# Catalyst-controlled switchable [4+1], [4+3] and [3+2] domino reactions of azadiene and MBH carbonate: diverse synthesis of benzothiophene fused derivatives

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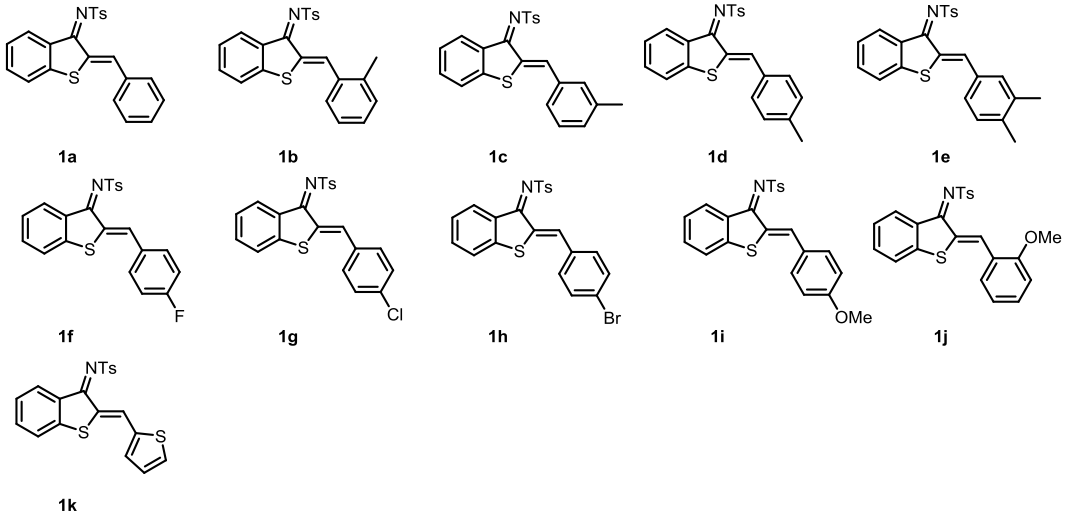
## 1. General information and materials

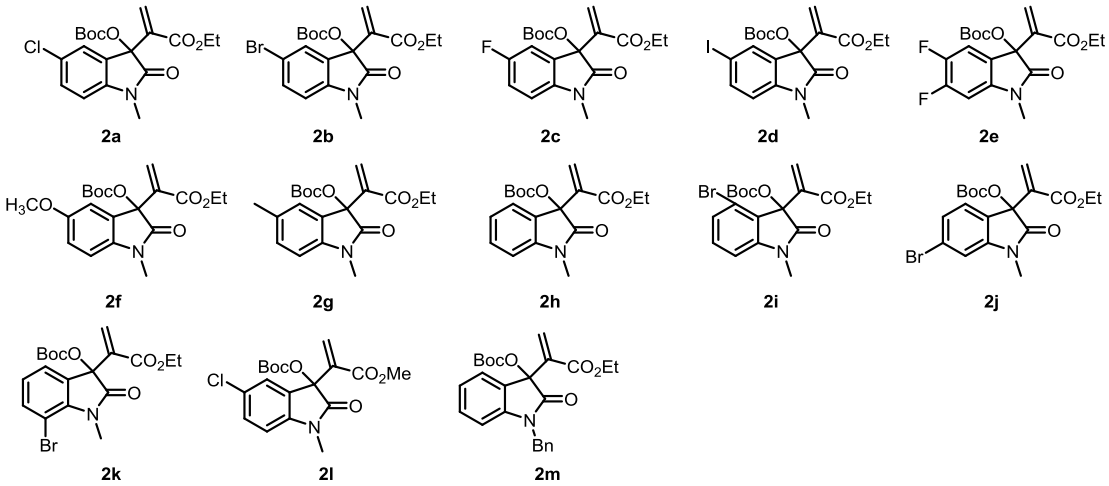
All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers (Aldrich, TCI or Alfa Aesar) and used without further purification. All solvents were purified and dried according to standard methods prior to use. TLC monitored all reactions with silica gel-coated plates. Flash column chromatography was performed using 200-300 mesh silica gel. $^{1}$H- and $^{13}$C NMR spectra were recorded at ambient temperature on Bruker 400 or 600 instruments. All spectra were referenced to $CDCl_3$ ($^{1}$H δ 7.26 ppm and $^{13}$C NMR δ 77.00 ppm). HRMS were obtained on Waters Xevo Q-TOF MS with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. IR was measured on a Perkin-Elmer 983G apparatus. Compound **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k** was synthesized according to the reported method[1, 2, 3] , and the synthesis method of **1j** are similar to **1a**. Compound **2a**, **2b**, **2c**, **2f**, **2g**, **2h**, **2l**, **2m**, **2n** was synthesized according to the reported method[4, 5, 6] , and the synthesis method of **2d**, **2e**, **2i**, **2j**, **2k** are similar to **2a**.

## 2. The structure of azadiene 1 and MBH carbonates 2

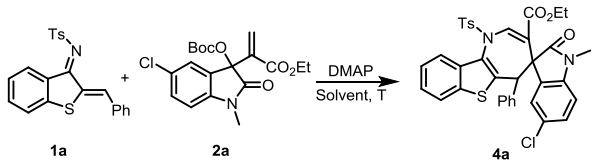
azadiene **1**




MBH carbonates **2**



**3. Table S1 Optimization of reaction conditions for product 4[a]**

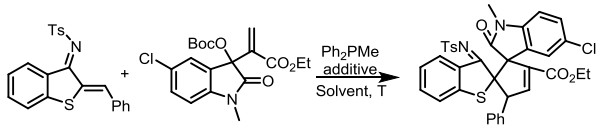



1a 2a 4a

| Solvent | **1a**:**2a**:DMAP | Time(min) | T(°C) | Yield/%[b] |
|---|---|---|---|---|
| THF | 1:2:0.25 | 10 | 67 | 28% |
| $CH_3CN$ | 1:2:0.25 | 10 | 67 | 40% |
| $CH_3CH_2OH$ | 1:2:0.25 | 10 | 67 | Trace |
| $CHCl_3$ | 1:2:0.25 | 5 | 67 | 26% |
| DCE | 1:2:0.25 | 5 | 67 | 23% |
| 1,4-dioxane | 1:2:0.25 | 6 | 67 | 30% |
| DMF | 1:2:0.25 | 10 | 67 | 54% |
| DMSO | 1:2:0.25 | 10 | 67 | 47% |
| $CH_3OH$ | 1:2:0.25 | 8 | 67 | 16% |
| Toluene | 1:2:0.25 | 3 h | 67 | 14% |
| DMF | 1:2:0.25 | 10 | 90 | 50% |
| DMF | 1:2:0.25 | 10 | 110 | 47% |
| DMF | 1:2:0.25 | 10 | 130 | 52% |
| DMF | 1:2:0.25 | 10 | 150 | 28% |
| DMF | 1:2.5:0.25 | 10 | 67 | 33% |
| DMF | 1:1.5:0.25 | 10 | 67 | 26% |
| DMF | 1:2:0.50 | 10 | 67 | 35% |
| DMF | 1:2:0.15 | 40 | 67 | 37% |

[a] Reaction conditions: **1a** (0.05 mmol), **2a** (0.15 mmol), DMAP (0.0125 mmol) in solvent (1 mL). [b] Isolated yields.

**4. Table S2 Optimization of reaction conditions for product 5[a]**




1a 2a 5a

| Entry | Solvent | Additive | Time | Yield/%[b] |
|---|---|---|---|---|
| 1 | toluene | benzoic acid | 10 min | 76% |
| 2 | THF | benzoic acid | 26 min | 45% |
| 3 | $CH_3CH_2OH$ | benzoic acid | 10 min | 22% |
| 4 | $CH_3CN$ | benzoic acid | 10 min | 40% |
| 5 | $CHCl_3$ | benzoic acid | 10 min | 84% |
| 6 | DCE | benzoic acid | 20 min | 65% |
| 7 | $CH_3OH$ | benzoic acid | 10 min | Trace |
| 8 | DMSO | benzoic acid | 10 min | Trace |
| 9 | dioxane | benzoic acid | 20 min | 77% |
| 10 | DMF | benzoic acid | 10 min | 28% |
| 11 | $CHCl_3$ | 4-(trifluoromethyl)benzoic acid | 30 min | 86% |
| 12 | $CHCl_3$ | ----- | 8 h | n.r |
| 13[c] | $CHCl_3$ | benzoic acid | 25 min | 70% |
| 14[d] | $CHCl_3$ | benzoic acid | 15 min | 82% |
| 15[e] | $CHCl_3$ | benzoic acid | 10 min | 92% |
| 16[f] | $CHCl_3$ | benzoic acid | 30 min | 92% |
| 17[g] | $CHCl_3$ | benzoic acid | 6 h | 91% |

[a] Reaction conditions: **1a** (0.05 mmol), **2a** (0.15 mmol), additive (0.0125 mmol) and $Ph_2PMe$ (0.0125 mmol) in solvent (1 mL) at 60 ℃. [b]Isolated yields. [c] **1a**:**2a**:additive:$Ph_2PMe$= 1.0:3.0:0.25:0.25. [d] **1a**:**2a**:additive:$Ph_2PMe$ = 1.0:3.5:0.25:0.25. [e] **1a**:**2a**:additive:$Ph_2PMe$ = 1.0:3.0:0.25:0.50. [f] **1a**:**2a**:additive:$Ph_2PMe$ = 1.0:3.0:0.25:0.15. [g] Reaction temperature is room temperature.

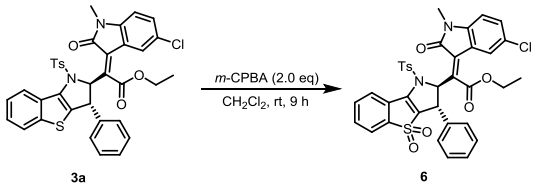
**5. Procedure for gram-scale reaction of 3a, 4a and 5a**

Under Ar atmosphere, to a $CH_3CN$ (20 mL) solution of **1a** (391.5 mg, 1.0 mmol) and **2a** (989.6 mg, 2.5 mmol) was added DABCO (28.0 mg, 0.25 mmol) at 67 °C. After completion of the reaction (monitored by TLC), the solvent is evaporated in vacuo. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to obtain **3a** (176 mg, 26%) as a yellow solid.

Under Ar atmosphere, to a DMF (20 mL) solution of **1a** (391.5 mg, 1.0 mmol) and **2a** (791.7 mg, 2.0 mmol) was added DMAP (30.5 mg, 0.25 mmol) at 67 °C. After completion of the reaction (monitored by TLC), remove the solvent by distillation under reduced pressure. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to obtain **4a** (317 mg, 47%) as a white solid.

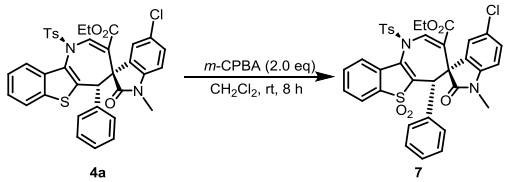
Under Ar atmosphere, to a $CHCl_3$ (20 mL) of **1a** (391.5 mg, 0.10 mmol) and **2a** (1187.5 mg, 3.0 mmol) was added benzoic acid (30.5 mg, 0.25 mmol) and $Ph_2PMe$ (27.8 ul, 0.15 mmol) at room temperature. After completion the reaction (monitored by TLC), the reaction mixture was evaporated in vacuo to remove the solvent. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to obtain **5a** (465 mg, 69%) as a yellow solid.

**6. Synthetic procedure for 6, 7, 8, 9 and 10**



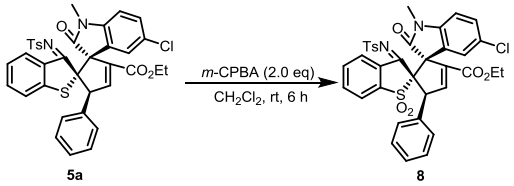

3a 6

Under Ar atmosphere, to a solution of **3a** (53.54 mg, 0.08 mmol) in DCM 2 mL was added *m*-CPBA (27.61 mg, 0.16 mmol). The reaction mixture was stirred at room temperature for 9 hours. After the reaction completed (monitored by TLC), the solvent was removed in vacuum. The reside was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to give **6** (24 mg, 42%) as a yellow solid.



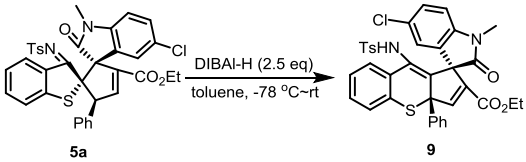

4a 7

Under Ar atmosphere, to a solution of **4a** (53.54 mg, 0.08 mmol) in $CH_2Cl_2$ 2 mL was added *m*-CPBA (27.61 mg, 0.16 mmol). The reaction mixture was stirred at room temperature for 8 hours. After the reaction complete (monitored by TLC), the solvent was removed in vacuum. The reside was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to give **7** (39 mg, 69%) as a white solid.



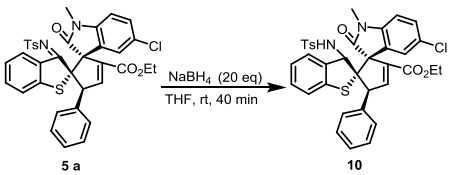

5a 8

Under Ar atmosphere, to a solution of **5a** (53.54 mg, 0.08 mmol) in $CH_2Cl_2$ 2 mL was added *m*-CPBA (27.61 mg, 0.16 mmol). The reaction mixture was stirred at room temperature for 6 hours. After the reaction complete (monitored by TLC), the solvent was removed in vacuum. The reside was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to give **8** (20 mg, 36%) as a yellow solid.




5a 9

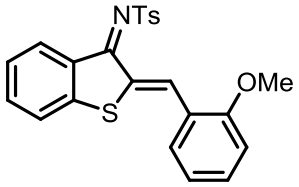
Under Ar atmosphere, to a solution of **5a** (53.54mg, 0.08 mmol) in toluene 2 mL was added DIBAl-H (2.5 M in toluene) 0.8 mL. The reaction mixture was stirred at -78 °C for 30 minutes, then move to room temperature and react for 3 days. After the reaction completed (monitored by TLC), quench with a small amount of water, the combined aqueous layers were extracted with $CH_2Cl_2$ (20 mL × 4). The combined organic layers were dried over $MgSO_4$ and concentrated. The reside was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to give **9** (33 mg, 62%) as a white solid.




5 a 10

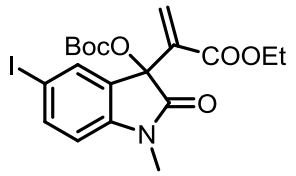
Under Ar atmosphere, to a solution of **5a** (53.54 mg, 0.08 mmol) in THF 2 mL was added $NaBH_4$ (60.53 mg, 1.6 mmol). The reaction mixture was stirred at room temperature for 40 min. After the reaction completed (monitored by TLC), quench with a small amount of water, the solvent was removed in vacuum, then the combined aqueous layers were extracted with $CH_2Cl_2$ (20 mL × 4). The combined organic layers were dried over $MgSO_4$ and concentrated. The reside was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to give **10** (22 mg, 40%) as a white solid.

**7. Characterization of all new compounds**



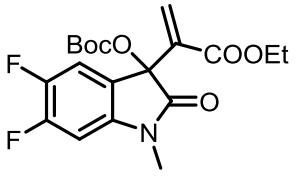

**N-((Z)-2-((Z)-2-methoxybenzylidene)benzo[b]thiophen-3(2H)-ylidene)-4-methylbenzenesulfonamide (1j)**

Red solid: 310 mg (yield 10%); mp 162-164 ℃; IR (KBr) 2927, 1608, 1512, 1288, 1136, 739, 557 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.0 Hz, 1H), 8.68 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.31 (m, 4H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 2.46 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.4, 159.2, 147.7, 142.8, 140.3, 135.1, 132.4, 132.3, 132.1, 131.9, 130.2, 129.3, 129.0, 126.7, 125.6, 123.9, 123.3, 120.9, 111.0, 55.8, 21.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{23}H_{20}NO_3S_2^+$ 422.0879, found 422.0905.




**Ethyl 2-(3-((tert-butoxycarbonyl)oxy)-5-iodo-1-methyl-2-oxoindolin-3-yl)acrylate (2d)**

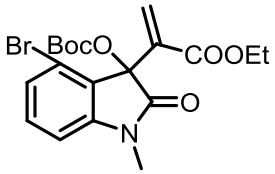
White solid: 1.33 g (yield 53%); mp 163-165 ℃; IR (KBr) 2981, 1753, 1727, 1606, 1259, 976, 671 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 6.65 – 6.59 (m, 2H), 6.53 (s, 1H), 4.07 – 3.94 (m, 2H), 3.25 (s, 3H), 1.36 (s, 9H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.1, 163.4, 149.8, 145.7, 139.2, 136.2, 131.9, 129.1, 128.9, 110.3, 84.4, 83.8, 79.1, 61.2, 27.6, 26.8, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{19}H_{23}INO_6^+$ 488.0565, found 488.0553.




**Ethyl 2-(3-((tert-butoxycarbonyl)oxy)-5,6-difluoro-1-methyl-2-oxoindolin-3-yl)acrylate (2e)**

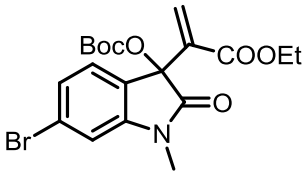
White solid: 1.27 g (yield 47%); mp 123-125 ℃; IR (KBr) 2986, 1735, 1627, 1514, 1254, 774, 619 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.02 (m, 1H, 6.67 (dd, J = 10.0, 6.4 Hz, 1H), 6.60 (s, 1H), 6.51 (s, 1H), 4.09 – 3.96 (m, 2H), 3.25 (s, 3H), 1.37 (s, 9H), 1.15 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR

(100 MHz, $CDCl_3$) δ 172.49, 163.41, 151.8 (d, J = 248.2 Hz), 151.7 (d, J = 248.1 Hz), 149.84, 147.6 (d, J = 13.5 Hz), 145.1 (d, J = 13.4 Hz), 142.60 (d, J = 2.3 Hz), 142.5 (d, J = 2.2 Hz), 135.99, 129.12, 113.5 (d, J = 1.1 Hz), 113.3 (d, J = 1.0 Hz), 98.7 (d, J = 23.2 Hz), 83.9, 79.1, 61.2, 27.6, 27.0, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{19}H_{22}F_2NO_6^+$ 398.1410, found 398.1412.



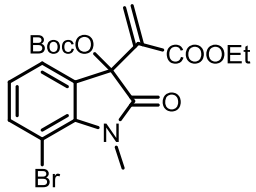

**Ethyl 2-(4-bromo-3-((tert-butoxycarbonyl)oxy)-1-methyl-2-oxoindolin-3-yl)acrylate (2i)**

White solid: 1.3 g (yield 50%); mp 121-123 °C; IR (KBr) 2984, 1748, 1715, 1612, 1287, 983, 725 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 1.6 Hz, 1H), 6.59 (s, 1H), 6.52 (s, 1H), 4.08 – 3.91 (m, 2H), 3.27 (s, 3H), 1.36 (s, 9H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.5, 163.5, 149.9, 147.2, 136.2, 128.8, 125.6, 125.2, 124.5, 124.3, 111.9, 83.7, 79.2, 6.14, 27.6, 26.8, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{19}H_{23}BrNO_6^+$ 440.0703, found 440.0696.



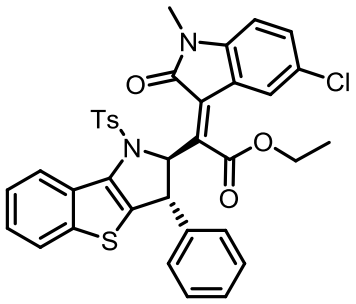

**Ethyl 2-(6-bromo-3-((tert-butoxycarbonyl)oxy)-1-methyl-2-oxoindolin-3-yl)acrylate (2j)**

White solid: 1.41 g (yield 54%); mp 119-121 ℃; IR (KBr) 2984, 1747, 1716, 1611, 1288, 983, 726, 568 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 1.2 Hz, 1H), 6.58 (s, 1H), 6.52 (s, 1H), 4.08 – 3.92 (m, 2H), 3.26 (s, 3H), 1.35 (s, 9H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.5, 163.5, 149.9, 147.2, 136.2, 128.8, 125.6, 125.2, 124.5, 124.3, 111.9, 83.7, 79.2, 61.1, 27.6, 26.8, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{19}H_{23}BrNO_6^+$ 440.0703, found 440.0721.



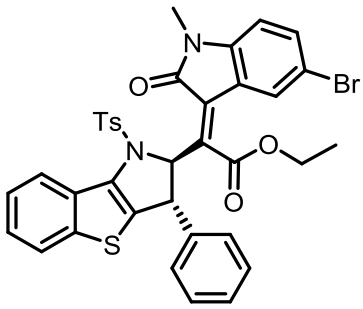

**Ethyl 2-(7-bromo-3-((tert-butoxycarbonyl)oxy)-1-methyl-2-oxoindolin-3-yl)acrylate (2k)**

White solid: 1.6 g (yield 60%); mp 124-126 ℃; IR (KBr) 2982, 1735, 1713, 1611, 1256, 979, 792 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.08 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.88 – 6.79 (m, 1H), 6.60 (s, 1H), 6.53 (s, 1H), 4.08 – 3.91 (m, 2H), 3.65 (s, 3H), 1.35 (s, 9H), 1.12 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.3, 163.5, 149.7, 143.3, 136.4, 136.0, 129.8, 129.0, 123.6, 122.3, 102.5, 83.7, 78.9, 61.2, 30.3, 27.6, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{19}H_{23}BrNO_6^+$ 440.0703, found 440.0692.



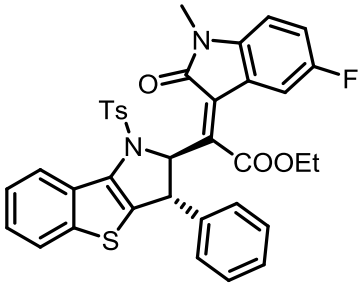

**Ethyl (*E*)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3a)**

Yellow solid: 46 mg (yield 68%); mp 225-227 ℃; IR (KBr) 2978, 1705, 1605, 1364, 1172, 815, 761, 704 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.42 – 7.36 (m, 1H), 7.35 (d, *J* = 4.4 Hz, 1H), 7.29 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.26 – 7.25 (m, 1H), 7.18 – 7.08 (m, 3H), 6.97 (s, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.44 (d, *J* = 7.2 Hz, 2H), 4.73 (d, *J* = 4.0 Hz, 1H), 4.28 – 4.04 (m, 2H), 3.17 (s, 3H), 2.39 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0, 165.7, 144.18, 144.15, 142.3, 142.1, 140.6, 138.3, 133.1, 132.2, 130.4, 129.8, 128.9, 128.6, 128.2, 127.6, 127.5, 127.2, 125.2, 124.8, 123.8, 123.76, 123.70, 123.5, 121.5, 109.0, 70.8, 62.2, 52.0, 26.3, 21.6, 13.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}ClN_2O_5S_2^+$ 669.1279, found 669.1248.



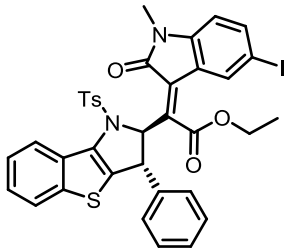

**Ethyl(*E*)-2-(5-bromo-1-methyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3b)**

White solid: 42 mg (yield 59%); mp 237-239 ℃; IR (KBr) 2964, 1710, 1603, 1362, 1167, 677, 545 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.45 – 7.42 (m, 1H), 7.41 – 7.36 (m, 2H), 7.34 (d, *J* = 4.0 Hz, 1H), 7.18 – 7.08 (m, 3H), 6.99 (t, *J* = 7.8 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 2H), 4.73 (d, *J* = 4.0 Hz, 1H), 4.28 – 4.05 (m, 2H), 3.16 (s, 3H), 2.39 (s, 3H), 1.05 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.9, 165.7, 144.2, 144.2, 142.7, 142.1, 140.6, 138.3, 133.2, 133.1, 132.2, 129.8, 128.9, 128.6, 128.2, 127.5, 127.1, 126.4, 125.2, 124.8, 123.8, 123.7, 123.3, 121.9, 114.8, 109.5, 70.9, 62.2, 52.0, 26.3, 21.6, 13.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}BrN_2O_5S_2^+$ 713.0774, found 713.0786.



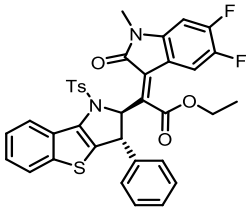
**Ethyl(*E*)-2-(5-fluoro-1-methyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3c)**

Yellow solid: 24 mg (yield 37%); mp 201-203 ℃; IR (KBr) 2976, 1724, 1602, 1325, 1277, 1173, 862, 817, 761 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.42 – 7.34 (m, 2H), 7.18 – 7.08 (m, 3H), 7.06 – 6.97 (m, 4H), 6.71 (dd, *J* = 9.4, 4.2 Hz, 1H), 6.45 (d, *J* = 7.2 Hz, 2H), 4.72 (d, *J* = 4.0 Hz, 1H), 4.23 – 4.15 (m, 1H), 4.12 – 4.04 (m, 1H), 3.17 (s, 3H), 2.38 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 165.7, 144.17, 144.13, 142.05, 140.01, 140.00, 139.4 (d, *J* = 233.5 Hz), 133.1, 132.3, 129.85, 129.85, 128.9, 128.6, 128.2, 127.5, 127.1, 125.2, 124.8, 123.7 (d, *J* = 8.5 Hz), 121.2, 121.1, 117.0 (d, *J* = 23.7 Hz ), 111.2 (d, *J* = 26.3 Hz), 108.6, 108.5, 70.8, 62.2, 52.0, 26.3, 21.6, 13.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}FN_2O_5S_2^+$ 653.1575, found 653.1599.




**Ethyl(*E*)-2-(5-iodo-1-methyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3d)**

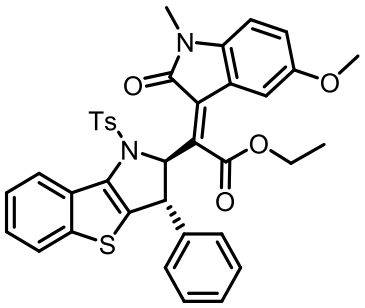
Yellow solid: 42 mg (yield 55%); mp 241-243 ℃; IR (KBr) 2989, 1708, 1599, 1364, 1169, 761, 564 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.56 – 7.47 (m, 4H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 4.0 Hz, 1H), 7.18 – 7.08 (m, 3H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 7.2 Hz, 2H), 4.73 (d, *J* = 4.0 Hz, 1H), 4.27 – 4.06 (m, 2H), 3.15 (s, 3H), 2.38 (s, 3H), 1.08 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.8, 165.7, 144.2, 143.3, 142.0, 140.6, 139.1, 138.3, 133.1, 132.24, 132.0, 129.8, 128.9, 128.6, 128.2, 127.5, 127.1, 125.2, 124.8, 123.75, 123.69, 123.0, 122.3, 110.1, 84.5, 70.9, 62.2, 52.0, 26.2, 21.6, 13.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}IN_2O_5S_2^+$ 761.0635, found 761.0640.




**Ethyl (*E*)-2-(5,6-difluoro-1-methyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3e)**

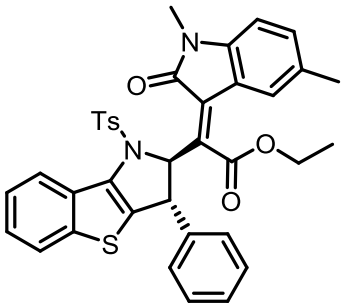
Yellow solid: 37 mg (yield 55%); mp 232-234 ℃; IR (KBr) 2928, 1716, 1360, 1268, 1153, 768, 590 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.41 – 7.36 (m, 1H), 7.32 (d, *J* = 4.4 Hz, 1H), 7.22 – 7.09 (m, 4H), 6.99 (t, *J* = 7.8 Hz, 2H), 6.61 (dd, *J* = 10.0, 6.4 Hz, 1H), 6.43 (d, *J* = 7.2 Hz, 2H), 4.71 (d, *J* = 4.0 Hz, 1H), 4.28 – 4.01 (m, 2H), 3.14 (s, 3H), 2.39 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 165.6, 144.2, 144.1, 141.6, 141.59, 141.56, 140.77, 140.75, 140.68, 140.66, 140.6, 138.3, 133.1, 132.2, 128.8(d, *J* = 21.6 Hz), 128.7 (d, *J* = 240.6 Hz), 128.21, 127.19, 125.0 (d, *J* = 47.0 Hz), 123.7 (d, *J* = 5.5 Hz),

123.32, 123.29, 113.3 (d, $J$ = 21.7 Hz), 100.0, 98.2 (d, $J$ = 23.0 Hz), 70.8, 62.3, 52.1, 26.4, 21.6, 13.5 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}F_2N_2O_5S_2^+$ 671.1480, found 671.1492.



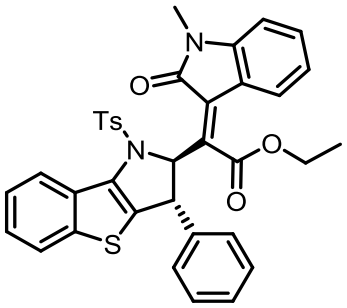

**Ethyl(*E*)-2-(5-methoxy-1-methyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3f)**

Red solid: 24 mg (yield 36%); mp 204-206 °C; IR (KBr) 2966, 1694, 1597, 1356, 1166, 690, 669, 562 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.70 (d, $J$ = 8.4 Hz, 1H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.42 (d, $J$ = 4.0 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.14 (t, $J$ = 7.4 Hz, 1H), 7.09 (d, $J$ = 8.0 Hz, 2H), 6.99 (t, $J$ = 7.6 Hz, 2H), 6.93 – 6.83 (m, 2H), 6.69 (d, $J$ = 8.4 Hz, 1H), 6.47 (d, $J$ = 7.2 Hz, 2H), 4.72 (d, $J$ = 3.6 Hz, 1H), 4.23 – 4.15 (m, 1H), 4.09 – 3.99 (m, 1H), 3.74 (s, 3H), 3.16 (s, 3H), 2.38 (s, 3H), 1.01 (t, $J$ = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 166.1, 155.5, 144.15, 144.05, 140.9, 140.7, 138.3, 137.9, 133.1, 132.4, 129.8, 129.0, 128.6, 128.2, 127.5, 127.0, 125.2, 124.7, 124.6, 123.8, 123.7, 121.0, 115.7, 110.3, 108.4, 70.8, 62.0, 55.9, 52.0, 26.2, 21.6, 13.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{33}N_2O_6S_2^+$ 665.1775, found 665.1777.



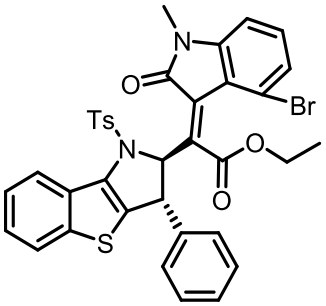

**Ethyl(*E*)-2-(1,5-dimethyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3g)**

Red solid: 36 mg (yield 55%); mp 232-234 ℃; IR (KBr) 2977, 2923, 1730, 1696, 1361, 1170, 669, 556 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.71 (d, $J$ = 8.0 Hz, 1H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.43 – 7.36 (m, 2H), 7.18 – 7.11 (m, 2H), 7.09 (d, $J$ = 7.6 Hz, 3H), 6.99 (t, $J$ = 7.6 Hz, 2H), 6.68 (d, $J$ = 8.0 Hz, 1H), 6.46 (d, $J$ = 7.6 Hz, 2H), 4.73 (d, $J$ = 4.0 Hz, 1H), 4.22 – 4.13 (m, 1H), 4.10 – 4.02 (m, 1H), 3.16 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H), 1.03 (t, $J$ = 7.0 Hz, 3H) ppm. $^{13}C$ NMR$\{^1H\}$ (100 MHz, $CDCl_3$) δ 166.4, 166.3, 144.2, 144.0, 141.7, 140.7, 140.3, 138.4, 133.1, 132.4, 131.5, 131.1, 129.8, 129.0, 128.6, 128.2, 128.1, 127.9, 127.5, 127.0, 125.1, 124.7, 124.4, 124.0, 123.8, 123.6, 120.2, 107.9, 70.8, 61.9, 52.0, 26.2, 21.6, 21.2, 13.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{33}N_2O_5S_2^+$ 649.1852, found 649.1835.



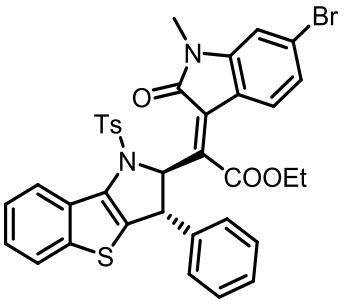
**Ethyl(*E*)-2-(1-methyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3h)**

Yellow solid: 41 mg (yield 64%); mp 217-219 ℃; IR (KBr) 2979, 1697, 1604, 1358, 1170, 755, 582 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.4, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.28 (m, 4H), 7.18 – 7.06 (m, 3H), 7.01 – 6.96 (m, 3H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 7.2 Hz, 2H), 4.74 (d, *J* = 4.0 Hz, 1H), 4.24 – 4.14 (m, 1H), 4.12 – 3.99 (m, 1H), 3.18 (s, 3H), 2.38 (s, 3H), 1.00 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.4, 166.2, 144.2, 144.1, 143.9, 140.7, 140.7, 138.4, 133.1, 132.4, 130.8, 129.8, 129.0, 128.6, 128.2, 127.5, 127.0, 125.2, 124.7, 124.2, 123.8, 123.7, 123.2, 122.2, 120.2, 108.7, 70.9, 62.0, 52.0, 26.2, 21.6, 13.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{31}N_2O_5S_2^+$ 635.1669, found 635.1669.



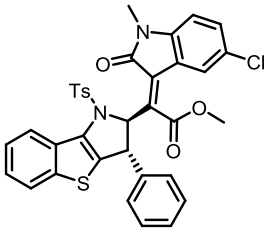
**Ethyl (*E*)-2-(4-bromo-1-methyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3i)**

Yellow solid: 34 mg (yield 48%); mp 219-221 °C; IR (KBr) 2954, 1711, 1598, 1362, 1275, 1167, 688, 579 $cm^{-1}$; $^1H$ NMR (400 MHz, CDCl3) δ 8.70 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.41 – 7.35 (m, 1H), 7.32 (d, J = 4.4 Hz, 1H), 7.18 – 7.08 (m, 5H), 6.99 (t, J = 7.6 Hz, 2H), 6.95 (d, J = 1.6 Hz, 1H), 6.43 (d, J = 7.2 Hz, 2H), 4.72 (d, J = 4.0 Hz, 1H), 4.24 – 4.13 (m, 1H), 4.11 – 3.98 (m, 1H), 3.16 (s, 3H), 2.39 (s, 3H), 0.98 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CDCl3) δ 166.2, 165.9, 144.9, 144.2, 144.1, 141.4, 140.6, 139.0, 133.0, 132.3, 129.8, 128.9, 128.6, 128.2, 127.5, 127.1, 125.2, 125.1, 124.74, 124.69, 124.4, 123.8, 123.7, 123.5, 119.1, 111.6, 70.9, 62.1, 52.0, 26.3, 21.6, 13.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}BrN_2O_5S_2$ 713.0774, found 713.0766.



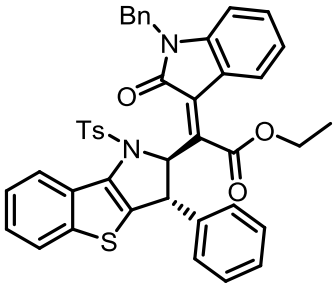
**Ethyl(*E*)-2-(6-bromo-1-methyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3j)**

Yellow solid: 54 mg (yield 75%); mp 218-220 ℃; IR (KBr) 2975, 1711, 1560, 1364, 1168, 755, 582 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 4.4 Hz, 1H), 7.18 – 7.08 (m, 5H), 6.99 (t, *J*=7.6Hz, 2H), 6.95 (d, *J*=1.2 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 2H), 4.72 (d, *J* = 4.0 Hz, 1H), 4.20 – 4.00 (m, 2H), 3.16 (s, 3H), 2.39 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 144.9, 144.1, 141.4, 140.6, 138.3, 133.0, 132.3, 129.8, 128.9, 128.6, 128.2, 127.5, 127.1, 125.2, 125.1, 124.74, 124.69, 124.4, 123.8, 123.7, 123.5, 119.1, 111.6, 70.9, 62.1, 52.0, 26.3, 21.6, 13.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}BrN_2O_5S_2^+$ 713.0774, found 71.0799.




**Methyl(*E*)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3k)**

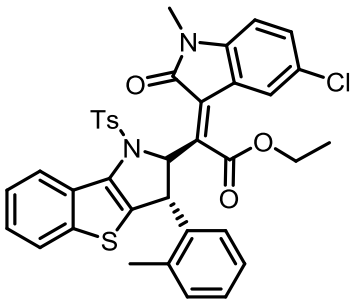
Red solid: 20 mg (yield 31%); mp 223-225 °C; IR (KBr) 2946, 1712, 1609, 1354, 1261, 1158, 703, 635, 580 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 3H), 7.42 – 7.35 (m, 2H), 7.30 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.18 – 7.12 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.99 (t, *J* = 7.8 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.47 (d, *J* = 7.2 Hz, 2H), 4.72 (d, *J* = 4.0 Hz, 1H), 3.62 (s, 3H), 3.18 (s, 3H), 2.38 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 144.2, 144.1, 142.3, 141.7, 140.4, 138.2, 133.2, 132.2, 130.5, 129.8, 128.9, 128.6, 128.2, 127.7, 127.5, 127.1, 125.3, 124.8, 123.7, 123.7, 123.6, 123.4, 121.4, 109.1, 70.8, 52.6, 51.9, 26.3, 21.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{35}H_{28}ClN_2O_5S_2^+$ 655.1123, found 655.1111.




**Ethyl(*E*)-2-(1-benzyl-5-chloro-2-oxoindolin-3-ylidene)-2-(3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3l)**

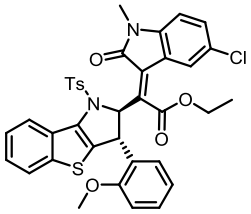
Yellow solid: 44 mg (yield 62%); mp 207-209 °C; IR (KBr) 2926, 1724, 1697, 1358, 1176, 742, 697, 557 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.45 (d, *J* = 4.8 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.37 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 7.25-7.24 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 2H), 4.99 (d, *J* = 15.6 Hz, 1H), 4.82 – 4.73 (m, 2H), 4.29 – 4.20 (m, 1H), 4.16 – 4.05 (m, 1H), 2.39 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 166.1, 144.2, 144.1, 142.9, 141.2, 140.8, 138.4, 135.7, 133.0, 132.2, 130.7, 129.8, 129.0, 128.7, 128.2, 127.61, 127.58, 127.3, 127.2, 125.2, 124.7,

124.1, 123.8, 123.7, 123.3, 122.3, 120.3, 109.1, 71.1, 62.0, 52.3, 43.5, 21.6, 13.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{42}H_{35}N_2O_5S_2^+$ 711.1982, found 711.1966.



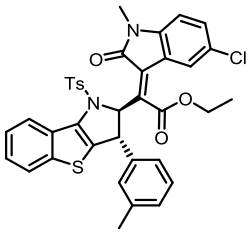
**Ethyl(*E*)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-(3-(o-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3m)**

Red solid: 35 mg (yield 51%); mp 216-218 ℃; IR (KBr) 2955, 1705, 1358, 1171, 1097, 730, 568 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.41 – 7.35 (m, 1H), 7.34 (d, *J* = 4.0 Hz, 1H), 7.29 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.06 – 6.98 (m, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.60 – 6.46 (m, 1H), 5.71 (d, *J* = 7.6 Hz, 1H), 5.07 (d, *J* = 4.0 Hz, 1H), 4.19 – 4.07 (m, 2H), 3.19 (s, 3H), 2.38 (s, 3H), 2.21 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.1, 165.8, 144.2, 144.2, 142.3, 141.9, 139.0, 138.4, 135.4, 133.2, 132.7, 130.4, 123.0, 129.9, 128.9, 128.6, 127.7, 127.4, 126.7, 125.9, 125.2, 124.7, 123.7, 123.7, 123.5, 121.4, 109.1, 70.2, 62.3, 47.0, 26.3, 21.6, 19.7, 13.5 ppm.



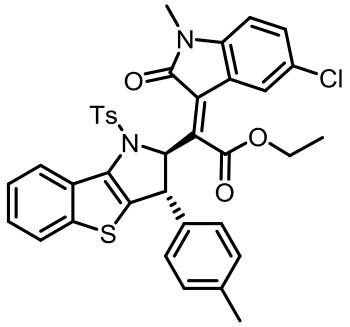
**Ethyl (*E*)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-(3-(2-methoxyphenyl)-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3n)**

Yellow solid: 53 mg (yield 76%); mp 219-221 ℃; IR (KBr) 2954, 1711, 1362, 1257, 1170, 783, 570 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.40 – 7.35 (m, 2H), 7.32 – 7.27 (m, 2H), 7.14 – 7.08 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.76 – 6.67 (m, 2H), 6.38 – 6.29 (m, 1H), 5.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.16 (d, *J* = 4.0 Hz, 1H), 4.22 – 4.02 (m, 2H), 3.51 (s, 3H), 3.20 (s, 3H), 2.35 (s, 3H), 0.94 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 165.8, 156.4, 144.2, 144.1, 142.7, 142.0, 138.9, 132.9, 132.2, 130.2, 129.7, 129.6, 129.2, 128.5, 128.0, 127.6, 127.5, 125.1, 124.6, 123.8, 123.7, 123.6, 123.5, 121.7, 119.8, 109.3, 108.8, 70.2, 62.1, 54.5, 44.7, 26.1, 21.6, 13.5 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{32}ClN_2O_6S_2^+$ 699.1385, found 699.1358.



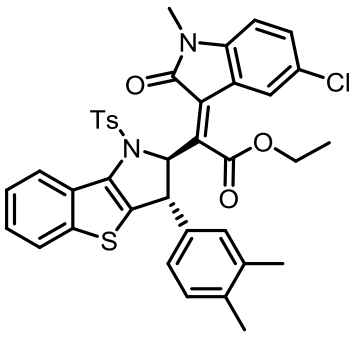
**Ethyl(*E*)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-(3-(m-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3o)**

Yellow solid: 43 mg (yield 63%); mp 210-212 ℃; IR (KBr) 2977, 2924, 1705, 1602, 1358, 1176, 721, 594 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.47 (m, 3H), 7.42 – 7.34 (m, 2H), 7.31 – 7.26 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H), 6.25 (d, *J* = 7.6 Hz, 1H), 4.72 (d, *J* = 4.0 Hz, 1H), 4.28 – 4.06 (m, 2H), 3.16 (s, 3H), 2.37 (s, 3H), 2.12 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0, 165.7, 144.2, 144.0, 142.3, 142.2, 140.5, 138.1, 137.7, 133.2, 132.4, 130.3, 129.7, 128.9, 128.7, 128.2, 128.10, 128.06, 127.6, 125.2, 124.7, 124.6, 123.72, 123.67, 123.5, 121.5, 109.0, 70.8, 62.2, 51.9, 26.3, 21.7, 21.4, 13.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{32}ClN_2O_5S_2^+$ 683.1436, found 683.1437.




**Ethyl(*E*)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-(3-(p-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3p)**

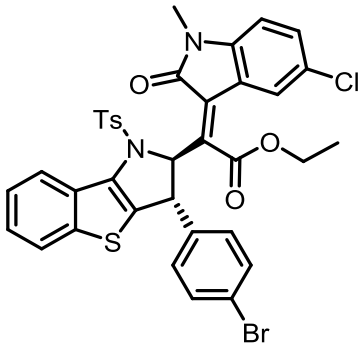
Yellow solid: 48 mg (yield 70%); mp 185-187 °C; IR (KBr) 2960, 1711, 1605, 1360, 1170, 809, 571 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.46 (m, 3H), 7.41 – 7.35 (m, 1H), 7.34 (d, *J* = 4.0 Hz, 1H), 7.29 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.24 (d, *J* = 1.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.34 (d, *J* = 8.4 Hz, 2H), 4.70 (d, *J* = 4.0 Hz, 1H), 4.26 – 4.02 (m, 2H), 3.18 (s, 3H), 2.39 (s, 3H), 2.28 (s, 3H), 1.03 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0, 165.7, 144.15, 144.13, 142.34, 142.2, 138.0, 137.6, 136.6, 133.4, 132.4, 130.3, 129.8, 128.9, 128.6, 127.6, 127.3, 125.2, 124.7, 123.68, 123.60, 123.6, 123.3, 121.5, 109.0, 70.9, 62.2, 51.7, 26.3, 21.6, 21.2, 13.6 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{32}ClN_2O_5S_2^+$ 683.1436, found 683.1437.




**Ethyl (*E*)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-(3-(3,4-dimethylphenyl)-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3q)**

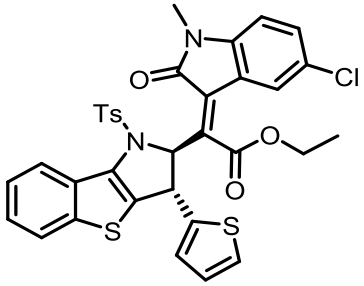
Yellow solid: 41 mg (yield 59%); mp 220-222 °C; IR (KBr) 2965, 1711, 1605, 1359, 1170, 1099, 808, 562 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.40 – 7.34 (m, 2H), 7.31 – 7.26 (m, 2H), 7.13（d，*J*= 8.0 Hz,

2H）, 6.74 (dd, *J* = 13.2, 8.0 Hz, 2H), 6.30 (s, 1H), 6.17 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.70 (d, *J* = 4.4 Hz, 1H), 4.27 – 4.07 (m, 1H), 3.17 (s, 2H), 2.38 (s, 3H), 2.17 (s, 3H), 2.01 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm.$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 166.0, 165.8, 144.15, 144.07, 142.5, 142.3, 138.1, 137.8, 136.3, 135.5, 133.5, 132.5, 130.3, 129.7, 129.5, 128.9, 128.7, 127.6, 125.2, 124.9, 124.6, 123.7, 123.69, 123.67, 123.4, 121.6, 109.0, 70.9, 62.2, 51.8, 26.3, 21.7, 19.8, 19.6, 13.6 ppm. HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{38}H_{34}ClN_2O_5S_2^+$ 697.1592, found 697.1609.



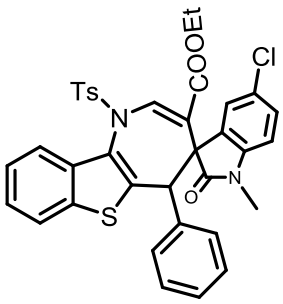

**Ethyl (*E*)-2-(3-(4-bromophenyl)-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)acetate (3r)**

Yellow solid: 22 mg (yield 31%); mp 219-221 °C; IR (KBr) 2942, 1712, 1607, 1465, 1363, 1166, 798, 573 cm$^{-1}$; $^{1}$H NMR (400 MHz, CDCl3) δ 8.68 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.44 – 7.35 (m, 2H), 7.30 (dd, J = 8.4, 2.0 Hz, 1H), 7.21 (d, J = 2.0 Hz, 1H), 7.14 – 7.06 (m, 4H), 6.74 (d, J = 8.4 Hz, 1H), 6.37 (d, J = 8.4 Hz, 2H), 4.65 (d, J = 3.6 Hz, 1H), 4.18 – 4.00 (m, 2H), 3.21 (s, 3H), 2.41 (s, 3H), 1.01 (t, J = 7.0 Hz, 3H) ppm. 13C NMR (100 MHz, CDCl3) δ 166.1, 165.6, 144.5, 144.1, 142.3, 141.8, 139.6, 138.6, 132.4, 132.3, 131.3, 130.5, 129.8, 129.1, 128.8, 128.5, 127.7, 125.3, 125.0, 123.9, 123.7, 123.6, 123.4, 121.4, 121.1, 109.1, 70.6, 62.3, 51.1, 26.4, 21.7, 13.6 ppm. HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{36}H_{28}BrClN_2O_5S_2$ 747.0384, found 747.0379.



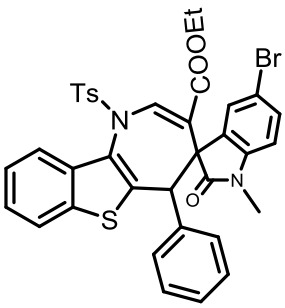

**Ethyl(*E*)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-(3-(thiophen-2-yl)-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (3s)**

White solid: 30 mg (yield 44%); mp 201-203 ℃; IR (KBr) 2965, 1709, 1605, 1363, 1171,1100, 690, 568 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.44 (d, *J* = 3.6 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.30 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.10 – 7.04 (m, 3H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.67 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.18 (d, *J* = 3.6 Hz, 1H), 4.94 (d, *J* = 3.6 Hz, 1H), 4.21 – 4.02 (m, 2H), 3.23 (s, 3H), 2.34 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 166.1, 165.6, 144.2, 144.0, 143.8, 142.3, 141.7, 138.1, 132.6, 132.2, 130.5, 129.8, 128.7, 128.4, 127.7, 126.6, 125.5, 125.3, 125.04, 124.98, 123.9, 123.7, 123.6, 121.4, 109.1, 71.2, 62.3, 47.0, 26.4, 21.6, 13.6 ppm. HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{34}H_{28}ClN_2O_5S_3^+$ 675.0843, found 675.0827.



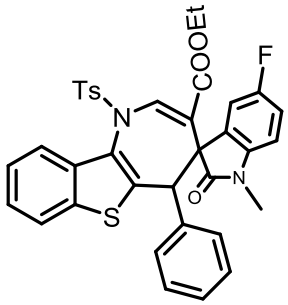

**Ethyl5'-chloro-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylat (4a)**

White solid: 36 mg (yield 54%); mp 152-154 ℃; IR (KBr) 2976, 1709, 1613, 1376, 1098, 736, 567 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.38 – 7.31 (m, 1H), 7.11 – 6.95 (m, 3H), 6.90 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.38 (d, *J* = 2.0 Hz, 1H), 6.16 (d, *J* = 8.0 Hz, 1H), 3.97 – 3.83 (m, 2H), 3.66 (s, 1H), 2.97 (s, 3H), 2.63 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.9, 176.3, 162.6, 150.7, 150.2, 143.7, 142.2, 139.1, 136.6, 135.87, 135.00, 134.96, 132.0, 129.4, 129.03, 129.01, 128.2, 127.9, 127.3, 127.2, 125.6, 125.1, 124.1, 123.1, 102.2, 68.1, 60.6, 55.9, 30.5, 21.8, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{36}H_{29}ClN_2NaO_5S_2^+$ 691.1299, found 691.1097.



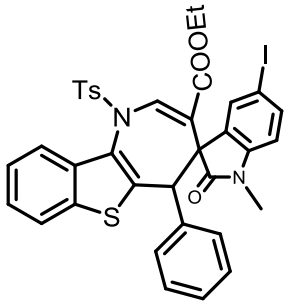

**Ethyl5'-bromo-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4b)**

White solid: 37 mg (yield 52%); mp 115-117 ℃; IR (KBr) 2973, 1709, 1611, 1376, 1262, 1067，735, 567 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.13 – 6.93 (m, 4H), 6.55 (d, *J* = 2.0 Hz, 1H), 6.12 (d, *J* = 8.0 Hz, 1H), 4.01 – 3.83 (m, 2H), 3.62 (s, 1H), 2.96 (s, 3H), 2.64 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.6, 165.2, 145.6, 142.4, 139.9, 138.0, 136.73, 135.9, 135.8, 134.3, 133.5, 130.9, 130.7, 129.6, 128.2, 127.7, 127.5, 125.0, 124.64, 124.61, 123.5, 122.0, 120.8, 114.1, 108.8, 61. 3, 56.6, 49.7, 26.1, 21.8, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}N_2O_5S_2^+$ 713.0774, found 713.0765.



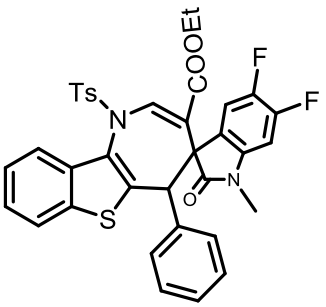

**Ethyl5'-fluoro-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4c)**

White solid: 30 mg (yield 44%); mp 159-161 ℃; IR (KBr) 2979, 1708, 1620, 1375, 1263, 1098，736, 566 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.43 (m, 1H), 7.37 – 7.27 (m, 1H), 7.15 – 6.94 (m, 3H), 6.64-6.13 (m, 1H), 6.18 (dd, *J* = 8.6, 4.2 Hz, 1H), 6.10 (dd, *J* = 7.8, 2.6 Hz, 1H), 3.97 – 3.81 (m, 2H), 3.71 (s, 1H), 2.99 (s, 3H), 2.60 (s, 3H), 0.99 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.8, 165.2, 158.7 (d, *J* = 239.1 Hz), 145.6, 139.6, 139.5, 138.2, 136.7, 135.90, 135.89, 134.5, 133.0 (d, *J* = 8.0 Hz), 130.5, 129.5, 128.2, 127.8, 127.5, 124.9, 124.6, 123.5, 122.0, 120.8, 114.4, 114.2, 109.6(d, *J* = 25.2 Hz), 107.9 (d, *J* = 7.9 Hz), 61.2, 56.8, 49.6, 26.2, 21.6, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{36}H_{29}FN_2NaO_5S_2^+$ 675.1394, found 675.1393.



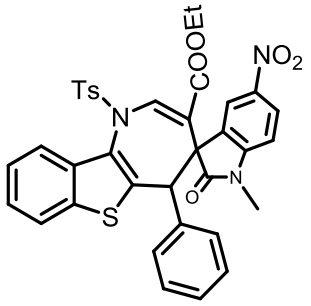

**Ethyl5'-iodo-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4d)**

White solid: 33 mg (yield 43%); mp 171-173 ℃; IR (KBr) 2972, 1706, 1605, 1376, 1171, 1098，737, 563 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.64 (dd, *J* = 15.6, 8.0 Hz, 3H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.13 – 6.93 (m, 3H), 6.76 (s, 1H), 6.02 (d, *J* = 8.4 Hz, 1H), 4.03 – 3.80 (m, 2H), 3.55 (s, 1H), 2.96 (s, 3H), 2.67 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.4, 165.2, 145.6, 143.1, 139.8, 138.1, 136.9, 136.7, 135.9, 135.6, 134.3, 133.8, 130.7, 130.2, 129.4, 128.2, 127.7, 127.4, 125.0, 124.6, 123.6, 122.0, 120.7, 109.5, 83.7, 61.3, 56.4, 49.7, 26.1, 22.0, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}IN_2O_5S_2^+$ 761.0635, found 761.0673.



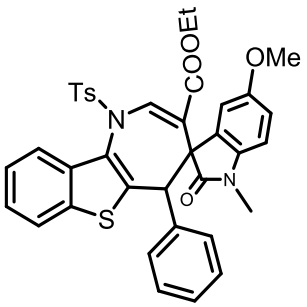

**Ethyl5',6'-difluoro-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4e)**

White solid: 34 mg (yield 50%); mp 258-260 ℃; IR (KBr) 2977, 1711, 1621, 1379, 1261, 1084，737, 568 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.38 – 7.31 (m, 1H), 7.15 – 6.97 (m, 3H), 6.20 – 6.15 (m, 1H), 6.10 (dd, *J* = 9.8, 6.2 Hz, 1H), 3.99 – 3.85 (m, 2H), 3.70 (s, 1H), 2.96 (s, 3H), 2.61 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.90, 165.13, 145.68, 139.89, 139.87, 139.81, 137.4 (d, *J* = 125.6 Hz), 135.83, 135.1 (d, *J* = 158.4 Hz), 129.58, 129.1 (d, *J* = 273.7 Hz), 128.38, 127.67, 127.66, 126.96, 126.92, 126.90, 125.00, 124.65, 122.8 (d, *J* = 122.8 Hz), 120.61, 111.11, 110.91, 110.90, 97.88, 97.65, 61.34, 56.37, 49.62, 26.33, 21.6, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}F_2N_2O_5S_2^+$ 671.1480, found 671.1472.



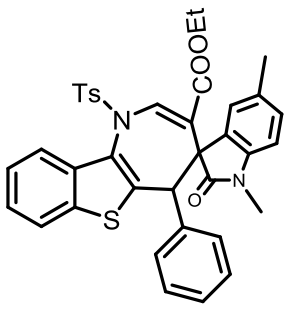

**Ethyl 1'-methyl-5'-nitro-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-b]azepine-4,3'-indoline]-3-carboxylate (4f)**

White solid: 16 mg (yield 23%); mp 278-280 ℃; IR (KBr) 3069, 1712, 1611, 1498, 1275, 1074, 730, 554 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.94 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.70 – 7.64 (m, 3H), 7.52 – 7.45 (m, 1H), 7.41 – 7.33 (m, 2H), 7.13 – 6.79 (m, 3H), 6.35 (d, *J* = 8.4 Hz, 1H), 4.08 – 3.78 (m, 2H), 3.63 (s, 1H), 3.08 (s, 3H), 2.59 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.4, 165.1, 149.2, 146.1, 142.6, 140.7, 137.5, 136.7, 135.8, 135.3, 134.0, 132.6, 130.9, 129.5, 128.5, 127.6, 125.7, 125.1, 124.7, 123.7, 122.1, 119.8, 117.1, 106.9, 61.6, 56.2, 49.4, 26.5, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}N_3O_7S_2^+$ 680.1520, found 680.1534.



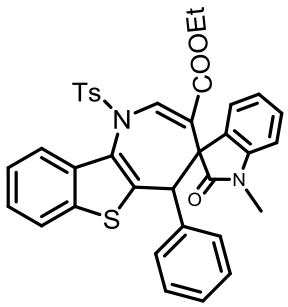

**Ethyl 5'-methoxy-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4g)**

White solid: 20 mg (yield 30%); mp 233-235 °C; IR (KBr) 3063, 2935, 1713, 1604, 1373, 1171, 736, 571 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.42 (m, 1H), 7.36 – 7.28 (m, 1H), 7.11 – 6.93 (m, 3H), 6.44 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.16 (d, *J* = 8.4 Hz, 1H), 6.03 (d, *J* = 2.8 Hz, 1H), 3.91 – 3.79 (m, 2H), 3.72 (s, 3H), 3.70 (s, 1H), 2.98 (s, 3H), 2.58 (s, 3H), 0.95 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.7, 165.4, 155.6, 145.3, 139.1, 138.8, 137.1, 136.7, 136.0, 135.8, 134.9, 132.7, 130.4, 129.2, 128.0, 127.8, 127.4, 124.8, 124.5, 123.6, 122.0, 121.3, 111.6, 110.1, 107.5, 61.0, 56.8, 55.8, 49.7, 26.2, 21.7, 13.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{33}N_2O_6S_2^+$ 665.1775, found 665.1744.



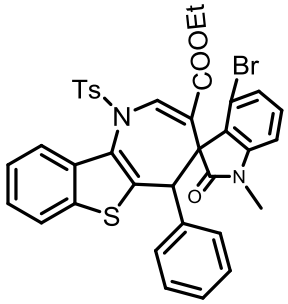

**Ethyl1',5'-dimethyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4h)**

White solid: 32 mg (yield 49%); mp 133-135 ℃; IR (KBr) 2974, 1702, 1619, 1371, 1260, 1094，735, 568 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.10 – 6.89 (m, 4H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.24 (s, 1H), 6.14 (d, *J* = 8.0 Hz, 1H), 3.94 – 3.72 (m, 2H), 3.68 (s, 1H), 2.98 (s, 3H), 2.59 (s, 3H), 2.24 (s, 3H), 0.92 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.0, 165.5, 145.0, 141.0, 138.93, 138.86, 136.7, 136.0, 135.9, 134.9, 131.3, 131.1, 130.4, 129.2, 128.5, 127.9, 127.3, 124.8, 124.5 123.5, 122.3, 122.0, 121.6, 107.1, 61.0, 56.6, 49.7, 26.10, 21.7, 21.1, 13.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{33}N_2O_5S_2^+$ 649.1825, found 649.1825.



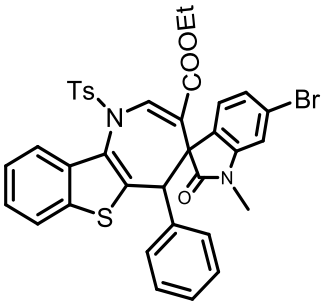

**Ethyl 1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4i)**

Yellow solid: 41 mg (yield 65%); mp 216-218 °C; IR (KBr) 2978, 1716, 1612, 1374, 1171, 739, 570 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.35 – 7.31 (m, 1H), 7.09 – 6.91 (m, 4H), 6.82 – 6.75 (m, 1H), 6.45 (d, *J* = 7.2 Hz, 1H), 6.27 (d, *J* = 7.6 Hz, 1H), 3.88 – 3.76 (m, 2H), 3.70 (s, 1H), 3.01 (s, 3H), 2.58 (s, 3H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.0, 165.5, 145.2, 143.5, 138.9, 138.9, 136.7, 135.9, 135.6, 134.9, 131.4, 130.3, 129.1, 128.4, 128.0, 127.8, 127.3, 124.8, 124.5, 123.6, 122.0, 121.8, 121.4, 121.3, 107.4, 61.0, 56.5, 49.7, 26.1, 21.7, 13.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{31}N_2O_5S_2^+$ 635.1669, found 635.1666.



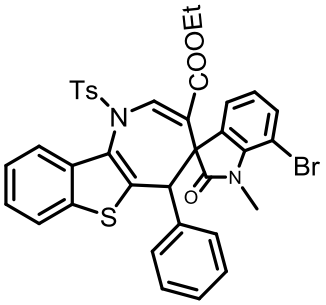

**Ethyl 4'-bromo-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4j)**

White solid: 49 mg (yield 69%); mp 261-263 ℃; IR (KBr) 2939, 1713, 1601, 1372, 1266, 1174, 1091, 731, 558 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.38 – 7.29 (m, 1H), 7.14 – 6.96 (m, 3H), 6.92 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.42 (d, *J* = 1.6 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 3.98 – 3.75 (m, 2H), 3.66 (s, 1H), 2.98 (s, 3H), 2.59 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.9, 165.3, 145.3, 144.8, 139.4, 138.5, 136.7, 135.8, 135.6, 134.5, 130.5, 130.3, 129.1, 128.3, 127.8, 127.6, 124.9, 124.6, 124.5, 123.6, 122.5, 122.1, 121.8, 120.7, 111.0, 61.2, 56.2, 49.4, 26.2, 21.8, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}N_2O_5S_2^+$ 713.0774, found 713.0746.



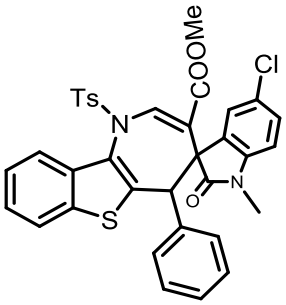
**Ethyl 5'-bromo-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4k)**

White solid: 29 mg (yield 41%); mp 243-245 °C; IR (KBr) 2960, 1718, 1602, 1372, 1173, 731, 559 $cm^{-1}$;$^1$H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.46 – 7.44 (m, 1H), 7.37 – 7.30 (m, 2H), 7.15 – 7.04 (m, 2H), 7.02 – 6.98 (m, 1H), 6.92 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.42 (d, *J* = 1.2 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 3.95 – 3.79 (m, 2H), 3.66 (s, 1H), 2.98 (s, 3H), 2.58 (s, 3H), 0.99 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 174.9, 165.3, 145.3, 144.8, 139.4, 138.5, 136.7, 135.8, 135.6, 134.5, 130.5, 130.3, 129.1, 128.3, 127.8, 127.6, 124.92, 124.6, 124.5, 123.6, 122.5, 122.05, 121.8, 120.7, 111.0, 61.2, 56.2, 49.4, 26.2, 21.7, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}BrN_2O_5S_2^+$ 713.0774, found 713.0778.




**Ethyl7'-bromo-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4l)**

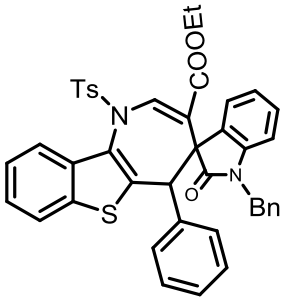
White solid: 32 mg (yield 45%); mp 276-278 °C; IR (KBr) 2975, 1715, 1602, 1371, 1263, 1173, 1098, 727, 567 $cm^{-1}$;$^1$H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.36 – 7.32 (m, 1H), 7.28 – 7.26 (m, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 1.2 Hz, 1H), 7.02 (d, *J* = 0.8 Hz, 1H), 6.65 – 6.58 (m, 1H), 6.34 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.94 – 3.79 (m, 2H), 3.63 (s, 1H), 3.40 (s, 3H), 2.57 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 175.5, 165.3, 145.3, 140.9, 139.3, 138.4, 136.7, 135.8, 135.6, 134.5, 134.3, 133.8, 130.3, 129.1, 128.4, 127.8, 127.4, 124.9, 124.6, 123.6, 122.8, 122.1, 120.7, 120.4, 101.8, 61.2, 56.3, 50.1, 29.7, 21.7, 13.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}BrN_2O_5S_2^+$ 713.0774, found 713.0803.




**Methyl 5'-chloro-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4m)**

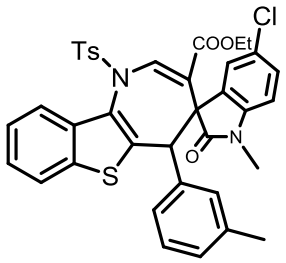
White solid: 37 mg (yield 55%); mp 248-250 °C; IR (KBr) 2941, 1720, 1611, 1374, 1278, 740, 551 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.43 (m, 1H), 7.37 – 7.31 (m, 1H), 7.14 – 6.94 (m, 3H), 6.90 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 6.17 (d, *J* = 8.0 Hz, 1H), 3.67 (s, 1H), 3.51

(s, 3H), 2.98 (s, 3H), 2.63 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.7, 165.5, 145.7, 142.0, 140.1, 138.1, 136.7, 135.9, 135.9, 134.3, 133.1, 130.7, 129.6, 128.2, 128.1, 127.7, 127.5, 126.9, 125.0, 124.6, 123.5, 122.1, 121.8, 120.8, 108.4, 56.6, 52.3, 49.5, 26.2, 21.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{35}H_{28}ClN_2O_5S_2^+$ 655.1123, found 655.1125.



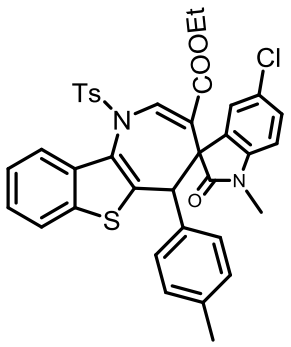

**Ethyl 1'-benzyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4n)**

Yellow solid: 58 mg (yield 82%); mp 146-148 °C; IR (KBr) 3049, 1714, 1609, 1371, 1171, 745, 551 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.33 – 7.26 (m, 3H), 7.26 – 7.23 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.91 – 6.84 (m, 3H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 6.8 Hz, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 5.05 (d, *J* = 15.2 Hz, 1H), 4.30 (d, *J* = 15.2 Hz, 1H), 3.91 – 3.76 (m, 1H), 3.70 (s, 1H), 3.59 – 3.39 (m, 1H), 2.57 (s, 3H), 0.65 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.1, 165.5, 145.2, 143.0, 139.0, 138.8, 136.7, 135.9, 135.6, 135.5, 134.9, 131.4, 130.3, 128.8, 128.6, 128.5, 128.2, 127.9, 127.9, 127.7, 127.4, 124.8, 124.5, 123.7, 122.1, 121.8, 121.6, 121.3, 108.4, 60.9, 56.3, 49.9, 44.6, 21.7, 13.5 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{42}H_{35}N_2O_5S_2^+$ 711.1982, found 711.1982.



