Supporting Information

Metal-Free C-H Amination for Indole Synthesis

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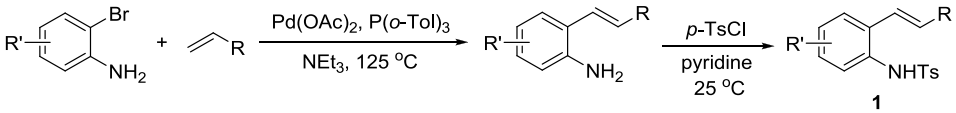
General Information

Nuclear Magnetic Resonance spectra were recorded on 300, 400, and 600 MHz instruments. Spectra were recorded in $CDCl_3$ solutions referenced to TMS or solvent residual peak. IR spectra were taken as a KBr pellet using FT-IR Spectrophotometer. High Resolution Mass Spectra were measured using EI at 70 eV. GC-MS spectra were recorded on a Perkin Elmer's Clarus 600S GC-system with Turbo mass ver.5.4.2 inert Mass Selective Detector (EI) and 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 ℃), after holding this temperature for 5 min, the column is heated to the temperature T_1 (ramp, 300 ℃, 10 ℃/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. CH_2Cl_2, CCl_4, CH_3CCl_3, and MeCN were distilled from CaH_2 immediately prior to use. Thin layer chromatograms (TLC) was visualized via UV.

General Procedure for the Preparation of 2-Styrylaniline Derivatives 1



1

Method A: 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 ℃ 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 (EtOAc : *n*-Hexane = 1:5) to afford the corresponding 2-styrylaniline product (e.g., R = Ph, R′ = H: 88%, a yellow solid).

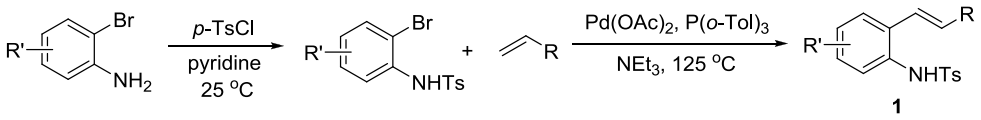
^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.85 (br s, 2H), 6.73 (d, J = 8.0 Hz, 1H), 6.81 (t, J = 7.6 Hz, 1H), 6.99 (d, J = 16.0 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 16.4 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 116.2, 119.1, 123.8, 124.2, 126.4, 127.2, 127.5, 128.7, 130.3, 137.6, 144.0 (1 carbon is missing due to overlapping). EIMS *m*/*z* 195 (M^+), 194, 165, 118, 89.

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

To a solution of 2-styrylaniline (2.3 g, 11.99 mmol, 1 equiv) in pyridine (60.0 mL, 0.2 M) was added *p*-toluenesulfonyl chloride (2.6 g, 13.19 mmol, 1.1 equiv) at 0 ℃. After being stirred at 25 ℃ for 2 hours, the reaction mixture was poured into water and then the product was extracted with

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

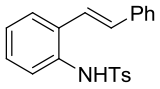
CH_2Cl_2 (three times), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give the corresponding product **1** (e.g., R = Ph, R′ = H (**1a**): 79%).



1

Method B: To a solution of 2-bromoaniline (319.3 mg, 1.856 mmol, 1 equiv) in pyridine (9.3 mL, 0.2 M) was added *p*-toluenesulfonyl chloride (397.2 mg, 2.042 mmol, 1.1 equiv) at 0 ℃. After being stirred at 25 ℃ 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 (EtOAc : *n*-Hexane = 1:8) to give the corresponding product (e.g., R′ = H: 91%). To a solution of *N*-Ts-2-bromoaniline (1 equiv) in NEt_3 (1.0 M) were added $Pd(OAc)_2$ (1 mol%), $P(o\text{-Tol})_3$ (8 mol%), and olefin (1.2 equiv). After being stirred at 125 ℃ 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.

(*E*)-4-Methyl-*N*-(2-styrylphenyl)benzenesulfonamide (1a)

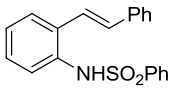


Following the Method A: 88% (step 1), 79% (step 2), a white solid (EtOAc : *n*-Hexane = 1:5 (step 1), 1:5 (step 2)). mp 138-141 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 6.62 (br s, 1H), 6.77 (d, J = 16.0 Hz, 1H), 6.83 (d, J = 16.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.23-7.38 (m, 8H), 7.49 (d, J = 6.4 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 122.6, 126.5, 126.6, 126.7, 127.06, 127.13, 128.1, 128.4, 128.6, 129.7, 132.2, 133.2, 136.5, 136.6, 143.9 (1 carbon is missing due to overlapping). EIMS *m*/*z* 349 (M^+), 194, 165, 117, 91.

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

(*E*)-*N*-(2-Styrylphenyl)benzenesulfonamide



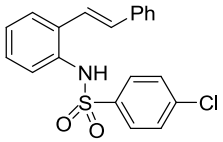
Following the Method A using benzenesulfonyl chloride as a sulfonylation reagent in place of *p*-TsCl: 83% (step 2), a pale yellow solid (EtOAc : *n*-Hexane = 1:2 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.45 (br s, 1H), 6.75 (d, J = 16.4 Hz, 1H), 6.80 (d, J = 16.0 Hz, 1H), 7.21-7.37 (m, 8H), 7.41 (t, J = 7.8 Hz, 2H), 7.47-7.52 (m, 2H), 7.73 (d, J = 7.2 Hz, 2H). ^{13}C NMR

[2] Bihn, J. H.; Kim, B. S.; Youn, S. W. *Org. Lett.* **2011**, *13*, 3738.

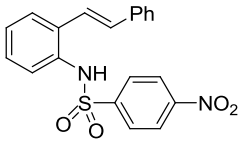
($CDCl_3$, 100 MHz) δ 122.5, 126.56, 126.62, 126.7, 127.1, 128.1, 128.4, 128.6, 129.0, 132.3, 133.00, 133.02, 133.2, 136.6, 139.4 (1 carbon is missing due to overlapping). EIMS *m*/*z* 335 (M^+), 194, 165, 152, 139, 128, 117, 97, 89, 77, 65, 51.

(*E*)-4-Chloro-*N*-(2-styrylphenyl)benzenesulfonamide



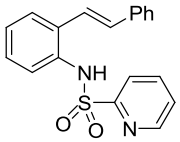
Following the Method A using 4-chlorobenzenesulfonyl chloride as a sulfonylation reagent in place of *p*-TsCl: 96% (step 2), a white solid (EtOAc : *n*-Hexane = 1:5 (step 2)).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.53 (br s, 1H), 6.77 (d, *J* = 16.4 Hz, 1H), 6.82 (d, *J* = 16.0 Hz, 1H), 7.24-7.38 (m, 10H), 7.49-7.51 (dd, *J* = 3.4, 5.4 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.4, 126.6, 126.7, 127.0, 127.5, 128.2, 128.4, 128.6, 128.7, 129.3, 132.4, 132.6, 133.6, 136.5, 137.7, 139.6. EIMS *m*/*z* 369 (M^+), 194, 177, 165, 152, 139, 118, 102, 89, 84, 65, 51.

(*E*)-4-Nitro-*N*-(2-Styrylphenyl)benzenesulfonamide



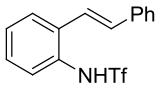
Following the Method A using 4-nitrobenzenesulfonyl chloride as a sulfonylation reagent in place of *p*-TsCl: 79% (step 2), a yellow solid (EtOAc : *n*-Hexane = 1:5 (step 2)).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.60 (br s, 1H), 6.71 (d, *J* = 16.4 Hz, 1H), 6.76 (d, *J* = 16.4 Hz, 1H), 7.23-7.38 (m, 8H), 7.50-7.52 (m, 1H), 7.85 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.1, 124.1, 126.4, 126.7, 127.8, 128.2, 128.4, 128.5, 128.7, 128.8, 131.9, 132.6, 134.0, 136.2, 144.9, 150.0. EIMS *m*/*z* 380 (M^+), 252, 207, 194, 165, 152, 117, 89, 76, 63, 51.

(*E*)-*N*-(2-Styrylphenyl)pyridine-2-sulfonamide



Following the Method A using 2-pyridinylsulfonyl chloride as a sulfonylation reagent in place of *p*-TsCl: 95% (step 2), a white solid (EtOAc : *n*-Hexane = 1:5 (step 2)).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.88 (d, *J* = 16.0 Hz, 1H), 7.19-7.23 (m, 3H), 7.29-7.39 (m, 6H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.48-7.53 (m, 1H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 8.65 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.9, 123.1, 126.1, 126.8, 126.9, 127.1, 127.2, 128.0, 128.2, 128.6, 131.6, 132.7, 133.5, 136.7, 137.9, 150.0, 156.5. EIMS *m*/*z* 336 (M^+), 194, 165, 78.

(*E*)-1,1,1-Trifluoro-*N*-(2-Styrylphenyl)methanesulfonamide

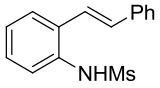


Following the Method A using Tf_2O as a sulfonylation reagent in place of *p*-TsCl: 87% (step 2), a white solid (EtOAc : *n*-Hexane = 1:5 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.65 (br s, 1H), 7.09 (d, J = 16.0 Hz, 1H), 7.28-7.42 (m, 6H), 7.46 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 7.2 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 119.9 (q, J = 213.6 Hz), 121.9, 126.9, 127.3, 128.66, 128.71, 128.8, 128.9, 129.0, 130.8, 133.7, 134.3, 136.6. EIMS *m*/*z* 327 (M^+), 194, 165, 117, 89.

Spectral data were consistent with data reported in the literature.[3]

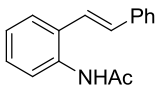
(*E*)-*N*-(2-Styrylphenyl)methanesulfonamide



Following the Method A using MsCl as a sulfonylation reagent in place of *p*-TsCl: 92% (step 2), a white solid (EtOAc : *n*-Hexane = 1:2 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.03 (s, 3H), 6.46 (br s, 1H), 7.06 (d, J = 16.0 Hz, 1H), 7.28-7.34 (m, 4H), 7.39 (t, J = 7.4 Hz, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.8, 122.7, 125.2, 126.8, 126.9, 128.2, 128.6, 128.7, 132.5, 132.6, 133.3, 136.7 (1 carbon is missing due to overlapping). EIMS *m*/*z* 273 (M^+), 194, 165, 117, 89.

(*E*)-*N*-(2-Styrylphenyl)acetamide



Following the Method A using AcCl in place of *p*-TsCl: 88% (step 2), a white solid (EtOAc : *n*-Hexane = 1:5 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.23 (s, 3H), 7.01 (d, J = 16.0 Hz, 1H), 7.14 (d, J = 16.0 Hz, 1H), 7.15 (br s, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.1, 123.5, 124.5, 125.6, 126.56, 126.63, 128.0, 128.2, 128.7, 130.5, 132.0, 134.6, 137.0, 168.8. EIMS *m*/*z* 237 (M^+), 194, 165, 118, 89.

Spectral data were consistent with data reported in the literature.[4]

(*E*)-2,2,2-Trifluoro-*N*-(2-styrylphenyl)acetamide

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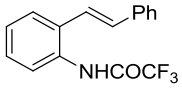
[3] Swingle, K. F.; Harrington, J. K.; Moore, G. G. I. *J. Med. Chem.* **1975**, *18*, 386.

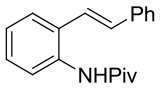
[4] Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9982.



Following the Method A using $(CF_3CO)_2O$ in place of *p*-TsCl: 93% (step 2), a white solid (EtOAc : *n*-Hexane = 1:10 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.04 (d, J = 16.4 Hz, 1H), 7.09 (d, J = 16.0 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 6.8 Hz, 1H), 7.35 (t, J = 6.8 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.94 (br s, 1H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 116.0 (q, J = 191.4 Hz), 122.0, 124.0, 126.9, 127.5, 127.6, 128.68, 128.73, 129.0, 131.1, 131.7, 134.3, 136.5, 155.3 (q, J = 24.7 Hz). EIMS *m*/*z* 291 (M^+), 194, 165, 89, 69.

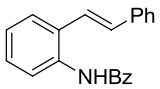
(*E*)-*N*-(2-Styrylphenyl)pivalamide



Following the Method A using PivCl in place of *p*-TsCl: 99% (step 2), a white solid (EtOAc : *n*-Hexane = 1:5 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (s, 9H), 7.00 (d, J = 16.4 Hz, 1H), 7.13 (d, J = 16.4 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.8 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.45 (br s, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.7, 39.7, 123.2, 123.9, 125.2, 126.4, 126.9, 128.1, 128.3, 128.8, 130.2, 132.6, 134.8, 136.9, 176.6. EIMS *m*/*z* 279 (M^+), 194, 118, 57.

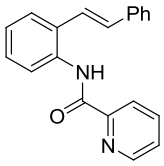
(*E*)-*N*-(2-Styrylphenyl)benzamide



Following the Method A using BzCl in place of *p*-TsCl: 78% (step 2), a white solid (EtOAc : *n*-Hexane = 1:3 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.06 (d, J = 16.0 Hz, 1H), 7.20-7.24 (m, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.4 Hz, 3H), 7.49 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 7.58 (t, J = 8.6 Hz, 2H), 7.88 (br s, 1H), 7.90 (d, J = 7.2 Hz, 2H), 7.99 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.3, 124.1, 125.7, 126.7, 127.1, 128.1, 128.4, 128.8, 128.9, 130.6, 131.9, 132.9, 134.6, 134.7, 136.8, 165.7 (1 carbon is missing due to overlapping). EIMS *m*/*z* 299 (M^+), 194, 165, 117, 105, 77.

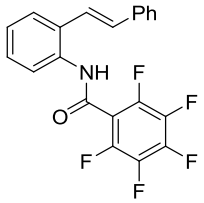
(*E*)-*N*-(2-Styrylphenyl)picolinamide



To the stirred suspension of picolinic acid (250.0 mg, 2.031 mmol, 1 equiv) in CH_2Cl_2 (4.1 mL, 0.5

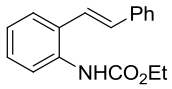
M) was added oxalyl chloride (199 μL, 2.234 mmol, 1.1 equiv) dropwise over a 15 minute period at 0 ℃ followed by addition of DMF (47 μL, 0.203 mmol, 10 mol %) in one portion, producing a rust-red color and the evolution of a gas. The mixture was kept in the cooling bath for 1 h and then allowed to warm to room temperature. After gas evolution ceased (ca. 5 h), the mixture was again cooled to 0 ℃ and NEt_3 (572 μL, 4.061 mmol, 2 equiv) was added dropwise over a 15 minute period followed by 2-styrylaniline (436.2 mg, 2.234 mmol, 1.1 equiv) added dropwise over a 15 minute period. The brown mixture was left in the cooling bath for 30 minutes and then allowed to warm to room temperature. Stirring was continued at room temperature for 14 h and then the precipitate formed was collected by gravity filtration through filter paper. The precipitate was washed with THF (2 x 75 mL) and the filtrate and washes were combined. Removal of the solvents *in vacuo* gave a crude brown solid. The solid was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:8) to give the corresponding product (588 mg, 96%) as a brown solid.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.11 (d, J = 16.0 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.29-7.41 (m, 5H), 7.49 (dd, J = 4.8, 7.2 Hz, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.93 (td, J = 1.2, 7.7 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 7.6 Hz, 1H), 8.62 (d, J = 4.0 Hz, 1H), 10.32 (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.4, 122.5, 123.3, 125.0, 126.4, 126.7, 127.0, 128.0, 128.4, 128.7, 129.5, 132.5, 134.7, 137.2, 137.6, 148.1, 149.9, 162.0. EIMS *m*/*z* 300 (M^+), 194, 78, 52.

(*E*)-2,3,4,5,6-Pentafluoro-*N*-(2-styrylphenyl)benzamide



As above using pentafluorobenzoic acid in place of picolinic acid: 44%, a brown solid (EtOAc : *n*-Hexane = 1:8).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.12 (d, J = 16.0 Hz, 1H), 7.14 (d, J = 16.8 Hz, 1H), 7.32-7.36 (m, 3H), 7.40-7.43 (m, 3H), 7.53 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 111.4 (t, J = 19.4 Hz), 120.9, 126.7, 126.8, 128.5, 128.6, 128.8, 129.0, 130.8, 132.8, 133.7, 136.30, 136.34, 137.5 (dt, J = 257.4, 15.9 Hz), 142.8 (dt, J = 257.4, 13.6 Hz), 143.1 (d, J = 251.5 Hz), 160.2. EIMS *m*/*z* 389 (M^+), 388, 165, 117, 89.

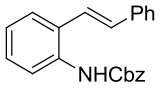
(*E*)-Ethyl 2-Styrylphenylcarbamate



Following the Method A using $ClCO_2Et$ in place of *p*-TsCl: 86% (step 2), a white solid (EtOAc : *n*-Hexane = 1:10 (step 2)).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.32 (t, J = 7.4 Hz, 3H), 4.24 (q, J = 7.1 Hz, 2H), 6.56 (br s, 1H), 7.00 (d, J = 16.0 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 16.0 Hz, 1H), 7.30 (d, J = 7.8 Hz,

2H), 7.39 (t, J = 7.6 Hz, 2H), 7.51-7.53 (m, 3H), 7.81 (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 61.2, 123.2, 124.5, 126.5, 127.9, 128.2, 128.6, 132.1, 134.8, 136.9, 154.0 (3 carbons are missing due to overlapping). EIMS m/z 267 (M^+), 194, 165, 117.

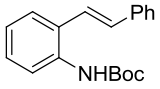
(*E*)-Benzyl 2-Styrylphenylcarbamate



Following the Method A using $ClCO_2Bn$ in place of *p*-TsCl: 73% (step 2), a white solid (EtOAc : *n*-Hexane = 1:5 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.23 (s, 2H), 6.67 (br s, 1H), 6.99 (d, J = 16.4 Hz, 1H), 7.14 (d, J = 14.0 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.29-7.46 (m, 9H), 7.50 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.83 (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 67.1, 123.1, 124.7, 126.6, 126.8, 128.0, 128.29, 128.35, 128.5, 128.7, 132.5, 134.7, 135.9, 136.8, 153.8 (3 carbons are missing due to overlapping). EIMS m/z 329 (M^+), 221, 194, 91.

(*E*)-*tert*-Butyl 2-Styrylphenylcarbamate

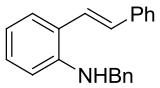


Following the Method A using $(Boc)_2O$ in $ClCH_2CH_2Cl$ in place of *p*-TsCl in pyridine: 64% (step 2), a white solid (EtOAc : *n*-Hexane = 1:15 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.61 (s, 9H), 6.56 (br s, 1H), 7.06 (d, J = 16.0 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.24 (d, J = 16.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.2 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.86 (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.3, 80.6, 122.3, 123.5, 124.3, 126.7, 126.9, 128.0, 128.4, 128.8, 129.2, 132.3, 135.4, 137.2, 153.2. EIMS m/z 295 (M^+), 239, 194, 165, 118, 89, 57.

Spectral data were consistent with data reported in the literature.[5]

(*E*)-*N*-Benzyl-2-styrylaniline



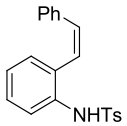
Following the Method A using BnCl in place of *p*-TsCl: 17% (step 2), a brown solid (EtOAc : *n*-Hexane = 1:8 (step 2)).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.38 (s, 2H), 6.67 (d, J = 8.4 Hz, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 15.9 Hz, 1H), 7.13-7.41 (m, 13H), 7.49 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 48.4, 111.3, 117.8, 124.2, 126.4, 127.26, 127.32, 127.5, 127.6, 128.7, 128.9, 131.0, 137.5, 139.1,

[5] (a) Hogan, A.-M. L.; O'Shea, D. F. *J. Org. Chem.* **2007**, *72*, 9557. (b) Hogan, A.-M. L.; O'Shea, D. F. *Org. Lett.* **2006**, *8*, 3769.

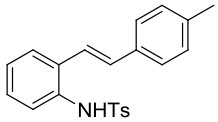
145.3 (2 carbons are missing due to overlapping). EIMS *m*/*z* 285 (M^+), 194, 167, 117, 91.
Spectral data were consistent with data reported in the literature.[5]

(*Z*)-4-Methyl-*N*-(2-styrylphenyl)benzenesulfonamide ((*Z*)-1a)



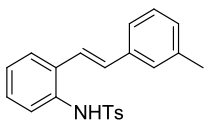
Following the Method A: In step 1, the requisite (*Z*)-2-styrylaniline was prepared from 2-bromonitrobenzene following the method reported by Driver and co-workers.[1] In step 2: 88%, (EtOAc : *n*-Hexane = 1: 8), a yellow solid. mp 99-101 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 6.18 (d, J = 12.0 Hz, 1H), 6.67 (d, J = 12.4 Hz, 1H), 6.75 (br s, 1H), 6.96 (d, J = 7.6 Hz, 2H), 7.03-7.28 (m, 8H), 7.56 (d, J = 9.2 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 121.7, 124.5, 125.1, 127.1, 127.9, 128.3, 128.4, 128.7, 129.5, 129.55, 129.64, 133.6, 134.0, 135.3, 136.3, 143.7. EIMS *m*/*z* 349 (M^+), 194, 165, 117, 89.

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



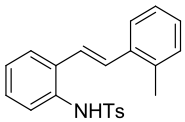
Following the Method A: 64% (step 1), 92% (step 2), a white solid (EtOAc : *n*-Hexane = 1:5 (step 1), 1:5 (step 2)). mp 159-160 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 2.37 (s, 3H), 6.38 (s, 1H), 6.68 (d, J = 16.0 Hz, 1H), 6.76 (d, J = 16.4 Hz, 1H), 7.14-7.29 (m, 8H), 7.38 (dd, J = 2.0, 7.6 Hz, 1H), 7.46 (dd, J = 2.4, 7.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 21.5, 121.5, 126.5, 127.0, 127.1, 128.2, 129.3, 129.6, 132.3, 133.1, 133.2, 133.9, 136.5, 138.1, 143.9 (2 carbons are missing due to overlapping). EIMS *m*/*z* 363 (M^+), 208, 193, 165, 91, 65.

(*E*)-4-Methyl-*N*-(2-(3-methylstyryl)phenyl)benzenesulfonamide (1c)



Following the Method A: 50% (step 1), 87% (step 2), a white solid (EtOAc : *n*-Hexane = 1:5 (step 1), 1:6 (step 2)). mp 96-100 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 2.38 (s, 3H), 6.43 (s, 1H), 6.70 (d, J = 16.0 Hz, 1H), 6.76 (d, J = 16.0 Hz, 1H), 7.11 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 7.22-7.26 (m, 3H), 7.39 (d, J = 8.8 Hz, 1H), 7.47 (dd, J = 1.6, 7.2 Hz 1H), 7.61 (,d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.27, 21.33, 122.3, 123.9, 126.3, 126.8, 126.9, 127.0, 127.2, 128.1, 128.4, 128.7, 129.5, 132.0, 133.1, 133.3, 136.4, 136.6, 138.0, 143.7. EIMS *m*/*z* 363 (M^+), 208, 193, 178, 165, 152, 117, 91, 77, 65, 51.

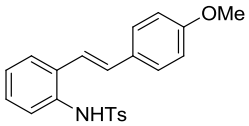
(*E*)-4-Methyl-*N*-(2-(2-methylstyryl)phenyl)benzenesulfonamide (1d)



Following the Method A: 49% (step 1), 73% (step 2), a white solid (Et_2O : *n*-Hexane = 1:1 (step 1), EtOAc : *n*-Hexane = 1:8 (step 2)). mp 146-151 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 6H), 6.47 (br s, 1H), 6.64 (d, J = 16.0 Hz, 1H), 7.05 (d, J = 16.4 Hz, 1H), 7.18-7.28 (m, 8H), 7.39 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.8, 21.4, 123.9, 125.4, 126.1, 126.5, 126.7, 126.9, 127.1, 128.0, 128.4, 129.6, 130.1, 130.4, 133.3, 135.7, 135.8, 136.6, 143.8 (1 carbon is missing due to overlapping). EIMS *m*/*z* 363 (M^+), 208, 193, 165, 91, 65.

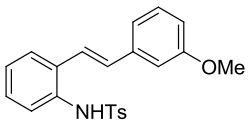
(*E*)-*N*-(2-(4-Methoxystyryl)phenyl)-4-methylbenzenesulfonamide (1e)



Following the Method A: 78% (step 1), 89% (step 2), a pale yellow solid (EtOAc : *n*-Hexane = 1:5 (step 1), 1:5 (step 2)). mp 128-135 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 3.84 (s, 3H), 6.49 (s, 1H), 6.62 (d, J = 16.0 Hz, 1H), 6.73 (d, J = 16.0 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 7.16-7.26 (m, 6H), 7.35-7.38 (m, 1H), 7.44-7.46 (m, 1H), 7.61 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 55.3, 113.9, 120.3, 126.2, 126.6, 126.9, 127.1, 127.88 127.91, 129.5, 131.5, 133.0, 133.5, 136.4, 143.8, 159.5 (1 carbon is missing due to overlapping). EIMS *m*/*z* 379 (M^+), 224, 180, 91.

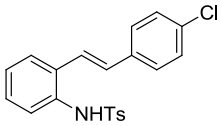
(*E*)-*N*-(2-(3-Methoxystyryl)phenyl)-4-methylbenzenesulfonamide (1f)



Following the Method A: 49% (step 1), 85% (step 2), a yellow solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:6 (step 2)). mp 125-126 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 3.84 (s, 3H), 6.65-6.72 (m, 1H), 6.75 (d, J = 9.2 Hz, 1H), 6.77 (s, 1H), 6.82-6.84 (m, 2H), 6.90 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.20-7.26 (m, 3H), 7.38 (d, J = 7.6 Hz, 1H), 7.48 (dd, J = 1.6, 7.2 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 55.3, 111.9, 113.6, 119.3, 122.9, 126.6, 126.8, 127.1, 128.5, 129.6, 129.7, 132.1, 133.1, 133.2, 136.4, 138.1, 143.9, 159.8 (1 carbon is missing due to overlapping). EIMS *m*/*z* 379 (M^+), 224, 180, 91.

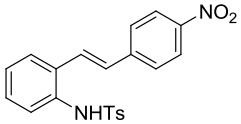
(*E*)-*N*-(2-(4-Chlorostyryl)phenyl)-4-methylbenzenesulfonamide (1g)



Following the Method A: 23% (step 1), 43% (step 2), a white solid (EtOAc : *n*-Hexane = 1:20 (step 1), 1:5 (step 2)). mp 195-196 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 6.36 (br s, 1H), 6.75 (d, J = 16.4 Hz, 1H), 6.81 (d, J = 16.4 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.23-7.32 (m, 7H), 7.49 (br s, 1H), 7.60 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 123.4, 126.5, 127.0, 127.18, 127.22, 127.8, 128.6, 128.8, 129.7, 130.6, 133.1, 133.2, 133.7, 135.2, 136.4, 144.0. EIMS *m*/*z* 383 (M^+), 228, 193, 165, 139, 117, 91, 77, 65, 51.

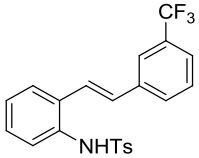
(*E*)-4-Methyl-*N*-(2-(4-nitrostyryl)phenyl)benzenesulfonamide (1h)



Following the Method A: 22% (step 1), 53% (step 2), a yellow solid (EtOAc : *n*-Hexane = 1:5 (step 1), 1:3 (step 2)). mp 200-209 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 6.68 (s, 1H), 6.90 (d, J = 16.4 Hz, 1H), 7.18-7.29 (m, 6H), 7.49 (d, J = 8.4 Hz, 2H), 7.57-7.60 (m, 1H), 7.62 (d, J = 8.0 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 124.0, 126.6, 127.1, 127.3, 127.4, 127.5, 127.8, 129.0, 129.4, 129.7, 132.9, 133.6, 136.3, 143.3, 144.1, 147.0. EIMS *m*/*z* 394 (M^+), 239, 207, 193, 165, 139, 117, 91, 65, 51.

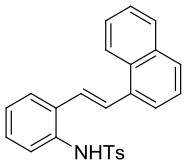
(*E*)-4-Methyl-*N*-(2-(3-(trifluoromethyl)styryl)phenyl)benzenesulfonamide (1i)



Following the Method A: 73% (step 1), 53% (step 2), a pale yellow solid (EtOAc : *n*-Hexane = 1:5 (step 1), 1:1 (step 2)). mp 144-147 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.24 (s, 3H), 6.76 (d, J = 16.0 Hz, 1H), 6.91 (d, J = 16.4 Hz, 1H), 6.99 (s, 1H), 7.12 (d, J = 7.6 Hz, 2H), 7.22-7.29 (m, 2H), 7.38 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.48-7.54 (m, 4H), 7.59 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 123.2 (q, J = 3.7 Hz), 124.0 (q, J = 271.0 Hz), 124.3 (q, J = 3.7 Hz), 124.6, 126.4, 127.0, 127.3, 127.6, 128.9, 129.0, 129.6, 129.7, 130.1, 130.9 (q, J = 32.2 Hz), 133.0, 133.3, 136.3, 137.5, 144.0. EIMS *m*/*z* 417 (M^+), 262, 242, 222, 193, 165, 139, 117, 91, 77, 65, 51.

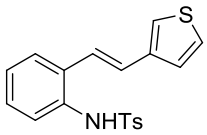
(*E*)-4-Methyl-*N*-(2-(2-(naphthalen-1-yl)vinyl)phenyl)benzenesulfonamide (1j)



Following the Method A: 16% (step 1), 84% (step 2), a pale yellow solid (EtOAc : *n*-Hexane = 1:20 (step 1), 1:5 (step 2)). mp 143-150 ℃.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.07 (s, 3H), 6.96-7.01 (m, 3H), 7.09 (br s, 1H), 7.20-7.23 (m, 2H), 7.34-7.39 (m, 2H), 7.44-7.60 (m, 7H), 7.73 (d, J = 8.1 Hz, 1H), 7.79-7.82 (m, 1H), 8.00-8.03 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 123.3, 123.8, 125.5, 125.7, 126.0, 126.5, 126.96, 127.03, 128.2, 128.4, 128.5, 129.4, 131.0, 133.2, 133.5, 134.1, 136.3, 143.7 (4 carbons are missing due to overlapping). EIMS *m*/*z* 399 (M^+), 244, 117, 91.

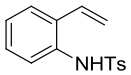
(*E*)-4-Methyl-*N*-(2-(2-(thiophen-2-yl)vinyl)phenyl)benzenesulfonamide (1k)



Following the Method B and using **1l** and 3-bromothiophene in step 2: 49% (step 2), a white solid (Acetone : *n*-Hexane = 1:1 (step 2)). mp 175-179 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 6.53 (br s, 1H), 6.62 (d, J = 16.0 Hz, 1H), 6.79 (d, J = 16.4 Hz, 1H), 7.12 (d, J = 5.2 Hz, 1H), 7.16 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.21-7.24 (m, 2H), 7.30 (dd, J = 2.8, 4.8 Hz, 1H), 7.36 (dd, J = 1.6, 6.8 Hz, 1H), 7.44 (dd, J = 2.4, 6.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 122.0, 122.4, 126.1, 126.7, 126.8, 127.2, 129.0, 129.6, 131.0, 131.9, 133.8, 136.3, 136.5, 143.7, 149.6, 154.9. EIMS *m*/*z* 355 (M^+), 206, 193, 165, 89.

4-Methyl-*N*-(2-vinylphenyl)benzenesulfonamide (1l)

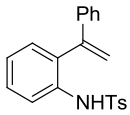


Following the Method B and step 2 is as follows. To a solution of *N*-Ts-2-bromoaniline (3.127 mmol, 1.02 g) in 1,4-dioxane (0.13 M, 24.0 ml) were added $Pd(pph_3)_4$ (2 mol%, 0.0625 mmol, 72.3 mg), tributyl(vinyl)tin (1.2 equiv, 3.752 mmol, 1.1 mL). The resulting mixture was heated to 125 ℃ for 4 hour. After the reaction mixture was cooled to room temperature and 10% KF solution (0.08 M, 39.0 ml) was added to the mixture, the mixture was allowed to stand for 2 h and then celite filtered. The reaction mixture was extracted with EtOAc (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 = 1:5) to give **1l** (474.0 mg, 56%) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 5.27 (d, J = 10.8 Hz, 1H), 5.51 (d, J = 17.2 Hz, 1H), 6.40 (br s , 1H), 6.50 (dd, J = 11.0, 17.4 Hz, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 8.0 Hz, 3H), 7.34 (t, J = 7.8 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 118.3, 124.8,

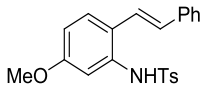
126.4, 126.9, 127.2, 128.6, 129.6, 131.5, 132.7, 133.1, 136.4, 143.9. EIMS *m*/*z* 273 (M^+), 118, 91. Spectral data were consistent with data reported in the literature.[6]

4-Methyl-*N*-(2-(1-phenylvinyl)phenyl)bnzenesulfonamide (1m)



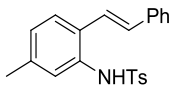
Following the Method A: In step 1, the requisite 2-vinylaniline was prepared from 2-bromoaniline and 1-phenylvinylboronic acid following the method reported by Driver and co-workers (EtOAc : *n*-Hexane = 1:10, 92%).[1] In step 2: 74%, (EtOAc : *n*-Hexane = 1:8), a white solid. mp 90-92 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 4.89 (s, 1H), 5.69 (s, 1H), 6.53 (s, 1H), 7.01 (d, J = 7.6 Hz, 2H), 7.04-7.12 (m, 4H), 7.20-7.33 (m, 4H), 7.43 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 117.2, 121.1, 124.7, 126.3, 127.2, 128.5, 128.76, 128.82, 129.4, 130.4, 133.0, 134.2, 136.0, 138.6, 143.7, 144.9. EIMS *m*/*z* 349 (M^+), 195, 177, 165, 152, 139, 116, 91, 77, 65, 52.

(*E*)-*N*-(5-Methoxy-2-styrylphenyl)-4-methylbenzenesulfonamide (1n)



Following the Method A: In step 1, the requisite 2-vinylaniline was prepared from 1-bromo-4-methoxy-2-nitrobenzene following the method reported by Driver and co-workers.[1] In step 2: 79%, (Acetone : *n*-Hexane = 1:7), a white solid.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 3.80 (s, 3H), 6.45 (br s, 1H), 6.63 (d, J = 16.4 Hz, 1H), 6.69 (d, J = 16.0 Hz, 1H), 7.78 (dd, J = 2.4, 8.4 Hz, 1H), 6.97 (d, J = 2.8 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.26-7.28 (m, 3H), 7.31-7.35 (t, J = 7.4 Hz, 2H), 7.38 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 55.5, 110.8, 113.6, 122.1, 125.1, 126.4, 127.2, 127.5, 127.7, 128.6, 129.7, 130.5, 134.3, 136.5, 136.9, 144.0, 159.6. EIMS *m*/*z* 379 (M^+), 224, 193, 91.

(*E*)-4-Methyl-*N*-(5-methyl-2-styrylphenyl)benzenesulfonamide (1o)



Following the Method A: 31% (step 1, using 2-bromo-5-methylaniline), 51% (step 2), a yellow solid (EtOAc : *n*-Hexane = 1:8 (step 1), 1:6 (step 2)). mp 155-157 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25 (s, 3H), 2.31 (s, 3H), 6.61 (br s, 1H), 6.70 (s, 2H), 7.02 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.20 (s, 1H), 7.24-7.32 (m, 5H), 7.36 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 21.4, 122.5, 126.2, 126.5, 127.1, 127.5, 127.9, 128.0, 128.5, 129.6, 130.3, 131.1, 132.9, 136.5, 136.8, 138.6, 143.8. EIMS *m*/*z* 363 (M^+), 208, 193, 165, 91.

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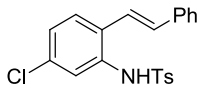
[6] Krolski, M. E.; Renaldo, A. F.; Rudisill, D. E.; Stille, J. K. *J. Org. Chem.* **1988**, *53*, 1170.

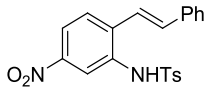
(*E*)-*N*-(5-Chloro-2-styrylphenyl)-4-methylbenzenesulfonamide (1p)



Following the Method A: 62% (step 1, using 5-chloro-2-iodoaniline), 66% (step 2), a yellow solid (EtOAc : *n*-Hexane = 1:8 (step 1), 1:6 (step 2)). mp 142-145 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.21 (s, 3H), 6.66 (d, J = 16.0 Hz, 1H), 6.76 (dd, J = 4.4, 16.0 Hz, 1H), 7.07-7.14 (m, 4H), 7.20-7.26 (m, 5H), 7.33 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 2.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 121.4, 126.2, 126.7, 127.0, 127.1, 127.3, 128.2, 128.6, 129.7, 131.3, 132.5, 133.4, 134.2, 136.0, 136.3, 144.2. EIMS *m*/*z* 383 (M^+), 228, 193, 165, 91, 65.

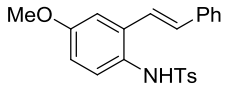
(*E*)-4-Methyl-*N*-(5-nitro-2-styrylphenyl)benzenesulfonamide (1q)



Following the Method A: 59% (step 1, using 2-bromo-5-nitroaniline), 82% (step 2), a yellow solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:4 (step 2)). mp 202-204 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 6.61 (br s, 1H), 6.89 (d, J = 16.0 Hz, 1H), 7.00 (d, J = 16.4 Hz, 1H), 7.24-7.29 (m, 3H), 7.37-7.39 (m, 4H), 7.65 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 8.05 (dd, J = 2.2, 9.0 Hz, 1H), 8.17 (d, J = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 120.7, 120.9, 121.4, 127.06, 127.13, 127.2, 128.8, 129.2, 130.0, 134.0, 135.7, 136.0, 139.0, 144.7 (2 carbons are missing due to overlapping). EIMS *m*/*z* 394 (M^+), 239, 193, 91, 65.

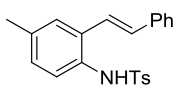
(*E*)-*N*-(4-Methoxy-2-styrylphenyl)-4-methylbenzenesulfonamide (1r)



Following the Method A: 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.[1] In step 2: 73 %, (EtOAc : *n*-Hexane = 1:6), a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.26 (s, 3H), 3.83 (s, 3H), 6.28 (br s, 1H), 6.75 (s, 2H), 6.79 (dd, J = 2.6, 8.6 Hz, 1H), 7.02 (d, J = 2.8 Hz, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.8 Hz, 1H), 7.26-7.34 (m, 5H), 7.57 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 55.4, 110.7, 113.9, 122.9, 125.9, 126.7, 127.2, 128.0, 128.5, 129.5, 130.1, 131.4, 135.9, 136.4, 136.6, 143.7, 158.8. EIMS *m*/*z* 379 (M^+), 224, 209, 180, 165, 152, 132, 104, 91, 77, 65, 52.

(*E*)-4-Methyl-*N*-(4-methyl-2-styrylphenyl)benzenesulfonamide (1s)

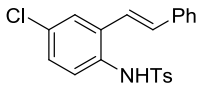


Following the Method A: 66% (step 1, using 2-bromo-4-methylaniline), 72 % (step 2), a white solid

(EtOAc : *n*-Hexane = 1:10 (step 1), 1:8 (step 2)). mp 114-120 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 2.35 (s, 3H), 6.35 (br s, 1H), 6.73 (d, J = 16.4 Hz, 1H), 6.79 (d, J = 16.0 Hz, 1H), 7.06 (dd, J = 1.2, 8.4 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.4 Hz, 1H), 7.27-7.36 (m, 6H), 7.60 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 21.5, 122.8, 126.6, 126.9, 127.2, 127.5, 128.0, 128.6, 129.3, 129.7, 130.5, 131.7, 133.4, 136.6, 136.7, 137.2, 143.8. EIMS *m*/*z* 363 (M^+), 208, 193, 165, 91, 65.

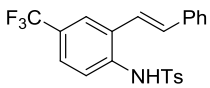
(*E*)-*N*-(4-Chloro-2-styrylphenyl)-4-methylbenzenesulfonamide (1t)



Following the Method A: 81% (step 1, using 2-bromo-4-chloroaniline), 90 % (step 2), a yellow solid (EtOAc : *n*-Hexane = 1:10 (step 1), 1:7 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.21 (s, 3H), 6.68 (d, J = 16.0 Hz, 1H), 6.76 (d, J = 16.0 Hz, 1H), 6.93 (s, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.13 (dd, J = 2.0, 8.4 Hz, 1H), 7.20-7.29 (m, 6H), 7.40 (d, J = 2.0 Hz, 1H), 7.56 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 121.4, 126.1, 126.8, 127.1, 128.1, 128.3, 128.4, 128.6, 129.7, 131.6, 132.8, 133.0, 135.1, 136.1, 136.2, 144.1. EIMS *m*/*z* 383 (M^+), 228, 193, 165, 151, 139, 115, 91, 77, 65, 51.

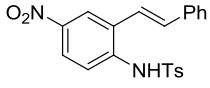
(*E*)-4-Methyl-*N*-(2-styryl-4-(trifluoromethyl)phenyl)benzenesulfonamide (1u)



Following the Method A: 34% (step 1, using 2-bromo-4-(trifluoromethyl)aniline), 83 % (step 2), a white solid (EtOAc : *n*-Hexane = 1:10 (step 1), 1:7 (step 2))

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 6.80 (d, J = 16.4 Hz, 1H), 6.84 (br s, 1H), 6.86 (d, J = 16.0 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.32-7.40 (m, 5H), 7.48 (d, J = 10.0 Hz, 1H), 7.53 (t, J = 8.8 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.68 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 121.1, 123.8 (q, J = 270.5 Hz), 123.9 (q, J = 3.6 Hz), 124.6, 125.1 (q, J = 3.6 Hz), 126.9, 127.1, 128.3 (q, J = 32.7 Hz), 128.6, 128.7, 129.9, 132.2, 134.3, 136.0, 136.1, 136.5, 144.4. EIMS *m*/*z* 417 (M^+), 262, 242, 222, 193, 185, 165, 155, 139, 115, 91, 65, 51.

(*E*)-4-Methyl-*N*-(4-nitro-2-styrylphenyl)benzenesulfonamide (1v)

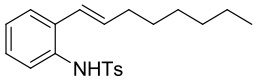


Following the Method A: 60% (step 1, using 2-bromo-4-nitrolaniline), 46 % (step 2), a yellow solid (EtOAc : *n*-Hexane = 1:10 (step 1), 1:6 (step 2)).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 6.85 (d, J = 15.6 Hz, 1H), 6.95 (d, J = 16.0 Hz, 1H), 7.19 (s, 1H), 7.24-7.28 (m, 2H), 7.34-7.43 (m, 5H), 7.61 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 8.06 (dd, J = 2.4, 9.2 Hz, 1H), 8.30 (d, J = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 120.0, 122.3, 122.4, 123.1, 127.0, 127.1, 128.7, 128.8, 130.0, 131.3, 135.5, 135.65, 135.70, 139.2,

144.8 (1 carbon is missing due to overlapping). EIMS *m*/*z* 394 (M^+), 281, 252, 239, 207, 193, 180, 165, 155, 139, 91, 77, 65, 51.

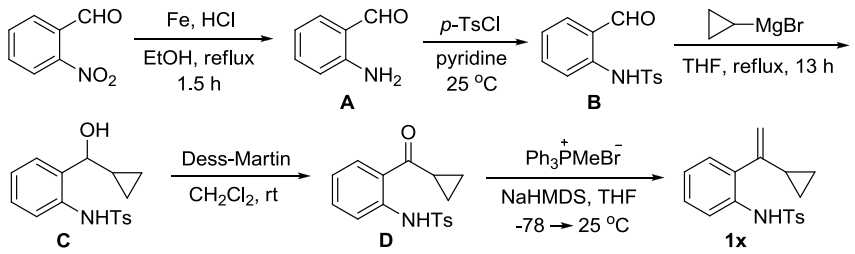
(*E*)-4-Methyl-*N*-(2-(oct-1-enyl)phenyl)benzenesulfonamide (1w)



In step 1, the requisite 2-vinylaniline was prepared from 2-bromoaniline and *trans*-1-octen-1-ylboronic acid following the method reported by Driver and co-workers (EtOAc : *n*-Hexane = 1:5, 97%).[1] In step 2: 86 % (EtOAc : *n*-Hexane = 1:8), a pale yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, J = 6.4 Hz, 3H), 1.25-1.29 (m, 8H), 2.07 (quartet, J = 6.5 Hz, 2H), 2.38 (s, 3H), 5.91 (dt, J = 6.8, 15.6 Hz, 1H), 6.04 (d, J = 15.6 Hz, 1H), 6.44 (s, 1H), 7.11 (t, J = 7.0 Hz, 1H), 7.15-7.26 (m, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.36 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 21.4, 22.5, 28.8, 28.9, 31.6, 33.1, 123.7, 124.8, 126.2, 126.8, 127.1, 127.5, 129.4, 132.7, 135.6, 136.5, 143.6 (1 carbon is missing due to overlapping). EIMS *m*/*z* 357 (M^+), 202, 155, 144, 130, 118, 106, 91, 77, 65, 55.

***N*-(2-(1-Cyclopropylvinyl)phenyl)-4-methylbenzenesulfonamide (1x)**



To a solution of the 2-nitrobenzaldehyde (338.7 mg, 2.241 mmol) and Fe powder (376.0 mg, 6.724 mmol, 3 equiv) in EtOH (6.4 mL, 0.35 M) was slowly added diluted HCl (1 M, 2.2 mL, 1 equiv) and heated under Ar atmosphere. After refluxing for 1.5 h, the mixture was washed with CH_2Cl_2 and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:8) to afford **A** (249.8 mg, 92%) as a yellow oil.

To a solution of **A** (249.8 mg, 2.062 mmol) in pyridine (10.3 mL, 0.2 M) was added *p*-toluenesulfonyl chloride (481.4 mg, 2.474 mmol, 1.2 equiv) at room temperature. After being stirred for 12 h, the mixture was washed with CH_2Cl_2 and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:4) to afford **B** (84.7 mg, 13%) as a yellow solid.

To a solution of **B** (84.2 mg, 0.267 mmol) in anhydrous THF (4.5 mL, 0.06 M) was added cyclopropylmagnesium bromide (1.0 M THF solution, 0.801 mmol, 0.8 mL, 3 equiv) at room temperature. The resulting mixture was refluxed for 13 h. On completion on the basis of TLC analysis, the mixture was quenched with sat. aq. NH_4Cl, washed with CH_2Cl_2 and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:3) to afford **C** (69.8 mg, 82%) as a yellow solid.

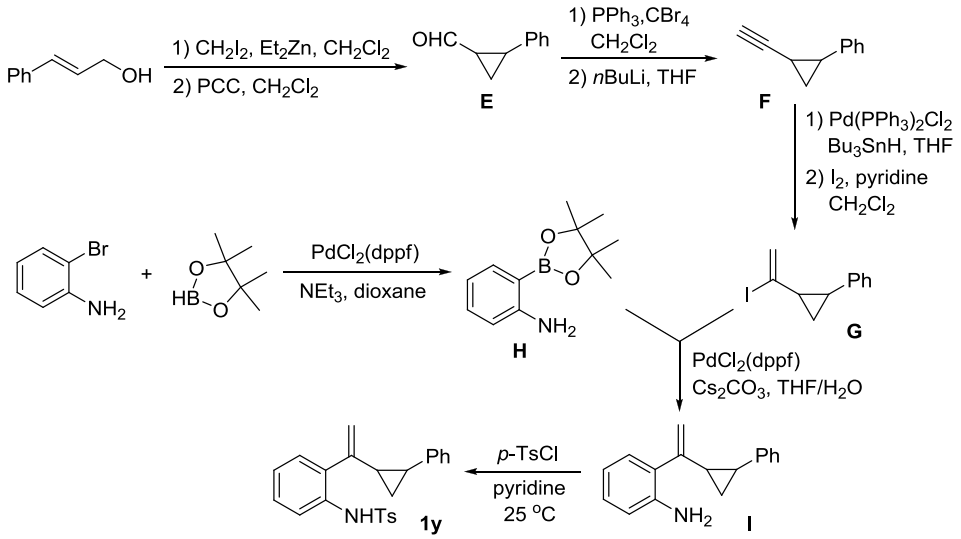
To a solution **C** (177.1 mg, 0.558 mmol) in CH_2Cl_2 (2.8 mL, 0.2 M) was added Dess-Martin periodinane (2.0 mL, 0.669 mmol, 1.2 equiv) at room temperature under Ar. After being stirred for 3 h, the reaction mixture was quenched with a premixed $Na_2S_2O_3$-$NaHCO_3$ solution (0.2 M, 1:1, 2.8 mL) at 0 ℃ and stirred for 1 h. The mixture was washed with CH_2Cl_2 and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:4) to afford **D** (50.0 mg, 28%) as a yellow solid.

$Ph_3P^+MeBr^-$ (104.5 mg, 0.286 mmol, 2 equiv) was dissolved in THF (0.7 mL, 0.2 M) under Ar at -78 ℃ and then NaHMDS (0.3 mL, 0.286 mmol, 2 equiv) was added and stirred for 30 min. **D** (45.2 mg, 0.143 mmol) in THF (0.2 mL, 0.7 M) was added and then warmed to 25 ℃. After being stirred for 11 h, the reaction mixture was quenched with sat. aq. NH_4Cl, washed with CH_2Cl_2 and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to afford **1x** (49.3 mg, 66 %) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.28-0.31 (m, 2H), 0.63-0.67 (m, 2H), 1.32-1.36 (m, 1H), 2.36 (s, 3H), 4.47 (s, 1H), 5.12 (s, 1H), 6.96 (d, J = 7.6 Hz, 2H), 7.01 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.21-7.24 (m, 1H), 7.62-7.66 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 6.5, 17.0, 21.5, 113.6, 119.3, 123.8, 127.3, 128.3, 129.3, 129.5, 131.7, 133.9, 136.3, 143.9, 147.2. EIMS *m*/*z* 313 (M^+), 158, 130, 117, 91.

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

4-Methyl-*N*-(2-(1-(2-phenylcyclopropyl)vinyl)phenyl)benzenesulfonamide (1y)



To a dried 500 mL flask were added CH_2I_2 (1.3 mL, 15.6 mmol, 2 equiv) and CH_2Cl_2 (46 mL, 0.17 M). After cooling to 0 ℃, Et_2Zn (1 M in hexane, 9.8 mL, 9.77 mmol, 1.25 equiv) was added. The resulting mixture was stirred at this temperature for 30 min. To another flask were added cinnamyl alcohol (1.0 g, 7.81 mmol) and CH_2Cl_2 (24 mL, 0.33 M). After cooling to 0 ℃, Et_2Zn (1 M in hexane, 9.8 mL, 9.77 mmol, 1.25 equiv) was added. The resulting mixture was stirred at this

[7] Kothandaraman, P.; Huang, C.; Susanti, D.; Rao, W.; Chan, P. W. H. *Chem. Eur. J.* **2011**, *17*, 10081.

temperature for 30 min. This reaction mixture was then added to the reaction mixture in the 500 mL flask. After stirred at 0 ℃ for 30 min, the resulting mixture was allowed to warm to room temperature and then stirred for 18 h. The reaction mixture was quenched with sat. aq. NH_4Cl and 1 M aq. HCl. The organic layer was separated. The aqueous layer was then extracted twice with CH_2Cl_2 (200 mL). 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 = 1:5) to give *trans*-2-phenylcyclopropanemethanol (1.2 g, 100%) as a colorless oil.[8]

To a solution of *trans*-2-phenylcyclopropanemethanol (432.0 mg, 2.915 mmol) in CH_2Cl_2 (11.7 mL, 0.4 M) was added PCC (942.5 mg, 4.372 mmol, 1.5 equiv) at room temperature under Ar atmosphere. After 1 h, the reaction mixture was filtered through a pad of Celite and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford **E** (362.8 mg, 85%) as colorless oil.[9]

To a solution of PPh_3 (4.50 g, 17.264 mmol, 4 equiv) in anhydrous CH_2Cl_2 (9.4 mL, 0.46 M) at 0 ℃ was added a solution of CBr_4 (2.80 g, 8.632 mmol, 2 equiv) in CH_2Cl_2 (3.2 mL, 1.34 M). After stirring at 0 ℃ for 5 min a solution of **E** (631.0 mg, 4.316 mmol) in CH_2Cl_2 (3.2 mL, 1.34 M) was then added dropwise. The mixture was stirred at 0 ℃ for an additional 30 min. The solution was then quenched with water, diluted with CH_2Cl_2 and the layers were separated. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (only *n*-Hexane) to give the desired dibromoolefin (1.1 g, 87%) as a light yellow oil.[10]

To a solution of the dibromoolefin (1.1 g, 3.64 mmol) in anhydrous THF (18.7 mL, 0.2 M) was added *n*BuLi (3.4 mL, 8.595 mmol, 2.45 M in hexane, 2.3 equiv) dropwise at -78 ℃. After stirred at -78 ℃ for 30 min, water was slowly added and the resulting solution was diluted with Et_2O and the layers were separated. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (only *n*-Hexane) to give **F** (545.0 mg, 100%) as a colorless oil.[10]

A solution of Bu_3SnH (580 μL, 2.186 mmol, 1 equiv) dissolved in THF (1.6 mL, 1.3 M) was added dropwise to a solution of **F** (310.8 mg, 2.186 mmol) and $Pd(PPh_3)_2Cl_2$ (30.7 mg, 0.0437 mmol, 2 mol%) in THF (4.9 mL, 0.45 M). Upon complete addition, the reaction mixture appeared opaque and brown. The solvent was removed by rotary evaporation yielding a brown oil. The residue was purified by column chromatography on silica gel (only *n*-Hexane) to give the desired stannylethene (567.3 mg, 60%) as a colorless oil.[11]

A solution of I_2 (123.9 g, 0.976 mmol, 1 equiv) in CH_2Cl_2 (32.5 mL, 0.03 M) was added dropwise to a solution of stannylethene (422.7 mg, 0.976 mmol) and pyridine (353 μL, 4.390 mmol, 4.5 equiv) in CH_2Cl_2 (8.9 mL, 0.1 M). After addition, the reaction mixture was allowed to stir for 0.5 h and

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[8] Itoh, T.; Shimizu, Y.; Kanai, M. *Org. Lett.* **2014**, *16*, 2736.

[9] Tzirakis, M. D.; Alberti, M. N.; Orfanopoulos, M. *Org. Lett.* **2011**, *13*, 3364.

[10] Charette, A. B.; Giroux, A. *J. Org. Chem.* **1996**, *61*, 8718.

[11] Milnes, K. K.; Gottschling, S. E.; Baines, K. M. *Org. Biomol. Chem.* **2004**, *2*, 3530.

was then quenched with a saturated solution of $Na_2S_2O_3$. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (three times). The combined organic layers were dried over $MgSO_4$, the solids were removed by gravity filtration and the solvent was removed by rotary evaporation yielding a yellow oil. Hexanes were added to the crude product. The salts were removed by gravity filtration and the hexanes removed from the filtrate by rotary evaporation. The product was dissolved in EtOAc and an aqueous solution of excess KF was added. The biphasic solution was allowed to stir vigorously for 18 h. The layers were separated and the aqueous layer was extracted with EtOAc (three times). The combined organic layers were dried over $MgSO_4$, the solids were removed by gravity filtration and the solvent was removed by rotary evaporation. The product was triturated with CH_3CN to remove any remaining KF. The product was further purified by column chromatography on silica gel (only *n*-Hexane) to give a mixture of **G** and destannylation product (208.4 mg, **G** : destannylation = 1:0.74, 45% of **G**) as a colorless oil.[11]

To a solution of 2-bromoaniline (1.0 g, 5.813 mmol), Et_3N (3.2 mL, 23.252 mmol, 4 equiv), $PdCl_2$(dppf) (237.4 mg, 0.291 mmol, 5 mol%) in 1,4-dioxane (17.6 mL, 0.33 M) was added dropwise 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.5 mL, 17.439 mmol, 3 equiv). The resultant mixture was heated to 100 ℃. After 12 h, the mixture was cooled to room temperature and diluted with sat. aq. NH_4Cl. The resulting aqueous phase was extracted with CH_2Cl_2 (three times). The combined organic phases were 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 **H** as a light yellow solid (1.1 g, 87%).[12]

To a solution of a mixture containing **G** (85.5 mg, 0.317 mmol) in THF/H_2O (1:1, 6.34 mL, 0.05 M) were added **H** (90.2 mg, 0.411 mmol, 1.3 equiv), Cs_2CO_3 (144.6 mg, 0.444 mmol, 1.4 equiv) and $PdCl_2$(dppf)·CH_2Cl_2 (25.9 mg, 0.0317 mmol, 10 mol%). The mixture was heated at 90 ℃ then THF was removed under reduced pressure. The residue was dissolved in EtOAc, washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:12) to give **I** (23.2 mg, 31%) as a yellow oil.[13]

To a solution of **I** (31.1 mg, 0.132 mmol, 1 equiv) in pyridine (0.7 mL, 0.2 M) was added *p*-toluenesulfonyl chloride (27.7 mg, 0.145 mmol, 1.1 equiv) at 0 ℃. After being stirred at 25 ℃ for 3 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 = 1:8) to give the corresponding product **1y** (38.1 mg, 74%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.00 (dt, J = 5.5, 9.2 Hz, 1H), 1.11 (dt, J = 5.5, 8.2 Hz, 1H), 1.51 (dt, J = 5.2, 8.0 Hz, 1H), 1.86 (dt, J = 4.8, 9.0 Hz, 1H), 2.32 (s, 3H), 4.59 (s, 1H), 5.20 (s, 1H), 6.95 (br s, 1H), 7.00-7.05 (m, 4H), 7.12 (d, J = 8.0 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 7.21-7.28 (m, 3H), 7.60 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.8, 21.5, 25.4, 29.1,

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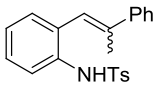
[12] Sun, K.; Liu. S.; Bec, P. M.; Driver, T. G. *Angew. Chem., Int. Ed.* **2011**, *50*, 1702.

[13] Queiroz, M. J. R. P.; Abreu, A. S.; Calhelha, R. C.; Carvalho, M. S. D.; Ferreira, P. M. T. *Tetrahedron* **2008**, *64*, 5139.

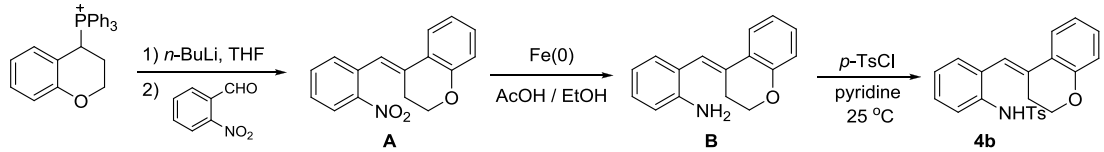
114.1, 119.6, 124.0, 125.8, 126.0, 127.2, 128.4, 129.1, 129.5, 131.9, 133.8, 136.2, 141.4, 143.8, 146.0 (1 carbon is missing due to overlapping). EIMS *m*/*z* 389 (M^+), 234, 207, 130, 91.

4-Methyl-*N*-(2-(2-phenylprop-1-enyl)phenyl)benzenesulfonamide (4a)



In step 1, the requisite 2-vinylaniline was prepared following the method reported by Driver and co-workers.[12] In step 2: 96 %, *E*:*Z* = 1:0.7, (EtOAc : *n*-Hexane = 1:5), a yellow solid, mp 98-100 ℃. Signals corresponding to (*E*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.90 (s, 3H), 2.38 (s, 3H), 6.19 (s, 1H), 6.53 (br s, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 7.02-7.12 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.17-7.37 (m, 7H), 7.61 (d, *J* = 7.6 Hz, 2H). Signals corresponding to (*Z*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.16 (s, 3H), 2.38 (s, 3H), 5.95 (s, 1H), 6.53 (br s, 1H), 6.77 (d, *J* = 7.2 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 7.07-7.17 (m, 3H), 7.19-7.37 (m, 5H), 7.56-7.62 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.8, 21.3, 25.5, 121.4, 121.5, 122.4, 122.7, 124.8, 125.1, 125.6, 126.9, 127.1, 127.2, 127.3, 127.7, 127.8, 127.9, 128.1, 128.2, 129.39, 129.43, 130.0, 130.5, 130.8, 130.9, 133.6, 134.3, 136.6, 139.9, 141.1, 141.2, 141.6, 141.7, 141.8, 143.6 (1 carbon is missing due to overlapping). EIMS *m*/*z* 363 (M^+), 208, 193, 91.

(*E*)-*N*-(2-(Chroman-4-ylidenemethyl)phenyl)-4-methylbenzenesulfonamide (4b)



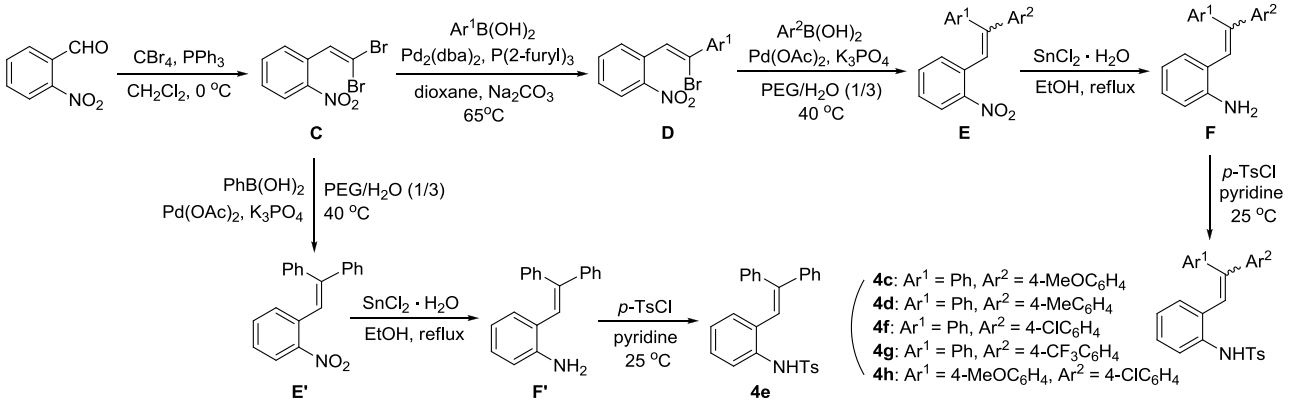
To a solution of the phosphonium salt[12] (1.5 g, 3.894 mmol, 1 equiv) in THF (12 mL, 0.3 M) was added *n*-BuLi (2.5 M in hexanes, 1.6 mL, 1 equiv) dropwise at -78 ℃. After stirring for 1 h at -78 ℃, the mixture was warmed to room temperature and stirred for additional 1 h. Then 2-nitrobenzaldehyde (647.3 mg, 4.283 mmol, 1.1 equiv) was added and the mixture was stirred for 1 h at rt. The resulting mixture was diluted with water and extracted with CH_2Cl_2 (three times). The resulting organic phase was washed with brine and dried over $MgSO_4$. After filtration, the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:20) to give **A** (448.8 mg, 43%) as a green solid.

To a solution of **A** (448.8 mg, 1.679 mmol, 1 equiv) in AcOH (8.4 mL, 0.2 M) and EtOH (8.4 mL, 0.2 M) was added Fe powder (750.2 mg, 13.433 mmol, 8 equiv). After stirring for 3 h at 80 ℃, the reaction mixture was cooled down to rt. The resulting mixture was filtered through a pad of Celite. The filtrate was diluted with water and washed with CH_2Cl_2 (three times). The resulting organic phase was washed with brine and dried over $MgSO_4$. The resulting mixture was filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:7) to give **B** (300.4 mg, 75%) as a white solid.

4b was prepared from **B** following a general procedure for tosylation as a white solid in 75 % yield (369.8 mg, EtOAc : *n*-Hexane = 1:5).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 2.53 (t, J = 4.8 Hz, 2H), 4.07 (t, J = 5.6 Hz, 2H), 6.37 (s, 1H), 6.52 (s, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 6.8 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 7.20-7.32 (m, 5H), 7.57 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 26.6, 66.0, 115.4, 117.7, 120.7, 121.4, 122.9, 124.3, 125.2, 127.1, 128.3, 129.5, 129.7, 129.9, 130.3, 134.7, 134.9, 136.9, 144.0, 154.8. EIMS *m*/*z* 391 (M^+), 236, 131, 91.

General Procedure for the Preparation of β,β-Disubstituted 2-Alkenylaniline Derivatives 4c-h



To a solution of 2-nitrobenzaldehyde (976.2 mg, 6.459 mmol, 1 equiv) and CBr_4 (4.3 g, 12.91 mmol, 2 equiv) in CH_2Cl_2 (16.1 ml, 0.4 M) at 0 ℃ was added dropwise a solution of PPh_3 (6.8 g, 25.84 mmol, 4 equiv) in CH_2Cl_2 (16 ml, 0.4 M). After addition (~1 h), the mixture was stirred for another 0.5 h before warmed to rt, and stirred for an additional 1 h. The reaction mixture was filtered through a short plug of silical gel, and was washed with a copious amount of CH_2Cl_2 until no product was found. Solvent was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:7) to give the corresponding product **C** (1.7 g, 85%) as an orange solid.

A mixture of **C** (1 equiv), $Pd_2(dba)_3$ (3 mol%), P(2-furyl)$_3$ (15 mol%), and $Ar^1B(OH)_2$ (1 equiv) in 1,4-dioxane (0.1 M) was stirred at rt under argon for 5 min. An aq. Na_2CO_3 solution (1.0 M, 2 equiv) was added and the reaction mixture was heated at 65 ℃ for 23 h. The reaction mixture was then extracted with ether (3 times) and dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product **D**.

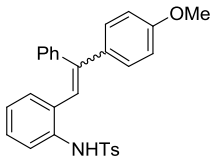
To a solution of **D** in mixed solvent (PEG : H_2O = 1:3, 0.15 M) were added $Ar^2B(OH)_2$ (1.25 equiv), $Pd(OAc)_2$ (4 mol%), and K_3PO_4 (2 equiv). The reaction mixture was stirred at 40 °C for 24 h. After cooling to rt, the mixture was diluted with water, extracted with CH_2Cl_2 (3 times), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give the corresponding product **E**.

The suspension of **E** (1 equiv) and $SnCl_2 \cdot H_2O$ (5 equiv) in EtOH (0.4 M) was heated at 100 °C for 30 min, and then cooled to rt. After most of EtOH was removed, the residue was taken into Et_2O and sat. K_2CO_3 solution. The reaction mixture was extracted with EtOAc (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 **F**.

4c-**d** and **4f**-**h** were prepared from **F** following a general procedure for tosylation. The stereochemistry of **4c**-**d** and **4f**-**h** was assigned based on spectral correlation with their precursors **F** which are known in the literature.[12]

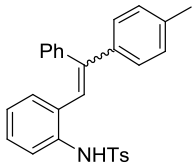
***N*-(2-(2-(4-Methoxyphenyl)-2-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (4c)**



E:*Z* = 1:0.6, a yellow solid (EtOAc : *n*-Hexane = 1:6), mp 60-66 ℃.

Signals corresponding to (*E*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 3.78 (s, 3H), 6.24 (s, 1H), 6.46 (s, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.76-6.96 (m, 4H), 7.02 (d, *J* = 9.2 Hz, 1H), 7.07-7.24 (m, 5H), 7.29-7.33 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H). Representative signals corresponding to (*Z*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 3.85 (s, 3H), 6.24 (s, 1H), 6.48 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 55.1, 55.3, 113.5, 113.8, 120.8, 122.0, 123.8, 123.9, 125.3, 125.4, 127.1, 127.7, 127.8, 128.0, 128.1, 128.3, 129.1, 129.56, 129.57, 130.2, 130.48, 130.50, 130.9, 131.36, 131.40, 131.5, 133.7, 134.0, 134.8, 136.8, 136.9, 139.1, 142.6, 143.6, 145.6, 145.7, 159.2, 159.6 (5 carbons are missing due to overlapping). EIMS *m*/*z* 455 (M^+), 300, 285, 208, 193, 165, 91.

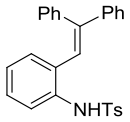
4-Methyl-*N*-(2-(2-phenyl-2-*p*-tolylvinyl)phenyl)benzenesulfonamide (4d)



E:*Z* = 1:0.6, a pale yellow solid (CH_2Cl_2 : *n*-Hexane = 1:3), mp 66-72 ℃.

Signals corresponding to (*E*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.20 (s, 3H), 2.32 (s, 3H), 6.21 (s, 1H), 6.61-6.90 (m, 7H), 6.97-7.25 (m, 8H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 2H). Representative signals corresponding to (*Z*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.27 (s, 3H), 2.32 (s, 3H), 6.22 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.16, 21.24, 21.6, 121.7, 122.3, 123.8, 124.0, 124.5, 125.3, 125.4, 125.9, 127.1, 127.6, 127.9, 128.0, 128.07, 128.10, 128.4, 128.9, 129.1, 129.2, 129.4, 129.6, 129.7, 130.1, 130.3, 130.5, 131.2, 131.3, 133.8, 134.0, 135.7, 136.9, 137.8, 138.1, 139.0, 139.5, 142.5, 143.7, 146.1, 146.2 (3 carbons are missing due to overlapping). EIMS *m*/*z* 439 (M^+), 284, 165, 91.

***N*-(2-(2,2-Diphenylvinyl)phenyl)-4-methylbenzenesulfonamide (4e)**



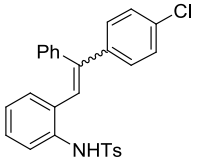
To a solution of **C** (351.1 mg, 1.144 mmol, 1 equiv) in mixed solvent (PEG : H_2O = 1:3, 7.6 mL, 0.15 M) were added phenylboronic acid (320.8 mg, 2.631 mmol, 2.3 equiv), $Pd(OAc)_2$ (11.2 mg, 0.0458 mmol, 4 mol%), and K_3PO_4 (485.6 mg, 2.288 mmol, 2 equiv). The reaction mixture was stirred at 40 ^oC for 18 h. After cooling to rt, the mixture was diluted with water, 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 (MeOH : CH_2Cl_2 : *n*-Hexane = 1:100:300) to give the corresponding product **E′** (189.1 mg, 56%) as a yellow oil.

The suspension of **E′** (210.1 mg, 0.697 mmol, 1 equiv) and $SnCl_2 \cdot H_2O$ (891.2 mg, 3.486 mmol, 5 equiv) in EtOH (1.7 mL, 0.4 M) was heated at 100 ^oC for 30 min, and then cooled to rt. After most of EtOH was removed, the residue was taken into Et_2O and sat. K_2CO_3 solution. The reaction mixture was extracted with EtOAc (three times), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (MeOH : CH_2Cl_2 : *n*-Hexane = 1:100:300) to give the corresponding product **F′** (124.8 mg, 66%) as a yellow solid.

4e was prepared from **F′** following a general procedure for tosylation as a white solid in 86 % yield (183.7 mg, EtOAc : *n*-Hexane = 1:10, mp 122-124 ℃).

^1H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 6.31 (s, 1H), 6.45 (br s, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.87-6.92 (m, 3H), 7.07-7.24 (m, 8H), 7.29-7.33 (m, 3H), 7.43 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 122.5, 123.9, 125.4, 127.1, 127.9, 128.0, 128.1, 128.2, 128.4, 129.6, 130.3, 130.5, 131.2, 134.0, 136.9, 138.9, 142.3, 143.7, 146.2 (1 carbon is missing due to overlapping). EIMS *m*/*z* 425 (M^+), 270, 193, 165, 91.

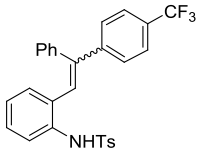
_N_-(2-(2-(4-Chlorophenyl)-2-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (4f)



E:*Z* = 1:0.3, a yellow solid (EtOAc : *n*-Hexane = 1:8), mp 128-131 ℃.

Signals corresponding to (*E*)-isomer: ^1H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 6.37 (s, 1H), 6.57 (br s, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 6.89 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.2 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.13-7.26 (m, 1H), 7.31-7.38 (m, 3H), 7.42 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H). Representative signals corresponding to (*Z*)-isomer: ^1H NMR ($CDCl_3$, 400 MHz) δ 2.38 (s, 3H), 6.33 (s, 1H), 6.62 (br s, 1H), 7.00 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 122.6, 123.1, 123.8, 124.4, 124.6, 125.2, 125.5, 125.8, 127.08, 127.12, 127.6, 127.9, 128.1, 128.2, 128.3, 128.47, 128.53, 129.0, 129.2, 129.3, 129.6, 129.8, 130.2, 130.3, 130.4, 130.89, 130.94, 131.7, 133.6, 133.9, 134.1, 134.3, 136.6, 136.8, 137.4, 140.9, 141.9, 143.7, 143.8, 145.0 (1 carbon is missing due to overlapping). EIMS *m*/*z* 459 (M^+), 228, 193, 165, 91.

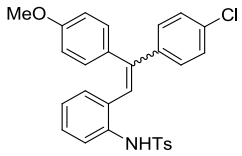
4-Methyl-_N_-(2-(2-phenyl-2-(4-(trifluoromethyl)phenyl)vinyl)phenyl)benzenesulfonamide (4g)



E:*Z* = 1:0.5, a white solid (EtOAc : *n*-Hexane = 1:10), mp 63-65 ℃.

Signals corresponding to (*E*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 6.47 (s, 1H), 6.62-6.69 (m, 1H), 6.69 (br s, 1H), 6.85 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 2H), 7.07-7.22 (m, 5H), 7.31-7.50 (m, 6H), 7.60 (d, *J* = 8.0 Hz, 2H). Representative signals corresponding to (*Z*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 6.89 (t, *J* = 7.2 Hz, 1H), 7.59 (d, *J* =7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 123.9, 124.0 (q, *J* = 271.0 Hz), 124.5, 125.2 (q, *J* = 3.7 Hz), 125.5, 125.8, 127.1, 127.2, 127.6, 127.9, 128.2 (q, *J* = 3.7 Hz), 128.36, 128.42, 128.6, 129.2 (q, *J* = 34.5 Hz), 129.45, 129.66, 129.69, 129.8, 130.2, 130.4, 130.5, 130.8, 131.3, 133.7, 134.5, 136.6, 136.9, 138.3, 138.9, 141.7, 142.9, 143.8, 143.86, 143.93, 144.9 (5 carbons are missing due to overlapping). EIMS *m*/*z* 493 (M^+), 338, 193, 165, 91.

_N_-(2-(2-(4-Chlorophenyl)-2-(4-methoxyphenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (4h)



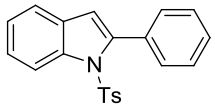
Stereochemistry of olefin could not be determined. a yellow solid (EtOAc : *n*-Hexane = 1:10), mp 129-139 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 3.78 (s, 3H), 6.23 (s, 1H), 6.43 (br s, 1H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 7.4 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 55.1, 114.0, 122.5, 124.3, 125.6, 127.1, 128.0, 128.3, 129.3, 129.6, 130.5, 131.5, 133.8, 134.0, 137.0, 141.2, 143.7, 144.4, 159.4 (2 carbons are missing due to overlapping). EIMS *m*/*z* 489 (M^+), 334, 299, 284, 254, 227, 208, 180, 165, 152, 127, 91, 65, 51.

General Procedure for the DDQ-Mediated C-H Amination of *N*-Ts-2-Alkenylanilines

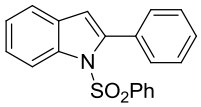
To a solution of the substrate **1** or **4** (0.05 mmol, 1 equiv) in CH_3CCl_3 (0.5 mL, 0.1 M) were added DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) (22.7 mg, 0.1 mmol, 2 equiv). The resulting mixture was stirred at the reported temperature (120 or 150 ℃) for the reported time under Ar atmosphere. After the reaction was completed, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product.

_N_-Ts-2-Phenylindole (2a)



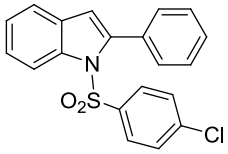
96% from (*E*)-**1a**; 76% from (*Z*)-**1a**, a white solid (EtOAc : *n*-Hexane = 1:7), mp 142-144 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H), 6.54 (s, 1H), 7.03 (d, J = 8.0 Hz, 2H), 7.24-7.28 (m, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.42-7.45 (m, 4H), 7.49-7.51 (m, 2H), 8.31 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 113.6, 116.6, 120.7, 124.3, 124.7, 126.8, 127.5, 128.6, 129.2, 130.3, 130.5, 132.4, 134.6, 138.3, 142.1, 144.5. EIMS *m*/*z* 347 (M^+), 208, 192, 177, 165, 139, 115, 91, 77, 65, 51.
Spectral data were consistent with data reported in the literature.[2, 14]

_N_-(Benzenesulfonyl)-2-phenylindole



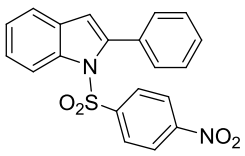
85%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 98-101 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.55 (s, 1H), 7.25 (t, J = 8.2 Hz, 2H), 7.28 (d, J = 7.6 Hz, 1H), 7.34-7.50 (m, 10H), 8.32 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 113.7, 116.6, 120.8, 124.4, 124.9, 126.7, 127.5, 128.6, 128.7, 130.3, 130.5, 132.3, 133.5, 137.5, 138.3, 142.1. EIMS *m*/*z* 333 (M^+), 192, 165, 139, 115, 89, 77, 63, 51.
Spectral data were consistent with data reported in the literature.[14]

_N_-(4-Chlorophenylsulfonyl)-2-phenylindole



89%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 150-158 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.58 (s, 1H), 7.22 (d, J = 8.8 Hz, 2H), 7.27 (t, J = 6.4 Hz, 1H), 7.30 (d, J = 8.8 Hz, 2H), 7.38 (t, J = 7.8 Hz, 1H), 7.44-7.51 (m, 6H), 8.30 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 114.2, 116.7, 120.9, 124.7, 125.1, 127.6, 128.2, 128.85, 128.91, 130.3, 130.7, 132.1, 135.7, 138.2, 140.2, 142.0. EIMS *m*/*z* 367 (M^+), 367, 192, 165, 139, 126, 111, 89, 75, 63, 51.

_N_-Ns-2-Phenylindole

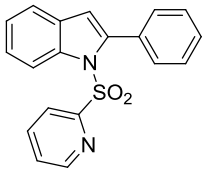


83%, a yellow solid (EtOAc : *n*-Hexane = 1:7), mp 140-147 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.61 (s, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.45-7.57 (m, 8H), 8.09 (d, J = 8.4 Hz, 2H), 8.30 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 114.8, 116.7, 121.2, 123.8, 125.2, 125.4, 127.8, 128.1, 129.1, 130.2, 130.8, 131.7, 138.1, 141.9,

[14] Yin, Y.; Ma, W.; Chai, Z.; Zhao, G. *J. Org. Chem.* **2007**, *72*, 5731.

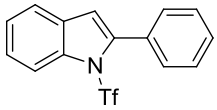
142.2, 150.4. EIMS *m*/*z* 378 (M^+), 192, 165, 139, 122, 115, 96, 89, 76, 63, 51.
Spectral data were consistent with data reported in the literature.[14]

_N_-(Pyridin-2-ylsulfonyl)-2-phenylindole



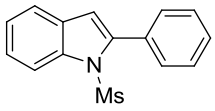
80%, a white solid (EtOAc : *n*-Hexane = 1:7).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.60 (s, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.32-7.41 (m, 5H), 7.49-7.53 (m, 3H), 7.65 (d, J = 7.6 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.49 (d, J = 3.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 112.6, 116.1, 120.7, 122.3, 124.2, 124.7, 127.3, 127.4, 128.6, 130.0, 130.4, 132.3, 137.6, 138.0, 142.3, 150.0, 155.3. EIMS *m*/*z* 334 (M^+), 269, 241, 215, 208, 192, 177, 165, 139, 127, 115, 102, 89, 78, 63, 51.

_N_-Tf-2-Phenylindole



66%, a white solid (EtOAc : *n*-Hexane = 1:7).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.77 (s, 1H), 7.39-7.47 (m, 5H), 7.50 (d, J = 8.0 Hz, 2H), 7.61 (dd, J = 2.4, 6.0 Hz, 1H), 8.05 (dd, J = 2.4, 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 114.8, 115.7, 118.0, 121.3, 125.6, 125.8, 127.7, 129.3, 130.0, 130.3, 130.8, 137.3, 141.7. EIMS *m*/*z* 325 (M^+), 192, 165, 139, 96, 89, 69, 63, 51.

_N_-Ms-2-Phenylindole



83%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 107-108 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.74 (s, 3H), 6.73 (s, 1H), 7.39 (t, J = 7.4 Hz, 2H), 7.45 (m, 3H), 7.58-7.63 (m, 3H), 8.15 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.5, 113.1, 115.8, 121.1, 124.6, 125.2, 127.7, 128.9, 130.1, 130.3, 132.0, 138.0, 142.0. EIMS *m*/*z* 271 (M^+), 192, 165, 139, 115, 96, 89, 63, 51.
Spectral data were consistent with data reported in the literature.[14-15]

_N_-(Ethoxycarbonyl)-2-phenylindole

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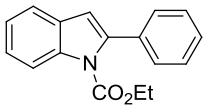
[15] Li, P.; Wang, L.; Wang, M.; You, F. *Eur. J. Org. Chem.* **2008**, 5946.

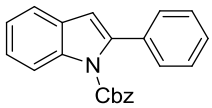


32%, a colorless oil. (EtOAc : *n*-Hexane = 1:10).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10 (t, J = 6.9 Hz, 3H), 4.25 (q, J = 7.2 Hz, 2H), 6.60 (s, 1H), 7.25-7.44 (m, 7H), 7.56 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 8.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 62.9, 110.5, 115.4, 120.5, 123.2, 124.5, 127.68, 127.74, 128.0, 128.1, 128.8, 129.0, 134.1, 151.2. EIMS *m*/*z* 265 (M^+), 236, 220, 206, 193, 165, 139, 115, 106, 89, 77, 63, 51.

Spectral data were consistent with data reported in the literature.[16]

_N_-Cbz-2-Phenylindole

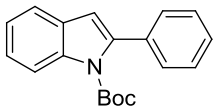


16%, a colorless oil. (EtOAc : *n*-Hexane = 1:10).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.23 (s, 2H), 6.59 (s, 1H), 7.07 (dd, J = 2.0, 7.2 Hz, 2H), 7.26-7.41 (m, 10H), 7.55 (d, J = 7.6 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 68.6, 105.0, 110.9, 115.5, 120.5, 123.3, 124.6, 127.8, 128.3, 128.37, 128.44, 128.8, 129.4, 134.2, 134.5, 137.3, 140.5, 151.6. EIMS *m*/*z* 327 (M^+), 283, 206, 193, 178, 165, 140, 102, 91, 65, 51.

Spectral data were consistent with data reported in the literature.[17]

_N_-Boc-2-Phenylindole

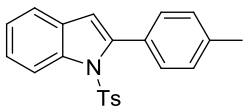


24%, a colorless oil. (EtOAc : *n*-Hexane = 1:10).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (s, 9H), 6.56 (s, 1H), 7.24-7.43 (m, 7H), 7.56 (d, J = 7.6 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.5, 83.4, 109.9, 115.2, 120.4, 122.9, 124.3, 127.6, 127.8, 128.7, 129.2, 135.0, 137.4, 140.5, 150.2. EIMS *m*/*z* 293 (M^+), 237, 193, 165, 139, 115, 96, 89, 82, 57.

Spectral data were consistent with data reported in the literature.[15]

_N_-Ts-2-_p_-Tolylindole (2b)



42%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 99-103 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 2.45 (s, 3H), 6.52 (s, 1H), 7.04 (d, J = 8.0 Hz, 2H), 7.25

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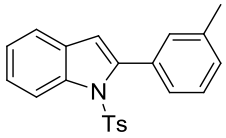
[16] Hiroya, K.; Itoh, S.; Sakamoto, T. *J. Org. Chem.* **2004**, *69*, 1126.

[17] Ackermann, L.; Barfüßer, S.; Potukuchi, H. K. *Adv. Synth. Catal.* **2009**, *351*, 1064.

(d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.46, 21.53, 113.3, 116.7, 120.6, 124.3, 124.6, 126.8, 128.3, 129.2, 129.5, 130.2, 130.7, 134.6, 138.2, 138.6, 142.3, 144.5. EIMS *m*/*z* 361 (M^+), 206, 191, 179, 164, 152, 139, 115, 102, 91, 77, 65, 51.

Spectral data were consistent with data reported in the literature.[18]

_N_-Ts-2-_m_-Tolylindole (2c)

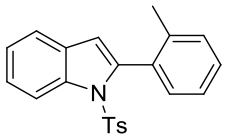


84%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 140-144 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.20 (s, 3H), 2.33 (s, 3H), 6.44 (s, 1H), 6.95 (d, *J* = 7.6 Hz, 2H), 7.17-7.28 (m, 8H), 7.35 (d, *J* = 7.6 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 21.5, 113.4, 116.6, 120.7, 124.3, 124.7, 126.8, 127.4, 129.2, 129.4, 130.6, 131.0, 132.3, 134.7, 137.0, 138.2, 142.3, 144.5 (1 carbon is missing due to overlapping). EIMS *m*/*z* 361 (M^+), 222, 206, 191, 179, 164, 152, 139, 115, 102, 91, 77, 65, 51.

Spectral data were consistent with data reported in the literature.[19]

_N_-Ts-2-_o_-Tolylindole (2d)



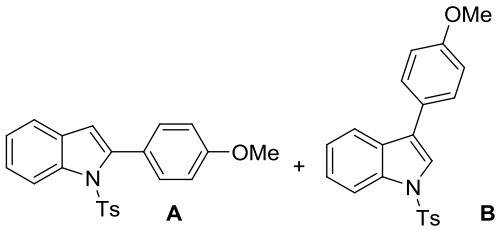
90%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 82-89 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25 (s, 3H), 2.33 (s, 3H), 6.49 (s, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.38-7.40 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5, 21.5, 112.3, 115.7, 120.6, 123.8, 124.5, 124.6, 126.9, 129.1, 129.3, 129.6, 130.0, 130.8, 132.0, 135.5, 137.2, 139.3, 140.3, 144.6. EIMS *m*/*z* 361 (M^+), 222, 206, 178, 151, 128, 115, 101, 91, 77, 65, 51. HREIMS *m/z* 361.1138 $(M)^+$, calcd for $C_{22}H_{19}NO_2S$ 361.1136.

_N_-Ts-2-(4-Methoxyphenyl)indole (A) & _N_-Ts-3-(4-Methoxyphenyl)indole (B) (2e)

[18] Palimkar, S. S.; Kumar, P. H.; Lahoti, R. J.; Srinivasan, K. V. *Tetrahedron* **2006**, *62*, 5109.

[19] Monguchi, Y.; Mori, S.; Aoyagi, S.; Tsutsui, A.; Maegawa, T.; Sajiki, H. *Org. Biomol. Chem.* **2010**, *8*, 3338.

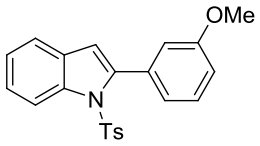


99% (**A**:**B** = 5.6:1), a colorless oil (EtOAc : *n*-Hexane = 1:7).

Signals corresponding to **A**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 3.94 (s, 3H), 6.53 (s, 1H), 7.01 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.28-7.35 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.47 (d, J = 8.8 Hz, 3H), 8.36 (d, J = 8.4 Hz, 1H). Representative signals corresponding to **B**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 3.91 (s, 3H), 7.58 (d, J = 8.8 Hz, 2H), 7.68 (s, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 55.3, 55.4, 112.9, 113.0, 113.8, 114.4, 116.7, 120.4, 120.5, 122.3, 123.5, 124.3, 124.5, 124.7, 124.8, 126.8, 126.9, 129.0, 129.2, 130.0, 130.6, 131.7, 134.7, 138.2, 142.0, 144.5, 160.0 (8 carbons are missing due to overlapping). EIMS (**A**) *m*/*z* 377 (M^+), 222, 207, 195, 178, 165, 152, 139, 126, 102, 91, 77, 65, 51. EIMS (**B**) *m*/*z* 377 (M^+), 222, 207, 190, 178, 152, 139, 126, 113, 91, 77, 65, 51.

Spectral data of **A** were consistent with data reported in the literature.[18]

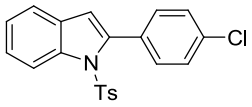
_N_-Ts-2-(3-Methoxyphenyl)indole (2f)



74%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 98-104 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H), 3.86 (s, 3H), 6.55 (s, 1H), 6.99 (d, J = 8.0 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 7.05 (s, 1H), 7.09 (d, J = 8.4 Hz, 1H), 7.24-7.37 (m, 5H), 7.44 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 55.3, 113.7, 114.5, 115.9, 116.7, 120.7, 122.8, 124.3, 124.8, 126.8, 128.5, 129.2, 130.5, 133.6, 134.6, 138.3, 141.9, 144.5, 158.7. EIMS *m*/*z* 377 (M^+), 313, 297, 238, 222, 207, 191, 178, 165, 152, 139, 126, 102, 91, 77, 65, 51. HREIMS *m*/*z* 377.1086 $(M)^+$, calcd for $C_{22}H_{19}NO_3S$ 377.1086.

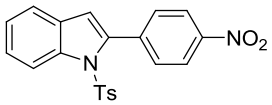
_N_-Ts-2-(4-Chlorophenyl)indole (2g)



86%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 133-135 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25 (s, 3H), 6.51 (s, 1H), 7.01 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.6 Hz, 3H), 7.32-7.42 (m, 6H), 8.28 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 114.1, 116.7, 120.8, 124.5, 125.1, 126.7, 127.8, 129.3, 130.4, 130.9, 131.5, 134.4, 134.8, 138.3, 140.8, 144.7. EIMS *m*/*z* 381 (M^+), 242, 226, 199, 190, 164, 155, 139, 113, 91, 75, 65, 51. HREIMS *m*/*z* 381.0588 $(M)^+$, calcd for $C_{21}H_{16}ClNO_2S$ 381.0590.

_N_-Ts-2-(4-Nitrophenyl)indole (2h)

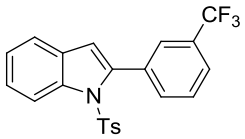


73%, a yellow solid (EtOAc : *n*-Hexane = 1:7), mp 170-175 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 6.69 (s, 1H), 7.06 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 8.29 (d, J = 8.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 116.1, 116.8, 121.3, 122.9, 124.9, 125.9, 126.6, 129.4, 130.3, 130.7, 133.9, 138.8, 138.9, 139.6, 145.1, 147.6.

Spectral data were consistent with data reported in the literature.[20]

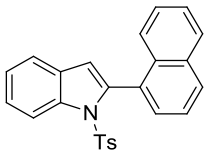
_N_-Ts-2-(3-(Trifluoromethyl)phenyl)indole (2i)



94%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 55-60 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 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 = 7.4 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.63 (s, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 114.4, 116.6, 121.0, 124.0 (q, J = 270.9 Hz), 124.5, 125.28 (q, J = 3.6 Hz), 125.33, 126.6, 126.7 (q, J = 3.8 Hz), 128.0, 129.4, 130.0 (q, J = 32.3 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. HREIMS *m/z* 415.0853 $(M)^+$, calcd for $C_{22}H_{16}F_3NO_2S$ 415.0854.

_N_-Ts-2-(1-Naphthyl)indole (2j)



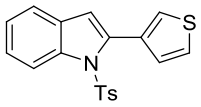
99%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 138-142 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.24 (s, 3H), 6.66 (s, 1H), 6.95 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.40-7.55 (m, 5H), 7.65 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 113.7, 115.8, 120.8, 124.0, 124.5, 124.8, 125.8, 126.1, 126.3, 126.9, 128.1, 129.3, 129.4, 129.6, 129.9, 130.0, 133.1, 133.4, 135.3, 137.6, 138.8, 144.6. EIMS *m/z* 397 (M^+), 242, 213, 187, 163, 155, 127, 121, 107, 91, 77, 65, 51.

Spectral data were consistent with data reported in the literature.[18-19]

[20] Kurisaki, T.; Naniwa, T.; Yamamoto, T.; Imagawa, H.; Nishizawa, M. *Tetrahedron Lett.* **2007**, *48*, 1871.

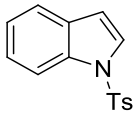
_N_-Ts-2-(3-Thienyl)indole (2k)



86%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 135-138 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H), 6.56 (s, 1H), 7.04 (d, J = 8.0 Hz, 2H), 7.24-7.30 (m, 4H), 7.34-7.37 (m, 3H), 7.44 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 113.1, 116.3, 120.6, 124.2, 124.3, 124.8, 125.7, 126.7, 129.3, 130.2, 130.3, 132.6, 134.9, 136.6, 138.0, 144.6. EIMS *m*/*z* 353 (M^+), 289, 273, 214, 198, 171, 154, 140, 127, 108, 101, 91, 77, 65, 51. HREIMS *m/z* 353.0542 $(M)^+$, calcd for $C_{19}H_{15}NO_2S_2$ 353.0544.

_N_-Ts-Indole (2l)

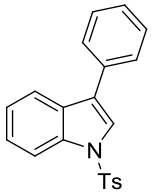


50%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 68-71 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 6.65 (d, J = 3.2 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 6.8 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 3.6 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 109.0, 113.5, 121.4, 123.3, 124.5, 126.3, 126.8, 129.9, 130.7, 134.8, 135.3, 144.9. EIMS *m*/*z* 271 (M^+), 206, 178, 155, 139, 116, 91, 77, 65, 51.

Spectral data were consistent with data reported in the literature.[21]

_N_-Ts-3-Phenylindole (2m)



95%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 145-147 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.22 (s, 3H), 7.23 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H), 7.73 (s, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 113.9, 120.5, 123.0, 123.6, 124.0, 124.9, 126.9, 127.6, 127.9, 128.9, 129.3, 130.0, 133.1, 135.2, 135.5, 145.1. EIMS *m*/*z* 347 (M^+), 267, 192, 165, 139, 115, 102, 91, 77, 65, 51.

Spectral data were consistent with data reported in the literature.[22]

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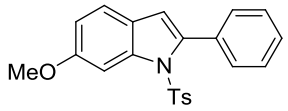
[21] Hightower, T. R.; Hasvold, L. A.; Peterson, K. P.; Larock, R. C. *J. Org. Chem.* **1996**, *61*, 3584.

[22] Kudo, N.; Perseghini, M.; Fu, G. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 1282.

_N_-Ts-6-Methoxy-2-phenylindole (2n)

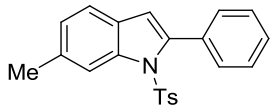


57%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 124-128 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 3.94 (s, 3H), 6.46 (s, 1H), 6.90 (dd, J = 2.0, 8.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.8 Hz, 1H), 7.37-7.41 (m, 3H), 7.45-7.48 (m, 2H), 7.88 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 55.8, 101.0, 113.4, 113.5, 121.1, 124.4, 126.7, 127.4, 128.3, 129.2, 130.2, 132.6, 134.5, 139.5, 140.9, 144.5, 157.9. EIMS *m*/*z* 377 (M^+), 281, 222, 207, 195, 179, 152, 139, 103, 91, 76, 65, 51.

Spectral data were consistent with data reported in the literature.[23]

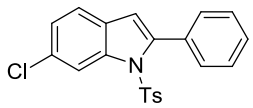
_N_-Ts-6-Methyl-2-phenylindole (2o)



6%, a yellow solid (EtOAc : *n*-Hexane = 1:7), mp 145-152 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 2.53 (s, 3H), 6.49 (s, 1H), 7.04 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.6 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.6 Hz, 1H), 7.41-7.42 (m, 3H), 7.47-7.49 (m, 2H), 8.13 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 22.1, 113.6, 116.8, 120.2, 125.7, 126.8, 127.4, 128.3, 128.5, 129.2, 130.2, 132.6, 134.7, 134.9, 138.7, 141.4, 144.4. HREIMS *m/z* 361.1138 $(M)^+$, calcd for $C_{22}H_{19}NO_2S$ 361.1136.

_N_-Ts-6-Chloro-2-phenylindole (2p)

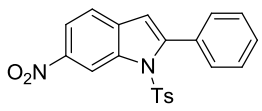


87%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 140-144 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.22 (s, 3H), 6.41 (s, 1H), 6.98 (d, J = 7.6 Hz, 2H), 7.16 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.8 Hz, 1H), 7.33-7.38 (m, 5H), 8.27 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 112.9, 116.7, 121.4, 124.9, 126.8, 127.5, 128.89, 128.91, 129.4, 130.4, 130.6, 131.9, 134.5, 138.6, 142.7, 144.9. EIMS *m*/*z* 381 (M^+), 226, 199, 190, 164, 155, 123, 113, 91, 73, 65, 51.

Spectral data were consistent with data reported in the literature.[23]

_N_-Ts-6-Nitro-2-phenylindole (2q)

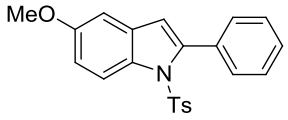


[23] Inamoto, K.; Asano, N; Nakamura, Y.; Yonemoto, M.; Kondo, Y. *Org. Lett.* **2012**, *14*, 2622.

100%, a yellow solid (EtOAc : *n*-Hexane = 1:7), mp 146-149 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 6.63 (s, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.43-7.51 (m, 5H), 7.55 (d, J = 8.8 Hz, 1H), 8.18 (dd, J = 1.6, 8.8 Hz, 1H), 9.25 (s, 1H).^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 112.3, 112.8, 119.6, 120.7, 126.9, 127.7, 129.59, 129.62, 130.5, 131.1, 134.4, 135.0, 136.9, 145.0, 145.5, 147.2. EIMS *m/z* 392 (M^+), 281, 253, 237, 207, 190, 179, 163, 155, 139, 126, 91, 77, 65, 51. HREIMS *m/z* 392.0832 $(M)^+$, calcd for $C_{21}H_{16}N_2O_4S$ 392.0831.

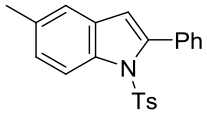
_N_-Ts-5-Methoxy-2-phenylindole (2r)



100%, a colorless oil (EtOAc : *n*-Hexane = 1:7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 3.83 (s, 3H), 6.49 (s, 1H), 6.89 (d, J = 2.0 Hz, 1H), 6.96 (dd, J = 2.2, 9.4 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.44 (m, 3H), 7.51-7.53 (m, 2H), 8.20 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 55.5, 103.1, 113.4, 113.9, 117.7, 126.8, 127.5, 128.6, 129.1, 130.2, 131.7, 132.4, 132.8, 134.3, 143.1, 144.4, 157.0. EIMS *m/z* 377 (M^+), 222, 207, 195, 179, 152, 127, 102, 91, 76, 65, 51. HREIMS *m/z* 377.1085 $(M)^+$, calcd for $C_{22}H_{19}NO_3S$ 377.1086.

