Supporting Information

Unusual 1,2-Aryl Migration in Pd(II)-Catalyzed Aza-Wacker-Type Cyclization of 2-Alkenylanilines

So Won Youn* and So Ra Lee

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

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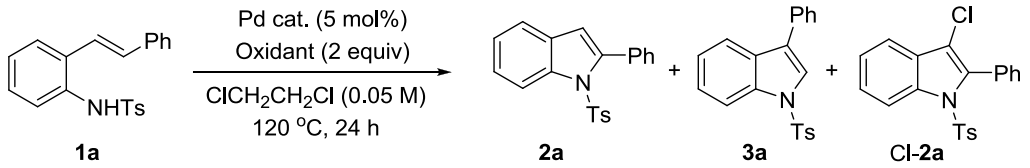
General Information

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

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

Table S1. Full Data of Optimization Studies



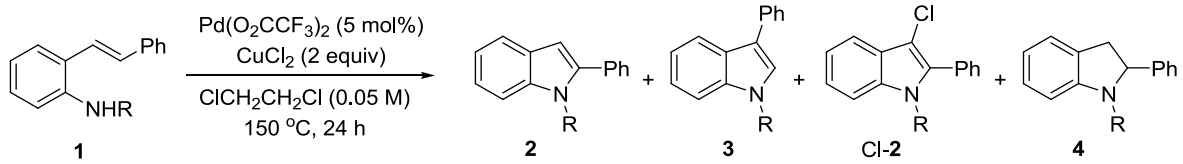
1a **2a** **3a** **Cl-2a**

Entry	Pd cat.	Oxidant	Additive (mol%)	Yield (%)[a]	**2a**:**3a**:Cl-**2a**[b]
1	$Pd(O_2CCF_3)_2$	$Cu(OAc)_2$	-	20	1:0:0
2	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	(84)	1:0.5:0
3	$Pd(O_2CCF_3)_2$	$CuBr_2$	-	36	1:0:0
4	$Pd(O_2CCF_3)_2$	Ag_2O	-	32	1:0:0
5	$Pd(O_2CCF_3)_2$	AgOAc	-	81	1:0:0
6	$Pd(O_2CCF_3)_2$	Ag_2CO_3	-	87	1:0.3:0
7	$Pd(O_2CCF_3)_2$	BQ or CuCl	-	0	-
8	$Pd(O_2CCF_3)_2$	*t*BuOOH	-	34	1:0:0
9	$Pd(O_2CCF_3)_2$	$Ce(SO_4)_2$	-	48	1:0.1:0
10	$Pd(O_2CCF_3)_2$	$PhI(OAc)_2$	-	12	1:0:trace[c]
11	$Pd(O_2CCF_3)_2$	$K_2S_2O_8$	-	34	1:0:0
12	$Pd(O_2CCF_3)_2$	Oxone	-	31	1:0:0
13	$Pd(O_2CCF_3)_2$	selectfluor	-	6	1:0.2:0
14[d]	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	40	1:0.2:0
15[e]	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	56	1:0.3:0.2
16[f]	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	16-33	1:0:0
17[g]	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	67-74	1:0:0
18[h]	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	24	1:0.3:0
19[i]	**$Pd(O_2CCF_3)_2$**	**$CuCl_2$**	-	**100 (91)**	**1:0.6:0**
20[i-j]	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	61	1:0.5:0
21[i, k]	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	100	1:1:0.7
22[i]	$Pd(O_2CCF_3)_2$	-	-	7	1:0:0
23[i, l]	$Pd(O_2CCF_3)_2$	-	-	69	1:0:0
24[i]	-	$CuCl_2$	-	85	1:0:0
25[i, m]	-	$CuCl_2$	-	(27)	1:0:0
26	$Pd(OAc)_2$	$CuCl_2$	-	89	1:1.3:0
27[i]	**$Pd(OAc)_2$**	**$CuCl_2$**	-	**98 (92)**	**1:2.1:0**
28[i]	$Pd(OAc)_2$	$Cu(OAc)_2$	-	17	1:0:0
29	$PdCl_2$	$CuCl_2$	-	86	1:0.9:0.2
30	$PdCl_2(MeCN)_2$	$CuCl_2$	-	87	1:0.9:0
31	$PdCl_2(PPh_3)_2$	$CuCl_2$	-	77	1:0:trace
32	$PdCl_2$(dppf)	$CuCl_2$	-	68	1:0.9:0
33[i]	$PdCl_2$(dppf)	$CuCl_2$	-	55	1:1:0
34	$Pd(OAc)_2$	$CuCl_2$	LiCl (200)	83	1:1:0
35[i]	**$Pd(OAc)_2$**	**$CuCl_2$**	**LiCl (200)**	**95 (92)**	**1:1.8:0**
36[i]	$PdCl_2$(dppf)	$CuCl_2$	LiCl (200)	46	1:1.4:0
37	$Pd(OAc)_2$	$CuCl_2$	LiBr (200)	58	1:0.5:0.3
38	$Pd(OAc)_2$	$CuCl_2$	NaI (200)	72	1:0.3:0
39	$Pd(OAc)_2$	$CuCl_2$	*n*Bu_4NCl (200)	47	1:0:0
40	$Pd(OAc)_2$	$CuCl_2$	dppf (5)	38[n]	1:0.1:0
41[i]	$Pd(OAc)_2$	$CuCl_2$	dppf (5)	15	1:0:0
42	$Pd(OAc)_2$	$CuCl_2$	dppp (5)	86	1:0:0.1
43	$Pd(OAc)_2$	$CuCl_2$	dppe (5)	64	1:trace:0

44	$Pd(OAc)_2$	$CuCl_2$	(*S*)-BINAP (5)	85	1:trace:0.1
45	$Pd(OAc)_2$	$CuCl_2$	Xantphos (5)	80	1:trace:0.1
46	$Pd(OAc)_2$	$CuCl_2$	Sphos (10)	68	1:0:0
47	$Pd(OAc)_2$	$CuCl_2$	P(*o*-Tol)$_3$ (10)	59	1:0:0.1
48	$Pd(OAc)_2$	$CuCl_2$	2,2'-bipyridine (5)	85	1:0.1:0.1
49	$Pd(OAc)_2$	$CuCl_2$	phenanthroline (5)	95	1:0.1:0.1
50	$Pd(OAc)_2$	$CuCl_2$	TMEDA (5)	75	1:trace:0
51	$Pd(OAc)_2$	$CuCl_2$	IMes·HCl (10)	93	1:0:0
52[i, o]	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	(100)	1:0.3:0
53[i, p]	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	(88)	1:0.06:0
54[i, q]	$Pd(O_2CCF_3)_2$	$CuCl_2$	-	20-57	1:0:0

All reactions were carried out 2-5 times repetitively and the average values of both yields and ratios are given. [a] Yields were determined by ^{1}H NMR using trichloroethylene as an internal standard. Value in parentheses indicates an isolated yield. [b] Ratios of inseparable isomers were determined by ^{1}H NMR. [c] Instead of Cl, OAc was introduced at C3 position. [d] In toluene. [e] In heptane. [f] In 1,4-dioxane, MeCN, EtOAc, or DMF. [g] In DMSO or AcOH. [h] At 100 ℃. [i] At 150 ℃. [j] Using 1 equiv $CuCl_2$. [k] Using 3 equiv $CuCl_2$. [l] Using 1 equiv $Pd(O_2CCF_3)_2$. [m] Using 20 mol% $CuCl_2$ under O_2 (1 atm). [n] *N*-Ts-2-phenylindoline was obtained in 8%. [o] In the presence of 1 equiv Na_2CO_3. [p] In the presence of 1 equiv K_2CO_3. [q] In the presence of 1 equiv NEt_3, $(iPr)_2NEt$, or DMAP.

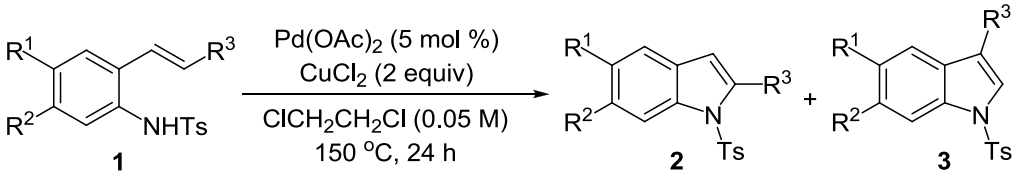
Table S2. Effect of *N*-Protecting Groups



Entry	R	Yield (%)[a]	**2**:**3**:Cl-**2**[b]
1	Ts (**1a**)	**91 (0)**	**1:0.6:0**
2	$PhSO_2$	88 (0)	1:0.2:0
3	*p*-$NO_2C_6H_4SO_2$	85 (0)	1:0.4:0
4	(2-pyridinyl)SO_2	80 (0)	1:0:0
5	Tf	96 (0)	1:0:0
6	Ms	90 (15)	1:0.3:0
7	Ac	-[c-d]	-
8	Piv	-[c]	-
9	Bz	-[c-d]	-
10	C_6F_5CO	-[c-d]	-
11	(2-pyridinyl)CO	-[c]	-
12	CO_2Et	68 (11)	1:0:0.3
13	Cbz	66 (5)	1:0:0.5
14	Boc	-[e]	-
15	Bn	-[d-e]	-
16	H	-[d-e]	-

All reactions were carried out 2-5 times repetitively and the average values of both yields and ratios are given. [a] Isolated yield. Value in parentheses indicates a yield of **4**. [b] Ratios of inseparable isomers were determined by ^{1}H NMR. [c] Complex mixture. [d] 30-60% of starting material remained unreacted. [e] Decomposed.

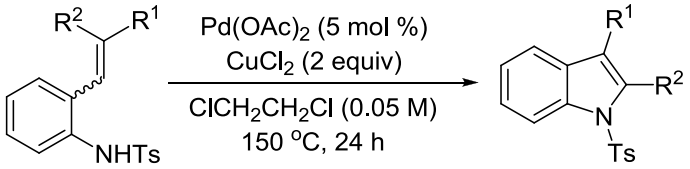
Table S3. Substrate Scope: β-Monosubstituted Alkenes

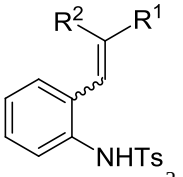
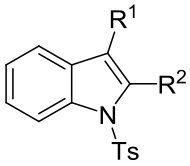
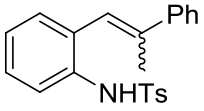
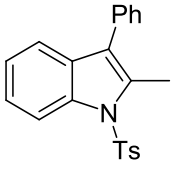
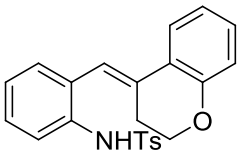
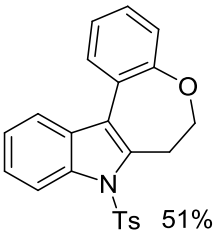
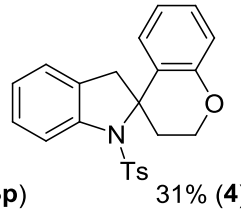


Entry	R^1	R^2	R^3	Yield (%)[a]	**2**:**3**[b]
1	H	H	Ph (**1a**)	92	1:2.1
2	H	H	Ph ((*Z*)-**1a**)	87[c]	1:0.7
3[d]	H	H	4-$MeOC_6H_4$ (**1b**)	80[c]	1:2.1 (:0.5)[e]
4	H	H	4-MeC_6H_4	93[c]	1:1.9 (:0.2)[e]
5	H	H	3-MeC_6H_4 (**1c**)	77[c, f]	1:0.9
6	H	H	2-MeC_6H_4	92[c]	1:2.1
7	H	H	4-ClC_6H_4 (**1d**)	85	1:0.6
8	H	H	4-$NO_2C_6H_4$ (**1e**)	91	1:0
9	H	H	3-$CF_3C_6H_4$	90	1:0
10[g]	H	H	CO_2Me (**1f**)	60[f]	1:0
11	H	H	*n*Hex (**1g**)	20	1:0
12	Me	H	Ph (**1h**)	85[c]	1:0.5
13	Cl	H	Ph	91	1:2
14[h]	NO_2	H	Ph (**1i**)	90	1:3.8
15	H	Me	Ph	89	1:0.3 (:0.1)[e]
16[h]	H	Cl	Ph (**1j**)	98	1:0.8
17[h]	H	NO_2	Ph (**1k**)	82[f]	1:1.1

All reactions were carried out 3-5 times repetitively and the average values of both yields and ratios are given. [a] Isolated yield. [b] Ratios of inseparable isomers were determined by ^{1}H NMR. [c] ~5% of the corresponding 2-substituted indoline was obtained. [d] For 6 h. [e] The ratio of *N*-Ts-2-aryl-3-chloro-substituted indole (Cl-**2**). [f] The remainder of the mass balance was unreacted starting material. [g] Using 20 mol% $Pd(OAc)_2$. [h] Using 10 mol% $Pd(OAc)_2$.

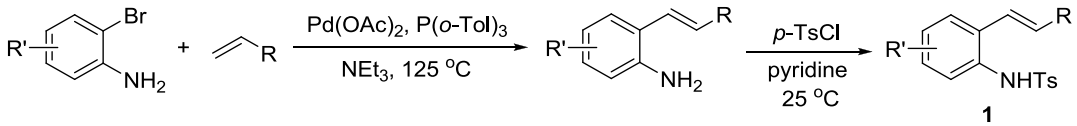
Table S4. Substrate Scope: β,β-Disubstituted Alkenes



Entry	Substrate		Product (%)[a]
			
	R^1	R^2	
1	4-$MeOC_6H_4$	4-$CF_3C_6H_4$ (**1l**)	78% (85%) (**3l**)
2	4-MeC_6H_4	4-$CF_3C_6H_4$ (**1m**)	47% (96%) (**3m**)
3	Ph	4-$CF_3C_6H_4$ (**1n**)	42% (89%) (**3n**)[b]
4	Ph	Ph	73% (94%)
5[c]	 **1o**		 64% (83%) (**3o**)
6[c]	 **1p**		 51% (**3p**)  31% (**4**)

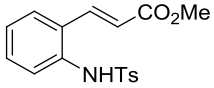
[a] Isolated yield. Value in parentheses indicates a yield based on recovered starting material. [b] ~5% of **2a** was obtained. [c] Using 10 mol% $Pd(OAc)_2$.

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



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 to afford the corresponding 2-styrylaniline product. To a solution of 2-styrylaniline (1 equiv) in pyridine (0.2 M) was added *p*-toluenesulfonyl chloride (1.1 equiv) at 0 ℃. 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 **1**.

(*E*)-Methyl 3-(2-(4-Methylphenylsulfonamido)phenyl)acrylate (1f)

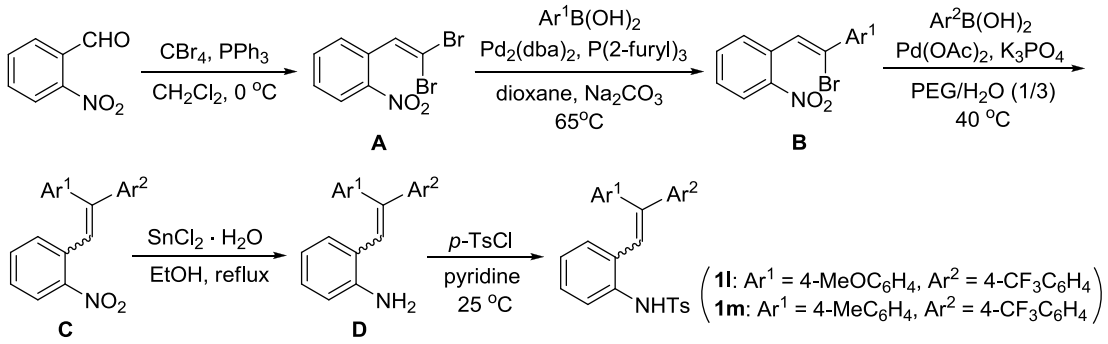


Following the general procedure: 32% (step 1), 85% (step 2), a yellow solid (EtOAc : *n*-Hexane = 1:4 (step 1), 1:2 (step 2)), mp 160-162 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (S, 3H), 3.79 (s, 3H), 6.15 (d, J = 15.6 Hz, 1H), 6.70 (br s, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.51 (d, J = 16.0 Hz, 1H), 7.56 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 51.9, 120.4, 127.2, 127.3, 129.6, 129.7, 130.3, 130.9, 134.6, 135.8, 138.98, 139.03, 144.0, 166.8. EIMS *m*/*z* 331 (M^+), 234, 176, 144, 132, 117, 91, 65, 51.

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

General Procedure for the Preparation of β,β-Disubstituted 2-Alkenylanilines



[2] Zhu, J.-B.; Wang, P.; Liao, S.; Tang, Y. *Org. Lett.* **2013**, *15*, 3054.

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 **A** (1.7 g, 85%) as an orange solid.

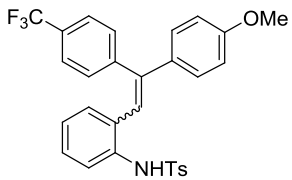
A mixture of **A** (1 equiv), $Pd_2(dba)_3$ (3 mol%), P(2-furyl)$_3$ (15 mol%), and $Ar^1B(OH)_2$ (1 equiv) in 1,4-dioxane (0.1 M) was stirred at rt under argon for 5 min. An aq. Na_2CO_3 solution (1.0 M, 2 equiv) was added and the reaction mixture was heated at 65 ℃ for 23 h. The reaction mixture was 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 **B**.

To a solution of **B** 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 ^oC 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 **C**.

The suspension of **C** (1 equiv) and $SnCl_2 \cdot H_2O$ (5 equiv) in EtOH (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 to give the corresponding product **D**.

1l-1m were prepared from **D** following a general procedure for tosylation. The stereochemistry of olefin **1l-1m** could not be determined.

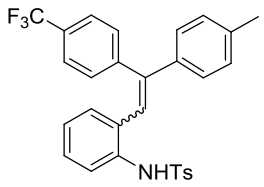
***N*-(2-(2-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (1l)**



E/*Z* mixture was obtained with a 3:1 ratio. an orange solid (EtOAc : *n*-Hexane = 1 : 4), mp 70-72 ℃. Signals corresponding to major isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ δ 2.41 (s, 3H), 3.82 (s, 3H), 6.42 (s, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.81-6.89 (m, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 4H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 3H), 7.59 (d, *J* = 8.4 Hz, 2H). Representative signals corresponding to minor isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 3.77 (s, 3H), 6.40 (s, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.93 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5,

55.1, 55.3, 113.6, 113.7, 114.0, 122.2, 123.8 (q, J = 270.6 Hz), 123.9, 124.1, 124.5, 125.0 (q, J = 4.4 Hz), 125.1 (q, J = 3.7 Hz), 125.5, 125.6, 127.08, 127.14, 128.1, 128.2, 128.3, 129.05 (q, J = 33.8 Hz), 129.09, 129.5, 129.6, 130.4, 130.6 (q, J = 30.8 Hz), 130.8, 131.5 134.0, 134.2, 134.5, 136.9, 143.2, 143.7, 143.8, 144.0, 144.4, 146.4, 149.6, 159.4, 159.8 (only distinguishable peaks; 5 carbons are missing due to overlapping). HREIMS *m/z* 546.1321 $(M+Na)^+$, calcd for $C_{29}H_{24}F_3NNaO_3S$ 546.1321.

4-Methyl-*N*-(2-(2-*p*-tolyl-2-(4-(trifluoromethyl)phenyl)vinyl)phenyl)benzenesulfonamide (1m)



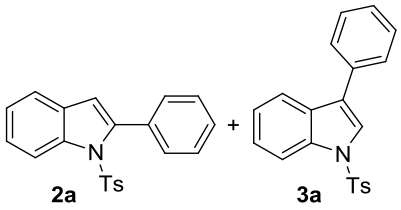
E/*Z* mixture was obtained with a 2.3:1 ratio. a yellow solid (EtOAc : *n*-Hexane = 1 : 6), mp 168-170 ℃.

Signals corresponding to major isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 2.43 (s, 3H), 6.41 (s, 1H), 6.55 (br s, 1H), 6.67 (d, J = 7.6 Hz, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 7.13-7.21 (m, 1H), 7.14 (d, J = 7.6 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H). Representative signals corresponding to minor isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.43 (s, 3H), 6.37 (s, 1H), 6.43 (br s, 1H), 6.80 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 21.3, 21.57, 21.58, 122.9, 123.6, 124.0 (q, J = 269.8 Hz), 124.4, 124.5, 125.0 (q, J = 3.7 Hz), 125.1 (q, J = 3.7 Hz), 125.5, 125.7, 127.1, 127.2, 127.5, 127.8, 128.3, 129.1, 129.4, 129.6, 129.7, 129.8, 130.1, 130.4, 130.5, 130.6, 130.7, 131.3, 133.6, 133.9, 134.5, 135.1, 136.9, 137.0, 138.3, 138.6, 138.8, 143.0, 143.8, 144.0, 144.6, 145.1, 146.2 (only distinguishable peaks; 2 carbons are missing due to overlapping). HREIMS *m/z* 530.1372 $(M+Na)^+$, calcd for $C_{29}H_{24}F_3NNaO_2S$ 530.1372.

General Procedure for the Pd(II)-Catalyzed Aza-Wacker-Type Cyclization of *N*-Ts-2-Alkenylanilines 1

To a solution of **1** (0.0677 mmol, 1 equiv) in $ClCH_2CH_2Cl$ (1.3 mL, 0.05 M) in pressure tube were added $Pd(OAc)_2$ (0.8 mg, 0.00339 mmol, 5 mol %) and $CuCl_2$ (18.2 mg, 0.136 mmol, 2 equiv). The resulting mixture was stirred at 150 °C for the reported time. After the reaction was completed, the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding product **2** or **3**. All reactions were carried out 3-5 times repetitively and the average values of both yields and ratios are given. In most cases, the remainder of the mass balance was unreacted starting material.

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

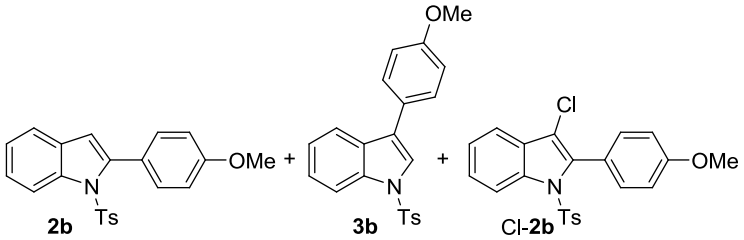


92% (**2a** : **3a** = 1 : 2.1), 87% (**2a** : **3a** = 1 : 0.7, from (*Z*)-**1a**), a white solid (EtOAc : *n*-Hexane = 1 : 8).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H of **2a**), 2.34 (s, 3H of **3a**) 6.55 (s, 1H of **2a**), 7.04 (d, *J* = 8.4 Hz, 2H of **2a**), 7.23 (d, *J* = 8.4 Hz, 2H of **3a**), 7.26-7.31 (m, 3H of **2a** & 1H of **3a**), 7.36-7.40 (m, 1H of **2a** & 2H of **3a**), 7.44-7.53 (m, 6H of **2a** & 2H of **3a**), 7.61 (d, *J* = 7.2 Hz, 2H of **3a**), 7.71 (s, 1H of **3a**), 7.79 (d, *J* = 8.4 Hz, 1H of **3a**), 7.82 (d, *J* = 8.4 Hz, 2H of **3a**), 8.07 (d, *J* = 8.4 Hz, 1H of **3a**), 8.33 (d, *J* = 8.0 Hz, 1H of **2a**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.49, 21.54, 113.6, 113.8, 116.6, 120.4, 120.7, 122.9, 123.5, 123.9, 124.3, 124.7, 124.9, 126.8, 126.9, 127.46, 127.51, 127.9, 128.6, 128.9, 129.2, 129.3, 129.9, 130.3, 130.5, 132.4, 133.0, 134.6, 135.1, 135.5, 138.2, 142.1, 144.5, 145.0. EIMS (**2a**) *m*/*z* 347 (M^+), 208, 192, 177, 165, 139, 115, 91, 77, 65, 51. EIMS (**3a**) *m*/*z* 347 (M^+), 267, 192, 165, 139, 115, 102, 91, 77, 65, 51.

Spectral data of **2a**[1, 3] and **3a**[1, 4] were consistent with data reported in the literature.

***N*-Ts-2-(4-Methoxyphenyl)indole (2b), *N*-Ts-3-(4-Methoxyphenyl)indole (3b), & *N*-Ts-3-Chloro-2-(4-methoxyphenyl)indole (Cl-2b)**



80% (**2b** : **3b** : Cl-**2b** = 1 : 2.1 : 0.5), a yellow solid (EtOAc : *n*-Hexane = 1 : 7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H of **2b**), 2.31 (s, 3H of Cl-**2b**), 2.34 (s, 3H of **3b**), 3.87 (s, 3H of **3b**), 3.89 (s, 3H of **2b**), 3.91 (s, 3H of Cl-**2b**), 6.48 (s, 1H of **2b**), 6.96 (d, *J* = 8.8 Hz, 2H of **2b**), 7.00 (d, *J* = 8.8 Hz, 2H of **3b**), 7.04 (d, *J* = 8.4 Hz, 2H of **2b**), 7.07 (d, *J* = 8.0 Hz, 2H of Cl-**2b**), 7.21-7.47 (m, 7H of **2b**, 4H of **3b**, & 9H of Cl-**2b**), 7.53 (d, *J* = 8.0 Hz, 2H of **3b**), 7.63 (s, 1H of **3b**), 7.74 (d, *J* = 7.6 Hz, 1H of **3b**), 7.80 (d, *J* = 8.0 Hz, 2H of **3b**), 8.05 (d, *J* = 8.4 Hz, 1H of **3b**), 8.31 (d, *J* = 8.8 Hz, 1H of **2b**), 8.35 (d, *J* = 8.4 Hz, 1H of Cl-**2b**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.48, 21.53, 55.28, 55.34, 112.8, 112.9, 113.0, 113.8, 113.9, 114.3, 116.5, 116.6, 118.5, 120.37, 120.44, 121.3, 122.3, 123.4, 123.7, 124.2, 124.5, 124.6, 124.7, 124.8, 125.4, 125.9, 126.76, 126.84, 127.05, 127.11, 127.3, 129.0, 129.1, 129.3, 129.46, 129.52, 129.9, 130.6, 131.6, 132.8, 134.7, 135.2,

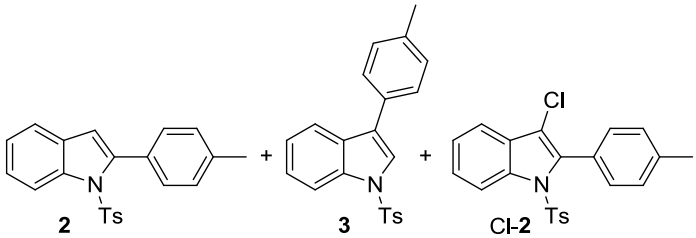
[3] Yin, Y.; Ma, W.; Chai, Z.; Zhao, G. *J. Org. Chem.* **2007**, *72*, 5731.

