Electronic Supplementary Material (ESI) for Chemical Science.


# Rhodium-Catalyzed Atroposelective Access to Trisubstituted Olefins via C-H Bond Olefination of Diverse Arenes

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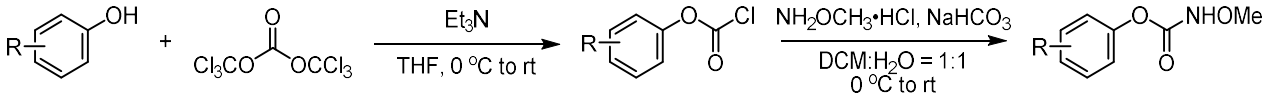
## 1. General Information

Commercially available chemicals were obtained from Adamas, Acros Organics, Aldrich Chemical Co., Alfa Aesar, and TCI and used as received unless otherwise noted. All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon. The $^{1}$H NMR spectra were recorded on 600 MHz NMR spectrometer. The $^{13}$C NMR spectra were recorded at 150 MHz. The $^{19}$F NMR spectra were recorded at 376 MHz. The $^{31}$P NMR spectra were recorded at 243 MHz. Chemical shifts were expressed in parts per million ($\delta$) downfield from the internal standard tetramethylsilane (TMS), and were reported as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), and m (multiplet). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: $\delta$ H = 7.26 ppm, $\delta$ C = 77.16 ppm). The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained via ESI mode by using a MicroTOF mass spectrometer. Column chromatography was performed on silica gel 200-300 mesh. The enantiomeric ratio (e.r.) of the products were determined by high-performance liquid chromatography (HPLC) with a chiral stationary phase in comparison with the authentic racemate sample with $^{n}$hexane and $^{i}$PrOH as solvents. All the chiral stationary phases including Chiralcel IE, IA, OD-H used in this study were purchased from Daicel Chirsal Technologies. Optical rotations were reported as follows: $[\alpha]_D^T$ = (c: g/100mL, in $CHCl_3$).

Chiral rhodium catalysts,[1] phenyl *N*-methoxycarbamates,[2] and alkynes[3], were prepared according to published procedures.

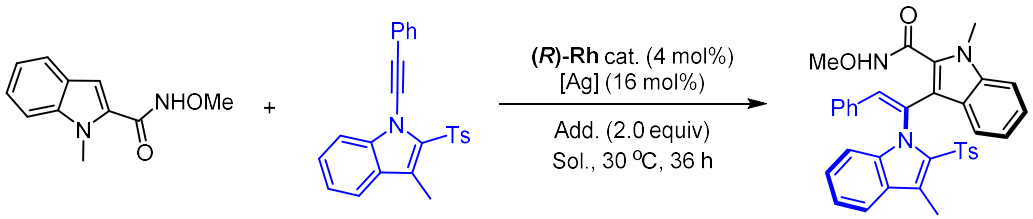
## 2. Experimental Section

### 2.1 General Procedure for the Synthesis of phenyl *N*-methoxycarbamates




The phenyl *N*-methoxycarbamates synthesis was completed by following a modified literature procedure. [2] To a round bottom flask charged with a stir bar was added the Triphosgene (1.65 mmol) and THF (30 mL) The mixture was cooled at 0 °C, then $Et_3N$ (0.7 mL) and phenol (5 mmol) were slowly added to the flask. The mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was evaporated under vacuum which was used in the subsequent step without further purification. *O*-Methyl-hydroxylamine hydrochloride (6 mmol) was dissolved in $CH_2Cl_2$: $H_2O$ = (10 mL:10 mL) in a 50 mL round-bottom flask. The solution was cooled to 0 °C, then $NaHCO_3$ (11 mmol) was added and phenyl chloroformate (5 mmol) was added dropwise over 10 min. The resulting solution was stirred at room temperature for 5 h. The mixture was transferred to a separatory funnel containing water (50 mL), organic phase was separated and aqueous phases were extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and concentrated. The residue was purified by flash silica gel chromatography to afford the phenyl *N*-methoxycarbamates.

### 2.2 Tables of the Optimization of Reaction Conditions of synthesis of 41.




39 2a 41

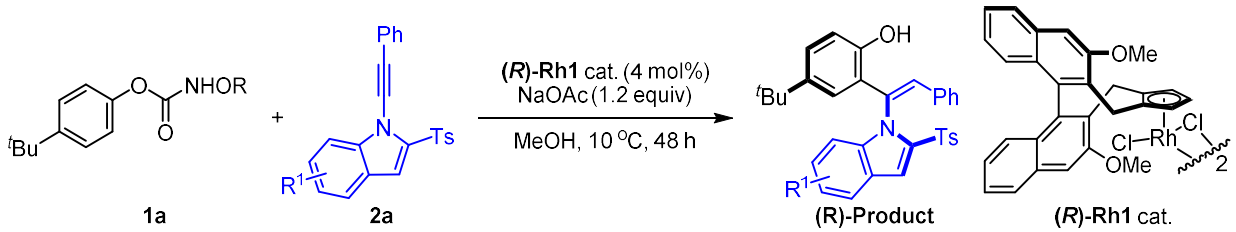
| Entry | Rh | [Ag] | Add. | Sol. | yield [%] | e.r. |
|---|---|---|---|---|---|---|
| 1 | (*R*)-Rh1 | $AgSbF_6$ | HOPiv | EA | Trace | - |
| 2 | (*R*)-Rh4 | $AgSbF_6$ | HOPiv | EA | 45 | 93:7 |
| 3 | (*R*)-Rh4 | $AgSbF_6$ | HOPiv | MeOH | 50 | 98:2 |
| 4 | (*R*)-Rh4 | $AgSbF_6$ | MesCOOH | MeOH | Trace | - |
| 5 | (*R*)-Rh4 | $AgSbF_6$ | HOAc | MeOH | 26 | 98:2 |
| 6 | (*R*)-Rh4 | $AgSbF_6$ | NaOAc | MeOH | 70 | 99:1 |
| 7 | (*R*)-Rh4 | - | NaOAc | MeOH | Trace | - |

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | (*R*)-Rh4 | $AgSbF_6$ | NaOAc | DCM | 75 | 94.5:5.5 |
| 9 | (*R*)-Rh4 | $AgSbF_6$ | NaOAc | THF | 31 | 99:1 |
| 10 | (*R*)-Rh4 | $AgSbF_6$ | NaOAc | PhMe | 71 | 89:11 |
| 11 | (*R*)-Rh4 | $AgSbF_6$ | NaOAc | EA | 88 | 97.5:2.5 |
| 12 | (*R*)-Rh4 | $AgSbF_6$ | NaOAc | PhCl | 53 | 96.5:3.5 |
| 13 | (*R*)-Rh4 | $AgSbF_6$ | NaOAc | TFE | Trace | - |
| 14 | (*R*)-Rh4 | $AgSbF_6$ | NaOAc | EtOH | 82 | 99:1 |
| 15 | (*R*)-Rh4 | $AgSbF_6$ | NaOAc | $^i$PrOH | 92 | 99:1 |

Reaction conditions: **39** (0.1 mmol), alkyne **2** (0.12 mmol), **(*R*)-Rh** cat (4 mol%), $AgSbF_6$ (16 mol%), Add (0.2 mmol) in Sol. (2 mL), 30 ºC, 36 h, isolated yield. The e.r. was determined by HPLC analysis using a chiral stationary phase.

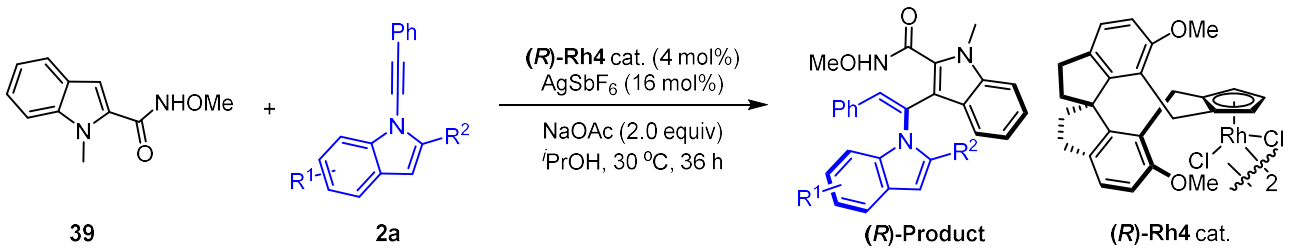
### 2.3 Typical General Procedure for the Asymmetric Catalysis

**General procedure for the synthesis of 3-38.**




A scew-cap vial (8 mL) was charged with alkyne **2a** (0.1 mmol, 1.0 equiv), **(*R*)-Rh1** (4 mol%) and NaOAc (0.12 mmol, 1.2 equiv) in MeOH (2 mL) and the mixture was stirred at 10 ºC. The resulted mixture was kept at 10 ºC for 15 min, to which was added *O*-phenyl carbamate **1a** (0.12 mmol, 1.2 equiv). The reaction was maintained at 10 ºC for 48 h. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding product **3-38**.

**General procedure for the synthesis of 40-49.**




A scew-cap vial (8 mL) was charged with *N*-methoxy-1-methyl-1H-indole-2-carboxamide **39** (0.1 mmol, 1 equiv), alkyne **2a** (0.12 mmol, 1.2 equiv), **(*R*)-Rh4** (4 mol%), $AgSbF_6$ (16 mol%) and NaOAc (0.2 mmol, 2.0 equiv) in $^i$PrOH (2 mL) and the reaction mixture was stirred at 30 ºC for 36 h under $N_2$.

The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding product **40-49**.

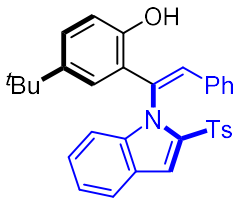
**General procedure for the synthesis of racemic product 3-38.**

A similar synthetic procedure was followed for synthesis of racemic products except that $[Cp^*RhCl_2]_2$ (4 mol %) was used at 60 $^oC$ for 24 h.

**General procedure for the synthesis of racemic product 40-49.**

A similar synthetic procedure was followed for synthesis of racemic products except that $[Cp^*RhCl_2]_2$ (4 mol %) was used in DCM at 50 $^oC$ for 24 h.

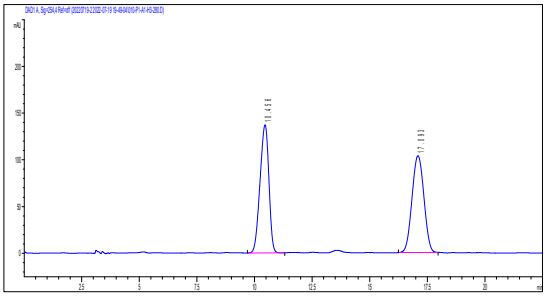
## 3. Characterization Data and HPLC Chromatograms



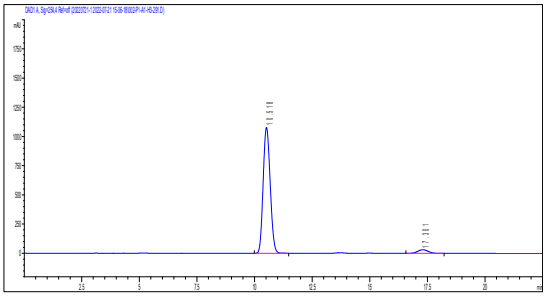

**(*R*, Z)-4-(tert-butyl)-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (3)**

The title compound was isolated as a pale-yellow solid (47.9 mg, 92%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.73 (d, $J$ = 8.0 Hz, 1H), 7.62 (s, 1H), 7.37 (d, $J$ = 8.3 Hz, 2H), 7.22 – 7.18 (m, 2H), 7.18 – 7.14 (m, 2H), 7.10 (dd, $J$ = 8.6, 2.5 Hz, 1H), 7.06 – 7.02 (m, 1H), 7.02 – 6.98 (m, 2H), 6.90 (dd, $J$ = 10.4, 8.3 Hz, 3H), 6.71 – 6.67 (m, 2H), 6.38 (d, $J$ = 2.4 Hz, 1H), 6.23 (s, br, 1H), 2.22 (s, 3H), 0.88 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.5, 143.5, 143.3, 138.7, 137.8, 134.6, 134.0, 132.3, 129.4, 129.2, 128.5, 128.4, 128.3, 127.1, 127.0, 126.9, 125.9, 125.4, 124.2, 122.7, 122.1, 117.6, 113.5, 111.9, 33.8, 31.1, 21.5. **HRMS (ESI)**: calcd. for $C_{33}H_{31}NNaO_3S^+$ $[M+Na]^+$ : 544.1917, found : 544.1906. **$[\alpha]_D^{20}$** = +98 (c = 0.1, $CHCl_3$).

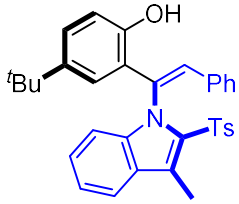
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 10.518 min, tr (minor) = 17.301 min, 96.5:3.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.456 | 3663.1 | 49.65 |
| 2 | 17.093 | 3714.1 | 50.35 |



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.518 | 22990.6 | 96.27 |
| 2 | 17.301 | 890.8 | 3.73 |

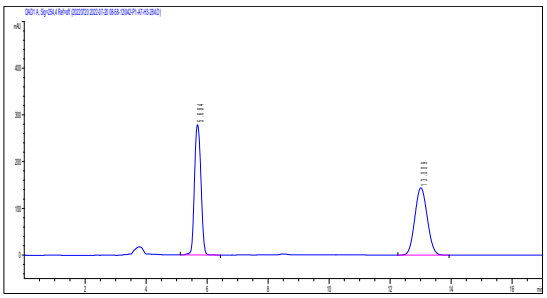



**(*R*, *Z*)-4-(tert-butyl)-2-(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-phenol (4)**

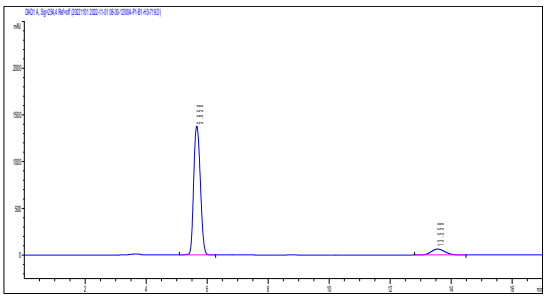
The title compound was isolated as a white solid (48.7 mg, 91%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.69 (d, $J$ = 8.1 Hz, 1H), 7.25 – 7.19 (m, 4H), 7.18 – 7.12 (m, 3H), 7.10 – 7.03 (m, 3H), 6.97 (d, $J$ = 8.6 Hz, 1H), 6.91 (d, $J$ = 8.1 Hz, 2H), 6.86 (dd, $J$ = 8.0, 1.8 Hz, 2H), 6.38 (s, br, 1H), 6.35 (d, $J$ = 2.4 Hz, 1H), 2.75 (s, 3H), 2.25 (s, 3H), 0.89 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.5, 143.5, 143.3, 139.0, 137.6, 134.3, 131.5, 130.0, 129.7, 129.4, 128.6, 128.5, 128.3, 127.4, 127.3, 127.0, 126.5, 126.4, 123.8, 123.0, 121.5, 120.7, 117.9, 111.8, 33.8, 31.2, 21.6,

10.4. **HRMS (ESI)**: calcd. for $C_{34}H_{33}NNaO_3S^+$ $[M+Na]^+$ : 558.2073, found : 558.2076. **$[\alpha]_D^{20}$** = +114 (c = 0.1, $CHCl_3$).

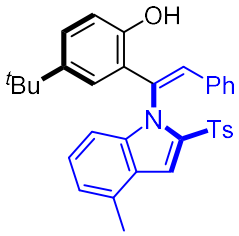
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 50:50, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 5.658 min, tr (minor) = 13.558 min, 91.5:8.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 5.684 | 4102.4 | 50.24 |
| 2 | 13.009 | 4063.2 | 49.76 |



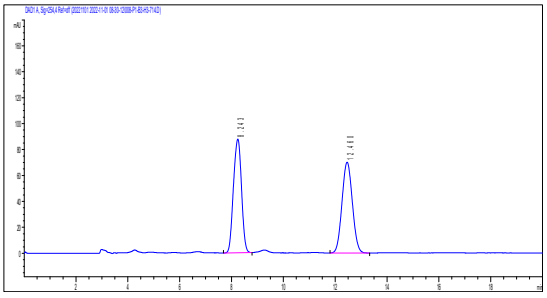
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 5.658 | 20843.3 | 91.41 |
| 2 | 13.558 | 1959.5 | 8.59 |

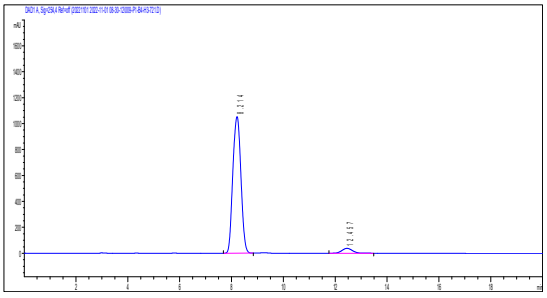



**(*R*, *Z*)-4-(tert-butyl)-2-(1-(4-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-phenol (5)**

The title compound was isolated as a white solid (48.7 mg, 91%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.68 (s, 1H), 7.42 – 7.37 (m, 2H), 7.24 (s, 1H), 7.12 – 7.07 (m, 2H), 7.06 – 6.97 (m, 4H), 6.94 (d, $J$ = 7.0 Hz, 1H), 6.89 (dd, $J$ = 8.4, 4.9 Hz, 3H), 6.67 (d, $J$ = 7.1 Hz, 2H), 6.41 (d, $J$ = 2.5 Hz, 1H), 2.63 (s, 3H), 2.22 (s, 3H), 0.90 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.6, 143.4, 143.2, 138.7, 137.8, 134.1, 133.8, 132.34, 132.27, 129.38, 129.35, 128.5, 128.4, 128.3, 127.08, 127.06, 127.0, 126.1, 125.5, 124.3, 122.1, 117.5, 112.2, 109.5, 33.8, 31.2, 21.5, 18.7. **HRMS (ESI)**: calcd. for $C_{34}H_{33}NNaO_3S^+$ $[M+Na]^+$ : 558.2073, found : 558.20763. **$[\alpha]_D^{20}$** = +74 (c = 0.1, $CHCl_3$).

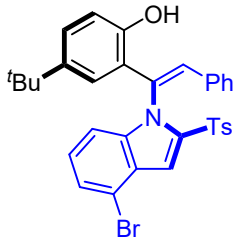
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 8.214 min, tr (minor) = 12.457 min, 95.5:4.5 e.r.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.243 | 1892.0 | 49.32 |
| 2 | 12.460 | 1944.2 | 50.68 |

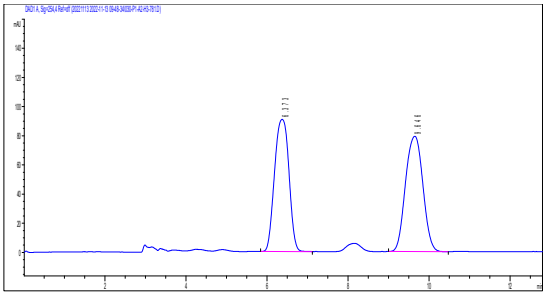
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.214 | 22828.5 | 95.61 |
| 2 | 12.457 | 1047.2 | 4.39 |

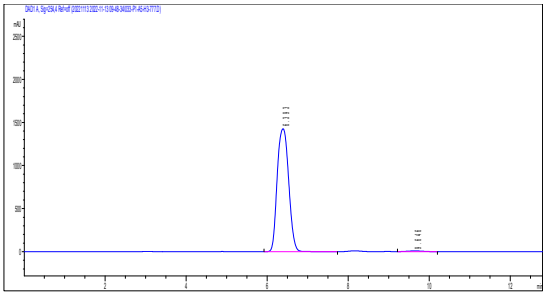



**(*R*, *Z*)-2-(1-(4-bromo-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-4-(tert-butyl)-phenol (6)**

The title compound was isolated as a pale-yellow solid (41.3 mg, 69%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.67 (d, $J$ = 0.8 Hz, 1H), 7.38 (d, $J$ = 8.4 Hz, 2H), 7.33 (dd, $J$ = 7.5, 0.8 Hz, 1H), 7.24 (s, 1H), 7.15 – 7.09 (m, 2H), 7.08 – 7.00 (m, 4H), 6.93 – 6.88 (m, 3H), 6.72 – 6.62 (m, 2H), 6.36 (d, $J$ = 2.5 Hz, 1H), 6.19 (s, br, 1H), 2.23 (s, 3H), 0.90 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.5, 143.8, 143.5, 138.7, 137.4, 135.5, 133.8, 132.6, 129.5, 129.0, 128.7, 128.6, 128.3, 127.5, 127.3, 127.2, 126.8, 125.1, 124.1, 117.7, 116.4, 113.2, 111.2, 33.8, 31.2, 21.6. **HRMS (ESI)**: calcd. for $C_{33}H_{30}BrNNaO_3S^+$ $[M+Na]^+$ : 622.1022, found : 622.1012. **$[\alpha]_D^{20}$** = +44 (c = 0.1, $CHCl_3$).

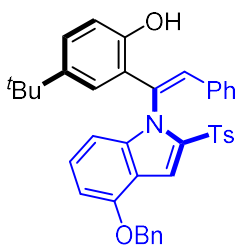
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 6.393 min, tr (minor) = 9.646 min, 99:1 e.r.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.373 | 2243.0 | 48.74 |
| 2 | 9.646 | 2358.8 | 51.26 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.393 | 27996.1 | 99.24 |
| 2 | 9.646 | 210.0 | 0.76 |

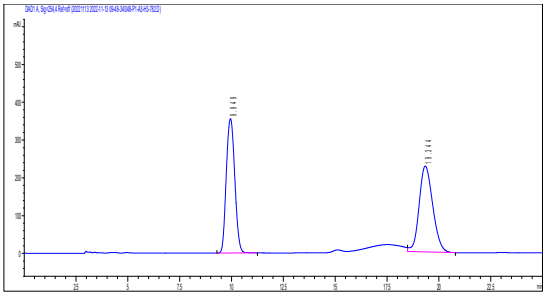



**(*R*, *Z*)-2-(1-(4-(benzyloxy)-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-4-(tert-butyl)phenol (7)**

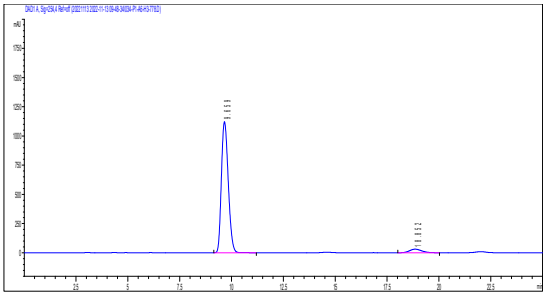
The title compound was isolated as a pale-yellow solid (48.9 mg, 78%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.81 (s, 1H), 7.56 (d, $J$ = 7.3 Hz, 2H), 7.46 (t, $J$ = 7.6 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.21 – 7.18 (m, 1H), 7.14 – 7.09 (m, 2H), 7.09 – 7.01

(m, 3H), 6.91 (d, $J$ = 8.6 Hz, 1H), 6.87 (d, $J$ = 8.1 Hz, 2H), 6.79 (d, $J$ = 8.4 Hz, 1H), 6.74 – 6.68 (m, 2H), 6.60 (d, $J$ = 7.7 Hz, 1H), 6.44 (d, $J$ = 2.5 Hz, 1H), 6.32 (s, br, 1H), 5.26 – 5.18 (m, 2H), 2.22 (s, 3H), 0.91 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 153.5, 151.5, 143.4, 143.3, 140.1, 137.9, 136.8, 134.0, 133.0, 132.3, 129.32, 129.27, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.6, 127.1, 127.0, 125.5, 124.3, 117.8, 117.6, 111.5, 104.9, 102.3, 70.2, 33.8, 31.2, 21.5. **HRMS (ESI)**: calcd. for $C_{40}H_{37}NNaO_4S^+$ $[M+Na]^+$ : 650.2336, found : 650.2347. **$[\alpha]_D^{20}$** = +86 (c = 0.1, $CHCl_3$).

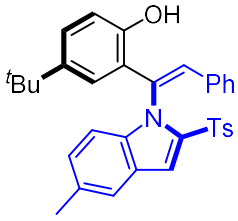
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.659 min, tr (minor) = 18.852 min, 95.5:4.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.949 | 10116.8 | 49.46 |
| 2 | 19.344 | 10337.5 | 50.54 |



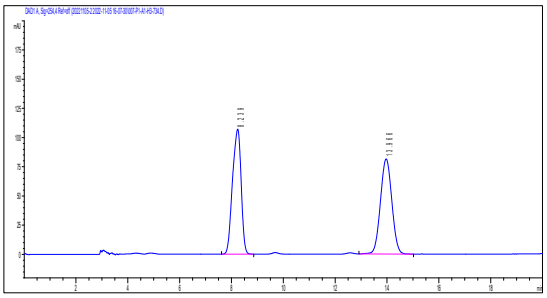
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.659 | 25736.6 | 95.47 |
| 2 | 18.852 | 1222.4 | 4.53 |



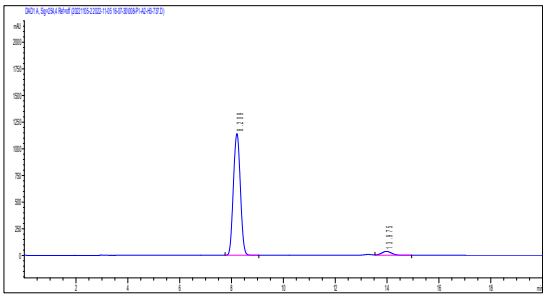

**(*R*, *Z*)-4-(tert-butyl)-2-(1-(5-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-phenol (8)**

The title compound was isolated as a yellow solid (47.6 mg, 89%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.55 (d, $J$ = 0.8 Hz, 1H), 7.50 - 7.47 (m, 1H), 7.36 (d, $J$ = 8.3 Hz, 2H), 7.18 (s, 1H), 7.09 (dd, $J$ = 8.6, 2.5 Hz, 1H), 7.07 – 6.99 (m, 5H), 6.89 (dd, $J$ = 10.2, 8.3 Hz, 3H), 6.73 – 6.67 (m, 2H), 6.40 (d, $J$ = 2.5 Hz, 1H), 6.26 (s, br, 1H), 2.39 (s, 3H), 2.22 (s, 3H), 0.89 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.5, 143.4, 143.3, 137.9, 137.2, 134.14, 134.05, 132.1, 131.5, 129.3, 129.0, 128.5, 128.4, 128.3, 127.03, 126.98, 126.1, 125.6, 124.3, 121.9, 117.6, 113.1, 111.6, 33.8, 31.2, 21.54, 21.50. **HRMS (ESI)**: calcd. for $C_{34}H_{33}NNaO_3S^+$ $[M+Na]^+$ : 558.2073, found : 558.2088; **$[\alpha]_D^{20}$** = +28 (c = 0.1, $CHCl_3$).

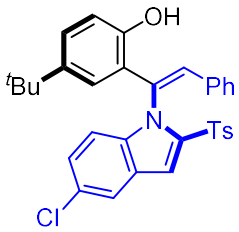
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 8.209 min, tr (minor) = 13.975 min, 95.5:4.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.239 | 2470.0 | 49.83 |
| 2 | 13.966 | 2486.7 | 50.17 |



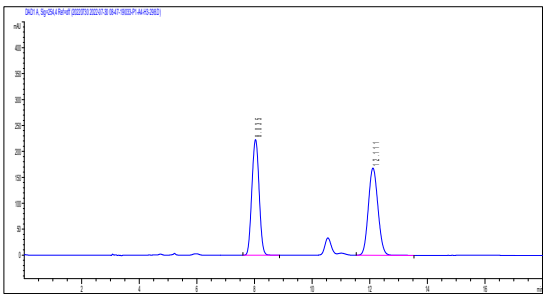
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.209 | 21276.8 | 95.53 |
| 2 | 13.975 | 996.4 | 4.47 |



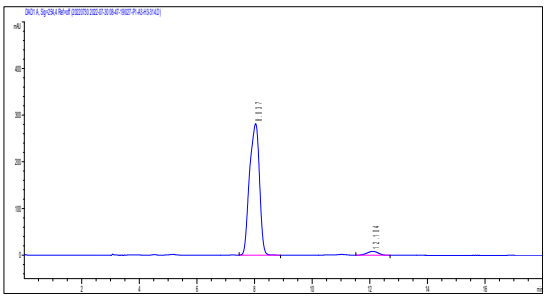

**(*R, Z*)-4-(tert-butyl)-2-(1-(5-chloro-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-phenol (9)**

The title compound was isolated as a white solid (46.6 mg, 84%). **$^1$H NMR (600 MHz, CDCl$_3$)** $\delta$ 7.70 (d, $J$ = 1.9 Hz, 1H), 7.56 (d, $J$ = 0.8 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.24 (s, 1H), 7.14 (dd, $J$ = 8.9, 2.0 Hz, 1H), 7.12 – 7.05 (m, 3H), 7.04 – 7.00 (m, 2H), 6.90 (d, $J$ = 8.6 Hz, 3H), 6.71 – 6.66 (m, 2H), 6.33 (d, $J$ = 2.5 Hz, 1H), 6.20 (s, br, 1H), 2.23 (s, 3H), 0.89 (s, 9H). **$^{13}$C NMR (150 MHz, CDCl$_3$)** $\delta$ 151.5, 143.8, 143.5, 137.4, 136.9, 136.1, 133.8, 132.4, 129.5, 128.9, 128.7, 128.6, 128.3, 127.7, 127.4, 127.2, 127.1, 126.6, 125.1, 124.0, 121.9, 117.6, 113.2, 112.4, 33.8, 31.2, 21.6. **HRMS (ESI)**: calcd. for $C_{33}H_{30}ClNNaO_3S^+$ $[M+Na]^+$ : 578.1527, found : 578.1513. **$[\alpha]_D^{20}$** = +36 (c = 0.1, $CHCl_3$).

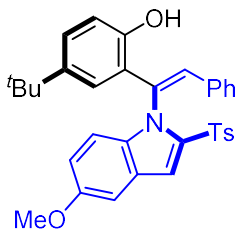
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 8.037 min, tr (minor) = 12.104 min, 96.5:3.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.035 | 3900.4 | 50.00 |
| 2 | 12.111 | 3900.3 | 50.00 |



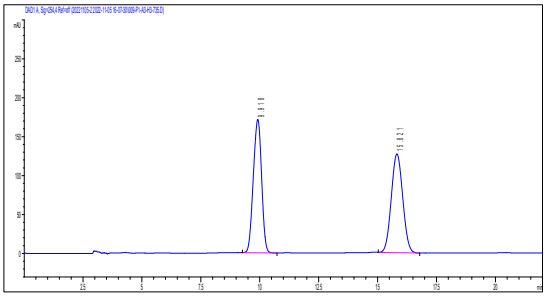
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.037 | 6727.3 | 96.71 |
| 2 | 12.104 | 228.9 | 3.29 |



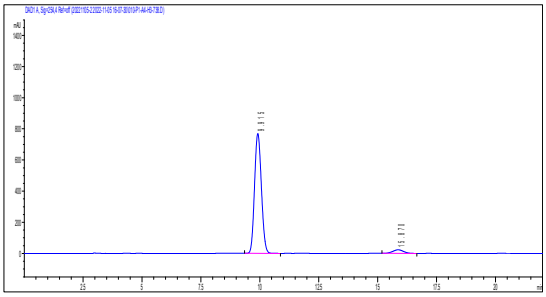

**(*R*, *Z*)-4-(tert-butyl)-2-(1-(5-methoxy-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-phenol (10)**

The title compound was isolated as a pale-yellow solid (53.4 mg, 97%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.54 (d, $J$ = 0.9 Hz, 1H), 7.36 (dd, $J$ = 8.3, 1.5 Hz, 2H), 7.19 (d, $J$ = 2.2 Hz, 1H), 7.11 - 7.08 (m, 2H), 7.07 – 7.04 (m, 2H), 7.03 – 6.99 (m, 2H), 6.91 – 6.85 (m, 4H), 6.72 – 6.68 (m, 2H), 6.38 (d, $J$ = 2.5 Hz, 1H), 6.27 (s, br, 1H), 3.83 (s, 3H), 2.22 (s, 3H), 0.89 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 155.4, 151.5, 143.4, 143.3, 137.9, 134.3, 133.98, 133.95, 132.1, 129.4, 129.3, 128.5, 128.40, 128.36, 127.1, 127.0, 126.3, 125.5, 124.2, 118.5, 117.6, 112.9, 112.8, 102.4, 55.7, 33.8, 31.2, 21.5. **HRMS (ESI)**: calcd. for $C_{34}H_{33}NNaO_4S^+$ $[M+Na]^+$ : 574.2023, found : 574.2019. **$[\alpha]_D^{20}$** = +40 (c = 0.1, $CHCl_3$).

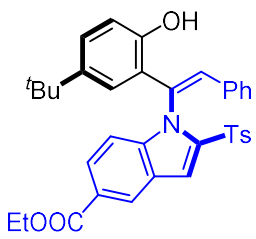
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.915 min, tr (minor) = 15.870 min, 95.5:4.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.918 | 4187.1 | 49.52 |
| 2 | 15.821 | 4267.8 | 50.48 |



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.915 | 15544.4 | 95.51 |
| 2 | 15.870 | 731.2 | 4.49 |

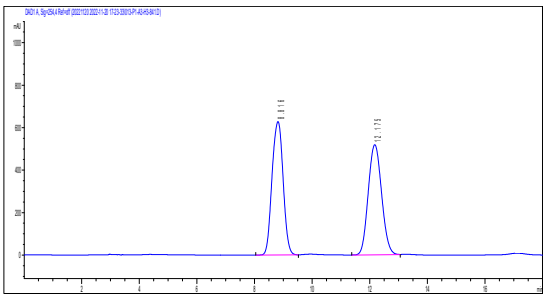



**ethyl (*R*, *Z*)-1-(1-(5-(tert-butyl)-2-hydroxyphenyl)-2-phenylvinyl)-2-tosyl-1H-indole-5-carboxylate (11)**

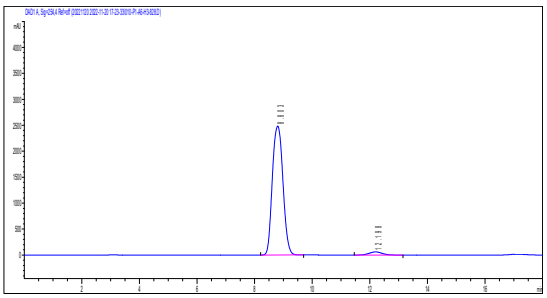
The title compound was isolated as a pale-yellow solid (49.8 mg, 84%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 8.53 – 8.49 (m, 1H), 7.88 (dd, $J$ = 8.9, 1.6 Hz, 1H), 7.71 (s, 1H), 7.38 (d, $J$ = 8.3 Hz, 2H), 7.29 – 7.27 (m, 1H), 7.19 (d, $J$ = 8.9 Hz, 1H), 7.10 (dd, $J$ = 8.5, 2.4 Hz, 1H), 7.06 – 7.03 (m, 1H), 7.02 – 6.98 (m, 2H), 6.90 (d, $J$ = 8.4 Hz, 3H), 6.70 (d, $J$ = 7.3 Hz, 2H), 6.32 (d, $J$ = 2.4 Hz, 1H), 6.27 – 6.19 (m, 1H), 4.37 (qd, $J$ = 7.1, 1.2 Hz, 2H), 2.22 (s, 3H), 1.39 (t, $J$ = 7.1 Hz, 3H), 0.87 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 166.9, 151.5, 143.8, 143.5, 140.8, 137.4, 136.6, 133.8, 132.6, 129.5, 128.9, 128.64, 128.55, 128.3, 127.6, 127.22, 127.15, 125.8, 125.3, 124.9,

124.7, 124.0, 117.6, 114.3, 111.7, 61.1, 33.8, 31.1, 21.6, 14.5. **HRMS (ESI)**: calcd. for $C_{36}H_{35}NNaO_5S^+$ $[M+Na]^+$ : 616.2128, found : 616.2140. **$[\alpha]_D^{20}$** = +10 (c = 0.1, $CHCl_3$).

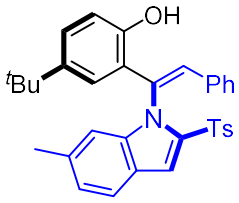
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 8.803 min, tr (minor) = 12.198 min, 97:3 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.816 | 16740.7 | 50.12 |
| 2 | 12.175 | 16662.3 | 49.88 |



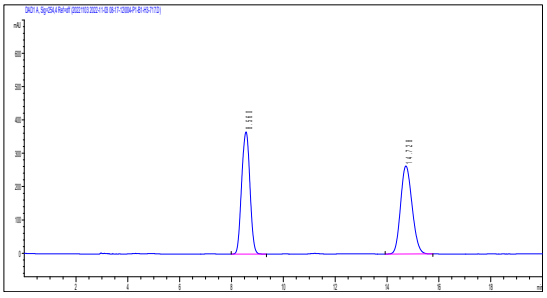
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.803 | 63469.9 | 97.14 |
| 2 | 12.198 | 1869.9 | 2.86 |

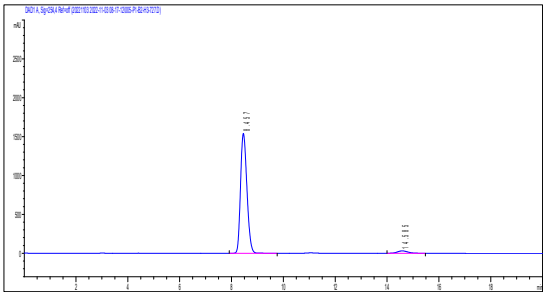



**(*R*, *Z*)-4-(tert-butyl)-2-(1-(6-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-phenol (12)**

The title compound was isolated as a pale-yellow solid (49.8 mg, 93%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.60 (d, $J$ = 8.4 Hz, 1H), 7.59 (d, $J$ = 0.9 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.23 (s, 1H), 7.10 (dd, $J$ = 8.6, 2.5 Hz, 1H), 7.07 – 7.03 (m, 1H), 7.02 – 6.97 (m, 4H), 6.92 – 6.86 (m, 3H), 6.72 – 6.66 (m, 2H), 6.42 (d, $J$ = 2.5 Hz, 1H), 6.33 (s, br, 1H), 2.28 (s, 3H), 2.22 (s, 3H), 0.91 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.5, 143.4, 143.2, 139.3, 137.9, 137.3, 134.1, 133.7, 132.3, 129.4, 129.3, 128.5, 128.2, 127.1, 127.0, 125.5, 124.40, 124.38, 124.3, 123.8, 122.2, 117.6, 113.6, 111.5, 33.8, 31.2, 22.2, 21.5. **HRMS (ESI)**: calcd. for $C_{34}H_{33}NNaO_3S^+$ $[M+Na]^+$ : 558.2073, found : 558.2064. **$[\alpha]_D^{20}$** = +52 (c = 0.1, $CHCl_3$).

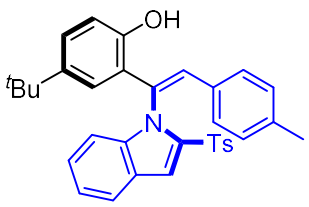
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 8.457 min, tr (minor) = 14.585 min, 97:3 e.r.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.560 | 8130.0 | 49.98 |
| 2 | 14.728 | 8136.3 | 50.02 |

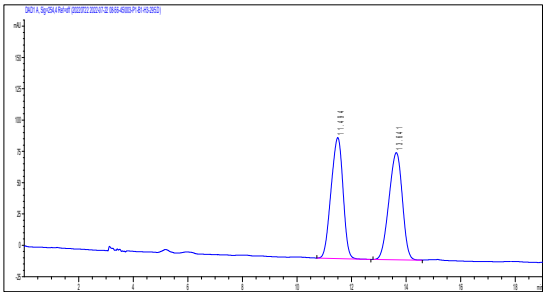
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.457 | 26299.7 | 97.01 |
| 2 | 14.585 | 812.1 | 2.99 |

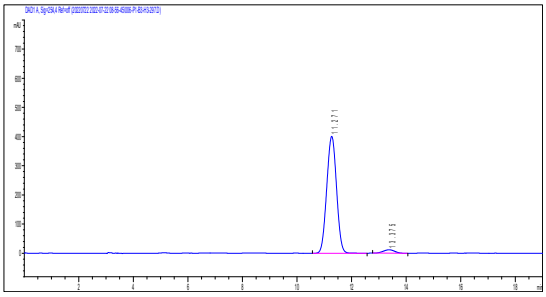



**(*R, Z*)-4-(tert-butyl)-2-(2-(p-tolyl)-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (13)**

The title compound was isolated as a pale-yellow solid (51.9 mg, 97%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.73 (dd, $J$ = 8.0, 1.1 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.41 – 7.34 (m, 2H), 7.23 – 7.14 (m, 4H), 7.10 (dd, $J$ = 8.6, 2.5 Hz, 1H), 6.93 – 6.83 (m, 5H), 6.46 (s, br, 1H), 6.45 – 6.40 (m, 2H), 6.28 – 6.15 (m, 1H), 2.22 (s, 3H), 2.06 (s, 3H), 0.89 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.5, 143.5, 143.4, 138.8, 137.9, 134.6, 133.9, 132.6, 129.44, 129.37, 129.2, 129.0, 128.4, 127.11, 127.08, 127.04, 127.02, 126.9, 126.0, 125.7, 125.4, 124.3, 122.6, 122.1, 117.7, 113.4, 112.0, 33.8, 31.2, 21.5, 21.4. **HRMS (ESI)**: calcd. for $C_{34}H_{33}NNaO_3S^+$ $[M+Na]^+$ : 558.2073, found : 558.2070. **$[\alpha]_D^{20}$** = +64 (c = 0.1, $CHCl_3$).

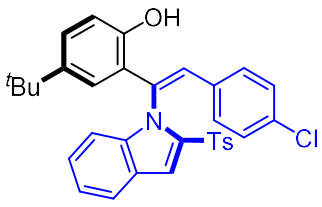
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 11.271 min, tr (minor) = 13.375 min, 96.5:3.5 e.r.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.494 | 2938.6 | 50.20 |
| 2 | 13.641 | 2915.3 | 49.80 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.271 | 9987.1 | 96.65 |
| 2 | 13.375 | 345.8 | 3.35 |

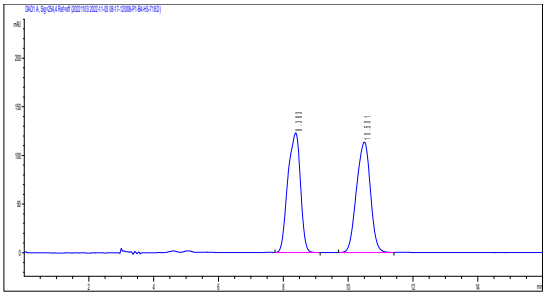



**(*R, Z*)-4-(tert-butyl)-2-(2-(4-chlorophenyl)-1-(2-tosyl-1H-indol-1-yl)-vinyl)phenol (14)**

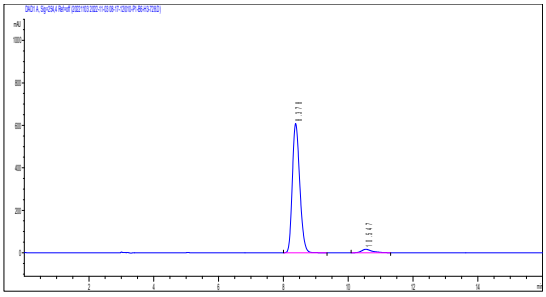
The title compound was isolated as a pale-yellow solid (50.5 mg, 91%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.77 – 7.72 (m, 1H), 7.67 – 7.62 (m, 1H), 7.40

(dd, $J$ = 8.5, 2.0 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.20 – 7.14 (m, 2H), 7.09 (dd, $J$ = 8.5, 2.3 Hz, 1H), 6.94 (d, $J$ = 8.5 Hz, 2H), 6.91 – 6.85 (m, 3H), 6.56 (d, $J$ = 8.6 Hz, 2H), 6.38 – 6.34 (m, 1H), 6.32 - 6.25 (m, 1H), 2.23 (s, 3H), 0.89 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.5, 143.7, 143.4, 138.6, 137.5, 134.6, 134.0, 132.6, 131.0, 130.0, 129.6, 129.4, 128.7, 127.2, 127.1, 125.9, 125.1, 124.3, 122.8, 122.3, 117.6, 113.6, 111.8, 33.8, 31.1, 21.5. **HRMS (ESI)**: calcd. for $C_{33}H_{30}ClNNaO_3S^+$ $[M+Na]^+$ : 578.1527, found : 578.1524. **$[\alpha]_D^{20}$** = +30 (c = 0.1, $CHCl_3$).

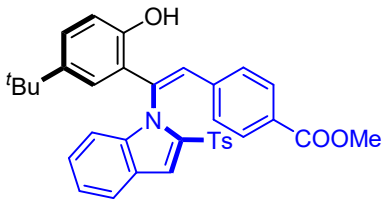
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 8.378 min, tr (minor) = 10.547 min, 96.5:3.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.383 | 3312.3 | 49.52 |
| 2 | 10.501 | 3376.4 | 50.48 |



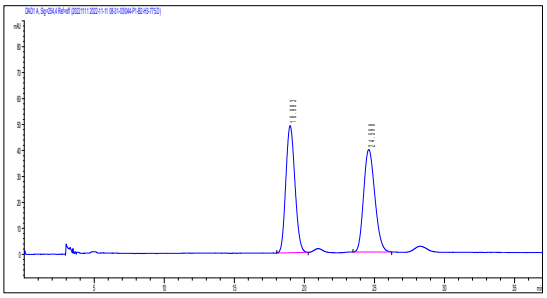
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.378 | 9676.0 | 96.42 |
| 2 | 10.547 | 358.9 | 3.58 |



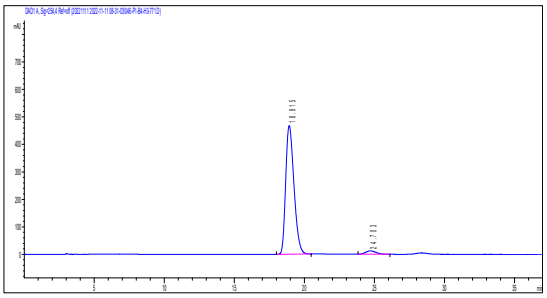

**methyl (*R*, *Z*)-4-(2-(5-(tert-butyl)-2-hydroxyphenyl)-2-(2-tosyl-1H-indol-1-yl)vinyl)benzoate (15)**

The title compound was isolated as a pale-yellow solid (51.5 mg, 89%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.75 – 7.71 (m, 1H), 7.68 – 7.61 (m, 3H), 7.40 (d, $J$ = 8.4 Hz, 2H), 7.33 (s, 1H), 7.21 – 7.14 (m, 2H), 7.14 – 7.08 (m, 2H), 6.90 – 6.85 (m, 3H), 6.72 (d, $J$ = 8.5 Hz, 2H), 6.35 (d, $J$ = 2.5 Hz, 1H), 6.34 (s, br, 1H), 3.82 (s, 3H), 2.20 (s, 3H), 0.89 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 166.7, 151.6, 143.7, 143.4, 138.7, 137.5, 134.7, 131.7, 131.1, 129.7, 129.4, 129.3, 128.2, 127.4, 127.2, 127.0, 125.9, 124.9, 124.4, 122.8, 122.3, 117.6, 113.7, 111.7, 52.2, 33.8, 31.1, 21.5. **HRMS (ESI)**: calcd. for $C_{35}H_{33}NNaO_5S^+$ $[M+Na]^+$ : 602.1972, found : 602.1967. **$[\alpha]_D^{20}$** = +60 (c = 0.1, $CHCl_3$).

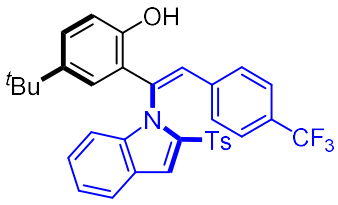
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 18.915 min, tr (minor) = 24.703 min, 97:3 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 18.983 | 2209.3 | 50.10 |
| 2 | 24.598 | 2200.5 | 49.90 |



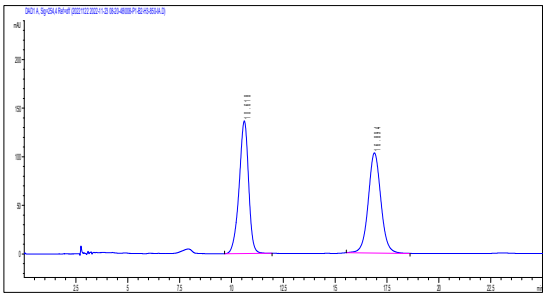
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 18.915 | 19199.5 | 96.86 |
| 2 | 24.703 | 622.9 | 3.14 |



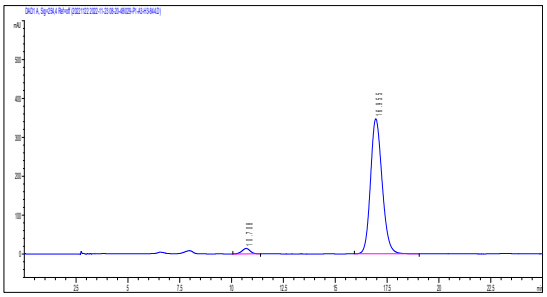

**(*R*, *Z*)-4-(tert-butyl)-2-(1-(2-tosyl-1H-indol-1-yl)-2-(4-(trifluoromethyl)phenyl)vinyl)phenol (16)**

The title compound was isolated as a pale-yellow solid (48.9 mg, 83%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.75 (dt, $J$ = 8.0, 1.0 Hz, 1H), 7.65 (d, $J$ = 0.8 Hz, 1H), 7.40 (d, $J$ = 8.3 Hz, 2H), 7.31 (s, 1H), 7.25 – 7.17 (m, 4H), 7.14 (dd, $J$ = 8.3, 1.0 Hz, 1H), 7.12 (dd, $J$ = 8.6, 2.4 Hz, 1H), 6.91 – 6.86 (m, 3H), 6.73 (d, $J$ = 8.2 Hz, 2H), 6.39 (d, $J$ = 2.5 Hz, 1H), 6.23 (s, br, 1H), 2.21 (s, 3H), 0.90 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.6, 143.8, 143.6, 138.7, 137.5, 134.6, 131.8, 130.7, 129.7 (q, $J_{C\text{-}F}$ = 32.6 Hz), 129.4, 128.6, 127.5, 127.22, 127.20, 125.9, 125.4 (q, $J_{C\text{-}F}$ = 3.9 Hz), 124.9, 124.5, 123.9 (q, $J_{C\text{-}F}$ = 271.9 Hz). 123.0, 122.9, 122.4, 117.8, 113.8, 111.7, 33.8, 31.1, 21.5. **$^{19}$F NMR (376 MHz, $CDCl_3$)** $\delta$ -62.7. **HRMS (ESI)**: calcd. for $C_{34}H_{30}F_3NNaO_3S^+$ $[M+Na]^+$ : 612.1791, found : 612.1789. **$[\alpha]_D^{20}$** = +22 (c = 0.1, $CHCl_3$).

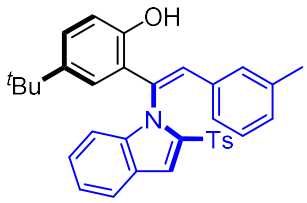
**HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 16.955 min, tr (minor) = 10.708 min, 97:3 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.618 | 4313.8 | 49.84 |
| 2 | 16.894 | 4342.3 | 50.16 |



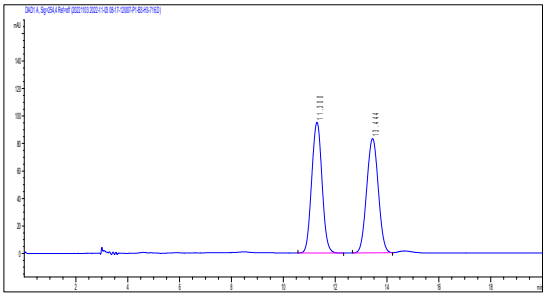
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.708 | 384.6 | 2.77 |
| 2 | 16.955 | 13497.6 | 97.23 |



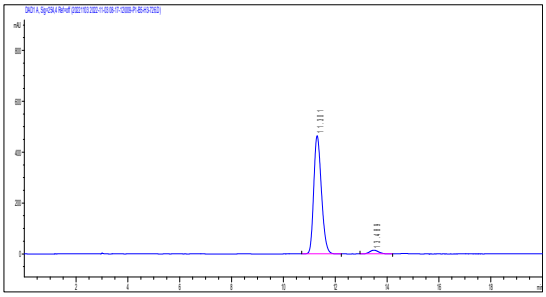
**(*R, Z*)-4-(tert-butyl)-2-(2-(m-tolyl)-1-(2-tosyl-1H-indol-1-yl)vinyl)-phenol (17)**

The title compound was isolated as a pale-yellow solid (44.9 mg, 84%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.73 (dt, $J$ = 8.0, 1.1 Hz, 1H), 7.63 (d, $J$ = 0.8 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.23 – 7.19 (m, 1H), 7.19 – 7.14 (m, 3H), 7.10 (dd, $J$ = 8.5, 2.4 Hz, 1H), 6.93 – 6.84 (m, 5H), 6.46 (s, br, 1H), 6.42 (d, $J$ = 2.6 Hz, 2H), 6.26 (s, 1H), 2.22 (s, 3H), 2.06 (s, 3H), 0.89 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.5, 143.5, 143.3, 138.8, 137.9, 137.8, 134.5, 133.8, 132.5, 129.43, 129.36, 129.2, 128.9, 128.4, 127.1, 127.0, 126.9, 125.9, 125.6, 125.3, 124.3, 122.6, 122.1, 117.6, 113.4, 112.0, 33.8, 31.2, 21.6, 21.4. **HRMS (ESI)**: calcd. for $C_{34}H_{33}NNaO_3S^+$ $[M+Na]^+$ : 558.2073, found : 558.2066; **$[\alpha]_D^{20}$** = +56 (c = 0.1, $CHCl_3$).

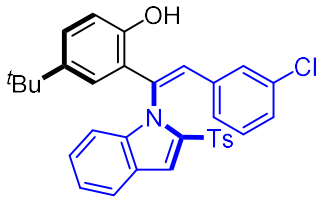
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 11.301 min, tr (minor) = 13.489 min, 96.5:3.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.300 | 2632.9 | 50.43 |
| 2 | 13.444 | 2587.7 | 49.57 |



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.301 | 9552.7 | 96.45 |
| 2 | 13.489 | 351.3 | 3.55 |

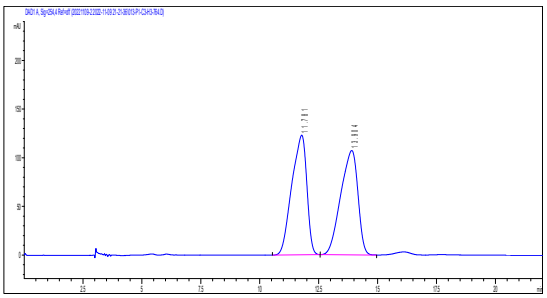


**(*R, Z*)-4-(tert-butyl)-2-(2-(3-chlorophenyl)-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (18)**

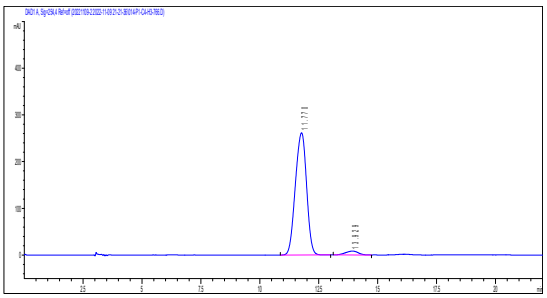
The title compound was isolated as a pale-yellow solid (47.7 mg, 86%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.75 (dt, $J$ = 8.0, 1.0 Hz, 1H), 7.66 (s, 1H), 7.42 (d, $J$ = 8.0 Hz, 2H), 7.25 – 7.16 (m, 3H), 7.16 – 7.13 (m, 1H), 7.11 (dd, $J$ = 8.5, 2.4 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.90 (d, $J$ = 8.1 Hz, 2H), 6.89 – 6.84 (m, 2H), 6.67 – 6.62 (m, 1H), 6.45 – 6.41 (m, 1H), 6.40 (d, $J$ = 2.5 Hz, 1H), 6.29 (s, br, 1H), 2.23 (s, 3H), 0.90 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.6, 143.7, 143.5, 138.7, 137.5, 135.9, 134.6, 134.2, 130.9, 130.8, 129.7, 129.4, 128.7, 128.2, 127.3, 127.2, 127.1, 126.0, 125.9, 125.0, 124.5, 122.9, 122.3, 117.7, 113.7, 111.7, 33.8, 31.2, 21.6. **HRMS**

**(ESI)**: calcd. for $C_{33}H_{30}ClNNaO_3S^+$ $[M+Na]^+$ : 578.1527, found : 578.1523. **$[\alpha]_D^{20}$** = +60 (c = 0.1, $CHCl_3$).

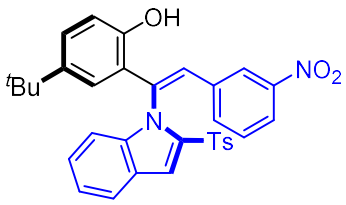
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 11.770 min, tr (minor) = 13.929 min, 96.5:3.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.781 | 5450.3 | 50.06 |
| 2 | 13.904 | 5437.2 | 49.94 |



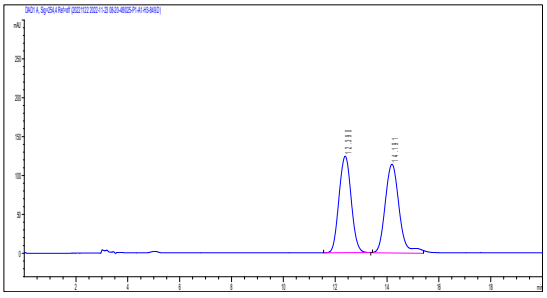
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 11.770 | 8653.7 | 96.51 |
| 2 | 13.929 | 313.0 | 3.49 |

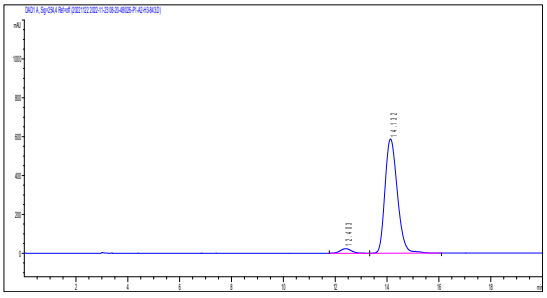



**(*R, Z*)-4-(tert-butyl)-2-(2-(3-nitrophenyl)-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (19)**

The title compound was isolated as a yellow solid (35.1 mg, 62%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.86 (dt, $J$ = 8.4, 1.5 Hz, 1H), 7.78 – 7.34 (m, 1H), 7.67 (s, 1H), 7.48 (s, 1H), 7.43 (d, $J$ = 8.0 Hz, 2H), 7.37 (s, 1H), 7.24 – 7.16 (m, 2H), 7.16 – 7.09 (m, 3H), 6.92 – 6.84 (m, 4H), 6.45 – 6.39 (m, 1H), 6.25 – 6.19 (m, 1H), 2.21 (s, 3H), 0.91 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.6, 148.2, 143.9, 143.7, 138.5, 137.4, 135.9, 134.7, 133.6, 132.7, 129.7, 129.4, 127.7, 127.33, 127.26, 126.0, 124.7, 124.5, 123.4, 123.1, 122.6, 122.5, 117.8, 114.0, 111.5, 33.9, 31.2, 21.5. **HRMS (ESI)**: calcd. for $C_{33}H_{30}N_2NaO_5S^+$ $[M+Na]^+$ : 589.1768, found : 589.1765. **$[\alpha]_D^{20}$** = +56 (c = 0.1, $CHCl_3$).

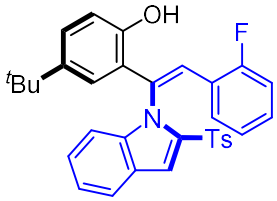
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 14.132 min, tr (minor) = 12.403 min, 96.5:3.5 e.r.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.390 | 4051.8 | 48.70 |
| 2 | 14.191 | 4268.9 | 51.30 |

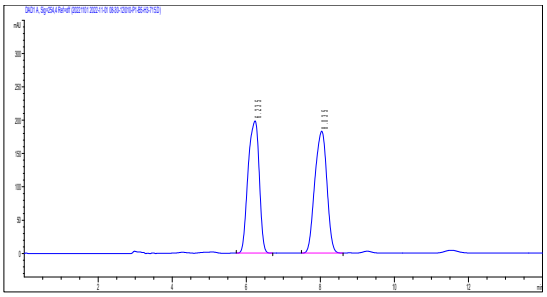
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.403 | 680.0 | 3.38 |
| 2 | 14.132 | 19431.1 | 96.62 |



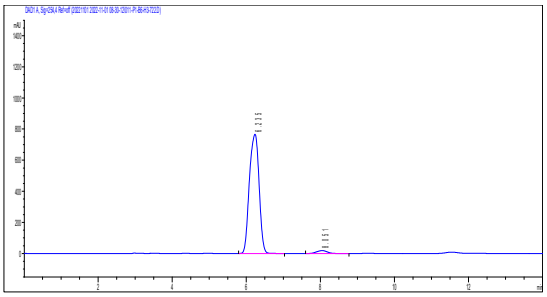

**(*R, Z*)-4-(tert-butyl)-2-(2-(2-fluorophenyl)-1-(2-tosyl-1H-indol-1-yl)vinyl)-phenol (20)**

The title compound was isolated as a pale-yellow solid (41.5 mg, 77%). **$^{1}$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.70 (dd, $J$ = 8.1, 1.1 Hz, 1H), 7.62 (d, $J$ = 0.9 Hz, 1H), 7.44 (s, 1H), 7.37 (d, $J$ = 8.3 Hz, 2H), 7.23 – 7.12 (m, 3H), 7.10 (dd, $J$ = 8.6, 2.4 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.95 - 6.86 (m, 4H), 6.64 – 6.56 (m, 1H), 6.41 – 6.35 (m, 2H), 6.22 (s, br, 1H), 2.23 (s, 3H), 0.89 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 160.4 (d, $J$ = 249.8 Hz), 151.7, 143.5, 143.3, 138.8, 137.6, 134.8, 131.4, 129.9 (d, $J$ = 8.3 Hz), 129.4, 127.8, 127.4, 127.01, 126.98, 126.5, 125.8, 125.0, 124.5, 124.25 (d, $J$ = 3.3 Hz), 123.9 (d, $J$ = 6.1 Hz), 122.7, 122.3 (d, $J$ = 12.1 Hz), 122.2, 120.8, 117.6, 115.2 (d, $J$ = 22.0 Hz), 113.7, 111.7, 33.8, 31.1, 21.6. **$^{19}$F NMR (376 MHz, $CDCl_3$)** $\delta$ -115.3. **HRMS (ESI)**: calcd. for $C_{33}H_{30}FNNaO_3S^+$ $[M+Na]^+$ : 562.1823, found : 562.1818. **$[\alpha]_D^{20}$** = +32 (c = 0.1, $CHCl_3$).

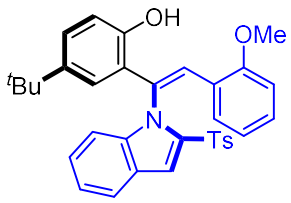
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 6.235 min, tr (minor) = 8.051 min, 97.5:2.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.235 | 4147.1 | 50.05 |
| 2 | 8.035 | 4138.7 | 49.95 |



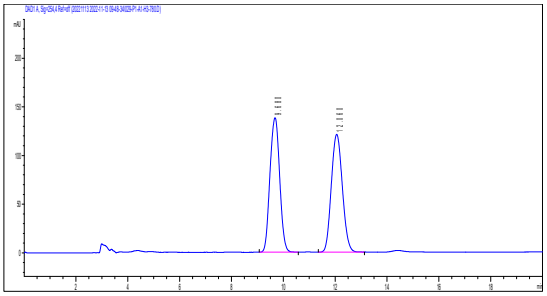
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.235 | 13898.9 | 97.40 |
| 2 | 8.051 | 371.0 | 2.60 |



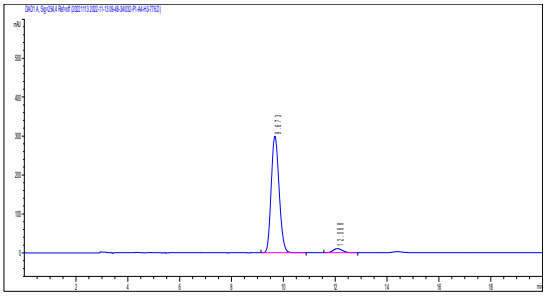
**(*R*, *Z*)-4-(tert-butyl)-2-(2-(2-methoxyphenyl)-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (21)**

The title compound was isolated as a pale-yellow solid (30.9 mg, 56%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.70 – 7.65 (m, 1H), 7.58 (s, 1H), 7.47 (s, 1H), 7.34 (d, $J$ = 8.3 Hz, 2H), 7.18 (d, $J$ = 3.7 Hz, 2H), 7.15 – 7.09 (m, 1H), 7.08 (dd, $J$ = 8.6, 2.5 Hz, 1H), 7.04 - 7.00 (m, 1H), 6.90 (dd, $J$ = 8.4, 2.9 Hz, 3H), 6.74 (d, $J$ = 8.2 Hz, 1H), 6.54 – 6.49 (m, 1H), 6.48 – 6.43 (m, 1H), 6.34 (d, $J$ = 2.5 Hz, 1H), 6.24 (s, br, 1H), 3.83 (s, 3H), 2.24 (s, 3H), 0.86 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 157.0, 151.7, 143.3, 143.1, 138.9, 138.0, 134.8, 129.6, 129.4, 129.2, 127.5, 127.01, 126.95, 126.9, 126.7, 125.8, 125.6, 124.3, 123.3, 122.5, 121.9, 120.7, 117.4, 113.4, 112.0, 110.3, 55.6, 33.7, 31.2, 21.6. **HRMS (ESI)**: calcd. for $C_{34}H_{33}NNaO_4S^+$ $[M+Na]^+$ : 574.2023, found : 574.2018. **$[\alpha]_D^{20}$** = +102 (c = 0.1, $CHCl_3$).