_N_-Ts-5-Methyl-2-phenylindole (2s)

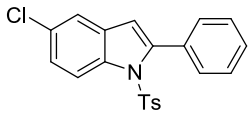


20%, a colorless oil (EtOAc : *n*-Hexane = 1:7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 2.42 (s, 3H), 6.48 (s, 1H), 7.05 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.8 Hz, 1H), 7.23 (s, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.43-7.53 (m, 5H), 8.18 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 21.5, 113.6, 116.4, 116.8, 120.2, 120.6, 126.1, 126.8, 127.5, 128.46, 128.54, 129.1, 130.3, 130.8, 132.5, 134.0, 144.4. EIMS *m/z* 361 (M^+), 222, 206, 179, 152, 128, 102, 91, 77, 65, 51.

Spectral data were consistent with data reported in the literature.[14, 18]

_N_-Ts-5-Chloro-2-phenylindole (2t)

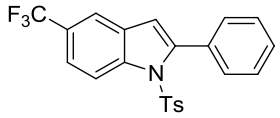


86%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 136-137 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 6.47 (s, 1H), 7.05 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.30 (dd, J = 1.6, 9.2 Hz, 1H), 7.40-7.48 (m, 6H), 8.23 (d, J = 9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 112.6, 117.7, 120.2, 124.9, 126.8, 127.5, 128.9, 129.3, 130.0, 130.3,

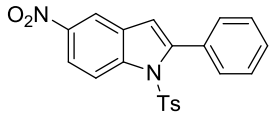
131.7, 131.8, 134.4, 136.6, 143.5, 144.8. EIMS *m*/*z* 381 (M^+), 242, 226, 199, 190, 164, 155, 139, 123, 91, 73, 65, 51.
Spectral data were consistent with data reported in the literature.[14]

_N_-Ts-2-Phenyl-5-(trifluoromethyl)indole (2u)



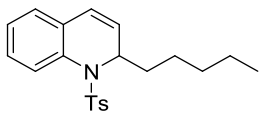
99%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 120-124 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 6.60 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.42-7.49 (m, 5H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.75 (s, 1H), 8.43 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 112.7, 116.6, 118.1 (q, *J* = 4.4 Hz), 121.3 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 270.6 Hz), 126.5 (q, *J* = 32.3 Hz), 126.8, 127.6, 129.1, 129.4, 130.0, 130.5, 131.6, 134.7, 139.6, 143.7, 145.1. EIMS *m*/*z* 415 (M^+), 396, 350, 335, 276, 260, 240, 233, 190, 183, 155, 137, 107, 91, 77, 65, 51. HREIMS *m*/*z* 415.0855 $(M)^+$, calcd for $C_{22}H_{16}F_3NO_2S$ 415.0854.

_N_-Ts-5-Nitro-2-phenylindole (2v)



96%, a yellow solid (EtOAc : *n*-Hexane = 1:7), mp 142-152 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 6.66 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.42-7.49 (m, 5H), 8.25 (dd, *J* = 2.0, 9.2 Hz, 1H), 8.38 (d, *J* = 2.0 Hz, 1H), 8.45 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 112.7, 116.5, 116.7, 119.7, 126.8, 127.6, 129.4, 129.6, 130.0, 130.5, 131.1, 134.5, 141.0, 144.7, 144.9, 145.5. EIMS *m*/*z* 392 (M^+), 253, 237, 207, 190, 179, 163, 155, 139, 126, 91, 77, 65, 51.
Spectral data were consistent with data reported in the literature.[14]

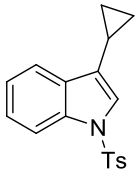
_N_-Ts-2-Pentyl-1,2-dihydroquinoline (2w′)



31%, a colorless oil (EtOAc : *n*-Hexane = 1:7).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.83 (t, *J* = 6.8 Hz, 3H), 1.22-1.25 (m, 5H), 1.33-1.35 (m, 3H), 2.29 (s, 3H), 4.72 (dt, *J* = 5.6, 6.8 Hz, 1H), 5.60 (dd, *J* = 5.6, 9.6 Hz, 1H), 5.93 (d, *J* = 9.2 Hz, 1H), 6.89 (d, *J* = 6.8 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 21.5, 22.5, 24.9, 31.4, 33.2, 55.1, 123.7, 126.2, 126.4, 127.2, 127.86, 127.88, 128.8, 128.9, 129.1, 132.8, 136.3, 143.1. EIMS *m*/*z* 355 (M^+), 284, 207, 155, 130, 102, 91, 77, 65, 51.

Spectral data were consistent with data reported in the literature.[24]

_N_-Ts-3-Cyclopropylindole (2x)

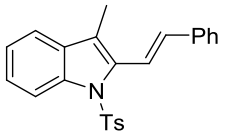


57%, a yellow solid (EtOAc : *n*-Hexane = 1:10), mp 160-165 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.63-0.67 (m, 2H), 0.89-0.94 (m, 2H), 1.82-1.86 (m, 1H), 2.33 (s, 3H), 7.19 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.4 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 5.9, 6.3, 21.5, 113.7, 119.6, 121.5, 123.0, 124.7, 125.9, 126.7, 129.5, 129.8, 131.6, 135.3, 144.7. EIMS *m*/*z* 311 (M^+), 156, 128, 91.

The chemical structure of compound **2x** was assigned based on spectral correlation with its des-tosyl congener.[25]

(*E*)-*N*-Ts-3-Methyl-2-styrylindole (2y′)

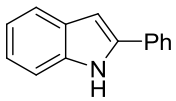


5%, a colorless solid (Et_2O : *n*-Hexane = 1:12).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H), 2.32 (s, 3H), 6.66 (d, *J* = 16.4 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 3H), 7.41-7.44 (m, 3H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 16.8 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H). EIMS *m*/*z* 387 (M^+), 281, 232, 217, 207, 191, 91.

The chemical structure of compound **2y′** was assigned based on spectral correlation with its *N*-(2-pyridylsulfonyl)indole congener.[26]

2-Phenylindole (3)



To a solution of **2a** (19.8 mg, 0.0570 mmol, 1 equiv) in MeOH (1.14 mL, 0.05 M) was added Mg (20.8 mg, 0.855 mmol, 15 equiv).[27] After being stirred at 50 ℃ for 6 h, the reaction mixture was poured into aq. NH_4Cl and then the product was extracted with CH_2Cl_2 (three times). The combined

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[24] Theeraladanon, C.; Arisawa, M.; Nakagawa, M.; Nishida, A. *Tetrahedron*: *Asymmetry* **2005**, *16*, 827.

[25] LaPorte, M.; Hong, K. B.; Xu, J.; Wipf, P. *J. Org. Chem*. **2013**, *78*, 167.

[26] García-Rubia, A.; Arrayás, R. G.; Carretero, J. C. *Angew. Chem. Int. Ed*. **2009**, *48*, 6511.

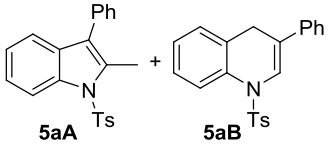
[27] Muratake, H.; Natsume, M. *Heterocycles* **1989**, *29*, 783.

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 afford **3** (10.6 mg, 95%) as a colorless solid (mp 178-180 ℃).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.85 (s, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.65 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 8.33 (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 100.0, 110.9, 120.2, 120.6, 122.3, 125.1, 127.7, 129.0, 129.2, 132.3, 136.8, 137.8. EIMS *m*/*z* 193 (M^+), 165, 139, 115, 96, 89, 83, 63, 51.

Spectral data were consistent with data reported in the literature.[28]

_N_-Ts-2-Methyl-3-phenylindole (5aA) & _N_-Ts-3-Phenyl-1,4-dihydroquinoline (5aB)

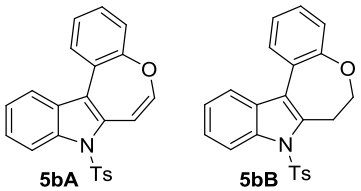


48% (**5aA**:**5aB** = 1.1:1), a colorless oil (EtOAc : *n*-Hexane = 1:7).

Signals corresponding to **5aA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 2.60 (s, 3H), 7.22-7.24 (m, 1H), 7.23 (d, J = 7.6 Hz, 2H), 7.30-7.39 (m, 4H), 7.41-7.48 (m, 3H), 7.73 (d, J = 8.4 Hz, 2H), 8.27 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.5, 21.56, 114.5, 119.2, 122.5, 123.5, 124.2, 126.4, 127.3, 128.5, 129.90, 129.94, 130.05, 133.07, 133.11, 136.3, 136.4, 144.7. Representative signals corresponding to **5aB**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 5.10 (s, 2H), 7.92 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.60, 37.6, 114.8, 120.6, 123.9, 126.1, 127.1, 127.3, 128.2, 128.8, 129.76, 129.79, 131.7, 131.9, 135.8, 136.5, 145.1 (1 carbon is missing due to overlapping). EIMS (**5aA**) *m*/*z* 361 (M^+), 206, 178, 165, 152, 128, 115, 91, 77, 65, 51. EIMS (**5aB**) *m*/*z* 361 (M^+), 207, 178, 165, 152, 139, 128, 115, 91, 77, 65, 51.

Spectral data of **5aA** were consistent with data reported in the literature.[29]

Indoles (5bA) & (5bB)



5aA: 40%, a colorless oil (EtOAc : *n*-Hexane = 1:7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 6.62 (d, J = 5.6 Hz, 1H), 6.98 (d, J = 5.2 Hz, 1H), 7.17 (d, J = 8.4 Hz, 3H), 7.26-7.33 (m, 2H), 7.37-7.38 (m, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 111.0, 115.4, 120.1, 121.5, 122.4, 124.2, 125.2, 125.5, 126.59, 126.63, 128.25, 128.32, 129.7, 129.8,

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[28] Wang, R. P.; Mo, S.; Lu, Y. Z.; Shen, Z. M. *Adv. Synth. Catal.* **2011**, *353*, 713.

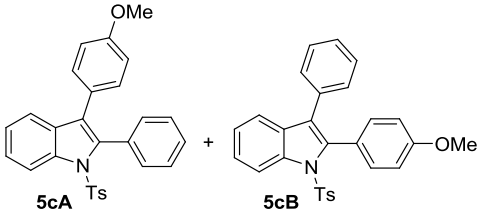
[29] Zhu, C.; Ma, S. *Org. Lett.* **2013**, *15*, 2782.

133.2, 134.9, 136.7, 145.0, 146.5, 156.9. EIMS *m/z* 387 (M^+), 281, 232, 207, 203, 176, 151, 133, 103, 91, 73, 65, 51. HREIMS *m/z* 387.0931 $(M)^+$, calcd for $C_{23}H_{17}NO_3S$ 387.0929.

5aB: 17%, a colorless oil (EtOAc : *n*-Hexane = 1:7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 3.60 (t, J = 6.0 Hz, 2H), 4.43 (t, J = 5.8 Hz, 2H), 7.12 (d, J = 8.0 Hz, 1H), 7.16-7.37 (m, 6H), 7.67 (d, J = 8.0 Hz, 2H), 7.87-7.89 (m, 2H), 8.31 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 30.5, 73.4, 114.9, 118.2, 120.0, 121.4, 123.5, 123.7, 124.6, 125.7, 126.3, 127.9, 128.7, 129.6, 130.0, 135.7, 136.1, 137.1, 145.0, 158.9. EIMS *m/z* 389 (M^+), 307, 281, 267, 234, 207, 204, 165, 152, 133, 102, 96, 91, 73, 65, 55. HREIMS *m/z* 389.1087 $(M)^+$, calcd for $C_{23}H_{19}NO_3S$ 389.1086.

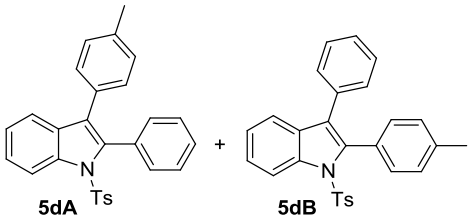
N-Ts-3-(4-Methoxyphenyl)-2-phenylindole (5cA) & *N*-Ts-2-(4-Methoxyphenyl)-3-phenylindole (5cB)



100% (**5cA**:**5cB** = 10:1), a white solid (EtOAc : *n*-Hexane = 1:5), mp 144-150 ℃.

Signals corresponding to **5cA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.76 (s, 3H), 6.77 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.23-7.35 (m, 8H), 7.41 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 55.1, 113.7, 116.2, 120.0, 124.1, 124.4, 124.8, 125.1, 126.9, 127.3, 128.4, 129.3, 130.7, 130.9, 131.1, 132.0, 135.3, 136.5, 137.2, 144.5, 158.5. Representative signals corresponding to **5cB**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.84 (s, 3H), 6.81 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.7, 112.8, 119.8, 128.2, 129.8, 133.4. HREIMS *m/z* 453.1397 $(M)^+$, calcd for $C_{28}H_{23}NO_3S$ 453.1399.

N-Ts-2-Phenyl-3-*p*-tolylindole (5dA) & *N*-Ts-3-Phenyl-2-*p*-tolylindole (5dB)

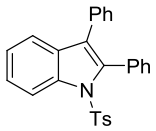


68% (**5dA**:**5dB** = 3.3:1), a white solid (EtOAc : *n*-Hexane = 1:5), mp 160-165 ℃.

Signals corresponding to **5dA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H), 2.30 (s, 3H), 6.97 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 7.6 Hz, 2H), 7.24-7.34 (m, 8H), 7.40 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 21.6, 116.2, 120.0, 124.1, 124.7, 125.1, 126.9, 127.3, 128.4, 128.9, 129.3, 129.6, 129.7, 130.6, 131.1, 132.1, 135.3, 136.6, 137.3, 144.5 (1 carbon is missing due to overlapping). Representative signals corresponding to **5dB**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 2.37 (s, 3H), 7.08 (d, J =

8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 116.3, 119.9, 125.0, 126.9, 127.9, 128.1, 128.2, 129.9, 131.9, 132.8, 138.3. EIMS (**5dA**) *m*/*z* 437 (M^+), 282, 267. EIMS (**5dB**) *m*/*z* 437 (M^+), 282, 267. HREIMS *m*/*z* 437.1449 $(M)^+$, calcd for $C_{28}H_{23}NO_2S$ 437.1449.

***N*-Ts-2,3-Diphenylindole (5e)**

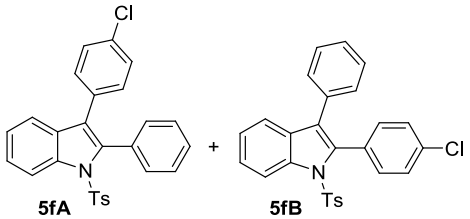


87%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 137-149 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 7.07-7.10 (m, 4H), 7.19-7.36 (m, 9H), 7.34 (d, J = 8.4 Hz, 2H), 7.41 (t, J = 7.8 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 116.2, 120.0, 124.2, 124.7, 125.2, 126.9, 127.3, 128.2, 128.5, 129.3, 129.8, 130.4, 130.9, 132.1, 132.7, 135.3, 136.8, 137.2, 144.6 (1 carbon is missing due to overlapping). EIMS *m*/*z* 423 (M^+), 268, 239, 213, 190, 165, 134, 120, 91, 65, 51.

Spectral data were consistent with data reported in the literature.[30]

***N*-Ts-3-(4-Chlorophenyl)-2-phenylindole (5fA) & *N*-Ts-2-(4-Chlorophenyl)-3-phenylindole (5fB)**

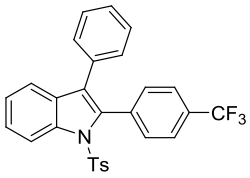


79% (**5fA**:**5fB** = 1:1.5), a white solid (EtOAc : *n*-Hexane = 1:5), mp 176-178 ℃.

Representative signals corresponding to **5fA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 7.02 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 7.6 Hz, 2H), 8.41 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 116.2, 119.6, 123.3, 124.2, 125.27, 126.9, 127.4, 128.4, 128.6, 129.3, 129.9, 130.5, 131.0, 131.1, 132.0, 132.8, 135.3, 137.0, 137.1, 144.6. Representative signals corresponding to **5fB**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 7.09 (d, J = 8.0 Hz, 4H), 8.40 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 116.3, 120.0, 124.3, 125.32, 125.4, 126.8, 127.1, 127.6, 128.1, 128.3, 129.4, 129.7, 130.4, 132.2, 133.2, 134.5, 135.0, 135.4, 137.3, 144.7. HREIMS *m*/*z* 457.0902 $(M)^+$, calcd for $C_{27}H_{20}ClNO_2S$ 457.0903.

***N*-Ts-3-Phenyl-2-(4-(trifluoromethyl)phenyl)indole (5gB)**

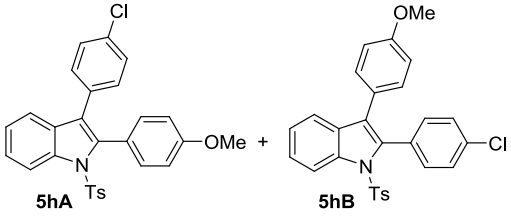
[30] Larock, R. C.; Yum, E. K.; Refvik, M. D. *J. Org. Chem.* **1998**, *63*, 7652.



30%, a white solid (EtOAc : *n*-Hexane = 1:7), mp 117-121 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 7.04-7.06 (m, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 7.2 Hz, 3H), 7.31 (d, J = 8.4 Hz, 3H), 7.39 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 8.6 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 8.40 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 116.4, 120.2, 124.2 (q, J = 3.7 Hz), 124.5, 125.7, 126.1, 126.8, 127.4, 128.4, 129.4, 129.8, 130.2 (q, J = 32.2 Hz), 130.5, 132.0, 132.2, 134.8, 134.9, 135.1, 137.5, 144.9 (1 carbon is missing due to overlapping). HREIMS *m/z* 491.1168 $(M)^+$, calcd for $C_{28}H_{20}F_3NO_2S$ 491.1167.

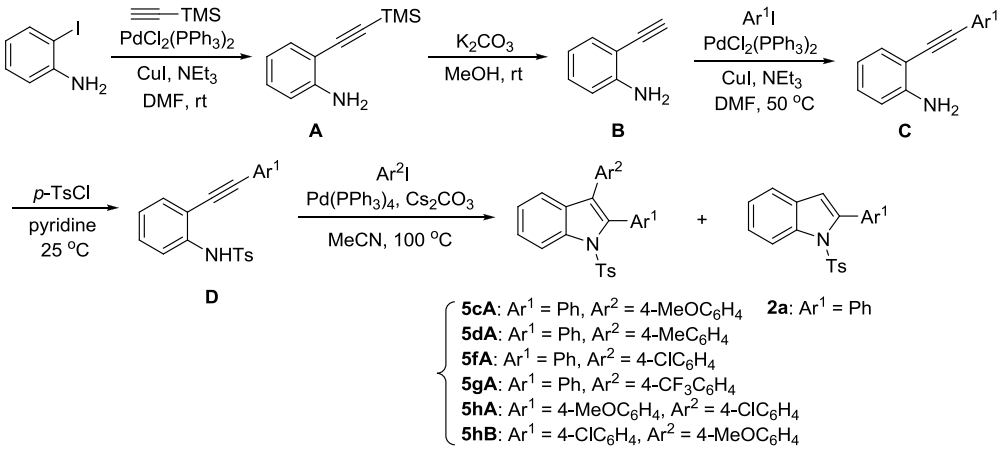
_N_-Ts-3-(4-Chlorophenyl)-2-(4-methoxyphenyl)indole (5hA) & _N_-Ts-2-(4-Chlorophenyl)-3-(4-methoxyphenyl)indole (5hB)



100% (**5hA**:**5hB** = 1:13.5), a white solid (EtOAc : *n*-Hexane = 1:7), mp 150-154 ℃.

Representative signals corresponding to **5hA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.85 (s, 3H), 7.03 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H). Signals corresponding to **5hB**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.78 (s, 3H), 6.79 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 8.8 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 8.39 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 55.1, 113.8, 116.3, 120.1, 124.3, 124.4, 125.1, 125.3, 126.8, 127.6, 129.3, 129.6, 130.6, 130.9, 133.3, 134.4, 135.1, 137.3, 144.7, 158.6 (1 carbon is missing due to overlapping). HREIMS *m/z* 487.1010 $(M)^+$, calcd for $C_{28}H_{22}ClNO_3S$ 487.1009.

General Procedure for the Preparation of 2,3-Disubstituted *N*-Ts-Indoles 5c-d & 5f-h



5cA: Ar^1 = Ph, Ar^2 = 4-$MeOC_6H_4$ **2a**: Ar^1 = Ph
5dA: Ar^1 = Ph, Ar^2 = 4-MeC_6H_4
5fA: Ar^1 = Ph, Ar^2 = 4-ClC_6H_4
5gA: Ar^1 = Ph, Ar^2 = 4-$CF_3C_6H_4$
5hA: Ar^1 = 4-$MeOC_6H_4$, Ar^2 = 4-ClC_6H_4
5hB: Ar^1 = 4-ClC_6H_4, Ar^2 = 4-$MeOC_6H_4$

To a solution of 2-iodoaniline (250.8 mg, 1.145 mmol) was dissolved in mixed DMF (0.6 mL, 2 M) and ethynyltrimethylsilane (243 μL, 1.718 mmol, 1.5 equiv), $PdCl_2(PPh_3)_2$ (8.0 mg, 0.0115 mmol, 1 mol%), CuI (2.2 mg, 0.0115 mmol, 1 mol%) and Et_3N (0.8 mL, 1.4 M) were added. The reaction mixture was stirred at room temperture for 2 h. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 times). The resulting organic phase was washed with brine and dried over $MgSO_4$. The resulting mixture was filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:20) to give the corresponding product **A** (173.4 mg, 80 %) as a yellow oil.

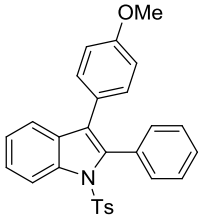
To a solution of **A** (173.4 mg, 0.916 mmol, 1 equiv) in MeOH (4.6 mL, 0.2 M) was added K_2CO_3 (253.0 mg, 1.832 mmol, 2 equiv). After being stirred at room temperature for1 h, the reaction mixture was poured into water and then the product was extracted with CH_2Cl_2 (three times). The combined organic 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 = 1:10) to afford the corresponding product **B** (82.4 mg, 77%) as a yellow oil.

To a solution of **B** (1 equiv) in DMF (0.25 M) were added Ar^1I (1equiv), $PdCl_2(PPh_3)_2$ (1 mol%), CuI (1 mol%), and Et_3N (8 equiv). After being stirred at 50 ℃ for 8-12 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 to afford the corresponding product **C**.

To a solution of **C** (1 equiv) in pyridine (0.2 M) was added *p*-TsCl (1.1 equiv) at 0 ℃. After being stirred at 25 ℃ 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 **D**.

To a solution of **D** (1 equiv) in MeCN (0.13 M) were added subsequently Cs_2CO_3 (2.2 equiv), $Pd(PPh_3)_4$ (5 mol%), and Ar^2I (2.2 equiv). After being stirred at 100 ^oC for 1 h, the reaction mixture was cooled to room temperature. 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 **5 (**or the the mixture of **5** and **2a**).

***N*-Ts-3-(4-Methoxyphenyl)-2-phenylindole (5cA)**

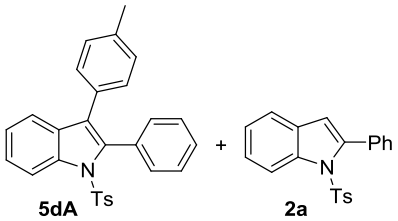


a white solid (EtOAc : *n*-Hexane = 1:10).

^1H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.76 (s, 3H), 6.77 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.24-7.37 (m, 8H), 7.41 (t, J = 7.8 Hz, 1H), 7.47 (d, J = 8.4 Hz,

1H), 8.40 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 55.1, 113.7, 116.2, 120.0, 124.1, 124.4, 124.8, 125.1, 126.9, 127.3, 128.4, 129.3, 130.7, 130.9, 131.1, 132.1, 135.3, 136.5, 137.2, 144.5, 158.4.

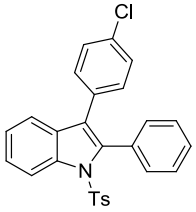
***N*-Ts-2-Phenyl-3-*p*-tolylindole (5dA) & *N*-Ts-2-Phenylindole (2a)**



5dA:**2a** = 3.3:1, a white solid (EtOAc : *n*-Hexane = 1:10).

Signals corresponding to **5dA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 2.32 (s, 3H), 6.98 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.24-7.35 (m, 8H), 7.41 (t, J = 7.8 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 21.5, 116.2, 120.0, 124.1, 124.7, 125.1, 126.9, 127.2, 128.4, 128.9, 129.3, 129.5, 129.6, 130.6, 131.0, 132.1, 135.3, 136.6, 137.2, 144.5 (1 carbon is missing due to overlapping).

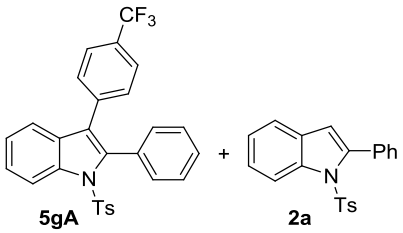
***N*-Ts-3-(4-Chlorophenyl)-2-phenylindole (5fA)**



a yellow solid (EtOAc : *n*-Hexane = 1:10).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 7.02 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 7.28-7.37 (m, 6H), 7.39-7.46 (m, 2H), 8.41 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 116.2, 119.6, 123.3, 124.2, 125.3, 126.9, 127.4, 128.4, 128.6, 129.3, 129.9, 130.5, 131.0, 131.1, 132.0, 132.8, 135.3, 137.0, 137.1, 144.6.

***N*-Ts-3-Phenyl-2-(4-(trifluoromethyl)phenyl)indole (5gA) & *N*-Ts-2-Phenylindole (2a)**

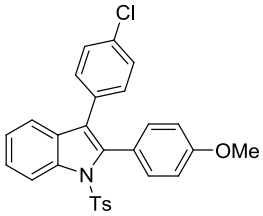


5gA:**2a** = 1:0.6, a white solid (EtOAc : *n*-Hexane = 1:10).

Representative signals corresponding to **5gA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 7.10 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 6.4 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 8.0 Hz, 1H), 8.45 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 116.2, 119.5, 123.1, 124.3, 125.1 (q, J = 3.8

Hz), 125.4, 126.9, 128.7, 128.8, 129.4, 129.6, 130.1, 132.0, 135.4, 136.7, 137.1, 137.5, 144.8 (3 carbons are missing due to overlapping).

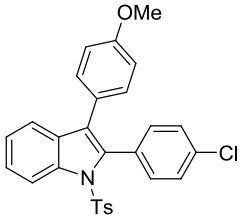
_N_-Ts-3-(4-Chlorophenyl)-2-(4-methoxyphenyl)indole (5hA)



a white solid (EtOAc : *n*-Hexane = 1:10).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.85 (s, 3H), 6.82 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 55.2, 112.9, 116.3, 119.5, 122.6, 123.0, 124.2, 125.1, 126.9, 128.5, 129.3, 130.0, 131.1, 131.4, 132.7, 133.3, 135.4, 137.0, 137.1, 144.6, 159.8.

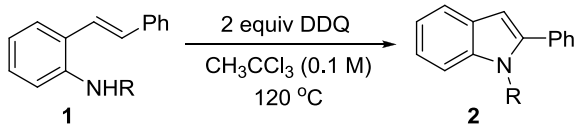
_N_-Ts-2-(4-Chlorophenyl)-3-(4-methoxyphenyl)indole (5hB)



a white solid (EtOAc : *n*-Hexane = 1:5).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.78 (s, 3H), 6.79 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 8.39 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 55.1, 113.8, 116.3, 120.1, 124.3, 124.4, 125.1, 125.3, 126.8, 127.6, 129.3, 129.6, 130.6, 130.9, 133.3, 134.5, 135.1, 137.3, 144.7, 158.6 (1 carbon is missing due to overlapping).

Effects of *N*-Protecting Group

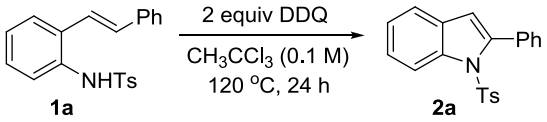


Entry	R	Time (h)	Yield (%)[a]	Entry	R	Time (h)	Yield (%)[a]
1	Ts (**1a**)	24	96 (**2a**)	10	Piv	24	-[b]
2	$PhSO_2$	11	85	11	Bz	24	-[b]
3	*p*-$ClC_6H_4SO_2$	6	89	12	C_6F_5CO	24	-
4	*p*-$NO_2C_6H_4SO_2$	24	83	13	(2-pyridinyl)CO	24	-
5	(2-pyridinyl)SO_2	6	80	14	CO_2Et	24	32
6	Tf	2	66	15	Cbz	24	16
7	Ms	18	83	16	Boc	24	24
8	Ac	24	trace	17	Bn	20	-[b]
9	CF_3CO	24	trace	18	H	1	-[c]

[a] Isolated yield. [b] Complex mixture. [c] Decomposed.

Mechanistic Studies

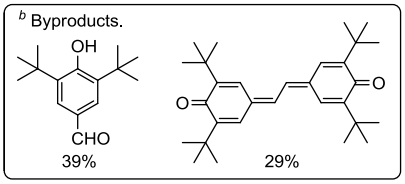
1) With Radical Scavenger



Radical scavenger	**1a** (%)[a]	**2a** (%)[a]
-	-	96
BHT (1 equiv)[b]	64 (72)	0 (trace)
TEMPO (1 equiv)	(85)	(15)

[a] Isolated yields (Yields determined by ^1H NMR).
[b] Complex mixture including two byproducts (see right).

[b] Byproducts.

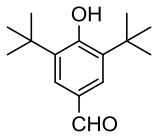


Inclusion of BHT or TEMPO as an additive had deleterious effect on the efficiency of the indole formation, while the corresponding trapping products were not obtained in both cases. While these results could suggest that a radical might be involved in this reaction, care must be taken when generalizing this, as they are both potential substrates for DDQ oxidation. Although there are a couple of examples wherein the addition of TEMPO did not have a significant effect on the product yield in the DDQ-mediated oxidative reactions (suggesting that DDQ has NOT been consumed through its direct reaction with TEMPO),[31] however, it

[31] (a) Zhang, G.; Wang, S.; Ma, Y.; Kong, W.; Wang, R. *Adv. Synth. Catal.* **2013**, *355*, 874. (b) Wang, Z.-L.; Li, H.-L.; Ge, L.-S.; An, X.-L.; Zhang, Z.-G.; Luo, X.; Fossey, J. S.; Deng, W.-P. *J. Org. Chem.* **2014**, *79*, 1156.

cannot be ruled out that DDQ was consumed by its direct reaction with TEMPO and/or BHT, and thus indole formation reactions were shut down either completely or to a large extent.

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

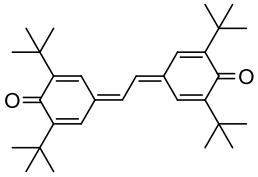


39%, a yellow solid (EtOAc : *n*-Hexane = 1:7), mp 166-171 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.48 (s, 18H), 5.85 (s, 1H), 7.73 (s, 2H), 9.85 (s, 1H). EIMS *m*/*z* 234 (M^+), 219, 191, 175, 159, 147, 128, 115, 102, 91, 77, 65, 57, 53.

Spectral data were consistent with data reported in the literature.[32]

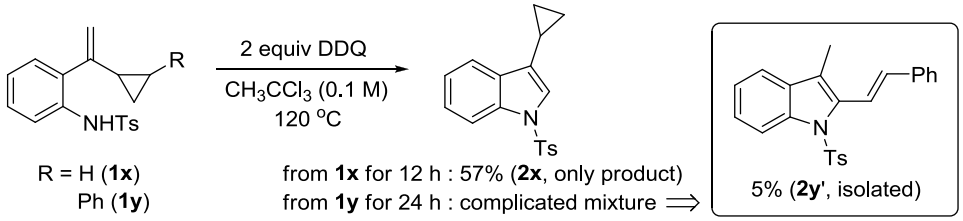
4,4'-(Ethane-1,2-diylidene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dienone)



29%, a yellow solid (EtOAc : *n*-Hexane = 1:7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 18H), 1.37 (s, 18H), 7.03 (d, *J* = 1.6 Hz, 2H), 7.25 (s, 2H), 7.52 (s, 2H). EIMS *m*/*z* 434 (M^+), 419, 378, 363, 349, 307, 281, 231, 219, 207, 189, 175, 159, 145, 133, 119, 91, 73, 57.[33]

2) Radical Clock Experiments



Radical clock experiments using **1x** and **1y** were conducted under the optimized conditions and gave very different outcomes: The first afforded **2x** as the sole product of which cyclopropyl ring remained intact, presumably because a ring opening reaction of the cyclopropyl benzyl radical is slower than its competitive oxidation to benzylic cation.[34] In sharp contrast, the latter using **1y**, in which a phenyl group would allow for a fast ring cleavage to result in a benzyl radical, led to a complicated mixture and **2y′** could be isolated,

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

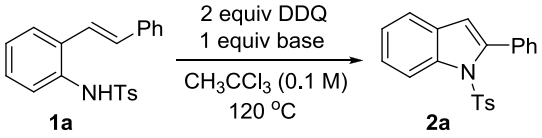
[33] B. Barton, C. G. Logie, B. M. Schoonees, B. Zeelie, *Org. Process Res. Dev.* **2005**, *9*, 62.

[34] Maity, S.; Zheng, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 9562.

albeit in a low yield. This product is likely to be formed through a cyclopropane ring opening, suggesting that a carbon radical intermediate was involved during the reaction.

3) Addition of Base

: to facilitate the generation of nitrogen radical cation or to enhance the nucleophilicitiy of sulfonamide

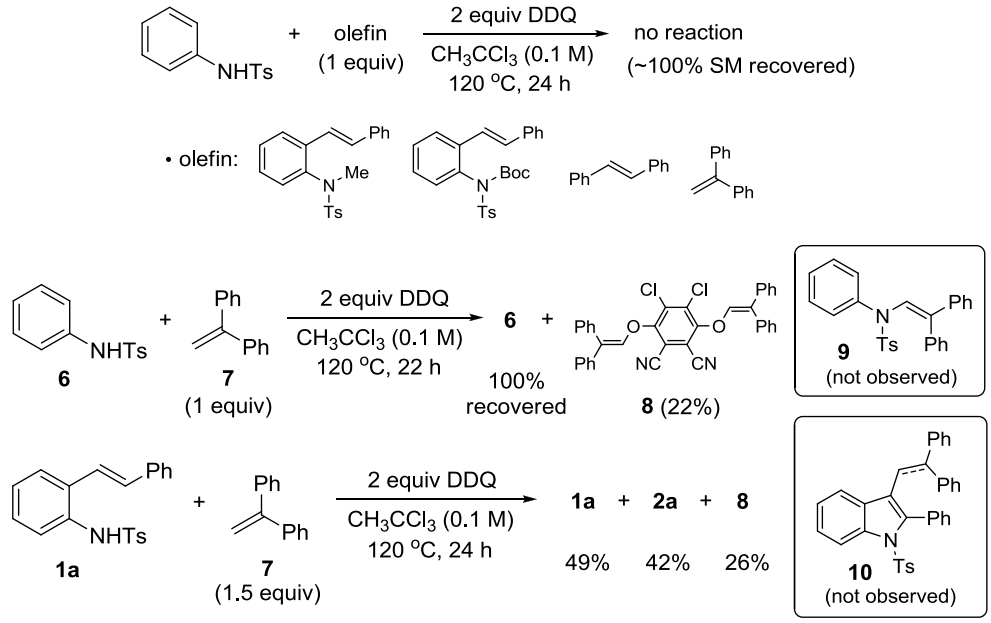


base	*t* (h)	**1a** (%)	**2a** (%)
-	24	-	96
LiOMe	21	-	62[a]
Na_2CO_3	24	4	91[a]
K_2CO_3	24	-	90[a]

[a] Determined by ^{1}H NMR.

Addition of LiOMe was detrimental, while both Na_2CO_3 and K_2CO_3 gave no beneficial effect.

4) Intermolecular Reaction with Various Olefins

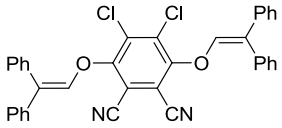


In stark contrast to the Chemler's work wherein C-H amination products such as **9** were formed through nitrogen-radical addition to various radical acceptors (e.g., **7**),[35] an intermolecular variant of our protocol did not proceed, giving fully recovered **6** and a byproduct **8** derived from **7** and DDQ. The introduction of a radical acceptor **7** to our

[35] T. W. Liwosz, S. R. Chemler, *Chem. Eur. J.* **2013**, *19*, 12771.

standard reaction conditions using **1a** as the substrate afforded **2a** and the same byproduct **8** without **10** which could be formed through interception of a radical intermediate by alkene **7** in domino C-H amination/intermolecular Heck-type coupling reaction.[36] These findings indicate that oxidation of the carbon radical, which is resulted from the intramolecular nucleophilic attack by the *ortho*-sulfonamide group toward an olefin radical cation (or electrophilic addition of nitrogen-centered radical cation to an alkene), to the corresponding benzylic carbocation intermediate followed by the deprotonation is much faster than intermolecular addition of the radical to an alkene (e.g., **7**). In addition, intermolecular C-N and C-C bond formations under our conditions appear to be unfavorable.

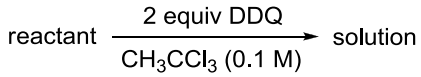
4,5-Dichloro-3,6-bis(2,2-diphenylvinyloxy)phthalonitrile (8)



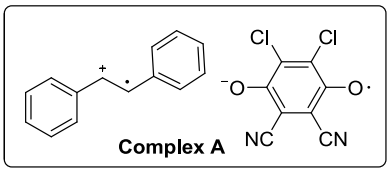
11% (from the 1st reaction), 13% (from the 2nd reaction), a yellow solid (CH_2Cl_2 : *n*-Hexane = 1:2).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.73 (s, 2H), 7.28-7.33 (m, 11H), 7.38 (t, J = 7.4 Hz, 5H), 7.46 (d, J = 7.2 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 108.0, 111.4, 127.9, 128.1, 128.22, 128.24, 128.6, 130.1, 134.3, 135.6, 138.1, 139.3, 144.9, 153.0. IR (KBr) ν_{max} 3055, 2920, 2236, 1415, 1358, 1244, 1170, 1085, 1071, 763, 696 cm^{-1}. HREIMS *m/z* 584.1050 $(M)^+$, calcd for $C_{36}H_{22}Cl_2N_2O_2$ 584.1058.

5) Color Change of Solution after Addition of DDQ



Reactant	Color of Solution	
	w/o DDQ	w/ DDQ
PhNHTs	clear	brown
	clear	deep green



When a solution of stilbene was combined with DDQ, we observed the immediate formation of a deep green color, whereas a color change to brown was observed when a solution of *N*-Ts-aniline was combined with DDQ. Apparently, a radical ion pair complex **A** might be generated through a single-electron transfer process between the stilbene double bond and DDQ.[37]

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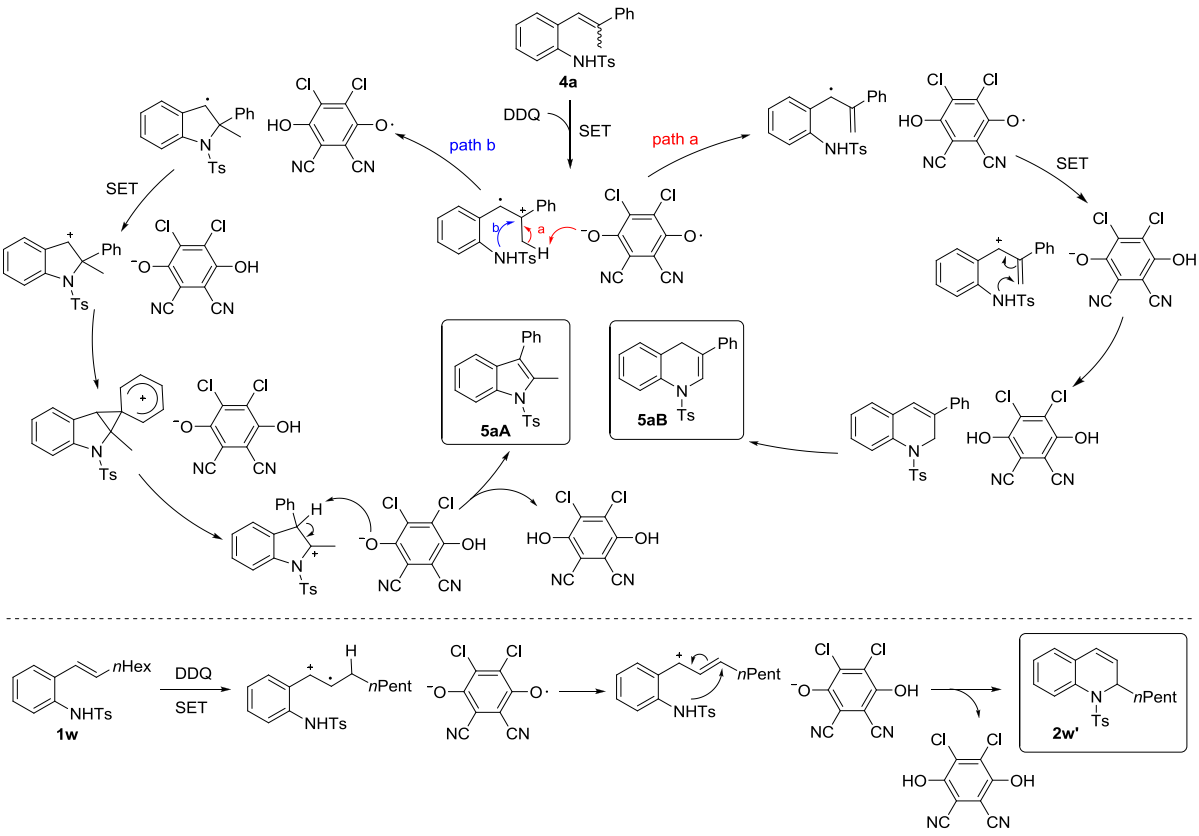
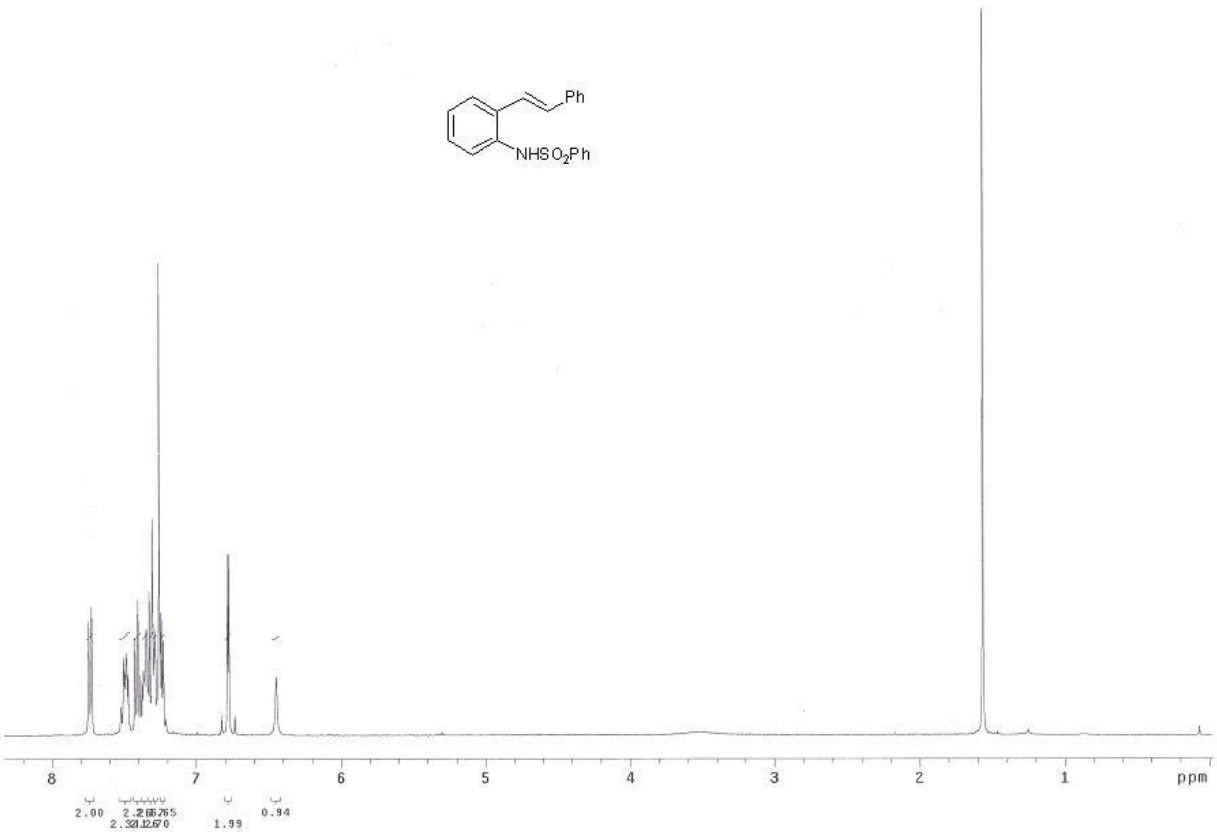
[36] T. W. Liwosz, S. R. Chemler, *J. Am. Chem. Soc.* **2012**, *134*, 2020.

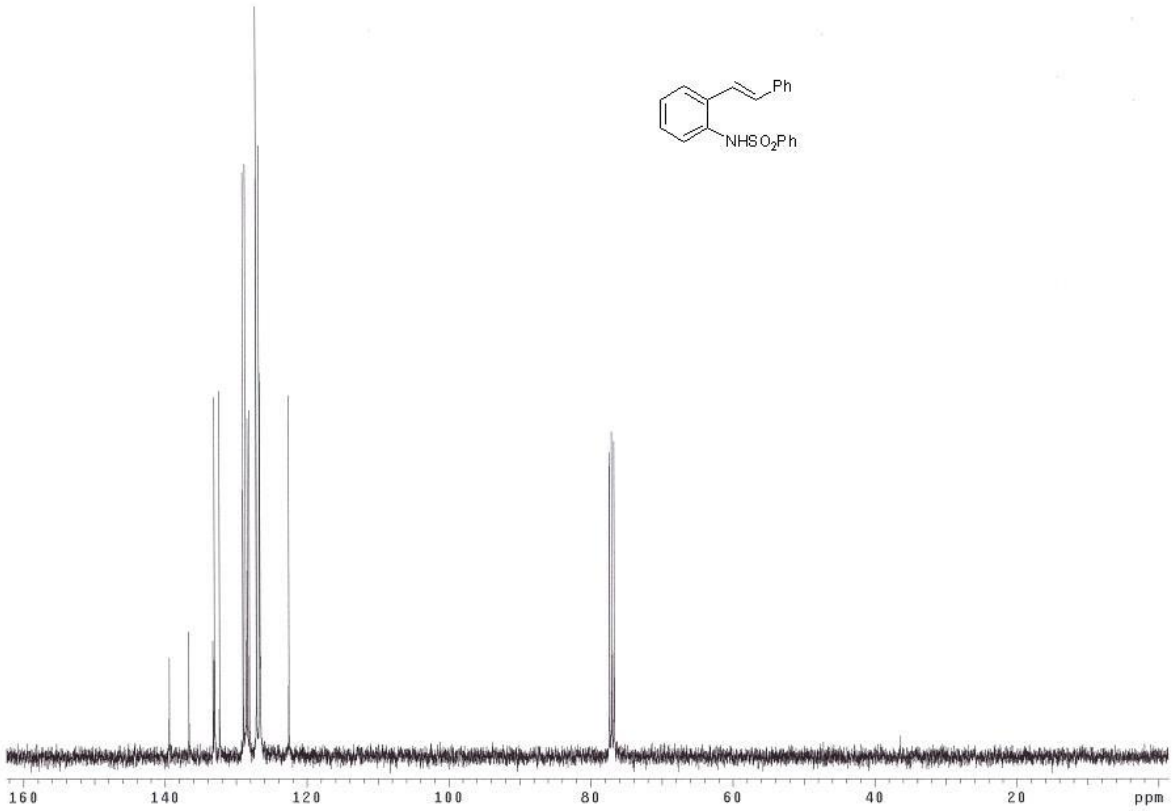
[37] (a) D. Cheng, W. L. Bao, *Adv. Synth. Catal.* **2008**, *350*, 1263. (b) Kim, K. H.; Lim, C. H.; Lim, J. W.; Kim, J. N. *Adv. Synth. Catal.* **2014**, *356*, 697.

Proposed Mechanism for the Reactions of 4a and 1w

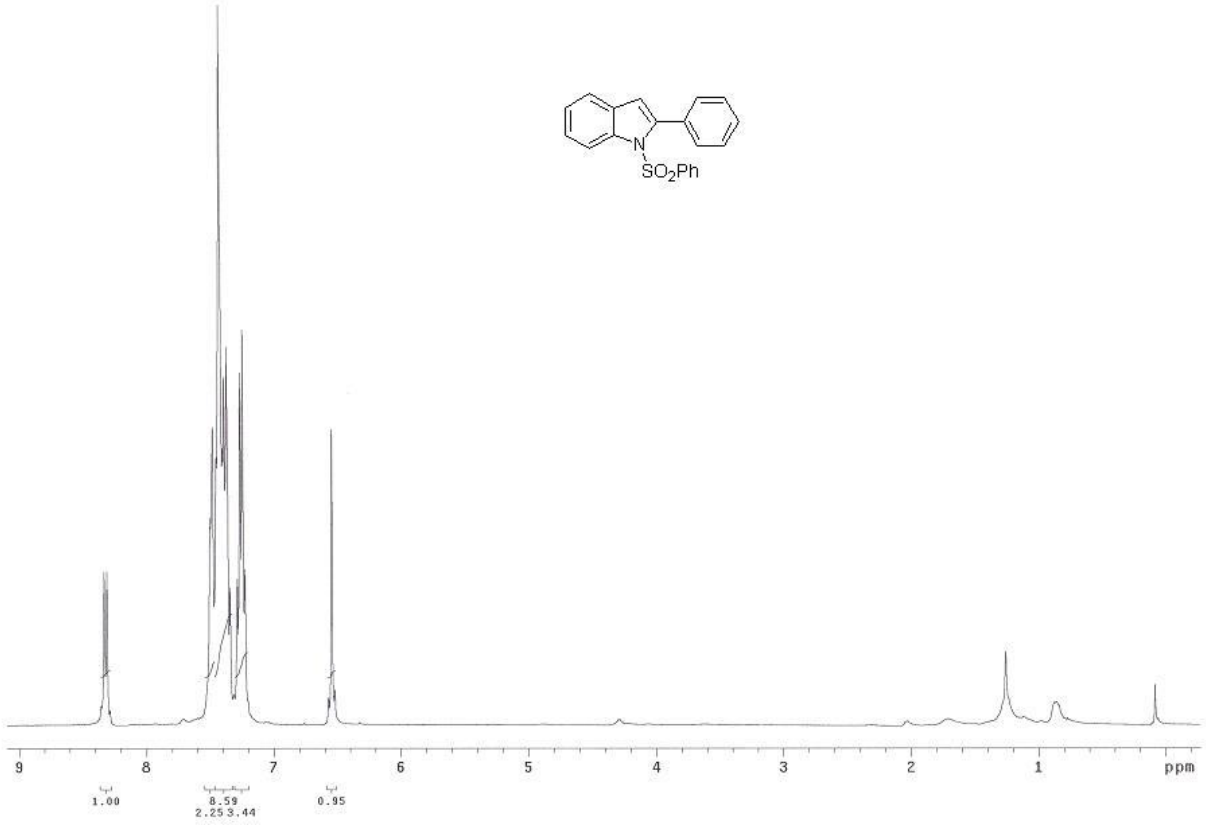




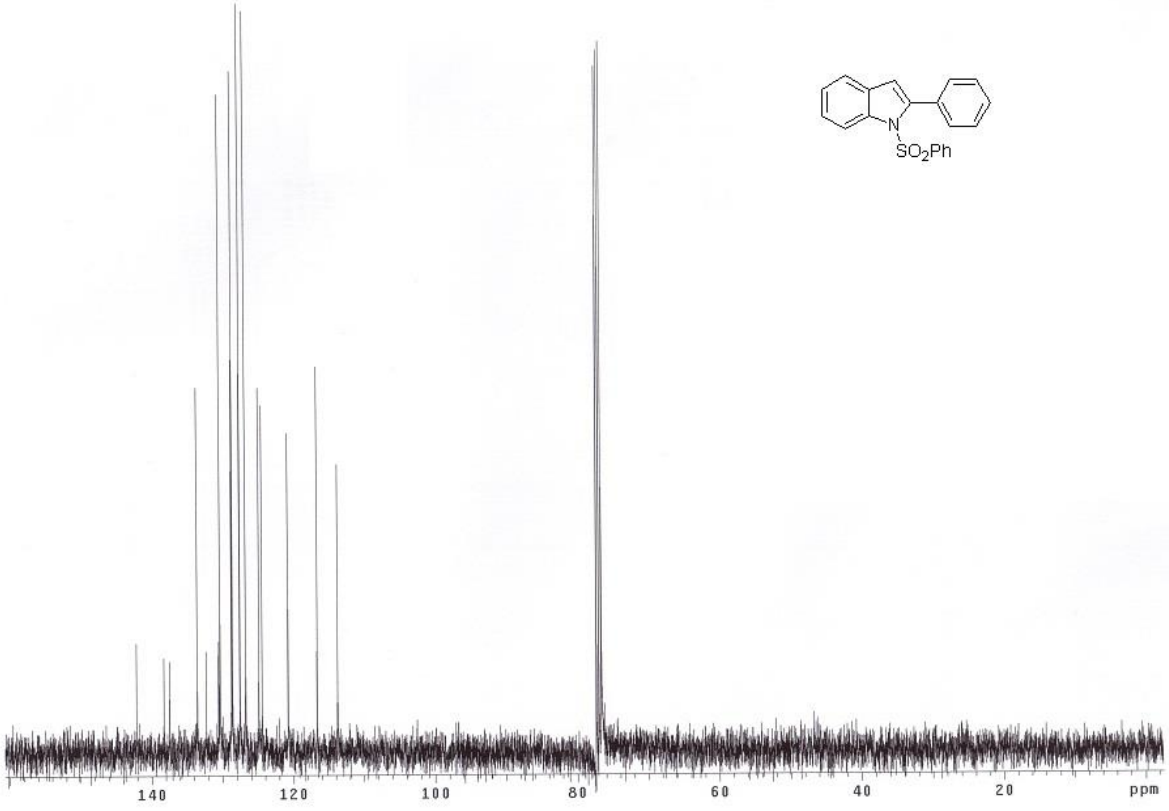
^{1}H NMR Spectrum of Compound *N*-Bs-**1** ($CDCl_3$, 400 MHz)



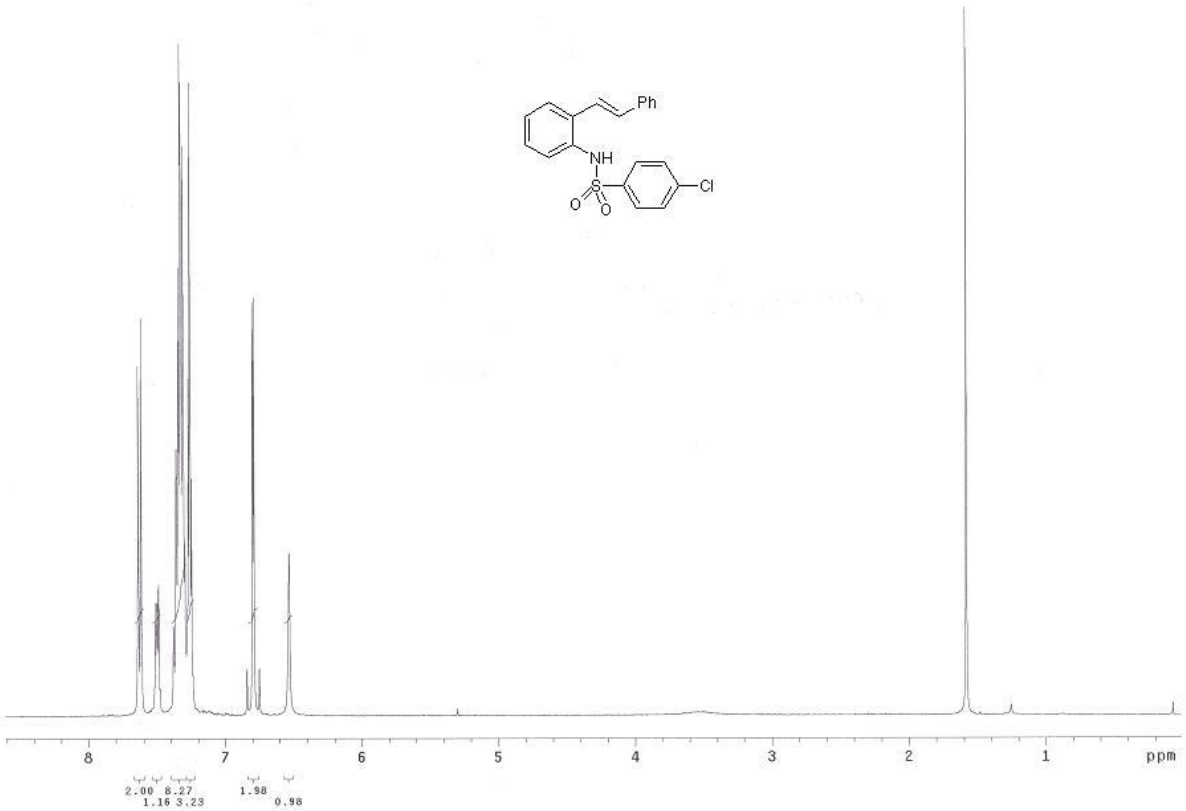
^{13}C NMR Spectrum of Compound *N*-Bs-**1** ($CDCl_3$, 100 MHz)



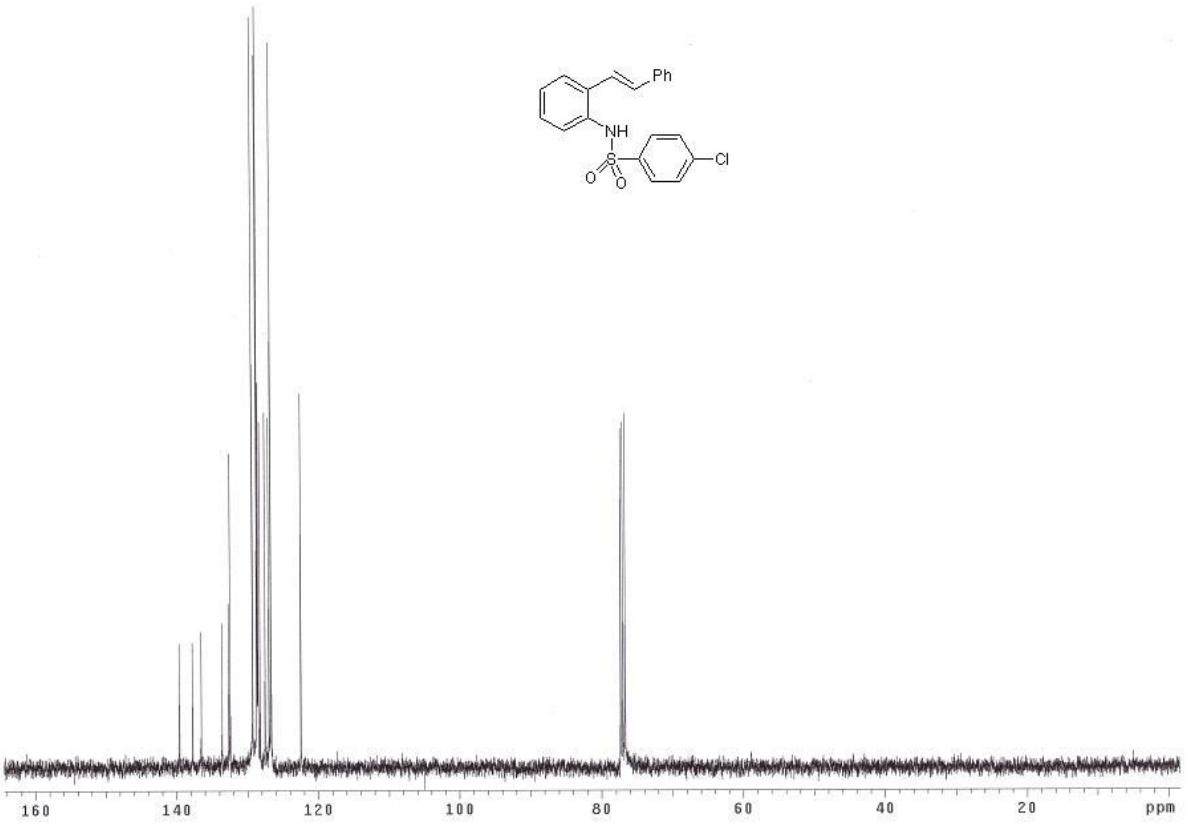
^{1}H NMR Spectrum of Compound *N*-Bs-**2** ($CDCl_3$, 400 MHz)



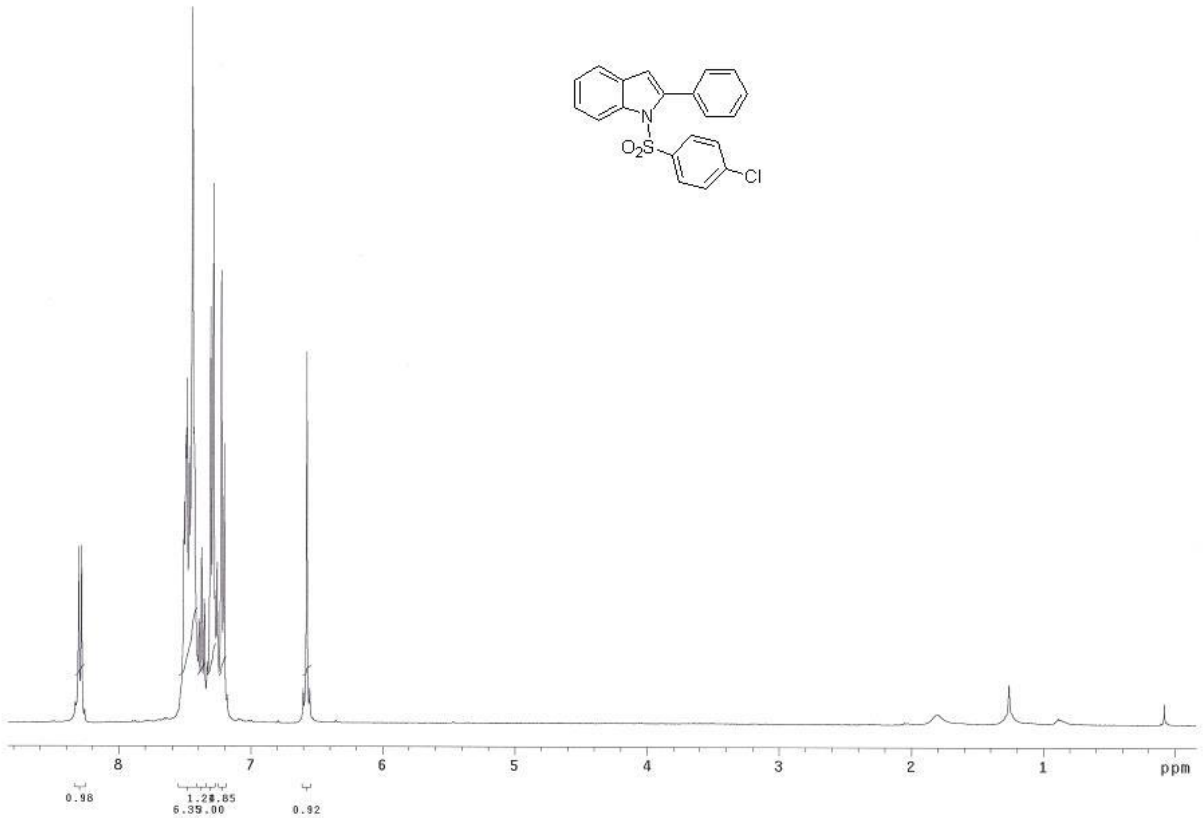
^{13}C NMR Spectrum of Compound *N*-Bs-**2** ($CDCl_3$, 100 MHz)



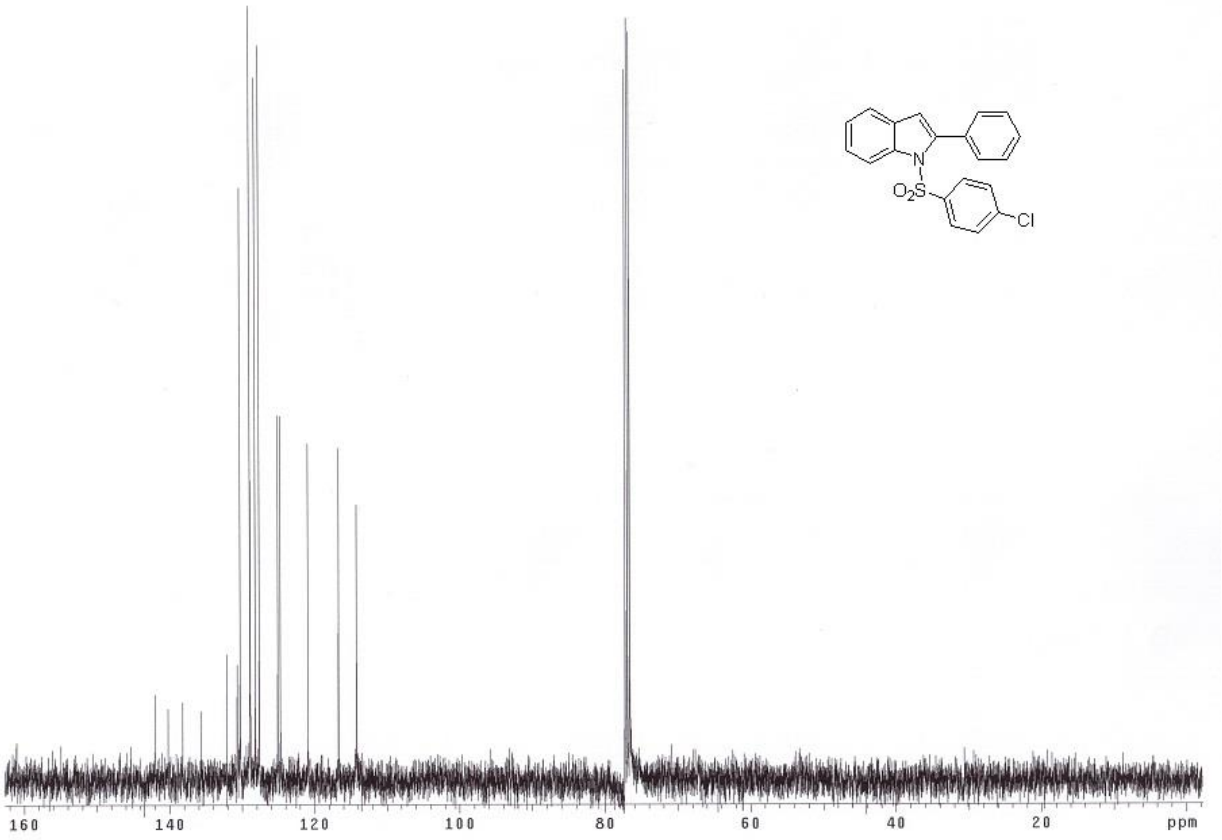
^{1}H NMR Spectrum of Compound *N*-*p*-$ClC_6H_4SO_2$-**1** ($CDCl_3$, 400 MHz)



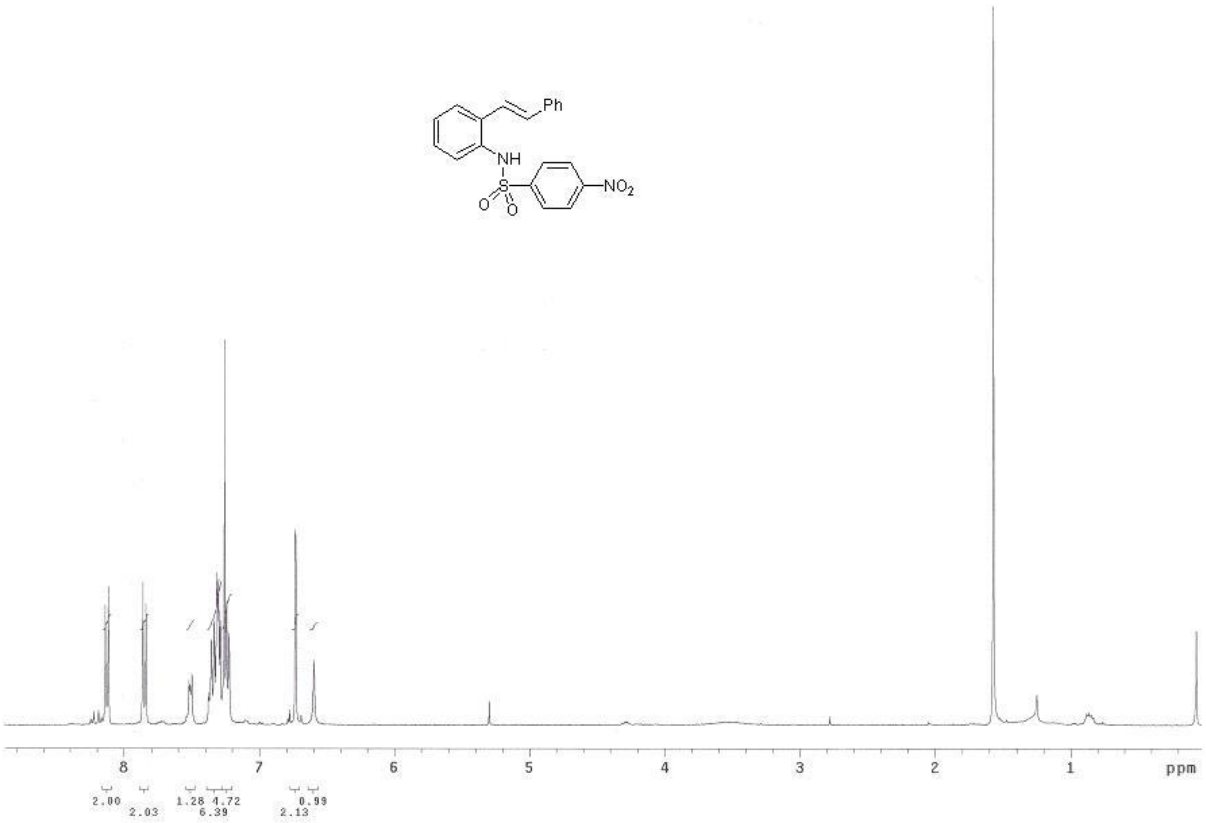
^{13}C NMR Spectrum of Compound *N*-*p*-$ClC_6H_4SO_2$-**1** ($CDCl_3$, 100 MHz)



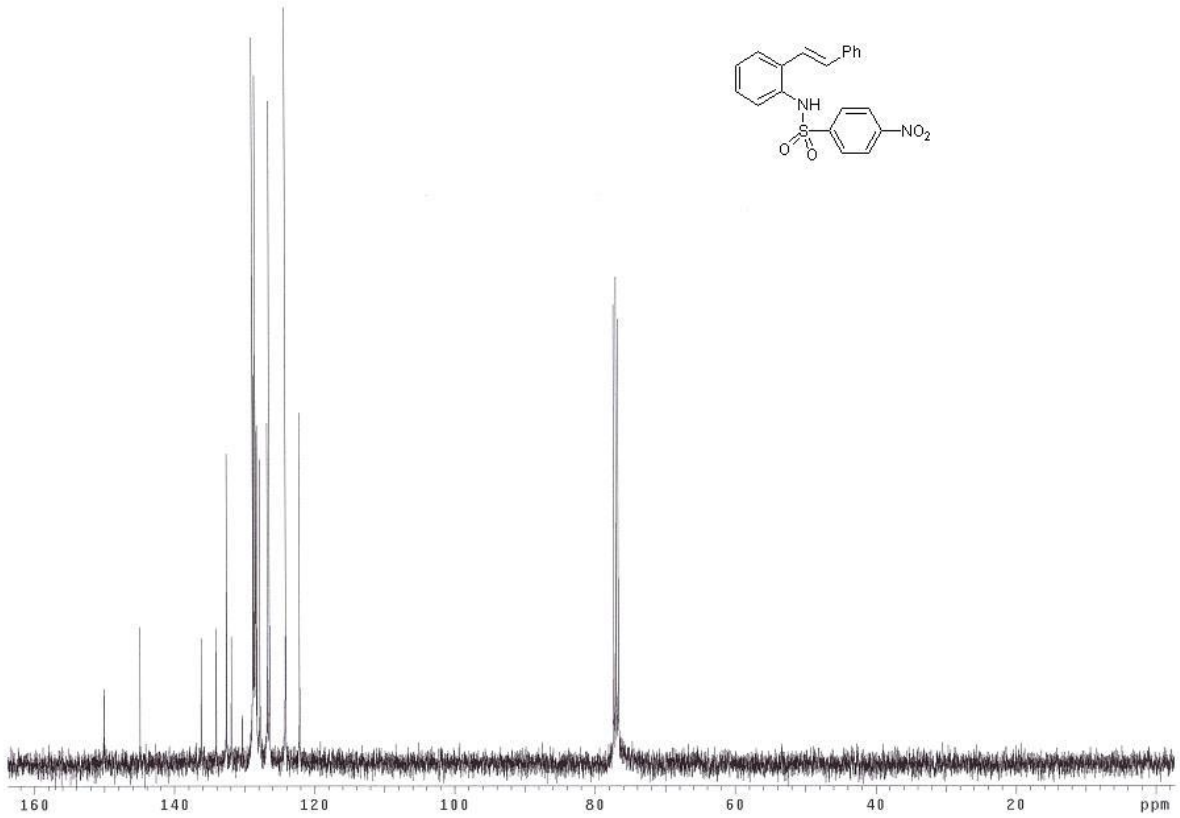
^{1}H NMR Spectrum of Compound *N*-*p*-$ClC_6H_4SO_2$-**2** ($CDCl_3$, 400 MHz)



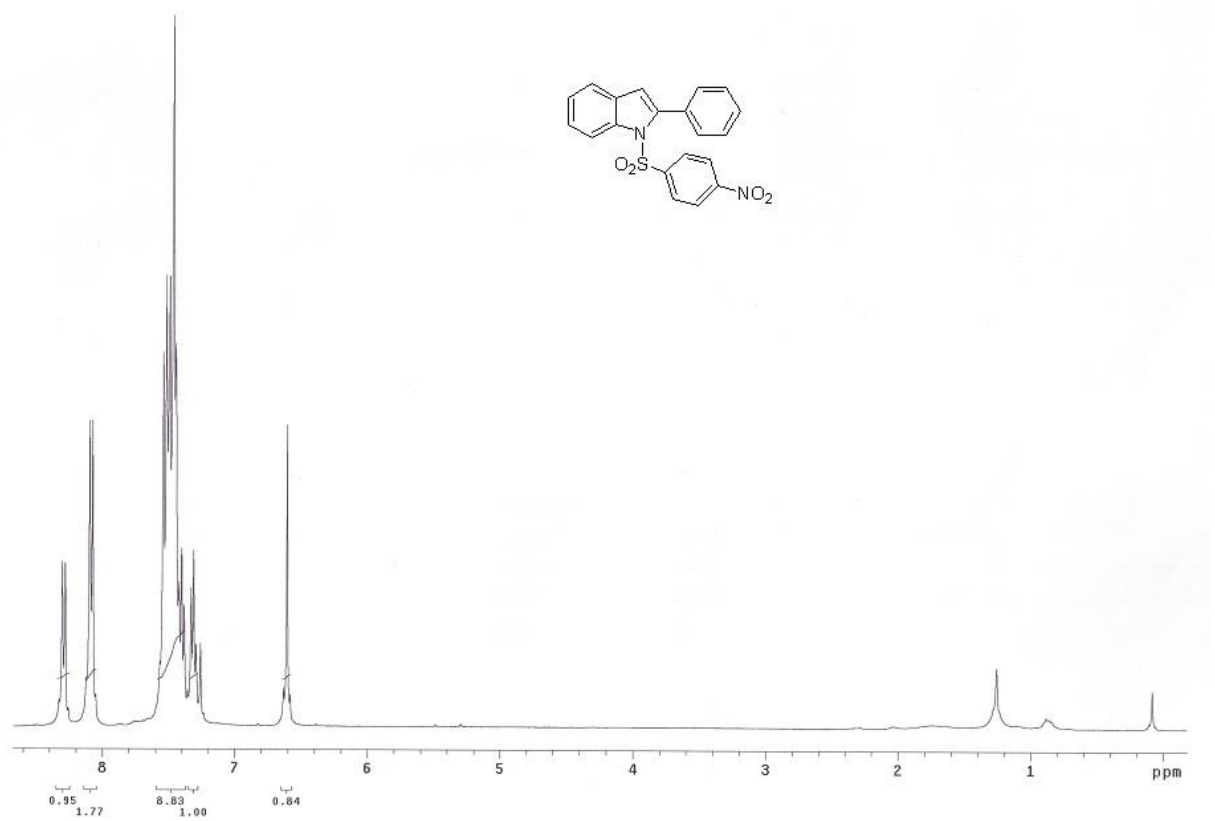
^{13}C NMR Spectrum of Compound *N*-*p*-$ClC_6H_4SO_2$-**2** ($CDCl_3$, 100 MHz)



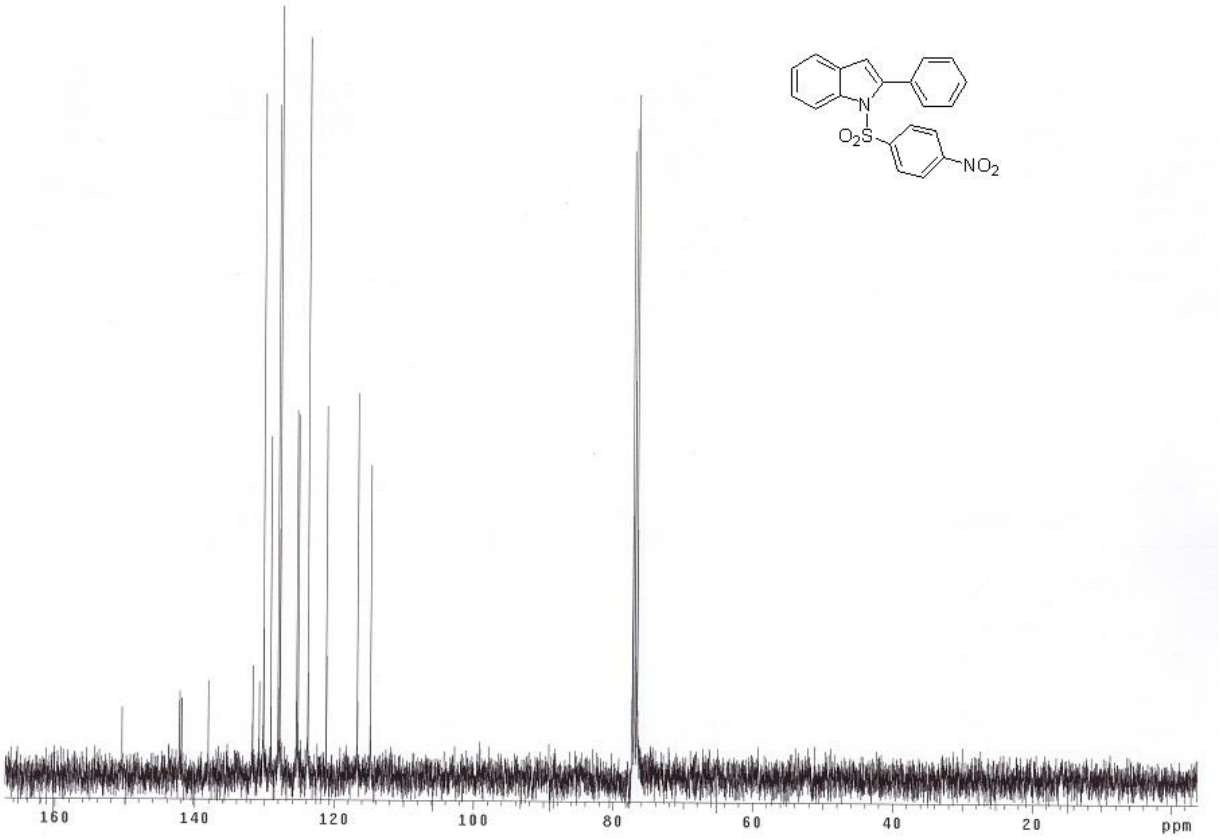
^{1}H NMR Spectrum of Compound *N*-Ns-**1** ($CDCl_3$, 400 MHz)



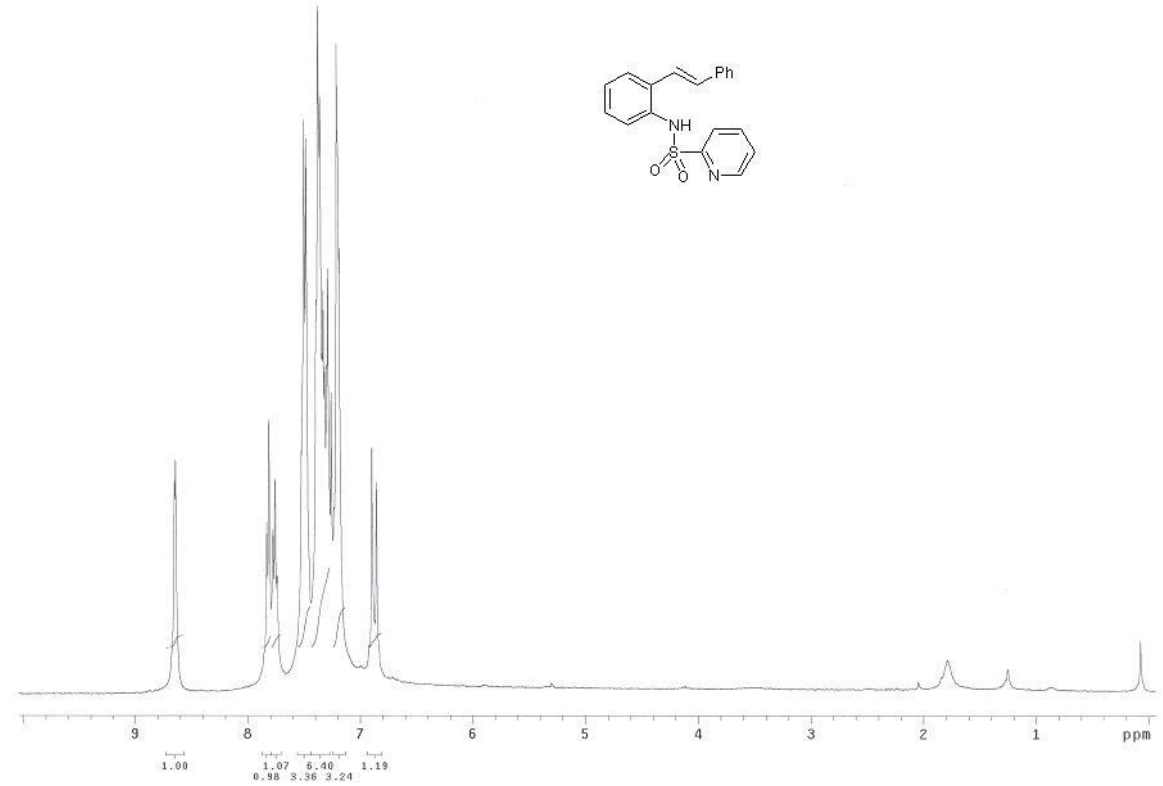
^{13}C NMR Spectrum of Compound *N*-Ns-**1** ($CDCl_3$, 100 MHz)



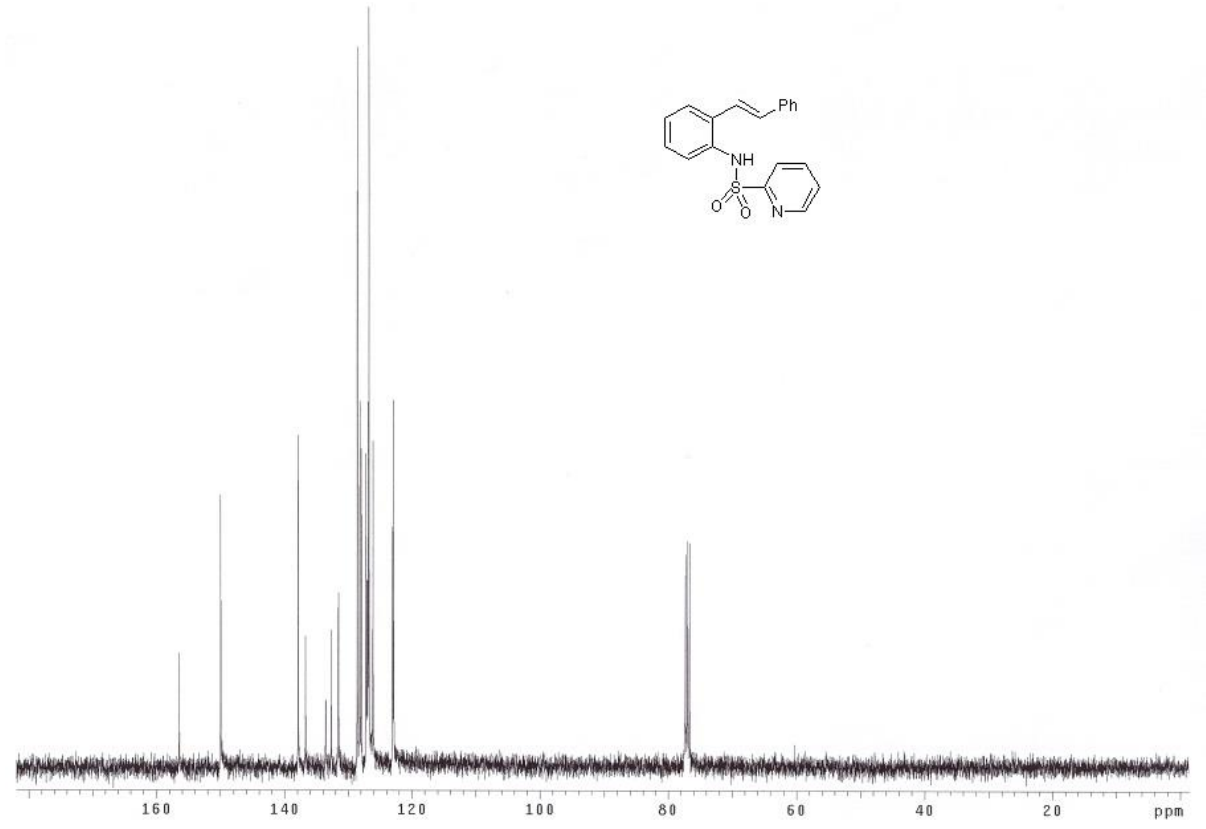
^{1}H NMR Spectrum of Compound *N*-Ns-**2** ($CDCl_3$, 400 MHz)



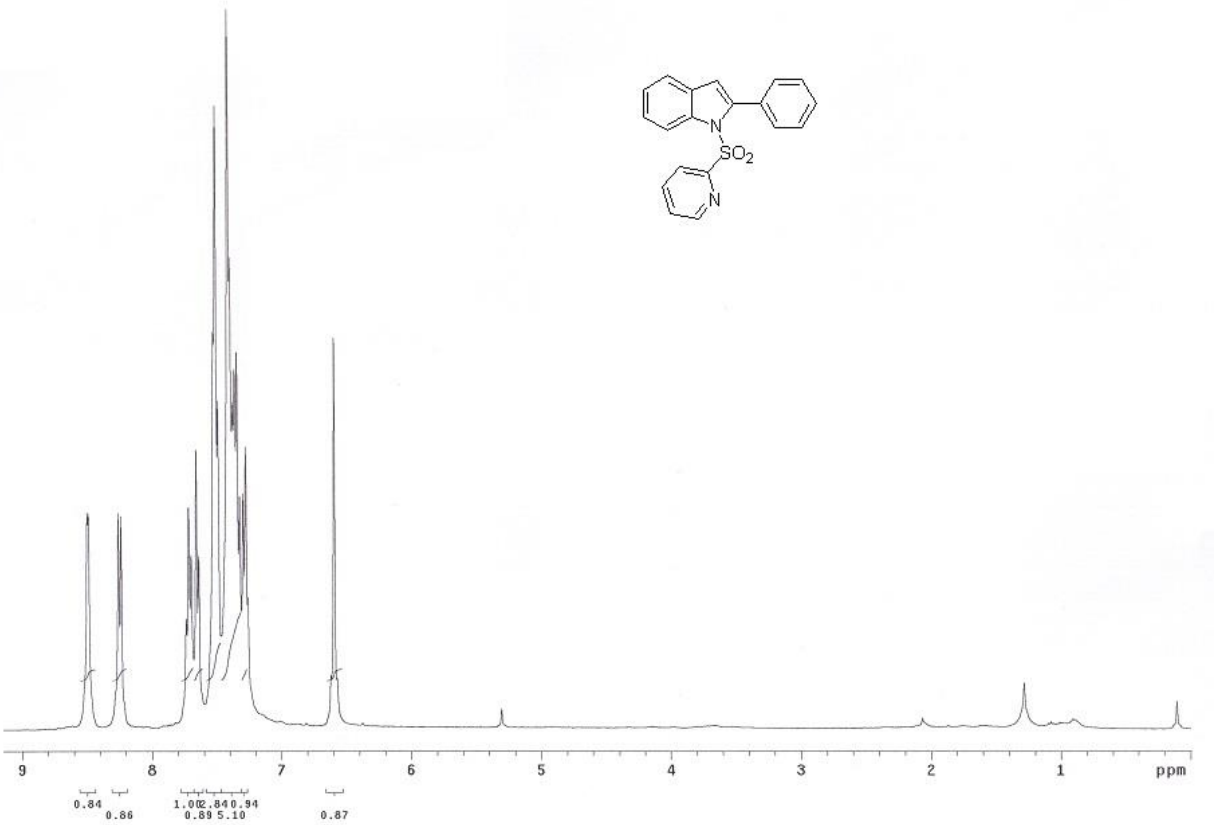
^{13}C NMR Spectrum of Compound *N*-Ns-**2** ($CDCl_3$, 100 MHz)



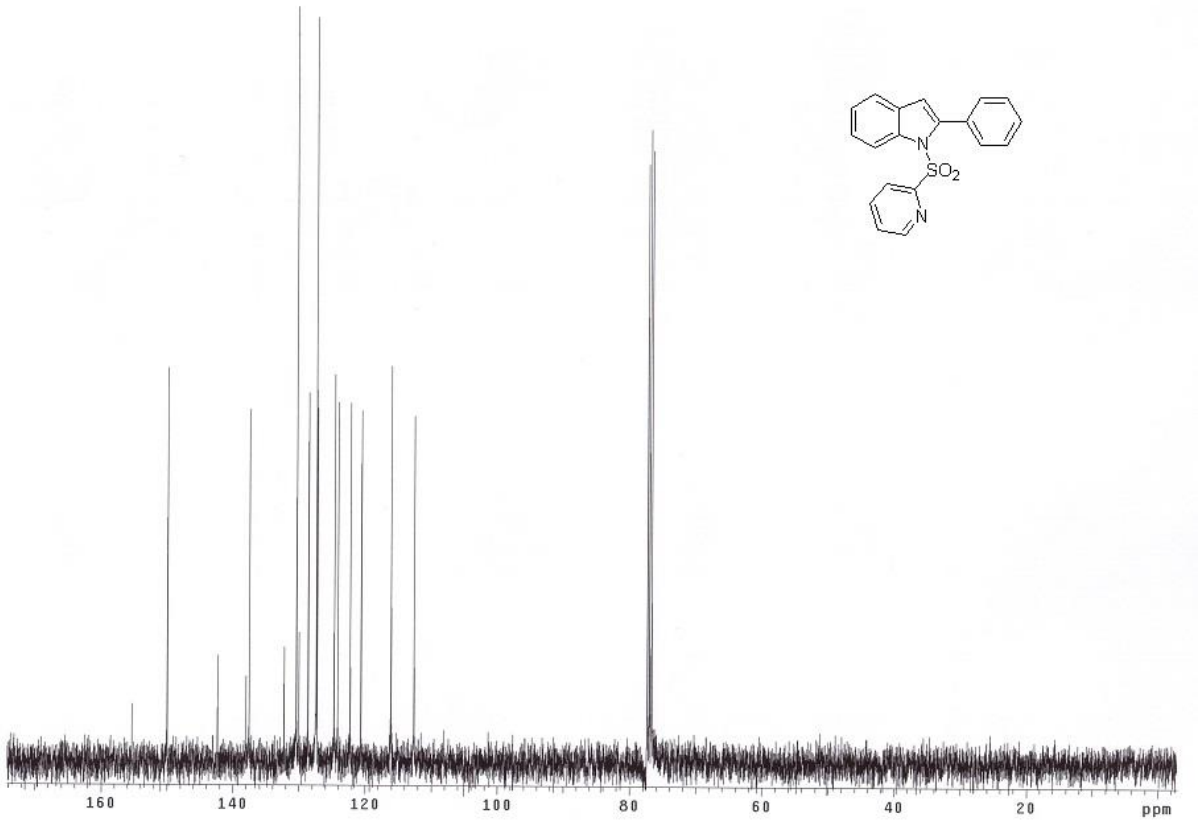
^{1}H NMR Spectrum of Compound *N*-(2-pyridinyl)SO_2-**1** ($CDCl_3$, 400 MHz)



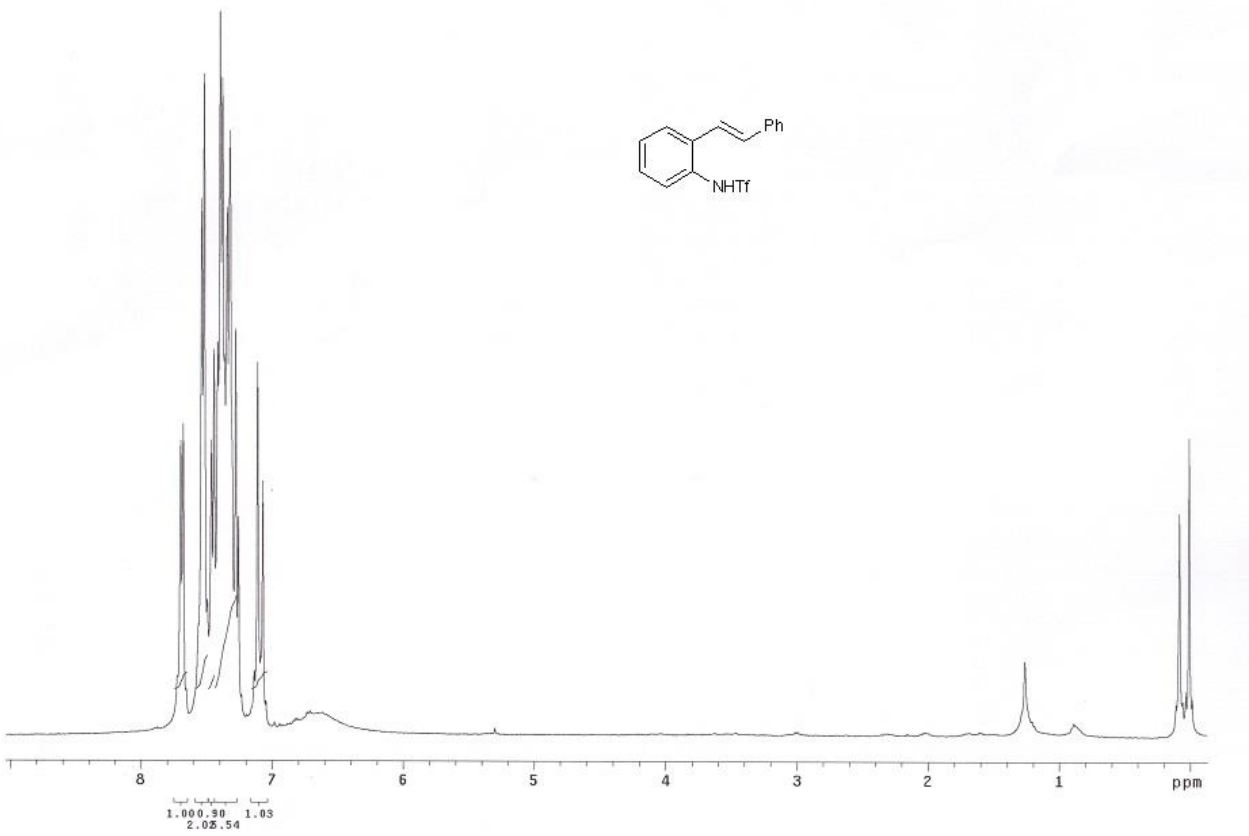
^{13}C NMR Spectrum of Compound *N*-(2-pyridinyl)SO_2-**1** ($CDCl_3$, 100 MHz)



