# Supporting Information

## Cooperative $FeCl_3$/DDQ System for the Regioselective Synthesis of 3-Arylindoles from β-Monosubstituted 2-Alkenylanilines

Su San Jang and So Won Youn*

*Center for New Directions in Organic Synthesis, Department of Chemistry and Research Institute for Natural Sciences, Hanyang University, Seoul 133-791, Korea.*

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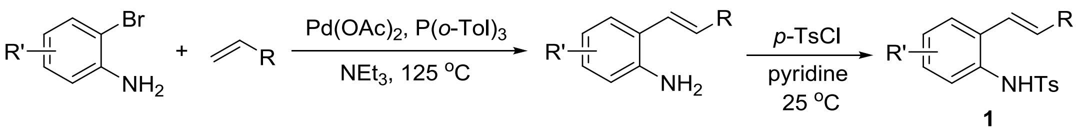
## General Information

Nuclear Magnetic Resonance spectra were recorded on 400 MHz instruments. Spectra were recorded in $CDCl_3$ solution referenced to TMS or solvent residual peak. High Resolution Mass Spectra were measured using EI at 70 eV. GC-MS spectra were recorded with EI ionization and an Elite-1 column (0.25 mm x 30 m, Film: 0.25 μm). For control of the conversion and characterization of the products, the following method was used: The method starts with the injection temperature $T_0$ (50 °C), after holding this temperature for 5 min, the column is heated to the temperature $T_1$ (ramp, 300 °C, 10 °C/min) and hold for additional 10 min. Flash chromatography was performed on silica gel 230-400 mesh. All catalysts were purchased from Sigma-Aldrich or Strem and used as received. Unless otherwise noted, all commercially obtained reagents and solvents were used as received. Anhydrous DMF, toluene, $ClCH_2CH_2Cl$, and dioxane were purchased from Sigma-Aldrich in a SureSeal™ bottle and used as received. THF was distilled from sodium benzophenone ketyl immediately prior to use. *n*-Heptane and MeCN were distilled from $CaH_2$ immediately prior to use. Thin layer chromatograms (TLC) was visualized via UV.

Preparation and spectral data of substrates **1a-h**, **1r-s**, and products **2s**, **3t** are available in our previous report.[1]

## General Procedure for the Preparation of *N*-Ts-2-Alkenylanilines 1

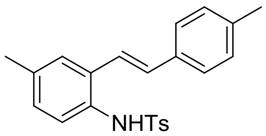



To a solution of 2-bromoaniline (2.7 g, 15.52 mmol, 1 equiv) in $NEt_3$ (15.0 mL, 1.0 M) were added $Pd(OAc)_2$ (34.8 mg, 0.155 mmol, 1 mol%), P(*o*-Tol)$_3$ (398.0 mg, 1.241 mmol, 8 mol%), and olefin (18.62 mmol, 1.2 equiv). After being stirred at 125 °C overnight, the reaction mixture was poured into water and then the product was extracted with $CH_2Cl_2$ (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding 2-styrylaniline product.

To a solution of 2-styrylaniline (1 equiv) in pyridine (0.2 M) was added *p*-toluenesulfonyl chloride (1.1 equiv) at 0 °C. After being stirred at 25 °C for 2 hours, the reaction mixture was poured into water and then the product was extracted with $CH_2Cl_2$ (three times), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give the corresponding product **1**.

[1] (a) Jang, Y. H.; Youn, S. W. *Org. Lett.* **2014**, *16*, 3720. (b) Youn, S. W.; Ko, T. Y.; Jang, M. J.; Jang, S. S. *Adv. Synth. Catal.* **2015**, *357*, 227. (c) Youn, S. W.; Lee, S. R. *Org. Biomol. Chem.* **2015**, *13*, 4652.

**(*E*)-4-Methyl-*N*-(4-methyl-2-(4-methylstyryl)phenyl)benzenesulfonamide (1i)**

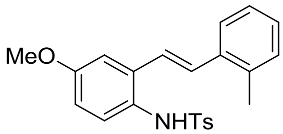



76% (step 1, step 1, using 2-bromo-4-methylaniline), 87% (step 2), a white solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:5 (step 2)), mp 134-135 ℃.

$^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.30 (s, 3H), 2.34 (s, 3H), 2.37 (s, 3H), 6.28 (s, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.1, 21.2, 21.4, 121.7, 126.5, 126.7, 127.1, 127.3, 128.9, 129.2, 129.5, 130.4, 131.4, 133.5, 134.0, 136.5, 137.0, 137.8, 143.7. MS (EI) *m/z* 377 ($M^+$), 222, 207, 191, 178, 165, 152, 130, 115, 103, 91, 77, 65, 53.

Spectral data were consistent with data reported in the literature.[2]

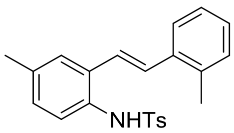
**(*E*)-*N*-(4-Methoxy-2-(2-methylstyryl)phenyl)-4-methylbenzenesulfonamide (1j)**




In step 1, the requisite 2-vinylaniline was prepared from 2-iodo-4-methoxy-1-nitrobenzene following the method reported by Driver and co-workers.[3] In step 2: 79 %, (EtOAc : *n*-Hexane = 1:4), a white solid.

$^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.31 (s, 3H), 2.33 (s, 3H), 3.84 (s, 3H), 6.24 (s, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.80 (dd, *J* = 2.6, 8.6 Hz, 1H), 7.01 (d, *J* = 15.6 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 7.15-7.21 (m, 6H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 19.8, 21.4, 55.4, 111.2, 113.5, 124.1, 125.4, 125.9, 126.0, 127.2, 127.9, 129.3, 129.5, 130.0, 130.3, 135.6, 135.7, 136.1, 136.5, 143.6, 158.7.

**(*E*)-4-Methyl-*N*-(4-methyl-2-(2-methylstyryl)phenyl)benzenesulfonamide (1k)**




63% (step 1, using 2-bromo-4-methylaniline), 77% (step 2), a white solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:5 (step 2)), mp 139-140 ℃.

$^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.32 (s, 3H), 2.348 (s, 3H), 2.352 (s, 3H), 6.43 (br s, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 7.03 (d, *J* = 16.4 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 1H), 7.16-7.22 (m, 3H), 7.17 (d, *J* = 6.8 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 2H), 7.30 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz)

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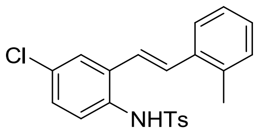
[2] Li, Y.-L.; Li, J.; Ma, A.-L.; Huang, Y.-N.; Deng J. *J. Org. Chem.* **2015**, *80*, 3841.

[3] Shen, M.; Leslie, B. E.; Driver, T. G. *Angew. Chem., Int. Ed.* **2008**, *47*, 5056.

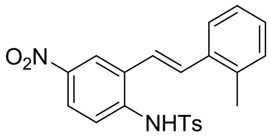
$\delta$ 19.8, 21.1, 21.4, 124.1, 125.4, 126.1, 126.9, 127.16, 127.24, 127.9, 129.2, 129.5, 129.6, 130.3, 130.6, 133.5, 135.7, 135.8, 136.7, 137.0, 143.7. MS (EI) *m*/*z* 377 ($M^+$), 222, 207, 178, 165, 130, 115, 103, 91, 77, 65, 51.

**(*E*)-*N*-(4-Chloro-2-(2-methylstyryl)phenyl)-4-methylbenzenesulfonamide (1l)**



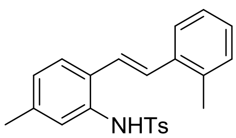

42% (step 1, using 2-bromo-4-chloroaniline), 54% (step 2), a white solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:5 (step 2)), mp 155-156 ℃.
$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.34 (s, 3H), 2.35 (s, 3H), 6.34 (br s, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 7.04 (d, *J* = 16.0 Hz, 1H), 7.16-7.23 (m, 7H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 1.2 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 19.8, 21.4, 122.6, 125.5, 126.2, 126.3, 127.1, 128.17, 128.21, 128.3, 129.7, 130.4, 130.9, 131.7, 132.7, 135.16, 135.20, 136.0, 136.2, 144.1. MS (EI) *m*/*z* 397 ($M^+$), 242, 207, 178, 165, 151, 130, 115, 102, 91, 77, 65, 51.

**(*E*)-4-Methyl-*N*-(2-(2-methylstyryl)-4-nitrophenyl)benzenesulfonamide (1m)**



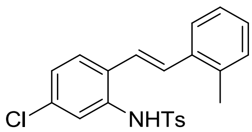

38% (step 1, using 2-bromo-4-nitrolaniline), 32% (step 2), a yellow solid ($Et_2O$ : $CH_2Cl_2$ : *n*-Hexane = 1:3:5 (step 1), EtOAc : *n*-Hexane = 1:6 (step 2)), mp 160-162 ℃.
$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.38 (s, 6H), 6.72 (d, *J* = 16.0 Hz, 1H), 7.12 (s, 1H), 7.18-7.27 (m, 6H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 8.08 (dd, *J* = 2.6, 8.6 Hz, 1H), 8.28 (d, *J* = 2.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 19.9, 21.6, 121.3, 122.0, 122.8, 123.4, 125.6, 126.3, 127.2, 129.0, 130.1, 130.7, 131.2, 134.0, 134.7, 135.9, 136.4, 139.4, 144.8, 144.9.

**(*E*)-4-Methyl-*N*-(5-methyl-2-(2-methylstyryl)phenyl)benzenesulfonamide (1n)**




55% (step 1, using 2-bromo-5-methylaniline), 92% (step 2), a white solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:5 (step 2)), mp 111-112 ℃.
$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.33 (s, 6H), 2.34 (s, 3H), 6.42 (s, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.99 (d, *J* = 16.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.14-7.21 (m, 6H), 7.24 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 19.8, 21.2, 21.4, 123.7, 125.3, 126.1, 126.4, 127.1, 127.2, 127.8, 127.9, 129.1, 129.6, 130.3, 130.4, 133.0, 135.7, 135.8, 136.7, 138.6, 143.8 . MS (EI) *m*/*z* 377 ($M^+$), 222, 207, 178, 165, 130, 115, 103, 91, 77, 65, 51.

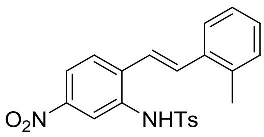
**(*E*)-*N*-(5-Chloro-2-(2-methylstyryl)phenyl)-4-methylbenzenesulfonamide (1o)**




42% (step 1, using 2-iodo-5-chloroaniline), 82% (step 2), a white solid (EtOAc : *n*-Hexane = 1:7 (step 1), 1:5 (step 2)), mp 153-155 ℃.

$^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.33 (s, 6H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.72 (s, 1H), 7.02 (d, *J* = 16.0 Hz, 1H), 7.17-7.24 (m, 6H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 19.8, 21.4, 122.6, 125.4, 125.9, 126.2, 126.9, 127.1, 127.6, 128.2, 129.7, 130.4, 130.5, 131.4, 133.5, 134.2, 135.3, 135.8, 136.2, 144.1. MS (EI) *m*/*z* 397 ($M^+$), 242, 207, 178, 165, 151, 130, 115, 91, 77, 65, 51.

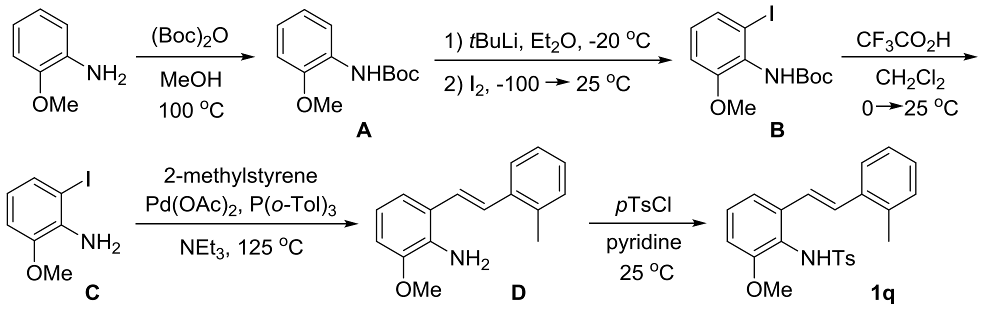
**(*E*)-4-Methyl-*N*-(2-(2-methylstyryl)-5-nitrophenyl)benzenesulfonamide (1p)**




63% (step 1, using 2-bromo-5-nitroaniline), 86% (step 2), a yellow solid (EtOAc : *n*-Hexane = 1:5 (step 1), $CH_2Cl_2$ : *n*-Hexane = 8:1 (step 2)), mp 195-196 ℃.

$^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.35 (s, 3H), 2.38 (s, 3H), 6.81 (d, *J* = 15.6 Hz, 1H), 6.83 (s, 1H), 7.18-7.27 (m, 6H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 8.04 (dd, *J* = 2.0, 8.4 Hz, 1H), 8.20 (d, *J* = 2.0 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 19.8, 21.5, 120.4, 121.3, 121.9, 125.7, 126.4, 127.26, 127.28, 129.1, 130.0, 130.7, 133.9, 134.1, 134.7, 135.9, 136.4, 139.0, 144.7, 147.0.

**(*E*)-*N*-(2-Methoxy-6-(2-methylstyryl)phenyl)-4-methylbenzenesulfonamide (1q)**




To a solution of the 2-methoxyaniline (411.0 mg, 3.337 mmol) in MeOH (10.1 mL, 0.33 M) was added $(Boc)_2O$ (1.0 ml, 4.005 mmol, 1.2 equiv). After being stirred at 100 ℃ for 4 h, the solvent was evaporated. The residue was extracted with $CH_2Cl_2$ (3 times), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:10) to give the corresponding product **A** (735.2 mg, 99 %) as a colorless liquid.[4]

[4] Kondo, Y.; Kojima, S.; Sakamoto, T. *J. Org. Chem.* **1997**, *62*, 6507.

To a solution of **A** (663.6 mg, 2.972 mmol, 1 equiv) in dry $Et_2O$ (3.6 mL, 0.83 M) was added *t*BuLi (1.7 M solution in pentane, 3.8 ml, 6.539 mmol, 2.2 equiv) under an argon atmosphere at -20 °C. After 3 h, $I_2$ (313.0 mg, 2.467 mmol, 0.83 equiv) in dry $Et_2O$ (8.3 mL, 0.36 M) was added at -100 °C. The reaction mixture was slowly warmed up to room temperature and stirred for 12 h. After addition of sat. aq. $Na_2S_2O_3$ solution (12 mL), the reaction mixture was extracted with $Et_2O$ (3 times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:7) to give the corresponding product **B** (435.1 mg, 42 %) as a yellow solid.[4]

To a solution of **B** (223.6 mg, 0.640 mmol, 1 equiv) in $CH_2Cl_2$ (1.3 mL, 0.5 M) was added $CF_3CO_2H$ (0.3 mL, 3.906 mmol, 6.1 equiv) at 0 °C. After being stirred at room temperature for 1.5 h, the volatiles were removed by evaporation and the residue was treated with sat. aq. $NaHCO_3$. The mixture was extracted with $Et_2O$ (3 times) and the combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:10) to give the corresponding product **C** (145.9 mg, 92 %) as a yellow liquid.[5]

To a solution of **C** (145.9 mg, 0.586 mmol, 1 equiv) in $NEt_3$ (0.6 mL, 1.0 M) were added $Pd(OAc)_2$ (1.3 mg, 0.006 mmol, 1 mol%), P(*o*-Tol)$_3$ (15.0 mg, 0.047 mmol, 8 mol%), and 2-methylstyrene (96 μL, 0.733 mmol, 1.2 equiv). After being stirred at 125 °C for 16.5 h, the reaction mixture was poured into water and then the product was extracted with $CH_2Cl_2$ (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:7) to give the corresponding product **D** (79.9 mg, 57 %) as a brown solid.

To a solution of **D** (79.0 mg, 0.330 mmol, 1 equiv) in pyridine (1.7 mL, 0.2 M) was added *p*-TsCl (89.9 mg, 0.462 mmol, 1.4 equiv) at 0 °C. After being stirred at 25 °C for 15 hours, the reaction mixture was poured into water and then the product was extracted with $CH_2Cl_2$ (three times), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:3) to give the corresponding product **1q** (93%, 120.6 mg, mp 112-113 °C) as a white solid.

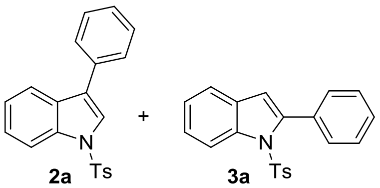
$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.32 (s, 3H), 2.44 (s, 3H), 3.31 (s, 3H), 6.36 (s, 1H), 6.57 (d, $J$ = 7.6 Hz, 1H), 7.13 (d, $J$ = 8.0 Hz, 2H), 7.17-7.22 (m, 4H), 7.32 (d, $J$ = 16.4 Hz, 1H), 7.39 (d, $J$ = 8.0 Hz, 1H), 7.54 (d, $J$ = 8.0 Hz, 2H), 7.58 (d, $J$ = 16.4 Hz, 1H), 7.64 (d, $J$ = 7.2 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 19.9, 21.4, 55.0, 109.0, 117.8, 122.5, 126.1, 126.2, 126.3, 127.46, 127.51, 127.6, 128.0, 128.8, 130.1, 135.6, 136.4, 136.5, 137.4, 143.3, 154.4. MS (EI) *m/z* 393 ($M^+$), 238, 223, 207, 194, 180, 165, 152, 132, 115, 104, 91, 77, 65, 51.

[5] Lautens, M.; Tayama, E.; Herse, C. *J. Am. Chem. Soc*. **2005**, *127*, 72.

## General Procedure for the Fe(III)-Catalyzed Regioselective Synthesis of 3-Arylindoles from β-Monosubstituted 2-Alkenylanilines

To a solution of **1** (0.05~0.1 mmol, 1 equiv) in $ClCH_2CH_2Cl$ (1~2 mL, 0.05 M) in pressure tube were added $FeCl_3 \cdot 6H_2O$ (5~25 mol %) and DDQ (0.1~0.2 mmol, 2 equiv). The resulting mixture was stirred at 80 °C for the reported time under Ar atmosphere. After the reaction was completed, the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding product **2**/**3**. All reactions were carried out 3-5 times repetitively and the average values of both yields and ratios are given.

### *N*-Ts-3-Phenylindole (2a) & *N*-Ts-2-Phenylindole (3a)



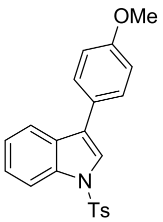

75% (**2a**:**3a** = 8:1), a white solid (EtOAc : *n*-Hexane = 1:5).

Signals corresponding to **2a**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.34 (s, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.70 (s, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.5, 113.8, 120.4, 122.9, 123.5, 123.9, 124.9, 126.9, 127.51, 127.9, 128.9, 129.3, 129.9, 133.0, 135.2, 135.5, 145.0. MS (EI) *m*/*z* 347 ($M^+$), 267, 192, 165, 139, 115, 91, 77, 65, 51.

Representative signals corresponding to **3a**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.28 (s, 3H), 6.55 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.5, 113.6, 116.6, 120.7, 124.3, 124.7, 126.8, 127.46, 128.6, 129.2, 130.3, 130.5, 132.4, 134.6, 138.2, 142.1, 144.5.

Spectral data of **2a** and **3a** were consistent with data reported in the literature.[1]

### *N*-Ts-3-(4-Methoxyphenyl)indole (2b)

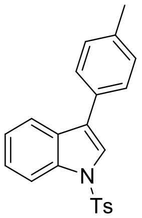



32%, a white solid (EtOAc : *n*-Hexane = 1:5), mp 111-114 ℃.

$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.34 (s, 3H), 3.87 (s, 3H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.63 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.6, 55.3, 113.8, 114.3, 120.4, 122.3, 123.4, 123.7, 124.8, 125.4, 126.8, 129.0, 129.5, 129.9, 135.2, 135.5, 144.9, 159.1.

Spectral data were consistent with data reported in the literature.[1-2]

**$N$-Ts-3-$p$-Tolylindole (2c)**

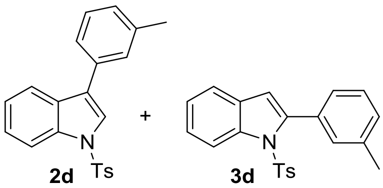


57%, a white solid (EtOAc : $n$-Hexane = 1:5), mp 93-95 °C.

$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.33 (s, 3H), 2.41 (s, 3H), 7.22 (d, $J$ = 8.0 Hz, 2H), 7.25-7.28 (m, 3H), 7.35 (t, $J$ = 7.8 Hz, 1H), 7.50 (d, $J$ = 7.6 Hz, 2H), 7.66 (s, 1H), 7.76 (d, $J$ = 8.4 Hz, 1H), 7.80 (d, $J$ = 8.0 Hz, 2H), 8.05 (d, $J$ = 8.0 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.2, 21.5, 113.8, 120.4, 122.6, 123.4, 123.9, 124.8, 126.8, 127.7, 129.4, 129.6, 129.9, 130.1, 135.2, 135.5, 137.3, 144.9. MS (EI) $m/z$ 361 ($M^+$), 206, 178, 164, 152, 139, 115, 103, 91, 77, 65, 51.

Spectral data were consistent with data reported in the literature.[1c, 2]

**$N$-Ts-3-$m$-Tolylindole (2d) & $N$-Ts-2-$m$-Tolylindole (3d)**




**2d** **3d**

74% (**2d**:**3d** = 8:1), a white solid (EtOAc : $n$-Hexane = 1:5).

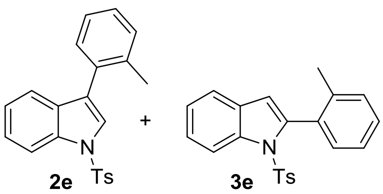
Signals corresponding to **2d**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.34 (s, 3H), 2.43 (s, 3H), 7.19 (d, $J$ = 7.6 Hz, 1H), 7.23 (d, $J$ = 8.4 Hz, 2H), 7.29 (t, $J$ = 8.0 Hz, 1H), 7.35-7.38 (m, 2H), 7.39 (d, $J$ = 7.2 Hz, 1H), 7.43 (s, 1H), 7.69 (s, 1H), 7.79 (d, $J$ = 8.0 Hz, 1H), 7.81 (d, $J$ = 8.4 Hz, 2H), 8.06 (d, $J$ = 8.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.5, 21.6, 113.8, 120.5, 122.9, 123.5, 124.0, 124.8, 124.9, 126.9, 128.3, 128.5, 128.8, 129.3, 129.9, 132.9, 135.1, 135.5, 138.6, 145.0.

Representative signals corresponding to **3d**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.29 (s, 3H), 2.43 (s, 3H), 6.53 (s, 1H), 7.05 (d, $J$ = 8.0 Hz, 2H), 8.31 (d, $J$ = 8.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.4, 113.4, 116.6, 120.6, 124.2, 124.6, 126.8, 127.4, 129.1, 129.4, 131.0, 137.0.

HRMS (EI) $[M]^+$ $m/z$ calcd for $C_{22}H_{19}NO_2S$ 361.1136, found 361.1139.

Spectral data of **2d**[1c] and **3d**[1] were consistent with data reported in the literature.

**$N$-Ts-3-$o$-Tolylindole (2e) & $N$-Ts-2-$o$-Tolylindole (3e)**



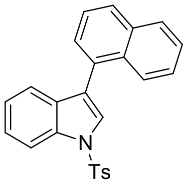

**2e** **3e**

97% (**2e**:**3e** = 8:1), a pale yellow oil (EtOAc : $n$-Hexane = 1:5).

Signals corresponding to **2e**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.21 (s, 3H), 2.34 (s, 3H), 7.20-7.35 (m,

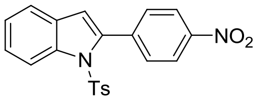
9H), 7.53 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.4, 21.6, 113.7, 120.7, 123.3, 123.4, 124.0, 124.7, 125.7, 126.8, 127.9, 129.8, 130.4, 130.5, 130.7, 131.9, 134.9, 135.1, 136.8, 144.9.
Representative signals corresponding to **3e**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.21 (s, 3H), 2.31 (s, 3H), 6.46 (s, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.5, 112.3, 115.7, 123.8, 124.5, 124.6, 126.9, 129.1, 129.3, 129.6, 130.8, 139.3, 144.6.
HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{19}NO_2S$ 361.1136, found 361.1137.
Spectral data of **2e**[1c] and **3e**[1] were consistent with data reported in the literature.

**N-Ts-3-(1-Naphthyl)indole (2f)**



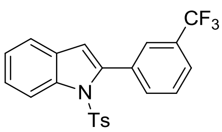

59%, a white solid (EtOAc : *n*-Hexane = 1:5), mp 38-43 ℃.
$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.38 (s, 3H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.49-7.56 (m, 3H), 7.73 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.6, 113.8, 121.0, 122.6, 123.4, 124.8, 124.9, 125.4, 125.9, 126.0, 126.1, 126.9, 127.8, 128.4, 129.9, 130.3, 131.1, 132.1, 133.8, 135.0, 135.2, 145.0 (1 carbon is missing due to overlapping). HRMS (EI) $[M]^+$ *m/z* calcd for $C_{25}H_{19}NO_2S$ 397.1136, found 397.1135.

**N-Ts-2-(4-Nitrophenyl)indole (3g)**




84%, a yellow solid (EtOAc : *n*-Hexane = 1:6), mp 170-172 ℃.
$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.29 (s, 3H), 6.69 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.5, 116.1, 116.8, 121.2, 122.9, 124.8, 125.9, 126.6, 129.4, 130.3, 130.7, 133.9, 138.8, 138.9, 139.6, 145.0, 147.6. MS (EI) *m/z* 392 ($M^+$), 253, 237, 190, 178, 164, 155, 140, 91, 65.
Spectral data were consistent with data reported in the literature.[1]

**N-Ts-2-(3-(Trifluoromethyl)phenyl)indole (3h)**

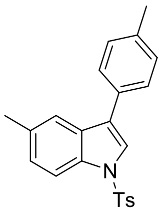


92%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 57-60 °C.

$^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.30 (s, 3H), 6.61 (s, 1H), 7.05 (d, $J$ = 8.4 Hz, 2H), 7.23 (d, $J$ = 8.0 Hz, 2H), 7.30 (t, $J$ = 7.6 Hz, 1H), 7.41 (t, $J$ = 7.6 Hz, 1H), 7.48 (d, $J$ = 8.0 Hz, 1H), 7.57 (t, $J$ = 7.8 Hz, 1H), 7.62 (s, 1H), 7.70 (d, $J$ = 7.8 Hz, 1H), 7.77 (d, $J$ = 8.0 Hz, 1H), 8.33 (d, $J$ = 8.6 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.5, 114.4, 116.6, 121.0, 124.0 (q, $J$ = 270.9 Hz), 124.5, 125.2 (q, $J$ = 3.8 Hz), 125.3, 126.6, 126.7 (q, $J$ = 3.8 Hz), 128.0, 129.4, 130.0 (q, $J$ = 32.1 Hz), 130.2, 133.1, 134.0, 134.5, 138.4, 140.2, 145.0. EIMS *m*/*z* 415 ($M^+$), 396, 350, 335, 276, 260, 240, 233, 220, 190, 165, 155, 139, 91, 65, 51.