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

135.5, 138.1, 142.0, 144.4, 144.9, 159.2, 160.0, 160.2 (4 carbons are missing due to overlapping). EIMS (**2b**) *m*/*z* 377 (M), 222, 207, 195, 178, 165, 152, 139, 126, 102, 91, 77, 65. EIMS (**3b**) *m*/*z* 377 (M^+), 222, 207, 178, 152, 91, 65, 51. EIMS (Cl-**2b**) *m*/*z* 411 (M^+), 355, 327, 281, 256, 207, 178, 133, 96, 73, 65, 51.

Spectral data of **2b** and **3b** were consistent with data reported in the literature.[1, 5-6]

***N*-Ts-2-*p*-Tolylindole (2), *N*-Ts-3-*p*-Tolylindole (3), & *N*-Ts-3-Chloro-2-*p*-tolylindole (Cl-2)**

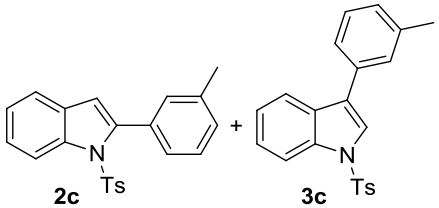


93% (**2** : **3** : Cl-**2** = 1 : 1.9 : 0.2), a yellow oil (EtOAc : *n*-Hexane = 1 : 7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.27 (s, 3H of **2**), 2.30 (s, 3H of Cl-**2**), 2.32 (s, 3H of **2**), 2.40 (s, 3H of **3**), 2.43 (s, 3H of **2**), 2.45 (s, 3H of Cl-**2**), 6.50 (s, 1H of **2**), 7.03 (d, *J* = 7.6 Hz, 2H of **2**), 7.07 (m, 2H of Cl-**2**), 7.14-7.31 (m, 5H of **2**, 4H of **3**, & 9H of Cl-**2**), 7.31-7.43 (m, 4H of **2** & 2H of **3**), 7.49 (d, *J* = 7.6 Hz, 2H of **3**), 7.66 (s, 1H of **3**), 7.76 (d, *J* = 8.4 Hz, 1H of **3**), 7.79 (d, *J* = 8.0 Hz, 2H of **3**), 8.04 (d, *J* = 8.4 Hz, 1H of **3**), 8.29 (d, *J* = 8.0 Hz, 1H of **2**), 8.33 (d, *J* = 8.2 Hz, 1H of Cl-**2**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 21.42, 21.49, 21.54, 113.3, 113.8, 116.5, 116.6, 118.6, 120.4, 120.5, 122.7, 123.5, 124.0, 124.2, 124.4, 124.58, 124.64, 124.8, 125.9, 126.0, 126.8, 126.9, 127.1, 127.7, 128.2, 128.3, 129.1, 129.2, 129.3, 129.4, 129.47, 129.52, 129.6, 129.9, 130.1, 130.2, 130.6, 131.2, 134.6, 135.2, 135.5, 137.3, 138.2, 138.6, 142.3, 144.4, 144.9 (6 carbons are missing due to overlapping). EIMS (**2)** *m*/*z* 361 (M^+), 206, 179, 65. EIMS (**3)** *m*/*z* 361 (M^+), 206, 178, 91, 65. EIMS (Cl-**2)** *m*/*z* 395 (M^+), 240, 213, 205, 155, 123.

Spectral data of **2** were consistent with data reported in the literature.[1, 5]

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



77% (**2c** : **3c** = 1 : 0.9), a yellow solid (EtOAc : *n*-Hexane = 1 : 7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H of **2c**), 2.34 (s, 3H of **3c**), 2.42 (s, 3H of **2c**), 2.43 (s, 3H of **3c**), 6.53 (s, 1H of **2c**), 7.05 (d, *J* = 8.0 Hz, 2H of **2c**), 7.19-7.36 (m, 8H of **2c** & 6H of **3c**), 7.42 (d, *J* = 8.0 Hz, 2H of **3c**), 7.44 (d, *J* = 9.2 Hz, 1H of **2c**), 7.69 (s, 1H of **3c**), 7.79 (d, *J* = 8.0 Hz, 1H

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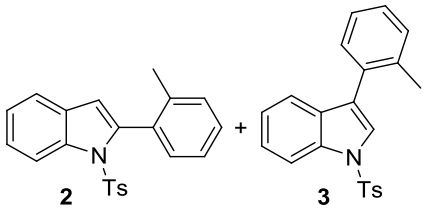
[5] Palimkar, S. S.; Kumar, P. H.; Lahoti, R. J.; Srinivasan, K. V. *Tetrahedron* **2006**, *62*, 5109.

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

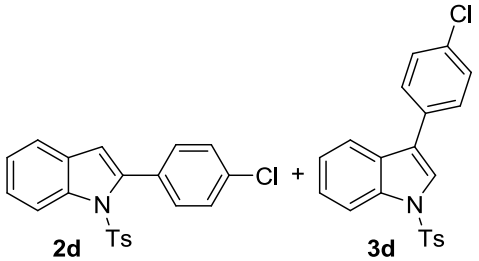
of **3c**), 7.81 (d, *J* = 8.4 Hz, 2H of **3c**), 8.06 (d, *J* = 8.4 Hz, 1H of **3c**), 8.31 (d, *J* = 8.4 Hz, 1H of **2c**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 21.49, 21.54, 113.3, 113.8, 116.6, 120.5, 120.6, 122.9, 123.5, 124.1, 124.2, 124.7, 124.8, 125.0, 126.8, 126.9, 127.4, 128.3, 128.6, 128.8, 129.1, 129.4, 129.9, 130.5, 131.0, 132.3, 133.0, 134.8, 135.2, 135.5, 137.0, 138.2, 138.6, 142.3, 144.4, 145.0 (3 carbons are missing due to overlapping). EIMS (**2c**) *m*/*z* 361 (M^+), 222, 206, 191, 179, 164, 152, 139, 115, 102, 91, 77, 65, 51. EIMS (**3c**) *m*/*z* 361 (M^+), 206, 178, 152, 91, 77, 65, 51.
Spectral data of **2c** were consistent with data reported in the literature.[1, 6]

_N_-Ts-2-_o_-Tolylindole (2) & _N_-Ts-3-_o_-Tolylindole (3)



92% (**2** : **3** = 1 : 2.1), a yellow oil (EtOAc : *n*-Hexane = 1 : 7).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.22 (s, each 3H of **2** & **3**), 2.32 (s, 3H of **2**), 2.35 (s, 3H of **3**), 6.46 (s, 1H of **2**), 7.09 (d, *J* = 8.4 Hz, 3H of **2**), 7.19-7.36 (m, 7H of **2** & 9H of **3**), 7.50 (d, *J* = 7.6 Hz, 1H of **2**), 7.53 (s, 1H of **3**), 7.80 (d, *J* = 8.4 Hz, 2H of **3**), 8.05 (d, *J* = 9.2 Hz, 1H of **3**), 8.33 (d, *J* = 8.4 Hz, 1H of **2**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.4, 20.5, 21.51, 21.54, 112.3, 113.8, 115.7, 120.6, 120.7, 123.4, 123.5, 123.8, 124.1, 124.55, 124.64, 124.7, 125.8, 126.8, 126.9, 127.9, 129.1, 129.3, 129.6, 129.9, 130.1, 130.5, 130.7, 130.9, 131.9, 132.1, 134.9, 135.2, 135.6, 136.8, 137.3, 139.3, 140.3, 144.6, 144.9 (1 carbon is missing due to overlapping). EIMS (**2**) *m*/*z* 361 (M^+), 222, 206, 178, 151, 128, 115, 101, 91, 77, 65, 51. EIMS (**3**) *m*/*z* 361 (M^+), 206, 178, 152, 128, 115, 103, 91, 77, 65, 51. HREIMS *m*/*z* 361.1138 $(M)^+$, calcd for $C_{22}H_{19}NO_2S$ 361.1136.
Spectral data of **2** were consistent with data reported in the literature.[1]

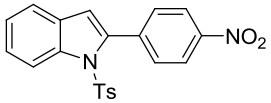
_N_-Ts-2-(4-Chlorophenyl)indole (2d) & _N_-Ts-3-(4-Chlorophenyl)indole (3d)



85% (**2d** : **3d** = 1 : 0.6), an orange solid (EtOAc : *n*-Hexane = 1 : 7).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H of **2d**), 2.35 (s, 3H of **3d**), 6.55 (s, 1H of **2d**), 7.05 (d, *J* = 8.0 Hz, 2H of **2d**), 7.23-7.32 (m, 3H of **2d** & 1H of **3d)**, 7.36-7.46 (m, 6H of **2d** & 5H of **3d**), 7.54 (d, *J* = 8.0 Hz, 2H of **3d**), 7.70 (s, 1H of **3d**), 7.72 (d, *J* = 8.4 Hz, 1H of **3d**), 7.82 (d, *J* = 7.6 Hz, 2H of **3d**), 8.06 (d, *J* = 8.4 Hz, 1H of **3d**), 8.31 (d, *J* = 8.8 Hz, 1H of **2d**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.6, 113.9, 114.0, 116.7, 120.1, 120.8, 122.7, 123.0, 123.6, 124.4, 125.0, 126.7, 126.9, 127.8, 128.9, 129.1, 129.3, 130.0, 130.4, 130.9, 131.45, 131.54, 133.4, 134.5, 134.7, 135.1, 135.4,

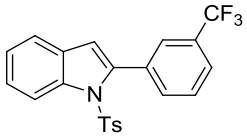
138.3, 140.8, 144.7, 145.1 (2 carbons are missing due to overlapping). EIMS (**2d**) *m*/*z* 381 (M^+), 242, 226, 199, 190, 164, 155, 139, 113, 91, 75, 65, 51. EIMS (**3d**) *m*/*z* 381 (M^+), 226, 199, 190, 163, 155, 137, 113, 91, 65, 51. HREIMS *m/z* 381.0588 $(M)^+$, calcd for $C_{21}H_{16}ClNO_2S$ 381.0590.
Spectral data of **2d** were consistent with data reported in the literature.[1]

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



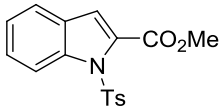
91%, a yellow solid (EtOAc : *n*-Hexane = 1 : 7), mp 170-171 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 6.69 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 8.30 (d, *J* = 8.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 116.1, 116.8, 121.2, 122.8, 124.8, 125.8, 126.6, 129.4, 130.3, 130.6, 133.8, 138.7, 138.9, 139.6, 145.0, 147.5. EIMS *m*/*z* 392 (M^+), 253, 237, 190, 178, 164, 155, 140, 91, 65.
Spectral data were consistent with data reported in the literature.[1, 7]

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



90%, an orange solid (EtOAc : *n*-Hexane = 1 : 7), mp 55-60 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 6.60 (s, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.60 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 114.3, 116.6, 120.9, 124.0 (q, *J* = 270.9 Hz), 124.5, 125.25 (q, *J* = 3.7 Hz), 125.29, 126.6, 126.7 (q, *J* = 3.7 Hz), 127.9, 129.3, 130.0 (q, *J* = 32.0 Hz), 130.2, 133.1, 134.0, 134.5, 138.4, 140.2, 144.9. 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.
Spectral data were consistent with data reported in the literature.[1]

Methyl _N_-Ts-Indole-2-carboxylate (2f)



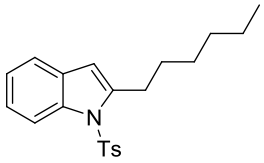
60%, a yellow solid (EtOAc : *n*-Hexane = 1 : 3), mp 52-54 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 3.94 (s, 3H), 7.16 (s, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 8.13

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

(d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 52.7, 115.4, 116.8, 122.5, 124.0, 127.0, 127.4, 128.1, 129.5, 131.4, 135.7, 138.2, 144.9, 161.8. EIMS m/z 329 (M^+), 265, 155, 143, 139, 115, 91, 89, 65, 51.

Spectral data were consistent with data reported in the literature.[8]

_N_-Ts-2-_n_-Hexylindole (2g)

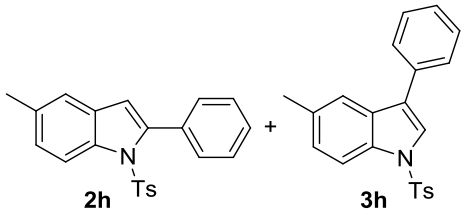


20%, a yellow solid (EtOAc : _n_-Hexane = 1 : 6), mp 73-74 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (m, 3H), 1.32 (m, 4H), 1.41 (m, 2H), 1.74 (quintet, J = 7.5 Hz, 2H), 2.33 (s, 3H), 2.97 (t, J = 7.6 Hz, 2H), 6.38 (s, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.21 (t, J = 6.4 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 21.5, 22.6, 28.8, 28.97, 29.02, 31.6, 108.5, 114.8, 120.0, 123.4, 123.7, 126.2, 129.7, 129.8, 136.2, 137.1, 142.5, 144.5. EIMS m/z 355 (M^+), 285, 221, 200, 170, 156, 143, 130, 118, 103, 91, 77, 65, 55.

Spectral data were consistent with data reported in the literature.[1, 9]

_N_-Ts-5-Methyl-2-phenylindole (2h) & _N_-Ts-5-Methyl-3-phenylindole (3h)



85% (**2h** : **3h** = 1 : 0.5), a white solid (EtOAc : _n_-Hexane = 1 : 7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H of **2h**), 2.34 (s, 3H of **3h**), 2.41 (s, 3H of **2h**), 2.43 (s, 3H of **3h**), 6.47 (s, 1H of **2h**), 7.04 (d, J = 8.0 Hz, 2H of **2h**), 7.16-7.32 (m, 4H of **2h** & 3H of **3h**), 7.35-7.51 (m, 5H of **2h** & 3H of **3h**), 7.55 (s, 1H of **3h**), 7.59 (d, J = 7.6 Hz, 2H of **3h**), 7.65 (s, 1H of **3h**), 7.79 (d, J = 8.0 Hz, 2H of **3h**), 7.93 (d, J = 8.8 Hz, 1H of **3h**), 8.18 (d, J = 8.4 Hz, 1H of **2h**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 21.4, 21.50, 21.54, 113.5, 113.6, 116.4, 120.2, 120.6, 123.1, 123.8, 126.1, 126.3, 126.78, 126.83, 127.4, 127.9, 128.5, 128.9, 129.1, 129.3, 129.5, 129.9, 130.2, 130.8, 131.4, 132.5, 133.2, 133.8, 133.9, 134.6, 135.2, 136.5, 142.2, 144.4, 144.9. EIMS (**2h**) m/z 361 (M^+), 222, 206, 179, 152, 128, 102, 91, 77, 65, 51. EIMS (**3h**) m/z 361 (M^+), 281, 206, 178, 152, 128, 102, 91, 77, 65, 51.

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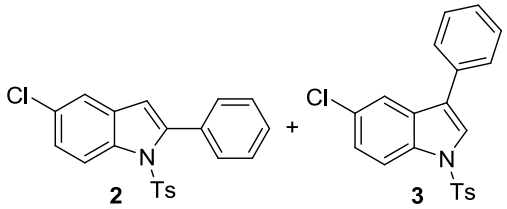
[8] (a) Blessley, G.; Holden, P.; Walker, M.; Brown, J. M.; Gouverneur, V. *Org. Lett.* **2012**, *14*, 2754. (b) Karadeolian, A.; Kerr**,** M. A. *J. Org. Chem.* **2010**, *75*, 6830. (c) Vieira, T. O.; Meaney, L. A.; Shi, Y.-L.; Alper, H. *Org. Lett.* **2008**, *10*, 4899.

[9] Yamagishi, M.; Nishigai, K.; Ishii, A.; Hata, T.; Urabe, H. *Angew. Chem. Int. Ed*. **2012**, *51*, 6471.

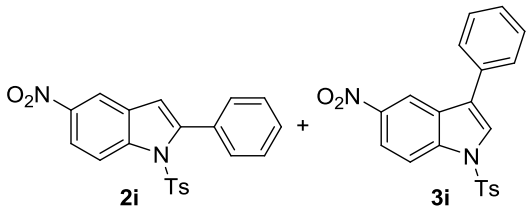
Spectral data of **2h** were consistent with data reported in the literature.[1, 3, 5]

***N*-Ts-5-Chloro-2-phenylindole (2) & *N*-Ts-5-Chloro-3-phenylindole (3)**



91% (**2** : **3** = 1 : 2), a pale yellow solid (EtOAc : *n*-Hexane = 1 : 7).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H of **2**), 2.35 (s, 3H of **3**), 6.48 (s, 1H of **2**), 7.06 (d, J = 8.4 Hz, 2H of **2**), 7.24 (d, J = 9.2 Hz, each 2H of **2** & **3**), 7.29-7.33 (m, each 1H of **2** & **3**), 7.37-7.49 (m, 6H of **2** & 3H of **3**), 7.55 (d, J = 7.6 Hz, 2H of **3**), 7.70 (s, 1H of **3**), 7.73 (d, J = 1.6 Hz, 1H of **3**), 7.78 (d, J = 8.4 Hz, 2H of **3**), 7.98 (d, J = 8.8 Hz, 1H of **3**), 8.23 (d, J = 8.8 Hz, 1H of **2**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.6, 112.6, 114.9, 117.7, 120.1, 120.2, 123.5, 124.2, 124.9, 125.1, 126.75, 126.84, 127.5, 127.8, 128.95, 129.03, 129.3, 129.6, 130.0, 130.3, 130.5, 131.7, 131.8, 132.4, 133.8, 134.4, 134.9, 136.5, 143.5, 144.8, 145.3 (2 carbons are missing due to overlapping). EIMS (**2**) m/z 381(M^+), 242, 226, 199, 190, 164, 155, 139, 123, 91, 73, 65, 51. EIMS (**3**) m/z 381(M^+), 226, 199, 190, 163, 155, 139, 126, 91, 65, 51.
Spectral data of **2**[1, 3] and **3**[10] were consistent with data reported in the literature.

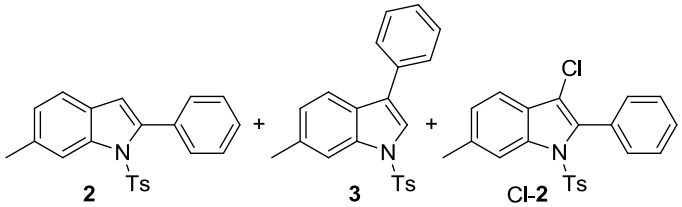
***N*-Ts-5-Nitro-2-phenylindole (2i) & *N*-Ts-5-Nitro-3-phenylindole (3i)**



90% (**2i** : **3i** = 1 : 3.8), a yellow oil (EtOAc : *n*-Hexane = 1 : 7).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H of **2i**), 2.38 (s, 3H of **3i**), 6.65 (s, 1H of **2i**), 7.09 (d, J = 8.4 Hz, 2H of **2i**), 7.29 (d, J = 8.4 Hz, each 2H of **2i** & **3i**), 7.42-7.45 (m, 5H of **2i** & 1H of **3i**), 7.52 (t, J = 7.4 Hz, 2H of **3i**), 7.58 (d, J = 7.6 Hz, 2H of **3i**), 7.837 (s, 1H of **3i**), 7.838 (d, J = 8.0 Hz, 2H of **3i**), 8.15 (d, J = 8.8 Hz, 1H of **3i**), 8.24 (dd, J = 2.0, 6.8 Hz, 1H of **2i**), 8.26 (dd, J = 2.0, 7.2 Hz, 1H of **3i**), 8.38 (d, J = 2.0 Hz, 1H of **2i**), 8.44 (d, J = 9.2 Hz, 1H of **2i**), 8.68 (d, J = 1.6 Hz, 1H of **3i**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.58, 21.64, 112.7, 114.0, 116.5, 116.8, 117.0, 119.7, 120.1, 124.6, 125.4, 126.8, 127.0, 127.6, 127.9, 128.3, 129.3, 129.4, 129.6, 130.3, 130.5, 131.1, 131.5, 134.6, 138.2, 141.0, 144.5, 144.7, 144.9, 145.5, 146.0 (3 carbons are missing due to overlapping). EIMS (**2i**) m/z 392 (M^+), 237, 207, 179, 155, 139, 127, 91, 77, 65, 51. EIMS (**3i**) m/z 392 (M^+), 237, 207, 191, 164, 155, 139, 91, 77, 65, 51.
Spectral data of **2i** were consistent with data reported in the literature.[1, 3]

[10] Miyagi, T.; Hari, Y.; Aoyama, T. *Tetrahedron Lett.* **2004**, *45*, 6303.

***N*-Ts-6-Methyl-2-phenylindole (2), *N*-Ts-6-Methyl-3-phenylindole (3), & *N*-Ts-3-Chloro-6-methyl-2-phenylindole (Cl-2)**

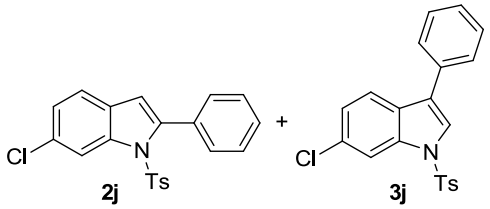


89% (**2** : **3** : Cl-**2** = 1 : 0.3 : 0.1), a pale yellow solid (EtOAc : *n*-Hexane = 1 : 7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H of **2**), 2.32 (s, 3H of Cl-**2**), 2.35 (s, 3H of **3**), 2.51 (s, 3H of **3**), 2.53 (s, 3H of **2**), 2.56 (s, 3H of Cl-**2**), 6.49 (s, 1H of **2**), 7.03-7.12 (m, each 2H of **3** & Cl-**2**), 7.04 (d, *J* = 8.0 Hz, 2H of **2**), 7.09 (d, *J* = 7.6 Hz, 1H of **2**), 7.20-7.49 (m, 4H of **3** & 9H of Cl-**2**), 7.27 (d, *J* = 8.0 Hz, 2H of **2**), 7.32 (d, *J* = 7.6 Hz, 1H of **2**), 7.41-7.49 (m, 5H of **2**), 7.60 (d, *J* = 7.6 Hz, 2H of **3**), 7.63 (s, 1H of **3**), 7.65 (d, *J* = 8.0 Hz, 1H of **3**), 7.80 (d, *J* = 8.0 Hz, 2H of **3**), 7.87 (s, 1H of **3**), 8.13 (s, 1H of **2**), 8.17 (s, 1H of Cl-**2**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.6, 21.9, 22.1, 113.6, 113.9, 114.9, 116.6, 116.8, 117.6, 118.3, 120.0, 120.2, 120.6, 121.2, 122.3, 123.9, 125.1, 125.7, 126.2, 126.77, 126.83, 127.0, 127.4, 127.8, 128.3, 128.5, 128.9, 129.1, 129.4, 129.9, 130.2, 131.4, 132.6, 133.2, 133.6, 134.7, 134.9, 135.1, 135.3, 135.9, 138.7, 141.4, 144.1, 144.4, 144.9 (8 carbons are missing due to overlapping). EIMS (**2**) *m*/*z* 361 (M^+), 222, 206, 179, 152, 128, 102, 91, 77, 65, 51. EIMS (**3**) *m*/*z* 361 (M^+), 222, 206, 178, 152, 128, 102, 91, 77, 65, 51. EIMS (Cl-**2**) *m*/*z* 395 (M^+), 361, 281, 240, 213, 204, 178, 151, 139, 102, 91, 65, 51. HREIMS *m/z* 361.1138 $(M)^+$, calcd for $C_{22}H_{19}NO_2S$ 361.1136.

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

***N*-Ts-6-Chloro-2-phenylindole (2j) & *N*-Ts-6-Chloro-3-phenylindole (3j)**

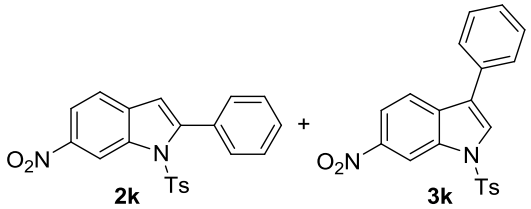


98% (**2j** : **3j** = 1 : 0.8), a pink solid (EtOAc : *n*-Hexane = 1 : 7).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H of **2j**), 2.37 (s, 3H of **3j**), 6.50 (s, 1H of **2j**), 7.07 (d, *J* = 7.6 Hz, 2H of **2j**), 7.27 (d, *J* = 6.8 Hz, 3H of **2j** & 2H of **3j**), 7.36 (d, *J* = 8.0 Hz, 1H of **2j**), 7.38-7.48 (m, 5H of **2j** & 4H of **3j**), 7.56 (d, *J* = 7.2 Hz, 2H of **3j**), 7.67 (s, 1H of **3j**), 7.68 (d, *J* = 7.6 Hz, 1H of **3j**), 7.81 (d, *J* = 8.4 Hz, 2H of **3j**), 8.08 (d, *J* = 0.8 Hz, 1H of **3j**), 8.35 (s, 1H of **2j**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.55, 21.61, 112.8, 114.0, 116.7, 121.2, 121.3, 123.3, 123.7, 124.2, 124.9, 126.8, 126.9, 127.5, 127.76, 127.81, 128.9, 129.0, 129.3, 130.1, 130.4, 130.6, 130.9, 131.8, 132.5, 134.5, 134.9, 135.8, 138.5, 142.6, 144.9, 145.4 (2 carbons are missing due to overlapping). EIMS (**2j**) *m*/*z* 381 (M^+), 226, 199, 190, 164, 155, 123, 113, 91, 73, 65, 51. EIMS (**3j**) *m*/*z* 381 (M^+), 226, 199, 190, 163, 155, 91, 65, 51.