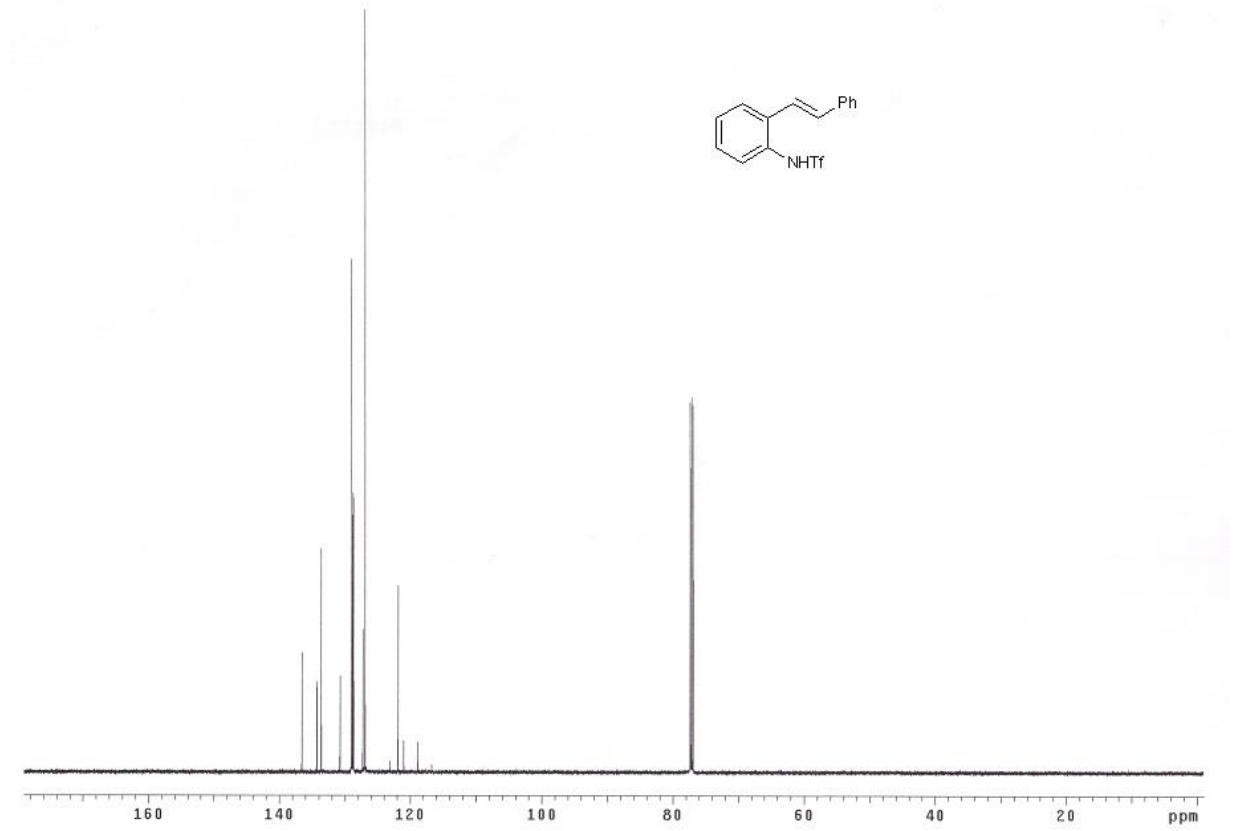
^{1}H NMR Spectrum of Compound *N*-(2-pyridinyl)SO_2-**2** ($CDCl_3$, 400 MHz)



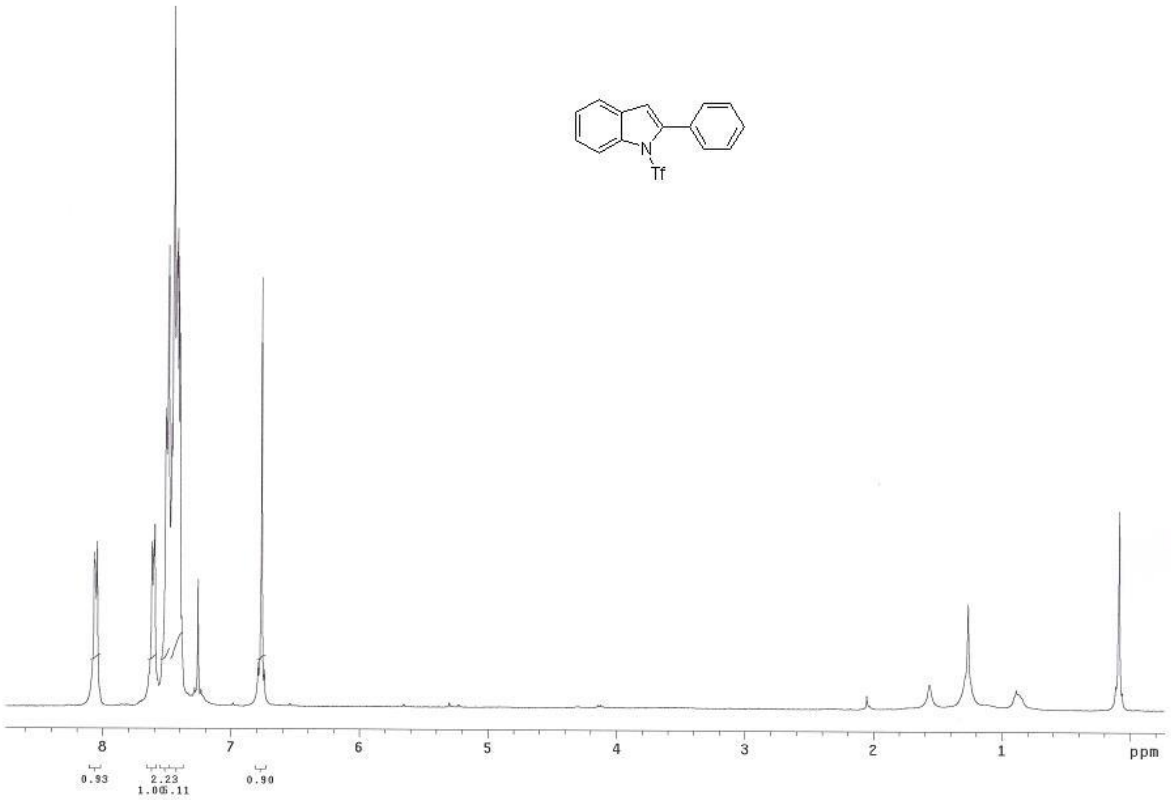
^{13}C NMR Spectrum of Compound *N*-(2-pyridinyl)SO_2-**2** ($CDCl_3$, 100 MHz)



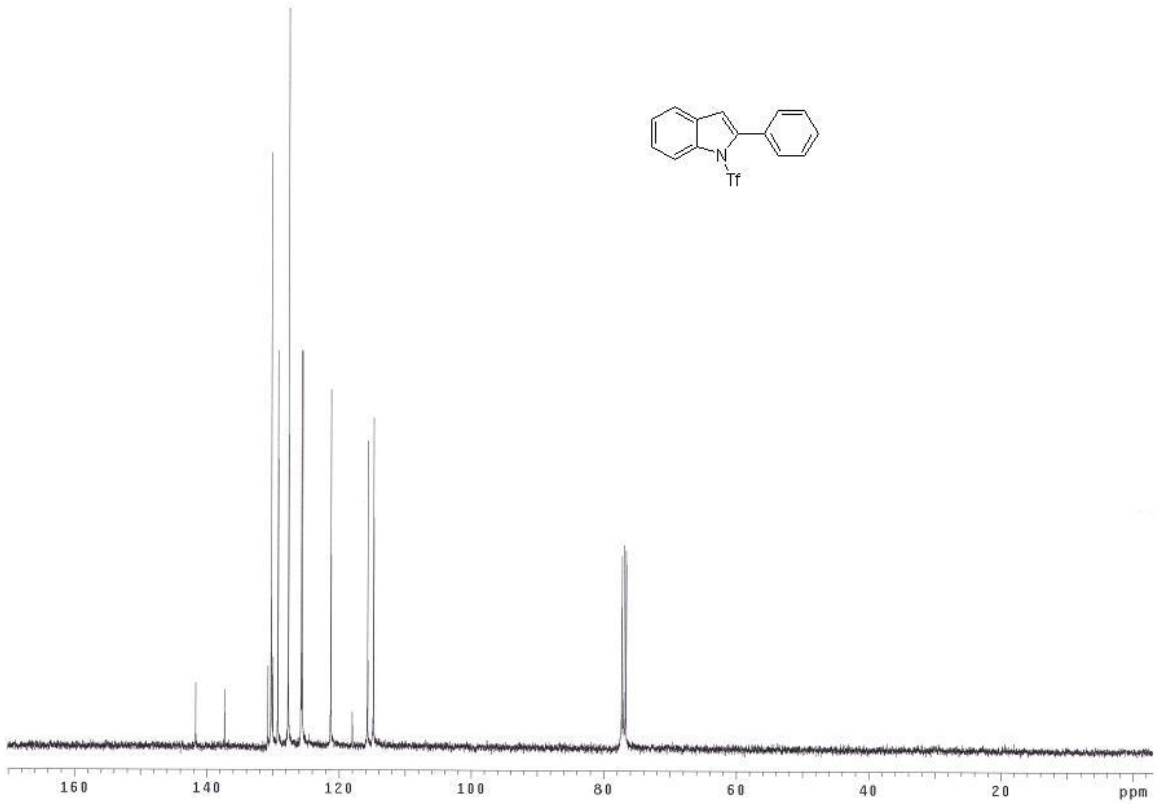
^{1}H NMR Spectrum of Compound *N*-Tf-**1** ($CDCl_3$, 400 MHz)



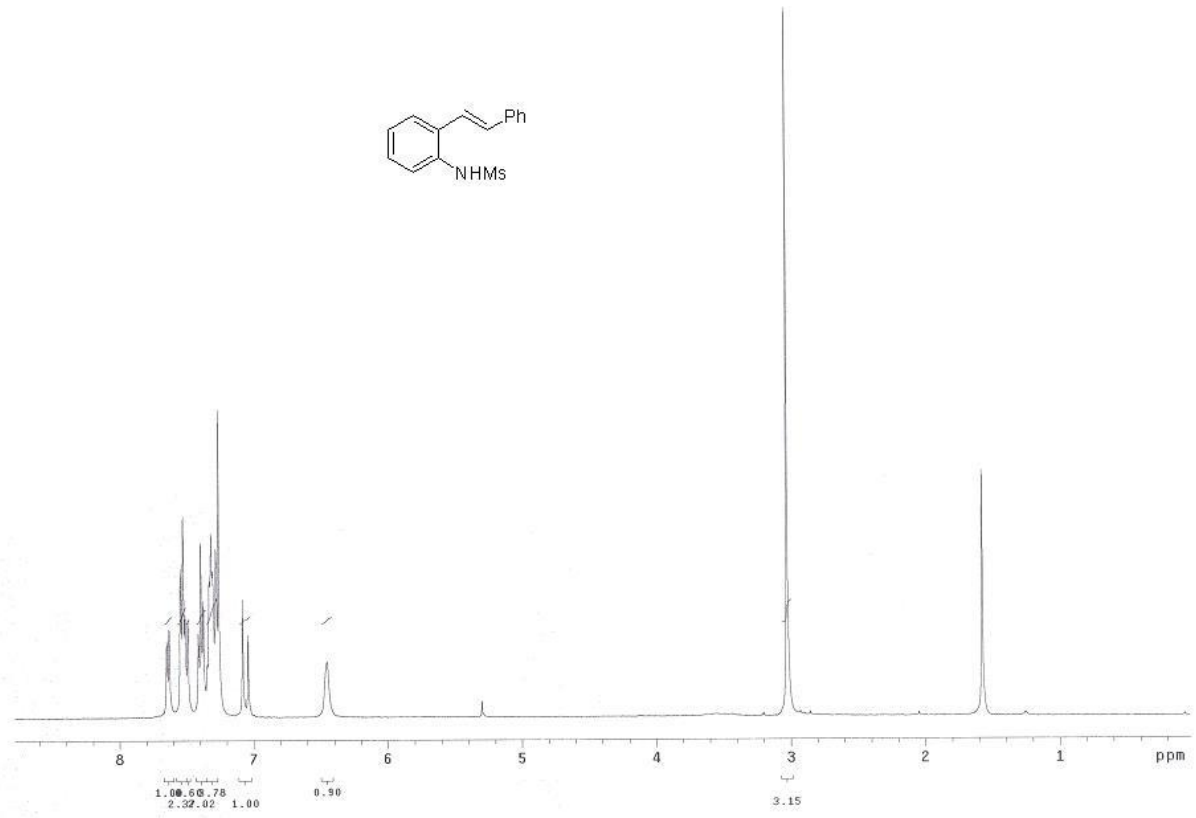
^{13}C NMR Spectrum of Compound *N*-Tf-**1** ($CDCl_3$, 100 MHz)



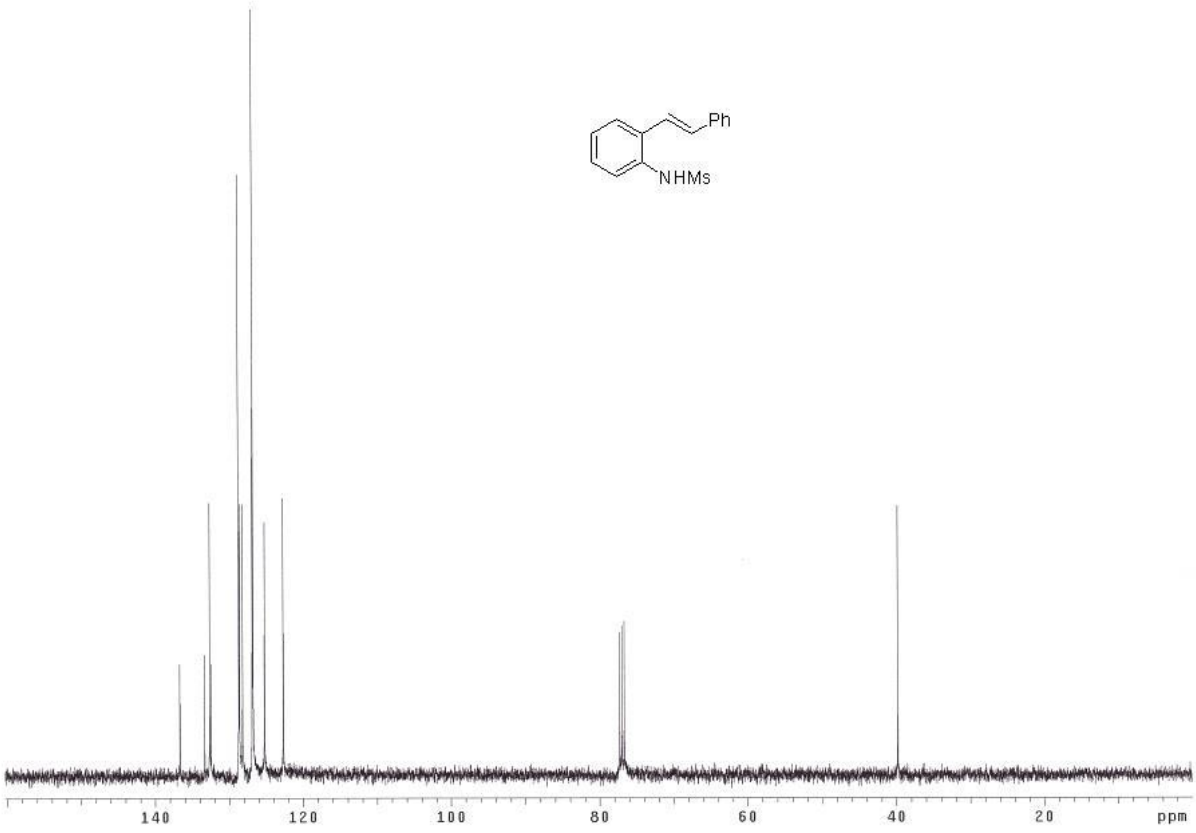
^{1}H NMR Spectrum of Compound *N*-Tf-**2** ($CDCl_3$, 400 MHz)



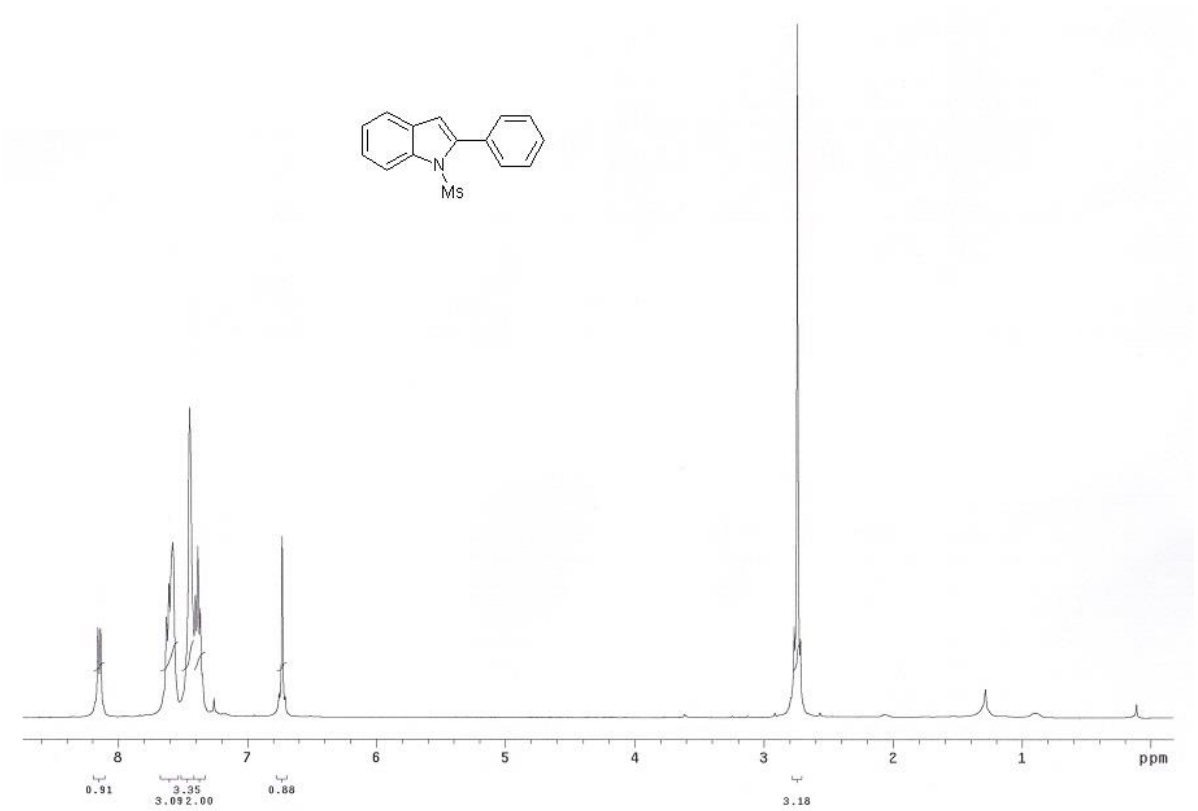
^{13}C NMR Spectrum of Compound *N*-Tf-**2** ($CDCl_3$, 100 MHz)



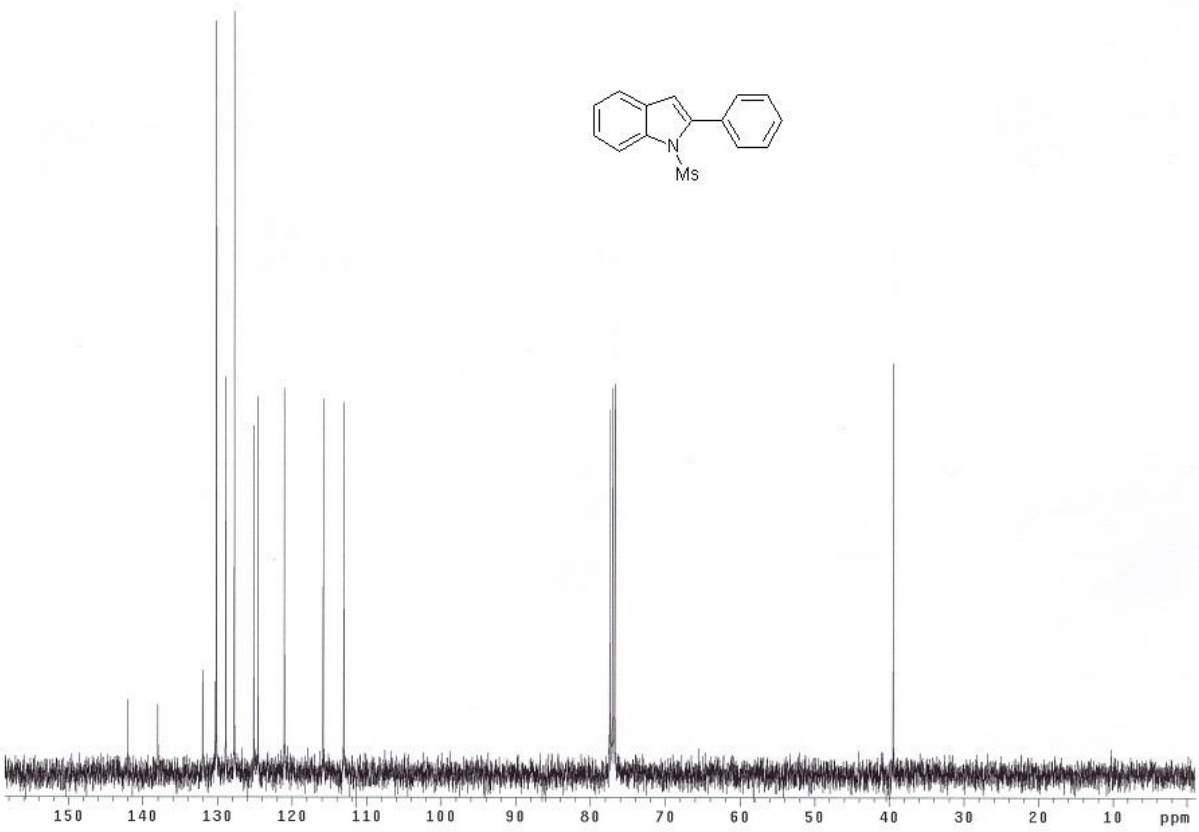
^{1}H NMR Spectrum of Compound *N*-Ms-**1** ($CDCl_3$, 400 MHz)



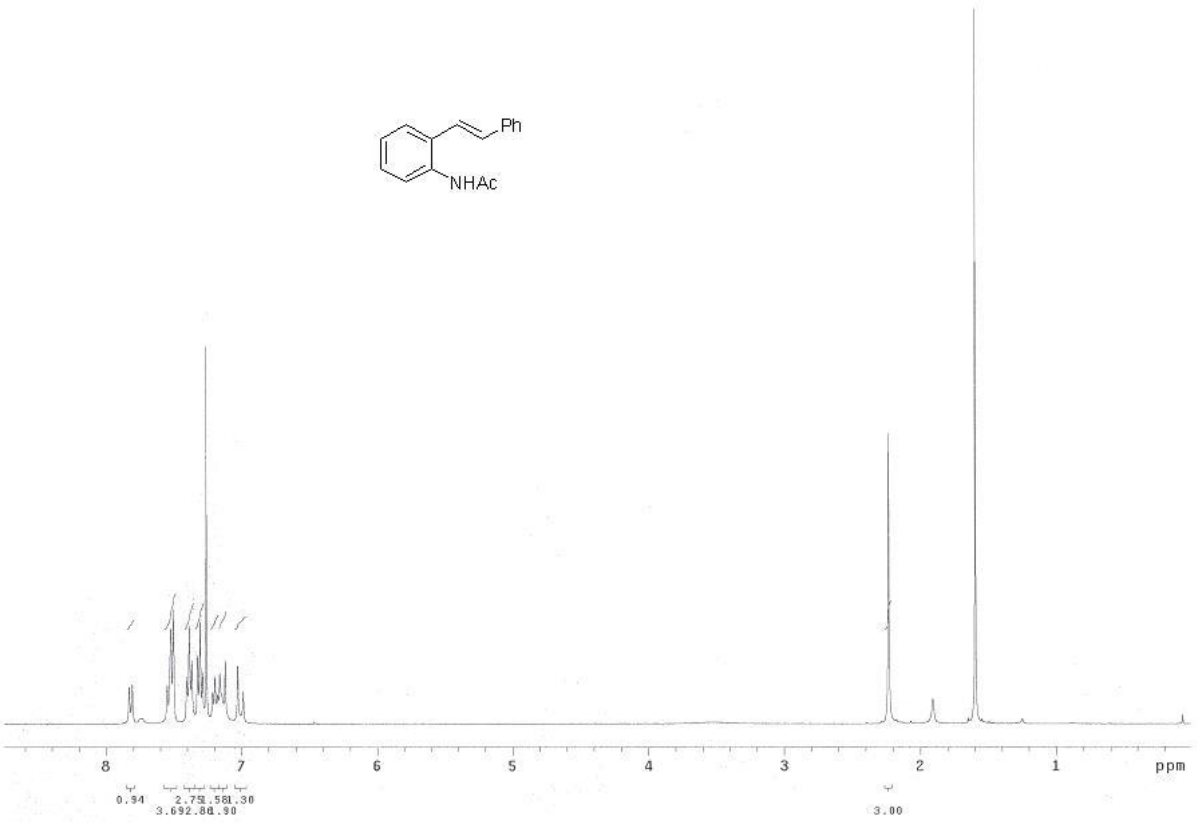
^{13}C NMR Spectrum of Compound *N*-Ms-**1** ($CDCl_3$, 100 MHz)



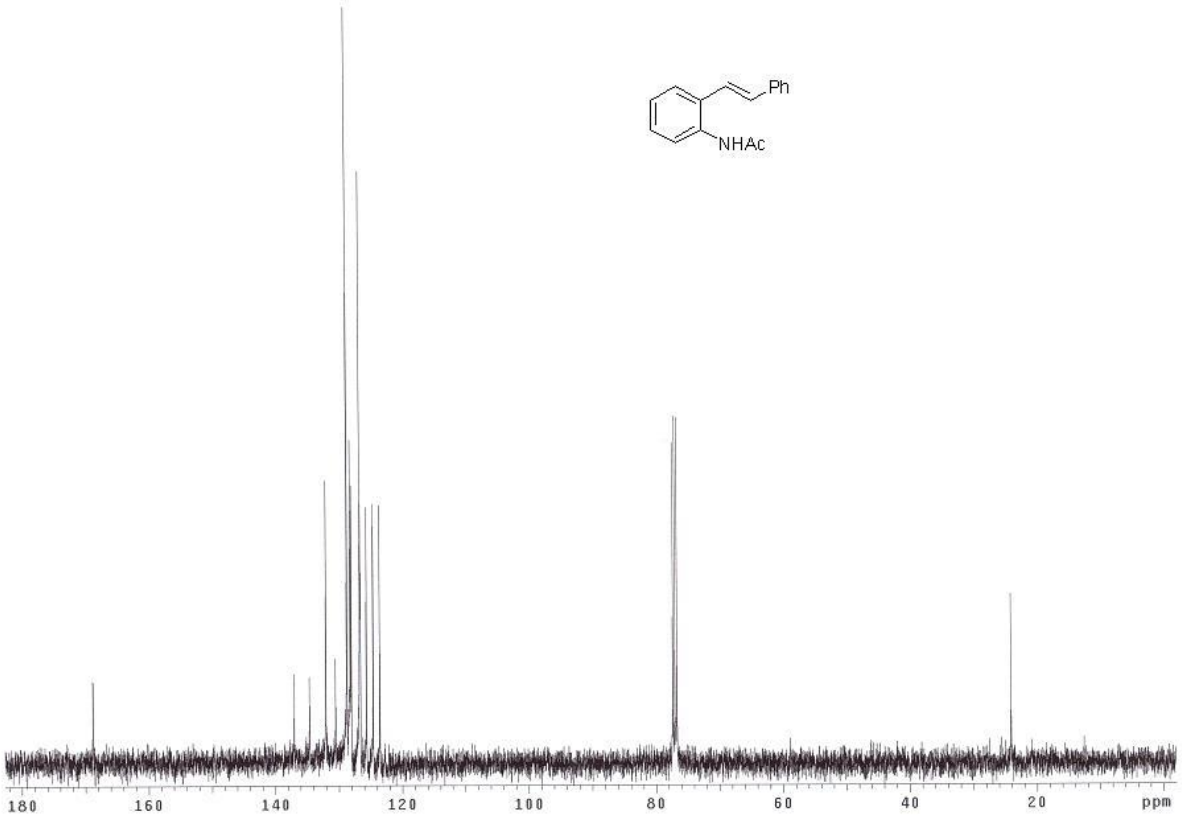
^{1}H NMR Spectrum of Compound *N*-Ms-**2** ($CDCl_3$, 400 MHz)



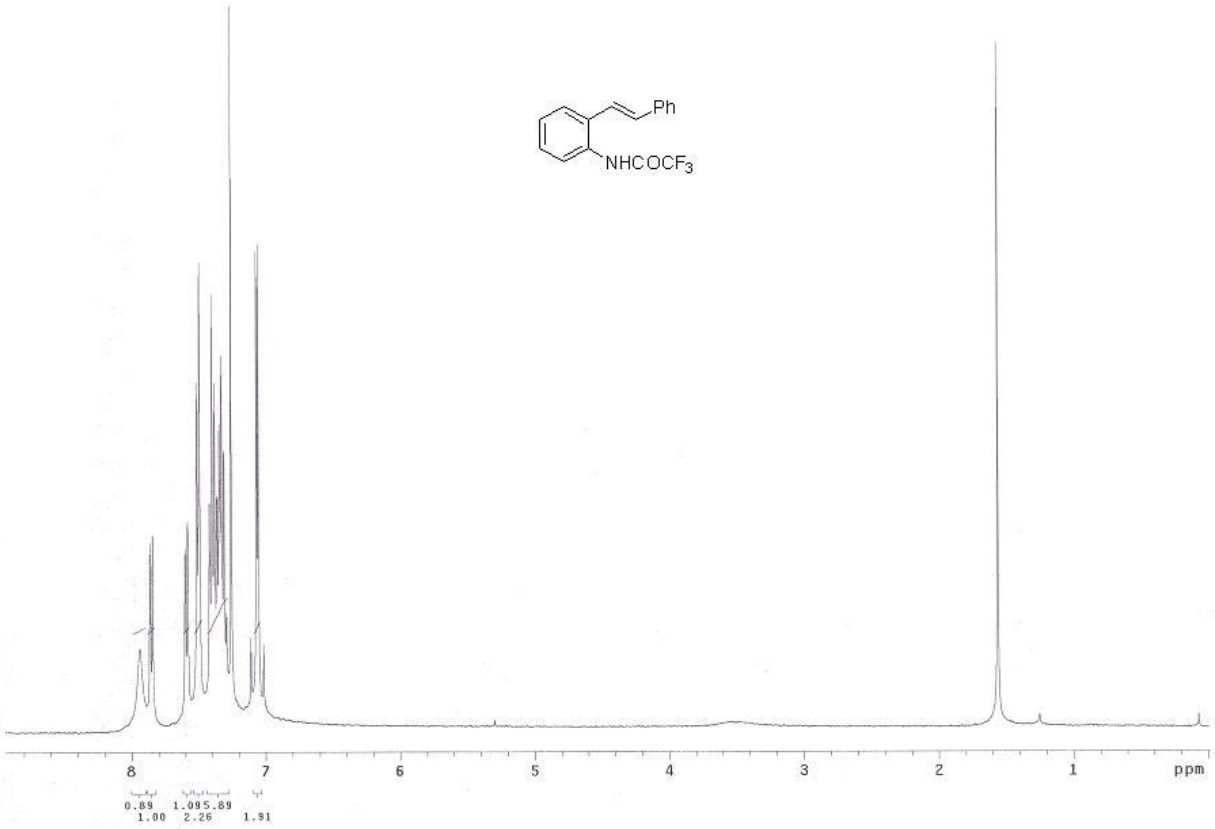
^{13}C NMR Spectrum of Compound *N*-Ms-**2** ($CDCl_3$, 100 MHz)



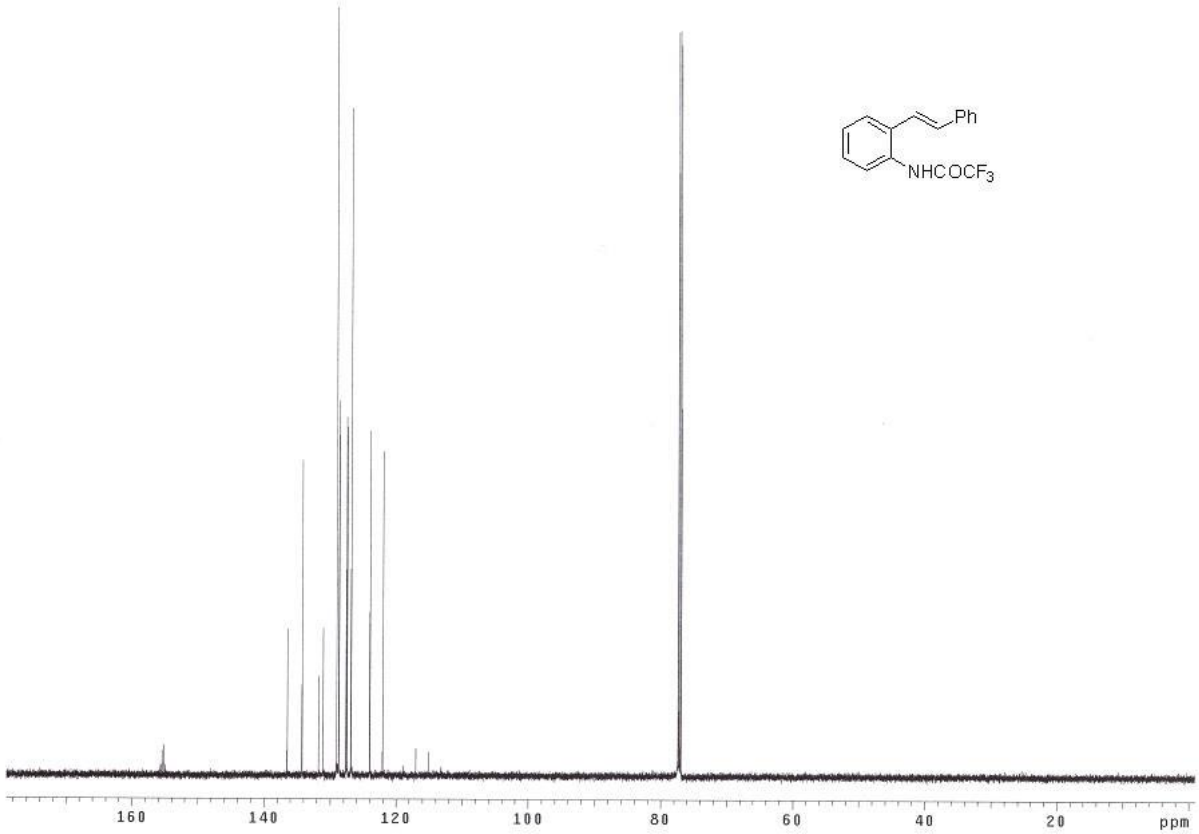
^{1}H NMR Spectrum of Compound *N*-Ac-**1** ($CDCl_3$, 400 MHz)



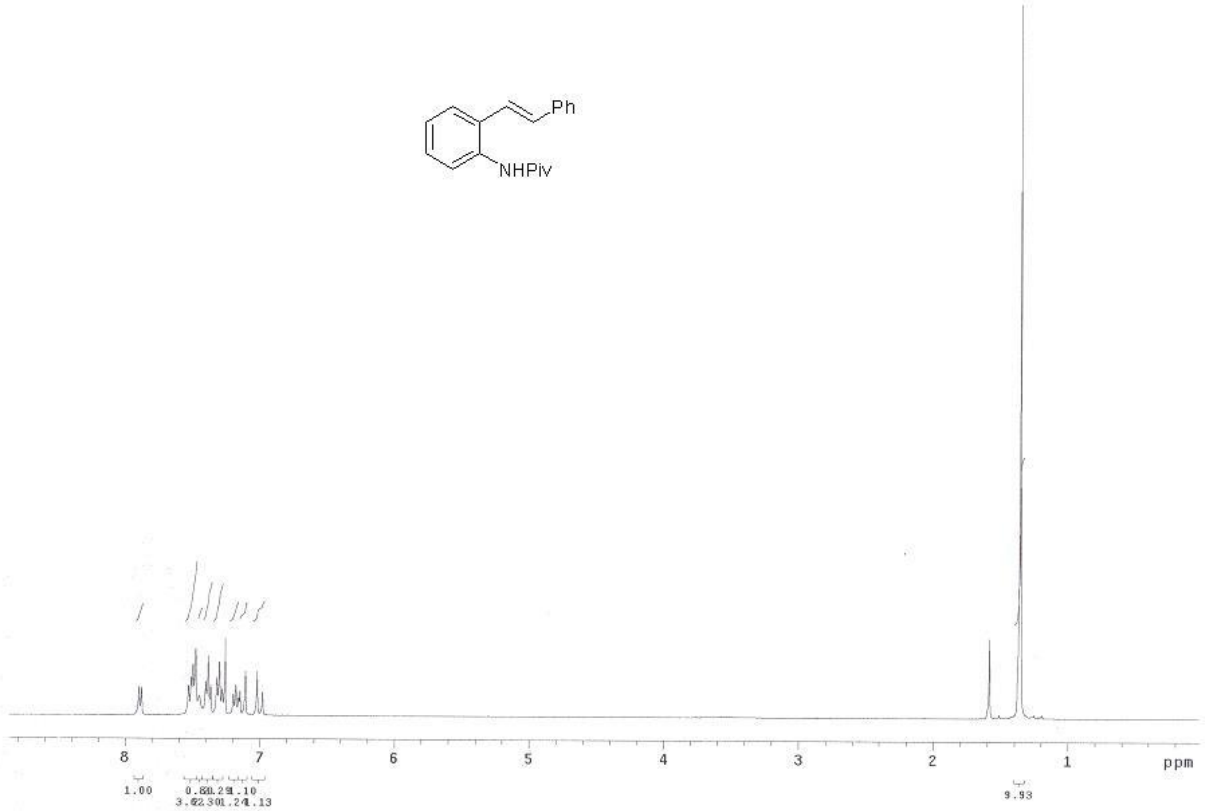
^{13}C NMR Spectrum of Compound *N*-Ac-**1** ($CDCl_3$, 100 MHz)



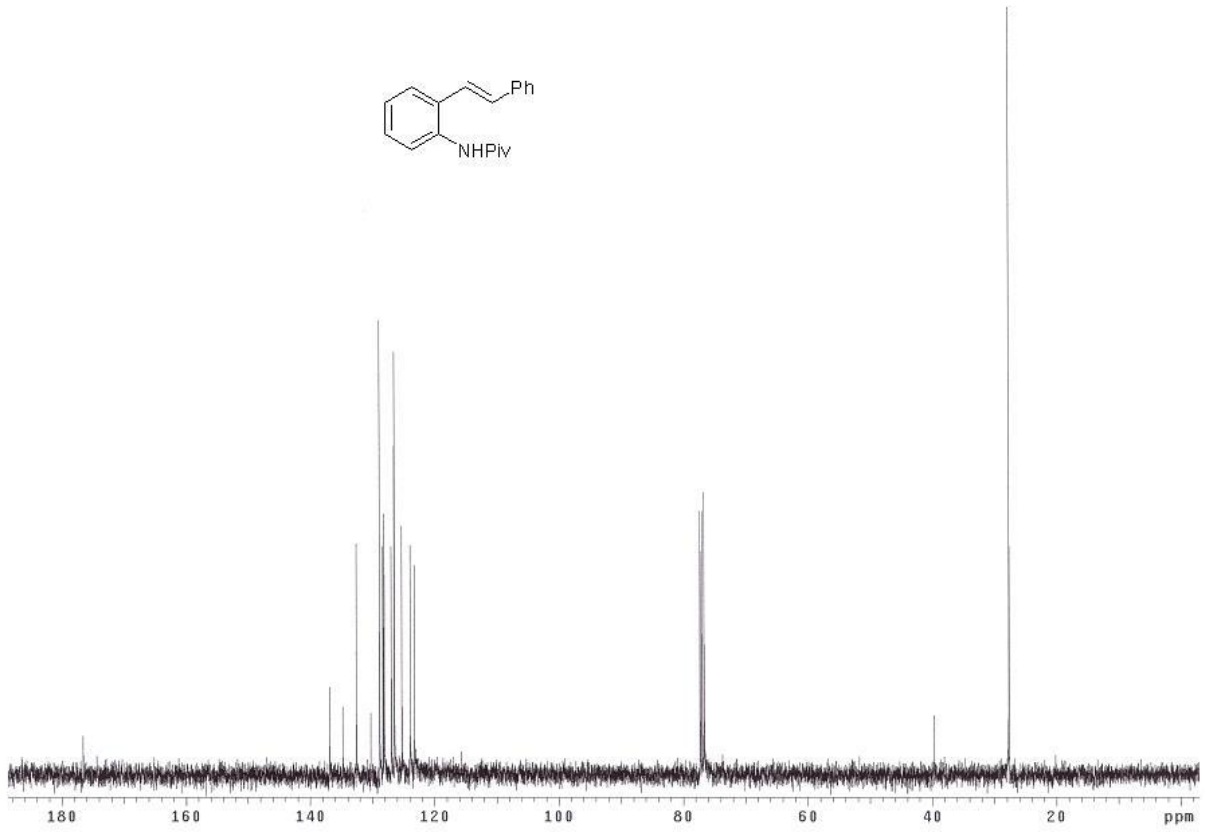
^{1}H NMR Spectrum of Compound *N*-CF_3CO-**1** ($CDCl_3$, 400 MHz)



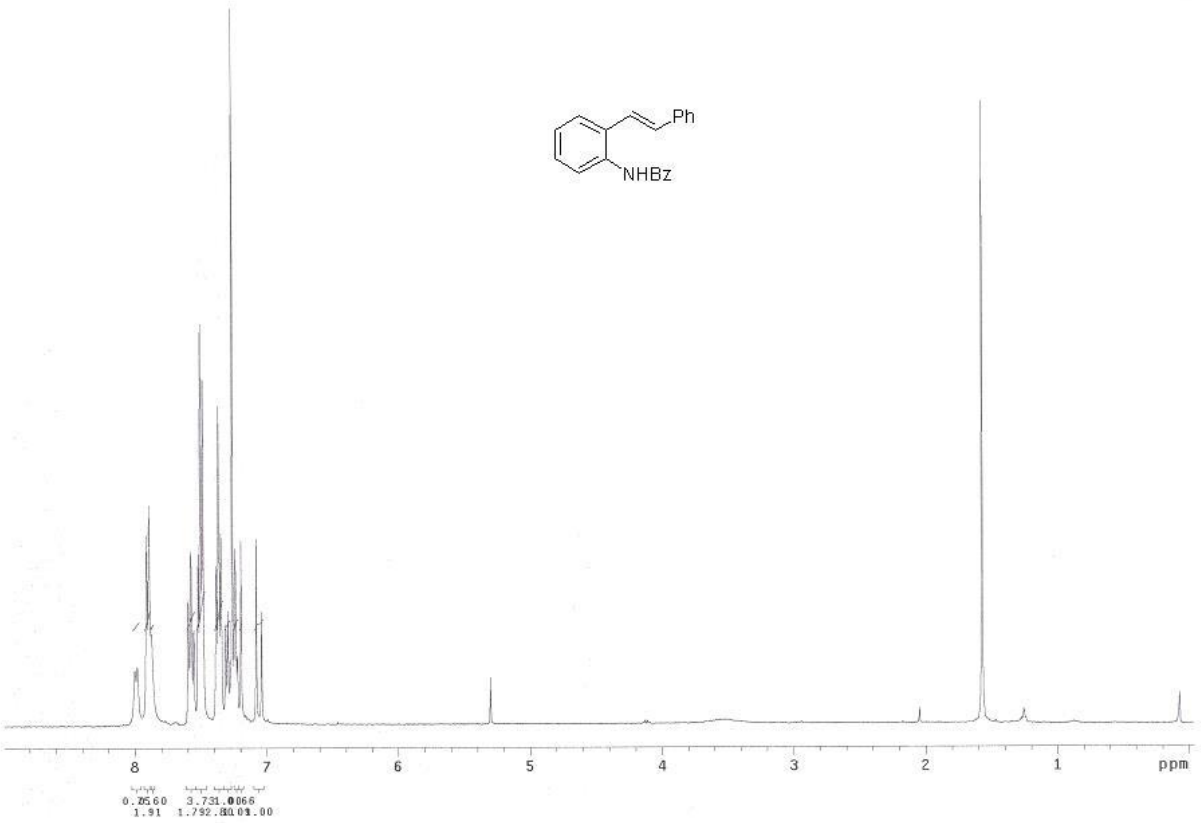
^{13}C NMR Spectrum of Compound *N*-CF_3CO-**1** ($CDCl_3$, 150 MHz)



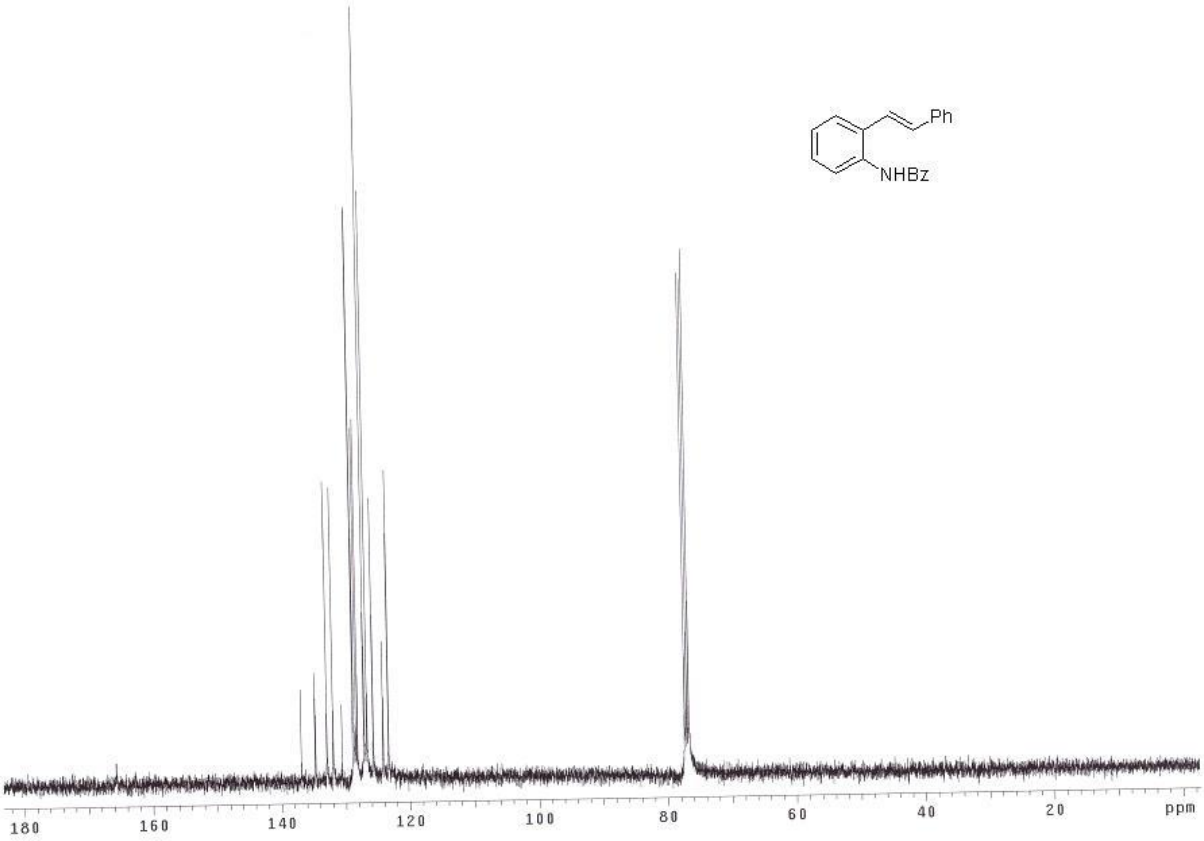
^{1}H NMR Spectrum of Compound *N*-Piv-**1** ($CDCl_3$, 400 MHz)



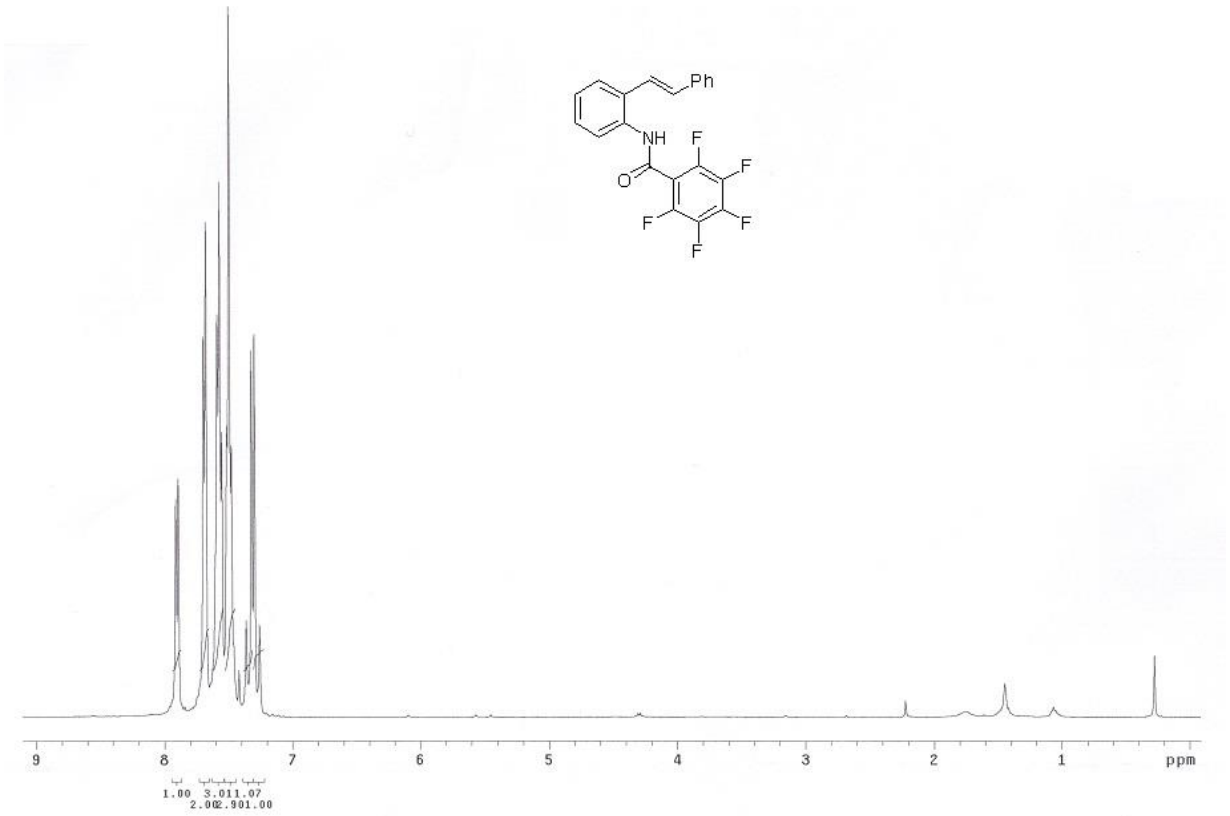
^{13}C NMR Spectrum of Compound *N*-Piv-**1** ($CDCl_3$, 100 MHz)



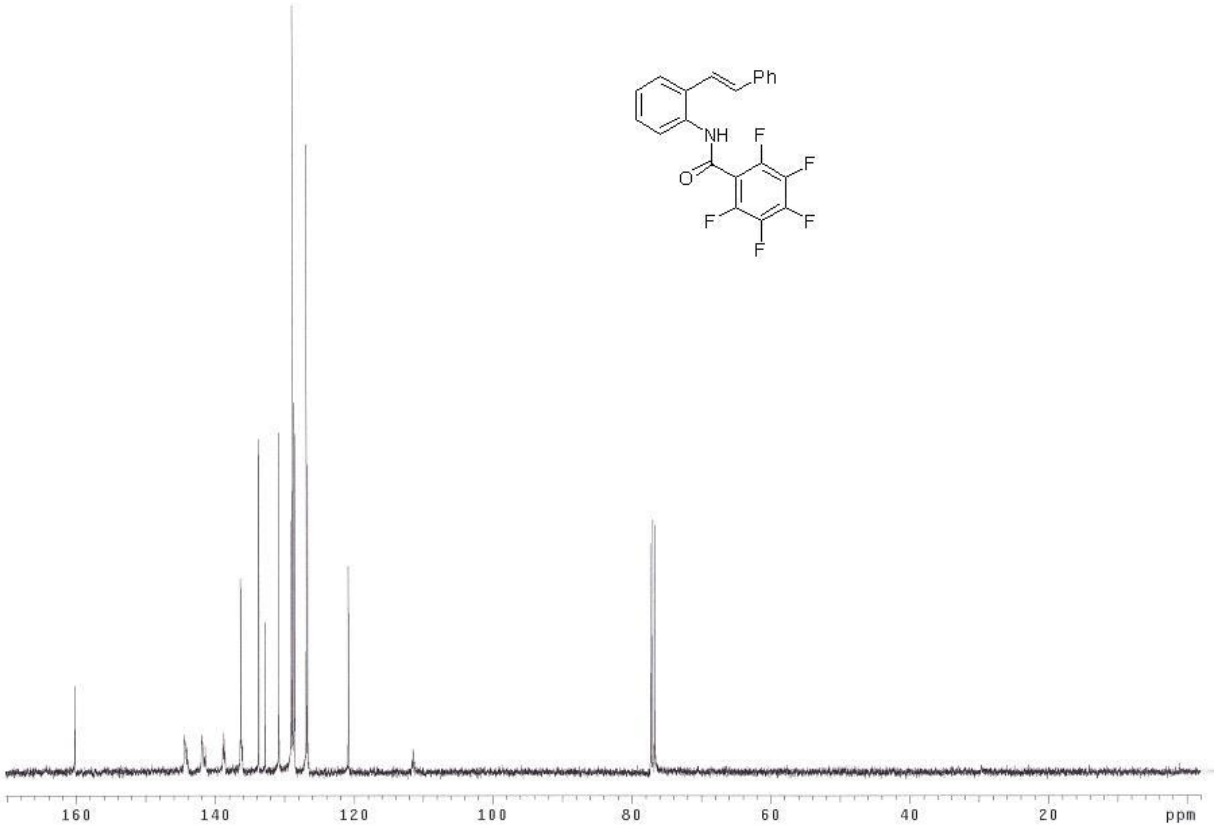
^{1}H NMR Spectrum of Compound *N*-Bz-**1** ($CDCl_3$, 400 MHz)



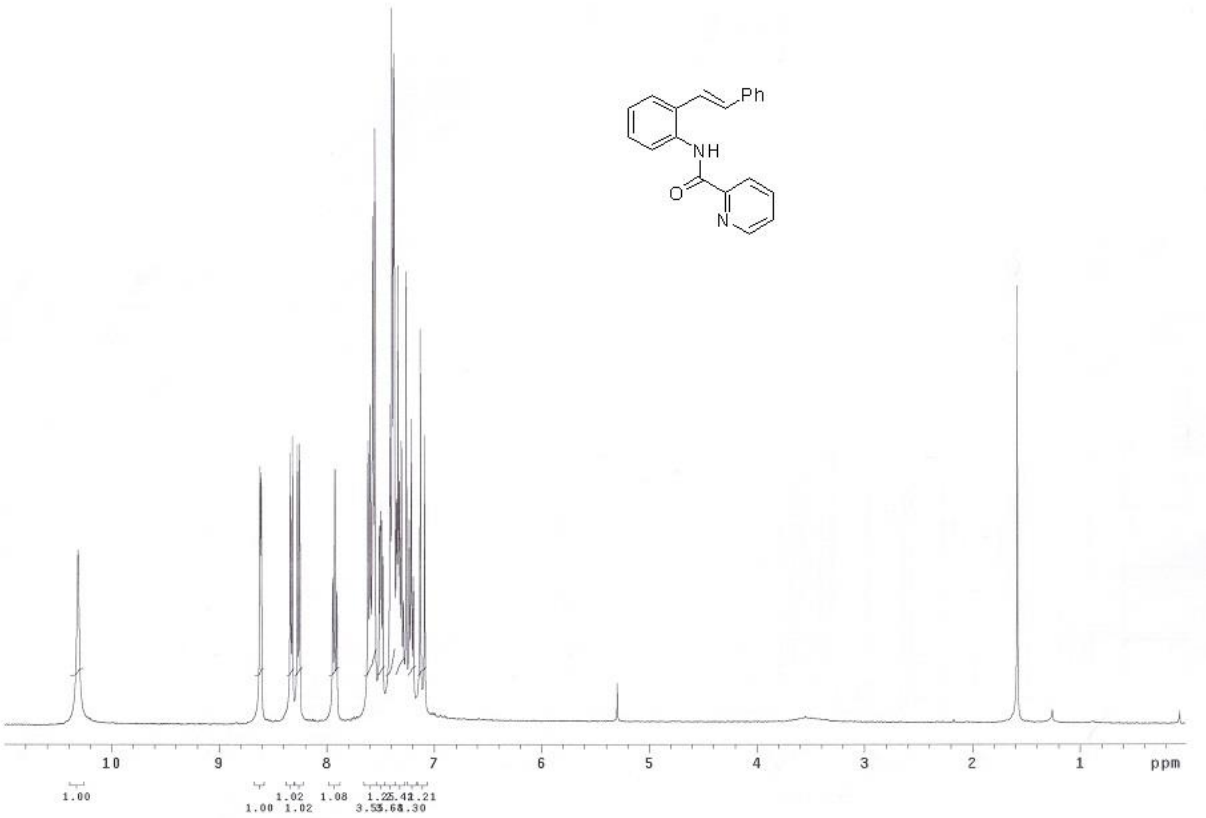
^{13}C NMR Spectrum of Compound *N*-Bz-**1** ($CDCl_3$, 100 MHz)



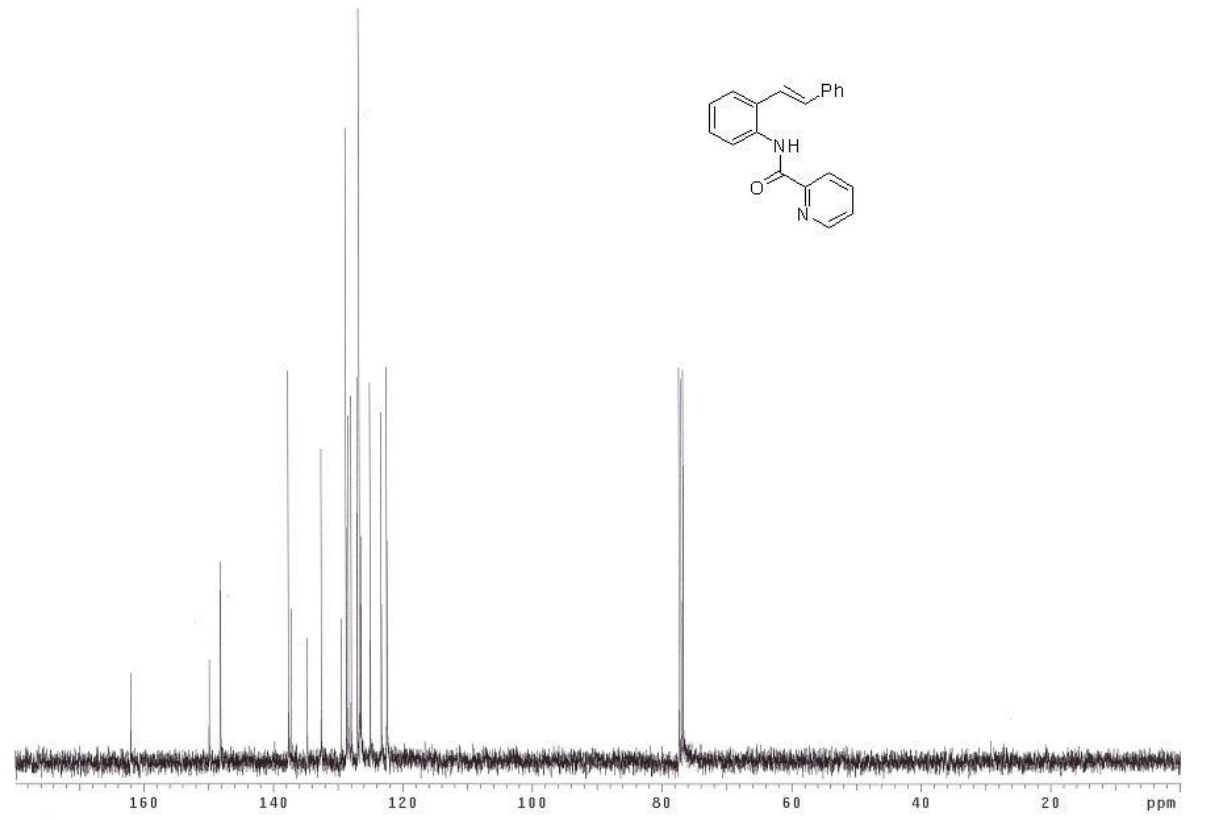
^{1}H NMR Spectrum of Compound *N*-C_6F_5CO-**1** ($CDCl_3$, 400 MHz)



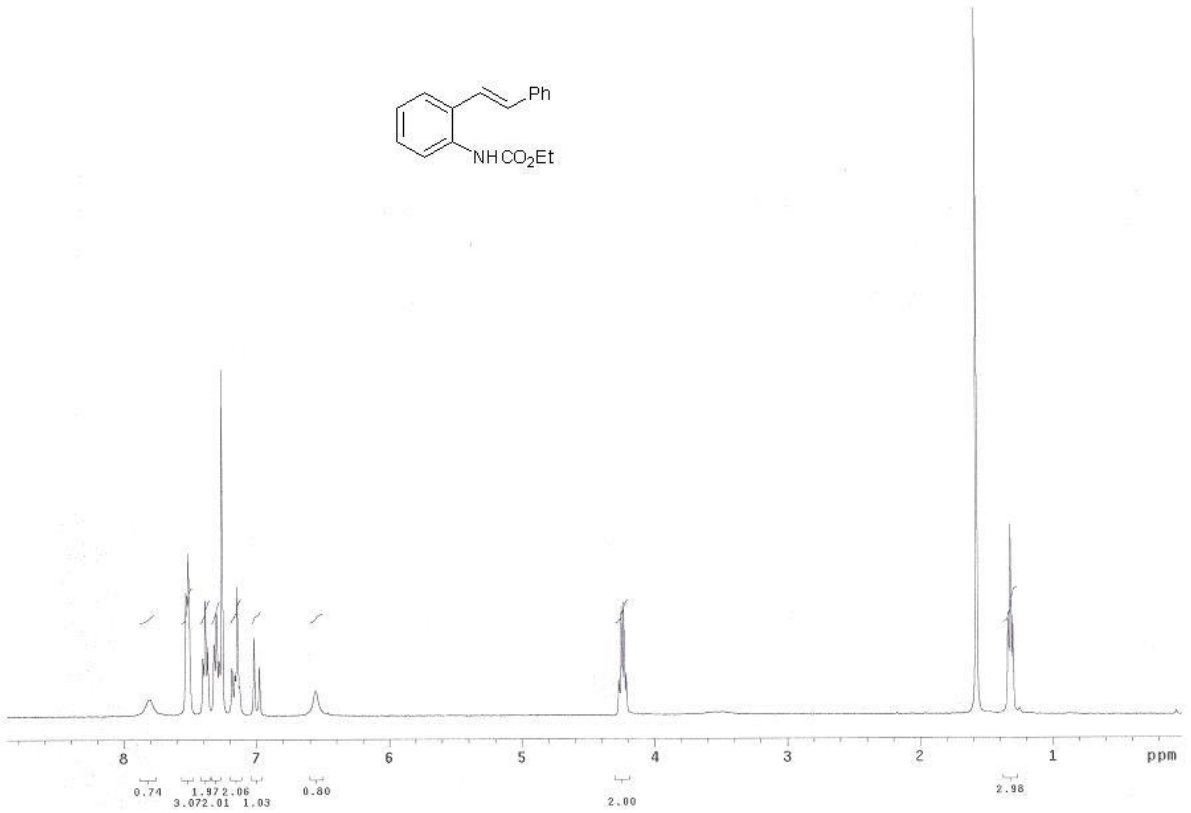
^{13}C NMR Spectrum of Compound *N*-C_6F_5CO-**1** ($CDCl_3$, 100 MHz)



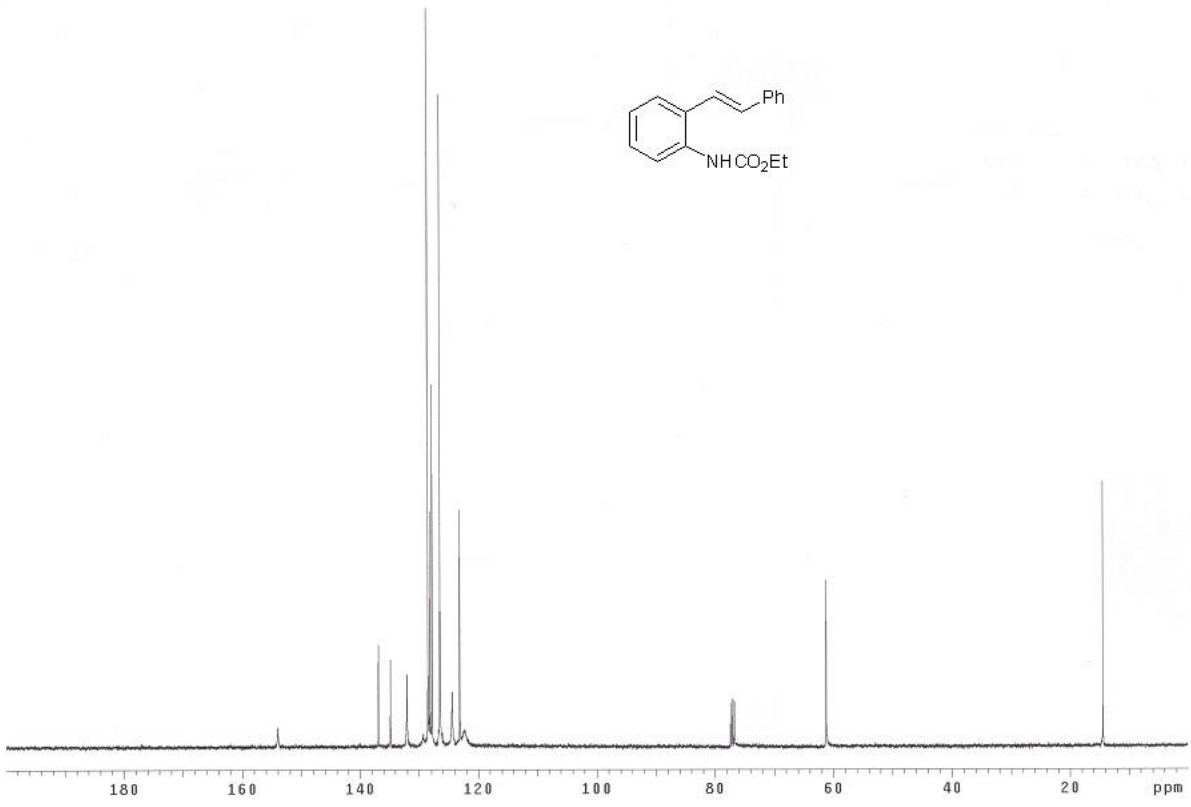
^{1}H NMR Spectrum of Compound *N*-(2-Pyridinyl)CO-**1** ($CDCl_3$, 400 MHz)



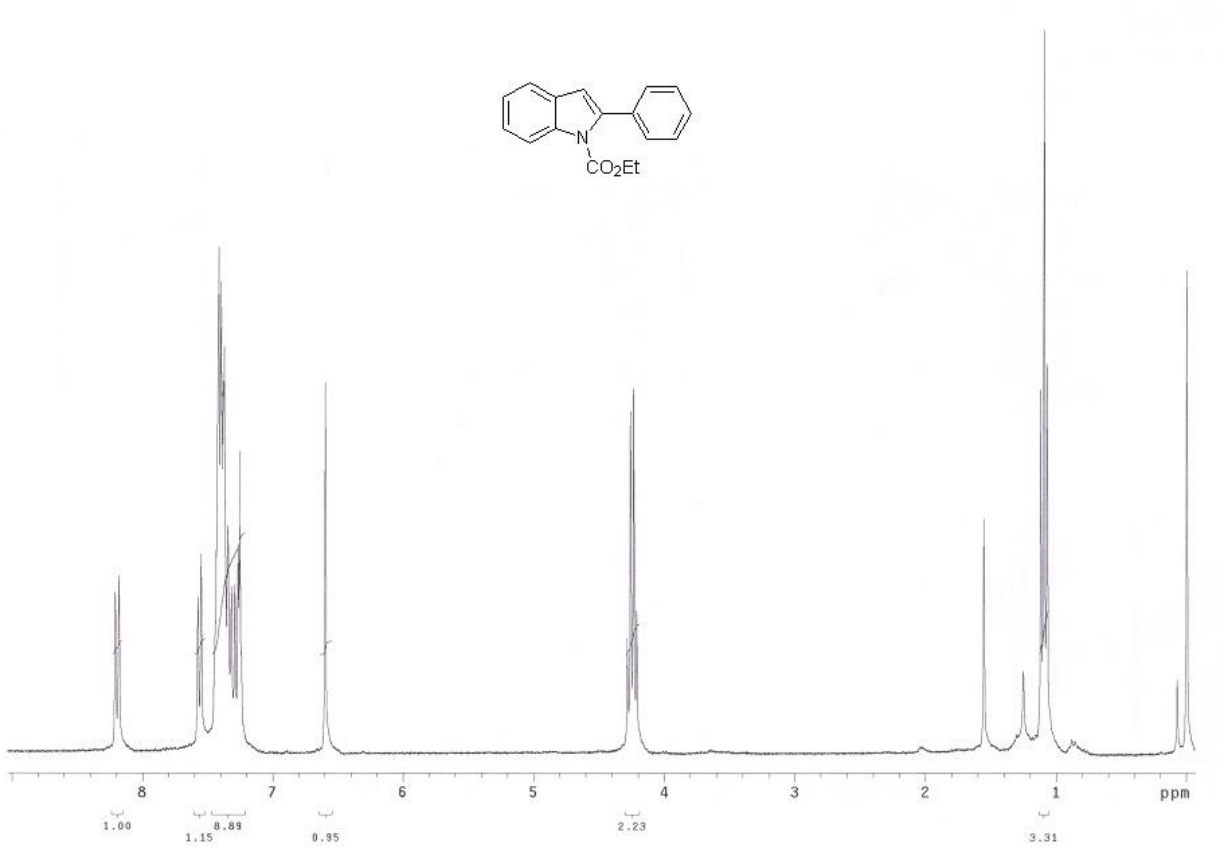
^{13}C NMR Spectrum of Compound *N*-(2-Pyridinyl)CO-**1** ($CDCl_3$, 100 MHz)



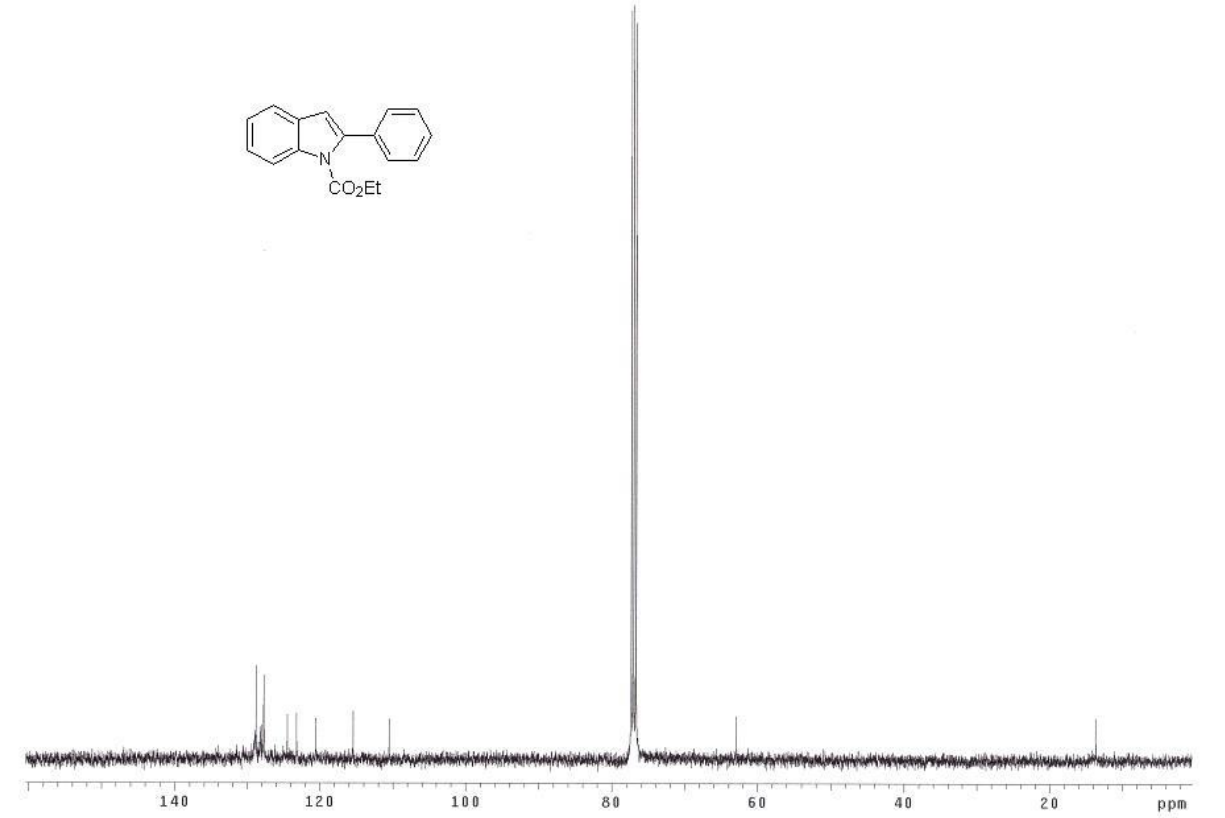
^{1}H NMR Spectrum of Compound *N*-CO_2Et-**1** ($CDCl_3$, 400 MHz)



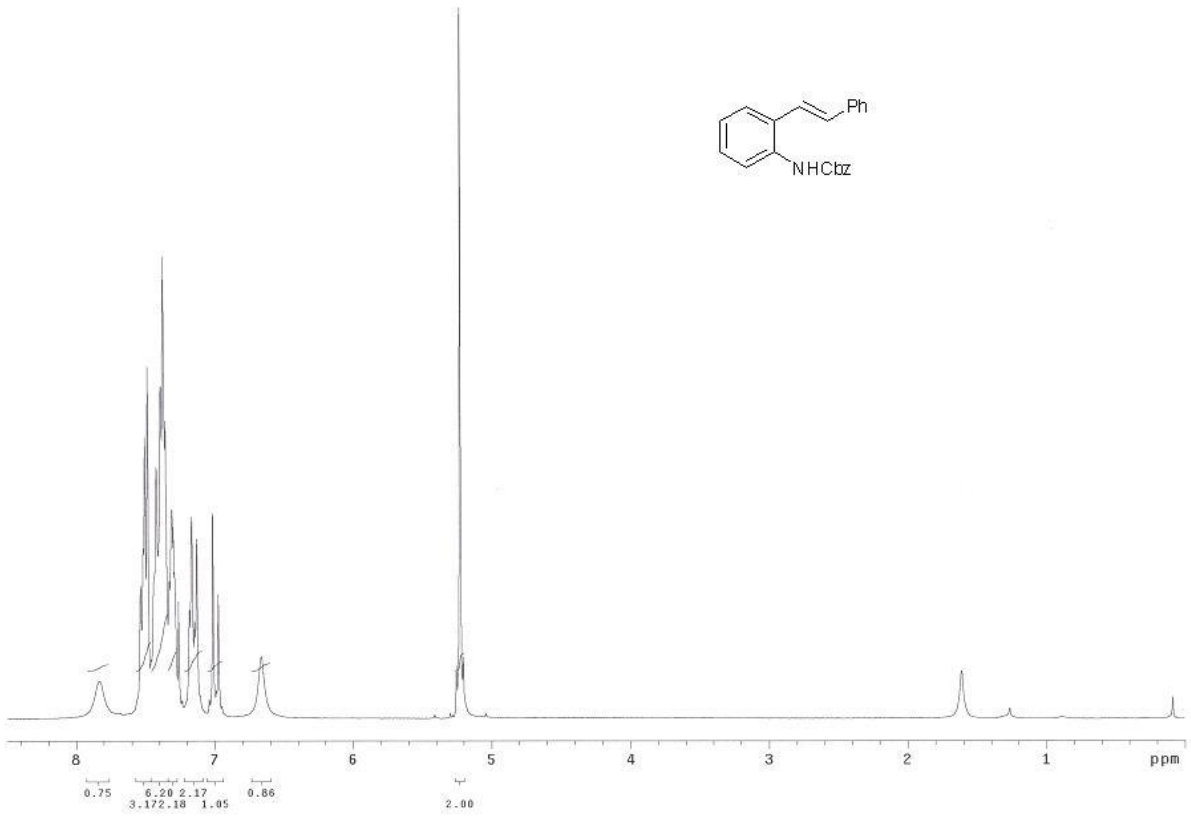
^{13}C NMR Spectrum of Compound *N*-CO_2Et-**1** ($CDCl_3$, 100 MHz)



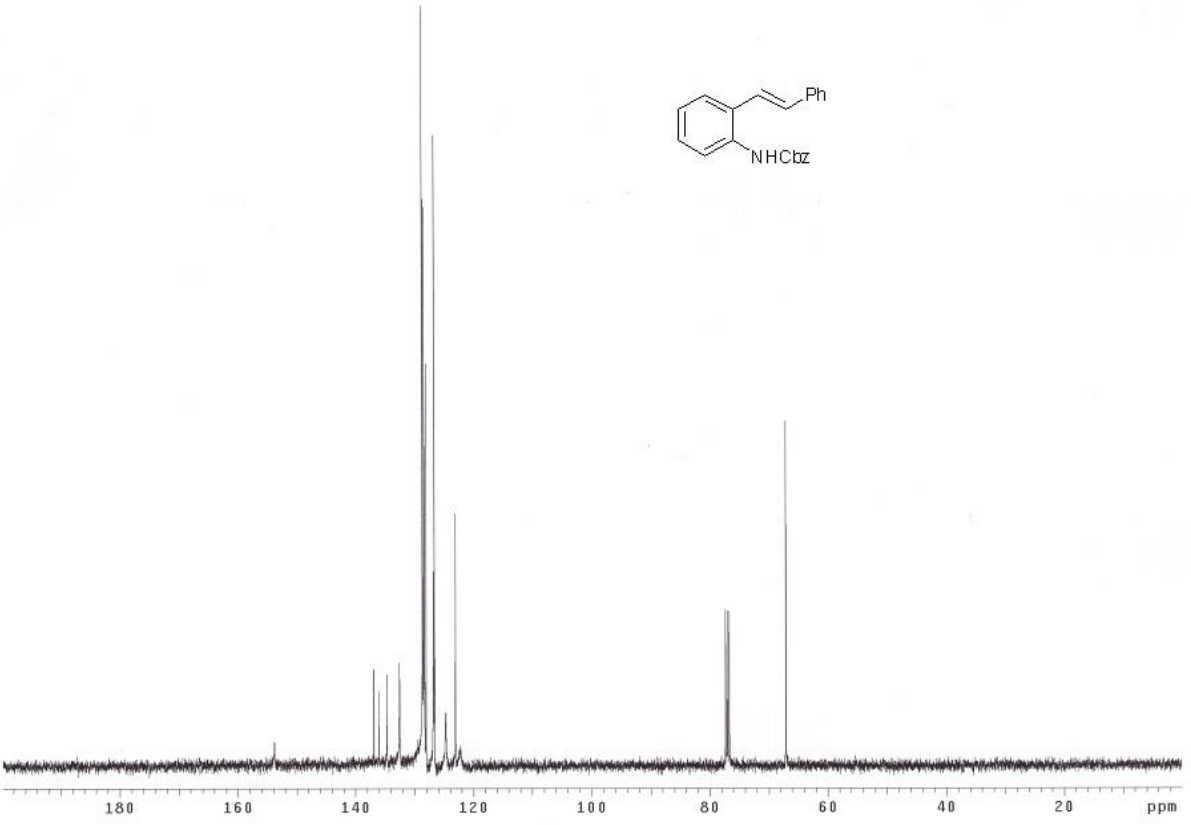
^{1}H NMR Spectrum of Compound *N*-CO_2Et-**2** ($CDCl_3$, 300 MHz)



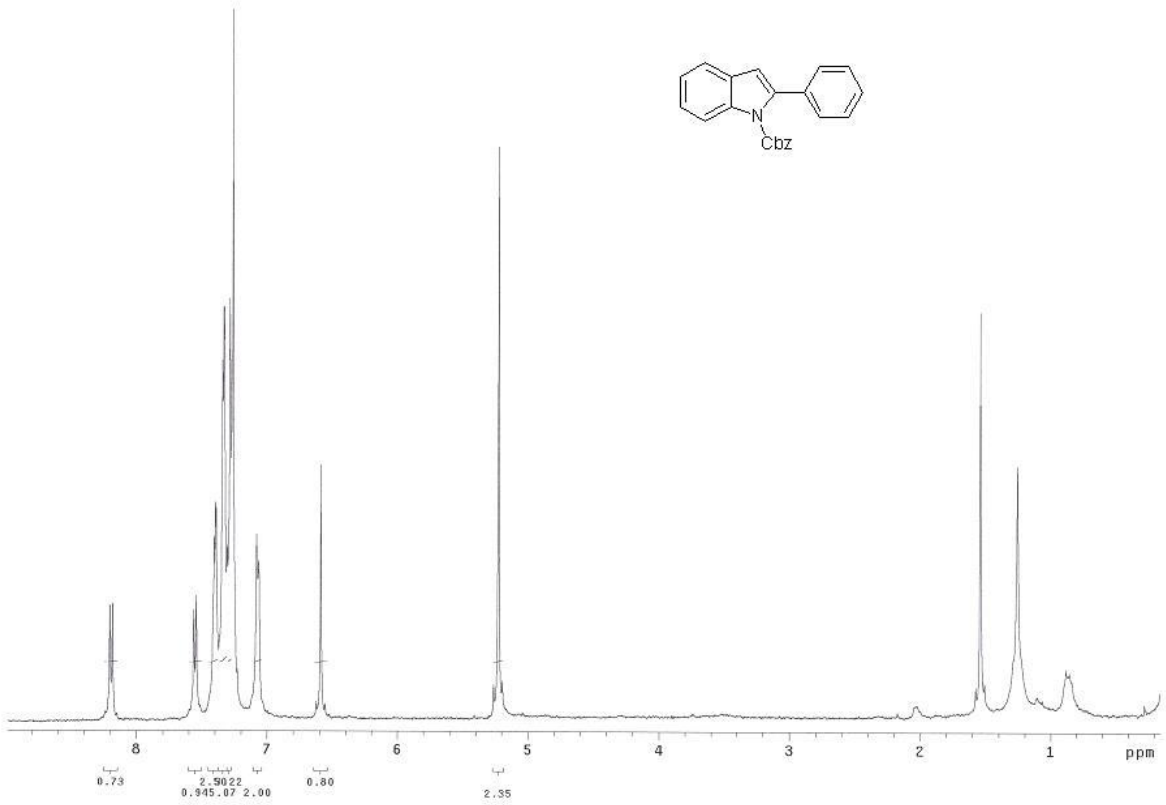
^{13}C NMR Spectrum of Compound *N*-CO_2Et-**2** ($CDCl_3$, 100 MHz)



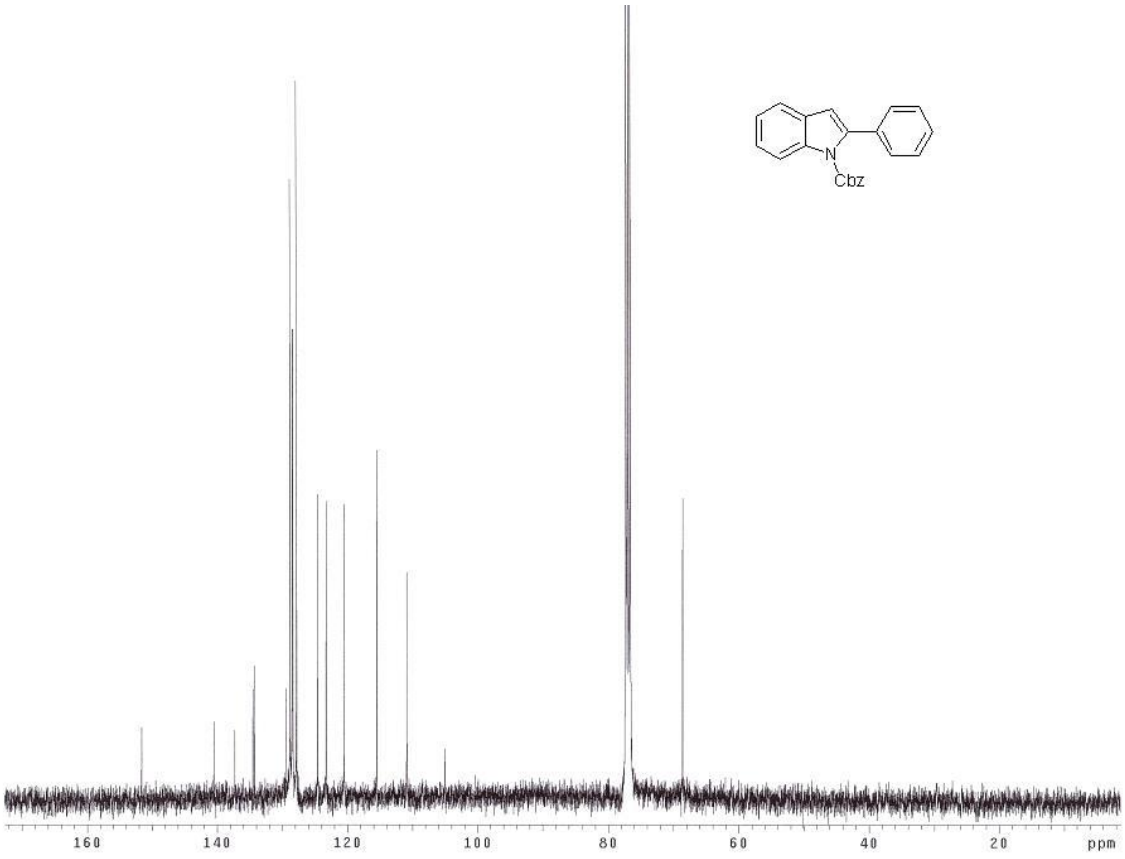
^{1}H NMR Spectrum of Compound *N*-Cbz-**1** ($CDCl_3$, 400 MHz)



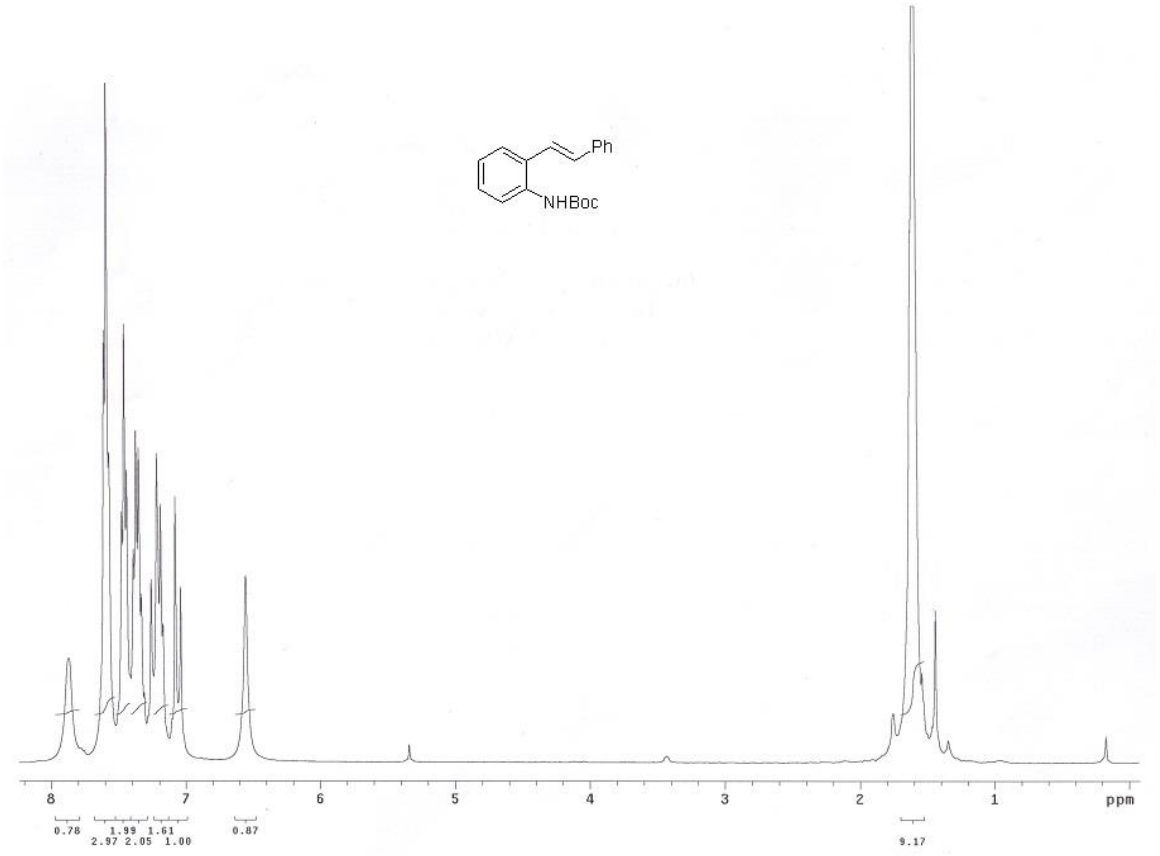
^{13}C NMR Spectrum of Compound *N*-Cbz-**1** ($CDCl_3$, 100 MHz)



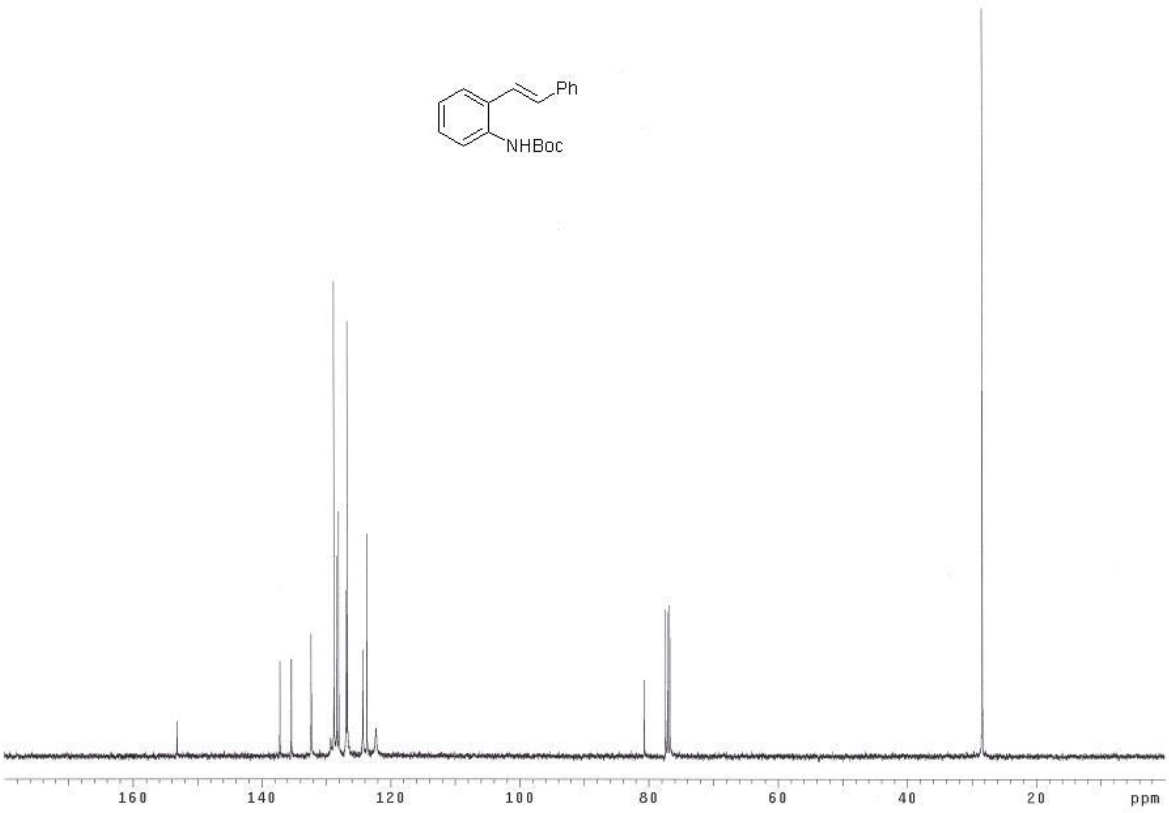
^{1}H NMR Spectrum of Compound *N*-Cbz-**2** ($CDCl_3$, 400 MHz)



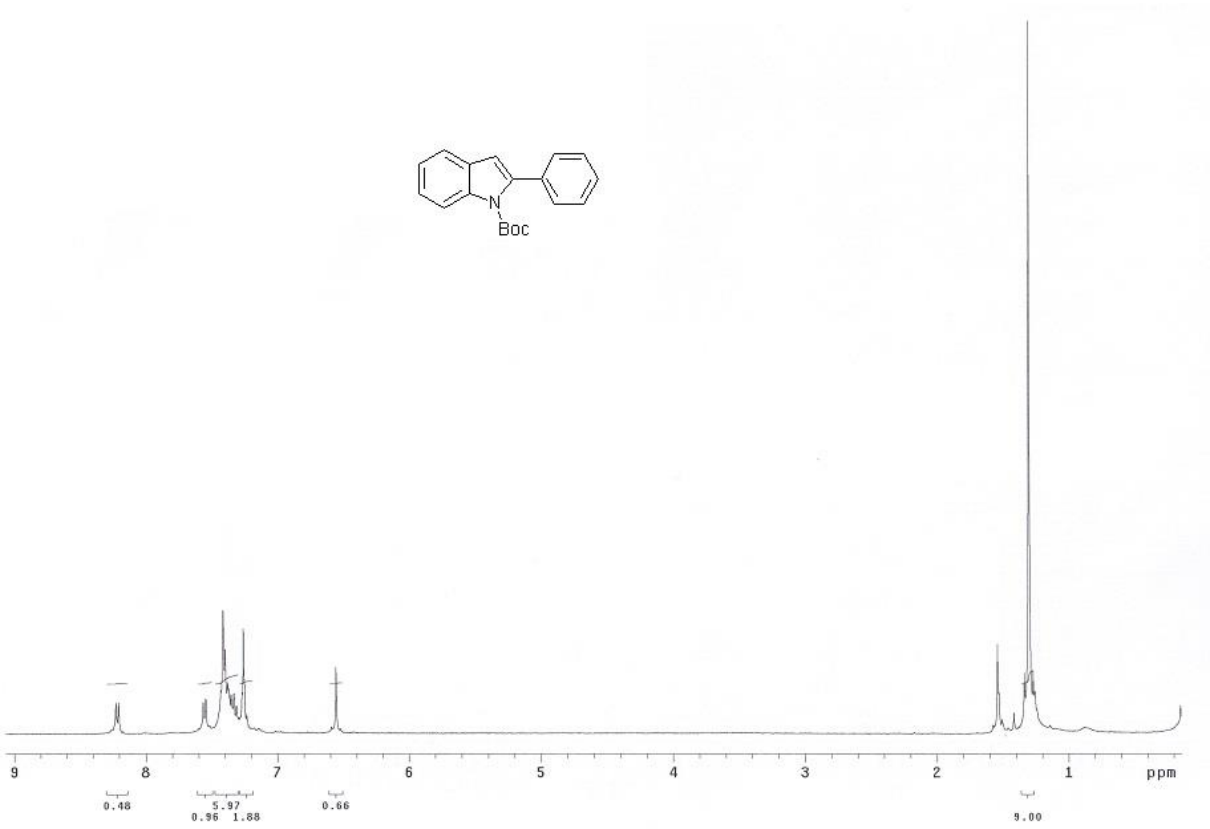
^{13}C NMR Spectrum of Compound *N*-Cbz-**2** ($CDCl_3$, 100 MHz)



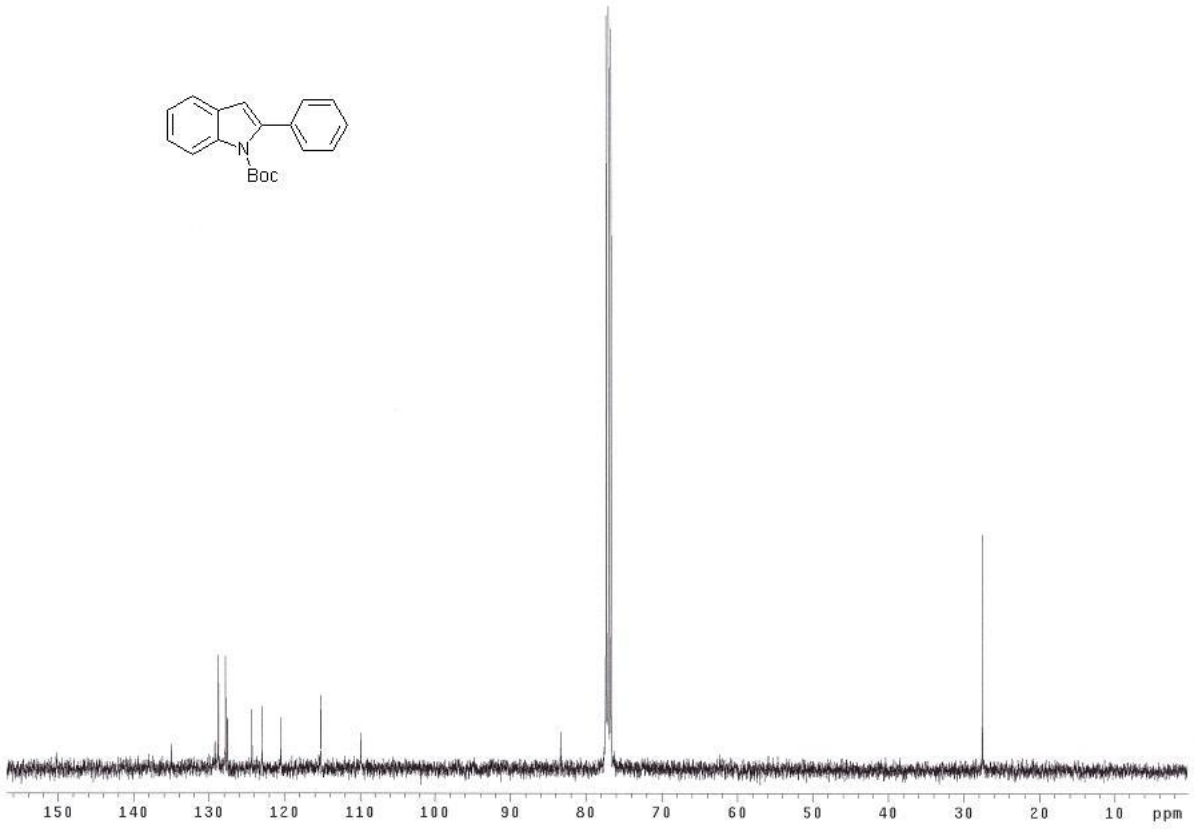
^{1}H NMR Spectrum of Compound *N*-Boc-**1** ($CDCl_3$, 400 MHz)