Spectral data were consistent with data reported in the literature.[1]

**_N_-Ts-5-Methyl-3-_p_-tolylindole (2i)**

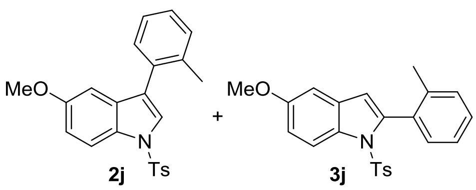



48%, a yellow oil (EtOAc : *n*-Hexane = 1:6).

$^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.33 (s, 3H), 2.42 (s, 6H), 7.17 (d, $J$ = 8.8 Hz, 1H), 7.21 (d, $J$ = 8.0 Hz, 2H), 7.28 (d, $J$ = 7.6 Hz, 2H), 7.48 (d, $J$ = 7.6 Hz, 2H), 7.53 (s, 1H), 7.61 (s, 1H), 7.78 (d, $J$ = 8.0 Hz, 2H), 7.92 (d, $J$ = 8.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.2, 21.4, 21.5, 113.5, 120.3, 122.8, 123.8, 126.2, 126.8, 127.8, 129.5, 129.7, 129.8, 130.2, 133.1, 133.7, 135.2, 137.3, 144.8. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{23}H_{21}NO_2S$ 375.1293, found 375.1294.

Spectral data were consistent with data reported in the literature.[2]

**_N_-Ts-5-Methoxy-3-_o_-tolylindole (2j) & _N_-Ts-5-Methoxy-2-_o_-tolylindole (3j)**



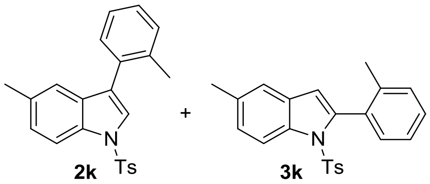

79% (**2j**:**3j** = 20:1), a white solid (EtOAc : *n*-Hexane = 1:4), mp 124-125 °C.

Signals corresponding to **2j**: $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.21 (s, 3H), 2.35 (s, 3H), 3.74 (s, 3H), 6.74 (d, $J$ = 1.6 Hz, 1H), 6.96 (dd, $J$ = 1.8, 9.0 Hz, 1H), 7.23 (d, $J$ = 8.4 Hz, 2H), 7.29-7.32 (m, 4H), 7.48 (s, 1H), 7.77 (d, $J$ = 8.4 Hz, 2H), 7.94 (d, $J$ = 8.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.4, 21.6, 55.6, 102.8, 113.9, 114.7, 123.6, 124.9, 125.8, 126.8, 127.9, 129.8, 130.4, 130.5, 131.7, 132.0, 135.1, 136.8, 144.8, 156.6 (1 carbon is missing due to overlapping).

Representative signals corresponding to **3j**: $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.24 (s, 3H), 2.32 (s, 3H), 3.85 (s, 3H), 6.40 (s, 1H), 7.09 (d, $J$ = 8.4 Hz, 4H), 8.21 (d, $J$ = 8.8 Hz, 1H).

HRMS (EI) $[M]^+$ *m/z* calcd for $C_{23}H_{21}NO_3S$ 391.1242, found 391.1244.

**N-Ts-5-Methyl-3-o-tolylindole (2k) & N-Ts-5-Methyl-2-o-tolylindole (3k)**



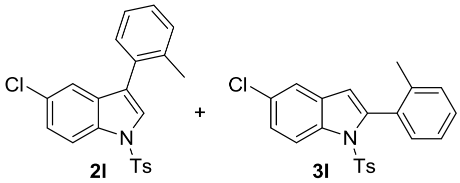
80% (**2k**:**3k** = 10:1), a pale brown oil (EtOAc : *n*-Hexane = 1:6).

Signals corresponding to **2k**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.20 (s, 3H), 2.32 (s, 3H), 2.35 (s, 3H), 7.10 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.25-7.30 (m, 4H), 7.47 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.39, 21.3, 21.5, 113.4, 120.4, 123.3, 124.2, 125.7, 126.1, 126.7, 127.8, 129.8, 130.4, 130.9, 132.0, 133.09, 133.14, 135.1, 136.8, 144.8 (1 carbon is missing due to overlapping).

Representative signals corresponding to **3k**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.22 (s, 3H), 2.29 (s, 3H), 2.42 (s, 3H), 6.38 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.44, 21.2, 112.2, 115.4, 120.6, 124.6, 125.9, 126.8, 129.0, 129.3, 129.6, 130.8.

HRMS (EI) $[M]^+$ *m/z* calcd for $C_{23}H_{21}NO_2S$ 375.1293, found 375.1296.

**N-Ts-5-Chloro-3-o-tolylindole (2l) & N-Ts-5-Chloro-2-o-tolylindole (3l)**



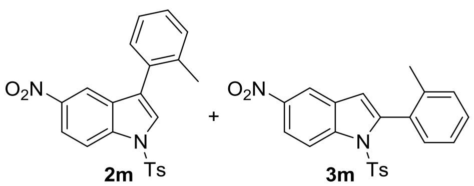
91% (**2l**:**3l** = 11:1), a white solid (EtOAc : *n*-Hexane = 1:6).

Signals corresponding to **2l**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.20 (s, 3H), 2.36 (s, 3H), 7.24-7.31 (m, 8H), 7.53 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 9.6 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.4, 21.6, 114.8, 120.3, 122.9, 125.0, 125.3, 125.9, 126.8, 128.2, 129.4, 130.0, 130.3, 130.6, 131.2, 132.0, 133.2, 134.8, 136.7, 145.3.

Representative signals corresponding to **3l**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.20 (s, 3H), 2.33 (s, 3H), 6.40 (s, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 3H), 7.46 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 111.4, 116.7, 124.7, 126.9, 129.3, 129.7, 130.8, 139.2, 141.7, 145.0.

HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{18}ClNO_2S$ 395.0747, found 395.0748.

**N-Ts-5-Nitro-3-o-tolylindole (2m) & N-Ts-5-Nitro-2-o-tolylindole (3m)**



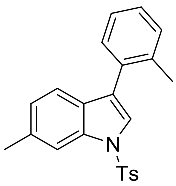
100% (**2m**:**3m** = 8:1), a yellow solid (EtOAc : *n*-Hexane = 1:6).

Signals corresponding to **2m**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.22 (s, 3H), 2.39 (s, 3H), 7.27-7.36 (m, 6H), 7.69 (s, 1H), 7.84 (d, $J$ = 8.0 Hz, 2H), 8.15 (d, $J$ = 9.2 Hz, 1H), 8.24 (d, $J$ = 9.2 Hz, 1H), 8.26 (s, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.4, 21.6, 113.9, 117.2, 120.0, 123.9, 126.1, 126.6, 126.9, 128.6, 130.2, 130.3, 130.4, 130.7, 130.8, 134.6, 136.7, 137.6, 144.4, 145.9.

Representative signals corresponding to **3m**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.14 (s, 3H), 2.36 (s, 3H), 6.60 (s, 1H), 7.07 (d, $J$ = 7.2 Hz, 1H), 7.15 (d, $J$ = 8.0 Hz, 2H), 8.43 (d, $J$ = 2.0 Hz, 1H), 8.46 (d, $J$ = 8.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.3, 111.8, 115.6, 116.8, 119.6, 124.8, 127.0, 129.66, 129.70, 130.9, 139.2, 145.6.

HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{18}N_2O_4S$ 406.0987, found 406.0987.

**_N_-Ts-6-Methyl-3-_o_-tolylindole (2n)**

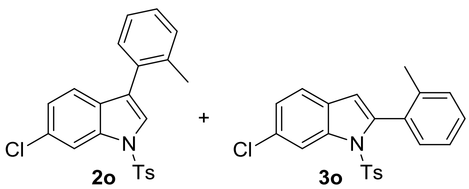



67%, a pale yellow oil (EtOAc : *n*-Hexane = 1:6).

$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.21 (s, 3H), 2.36 (s, 3H), 2.49 (s, 3H), 7.05 (d, $J$ = 8.4 Hz, 1H), 7.21-7.30 (m, 3H), 7.24 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 7.2 Hz, 2H), 7.45 (s, 1H), 7.79 (d, $J$ = 8.0 Hz, 2H), 7.86 (s, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.4, 21.6, 21.9, 113.8, 120.3, 123.37, 123.43, 124.9, 125.7, 126.8, 127.8, 128.5, 129.8, 130.40, 130.43, 132.1, 134.9, 135.3, 136.8, 144.8 (1 carbon is missing due to overlapping).

HRMS (EI) $[M]^+$ *m/z* calcd for $C_{23}H_{21}NO_2S$ 375.1293, found 375.1292.

**_N_-Ts-6-Chloro-3-_o_-tolylindole (2o) & _N_-Ts-6-Chloro-2-_o_-tolylindole (3o)**



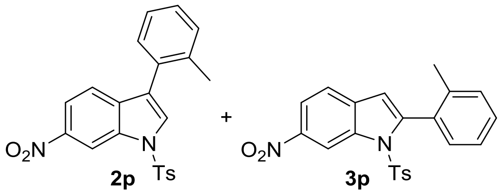

96% (**2o**:**3o** = 10:1), a white solid (EtOAc : *n*-Hexane = 1:6).

Signals corresponding to **2o**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.19 (s, 3H), 2.38 (s, 3H), 7.19-7.36 (m, 8H), 7.51 (s, 1H), 7.80 (d, $J$ = 8.4 Hz, 2H), 8.08 (s, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.3, 21.6, 113.9, 121.5, 123.2, 124.1, 124.5, 125.8, 126.8, 128.1, 129.2, 130.0, 130.4, 130.5, 130.8, 131.4, 134.9, 135.2, 136.7, 145.3.

Representative signals corresponding to **3o**: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.17 (s, 3H), 2.34 (s, 3H), 6.42 (s, 1H), 7.06 (d, $J$ = 7.6 Hz, 1H), 7.13 (d, $J$ = 8.0 Hz, 2H), 7.41 (d, $J$ = 8.0 Hz, 2H), 8.37 (s, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 111.6, 115.8, 121.3, 124.4, 124.7, 127.0, 129.3, 129.5, 129.6, 130.9, 131.5, 135.4, 139.3, 145.0.

HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{18}ClNO_2S$ 395.0747, found 395.0743.

**_N_-Ts-6-Nitro-3-_o_-tolylindole (2p) & _N_-Ts-6-Nitro-2-_o_-tolylindole (3p)**



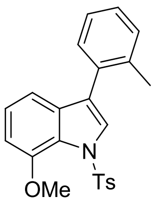

98% (**2p**:**3p** = 8:1), a yellow solid (EtOAc : *n*-Hexane = 1:5).

Signals corresponding to **2p**: $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.20 (s, 3H), 2.39 (s, 3H), 7.27-7.35 (m, 4H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.79 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 8.12 (dd, *J* = 1.6, 8.4 Hz, 1H), 8.96 (d, *J* = 1.6 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.3, 21.6, 110.1. 118.6, 120.9, 123.1, 126.0, 127.0, 128.5, 128.8, 130.3, 130.4, 130.5, 130.7, 133.6, 134.5, 135.2, 136.7, 145.2, 145.9.

Representative signals corresponding to **3p**: $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.15 (s, 3H), 2.36 (s, 3H), 6.56 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 8.20 (dd, *J* = 1.6, 8.4 Hz, 1H), 9.27 (s, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 111.3, 111.9, 119.1, 120.6, 124.8, 127.2, 129.7, 129.8, 145.6.

HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{18}N_2O_4S$ 406.0987, found 406.0988.

**_N_-Ts-7-Methoxy-3-_o_-tolylindole (2q)**

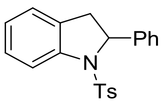



67%, a white solid (EtOAc : *n*-Hexane = 1:5), mp 104-105 ℃.

$^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.30 (s, 3H), 2.41 (s, 3H), 3.73 (s, 3H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.28-7.38 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.81 (s, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.5, 21.6, 55.5, 107.0, 113.2, 121.2, 124.0, 124.5, 125.7, 126.4, 127.3, 127.8, 129.3, 130.4, 130.7, 132.2, 133.5, 137.0, 137.3, 144.1, 147.5.

HRMS (EI) $[M]^+$ *m/z* calcd for $C_{23}H_{21}NO_3S$ 391.1242, found 391.1243.

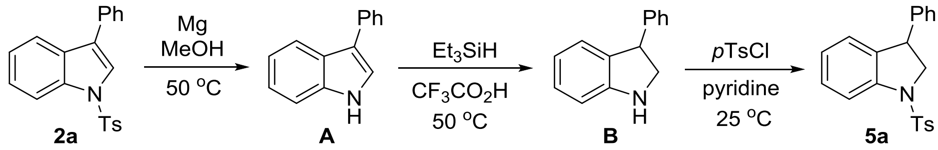
**_N_-Ts-2-Phenylindoline (4a)**




To a solution of the **1a** (20.0 mg, 0.06 mmol, 1 equiv) in $ClCH_2CH_2Cl$ (1.1 mL, 0.05 M) was added $Cu(OTf)_2$ (4.1 mg, 0.012 mmol, 20 mol%). After being stirred at 120 ℃ for 36 h under Ar atmosphere, the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:8) to give the corresponding **4a** (17.2 mg, 86 %) as a white solid.

$^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.36 (s, 3H), 2.88 (dd, *J* = 2.6, 16.2 Hz, 1H), 3.28 (dd, *J* = 10.0, 16.4 Hz, 1H), 5.33 (dd, *J* = 2.8, 10.0 Hz, 1H), 7.03-7.05 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.23-7.32 (m, 6H), 7.54 (d, $J$ = 8.4 Hz, 2H), 7.71 (d, $J$ = 8.0 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.5, 37.9, 64.8, 116.5, 124.5, 125.0, 126.0, 127.1, 127.6, 127.9, 128.6, 129.5, 131.2, 135.4, 141.9, 142.7, 143.8.

**$N$-Ts-3-Phenylindoline (5a)**




To a solution of **2a** (127.6 mg, 0.367 mmol, 1 equiv) in MeOH (7.3 mL, 0.05 M) was added Mg (134.6 mg, 5.509 mmol, 15 equiv). After being stirred at 50 °C for 6 h, the reaction mixture was poured into sat. aq. $NH_4Cl$ and then the product was extracted with $CH_2Cl_2$ (3 times). The combined organic layer was washed with brine, dried over MgSO4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : $n$-Hexane = 1:7) to give the **A** (58.6 mg, 83%) as a colorless solid.[1a]

To a solution **A** (57.6 mg, 0.298 mmol, 1 equiv) in $CF_3CO_2H$ (0.7 mL, 0.43 M) was added $Et_3SiH$ (96 µL, 0.596 mmol, 2 equiv) was added. After being stirred at 50 °C for 72 h, the reaction mixture was cooled to room temperature, diluted with water, brought to pH ~9 with a sat. aq. $NaHCO_3$, and extracted with $CH_2Cl_2$ (3 times). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : $n$-Hexane = 1:4) to give the corresponding product **B** (37.6 mg, 65%) as a yellow liquid.[6]

To a solution of **B** (37.6 mg, 0.193 mmol, 1 equiv) in pyridine (1.0 mL, 0.2 M) was added $p$-TsCl (41.3 mg, 0.212 mmol, 1.1 equiv) at 0 °C. After being stirred at 25 °C for 0.5 hours, the reaction mixture was poured into water and then the product was extracted with $CH_2Cl_2$ (three times), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : $n$-Hexane = 1:4) to give the corresponding product **5a** (91%, 61.2 mg) as a white solid.

$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.41 (s, 3H), 3.78 (dd, $J$ = 12.8, 16.0 Hz, 1H), 4.32-4.39 (m, 2H), 6.86-6.89 (m, 3H), 6.98 (t, $J$ = 7.4 Hz, 1H), 7.20-7.28 (m, 6H), 7.70 (d, $J$ = 7.6 Hz, 2H), 7.76 (d, $J$ = 8.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.5, 46.2, 58.4, 114.9, 124.0, 125.6, 127.0, 127.4, 127.7, 128.3, 128.7, 129.7, 133.7, 134.8, 142.0, 142.4, 144.1.

Spectral data were consistent with data reported in the literature.[7]

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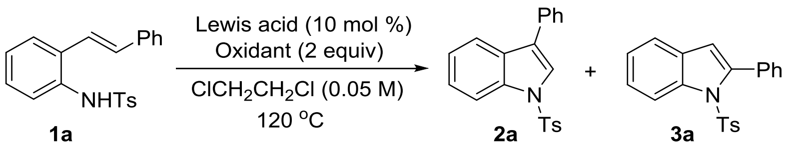
[6] Johnson, K. F.; Zeeland, R. V.; Stanley, L. M. *Org. Lett.* **2015**, *15*, 2798.

[7] (a) Kuwano, R.; Kaneda, K.; Ito, T.; Sato, K.; Kurokawa, T.; Ito, Y. *Org. Lett.* **2004**, *6*, 2213. (b) Kuwano, R.; Kashiwabara, M.; Sato, K.; Ito, T.; Kaneda, K.; Ito, Y. *Tetrahedron: Asymmetry* **2006**, *17*, 521. (c) Pineschi, M.; Bertolini, F.; Crotti, P.; Macchia, F. *Org. Lett.* **2006**, *8*, 2627. (d) Takeda, Y.; Ikeda, Y. Kuroda, A.; Tanaka, S.; Minakata, S. *J. Am. Chem. Soc.* **2014**, *136*, 8544. (e) Soldi, C.; Lamb, K. L.; Squitieri, R. A.; González-López, M.; Maso, M. J.; Shaw. J. T. *J. Am. Chem. Soc.* **2014**, *136*, 15142.

## Full Data of Optimization Studies

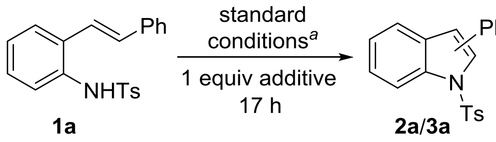



| Entry | Lewis Acid | Oxidant | Time (h) | Yield (%)[a] | **2a**:**3a**[b] |
|---|---|---|---|---|---|
| 1 | $FeCl_3$ | DDQ | 6 | 91 (71) | 7:1 |
| 2 | $FeBr_3$ | DDQ | 5 | 90 | 1:7 |
| 3 | $Fe_2(SO_4)_3 \cdot xH_2O$ | DDQ | 7 | 100 | 0:1 |
| 4 | $FeSO_4 \cdot 7H_2O$ | DDQ | 0.5 | 100 | 1:7 |
| 5 | $Fe(NO_3)_2 \cdot 9H_2O$ | DDQ | 5 | 100 | 1:29 |
| 6 | $FeCl_2$ | DDQ | 8 | 100 | 1:7 |
| 7 | $Fe(OTf)_2$ | DDQ | 24 | 100 | 0:1 |
| 8 | $InCl_3$ | DDQ | 24 | 100 | 2:1 |
| 9 | $Sc(OTf)_3$ | DDQ | 24 | 81 | 1:2 |
| 10 | $Yb(OTf)_3$ | DDQ | 24 | 94 | 1:8 |
| 11 | $CuCl_2$ | DDQ | 24 | 100 | 1:24 |
| 12 | $ZnCl_2$ | DDQ | 24 | 100 | 1:24 |
| 13 | $SnCl_2$ | DDQ | 24 | 100 | 1:17 |
| 14 | $Bi(OTf)_3$ | DDQ | 24 | 74 | 1:10 |
| 15 | $MgCl_2$ | DDQ | 24 | 100 | 1:12 |
| 16 | Others[c] | DDQ | 24 | 50-100 | 0:1 |
| 17 | $FeCl_3$ | BQ | 24 | 10 | 2:1 |
| 18 | $FeCl_3$ | $Cu(OAc)_2$ | 24 | 52 | 1:12 |
| 19 | $FeCl_3$ | *t*BuOO*t*Bu | 24 | 40 | 1:1.4 |
| 20[d] | $FeCl_3$ | DDQ | 7/24 | 100 | 1:4 |
| 21[e] | $FeCl_3$ | DDQ | 24 | 46 | 1:1 |
| 22[f] | $FeCl_3$ | DDQ | 24 | 15-97 | 0:1 |
| 23[g] | $FeCl_3$ | DDQ | 4 | (72) | 8:1 |
| 24[h] | $FeCl_3$ | DDQ | 5 | (63) | 9:1 |
| 25[g, i] | $FeCl_3$ | DDQ | 24 | (59) | 7:1 |
| **26**[g] | **$FeCl_3 \cdot 6H_2O$** | **DDQ** | **4** | **(75)** | **8:1** |
| 27[g, j] | - | DDQ | 24 | (30) | 0:1 |
| 28[g, j-k] | $FeCl_3 \cdot 6H_2O$ | - | 24 | (7) | 10:1 |

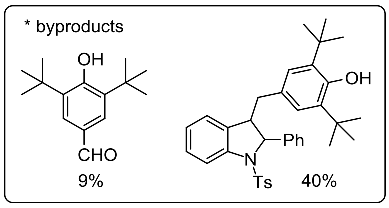
[a] Yields were determined by $^1H$ NMR using trichloroethylene as an internal standard. Value in parentheses indicates an isolated yield. [b] Ratios of inseparable isomers were determined by $^1H$ NMR. [c] Other Lewis acids such as $PdCl_2$, $PtCl_2$, AuCl, $RuCl_3$, AgOTf, and $AlCl_3$. [d] In *n*-heptane or MeCN, respectively. [e] In toluene. [f] In other solvents such as $CH_3CCl_3$, 1,4-dioxane, *t*BuOH, and DMF. [g] At 80 °C. [h] At 60 °C. [i] Using 1 equiv DDQ. [j] **1a** was recovered in 43-46% yield. [k] *N*-Ts-2-Phenylindoline (**4a**) was obtained in 40% yield.

## Mechanistic Studies

### 1) With Radical Scavenger

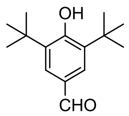



| Additive | **1a** | **2a**+**3a** (**2a**:**3a**) |
|---|---|---|
| TEMPO | 100% | - |
| BHT* | 17% | 11% (5:1) |
| ascorbic acid | 46% | 34% (1:1.3) |



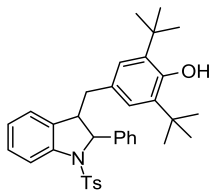

[a] 10 mol % $FeCl_3 \cdot 6H_2O$ and 2 equiv DDQ in $ClCH_2CH_2Cl$ (0.05 M) at 80 °C.

**3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde**



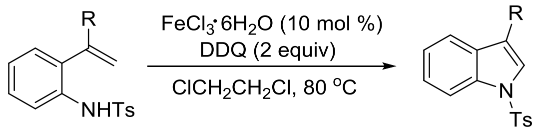

9%, a yellow solid (EtOAc : *n*-Hexane = 1:7).
$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.48 (s, 18H), 5.85 (s, 1H), 7.73 (s, 2H), 9.85 (s, 1H).
Spectral data were consistent with data reported in the literature.[1a, 8]

**2,6-Di-*tert*-butyl-4-((2-phenyl-1-tosylindolin-3-yl)methyl)phenol**




40%, a brown oil (EtOAc : *n*-Hexane = 1:7).
$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.42 (s, 18H), 1.94 (dd, $J$ = 10.2, 13.6 Hz, 1H), 2.32 (t, $J$ = 6.4 Hz, 1H), 2.37 (s, 3H), 3.20 (dd, $J$ = 6.8, 7.6 Hz, 1H), 4.93 (s, 1H), 5.14 (s, 1H), 6.69 (s, 2H), 6.75 (d, $J$ = 7.6 Hz, 1H), 6.90-6.91 (m, 2H), 6.99 (t, $J$ = 7.4 Hz, 1H), 7.15-7.17 (m, 3H), 7.24 (d, $J$ = 8.0 Hz, 2H), 7.30 (t, $J$ = 7.6 Hz, 1H), 7.66 (d, $J$ = 8.0 Hz, 2H), 7.84 (d, $J$ = 8.0 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.6, 30.3, 34.3, 43.0, 53.5, 69.6, 116.0, 124.1, 125.4, 125.5, 125.7, 127.18, 127.22, 128.3, 128.4, 128.5, 129.5, 134.0, 135.4, 136.1, 141.7, 142.7, 144.0, 152.5. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{36}H_{41}NO_3S$ 567.2807, found 567.2809.

### 2) Reactivity of Terminal Alkenes




R = Ph (**1r**)
H (**1s**)

from **1r** for 30 h : **2a** (70%)
from **1s** for 24h : **2s** (5%) + recovered **1s** (18%)
+ some unidentified dimer-like compounds (< 10%)

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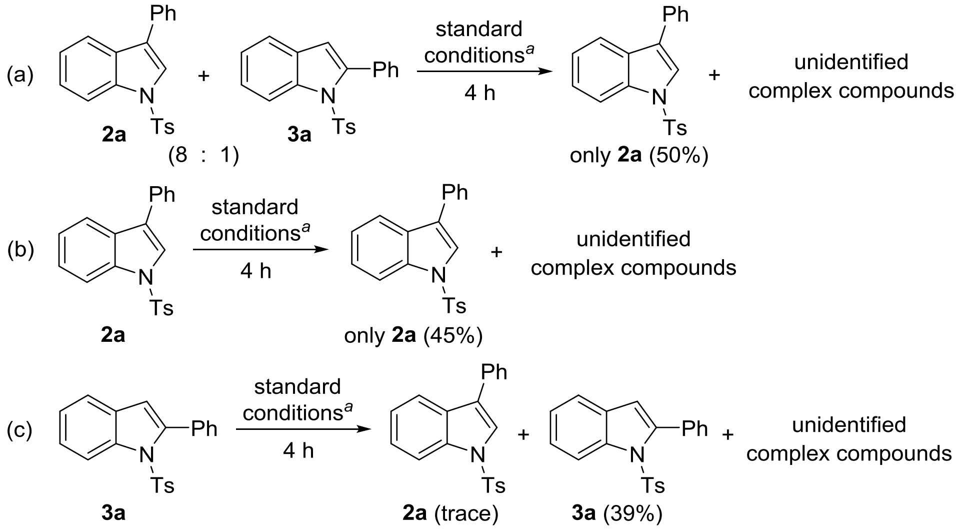
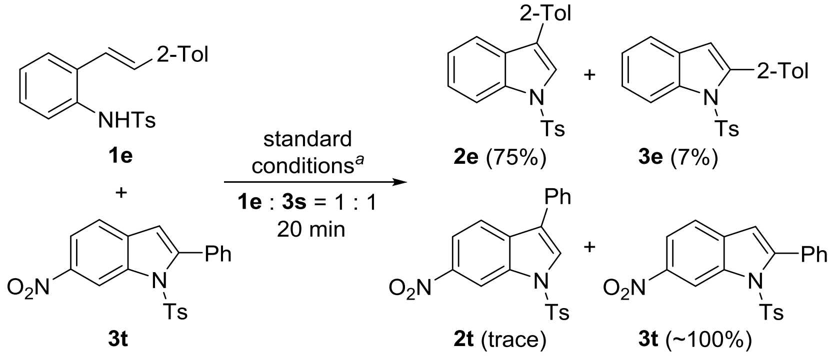
[8] Ozanne, A.; Pouységu, L.; Depernet, D.; François, B.; Quideau, S. *Org. Lett.* **2003**, *5*, 2903.