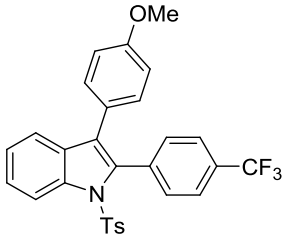
Spectral data of **2j** were consistent with data reported in the literature.[1, 11]

***N*-Ts-6-Nitro-2-phenylindole (2k) & *N*-Ts-6-Nitro-3-phenylindole (3k)**



82% (**2k** : **3k** = 1 : 1.1), a dark brown solid (EtOAc : *n*-Hexane = 1 : 7).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H of **2k**), 2.38 (s, 3H of **3k**), 6.62 (s, 1H of **2k**), 7.09 (d, J = 8.4 Hz, 2H of **2k**), 7.28-7.31 (m, each 2H of **2k** & **3k**), 7.42-7.52 (m, 5H of **2k** & 3H of **3k**), 7.55 (d, J = 8.4 Hz, 1H of **2k**), 7.57 (d, J = 6.4 Hz, 2H of **3k**), 7.86 (d, J = 8.4 Hz, 1H of **3k**), 7.87 (d, J = 7.6 Hz, 2H of **3k**), 7.94 (s, 1H of **3k**), 8.18 (d, J = 9.2 Hz, each 1H of **2k** & **3k**), 8.96 (s, 1H of **3k**), 9.25 (s, 1H of **2k**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.57, 21.64, 110.2, 112.3, 112.8, 118.7, 119.6, 120.6, 120.7, 123.8, 126.9, 127.1, 127.6, 127.7, 127.9, 128.2, 129.2, 129.57, 129.59, 130.3, 130.5, 131.1, 131.7, 133.8, 134.2, 134.4, 134.5, 135.0, 136.9, 145.0, 145.2, 145.4, 146.0, 147.2. EIMS (**2k**) *m*/*z* 392 (M^+), 281, 253, 237, 207, 190, 179, 163, 155, 139, 91, 77, 65, 51. EIMS (**3k**) *m*/*z* 392 (M^+), 282, 252, 237, 207, 190, 179, 163, 155, 139, 126, 91, 65, 51. HREIMS *m/z* 392.0832 $(M)^+$, calcd for $C_{21}H_{16}N_2O_4S$ 392.0831.
Spectral data of **2k** were consistent with data reported in the literature.[1]

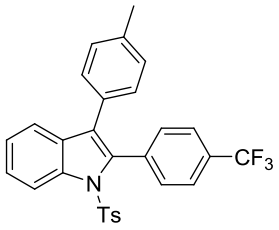
***N*-Ts-3-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)indole (3l)**



78%, a greenish solid (EtOAc : *n*-Hexane = 1 : 8), mp 140-142 ℃. *E*/*Z* mixture of **1l** (3:1) was used and recovered in 8% yield with a 1:1 ratio.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 3.77 (s, 3H), 6.78 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 8.39 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 55.1, 113.9, 116.3, 120.2, 124.079 (q, J = 270.6 Hz), 124.082, 124.2 (q, J = 3.7 Hz), 124.4, 125.6, 125.9, 126.8, 129.4, 130.1 (q, J = 32.3 Hz), 130.7, 130.9, 132.2, 134.7, 134.9, 135.0, 137.4, 144.8, 158.8. HREIMS *m/z* 544.1165 $(M+Na)^+$, calcd for $C_{29}H_{22}F_3NNaO_3S$ 544.1165.

***N*-Ts-3-*p*-Tolyl-2-(4-(trifluoromethyl)phenyl)indole (3m)**

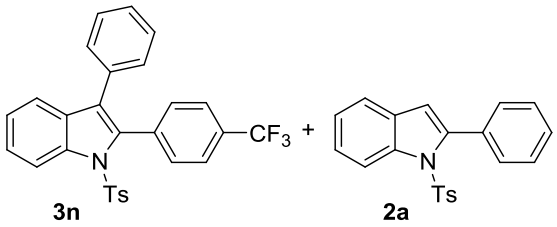
[11] Inamoto, K.; Asano, N; Nakamura, Y.; Yonemoto, M.; Kondo, Y. *Org. Lett.* **2012**, *14*, 2622.



47%, a yellow solid (EtOAc : *n*-Hexane = 1 : 6). *E*/*Z* mixture of **1m** (2.3:1) was used and recovered in 51% yield with a 1.1:1 ratio.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 2.32 (s, 3H), 6.93 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 8.4 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 8.39 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 21.6, 116.4, 120.3, 124.1 (q, J = 270.6 Hz), 124.2 (q, J = 3.7 Hz), 124.4, 125.6, 126.1, 126.8, 128.9, 129.1, 129.4, 129.6, 130.1 (q, J = 32.2 Hz), 130.6, 132.2, 134.86, 134.91, 137.1, 137.5, 144.8 (1 carbon is missing due to overlapping). HREIMS *m/z* 528.1215 $(M+Na)^+$, calcd for $C_{29}H_{22}F_3NNaO_2S$ 528.1216.

_N_-Ts-3-Phenyl-2-(4-(trifluoromethyl)phenyl)indole (3n) & _N_-Ts-2-Phenylindole (2a)

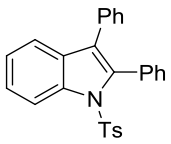


42% (**3n** : **2a** = 1 : 0.1), a yellow solid (EtOAc : *n*-Hexane = 1 : 7). *E*/*Z* mixture of **1n** (1.7:1) was used and recovered in 53% yield with a 1.4:1 ratio.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H of **2a**), 2.32 (s, 3H of **3n**), 6.54 (s, 1H of **2a**), 7.04-7.06 (m, 2H of **3n** & 2H of **2a**), 7.09 (d, J = 8.0 Hz, 2H of **3n**), 7.20-7.34 (m, 6H of **3n** & 4H of **2a**), 7.38 (d, J = 8.0 Hz, 2H of **3n**), 7.42-7.49 (m, 2H of **3n** & 6H of **2a**), 7.53 (d, J = 8.0 Hz, 2H of **3n**), 8.31 (d, J = 8.4 Hz, 1H of **2a**), 8.40 (d, J = 8.8 Hz, 1H of **3n**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.6, 113.6, 116.4, 116.6, 120.2, 120.7, 124.1 (q, J = 271.3 Hz), 124.2 (q, J = 3.7 Hz), 124.5, 124.7, 125.7, 126.1, 126.8, 126.9, 127.3, 127.5, 128.4, 128.6, 129.2, 129.4, 129.8, 130.2 (q, J = 32.2 Hz), 130.3, 130.45, 130.53, 132.0, 132.2, 132.4, 134.6, 134.8, 134.9, 135.1, 137.4, 138.2, 142.1, 144.5, 144.9 (1 carbon is missing due to overlapping). EIMS (**3n**) *m*/*z* 491 (M^+), 336, 267, 239, 163, 155, 134, 91, 65, 51. EIMS (**2a**) *m*/*z* 347 (M^+), 208, 192, 165, 139, 115, 91, 65. HREIMS *m/z* 491.1168 $(M)^+$, calcd for $C_{28}H_{20}F_3NO_2S$ 491.1167.

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

_N_-Ts-2,3-Diphenylindole

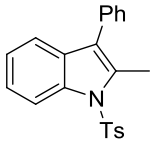


73%, a pale yellow solid (EtOAc : *n*-Hexane = 1 : 5), mp 173-175 ℃. Unreacted starting material was recovered in 22% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 7.07-7.09 (m, 4H), 7.20-7.31 (m, 9H), 7.34 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.6 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 21.5, 116.2, 119.9, 124.1, 124.7, 125.1, 126.9, 127.2, 128.1, 128.4, 129.3, 129.8, 130.4, 130.8, 132.0, 132.6, 135.2, 136.8, 137.2, 144.5 (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.[1, 12]

_N_-Ts-2-Methyl-3-phenylindole (3o)

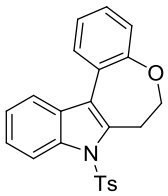


64%, a yellow oil (EtOAc : *n*-Hexane = 1 : 6). Unreacted **1o** was recovered in 23% yield.

^{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), 7.30-7.38 (m, 4H), 7.41-7.47 (m, 3H), 7.73 (d, J = 8.0 Hz, 2H), 8.27 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.5, 21.6, 114.5, 119.2, 122.5, 123.5, 124.2, 126.4, 127.3, 128.5, 129.9, 130.0, 133.05, 133.10, 136.2, 136.3, 144.7 (1 carbon is missing due to overlapping). EIMS *m*/*z* 361 (M^+), 206, 178, 165, 152, 128, 115, 91, 77, 65, 51.

Spectral data were consistent with data reported in the literature.[1, 13]

_N_-Ts-7,8-Dihydro-6*H*-benzo[6,7]oxepino[4,5-*b*]indole (3p)



51%, a yellow solid (EtOAc : *n*-Hexane = 1 : 7), mp 109-110 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 3.60 (t, J = 6.2 Hz, 2H), 4.44 (t, J = 6.0 Hz, 2H), 7.13 (d, J = 7.6 Hz, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.20-7.26 (m, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.87-7.89 (m, 2H), 8.32 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 30.5, 73.4, 114.9, 118.2, 120.0, 121.4, 123.5, 123.7, 124.6, 125.6, 126.3, 127.9, 128.6, 129.6, 130.0, 135.6, 136.1, 137.0, 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.

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

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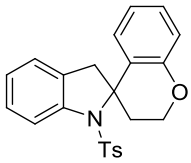
[12] Larock, R. C.; Yum, E. K.; Refvik, M. D. *J. Org. Chem.* **1998**, *63*, 7652.

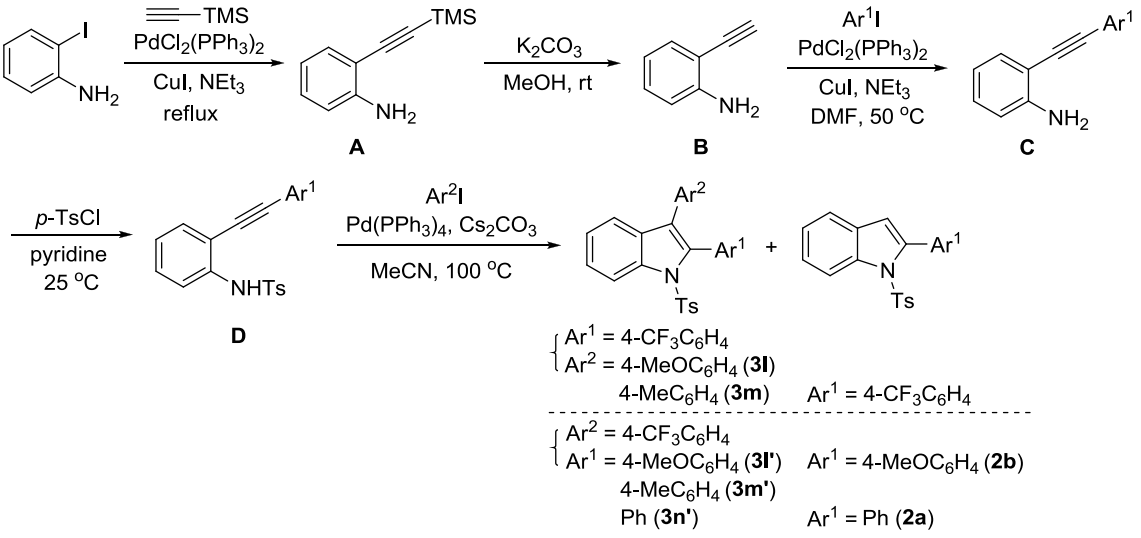
[13] (a) Zhu, C.; Ma, S. *Org. Lett.* **2013**, *15*, 2782. (b) McAusland, D.; Seo, S.; Pintori, D. G.; Finlayson, J.; Greaney, M. F. *Org. Lett.* **2011**, *13*, 3667.

***N*-Ts-Spiro(chroman-4,2'-indoline) (4)**



31%, a yellow solid (EtOAc : *n*-Hexane = 1 : 7), mp 168-170 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.07 (d, J = 13.2 Hz, 1H), 2.38 (s, 3H), 3.27 (d, J = 16.0 Hz, 1H), 3.29 (td, J = 4.0, 12.6 Hz, 1H), 3.54 (d, J = 16.0 Hz, 1H), 4.21 (td, J = 1.9, 11.6 Hz, 1H), 4.21 (dt, J = 3.8, 11.3 Hz, 1H), 6.72 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 7.2 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 8.8 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 7.23 (t, J = 8.4 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 35.0, 48.6, 64.1, 69.3, 113.8, 117.2, 120.6, 123.0, 125.1, 126.3, 126.9, 127.0, 127.1, 128.1, 128.9, 129.4, 138.4, 142.4, 143.6, 154.3. EIMS *m/z* 391 (M^+), 355, 326, 254, 236, 220, 180, 165, 152, 143, 131, 91, 65, 51. HREIMS *m/z* 414.1133 $(M+Na)^+$, calcd for $C_{23}H_{21}NNaO_3S$ 414.1140.

General Procedure for the Preparation of 2,3-Disubstituted *N*-Ts-Indoles 3 & 3'



Authentic samples of 2-aryl-3-aryl'-substituted indoles (**3** and **3'**) were prepared as follows[14] and the products from our protocol were identified by comparison with ^{1}H & ^{13}C NMR spectra of each corresponding isomer.

To a solution of 2-iodoaniline (800.4 mg, 3.654 mmol) was dissolved in mixed ethynyltrimethylsilane (607 μL, 4.385 mmol, 1.2 equiv), $PdCl_2(PPh_3)_2$ (256.5 mg, 0.365 mmol, 10 mol%), CuI (69.6 mg, 0.365 mmol, 10 mol%) and Et_3N (28.1 mL, 0.13 M) were added. The

[14] Cacchi, S.; Fabrizi, G.; Lamba, D.; Marinelli, F.; Parisi, L. M. *Synthesis* **2003**, 728.

reaction mixture was stirred at reflux for 3 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** (520.8 mg, 75 %) as a yellow oil.

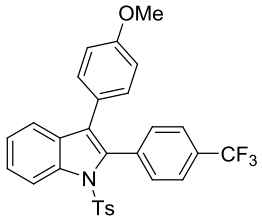
To a solution of **A** (520.8 mg, 2.751 mmol, 1 equiv) in MeOH (13.8 mL, 0.2 M) was added K_2CO_3 (760.4 mg, 5.502 mmol, 2 equiv). After being stirred at room temperature for 16 h, the reaction mixture was poured into water and then the product was extracted with CH_2Cl_2 (3 times). The combined organic 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 = 1:10) to afford the corresponding product **B** (315.6 mg, 98%) 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 ℃ 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 **3** or **3' (**or the mixture of **3** or **3'** and **2**).

***N*-Ts-3-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)indole (3l)**

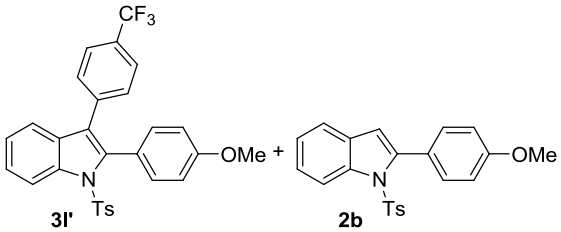


a white solid (EtOAc : *n*-Hexane = 1 : 8).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.77 (s, 3H), 6.79 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 8.39 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 55.2, 113.9, 116.4, 120.2, 124.09, 124.10 (q, J = 270.6 Hz), 124.2 (q, J = 3.7 Hz), 124.4, 125.6, 125.9, 126.8, 129.4, 130.1 (q, J = 32.2 Hz), 130.7,

130.9, 132.2, 134.7, 134.9, 135.0, 137.4, 144.8, 158.8. HREIMS *m/z* 544.1163 $(M+Na)^+$, calcd for $C_{29}H_{22}F_3NNaO_3S$ 544.1165.

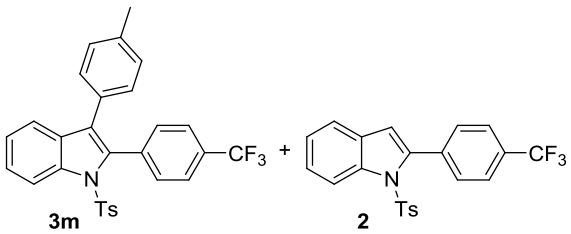
***N*-Ts-2-(4-Methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)indole (3l') & *N*-Ts-2-(4-Methoxyphenyl)indole (2b)**



3l' : **2b** = 9.6 : 1, a white solid (EtOAc : *n*-Hexane = 1 : 5).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H of **2b**), 2.32 (s, 3H of **3l'**), 3.85 (s, 3H of **3l'**), 3.89 (s, 3H of **2b**), 6.48 (s, 1H of **2b**), 6.82 (d, *J* = 8.4 Hz, 2H of **3l'**), 6.95 (d, *J* = 8.4 Hz, 2H of **2b**), 7.03 (d, *J* = 7.6 Hz, 2H of **2b**), 7.09 (d, *J* = 8.0 Hz, 2H of **3l'**), 7.12 (d, *J* = 8.4 Hz, 2H of **3l'**), 7.20-7.50 (m, 7H of **2b**), 7.21 (d, *J* = 8.4 Hz, 2H of **3l'**), 7.30 (t, *J* = 7.6 Hz, 1H of **3l'**), 7.33 (d, *J* = 8.0 Hz, 2H of **3l'**), 7.43 (t, *J* = 7.6 Hz, 1H of **3l'**), 7.44 (d, *J* = 8.8 Hz, 1H of **3l'**), 7.48 (d, *J* = 8.8 Hz, 2H of **3l'**), 8.30 (d, *J* = 8.0 Hz, 1H of **2b**), 8.42 (d, *J* = 8.0 Hz, 1H of **3l'**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.6, 55.2, 55.3, 112.9, 113.0, 116.3, 116.7, 119.4, 120.5, 122.3, 122.8, 124.1 (q, *J* = 270.6 Hz), 124.2, 124.3, 124.5, 125.1 (q, *J* = 3.7 Hz), 125.3, 126.8, 126.9, 128.7 (q, *J* = 32.3 Hz), 129.1, 129.2, 129.3, 129.7, 130.0, 130.6, 131.6, 133.4, 135.4, 136.9, 137.1, 137.5, 144.5, 144.7, 160.0. (5 carbons are missing due to overlapping). HREIMS (**3l'**) *m/z* 544.1163 $(M+Na)^+$, calcd for $C_{29}H_{22}F_3NNaO_3S$ 544.1165. HREIMS (**2b**) *m/z* 400.0983 $(M+Na)^+$, calcd for $C_{22}H_{19}NNaO_3S$ 400.0978.

***N*-Ts-3-*p*-Tolyl-2-(4-(trifluoromethyl)phenyl)indole (3m) & *N*-Ts-2-(4-(Trifluoromethyl)phenyl)indole (2)**

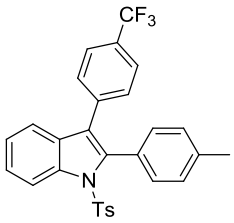


3m : **2** = 1 : 0.3, a beige solid (CH_2Cl_2 : *n*-Hexane = 1 : 1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H of **2**), 2.30 (s, 3H of **3m**), 2.31 (s, 3H of **3m**), 6.60 (s, 1H of **2**), 6.93 (d, *J* = 8.0 Hz, 2H of **3m**), 7.05 (d, *J* = 9.0 Hz, 2H of **3m**), 7.07 (d, *J* = 8.8 Hz, 2H of **3m**), 7.04-7.09 (m, 2H of **2**), 7.29 (t, *J* = 7.2 Hz, 1H of **3m**), 7.30 (d, *J* = 8.4 Hz, 2H of **3m**), 7.24-7.27 (m, 3H of **2**), 7.36-7.40 (m, 2H of **2**), 7.39 (d, *J* = 8.0 Hz, 2H of **3m**), 7.43 (t, *J* = 8.2 Hz, 1H of **3m**), 7.45 (d, *J* = 7.2 Hz, 1H of **3m**), 7.53 (d, *J* = 7.6 Hz, 2H of **3m**), 7.63 (d, *J* = 8.4 Hz, 2H of **2**), 7.68 (d, *J* = 8.8 Hz, 2H of **2**), 8.31 (d, *J* = 8.4 Hz, 1H of **2**), 8.39 (d, *J* = 8.0 Hz, 1H of **3m**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 21.49, 21.52, 115.0, 116.3, 116.7, 120.3, 121.0, 124.1 (q, *J* = 270.6 Hz), 124.2 (q, *J* = 3.7 Hz), 124.4, 124.5 (q, *J* = 3.7 Hz), 124.6, 125.4, 125.6, 126.2, 126.7, 126.8, 128.9,

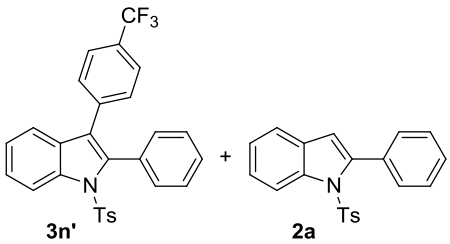
129.1, 129.3, 129.4, 129.6, 130.1 (q, *J* = 32.3 Hz), 130.37, 130.4 (q, *J* = 33.0 Hz), 130.6, 132.2, 134.2, 134.87, 134.92, 136.0, 137.1, 137.5, 138.5, 140.4, 144.8 (4 carbons are missing due to overlapping). HREIMS (**3m**) *m/z* 528.1213 $(M+Na)^+$, calcd for $C_{29}H_{22}F_3NNaO_2S$ 528.1216. HREIMS (**2**) *m/z* 438.0751 $(M+Na)^+$, calcd for $C_{22}H_{16}F_3NNaO_2S$ 438.0746.

_N_-Ts-2-_p_-Tolyl-3-(4-(trifluoromethyl)phenyl)indole (3m')



a light yellow solid (CH_2Cl_2 : *n*-Hexane = 1 : 2), mp 188-190 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 2.39 (s, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 6.8 Hz, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 8.42 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.47, 21.54, 116.3, 119.4, 122.9, 124.1 (q, *J* = 271.3 Hz), 124.3, 125.1 (q, *J* = 3.6 Hz), 125.3, 126.9, 127.3, 128.3, 128.8 (q, *J* = 32.3 Hz), 129.3, 129.8, 130.0, 131.8, 135.3, 136.8, 137.1, 137.7, 138.8, 144.7. HREIMS *m/z* 528.1214 $(M+Na)^+$, calcd for $C_{29}H_{22}F_3NNaO_2S$ 528.1216.

_N_-Ts-2-Phenyl-3-(4-(trifluoromethyl)phenyl)indole (3n') & _N_-Ts-2-Phenylindole (2a)

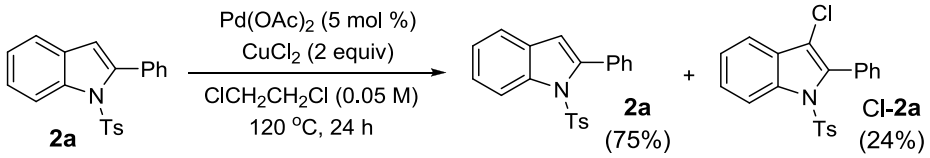


55% (**3n'** : **2a** = 1 : 0.6), a white solid (EtOAc : *n*-Hexane = 1 : 10).
Representative signals corresponding to **3n'**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 6.4 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 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). EIMS (**3n'**) *m/z* 491 (M^+), 336, 267, 239, 155, 134, 91. EIMS (**2a**) *m/z* 347 (M^+), 208, 192, 165, 139, 115, 91, 65.
Spectral data of **3n'** were consistent with data reported in the literature.[1]

Mechanistic Studies

1) Reaction of 2a under the Standard Reaction Conditions

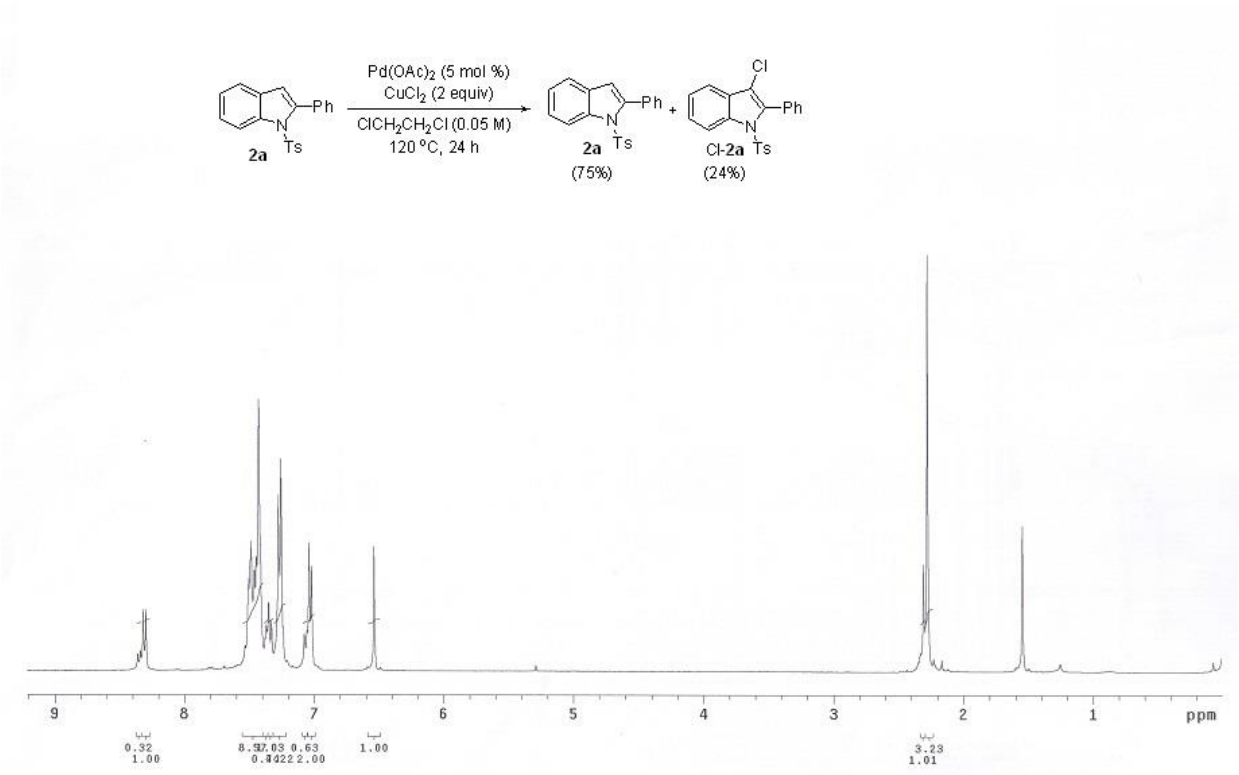
To a solution of **2a** (25.0 mg, 0.0715 mmol, 1 equiv) in $ClCH_2CH_2Cl$ (1.4 mL, 0.05 M) in pressure tube were added $Pd(OAc)_2$ (0.8 mg, 0.00358 mmol, 5 mol %) and $CuCl_2$ (19.2 mg, 0.143 mmol, 2 equiv). After the resulting mixture was stirred at 150 °C for 24 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the mixture of **2a** and Cl-**2a** (25.3 mg, 99%, **2a** and Cl-**2a** = 1:0.3).