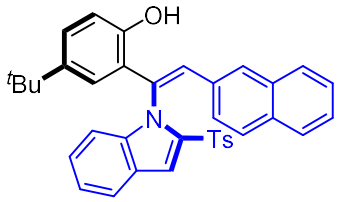
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.673 min, tr (minor) = 12.088 min, 96:4 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.680 | 3582.6 | 50.04 |
| 2 | 12.060 | 3576.7 | 49.96 |



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.673 | 6354.3 | 95.91 |
| 2 | 12.088 | 270.7 | 4.09 |

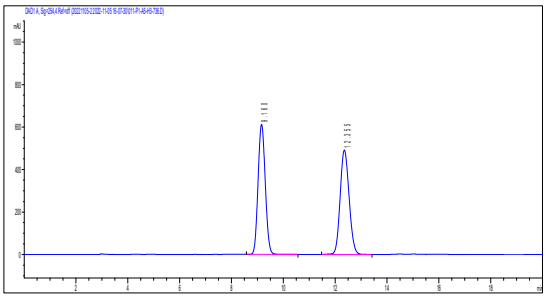


**(*R*, *Z*)-4-(tert-butyl)-2-(2-(naphthalen-2-yl)-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (22)**

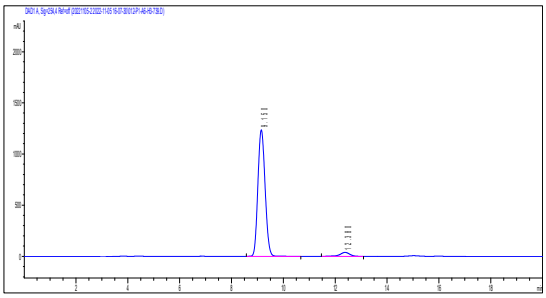
The title compound was isolated as a pale-yellow solid (39.4 mg, 69%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.79 – 7.74 (m, 1H), 7.70 (s, 1H), 7.63 – 7.58 (m, 1H), 7.55 – 7.50 (m, 1H), 7.43 – 7.39 (m, 3H), 7.39 – 7.33 (m, 3H), 7.26 – 7.24 (m, 1H), 7.23 – 7.20 (m, 1H), 7.19 – 7.11 (m, 3H), 6.92 (d, $J$ = 8.6 Hz, 1H), 6.79 (d, $J$ = 8.0 Hz, 2H), 6.52 (dd, $J$ = 8.7, 1.8 Hz, 1H), 6.48 (d, $J$ = 2.5 Hz, 1H), 6.37 (s, br, 1H), 2.08 (s, 3H), 0.93 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.6, 143.6, 143.4, 139.0, 137.6, 134.7, 133.2, 133.0, 132.4, 131.7, 129.6, 129.3,

129.2, 128.4, 128.2, 127.4, 127.2, 127.1, 127.0, 126.6, 126.2, 125.9, 125.6, 125.0, 124.5, 122.8, 122.2, 117.7, 113.6, 111.9, 33.8, 31.2, 21.4. **HRMS (ESI)**: calcd. for $C_{37}H_{33}NNaO_3S^+$ $[M+Na]^+$ : 594.2073, found : 594.2069. **$[\alpha]_D^{20}$** = +14 (c = 0.1, $CHCl_3$).

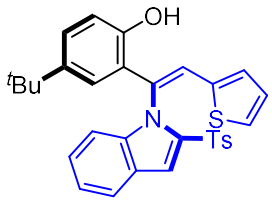
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 9.150 min, tr (minor) = 12.380 min, 96:4 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.160 | 11789.6 | 50.05 |
| 2 | 12.355 | 11766.1 | 49.95 |



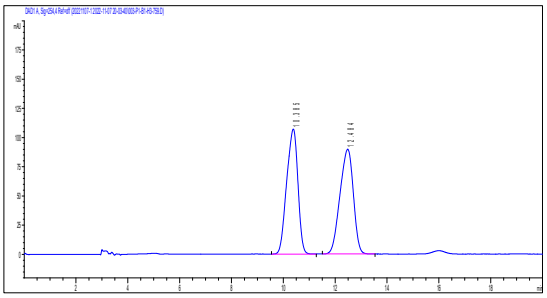
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.150 | 23783.8 | 95.94 |
| 2 | 12.380 | 1007.4 | 4.06 |



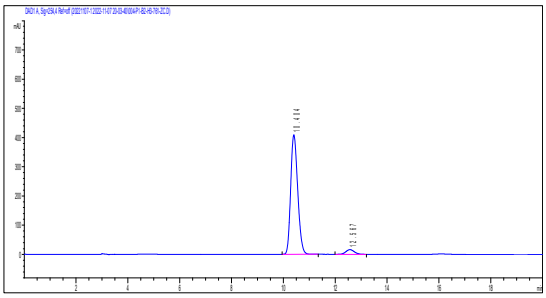

**(*R, Z*)-4-(tert-butyl)-2-(2-(thiophen-2-yl)-1-(2-tosyl-1H-indol-1-yl)vinyl)-phenol (23)**

The title compound was isolated as a yellow solid (45.3 mg, 86%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.79 (dt, $J$ = 8.1, 1.0 Hz, 1H), 7.68 (s, 1H), 7.64 (d, $J$ = 0.9 Hz, 1H), 7.43 (d, $J$ = 8.3 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.26 – 7.21 (m, 2H), 7.07 (dd, $J$ = 8.5, 2.4 Hz, 1H), 6.97 (dt, $J$ = 5.0, 1.0 Hz, 1H), 6.89 – 6.84 (m, 4H), 6.79 (dd, $J$ = 5.0, 3.7 Hz, 1H), 6.28 (d, $J$ = 2.4 Hz, 1H), 6.07 (s, br, 1H), 2.21 (s, 3H), 0.87 (s, 10H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.20, 151.18, 143.6, 143.3, 139.1, 137.5, 137.3, 134.3, 130.1, 129.3, 128.5, 127.6, 127.5, 126.9, 126.8, 126.5, 126.3, 126.2, 124.4, 124.2, 122.9, 122.2, 117.4, 113.4, 111.8, 33.8, 31.1, 21.5. **HRMS (ESI)**: calcd. for $C_{31}H_{29}NNaO_3S_2^+$ $[M+Na]^+$ : 550.1481, found : 550.1478. **$[\alpha]_D^{20}$** = +80 (c = 0.1, $CHCl_3$).

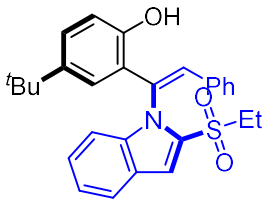
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 10.404 min, tr (minor) = 12.567 min, 95.5:4.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.385 | 3216.2 | 50.01 |
| 2 | 12.484 | 3215.6 | 49.99 |



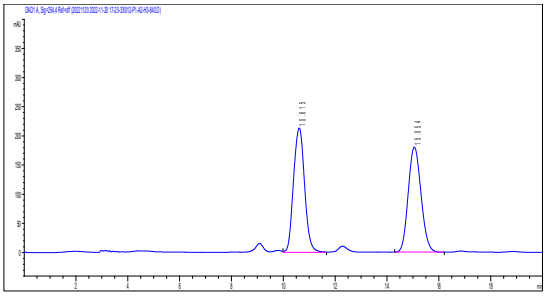
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.404 | 7690.5 | 95.50 |
| 2 | 12.567 | 362.4 | 4.50 |



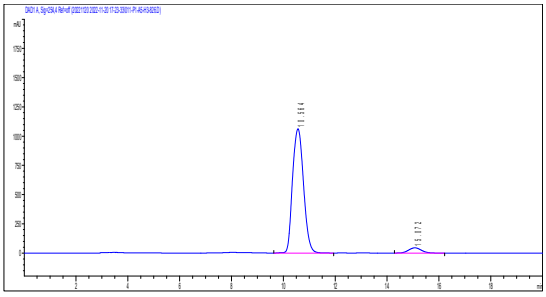
**(*R*, *Z*)-4-(tert-butyl)-2-(1-(2-(ethylsulfonyl)-1H-indol-1-yl)-2-phenylvinyl)-phenol (24)**

The title compound was isolated as a pale-yellow solid (28.5 mg, 62%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.75 – 7.70 (m, 1H), 7.45 (s, 1H), 7.28 (dd, $J$ = 8.6, 2.5 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.20 – 7.15 (m, 2H), 7.09 – 7.01 (m, 4H), 6.85 – 6.79 (m, 2H), 6.70 (d, $J$ = 2.4 Hz, 1H), 6.21 (s, br, 1H), 2.46 (dq, $J$ = 14.8, 7.4 Hz, 1H), 1.99 (dq, $J$ = 14.5, 7.3 Hz, 1H), 1.06 (s, 9H), 1.00 (t, $J$ = 7.4 Hz, 3H), **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.8, 144.0, 138.5, 134.0, 131.6, 131.4, 128.8, 128.7, 128.6, 128.3, 127.9, 127.1, 126.1, 125.6, 124.3, 122.8, 122.2, 118.1, 115.1, 112.0, 49.8, 34.0, 31.4, 7.8. **HRMS (ESI)**: calcd. for $C_{28}H_{29}NNaO_3S^+$ $[M+Na]^+$ : 482.1760, found : 482.1754. **$[\alpha]_D^{20}$** = +140 (c = 0.1, $CHCl_3$).

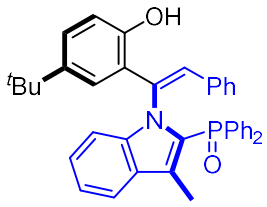
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 10.564 min, tr (minor) = 15.072 min, 95.5:4.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.615 | 6329.2 | 50.55 |
| 2 | 15.054 | 6191.2 | 49.45 |



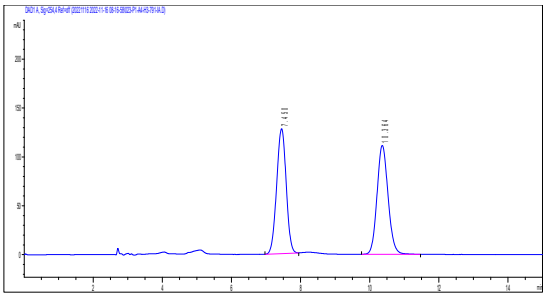
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.564 | 31299.5 | 95.34 |
| 2 | 15.072 | 1528.9 | 4.66 |



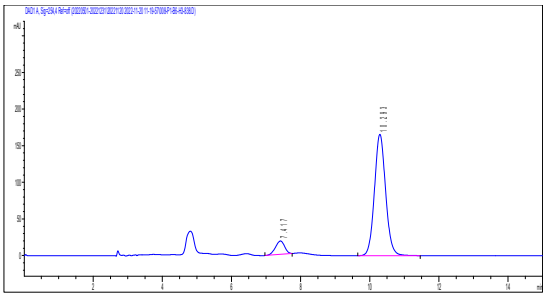
**(*R, Z*)-(1-(1-(5-(tert-butyl)-2-hydroxyphenyl)-2-phenylvinyl)-3-methyl-1H-indol-2-yl)diphenylphosphine oxide (25)**

The title compound was isolated as a white solid (31.4 mg, 54%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 9.27 (s, 1H), 7.60 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.55 - 7.50 (m, 1H), 7.50 – 7.45 (m, 2H), 7.43 – 7.33 (m, 5H), 7.30 (d, $J$ = 8.4 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.16 - 7.11 (m, 1H), 7.09 – 7.03 (m, 3H), 7.00 (s, 1H), 6.97 – 6.92 (m, 2H), 6.90 (dd, $J$ = 8.5, 2.4 Hz, 1H), 6.67 (d, $J$ = 8.6 Hz, 1H), 6.53 (d, $J$ = 2.4 Hz, 1H), 1.80 (s, 3H), 0.96 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 152.3, 142.2, 139.1 (d, $J$ = 8.1 Hz), 135.5, 133.3 (d, $J$ = 111.6 Hz), 132.4 (d, $J$ = 2.8 Hz), 132.1, 131.9 (d, $J$ = 2.8 Hz), 131.84, 131.76, 131.44, 131.37, 130.4 (d, $J$ = 110.2 Hz), 130.1, 128.9, 128.8, 128.6, 128.5, 128.42 (d, $J$ = 12.6 Hz), 128.40, 128.3, 127.6, 126.9, 125.9, 124.3, 123.9 (d, $J$ = 15.1 Hz), 122.7 (d, $J$ = 120.4 Hz), 120.6, 119.7, 119.2, 111.6, 33.7, 31.4, 10.9. **$^{31}$P NMR (243 MHz, $CDCl_3$)** $\delta$ 26.3; **HRMS (ESI)**: calcd. for $C_{39}H_{36}NNaO_2P^+$ $[M+Na]^+$ : 604.2376, found : 604.2374. **$[\alpha]_D^{20}$** = +26 (c = 0.1, $CHCl_3$).

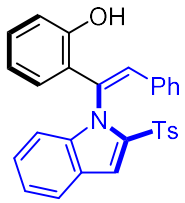
**HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.293 min, tr (minor) = 7.417 min, 91.5:8.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.450 | 2448.6 | 49.76 |
| 2 | 10.364 | 2472.1 | 50.24 |



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.417 | 334.9 | 8.26 |
| 2 | 10.293 | 3719.9 | 91.74 |

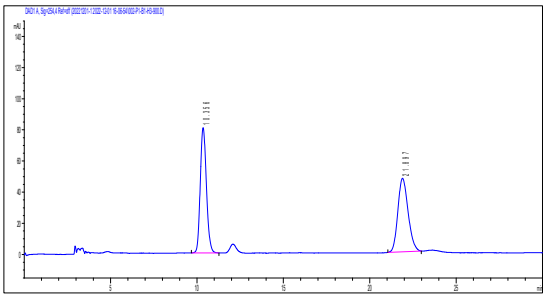


**(*R, Z*)-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (26)**

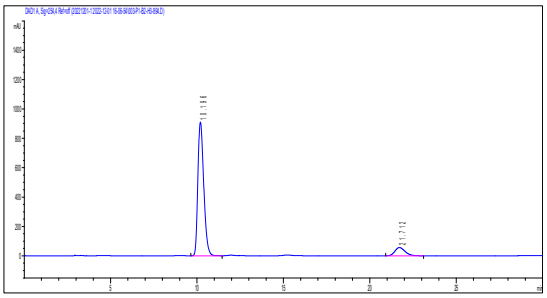
The title compound was isolated as a pale-yellow solid (23.3 mg, 50%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.76 – 7.70 (m, 1H), 7.60 (s, 1H), 7.39 (d, $J$ = 8.1 Hz, 2H), 7.27 (s, 1H), 7.23 – 7.14 (m, 3H), 7.11 – 7.06 (m, 1H), 7.06 – 7.02 (m, 1H), 7.01 – 6.95 (m, 3H), 6.90 (d, $J$ = 8.0 Hz, 2H), 6.66 – 6.59 (m, 2H), 6.51 – 6.46 (m, 1H), 6.46 – 6.39 (m, 2H), 2.23 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 153.8, 143.7, 138.5, 137.6, 134.5, 133.9, 132.6, 130.0, 129.4,

128.7, 128.5, 128.4, 127.8, 127.1, 126.9, 126.3, 125.9, 122.7, 122.2, 120.8, 118.0, 113.4, 112.0, 21.5. **HRMS (ESI)**: calcd. for $C_{29}H_{23}NNaO_3S^+$ $[M+Na]^+$ : 488.1291, found : 488.1292. **$[\alpha]_D^{20}$** = +42 (c = 0.1, $CHCl_3$).

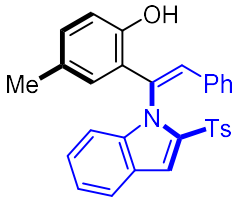
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 10.196 min, tr (minor) = 21.712 min, 90.5:9.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.356 | 1994.6 | 50.59 |
| 2 | 21.897 | 1948.4 | 49.41 |



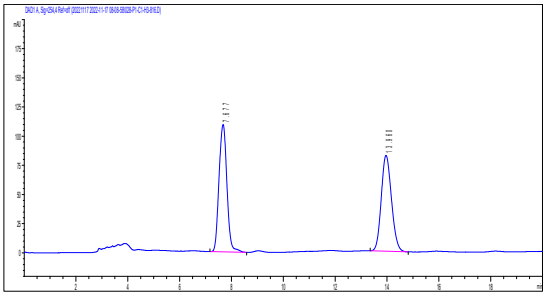
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.196 | 21543.6 | 90.38 |
| 2 | 21.712 | 2291.9 | 9.62 |

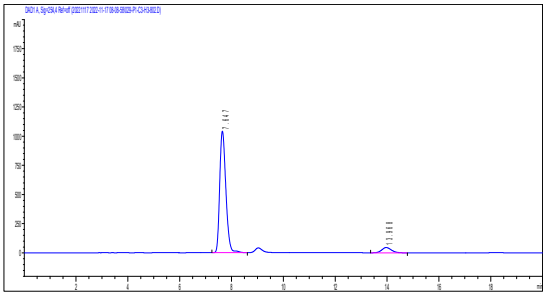



**(*R, Z*)-4-methyl-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (27)**

The title compound was isolated as a pale-yellow solid (29.7 mg, 62%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.74 (d, $J$ = 7.8 Hz, 1H), 7.64 (s, 1H), 7.35 (d, $J$ = 8.0 Hz, 2H), 7.24 (s, 1H), 7.21 – 7.13 (m, 3H), 7.05 – 6.96 (m, 3H), 6.93 – 6.82 (m, 4H), 6.63 (d, $J$ = 7.7 Hz, 2H), 6.21 (s, br, 1H), 6.12 (s, 1H), 2.25 (s, 3H), 1.82 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 151.9, 143.4, 138.5, 137.7, 134.4, 134.0, 132.2, 130.7, 129.9, 129.2, 128.8, 128.5, 128.32, 128.29, 127.9, 127.0, 126.8, 125.9, 125.7, 122.7, 122.1, 118.0, 113.5, 112.1, 21.5, 20.3. **HRMS (ESI)**: calcd. for $C_{30}H_{25}NNaO_3S^+$ $[M+Na]^+$ : 502.1447, found : 502.1443. **$[\alpha]_D^{20}$** = +34 (c = 0.1, $CHCl_3$).

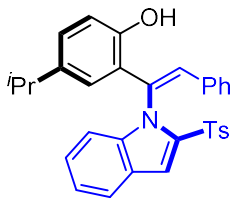
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 70:30, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 7.647 min, tr (minor) = 13.968 min, 94:6 e.r.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.677 | 2314.7 | 50.72 |
| 2 | 13.960 | 2248.8 | 49.28 |

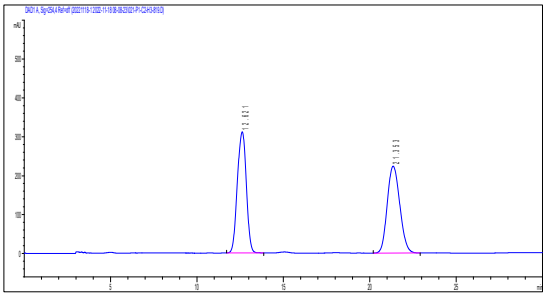
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.647 | 17175.0 | 93.75 |
| 2 | 13.968 | 1145.9 | 6.25 |

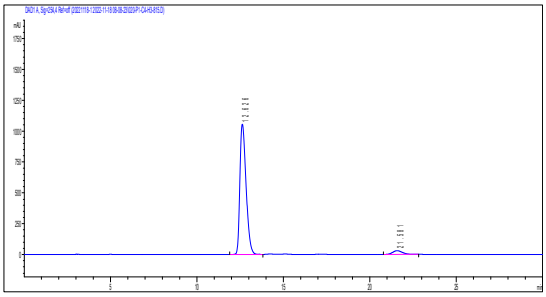



**(*R*, *Z*)-4-isopropyl-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (28)**

The title compound was isolated as a pale-yellow solid (37.5 mg, 74%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.73 (d, $J$ = 7.8 Hz, 1H), 7.63 (s, 1H), 7.36 (d, $J$ = 8.3 Hz, 2H), 7.22 – 7.14 (m, 4H), 7.06 – 6.95 (m, 4H), 6.93 (d, $J$ = 8.4 Hz, 1H), 6.90 (d, $J$ = 8.1 Hz, 2H), 6.69 – 6.62 (m, 2H), 6.30 – 6.21 (m, 2H), 2.42 – 2.34 (m, 1H), 2.23 (s, 3H), 0.87 (d, $J$ = 6.9 Hz, 3H), 0.85 (d, $J$ = 6.9 Hz, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.9, 143.5, 141.1, 138.6, 137.8, 134.5, 134.0, 132.4, 129.4, 129.0, 128.5, 128.4, 128.3, 127.7, 127.0, 126.9, 125.94, 125.90, 125.6, 122.7, 122.1, 118.1, 113.5, 112.0, 33.0, 23.93, 23.86, 21.5. **HRMS (ESI)**: calcd. for $C_{32}H_{29}NNaO_3S^+$ $[M+Na]^+$ : 530.1760, found : 530.1756. **$[\alpha]_D^{20}$** = +48 (c = 0.1, $CHCl_3$).

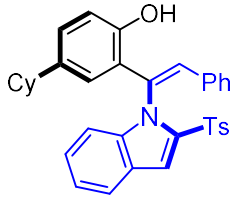
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 12.626 min, tr (minor) = 21.581 min, 95.5:4.5 e.r.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.621 | 11245.8 | 49.94 |
| 2 | 21.353 | 11274.7 | 50.06 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.626 | 26227.0 | 95.65 |
| 2 | 21.581 | 1194.1 | 4.35 |

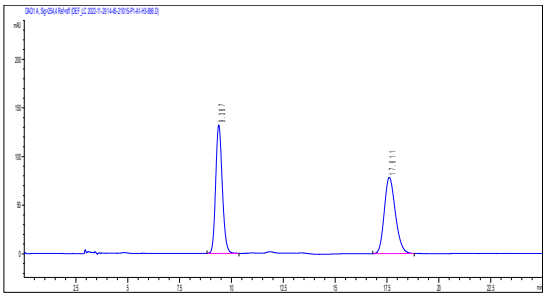



**(*R*, *Z*)-4-cyclohexyl-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (29)**

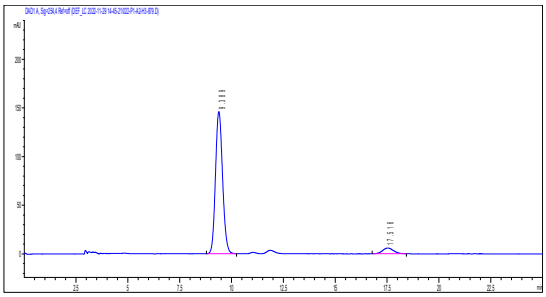
The title compound was isolated as a pale-yellow solid (26.3 mg, 48%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.76 – 7.72 (m, 1H), 7.65 (s, 1H), 7.34 (d, $J$ = 8.4 Hz, 2H), 7.22 – 7.14 (m, 4H), 7.05 – 6.92 (m, 5H), 6.89 (d, $J$ = 8.1 Hz, 2H), 6.67 – 6.61 (m, 2H), 6.26 (s, br, 1H), 6.24 (d, $J$ = 2.0 Hz, 1H), 2.23 (s, 3H), 1.96 (tt, $J$ = 12.0, 3.4 Hz, 1H), 1.69 – 1.63 (m, 2H), 1.63 – 1.57 (m, 1H), 1.50 – 1.45 (m, 1H), 1.36 – 1.31 (m, 1H), 1.21 – 1.11 (m, 2H), 1.07 (tt,

$J$ = 12.4, 3.2 Hz, 1H), 1.00 (qd, $J$ = 12.4, 12.0, 3.4 Hz, 2H). **$^{13}$C NMR (150 MHz, CDCl$_3$)** $\delta$ 152.0, 143.5, 140.4, 138.6, 137.7, 134.5, 134.0, 132.3, 129.4, 129.0, 128.5, 128.4, 128.3, 128.1, 127.0, 126.9, 126.1, 126.0, 125.9, 122.6, 122.1, 118.0, 113.5, 112.1, 43.3, 34.39, 34.35, 26.8, 26.0, 21.5. **HRMS (ESI)**: calcd. for $C_{35}H_{33}NNaO_3S^+$ $[M+Na]^+$ : 570.2073, found : 570.2079. **$[\alpha]_D^{20}$** = +18 (c = 0.1, $CHCl_3$).

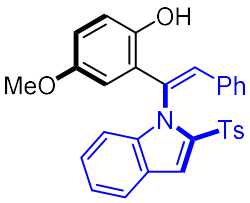
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 9.389 min, tr (minor) = 17.516 min, 94:6 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.387 | 2918.3 | 50.05 |
| 2 | 17.611 | 2912.2 | 49.95 |



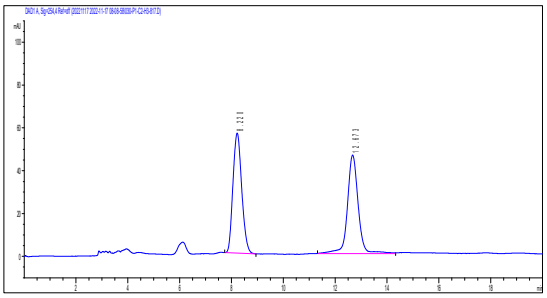
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.389 | 3468.8 | 94.00 |
| 2 | 17.516 | 221.6 | 6.00 |



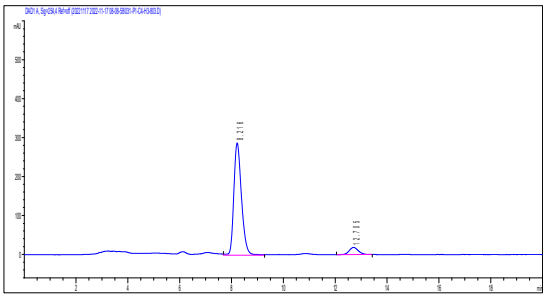

**(*R*, *Z*)-4-methoxy-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (30)**

The title compound was isolated as a pale-yellow solid (21.3 mg, 43%). **$^1$H NMR (600 MHz, CDCl$_3$)** $\delta$ 7.73 – 7.70 (m, 1H), 7.61 (s, 1H), 7.41 – 7.36 (m, 2H), 7.27 – 7.26 (m, 1H), 7.21 – 7.17 (m, 1H), 7.17 – 7.12 (m, 2H), 7.05 – 7.01 (m, 1H), 7.00 – 6.95 (m, 2H), 6.94 – 6.88 (m, 3H), 6.67 – 6.59 (m, 3H), 6.00 (s, br, 1H), 5.91 (d, $J$ = 3.0 Hz, 1H), 3.37 (s, 3H), 2.25 (s, 3H). **$^{13}$C NMR (150 MHz, CDCl$_3$)** $\delta$ 153.6, 147.9, 143.6, 138.6, 137.7, 134.4, 133.9, 132.8, 129.3, 128.6, 128.50, 128.46, 128.4, 127.1, 127.0, 126.9, 125.9, 122.8, 122.2, 119.0, 115.4, 113.7, 112.8, 112.0, 55.5, 21.5. **HRMS (ESI)**: calcd. for $C_{30}H_{25}NNaO_4S^+$ $[M+Na]^+$ : 518.1397, found : 518.1396. **$[\alpha]_D^{20}$** = +72 (c = 0.1, $CHCl_3$).

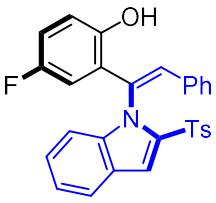
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 70:30, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 8.216 min, tr (minor) = 12.705 min, 93:7 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.220 | 1320.8 | 49.87 |
| 2 | 12.673 | 1327.8 | 50.13 |



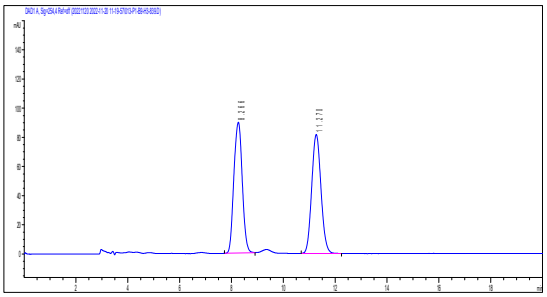
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.216 | 5920.7 | 92.97 |
| 2 | 12.705 | 447.7 | 7.03 |



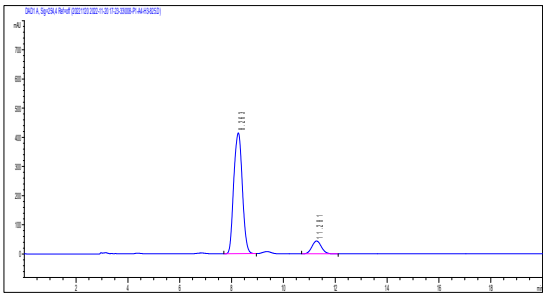

**(R, Z)-4-fluoro-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (31)**

The title compound was isolated as a pale-yellow solid (21.7 mg, 45%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.74 (dd, $J$ = 7.9, 1.3 Hz, 1H), 7.62 (s, 1H), 7.42 (d, $J$ = 8.5 Hz, 2H), 7.29 (s, 1H), 7.24 – 7.16 (m, 2H), 7.15 – 7.11 (m, 1H), 7.07 – 7.03 (m, 1H), 6.98 (t, $J$ = 7.7 Hz, 2H), 6.94 (d, $J$ = 8.1 Hz, 2H), 6.90 (dd, $J$ = 9.0, 4.8 Hz, 1H), 6.75 (m, 1H), 6.65 – 6.60 (m, 2H), 6.29 – 6.23 (m, 1H), 6.06 (dd, $J$ = 9.2, 3.1 Hz, 1H), 2.25 (s, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 156.9 (d, $J_{C\text{-}F}$ = 239.4 Hz), 150.0 (d, $J_{C\text{-}F}$ = 2.2 Hz), 144.0, 138.4, 137.6, 134.3, 133.57, 133.56, 129.5, 128.7, 128.6, 128.5, 127.8, 127.3 (d, $J_{C\text{-}F}$ = 7.3 Hz), 127.2, 127.0, 126.0, 122.9, 122.4, 119.2 (d, $J_{C\text{-}F}$ = 8.1 Hz), 116.5 (d, $J_{C\text{-}F}$ = 23.2 Hz), 113.84, 113.81 (d, $J_{C\text{-}F}$ = 23.9 Hz), 111.8, 21.5. **$^{19}$F NMR (376 MHz, $CDCl_3$)** $\delta$ -123.4; **HRMS (ESI)**: calcd. for $C_{29}H_{22}FNNaO_3S^+$ $[M+Na]^+$ : 506.1197, found : 506.1196. **$[\alpha]_D^{20}$** = +28 (c = 0.1, $CHCl_3$).

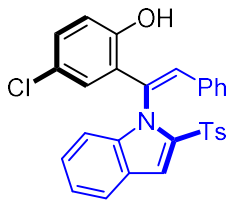
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 8.263 min, tr (minor) = 11.281 min, 90:10 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.266 | 2012.9 | 49.84 |
| 2 | 11.27 | 2026.1 | 50.16 |



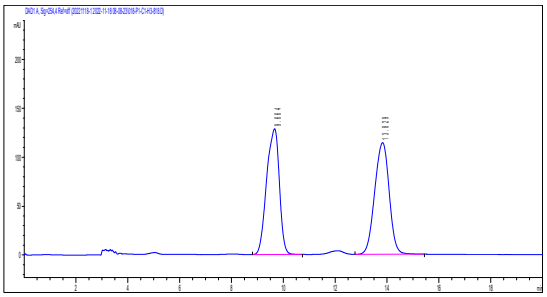
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.263 | 9540.8 | 90.00 |
| 2 | 11.281 | 1060.1 | 10.00 |



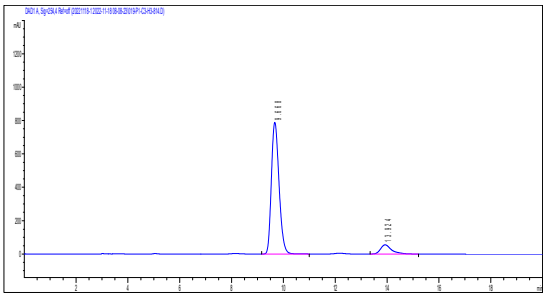

**(*R, Z*)-4-chloro-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (32)**

The title compound was isolated as a pale-yellow solid (32.4 mg, 65%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.78 – 7.72 (m, 1H), 7.65 (s, 1H), 7.41 – 7.36 (m, 2H), 7.24 (s, 1H), 7.22 – 7.16 (m, 2H), 7.12 – 7.09 (m, 1H), 7.07 – 7.03 (m, 1H), 7.01 – 6.92 (m, 5H), 6.88 (d, $J$ = 8.7 Hz, 1H), 6.66 – 6.58 (m, 2H), 6.44 (s, br, 1H), 6.28 (d, $J$ = 2.6 Hz, 1H), 2.27 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 152.7, 144.0, 138.5, 137.5, 134.0, 133.6, 133.4, 129.7, 129.5, 128.8, 128.6, 128.5, 127.6, 127.5, 127.3, 127.1, 126.8, 125.9, 125.8, 122.9, 122.4, 119.5, 114.0, 111.9, 21.6. **HRMS (ESI)**: calcd. for $C_{29}H_{22}ClNNaO_3S^+$ $[M+Na]^+$ : 522.0901, found : 522.0900. **$[\alpha]_D^{20}$** = +36 (c = 0.1, $CHCl_3$).

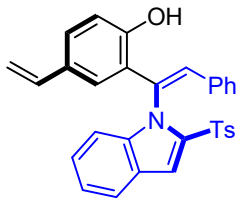
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 9.668 min, tr (minor) = 13.924 min, 91:9 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.664 | 4378.8 | 49.69 |
| 2 | 13.829 | 4433.7 | 50.31 |



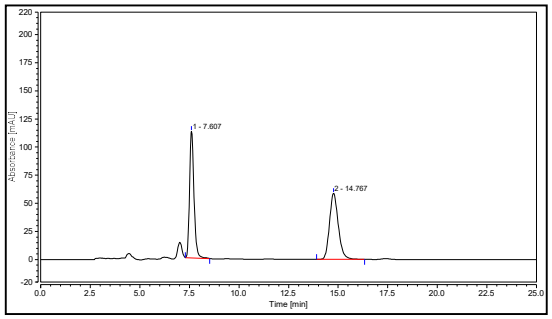
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.668 | 16214.5 | 90.91 |
| 2 | 13.924 | 1620.5 | 9.09 |

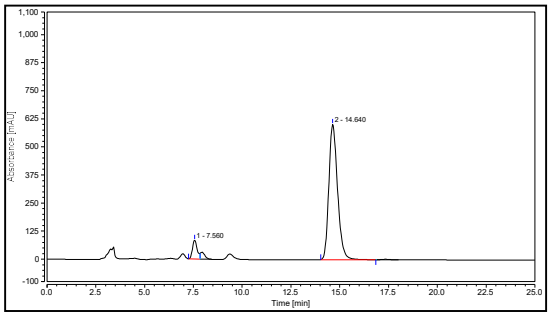



**(*R, Z*)-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)-4-vinylphenol (33)**

The title compound was isolated as a pale-yellow solid (26.5 mg, 54%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.75 – 7.72 (m, 1H), 7.64 (s, 1H), 7.33 (d, $J$ = 8.3 Hz, 2H), 7.22 – 7.12 (m, 5H), 7.06 – 7.02 (m, 1H), 7.01 – 6.96 (m, 2H), 6.92 (d, $J$ = 8.5 Hz, 1H), 6.87 (d, $J$ = 8.1 Hz, 2H), 6.67 – 6.61 (m, 2H), 6.37 (s, 1H), 6.31 (d, $J$ = 2.2 Hz, 1H), 6.16 (dd, $J$ = 17.5, 10.9 Hz, 1H), 5.20 (d, $J$ = 17.5 Hz, 1H), 4.90 (d, $J$ = 10.9 Hz, 1H), 2.21 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 153.8, 143.7, 138.6, 137.5, 135.6, 134.3, 133.9, 132.5, 130.7, 129.4, 128.6, 128.53, 128.51, 128.4, 127.1, 127.0, 126.8, 126.3, 125.94, 125.93, 122.8, 122.2, 118.4, 113.8, 112.1, 112.0, 21.5. **HRMS (ESI)**: calcd. for $C_{31}H_{25}NNaO_3S^+$ $[M+Na]^+$ : 514.1447, found : 514.1456. **$[\alpha]_D^{20}$** = +28 (c = 0.1, $CHCl_3$).

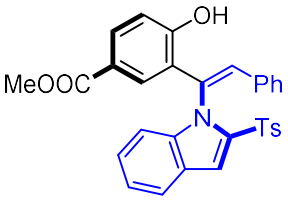
**HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 14.640 min, tr (minor) = 7.560 min, 93:7 e.r.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.607 | 29.4 | 49.30 |
| 2 | 14.767 | 30.2 | 50.70 |

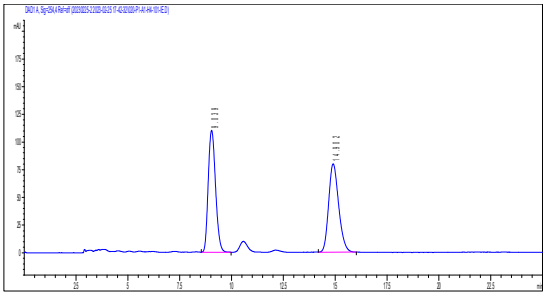
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 7.560 | 23.6 | 7.01 |
| 2 | 14.640 | 312.7 | 92.99 |

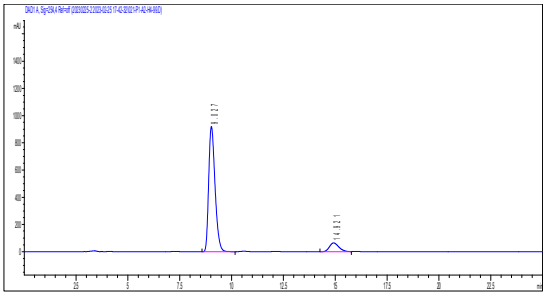



**methyl (*R, Z*)-4-hydroxy-3-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)-benzoate (34)**

The title compound was isolated as a pale-yellow solid (22.5 mg, 43%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.77 – 7.71 (m, 2H), 7.65 (s, 1H), 7.36 (d, $J$ = 8.1 Hz, 2H), 7.23 – 7.13 (m, 4H), 7.11 (d, $J$ = 8.2 Hz, 1H), 7.06 – 6.94 (m, 5H), 6.87 (d, $J$ = 8.1 Hz, 2H), 6.58 (d, $J$ = 7.6 Hz, 2H), 3.69 (s, 3H), 2.21 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 166.1, 158.2, 143.8, 138.7, 137.5, 133.9, 133.7, 133.0, 131.7, 130.3, 129.4, 128.7, 128.5, 128.4, 128.2, 127.1, 126.9, 126.0, 125.8, 122.9, 122.7, 122.4, 118.0, 114.3, 112.1, 51.9, 21.5. **HRMS (ESI)**: calcd. for $C_{31}H_{25}NNaO_5S^+$ $[M+Na]^+$ : 546.1346, found : 546.1358. **$[\alpha]_D^{20}$** = +18 (c = 0.1, $CHCl_3$).

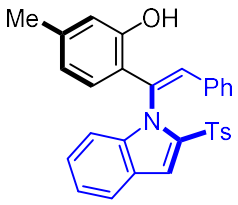
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 75:15, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 9.027 min, tr (minor) = 14.921 min, 90.5:9.5 e.r.





| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.039 | 2703.1 | 50.24 |
| 2 | 14.902 | 2677.7 | 49.76 |

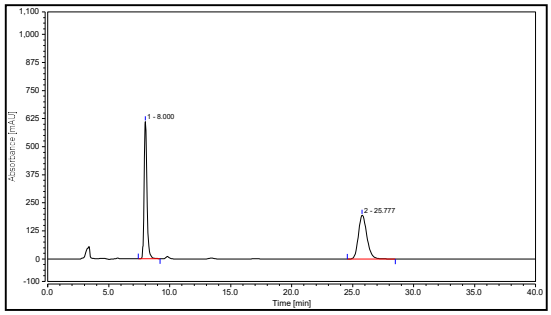
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.027 | 19535.4 | 90.61 |
| 2 | 14.921 | 2024.2 | 9.39 |



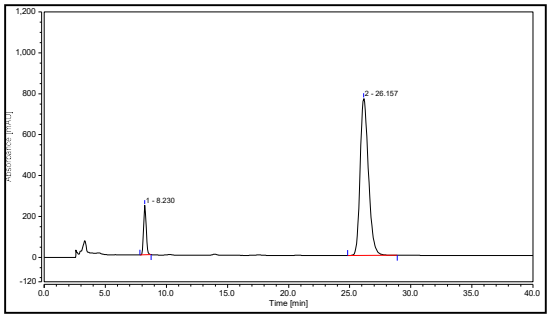

**(*R*, *Z*)-5-methyl-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (35)**

The title compound was isolated as a pale-yellow solid (40.2 mg, 84%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.76 – 7.71 (m, 1H), 7.65 – 7.60 (m, 1H), 7.45 – 7.37 (m, 2H), 7.25 – 7.14 (m, 4H), 7.05 – 7.00 (m, 1H), 6.97 (t, $J$ = 7.5 Hz, 2H), 6.90 (d, $J$ = 8.1 Hz, 2H), 6.76 (s, 1H), 6.66 – 6.60 (m, 2H), 6.38 – 6.28 (m, 1H), 6.25 (s, br, 2H), 2.25 (s, 3H), 2.22 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 153.6, 143.5, 140.6, 138.5, 137.6, 134.4, 134.0, 131.7, 129.2, 128.9, 128.4, 128.3, 128.2, 127.7, 127.12, 127.10, 126.8, 125.8, 123.2, 122.7, 122.1, 121.5, 118.3, 113.5, 112.1, 21.6, 21.3. **HRMS (ESI)**: calcd. for $C_{30}H_{25}NNaO_3S^+$ $[M+Na]^+$ : 502.1447, found : 502.1448. **$[\alpha]_D^{20}$** = +64 (c = 0.1, $CHCl_3$).

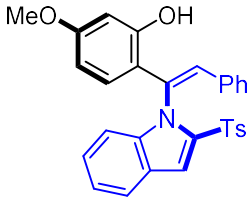
**HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 26.157 min, tr (minor) = 8.230 min, 91:9 e.r.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.000 | 165.0 | 51.15 |
| 2 | 25.777 | 157.6 | 48.85 |



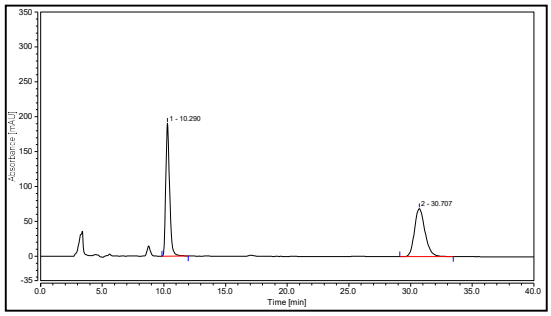

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.230 | 59.2 | 8.89 |
| 2 | 26.157 | 606.2 | 91.11 |



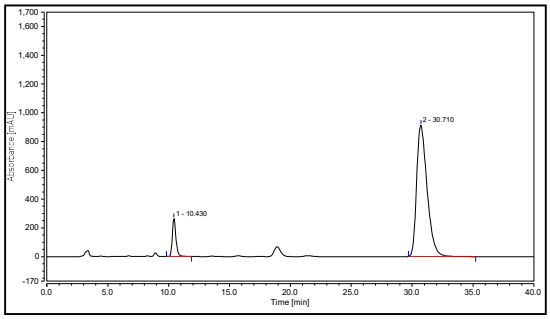

**(*R*, *Z*)-5-methoxy-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (36)**

The title compound was isolated as a pale-yellow solid (37.1 mg, 75%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.76 – 7.70 (m, 1H), 7.61 (s, 1H), 7.40 (d, $J$ = 8.1 Hz, 2H), 7.22 – 7.14 (m, 3H), 7.11 (s, 1H), 7.04 – 6.96 (m, 3H), 6.92 (d, $J$ = 8.0 Hz, 2H), 6.69 – 6.61 (m, 2H), 6.48 (d, $J$ = 2.5 Hz, 1H), 6.43 (s, br, 1H), 6.28 (d, $J$ = 8.7 Hz, 1H), 5.99 (dd, $J$ = 8.7, 2.6 Hz, 1H), 3.73 (s, 3H), 2.26 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 161.4, 155.1, 143.5, 138.5, 137.8, 134.3, 134.1, 130.8, 129.3, 128.9, 128.8, 128.5, 128.3, 128.2, 127.0, 126.9, 125.9, 122.7, 1222, 118.9, 113.7, 112.1, 107.2, 102.9, 55.4, 21.5. **HRMS (ESI)**: calcd. for $C_{30}H_{25}NNaO_4S^+$ $[M+Na]^+$ : 518.1397, found : 518.1390. **$[\alpha]_D^{20}$** = +52 (c = 0.1, $CHCl_3$).

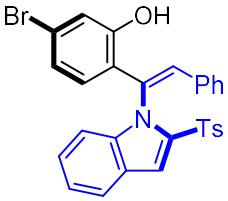
**HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 30.710 min, tr (minor) = 10.430 min, 91:9 e.r.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.290 | 68.0 | 49.87 |
| 2 | 30.707 | 68.4 | 50.13 |



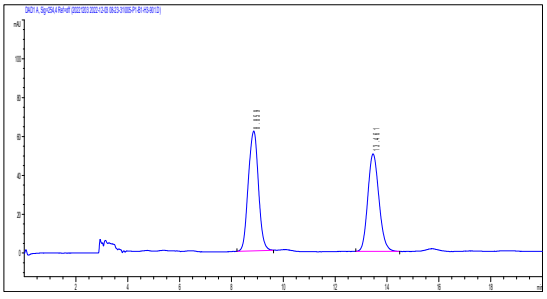

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.430 | 90.1 | 9.05 |
| 2 | 30.710 | 906.1 | 90.95 |



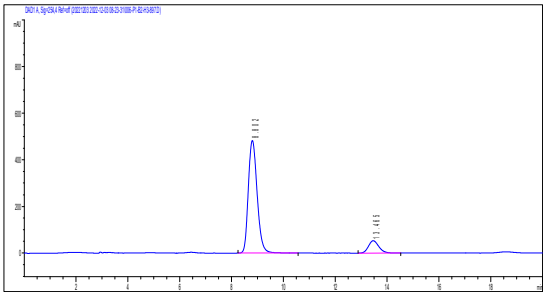

**(*R*, *Z*)-5-bromo-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (37)**

The title compound was isolated as a pale-yellow solid (25.0 mg, 46%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.74 (d, $J$ = 7.9 Hz, 1H), 7.66 (s, 1H), 7.38 (d, $J$ = 8.0 Hz, 2H), 7.22 – 7.15 (m, 3H), 7.13 – 7.03 (m, 3H), 7.02 – 6.95 (m, 4H), 6.67 (d, $J$ = 7.6 Hz, 2H), 6.55 – 6.43 (m, 2H), 6.18 (d, $J$ = 8.3 Hz, 1H), 2.32 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 154.5, 144.1, 138.4, 137.4, 134.0, 133.7, 132.6, 129.5, 129.0, 128.7, 128.6, 128.4, 127.8, 127.1, 126.8, 125.9, 125.1, 123.8, 123.5, 122.9, 122.3, 121.1, 114.1, 111.9, 21.7. **HRMS (ESI)**: calcd. for $C_{29}H_{22}BrNNaO_3S^+$ $[M+Na]^+$ : 566.0396, found : 566.0389. **$[\alpha]_D^{20}$** = +28 (c = 0.1, $CHCl_3$).

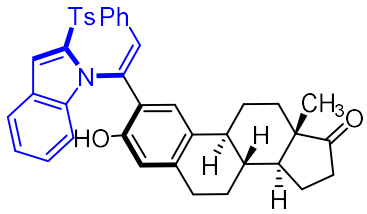
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 8.802 min, tr (minor) = 13.465 min, 88.5:11.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.859 | 1674.7 | 52.62 |
| 2 | 13.461 | 1508.2 | 47.38 |



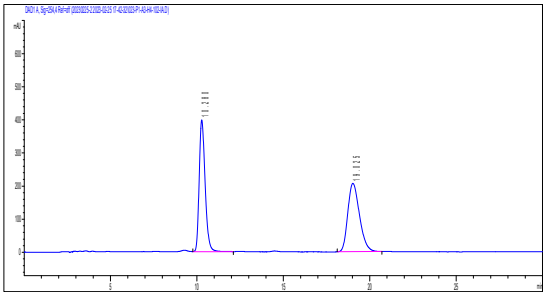
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.802 | 11410.0 | 88.63 |
| 2 | 13.465 | 1463.6 | 11.37 |



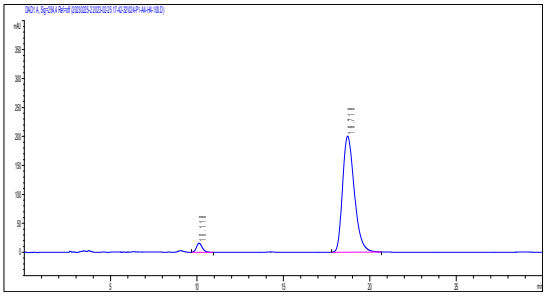

**(8R,9S,13S,14S)-3-hydroxy-13-methyl-2-((*R, Z*)-2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (38)**

The title compound was isolated as a pale-yellow solid (30.1 mg, 47%, 2.5:1 d.r.). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.73 (d, $J$ = 7.9 Hz, 1H), 7.65 (s, 1H), 7.40 (d, $J$ = 8.0 Hz, 2H), 7.22 – 7.10 (m, 4H), 7.05 – 6.95 (m, 4H), 6.92 (d, $J$ = 8.0 Hz, 2H), 6.70 (s, 1H), 6.65 (d, $J$ = 7.7 Hz, 2H), 6.27 (s, br, 1H), 6.14 (s, 1H), 2.97 – 2.88 (m, 1H), 2.86 – 2.73 (m, 2H), 2.55 – 2.38 (m, 2H), 2.27 (s, 3H), 2.18 – 1.87 (m, 6H), 1.70 – 1.42 (m, 6H), 1.39 – 1.14 (m, 5H), 0.91 (s, 1H), 0.78 (s, 3H), 0.69 – 0.59 (m, 1H); **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.8, 149.1, 143.0, 139.1, 138.5, 138.3, 138.1, 138.0, 134.4, 134.1, 132.0, 131.2, 129.20, 129.16, 128.5, 128.3, 128.2, 127.3, 126.9, 126.6, 125.8, 124.6, 123.8, 122.8, 122.2, 121.0, 118.2, 117.9, 113.9, 112.0, 50.6, 50.4, 48.1, 47.9, 44.3, 43.5, 38.3, 38.1, 36.0, 35.9, 31.7, 31.3, 29.6, 29.4, 26.5, 26.4, 25.9, 25.1, 21.8, 21.72, 21.66, 14.0, 13.8. **HRMS (ESI)**: calcd. for $C_{41}H_{39}NNaO_4S^+$ $[M+Na]^+$ : 664.2492, found : 664.2500. **$[\alpha]_D^{20}$** = +104 (c = 0.1, $CHCl_3$).

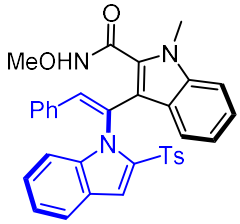
**HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 75:25, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 18.718 min, tr (minor) = 10.118 min, 96.5:3.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.280 | 9486.5 | 49.39 |
| 2 | 19.025 | 9722.9 | 50.61 |



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.118 | 367.4 | 3.74 |
| 2 | 18.718 | 9464.2 | 96.26 |

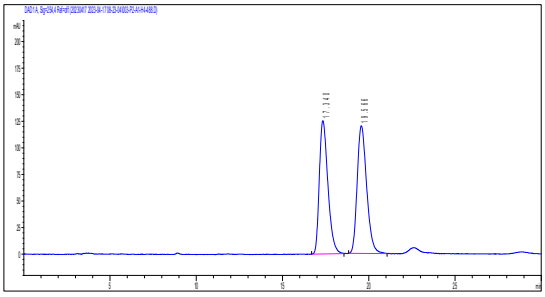



**(*R, Z*)-N-methoxy-1-methyl-3-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)-1H-indole-2-carboxamide (40)**

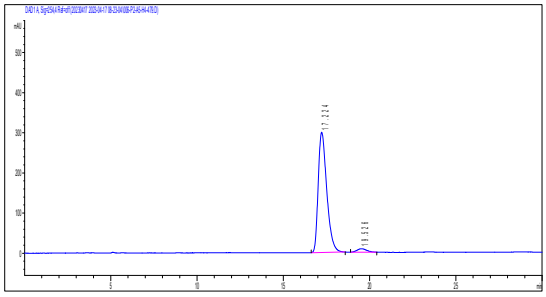
The title compound was isolated as a pale-yellow solid (55.8 mg, 97%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 11.04 (s, br, 1H), 7.82 – 7.75 (m, 2H), 7.21 – 7.16 (m, 3H), 7.07 – 7.01 (m, 5H), 6.99 - 6.95 (m, 1H), 6.94 – 6.88 (m, 4H), 6.54 (d, $J$ = 8.1 Hz, 2H), 6.48 (t, $J$ = 7.6

Hz, 1H), 5.52 (d, $J$ = 8.2 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 2.14 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 159.7, 143.1, 138.3, 137.1, 136.1, 134.4, 133.1, 130.2, 128.7, 128.22, 128.19, 128.15, 128.0, 127.1, 126.4, 125.5, 125.1, 124.7, 123.5, 122.8, 122.4, 121.3, 120.2, 116.1, 114.5, 113.1, 109.7, 63.9, 31.0, 21.6. **HRMS (ESI)**: calcd. for $C_{34}H_{29}N_3NaO_4S^+$ $[M+Na]^+$ : 598.1771, found : 598.1766. **$[\alpha]_D^{20}$** = +20 (c = 0.1, $CHCl_3$).

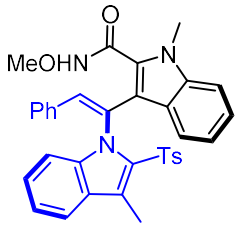
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 65:35, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 17.224 min, tr (minor) = 19.526 min, 97:3 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 17.340 | 4336.7 | 48.52 |
| 2 | 19.566 | 4600.7 | 51.48 |



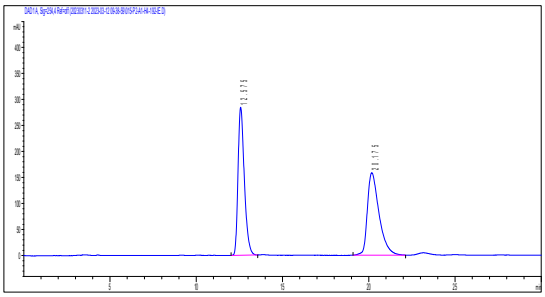
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 17.224 | 10306.7 | 96.90 |
| 2 | 19.526 | 329.3 | 3.10 |



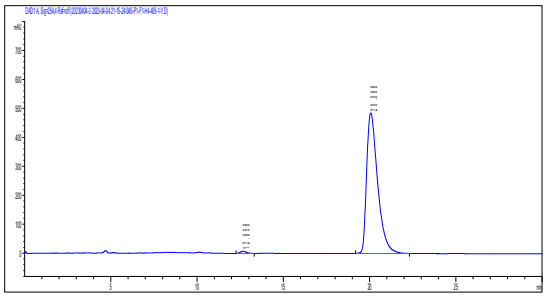

**(*R, Z*)-N-methoxy-1-methyl-3-(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-1H-indole-2-carboxamide (41)**

The title compound was isolated as a pale-yellow solid (54.2 mg, 92%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 11.13 (s, br, 1H), 7.81 – 7.74 (m, 1H), 7.22 - 7.15 (m, 3H), 7.09 – 6.94 (m, 8H), 6.89 (d, $J$ = 9.3 Hz, 2H), 6.53 (d, $J$ = 7.9 Hz, 2H), 6.47 (t, $J$ = 7.7 Hz, 1H), 5.36 (d, $J$ = 8.2 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 2.91 (s, 3H), 2.15 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 159.9, 142.9, 137.4, 137.0, 136.9, 134.7, 130.0, 128.7, 128.3, 128.0, 127.97, 127.7, 127.6, 127.13, 127.09, 125.6, 124.6, 124.2, 123.4, 121.7, 121.2, 120.9, 120.2, 115.0, 113.0, 109.6, 63.9, 31.0, 21.6, 10.8. **HRMS (ESI)**: calcd. for $C_{35}H_{31}N_3NaO_4S^+$ $[M+Na]^+$ : 612.1927, found : 612.1917. **$[\alpha]_D^{20}$** = -8 (c = 0.1, $CHCl_3$).

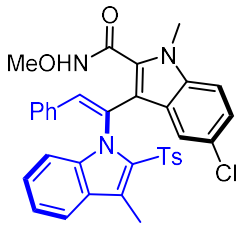
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 60:40, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 20.068 min, tr (minor) = 12.658 min, 99:1 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.575 | 7228.9 | 49.24 |
| 2 | 20.175 | 7453.6 | 50.76 |



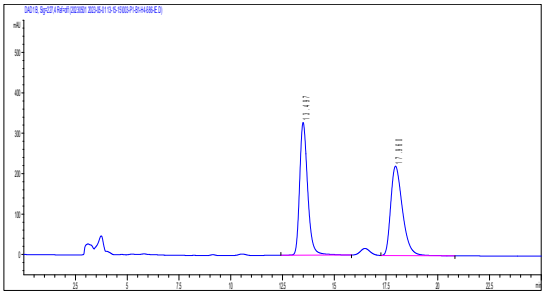
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.658 | 188.3 | 0.87 |
| 2 | 20.068 | 21516.5 | 99.13 |



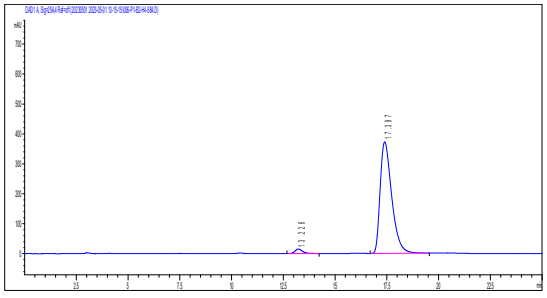

**(*R, Z*)-5-chloro-N-methoxy-1-methyl-3-(1-(3-methyl-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-1H-indole-2-carboxamide (42)**

The title compound was isolated as a pale-yellow solid (49.8 mg, 80%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 11.08 (s, br, 1H), 7.83 – 7.77 (m, 1H), 7.24 – 7.18 (m, 2H), 7.15 – 7.11 (m, 1H), 7.09 – 6.98 (m, 7H), 6.91 (d, $J$ = 8.5 Hz, 1H), 6.88 (s, 1H), 6.81 (d, $J$ = 8.8 Hz, 1H), 6.63 (d, $J$ = 7.9 Hz, 2H), 5.22 (s, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 2.93 (s, 3H), 2.17 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 159.6, 143.1, 137.6, 136.9, 135.4, 134.5, 131.1, 128.7, 128.4, 128.19, 128.17, 128.1, 127.94, 127.90, 127.2, 126.7, 126.6, 126.0, 125.4, 124.4, 123.8, 122.0, 121.1, 119.9, 114.7, 112.7, 110.7, 63.9, 31.2, 21.6, 10.8. **HRMS (ESI)**: calcd. for $C_{35}H_{30}ClN_3NaO_4S^+$ $[M+Na]^+$ : 646.1538, found : 646.1537. **$[\alpha]_D^{20}$** = -22 (c = 0.1, $CHCl_3$).

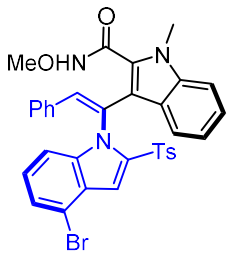
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 75:25, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 17.397 min, tr (minor) = 13.226 min, 97.5:2.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.497 | 8796.9 | 50.21 |
| 2 | 17.960 | 8724.4 | 49.79 |



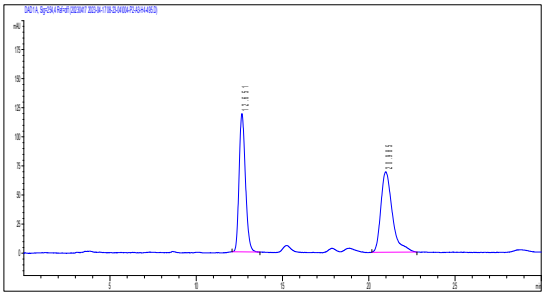
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 13.226 | 375.7 | 2.54 |
| 2 | 17.397 | 14439.8 | 97.46 |



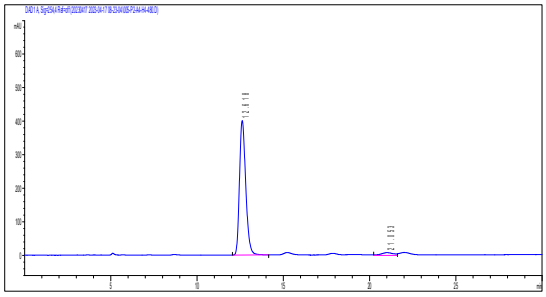

**(*R, Z*)-3-(1-(4-bromo-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-N-methoxy-1-methyl-1H-indole-2-carboxamide (43)**

The title compound was isolated as a pale-yellow solid (56.8 mg, 87%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 10.98 (s, br, 1H), 7.85 – 7.81 (m, 1H), 7.34 (d, $J$ = 7.5 Hz, 1H), 7.14 (d, $J$ = 8.5 Hz, 1H), 7.08 – 6.97 (m, 7H), 6.95 – 6.87 (m, 4H), 6.55 (d, $J$ = 8.1 Hz, 2H), 6.52 (t, $J$ = 7.6 Hz, 1H), 5.48 (d, $J$ = 8.2 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 2.15 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 159.6, 143.4, 138.4, 137.1, 135.7, 134.14, 134.08, 130.3, 128.8, 128.5, 128.4, 128.13, 128.10, 127.8, 126.4, 126.3, 125.4, 125.2, 124.5, 123.6, 121.5, 119.9, 116.5, 115.7, 114.0, 112.4, 109.8, 63.9, 31.1, 21.6. **HRMS (ESI)**: calcd. for $C_{34}H_{28}BrN_3NaO_4S^+$ $[M+Na]^+$ : 676.0876, found : 676.0868. **$[\alpha]_D^{20}$** = -48 (c = 0.1, $CHCl_3$).

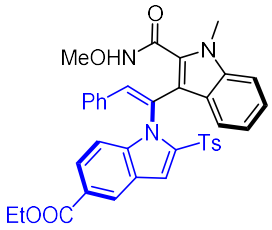
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 65:35, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 12.618 min, tr (minor) = 21.053 min, 96:4 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.651 | 3024.2 | 48.45 |
| 2 | 20.985 | 3218.3 | 51.55 |



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.618 | 10081 | 95.97 |
| 2 | 21.053 | 423.2 | 4.03 |

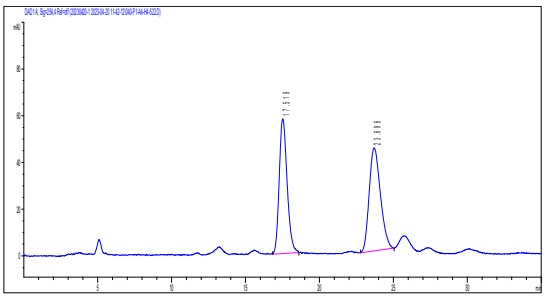



**ethyl (*R, Z*)-1-(1-(2-(methoxycarbamoyl)-1-methyl-1H-indol-3-yl)-2-phenylvinyl)-2-tosyl-1H-indole-5-carboxylate (44)**

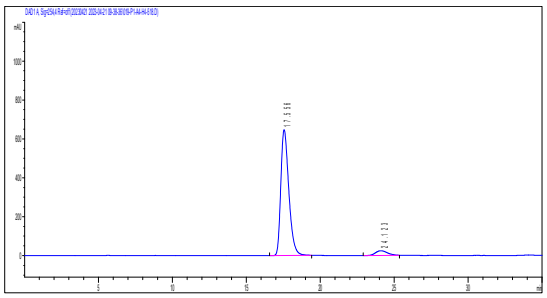
The title compound was isolated as a pale-yellow solid (48.5 mg, 75%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 10.98 (s, br, 1H), 8.56 (d, $J$ = 1.6 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.22 (d, $J$ = 8.9 Hz, 1H), 7.08 – 7.02 (m, 5H), 6.98 (t, $J$ = 7.6 Hz, 1H), 6.96 – 6.89 (m, 4H), 6.55 (d, $J$ = 8.0 Hz, 2H), 6.47 (t, $J$ = 7.5 Hz, 1H), 5.45 (d, $J$ = 8.2 Hz, 1H), 4.38 (q, $J$ = 7.1 Hz, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 2.14 (s, 3H), 1.39 (t, $J$ = 7.1 Hz, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 166.7, 159.6, 143.4, 140.4, 137.1, 135.7, 135.0, 134.1, 130.3, 128.8, 128.6, 128.4, 128.12, 128.08, 127.8, 126.1, 125.9, 125.1, 125.0, 124.9, 124.4, 123.6, 121.4, 119.8, 116.9, 113.9, 112.9, 109.9, 63.9,

61.1, 31.1, 21.6, 14.5. **HRMS (ESI)**: calcd. for $C_{37}H_{33}N_3NaO_6S^+$ $[M+Na]^+$ : 670.1982, found : 670.1980. **$[\alpha]_D^{20}$** = -54 (c = 0.1, $CHCl_3$).

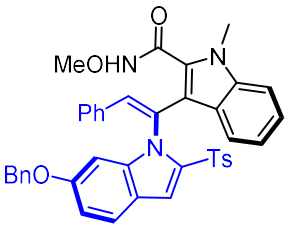
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 65:35, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 17.556 min, tr (minor) = 24.123 min, 94.5:5.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 17.519 | 2138.0 | 47.87 |
| 2 | 23.696 | 2328.5 | 52.13 |



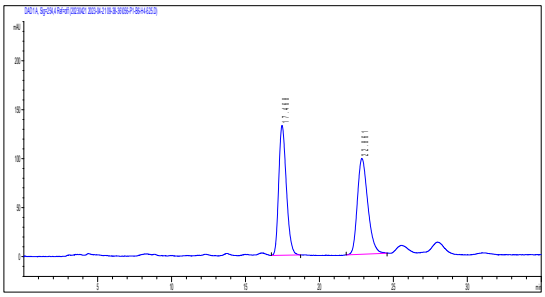
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 17.556 | 24280.2 | 94.66 |
| 2 | 24.123 | 1369.9 | 5.34 |



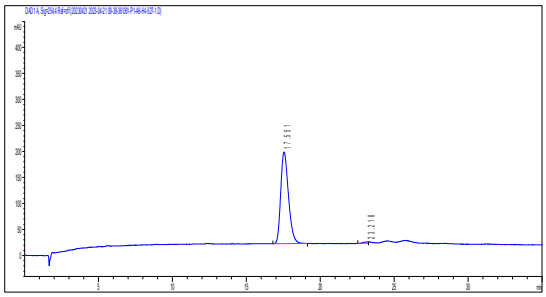

**(*R, Z*)-3-(1-(6-(benzyloxy)-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-N-methoxy-1-methyl-1H-indole-2-carboxamide (45)**

The title compound was isolated as a pale-yellow solid (44.9 mg, 66%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 11.08 (s, br, 1H), 7.73 (s, 1H), 7.64 (d, $J$ = 8.9 Hz, 1H), 7.31 – 7.24 (m, 5H), 7.08 – 7.02 (m, 5H), 7.02 – 6.97 (m, 1H), 6.97 – 6.92 (m, 2H), 6.92 – 6.86 (m, 3H), 6.65 (d, $J$ = 2.1 Hz, 1H), 6.56 - 6.50 (m, 3H), 5.62 (d, $J$ = 8.1 Hz, 1H), 4.81 (d, $J$ = 11.3 Hz, 1H), 4.60 (d, $J$ = 11.3 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 2.15 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 159.7, 159.2, 142.8, 139.5, 137.1, 136.44, 136.42, 134.6, 131.5, 130.2, 128.8, 128.6, 128.21, 128.15, 128.0, 127.9, 127.7, 126.6, 124.9, 124.7, 123.7, 123.5, 121.4, 120.3, 119.9, 116.7, 115.0, 114.4, 109.7, 95.7, 70.4, 63.9, 31.0, 21.6. **HRMS (ESI)**: calcd. for $C_{41}H_{35}N_3NaO_5S^+$ $[M+Na]^+$ : 704.2190, found : 704.2187. **$[\alpha]_D^{20}$** = +42 (c = 0.1, $CHCl_3$).