## 3) Stability of Indole Products 2 & 3 Under the Standard Reactions Conditions



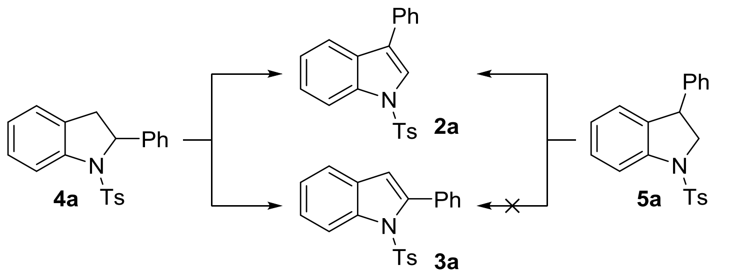
[a] 10 mol % $FeCl_3 \cdot 6H_2O$ and 2 equiv DDQ in $ClCH_2CH_2Cl$ (0.05 M) at 80 °C.

## 4) Crossover Experiments



[a] 10 mol % $FeCl_3 \cdot 6H_2O$ and 2 equiv DDQ in $ClCH_2CH_2Cl$ (0.05 M) at 80 °C.

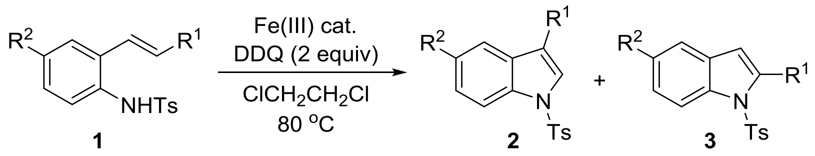
## 5) Reaction of Possible Intermediates



| Reaction Conditions[a] | < Reaction of **4a** > | | | < Reaction of **5a** > | | |
|---|---|---|---|---|---|---|
| | t (h) | **2a**+**3a** (**2a**:**3a**) | **4a** | t (h) | only **2a** | **5a** |
| $Fe^{3+}$ + DDQ | 4 | 28% (1.4:1) | 21% | 1 | 100% | 0% |
| | 24 | 28% (2.8:1) | 4% | | | |
| only $Fe^{3+}$ | 24 | 0% | 100% | 24 | 0% | 100% |
| only DDQ | 24 | 88% (only **3a**) | 10% | 1 | 100% | 0% |

[a] In $ClCH_2CH_2Cl$ (0.05 M) at 80 °C ($Fe^{3+}$ = 10 mol % $FeCl_3 \cdot 6H_2O$, DDQ = 2 equiv DDQ).

## 6) Effects of Fe(III) Loading




| $R^1$ = Ph, $R^2$ = H (**1a**) | | | | $R^1$ = 2-Me$C_6H_4$, $R^2$ = MeO (**1j**) | | | | $R^1$ = 2-Me$C_6H_4$, $R^2$ = Cl (**1l**) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $FeCl_3$ (mol %) | Time (h) | Yield (%)[a] | **2a**:**3a**[b] | $FeCl_3\cdot 6H_2O$ (mol %) | Time (min) | Yield (%)[a] | **2j**:**3j**[b] | $FeCl_3\cdot 6H_2O$ (mol %) | Time (h) | Yield (%)[a] | **2l**:**3l**[b] |
| 2 | 24 | 75 | 5:1 | 3 | 30 | 98 | 6:1 | 5 | 24 | 91 | 2:1 |
| 5 | 24 | 74 | 6:1 | 10 | 10 | 78 | 13:1 | 10 | 6 | 94 | 9:1 |
| 10 | 4 | 72 | 8:1 | 15 | 10 | 79 | 20:1 | 15 | 2 | 92 | 10:1 |
| 15 | 2 | 48 | 27:1 | 20 | 5 | 55 | 53:1 | 20 | 1 | 91 | 11:1 |
| 20 | 1 | 34 | 1:0 | | | | | 25 | 0.5 | 86 | 11:1 |

[a] Isolated yield. [b] Determined by $^1$H NMR.

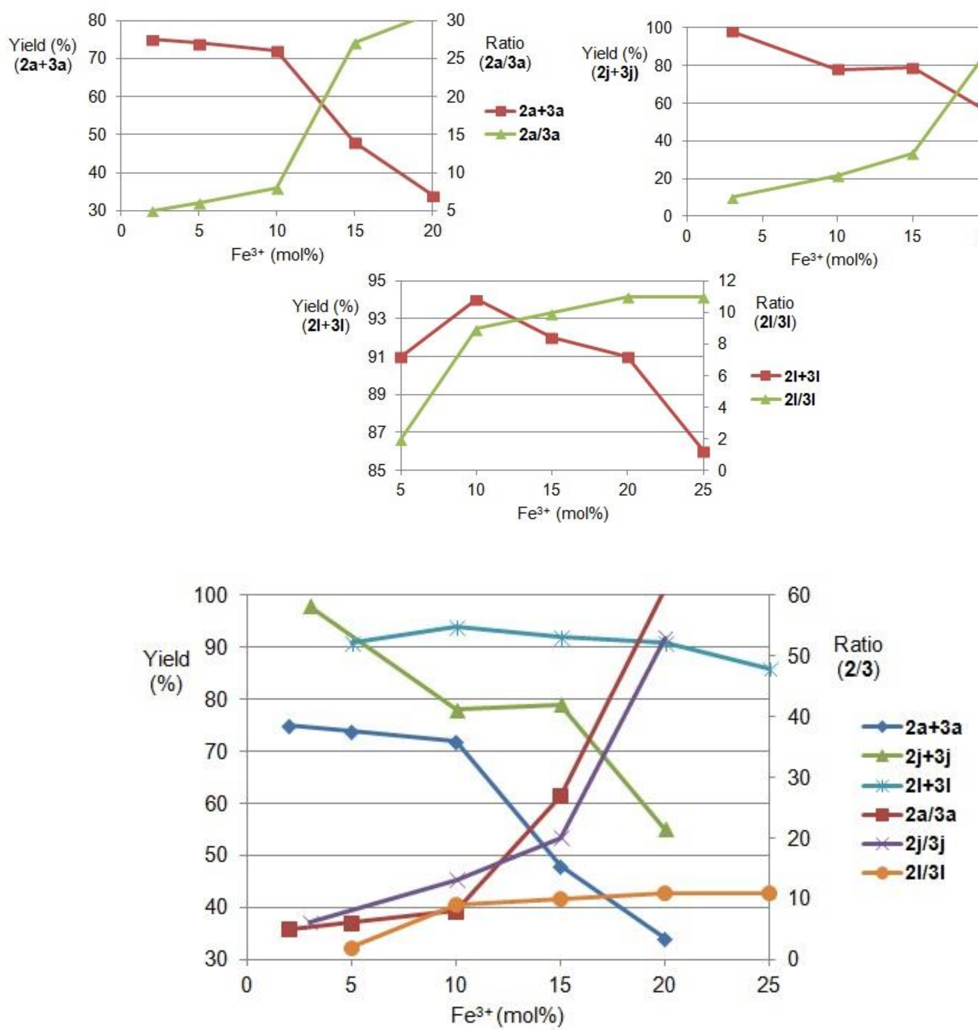
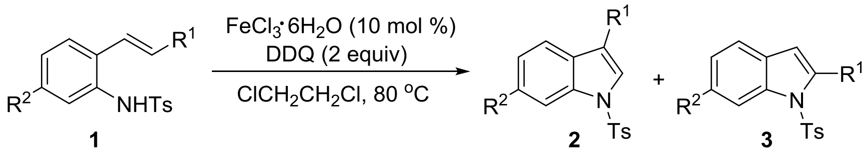



**Figure S1.** Plot of Yield and Ratio of **2** and **3** versus the Amount of $Fe^{3+}$ Catalyst Used

## 7) Analysis of the Reaction Mixture During the Reaction of 1




| R$^1$ = Ph, R$^2$ = H (**1a**) | | | | R$^1$ = 2-MeC$_6$H$_4$, R$^2$ = NO$_2$ (**1p**) | | | |
|---|---|---|---|---|---|---|---|
| Time (h) | **1a** (%)[a] | **2a**+**3a** (%)[a] | **2a**:**3a**[a] | Time (h) | **1p** (%)[a] | **2p**+**3p** (%)[a] | **2p**:**3p**[a] |
| 0.5 | 19 | 81 | 4.8:1 | 0.5 | 80 | 20 | 9.0:1 |
| 1 | 8 | 93 | 4.8:1 | 1 | 58 | 42 | 7.0:1 |
| 1.5 | - | 100 | 5.3:1 | 2 | 38 | 62 | 8.2:1 |
| 2 | - | 100 | 5.7:1 | 4 | 17 | 83 | 7.8:1 |
| 3 | - | 100 | 6.8:1 | 6 | 9 | 91 | 7.2:1 |
| 4 | - | 100 | 8.1:1 | 9 | 3 | 97 | 7.2:1 |
| | | | | 12 | - | 100 | 7.2:1 |

[a] Determined by $^1$H NMR.

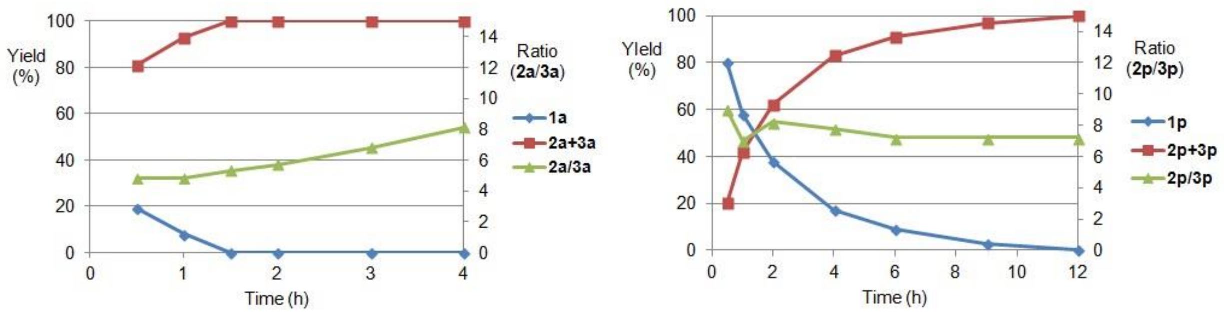
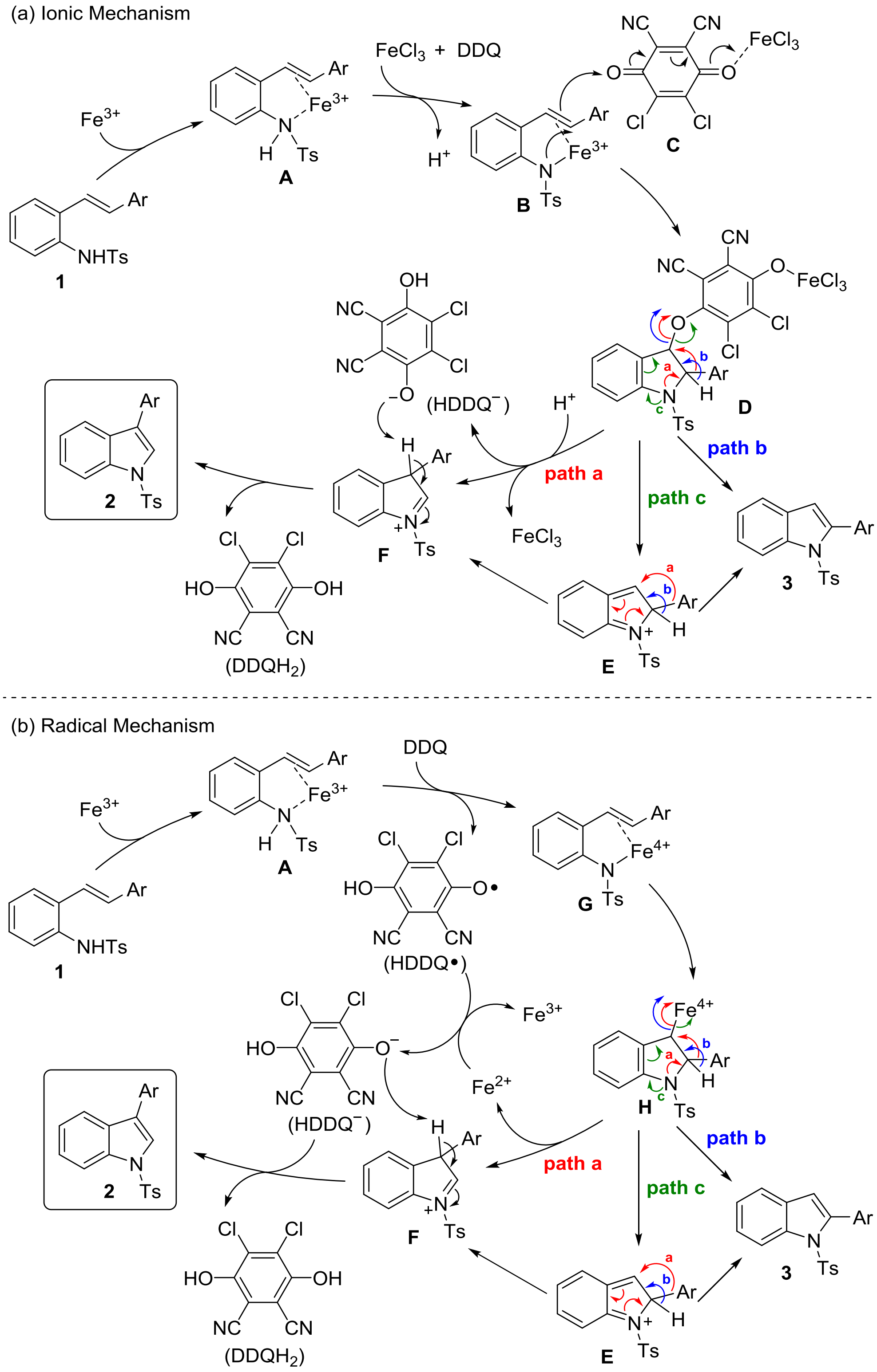



**Figure S2.** Plot of Yield and Ratio of **2** and **3** versus Time

## Proposed Mechanism[9]

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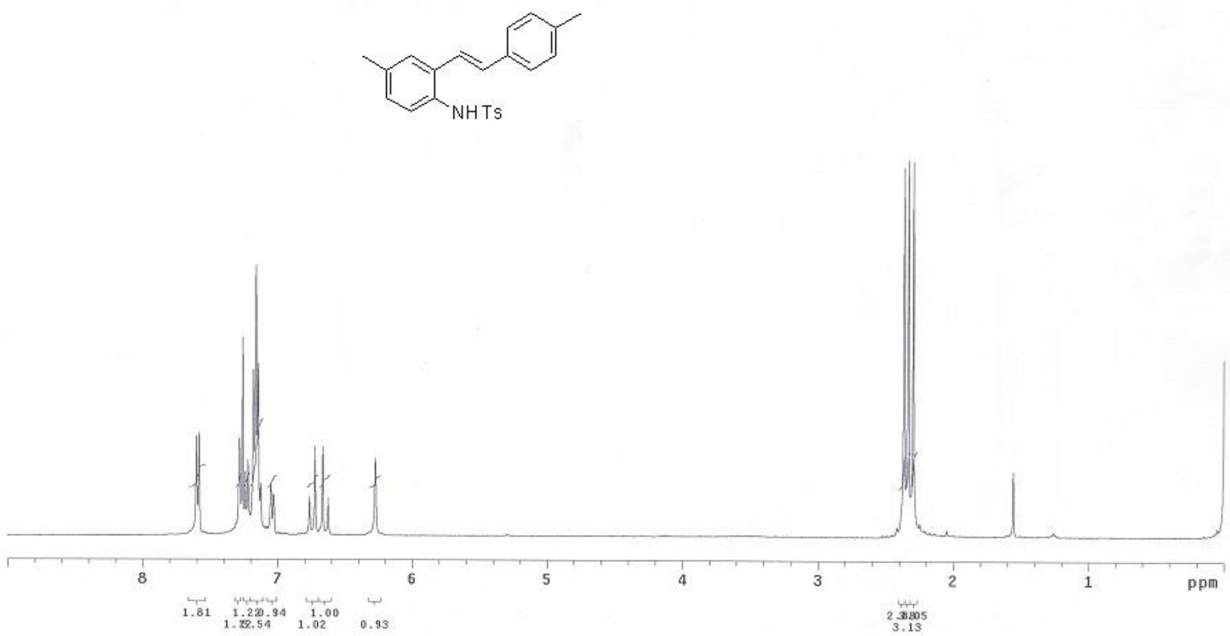
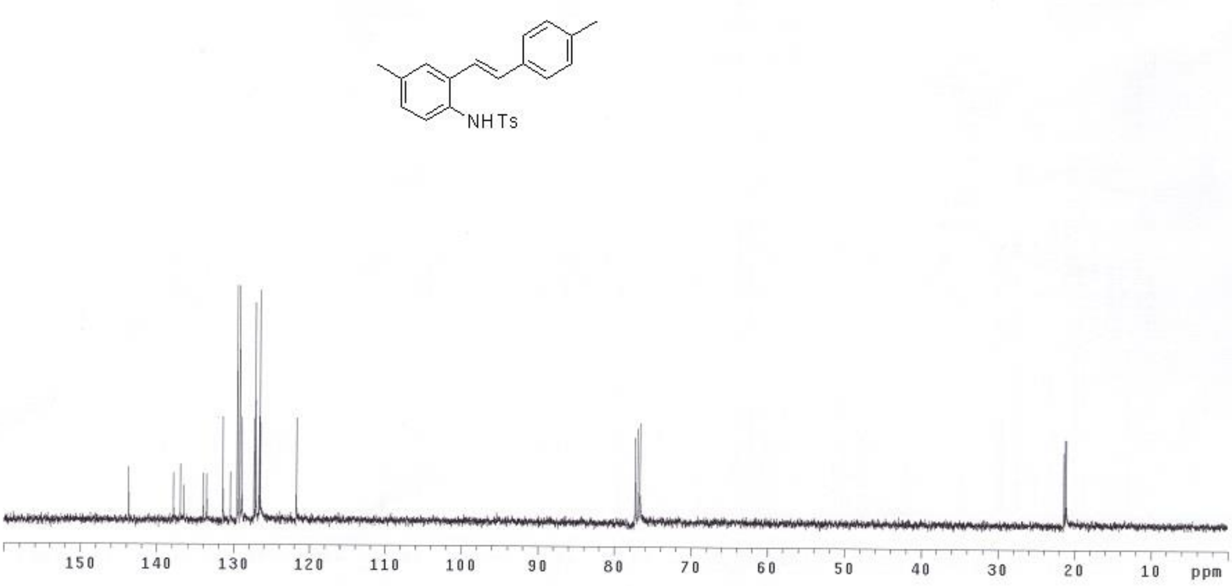
9 For the related ionic mechanism, see: (a) Liu, N.; Mao, L.-L.; Yang, B.; Yang, S.-D. *Chem. Commun.* **2014**, *50*, 10879. (b) Shimizu, M.; Itou, H.; Miura, M. *J. Am. Chem. Soc.* **2005**, *127*, 3296. For the related radical mechanism, see: (c) Kshirsagar, U. A.; Regev, C.; Parnes, R.; Pappo, D. *Org. Lett.* **2013**, *15*, 3174.

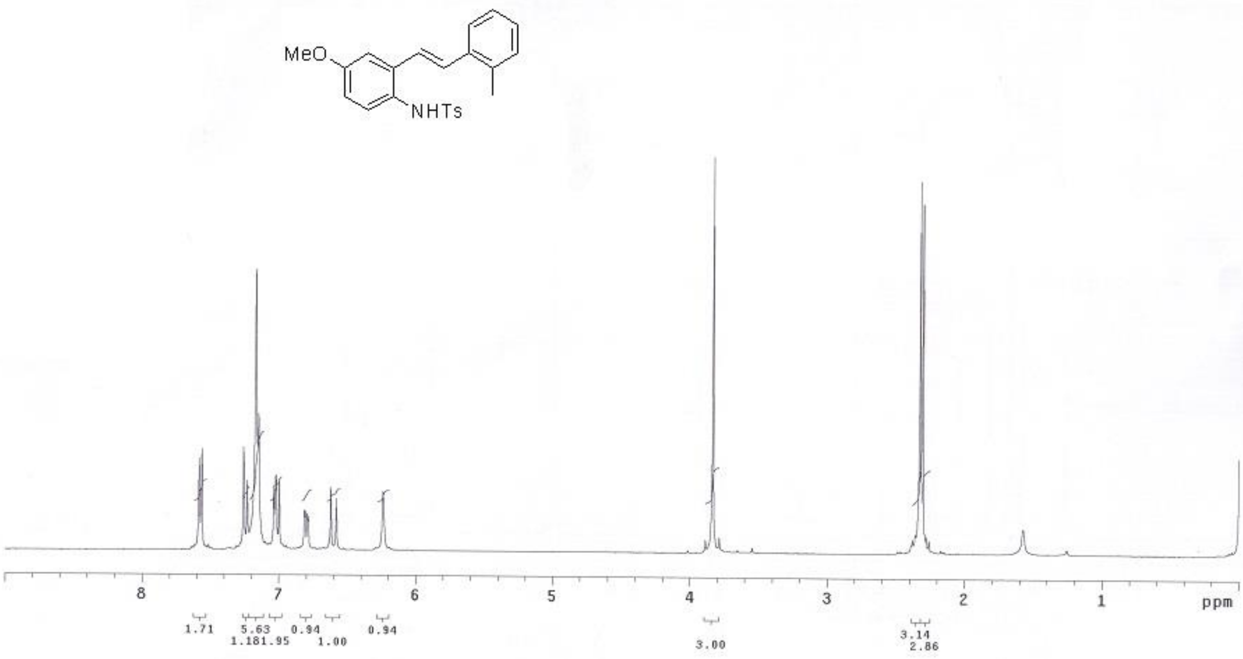
## Copies of NMR Spectra

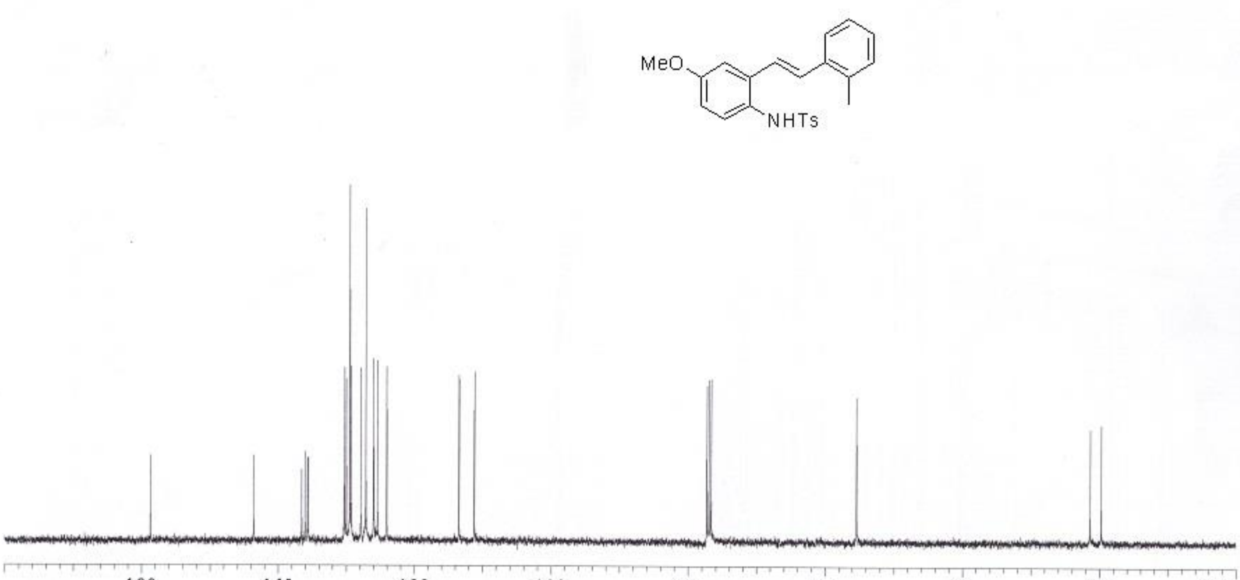
### (*E*)-4-Methyl-*N*-(4-methyl-2-(4-methylstyryl)phenyl)benzenesulfonamide (1i)



