Chemo- and diastereoselective synthesis of spiro-iminoindoline-pyrazolines as potential antioxidant reagents

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Supplementary Information

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1. General Information

General Procedures

- All reactions were performed in oven-dried or flame-dried reaction vessels, modified Schlenk flasks, or round-bottom flasks. The flasks were fitted with Teflon screw caps and reactions were conducted under an atmosphere of argon if needed. Gas-tight syringes with stainless steel needles were used to transfer air- and moisture-sensitive liquids. All moisture and/or air sensitive solid compounds were manipulated inside normal desiccators. Flash column chromatography was performed using silica gel (40 – 63 μm, 230 – 400 mesh).
- Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates (Merck) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and I_2.
- Organic solutions were concentrated at 30 – 50 °C on rotary evaporators at ~10 torr followed by drying on vacuum pump at ~1 torr. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated.

Materials

- Commercial reagents and solvents were purchased from Adamas-beta, Aldrich Chemical Co., Alfa Aesar, Macklin, Leyan, and Energy Chemical used as received with the following exceptions: THF was purified by refluxing over Na-benzophenone under positive argon pressure followed by distillation.[1] The 3-alkenyl-iminoindolines **1**[2] and hydrazonoyl chlorides **2**[3] were prepared according to literature procedure.

Instrumentation

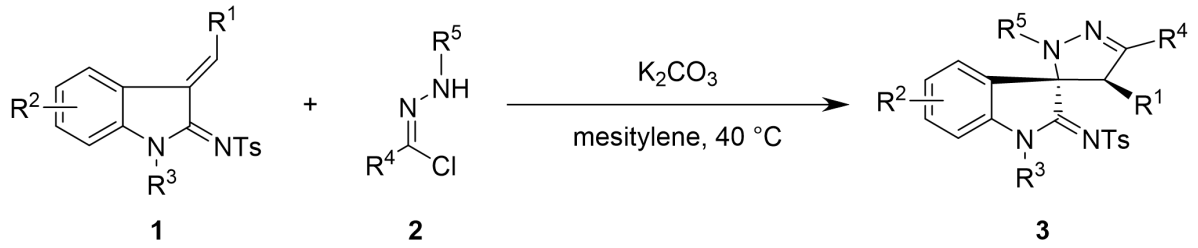
- Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with JEOL-600M. Proton chemical shifts are reported in parts per million (δ scale), and are referenced using residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ($CHCl_3$)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant(s) (Hz), integration].
- Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with JEOL 151 MHz spectrometers. Carbon chemical shifts are reported in parts per million (δ scale), and

are referenced using the carbon resonances of the solvent (δ 77.0 ($CHCl_3$)). Data are reported as follows: chemical shift [multiplicity (if not singlet), assignment (C_q = fully substituted carbon)].

- Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were recorded with JEOL 564 MHz spectrometers. Fluorine chemical shifts are reported in parts per million (δ scale).
- High resolution mass spectra (HRMS) were performed on an Agilent 6230 time-of-flight (TOF) LC/MS instrument or a Waters SYNAPT G2 mass spectrometer by using an electrospray ionization (ESI) source analyzed by quadrupole time-of-flight (Q-TOF).
- Melting points were determined on a SGW X-4 digital melting point apparatus using open glass capillaries and temperatures were not corrected, reported in degrees Celsius.

2. General Procedure for the Synthesis of Spiro-iminoindoline-pyrazolines

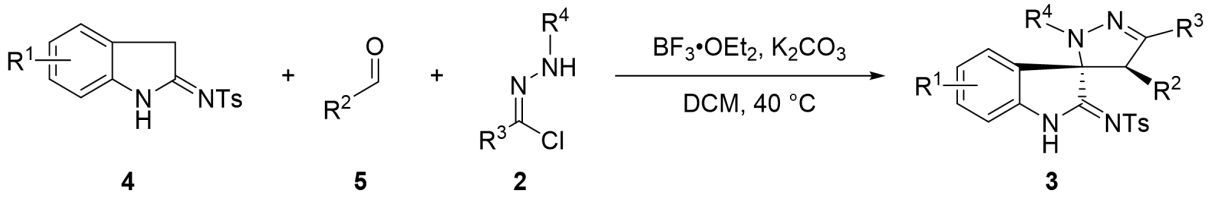
General procedure A*: the (2 + 3) cyclization of alkenyl-iminoindolines and hydrazonoyl chlorides*



An oven-dried 10 mL glass tube was charged with alkenyl-iminoindolines **1** (0.05 mmol), hydrazonoyl chlorides **2** (0.075 mmol) and K_2CO_3 (10.4 mg, 0.075 mmol) in mesitylene (0.5 mL). The mixture was then stirred rapidly at 40 ℃ in an oil bath for 4 h. Then the mixture was directly purified by column chromatography on silica gel with petroleum ether/ethyl acetate to afford the desired products **3a** – **3ax**, which were dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS.

Note: N-alkyl-substituted hydrazonoyl chlorides posed a challenge under the current conditions, likely due to the weaker acidity of the N–H bond.

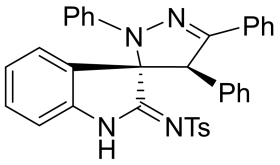
General procedure B: *formal (1 + 1 + 3) cyclization of iminoindolines, aldehydes and hydrazonoyl chlorides*



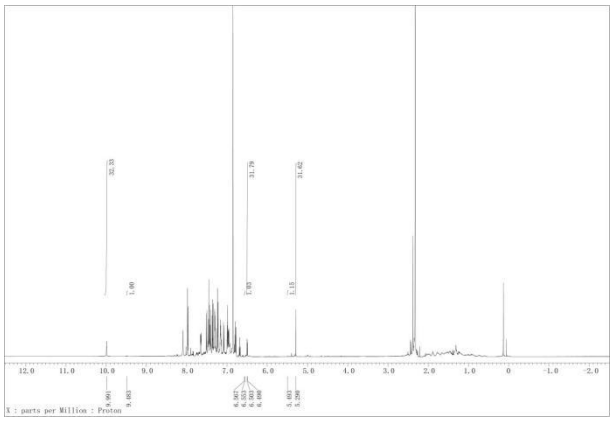
To an oven-dried 10 mL Schlenk tube were added iminoindolines **4** (0.05 mmol). The tube was evacuated and back-filled with argon three times. Under an argon atmosphere, anhydrous DCM (0.5 mL) was added *via* syringe, and the mixture was stirred at 0 °C. Subsequently, aldehydes **5** (0.075 mmol) and $BF_3{\cdot}OEt_2$ (0.075 mmol, 10.6 mg) were added to the solution. The reaction mixture was stirred at room temperature for 2 min. Afterward, under argon, hydrazonoyl chlorides **2** (0.075 mmol) and K_2CO_3 (0.2 mmol, 27.6 mg) were added sequentially. The mixture was stirred at 40 °C in an oil bath for 12 h. Upon completion, the crude mixture was directly purified by column chromatography on silica gel (petroleum

ether/ethyl acetate) to afford the desired product **3**, which was dried under vacuum and characterized by ^{1}H NMR, ^{13}C NMR, and HRMS.

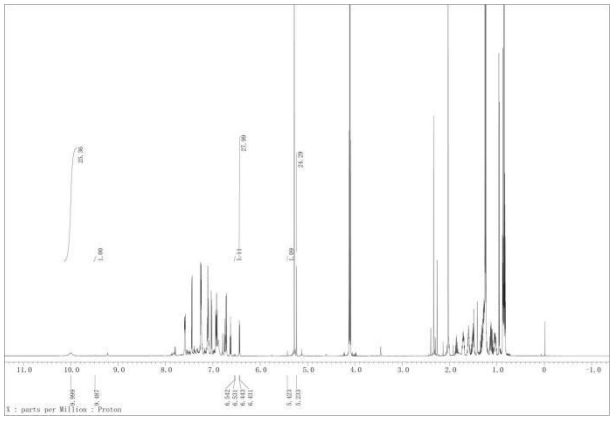
4-methyl-N-((Z)-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)benzenesulfonamide 3a



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3a** (28.1 mg, 99% yield) as a yellow solid.



Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3a** (23.0 mg, 81% yield) as a yellow solid.



Melting point, NMR and HRMS data for the product **3a**:

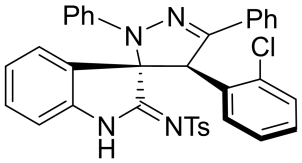
Melting point: 287.2 – 291.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.92 (s, 1H), 7.62 – 7.59 (m, 2H), 7.47 (d, *J* =8.4 Hz, 2H), 7.27 – 7.26 (m, 3H), 7.15 – 7.10 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.91 (m, 5H), 6.76 (t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 2H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.25 (s, 1H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.5, 149.2, 144.2, 142.9, 140.0, 138.1, 134.2, 131.5, 129.8, 129.3, 129.2, 128.8, 128.8, 128.6, 128.3, 128.0, 126.9, 126.4, 126.2, 126.0, 123.5, 121.1, 115.6, 111.1, 80.9, 64.7, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{28}N_4O_2SNa^+$: 591.1825, found: 591.1832.

N-((Z)-4'-(2-chlorophenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3b



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3b** (28.3 mg, 94% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3b**:

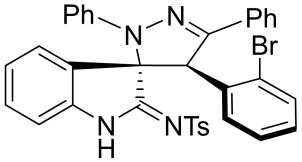
Melting point: 231.4 – 234.6 ºC.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.02 (s, 1H), 7.57 – 7.55 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.28 (m, 3H), 7.20 (t, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.14 – 7.10 (m, 3H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.95 – 6.92 (m, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 2H), 6.64 (t, *J* = 7.8 Hz, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 5.68 (s, 1H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 169.9, 148.7, 144.1, 142.8, 141.2, 138.1, 135.1, 132.4, 131.1, 130.7, 130.1, 129.5, 129.4, 129.2, 128.9, 128.8, 128.4, 126.9, 126.7, 126.2, 125.9, 125.6, 123.3, 121.3, 115.7, 111.3, 79.8, 60.1, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{35}ClN_4O_2SNa^+$: 625.1435, found: 625.1428; calculated for $C_{35}H_{27}{}^{37}ClN_4O_2SNa^+$: 627.1406, found: 627.1414.

N-((Z)-4'-(2-bromophenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3c



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3c** (29.1 mg, 90% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3c**:

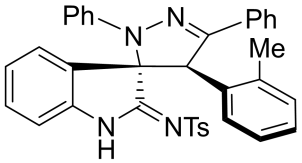
Melting point: 241.3 – 243.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.05 (s, 1H), 7.56 – 7.54 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.29 (m, 3H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 4.2 Hz, 2H), 7.05 – 6.99 (m, 4H), 6.95 – 6.92 (m, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.64 (t, *J* = 7.8 Hz, 1H), 6.29 (d, *J* = 7.8 Hz, 1H), 5.66 (s, 1H), 2.36 (s, 3H).

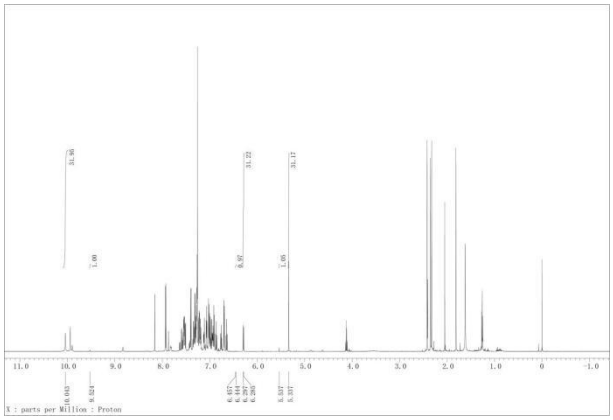
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 169.8, 149.0, 144.1, 142.9, 141.4, 138.2, 134.1, 132.9, 131.1, 130.9, 130.1, 129.6, 129.2, 128.9, 128.8, 128.4, 127.6, 126.8, 126.2, 126.2, 125.9, 125.5, 123.3, 121.4, 115.9, 111.4, 79.7, 62.5, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{79}BrN_4O_2SNa^+$: 669.0930, found: 669.0928; calculated for $C_{35}H_{27}{}^{81}BrN_4O_2SNa^+$: 671.0910, found: 671.0912.

N-((Z)-2',5'-diphenyl-4'-(o-tolyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3d



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3d** (24.4 mg, 84% yield) as a yellow solid.



Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3d** (18.9 mg, 65% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3d**:

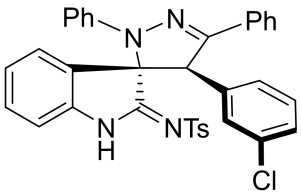
Melting point: 241.3 – 243.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.06 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.54 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.26 (m, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.13 – 7.12 (m, 1H), 7.08 – 7.05 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.94 – 6.90 (m, 3H), 6.76 (t, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.63 (t, *J* = 7.8 Hz, 1H), 6.29 (d, *J* = 7.8 Hz, 1H), 5.34 (s, 1H), 2.35 (s, 3H), 1.81 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.2, 150.1, 144.4, 142.8, 140.6, 138.1, 136.8, 132.5, 131.5, 130.5, 130.0, 129.6, 129.3, 129.2, 128.8, 128.3, 128.1, 126.8, 126.5, 126.4, 126.1, 125.8, 123.4, 121.1, 115.8, 111.2, 80.1, 59.9, 21.5, 19.2.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{36}H_{30}N_4O_2SNa^+$: 605.1982, found: 605.1977.

N-((Z)-4'-(3-chlorophenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3e



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel

chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3e** (20.5 mg, 68% yield) as a yellow solid.

Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3e** (16.6 mg, 55% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3e**:

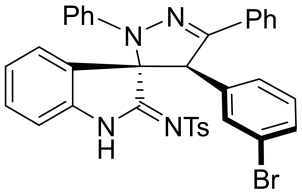
Melting point: 232.4 – 236.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.99 (s, 1H), 7.60 – 7.58 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.28 (m, 3H), 7.16 (t, *J* = 8.4 Hz, 1H), 7.13 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.07 – 7.05 (m, 3H), 6.97 – 6.93 (m, 3H), 6.90 – 6.82 (m, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.74 – 6.70 (m, 3H), 6.49 (d, *J* = 7.8 Hz, 1H), 5.19 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.1, 148.5, 143.9, 143.0, 140.1, 138.0, 136.4, 134.6, 131.1, 130.1, 129.9, 129.24, 129.18, 128.9, 128.8, 128.4, 128.3, 127.4, 126.8, 126.2, 125.5, 123.6, 121.3, 115.7, 111.4, 80.8, 64.0, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{35}ClN_4O_2SNa^+$: 625.1435, found: 625.1433; calculated for $C_{35}H_{27}{}^{37}ClN_4O_2SNa^+$: 627.1406, found: 627.1408.

N-((Z)-4'-(3-bromophenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3f



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3f** (22.6 mg, 70% yield) as a yellow solid.

Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3f** (12.3 mg, 38% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3f**:

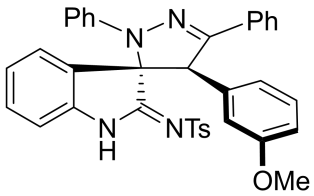
Melting point: 231.3 – 234.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.90 (s, 1H), 7.59 – 7.57 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.28 (m, 4H), 7.19 – 7.16 (m, 1H), 7.05 (d, *J* = 8.4 Hz, 3H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.96 – 6.94 (m, 3H), 6.87 (s, 1H), 6.78 (t, *J* = 6.6 Hz, 1H), 6.73 – 6.71 (m, 3H), 6.49 (d, *J* = 7.8 Hz, 1H), 5.17 (s, 1H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.1, 148.5, 144.0, 143.0, 140.0, 138.0, 136.6, 132.1, 131.3, 131.1, 130.2, 130.1, 129.2, 129.0, 128.8, 128.5, 127.9, 126.8, 126.3, 126.2, 125.5, 123.6, 122.7, 121.4, 115.7, 111.3, 80.8, 64.0, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{35}H_{27}{}^{79}BrN_4O_2SH^+$: 647.1111, found: 647.1109; calculated for $C_{35}H_{27}{}^{81}BrN_4O_2SH^+$: 649.1091, found: 649.1095.

N-((Z)-4'-(3-methoxyphenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3g



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3g** (16.2 mg, 54% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3g**:

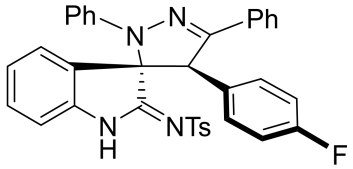
Melting point: 185.0 – 188.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.07 (s, 1H), 7.63 – 7.62 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.27 (m, 3H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.05 – 7.01 (m, 3H), 6.97 – 6.93 (m, 3H), 6.77 – 6.74 (m, 3H), 6.69 – 6.66 (m, 2H), 6.53 (d, *J* = 7.8 Hz, 2H), 6.44 – 6.41 (m, 1H), 5.22 (s, 1H), 3.59 (s, 3H), 2.35 (s, 3H).

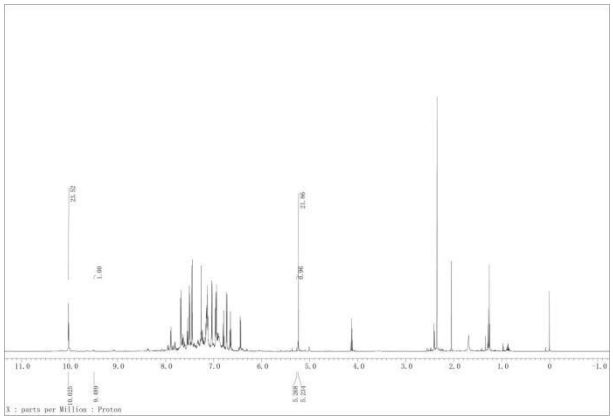
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.5, 159.6, 149.0, 144.1, 142.9, 140.1, 138.1, 135.7, 131.5, 129.8, 129.5, 129.2, 128.8, 128.7, 128.6, 128.3, 126.8, 126.2, 125.9, 123.5, 121.6, 121.0, 115.5, 114.7, 113.7, 111.3, 80.8, 64.6, 55.1, 21.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{36}H_{30}N_4NaO_3S^+$: 621.1931, found: 621.1931.

N-((Z)-4'-(4-fluorophenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3h



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3h** (14.9 mg, 51% yield) as a yellow solid.



Melting point, NMR and HRMS data for the product **3h**:

Melting point: 221.5 – 227.9 °C.

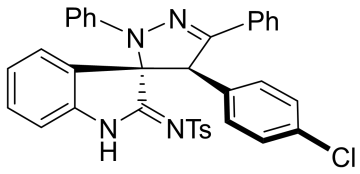
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.97 (s, 1H), 7.59 – 7.58 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.27 (m, 3H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.93 (m, 3H), 6.91 – 6.85 (m, 2H), 6.83 – 6.80 (m, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.73 – 6.69 (m, 3H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.25 (s, 1H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.3, 162.3 (d, $J_{C\text{-}F}$ = 248.5 Hz, 1C), 148.9, 144.0, 143.0, 140.0, 138.0, 131.3, 130.9 (d, $J_{C\text{-}F}$ = 7.2 Hz, 1C), 130.1 (d, $J_{C\text{-}F}$ = 2.9 Hz, 1C), 130.0, 129.2, 128.9, 128.8, 128.4, 126.9, 126.2, 125.8, 123.6, 121.2, 115.7, 115.6, 115.5, 111.3, 80.8, 63.9, 21.5.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -113.1 – -113.2 (m, 1F).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}FN_4O_2SNa^+$: 609.1731, found: 609.1726.

N-((Z)-4'-(4-chlorophenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3i



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3i** (24.9 mg, 83% yield) as a yellow solid.

Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3i** (18.4 mg, 61% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3i**:

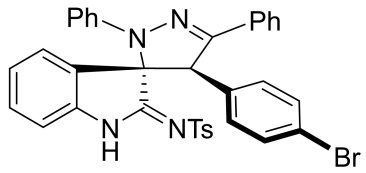
Melting point: 163.4 – 167.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.03 (s, 1H), 7.59 – 7.57 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.27 (m, 3H), 7.16 – 7.13 (m, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.96 – 6.92 (m, 3H), 6.85 – 6.84 (m, 2H), 6.77 (t, *J* = 7.8 Hz, 1H), 6.74 – 6.70 (m, 3H), 6.49 (d, *J* = 7.2 Hz, 1H), 5.24 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.2, 148.7, 144.0, 143.0, 140.1, 138.0, 134.0, 132.8, 131.2, 130.6, 130.1, 129.2, 128.9, 128.8, 128.4, 126.8, 126.21, 126.18, 125.6, 123.6, 121.2, 115.6, 111.5, 80.8, 63.9, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{35}ClN_4O_2SNa^+$: 625.1435, found: 625.1426; calculated for $C_{35}H_{27}{}^{37}ClN_4O_2SNa^+$: 627.1406, found: 627.1415.

N-((Z)-4'-(4-bromophenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3j



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3j** (20.1 mg, 62% yield) as a yellow solid.

Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3j** (13.6 mg, 42% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3j**:

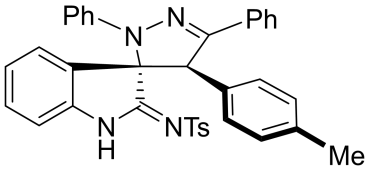
Melting point: 139.3 – 143.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.91 (s, 1H), 7.57 – 7.56 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.27 (m, 3H), 7.26 – 7.24 (m, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.93 (m, 3H), 6.78 – 6.76 (m, 3H), 6.74 – 6.71 (m, 3H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.21 (s, 1H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.2, 148.7, 144.0, 143.0, 140.0, 138.0, 133.3, 131.8, 131.2, 130.9, 130.1, 129.2, 128.9, 128.8, 128.4, 126.8, 126.3, 126.2, 125.6, 123.7, 122.2, 121.3, 115.7, 111.3, 80.7, 64.0, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{79}BrN_4O_2SNa^+$: 669.0930, found 669.0927; calculated for $C_{35}H_{27}{}^{81}BrN_4O_2SNa^+$: 671.0910, found: 671.0916.

<u>N-((Z)-2',5'-diphenyl-4'-(p-tolyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3k</u>



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel

chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3k** (14.6 mg, 50% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3k**:

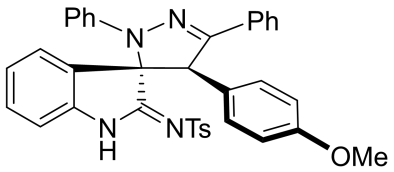
Melting point: 210.4 – 213.6 ºC.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.87 (s, 1H), 7.61 – 7.60 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.27 – 7.26 (m, 3H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.90 (m, 5H), 6.79 – 6.75 (m, 3H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 7.2 Hz, 1H), 5.21 (s, 1H), 2.35 (s, 3H), 2.22 (s, 3H).

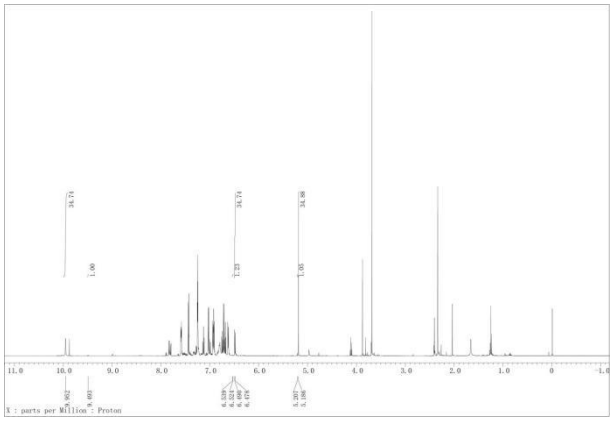
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.6, 149.5, 144.3, 142.9, 140.0, 138.1, 137.8, 131.6, 131.1, 129.8, 129.3, 129.2, 129.1, 128.8, 128.7, 128.3, 126.9, 126.5, 126.2, 126.1, 123.5, 121.1, 115.7, 111.0, 80.9, 64.4, 21.5, 21.1.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{36}H_{30}N_4O_2SNa^+$: 605.1982, found 605.1986.

N-((Z)-4'-(4-methoxyphenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3l



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3l** (12.3 mg, 41% yield) as a yellow solid.



Melting point, NMR and HRMS data for the product **3l**:

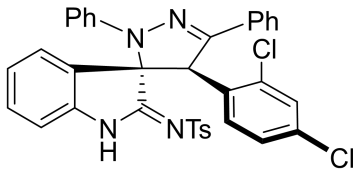
Melting point: 231.1 – 234.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.85 (s, 1H), 7.61 – 7.59 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.26 (m, 3H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.93 (m, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.73 – 6.69 (m, 3H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.51 (d, *J* = 6.6 Hz, 1H), 5.20 (s, 1H), 3.70 (s, 3H), 2.35 (s, 3H).

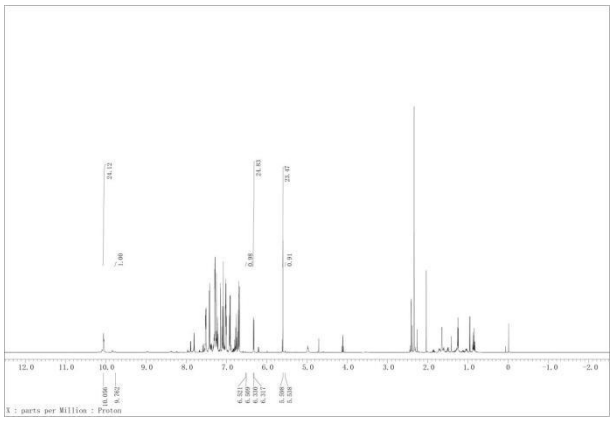
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.5, 159.2, 149.5, 144.3, 142.9, 140.0, 138.1, 131.6, 130.4, 129.8, 129.2, 128.8, 128.7, 128.3, 126.9, 126.5, 126.2, 126.1, 123.6, 121.1, 115.7, 114.0, 111.1, 80.9, 64.1, 55.2, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{36}H_{30}N_4O_3SH^+$: 599.2111, found 599.2116.

N-((Z)-4'-(2,4-dichlorophenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3m



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3m** (26.7 mg, 84% yield) as a yellow solid.



Melting point, NMR and HRMS data for the product **3m**:

Melting point: 134.1 – 137.1 °C.

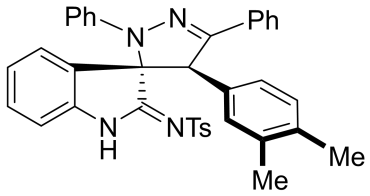
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.11 (s, 1H), 7.54 – 7.53 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.30 (m, 3H), 7.22 (t, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 1.8 Hz, 1H), 7.13 – 7.08 (m,

2H), 7.04 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.95 – 6.92 (m, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.73 – 6.70 (m, 3H), 6.34 (d, *J* = 7.8 Hz, 1H), 5.62 (s, 1H), 2.36 (s, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 169.7, 148.2, 143.9, 142.9, 141.2, 138.0, 135.8, 134.6, 131.5, 131.2, 130.9, 130.3, 129.4, 129.2, 129.0, 128.8, 128.5, 127.3, 126.7, 126.2, 125.7, 125.3, 123.5, 121.4, 115.7, 111.6, 79.7, 59.6, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{26}{}^{35}Cl^{35}ClN_4O_2SNa^+$: 659.1046, found: 659.1040; calculated for $C_{35}H_{26}{}^{37}Cl^{35}ClN_4O_2SNa^+$: 661.1016, found: 661.1021.

N-((Z)-4'-(3,4-dimethylphenyl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3n



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^1H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3n** (19.1 mg, 64% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3n**:

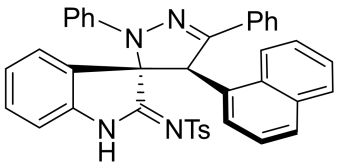
Melting point: 249.2 – 253.1 °C.

^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.90 (s, 1H), 7.62 – 7.60 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.26 (m, 3H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.91 (m, 3H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.77 – 6.72 (m, 3H), 6.67 – 6.64 (m, 3H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.15 (s, 1H), 2.35 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 170.6, 149.6, 144.3, 142.9, 140.0, 138.2, 136.8, 136.3, 131.7, 131.4, 130.3, 129.7, 129.2, 128.8, 128.6, 128.3, 126.9, 126.5, 126.2, 126.1, 123.4, 121.0, 115.6, 111.0, 80.9, 64.4, 21.5, 19.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{37}H_{32}N_4O_2SNa^+$: 619.2138, found 619.2139.

4-methyl-N-((Z)-4'-(naphthalen-1-yl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)benzenesulfonamide 3o



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3o** (15.1 mg, 49% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3o**:

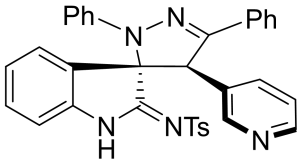
Melting point: 252.4 – 255.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.96 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 4.2 Hz, 1H), 7.58 (d, *J* = 6.0 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.31 – 7.29 (m, 3H), 7.25 – 7.22 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.93 (m, 2H), 6.85 (t, *J* = 7.8 Hz, 1H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.74 – 6.71 (m, 3H), 6.30 (t, *J* = 7.8 Hz, 1H), 6.19 (d, *J* = 7.8 Hz, 1H), 6.02 (s, 1H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.5, 149.3, 144.3, 143.0, 140.1, 138.1, 133.7, 131.8, 131.5, 130.3, 129.6, 129.2, 128.82, 128.75, 128.6, 128.4, 127.8, 126.9, 126.6, 126.2, 126.0, 125.9, 125.6, 125.0, 122.9, 122.0, 121.1, 115.6, 110.9, 80.3, 59.3, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{39}H_{30}N_4O_2SNa^+$: 641.1982, found: 641.1977.

N-((Z)-2',5'-diphenyl-4'-(pyridin-3-yl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3p



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3p** (18.8 mg, 66% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3p**:

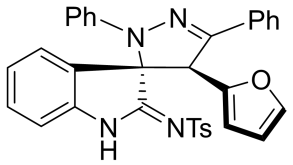
Melting point: 130.5 – 135.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.92 (s, 1H), 8.40 (d, *J* = 4.2 Hz, 1H), 8.14 (s, 1H), 7.56 – 7.55 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.27 (m, 4H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.11 – 7.08 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.96 – 6.94 (m, 3H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.73 – 6.70 (m, 3H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.30 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 169.9, 150.2, 149.2, 147.9, 143.8, 143.2, 140.0, 137.9, 136.8, 130.8, 130.42, 130.37, 129.3, 129.1, 129.0, 128.9, 128.5, 126.8, 126.3, 125.3, 123.8, 123.4, 121.5, 115.8, 111.6, 80.8, 62.0, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{34}H_{27}N_5O_2SH^+$: 570.1958, found: 570.1962.

N-((Z)-4'-(furan-2-yl)-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3q



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3q** (14.2 mg, 51% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3q**:

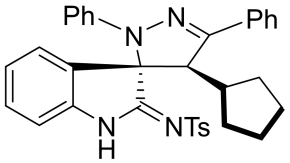
Melting point: 211.9 – 215.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.95 (s, 1H), 7.63 – 7.61 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.30 (m, 3H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.95 – 6.93 (m, 2H), 6.86 – 6.82 (m, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.13 (s, 1H), 6.05 (d, *J* = 3.0 Hz, 1H), 5.44 (s, 1H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.0, 147.6, 146.1, 143.8, 143.0, 142.7, 140.1, 138.0, 131.4, 130.2, 129.2, 128.9, 128.8, 128.4, 126.5, 126.2, 126.1, 125.7, 123.9, 121.1, 115.3, 111.2, 110.6, 110.6, 80.0, 58.5, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{33}H_{26}N_4O_3SNa^+$: 581.1618, found 581.1619.

N-((Z)-4'-cyclopentyl-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3r



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3r** (9.2 mg, 33% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3r**:

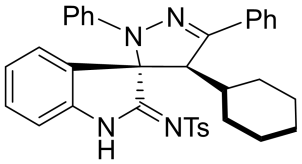
Melting point: 101.1 – 104.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.89 (s, 1H), 7.56 – 7.55 (m, 2H), 7.50 – 7.47 (m, 3H), 7.38 – 7.36 (m, 4H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.07 – 7.04 (m, 3H), 6.93 – 6.90 (m, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 2H), 4.08 (d, *J* = 7.8 Hz, 1H), 2.34 (s, 3H), 2.09 – 2.02 (m, 1H), 1.44 – 1.39 (m, 1H), 1.33 – 1.30 (m, 1H), 1.26 – 1.19 (m, 2H), 1.17 – 1.14 (m, 1H), 1.11 – 1.06 (m, 1H), 1.03 – 0.98 (m, 1H), 0.90 – 0.84 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 171.0, 153.0, 144.4, 143.0, 140.7, 138.0, 134.0, 130.4, 129.2, 128.74, 128.66, 128.2, 127.7, 126.3, 126.2, 124.0, 121.2, 116.2, 111.7, 81.1, 63.8, 40.4, 31.6, 25.3, 24.2, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{34}H_{32}N_4O_2SNa^+$: 583.2138, found 583.2138.

N-((Z)-4'-cyclohexyl-2',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3s



Prepared according to general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3s** (15.8 mg, 55% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3s**:

Melting point: 228.4 – 231.7 °C.

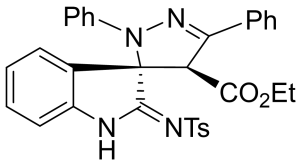
^{1}H NMR (600 MHz, CDCl3) δ (ppm): 9.93 (s, 1H), 7.61 – 7.59 (m, 2H), 7.48 (d, *J* = 7.8 Hz,

1H), 7.41 – 7.40 (m, 3H), 7.39 – 7.37 (m, 3H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.93 – 6.90 (m, 2H), 6.75 (t, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 7.2 Hz, 2H), 3.79 (d, *J* = 2.4 Hz, 1H), 2.34 (s, 3H), 1.96 (d, *J* = 13.2 Hz, 1H), 1.61 – 1.57 (m, 2H), 1.48 – 1.47 (m, 2H), 1.27 – 1.26 (m, 1H), 1.11 – 1.09 (m, 1H), 1.00 – 0.99 (m, 1H), 0.96 – 0.92 (m, 1H), 0.87 – 0.80 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 170.5, 152.8, 144.7, 142.8, 141.0, 138.2, 133.7, 130.5, 129.1, 128.9, 128.6, 128.3, 127.4, 126.6, 126.1, 125.9, 123.9, 121.2, 116.4, 112.0, 81.4, 63.0, 39.4, 33.8, 29.5, 27.0, 25.9, 25.7, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{35}H_{34}N_4O_2SH^+$: 575.2475, found: 575.2472.

ethyl-(Z)-2',5'-diphenyl-2-(tosylimino)-2',4'-dihydrospiro[indoline-3,3'-pyrazole]-4'-carboxylate 3t



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3t** (20.3 mg, 72% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3t**:

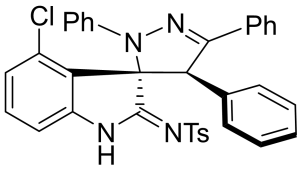
Melting point: 212.1 – 214.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.14 (s, 1H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.30 (d, *J* = 6.6 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.06 – 7.05 (m, 3H), 6.95 – 6.93 (m, 2H), 6.74 (t, *J* = 6.6 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 2H), 5.05 (s, 1H), 3.83 – 3.80 (m, 1H), 3.76 – 3.73 (m, 1H), 2.34 (s, 3H), 0.83 (t, *J* = 6.6 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 170.0, 166.5, 144.3, 143.2, 143.1, 140.6, 137.7, 131.3, 130.9, 129.2, 129.0, 128.8, 128.5, 126.2, 126.1, 126.0, 125.5, 124.3, 121.1, 115.0, 111.6, 77.9, 64.6, 61.7, 21.5, 13.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{32}H_{28}N_4O_4SNa^+$: 587.1723, found: 587.1720.

N-((Z)-4-chloro-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3u



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3u** (24.9 mg, 83% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3u**:

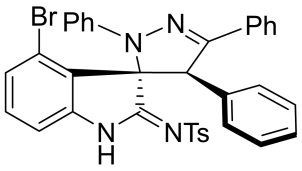
Melting point: 220.4 – 223.2 °C.

^{1}H NMR (600 MHz, CDCl3) δ (ppm): 10.07 (s, 1H), 7.62 – 7.60 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.28 – 7.27 (m, 3H), 7.19 – 7.15 (m, 3H), 7.08 – 7.05 (m, 3H), 6.97 – 6.95 (m, 2H), 6.90 – 6.86 (m, 3H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 2.4 Hz, 1H), 5.26 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.1, 149.1, 143.9, 143.1, 138.5, 137.9, 133.8, 131.3, 129.8, 129.3, 129.1, 128.9, 128.8, 128.40, 128.37, 127.8, 126.9, 126.6, 126.2, 121.3, 115.5, 112.1, 80.6, 65.0, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{35}H_{27}{}^{35}ClN_4O_2SNa^+$: 603.1616, found: 603.1621; calculated for $C_{35}H_{27}{}^{37}ClN_4O_2SNa^+$: 605.1587, found: 605.1600.

N-((Z)-4-bromo-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3v



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3v** (22.6 mg, 70% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3v**:

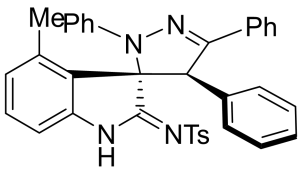
Melting point: 228.3 – 229.5 °C.

^{1}H NMR (600 MHz, CDCl3) δ (ppm): 10.10 (s, 1H), 7.62 – 7.61 (m, 2H), 7.46 – 7.42 (m, 2H), 7.29 – 7.27 (m, 3H), 7.24 – 7.18 (m, 4H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.98 – 6.95 (m, 2H), 6.90 – 6.90 (m, 2H), 6.85 – 6.78 (m, 2H), 6.73 – 6.72 (m, 2H), 6.51 – 6.51 (m, 1H), 5.25 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 169.9, 149.1, 143.9, 143.1, 139.0, 137.8, 133.8, 132.6, 131.3, 129.7, 129.4, 129.3, 129.1, 128.9, 128.8, 128.44, 128.38, 128.1, 126.9, 126.2, 121.3, 116.4, 115.52, 115.46, 80.7, 65.0, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{35}H_{27}{}^{79}BrN_4O_2SNa^+$: 647.1111, found: 647.1109; calculated for $C_{35}H_{27}{}^{81}BrN_4O_2SNa^+$: 649.1090, found: 649.1099.

4-methyl-N-((Z)-4-methyl-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)benzenesulfonamide 3w



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3w** (17.8 mg, 61% yield) as a yellow solid.

Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3w** (15.0 mg, 46% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3w**:

Melting point: 240.1 – 243.2 °C.

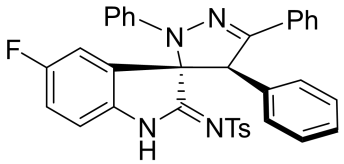
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.92 (s, 1 H), 7.61 – 7.60 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.26 (m, 3H), 7.15 – 7.12 (m, 3H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.95 – 6.93 (m, 4H), 6.78 – 6.73 (m, 4H), 6.45 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 7.2 Hz, 1H), 5.21 (s, 1H), 2.35 (s, 3H), 2.22 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.8, 149.3, 144.3, 142.8, 140.3, 140.2, 138.2, 134.3, 131.5, 129.3, 129.2, 128.8, 128.7, 128.6, 128.3, 128.0, 126.9, 126.2, 126.0, 124.2, 122.8,

121.0, 115.7, 112.0, 80.7, 64.3, 21.6, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{36}H_{30}N_4O_2SH^+$: 583.2162, found 583.2168.

N-((Z)-5-fluoro-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3x



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3x** (27.0 mg, 92% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3x**:

Melting point: 228.3 – 229.5 °C.

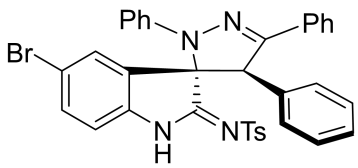
^{1}H NMR (600 MHz, CDCl3) δ (ppm): 9.99 (s, 1H), 7.60 – 7.58 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.25 (m, 4H), 7.16 – 7.12 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.96 – 6.91 (m, 3H), 6.78 (t, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 9.0 Hz, 2H), 6.65 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.38 – 6.32 (m, 2H), 5.21 (s, 1H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.6, 163.6 (d, J_{C-F} = 248.5 Hz, 1C), 149.3, 144.1, 143.2, 141.4 (d, J_{C-F} = 11.5 Hz, 1C), 137.8, 134.1, 131.4, 129.3, 129.2, 128.9, 128.8, 128.4, 128.2, 127.6 (d, J_{C-F} = 10.1 Hz, 1C), 126.9, 126.3, 121.4, 115.8, 110.2, 110.1, 99.8 (d, J_{C-F} = 27.5 Hz, 1C), 80.3, 64.5, 21.5.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -108.90 – -108.94 (m, 1F).

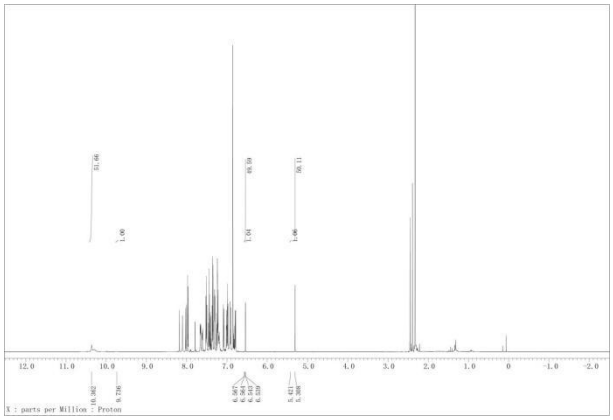
HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{35}H_{27}FN_4O_2SH^+$: 587.1912, found: 587.1901.

N-((Z)-5-bromo-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3y



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel

chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3y** (20.7 mg, 64% yield) as a yellow solid.



Melting point, NMR and HRMS data for the product **3y**:

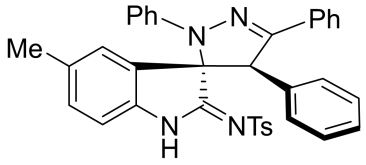
Melting point: 210.6 – 213.2 °C.

^{1}H NMR (600 MHz, CDCl3) δ (ppm): 10.08 (s, 1H), 7.62 – 7.61 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.27 (m, 3H), 7.22 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.20 – 7.16 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.97 – 6.94 (m, 2H), 6.89 (brs, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.74 – 6.72 (m, 2H), 6.51 (d, *J* = 1.8 Hz, 1H), 5.25 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ (ppm): 169.9, 149.0, 143.9, 143.1, 138.9, 137.8, 133.8, 132.6, 131.2, 129.4, 129.2, 129.1, 128.9, 128.8, 128.44, 128.37, 128.1, 126.9, 126.2, 121.2, 116.4, 115.4, 112.6, 80.6, 65.0, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{79}BrN_4O_2SNa^+$: 669.0930, found: 669.0919; calculated for $C_{35}H_{27}{}^{81}BrN_4O_2SNa^+$: 671.0910, found: 671.0904.

4-methyl-N-((Z)-5-methyl-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)benzenesulfonamide 3z



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3z** (18.9 mg, 65% yield) as a yellow solid.

Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel

chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3z** (16.2 mg, 50% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3z**:

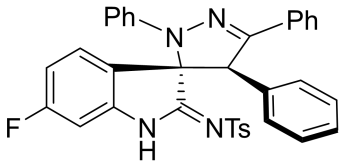
Melting point: 222.3 – 223.2 °C.

^{1}H NMR (600 MHz, CDCl3) δ (ppm): 9.86 (s, 1H), 7.61 – 7.59 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.26 (m, 3H), 7.15 – 7.12 (m, 3H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.93 (m, 4H), 6.76 (t, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 3H), 6.46 (d, *J* = 7.2 Hz, 1H), 6.30 (d, *J* = 8.4 Hz, 1H), 5.20 (s, 1H), 2.35 (s, 3H), 2.23 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.8, 149.3, 144.3, 142.8, 140.3, 140.2, 138.2, 134.3, 131.5, 129.3, 129.2, 128.8, 128.7, 128.6, 128.3, 128.0, 126.9, 126.2, 126.0, 124.3, 122.8, 121.1, 115.7, 111.9, 80.7, 64.3, 21.6, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{36}H_{30}N_4O_2SNa^+$: 583.2162, found 583.2162.

N-((Z)-6-fluoro-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3aa



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3aa** (21.4 mg, 73% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3aa**:

Melting point: 236.3 – 240.1 °C.

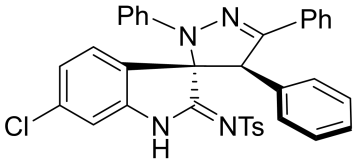
^{1}H NMR (600 MHz, CDCl3) δ (ppm): 10.12 (s, 1H), 7.62 – 7.60 (m, 2H), 7.48 – 7.47 (m, 2H), 7.28 – 7.27 (m, 3H), 7.16 – 7.14 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.98 – 6.95 (m, 2H), 6.92 – 6.86 (m, 2H), 6.79 (t, *J* = 6.6 Hz, 1H), 6.74 – 6.73 (m, 2H), 6.70 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.37 – 6.32 (m, 2H), 5.24 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.7, 163.5 (d, J_{C-F} = 250.1 Hz, 1C), 149.3, 144.1, 143.2, 141.4 (d, J_{C-F} = 11.6 Hz, 1C), 137.8, 134.1, 131.3, 129.3, 129.2, 128.83, 128.81, 128.7, 128.3, 128.2, 127.4 (d, J_{C-F} = 10.1 Hz, 1C), 126.9, 126.2, 121.4 (d, J_{C-F} = 2.9 Hz, 1C), 121.2, 115.7, 110.1 (d, J_{C-F} = 21.7 Hz, 1C), 100.1 (d, J_{C-F} = 28.8 Hz, 1C), 80.3, 64.5, 21.5.

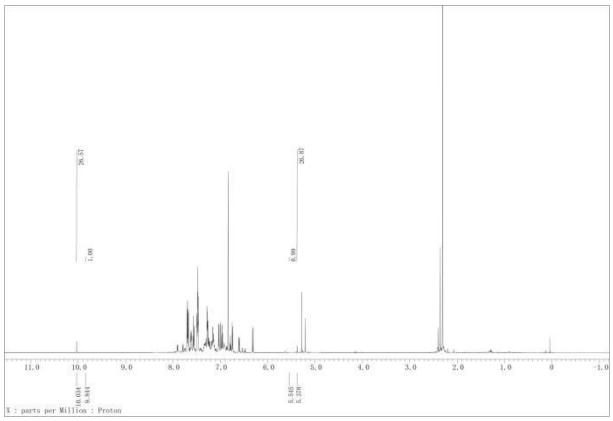
^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -108.89 – -108.93 (m, 1F).

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{35}H_{27}FN_4O_2SH^+$: 587.1912, found 587.1911.

N-((Z)-6-chloro-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3ab



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ab** (30.4 mg, 90% yield) as a yellow solid.



Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ab** (26.1 mg, 78% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ab**:

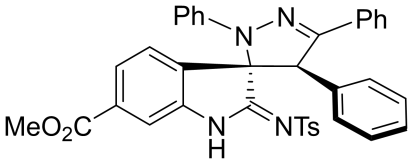
Melting point: 217.4 – 220.3 °C.

^{1}H NMR (600 MHz, CDCl3) δ (ppm): 10.10 (s, 1H), 7.62 – 7.60 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.26 (m, 3H), 7.17 – 7.13 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.98 – 6.95 (m, 3H), 6.92 – 6.87 (m, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.2 Hz, 2H), 6.62 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.33 (d, *J* = 7.8 Hz, 1H), 5.24 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.2, 149.3, 144.1, 143.1, 141.2, 137.8, 135.6, 134.0, 131.3, 129.3, 129.2, 128.9, 128.84, 128.78, 128.3, 128.2, 127.0, 126.9, 126.2, 124.4, 123.4, 121.3, 115.7, 112.0, 80.4, 64.6, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{35}H_{27}{}^{35}ClN_4O_2SNa^+$: 603.1616, found: 603.1621; calculated for $C_{35}H_{27}{}^{37}ClN_4O_2SNa^+$: 605.1587, found: 605.1600.

Methyl-(Z)-2',4',5'-triphenyl-2-(tosylimino)-2',4'-dihydrospiro[indoline-3,3'-pyrazole]-6-carboxylate 3ac



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ac** (25.0 mg, 80% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ac**:

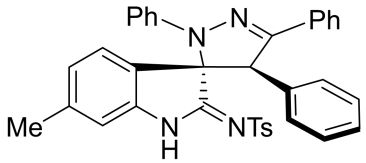
Melting point: 241.8 – 245.7 °C.

^{1}H NMR (600 MHz, CDCl3) δ (ppm): 10.11 (s, 1H), 7.64 (s, 1H), 7.61 – 7.60 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.27 – 7.26 (m, 3H), 7.14 – 7.11 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.91 (m, 4H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 1H), 5.30 (s, 1H), 3.85 (s, 3H), 2.35 (s, 3H).

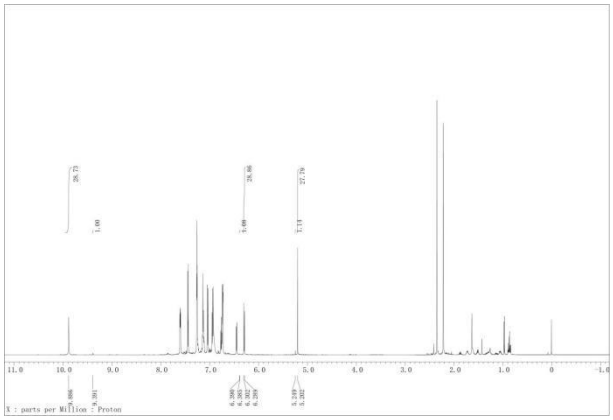
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.1, 165.9, 149.2, 144.0, 143.1, 140.4, 137.8, 133.8, 131.7, 131.2, 131.0, 129.2, 129.1, 128.9, 128.8, 128.34, 128.30, 126.9, 126.2, 126.1, 124.9, 121.3, 115.6, 112.0, 80.6, 65.0, 52.4, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{37}H_{30}N_4O_4SH^+$: 627.2061, found 627.2061.

4-methyl-N-((Z)-6-methyl-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)benzenesulfonamide 3ad



Prepared according to the general Procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ad** (23.9 mg, 82% yield) as a yellow solid.



Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ad** (15.7 mg, 54% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ad**:

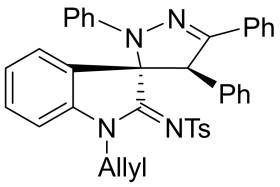
Melting point: 226.3 – 228.7 °C.

^{1}H NMR (600 MHz, CDCl3) δ (ppm): 9.37 (s, 1H), 7.55 – 7.53 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.24 – 7.22 (m, 5H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.13 – 7.10 (m, 2H), 6.99 – 6.96 (m, 5H), 6.90 – 6.84 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 3H), 6.73 (t, *J* = 7.2 Hz, 1H), 5.35 (s, 1H), 2.36 (s, 3H), 2.33 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ (ppm): 166.2, 147.0, 143.9, 142.5, 140.0, 138.1, 135.1, 132.0, 131.3, 130.0, 129.0, 128.9, 128.5, 128.24, 128.22, 128.1, 126.8, 126.7, 126.1, 120.2, 114.0, 109.2, 80.5, 64.5, 21.4, 17.3.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for $C_{36}H_{30}N_4O_2SNa^+$: 583.2162, found 583.2165.

N-((Z)-1-allyl-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3ae



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel

chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ae** (10.3 mg, 34% yield) as a yellow oil.

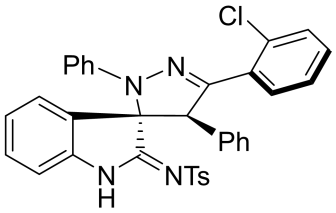
NMR and HRMS data for the product **3ae**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.61 (d, *J* = 7.8 Hz, 4H), 7.26 – 7.24 (m, 3H), 7.04 – 7.00 (m, 4H), 6.94 – 6.92 (m, 6H), 6.72 – 6.69 (m, 2H), 6.67 – 6.62 (m, 4H), 6.01 (s, 1H), 5.88 – 5.83 (m, 1H), 5.32 – 5.27 (m, 2H), 4.74 (dd, *J* = 15.6, 5.4 Hz, 1H), 4.64 (dd, *J* = 15.6, 5.4 Hz, 1H), 2.25 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 167.8, 149.0, 143.6, 141.9, 141.4, 139.7, 134.1, 131.8, 130.2, 129.7, 129.3, 128.7, 128.5, 128.2, 128.1, 127.7, 127.0, 126.9, 126.5, 126.1, 123.3, 120.6, 119.3, 115.2, 110.0, 80.6, 65.2, 46.0, 21.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{38}H_{32}N_4O_2SNa^+$: 631.2138, found: 631.2132.

N-((Z)-5'-(2-chlorophenyl)-2',4'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3af



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3af** (23.2 mg, 77% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3af**:

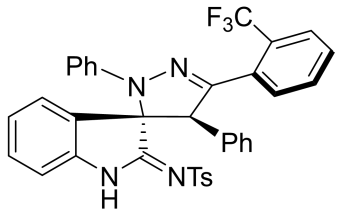
Melting point: 181.4 – 184.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.90 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.58 (m, 1H), 7.34 – 7.33 (m, 1H), 7.21 – 7.18 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.07 – 7.03 (m, 3H), 6.97 – 6.94 (m, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 2H), 6.79 – 6.75 (m, 3H), 6.68 (t, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 5.67 (s, 1H), 2.38 (s, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 170.2, 148.2, 143.9, 143.2, 139.8, 138.0, 133.3, 132.8, 130.8, 130.6, 129.9, 129.7, 129.4, 129.3, 128.8, 128.3, 127.9, 126.6, 126.5, 126.2, 125.3, 123.5, 121.5, 115.9, 111.1, 81.5, 66.5, 21.5.

HRMS(ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{35}ClN_4O_2SNa^+$: 625.1435, found: 625.1437; calculated for $C_{35}H_{27}{}^{37}ClN_4O_2SNa^+$: 627.1406, found: 627.1406.

N-((Z)-2',4'-diphenyl-5'-(2-(trifluoromethyl)phenyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3ag



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^1H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ag** (25.4 mg, 80% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ag**:

Melting point: 170.2 – 174.3 °C.

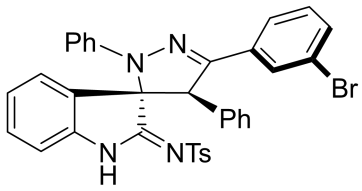
^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.15 (s, 1H), 7.79 – 7.78 (m, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.30 – 7.28 (m, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.04 – 7.01 (m, 1H), 7.01 – 6.96 (m, 3H), 6.94 – 6.91 (m, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.82 – 6.80 (m, 3H), 6.76 – 6.73 (m, 3H), 6.70 (t, J = 7.8 Hz, 1H), 5.63 (s, 1H), 2.39 (s, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 170.8, 145.7, 143.6, 143.4, 139.5, 137.8, 132.7, 131.4, 130.6, 130.2, 130.0, 129.39, 129.37, 128.83 (q, J_{C-F} =234.2 Hz, 1C), 128.80, 128.3, 127.8, 127.4 (q, J_{C-F} =5.7 Hz, 1C), 126.5, 126.0, 125.7 (q, J_{C-F} =199.6 Hz, 1C), 125.0, 123.6, 122.4 (q, J_{C-F} =274.8 Hz, 1C), 121.3, 115.3, 111.3, 81.8, 66.9, 21.5.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -57.7 (s, 3F).

HRMS(ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{36}H_{27}F_3N_4O_2SNa^+$: 659.1699, found: 659.1702.

N-((Z)-5'-(3-bromophenyl)-2',4'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3ah



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ah** (20.7 mg, 64% yield) as a yellow solid.

Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ah** (13.9 mg, 43% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ah**:

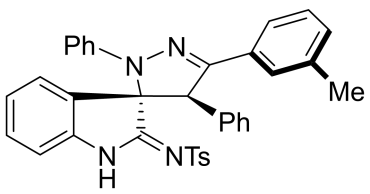
Melting point: 236.3 – 239.9 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.91 (s, 1H), 7.91 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.15 – 7.13 (m, 4H), 7.09 (t, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.96 – 6.93 (m, 3H), 6.89 (s, 1H), 6.81 – 6.77 (m, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 5.17 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.2, 147.7, 143.8, 143.1, 140.0, 138.0, 133.7, 133.6, 131.6, 130.0, 129.9, 129.4, 129.24, 129.16, 128.8, 128.7, 128.3, 126.4, 126.2, 125.6, 125.5, 123.6, 122.6, 121.4, 115.7, 111.2, 80.9, 64.3, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{79}BrN_4O_2SNa^+$: 669.0930, found: 669.0924; calculated for $C_{35}H_{27}{}^{81}BrN_4O_2SNa^+$: 671.0910, found: 671.0907.

N-((Z)-2',4'-diphenyl-5'-(m-tolyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3ai



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ai** (15.7 mg, 54% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ai**:

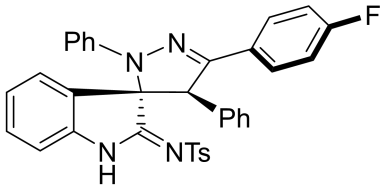
Melting point: 228.7 – 230.4 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.91 (s, 1H), 7.55 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.14 – 7.11 (m, 5H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.91 (m, 5H), 6.76 (t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 2H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 5.24 (s, 1H), 2.35 (s, 3H), 2.31 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.5, 149.4, 144.2, 142.9, 140.0, 138.1, 137.9, 134.3, 131.4, 129.8, 129.7, 129.23, 129.17, 128.8, 128.6, 128.2, 128.0, 127.4, 126.4, 126.2, 126.0, 124.2, 123.5, 121.1, 115.7, 111.1, 80.8, 64.7, 21.5, 21.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{36}H_{30}N_4O_2SNa^+$: 605.1982, found: 605.1980.

N-((Z)-5'-(4-fluorophenyl)-2',4'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3aj



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3aj** (12.9 mg, 44% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3aj**:

Melting point: 240.5 – 242.8 °C.

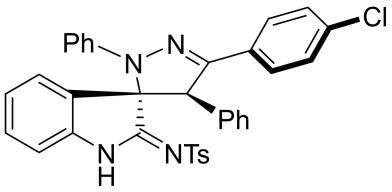
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.88 (s, 1H), 7.59 – 7.56 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.13 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.97 – 6.94 (m, 4H), 6.92 – 6.90 (m, 3H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.66 (t, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 5.20 (s, 1H), 2.36 (s, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 170.4, 163.0 (d, J_{C-F} = 250.0 Hz, 1C), 148.3, 144.1, 143.0, 140.0, 138.1, 134.0, 129.9, 129.2, 128.8, 128.73, 128.69, 128.2, 127.7 (d, J_{C-F} = 2.9 Hz, 1C), 126.4, 126.2, 125.8, 123.5, 121.2, 115.6, 115.5 (d, J_{C-F} = 21.7 Hz, 1C), 111.1, 80.9, 64.7, 21.5.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -111.66 – -111.71(m, 1F).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}FN_4NaO_2S^+$: 609.1731, found 609.1732.

N-((Z)-5'-(4-chlorophenyl)-2',4'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3ak



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^1H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ak** (21.4 mg, 71% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ak**:

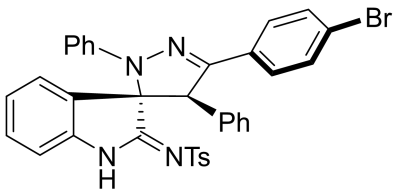
Melting point: 236.9 – 239.1 °C.

^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.94 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.15 – 7.11 (m, 4H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.95 – 6.92 (m, 3H), 6.88 – 6.82 (m, 2H), 6.77 (t, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 5.20 (s, 1H), 2.36 (s, 3H).

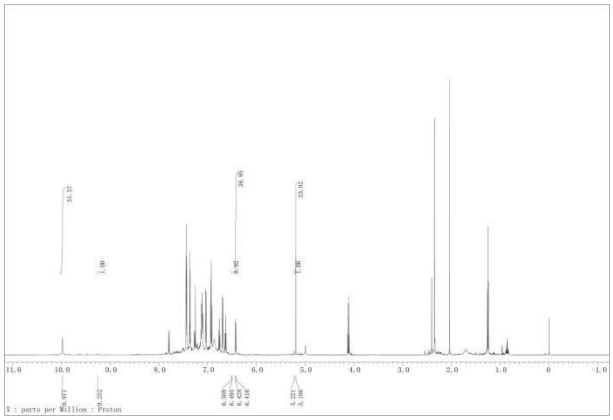
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 170.4, 148.1, 143.9, 143.0, 140.0, 138.0, 134.5, 133.9, 130.0, 129.9, 129.21, 129.18, 128.8, 128.7, 128.6, 128.2, 128.0, 126.3, 126.2, 125.7, 123.5, 121.3, 115.6, 111.2, 80.9, 64.5, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{35}ClN_4O_2SNa^+$: 625.1435, found: 625.1430; calculated for $C_{35}H_{27}{}^{37}ClN_4O_2SNa^+$: 627.1406, found: 627.1415.

N-((Z)-5'-(4-bromophenyl)-2',4'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3al



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3al** (19.7 mg, 61% yield) as a yellow solid.



Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3al** (13.2 mg, 41% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3al**:

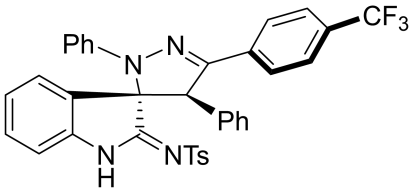
Melting point: 250.1 – 252.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.97 (s, 1H), 7.47 – 7.45 (m, 4H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.16 – 7.11 (m, 4H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.92 (m, 3H), 6.88 – 6.82 (m, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 2H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 1H), 5.20 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.3, 148.1, 143.9, 143.0, 140.0, 138.0, 133.9, 131.5, 130.4, 129.9, 129.21, 129.16, 128.8, 128.7, 128.3, 128.2, 126.3, 126.2, 125.7, 123.5, 122.9, 121.3, 115.6, 111.2, 80.9, 64.4, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{79}BrN_4O_2SNa^+$: 669.0930, found: 669.0929; calculated for $C_{35}H_{27}{}^{81}BrN_4O_2SNa^+$: 671.0910, found: 671.0917.