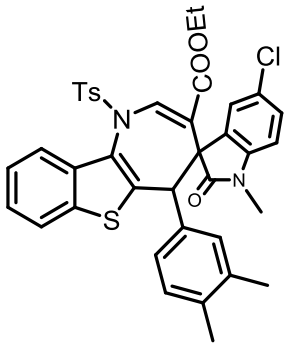

**Ethyl 5'-chloro-1'-methyl-2'-oxo-5-(m-tolyl)-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4p)**

Yellow solid: 20 mg (yield 29%); mp 297-299 °C; IR (KBr) 2976, 1710, 1612, 1374, 1264, 1174，742, 569 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.37 – 7.30 (m, 2H), 7.00 – 6.88 (m, 3H), 6.38 (d, *J* = 2.0 Hz, 1H), 6.17 (d, *J* = 8.4 Hz, 1H), 3.99 – 3.81 (m, 2H), 3.60 (s, 1H), 2.98 (s, 3H), 2.63 (s, 3H), 2.23 – 2.02 (m, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.7, 165.2, 145.5, 142.0, 139.8, 138.2, 137.2, 136.8, 135.94, 135.90, 134.2, 133.2, 130.7, 129.5, 128.7, 128.0, 127.8, 126.9, 124.9, 124.6, 123.5, 122.04, 121.99, 120.9, 120.9, 108.3, 61.3, 56.6, 49.6, 26.1, 21.8, 21.3, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{32}ClN_2O_5S_2^+$ 683.1436, found 683.1436.



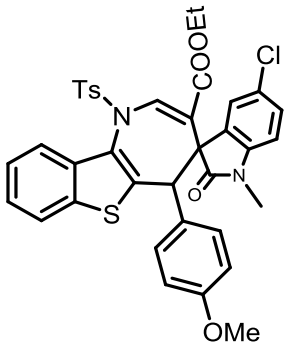

**Ethyl 5'-chloro-1'-methyl-2'-oxo-5-(p-tolyl)-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4q)**

White solid: 42 mg (yield 61%); mp 120-122 °C; IR (KBr) 2973, 1716, 1610, 1492, 1373, 1268, 1169, 736, 563 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.36 – 7.29 (m, 1H), 6.91 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.81 (s, 2H), 6.38 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 3.97 – 3.82 (m, 2H), 3.60 (s, 1H), 2.98 (s, 3H), 2.62 (s, 3H), 2.18 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.8, 165.2, 145.6, 142.0, 139.8, 138.6, 137.9, 136.7, 135.9, 135.8, 133.3, 131.3, 130.7, 129.4, 128.2, 128.0, 127.7, 126.9, 124.9, 124.6, 123.5, 122.0, 121.9, 120.9, 108.3, 61.3, 56.6, 49.2, 26.2, 21.7, 21.0, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{32}ClN_2O_5S_2^+$ 683.1436, found 683.1436.



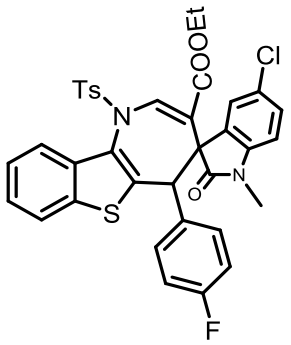

**Ethyl 5'-chloro-5-(3,4-dimethylphenyl)-1'-methyl-2'-oxo-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4r)**

White solid: 32 mg (yield 46%); mp 142-144 ℃; IR (KBr) 2976, 1715, 1610, 1373, 1271, 1102，660, 567 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.42 (m, 1H), 7.38 – 7.28 (m, 1H), 6.90 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.77 (s, 1H), 6.38 (d, *J* = 2.0 Hz, 1H), 6.18 (d, *J* = 8.0 Hz, 1H), 4.02 – 3.77 (m, 2H), 3.57 (s, 1H), 2.98 (s, 3H), 2.64 (s, 3H), 2.09 (s, 6H), 1.00 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.8, 165.3, 145.4, 142.0, 139.7, 138.8, 136.8, 136.4, 136.0, 135.9, 135.7, 133.3, 131.7, 130.7, 129.3, 128.6, 127.9, 127.7, 126.8, 124.8, 124.5, 123.5, 122.0, 121.9, 121.0, 108.3, 61.2, 56.6, 49.2, 26.1, 21.8, 19.6, 19.3, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{42}H_{35}N_2O_5S_2^+$ 697.1592, found 697.1548.



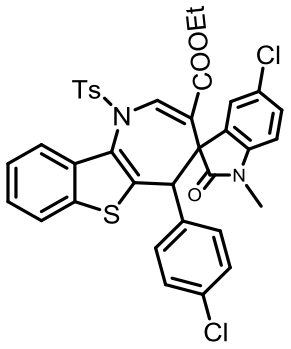

**Ethyl 5'-chloro-5-(4-methoxyphenyl)-1'-methyl-2'-oxo-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4s)**

White solid: 16 mg (yield 24%); mp 268-270 °C; IR (KBr) 2944, 1719, 1611, 1371, 1258, 1173, 1095, 742, 562 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.43 (m, 1H), 7.38 – 7.31 (m, 1H), 6.92 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.63 – 6.43 (m, 2H), 6.35 (d, *J* = 2.0 Hz, 1H), 6.20 (d, *J* = 8.4 Hz, 1H), 3.99 – 3.79 (m, 2H), 3.70 (s, 3H), 3.59 (s, 1H), 2.97 (s, 3H), 2.62 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.8, 165.2, 159.1, 145.5, 142.0, 139.8, 138.8, 136.7, 136.0, 135.9, 133.4, 130.6, 129.4, 128.0, 127.7, 126.9, 126.4, 124.9, 124.6, 123.5, 122.0, 121.8, 120.9, 112.7, 108.4, 61.3, 56.8, 55.2, 48.8, 26.2, 21.8, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{31}ClN_2O_6S_2^+$ 699.1385, found 699.1374.



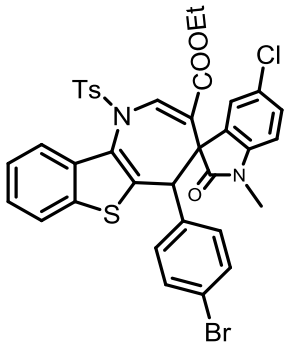

**Ethyl 5'-chloro-5-(4-fluorophenyl)-1'-methyl-3'-oxo-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,2'-indoline]-3-carboxylate (4t)**

White solid: 31 mg (yield 46%); mp 226-228 °C; IR (KBr) 2976, 1712, 1609, 1376, 1170, 1099，737, 564 $cm^{-1}$; $^1H$ NMR (400 MHz,$CDCl_3$) δ 8.50 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.39 – 7.32 (m, 1H), 6.94 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.71 (s, 2H), 6.36 (d, *J* = 2.0 Hz, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 4.01 – 3.79 (m, 2H), 3.67 (s, 1H), 2.98 (s, 3H), 2.62 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.6, 165.1, 162.2 (d, *J* = 247.1 Hz), 145.6, 141.9, 139.8, 137.7, 136.6, 135.92, 135.91, 133.1, 130.7, 130.3, 130.2, 129.7, 128.2, 127.8, 127.1, 125.1, 124.7, 123.7, 122.0, 121.8, 120.7, 114.4 (d, *J* = 21.0 Hz), 108.5, 61.3, 56.6, 48.8, 26.2, 21.8, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}ClFN_2O_5S_2^+$ 687.1185, found 687.1189.



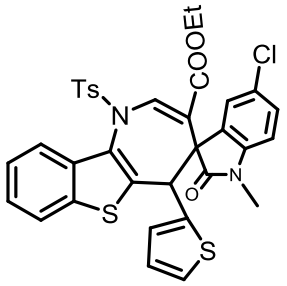

**Ethyl 5'-chloro-5-(4-chlorophenyl)-1'-methyl-2'-oxo-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4u)**

White solid: 41 mg (yield 58%); mp 260-262 °C; IR (KBr) 2961, 1714, 1613, 1375, 1267, 1096, 745, 558 $cm^{-1}$;$^1$H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.39 – 7.32 (m, 1H), 7.07 – 6.90 (m, 3H), 6.37 (d, J = 2.0 Hz, 1H), 6.24 (d, J = 8.4 Hz, 1H), 4.00 – 3.80 (m, 2H), 3.63 (s, 1H), 2.99 (s, 3H), 2.61 (s, 3H), 1.02 (t, J = 7.2 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (100 MHz, CDCl3) δ 174.6, 165.0, 145.6, 141.9, 139.8, 137.3, 136.6, 135.9, 134.2, 132.9, 130.7, 129.8, 128.38, 128.36, 127.8, 127.70, 127.68, 127.1, 125.1, 124.8, 123.6, 122.1, 121.8, 120.7, 108.6, 61.4, 56.5, 49.0, 26.3, 21.8, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}Cl_2N_2O_5S_2^+$ 703.0889, found 703.0880.



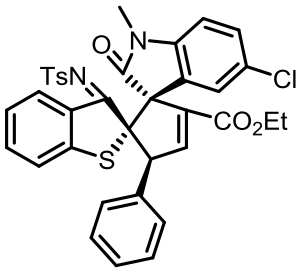

**Ethyl 5-(4-bromophenyl)-5'-chloro-1'-methyl-2'-oxo-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4v)**

White solid: 32 mg (yield 43%); mp 265-267 ℃; IR (KBr) 2976, 1715, 1612, 1491, 1376, 1270, 1170, 1091, 735, 561 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.38 – 7.32 (m, 1H), 7.23 – 7.04 (m, 2H), 6.96 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.37 (d, *J* = 2.0 Hz, 1H), 6.24 (d, *J* = 8.0 Hz, 1H), 4.03 – 3.77 (m, 2H), 3.62 (s, 1H), 2.99 (s, 3H), 2.61 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 174.5, 165.0, 145.6, 141.9, 139.8, 137.2, 136.6, 135.89, 135.88, 133.4, 132.9, 130.7, 129.8, 128.4, 127.8, 127.1, 125.1, 124.8, 123.6, 122.4, 122.1, 121.8, 120.7, 108.6, 61.4, 56.4, 49.1, 26.3, 21.8, 13.8. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}ClBrN_2O_5S_2^+$ 747.0384, found 747.0383.



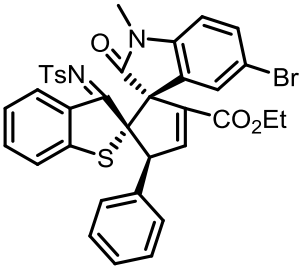

**Ethyl 5'-chloro-1'-methyl-2'-oxo-5-(thiophen-2-yl)-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate (4w)**

White solid: 32 mg (yield 47%); mp 113-115 °C; IR (KBr) 2967, 1710, 1612, 1378, 1263, 1098，730, 555 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.42 (m, 1H), 7.37 – 7.32 (m, 1H), 6.99 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.95 (d, *J* = 5.2 Hz, 1H), 6.81 (s, 1H), 6.77 – 6.73 (m, 1H), 6.37 (d, *J* = 2.0 Hz, 1H), 6.30 (d, *J* = 8.4 Hz, 1H), 3.98 – 3.82 (m, 2H), 3.77 (s, 1H), 3.03 (s, 3H), 2.62 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.3, 165.1, 145.8, 142.4, 139.6, 138.5, 136.7, 136.2, 136.1, 135.37, 135.35, 133.0, 131.0, 129.1, 128.3, 127.4, 127.2, 126.3, 126.1, 125.0, 124.7, 123.6, 122.1, 122.0, 120.7, 108.4, 61.3, 56.7, 43.8, 26.3, 21.9, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{34}H_{28}ClN_2O_5S_3^+$ 675.0843, found 675.0827.



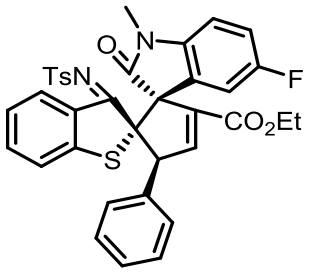

**Ethyl (*E*)-5''-chloro-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5a)**

Yellow solid: 61 mg (yield 91%); mp 215-217 °C; IR (KBr) 3064, 2979, 1707, 1604, 1582, 1319, 1153, 1089, 749, 671, 551 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.31 – 7.27 (m, 1H), 7.14 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.12 – 7.06 (m, 2H), 7.02 (d, *J* = 4.4 Hz, 4H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.54 (d, *J* = 1.2 Hz, 1H), 4.10 – 3.89 (m, 2H), 3.26 (s, 3H), 2.52 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.8, 175.3, 162.4, 150.5, 149.9, 143.6, 143.5, 139.0, 136.8, 135.8, 134.8, 132.1, 129.4, 129.2, 129.0, 128.5, 128.2, 127.9, 127.5, 127.3, 127.2, 125.3, 122.9, 108.9, 77.4, 68.2, 60.6, 56.6, 26.7, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}ClN_2O_5S_2^+$ 669.1279, found 669.1286.



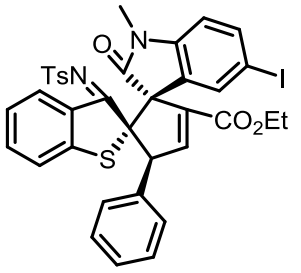
**Ethyl (*E*)-5''-bromo-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2, 1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5b)**

Yellow solid: 44 mg (yield 62%); mp 221-223 °C; IR (KBr) 3062, 2979, 1711, 1605, 1580, 1319, 1151, 1091, 670, 548 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.50 – 7.39 (m, 3H), 7.32 – 7.27 (m, 2H), 7.14 – 7.06 (m, 2H), 7.05 – 6.95 (m, 5H), 6.62 (d, *J* = 8.4 Hz, 1H), 5.53 (d, *J* = 2.0 Hz, 1H), 4.11 – 3.90 (m, 2H), 3.25 (s, 3H), 2.53 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.8, 175.1, 162.4, 150.5, 149.9, 143.9, 143.6, 139.0, 136.8, 135.8, 134.8, 132.11, 132.09, 129.7, 129.4, 129.0, 128.2, 127.9, 127.8, 127.4, 127.3, 125.2, 122.9, 115.9, 109.4, 77.5, 68.1, 60.6, 56.5, 26.6, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}BrN_2O_5S_2^+$ 713.0774, found 713.0763.




**Ethyl (*E*)-5''-fluoro-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5c)**

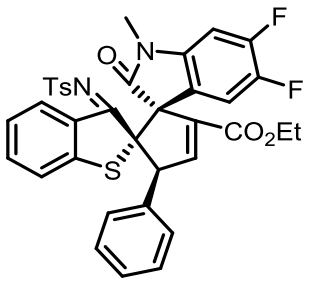
White solid: 54 mg (yield 83%); mp 207-209 °C; IR (KBr) 2979, 1709, 1579, 1314, 1090, 813, 673, 549 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.40 (m, 3H), 7.34 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.13 – 7.07 (m, 2H), 7.05 – 6.94 (m, 5H), 6.91-6.86 (m, 1H), 6.68 (dd, *J* = 8.6, 4.2 Hz, 1H), 5.56 (d, *J* = 2.0 Hz, 1H), 4.12 – 3.91 (m, 2H), 3.27 (s, 3H), 2.53 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.9, 175.4, 162.4, 159.2（d, *J* = 239.8 Hz), 150.8, 149.9, 143.6, 140.9, 139.1, 136.9, 135.8, 134.9, 132.1, 129.4, 129.0, 128.2, 127.8, 127.44, 127.37, 127.3, 125.2, 122.9, 115.5（d, *J* = 23.5 Hz), 115.2（d, *J* = 26.2 Hz), 108.4 (d, *J* = 8.7 Hz), 68.4, 60.6, 56.6, 26.7, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}FN_2O_5S_2^+$ 653.1575, found 653.1580.




**Ethyl (*E*)-5''-iodo-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5d)**

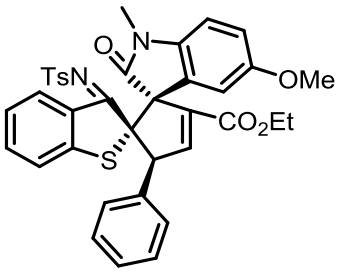
White solid: 50 mg (yield 66%); mp 202-204 °C; IR (KBr) 2983, 1710, 1603, 1581, 1320, 1152, 1091, 813, 671, 555 $cm^{-1}$; $^1H$ NMR (400 MHz,$CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 1.6 Hz, 1H), 7.51 – 7.40 (m, 4H), 7.31-7.26 (m, 2H), 7.12 – 7.05 (m, 2H), 7.05 – 6.98 (m, 5H), 6.52 (d, *J* = 8.0 Hz, 1H), 5.52 (d, *J* = 2.0 Hz, 1H), 4.13 – 3.90 (m, 2H), 3.25 (s, 3H), 2.53 (s, 3H), 1.05 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.8, 175.0, 162.4, 150.4, 149.9, 144.6, 143.5, 139.1, 138.2, 136.7, 135.7, 134.8, 132.1, 129.4, 129.0, 128.2, 127.99, 127.96, 127.4, 127.3,

125.2, 122.9, 109.9, 85.7, 77.5, 68.0, 60.6, 56.3, 26.6, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}IN_2O_5S_2^+$ 761.0635, found 761.0641.



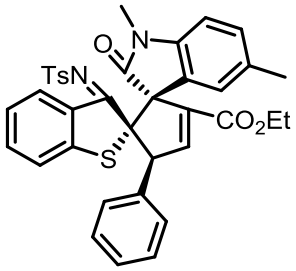

**Ethyl (*E*)-5'',6''-difluoro-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5e)**

Yellow solid: 44 mg (yield 66%); mp 195-197 °C; IR (KBr) 3055, 2984, 1713, 1600, 1577, 1501, 1316, 1086, 737, 669, 549 $cm^{-1}$; $^1H$ NMR (400 MHz,$CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.40 (m, 4H), 7.36 – 7.28 (m, 1H), 7.15 – 7.08 (m, 2H), 7.06 – 6.97 (m, 5H), 6.59 (dd, *J* = 9.6, 6.4 Hz, 1H), 5.53 (d, *J* = 2.0 Hz, 1H), 4.11 – 3.94 (m, 2H), 3.24 (s, 3H), 2.53 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.9, 175.6, 162.4, 151.0 (d, *J* = 234.4 Hz), 150.3 (d, *J* = 80.5 Hz), 148.7 (d, *J* = 201.0 Hz), 143.7, 141.528 (d, *J* = 11.1 Hz), 141.527 (d, *J* = 7.1 Hz), 139.0, 136.7, 135.9, 134.7, 132.1, 129.4, 128.9, 128.2, 127.7, 127.5, 127.3, 125.4, 123.0, 121.208 (d, *J* = 1.4 Hz), 121.202 (d, *J* = 10.1 Hz), 116.9 (d, *J* = 21.6 Hz), 98.2 (d, *J* = 23.1 Hz), 68.1, 60.7, 56.6, 26.8, 21.7, 14.0 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}F_2N_2O_5S_2^+$ 671.1480, found 671.1471.



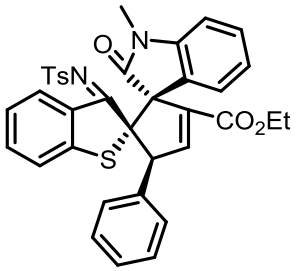

**Ethyl (*E*)-5''-methoxy-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5f)**

Yellow solid: 51 mg (yield 77%); mp 218-220 °C; IR (KBr) 3065, 2976, 1706, 1603, 1308, 1238, 1089, 670, 548 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.12 – 7.06 (m, 2H), 7.02 – 6.95 (m, 5H), 6.74 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 5.63 (d, *J* = 2.0 Hz, 1H), 4.09 – 3.93 (m, 2H), 3.68 (s, 3H), 3.26 (s, 3H), 2.53 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.4, 175.4, 162.7, 156.3, 151.3, 149.8, 143.5, 139.3, 138.5, 137.3, 135.7, 135.1, 131.9, 129.4, 128.9, 128.2, 128.0, 127.24, 127.19, 126.7, 125.1, 123.0, 115.8, 112.6, 108.7, 77.7, 68.9, 60.5, 56.5, 56.2, 26.6, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{33}N_2O_6S_2^+$ 665.1775, found 665.1772.



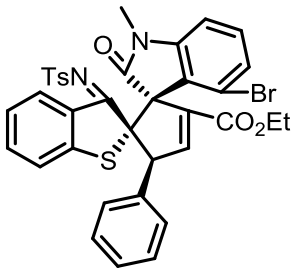

**Ethyl (*E*)-1'',5''-dimethyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5g)**

Yellow solid: 53 mg (yield 82%); mp 223-225 ℃; IR (KBr) 3061, 2984, 1706, 1602, 1579, 1315, 1089, 671, 550 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.38 (s, 1H), 7.26 – 7.22 (m, 1H), 7.11 – 7.05 (m, 2H), 7.04 – 6.98 (m, 4H), 6.98 – 6.91 (m, 2H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.55 (d, *J* = 2.0 Hz, 1H), 4.10 – 3.92 (m, 2H), 3.26 (s, 3H), 2.53 (s, 3H), 2.17 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.4, 175.6, 162.7, 151.0, 149.5, 143.4, 142.4, 139.4, 137.3, 135.5, 135.2, 132.6, 131.8, 129.3, 129.3, 129.0, 128.1, 127.6, 127.3, 127.2, 125.7, 124.9, 122.9, 107.6, 77.6, 68.4, 60.4, 56.2, 26.6, 21.7, 20.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{33}N_2O_5S_2^+$ 649.1825, found 649.1807.



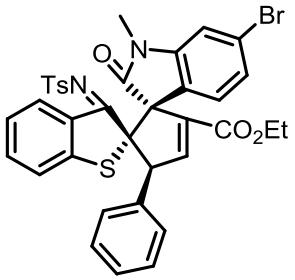

**Ethyl (*E*)-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5h)**

Yellow solid: 17 mg (yield 27%); mp 216-218 °C; IR (KBr) 3059, 2980, 1713, 1604, 1578, 1314, 1289, 749, 670, 546 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.30 – 7.27 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.12 – 7.06 (m, 2H), 7.03 – 6.97 (m, 4H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.56 (d, *J* = 2.0 Hz, 1H), 4.07 – 3.85 (m, 2H), 3.28 (s, 3H), 2.53 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.4, 175.7, 162.7, 151.0, 149.7, 144.9, 143.5, 139.3, 137.1, 135.6, 135.1, 132.0, 129.4, 129.2, 129.0, 128.2, 128.0, 127.3, 127.2, 126.6, 125.8, 125.0, 123.1, 122.9, 108.0, 77.5, 68.4, 60.5, 56.2, 26.5, 21.7, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{36}H_{30}N_2NaO_5S_2^+$ 657.1488, found 657.1505.



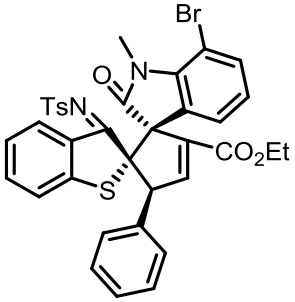

**Ethyl (*E*)-4''-bromo-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[b]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5i)**

Yellow solid: 27 mg (yield 38%); mp 246-248 °C; IR (KBr) 2955, 1714, 1590, 1304, 1243, 1089, 733, 538 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.34 – 7.28 (m, 1H), 7.13 – 7.07 (m, 2H), 7.05 – 6.95 (m, 6H), 6.91 (d, *J* = 2.0 Hz, 1H), 5.54 (d, *J* = 2.0 Hz, 1H), 4.12 – 3.90 (m, 2H), 3.26 (s, 3H), 2.53 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.1, 175.6, 162.5, 150.9, 150.0, 146.3, 143.6, 139.1, 136.8, 135.9, 134.8, 132.1, 129.4, 129.0, 128.2, 128.0, 127.7, 127.4, 127.2, 125.9, 125.3, 124.8, 123.1, 123.0, 111.7, 68.1, 60.7, 56.5, 26.7, 21.8, 14.0 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}BrN_2O_5S_2^+$ 713.0774, found 713.0786.



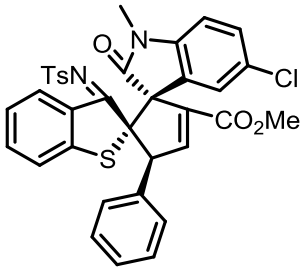

**Ethyl (*E*)-6''-bromo-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5j)**

Yellow solid: 34 mg (yield 48%); mp 219-221 ℃; IR (KBr) 3062, 2963, 1715, 1601, 1573, 1366, 1321, 1085, 668, 551 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.38 (m, 4H), 7.33 – 7.28 (m, 1H), 7.11 (d, *J* = 7.7 Hz, 2H), 7.05 – 6.96 (m, 6H), 6.91 (d, *J* = 1.6 Hz, 1H), 5.54 (d, *J* = 2.0 Hz, 1H), 4.07 – 3.95 (m, 2H), 3.25 (s, 3H), 2.53 (s, 3H), 1.06 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.1, 175.6, 162.5, 150.9, 149.9, 146.3, 143.6, 139.2, 136.8, 135.9, 134.8, 132.1, 129.4, 129.0, 128.2, 128.0, 127.8, 127.4, 127.2, 125.9, 125.3, 124.9, 123.1, 123.0, 111.7, 68.1, 60.7, 56.5, 26.7, 21.7, 14.0 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}BrN_2O_5S_2^+$ 713.0774, found 713.0795.



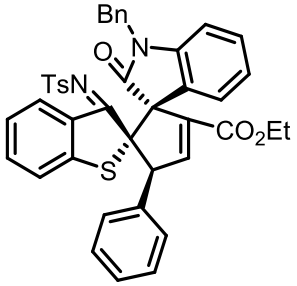

**Ethyl (*E*)-7''-bromo-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5k)**

Yellow solid: 45 mg (yield 63%); mp 181-183 °C; IR (KBr) 2982, 1713, 1560, 1452, 1319, 1293, 1084, 670, 550 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.47 – 7.42 (m, 3H), 7.33 – 7.26 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 1H), 7.11 – 7.06 (m, 1H), 7.01 – 6.93 (m, 5H), 6.74 (t, *J* = 7.8 Hz, 1H), 5.55 (d, *J* = 1.6 Hz, 1H), 4.09 – 3.91 (m, 2H), 3.67 (s, 3H), 2.54 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.1, 176.4, 162.8, 150.8, 150.3, 143.8, 142.3, 139.2, 136.7, 136.0, 135.11, 135.08, 132.1, 129.5, 129.14, 129.12, 128.3, 128.0, 127.42, 127.35, 125.7, 125.3, 124.2, 123.2, 102.4, 77.9, 68.2, 60.7, 56.0, 30.6, 21.9, 14.0 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}BrN_2O_5S_2^+$ 713.0774, found 713.0806.



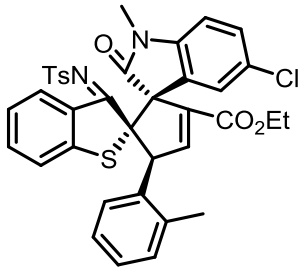

**Methyl (*E*)-5''-chloro-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5l)**

Yellow solid: 52 mg (yield 79%); mp 187-189 °C; IR (KBr) 3064, 2945, 1703, 1604, 1580, 1328, 1157, 821, 671, 554 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.30 – 7.27 (m, 1H), 7.14 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.11 – 7.06 (m, 2H), 7.05 – 6.96 (m, 5H), 6.68 (d, *J* = 8.4 Hz, 1H), 5.54 (d, *J* = 2.0 Hz, 1H), 3.61 (s, 3H), 3.26 (s, 3H), 2.53 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.8, 175.2, 162.9, 150.5, 150.0, 143.5, 143.4, 139.1, 136.5, 135.8, 134.7, 132.1, 129.35, 129.25, 129.0, 128.5, 128.2, 127.9, 127.5, 127.3, 127.2, 125.2, 122.9, 108.9, 77.4, 68.1, 56.7, 51.8, 26.7, 21.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{35}H_{28}ClN_2O_5S_2^+$ 655.1123, found 655.1138.



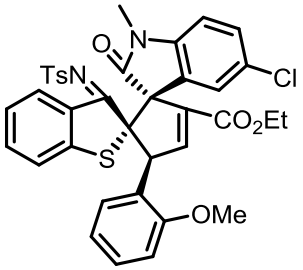

**Ethyl (*E*)-1''-benzyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5m)**

Yellow solid: 36 mg (yield 51%); mp 229-231 °C; IR (KBr) 2974, 1708, 1601, 1575, 1313, 1150, 1088, 751, 672, 548 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.47 – 7.40 (m, 4H), 7.37 – 7.26 (m, 4H), 7.12 – 7.03 (m, 3H), 7.01 – 6.98 (m, 4H), 6.98 – 6.93 (m, 1H), 6.88 – 6.82 (m, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.59 (d, *J* = 2.0 Hz, 1H), 5.06 – 4.94 (m, 2H), 4.11 – 4.00 (m, 1H), 3.91 – 3.82 (m, 1H), 2.54 (s, 3H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.3, 175.9, 162.7, 150.8, 150.0, 144.1, 143.6, 139.2, 137.1, 135.7, 135.5, 135.1, 132.1, 129.4, 129.12, 129.09, 128.6, 128.2, 128.1, 127.6, 127.5, 127.2, 126.60, 125.9, 125.1, 123.1, 122.8, 109.1, 77.8, 68.5, 60.5, 55.9, 44.2, 21.75, 13.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{42}H_{35}N_2O_5S_2^+$ 711.1982, found 711.1993.



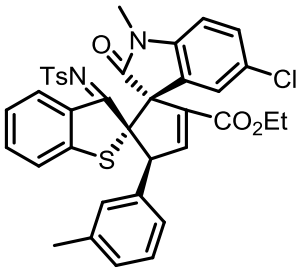
**Ethyl (*E*)-5''-chloro-1''-methyl-2''-oxo-5'-(o-tolyl)-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5n)**

Yellow solid: 22 mg (yield 32%); mp 215-217 °C; IR (KBr) 3075, 2927, 1718, 1603, 1578, 1318, 1297, 812, 670, 547 $cm^{-1}$;$^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.29 – 7.27 (m, 0H), 7.26 – 7.24 (m, 1H), 7.16 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.10 – 7.06 (m, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.02 – 6.89 (m, 4H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.00 (d, *J* = 2.0 Hz, 1H), 4.04 – 3.97 (m, 1H), 3.93-3.85 (m, 1H), 3.27 (s, 3H), 2.50 (s, 3H), 2.47 (s, 3H), 1.01 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 178.0, 175.4, 162.36, 151.1, 150.1, 143.7, 143.5, 139.1, 137.5, 137.3, 135.7, 132.9, 132.14, 132.09, 130.3, 129.6, 129.1, 128.4, 128.2, 128.0, 127.7, 127.4, 127.3, 125.8, 125.2, 122.6, 108.8, 79.2, 67.2, 60.5, 54.8, 26.7, 21.7, 20.9, 13.9 ppm. HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{37}H_{32}ClN_2O_5S_2^+$ 683.1436, found 683.1434.




**Ethyl (*E*)-5''-chloro-5'-(2-methoxyphenyl)-1''-methyl-2''-oxo-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5o)**

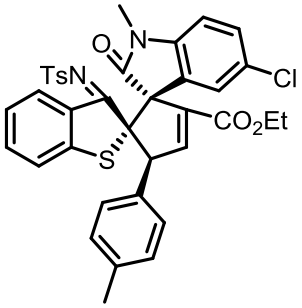
Yellow solid: 54 mg (yield 77%); mp 146-148 °C; IR (KBr) 2982, 1713, 1603, 1295, 1234, 815, 668, 542 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.14 – 7.02 (m, 3H), 6.98 – 6.92 (m, 1H), 6.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.68 – 6.59 (m, 3H), 5.98 (d, *J* = 2.0 Hz, 1H), 4.06 – 3.88 (m, 2H), 3.61 (s, 3H), 3.26 (s, 3H), 2.50 (s, 3H), 1.01 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 178.5, 175.4, 162.5, 157.6, 151.6, 151.5, 143.5, 139.2, 136.0, 135.5, 132.1, 132.0, 129.5, 129.0, 128.9, 128.3, 127.9, 127.6, 127.6, 127.3, 124.8, 123.1, 122.5, 120.0, 110.1, 108.7, 78.0, 67.8, 60.5, 55.0, 51.9, 26.7, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{37}H_{32}ClN_2O_6S_2^+$ 699.1385, found 699.1392.




**Ethyl (*E*)-5''-chloro-1''-methyl-2''-oxo-5'-(m-tolyl)-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5p)**

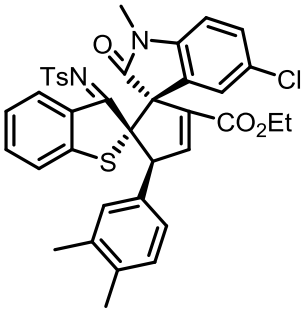
Yellow solid: 58 mg (yield 59%); mp 206-208 ℃; IR (KBr) 2973, 1711, 1605, 1578, 1312, 814, 771, 671, 548 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.49 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.14 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.94 – 6.85 (m, 4H), 6.68 (d, *J* = 8.4 Hz, 1H), 5.53 (d, *J* = 2.0 Hz, 1H), 4.11 – 3.90 (m, 2H), 3.26 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 178.1, 175.3, 162.4, 150.7, 150.0, 143.5, 143.5, 139.2,

137.7, 136.9, 135.7, 134.6, 132.1, 129.7, 129.5, 129.2, 128.5, 128.3, 128.0, 127.9, 127.5, 127.3, 127.2, 126.0, 125.2, 122.9, 108.8, 77.5, 68.0, 60.6, 56.9, 26.7, 21.7, 21.3, 13.9 ppm. HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{36}H_{32}ClN_2O_5S_2^+$ 683.1436, found 683.1439.



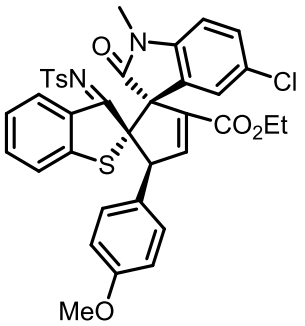

**Ethyl (*E*)-5''-chloro-1''-methyl-2''-oxo-5'-(p-tolyl)-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5q)**

Yellow solid: 54 mg (yield 79%); mp 2213-215 °C; IR (KBr) 2981,1712, 1606, 1580, 1318, 1291, 816, 667, 547 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.31 – 7.26 (m, 1H), 7.14 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.03 – 6.96 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.50 (d, *J* = 2.0 Hz, 1H), 4.10 – 3.88 (m, 2H), 3.26 (s, 3H), 2.53 (s, 3H), 2.20 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 177.9, 175.3, 162.5, 150.6, 150.3, 143.6, 143.4, 139.1, 137.0, 136.5, 135.7, 132.1, 131.6, 129.4, 129.1, 129.0, 128.9, 128.5, 127.9, 127.5, 127.3, 127.1, 125.2, 122.9, 108.8, 77.6, 68.2, 60.6, 56.2, 26.6, 21.7, 21.1, 13.9 ppm. HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{36}H_{32}ClN_2O_5S_2^+$ 683.1436, found 683.1431.



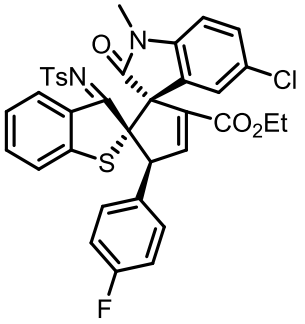

**Ethyl (*E*)-5''-chloro-5'-(3,4-dimethylphenyl)-1''-methyl-2''-oxo-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5r)**

Yellow solid: 44 mg (yield 63%); mp 121-123 °C; IR (KBr) 2978, 2930, 1171, 1604, 1310, 1288, 1245, 733, 543 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.13 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.85 (s, 1H), 6.80 – 6.73 (m, 2H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.50 (d, *J* = 2.0 Hz, 1H), 4.09 – 3.88 (m, 1H), 3.26 (s, 2H), 2.52 (s, 3H), 2.09 (s, 3H), 1.96 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 178.2, 175.3, 162.5, 150.8, 150.6, 143.47, 143.45, 139.2, 136.6, 136.2, 135.7, 132.0, 131.9, 130.4, 129.5, 129.4, 129.1, 128.5, 128.0, 127.5, 127.2, 126.5, 125.2, 122.9, 108.8, 77.6, 68.1, 60.6, 56.5, 26.7, 21.7, 19.6, 19.4, 13.9 ppm. HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{38}H_{34}ClN_2O_5S_2^+$ 697.1592, found 697.1620.



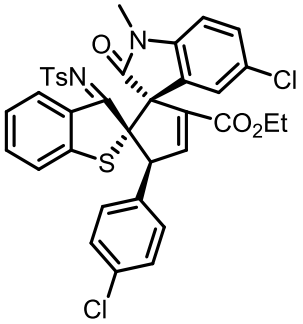

**Ethyl (*E*)-5''-chloro-5'-(4-methoxyphenyl)-1''-methyl-2''-oxo-3-(tosylimino)-3*H*-dispiro[benzo[b]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate（5s）**

Yellow solid: 23 mg (yield 33%); mp 241-243 ℃; IR (KBr) 2955, 1714, 1590, 1304, 1243, 1089, 733, 538 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.14 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.57 – 6.49 (m, 2H), 5.49 (d, *J* = 1.6 Hz, 1H), 4.10 – 3.88 (m, 2H), 3.69 (s, 3H), 3.26 (s, 3H), 2.52 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.0, 175.3, 162.5, 158.7, 150.6, 150.3, 143.6, 143.4, 139.1, 136.6, 135.7, 132.1, 130.3, 129.4, 129.1, 128.5, 127.9, 127.5, 127.4, 127.1, 126.7, 125.2, 122.9, 113.6, 108.8, 77.7, 68.1, 60.6, 56.0, 55.1, 26.7, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{37}H_{32}ClN_2O_6S_2^+$ 699.1385, found 699.1395.



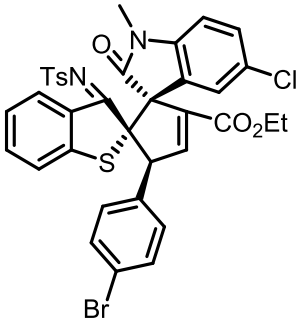

**Ethyl (*E*)-5''-chloro-5'-(4-fluorophenyl)-1''-methyl-2''-oxo-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5t)**

Yellow solid: 52 mg (yield 76%); mp 218-220 °C; IR (KBr) 3064, 2981, 1710, 1607, 1581, 1319, 1153, 1088, 785, 667, 550 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.14 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.04 – 6.95 (m, 3H), 6.74 – 6.65 (m, 3H), 5.50 (d, *J* = 1.6 Hz, 1H), 4.07 – 3.92 (m, 2H), 3.26 (s, 3H), 2.53 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.8, 175.2, 162.4, 162.0 (d, *J* = 245.0 Hz), 150.4, 149.4, 143.8, 143.4, 138.9, 137.0, 135.9, 132.1, 130.7 (d, *J* = 80.0 Hz), 130.5 (d, *J* = 32.0 Hz), 129.5, 129.2, 128.6, 127.8, 127.3, 127.1, 125.4, 122.9, 115.2, 115.0, 108.9, 77.5, 68.1, 60.7, 55.8, 26.7, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}ClFN_2O_5S_2^+$ 687.1185, found 687.1207.



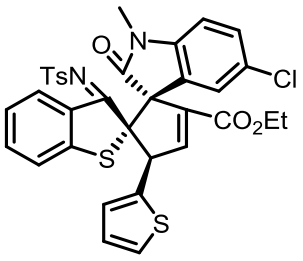

**Ethyl (*E*)-5''-chloro-5'-(4-chlorophenyl)-1''-methyl-2''-oxo-3-(tosylimino)-3*H*-dispiro[benzo[b]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate（5u）**

Yellow solid: 53 mg (yield 75%); mp 211-215 ℃; IR (KBr) 2954, 1714, 1591, 1488, 1316,1090, 797, 556 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.14 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.98 – 6.90 (m, 4H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.47 (d, *J* = 2.0 Hz, 1H), 4.09 – 3.88 (m, 2H), 3.26 (s, 3H), 2.53 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.7, 175.1, 162.3, 150.2, 149.2, 143.8, 143.4, 138.8, 136.9, 136.0, 133.3, 132.1, 130.4, 129.5, 129.3, 128.6, 128.4, 127.8, 127.3, 127.2, 127.0, 125.4, 123.0, 108.9, 68.3, 60.7, 55.6, 26.7, 21.8, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}Cl_2N_2O_5S_2^+$ 703.0889, found 703.0900.



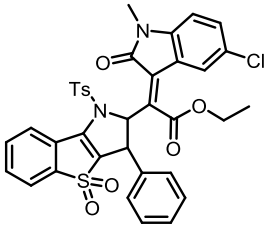

**Ethyl (*E*)-5'-(4-bromophenyl)-5''-chloro-1''-methyl-2''-oxo-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5v)**

Yellow solid: 25 mg (yield 33%); mp 205-207 ℃; IR (KBr) 2950, 1714, 1586, 1318, 1091, 799, 676 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.17 – 7.02 (m, 4H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.45 (d, *J* = 2.4 Hz, 1H), 4.10 – 3.92 (m, 1H), 3.26 (s, 2H), 2.53 (s, 2H), 1.04 (t, *J* = 7.2 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.6, 175.1, 162.3, 150.2, 149.1, 143.8, 143.4, 138.8, 136.9, 136.0, 133.9, 132.2, 131.3, 130.7, 129.5, 129.3, 128.6, 127.8, 127.4, 127.2, 126.9, 125.4, 123.0, 121.6, 108.9, 68.3, 60.7, 55.6, 26.7, 21.8, 13.9 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}BrClN_2O_5S_2^+$ 747.0384, found 747.0382.



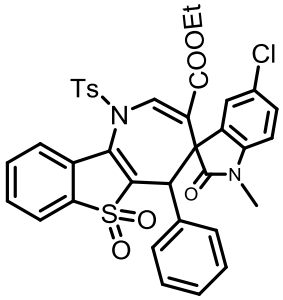
**Ethyl (*E*)-5''-chloro-1''-methyl-2''-oxo-5'-(thiophen-2-yl)-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (5w)**

Yellow solid: 65 mg (yield 96%); mp 196-198 °C; IR (KBr) 2978, 1711, 1606, 1580, 1321, 1150, 774, 668, 551 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.35 – 7.30 (m, 1H), 7.16 – 7.11 (m, 2H), 7.08 – 7.02 (m, 2H), 6.71 – 6.65 (m, 2H), 6.42 (d, *J* = 3.6 Hz, 1H), 5.68 (s, 1H), 4.09 – 3.90 (m, 2H), 3.25 (s, 3H), 2.51 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.5, 175.0, 162.3, 150.5, 149.3, 143.5, 143.4, 138.9, 136.9, 136.4, 135.8, 132.1, 129.3, 128.4, 128.1, 127.4, 127.2, 126.8, 126.63, 126.55, 125.6, 125.4, 123.1, 108.9, 68.0, 60.7, 52.9, 26.7, 21.7, 13.9 ppm. HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{34}H_{28}ClN_2O_5S_3^+$ 675.0843, found 675.0847.




**Ethyl (*E*)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-(4,4-dioxido-3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrol-2-yl)acetate (6)**

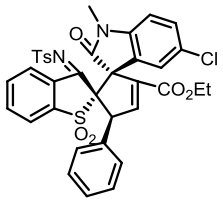
Yellow solid: 22 mg (yield 42%); mp 230-232 °C; IR (KBr) 2927, 1709, 1614, 1374, 1309, 1160, 589, 544 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.6 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.65 – 7.59 (m, 3H), 7.35 (d, *J* = 4.8 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.28 (s, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 2H), 4.66 (d, *J* = 4.4 Hz, 1H), 4.46 – 4.20 (m, 2H), 3.15 (s, 3H), 2.46 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.9, 165.1, 148.7, 145.5, 144.4, 142.5, 140.1, 137.5, 133.5, 131.8, 131.1, 130.9, 130.4, 129.5, 128.5, 128.4, 127.9, 127.8, 127.4, 125.2, 125.1, 124.2, 121.6, 121.1, 109.2, 71.3, 62.7, 49.1, 26.3, 21.7, 13.8 ppm. HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{36}H_{30}ClN_2O_7S_2^+$ 701.1177, found 701.1190.




**Ethyl 5'-chloro-1'-methyl-2'-oxo-5-phenyl-1-tosyl-1,5-dihydrospiro[benzo[4,5]thieno[3,2-*b*]azepine-4,3'-indoline]-3-carboxylate 6,6-dioxide (7)**

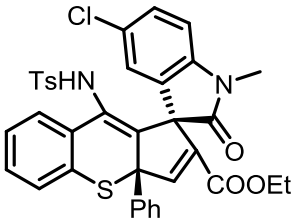
White solid: 36 mg (yield 69%); mp 209-211 °C; IR (KBr) 2982, 1718, 1611, 1377, 1175, 1164, 720, 543 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.61 (m, 5H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.90 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.18 (d, *J* = 8.4 Hz, 1H), 6.10 (d, *J* = 2.0 Hz, 1H), 5.73 (d, *J* = 7.6 Hz, 1H), 4.05 – 3.81 (m, 2H), 3.31 (s, 1H), 3.03 (s, 3H), 2.65 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.2, 164.6, 146.8, 142.4, 140.8, 137.6, 137.4, 137.3, 135.6, 132.8, 131.9, 131.3, 131.1, 130.6, 129.5, 129.2, 128.4, 128.0, 127.8, 127.4, 127.2, 126.8, 124.7, 122.00, 121.97,

120.9, 108.4, 61.6, 55.9, 49.5, 26.4, 21.9, 13.7 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}ClN_2O_7S_2^+$ 701.1177, found 701.1199.



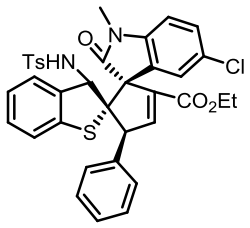

**Ethyl (*E*)-5''-chloro-1''-methyl-2''-oxo-5'-phenyl-3-(tosylimino)-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate 1,1-dioxide (8)**

White solid: 19 mg (yield 36%); mp 220-222 ℃; IR (KBr) 3086, 2982, 1718, 1611, 1378, 1316, 1164, 775, 720, 543 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.51 – 7.45 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.25 (m, 1H), 7.23 – 7.16 (m, 3H), 7.09 (d, *J* = 2.0 Hz, 1H), 7.08 – 7.02 (m, 3H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.16 (d, *J* = 1.6 Hz, 1H), 4.07 – 3.90 (m, 1H), 3.89 – 3.72 (m, 1H), 3.29 (s, 3H), 2.48 (s, 3H), 0.93 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.3, 166.9, 161.8, 145.8, 144.6, 144.5, 144.0, 137.8, 137.7, 136.2, 133.8, 132.8, 130.7, 130.2, 129.9, 129.3, 128.3, 128.3, 128.1, 127.74, 127.71, 127.67, 127.6, 121.5, 108.8, 85.1, 64.3, 60.7, 57.3, 27.2, 21.7, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}ClN_2O_7S_2^+$ 701.1177, found 701.1189.




**Ethyl (*E*)-5'-chloro-1'-methyl-2'-oxo-3a-phenyl-9-(tosylimino)-3a,9a-dihydro-9*H*-spiro[cyclopenta[*b*]thiochromene-1,3'-indoline]-2-carboxylate (9)**

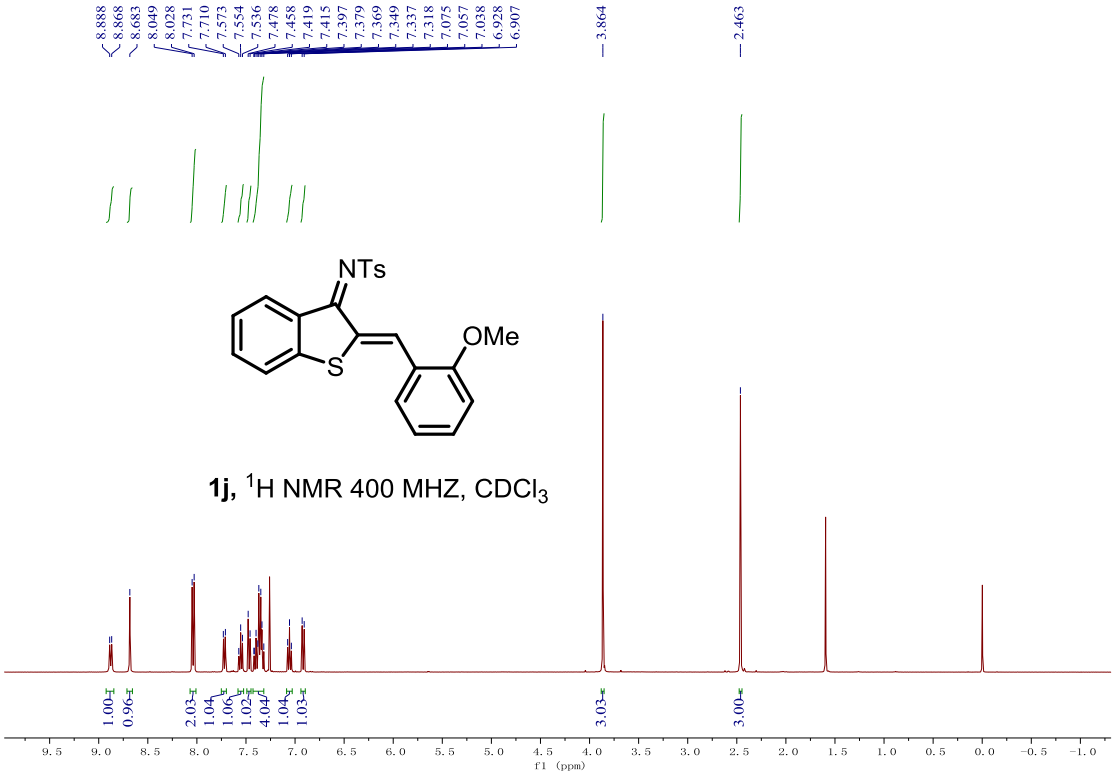
White solid: 31 mg (yield 62%); mp 224-226 °C; IR (KBr) 3177, 1721, 1694, 1610, 1490, 1341, 1162, 767, 661, 549 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.26 – 7.24 (m, 2H), 7.18 (s, 1H), 7.17 – 7.11 (m, 3H), 7.10 (s, 1H), 6.97 – 6.91 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.47 – 6.38 (m, 1H), 6.08 – 6.00 (m, 1H), 5.34 (s, 1H), 4.06 – 3.93 (m, 2H), 3.41 (s, 3H), 2.38 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.6, 161.8, 146.9, 144.2, 143.9, 139.4, 139.2, 138.4, 136.4, 131.94, 131.86, 131.8, 129.8, 129.7, 128.9, 128.9, 128.2, 128.0, 127.7, 127.3, 126.0, 125.5, 124.7, 109.3, 64.5, 62.5, 61.1, 27.0, 21.6, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}ClN_2O_5S_2^+$ 669.1279, found 669.1274.



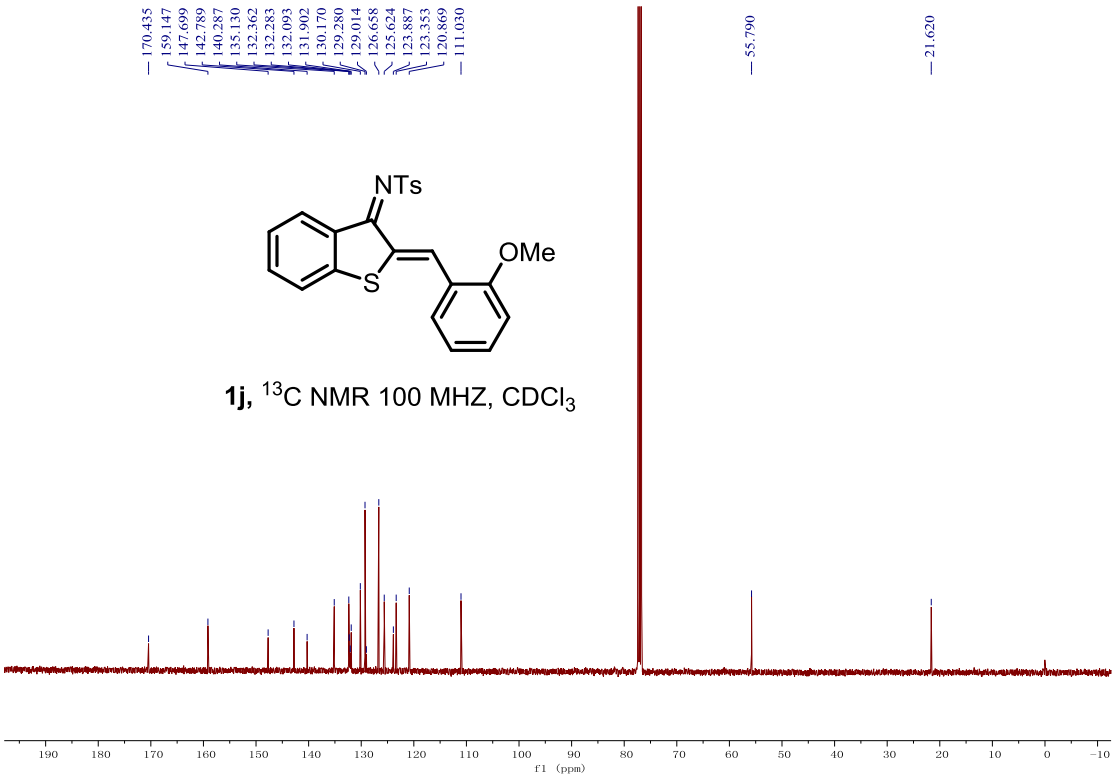

**Ethyl 5''-chloro-1''-methyl-3-((4-methylphenyl)sulfonamido)-2''-oxo-5'-phenyl-3*H*-dispiro[benzo[*b*]thiophene-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (10)**

White solid: 22 mg (yield 40%); mp 227-229 °C; IR (KBr) 3064, 2956, 1703, 1612, 1332, 1166, 1087, 753, 668, 551 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.16 – 7.07 (m, 3H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.70 – 6.64 (m, 1H), 6.37 (d, *J* = 7.6 Hz, 1H), 5.68 – 5.55 (m, 2H), 4.75 (d, *J* = 10.4 Hz, 1H), 4.09 – 3.99 (m, 1H), 3.92 – 3.82 (m, 1H), 3.25 (s, 3H), 2.43 (s, 3H), 1.01 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.0, 162.4, 148.9, 143.6, 143.4, 139.4, 138.6, 136.8, 136.1, 134.5, 129.9, 129.2, 128.8, 128.6, 128.0, 127.9, 127.8, 127.4, 126.9, 125.2, 123.5, 121.4, 109.1, 77.8, 67.3, 64.8, 60.6, 57.0, 26.7, 21.6, 13.8 ppm. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{36}H_{31}ClN_2O_5S_2^+$ 671.1436, found 671.1431.