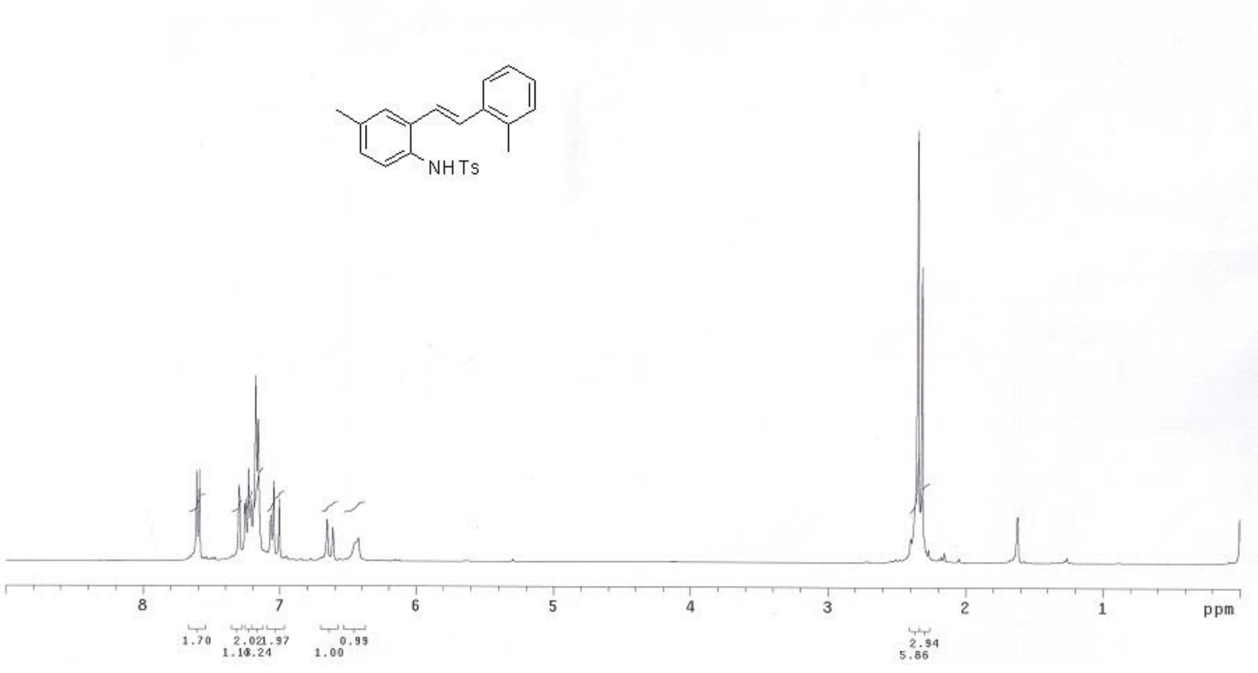



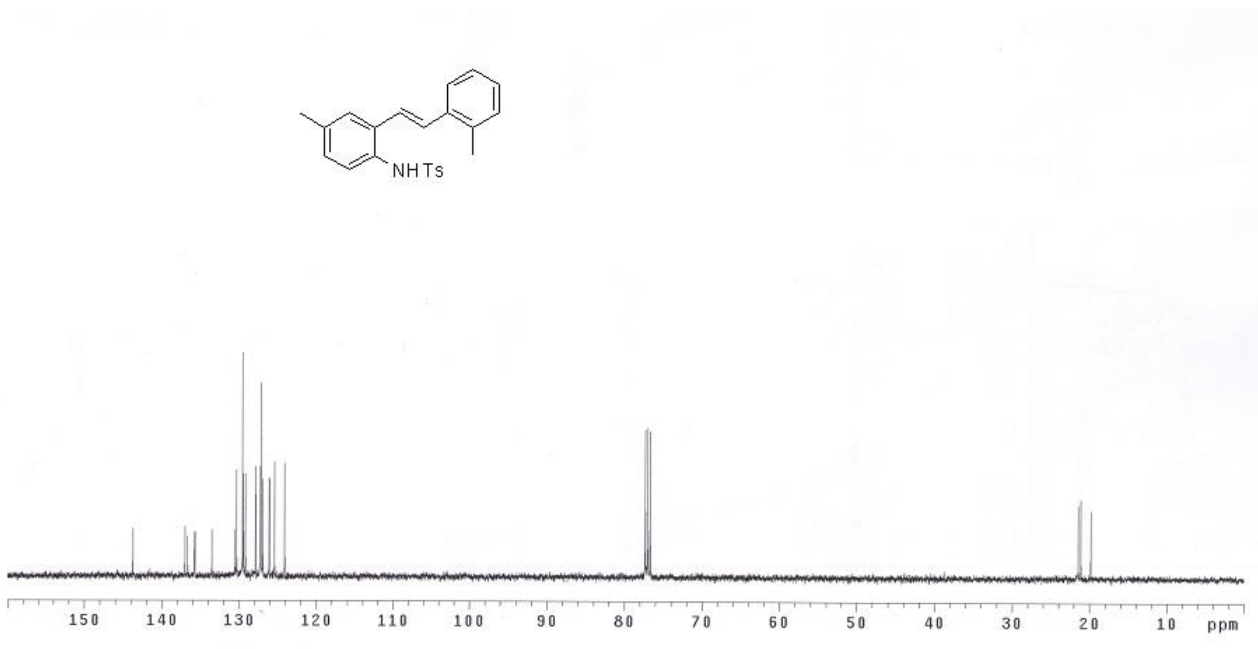
**(*E*)-*N*-(4-Methoxy-2-(2-methylstyryl)phenyl)-4-methylbenzenesulfonamide (1j)**



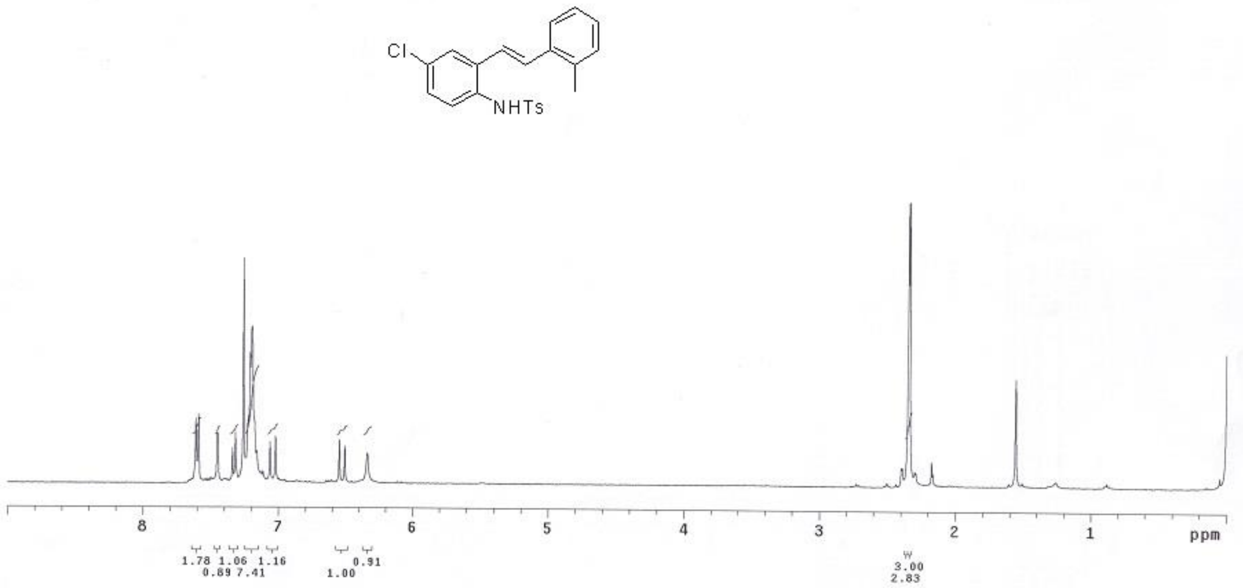



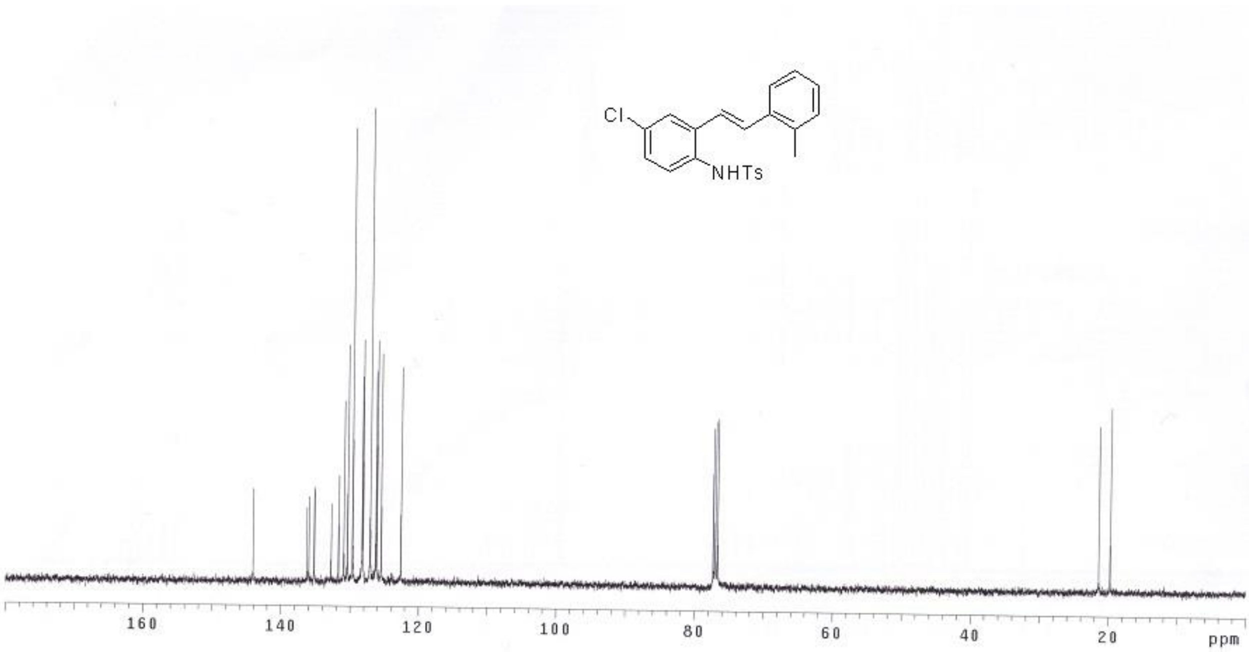
**(*E*)-4-Methyl-*N*-(4-methyl-2-(2-methylstyryl)phenyl)benzenesulfonamide (1k)**



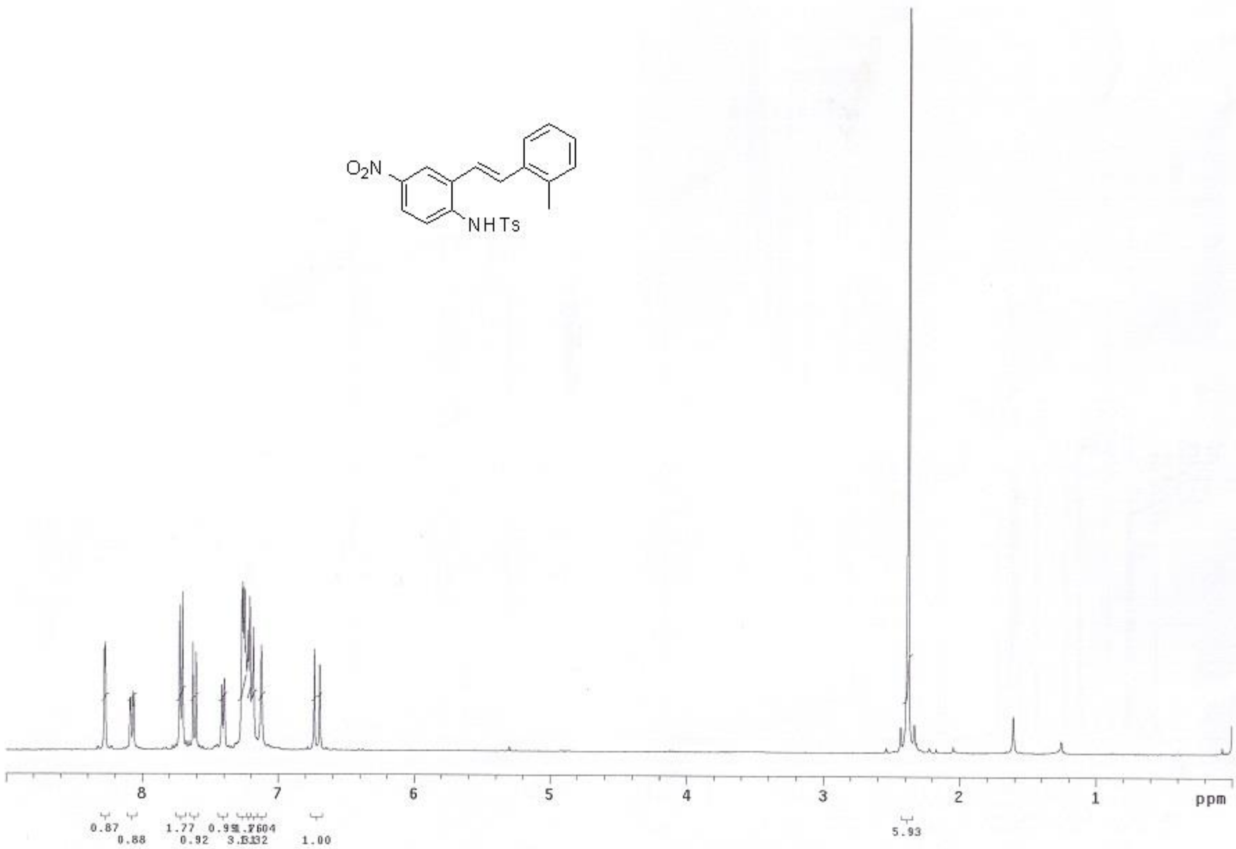



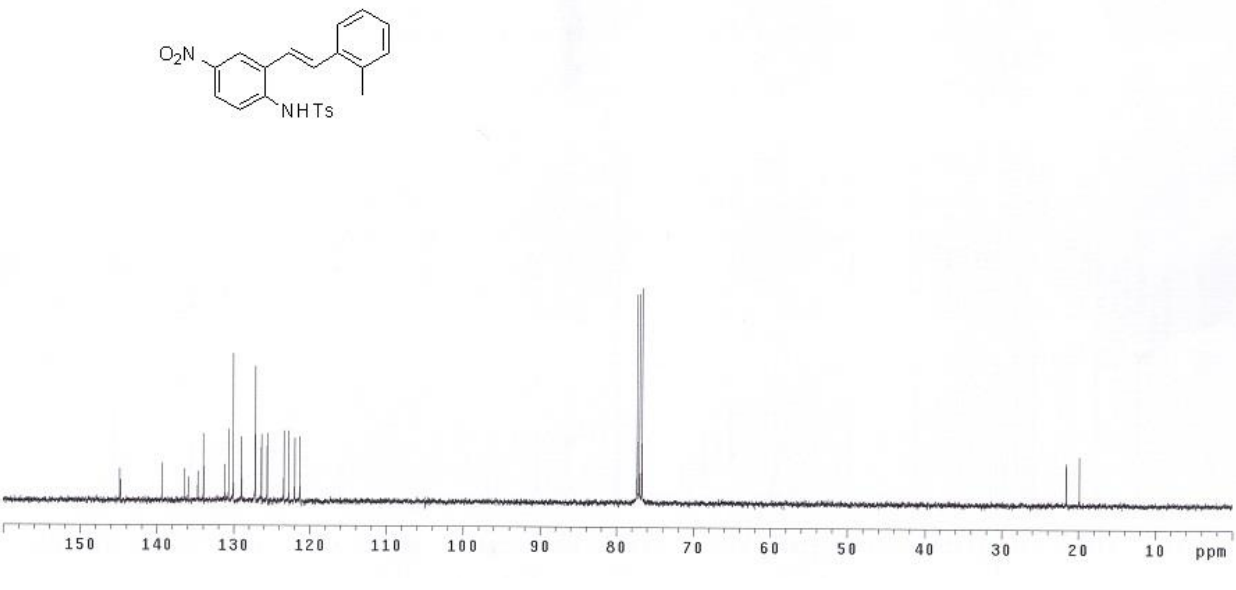
**(*E*)-*N*-(4-Chloro-2-(2-methylstyryl)phenyl)-4-methylbenzenesulfonamide (1l)**



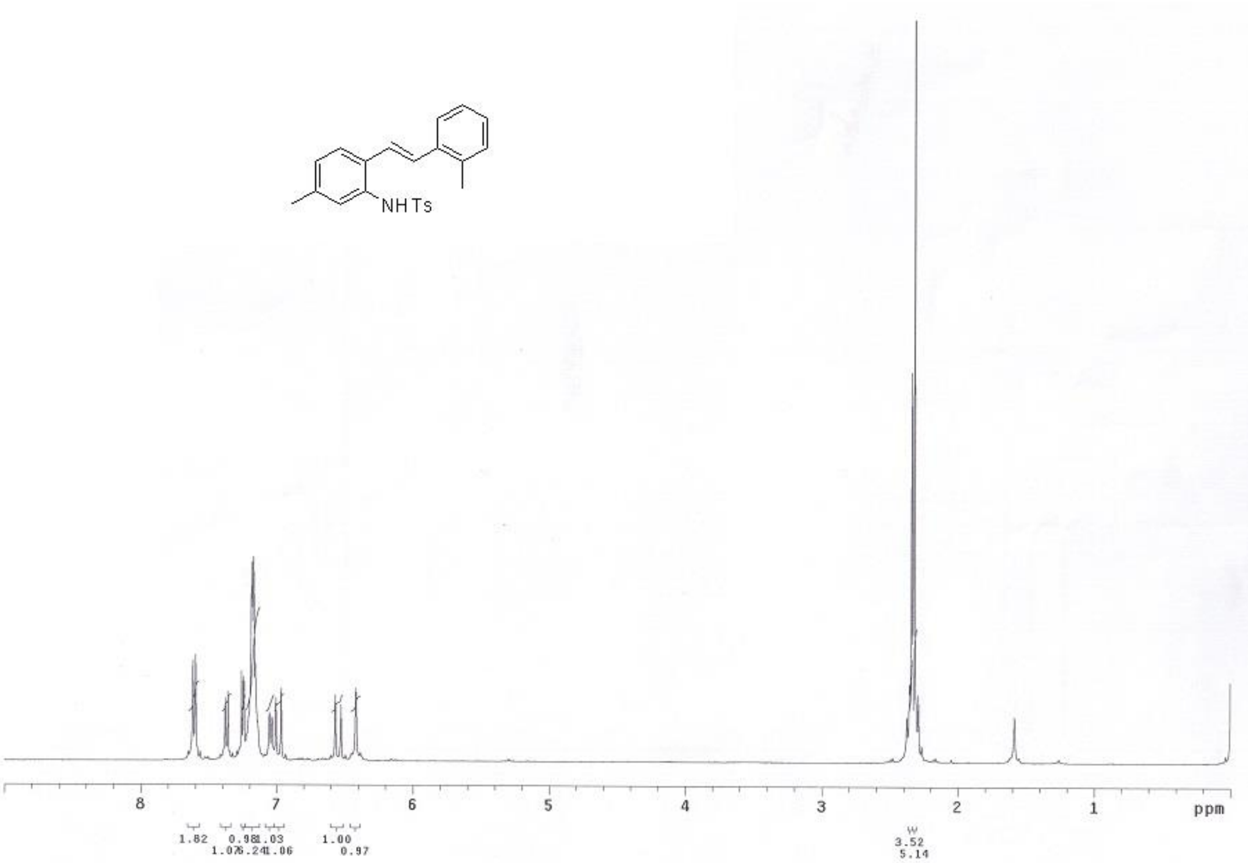



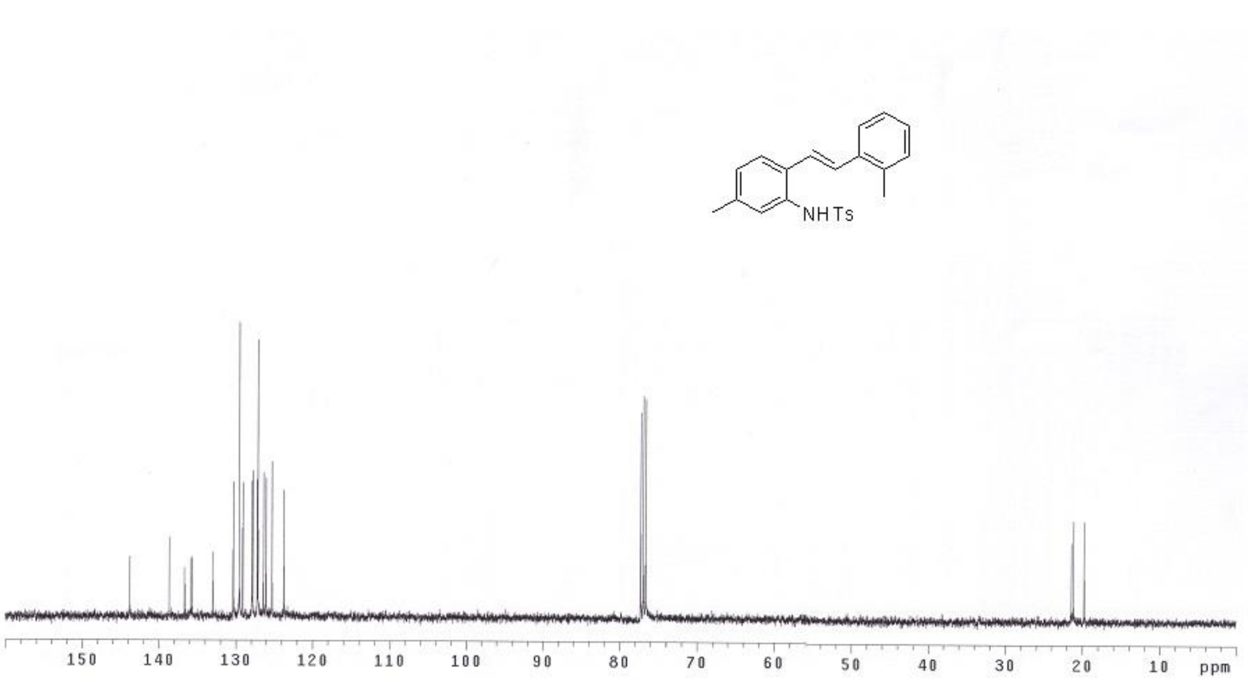
**(*E*)-4-Methyl-*N*-(2-(2-methylstyryl)-4-nitrophenyl)benzenesulfonamide (1m)**



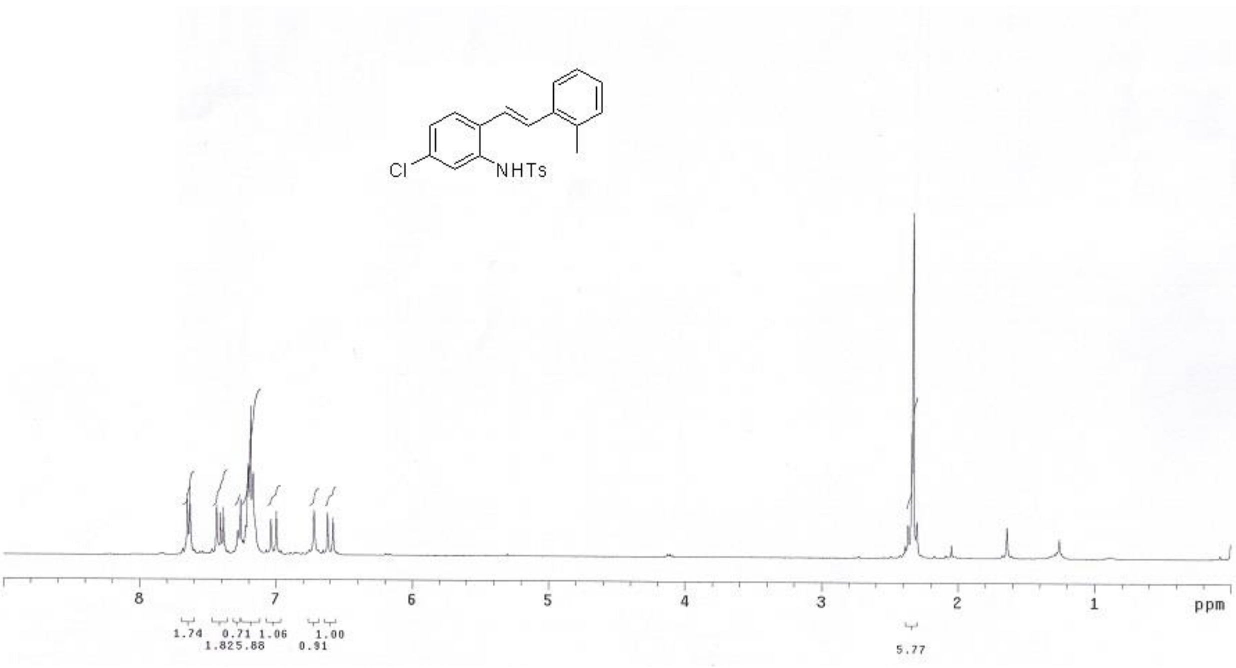



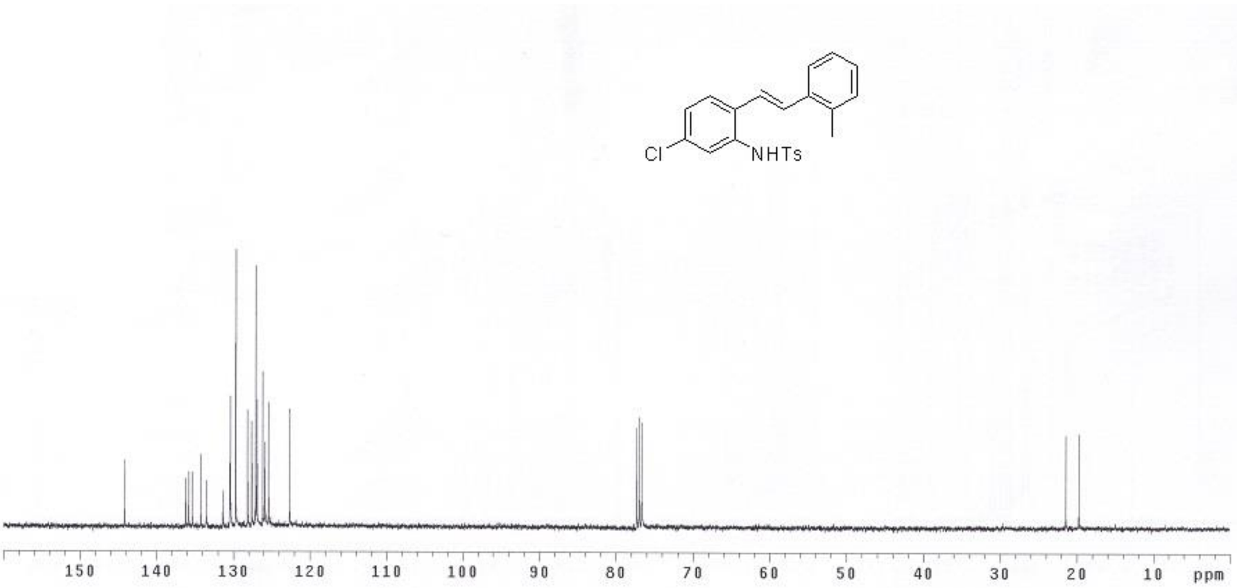
**(*E*)-4-Methyl-*N*-(5-methyl-2-(2-methylstyryl)phenyl)benzenesulfonamide (1n)**



