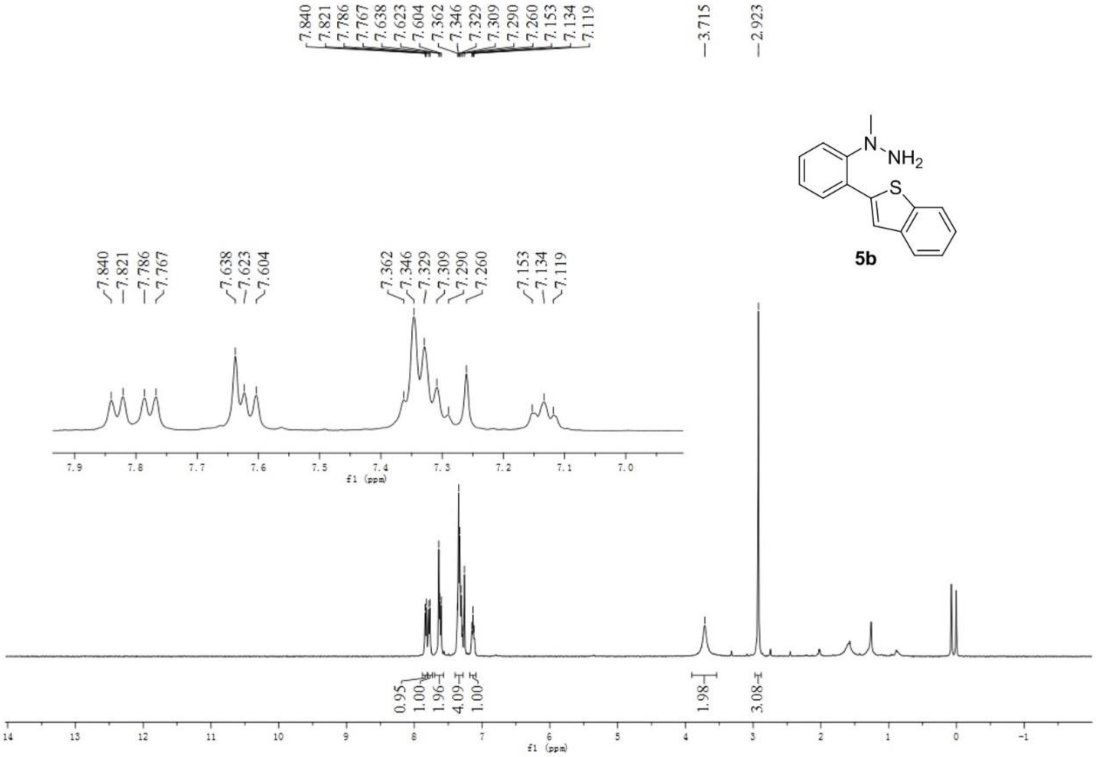
4m


140.78
137.04
131.79
126.67
119.65
112.06
109.70
35.27
33.13
N
N
O
N
140.78
137.04
131.79
130.88
129.37
128.21
127.33
127.16
126.67
122.47
120.43
119.65
112.06
109.70
140
136
132
128
124
120
116
112
108
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