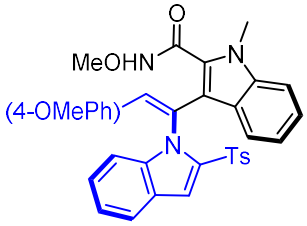
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 65:35, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 17.551 min, tr (minor) = 23.218 min, 99:1 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 17.468 | 4748.1 | 49.76 |
| 2 | 22.861 | 4793.3 | 50.24 |



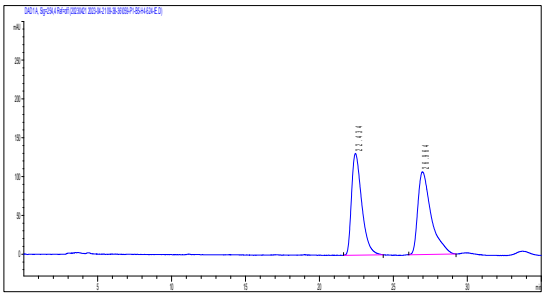
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 17.551 | 6422.3 | 99.01 |
| 2 | 23.218 | 64.0 | 0.99 |



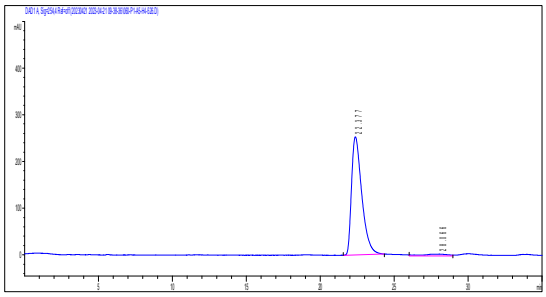

**(*R, Z*)-N-methoxy-3-(2-(4-methoxyphenyl)-1-(2-tosyl-1H-indol-1-yl)vinyl)-1-methyl-1H-indole-2-carboxamide (46)**

The title compound was isolated as a pale-yellow solid (53.2 mg, 88%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 11.01 (s, br, 1H), 7.83 – 7.75 (m, 2H), 7.23 – 7.17 (m, 3H), 7.05 (d, $J$ = 8.4 Hz, 2H), 6.99 – 6.94 (m, 1H), 6.89 (d, $J$ = 8.3 Hz, 1H), 6.85 (s, 1H), 6.81 (d, $J$ = 8.7 Hz, 2H), 6.58 – 6.55 (m, 2H), 6.53 (d, $J$ = 8.0 Hz, 2H), 6.46 (t, $J$ = 7.6 Hz, 1H), 5.51 (d, $J$ = 8.2 Hz, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 2.13 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 159.9, 159.3, 143.1, 138.3, 137.1, 136.1, 133.0, 129.81, 129.78, 128.02, 128.00, 127.2, 127.1, 125.5, 125.1, 124.6, 124.2, 123.5, 122.8, 122.4, 121.1, 120.2, 115.8, 114.8, 114.2, 113.2, 109.7, 64.0, 55.2, 31.0, 21.6. **HRMS (ESI)**: calcd. for $C_{35}H_{31}N_3NaO_5S^+$ $[M+Na]^+$ : 628.1877, found : 628.1878. **$[\alpha]_D^{20}$** = +16 (c = 0.1, $CHCl_3$).

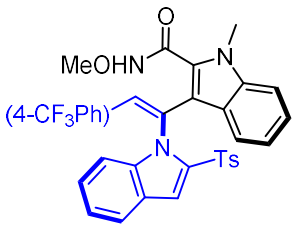
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 65:35, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 22.374 min, tr (minor) = 27.747 min, 99:1 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 22.434 | 6324.2 | 48.56 |
| 2 | 26.964 | 6699.5 | 51.44 |



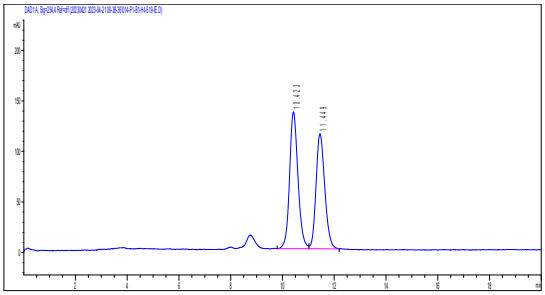
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 22.374 | 25544.9 | 98.83 |
| 2 | 27.747 | 303.0 | 1.17 |



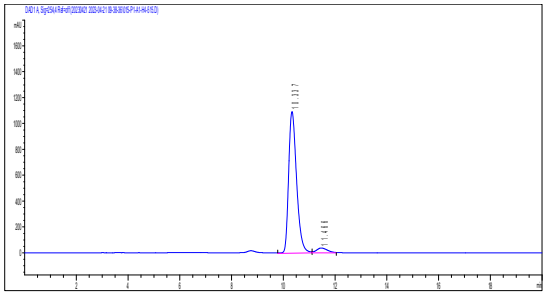

**(*R, Z*)-N-methoxy-1-methyl-3-(1-(2-tosyl-1H-indol-1-yl)-2-(4-(trifluoromethyl)phenyl)vinyl)-1H-indole-2-carboxamide (47)**

The title compound was isolated as a pale-yellow solid (57.2 mg, 89%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 11.00 (s, br, 1H), 7.84 - 7.76 (m, 2H), 7.29 (d, $J$ = 8.3 Hz, 2H), 7.23 - 7.19 (m, 2H), 7.18 – 7.14 (m, 1H), 7.05 (d, $J$ = 8.4 Hz, 2H), 7.03 – 6.97 (m, 3H), 6.92 (d, $J$ = 7.7 Hz, 2H), 6.55 (d, $J$ = 8.1 Hz, 2H), 6.50 (t, $J$ = 7.6 Hz, 1H), 5.49 (d, $J$ = 8.2 Hz, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 2.15 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 159.7, 143.3, 138.1, 137.9, 137.1, 136.0, 133.1, 130.6, 129.5 (q, $J_{C\text{-}F}$ = 32.2 Hz), 128.7, 128.3, 128.1, 127.5, 126.1, 125.7 (q, $J_{C\text{-}F}$ = 3.9 Hz), 125.6, 125.1, 124.6, 123.9 (q, $J_{C\text{-}F}$ = 272.0 Hz), 123.7, 123.1, 122.7, 121.6, 120.0, 116.4, 114.0, 112.7, 109.8, 64.0, 31.1, 21.6. **$^{19}$F NMR (376 MHz, $CDCl_3$)** $\delta$ -62.6. **HRMS (ESI)**: calcd. for $C_{35}H_{28}F_3N_3NaO_4S^+$ $[M+Na]^+$ : 666.1645, found : 666.1638. **$[\alpha]_D^{20}$** = +14 (c = 0.1, $CHCl_3$).

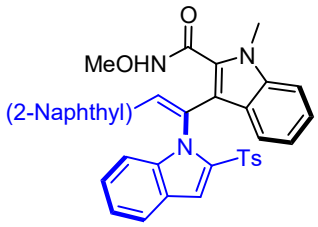
**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 65:35, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.337 min, tr (minor) = 11.466 min, 95.5:4.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.423 | 3063.4 | 52.45 |
| 2 | 11.449 | 2776.8 | 47.55 |



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.337 | 23351.9 | 95.67 |
| 2 | 11.466 | 1057 | 4.33 |

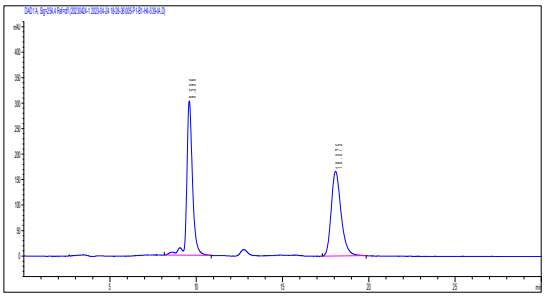



**(*R, Z*)-N-methoxy-1-methyl-3-(2-(naphthalen-2-yl)-1-(2-tosyl-1H-indol-1-yl)vinyl)-1H-indole-2-carboxamide (48)**

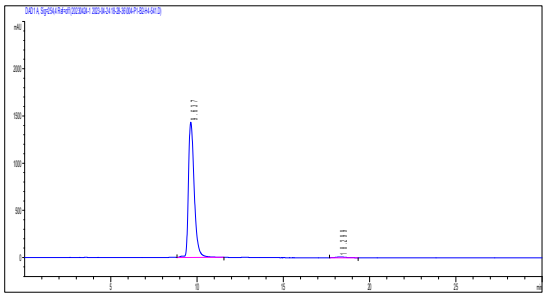
The title compound was isolated as a pale-yellow solid (37.5 mg, 60%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 11.06 (s, br, 1H), 7.85 (s, 1H), 7.79 (d, $J$ = 7.6 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.54 (s, 1H), 7.42 – 7.35 (m, 3H), 7.22 (d, $J$ = 8.1 Hz, 1H), 7.16 – 7.06 (m, 5H), 6.99 (t, $J$ = 7.7 Hz, 1H), 6.94 – 6.89 (m, 1H), 6.82 (d, $J$ = 8.6 Hz, 1H), 6.55 (d, $J$ = 8.0 Hz, 2H), 6.50 (t, $J$ = 7.6 Hz, 1H), 5.53 (d, $J$ = 8.2 Hz, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 2.15 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 159.8, 143.2, 138.6, 137.2, 136.1, 133.4, 133.1, 132.9, 132.2, 130.3, 129.0,

128.41, 128.35, 128.14, 128.07, 127.6, 127.3, 126.5, 126.3, 125.5, 125.1, 124.72, 124.69, 123.6, 122.9, 122.5, 121.3, 120.2, 116.2, 114.6, 113.1, 109.8, 64.0, 31.1, 21.6. **HRMS (ESI)**: calcd. for $C_{38}H_{31}N_3NaO_4S^+$ $[M+Na]^+$ : 648.1927, found : 648.1919. **$[\alpha]_D^{20}$** = +10 (c = 0.1, $CHCl_3$).

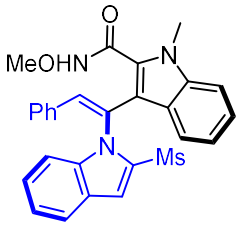
**HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 70:30, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 9.637 min, tr (minor) = 18.299 min, 99:1 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.596 | 7033.8 | 51.58 |
| 2 | 18.075 | 6600.9 | 48.42 |



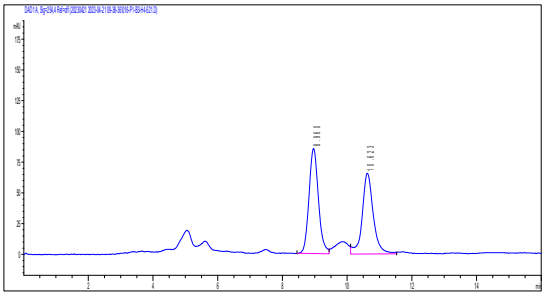
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.637 | 33366.2 | 99.09 |
| 2 | 18.299 | 305.6 | 0.91 |

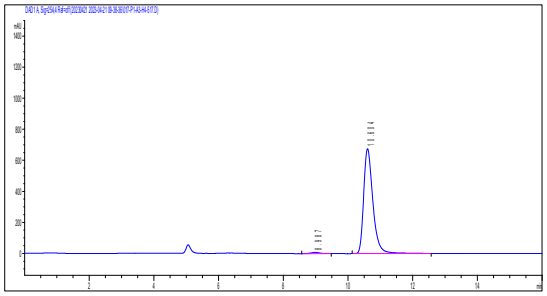



**(*R, Z*)-N-methoxy-1-methyl-3-(1-(2-(methylsulfonyl)-1H-indol-1-yl)-2-phenylvinyl)-1H-indole-2-carboxamide (49)**

The title compound was isolated as a pale-yellow solid (41.9 mg, 84%). **$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 10.77 (s, br, 1H), 7.78 – 7.72 (m, 1H), 7.57 (s, 1H), 7.35 (d, $J$ = 8.4 Hz, 1H), 7.26 – 7.17 (m, 4H), 7.05 – 6.98 (m, 4H), 6.89 – 6.84 (m, 2H), 6.74 (t, $J$ = 7.6 Hz, 1H), 5.87 (d, $J$ = 8.2 Hz, 1H), 3.98 (s, 3H), 3.64 (s, 3H), 2.24 (s, 3H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 159.7, 138.1, 137.3, 134.3, 134.1, 130.7, 128.7, 128.6, 128.3, 128.2, 127.3, 126.4, 125.5, 124.7, 124.6, 123.0, 122.5, 122.1, 119.9, 114.9, 114.5, 113.1, 110.5, 63.9, 44.6, 31.5. **HRMS (ESI)**: calcd. for $C_{28}H_{25}N_3NaO_4S^+$ $[M+Na]^+$ : 522.1458, found : 522.1456. **$[\alpha]_D^{20}$** = +82 (c = 0.1, $CHCl_3$).

**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 65:35, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 10.604 min, tr (minor) = 8.987 min, 99:1 e.r.



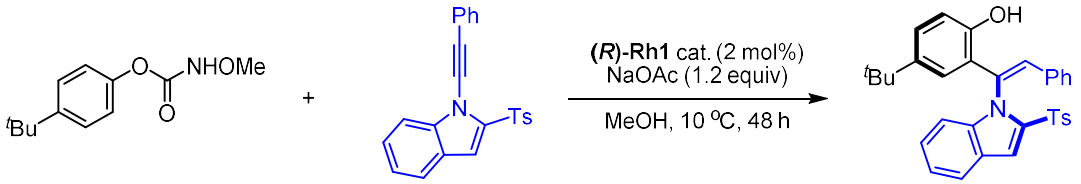


| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.96 | 1726.9 | 52.48 |
| 2 | 10.623 | 1563.8 | 47.52 |

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.987 | 151.7 | 1.12 |
| 2 | 10.604 | 13376.6 | 98.88 |

## 4. Synthetic applications

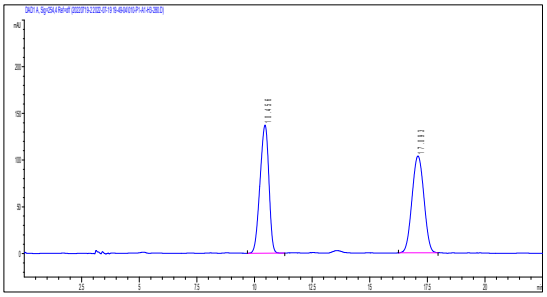
### 1 mmol-scale synthesis of 3.



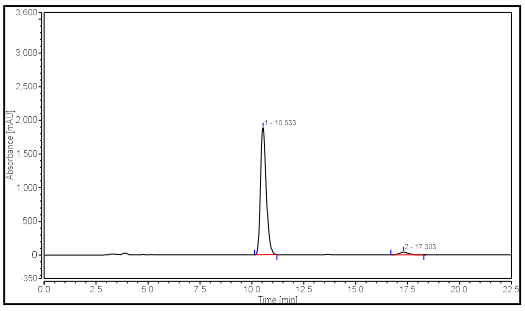

**1a** + **2a** (1 mmol) → **(*R*)-3** (90%, 96.5:3.5 e.r.)

A tube (15 mL) was charged with alkyne **2a** (1 mmol, 1.0 equiv), **(*R*)-Rh1** (2 mol%) and NaOAc (1.2mmol, 2.0 equiv) in MeOH (8 mL) and the mixture was stirred at 10 °C. The resulted mixture was kept at 10 °C for 15 min, to which was added *N*-alkoxycarbamate **1a** (1.2 mmol, 1.2 equiv). The reaction was maintained at 10 °C for 48 h. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding product **(*R*)-3** as a pale-yellow solid (468.9 mg, 90% yield, 96.5:3.5 e.r.).

**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.533 min, tr (minor) = 17.303 min, 96.5:3.5 e.r.

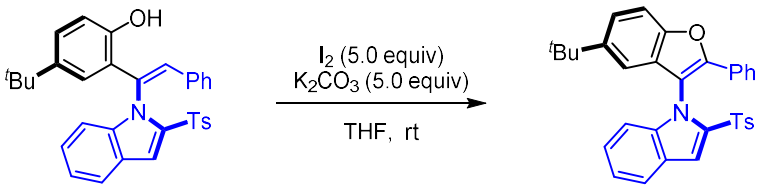


| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.456 | 3663.1 | 49.65 |
| 2 | 17.093 | 3714.1 | 50.35 |



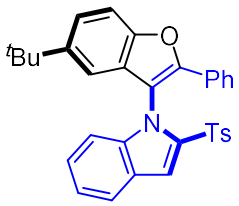
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 10.533 | 606.8 | 96.70 |
| 2 | 17.303 | 20.7 | 3.30 |

**Transformations and Synthetic Applications**




**3**, 96.5:3.5 e.r. **50**, 47%, 95.5:4.5 e.r.

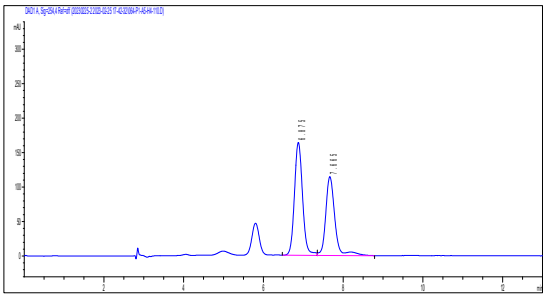
A scew-cap vial (8 mL) was charged with **3** (0.1 mmol, 52.1 mg) and $K_2CO_3$ (0.5 mmol, 69.1 mg) in THF (2 mL) was stirred at room temperature for 30 min, then iodine (0.5 mmol, 126.9 mg) was added in one portion, and the reaction was monitored by TLC. Saturate $Na_2S_2O_3$ solution was added, and the mixture was stirred for another 30 min. The product was extracted by $CH_2Cl_2$, washed with brine, dried over anhydrous $Na_2SO_4$, evaporated the solvent under vacuum, and purified by silica gel column chromatography to afford the product **50** as a pale-yellow solid (24.4 mg, 47% yield, 95.5:4.5 e.r.).[4]



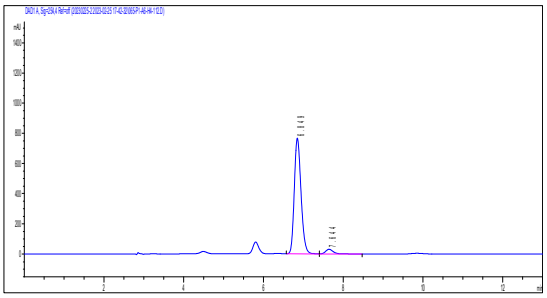

**(*R*, *Z*)-4-(tert-butyl)-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenol (50)**

**$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.87 (d, $J$ = 7.9 Hz, 1H), 7.79 (s, 1H), 7.51 (d, $J$ = 8.8 Hz, 1H), 7.42 (dd, $J$ = 8.8, 1.9 Hz, 1H), 7.30 – 7.27 (m, 3H), 7.26 – 7.22 (m, 1H), 7.15 – 7.12 (m, 1H), 7.05 (t, $J$ = 7.7 Hz, 2H), 6.98 (d, $J$ = 8.3 Hz, 1H), 6.92 (d, $J$ = 7.9 Hz, 2H), 6.87 (s, 1H), 6.76 (d, $J$ = 8.0 Hz, 2H), 2.09 (s, 3H), 1.24 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.6, 151.0, 146.9, 144.0, 140.1, 136.8, 136.7, 129.2, 128.9, 128.41, 128.39, 128.1, 127.4, 126.6, 125.8, 125.2, 123.6, 123.0, 122.3, 115.5, 113.3, 112.5, 111.7, 110.7, 34.9, 31.8, 21.6. **HRMS (ESI)**: calcd. for $C_{33}H_{29}NNaO_3S^+$ $[M+Na]^+$ : 542.1760, found : 542.1763. **$[\alpha]_D^{20}$** = +48 (c = 0.1, $CHCl_3$).

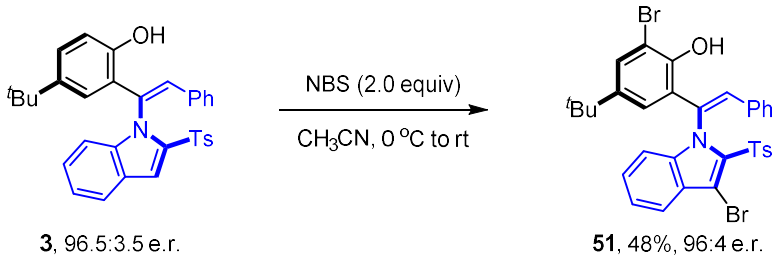
**HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 95:5, v = 1.0 mL/min, 40 ºC, 254 nm); tr (major) = 6.849 min, tr (minor) = 7.644 min, 95.5:4.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.875 | 1920.6 | 51.32 |
| 2 | 7.665 | 1821.5 | 48.68 |

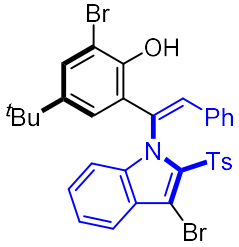


| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 6.849 | 8992.8 | 95.62 |
| 2 | 7.644 | 412.2 | 4.38 |




**3**, 96.5:3.5 e.r. **51**, 48%, 96:4 e.r.

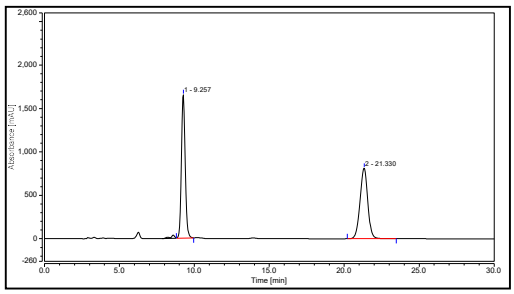
A scew-cap vial (8 mL) was charged with **3** (0.1 mmol, 52.1 mg) and $CH_3CN$ (2 mL) was stirred at 0 °C for 10 min. Then NBS (0.2 mmol, 35.6 mg) was added and the reaction was allowed to room temperature and stirred for 12 h. The mixture was quenched with 10 mL saturate $Na_2SO_3$ solution and the resulting mixture was extracted with EA (3 × 5 mL). The organic layers were combined, dried over anhydrous $Na_2SO_4$ and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the product **51** as a white solid (32.5 mg, 48% yield, 96:4 e.r.).[5]



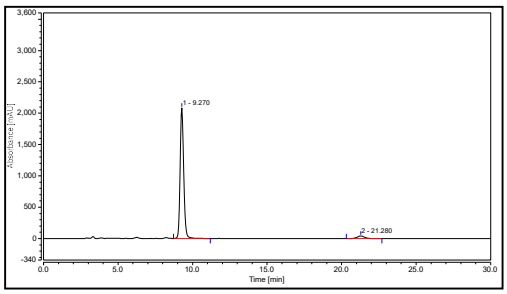

**(*R*, *Z*)-2-bromo-6-(1-(3-bromo-2-tosyl-1H-indol-1-yl)-2-phenylvinyl)-4-(tert-butyl)phenol (51)**

**$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.71 (d, $J$ = 7.5 Hz, 1H), 7.44 (d, $J$ = 8.3 Hz, 2H), 7.37 (s, 1H), 7.31 (d, $J$ = 2.3 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.19 – 7.16 (m, 1H), 7.11 – 7.05 (m, 3H), 6.96 (d, $J$ = 8.1 Hz, 2H), 6.91 – 6.88 (m, 2H), 6.46 (d, $J$ = 2.3 Hz, 1H), 6.04 (s, br, 1H), 2.27 (s, 3H), 0.97 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 147.9, 144.6, 144.2, 137.9, 137.1, 134.0, 132.5, 131.5, 129.7, 129.3, 128.8, 128.7, 128.6, 127.9, 126.9, 126.8, 126.2, 124.7, 122.8, 121.4, 112.4, 112.1, 101.8, 34.1, 31.1, 21.7. **HRMS (ESI)**: calcd. for $C_{33}H_{29}Br_2NNaO_3S^+$ $[M+Na]^+$ : 702.0107, found : 702.0104. **$[\alpha]_D^{20}$** = +22 (c = 0.1, $CHCl_3$).

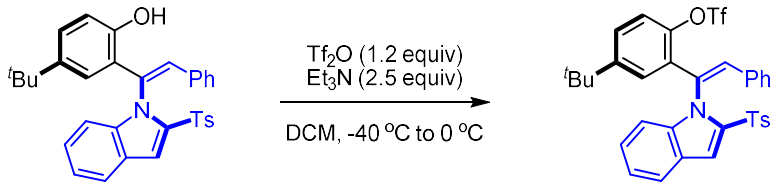
**HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.270 min, tr (minor) = 21.280 min, 96:4 e.r.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.257 | 490.9 | 50.15 |
| 2 | 21.330 | 488.0 | 49.85 |

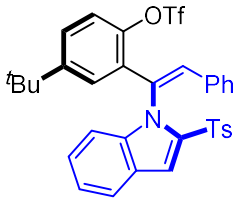



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 9.270 | 581.5 | 95.92 |
| 2 | 21.280 | 24.7 | 4.08 |




**3**, 96.5:3.5 e.r. **52**, 83%, 96.5:3.5 e.r.

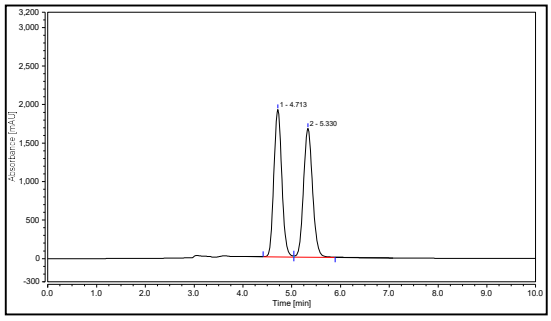
A scew-cap vial (8 mL) was charged with **3** (0.1 mmol, 52.1 mg) and DCM (2 mL). The resulted mixture was stirred at -40 °C, then $Tf_2O$ (0.12 mmol, 33.8 mg) was added slowly. The reaction was allowed warm to 0 °C and stirred for 12 h. After the reaction was completed, the solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography to afford the product **52** as a white solid (54.2 mg, 83% yield, 96.5:3.5 e.r.).[6]



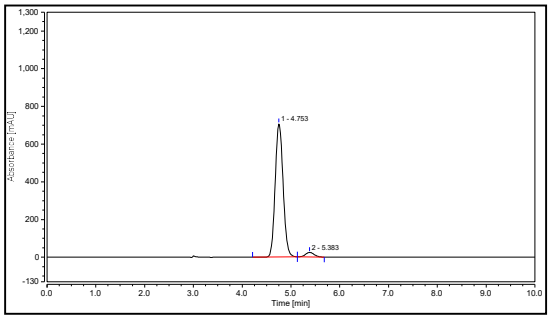

**(*R, Z*)-4-(tert-butyl)-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenyl trifluoroomethanesulfonate (52)**

**$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.79 (d, $J$ = 7.8 Hz, 1H), 7.68 (s, 1H), 7.56 (d, $J$ = 8.0 Hz, 2H), 7.41 (s, 1H), 7.29 (s, 2H), 7.25 – 7.18 (m, 3H), 7.00 (t, $J$ = 7.4 Hz, 1H), 6.88 – 6.83 (m, 4H), 6.67 (s, 1H), 6.41 (d, $J$ = 7.8 Hz, 2H), 2.15 (s, 3H), 1.02 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.3, 144.2, 143.9, 139.0, 137.2, 135.8, 135.3, 133.4, 130.4, 129.3, 129.1, 128.7, 128.3, 128.0, 127.0, 126.9, 126.8, 125.8, 122.9, 122.4, 121.3, 119.6, 117.5, 113.4, 112.0, 34.6, 30.9, 21.5. **$^{19}$F NMR (376 MHz, $CDCl_3$)** $\delta$ -73.9. **HRMS (ESI)**: calcd. for $C_{34}H_{30}F_3NNaO_5S_2^+$ $[M+Na]^+$ : 676.1410, found : 676.1409. **$[\alpha]_D^{20}$** = +19 (c = 0.1, $CHCl_3$).

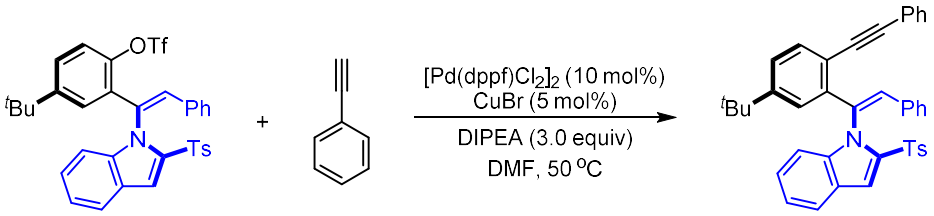
**HPLC analysis**: Daicel Chiralpak OD-H column (hexane: 2-propanol = 95:5, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 4.753 min, tr (minor) = 5.383 min, 96.5:3.5 e.r.




| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 4.713 | 362.3 | 50.17 |
| 2 | 5.330 | 359.9 | 49.83 |

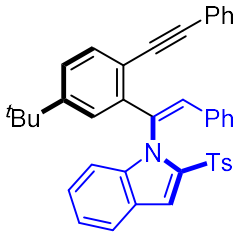



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 4.753 | 132.3 | 96.44 |
| 2 | 5.383 | 4.9 | 3.56 |




**52**, 96.5:3.5 e.r. **53**, 68%, 92.5:7.5 e.r.

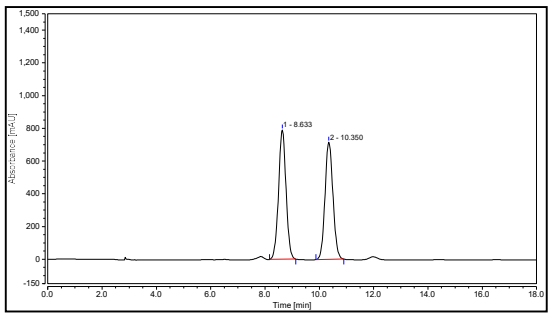
A scew-cap vial (8 mL) was charged with **52** (0.1 mmol, 65.3 mg), $Pd(dppf)Cl_2$ (10 mol%, 7.3 mg), CuBr (5 mol%, 0.7 mg) and DMF (1.0 mL). Phenylacetylene (0.3 mmol, 30.6 mg) and DIPEA (0.3 mol, 38.8 mg) was then added and the mixture was stirred at 50 °C for 12 h. The solvent was evaporated under vacuum and the residue was purified by flash column chromatography to afford the product **53** as a white solid (41.1 mg, 68% yield, 92.5:7.5 e.r.).[6]



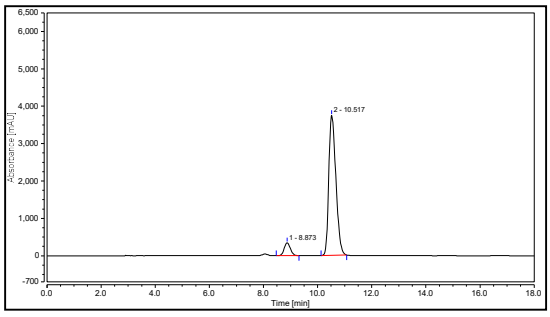

**(*R, Z*)-4-(tert-butyl)-2-(2-phenyl-1-(2-tosyl-1H-indol-1-yl)vinyl)phenyl trifluoromethanesulfonate (53)**

**$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.76 (s, 1H), 7.70 (d, $J$ = 7.9 Hz, 1H), 7.68 (s, 1H), 7.56 (d, $J$ = 8.1 Hz, 2H), 7.40 (d, $J$ = 8.1 Hz, 1H), 7.26 – 7.20 (m, 5H), 7.18 – 7.10 (m, 4H), 6.98 (t, $J$ = 7.5 Hz, 1H), 6.88 (t, $J$ = 7.7 Hz, 2H), 6.75 (d, $J$ = 8.1 Hz, 2H), 6.66 (s, 1H), 6.54 (d, $J$ = 7.8 Hz, 2H), 2.12 (s, 3H), 1.03 (s, 9H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 151.6, 143.4, 139.3, 139.1, 137.3, 135.6, 134.2, 133.9, 133.2, 131.6, 131.1, 129.2, 128.8, 128.3, 128.3, 128.2, 127.9, 126.5, 125.7, 125.0, 124.4, 123.5, 122.7, 121.9, 118.1, 113.3, 112.3, 93.5, 89.6, 34.6, 30.9, 21.5. **HRMS (ESI)**: calcd. for $C_{41}H_{35}NNaO_2S^+$ $[M+Na]^+$ : 628.2281, found : 628.2298. **$[\alpha]_D^{20}$** = -82 (c = 0.1, $CHCl_3$).

**HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 95:5, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.517 min, tr (minor) = 8.873 min, 92.5:7.5 e.r.



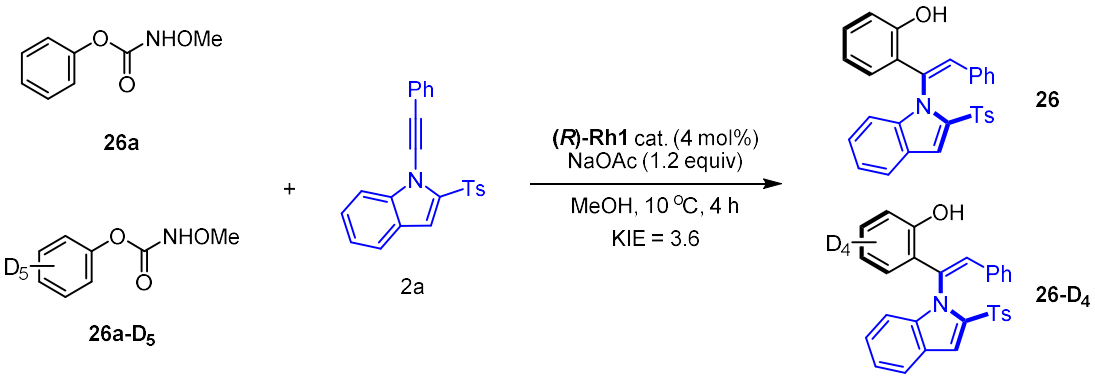

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.633 | 251.8 | 50.99 |
| 2 | 10.350 | 242.1 | 49.01 |



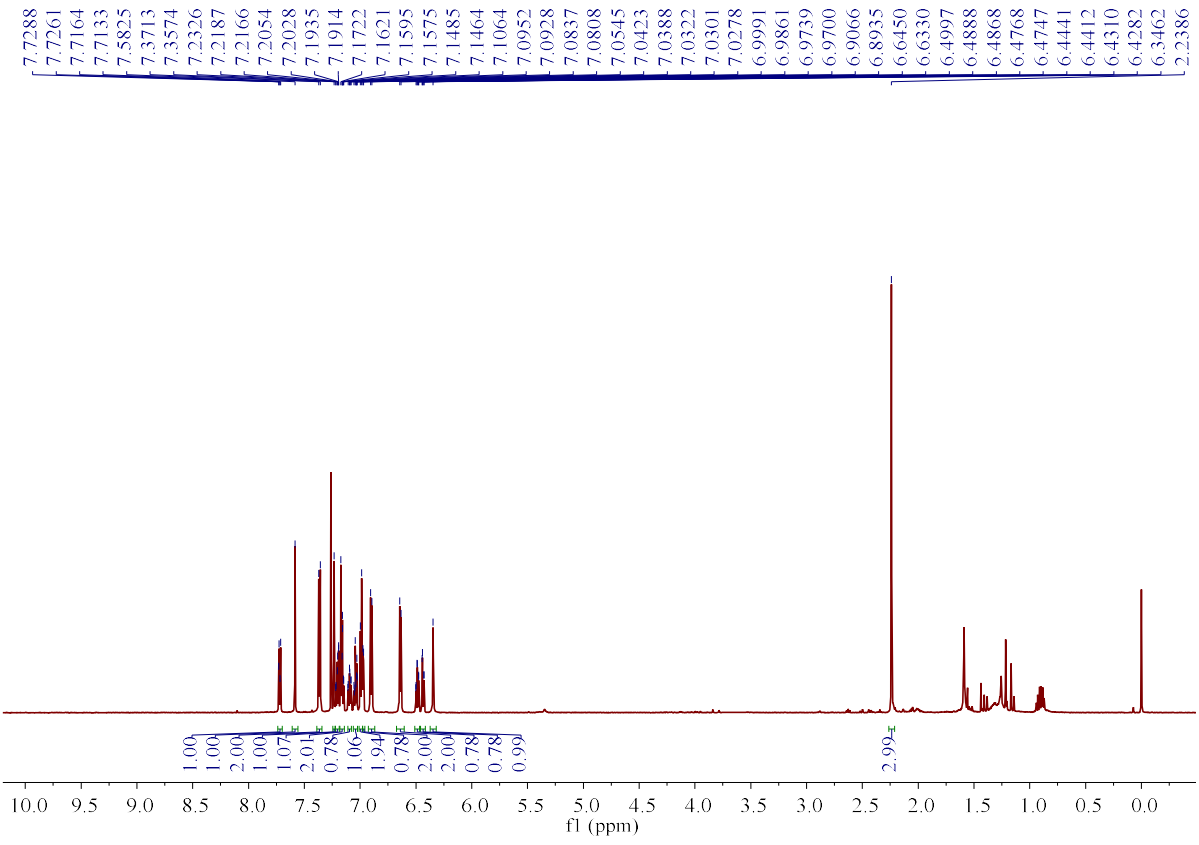

| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 8.873 | 90.7 | 7.37 |
| 2 | 10.517 | 1139.7 | 92.63 |

## 5. Mechanistic Studies

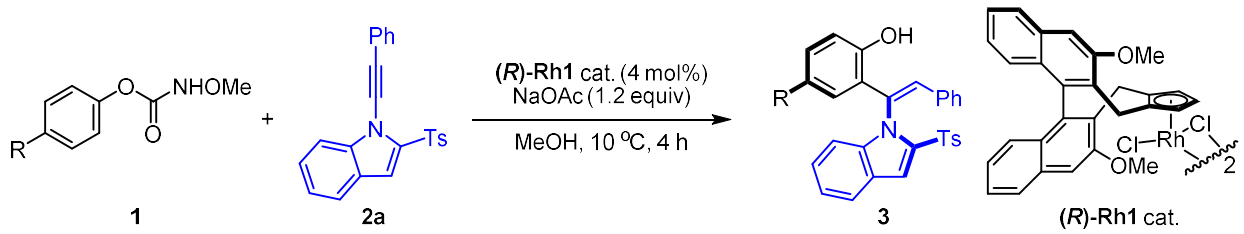
### 5.1 Parallel Experiments for KIE




Two scew-cap vials (8 mL) each was charged with alkynes **2a** (0.1 mmol, 1.0 equiv), **(*R*)-Rh1** (4 mol%) and NaOAc (0.12mmol, 2.0 equiv) in MeOH (2 mL) and the mixture was stirred at 10 ºC. The resulted mixture was kept at 10 ºC for 15 min, to which was added *N*-alkoxycarbamate **26a** (0.12 mmol, 1.2 equiv) or **26a-D5** (0.12 mmol, 1.2 equiv). The reaction was maintained at 10 ºC for 4 h. The two mixtures were combined and were rapidly evaporated under reduced pressure separately. The purification was performed by flash column chromatography on silica gel to afford the products. The KIE value was determined to be $k_H/k_D$ = 3.6 on the basis of $^1$H NMR analysis.

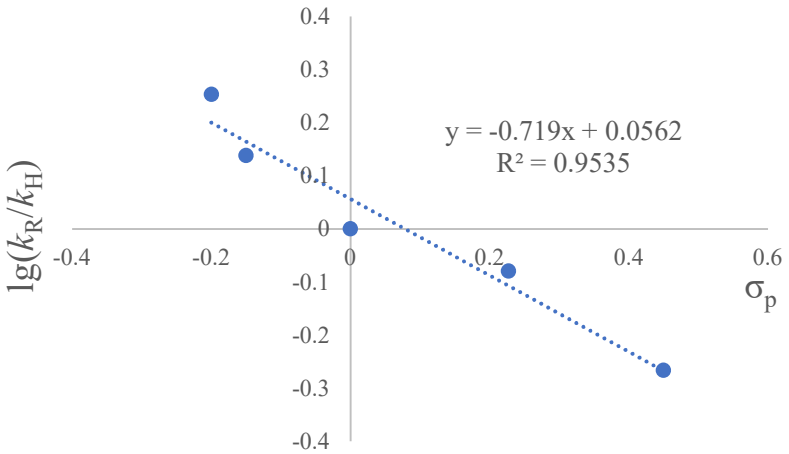


## 5.2 Hammett plot

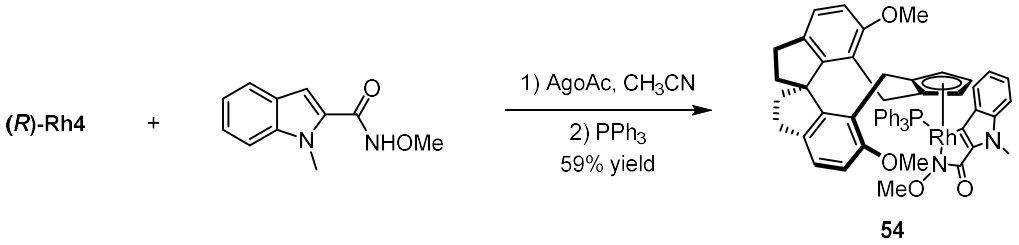



A scew-cap vial (8 mL) was charged with alkyne **2a** (0.1 mmol, 1.0 equiv), **(*R*)-Rh1** (4 mol%) and NaOAc (0.12mmol, 2.0 equiv) in MeOH (2 mL) and the mixture was stirred at 10 °C. The resulted mixture was kept at 10 °C for 15 min, to which was added *N*-alkoxycarbamate **1** (0.12 mmol, 1.2 equiv). The reaction was maintained at 10 °C for 4 h. The reaction mixture was evaporated under vacuum. The conversions were determined by $^1$H NMR with 1,3,5-trimethoxybenzene as an internal standard.

| Entry | R | σ(para) | Conv.(%) | lg($k_R$/$k_H$) |
|---|---|---|---|---|
| 1 | H | 0 | 24 | 0 |
| 2 | $^i$Pr | -0.15 | 33 | 0.138303 |
| 3 | $^t$Bu | -0.2 | 43 | 0.253257 |
| 4 | Cl | 0.227 | 20 | -0.07918 |
| 5 | COOMe | 0.45 | 13 | -0.26627 |



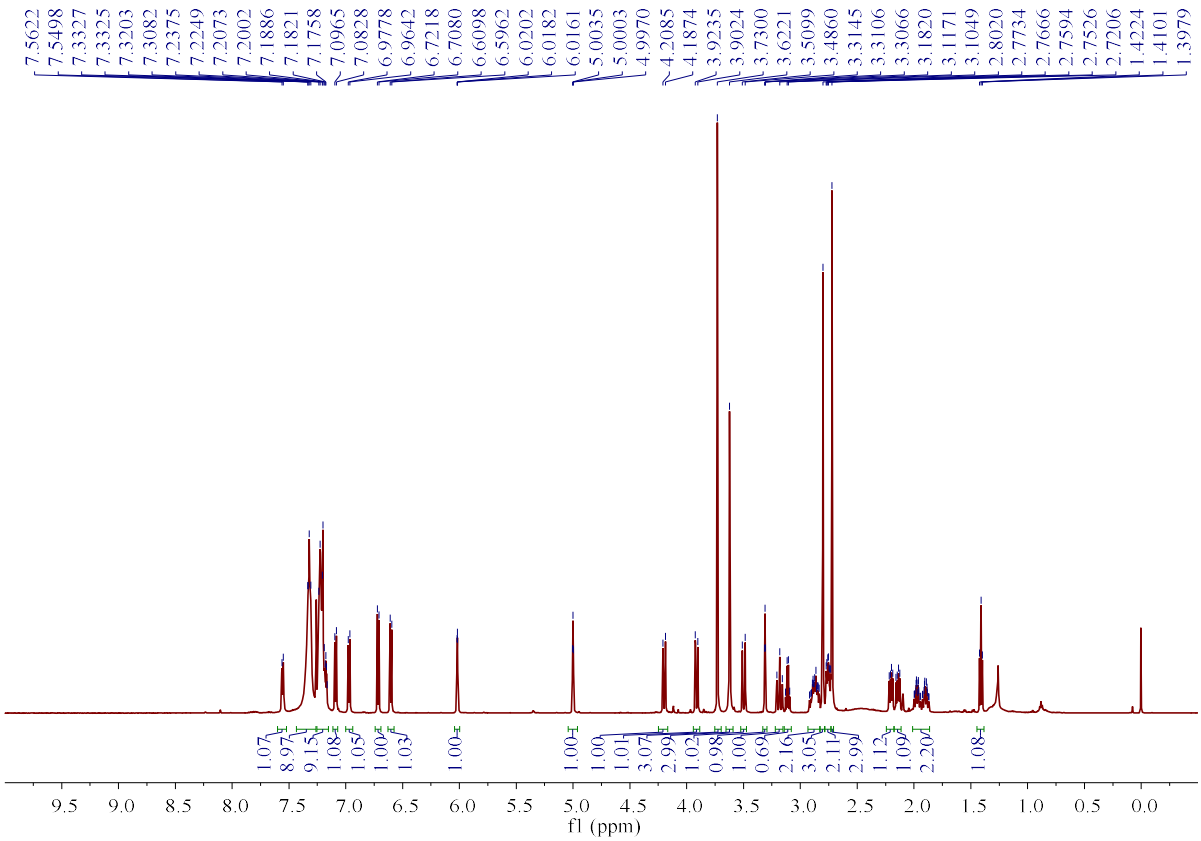
**5.3 Synthesis of Rhodium complexes 54.**



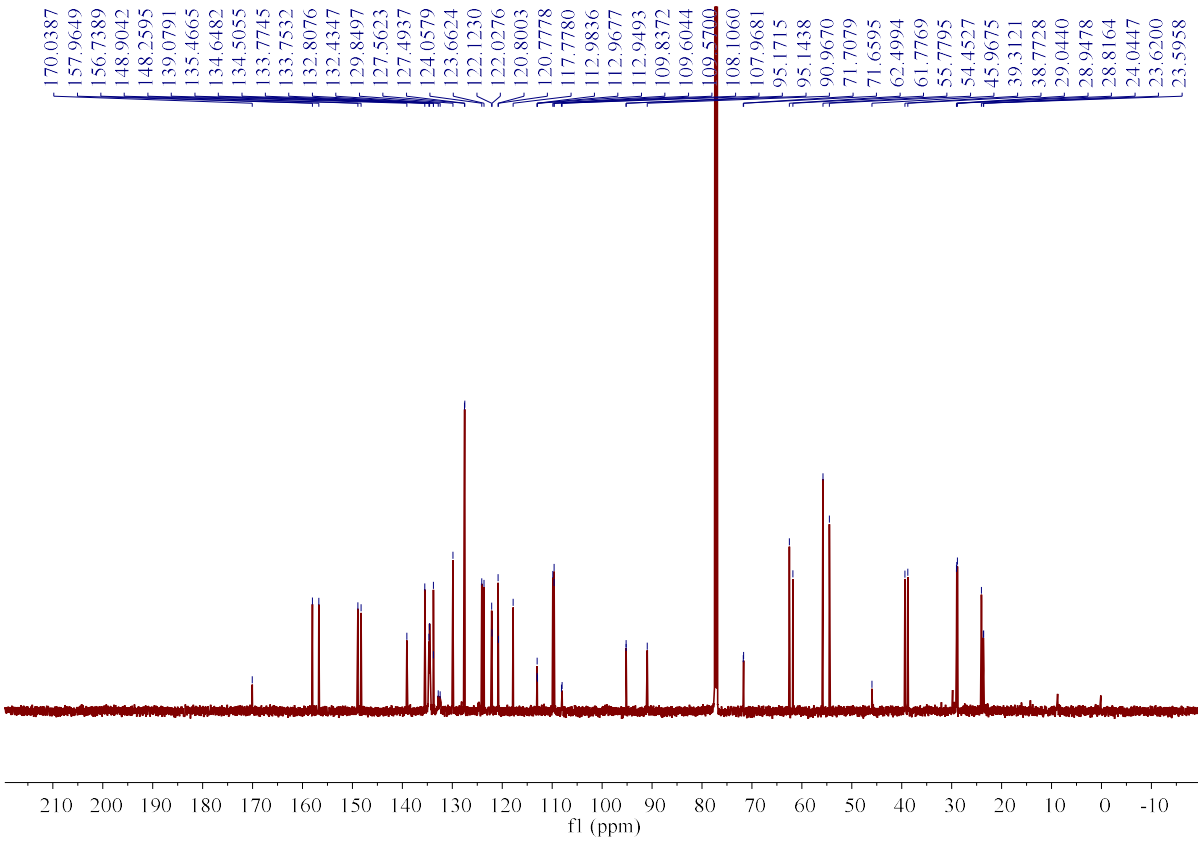

**54**

A mixture of N-methoxy-1-methyl-1H-indole-2-carboxamide (20.4 mg, 0.1 mmol, 2.0 equiv), **(*R*)-Rh4** compound (54.4 mg, 0.05 mmol) and silver acetate (33.4 mg, 0.2 mmol, 4.0 equiv) in acetonitrile (5 mL) was stirred for 30 min at room temperature under $N_2$ atmosphere. Another portion of triphenylphosphine (26.2 mg, 0.1 mmol, 2.0 equiv) was added and the mixture was allowed to stir for additional 50 min at room temperature. The resulting crude mixture was filtered through PTFE syringe filter washing with acetonitrile (10 mL) and concentrated under reduced pressure. **54** was purified by deactivated silica gel chromatography (by flushing with hexane-ethyl acetate-triethylaminen = 1:1:0.4 solution). Product **54** was isolated in 59% yield as a yellow solid.

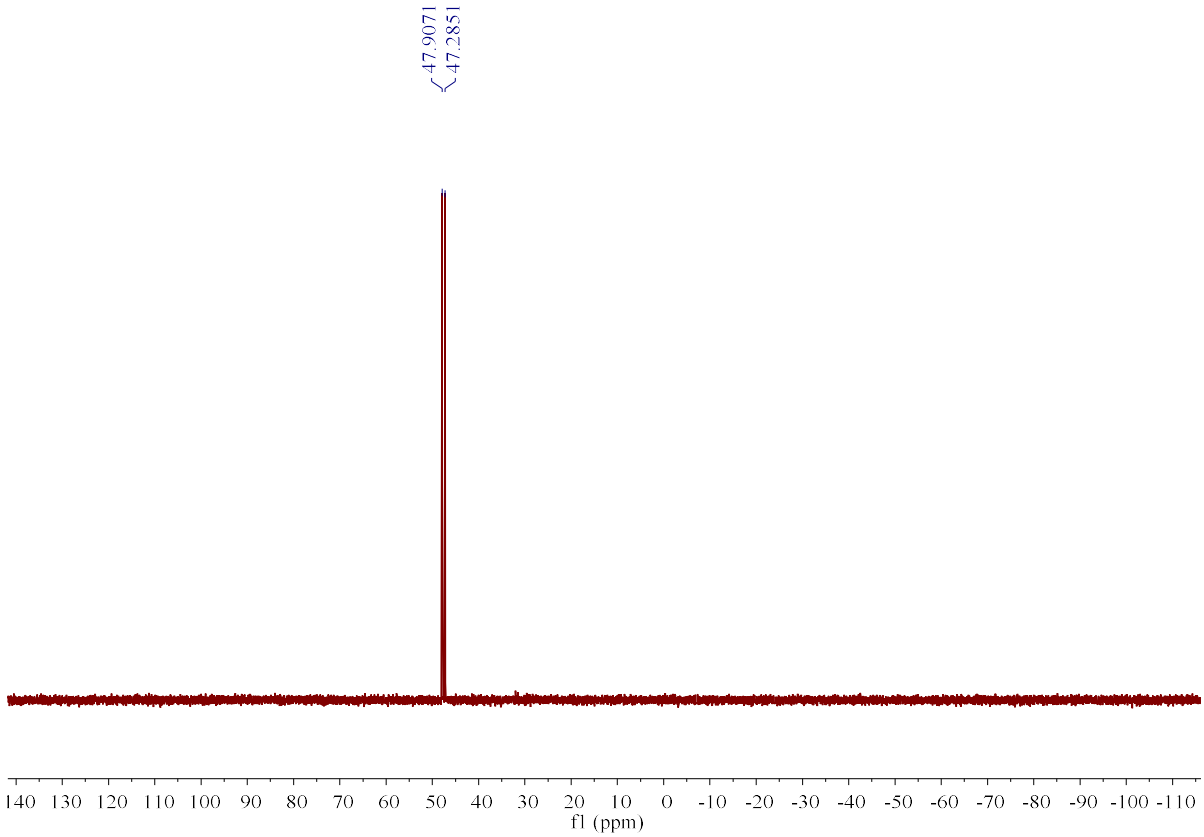
**$^1$H NMR (600 MHz, $CDCl_3$)** $\delta$ 7.56 (d, $J$ = 7.5 Hz, 1H), 7.43 – 7.26 (m, 9H), 7.25 – 7.15 (m, 9H), 7.09 (d, $J$ = 8.3 Hz, 1H), 6.97 (d, $J$ = 8.1 Hz, 1H), 6.71 (d, $J$ = 8.3 Hz, 1H), 6.60 (d, $J$ = 8.2 Hz, 1H), 6.04 – 6.00 (m, 1H), 5.04 – 4.96 (m, 1H), 4.20 (d, $J$ = 12.7 Hz, 1H), 3.91 (d, $J$ = 12.7 Hz, 1H), 3.73 (s, 3H), 3.62 (s, 3H), 3.50 (d, $J$ = 14.4 Hz, 1H), 3.31 (t, $J$ = 2.4 Hz, 1H), 3.18 (t, $J$ = 14.8 Hz, 1H), 3.11 (q, $J$ = 7.3 Hz, 1H), 2.93 – 2.83 (m, 2H), 2.80 (s, 3H), 2.78 - 2.73 (m, 2H), 2.72 (s, 3H), 2.20 (dd, $J$ = 12.1, 6.7 Hz, 1H), 2.14 (dd, $J$ = 12.6, 6.9 Hz, 1H), 2.01 – 1.86 (m, 2H), 1.41 (t, $J$ = 7.3 Hz, 1H). **$^{13}$C NMR (150 MHz, $CDCl_3$)** $\delta$ 170.1 (d, $J$ = 4.0 Hz), 157.4 (d, $J$ = 185.0 Hz), 148.6 (d, $J$ = 97.3 Hz), 139.1, 135.5, 134.7, 134.5 (br), 133.77, 133.75, 132.8, 132.5, 129.9, 127.6, 127.5, 123.9 (d, $J$ = 59.7 Hz), 122.1, 122.0, 120.80, 120.78, 117.8, 113.0 (t, $J$ = 2.4 Hz), 109.8, 109.60, 109.57, 108.1, 108.0, 95.2 (d, $J$ = 4.2 Hz), 91.0 (d, $J$ = 3.6 Hz), 71.7 (d, $J$ = 7.3 Hz), 62.5, 61.8, 55.8, 54.5, 46.0, 39.3, 38.8, 29.0 (d, $J$ = 14.5 Hz), 28.8, 24.0, 23.6 (d, $J$ = 3.7 Hz). **$^{31}$P NMR (243 MHz, $CDCl_3$)** $\delta$ 47.6 (d, $J$ = 151.1 Hz). **HRMS (ESI)**: calcd. for $C_{55}H_{51}N_2NaO_4PRh^+$ $[M+H]^+$ : 937.2636, found : 937.2635.



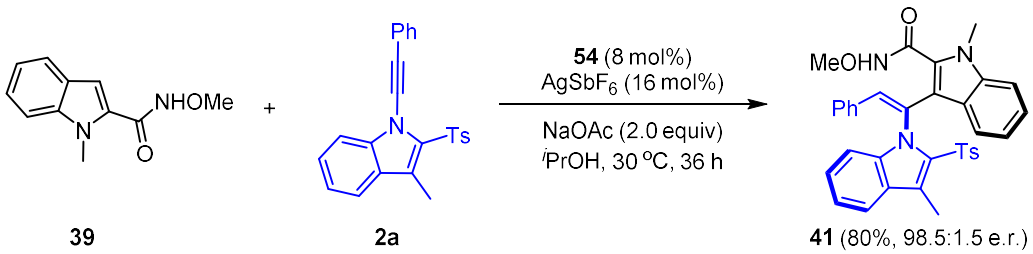

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 54.**




**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 54.**



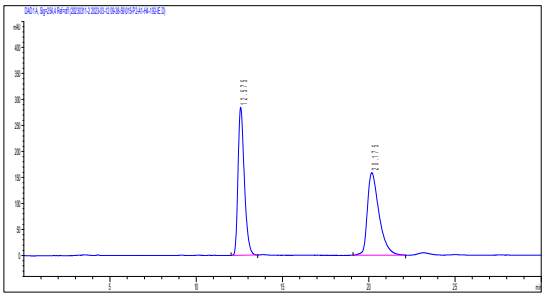

**$^{31}$P NMR (243 MHz, $CDCl_3$) spectrum of 54.**



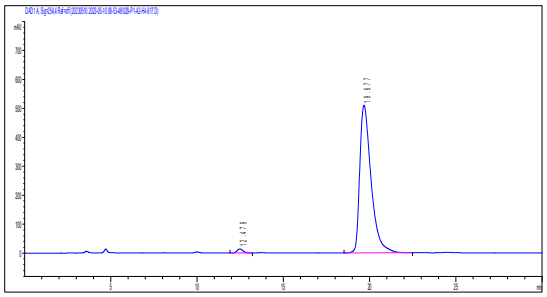

**39** **2a** **41** (80%, 98.5:1.5 e.r.)

A scew-cap vial (8 mL) was charged with *N*-methoxy-1-methyl-1H-indole-2-carboxamide **39** (0.1 mmol, 1 equiv), alkyne **2a** (0.12 mmol, 1.2 equiv), **54** (5 mol%), $AgSbF_6$ (16 mol%) and NaOAc (0.2 mmol, 2.0 equiv) in $^{i}$PrOH (2 mL) and the reaction mixture was stirred at 30 °C for 36 h under $N_2$. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding product **41** (47.1 mg, 80%, 98.5:1.5 e.r.).

**HPLC analysis**: Daicel Chiralpak IE column (hexane: 2-propanol = 60:40, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 19.677 min, tr (minor) = 12.479 min, 98.5:1.5 e.r.



| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.575 | 7228.9 | 49.24 |
| 2 | 20.175 | 7453.6 | 50.76 |



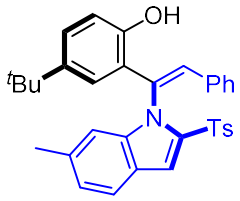
| No. | Time | Area | Area (%) |
|---|---|---|---|
| 1 | 12.479 | 335.4 | 1.42 |
| 2 | 19.677 | 23201.2 | 98.58 |

### 5.4 Rotational Barrier for Products 12 and 41.

The enantiomerisation barrier, corresponding to the barrier to rotation for the following atropisomers, was obtained by kinetic of racemisation of an enantiomer. The slope of the first order kinetic line gives the racemisation constant ($k_{racemisation}$ =2 × $k_{enantiomerisation}$). Eyring equation gives the enantiomerisation barrier ($\Delta G^{\ddagger}_{enaniomerization}$) from enantiomerisation constant ($k_{enantiomerisation}$), R = 8.31451 J •K$^{-1}$ • mol$^{-1}$, $h$ = 6.62608 × 10$^{-34}$ Js and $k_B$ = 1.38066 × 10$^{-23}$ J/K. Reactions were conducted at 1 mg/mL concentration. Enantiomeric excess values were determined by HPLC.

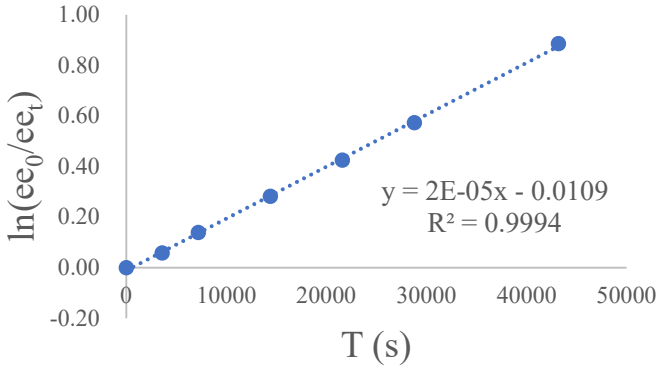
$$\Delta G^{\ddagger}_{enantiomerization} = RT\times \ln\frac{k_B\times T}{h\times k_{enantiomerisation}}$$

Racemization of **12** in PhMe at 80 °C.




**12.** $\Delta G^{\ddagger}$ = 28.9 kcal/mol (80 °C, PhMe)

| T/s | ee | ln(ee$_0$/ee$_t$) |
|---|---|---|
| 0 | 90 | 0.000000 |
| 3600 | 85 | 0.058269 |
| 7200 | 78 | 0.138841 |
| 14400 | 68 | 0.282001 |
| 21600 | 59 | 0.424400 |
| 28800 | 51 | 0.573024 |
| 43200 | 37 | 0.885687 |



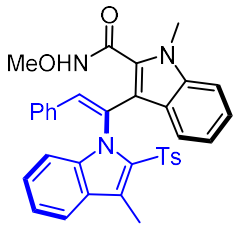

$k_{racemization}$ (80 °C) = 2.0×10$^{-5}$ s$^{-1}$

$k_{enantiomerization}$ (80 °C) = 1.0×10$^{-5}$ s$^{-1}$

Employing the Eyring equation: $\Delta G^{\ddagger}_{enantiomerization} = RT\times \ln\frac{k_B\times T}{hk_{enantiomerisation}}$

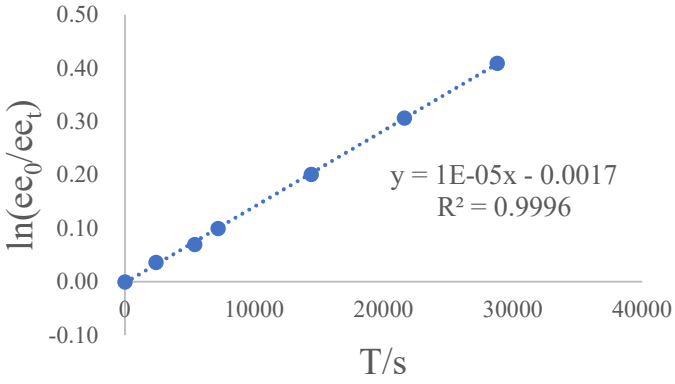
$$\Delta G^{\neq} = 8.314\ J\bullet K^{-1}\bullet\ mol^{-1}\times 353.15\ K\times\ln\frac{1.381\times10^{-23}\ J\bullet K^{-1}\times 353.15\ K}{1.0\times10^{-5}\ S^{-1}\times 6.626\times10^{-34}\ J\bullet s}$$

$$\Delta G^{\neq} = 120.8\ kJ\bullet mol^{-1} = 28.9\ kcal\bullet mol^{-1}$$




**41.** $\Delta G^{\ddagger}$ = 30.2 kcal/mol (90 ºC, PhMe)

| T/s | ee | $\ln(ee_0/ee_t)$ |
|---|---|---|
| 0 | 97.6 | 0.000000 |
| 2400 | 94.1 | 0.036519 |
| 5400 | 91.0 | 0.070018 |
| 7200 | 88.3 | 0.100137 |
| 14400 | 79.8 | 0.201354 |
| 21600 | 71.8 | 0.306993 |
| 28800 | 64.8 | 0.409572 |




$k_{racemization}$ (90 ºC) = $1.0\times10^{-5}$ $s^{-1}$

$k_{enantiomerization}$ (90 ºC) = $5.0\times10^{-6}$ $s^{-1}$

Employing the Eyring equation: $\Delta G^{\neq} = RT \ln(\frac{k_B \times T}{k_{ent} \times h})$

$$\Delta G^{\neq} = 8.314\, J \bullet mol^{-1} \bullet K^{-1} \times 363.15\, K \times \ln(\frac{1.381 \times 10^{-23} J \bullet K^{-1} \times 363.15}{5.0 \times 10^{-6} s^{-1} \times 6.626 \times 10^{-34} J \bullet s})$$

$$\Delta G^{\neq} = 126.4\, kJ \bullet mol^{-1} = 30.2\, kcal \bullet mol^{-1}$$

## 6. X-Ray Crystallographic Data

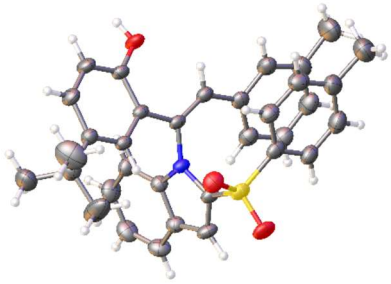


**Table 1 Crystal data and structure refinement for 17 (CCDC 2243043).**

| | |
|---|---|
| Identification code | 17 |
| Empirical formula | $C_{34}H_{33}NO_3S$ |
| Formula weight | 535.67 |
| Temperature/K | 200.00 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.1729(4) |
| b/Å | 15.6495(7) |
| c/Å | 19.8440(8) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2848.6(2) |
| Z | 4 |
| $\rho_{cal}$cg/cm$^3$ | 1.249 |
| μ/mm$^{-1}$ | 1.282 |
| F(000) | 1136.0 |
| Crystal size/mm$^3$ | 0.4 × 0.3 × 0.1 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 7.194 to 136.404 |
| Index ranges | $-10 \le h \le 11$, $-18 \le k \le 18$, $-23 \le l \le 23$ |
| Reflections collected | 44830 |
| Independent reflections | 5193 [$R_{int}$ = 0.0538, $R_{sigma}$ = 0.0255] |
| Data/restraints/parameters | 5193/0/358 |
| Goodness-of-fit on F2 | 1.051 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0424, $wR_2$ = 0.1180 |
| Final R indexes [all data] | $R_1$ = 0.0436, $wR_2$ = 0.1191 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.53/-0.18 |
| Flack parameter | 0.038(6) |

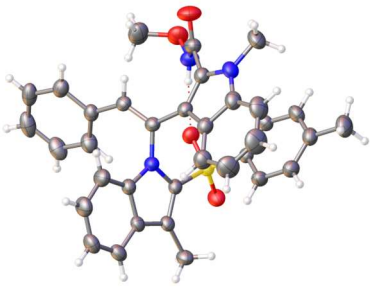


**Table 2 Crystal data and structure refinement for 41 (CCDC 2260294).**

| | |
|---|---|
| Identification code | 41 |
| Empirical formula | $C_{35}H_{31}N_3O_4S$ |
| Formula weight | 589.69 |
| Temperature/K | 255.00 |
| Crystal system | hexagonal |
| Space group | $P6_5$ |
| a/Å | 21.8313(6) |
| b/Å | 21.8313(6) |
| c/Å | 11.5605(4) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 120 |
| Volume/Å$^3$ | 4771.6(3) |
| Z | 6 |
| $\rho_{calc}$g/cm$^3$ | 1.231 |
| μ/mm$^{-1}$ | 1.241 |
| F(000) | 1860.0 |
| Crystal size/mm$^3$ | 0.4 × 0.3 × 0.3 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 8.966 to 136.984 |
| Index ranges | -26 ≤ h ≤ 26, -26 ≤ k ≤ 26, -13 ≤ l ≤ 12 |
| Reflections collected | 149628 |
| Independent reflections | 5768 [$R_{int}$ = 0.0426, $R_{sigma}$ = 0.0131] |
| Data/restraints/parameters | 5768/350/396 |
| Goodness-of-fit on F$^2$ | 1.053 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0268, $wR_2$ = 0.0710 |
| Final R indexes [all data] | $R_1$ = 0.0274, $wR_2$ = 0.0715 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.14/-0.24 |
| Flack parameter | 0.036(4) |

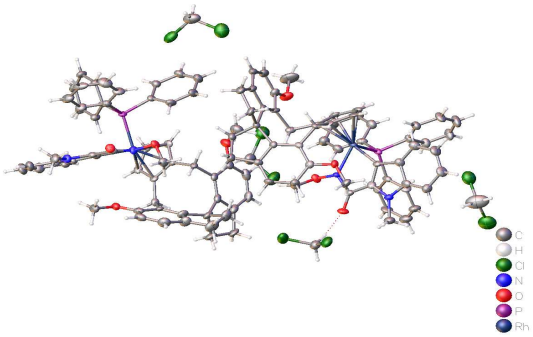


**Table 2 Crystal data and structure refinement for compound 54 (CCDC 2265864).**

| | |
|---|---|
| Identification code | 54 |
| Empirical formula | $C_{57}H_{54}Cl_4N_2O_4PRh$ |
| Formula weight | 1106.70 |
| Temperature/K | 153.00 |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| a/Å | 14.7897(15) |
| b/Å | 13.9358(14) |
| c/Å | 27.027(3) |
| α/° | 90 |
| β/° | 103.411(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 5418.6(9) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.357 |
| μ/mm$^{-1}$ | 5.010 |
| F(000) | 2280.0 |
| Crystal size/mm$^3$ | 0.4 × 0.3 × 0.2 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.144 to 136.872 |
| Index ranges | $-17 \le h \le 17$, $-16 \le k \le 16$, $-32 \le l \le 32$ |
| Reflections collected | 74916 |
| Independent reflections | 19422 [$R_{int}$ = 0.0533, $R_{sigma}$ = 0.0503] |
| Data/restraints/parameters | 19422/12/1251 |
| Goodness-of-fit on $F^2$ | 1.061 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0518, $wR_2$ = 0.1319 |
| Final R indexes [all data] | $R_1$ = 0.0527, $wR_2$ = 0.1327 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.60/-1.12 |
| Flack parameter | 0.153(9) |

## 7. References

[1] (a) B. Ye, N. Cramer. *J. Am. Chem. Soc*. **2013**, *135*, 636. (b) N. Zheng, W. Cui, C. Zheng, S. You. *J. Am. Chem. Soc.* **2016**, *138*, 5242.