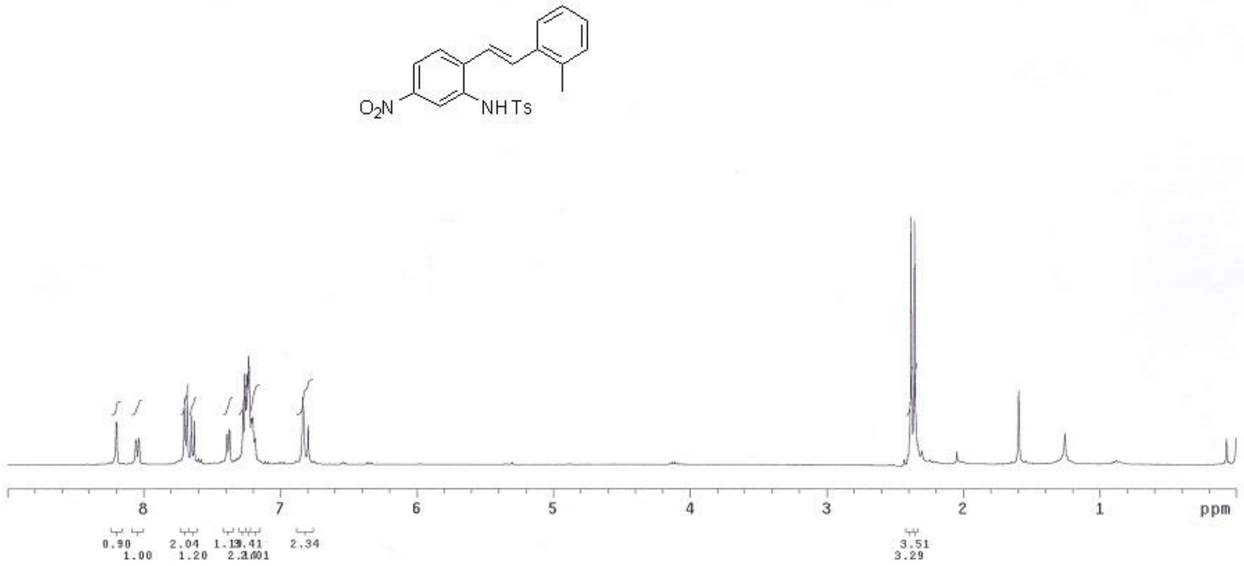



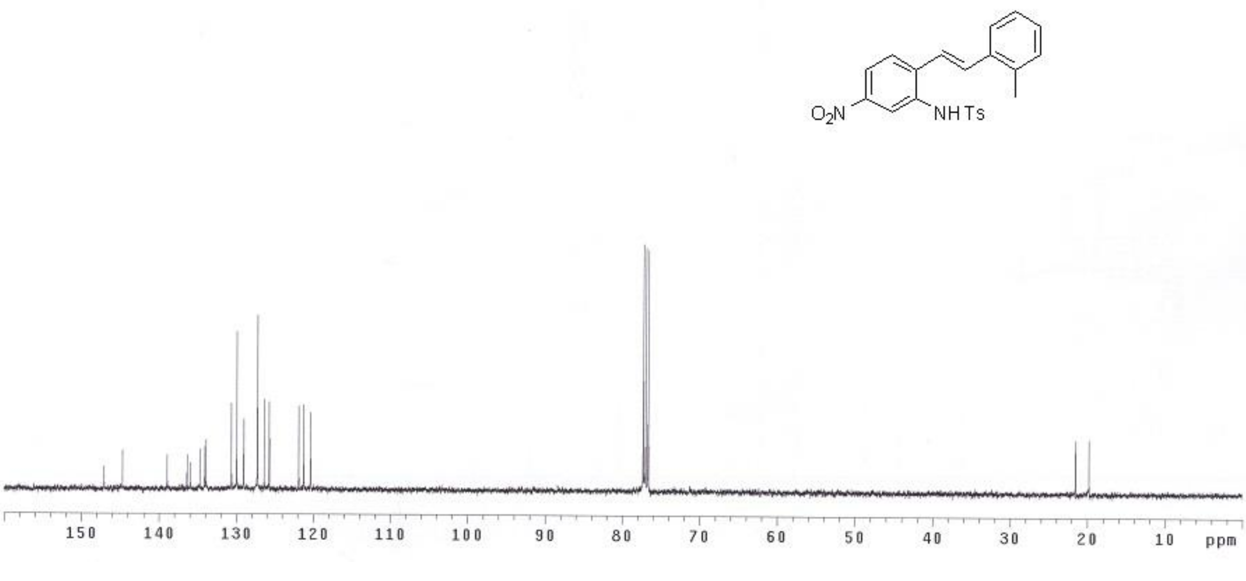
**(*E*)-*N*-(5-Chloro-2-(2-methylstyryl)phenyl)-4-methylbenzenesulfonamide (1o)**



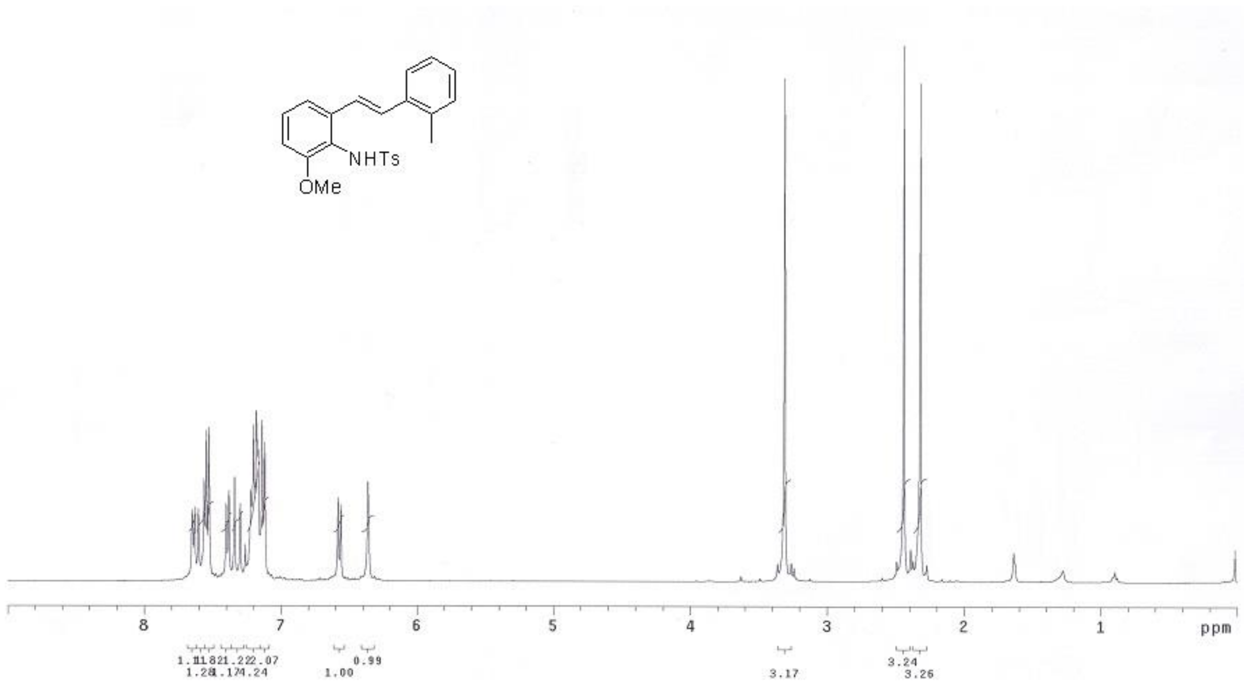



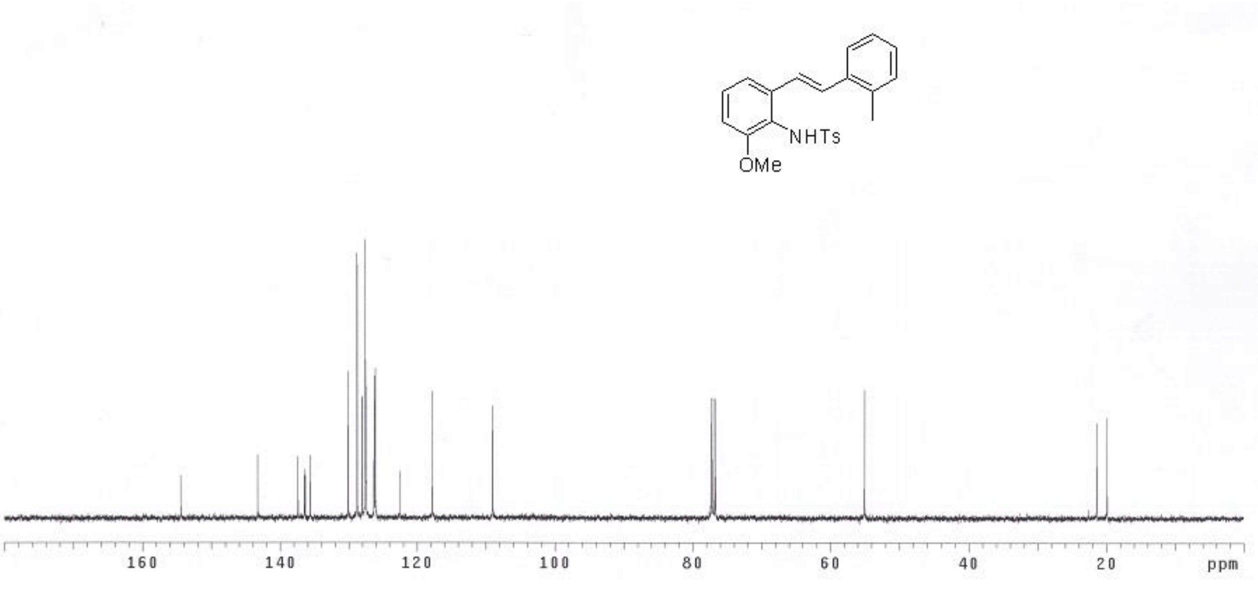
**(*E*)-4-Methyl-*N*-(2-(2-methylstyryl)-5-nitrophenyl)benzenesulfonamide (1p)**



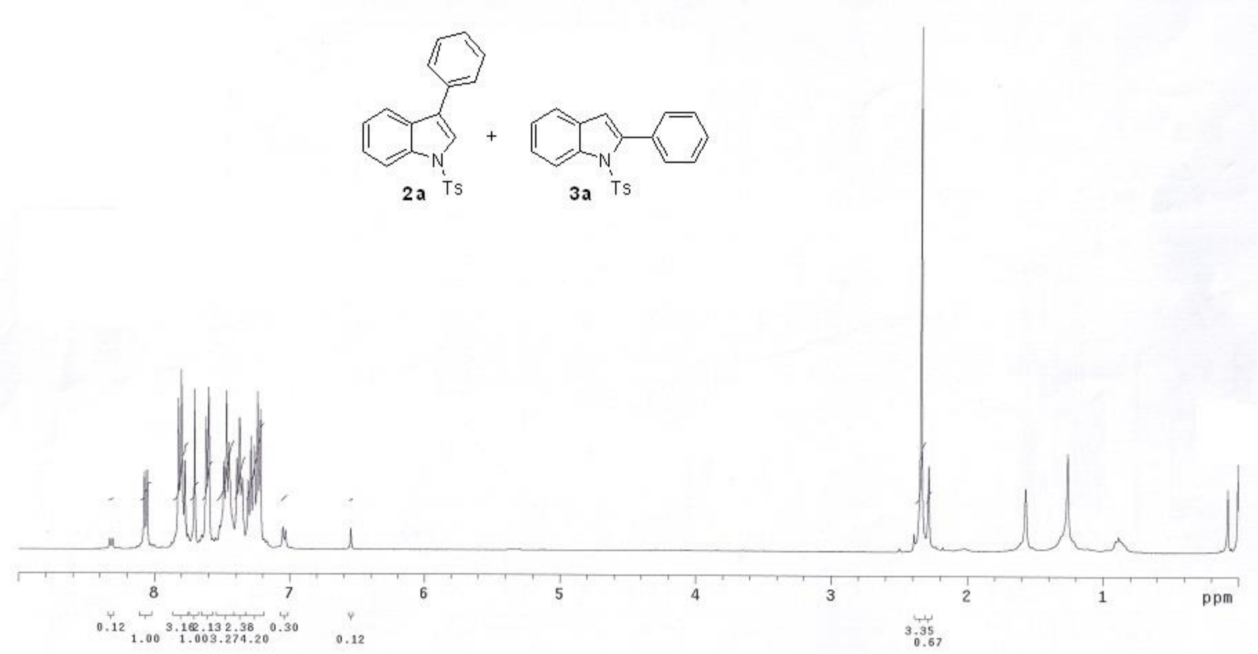


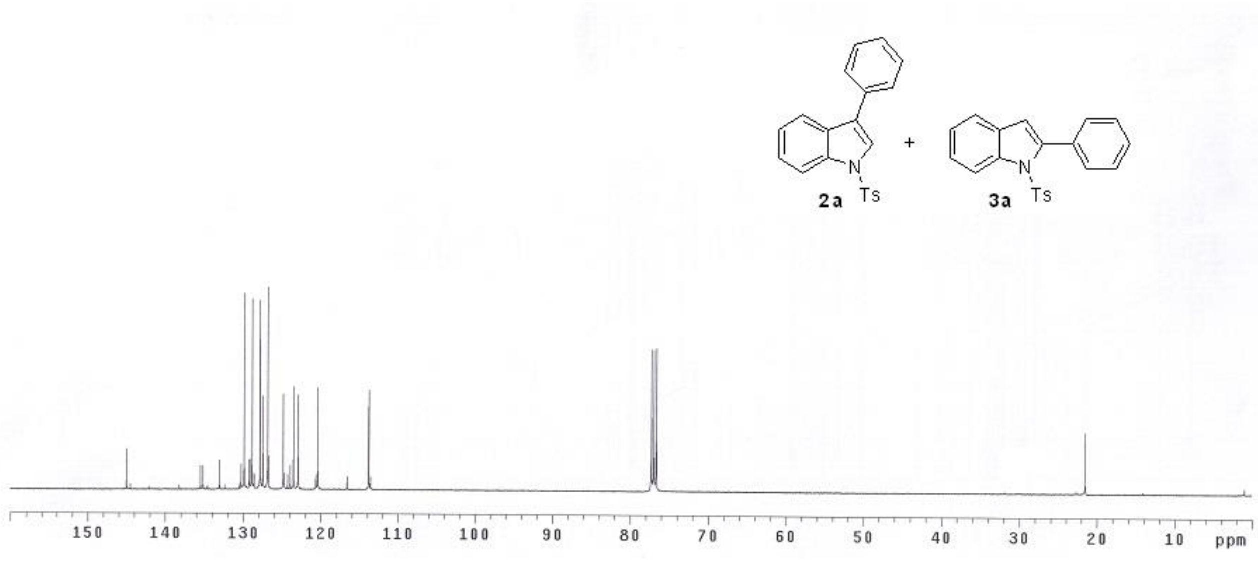
**(*E*)-*N*-(2-Methoxy-6-(2-methylstyryl)phenyl)-4-methylbenzenesulfonamide (1q)**



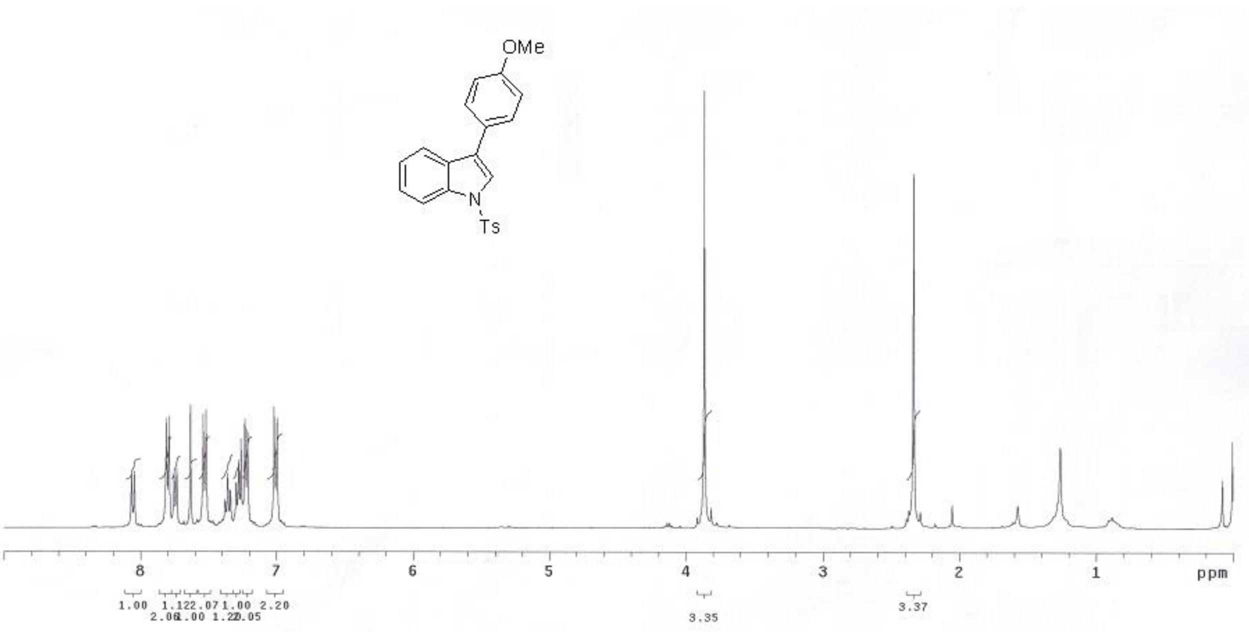



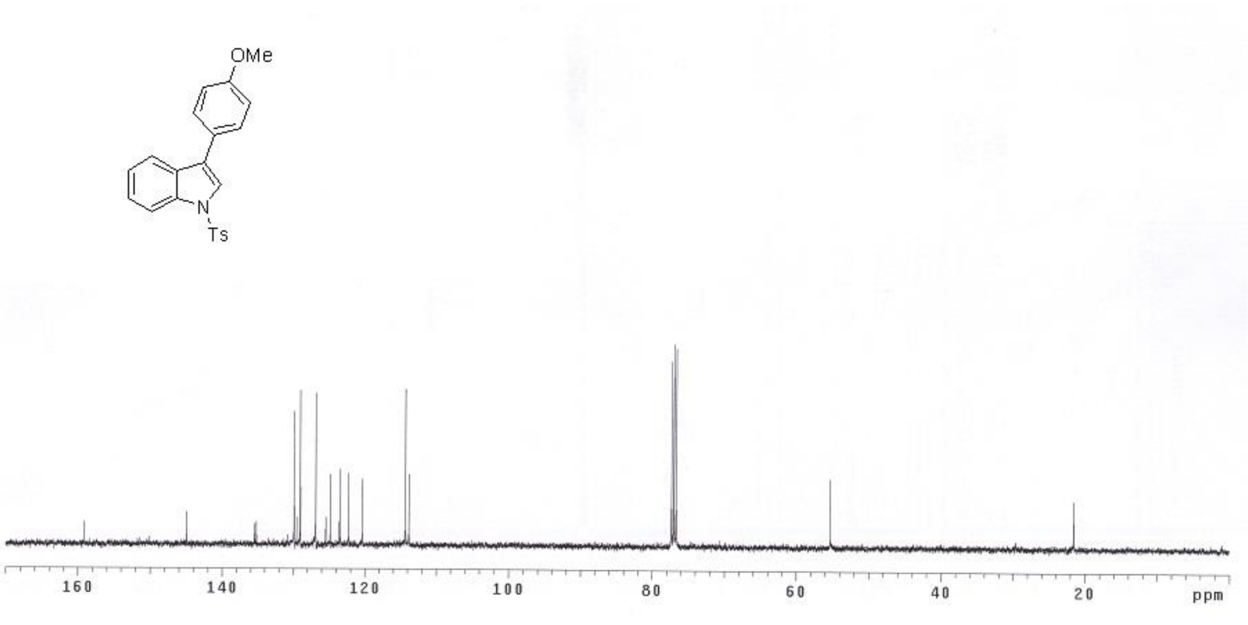
**N-Ts-3-Phenylindole (2a) & N-Ts-2-Phenylindole (3a)**



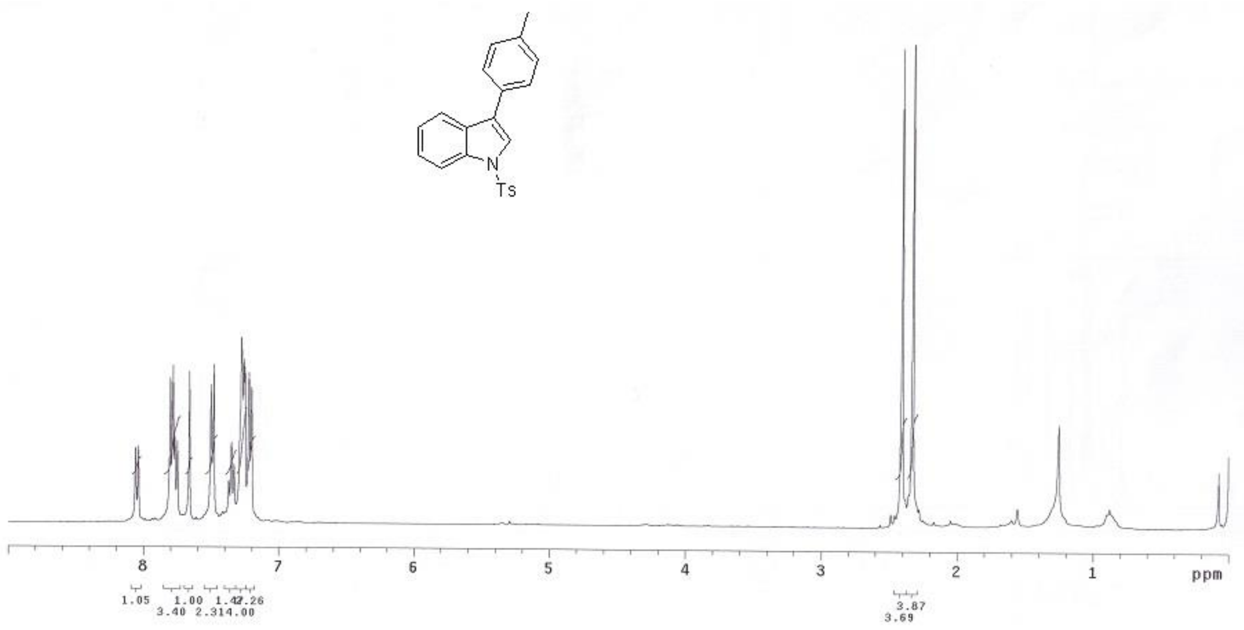


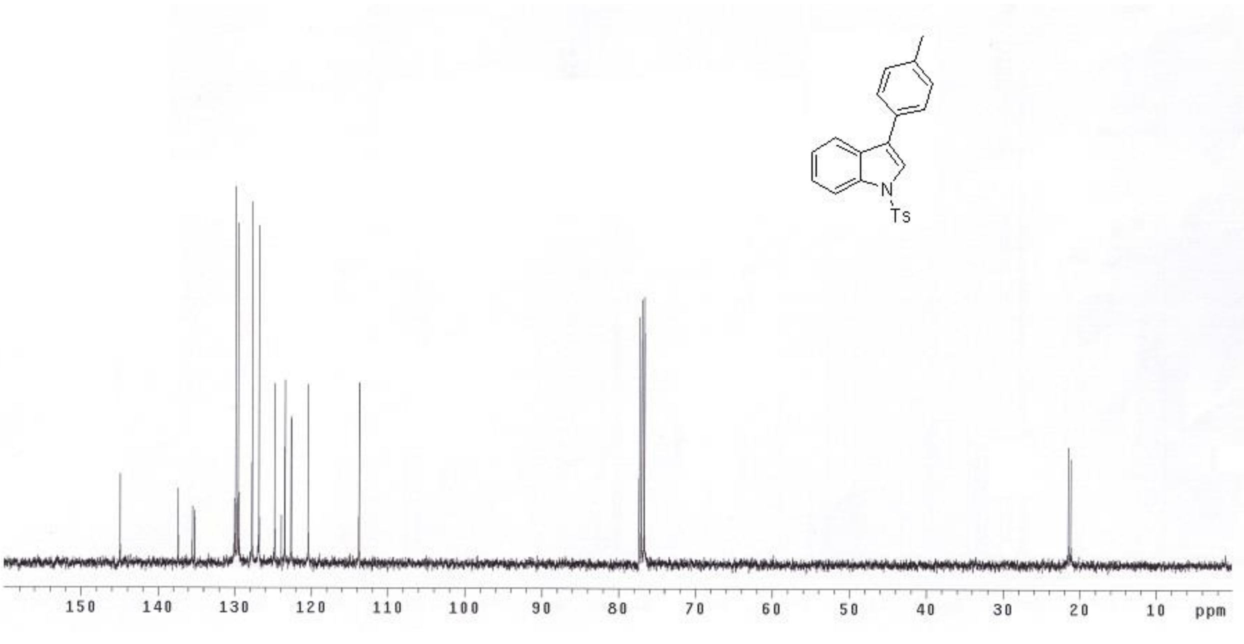
***N*-Ts-3-(4-Methoxyphenyl)indole (2b)**