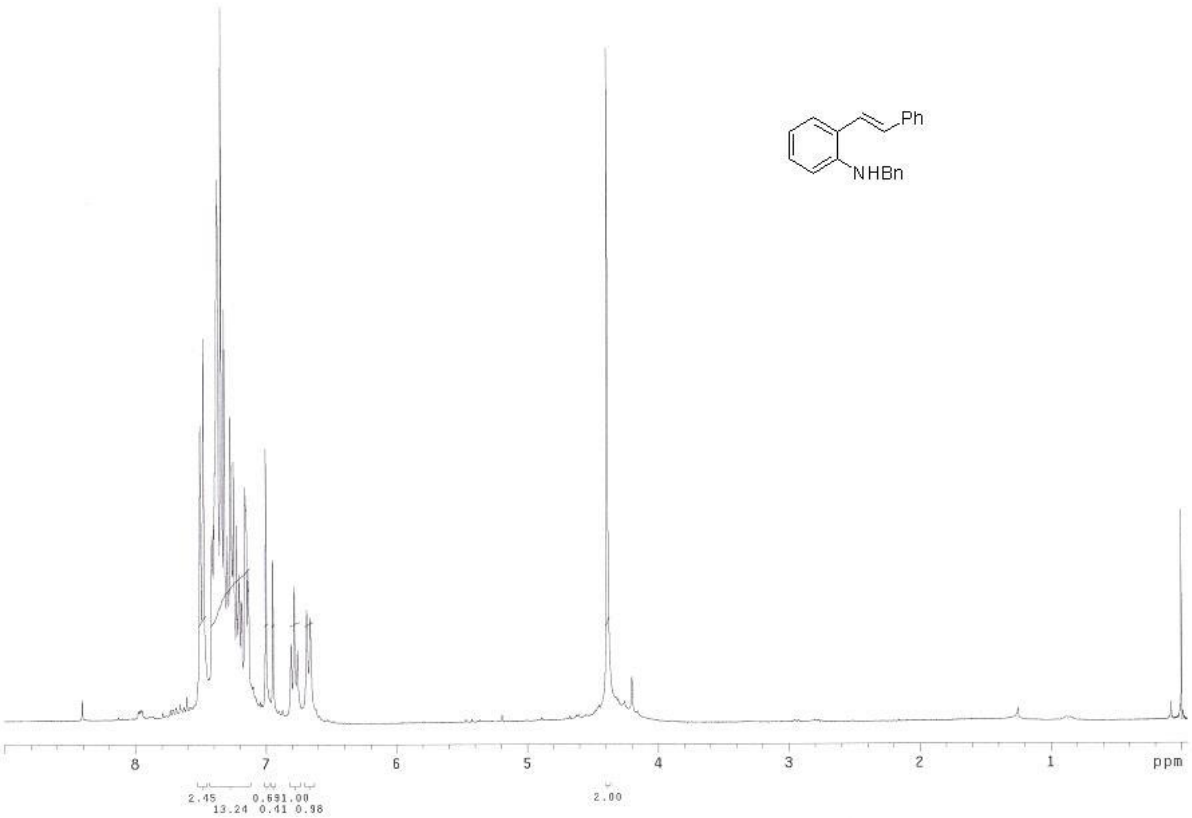
^{13}C NMR Spectrum of Compound *N*-Boc-**1** ($CDCl_3$, 100 MHz)



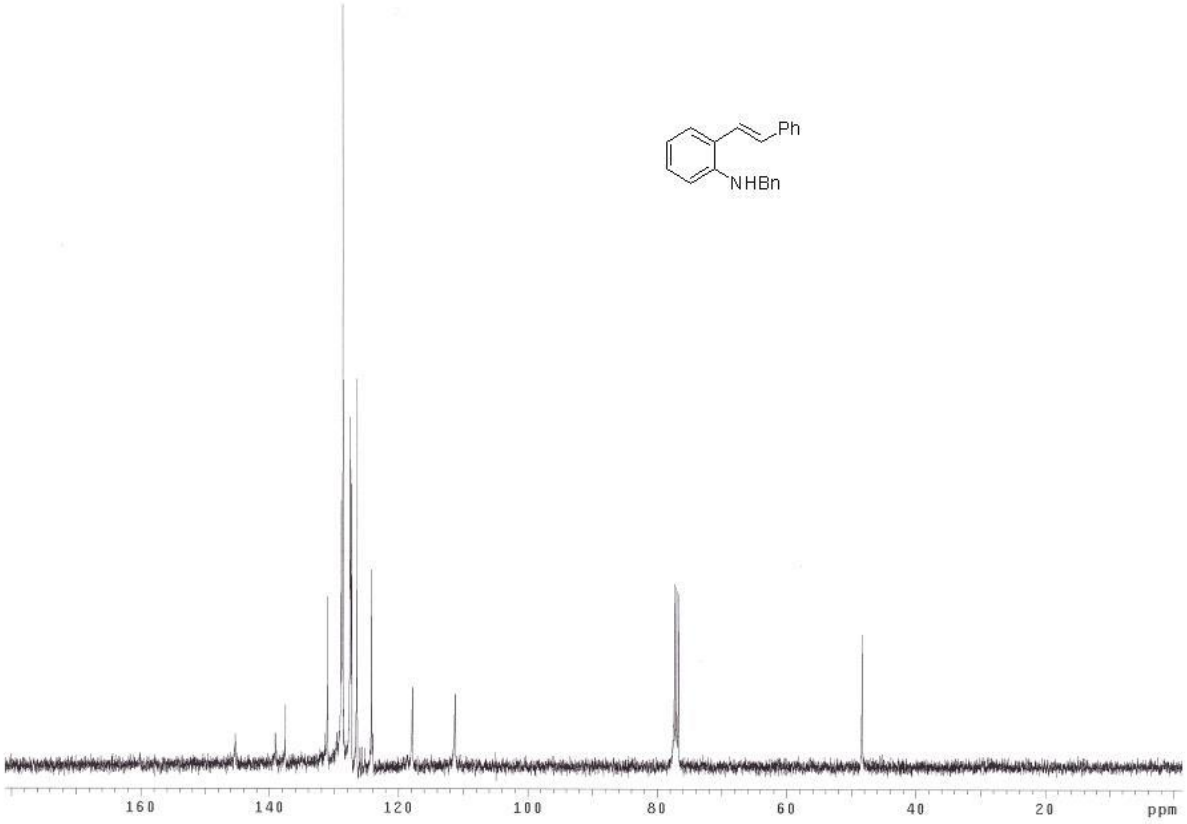
^{1}H NMR Spectrum of Compound *N*-Boc-**2** ($CDCl_3$, 400 MHz)



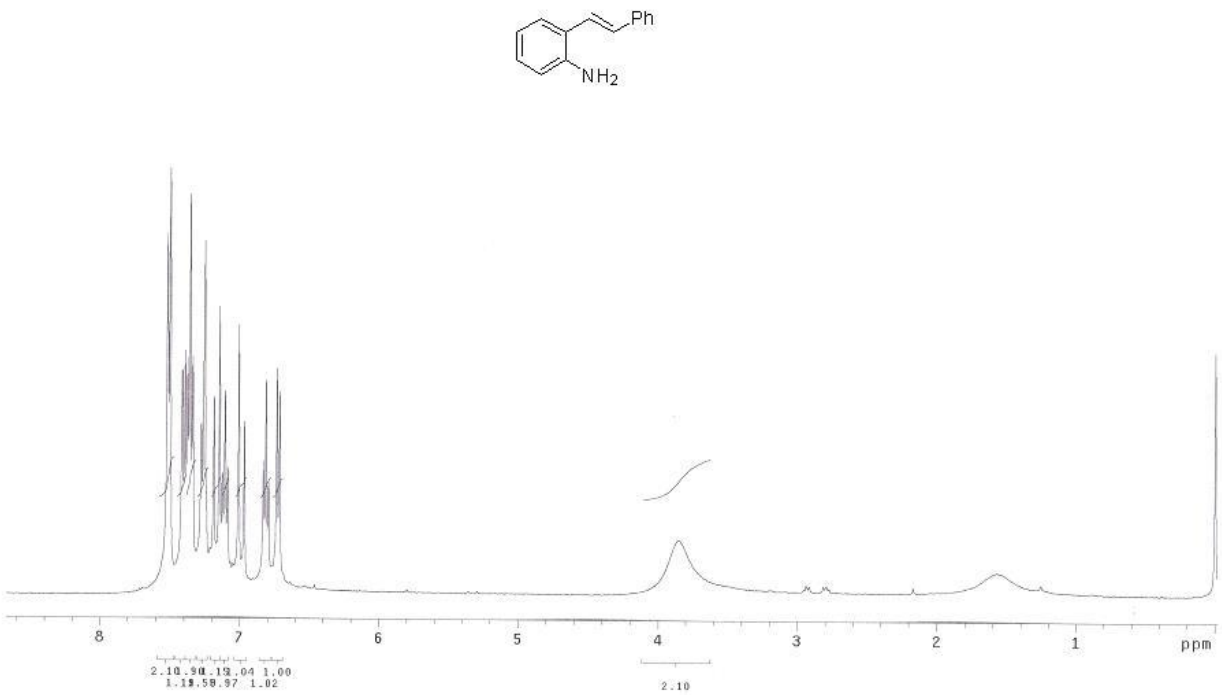
^{13}C NMR Spectrum of Compound *N*-Boc-**2** ($CDCl_3$, 100 MHz)



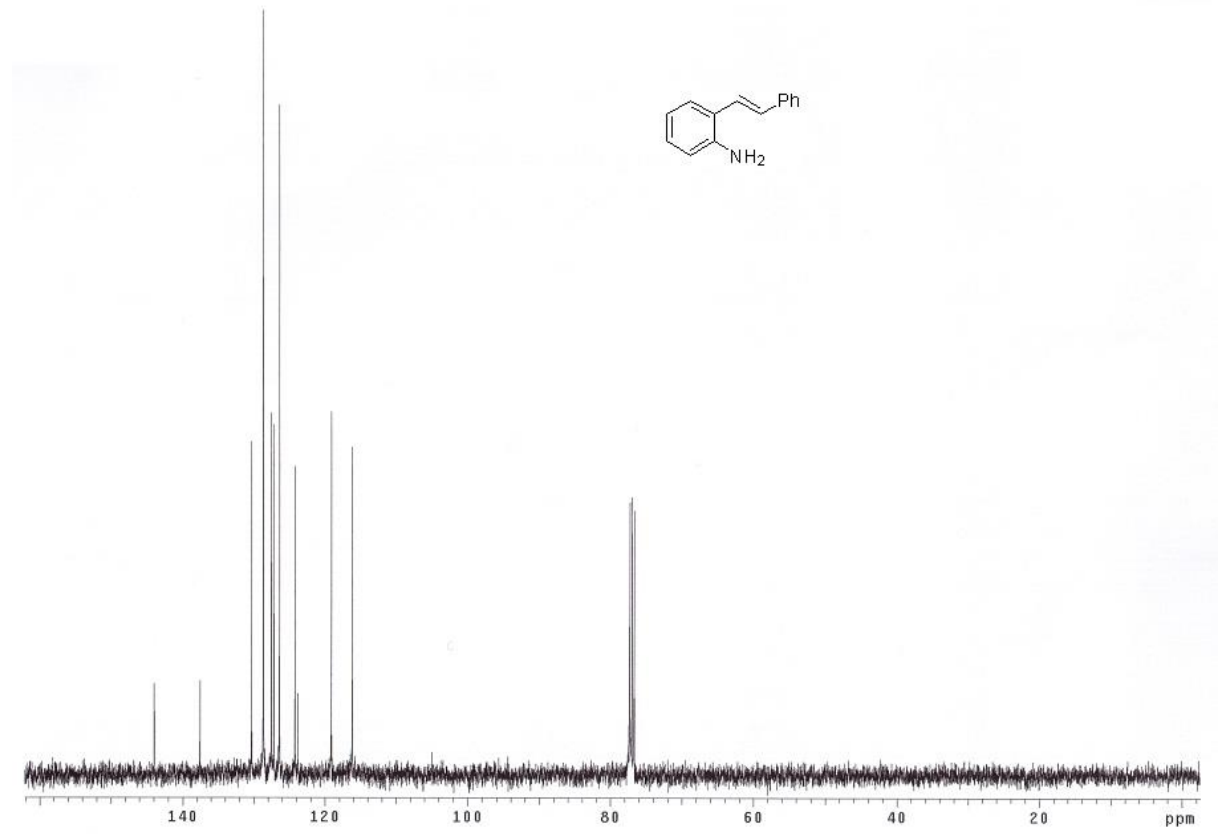
^{1}H NMR Spectrum of Compound *N*-Bn-**1** ($CDCl_3$, 300 MHz)



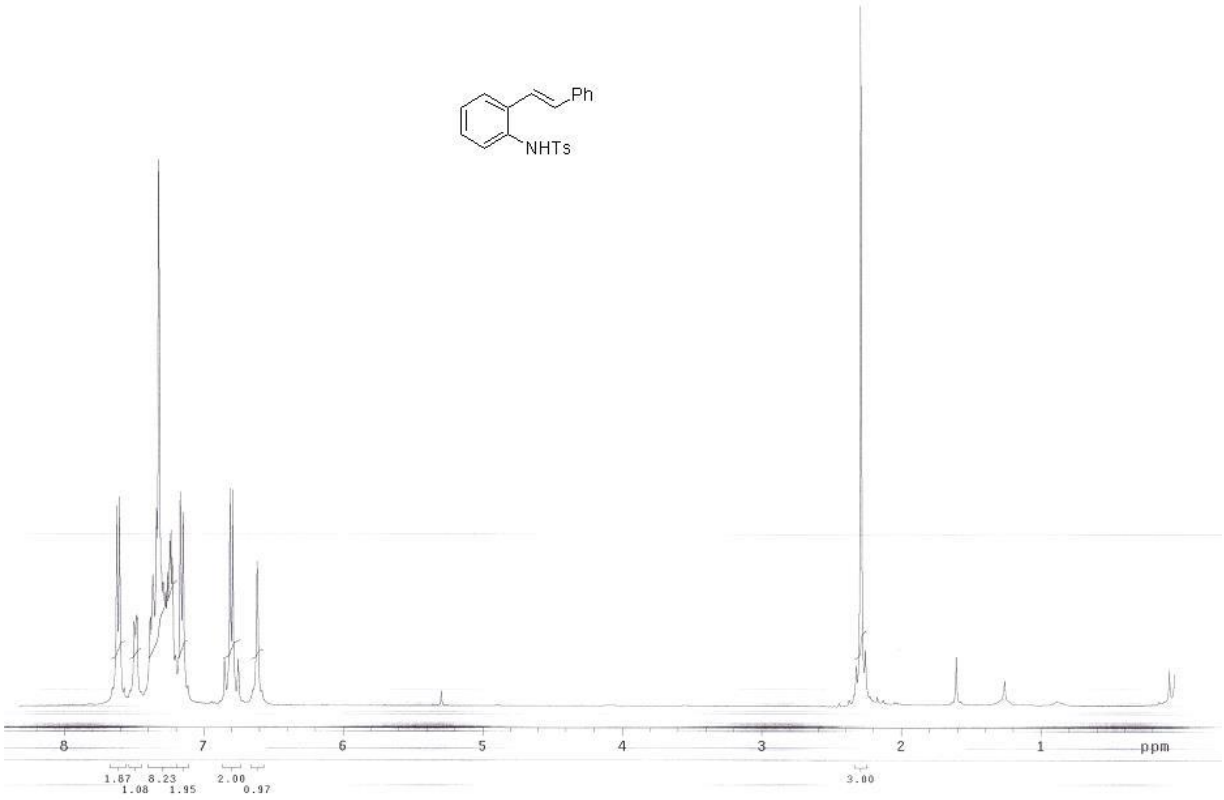
^{13}C NMR Spectrum of Compound *N*-Bn-**1** ($CDCl_3$, 100 MHz)



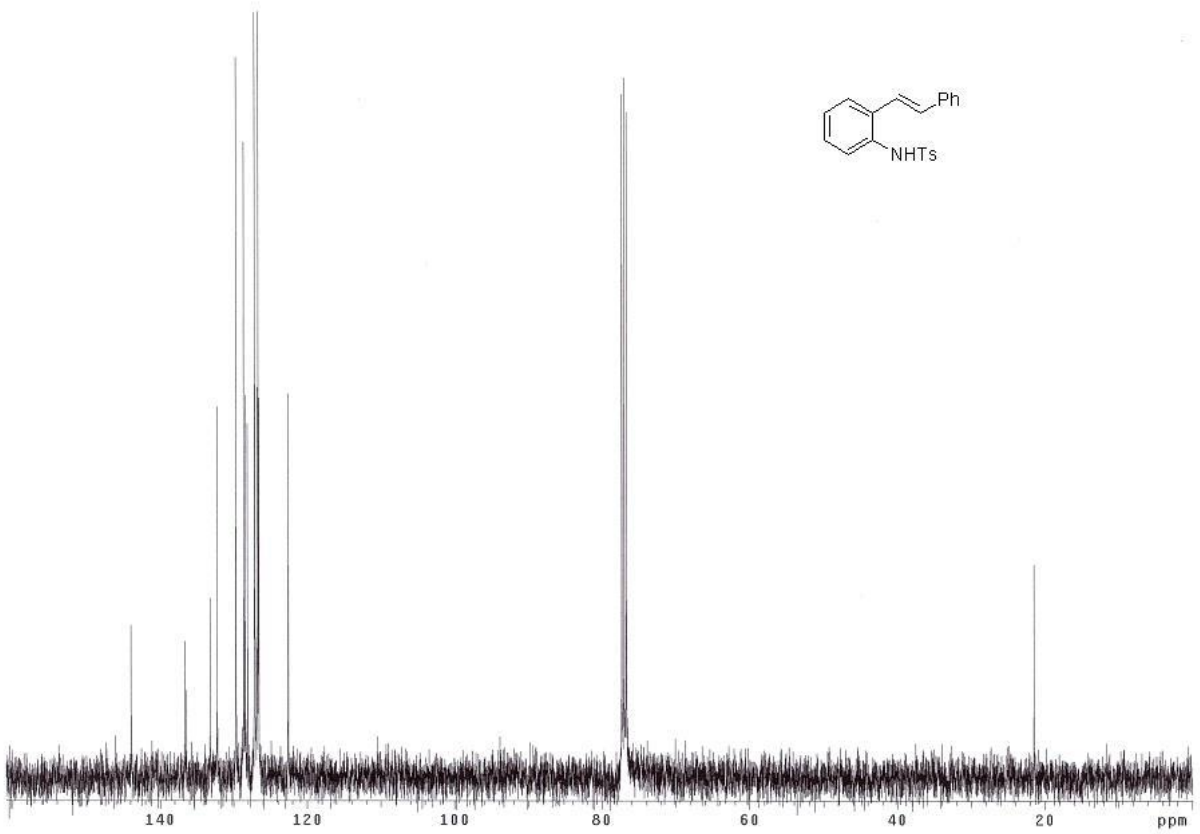
^{1}H NMR Spectrum of Compound *N*-H-**1** ($CDCl_3$, 400 MHz)



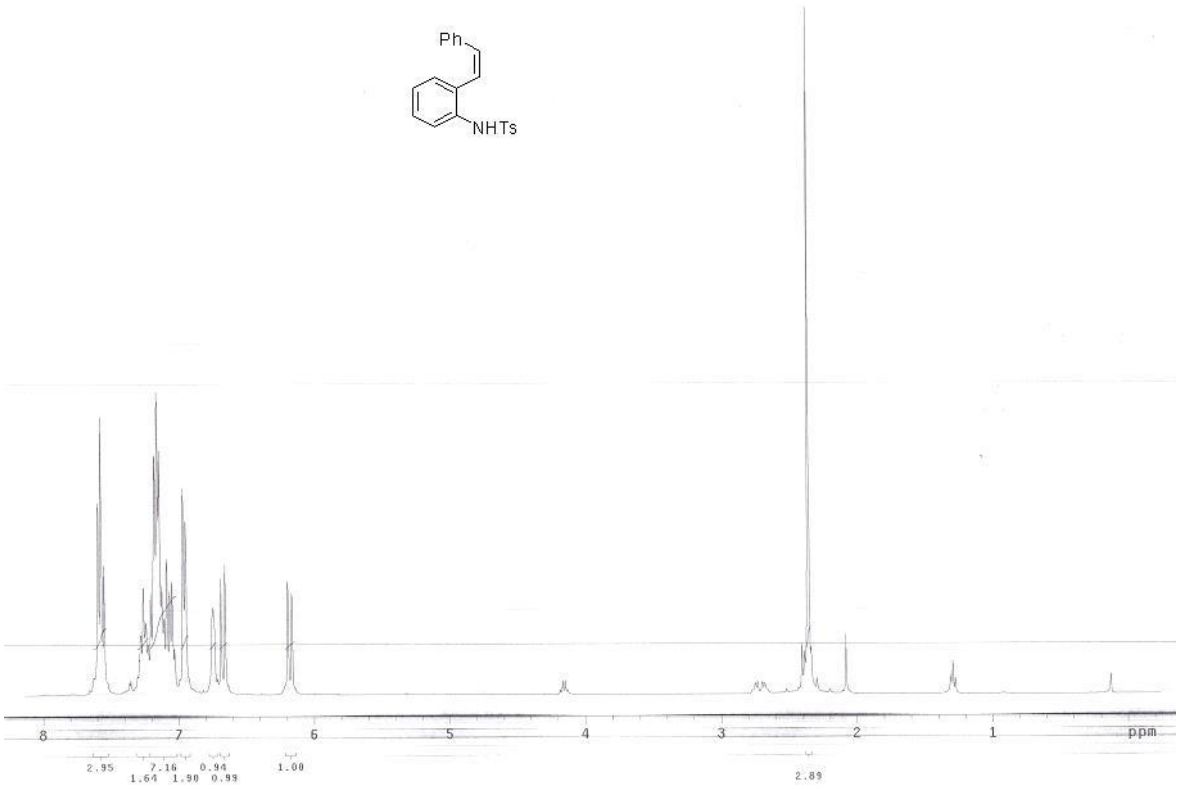
^{13}C NMR Spectrum of Compound *N*-H-**1** ($CDCl_3$, 100 MHz)



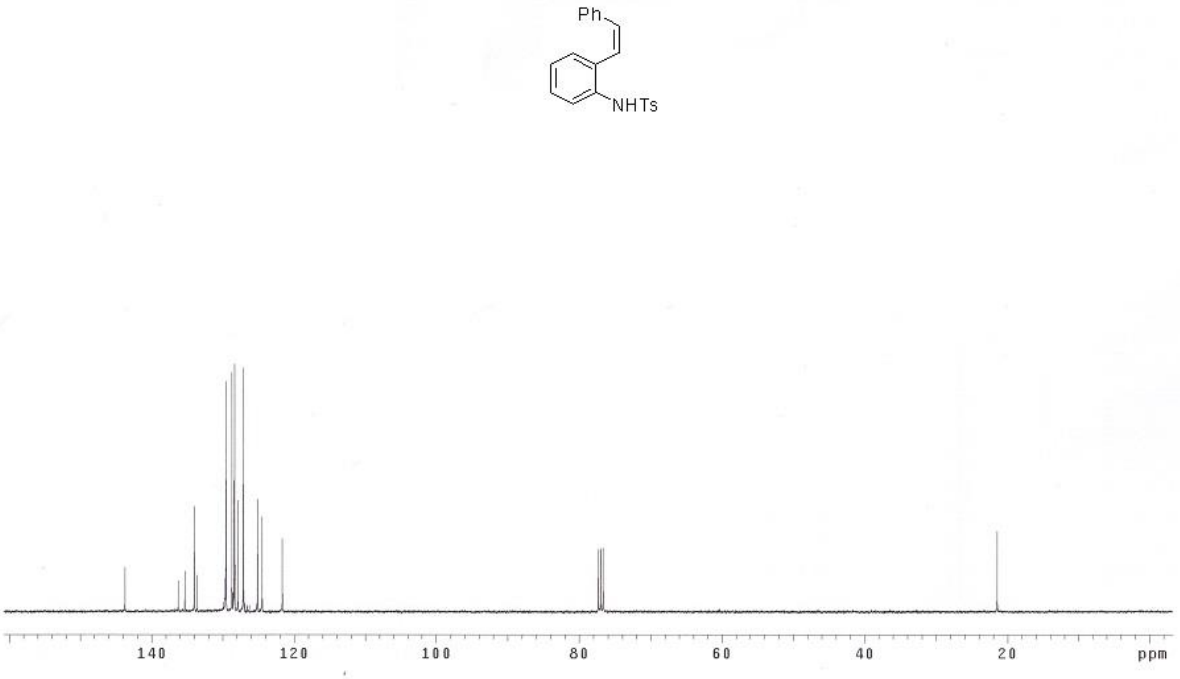
^{1}H NMR Spectrum of Compound **1a** ($CDCl_3$, 400 MHz)



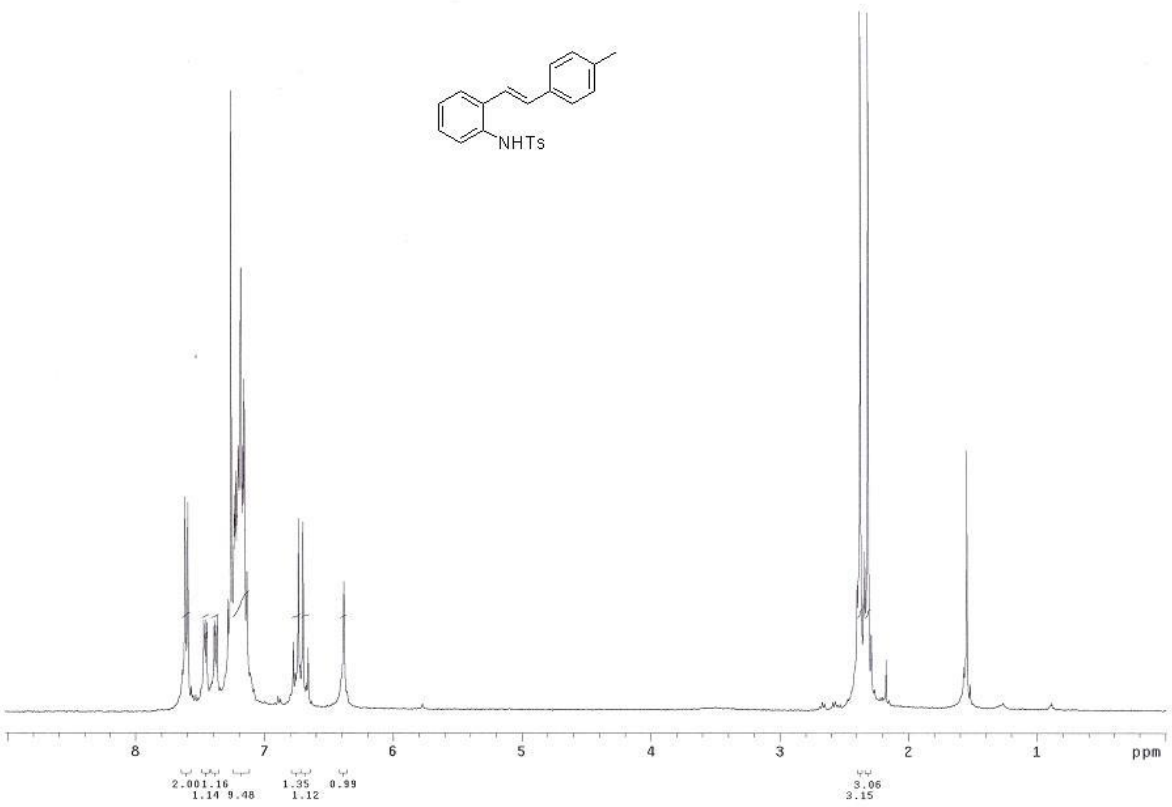
^{13}C NMR Spectrum of Compound **1a** ($CDCl_3$, 100 MHz)



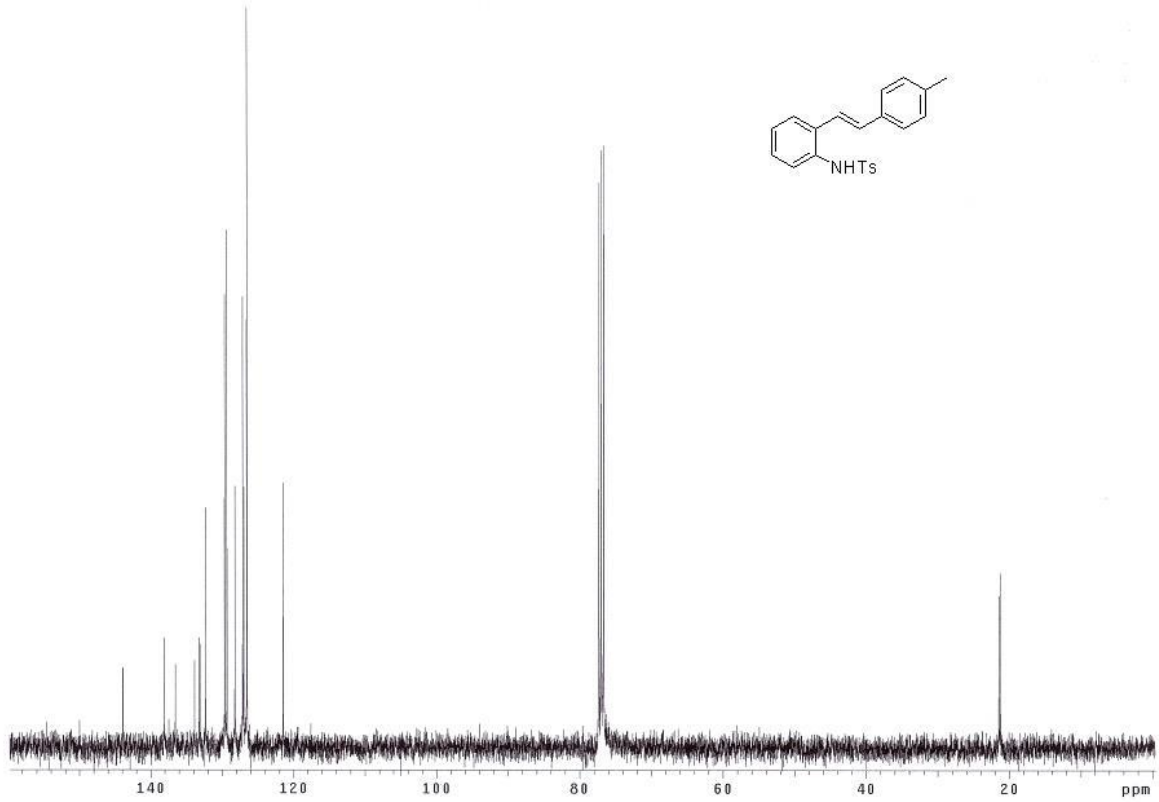
^{1}H NMR Spectrum of Compound (*Z*)-**1a** ($CDCl_3$, 400 MHz)



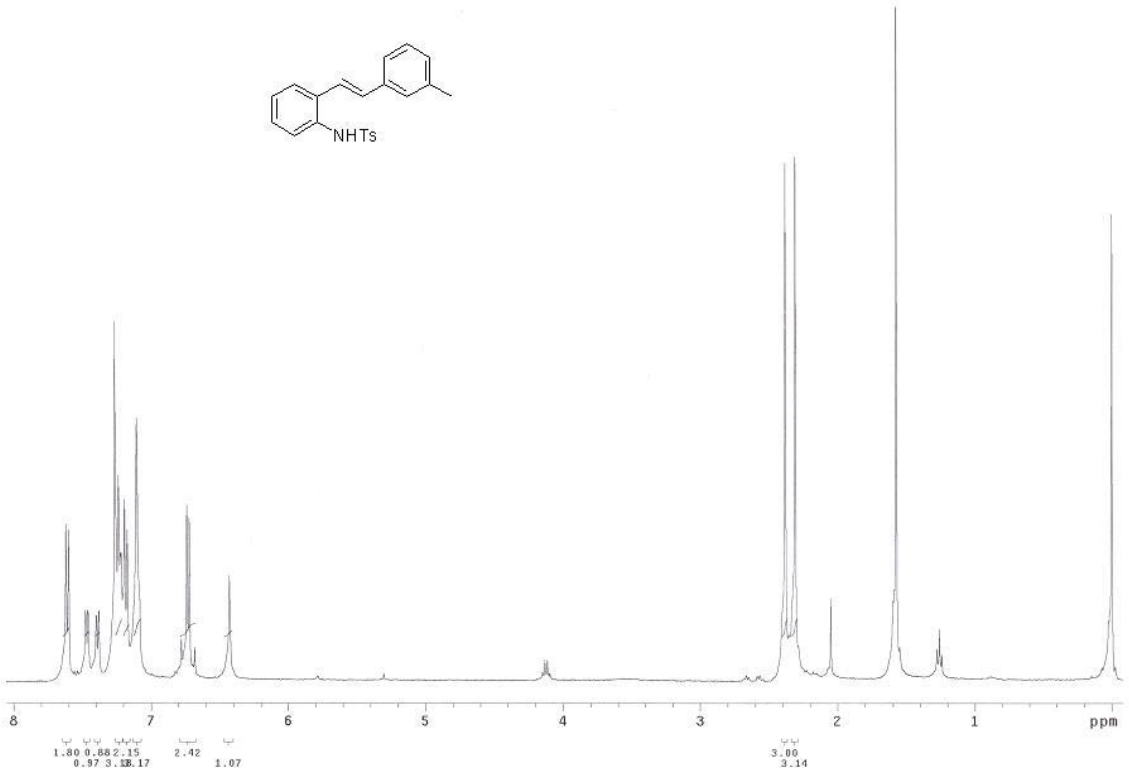
^{13}C NMR Spectrum of Compound (*Z*)-**1a** ($CDCl_3$, 100 MHz)



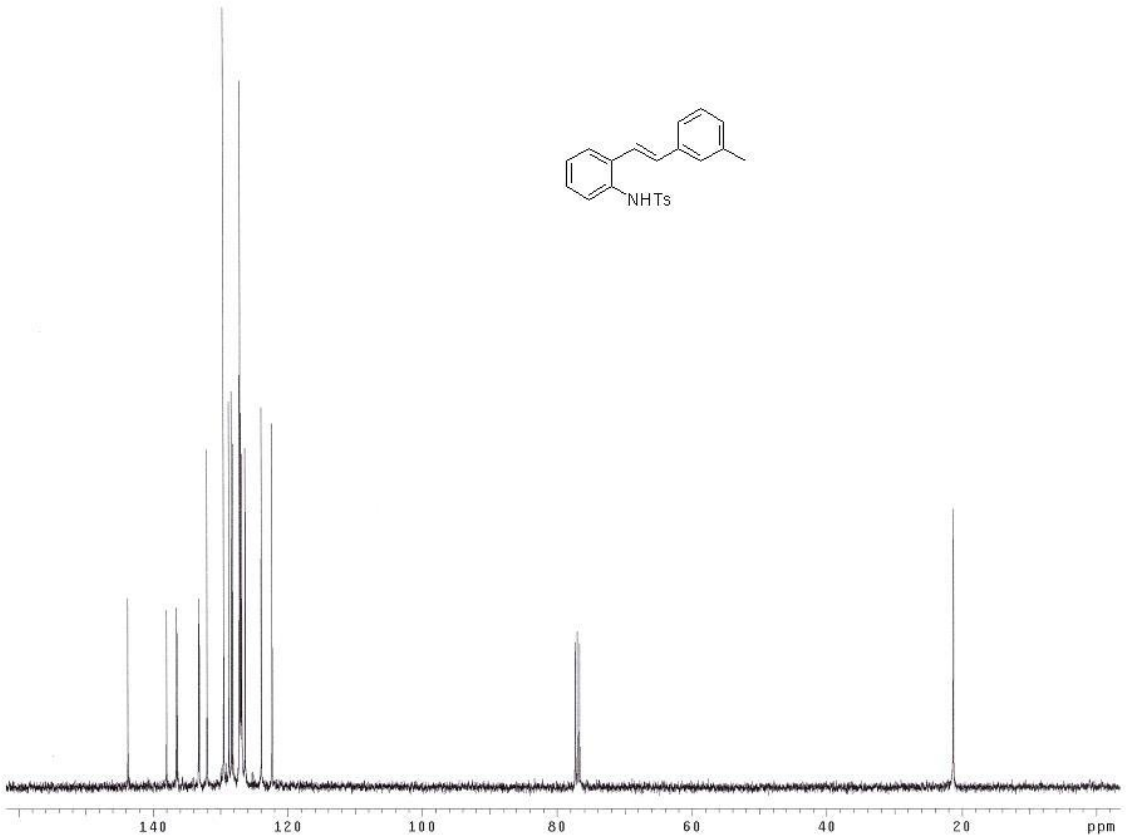
^{1}H NMR Spectrum of Compound **1b** ($CDCl_3$, 400 MHz)



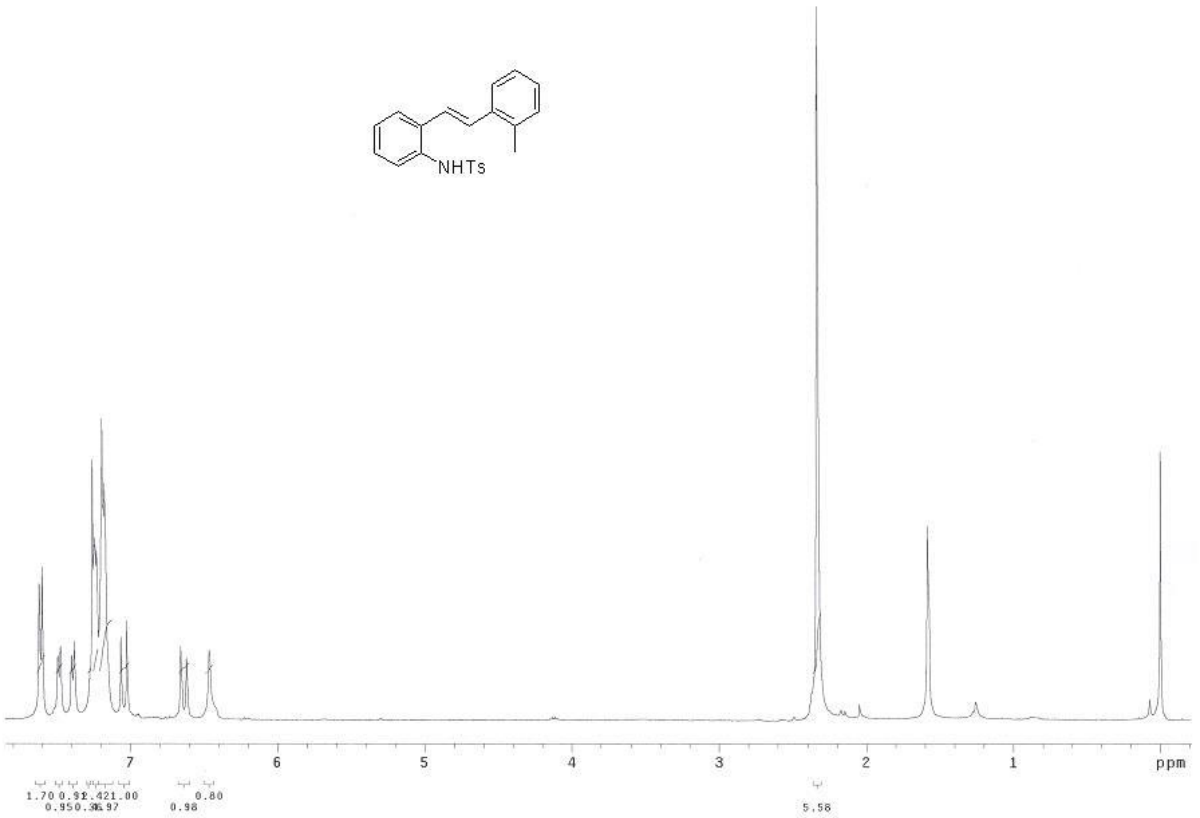
^{13}C NMR Spectrum of Compound **1b** ($CDCl_3$, 100 MHz)



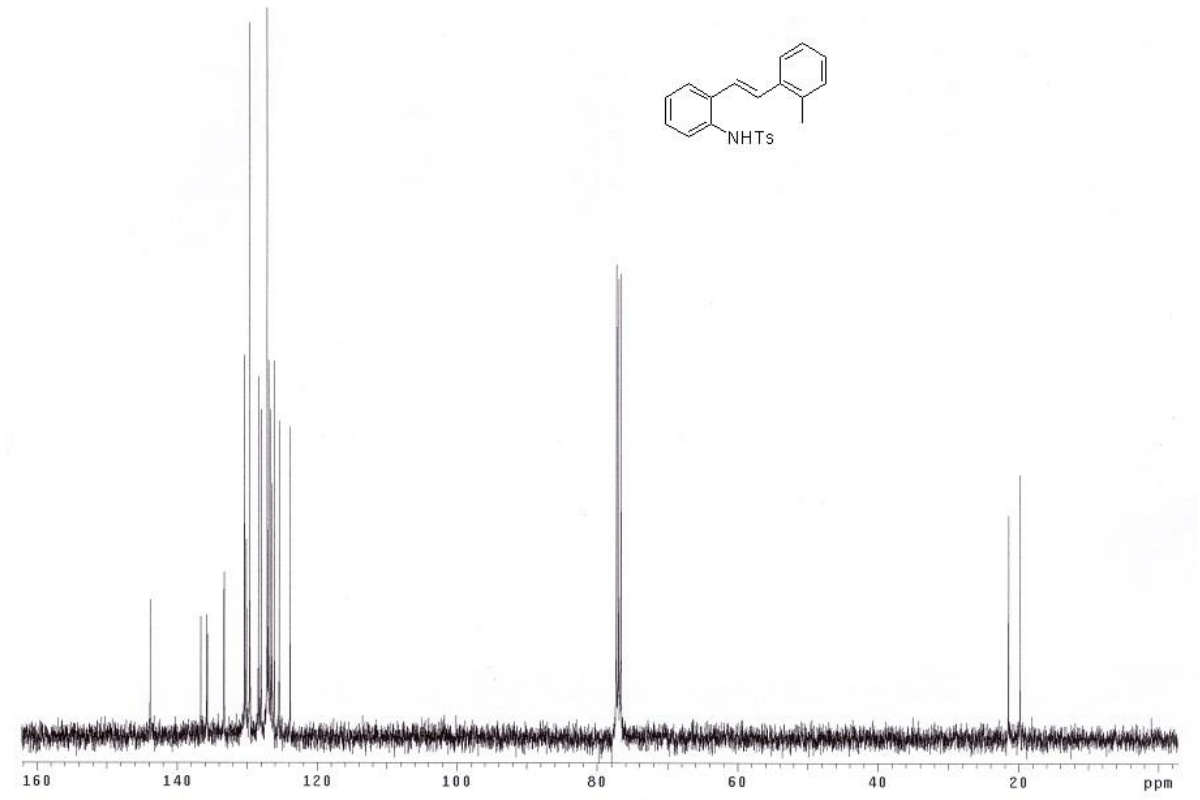
^{1}H NMR Spectrum of Compound **1c** ($CDCl_3$, 400 MHz)



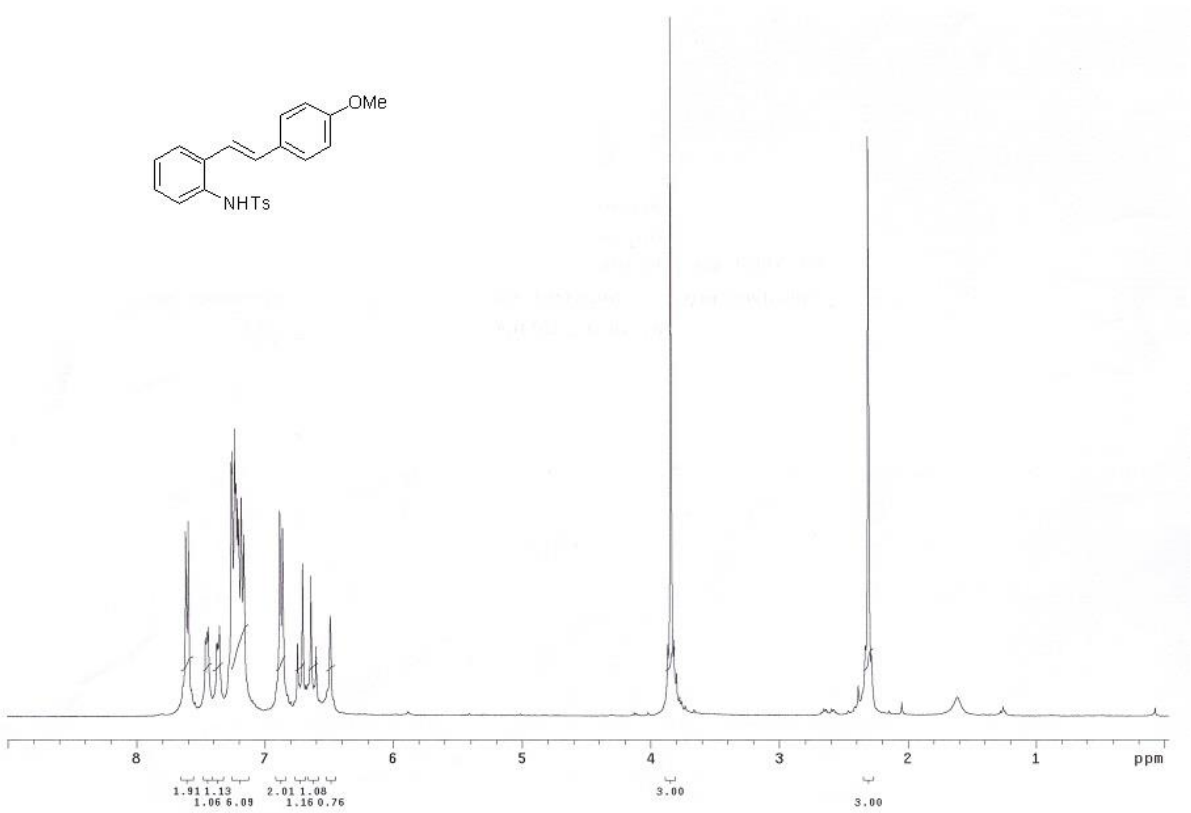
^{13}C NMR Spectrum of Compound **1c** ($CDCl_3$, 100 MHz)



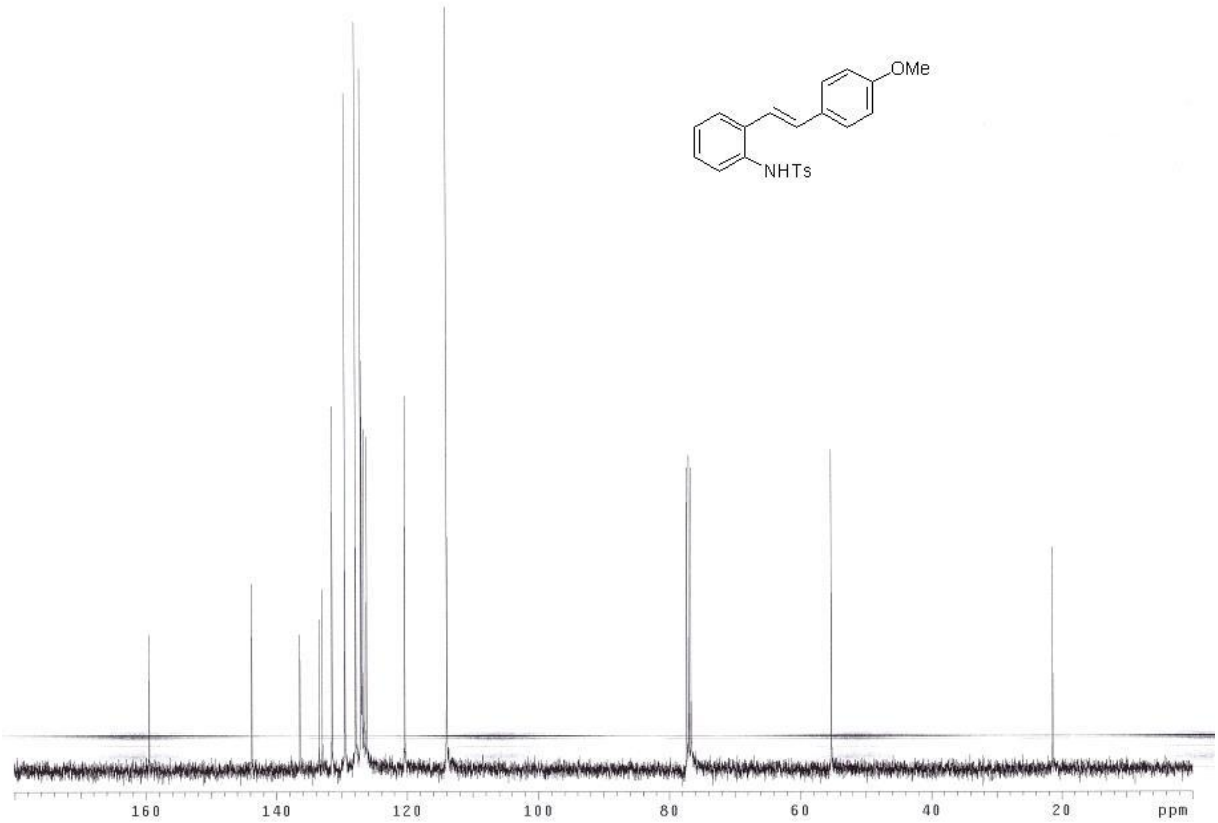
^{1}H NMR Spectrum of Compound **1d** ($CDCl_3$, 400 MHz)



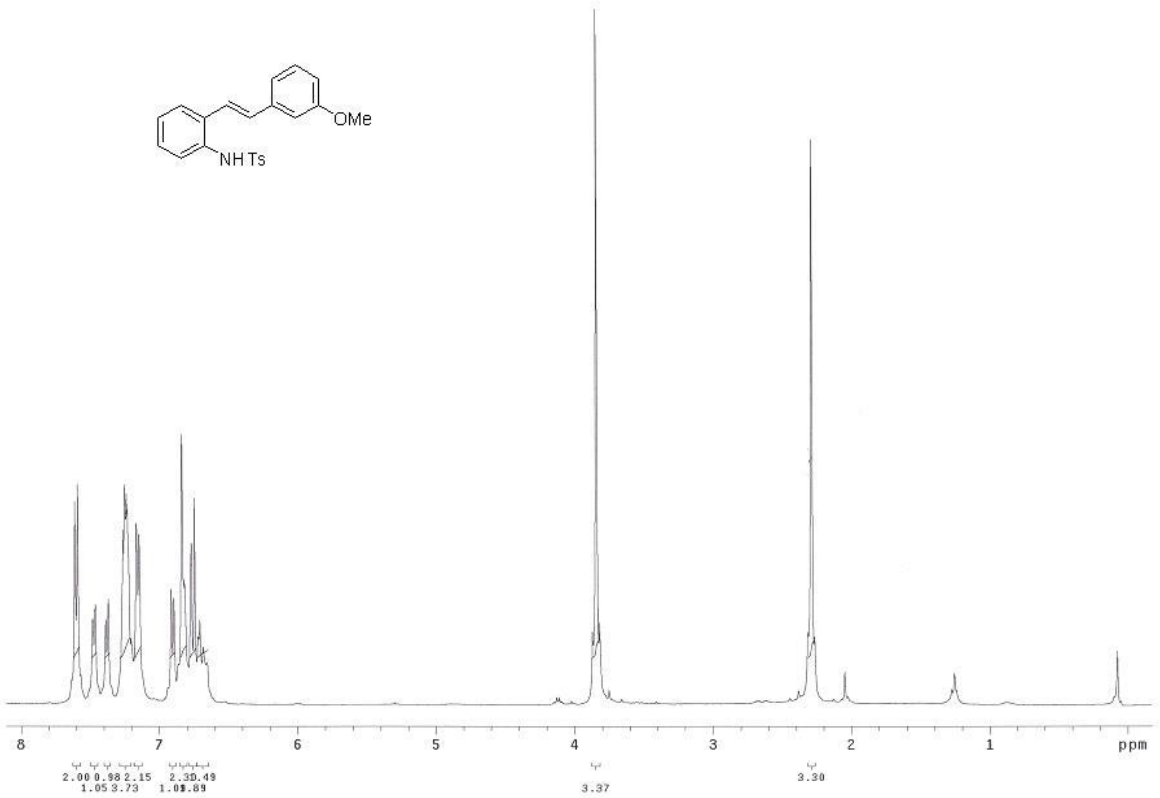
^{13}C NMR Spectrum of Compound **1d** ($CDCl_3$, 100 MHz)



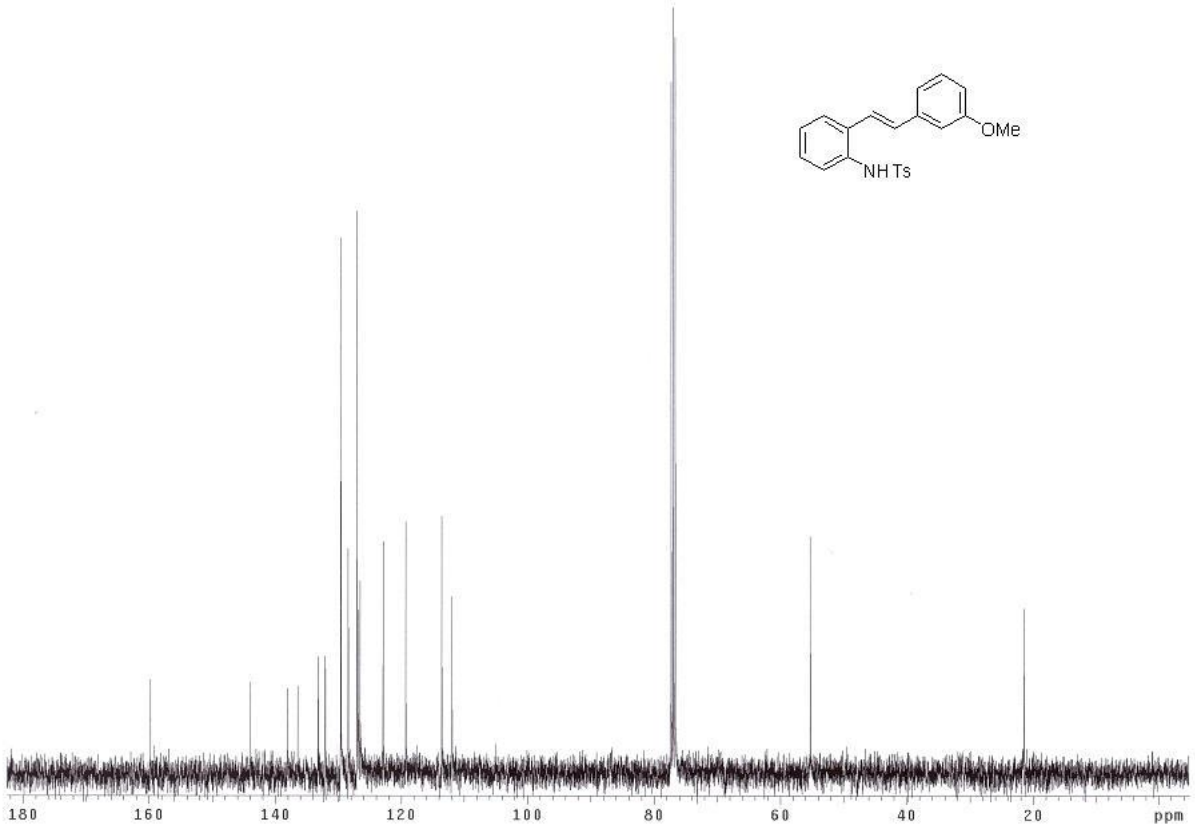
^{1}H NMR Spectrum of Compound **1e** ($CDCl_3$, 400 MHz)



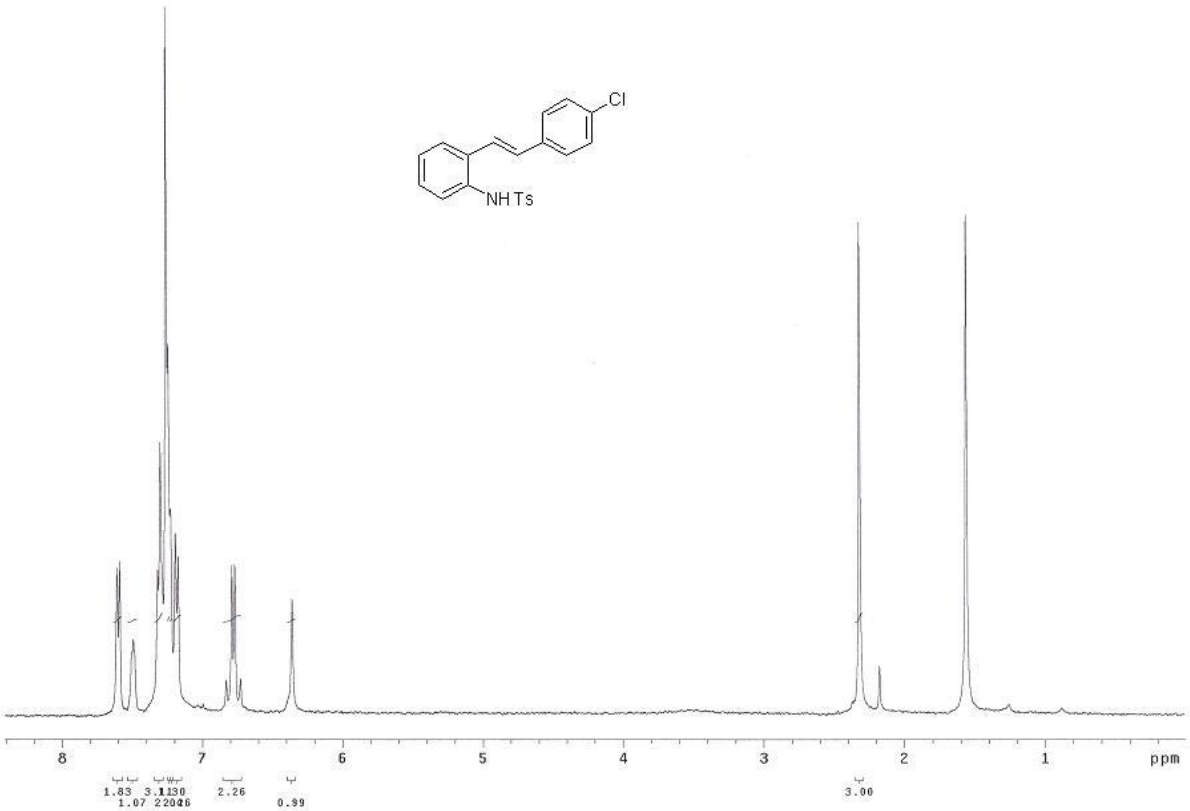
^{13}C NMR Spectrum of Compound **1e** ($CDCl_3$, 100 MHz)



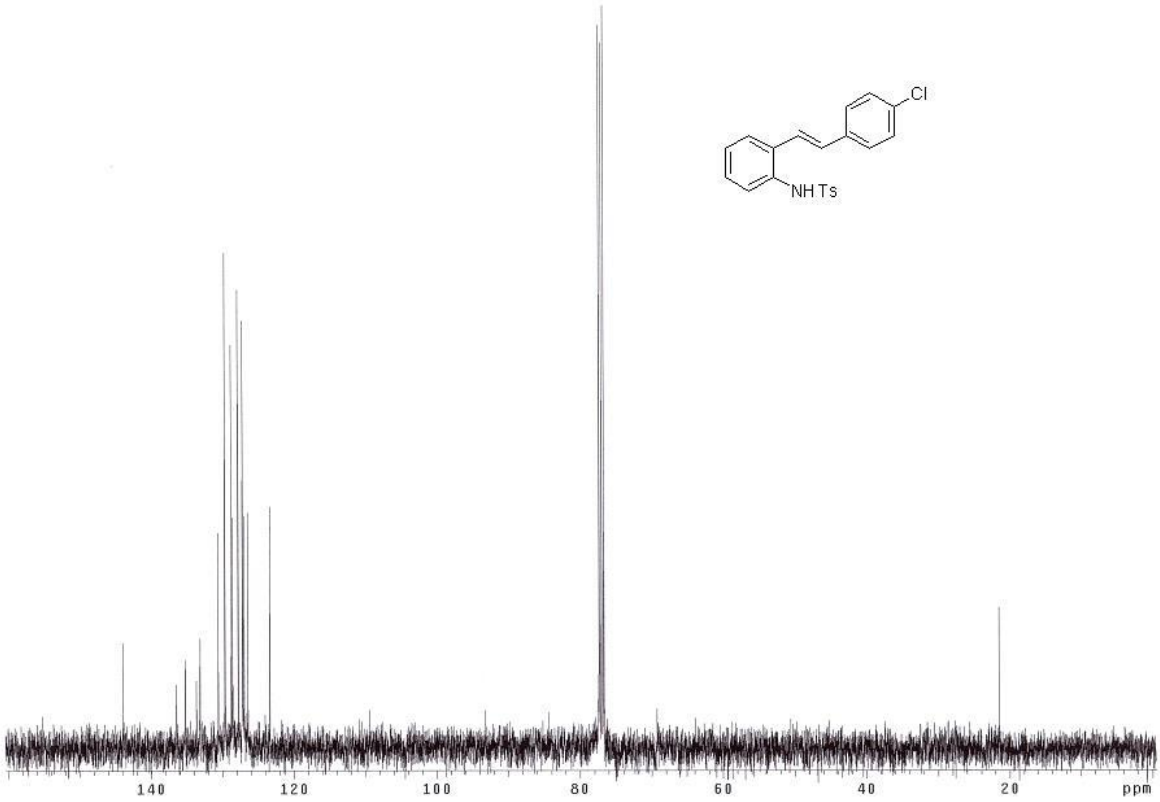
^{1}H NMR Spectrum of Compound **1f** ($CDCl_3$, 400 MHz)



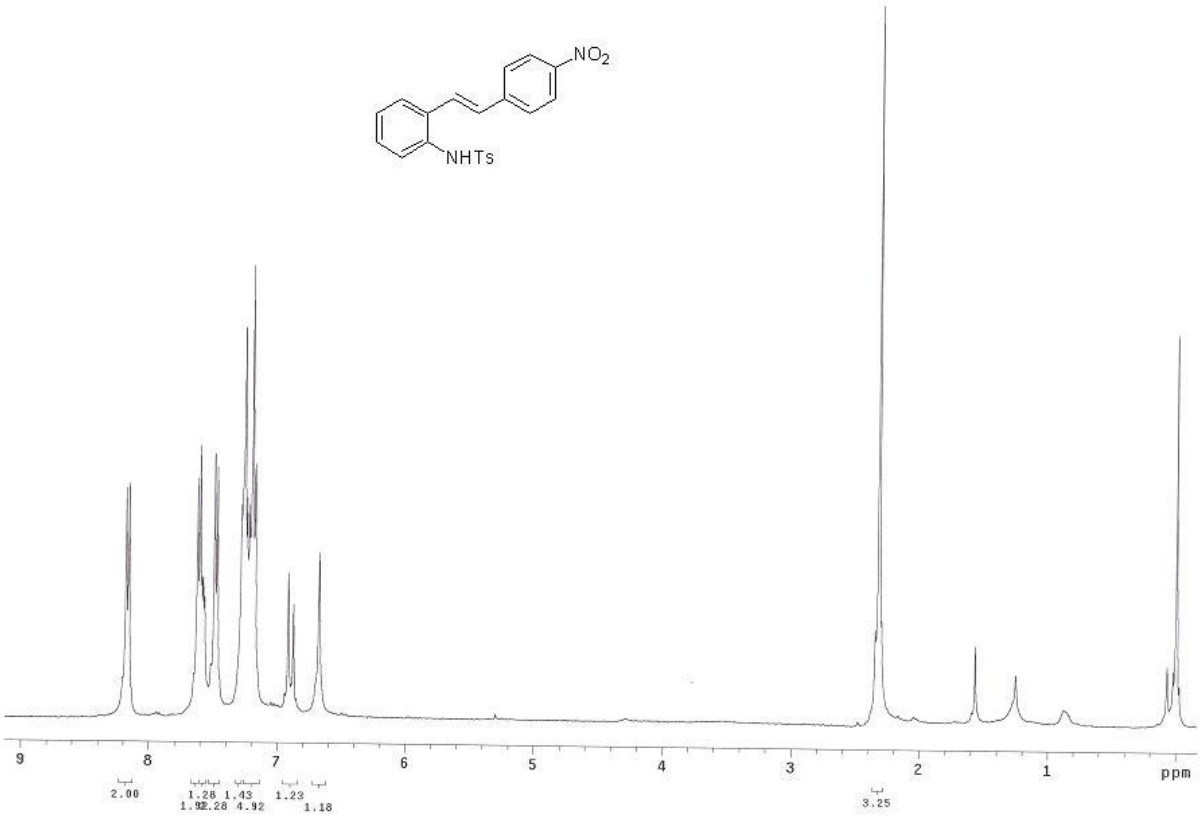
^{13}C NMR Spectrum of Compound **1f** ($CDCl_3$, 100 MHz)



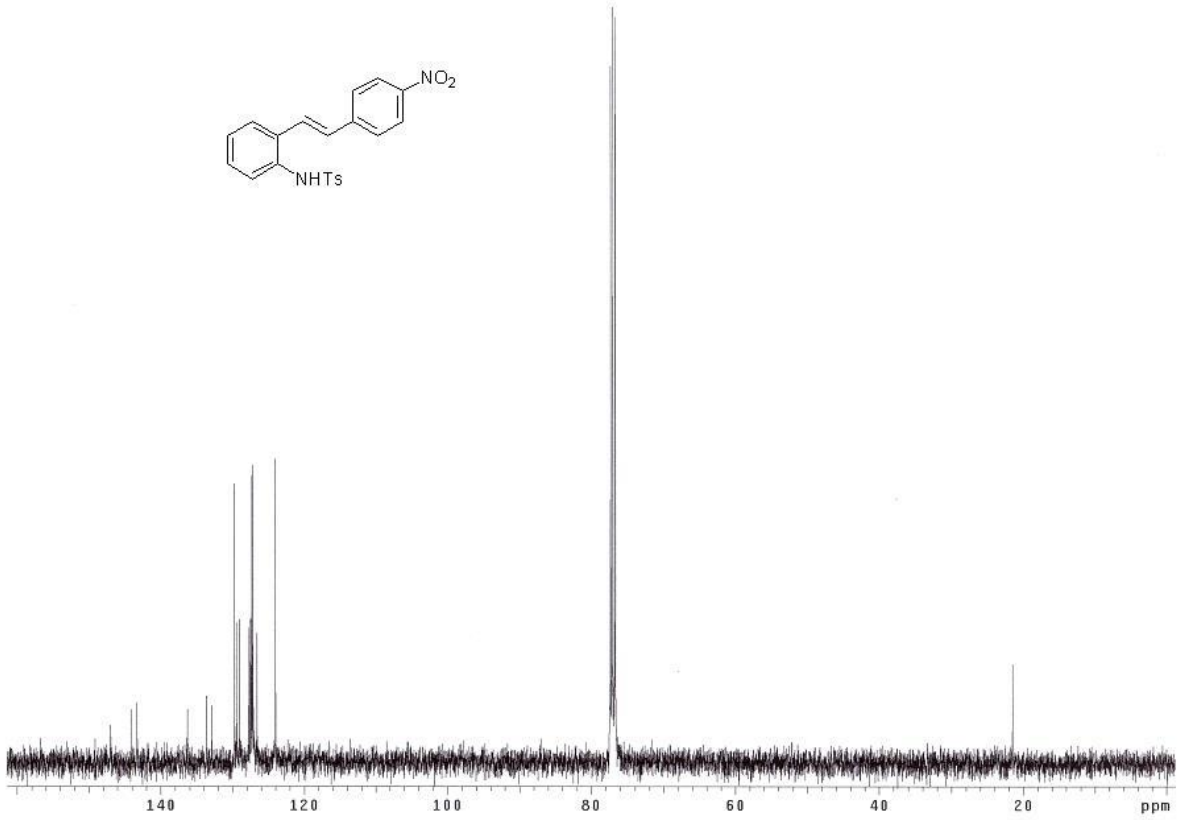
^{1}H NMR Spectrum of Compound **1g** ($CDCl_3$, 400 MHz)



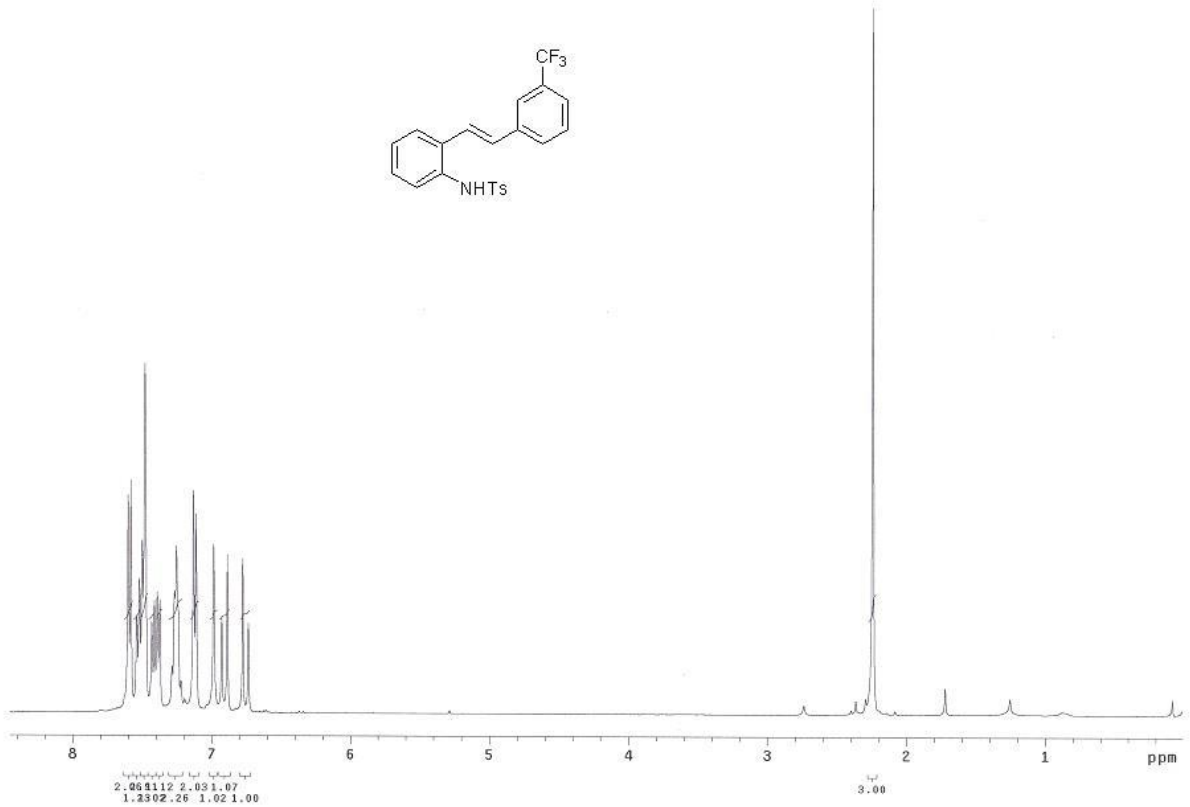
^{13}C NMR Spectrum of Compound **1g** ($CDCl_3$, 100 MHz)



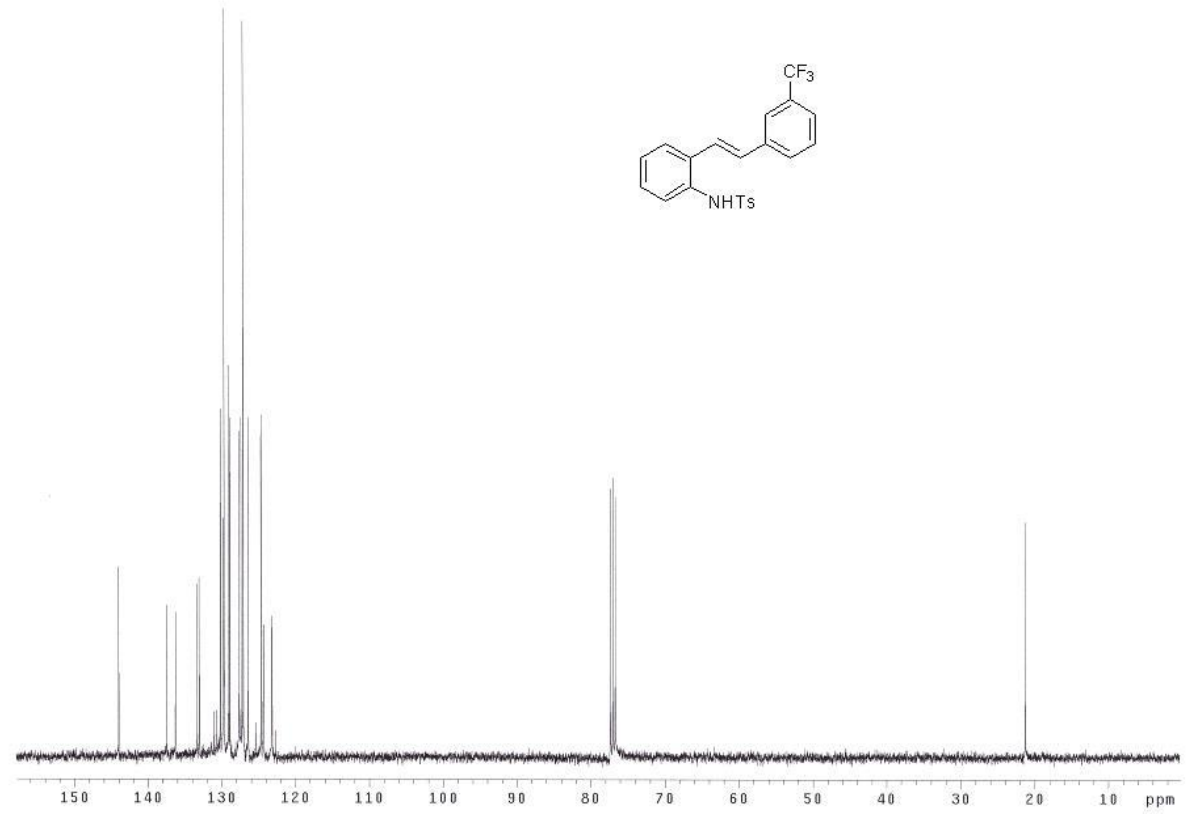
^{1}H NMR Spectrum of Compound **1h** ($CDCl_3$, 400 MHz)



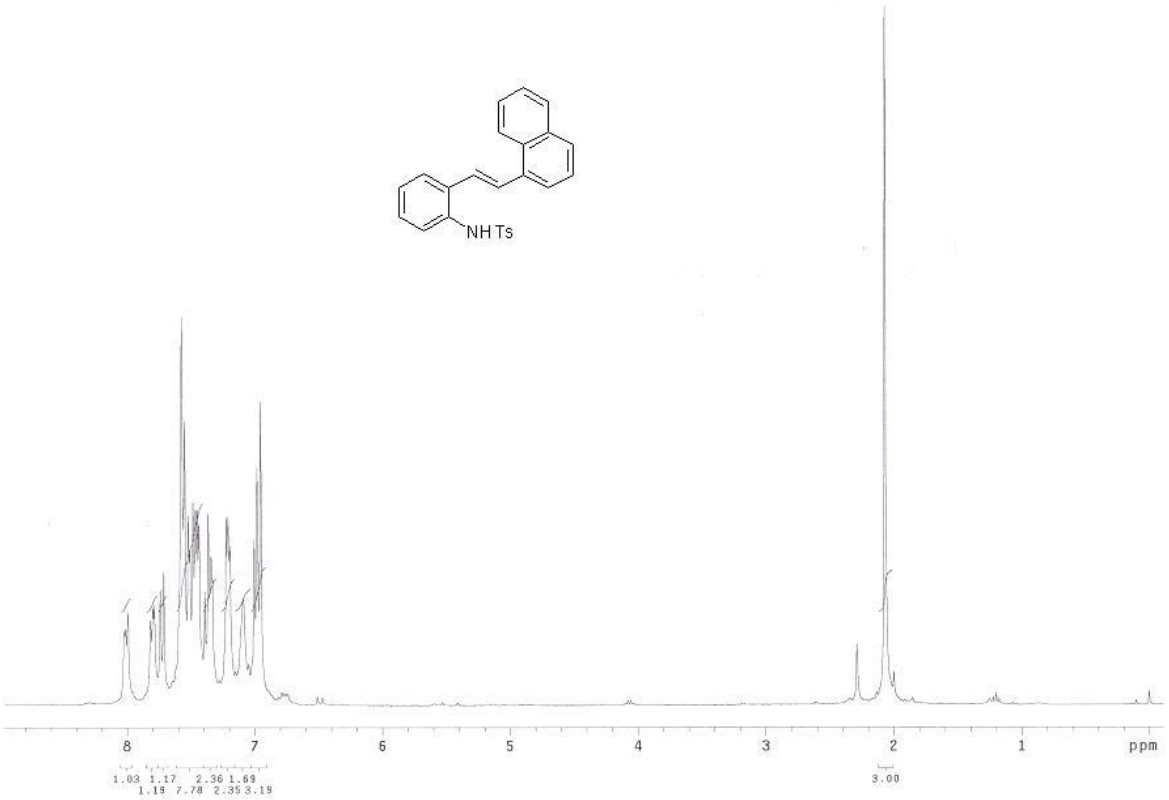
^{13}C NMR Spectrum of Compound **1h** ($CDCl_3$, 100 MHz)



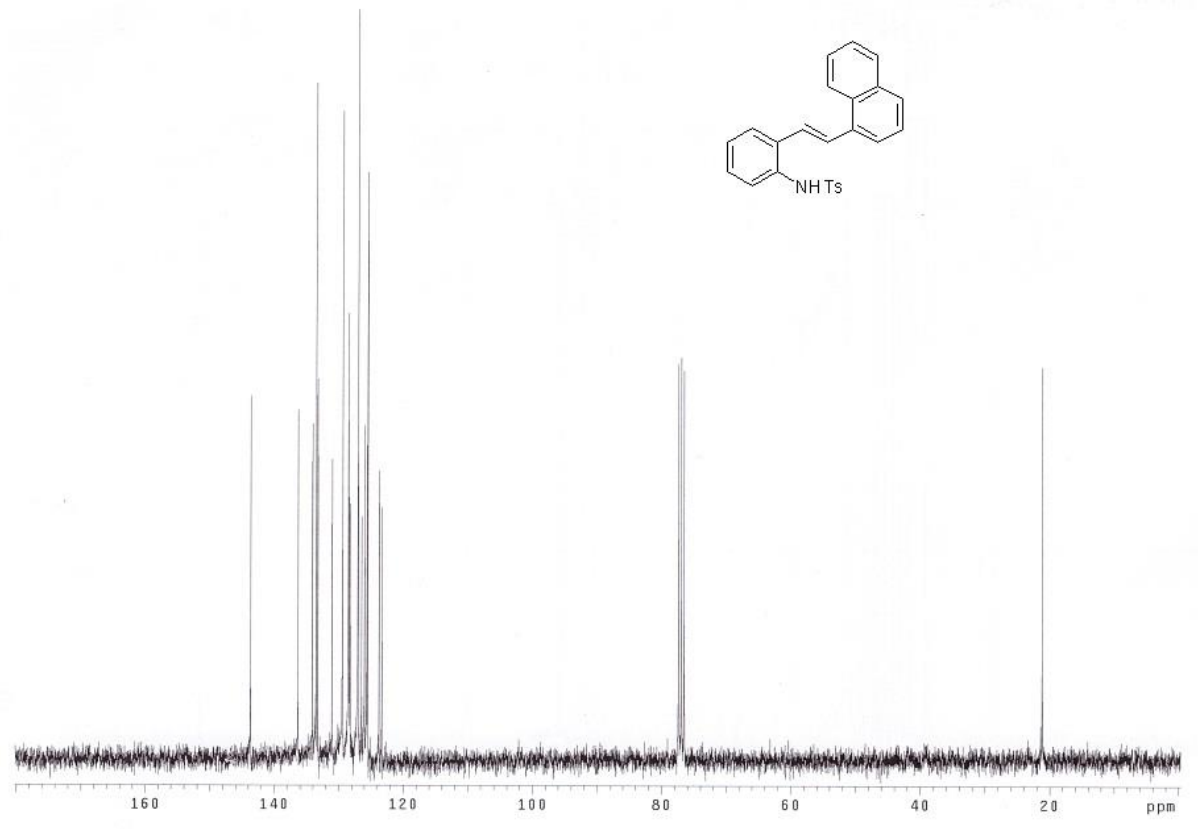
^{1}H NMR Spectrum of Compound **1i** ($CDCl_3$, 400 MHz)



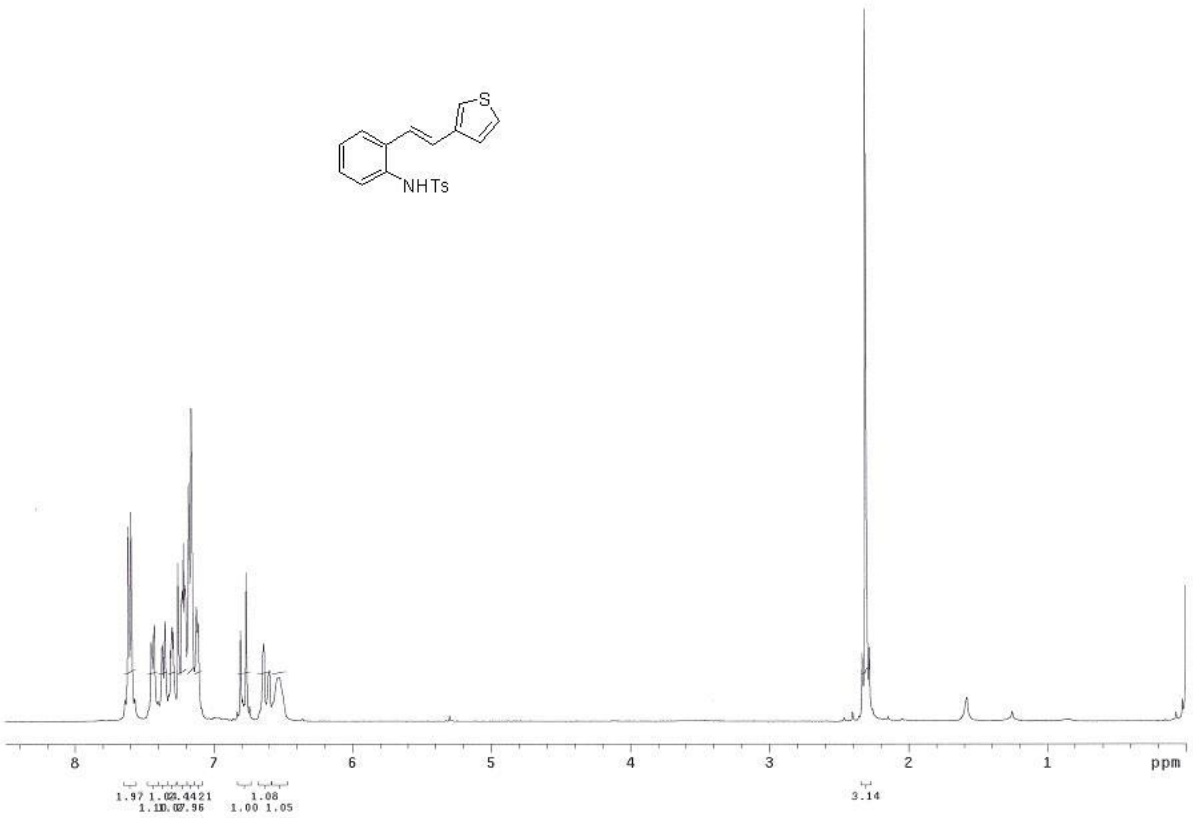
^{13}C NMR Spectrum of Compound **1i** ($CDCl_3$, 100 MHz)



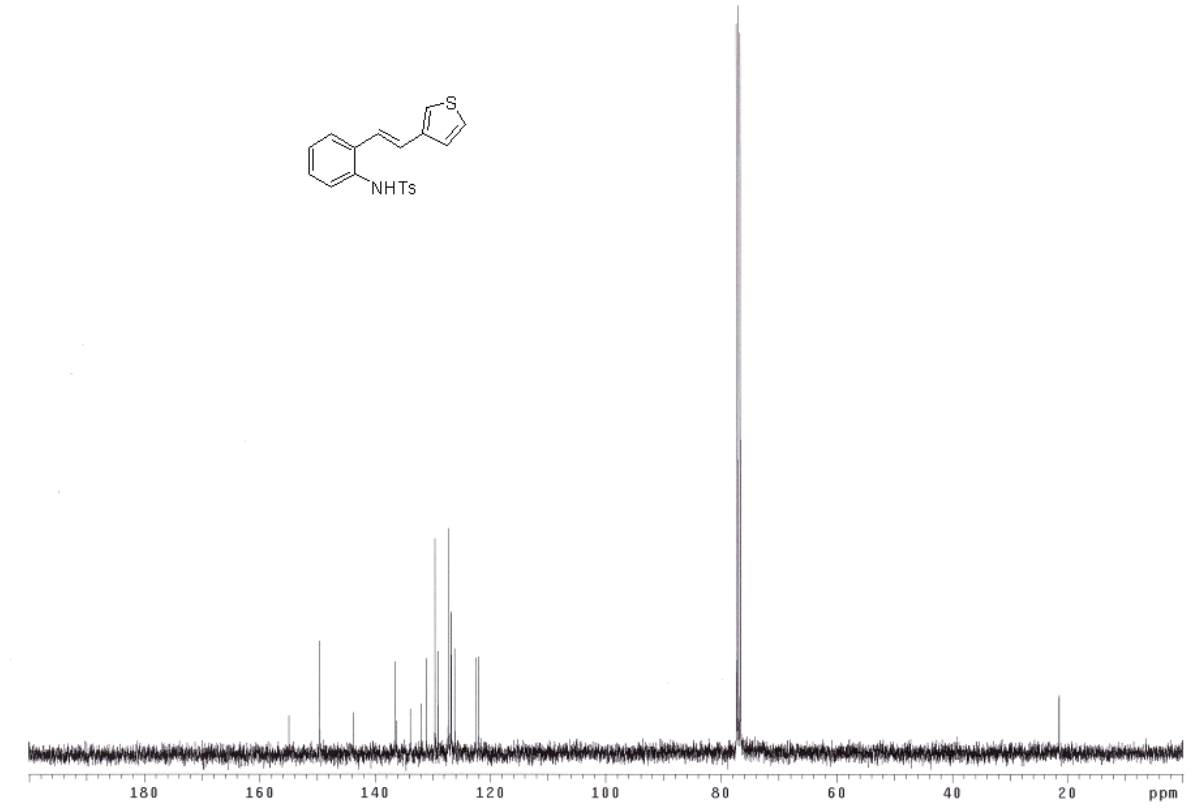
^{1}H NMR Spectrum of Compound **1j** ($CDCl_3$, 300 MHz)



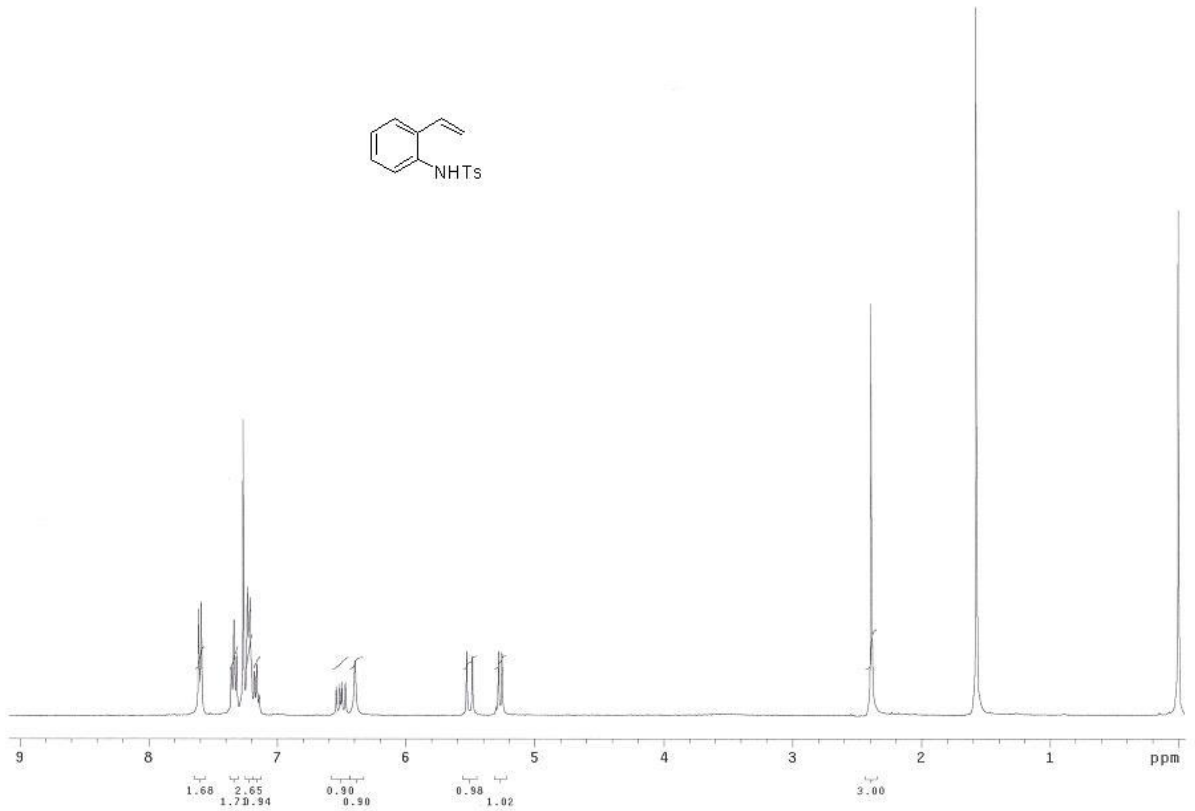
^{13}C NMR Spectrum of Compound **1j** ($CDCl_3$, 75 MHz)



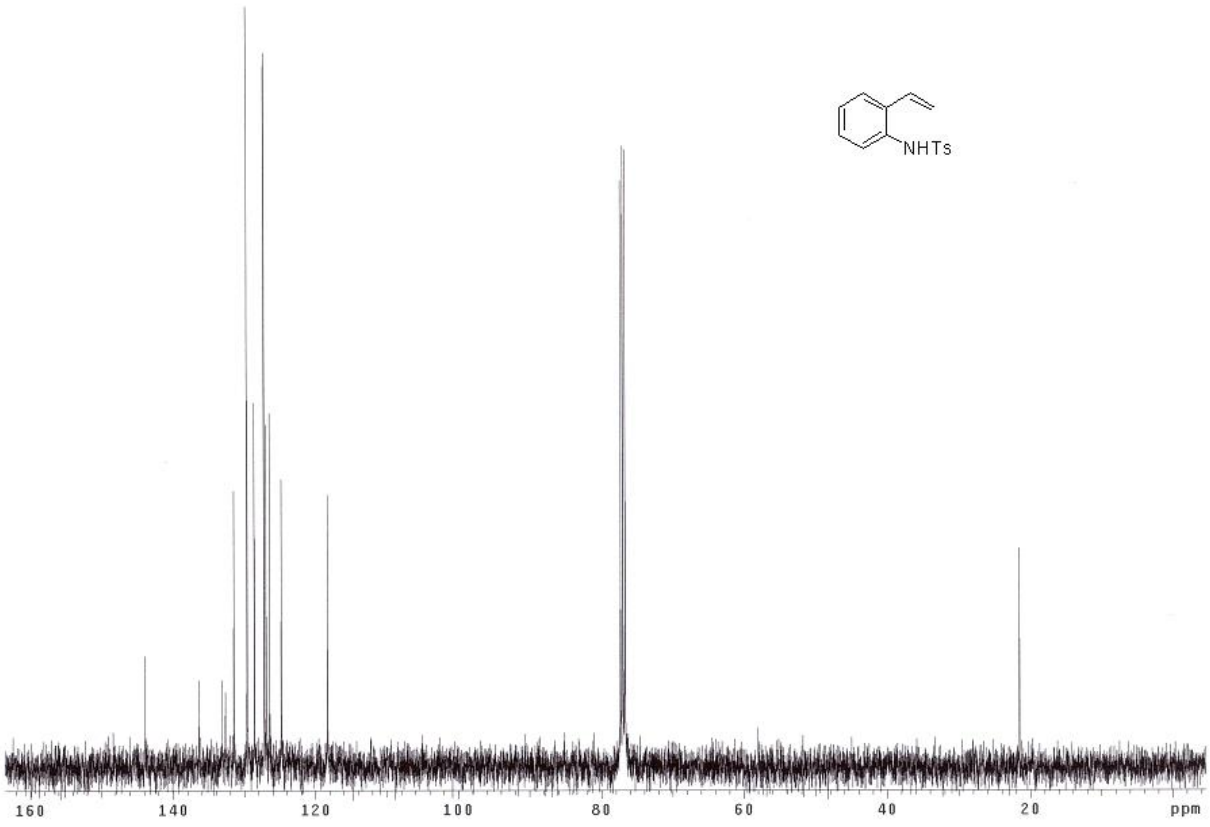
^{1}H NMR Spectrum of Compound **1k** ($CDCl_3$, 400 MHz)



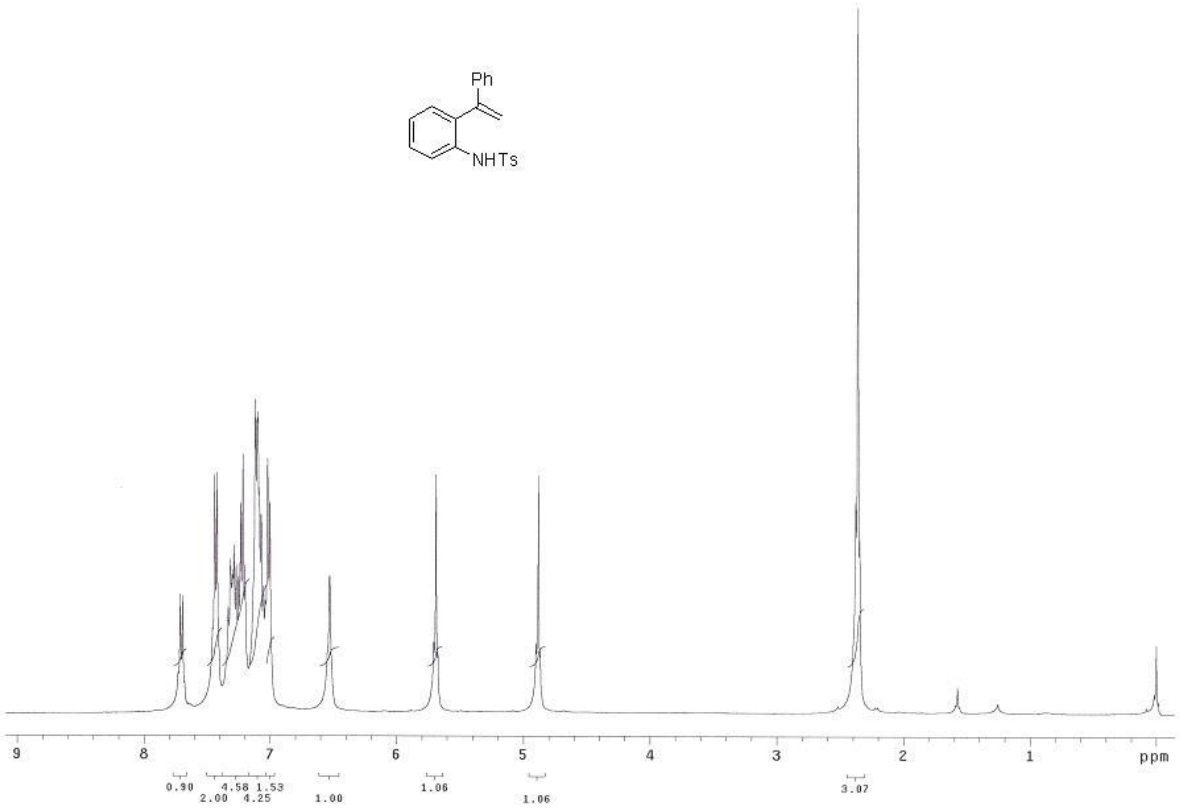
^{13}C NMR Spectrum of Compound **1k** ($CDCl_3$, 100 MHz)



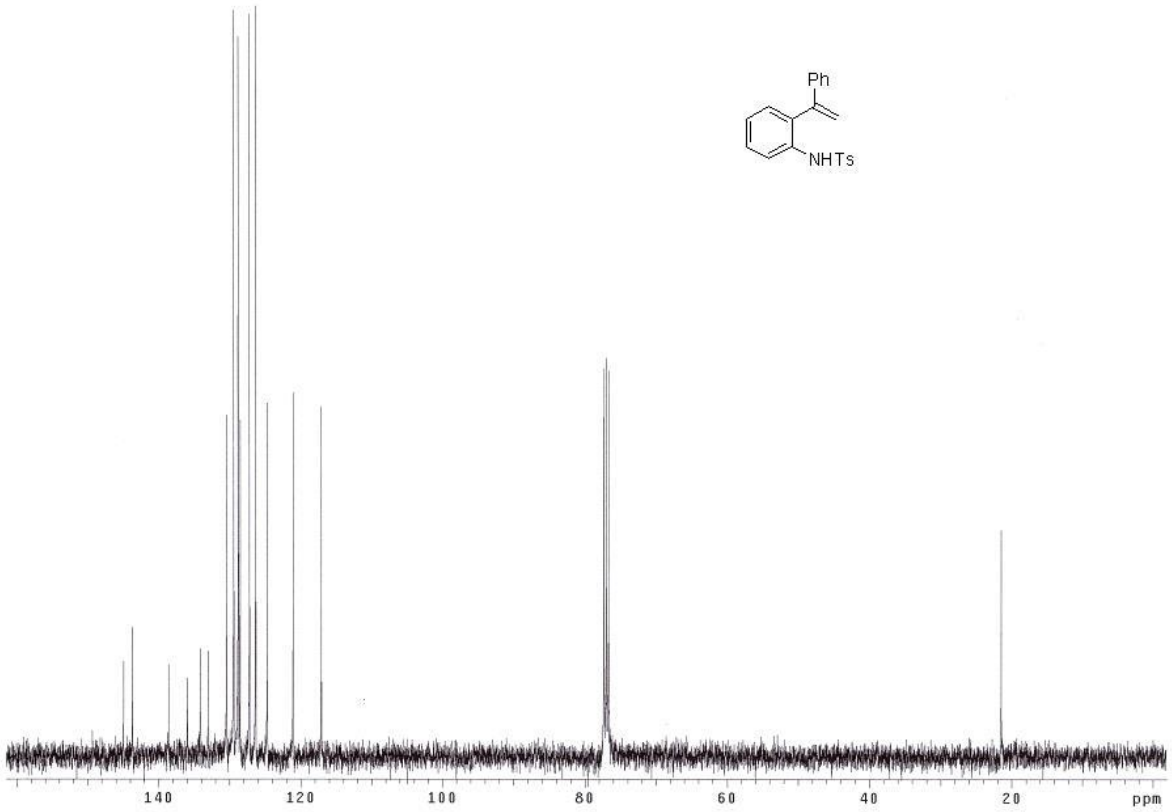
^{1}H NMR Spectrum of Compound **1l** ($CDCl_3$, 400 MHz)