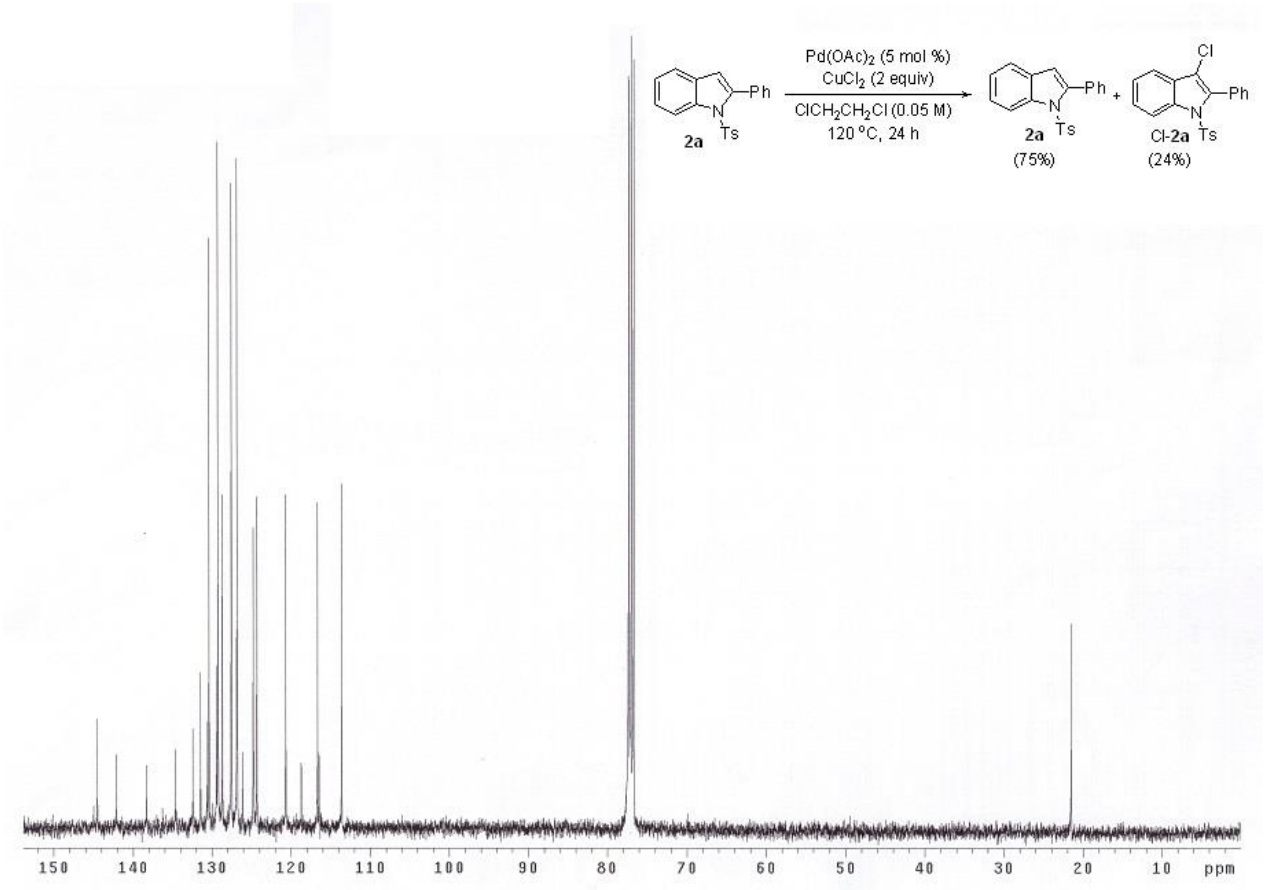
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H of **2a**), 2.31 (s, 3H of Cl-**2a**), 6.54 (s, 1H of **2a**), 7.03 (d, J = 7.6 Hz, 2H of **2a**), 7.07 (d, J = 8.0 Hz, 2H of Cl-**2a**), 7.24-7.28 (m, 1H of **2a** & 2H of Cl-**2a**), 7.27 (d, J = 8.4 Hz, 2H of **2a**), 7.33-7.38 (m, 1H of **2a** & 1H of Cl-**2a**), 7.43-7.53 (m, 6H of **2a** & 7H of Cl-**2a**), 8.31 (d, J = 8.4 Hz, 1H of **2a**), 8.35 (d, J = 8.8 Hz, 1H of Cl-**2a**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.6, 113.6, 116.4, 116.6, 118.7, 120.7, 124.3, 124.7, 124.8, 126.1, 126.8, 126.9, 127.47, 127.52, 128.6, 129.2, 129.4, 130.3, 130.5, 131.4, 132.4, 134.6, 136.3, 138.2, 142.1, 144.5, 145.0 (6 carbons are missing due to overlapping). EIMS (**2a**) *m*/*z* 347 (M^+), 208, 192, 177, 165, 139, 115, 91, 77, 65, 51. EIMS (Cl-**2a**) *m*/*z* 381 (M^+), 267, 226, 199, 190, 164, 155, 91, 65, 51.

Spectral data of **2a**[1, 3] and Cl-**2a**[15] were consistent with data reported in the literature.

[15] (a) Yamashita, M.; Noro, T.; Iida, A. *Tetrahderon Lett.* **2013**, *54*, 6848. (b) Shen, Z.; Lu, X. *Adv. Synth. Catal.* **2009**, *351*, 3107. (c) Dalton, L.; Humphrey, G. L.; Cooper, M. M.; Joule, J. A. *J. Chem. Soc., Perkin Trans.1:* **1983**, *10*, 2417.



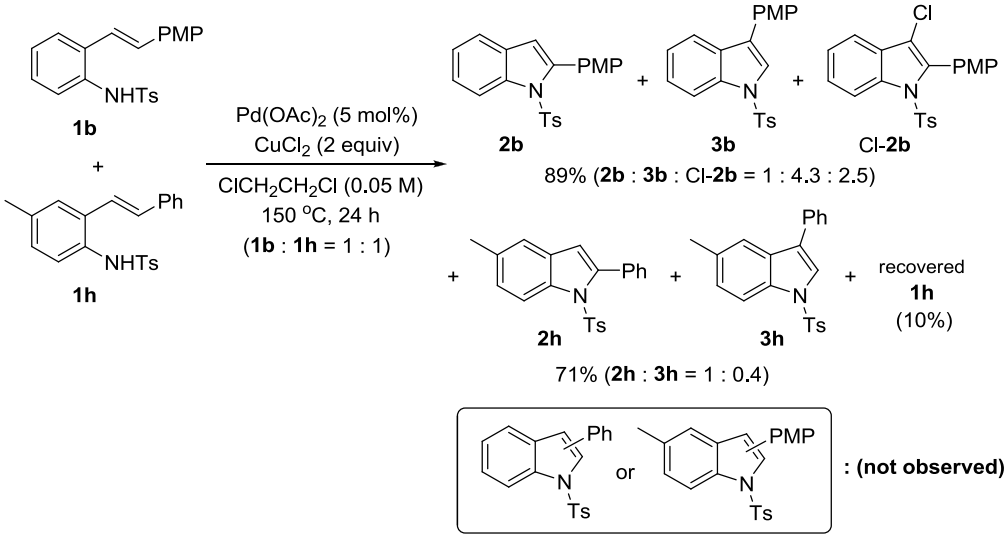
^{1}H NMR Spectrum of **2a** & Cl-**2a** Mixture ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2a** & Cl-**2a** Mixture ($CDCl_3$, 100 MHz)

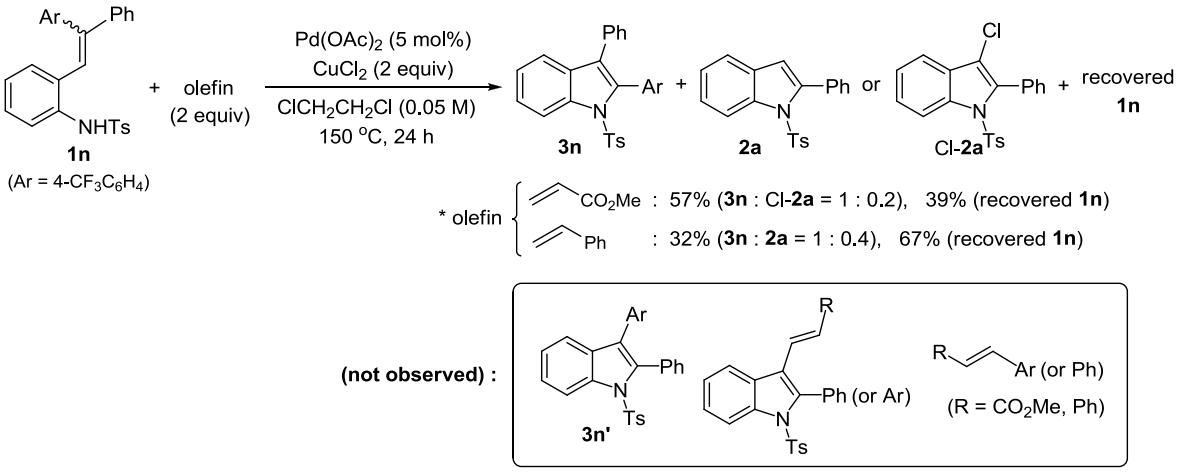
2) Crossover Experiments

To a solution of **1b** and **1h** (each 0.0361 mmol, 0.5 equiv) in $ClCH_2CH_2Cl$ (1.4 mL, 0.05 M) in pressure tube were added $Pd(OAc)_2$ (0.8 mg, 0.00361 mmol, 5 mol %) and $CuCl_2$ (19.4 mg, 0.144 mmol, 2 equiv). After the resulting mixture was stirred at 150 °C for 24 h, the reaction mixture was concentrated *in vacuo*. ^1H NMR of each crude mixture was taken first and then a few spots observed in TLC were separated by column chromatography on silica gel. ^1H NMR and GC-MS of each portion were taken to identify the structure of each compound.

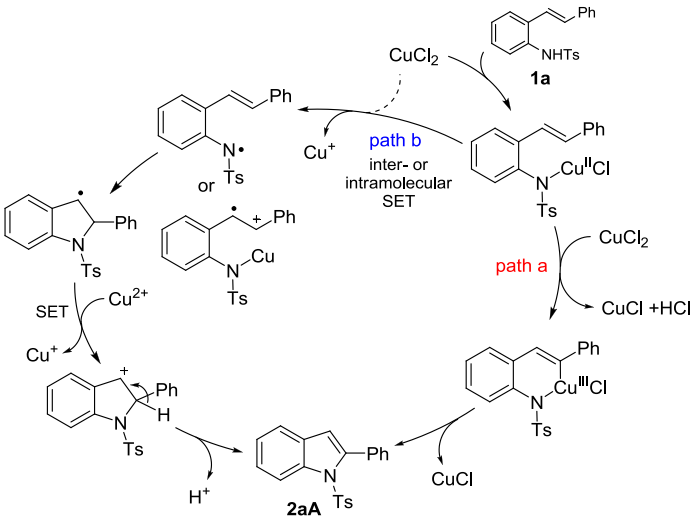


3) Addition of Olefins

To a solution of **1n** (26.0 mg, 0.0527 mmol, 1 equiv) in $ClCH_2CH_2Cl$ (1.1 mL, 0.05 M) in pressure tube were added olefin (0.105 mmol, 2 equiv), $Pd(OAc)_2$ (0.6 mg, 0.00264 mmol, 5 mol %), and $CuCl_2$ (14.2 mg, 0.105 mmol, 2 equiv). After the resulting mixture was stirred at 150 °C for 24 h, the reaction mixture was concentrated *in vacuo*. ^1H NMR of each crude mixture was taken first and then a few spots observed in TLC were separated by column chromatography on silica gel. ^1H NMR and GC-MS of each portion were taken to identify the structure of each compound.

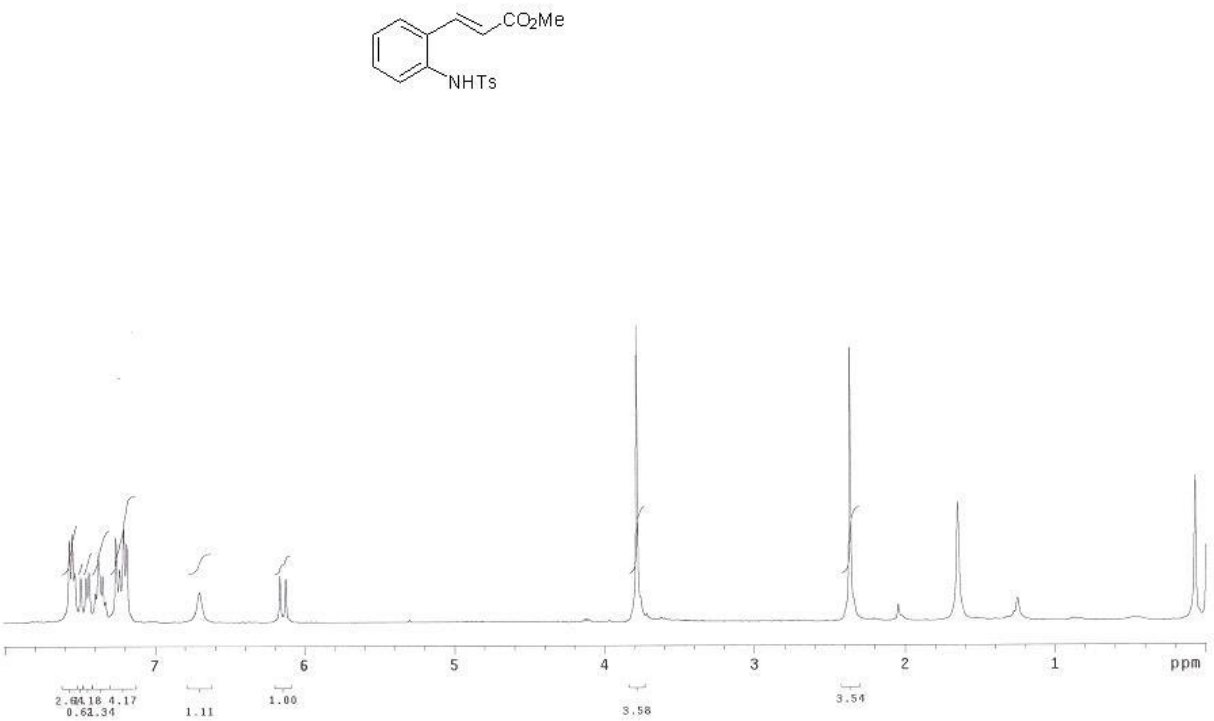


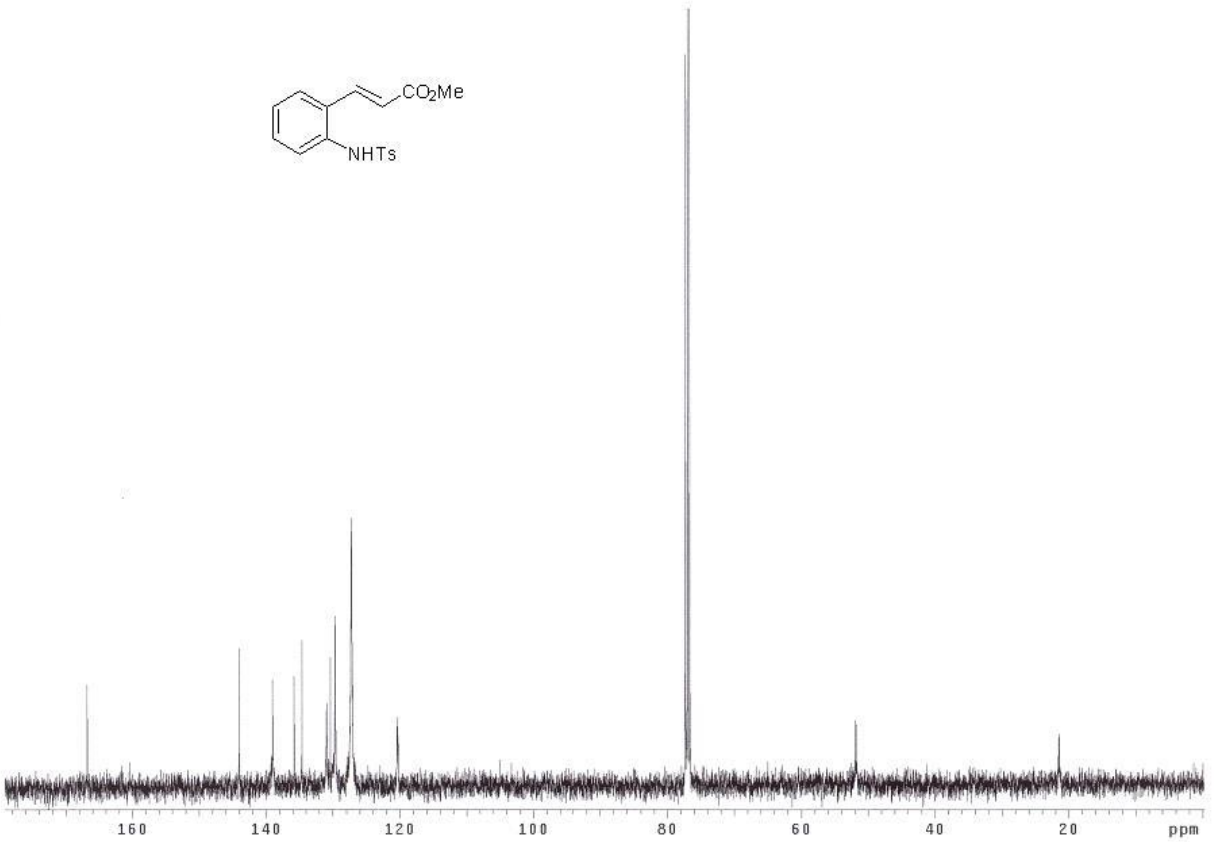
Proposed Mechanism for the Cu(II)-Mediated Reaction in the Absence of Pd(II) Catalyst (Entries 23-24 in Table S1)



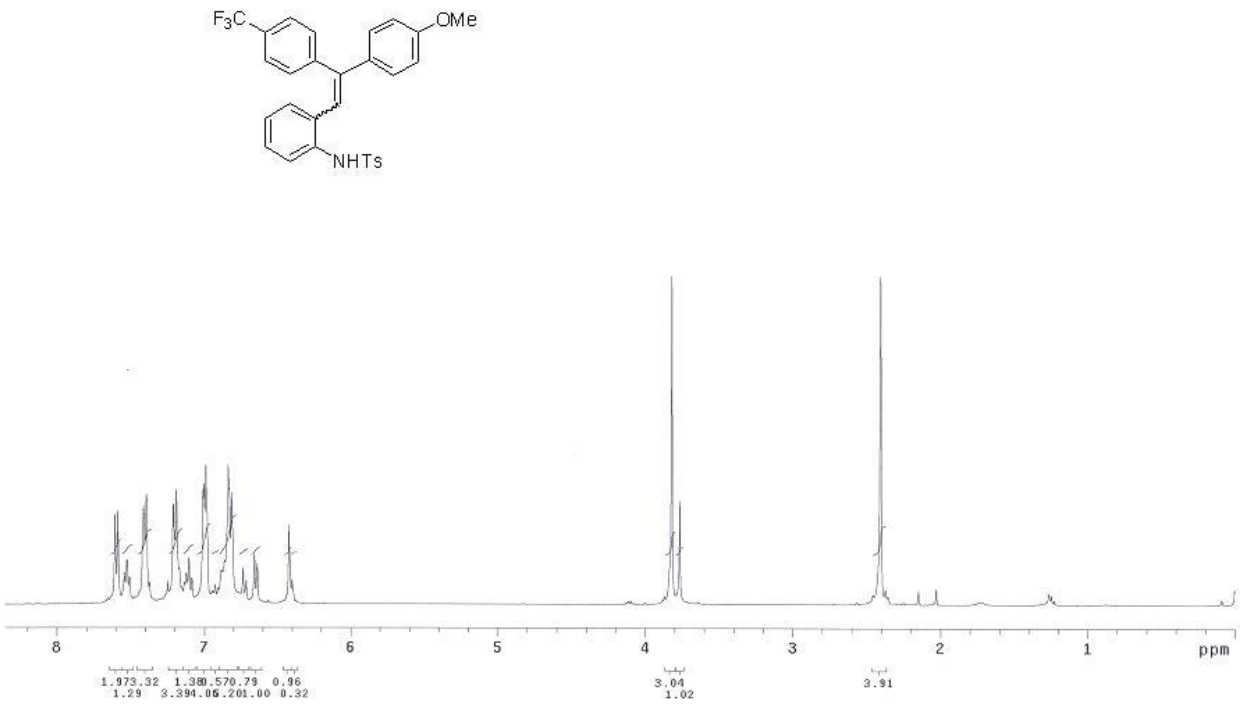
Copies of NMR Spectra

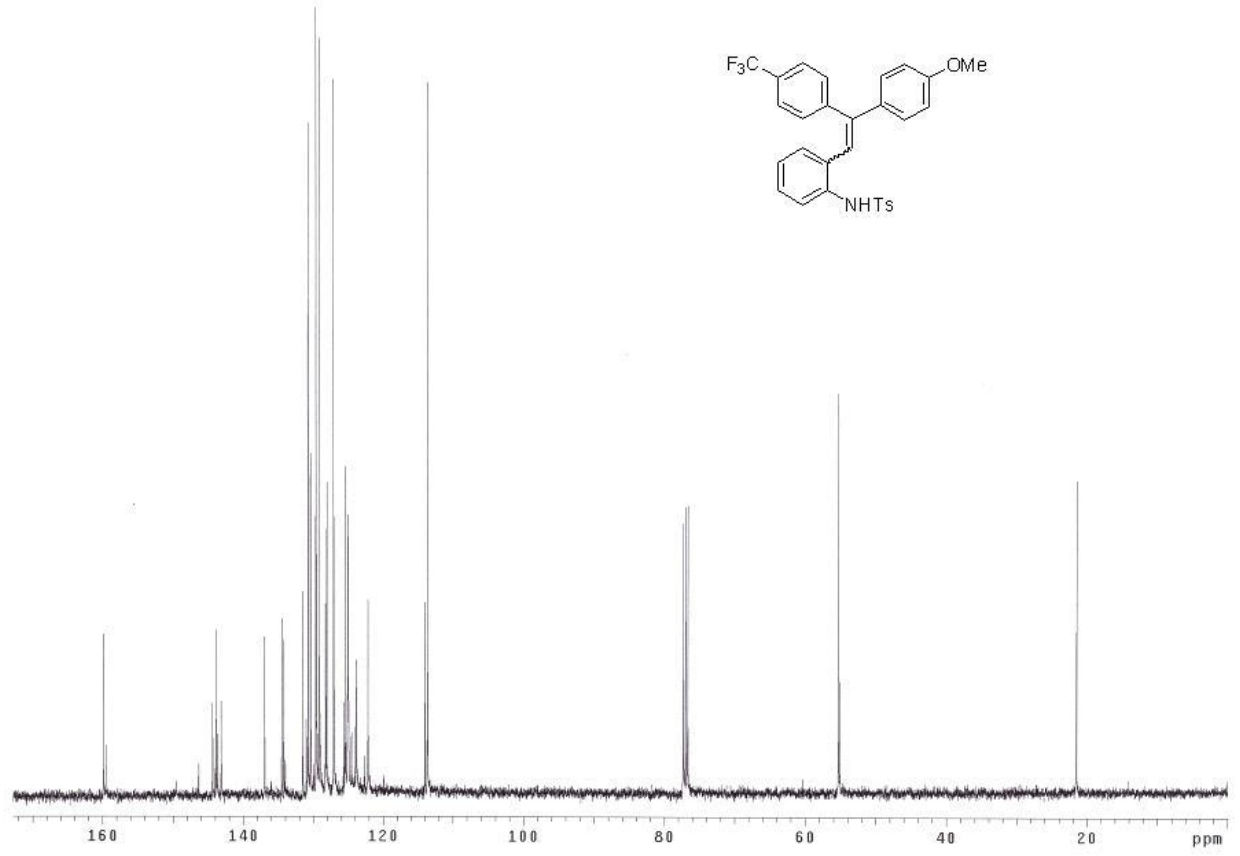
(*E*)-Methyl 3-(2-(4-Methylphenylsulfonamido)phenyl)acrylate (1f)