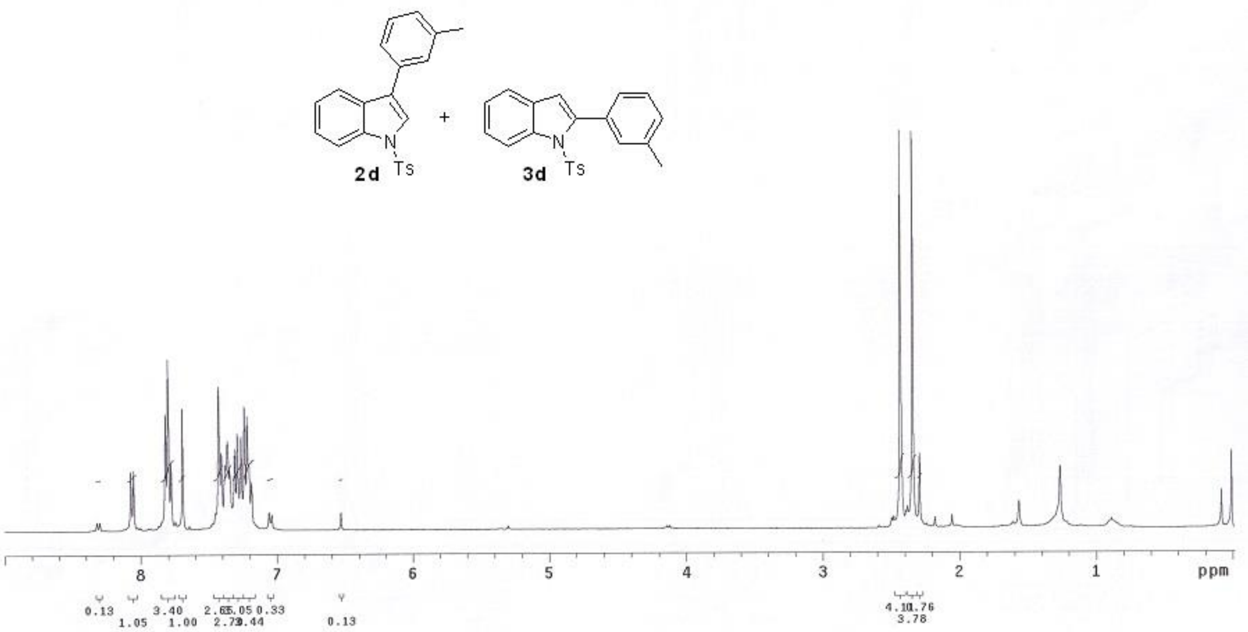



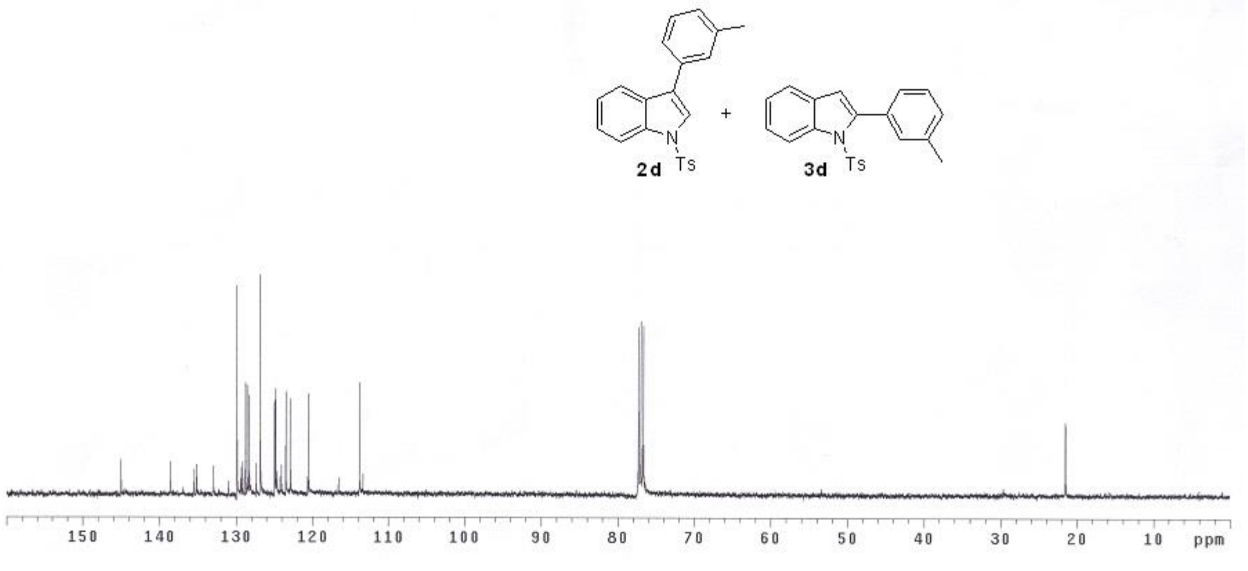
***N*-Ts-3-*p*-Tolylindole (2c)**



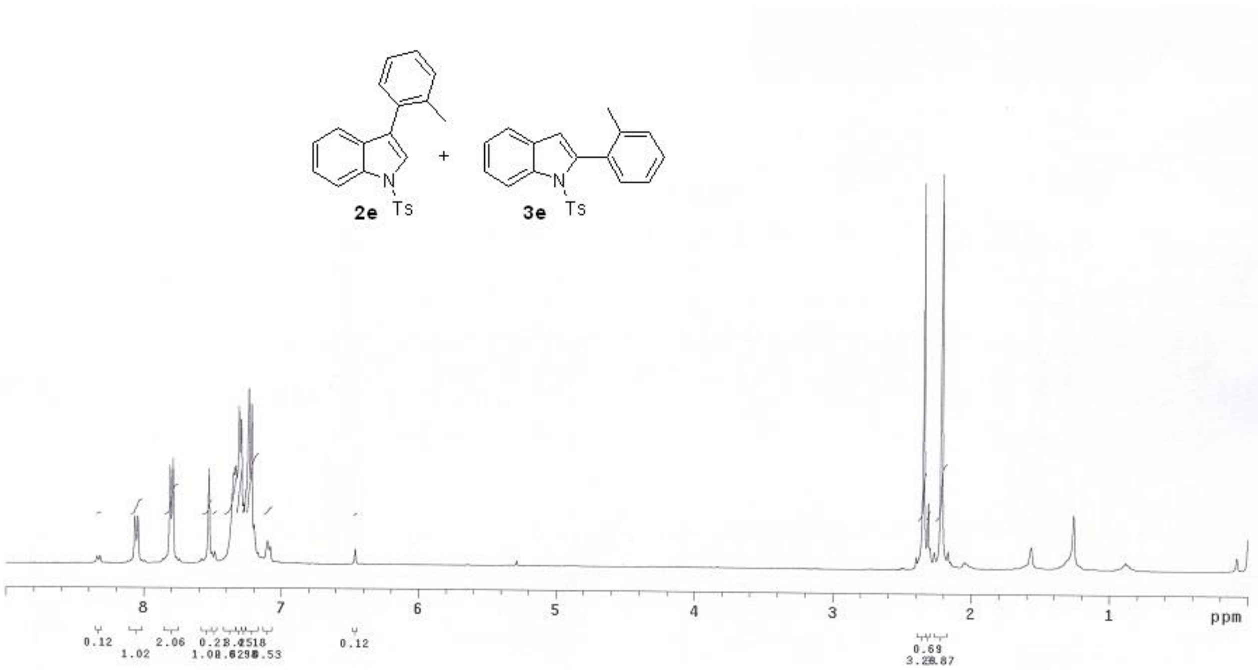



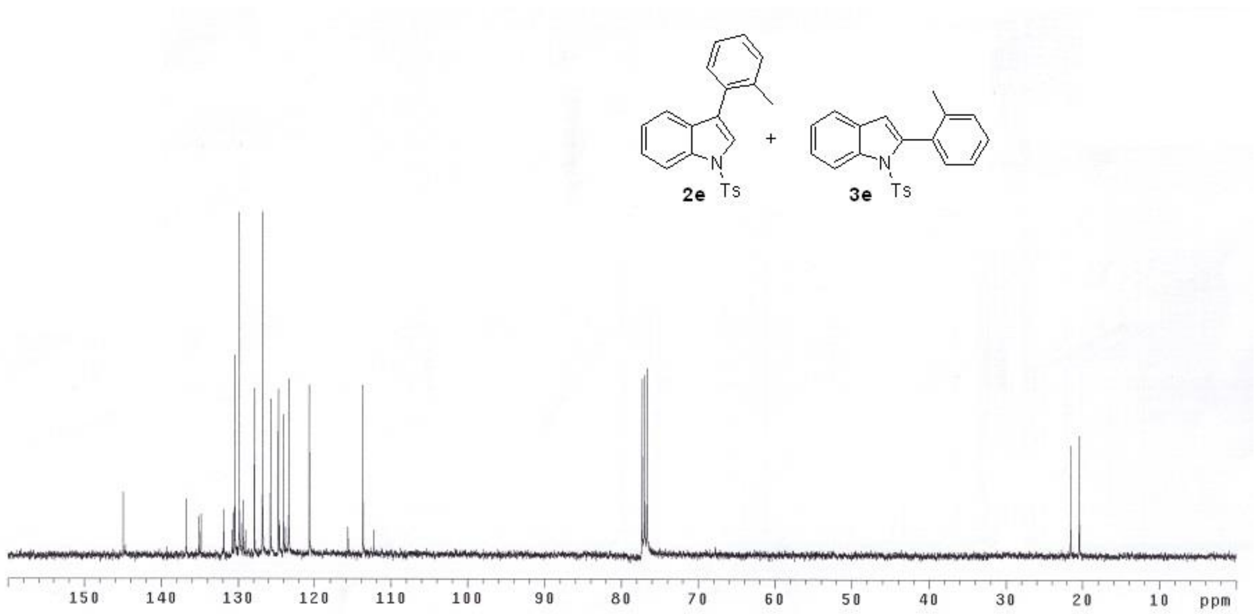
**N-Ts-3-m-Tolylindole (2d) & N-Ts-2-m-Tolylindole (3d)**



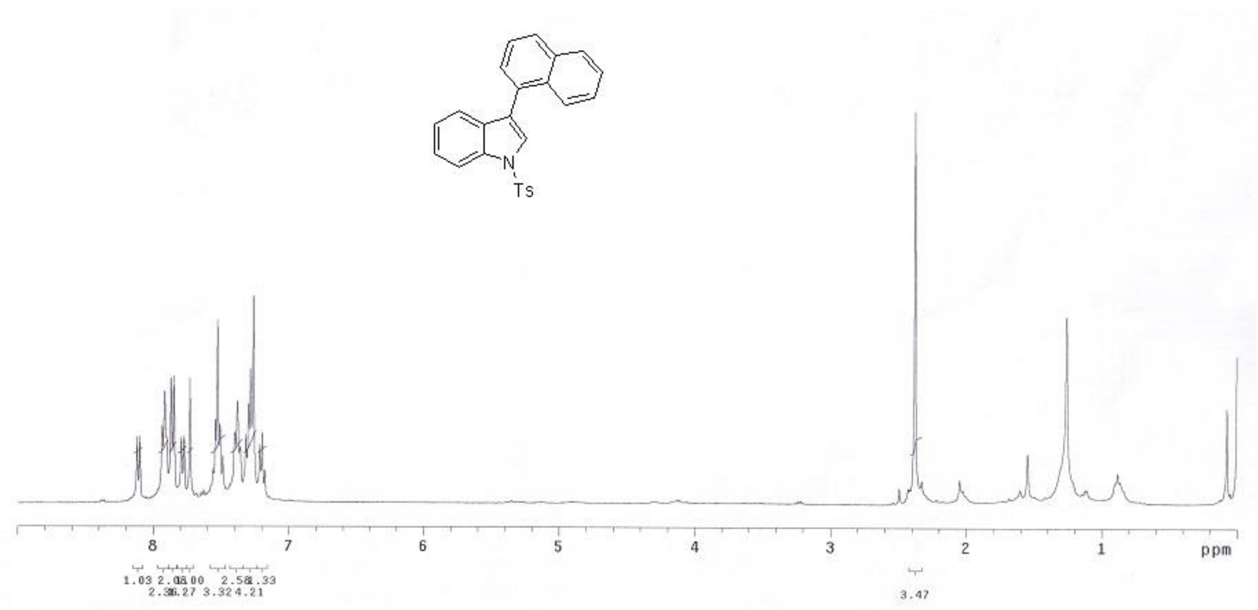



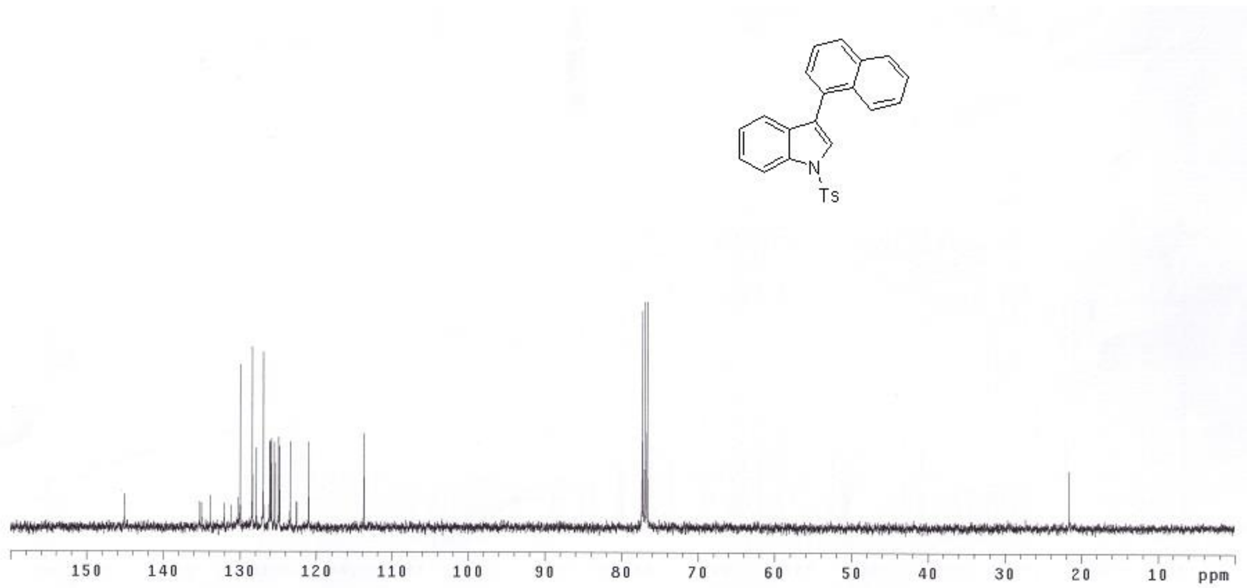
***N*-Ts-3-*o*-Tolylindole (2e) & *N*-Ts-2-*o*-Tolylindole (3e)**



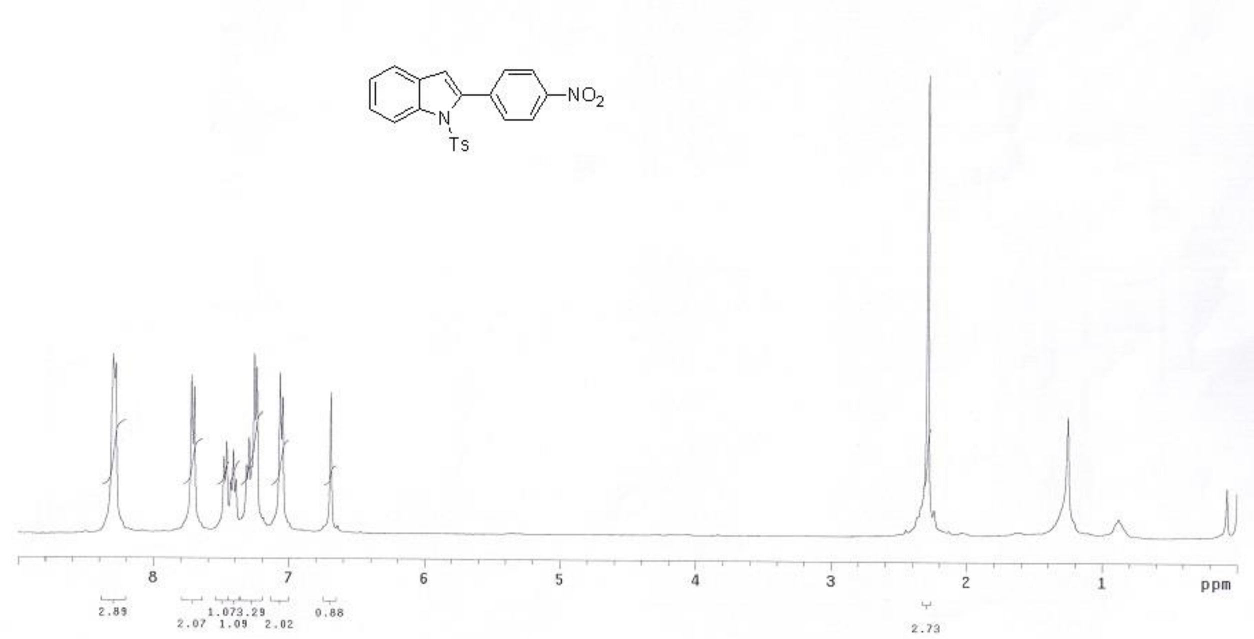



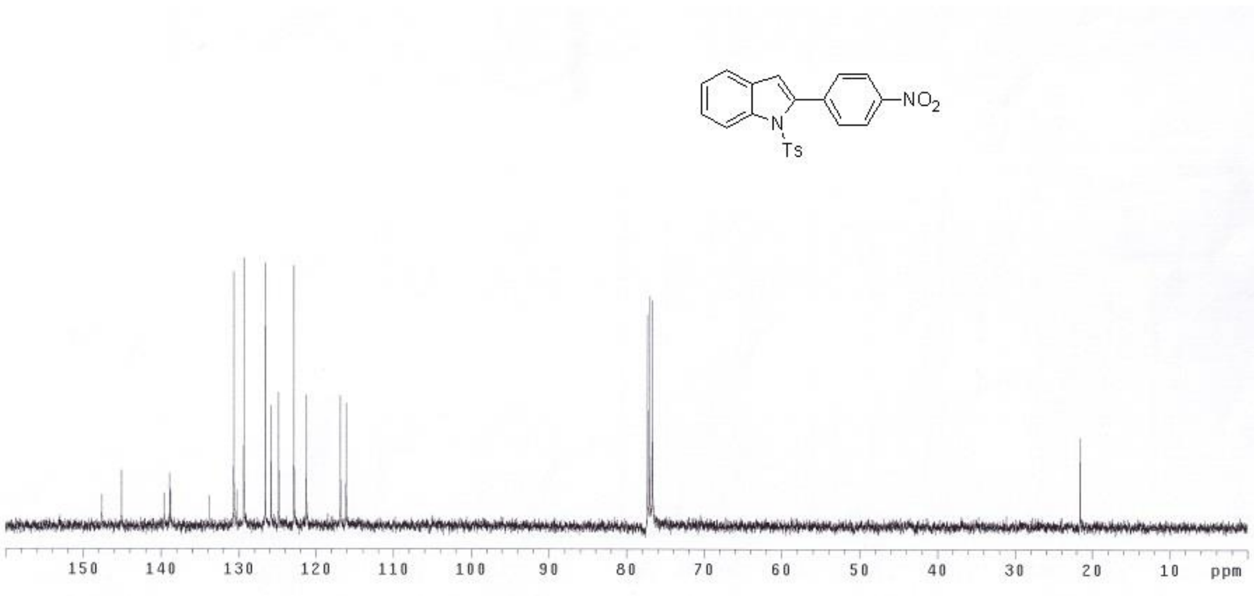
***N*-Ts-3-(1-Naphthyl)indole (2f)**



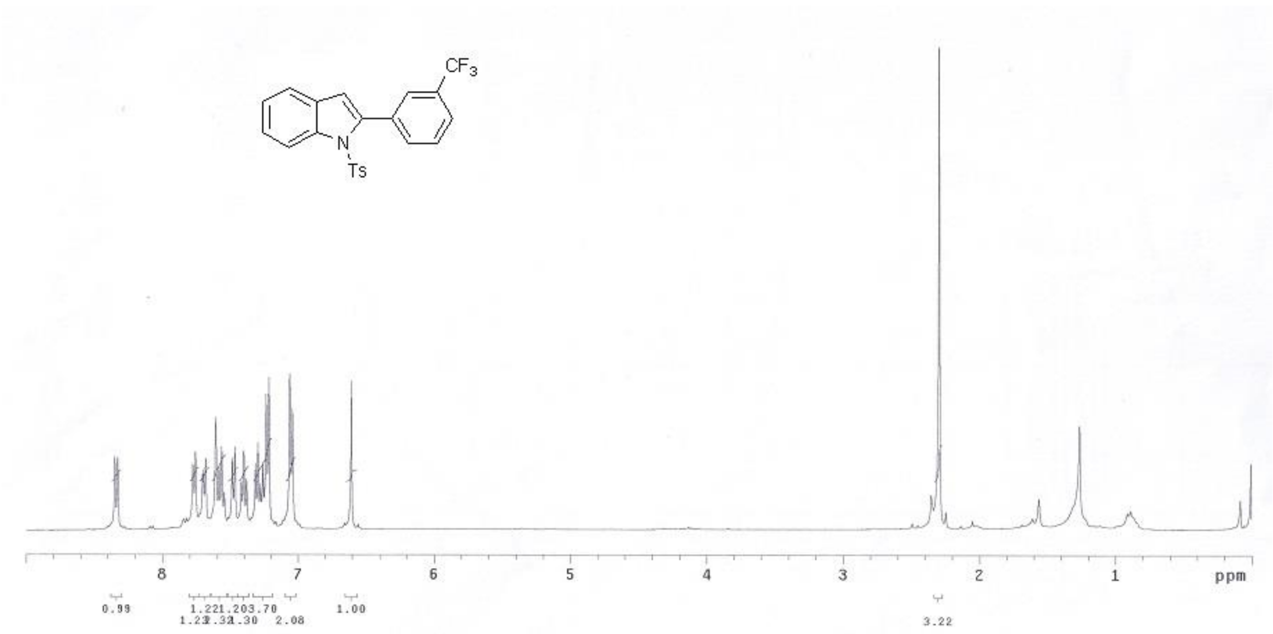



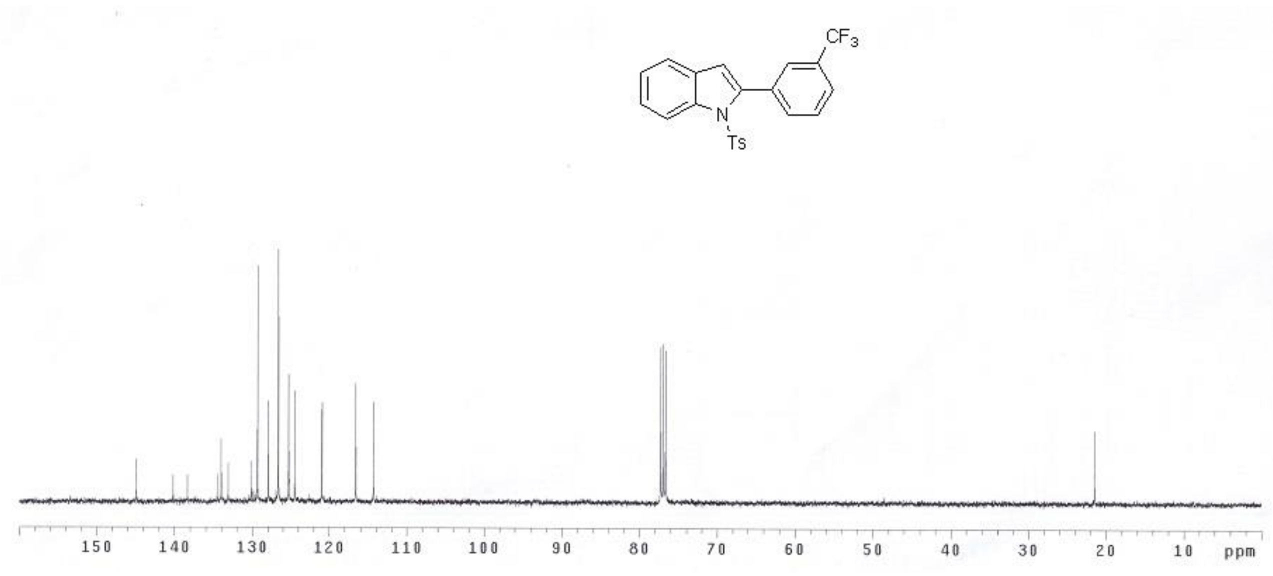
**_N_-Ts-2-(4-Nitrophenyl)indole (3g)**



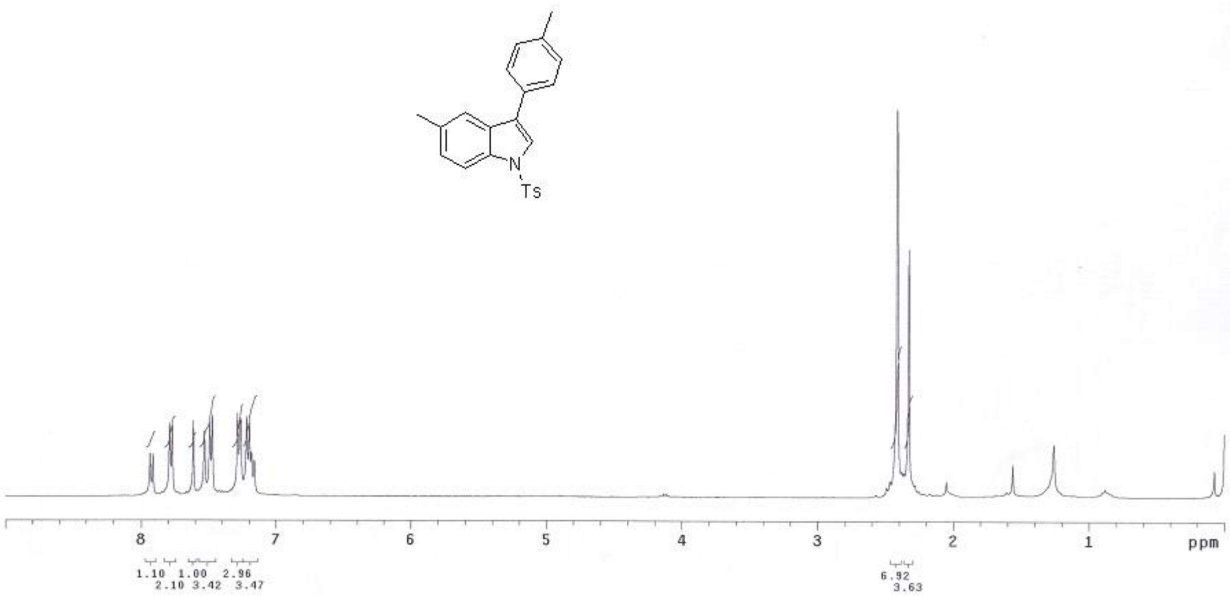



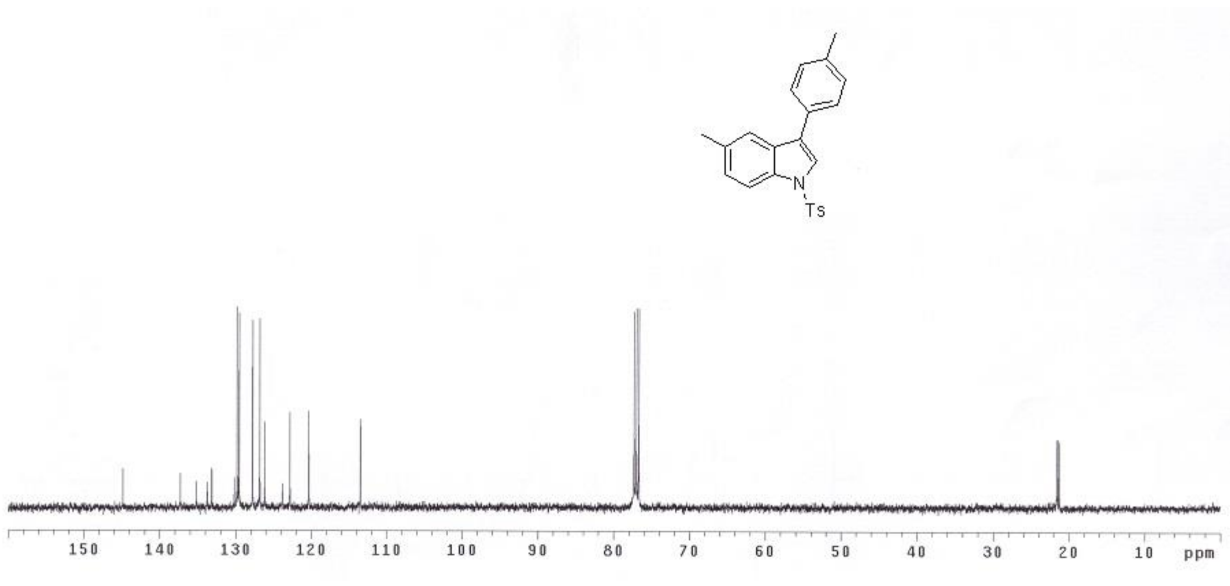
***N*-Ts-2-(3-(Trifluoromethyl)phenyl)indole (3h)**