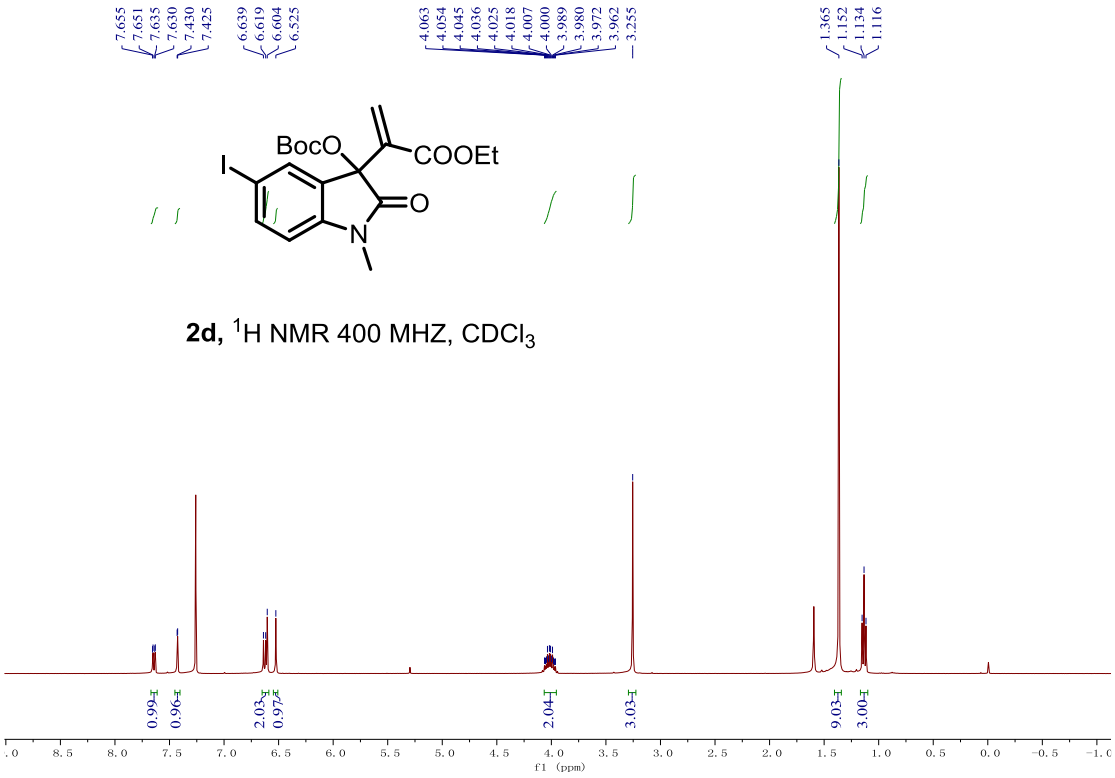
## 8. NMR spectra of all new compounds



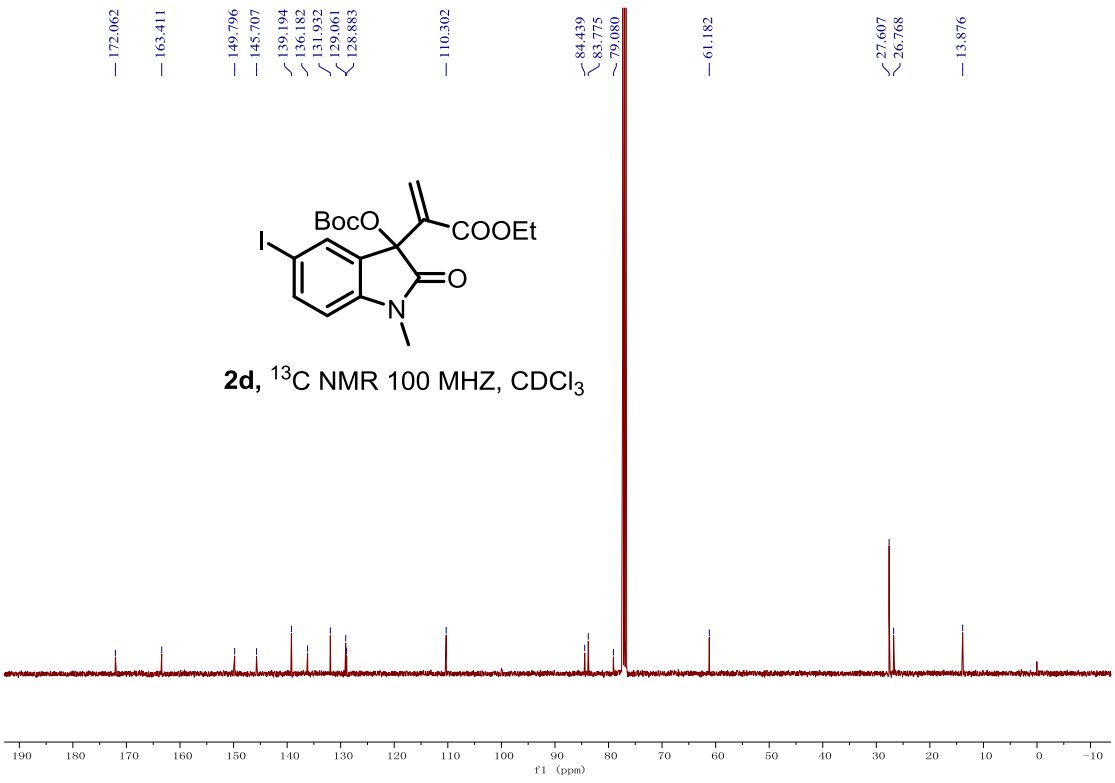

**1j,** $^{1}$H NMR 400 MHZ, $CDCl_3$



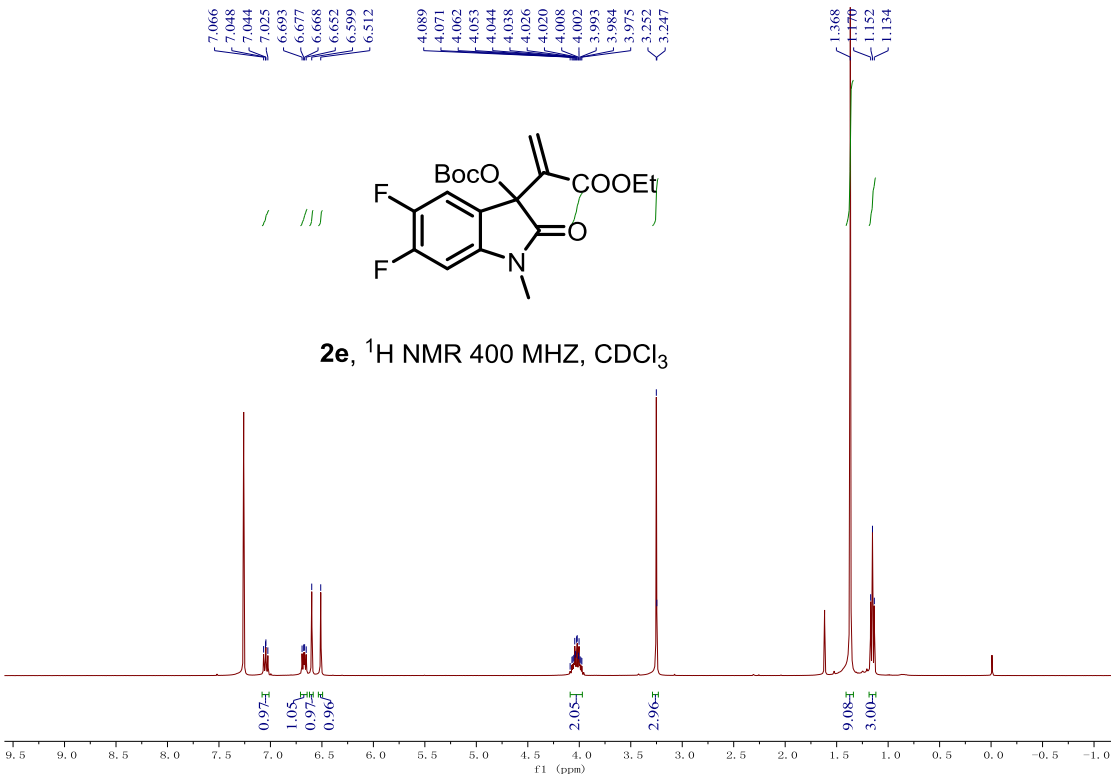

**1j,** $^{13}$C NMR 100 MHZ, $CDCl_3$



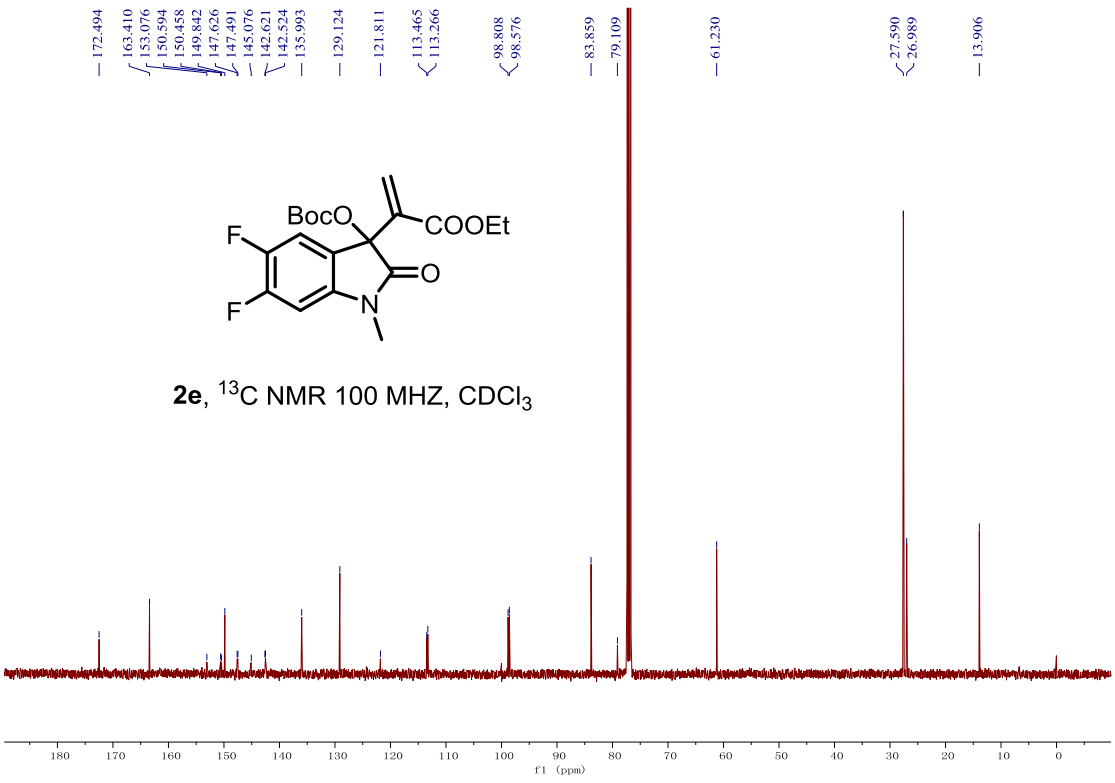

**2d,** $^{1}$H NMR 400 MHZ, $CDCl_3$



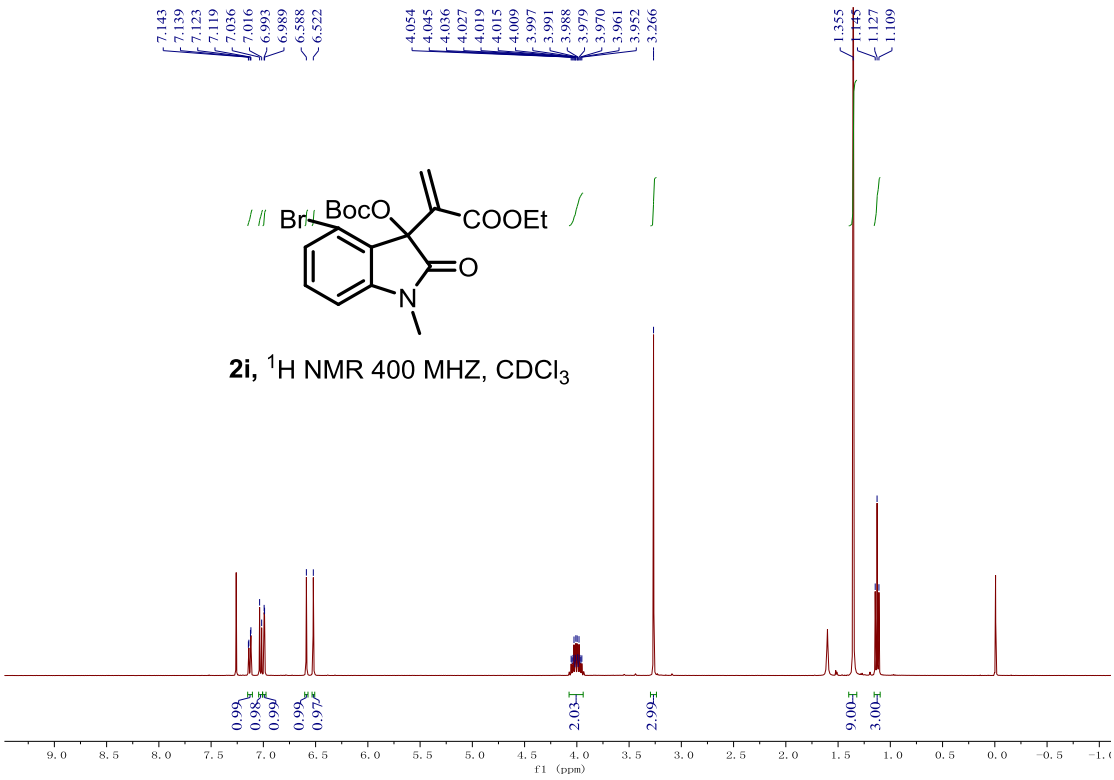

**2d,** $^{13}$C NMR 100 MHZ, $CDCl_3$



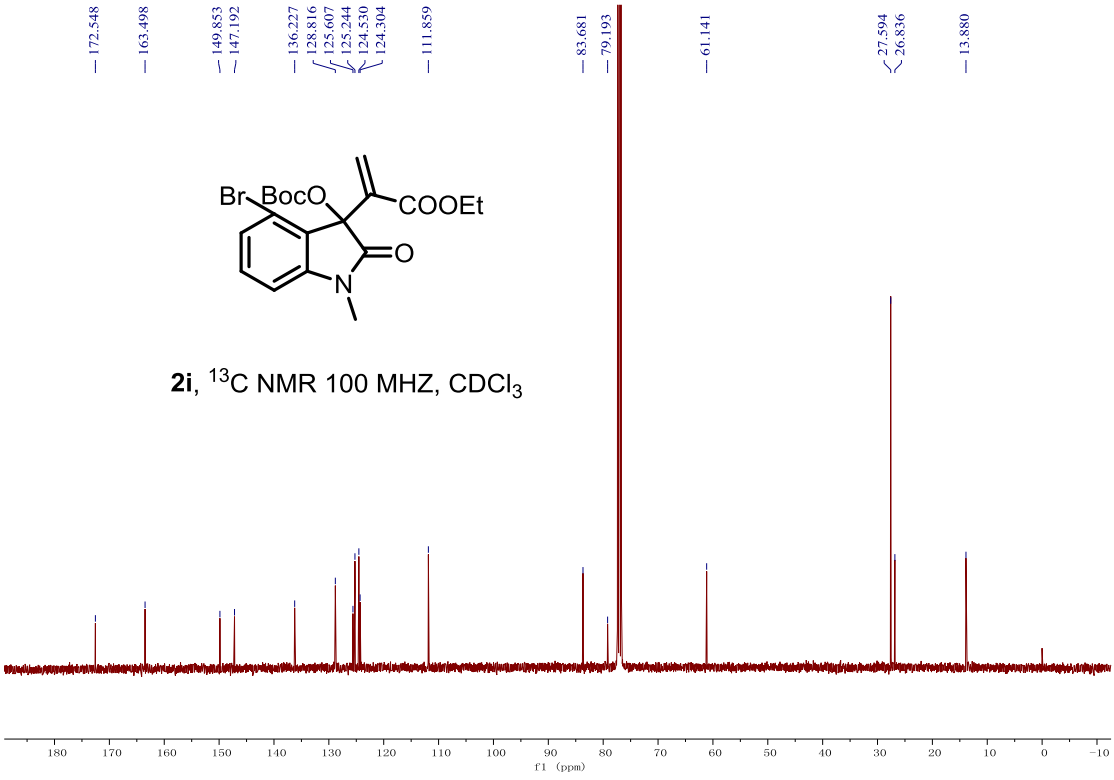

**2e**, $^{1}$H NMR 400 MHZ, $CDCl_3$



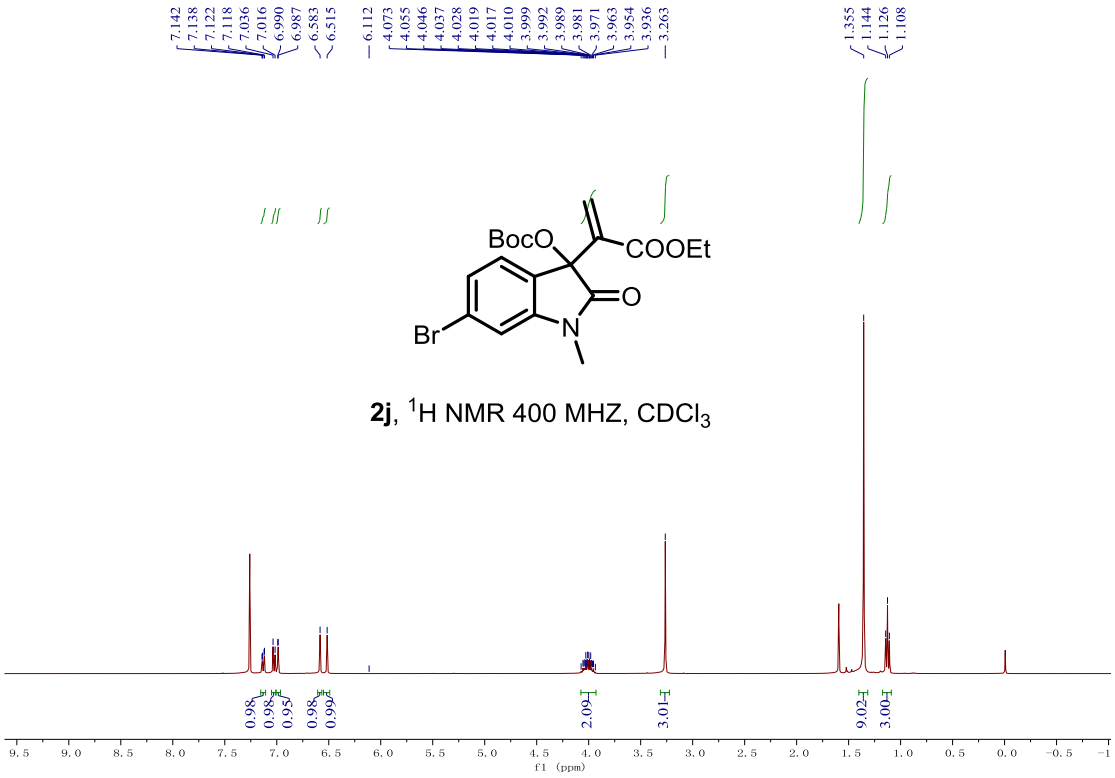

**2e**, $^{13}$C NMR 100 MHZ, $CDCl_3$



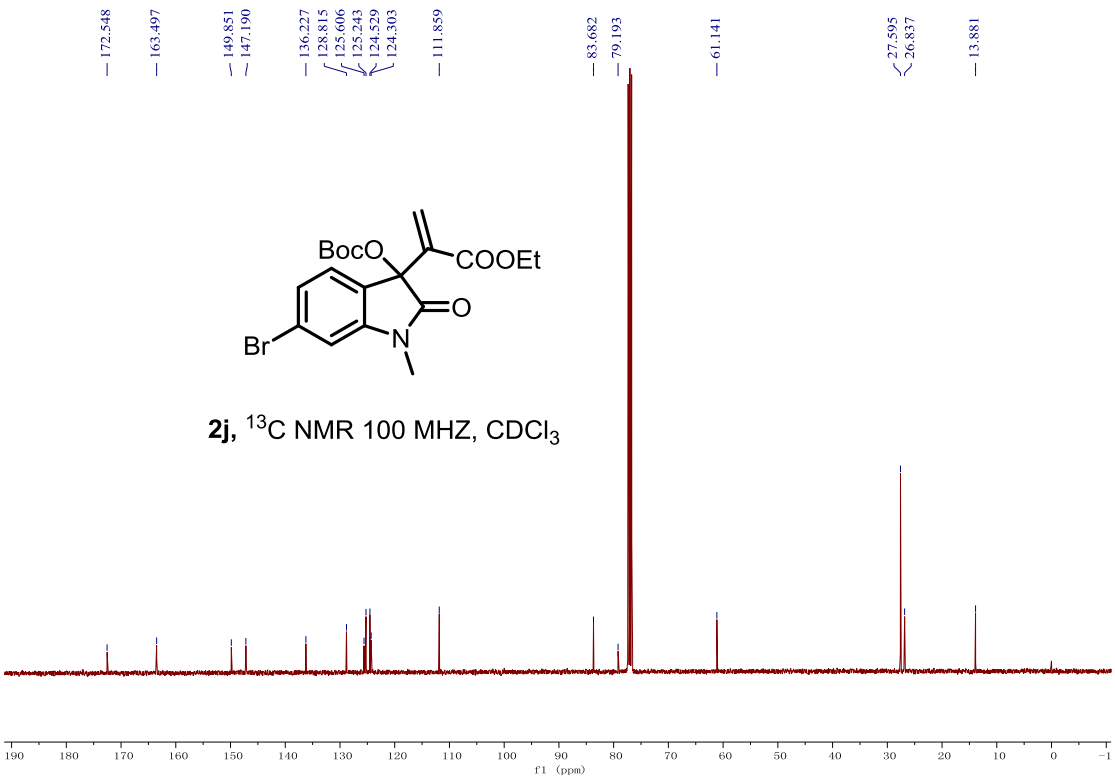

**2i,** $^{1}$H NMR 400 MHZ, $CDCl_3$



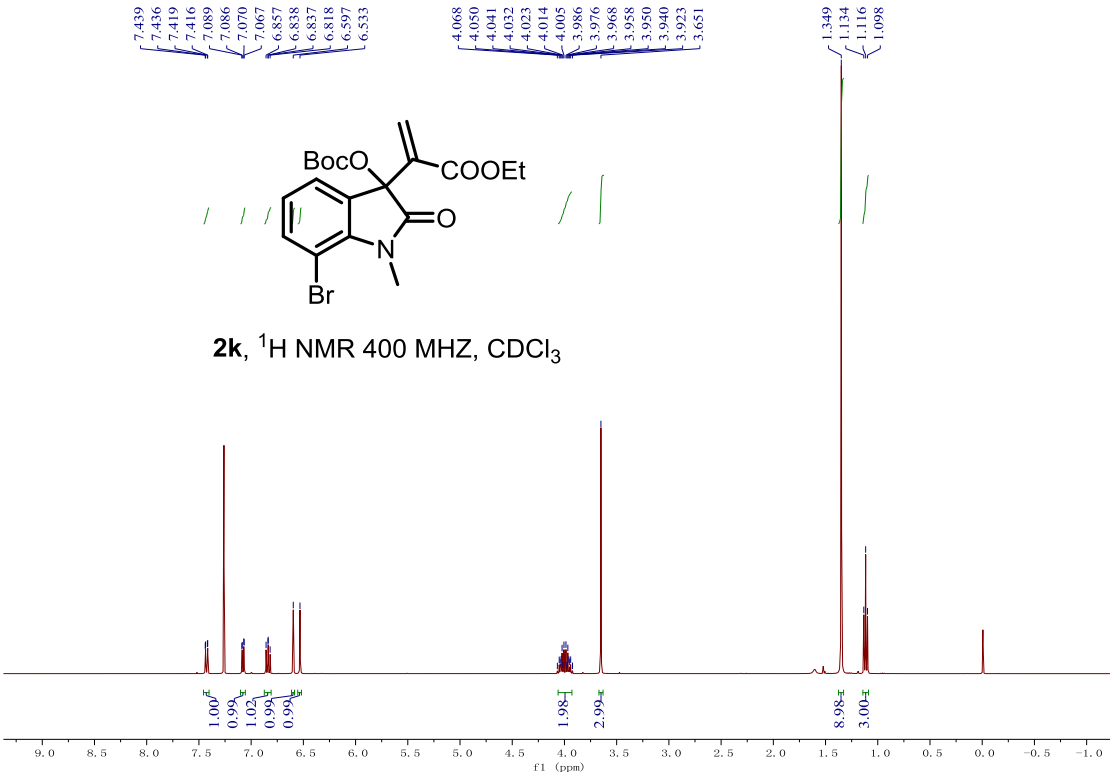

**2i**, $^{13}$C NMR 100 MHZ, $CDCl_3$



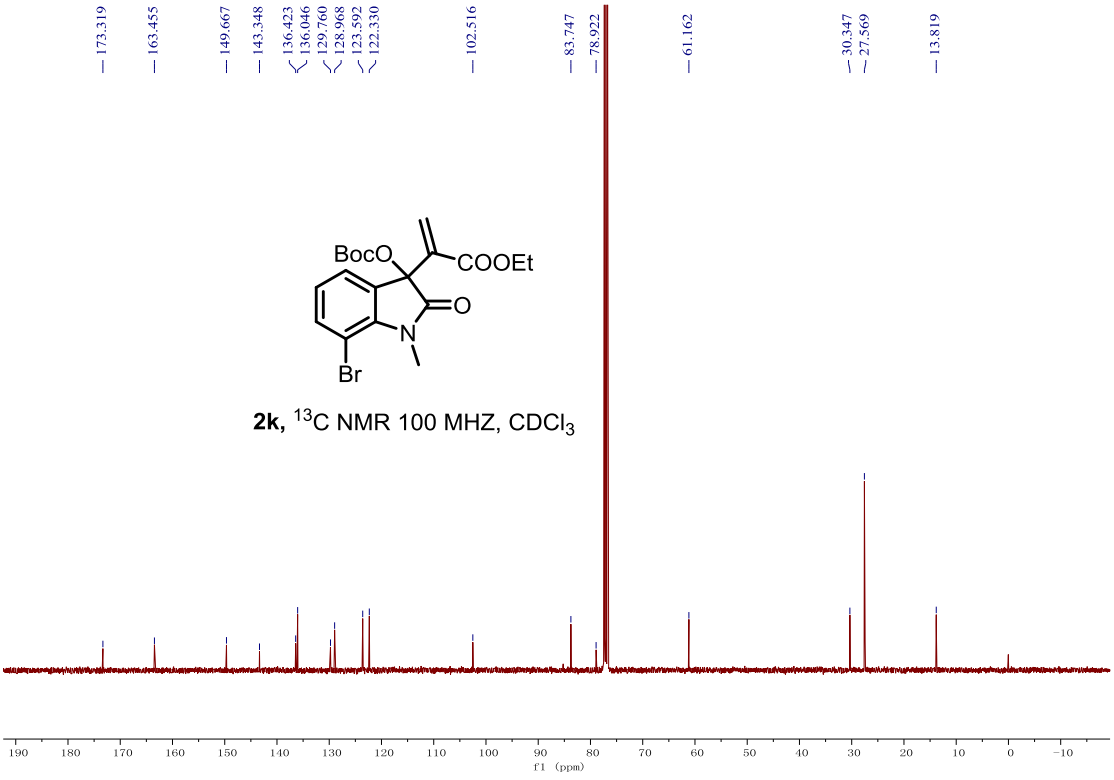

**2j**, $^{1}$H NMR 400 MHZ, $CDCl_3$



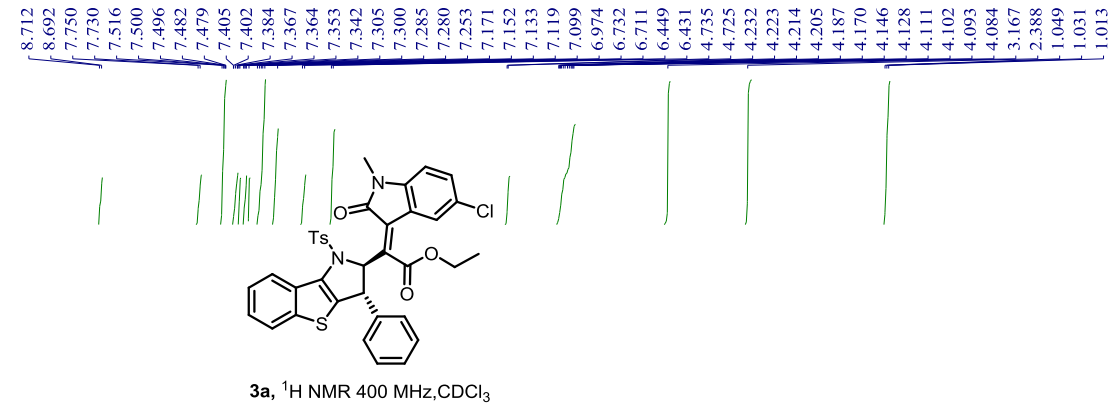

**2j,** $^{13}$C NMR 100 MHZ, $CDCl_3$



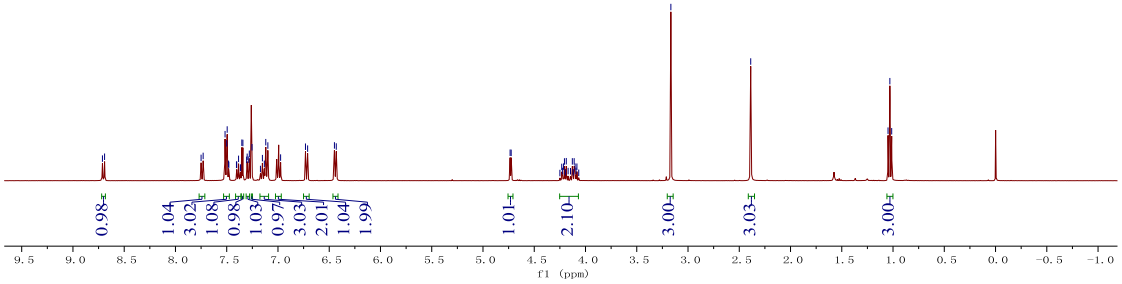

**2k**, $^{1}$H NMR 400 MHZ, $CDCl_3$

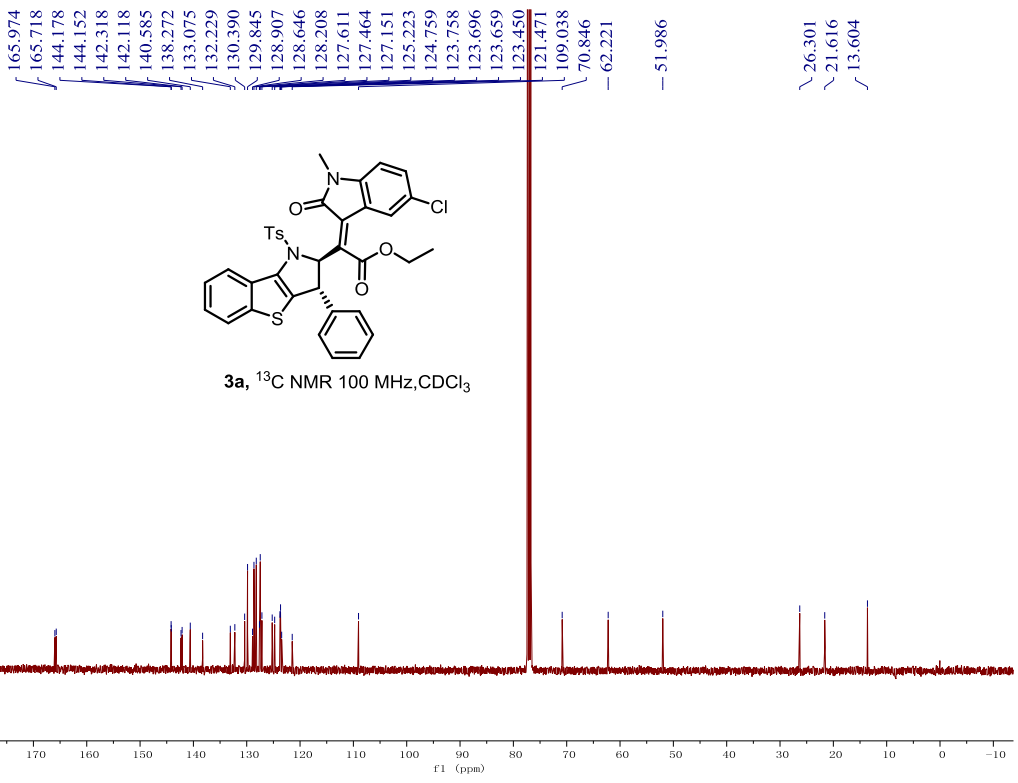



**2k,** $^{13}$C NMR 100 MHZ, $CDCl_3$

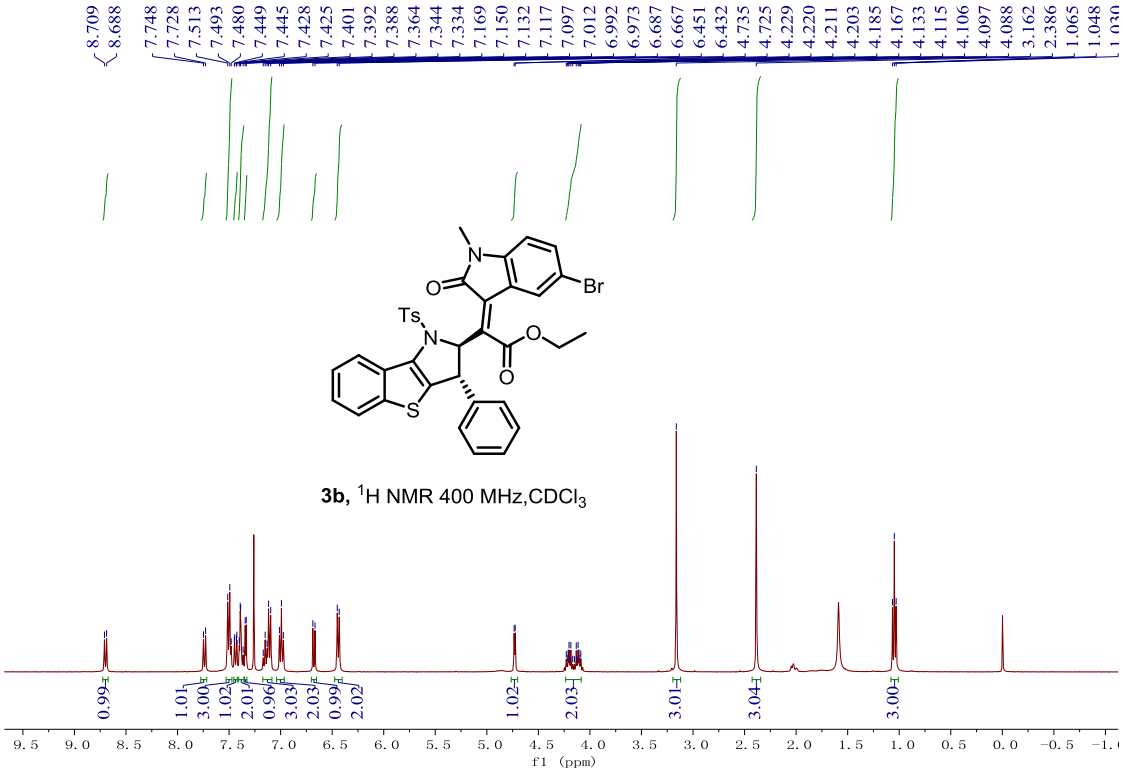



**3a,** $^{1}$H NMR 400 MHz,$CDCl_3$

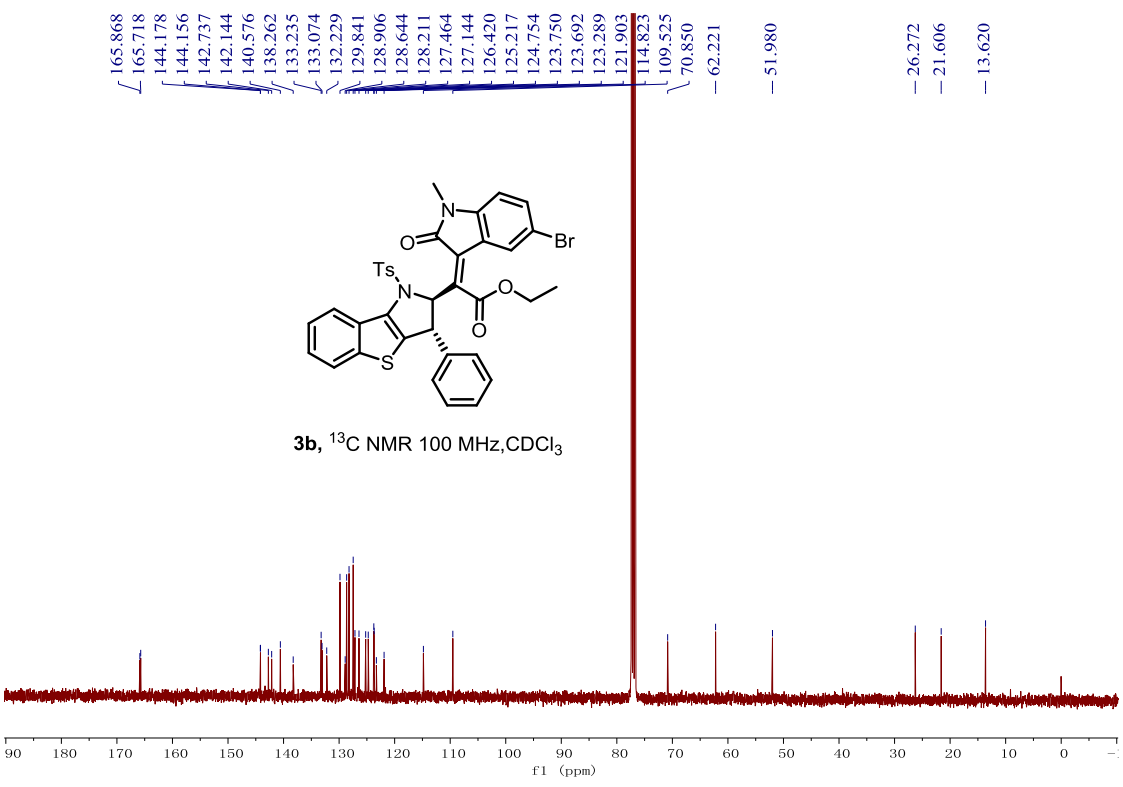


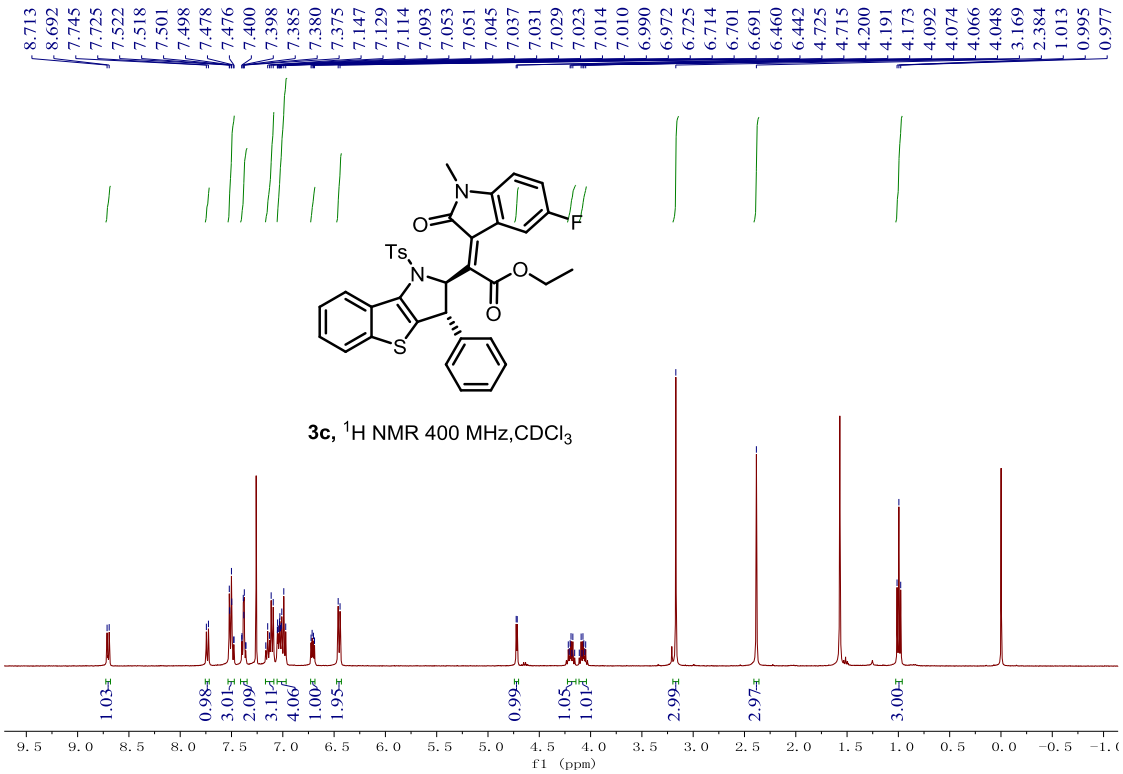

**3a,** $^{13}$C NMR 100 MHz,$CDCl_3$



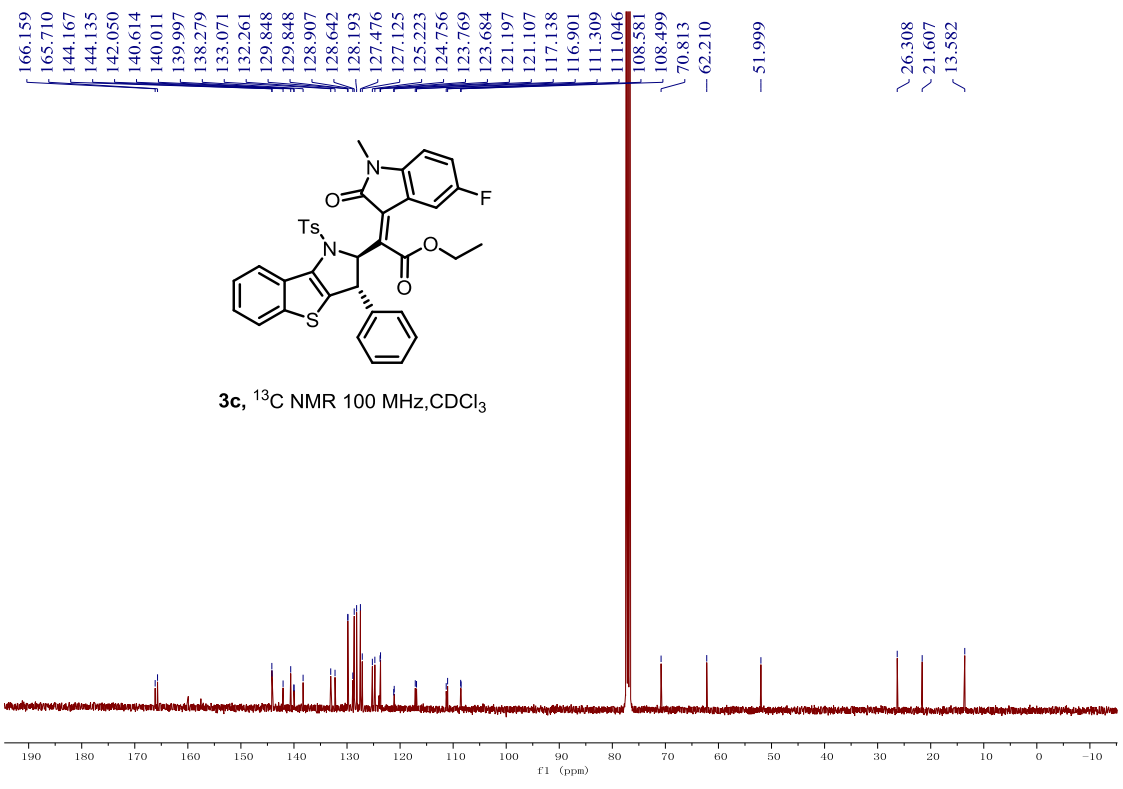

**3b,** $^{1}$H NMR 400 MHz,$CDCl_3$




**3b,** $^{13}$C NMR 100 MHz,$CDCl_3$




**3c,** $^{1}$H NMR 400 MHz,$CDCl_3$

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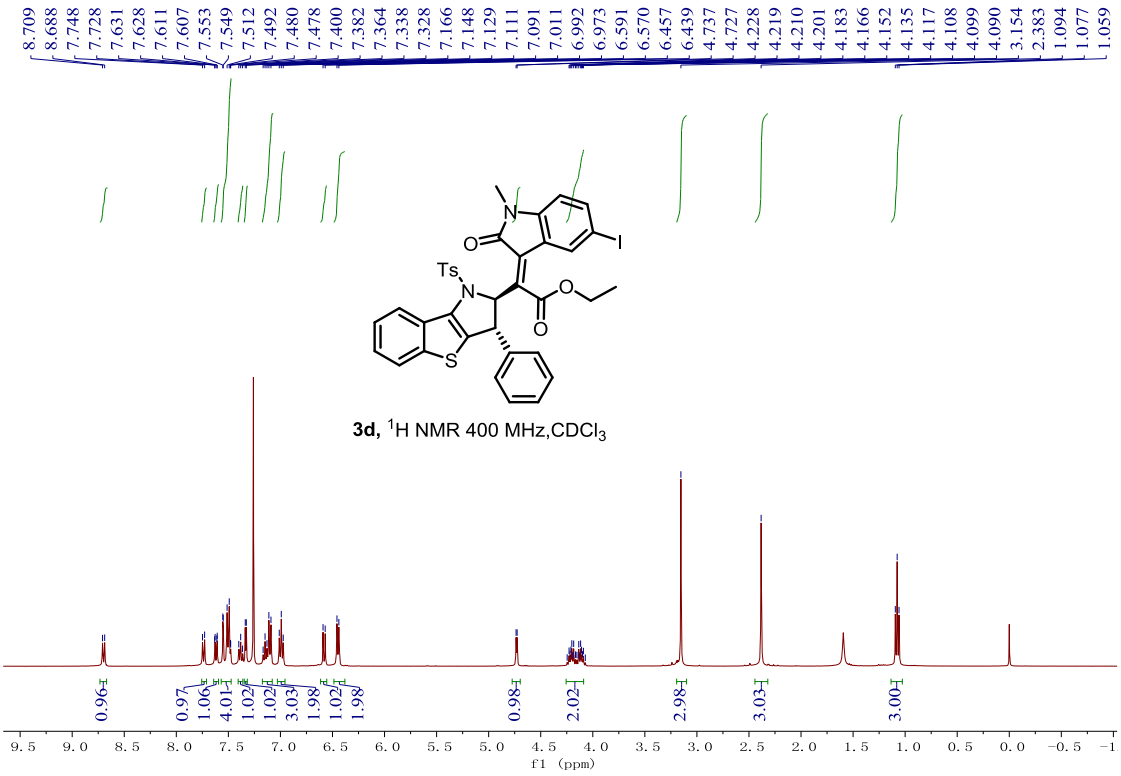


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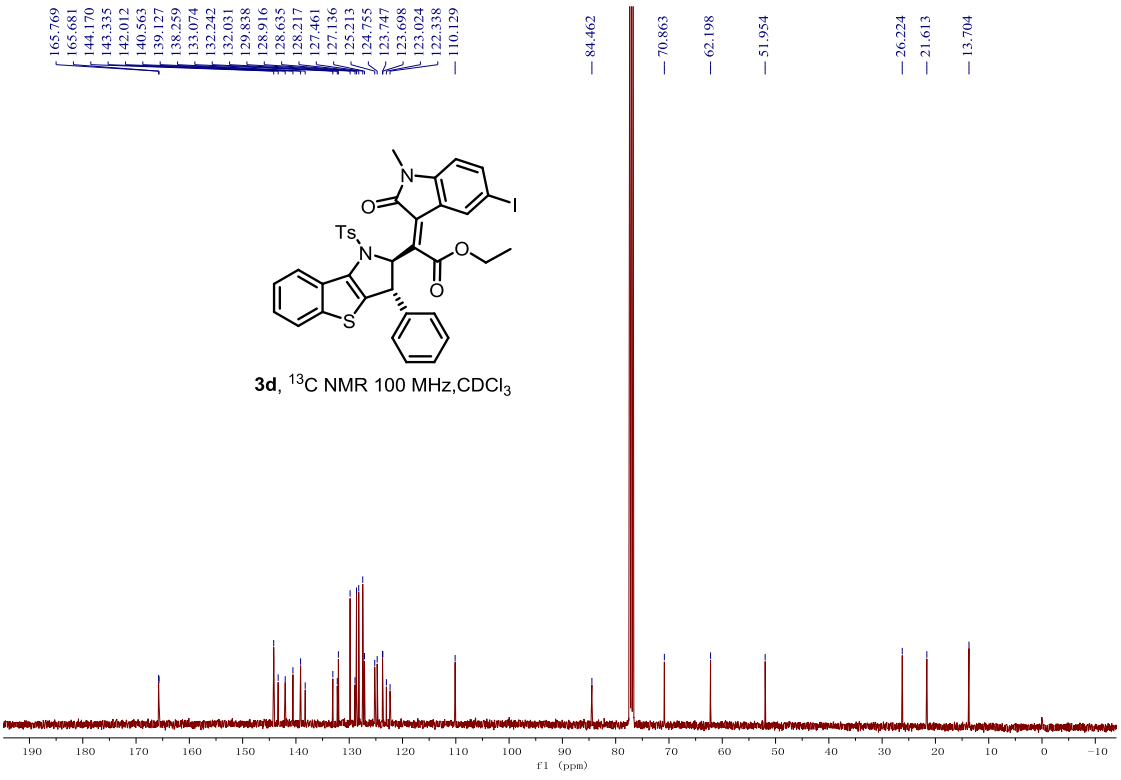


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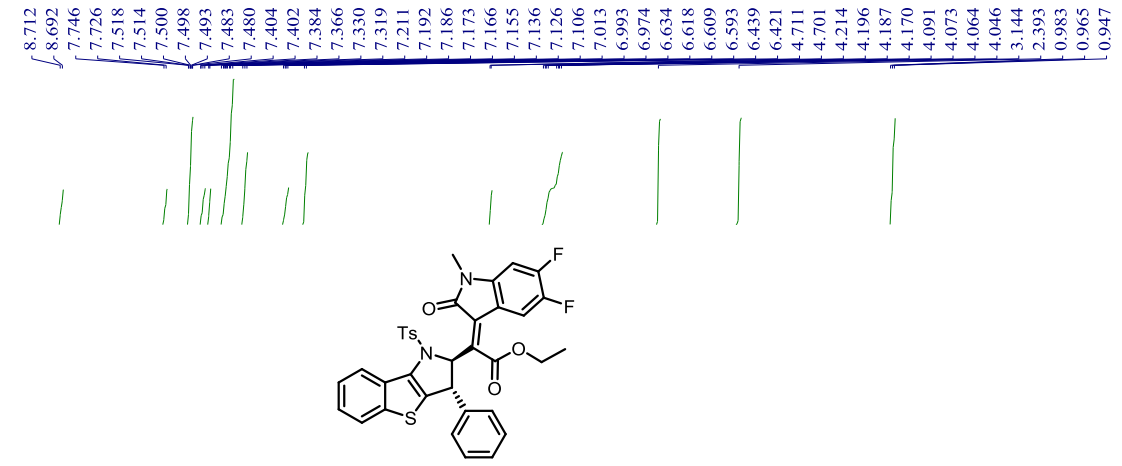


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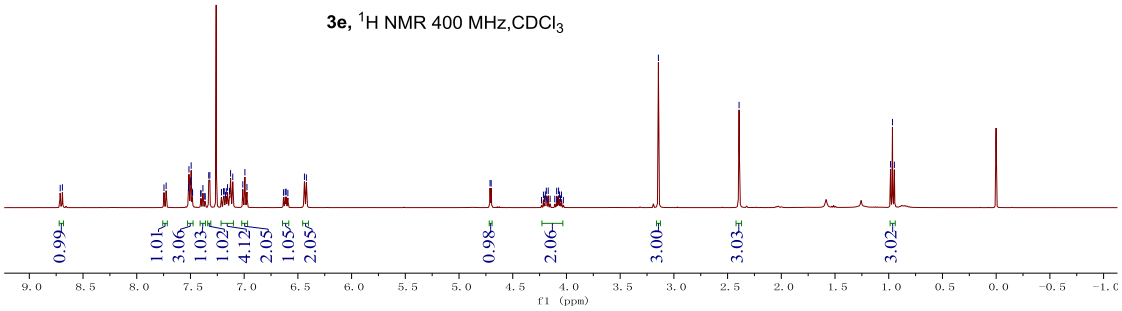


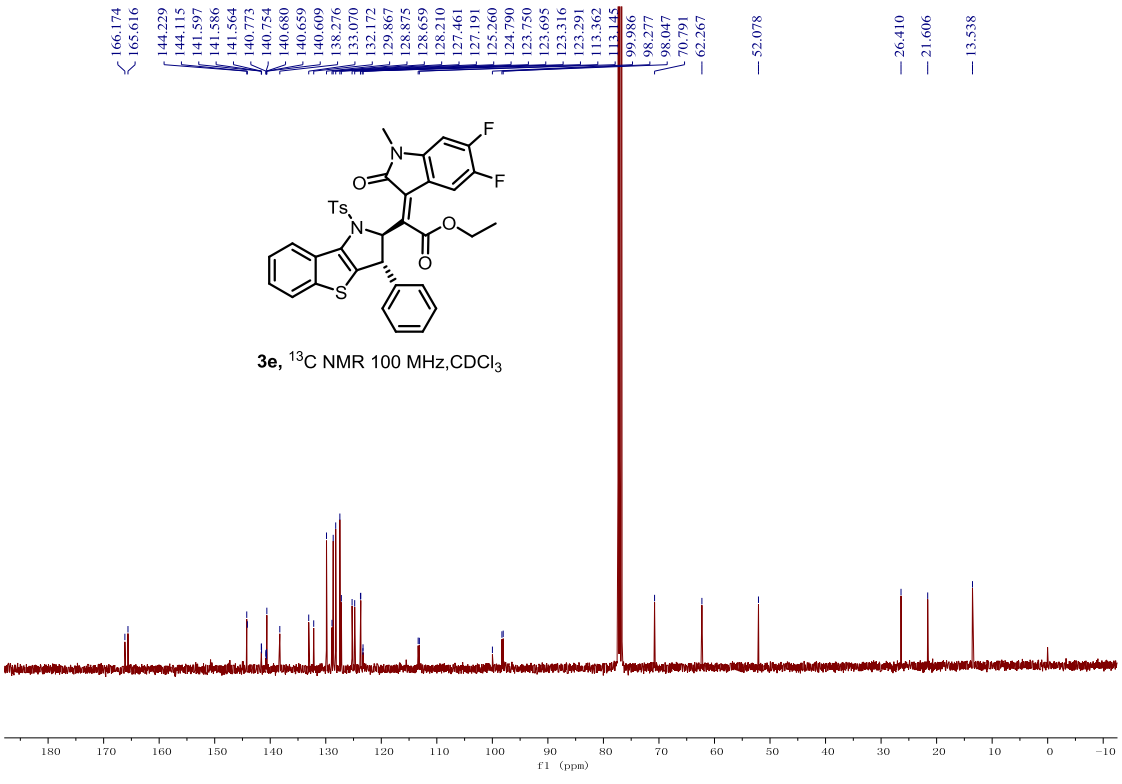


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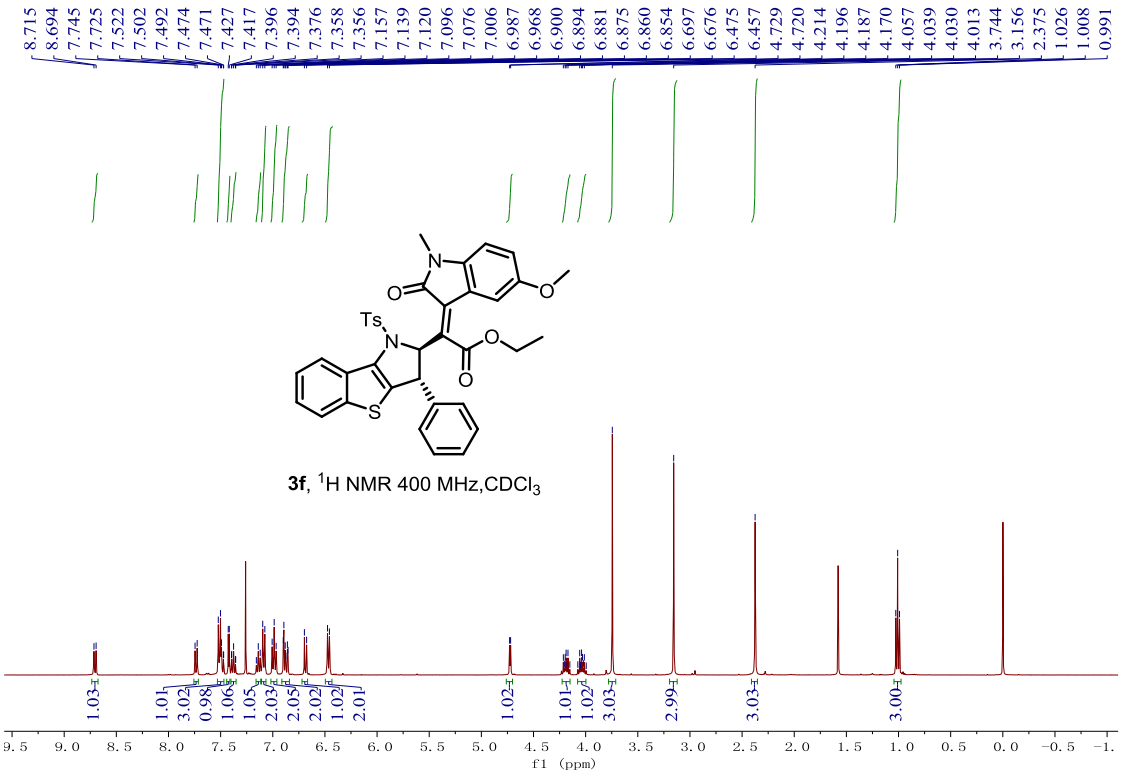
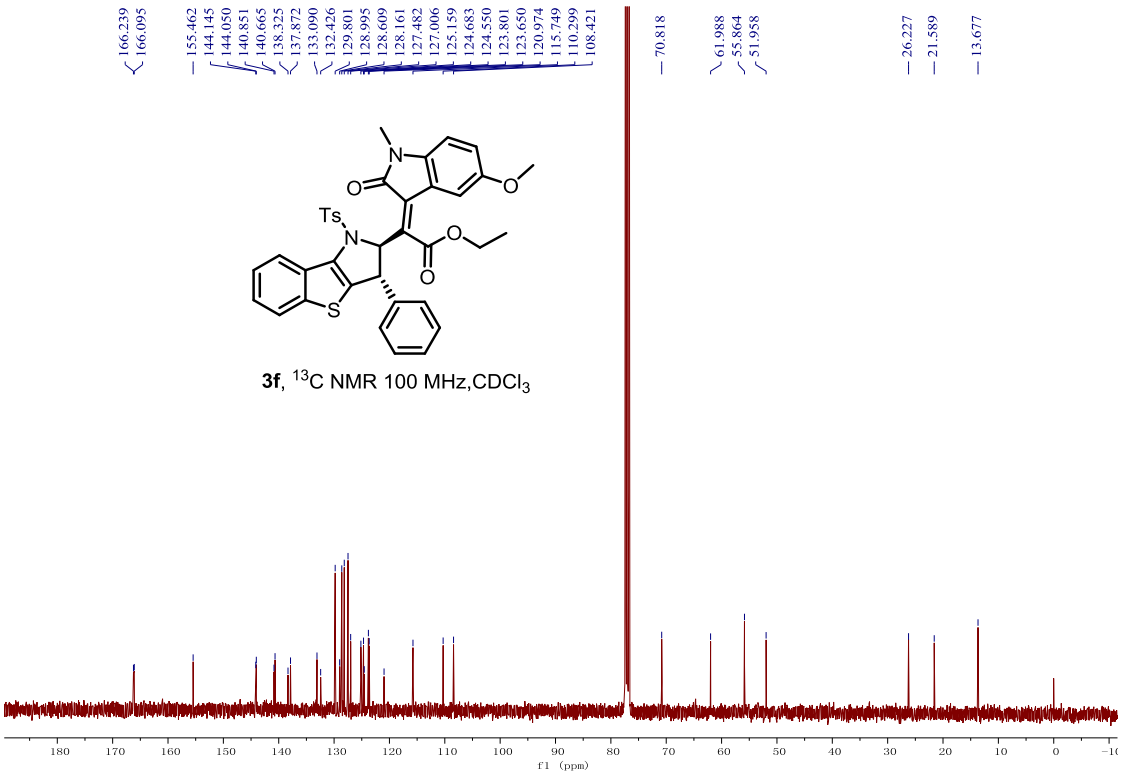
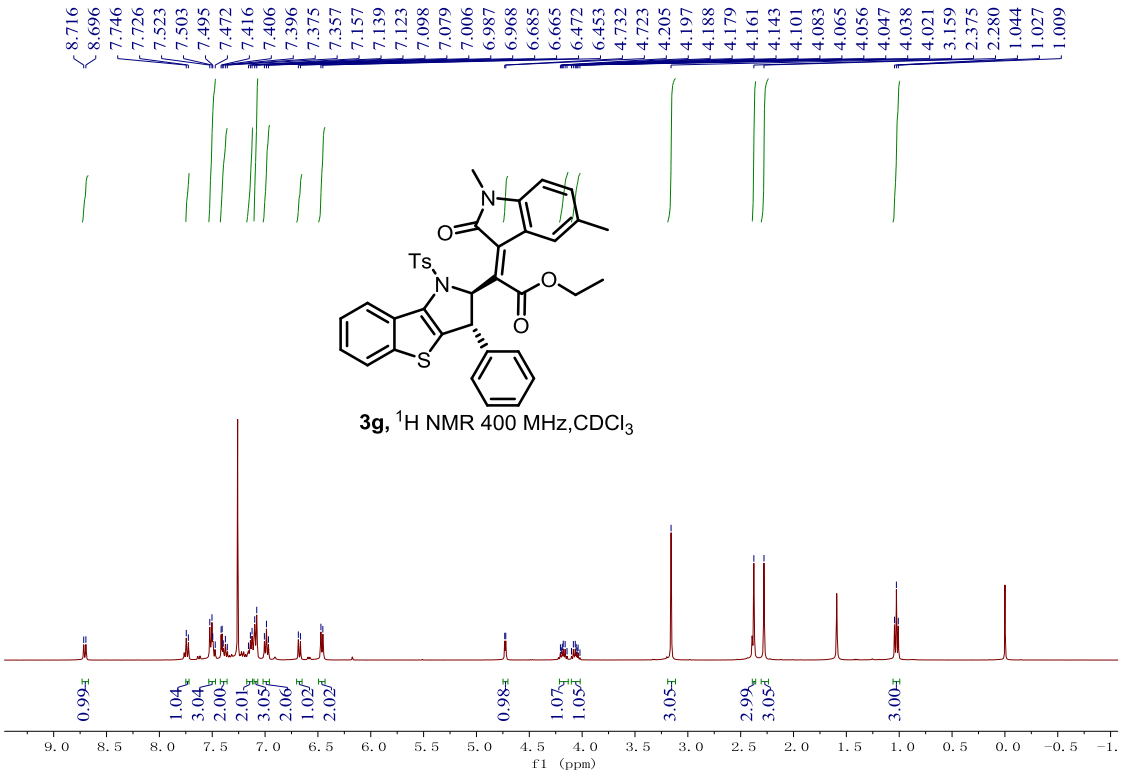



**3f**, $^{1}$H NMR 400 MHz,$CDCl_3$




**3f**, $^{13}$C NMR 100 MHz,$CDCl_3$

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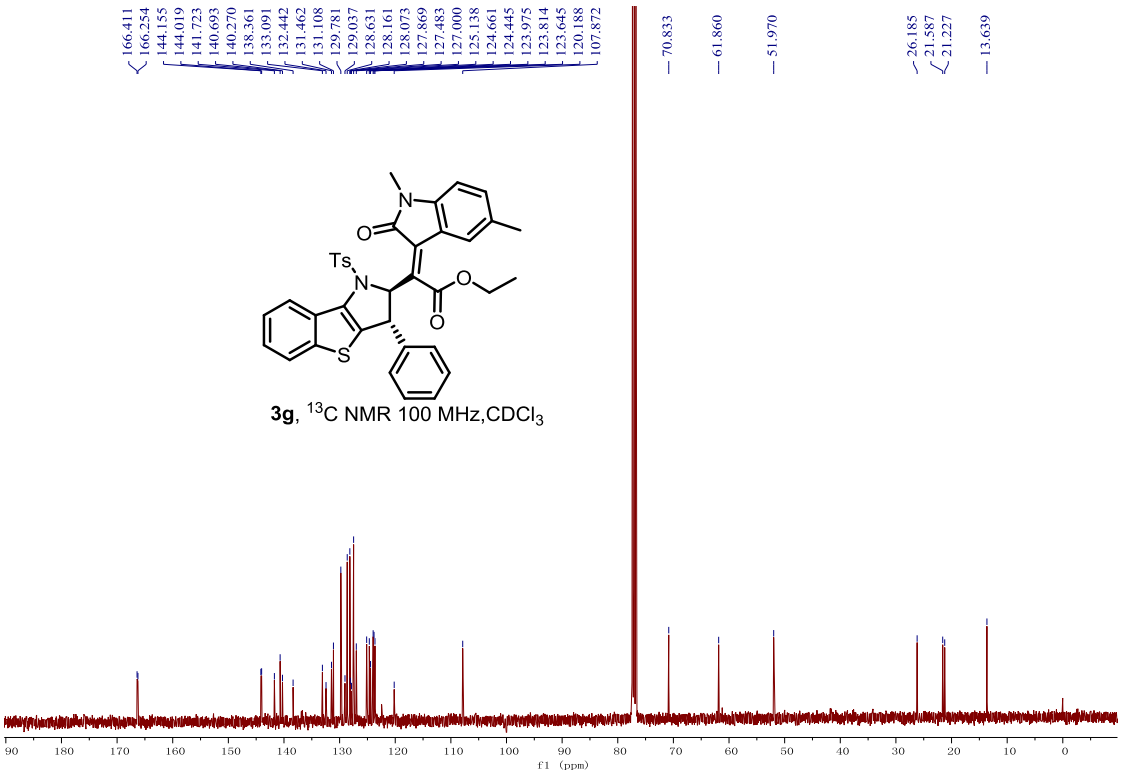


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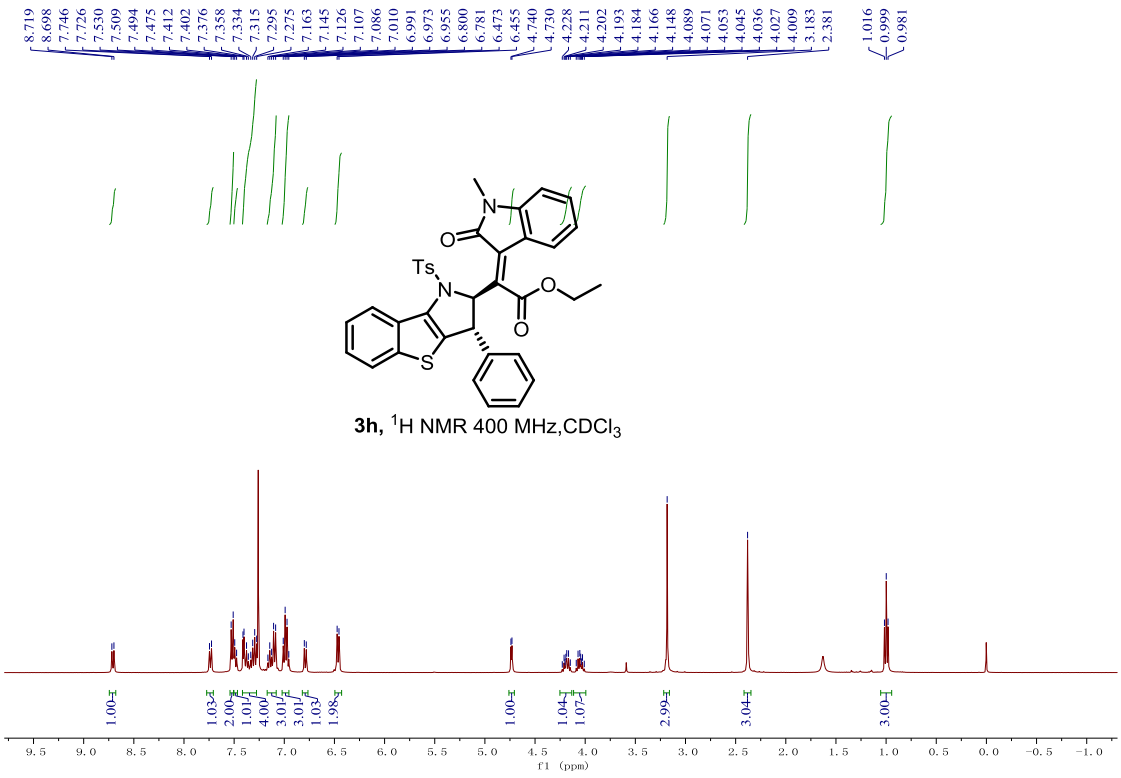


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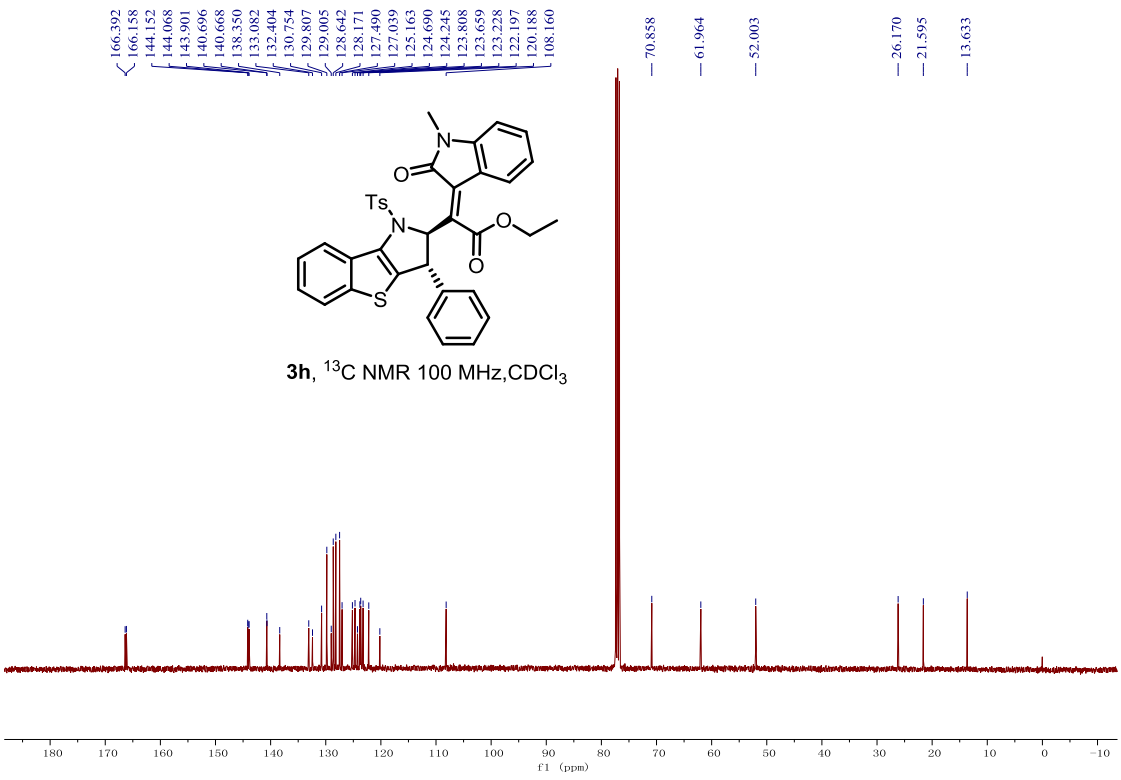


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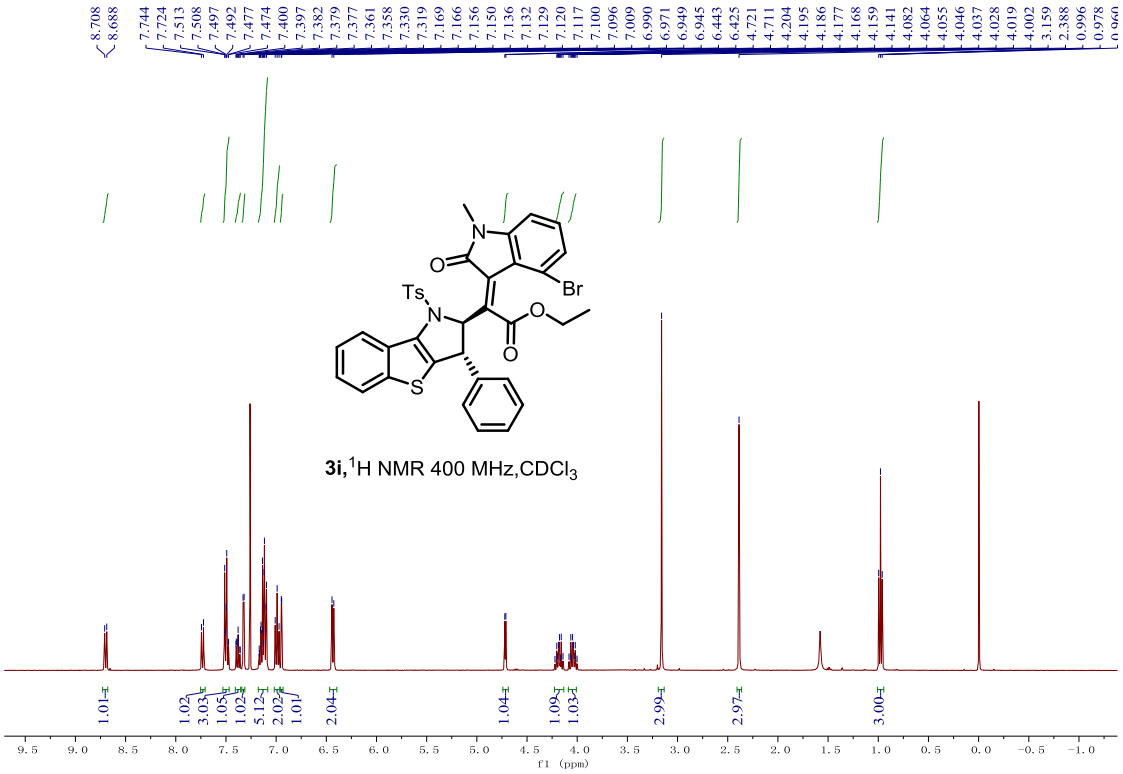
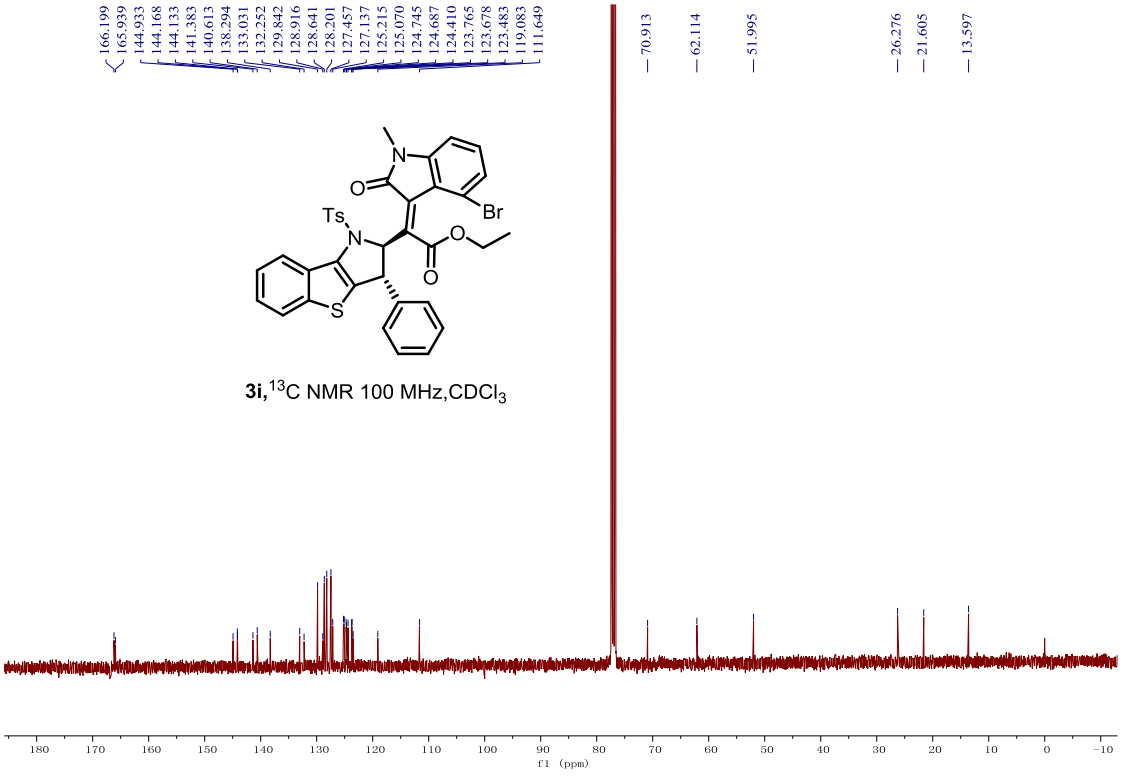
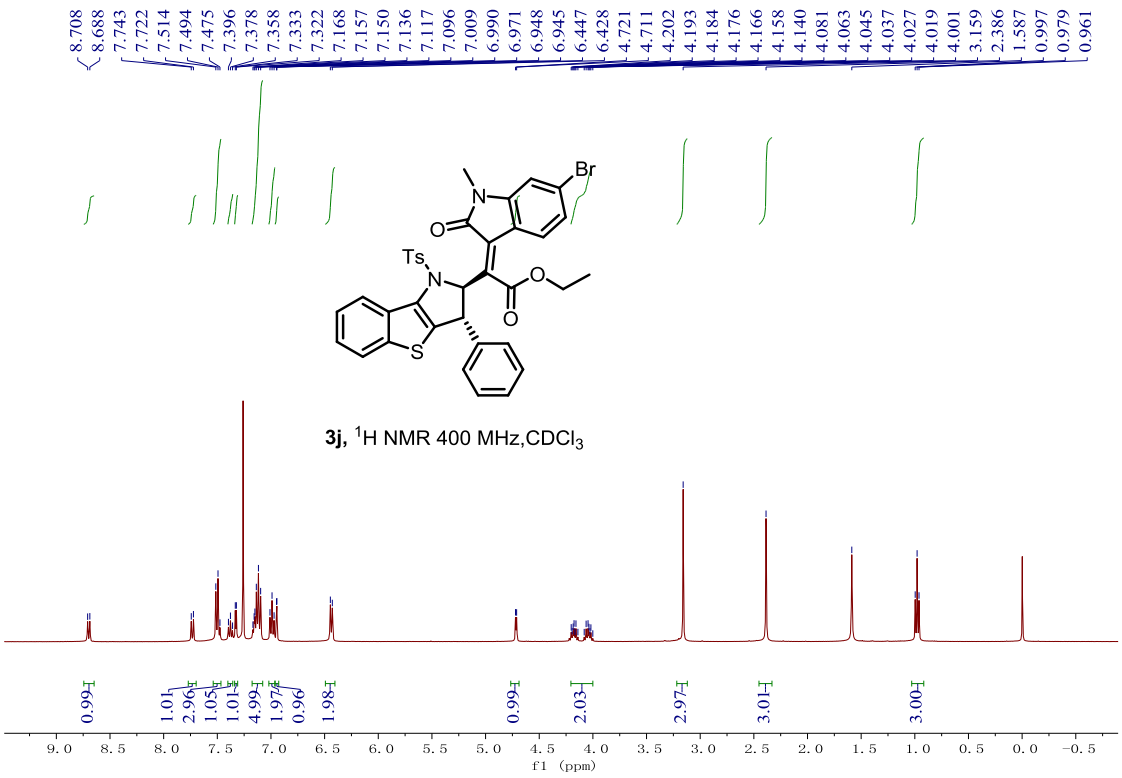


**3i,** $^{1}$H NMR 400 MHz,$CDCl_3$



**3i,** $^{13}$C NMR 100 MHz,$CDCl_3$

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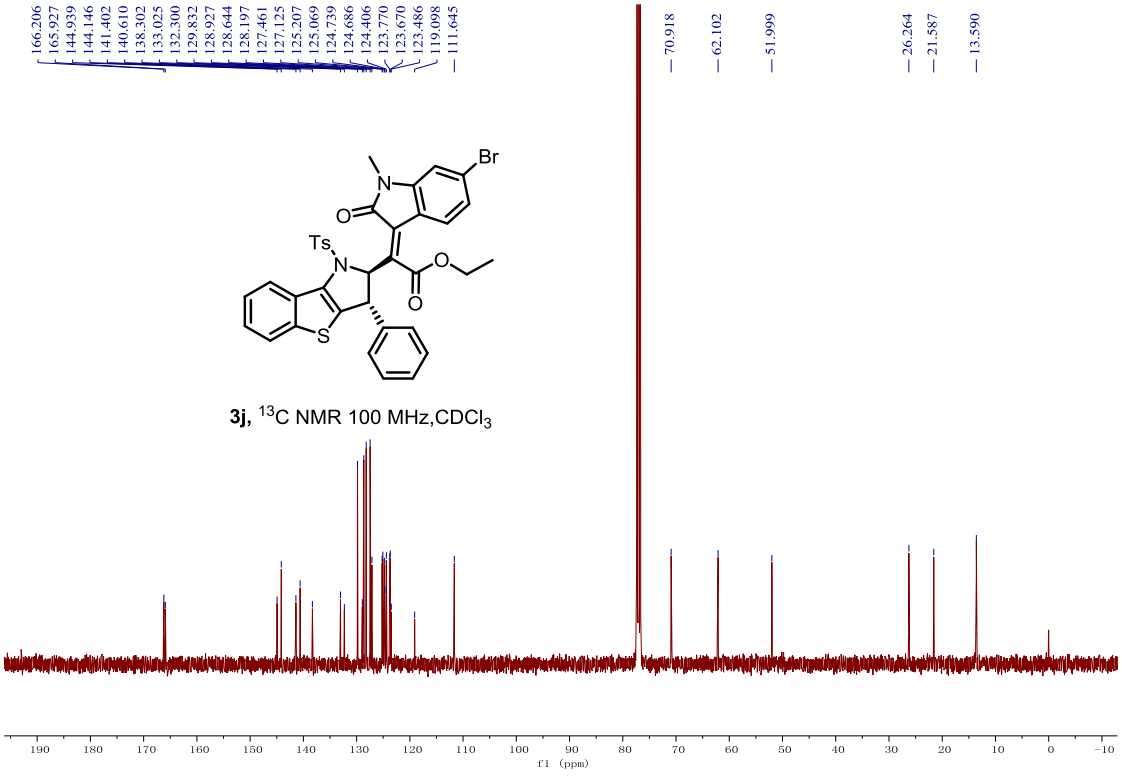