N-((Z)-2',4'-diphenyl-5'-(4-(trifluoromethyl)phenyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3am



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3am** (23.2 mg, 73% yield) as a yellow solid.

Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3am** (19.1 mg, 60% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3am**:

Melting point: 238.1 – 240.5 °C.

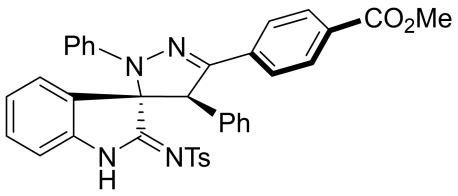
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.99 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.12 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.97 – 6.94 (m, 3H), 6.89 – 6.83 (m, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 6.6 Hz, 1H), 5.24 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.2, 147.6, 143.6, 143.1, 140.1, 138.0, 134.9, 133.7, 130.1 (q, $J_{C\text{-}F}$ = 31.9 Hz, 1C), 130.0, 129.2, 129.1, 128.9, 128.8, 128.3, 126.9, 126.3, 126.2, 125.5, 125.3 (q, $J_{C\text{-}F}$ = 4.4 Hz, 1C), 124.0 (q, $J_{C\text{-}F}$ =239.4 Hz, 1C), 123.6, 121.6 115.7, 111.3, 81.0, 64.3, 21.5.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -62.6 (s, 3F).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{36}H_{27}FN_4O_2SNa^+$: 659.1699, found: 659.1706.

Methyl-4-((Z)-2',4'-diphenyl-2-(tosylimino)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-5'-yl) benzoate 3an



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3an** (17.2 mg, 55% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3an**:

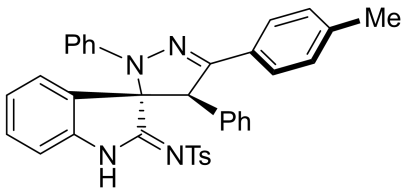
Melting point: 213.4 – 215.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.98 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.14 – 7.10 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.97 – 6.94 (m, 3H), 6.88 (br s, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.26 (s, 1H), 3.89 (s, 3H), 2.35 (s, 3H).

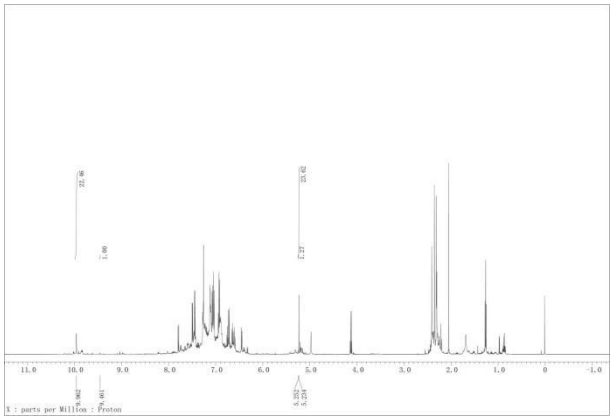
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.3, 166.7, 147.9, 143.6, 143.1, 140.0, 138.0, 135.7, 133.9, 130.0, 129.7, 129.6, 129.23, 129.15, 128.9, 128.7, 128.2, 126.6, 126.3, 126.2, 125.6, 123.5, 121.5, 115.7, 111.3, 81.0, 64.4, 52.1, 21.5.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for $C_{37}H_{30}N_4O_4SNa^+$: 649.1880, found 649.1884.

N-((Z)-2',4'-diphenyl-5'-(p-tolyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3ao



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ao** (21.0 mg, 72% yield) as a yellow solid.



Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ao** (14.8 mg, 51% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ao**:

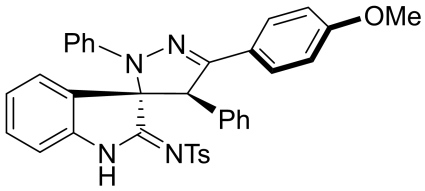
Melting point: 221.7 – 223.9 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.97 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.10 (m, 4H), 7.08 – 7.05 (m, 4H), 6.94 – 6.91 (m, 5H), 6.75 – 6.72 (m, 3H), 6.64 (t, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.24 (s, 1H), 2.36 (s, 3H), 2.32 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.6, 149.3, 144.3, 142.9, 140.0, 138.8, 138.1, 134.3, 129.8, 129.24, 129.17, 129.0, 128.8, 128.7, 128.5, 128.0, 126.9, 126.3, 126.2, 126.1, 123.4, 120.9, 115.5, 111.2, 80.8, 64.8, 21.5, 21.3.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for $C_{36}H_{30}N_4O_2SNa^+$: 605.1982, found: 605.1986.

N-((Z)-5'-(4-methoxyphenyl)-2',4'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3ap



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ap** (17.6 mg, 59% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ap**:

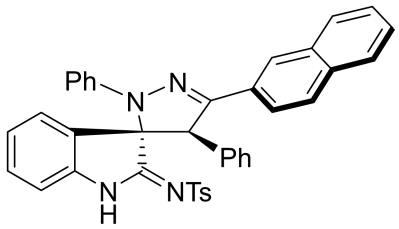
Melting point: 147.3 – 150.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.94 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.12 – 7.11 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.95 – 6.92 (m, 5H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.75 – 6.71 (m, 3H), 6.64 (t, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.22 (s, 1H), 3.77 (s, 3H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.7, 160.1, 149.1, 144.4, 142.9, 140.0, 138.2, 134.4, 129.8, 129.3, 129.2, 128.8, 128.6, 128.4, 128.0, 126.4, 126.2, 126.1, 124.2, 123.4, 120.9, 115.5, 113.8, 111.1, 80.8, 64.9, 55.2, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{36}H_{30}N_4O_3SNa^+$: 621.1931, found: 621.1926.

4-methyl-N-((Z)-5'-(naphthalen-2-yl)-2',4'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)benzenesulfonamide 3aq



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3aq** (27.5 mg, 89% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3aq**:

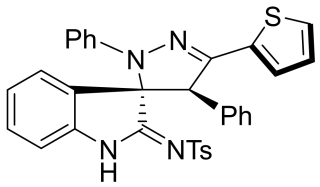
Melting point: 276.8 – 280.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.02 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.78 (m, 2H), 7.68 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 6.6 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.15 – 7.10 (m, 4H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.99 – 6.95 (m, 5H), 6.79 (m, 3H), 6.66 (t, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.37 (s, 1H), 2.32 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.4, 149.3, 144.1, 142.9, 140.1, 138.1, 134.3, 133.4, 133.0, 129.9, 129.23, 129.17, 129.0, 128.8, 128.6, 128.3, 128.1, 128.0, 127.6, 126.7, 126.5, 126.4, 126.2, 125.9, 124.3, 123.5, 121.2, 115.7, 111.2, 80.9, 64.6, 21.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{39}H_{30}N_4O_2SNa^+$: 641.1982, found: 641.1975.

N-((Z)-2',4'-diphenyl-5'-(thiophen-2-yl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3ar



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ar** (19.2 mg, 67% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ar**:

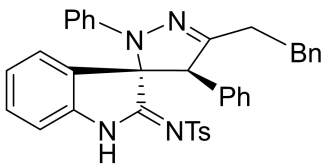
Melting point: 212.9 – 214.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.95 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 4.2 Hz, 1H), 7.15 – 7.12 (m, 3H), 7.11 – 7.08 (m, 3H), 6.93 – 6.89 (m, 5H), 6.84 (t, *J* = 4.8 Hz, 1H), 6.75 (t, *J* = 6.6 Hz, 1H), 6.70 – 6.65 (m, 4H), 6.56 (d, *J* = 7.2 Hz, 1H), 5.24 (s, 1H), 2.37 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.3, 145.2, 143.8, 143.0, 140.0, 138.0, 135.2, 133.8, 129.9, 129.4, 129.2, 128.8, 128.5, 128.2, 127.6, 127.2, 126.8, 126.4, 126.3, 125.7, 123.5, 121.1, 115.6, 111.2, 81.1, 65.7, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{33}H_{26}N_4O_2S_2Na^+$: 597.1389, found: 597.1388.

4-methyl-N-((Z)-5'-phenethyl-2',4'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)benzenesulfonamide 3as



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel

chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3as** (17.6 mg, 59% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3as**:

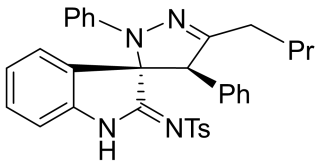
Melting point: 106.7 – 109.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.90 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.24 (m, 2H), 7.21 – 7.16 (m, 4H), 7.14 – 7.13 (m, 4H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.93 – 6.90 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.79 – 6.77 (m, 2H), 6.74 – 6.72 (m, 1H), 6.67 – 6.63 (m, 3H), 6.49 (d, *J* = 7.8 Hz, 1H), 4.73 (s,1H), 3.03 – 3.00 (m, 2H), 2.78 – 2.73 (m, 1H), 2.59 – 2.55 (m, 1H), 2.38 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.7, 153.0, 144.8, 143.1, 141.2, 139.9, 138.2, 133.1, 129.7, 129.5, 129.3, 128.7, 128.6, 128.5, 128.3, 128.1, 126.3, 126.2, 126.0, 123.4, 120.8, 115.5, 111.1, 80.5, 67.1, 32.5, 30.9, 21.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{37}H_{32}N_4O_2SNa^+$: 619.2138, found: 619.2139.

N-((Z)-5'-butyl-2',4'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3at



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3at** (18.4 mg, 67% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3at**:

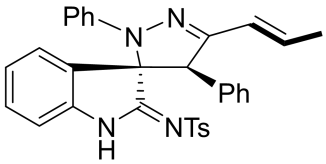
Melting point: 162.4 – 165.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.78 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.17 (m, 3H), 7.12 – 7.09 (m, 3H), 6.90 – 6.87 (m, 4H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.67 (t, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 7.8 Hz, 1H), 4.72 (s, 1H), 2.50 – 2.45 (m, 1H), 2.38 (s, 3H), 2.25 – 2.20 (m, 1H), 1.61 – 1.59 (m, 2H),1.46 – 1.41 (m, 1H), 1.39 – 1.34 (m, 1H), 0.89 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 170.5, 154.3, 145.0, 143.0, 140.0, 138.2, 133.4, 129.7, 129.5, 129.2, 128.7, 128.6, 128.2, 126.3, 126.23, 126.20, 123.4, 120.8, 115.8, 111.0, 80.3, 66.7, 28.7, 28.4, 22.3, 21.5, 13.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{33}H_{32}N_4O_2SNa^+$: 571.2138, found: 571.2141.

N-((Z)-2',4'-diphenyl-5'-((E)-prop-1-en-1-yl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3au



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^1H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3au** (16.0 mg, 60% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3au**:

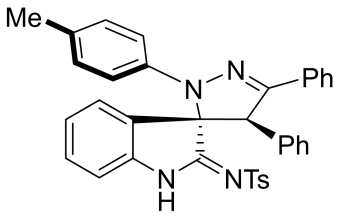
Melting point: 107.5 – 109.7 °C.

^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.87 (s, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.20 – 7.16 (m, 4H), 7.11 (t, J = 7.8 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 6.91 – 6.88 (m, 4H), 6.72 (t, J = 7.2 Hz, 1H), 6.65 – 6.60 (m, 3H), 6.47 – 6.41 (m, 2H), 5.61 – 5.55 (m, 1H), 4.95 (s, 1H), 2.36 (s, 3H), 1.72 (d, J = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 170.7, 150.6, 144.2, 142.9, 139.9, 138.2, 134.4, 133.9, 129.7, 129.20, 129.17, 128.8, 128.4, 127.9, 126.3, 126.2, 126.0, 123.42, 123.35, 120.9, 115.4, 111.0, 80.6, 64.2, 21.5, 18.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{32}H_{28}N_4O_2SNa^+$: 555.1825, found: 555.1822.

N-((Z)-4',5'-diphenyl-2'-(p-tolyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3av



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3av** (18.0 mg, 62% yield) as a yellow solid.

Prepared according to the general procedure B, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3av** (15.1 mg, 52% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3av**:

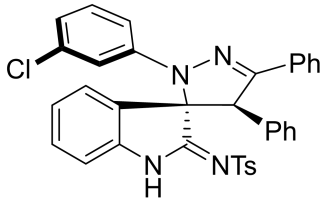
Melting point: 117.0 – 120.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.85 (s, 1H), 7.61 – 7.59 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.26 (m, 3H), 7.15 – 7.11 (m, 4H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.92 – 6.88 (m, 3H), 6.71 (d, *J* = 9.0 Hz, 2H), 6.66 (t, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 7.2 Hz, 1H), 5.22 (s, 1H), 2.37 (s, 3H), 2.17 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.4, 149.1, 142.9, 141.9, 140.1, 138.2, 134.3, 131.6, 130.7, 129.8, 129.3, 129.2, 129.1, 128.64, 128.59, 128.3, 128.0, 126.8, 126.5, 126.3, 126.1, 123.4, 116.2, 111.0, 81.2, 64.5, 21.5, 20.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{36}H_{30}N_4O_2SH^+$: 583.2162, found: 583.2162.

N-((Z)-2'-(3-chlorophenyl)-4',5'-diphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3aw



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel

chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3aw** (21.4 mg, 71% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3aw**:

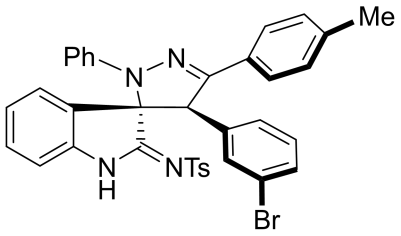
Melting point: 231.1 – 233.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.88 (s, 1H), 7.61 – 7.60 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.28 (m, 3H), 7.17 (t, *J* = 9.0 Hz, 1H), 7.14 – 7.12 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.00 (s, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.88 – 6.84 (m, 2H), 6.76 (t, *J* = 8.4 Hz, 1H), 6.68 – 6.65 (m, 2H), 6.44 (d, *J* = 7.2 Hz, 1H), 6.27 (dd, *J* = 7.8, 1.2 Hz, 1H), 5.27 (s, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 170.2, 149.9, 145.5, 143.2, 139.9, 137.9, 134.7, 134.1, 131.1, 130.1, 129.7, 129.24, 129.20, 129.1, 128.7, 128.4, 128.2, 127.1, 126.3, 126.1, 125.7, 123.6, 120.7, 116.0, 112.2, 111.3, 80.5, 64.8, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{35}H_{27}{}^{35}ClN_4O_2SH^+$: 603.1616, found: 603.1614; $[M + Na]^+$ calculated for $C_{35}H_{27}{}^{37}ClN_4O_2SNa^+$: 627.1406, found: 627.1427.

N-((Z)-4'-(3-bromophenyl)-2'-phenyl-5'-(p-tolyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide 3ax



Prepared according to the general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **3ax** (20.1 mg, 61% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **3ax**:

Melting point: 159.2 – 163.0 °C.

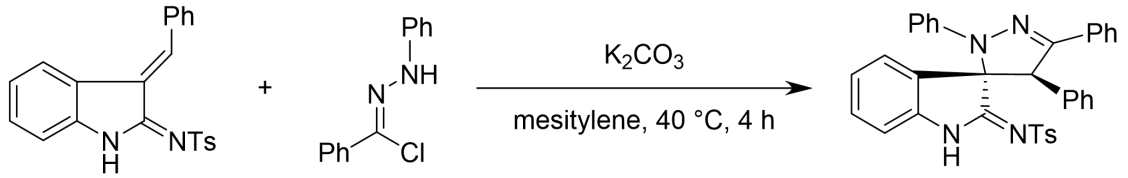
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.96 (s, 1H), 7.48 – 7.46 (m, 4H), 7.28 – 7.26 (m, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 3H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.96 – 6.92 (m, 3H), 6.86 (s, 1H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 3H), 6.48 (d, *J* = 7.2 Hz, 1H), 5.16 (s, 1H), 2.35 (s, 3H), 2.33 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 170.2, 148.7, 144.1, 143.0, 140.1, 139.1, 138.1, 136.8, 132.1, 131.2, 130.10, 130.08, 129.23, 129.19, 128.8, 128.4, 127.9, 126.8, 126.2, 125.6, 123.6, 122.7, 121.2, 115.7, 111.4, 80.7, 64.1, 21.5, 21.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{36}H_{29}{}^{79}BrN_4O_2SH^+$: 661.1267, found: 661.1273; calculated for $C_{36}H_{29}{}^{81}BrN_4O_2SH^+$: 663.1247, found: 663.1254.

3. Synthetic Application Studies of 3a

*3.1 Gram-scale synthesis of **3a***

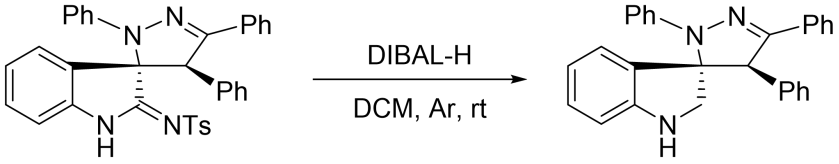


1a **2a** **3a**

An oven-dried 50 mL flask was charged with alkenyl-iminoindoline **1a** (2.0 mmol, 748.2 mg), hydrazonoyl chloride **2a** (3.0 mmol, 690.2 mg) and K_2CO_3 (3.0 mmol, 414.6 mg) in mesitylene (40.0 mL). The mixture was then stirred rapidly at 40 ℃ with an oil bath for 4 h. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate 15:1 to 4:1) to afford product **3a** (1.01 g, 89% yield) as a yellow solid.

*3.2 Reduction of iminyl to methylene of products **3a*** [4]

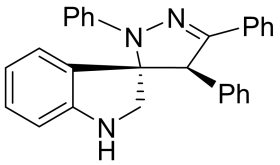
A. Procedure and characterization



3a **6**

To an oven-dried 10 mL Schlenk tube was added **3a** (0.10 mmol, 56.8 mg), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, dry DCM (1.0 mL) was added *via* syringe and stirred at 0 °C. To this solution was dropwise added DIBAL-H (0.3 mL, 1 M in n-hexane) using a syringe. The reaction mixture was stirred at room temperature for 2 h. The reaction was then quenched with saturated NaCl solution (2.0 mL) and extracted with ethyl acetate (3 × 5.0 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The crude product was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1 to 6:1) to afford **6** (28.0 mg, 70% yield) as a yellow solid , which was dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS.

2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazole] 6



Prepared according to procedure metioned above, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate= 20:1 to 6:1) to afford **6** (28.0 mg, 70% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **6**:

Melting point: 146.3 – 149.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.74 (d, *J* = 7.2 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.20 (m, 2H), 7.16 – 7.13 (m, 5H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.97 – 6.79 (m, 3H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.32 (t, *J* = 7.2 Hz, 1H), 6.17 (d, *J* = 7.8 Hz, 1H), 4.79 (s, 1H), 3.95 (d, *J* = 9.6 Hz, 1H), 3.80 (s, 1H), 3.50 (d, *J* = 9.6 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 150.5, 149.9, 144.3, 135.3, 132.5, 128.8, 128.6, 128.53, 128.45, 128.3, 127.4, 126.5, 126.3, 126.31, 120.26, 118.6, 116.9, 110.2, 81.1, 62.4, 54.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{28}H_{23}N_3H^+$: 402.1965, found: 402.1967.

B. Natural population analysis (NPA) & electrophilic index (ω_K) analysis

1) Computational method

Density functional theory (DFT) calculations were performed with Gaussian 16 suite of programs.[5] Geometry optimizations were operated to locate all of the stationary points, using the M06-2X density functional theory method[6] including Grimme empirical dispersion correction (D3BJ)[7] with 6-311++G(d,p) basis sets[8] for all atoms. The natural population analysis (NPA)[9] and reactivity index analysis (electrophilicity index ω and nucleophilicity index N)[10] for key optimized structures were performed to further investigate the electronic properties.

2) Energies and cartesian coordinates of all stationary points

Zero-point correction = 0.528968 (a.u.)
Thermal correction to Energy = 0.561168 (a.u.)
Thermal correction to Enthalpy = 0.562112 (a.u.)

Thermal correction to Gibbs Free Energy = 0.462922 (a.u.)

Sum of electronic and zero-point Energies = -2078.077629 (a.u.)

Sum of electronic and thermal Energies = -2078.045429 (a.u.)

Sum of electronic and thermal Enthalpies = -2078.044485 (a.u.)

Sum of electronic and thermal Free Energies = -2078.143675 (a.u.)

Imaginary frequency: 0 (cm^{-1})

Standard orientation:

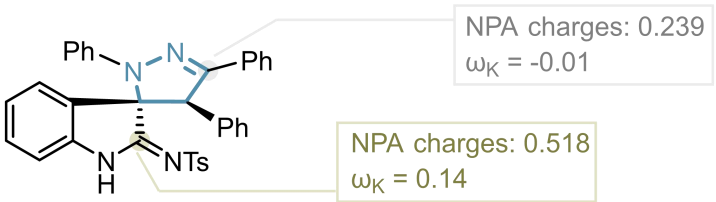
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	16	0	-0.529264	0.955770	-3.468879
2	8	0	-1.690432	0.190146	-3.874983
3	8	0	-0.490594	2.384330	-3.800446
4	7	0	-0.272958	0.739607	-1.840874
5	7	0	-0.815890	3.007314	-1.214227
6	1	0	-0.936168	3.386031	-2.148808
7	7	0	0.877497	-0.540852	0.906995
8	7	0	1.106661	0.803559	0.711442
9	6	0	-1.914589	-4.658983	1.842111
10	6	0	-2.774722	-3.570406	1.772169
11	1	0	-3.840436	-3.708738	1.908806
12	6	0	-2.271164	-2.296943	1.527483
13	1	0	-2.950969	-1.453631	1.485403
14	6	0	-0.899886	-2.103009	1.347824
15	6	0	-0.367372	-0.762008	1.074613
16	6	0	-1.212803	0.495240	1.037982
17	1	0	-2.032423	0.396648	0.321834
18	6	0	-0.158236	1.515220	0.476985
19	6	0	-0.422636	1.723625	-1.027869
20	6	0	0.924787	0.176712	-4.135534
21	6	0	2.179169	0.634130	-3.748582
22	1	0	2.279658	1.430821	-3.018052

23	6	0	3.301478	0.036215	-4.305384
24	1	0	4.286253	0.376408	-4.009498
25	6	0	3.157856	-0.997446	-5.229022
26	6	0	-0.707242	3.750299	-0.024779
27	6	0	-0.941618	5.101254	0.159318
28	1	0	-1.277585	5.731199	-0.655019
29	6	0	-0.715687	5.619693	1.435559
30	1	0	-0.886920	6.674477	1.613893
31	6	0	-0.267470	4.810099	2.475458
32	1	0	-0.090585	5.239610	3.453354
33	6	0	-0.042627	3.447499	2.268211
34	1	0	0.309512	2.813476	3.072777
35	6	0	-0.274288	2.922736	1.010978
36	6	0	2.288423	1.142273	0.018347
37	6	0	3.234906	0.157188	-0.290415
38	1	0	3.036987	-0.868567	-0.017407
39	6	0	4.405942	0.501158	-0.950431
40	1	0	5.123771	-0.277845	-1.181511
41	6	0	4.658444	1.816617	-1.330032
42	1	0	5.573800	2.077392	-1.847147
43	6	0	3.715458	2.792000	-1.028421
44	1	0	3.889021	3.823966	-1.310122
45	6	0	2.541290	2.467409	-0.356703
46	1	0	1.844712	3.257004	-0.110804
47	6	0	-0.544044	-4.470983	1.665894
48	1	0	0.129903	-5.317827	1.718177
49	6	0	-0.038409	-3.204411	1.420772
50	1	0	1.024009	-3.048903	1.279266
51	6	0	-1.774248	0.862128	2.396050
52	6	0	-1.127941	0.487626	3.573245
53	1	0	-0.230447	-0.121105	3.525489

54	6	0	-1.625299	0.894825	4.807165
55	1	0	-1.116408	0.596538	5.716133
56	6	0	-2.772450	1.678808	4.875189
57	1	0	-3.158809	1.995095	5.836748
58	6	0	-3.426484	2.049116	3.703865
59	6	0	-2.929457	1.639665	2.472243
60	1	0	-3.433775	1.937690	1.557908
61	6	0	0.758863	-0.857933	-5.044183
62	1	0	-0.239427	-1.190048	-5.301186
63	6	0	1.893549	-1.444927	-5.596355
64	1	0	1.786921	-2.253125	-6.309460
65	1	0	-4.322209	2.657003	3.749069
66	1	0	-2.306963	-5.650814	2.032418
67	1	0	4.038274	-1.459165	-5.660340

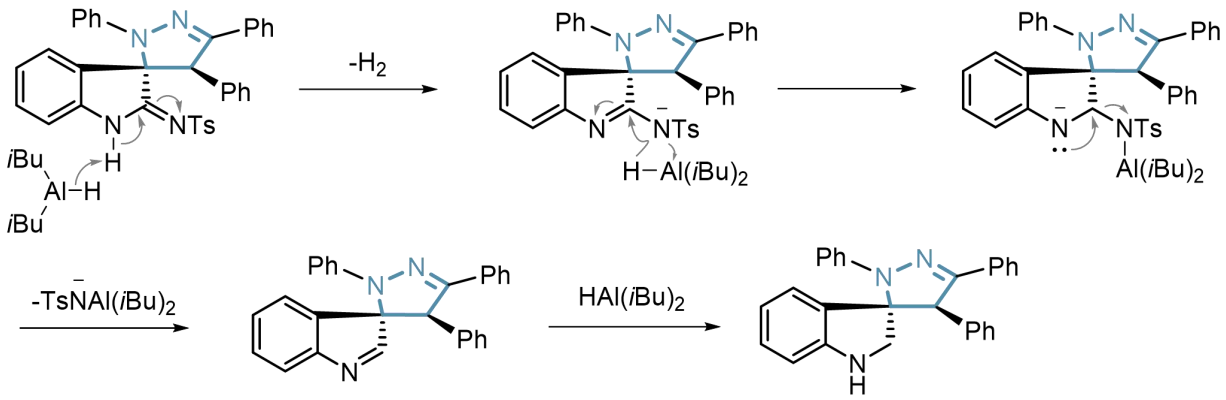
3) NPA & ω_K analysis result

The calculated charge on the imine carbon in the amidine moiety is +0.518, whereas that in the hydrazone is +0.239, indicating that the amidine imine is relatively more electron-deficient. This result is consistent with the analysis based on electrophilicity indices. The enhanced electrophilicity of the amidine imine may arise from the presence of the strongly electron-withdrawing *p*-toluenesulfonyl (Ts) group, thereby leading to its preferential reduction by DIBAL-H.



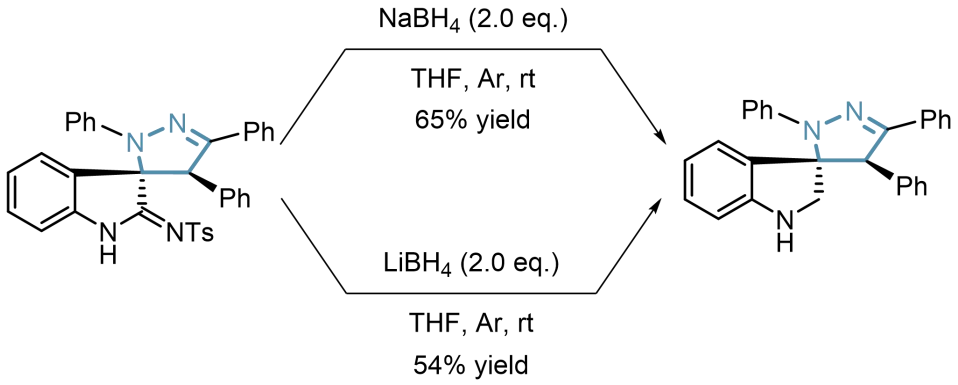
C. Proposed reduction mechanism

Considering the structural similarity between amidines and amides, and given that amides can be reduced to amines by hydride donors such as $LiAlH_4$, we propose that the reduction of amidines to amines by DIBAL-H may proceed *via* a similar mechanistic pathway. Based on this assumption, a plausible reaction mechanism is proposed below.

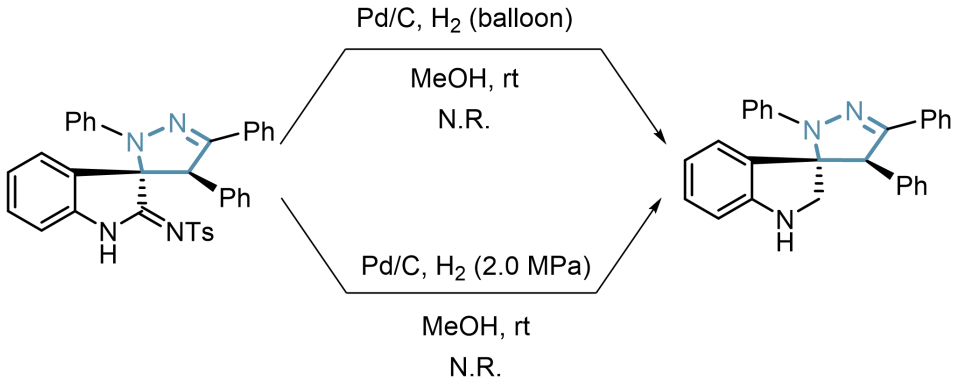


D. Experimental validation

Based on the proposed reaction mechanism, we further evaluated the reaction using alternative reducing agents to validate its generality. The results demonstrated that the reaction proceeded smoothly when $NaBH_4$ and $LiBH_4$ were employed as reductants, affording the desired product in 65% and 54% isolated yields, respectively.



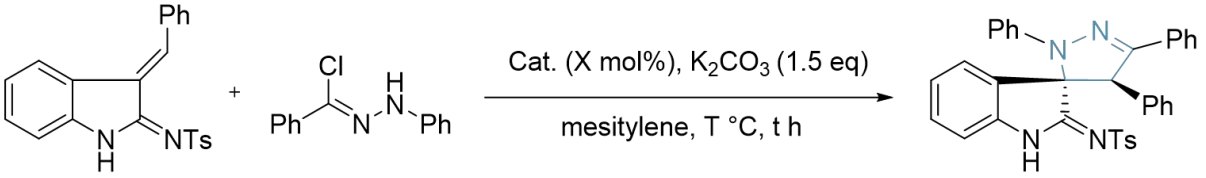
In contrast, when the reaction was carried out under hydrogenation conditions using Pd/C as a catalyst, no product formation was observed under either 1 atm or 2.0 MPa of H_2 pressure. This result further supports the hypothesis that a hydride species is essential for the reduction process.



3.3 Initial evaluation of the protocol's enantioselective potential

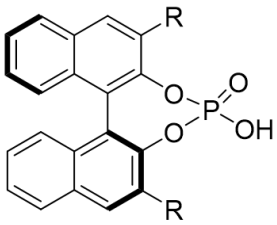
An initial evaluation of the enantioselective potential of the protocol was conducted by

screening a variety of chiral catalysts, including chiral phosphoric acids, chiral tertiary amine catalysts, and chiral phase-transfer catalysts. However, the desired product was obtained as a nearly racemic mixture, indicating no observable enantioselectivity under the conditions tested.

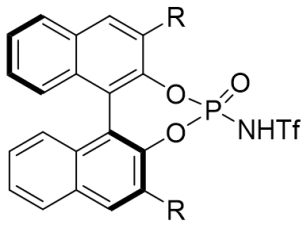


1a **2a** **3a**

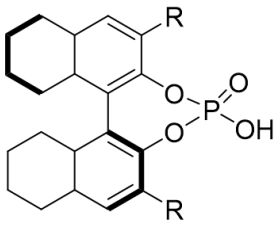
Cat. = CPA (10 mol%), 40 °C, 4 h
(CPA: Chiral Phosphoric Acid)



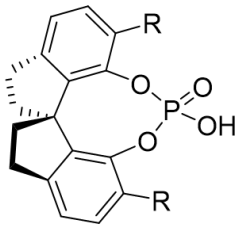
C1 R = 1-pyrenyl, 90% yield, 0 ee
C2 R = 4-Ph-C_6H_4, 93% yield, 0 ee
C3 R = 3,5-Me_2-C_6H_3, 92% yield, 0 ee
C4 R = 3,5-$(CF_3)_2$-C_6H_3, 90% yield, 0 ee
C5 R = 2,4,6-Cy_3-C_6H_2 91% yield, 0 ee



C6 R = Ph, 89% yield, 0 ee

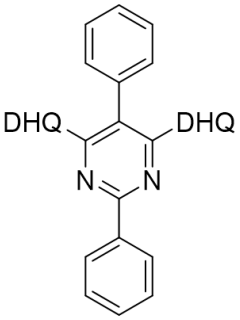


C7 R = triphenylsilyl, 94% yield, 0 ee
C8 R = 2,4,6-$(iPr)_3$-C_6H_4, 93% yield, 0 ee
C9 R = 9-anthryl, 90% yield, 0ee

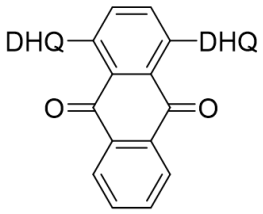


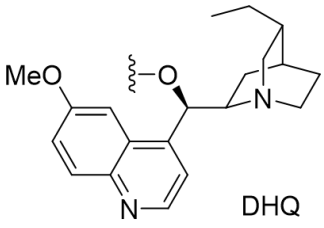
C10 R = 9-anthryl, 93% yield, 0 ee

Cat. = CTA (20 mol%), T °C, t h
(CTA: Chiral Tertiary Amine)



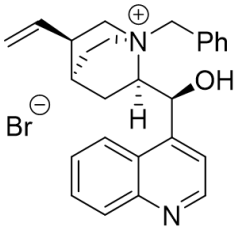
C11 $(DHQ)_2PYR$
40 °C, 4 h, 54% yield, 0 ee
20 °C, 8 h, 48% yield, 0 ee
0 °C, 12 h, 43% yield, 0 ee
-10 °C, 12 h, 32% yield, 0 ee



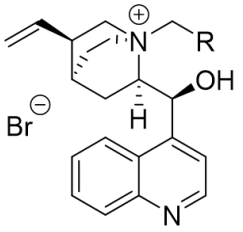


C12 $(DHQ)_2AQN$, 40 °C, 4 h, 46% yield, 0 ee

Cat. = CPTC (10 mol%), T °C, t h
(CPT: Chiral Phase-Transfer Catalyst)



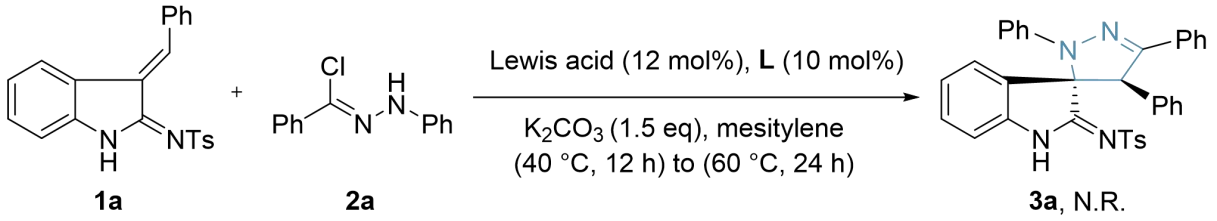
C13 40 °C, 4 h, 64% yield, 0 ee
0 °C, 8 h, 43% yield, 0 ee



C14 R= 4-Cl-C_6H_4
40 °C, 4 h,
68% yield, 0 ee

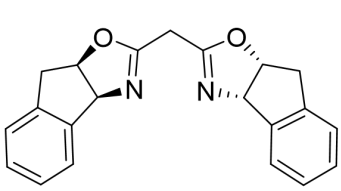
We subsequently investigated the use of metal-based Lewis acids in combination with

chiral oxazoline ligands in an effort to achieve enantioselective control. $Mg(ClO_4)_2$ and $Mg[N(OTf)_2]_2$ were employed as Lewis acids, while **L1–L8** served as chiral ligands. However, under standard reaction conditions, these metal–ligand systems appeared to significantly inhibit the reaction. Further attempts to improve the outcome by increasing the reaction temperature to 60 °C and extending the reaction time to 24 h also failed to produce any desired product.

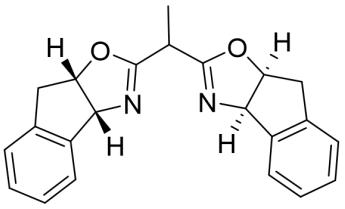


1a **2a** **3a**, N.R.

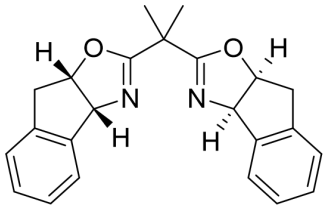
Lewis acid = $Mg(ClO_4)_2$ or $Mg[N(OTf)_2]_2$



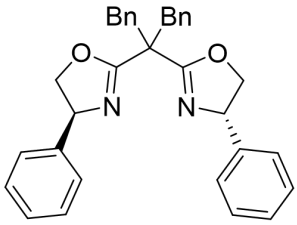
L1



L2



L3



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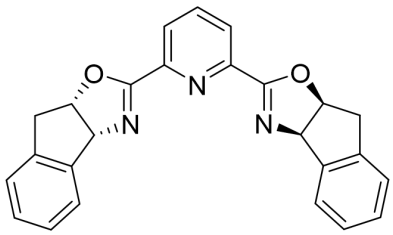
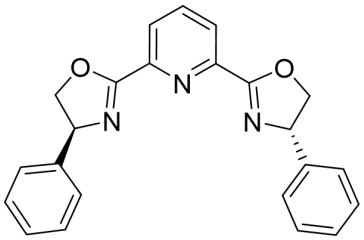


L5



L6

N.R.: no reaction

4. Assessment of Antioxidant Activity *via* DPPH Radical Scavenging Rate

*4.1 DPPH radical scavenging rate (S_R) of Compound **3***[11]

A. Preparation of solutions

1) DPPH Free radical solution

Accurately weigh 0.2 mg of DPPH and dissolve it in 20 mL of anhydrous methanol using a light-shielding brown volumetric flask. Store the solution under refrigeration to protect it from light-induced degradation.

2) Sample solution of compound **3**

Accurately weigh 1 mg of Compound **3**, and dissolve it in 1 mL of anhydrous methanol to obtain a solution with a concentration of 1 mg/mL.

3) Ascorbic acid (AA) solution

Weigh 1 mg of ascorbic acid, and dissolve it in 1 mL of anhydrous methanol to prepare a 1 mg/mL standard solution for use as a positive control.

B. Experimental method

All experimental steps were performed in a dark environment to minimize DPPH degradation.

1) Experimental group

Pipette 0.1 mL of Compound **3** solution and 0.1 mL of DPPH solution into a well of the 96-well microplate. Shake vigorously to ensure mixing. Incubate the mixture at 30 °C for 30 minutes. Measure the absorbance at 515 nm using an ELISA plate reader. Perform all measurements in duplicate, and record the average absorbance (A_i).

2) Positive control group

Pipette 0.1 mL of AA solution and 0.1 mL of DPPH solution into a well. Incubate at 30 °C for 30 minutes, then measure absorbance (A_i) at 515 nm.

3) Control group

Combine 0.1 mL of Compound **3** solution and 0.1 mL of anhydrous methanol in a well. After 30 minutes, measure absorbance (A_j).

4) Blank group

Mix 0.1 mL of DPPH solution and 0.1 mL of anhydrous methanol in a well. Measure absorbance after 30 minutes to obtain the value (A_o).

C. Calculation of DPPH Radical Scavenging Rate

The scavenging rate (S_R%) of Compound **3** on DPPH free radicals was calculated using the following formula:

$$S_R = (1 - \frac{A_i - A_j}{A_0}) \times 100\%$$

Where: A_i = Absorbance of sample with DPPH, A_j = Absorbance of sample without DPPH (control group), A_j = Absorbance of DPPH with methanol (blank).

Table S1. DPPH Radical Scavenging Rate (S_R) of Compound **3** and AA.

Compound	S_R (%)	Compound	S_R (%)	Compound	S_R (%)	Compound	S_R (%)
3a	59.6	**3l**	96.2	**3ah**	63.2	**3as**	20.3
3b	83.5	**3m**	55.4	**3ai**	96.5	**3at**	77.4
3c	38.3	**3n**	97.0	**3aj**	99.3	**3au**	96.2
3d	51.9	**3o**	99.8	**3ak**	78.9	**3av**	86.4
3e	82.7	**3p**	54.9	**3al**	36.1	**3aw**	77.4
3f	47.4	**3q**	87.2	**3am**	36.9	**3ax**	96.2
3g	96.2	**3r**	83.5	**3an**	41.4	**AA**	95.8
3h	97.0	**3t**	61.7	**3ao**	42.1		
3i	83.5	**3ae**	97.0	**3ap**	39.1		
3j	97.7	**3af**	63.2	**3aq**	99.3		
3k	97.7	**3ag**	73.7	**3ar**	96.2		

*4.2 Effect of different concentrations of Compound **3o** on DPPH radical scavenging rate*[11]

To investigate the dose-dependent antioxidant activity of Compound **3o**, a series of solutions at varying concentrations were prepared. Specifically, six concentrations of Compound 3o were tested: 0.2 mg/mL, 0.4 mg/mL, 0.6 mg/mL, 0.8 mg/mL, 1.0 mg/mL, and 1.2 mg/mL. The experimental procedure followed was consistent with that outlined in Section 1.1, employing the DPPH free radical scavenging assay under dark conditions. Each sample was mixed with an equal volume (0.1 mL) of freshly prepared DPPH solution and incubated at 30 °C for 30 minutes. Absorbance was measured at 515 nm using an ELISA plate reader.

The DPPH scavenging rate at each concentration was calculated using the following formula:

$$S_R = (1 - \frac{A_i - A_j}{A_0}) \times 100\%$$

Where: A_i = Absorbance of sample with DPPH, A_j = Absorbance of sample without DPPH (control group), A_j = Absorbance of DPPH with methanol (blank).

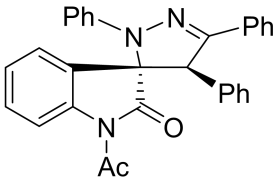
Table S2. DPPH Radical Scavenging Rate (S_R) of Compound **3o** at Different Concentrations

Experimental Data	**Compound 3o** concentration (mg/mL)					
	0.2	0.4	0.6	0.8	1.0	1.2
S_R (%)	22.6	49.6	73.7	90.9	99.8	99.9

4.3 Comparison of DPPH radical scavenging activities between spiro-pyrazoline-oxindoles and spiro-iminoindoline-pyrazolines

When N–H unprotected 3-alkenyl oxindole was used as the substrate, the reaction gave unsatisfactory results. Therefore, we employed N-acetyl-protected 3-alkenyl oxindole as the substrate, where the electron-withdrawing acetyl group enhances the electrophilicity of the oxindole moiety. This modification successfully enabled the synthesis of N-acetyl-protected spiro-pyrazoline-oxindole **7**.

1-acetyl-2',4',5'-triphenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one 7



Prepared according to the **Section 2** general procedure A, the diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis and the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1 to 4:1) to afford **7** (13.8 mg, 60% yield) as a yellow solid.

Melting point, NMR and HRMS data for the product **7**:

Melting point: 201.1 – 205.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.22 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.68 (m, 2H), 7.32 – 7.29 (m, 3H), 7.25 – 7.22 (m, 1H), 7.19 – 7.16 (m, 3H), 7.13 – 7.10 (m, 2H), 7.02 – 6.95 (m, 2H), 6.89 – 6.85 (m, 3H), 6.77 (t, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 1H), 5.09 (s, 1H), 2.65 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ (ppm): 176.5, 170.6, 148.8, 144.0, 139.3, 133.8, 131.3, 129.8, 129.2, 129.0, 129.0, 128.8, 128.4, 128.3, 126.8, 125.9, 124.8, 124.4, 121.7, 116.5, 115.8, 77.2, 63.4, 26.6.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{30}H_{23}N_3O_2Na^+$: 480.1682, found: 480.1687.

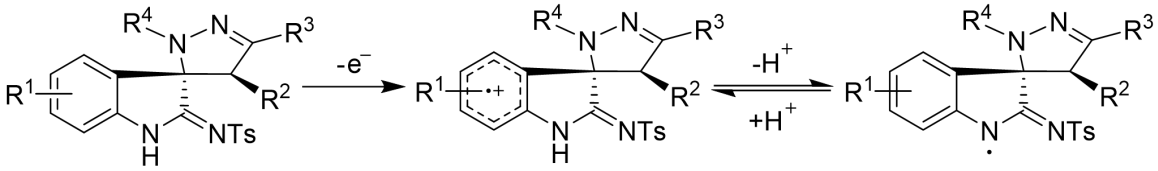
Subsequently, the DPPH radical scavenging rate of compound **7** was evaluated according to the experimental procedure described in **Section 4.1**. At a concentration of 1.0 mg/mL, compound **7** exhibited a scavenging rate of only 51.9%. In contrast, the N-protected spiro-iminoindoline-pyrazoline **3ae**, showed a significantly higher scavenging rate of 97%。

Table S3. DPPH Radical Scavenging Rate (S_R) of Compound **3ae** and **7**

Compound	S_R (%)	Compound	S_R (%)
3ae	97.0	**7**	51.9

4.4 Possible mechanism of DPPH radical scavenging

Owing to the electron-rich nature of the indole ring within the spiro-iminoindoline-pyrazolines, as illustrated in the figure below, the indole moiety is susceptible to oxidation in the presence of oxidants such as DPPH radicals.[12a,12b] Upon losing one electron, the indole forms a radical cation, which subsequently undergoes deprotonation to generate a conjugated nitrogen-centered radical. The released proton can then combine with the DPPH radical anion, leading to its reduction.

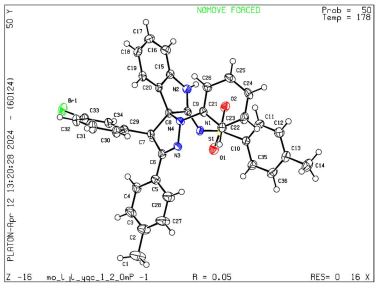


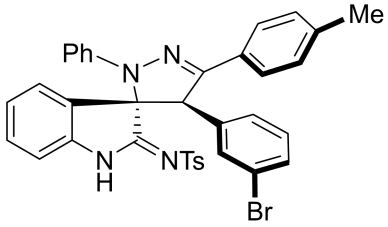
Moreover, according to the comparative experiments described in **Section 4.3**, the amidine moiety in spiro-iminoindoline-pyrazolines was found to play a significant role in contributing to the antioxidant activity of these compounds.

On the other hand, the hydrazone moiety within the spiro-pyrazoline scaffold may also contribute to the scavenging of DPPH radicals.[12c] This assumption is preliminarily supported by the excellent antioxidant activity observed for compound **3ae**, in which the N–H group is blocked.

5. Crystal Data and Structure Refinement

To a glass tube containing **3ax** (40 mg) was added 6.0 mL petroleum ether and 1.2 mL ethyl acetate. Tube was sealed up and kept aside for 3 days at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the structure of **3ax**. The data were collected by a Bruker APEX-II CCD equipped with a Mo radiation source (λ = 0.71073 Å) at 178.0 K. CCDC 2350984 (**3ax**) contains the crystallographic data for this paper.





3ax (**CCDC** 2350984)

Identification code	**3ax**
Empirical formula	$C_{40.5}H_{34}BrN_4O_3S$
Formula weight	736.68
Temperature/K	178.0
Crystal system	triclinic
Space group	P-1
a/Å	8.4871(19)
b/Å	12.362(3)
c/Å	17.148(4)
α/°	90.504(9)
β/°	97.493(10)
γ/°	103.217(9)
Volume/Å^3	1735.1(7)
Z	2
ρ_{calc}g/cm^3	1.410
μ/mm^{-1}	1.290
F(000)	760.0
Crystal size/mm^3	0.32 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.07 to 55.294
Index ranges	-10 ≤ h ≤ 11, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22
Reflections collected	24854
Independent reflections	7985 [R_{int} = 0.0780, R_{sigma} = 0.0814]
Data/restraints/parameters	7985/0/399
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0503, wR_2 = 0.1273
Final R indexes [all data]	R_1 = 0.0804, wR_2 = 0.1417
Largest diff. peak/hole / e Å^{-3}	0.50/-0.70

6. References and Notes

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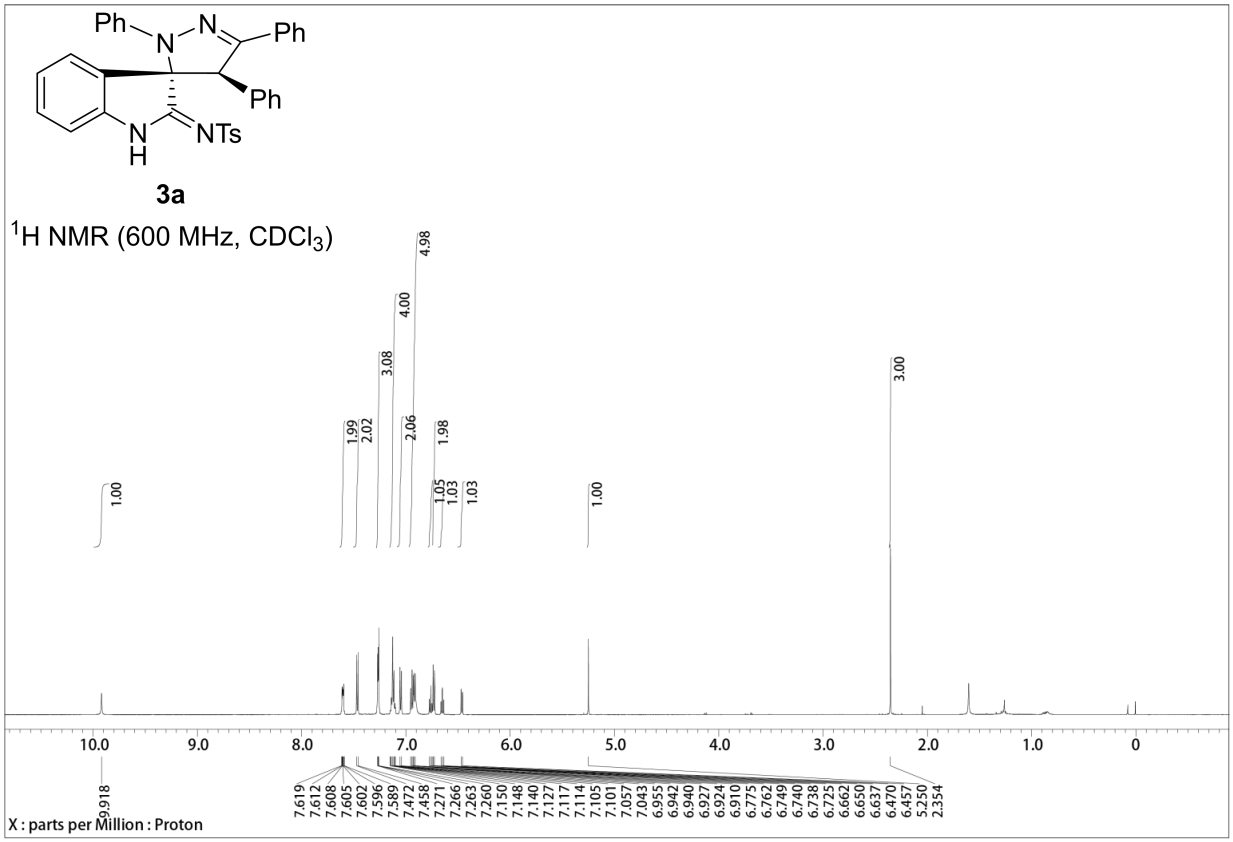
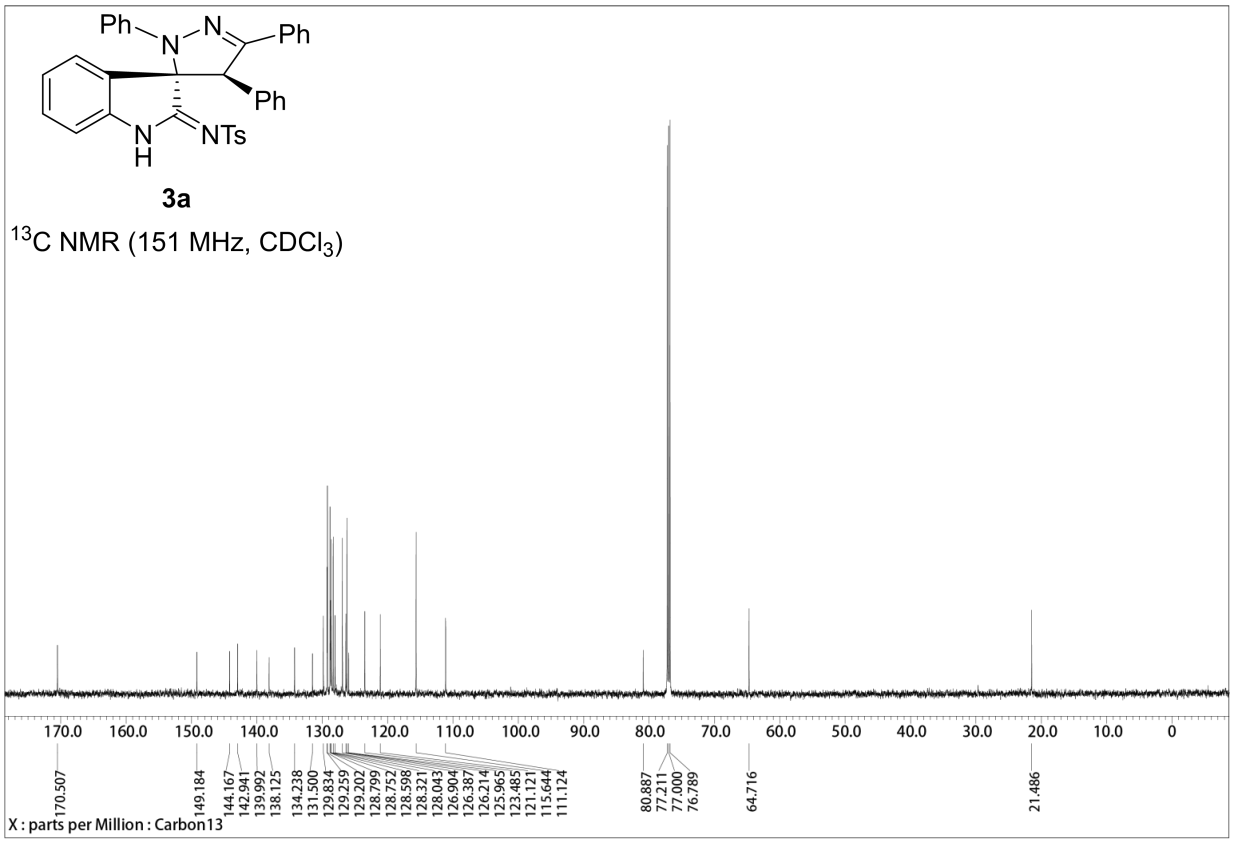
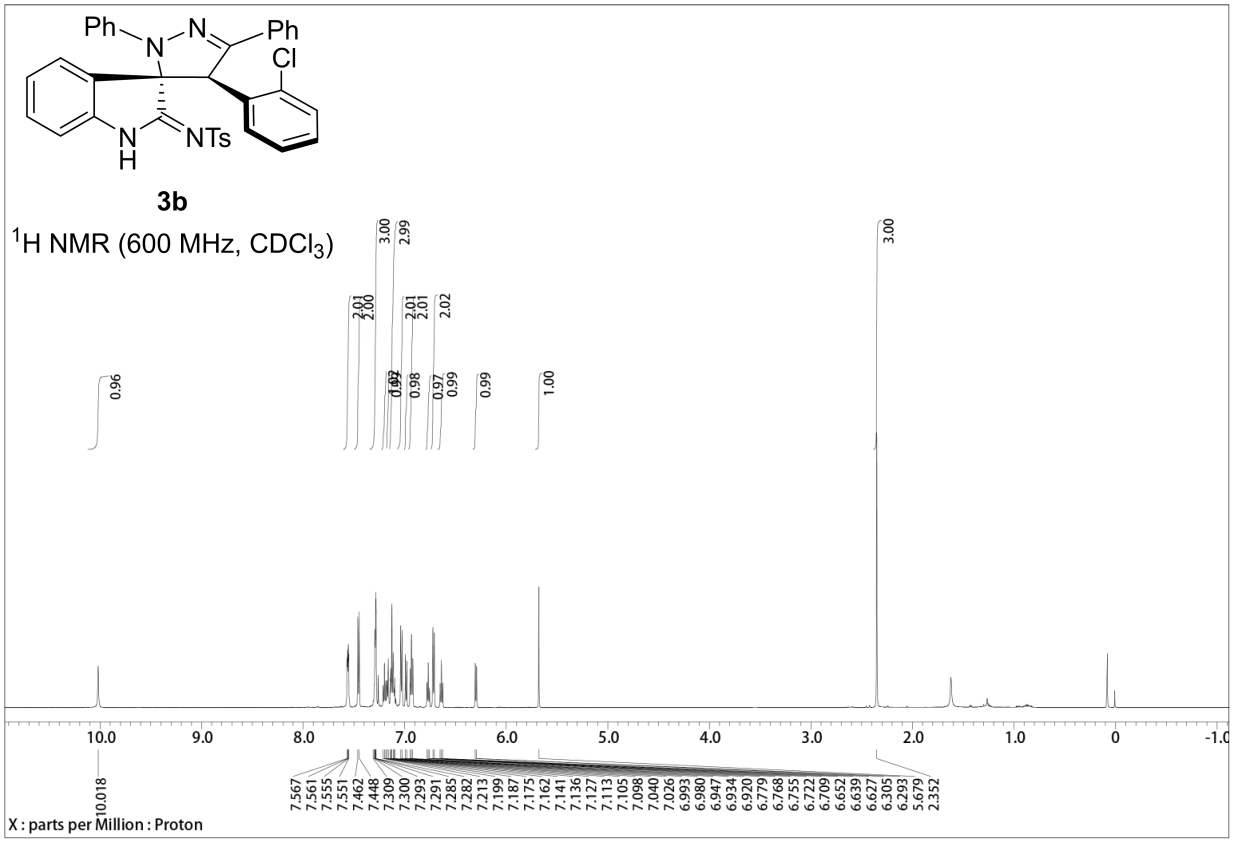
7. NMR Spectra