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[3] R. Mi, H. Chen, X. Zhou, N. Li, D. Ji, F. Wang, Y. Lan, X. Li, *Angew. Chem., Int. Ed*. **2022**, *61*, e202111860.

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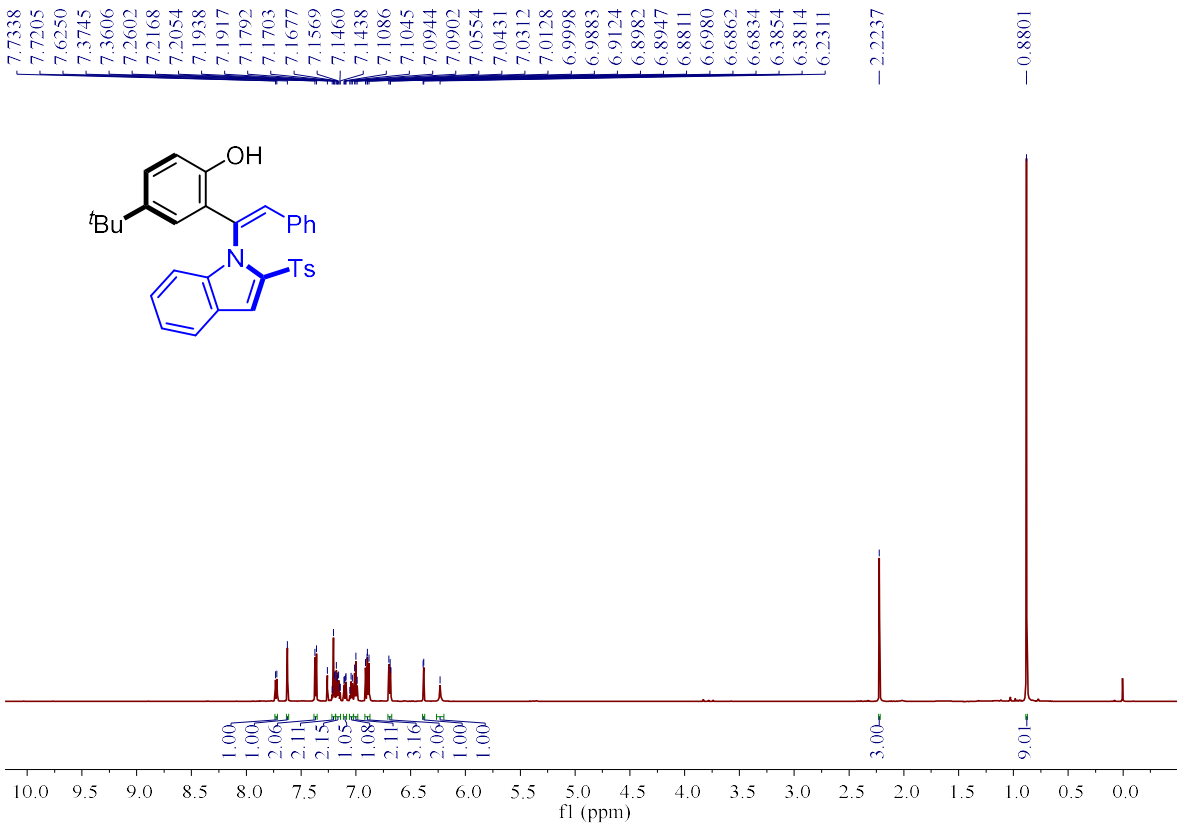
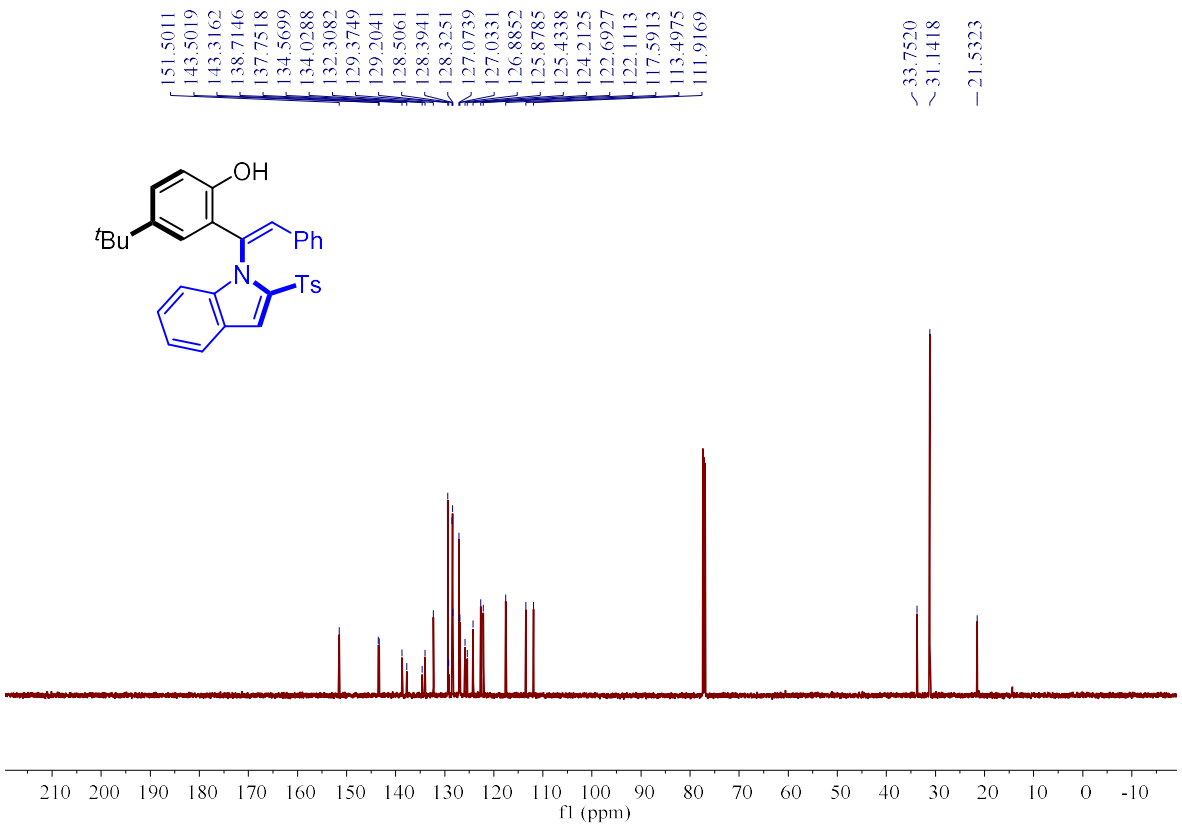
[5] A. Thevenon, A. Cyriac, D. Myers, A. White, C. Durr, C. Williams. *J. Am. Chem. Soc.* **2018**, *140*, 6893.

[6] P. Wang, Y. Huang, J. Jing, F. Wang, X. Li. *Org. Lett*. **2022**, *24*, 2531.