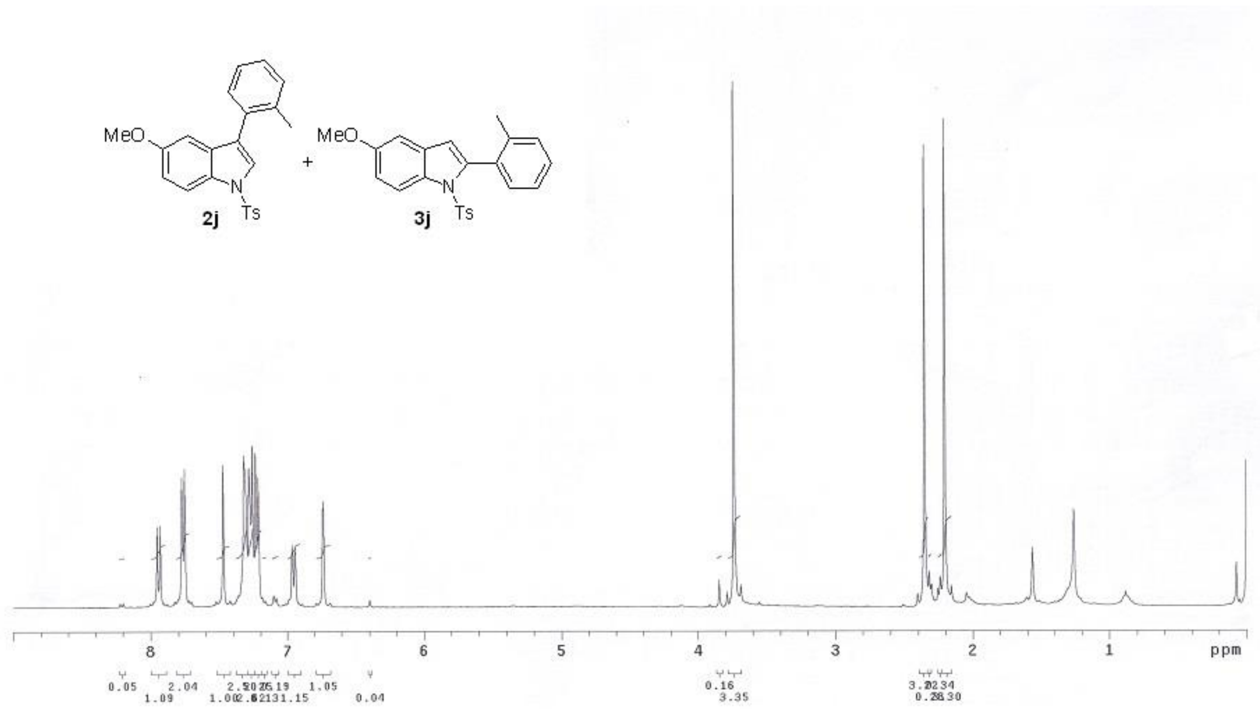



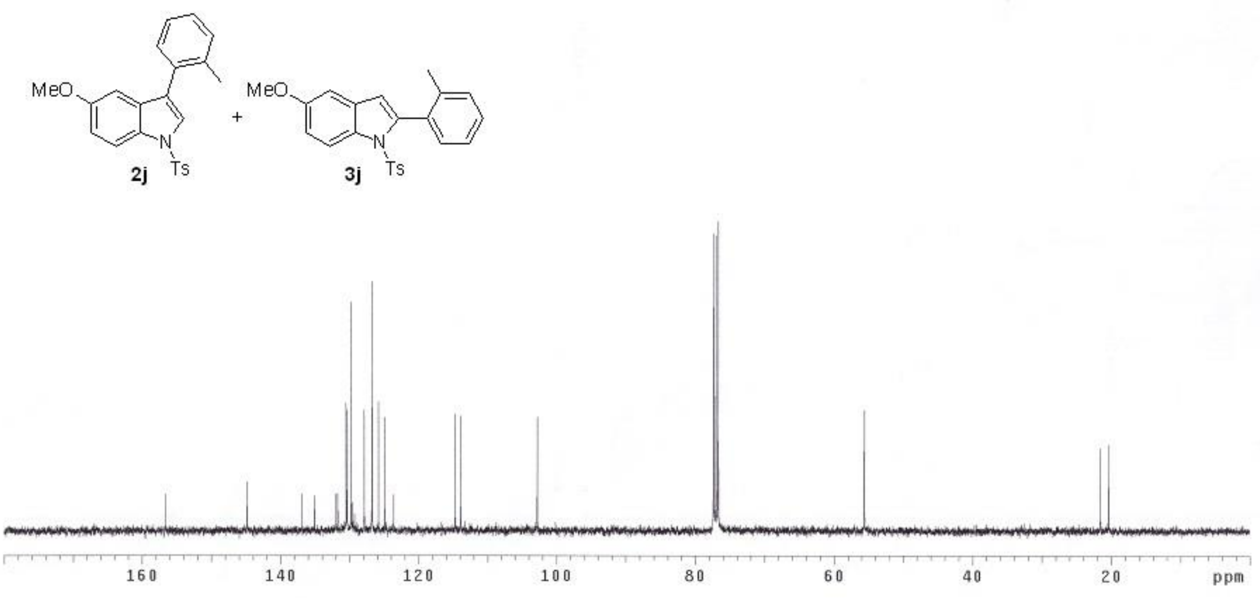
***N*-Ts-5-Methyl-3-*p*-tolylindole (2i)**



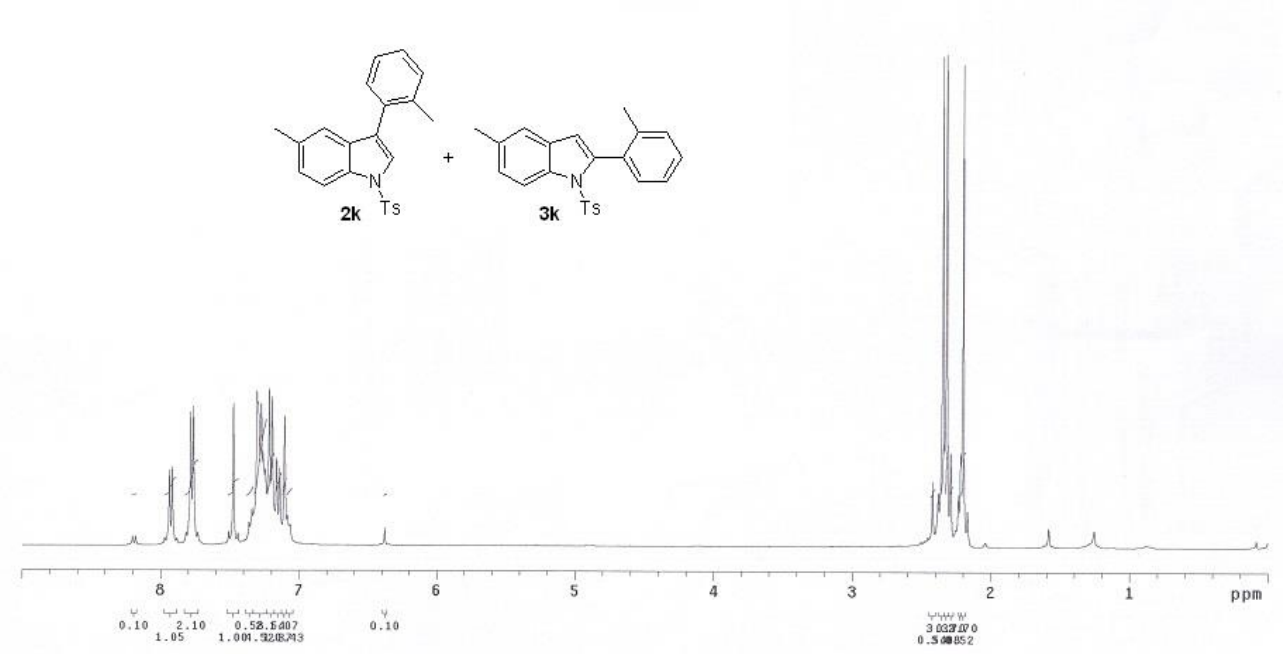



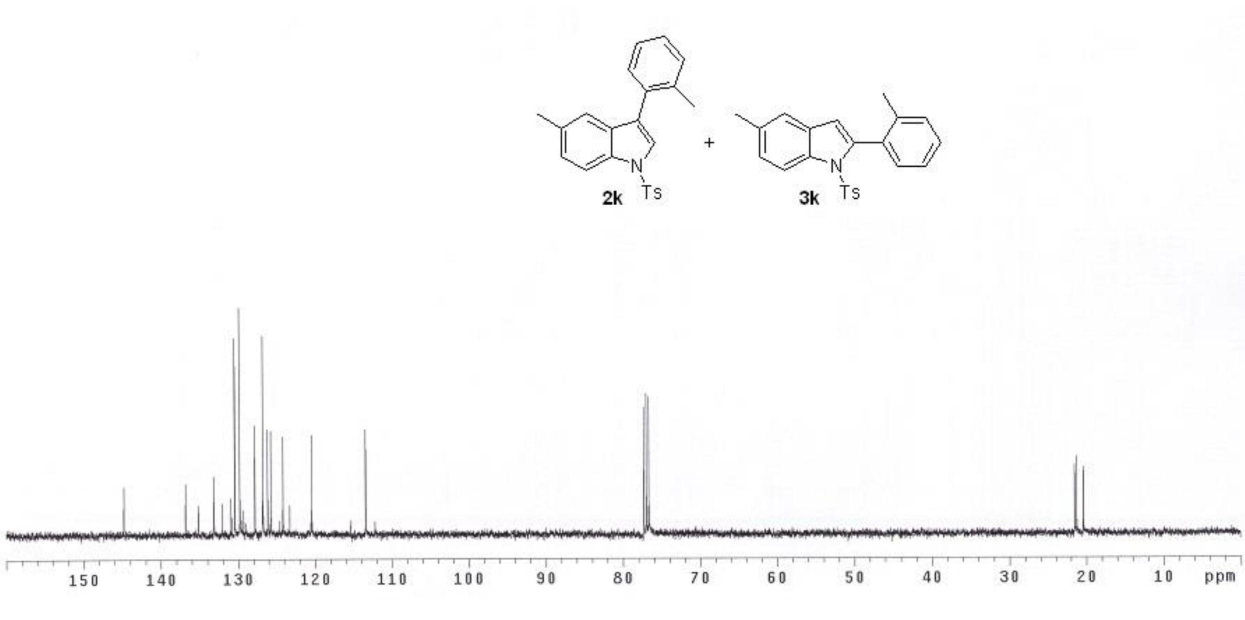
**_N_-Ts-5-Methoxy-3-_o_-tolylindole (2j) & _N_-Ts-5-Methoxy-2-_o_-tolylindole (3j)**



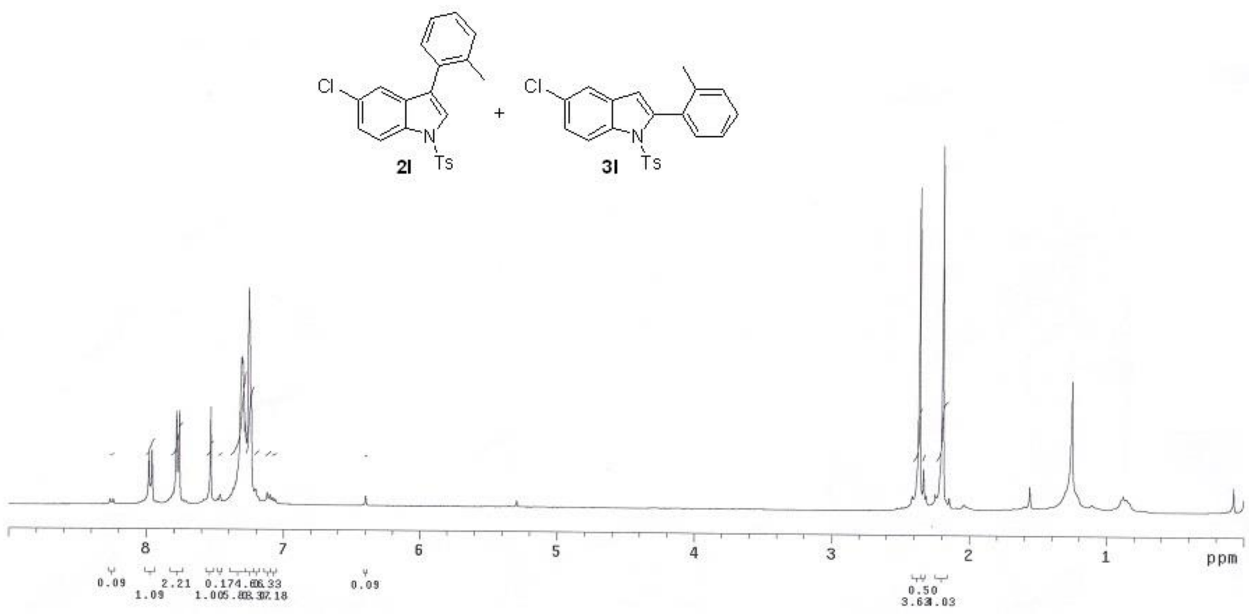



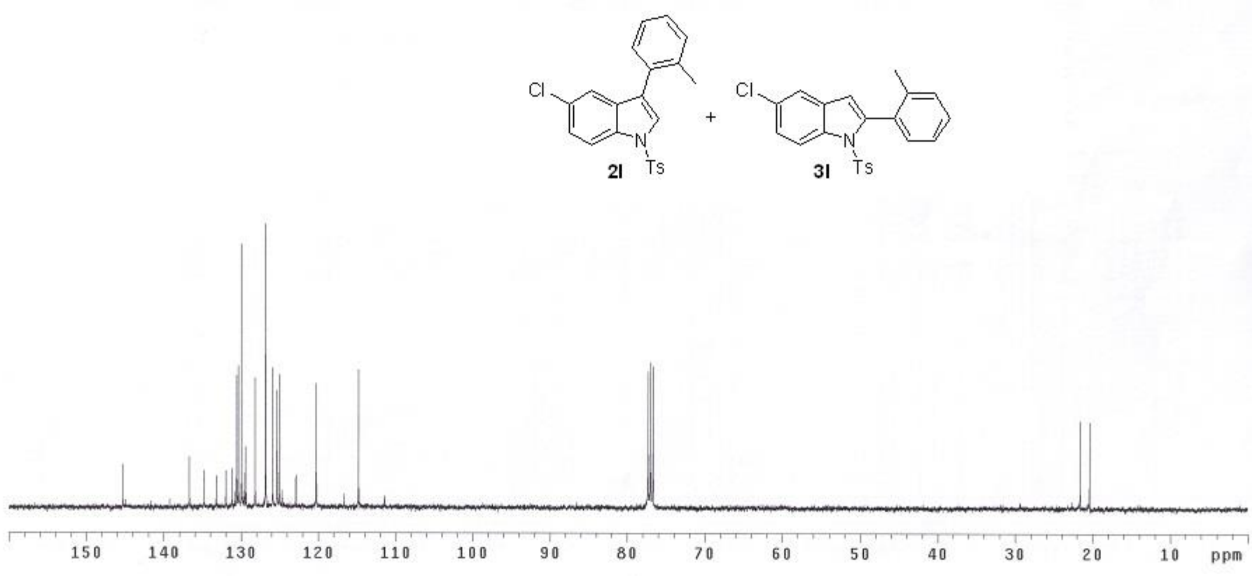
**_N_-Ts-5-Methyl-3-_o_-tolylindole (2k) & _N_-Ts-5-Methyl-2-_o_-tolylindole (3k)**



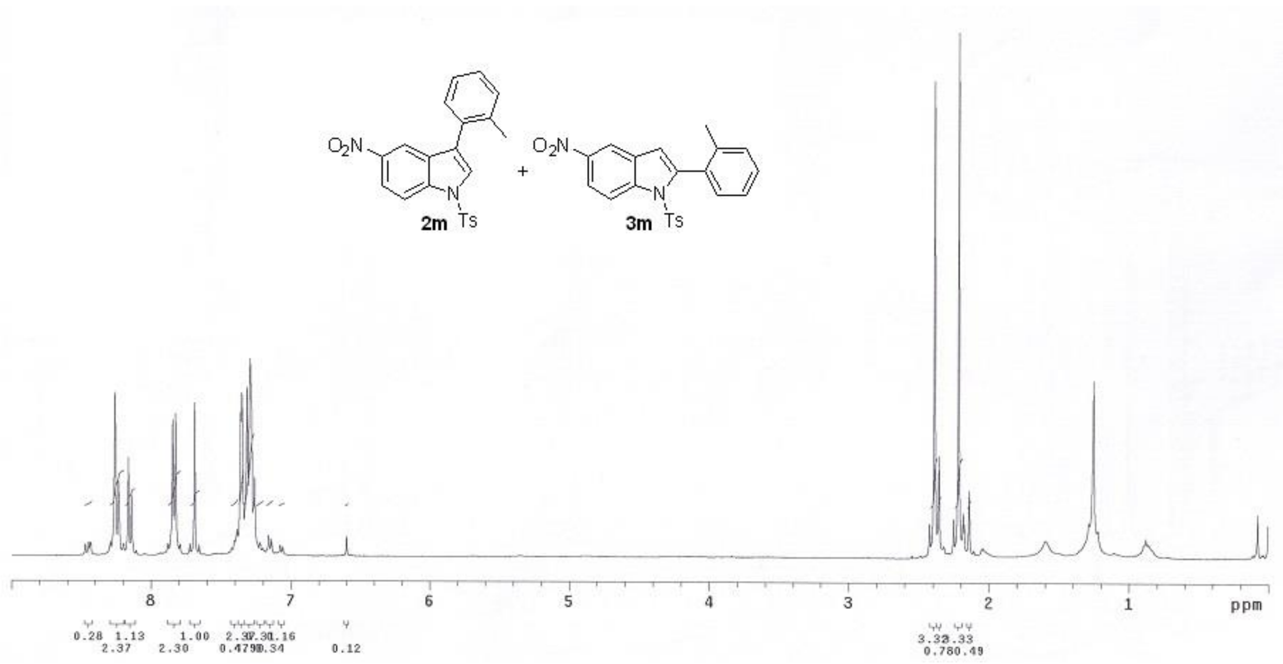



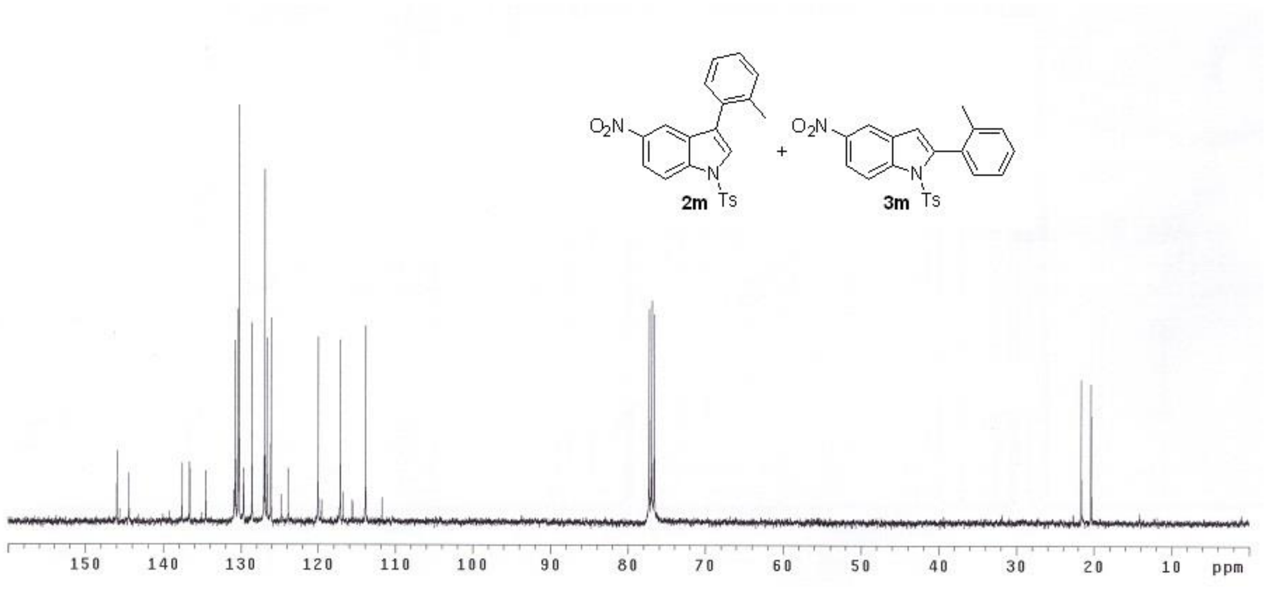
**_N_-Ts-5-Chloro-3-_o_-tolylindole (2l) & _N_-Ts-5-Chloro-2-_o_-tolylindole (3l)**



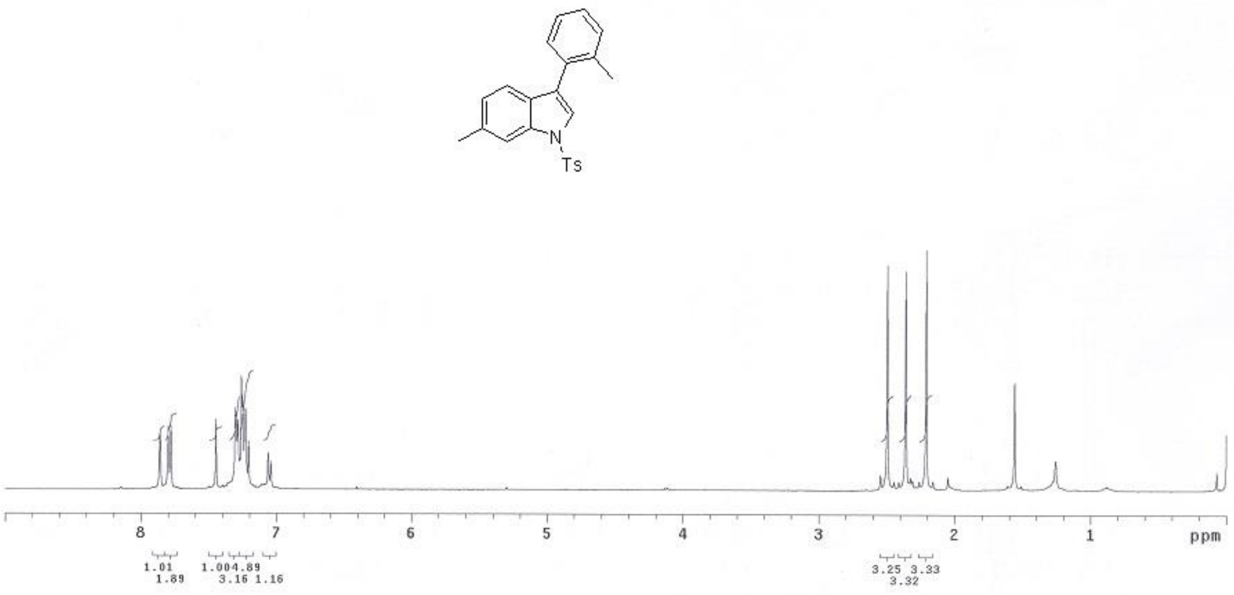



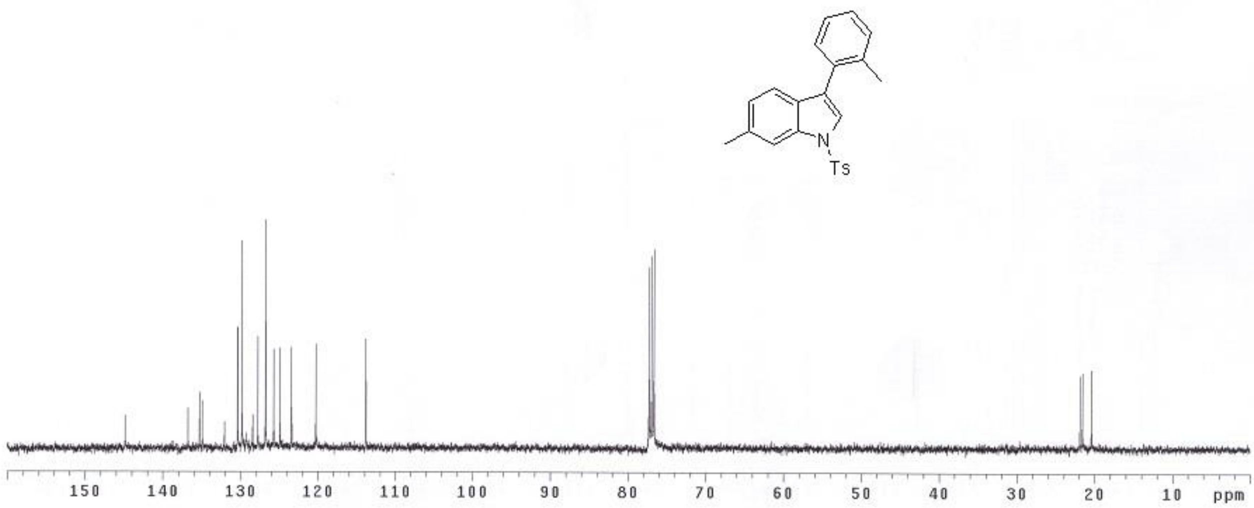
**N-Ts-5-Nitro-3-o-tolylindole (2m) & N-Ts-5-Nitro-2-o-tolylindole (3m)**