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NTs
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2.01
2.02
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6.293
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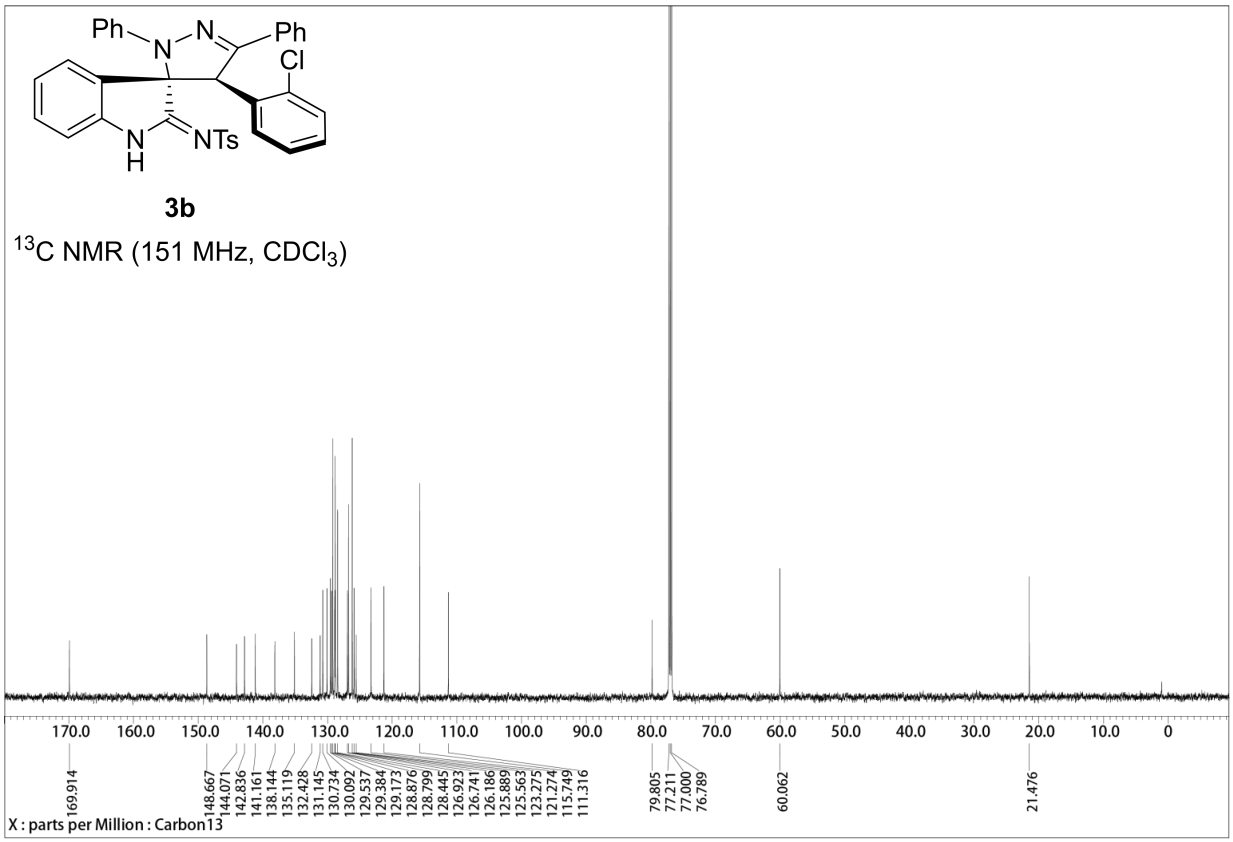
2.352
X : parts per Million : Proton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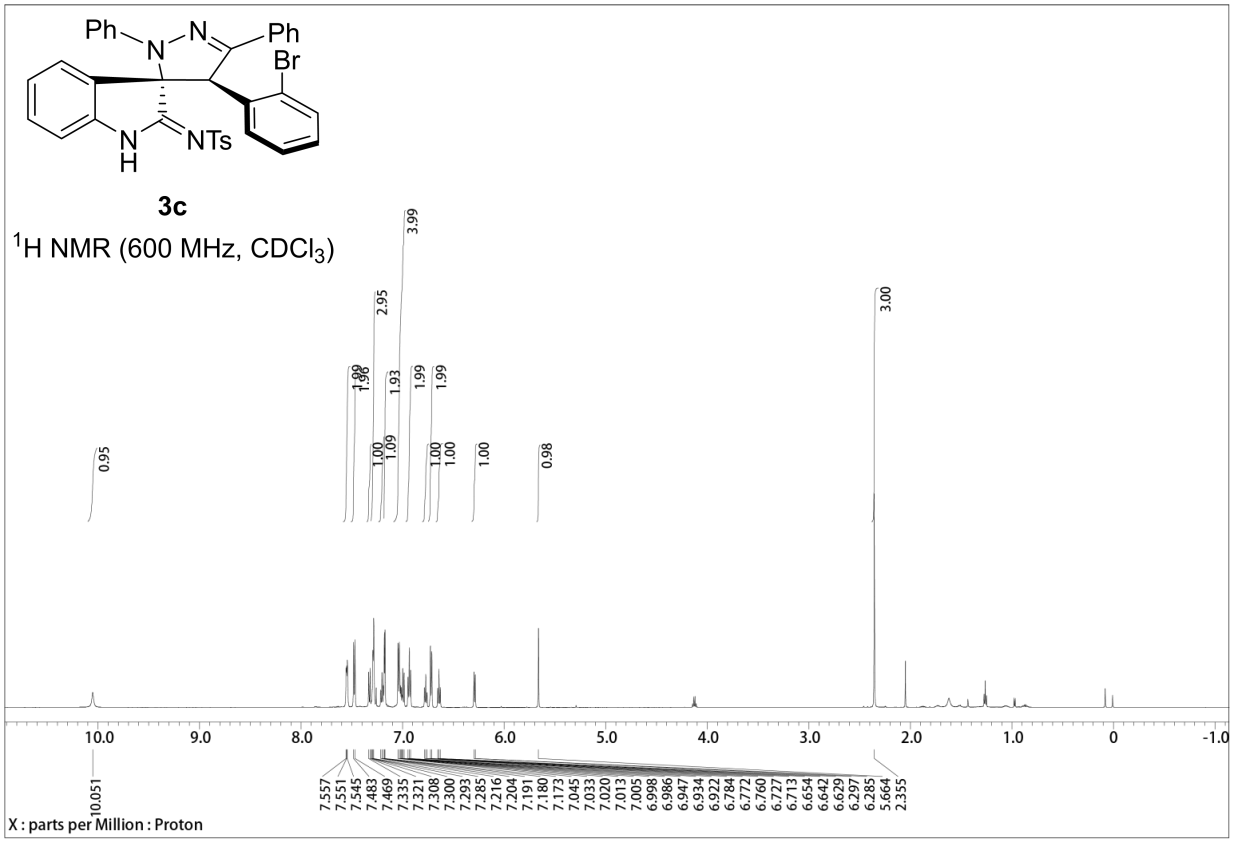
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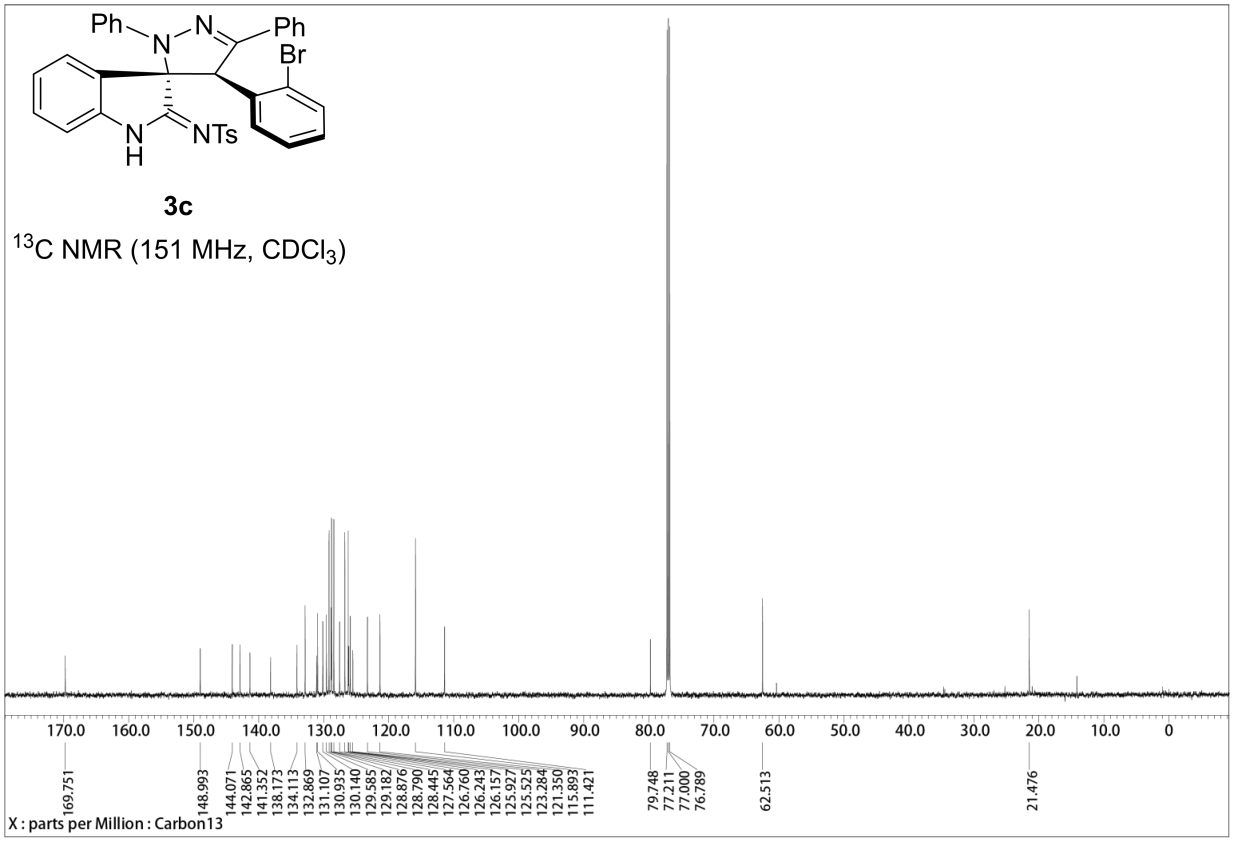
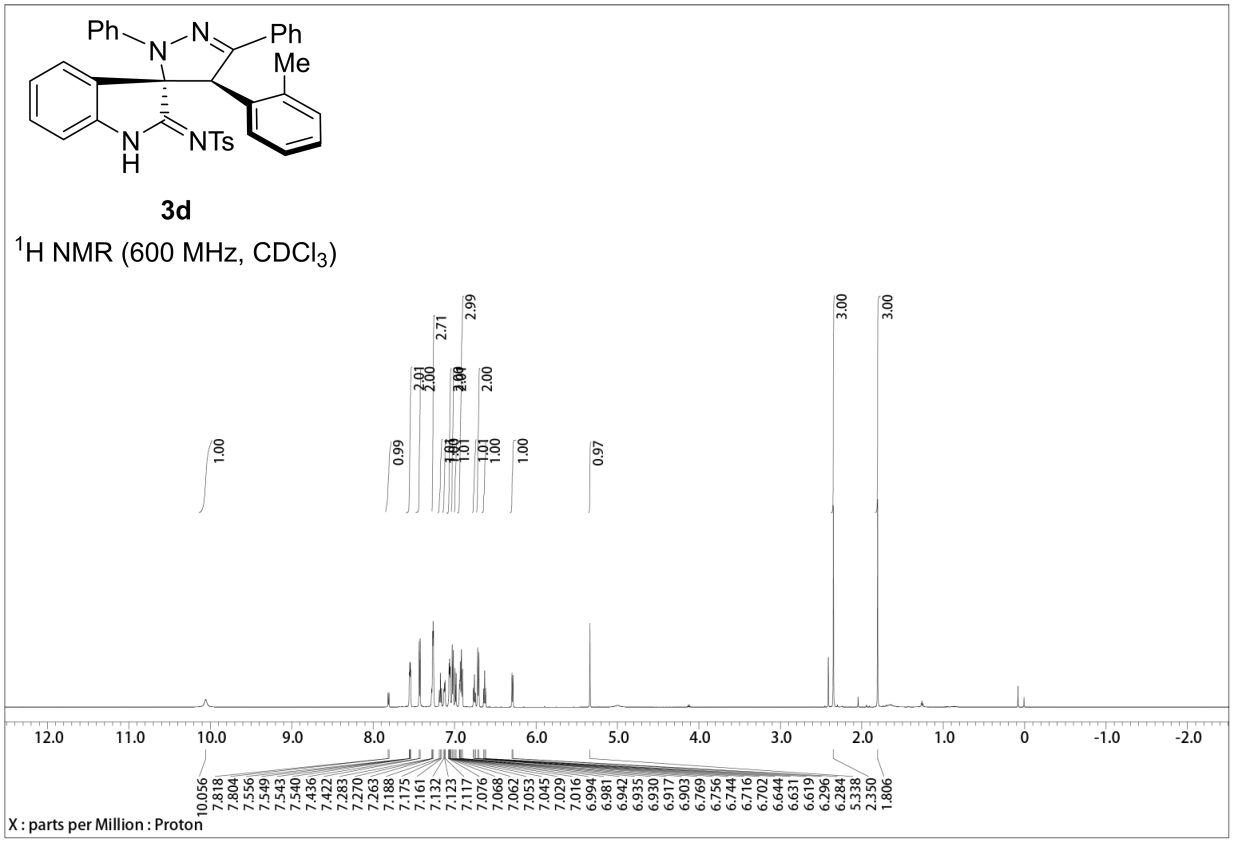
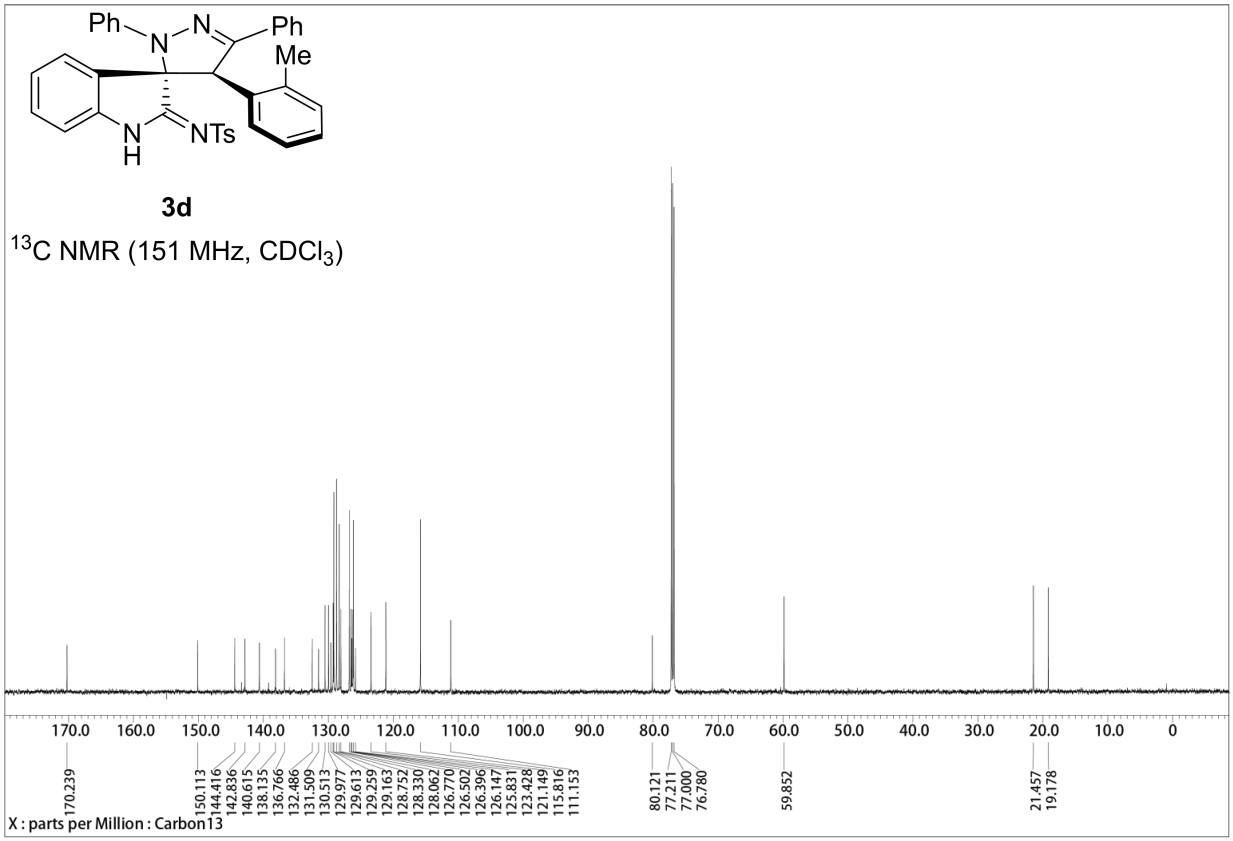
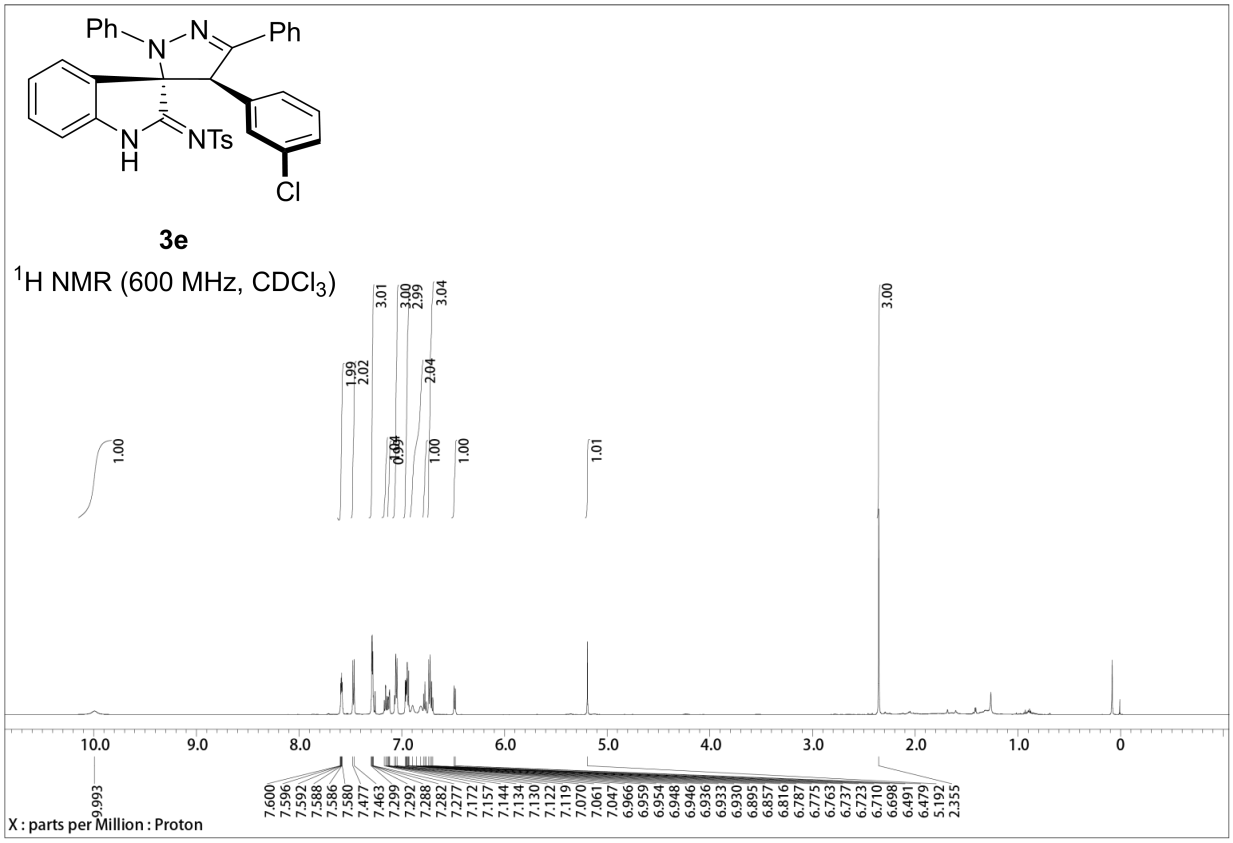
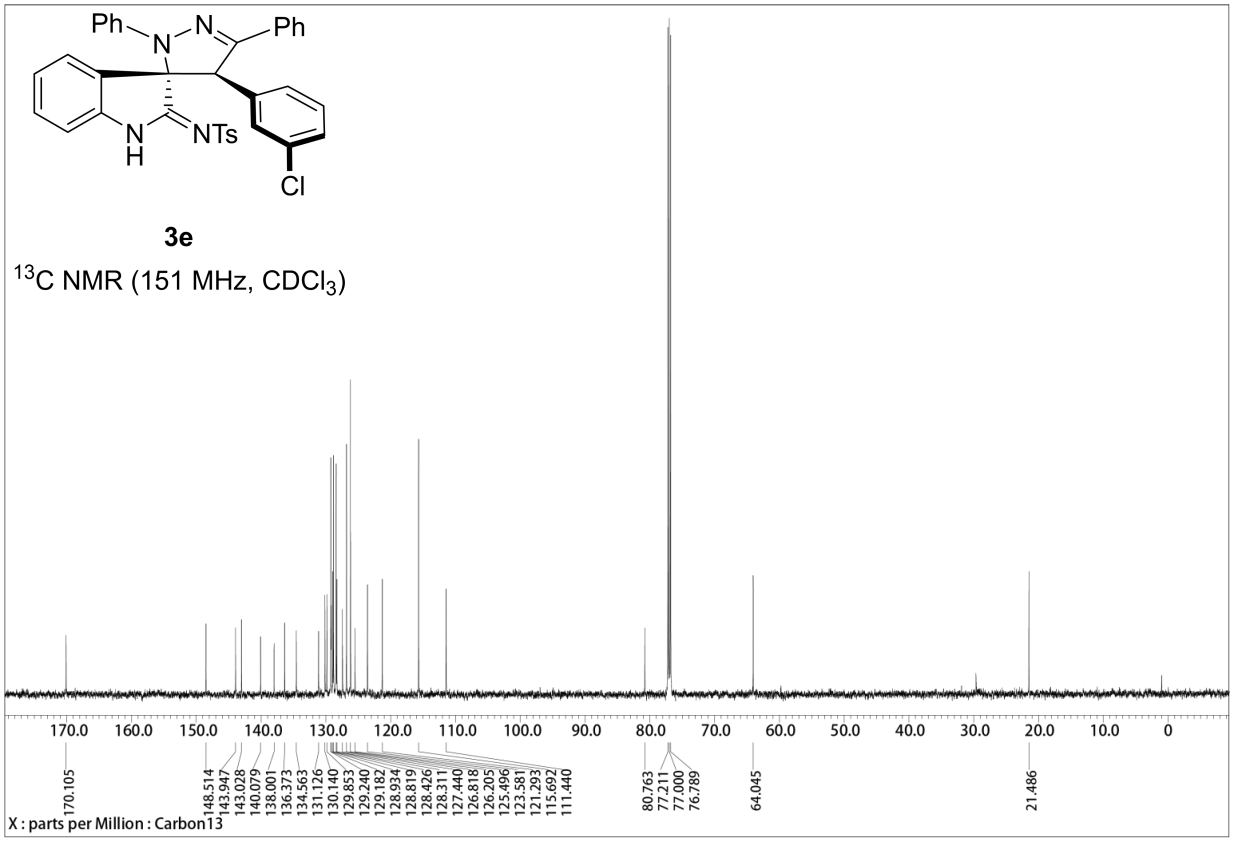
7.173
7.045
7.033
7.020
7.013
7.005
6.998
6.986
6.947
6.934
6.922
6.784
6.772
6.760
6.727
6.713
6.654
6.642
6.629
6.297
6.285
5.664
2.355
X : parts per Million : Proton

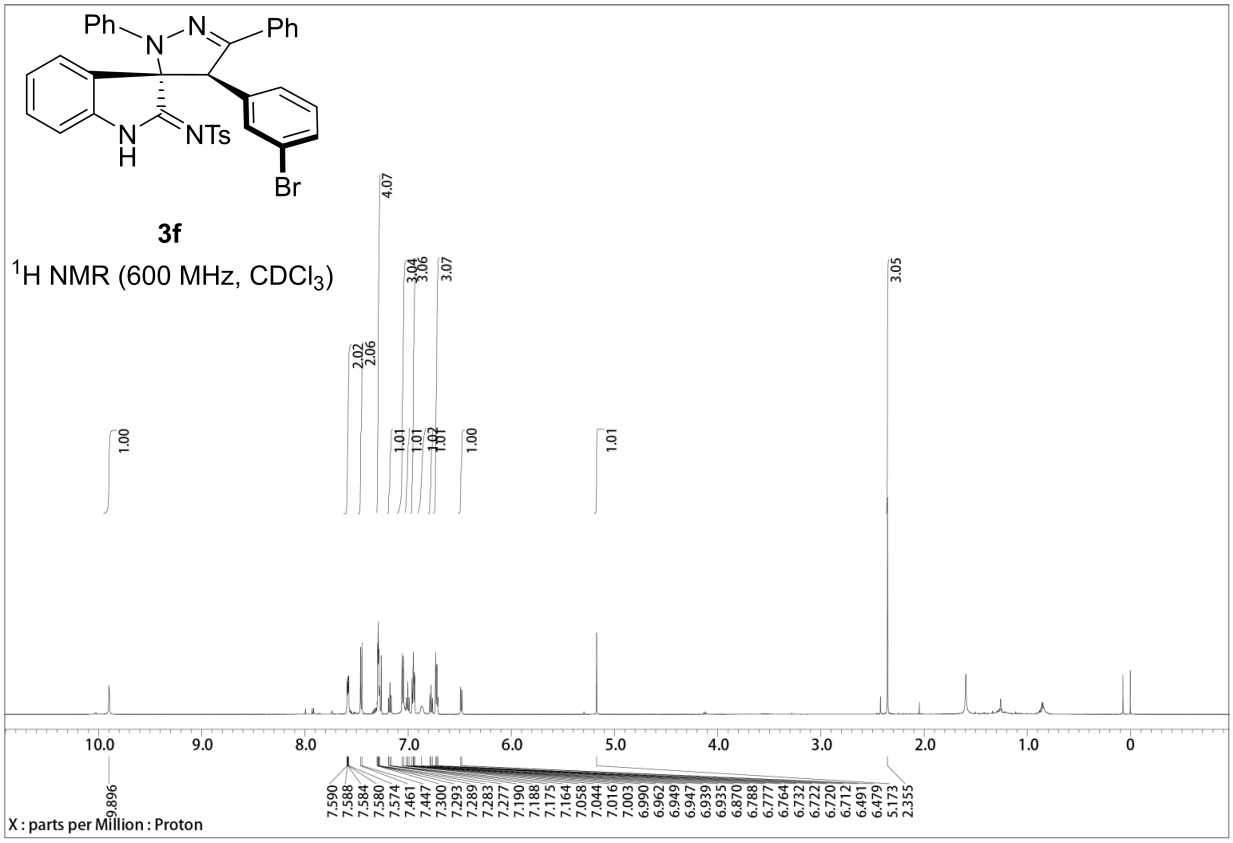

Ph
N
N
Ph
Br
N
H
NTs
3c
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.751
148.993
144.071
142.865
141.352
138.173
134.113
132.869
131.107
130.935
130.140
129.585
129.182
128.876
128.790
128.445
127.564
126.760
126.243
126.157
125.927
125.525
123.284
121.350
115.893
111.421
79.748
77.211
77.000
76.789
62.513
21.476
X : parts per Million : Carbon13

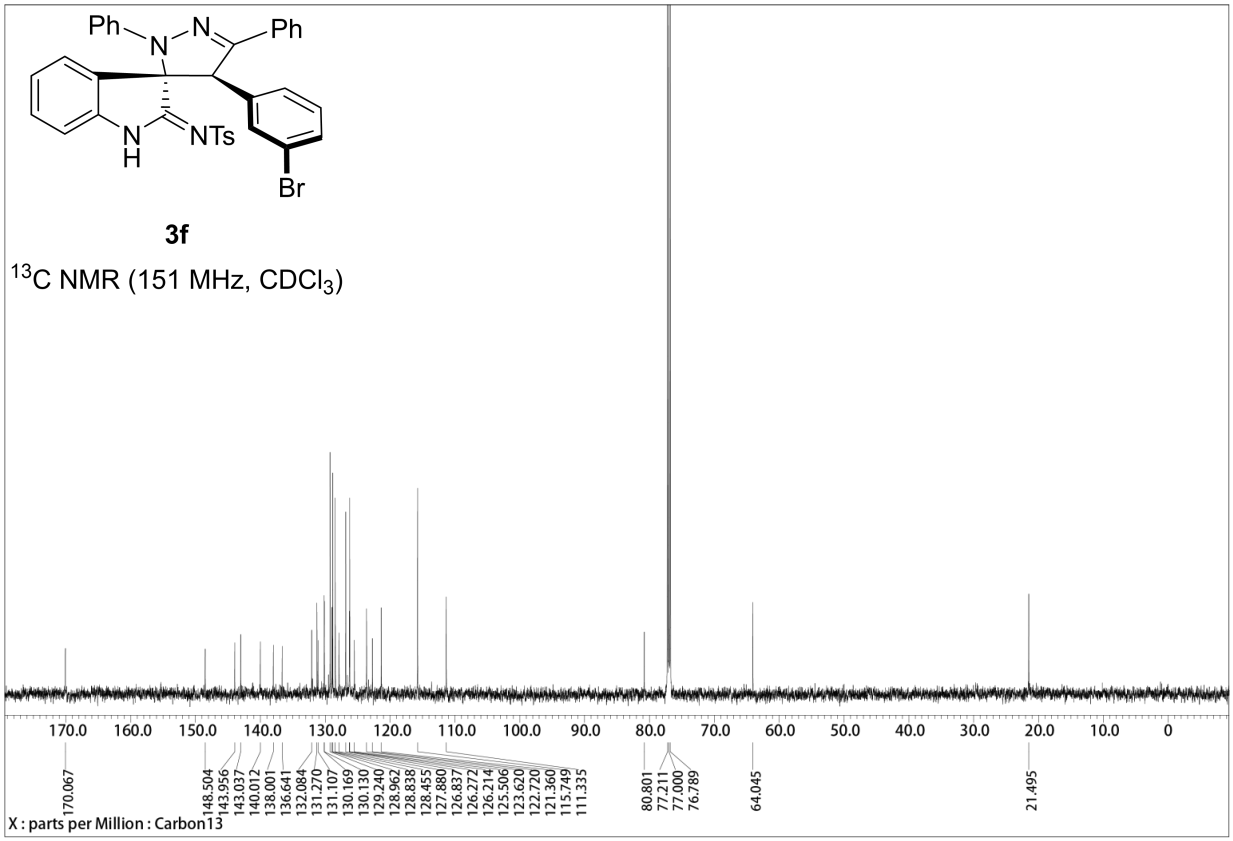

Ph
N
N
Ph
Me
N
H
NTs
3d
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton

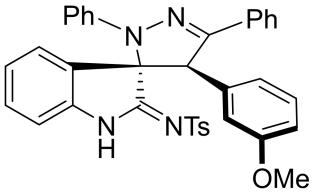

Ph
N
N
Ph
Me
N
H
NTs
3d
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13


Ph
N
N
Ph
N
H
NTs
Cl
3e
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


Ph
N
N
Ph
N
H
NTs
Cl
3e
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

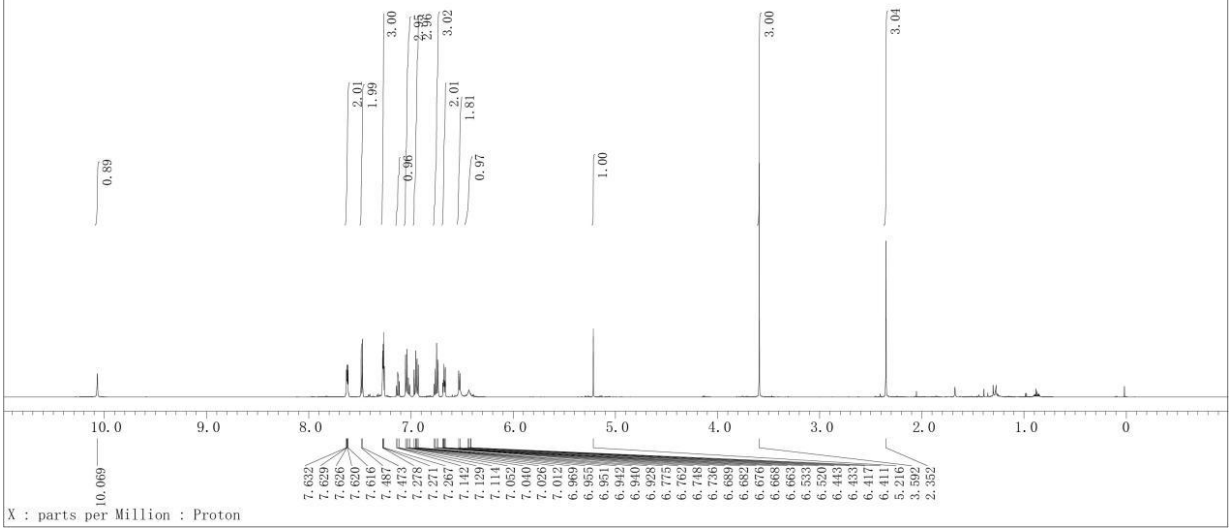

Ph
N
N
Ph
N
H
NTs
Br
3f
1H NMR (600 MHz, CDCl3)
4.07
3.04
3.06
3.07
3.05
2.02
2.06
1.00
1.01
1.01
1.02
1.01
1.00
1.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.896
7.590
7.588
7.584
7.580
7.574
7.461
7.447
7.300
7.293
7.289
7.283
7.277
7.190
7.188
7.175
7.164
7.058
7.044
7.016
7.003
6.990
6.962
6.949
6.947
6.939
6.935
6.870
6.788
6.777
6.764
6.732
6.722
6.720
6.712
6.491
6.479
5.173
2.355
X : parts per Million : Proton

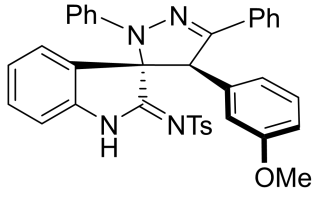

Ph
N
N
Ph
N
H
NTs
Br
3f
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.067
148.504
143.956
143.037
140.012
138.001
136.641
132.084
131.270
131.107
130.169
130.130
129.240
128.962
128.838
128.455
127.880
126.837
126.272
126.214
125.506
123.620
122.720
121.360
115.749
111.335
80.801
77.211
77.000
76.789
64.045
21.495
X : parts per Million : Carbon13



3g

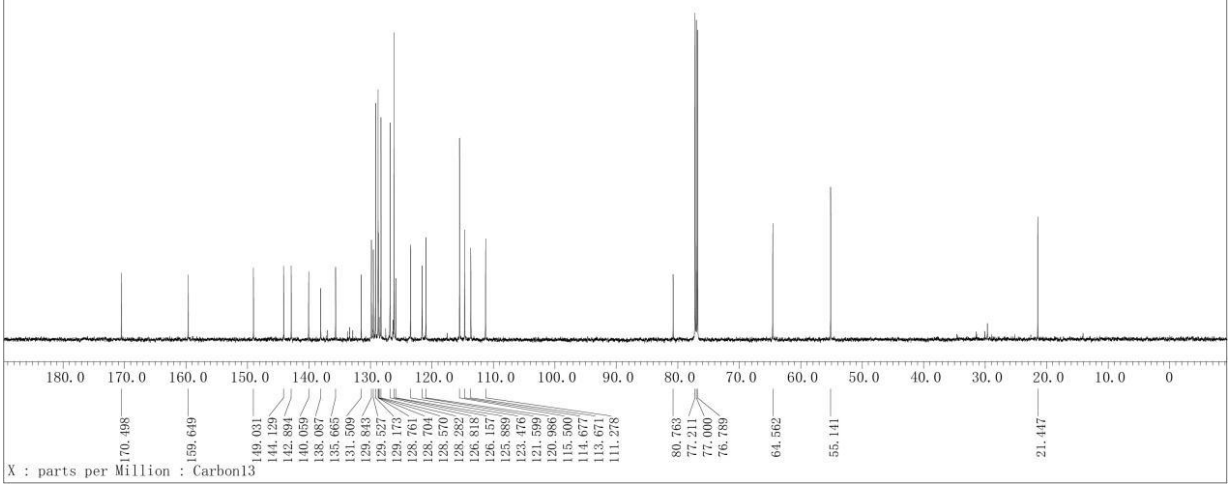
^{1}H NMR (600 MHz, $CDCl_3$)

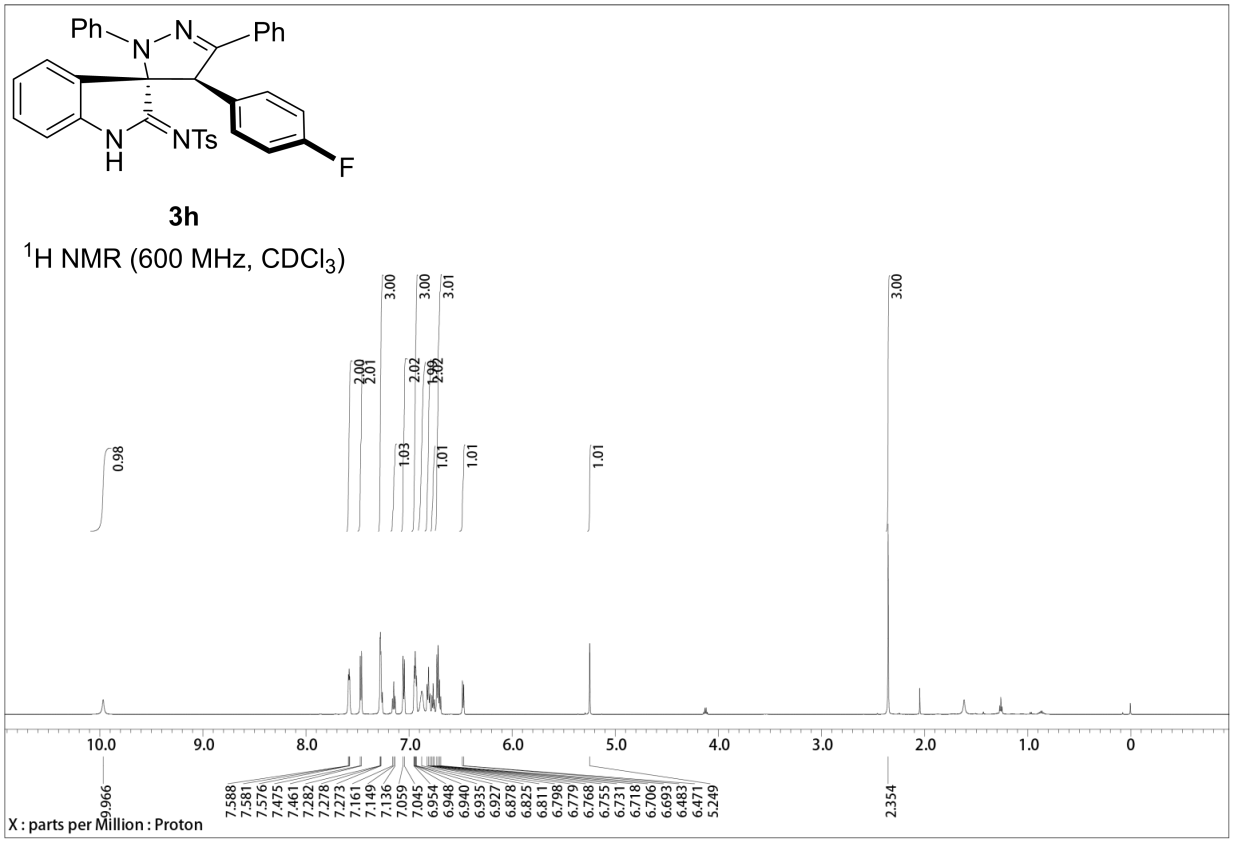


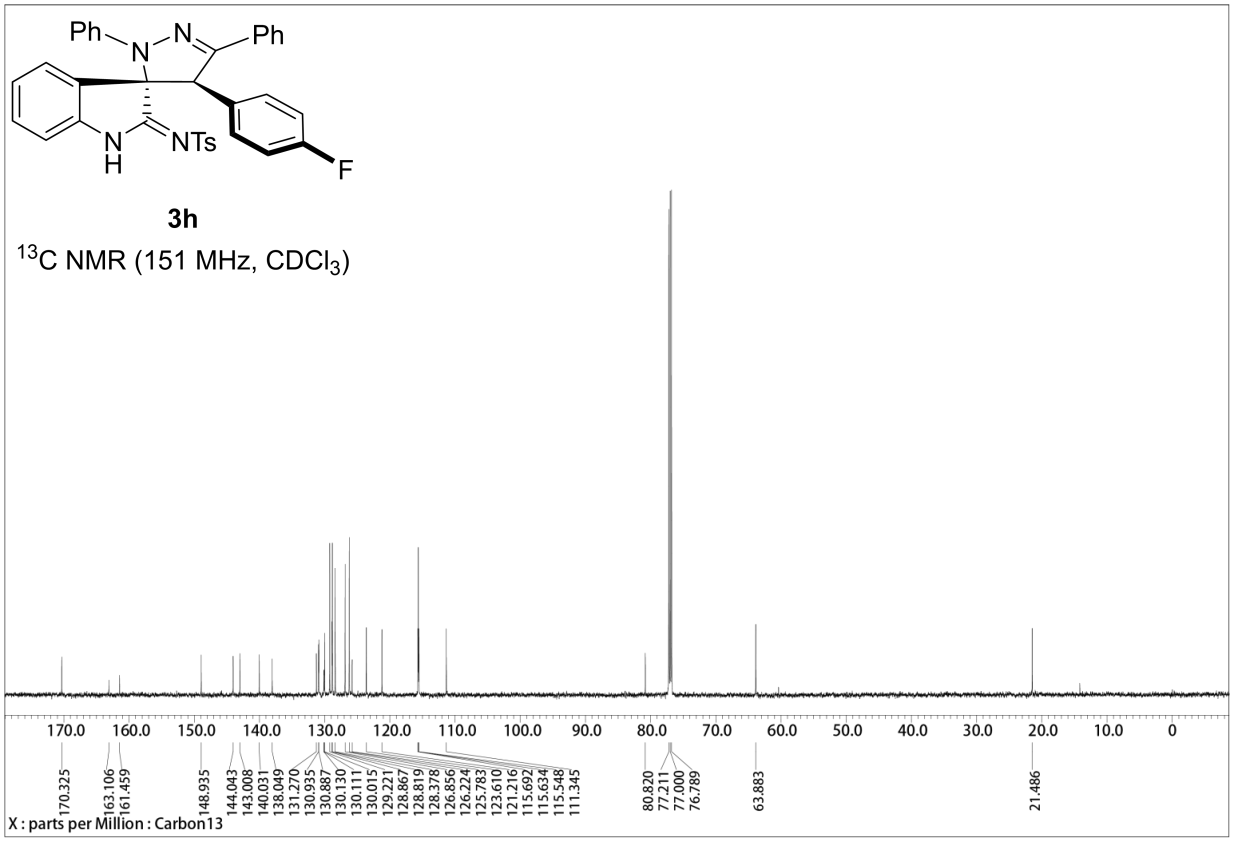


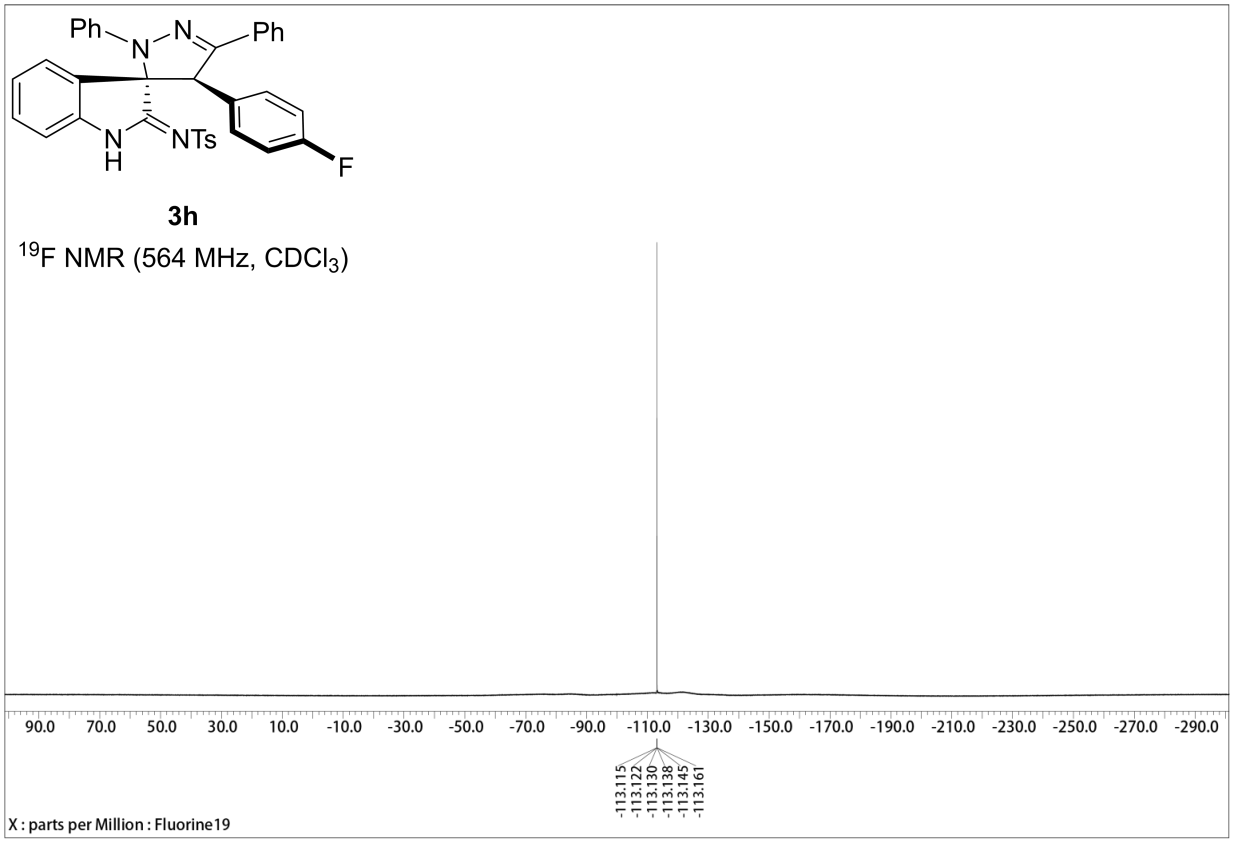
3g

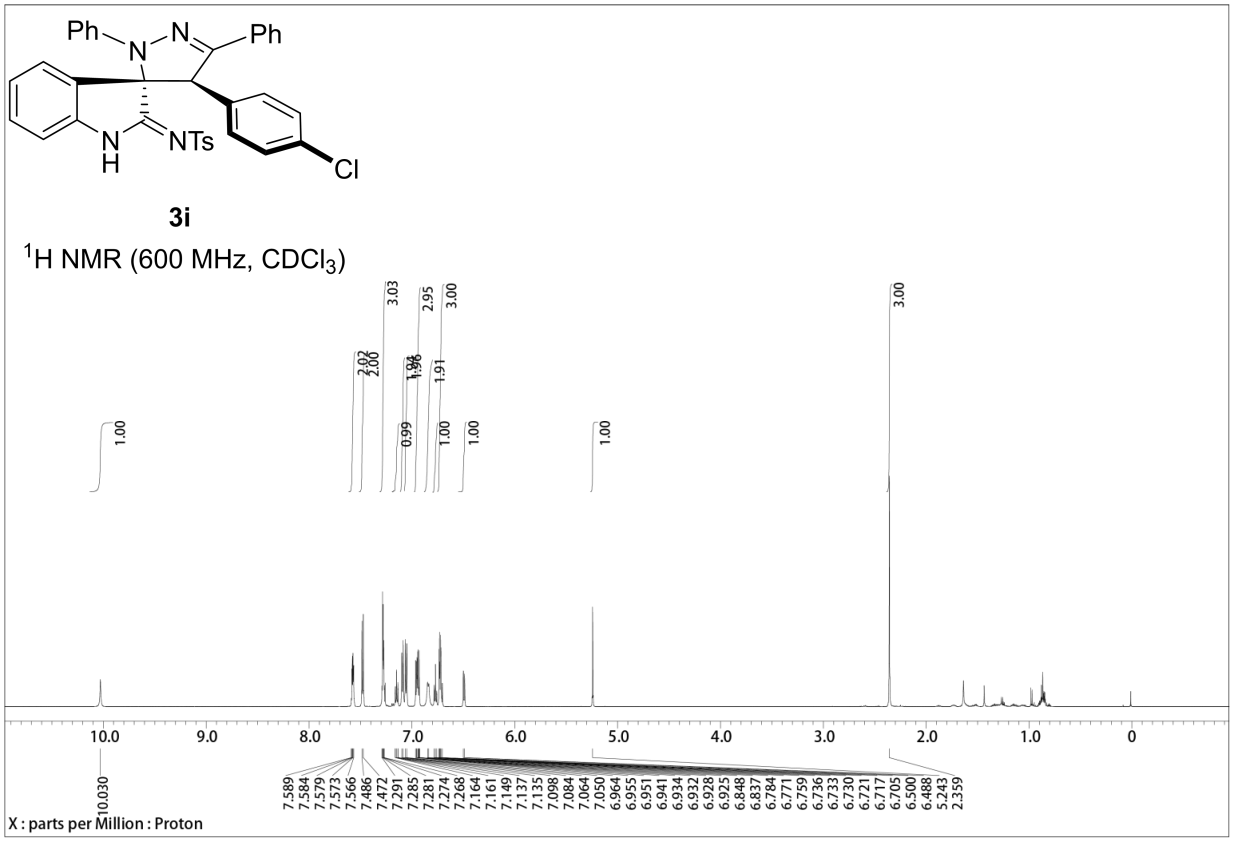
^{13}C NMR (151 MHz, $CDCl_3$)

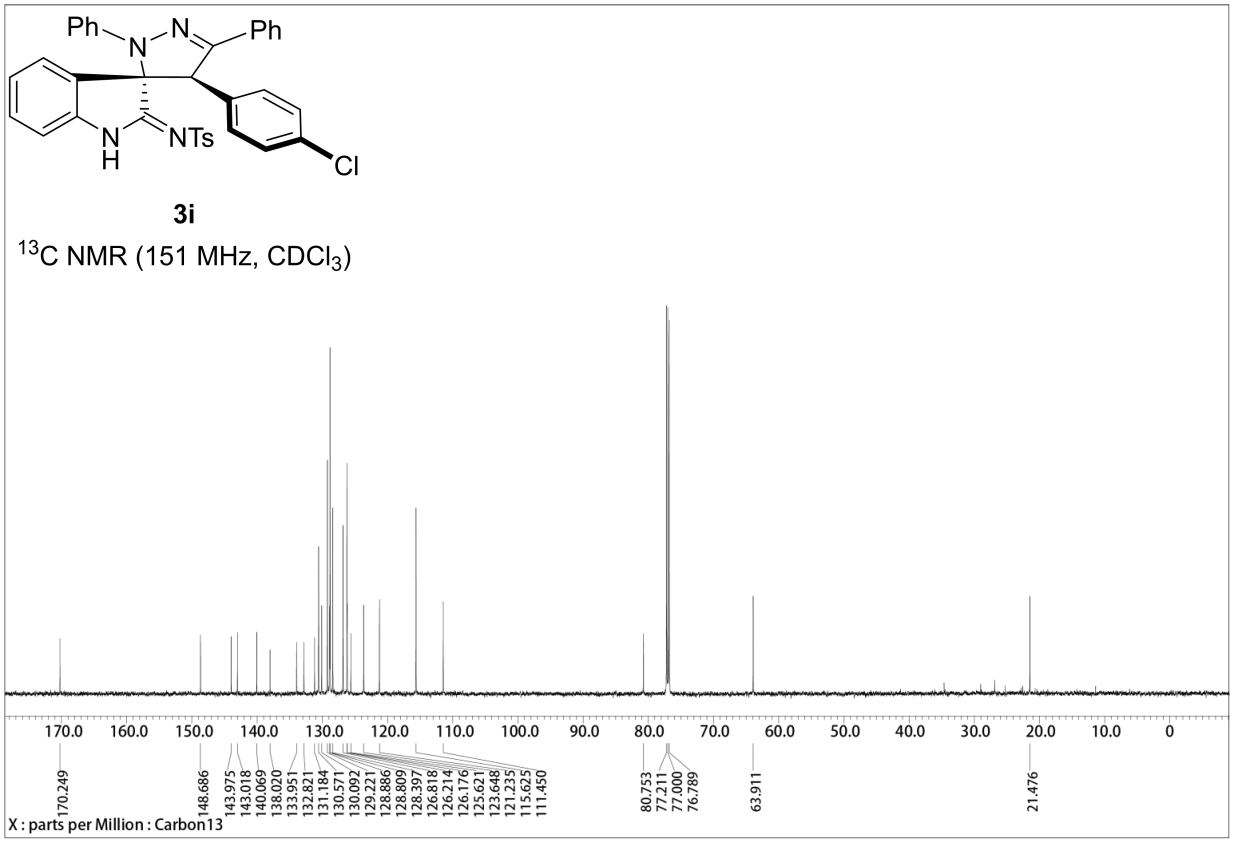


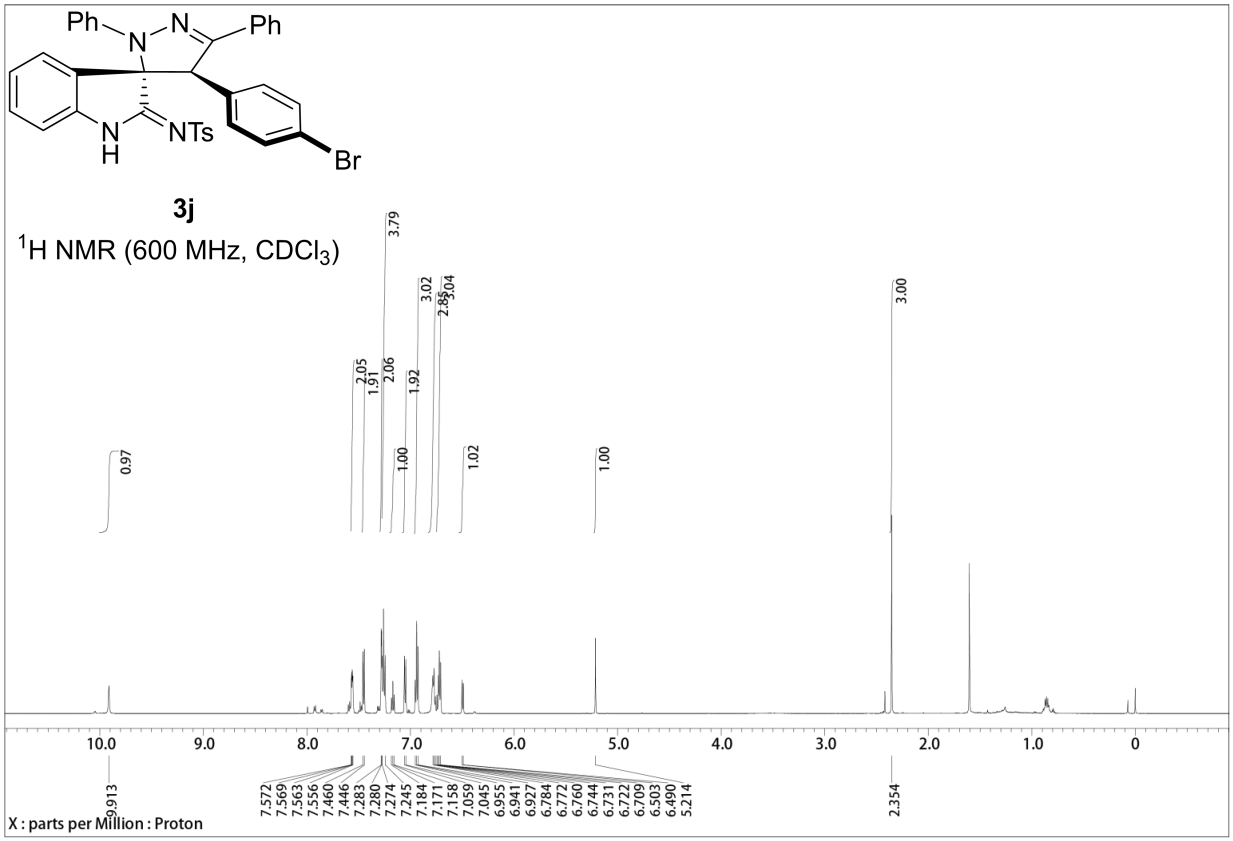

Ph
N
N
Ph
N
H
NTs
F
3h
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton

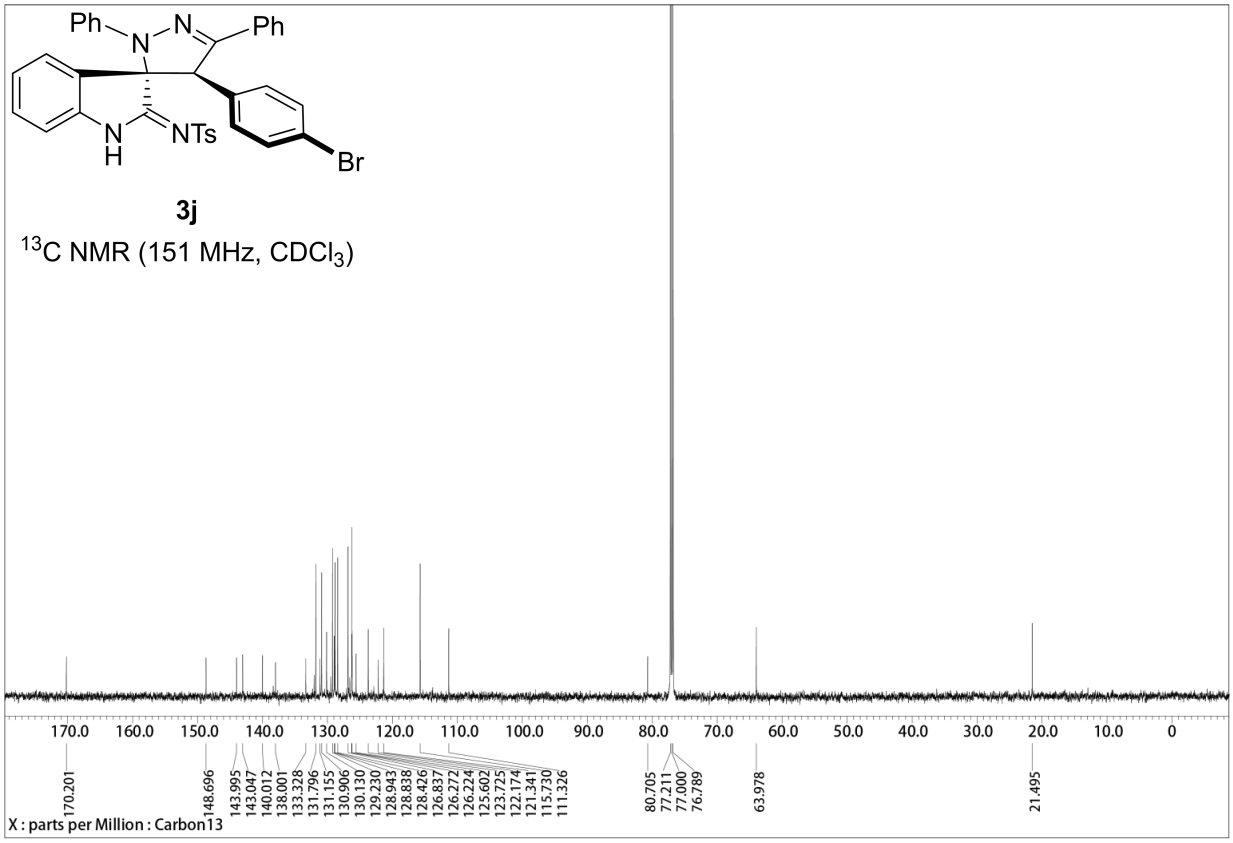

Ph
N
N
Ph
N
H
NTs
F
3h
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

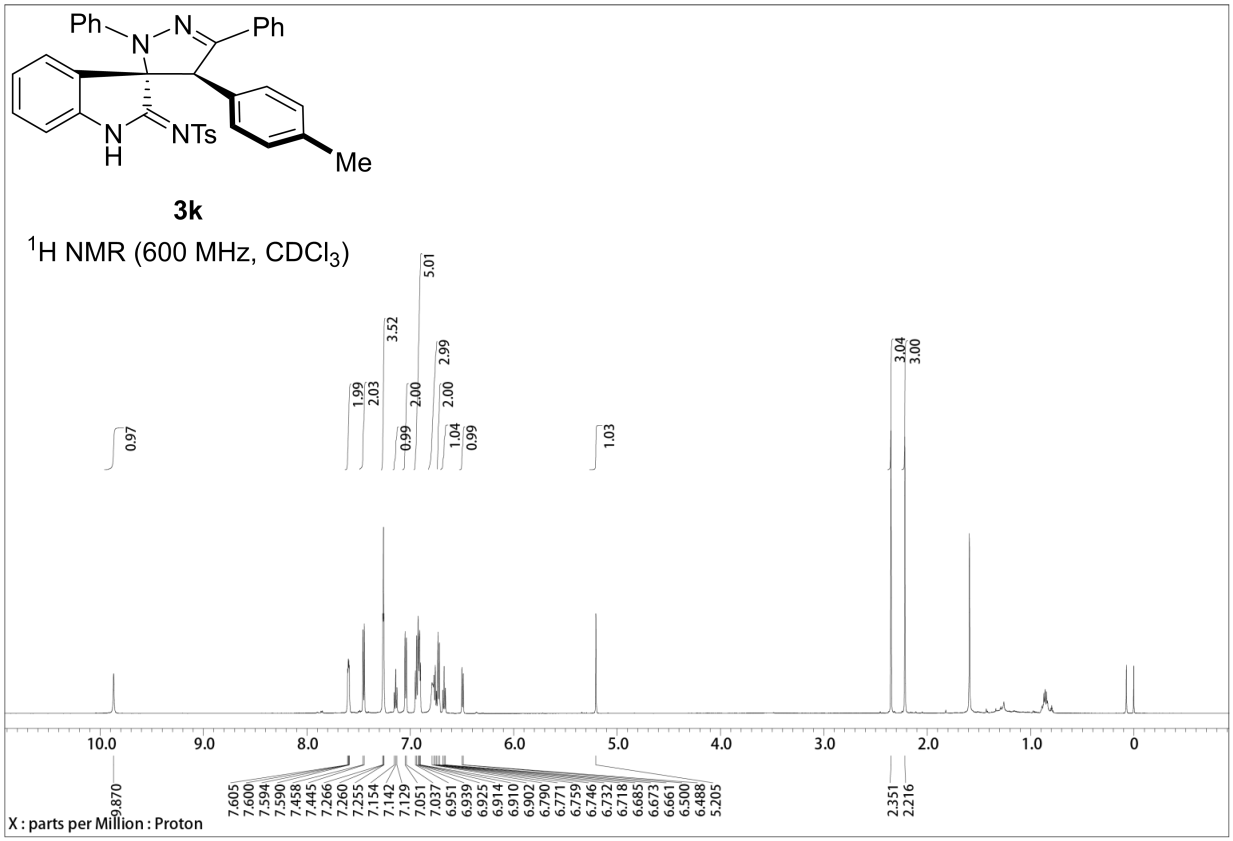

Ph
N
N
Ph
N
H
NTs
F
3h
19F NMR (564 MHz, CDCl3)
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0
-113.115
-113.122
-113.130
-113.138
-113.145
-113.161
X : parts per Million : Fluorine19