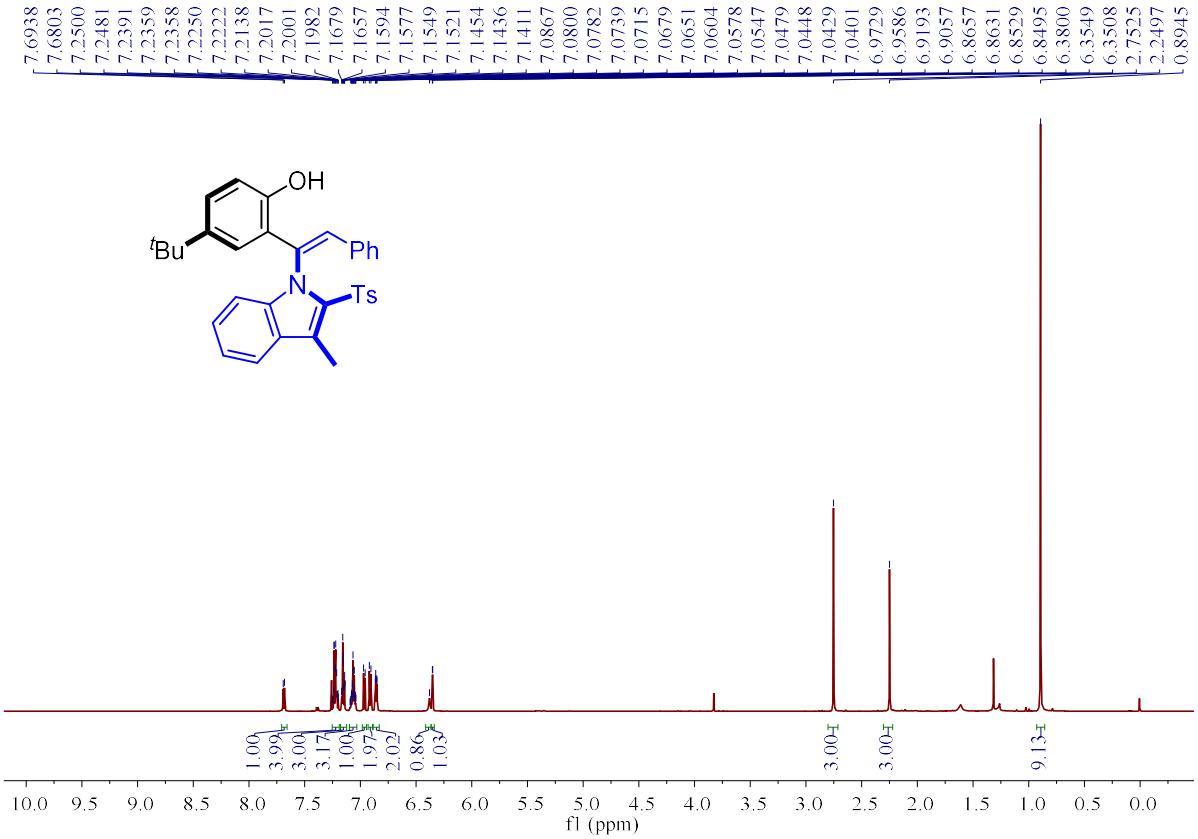
## 8. NMR Spectra



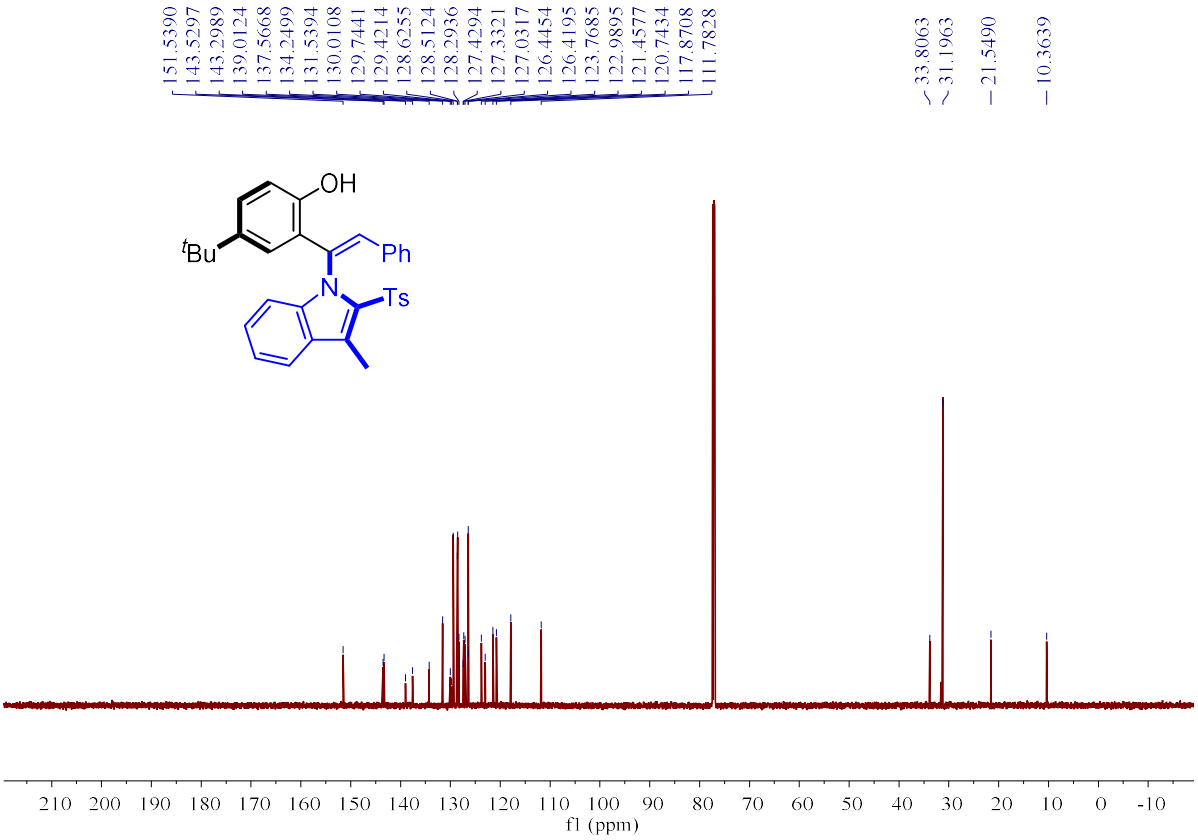

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 3.**



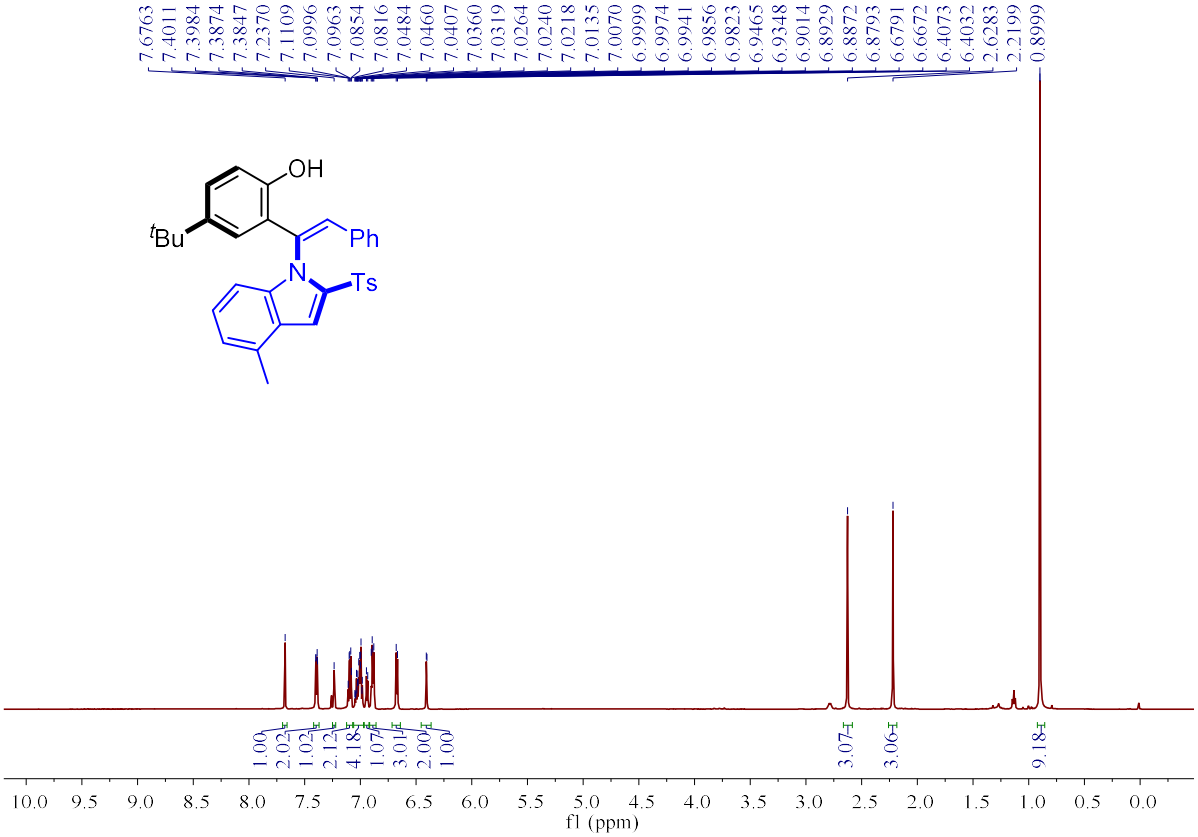

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 3.**



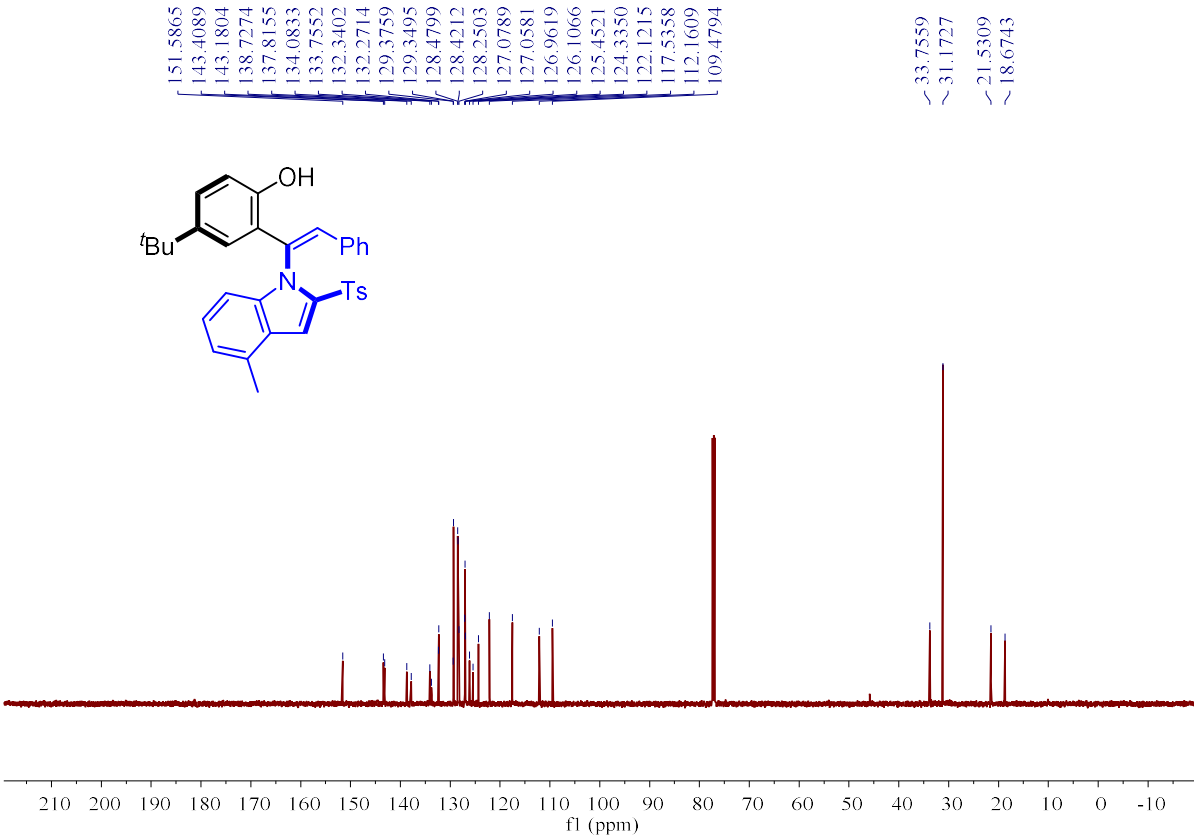

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 4.**



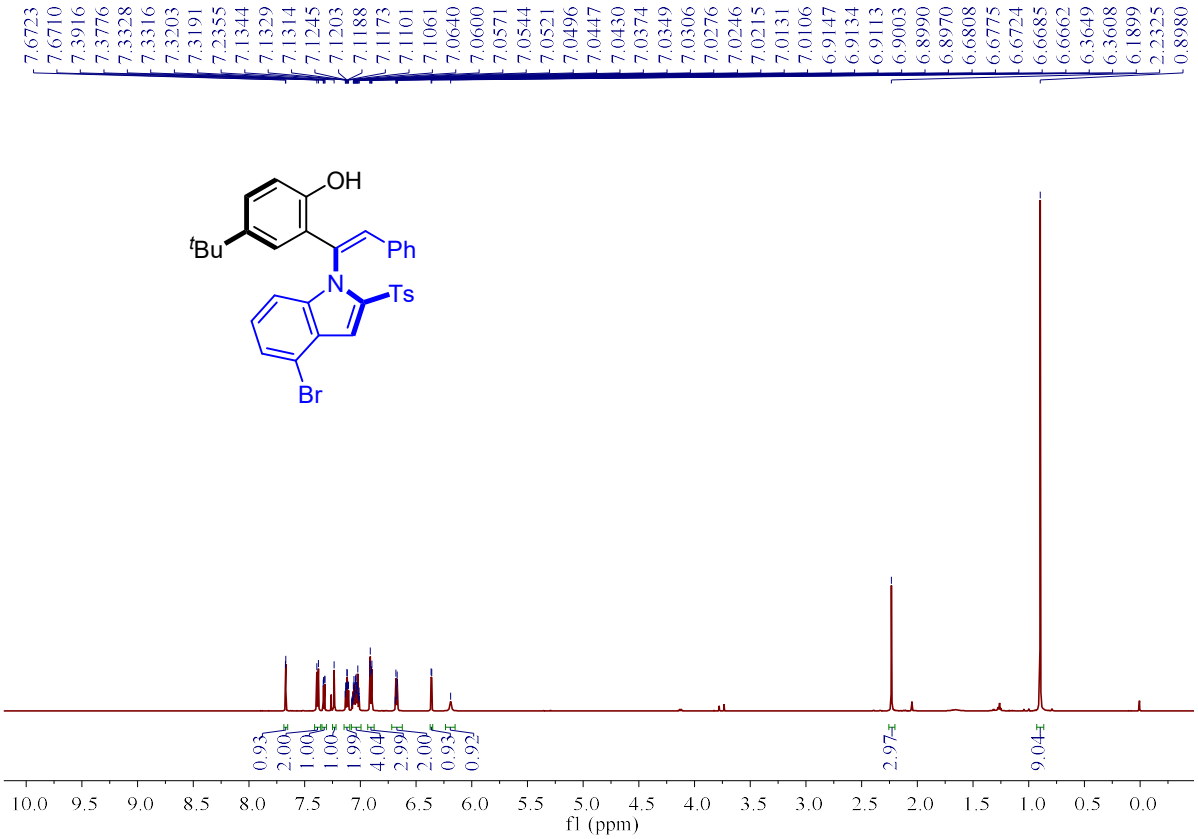

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 4.**



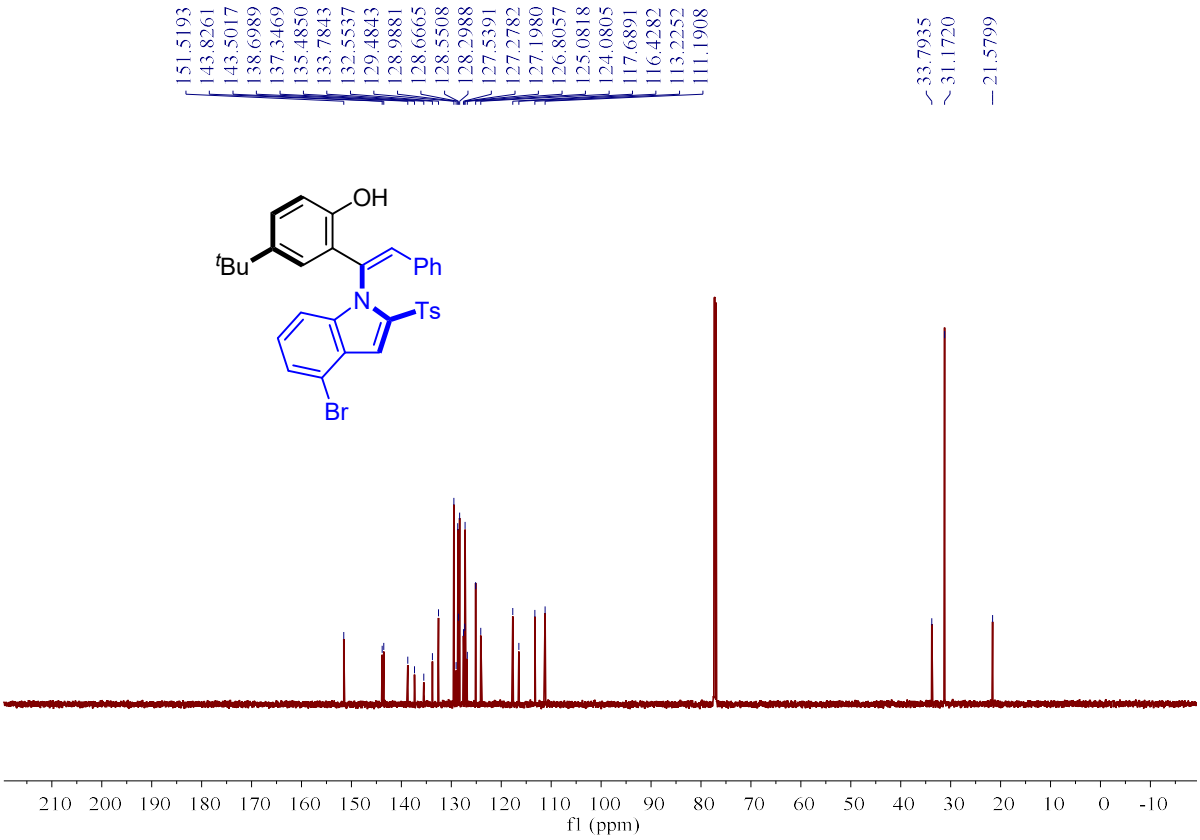

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 5.**



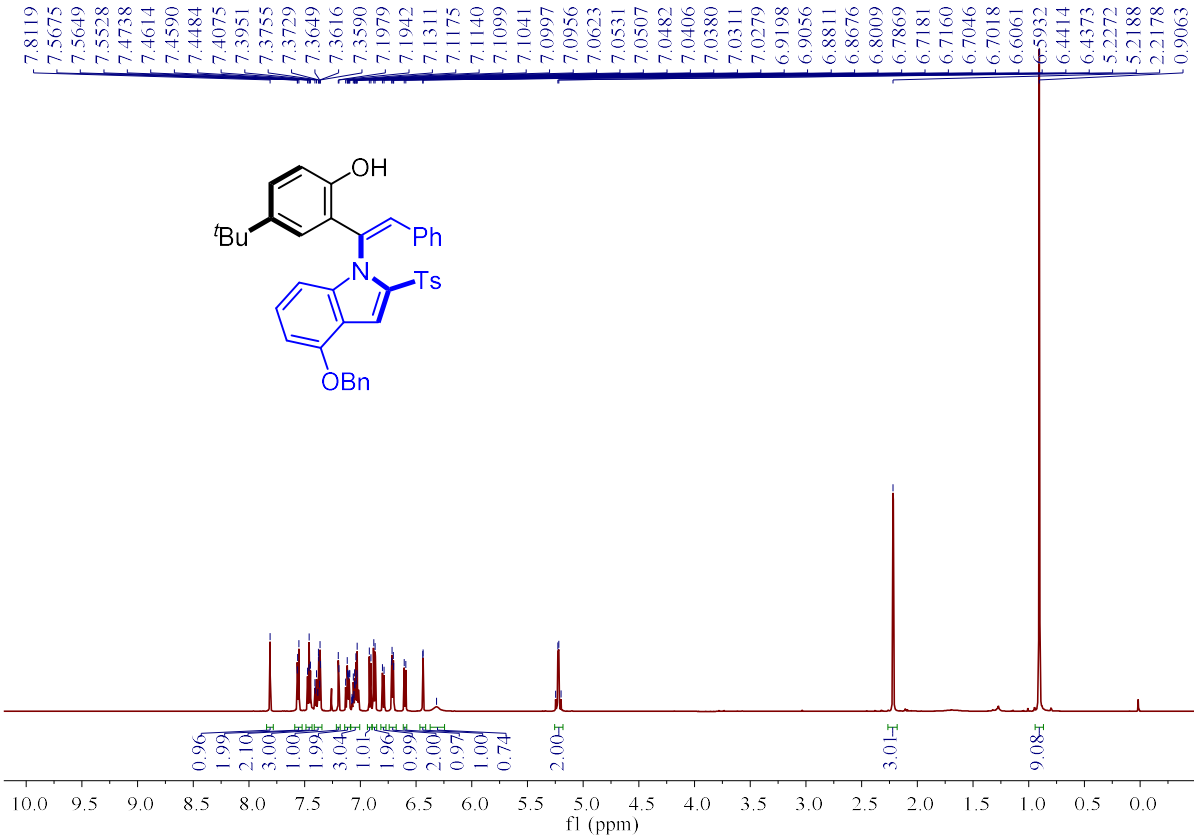

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 5.**



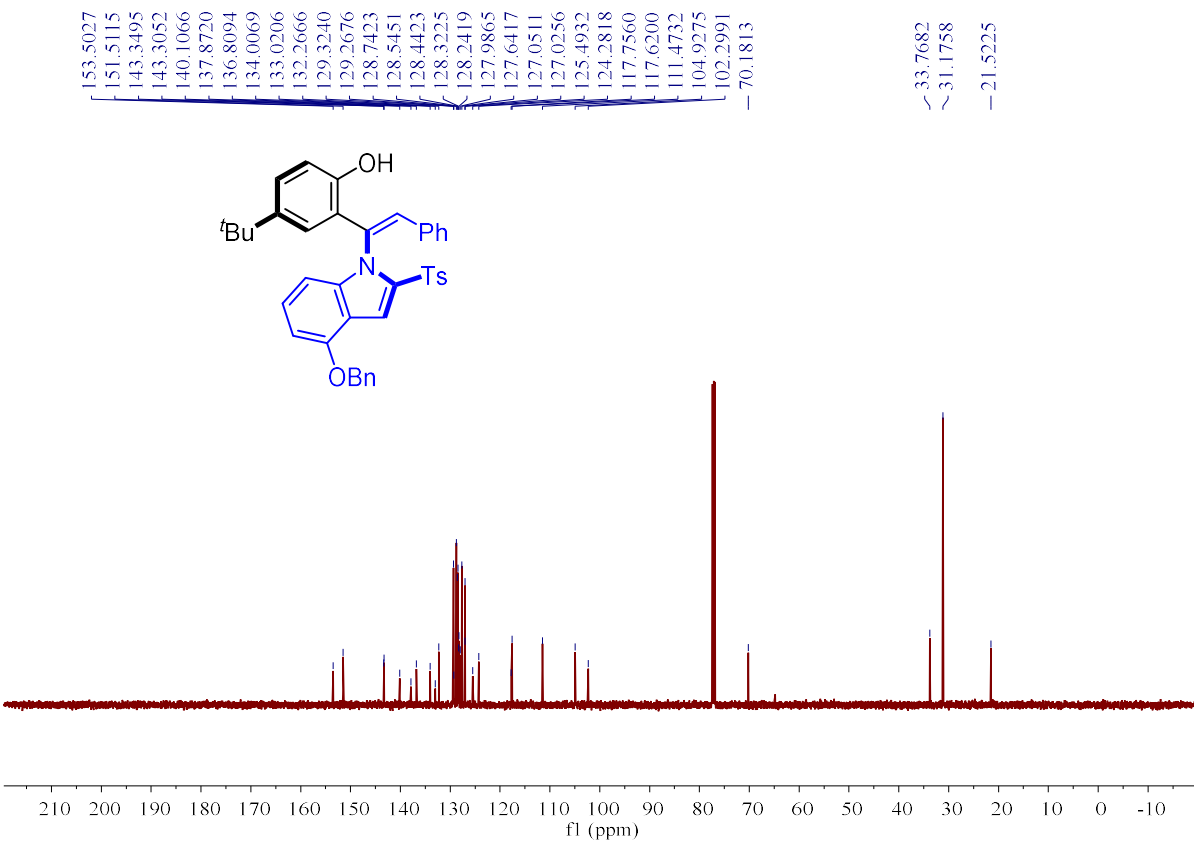

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 6.**



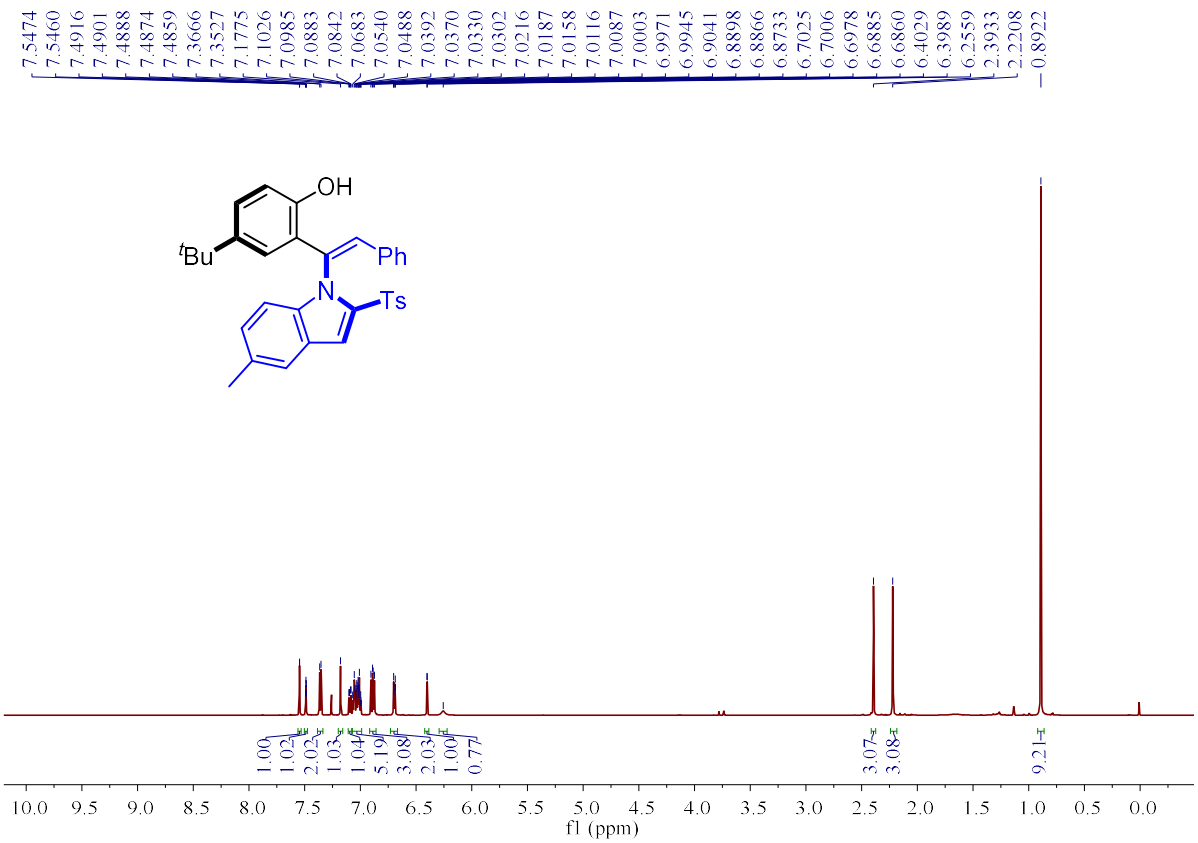

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 6.**



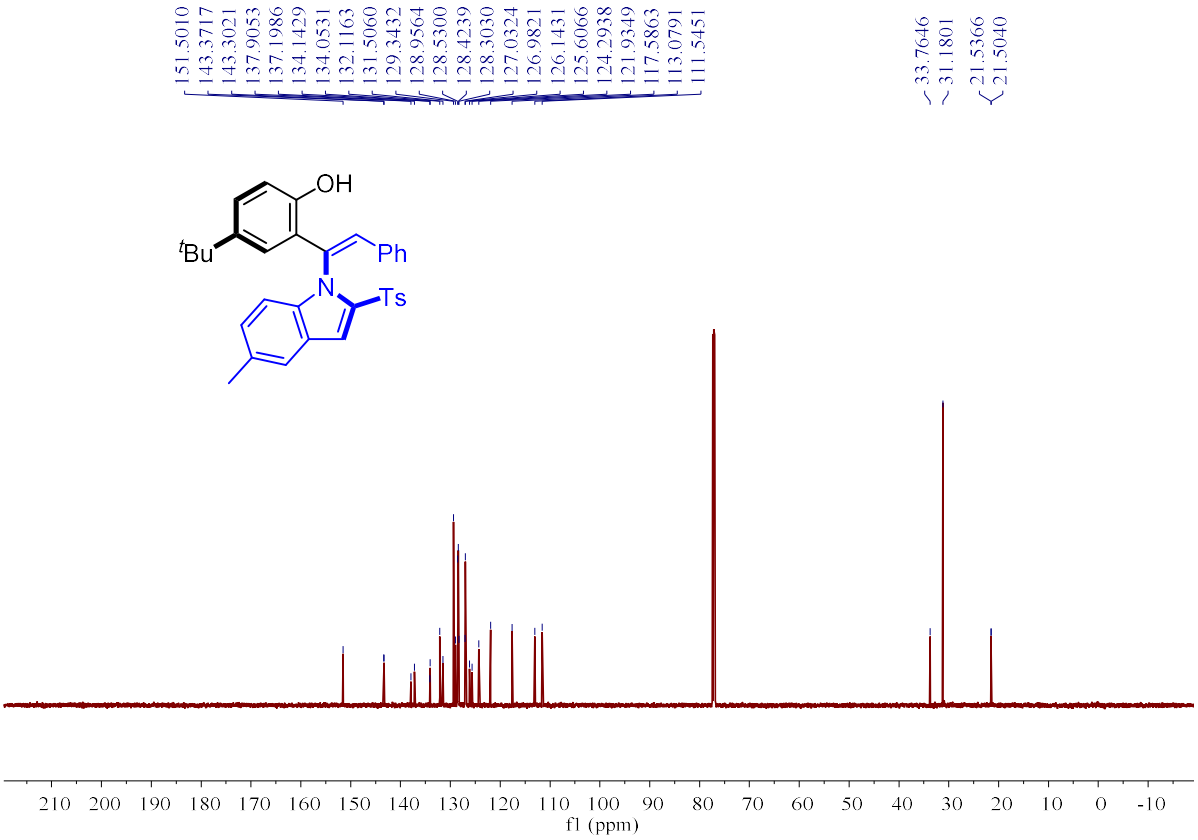

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 7.**



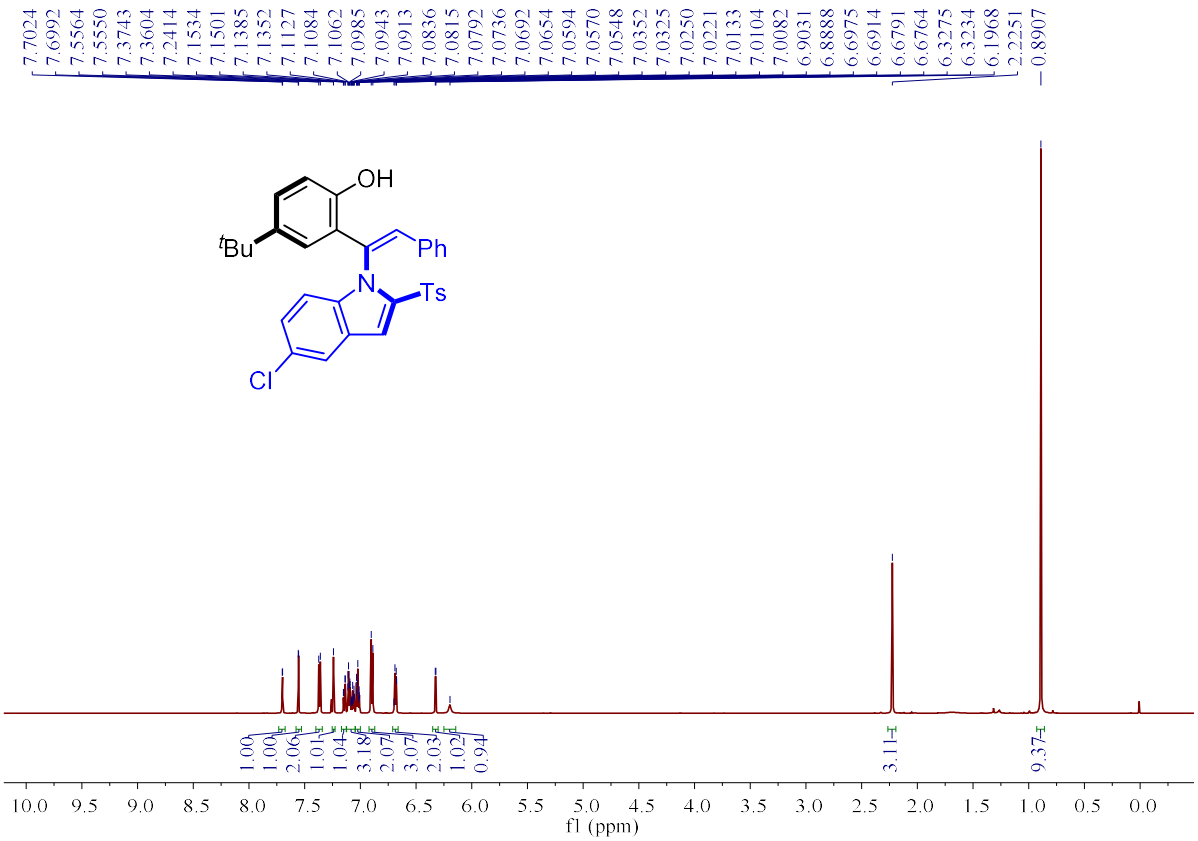

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 7.**



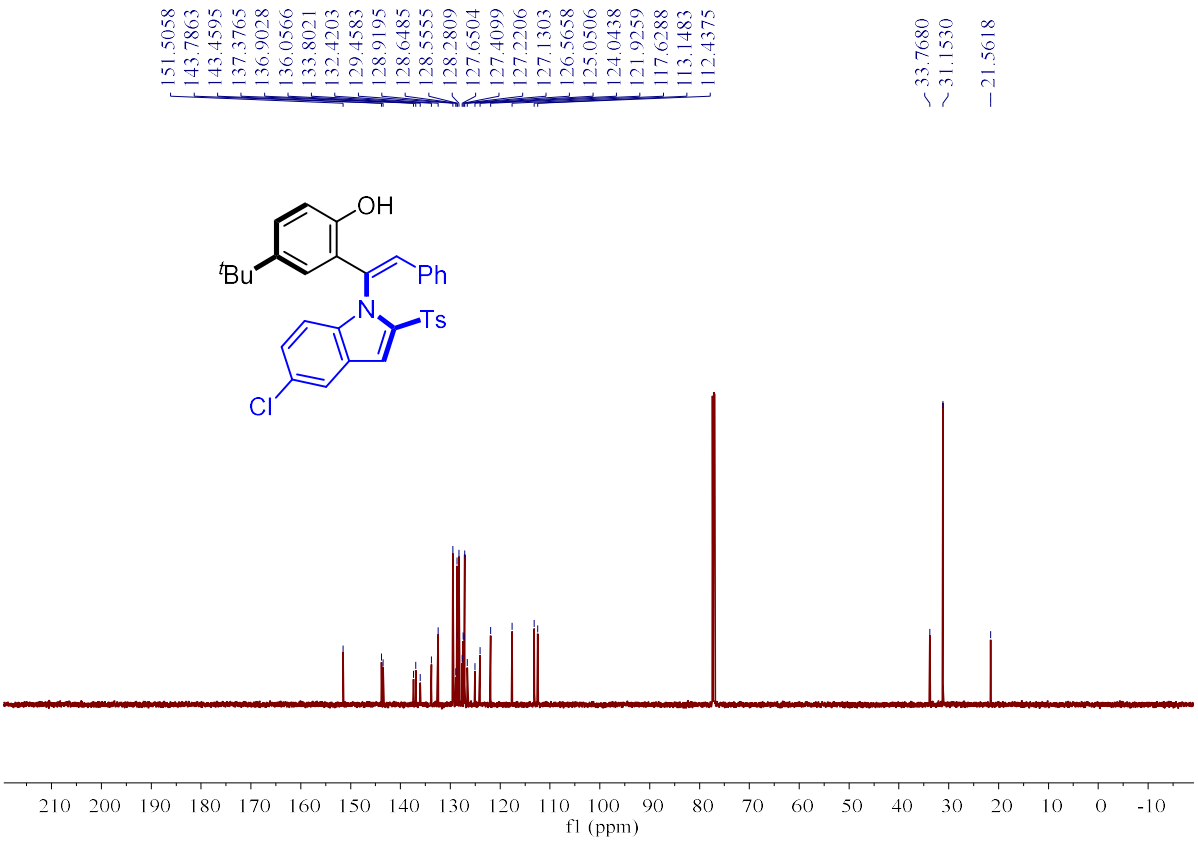

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 8.**



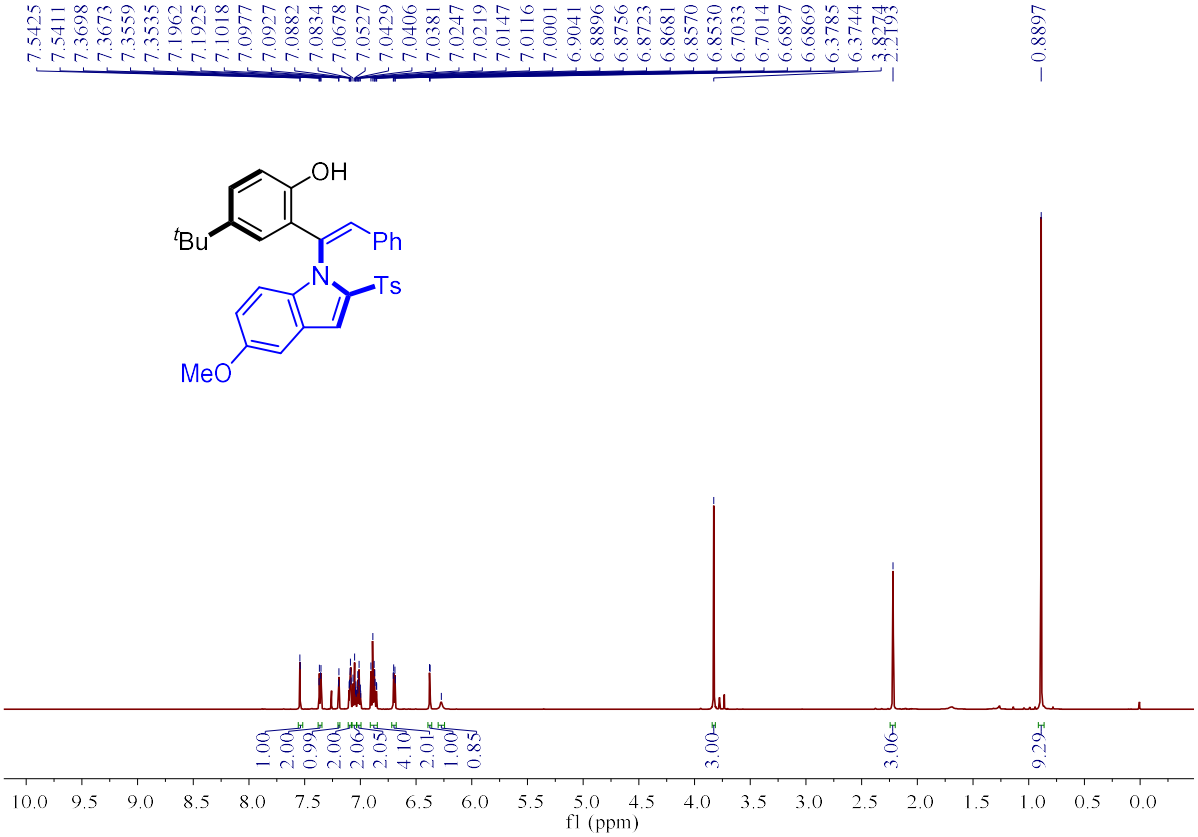

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 8.**



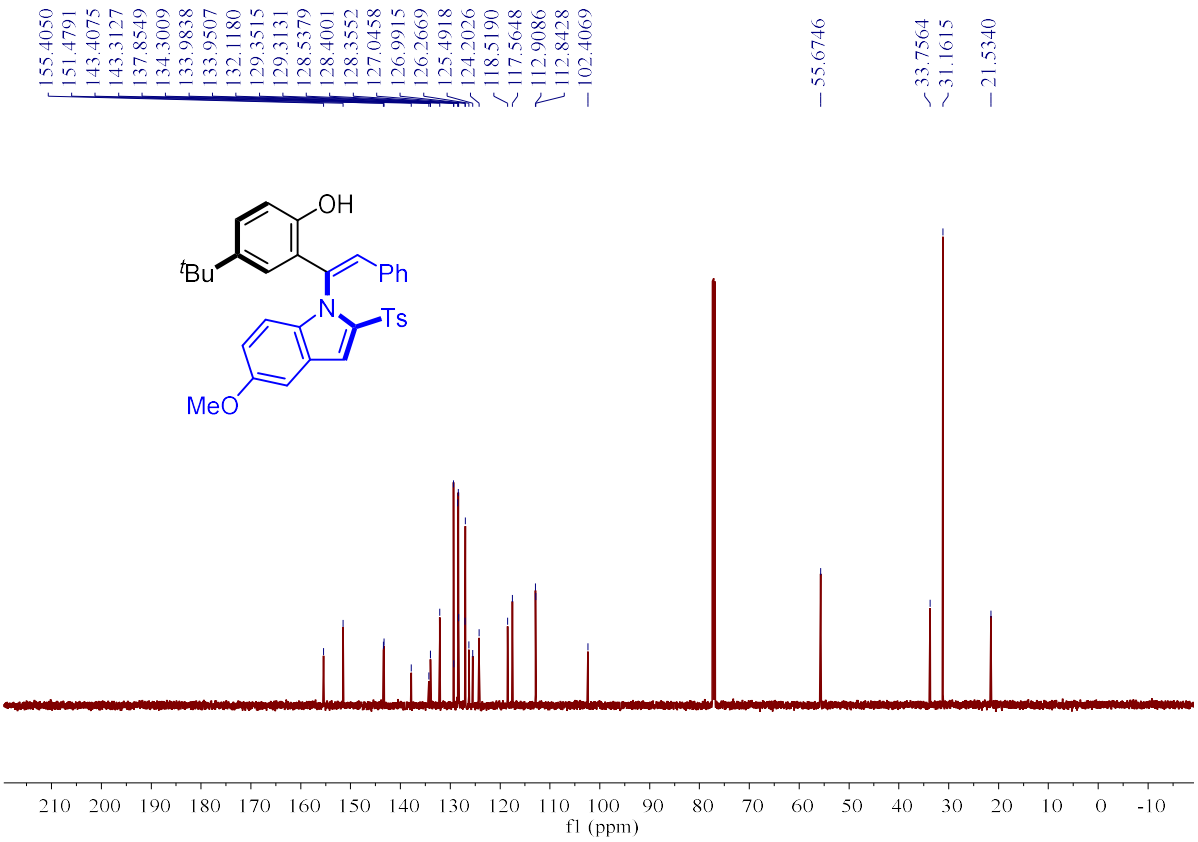

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 9.**



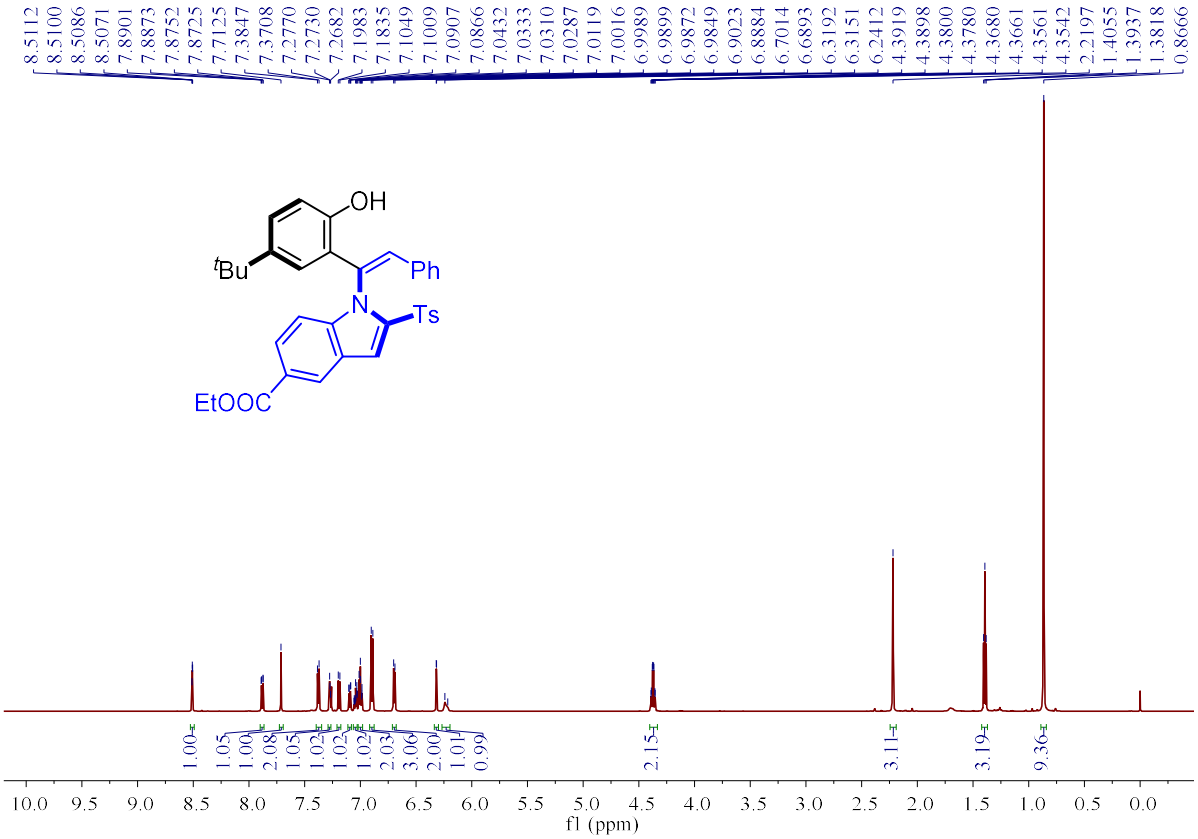

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 9.**



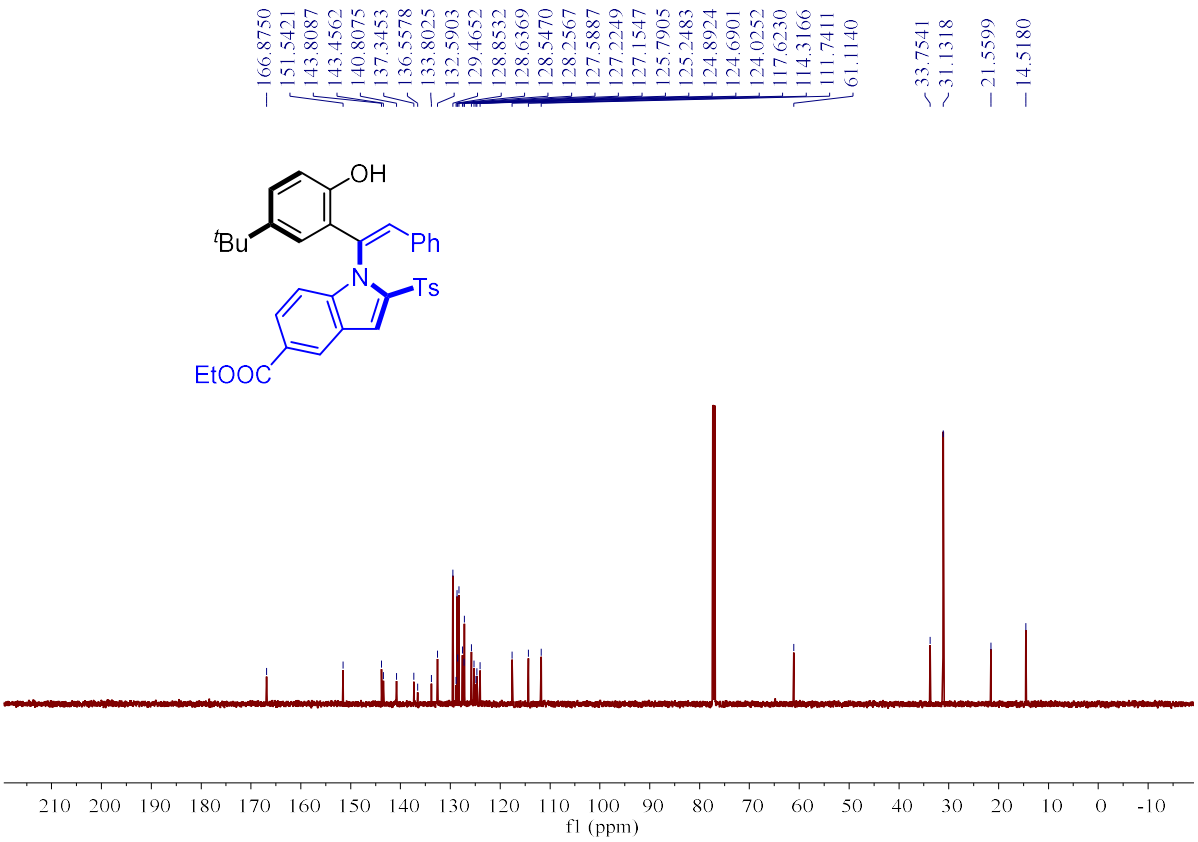

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 10.**



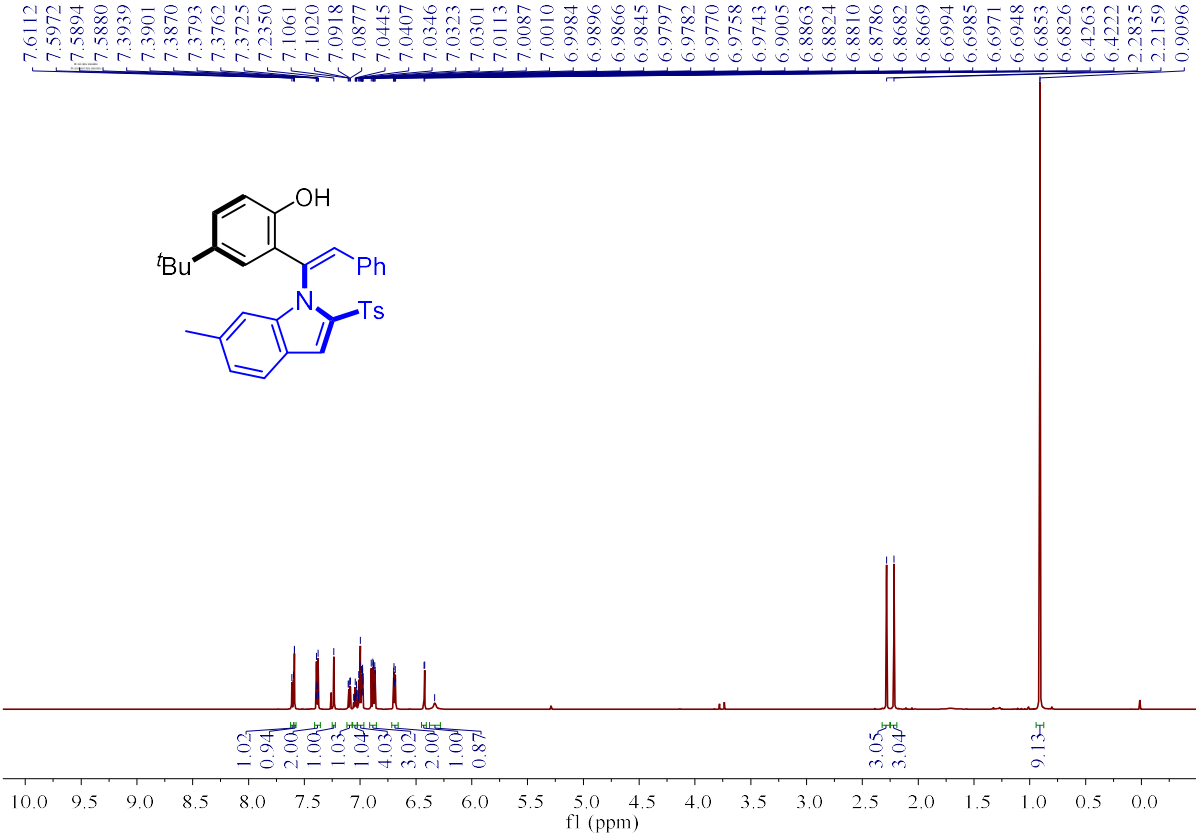

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 10.**



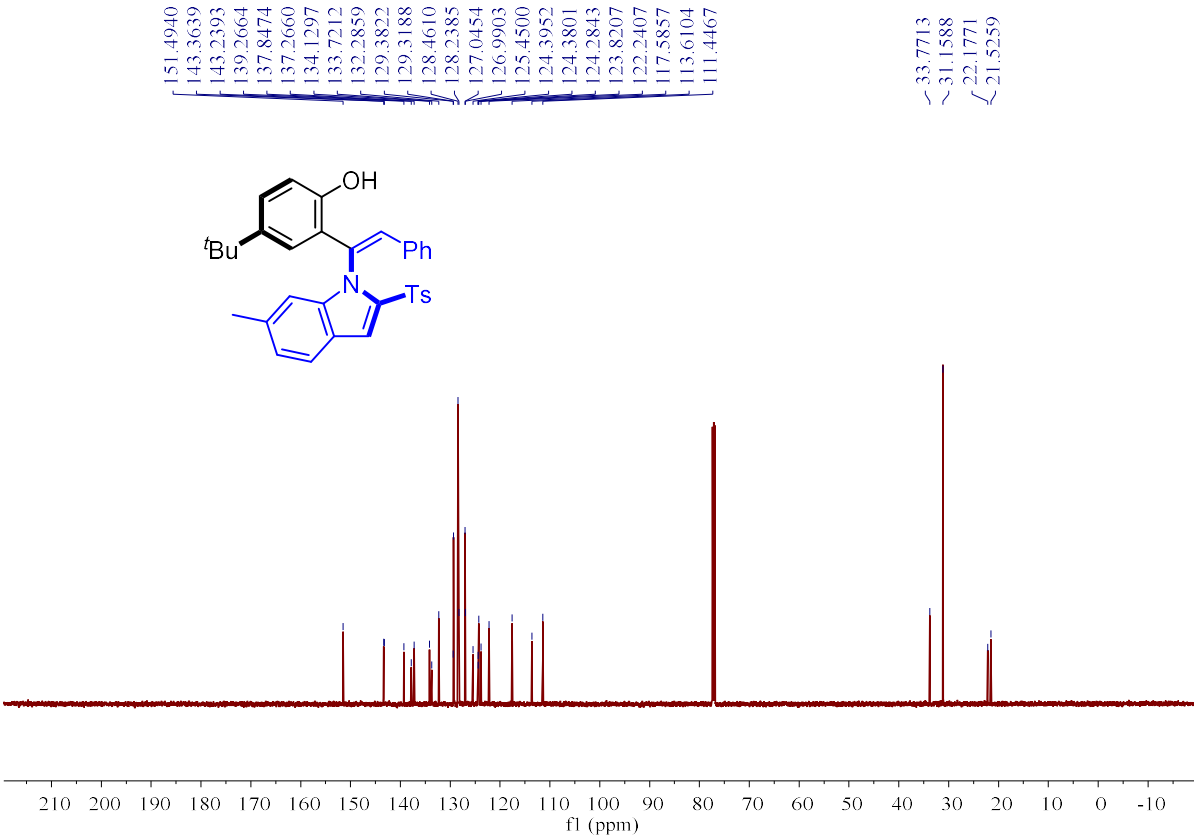

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 11.**



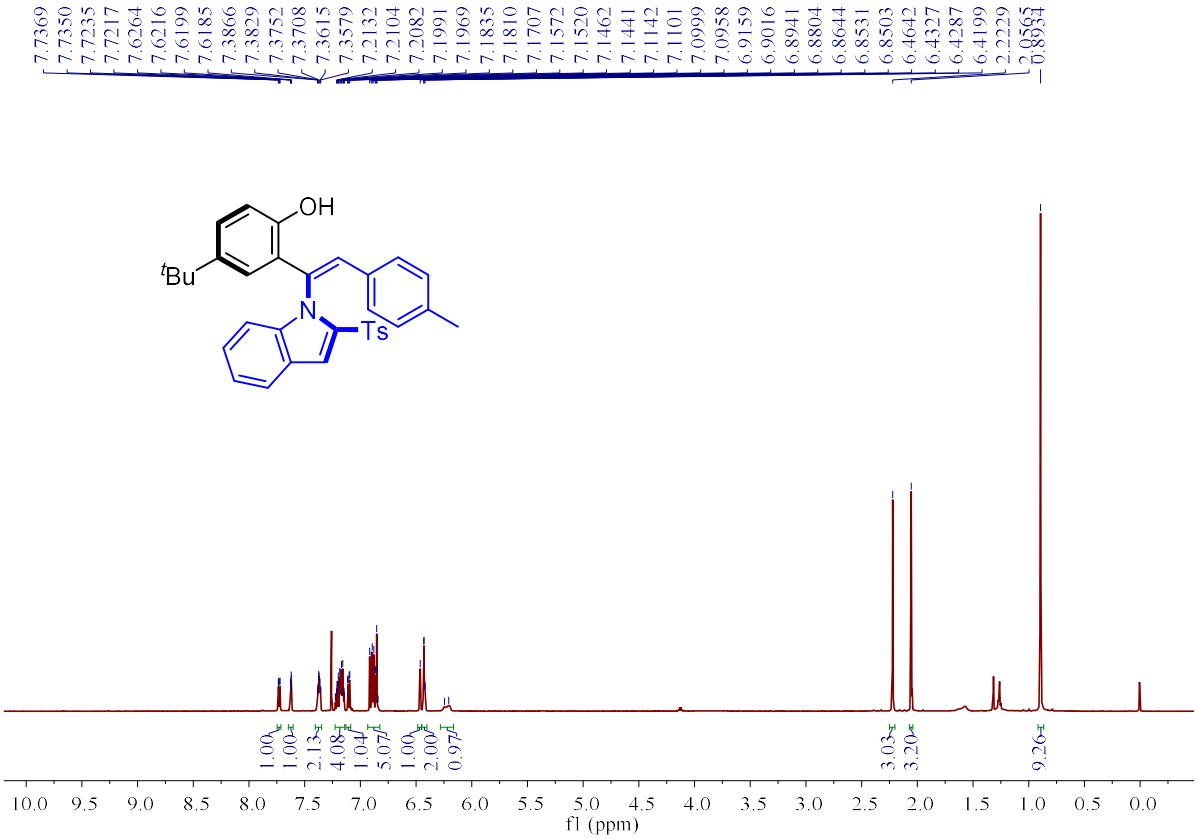

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 11.**



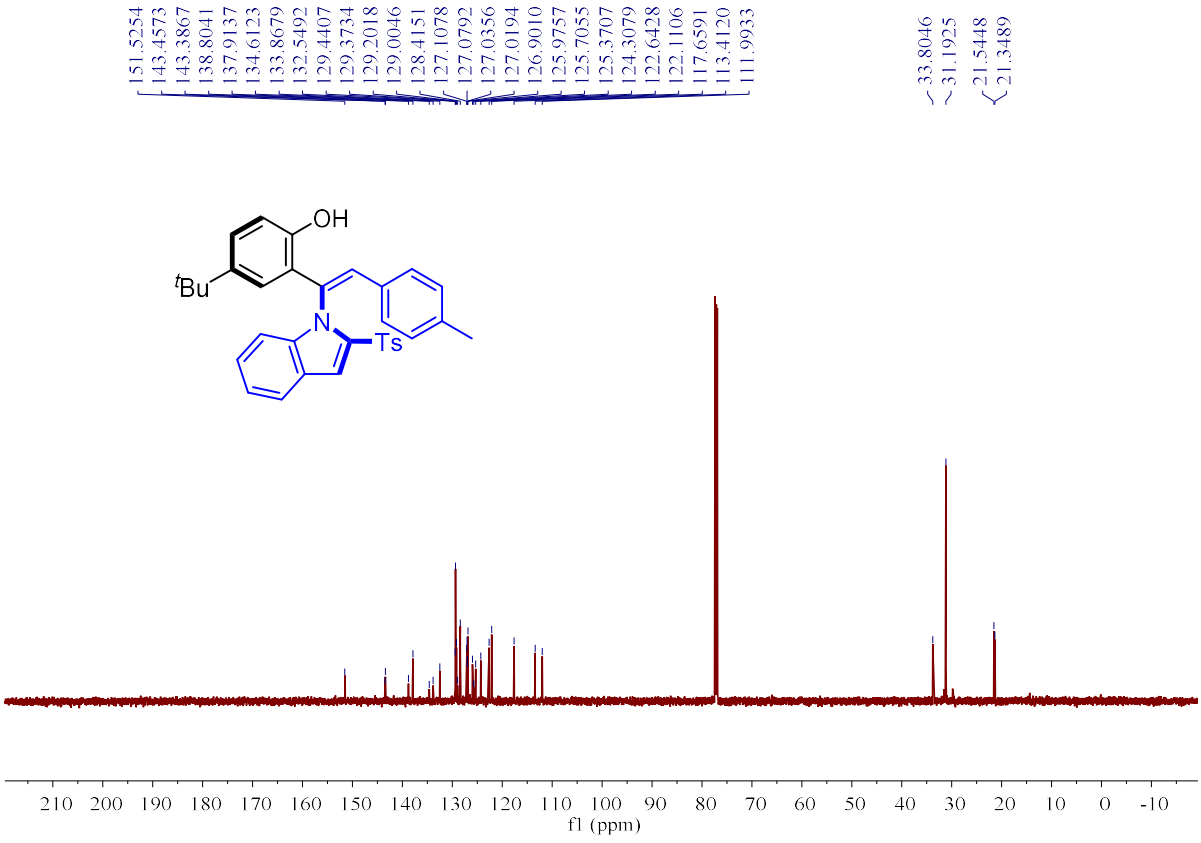

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 12.**



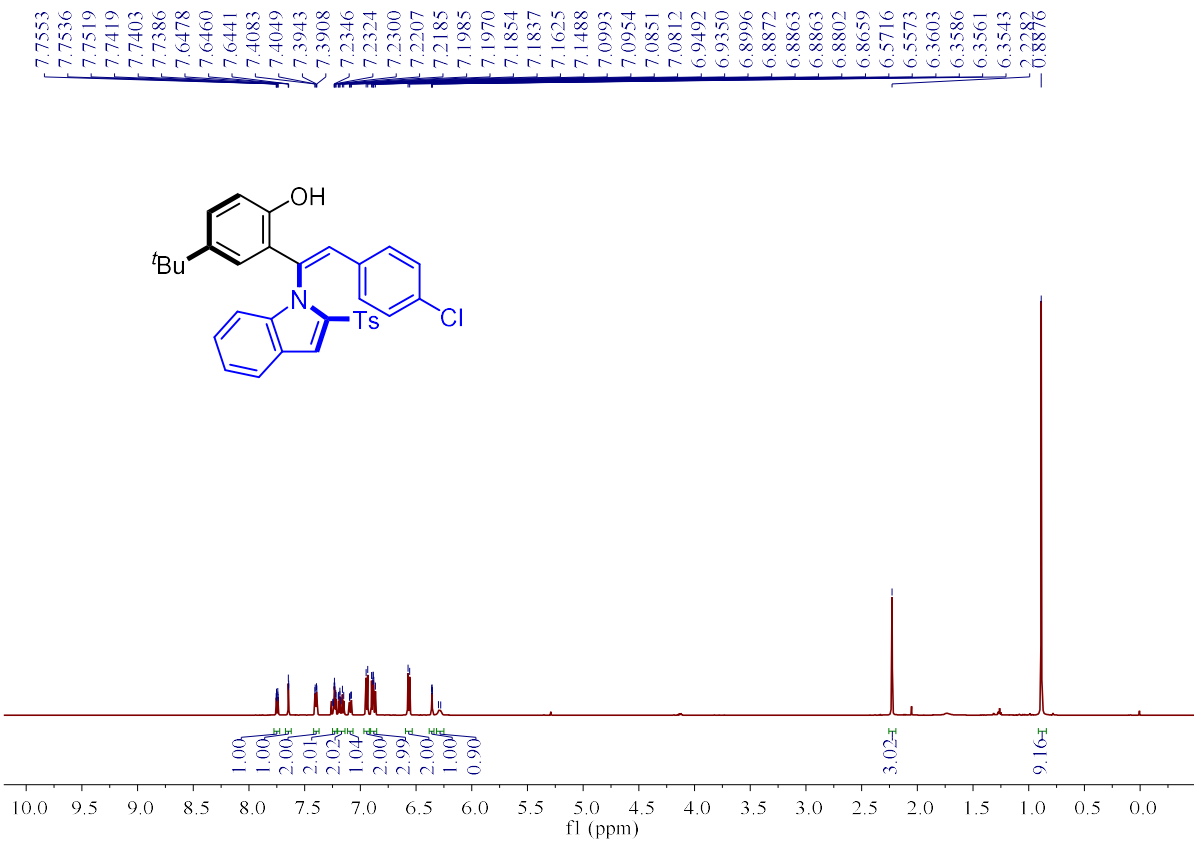

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 12.**



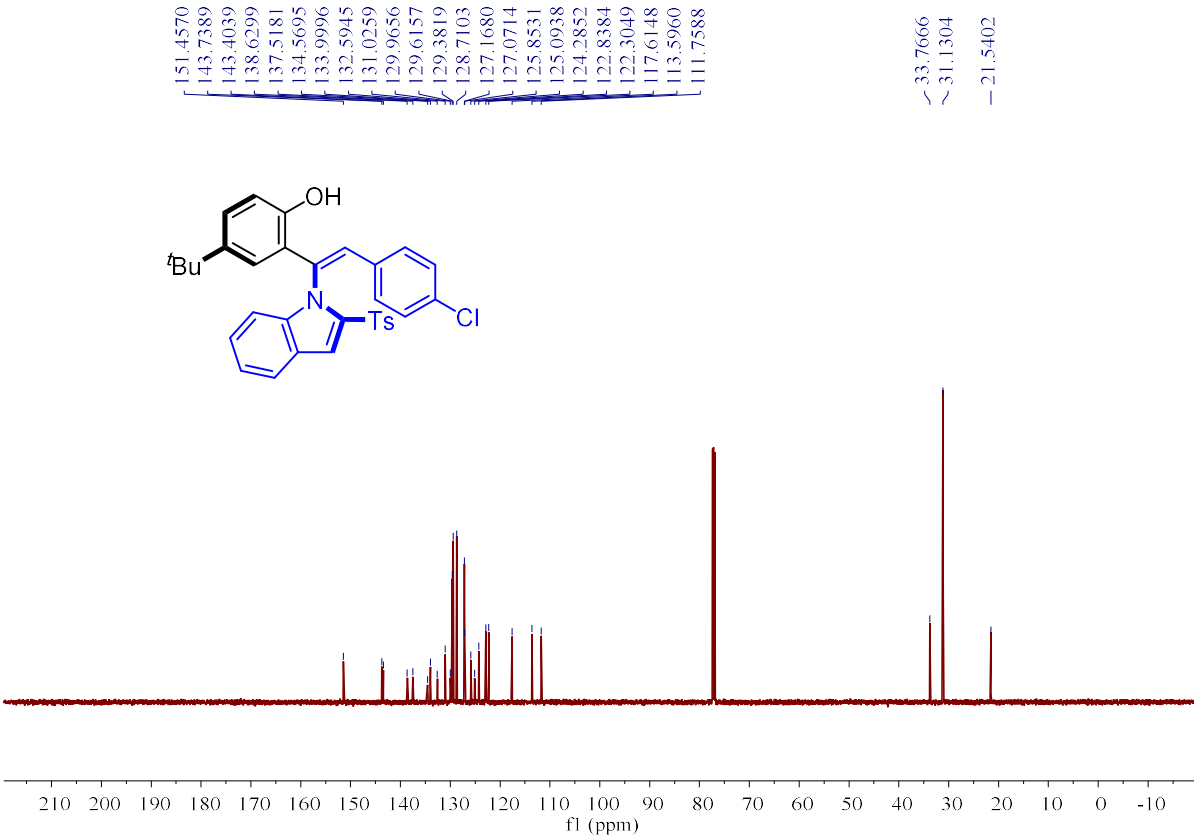

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 13.**



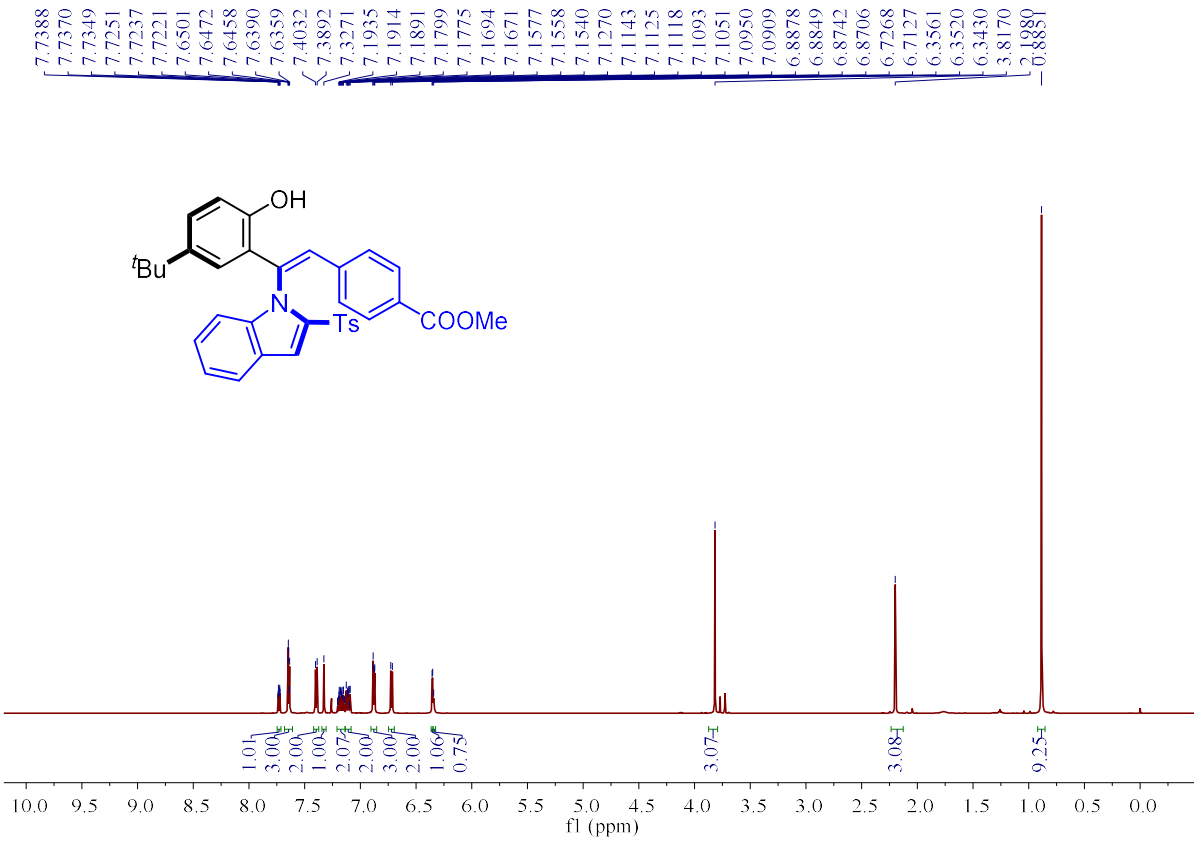

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 13.**



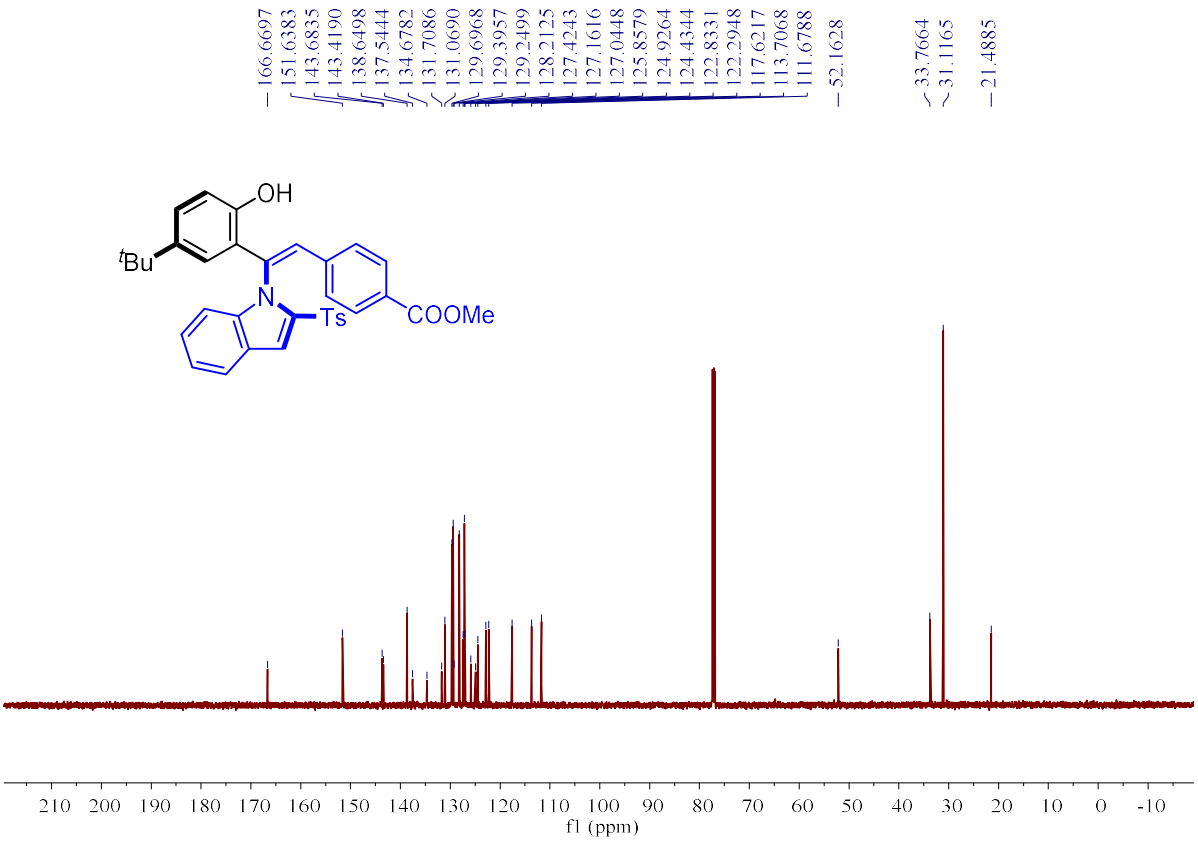

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 14.**



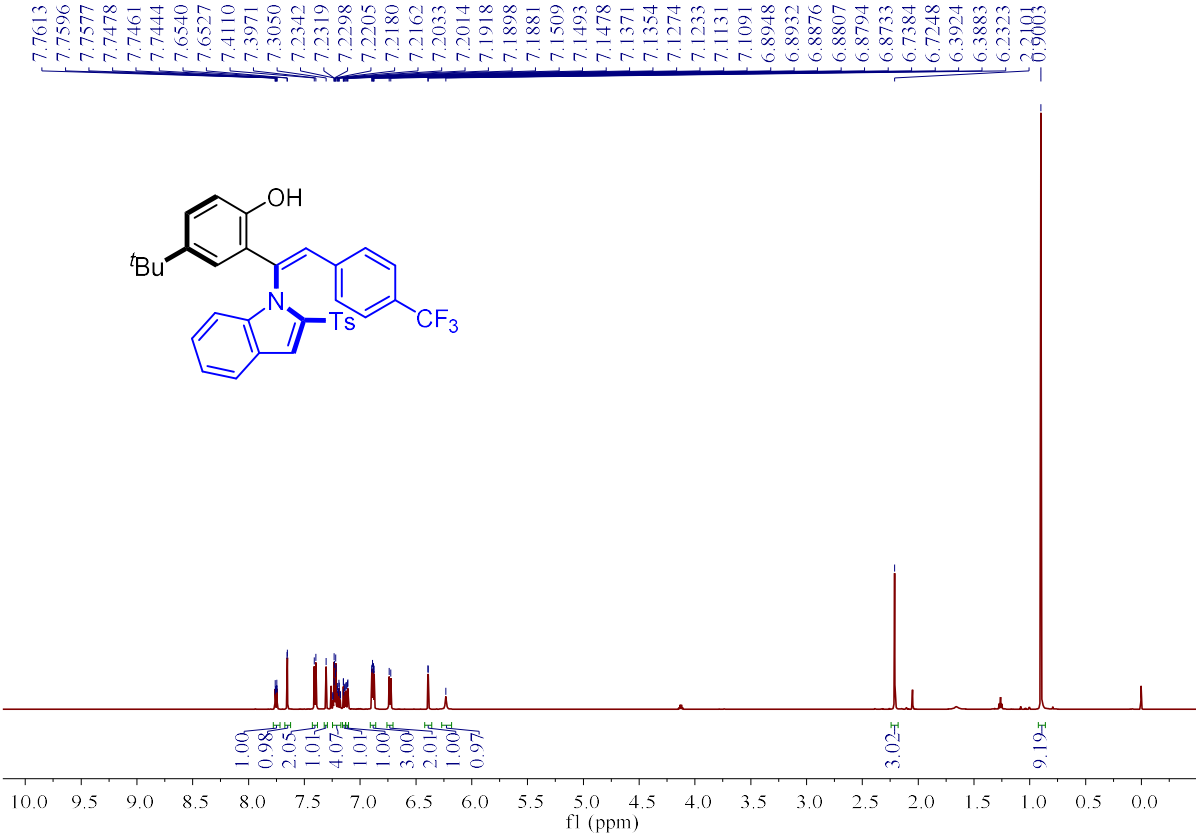

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 14.**



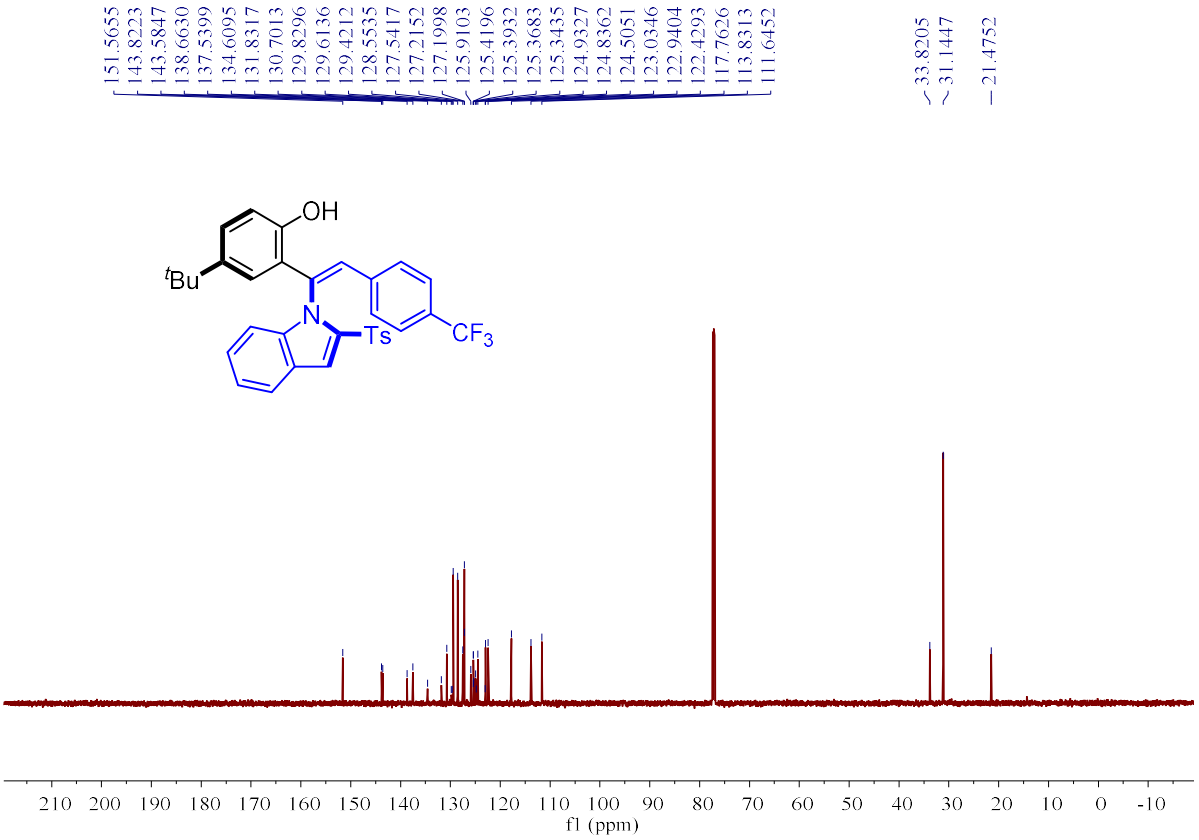

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 15.**



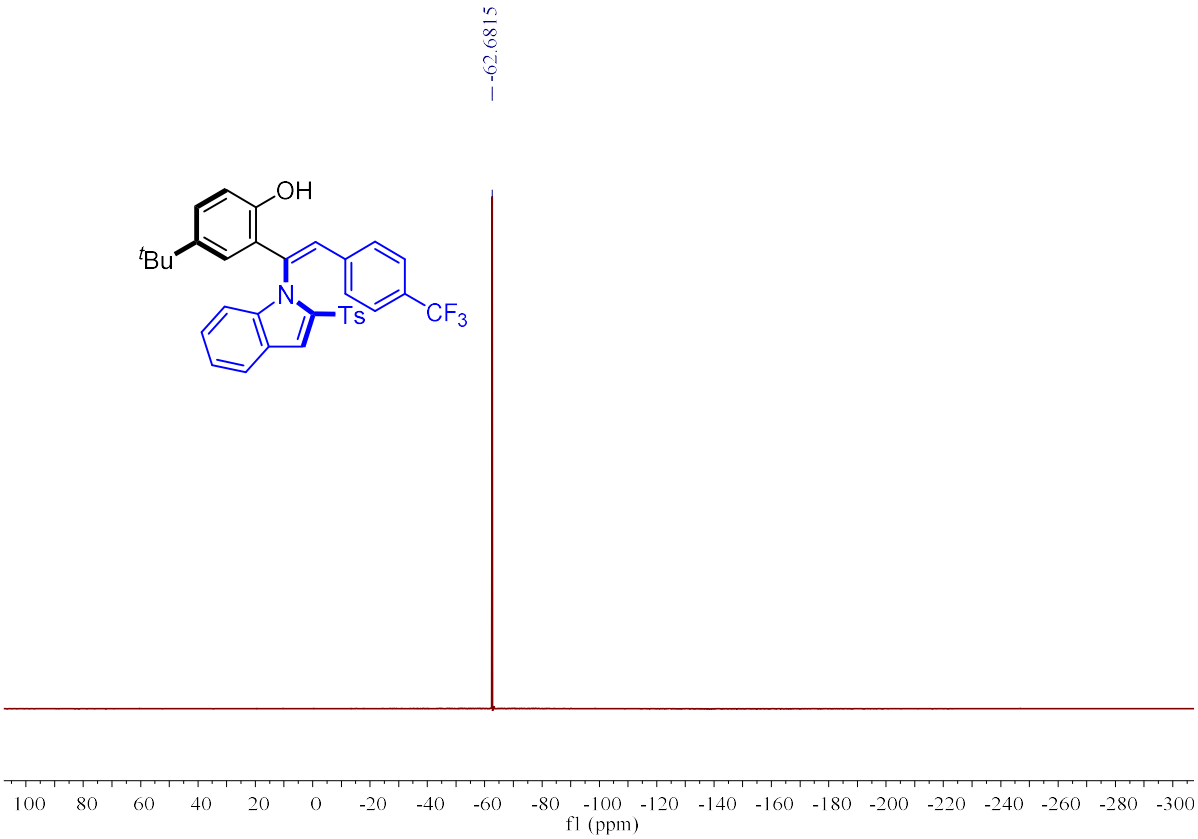

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 15.**



