

## Supplementary Information

# Diastereoselectivity construction of spiro-cyclopropyl-pyrazoles via a [2+1] annulation reaction of iminoindoline-derived alkenes and 4-bromo-pyrazolons

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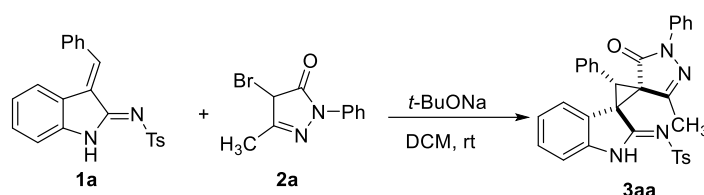
## 1. General Information

Commercial grade solvent was dried and purified by standard procedures as specified in Purification of Laboratory Chemicals.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance (400, 600 for  $^1\text{H}$  NMR, 100, 150 for  $^{13}\text{C}$  NMR) instrument. Data for  $^1\text{H}$  NMR are reported as chemical shift (ppm, tetramethylsilane as the internal standard), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz). Data for  $^{13}\text{C}$  NMR are reported as chemical shift. High resolution mass spectra were obtained with Thermo Scientific LTQ Orbitrap XL mass spectrometer. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. Reactions were monitored by TLC and visualized with ultraviolet light. Melting points were recorded on a Buchi Melting Point B-545. X-ray crystallographic analyses were obtained on Bruker D8 Venture.

## 2. General Procedure for the Syntheses of Reactants 1 and 2.

iminoindoline-derived alkenes <sup>1,2</sup> and 4-bromo pyrazolones <sup>3</sup> were prepared as reported procedures. Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification.

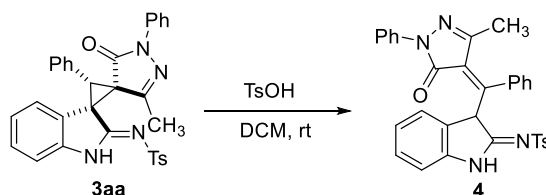
## 3. General procedure for the synthesis of 3aa



**Scheme S1** General procedure for the synthesis of **3aa**

A mixture of 0.1 mmol **1a** (37.4 mg), 0.12 mmol **2a** (30.2 mg) and 0.15 mmol *t*-BuONa (14.6 mg) in 1 ml DCM was stirred at room temperature. After the reaction was completed by TLC, the crude product was directly purified by silica gel chromatography with petroleum ether/ethyl acetate 10/1 to give the desired product **3aa** (48.3 mg,  $R_f$  = 0.2). Other reactants were operated by the same procedures.

## 4. transformation of product 3aa



**Scheme S2** Transformation of product **3aa**

A mixture of 0.1 mmol **3aa** (54.6 mg), 0.2 mmol TsOH (34.0 mg) in 1 ml DCM was stirred at room temperature. After the reaction was completed by TLC, the crude product was directly purified by silica gel chromatography with petroleum ether/ethyl acetate 8/1 to give the desired product **4** (38.2 mg,  $R_f$  = 0.2).

1 R. E. Harmon, G. Wellman, S. K. Gupta, *J. Org. Chem.* 1973, **38**, 11-16.

2 K. Moriyama, K. Ishida, H. Togo, *Chem. Commun.* 2015, **51**, 2273-2276.

3 Y. Zhang, D. Stephens, G. Hernandez, R. Mendoza, O. V. Larionov, *Chem.- Eur. J.*, 2012, **18**, 16612.

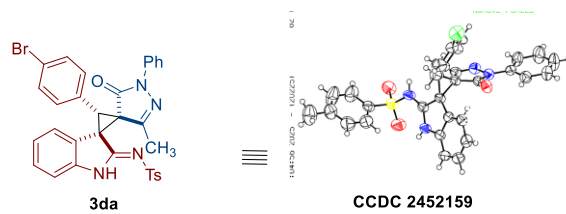
## 5. X-ray crystallographic data of compound **3da**

### 5.1 Sample preparation and crystal growth

Approximately 30 mg sample **3da** was dissolved in 1 mL of dichloromethane in a 5 mL transparent glass vial. Next, 3 mL n-hexane was slowly added to each solution. The vials were then loosely covered and placed in an undisturbed cabinet to allow for slow solvent evaporation. This process yielded a single crystal of sample, suitable for X-ray crystallographic analysis.

**Table 1 Crystal data and structure refinement for mo\_250226LCY\_0m.**

|                                                |                                          |
|------------------------------------------------|------------------------------------------|
| Identification code                            | mo_250226LCY_0m                          |
| Empirical formula                              | C32H26BrN4O3S                            |
| Formula weight                                 | 626.54                                   |
| Temperature/K                                  | 297.00                                   |
| Crystal system                                 | triclinic                                |
| Space group                                    | P-1                                      |
| a/Å                                            | 11.1261(4)                               |
| b/Å                                            | 12.1877(4)                               |
| c/Å                                            | 24.0151(8)                               |
| $\alpha/^\circ$                                | 84.6530(10)                              |
| $\beta/^\circ$                                 | 78.8130(10)                              |
| $\gamma/^\circ$                                | 78.2160(10)                              |
| Volume/Å <sup>3</sup>                          | 3122.41(18)                              |
| Z                                              | 4                                        |
| $\rho_{\text{calc}}/\text{cm}^3$               | 1.333                                    |
| $\mu/\text{mm}^{-1}$                           | 1.421                                    |
| F(000)                                         | 1284.0                                   |
| Crystal size/mm <sup>3</sup>                   | 0.2 × 0.15 × 0.1                         |
| Radiation                                      | MoK $\alpha$ ( $\lambda$ = 0.71073)      |
| 2 $\theta$ range for data collection/ $^\circ$ | 3.802 to 56.6                            |
| Index ranges                                   | -14 ≤ h ≤ 14, -13 ≤ k ≤ 16, -32 ≤ l ≤ 31 |
| Reflections collected                          | 79843                                    |
| Independent reflections                        | 15497 [Rint = 0.0806, Rsigma = 0.0657]   |
| Data/restraints/parameters                     | 15497/0/743                              |
| Goodness-of-fit on F <sup>2</sup>              | 1.054                                    |
| Final R indexes [ $I \geq 2\sigma(I)$ ]        | R1 = 0.0704, wR2 = 0.2164                |
| Final R indexes [all data]                     | R1 = 0.1189, wR2 = 0.2521                |
| Largest diff. peak/hole / e Å <sup>-3</sup>    | 1.06/-1.69                               |

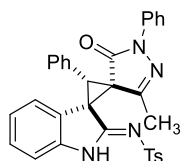


**Figure S1** XRD structure of **3da**: molecular structure shown as 50% probability ellipsoids

## 6. The data of the products

### (3aa)

**4-methyl-N-((2'S,3R,3'S,Z)-3''-methyl-5''-oxo-1'',3'-diphenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)benzenesulfonamide**



yellow solid, 86% yield, 45.3 mg; mp = 167.6-169.2 °C; dr 10:1;

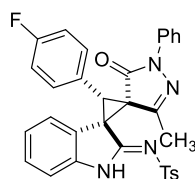
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 10.10 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.18 (m, 8H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.95 (dd, *J* = 7.6, 4.4 Hz, 3H), 6.82 (t, *J* = 7.8 Hz, 1H), 4.57 (s, 1H), 2.37 (s, 3H), 2.23 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 165.4, 164.6, 156.2, 144.1, 141.7, 138.3, 138.1, 130.6, 130.4, 129.9, 129.5, 128.9, 128.4, 127.9, 126.9, 125.2, 122.4, 120.0, 119.0, 110.6, 52.7, 51.0, 40.3, 21.8, 19.3.

**HRMS**(ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>26</sub>N<sub>4</sub>O<sub>3</sub>SNa<sup>+</sup> 569.1623, found 569.1622.

### (3ba)

**N-((2'S,3R,3'S,Z)-3''-(4-fluorophenyl)-3''-methyl-5''-oxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 92% yield, 51.9 mg; mp = 170.3-172.1 °C; dr 5:1

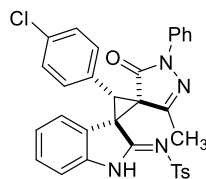
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.36 – 7.23 (m, 6H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 3H), 6.91 (t, *J* = 7.8 Hz, 1H), 4.58 (d, *J* = 1.8 Hz, 1H), 2.44 (s, 3H), 2.28 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 165.2, 164.6, 162.7 (d, *J* = 250 Hz), 156.1, 144.2, 141.8, 138.2, 138.0, 132.2 (d, *J* = 10 Hz), 130.4, 129.9, 129.6, 129.5, 129.0, 128.9, 126.9, 126.7, 125.3, 122.5, 119.8, 119.0, 115.5 (d, *J* = 20 Hz), 110.7, 52.6, 51.0, 39.4, 21.8, 19.3.

**HRMS**(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>FN<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 565.1710, found 565.1711.

### (3ca)

**N-((2'S,3R,3'S,Z)-3''-(4-chlorophenyl)-3''-methyl-5''-oxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 80% yield, 46.4 mg; mp = 173.9-175.7 °C; dr 5:1

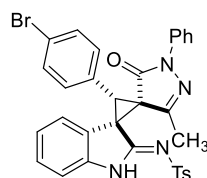
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 10.12 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.62 (m, 2H), 7.27 – 7.18 (m, 7H), 7.07 – 7.03 (m, 2H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.91 – 6.83 (m, 3H), 4.50 (s, 1H), 2.37 (s, 3H), 2.20 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*)  $\delta$  165.1, 164.5, 156.1, 144.2, 141.8, 138.1, 138.0, 134.4, 131.7, 131.1, 130.3, 129.9, 129.7, 129.6, 129.0, 128.9, 128.6, 128.1, 126.9, 126.6, 126.4, 125.3, 122.5, 119.7, 119.0, 110.8, 52.5, 50.9, 39.4, 21.8, 19.3.

**HRMS**(ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>ClN<sub>4</sub>O<sub>3</sub>SN<sup>+</sup> 603.1234, found 603.1235.

**(3da)**

**N-((2'S,3R,3'S,Z)-3'-(4-bromophenyl)-3''-methyl-5''-oxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 73% yield, 45.6 mg; mp = 160.1-161.6 °C; dr 5:1

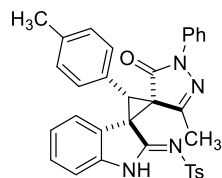
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*)  $\delta$  10.12 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.36 (dd, *J* = 19.4, 8.2 Hz, 2H), 7.27 – 7.19 (m, 5H), 7.06 (t, *J* = 7.7 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.84 (dd, *J* = 18.8, 8.0 Hz, 3H), 4.48 (s, 1H), 2.37 (s, 3H), 2.19 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*)  $\delta$  165.09, 164.49, 156.04, 144.22, 141.77, 138.12, 137.96, 132.06, 131.58, 131.45, 131.08, 130.31, 129.87, 129.70, 129.63, 129.00, 128.88, 126.97, 126.94, 126.60, 125.28, 122.57, 119.72, 119.10, 118.97, 110.73, 52.39, 50.85, 39.42, 21.77, 19.32.

**HRMS**(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>BrN<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 625.0909, found 625.0912.

**(3ea)**

**4-methyl-N-((2'S,3R,3'S,Z)-3''-methyl-5''-oxo-1''-phenyl-3'-(p-tolyl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)benzenesulfonamide**



yellow solid, 91% yield, 51.0 mg; mp = 170.4-172.1 °C; dr 10:1

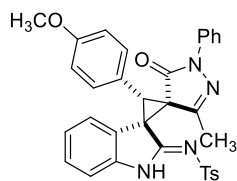
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*)  $\delta$  10.21 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.29 (m, 4H), 7.26 – 7.18 (m, 1H), 7.16 – 7.09 (m, 4H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.93 – 6.88 (m, 3H), 4.62 (s, 1H), 2.44 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*)  $\delta$  165.4, 164.6, 156.3, 144.1, 141.7, 138.3, 138.2, 138.1, 130.6, 130.2, 129.8, 129.4, 129.3, 129.1, 128.8, 126.9, 125.1, 124.7, 122.3, 120.1, 119.0, 110.6, 52.8, 51.1, 40.2, 21.7, 21.4, 19.3.

**HRMS**(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>33</sub>H<sub>28</sub>N<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 561.1960, found 561.1958.

**(3fa)**

**N-((2'S,3R,3'S,Z)-3'-(4-methoxyphenyl)-3''-methyl-5''-oxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 82% yield, 47.2 mg; mp = 171.6-173.1 °C; dr 10:1

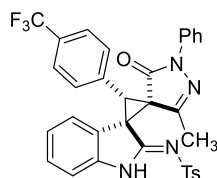
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 10.23 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.29 (m, 4H), 7.26 – 7.18 (m, 1H), 7.13 (dd, *J* = 25.2, 8.3 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.95 – 6.89 (m, 3H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.60 (s, 1H), 3.79 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 165.4, 164.7, 159.5, 156.3, 144.1, 141.7, 138.3, 138.1, 131.5, 131.0, 130.6, 129.8, 129.4, 129.3, 128.9, 128.8, 126.9, 126.7, 125.1, 122.4, 120.1, 119.7, 119.0, 113.8, 110.6, 55.3, 52.9, 51.1, 39.9, 21.7, 19.3.

**HRMS**(ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>33</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>SN<sup>+</sup> 599.1729, found 599.1727.

### (3ga)

**4-methyl-N-((2'S,3R,3'S,Z)-3''-methyl-5''-oxo-1''-phenyl-3'-(4-(trifluoromethyl)phenyl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)benzenesulfonamide**



yellow solid, 85% yield, 52.2 mg; mp = 168.6-169.2 °C; dr 5:1

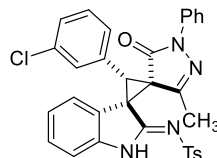
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 10.19 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.22 (ddd, *J* = 28.9, 14.7, 8.0 Hz, 5H), 7.02 (ddd, *J* = 29.8, 16.6, 7.9 Hz, 5H), 6.83 (t, *J* = 7.8 Hz, 1H), 4.56 (s, 1H), 2.36 (s, 3H), 2.21 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 164.9, 164.5, 156.0, 144.3, 141.9, 138.1, 137.9, 132.1, 130.8, 130.6 (d, *J* = 32.6 Hz), 130.3, 130.1, 129.9, 129.8, 129.6, 129.0, 128.9, 127.0, 126.6, 125.3 (dd, *J* = 7.0, 3.2 Hz), 124.0 (d, *J* = 275.3 Hz), 122.7, 119.6, 119.1, 119.0, 110.9, 52.3, 50.8, 39.4, 21.8, 19.3.

**HRMS**(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>33</sub>H<sub>25</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 615.1678, found 615.1679.

### (3ha)

**N-((2'S,3R,3'S,Z)-3'-(3-chlorophenyl)-3''-methyl-5''-oxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 83% yield, 48.1 mg; mp = 165.8-167.2 °C; dr 10:1

**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 10.14 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.64 (dd, *J* = 9.0, 4.8 Hz, 2H), 7.27 – 7.17 (m, 6H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.93 (td, *J* = 17.9, 8.3 Hz, 5H), 6.81 (t, *J* = 7.8 Hz, 1H), 4.57 (s, 1H), 2.36 (s, 3H), 2.23 (s, 3H).

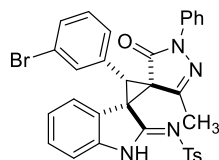
**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 165.0, 164.4, 156.0, 144.2, 141.8, 138.1, 138.0, 134.1, 130.3, 130.2, 130.0, 129.9, 129.7, 129.6, 129.53, 129.0, 128.9, 128.6, 126.9, 126.5, 125.3, 122.6, 119.6, 119.1, 119.0, 110.8, 52.3, 50.9,

39.2, 21.7, 19.3.

HRMS(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>ClN<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 581.1414, found 581.1415.

**(3ia)**

**N-((2'S,3R,3'S,Z)-3'-(3-bromophenyl)-3''-methyl-5''-oxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 65% yield, 40.6 mg; mp = 135.2-136.8 °C; dr 10:1

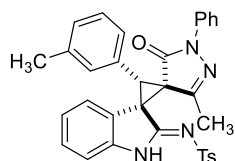
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 10.18 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.36 – 7.27 (m, 5H), 7.20 – 7.16 (m, 3H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.99 – 6.93 (m, 2H), 4.59 (d, *J* = 1.5 Hz, 1H), 2.45 (s, 3H), 2.29 (s, 3H).

<sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 165.0, 164.4, 156.0, 144.2, 141.8, 138.1, 137.1, 133.2, 131.5, 130.3, 130.3, 129.9, 129.9, 129.7, 129.1, 128.9, 127.0, 125.3, 122.6, 122.2, 119.6, 119.0, 110.8, 52.3, 50.9, 39.1, 21.8, 19.3.

HRMS(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>BrN<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 625.0909, found 625.0908.

**(3ja)**

**4-methyl-N-((2'S,3R,3'S,Z)-3''-methyl-5''-oxo-1''-phenyl-3'-(*m*-tolyl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)benzenesulfonamide**



yellow solid, 95% yield, 53.2 mg; mp = 170.1-171.8 °C; dr 10:1

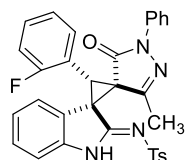
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 10.12 (d, *J* = 6.2 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.66 (m, 2H), 7.27 – 7.21 (m, 4H), 7.19 – 7.16 (m, 1H), 7.08 – 7.00 (m, 4H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.85 – 6.80 (m, 3H), 4.53 (s, 1H), 2.36 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H).

<sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 165.5, 164.6, 156.3, 144.1, 141.7, 138.3, 138.2, 138.1, 130.9, 130.7, 129.8, 129.5, 129.1, 128.9, 128.3, 127.8, 127.4, 126.9, 125.1, 122.4, 120.1, 119.0, 110.5, 52.7, 51.2, 40.3, 21.8, 21.5, 19.3.

HRMS(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>33</sub>H<sub>28</sub>N<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 561.1960, found 561.1964.

**(3ka)**

**N-((2'S,3R,3'S,Z)-3'-(2-fluorophenyl)-3''-methyl-5''-oxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 65% yield, 36.7 mg; mp = 173.2-174.8 °C; dr 10:1

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 10.17 – 10.10 (m, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.23 (m, 4H), 7.22 – 7.17 (m, 3H), 7.03 (t, *J* = 7.4 Hz, 1H), 7.01 – 6.93 (m, 4H), 6.84 (td, *J* = 7.8, 1.1 Hz, 1H), 4.34 (s, 1H), 2.36 (s, 3H), 2.22 (s, 3H).

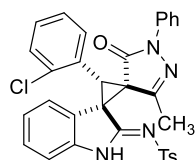


$^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  165.3, 164.9, 161.4 (d,  $J$  = 248.2 Hz), 155.9, 144.1, 141.8, 138.2, 138.03, 132.1, 132.1, 130.4 (d,  $J$  = 8.2 Hz), 129.9, 129.8, 129.6, 128.8, 126.9, 126.9, 125.2, 123.7, 123.7, 122.6, 120.3, 119.2, 115.8 (d,  $J$  = 21.2 Hz), 110.7, 51.2, 50.6, 34.6, 21.7, 19.3.

HRMS(ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{32}\text{H}_{25}\text{FN}_4\text{O}_3\text{SH}^+$  565.1710, found 565.1708.

### (3la)

**N-((2'S,3R,3'S,Z)-3'-(2-chlorophenyl)-3''-methyl-5''-oxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 88% yield, 51.0 mg; mp = 187.6-189.3 °C; dr 10:1

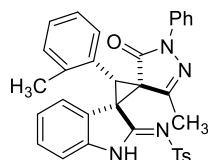
$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  10.27 (s, 1H), 7.90 (d,  $J$  = 8.1 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.37 – 7.27 (m, 8H), 7.21 (d,  $J$  = 7.8 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.06 (d,  $J$  = 7.8 Hz, 1H), 6.93 (t,  $J$  = 7.8 Hz, 1H), 4.44 (s, 1H), 2.44 (s, 3H), 2.34 (s, 3H).

$^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  165.2, 164.8, 156.1, 144.1, 141.7, 138.2, 138.1, 135.3, 132.1, 129.9, 129.9, 129.8, 129.8, 129.6, 128.8, 126.9, 126.6, 126.3, 125.3, 122.7, 120.4, 119.3, 110.7, 51.8, 51.7, 38.7, 21.7, 19.4.

HRMS(ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{32}\text{H}_{25}\text{ClN}_4\text{O}_3\text{SH}^+$  581.1414, found 581.1413.

### (3ma)

**4-methyl-N-((2'S,3R,3'S,Z)-3''-methyl-5''-oxo-1''-phenyl-3'-(*o*-tolyl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)benzenesulfonamide**



yellow solid, 92% yield, 51.5 mg; mp = 175.4-177.1 °C; dr 10:1

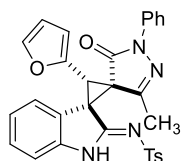
$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  10.19 (s, 1H), 7.86 – 7.78 (m, 2H), 7.30 (dd,  $J$  = 7.7, 1.8 Hz, 1H), 7.26 (dd,  $J$  = 9.7, 7.9 Hz, 3H), 7.23 – 7.14 (m, 6H), 7.00 – 6.93 (m, 4H), 6.75 (t,  $J$  = 7.8 Hz, 1H), 4.61 (d,  $J$  = 2.3 Hz, 1H), 2.35 (s, 3H), 2.22 (s, 3H).

$^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  165.4, 164.8, 156.3, 144.1, 141.5, 138.4, 138.1, 137.7, 130.7, 130.6, 130.0, 129.8, 129.5, 128.9, 128.6, 126.8, 126.5, 125.6, 125.2, 122.6, 120.5, 119.1, 110.6, 52.5, 51.3, 39.8, 21.8, 19.5, 19.4.

HRMS(ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{33}\text{H}_{28}\text{N}_4\text{O}_3\text{SNa}^+$  583.1780, found 583.1780.

### (3na)

**N-((2'S,3S,3'R,Z)-3'-(furan-2-yl)-3''-methyl-5''-oxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 53% yield, 28.4 mg; mp = 180.0-181.7 °C; dr 10:1

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  10.19 (s, 1H), 7.91 – 7.87 (m, 2H), 7.75 (dt,  $J$  = 8.1, 1.2 Hz, 2H), 7.35 – 7.29 (m,

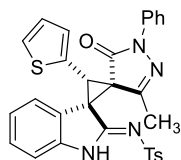
7H), 7.13 – 7.12 (m, 1H), 7.03 (ddt,  $J = 6.6, 4.4, 1.3$  Hz, 3H), 6.90 (td,  $J = 7.8, 1.1$  Hz, 1H), 4.65 (d,  $J = 1.1$  Hz, 1H), 2.45 (s, 3H), 2.31 (s, 3H).

**$^{13}\text{C}$  NMR** (150 MHz, Chloroform- $d$ )  $\delta$  165.4, 164.6, 156.2, 144.1, 141.7, 138.3, 138.1, 130.6, 130.4, 129.8, 129.5, 128.8, 128.4, 127.9, 126.9, 125.2, 122.4, 120.0, 119.0, 110.6, 52.7, 51.0, 40.3, 21.8, 19.3.