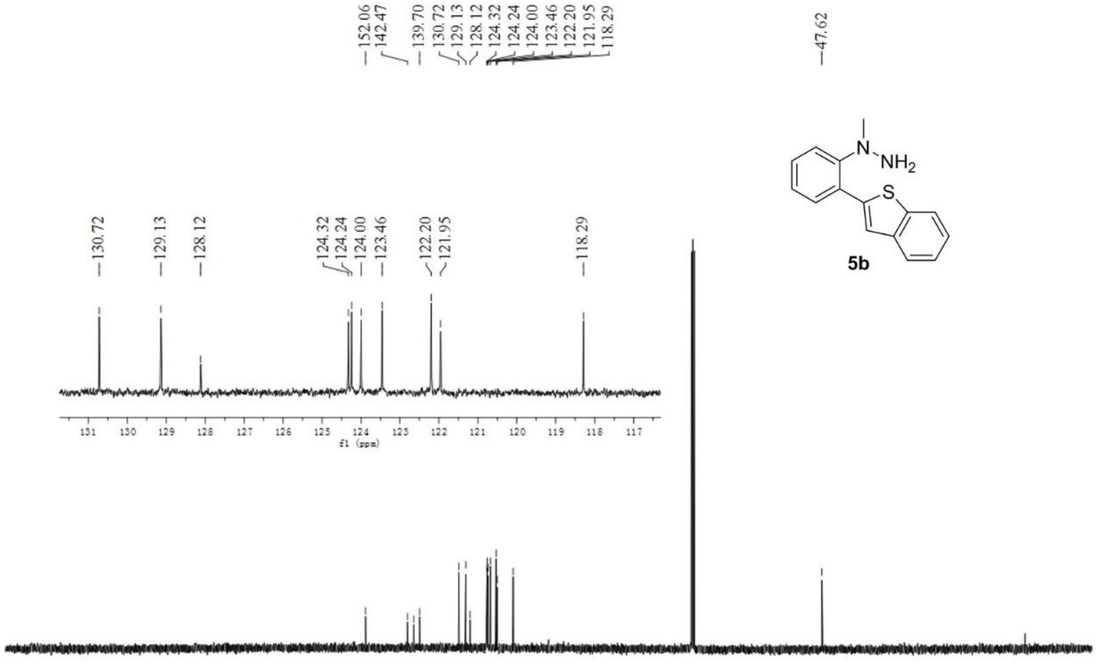
4m


7.873
7.853
7.807
7.788
7.325
6.810
6.792
6.773
6.749
6.728
4.540
2.870
NH
S
5a
7.873
7.853
7.807
7.788
7.411
7.390
7.373
7.369
7.354
7.346
7.340
7.325
7.305
7.260
6.810
6.792
6.773
6.749
6.728
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
0.96
1.00
5.13
1.04
1.05
1.00
3.14
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