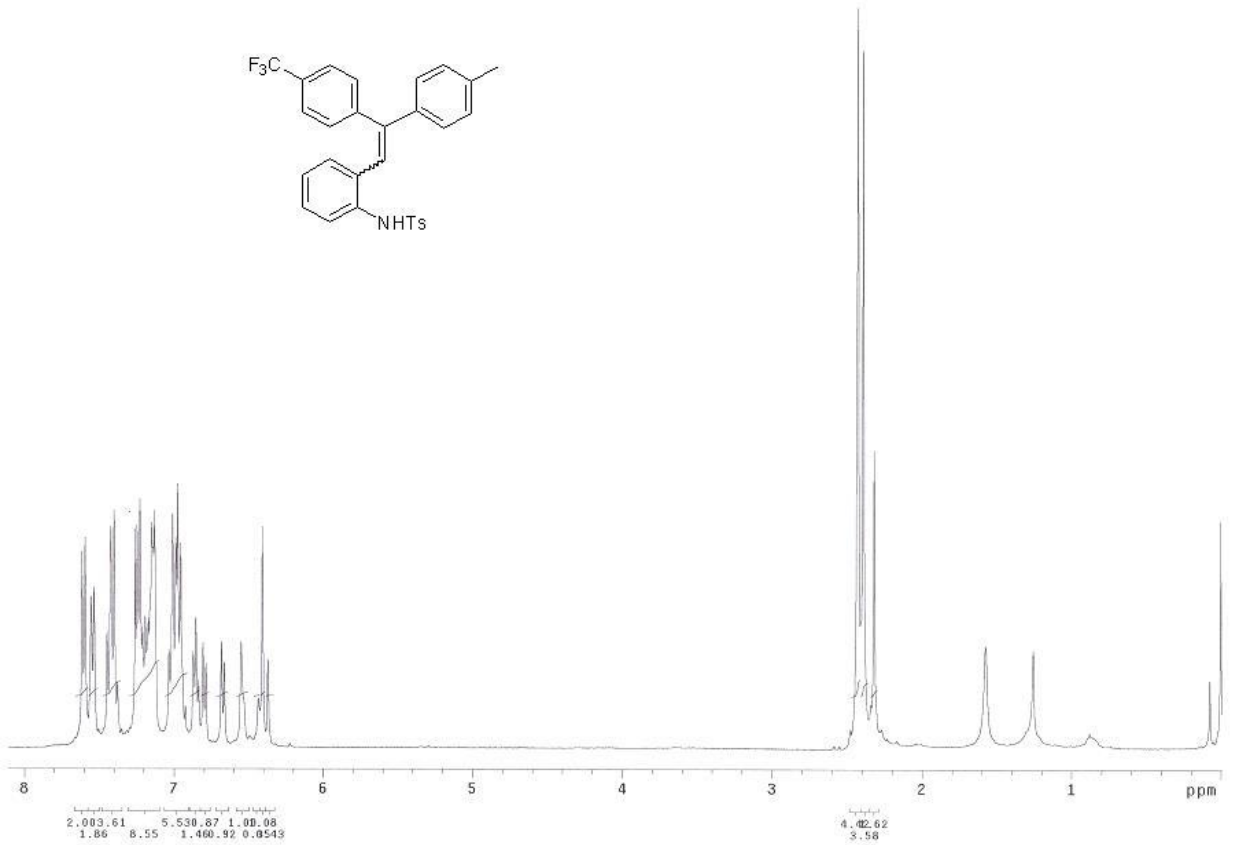


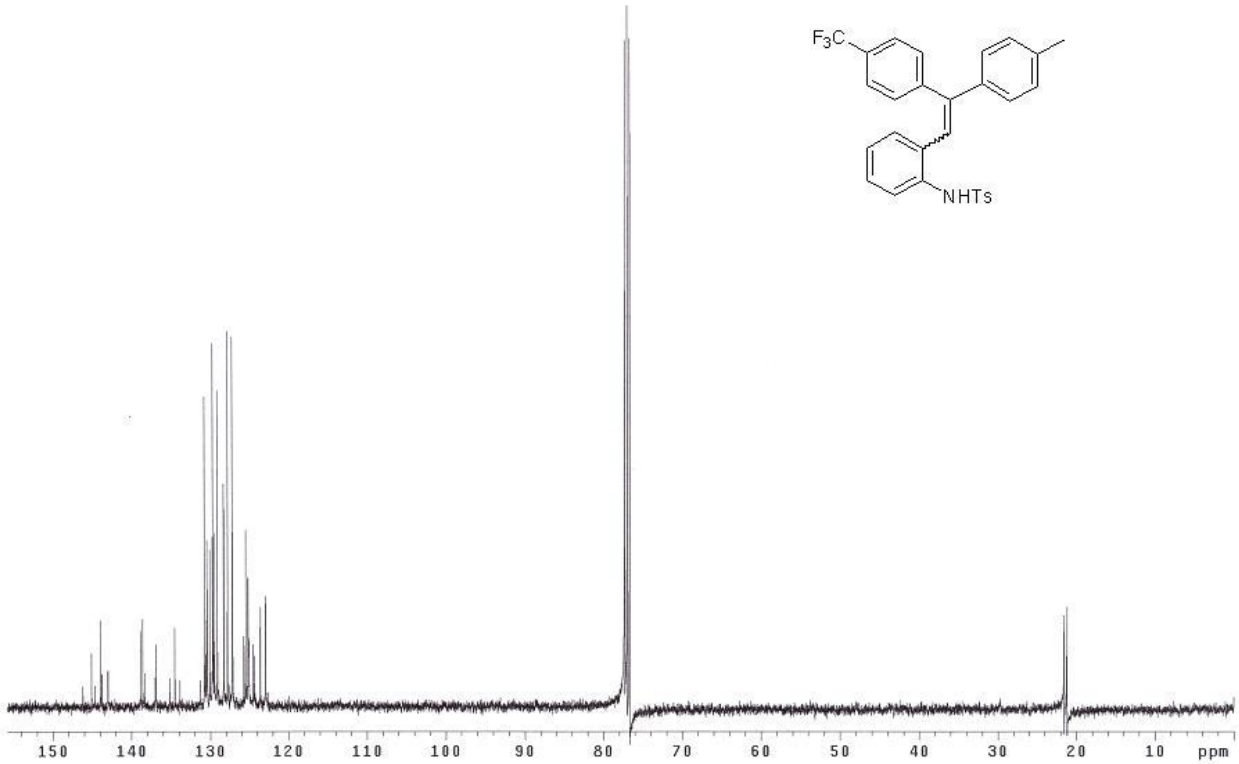
***N*-(2-(2-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (1l)**



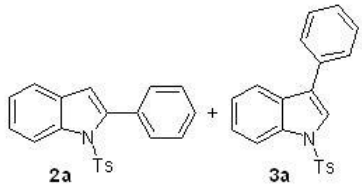


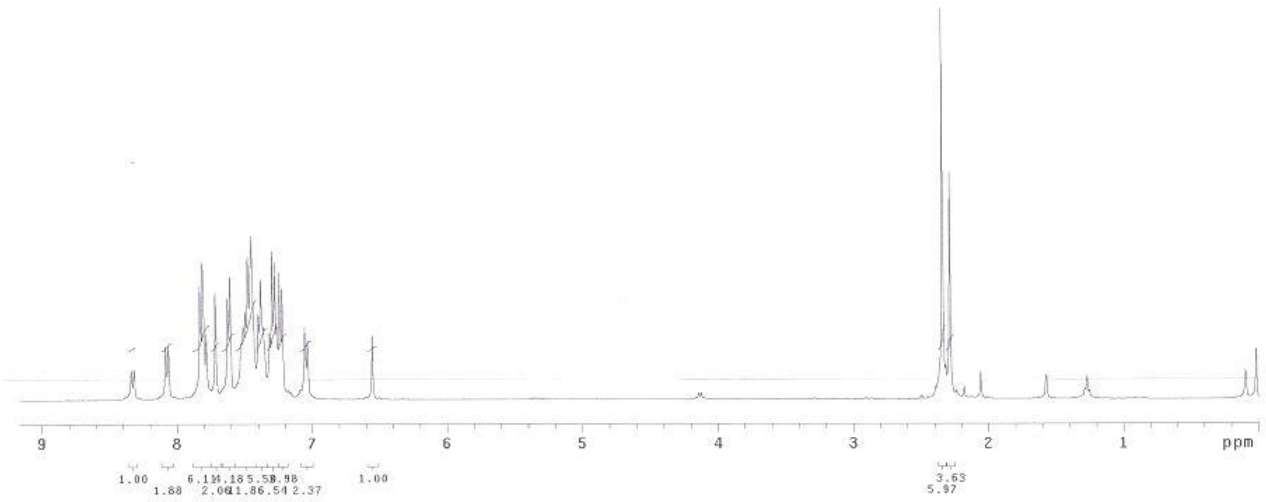
4-Methyl-*N*-(2-(2-*p*-tolyl-2-(4-(trifluoromethyl)phenyl)vinyl)phenyl)benzenesulfonamide (1m)

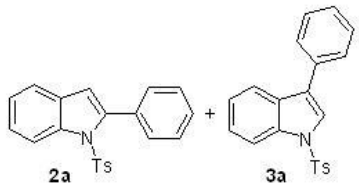




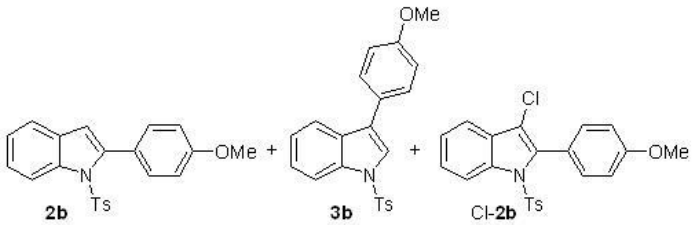
***N*-Ts-2-Phenylindole (2a) & *N*-Ts-3-Phenylindole (3a)**

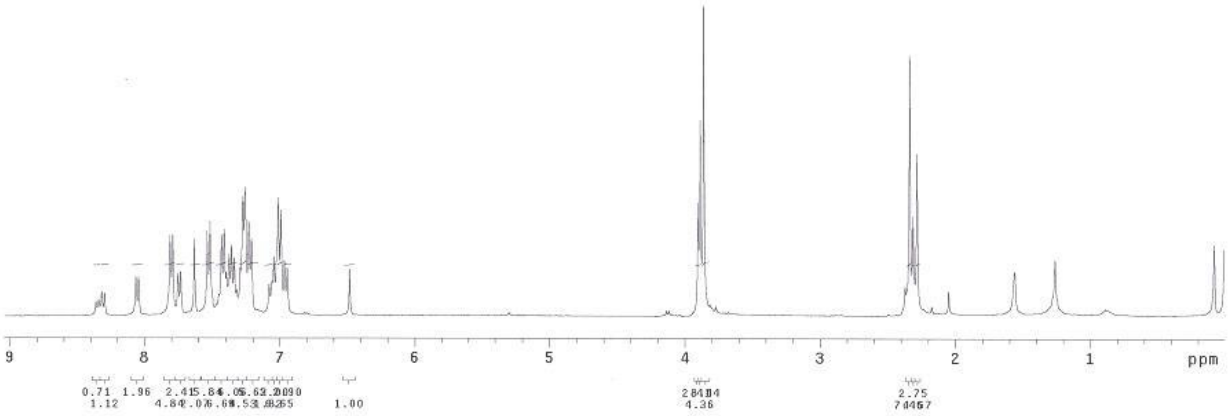


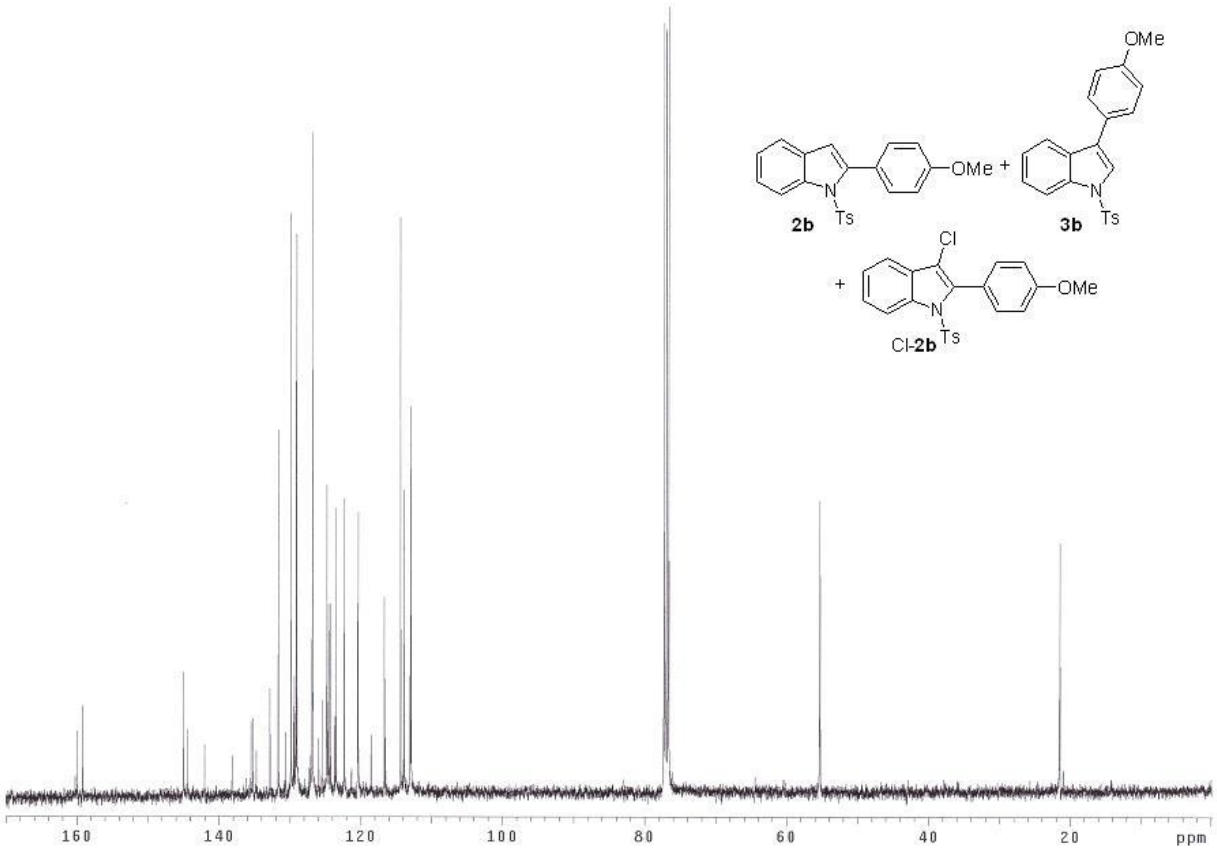




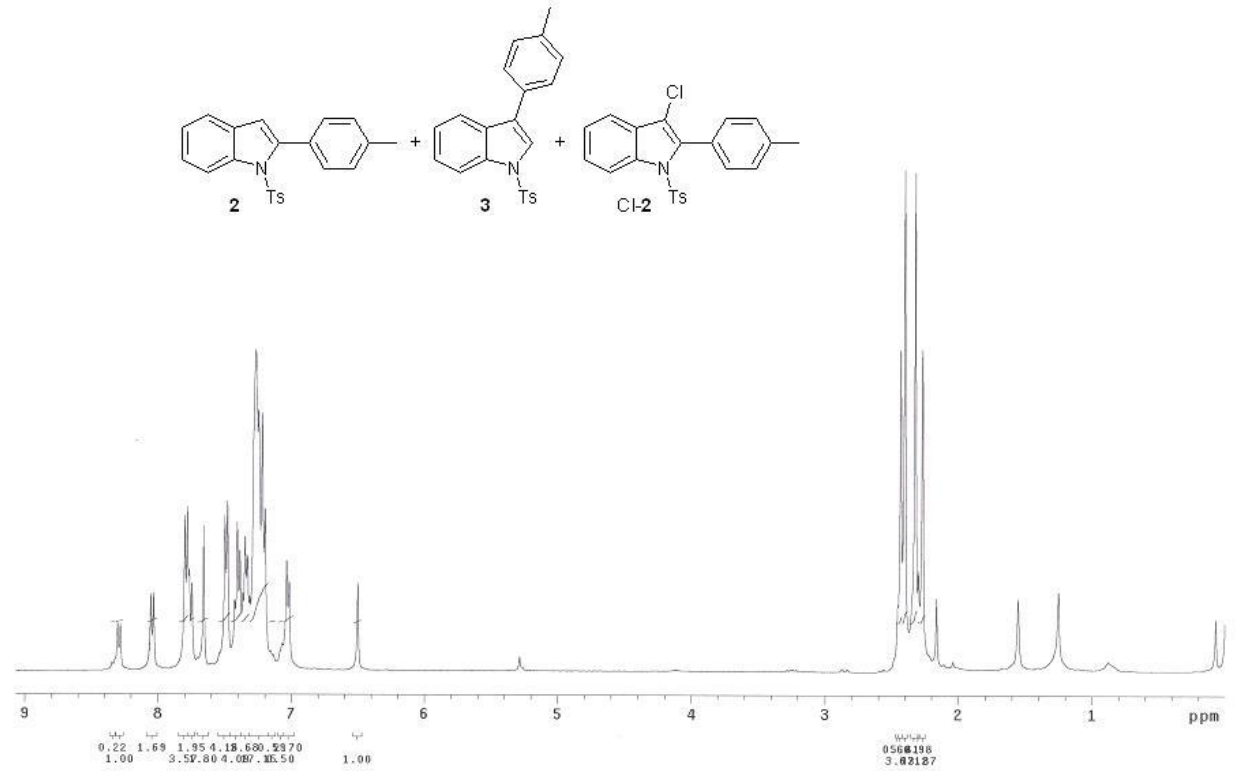
***N*-Ts-2-(4-Methoxyphenyl)indole (2b), *N*-Ts-3-(4-Methoxyphenyl)indole (3b), & *N*-Ts-3-Chloro-2-(4-methoxyphenyl)indole (Cl-2b)**

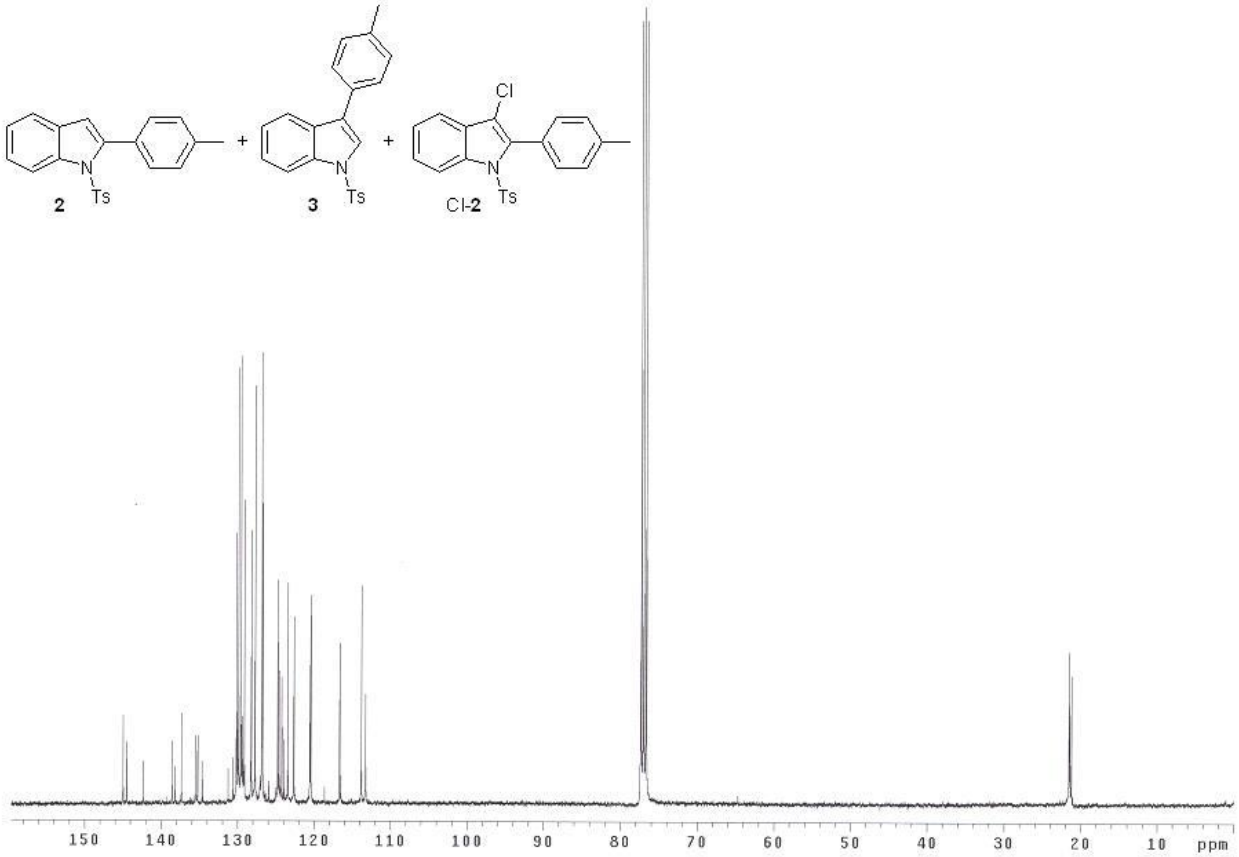




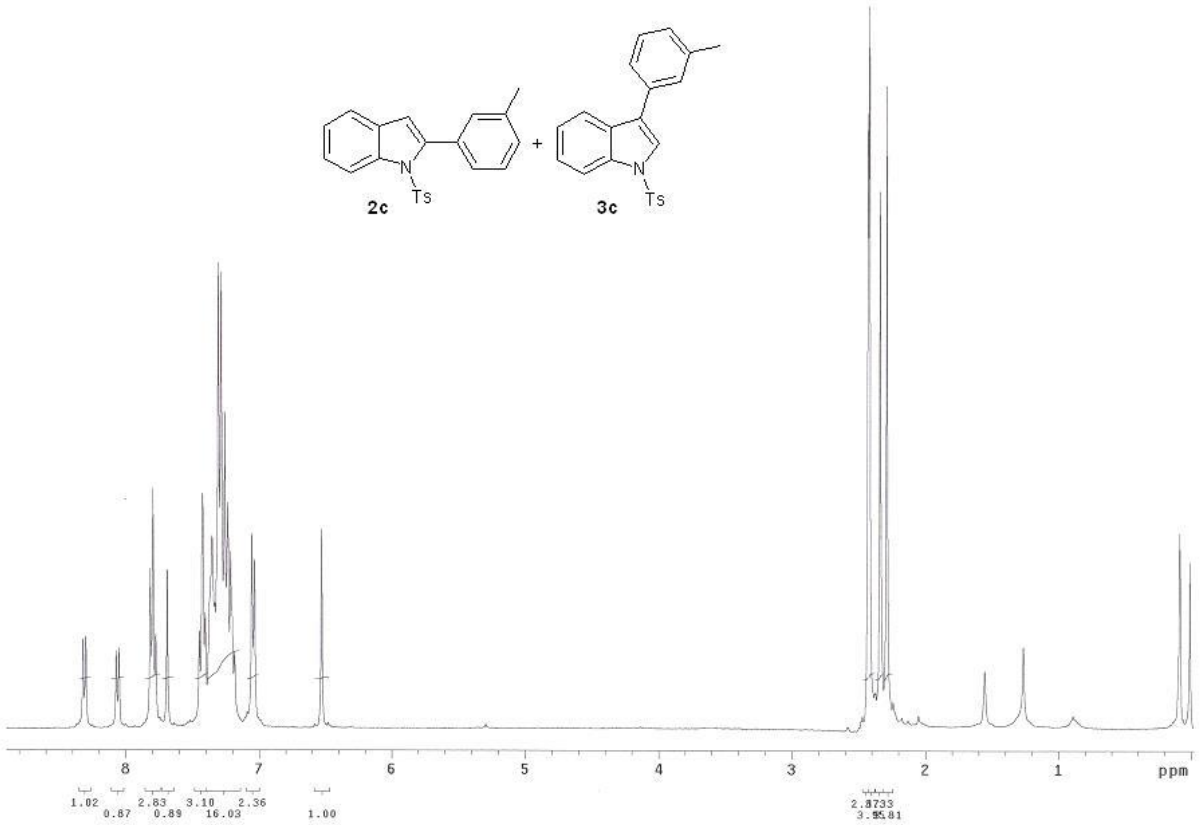


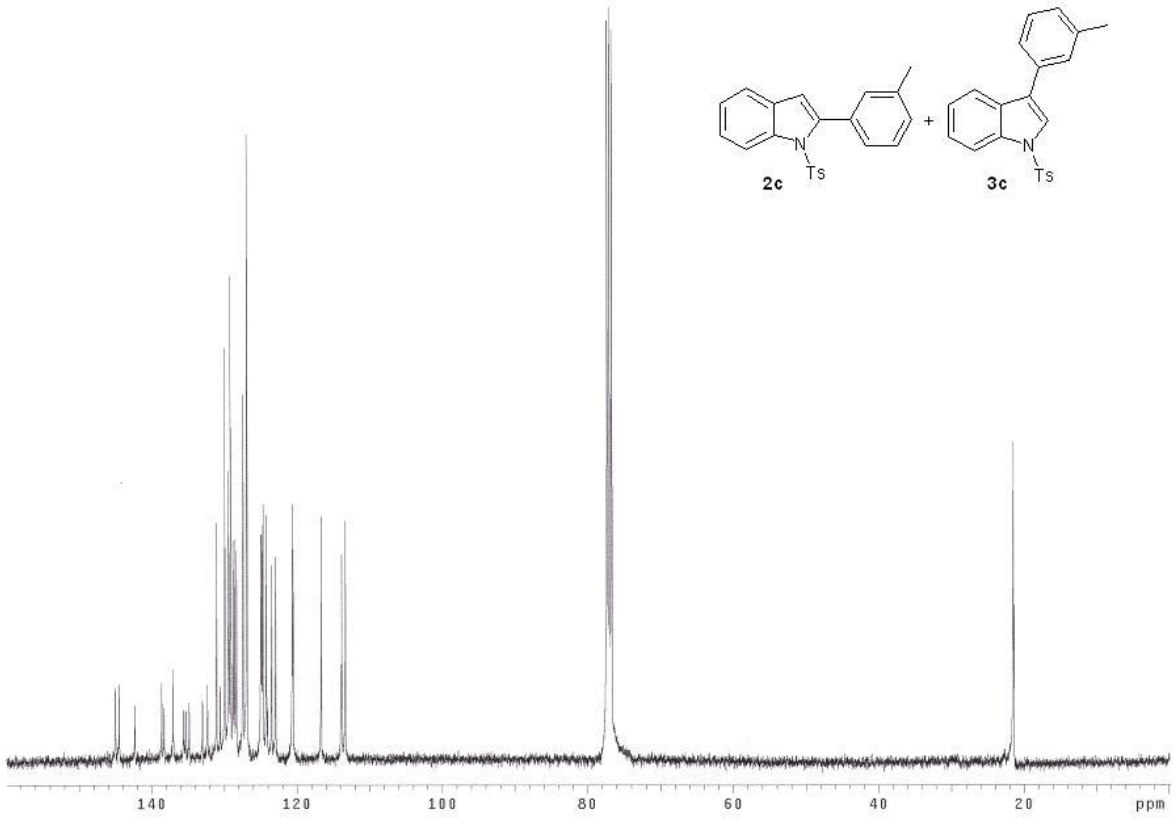
***N*-Ts-2-*p*-Tolylindole (2), *N*-Ts-3-*p*-Tolylindole (3), & *N*-Ts-3-Chloro-2-*p*-tolylindole (Cl-2)**