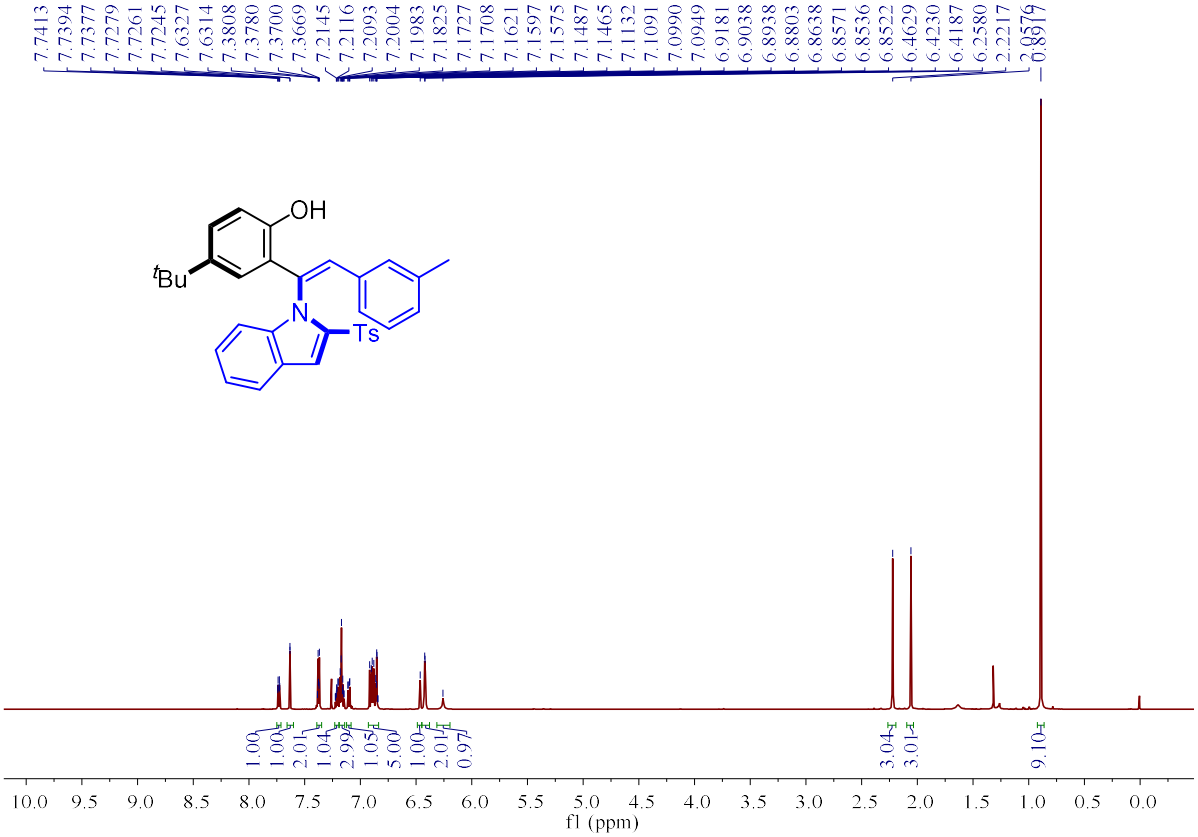

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 16.**



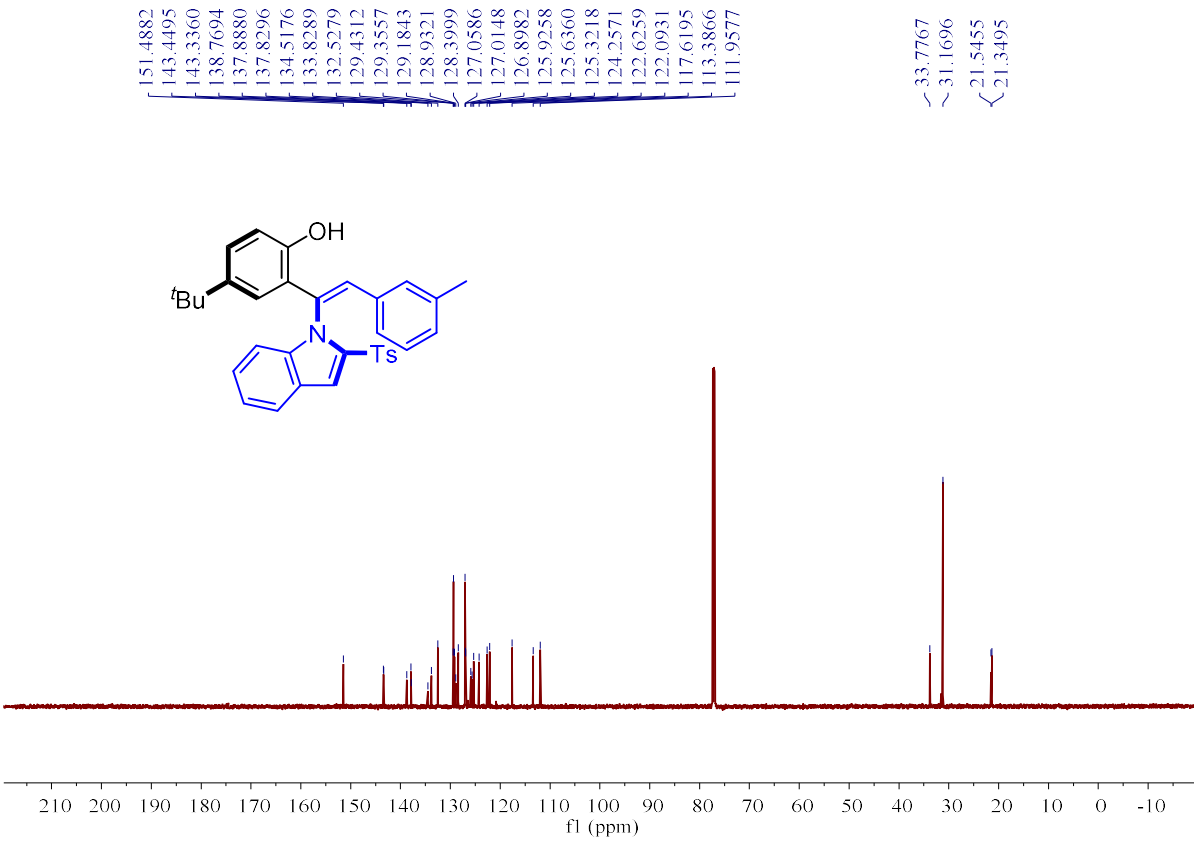

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 16.**



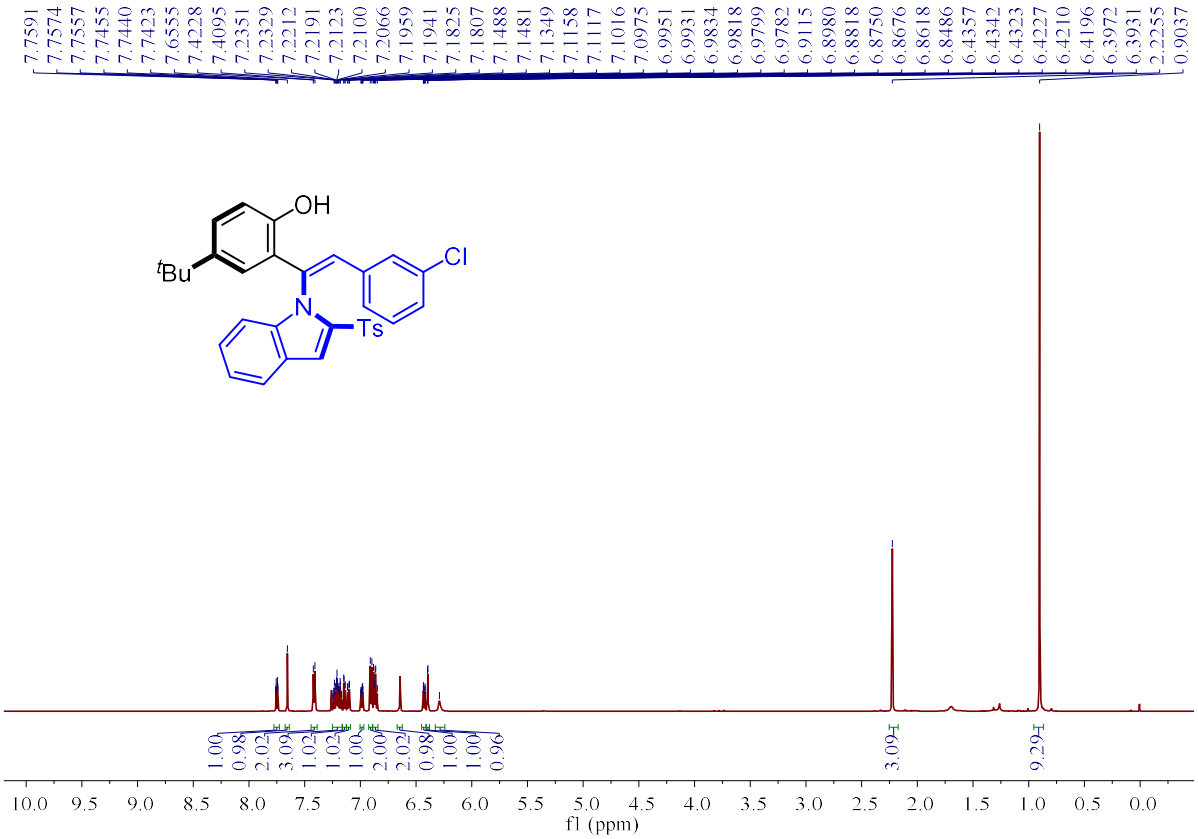

**$^{19}$F NMR (376 MHz, $CDCl_3$) spectrum of 16.**



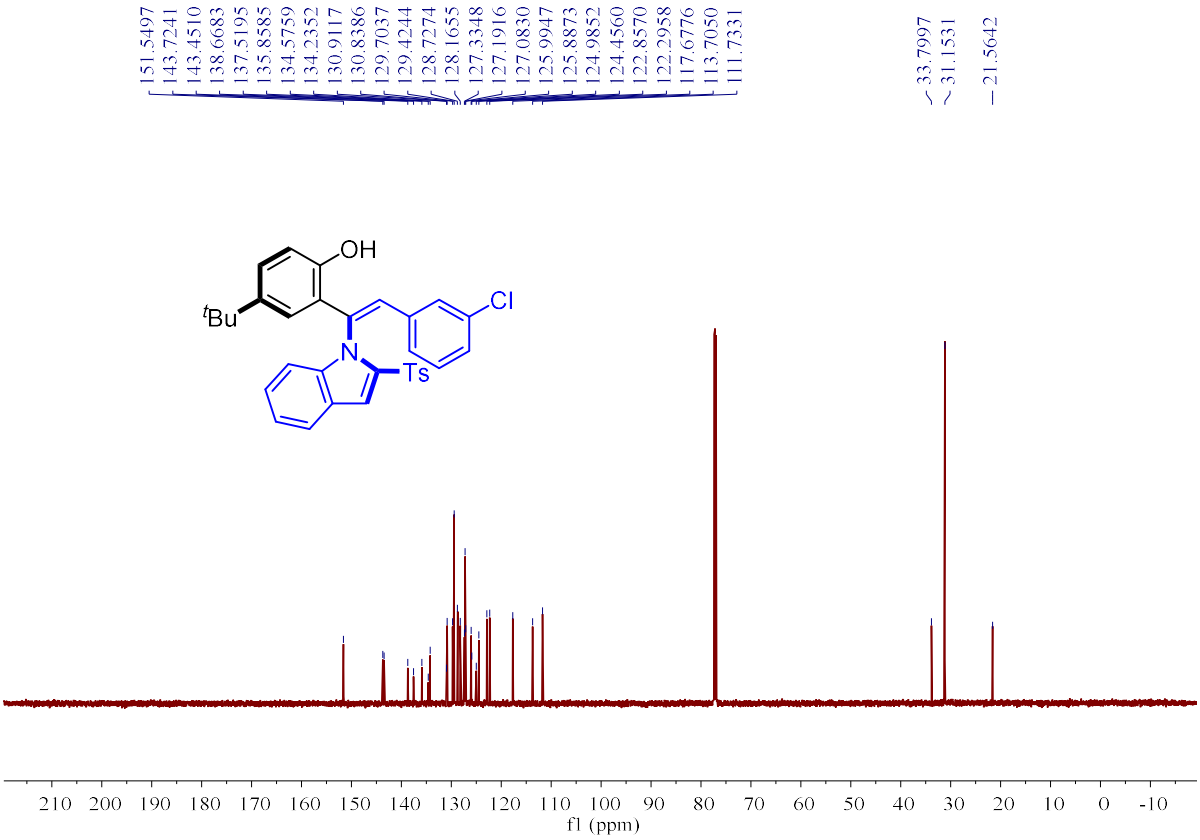

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 17.**



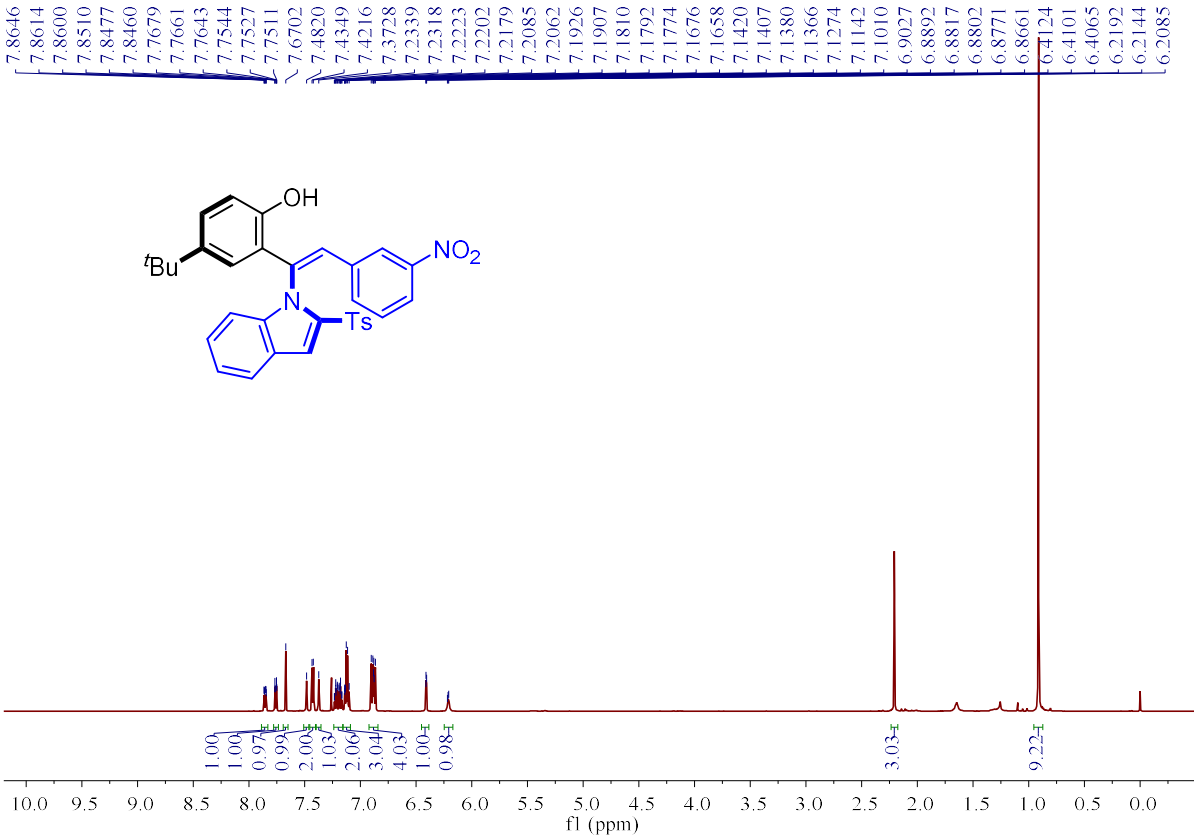

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 17.**



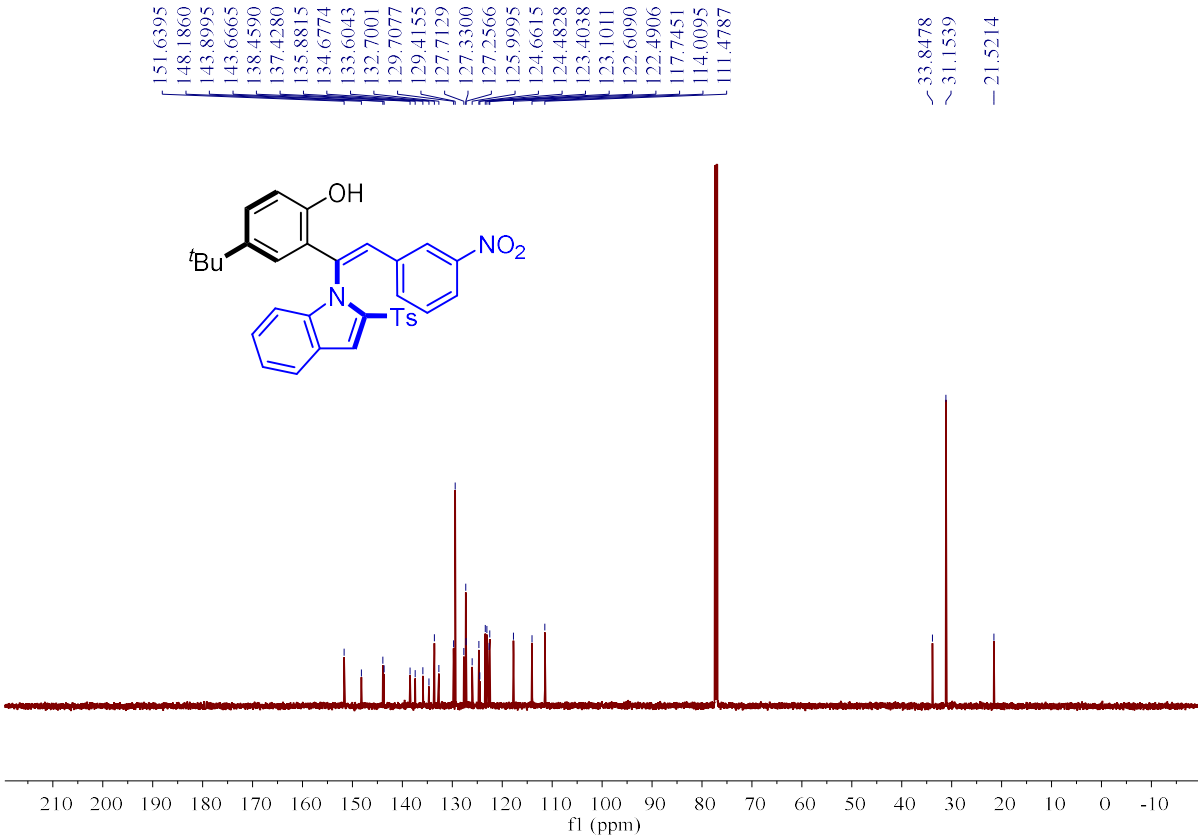

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 18.**



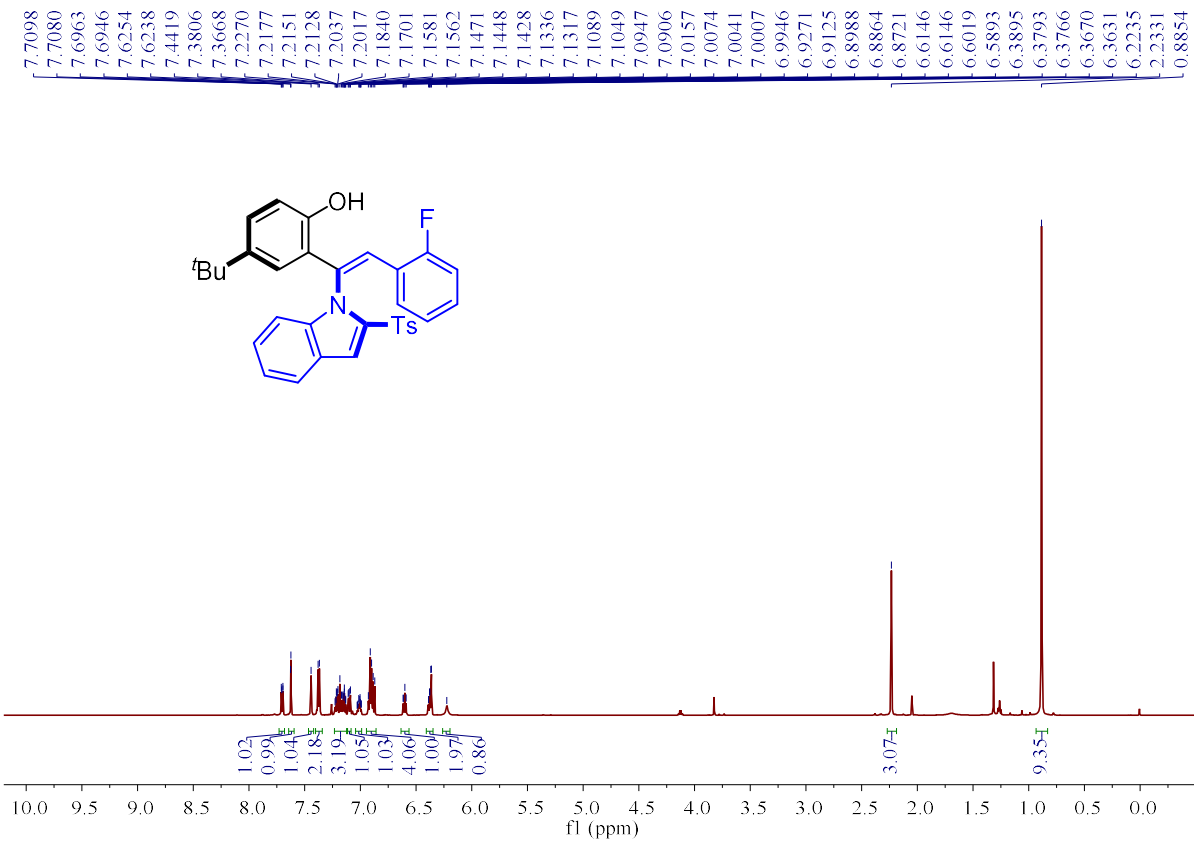

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 18.**



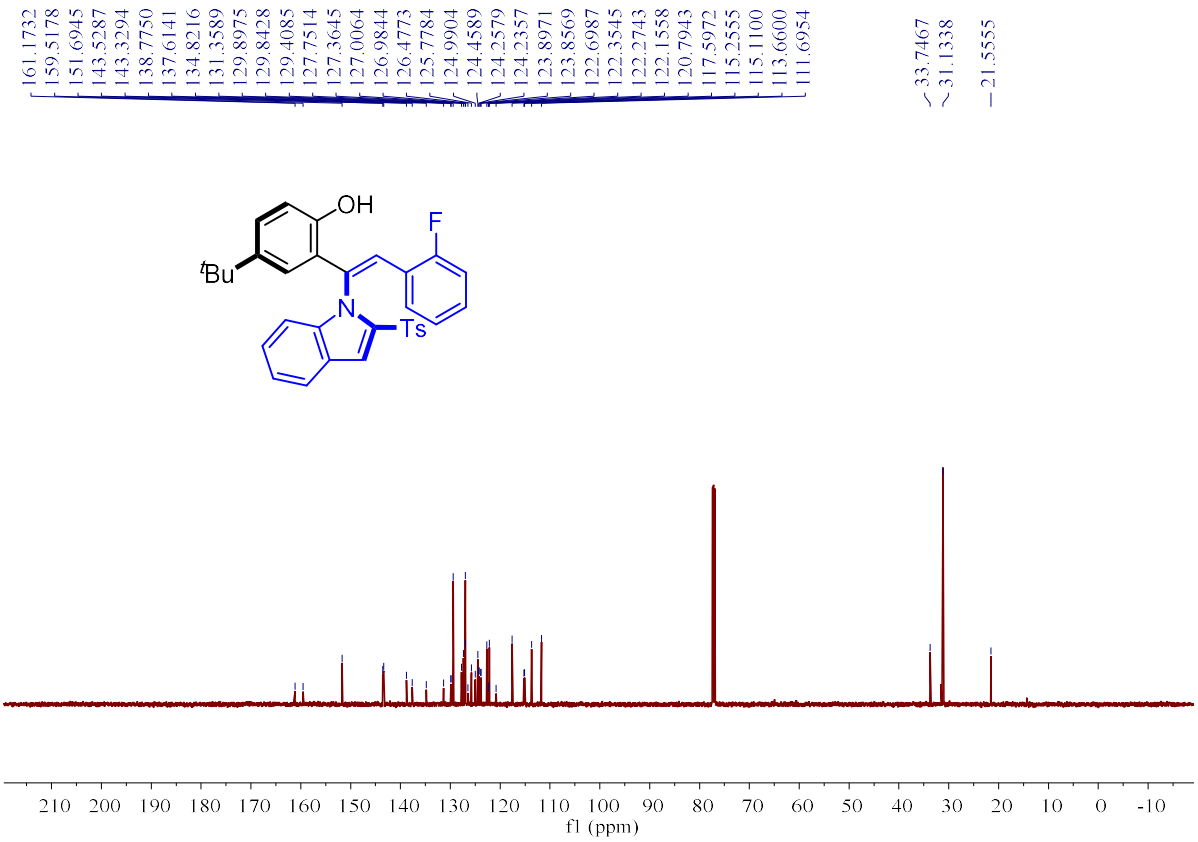

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 19.**



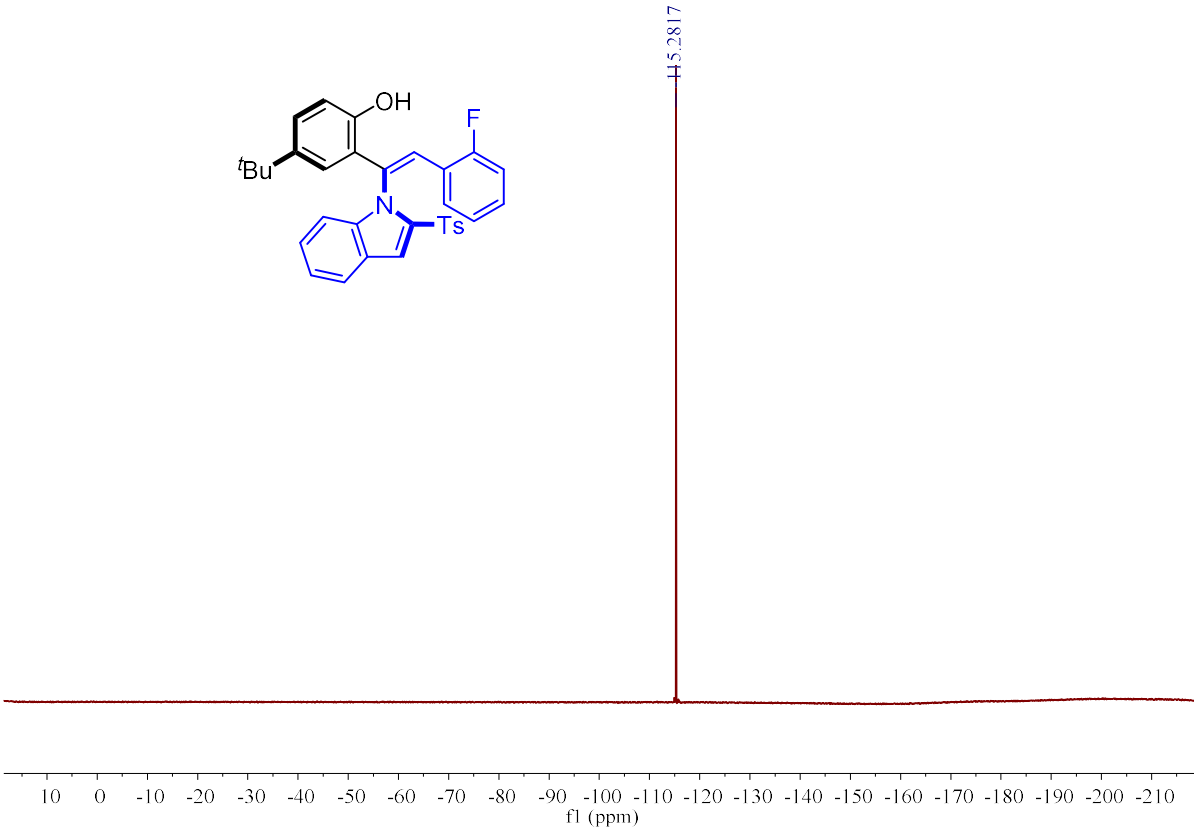

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 19.**



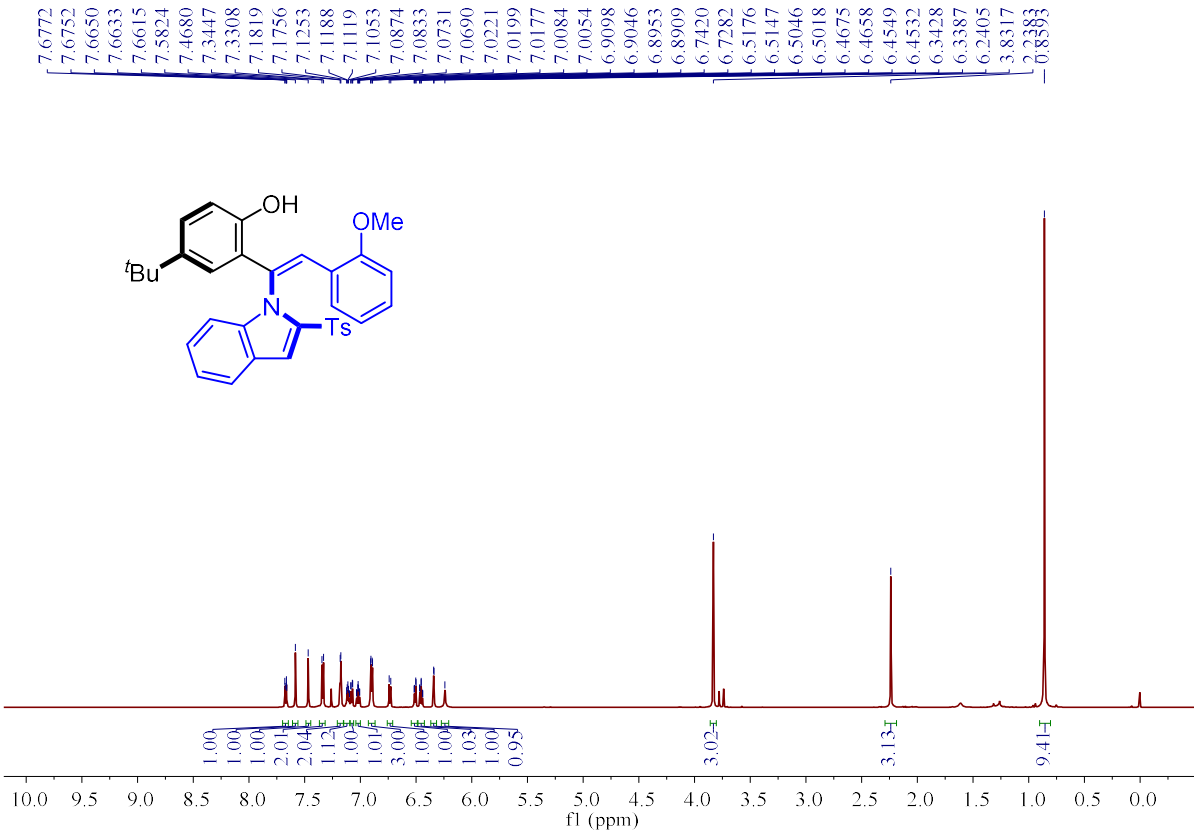

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 20.**



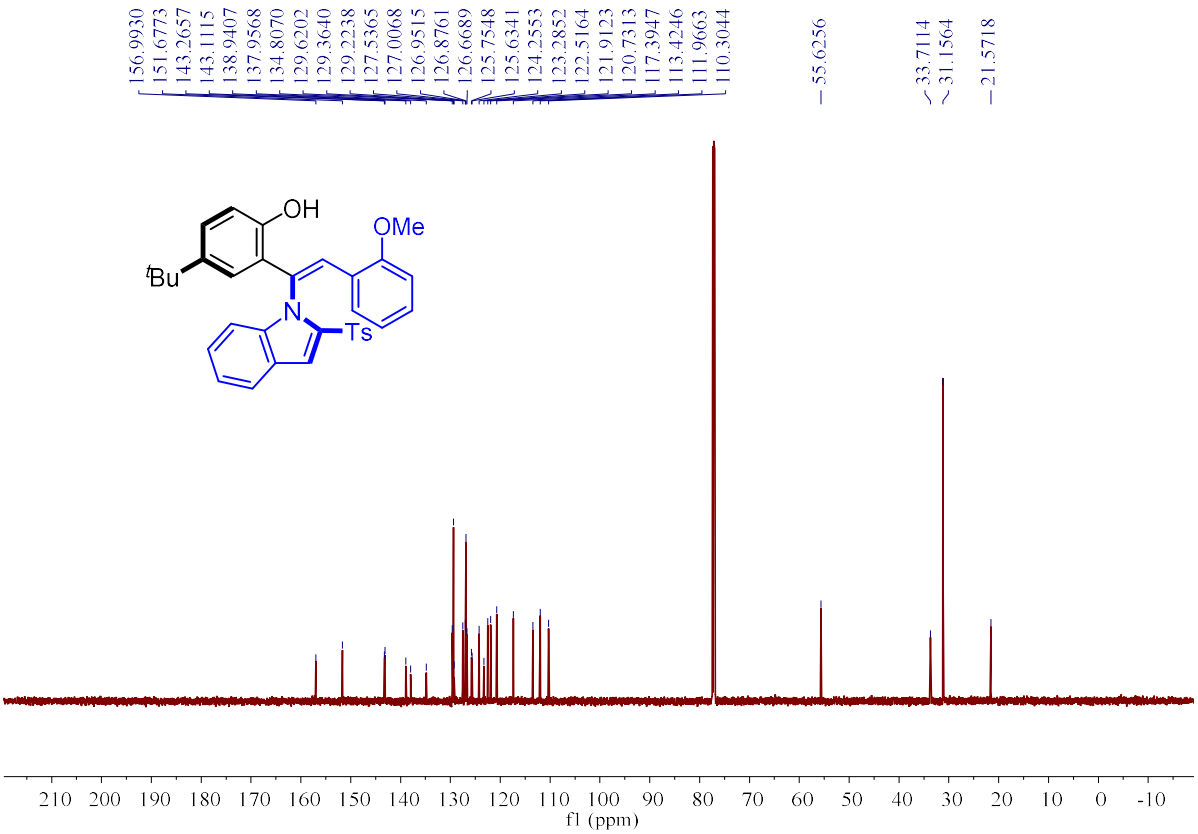

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 20.**



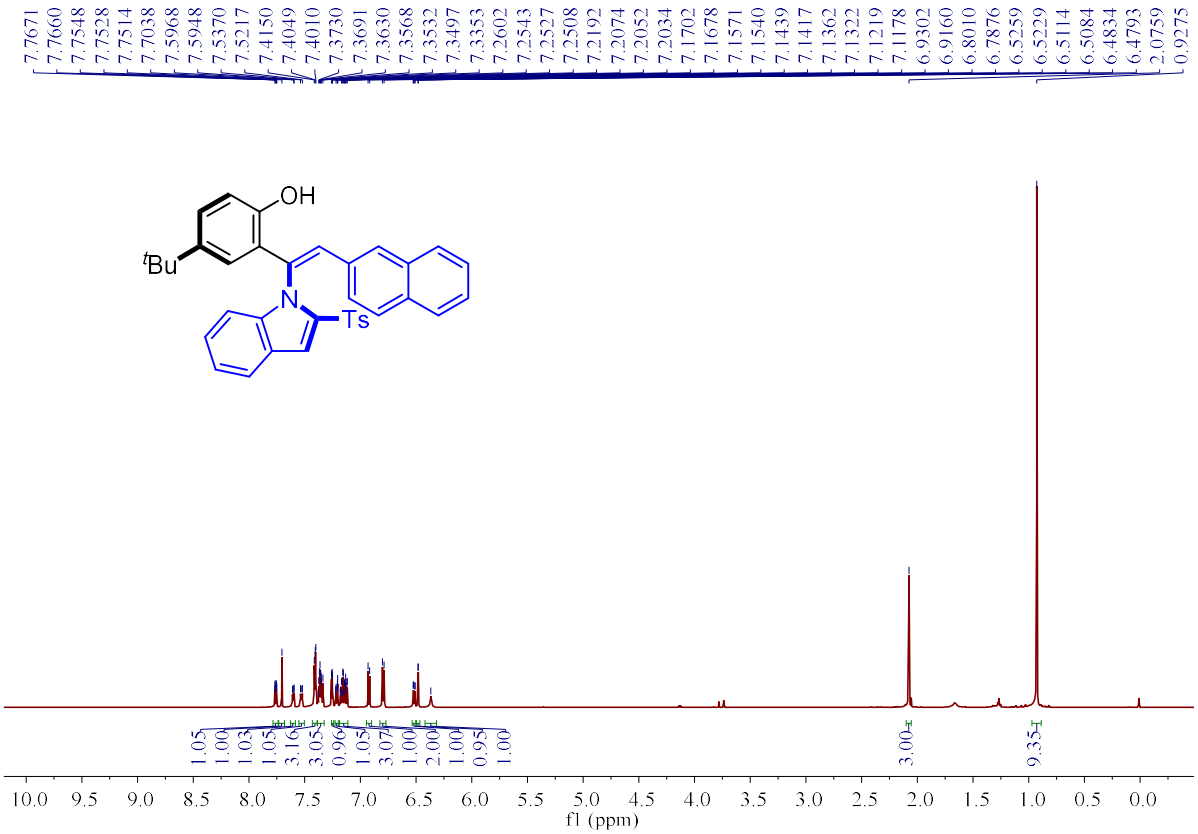

**$^{19}$F NMR (376 MHz, $CDCl_3$) spectrum of 20.**



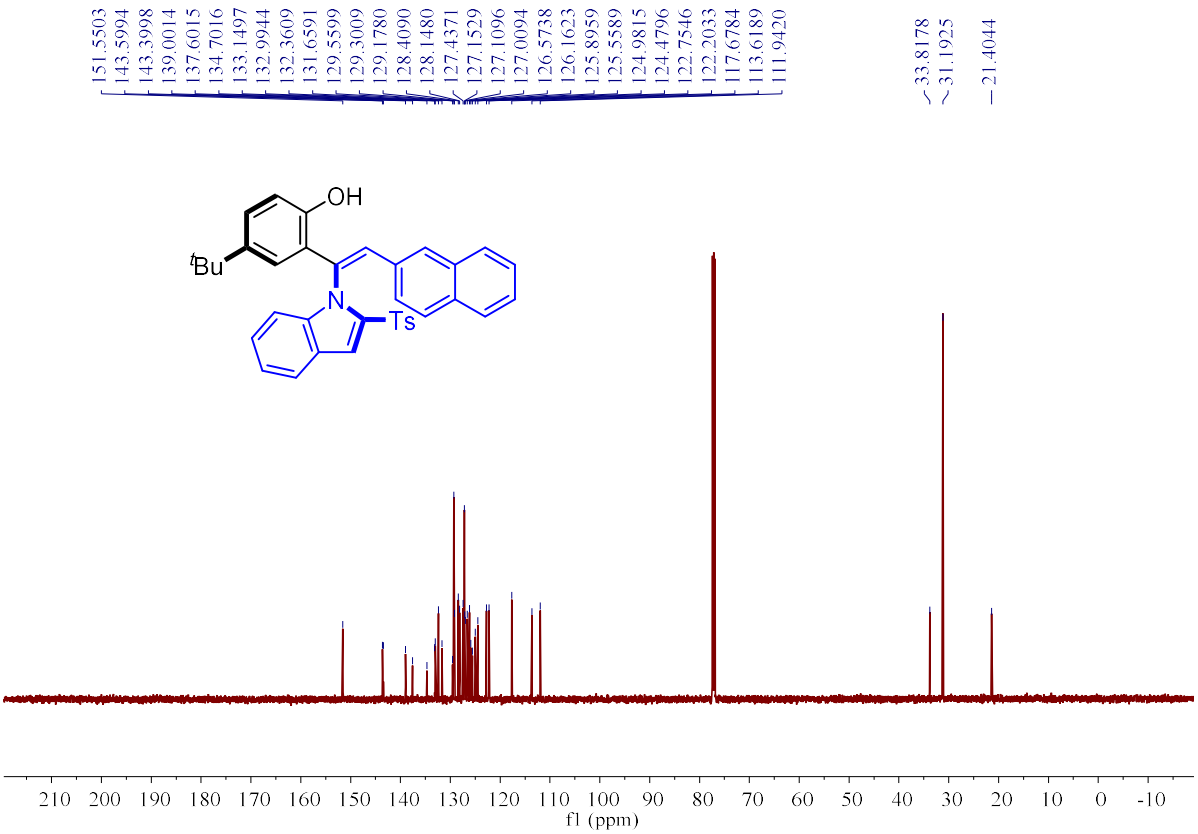

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 21.**



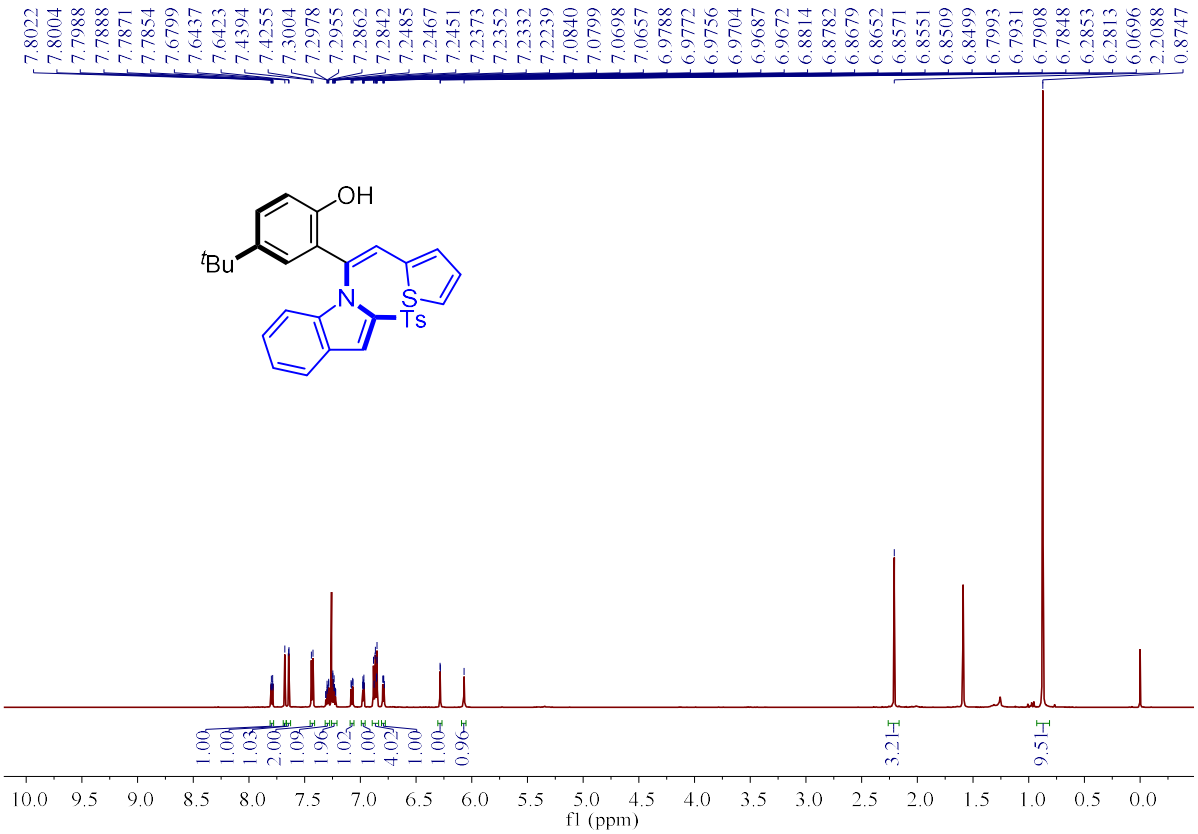

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 21.**



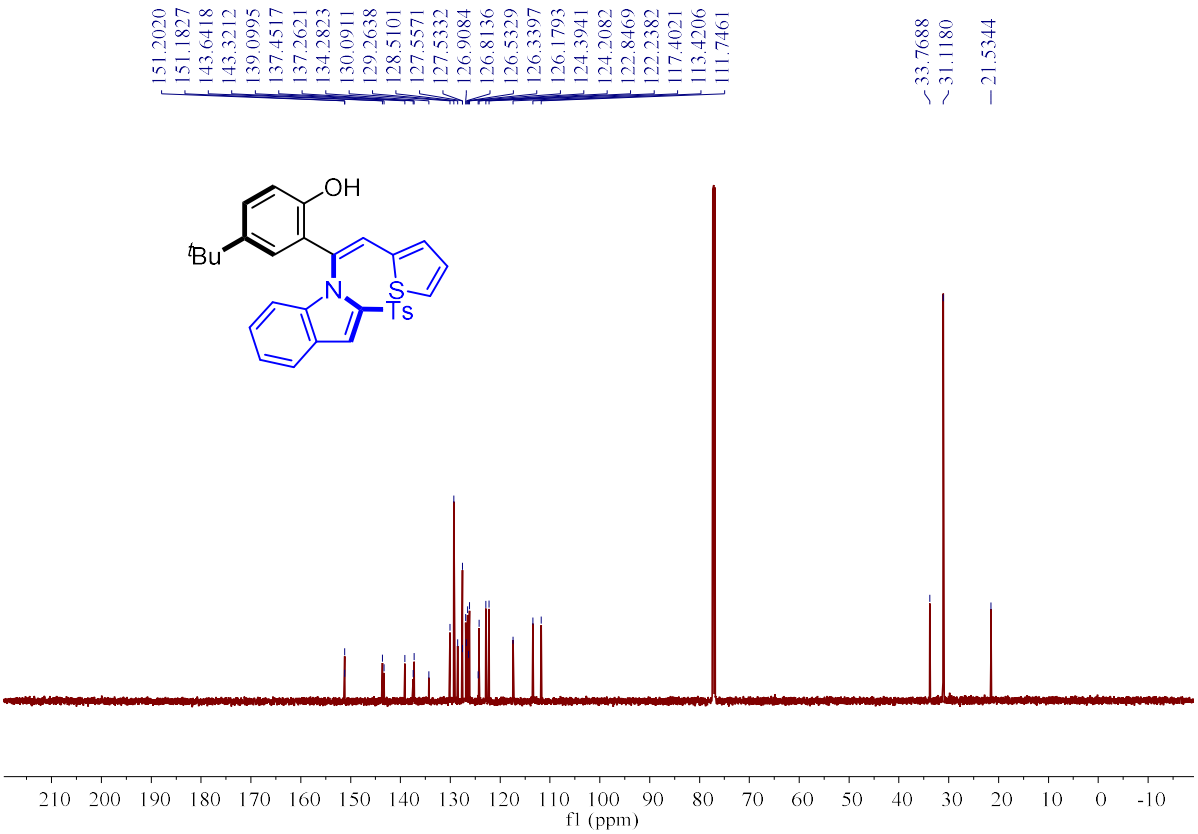

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 22.**



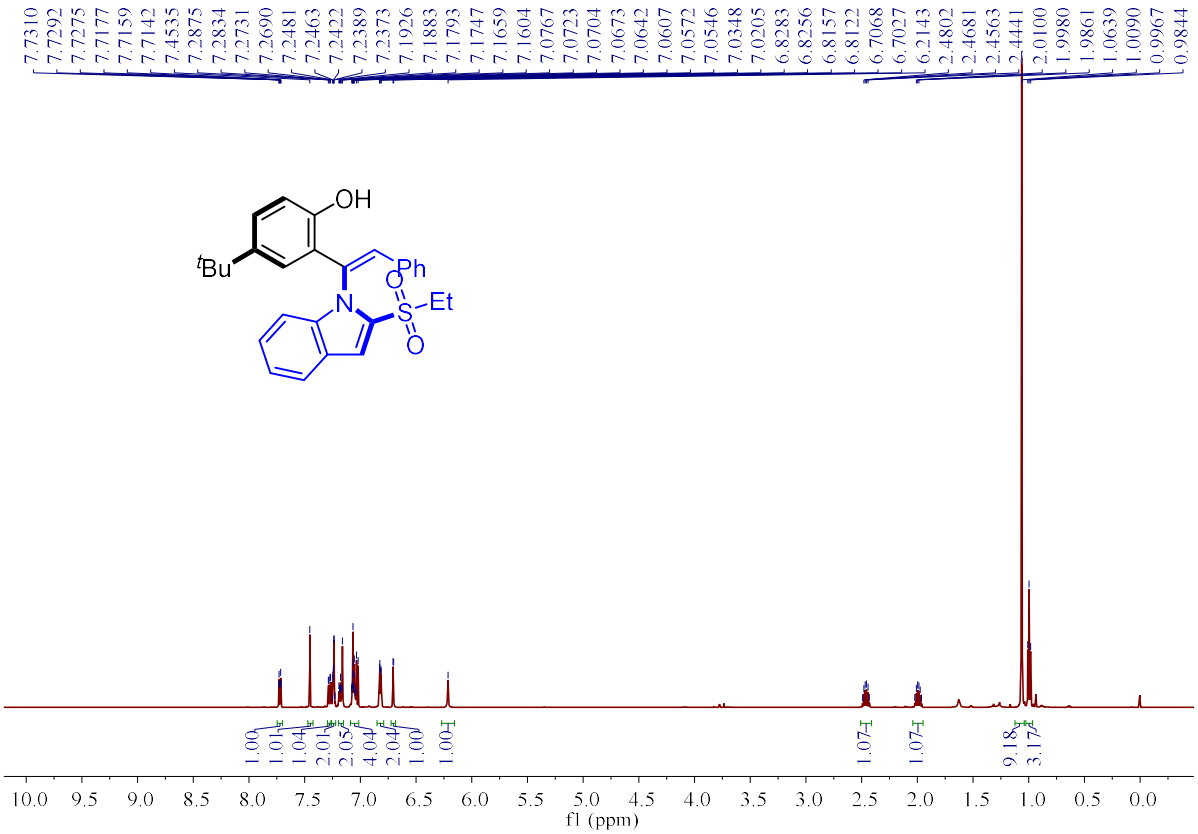

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 22.**



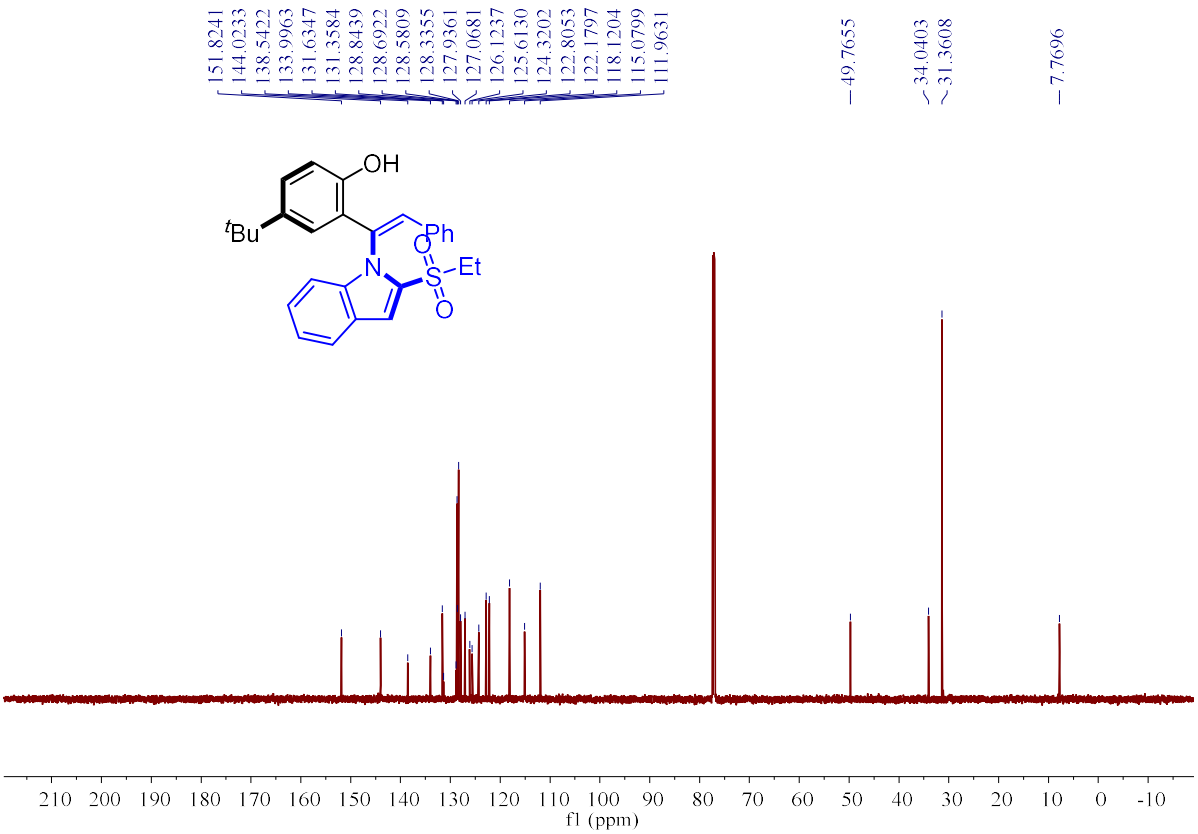

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 23.**



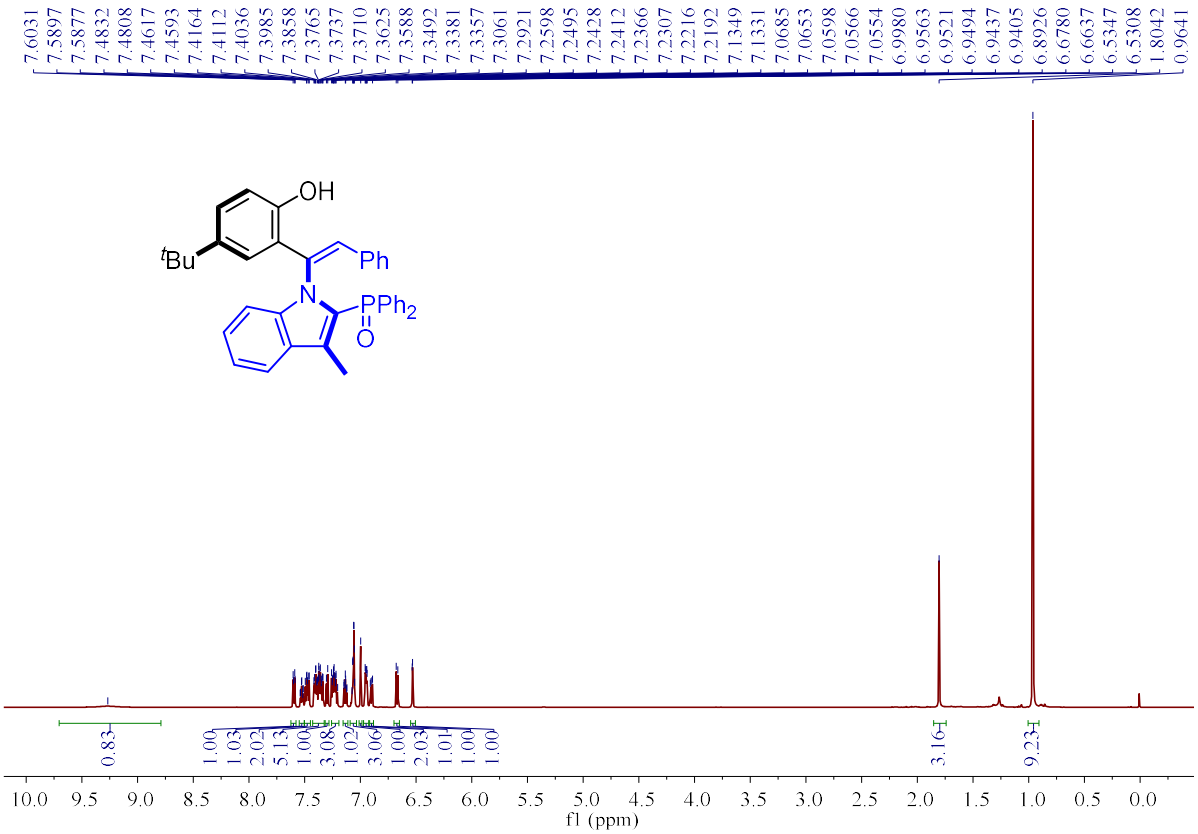

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 23.**



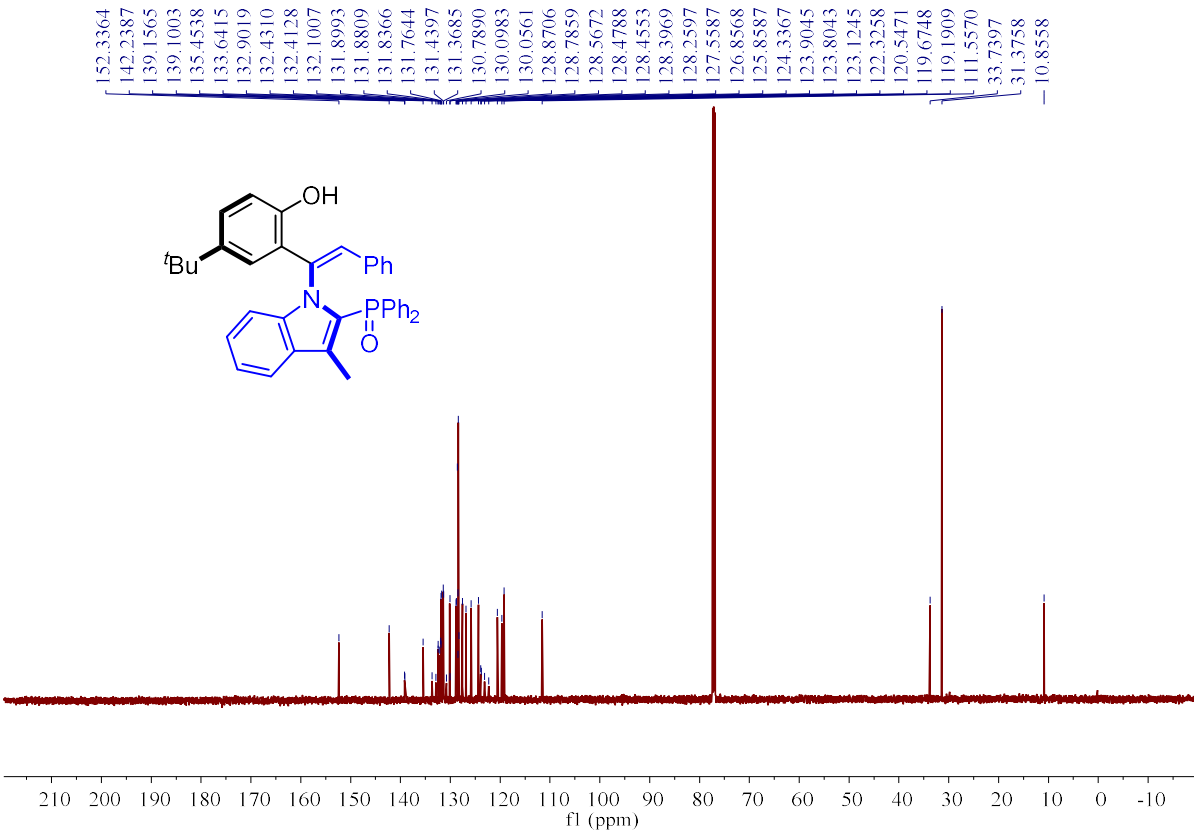

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 24.**



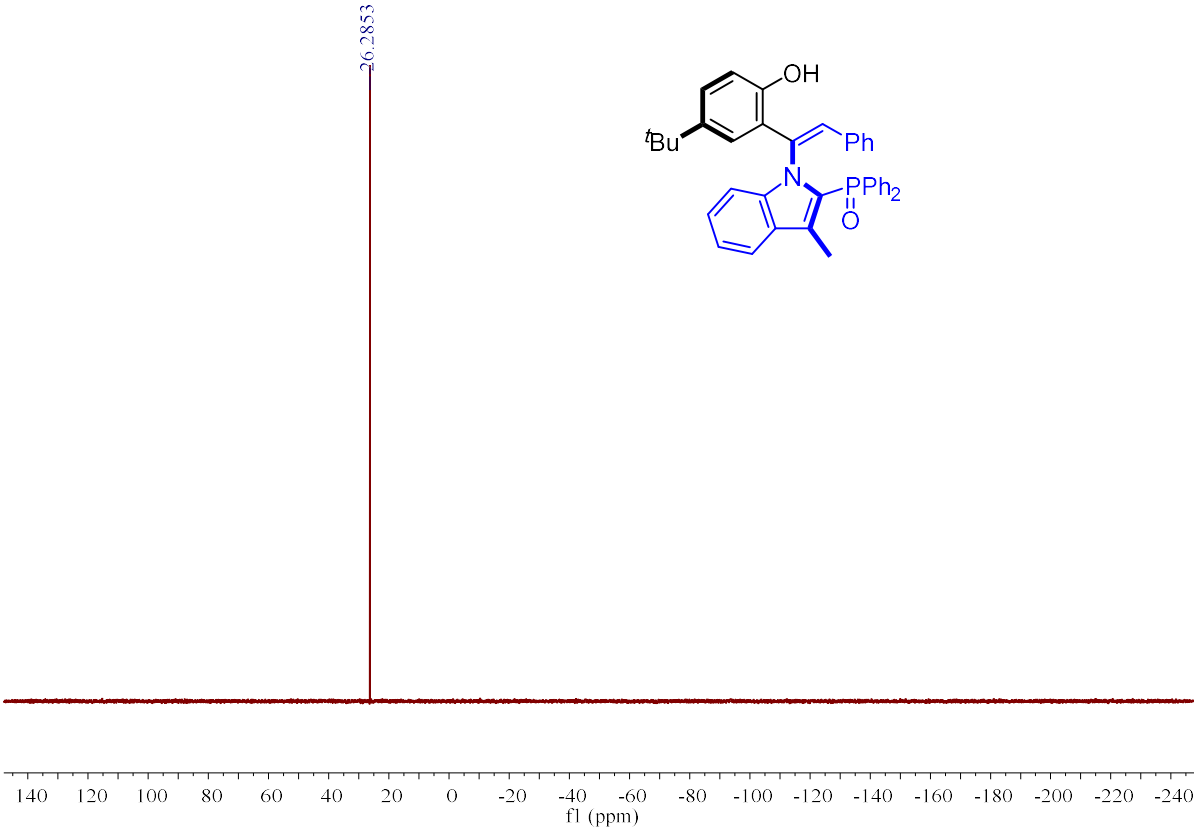

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 24.**



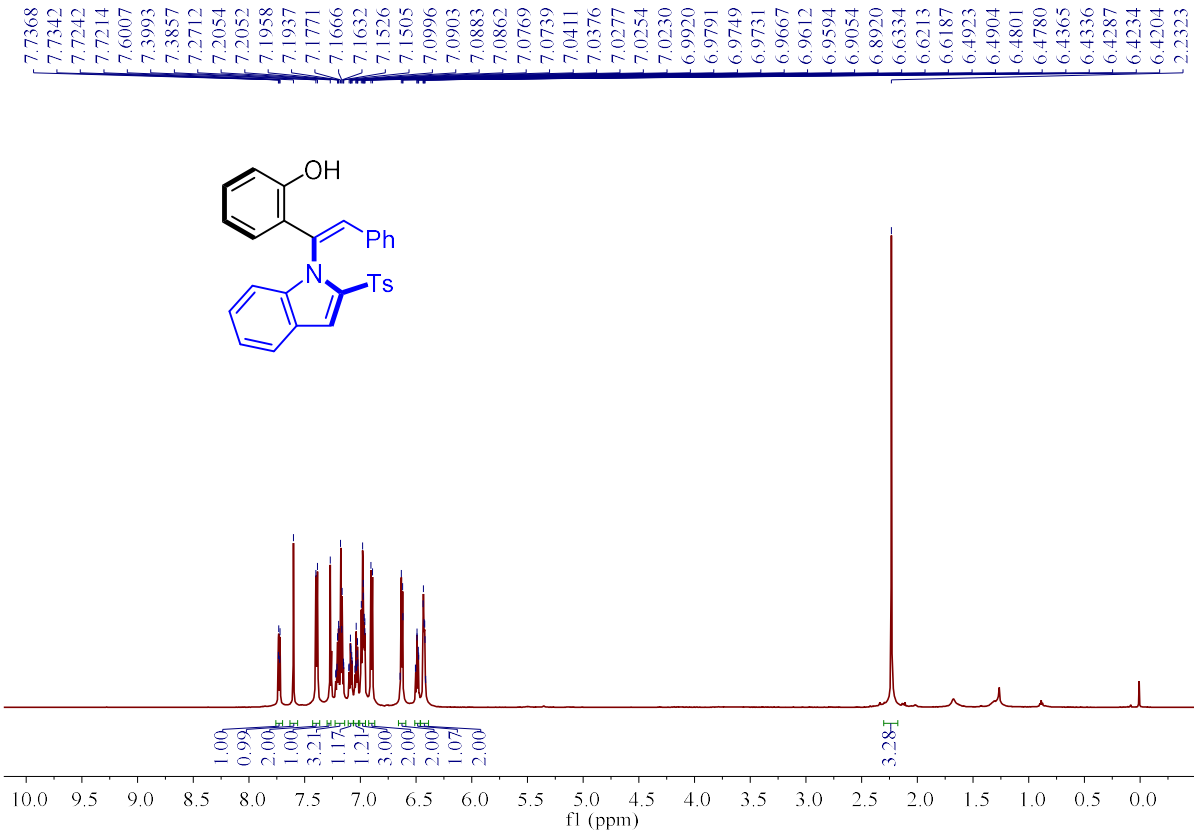

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 25.**



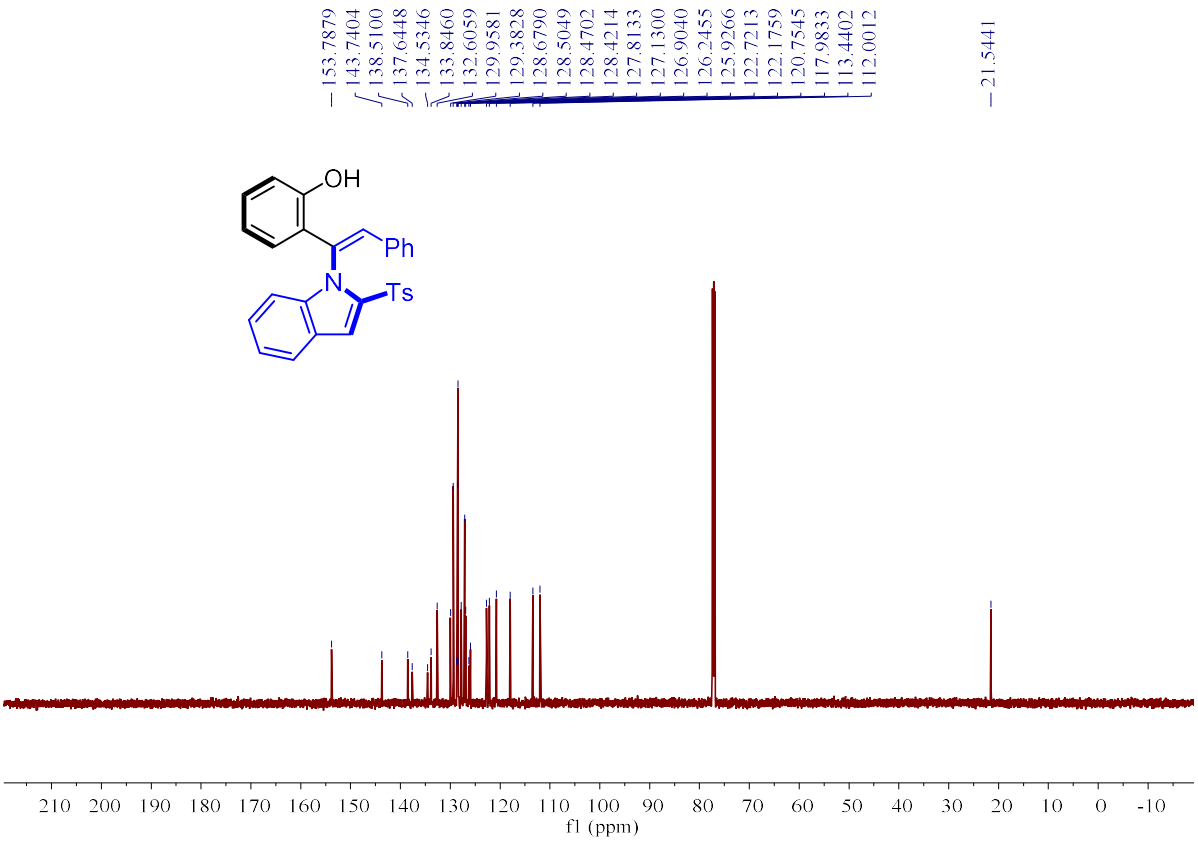

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 25.**



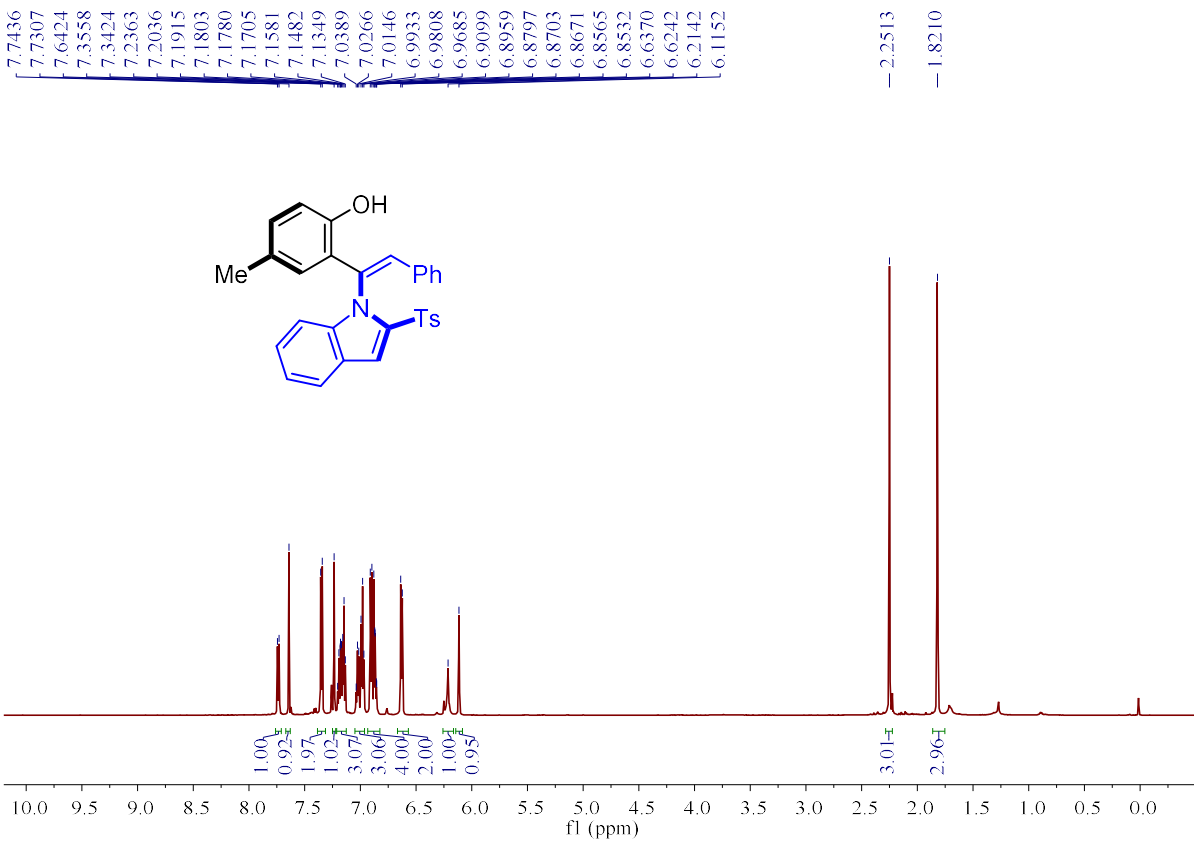

**$^{31}$P NMR (243 MHz, $CDCl_3$) spectrum of 25.**



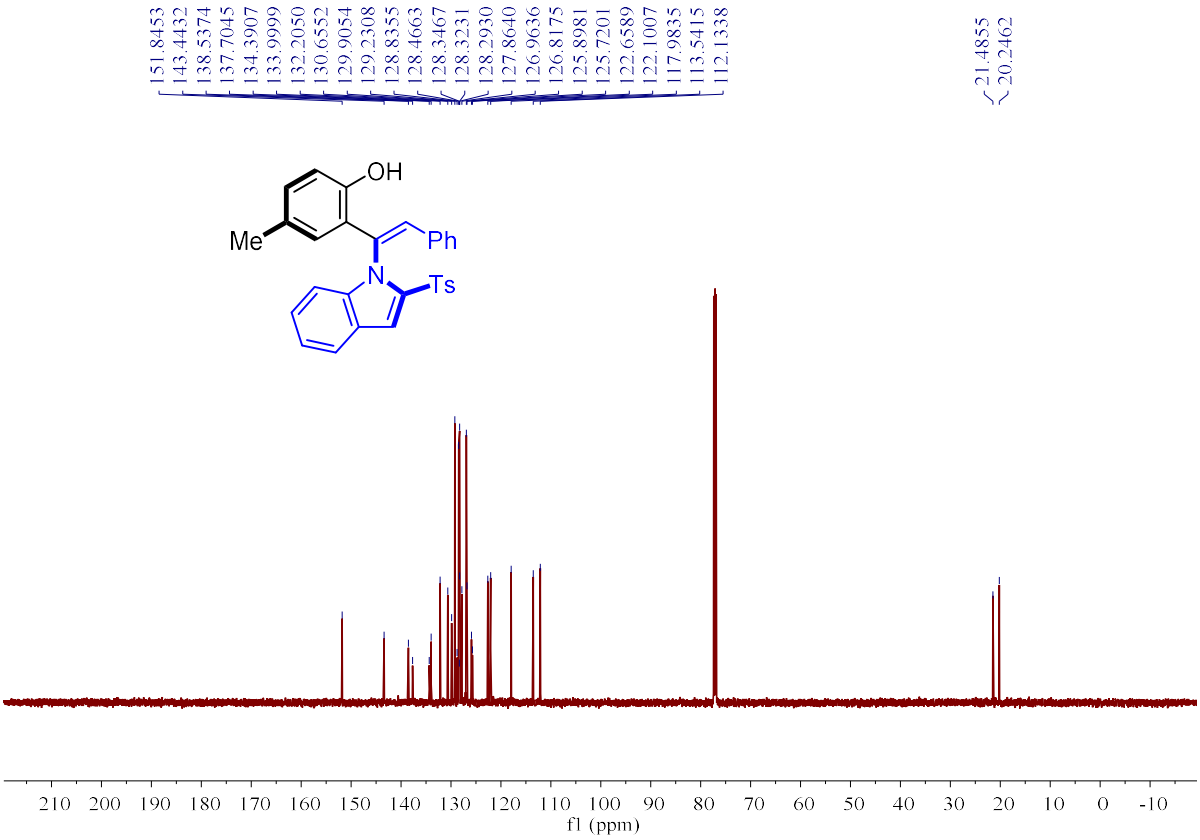

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 26.**



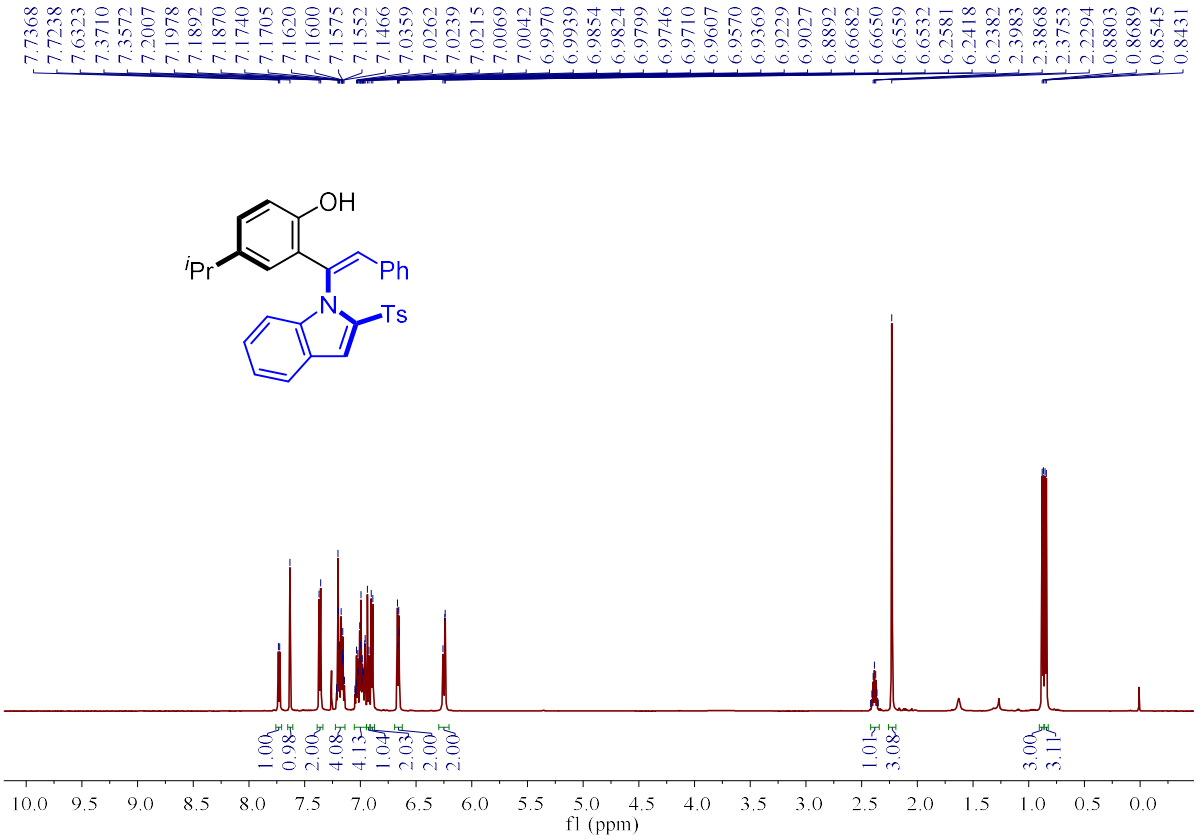

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 26.**



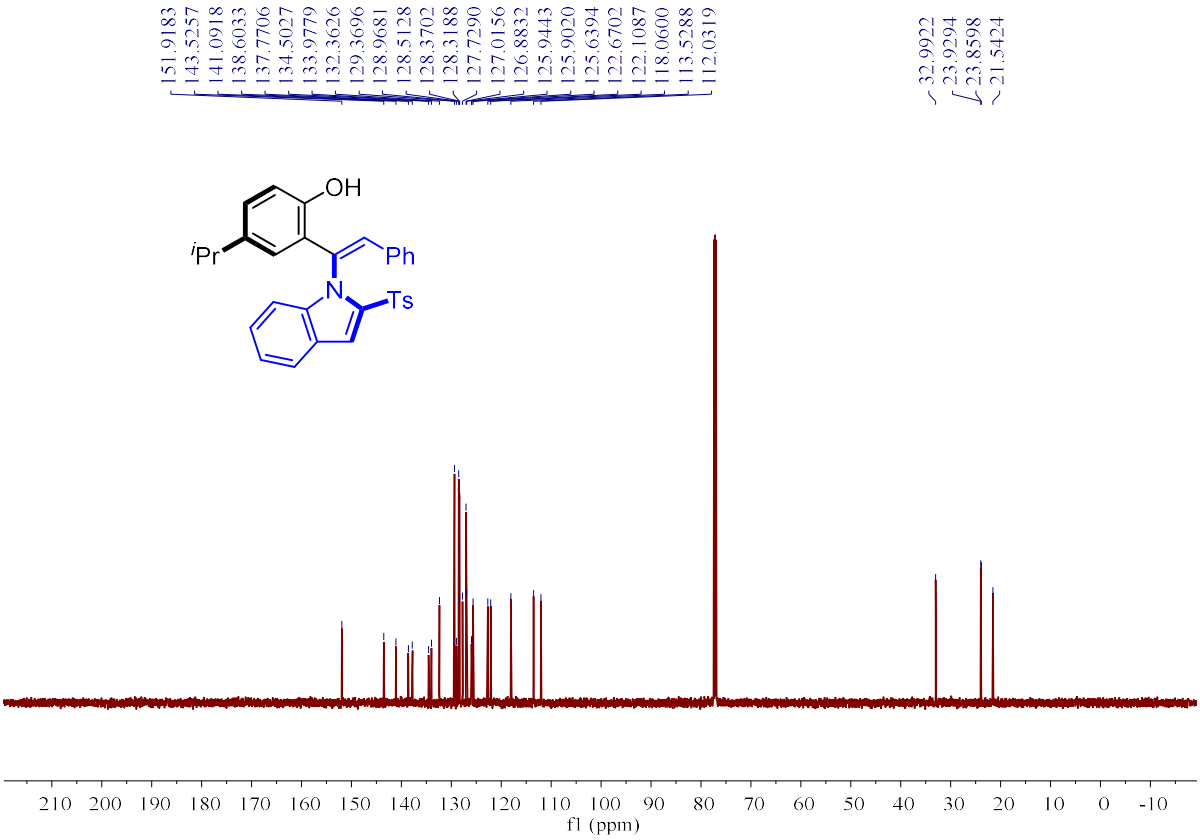

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 27.**