**HRMS**(ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_4\text{O}_4\text{SH}^+$  537.1597, found 537.1600.

#### (30a)

**4-methyl-N-((2'S,3R,3'S,Z)-3''-methyl-5''-oxo-1''-phenyl-3'-(thiophen-2-yl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)benzenesulfonamide**



yellow solid, 60% yield, 33.1 mg; mp = 159.1-160.8 °C; dr 10:1

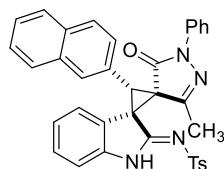
**$^1\text{H}$  NMR** (400 MHz, Chloroform- $d$ )  $\delta$  10.08 (s, 1H), 7.90 – 7.85 (m, 2H), 7.75 (d,  $J = 8.1$  Hz, 2H), 7.44 (d,  $J = 8.0$  Hz, 1H), 7.36 – 7.28 (m, 6H), 7.15 – 7.10 (m, 1H), 6.98 (dt,  $J = 13.7, 8.0$  Hz, 3H), 6.86 (dd,  $J = 3.6, 1.7$  Hz, 1H), 4.57 (s, 1H), 2.45 (s, 3H), 2.28 (s, 3H).

**$^{13}\text{C}$  NMR** (150 MHz, Chloroform- $d$ )  $\delta$  165.1, 164.5, 156.1, 144.2, 141.8, 138.1, 138.0, 134.4, 131.8, 130.4, 129.9, 129.7, 128.9, 128.7, 128.2, 127.0, 125.3, 122.6, 119.0, 110.7, 52.5, 50.9, 39.4, 21.8, 19.3.

**HRMS**(ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_4\text{O}_3\text{S}_2\text{H}^+$  553.1268, found 553.1270.

#### (3pa)

**4-methyl-N-((2'S,3S,3'R,Z)-3''-methyl-3'-(naphthalen-2-yl)-5''-oxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)benzenesulfonamide**



yellow solid, 85% yield, 50.7 mg; mp = 179.1-180.5 °C; dr 5:1

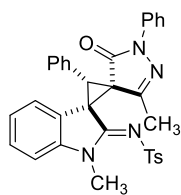
**$^1\text{H}$  NMR** (600 MHz, Chloroform- $d$ )  $\delta$  10.20 (s, 1H), 7.91 (d,  $J = 8.3$  Hz, 2H), 7.82 (d,  $J = 7.0$  Hz, 1H), 7.80 – 7.65 (m, 4H), 7.54 – 7.40 (m, 4H), 7.36 – 7.27 (m, 4H), 7.15 – 7.08 (m, 3H), 7.04 (d,  $J = 7.5$  Hz, 1H), 6.83 (td,  $J = 7.8, 1.1$  Hz, 1H), 4.86 – 4.77 (m, 1H), 2.45 (s, 3H), 2.34 (s, 3H).

**$^{13}\text{C}$  NMR** (150 MHz, Chloroform- $d$ )  $\delta$  165.4, 164.6, 156.2, 144.2, 141.7, 138.3, 138.1, 133.1, 133.0, 130.6, 129.9, 129.8, 129.5, 129.0, 128.9, 128.2, 128.0, 127.9, 127.6, 127.0, 126.6, 126.5, 126.2, 125.4, 125.2, 122.5, 120.0, 119.1, 119.0, 110.6, 52.8, 51.2, 40.4, 21.8, 19.4.

**HRMS**(ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{36}\text{H}_{28}\text{N}_4\text{O}_3\text{SNa}^+$  619.1780, found 619.1782.

#### (3qa)

**N-((2'S,3R,3'S,Z)-1,3''-dimethyl-5''-oxo-1'',3'-diphenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 45% yield, 25.2 mg; mp = 161.9-163.3 °C; dr 10:1

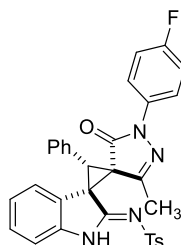
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 (qd, *J* = 10.8, 9.9, 4.7 Hz, 8H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 4.49 (s, 1H), 3.97 (s, 3H), 2.43 (s, 3H), 2.23 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 164.6, 161.6, 156.0, 145.4, 143.1, 140.4, 138.1, 130.3, 130.1, 129.6, 129.5, 129.0, 128.9, 128.4, 128.3, 128.3, 126.5, 125.1, 122.7, 120.7, 118.9, 109.3, 53.3, 50.9, 40.4, 34.4, 21.7, 19.7.

**HRMS**(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>33</sub>H<sub>28</sub>N<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 561.1960, found 561.1978.

### (3ab)

**N-((2'S,3R,3'S,Z)-1''-(4-fluorophenyl)-3''-methyl-5''-oxo-3'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 88% yield, 49.6 mg; mp = 170.3-172.1 °C; dr 10:1

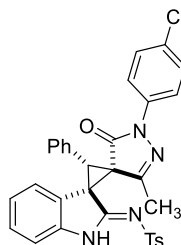
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 10.12 (s, 1H), 7.98 – 7.89 (m, 1H), 7.86 – 7.78 (m, 2H), 7.30 – 7.11 (m, 8H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.95 (dd, *J* = 19.4, 7.5 Hz, 3H), 6.83 (td, *J* = 7.7, 3.8 Hz, 1H), 4.59 (d, *J* = 9.6 Hz, 1H), 2.37 (s, 3H), 2.23 (d, *J* = 11.6 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 165.3, 164.5, 160.0 (d, *J* = 240 Hz), 156.4, 144.1, 141.7, 138.3 (d, *J* = 2.7 Hz), 130.6, 130.3, 129.9, 129.6, 128.4, 127.8, 126.9, 122.4, 120.8, 120.7, 119.9, 115.5 (d, *J* = 10 Hz), 110.6, 52.8, 51.0, 40.3, 21.8, 19.3.

**HRMS**(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>FN<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 565.1710, found 565.1714.

### (3ac)

**N-((2'S,3R,3'S,Z)-1''-(4-chlorophenyl)-3''-methyl-5''-oxo-3'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



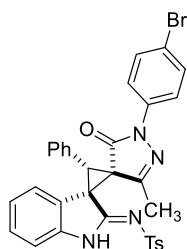
yellow solid, 95% yield, 55.1 mg; mp = 140.7-142.5 °C; dr 10:1

**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.85 (t, *J* = 2.0 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 3H), 7.30 (dd, *J* = 14.4, 7.5 Hz, 3H), 7.22 (t, *J* = 8.2 Hz, 1H), 7.09 (dd, *J* = 15.7, 7.9 Hz, 2H), 7.02 (dd, *J* = 14.4, 7.7 Hz, 3H), 6.91 (t, *J* = 7.8 Hz, 1H), 4.66 (s, 1H), 2.45 (s, 3H), 2.30 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*)  $\delta$  165.4, 165.3, 156.5, 144.1, 141.6, 138.3, 134.7, 131.6, 130.5, 130.4, 130.4, 129.8, 129.7, 129.4, 128.9, 128.3, 128.3, 127.8, 127.5, 126.9, 122.4, 119.9, 110.6, 52.7, 49.8, 40.1, 21.7, 19.3.  
**HRMS(ESI)** *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>ClN<sub>4</sub>O<sub>3</sub>SNa<sup>+</sup> 603.1234, found 603.1236.

**(3ad)**

**N-((2'S,3R,3'S,Z)-1''-(4-bromophenyl)-3''-methyl-5''-oxo-3'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 72% yield, 45.0 mg; mp = 168.5-170.2 °C; dr 10:1

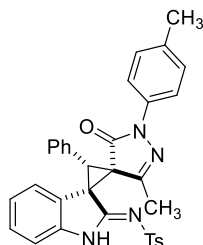
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*)  $\delta$  10.14 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.14 (m, 7H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.85 (t, *J* = 8.0 Hz, 2H), 4.51 (s, 1H), 2.37 (s, 3H), 2.22 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*)  $\delta$  165.2, 164.6, 156.7, 144.2, 141.8, 138.2, 137.2, 131.8, 130.5, 130.3, 129.9, 129.6, 128.5, 128.4, 127.72, 126.9, 122.4, 120.4, 119.8, 117.9, 110.6, 52.9, 51.0, 40.3, 21.8, 19.4.

**HRMS(ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>BrN<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 625.0909, found 625.0908.

**(3ae)**

**4-methyl-N-((2'S,3R,3'S,Z)-3''-methyl-5''-oxo-3'-phenyl-1''-(p-tolyl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)benzenesulfonamide**



yellow solid, 68% yield, 38.1 mg; mp = 148.6-150.3 °C; dr 10:1

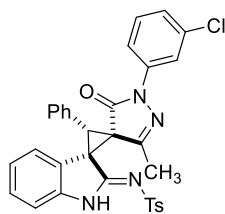
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*)  $\delta$  10.13 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.17 (m, 6H), 7.04 (dd, *J* = 10.3, 7.8 Hz, 3H), 6.96 – 6.93 (m, 3H), 6.80 (t, *J* = 7.8 Hz, 1H), 4.56 (s, 1H), 2.36 (s, 3H), 2.21 (d, *J* = 3.4 Hz, 6H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*)  $\delta$  165.4, 164.5, 156.0, 144.1, 141.7, 138.3, 135.7, 130.6, 130.4, 129.8, 129.4, 129.3, 128.3, 128.3, 127.9, 126.9, 122.4, 120.1, 119.1, 110.6, 52.6, 51.0, 40.3, 21.7, 21.0, 19.3.

**HRMS(ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>33</sub>H<sub>28</sub>N<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 561.1960, found 561.1958.

**(3af)**

**N-((2'S,3S,3'R,Z)-1''-(3-chlorophenyl)-3''-methyl-5''-oxo-3'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 78% yield, 45.3 mg; mp = 168.8-170.3 °C; dr 10:1

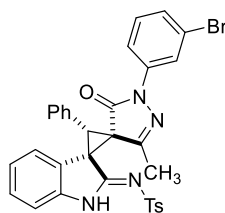
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 10.16 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.84 (t, *J* = 2.1 Hz, 1H), 7.37 – 7.27 (m, 7H), 7.22 (t, *J* = 8.2 Hz, 1H), 7.12 – 7.07 (m, 2H), 7.04 – 7.00 (m, 3H), 6.91 (td, *J* = 7.8, 1.1 Hz, 1H), 4.66 (s, 1H), 2.45 (s, 3H), 2.30 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 165.2, 164.7, 156.7, 144.2, 141.7, 139.1, 138.2, 134.6, 130.6, 130.3, 129.9, 129.7, 129.6, 128.5, 128.4, 127.7, 126.9, 125.0, 122.5, 119.8, 118.8, 116.7, 110.6, 52.9, 51.1, 40.3, 21.8, 19.3.

**HRMS(ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>ClN<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 581.1414, found 581.1416.

### (3ag)

**N-((2'S,3R,3'S,Z)-1''-(3-bromophenyl)-3''-methyl-5''-oxo-3'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 82% yield, 51.2 mg; mp = 169.5-171.3 °C; dr 10:1;

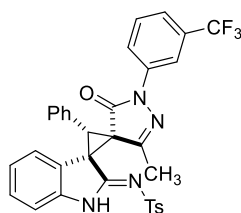
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 10.12 (s, 1H), 8.03 (d, *J* = 30.9 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.35 (dp, *J* = 15.2, 7.3 Hz, 7H), 7.24 – 7.07 (m, 3H), 7.01 (t, *J* = 6.3 Hz, 3H), 6.92 (t, *J* = 8.1 Hz, 1H), 4.65 (s, 1H), 2.45 (s, 3H), 2.30 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 165.2, 164.6, 156.7, 144.2, 141.8, 139.2, 138.2, 130.5, 130.3, 130.1, 129.9, 129.4, 129.4, 128.5, 128.4, 128.4, 127.9, 127.7, 126.9, 122.5, 121.6, 119.8, 117.2, 110.7, 53.0, 51.0, 40.3, 21.8, 19.3.

**HRMS(ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>25</sub>BrN<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 625.0909, found 625.0907.

### (3ah)

**4-methyl-N-((2'S,3R,3'S,Z)-3''-methyl-5''-oxo-3'-phenyl-1''-(4-(trifluoromethyl)phenyl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)benzenesulfonamide**



yellow solid, 80% yield, 49.1 mg; mp = 162.2-163.8 °C; dr 10:1

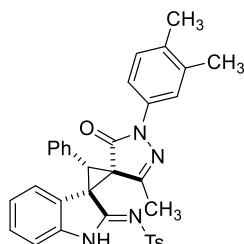
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 10.13 (s, 1H), 8.14 – 7.95 (m, 2H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.36 (tt, *J* = 18.2, 7.7 Hz, 8H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.02 (dd, *J* = 8.3, 3.7 Hz, 3H), 6.92 (t, *J* = 7.8 Hz, 1H), 4.67 (s, 1H), 2.46 (s, 3H), 2.32 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 165.1, 164.8, 156.9, 144.2, 141.8, 138.6, 138.2, 131.3 (d, *J* = 32.5 Hz), 130.5, 130.3, 129.9, 129.7, 129.4, 128.5, 128.5, 127.7, 126.9, 124.0 (d, *J* = 272.6 Hz), 122.5, 121.7, 121.4 (d, *J* = 3.9 Hz), 119.8, 115.6, 110.7, 53.1, 51.1, 40.4, 21.8, 19.3.

**HRMS**(ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>33</sub>H<sub>25</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>SN<sup>+</sup> 637.1497, found 637.1497.

**(3ai)**

**N-((2'S,3R,3'S,Z)-1''-(3,4-dimethylphenyl)-3''-methyl-5''-oxo-3'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)-4-methylbenzenesulfonamide**



yellow solid, 67% yield, 38.5 mg; mp = 183.6-185.2 °C; dr 10:1

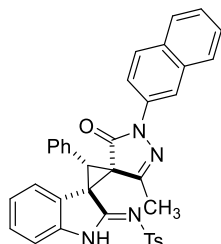
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 10.12 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.26 – 7.16 (m, 6H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.98 – 6.92 (m, 4H), 6.81 (td, *J* = 7.8, 1.1 Hz, 1H), 4.55 (d, *J* = 1.1 Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 165.5, 164.4, 156.0, 144.1, 141.7, 138.3, 137.1, 135.9, 133.6, 130.6, 130.4, 129.8, 129.8, 129.4, 128.3, 128.3, 128.0, 126.9, 122.4, 120.3, 120.1, 116.7, 110.5, 52.6, 51.0, 40.3, 21.7, 20.0, 19.4, 19.3.

**HRMS**(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>34</sub>H<sub>31</sub>N<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 575.2117, found 575.2120.

**(3aj)**

**4-methyl-N-((2'S,3R,3'S,Z)-3''-methyl-1''-(naphthalen-2-yl)-5''-oxo-3'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopropane-2',4''-pyrazol]-2-ylidene)benzenesulfonamide**



yellow solid, 97% yield, 57.8 mg; mp = 172.8-174.7 °C; dr 10:1

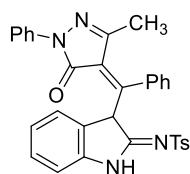
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 10.18 (s, 1H), 8.23 (s, 1H), 7.98 – 7.84 (m, 3H), 7.81 – 7.71 (m, 3H), 7.44 – 7.25 (m, 8H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.06 – 7.01 (m, 3H), 6.92 (t, *J* = 8.3 Hz, 1H), 4.68 (s, 1H), 2.44 (s, 3H), 2.35 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 165.4, 164.8, 156.4, 144.1, 141.8, 138.3, 135.7, 133.6, 131.1, 130.6, 130.4, 129.9, 129.6, 128.7, 128.4, 128.1, 127.9, 127.7, 126.9, 126.5, 125.4, 122.5, 120.0, 118.6, 116.1, 110.6, 52.8, 51.2, 40.4, 21.8, 19.4.

**HRMS**(ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>36</sub>H<sub>28</sub>N<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 597.1960, found 597.1965

(4)

**4-methyl-N-((Z)-3-((E)-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)(phenyl)methyl)indolin-2-ylidene)benzenesulfonamide**



yellow solid, 67% yield, 36.6 mg; mp = 174.5-176.3 °C;

**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 10.25 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (dt, *J* = 19.3, 7.7 Hz, 4H), 7.31 – 7.25 (m, 4H), 7.18 – 7.09 (m, 5H), 6.74 (t, *J* = 7.7 Hz, 1H), 5.93 (d, *J* = 8.1 Hz, 1H), 2.31 (s, 3H), 1.35 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 160.0, 154.9, 150.8, 144.1, 143.7, 140.7, 138.2, 137.6, 136.0, 130.9, 130.6, 129.8, 129.8, 129.0, 128.9, 126.7, 126.6, 126.5, 126.1, 125.3, 123.1, 122.4, 121.0, 111.5, 29.8, 21.7, 16.4.

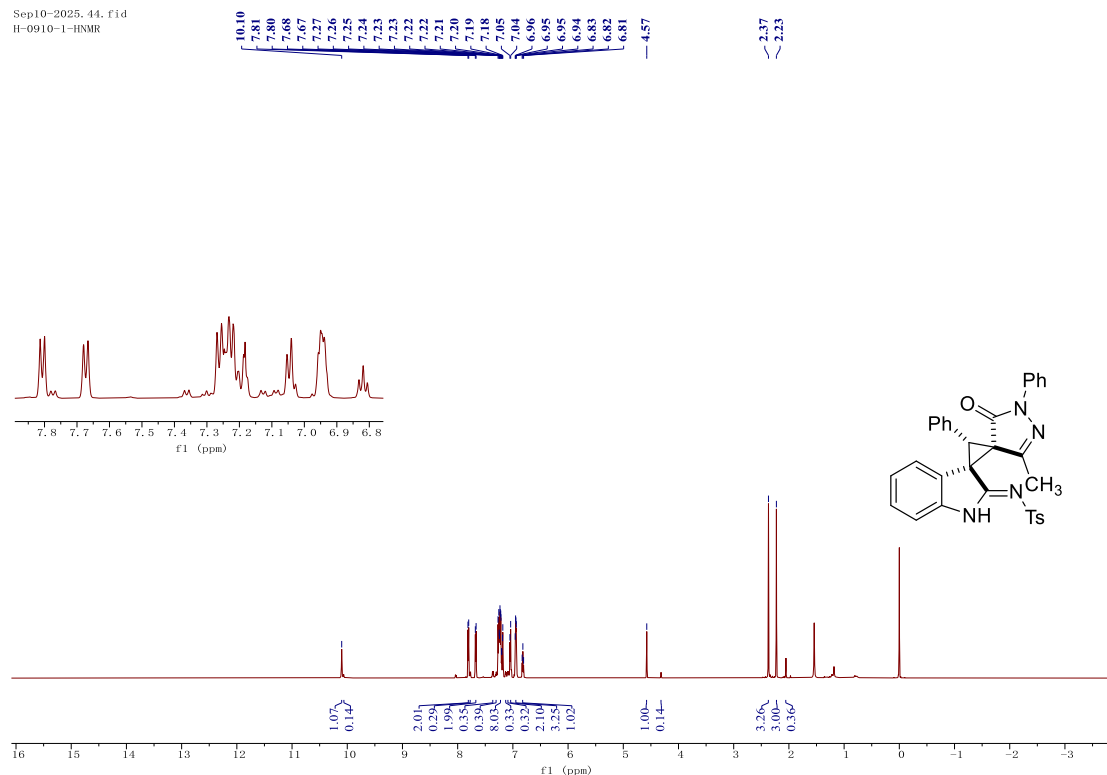
**HRMS(ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>26</sub>N<sub>4</sub>O<sub>3</sub>SH<sup>+</sup> 547.1804, found 547.1808.

## 7 The copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra for compounds

### 3aa

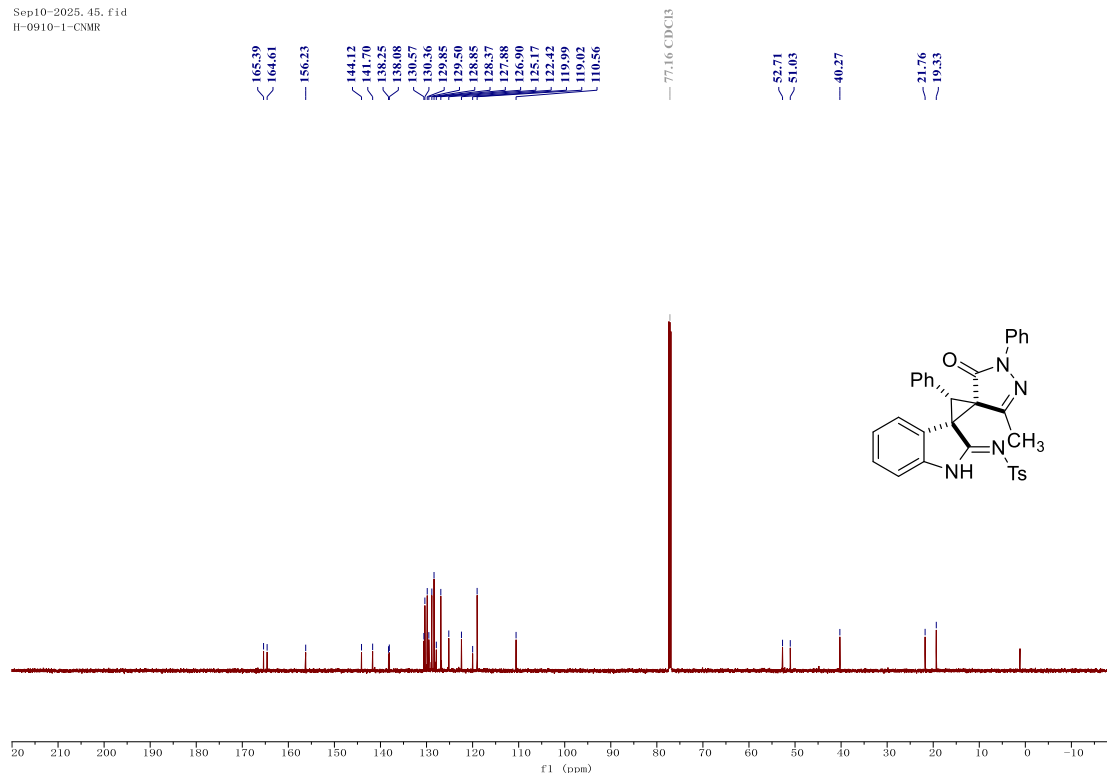
#### $^1\text{H}$ NMR (600 MHz, Chloroform- $d$ )