_N_-Ts-2-_m_-Tolylindole (2c) & _N_-Ts-3-_m_-Tolylindole (3c)





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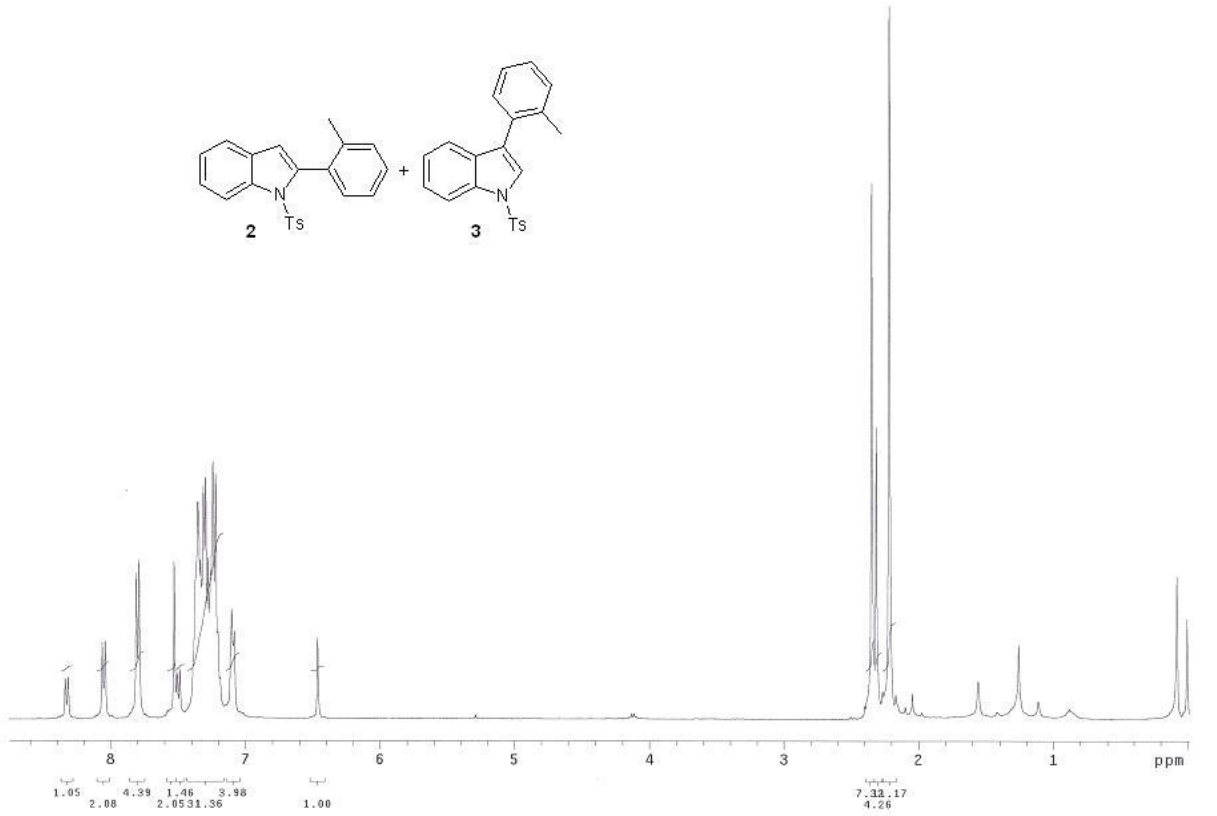
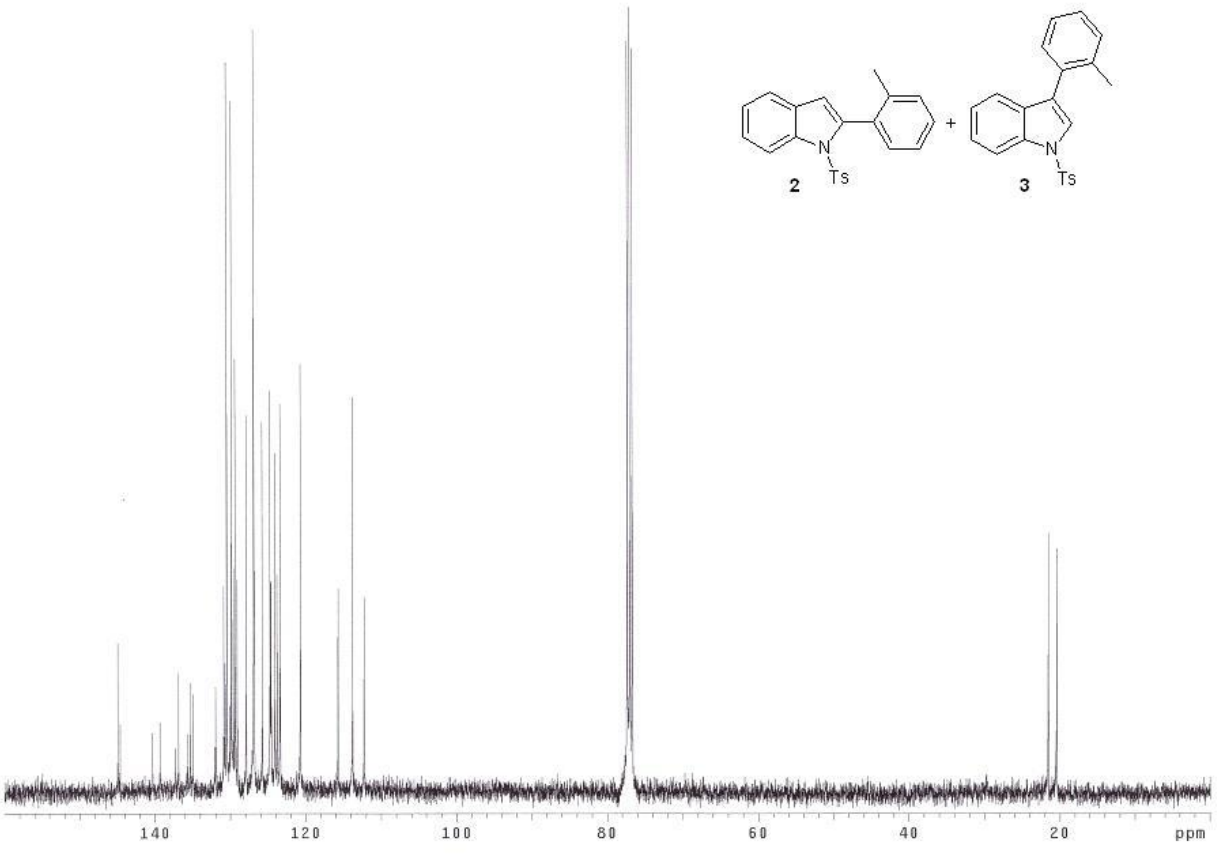
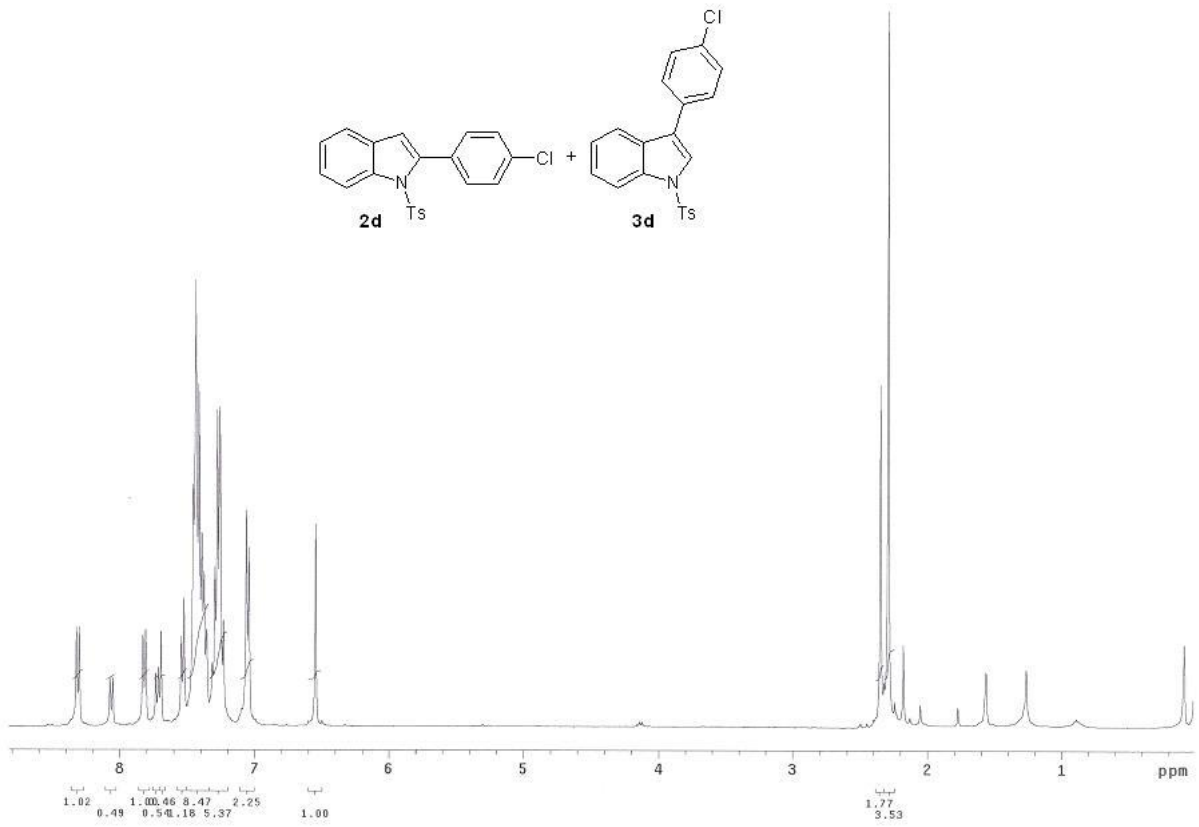
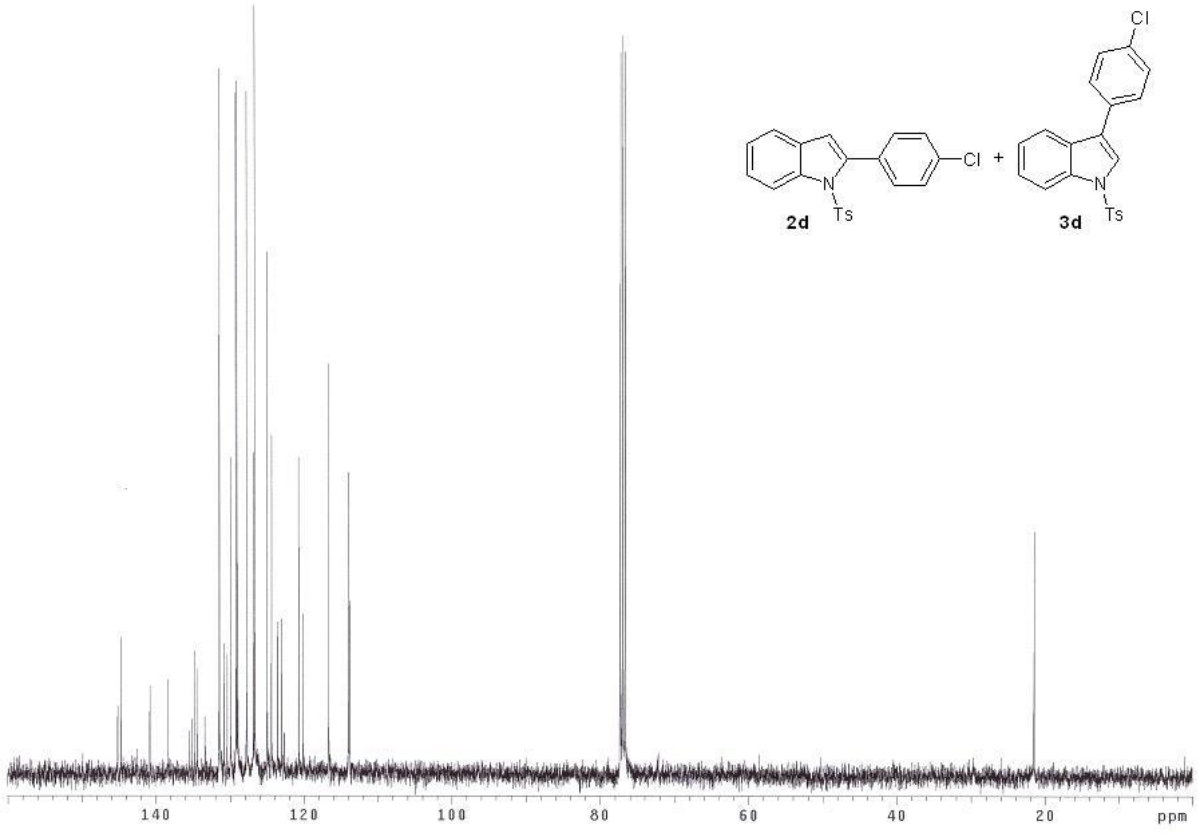


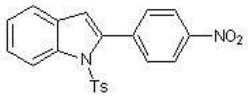


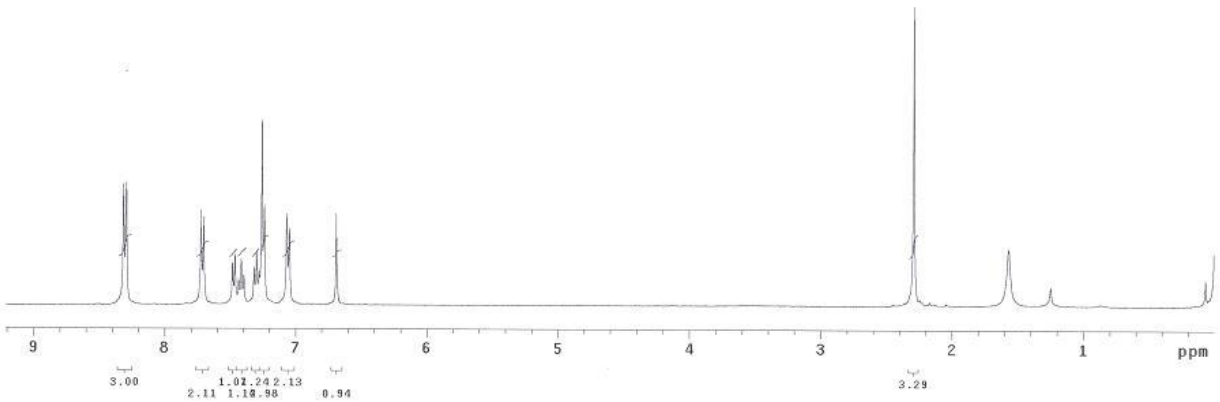
***N*-Ts-2-(4-Chlorophenyl)indole (2d) & *N*-Ts-3-(4-Chlorophenyl)indole (3d)**

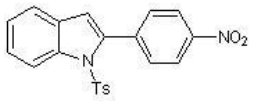




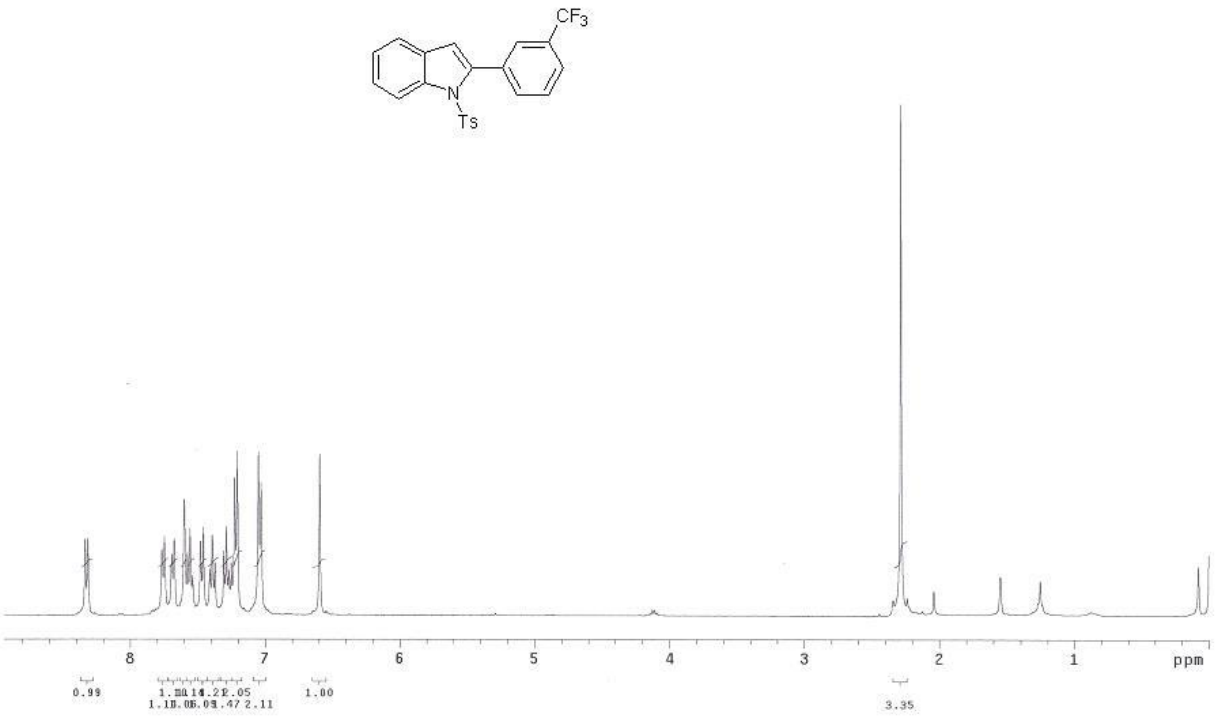
_N_-Ts-2-(4-Nitrophenyl)indole (2e)

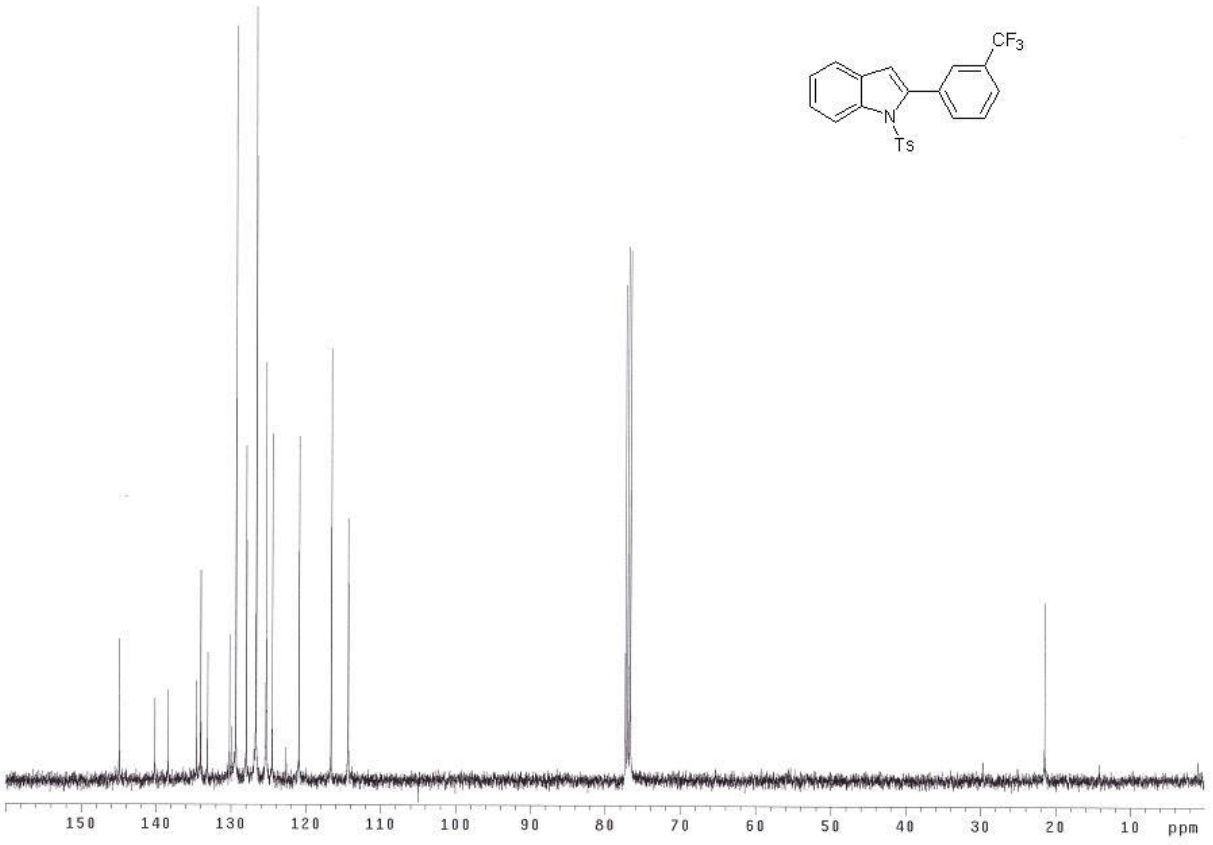




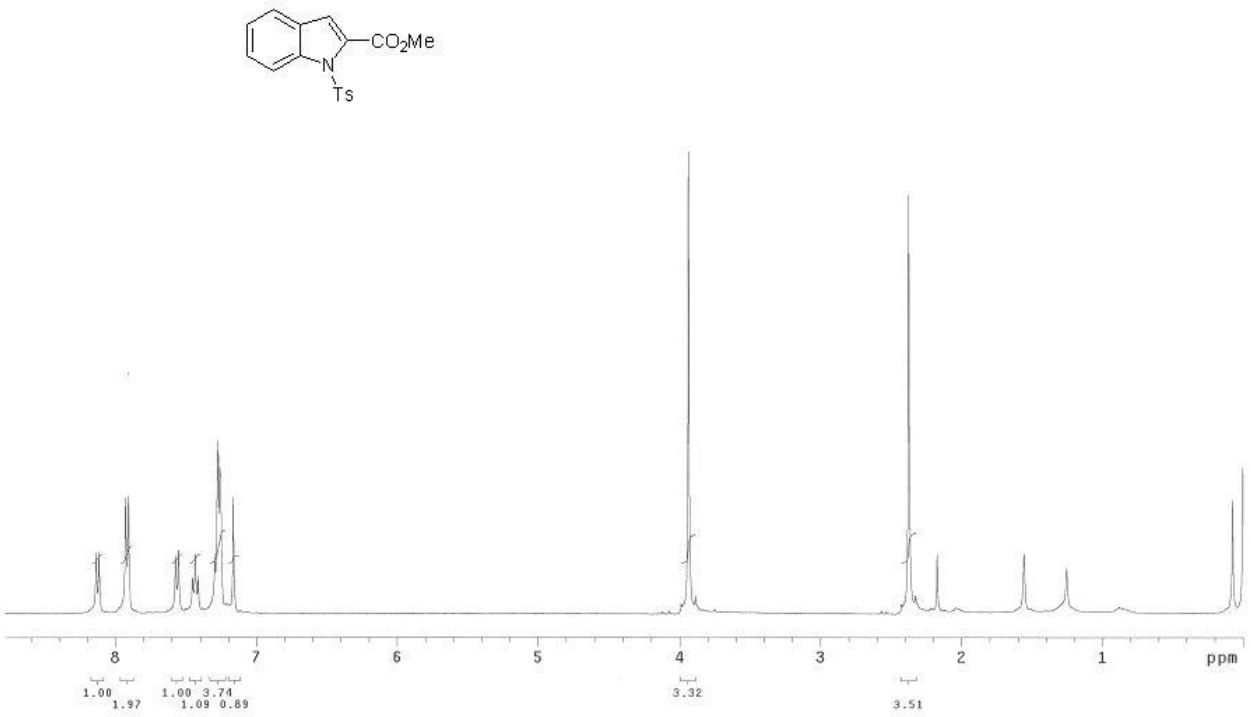


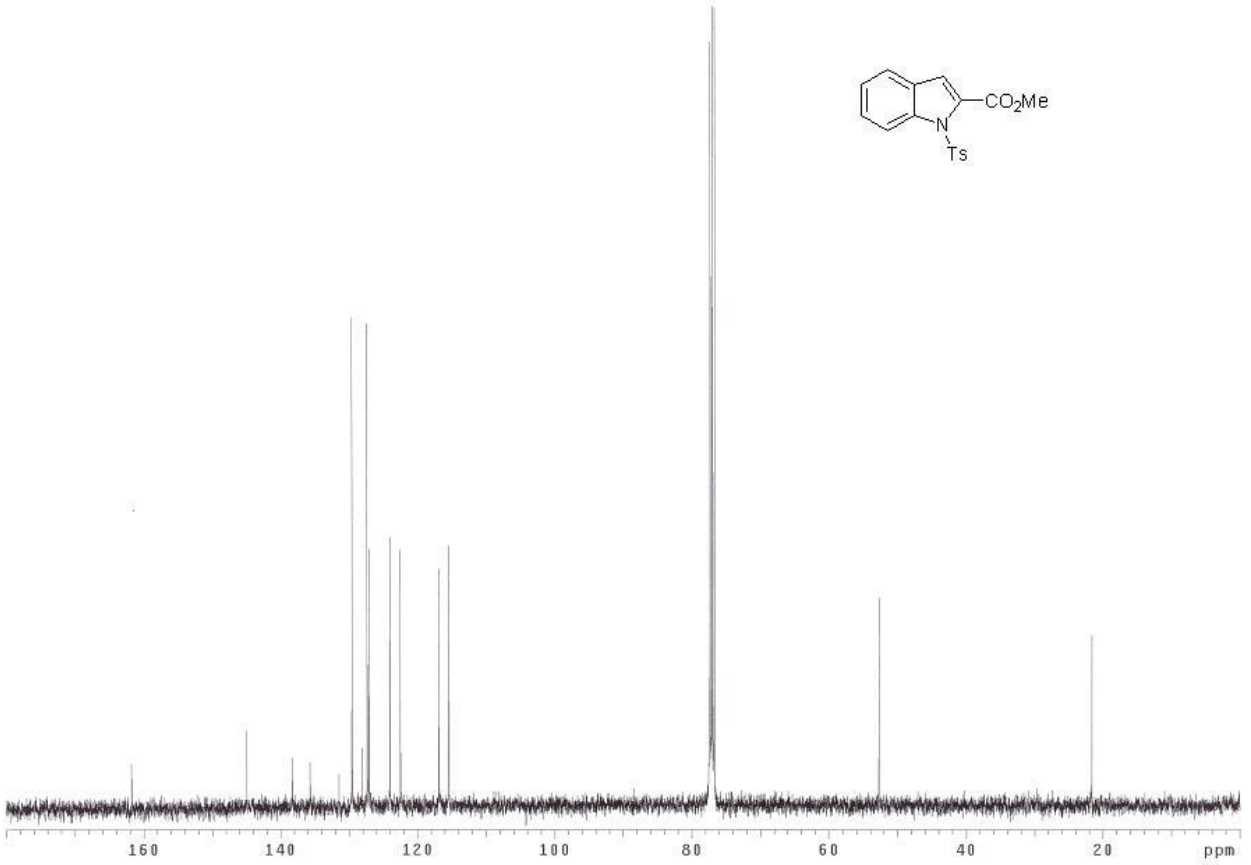
***N*-Ts-2-(3-(Trifluoromethyl)phenyl)indole**