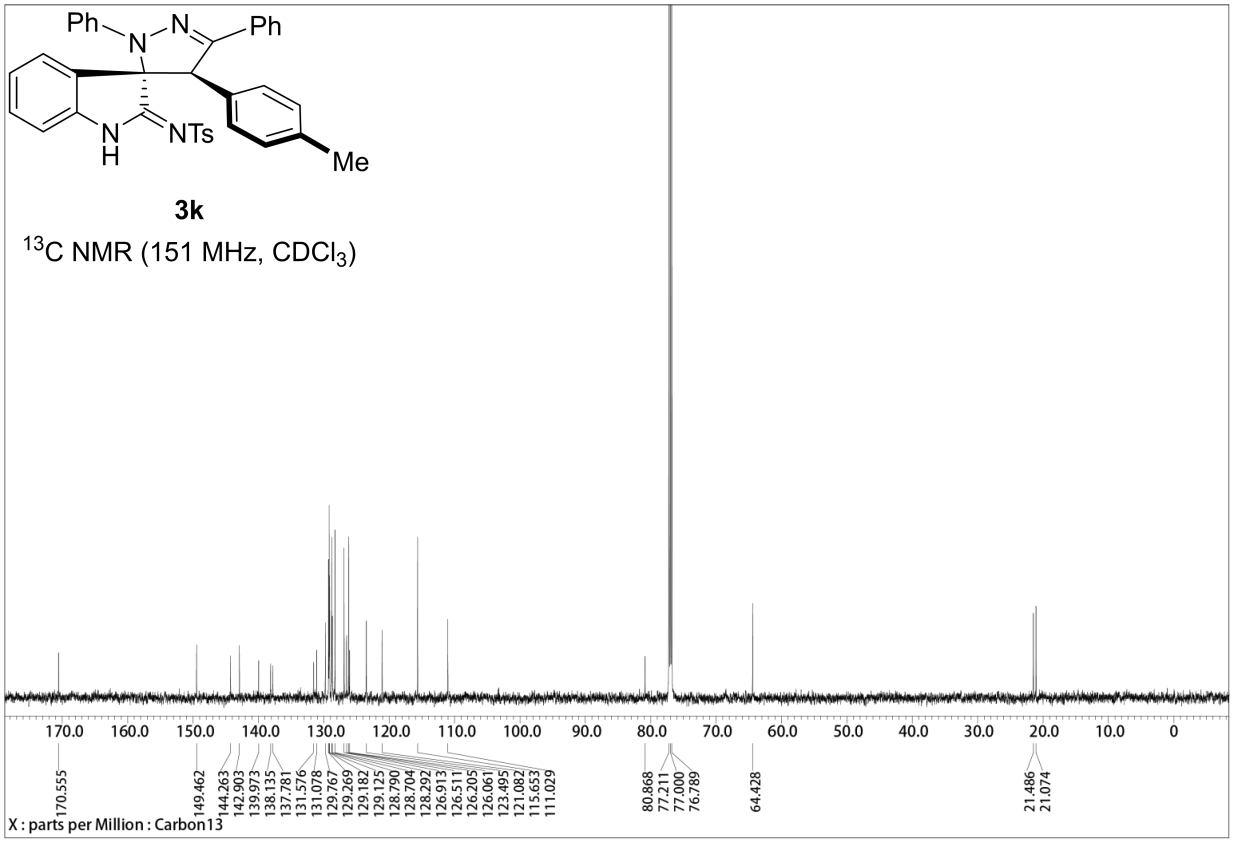

Ph
N
N
Ph
N
H
NTs
Cl
3i
1H NMR (600 MHz, CDCl3)
3.03
2.95
3.00
3.00
2.02
2.00
1.94
1.96
1.91
1.00
0.99
1.00
1.00
1.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
10.030
7.589 7.584 7.579 7.573 7.566 7.486 7.472 7.291 7.285 7.281 7.274 7.268 7.164 7.161 7.149 7.137 7.135 7.098 7.084 7.064 7.050 6.964 6.955 6.951 6.941 6.934 6.932 6.928 6.925 6.848 6.837 6.784 6.771 6.759 6.736 6.733 6.730 6.721 6.717 6.705 6.500 6.488 5.243 2.359
X : parts per Million : Proton

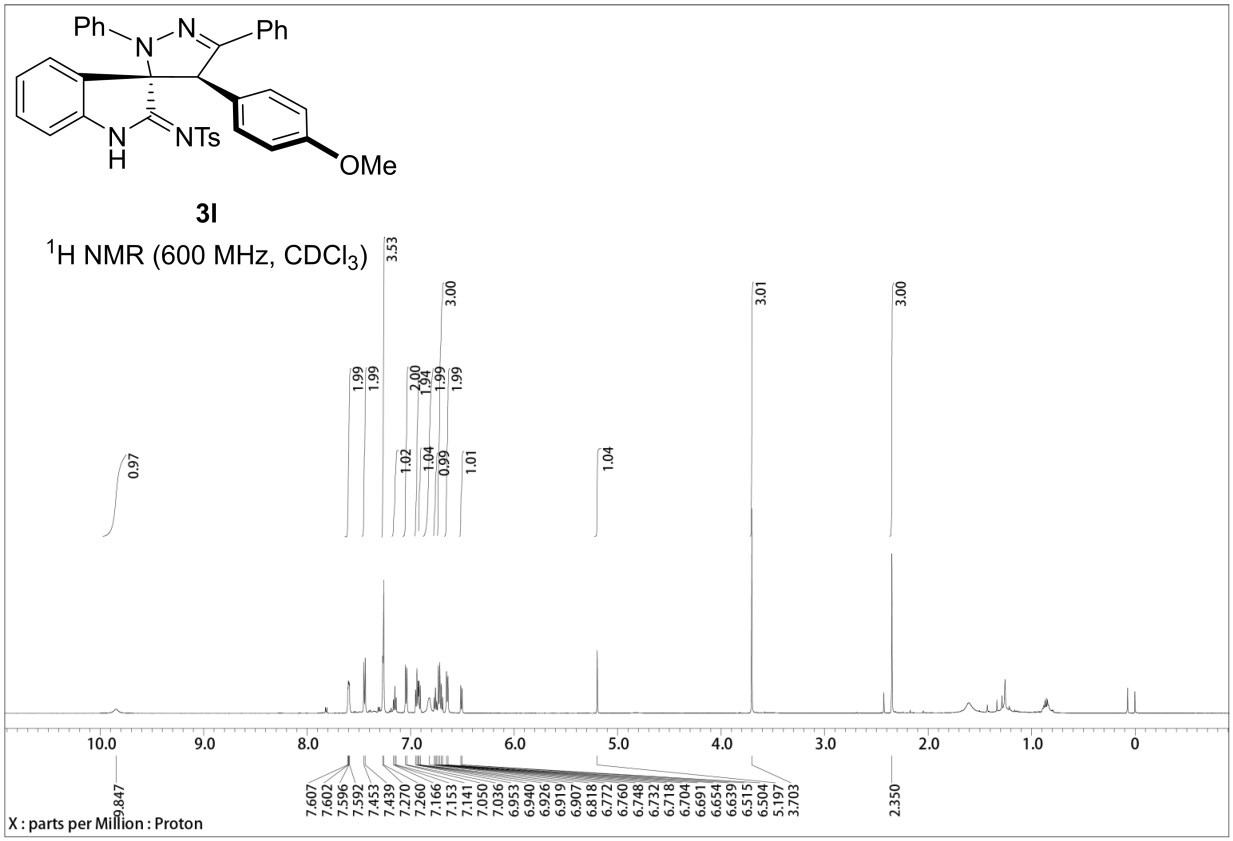

Ph
N
N
Ph
N
H
NTs
Cl
3i
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.249
148.686
143.975
143.018
140.069
138.020
133.951
132.821
131.184
130.571
130.092
129.221
128.886
128.809
128.397
126.818
126.214
126.176
125.621
123.648
121.235
115.625
111.450
80.753
77.211
77.000
76.789
63.911
21.476
X : parts per Million : Carbon13

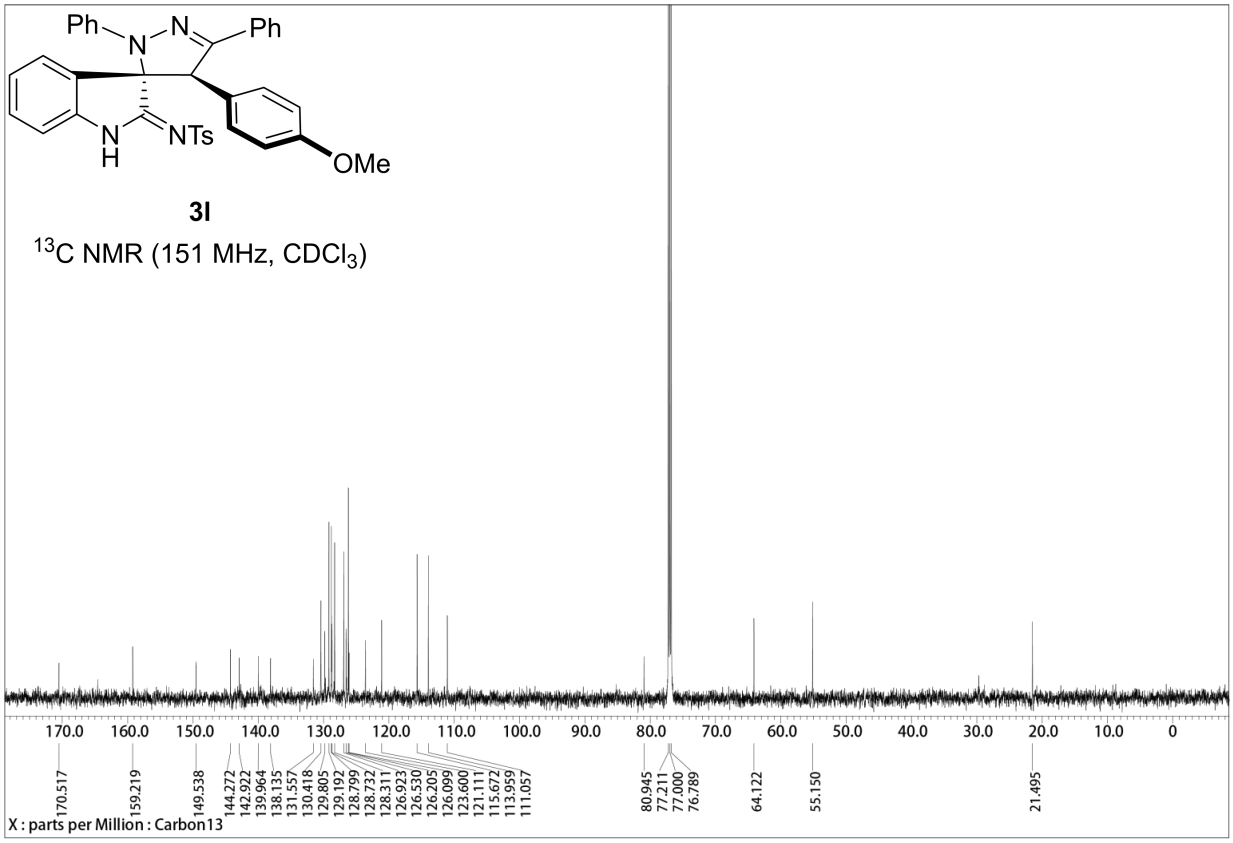

Ph
N
N
Ph
N
H
NTs
Br
3j
1H NMR (600 MHz, CDCl3)
3.79
3.02
2.88
3.04
2.05
1.91
2.06
1.92
0.97
1.00
1.02
1.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.913
7.572
7.569
7.563
7.556
7.460
7.446
7.283
7.280
7.274
7.245
7.184
7.171
7.158
7.059
7.045
6.955
6.941
6.927
6.784
6.772
6.760
6.744
6.731
6.722
6.709
6.503
6.490
5.214
2.354
X : parts per Million : Proton

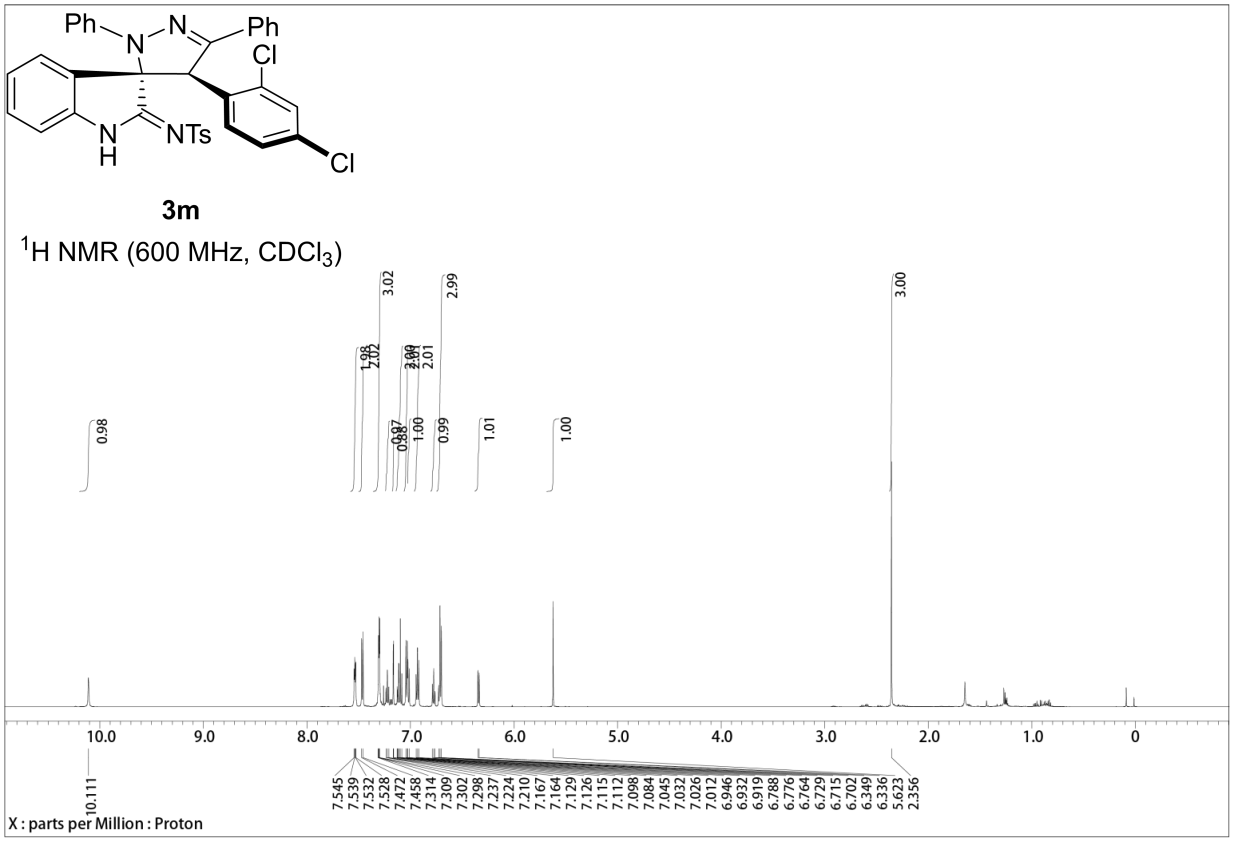

Ph
N
N
Ph
N
H
NTs
Br
3j
^{13}C NMR (151 MHz, CDCl$_3$)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.201
148.696
143.995
143.047
140.012
138.001
133.328
131.796
131.155
130.906
130.130
129.230
128.943
128.838
128.426
126.837
126.272
126.224
125.602
123.725
122.174
121.341
115.730
111.326
80.705
77.211
77.000
76.789
63.978
21.495
X : parts per Million : Carbon13

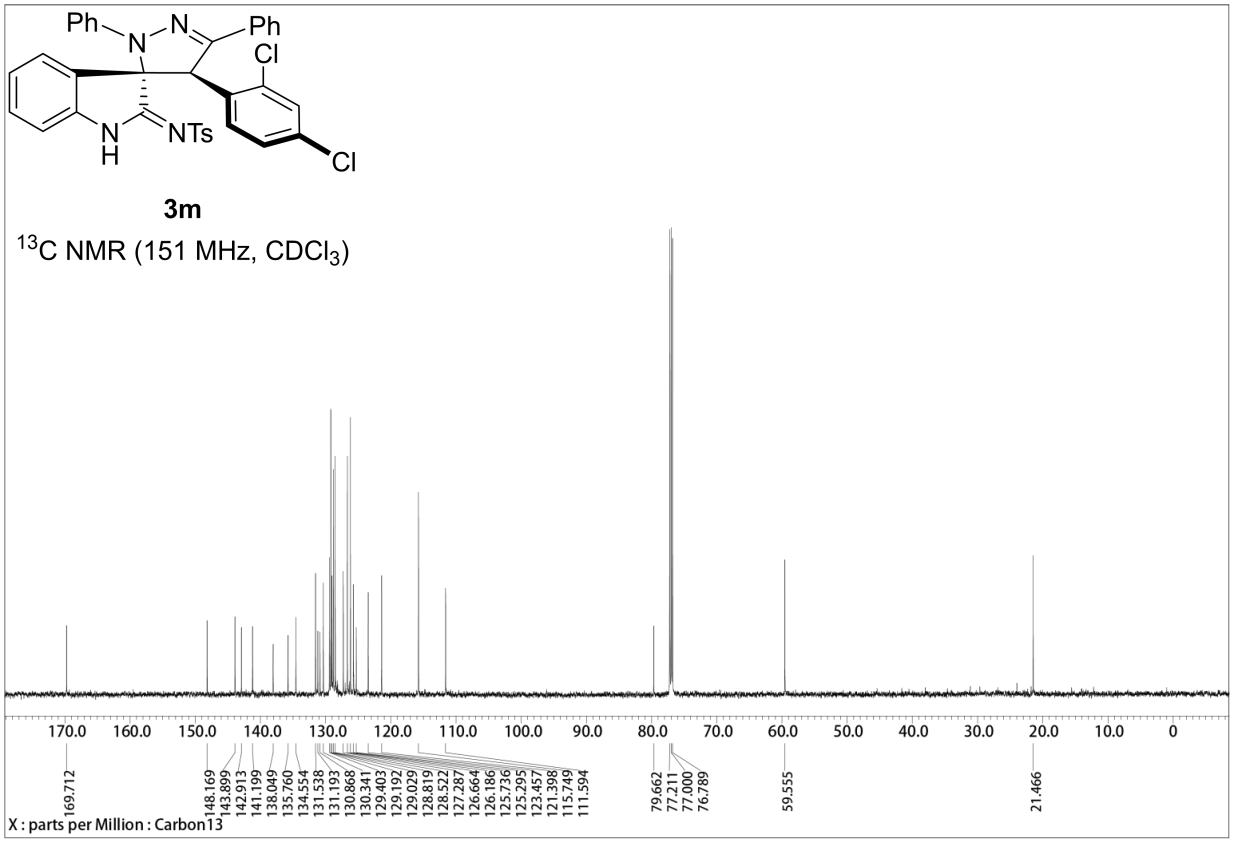

Ph
N
N
Ph
N
H
NTs
Me
3k
^{1}H NMR (600 MHz, CDCl$_3$)
0.97
1.99
2.03
3.52
5.01
0.99
2.00
2.99
2.00
1.04
0.99
1.03
3.04
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.870
7.605
7.600
7.594
7.590
7.458
7.445
7.266
7.260
7.255
7.154
7.142
7.129
7.051
7.037
6.951
6.939
6.925
6.914
6.910
6.902
6.790
6.771
6.759
6.746
6.732
6.718
6.685
6.673
6.661
6.500
6.488
5.205
2.351
2.216
X : parts per Million : Proton

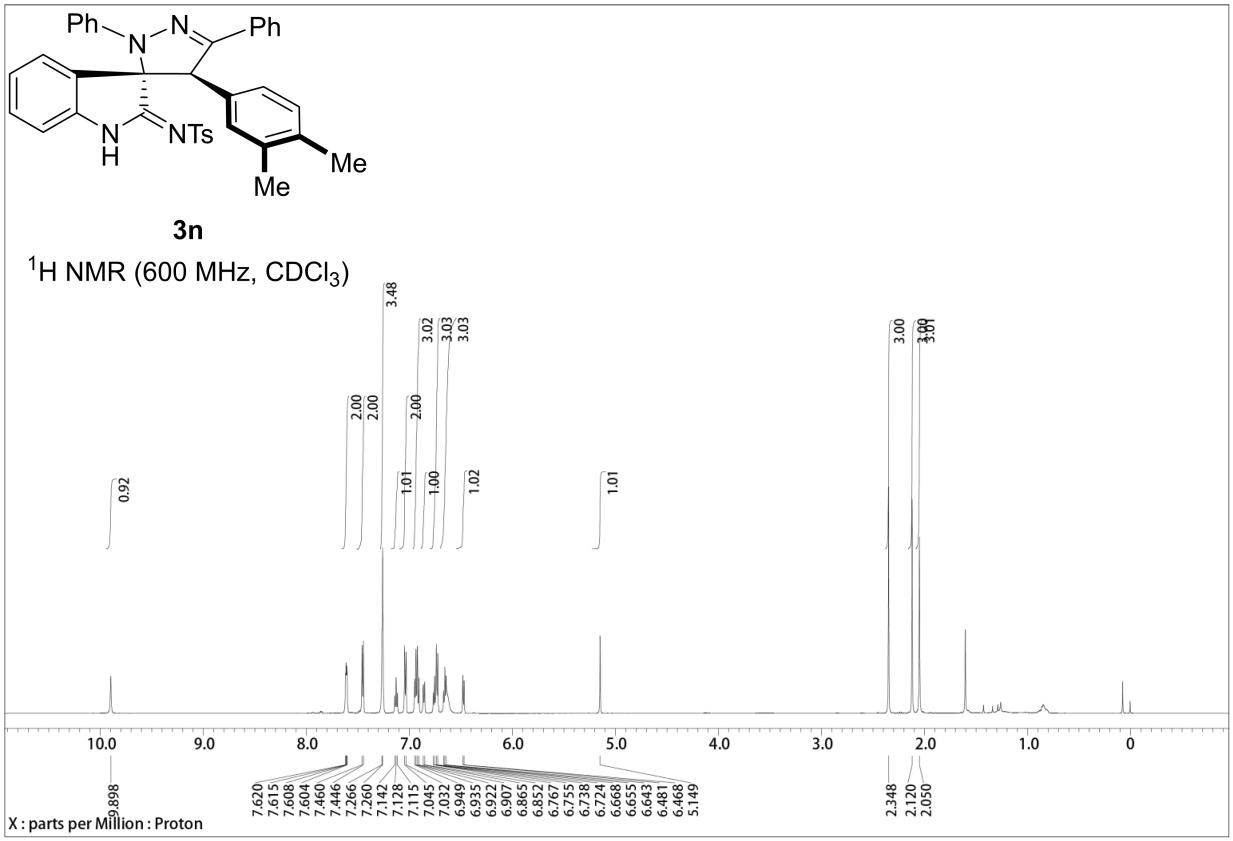

Ph
N
N
Ph
N
H
NTs
Me
3k
13C NMR (151 MHz, CDCl3)
170.555
149.462
144.263
142.903
139.973
138.135
137.781
131.576
131.078
129.767
129.269
129.182
129.125
128.790
128.704
128.292
126.913
126.511
126.205
126.061
123.495
121.082
115.653
111.029
80.868
77.211
77.000
76.789
64.428
21.486
21.074
X : parts per Million : Carbon13

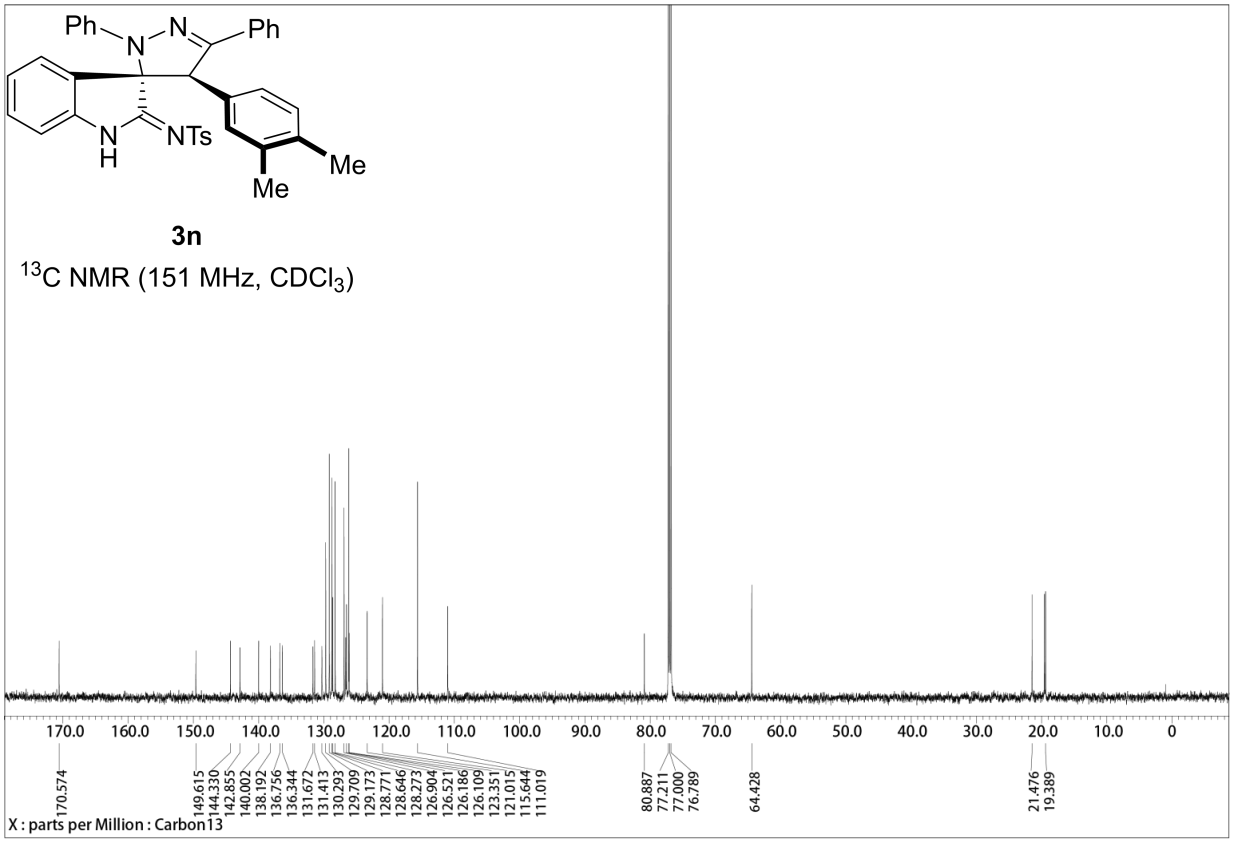

Ph
N
N
Ph
N
H
NTs
OMe
3l
1H NMR (600 MHz, CDCl3)
3.53
3.00
3.01
3.00
1.99
1.99
2.00
1.94
1.99
1.99
0.97
1.02
1.04
0.99
1.01
1.04
9.847
7.607
7.602
7.596
7.592
7.453
7.439
7.270
7.260
7.166
7.153
7.141
7.050
7.036
6.953
6.940
6.926
6.919
6.907
6.818
6.772
6.760
6.748
6.732
6.718
6.704
6.691
6.654
6.639
6.515
6.504
5.197
3.703
2.350
X : parts per Million : Proton

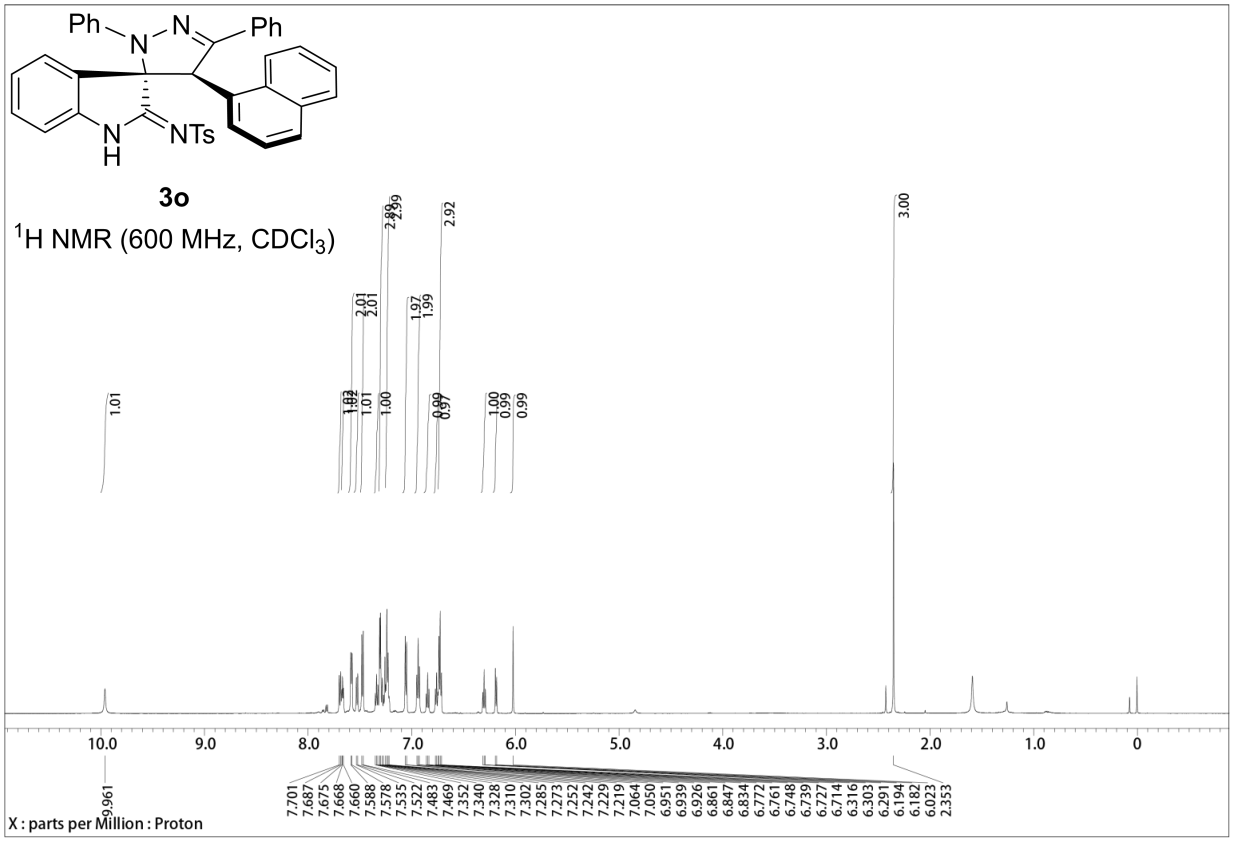

Ph
N
N
Ph
N
H
NTs
OMe
3l
13C NMR (151 MHz, CDCl3)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.517 159.219 149.538 144.272 142.922 139.964 138.135 131.557 130.418 129.805 129.192 128.799 128.732 128.311 126.923 126.530 126.205 126.099 123.600 121.111 115.672 113.959 111.057
80.945 77.211 77.000 76.789 64.122 55.150 21.495
X : parts per Million : Carbon13

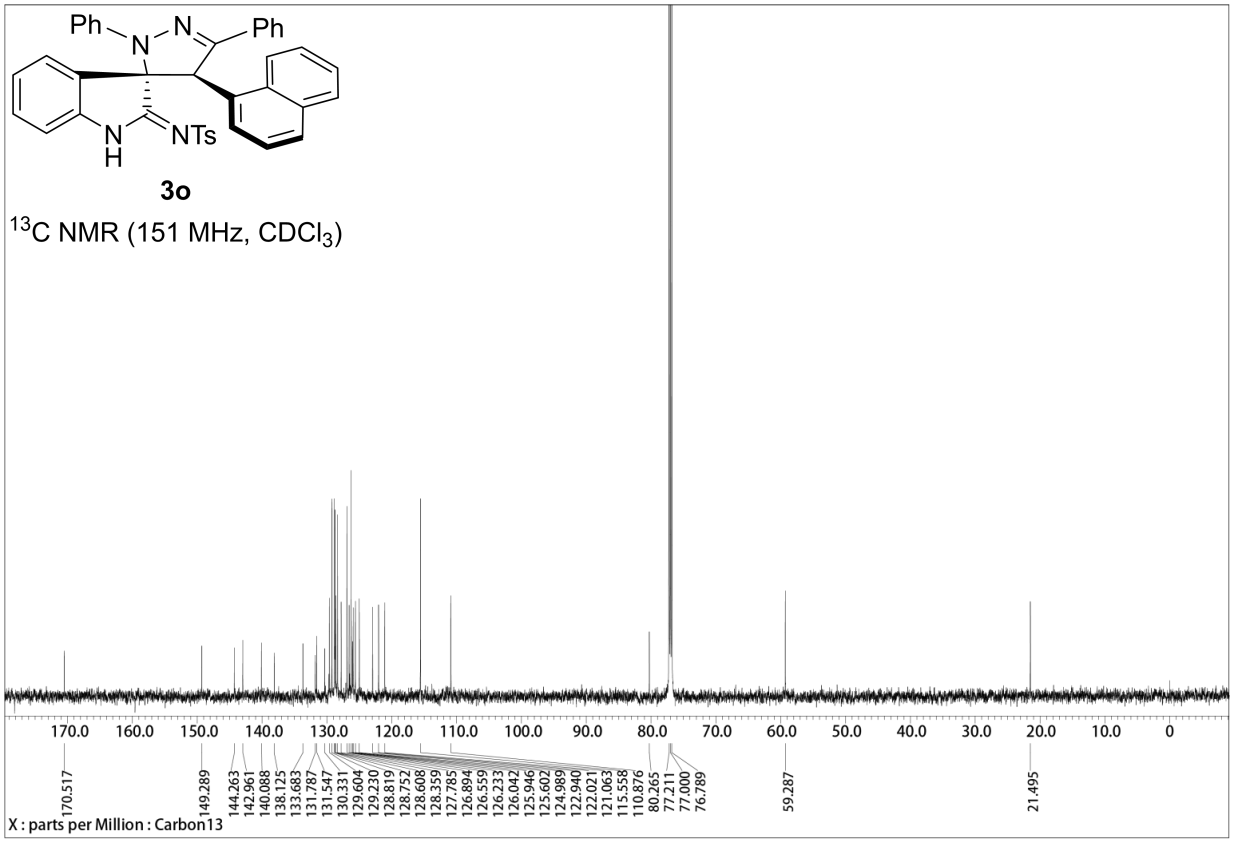

Ph
N
N
Ph
Cl
N
H
NTs
Cl
3m
1H NMR (600 MHz, CDCl3)
3.02 2.99 3.00
1.98 2.02 2.01
0.98 1.00 0.99 1.01 1.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
10.111
7.545 7.539 7.532 7.528 7.472 7.458 7.314 7.309 7.302 7.298 7.237 7.224 7.210 7.167 7.164 7.129 7.126 7.115 7.112 7.098 7.084 7.045 7.032 7.026 7.012 6.946 6.932 6.919 6.788 6.776 6.764 6.729 6.715 6.702 6.349 6.336 5.623 2.356
X : parts per Million : Proton

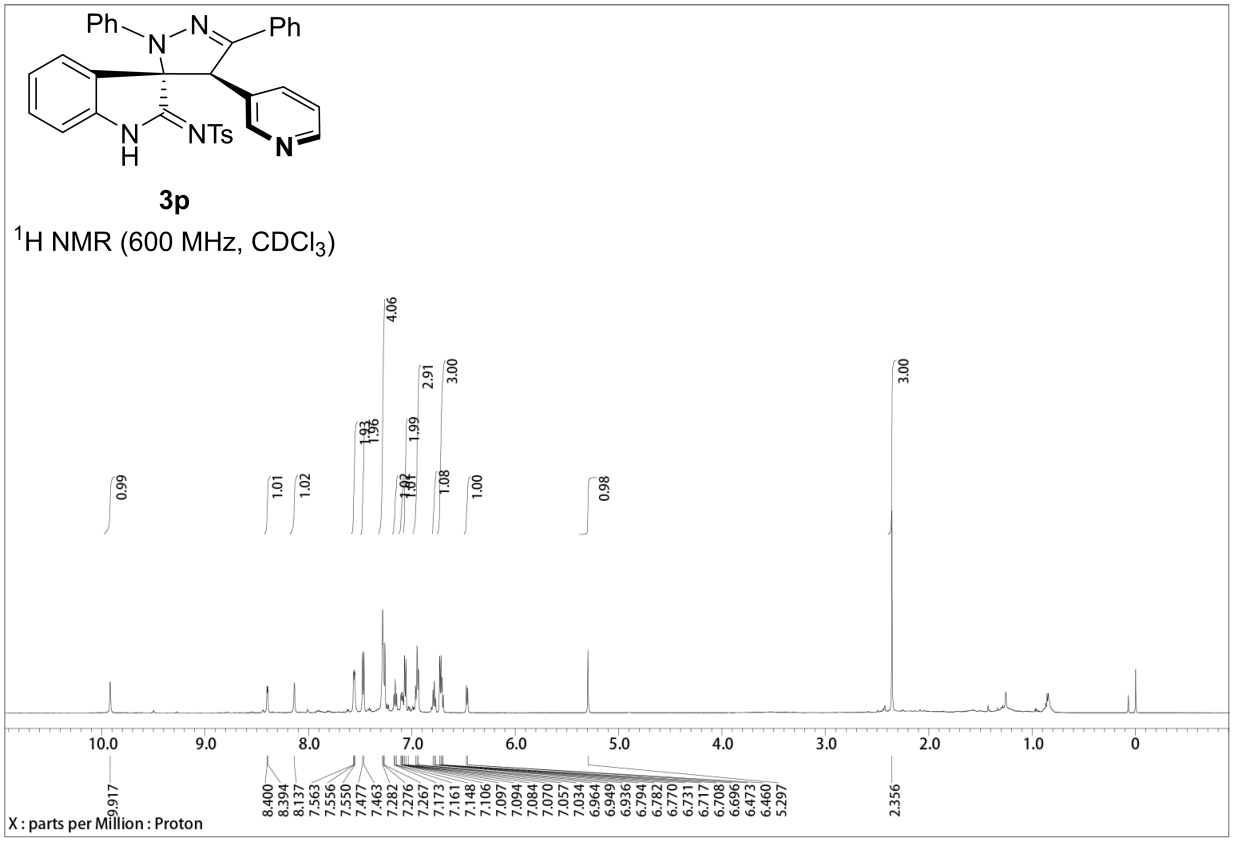

Ph
N
N
Ph
Cl
N
H
NTs
Cl
3m
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

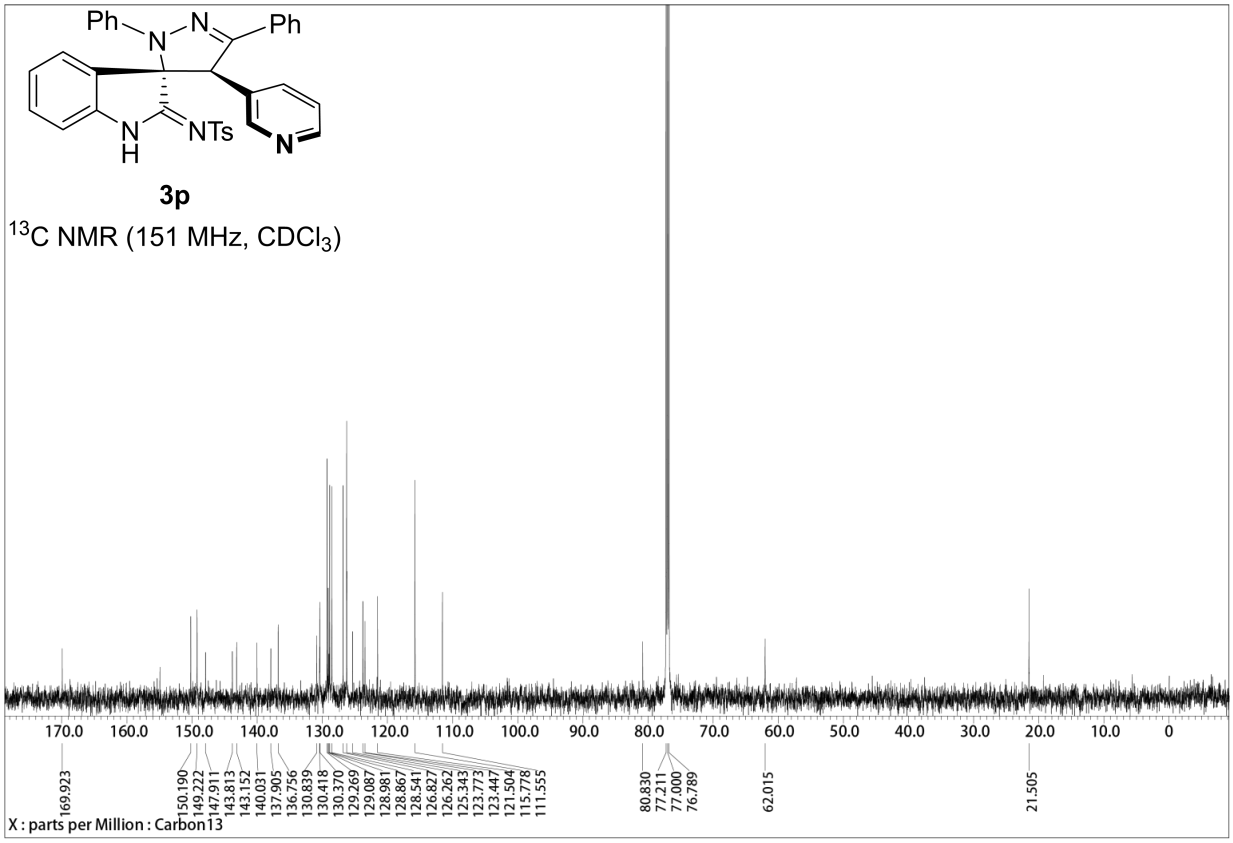

Ph
N
N
Ph
N
H
NTs
Me
Me
3n
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton

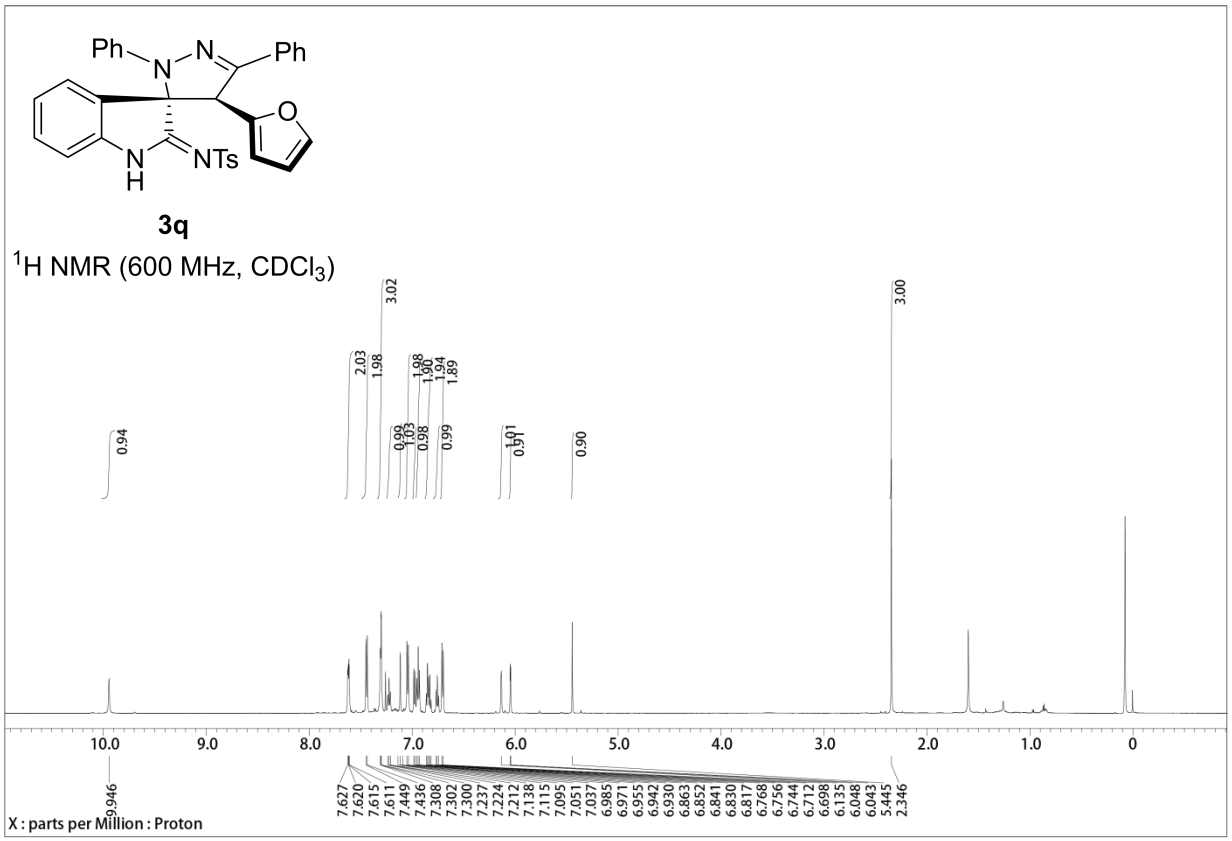

Ph
N
N
Ph
N
H
NTs
Me
Me
3n
13C NMR (151 MHz, CDCl3)
170.574
149.615
144.330
142.855
140.002
138.192
136.756
136.344
131.672
131.413
130.293
129.709
129.173
128.771
128.646
128.273
126.904
126.521
126.186
126.109
123.351
121.015
115.644
111.019
80.887
77.211
77.000
76.789
64.428
21.476
19.389
X : parts per Million : Carbon13

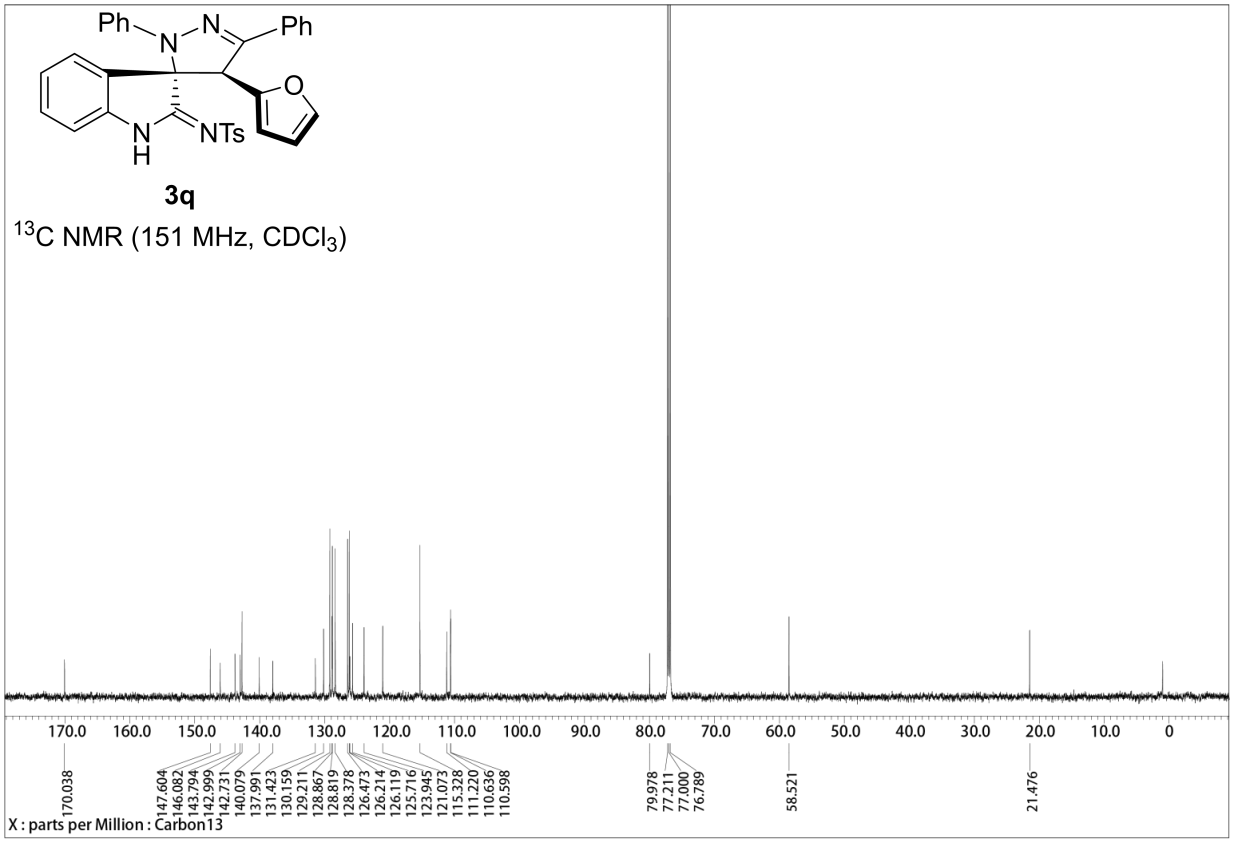

Ph
N
N
Ph
N
H
NTs
3o
1H NMR (600 MHz, CDCl3)
9.961
7.701
7.687
7.675
7.668
7.660
7.588
7.578
7.535
7.522
7.483
7.469
7.352
7.340
7.328
7.310
7.302
7.285
7.273
7.252
7.242
7.229
7.219
7.064
7.050
6.951
6.939
6.926
6.861
6.847
6.834
6.772
6.761
6.748
6.739
6.727
6.714
6.316
6.303
6.291
6.194
6.182
6.023
2.353
X : parts per Million : Proton

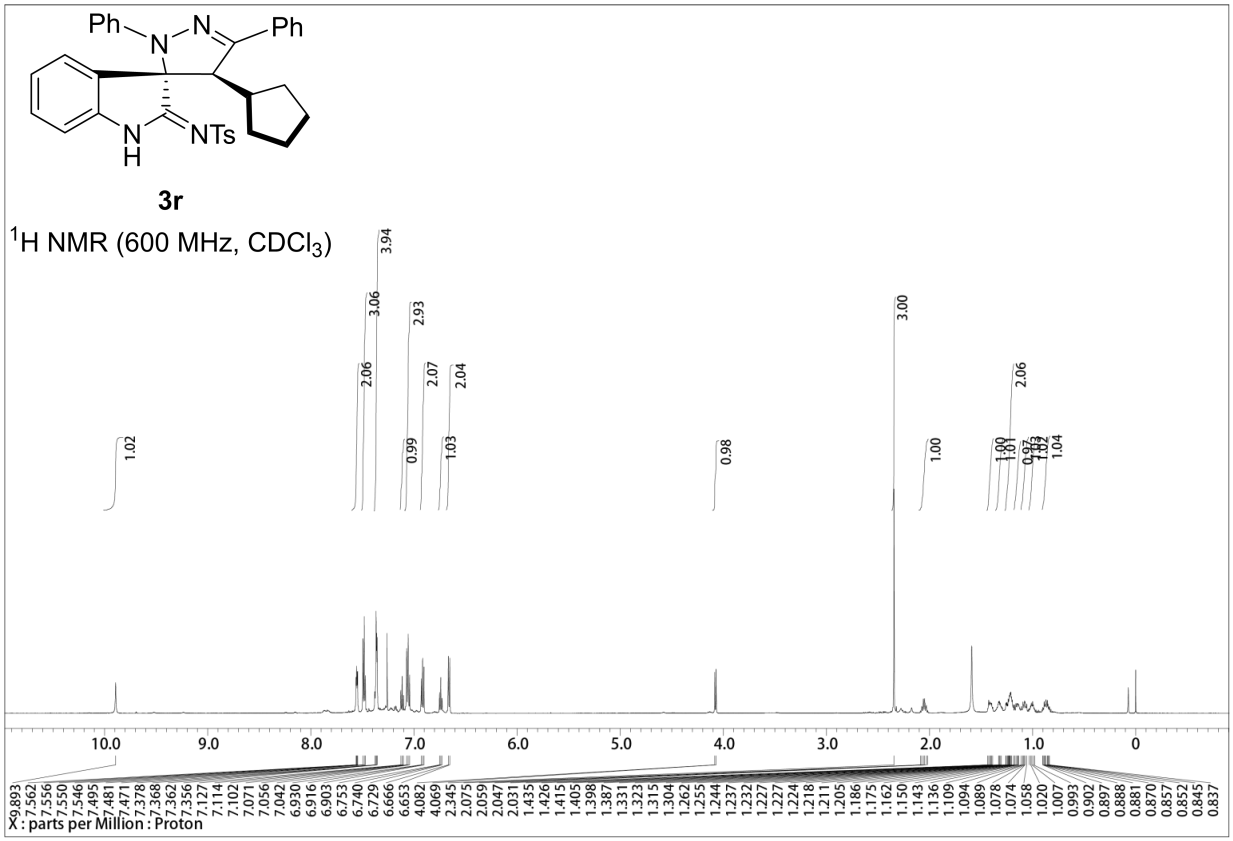

Ph
N
N
Ph
N
H
NTs
3o
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.517
149.289
144.263
142.961
140.088
138.125
133.683
131.787
131.547
130.331
129.604
129.230
128.819
128.752
128.608
128.359
127.785
126.894
126.559
126.233
126.042
125.946
125.602
124.989
122.940
122.021
121.063
115.558
110.876
80.265
77.211
77.000
76.789
59.287
21.495
X : parts per Million : Carbon13

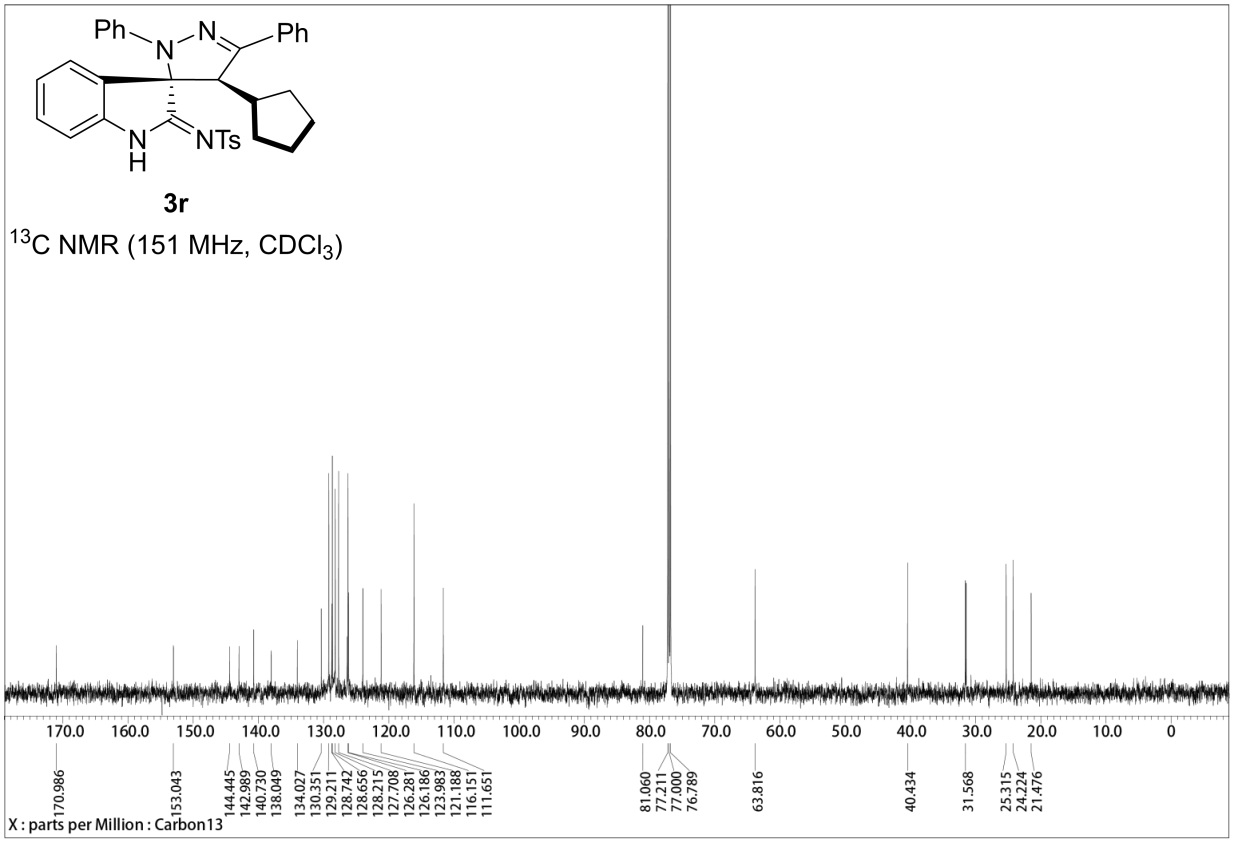

Ph
N
N
Ph
N
H
NTs
N
3p
1H NMR (600 MHz, CDCl3)
4.06
2.91
3.00
1.93
1.96
1.99
0.99
1.01
1.02
1.01
1.02
1.08
1.00
0.98
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.917
8.400
8.394
8.137
7.563
7.556
7.550
7.477
7.463
7.282
7.276
7.267
7.173
7.161
7.148
7.106
7.097
7.094
7.084
7.070
7.057
7.034
6.964
6.949
6.936
6.794
6.782
6.770
6.731
6.717
6.708
6.696
6.473
6.460
5.297
2.356
X : parts per Million : Proton

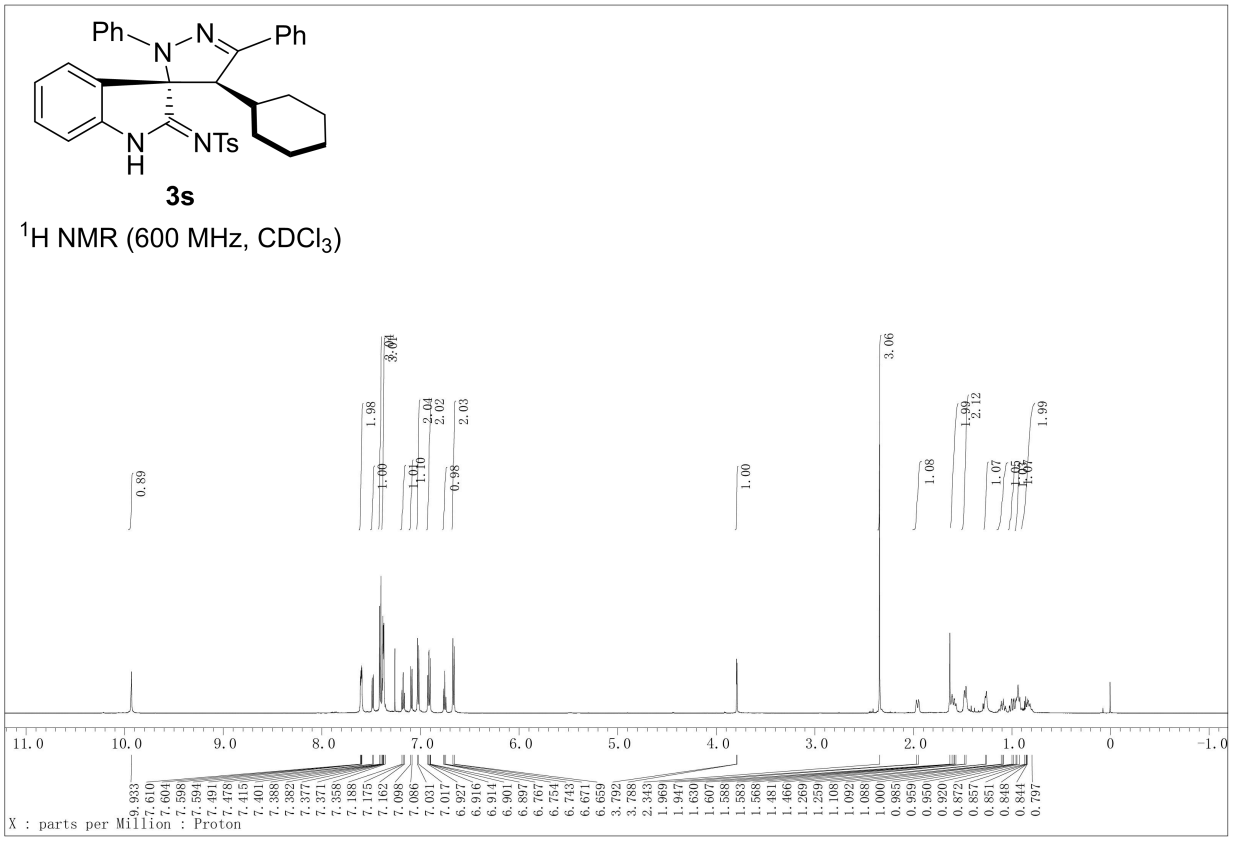

Ph
N
N
Ph
N
H
NTs
N
3p
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.923
150.190
149.222
147.911
143.813
143.152
140.031
137.905
136.756
130.839
130.418
130.370
129.269
129.087
128.981
128.867
128.541
126.827
126.262
125.343
123.773
123.447
121.504
115.778
111.555
80.830
77.211
77.000
76.789
62.015
21.505
X : parts per Million : Carbon13

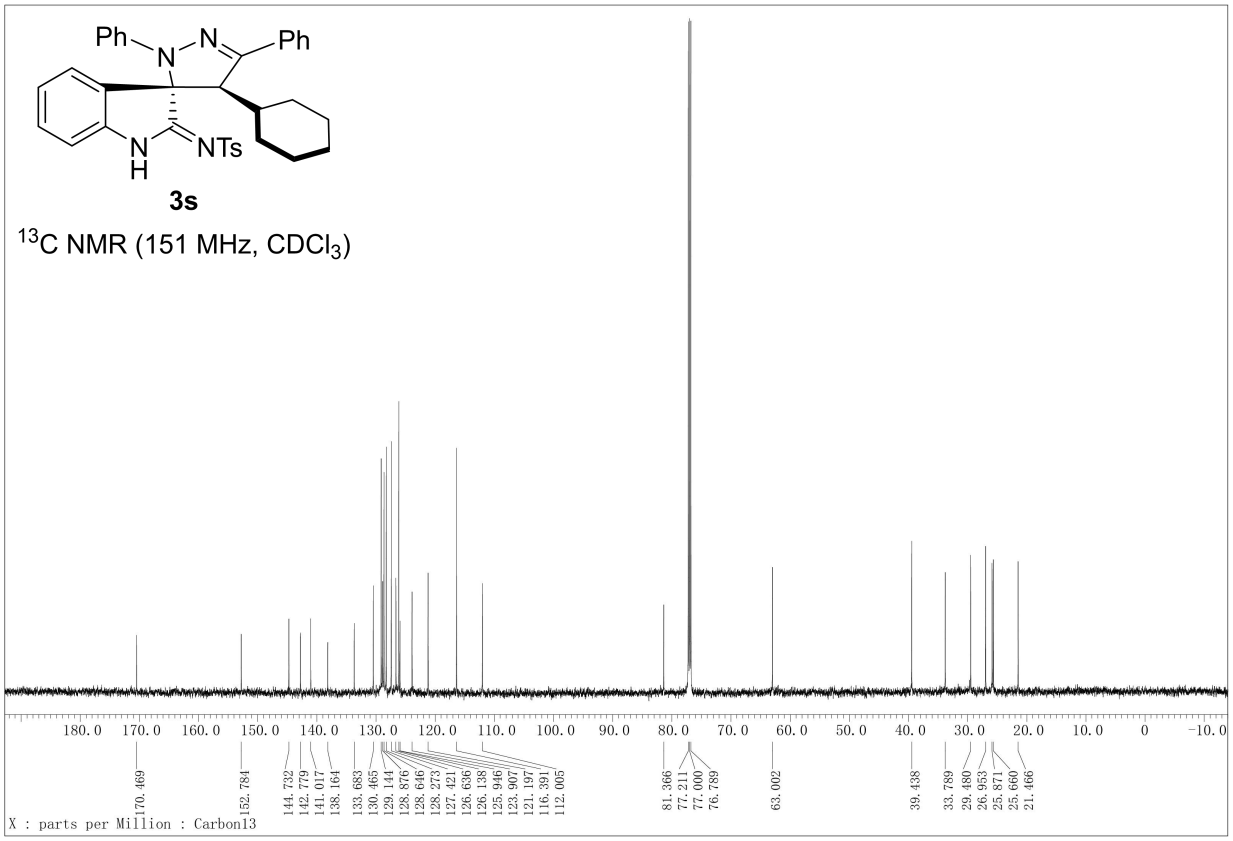

Ph
N
N
Ph
O
N
H
NTs
3q
1H NMR (600 MHz, CDCl3)
3.02
2.03
1.98
1.98
1.90
1.94
1.89
0.94
0.99
0.98
0.98
0.99
1.01
0.91
0.90
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.946
7.627
7.620
7.615
7.611
7.449
7.436
7.308
7.302
7.300
7.237
7.224
7.212
7.138
7.115
7.095
7.051
7.037
6.985
6.971
6.955
6.942
6.930
6.863
6.852
6.841
6.830
6.817
6.768
6.756
6.744
6.712
6.698
6.135
6.048
6.043
5.445
2.346
X : parts per Million : Proton