Sep10-2025. 44. f1d  
H-0910-1-HNMR



#### $^{13}\text{C}$ NMR (150 MHz, Chloroform- $d$ )

Sep10-2025. 45. f1d  
H-0910-1-CNMR

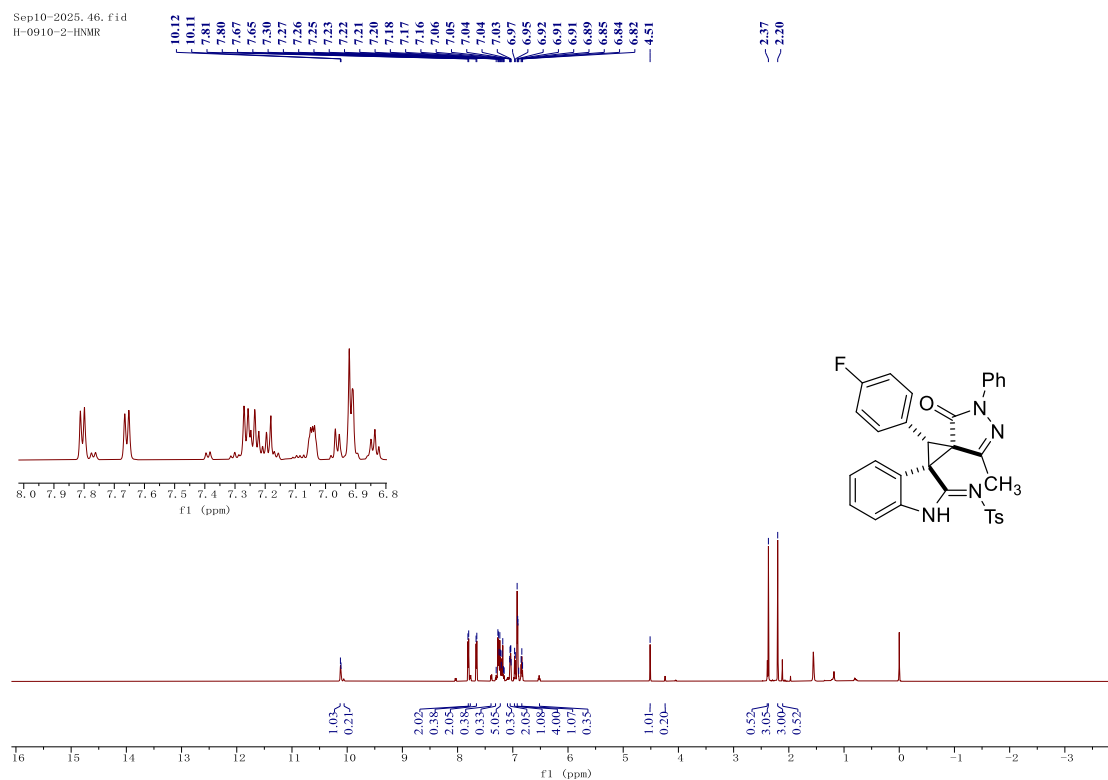




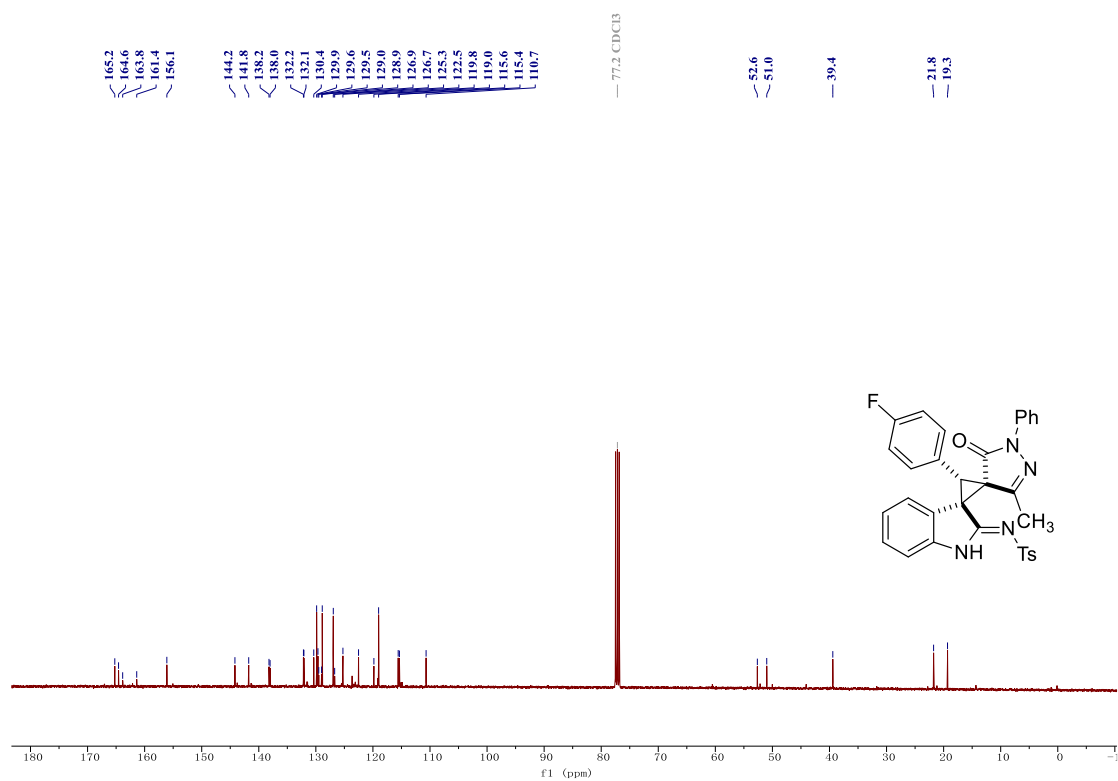
**3ba**

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**

Sep10-2025\_46.fid  
H-0910-2-HNMR



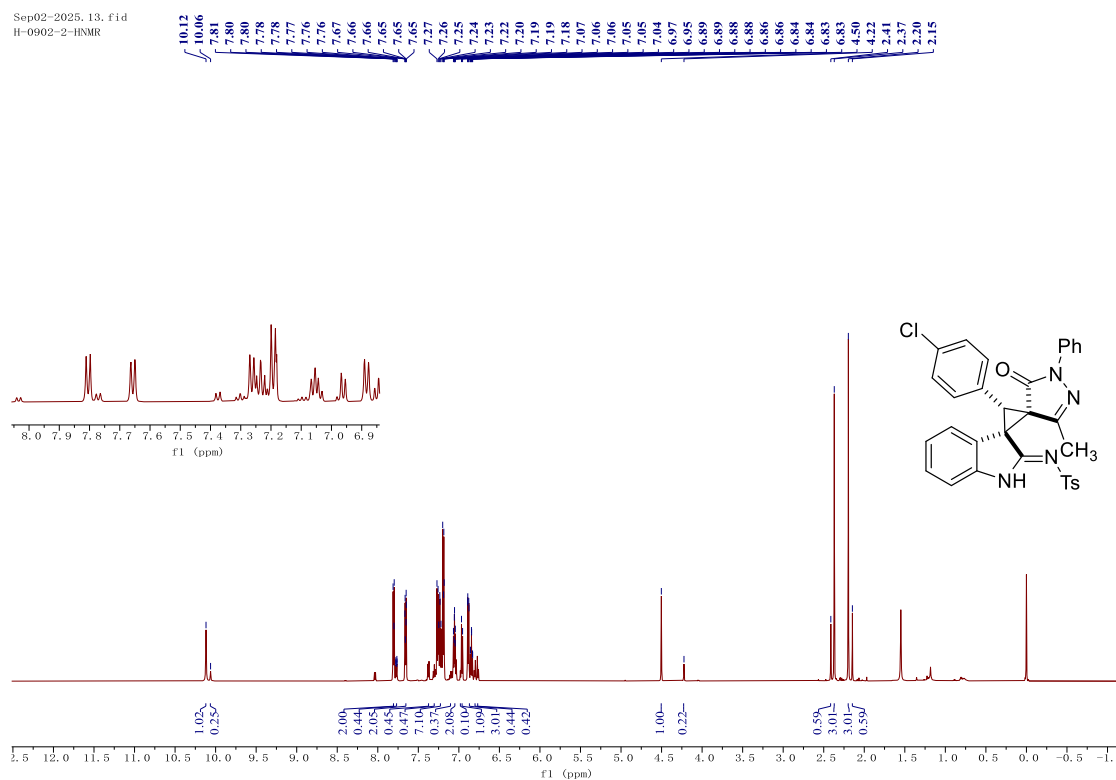
**<sup>13</sup>C NMR (100 MHz, Chloroform-*d*)**



### 3ca

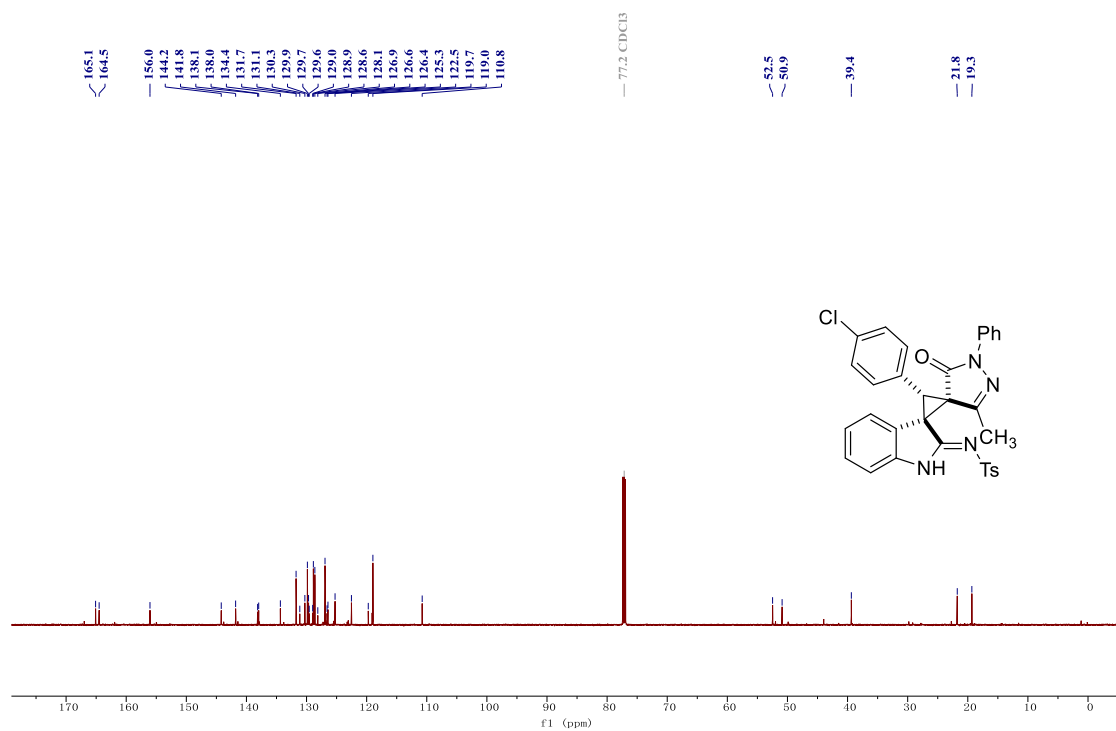
#### <sup>1</sup>H NMR (600 MHz, Chloroform-d)

Sep02-2025, 13, fid  
H-0902-2-1HMR



#### <sup>13</sup>C NMR (150 MHz, Chloroform-d)

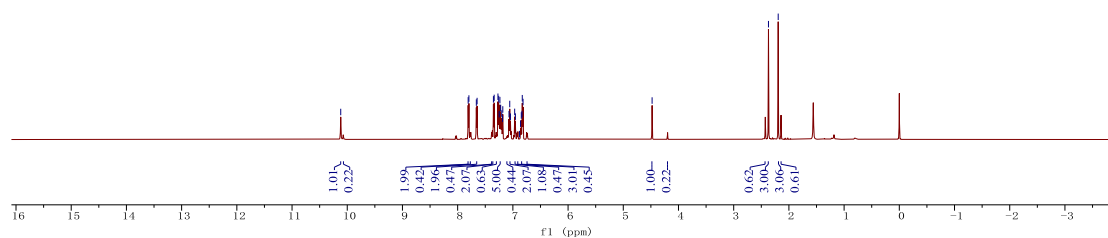
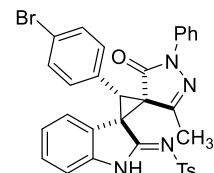
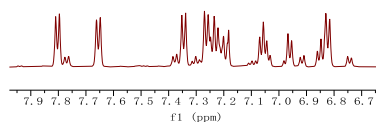
May06-2025, 18, fid  
HD-23



**3da**

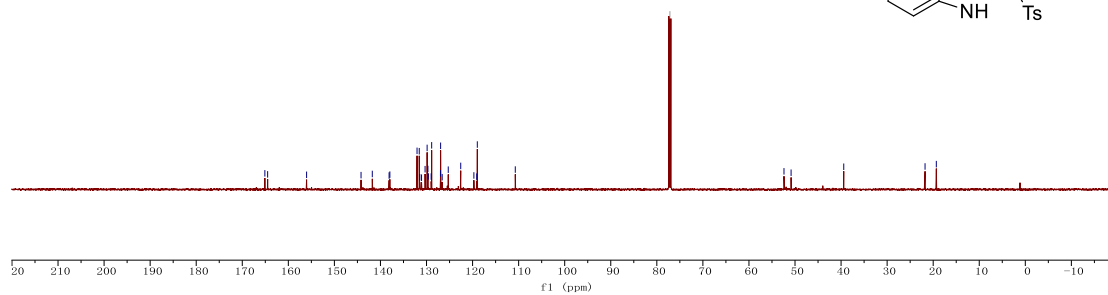
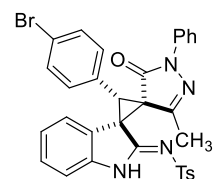
**<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)**

Sep11-2025, 33, fid  
H-0911-1-1H-NMR



**<sup>13</sup>C NMR (150 MHz, Chloroform-*d*)**

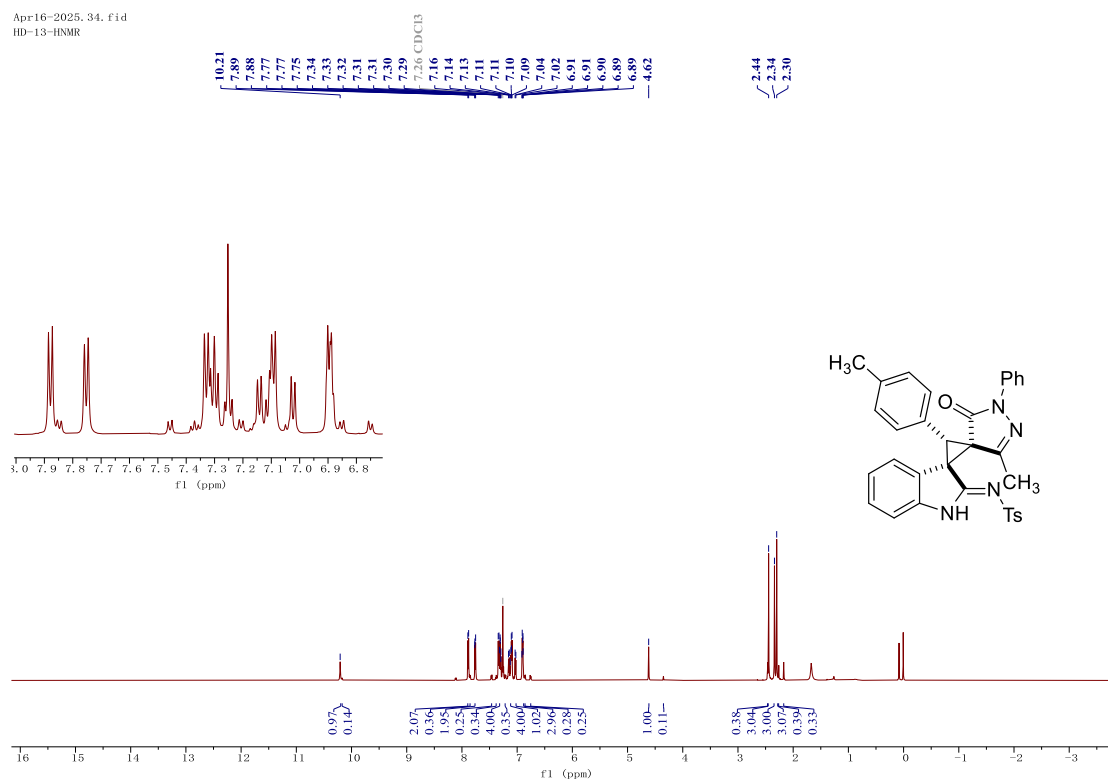
Sep11-2025, 34, fid  
H-0911-1-13C-NMR



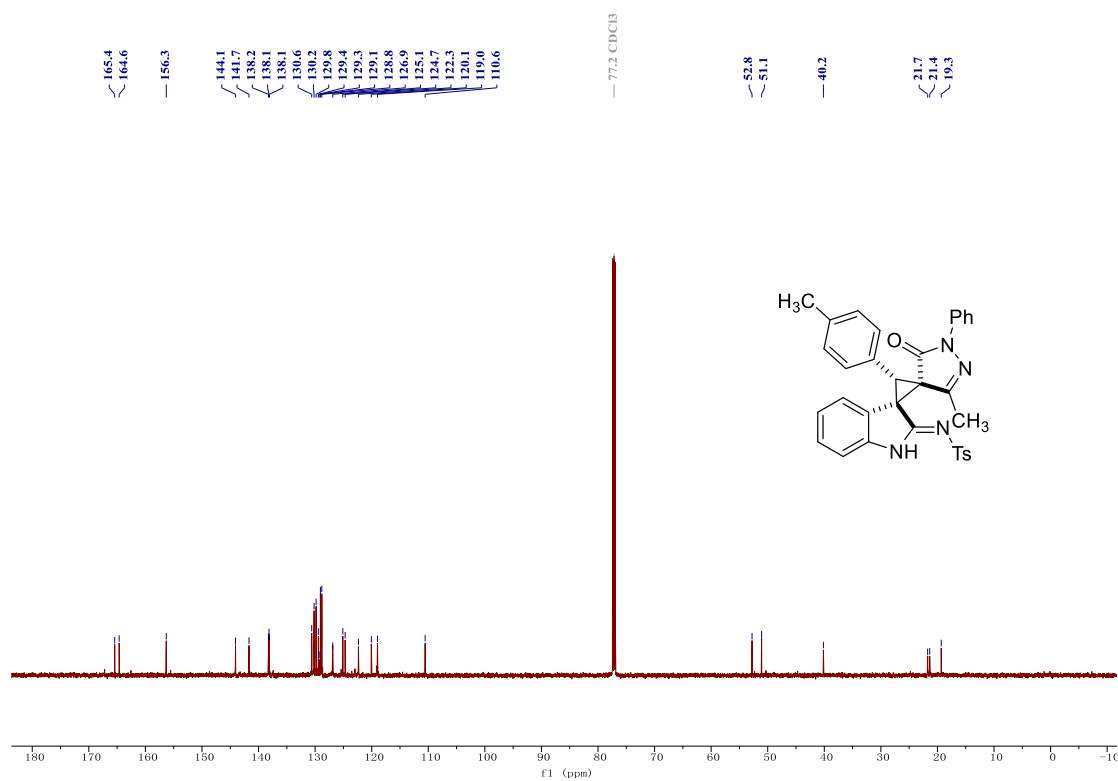
3ea

<sup>1</sup>H NMR (600 MHz, Chloroform-d)

Apr16-2025, 34, f1d  
HD-13-HNMR

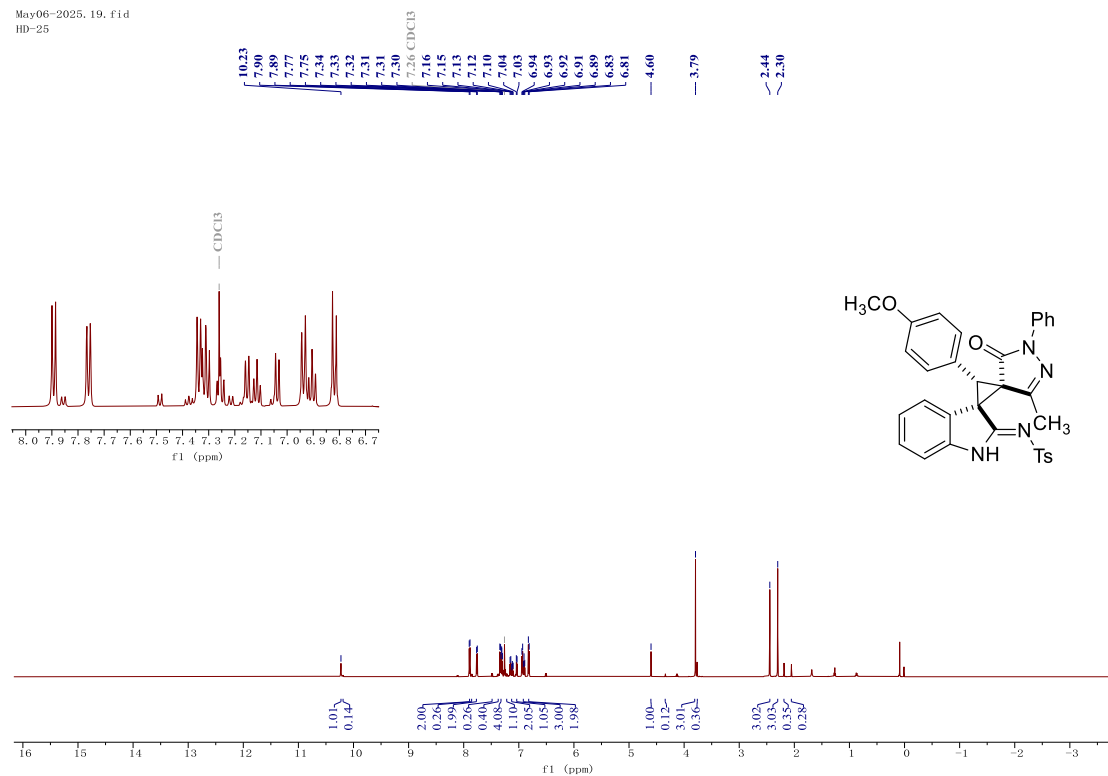


<sup>13</sup>C NMR (150 MHz, Chloroform-d)