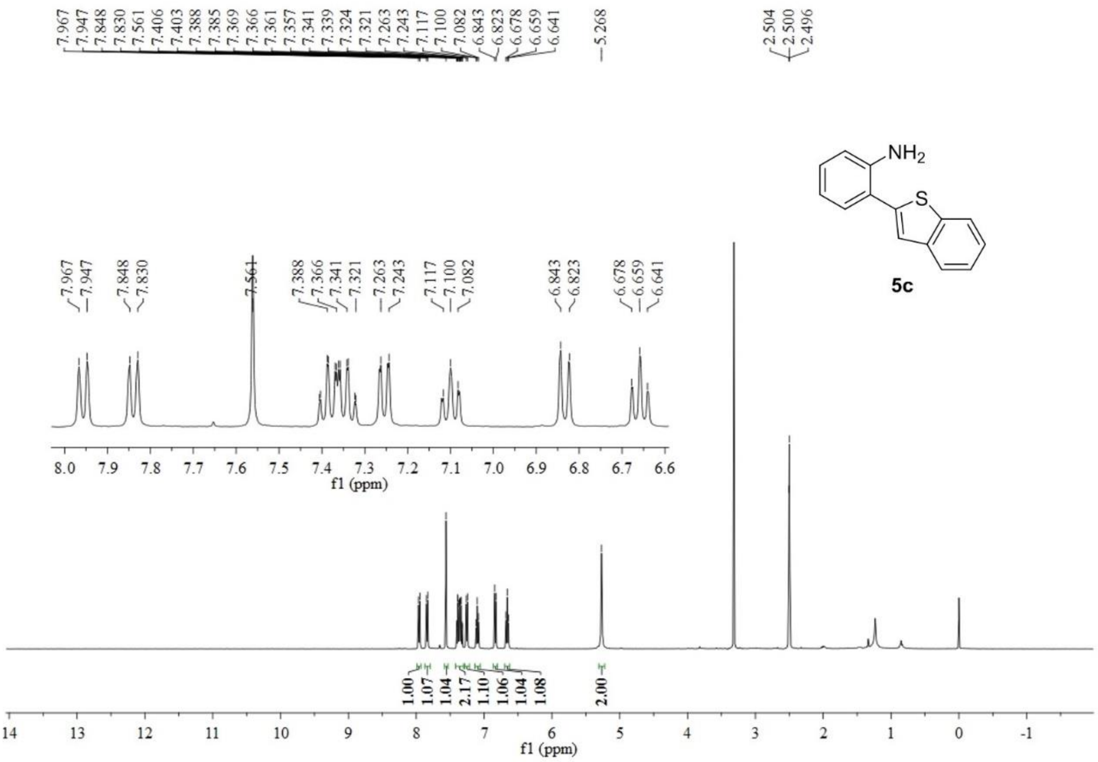

146.91
140.03
131.08
130.06
124.56
116.81
110.25
30.84
NH
S
5a
146.91
141.62
140.43
140.03
131.08
130.06
124.56
124.32
123.52
122.81
122.26
119.53
116.81
110.25
145 140 135 130 125 120 115 110
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.840
7.821
7.786
7.767
7.638
7.623
7.604
7.362
7.346
7.329
7.309
7.290
7.260
7.153
7.134
7.119
3.715
2.923
N
NH2
S
0.95
1.00
1.96
4.09
1.00
1.98
3.08
f1 (ppm)

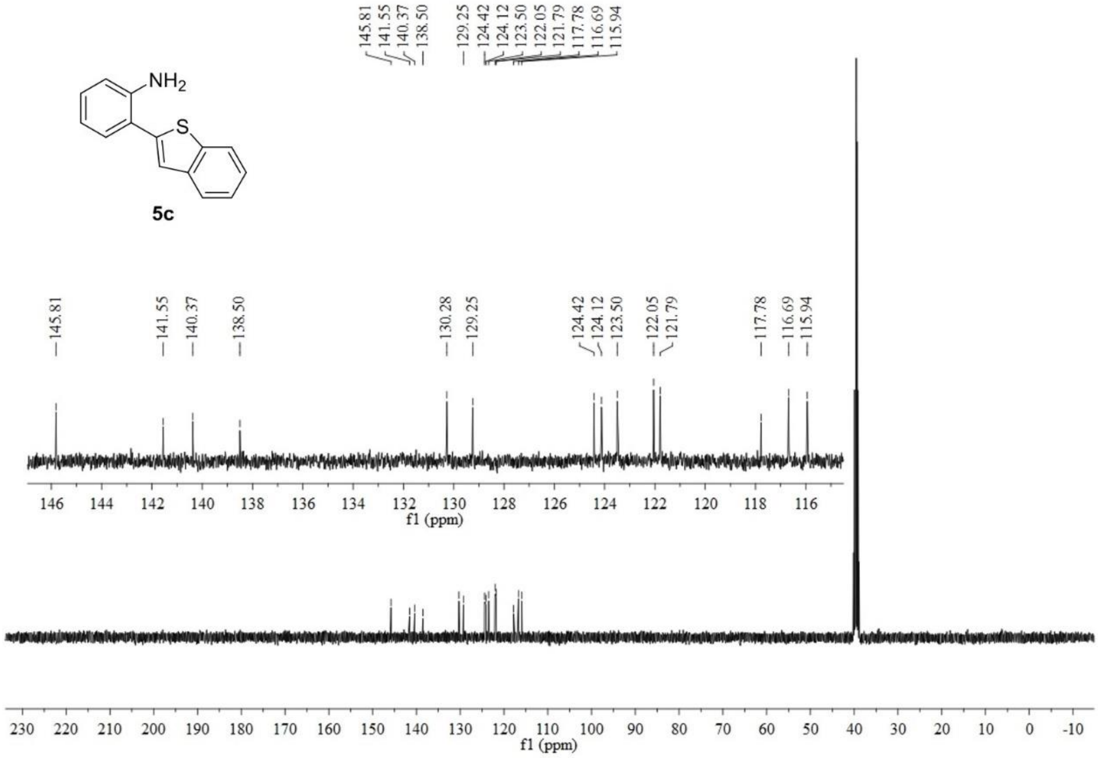
5b


152.06
142.47
139.70
130.72
129.13
128.12
124.32
124.24
124.00
123.46
122.20
121.95
118.29
47.62
N
NH2
S
f1 (ppm)