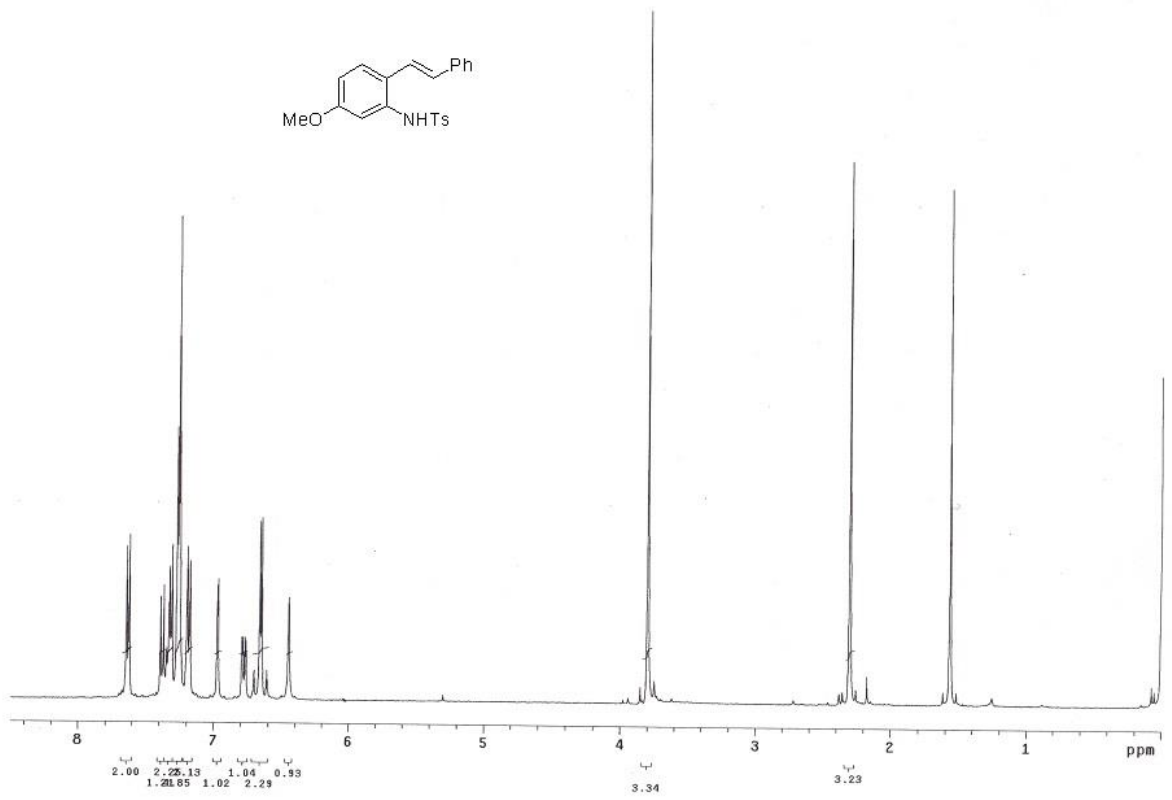
^{13}C NMR Spectrum of Compound **1l** ($CDCl_3$, 100 MHz)



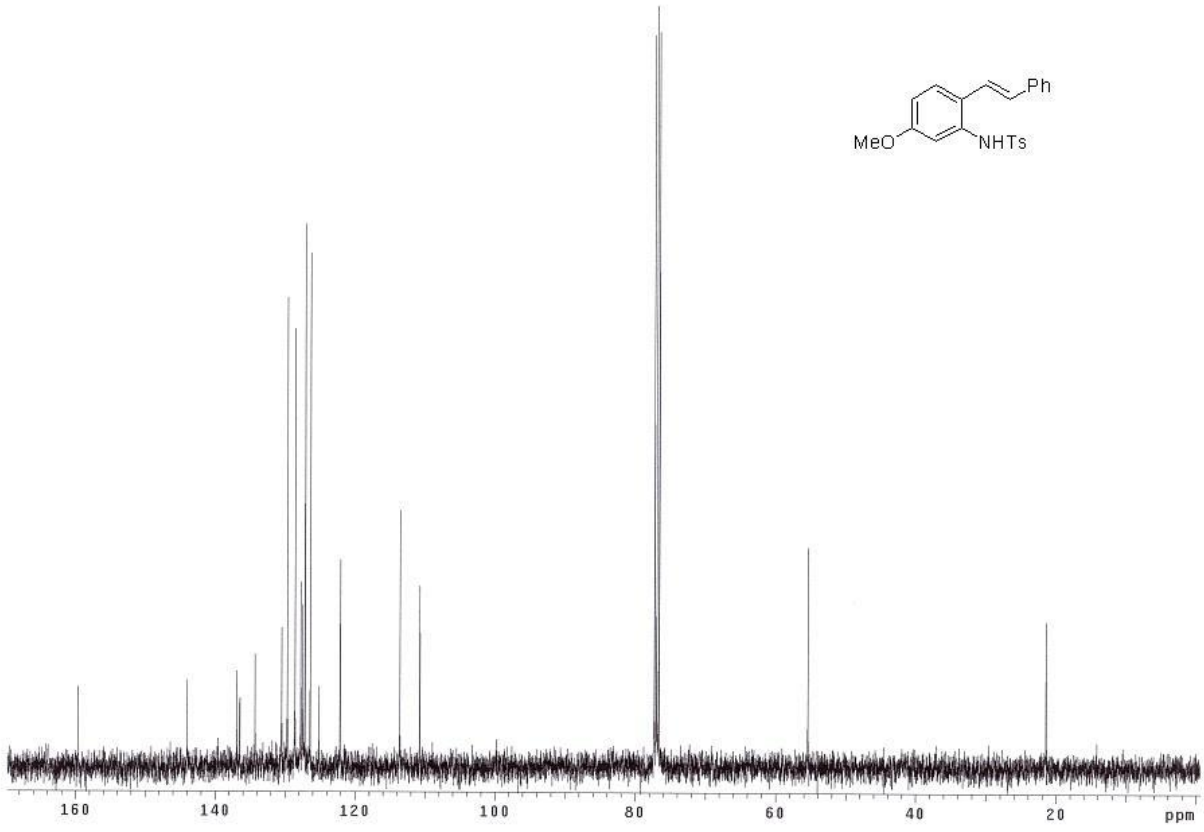
^{1}H NMR Spectrum of Compound **1m** ($CDCl_3$, 400 MHz)



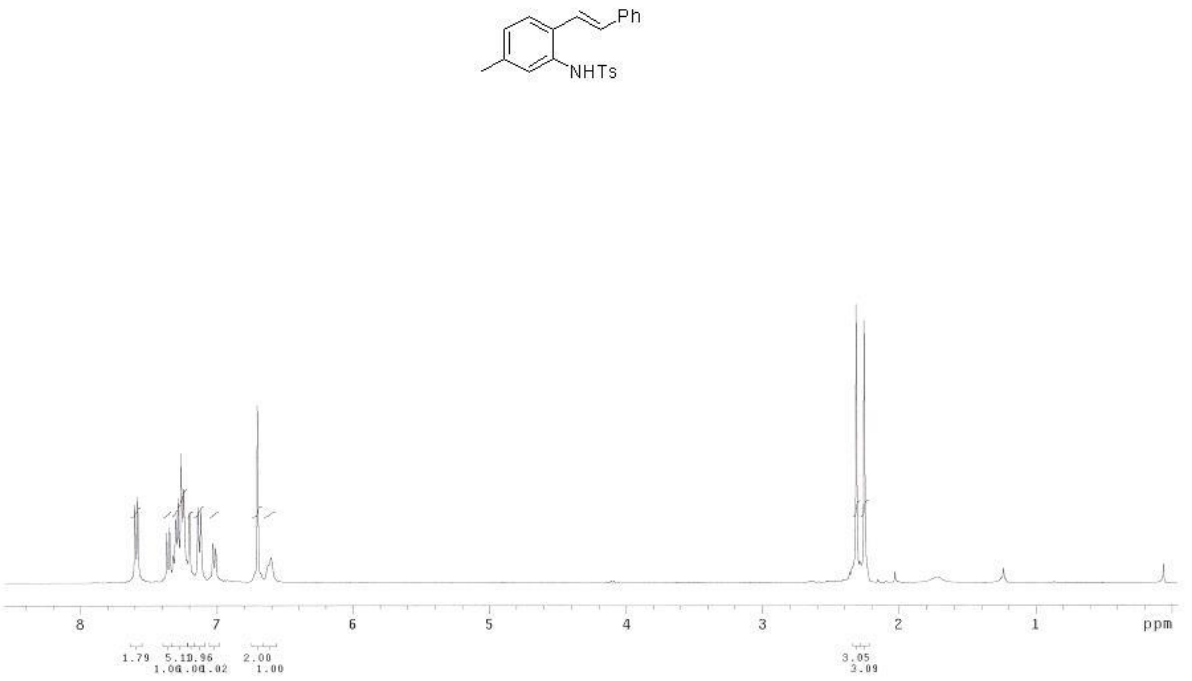
^{13}C NMR Spectrum of Compound **1m** ($CDCl_3$, 100 MHz)



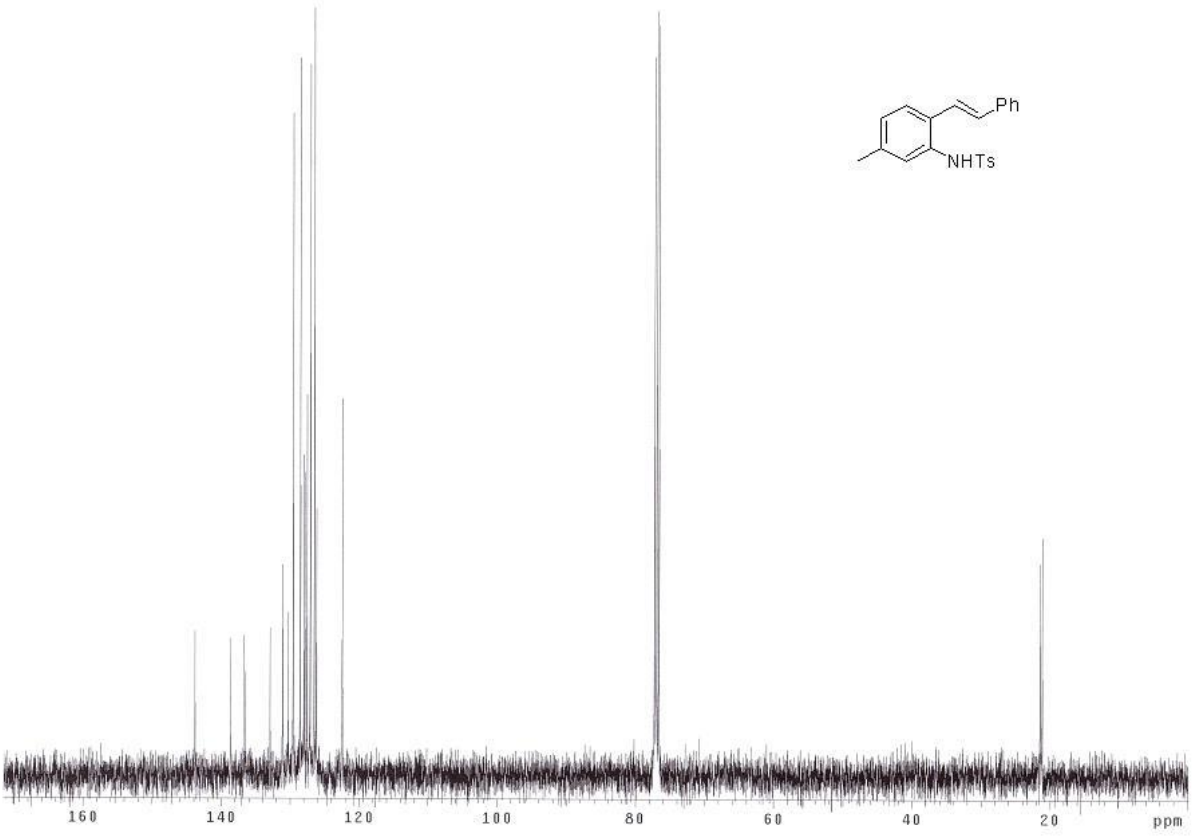
^{1}H NMR Spectrum of Compound **1n** ($CDCl_3$, 400 MHz)



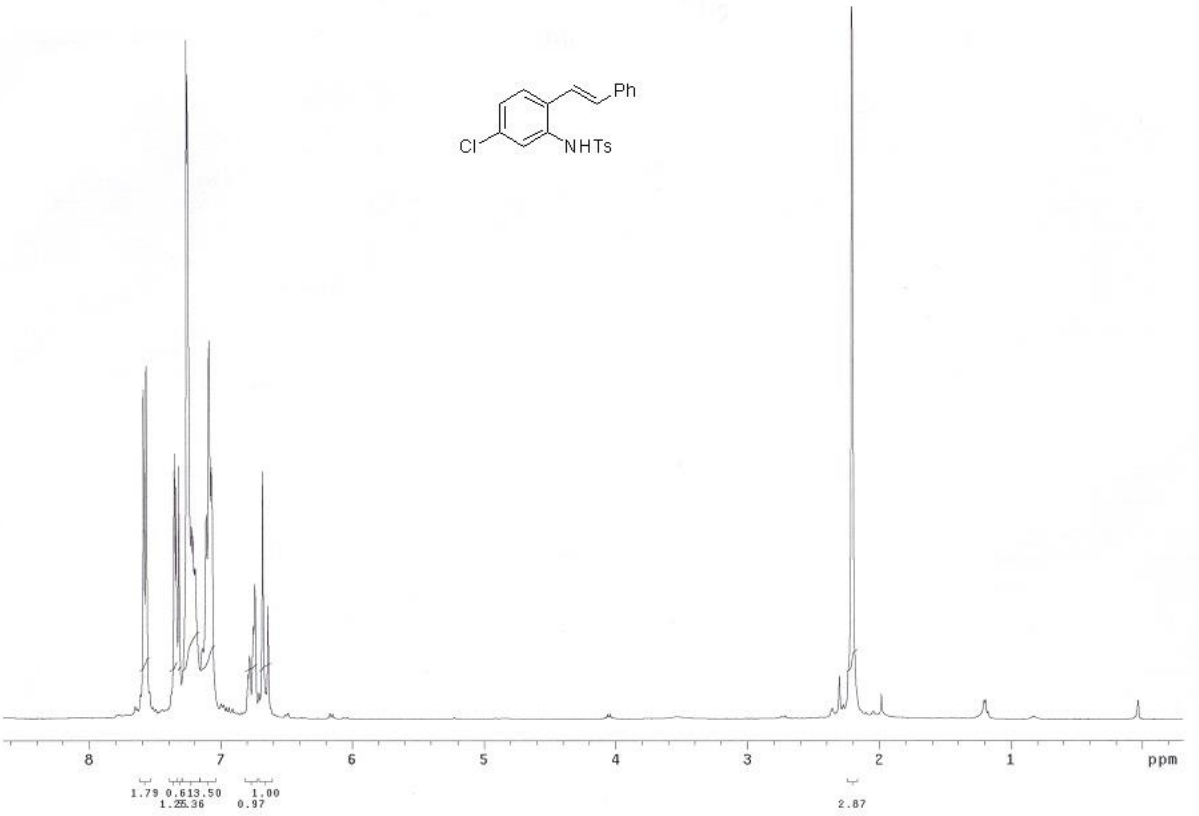
^{13}C NMR Spectrum of Compound **1n** ($CDCl_3$, 100 MHz)



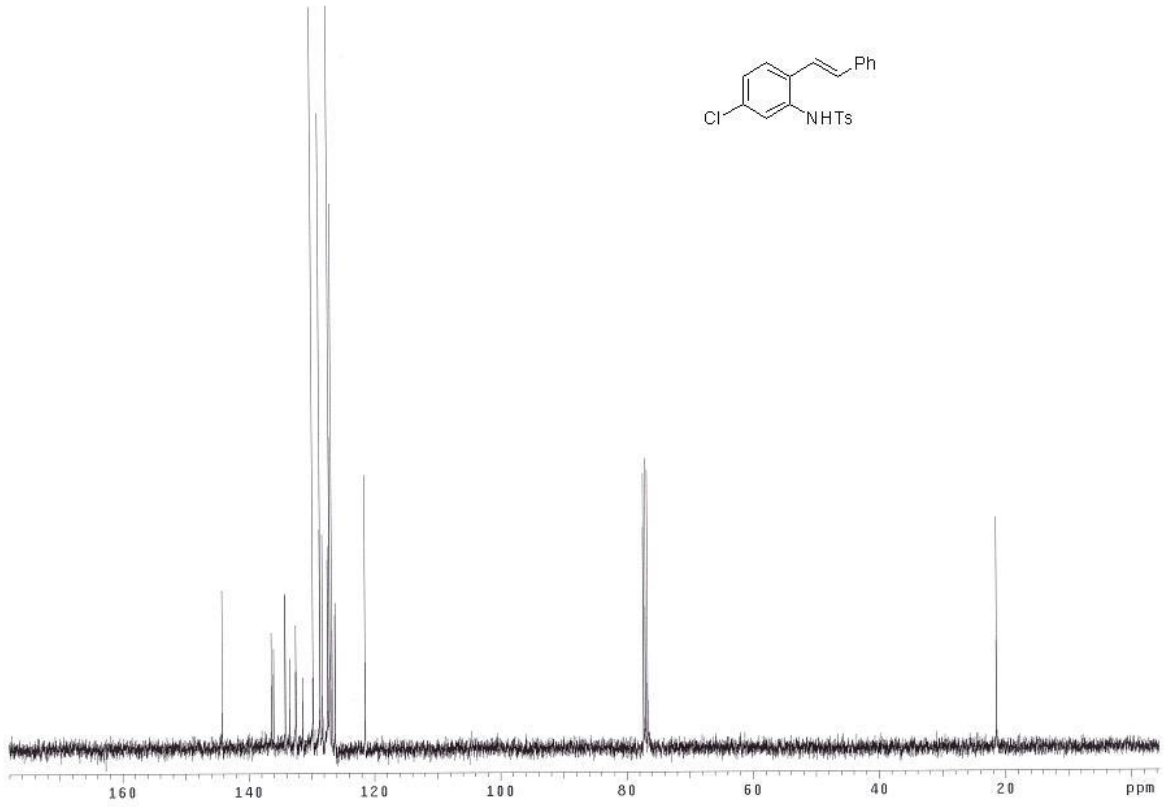
^{1}H NMR Spectrum of Compound **1o** ($CDCl_3$, 400 MHz)



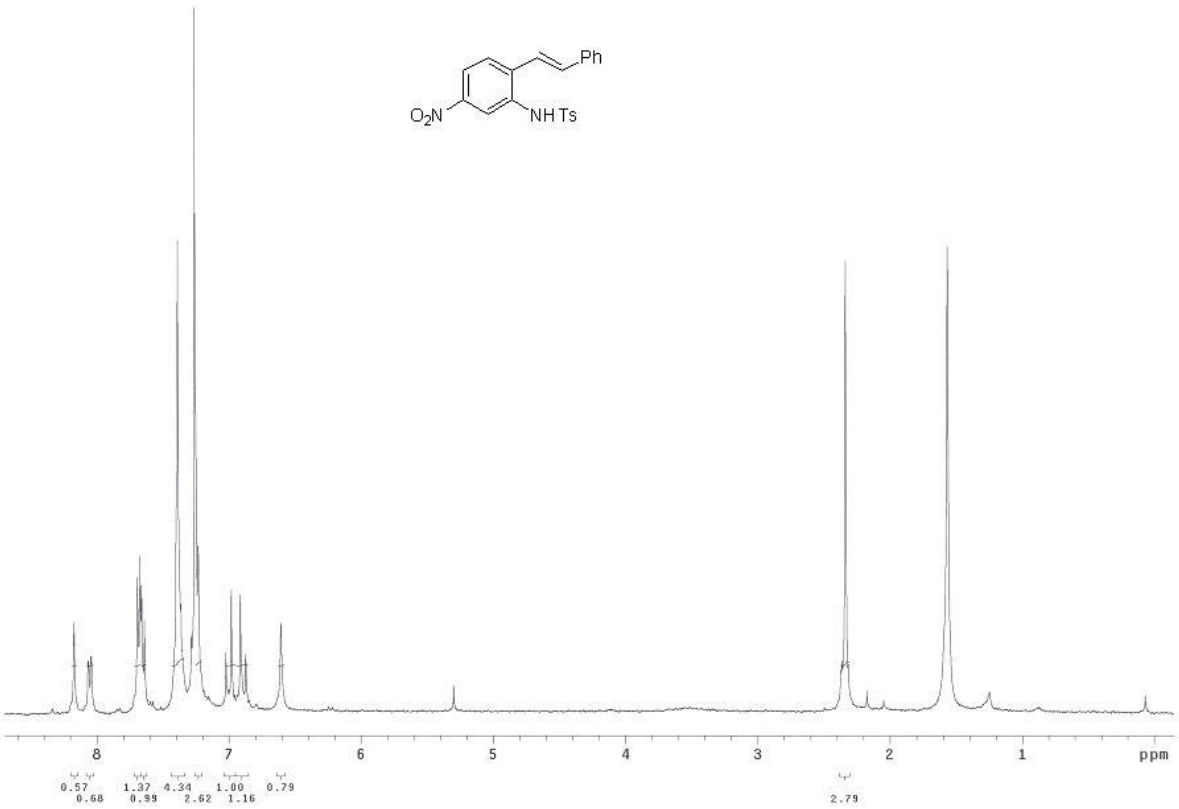
^{13}C NMR Spectrum of Compound **1o** ($CDCl_3$, 100 MHz)



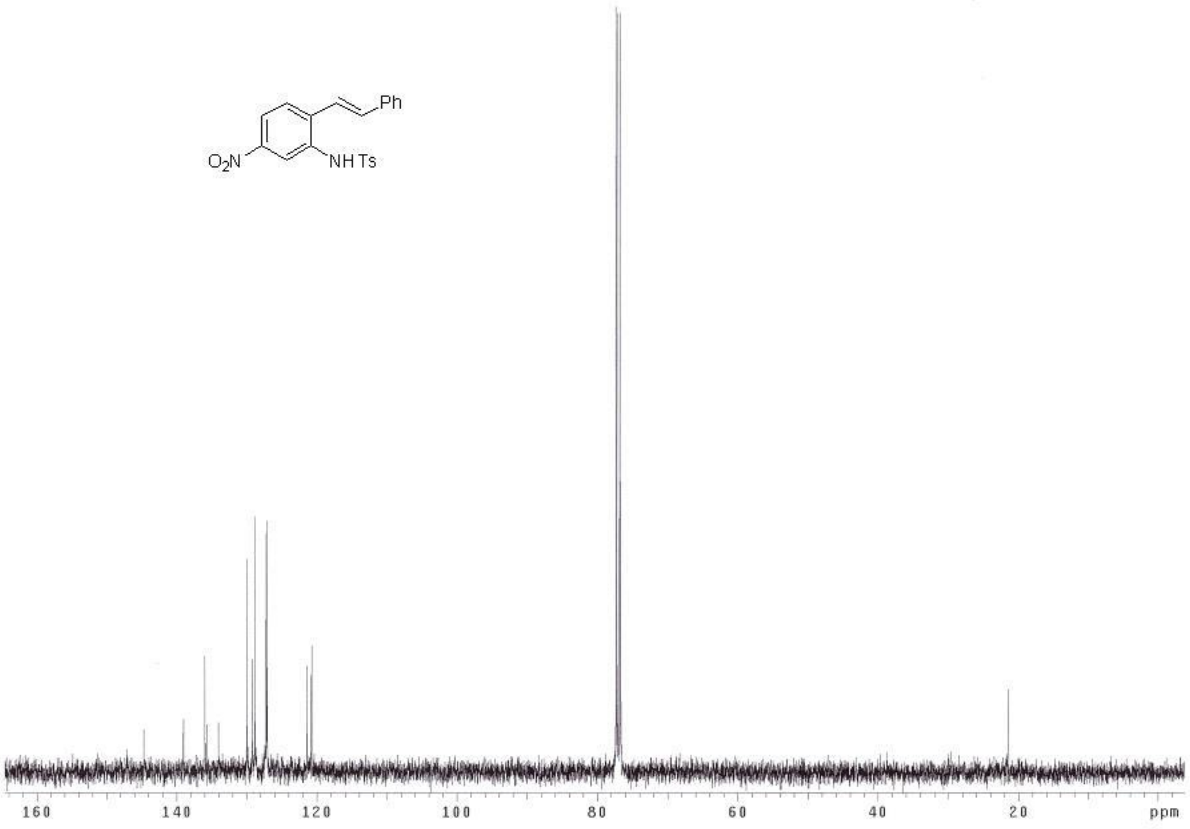
^{1}H NMR Spectrum of Compound **1p** ($CDCl_3$, 400 MHz)



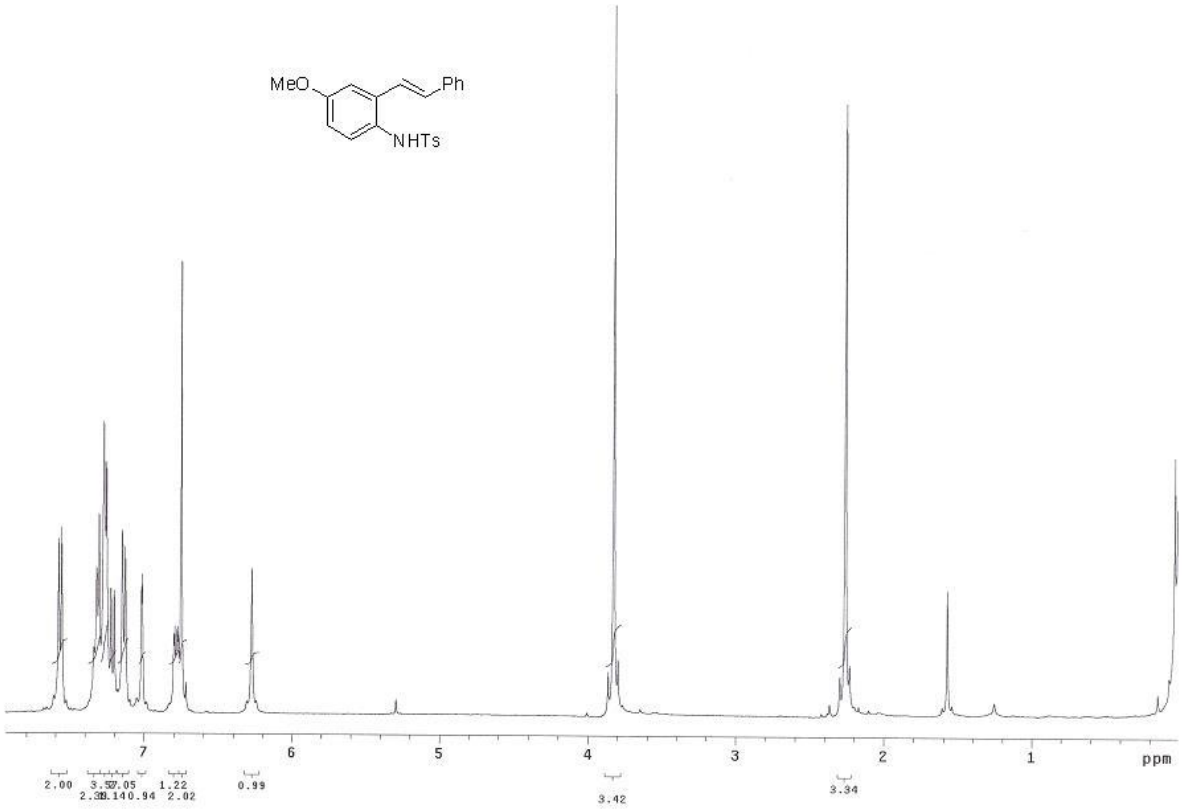
^{13}C NMR Spectrum of Compound **1p** ($CDCl_3$, 100 MHz)



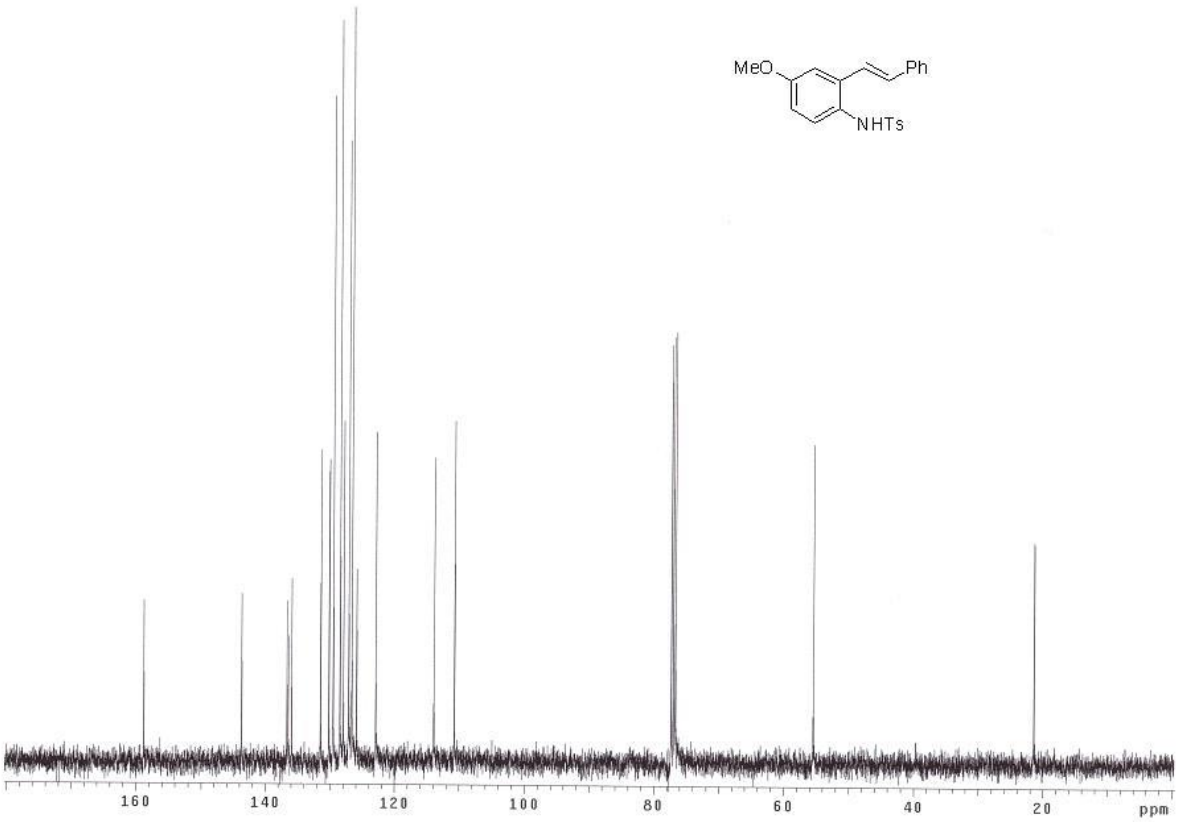
^{1}H NMR Spectrum of Compound **1q** ($CDCl_3$, 400 MHz)



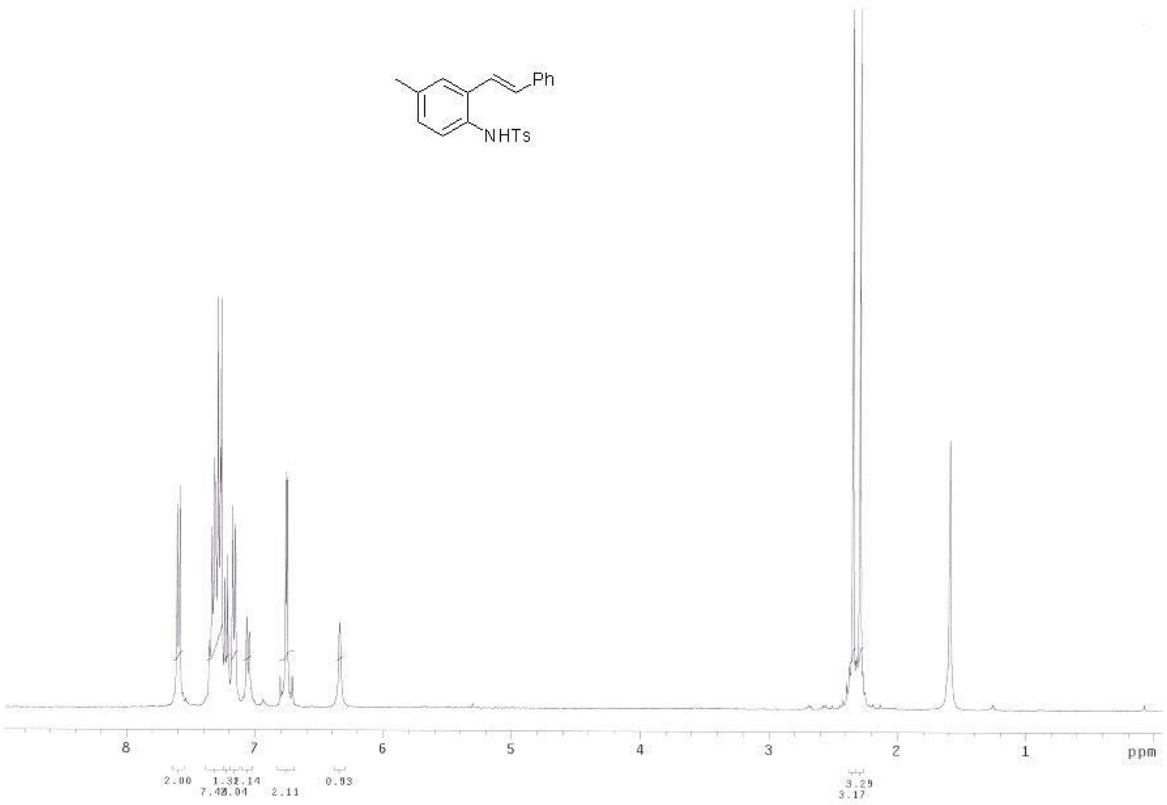
^{13}C NMR Spectrum of Compound **1q** ($CDCl_3$, 100 MHz)



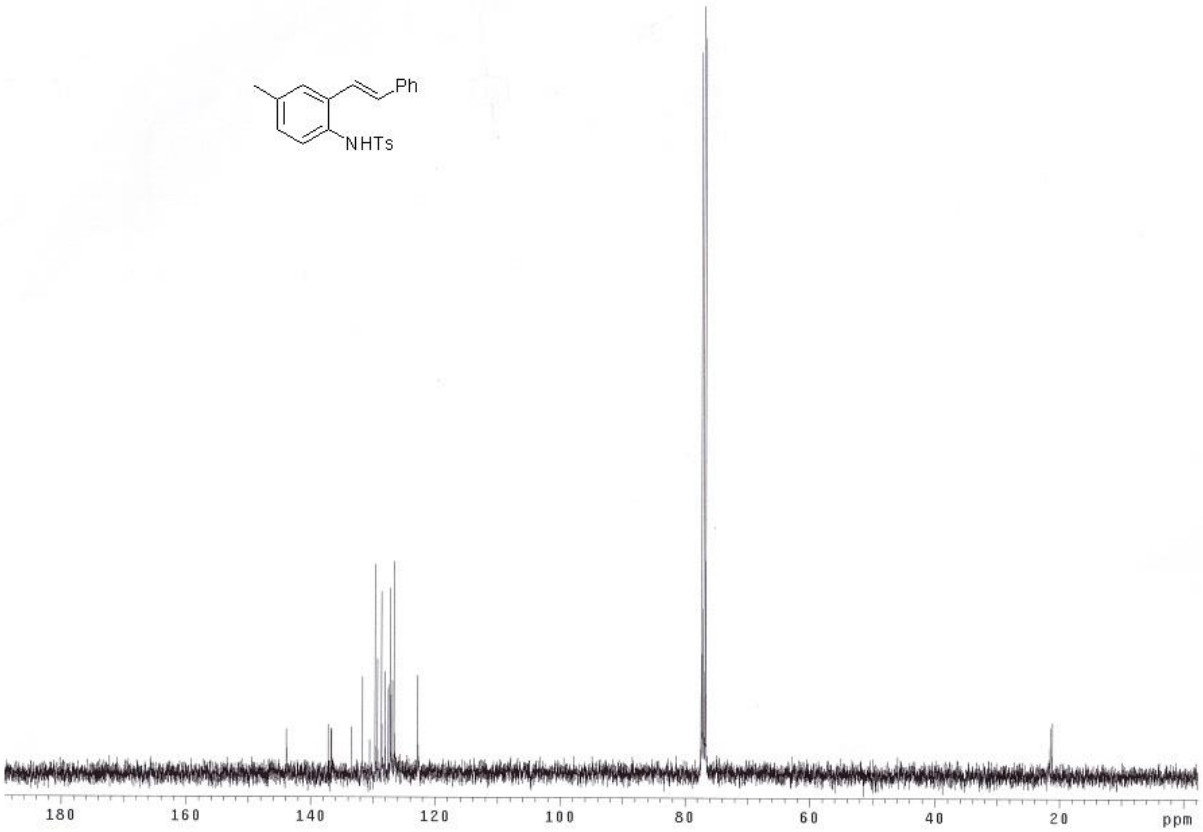
^{1}H NMR Spectrum of Compound **1r** ($CDCl_3$, 400 MHz)



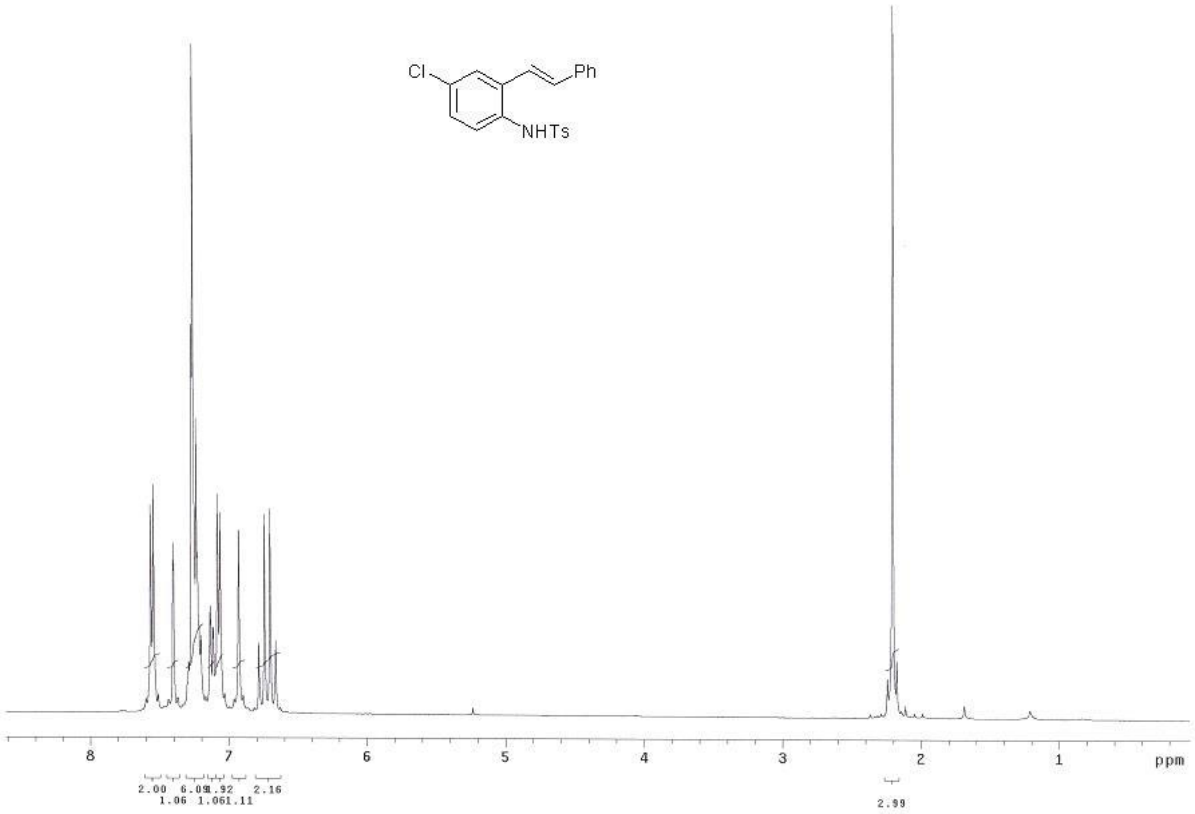
^{13}C NMR Spectrum of Compound **1r** ($CDCl_3$, 100 MHz)



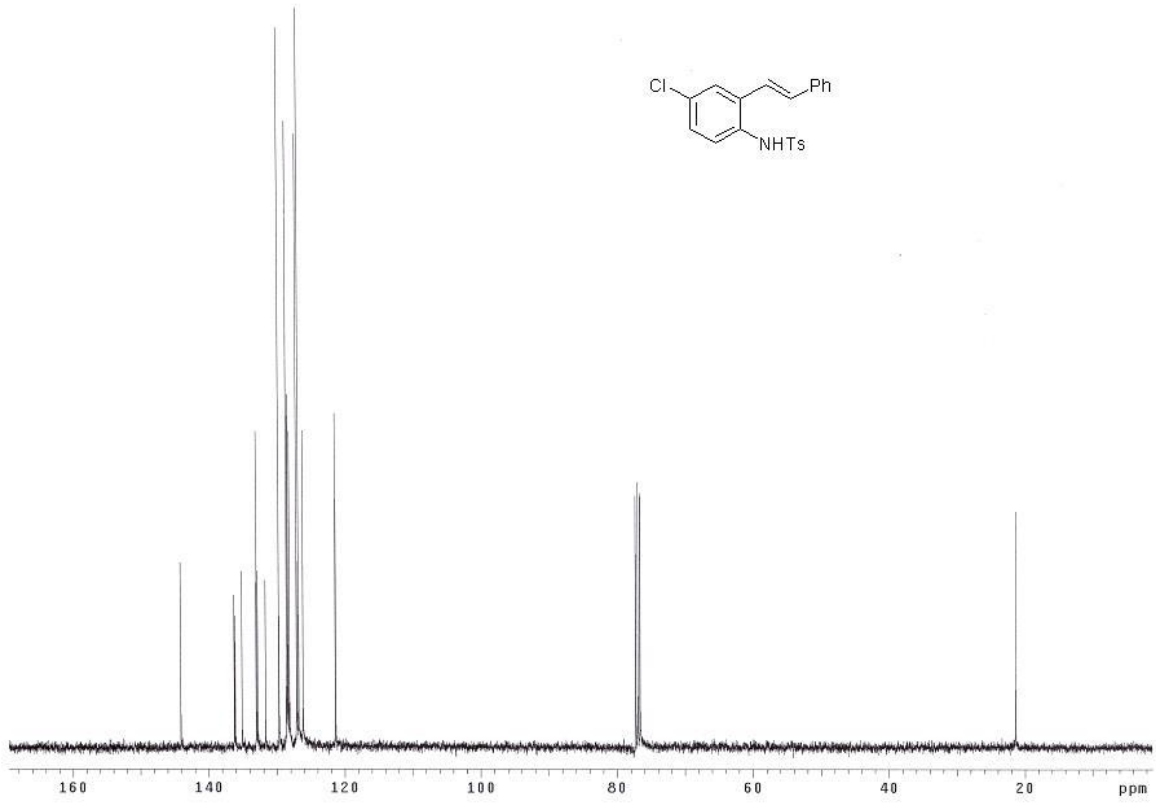
^{1}H NMR Spectrum of Compound **1s** ($CDCl_3$, 400 MHz)



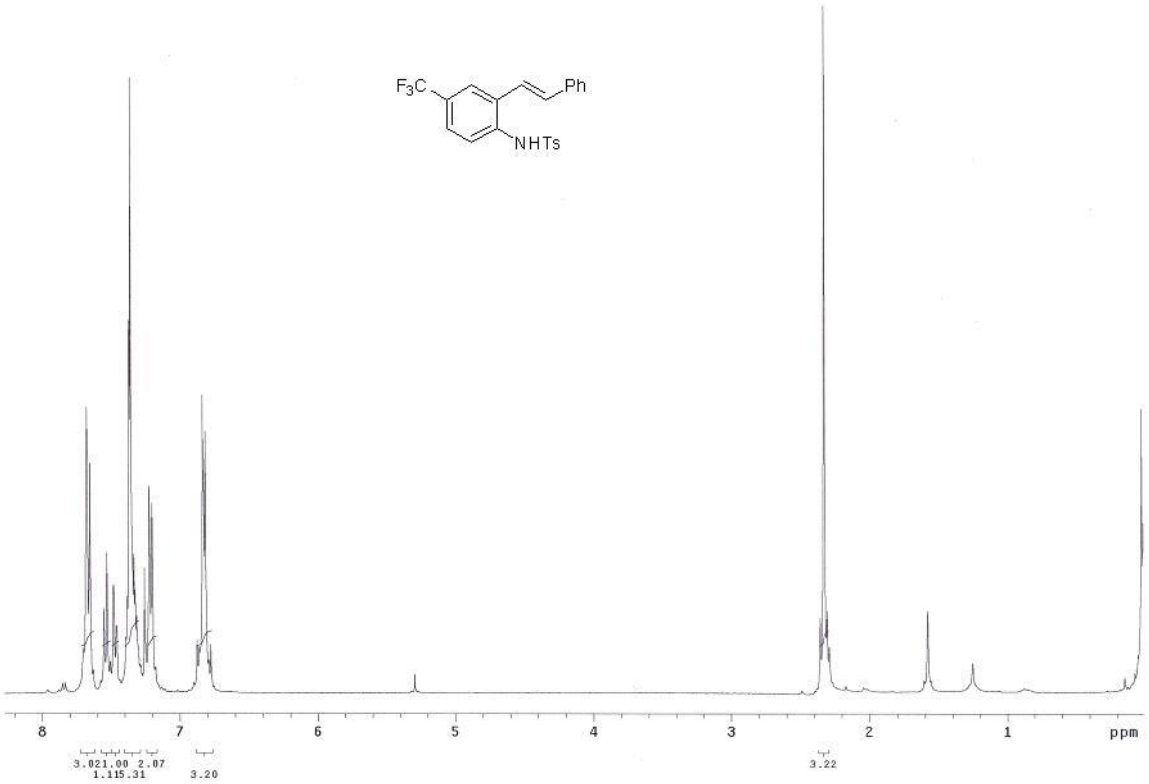
^{13}C NMR Spectrum of Compound **1s** ($CDCl_3$, 100 MHz)



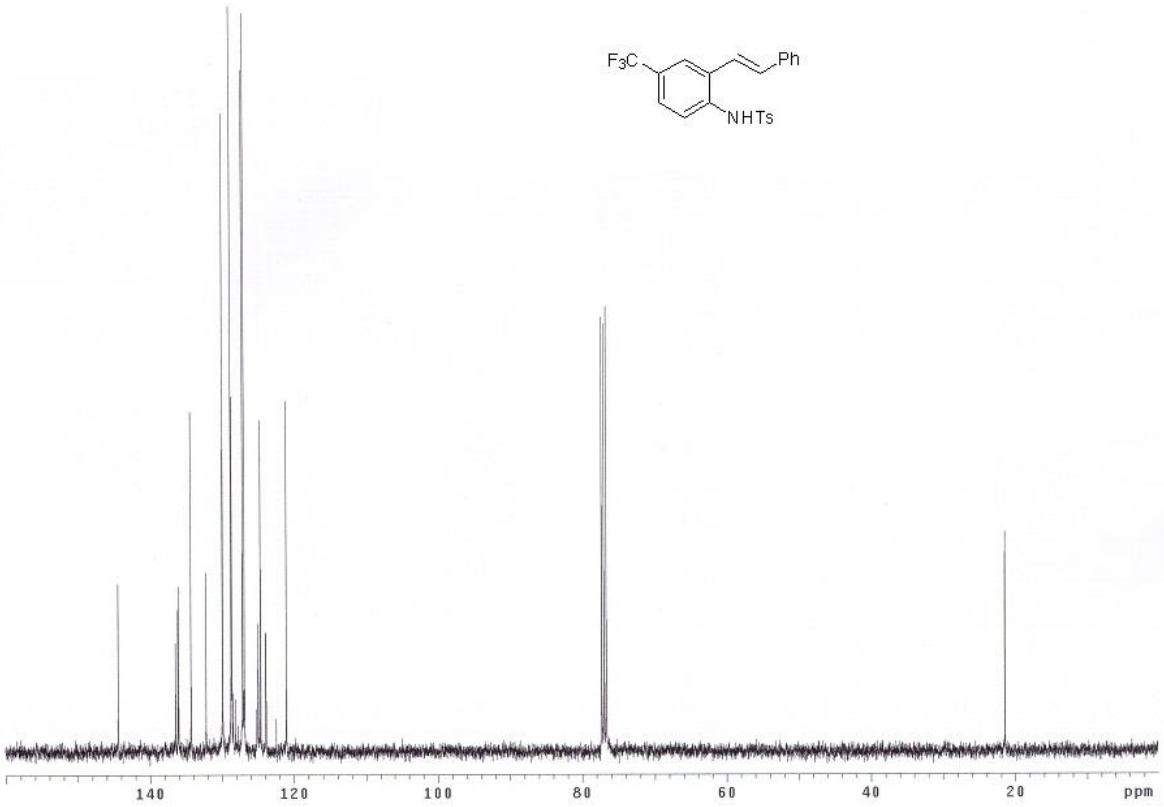
^{1}H NMR Spectrum of Compound **1t** ($CDCl_3$, 400 MHz)



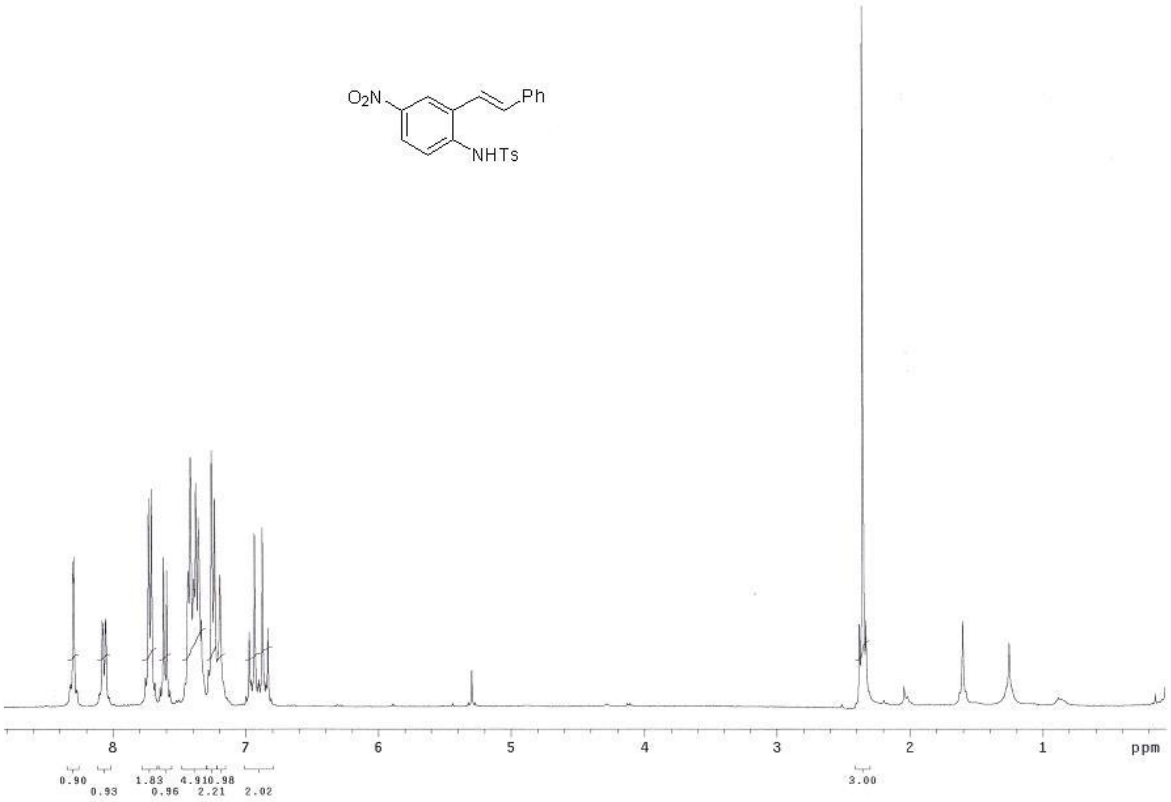
^{13}C NMR Spectrum of Compound **1t** ($CDCl_3$, 100 MHz)



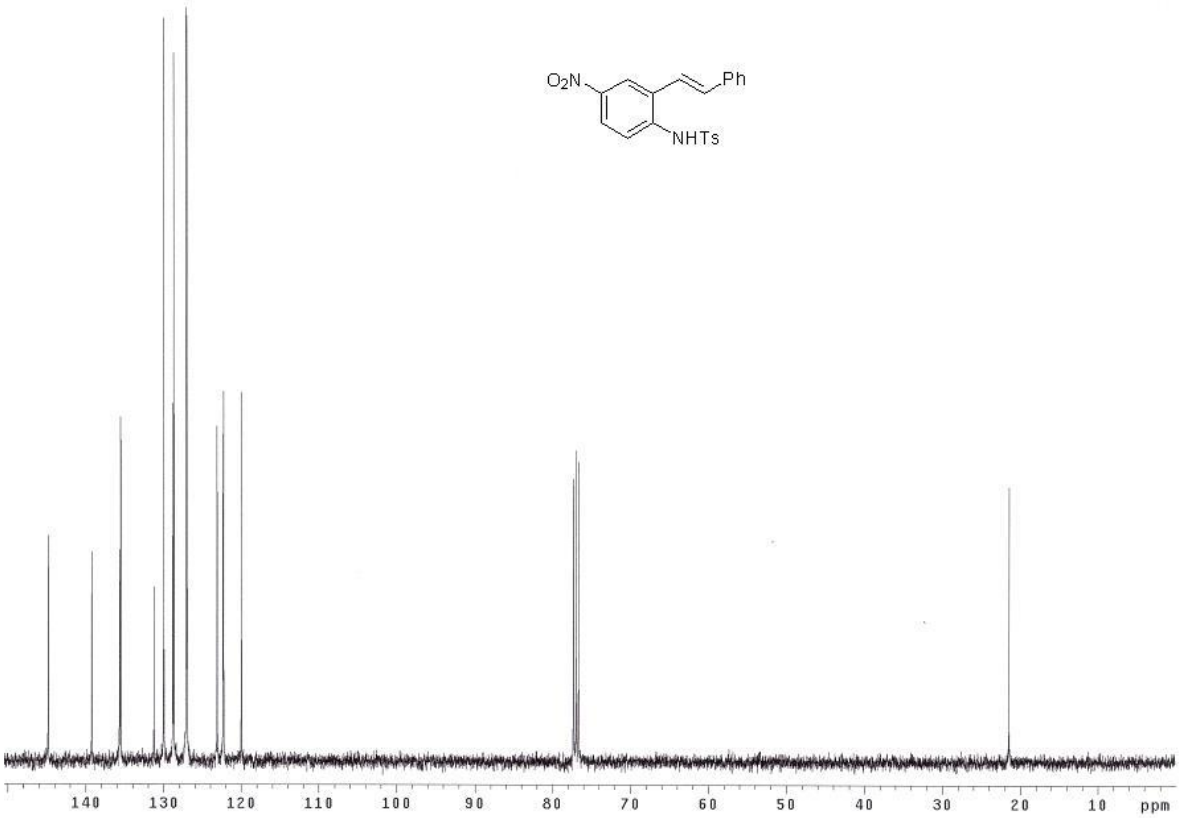
^{1}H NMR Spectrum of Compound **1u** ($CDCl_3$, 400 MHz)



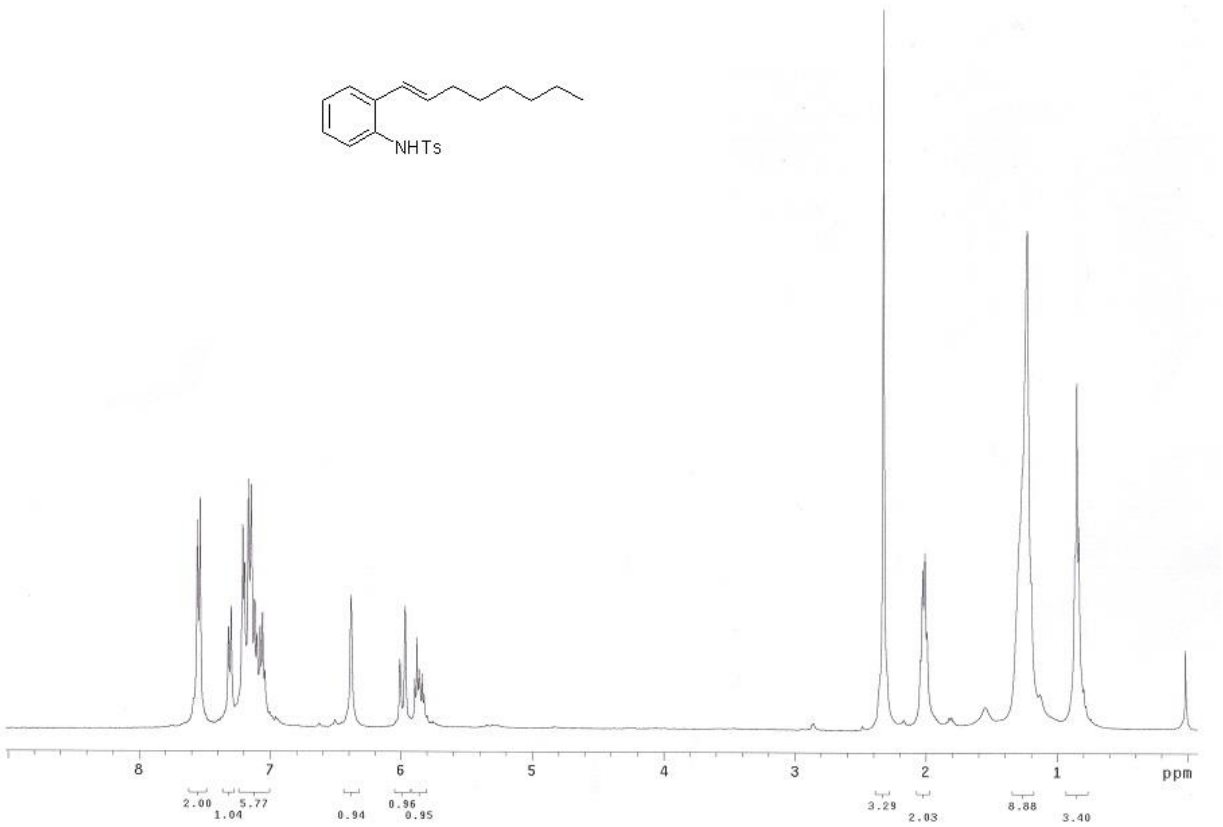
^{13}C NMR Spectrum of Compound **1u** ($CDCl_3$, 100 MHz)



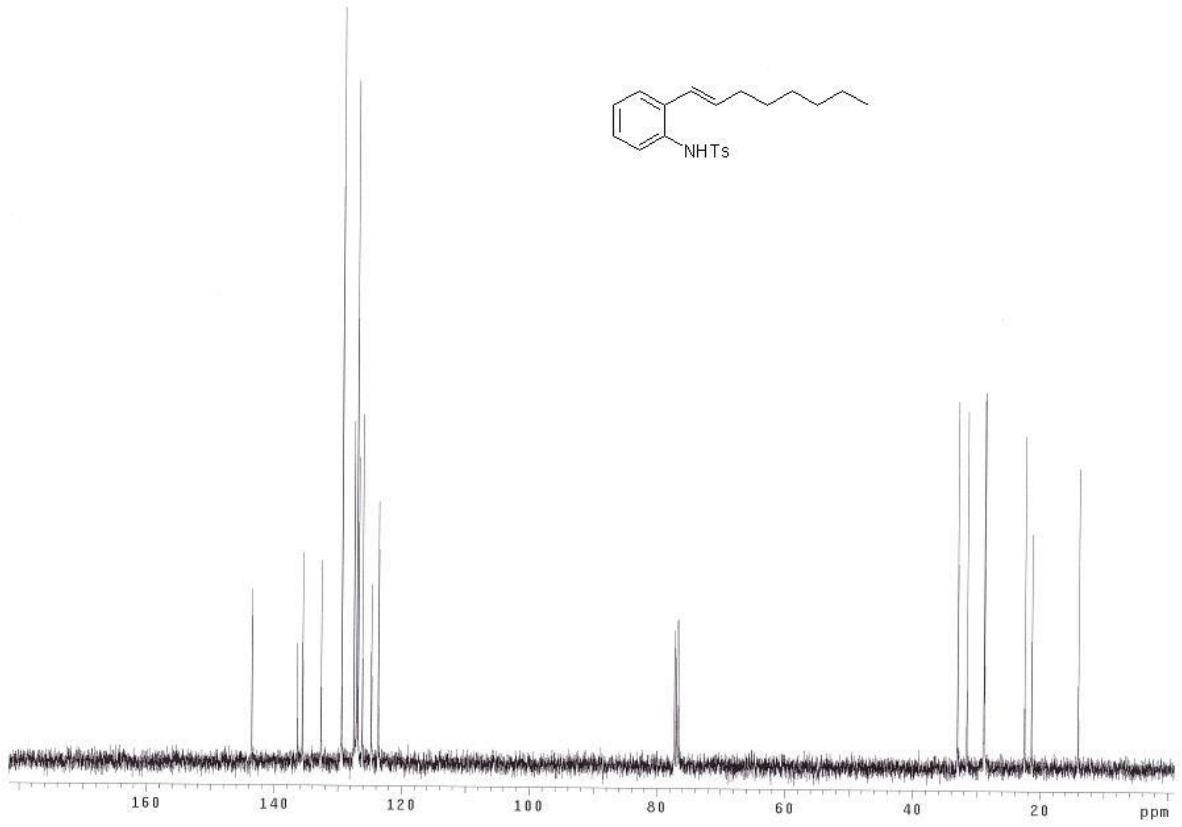
^{1}H NMR Spectrum of Compound **1v** ($CDCl_3$, 400 MHz)



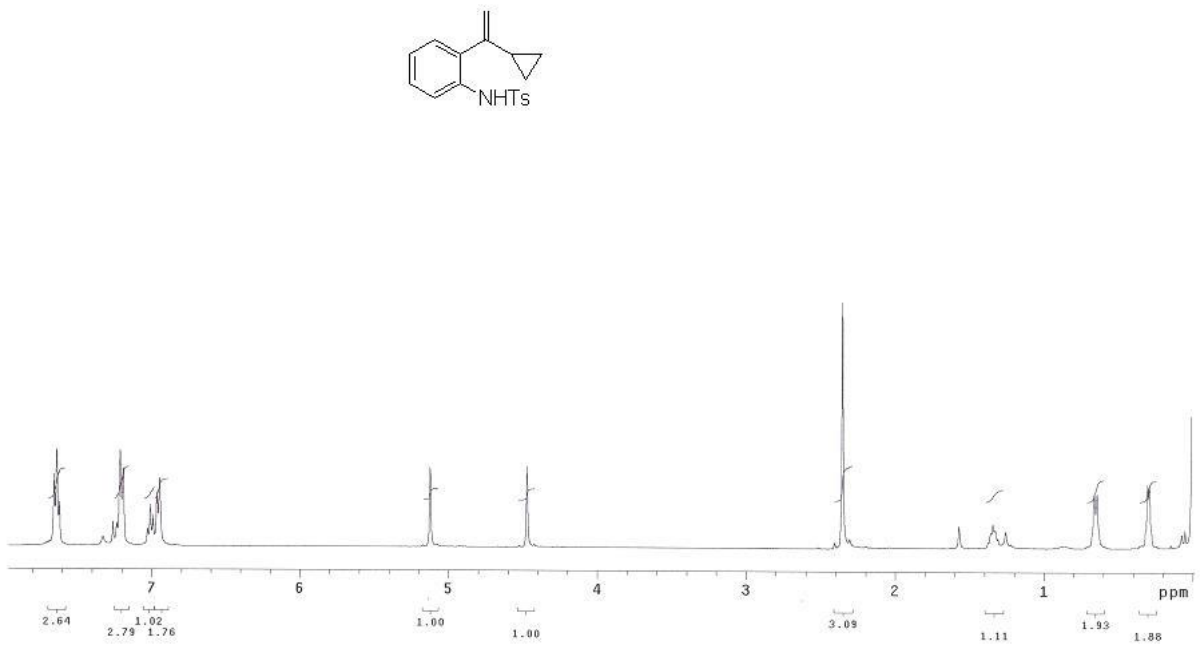
^{13}C NMR Spectrum of Compound **1v** ($CDCl_3$, 100 MHz)



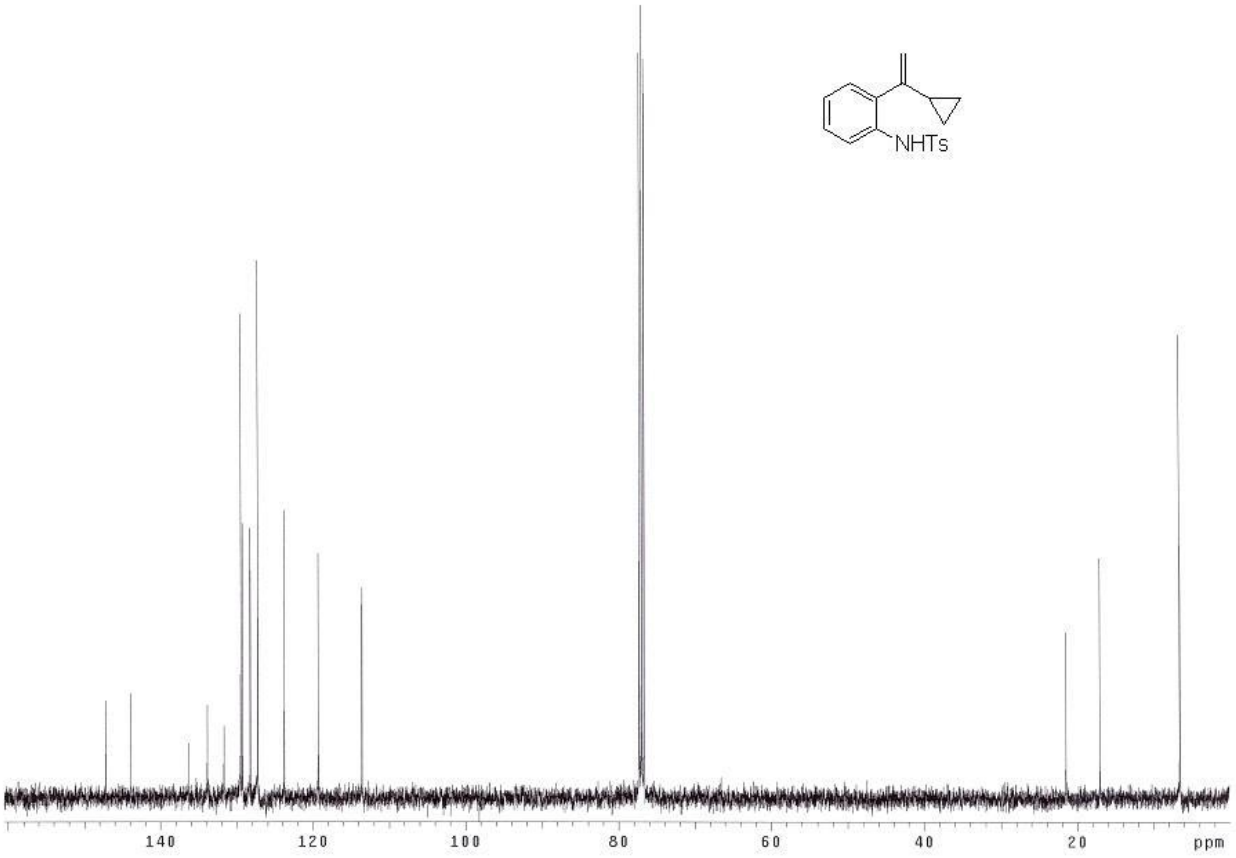
^{1}H NMR Spectrum of Compound **1w** ($CDCl_3$, 400 MHz)



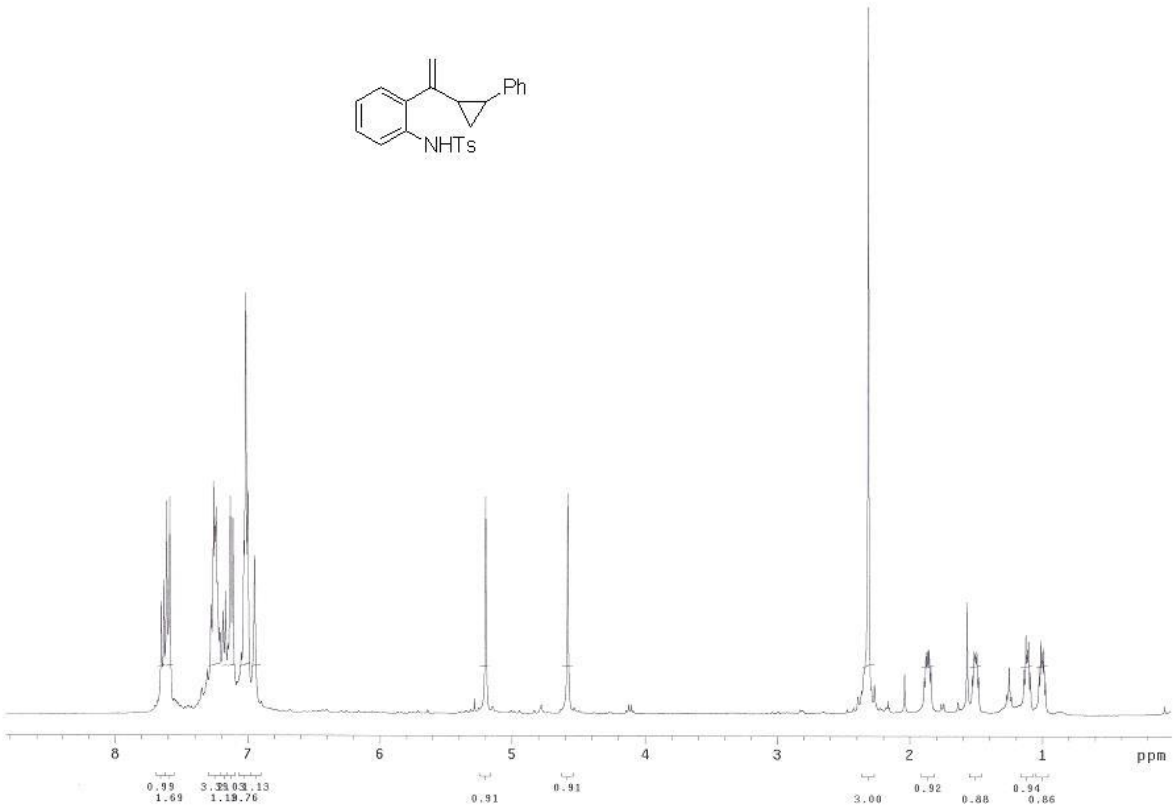
^{13}C NMR Spectrum of Compound **1w** ($CDCl_3$, 100 MHz)



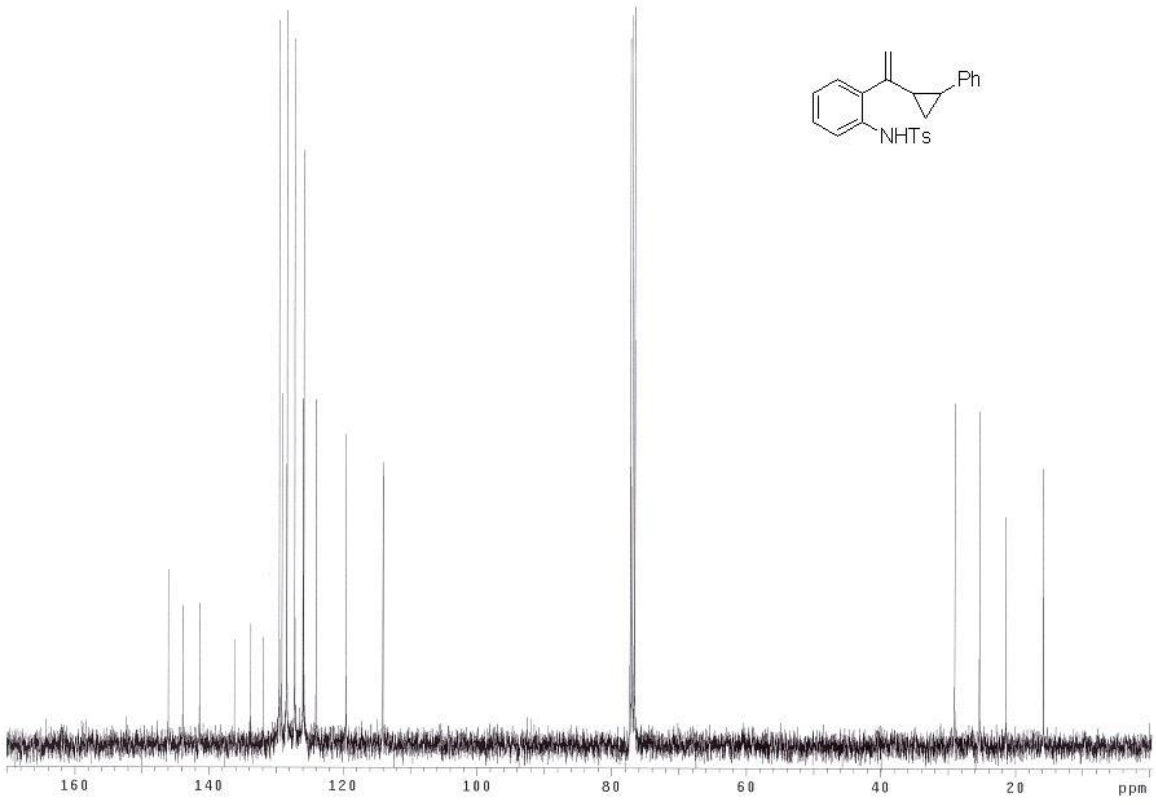
^{1}H NMR Spectrum of Compound **1x** ($CDCl_3$, 400 MHz)



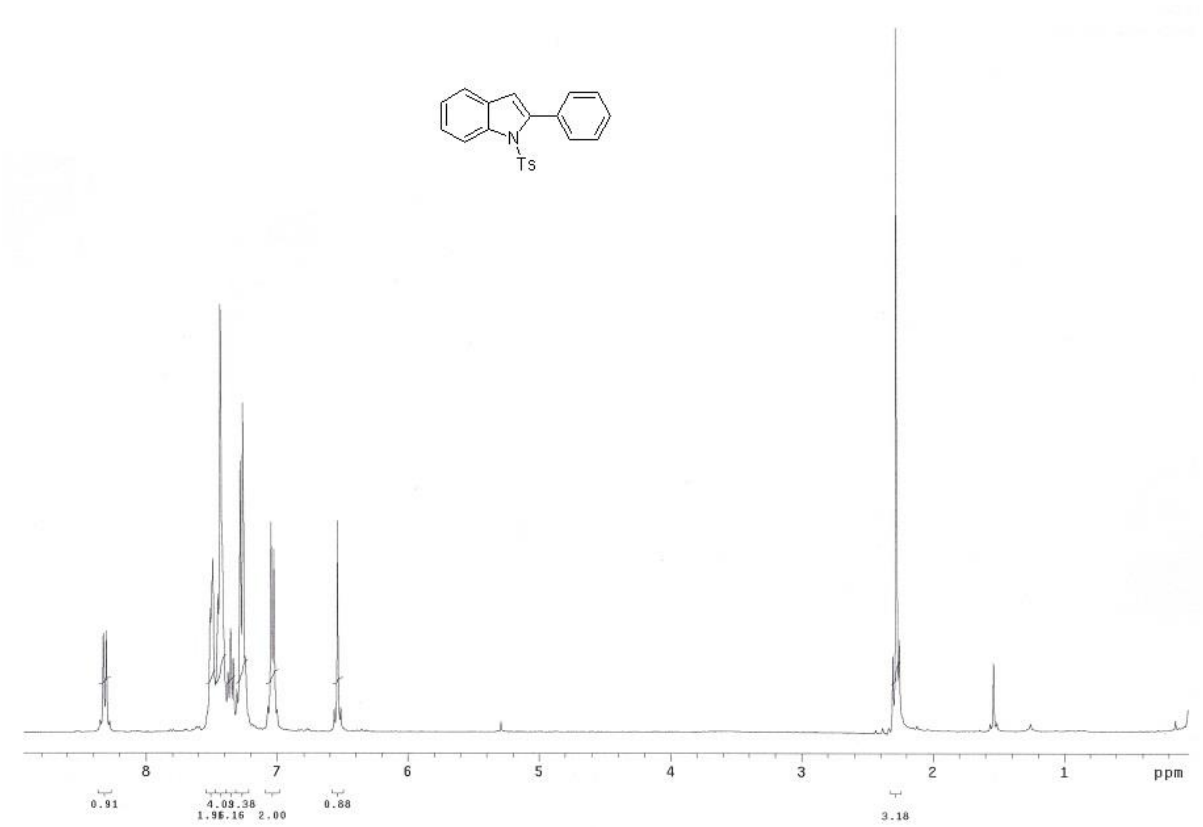
^{13}C NMR Spectrum of Compound **1x** ($CDCl_3$, 100 MHz)



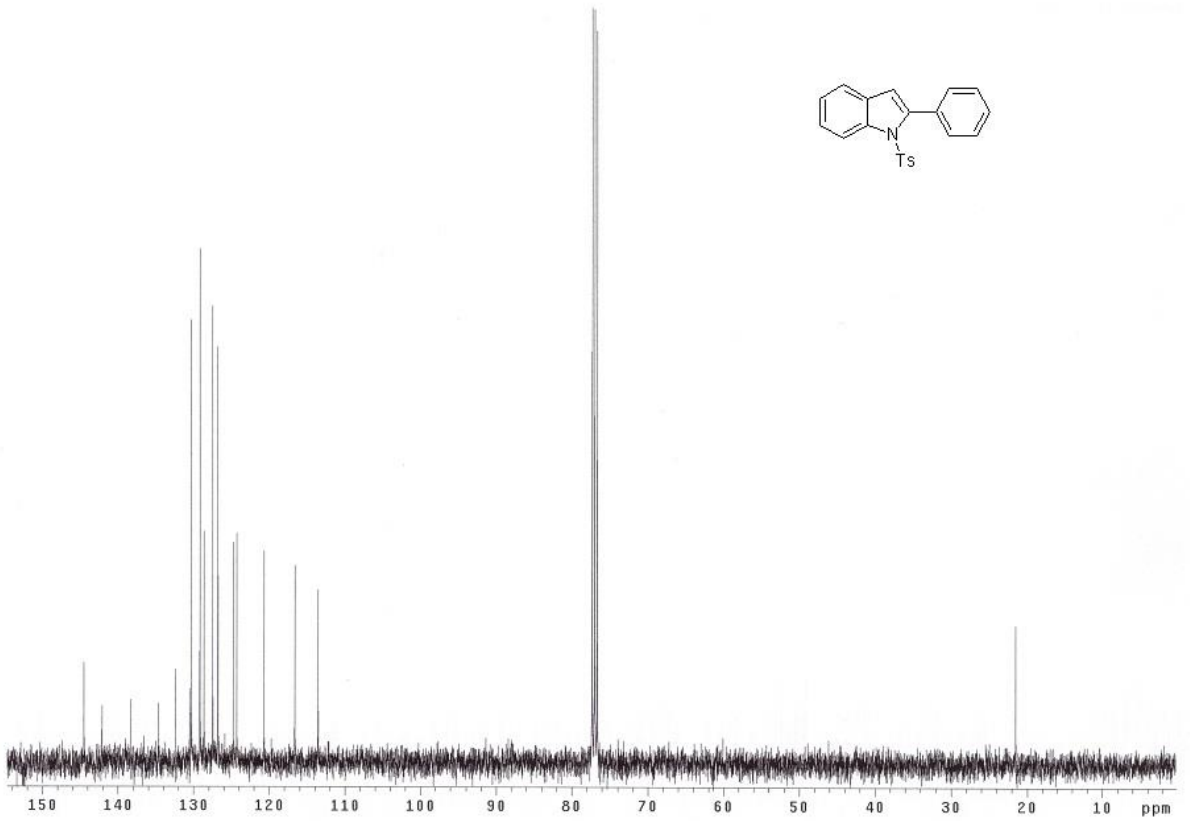
^{1}H NMR Spectrum of Compound **1y** ($CDCl_3$, 400 MHz)



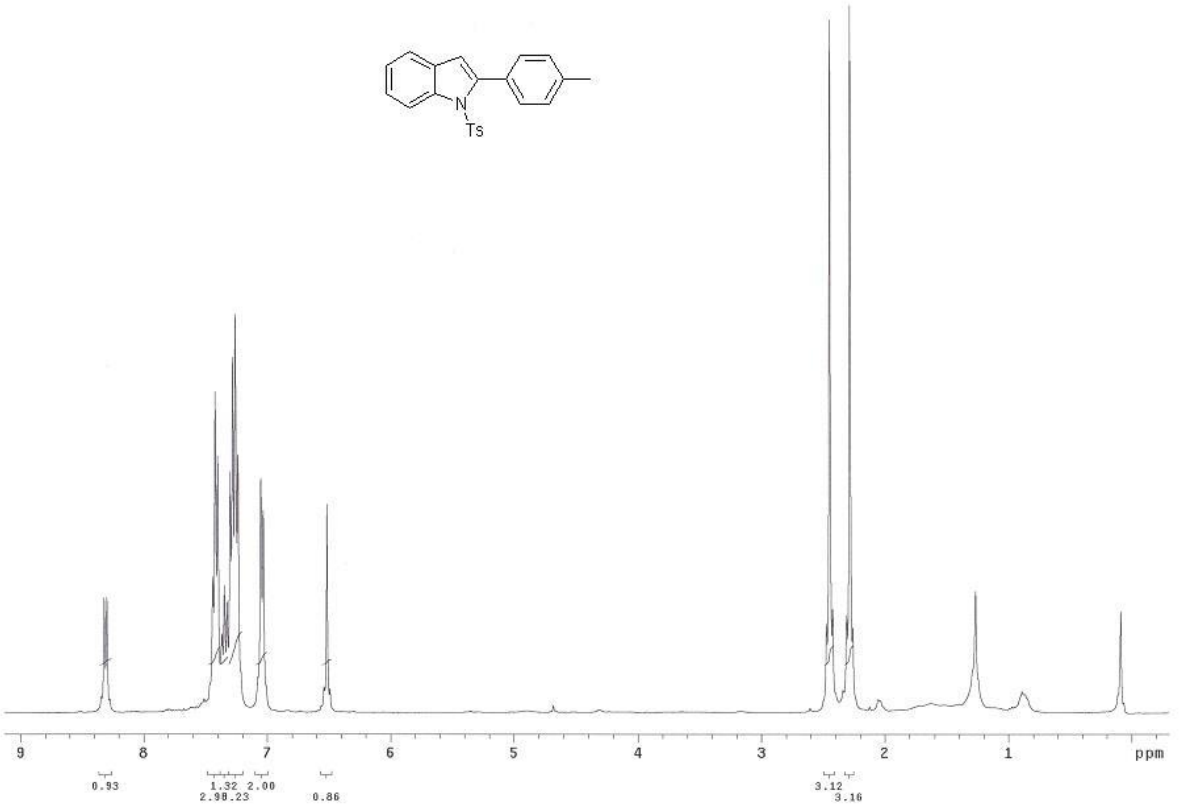
^{13}C NMR Spectrum of Compound **1y** ($CDCl_3$, 100 MHz)



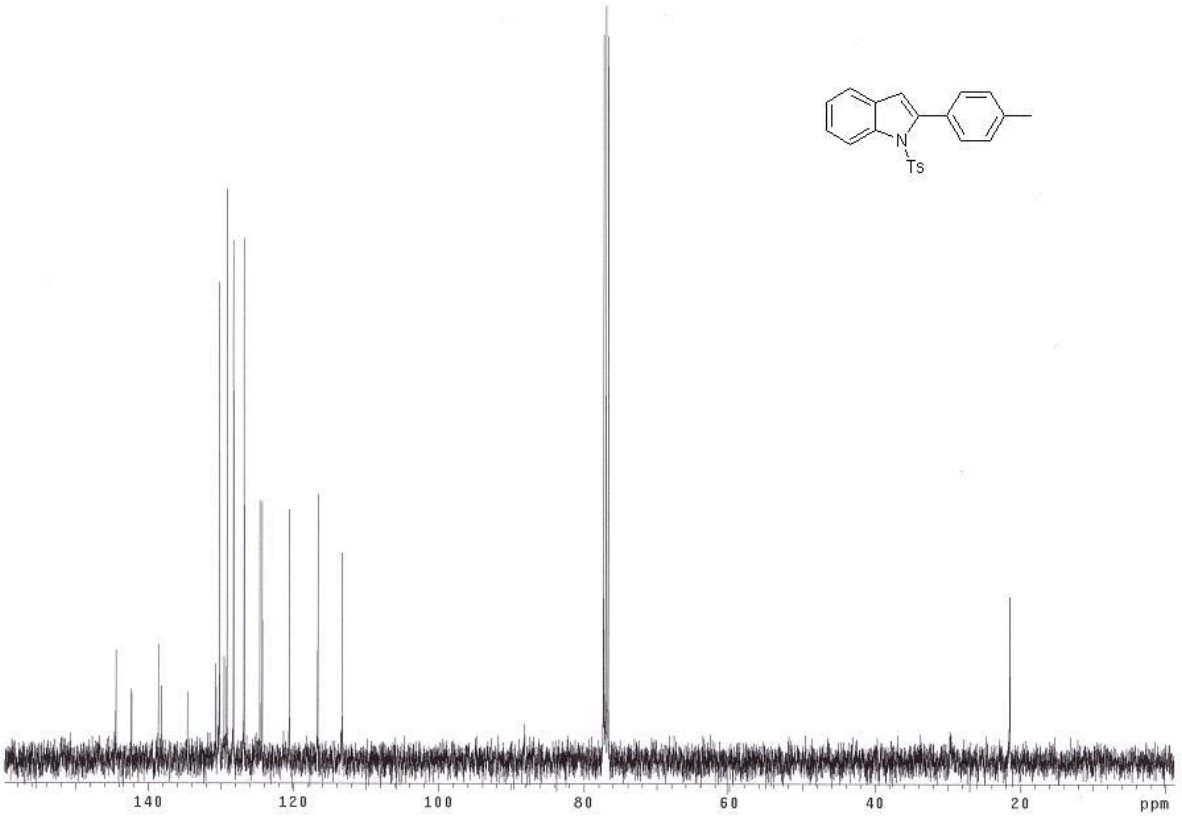
^{1}H NMR Spectrum of Compound **2a** ($CDCl_3$, 400 MHz)



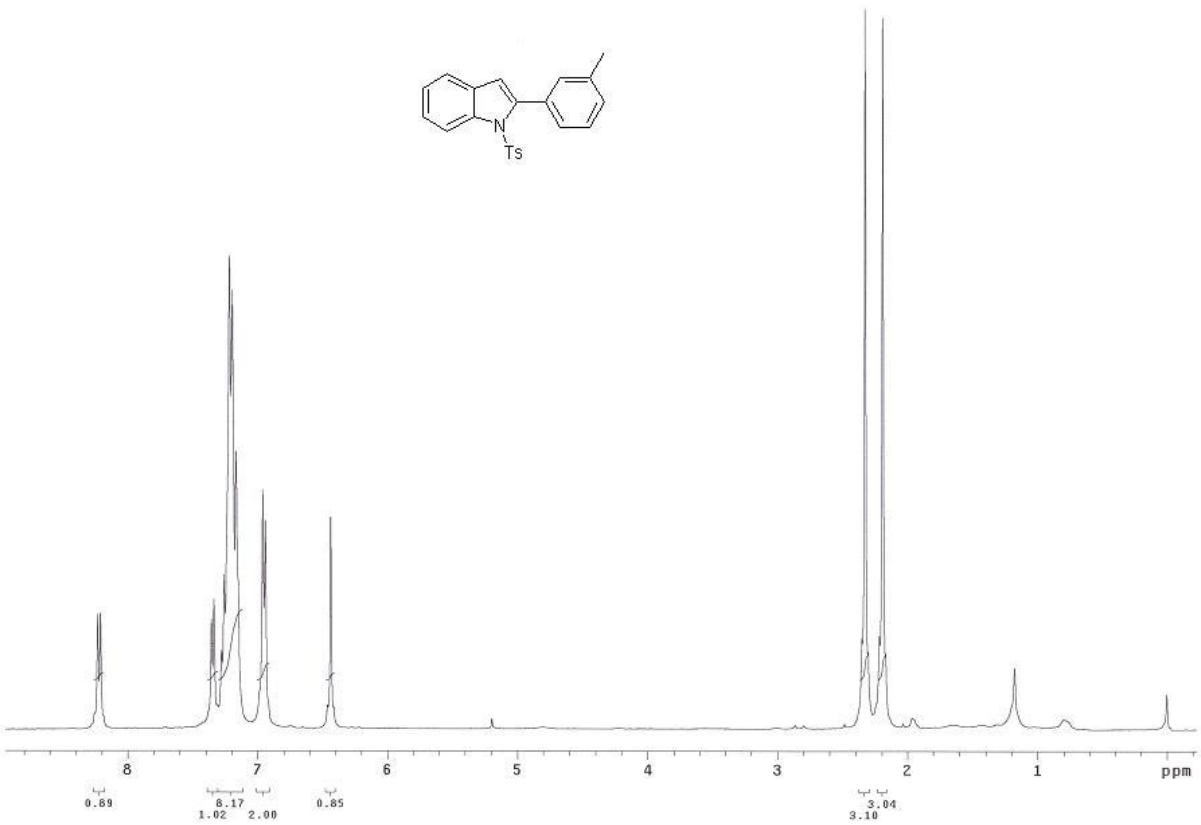
^{13}C NMR Spectrum of Compound **2a** ($CDCl_3$, 100 MHz)



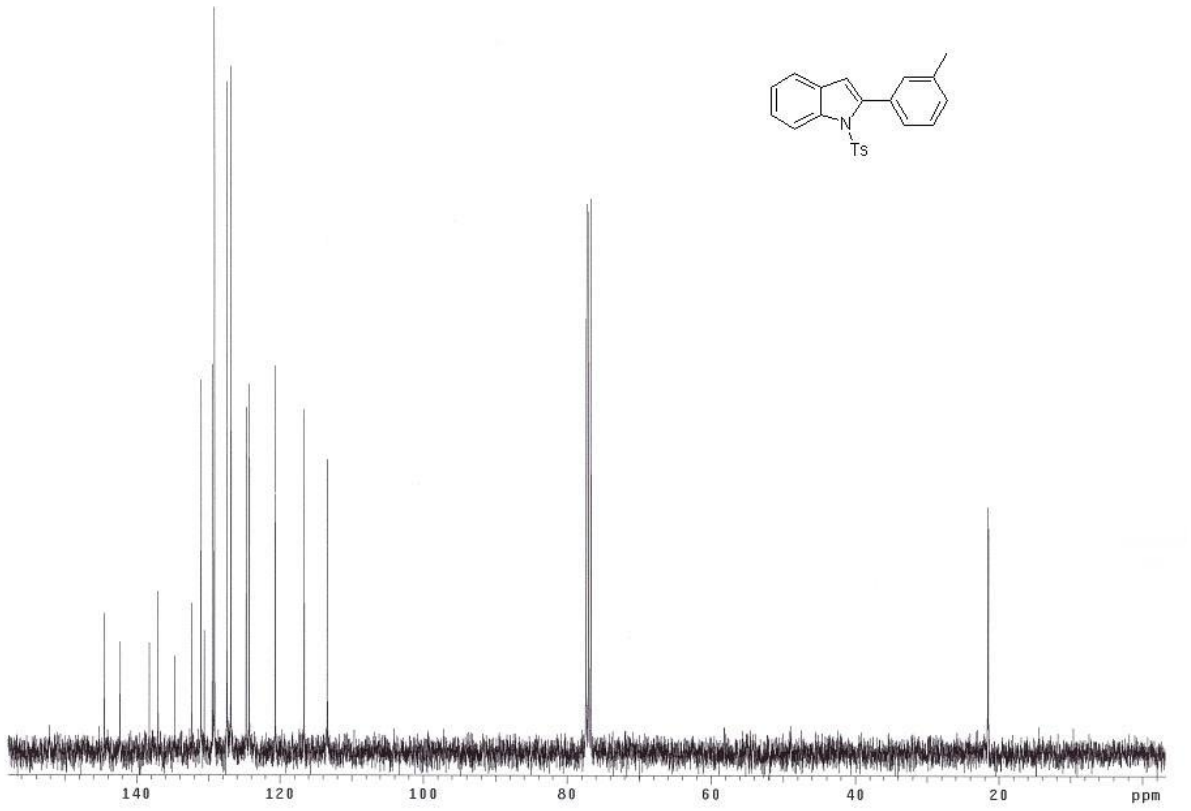
^{1}H NMR Spectrum of Compound **2b** ($CDCl_3$, 400 MHz)



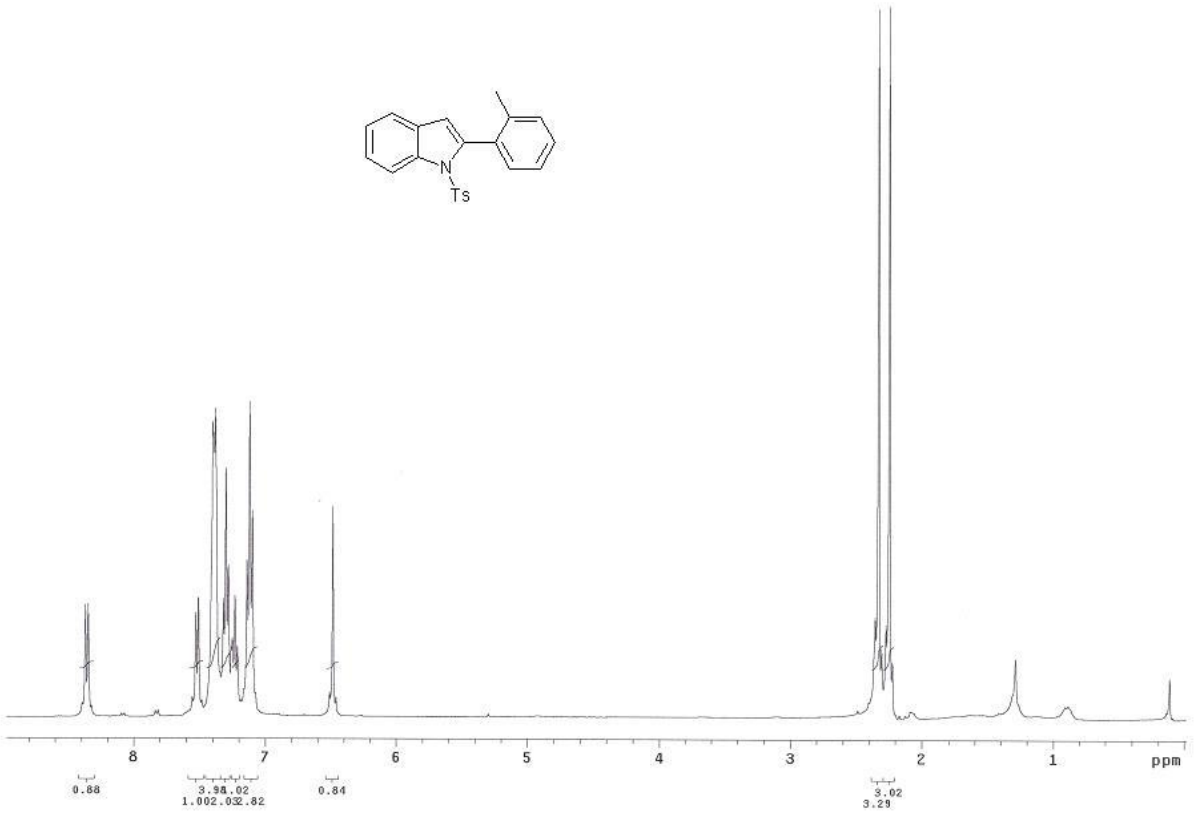
^{13}C NMR Spectrum of Compound **2b** ($CDCl_3$, 100 MHz)



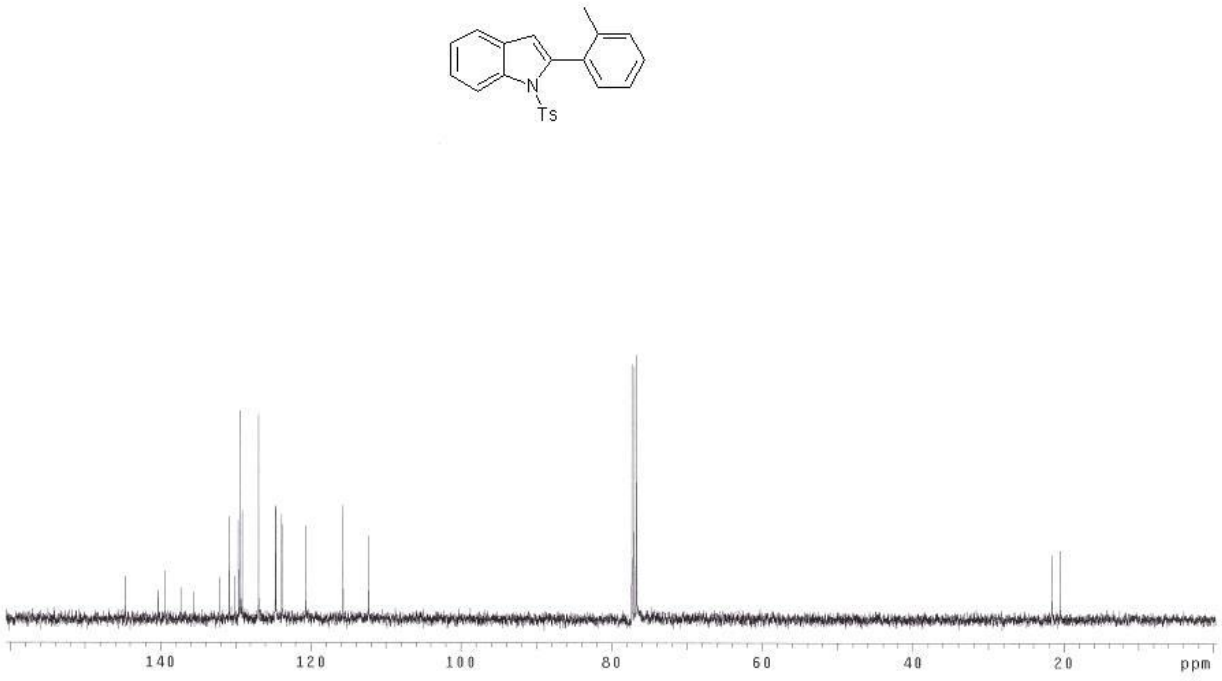
^{1}H NMR Spectrum of Compound **2c** ($CDCl_3$, 400 MHz)