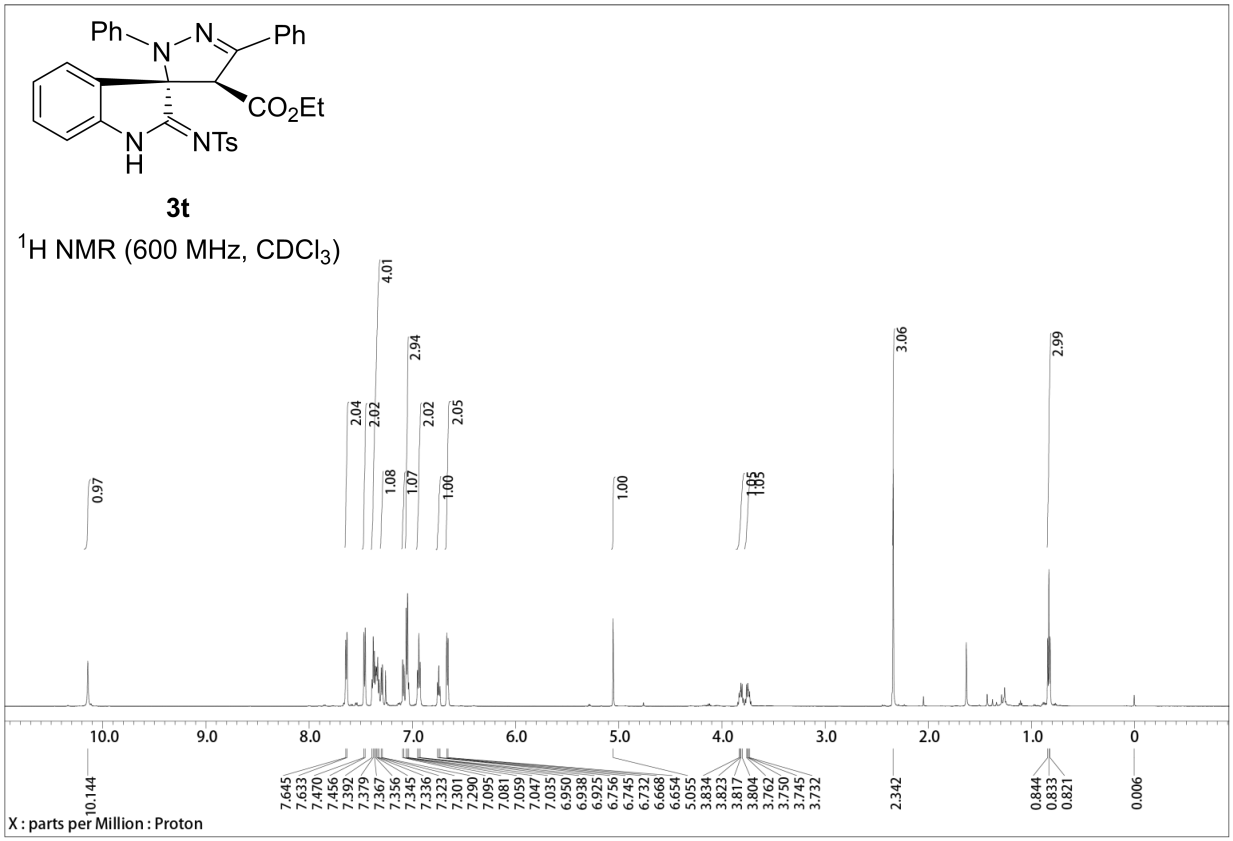

Ph
N
N
Ph
O
N
H
NTs
3q
13C NMR (151 MHz, CDCl3)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.038
147.604
146.082
143.794
142.999
142.731
140.079
137.991
131.423
130.159
129.211
128.867
128.819
128.378
126.473
126.214
126.119
125.716
123.945
121.073
115.328
111.220
110.636
110.598
79.978
77.211
77.000
76.789
58.521
21.476
X : parts per Million : Carbon13

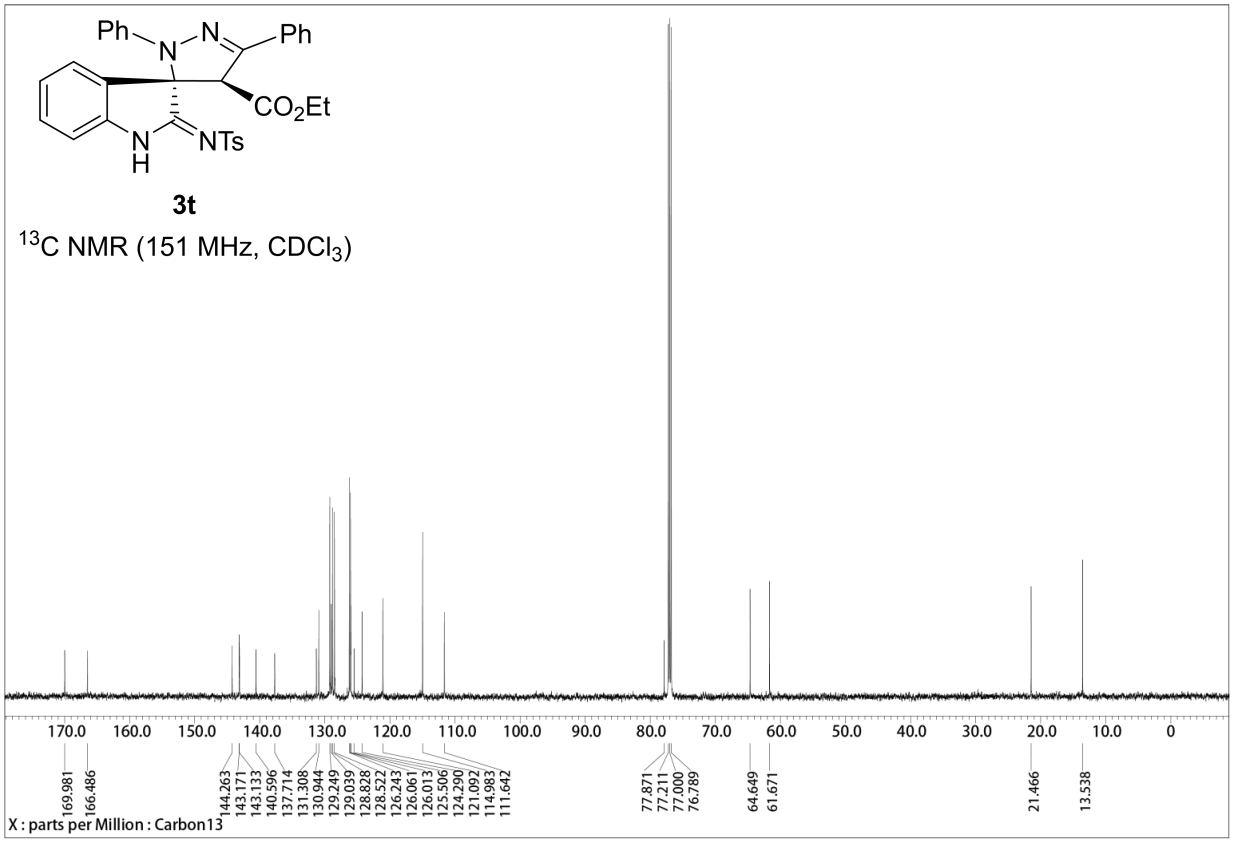

Ph
N
N
Ph
N
H
NTs
3r
1H NMR (600 MHz, CDCl3)
3.94
3.06
2.93
2.06
2.07
2.04
3.00
2.06
1.02
0.99
1.03
0.98
1.00
1.00
1.00
1.04
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.893
7.562
7.556
7.550
7.546
7.495
7.481
7.471
7.378
7.368
7.362
7.356
7.127
7.114
7.102
7.071
7.056
7.042
6.930
6.916
6.903
6.753
6.740
6.729
6.666
6.653
4.082
4.069
2.345
2.075
2.059
2.047
2.031
1.435
1.426
1.415
1.405
1.398
1.387
1.331
1.323
1.315
1.304
1.262
1.255
1.244
1.237
1.232
1.227
1.227
1.224
1.218
1.211
1.205
1.186
1.175
1.162
1.150
1.143
1.136
1.109
1.094
1.089
1.078
1.074
1.058
1.020
1.007
0.993
0.902
0.897
0.888
0.881
0.870
0.857
0.852
0.845
0.837
X : parts per Million : Proton

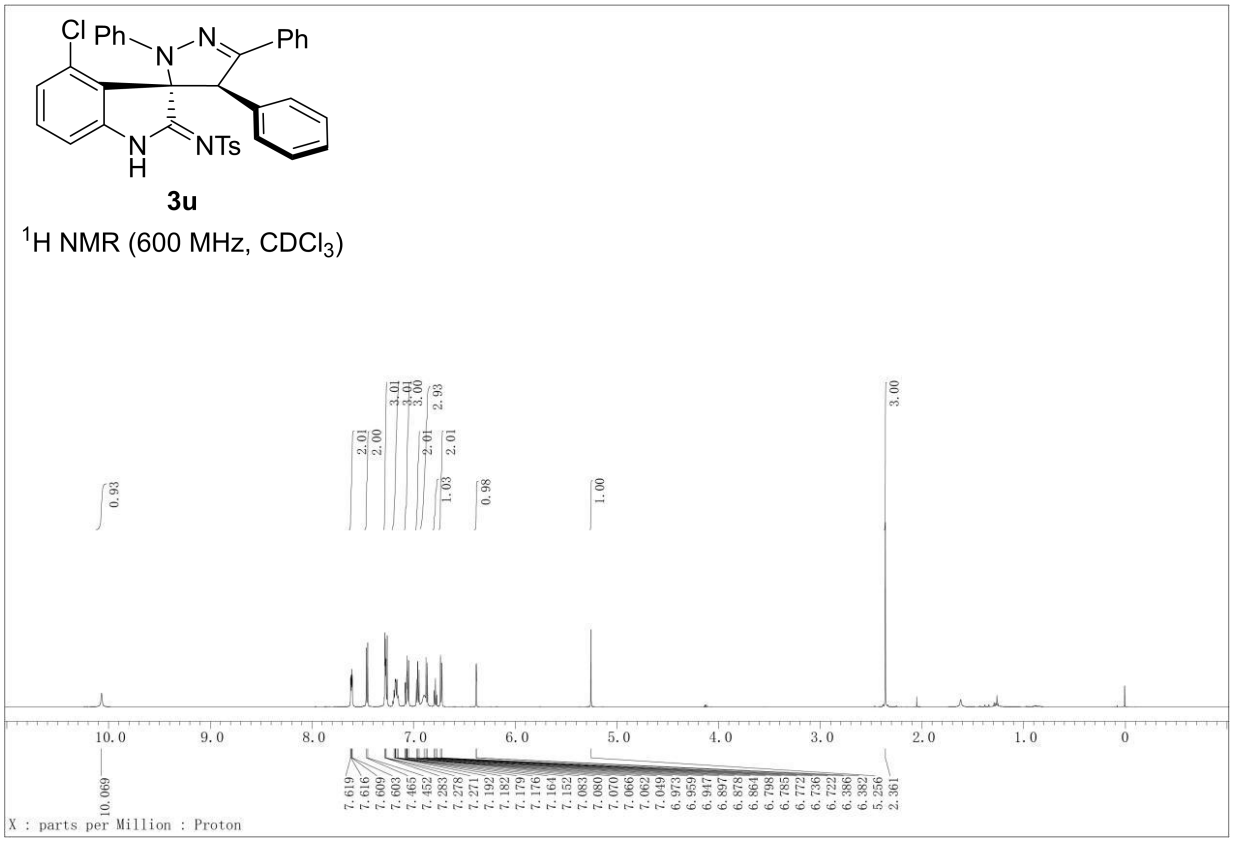

Ph
N
N
Ph
N
H
NTs
3r
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

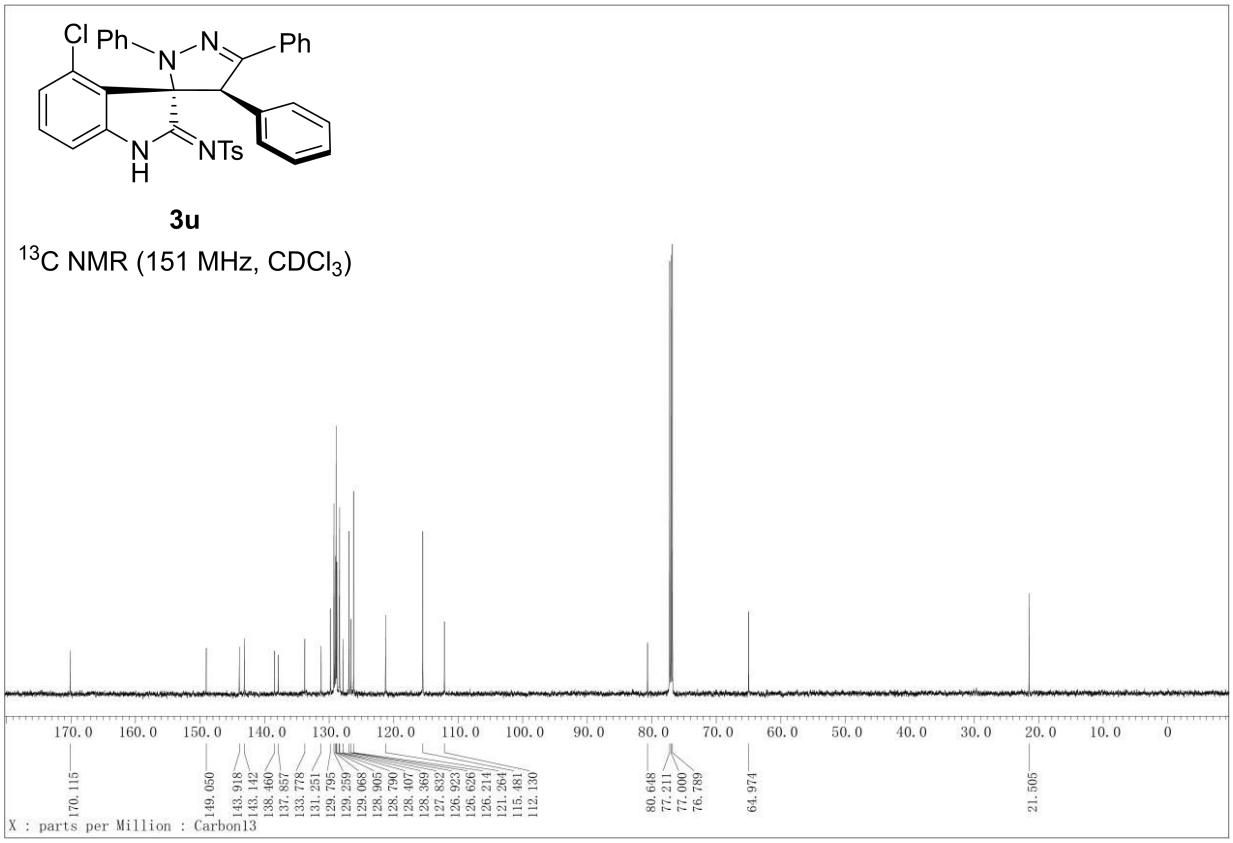

Ph
N
N
Ph
N
H
NTs
3s
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton

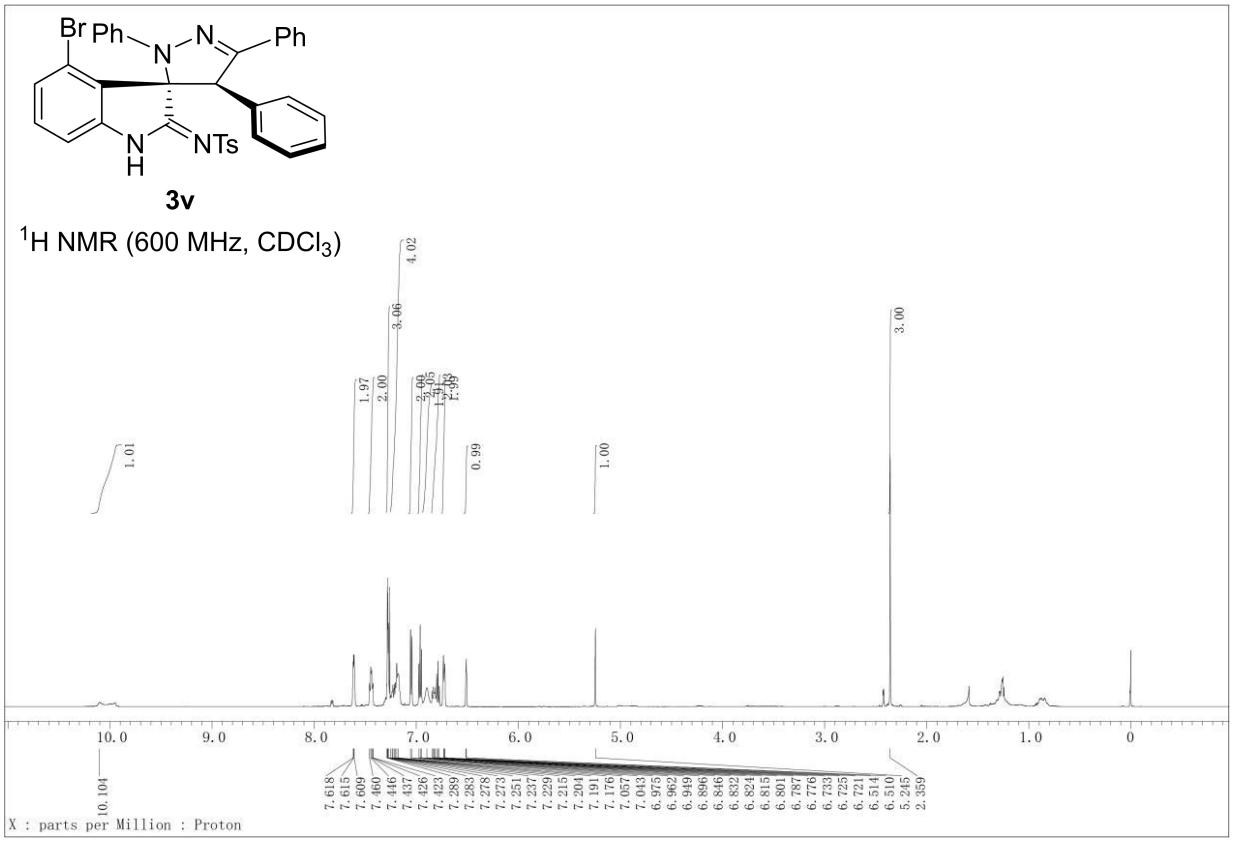

Ph
N
N
Ph
N
H
NTs
3s
13C NMR (151 MHz, CDCl3)
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
170.469
152.784
144.732
142.779
141.017
138.164
133.683
130.465
129.144
128.876
128.646
128.273
127.421
126.636
126.138
125.946
123.907
121.197
116.391
112.005
81.366
77.211
77.000
76.789
63.002
39.438
33.789
29.480
26.953
25.871
25.660
21.466
X : parts per Million : Carbon13

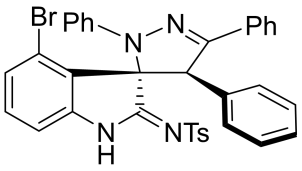

Ph
N
N
Ph
CO2Et
N
H
NTs
3t
1H NMR (600 MHz, CDCl3)
4.01
2.94
2.04
2.02
2.02
2.05
1.08
1.07
1.00
0.97
1.00
3.06
2.99
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
10.144
7.645
7.633
7.470
7.456
7.392
7.379
7.367
7.356
7.345
7.336
7.323
7.301
7.290
7.095
7.081
7.059
7.047
7.035
6.950
6.938
6.925
6.756
6.745
6.732
6.668
6.654
5.055
3.834
3.823
3.817
3.804
3.762
3.750
3.745
3.732
2.342
0.844
0.833
0.821
0.006
X : parts per Million : Proton


Ph
N
N
Ph
CO2Et
N
H
NTs
3t
13C NMR (151 MHz, CDCl3)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
169.981 166.486 144.263 143.171 143.133 140.596 137.714 131.308 130.944 129.249 129.039 128.828 128.522 126.243 126.061 126.013 125.506 124.290 121.092 114.983 111.642 77.871 77.211 77.000 76.789 64.649 61.671 21.466 13.538
X : parts per Million : Carbon13


Cl
Ph
N
N
Ph
N
H
NTs
3u
1H NMR (600 MHz, CDCl3)
0.93 2.01 2.00 3.01 3.01 3.00 2.93 2.01 2.01 1.03 0.98 1.00 3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
10.069 7.619 7.616 7.609 7.603 7.465 7.452 7.283 7.278 7.271 7.192 7.182 7.179 7.176 7.164 7.152 7.083 7.080 7.070 7.066 7.062 7.049 6.973 6.959 6.947 6.897 6.878 6.864 6.798 6.785 6.772 6.736 6.722 6.386 6.382 5.256 2.361
X : parts per Million : Proton

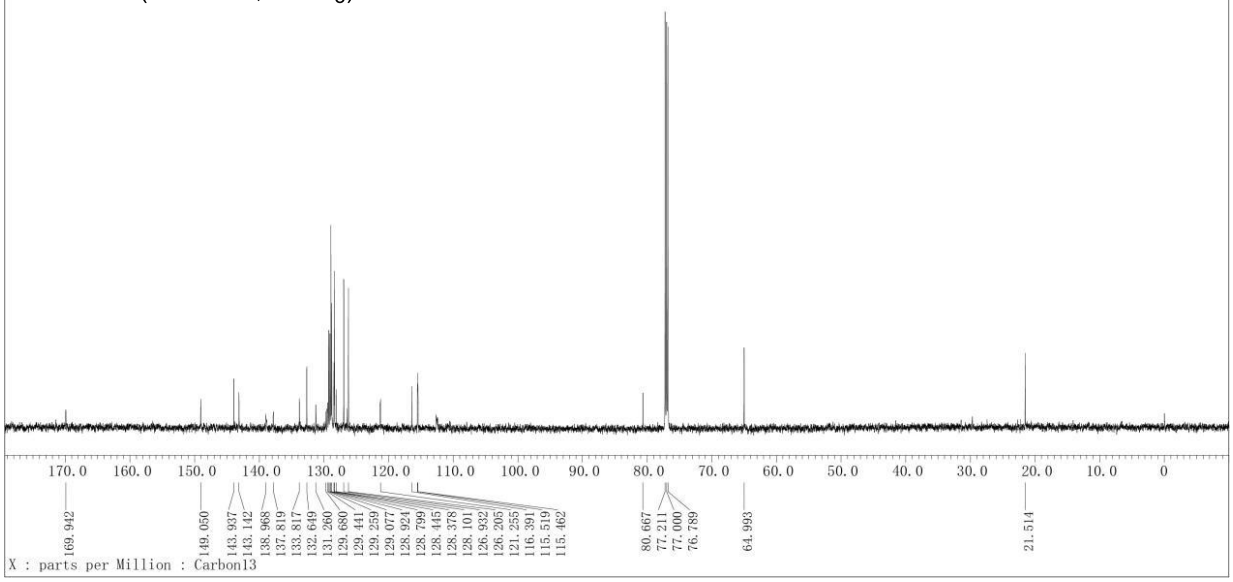

Cl
Ph
N
N
Ph
N
H
NTs
3u
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

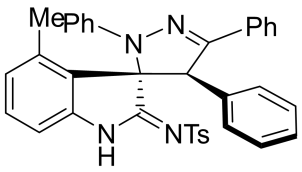

Br
Ph
N
N
Ph
N
H
NTs
3v
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton



3v

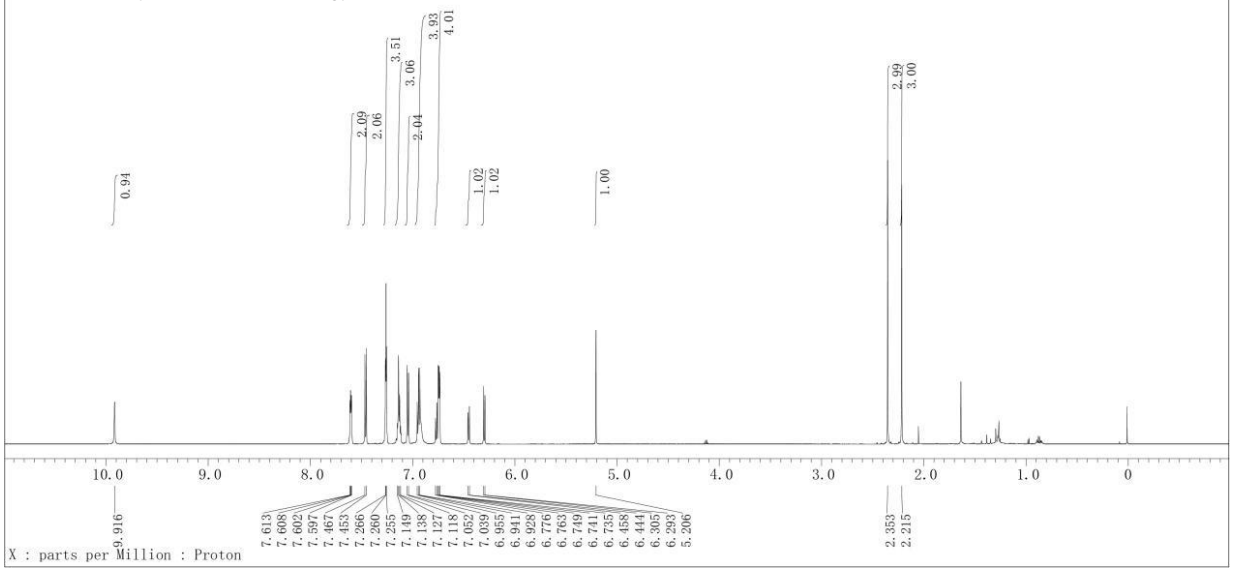
^{13}C NMR (151 MHz, $CDCl_3$)

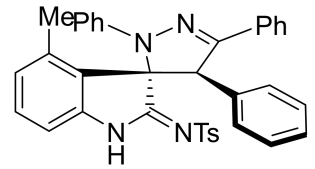




3w

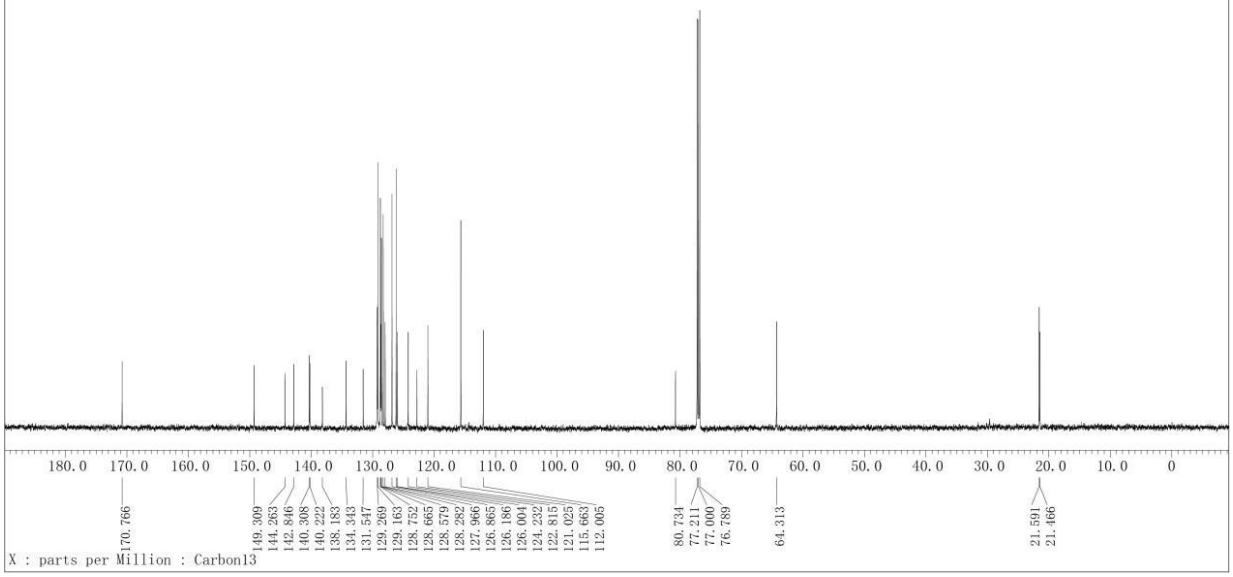
^{1}H NMR (600 MHz, $CDCl_3$)

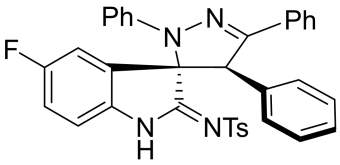




3w

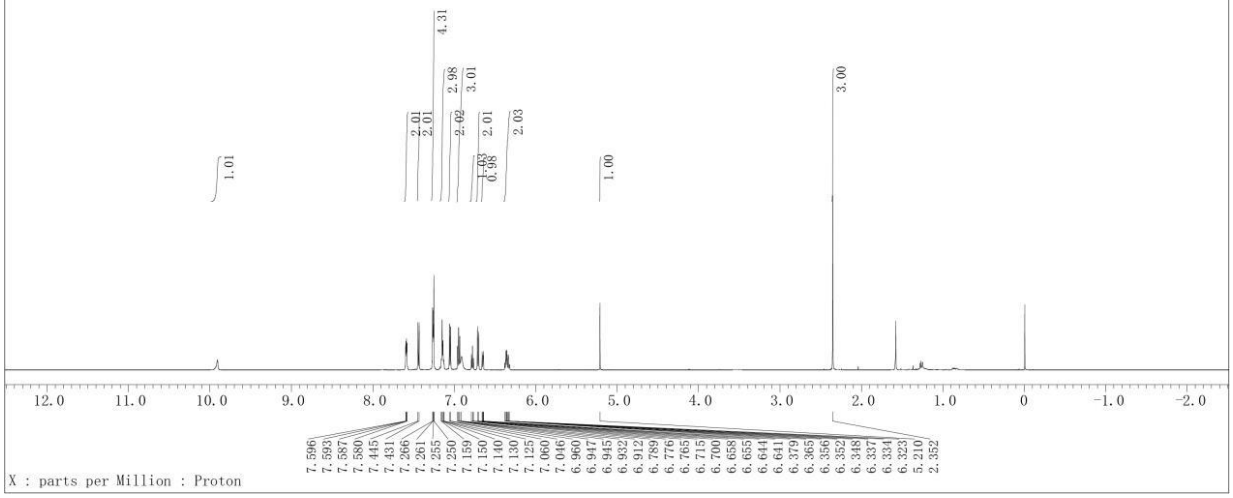
^{13}C NMR (151 MHz, $CDCl_3$)

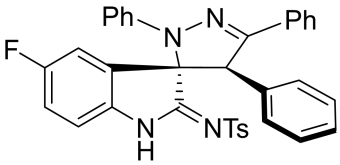




3x

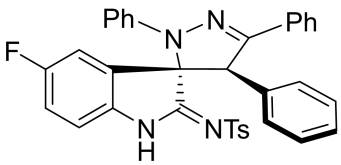
^{1}H NMR (600 MHz, $CDCl_3$)





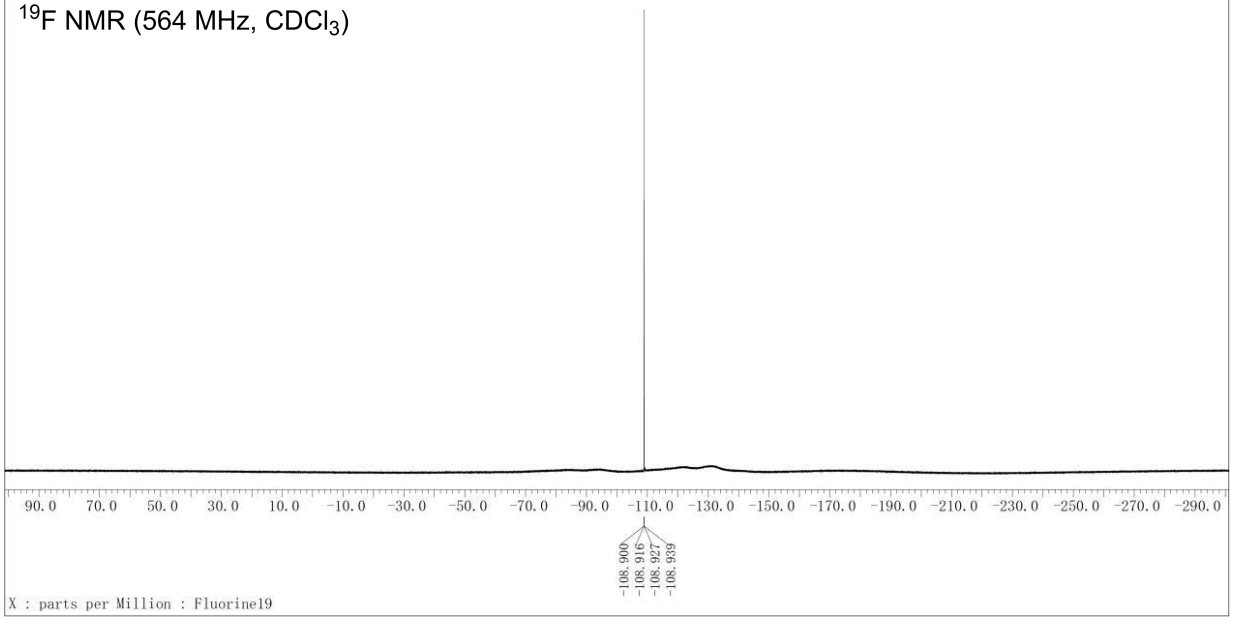
3x

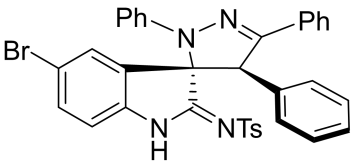
^{13}C NMR (151 MHz, $CDCl_3$)



3x

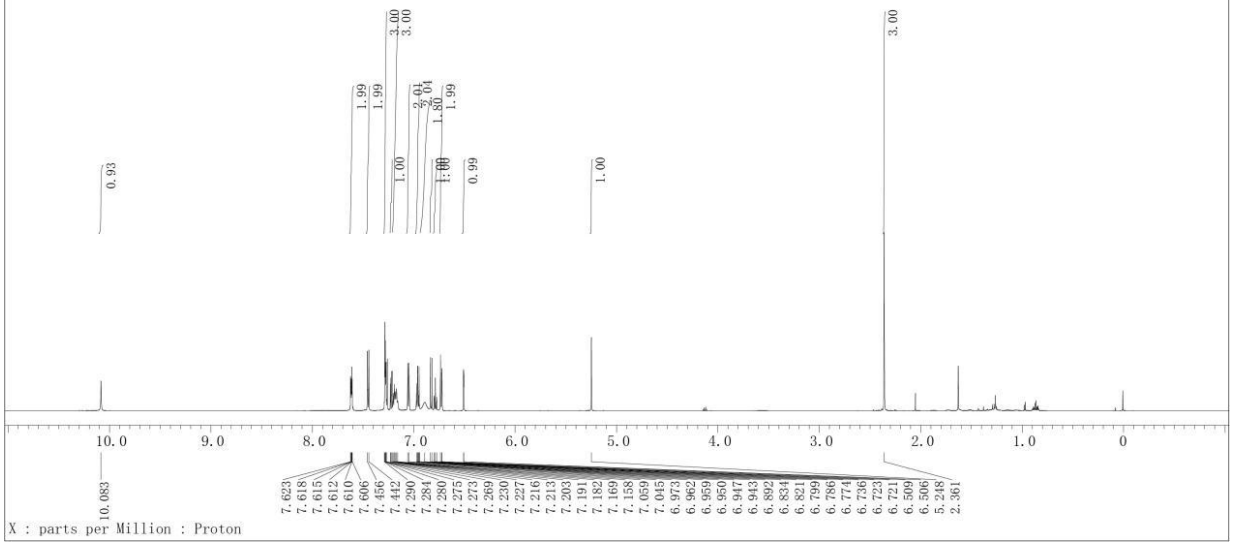
^{19}F NMR (564 MHz, $CDCl_3$)

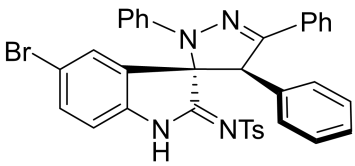




3y

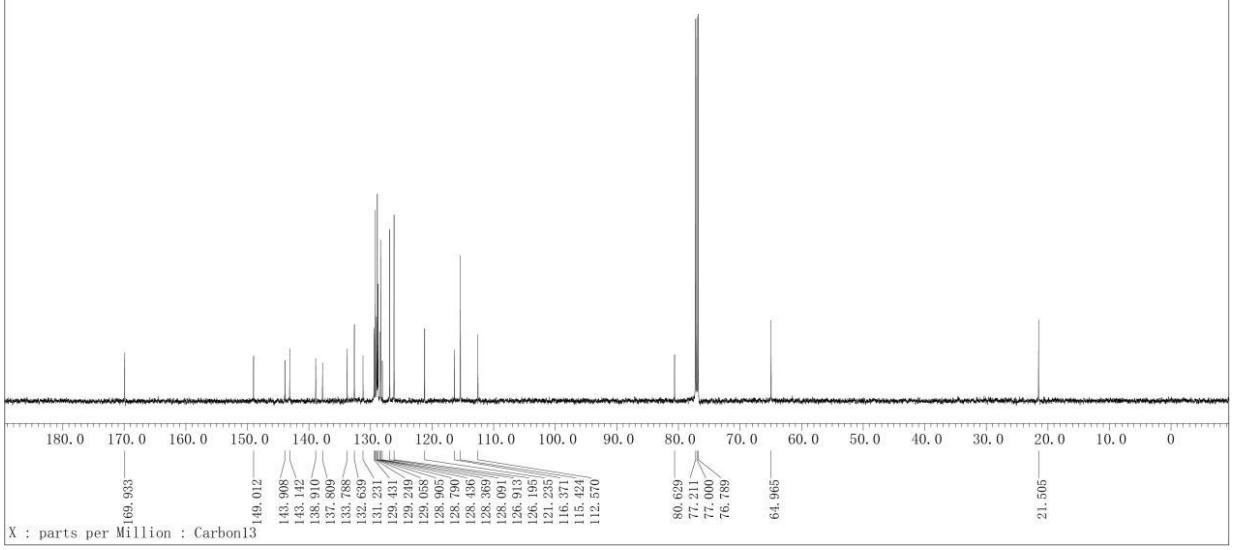
^{1}H NMR (600 MHz, $CDCl_3$)

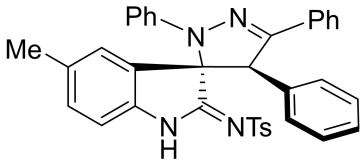




3y

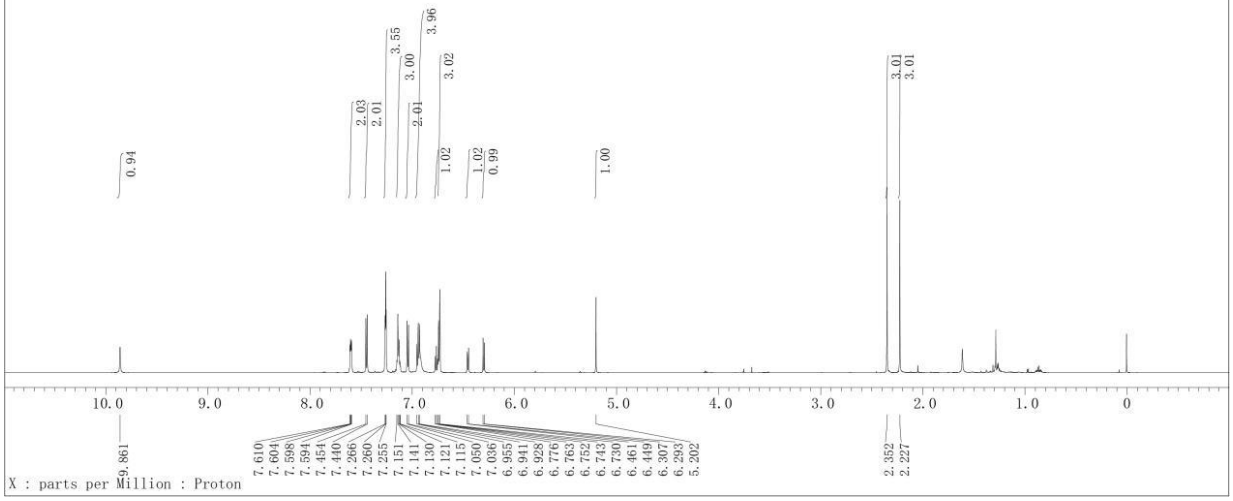
^{13}C NMR (151 MHz, $CDCl_3$)

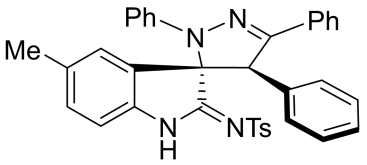




3z

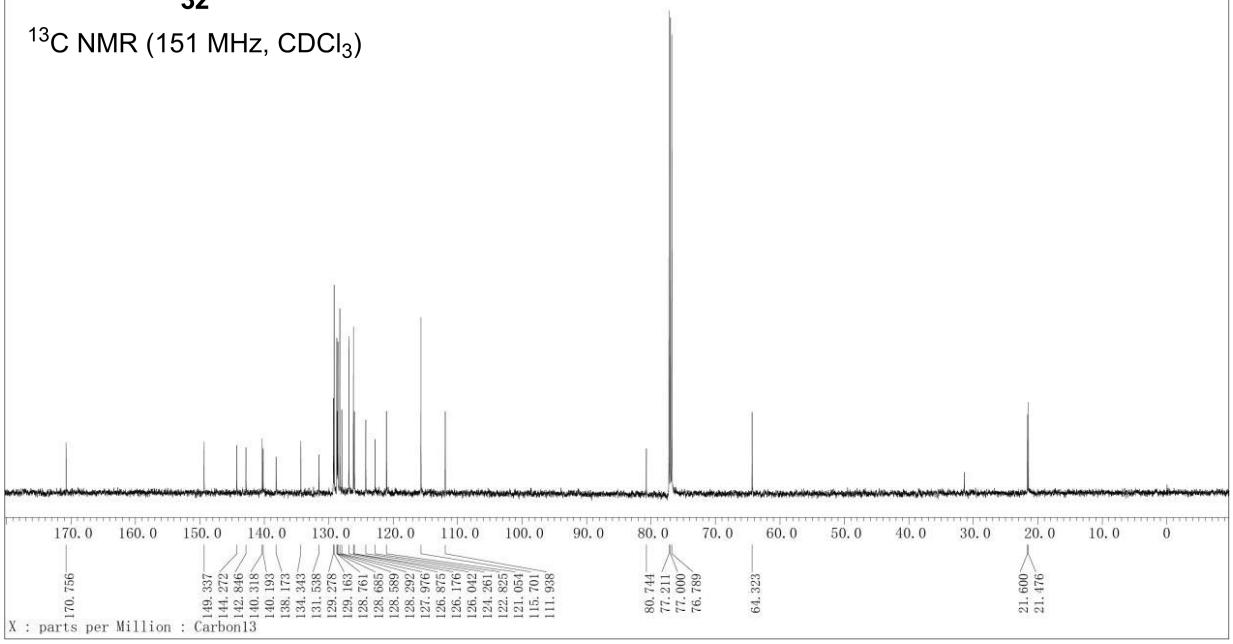
^{1}H NMR (600 MHz, $CDCl_3$)

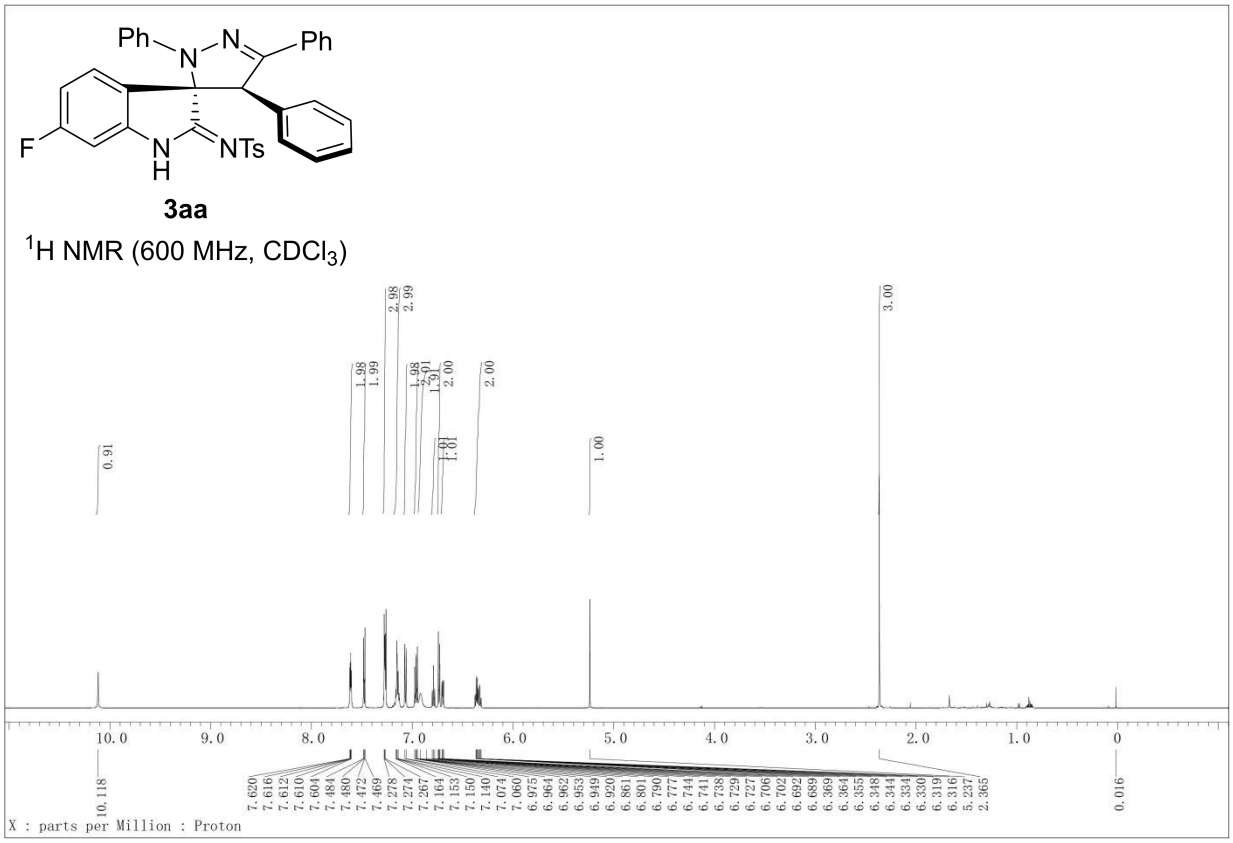


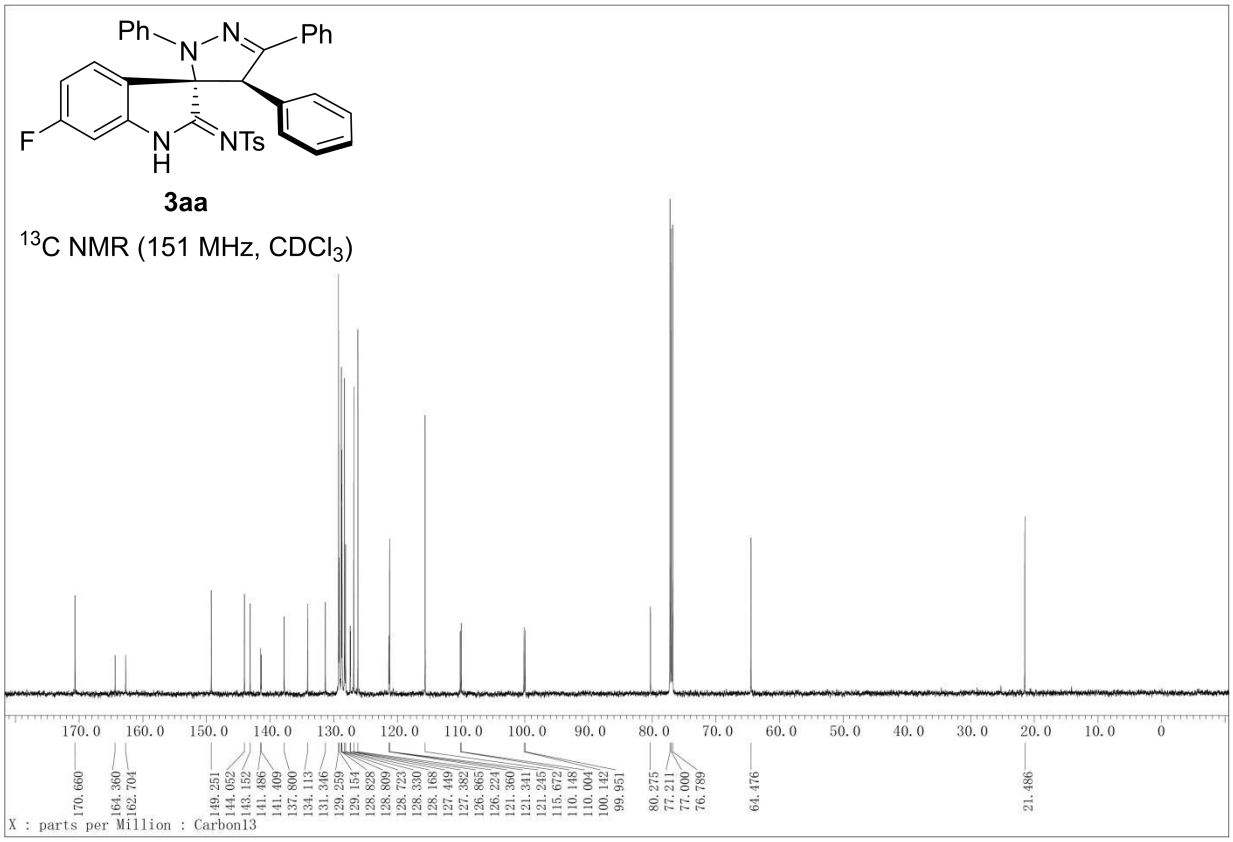


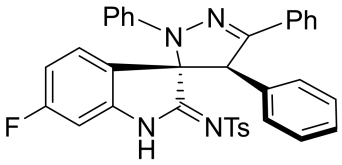
3z

^{13}C NMR (151 MHz, $CDCl_3$)



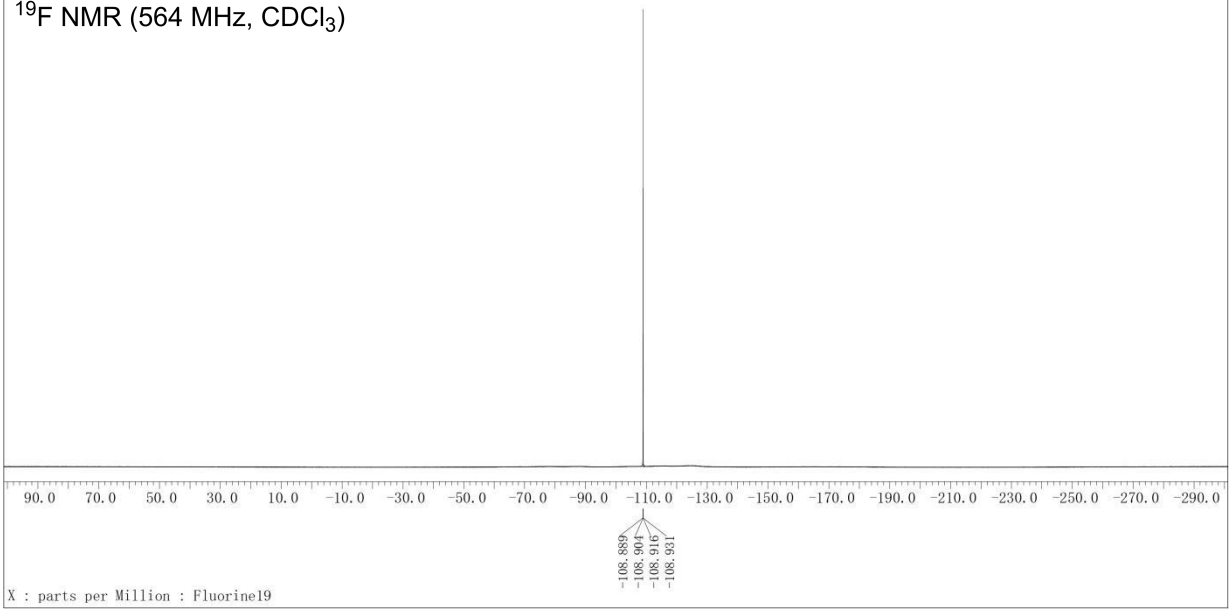

Ph
N
N
Ph
F
N
H
NTs
3aa
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton

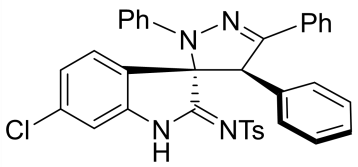

Ph
N
N
Ph
F
N
H
NTs
3aa
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



3aa

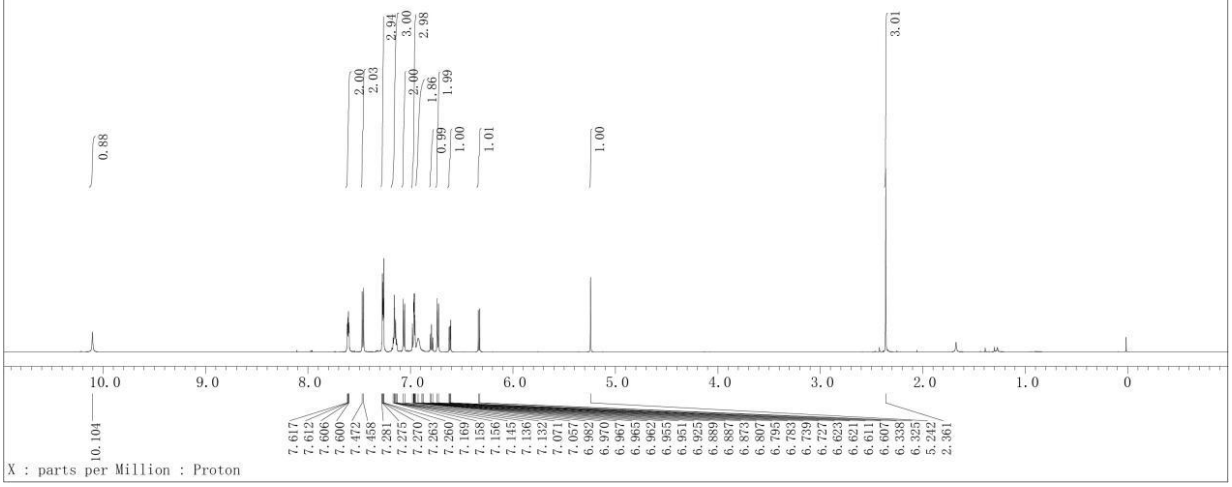
^{19}F NMR (564 MHz, $CDCl_3$)

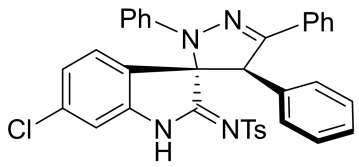




3ab

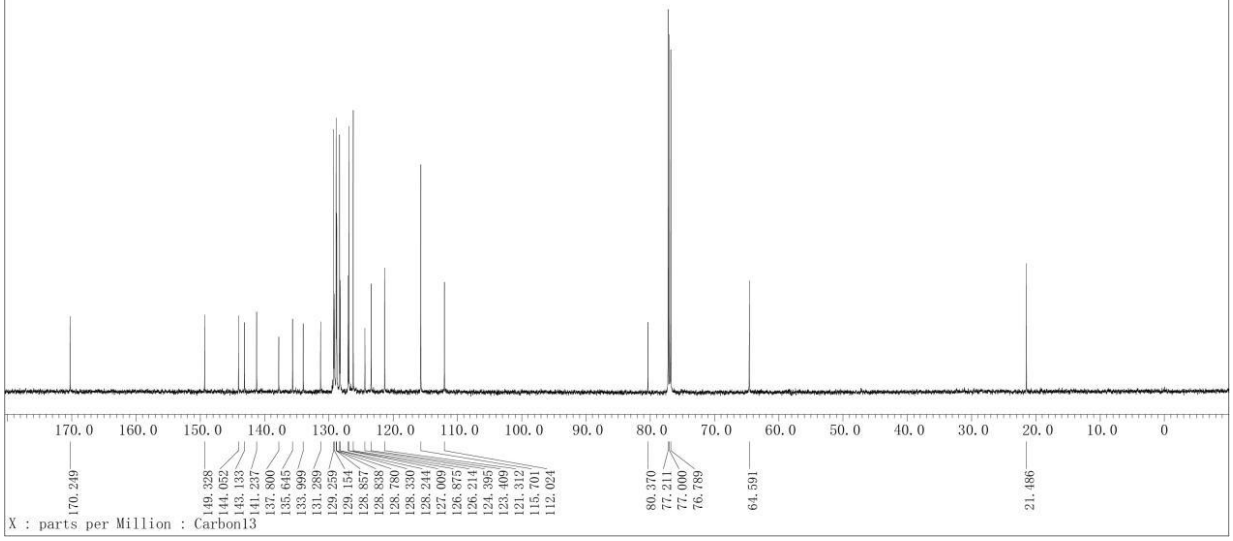
^{1}H NMR (600 MHz, $CDCl_3$)

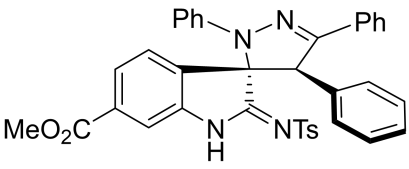




3ab

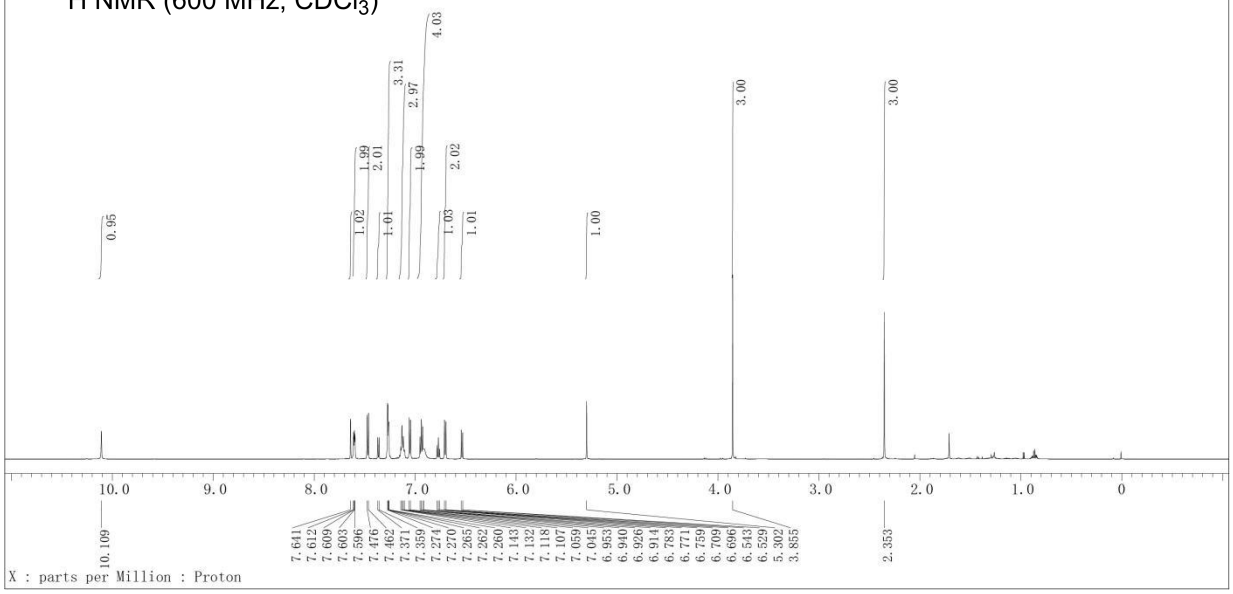
^{13}C NMR (151 MHz, $CDCl_3$)