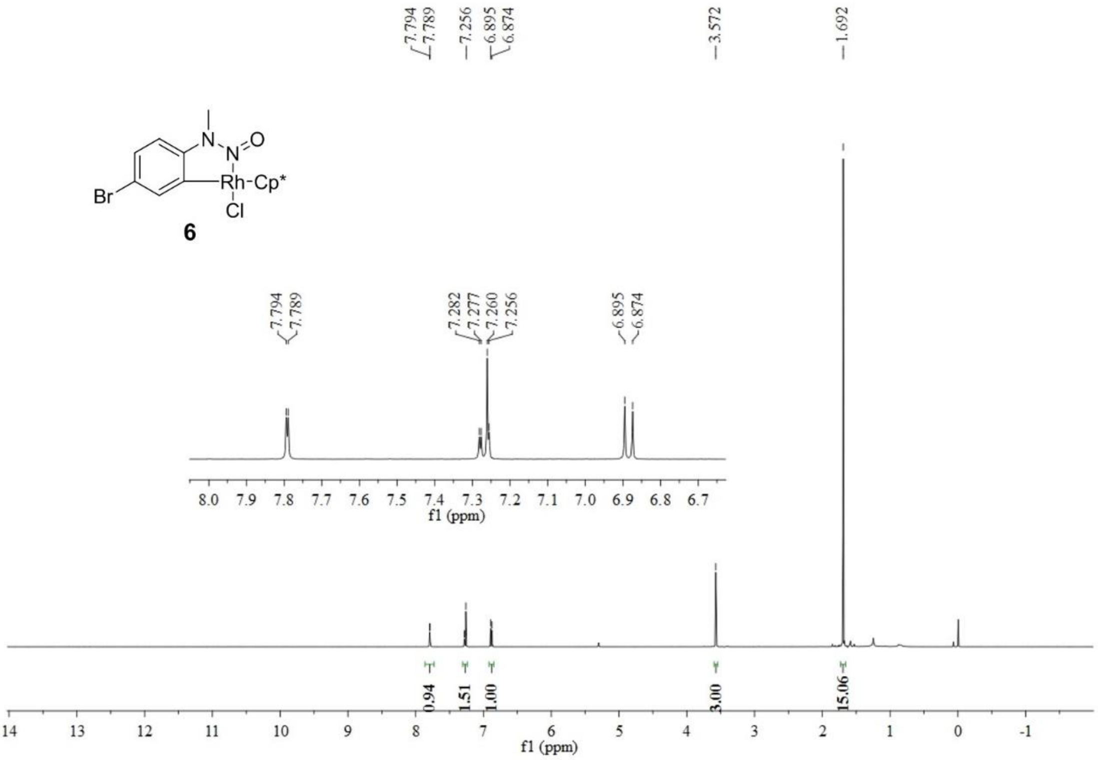
5b

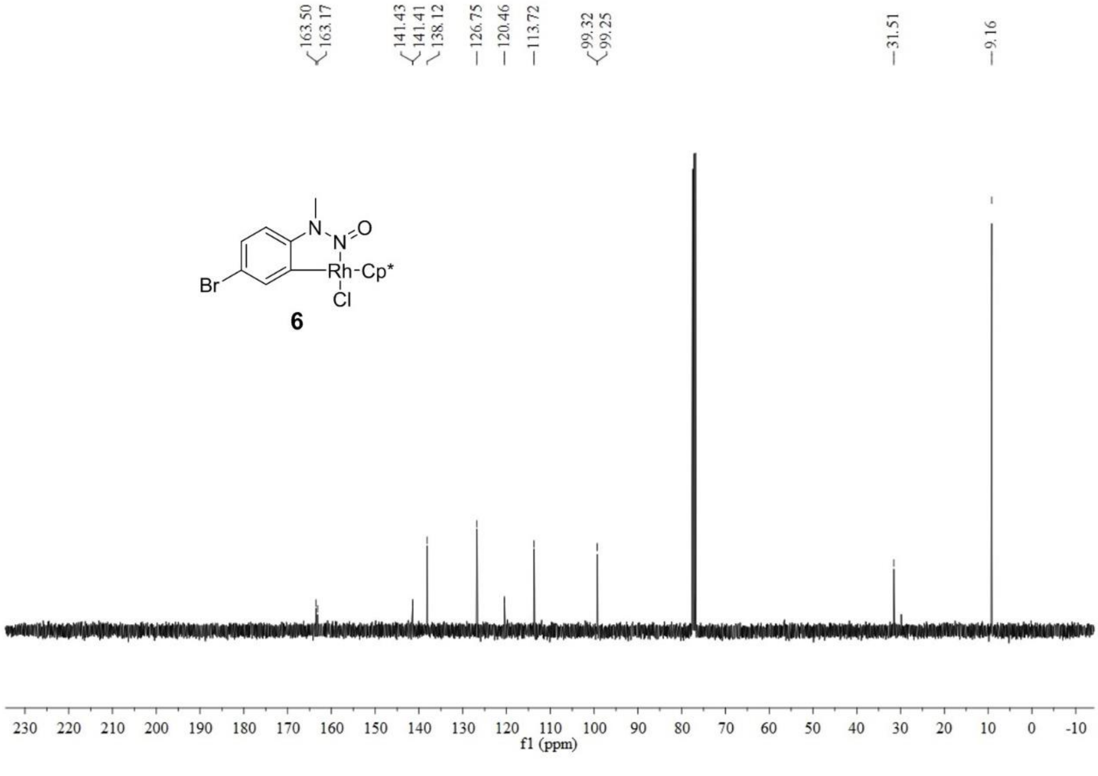

7.967
7.947
7.848
7.830
7.561
7.406
7.403
7.388
7.385
7.369
7.366
7.361
7.357
7.341
7.339
7.324
7.321
7.263
7.243
7.117
7.100
7.082
6.843
6.823
6.678
6.659
6.641
5.268
2.504
2.500
2.496
NH2
S
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
f1 (ppm)
1.00
1.07
1.04
2.17
1.10
1.06
1.04
1.08
2.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

5c


145.81
141.55
140.37
138.50
129.25
124.42
124.12
123.50
122.05
121.79
117.78
116.69
115.94
NH2
S
145.81
141.55
140.37
138.50
130.28
129.25
124.42
124.12
123.50
122.05
121.79
117.78
116.69
115.94
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

5c


7.794
7.789
7.256
6.895
6.874
3.572
1.692
Br
N
N
O
Rh-Cp*
Cl
6
7.794
7.789
7.282
7.277
7.260
7.256
6.895
6.874
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
0.94
1.51
1.00
3.00
15.06
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


163.50
163.17
141.43
141.41
138.12
126.75
120.46
113.72
99.32
99.25
31.51
9.16
Br
N
N
O
Rh-Cp*
Cl
6
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