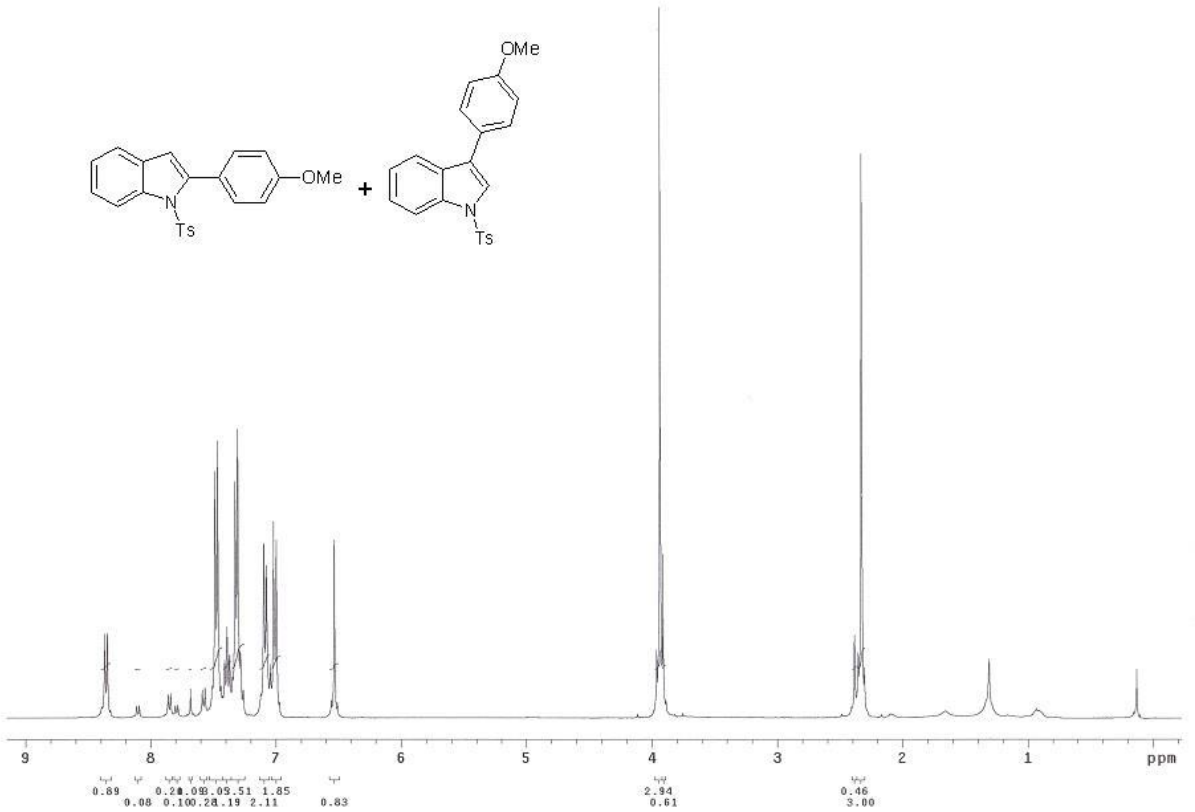
^{13}C NMR Spectrum of Compound **2c** ($CDCl_3$, 100 MHz)



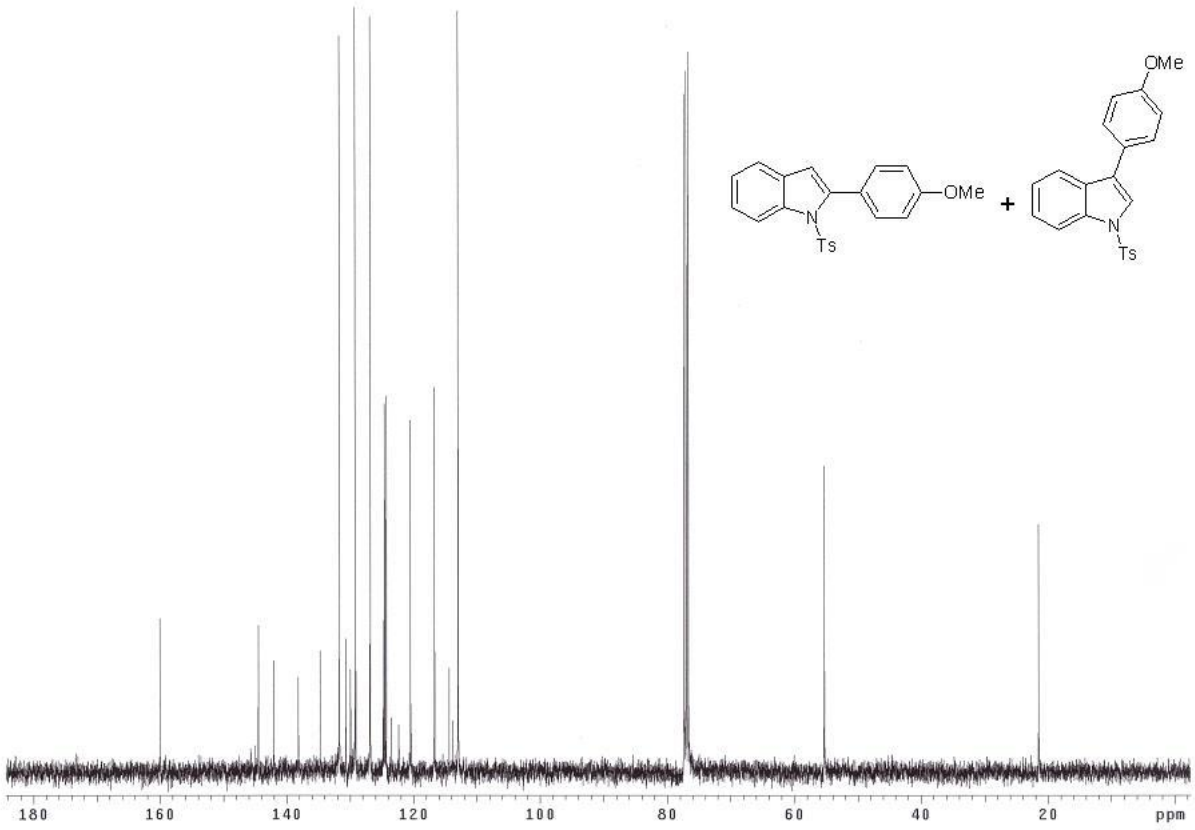
^{1}H NMR Spectrum of Compound **2d** ($CDCl_3$, 400 MHz)



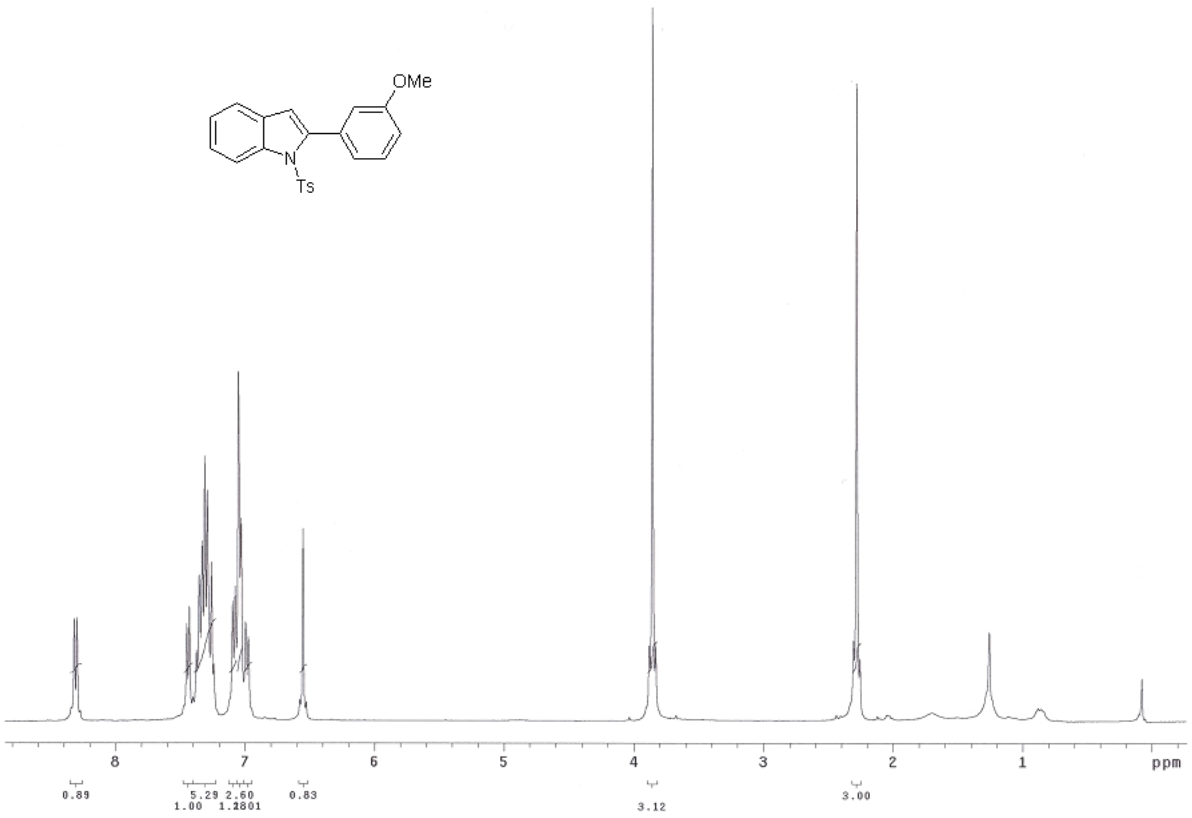
^{13}C NMR Spectrum of Compound **2d** ($CDCl_3$, 100 MHz)



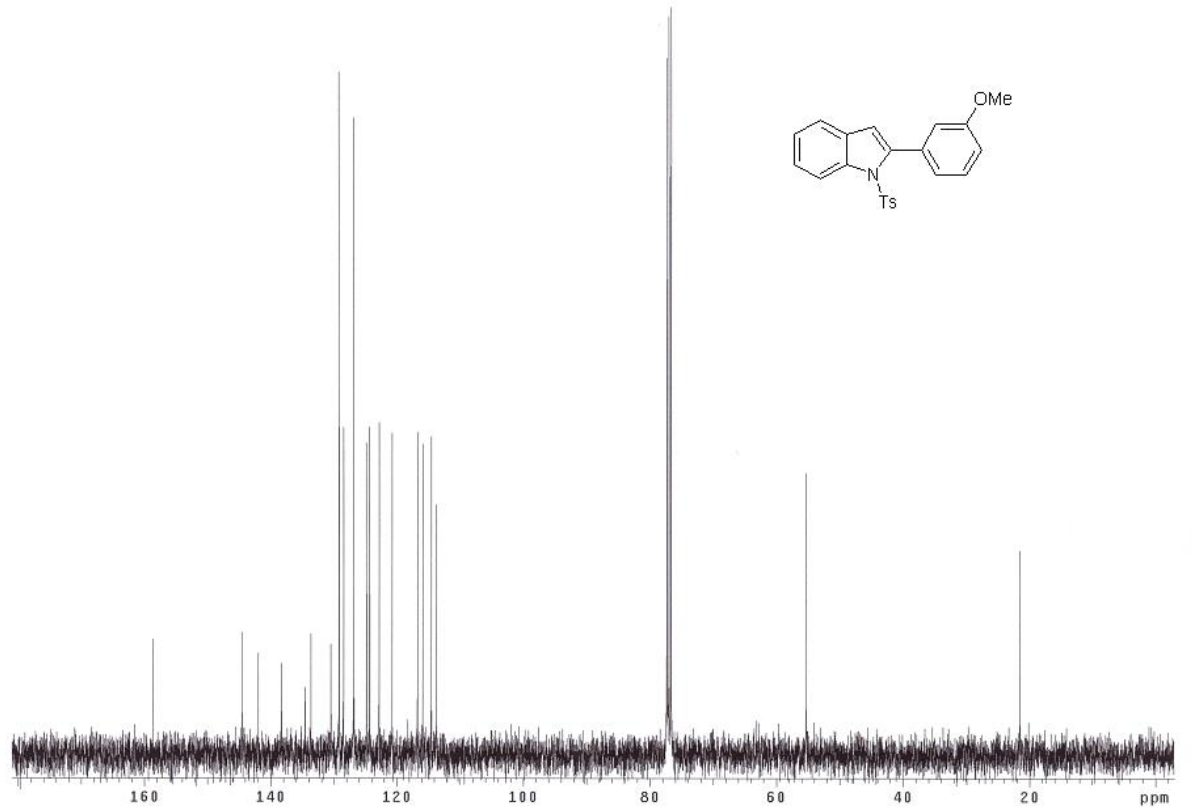
^{1}H NMR Spectrum of Compound **2e** ($CDCl_3$, 400 MHz)



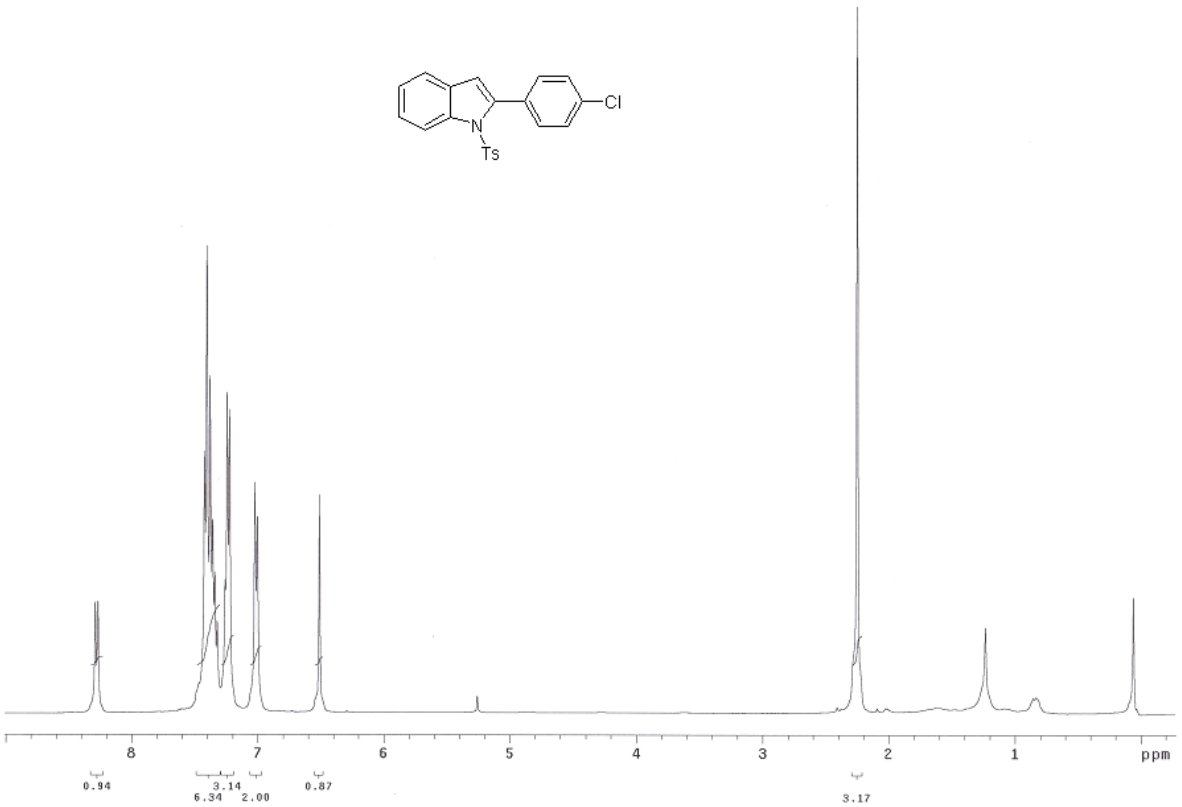
^{13}C NMR Spectrum of Compound **2e** ($CDCl_3$, 100 MHz)



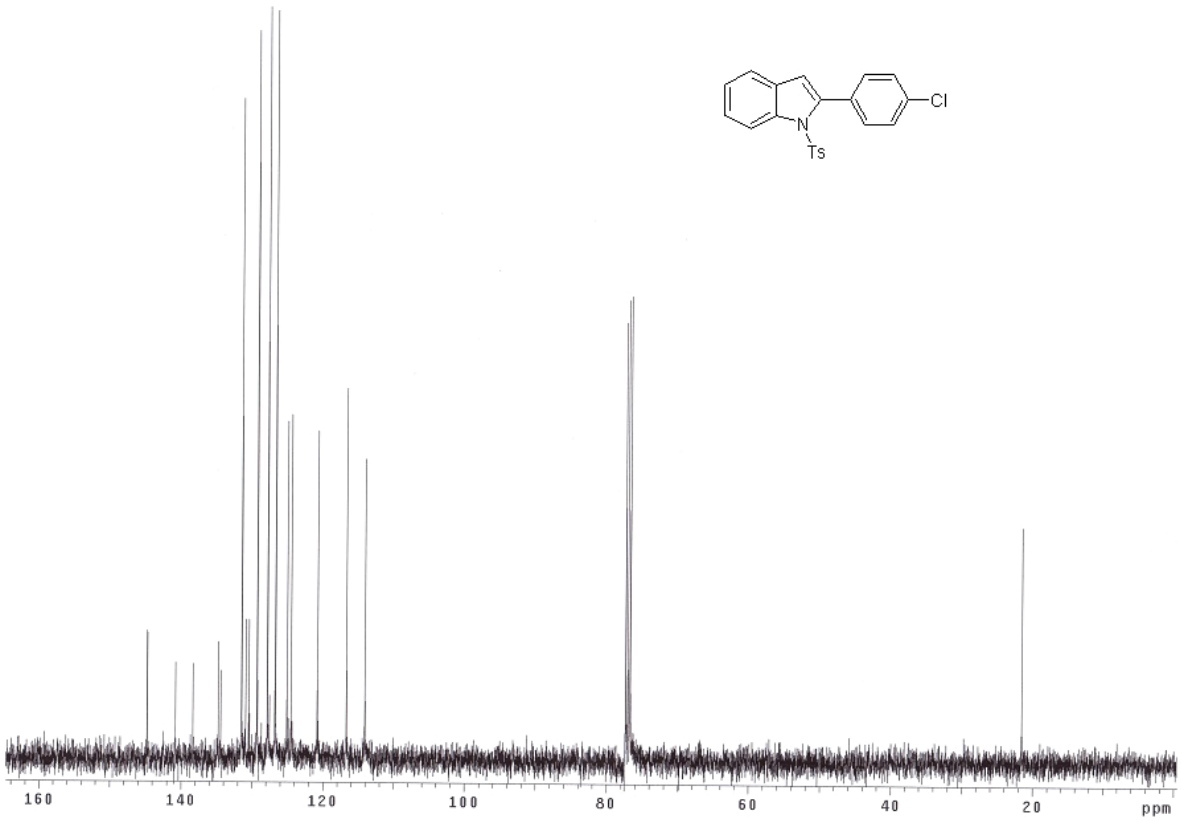
^{1}H NMR Spectrum of Compound **2f** ($CDCl_3$, 400 MHz)



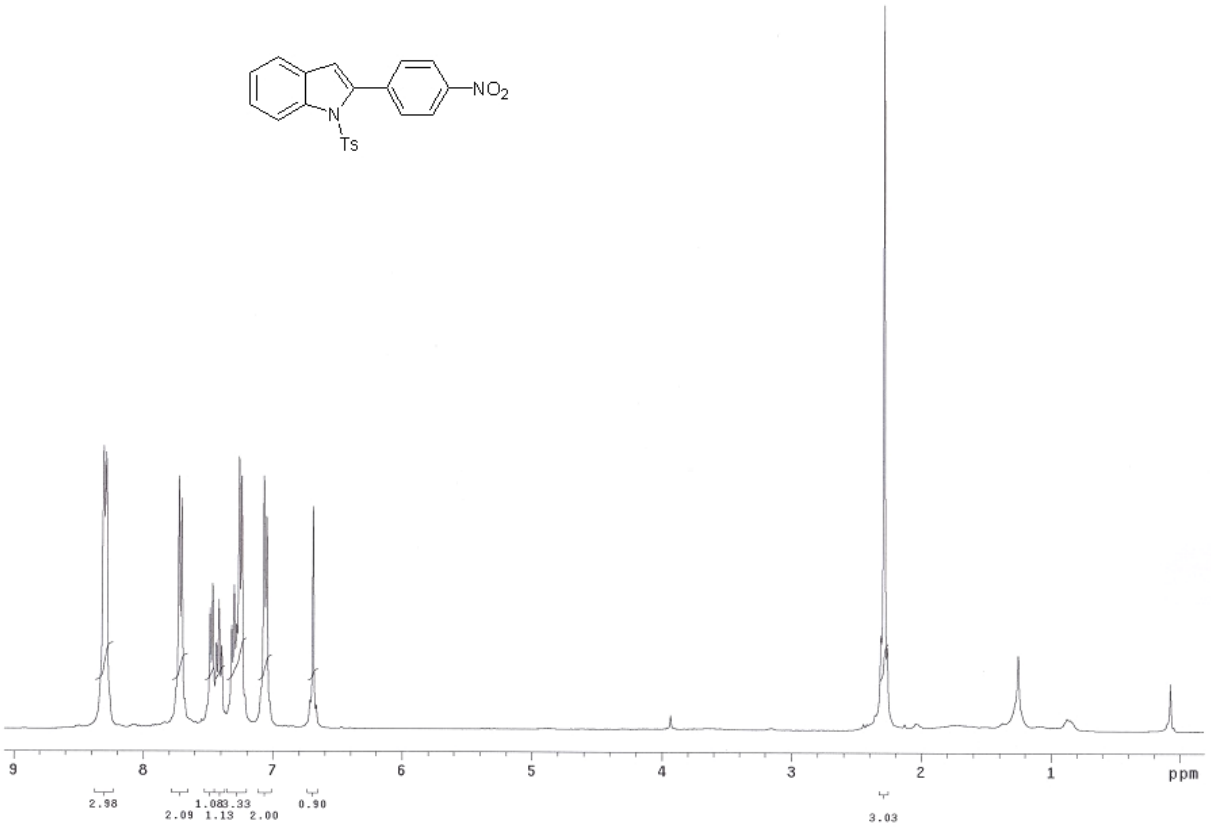
^{13}C NMR Spectrum of Compound **2f** ($CDCl_3$, 100 MHz)



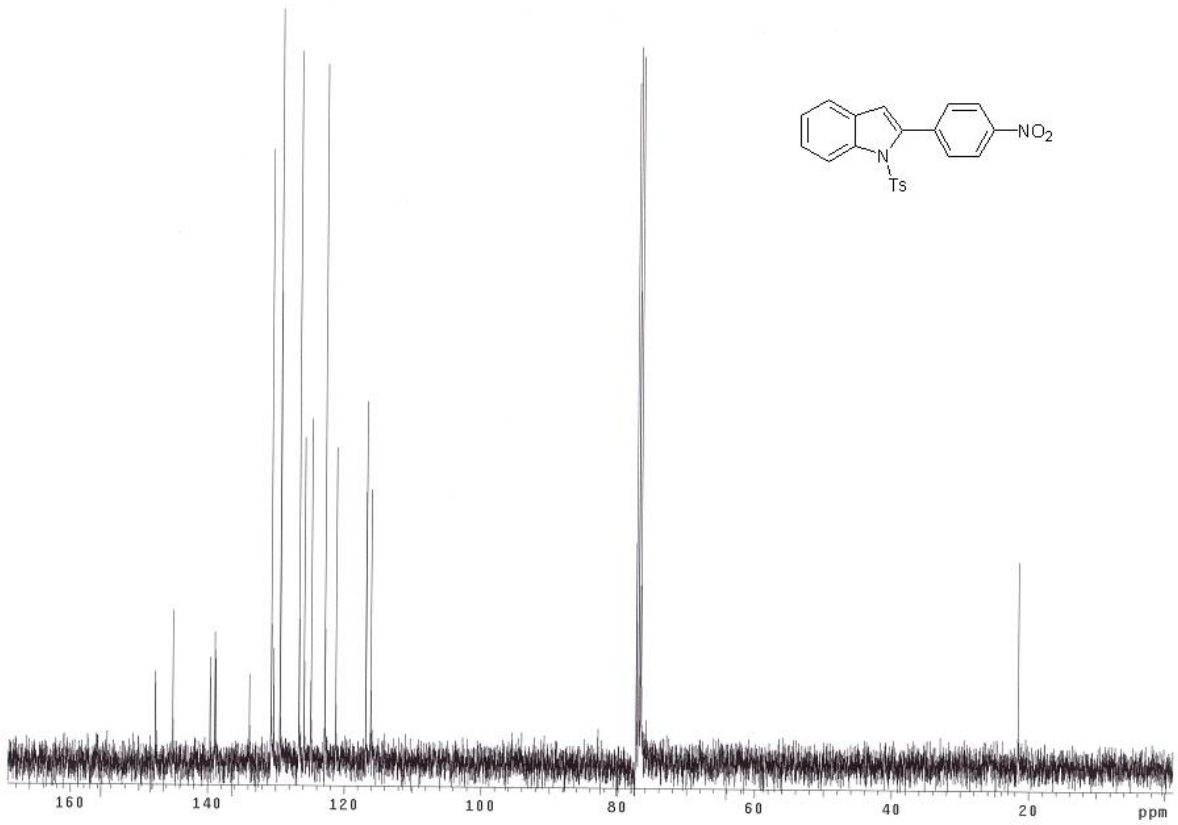
^{1}H NMR Spectrum of Compound **2g** ($CDCl_3$, 400 MHz)



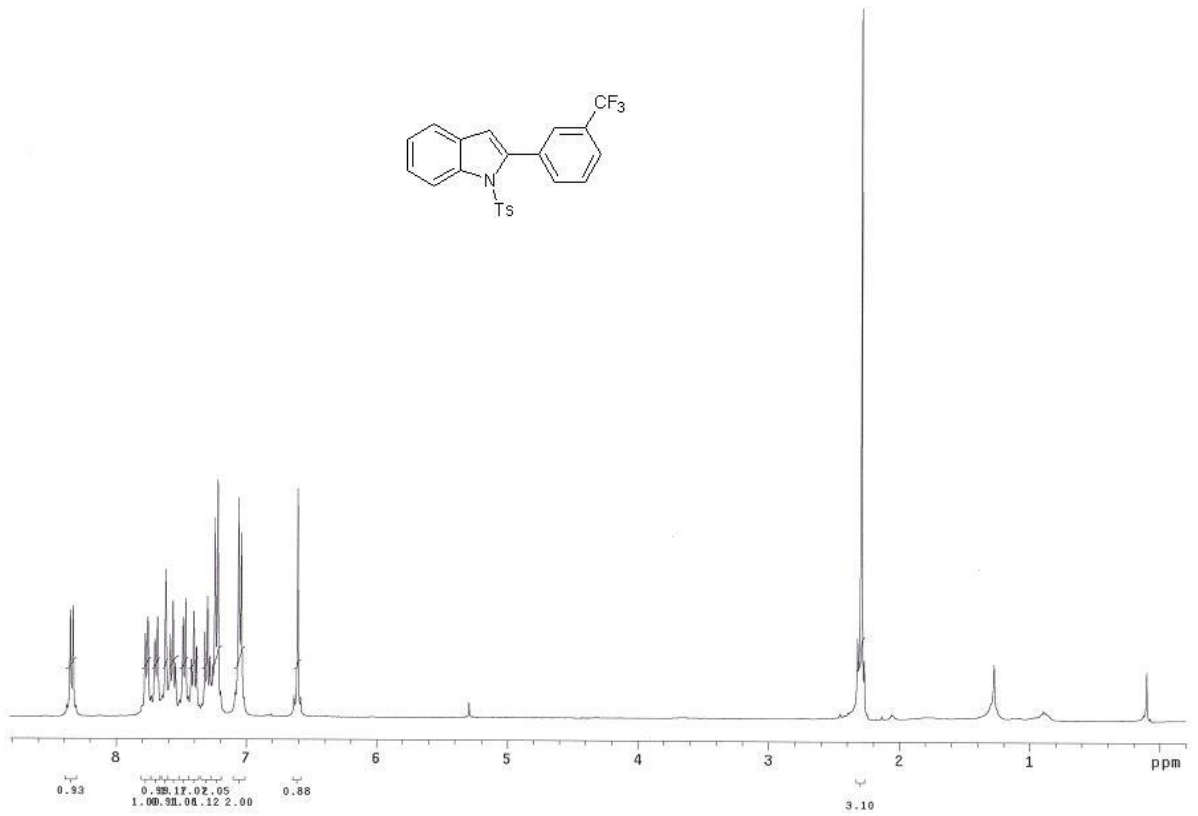
^{13}C NMR Spectrum of Compound **2g** ($CDCl_3$, 100 MHz)



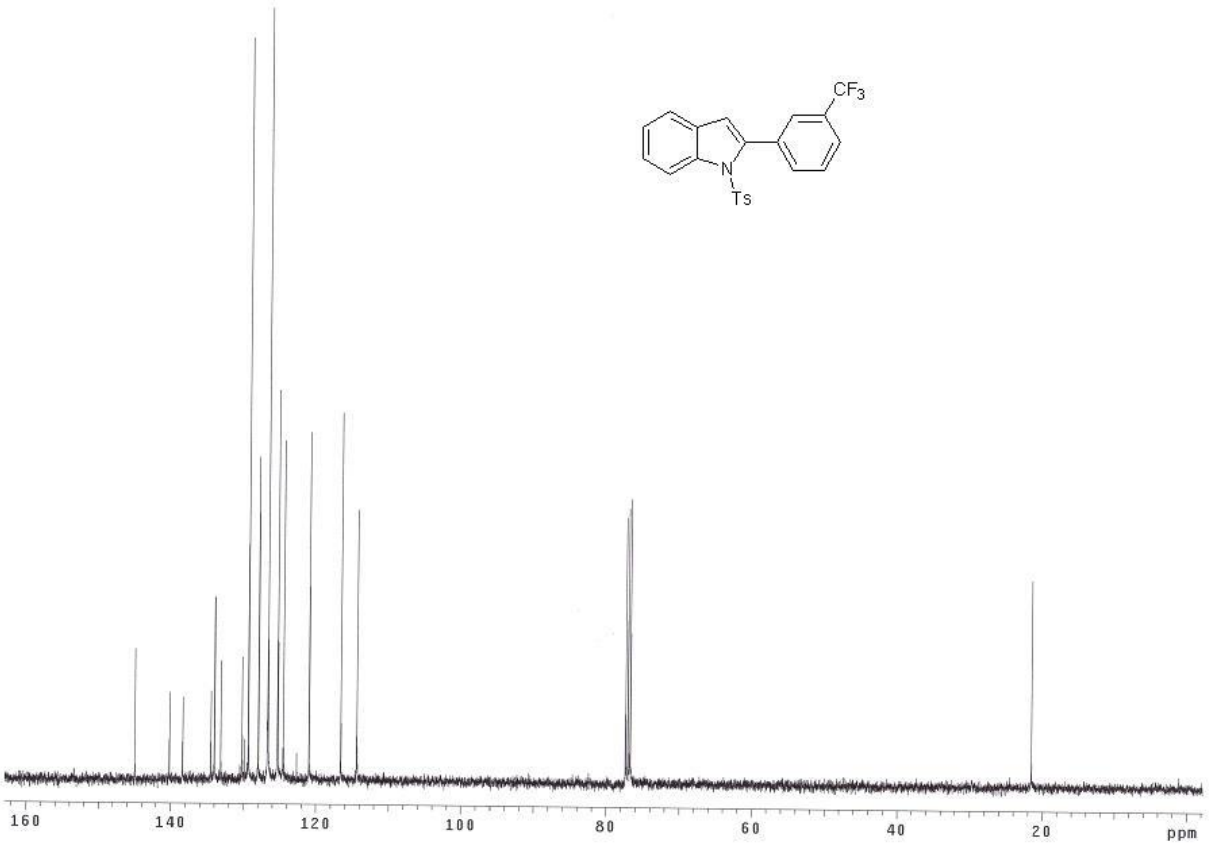
^{1}H NMR Spectrum of Compound **2h** ($CDCl_3$, 400 MHz)



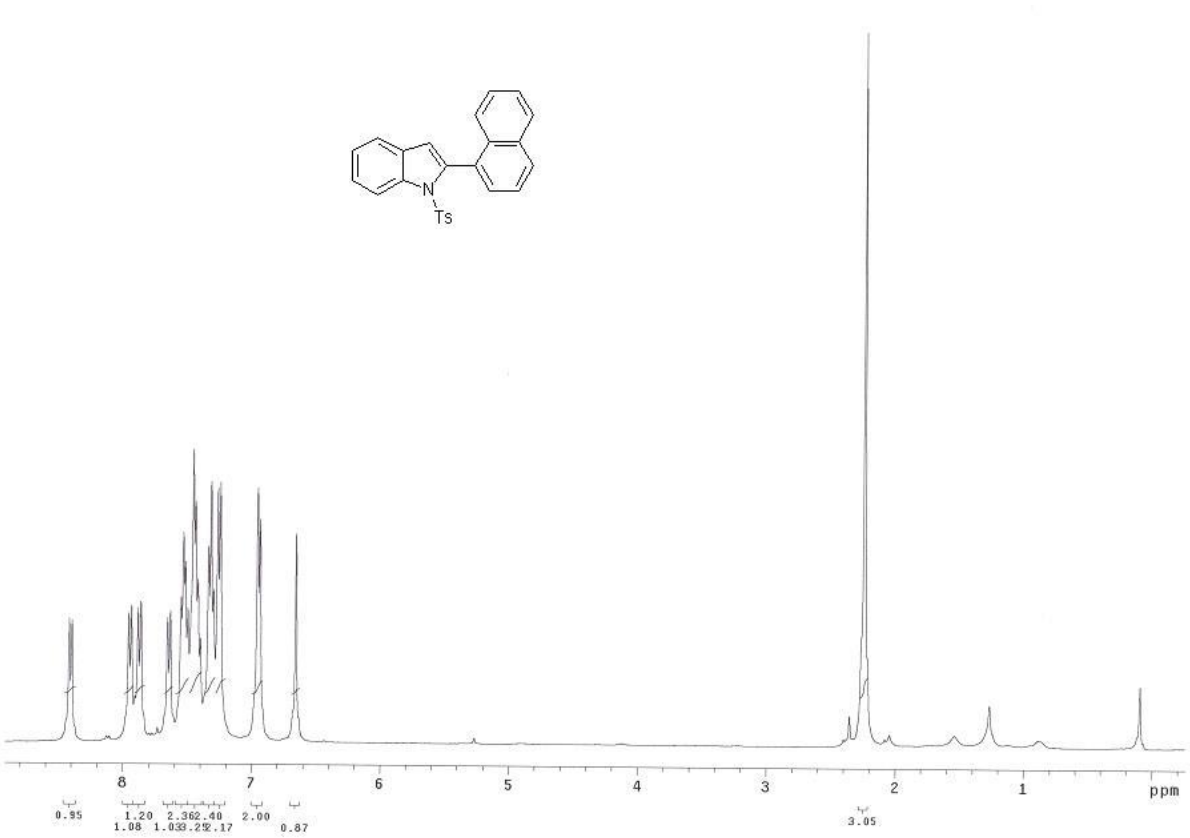
^{13}C NMR Spectrum of Compound **2h** ($CDCl_3$, 100 MHz)



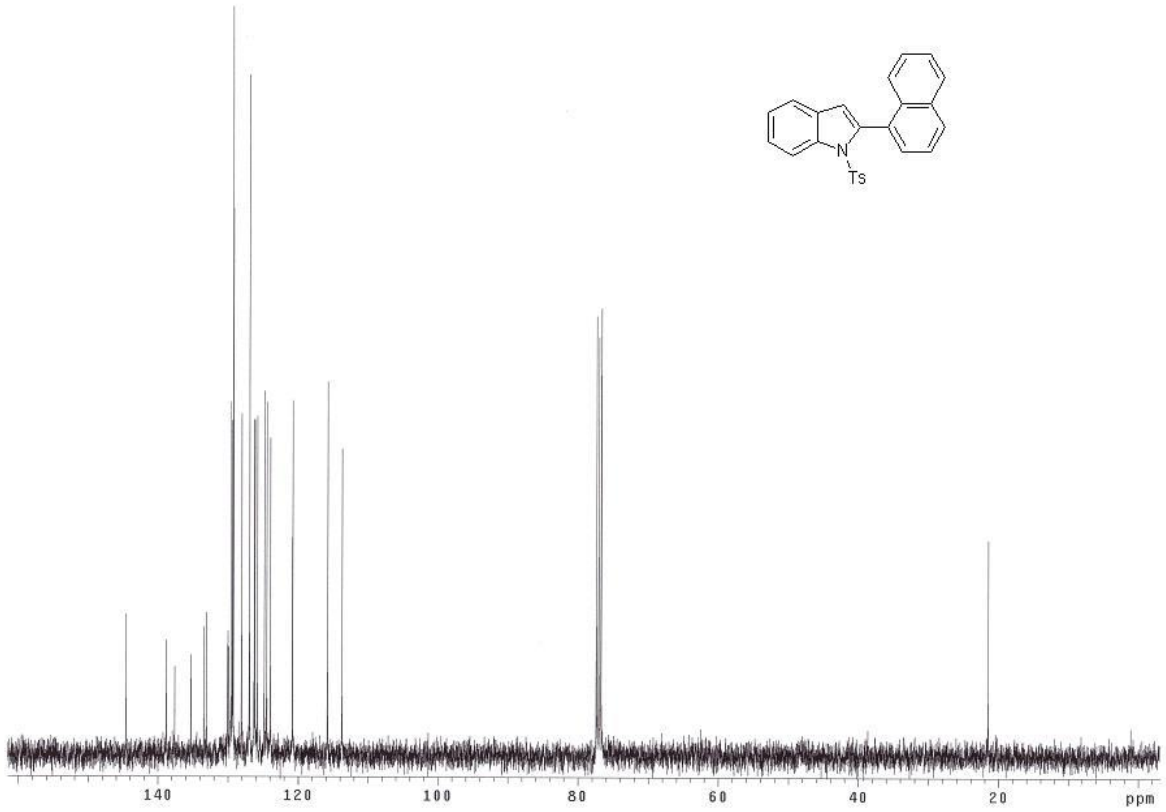
^{1}H NMR Spectrum of Compound **2i** ($CDCl_3$, 400 MHz)



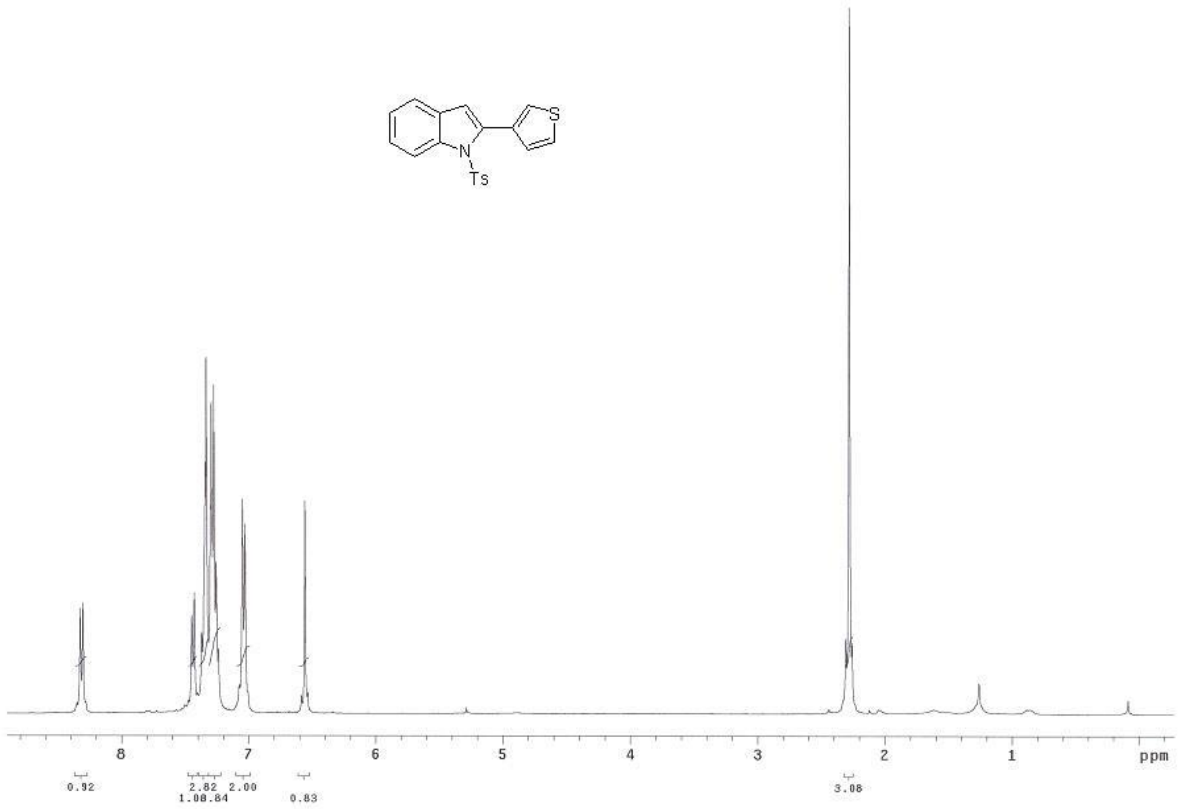
^{13}C NMR Spectrum of Compound **2i** ($CDCl_3$, 100 MHz)



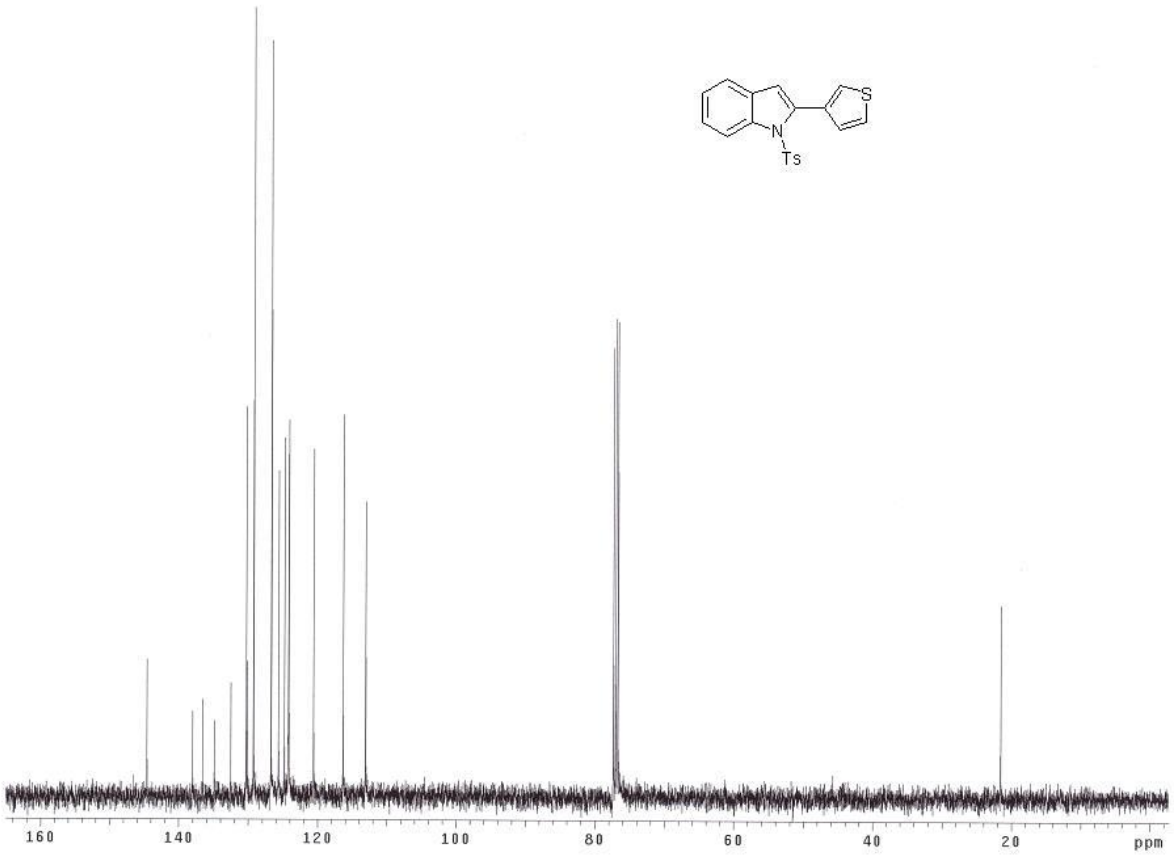
^{1}H NMR Spectrum of Compound **2j** ($CDCl_3$, 400 MHz)



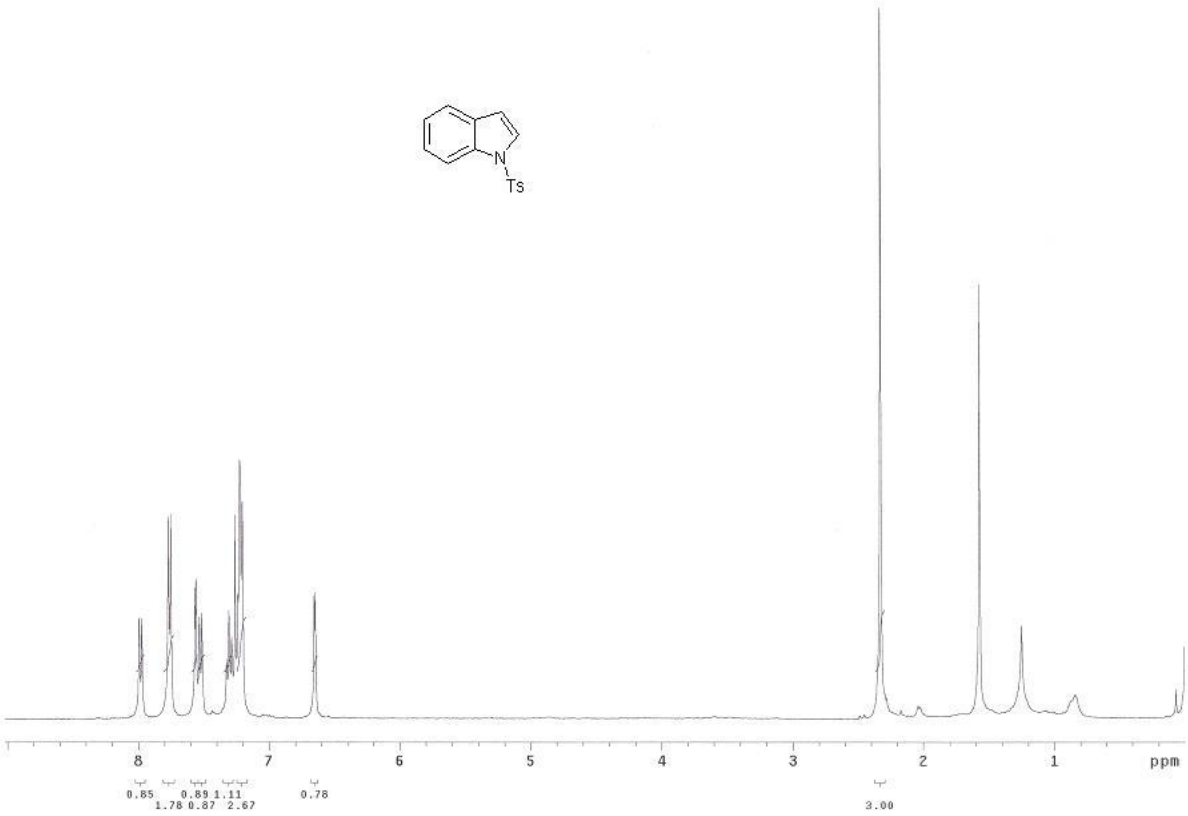
^{13}C NMR Spectrum of Compound **2j** ($CDCl_3$, 100 MHz)



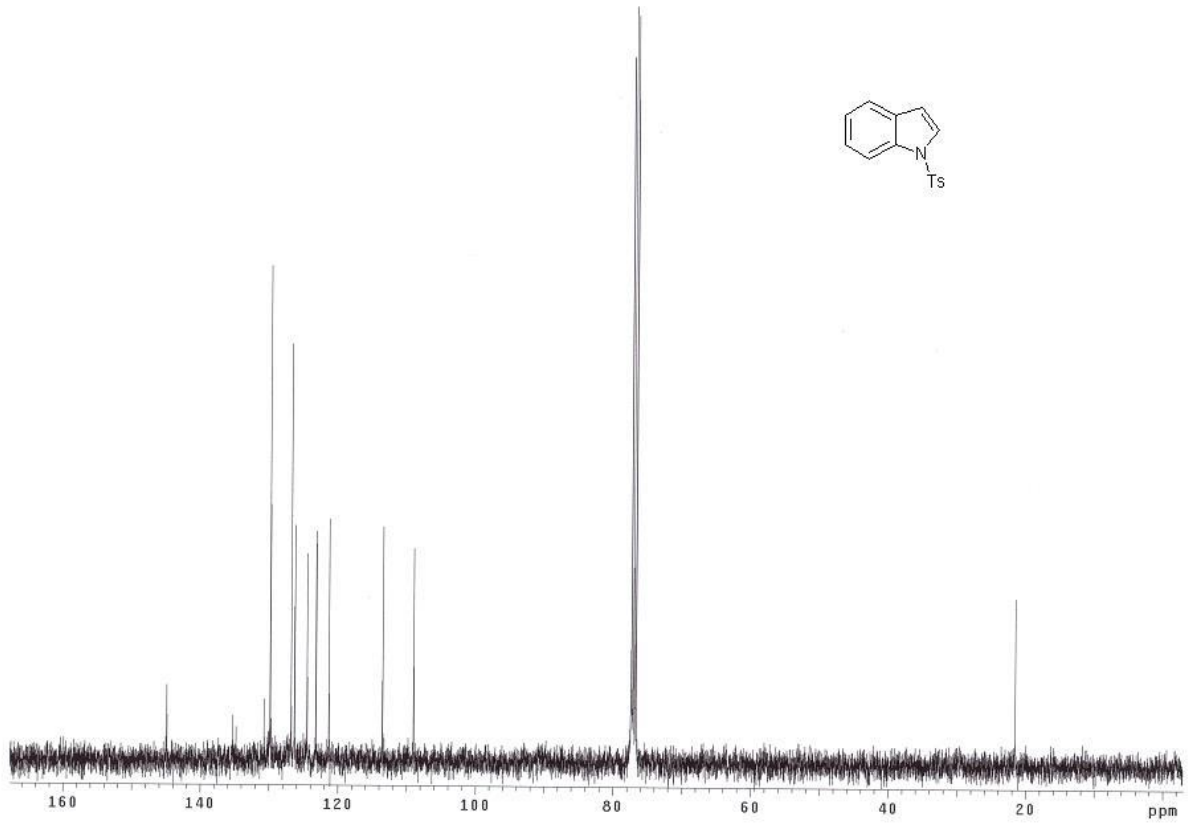
^{1}H NMR Spectrum of Compound **2k** ($CDCl_3$, 400 MHz)



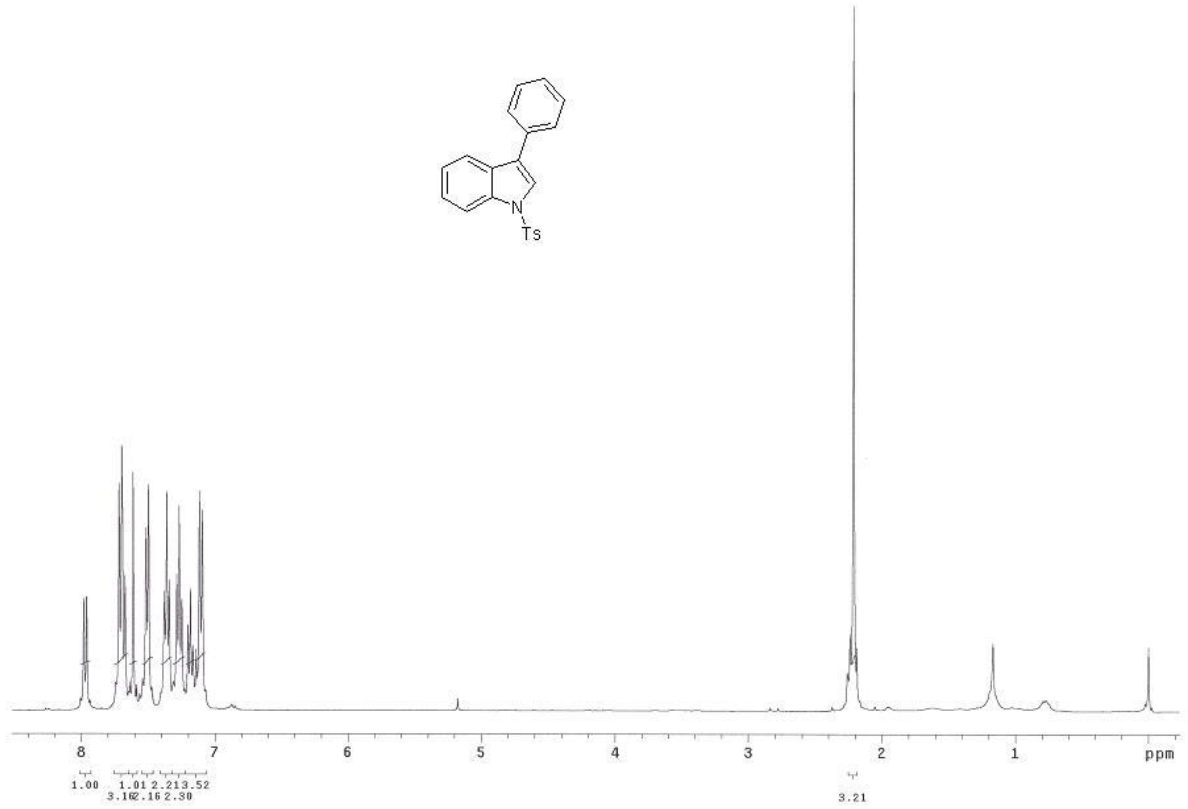
^{13}C NMR Spectrum of Compound **2k** ($CDCl_3$, 100 MHz)



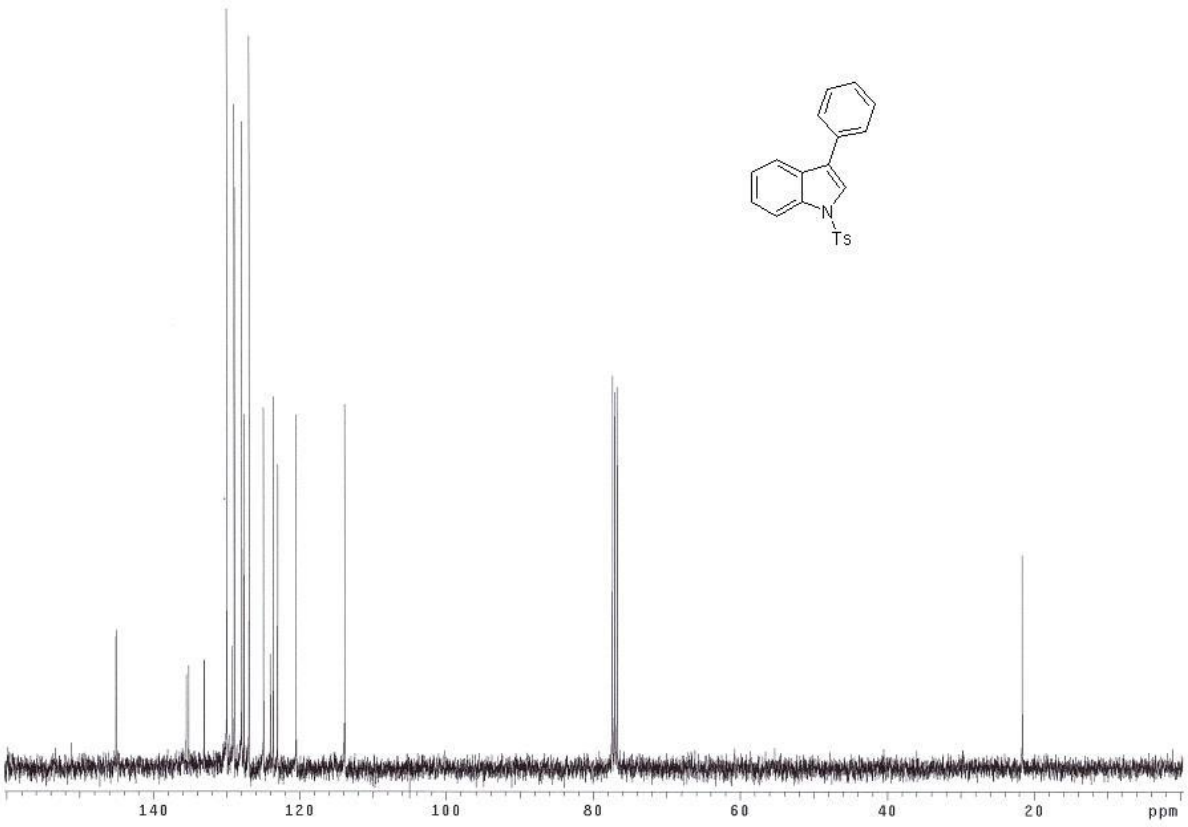
^{1}H NMR Spectrum of Compound **2l** ($CDCl_3$, 400 MHz)



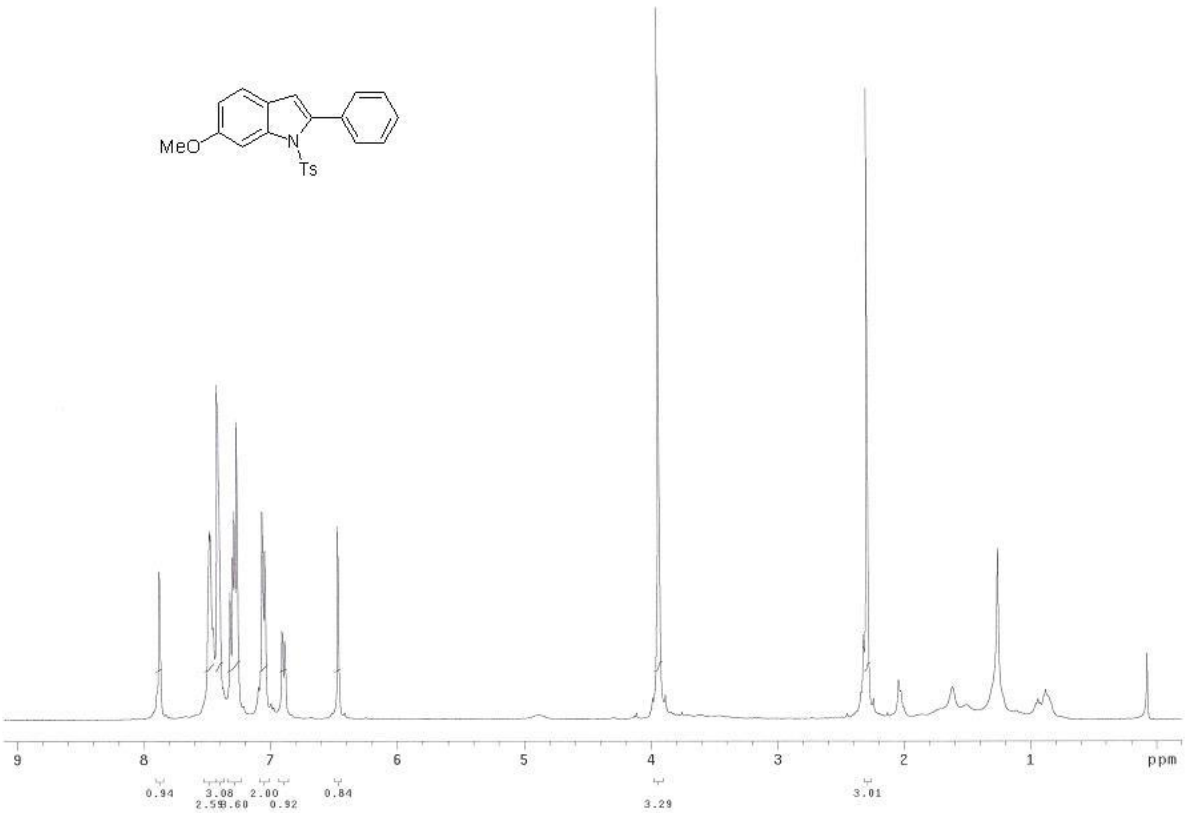
^{13}C NMR Spectrum of Compound **2l** ($CDCl_3$, 100 MHz)



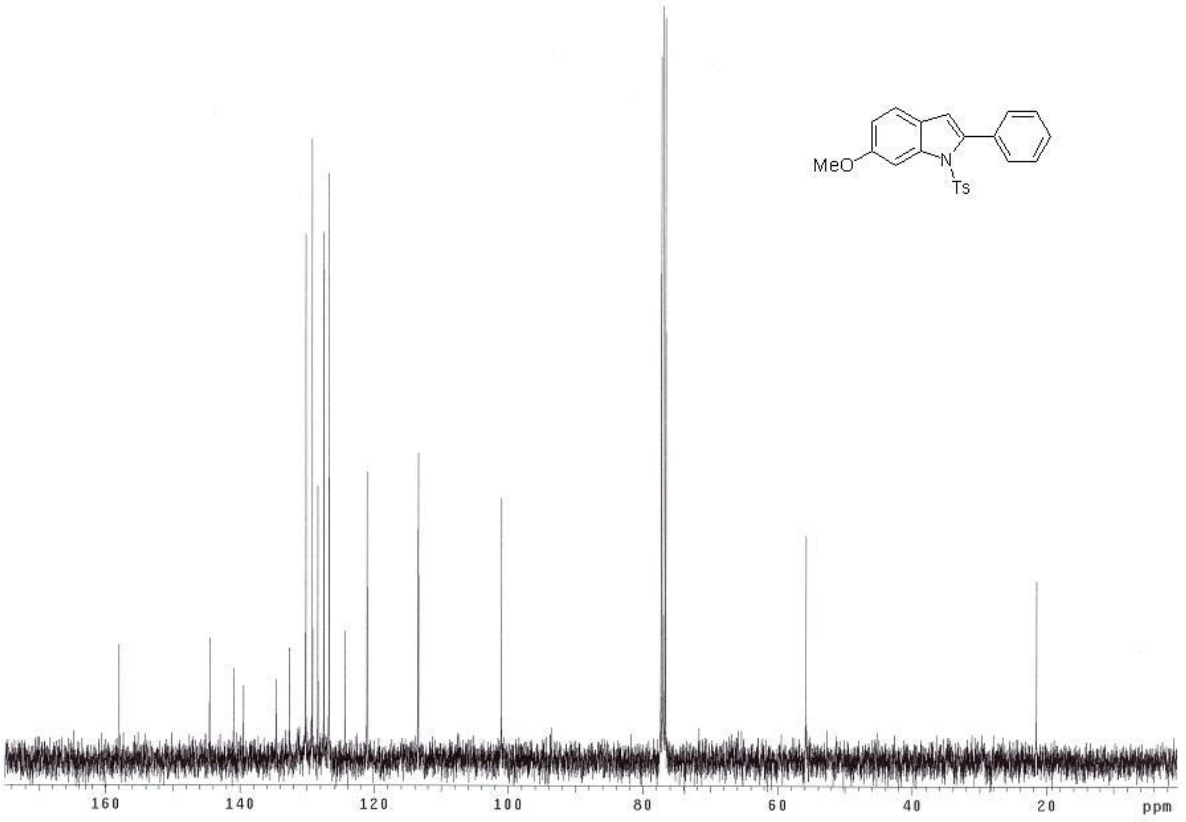
^{1}H NMR Spectrum of Compound **2m** ($CDCl_3$, 400 MHz)



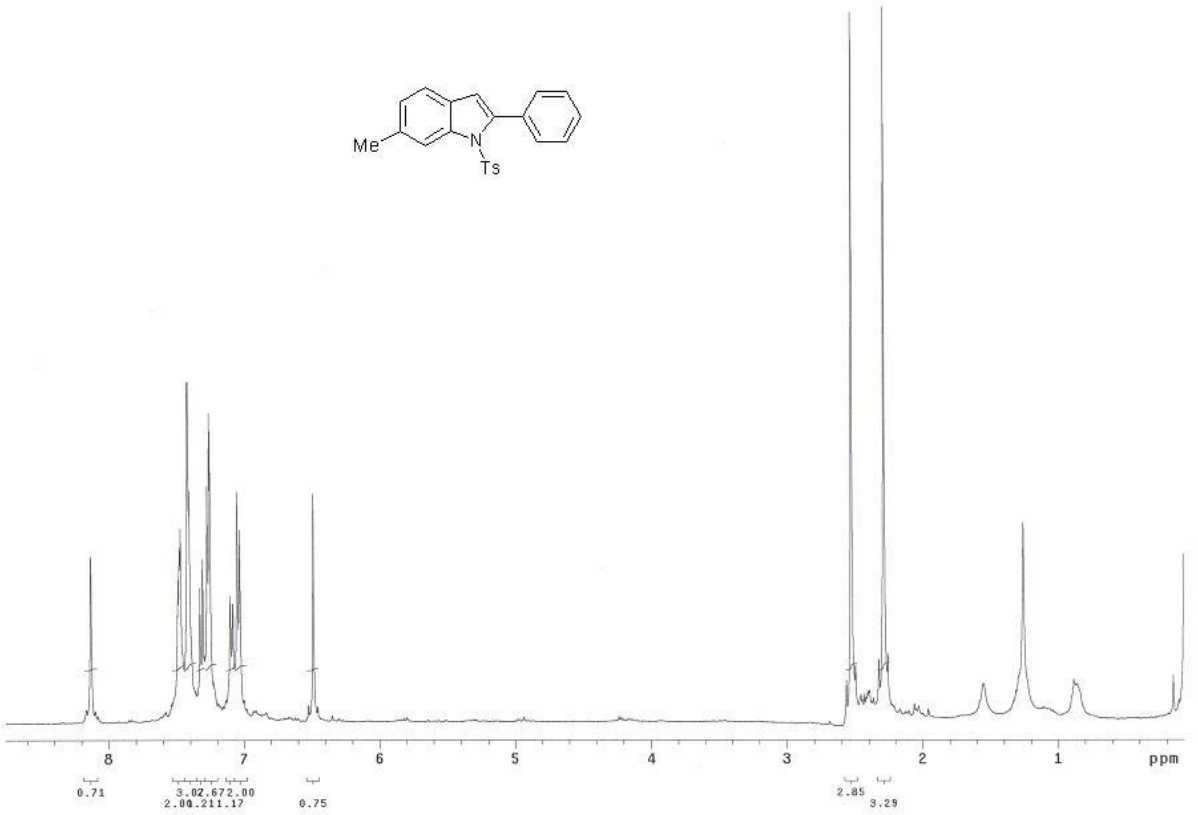
^{13}C NMR Spectrum of Compound **2m** ($CDCl_3$, 100 MHz)



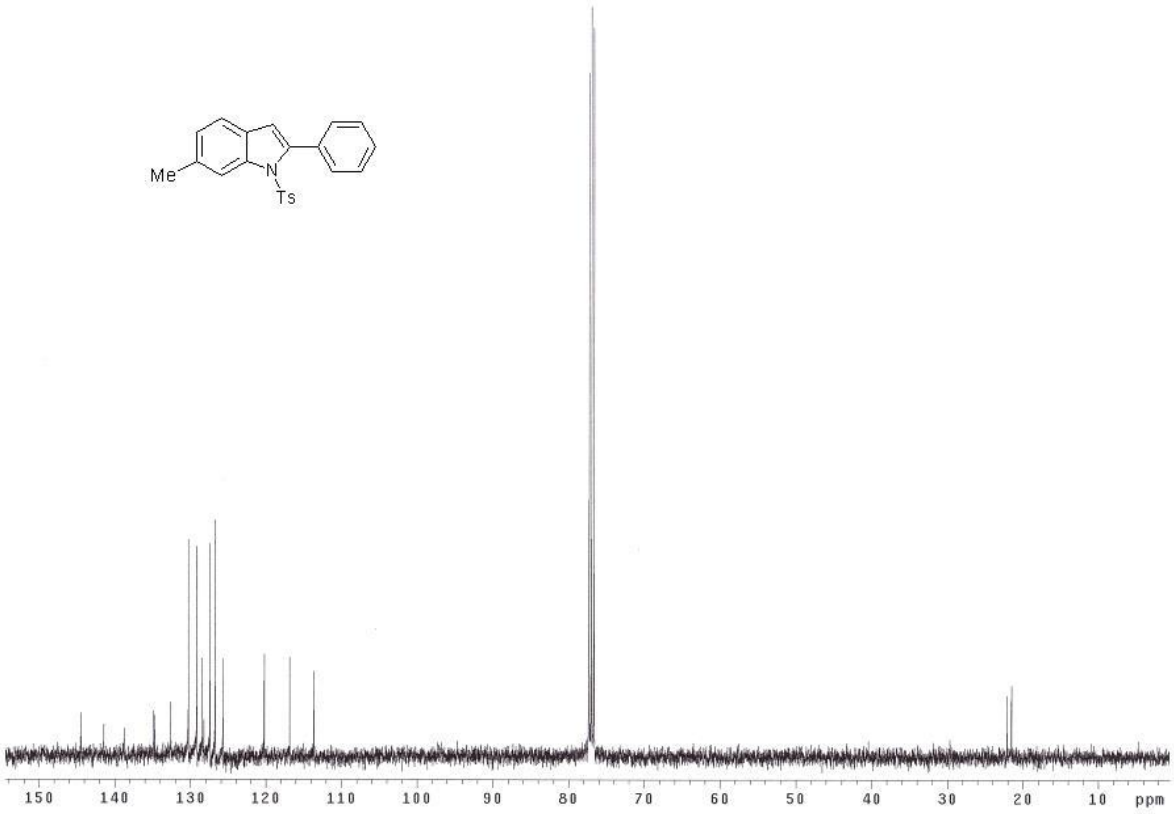
^{1}H NMR Spectrum of Compound **2n** ($CDCl_3$, 400 MHz)



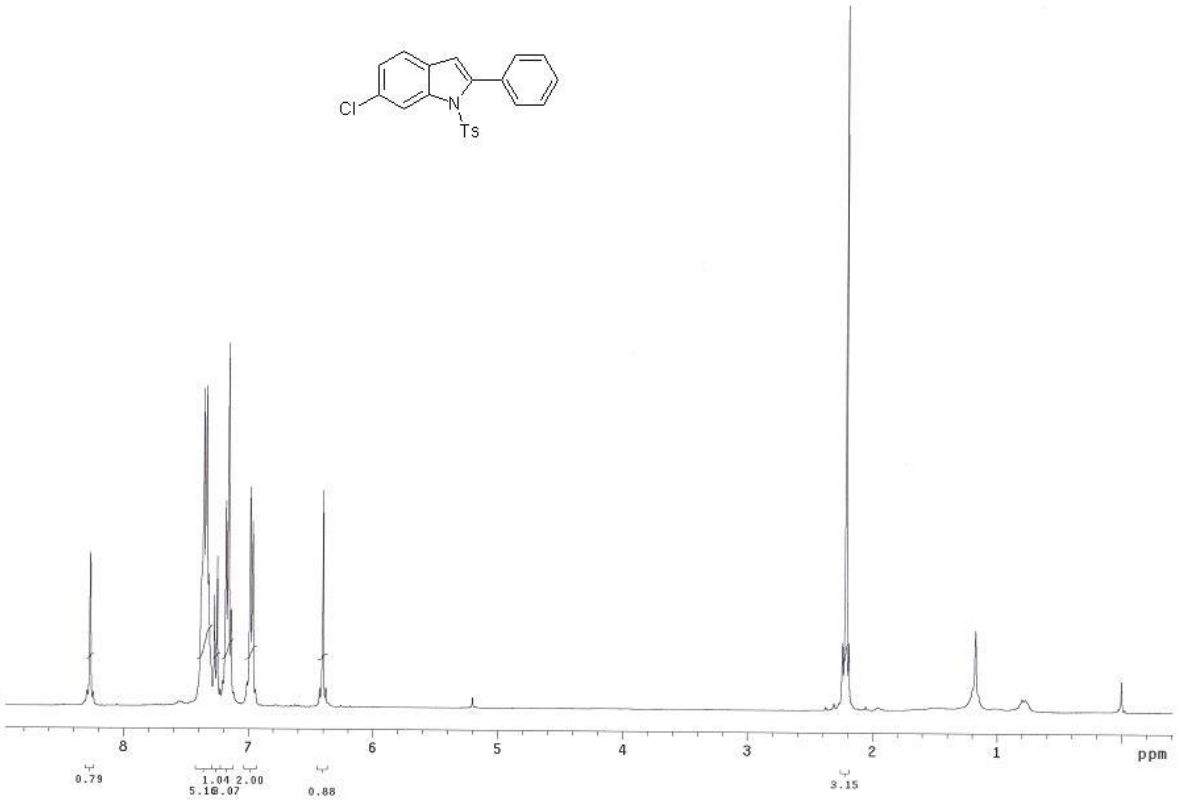
^{13}C NMR Spectrum of Compound **2n** ($CDCl_3$, 100 MHz)



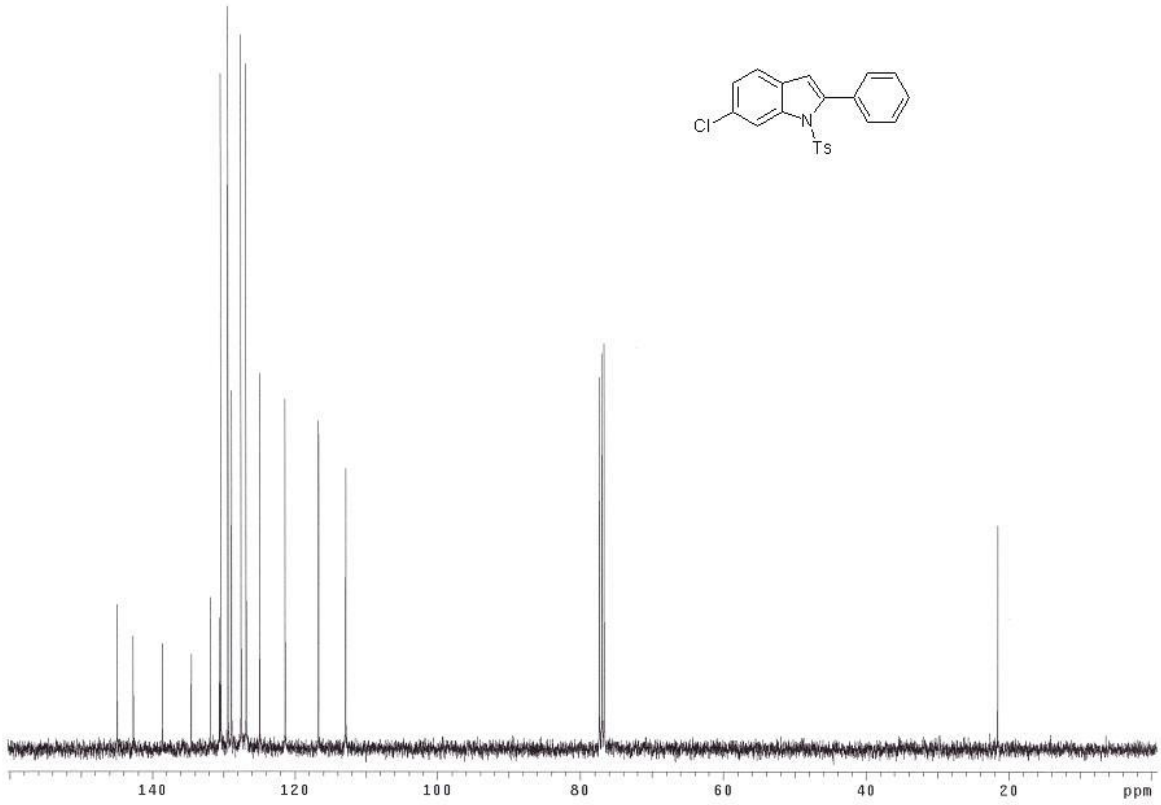
^{1}H NMR Spectrum of Compound **2o** ($CDCl_3$, 400 MHz)



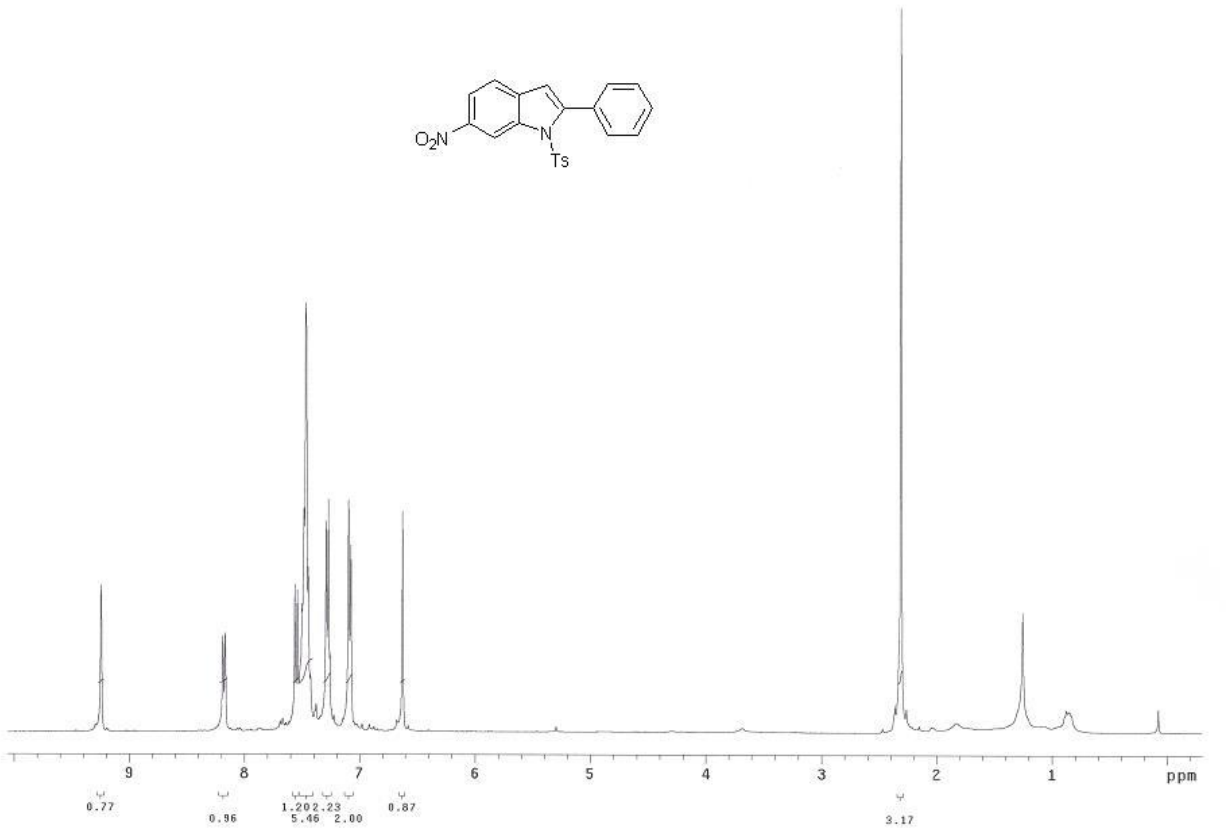
^{13}C NMR Spectrum of Compound **2o** ($CDCl_3$, 100 MHz)



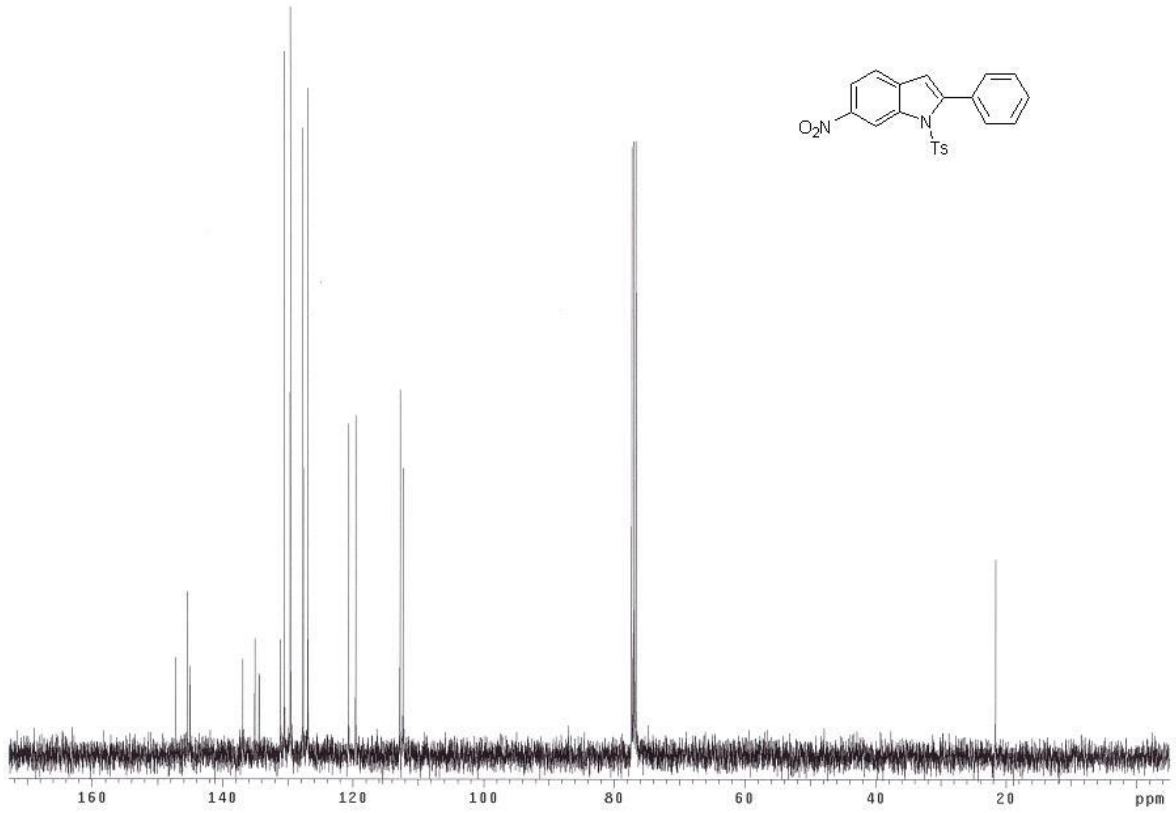
^{1}H NMR Spectrum of Compound **2p** ($CDCl_3$, 400 MHz)



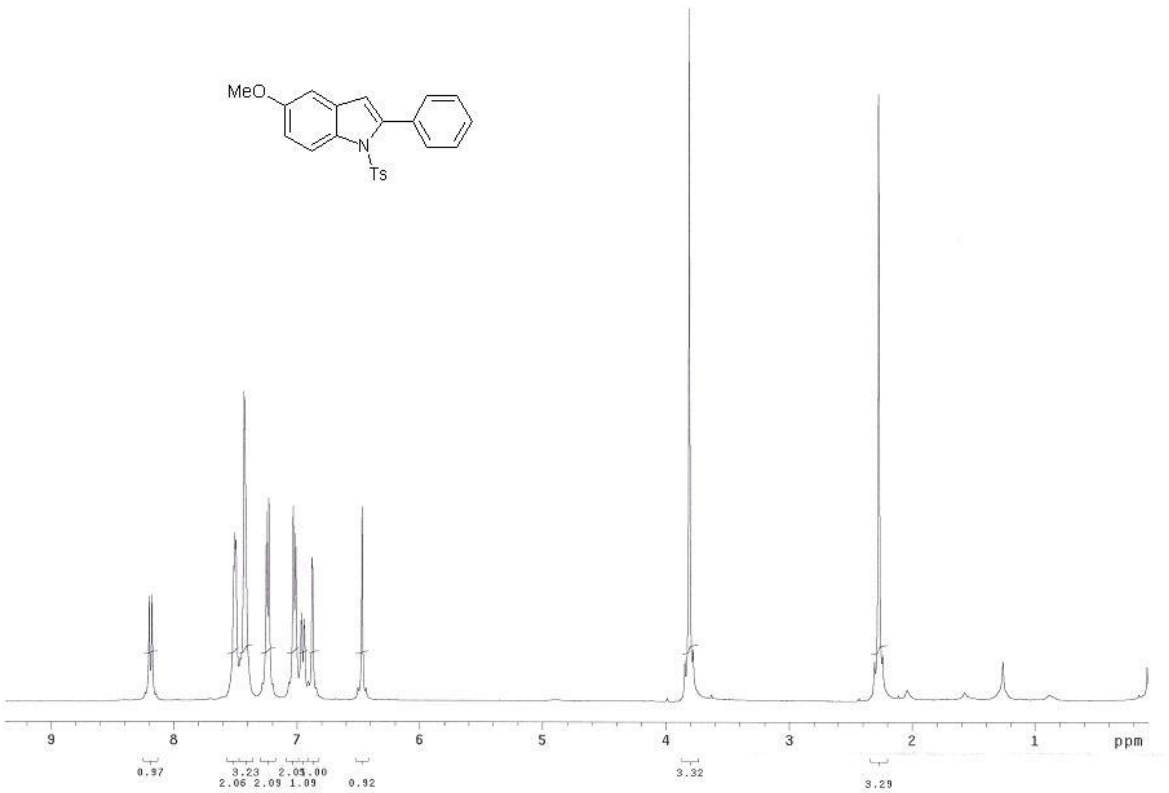
^{13}C NMR Spectrum of Compound **2p** ($CDCl_3$, 100 MHz)



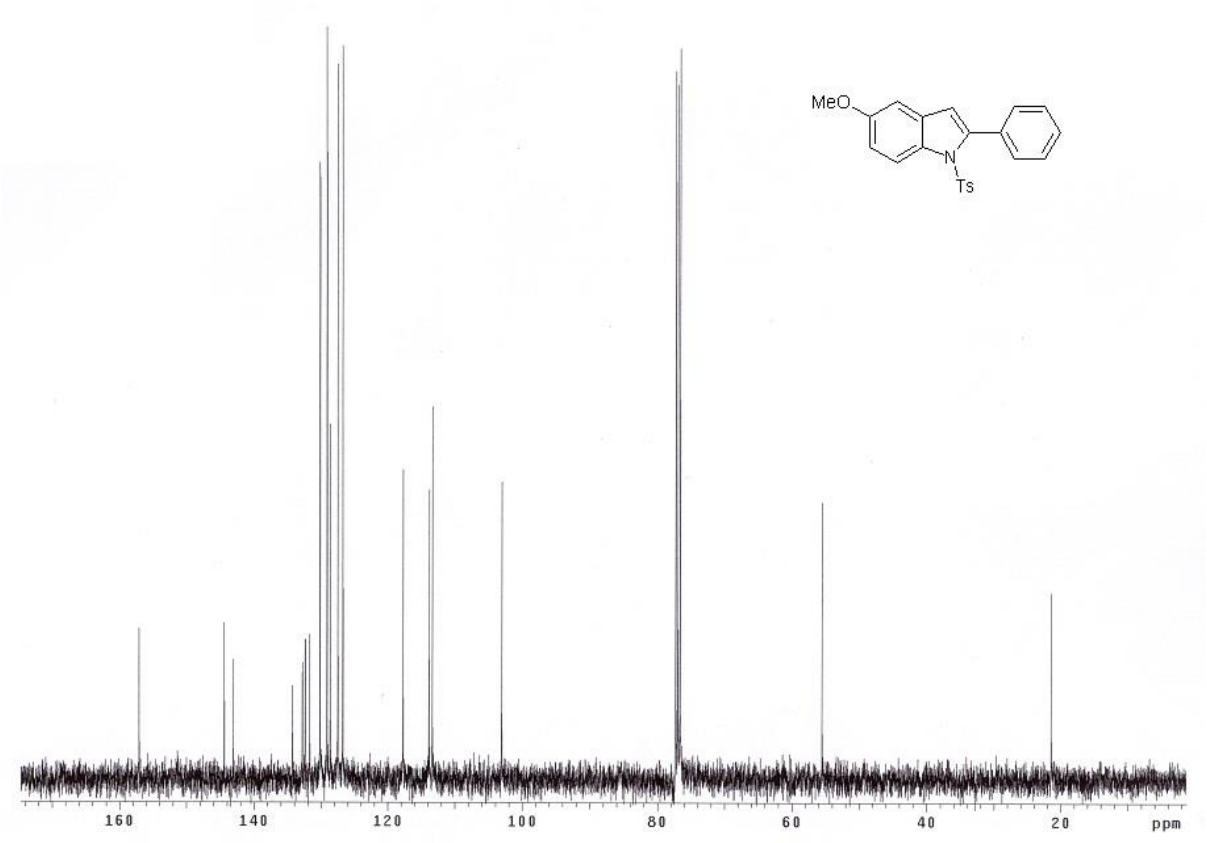
^{1}H NMR Spectrum of Compound **2q** ($CDCl_3$, 400 MHz)



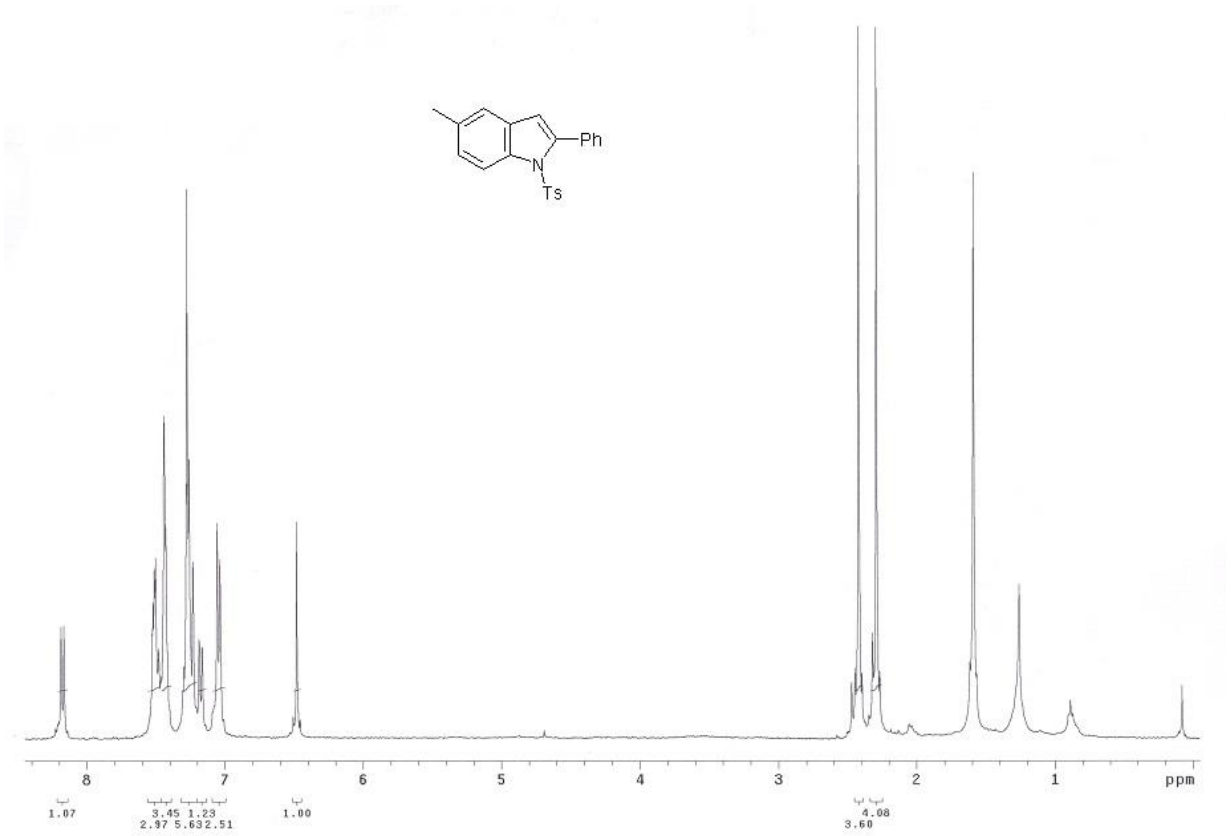
^{13}C NMR Spectrum of Compound **2q** ($CDCl_3$, 100 MHz)



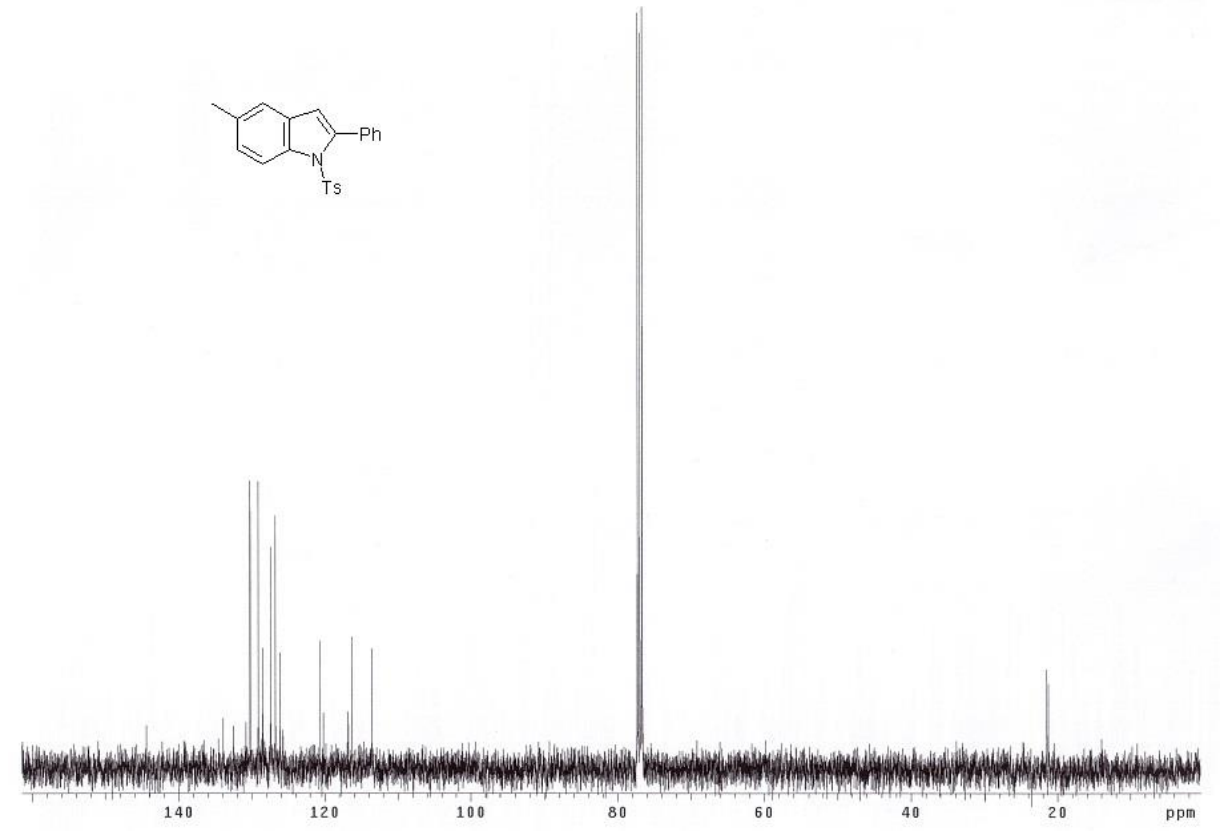
^{1}H NMR Spectrum of Compound **2r** ($CDCl_3$, 400 MHz)



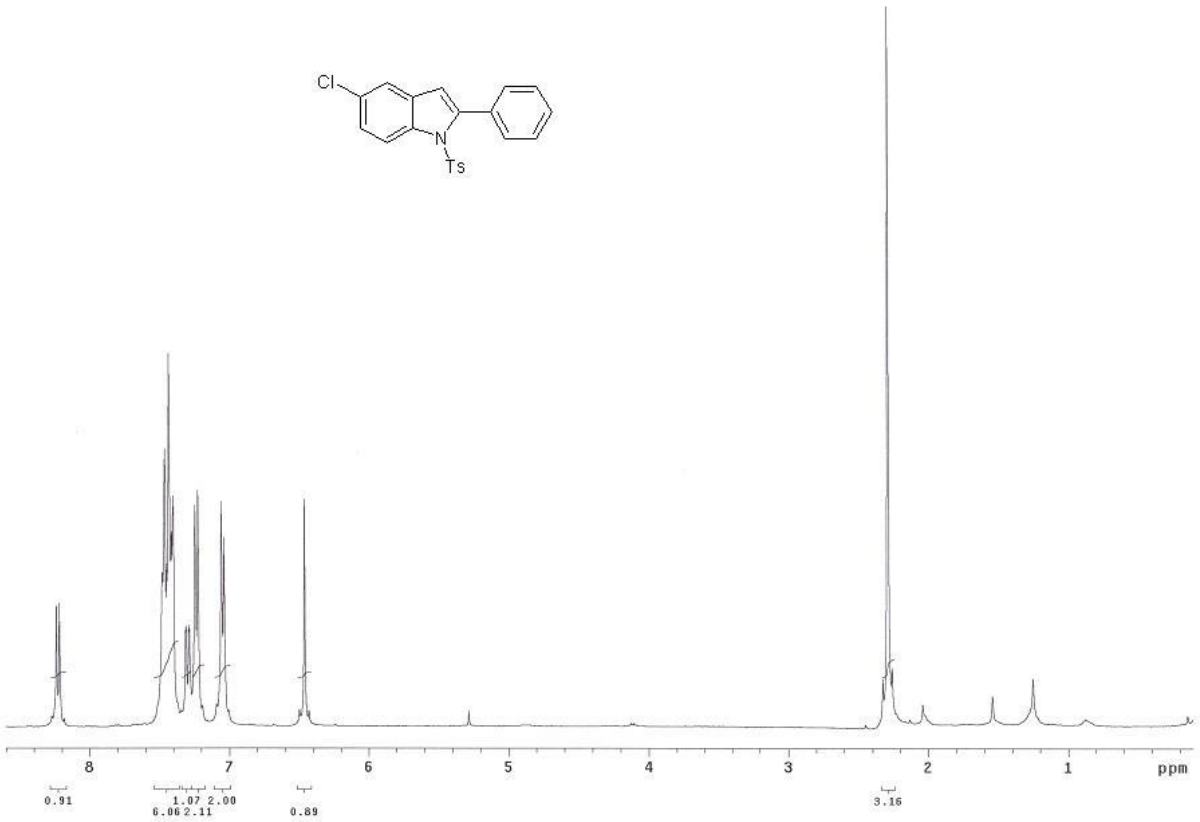
^{13}C NMR Spectrum of Compound **2r** ($CDCl_3$, 100 MHz)