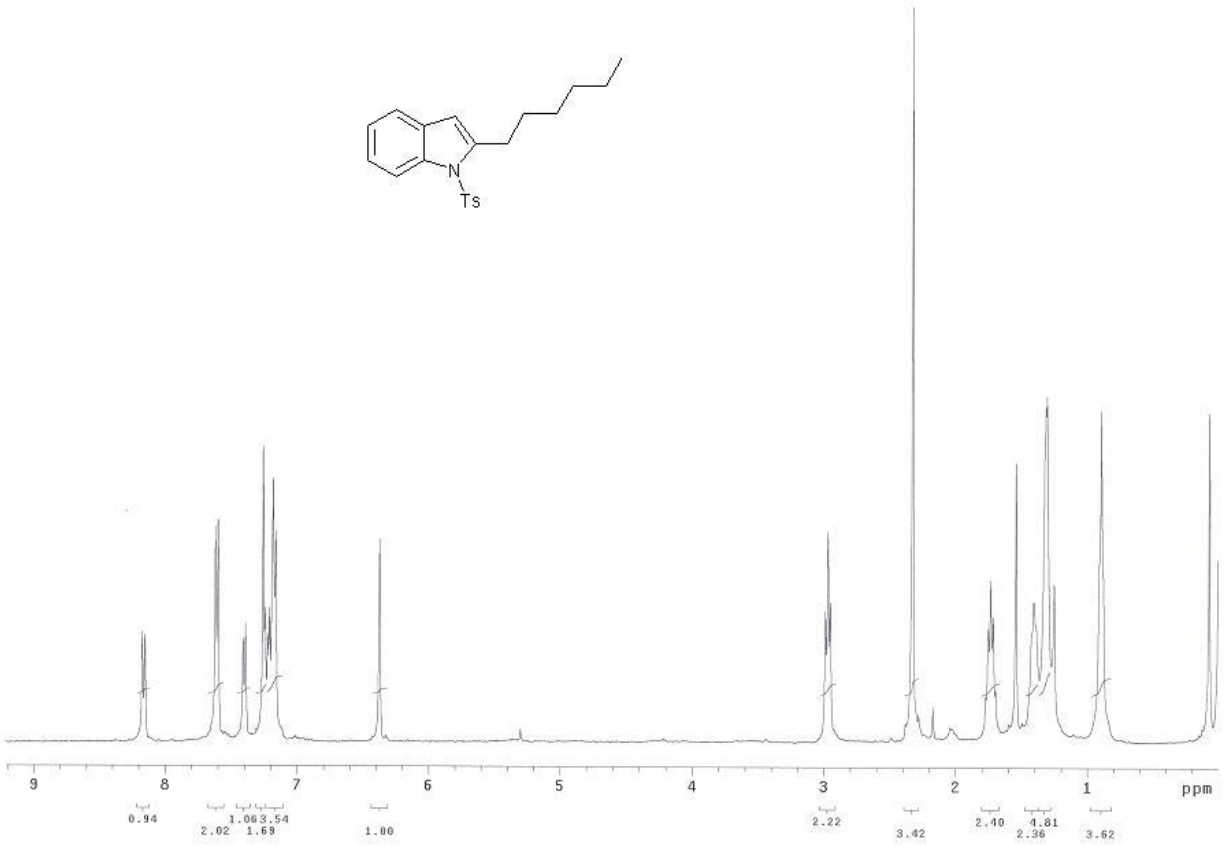


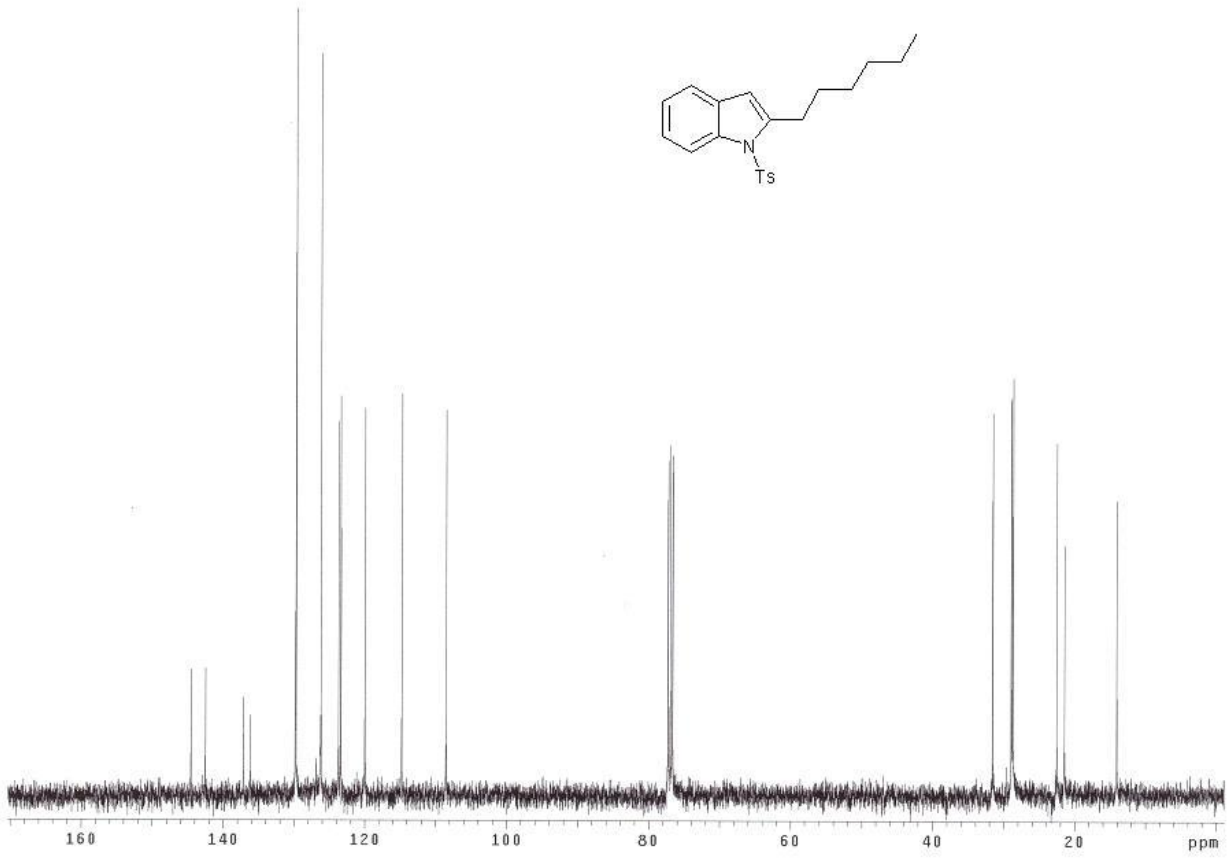
Methyl *N*-Ts-Indole-2-carboxylate (2f)



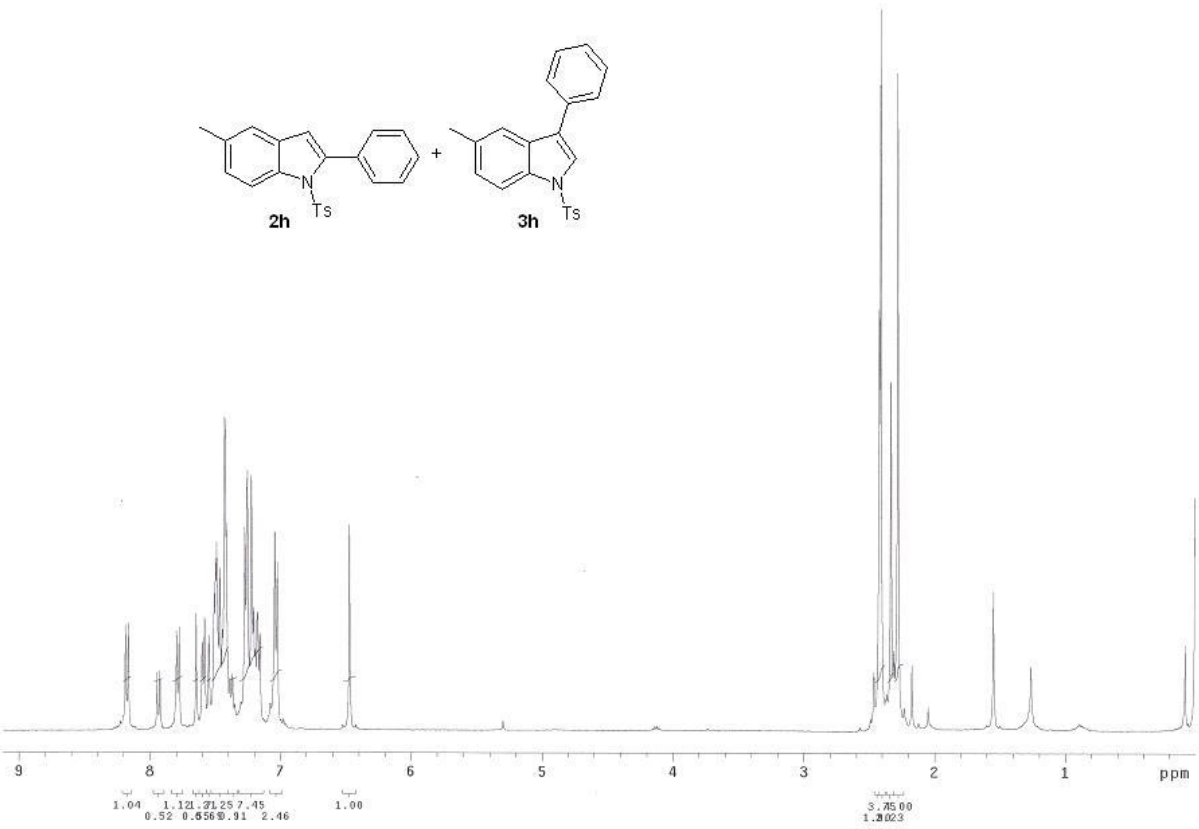


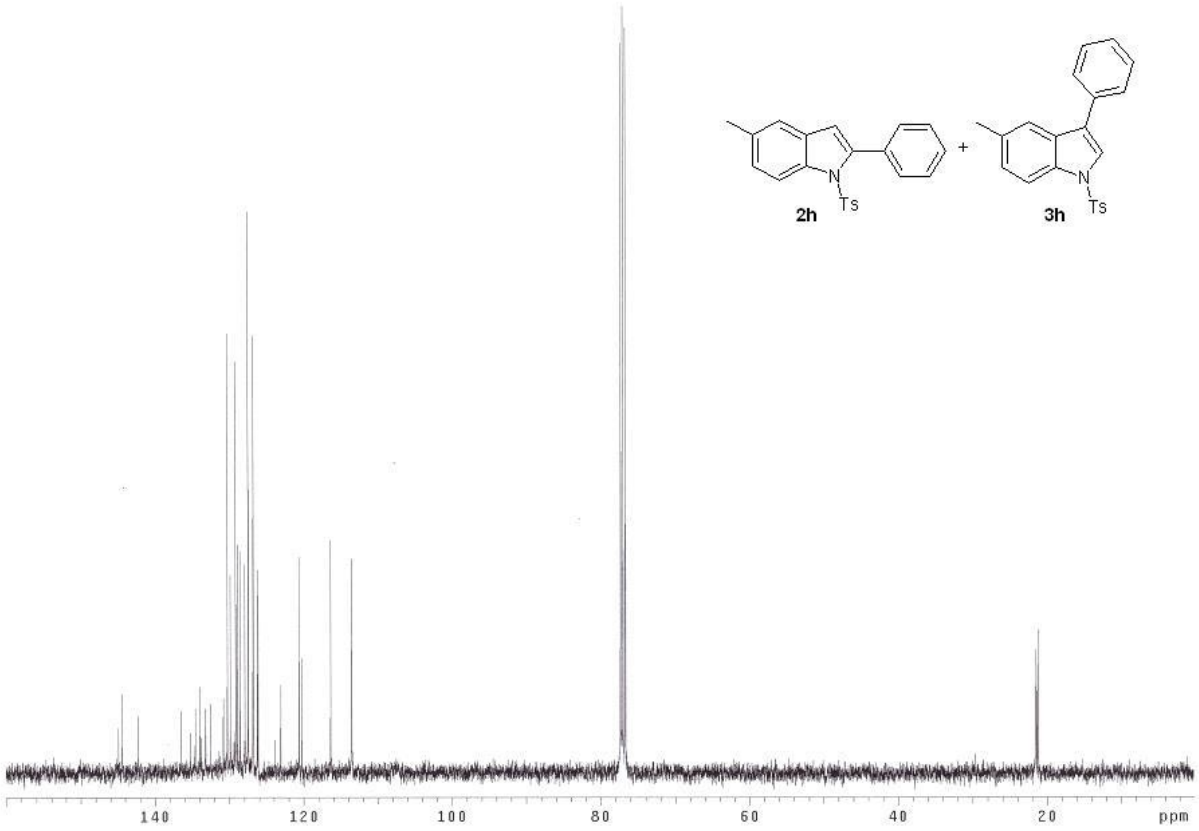
***N*-Ts-2-*n*-Hexylindole (2g)**



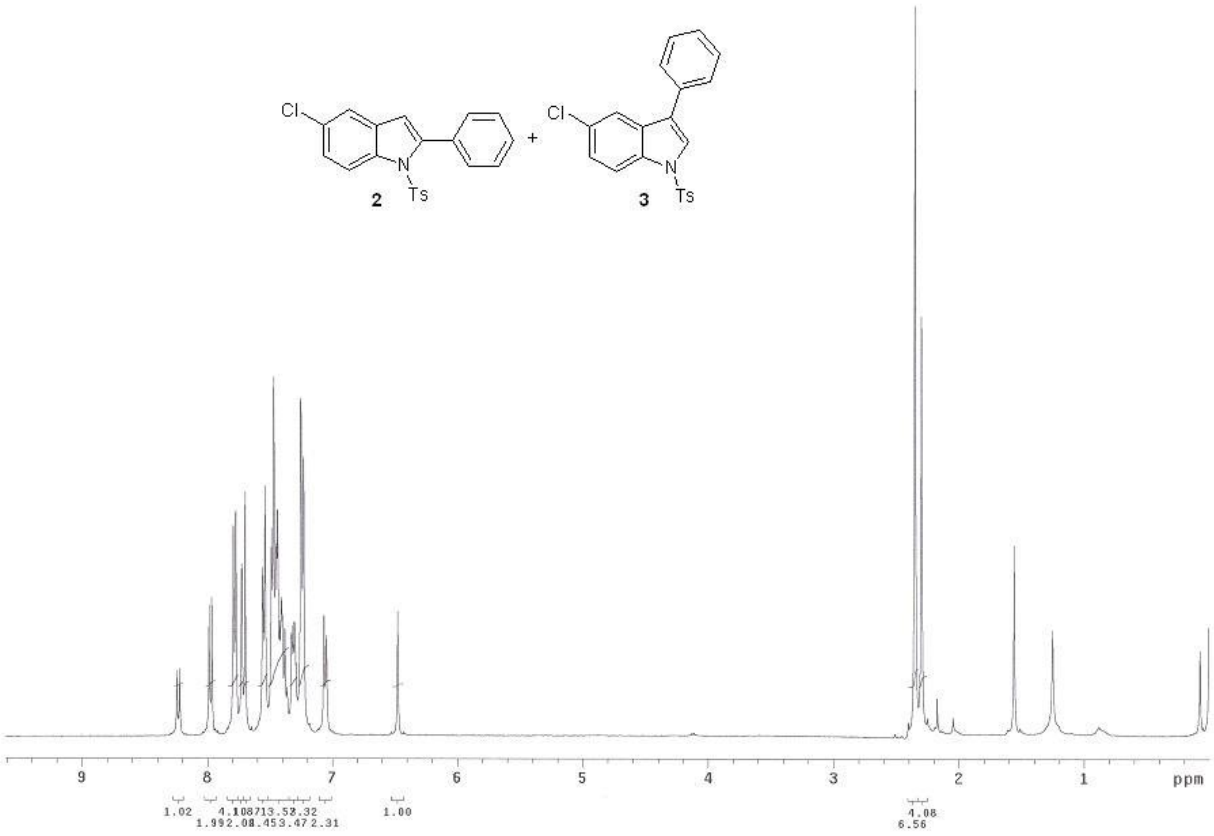


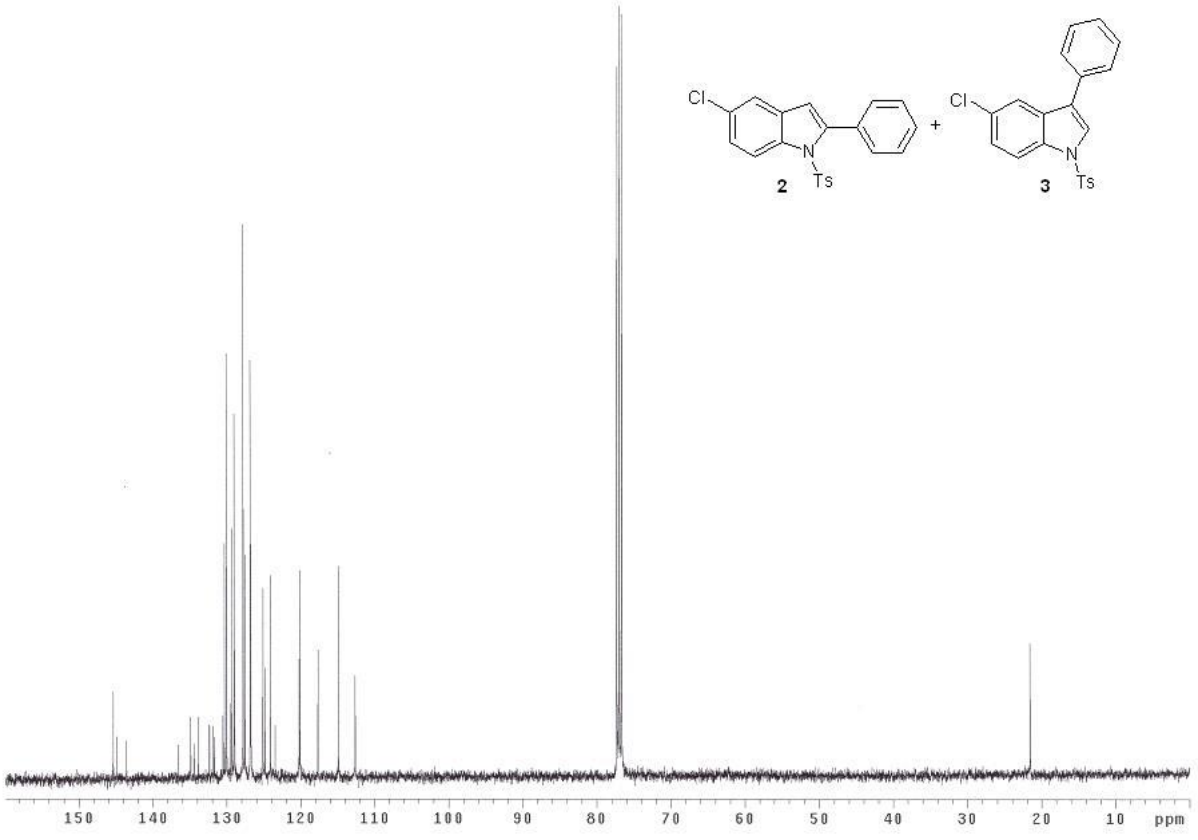
_N_-Ts-5-Methyl-2-phenylindole (2h) & _N_-Ts-5-Methyl-3-phenylindole (3h)



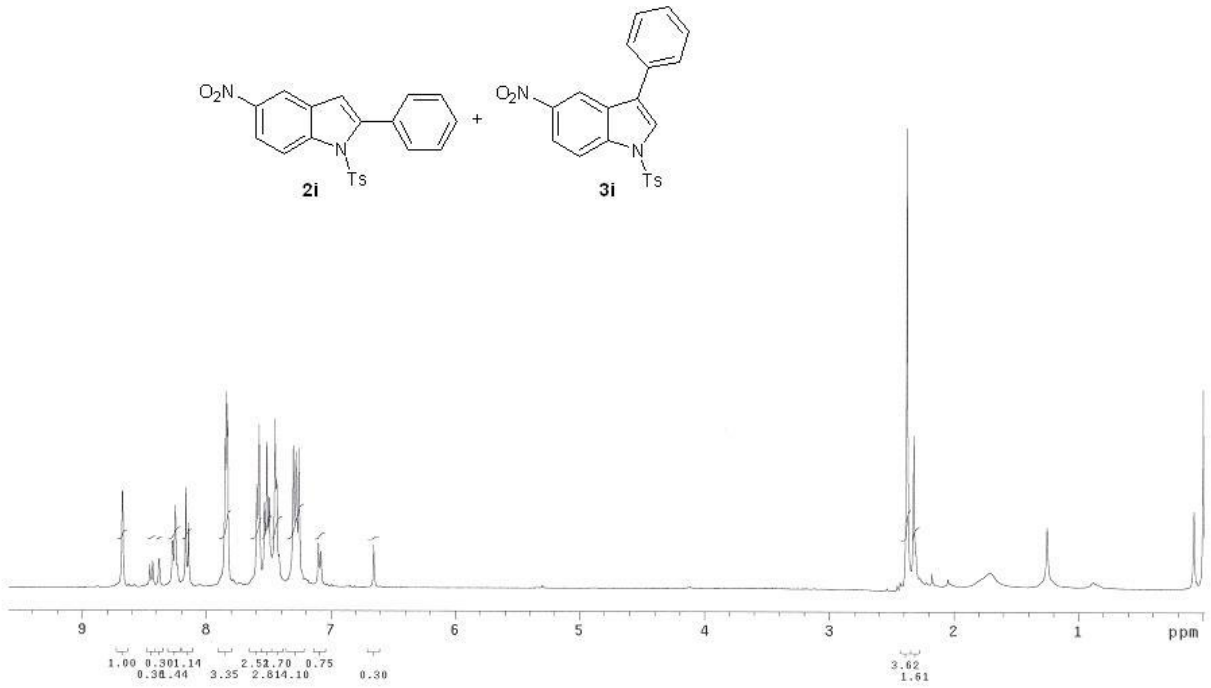


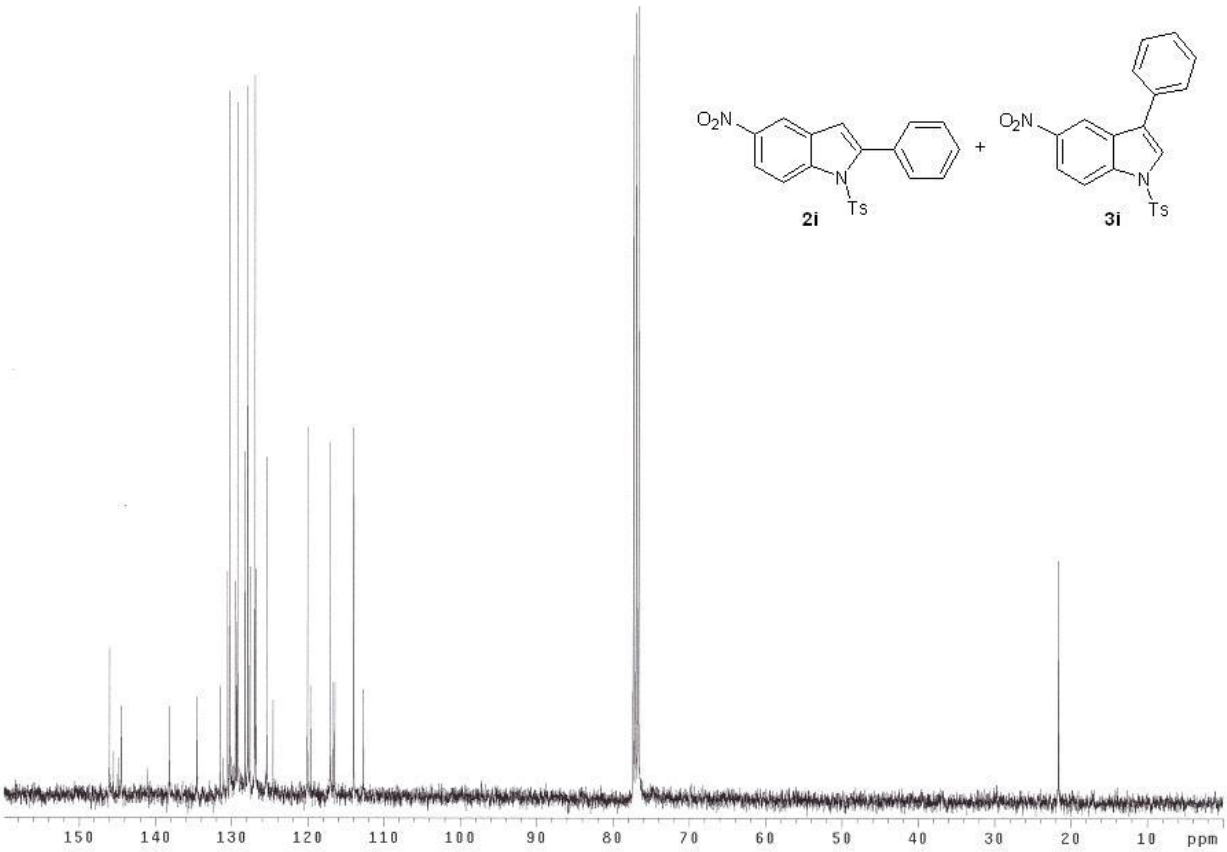
_N_-Ts-5-Chloro-2-phenylindole (2) & _N_-Ts-5-Chloro-3-phenylindole (3)