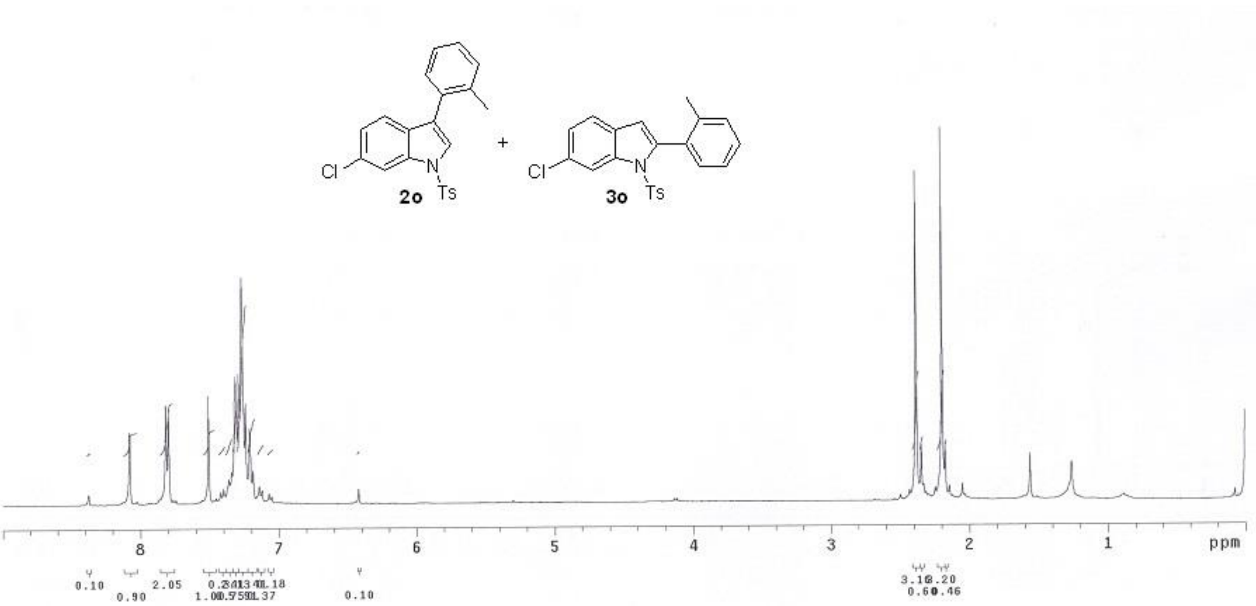



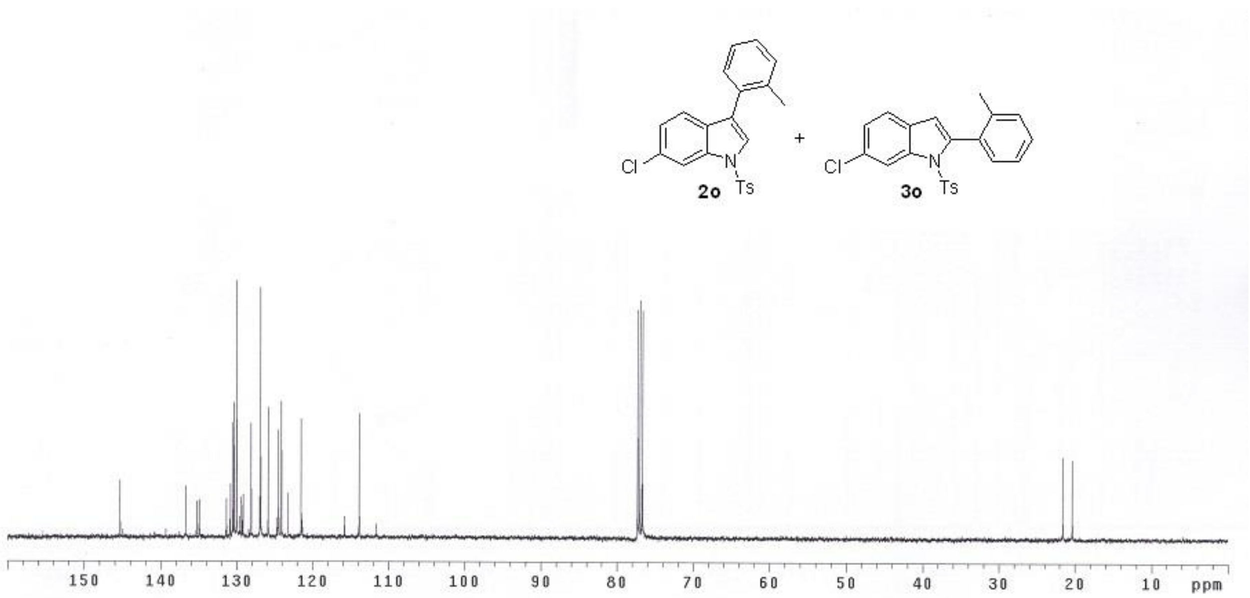
**N-Ts-6-Methyl-3-o-tolylindole (2n)**



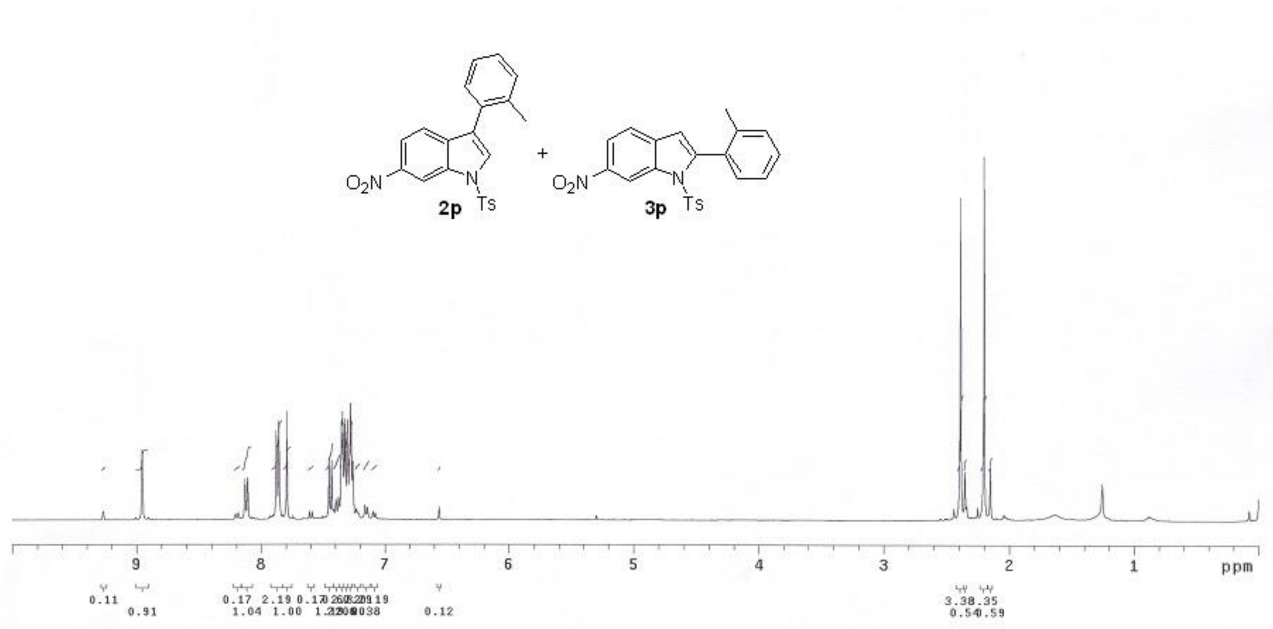



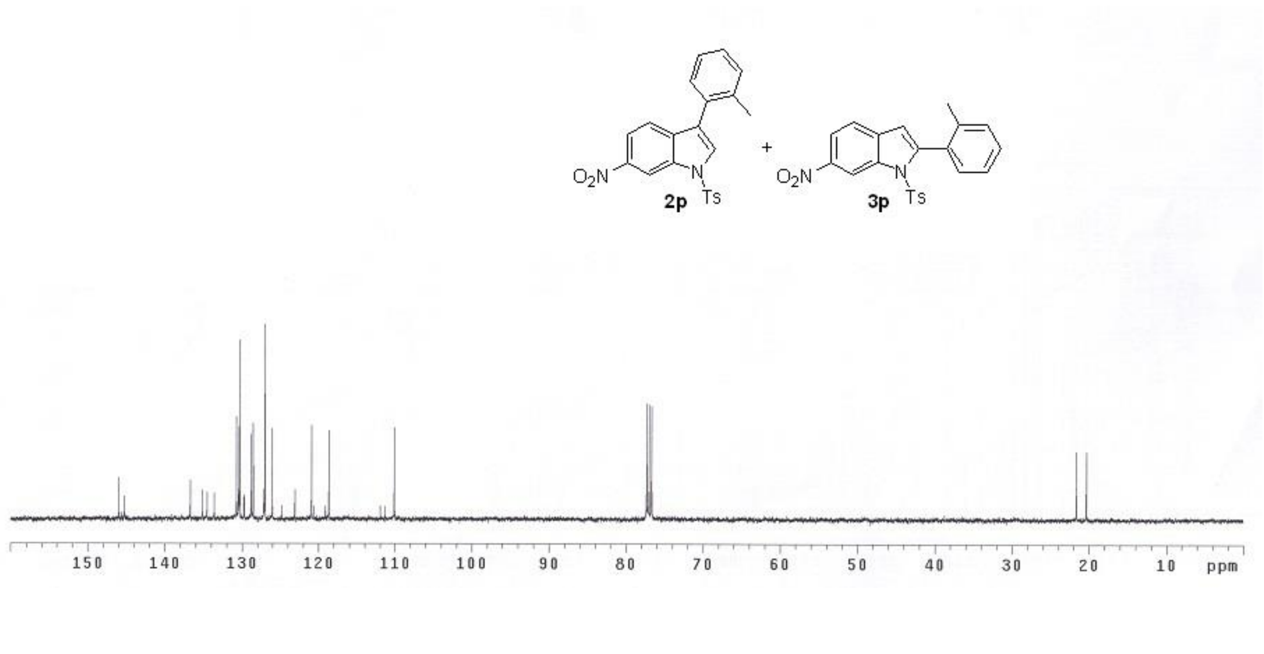
***N*-Ts-6-Chloro-3-*o*-tolylindole (2o) & *N*-Ts-6-Chloro-2-*o*-tolylindole (3o)**



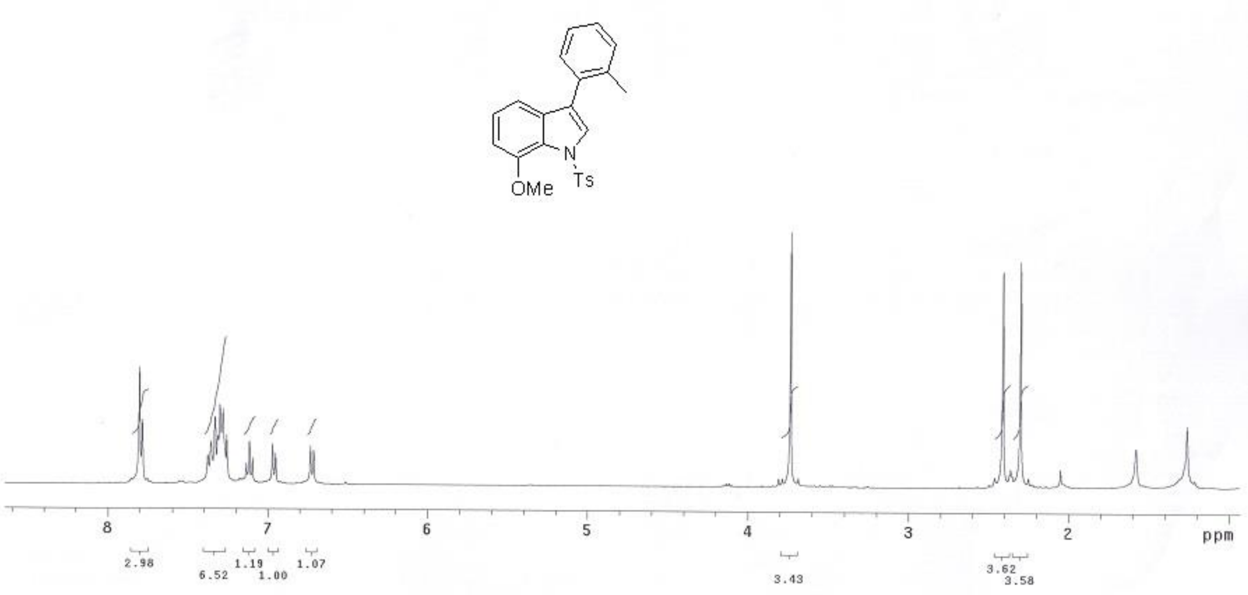



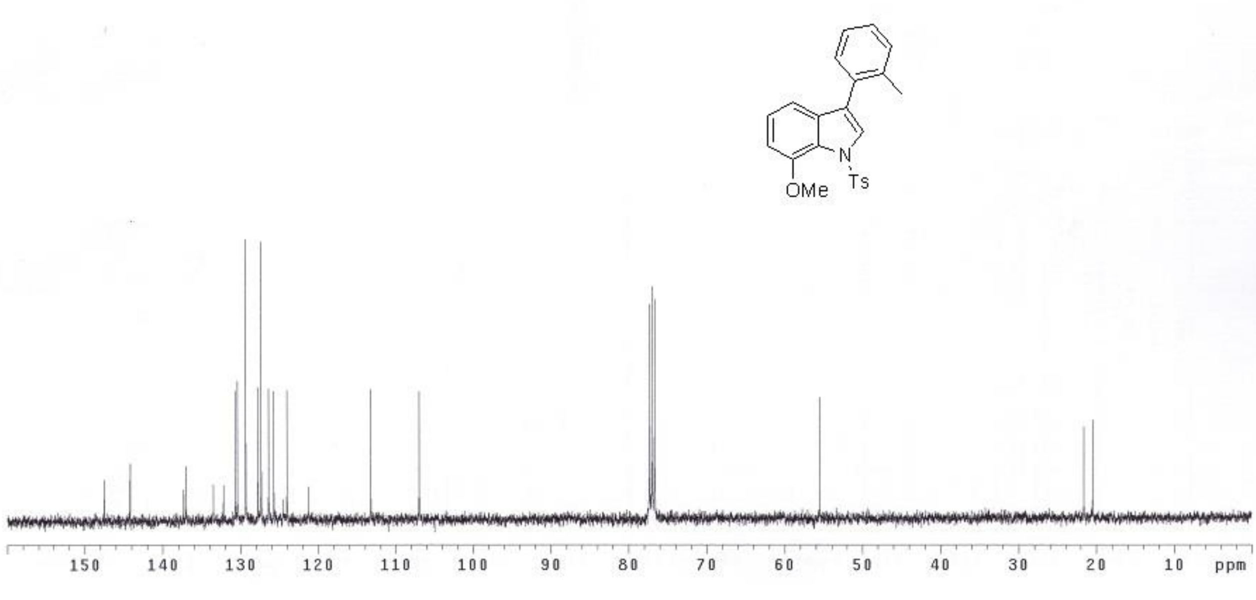
***N*-Ts-6-Nitro-3-*o*-tolylindole (2p) & *N*-Ts-6-Nitro-2-*o*-tolylindole (3p)**



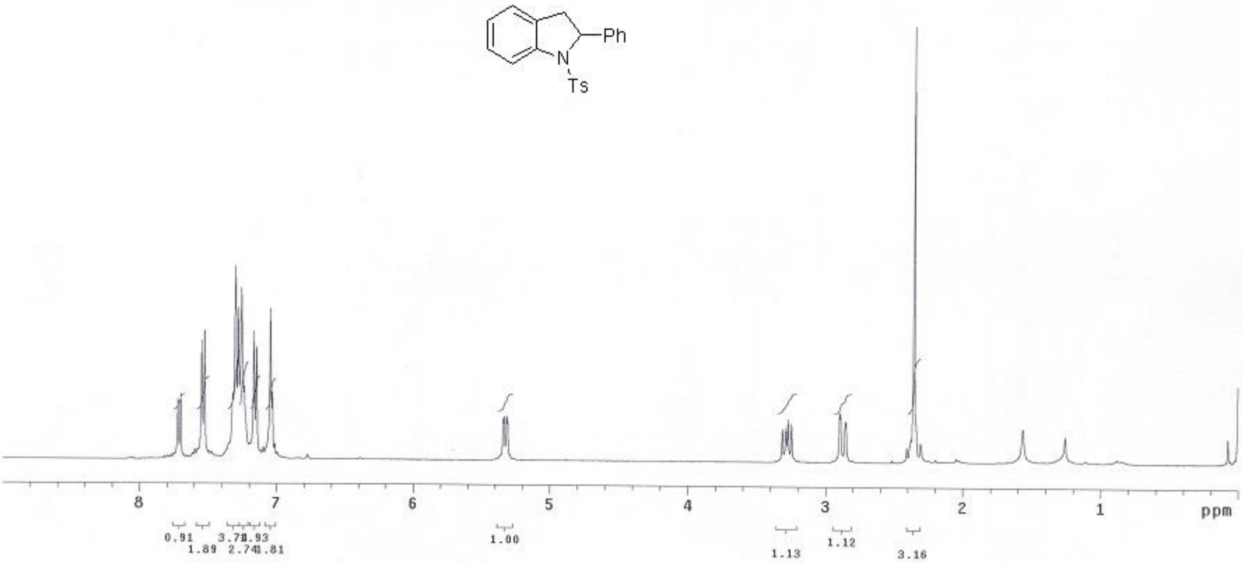



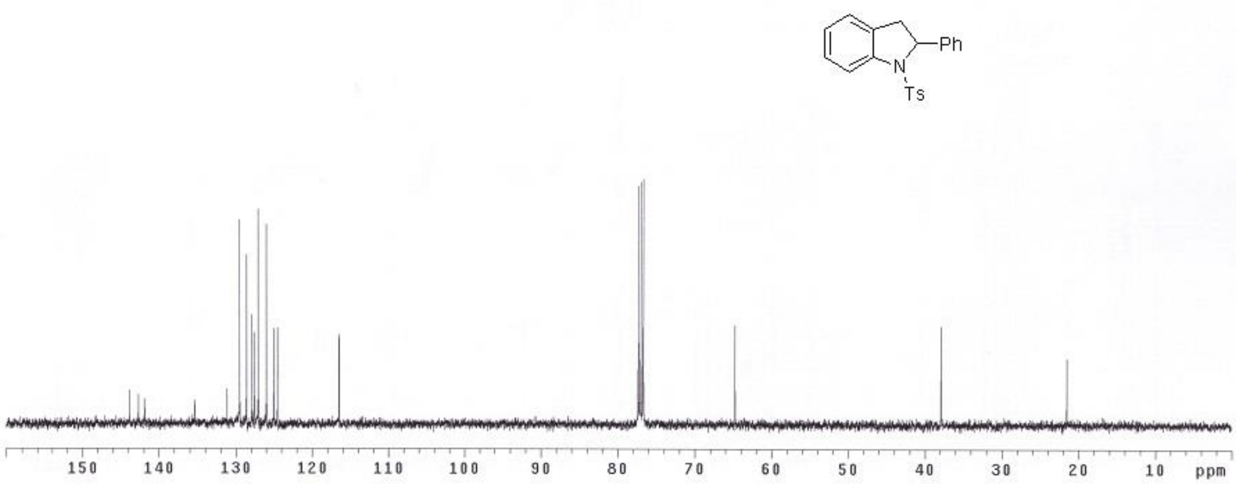
***N*-Ts-7-Methoxy-3-*o*-tolylindole (2q)**



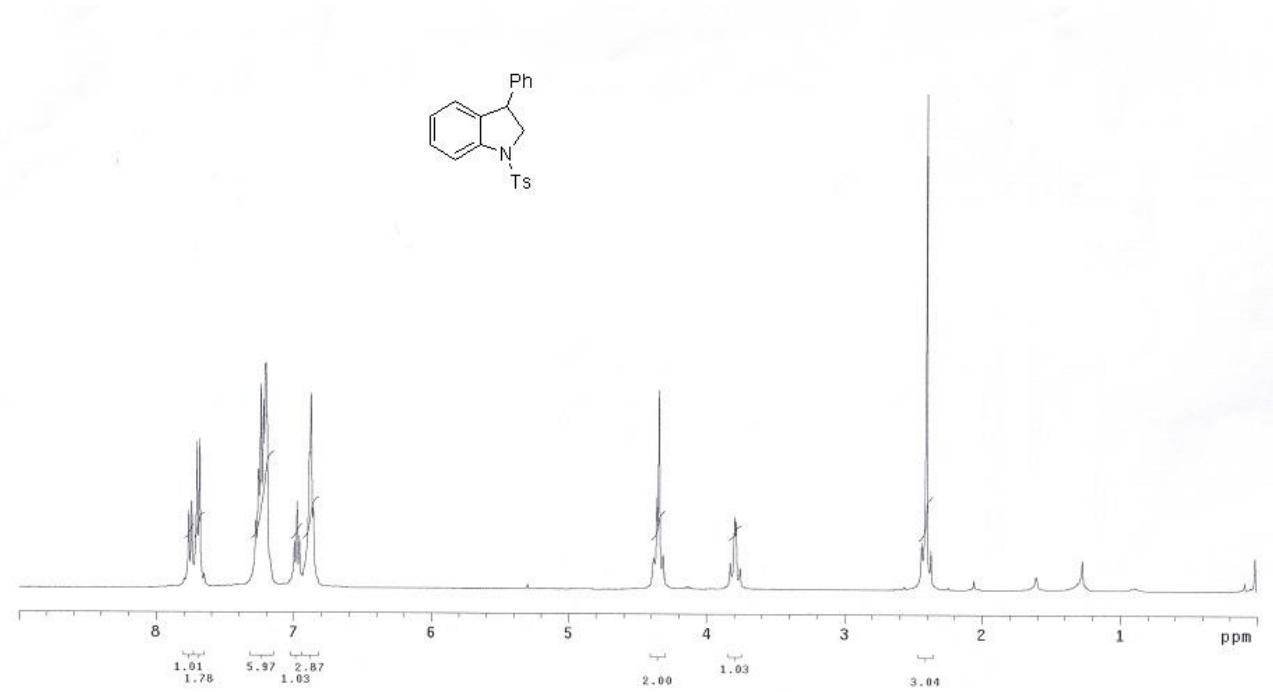



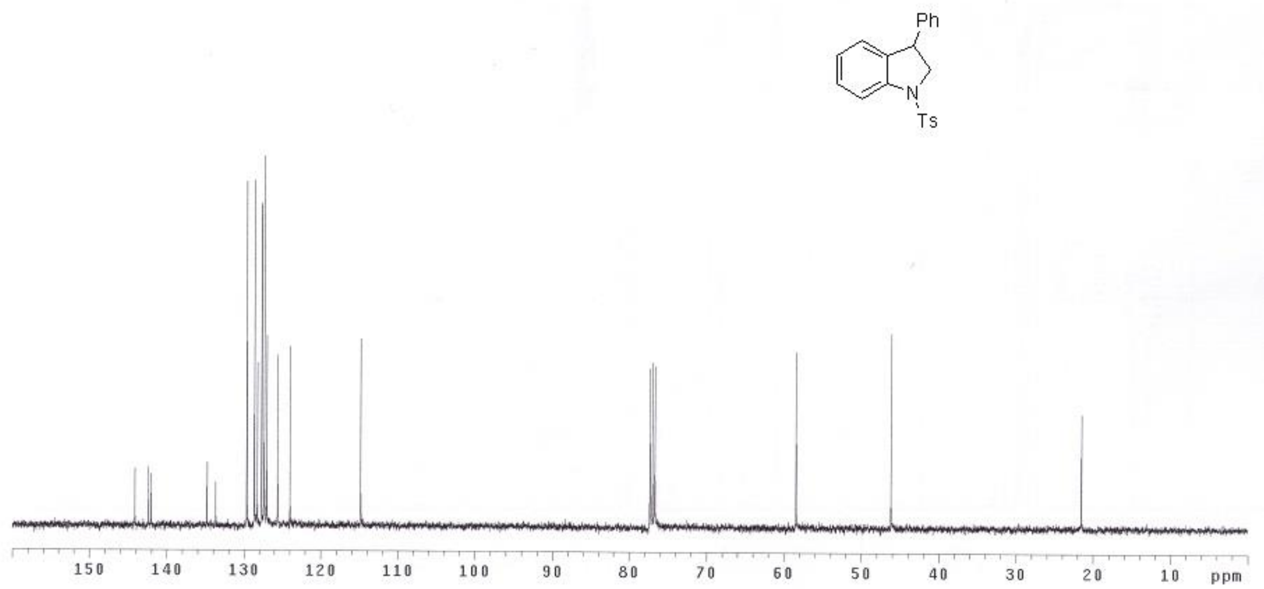
***N*-Ts-2-Phenylindoline (4a)**



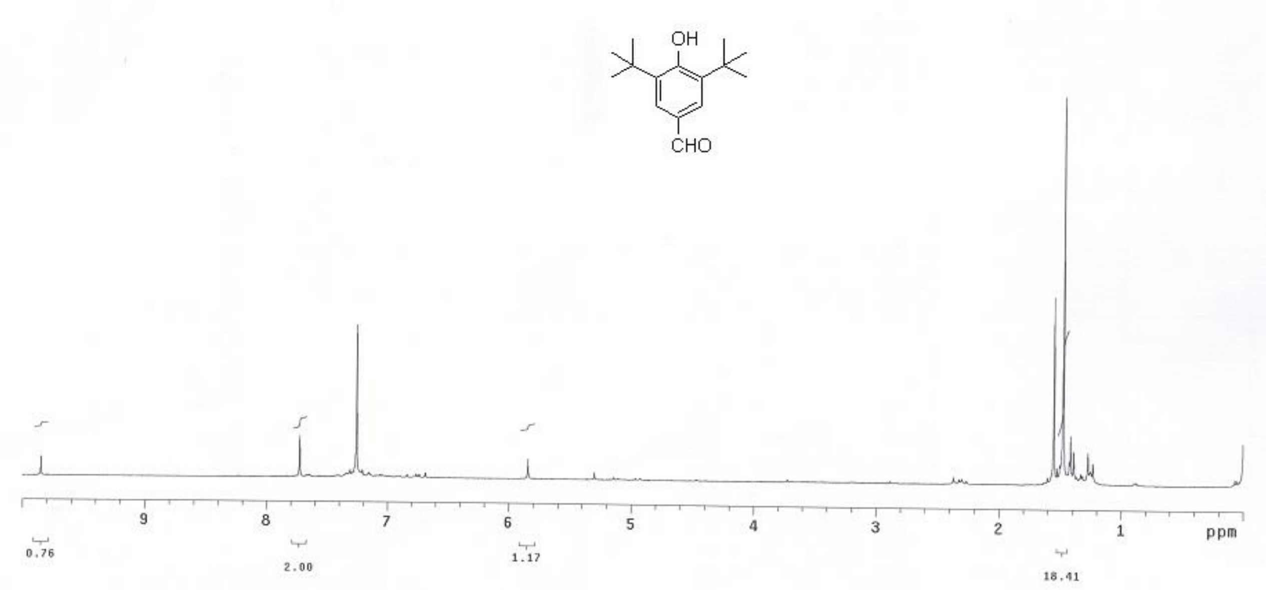



***N*-Ts-3-Phenylindoline (5a)**



**3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde**



**2,6-Di-*tert*-butyl-4-((2-phenyl-1-tosylindolin-3-yl)methyl)phenol**