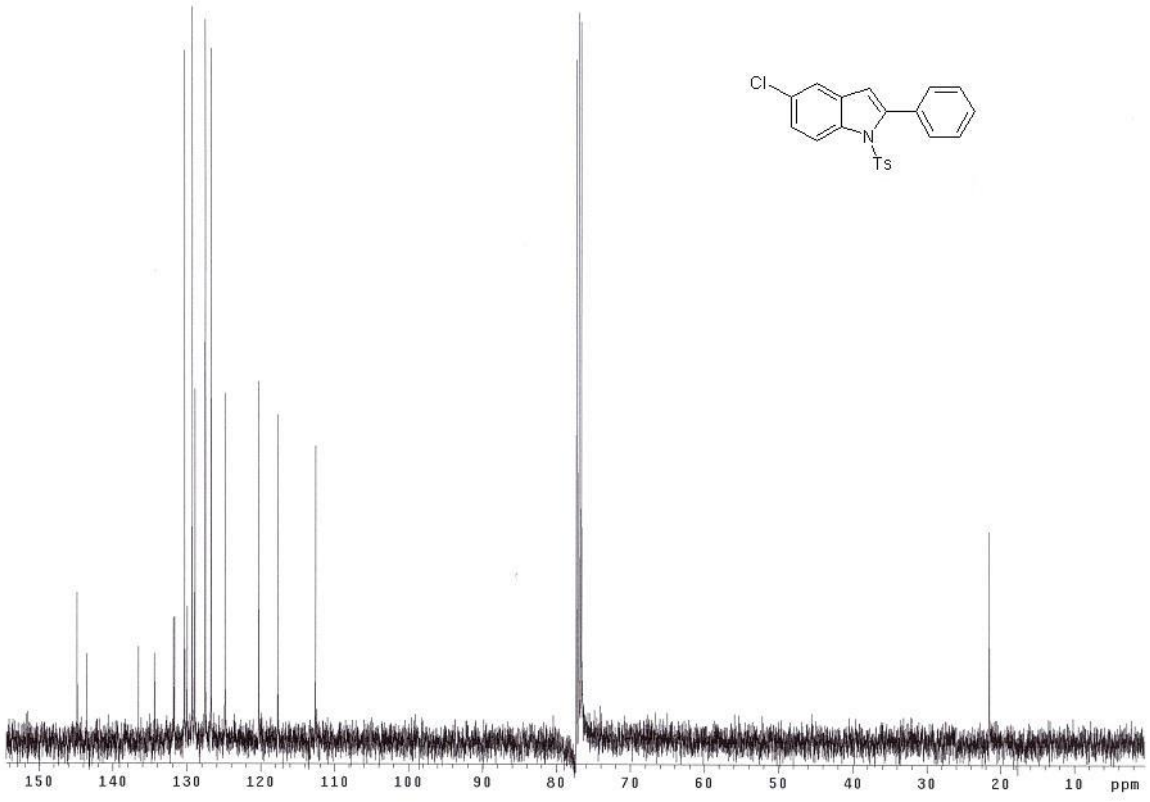
^{1}H NMR Spectrum of Compound **2s** ($CDCl_3$, 400 MHz)



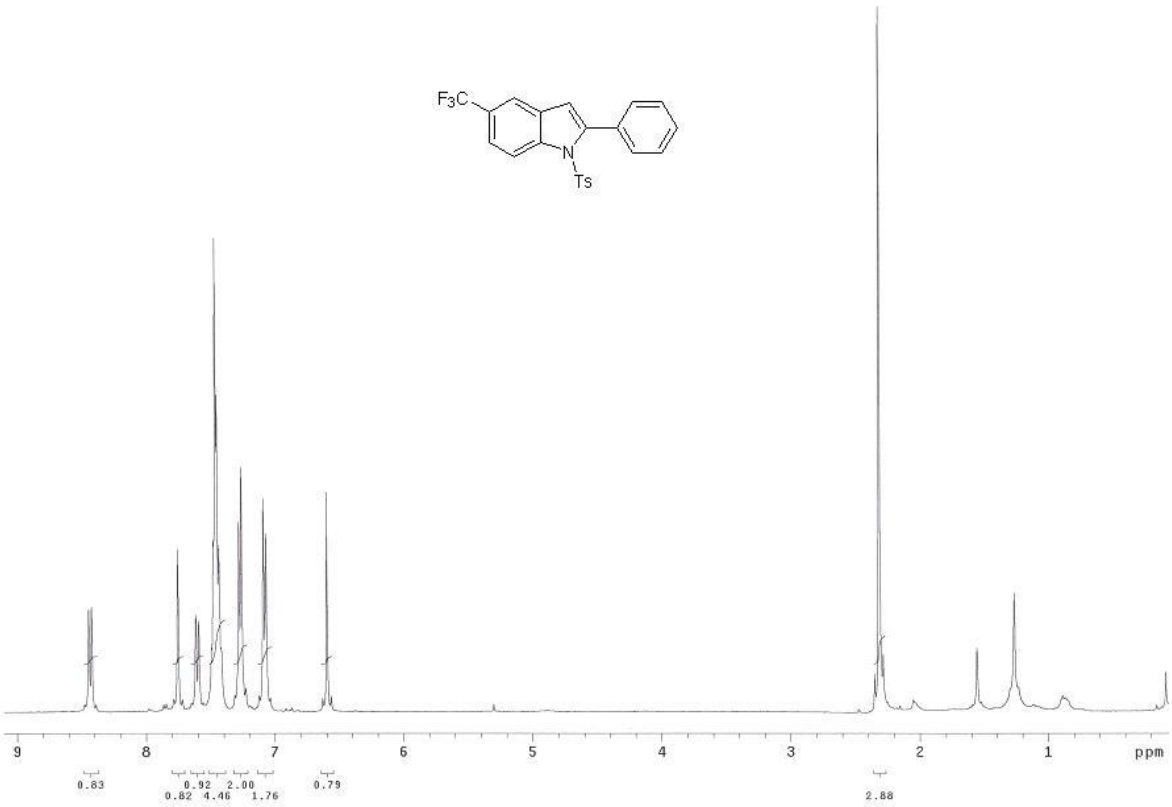
^{13}C NMR Spectrum of Compound **2s** ($CDCl_3$, 100 MHz)



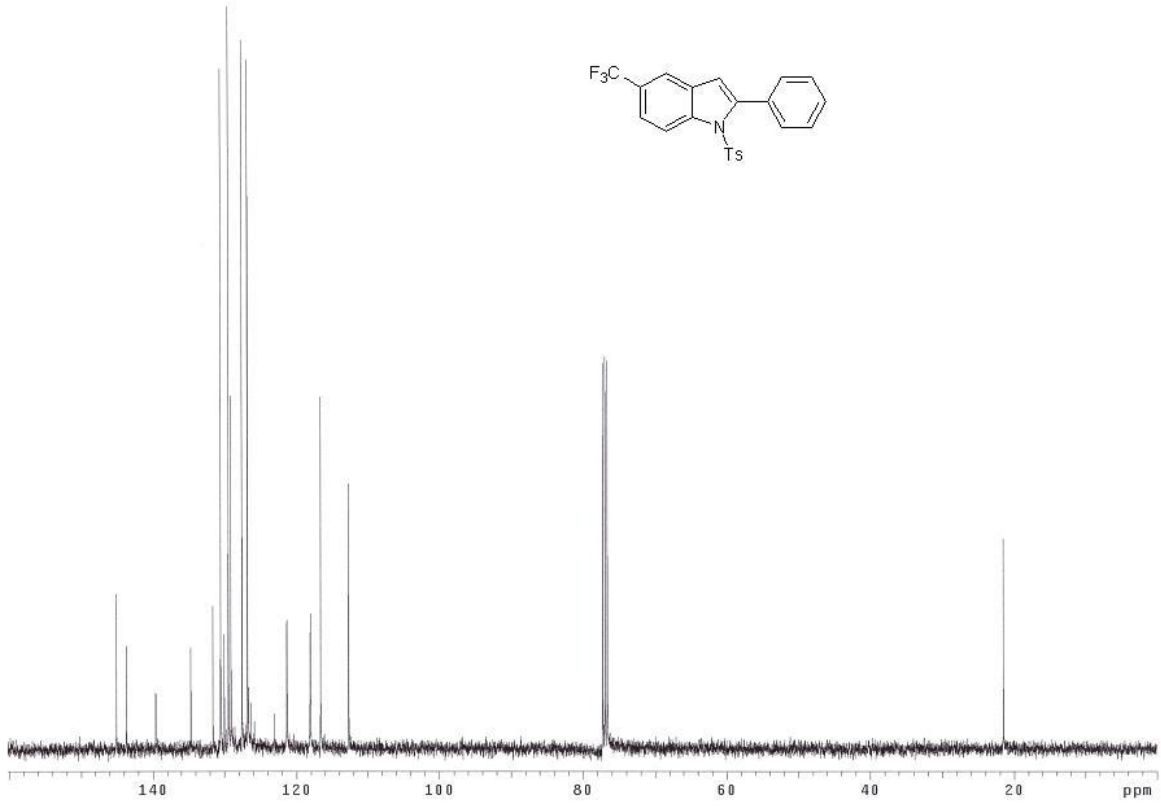
^{1}H NMR Spectrum of Compound **2t** ($CDCl_3$, 400 MHz)



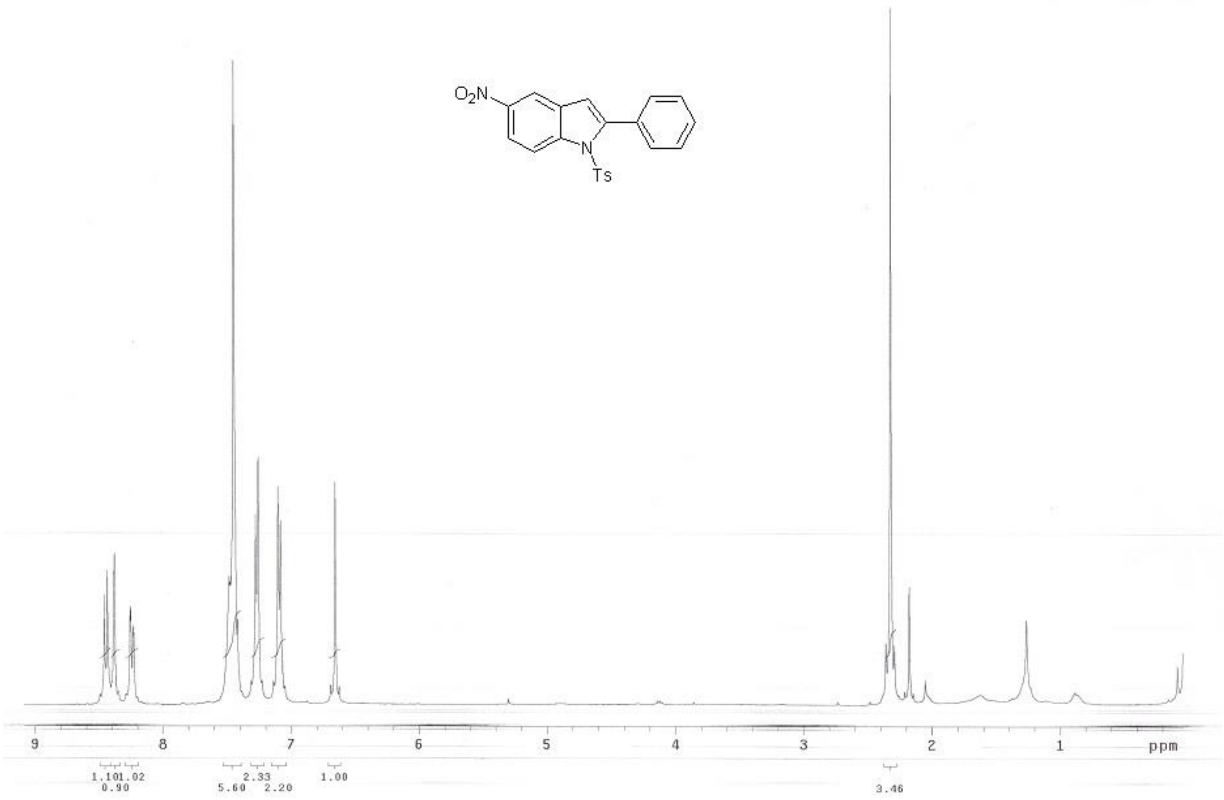
^{13}C NMR Spectrum of Compound **2t** ($CDCl_3$, 100 MHz)



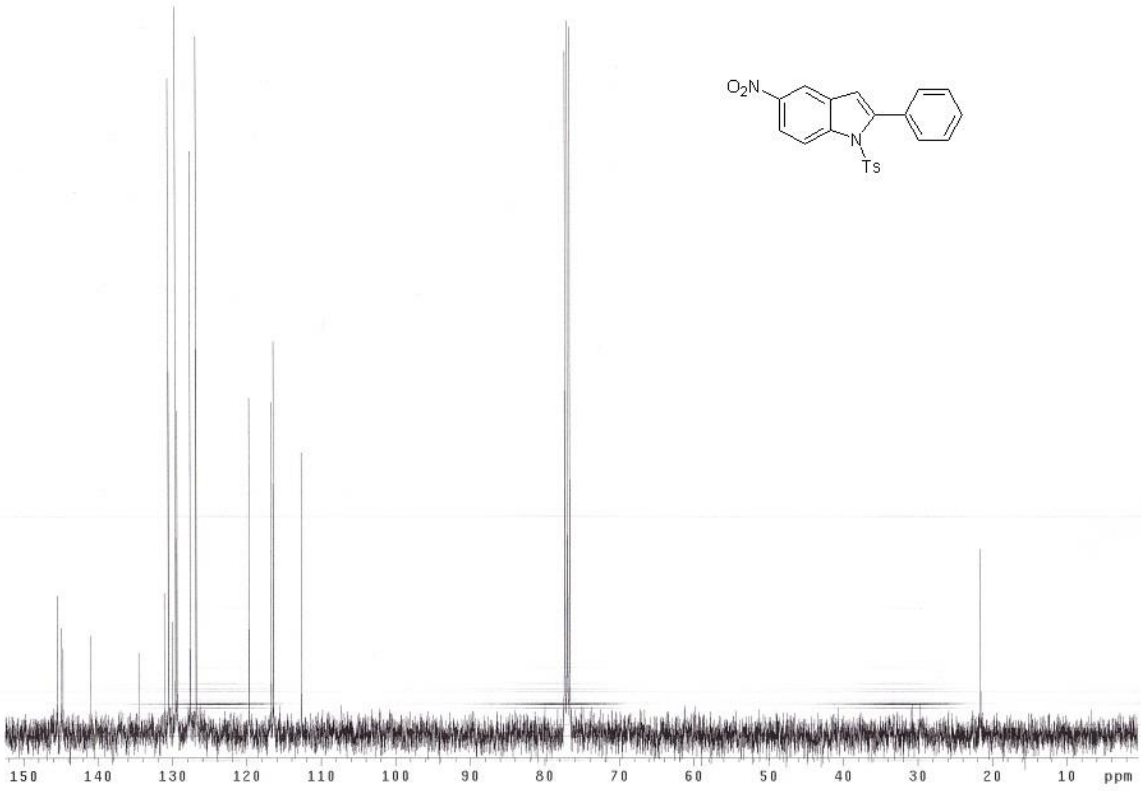
^{1}H NMR Spectrum of Compound **2u** ($CDCl_3$, 400 MHz)



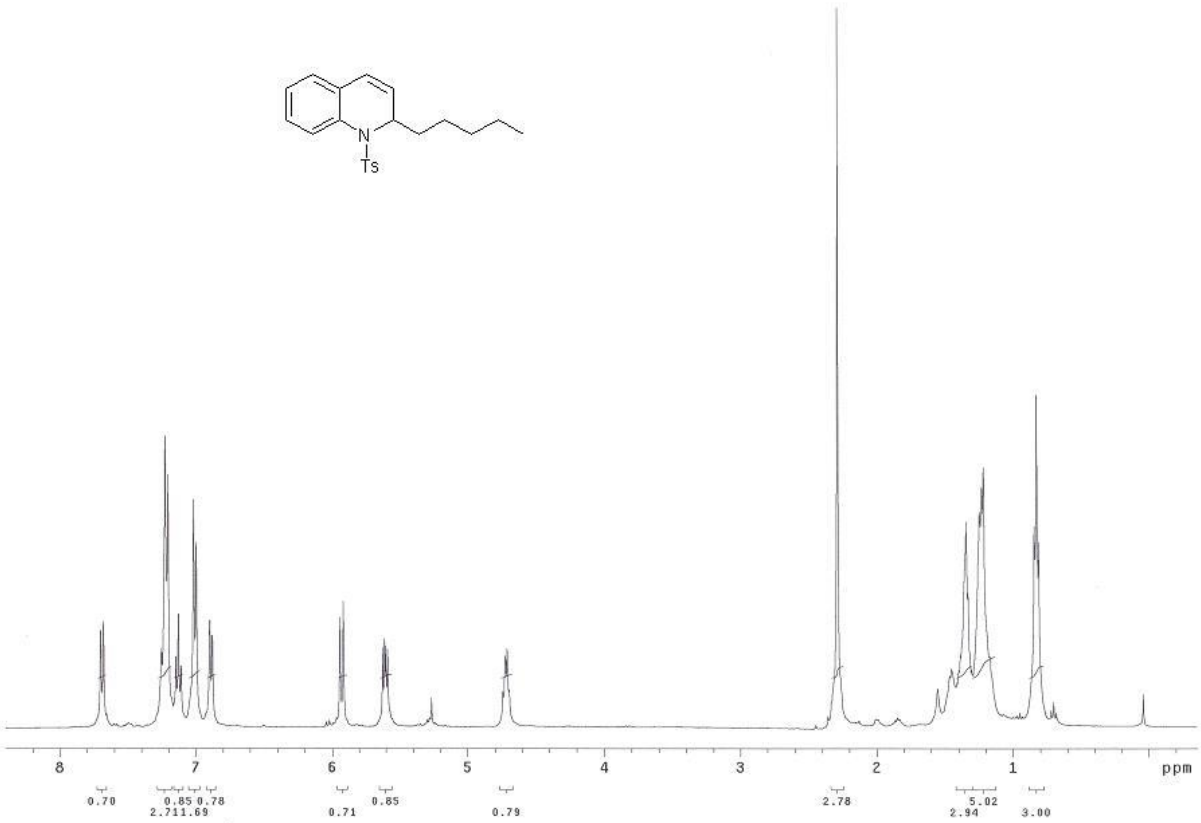
^{13}C NMR Spectrum of Compound **2u** ($CDCl_3$, 100 MHz)



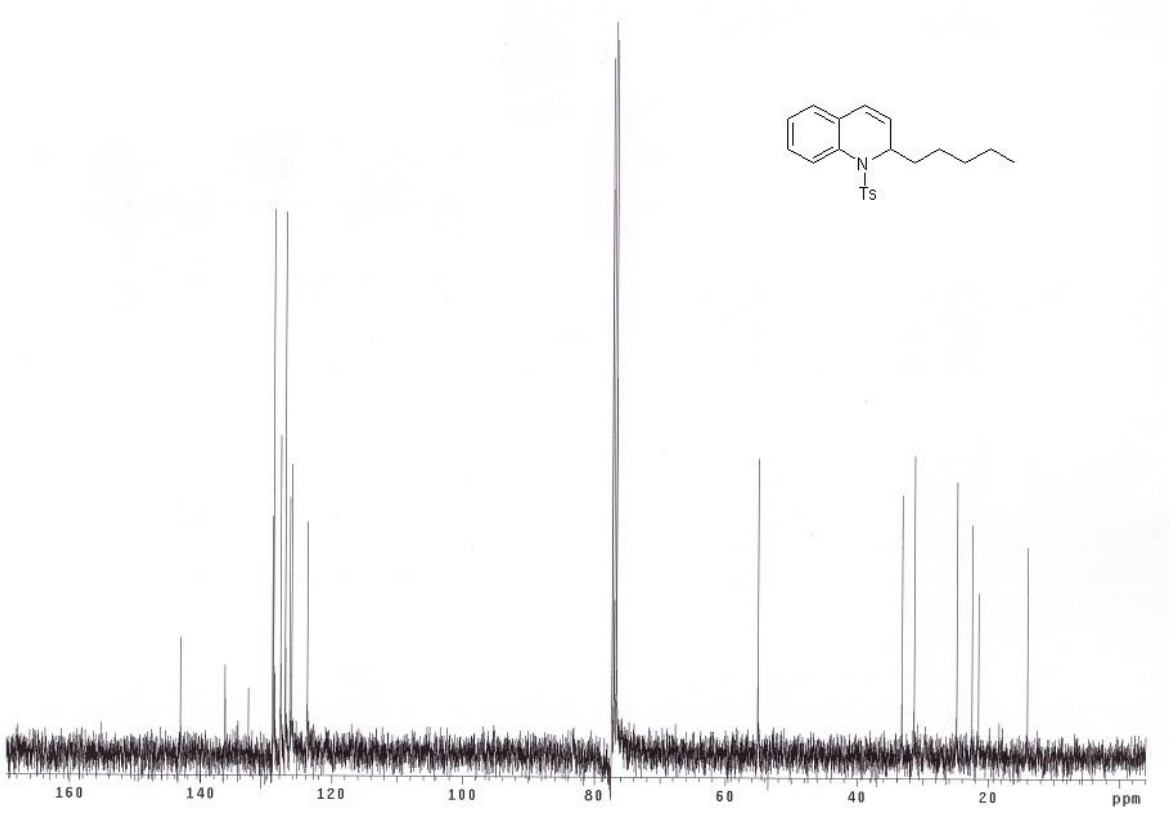
^{1}H NMR Spectrum of Compound **2v** ($CDCl_3$, 400 MHz)



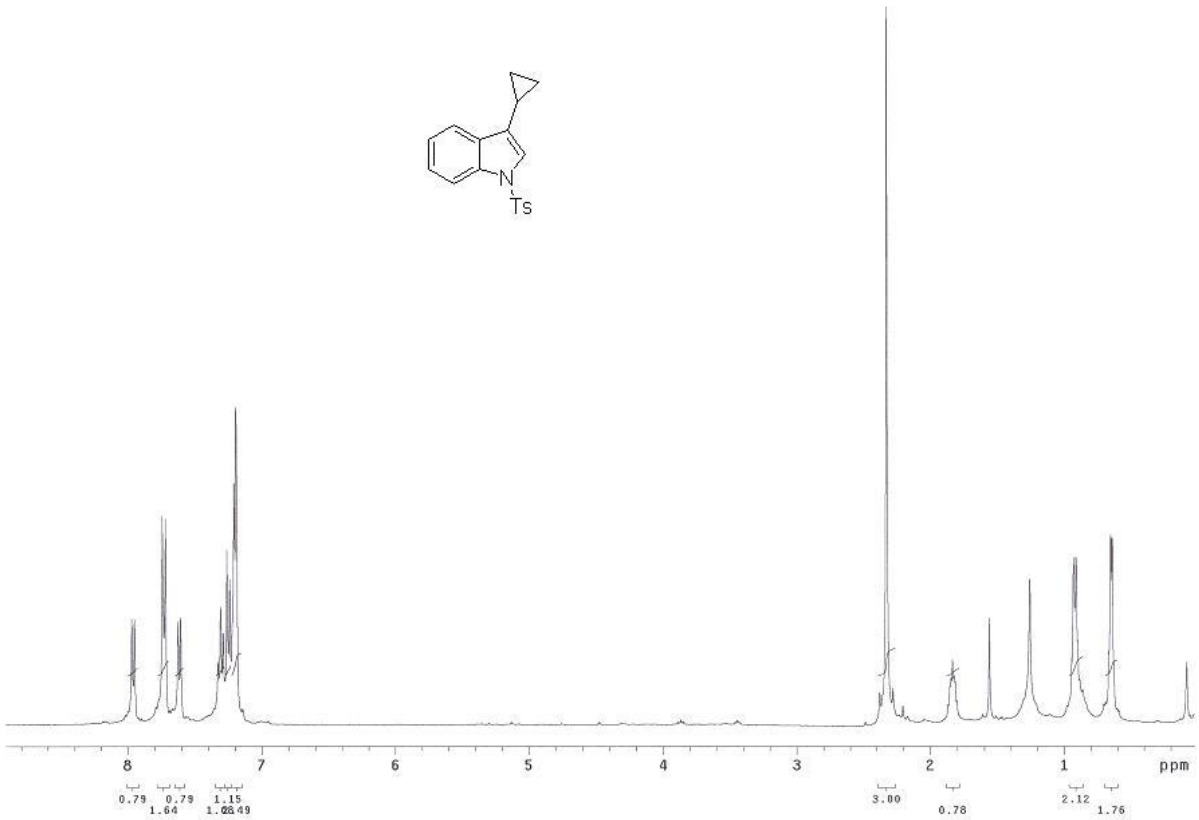
^{13}C NMR Spectrum of Compound **2v** ($CDCl_3$, 100 MHz)



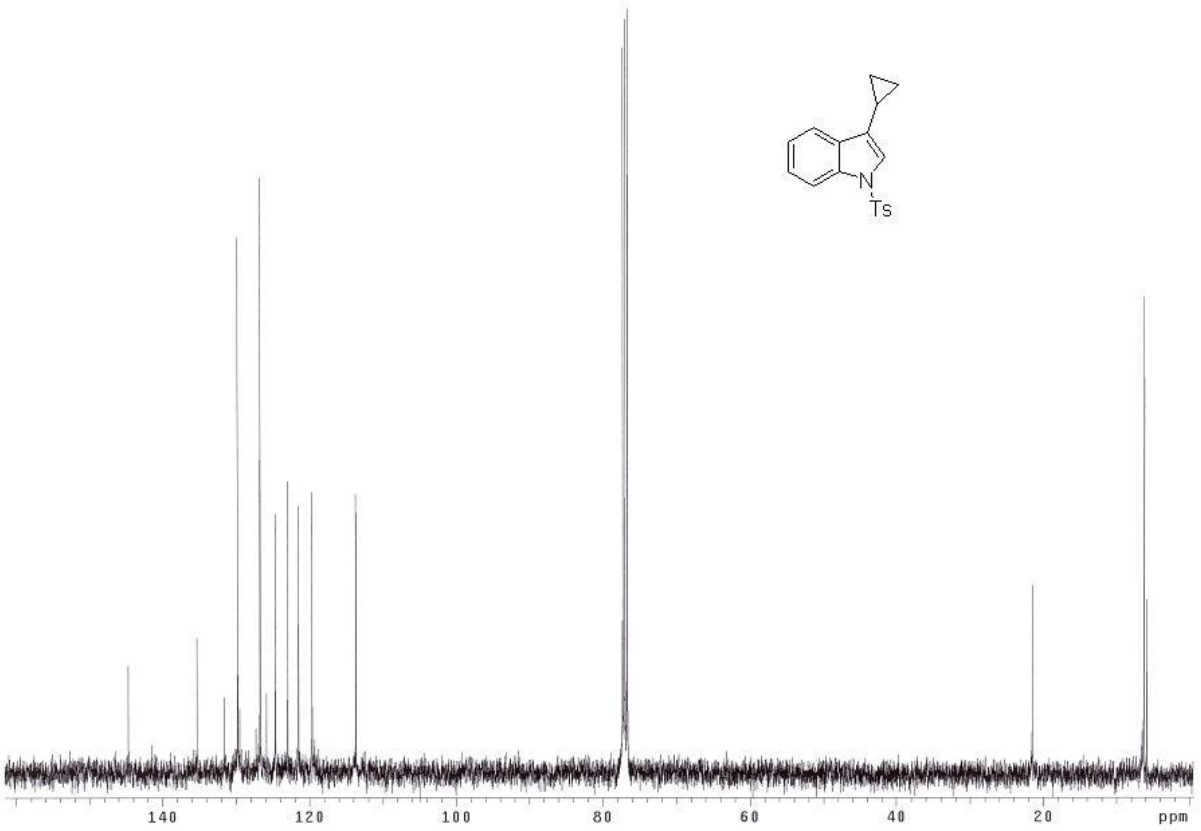
^{1}H NMR Spectrum of Compound **2w′** ($CDCl_3$, 400 MHz)



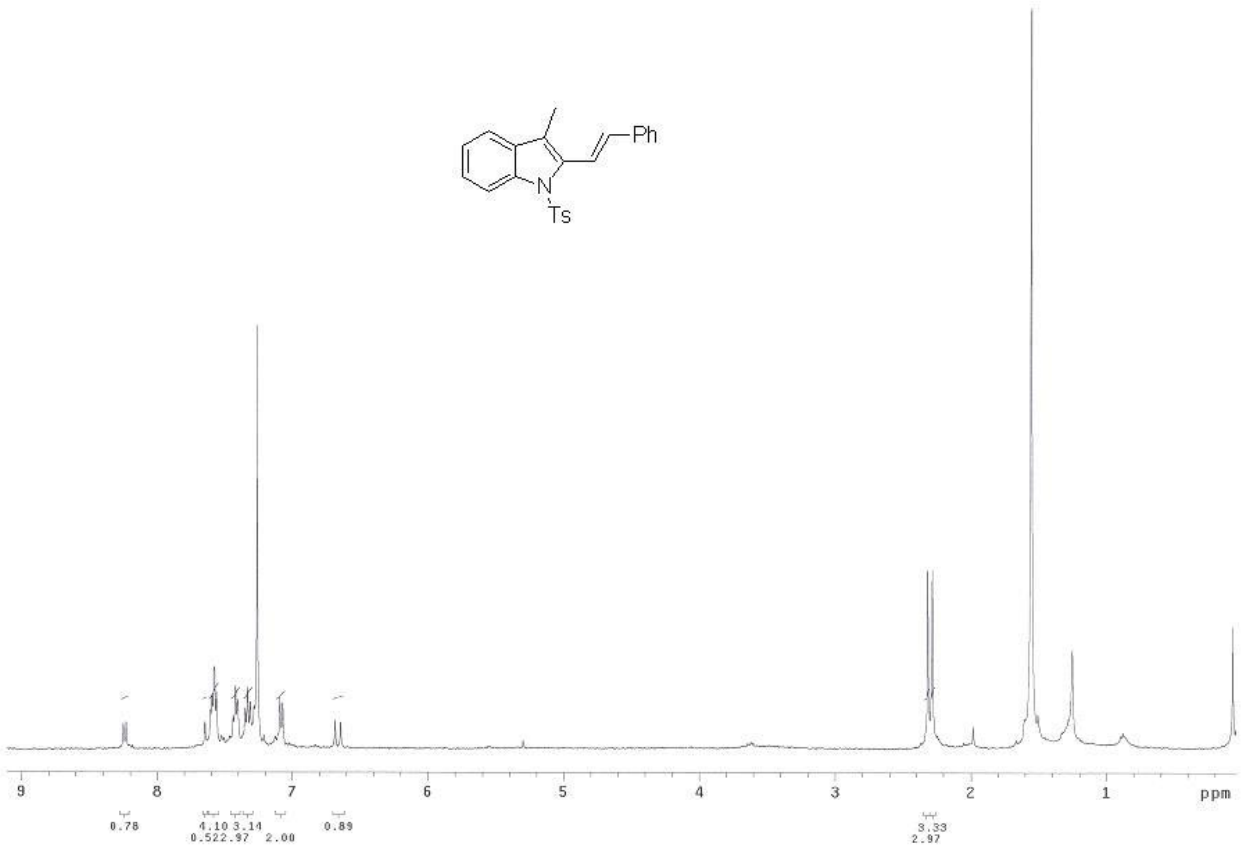
^{13}C NMR Spectrum of Compound **2w′** ($CDCl_3$, 100 MHz)



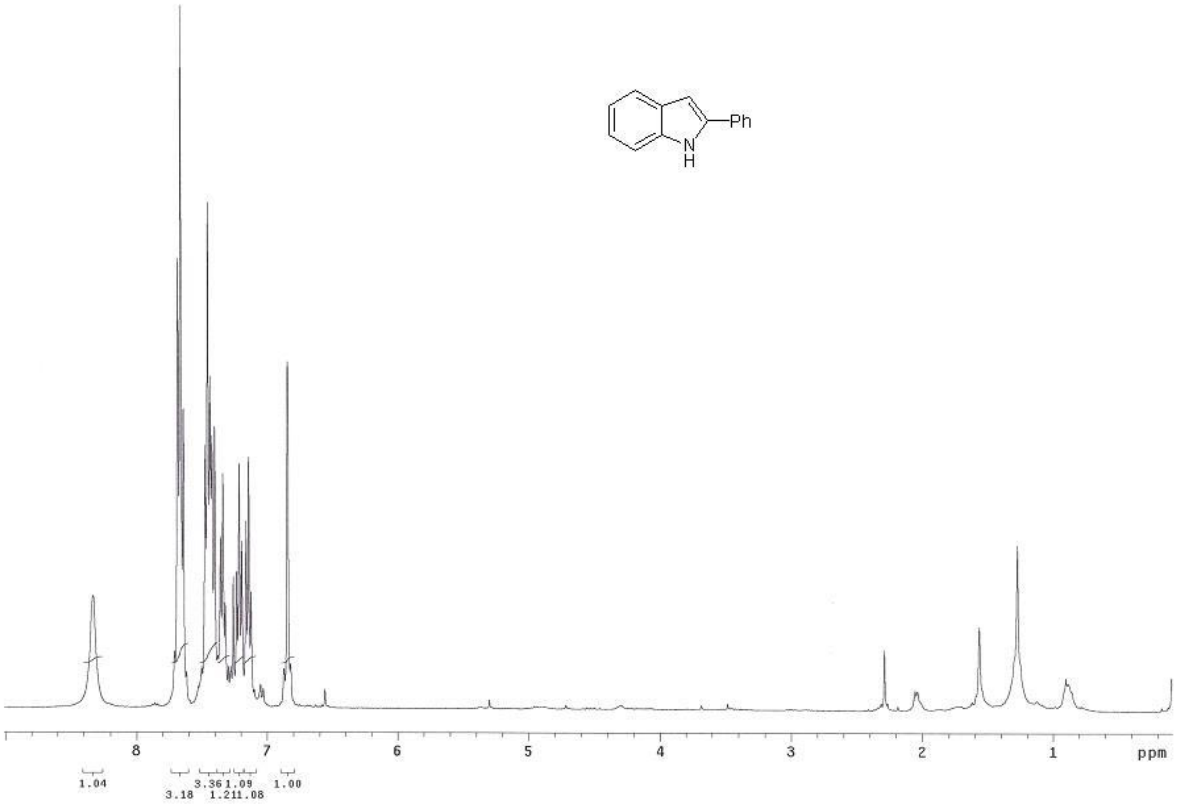
^{1}H NMR Spectrum of Compound **2x** ($CDCl_3$, 400 MHz)



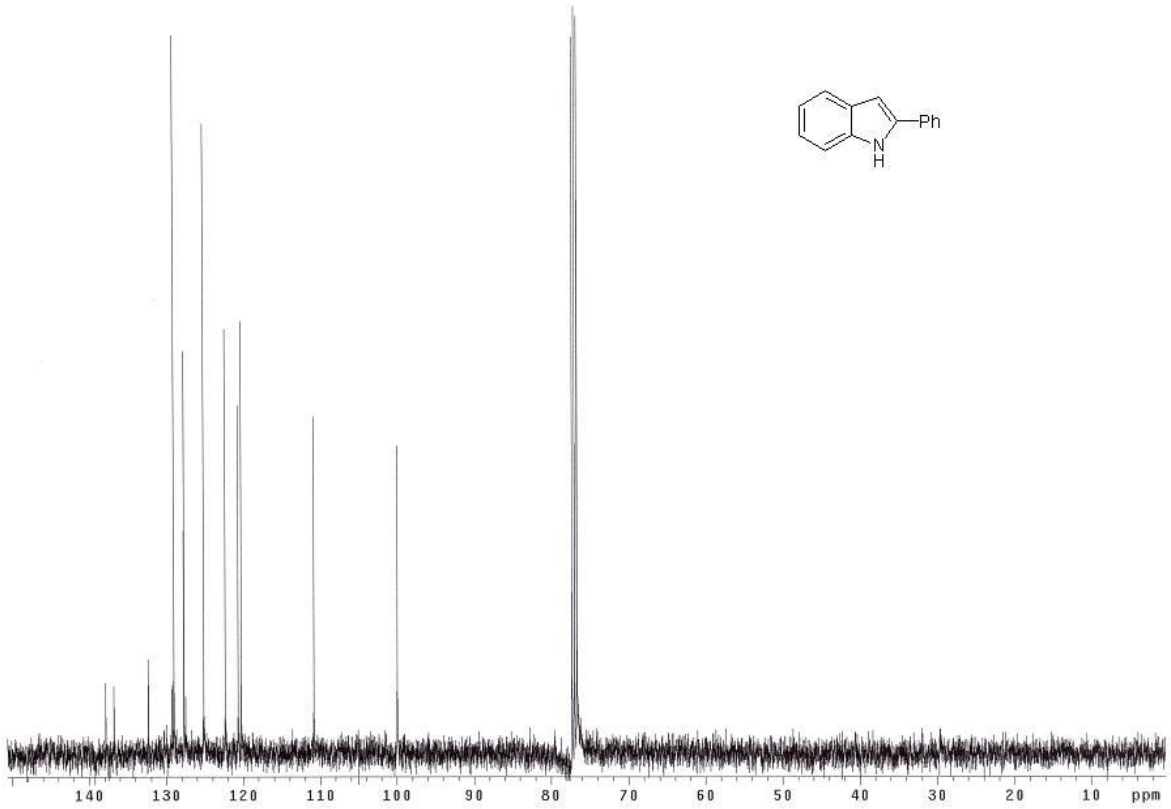
^{13}C NMR Spectrum of Compound **2x** ($CDCl_3$, 100 MHz)



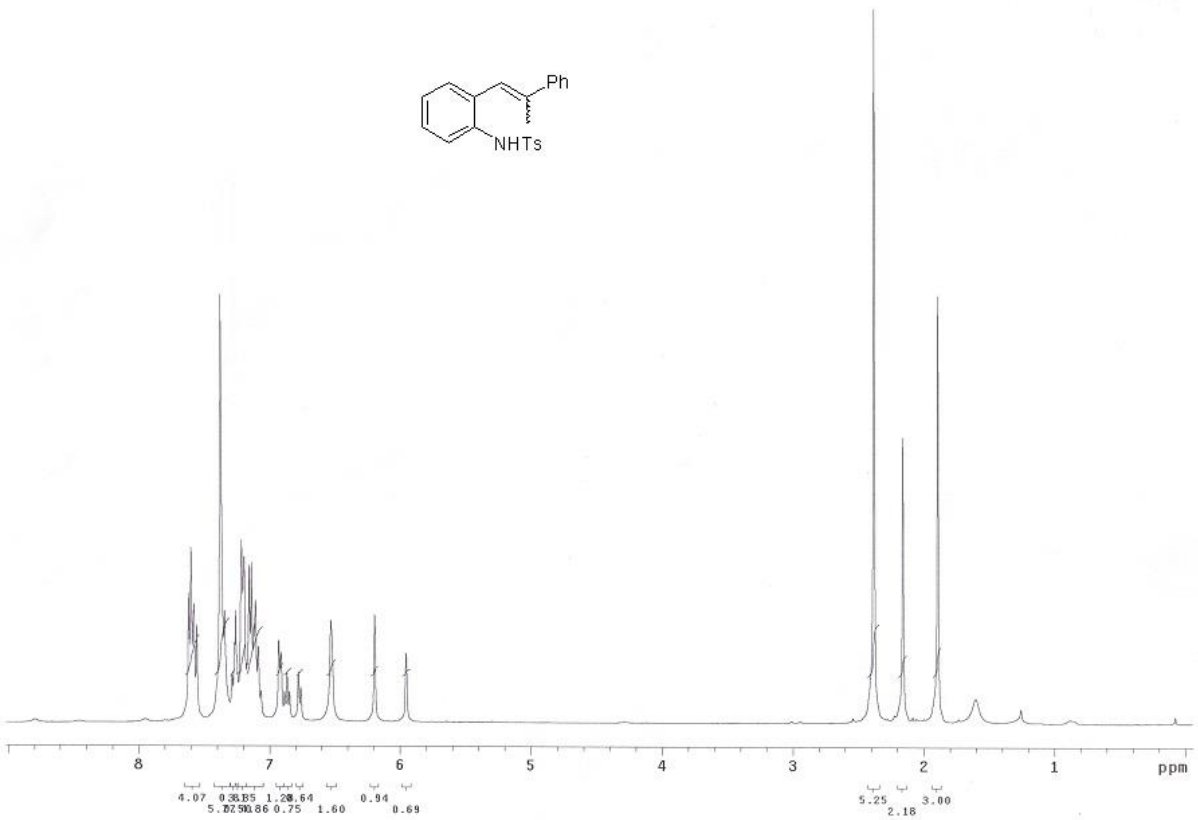
^{1}H NMR Spectrum of Compound **2y′** ($CDCl_3$, 400 MHz)



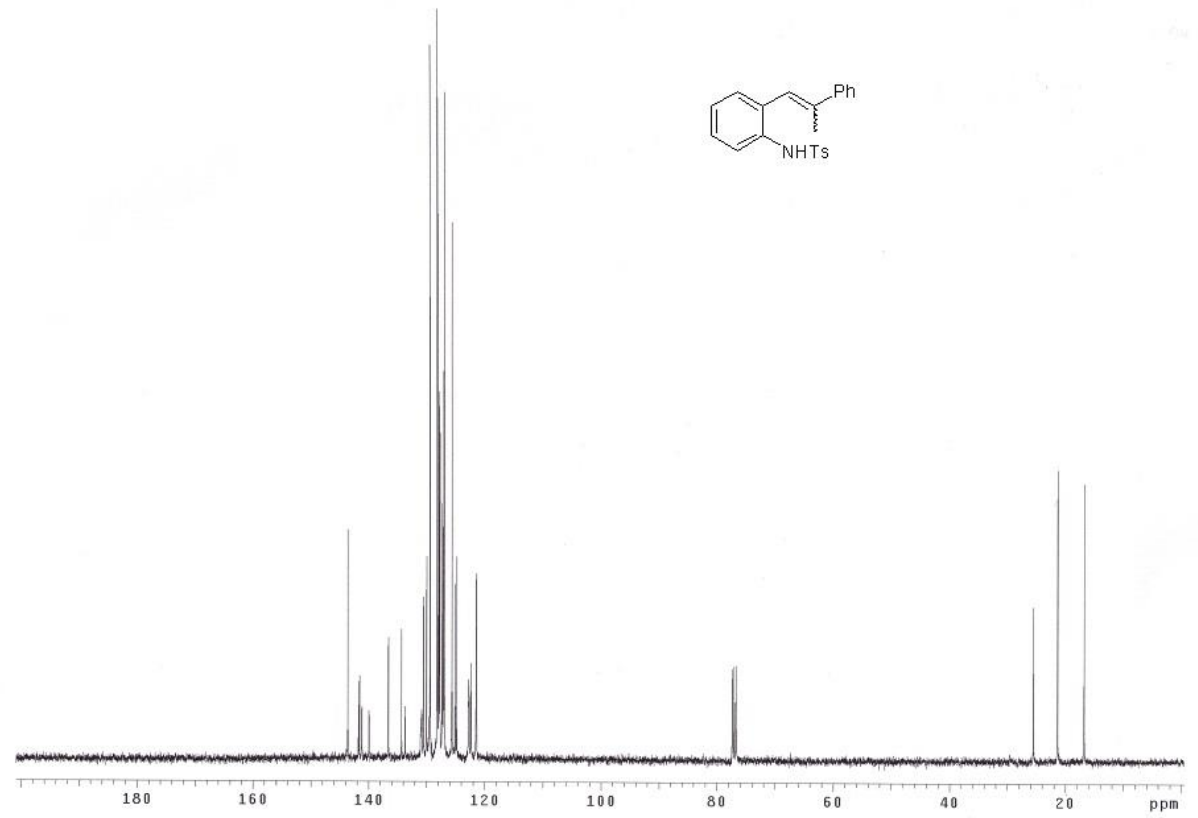
^{1}H NMR Spectrum of Compound **3** ($CDCl_3$, 400 MHz)



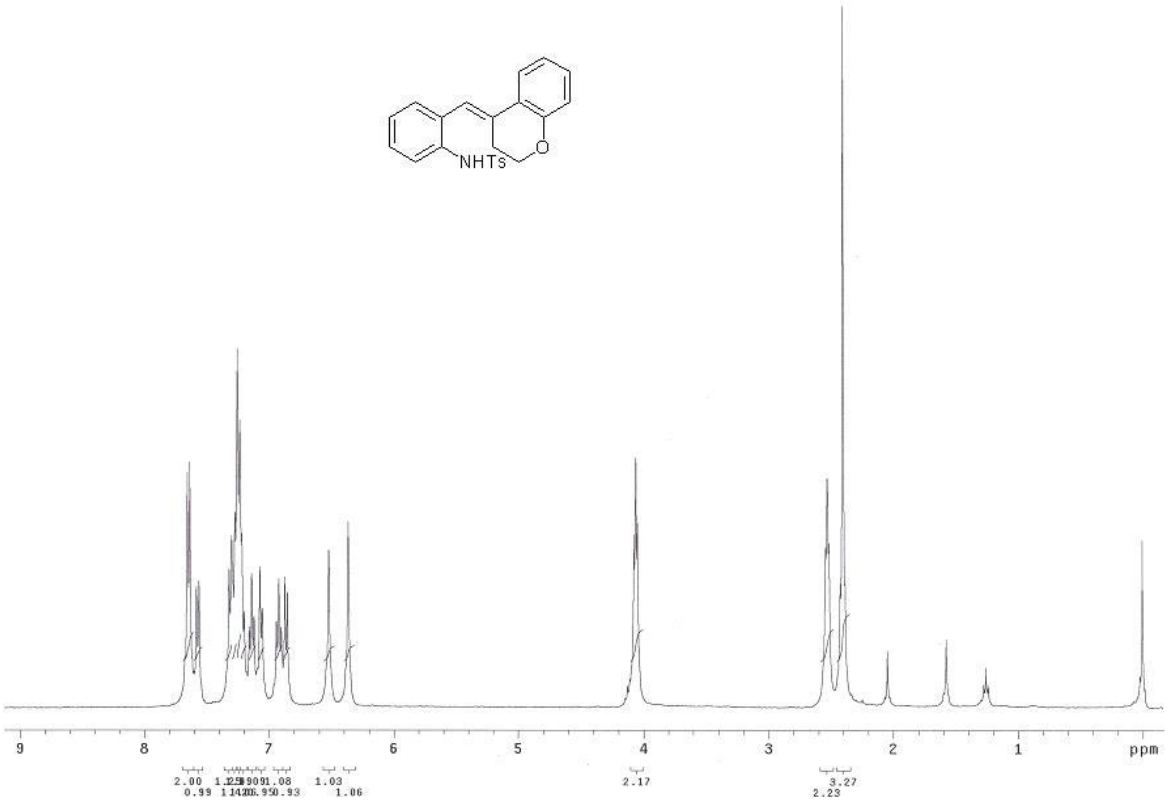
^{13}C NMR Spectrum of Compound **3** ($CDCl_3$, 100 MHz)



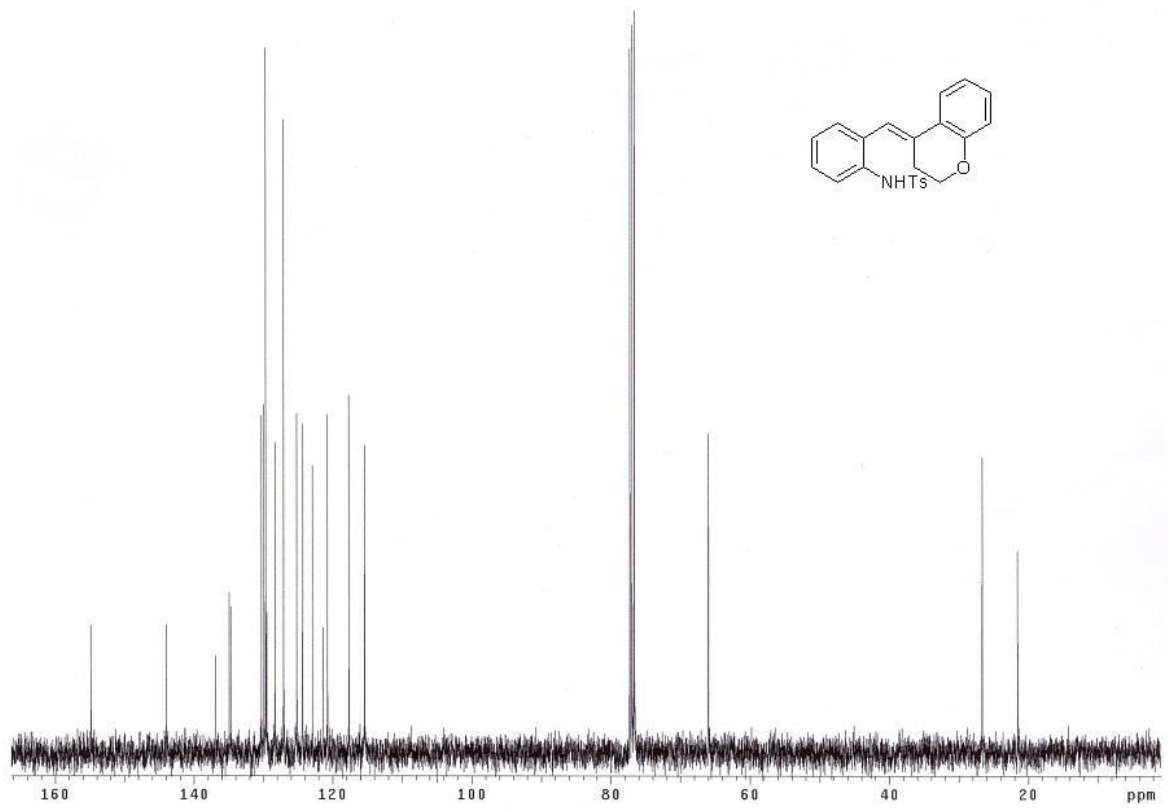
^{1}H NMR Spectrum of Compound **4a** ($CDCl_3$, 400 MHz)



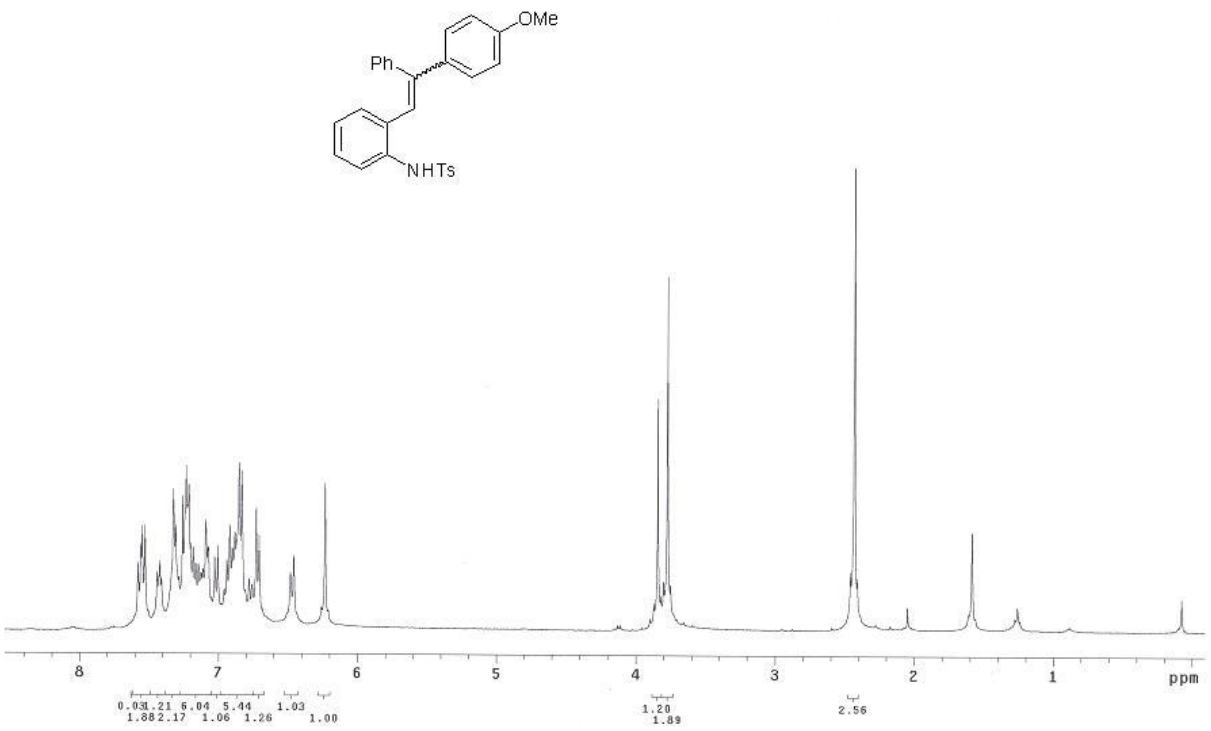
^{13}C NMR Spectrum of Compound **4a** ($CDCl_3$, 100 MHz)



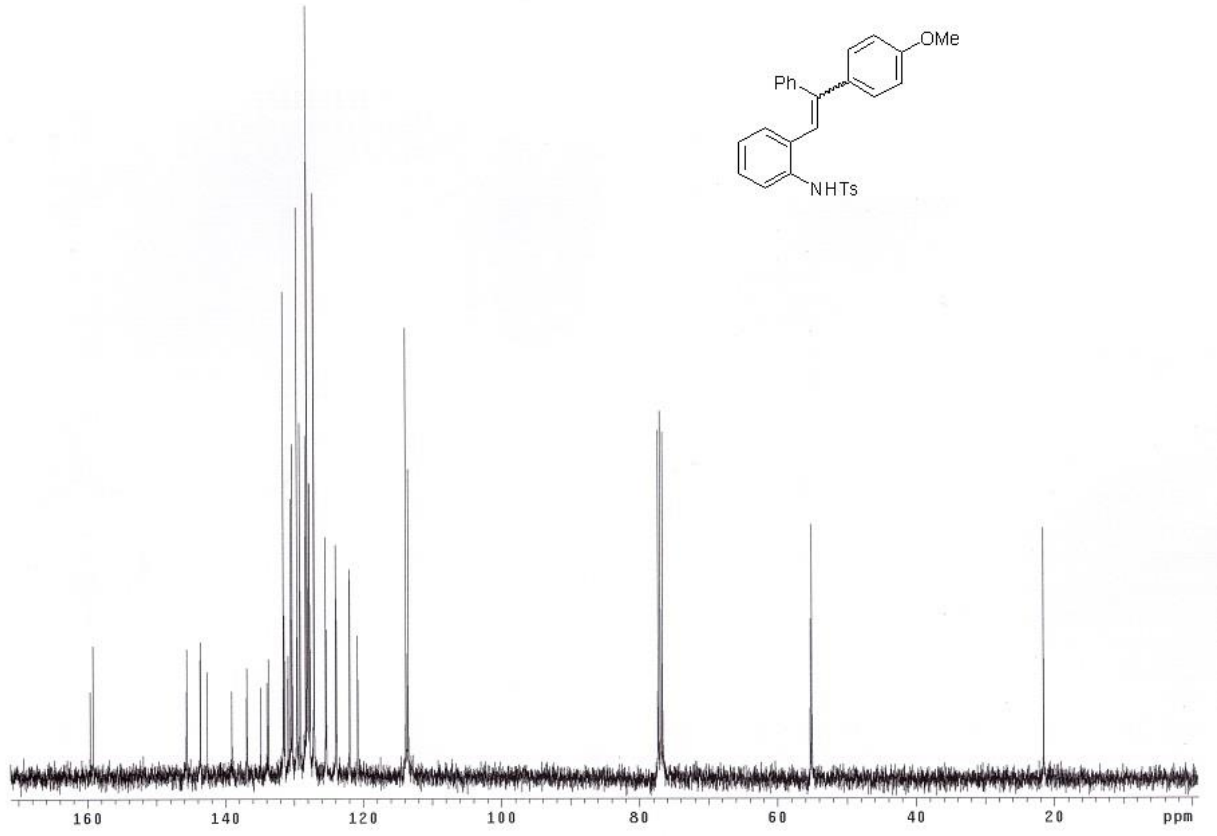
^{1}H NMR Spectrum of Compound **4b** ($CDCl_3$, 400 MHz)



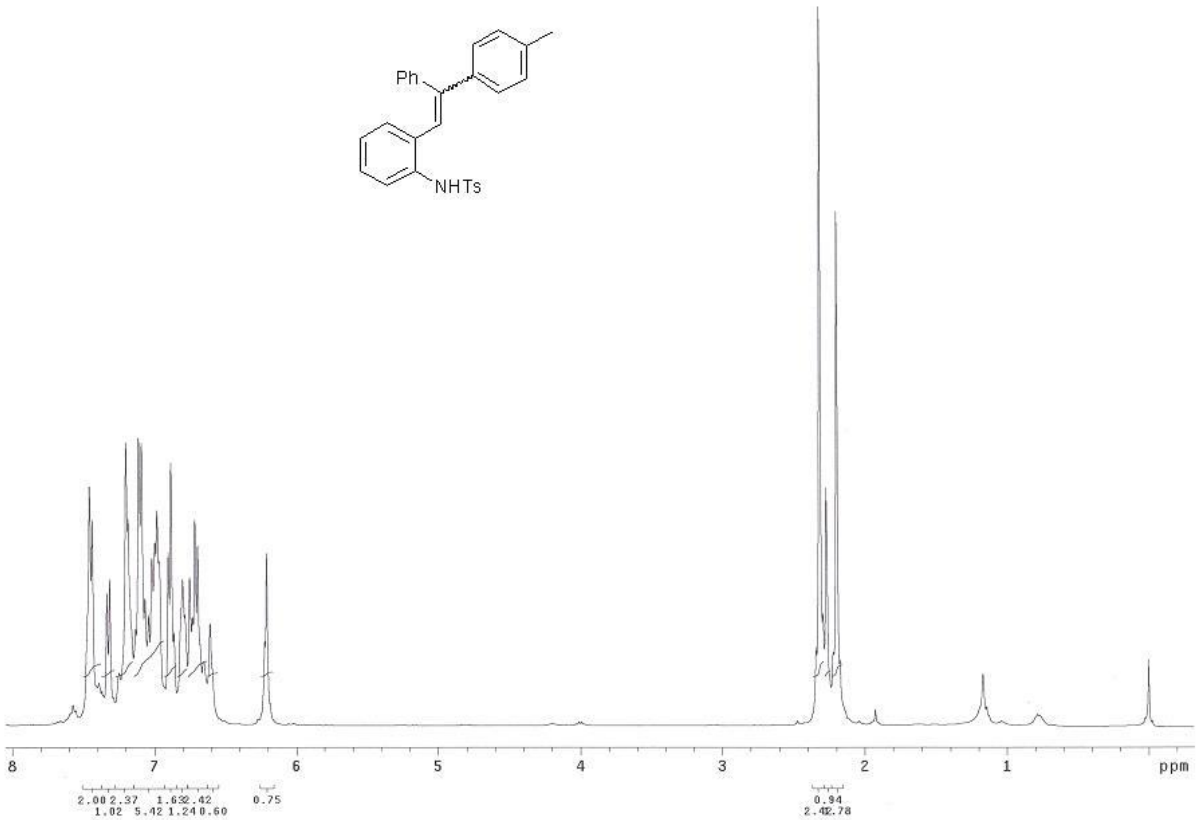
^{13}C NMR Spectrum of Compound **4b** ($CDCl_3$, 100 MHz)



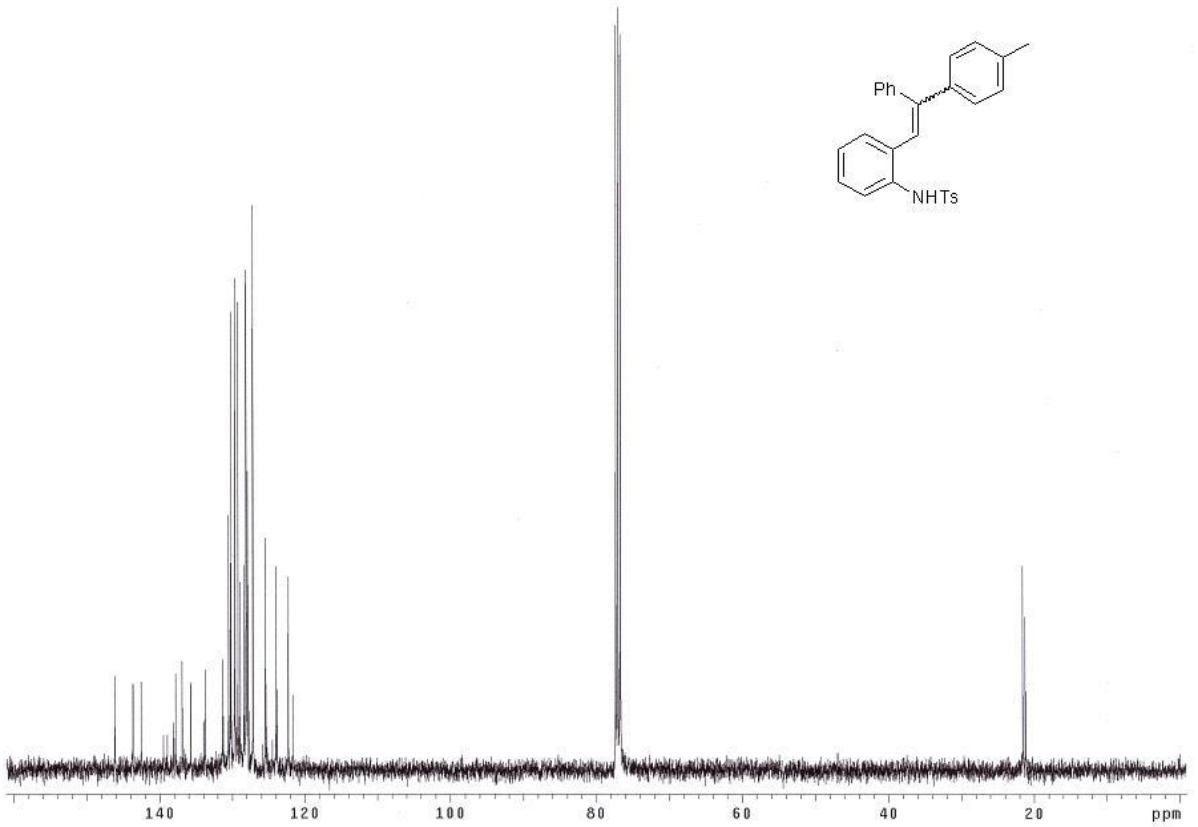
^{1}H NMR Spectrum of Compound **4c** ($CDCl_3$, 400 MHz)



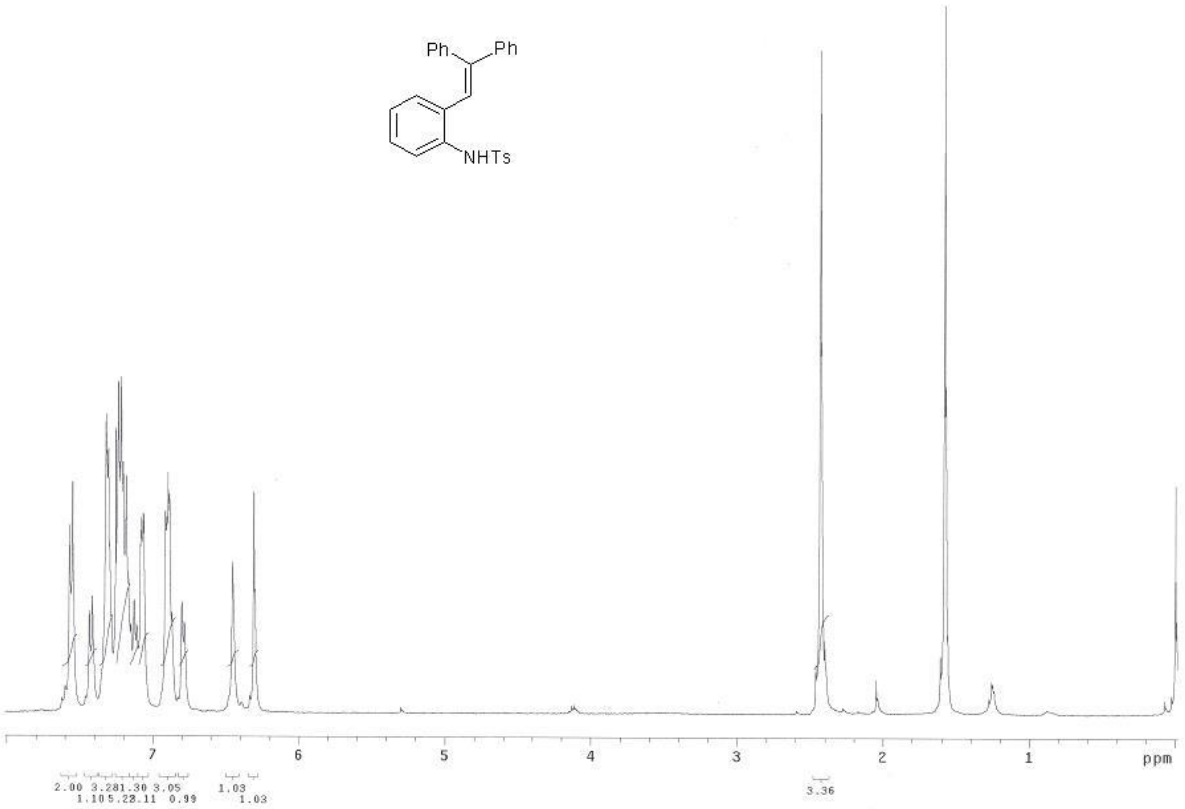
^{13}C NMR Spectrum of Compound **4c** ($CDCl_3$, 100 MHz)



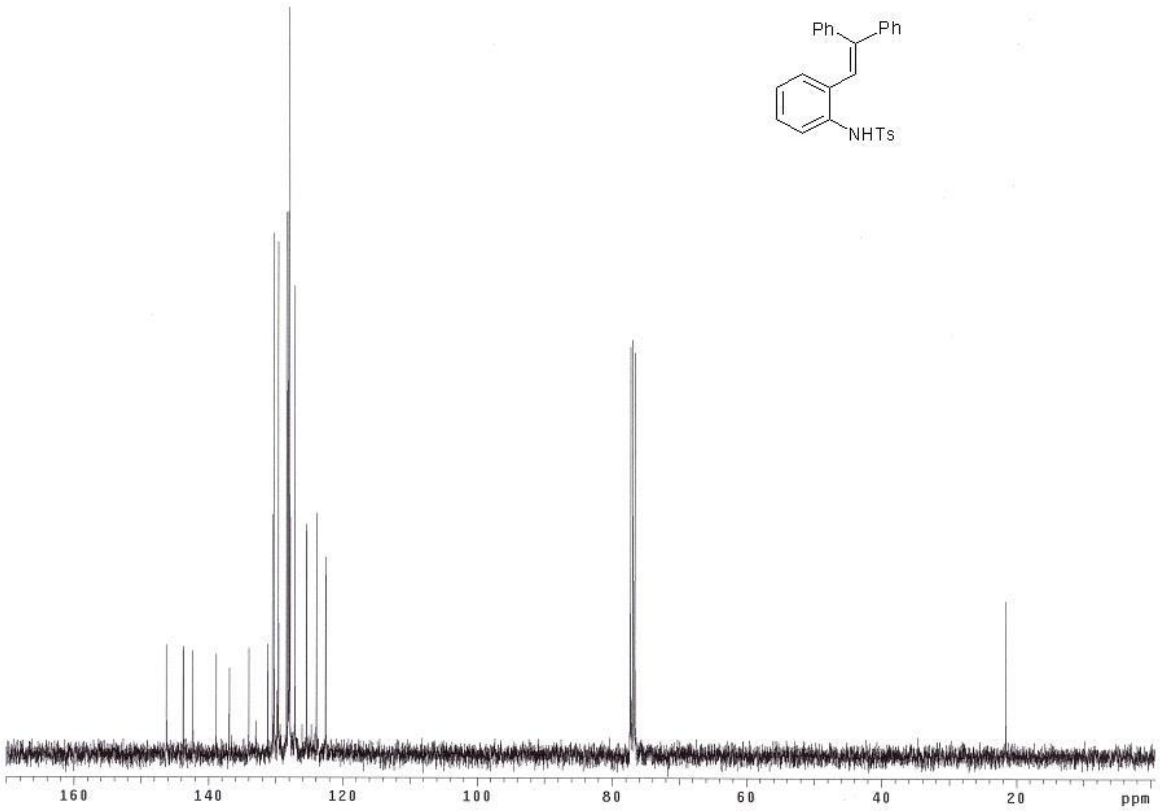
^{1}H NMR Spectrum of Compound **4d** ($CDCl_3$, 400 MHz)



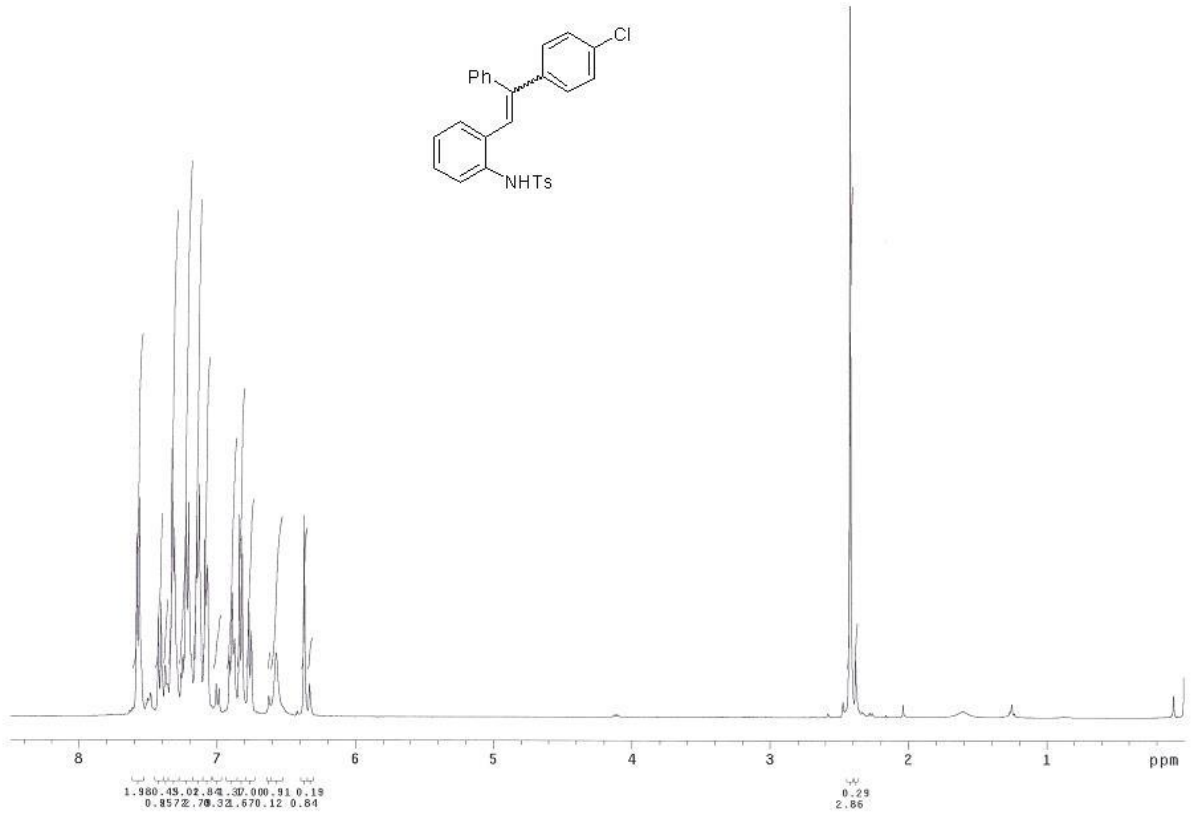
^{13}C NMR Spectrum of Compound **4d** ($CDCl_3$, 100 MHz)



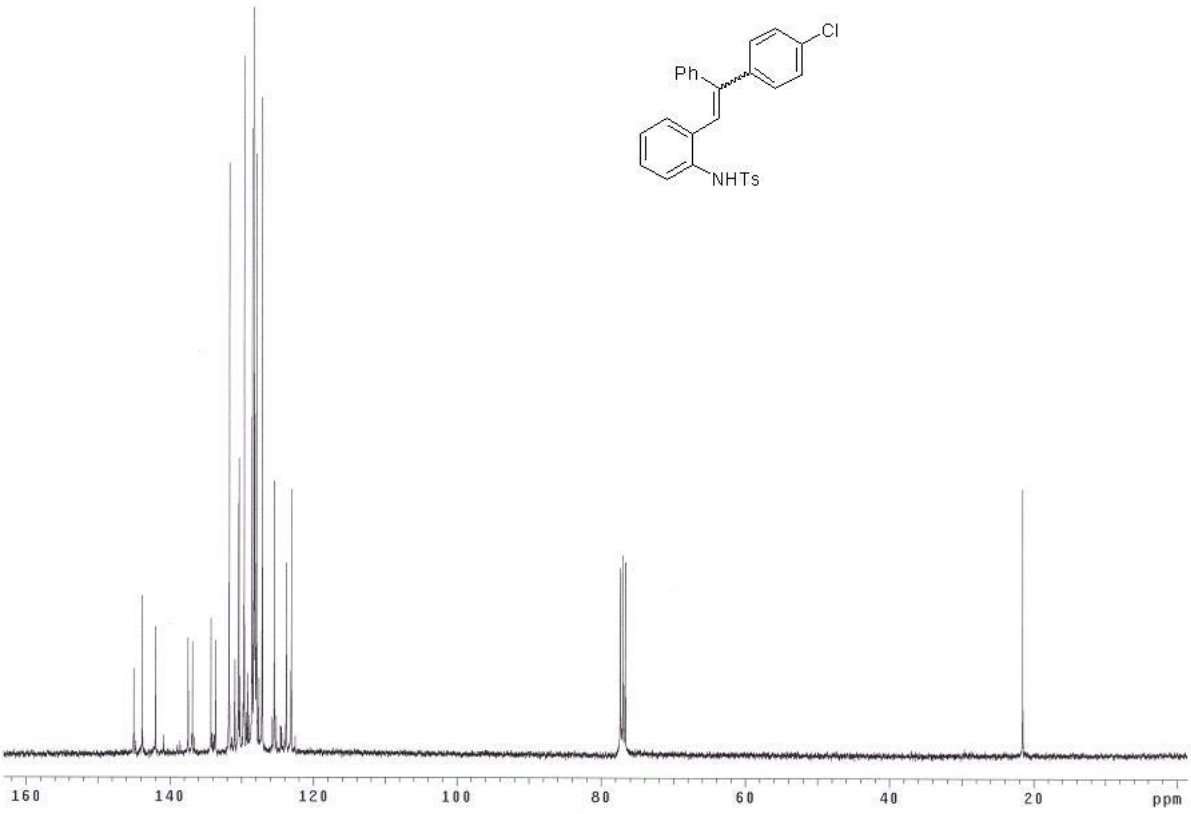
^{1}H NMR Spectrum of Compound **4e** ($CDCl_3$, 400 MHz)



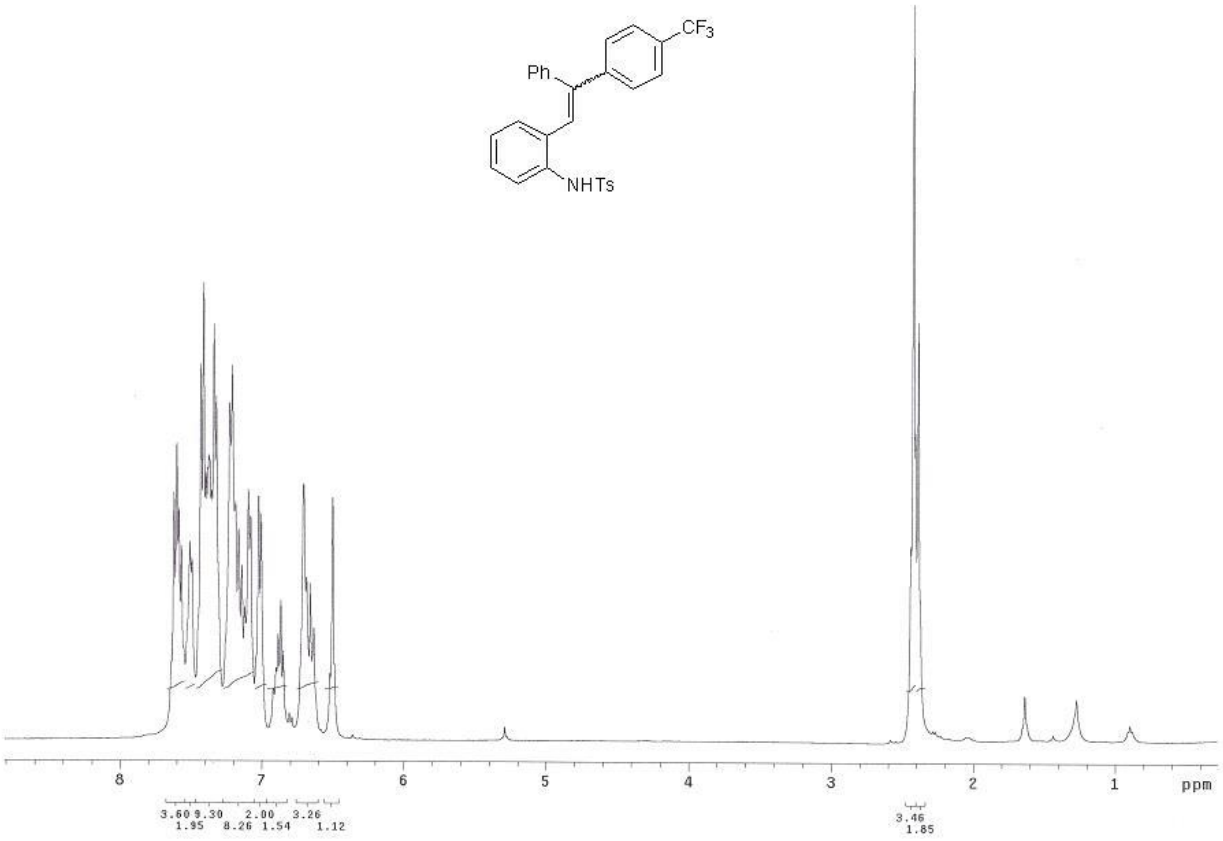
^{13}C NMR Spectrum of Compound **4e** ($CDCl_3$, 100 MHz)



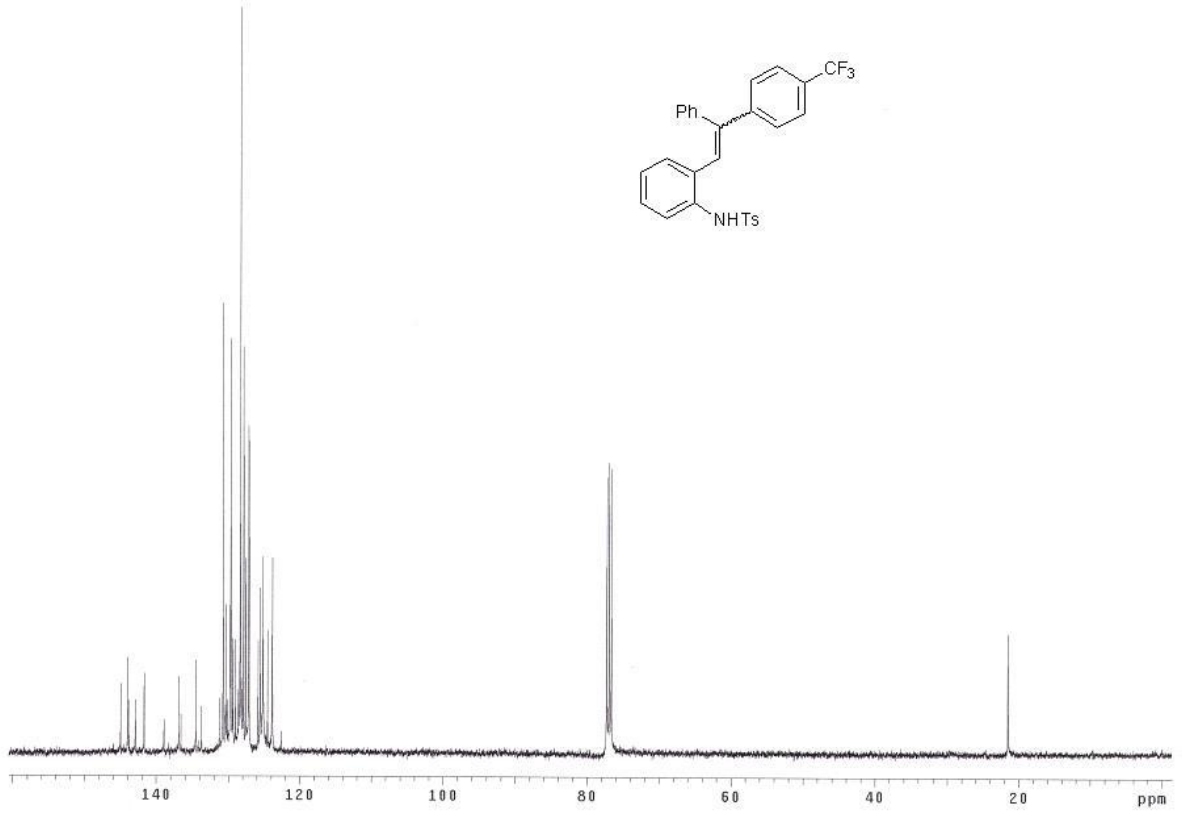
^{1}H NMR Spectrum of Compound **4f** ($CDCl_3$, 400 MHz)



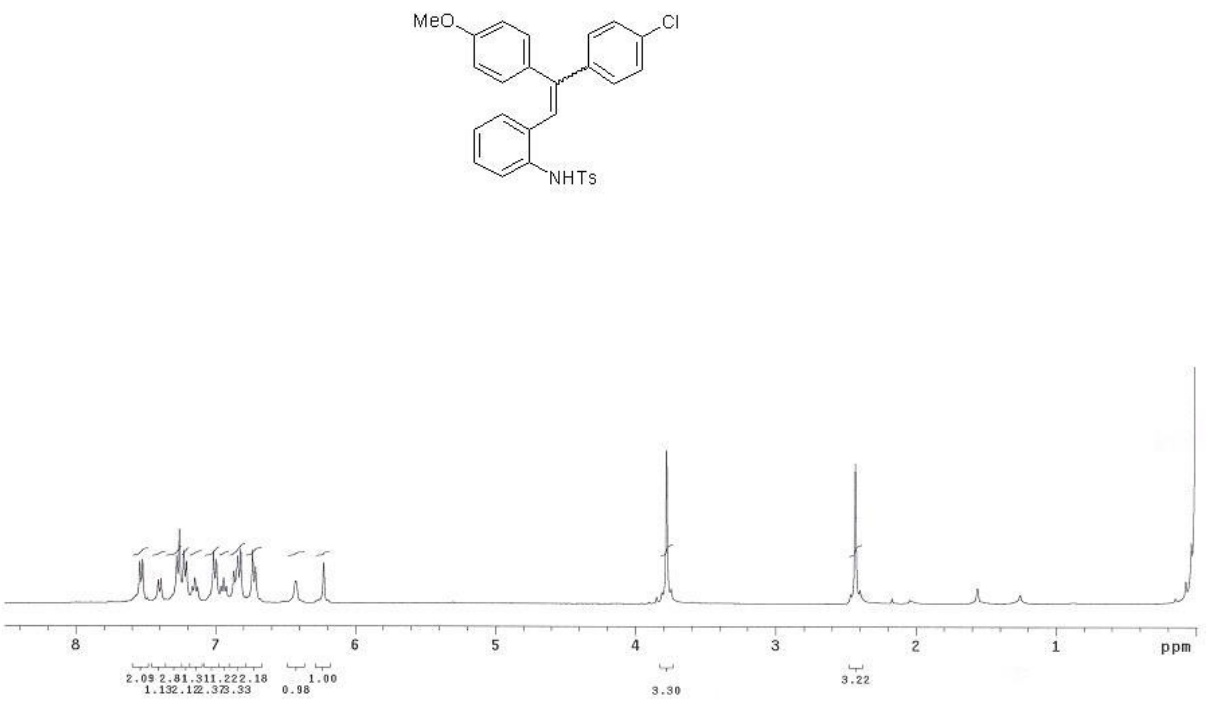
^{13}C NMR Spectrum of Compound **4f** ($CDCl_3$, 100 MHz)



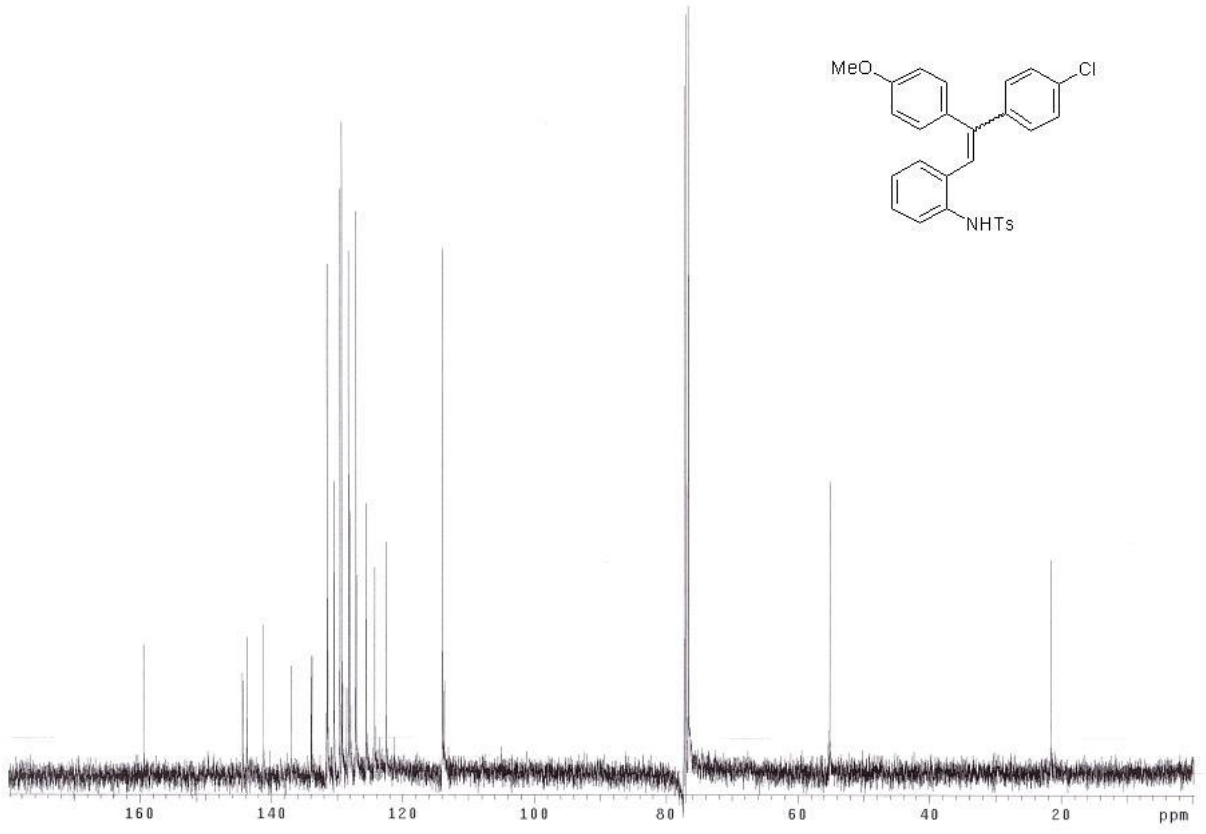
^{1}H NMR Spectrum of Compound **4g** ($CDCl_3$, 400 MHz)



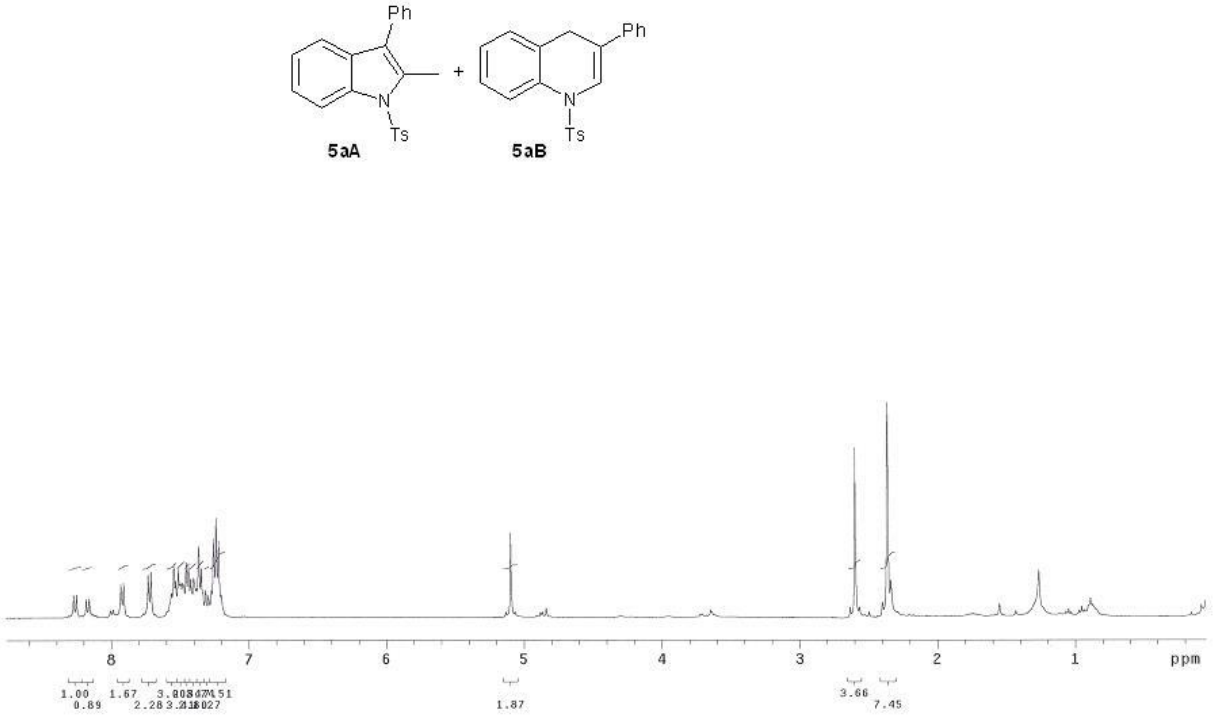
^{13}C NMR Spectrum of Compound **4g** ($CDCl_3$, 100 MHz)



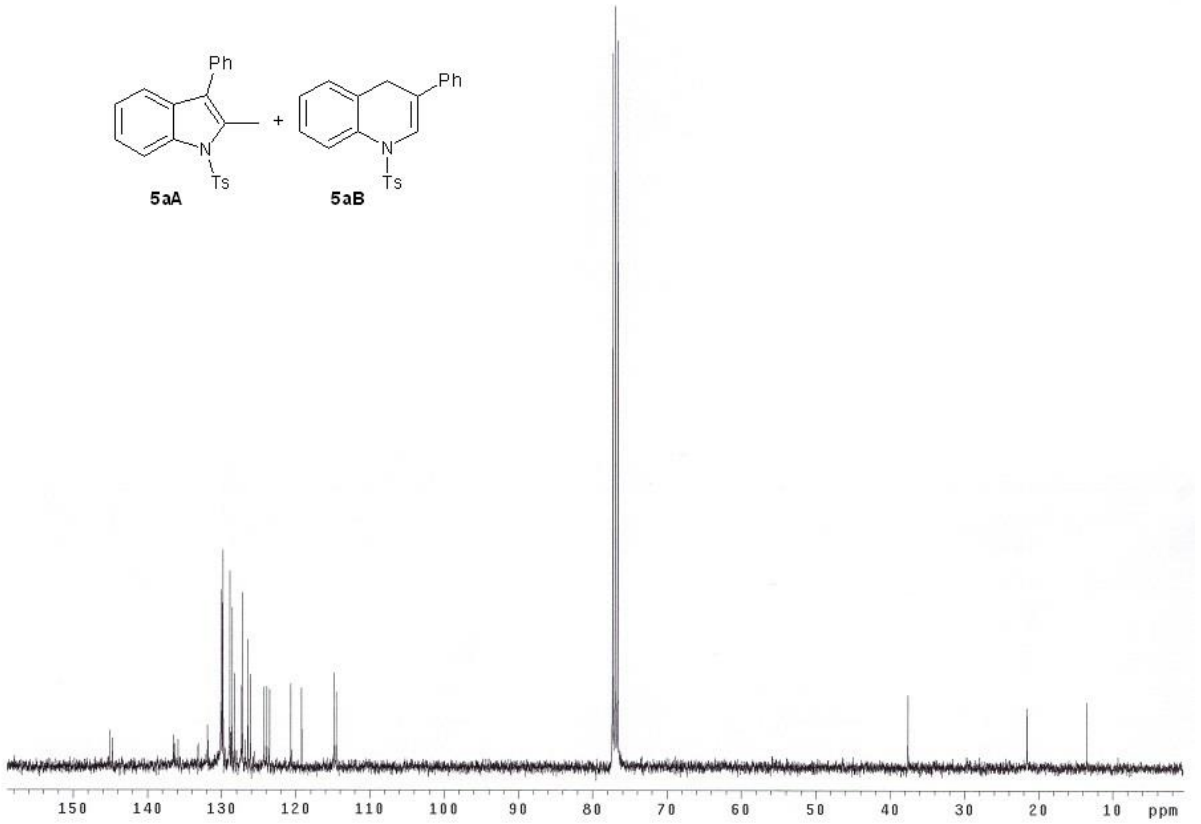
^{1}H NMR Spectrum of Compound **4h** ($CDCl_3$, 400 MHz)



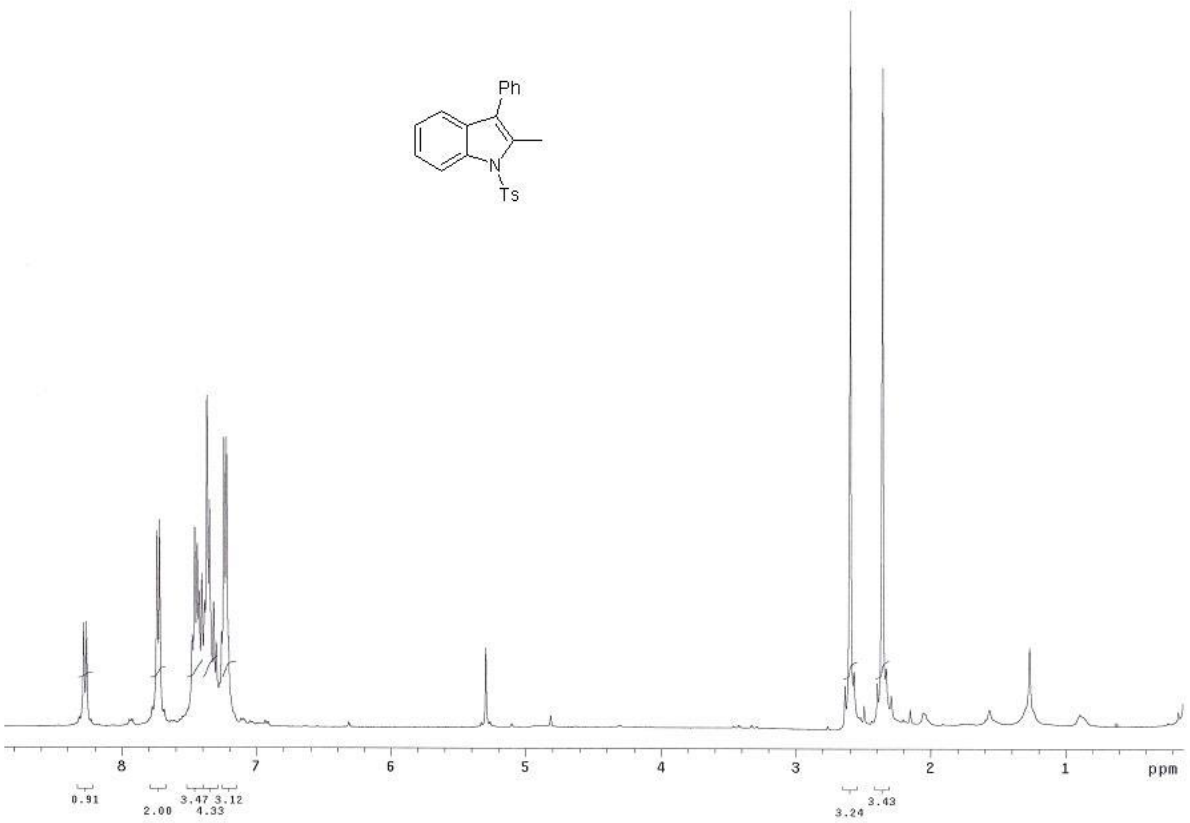
^{13}C NMR Spectrum of Compound **4h** ($CDCl_3$, 100 MHz)