XI. X-ray crystallographic data of complex 6

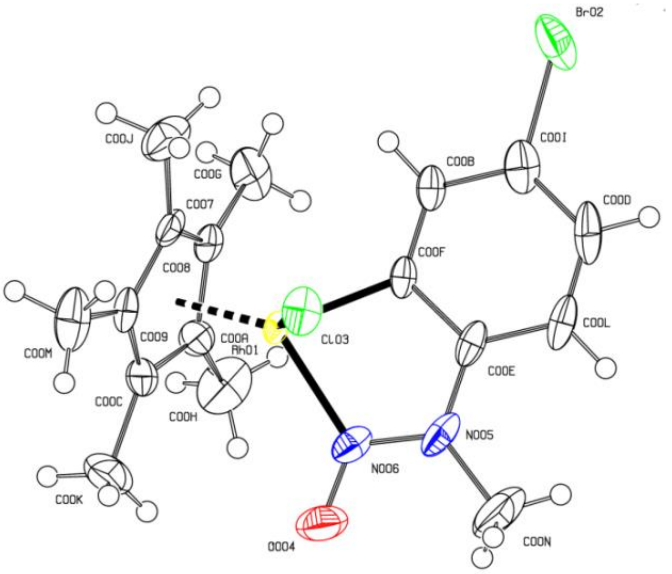


Figure S1. ORTEP diagram of complex **6** (CCDC: 1838256). Thermal ellipsoids are shown at the 50% probability level.

Table S2. Crystal data and structure refinement for complex **6**.

Identification code	hs-x-2
Empirical formula	$C_{17}H_{21}BrClN_2ORh$
Formula weight	487.63
Temperature/K	295.4(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	15.4304(5)
b/Å	14.9823(4)
c/Å	16.4747(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3808.67(19)
Z	8

ρ_{calc}g/cm^3	1.701
μ/mm^{-1}	11.034
F (000)	1936.0
Crystal size/mm^3	0.65 × 0.6 × 0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.826 to 134.146
Index ranges	$-18 \le h \le 18$, $-15 \le k \le 17$, $-19 \le l \le 19$
Reflections collected	19343
Independent reflections	3400 [R_{int} = 0.0867, R_{sigma} = 0.0414]
Data/restraints/parameters	3400/13/214
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.1466
Final R indexes [all data]	R_1 = 0.0587, wR_2 = 0.1519
Largest diff. peak/hole / e Å^{-3}	1.33/-1.81