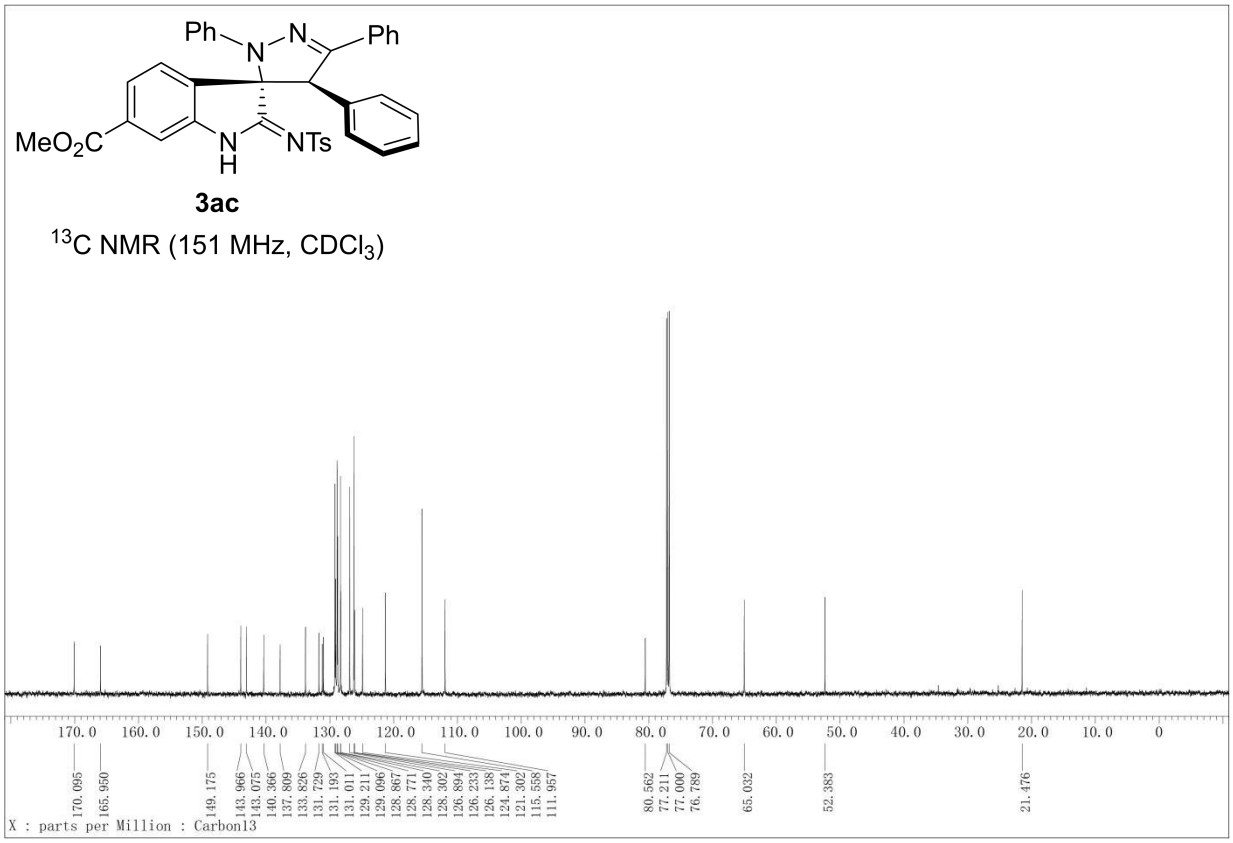


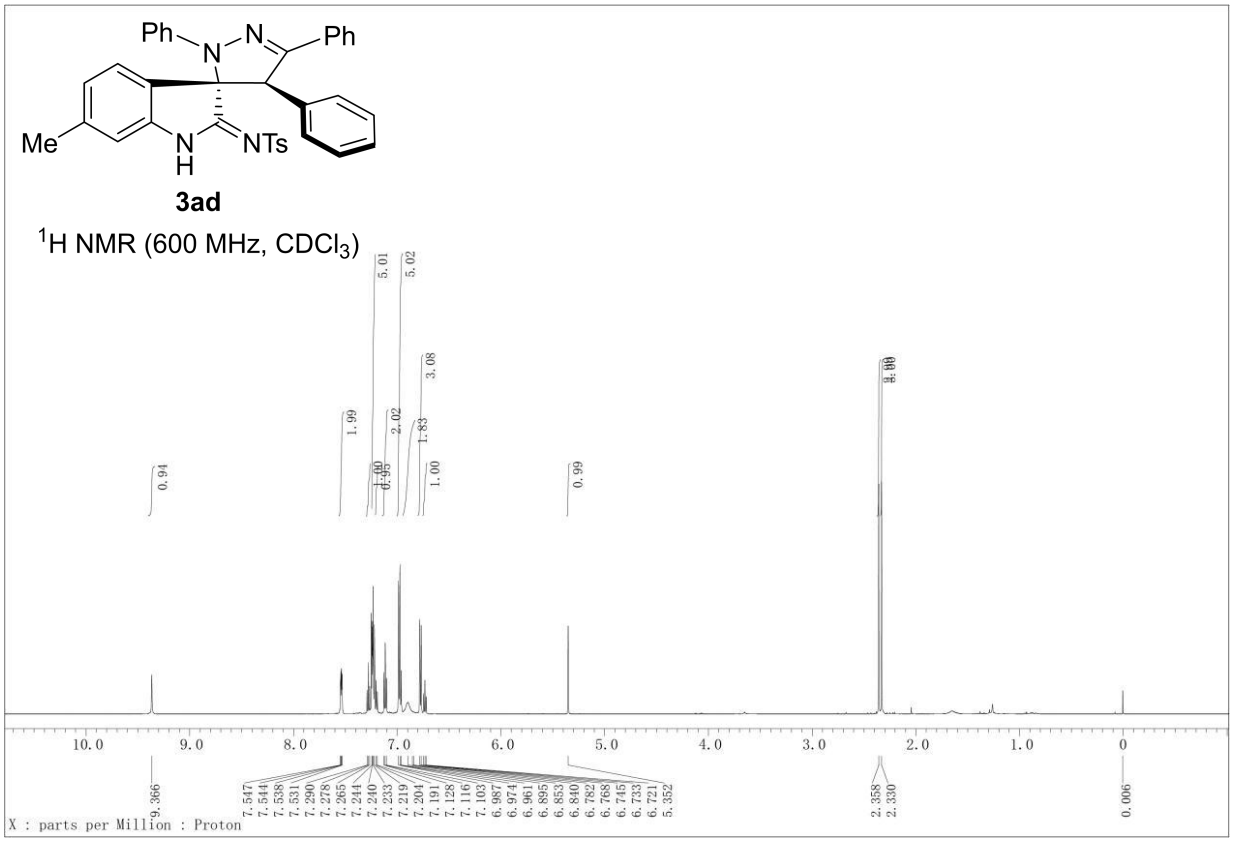


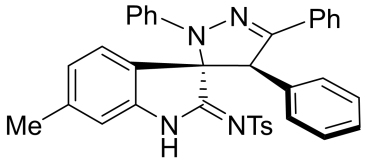
3ac

^{1}H NMR (600 MHz, $CDCl_3$)



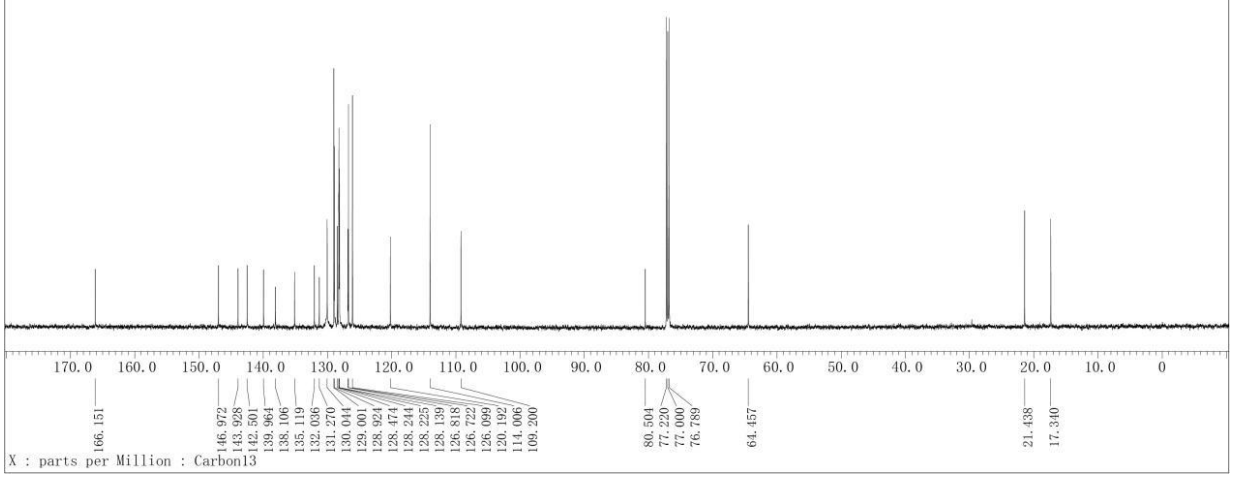

Ph
N
N
Ph
MeO2C
N
H
NTs
3ac
13C NMR (151 MHz, CDCl3)
170.095
165.950
149.175
143.966
143.075
140.366
137.809
133.826
131.729
131.193
131.011
129.211
129.096
128.867
128.771
128.340
128.302
126.894
126.233
126.138
124.874
121.302
115.558
111.957
80.562
77.211
77.000
76.789
65.032
52.383
21.476
X : parts per Million : Carbon13

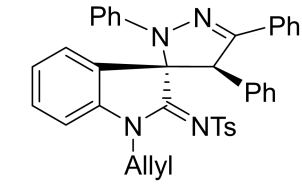

Ph
N
N
Ph
Me
N
H
NTs
3ad
1H NMR (600 MHz, CDCl3)
5.01
5.02
3.08
1.99
2.02
1.83
0.94
1.00
0.99
9.366
7.547
7.544
7.538
7.531
7.290
7.278
7.265
7.244
7.240
7.233
7.219
7.204
7.191
7.128
7.116
7.102
6.987
6.974
6.961
6.895
6.853
6.840
6.782
6.768
6.745
6.733
6.721
5.352
2.358
2.330
0.006
X : parts per Million : Proton



3ad

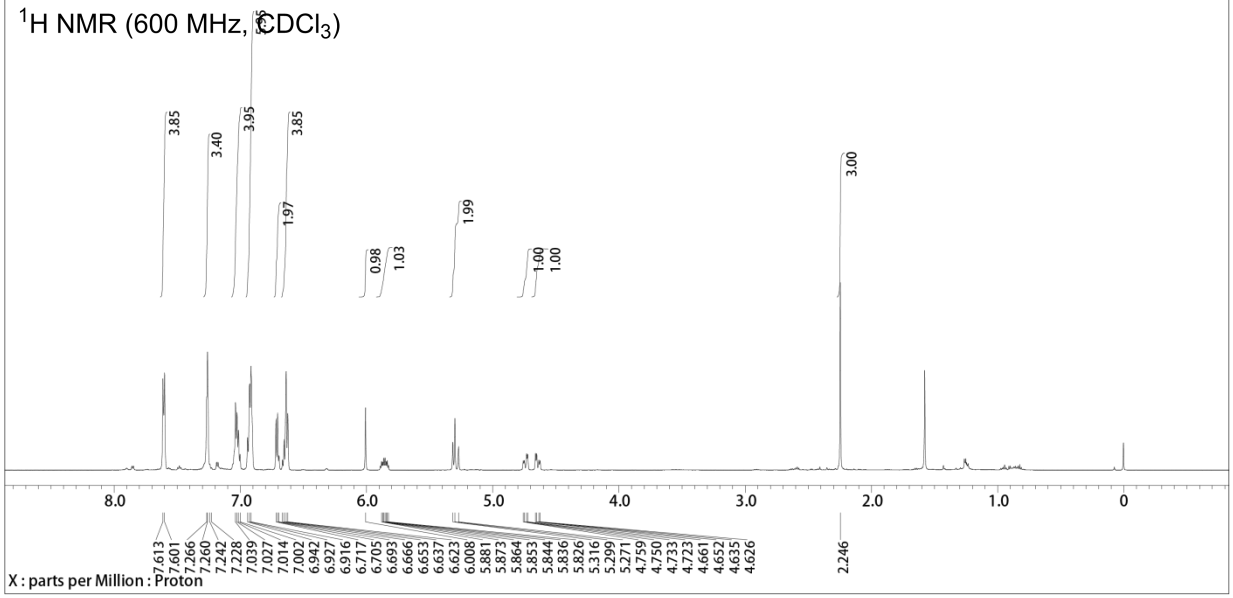
^{13}C NMR (151 MHz, $CDCl_3$)

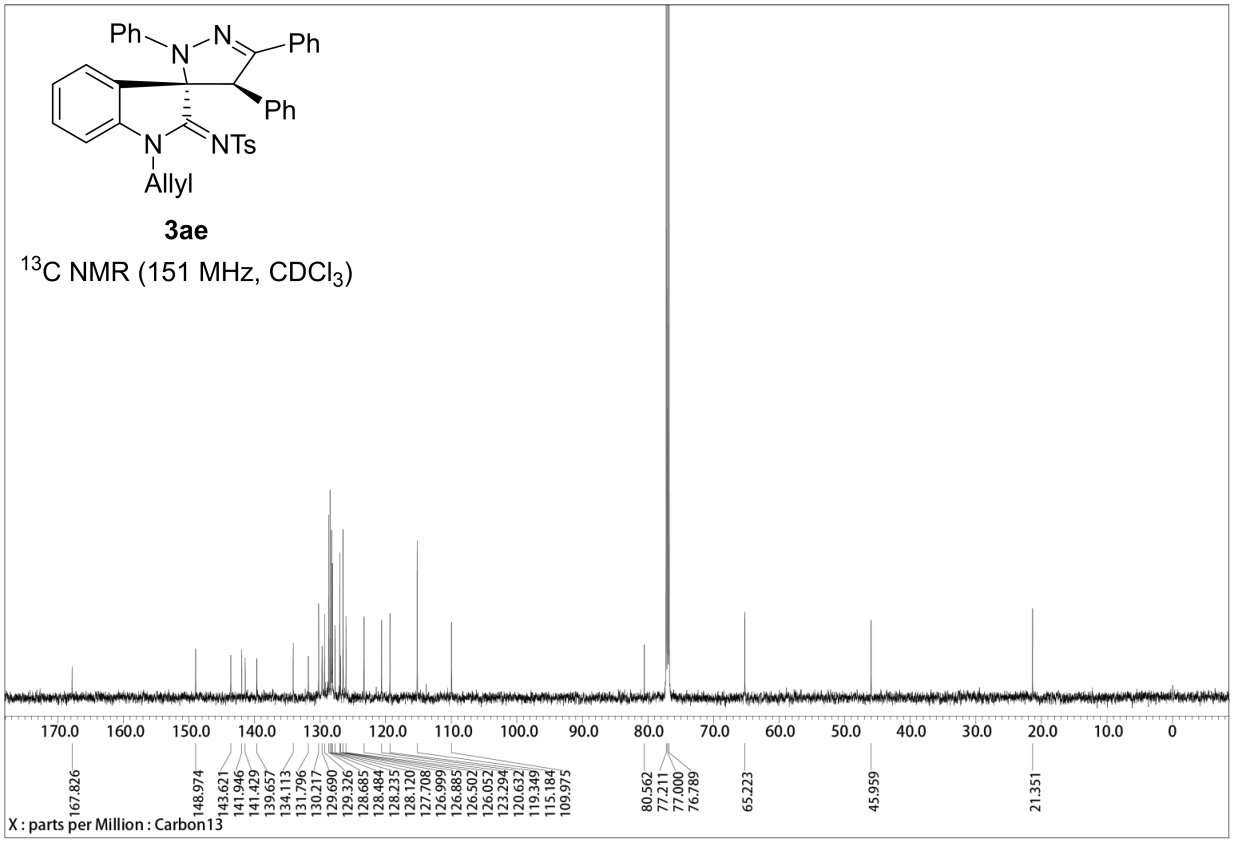


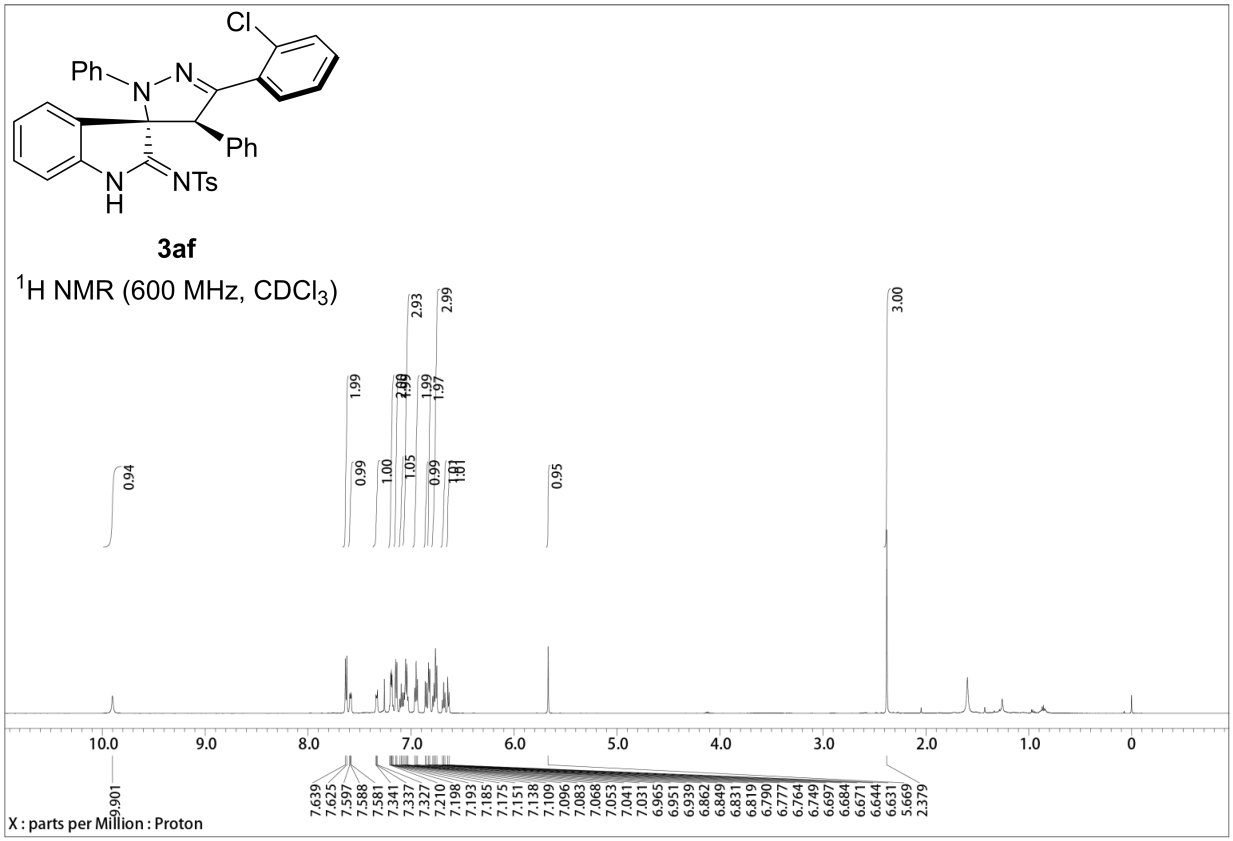


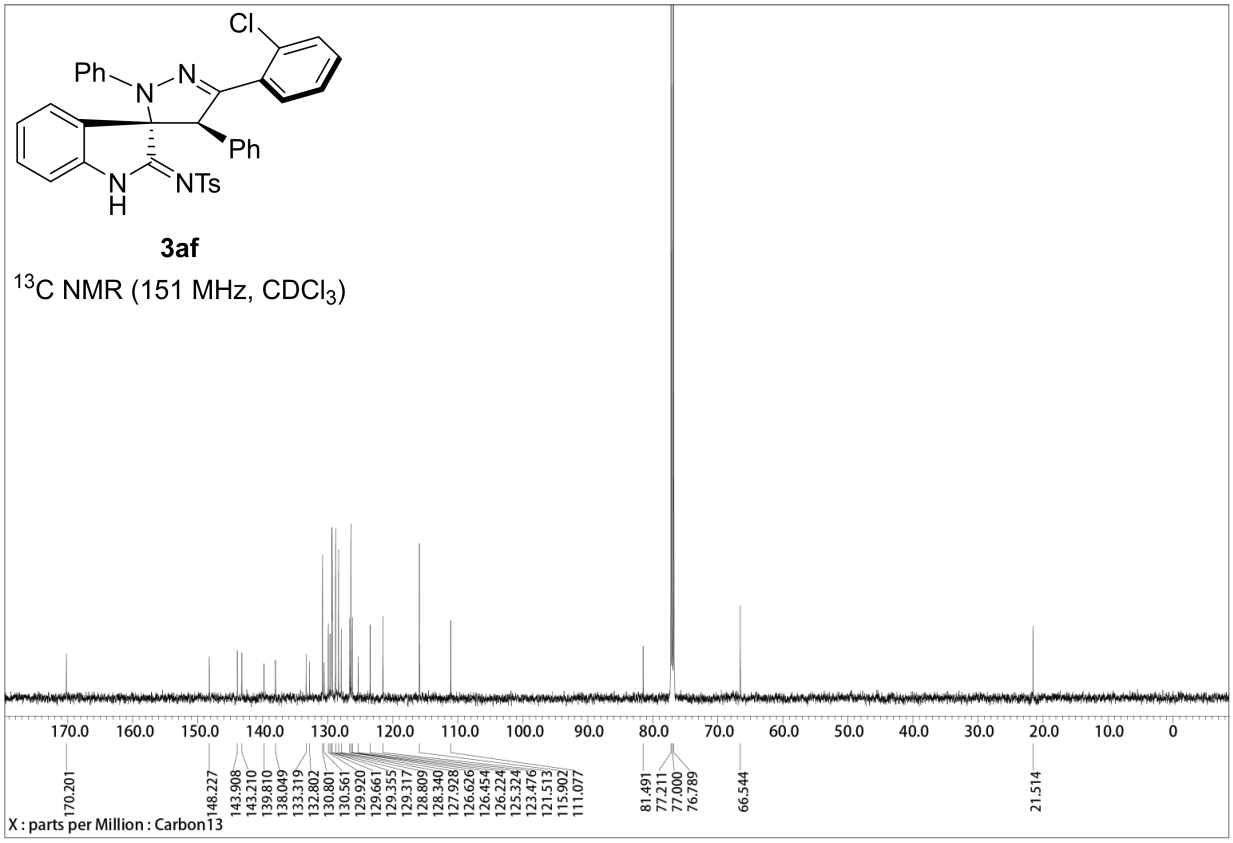
3ae

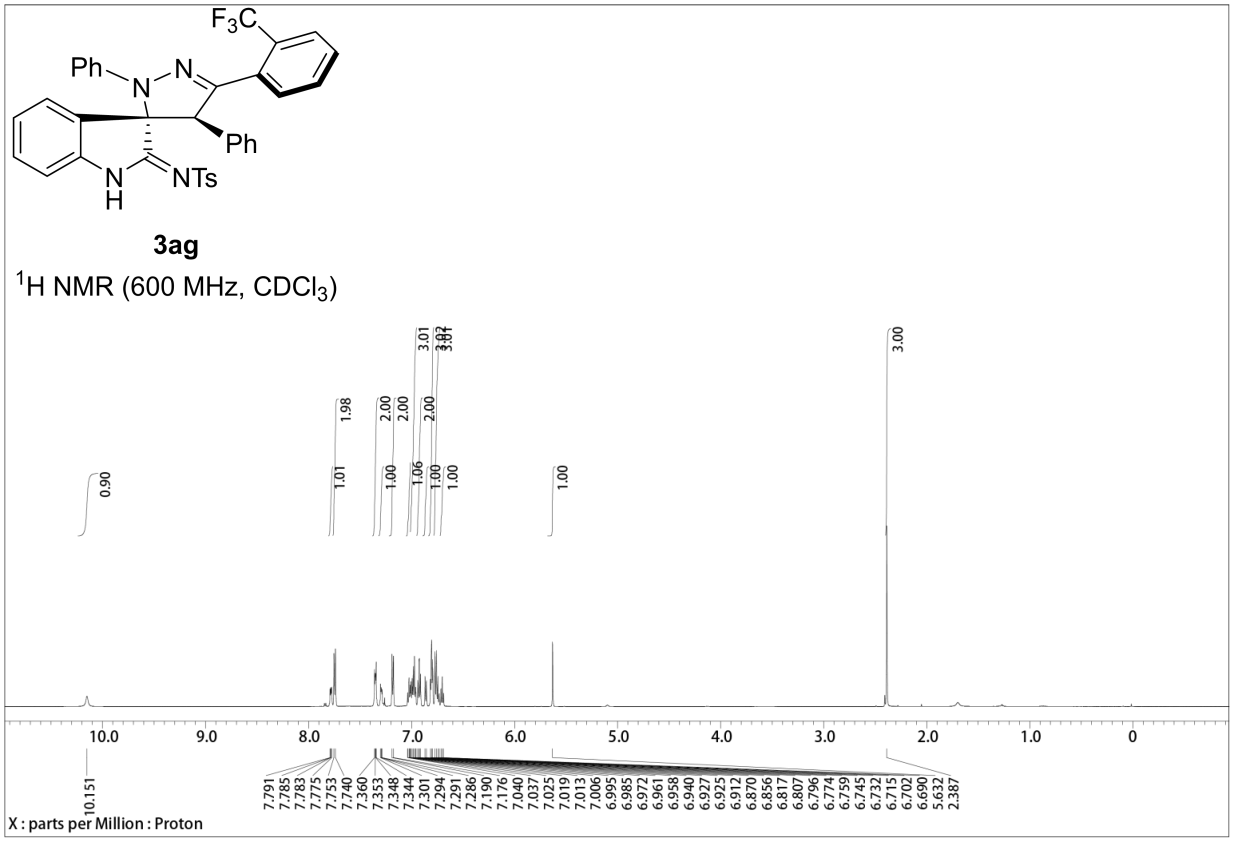
^{1}H NMR (600 MHz, $CDCl_3$)

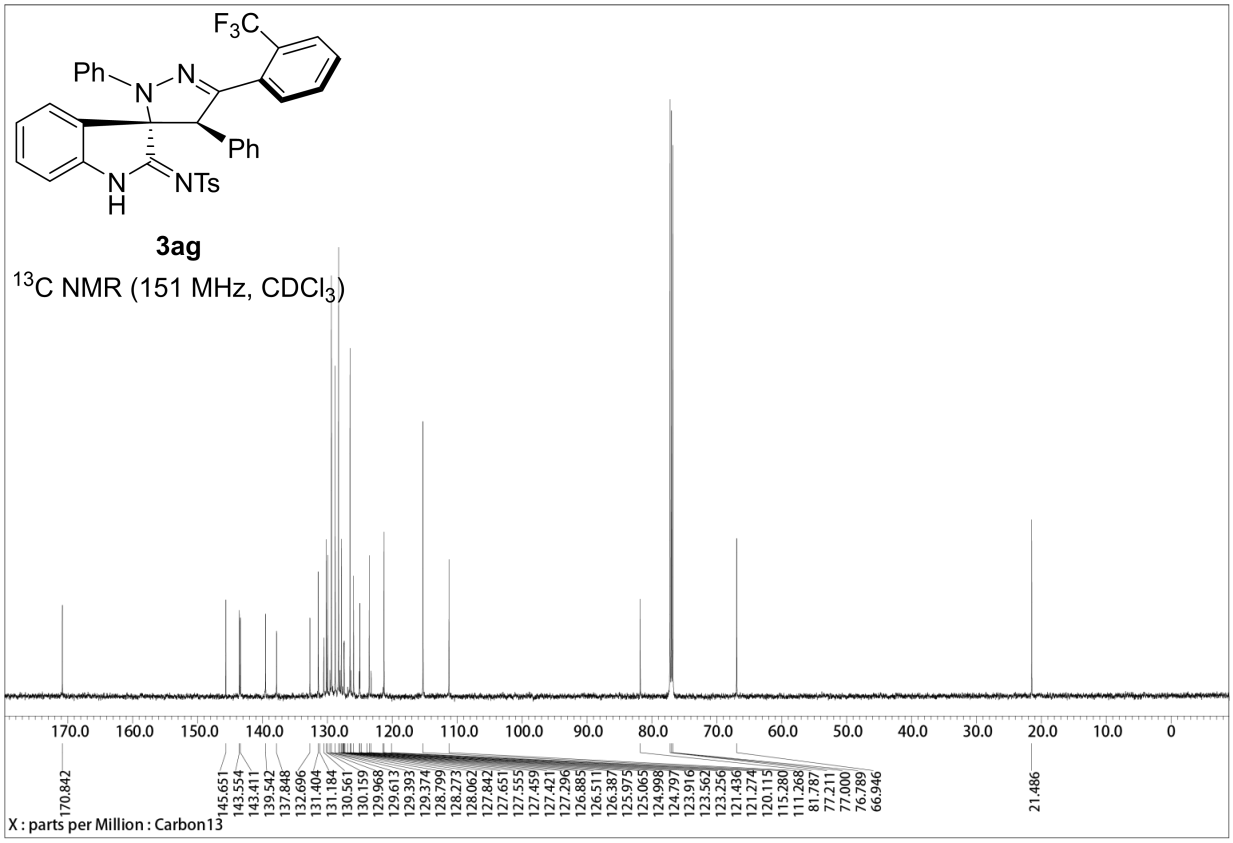


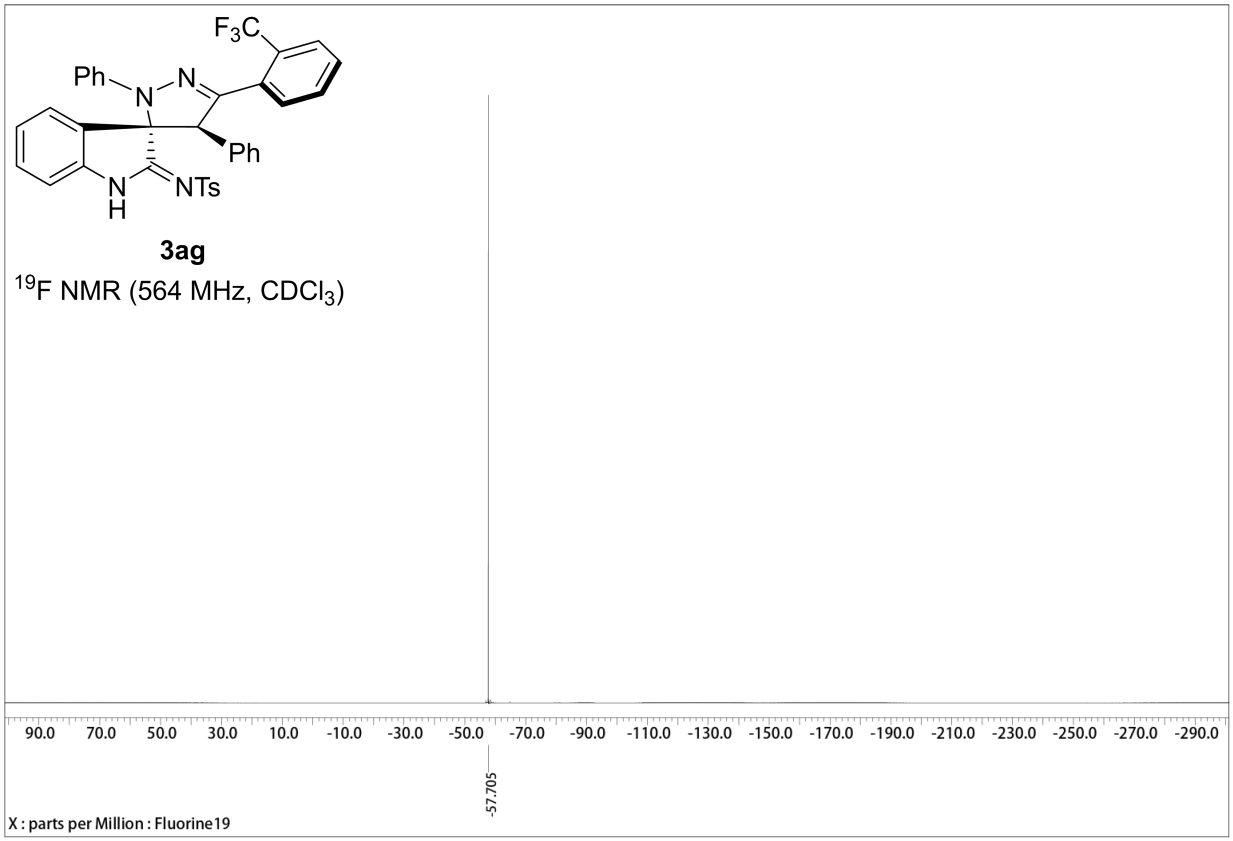

Ph
N
N
Ph
Ph
N
NTs
Allyl
3ae
13C NMR (151 MHz, CDCl3)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
167.826
148.974
143.621
141.946
141.429
139.657
134.113
131.796
130.217
129.690
129.326
128.685
128.484
128.235
128.120
127.708
126.999
126.885
126.502
126.052
123.294
120.632
119.349
115.184
109.975
80.562
77.211
77.000
76.789
65.223
45.959
21.351
X : parts per Million : Carbon13

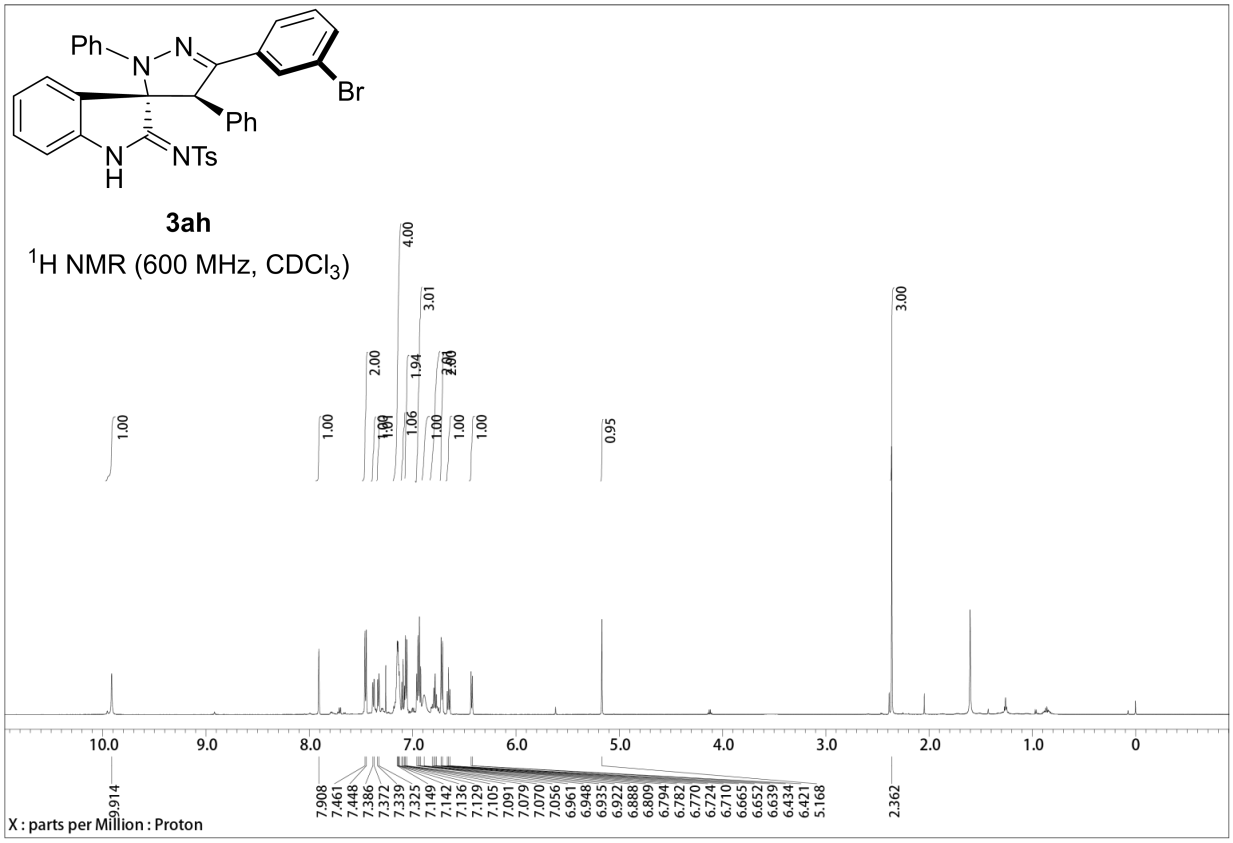

Cl
Ph
N
N
Ph
N
H
NTs
3af
1H NMR (600 MHz, CDCl3)
2.93
2.99
3.00
1.99
1.97
0.94
0.99
1.00
1.05
0.99
0.95
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.901
7.639
7.625
7.597
7.588
7.581
7.341
7.337
7.327
7.210
7.198
7.193
7.185
7.175
7.151
7.138
7.109
7.096
7.083
7.068
7.053
7.041
7.031
6.965
6.951
6.939
6.862
6.849
6.831
6.819
6.790
6.777
6.764
6.749
6.697
6.684
6.671
6.644
6.631
5.669
2.379
X : parts per Million : Proton

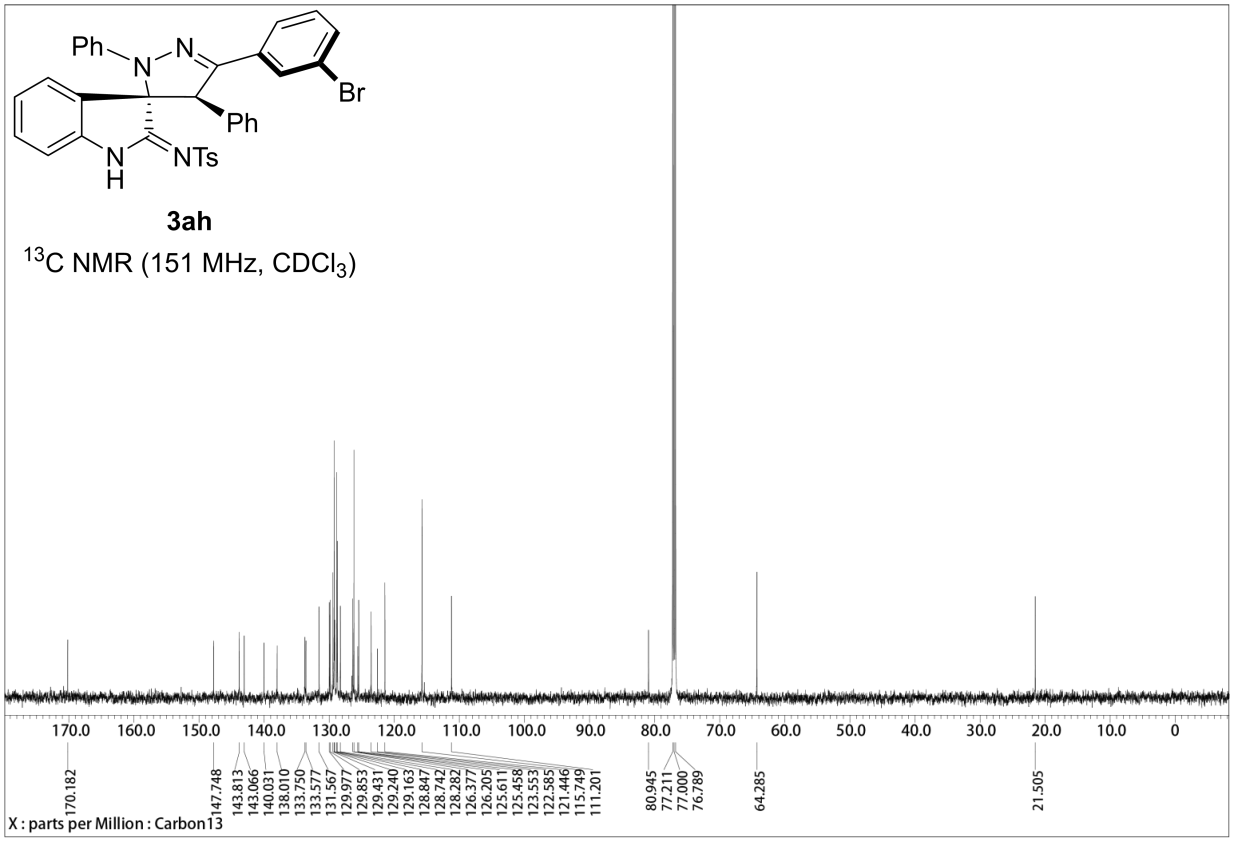

Cl
Ph
N
N
Ph
N
H
NTs
3af
13C NMR (151 MHz, CDCl3)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.201
148.227
143.908
143.210
139.810
138.049
133.319
132.802
130.801
130.561
129.920
129.661
129.355
129.317
128.809
128.340
127.928
126.626
126.454
126.224
125.324
123.476
121.513
115.902
111.077
81.491
77.211
77.000
76.789
66.544
21.514
X : parts per Million : Carbon13

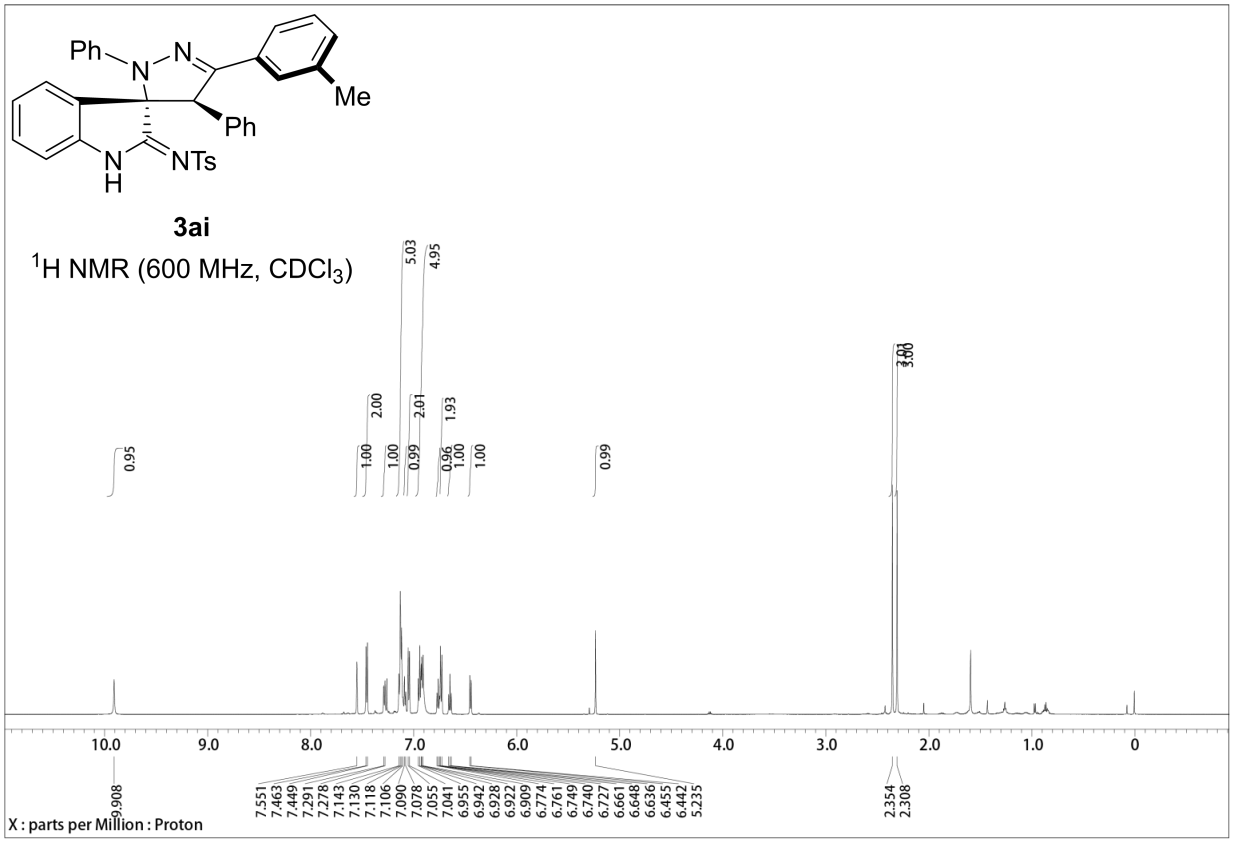

F3C
Ph
N
N
Ph
N
H
NTs
3ag
1H NMR (600 MHz, CDCl3)
0.90
1.01
1.98
1.00
2.00
2.00
1.06
2.00
1.00
1.00
1.00
3.01
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
10.151
7.791
7.785
7.783
7.775
7.753
7.740
7.360
7.353
7.348
7.344
7.301
7.294
7.291
7.286
7.190
7.176
7.040
7.037
7.025
7.019
7.013
7.006
6.995
6.985
6.972
6.961
6.958
6.940
6.927
6.925
6.912
6.870
6.856
6.817
6.807
6.796
6.774
6.759
6.745
6.732
6.715
6.702
6.690
5.632
2.387
X : parts per Million : Proton

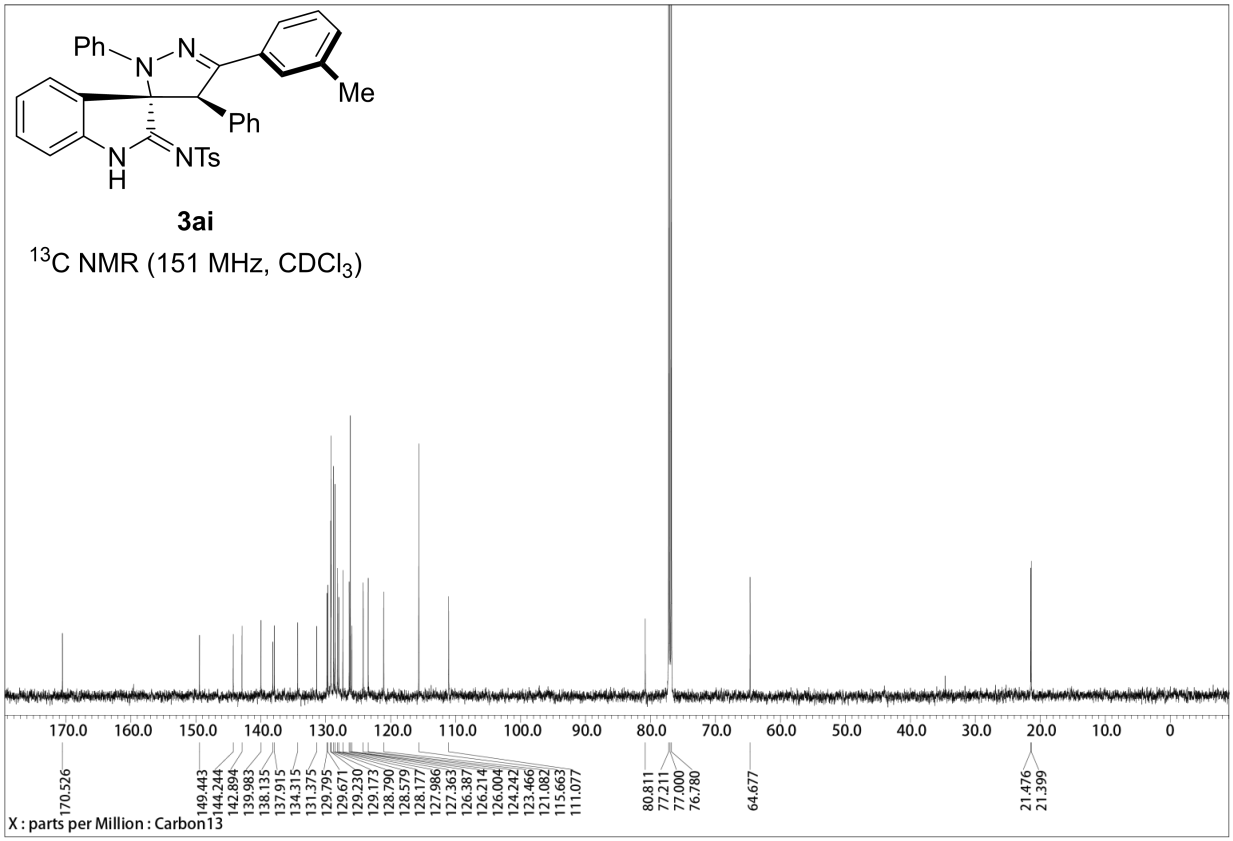

F3C
Ph
N
N
Ph
N
H
NTs
3ag
13C NMR (151 MHz, CDCl3)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.842
145.651 143.554 143.411 139.542 137.848 132.696 131.404 131.184 130.561 130.159 129.968 129.613 129.393 129.374 128.799 128.273 128.062 127.842 127.651 127.555 127.459 127.421 127.296 126.885 126.511 126.387 125.975 125.065 124.998 124.797 123.916 123.562 123.256 121.436 121.274 120.115 115.280 111.268 81.787 77.211 77.000 76.789 66.946
21.486
X : parts per Million : Carbon13

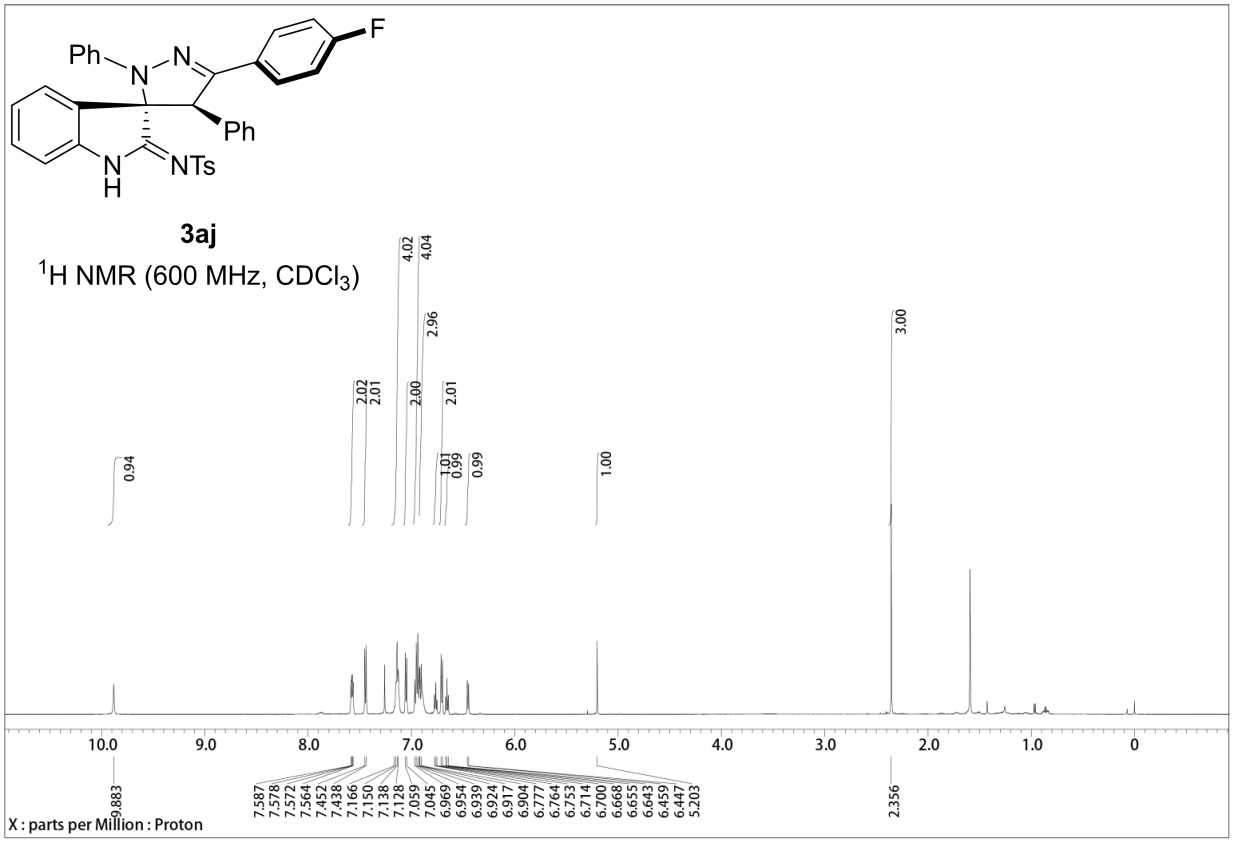

F3C
Ph
N
N
Ph
N
H
NTs
3ag
19F NMR (564 MHz, CDCl3)
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0
-57.705
X : parts per Million : Fluorine19

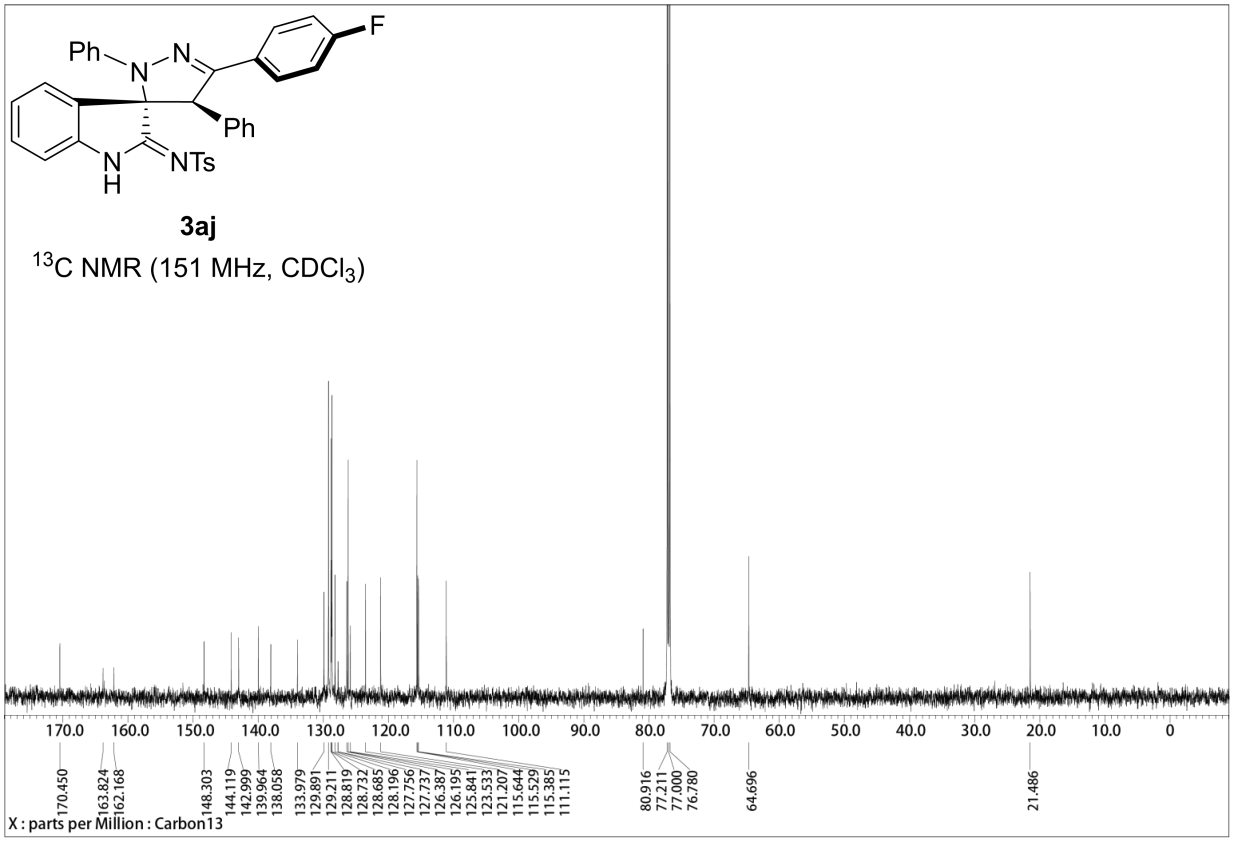

Ph
N
N
Br
Ph
N
H
NTs
3ah
1H NMR (600 MHz, CDCl3)
4.00
3.01
3.00
2.00
1.94
1.00
1.06
0.95
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.914
7.908
7.461
7.448
7.386
7.372
7.339
7.325
7.149
7.142
7.136
7.129
7.105
7.091
7.079
7.070
7.056
6.961
6.948
6.935
6.922
6.888
6.809
6.794
6.782
6.770
6.724
6.710
6.665
6.652
6.639
6.434
6.421
5.168
2.362
X : parts per Million : Proton

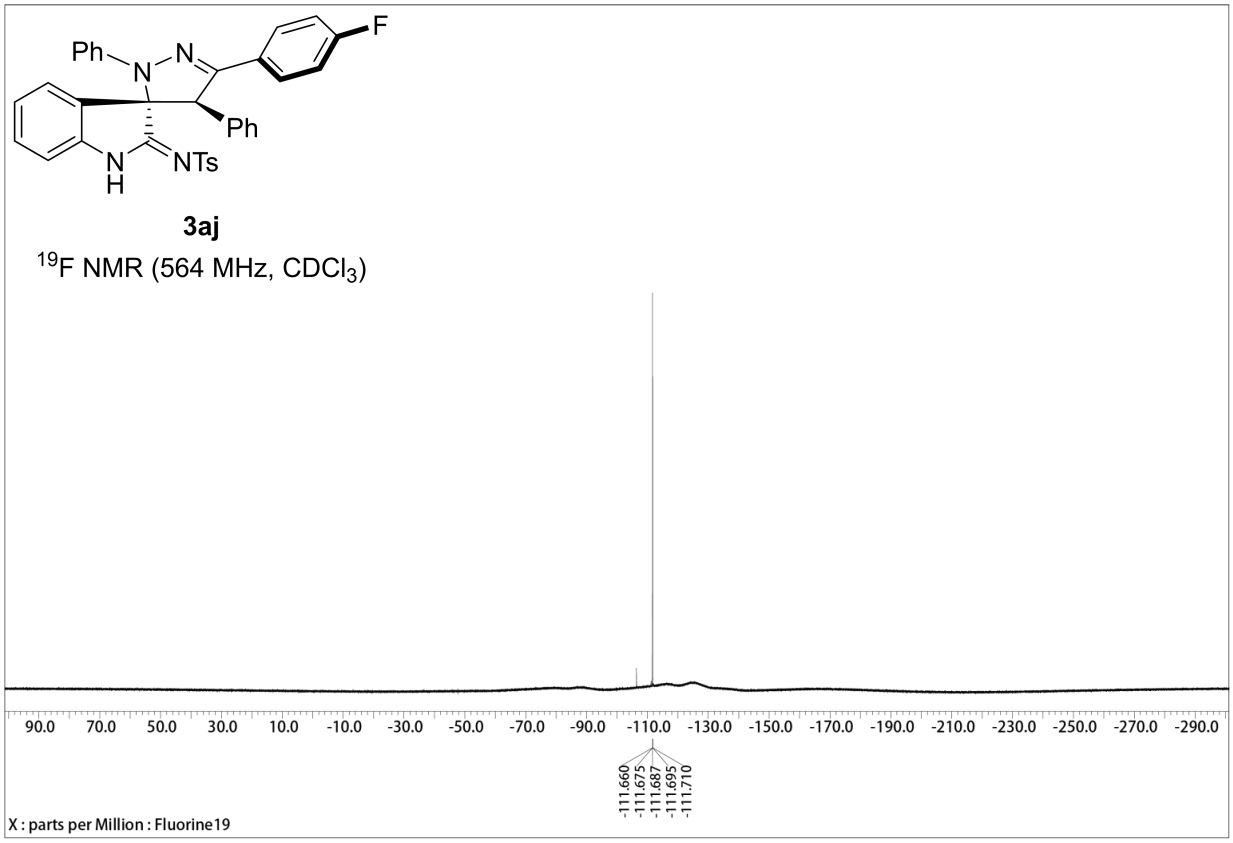

Ph
N
N
Br
Ph
N
H
NTs
3ah
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.182
147.748
143.813
143.066
140.031
138.010
133.750
133.577
131.567
129.977
129.853
129.431
129.240
129.163
128.847
128.742
128.282
126.377
126.205
125.611
125.458
123.553
122.585
121.446
115.749
111.201
80.945
77.211
77.000
76.789
64.285
21.505
X : parts per Million : Carbon13

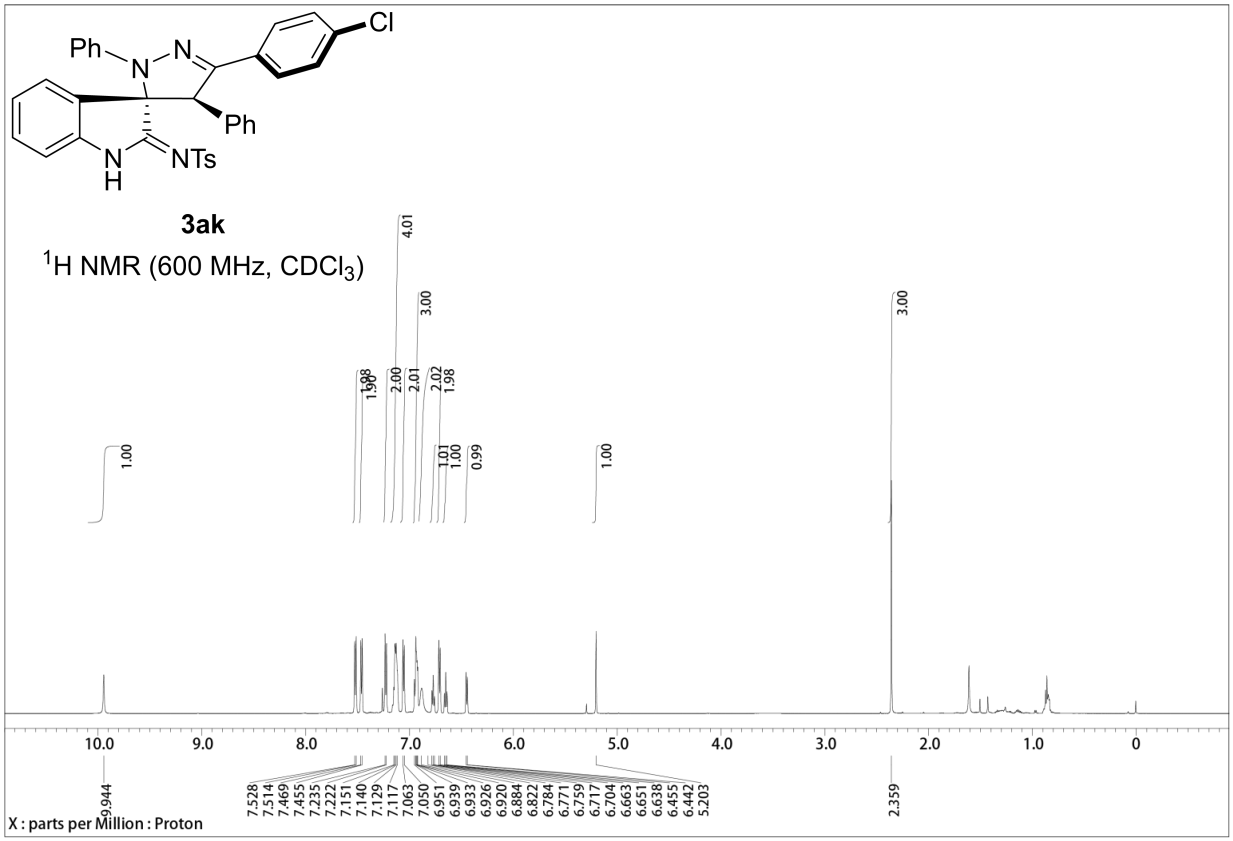

Ph
N
N
Me
Ph
N
H
NTs
3ai
1H NMR (600 MHz, CDCl3)
5.03
4.95
2.00
2.01
1.93
0.95
1.00
1.00
0.99
0.96
1.00
1.00
0.99
3.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.908
7.551
7.463
7.449
7.291
7.278
7.143
7.130
7.118
7.106
7.090
7.078
7.055
7.041
6.955
6.942
6.928
6.922
6.909
6.774
6.761
6.749
6.740
6.727
6.661
6.648
6.636
6.455
6.442
5.235
2.354
2.308
X : parts per Million : Proton