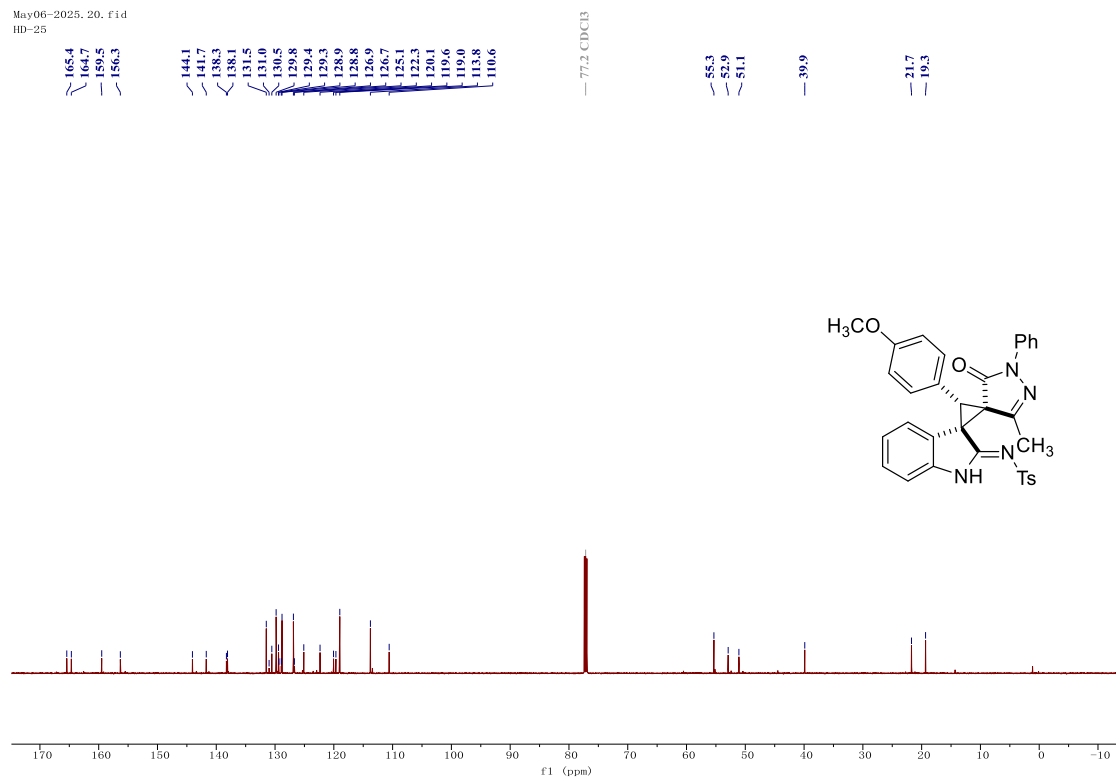


**3fa****<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)**

May06-2025, 19, fid  
HD-25

**<sup>13</sup>C NMR (150 MHz, Chloroform-*d*)**

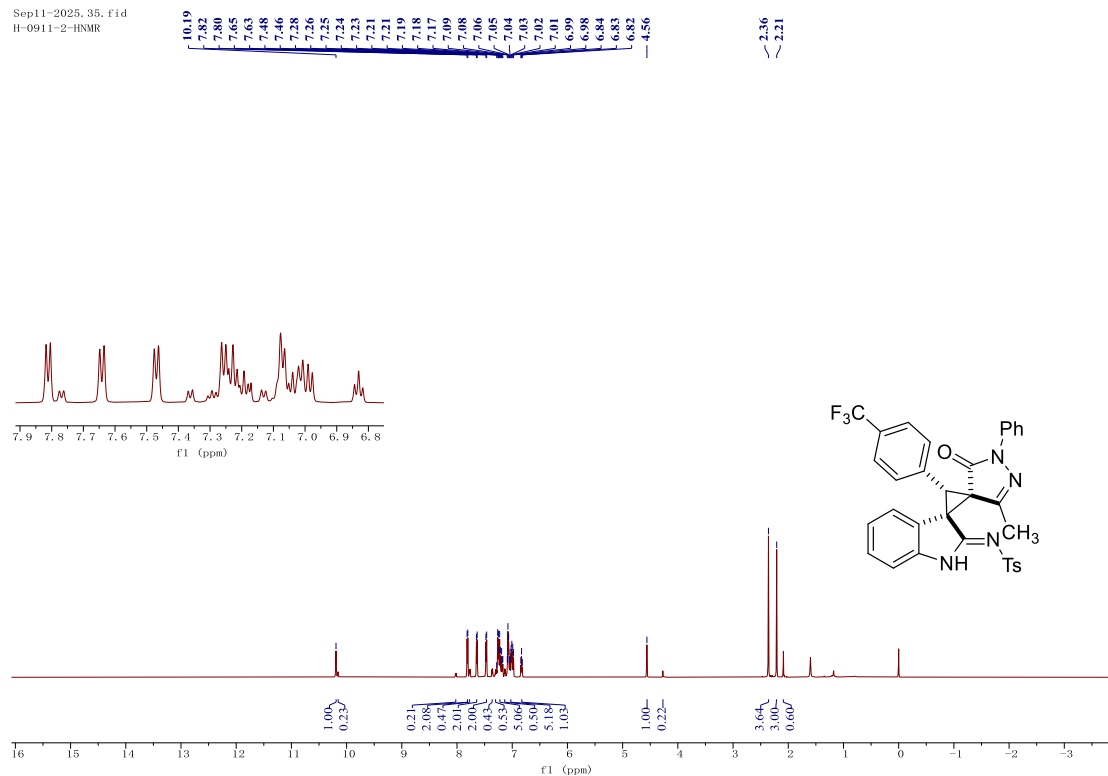
May06-2025, 20, fid  
HD-25



### 3ga

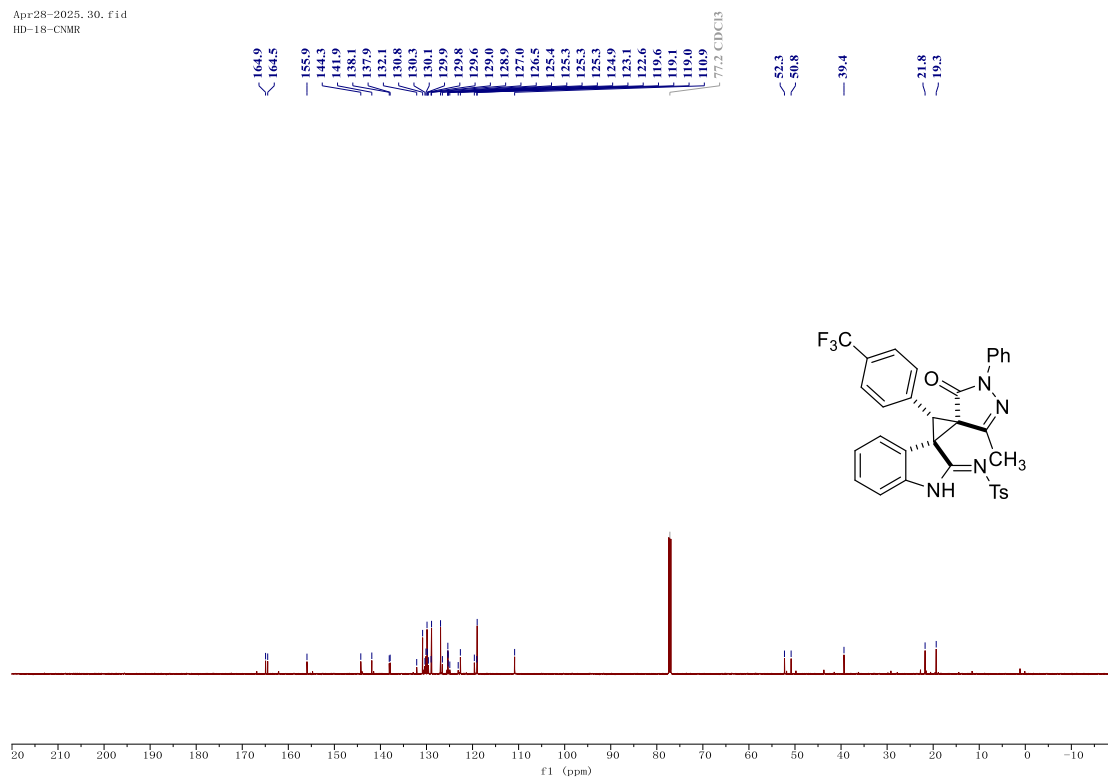
#### <sup>1</sup>H NMR (600 MHz, Chloroform-d)

Sep11-2025, 35, fid  
H-0911-2-HNMR



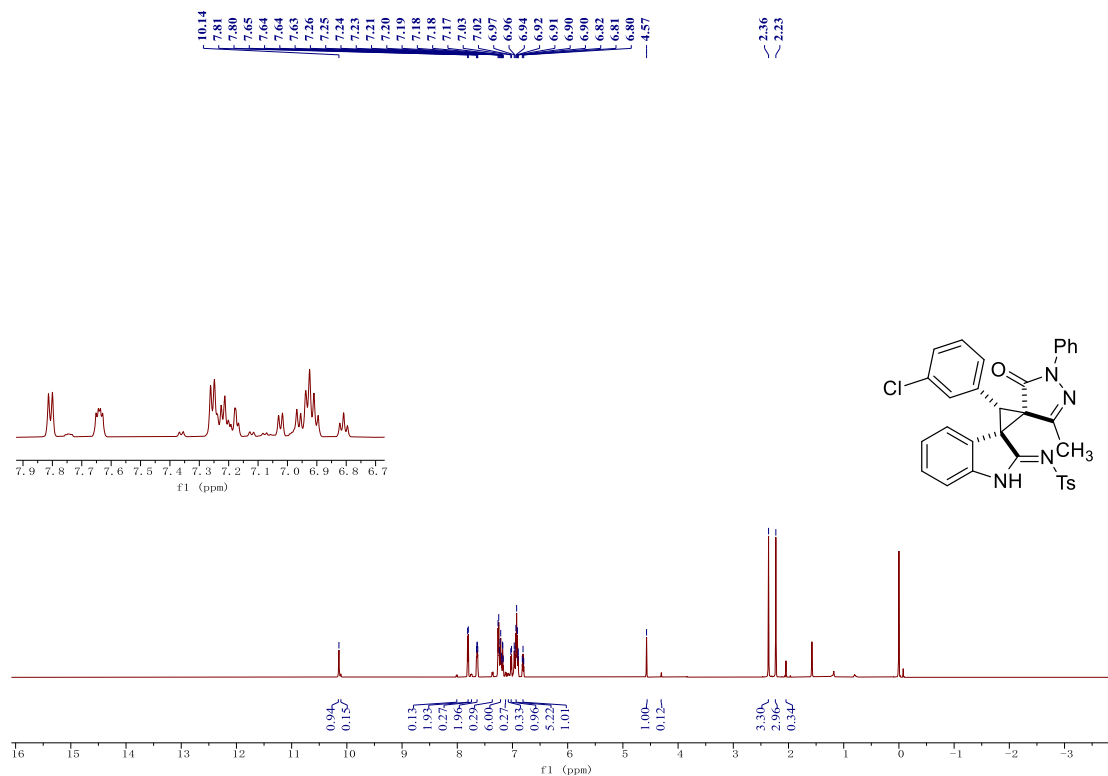
#### <sup>13</sup>C NMR (150 MHz, Chloroform-d)

Apr28-2025, 30, fid  
HD-18-CNMR

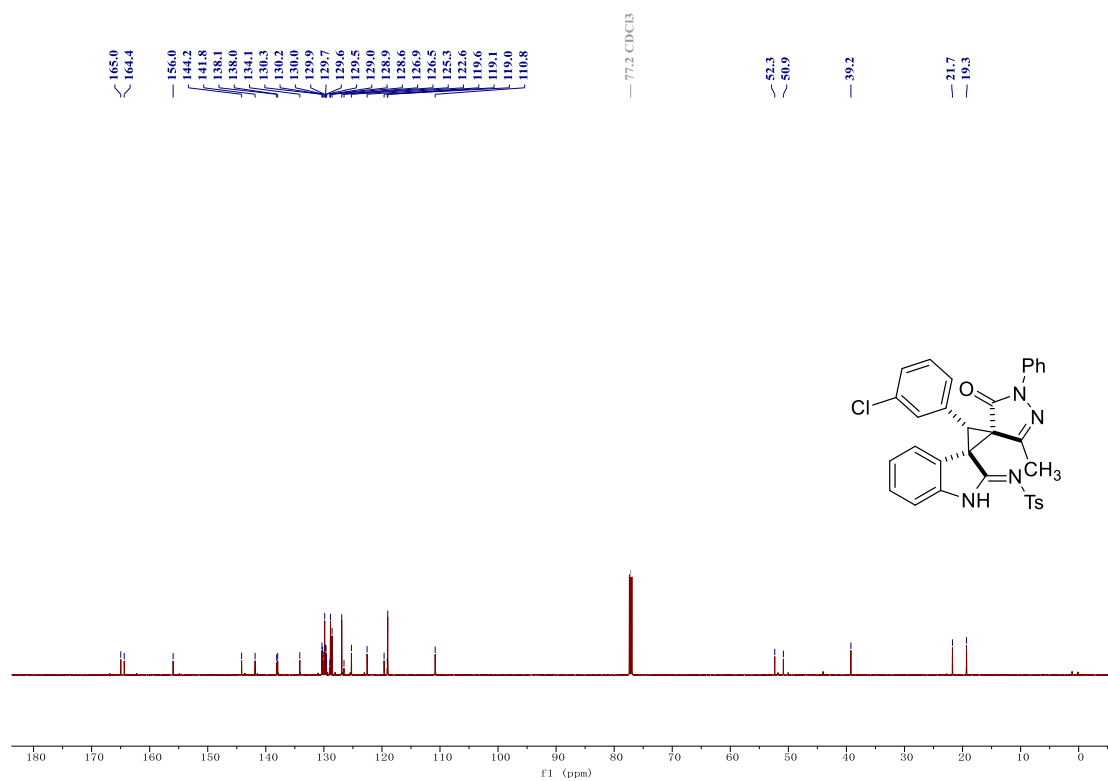


3ha

$^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )



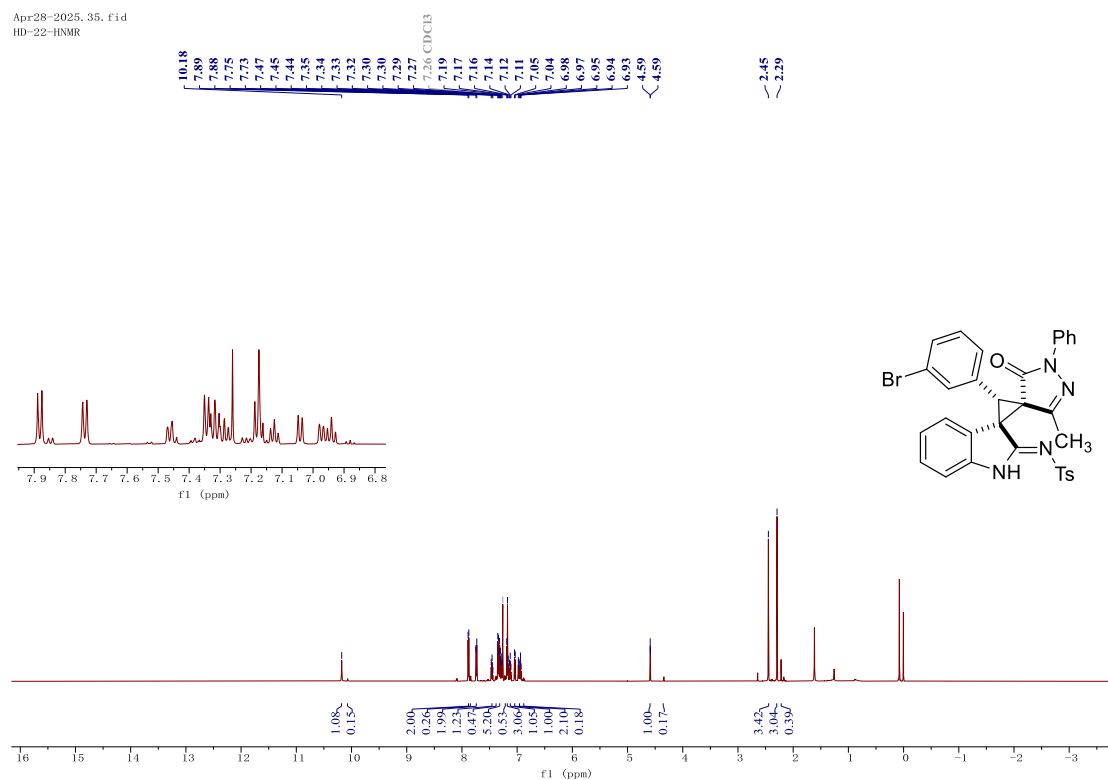
$^{13}\text{C}$  NMR (150 MHz, Chloroform- $d$ )



3ia

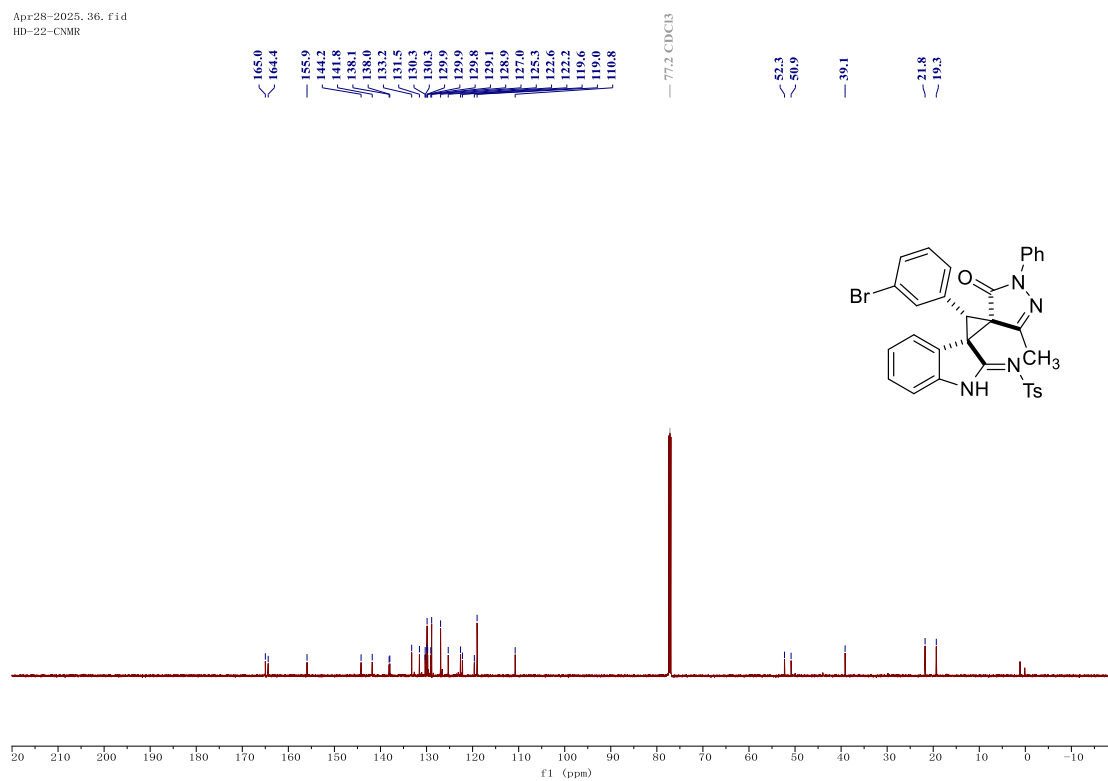
<sup>1</sup>H NMR (600 MHz, Chloroform-d)

Apr-28-2025, 35, f1d  
HD-22-HNMR



<sup>13</sup>C NMR (150 MHz, Chloroform-d)

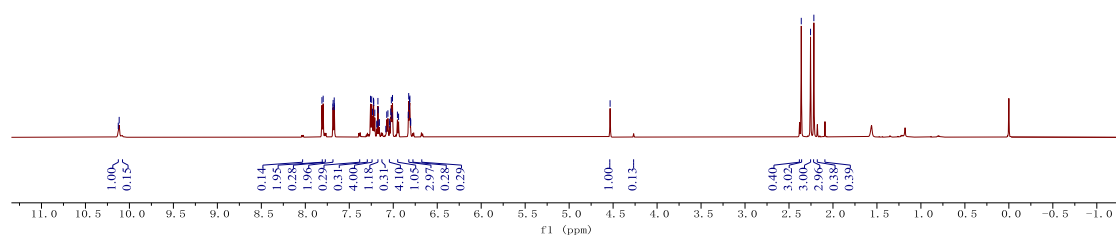
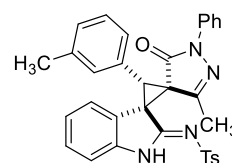
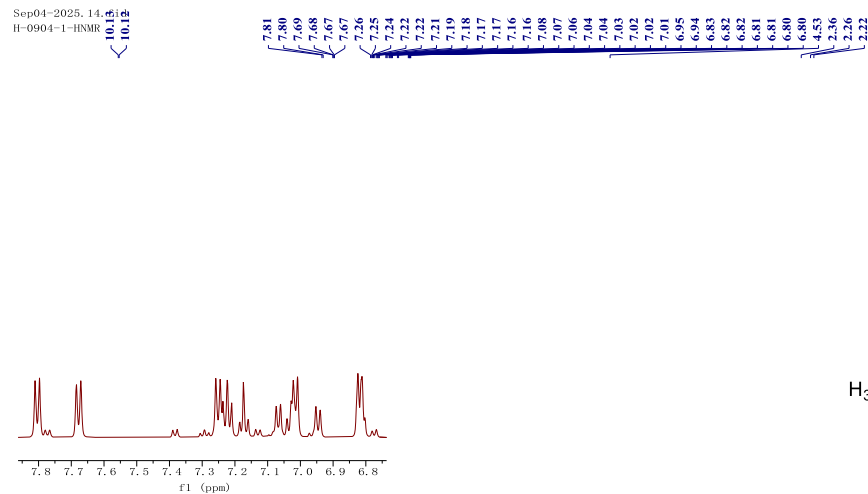
Apr-28-2025, 36, f1d  
HD-22-CNMR



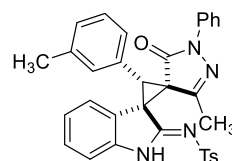
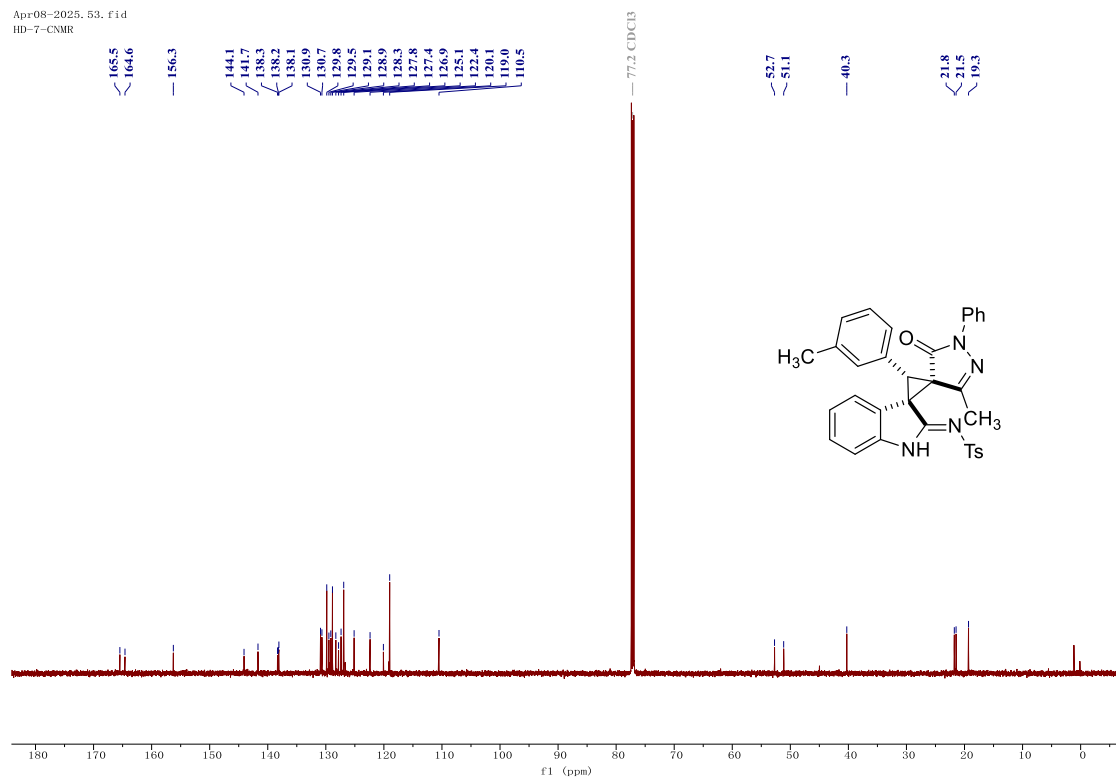


<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)