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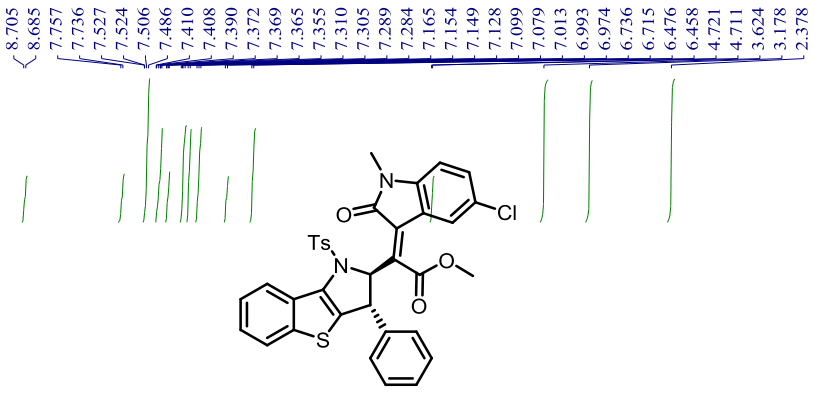


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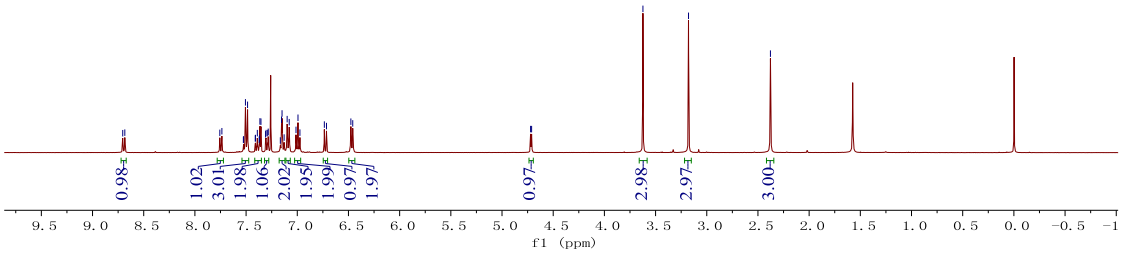
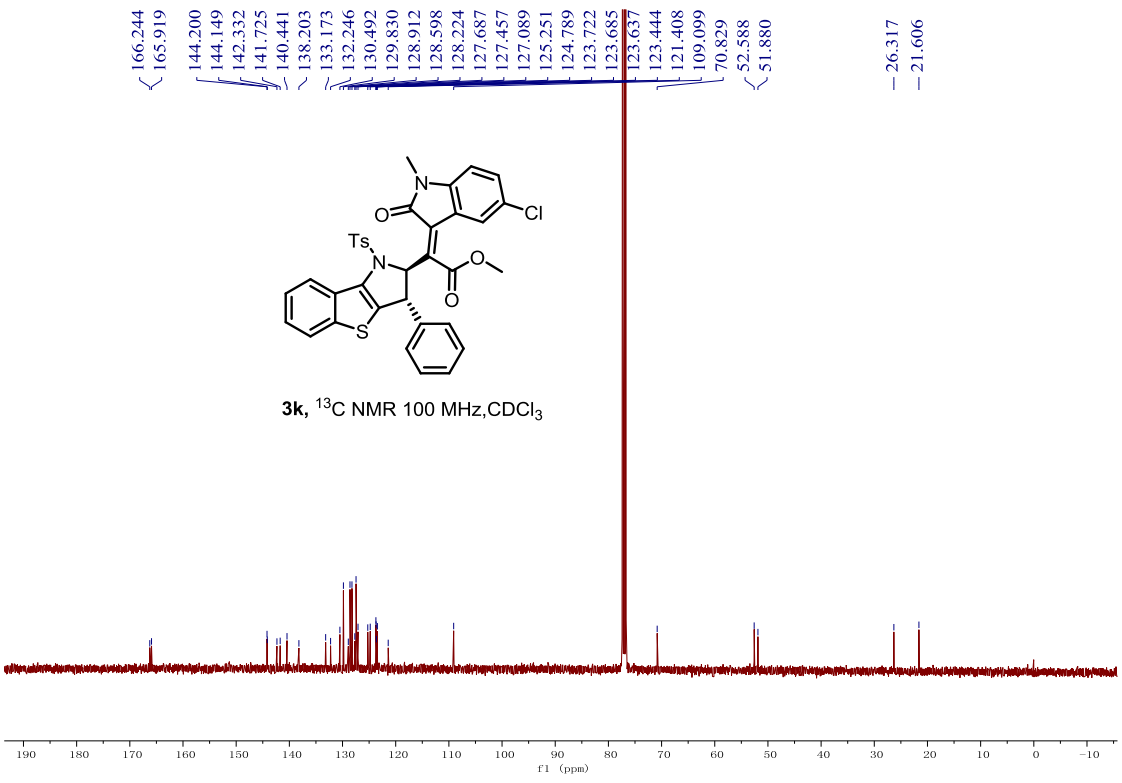
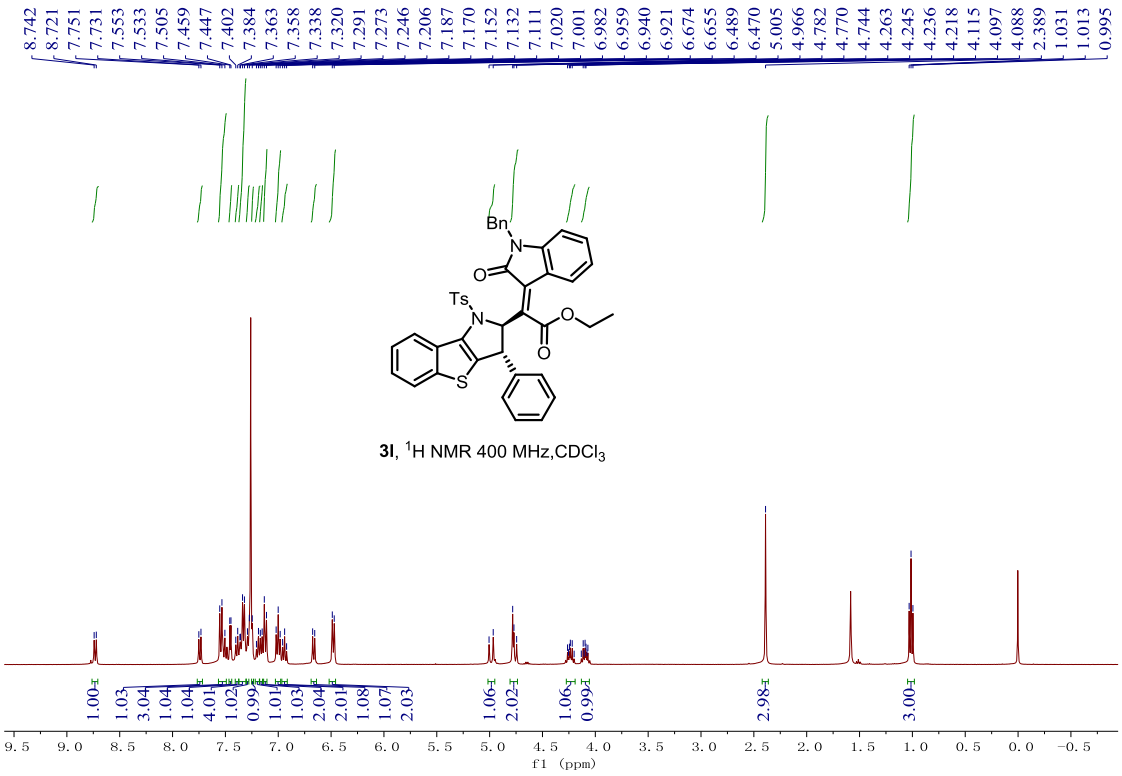
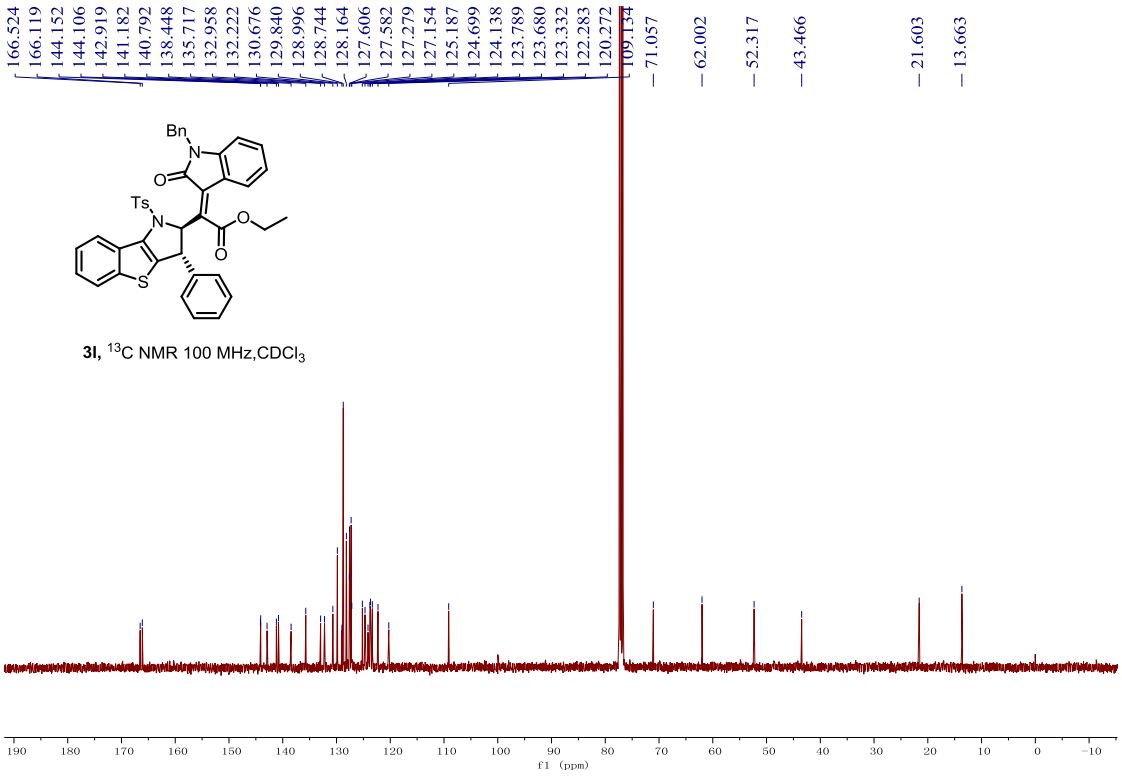