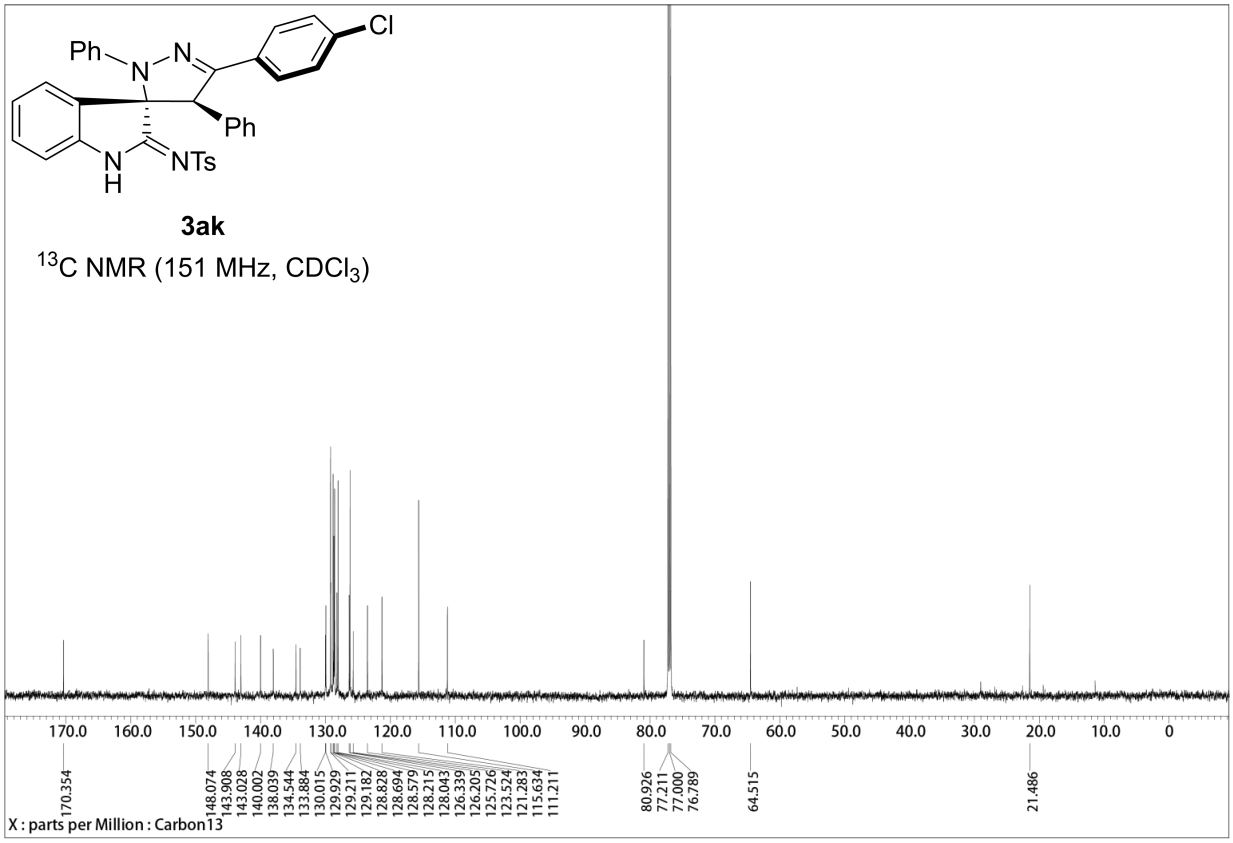

Ph
N
N
Me
Ph
N
H
NTs
3ai
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.526
149.443
144.244
142.894
139.983
138.135
137.915
134.315
131.375
129.795
129.671
129.230
129.173
128.790
128.579
128.177
127.986
127.363
126.387
126.214
126.004
124.242
123.466
121.082
115.663
111.077
80.811
77.211
77.000
76.780
64.677
21.476
21.399
X : parts per Million : Carbon13

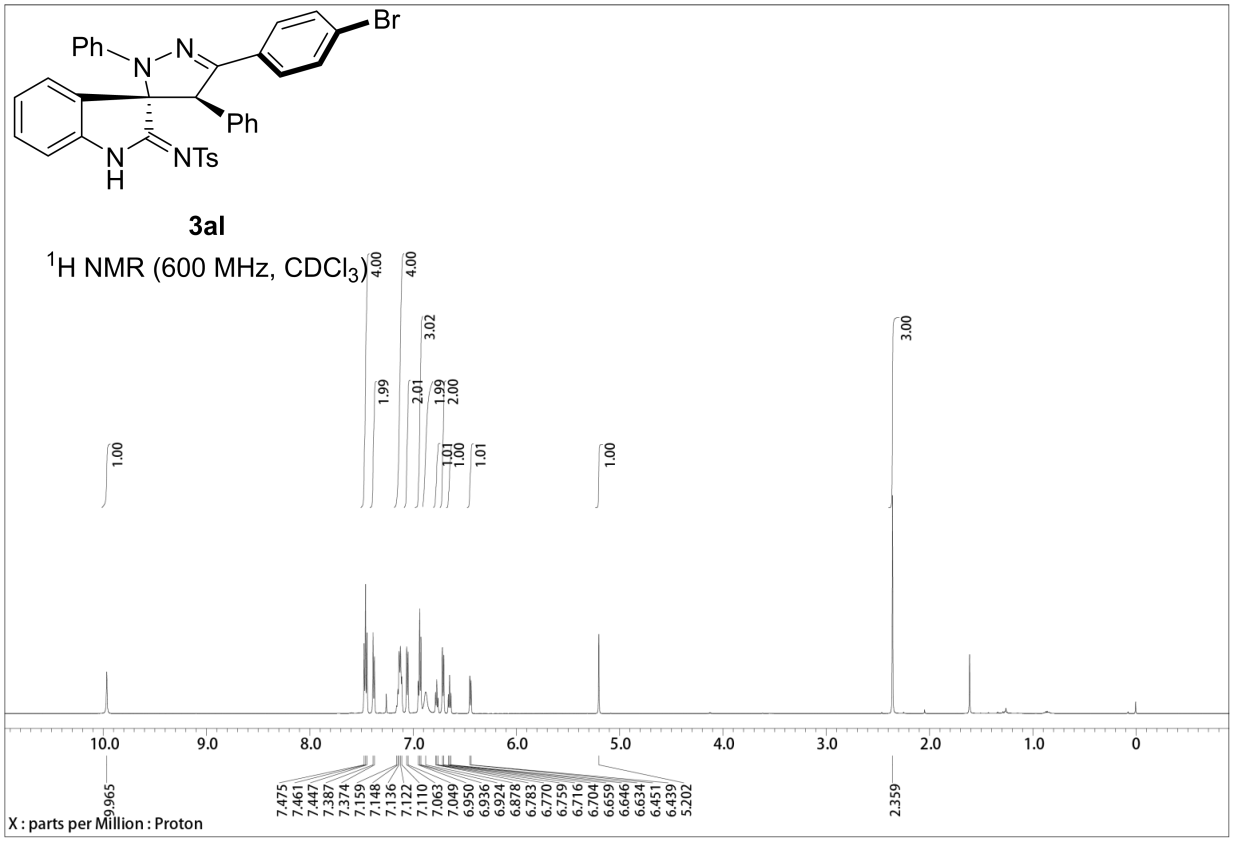

Ph
N
N
F
Ph
N
H
NTs
3aj
1H NMR (600 MHz, CDCl3)
4.02
4.04
2.96
3.00
2.02
2.01
2.00
2.01
0.94
1.01
0.99
0.99
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.883
7.587
7.578
7.572
7.564
7.452
7.438
7.166
7.150
7.138
7.128
7.059
7.045
6.969
6.954
6.939
6.924
6.917
6.904
6.777
6.764
6.753
6.714
6.700
6.668
6.655
6.643
6.459
6.447
5.203
2.356
X : parts per Million : Proton

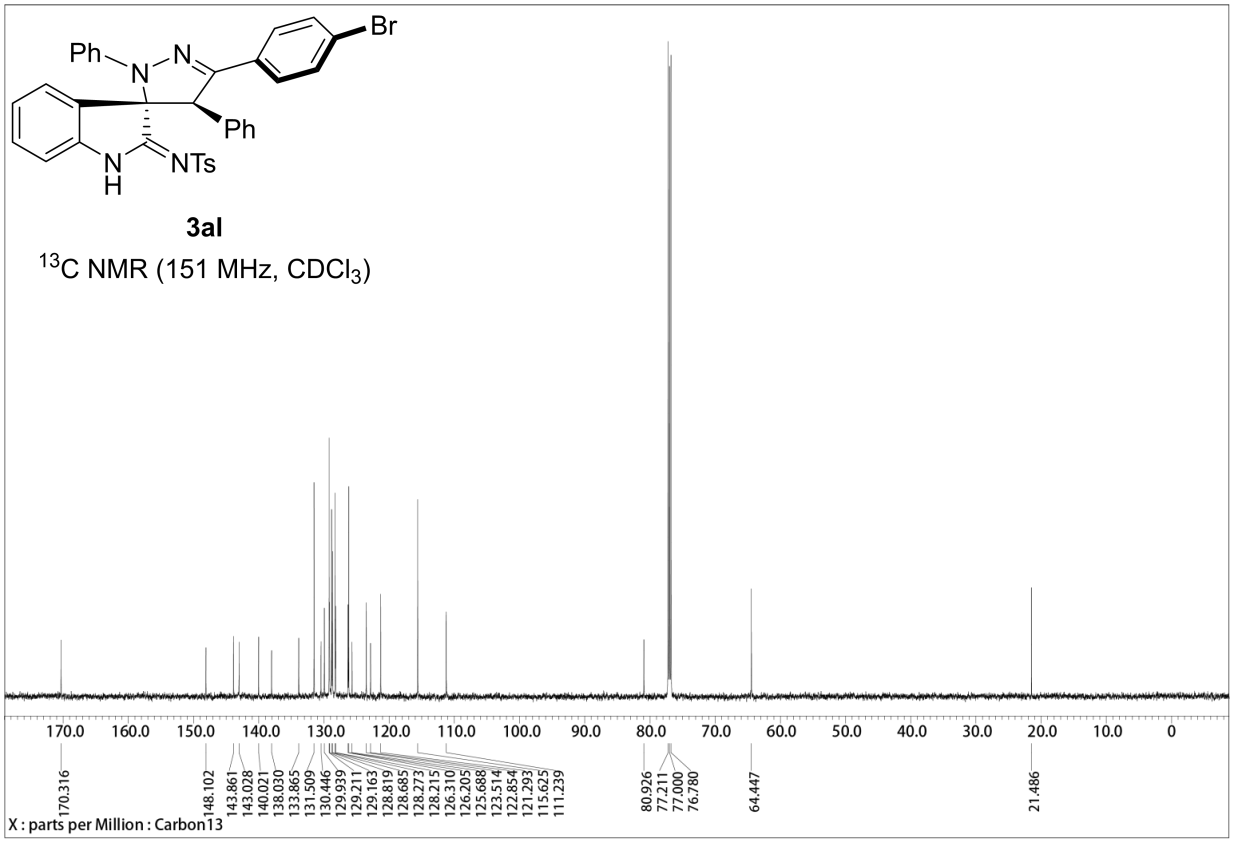

Ph
N
N
F
Ph
N
H
NTs
3aj
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.450
163.824
162.168
148.303
144.119
142.999
139.964
138.058
133.979
129.891
129.211
128.819
128.732
128.685
128.196
127.756
127.737
126.387
126.195
125.841
123.533
121.207
115.644
115.529
115.385
111.115
80.916
77.211
77.000
76.780
64.696
21.486
X : parts per Million : Carbon13

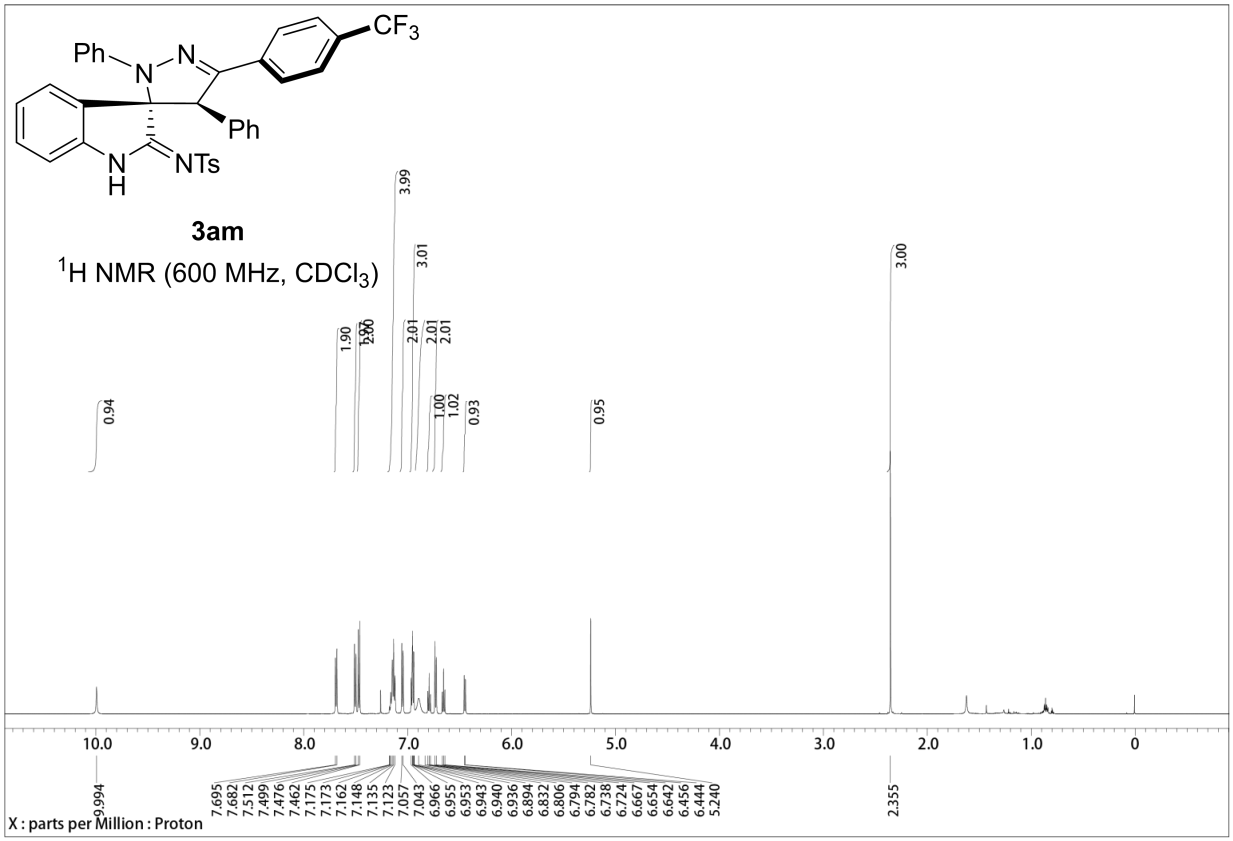

Ph
N
N
F
Ph
N
H
NTs
3aj
19F NMR (564 MHz, CDCl3)
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0
-111.660
-111.675
-111.687
-111.695
-111.710
X : parts per Million : Fluorine19

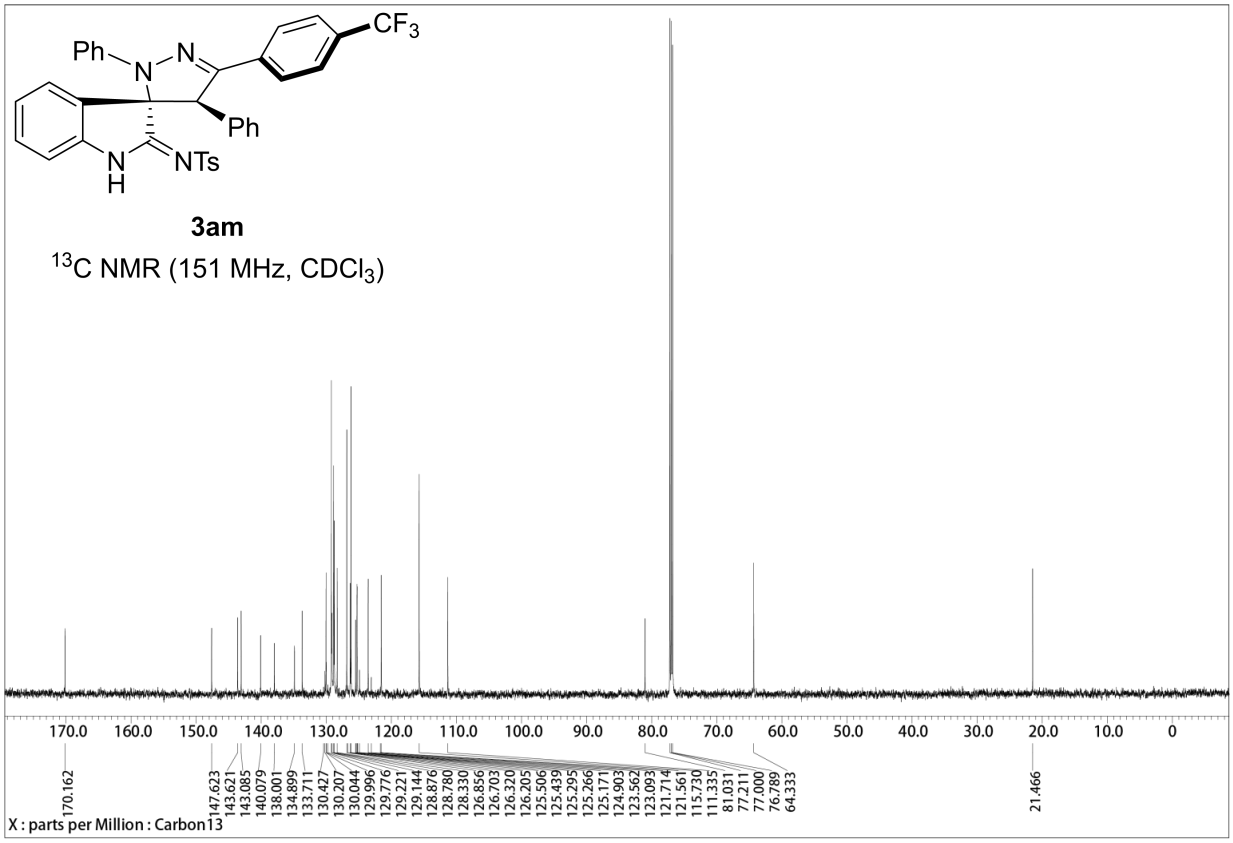

Ph
N
N
Cl
Ph
N
H
NTs
3ak
1H NMR (600 MHz, CDCl3)
4.01
3.00
3.00
2.00
2.01
2.02
1.98
1.00
1.00
1.00
0.99
1.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.944
7.528
7.514
7.469
7.455
7.235
7.222
7.151
7.140
7.129
7.117
7.063
7.050
6.951
6.939
6.933
6.926
6.920
6.884
6.822
6.784
6.771
6.759
6.717
6.704
6.663
6.651
6.638
6.455
6.442
5.203
2.359
X : parts per Million : Proton

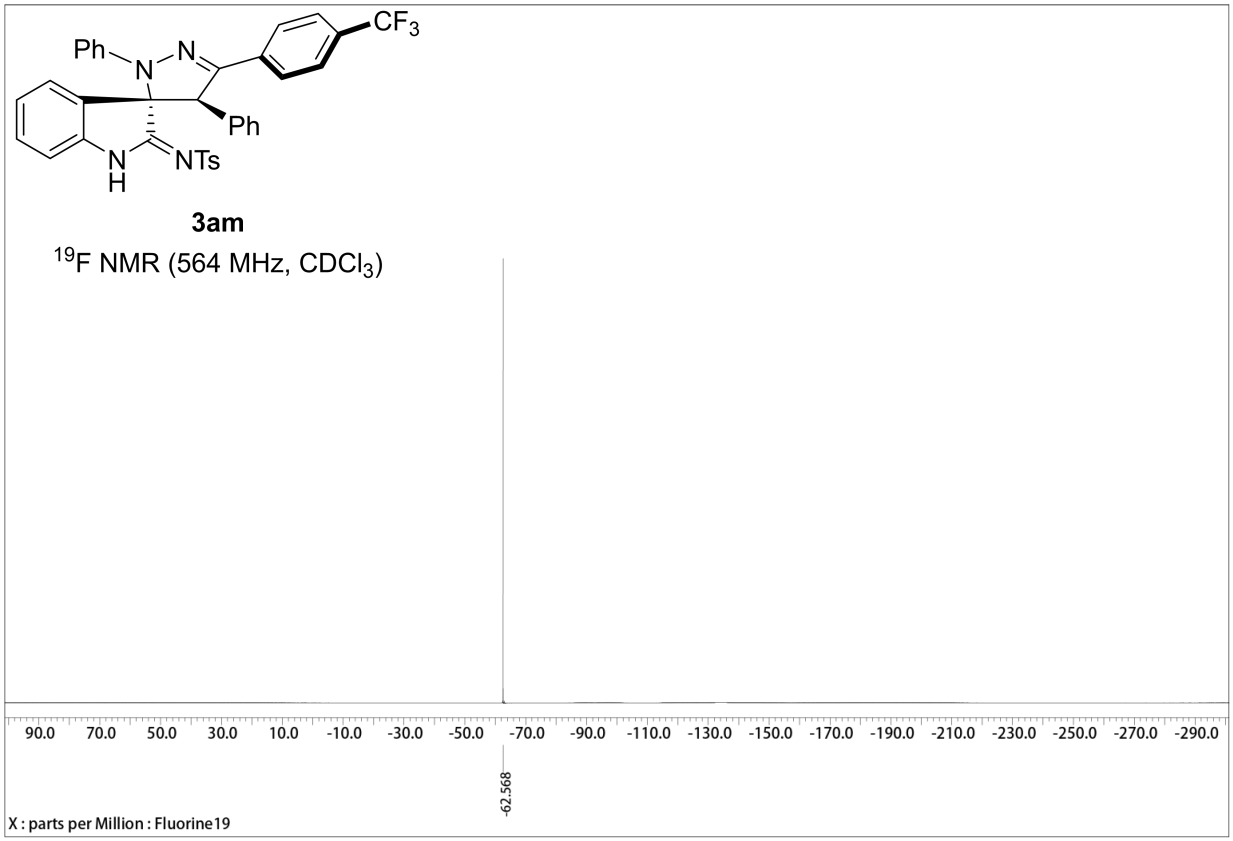

Ph
N
N
Cl
Ph
N
H
NTs
3ak
13C NMR (151 MHz, CDCl3)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.354
148.074 143.908 143.028 140.002 138.039 134.544 133.884 130.015 129.929 129.211 129.182 128.828 128.694 128.579 128.215 128.043 126.339 126.205 125.726 123.524 121.283 115.634 111.211
80.926 77.211 77.000 76.789
64.515
21.486
X : parts per Million : Carbon13

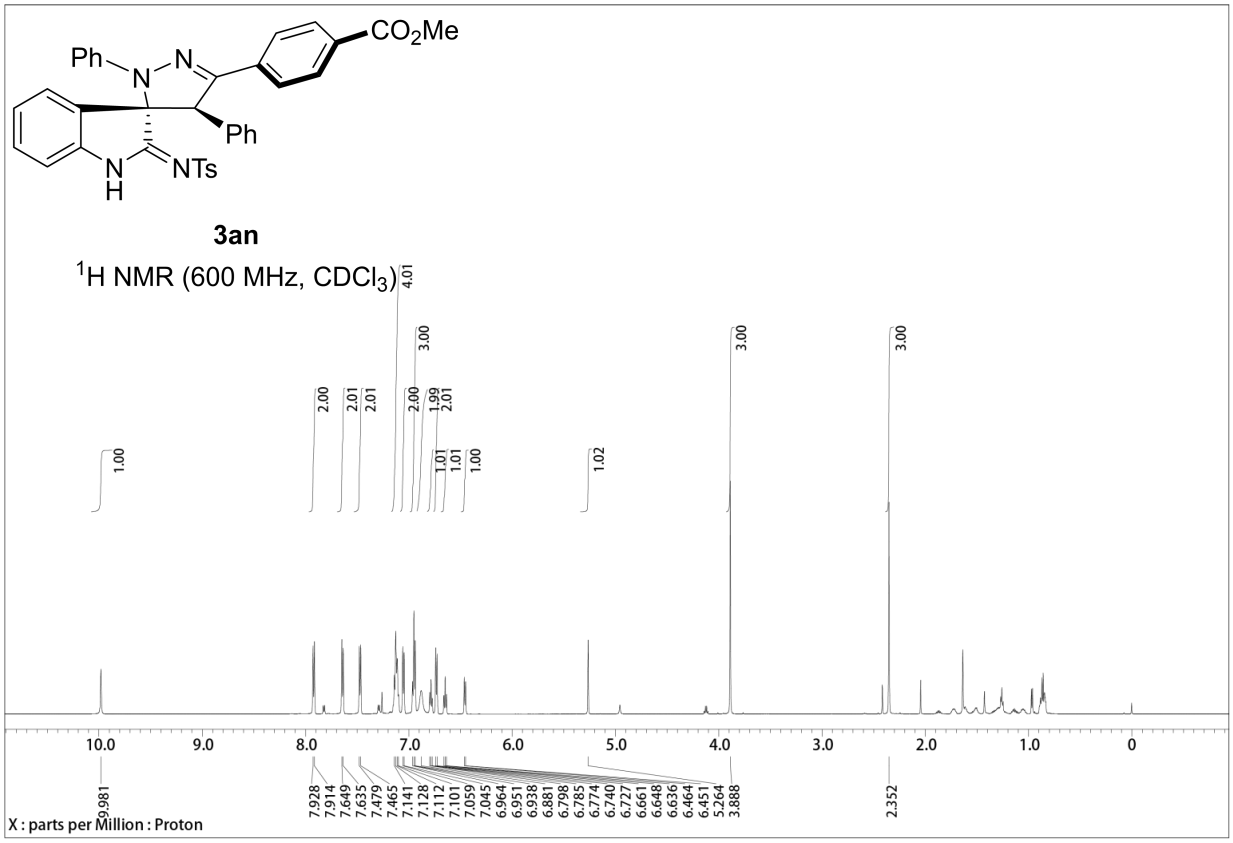

Ph
N
N
Br
Ph
N
H
NTs
3al
1H NMR (600 MHz, CDCl3)
4.00 4.00 3.02 3.00
1.99 2.01 1.99 2.00
1.00 1.01 1.00 1.01 1.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.965
7.475 7.461 7.447 7.387 7.374 7.159 7.148 7.136 7.122 7.110 7.063 7.049 6.950 6.936 6.924 6.878 6.783 6.770 6.759 6.716 6.704 6.659 6.646 6.634 6.451 6.439 5.202
2.359
X : parts per Million : Proton

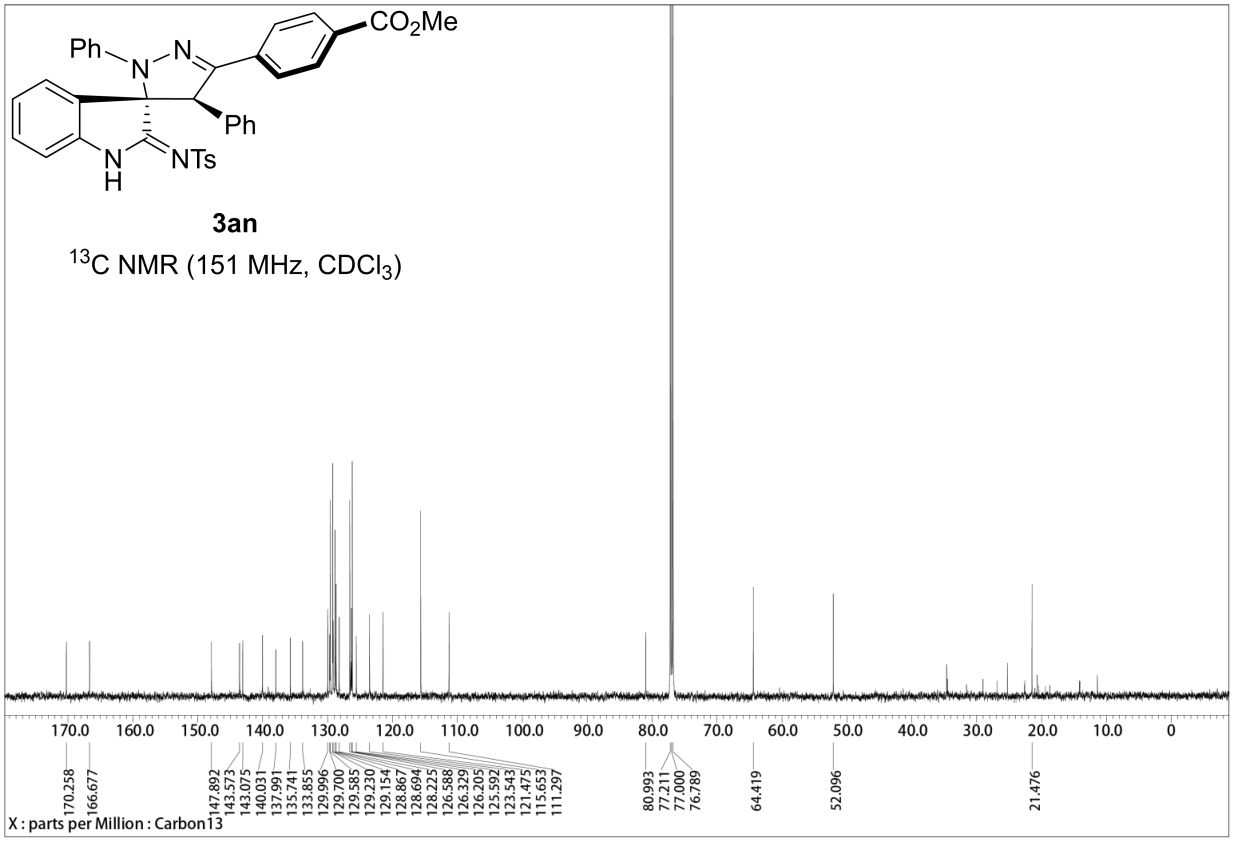

Ph
N
N
Br
Ph
N
H
NTs
3al
13C NMR (151 MHz, CDCl3)
170.316
148.102
143.861
143.028
140.021
138.030
133.865
131.509
130.446
129.939
129.211
129.163
128.819
128.685
128.273
128.215
126.310
126.205
125.688
123.514
122.854
121.293
115.625
111.239
80.926
77.211
77.000
76.780
64.447
21.486
X : parts per Million : Carbon13

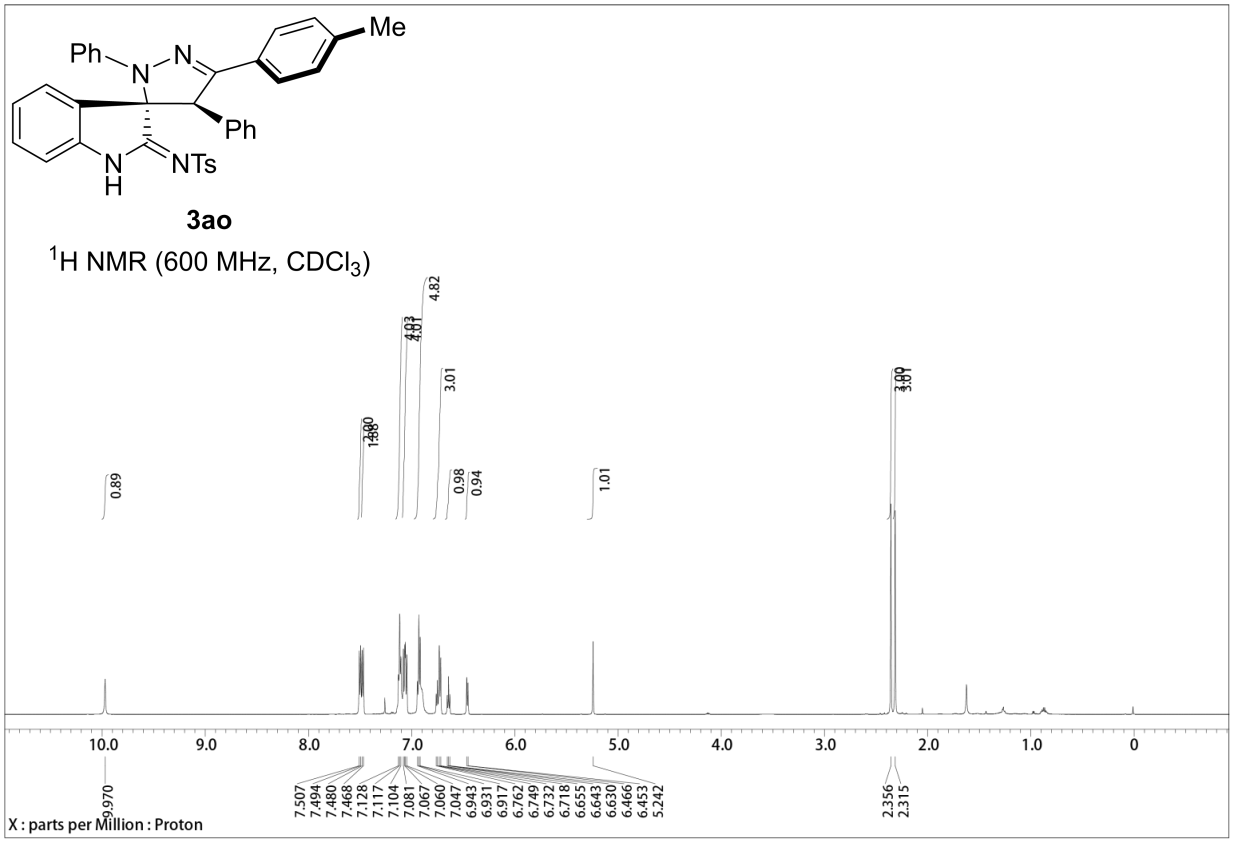

Ph
N
N
CF3
Ph
N
H
NTs
3am
1H NMR (600 MHz, CDCl3)
3.99
3.01
3.00
2.01
2.01
2.01
1.90
1.00
1.02
0.94
0.93
0.95
9.994
7.695
7.682
7.512
7.499
7.476
7.462
7.175
7.173
7.162
7.148
7.135
7.123
7.057
7.043
6.966
6.955
6.953
6.943
6.940
6.936
6.894
6.832
6.806
6.794
6.782
6.738
6.724
6.667
6.654
6.642
6.456
6.444
5.240
2.355
X : parts per Million : Proton

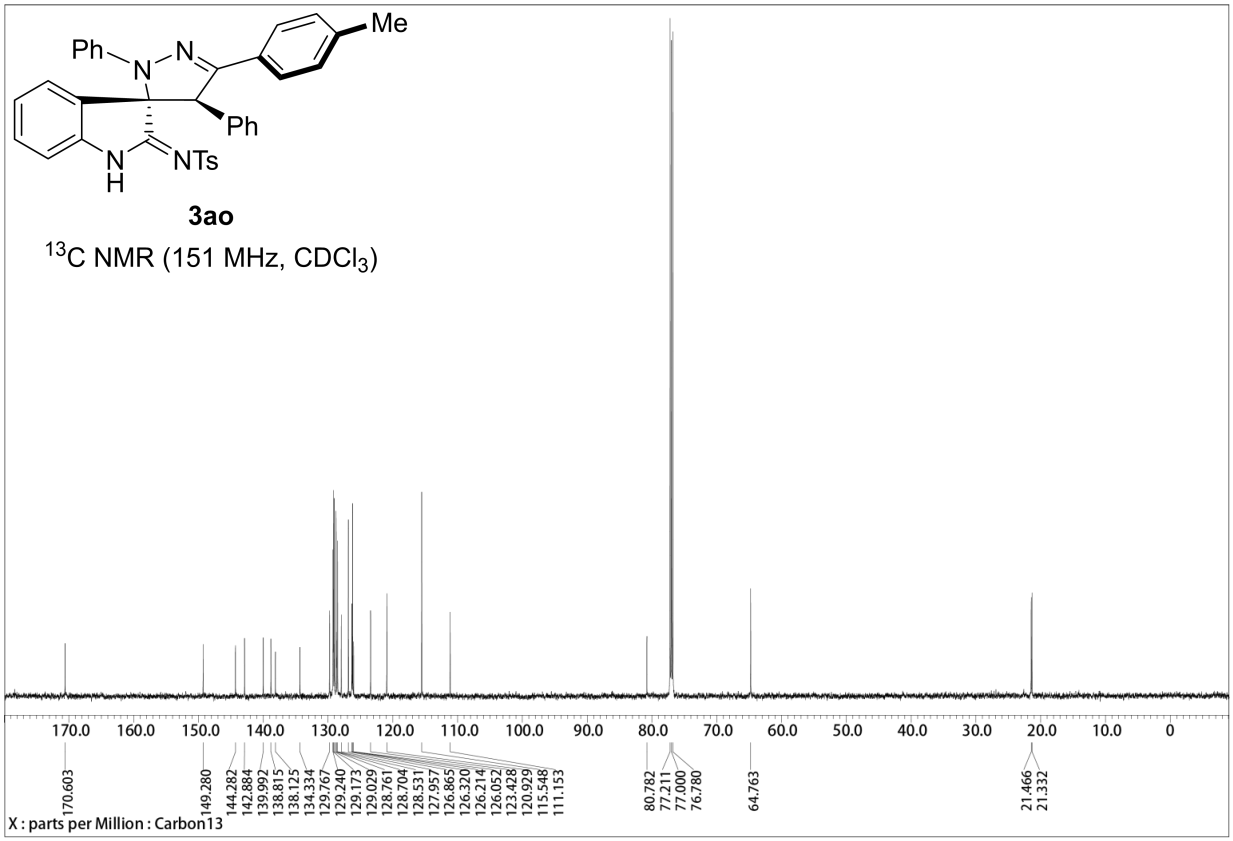

Ph
N
N
CF3
Ph
N
H
NTs
3am
13C NMR (151 MHz, CDCl3)
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.162
147.623
143.621
143.085
140.079
138.001
134.899
133.711
130.427
130.207
130.044
129.996
129.776
129.221
129.144
128.876
128.780
128.330
126.856
126.703
126.320
126.205
125.506
125.439
125.295
125.266
125.171
124.903
123.562
123.095
121.714
121.561
115.730
111.335
81.031
77.211
77.000
76.789
64.333
21.466
X : parts per Million : Carbon13

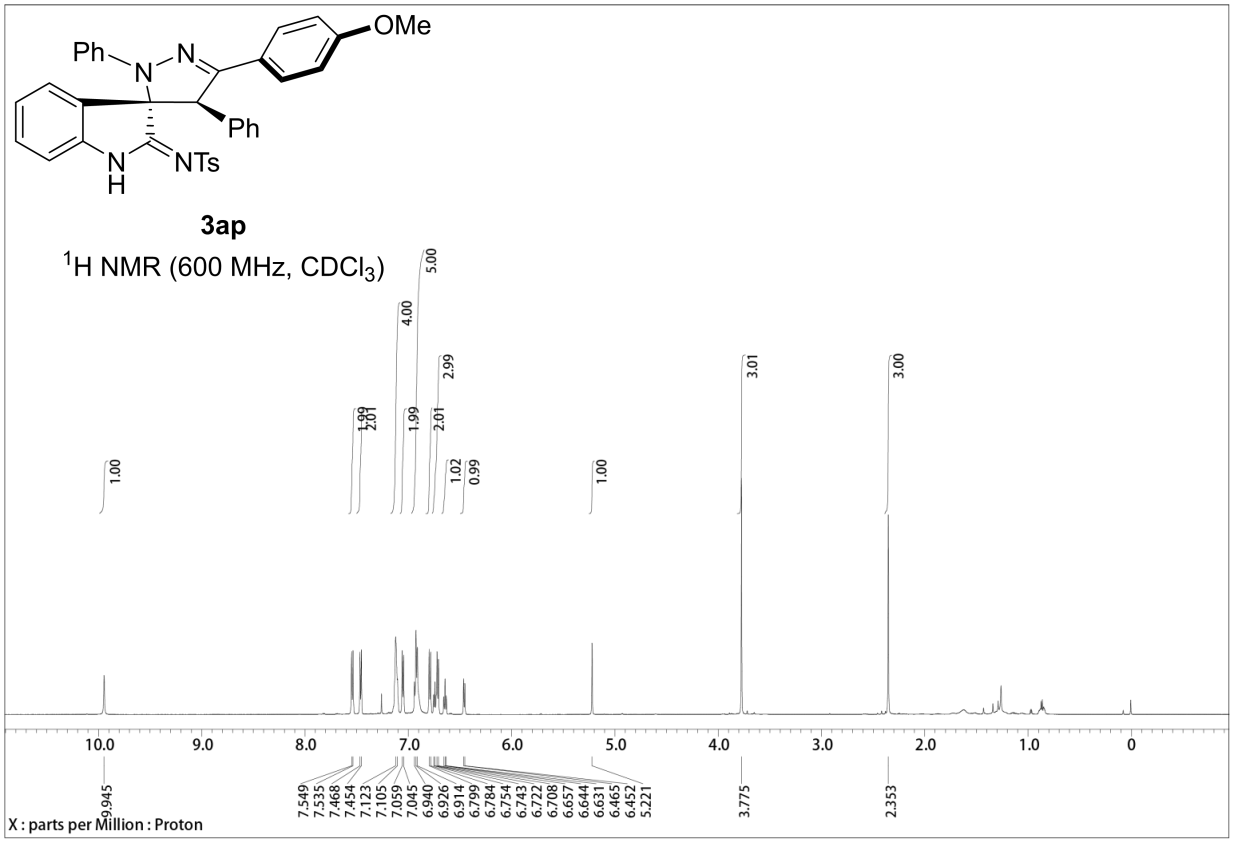

Ph
N
N
CF3
Ph
N
H
NTs
3am
19F NMR (564 MHz, CDCl3)
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0
-62.568
X : parts per Million : Fluorine19

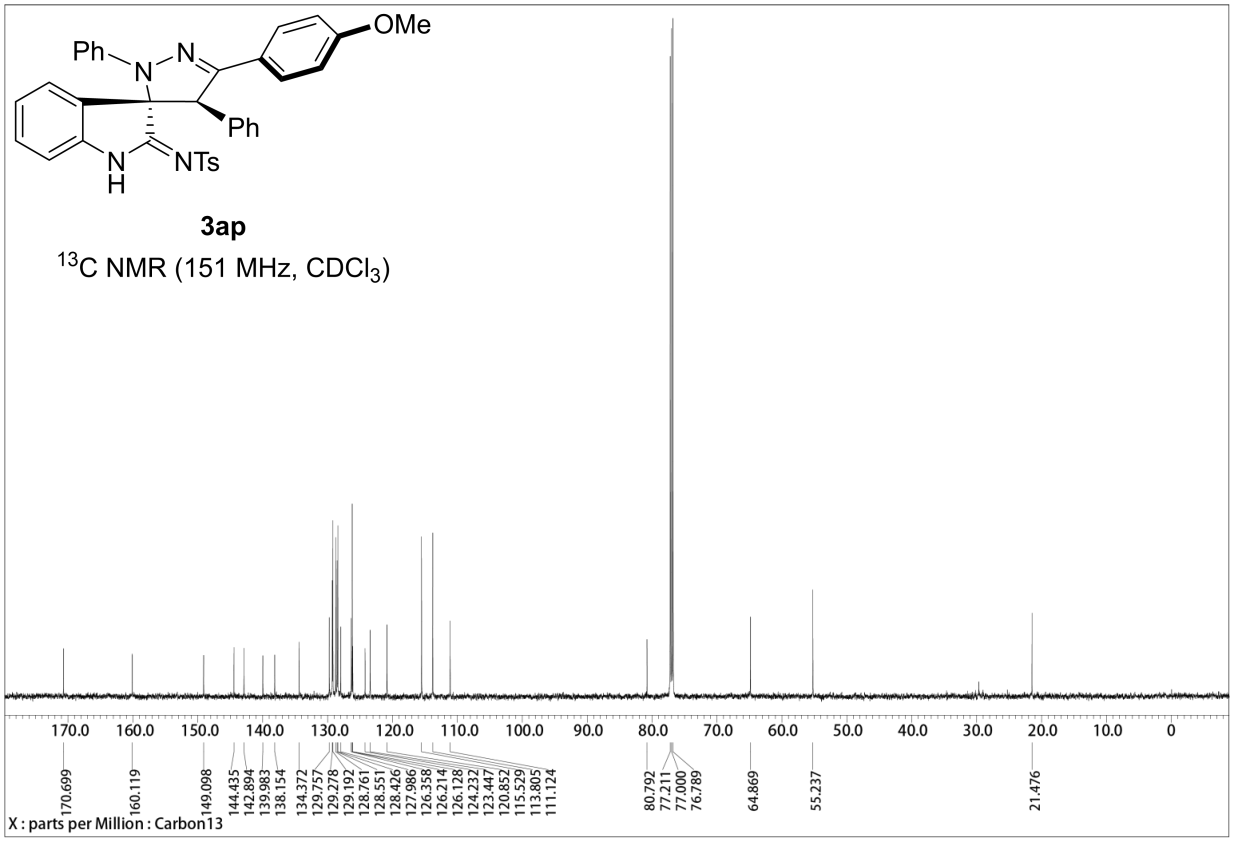

Ph
N
N
CO2Me
Ph
N
H
NTs
3an
1H NMR (600 MHz, CDCl3)
4.01
3.00
3.00
3.00
2.00
2.01
2.01
2.00
1.99
2.01
1.00
1.01
1.01
1.00
1.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.981
7.928
7.914
7.649
7.635
7.479
7.465
7.141
7.128
7.112
7.101
7.059
7.045
6.964
6.951
6.938
6.881
6.798
6.785
6.774
6.740
6.727
6.661
6.648
6.636
6.464
6.451
5.264
3.888
2.352
X : parts per Million : Proton

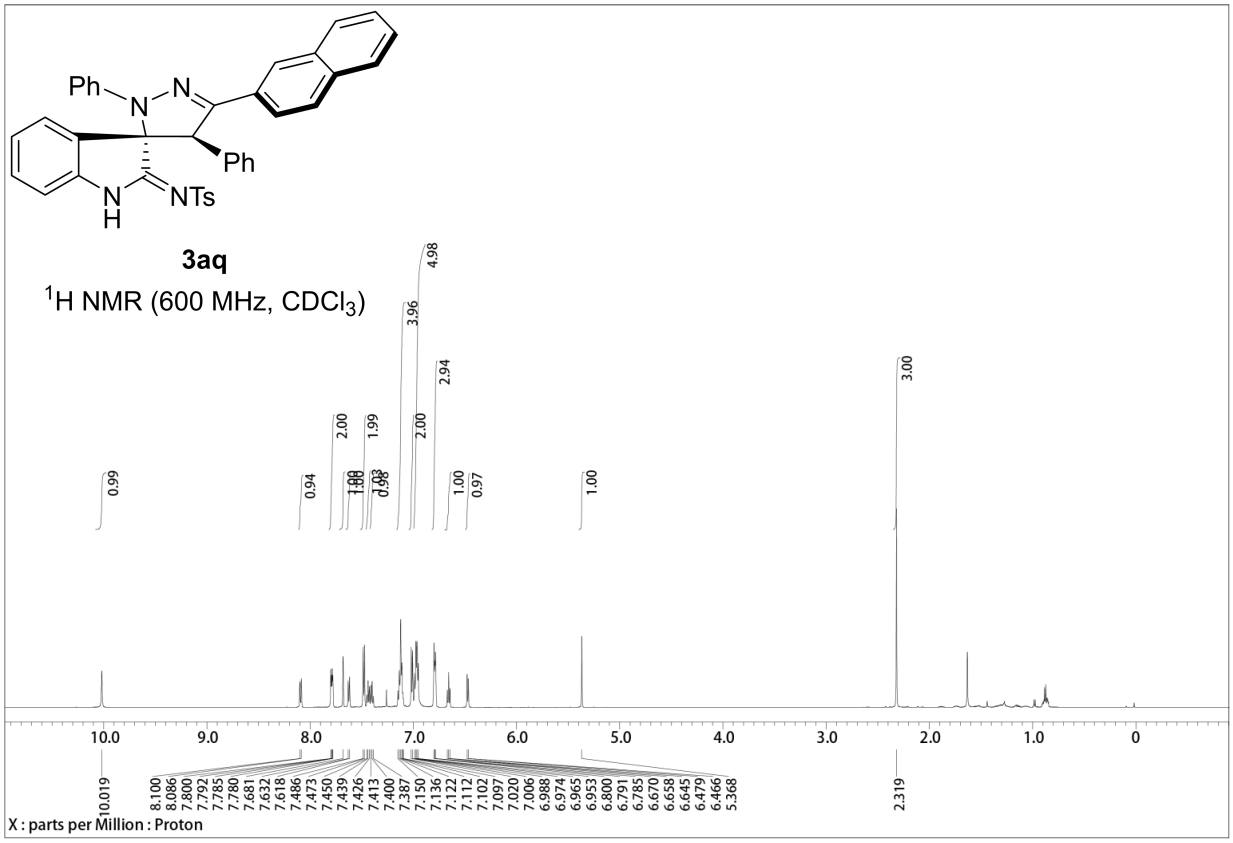

Ph
N
N
CO2Me
Ph
N
H
NTs
3an
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.258
166.677
147.892
143.573
143.075
140.031
137.991
135.741
133.855
129.996
129.700
129.585
129.230
129.154
128.867
128.694
128.225
126.588
126.329
126.205
125.592
123.543
121.475
115.653
111.297
80.993
77.211
77.000
76.789
64.419
52.096
21.476
X : parts per Million : Carbon13

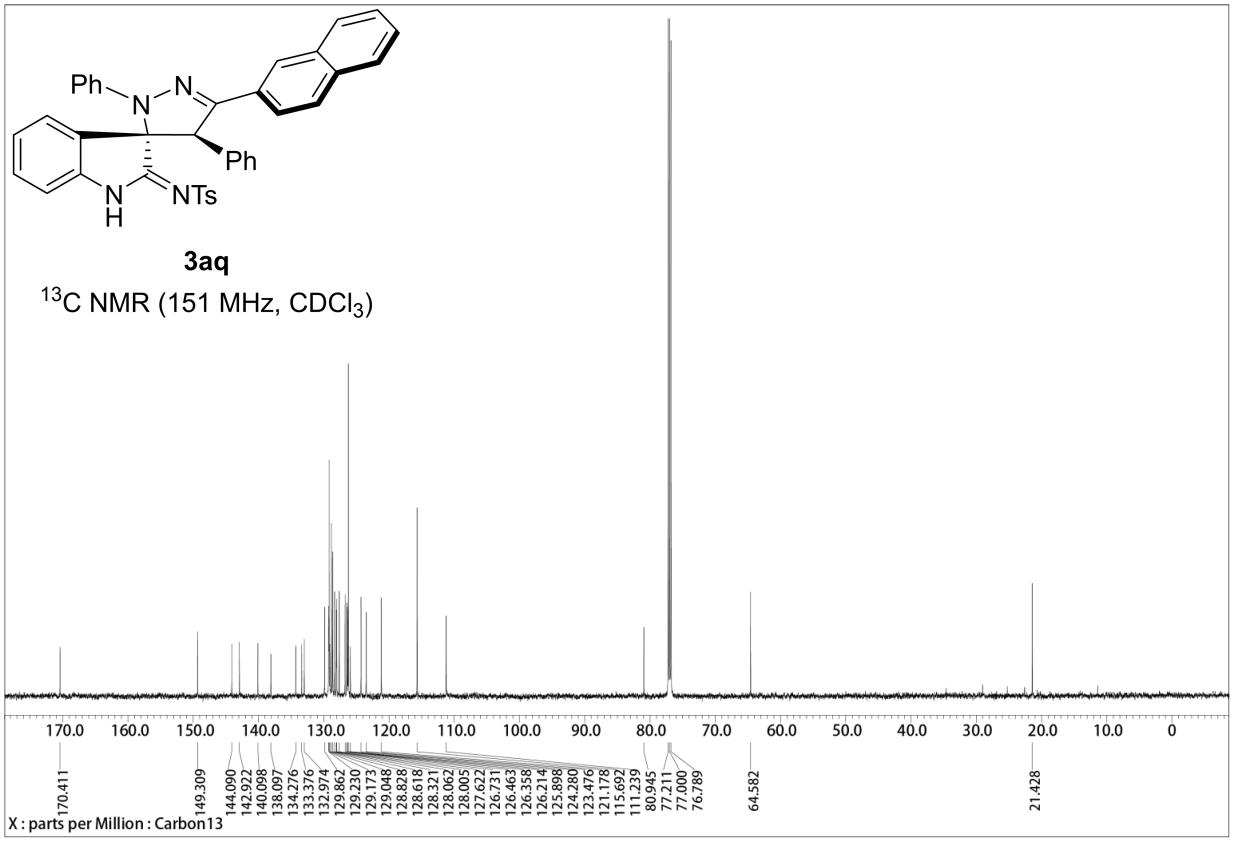

Ph
N
N
Me
Ph
N
H
NTs
3ao
1H NMR (600 MHz, CDCl3)
4.82
4.03
4.01
3.01
3.00
3.01
1.00
1.00
0.98
0.94
1.01
0.89
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.970
7.507
7.494
7.480
7.468
7.128
7.117
7.104
7.081
7.067
7.060
7.047
6.943
6.931
6.917
6.762
6.749
6.732
6.718
6.655
6.643
6.630
6.466
6.453
5.242
2.356
2.315
X : parts per Million : Proton

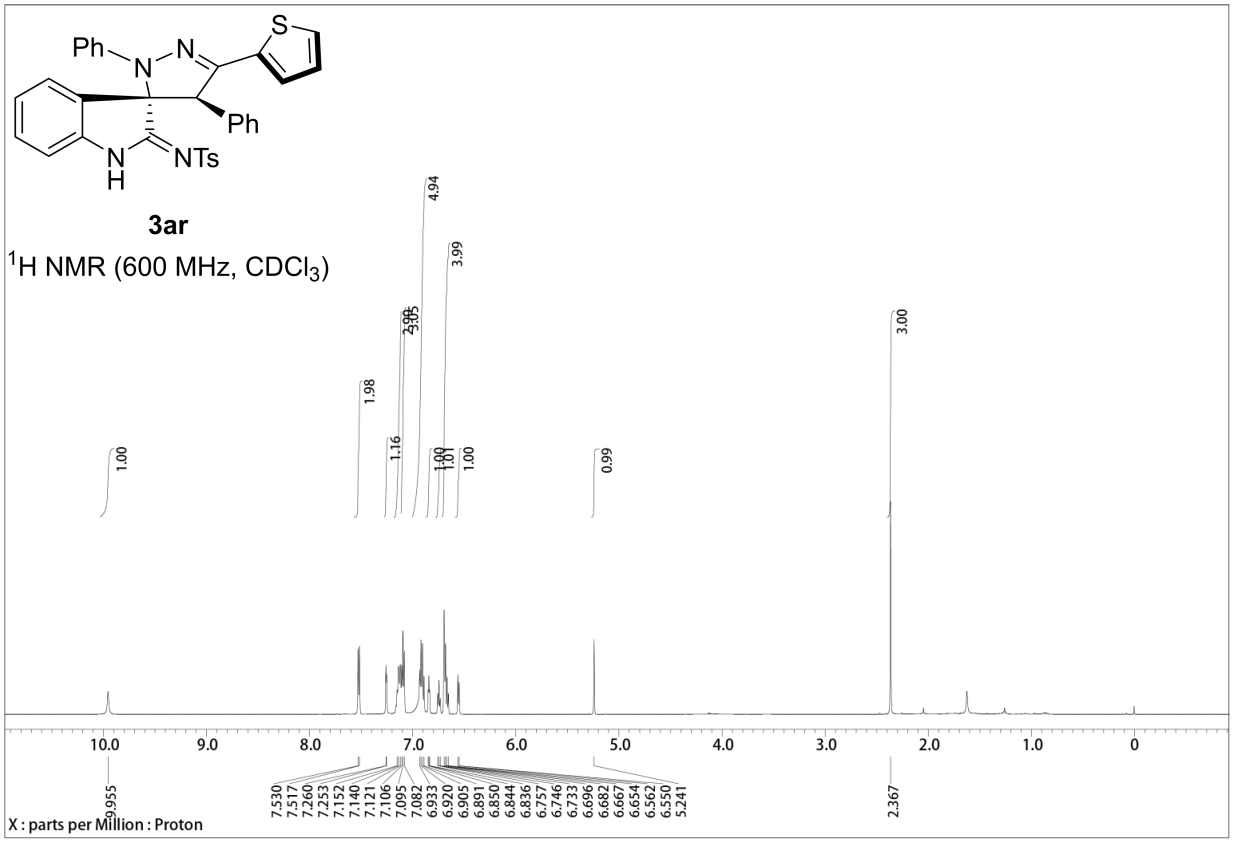

Ph
N
N
Me
Ph
N
H
NTs
3ao
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.603
149.280
144.282
142.884
139.992
138.815
138.125
134.334
129.767
129.240
129.173
129.029
128.761
128.704
128.531
127.957
126.865
126.320
126.214
126.052
123.428
120.929
115.548
111.153
80.782
77.211
77.000
76.780
64.763
21.466
21.332
X : parts per Million : Carbon13

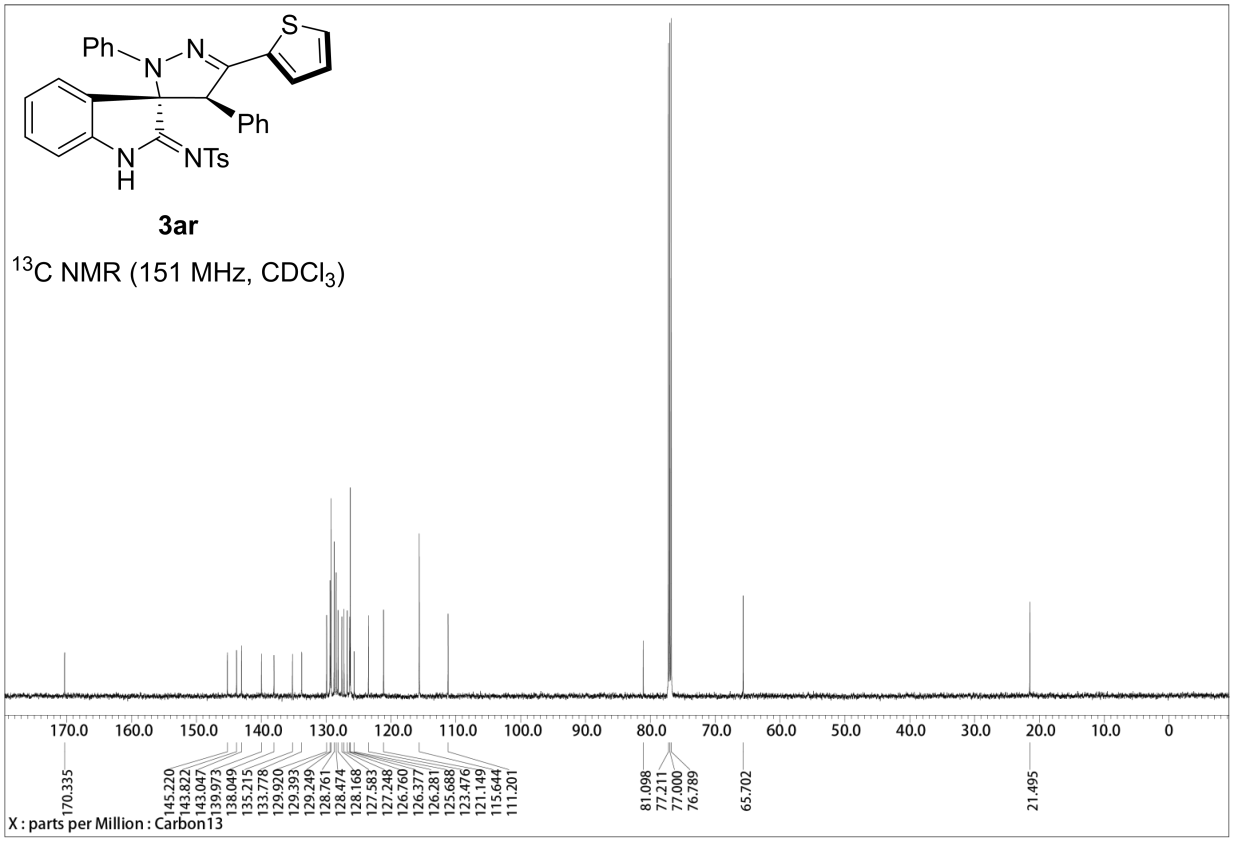

OMe
Ph
N
N
Ph
N
H
NTs
3ap
1H NMR (600 MHz, CDCl3)
5.00
4.00
3.01
3.00
2.99
2.01
1.99
1.99
1.02
1.00
1.00
0.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.945
7.549
7.535
7.468
7.454
7.123
7.105
7.059
7.045
6.940
6.926
6.914
6.799
6.784
6.754
6.743
6.722
6.708
6.657
6.644
6.631
6.465
6.452
5.221
3.775
2.353
X : parts per Million : Proton