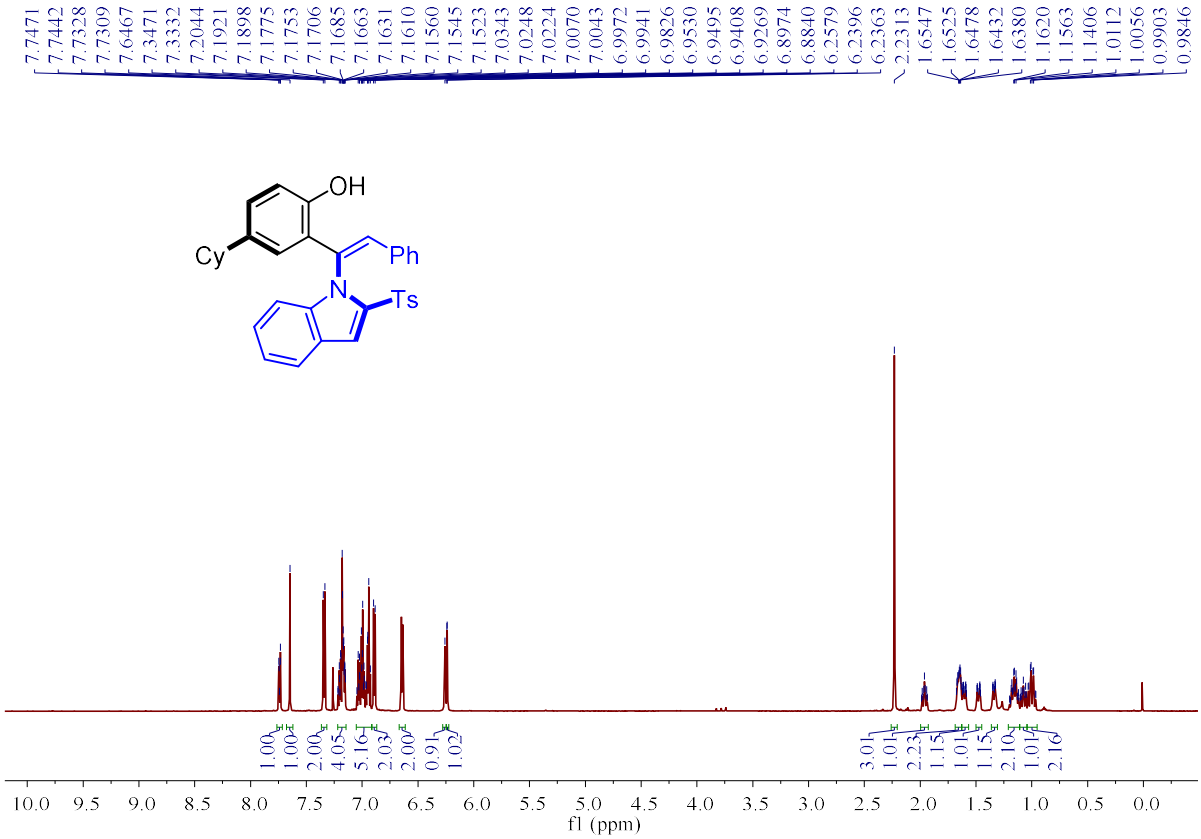

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 27.**



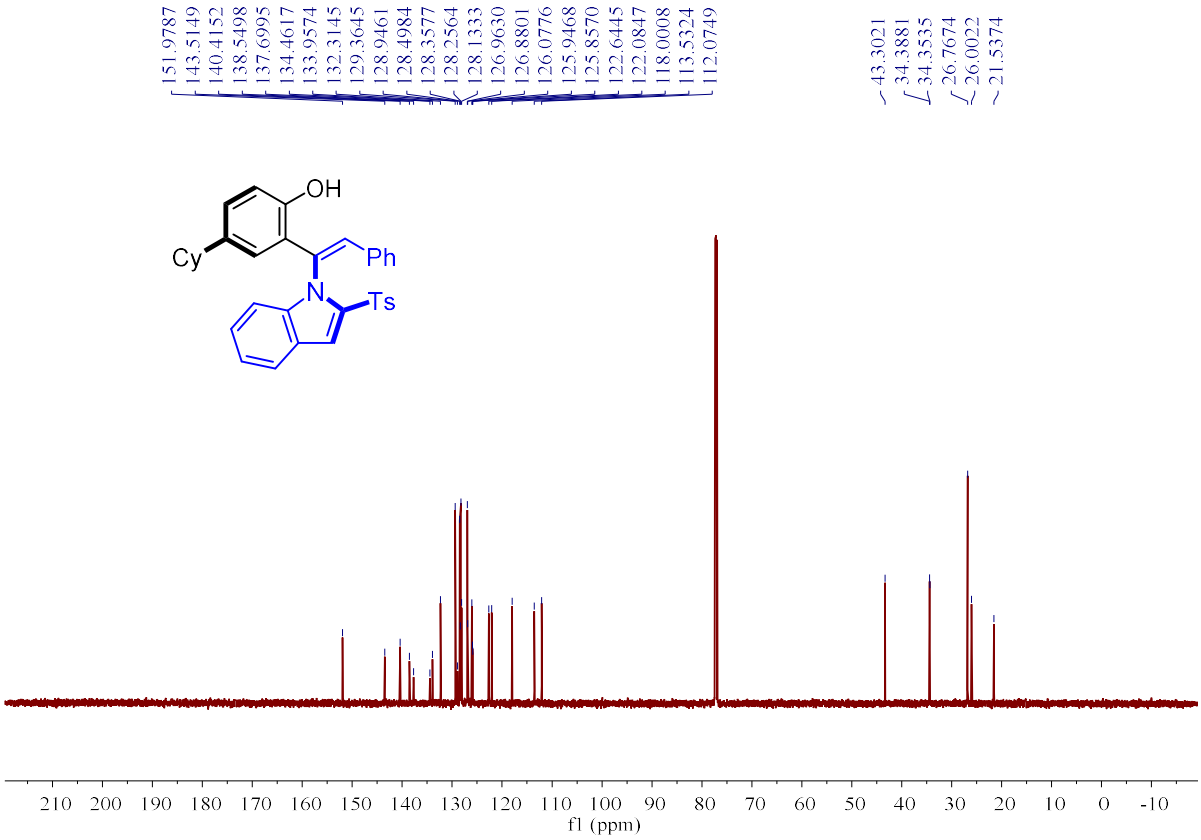

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 28.**



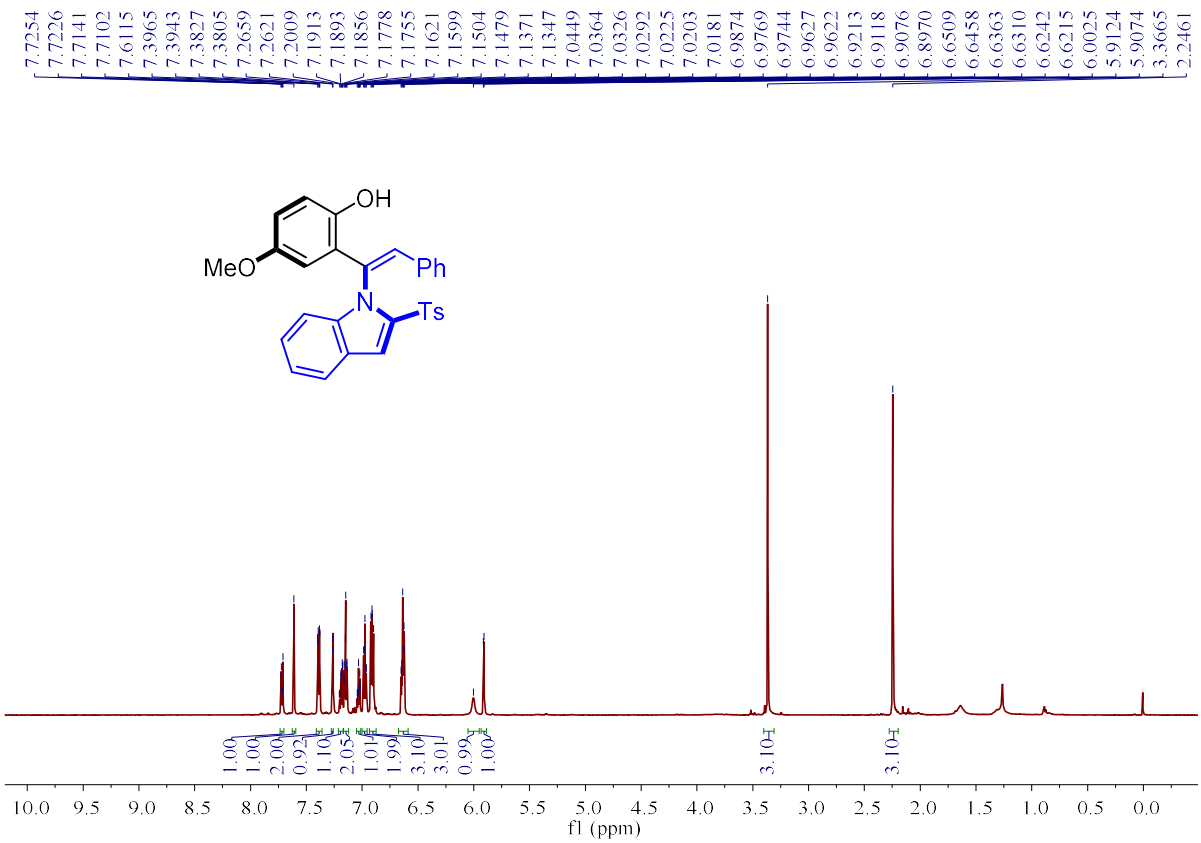

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 28.**



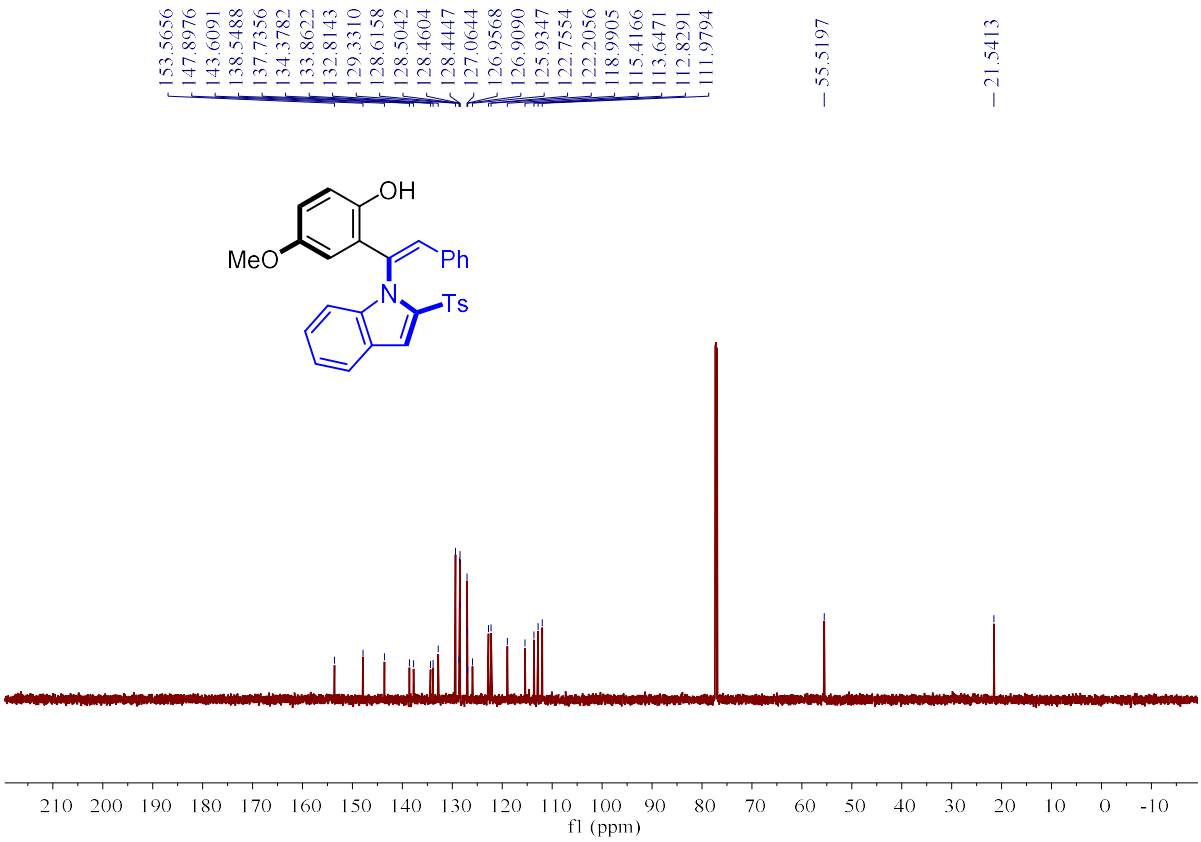

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 29.**



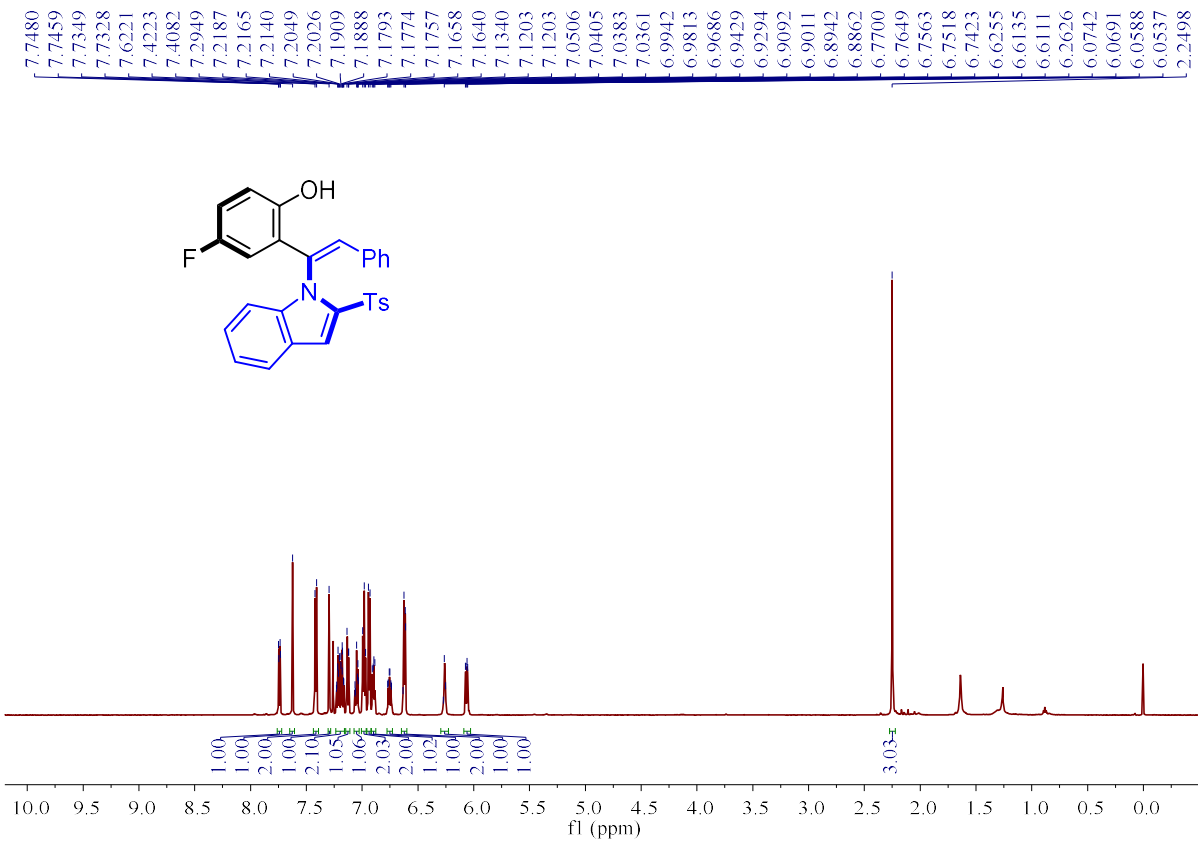

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 29.**



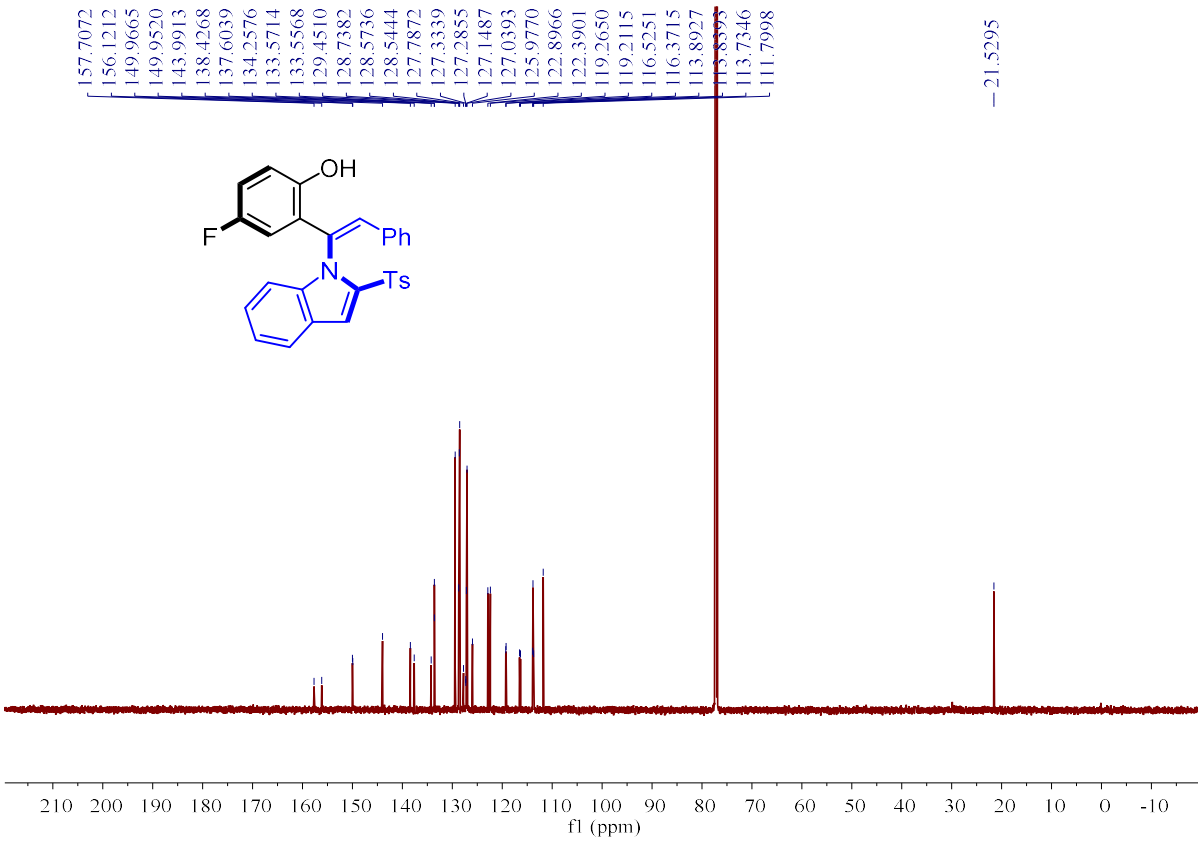

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 30.**



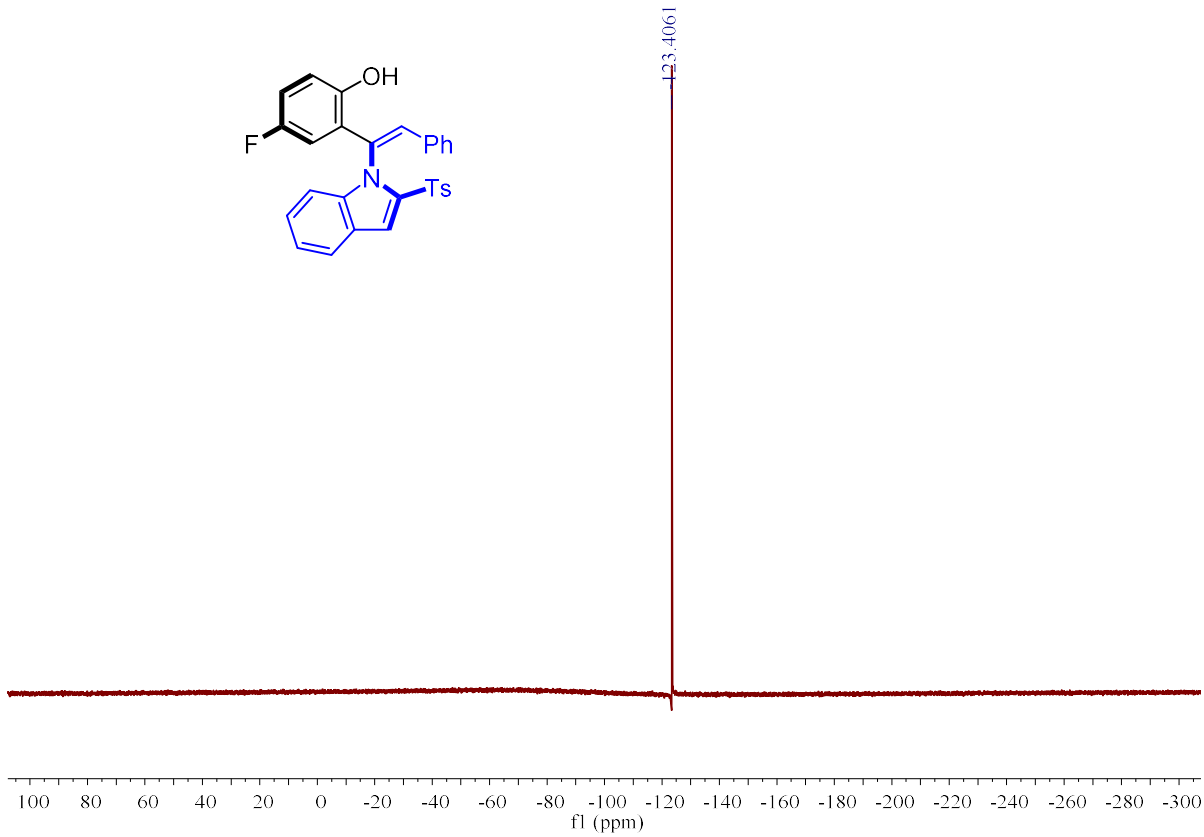

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 30.**



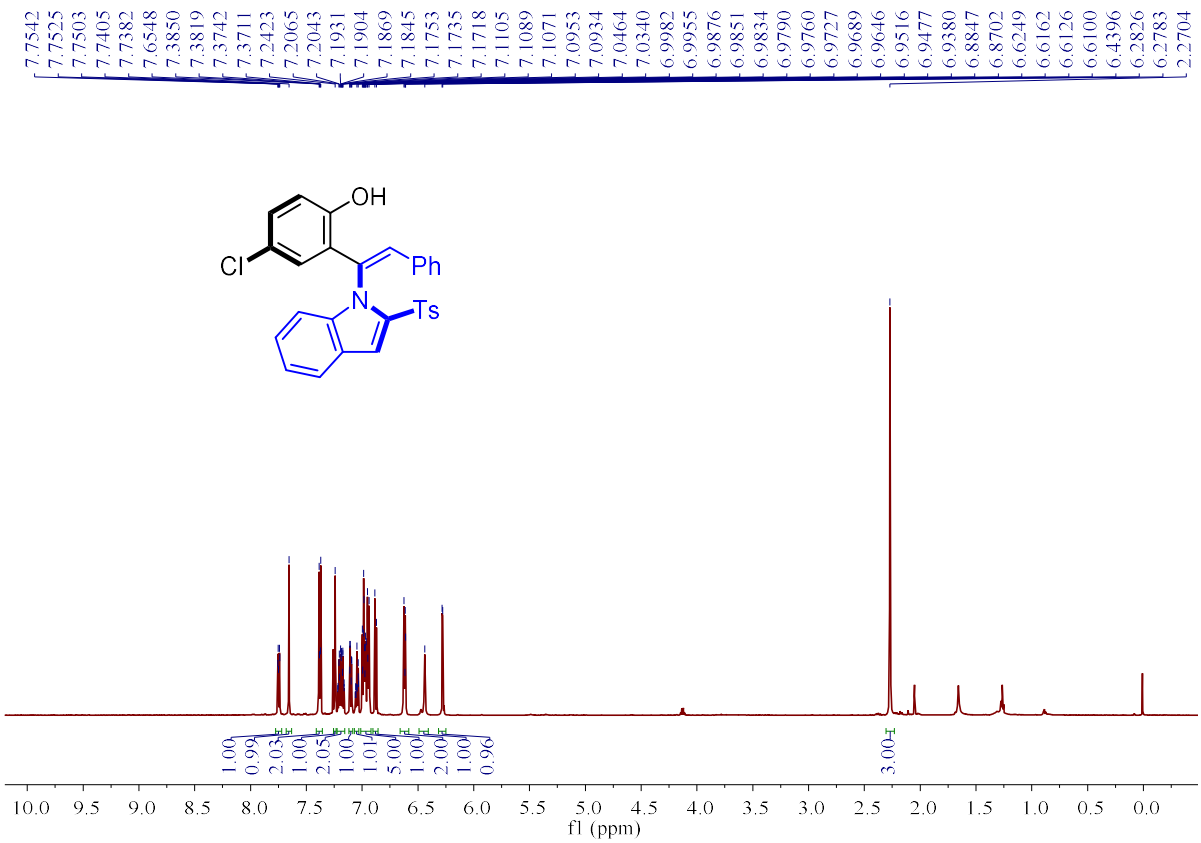

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 31.**



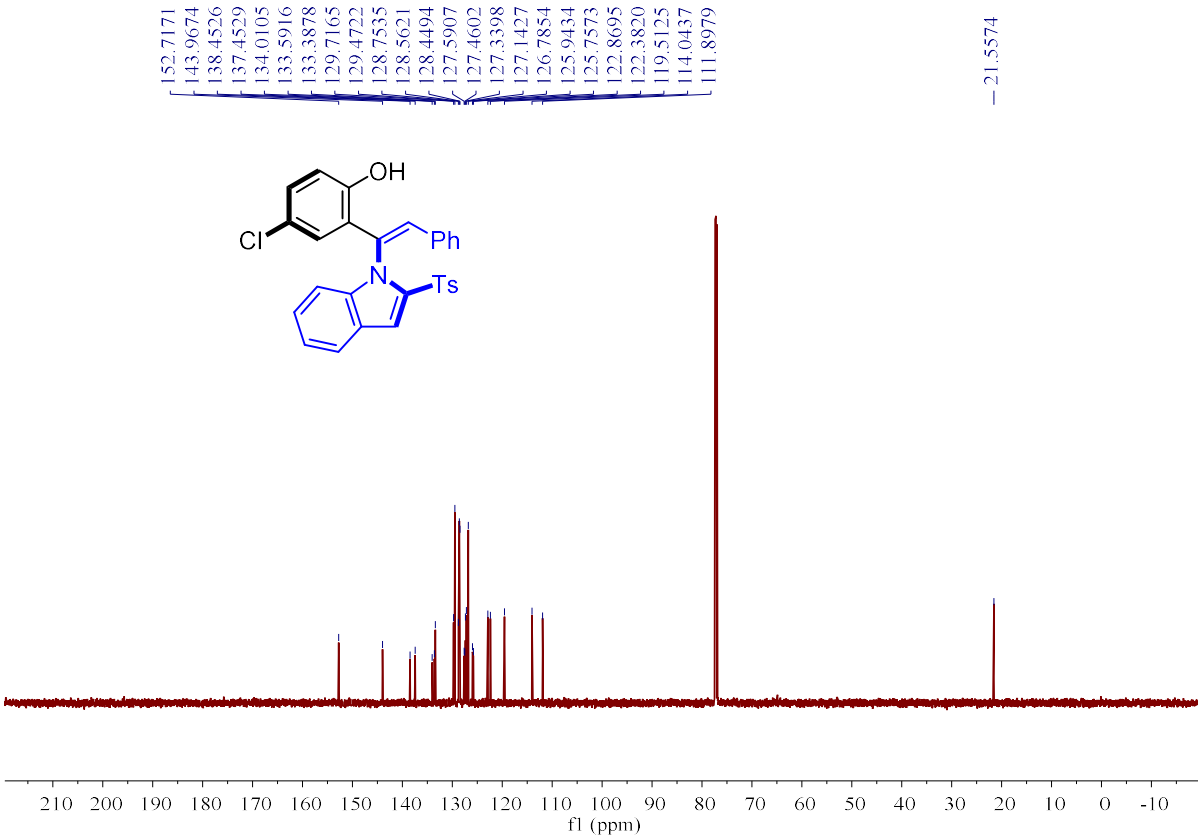

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 31.**



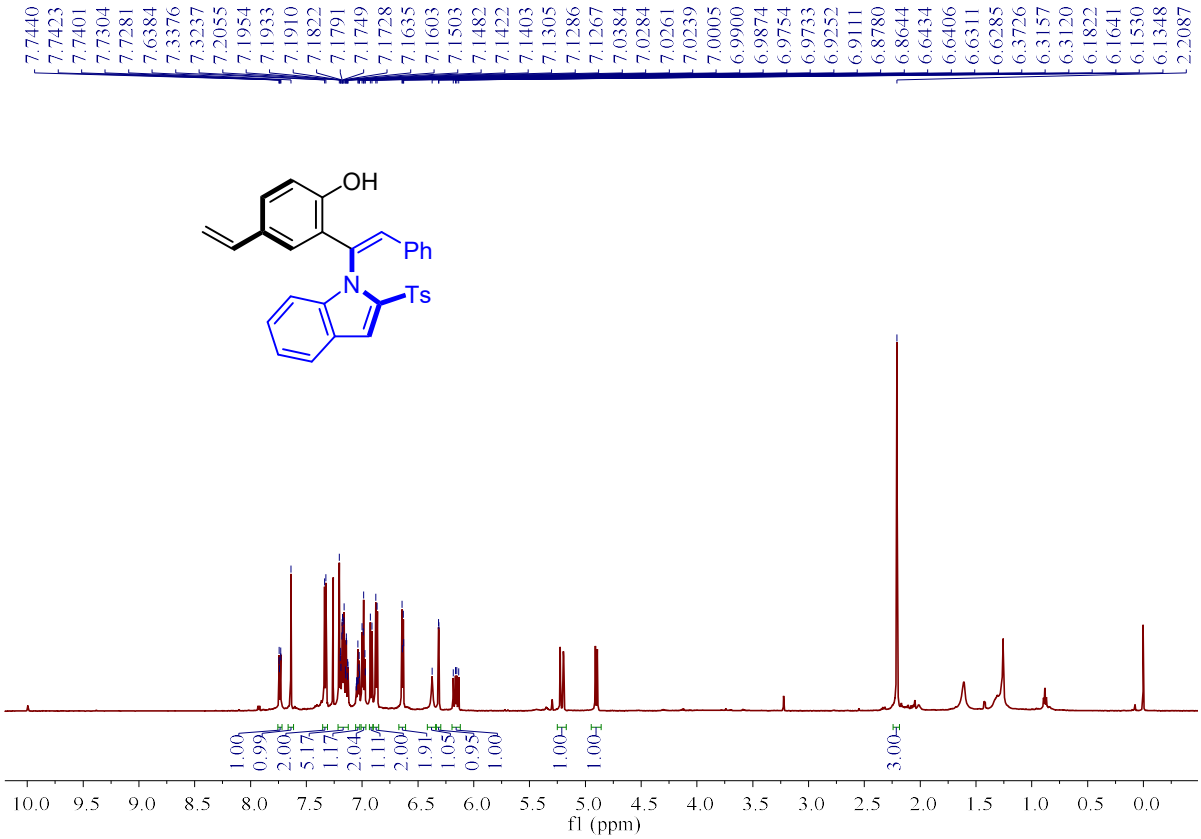

**$^{19}$F NMR (376 MHz, $CDCl_3$) spectrum of 31.**



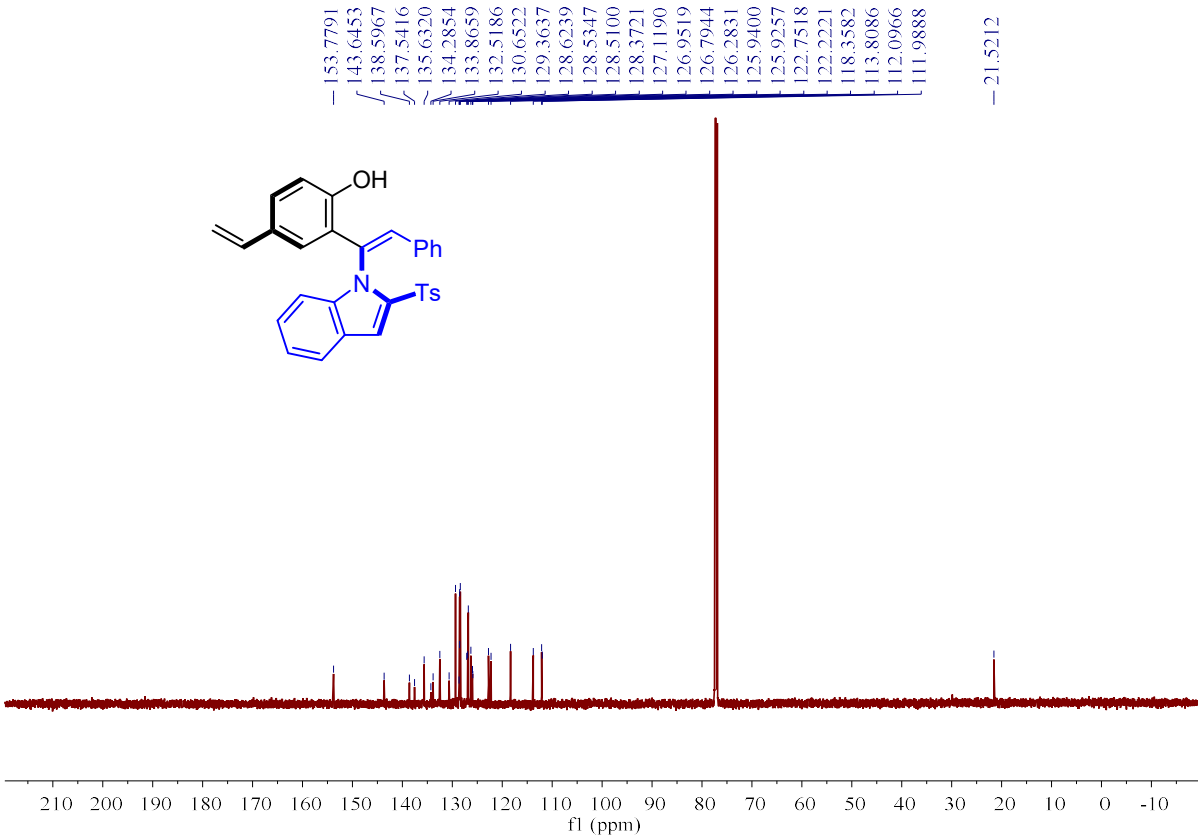

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 32.**



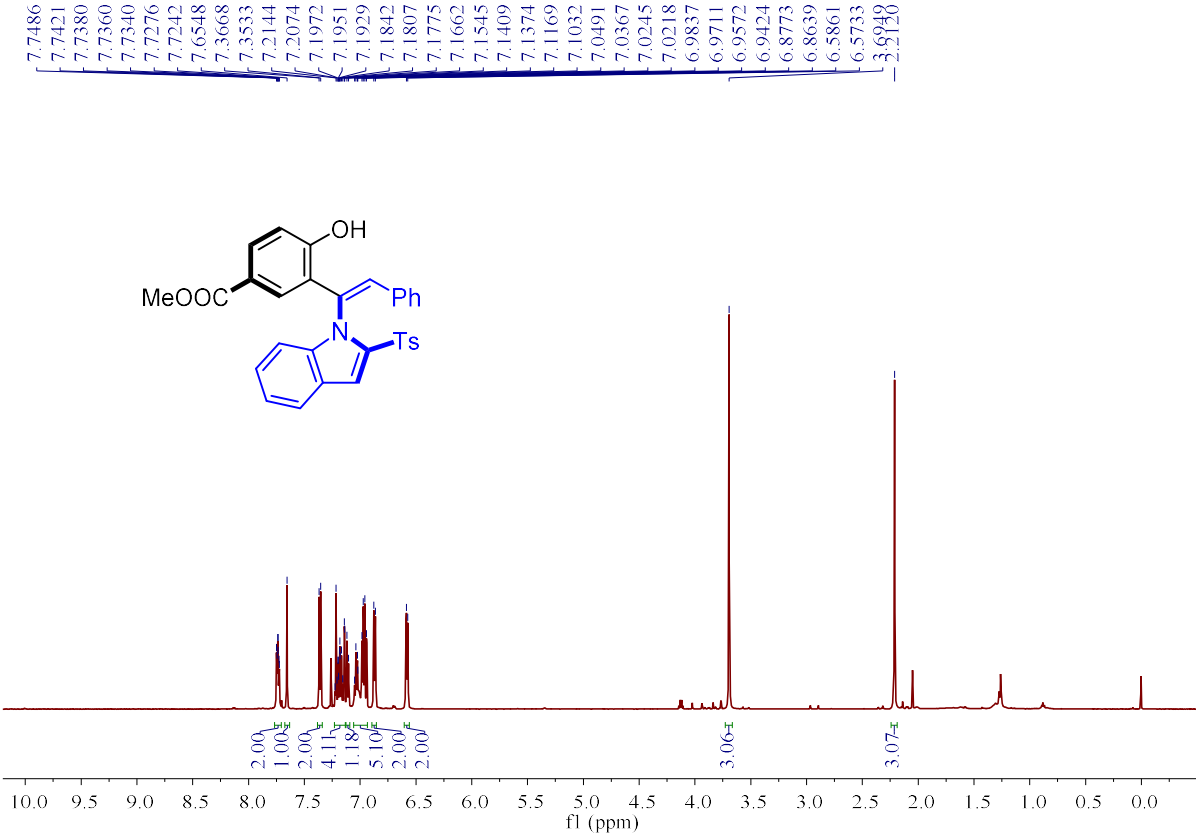

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 32.**



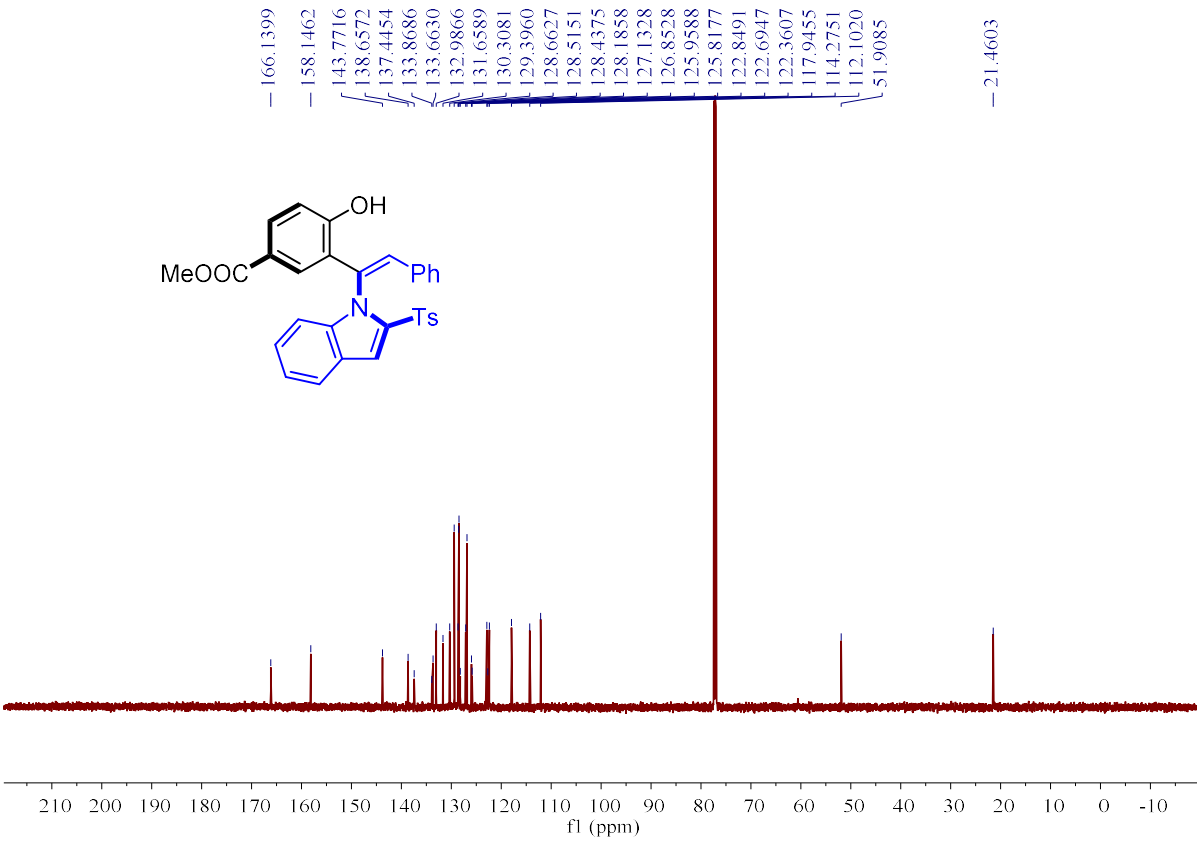

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 33.**



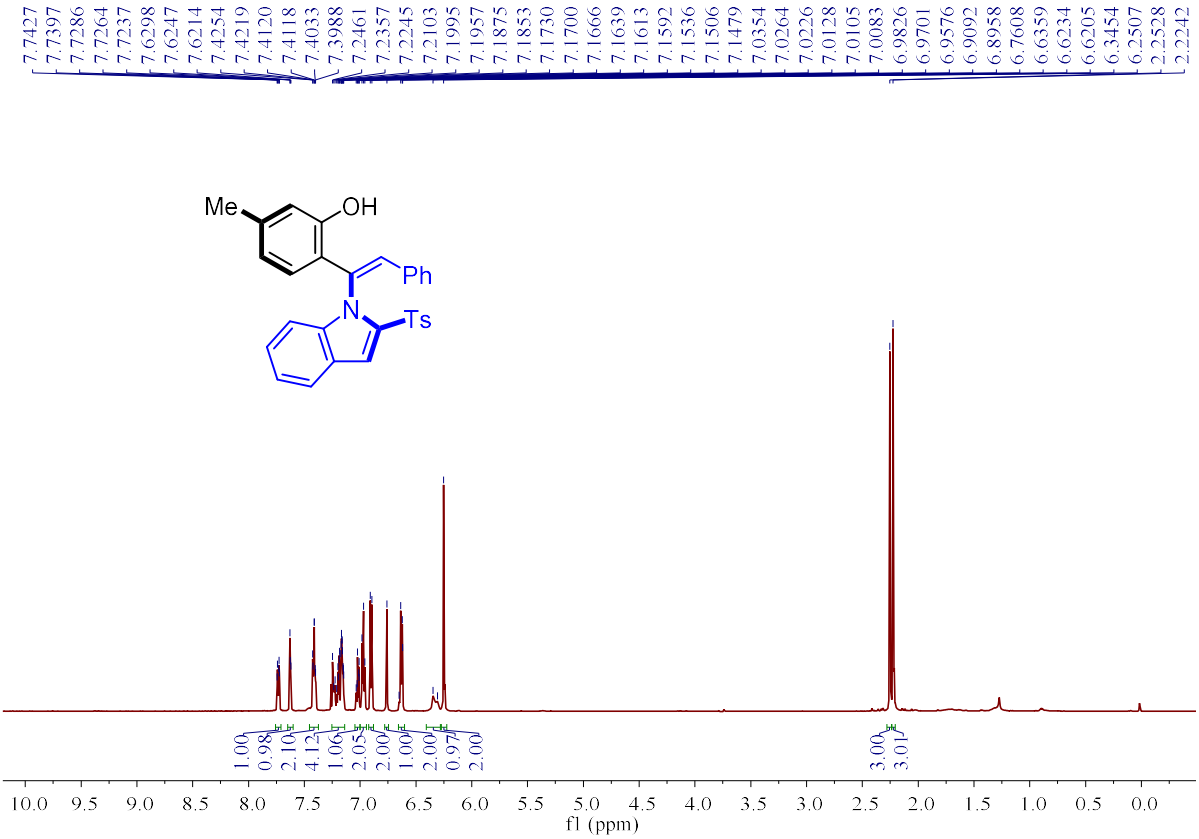

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 33.**



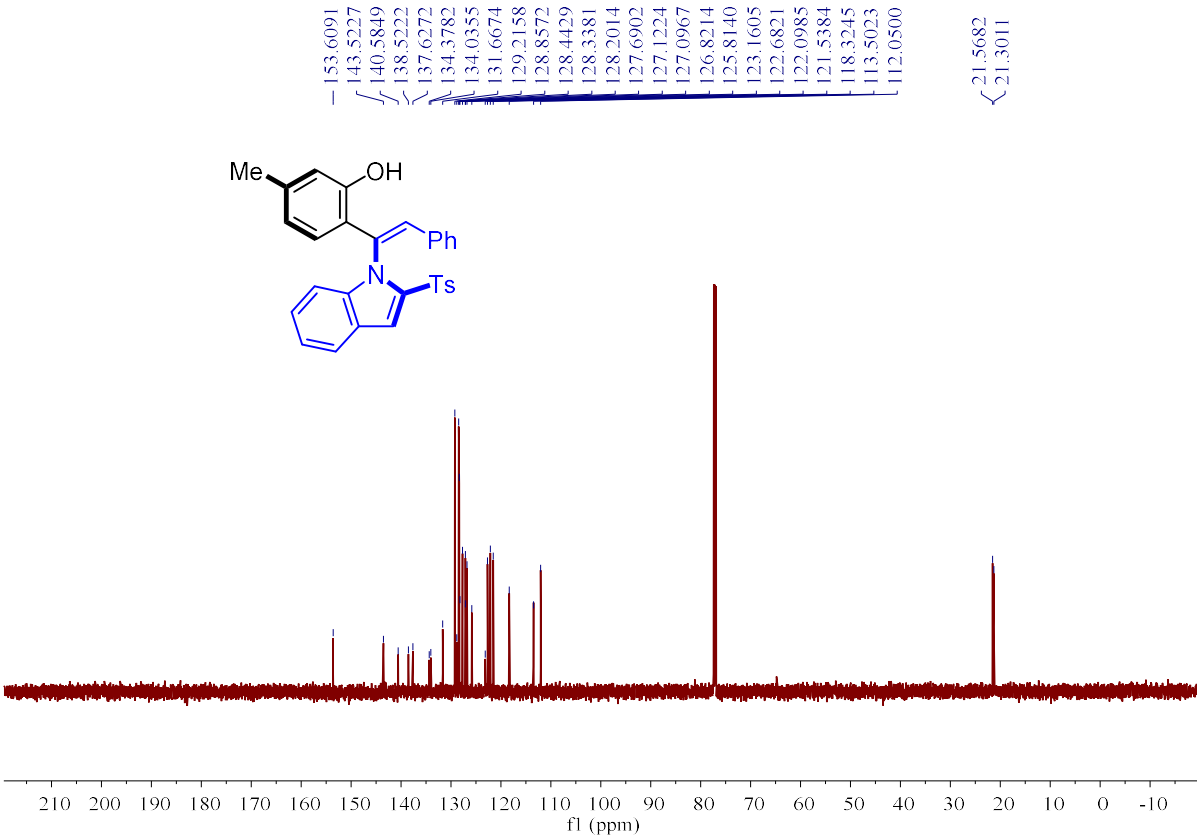

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 34.**



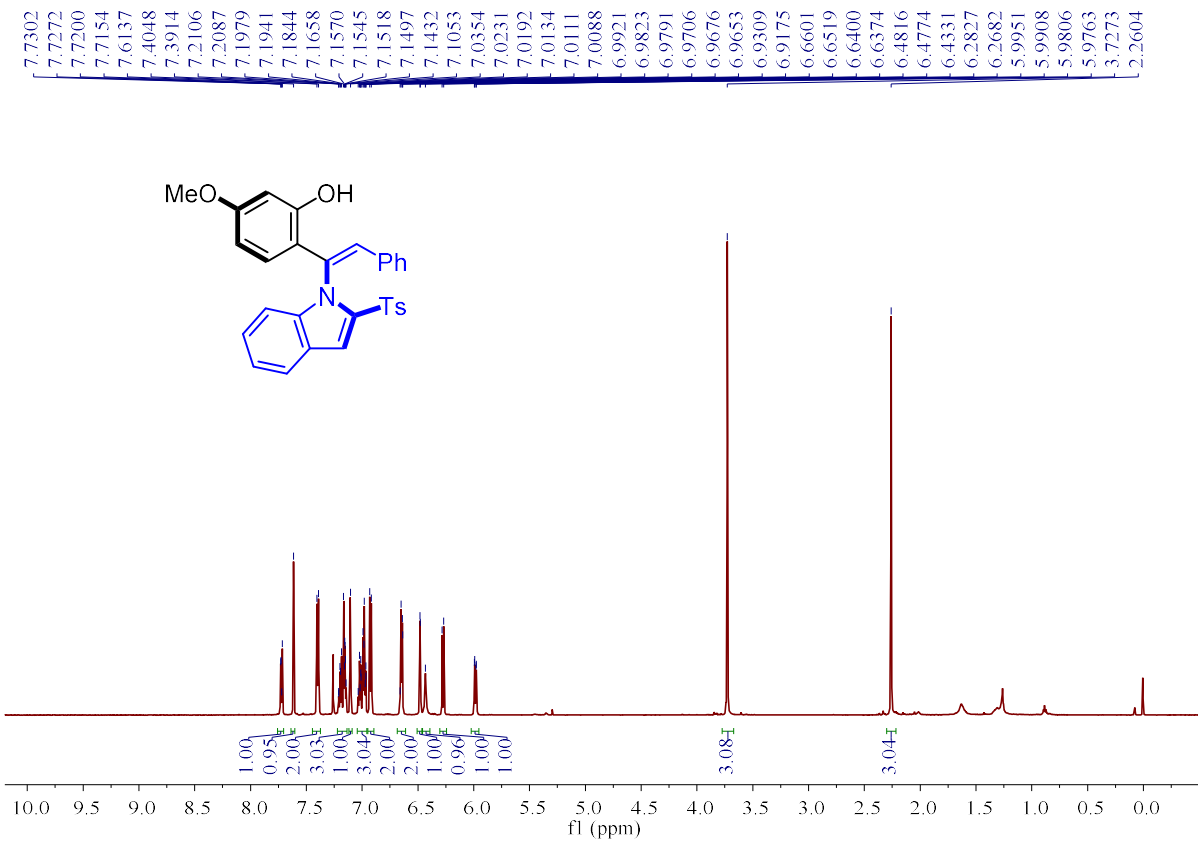

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 34.**



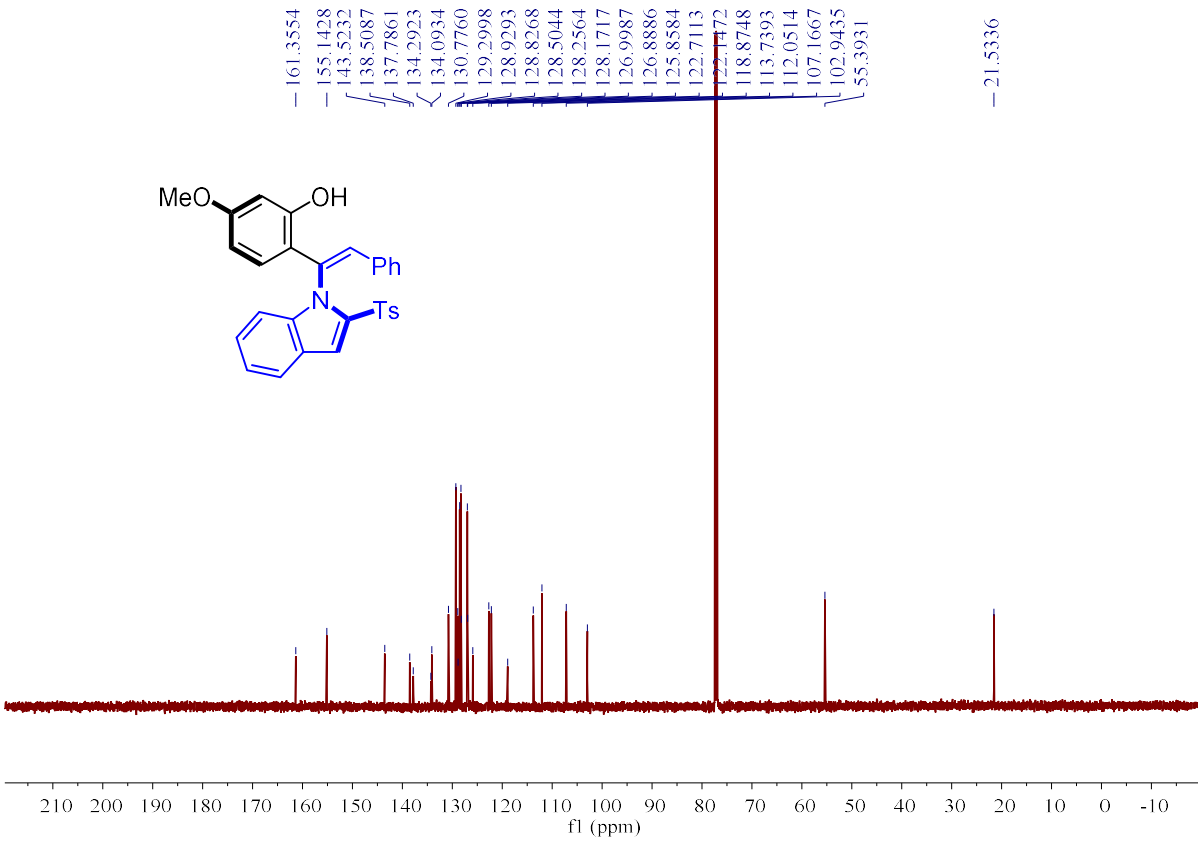

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 35.**



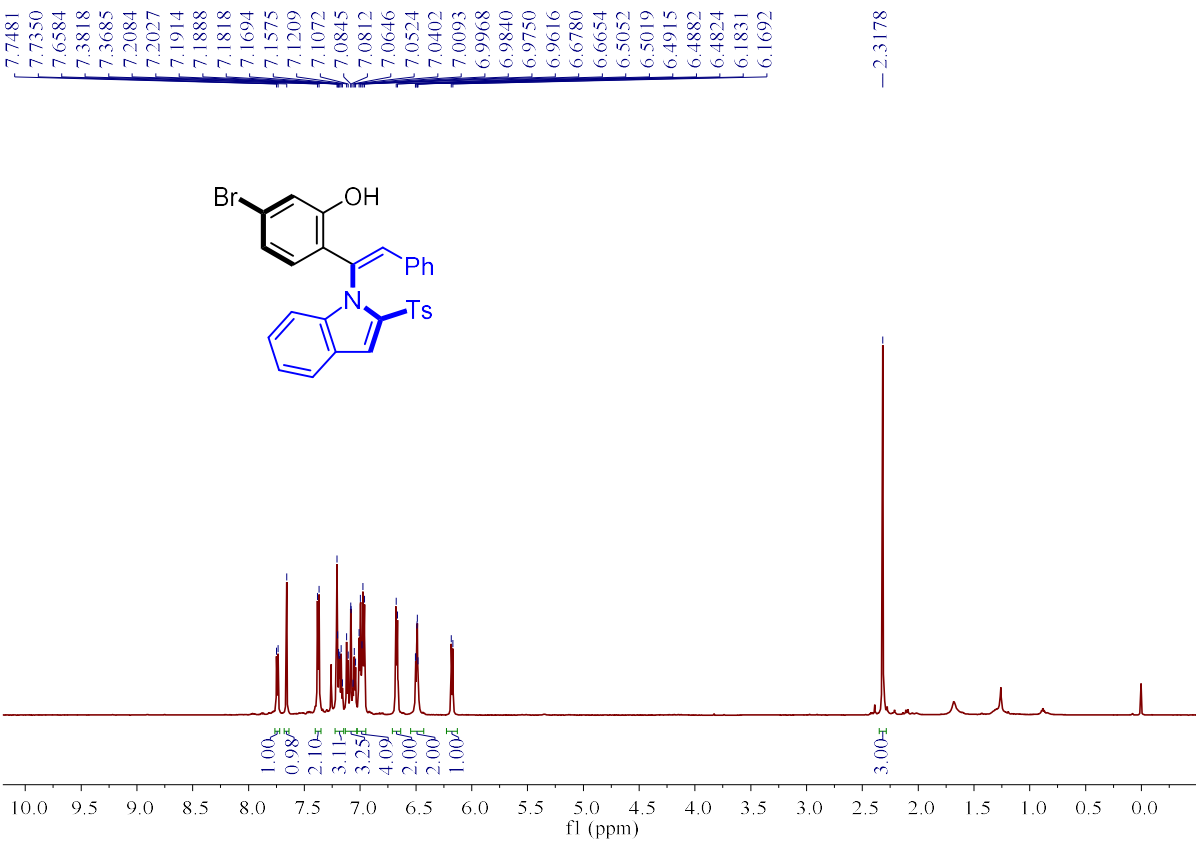

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 35.**



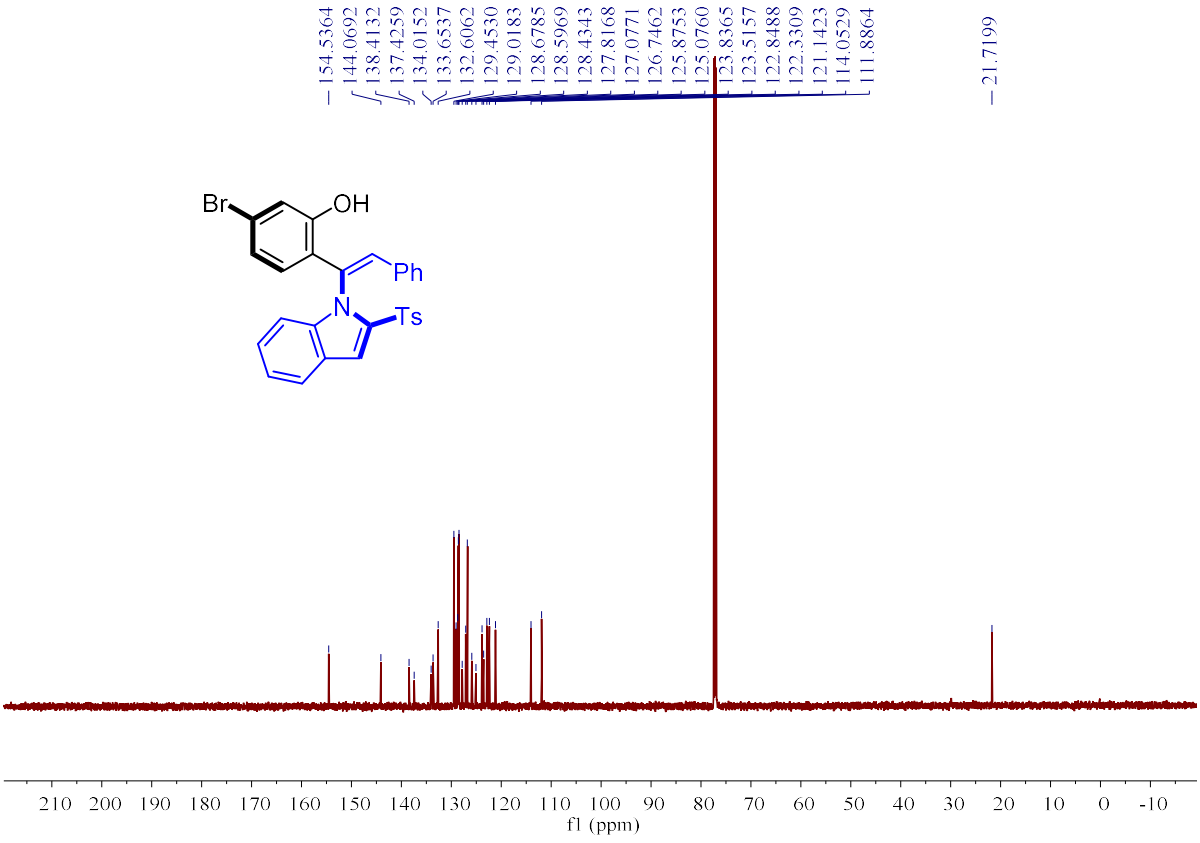

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 36.**



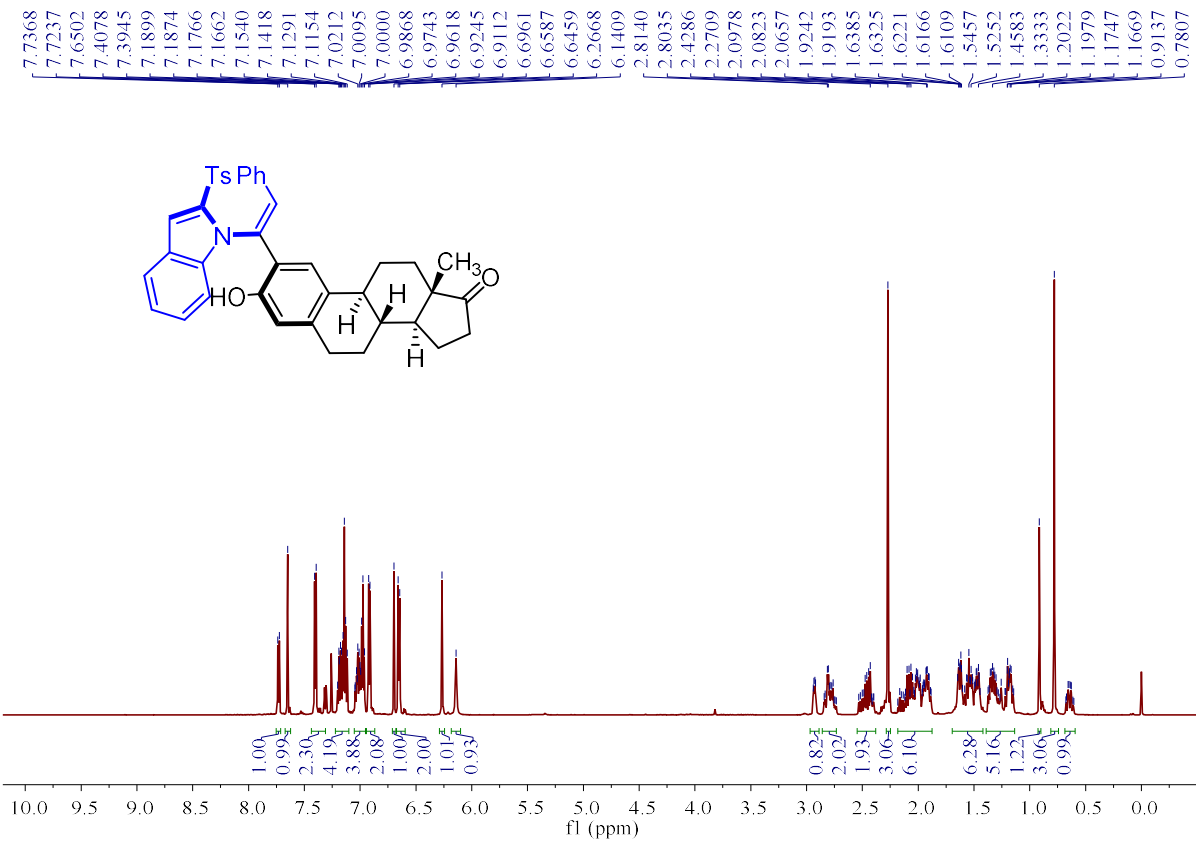

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 36.**



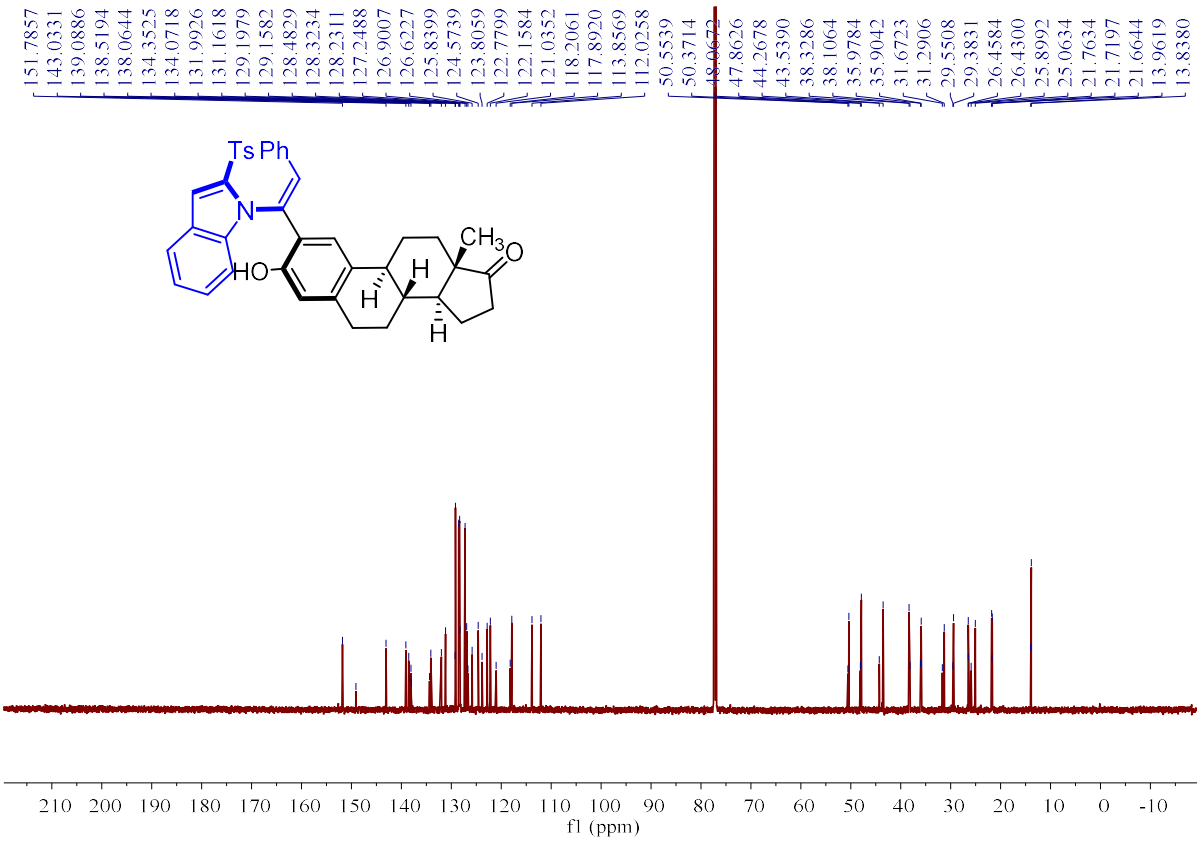

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 37.**



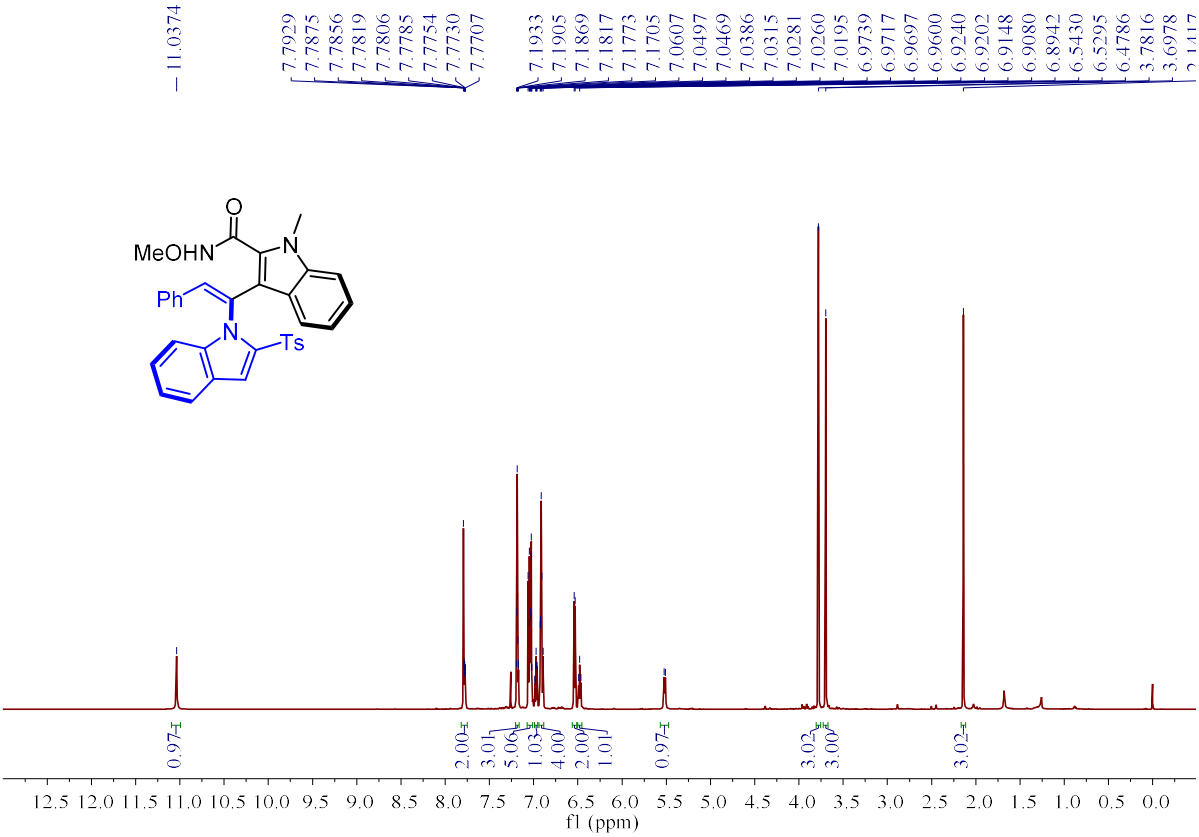

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 37.**



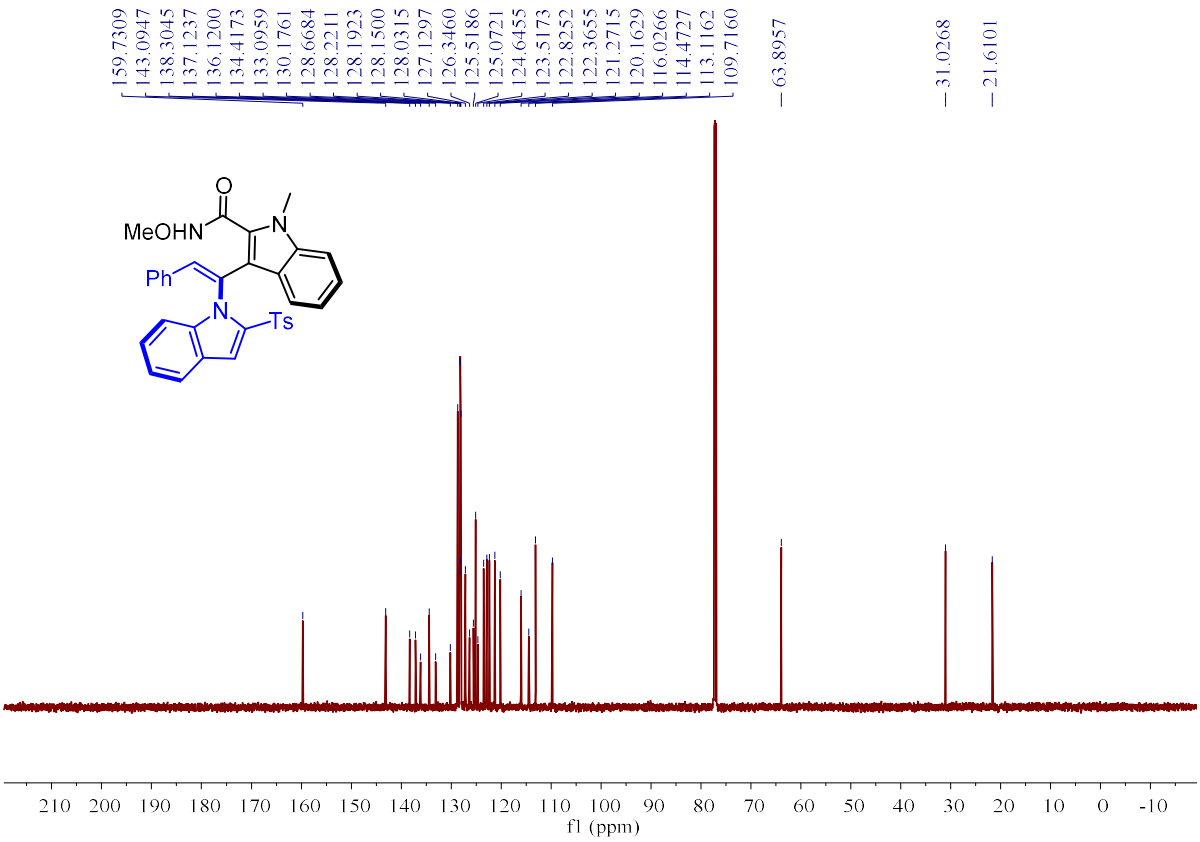

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 38.**



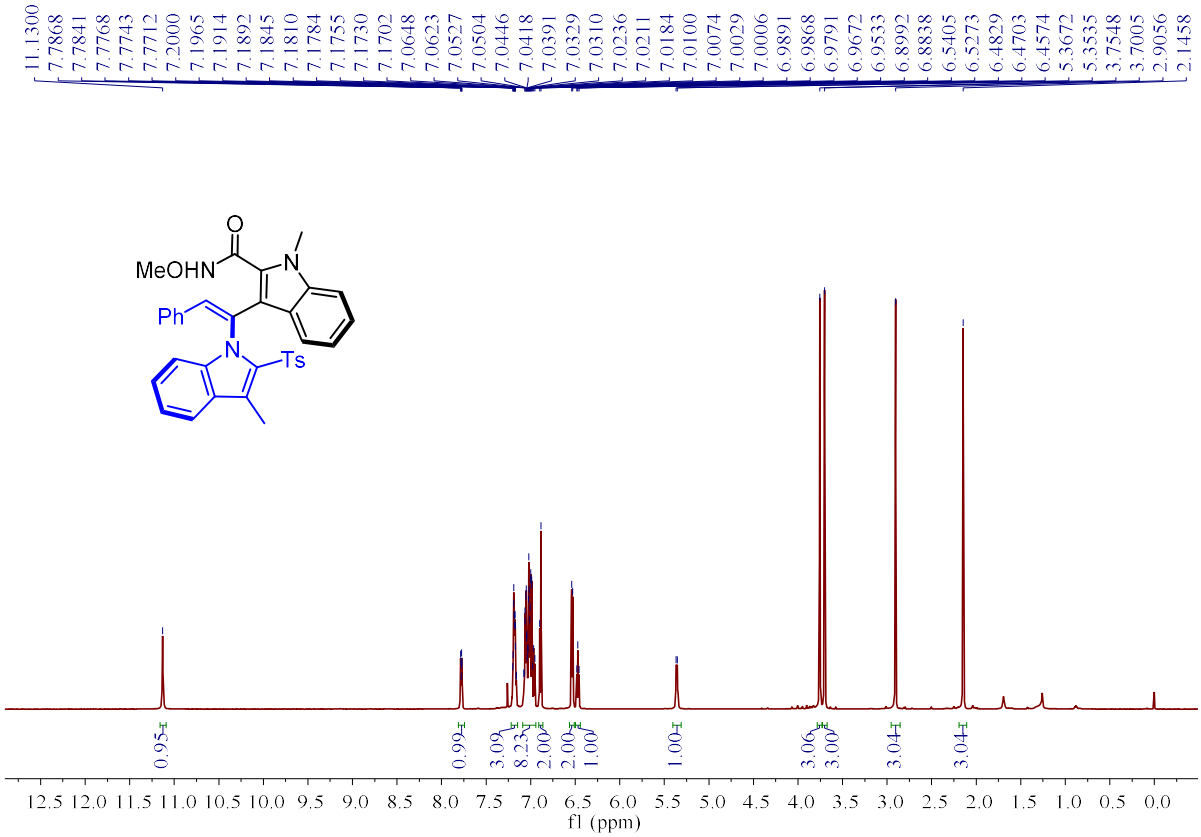

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 38.**



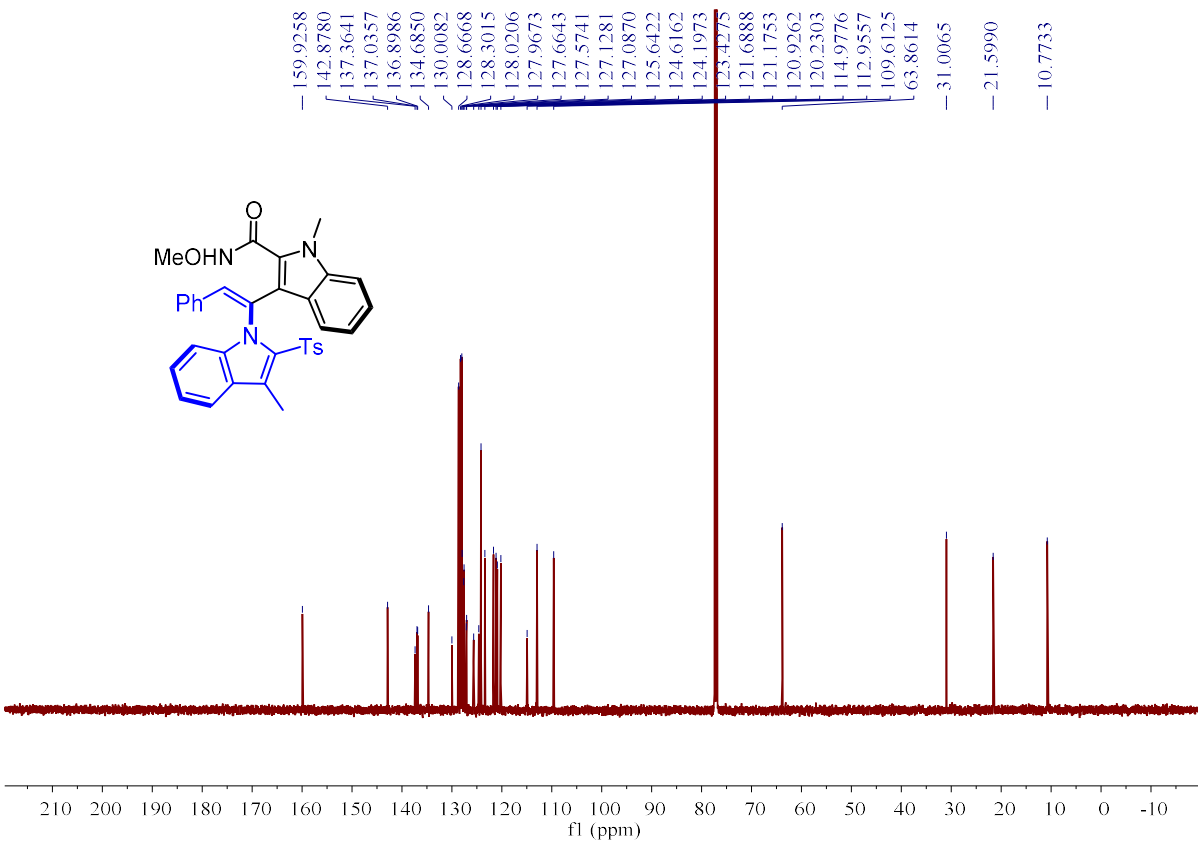

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 40.**



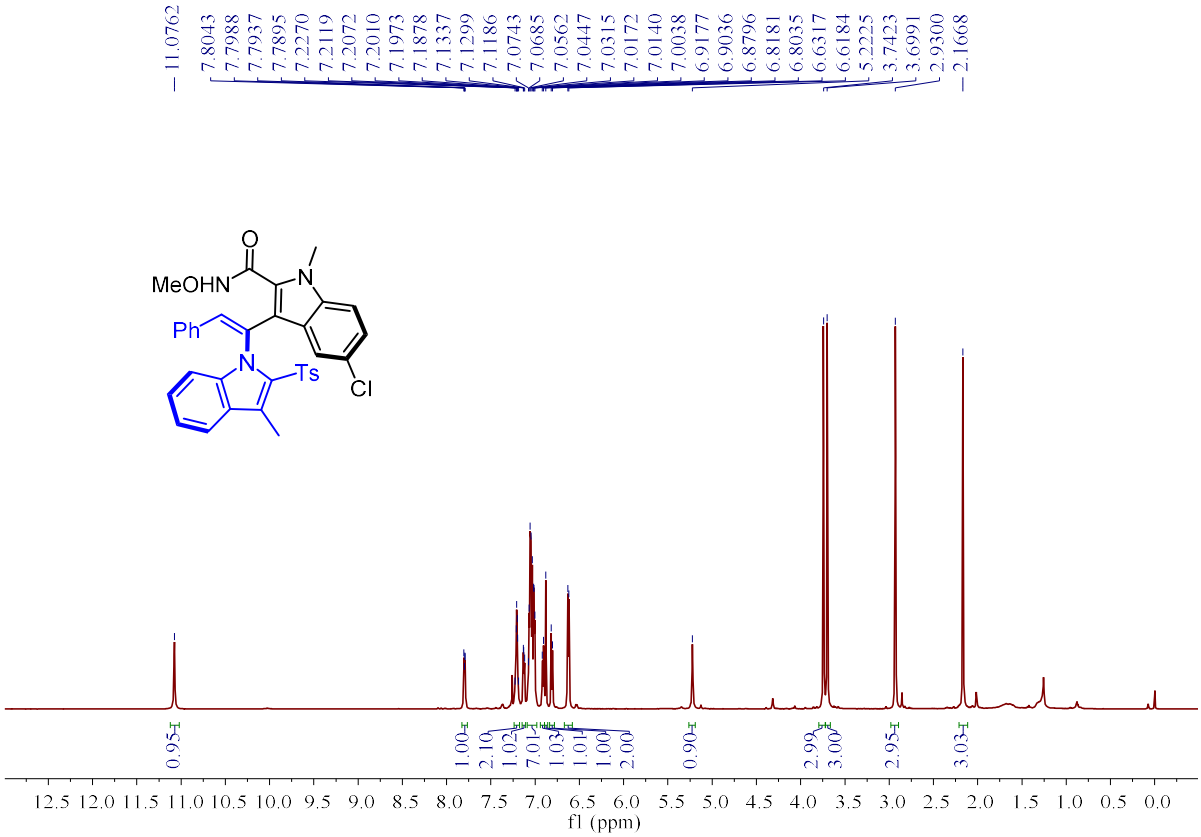

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 40.**



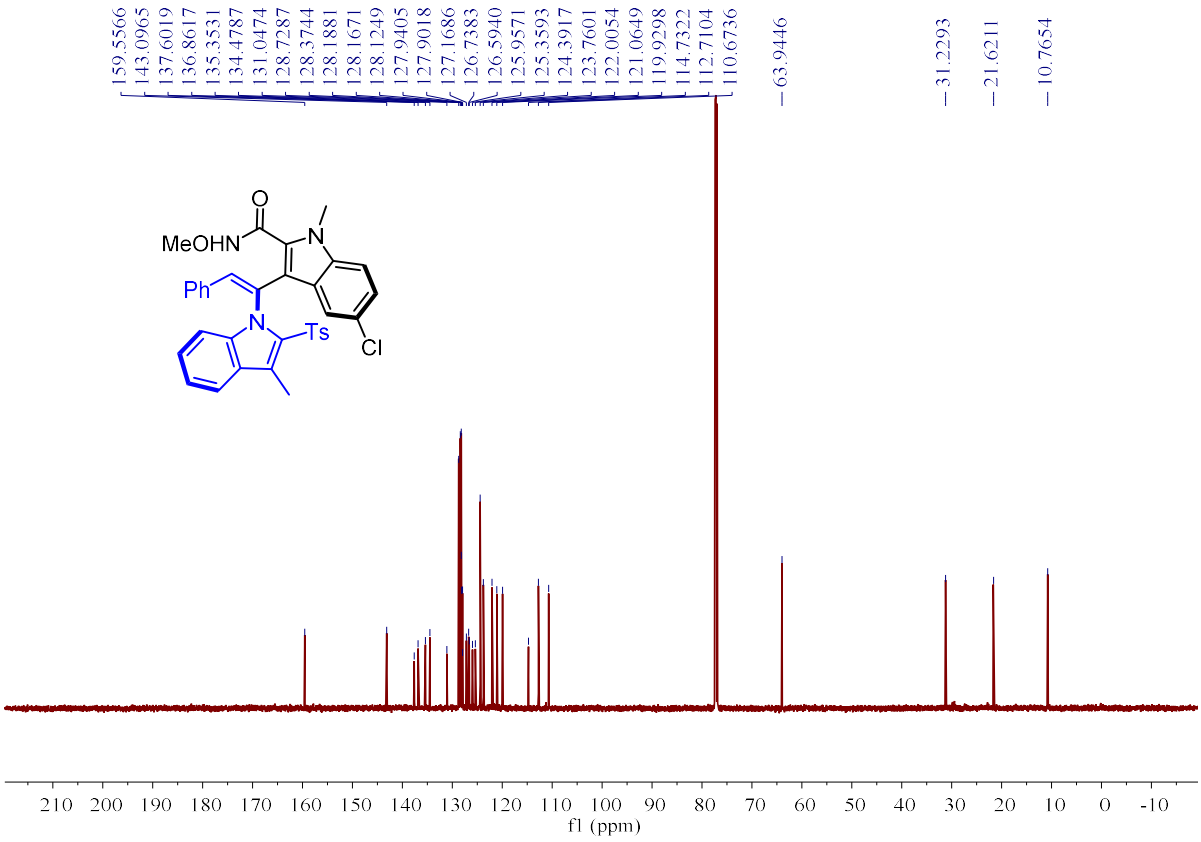