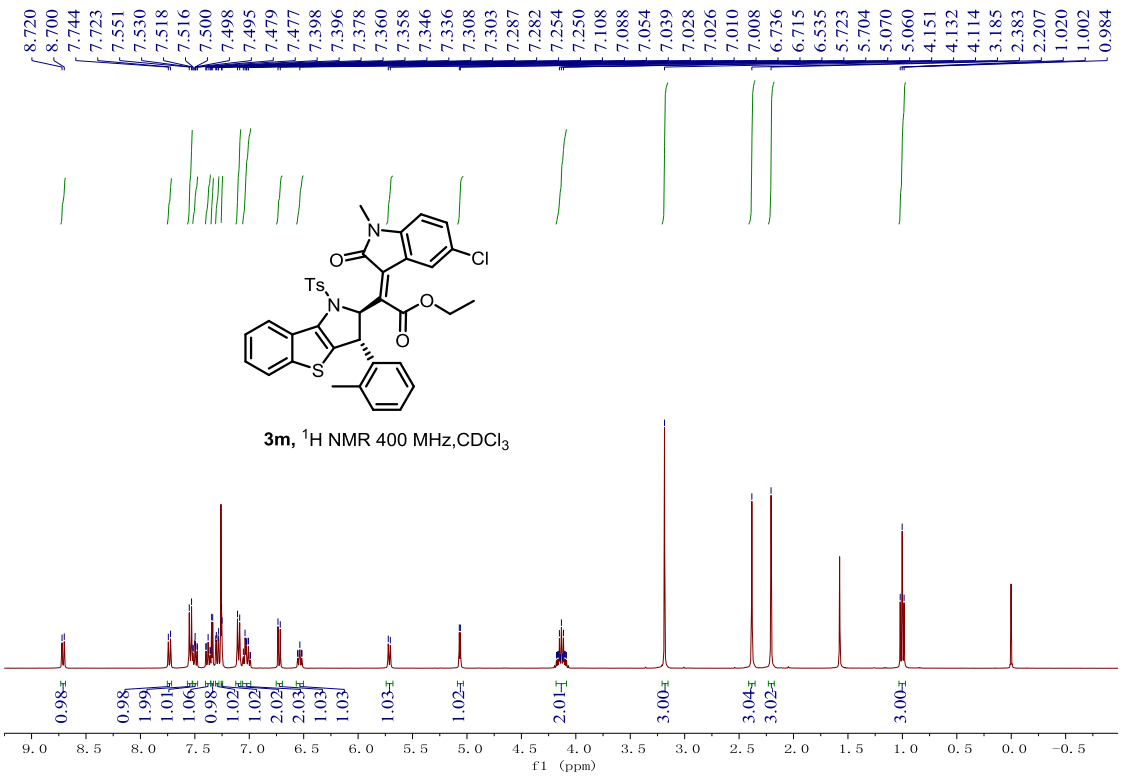

**3k,** $^{13}$C NMR 100 MHz,$CDCl_3$



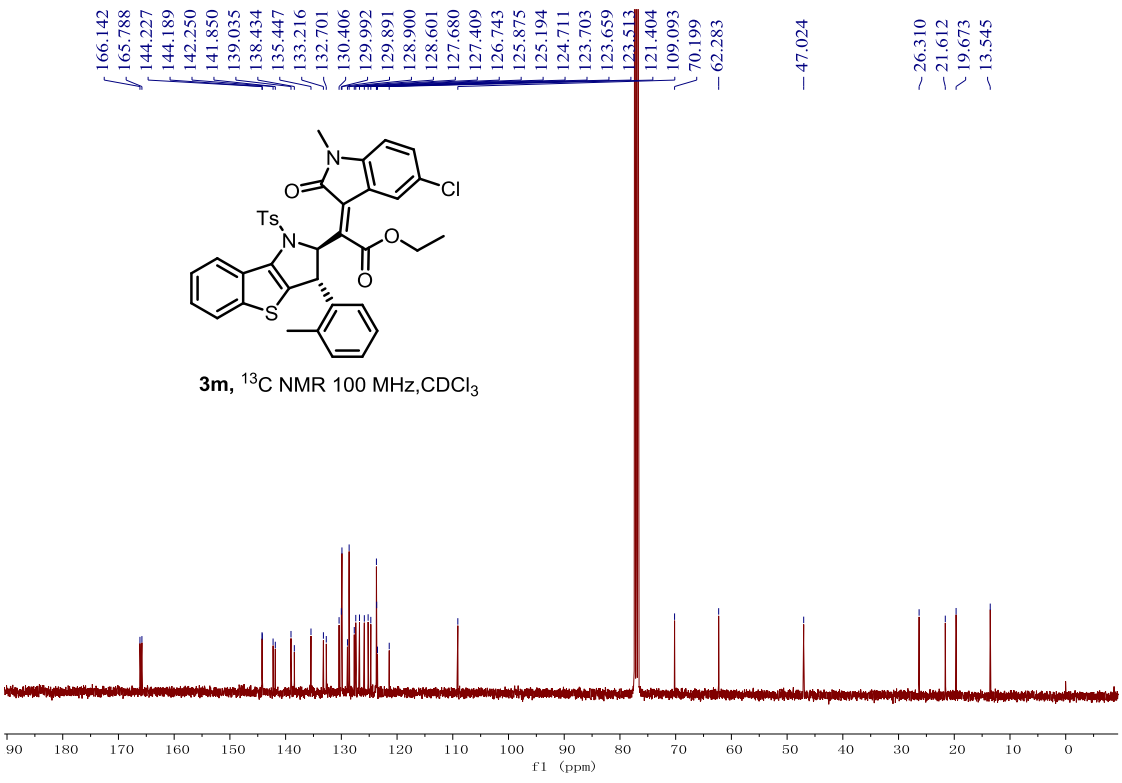

**3l**, $^{1}$H NMR 400 MHz,$CDCl_3$



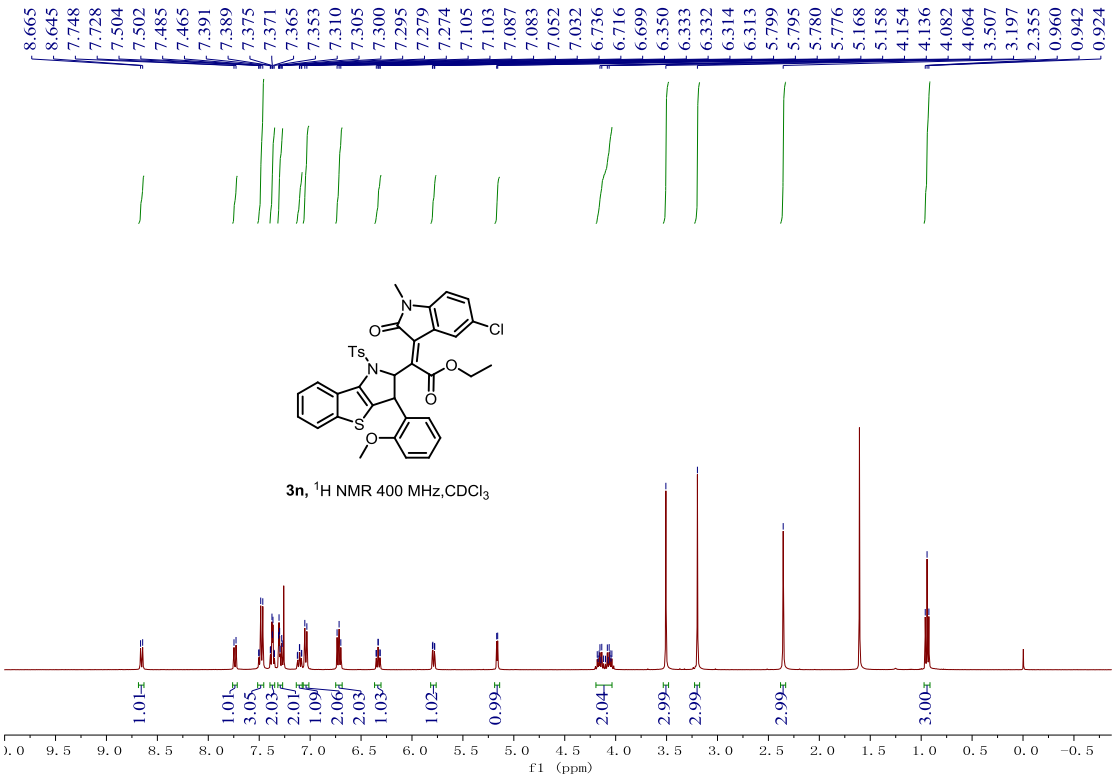

**3l**, $^{13}$C NMR 100 MHz,$CDCl_3$



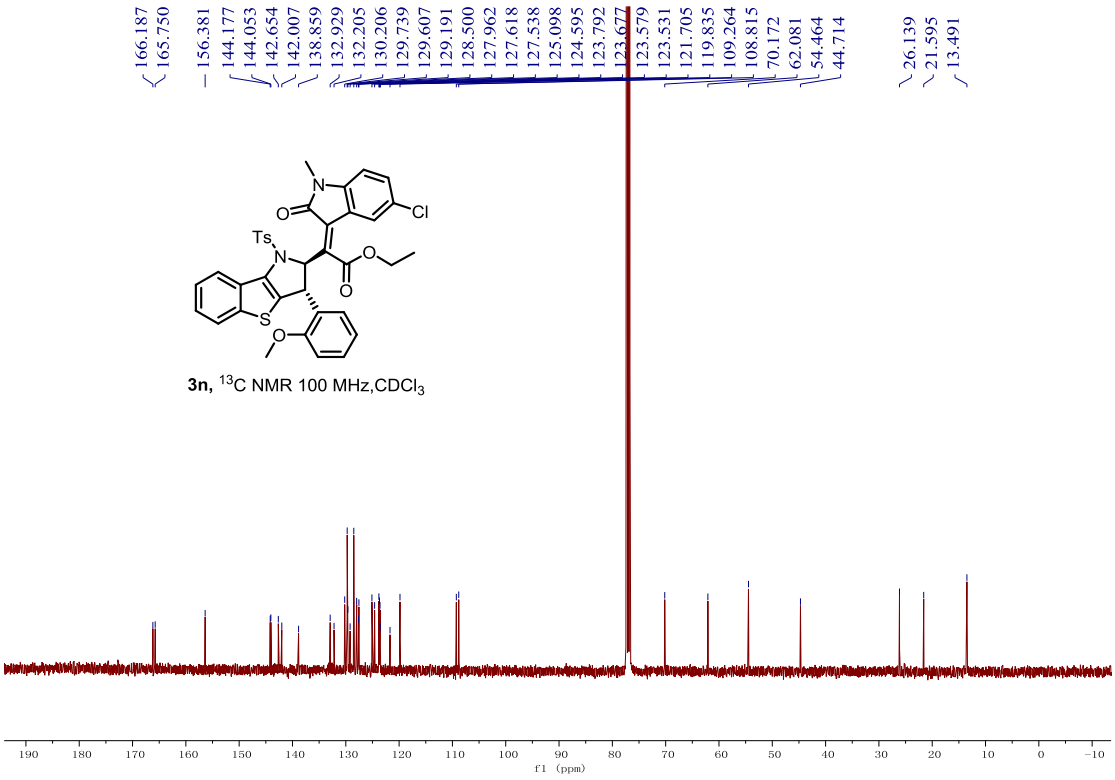

**3m,** $^{1}$H NMR 400 MHz,$CDCl_3$



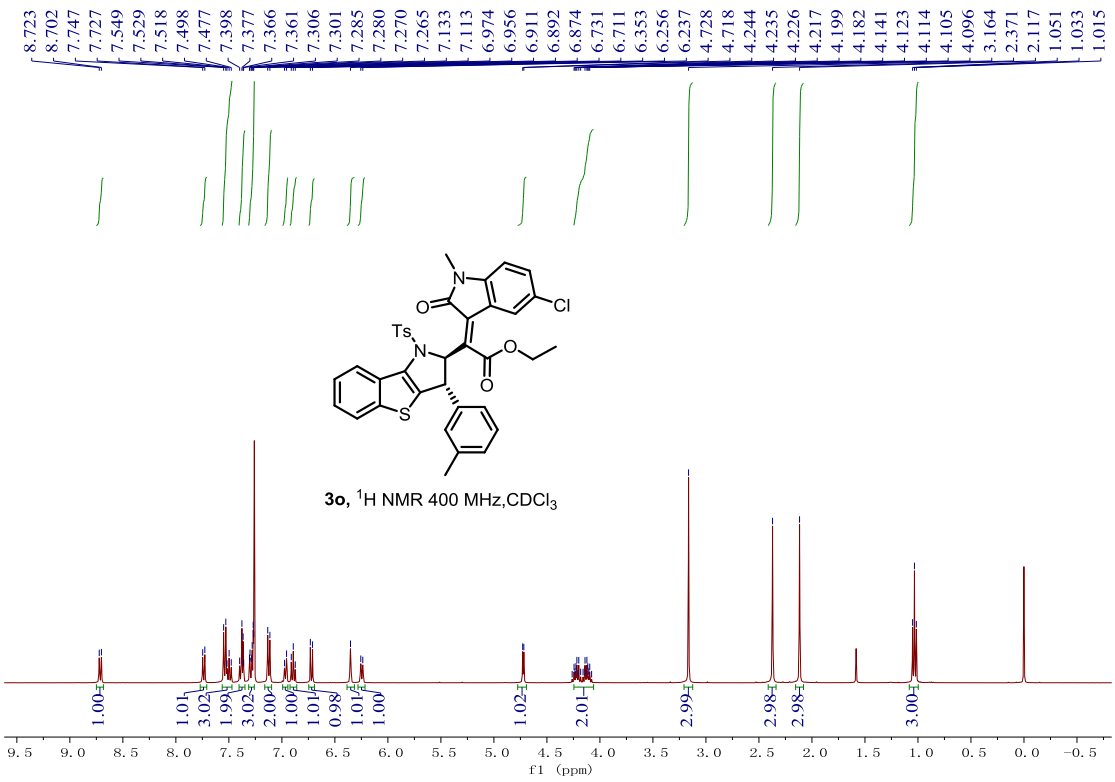

**3m,** $^{13}$C NMR 100 MHz,$CDCl_3$



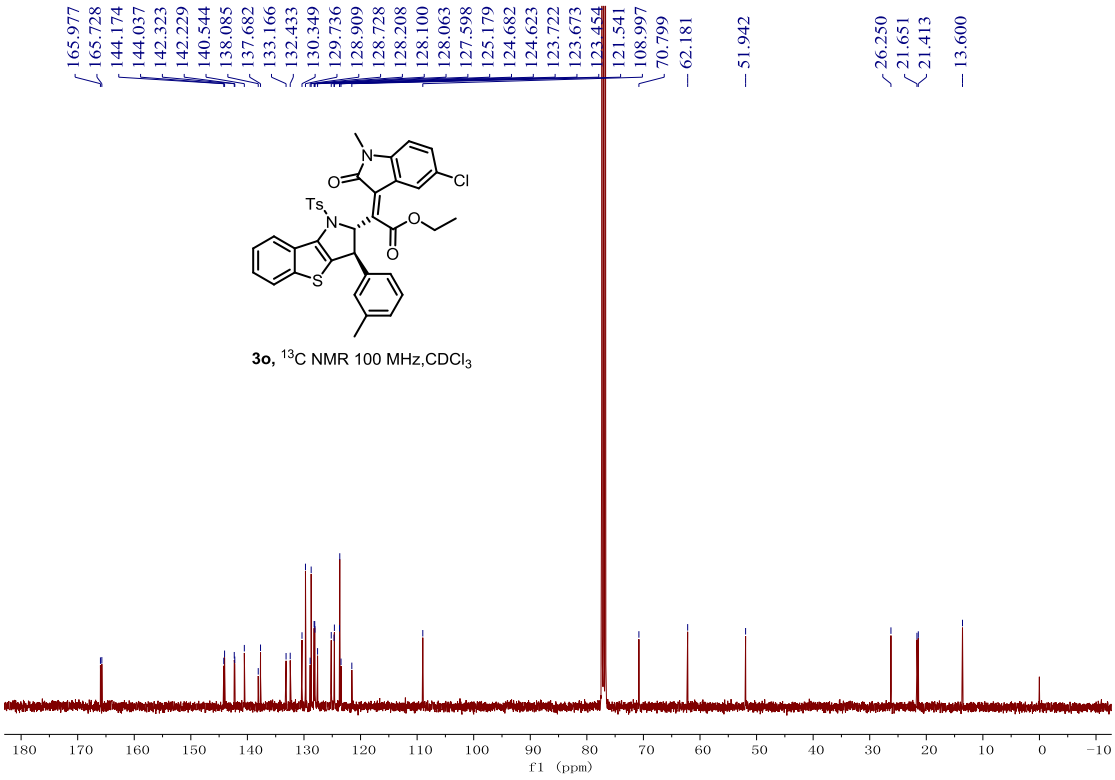

**3n,** $^{1}$H NMR 400 MHz,$CDCl_3$



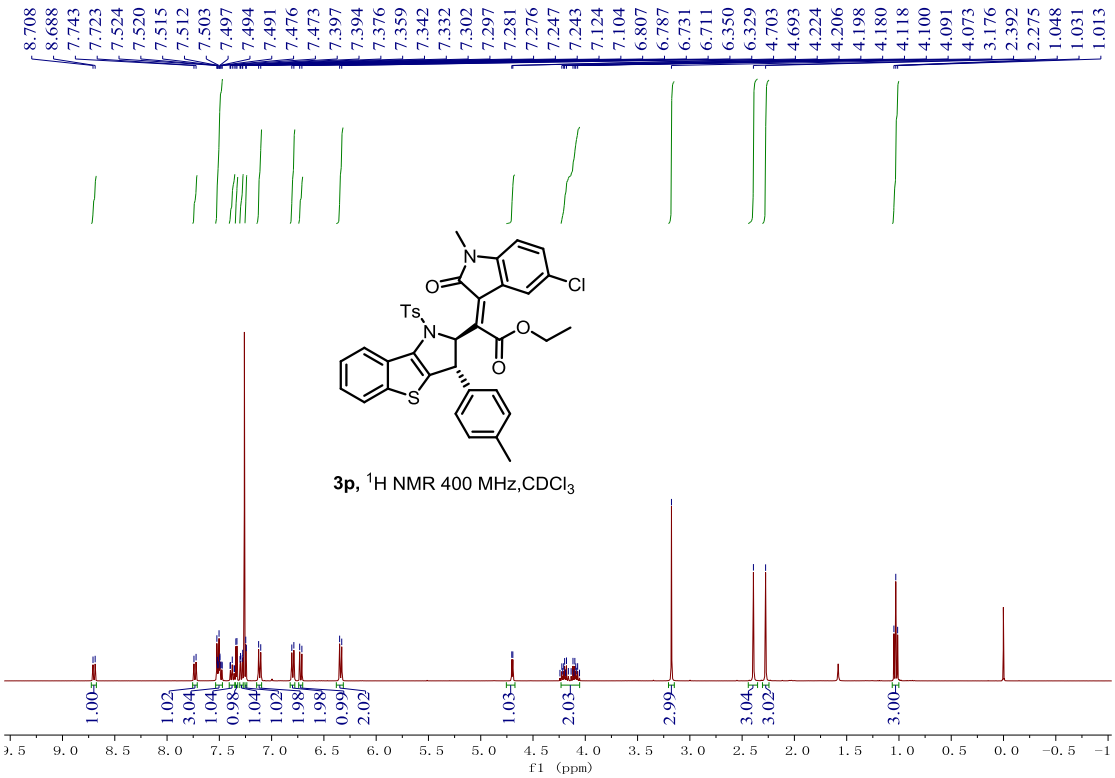

**3n,** $^{13}$C NMR 100 MHz,$CDCl_3$



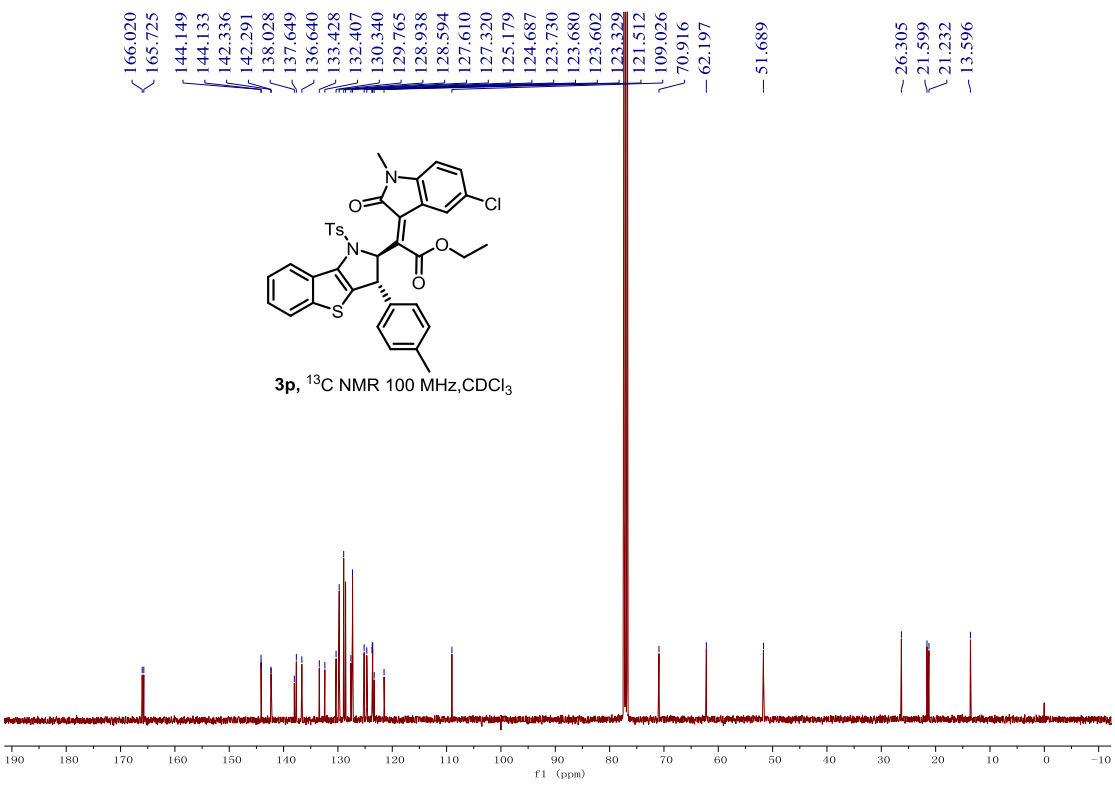

**3o,** $^{1}$H NMR 400 MHz,$CDCl_3$



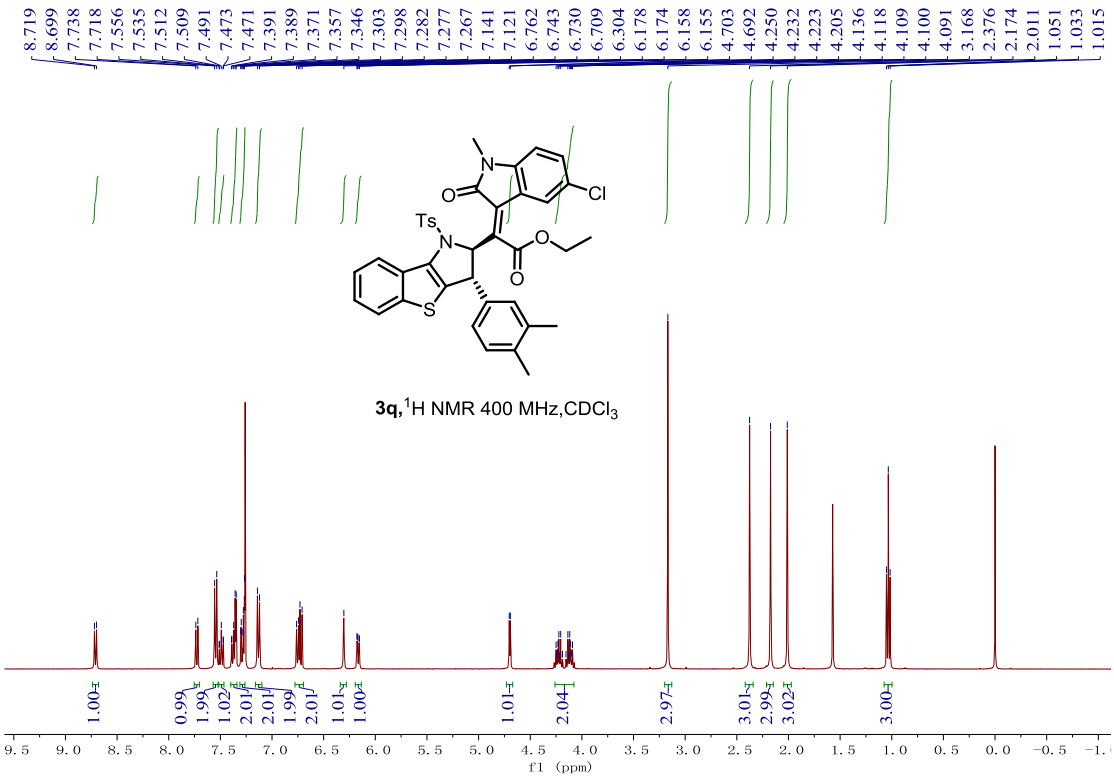

**3o,** $^{13}$C NMR 100 MHz,$CDCl_3$



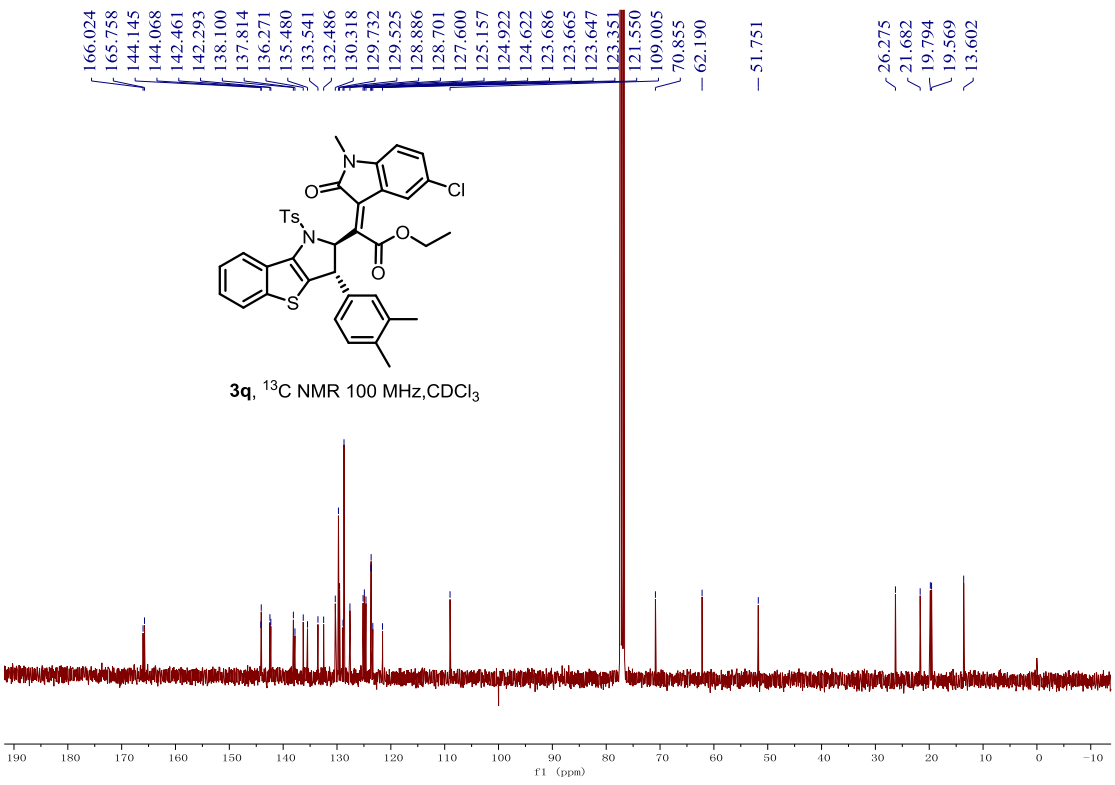

**3p,** $^{1}$H NMR 400 MHz,$CDCl_3$



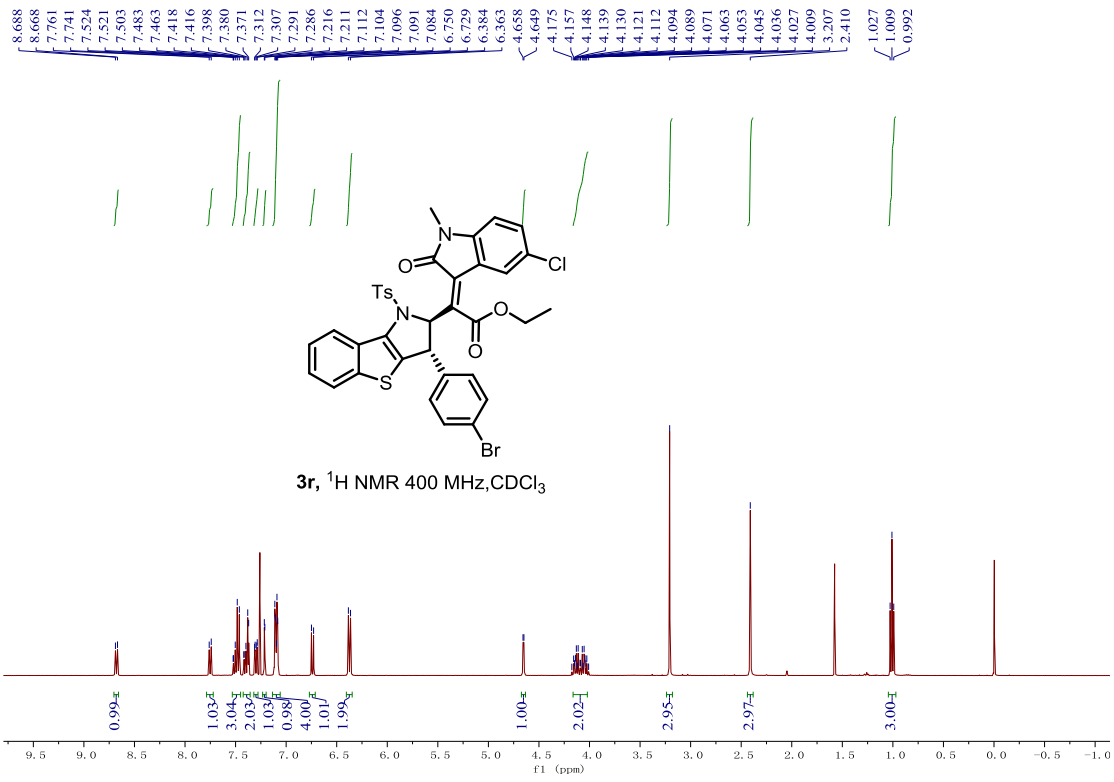

**3p,** $^{13}$C NMR 100 MHz,$CDCl_3$



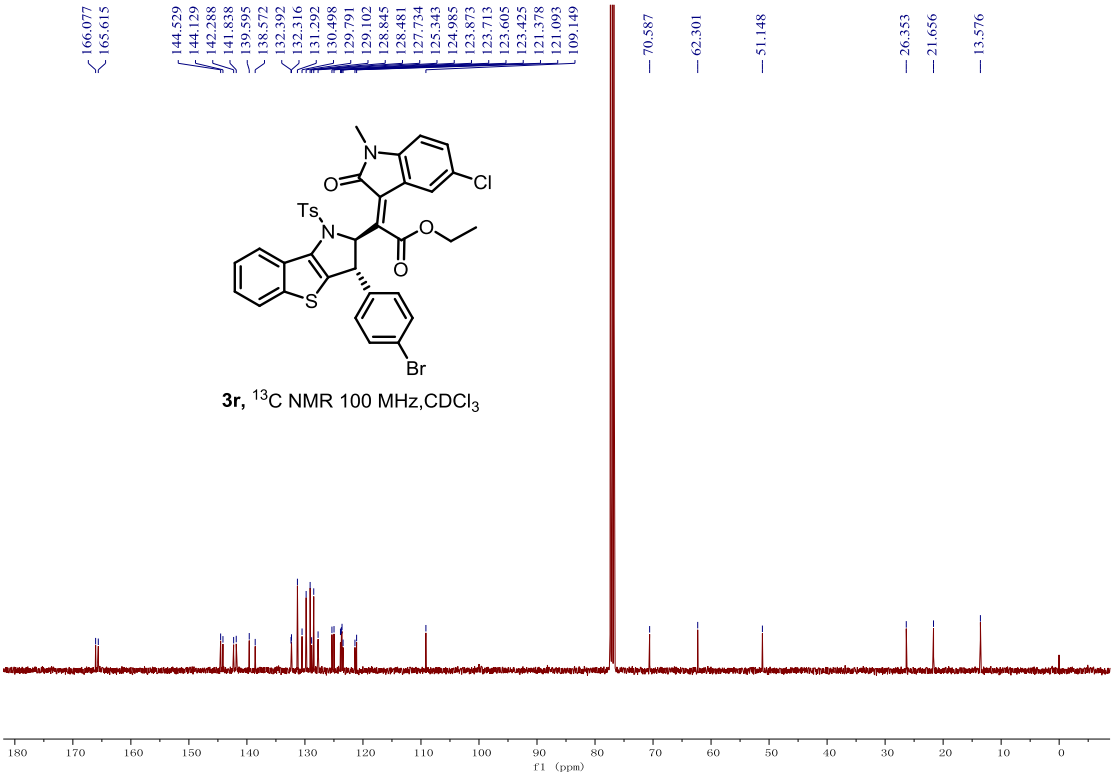

**3q,**$^{1}$H NMR 400 MHz,$CDCl_3$



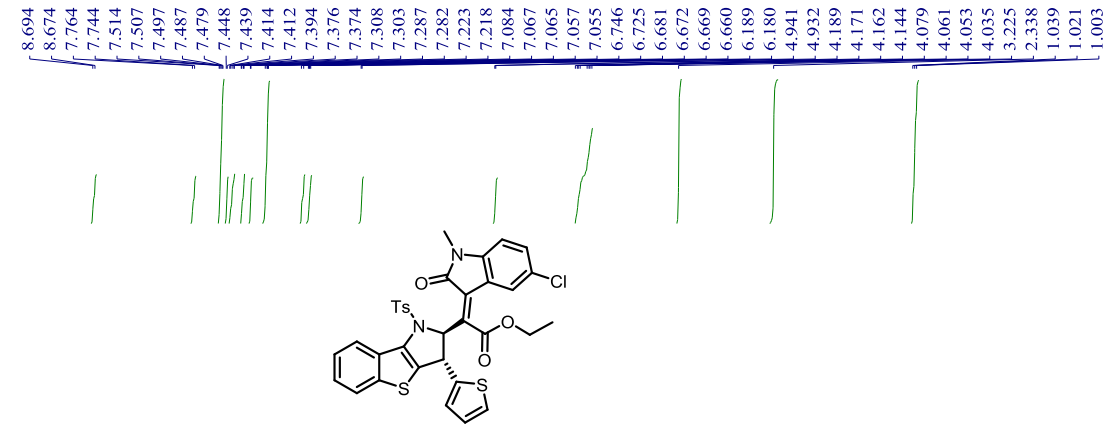

**3q**, $^{13}$C NMR 100 MHz,$CDCl_3$



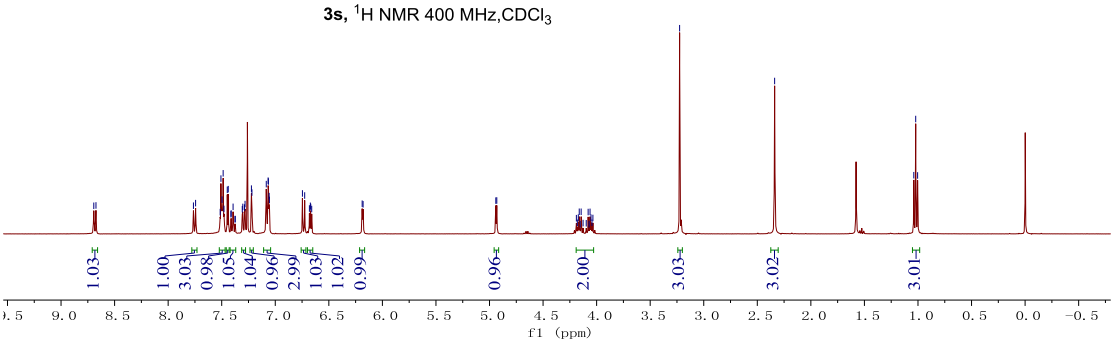

**3r,** $^{1}$H NMR 400 MHz,$CDCl_3$

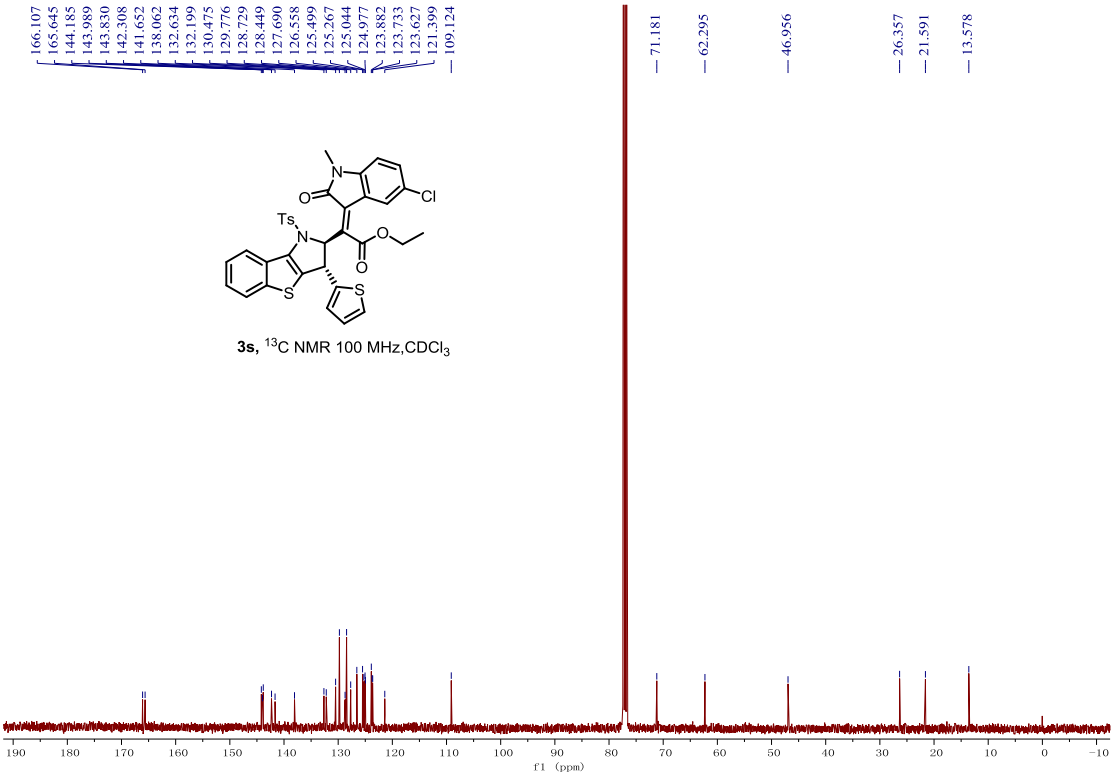



**3r,** $^{13}$C NMR 100 MHz,$CDCl_3$

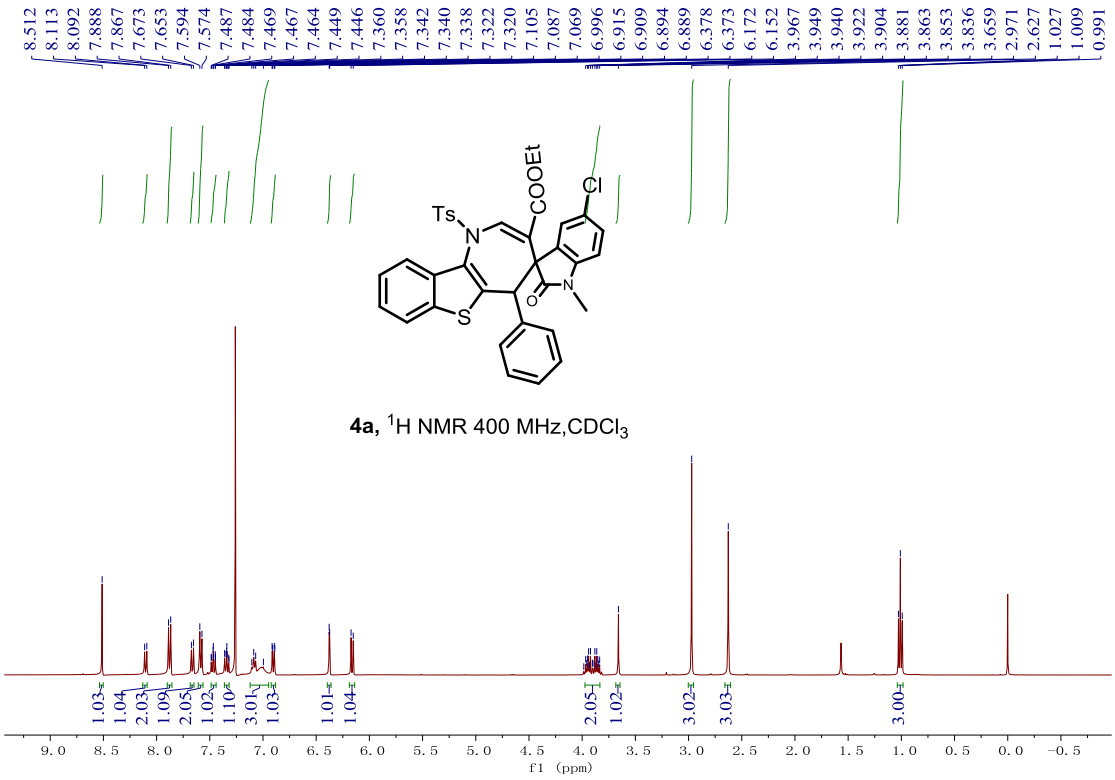



**3s,** $^{1}$H NMR 400 MHz,$CDCl_3$

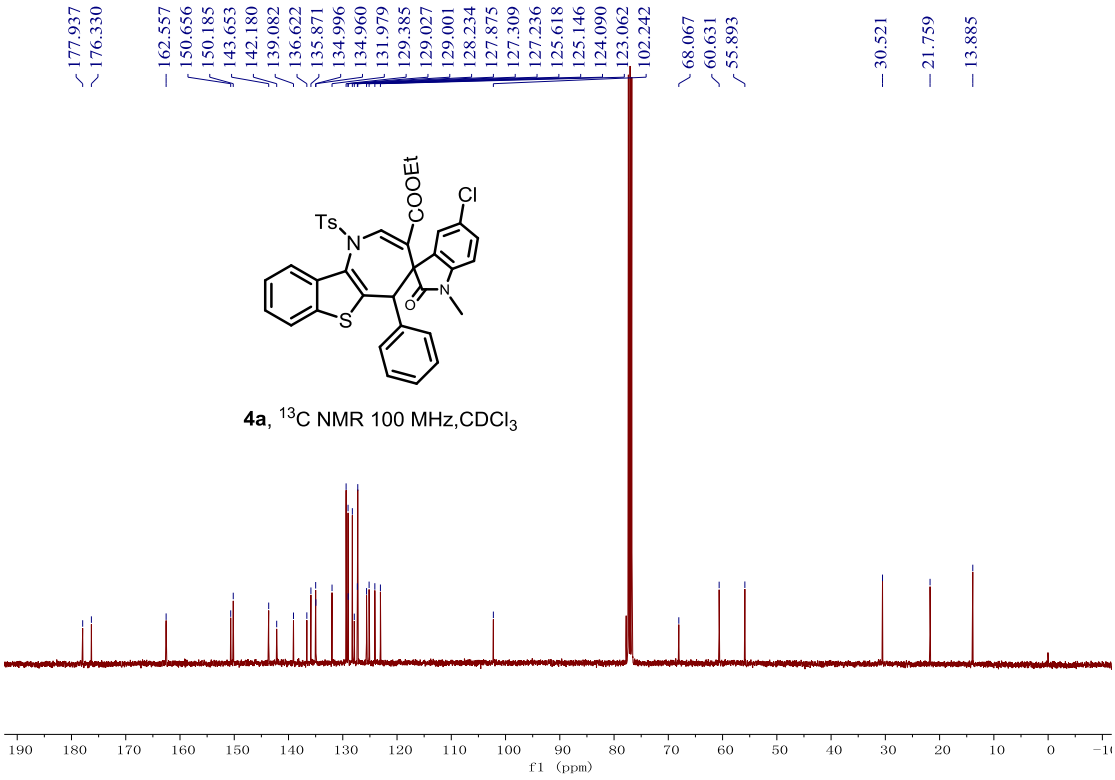


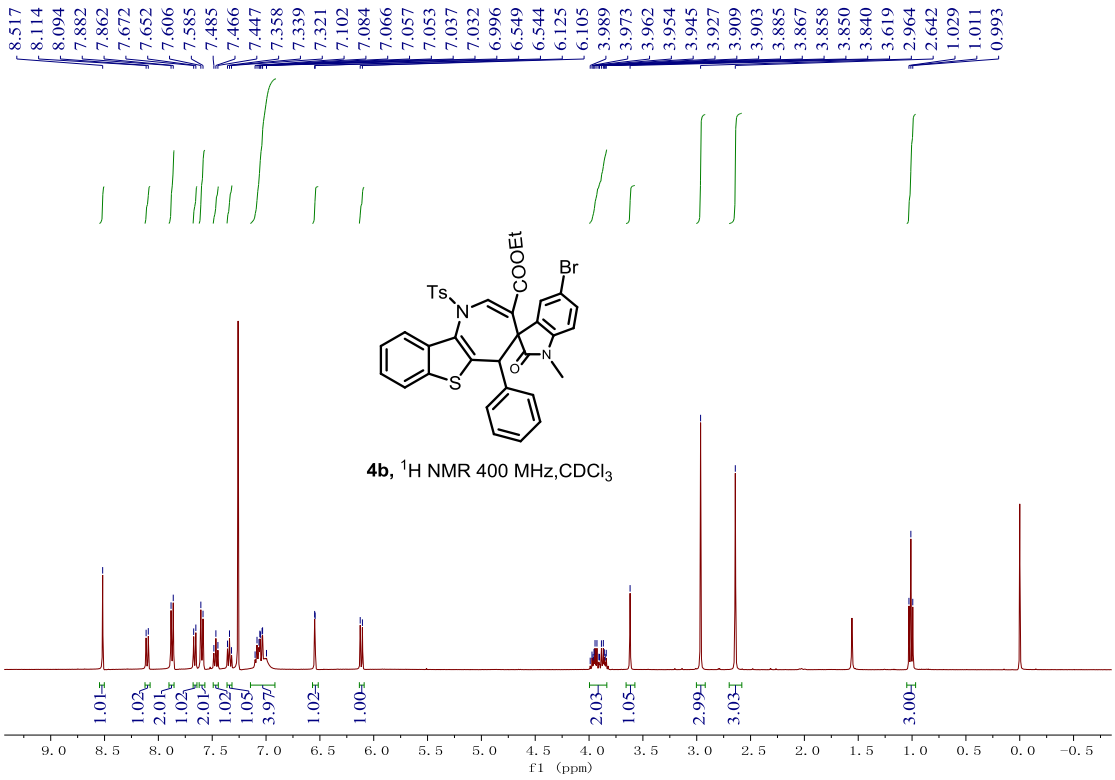

**3s,** $^{13}$C NMR 100 MHz,$CDCl_3$



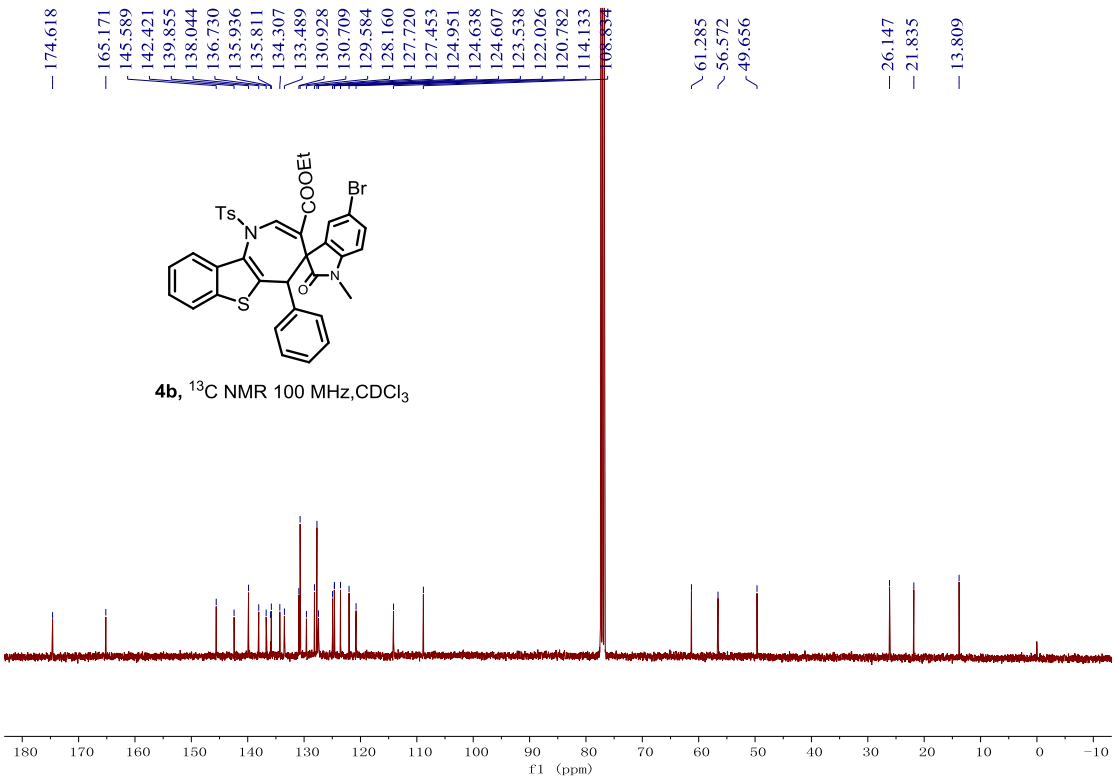

**4a,** $^{1}$H NMR 400 MHz,$CDCl_3$



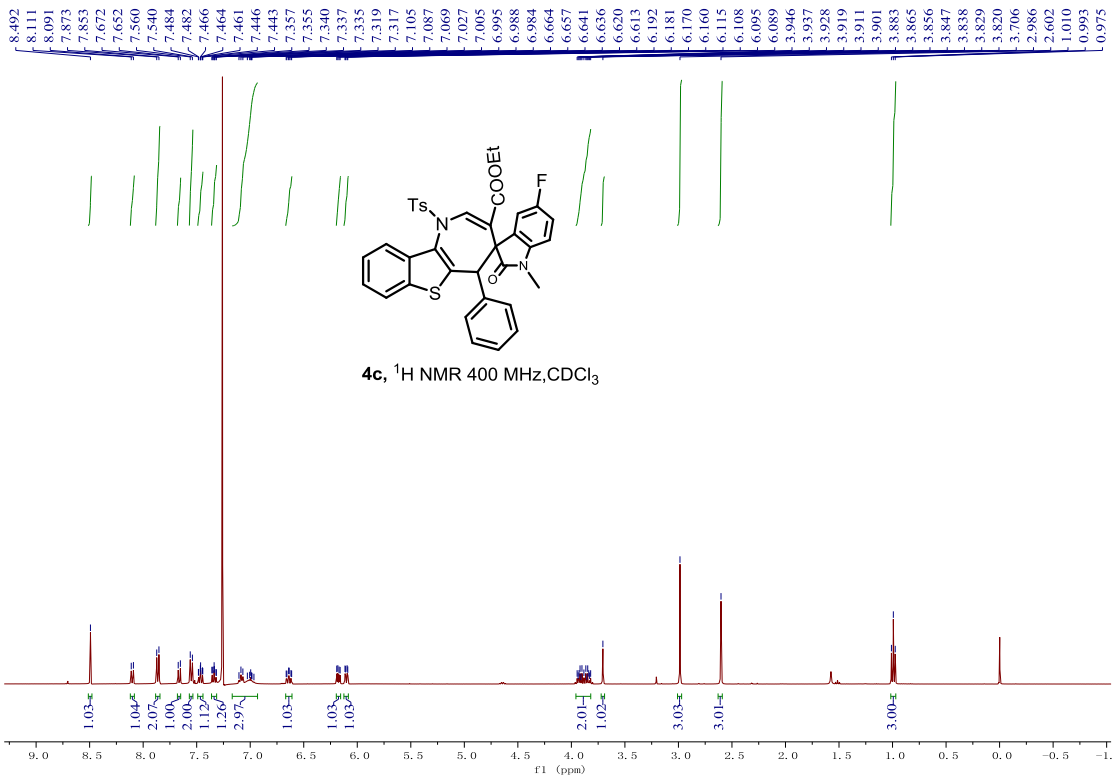

**4a**, $^{13}$C NMR 100 MHz,$CDCl_3$



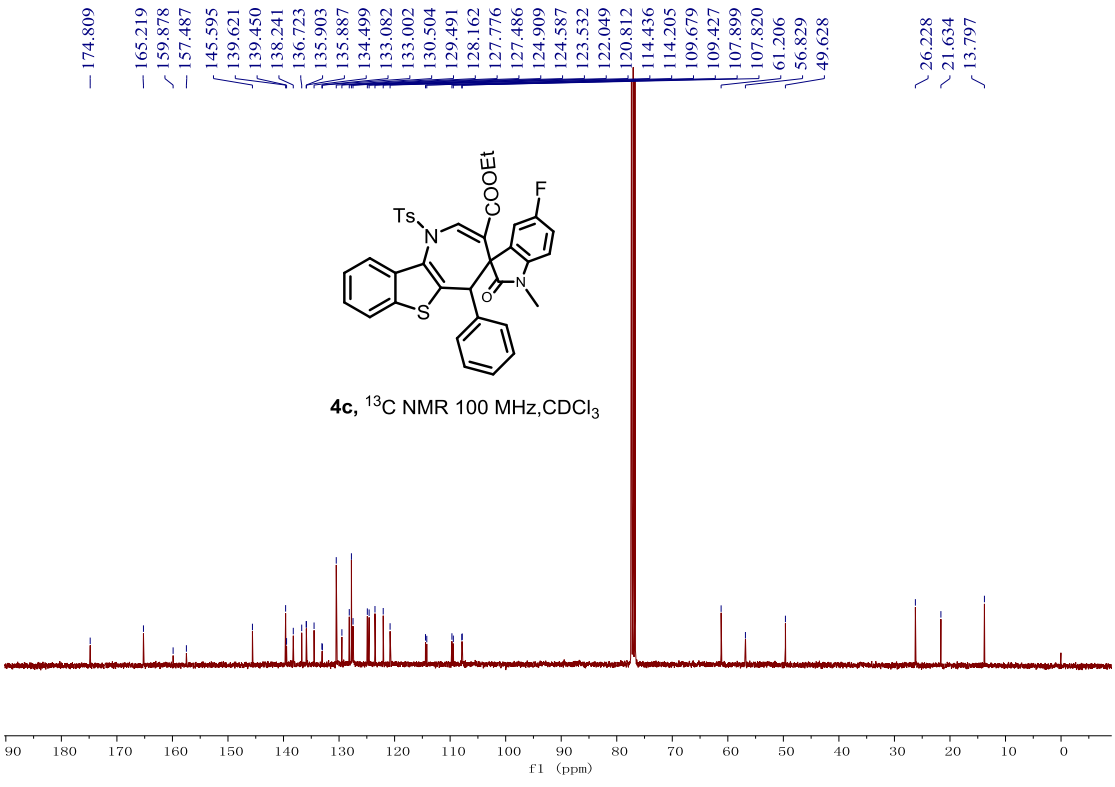

**4b,** $^{1}$H NMR 400 MHz,$CDCl_3$



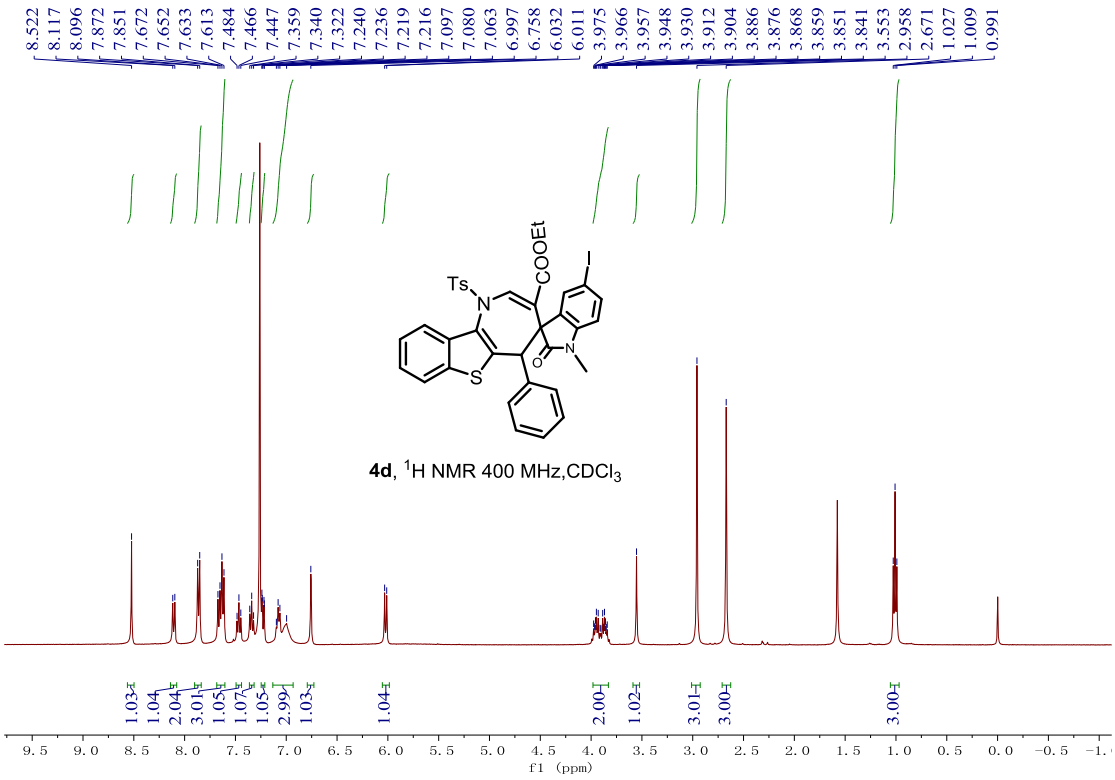

**4b,** $^{13}$C NMR 100 MHz,$CDCl_3$



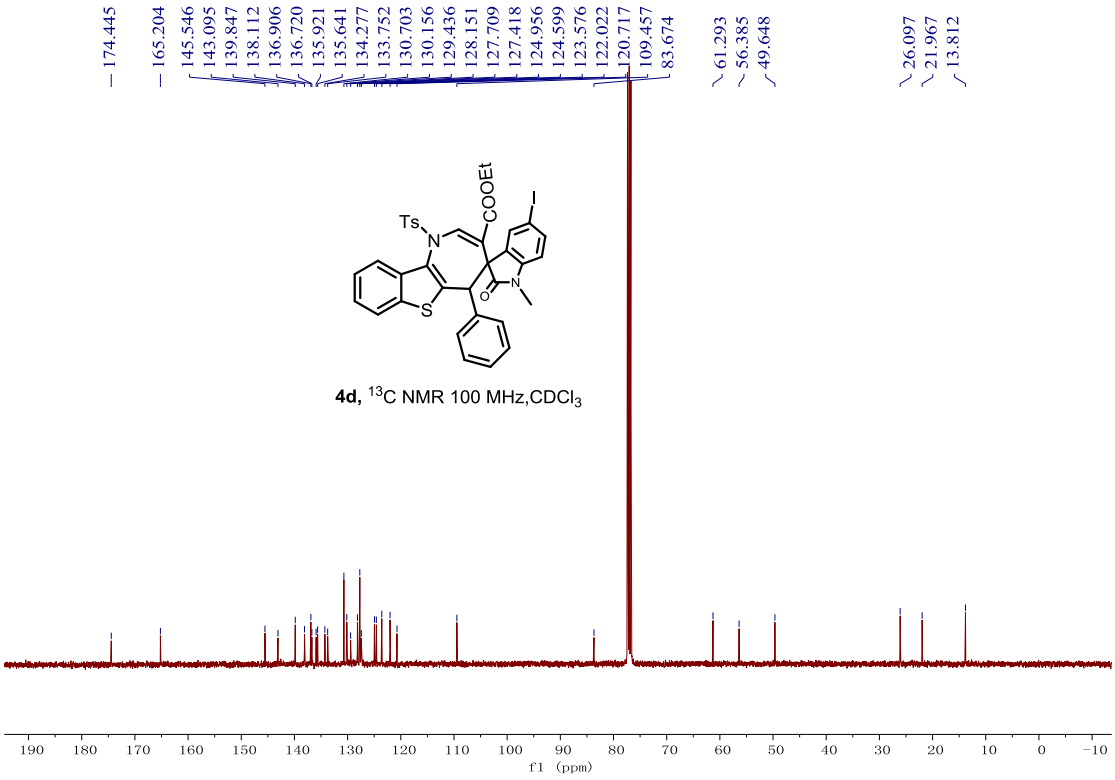

**4c,** $^{1}$H NMR 400 MHz,$CDCl_3$



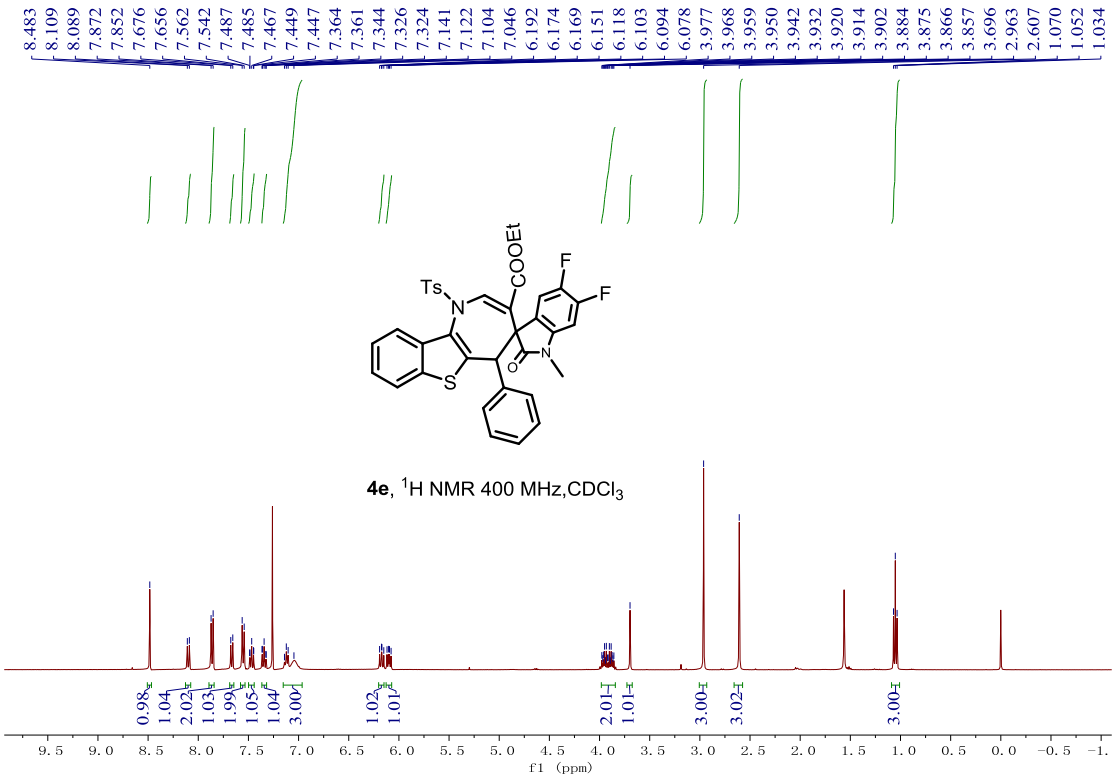

**4c,** $^{13}$C NMR 100 MHz,$CDCl_3$



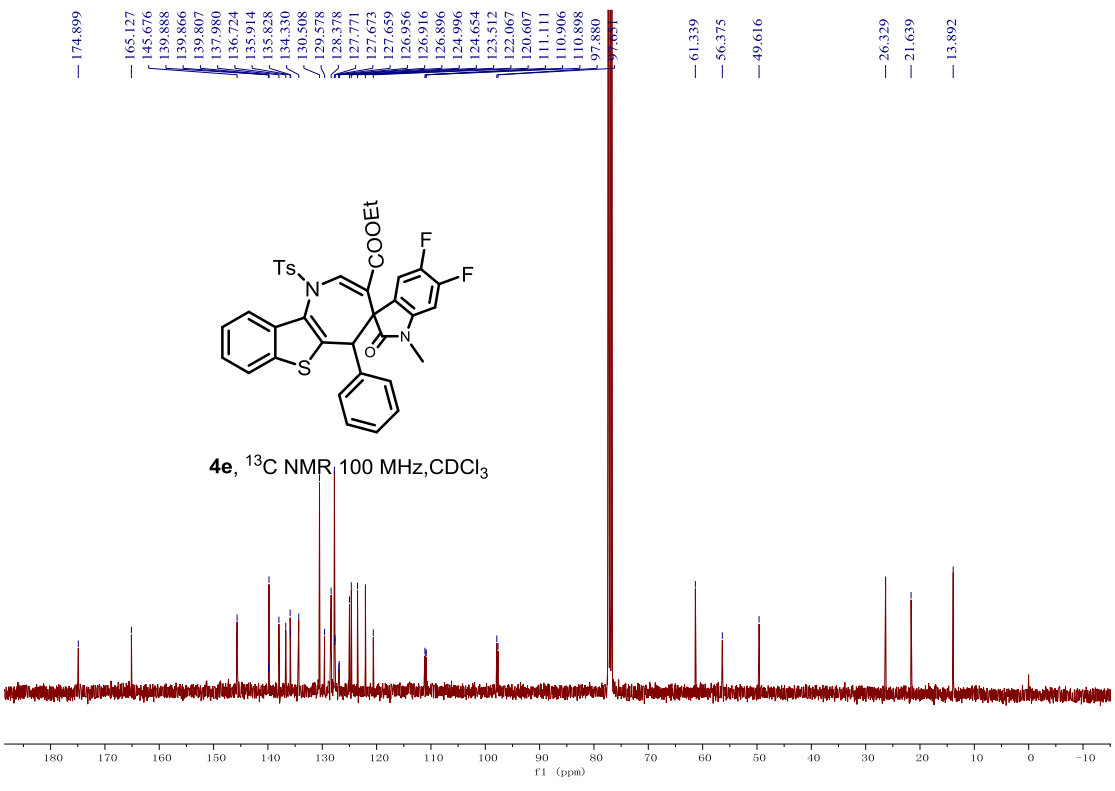

**4d**, $^{1}$H NMR 400 MHz,$CDCl_3$



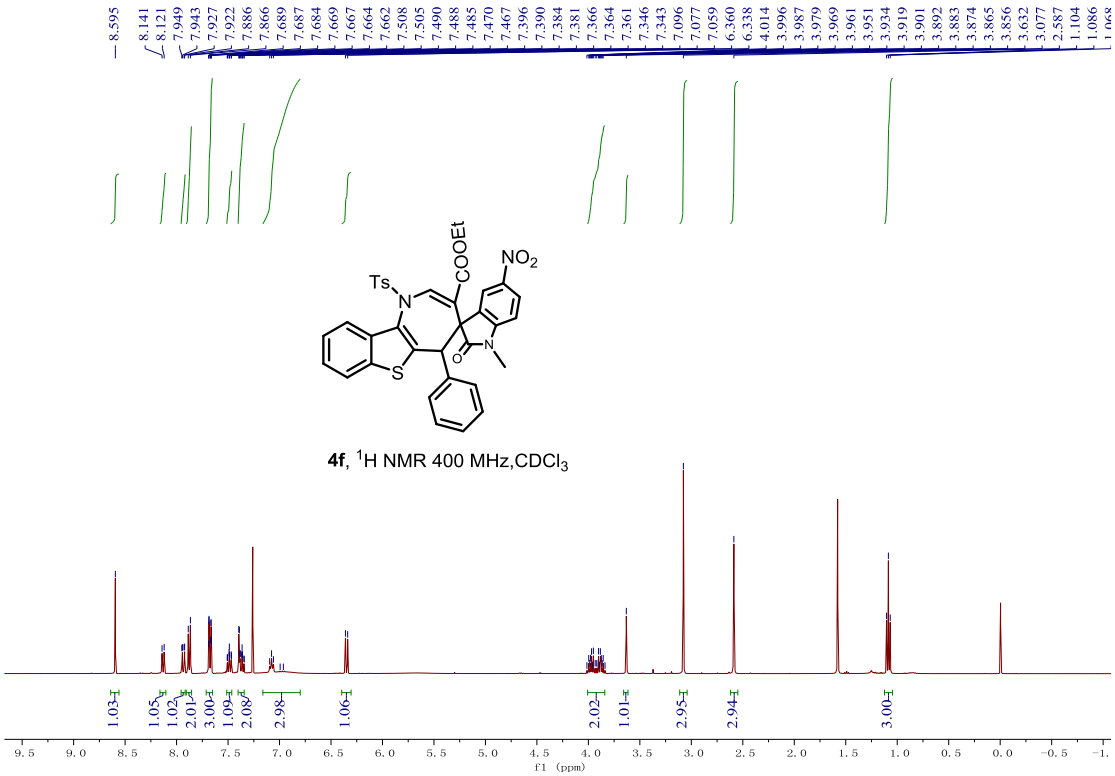

**4d,** $^{13}$C NMR 100 MHz,$CDCl_3$



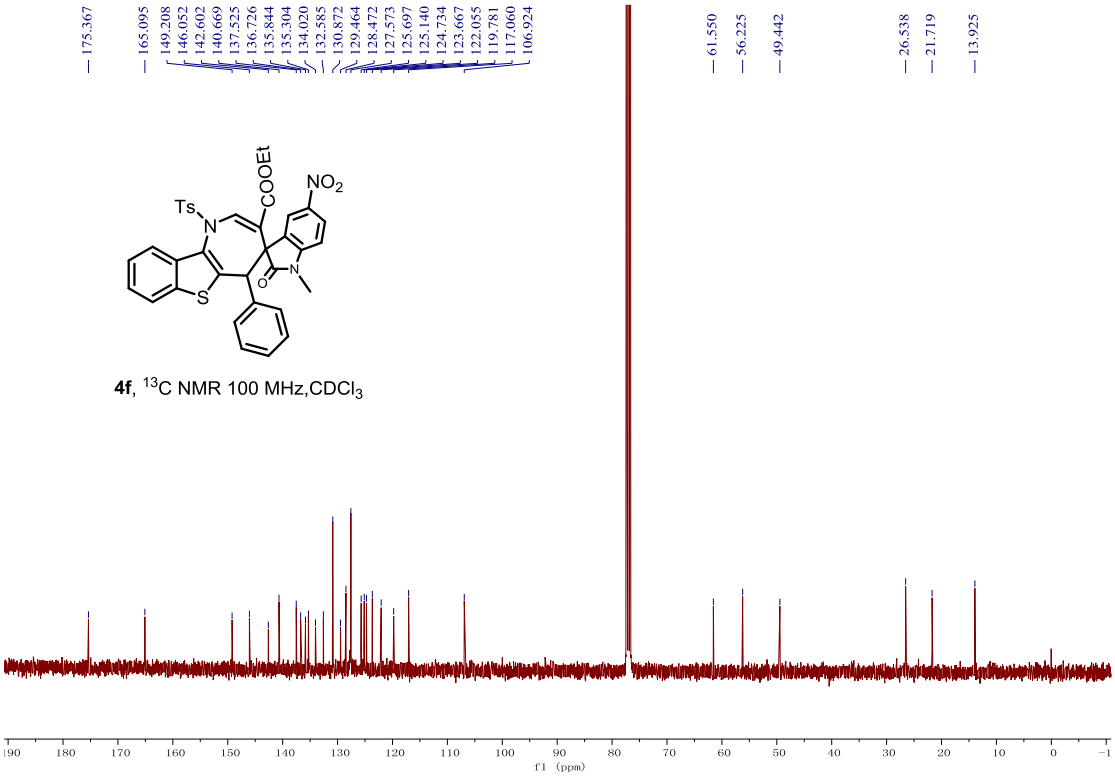

**4e**, $^{1}$H NMR 400 MHz,$CDCl_3$



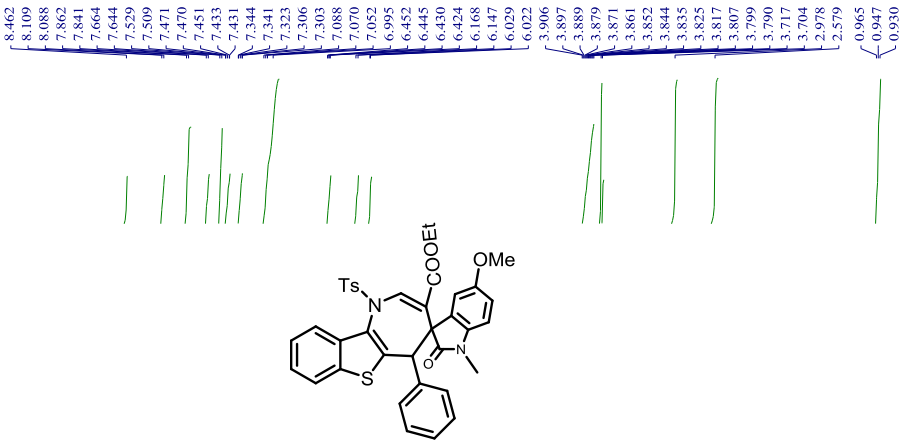

**4e**, $^{13}$C NMR 100 MHz,$CDCl_3$



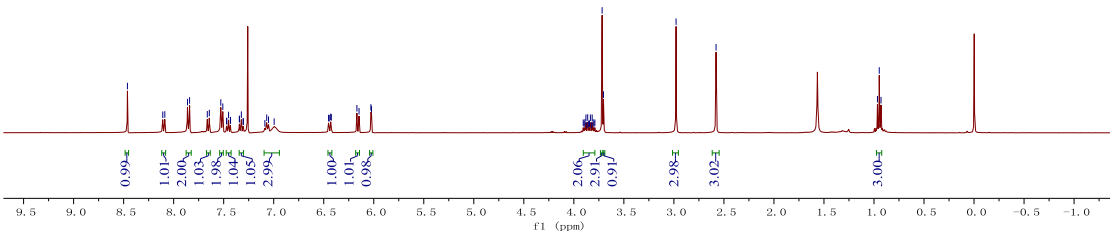

**4f**, $^{1}$H NMR 400 MHz,$CDCl_3$

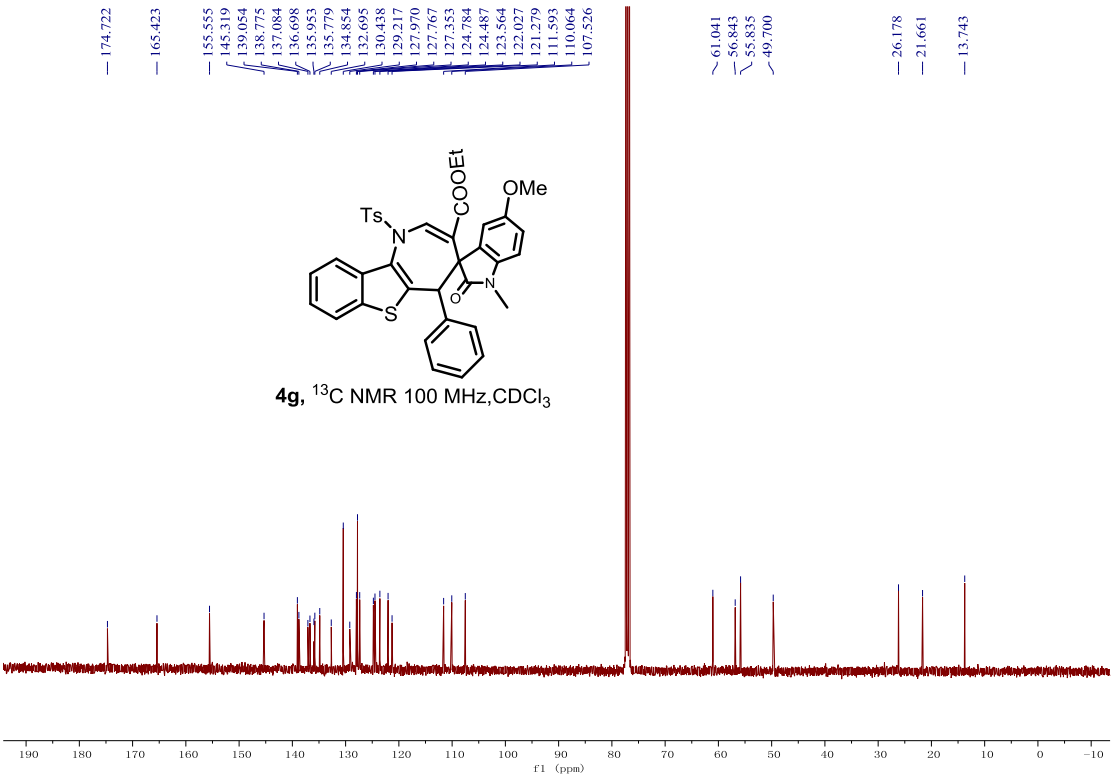



**4f**, $^{13}$C NMR 100 MHz,$CDCl_3$

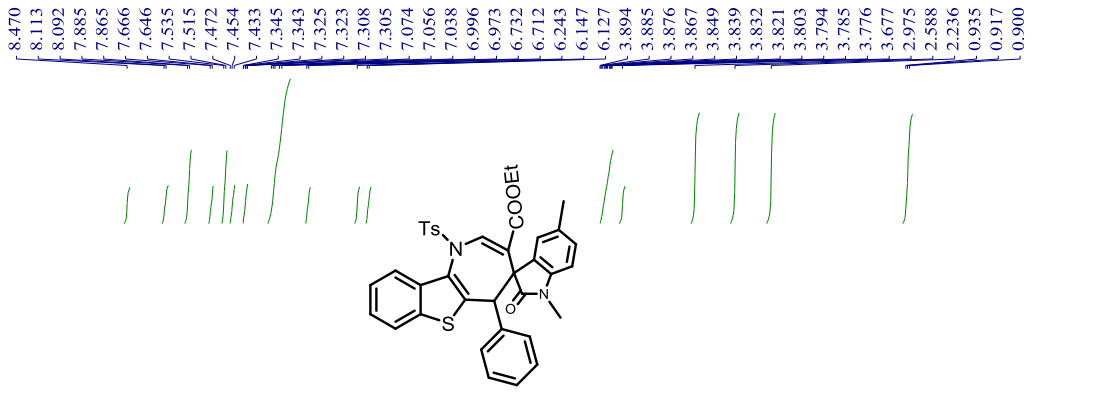



**4g,** $^{1}$H NMR 400 MHz,$CDCl_3$

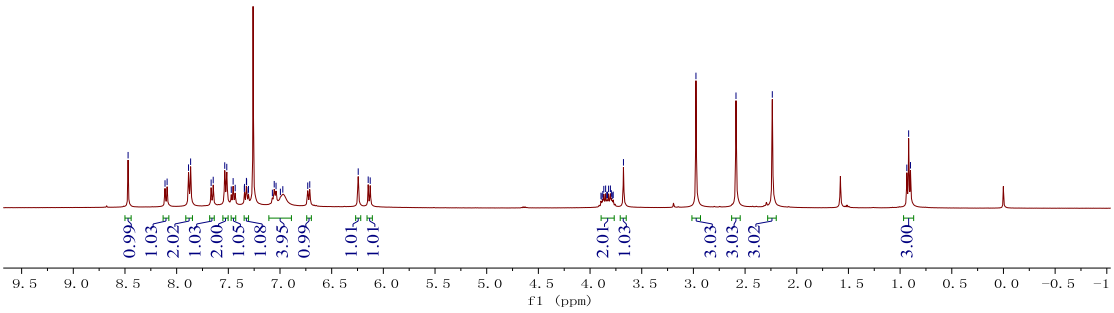


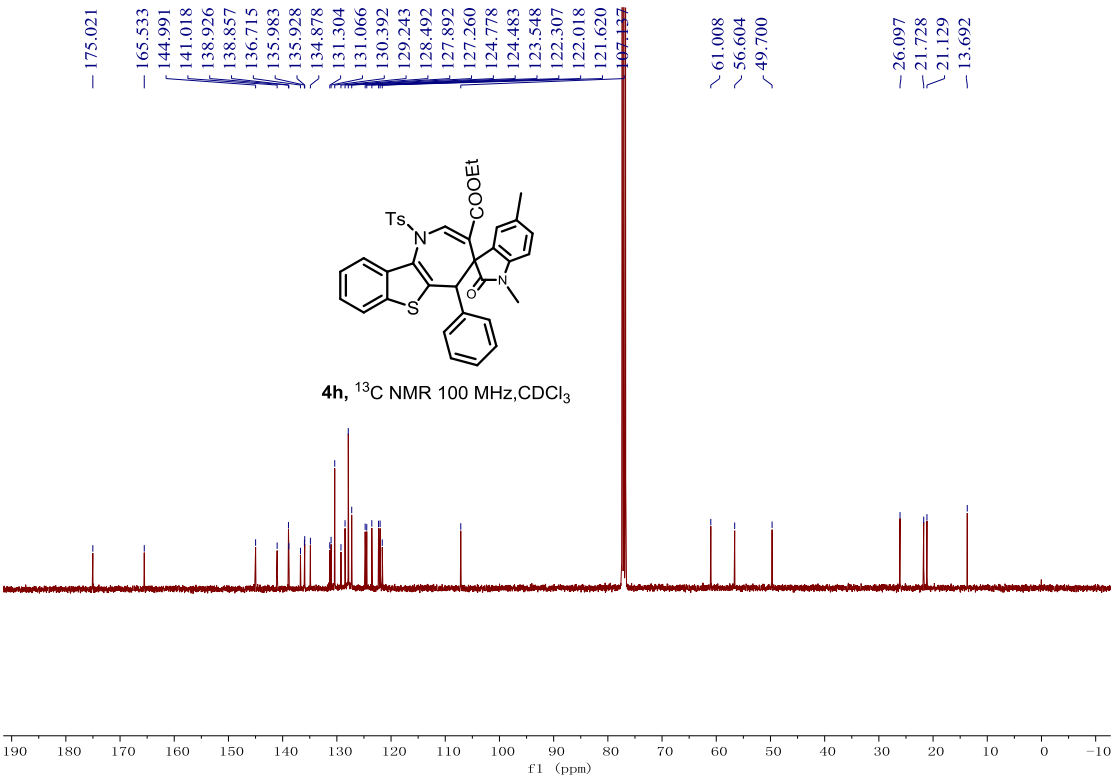




**4g,** $^{13}$C NMR 100 MHz,$CDCl_3$

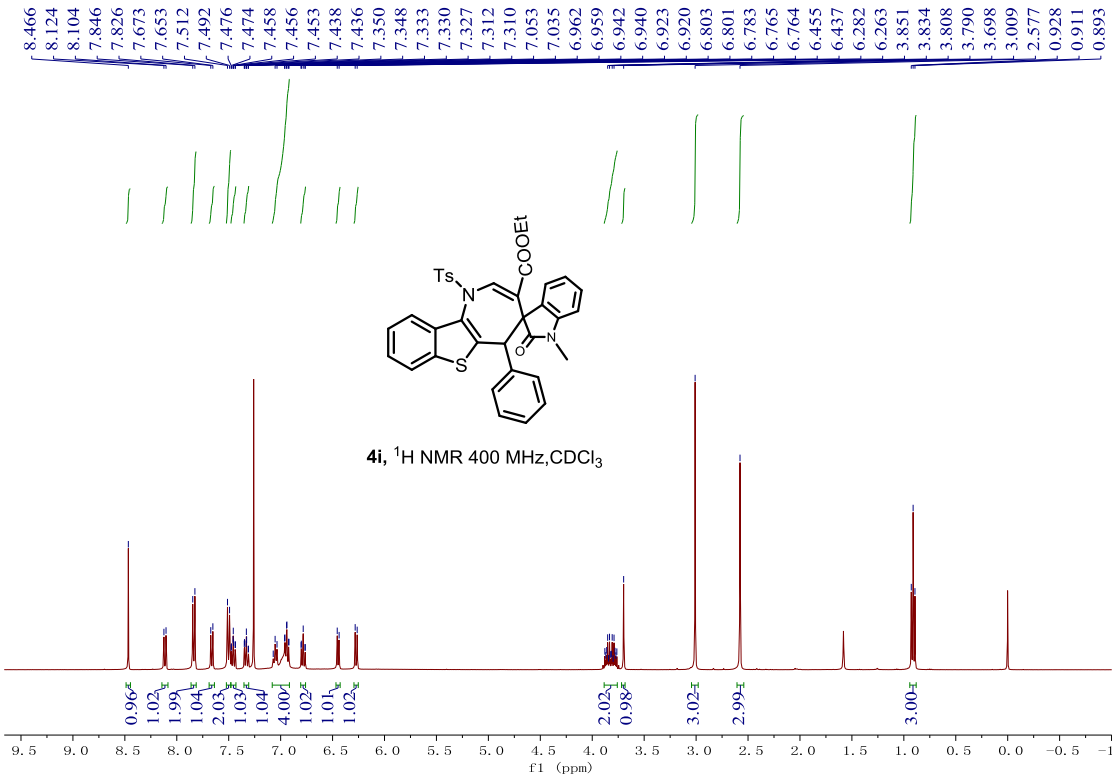



**4h,** $^{1}$H NMR 400 MHz,$CDCl_3$

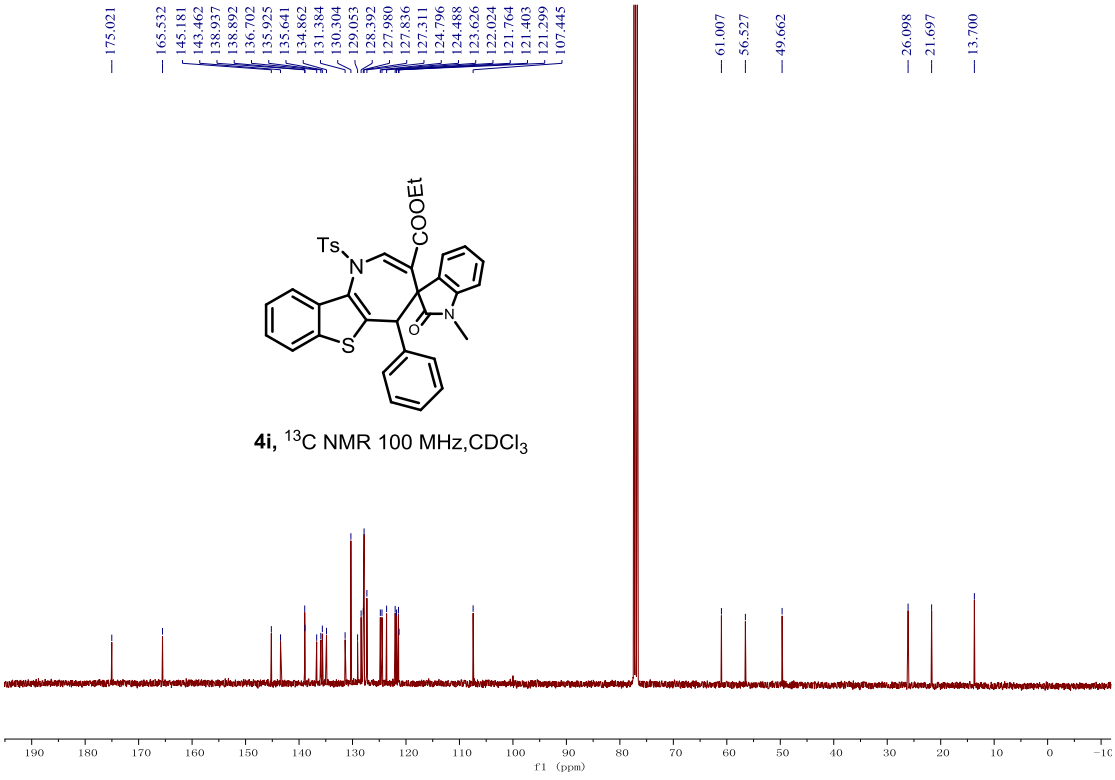


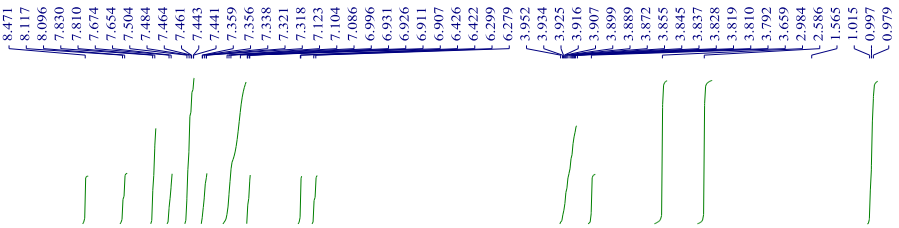

**4h,** $^{13}$C NMR 100 MHz,$CDCl_3$

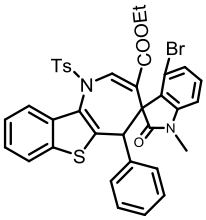



**4i,** $^{1}$H NMR 400 MHz,$CDCl_3$

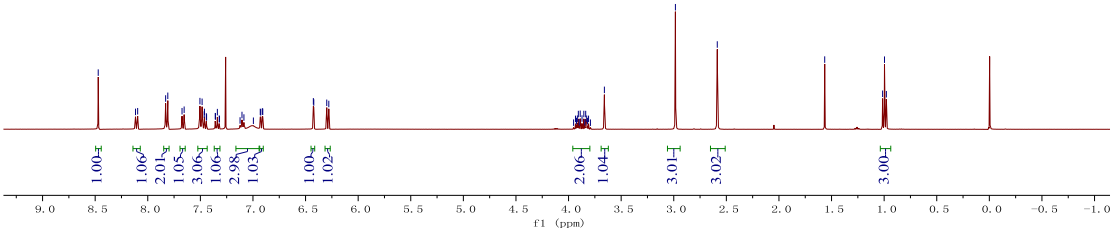



**4i,** $^{13}$C NMR 100 MHz,$CDCl_3$



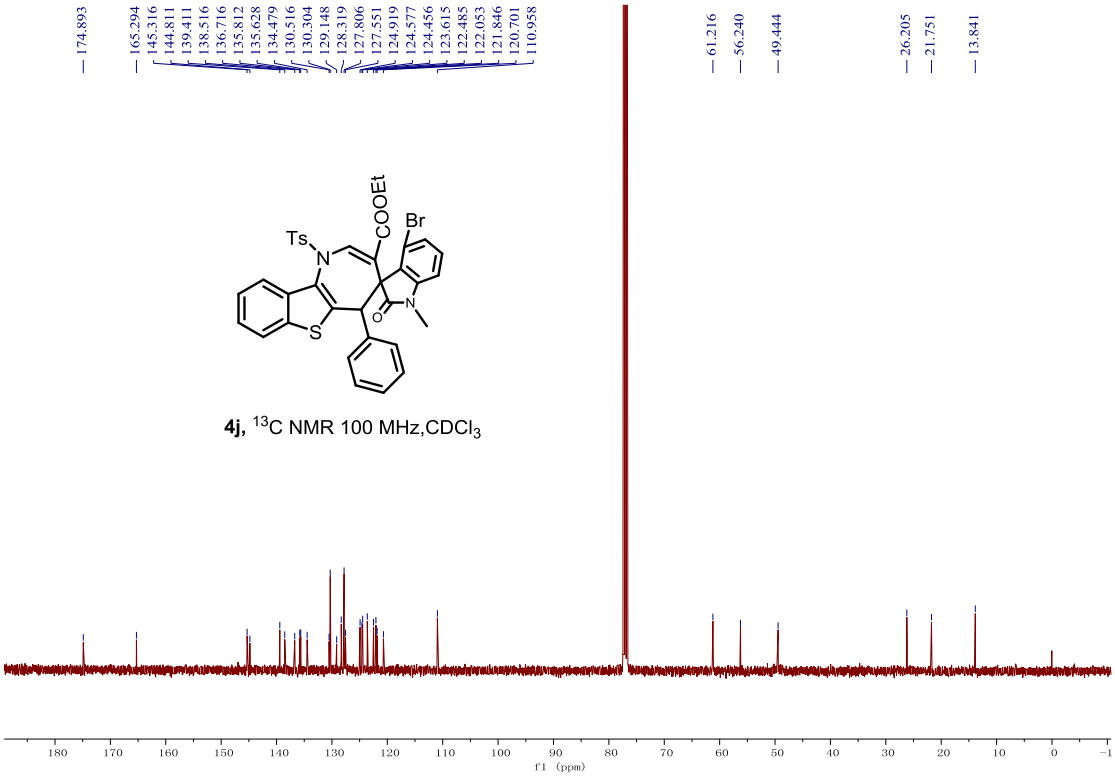

**4j,** $^{1}$H NMR 400 MHz,$CDCl_3$

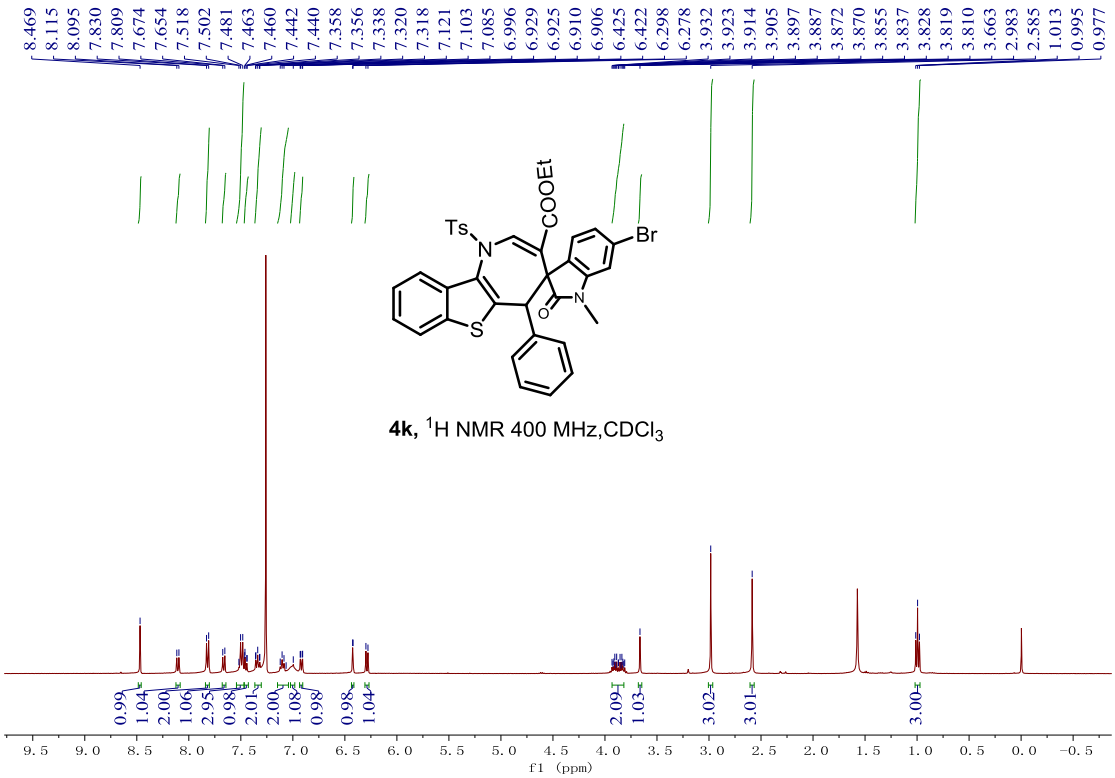




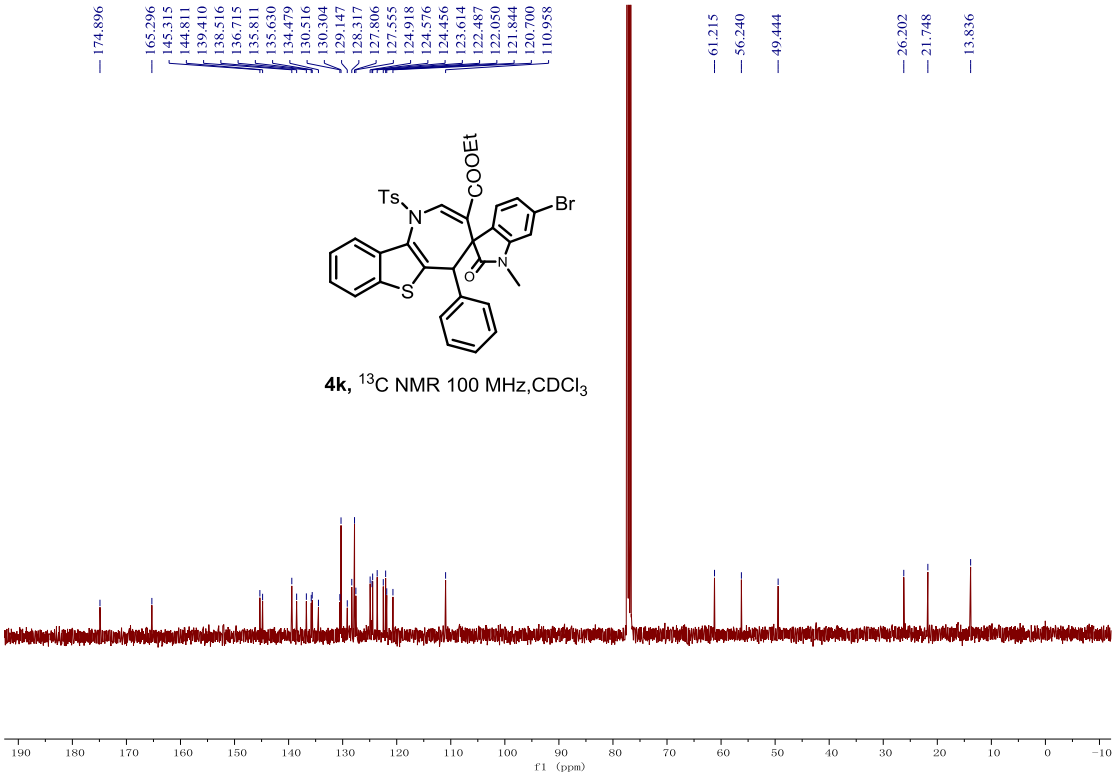


**4j,** $^{13}$C NMR 100 MHz,$CDCl_3$

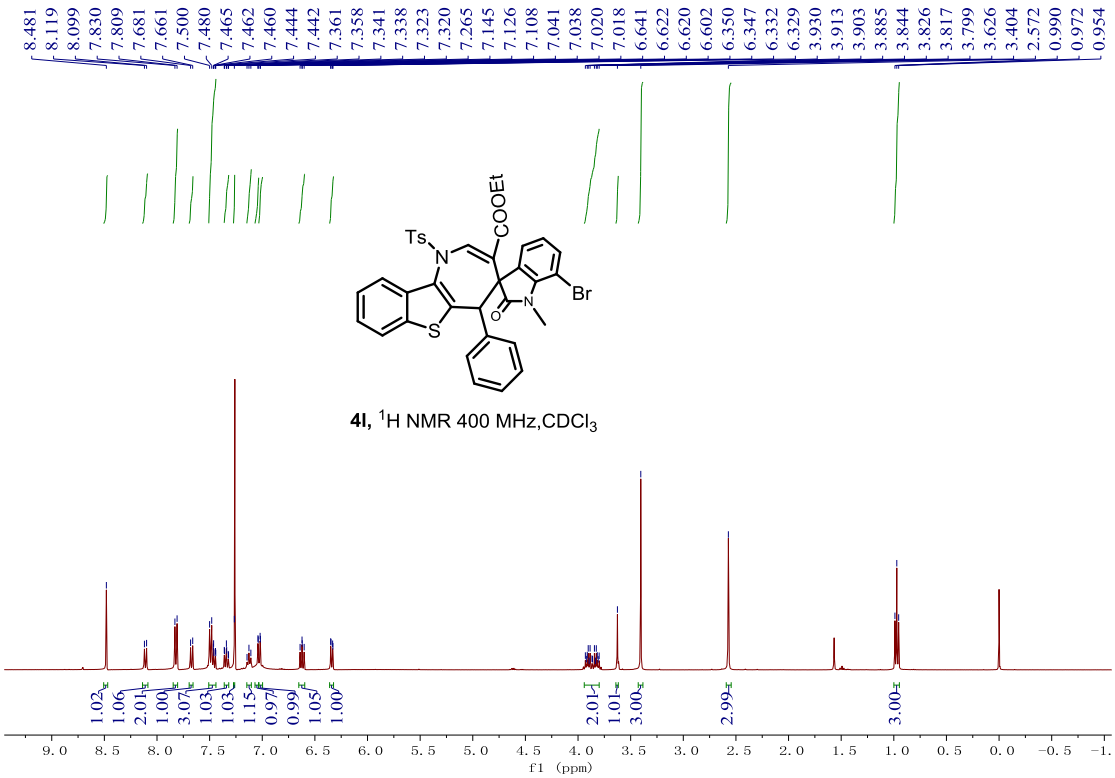




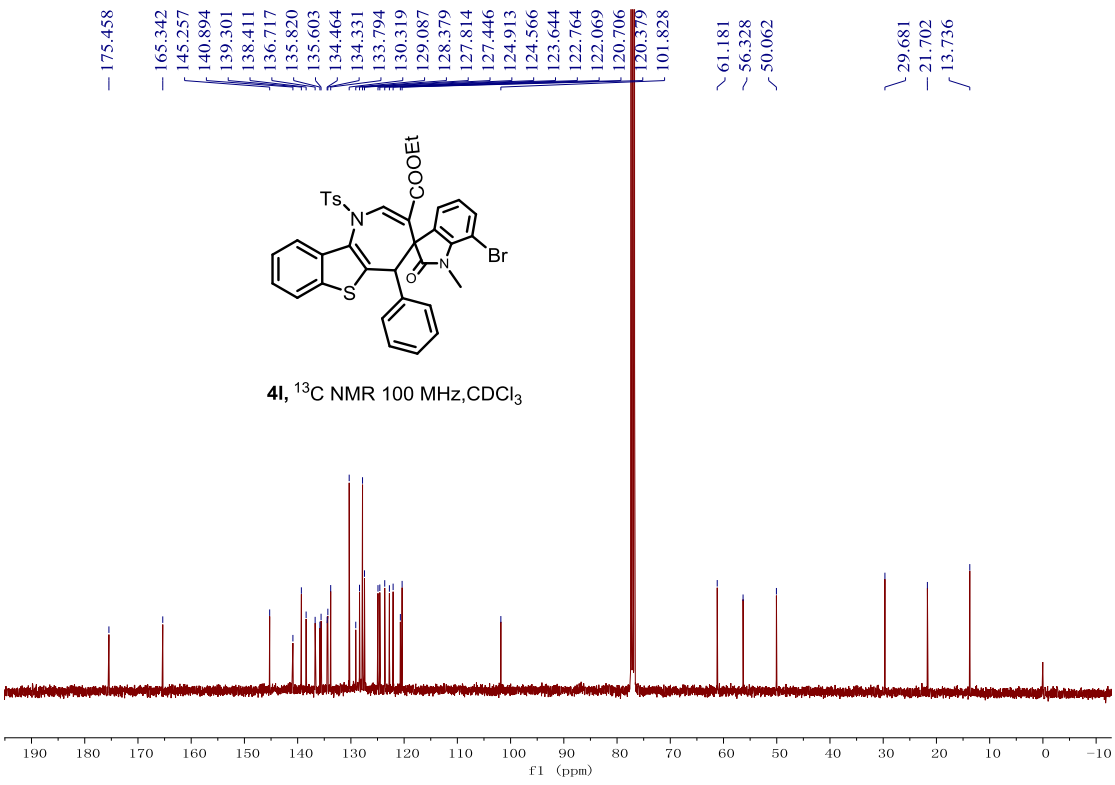

**4k,** $^{1}$H NMR 400 MHz,$CDCl_3$



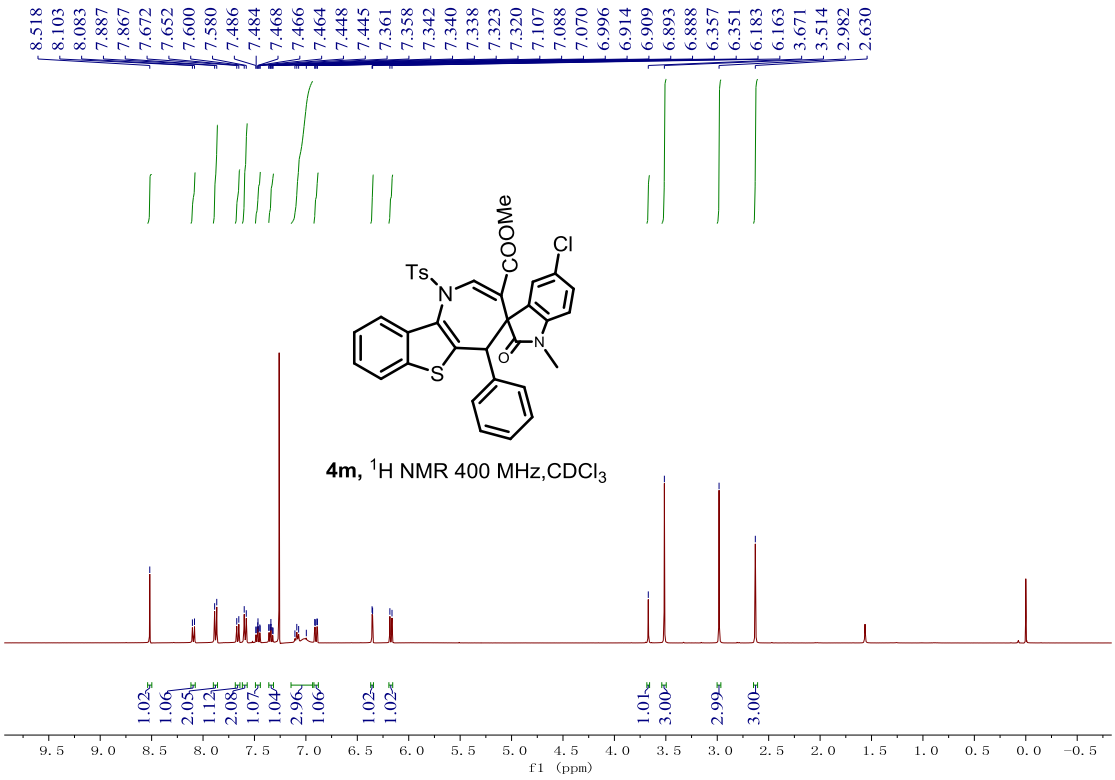

**4k,** $^{13}$C NMR 100 MHz,$CDCl_3$



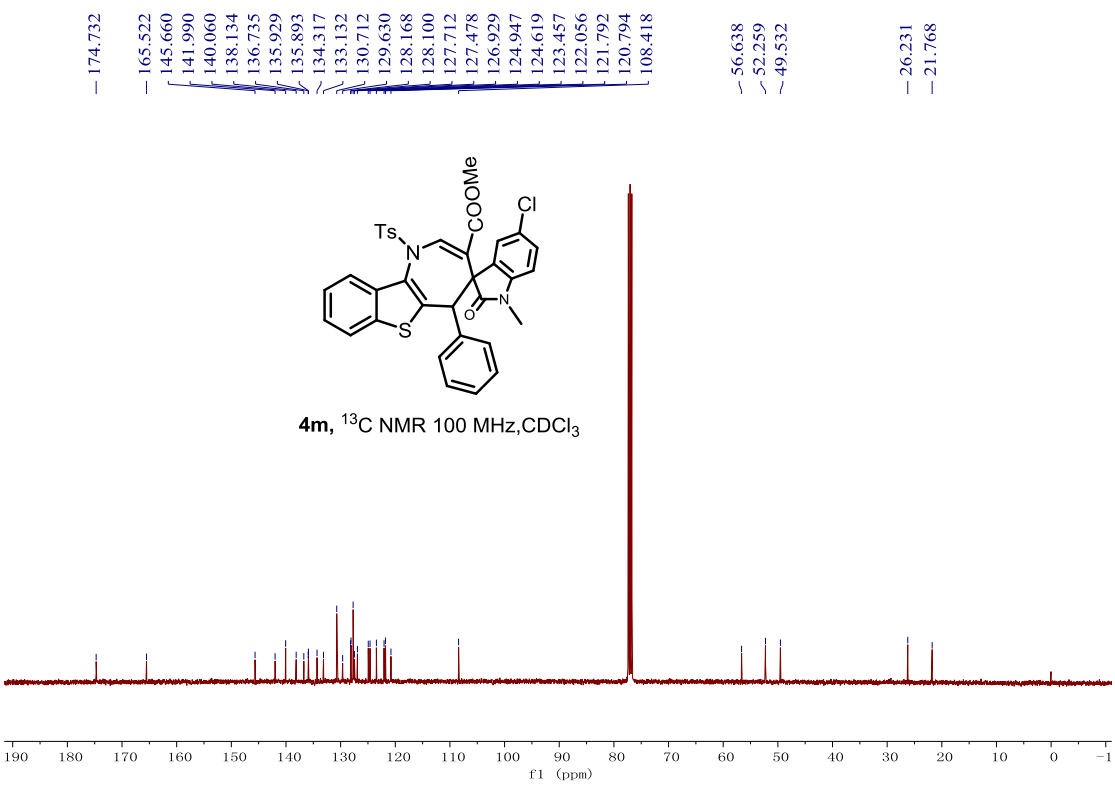

**4l**, $^{1}$H NMR 400 MHz,$CDCl_3$



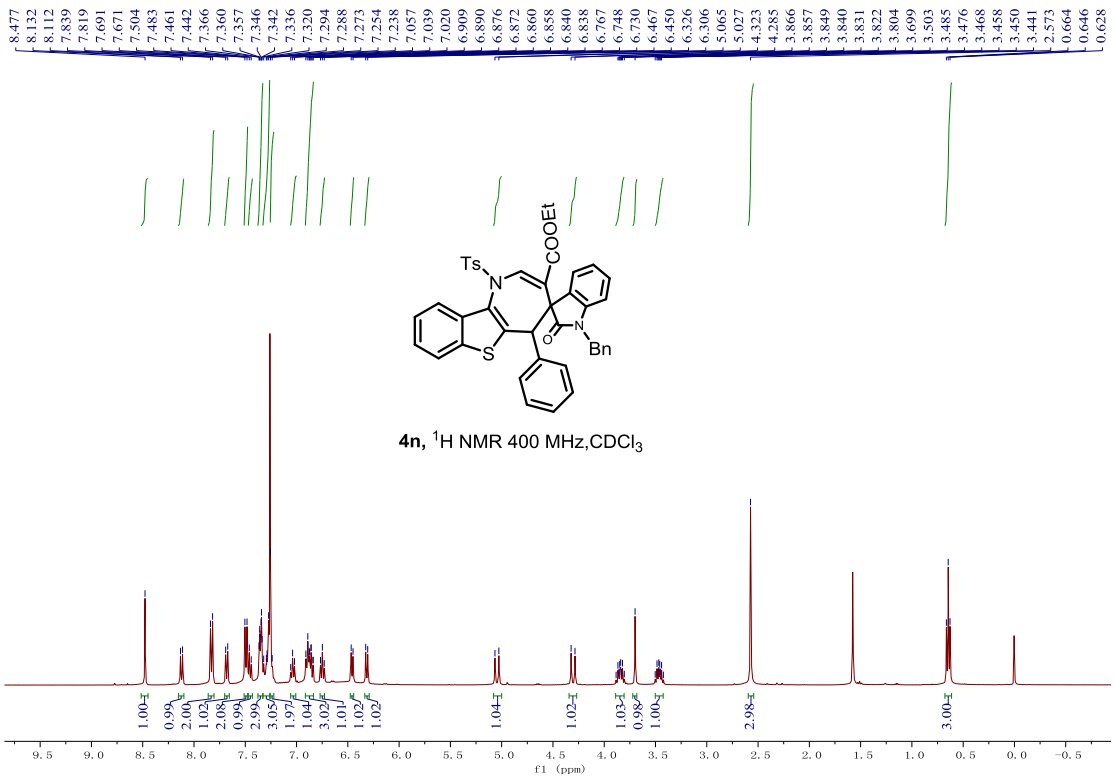

**4l**, $^{13}$C NMR 100 MHz,$CDCl_3$



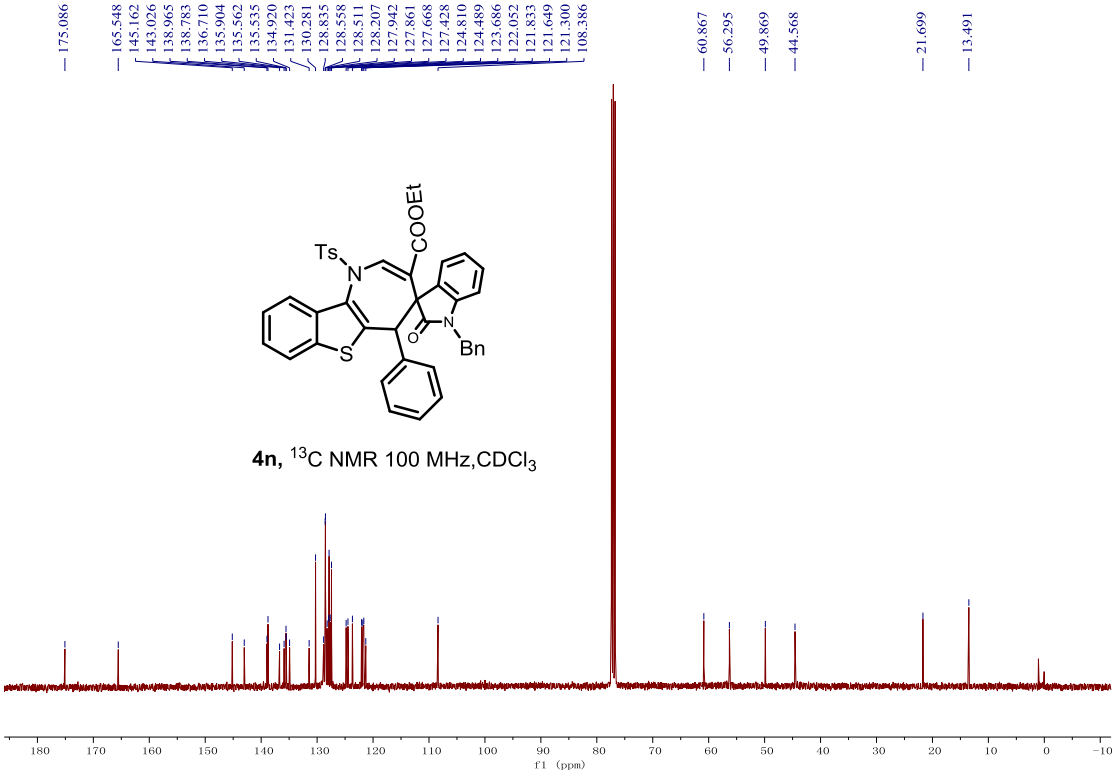