Sep04-2025. 14.81  
H-0904-1-HNMR 0.10 0.10

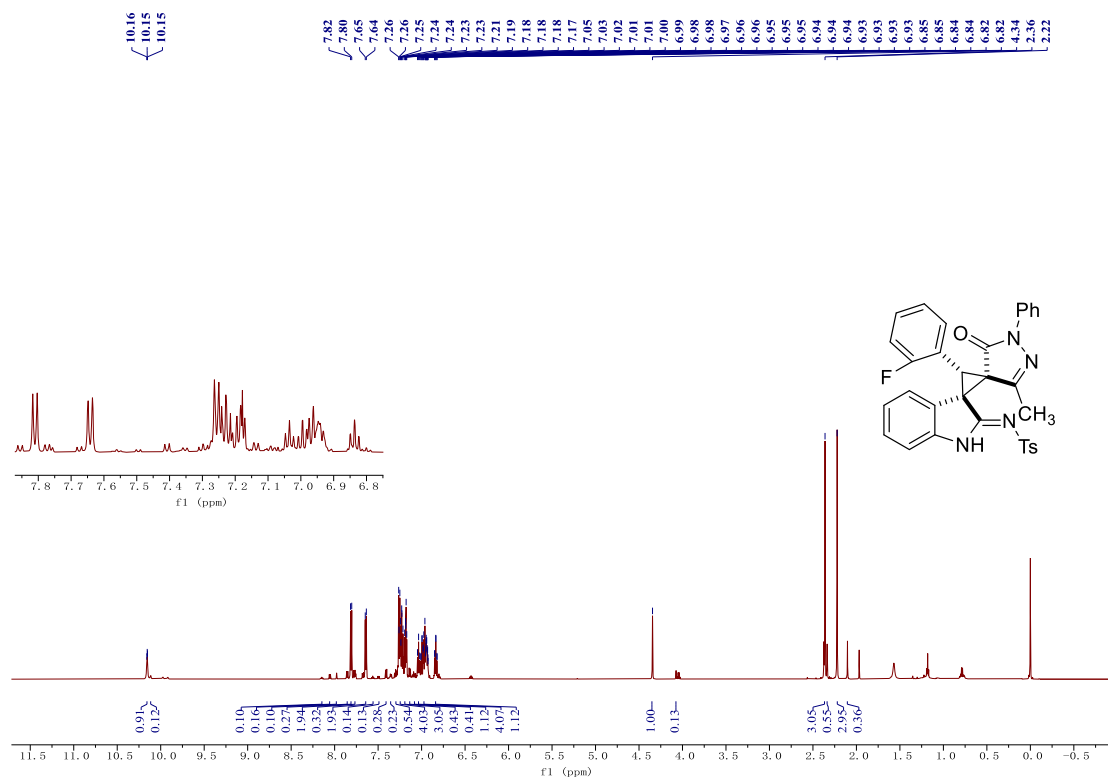


Apr08-2025. 53. fid  
HD-7-CNMR



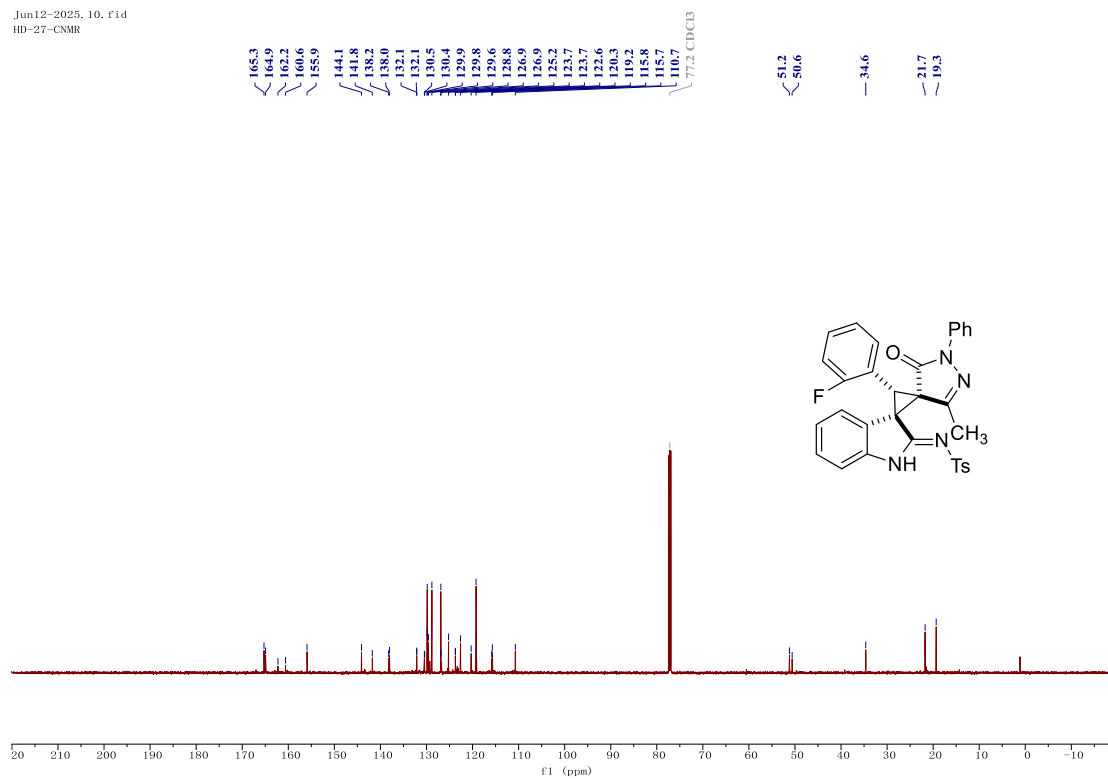
**3ka**

**<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)**



**<sup>13</sup>C NMR (150 MHz, Chloroform-*d*)**

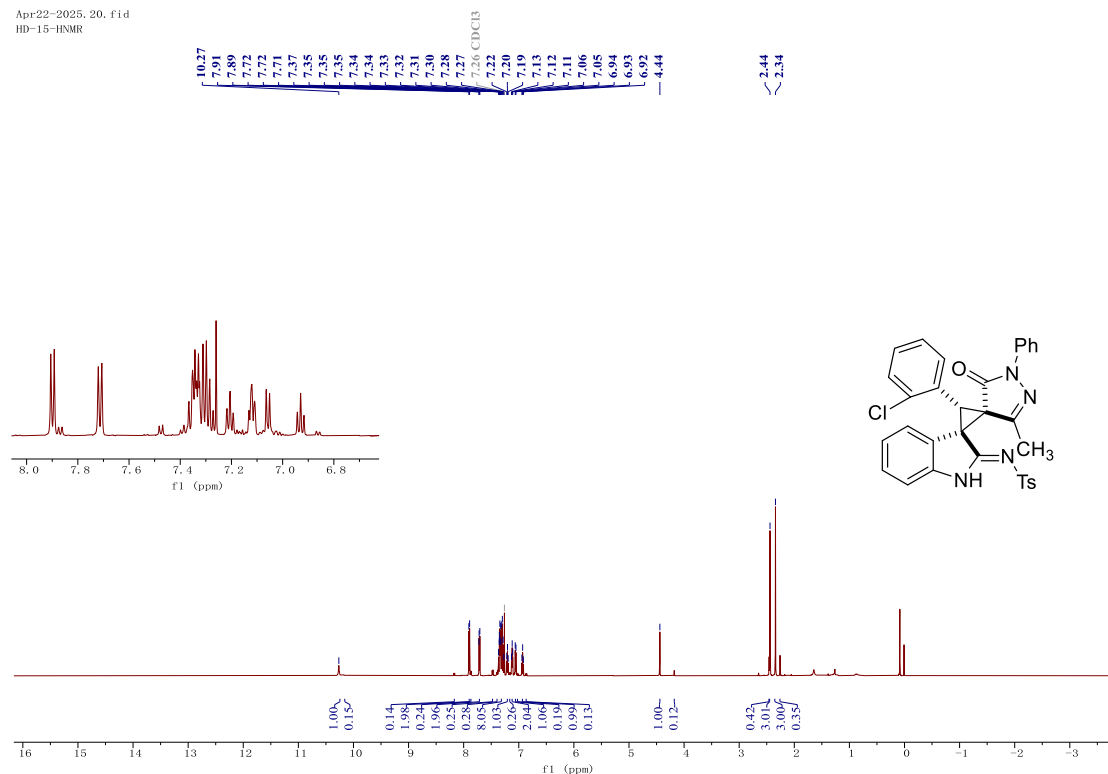
Jun12-2025, 10. fid  
HD-27-CNMR



3la

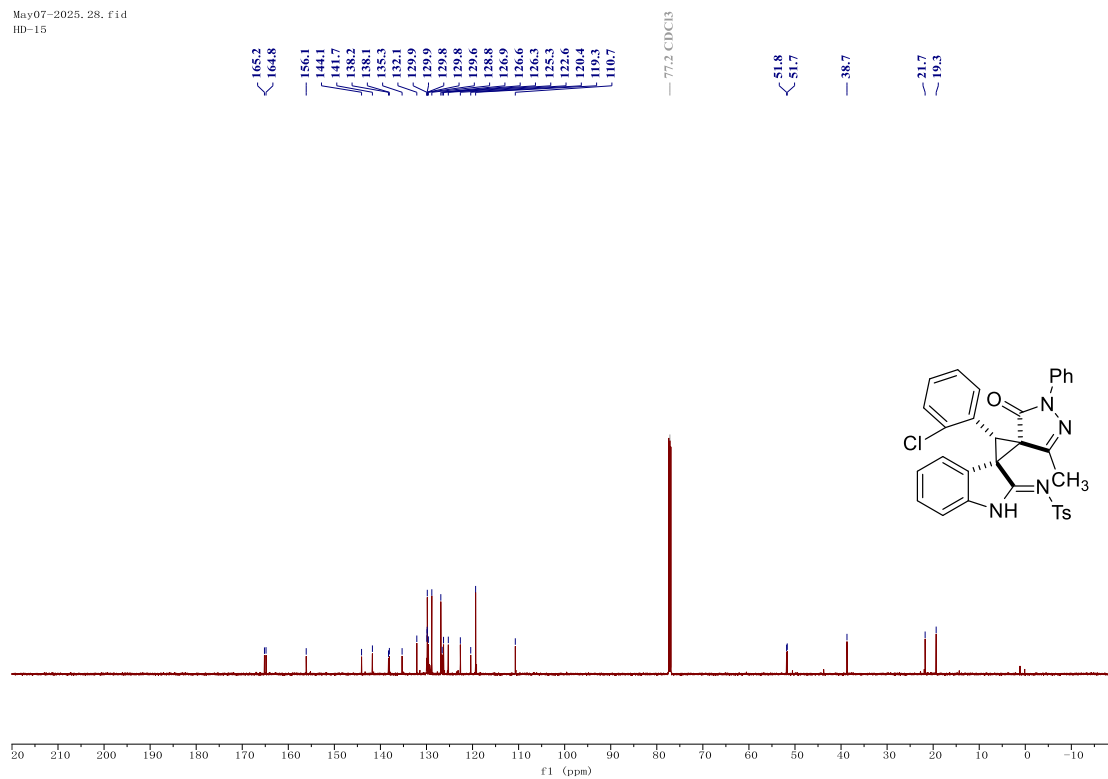
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)

Apr22-2025, 20, fid  
HD-15-HNMR



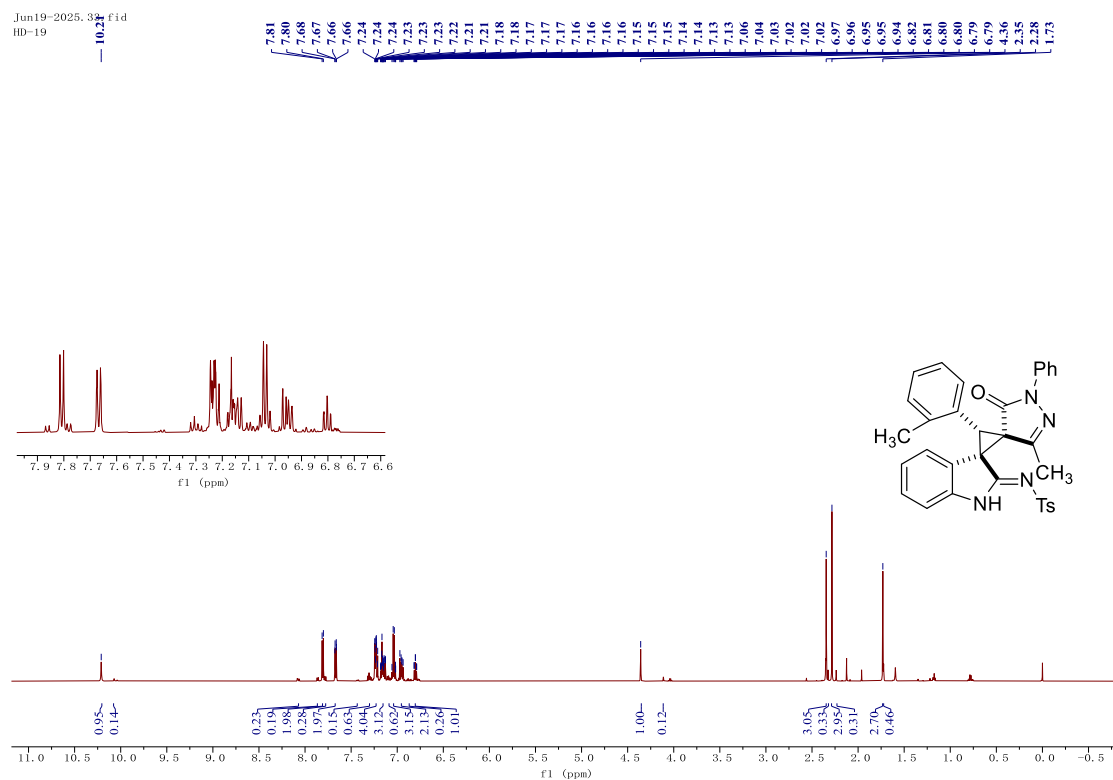
<sup>13</sup>C NMR (150 MHz, Chloroform-*d*)

May07-2025, 28, fid  
HD-15

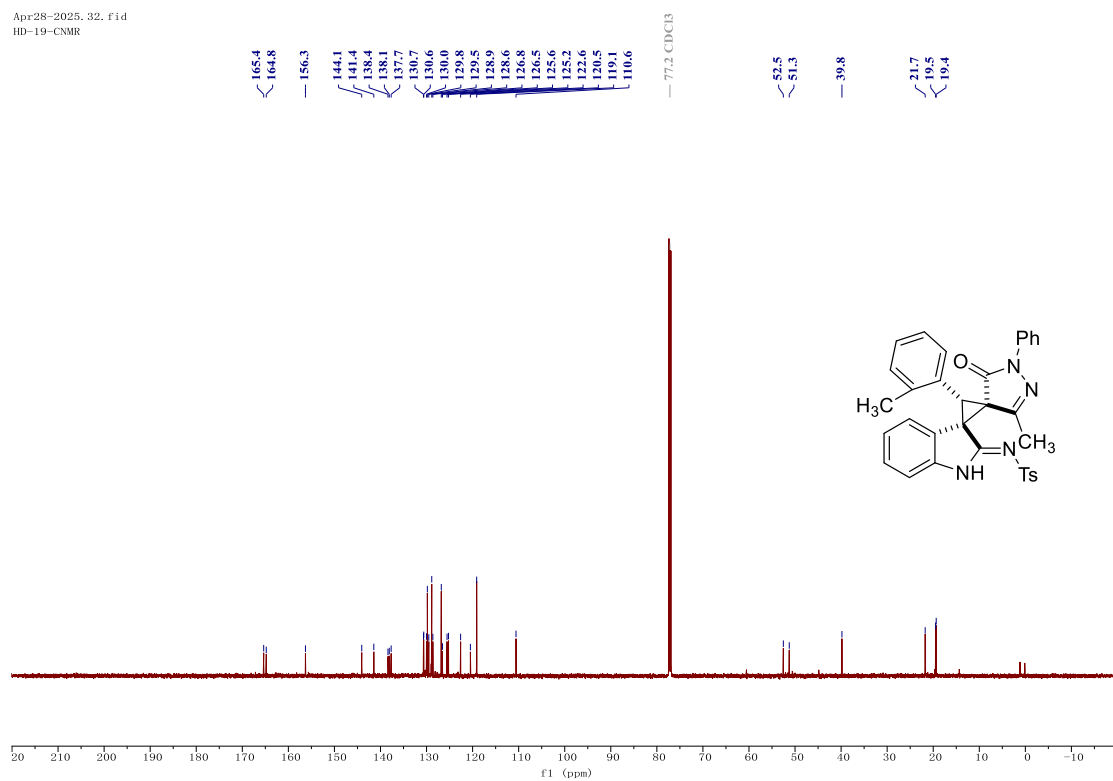


3ma

<sup>1</sup>H NMR (600 MHz, Chloroform-d)



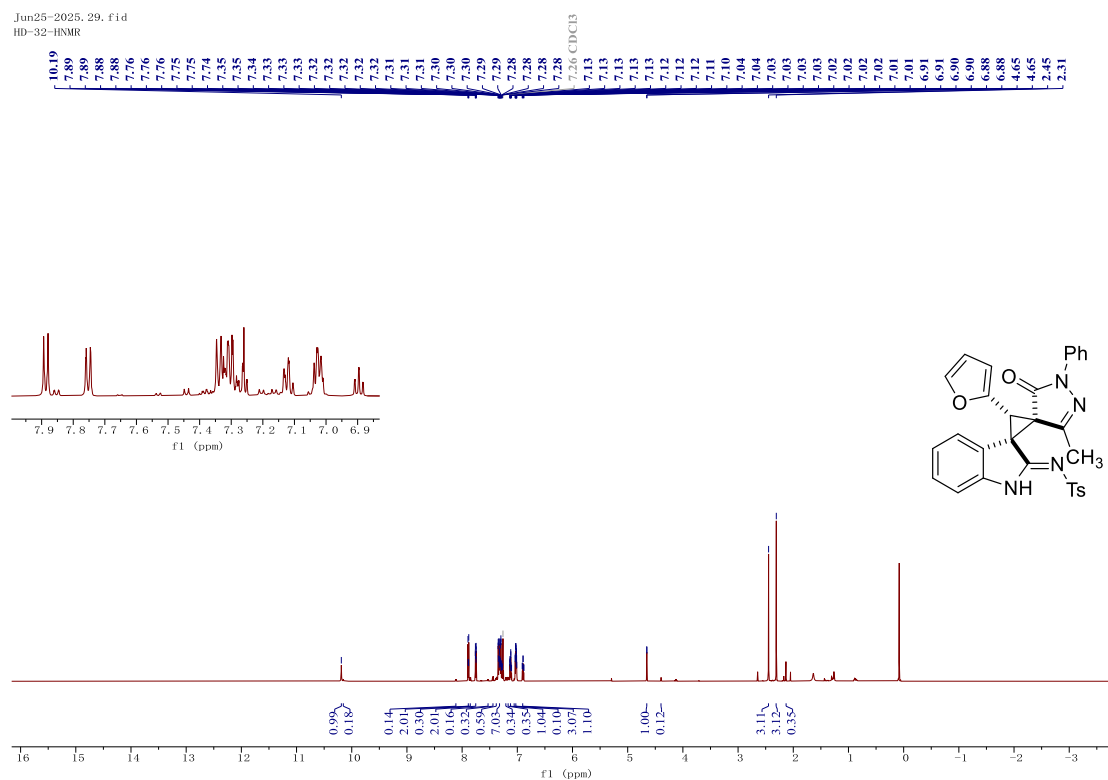
<sup>13</sup>C NMR (150 MHz, Chloroform-d)



### 3na

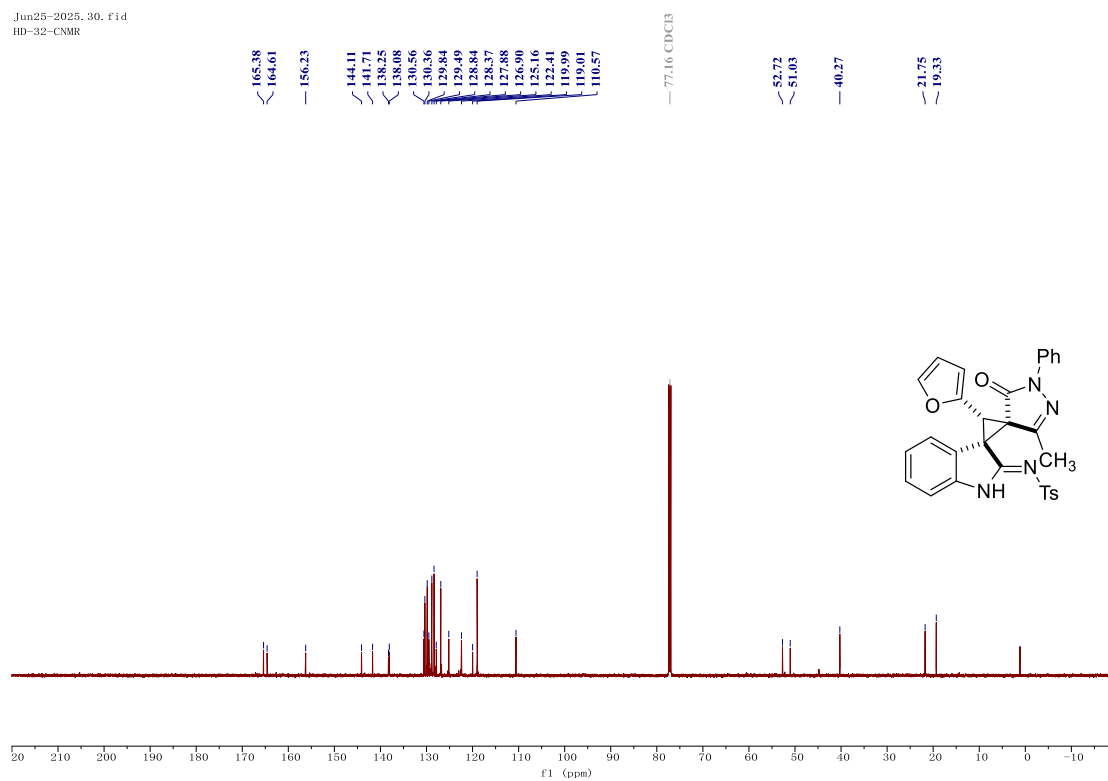
#### <sup>1</sup>H NMR (600 MHz, Chloroform-*d*)