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 41.**



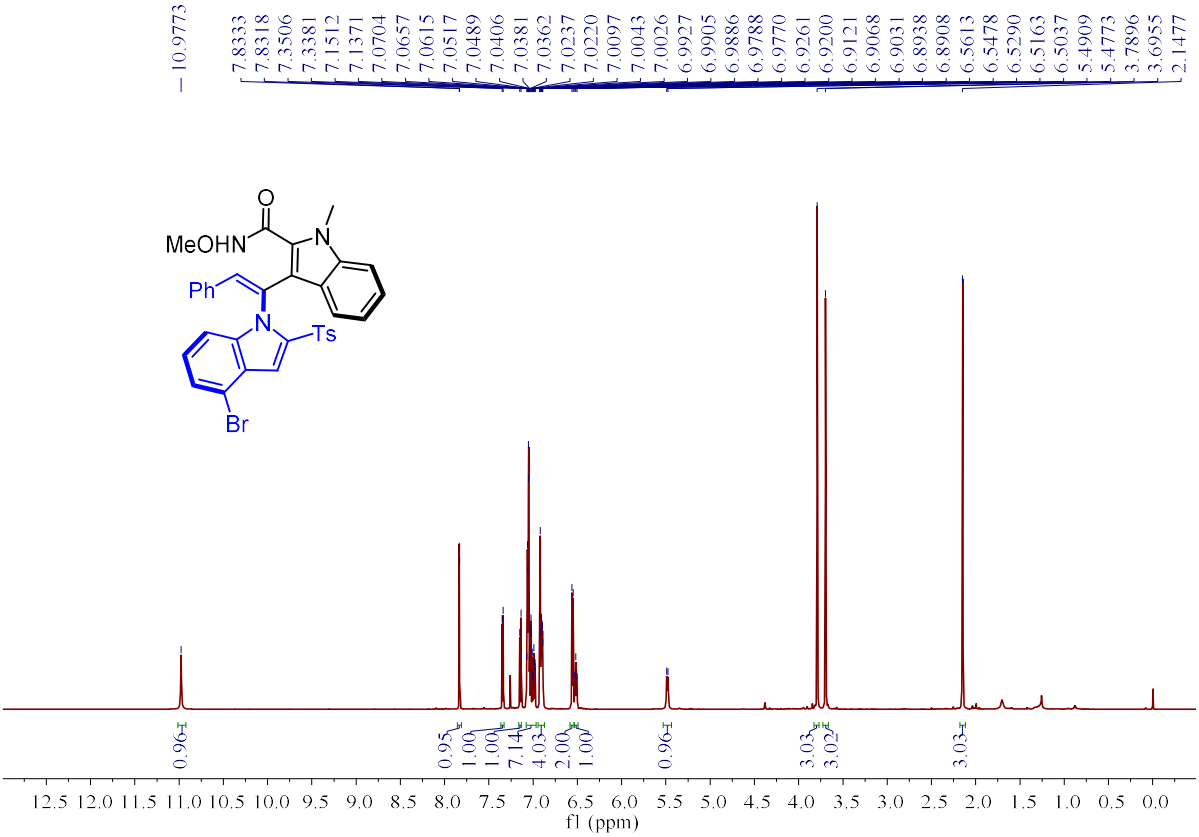

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 41.**



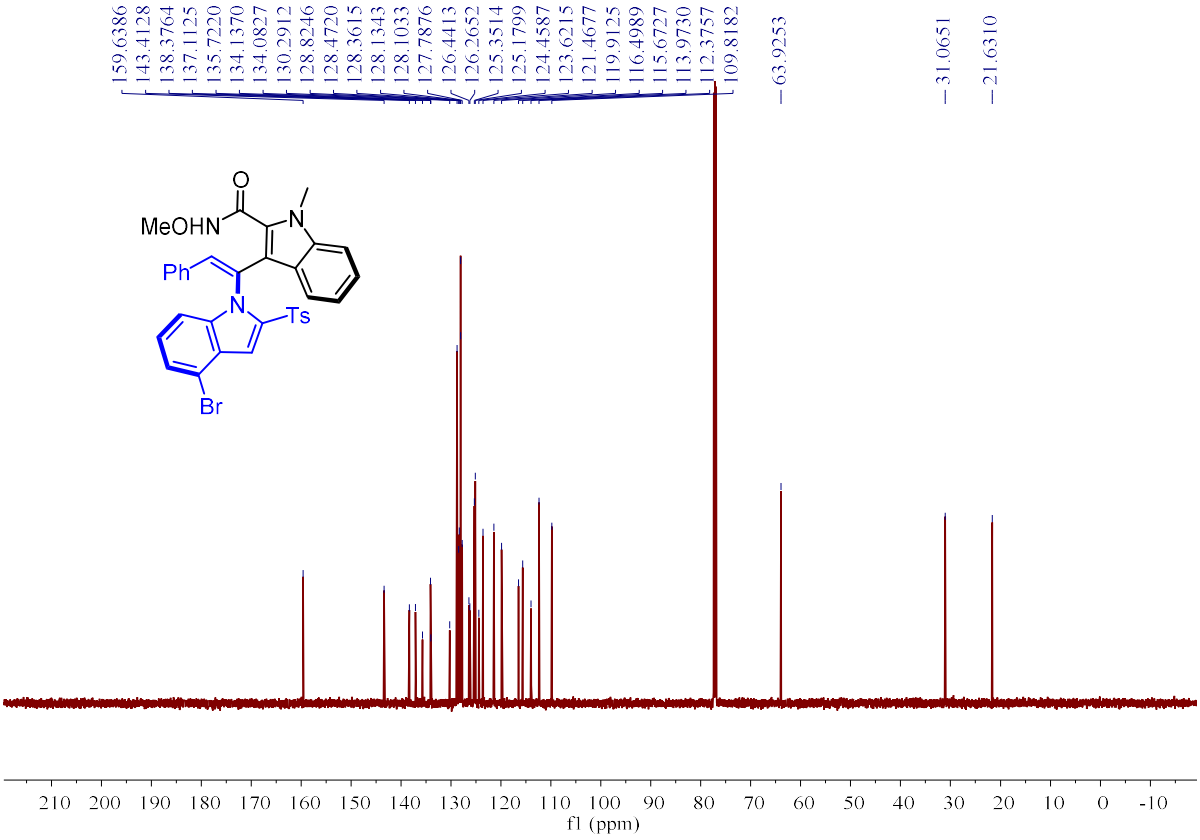

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 42.**



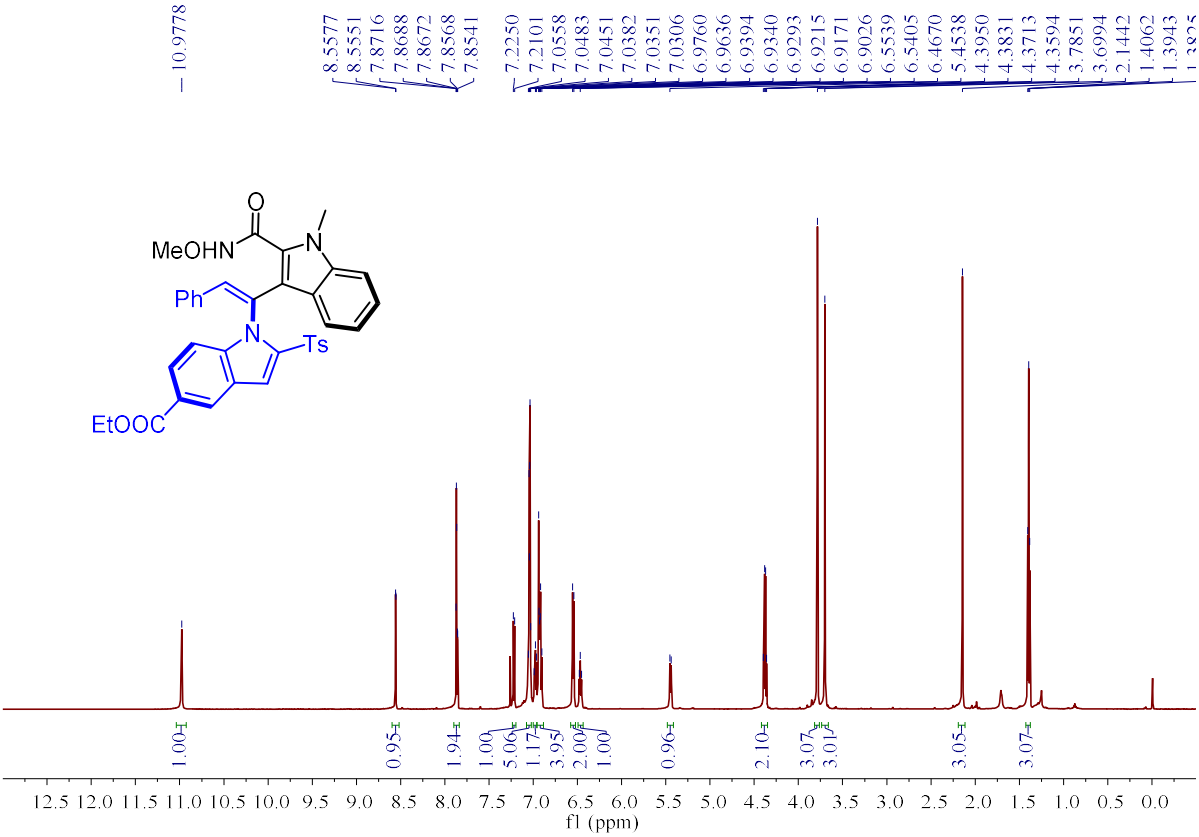

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 42.**



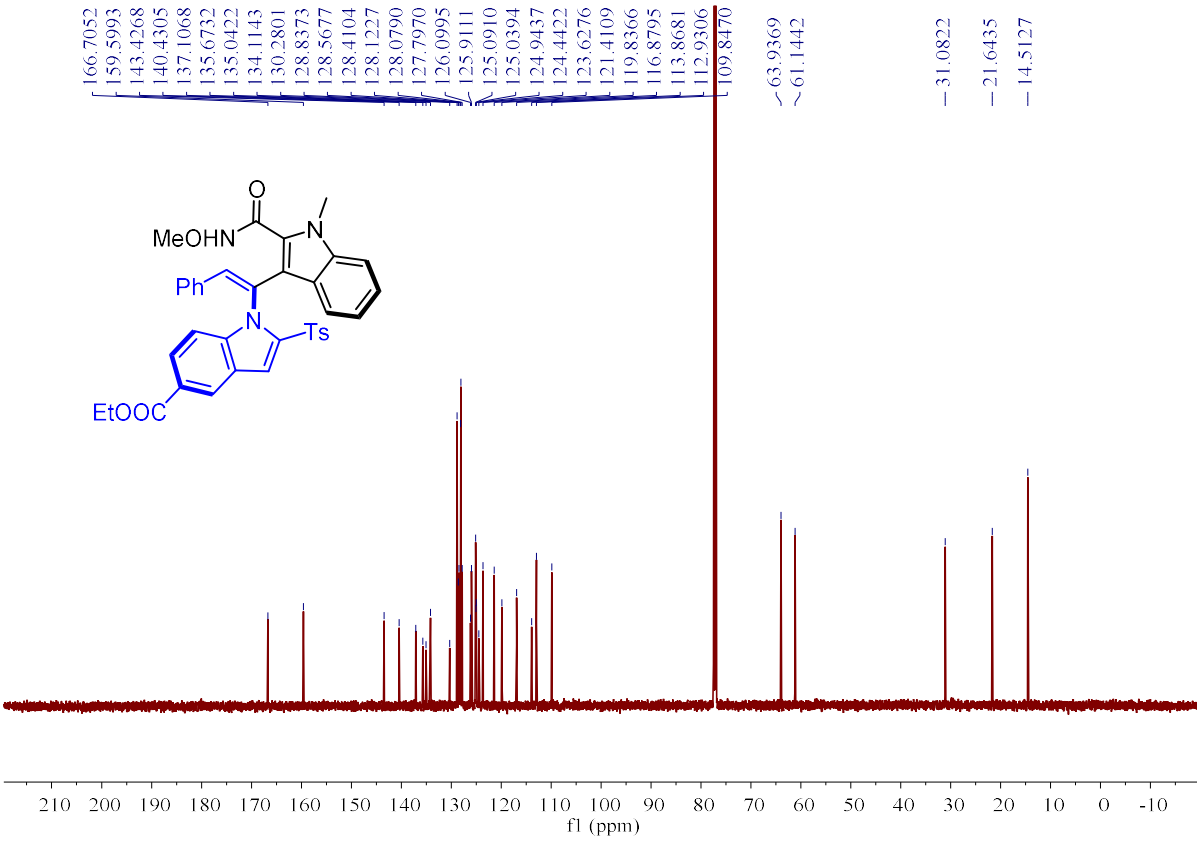

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 43.**



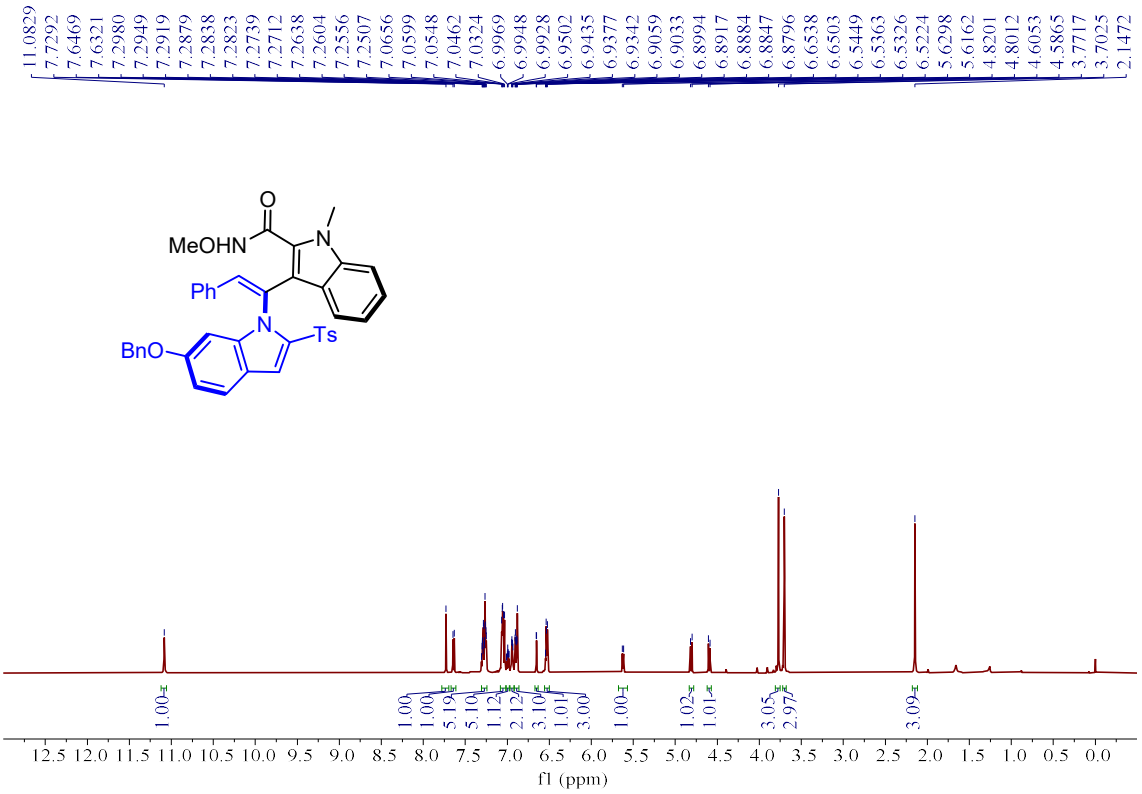

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 43.**



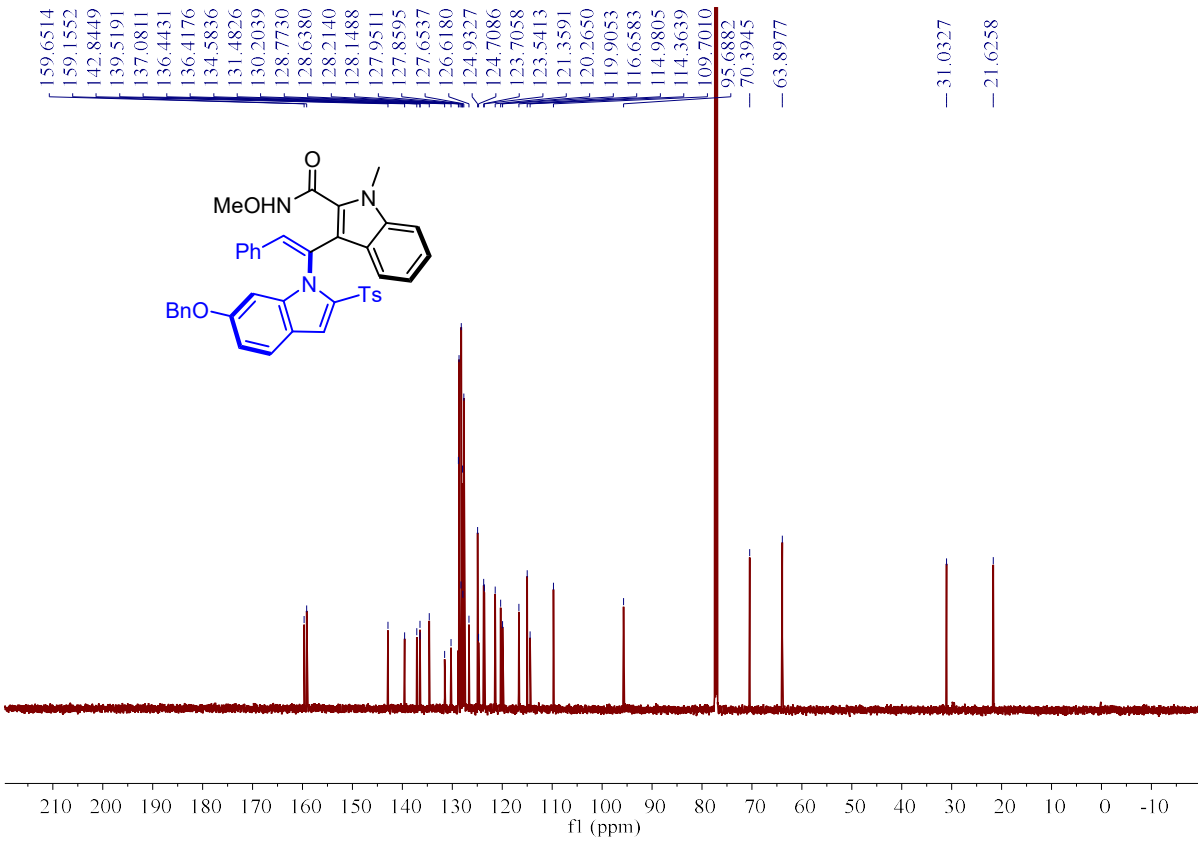

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 44.**



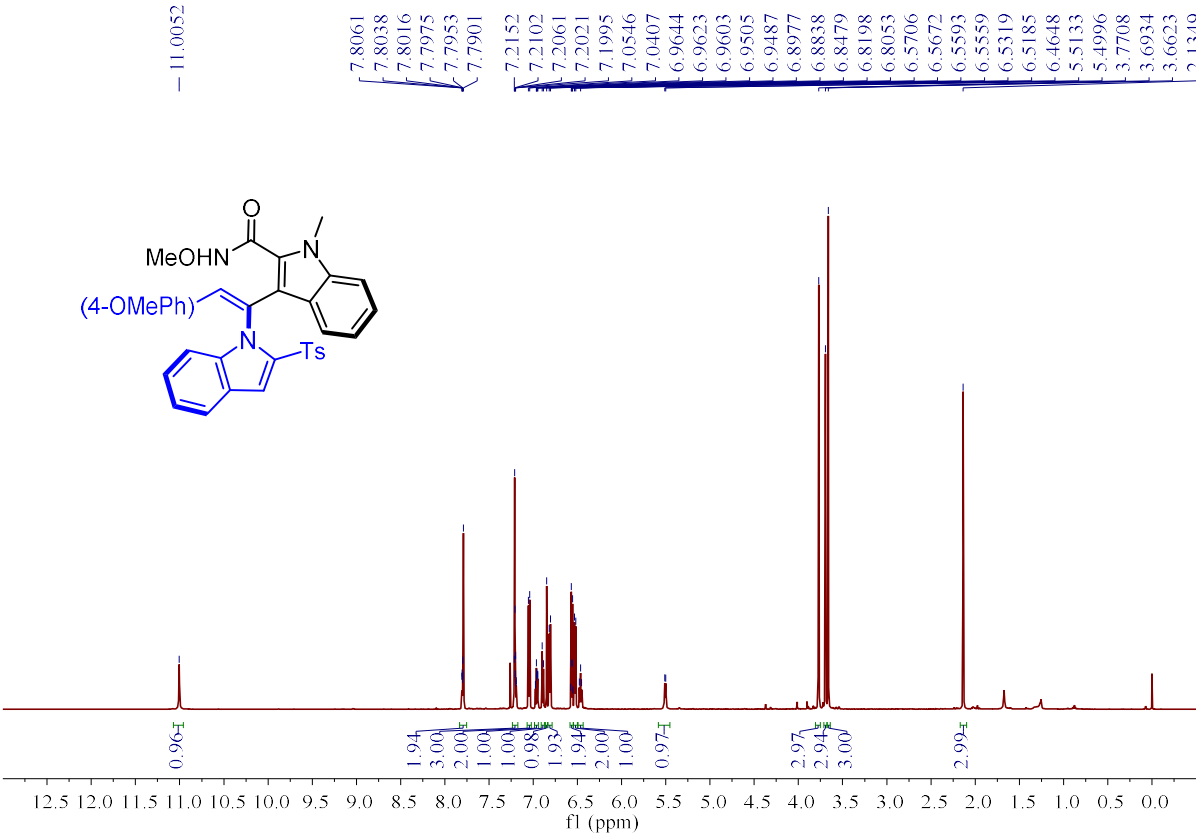

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 44.**



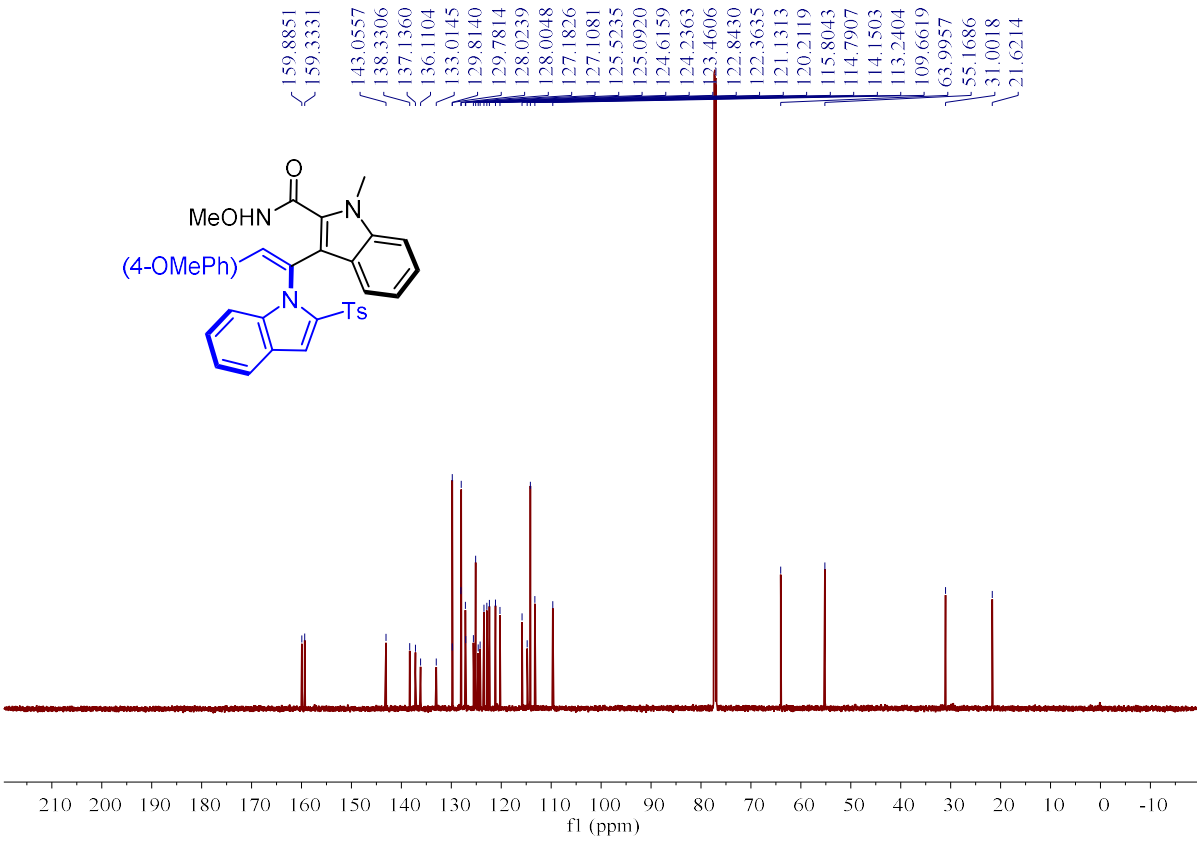

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 45.**



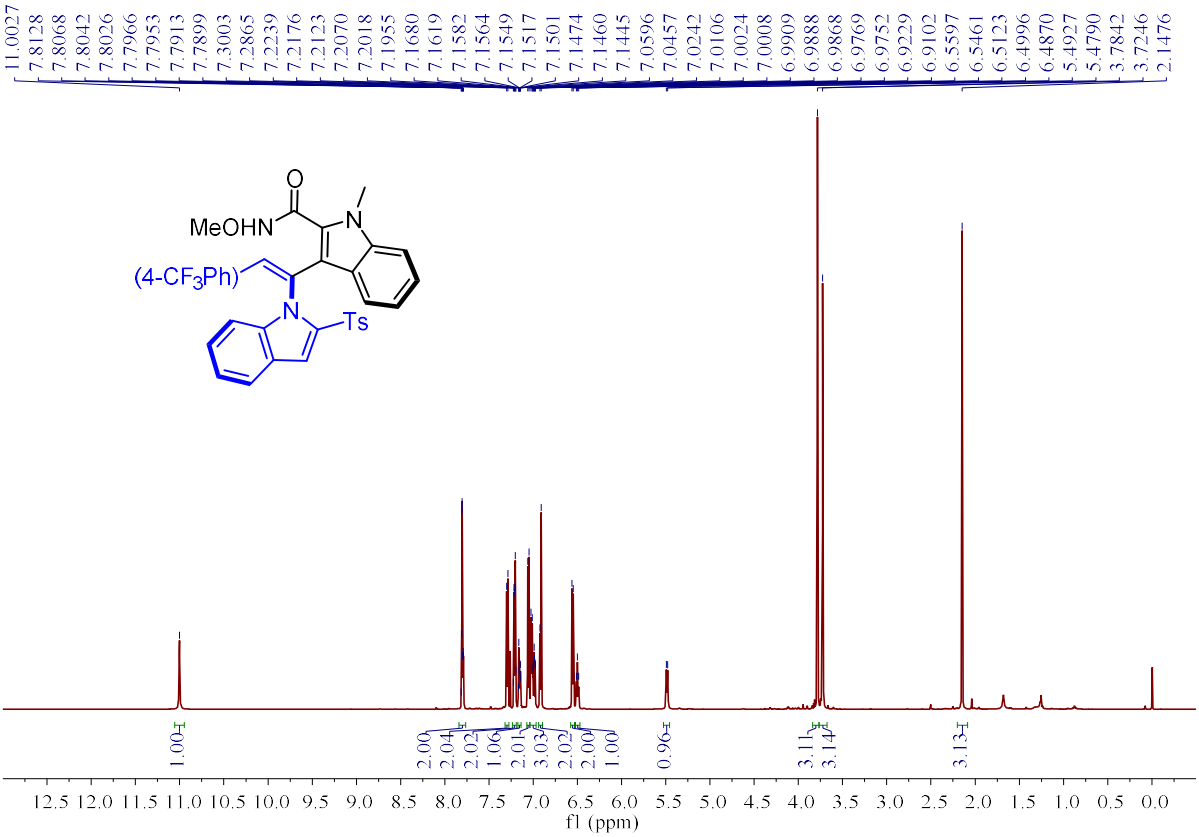

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 45.**



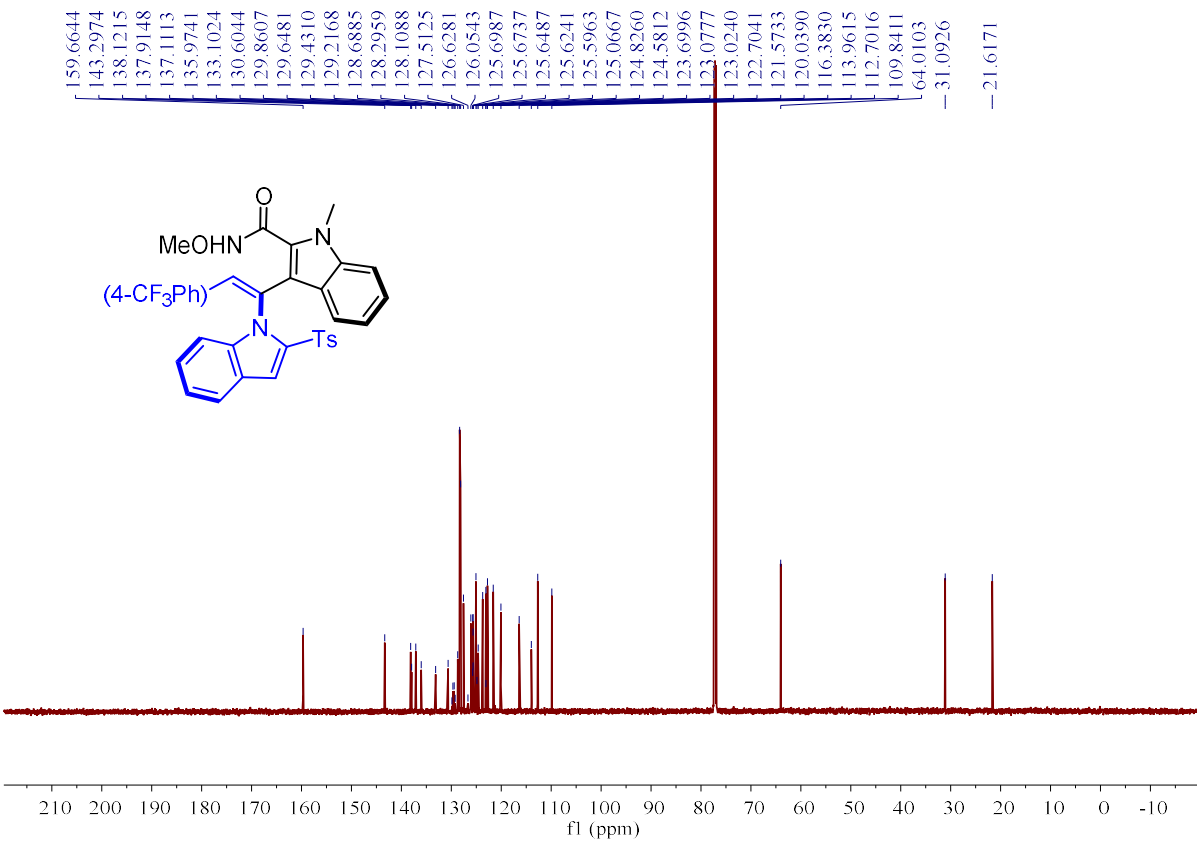

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 46.**



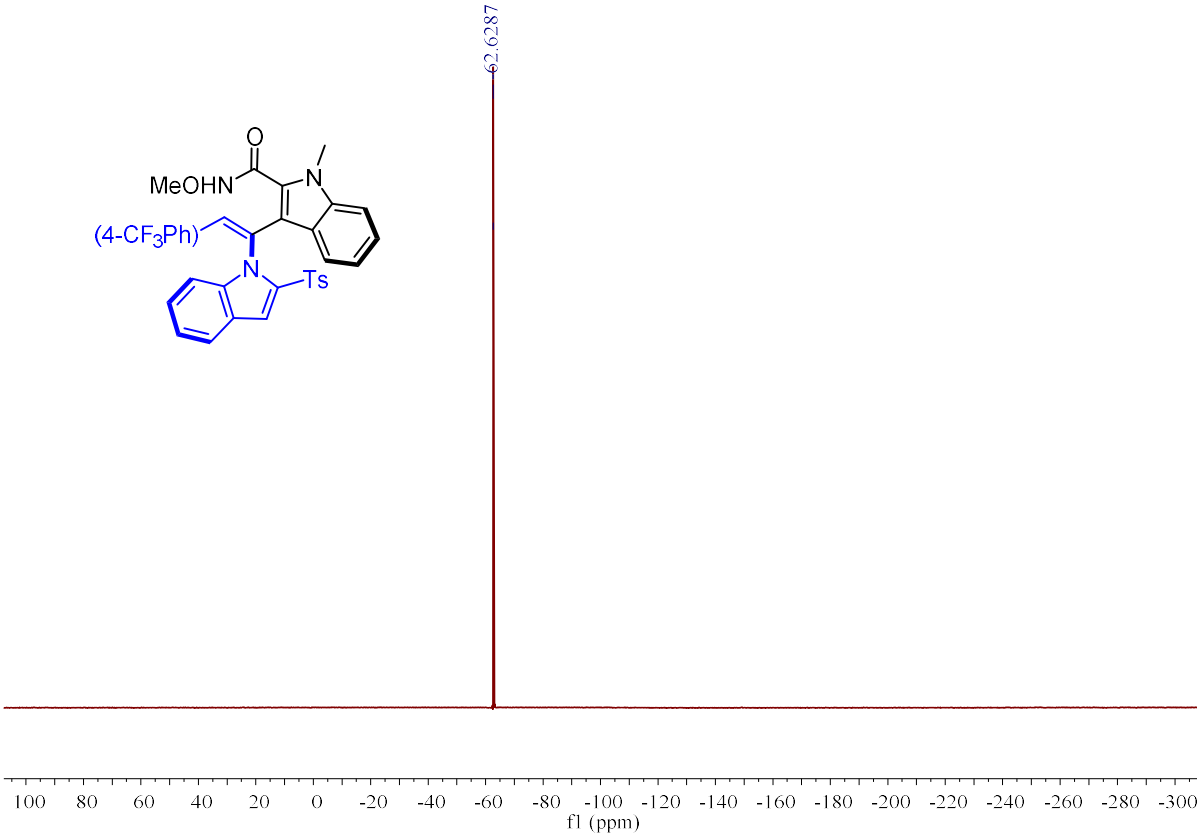

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 46.**



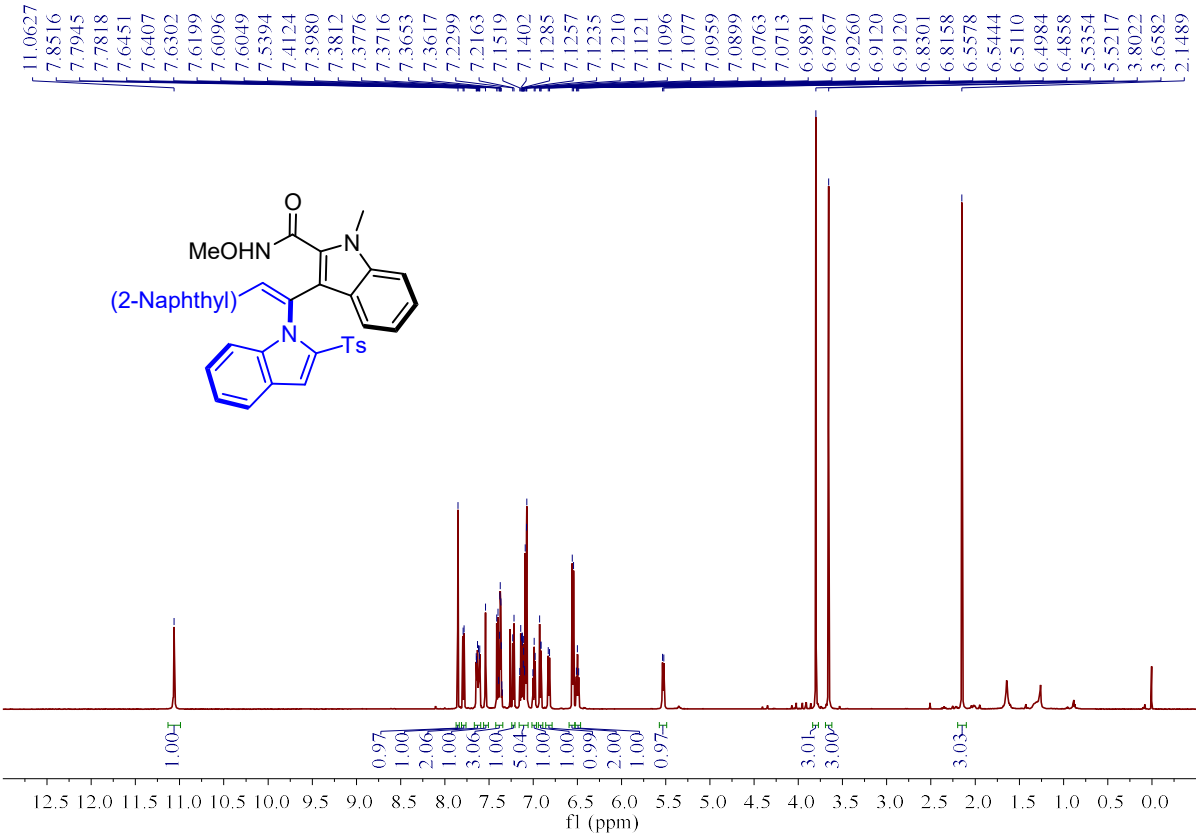

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 47.**



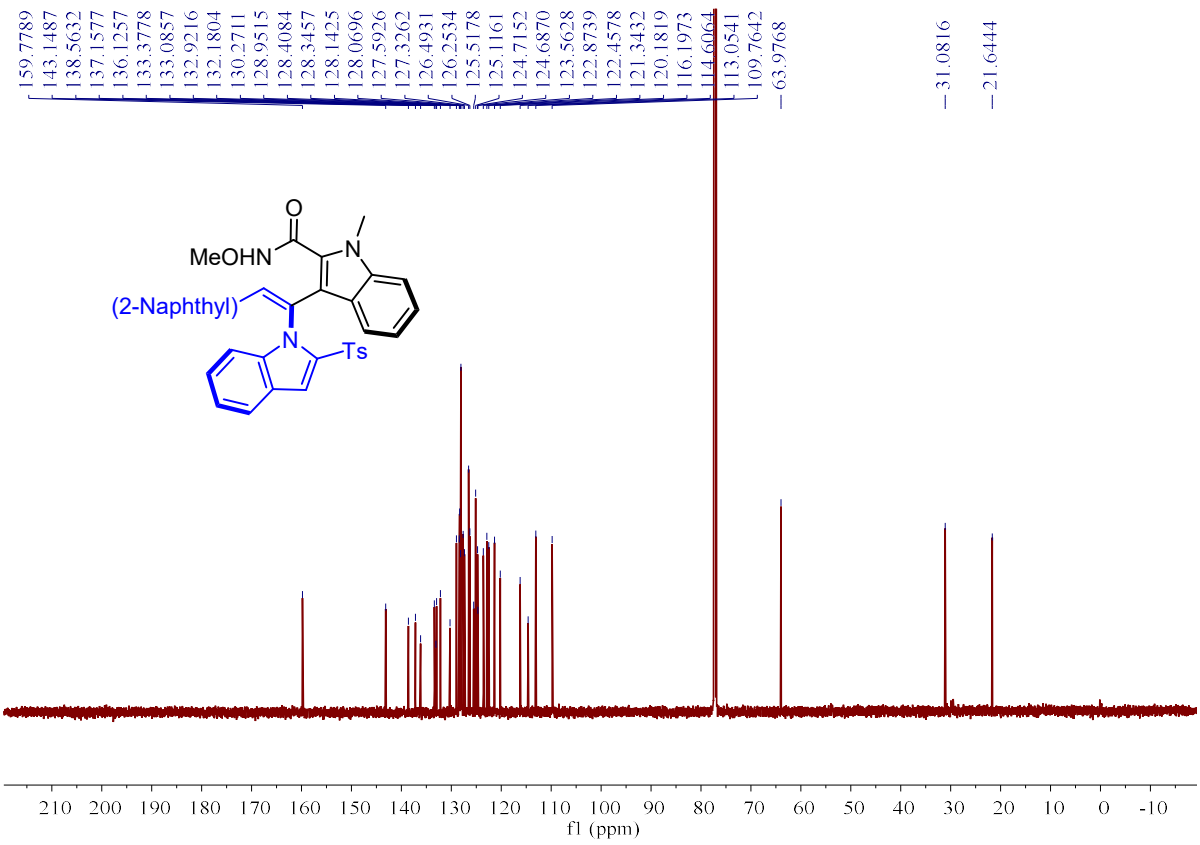

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 47.**



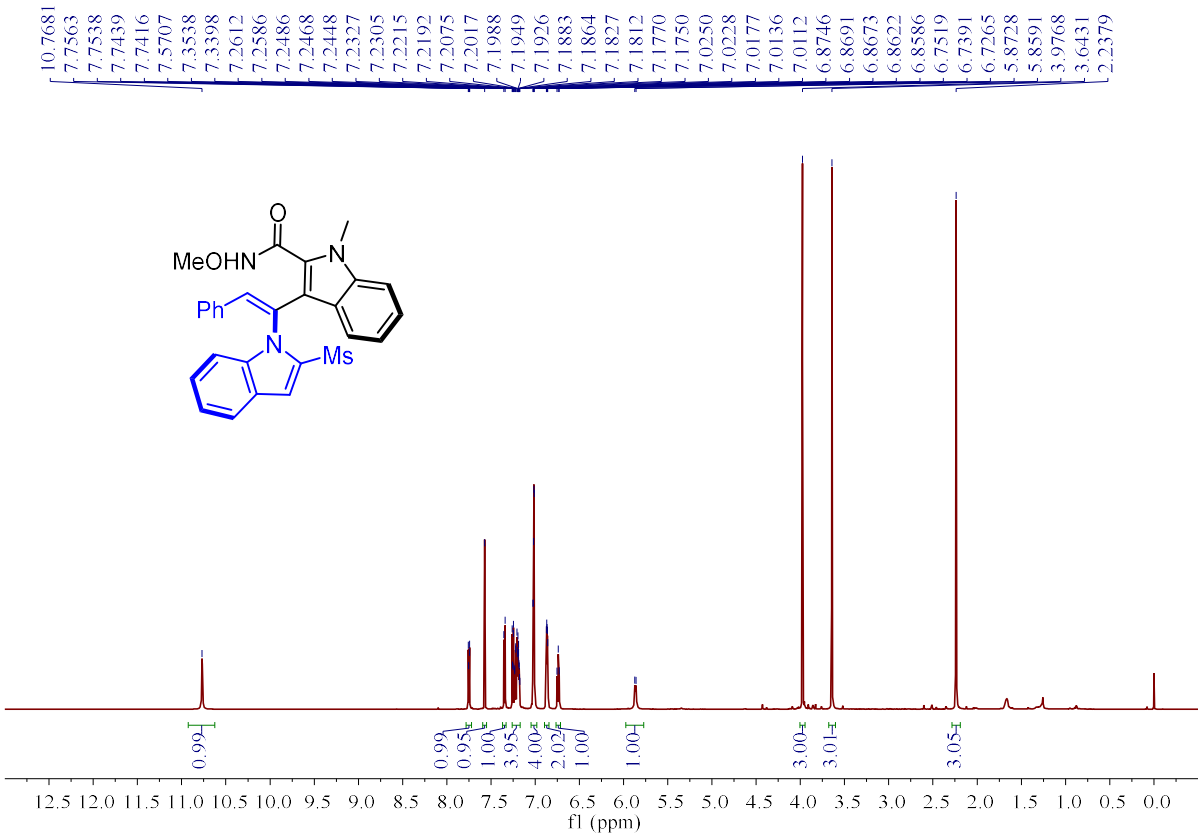

**$^{19}$F NMR (376 MHz, $CDCl_3$) spectrum of 47.**



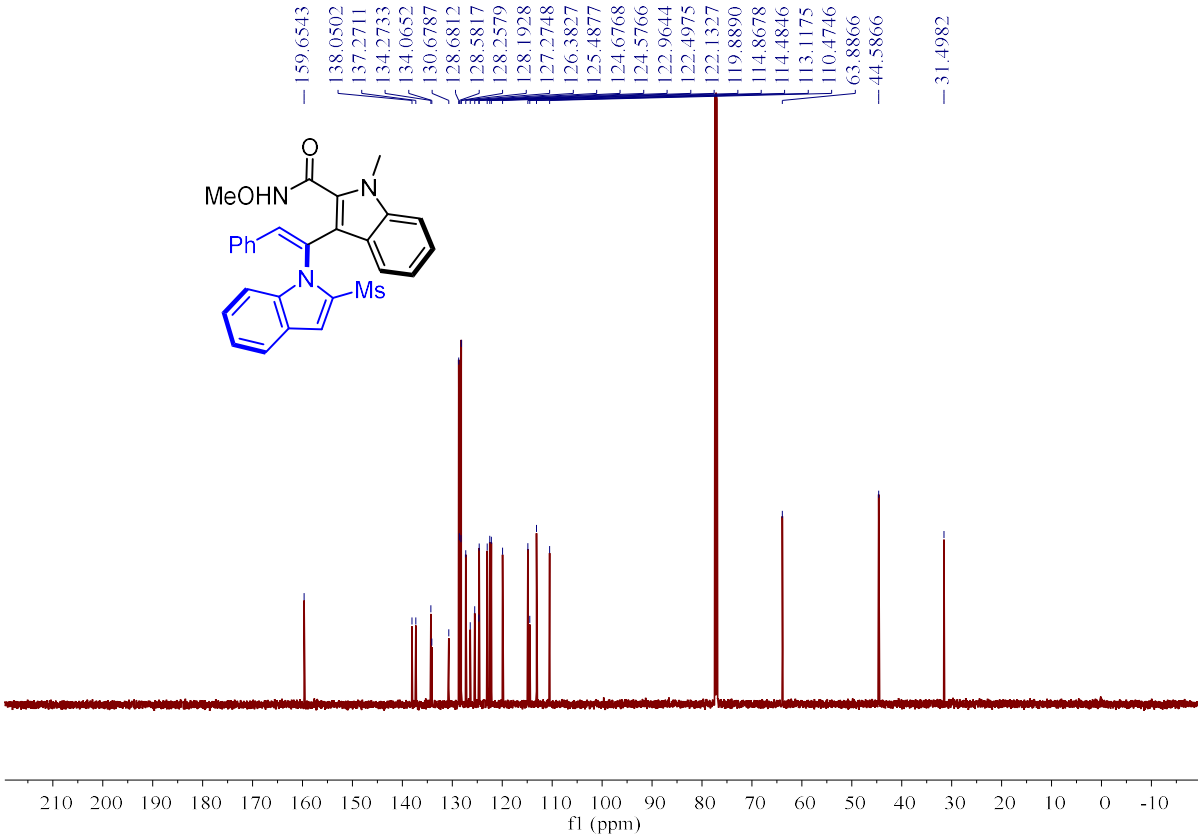

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 48.**



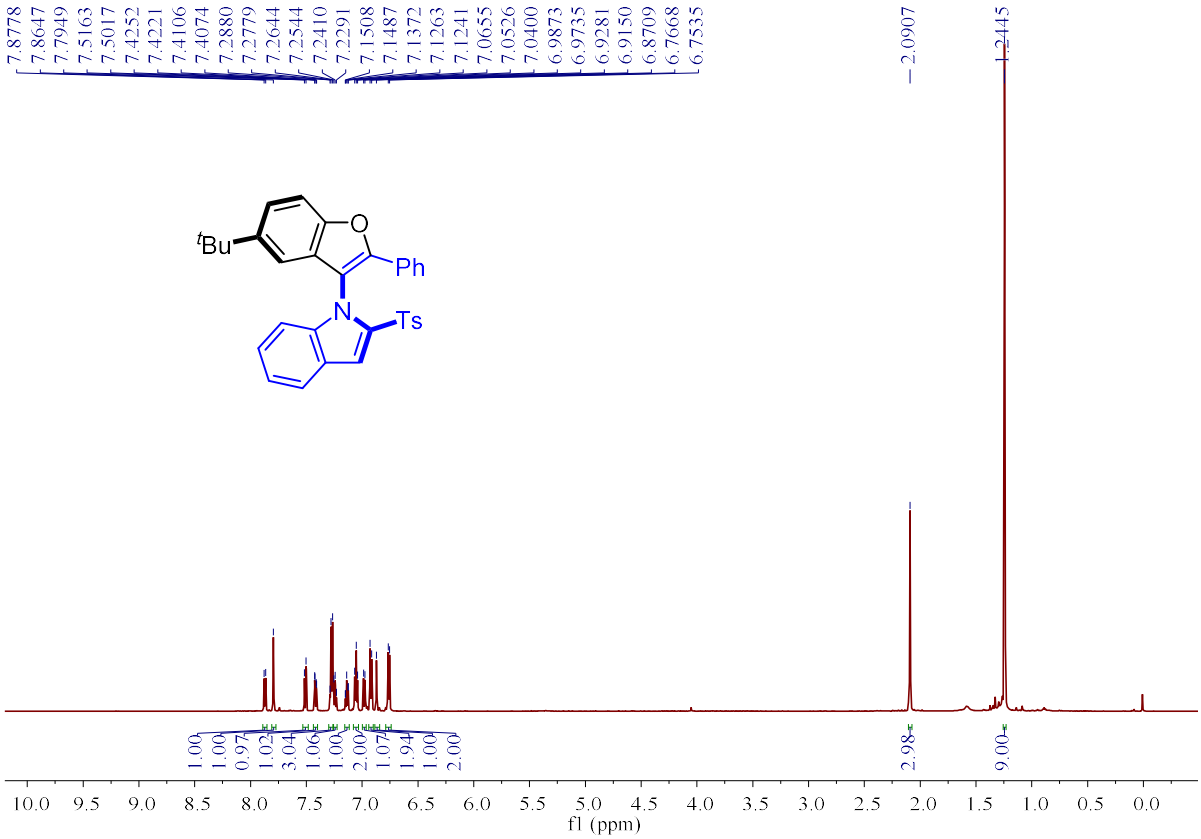

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 48.**



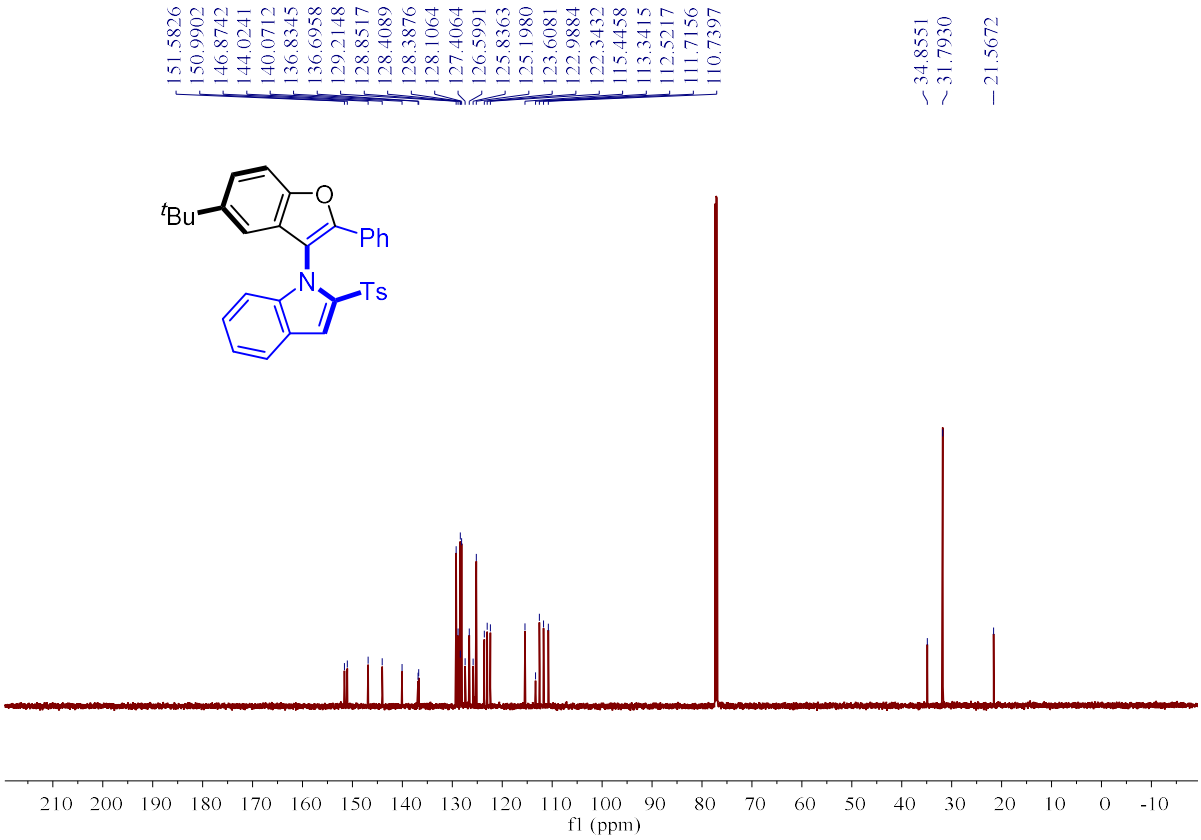

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 49.**



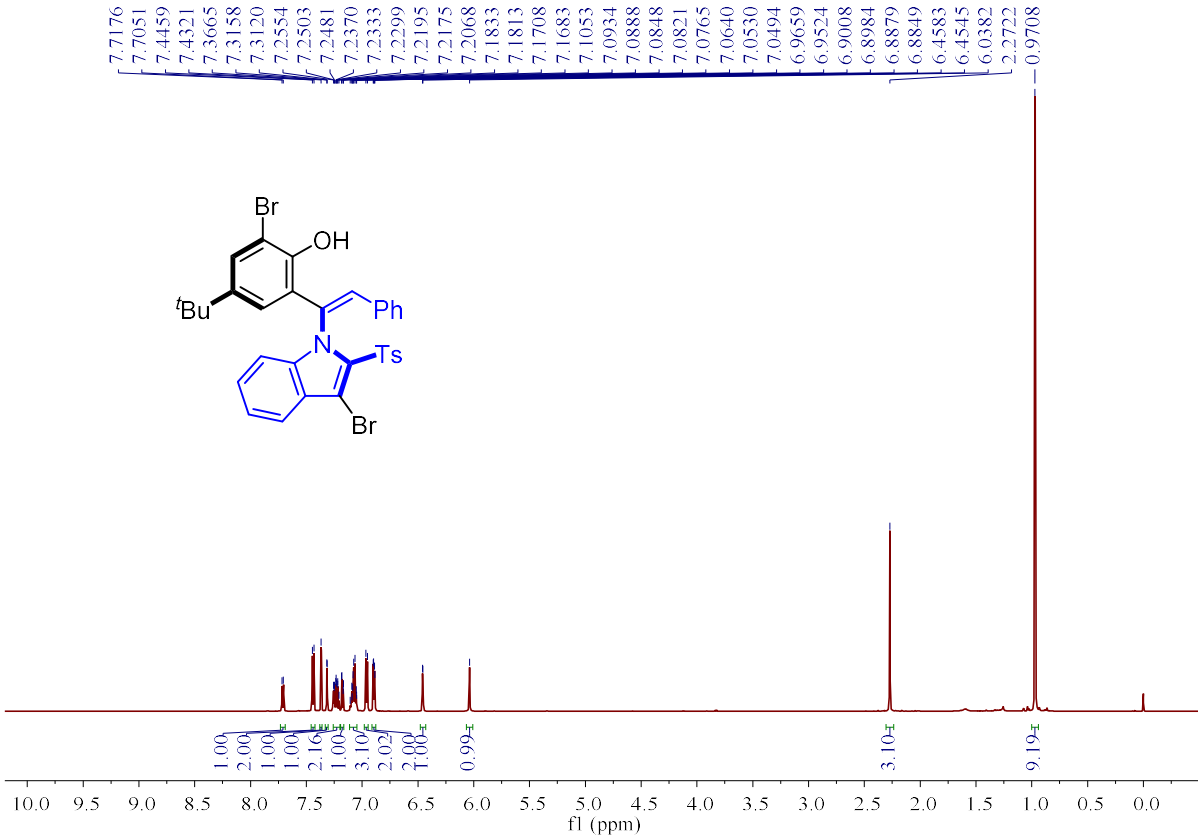

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 49.**



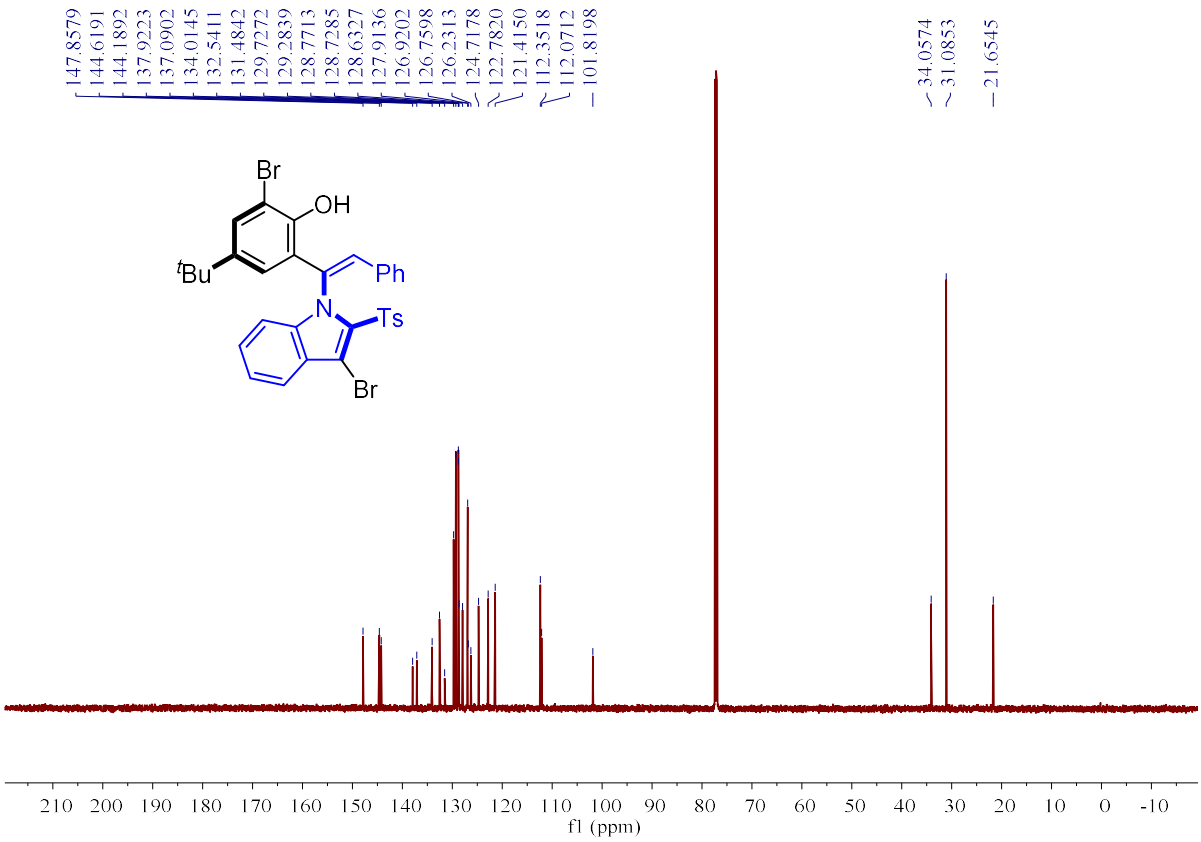

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 50.**



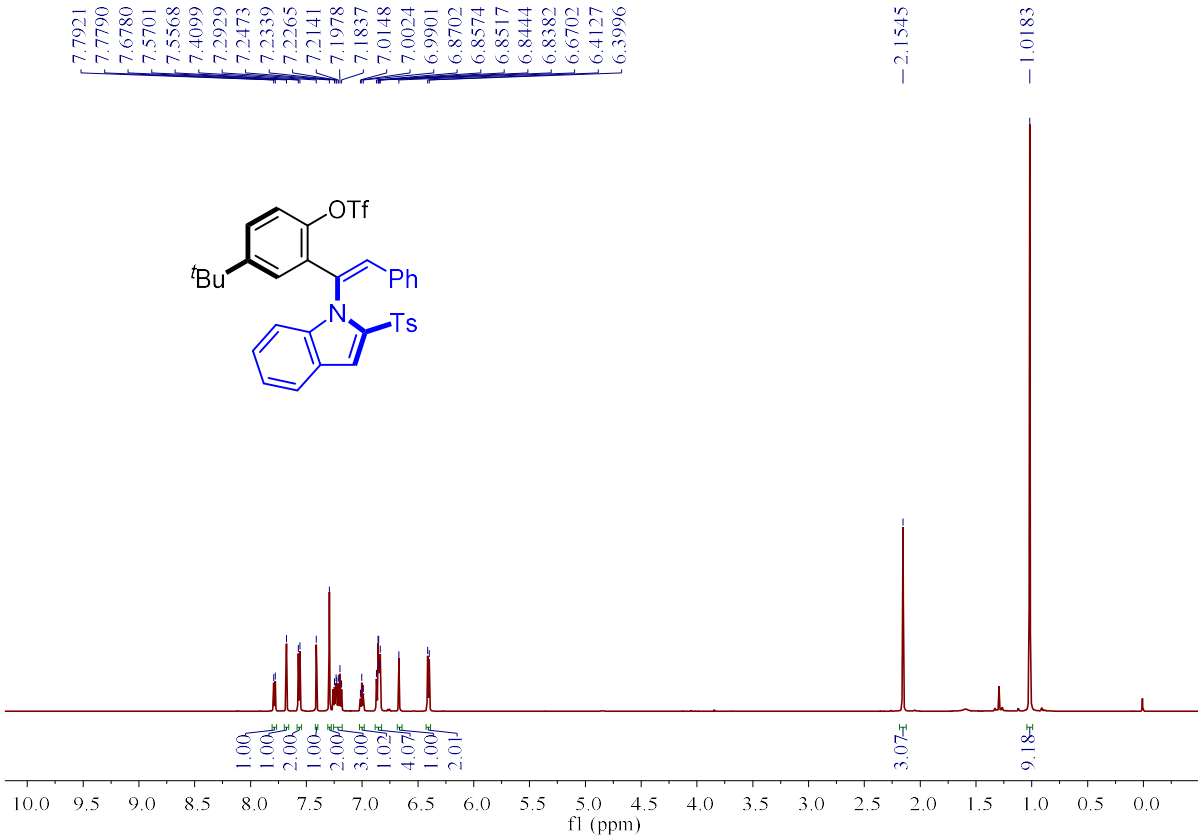

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 50.**



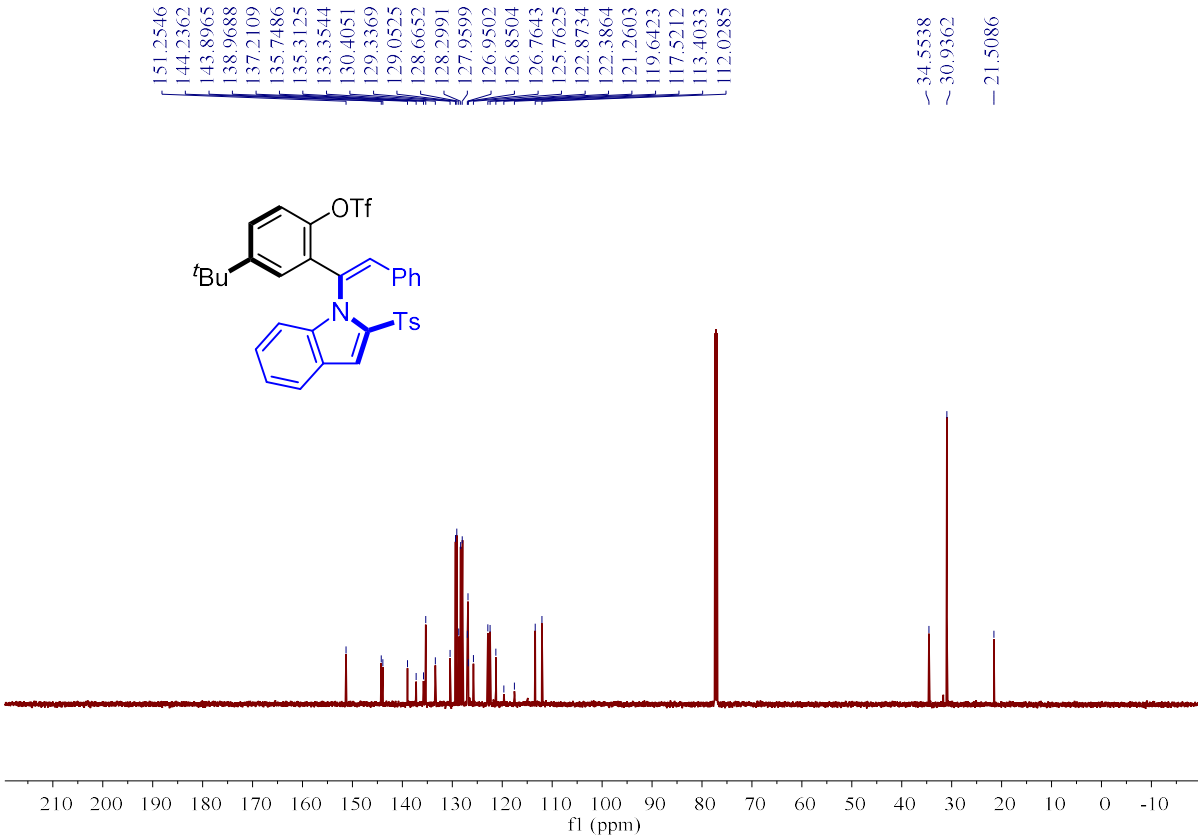

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 51.**



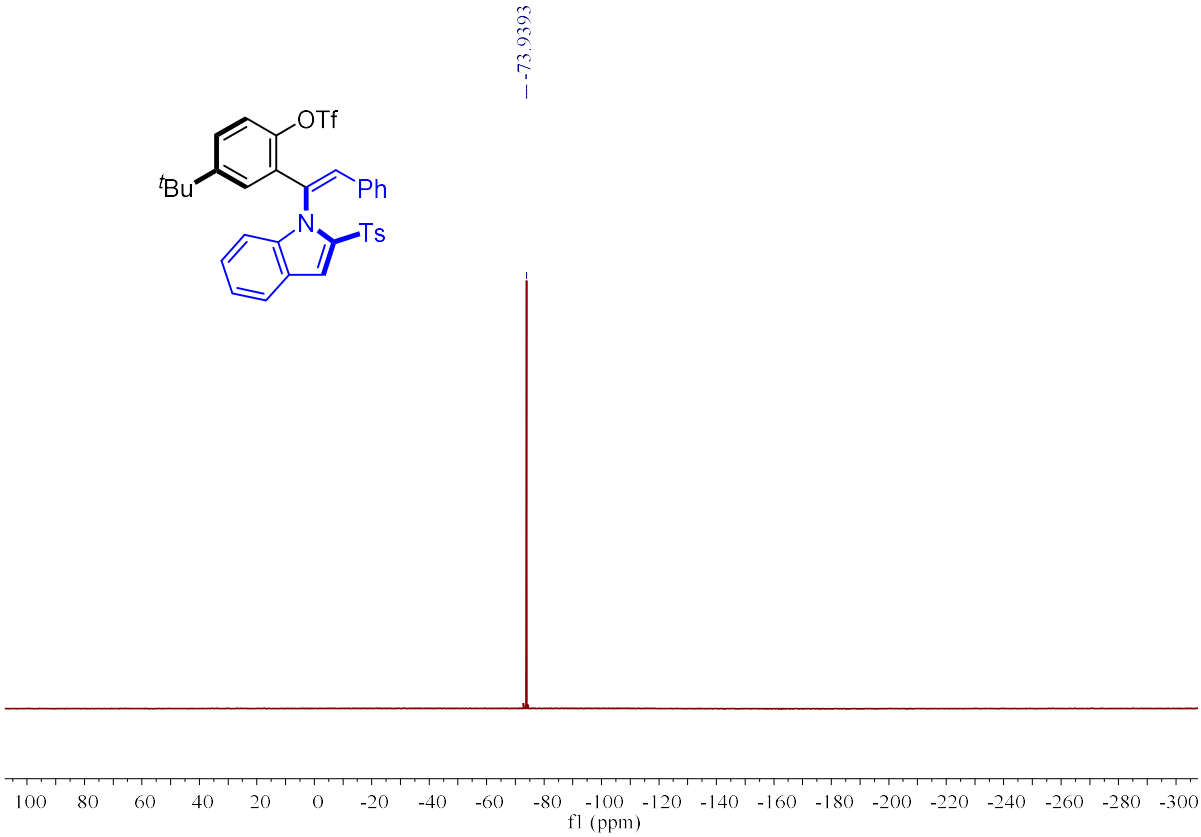

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 51.**



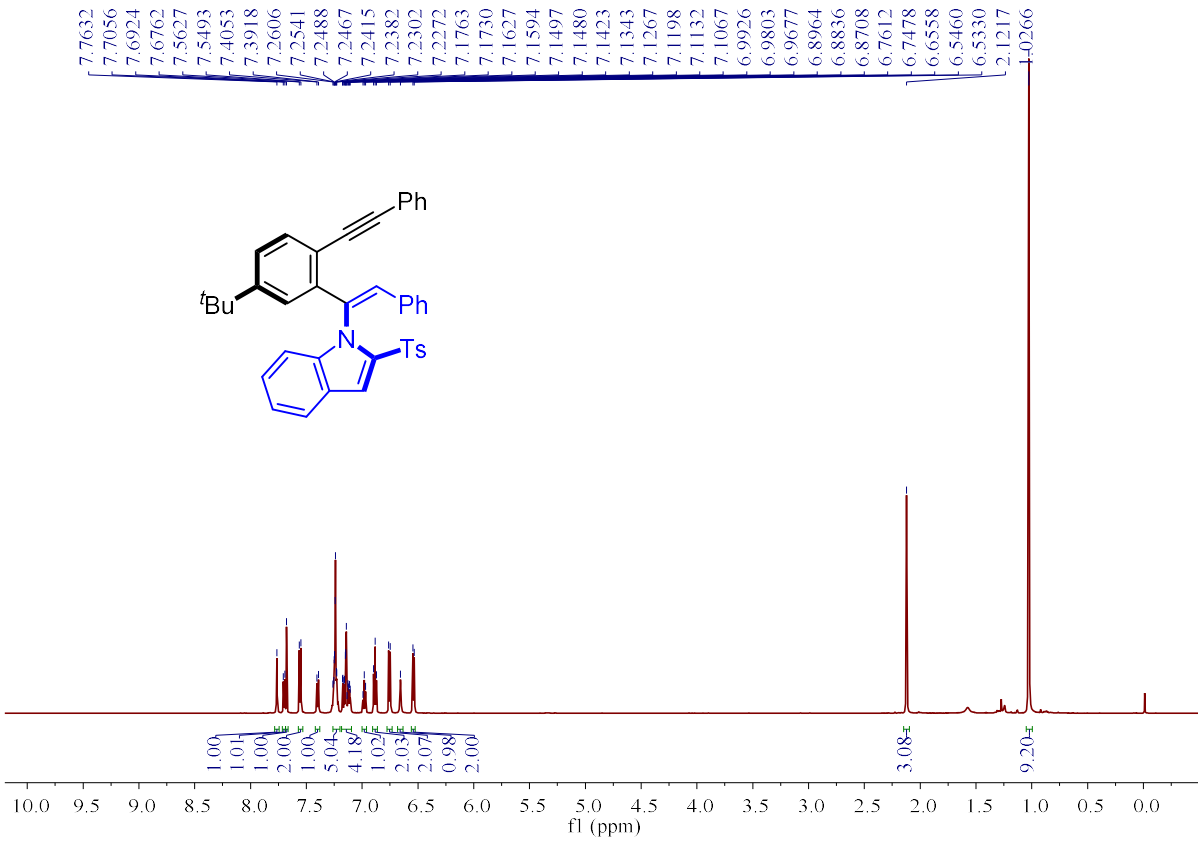

**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 52.**



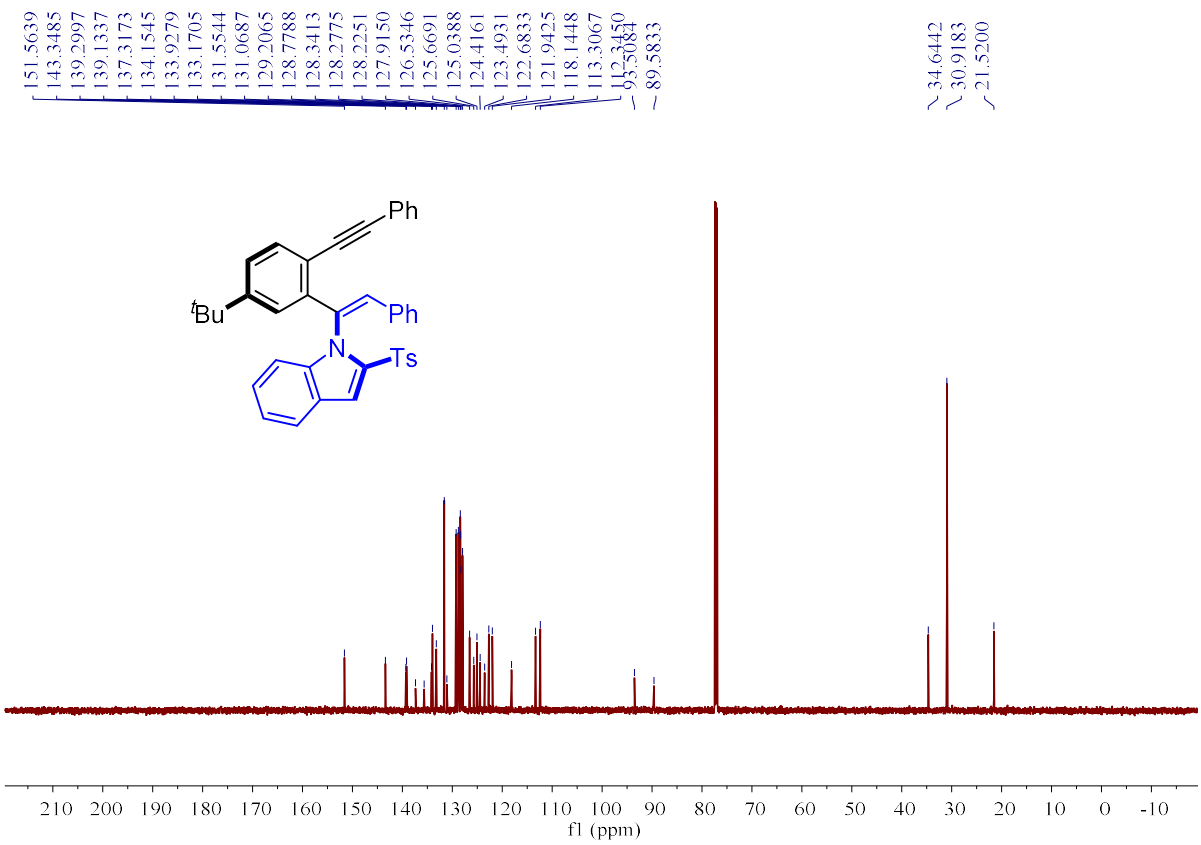

**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 52.**




**$^{19}$F NMR (376 MHz, $CDCl_3$) spectrum of 52.**




**$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of 53.**




**$^{13}$C NMR (150 MHz, $CDCl_3$) spectrum of 53.**