**4m,** $^{1}$H NMR 400 MHz,$CDCl_3$



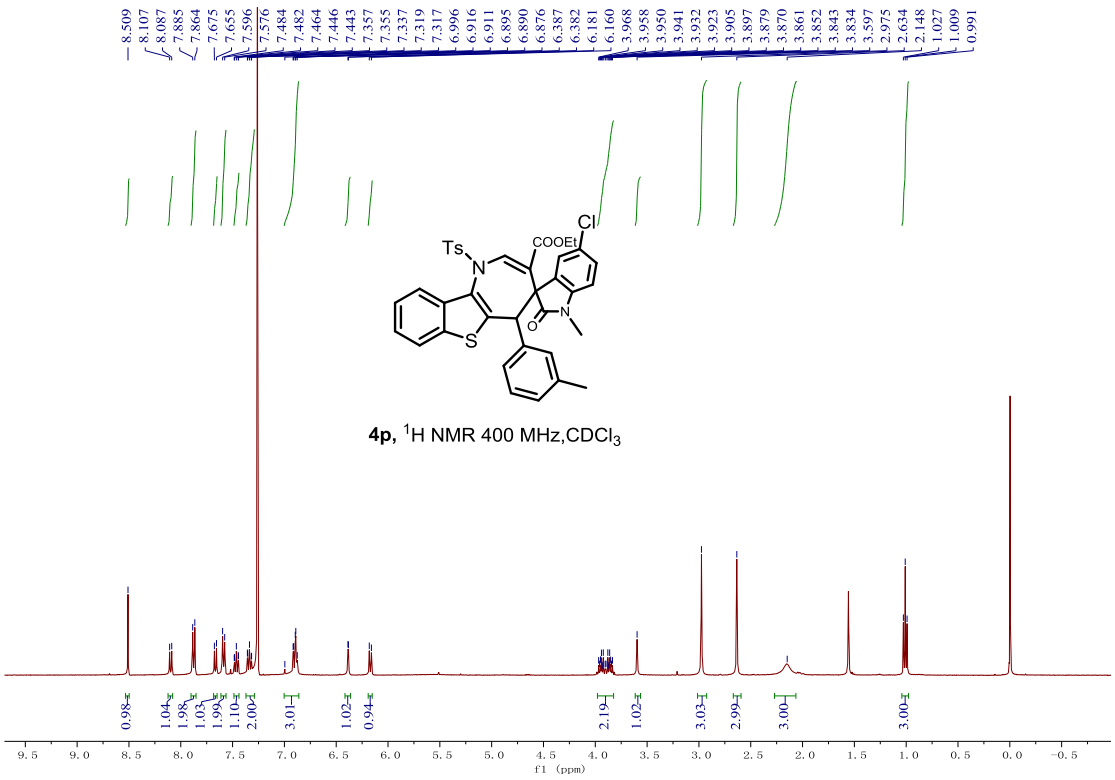

**4m,** $^{13}$C NMR 100 MHz,$CDCl_3$



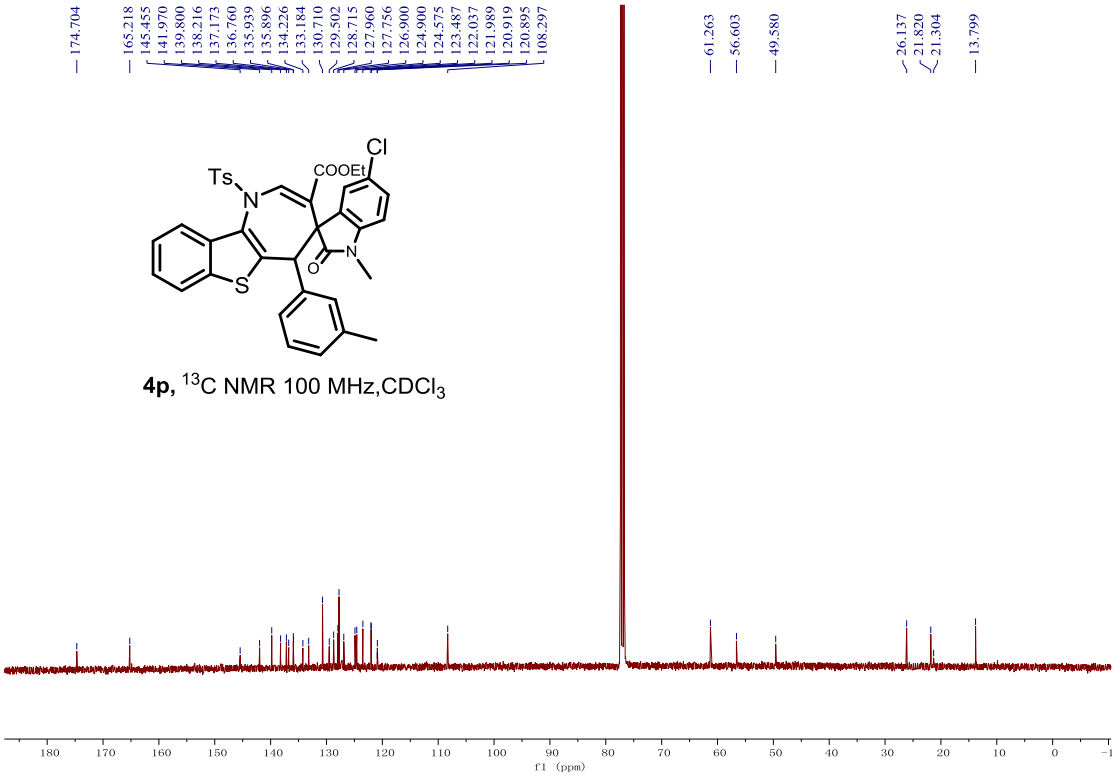

**4n,** $^{1}$H NMR 400 MHz,$CDCl_3$



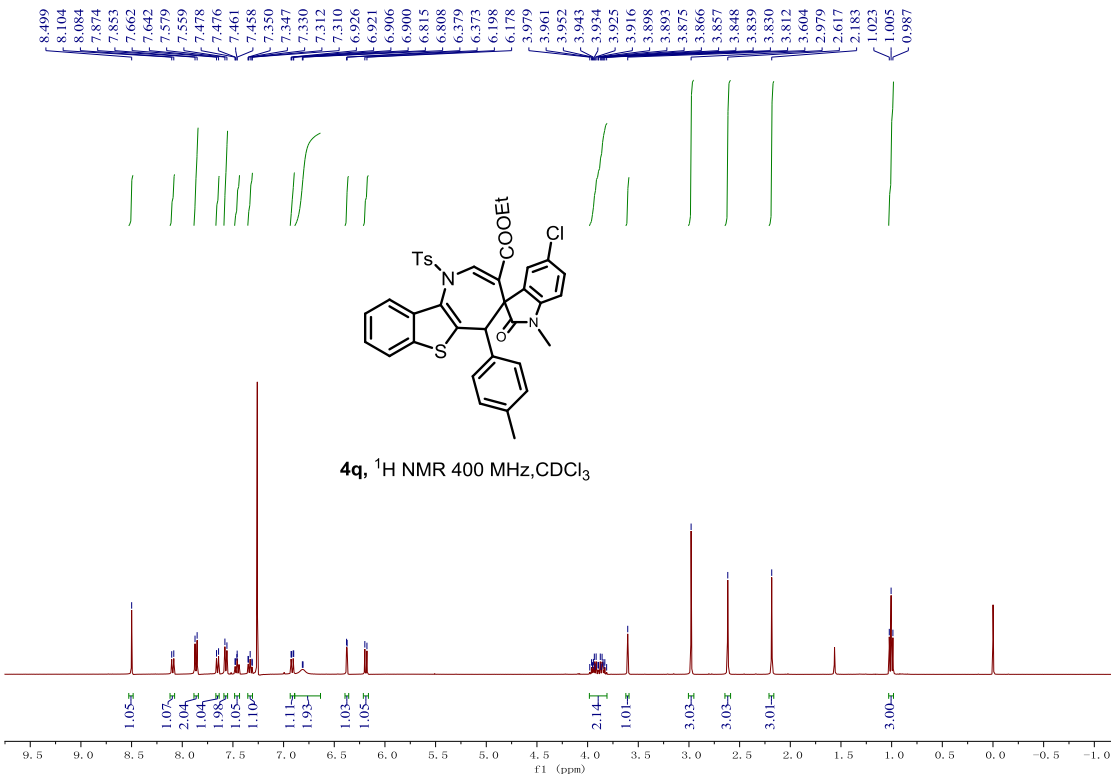

**4n,** $^{13}$C NMR 100 MHz,$CDCl_3$



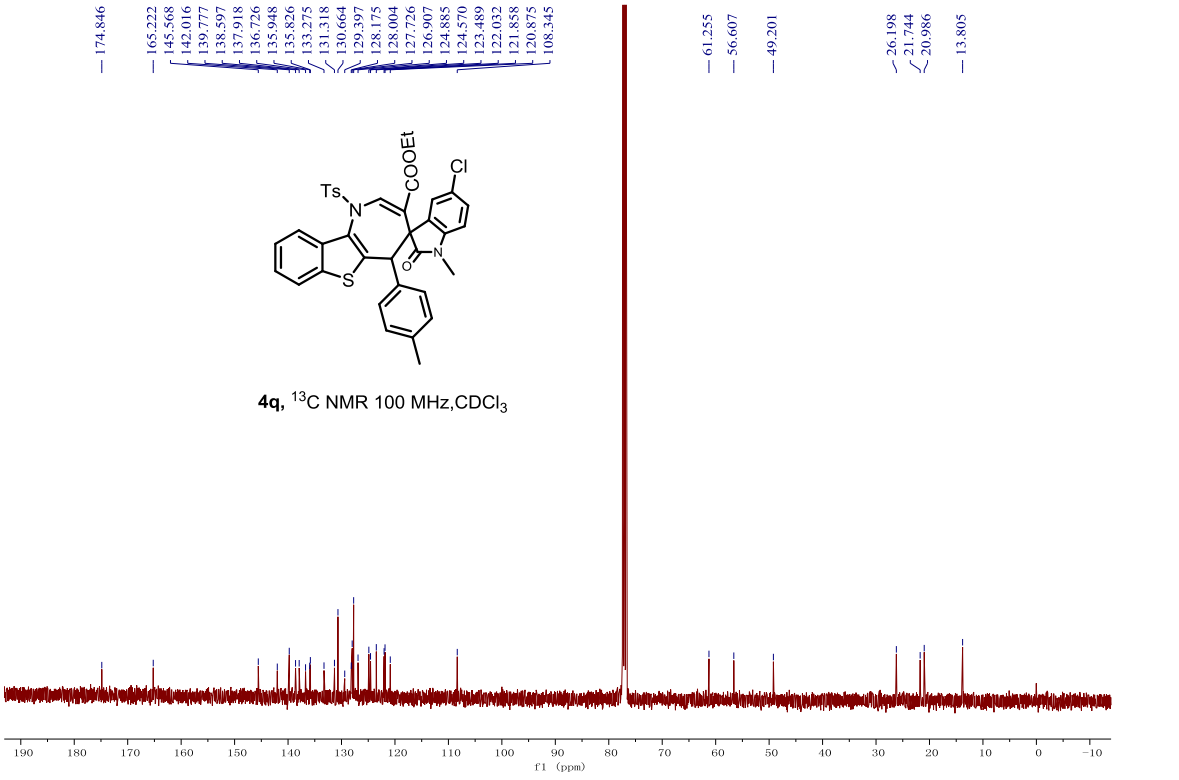

**4p,** $^{1}$H NMR 400 MHz,$CDCl_3$



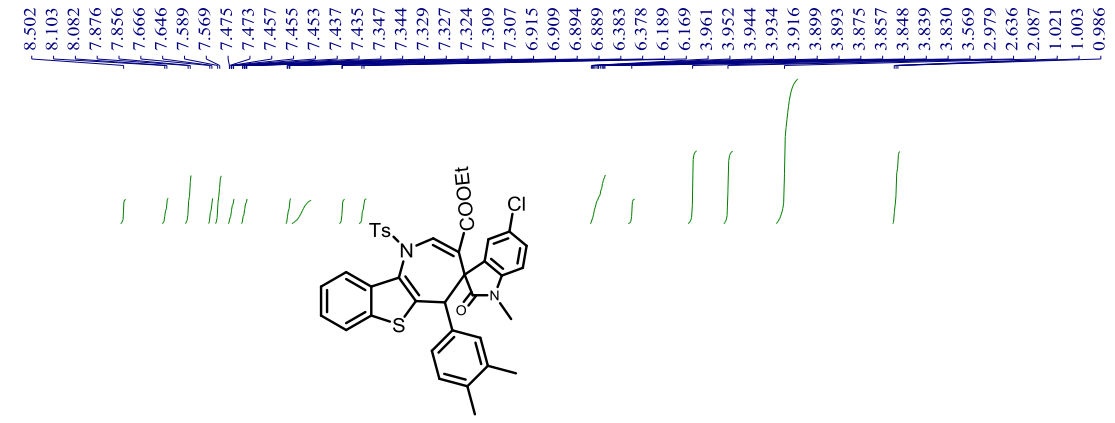

**4p,** $^{13}$C NMR 100 MHz,$CDCl_3$



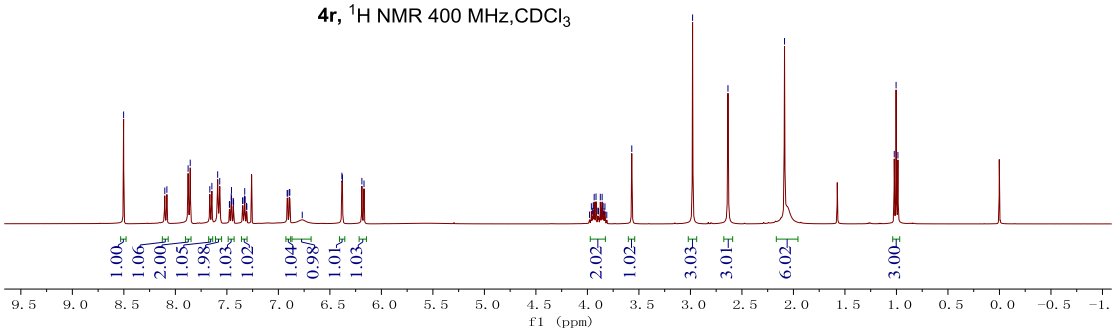

**4q,** $^{1}$H NMR 400 MHz,$CDCl_3$

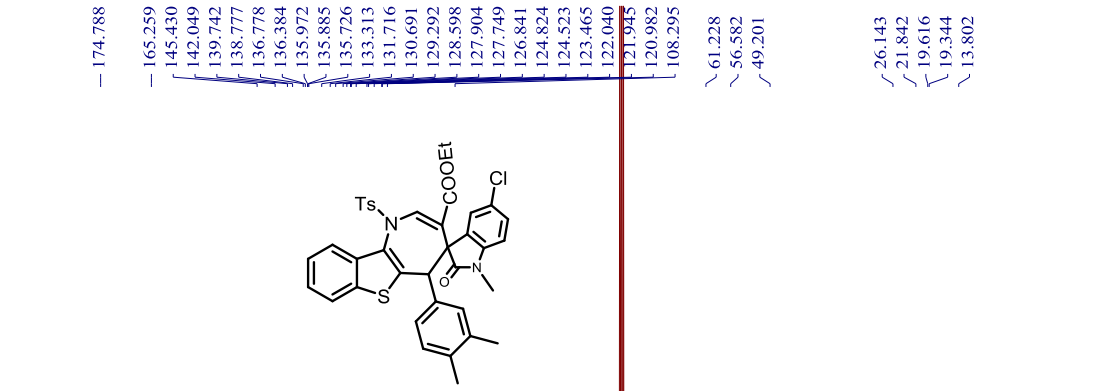



**4q,** $^{13}$C NMR 100 MHz,$CDCl_3$




**4r,** $^{1}$H NMR 400 MHz,$CDCl_3$

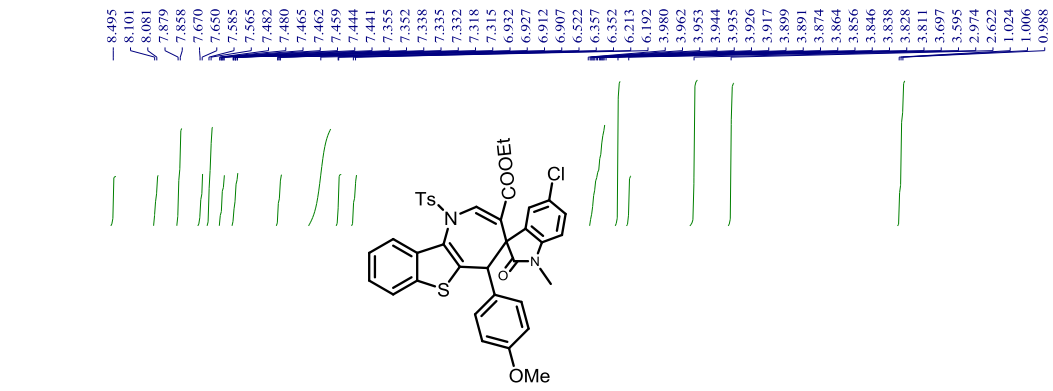


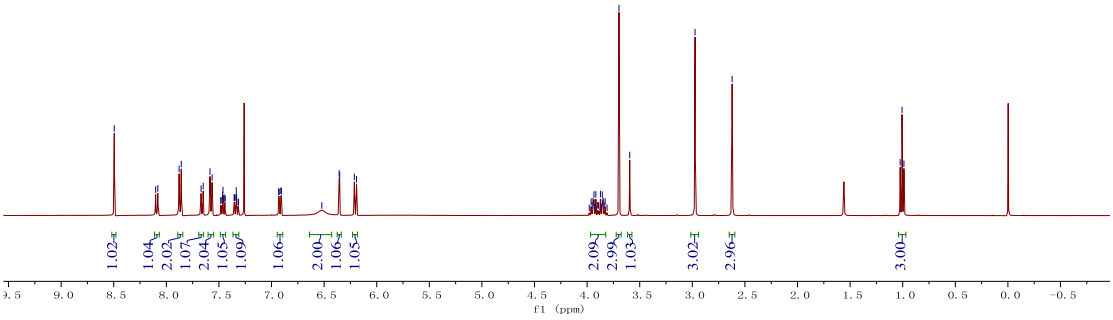


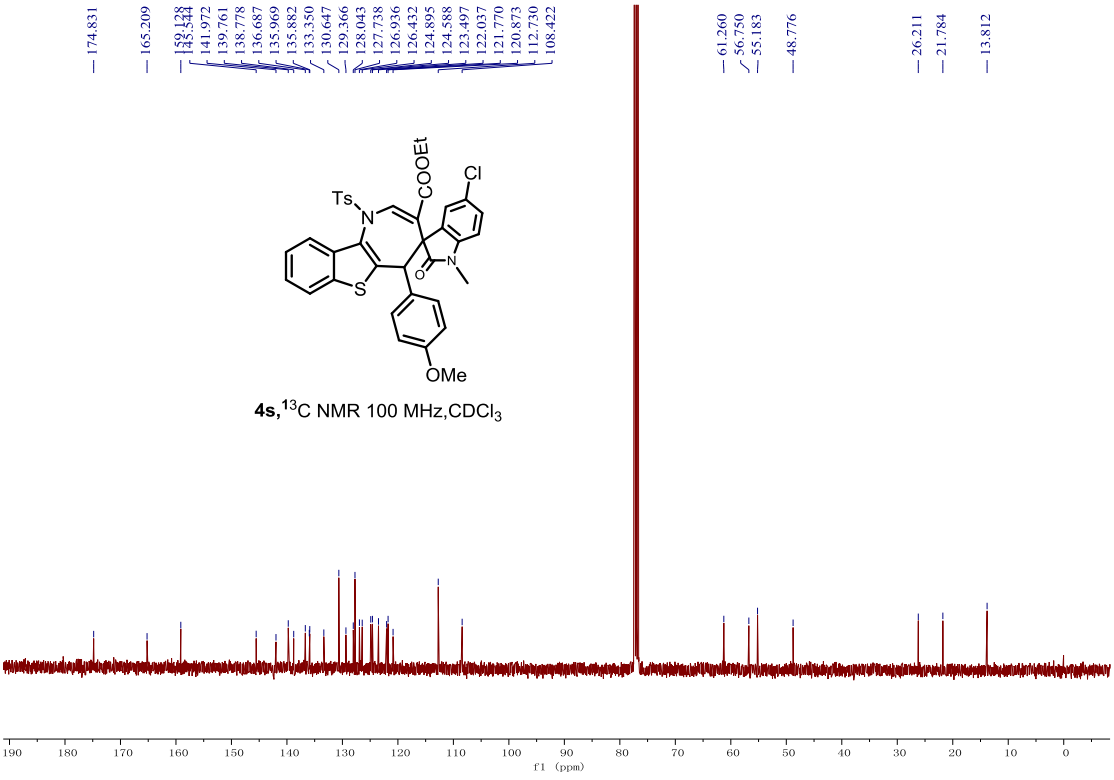


**4r,** $^{13}$C NMR 100 MHz,$CDCl_3$

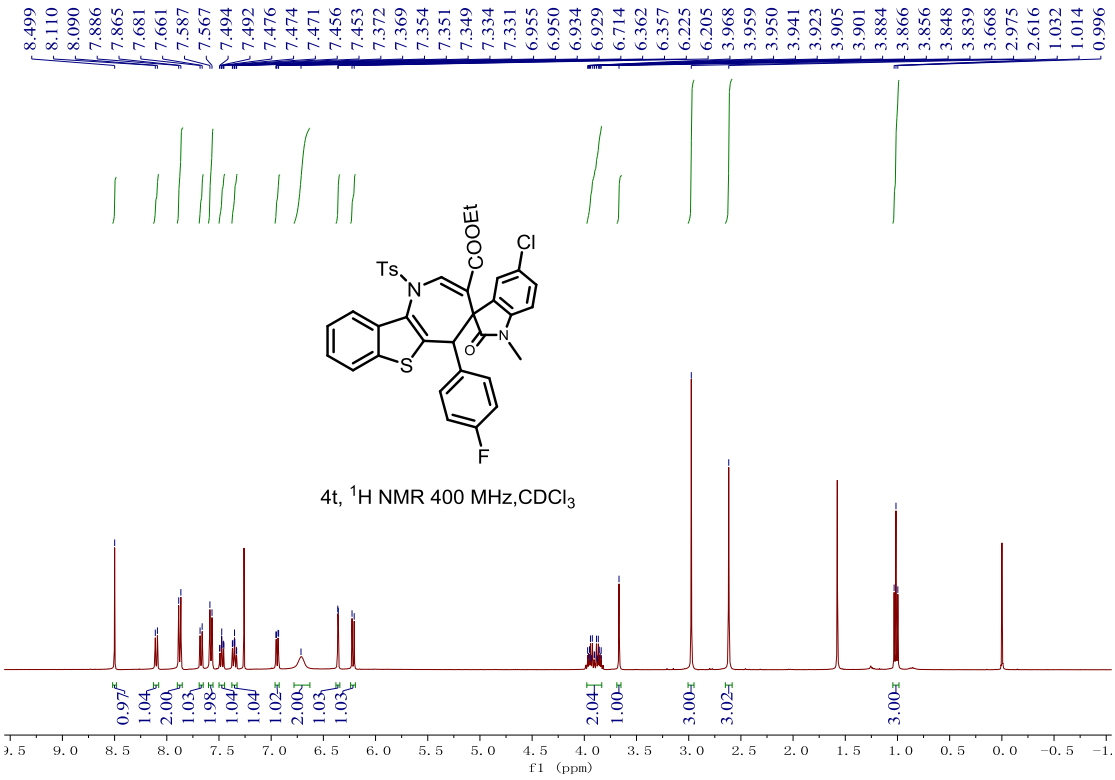



**4s,** $^{1}$H NMR 400 MHz,$CDCl_3$

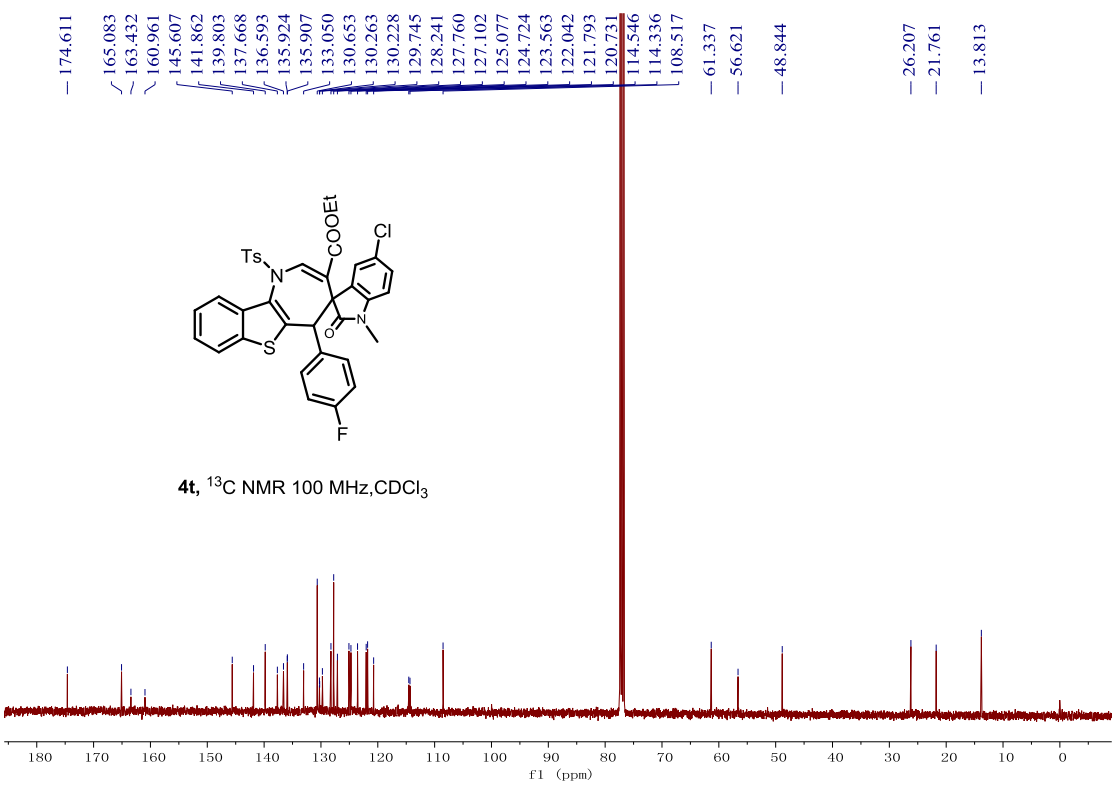


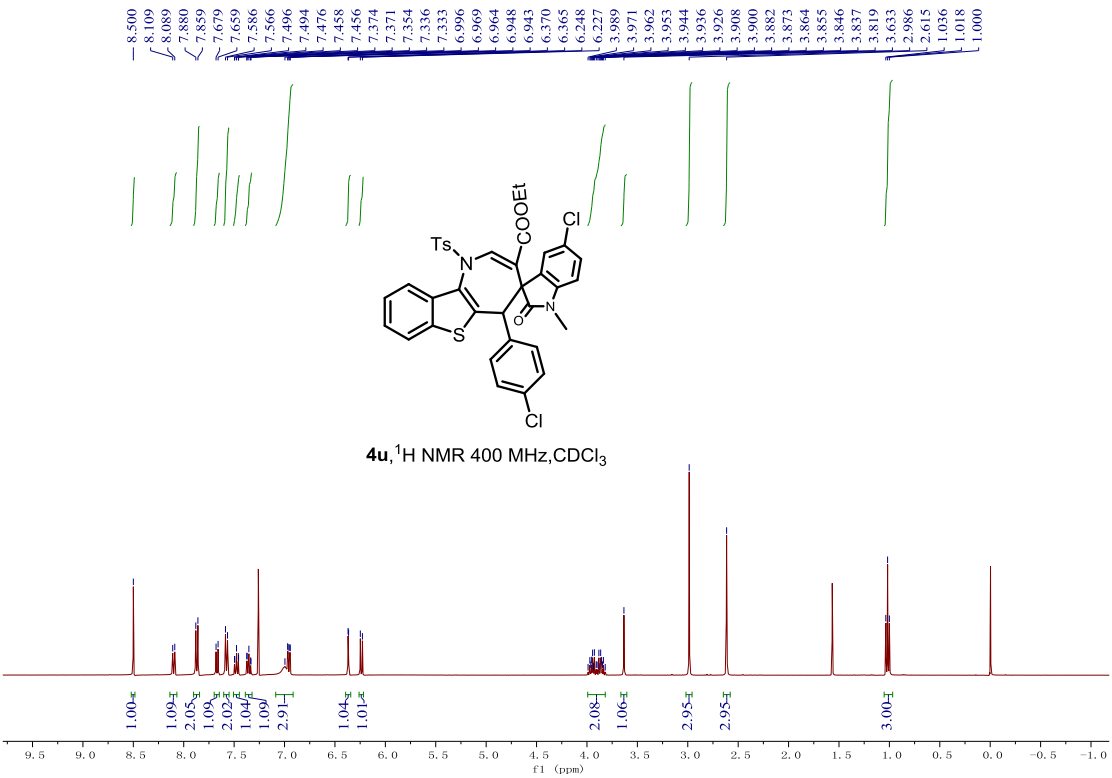

**4s,**$^{13}$C NMR 100 MHz,$CDCl_3$




4t, $^{1}$H NMR 400 MHz,$CDCl_3$

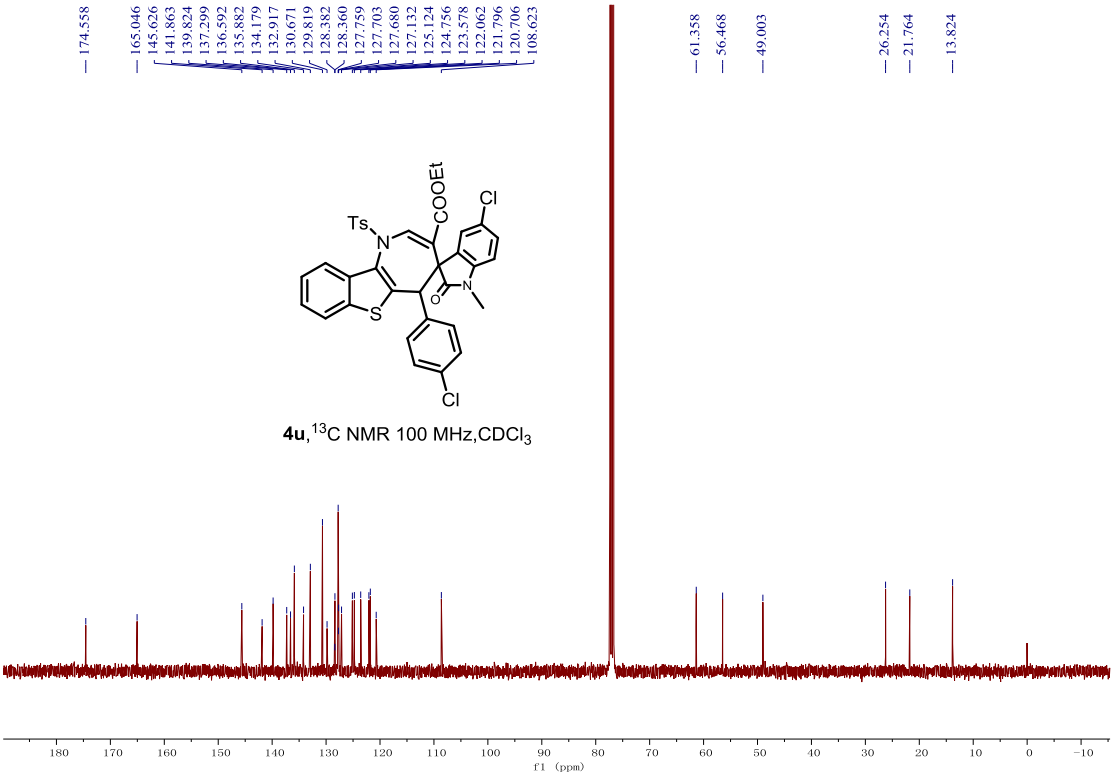



**4t,** $^{13}$C NMR 100 MHz,$CDCl_3$

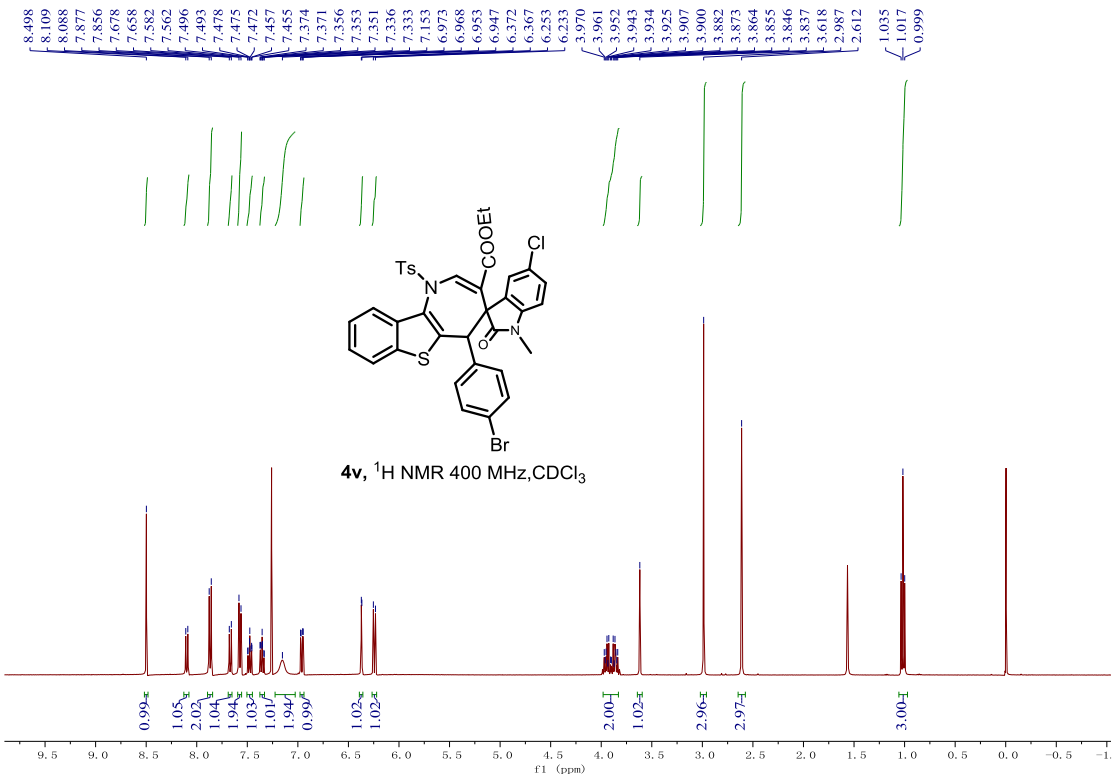



**4u**,$^{1}$H NMR 400 MHz,$CDCl_3$

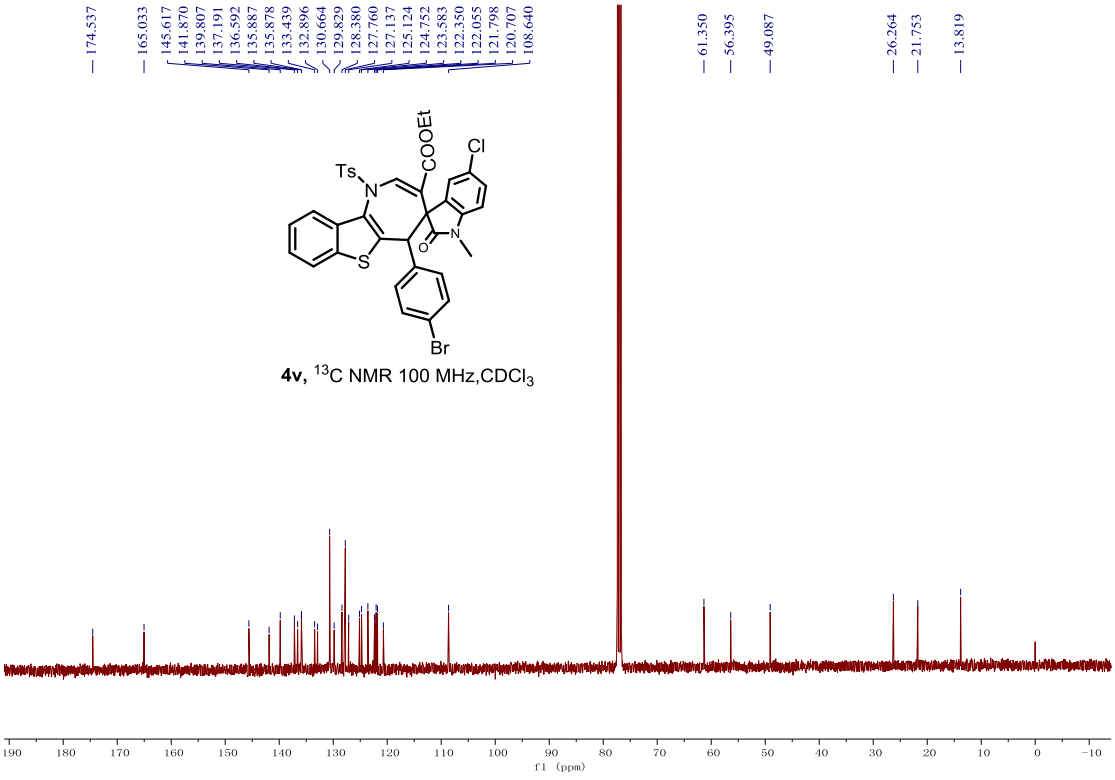


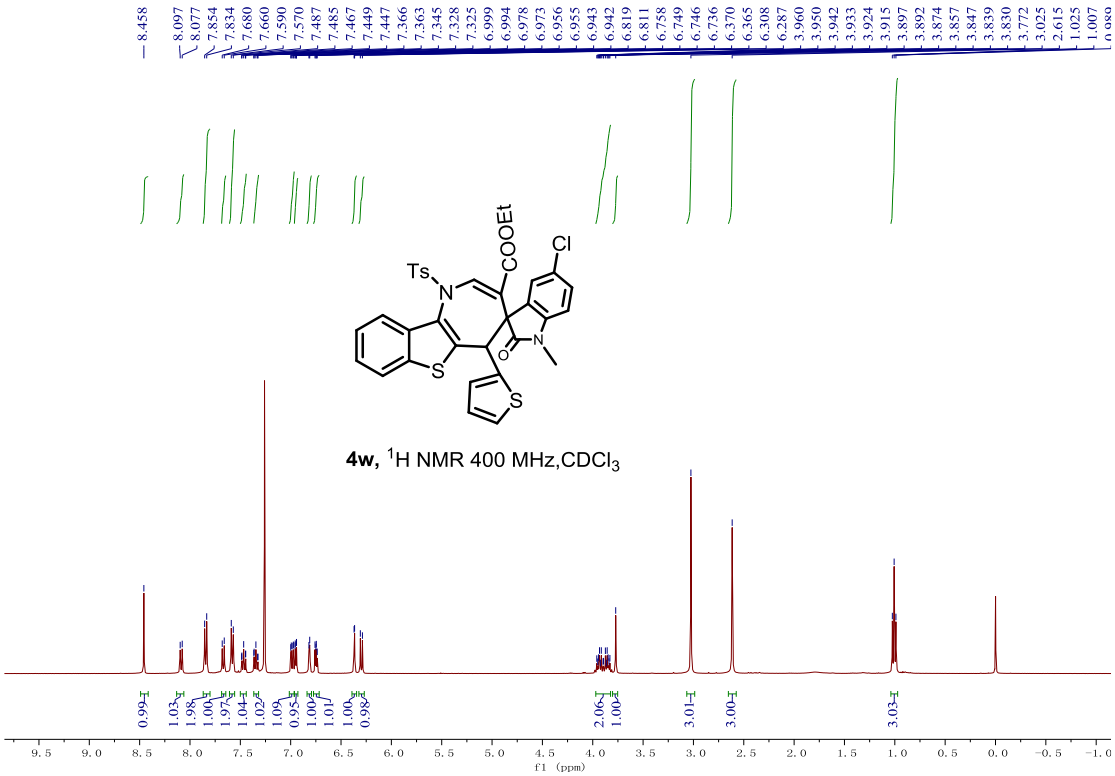

**4u**,$^{13}$C NMR 100 MHz,$CDCl_3$




**4v,** $^{1}$H NMR 400 MHz,$CDCl_3$




**4v,** $^{13}$C NMR 100 MHz,$CDCl_3$



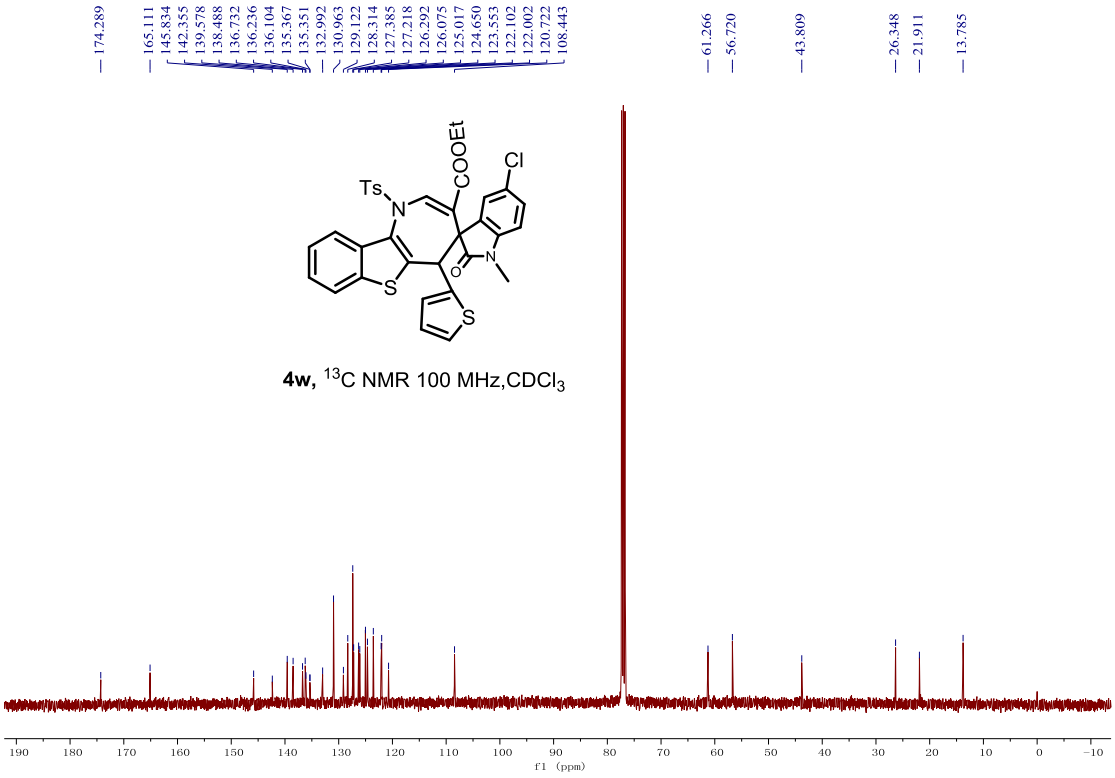

**4w,** $^{1}$H NMR 400 MHz,$CDCl_3$

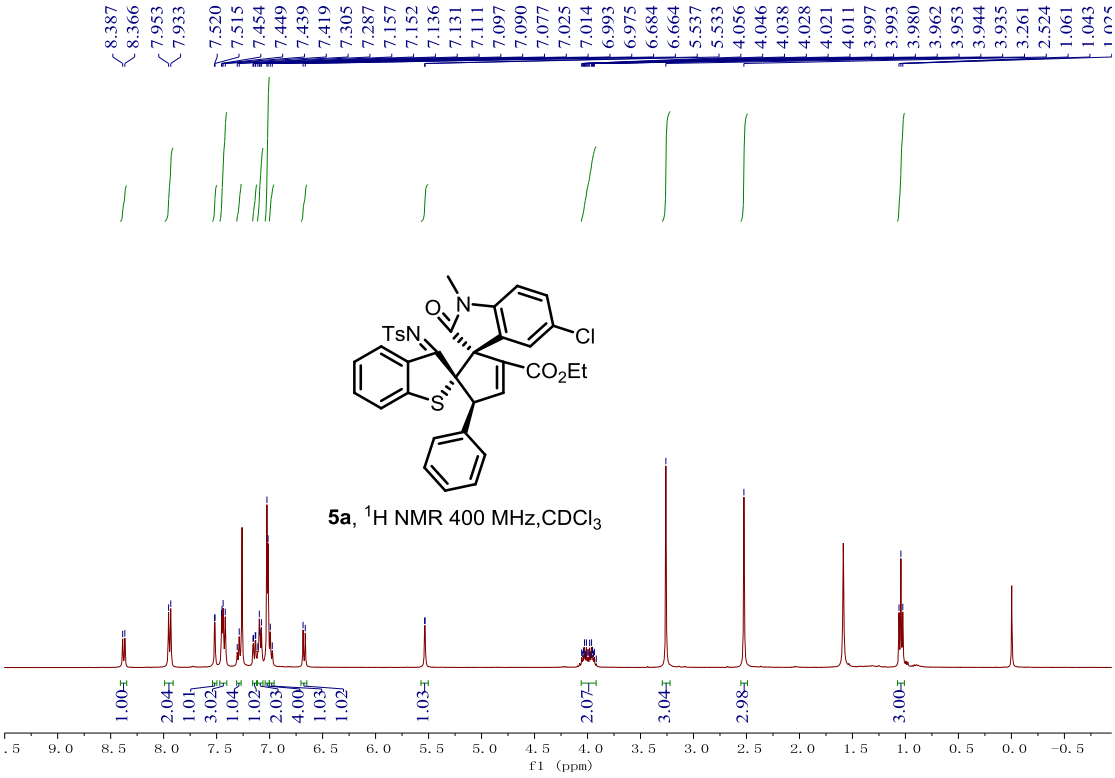




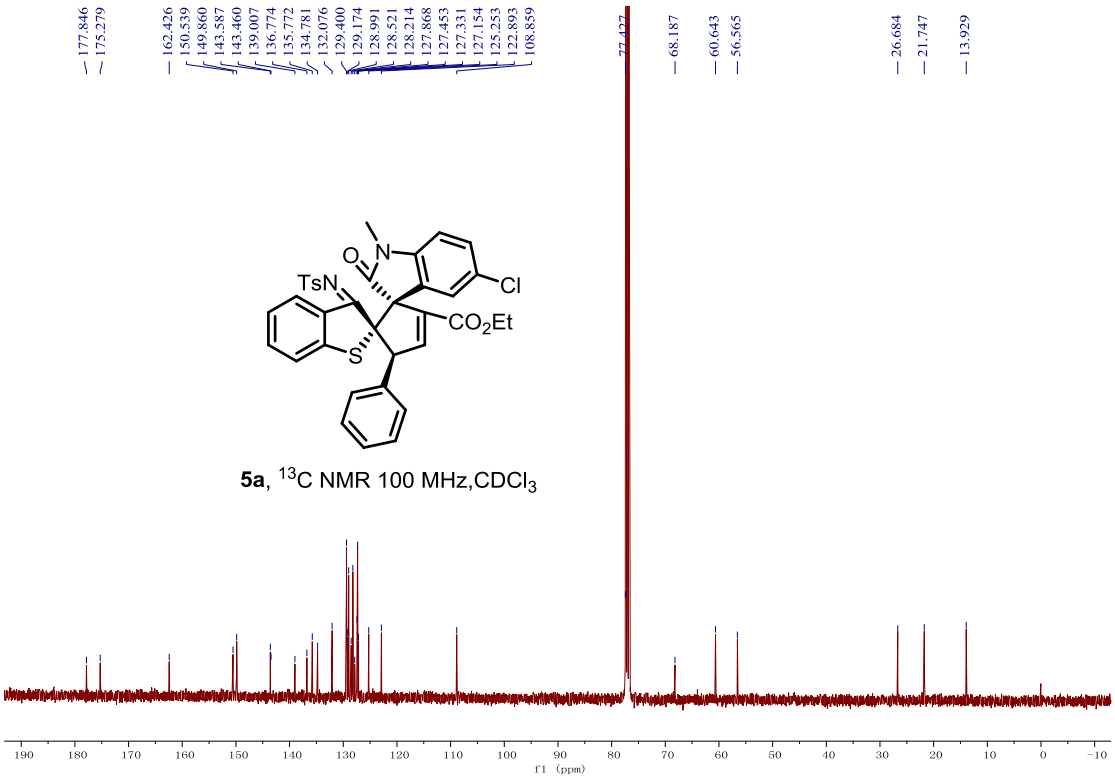


**4w,** $^{13}$C NMR 100 MHz,$CDCl_3$

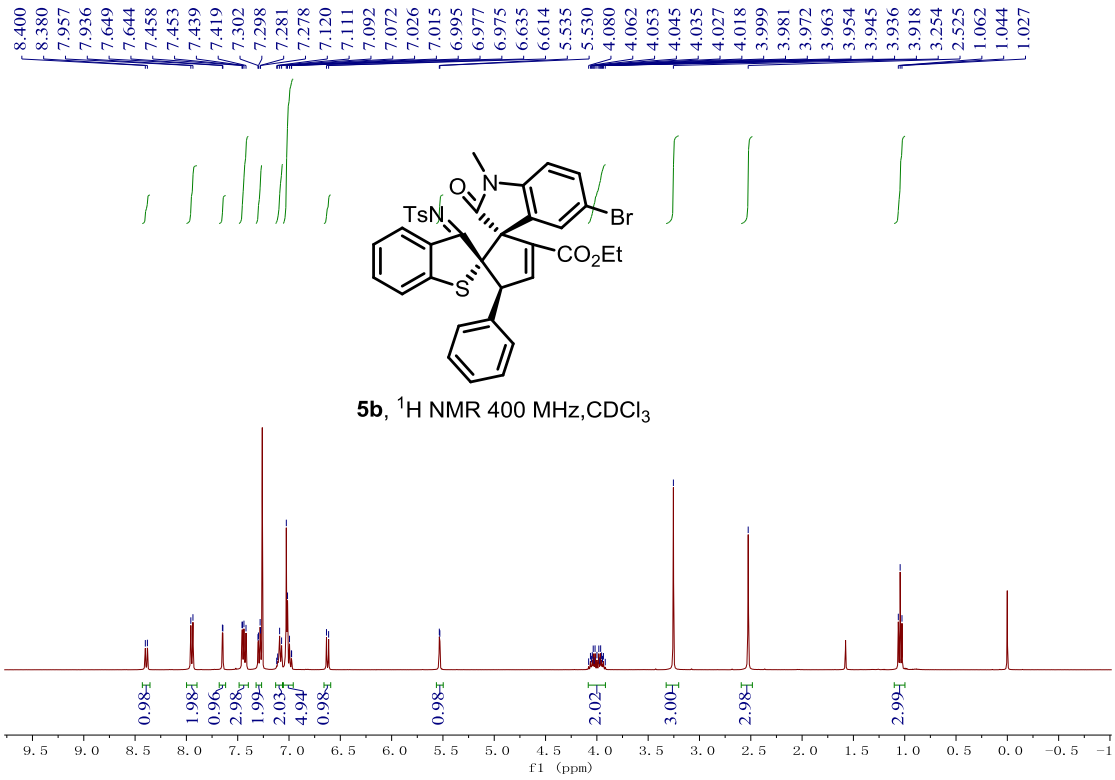




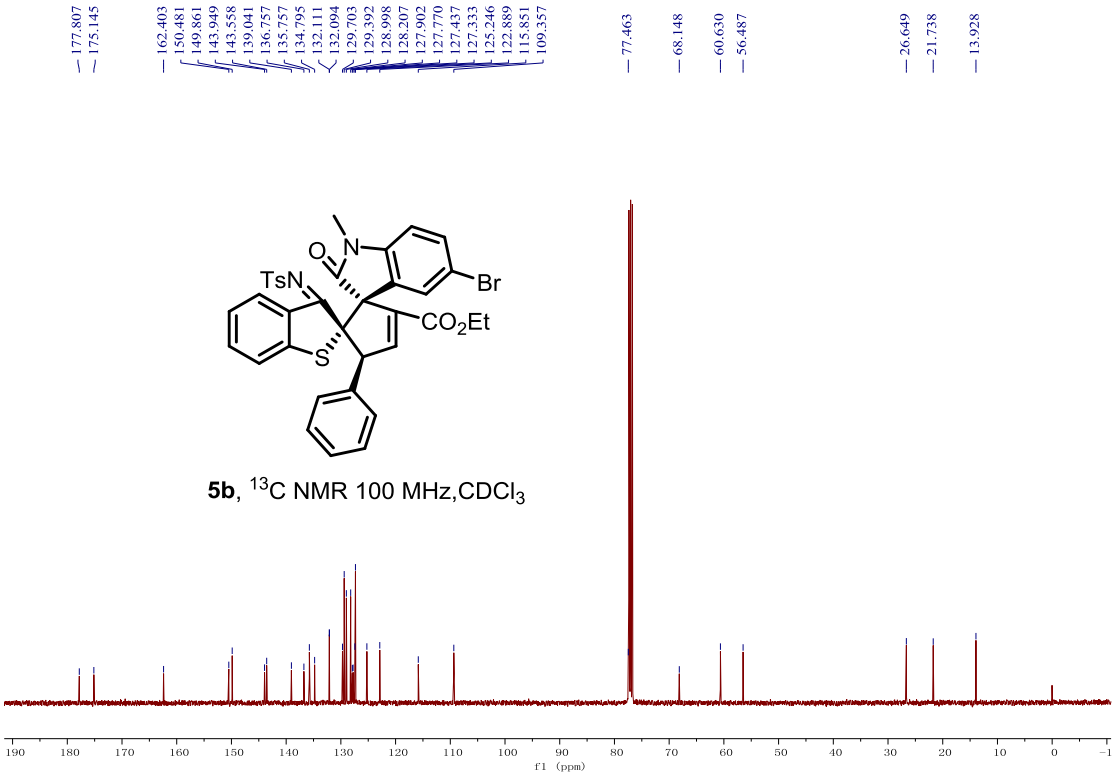

**5a**, $^{1}$H NMR 400 MHz,$CDCl_3$



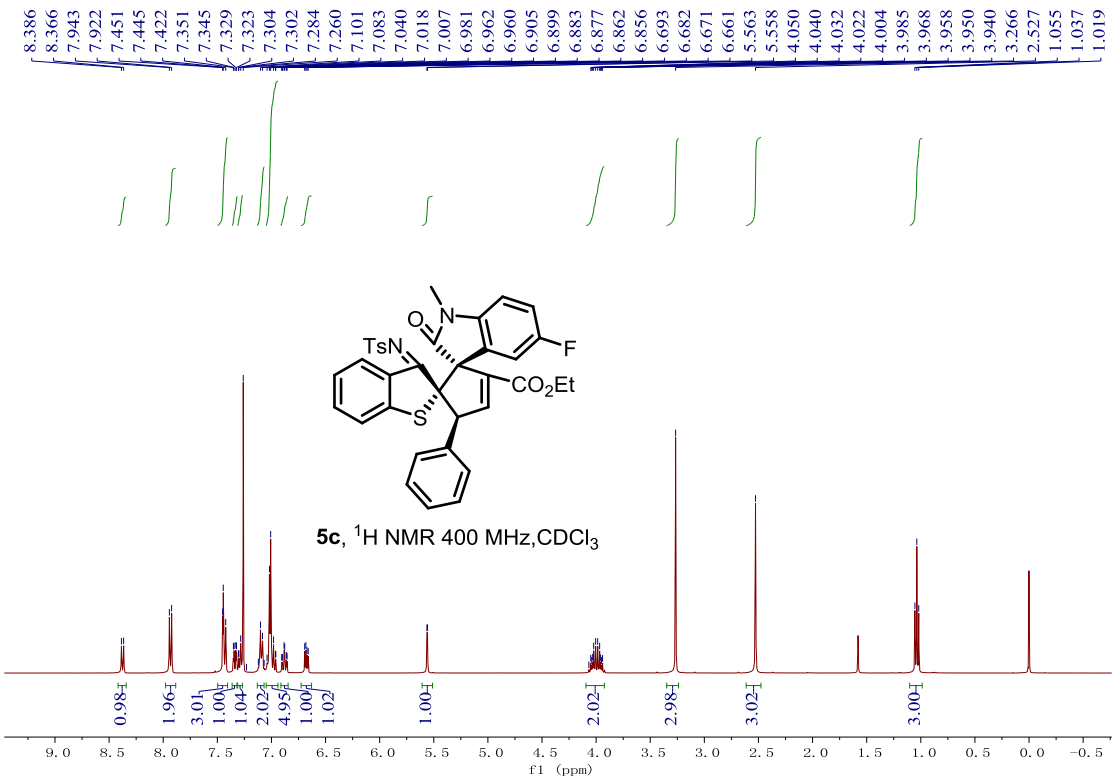

**5a**, $^{13}$C NMR 100 MHz,$CDCl_3$

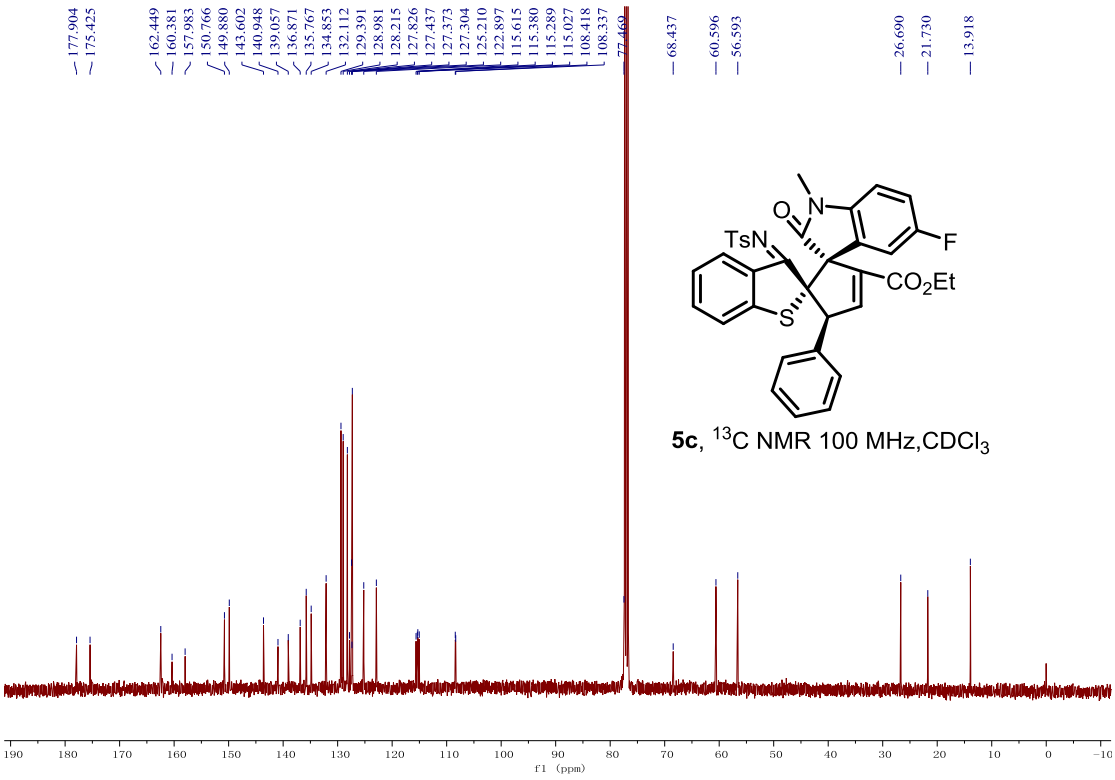


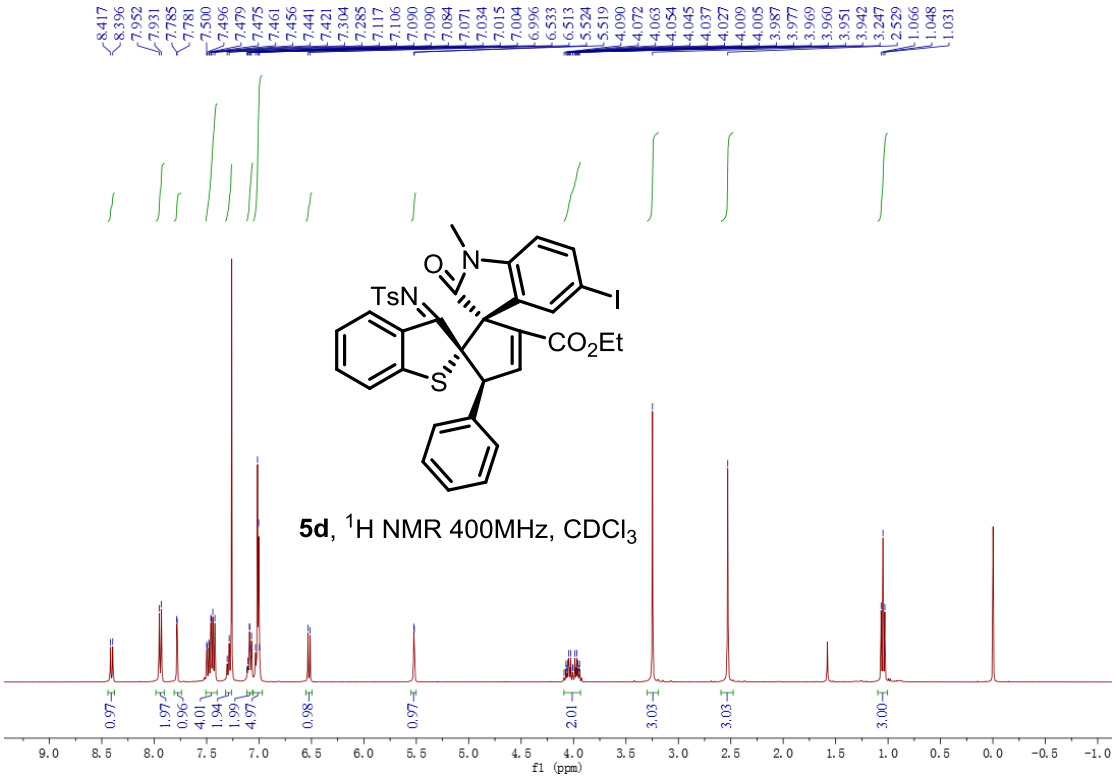

**5b**, $^{1}$H NMR 400 MHz,$CDCl_3$



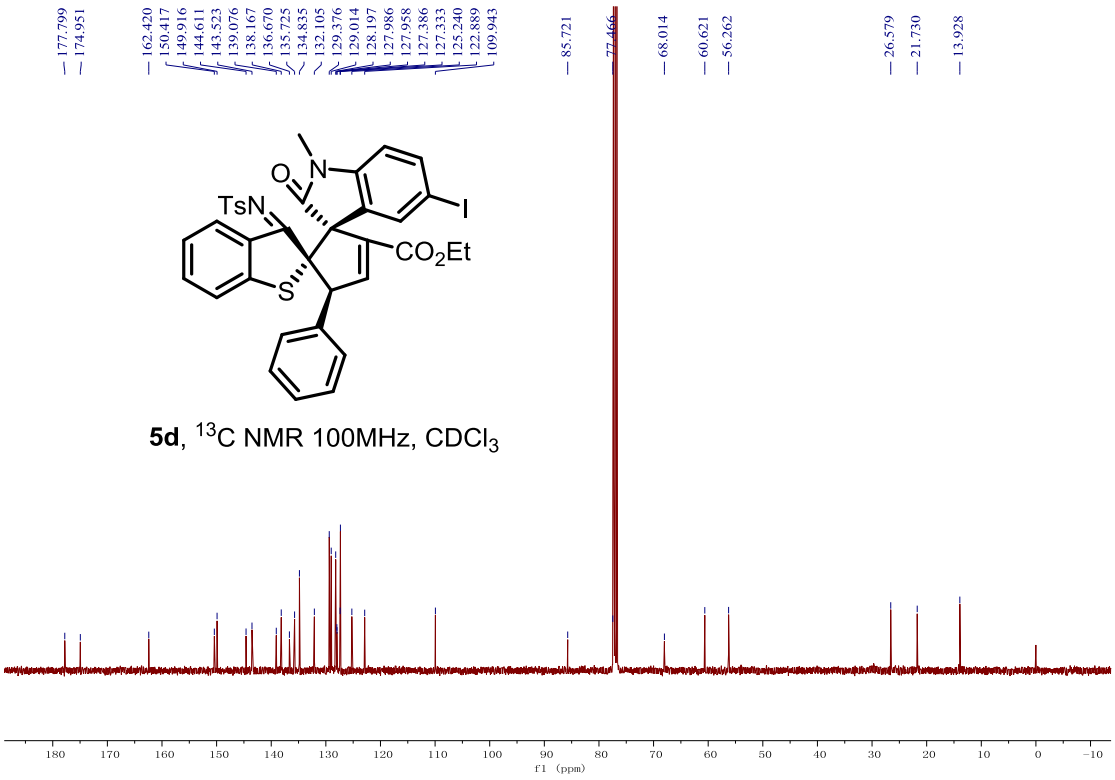

**5b**, $^{13}$C NMR 100 MHz,$CDCl_3$


8.386
8.366
7.943
7.922
7.451
7.445
7.422
7.351
7.345
7.329
7.323
7.304
7.302
7.284
7.260
7.101
7.083
7.040
7.018
7.007
6.981
6.962
6.960
6.905
6.899
6.883
6.877
6.862
6.856
6.693
6.682
6.671
6.661
5.563
5.558
4.050
4.040
4.032
4.022
4.004
3.985
3.968
3.958
3.950
3.940
3.266
2.527
1.055
1.037
1.019
TsN
O
N
F
CO2Et
S
5c, 1H NMR 400 MHz,CDCl3
0.98
1.96
3.01
1.00
1.04
2.02
4.95
1.00
1.02
1.00
2.02
2.98
3.02
3.00
f1 (ppm)

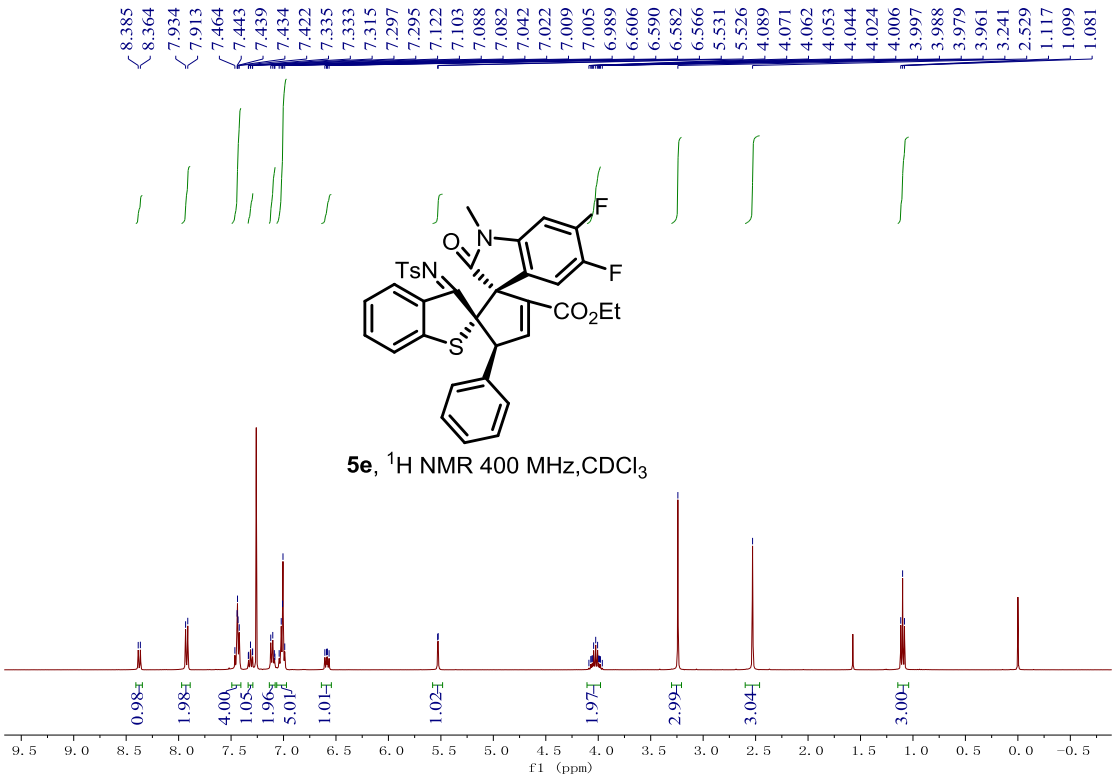

177.904
175.425
162.449
160.381
157.983
150.766
149.880
143.602
140.948
139.057
136.871
135.767
134.853
132.112
129.391
128.981
128.215
127.826
127.437
127.373
127.304
125.210
122.897
115.615
115.380
115.289
115.027
108.418
108.337
77.469
68.437
60.596
56.593
26.690
21.730
13.918
TsN
O
N
F
CO2Et
S
5c, 13C NMR 100 MHz,CDCl3
f1 (ppm)



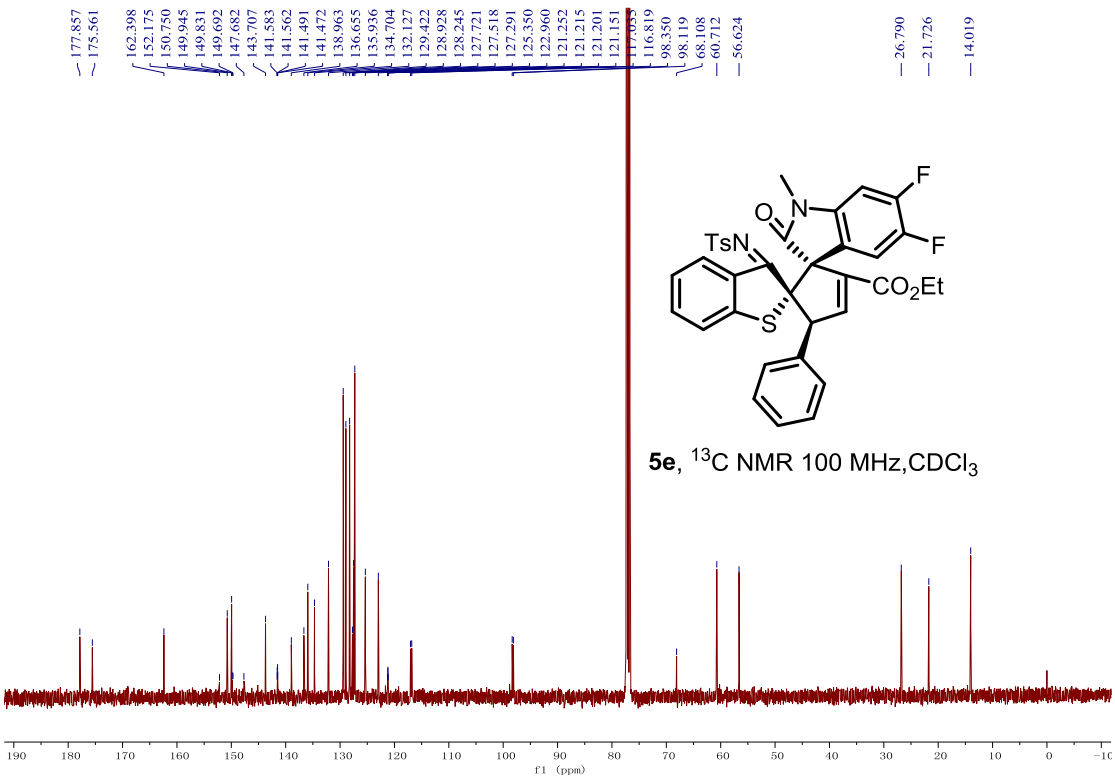

**5d**, $^{1}$H NMR 400MHz, $CDCl_3$



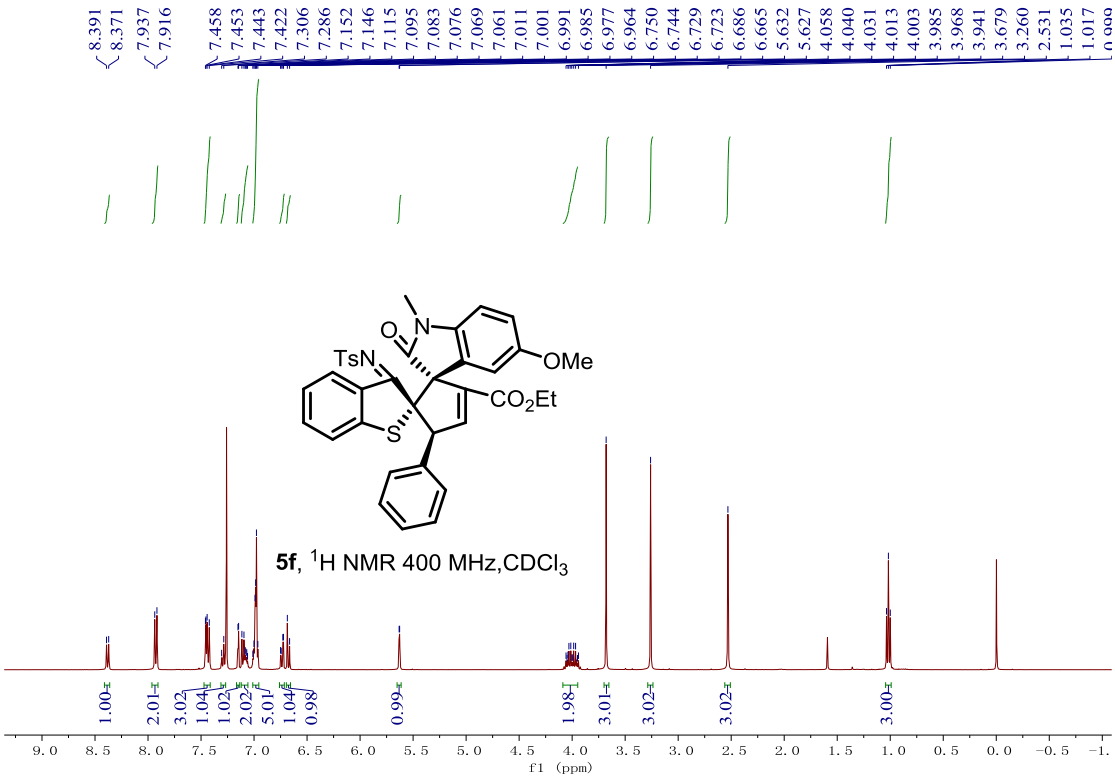

**5d**, $^{13}$C NMR 100MHz, $CDCl_3$

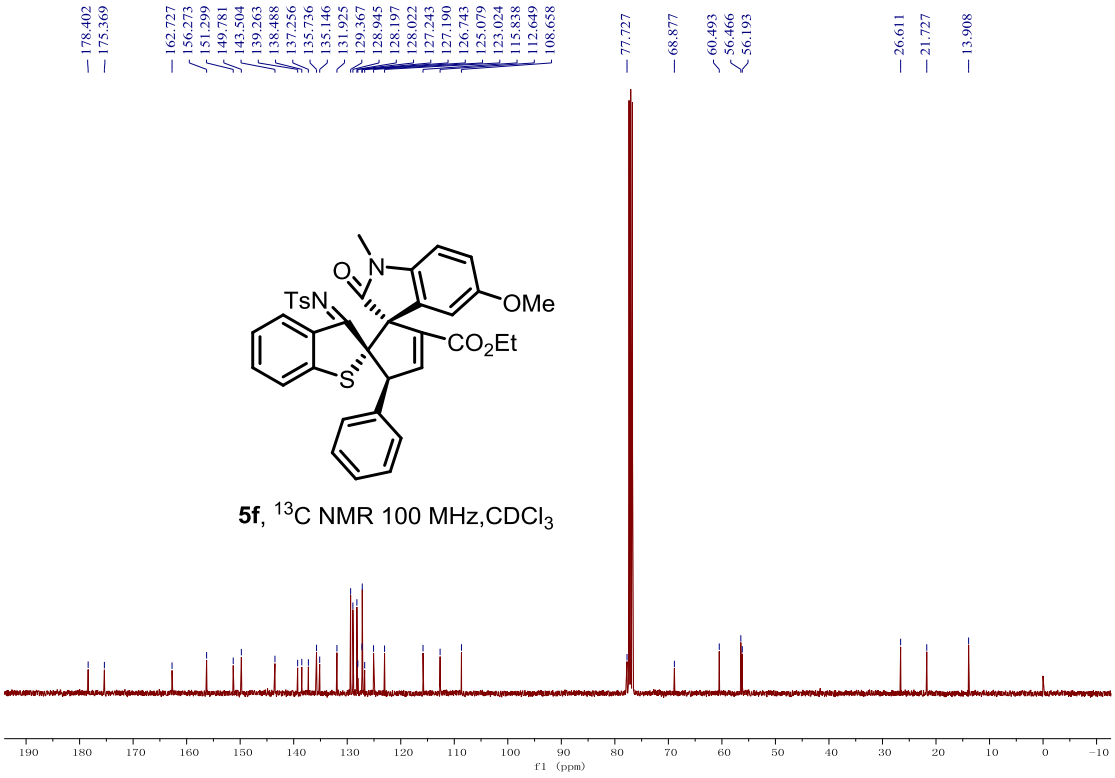


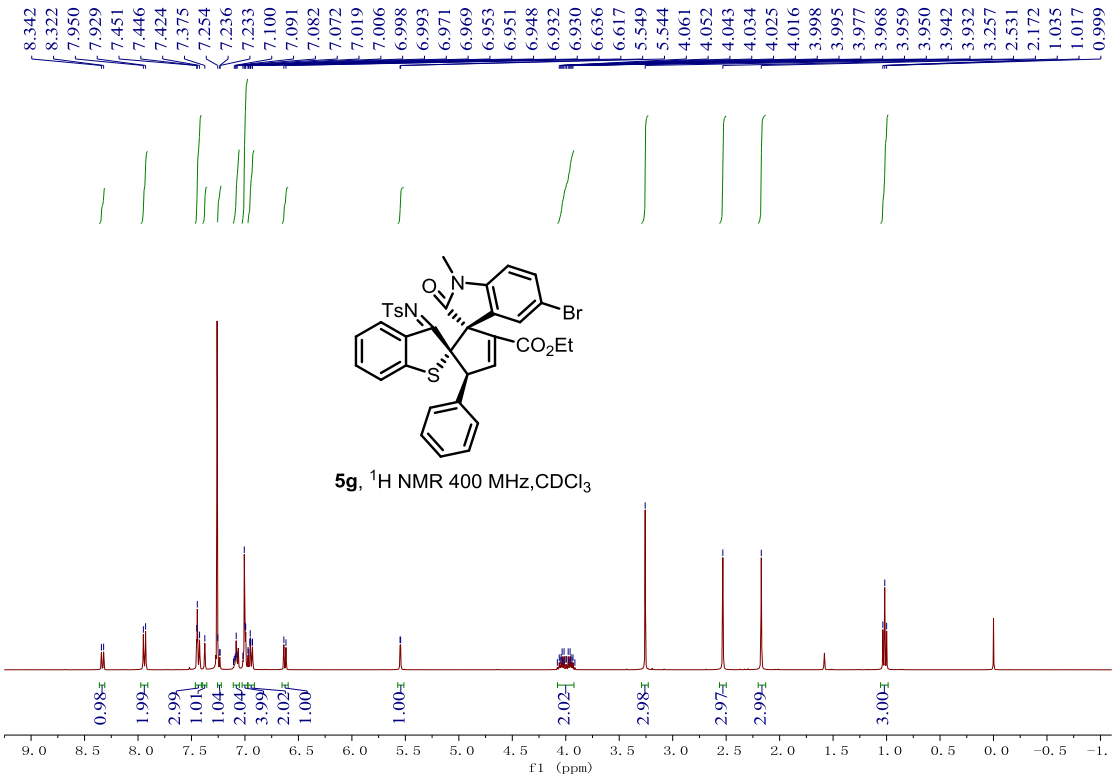

**5e**, $^{1}$H NMR 400 MHz,$CDCl_3$



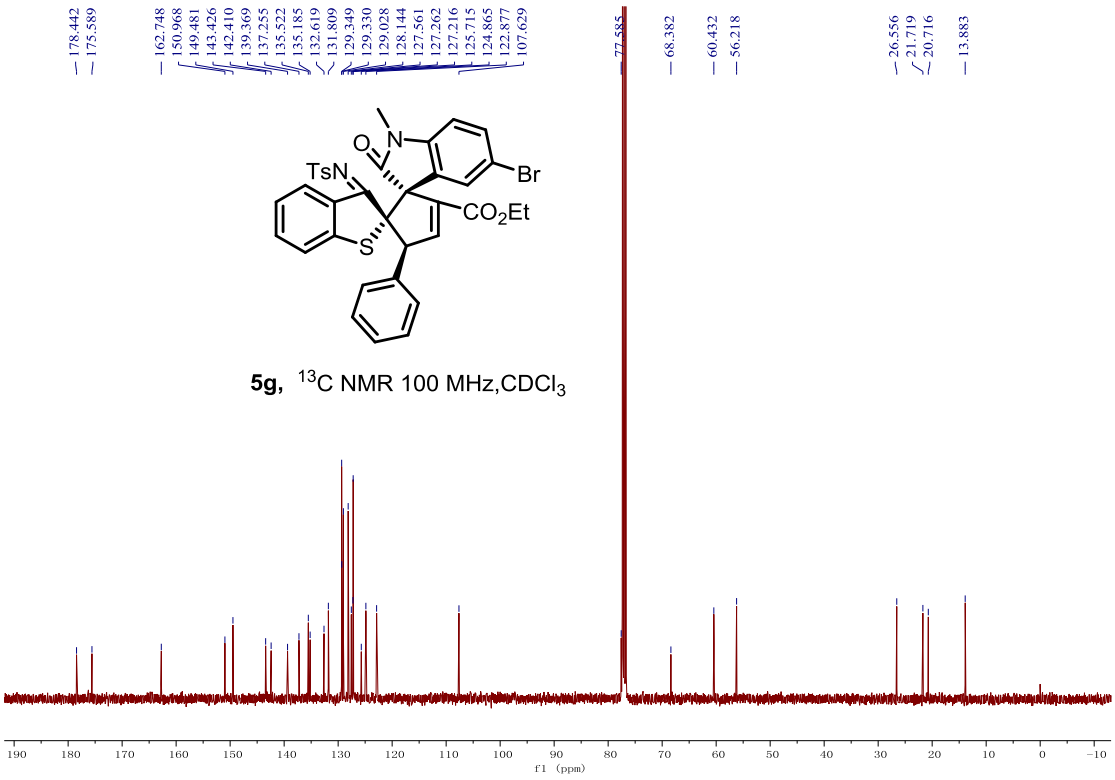

**5e**, $^{13}$C NMR 100 MHz,$CDCl_3$


8.391
8.371
7.937
7.916
7.458
7.453
7.443
7.422
7.306
7.286
7.152
7.146
7.115
7.095
7.083
7.076
7.069
7.061
7.011
7.001
6.991
6.985
6.977
6.964
6.750
6.744
6.729
6.723
6.686
6.665
5.632
5.627
4.058
4.040
4.031
4.013
4.003
3.985
3.968
3.941
3.679
3.260
2.531
1.035
1.017
TsN
O
N
OMe
CO2Et
S
5f, 1H NMR 400 MHz,CDCl3
1.00
2.01
3.02
1.04
1.02
2.02
5.01
1.04
0.98
0.99
1.98
3.01
3.02
3.02
3.00
f1 (ppm)