Jun25-2025, 29. fid  
HD-32-<sup>1</sup>H-NMR



#### <sup>13</sup>C NMR (150 MHz, Chloroform-*d*)

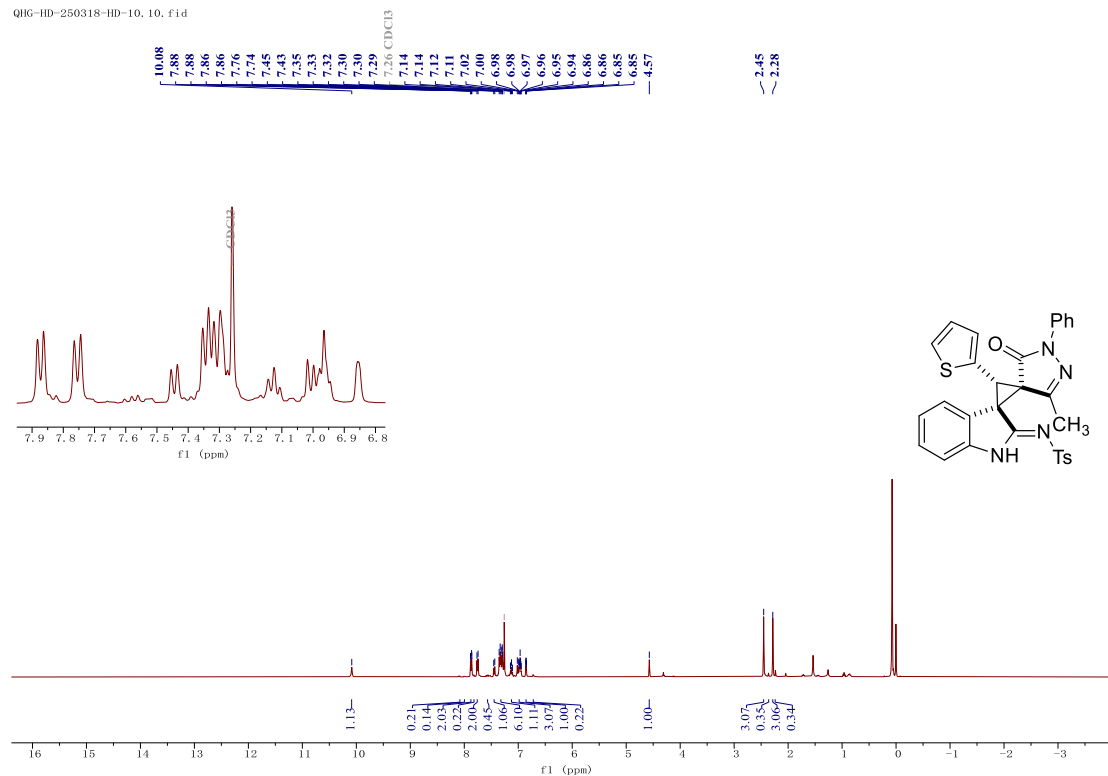
Jun25-2025, 30. fid  
HD-32-<sup>13</sup>C-NMR



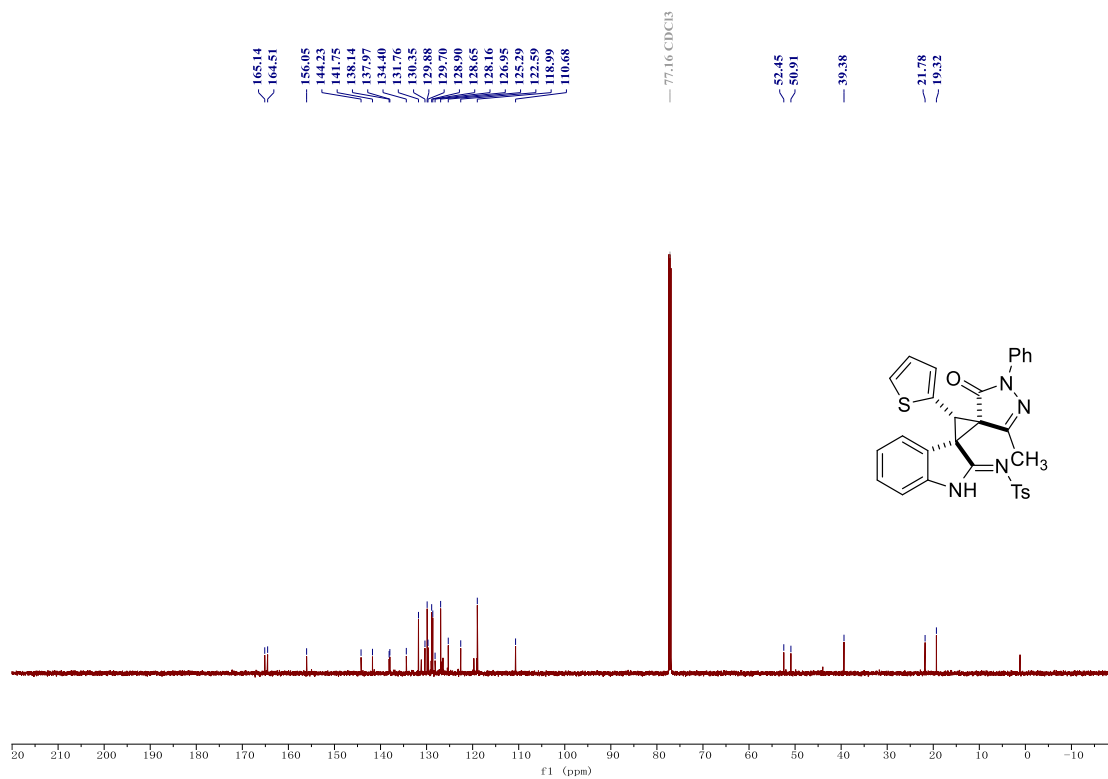
**30a**

**$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**

QMG-HD-250318-HD-10, 10, f1d



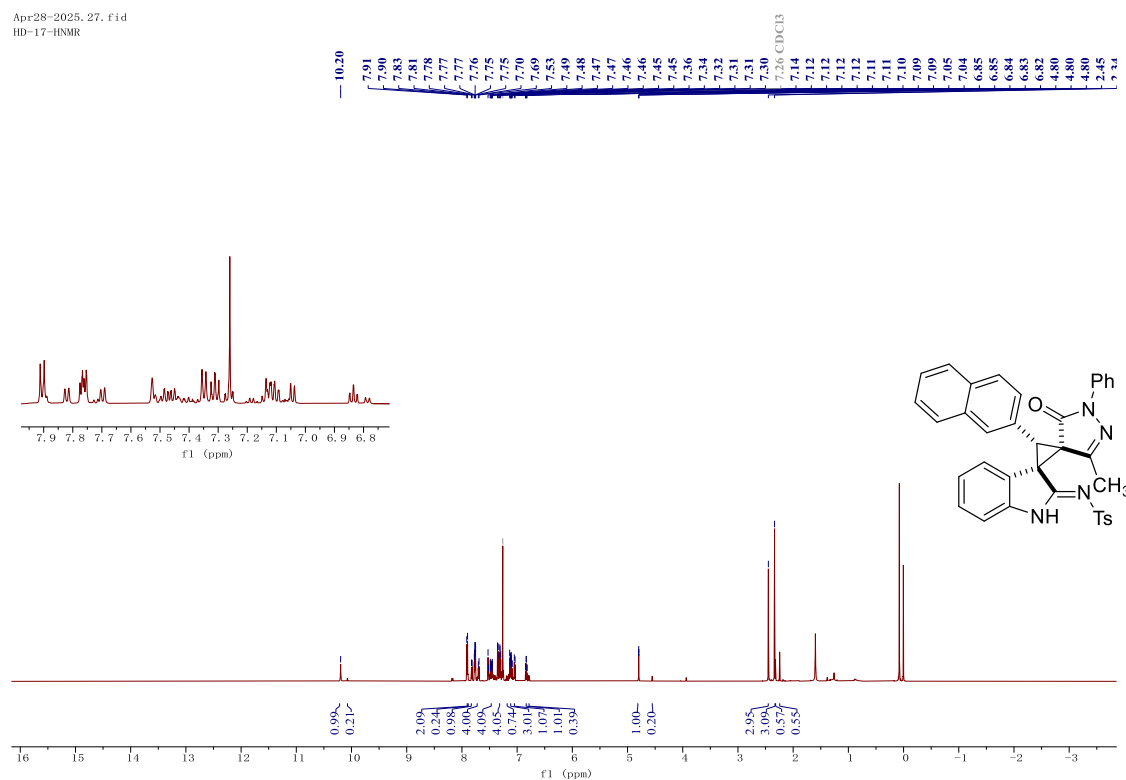
**$^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)**



3pa

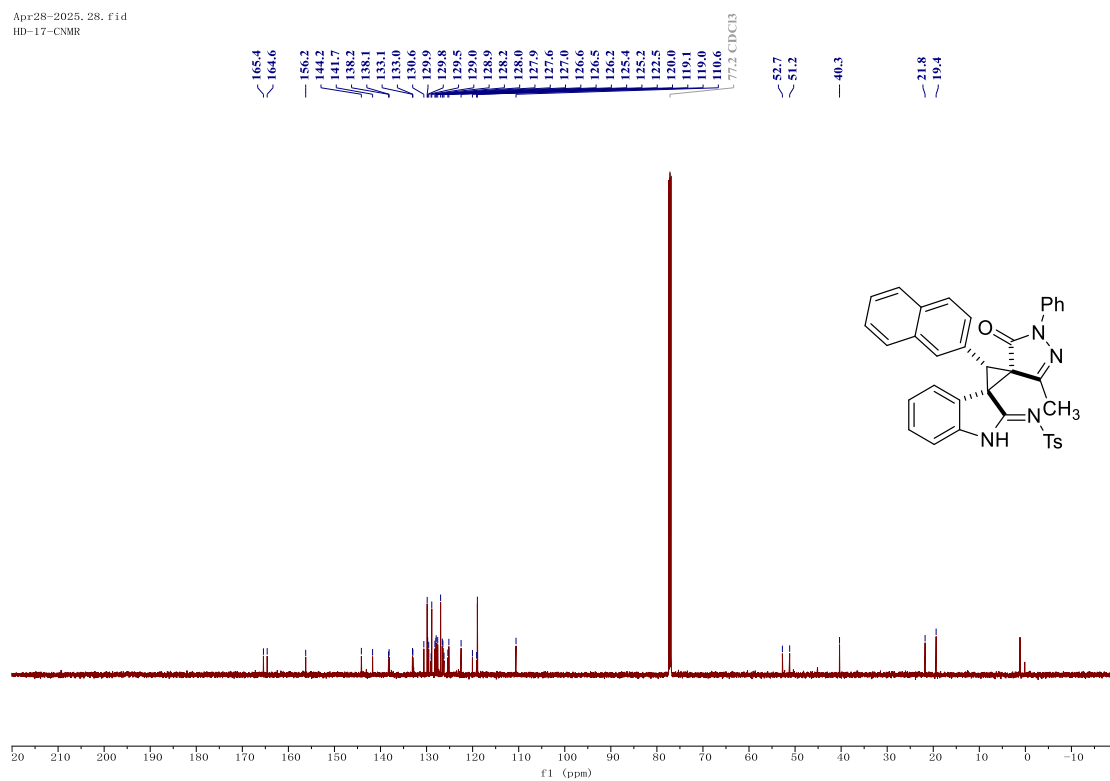
<sup>1</sup>H NMR (600 MHz, Chloroform-d)

Apr28-2025, 27, fid  
HD-17-HNMR



<sup>13</sup>C NMR (150 MHz, Chloroform-d)

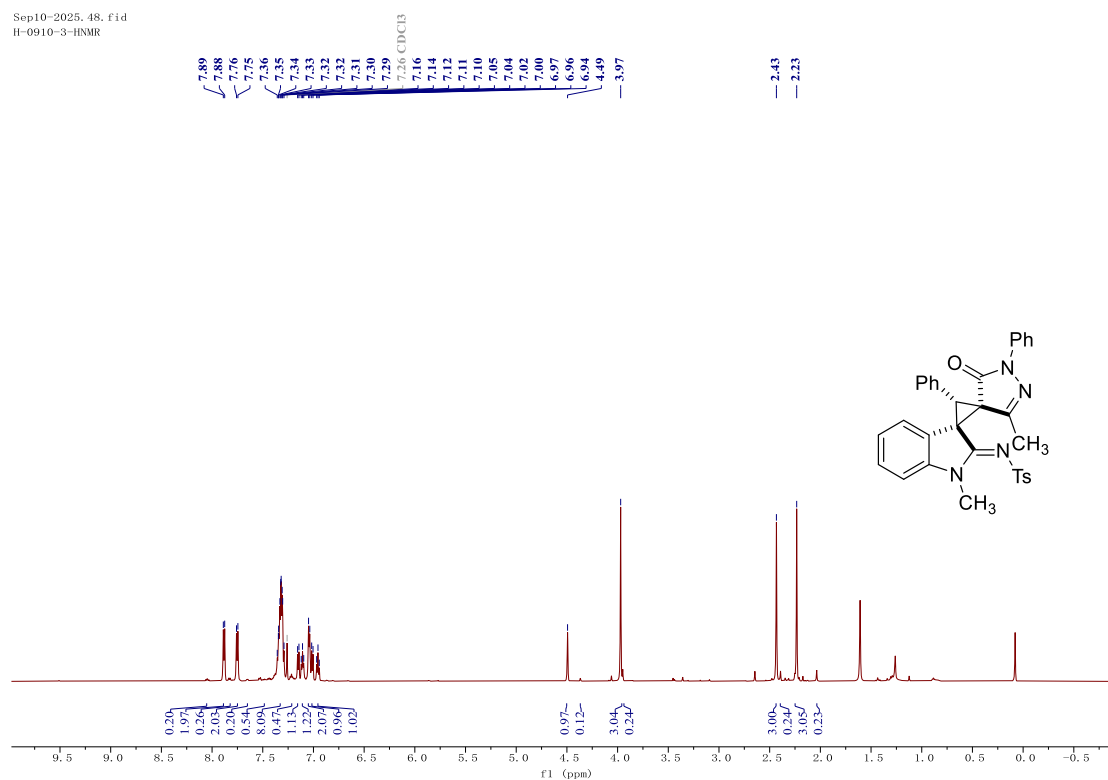
Apr28-2025, 28, fid  
HD-17-CNMR



### 3qa

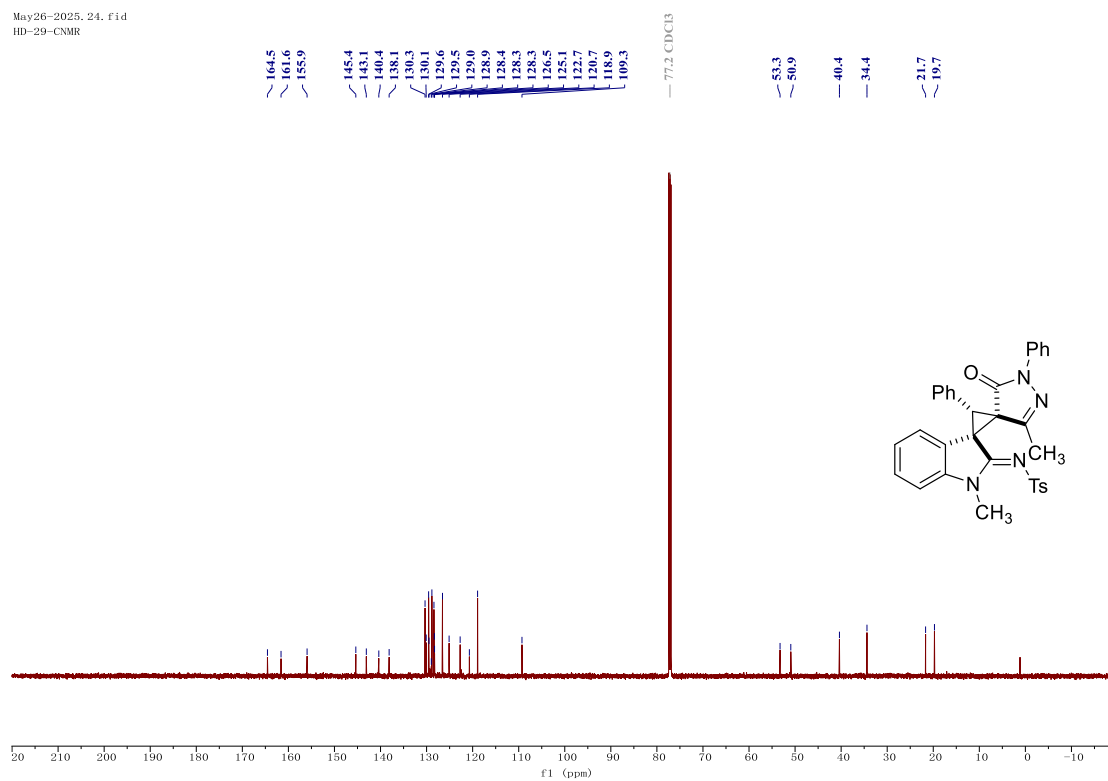
#### <sup>1</sup>H NMR (600 MHz, Chloroform-*d*)

Sep10-2025, 48, f1d  
H-0910-3-1H-NMR



#### <sup>13</sup>C NMR (150 MHz, Chloroform-*d*)

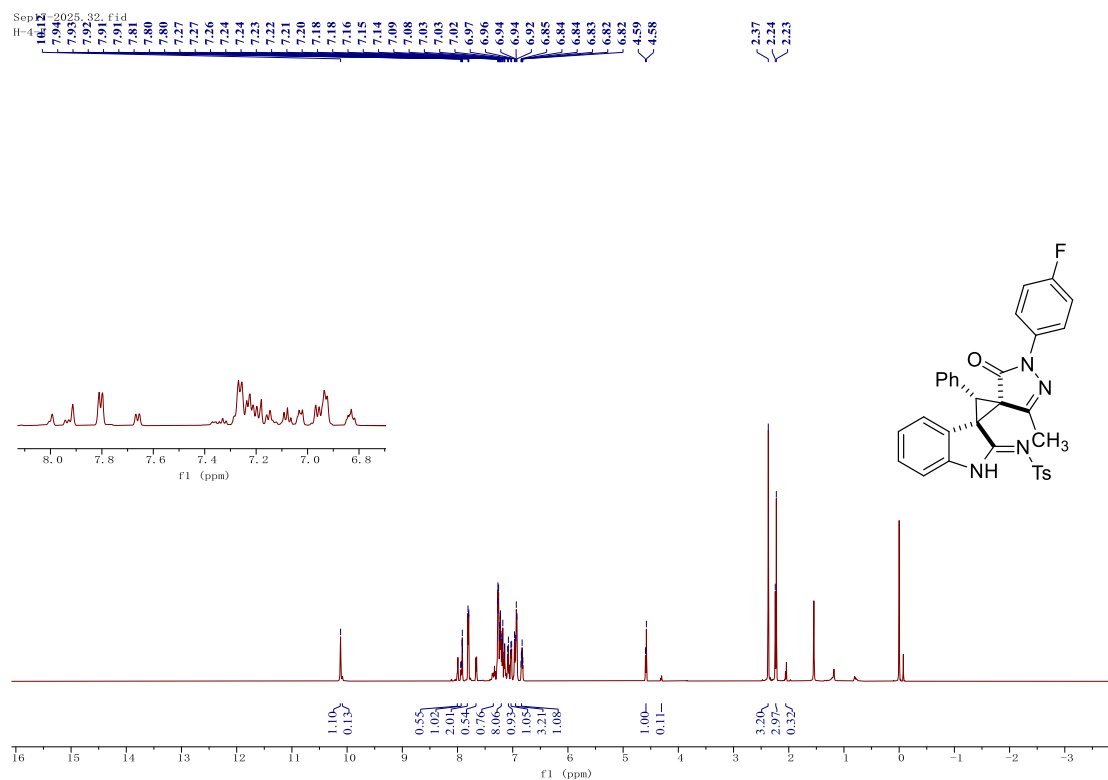
May26-2025, 24, f1d  
HD-29-13C-NMR



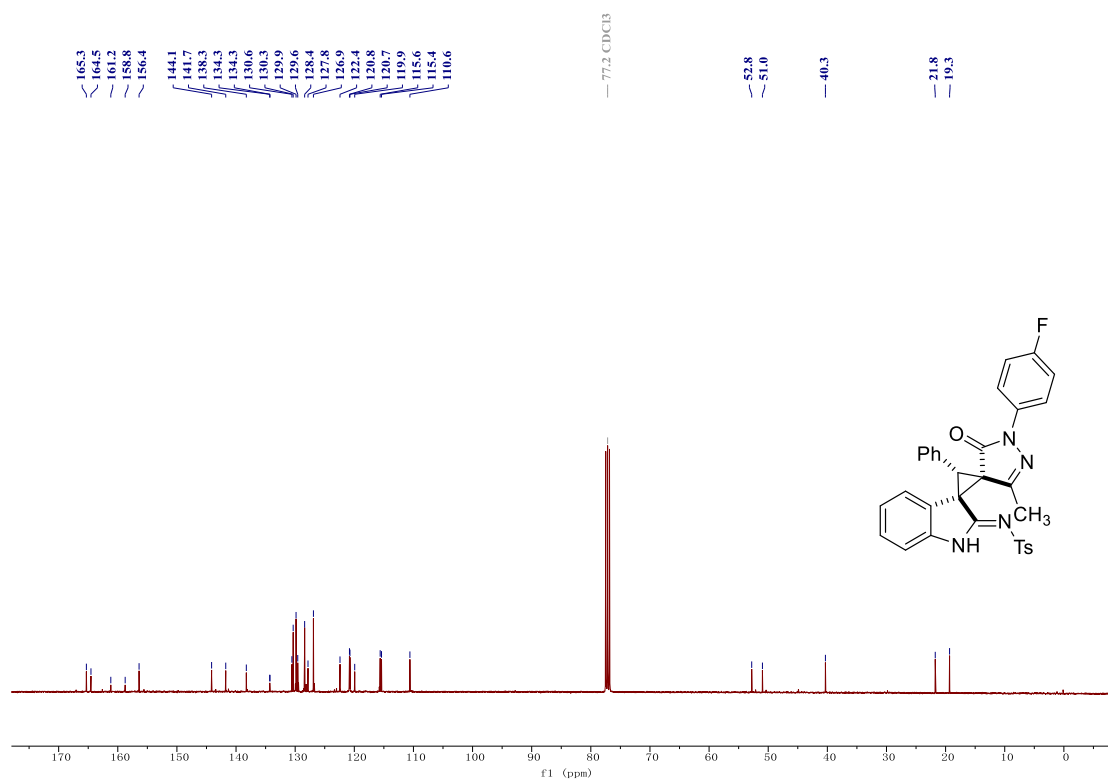


3ab

$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )



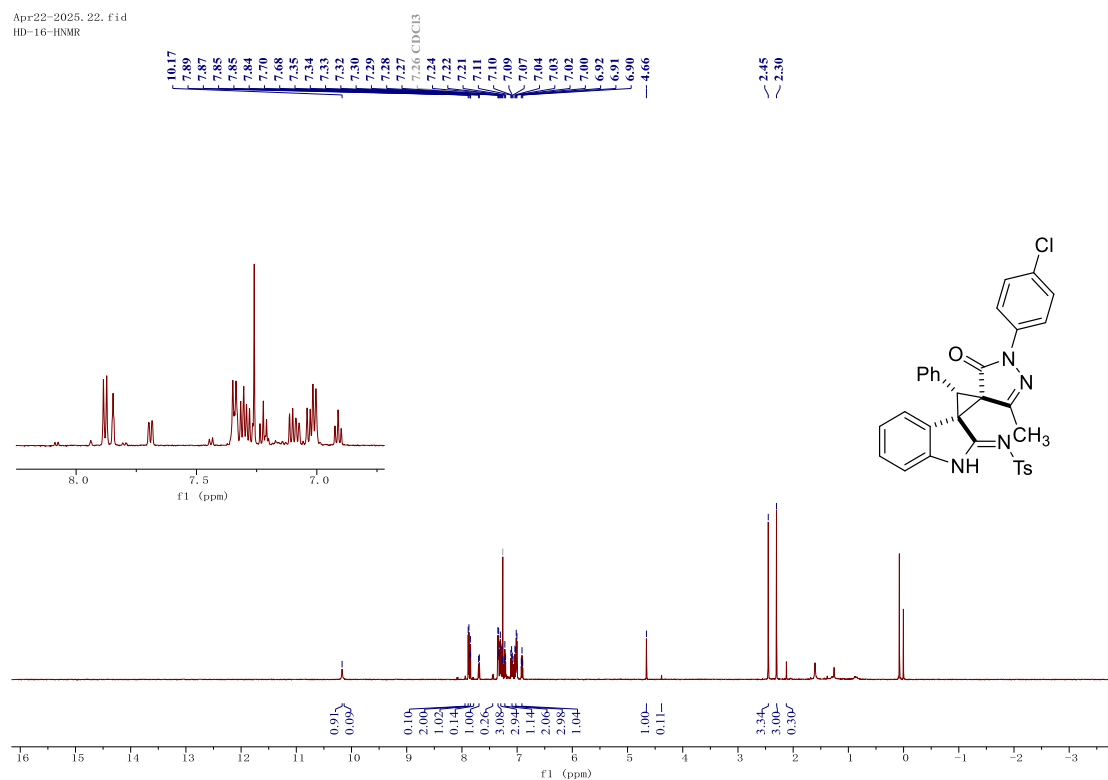
$^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )



**3ac**

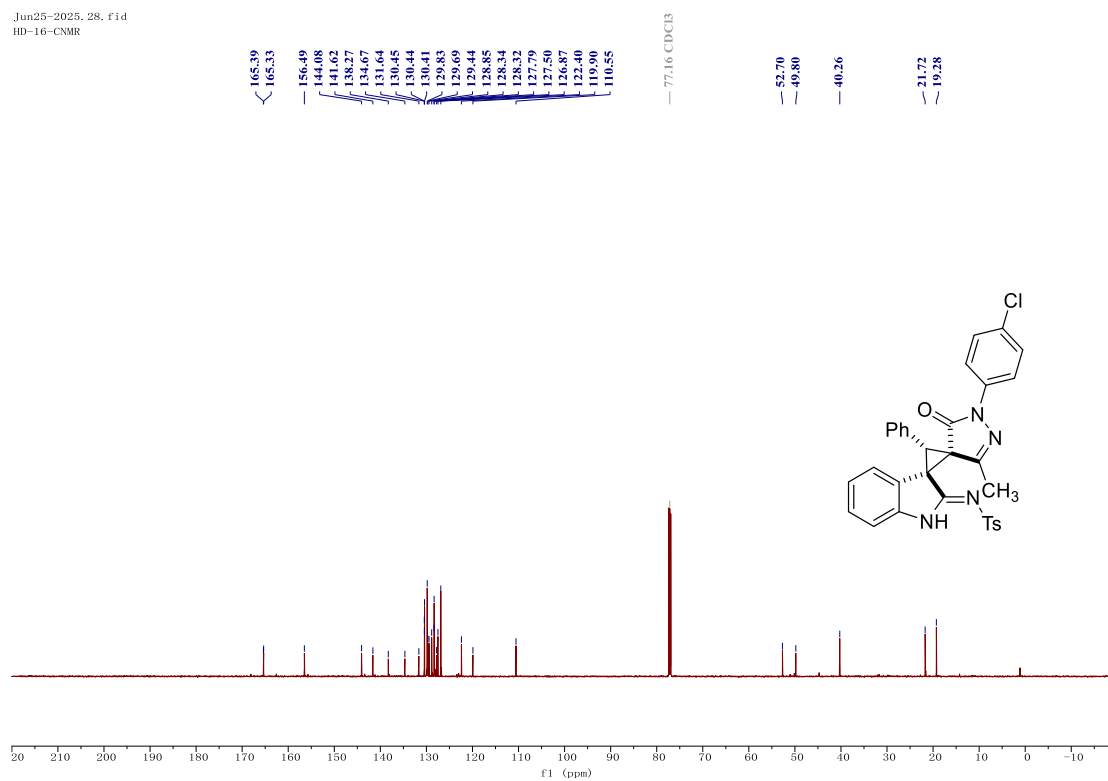
**<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)**

Apr22-2025, 22, fid  
HD-16-HNMR



**<sup>13</sup>C NMR (150 MHz, Chloroform-*d*)**

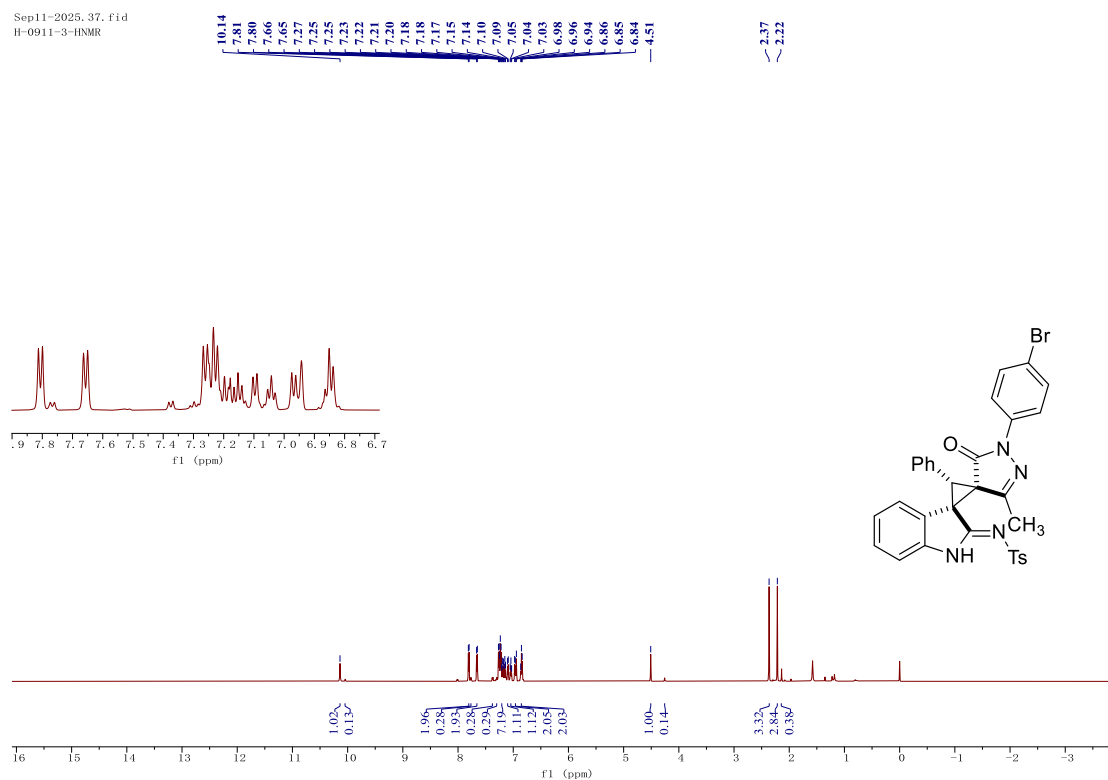
Jun25-2025, 28, fid  
HD-16-CNMR



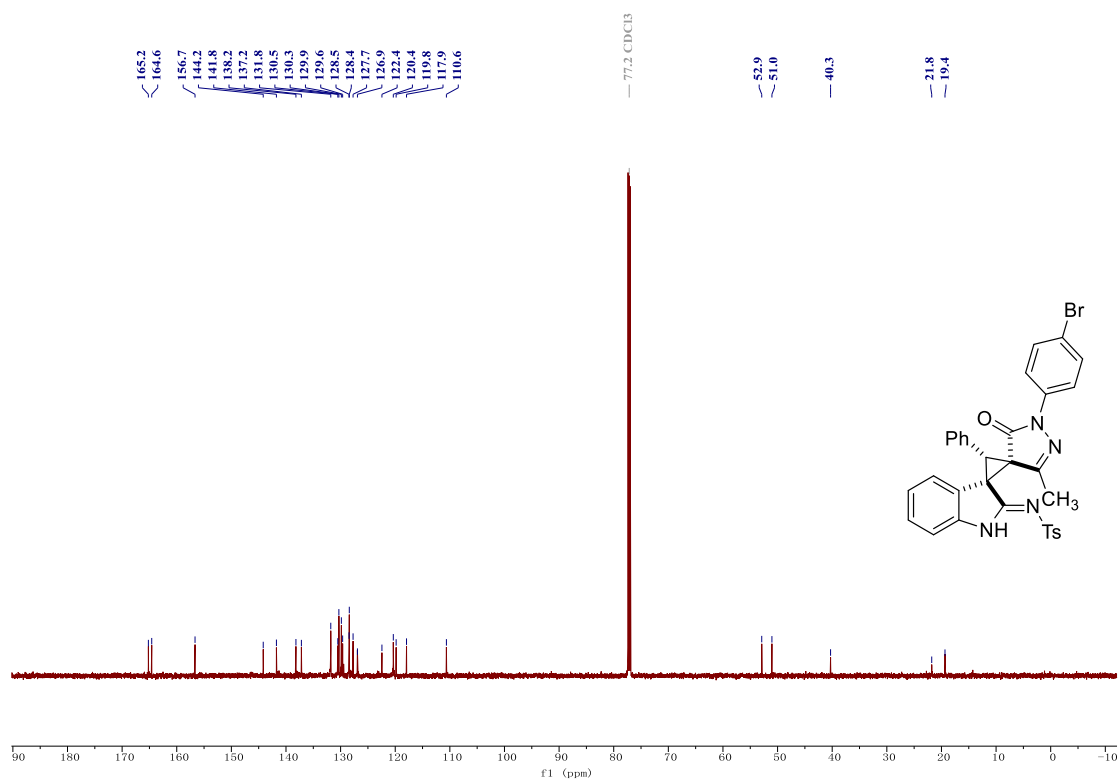
**3ad**

**<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)**

Sep11-2025, 37, fid  
H-0911-3-HNMR

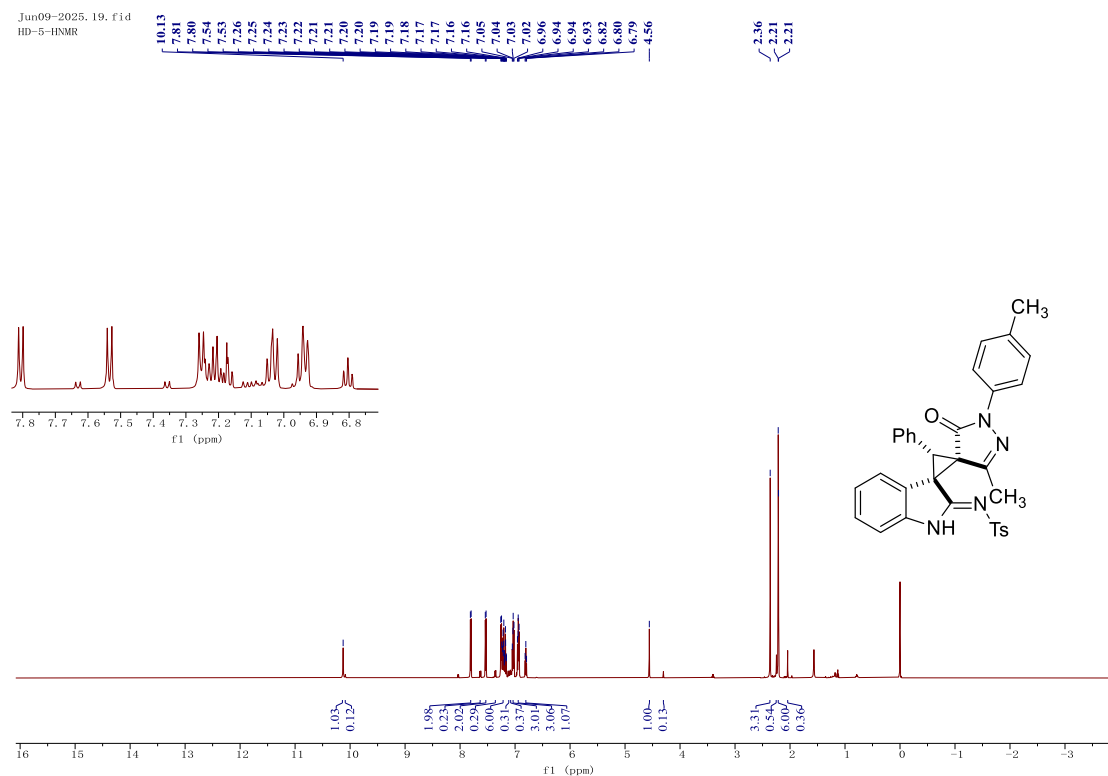


**<sup>13</sup>C NMR (150 MHz, Chloroform-*d*)**

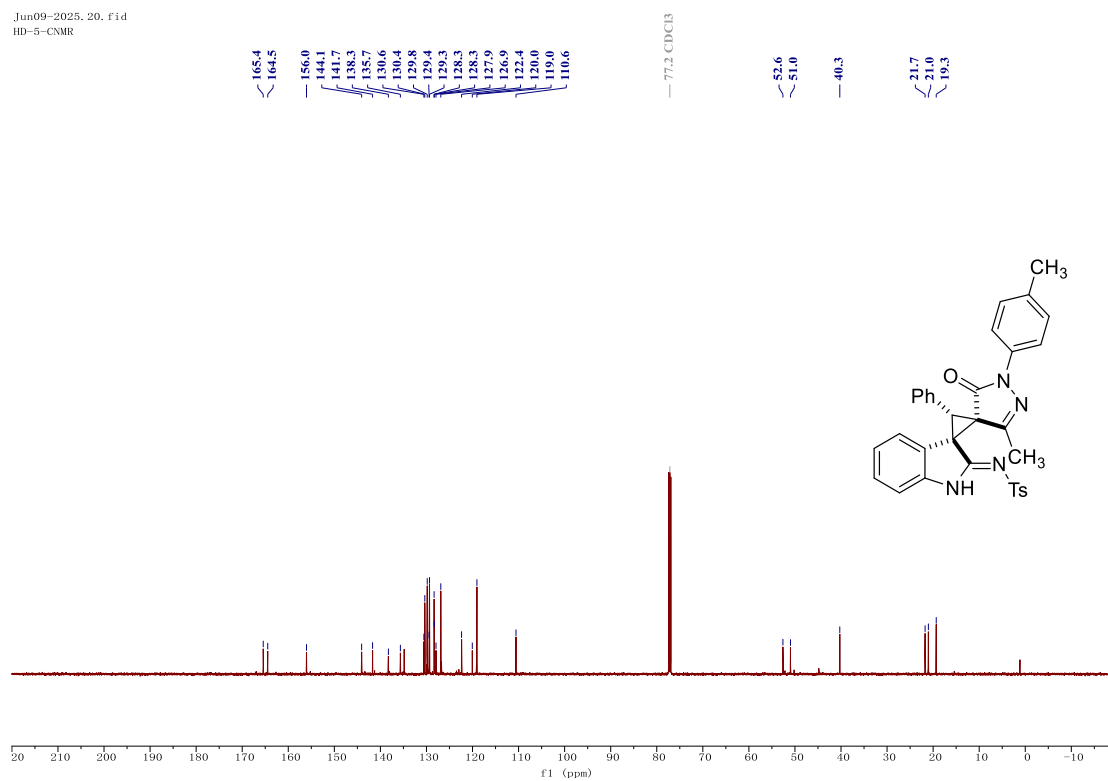


3ae

<sup>1</sup>H NMR (600 MHz, Chloroform-d)



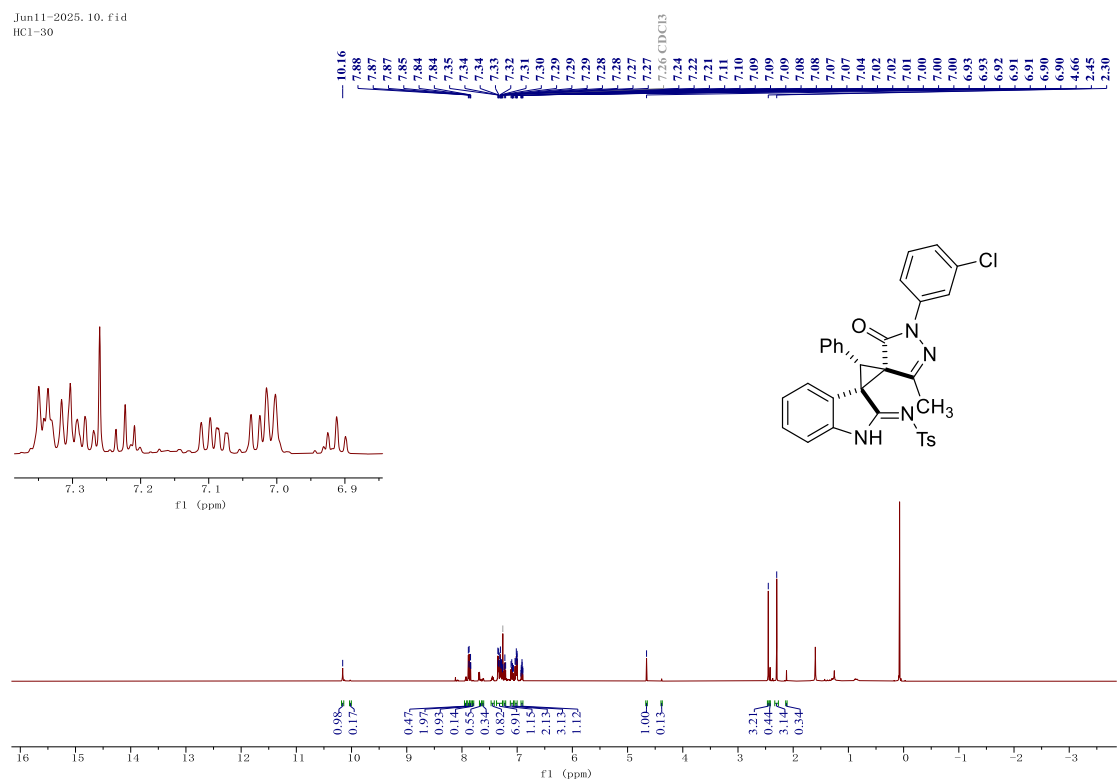
<sup>13</sup>C NMR (150 MHz, Chloroform-d)



**3af**

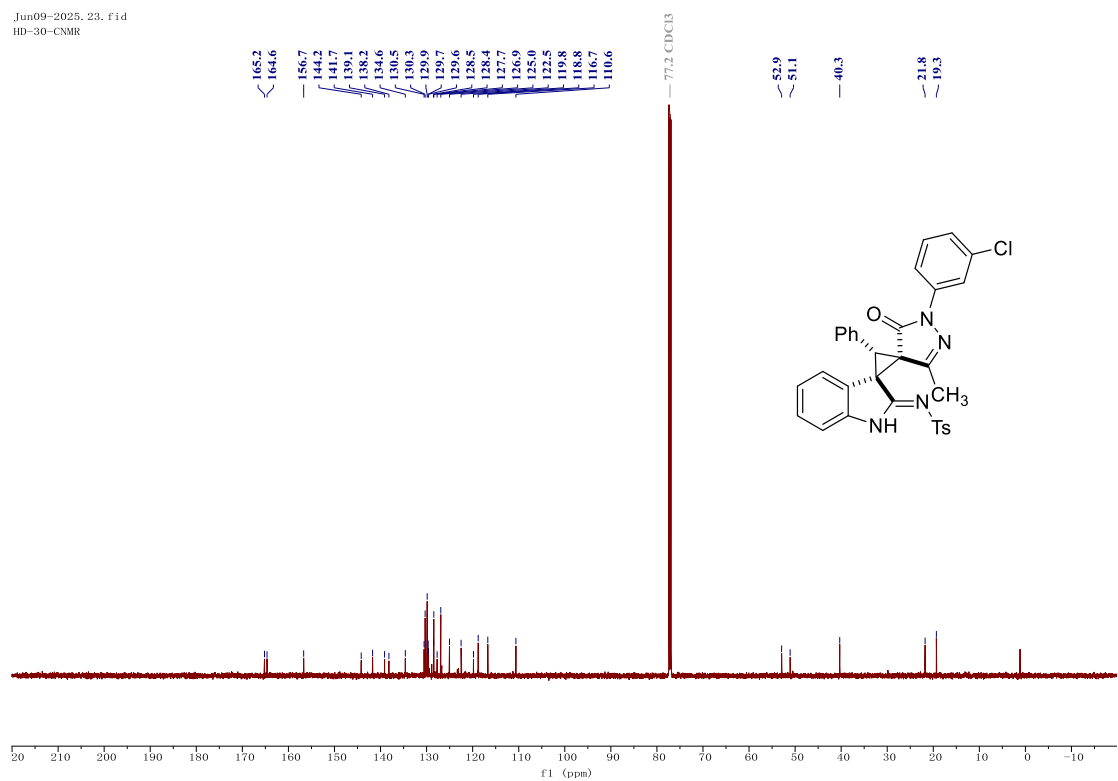
**$^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )**

Jun11-2025, 10. fid  
HC1-30



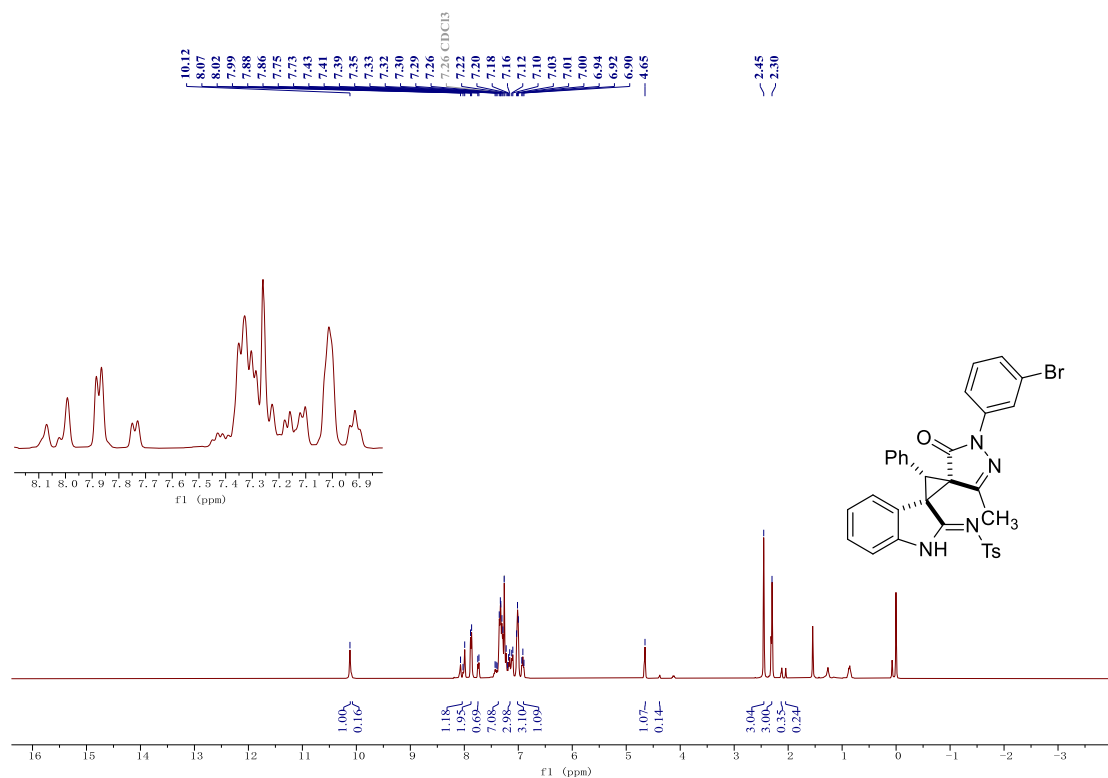
**$^{13}\text{C}$  NMR (150 MHz, Chloroform- $d$ )**