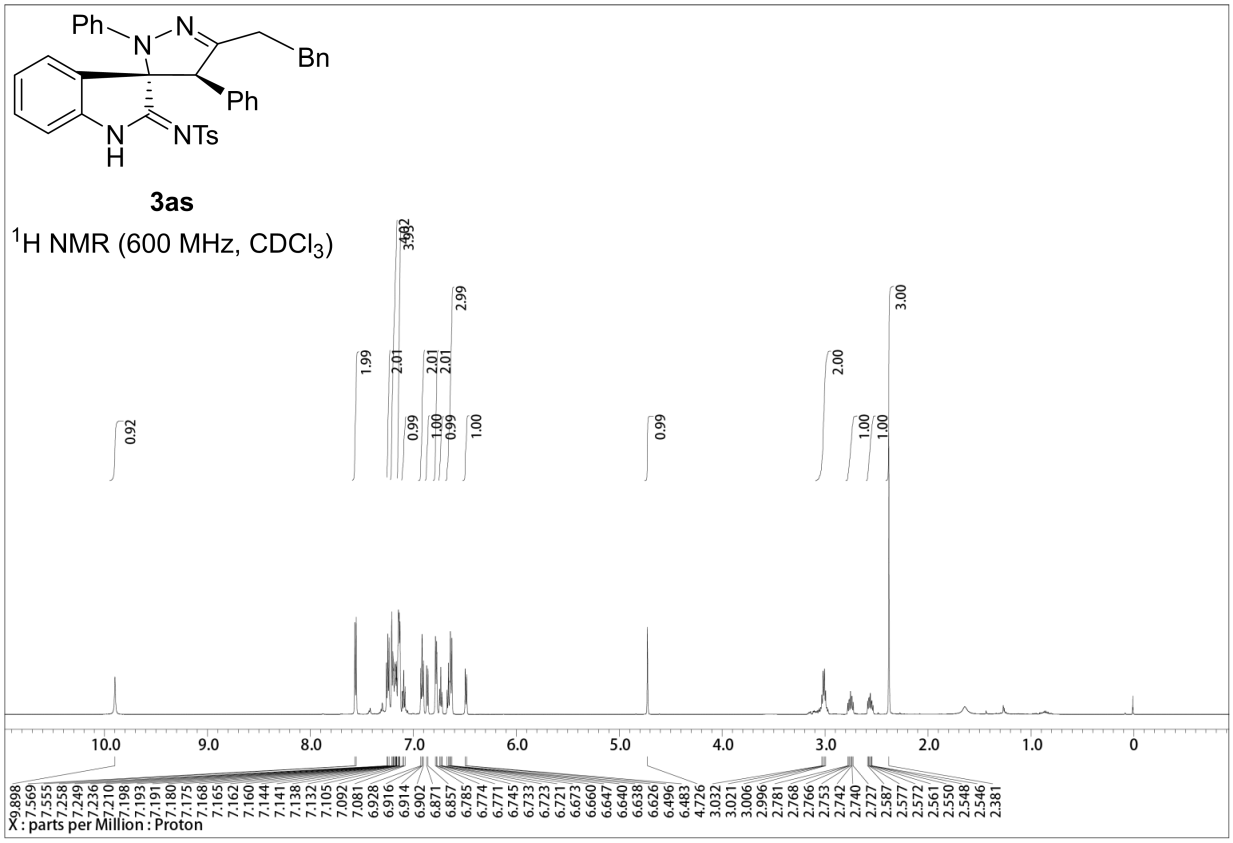

OMe
Ph
N
N
Ph
N
H
NTs
3ap
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.699
160.119
149.098
144.435
142.894
139.983
138.154
134.372
129.757
129.278
129.192
128.761
128.551
128.426
127.986
126.358
126.214
126.128
124.232
123.447
120.852
115.529
113.805
111.124
80.792
77.211
77.000
76.789
64.869
55.237
21.476
X : parts per Million : Carbon13

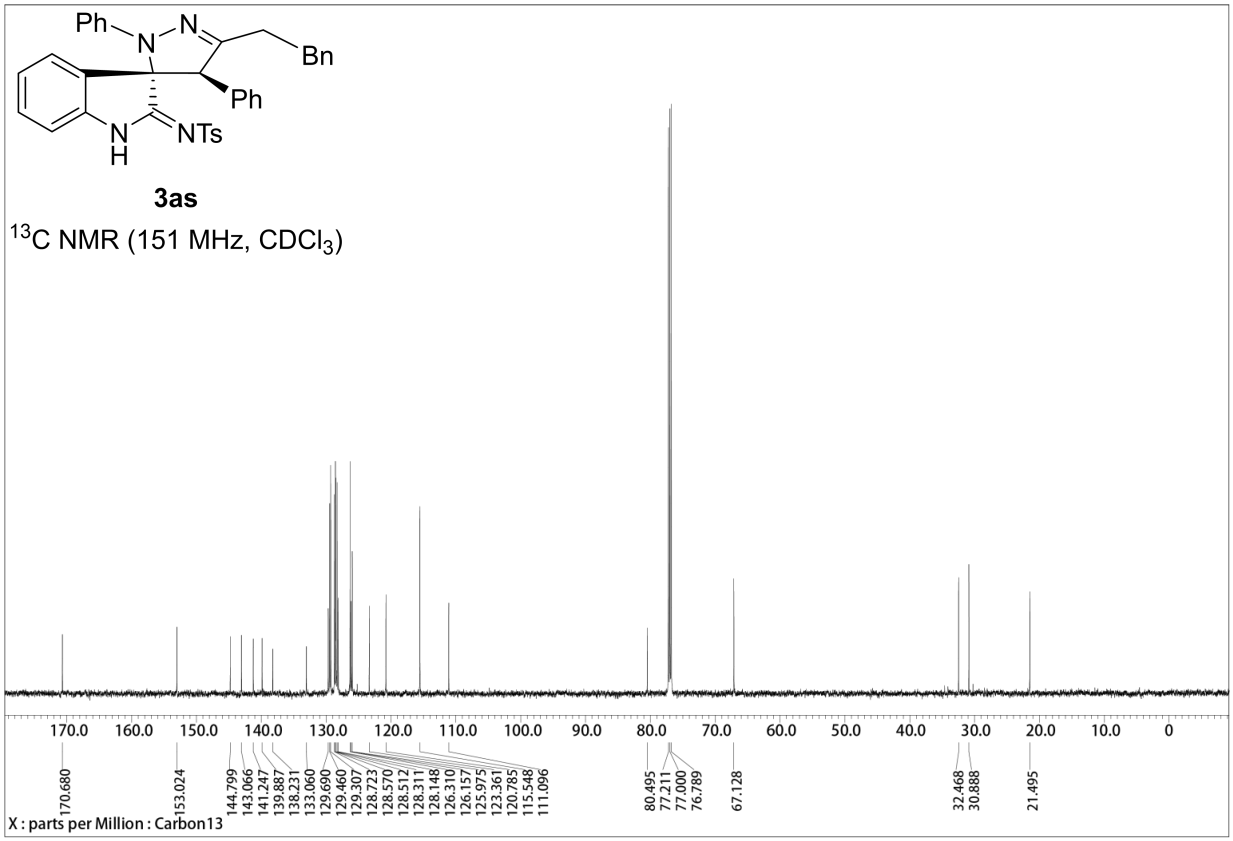

Ph
N
N
Ph
N
H
NTs
3aq
1H NMR (600 MHz, CDCl3)
4.98
3.96
2.94
3.00
2.00
1.99
2.00
0.99
0.94
1.00
0.97
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.019
2.319
X : parts per Million : Proton

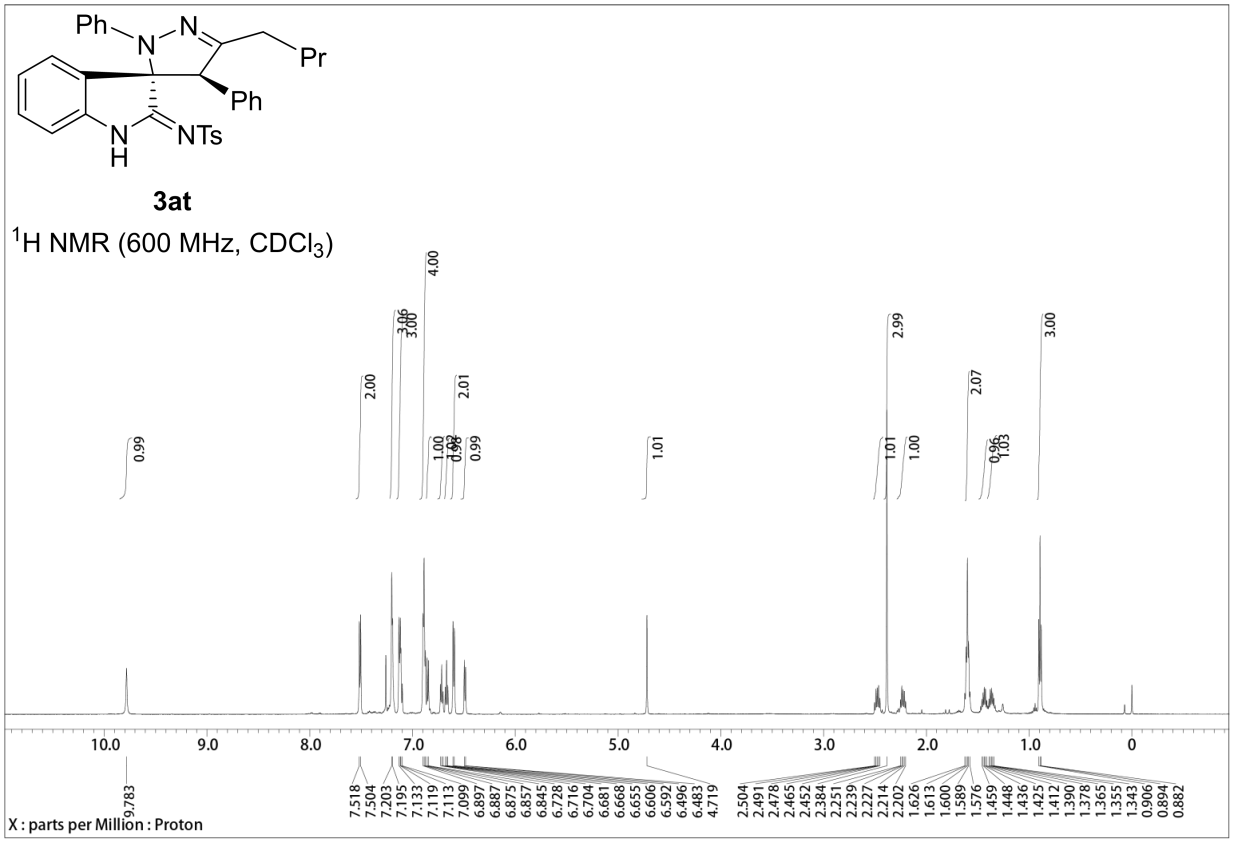

Ph
N
N
Ph
N
H
NTs
3aq
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.411
149.309
64.582
21.428
X : parts per Million : Carbon13

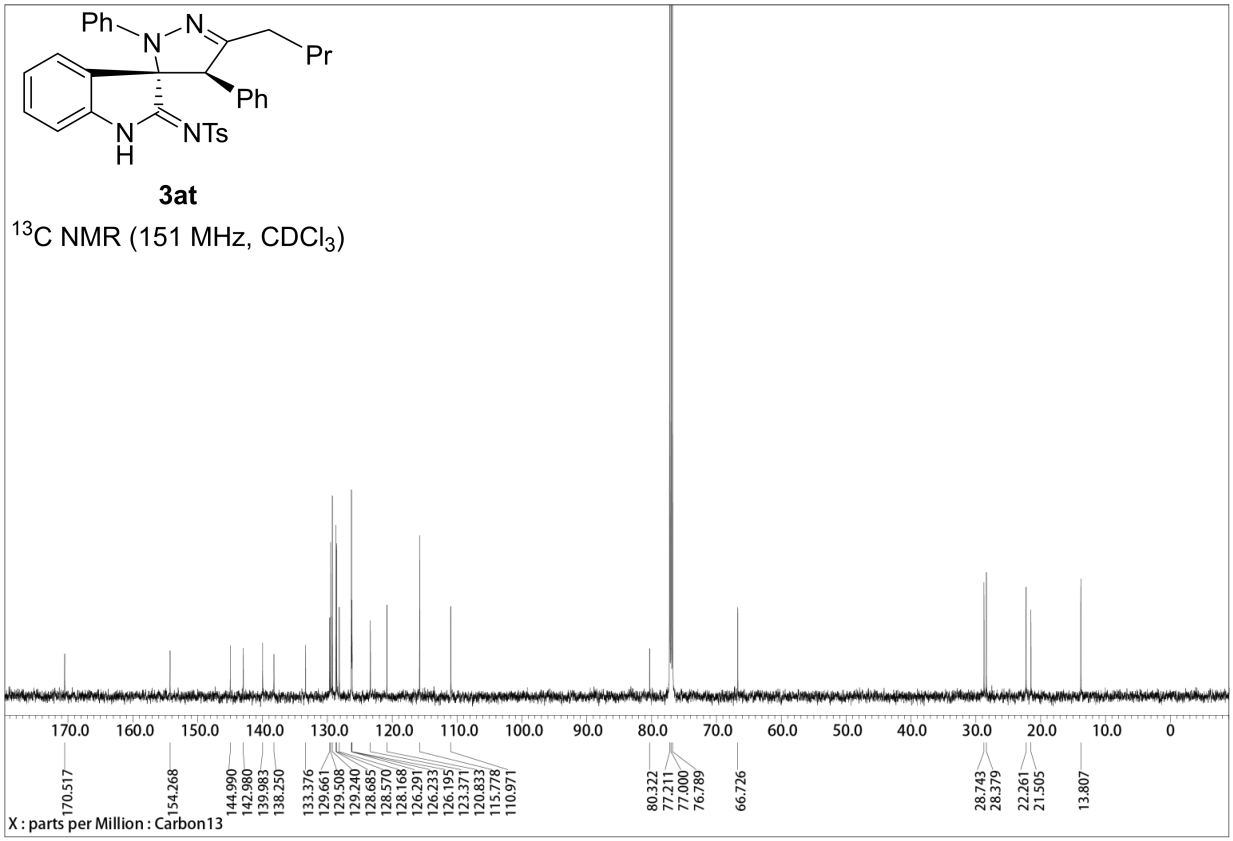

Ph
N
N
S
Ph
N
H
NTs
3ar
1H NMR (600 MHz, CDCl3)
4.94
3.99
3.00
1.98
1.16
1.00
0.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.955
7.530
7.517
7.260
7.253
7.152
7.140
7.121
7.106
7.095
7.082
6.933
6.920
6.905
6.891
6.850
6.844
6.836
6.757
6.746
6.733
6.696
6.682
6.667
6.654
6.562
6.550
5.241
2.367
X : parts per Million : Proton

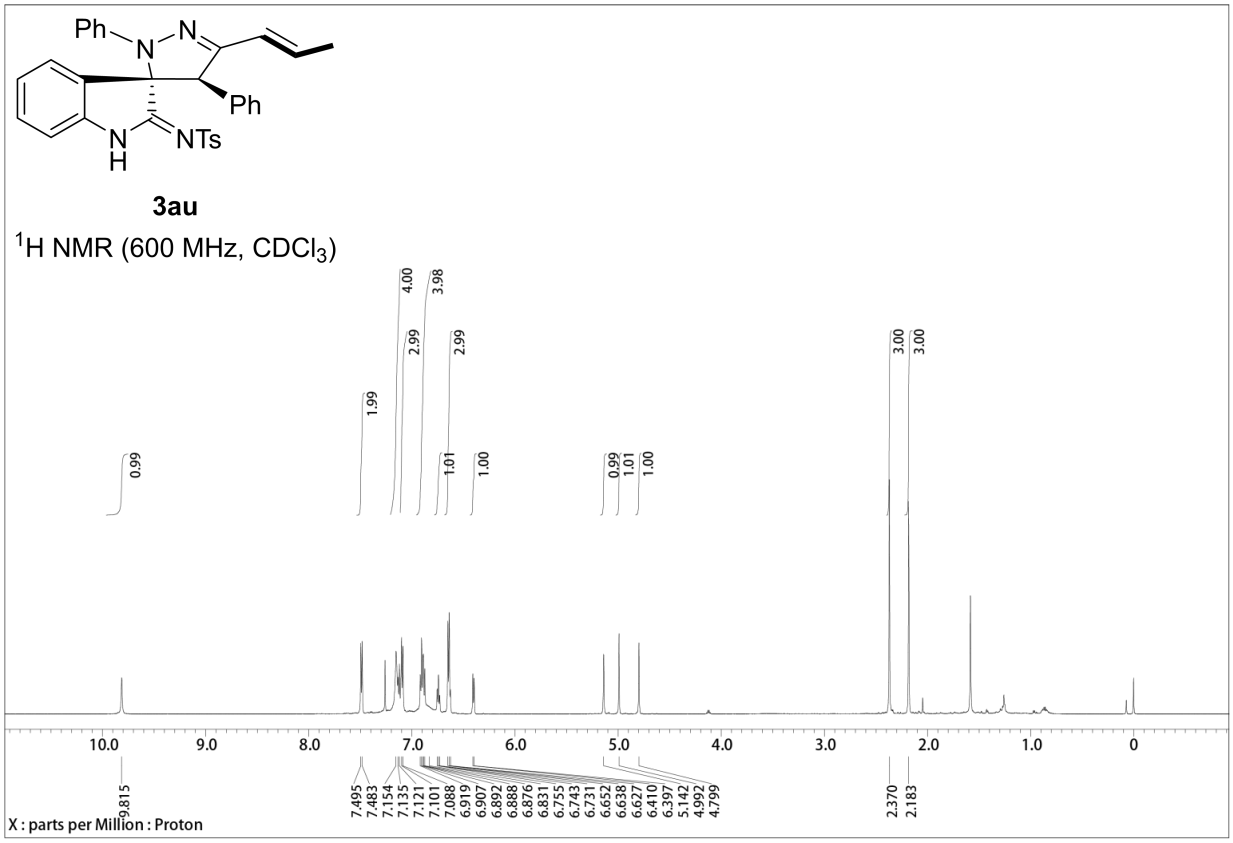

Ph
N
N
S
Ph
N
H
NTs
3ar
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.335
145.220
143.822
143.047
139.973
138.049
135.215
133.778
129.920
129.393
129.249
128.761
128.474
128.168
127.583
127.248
126.760
126.377
126.281
125.688
123.476
121.149
115.644
111.201
81.098
77.211
77.000
76.789
65.702
21.495
X : parts per Million : Carbon13

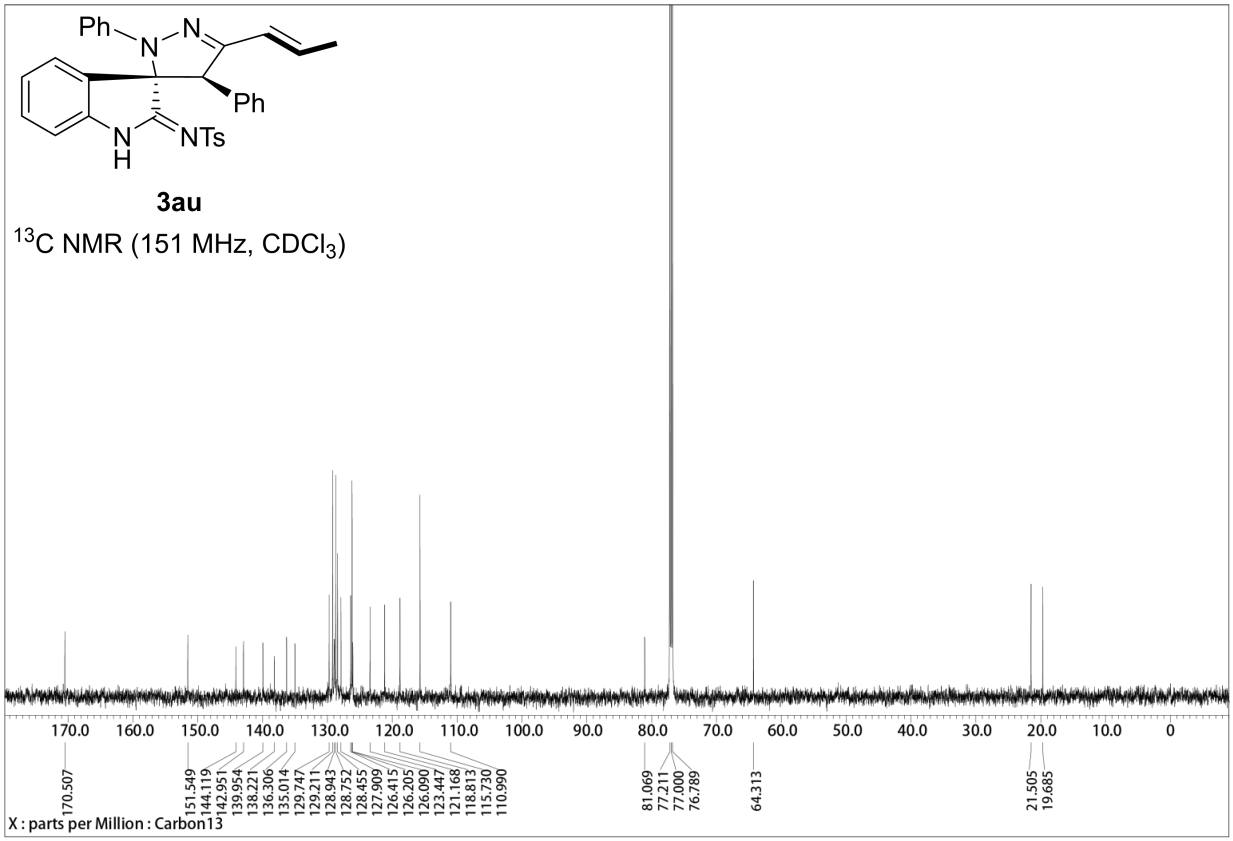

Ph
N
N
Bn
Ph
N
H
NTs
3as
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton

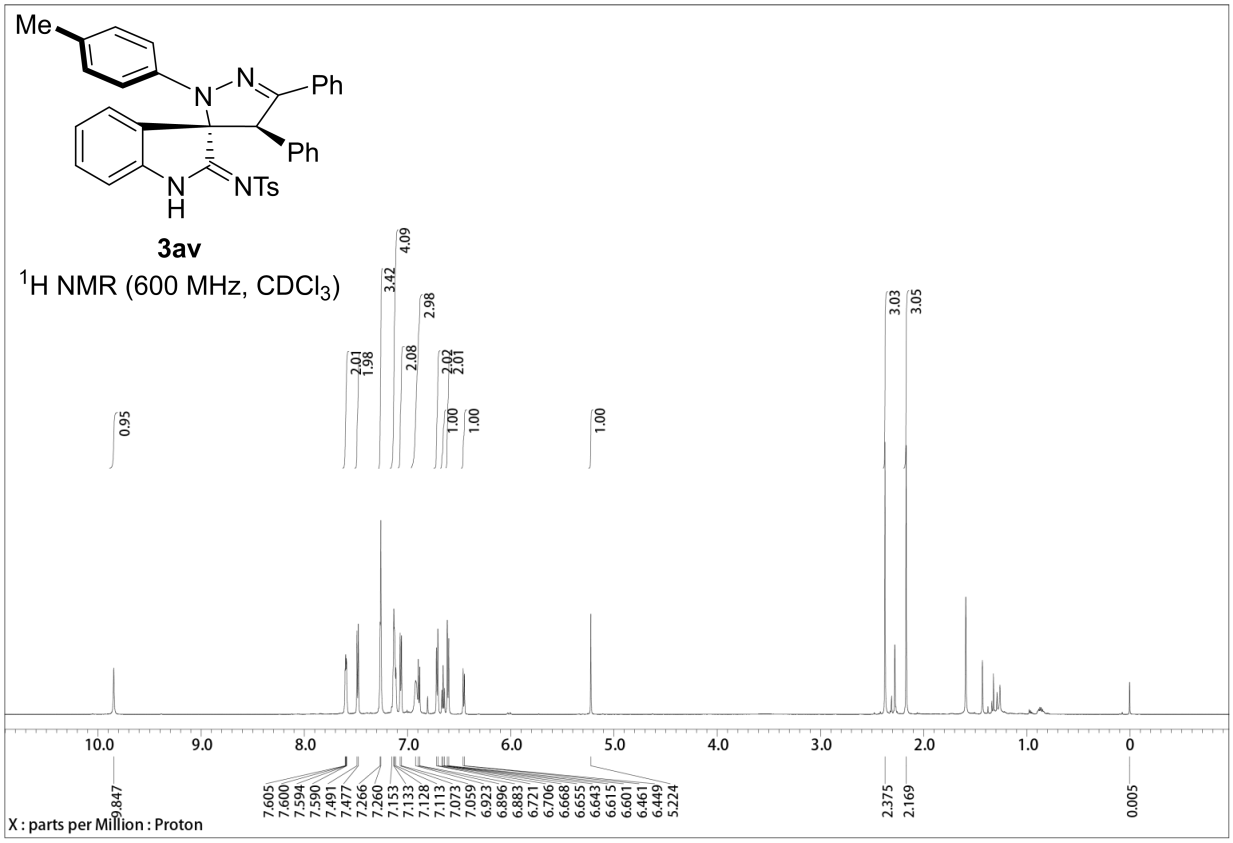

Ph
N
N
Bn
Ph
N
H
NTs
3as
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

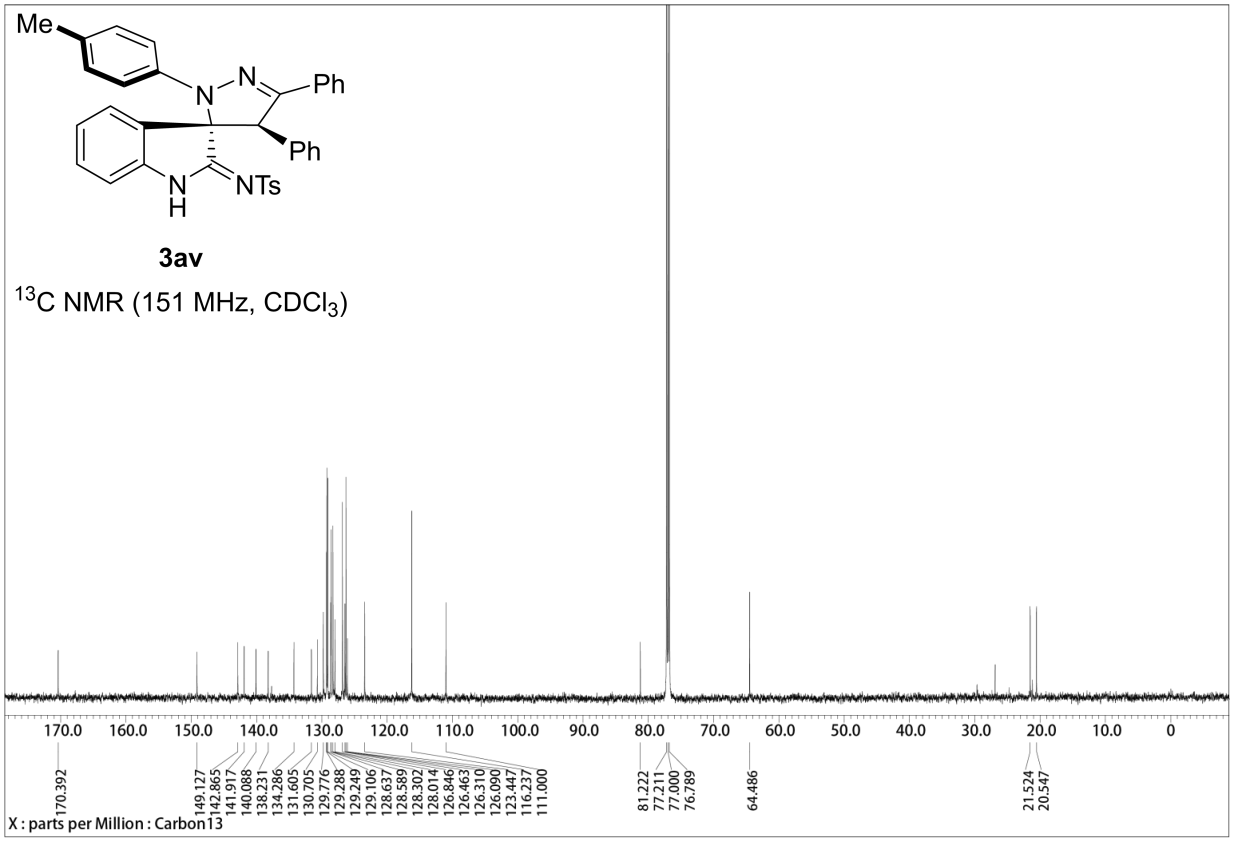

Ph
N
N
Pr
Ph
N
H
NTs
3at
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton

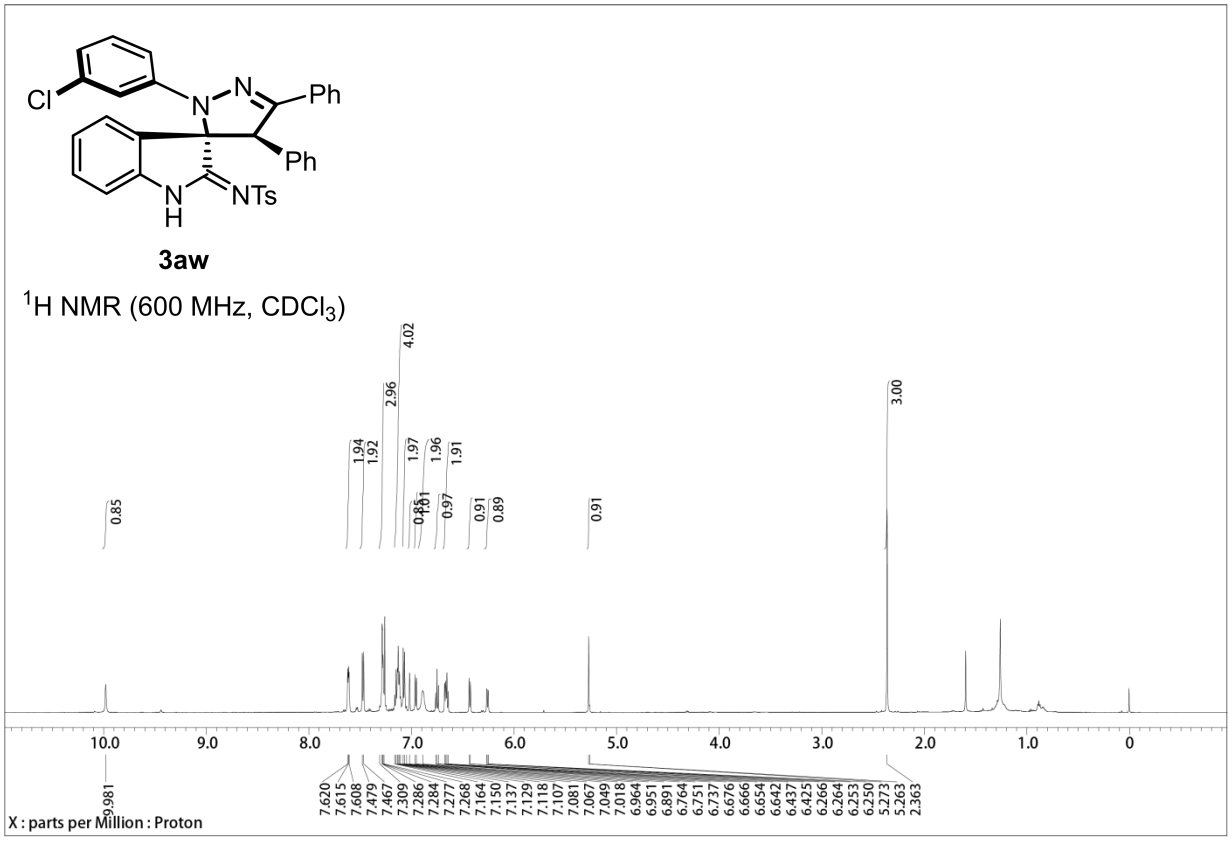

Ph
N
N
Pr
Ph
N
H
NTs
3at
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

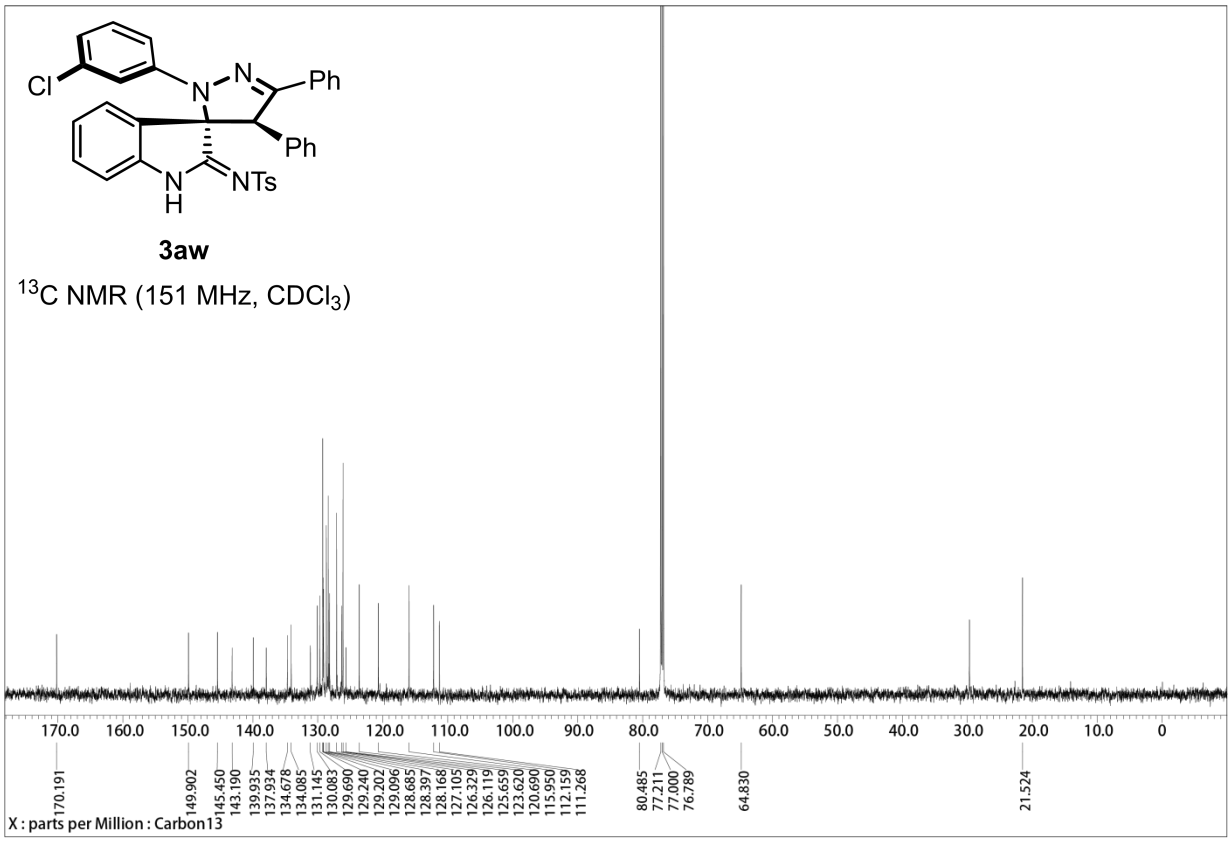

Ph
N
N
Ph
N
H
NTs
3au
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton

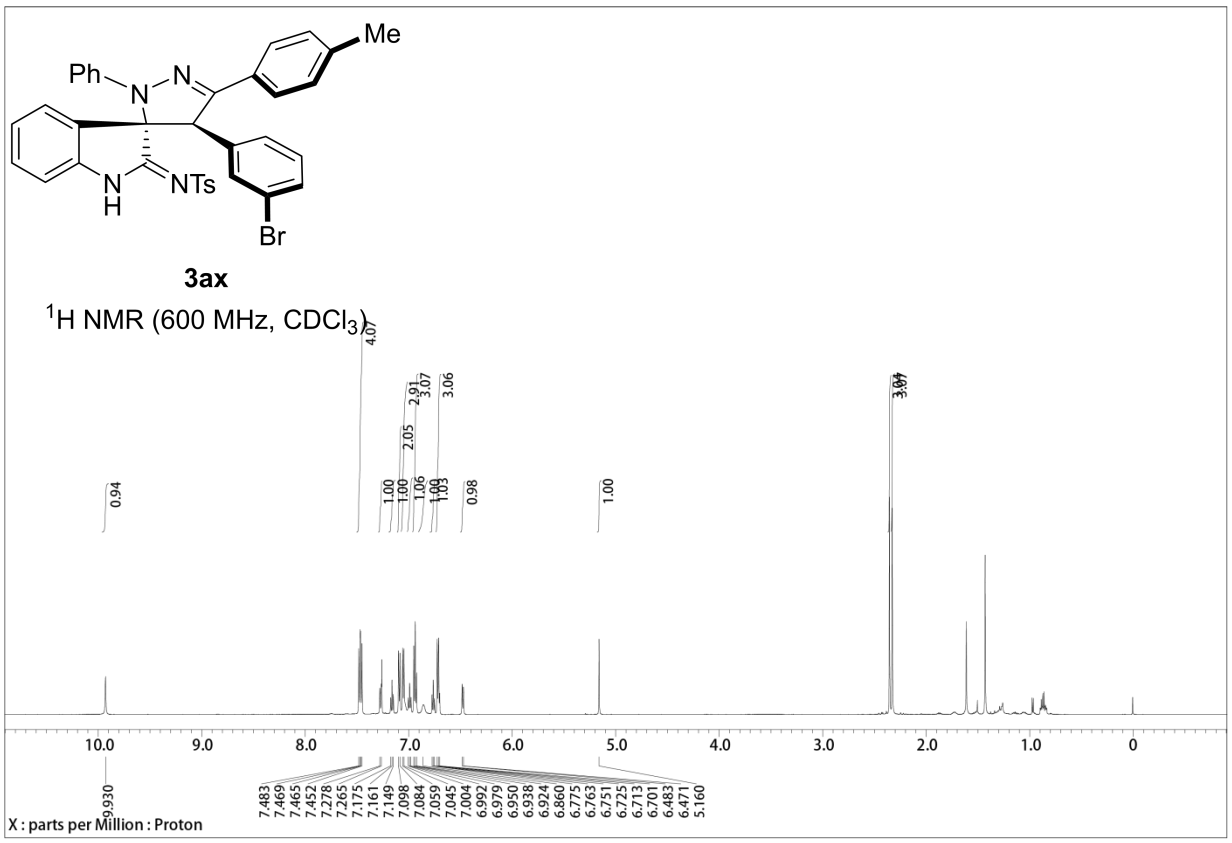

Ph
N
N
Ph
N
H
NTs
3au
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

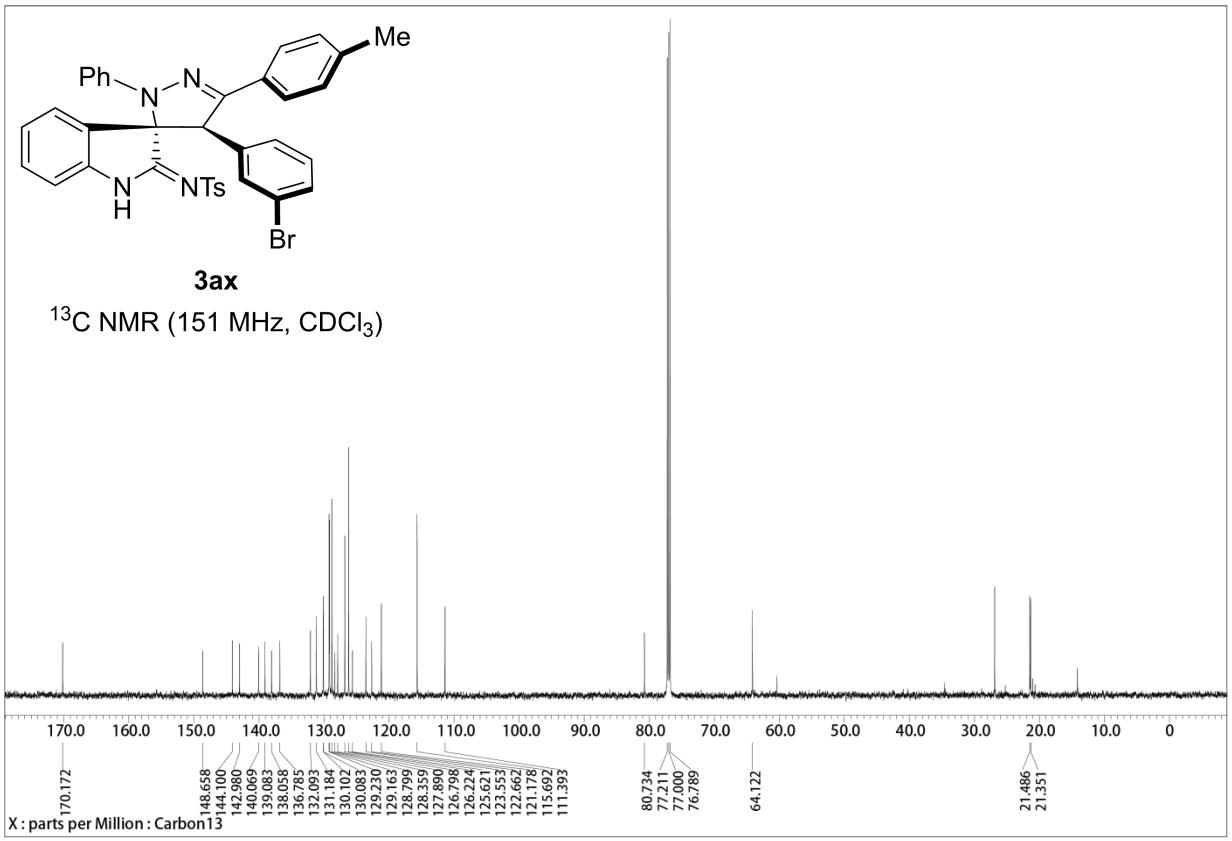

Me
N
N
Ph
Ph
N
H
NTs
3av
1H NMR (600 MHz, CDCl3)
4.09
3.42
2.98
3.03
3.05
2.01
1.98
2.08
2.02
2.01
0.95
1.00
1.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.847
7.605
7.600
7.594
7.590
7.491
7.477
7.266
7.260
7.153
7.133
7.128
7.113
7.073
7.059
6.923
6.896
6.883
6.721
6.706
6.668
6.655
6.643
6.615
6.601
6.461
6.449
5.224
2.375
2.169
0.005
X : parts per Million : Proton

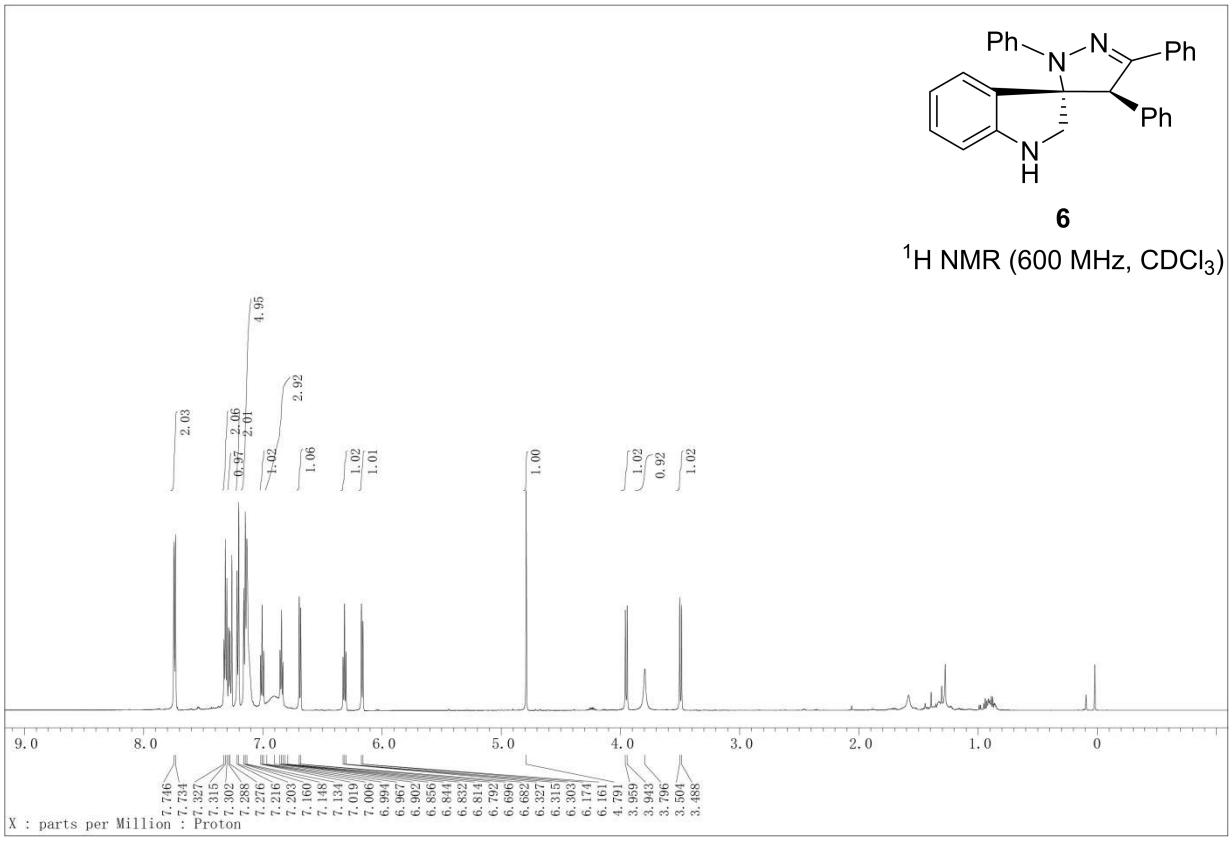

Me
N
N
Ph
Ph
N
H
NTs
3av
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.392
149.127
142.865
141.917
140.088
138.231
134.286
131.605
130.705
129.776
129.288
129.249
129.106
128.637
128.589
128.302
128.014
126.846
126.463
126.310
126.090
123.447
116.237
111.000
81.222
77.211
77.000
76.789
64.486
21.524
20.547
X : parts per Million : Carbon13

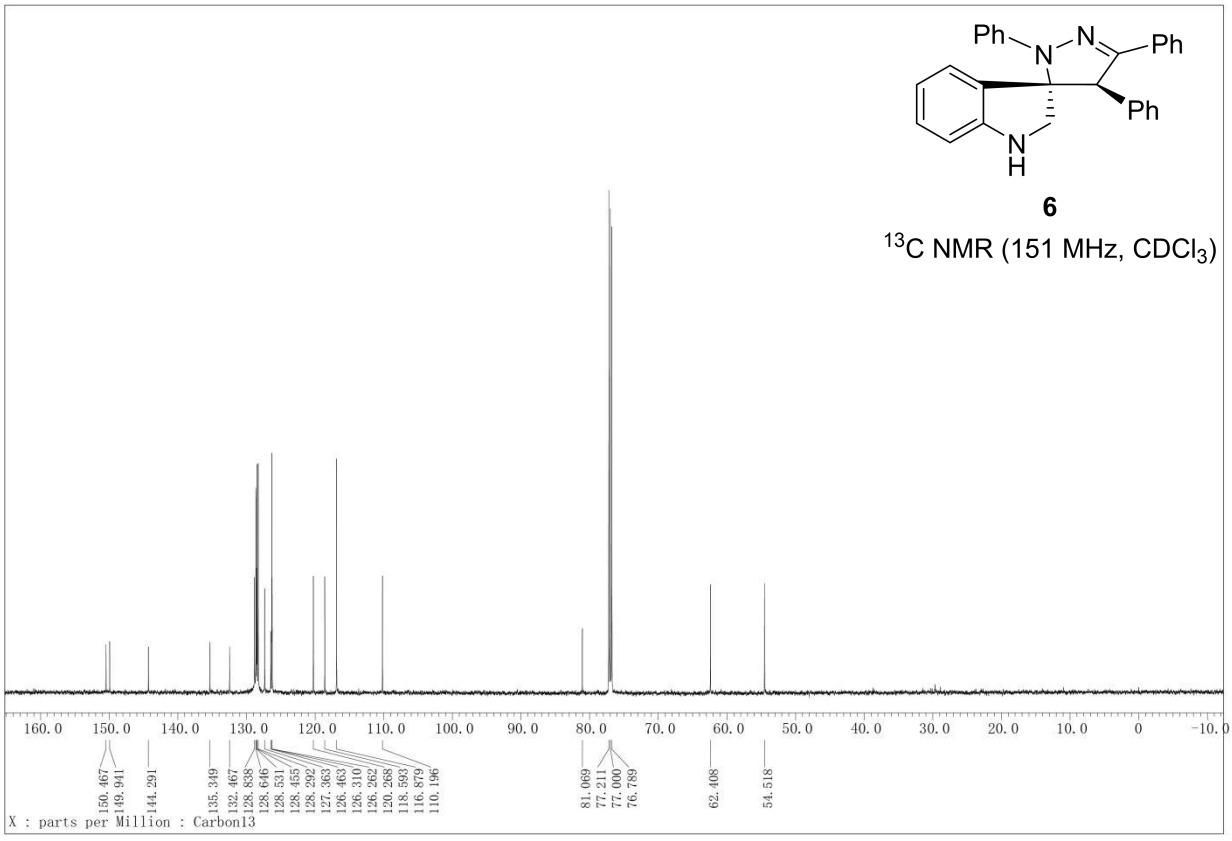

Cl
N
N
Ph
Ph
N
H
NTs
3aw
1H NMR (600 MHz, CDCl3)
4.02
2.96
3.00
1.94
1.92
1.97
1.96
1.91
0.85
0.91
0.97
0.91
0.89
0.91
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.981
7.620
7.615
7.608
7.479
7.467
7.309
7.286
7.284
7.277
7.268
7.164
7.150
7.137
7.129
7.118
7.107
7.081
7.067
7.049
7.018
6.964
6.951
6.891
6.764
6.751
6.737
6.676
6.666
6.654
6.642
6.437
6.425
6.266
6.264
6.253
6.250
5.273
5.263
2.363
X : parts per Million : Proton

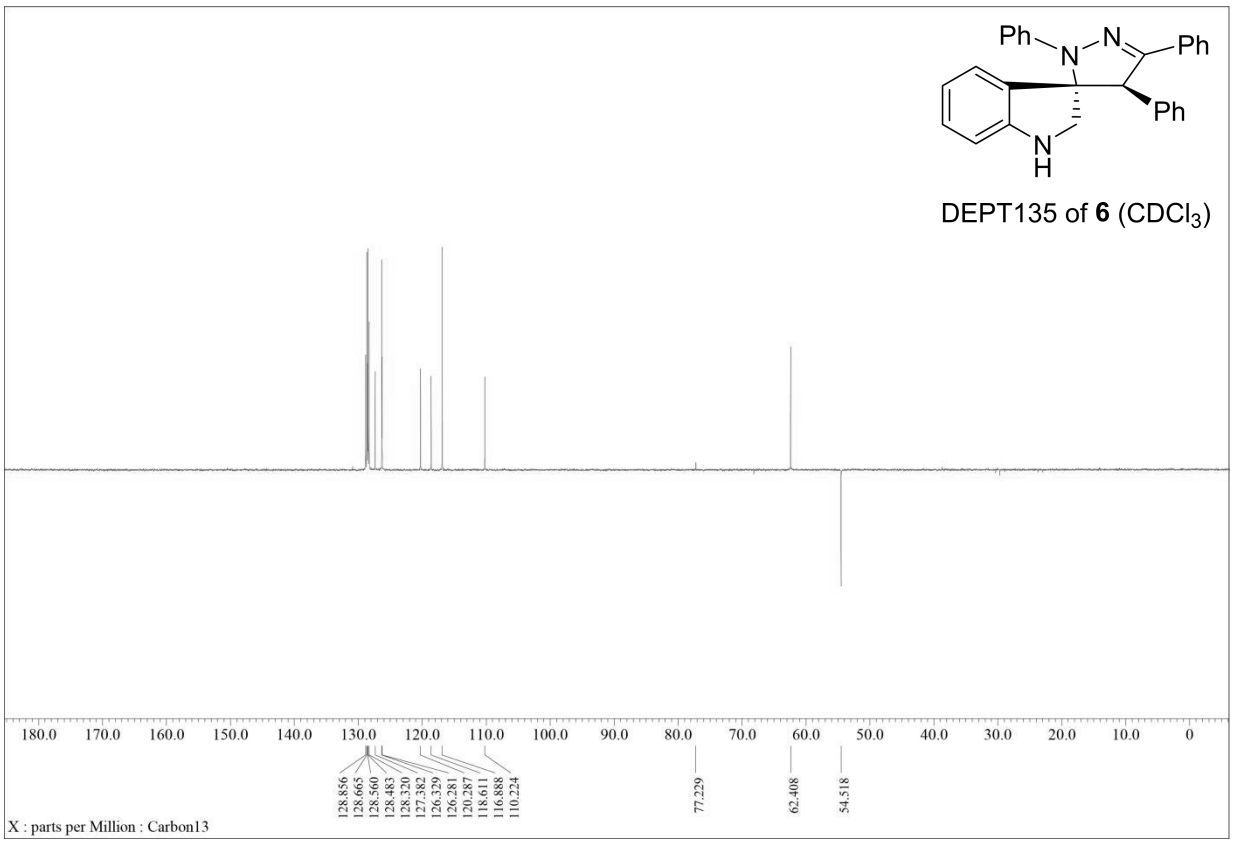

Cl
N
N
Ph
Ph
N
H
NTs
3aw
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.191
149.902
145.450
143.190
139.935
137.934
134.678
134.085
131.145
130.083
129.690
129.240
129.202
129.096
128.685
128.397
128.168
127.105
126.329
126.119
125.659
123.620
120.690
115.950
112.159
111.268
80.485
77.211
77.000
76.789
64.830
21.524
X : parts per Million : Carbon13

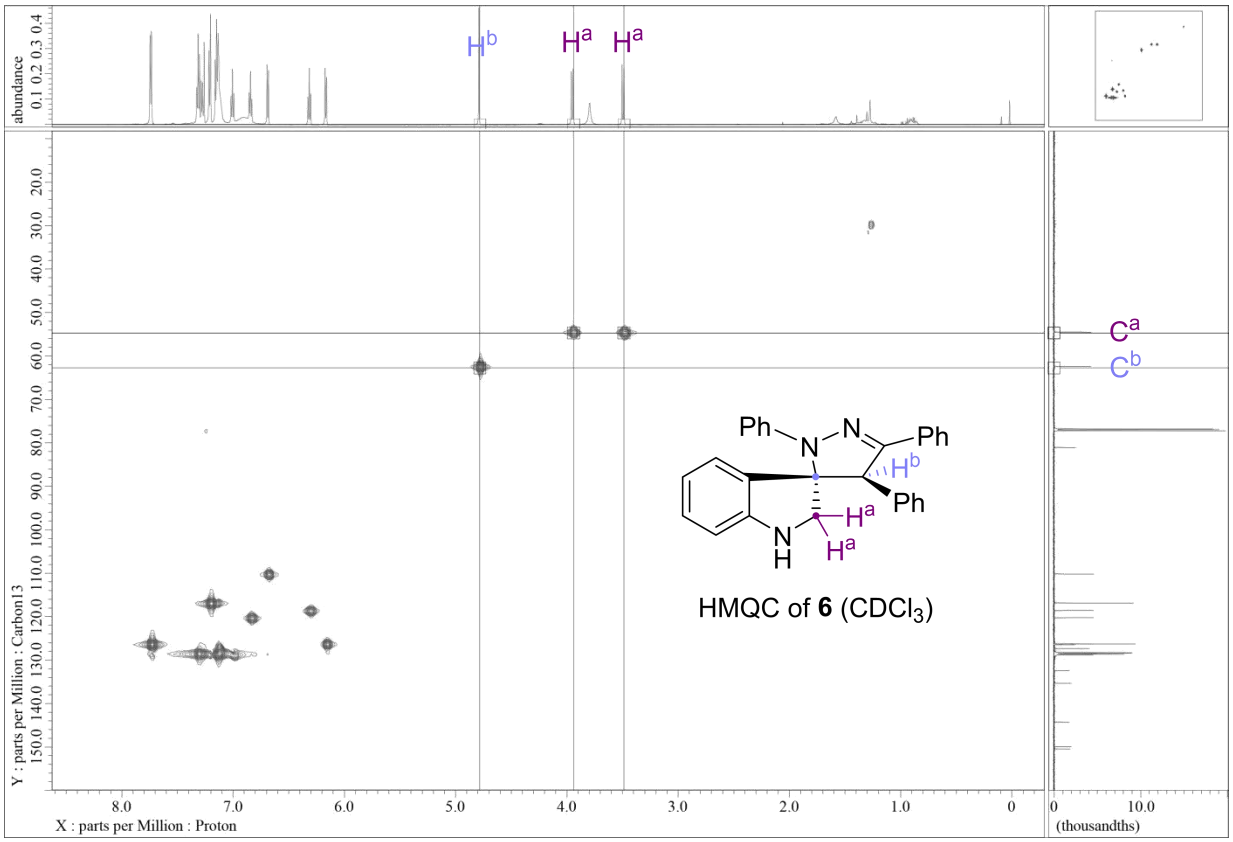

Me
Ph
N
N
N
H
NTs
Br
3ax
1H NMR (600 MHz, CDCl3)
4.07
2.91
3.07
3.06
2.05
0.94
1.00
1.00
1.06
1.00
1.03
0.98
1.00
3.07
3.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.930
7.483
7.469
7.465
7.452
7.278
7.265
7.175
7.161
7.149
7.098
7.084
7.059
7.045
7.004
6.992
6.979
6.950
6.938
6.924
6.860
6.775
6.763
6.751
6.725
6.713
6.701
6.483
6.471
5.160
X : parts per Million : Proton

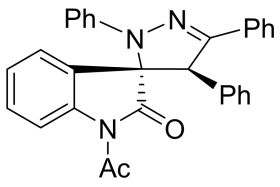

Me
Ph
N
N
N
H
NTs
Br
3ax
13C NMR (151 MHz, CDCl3)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.172
148.658
144.100
142.980
140.069
139.083
138.058
136.785
132.093
131.184
130.102
130.083
129.230
129.163
128.799
128.359
127.890
126.798
126.224
125.621
123.553
122.662
121.178
115.692
111.393
80.734
77.211
77.000
76.789
64.122
21.486
21.351
X : parts per Million : Carbon13


Ph
N
N
Ph
Ph
N
H
6
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


Ph
N
N
Ph
Ph
N
H
6
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

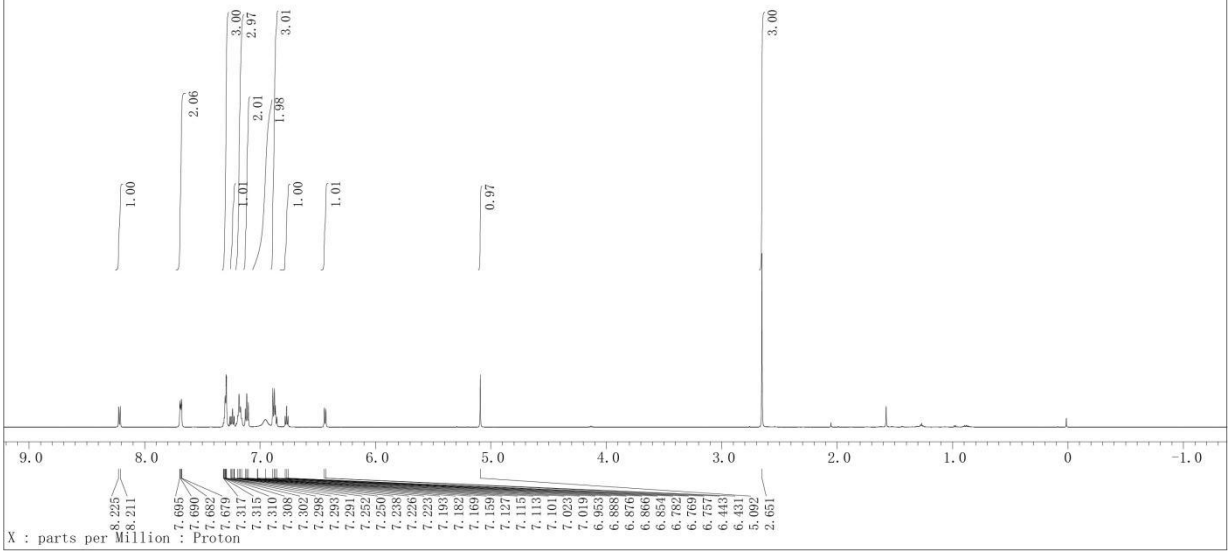

Ph
N
N
Ph
Ph
N
H
DEPT135 of 6 (CDCl3)
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
128.856
128.665
128.560
128.483
128.320
127.382
126.329
126.281
120.287
118.611
116.888
110.224
77.229
62.408
54.518
X : parts per Million : Carbon13

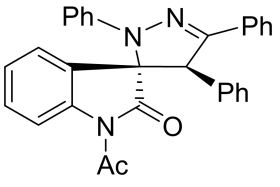

abundance
0.1 0.2 0.3 0.4
Hb
Ha
Ha
Ca
Cb
Ph
N
N
Ph
Hb
Ph
Ha
N
H
Ha
HMQC of 6 (CDCl3)
Y : parts per Million : Carbon13
20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0 120.0 130.0 140.0 150.0
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton
0 10.0
(thousandths)



7

^{1}H NMR (600 MHz, $CDCl_3$)





7

^{13}C NMR (151 MHz, $CDCl_3$)