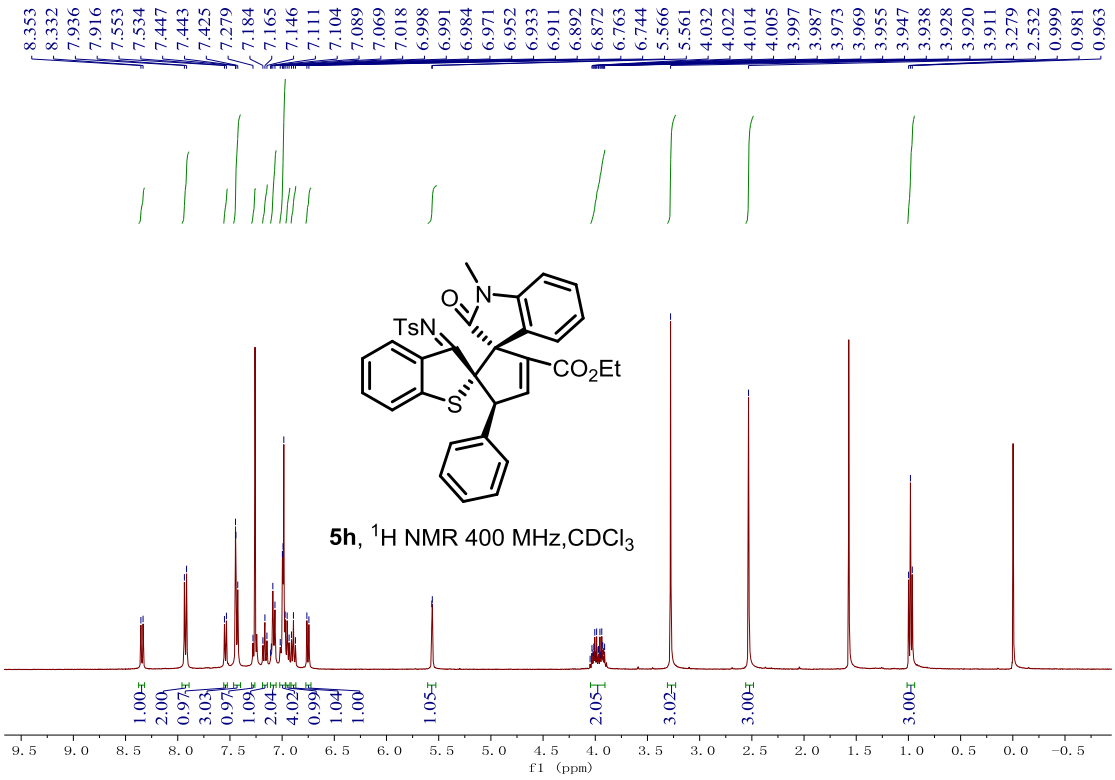

178.402
175.369
162.727
156.273
151.299
149.781
143.504
139.263
138.488
137.256
135.736
135.146
131.925
129.367
128.945
128.197
128.022
127.243
127.190
126.743
125.079
123.024
115.838
112.649
108.658
77.727
68.877
60.493
56.466
56.193
26.611
21.727
13.908
TsN
O
N
OMe
CO2Et
S
5f, 13C NMR 100 MHz,CDCl3
f1 (ppm)