Jun09-2025, 23. fid  
HD-30-CNMR



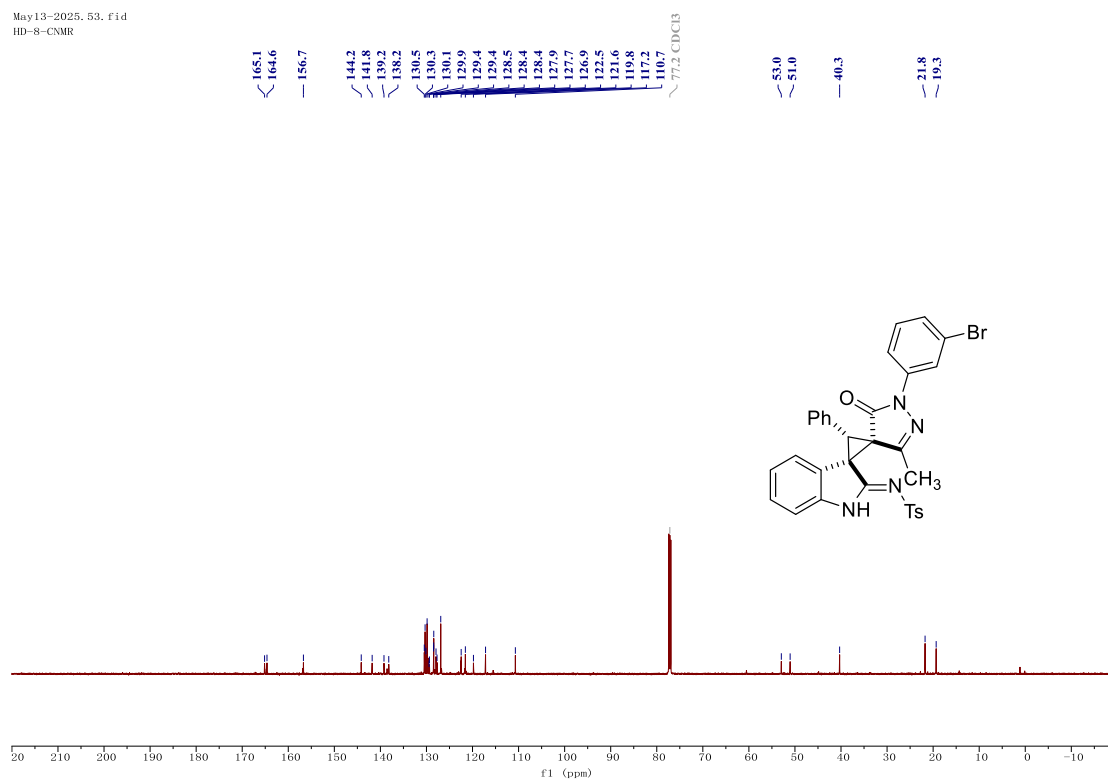
**3ag**

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**



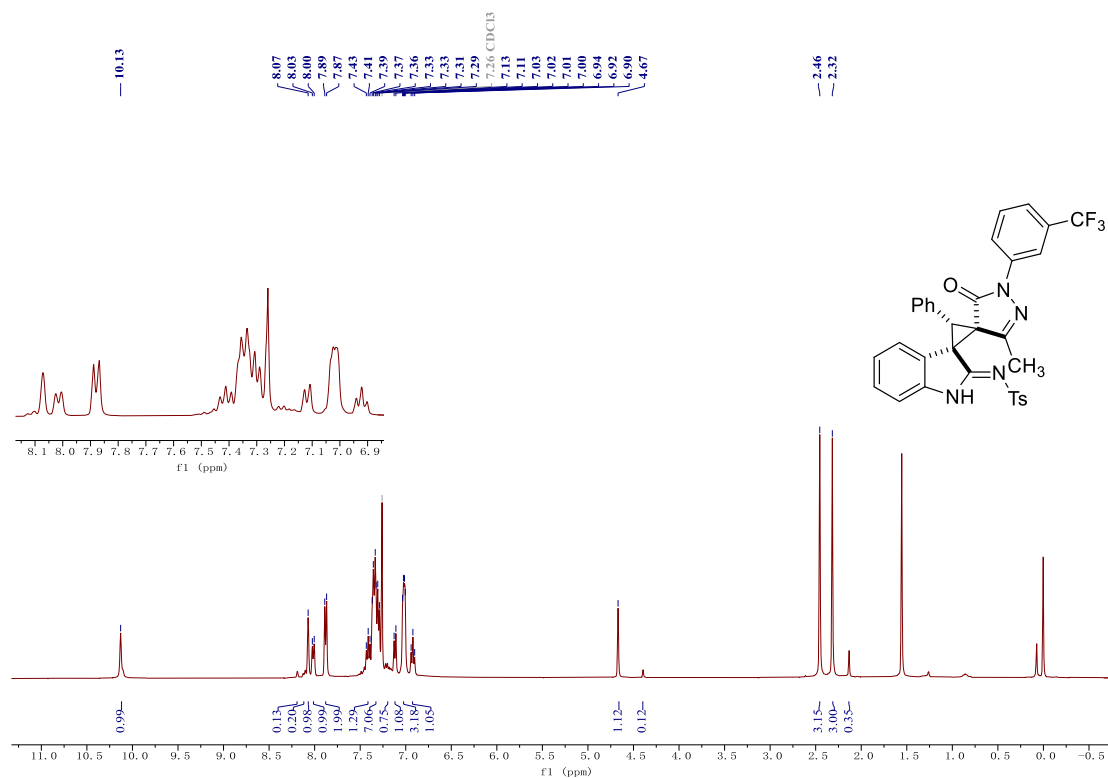
**<sup>13</sup>C NMR (150 MHz, Chloroform-*d*)**

May13-2025, 53, fid  
HD-8-CNMR



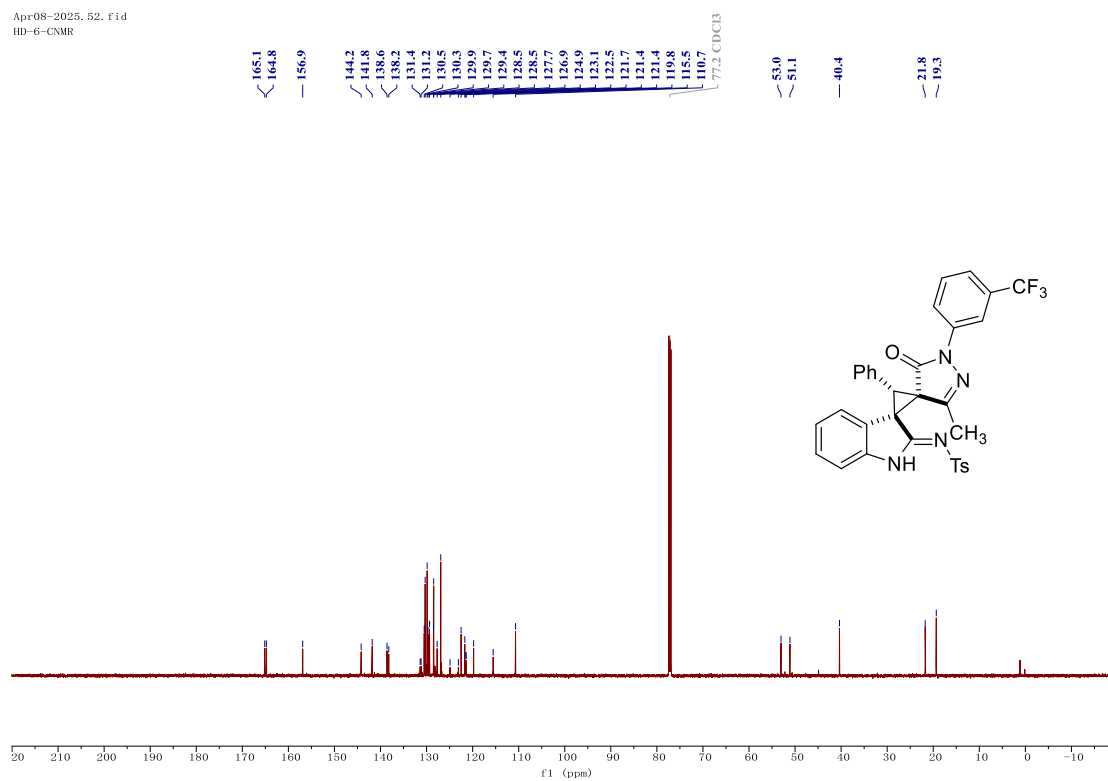
### 3ah

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)



$^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)

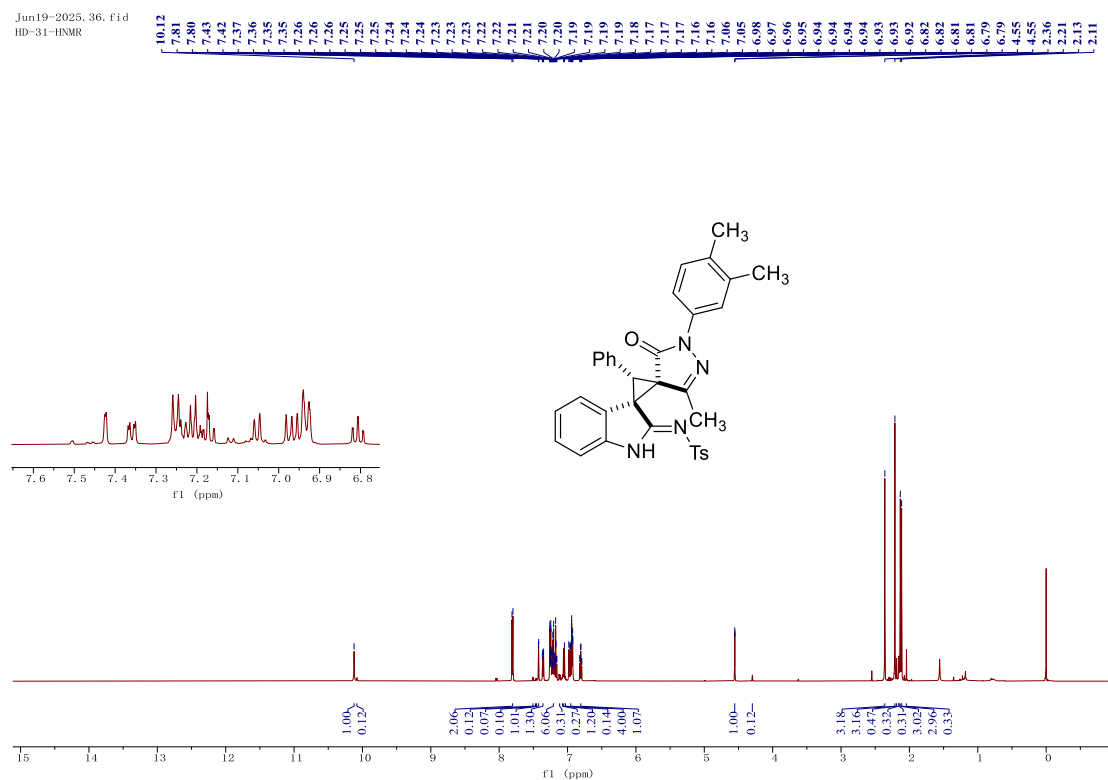
Apr08-2025, 52, fid  
HD-6-CNMR



3ai

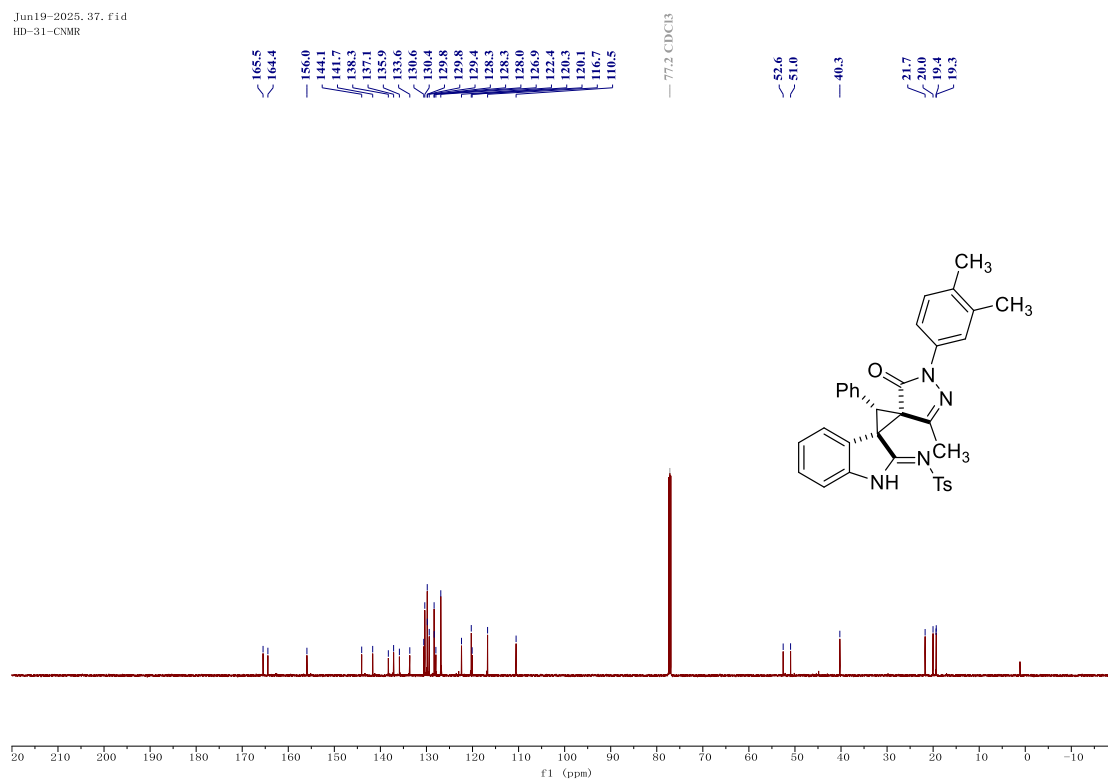
**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**

Jun19-2025, 36, fid  
HD-31-HNMR



**<sup>13</sup>C NMR (150 MHz, Chloroform-*d*)**

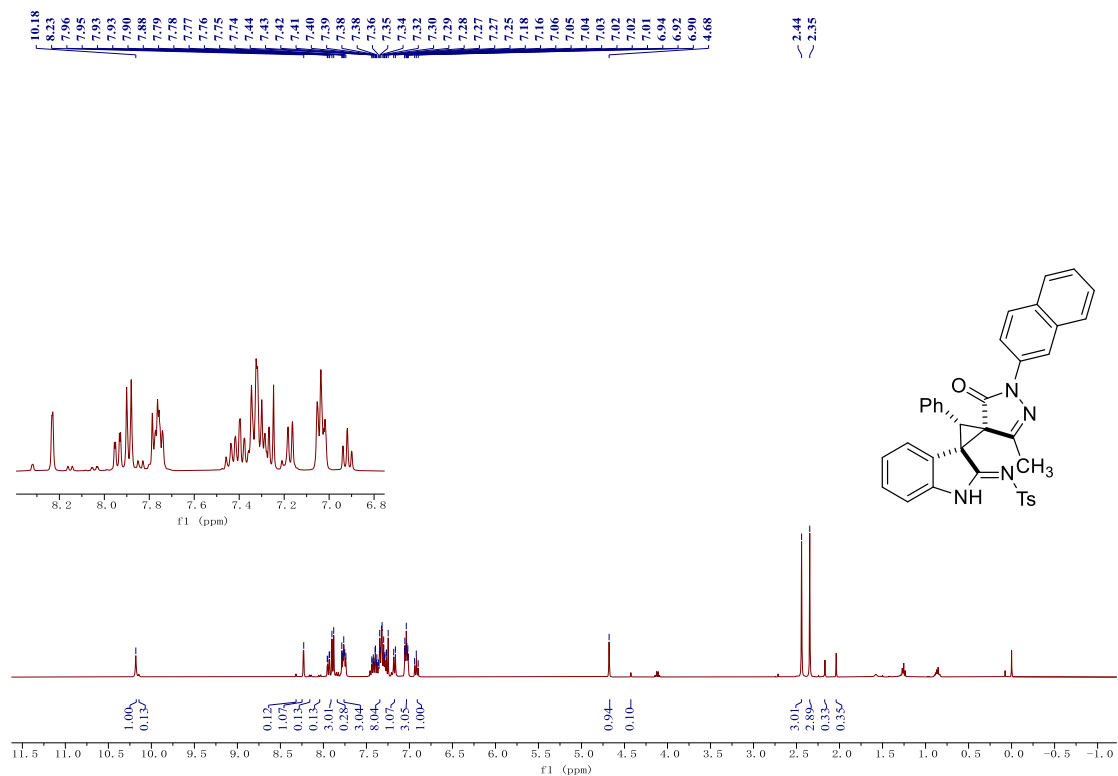
Jun19-2025, 37, fid  
HD-31-CNMR



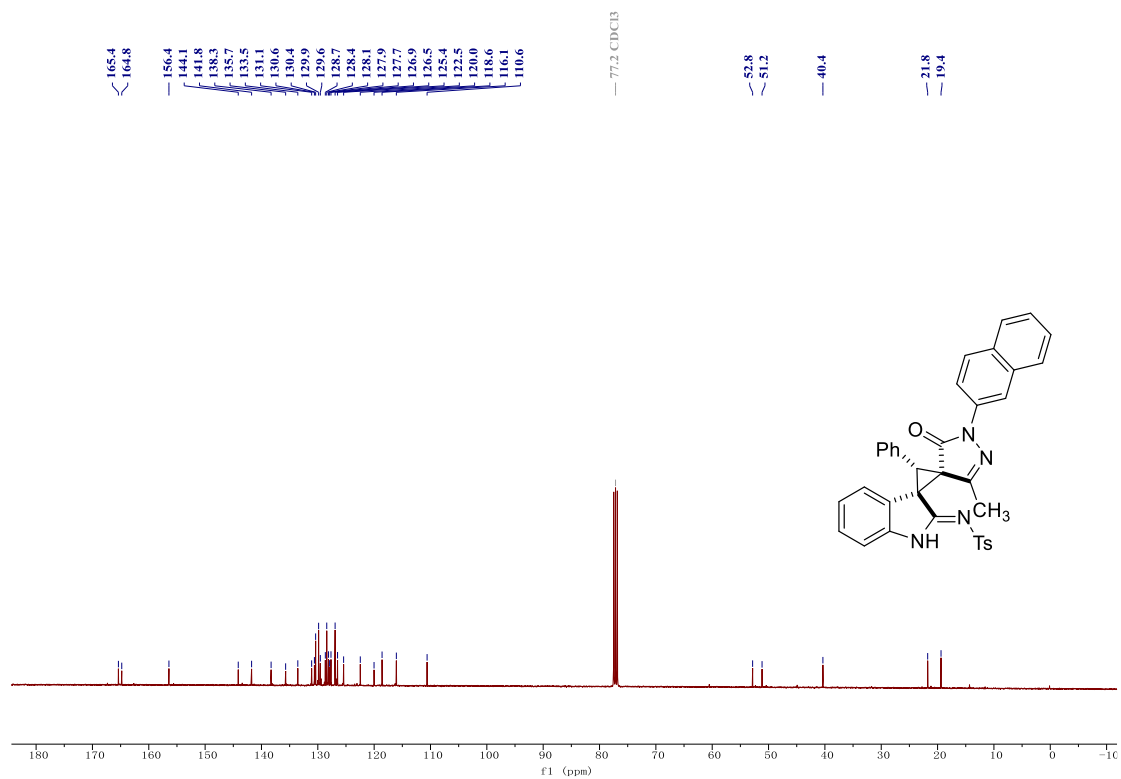


3aj

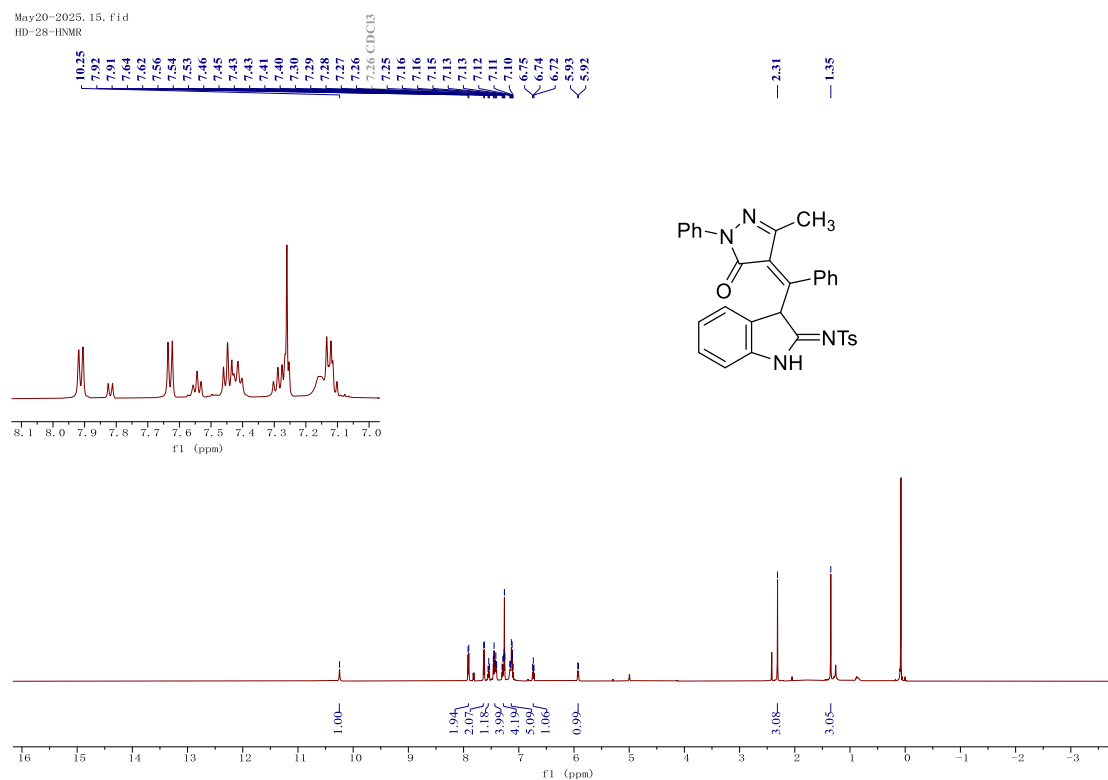
<sup>1</sup>H NMR (400 MHz, Chloroform-d)



<sup>13</sup>C NMR (100 MHz, Chloroform-d)



4

**<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)**May20-2025, 15, f1d  
HD-28-HNMR**<sup>13</sup>C NMR (150 MHz, Chloroform-*d*)**May20-2025, 16, f1d  
HD-28-CNMR