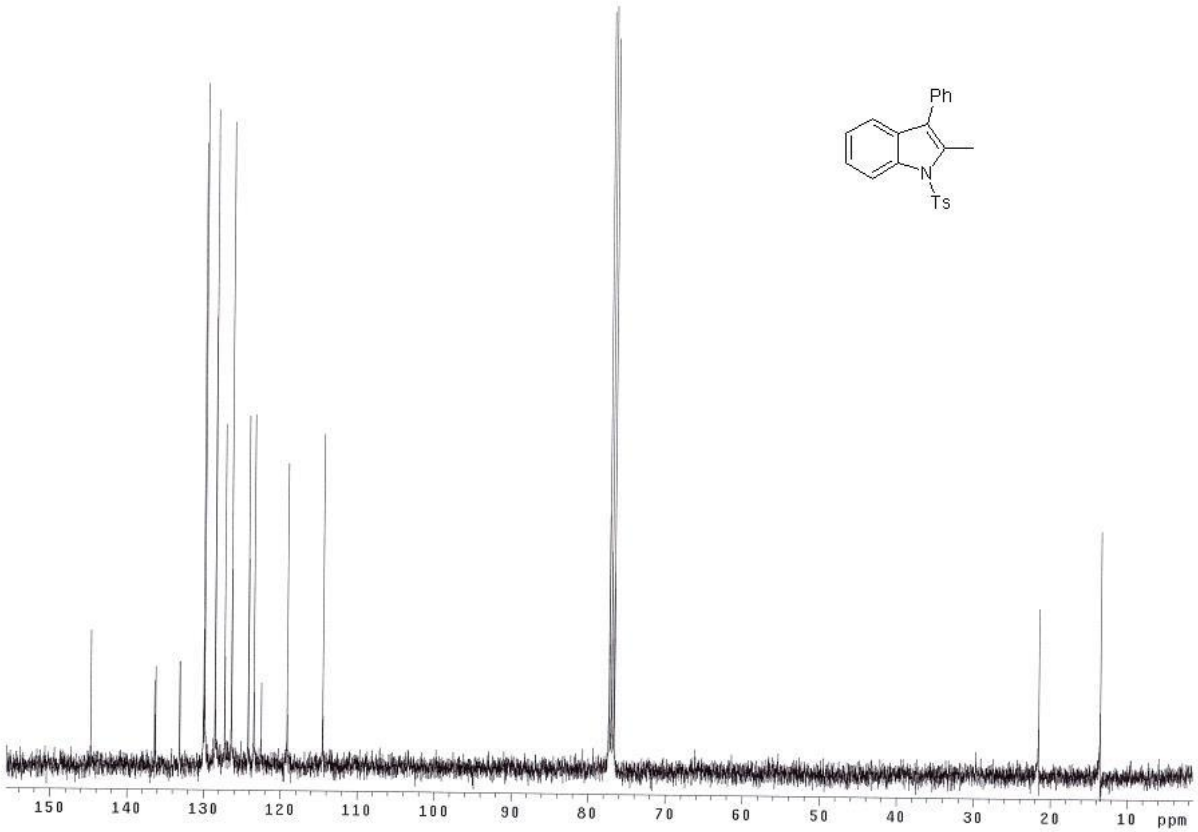
^{1}H NMR Spectrum of Compound **5aA** & **5aB** ($CDCl_3$, 400 MHz)



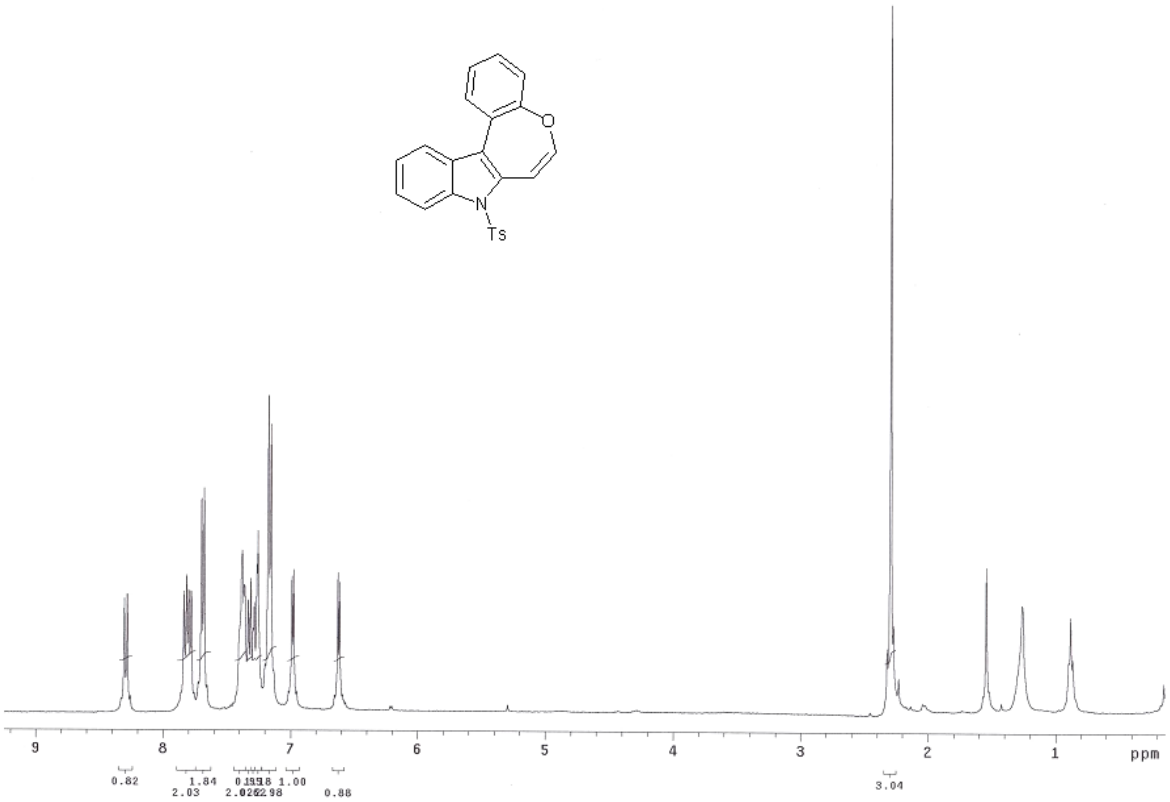
^{13}C NMR Spectrum of Compound **5aA** & **5aB** ($CDCl_3$, 100 MHz)



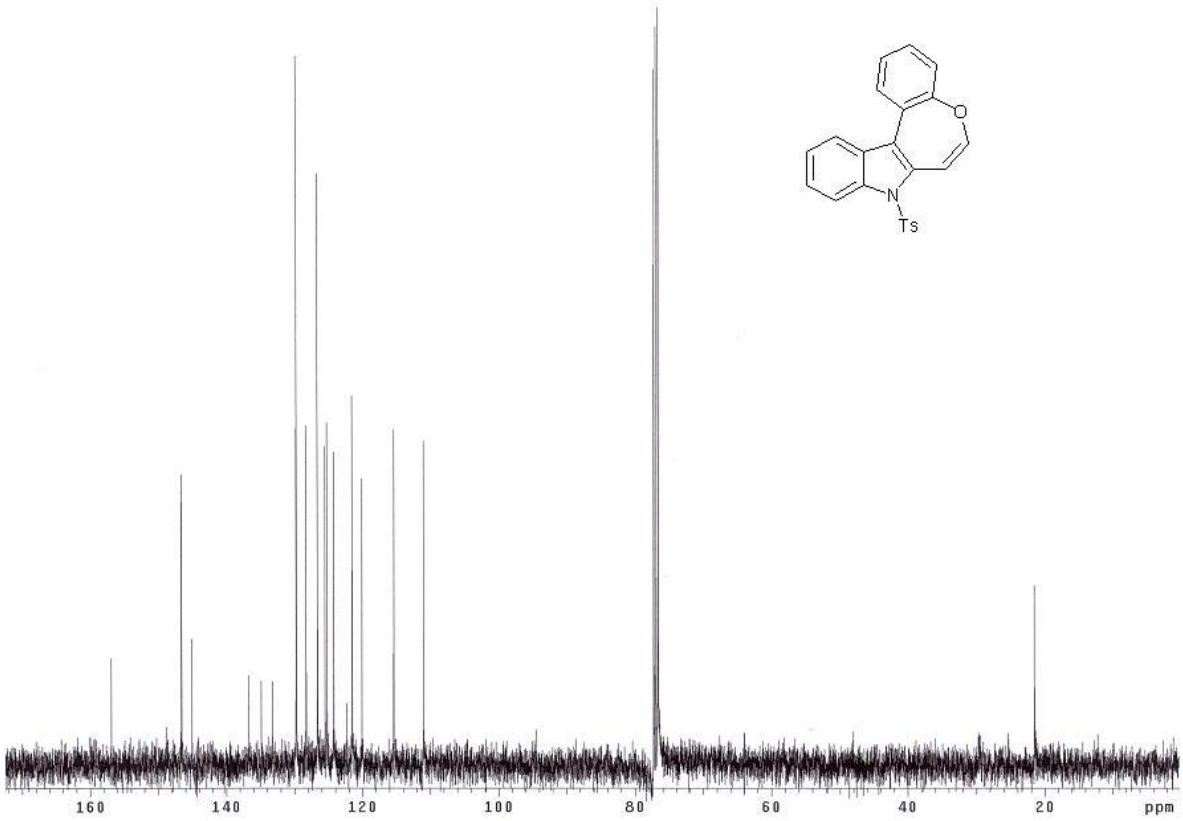
^{1}H NMR Spectrum of Compound **5aA** ($CDCl_3$, 400 MHz)



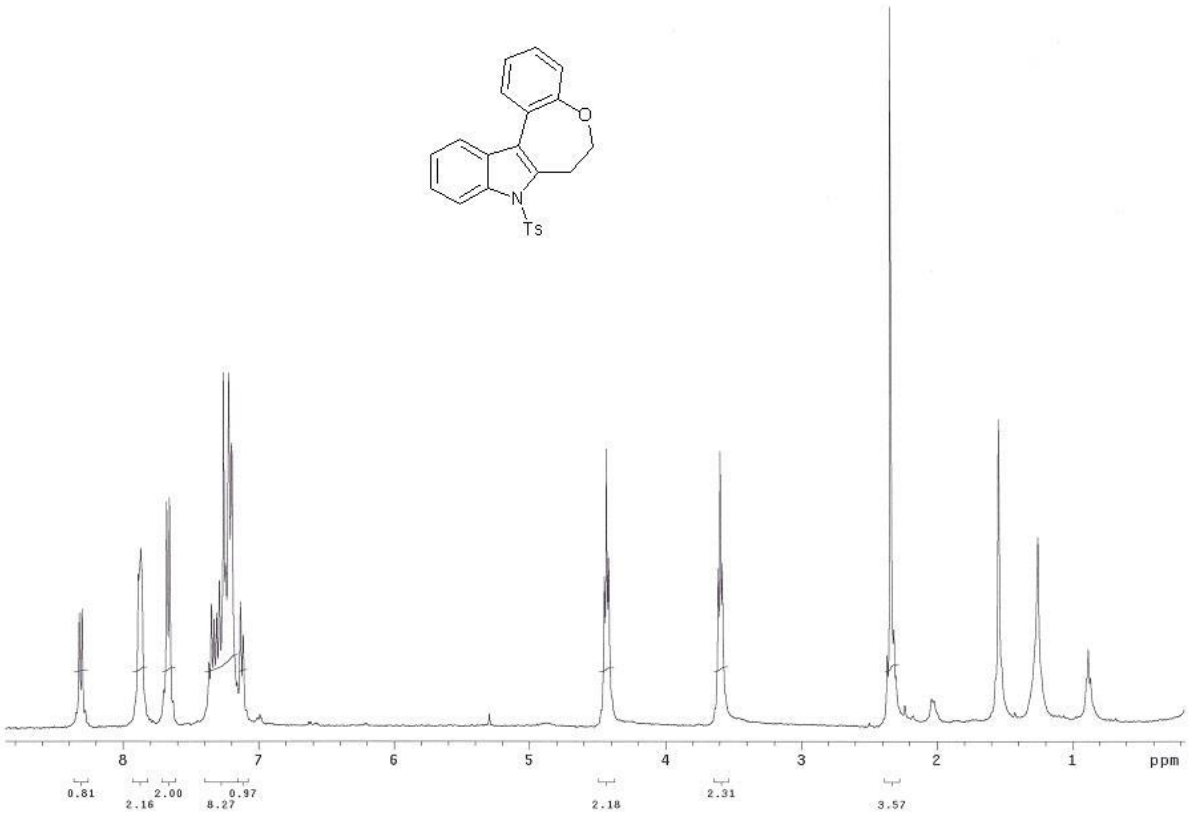
^{13}C NMR Spectrum of Compound **5aA** ($CDCl_3$, 100 MHz)



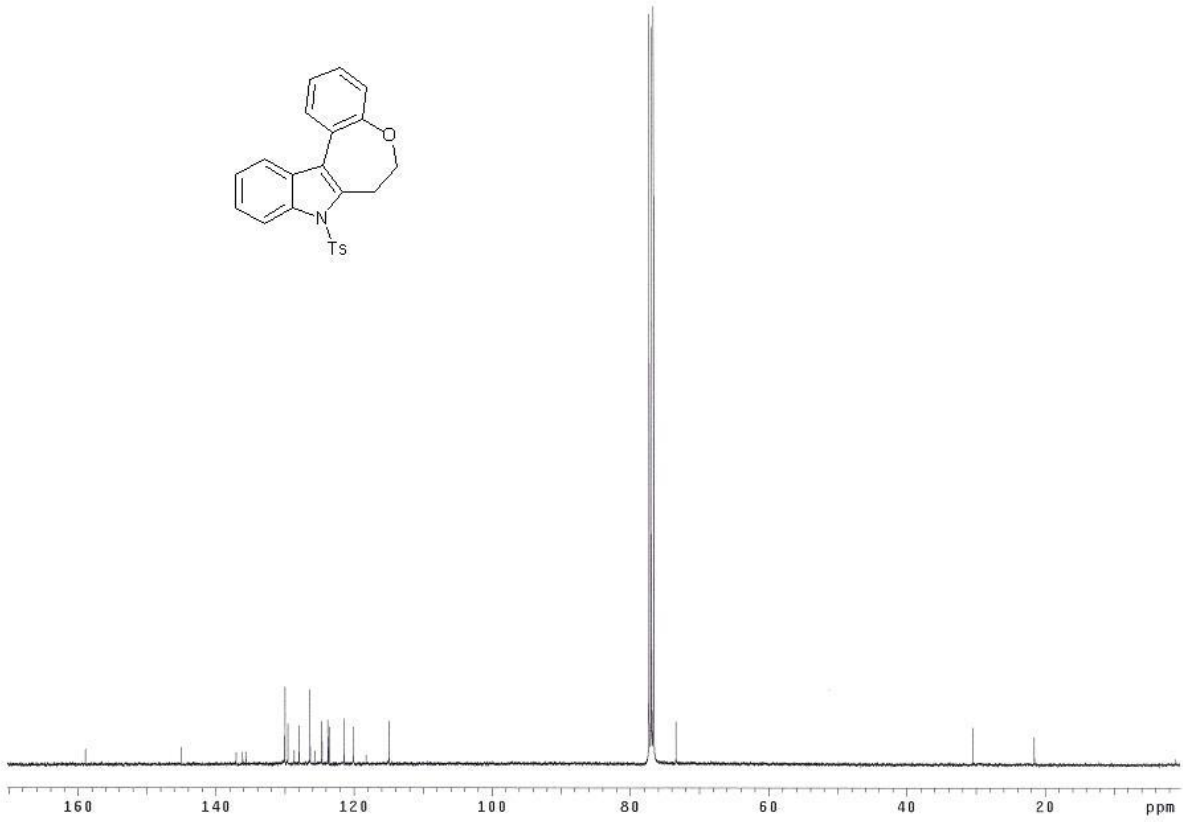
^{1}H NMR Spectrum of Compound **5bA** ($CDCl_3$, 400 MHz)



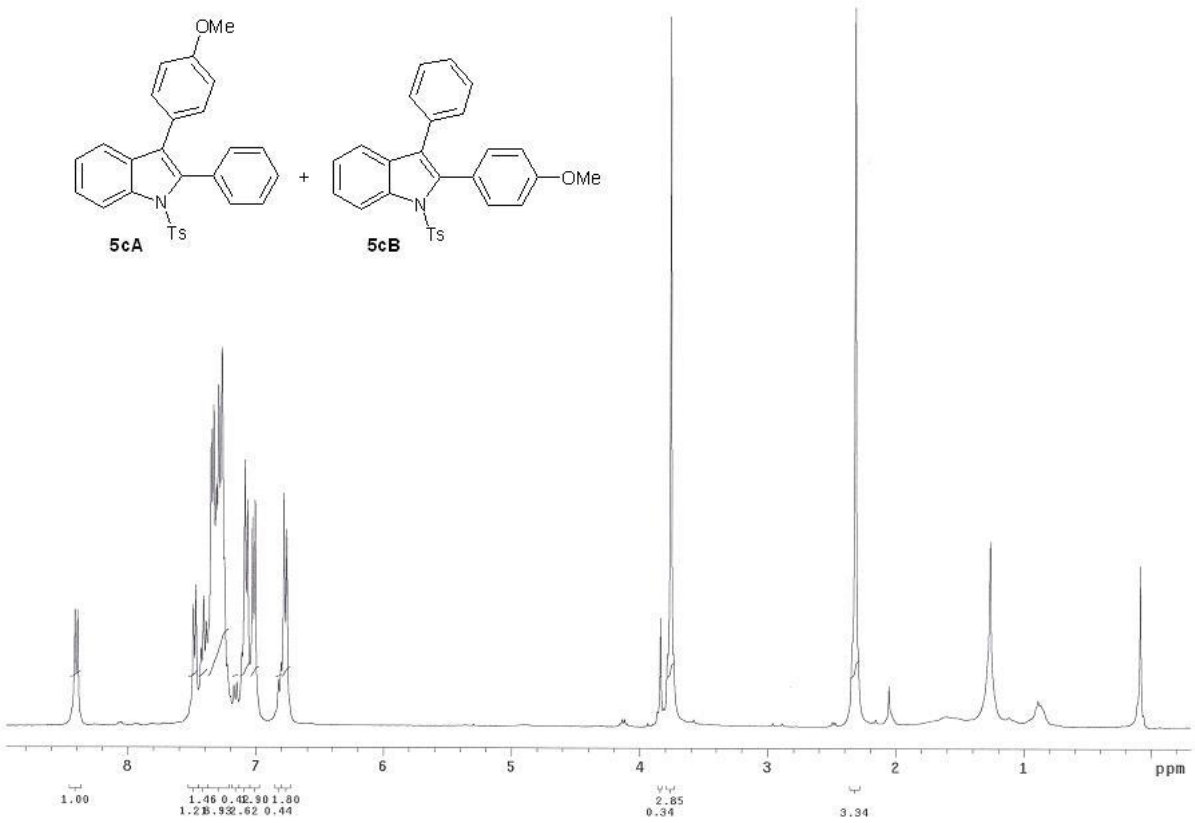
^{13}C NMR Spectrum of Compound **5bA** ($CDCl_3$, 100 MHz)



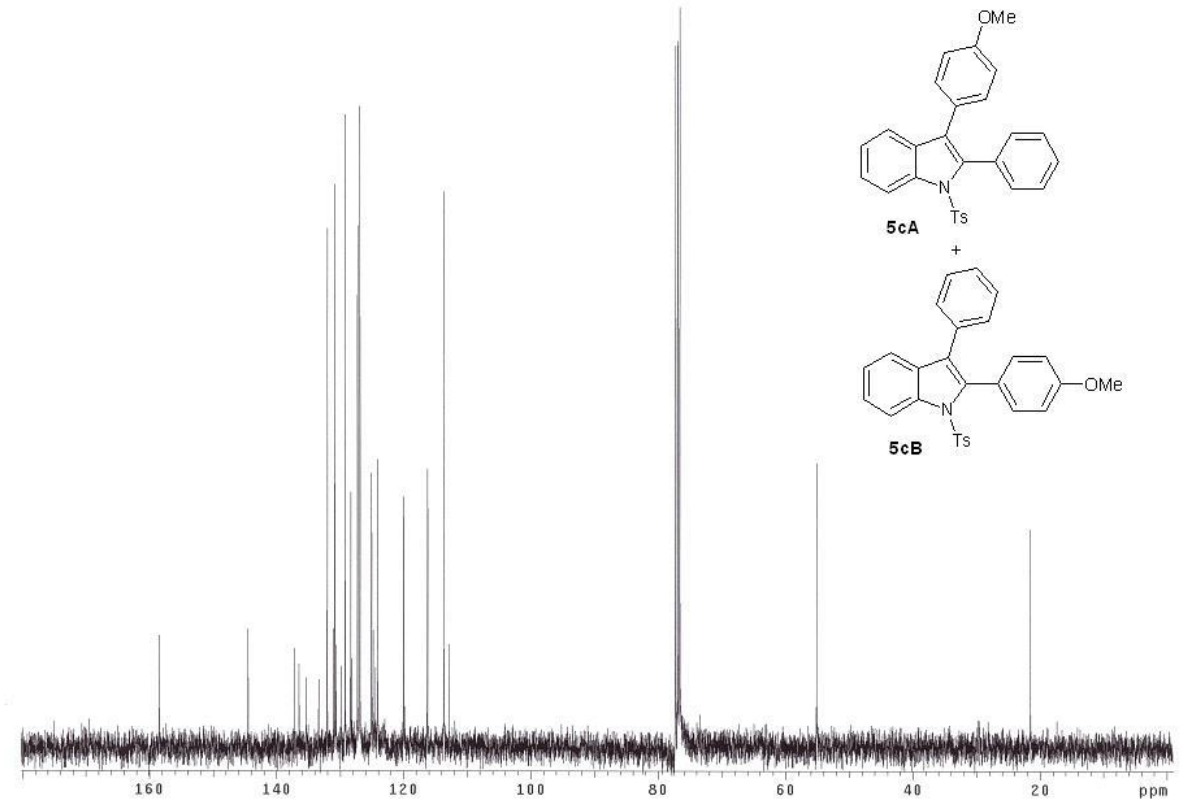
^{1}H NMR Spectrum of Compound **5bB** ($CDCl_3$, 400 MHz)



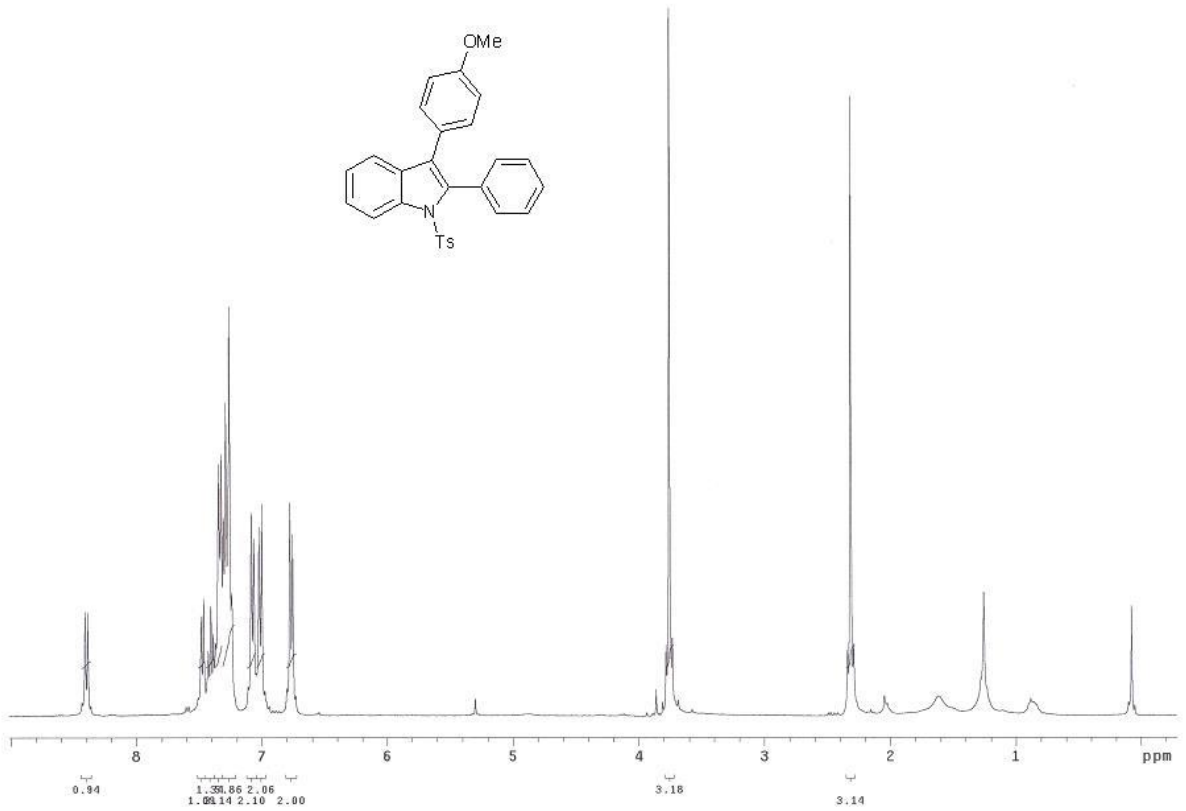
^{13}C NMR Spectrum of Compound **5bB** ($CDCl_3$, 100 MHz)



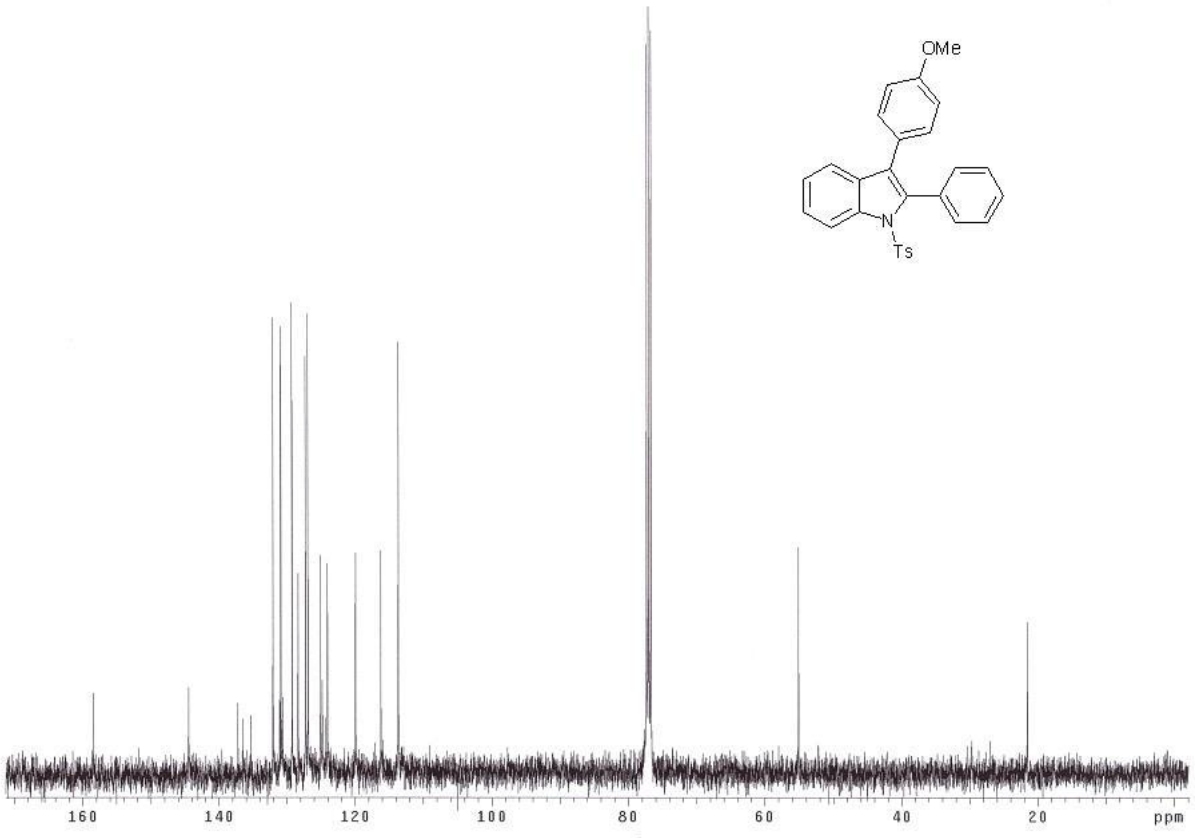
^{1}H NMR Spectrum of Compound **5cA** & **5cB** ($CDCl_3$, 400 MHz)



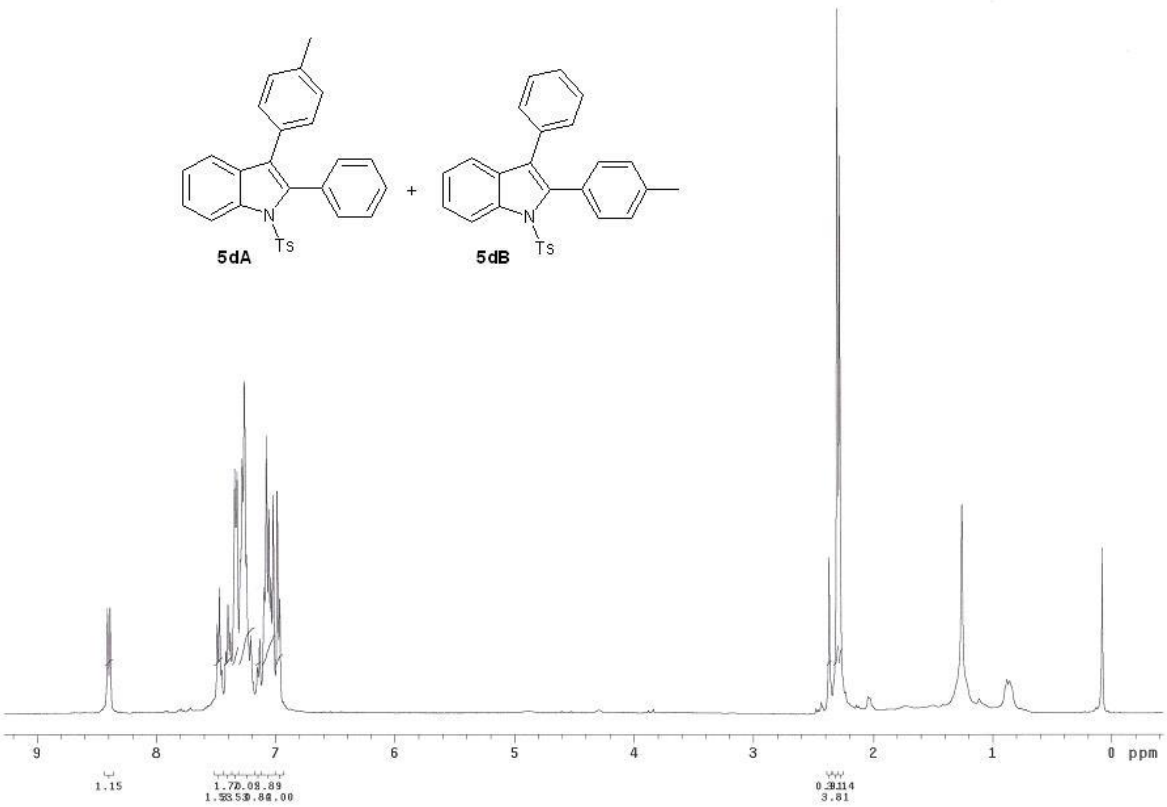
^{13}C NMR Spectrum of Compound **5cA** & **5cB** ($CDCl_3$, 100 MHz)



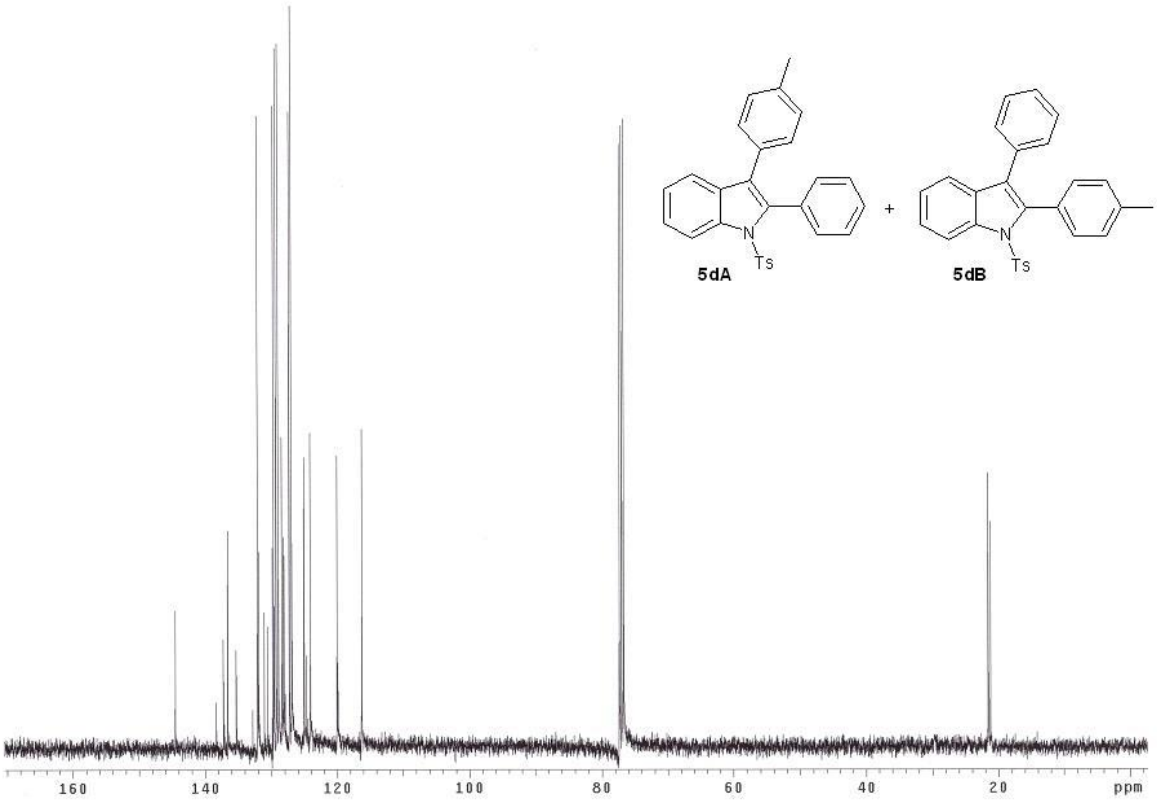
^{1}H NMR Spectrum of Compound **5cA** ($CDCl_3$, 400 MHz)



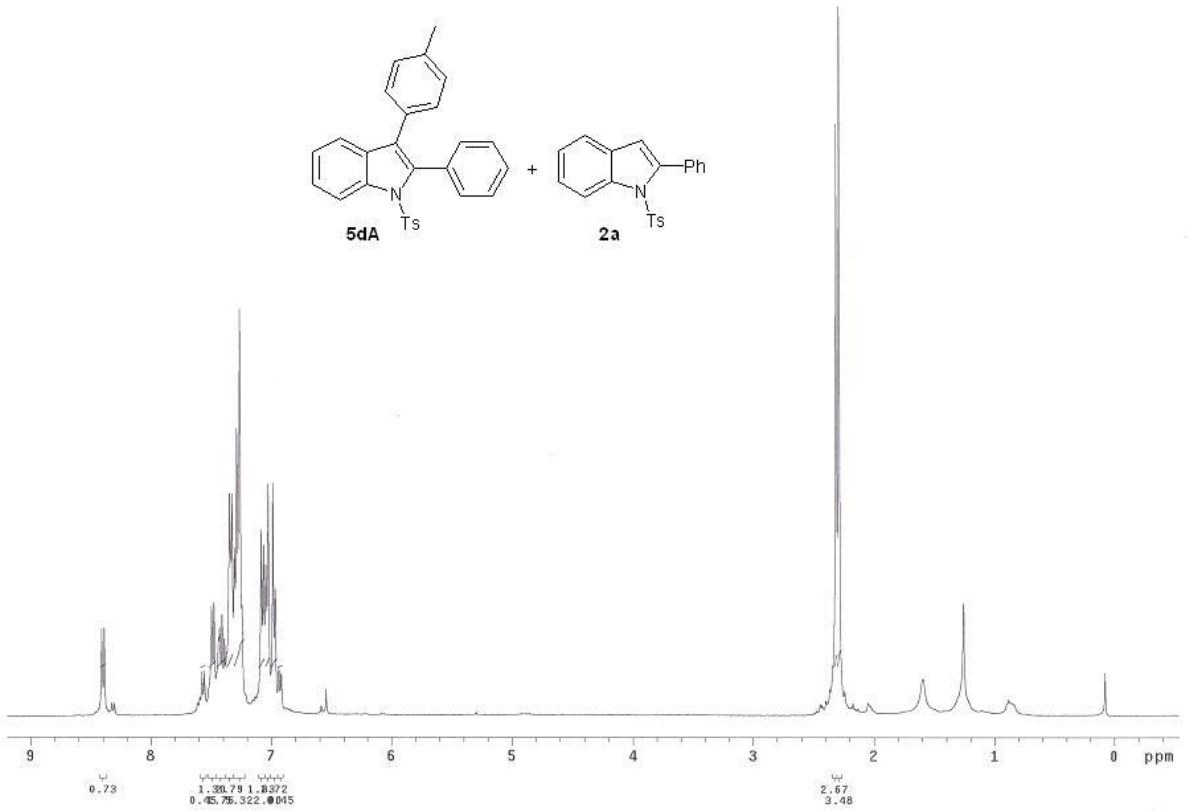
^{13}C NMR Spectrum of Compound **5cA** ($CDCl_3$, 100 MHz)



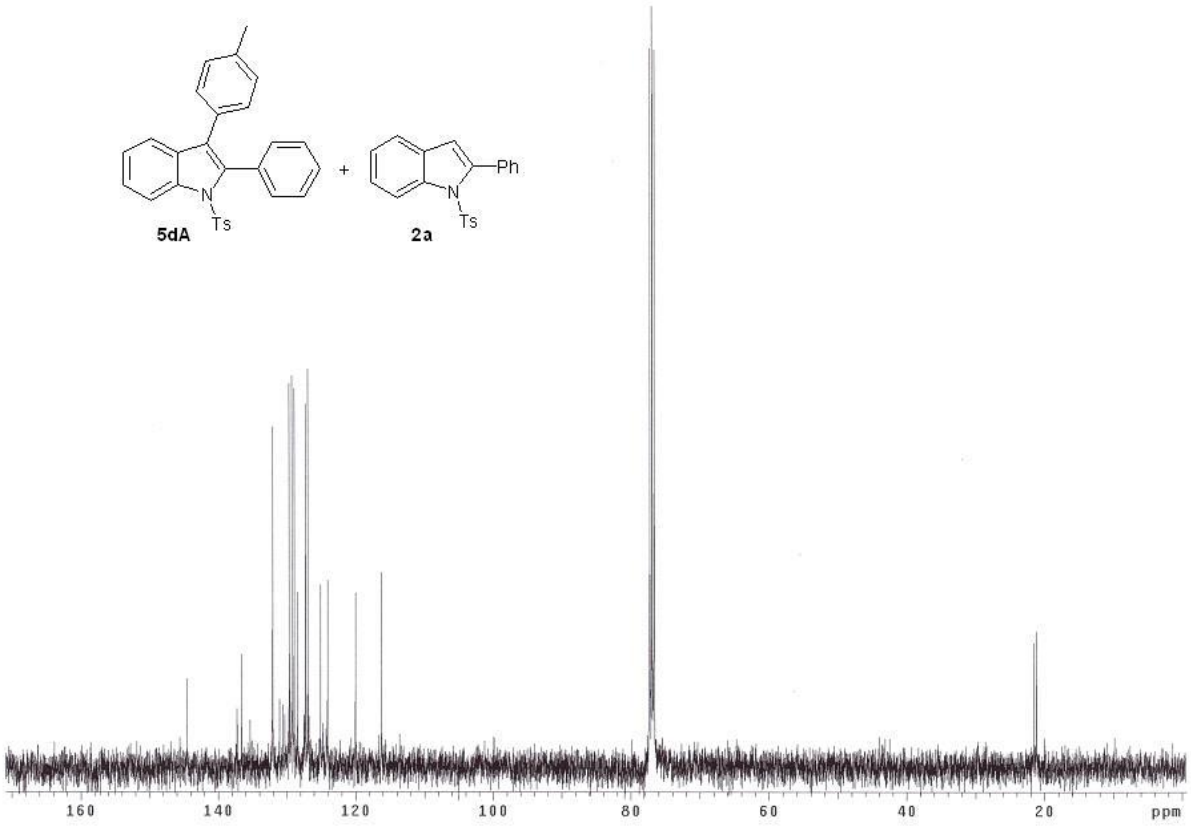
^{1}H NMR Spectrum of Compound **5dA** & **5dB** ($CDCl_3$, 400 MHz)



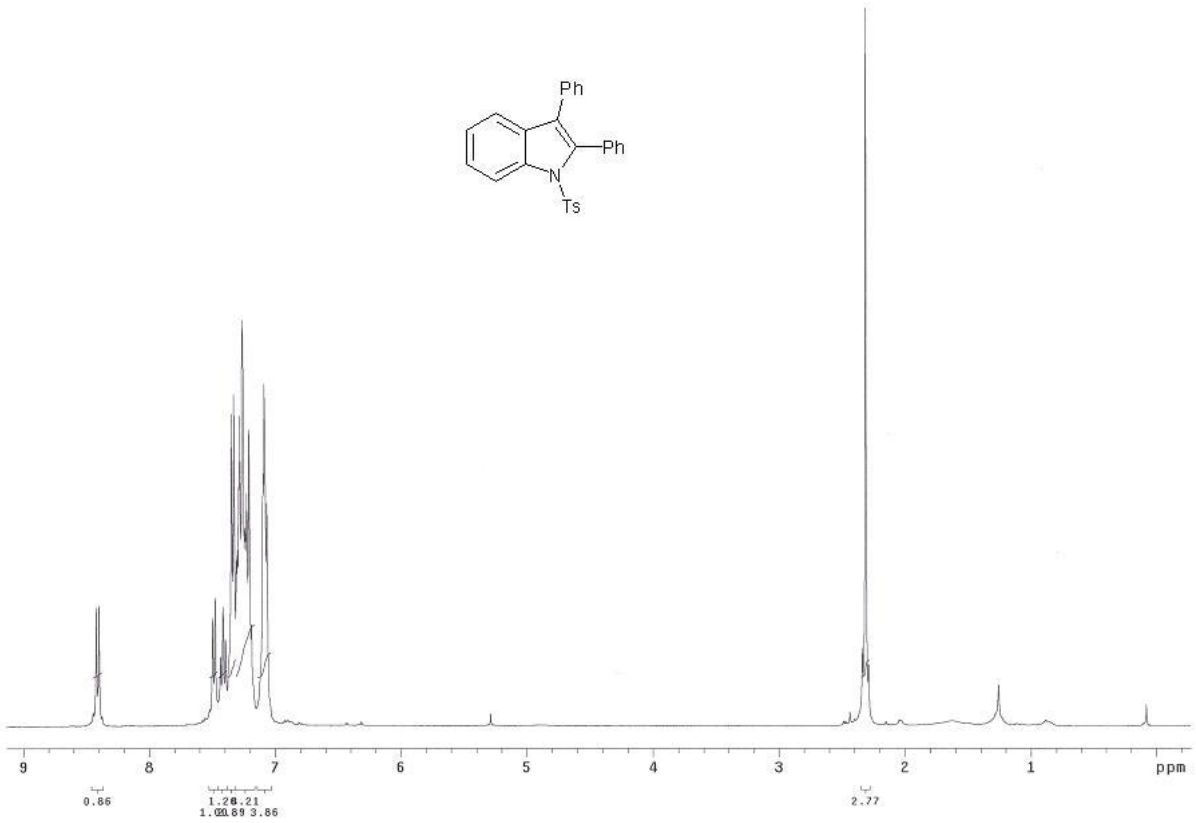
^{13}C NMR Spectrum of Compound **5dA** & **5dB** ($CDCl_3$, 100 MHz)



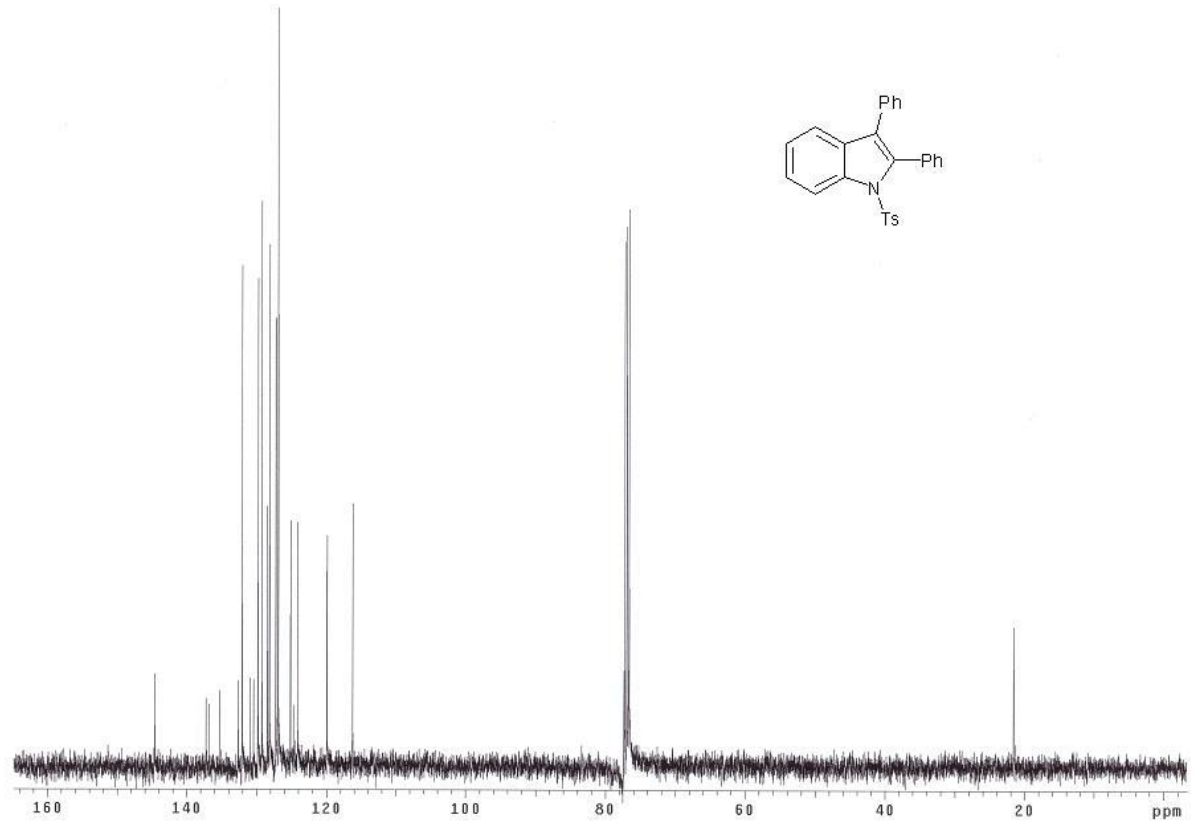
^{1}H NMR Spectrum of Compound **5dA** & **2a** ($CDCl_3$, 400 MHz)



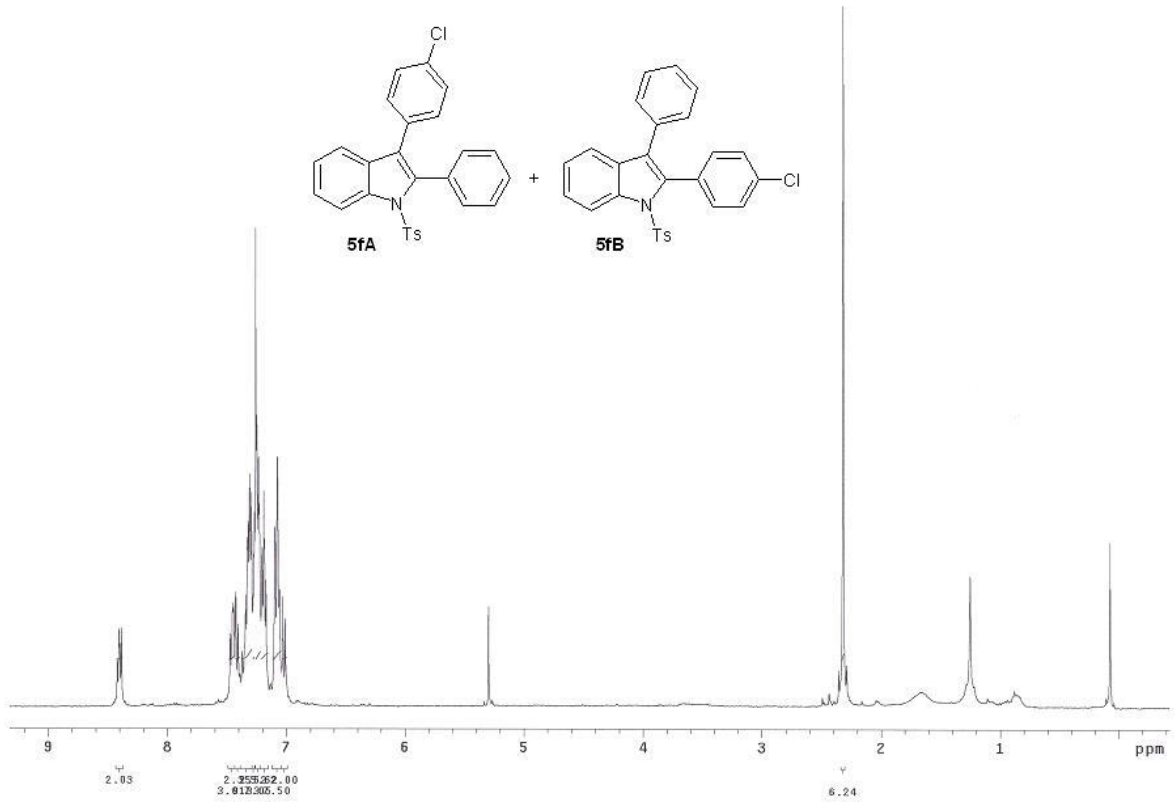
^{13}C NMR Spectrum of Compound **5dA** & **2a** ($CDCl_3$, 100 MHz)



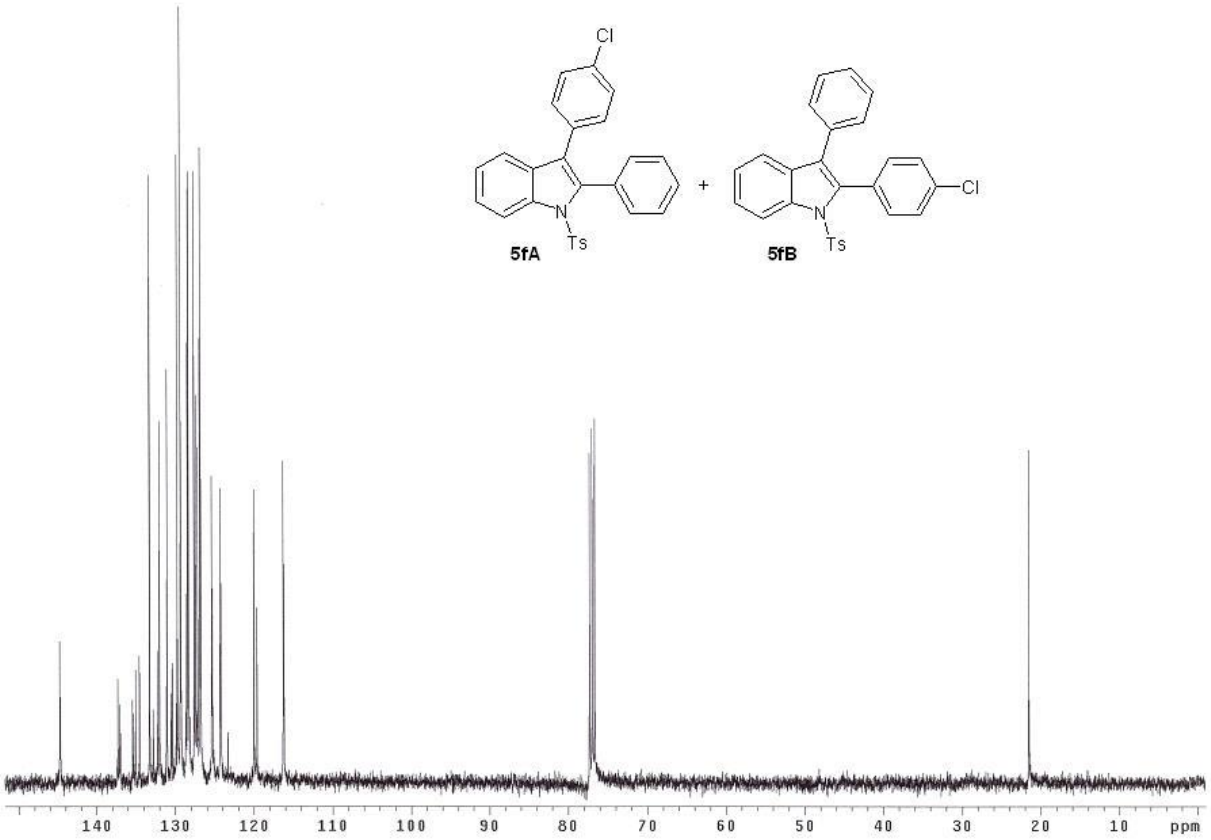
^{1}H NMR Spectrum of Compound **5e** ($CDCl_3$, 400 MHz)



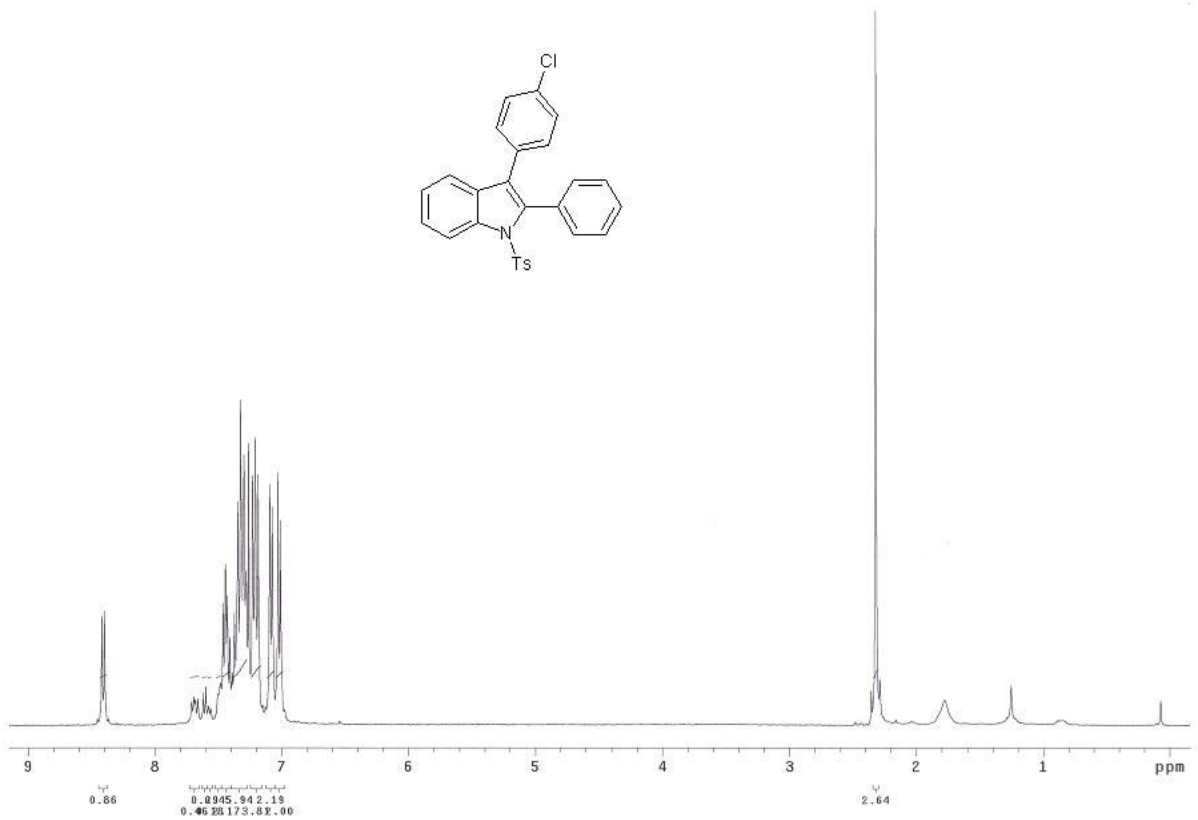
^{13}C NMR Spectrum of Compound **5e** ($CDCl_3$, 100 MHz)



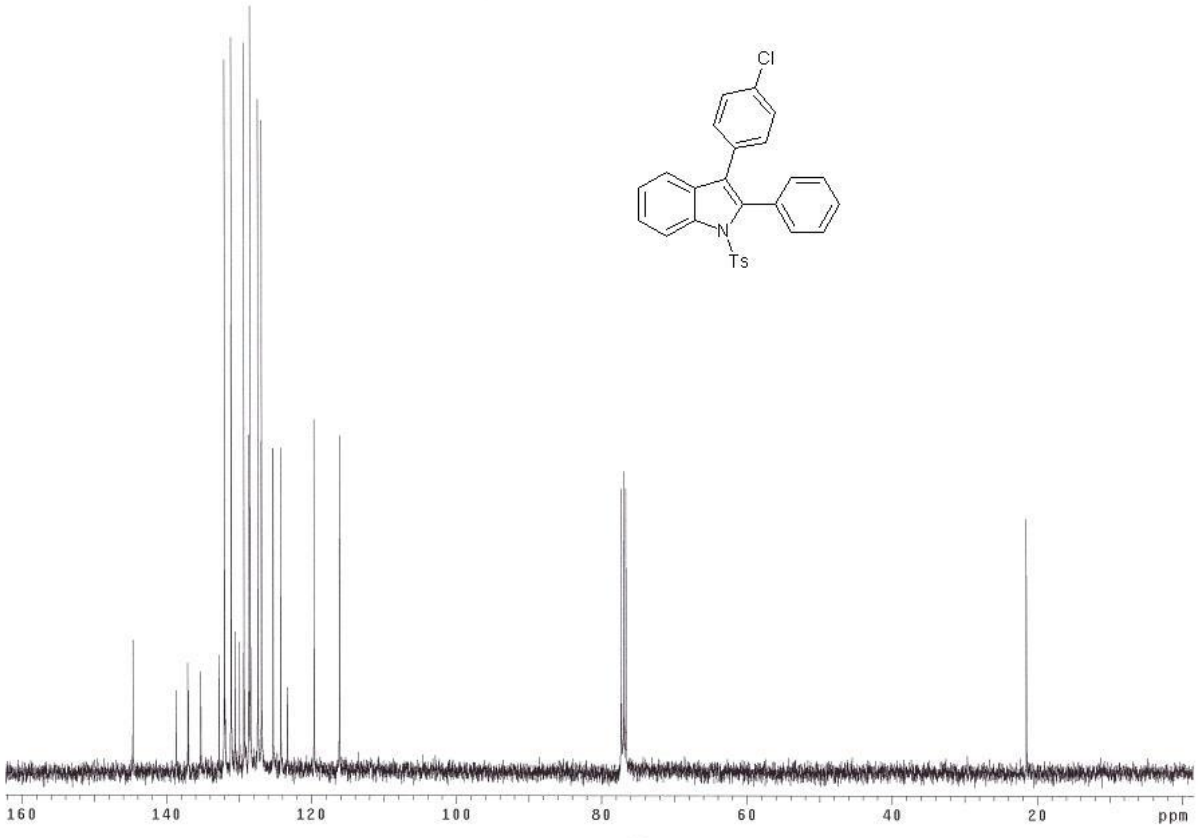
^{1}H NMR Spectrum of Compound **5fA** & **5fB** ($CDCl_3$, 400 MHz)



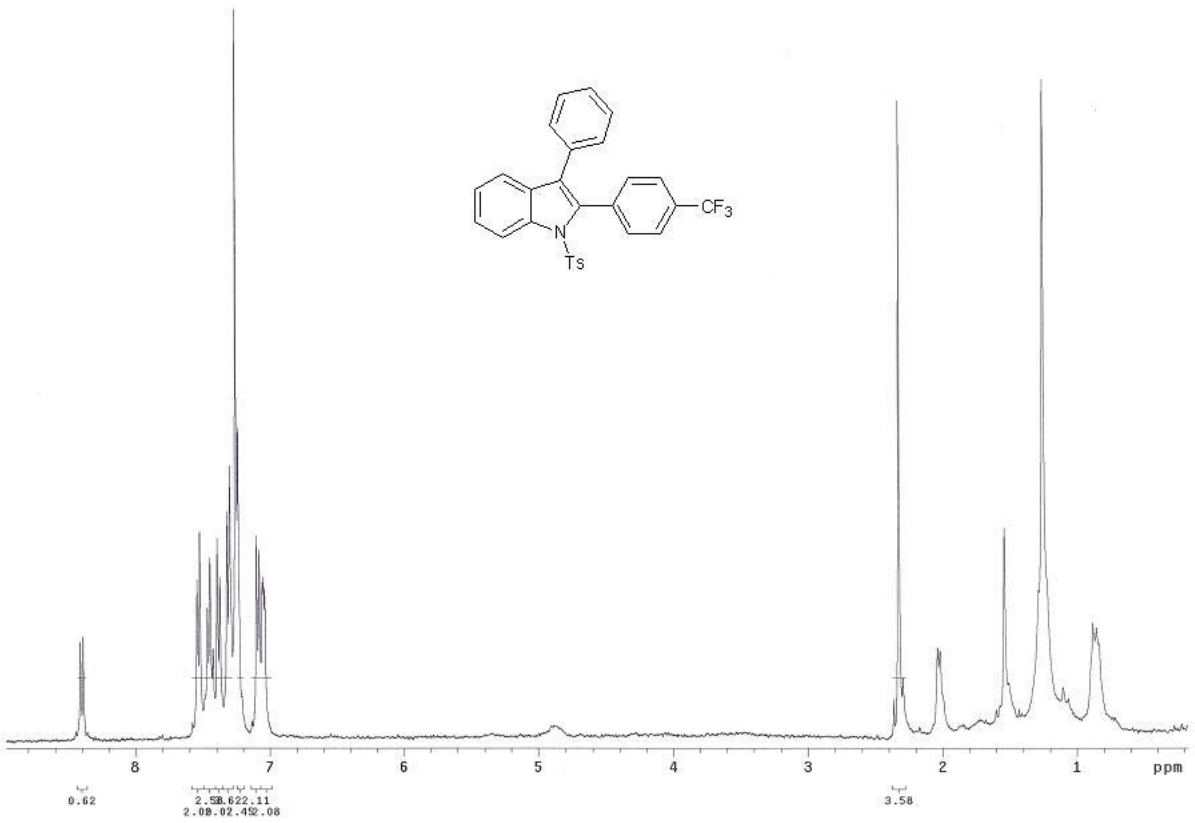
^{13}C NMR Spectrum of Compound **5fA** & **5fB** ($CDCl_3$, 100 MHz)



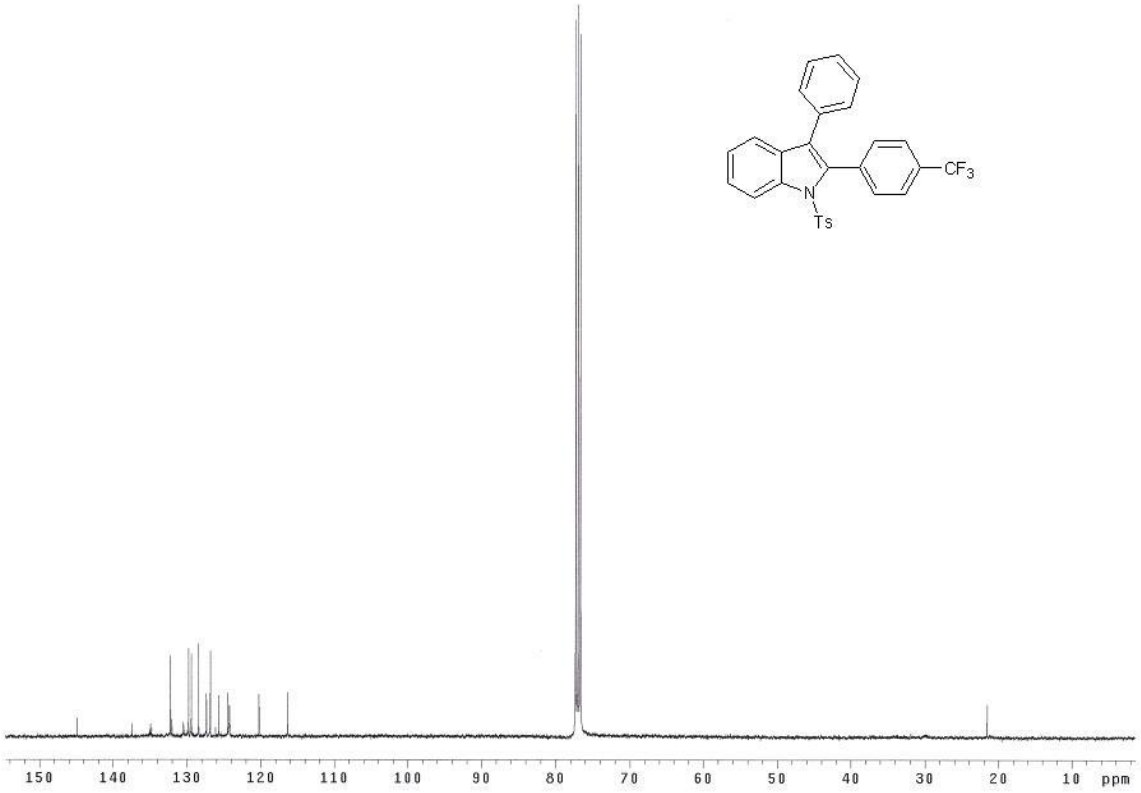
^{1}H NMR Spectrum of Compound **5fA** ($CDCl_3$, 400 MHz)



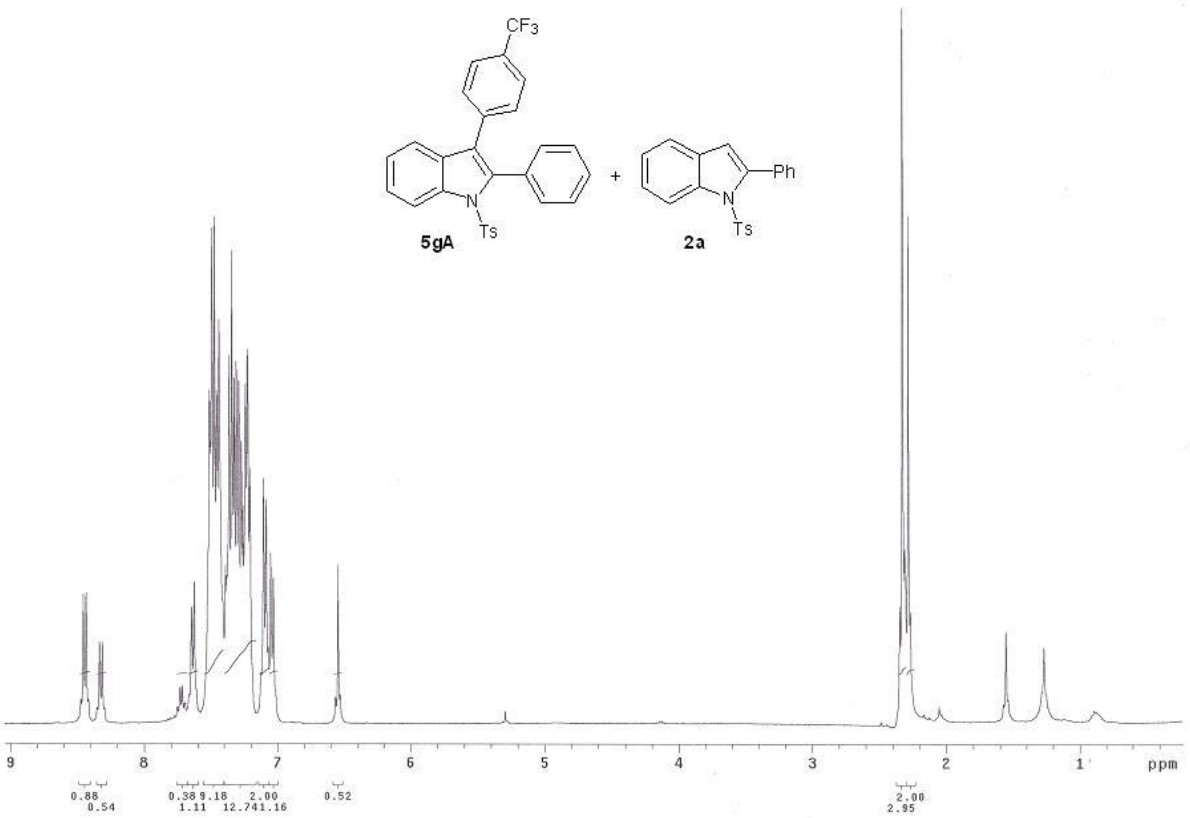
^{13}C NMR Spectrum of Compound **5fA** ($CDCl_3$, 100 MHz)



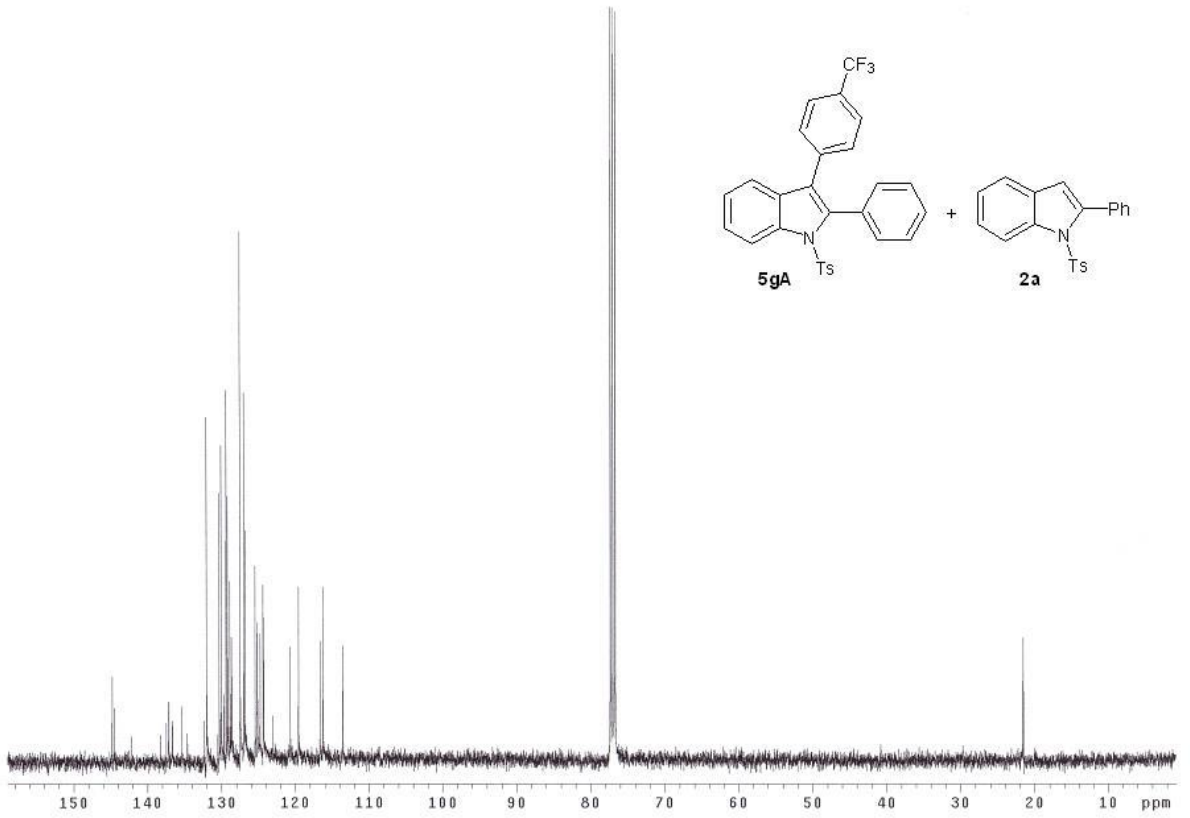
^{1}H NMR Spectrum of Compound **5gB** ($CDCl_3$, 400 MHz)



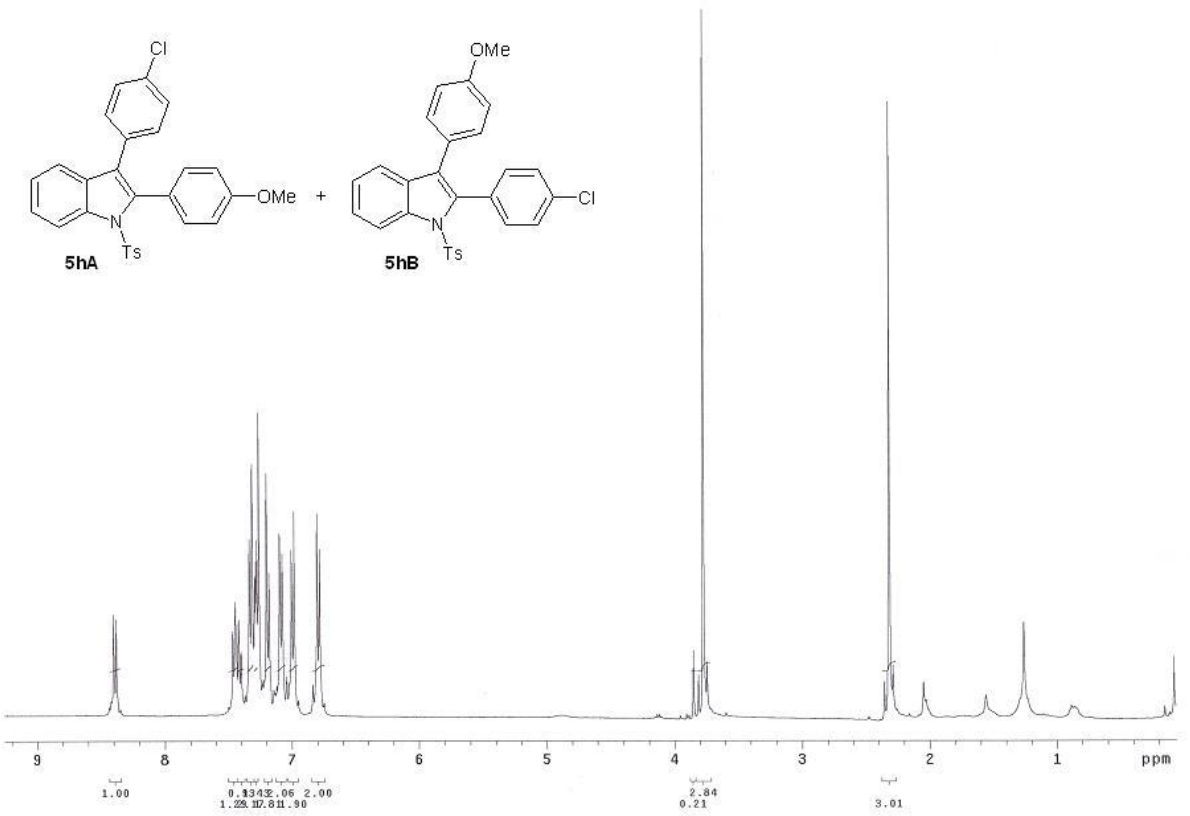
^{13}C NMR Spectrum of Compound **5gB** ($CDCl_3$, 100 MHz)



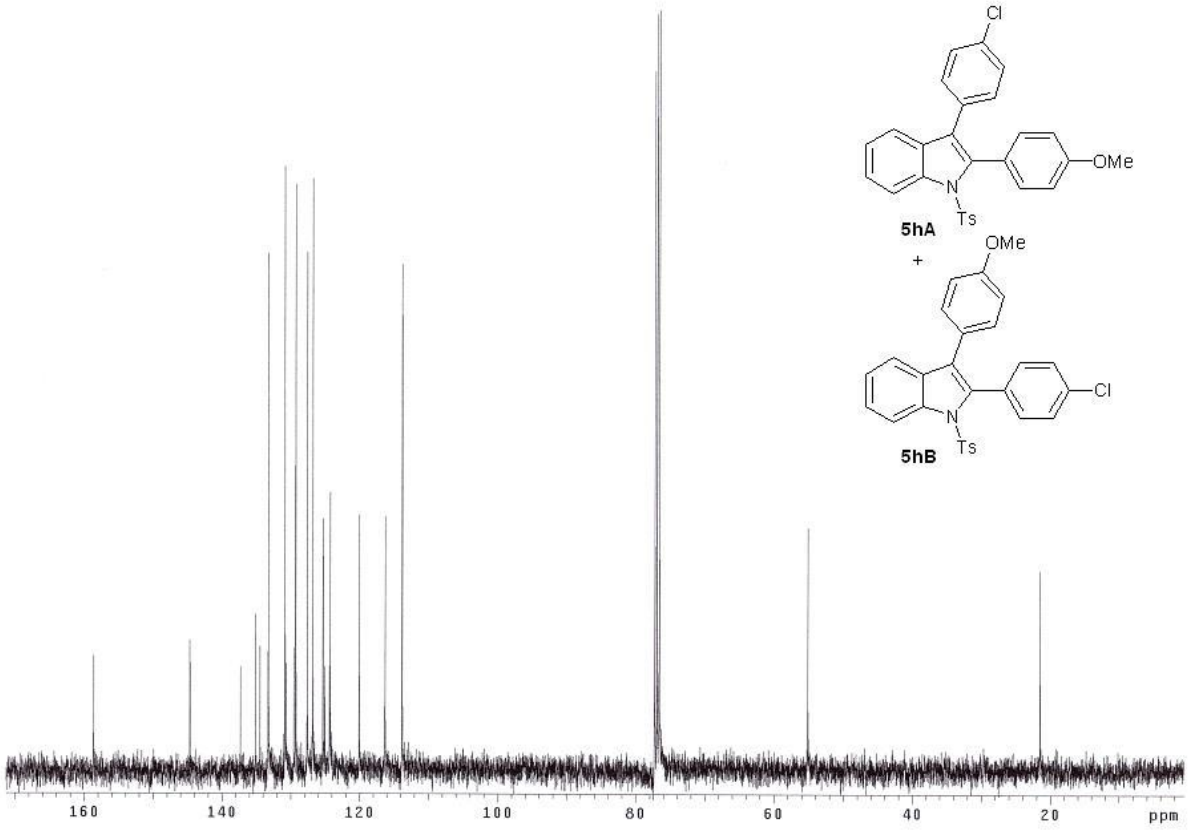
^{1}H NMR Spectrum of Compound **5gA** & **2a** ($CDCl_3$, 400 MHz)



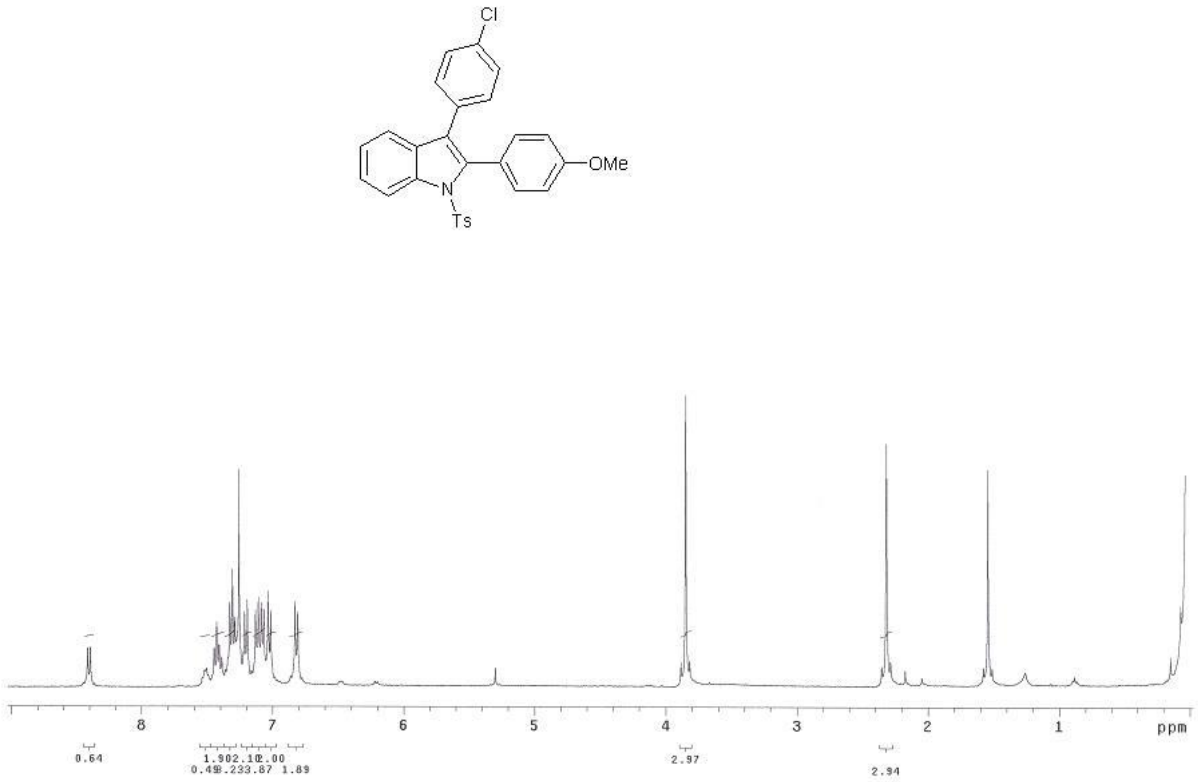
^{13}C NMR Spectrum of Compound **5gA** & **2a** ($CDCl_3$, 100 MHz)



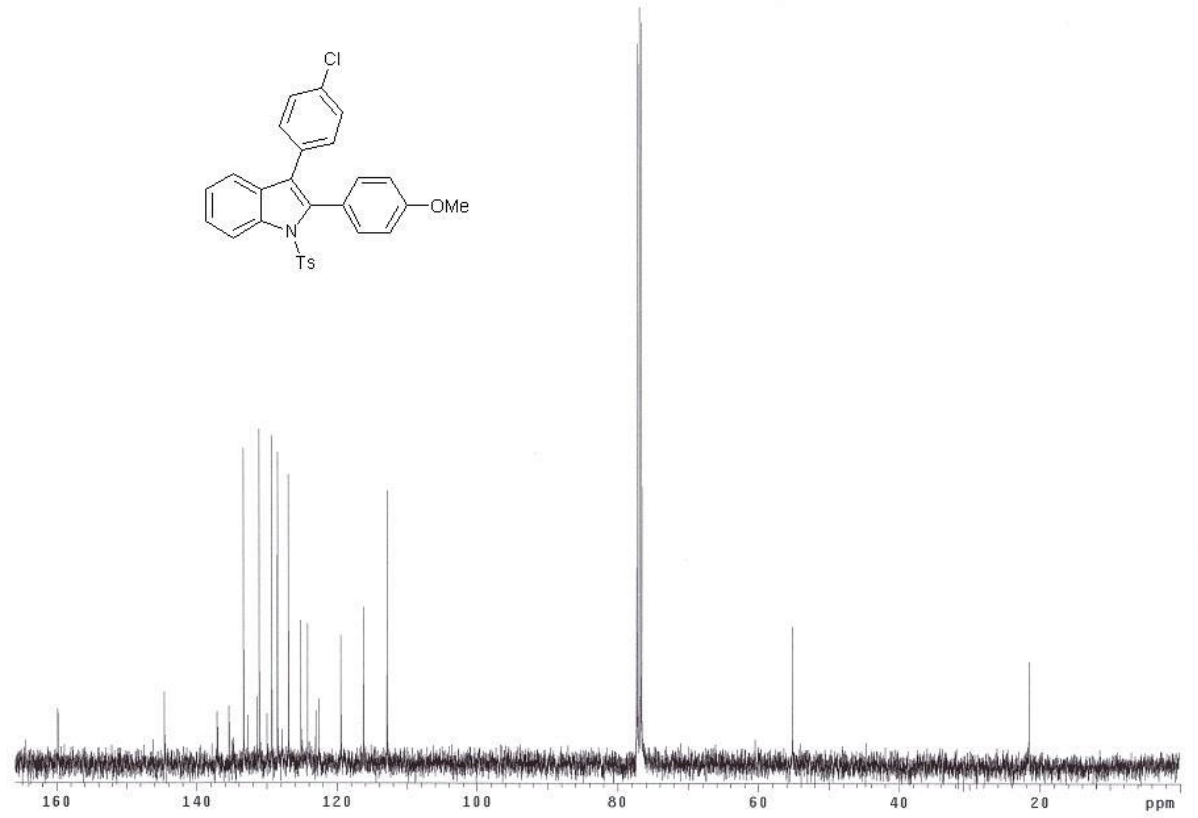
^{1}H NMR Spectrum of Compound **5hA** & **5hB** ($CDCl_3$, 400 MHz)



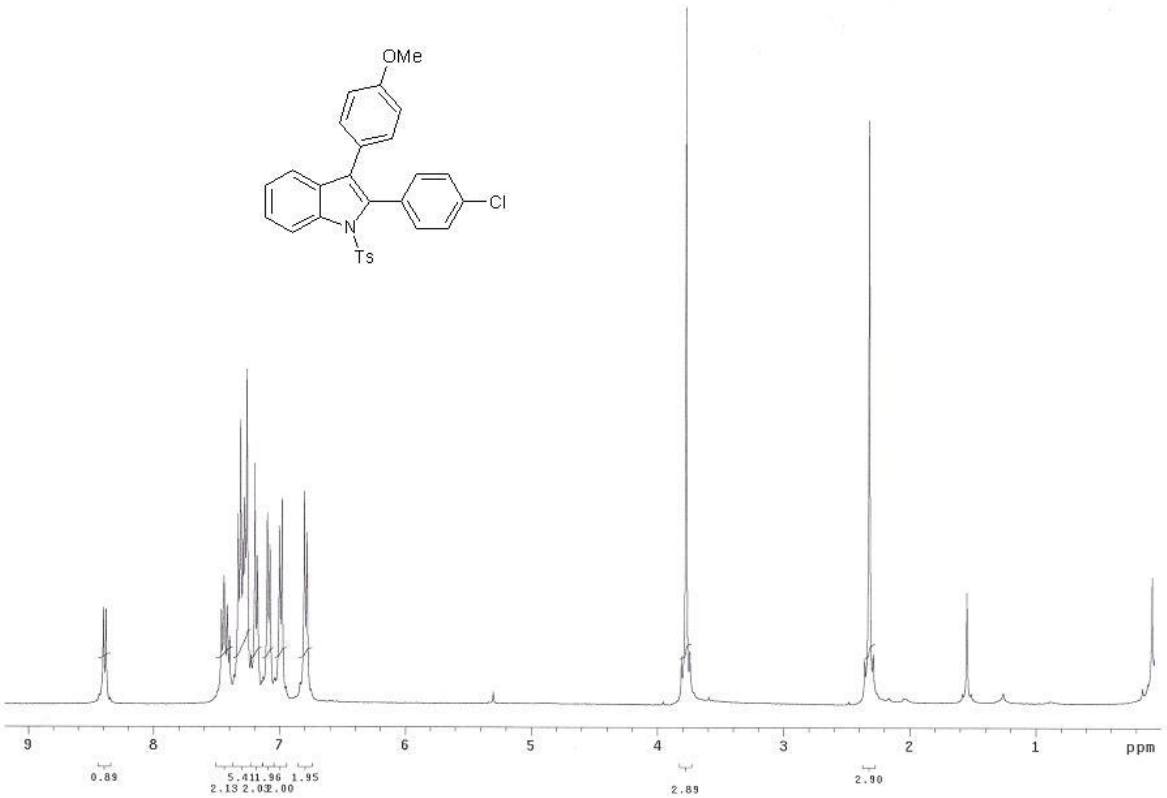
^{13}C NMR Spectrum of Compound **5hA** & **5hB** ($CDCl_3$, 100 MHz)



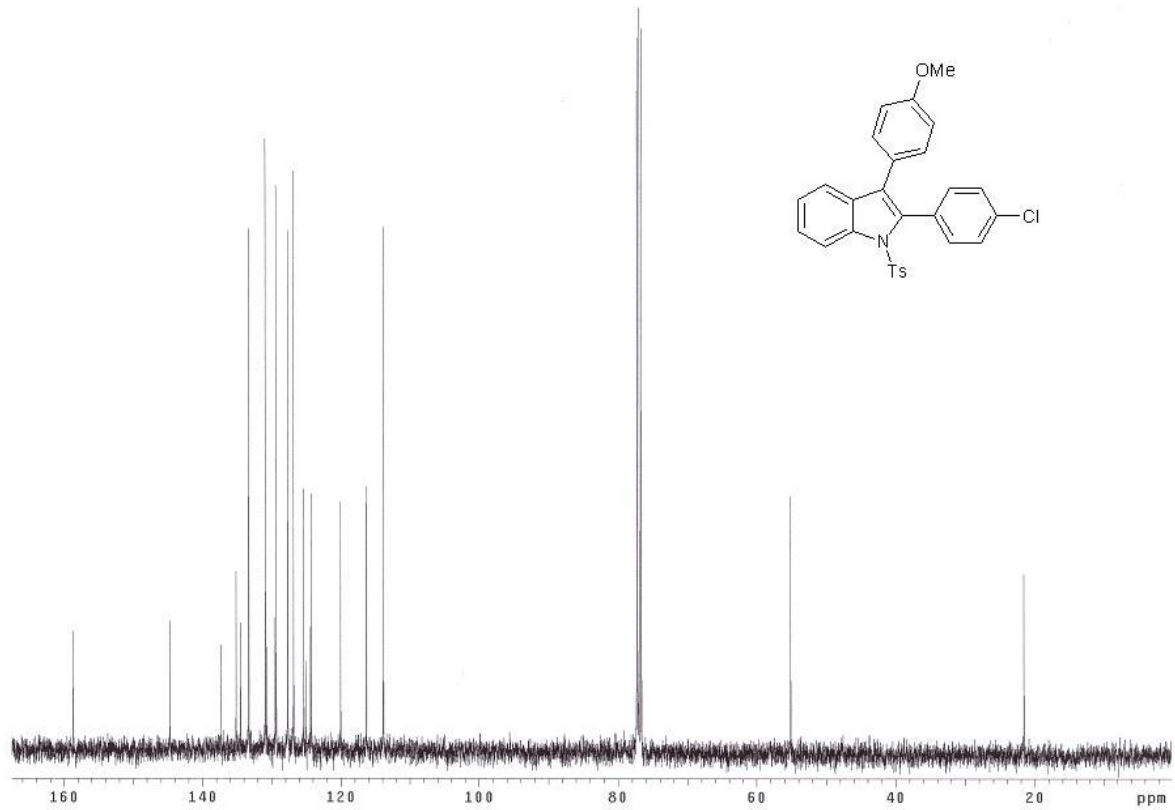
^{1}H NMR Spectrum of Compound **5hA** ($CDCl_3$, 400 MHz)



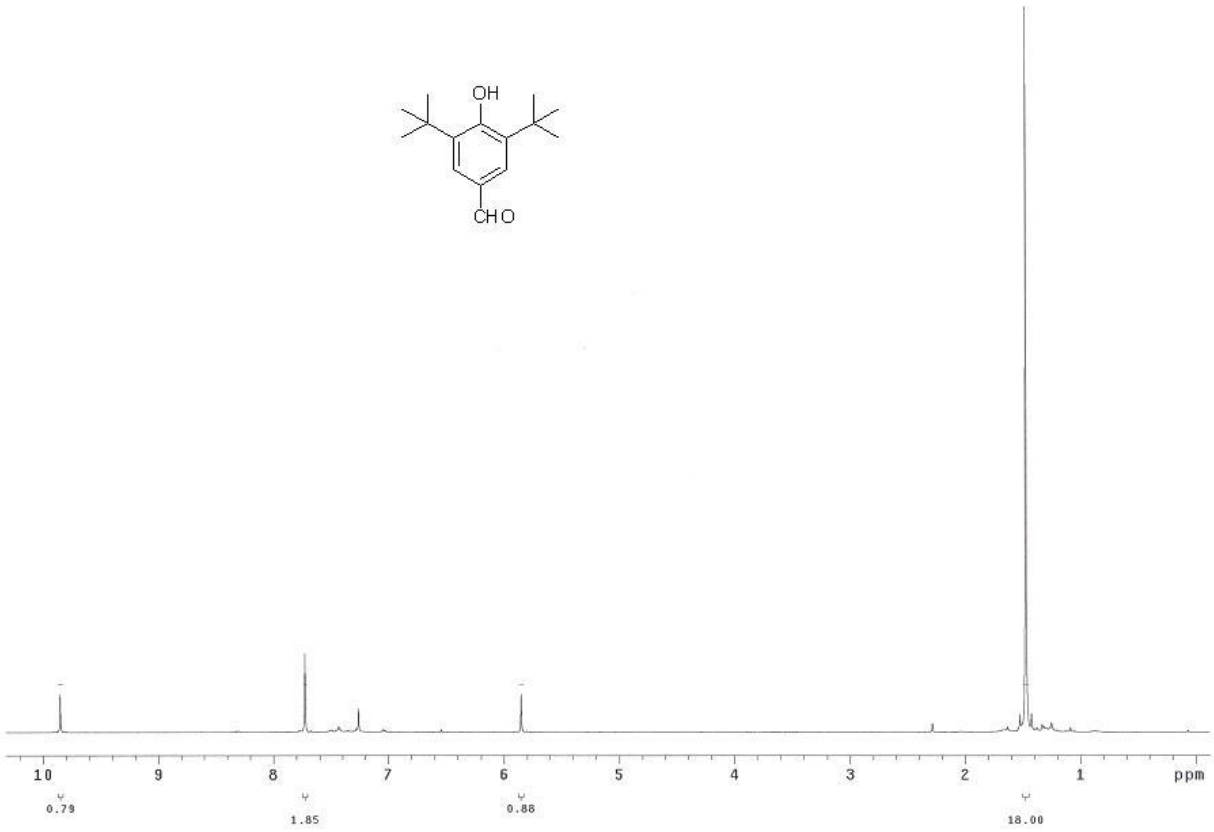
^{13}C NMR Spectrum of Compound **5hA** ($CDCl_3$, 100 MHz)



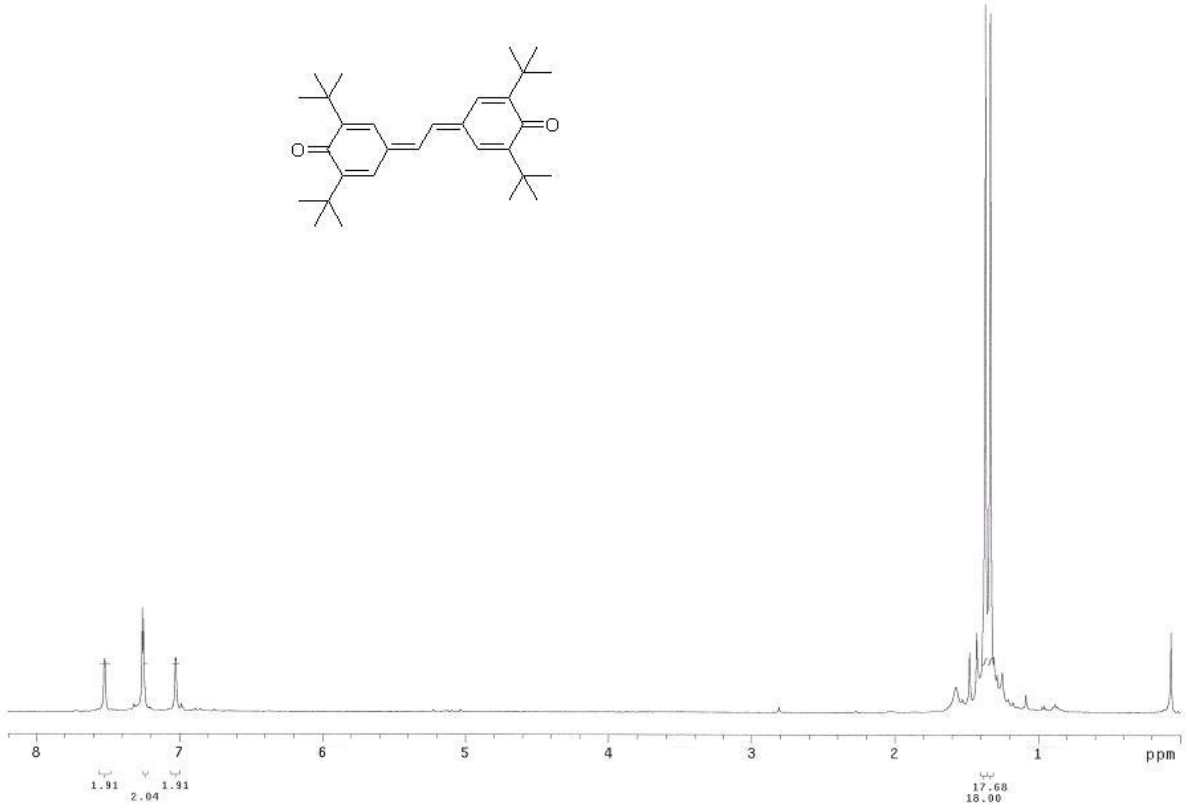
^{1}H NMR Spectrum of Compound **5hB** ($CDCl_3$, 400 MHz)



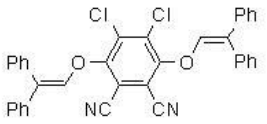
^{13}C NMR Spectrum of Compound **5hB** ($CDCl_3$, 100 MHz)

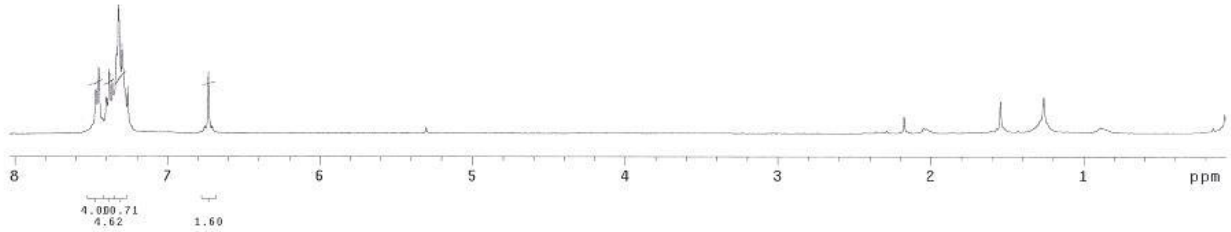


^{1}H NMR Spectrum of Byproduct from the Reaction in the Presence of BHT ($CDCl_3$, 400 MHz)

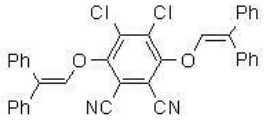


^{1}H NMR Spectrum of Byproduct from the Reaction in the Presence of BHT ($CDCl_3$, 400 MHz)





^{1}H NMR Spectrum of DDQ Adduct **8** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of DDQ Adduct **8** ($CDCl_3$, 100 MHz)