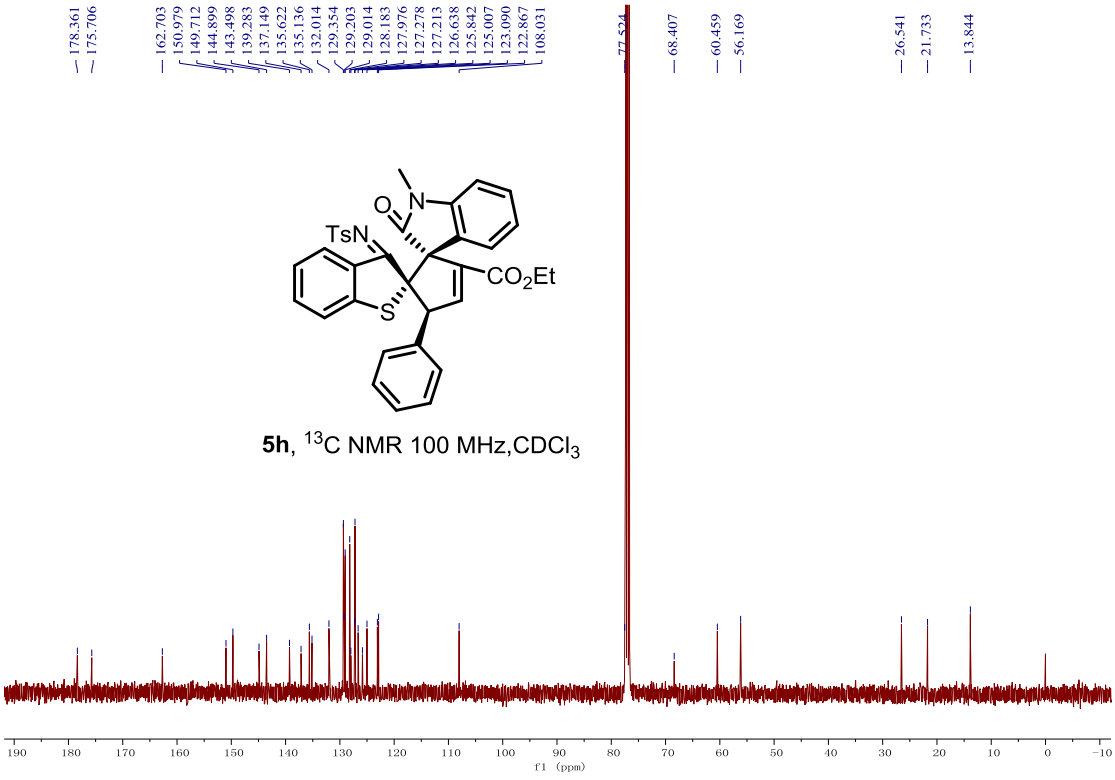

**5g**, $^{1}$H NMR 400 MHz,$CDCl_3$



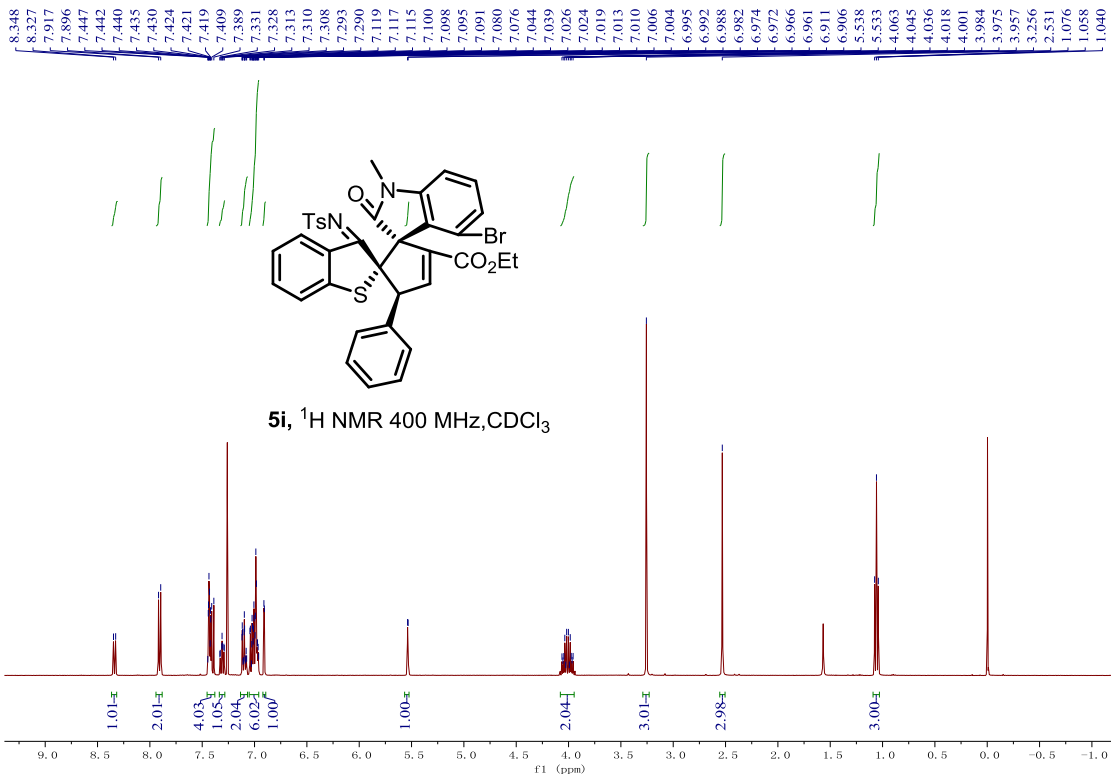

**5g,** $^{13}$C NMR 100 MHz,$CDCl_3$



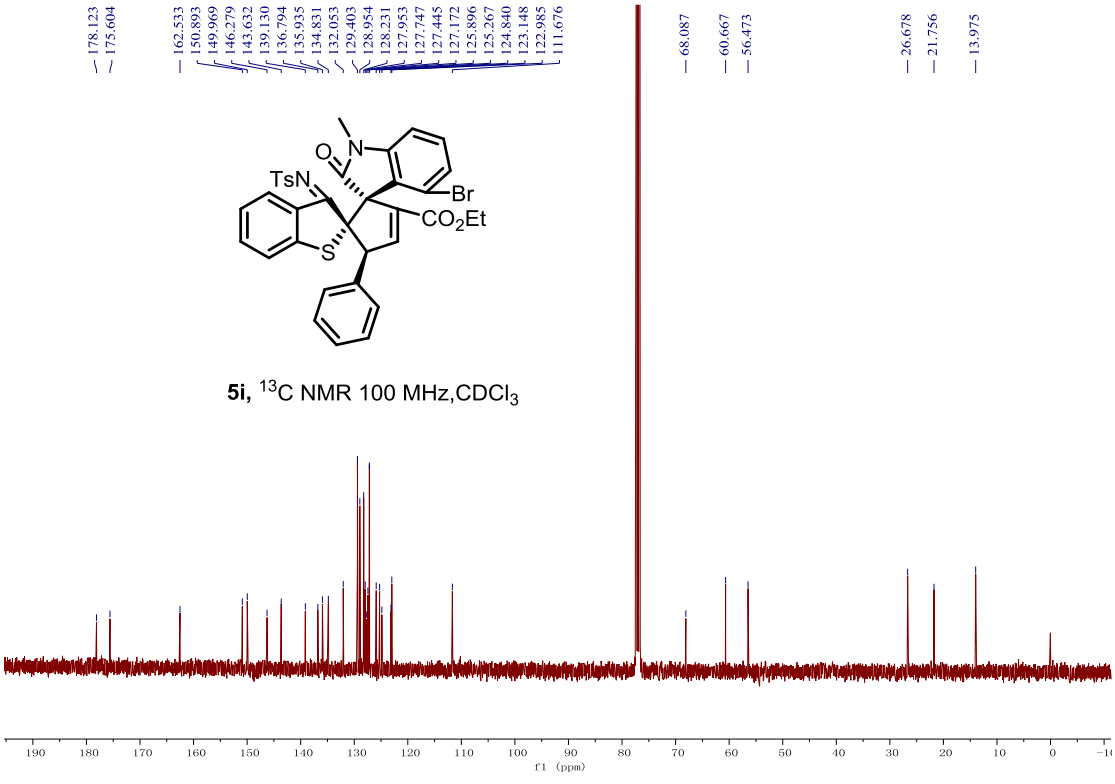

**5h**, $^{1}$H NMR 400 MHz,$CDCl_3$



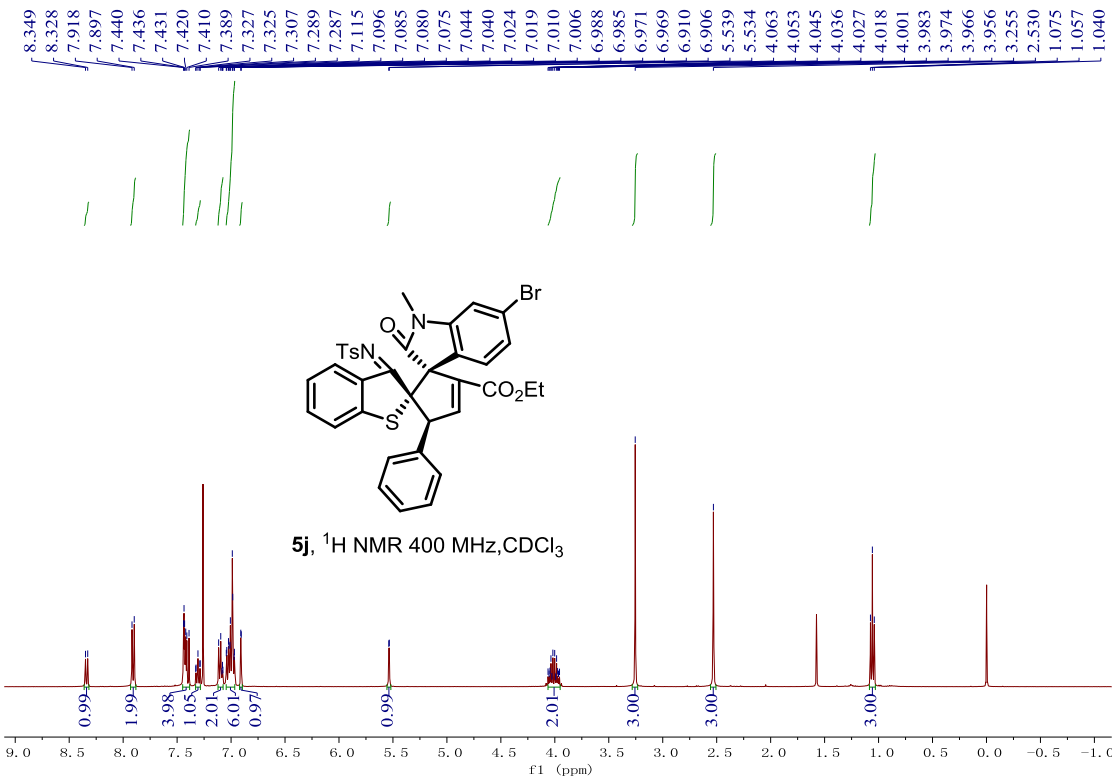

**5h**, $^{13}$C NMR 100 MHz,$CDCl_3$



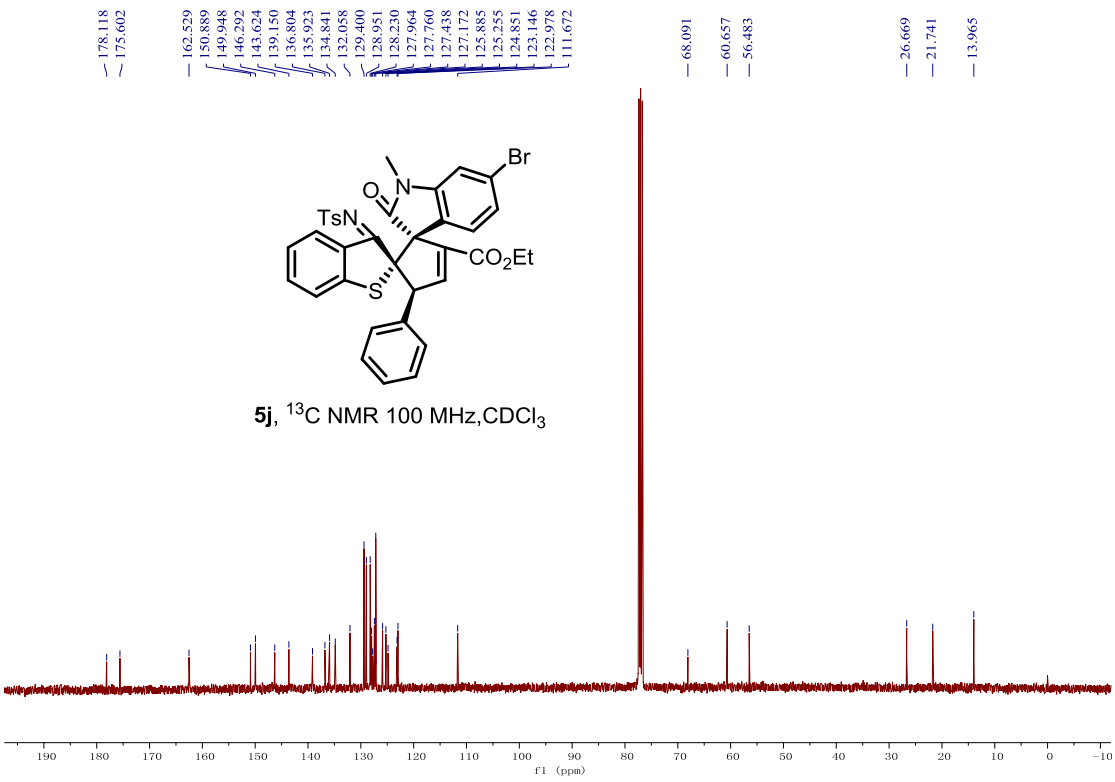

**5i,** $^{1}$H NMR 400 MHz,$CDCl_3$



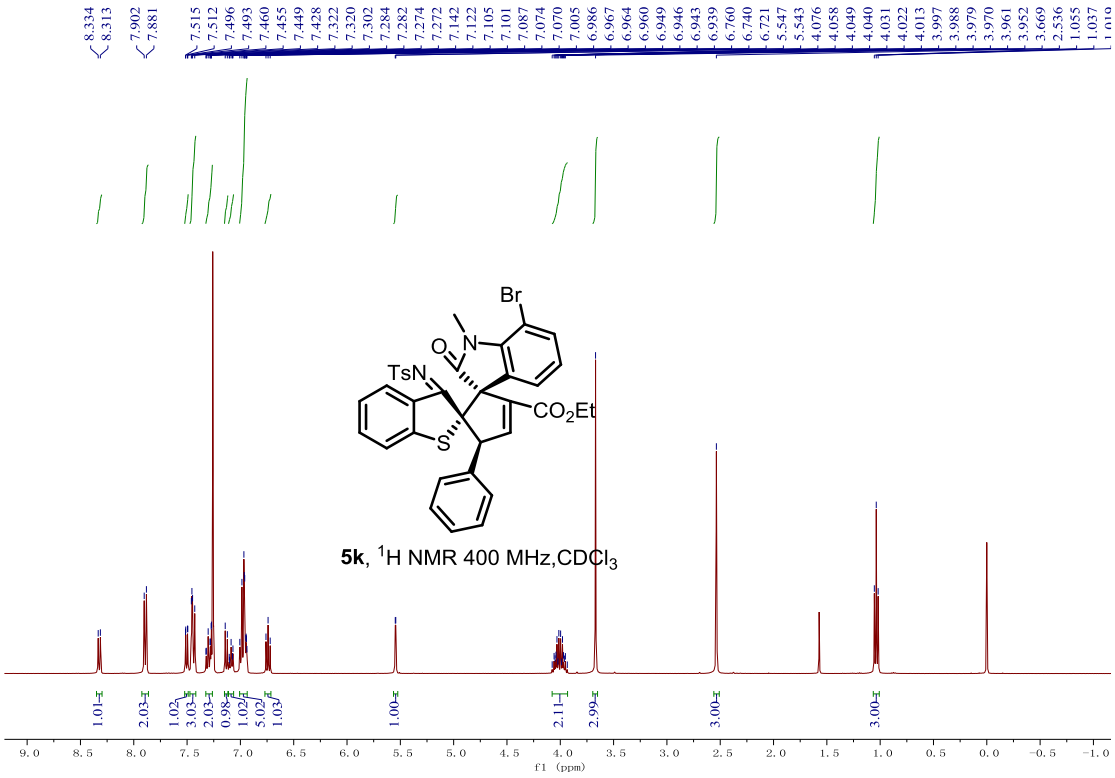

**5i,** $^{13}$C NMR 100 MHz,$CDCl_3$



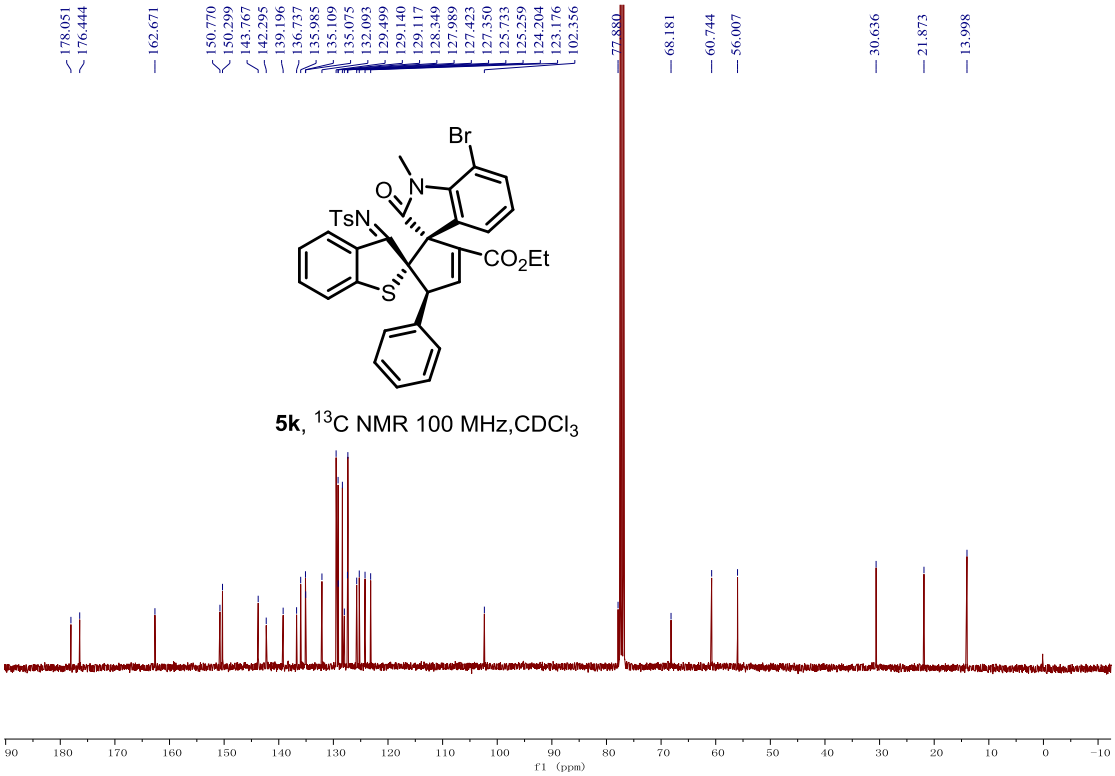

**5j**, $^{1}$H NMR 400 MHz,$CDCl_3$



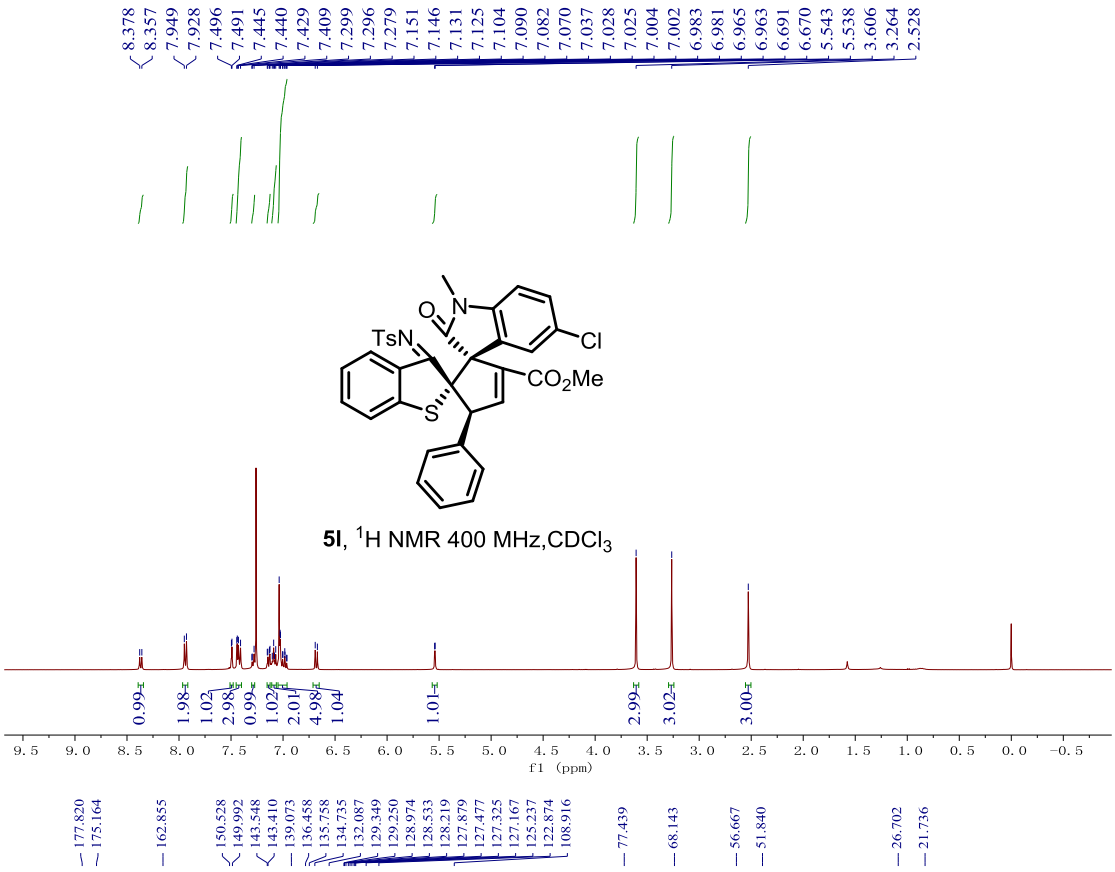

**5j**, $^{13}$C NMR 100 MHz,$CDCl_3$



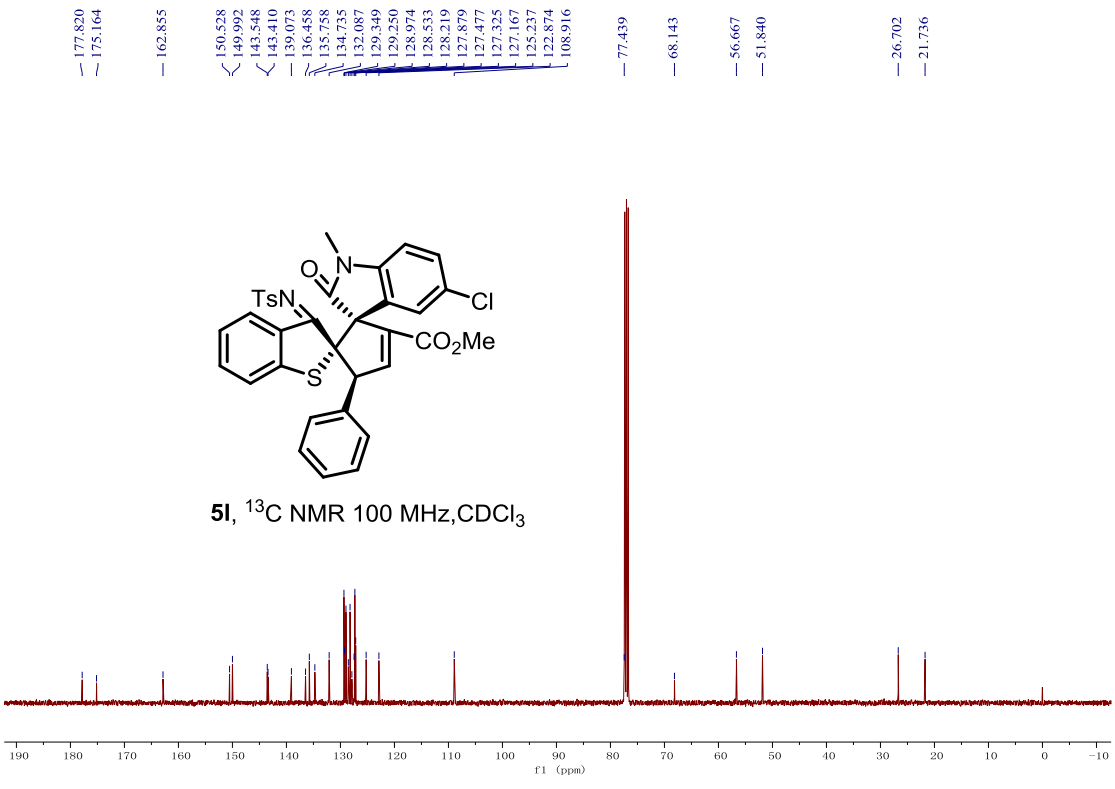

**5k**, $^{1}$H NMR 400 MHz,$CDCl_3$



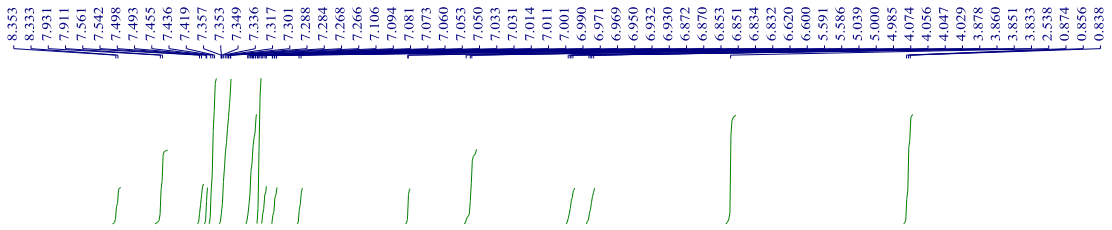

**5k**, $^{13}$C NMR 100 MHz,$CDCl_3$

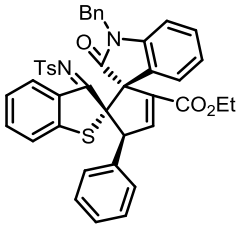



**5l**, $^{1}$H NMR 400 MHz,$CDCl_3$

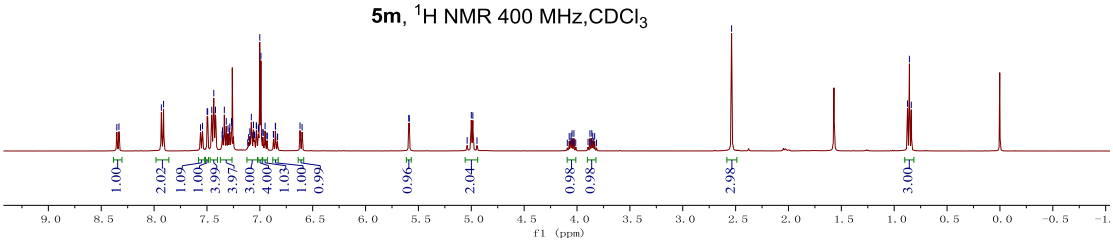


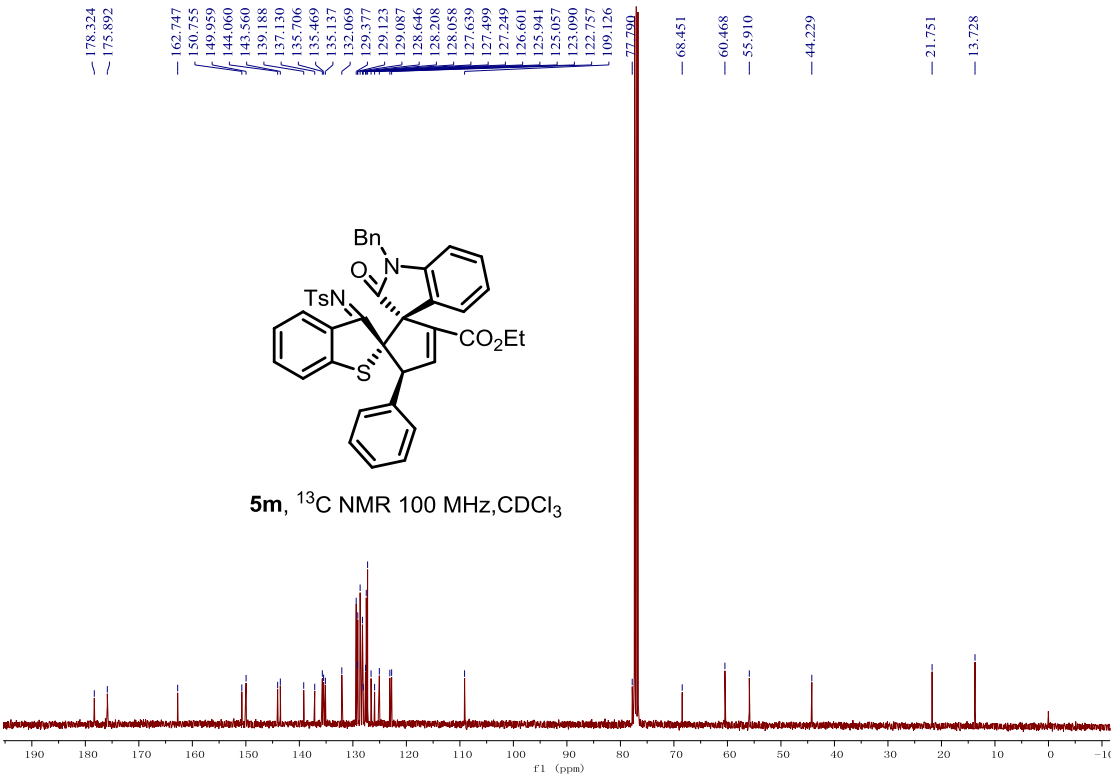

**5l**, $^{13}$C NMR 100 MHz,$CDCl_3$





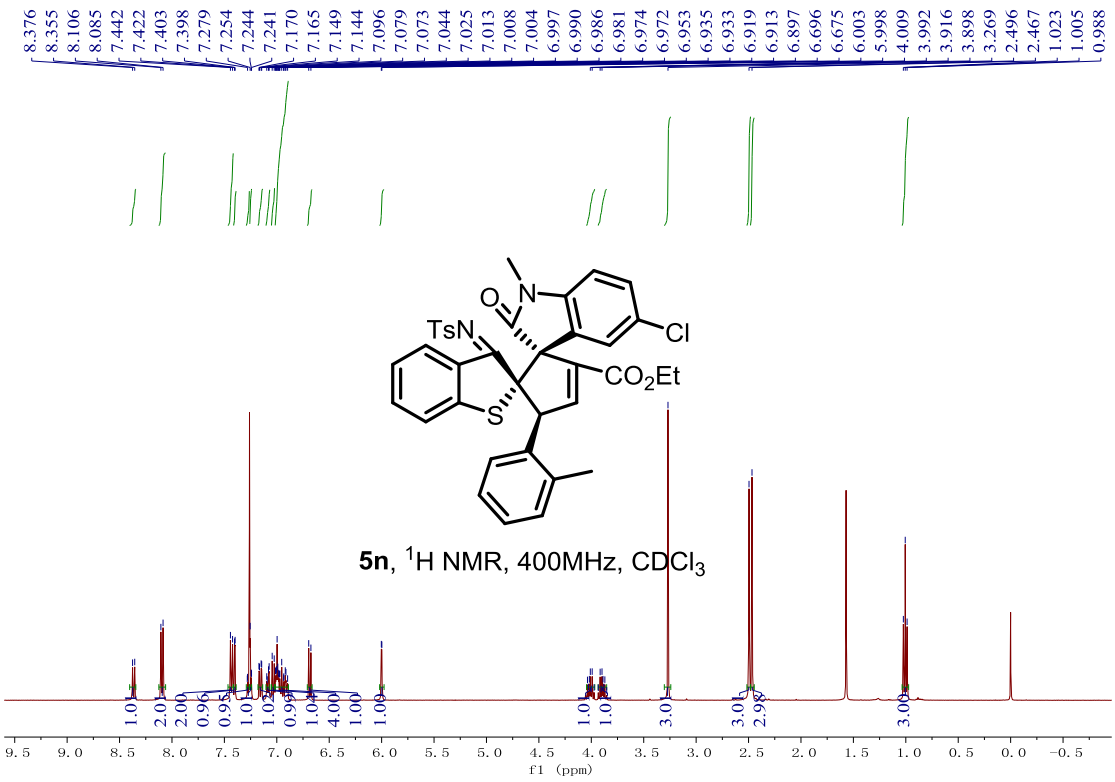

**5m**, $^{1}$H NMR 400 MHz,$CDCl_3$



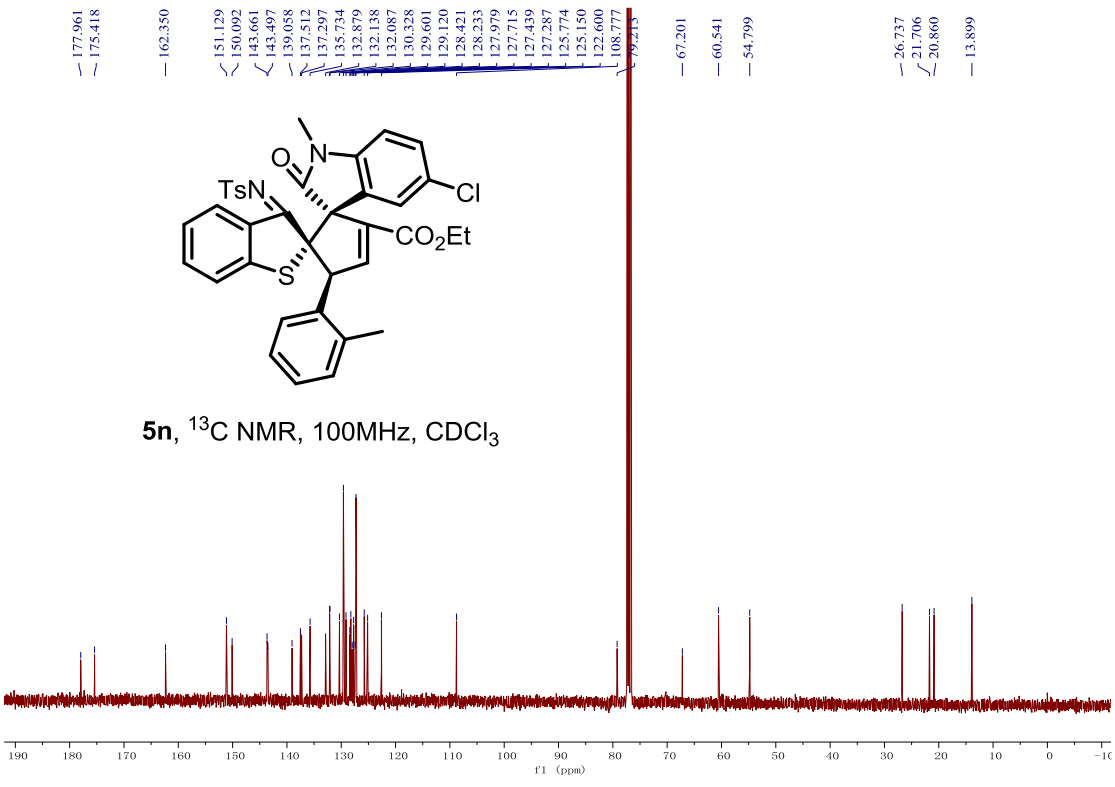




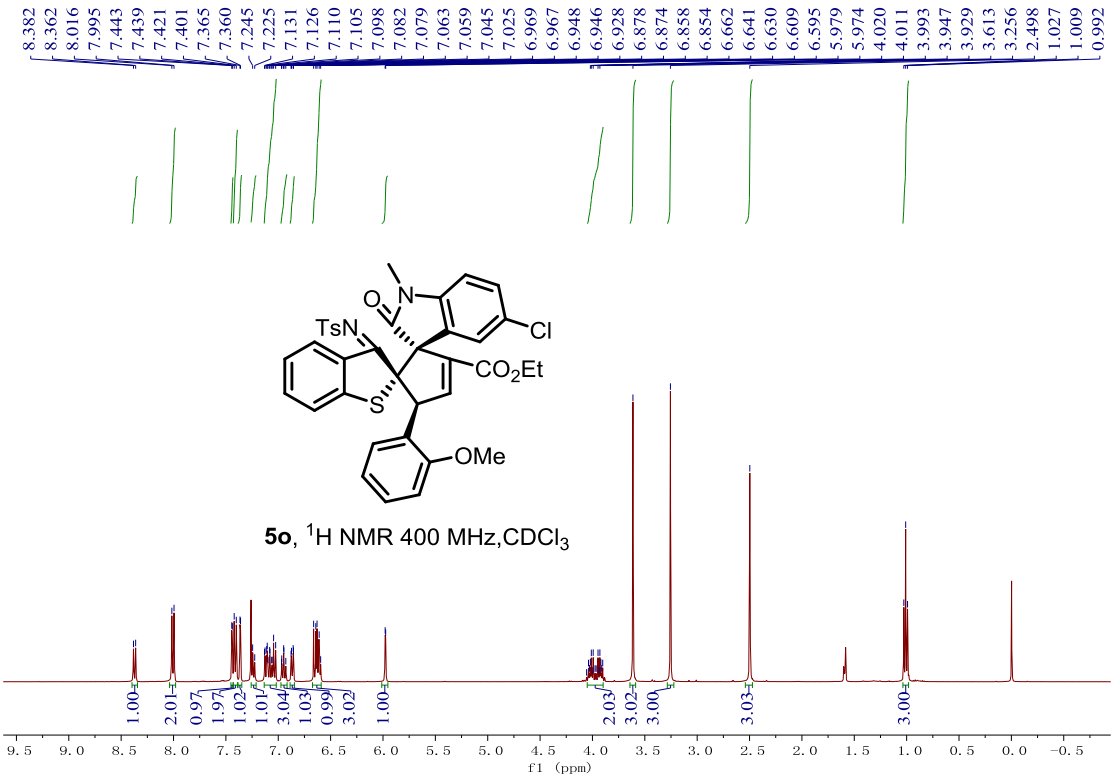

**5m**, $^{13}$C NMR 100 MHz,$CDCl_3$



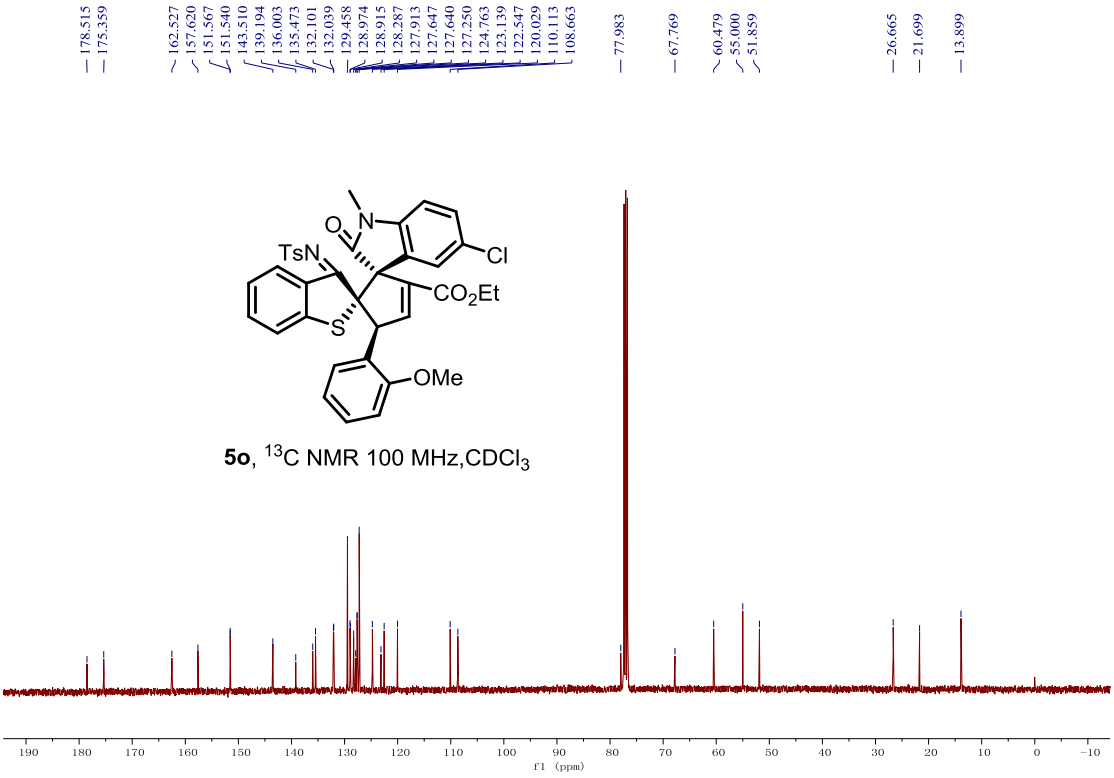

**5n**, $^{1}$H NMR, 400MHz, $CDCl_3$



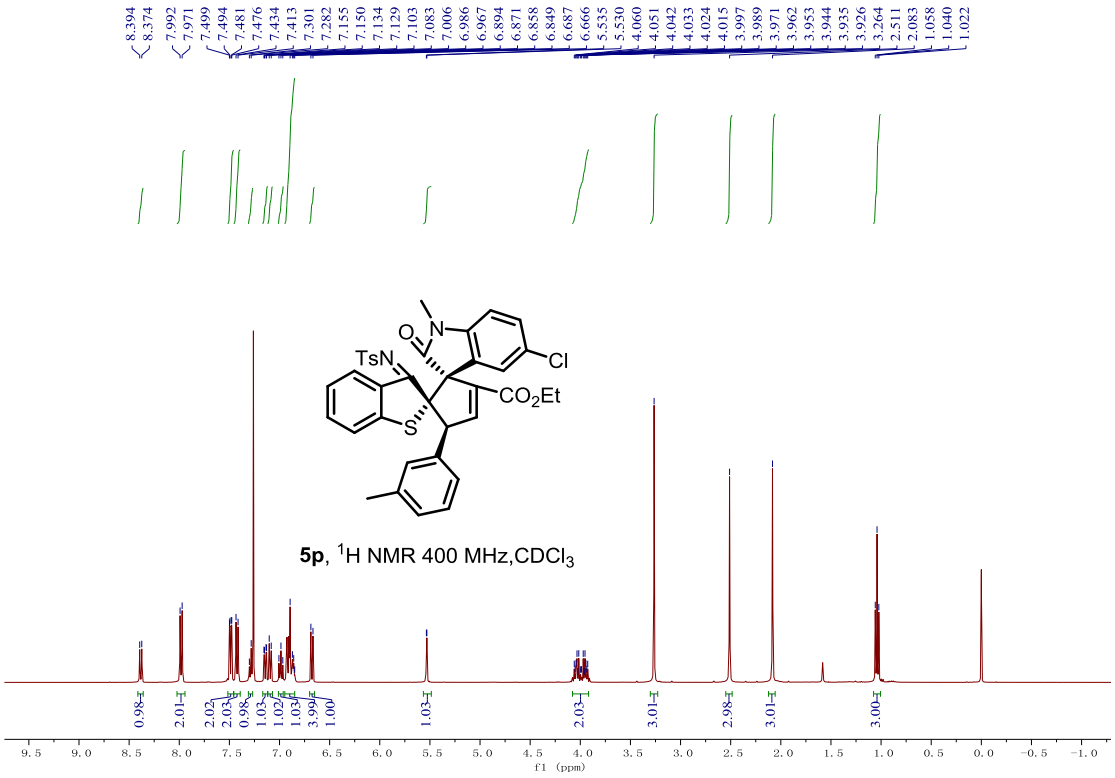

**5n**, $^{13}$C NMR, 100MHz, $CDCl_3$



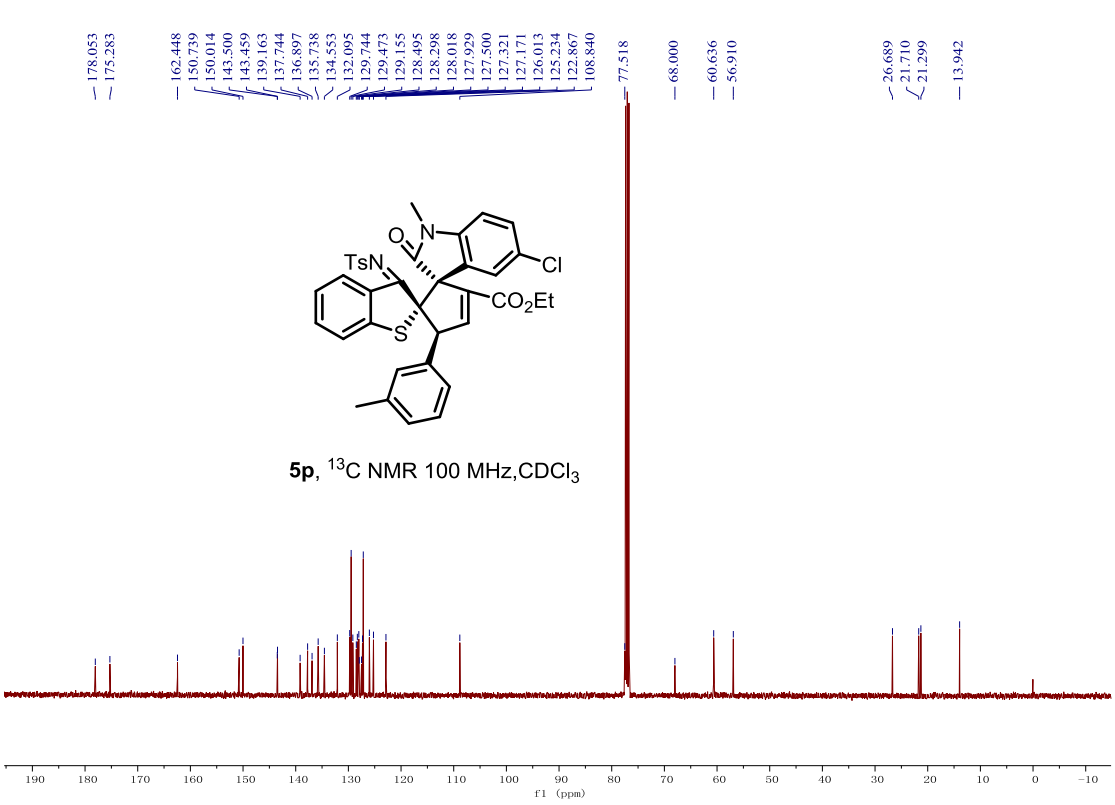

**5o**, $^{1}$H NMR 400 MHz,$CDCl_3$



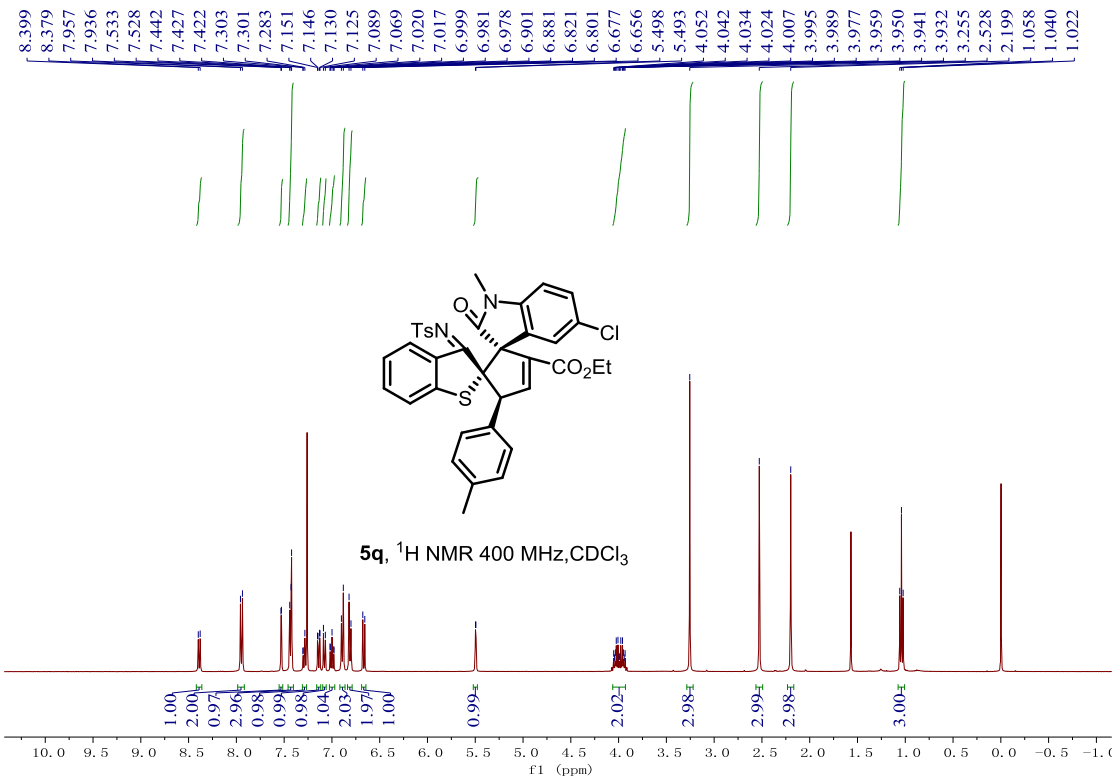

**5o**, $^{13}$C NMR 100 MHz,$CDCl_3$



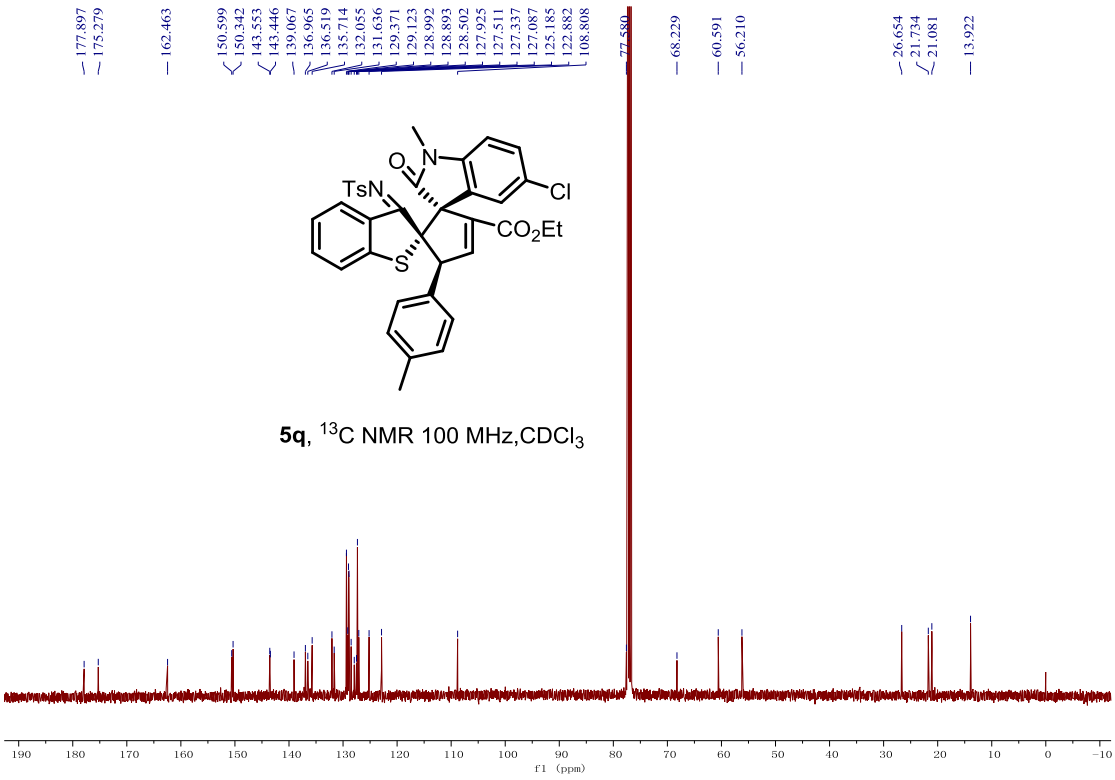

**5p**, $^{1}$H NMR 400 MHz,$CDCl_3$



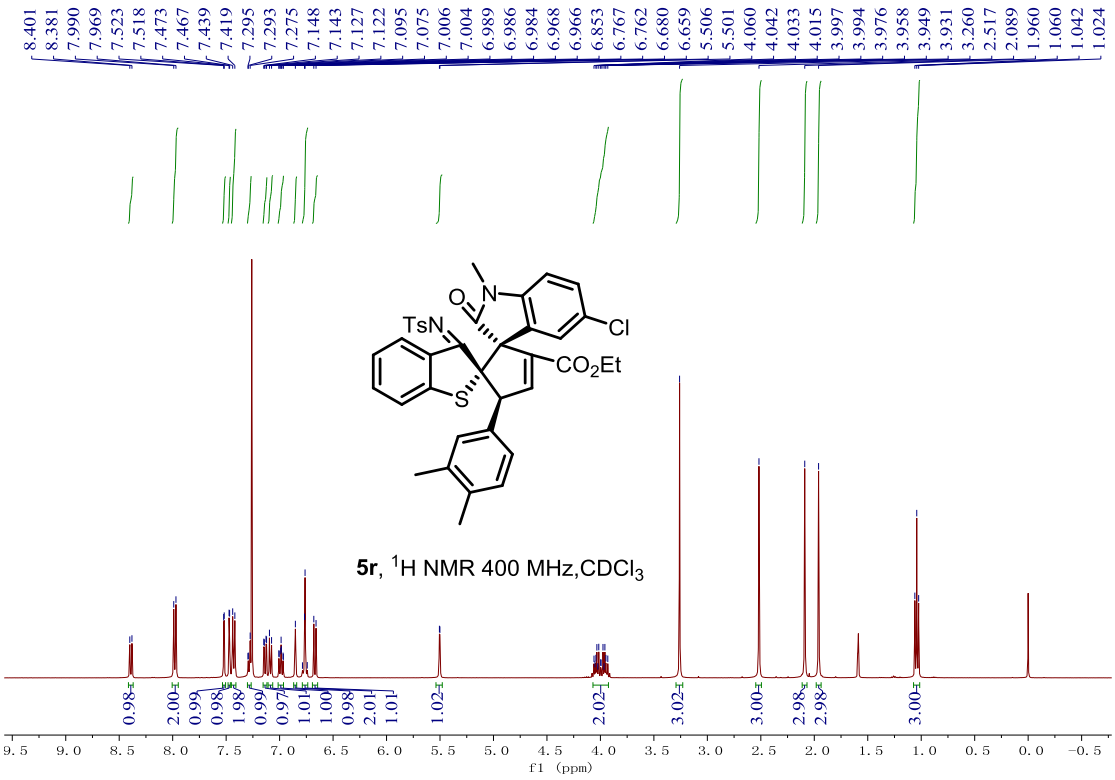

**5p**, $^{13}$C NMR 100 MHz,$CDCl_3$



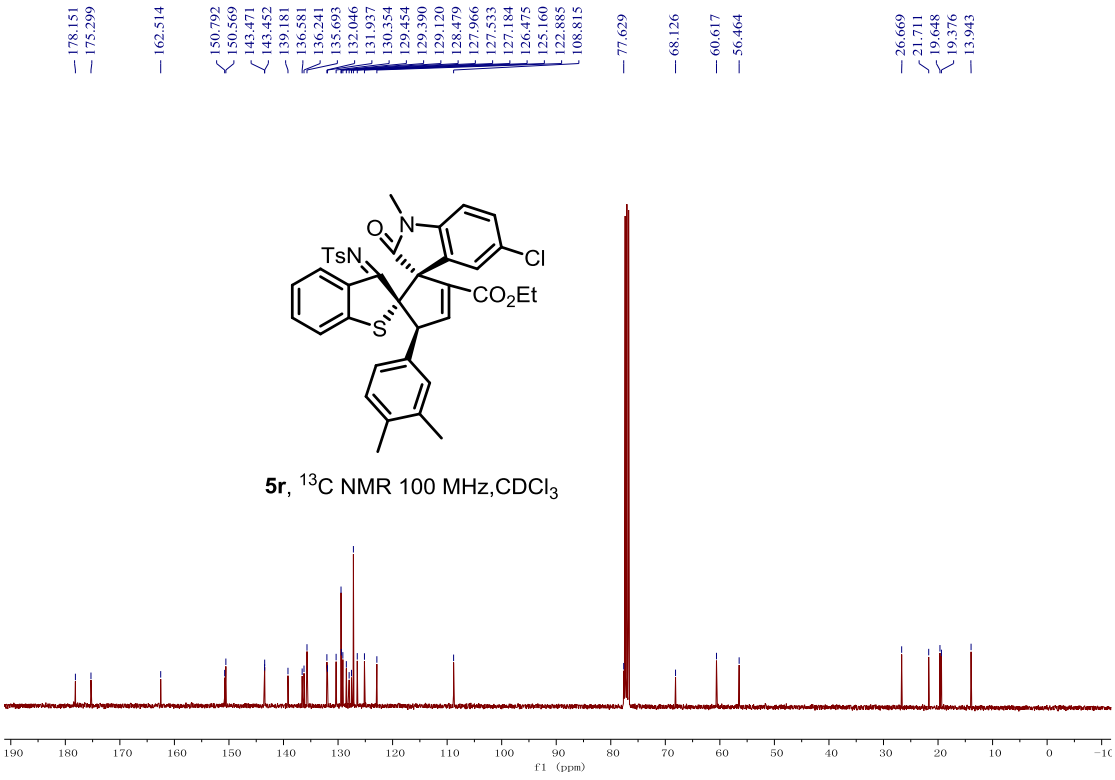

**5q**, $^{1}$H NMR 400 MHz,$CDCl_3$



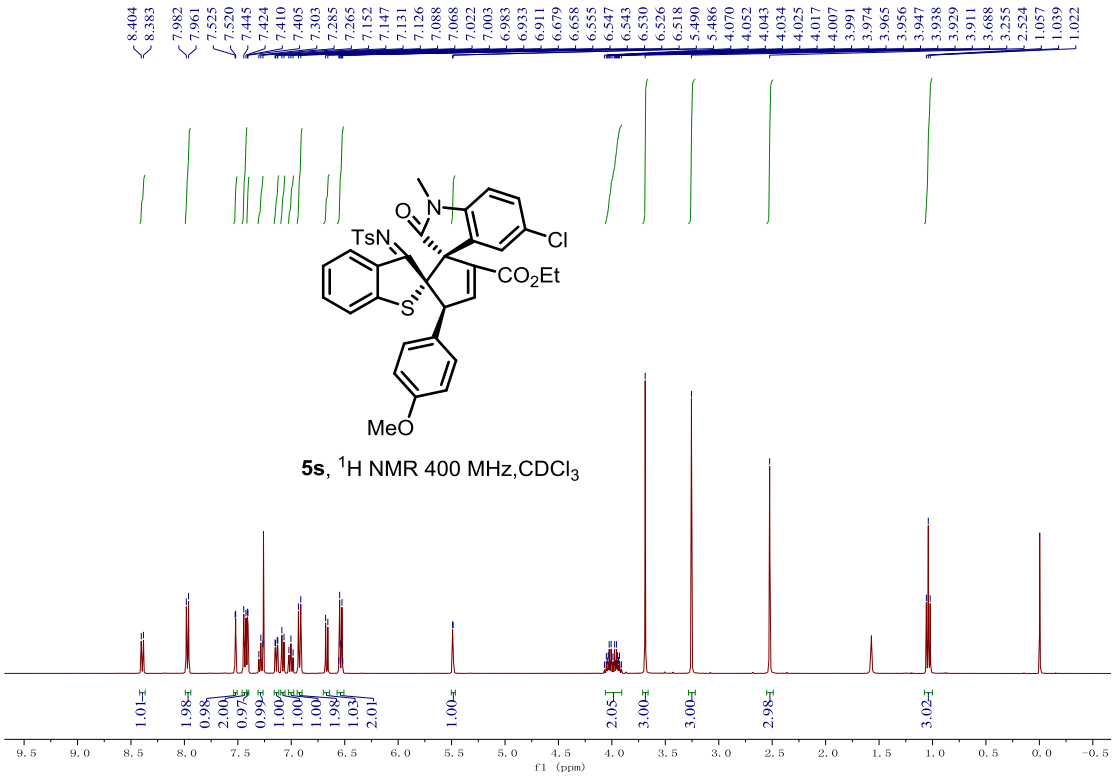

**5q**, $^{13}$C NMR 100 MHz,$CDCl_3$



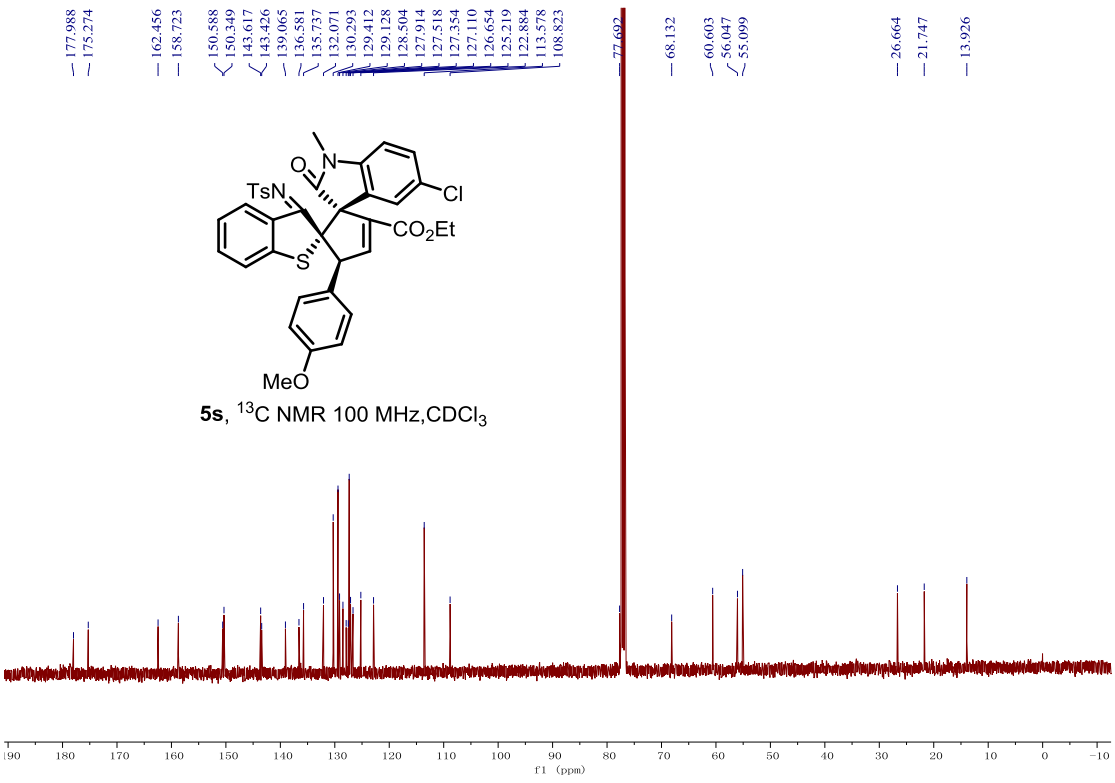

**5r**, $^{1}$H NMR 400 MHz,$CDCl_3$



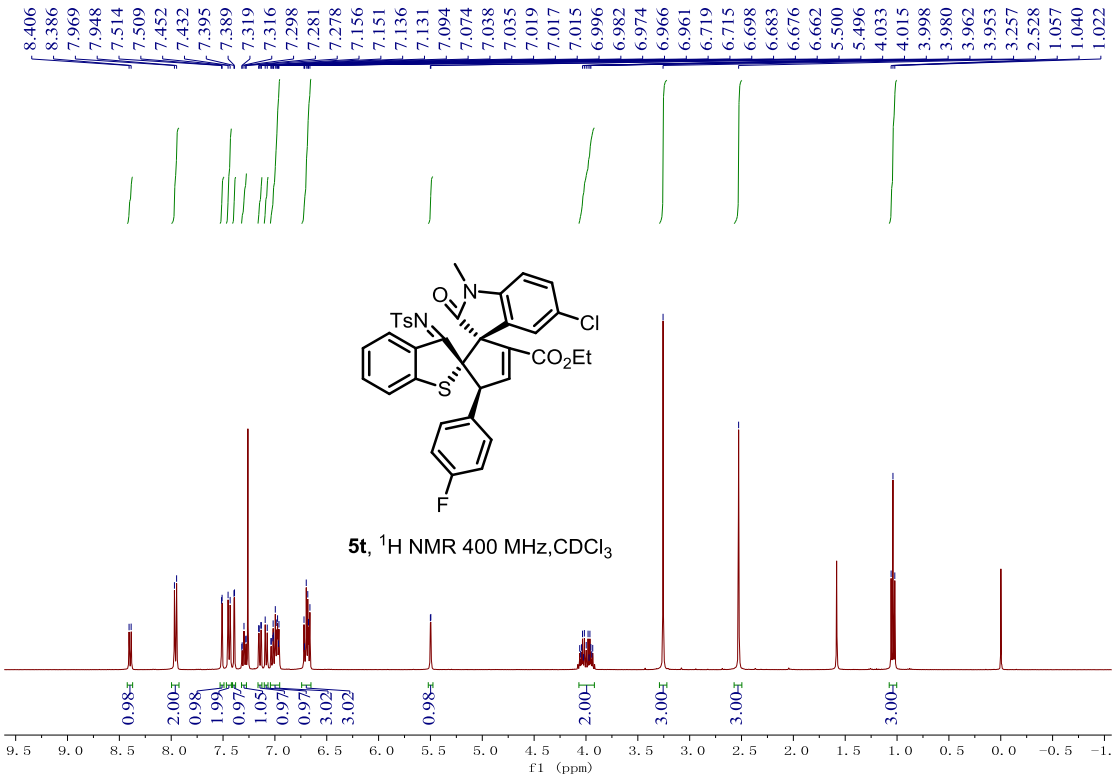

**5r**, $^{13}$C NMR 100 MHz,$CDCl_3$



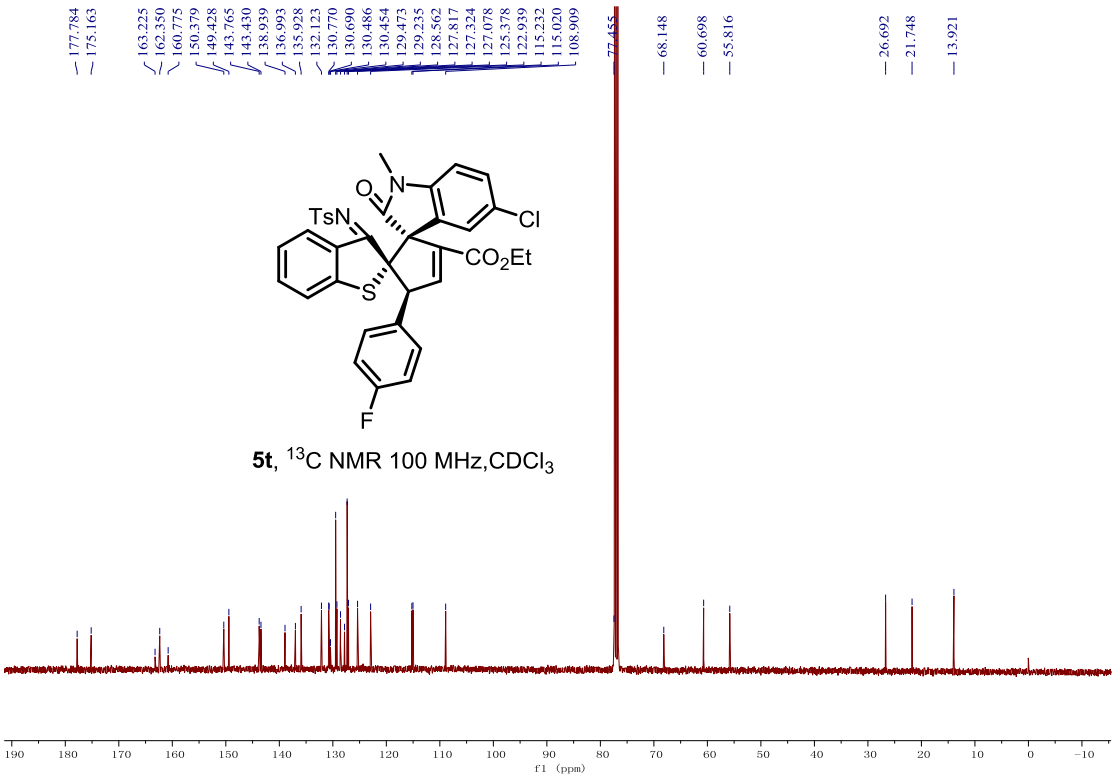

**5s**, $^{1}$H NMR 400 MHz,$CDCl_3$



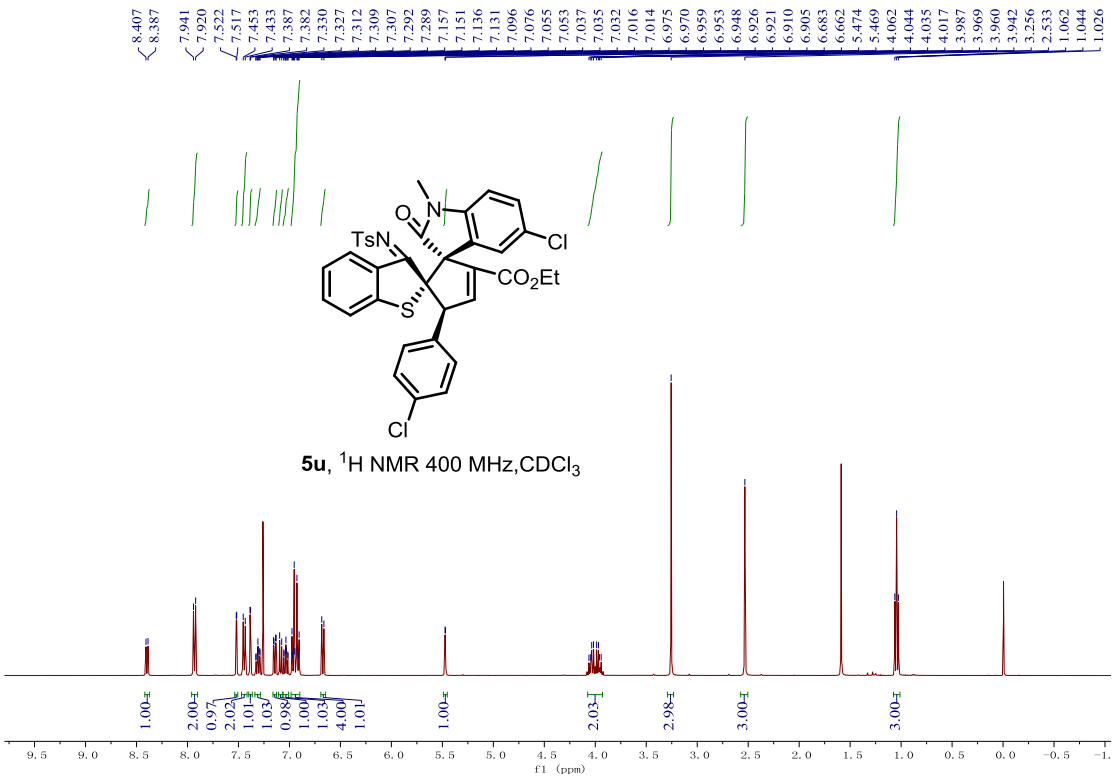

**5s**, $^{13}$C NMR 100 MHz,$CDCl_3$



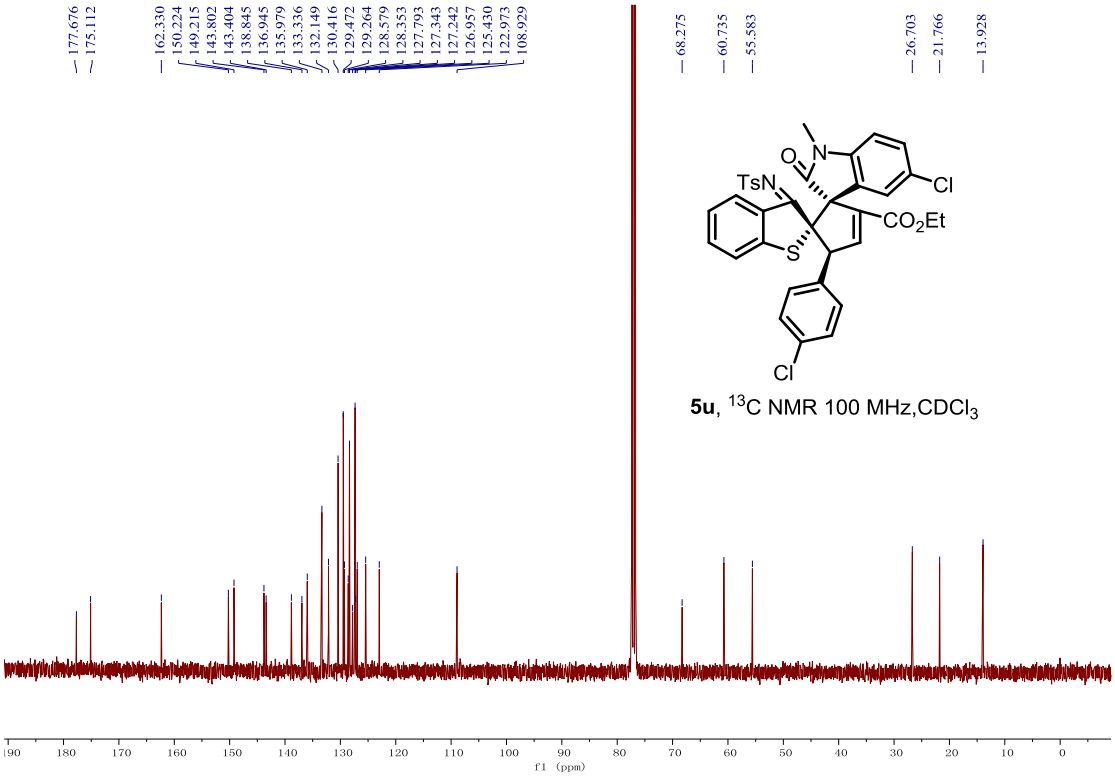

**5t**, $^{1}$H NMR 400 MHz,$CDCl_3$



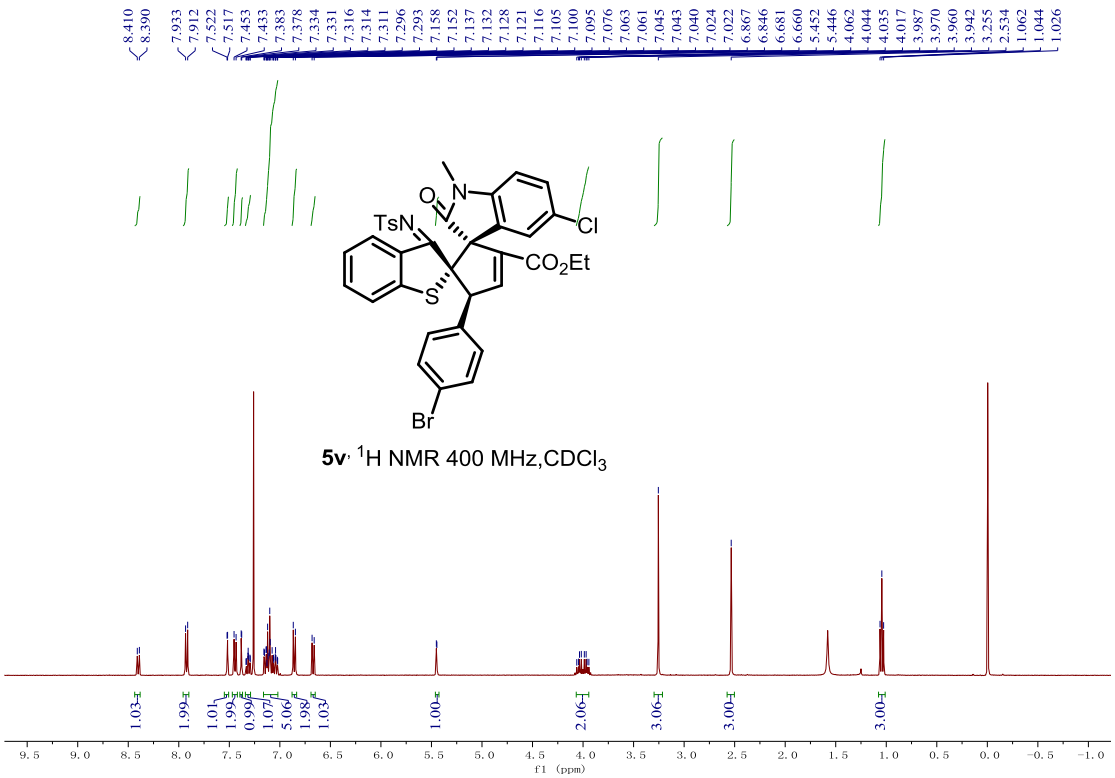

**5t**, $^{13}$C NMR 100 MHz,$CDCl_3$



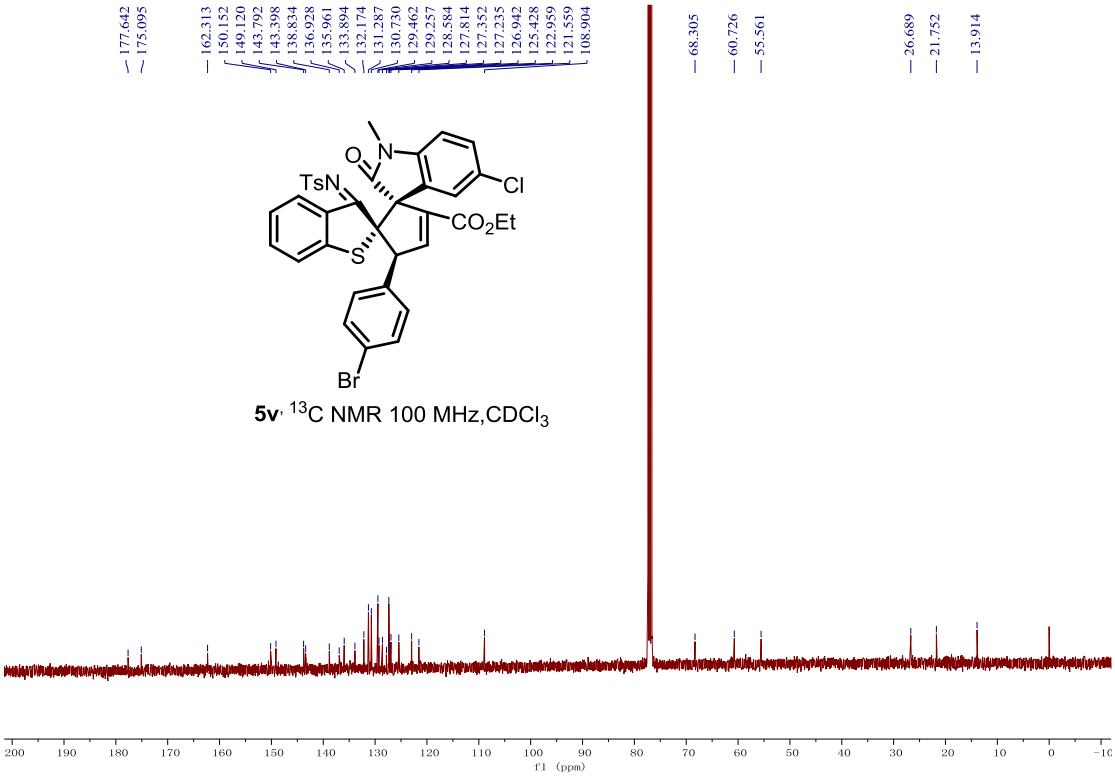

**5u**, $^{1}$H NMR 400 MHz,$CDCl_3$



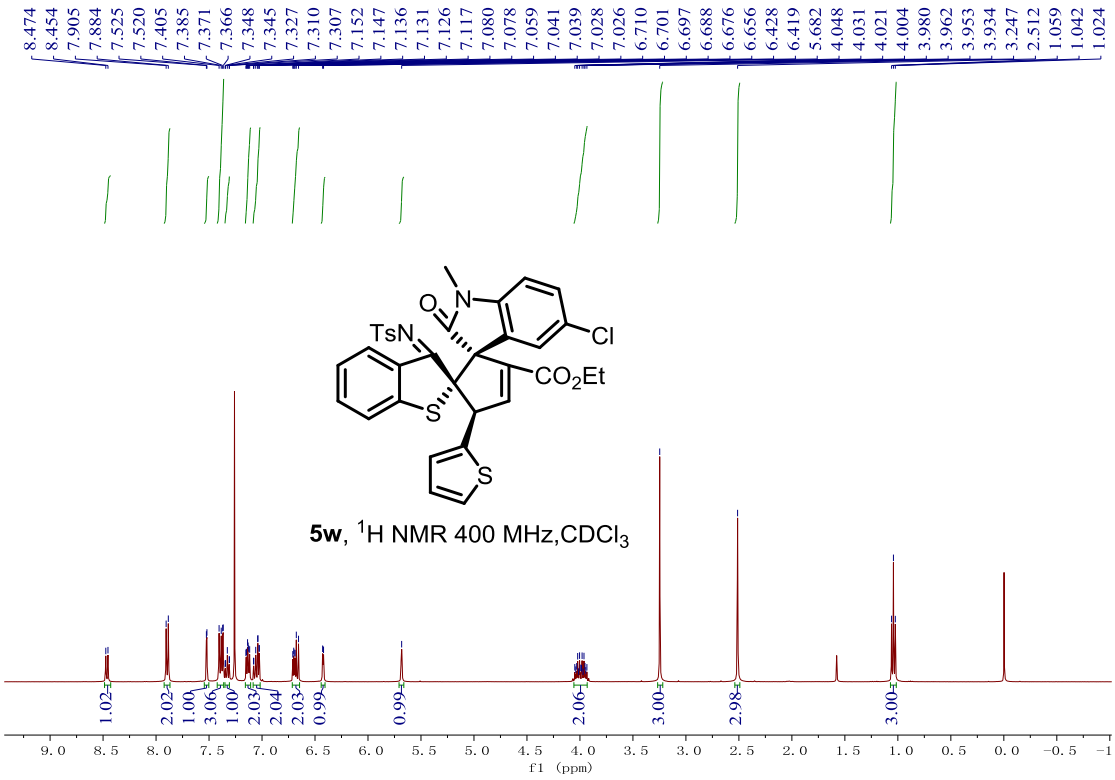

**5u**, $^{13}$C NMR 100 MHz,$CDCl_3$



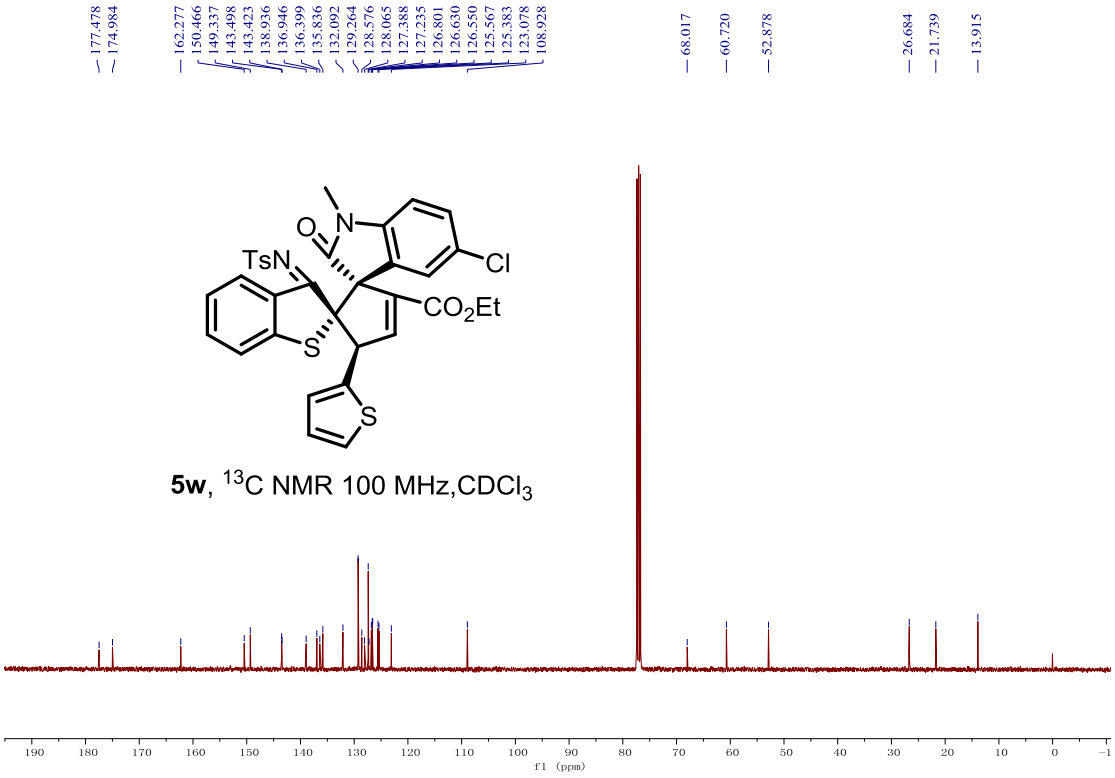

**5v**, $^{1}$H NMR 400 MHz,$CDCl_3$



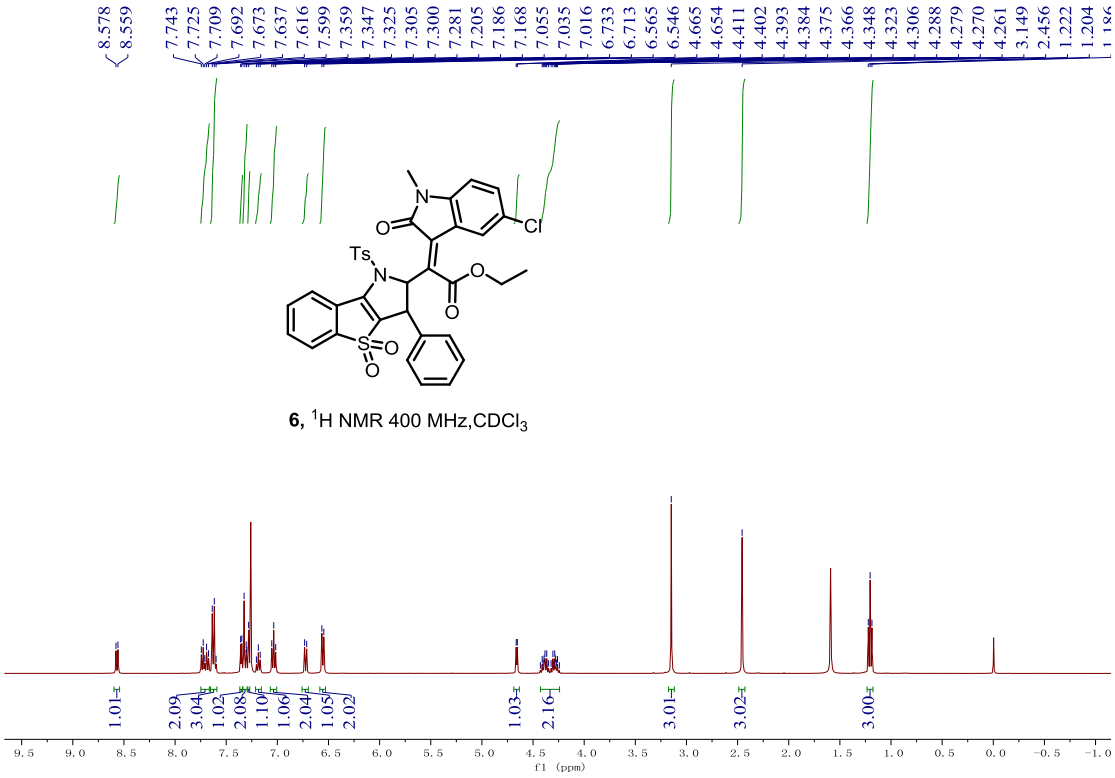

**5v**, $^{13}$C NMR 100 MHz,$CDCl_3$



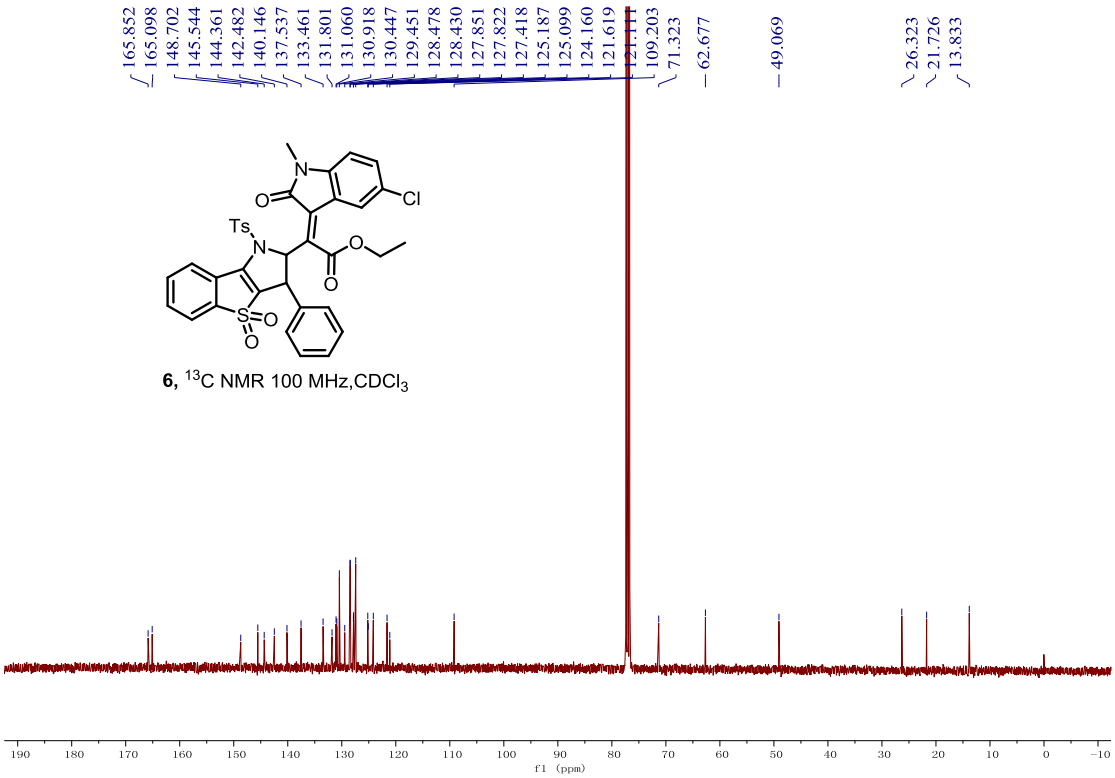

**5w**, $^{1}$H NMR 400 MHz,$CDCl_3$




**5w**, $^{13}$C NMR 100 MHz,$CDCl_3$

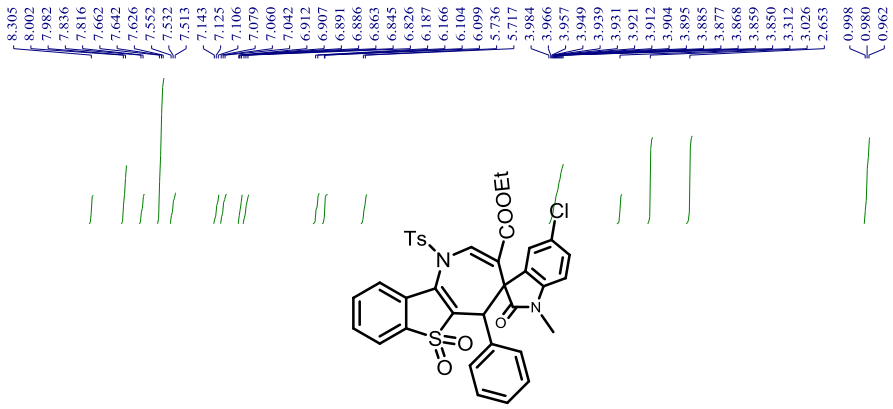


**6,** $^{1}$H NMR 400 MHz,$CDCl_3$

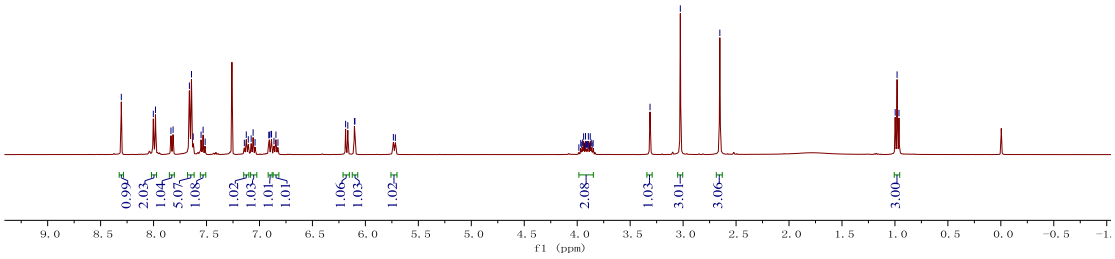


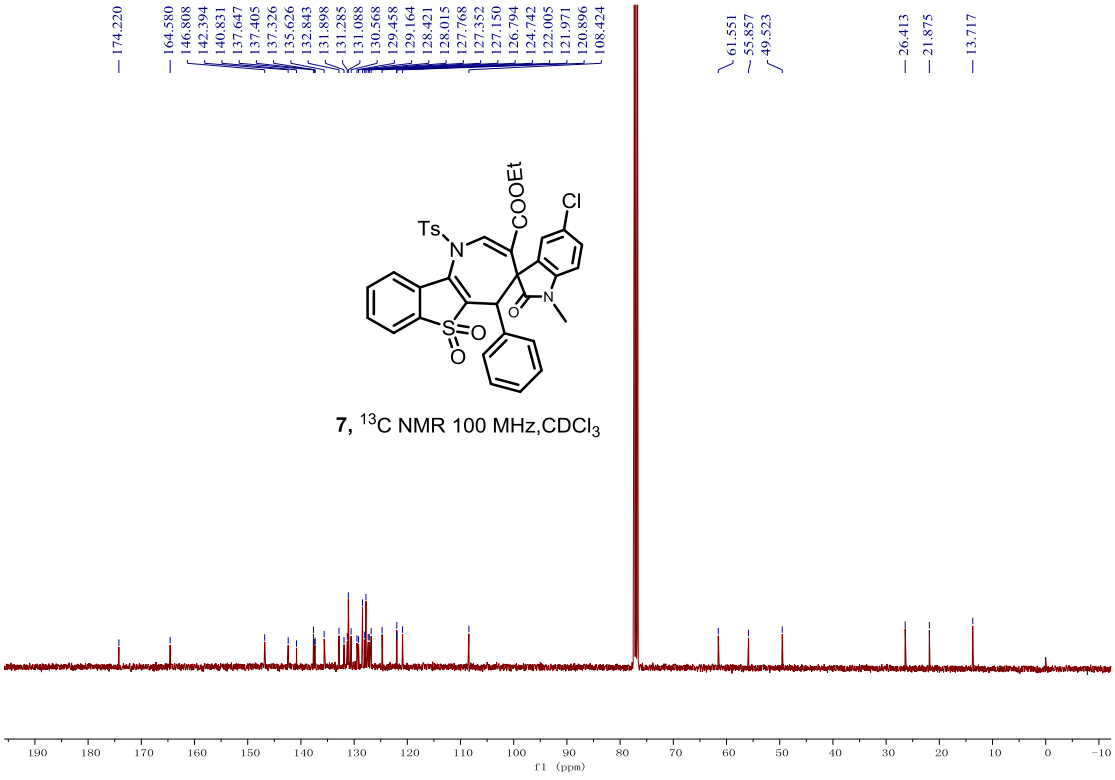


**6,** $^{13}$C NMR 100 MHz,$CDCl_3$

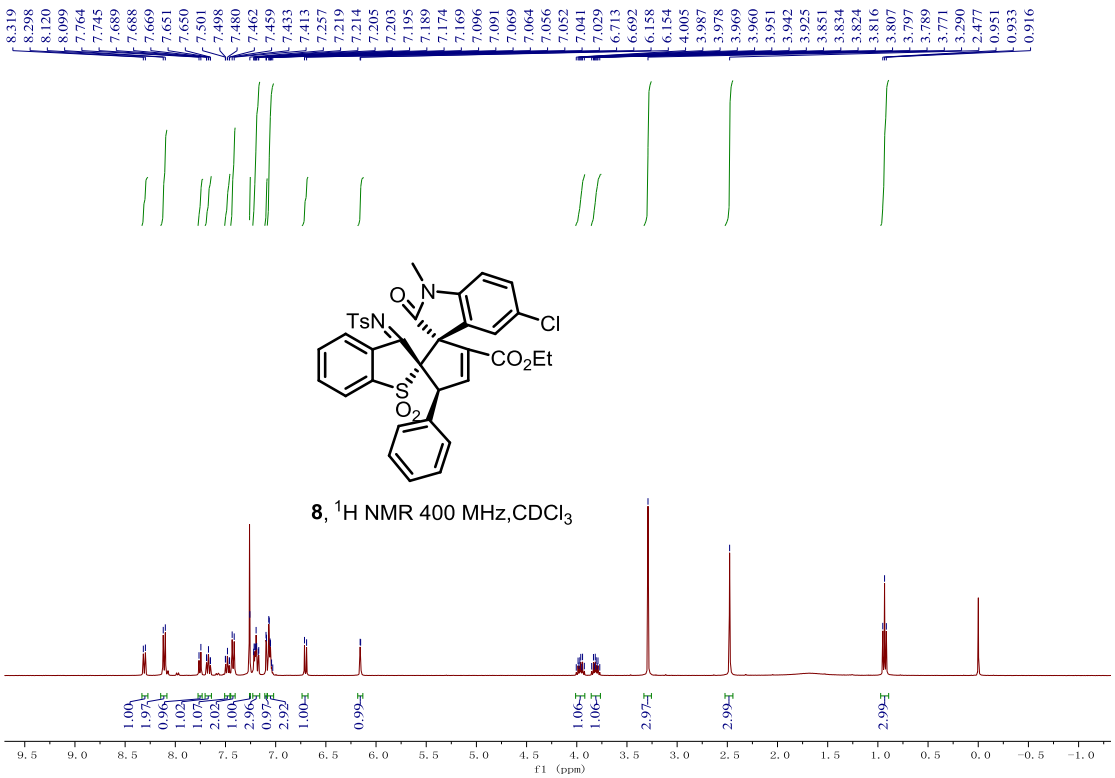



**7**, $^{1}$H NMR 400 MHz,$CDCl_3$

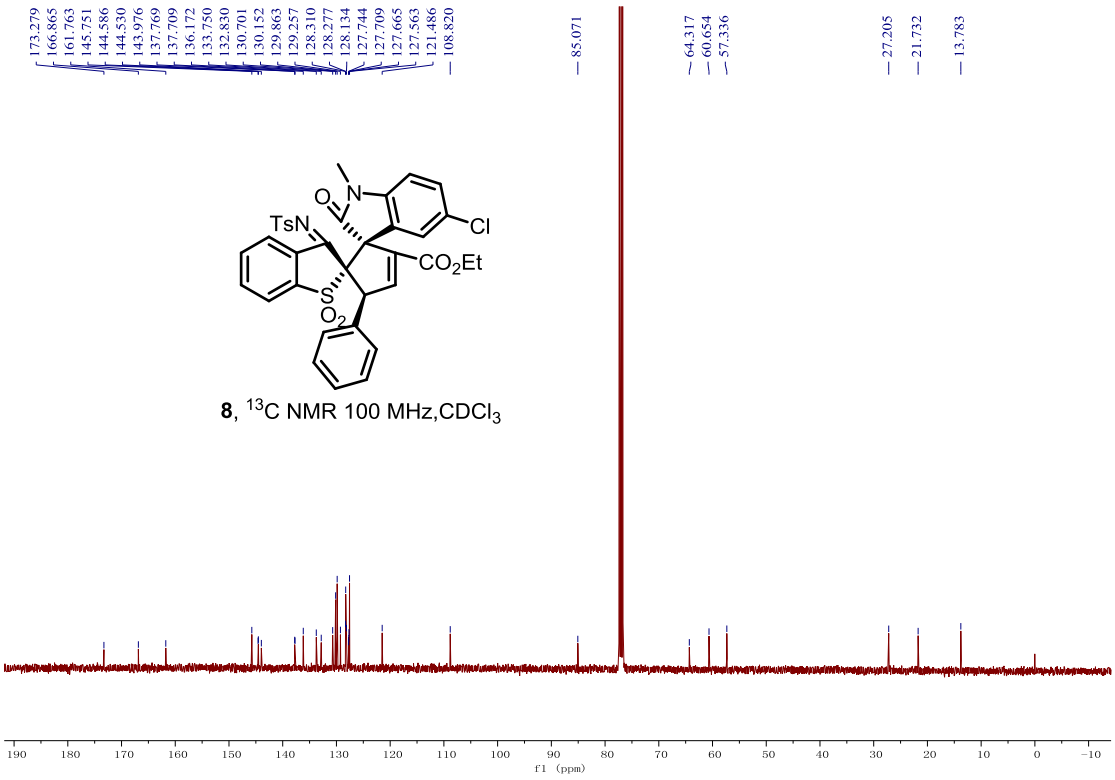


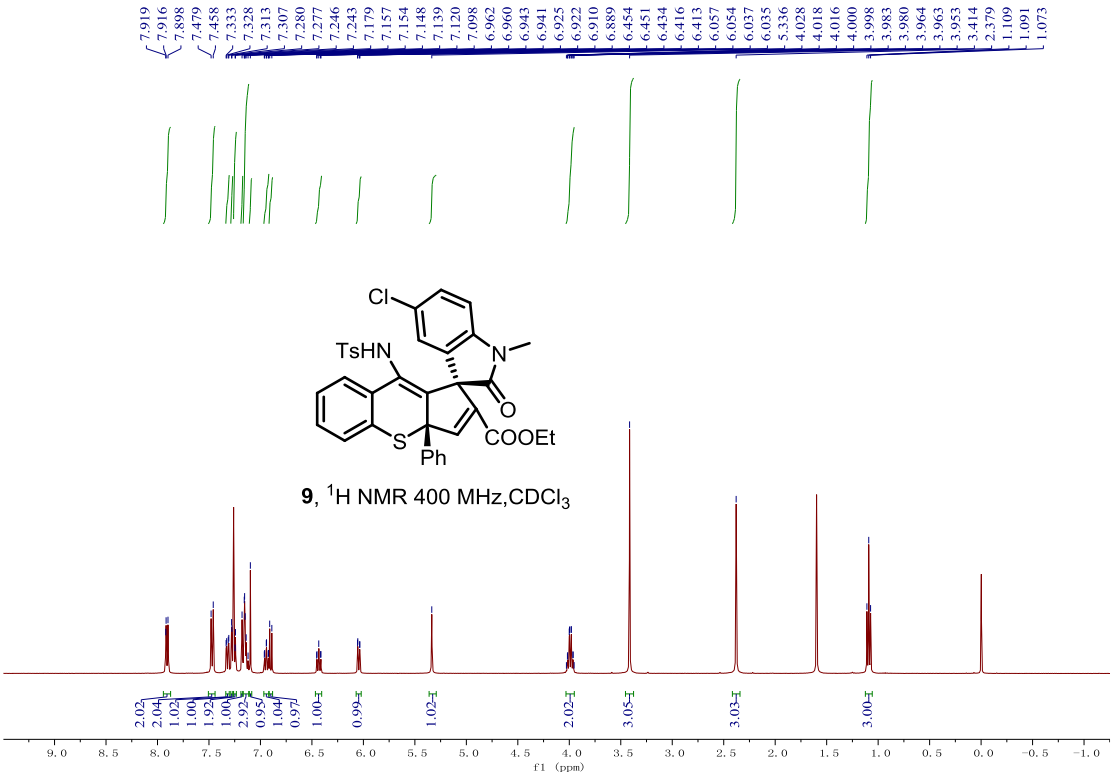

**7**, $^{13}$C NMR 100 MHz,$CDCl_3$



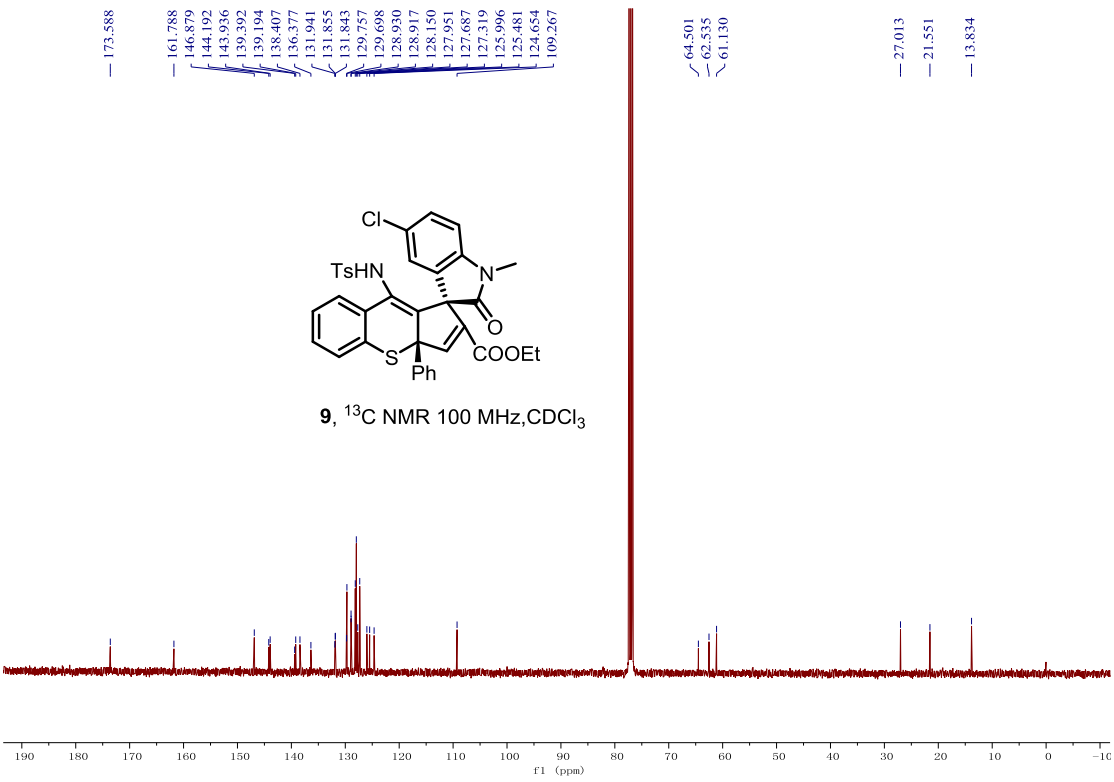

**8**, $^{1}$H NMR 400 MHz,$CDCl_3$



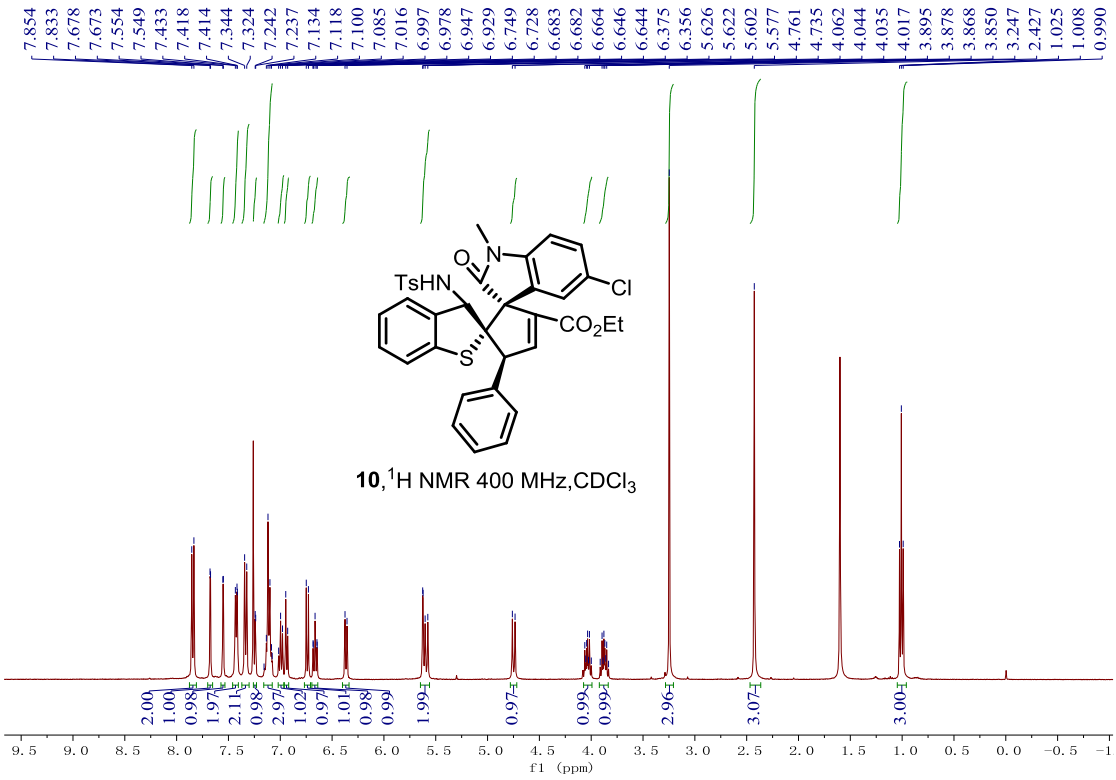

**8**, $^{13}$C NMR 100 MHz,$CDCl_3$



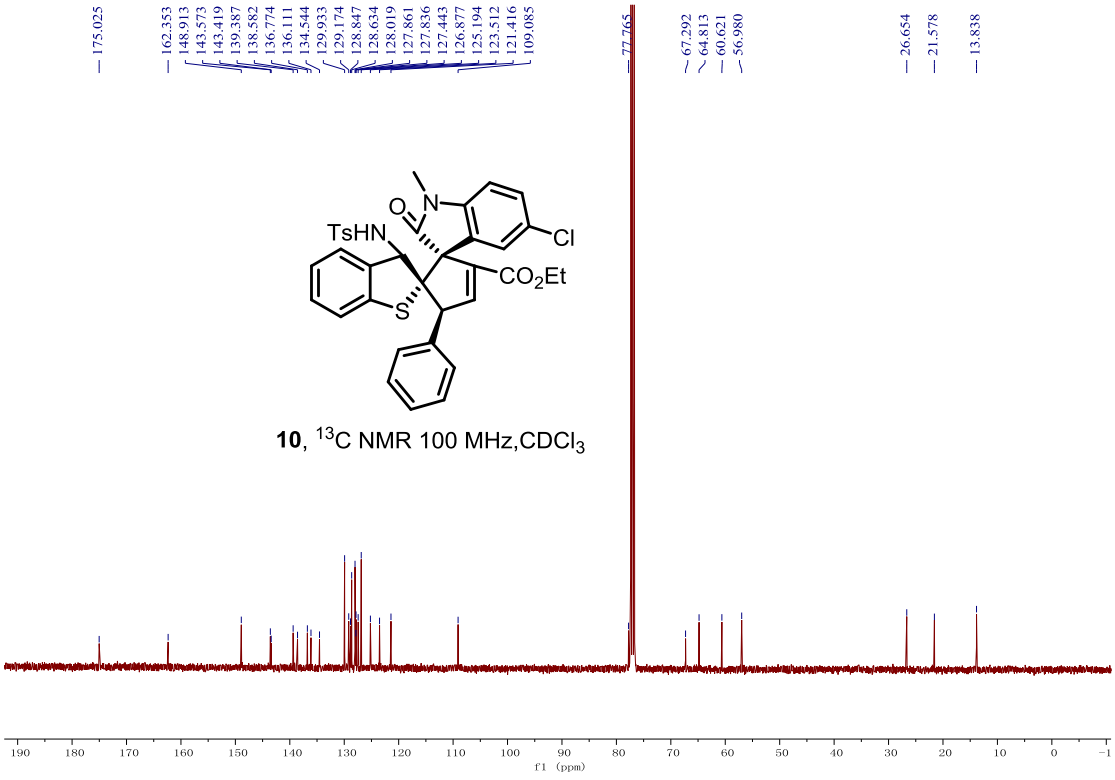

**9**, $^{1}$H NMR 400 MHz,$CDCl_3$




**9**, $^{13}$C NMR 100 MHz,$CDCl_3$

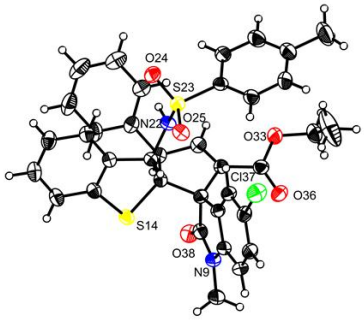



**10**,$^{1}$H NMR 400 MHz,$CDCl_3$




**10**, $^{13}$C NMR 100 MHz,$CDCl_3$

## 9. X-ray crystal structures

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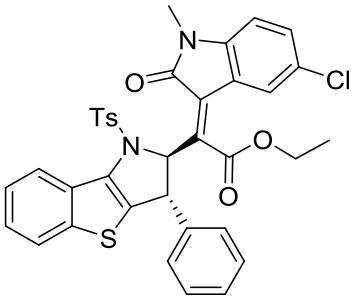
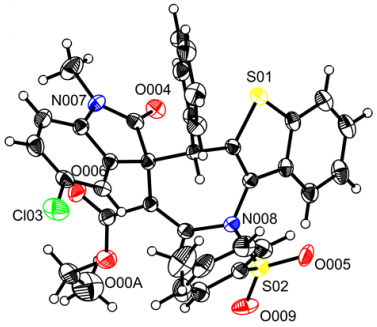



**3a**

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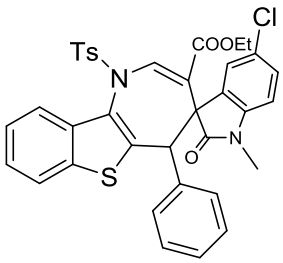
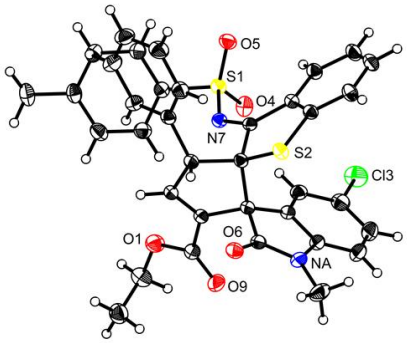



**4a**

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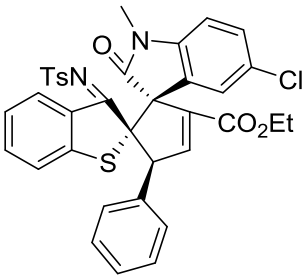
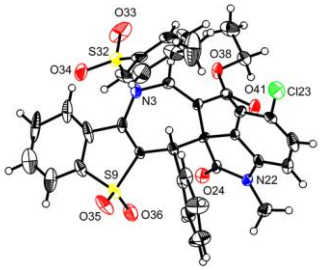



**5a**

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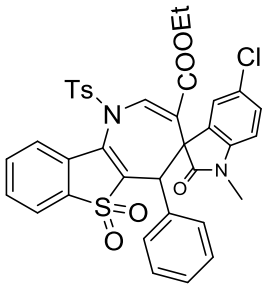
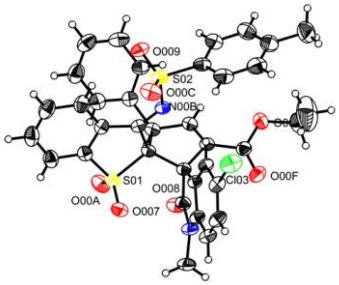



**7**

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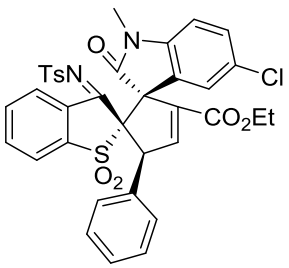
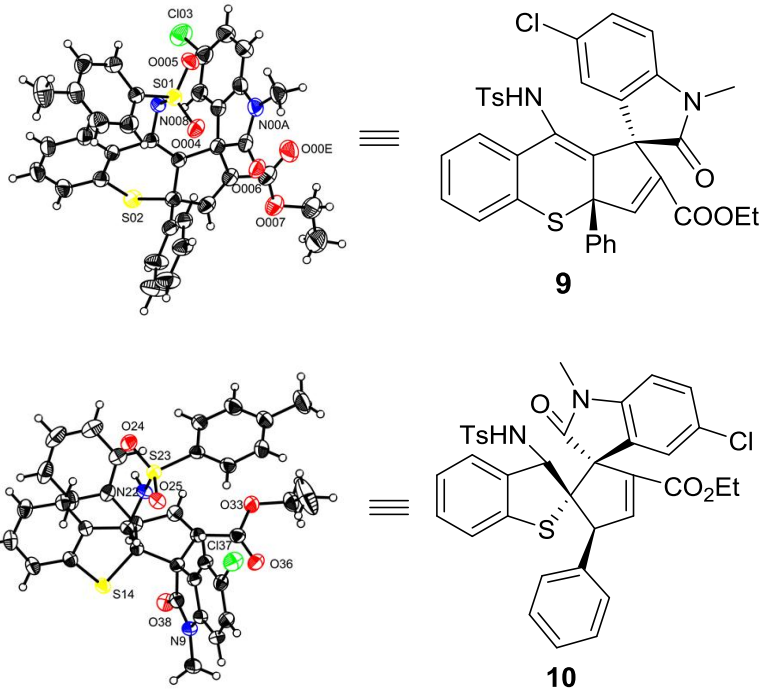



**8**




## 10. Computational Details

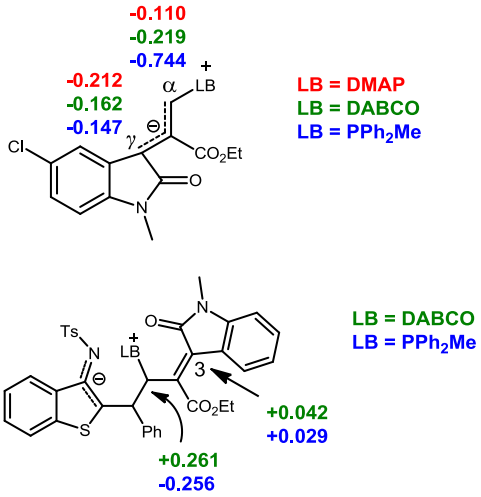



**Figure S1.** NBO charge distributions for intermediates **A** and **B**, calculated at the B3LYP/6-311+G*//B3LYP/6-31G* level of theory.

Calculations were performed using Gaussian 16 computational program.[7] The B3LYP density functional method[8] and the 6-31G* basis set were used in geometrical optimizations and frequency analyses (no imaginary frequency). Single point calculations were performed using the B3LYP method and the 6-311+G* level of theory.

**Table S1.** Cartesian coordinates of optimized structures

| Names | Cartesian Coordinates | | | |
|---|---|---|---|---|
| A-DABCO | 6 | 3.646071000 | -0.844437000 | -0.054646000 |
| | 6 | 2.574426000 | 0.052083000 | -0.354120000 |
| | 6 | 2.911505000 | 1.313196000 | -0.871008000 |
| | 6 | 4.256373000 | 1.666085000 | -1.041213000 |
| | 6 | 5.285702000 | 0.776469000 | -0.714212000 |
| | 6 | 4.983801000 | -0.500962000 | -0.221121000 |
| | 6 | 1.698719000 | -1.983399000 | 0.372770000 |
| | 6 | 1.340426000 | -0.650689000 | -0.060935000 |
| | 1 | 2.143945000 | 2.019562000 | -1.171532000 |
| | 1 | 4.499209000 | 2.647956000 | -1.440589000 |
| | 1 | 6.323647000 | 1.068037000 | -0.851722000 |
| | 1 | 5.774640000 | -1.206444000 | 0.019404000 |
| | 7 | 3.106862000 | -2.043573000 | 0.384650000 |
| | 6 | 3.853398000 | -3.219038000 | 0.768621000 |
| | 1 | 4.468516000 | -3.591836000 | -0.060176000 |
| | 1 | 4.510421000 | -3.013730000 | 1.622845000 |
| | 1 | 3.128241000 | -3.984816000 | 1.049694000 |
| | 8 | 0.984125000 | -2.954428000 | 0.707785000 |
| | 6 | -0.015014000 | -0.190713000 | -0.150680000 |
| | 6 | -1.087304000 | -1.028341000 | -0.013257000 |
| | 1 | -0.914268000 | -2.080442000 | 0.154140000 |
| | 6 | -0.190239000 | 1.290161000 | -0.387371000 |
| | 8 | -0.615962000 | 1.793861000 | -1.413897000 |
| | 8 | 0.181569000 | 1.997942000 | 0.686901000 |
| | 6 | 0.086666000 | 3.447285000 | 0.587114000 |
| | 6 | 0.576779000 | 4.023338000 | 1.900332000 |
| | 1 | -0.954575000 | 3.713748000 | 0.381847000 |
| | 1 | 0.695230000 | 3.777284000 | -0.259660000 |
| | 1 | 0.516543000 | 5.115954000 | 1.863337000 |
| | 1 | -0.036309000 | 3.672417000 | 2.736397000 |
| | 1 | 1.617717000 | 3.741044000 | 2.086133000 |
| | 6 | -4.470839000 | 0.666383000 | 0.784905000 |
| | 6 | -2.922084000 | 0.512945000 | 0.796405000 |
| | 1 | -4.737861000 | 1.690272000 | 0.509435000 |
| | 1 | -4.880051000 | 0.468042000 | 1.779182000 |
| | 1 | -2.439508000 | 1.389045000 | 0.371211000 |
| | 1 | -2.511901000 | 0.322509000 | 1.788614000 |
| | 6 | -4.502555000 | -0.059146000 | -1.497496000 |
| | 1 | -5.037666000 | -0.681900000 | -2.219860000 |
| | 1 | -4.647657000 | 0.986633000 | -1.782471000 |

| | | | | |
|---|---|---|---|---|
| | 6 | -2.989929000 | -0.418531000 | -1.506309000 |
| | 1 | -2.773714000 | -1.336496000 | -2.055452000 |
| | 1 | -2.357492000 | 0.379984000 | -1.891236000 |
| | 6 | -3.307726000 | -1.886707000 | 0.448146000 |
| | 1 | -2.960080000 | -2.747576000 | -0.124090000 |
| | 1 | -3.008634000 | -2.015404000 | 1.489710000 |
| | 6 | -4.829984000 | -1.635101000 | 0.274673000 |
| | 1 | -5.247718000 | -2.322945000 | -0.465551000 |
| | 1 | -5.346131000 | -1.808328000 | 1.223009000 |
| | 7 | -2.530352000 | -0.679895000 | -0.069600000 |
| | 7 | -5.092444000 | -0.260369000 | -0.166838000 |
| **A-DMAP** | 6 | -4.390704000 | -0.477346000 | -0.035628000 |
| | 6 | -3.224734000 | 0.343773000 | -0.126869000 |
| | 6 | -3.419644000 | 1.730856000 | -0.228030000 |
| | 6 | -4.716829000 | 2.258820000 | -0.243545000 |
| | 6 | -5.839771000 | 1.428450000 | -0.158771000 |
| | 6 | -5.682068000 | 0.039777000 | -0.052474000 |
| | 6 | -2.589680000 | -1.894630000 | 0.071462000 |
| | 6 | -2.076514000 | -0.544863000 | -0.072463000 |
| | 1 | -2.577429000 | 2.409194000 | -0.305900000 |
| | 1 | -4.848025000 | 3.335356000 | -0.324082000 |
| | 1 | -6.838671000 | 1.856564000 | -0.173431000 |
| | 1 | -6.545718000 | -0.615997000 | 0.017262000 |
| | 7 | -3.993700000 | -1.801280000 | 0.073888000 |
| | 6 | -4.871313000 | -2.942045000 | 0.198383000 |
| | 1 | -5.500087000 | -2.866724000 | 1.094432000 |
| | 1 | -5.525299000 | -3.040462000 | -0.676960000 |
| | 1 | -4.240216000 | -3.829150000 | 0.276123000 |
| | 8 | -1.991435000 | -2.987172000 | 0.177399000 |
| | 6 | -0.678240000 | -0.255011000 | -0.102746000 |
| | 6 | 0.297162000 | -1.196562000 | 0.112525000 |
| | 1 | 0.031739000 | -2.210281000 | 0.375629000 |
| | 6 | -0.272069000 | 1.172036000 | -0.384630000 |
| | 8 | -0.462073000 | 1.751764000 | -1.438733000 |
| | 8 | 0.336639000 | 1.728977000 | 0.674384000 |
| | 6 | 0.803574000 | 3.098026000 | 0.513211000 |
| | 6 | 1.482354000 | 3.500940000 | 1.807182000 |
| | 1 | -0.056817000 | 3.733606000 | 0.284592000 |
| | 1 | 1.487732000 | 3.131874000 | -0.339744000 |
| | 1 | 1.844335000 | 4.530974000 | 1.723654000 |
| | 1 | 0.784703000 | 3.448488000 | 2.648987000 |
| | 1 | 2.337372000 | 2.851548000 | 2.020280000 |
| | 6 | 2.262316000 | -0.225181000 | -1.006615000 |
| | 6 | 3.614018000 | -0.010909000 | -1.095774000 |

| | | | | |
|---|---|---|---|---|
| | 6 | 4.511108000 | -0.601498000 | -0.161981000 |
| | 6 | 3.905292000 | -1.415703000 | 0.838783000 |
| | 6 | 2.545188000 | -1.560865000 | 0.895380000 |
| | 7 | 1.701352000 | -0.968158000 | -0.004802000 |
| | 1 | 1.578527000 | 0.167481000 | -1.745915000 |
| | 1 | 3.971764000 | 0.588267000 | -1.921984000 |
| | 1 | 4.496474000 | -1.923501000 | 1.588523000 |
| | 1 | 2.062977000 | -2.147459000 | 1.666771000 |
| | 7 | 5.848596000 | -0.415337000 | -0.227176000 |
| | 6 | 6.734194000 | -1.088923000 | 0.723011000 |
| | 1 | 6.634858000 | -2.178428000 | 0.654210000 |
| | 1 | 7.765186000 | -0.823922000 | 0.493403000 |
| | 1 | 6.520604000 | -0.779202000 | 1.752500000 |
| | 6 | 6.424227000 | 0.431906000 | -1.271704000 |
| | 1 | 6.001443000 | 1.441983000 | -1.234894000 |
| | 1 | 7.499185000 | 0.506244000 | -1.113782000 |
| | 1 | 6.249382000 | 0.012123000 | -2.269678000 |
| **A-Ph$_2$PMe** | 6 | -4.262640000 | -1.286768000 | -0.139451000 |
| | 6 | -3.386793000 | -0.253199000 | 0.297275000 |
| | 6 | -3.962563000 | 0.931861000 | 0.771583000 |
| | 6 | -5.354552000 | 1.084066000 | 0.769114000 |
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