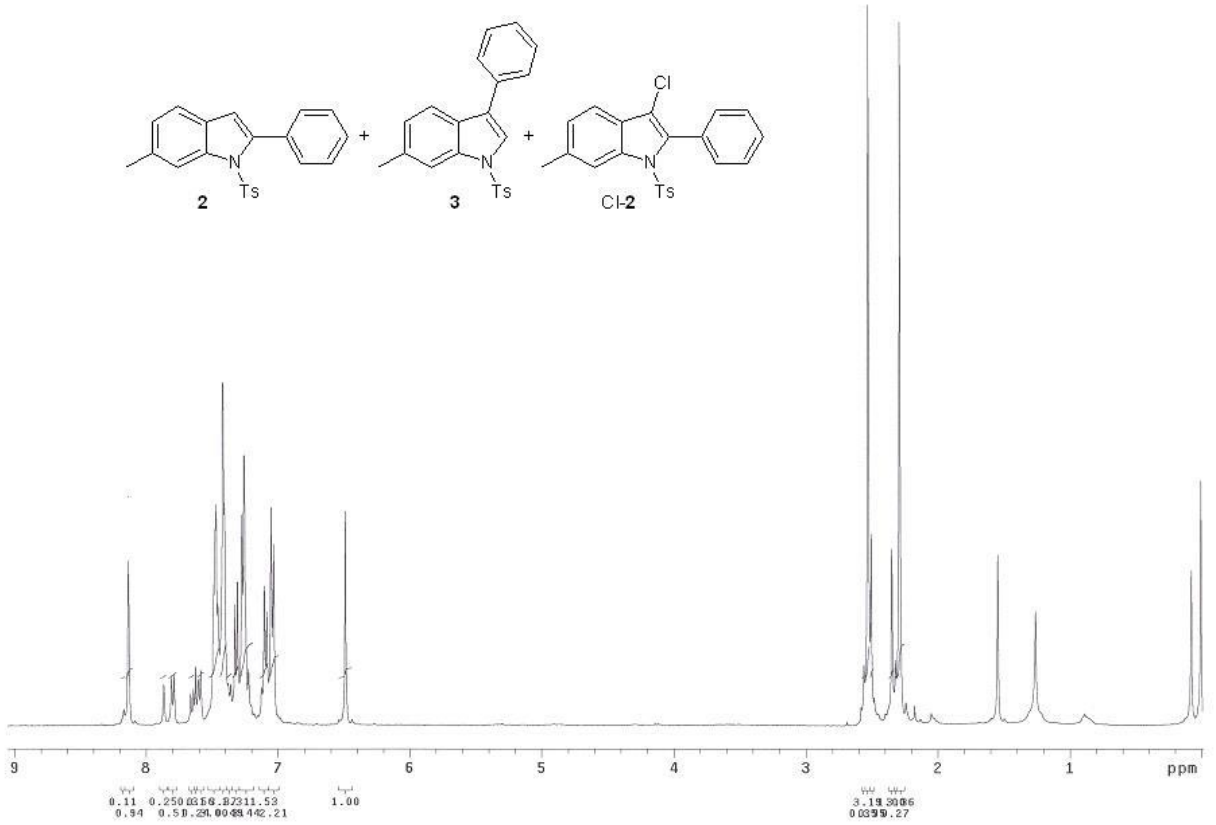


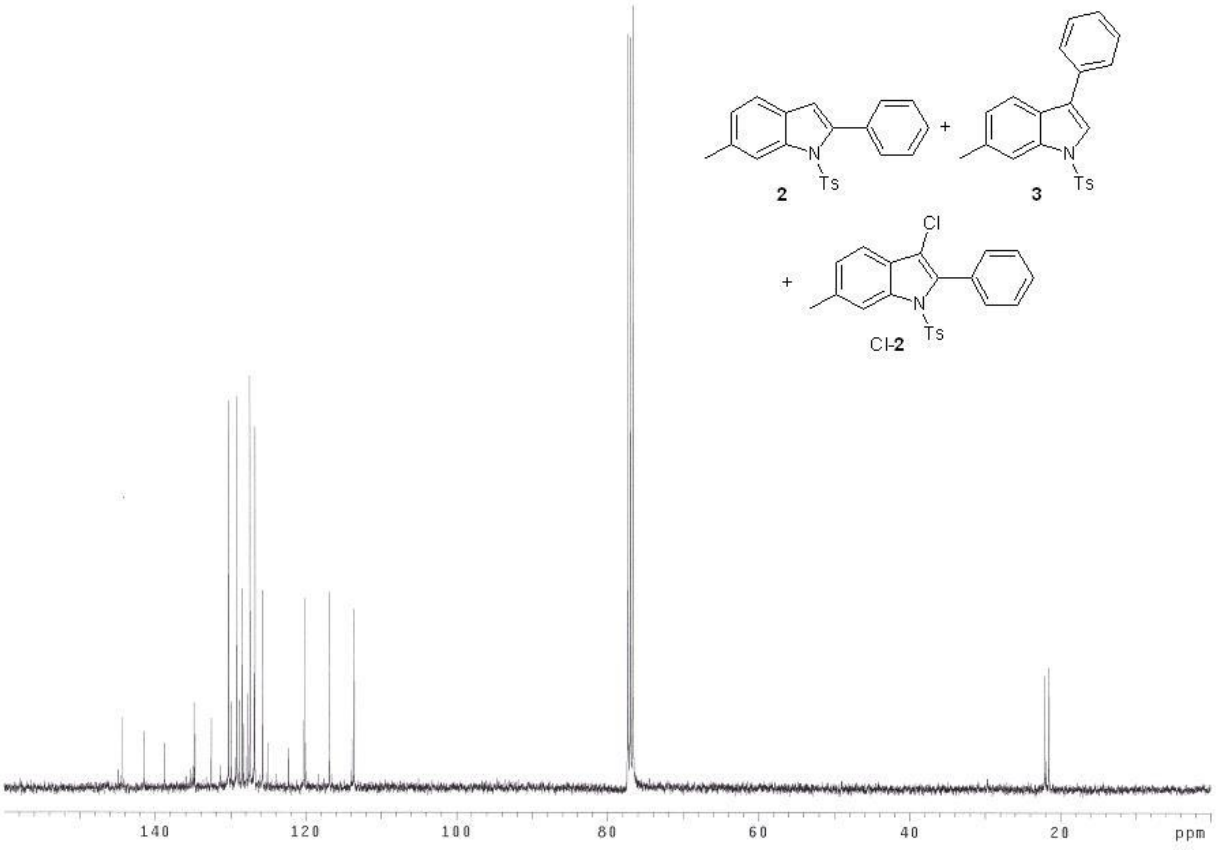
_N_-Ts-5-Nitro-2-phenylindole (2i) & _N_-Ts-5-Nitro-3-phenylindole (3i)



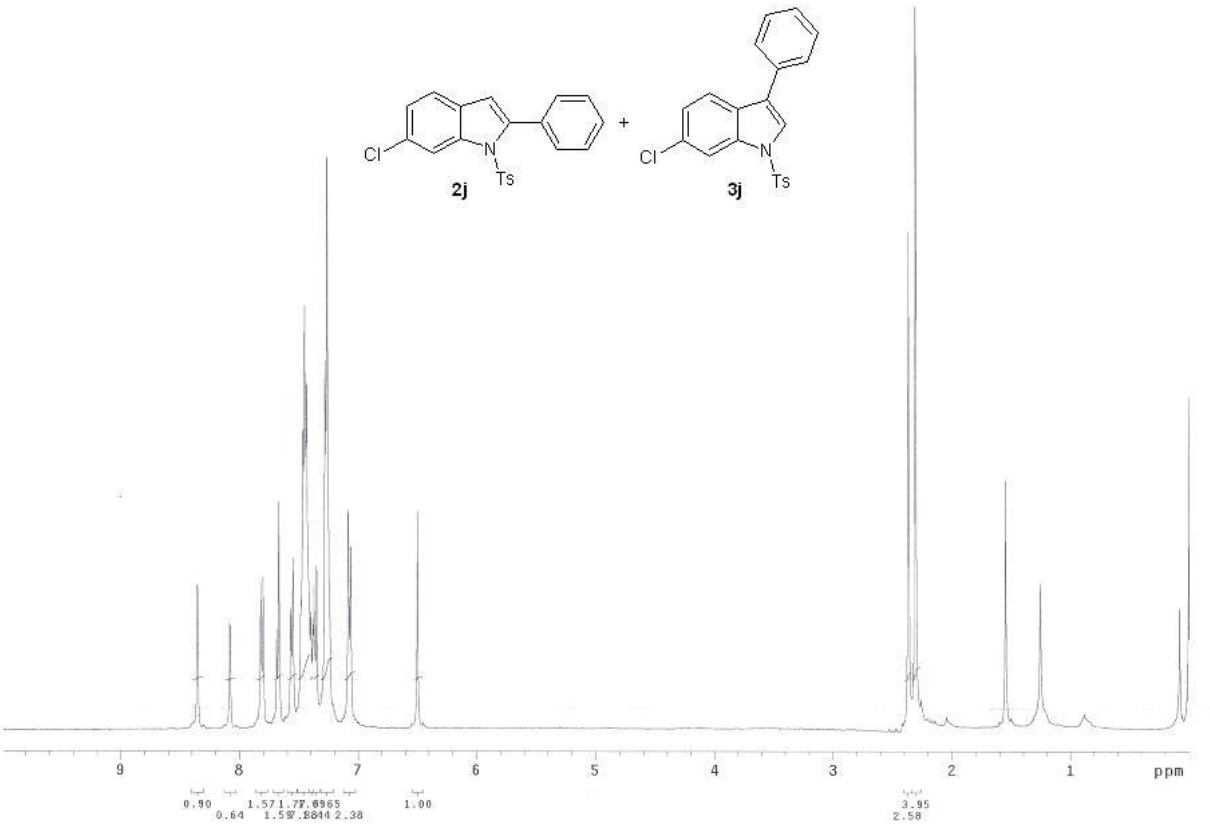


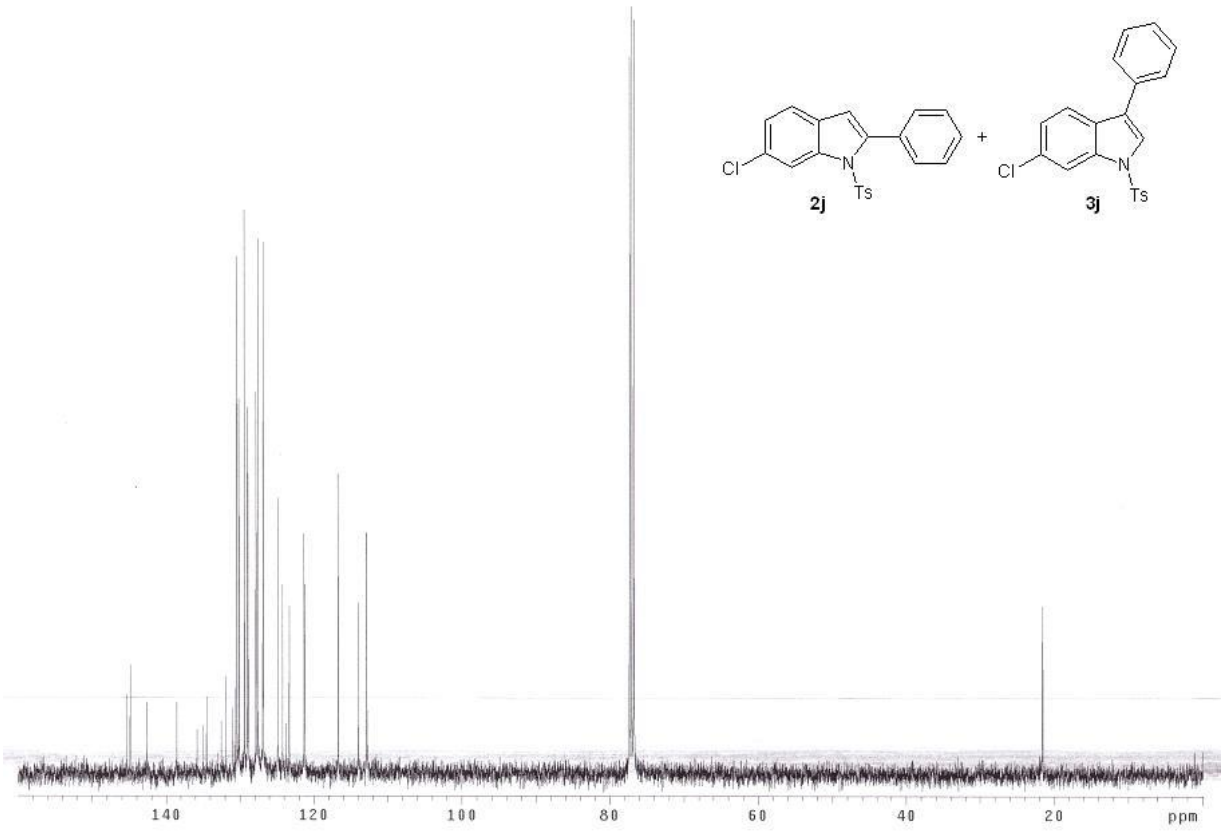
***N*-Ts-6-Methyl-2-phenylindole (2), *N*-Ts-6-Methyl-3-phenylindole (3), & *N*-Ts-3-Chloro-6-methyl-2-phenylindole (Cl-2)**



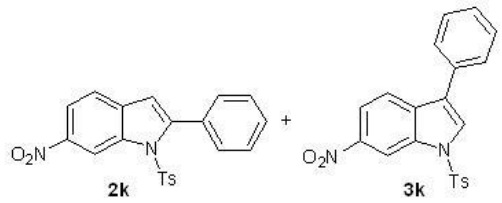


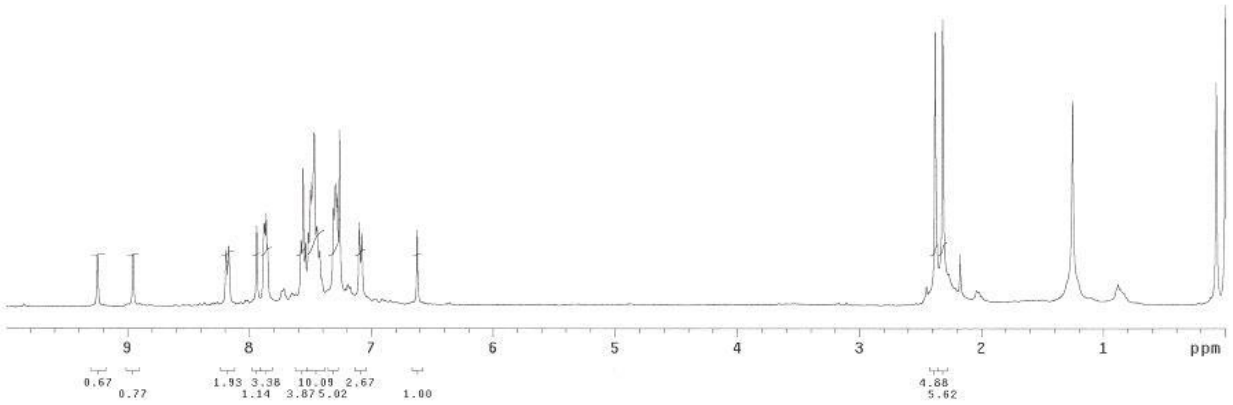
***N*-Ts-6-Chloro-2-phenylindole (2j) & *N*-Ts-6-Chloro-3-phenylindole (3j)**

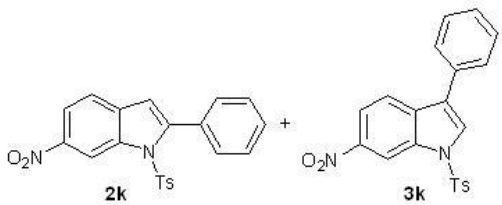




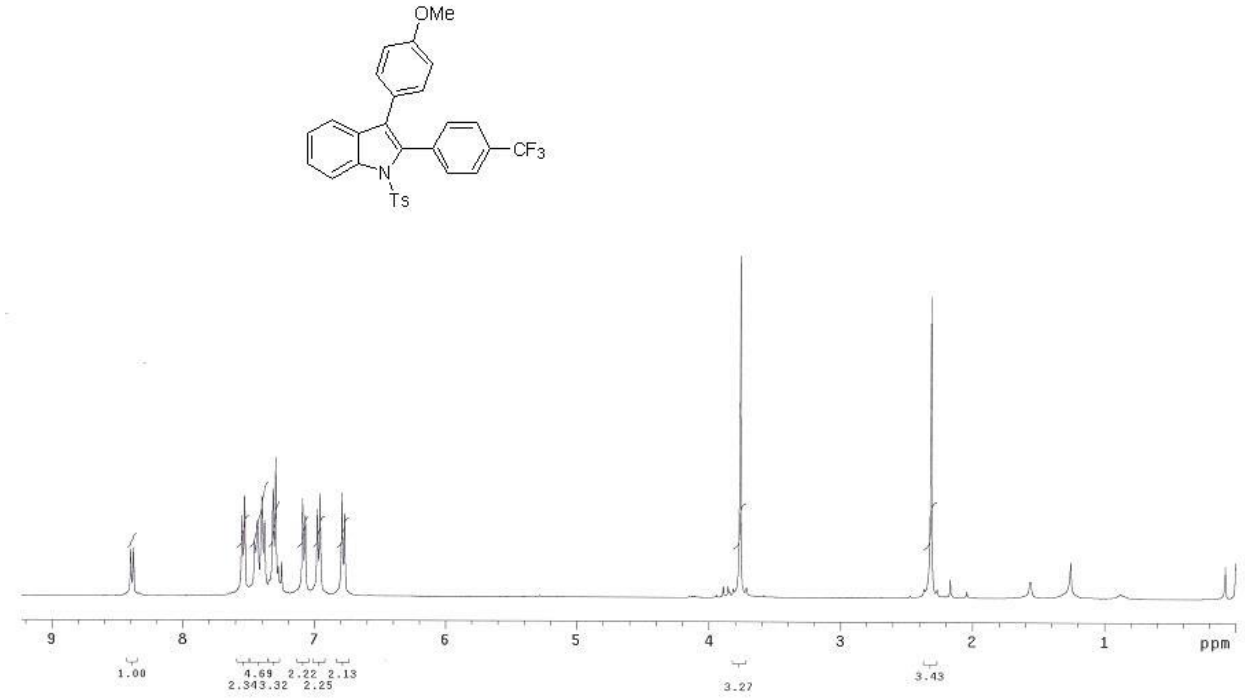
_N_-Ts-6-Nitro-2-phenylindole (2k) & _N_-Ts-6-Nitro-3-phenylindole (3k)

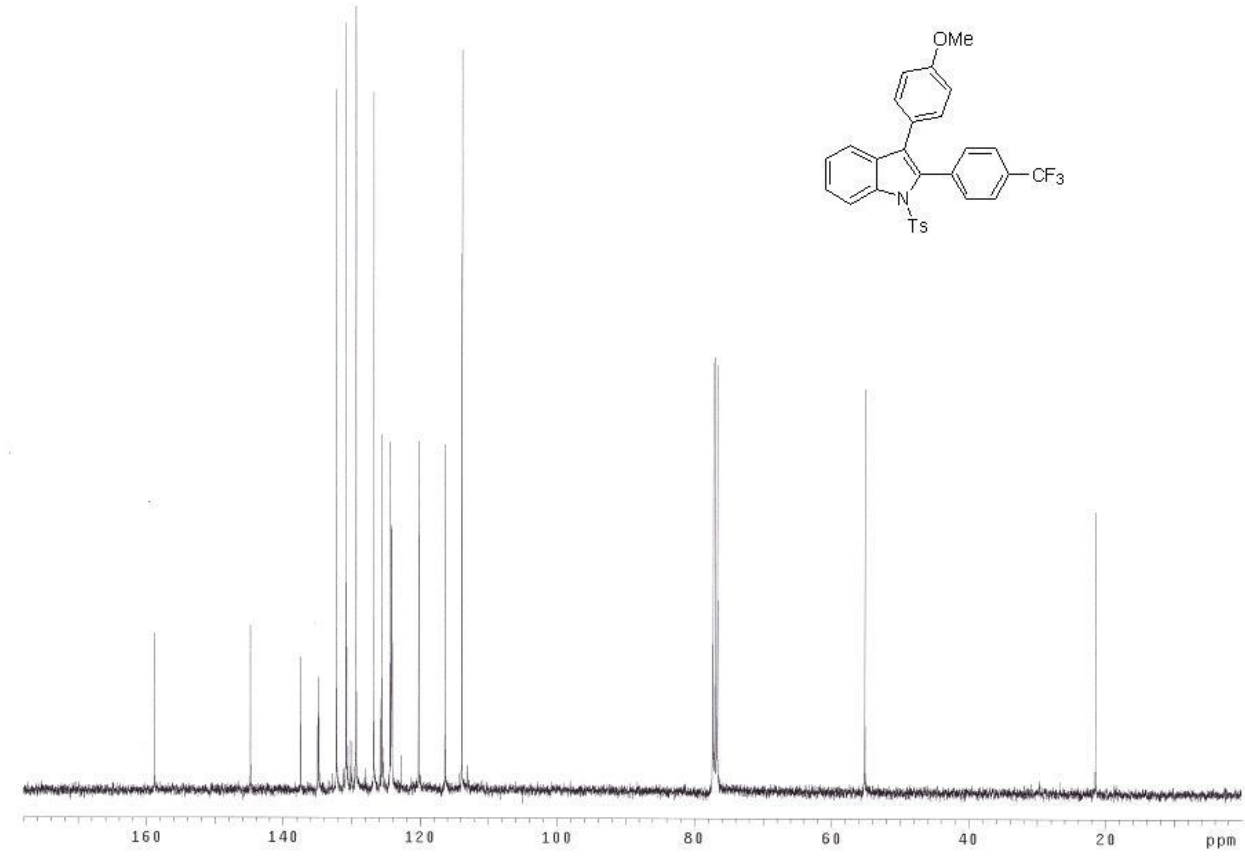




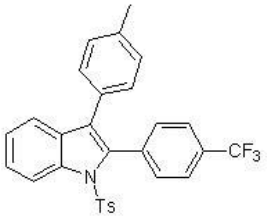


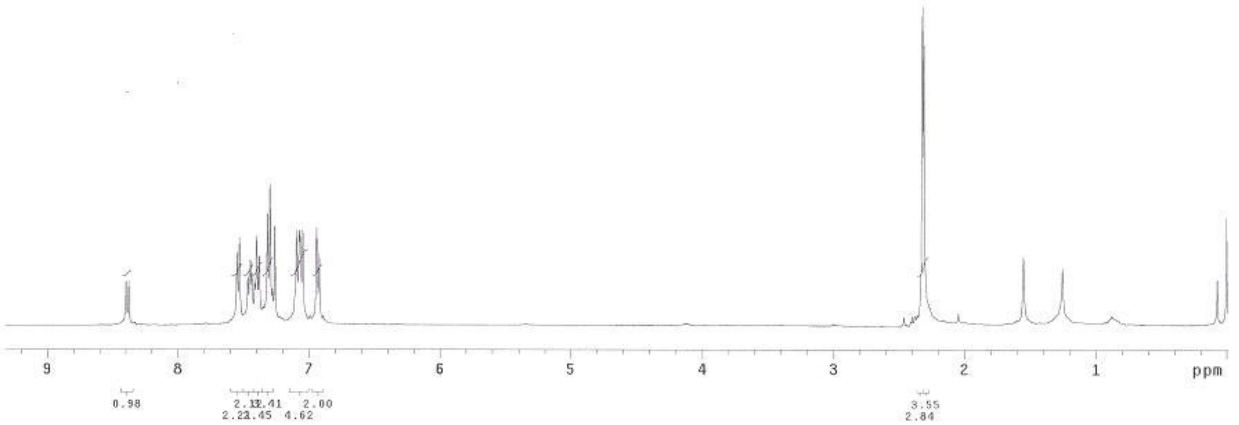
***N*-Ts-3-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)indole (3l)**

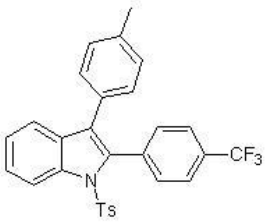


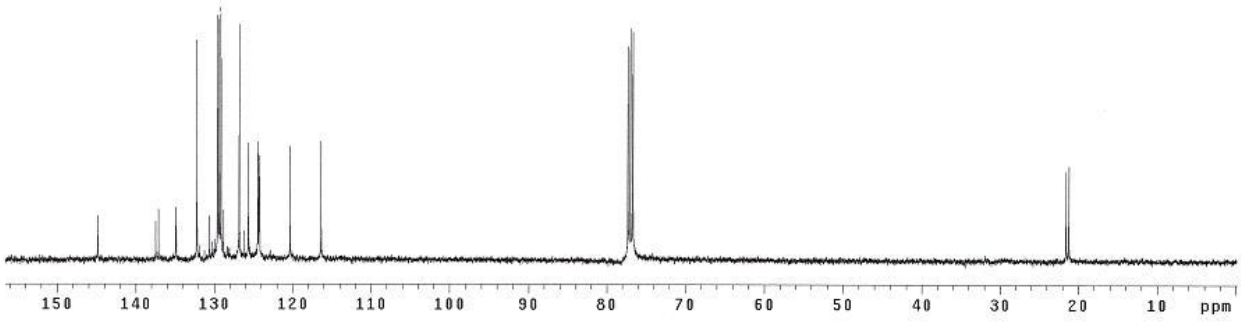


***N*-Ts-3-*p*-Tolyl-2-(4-(trifluoromethyl)phenyl)indole (3m)**

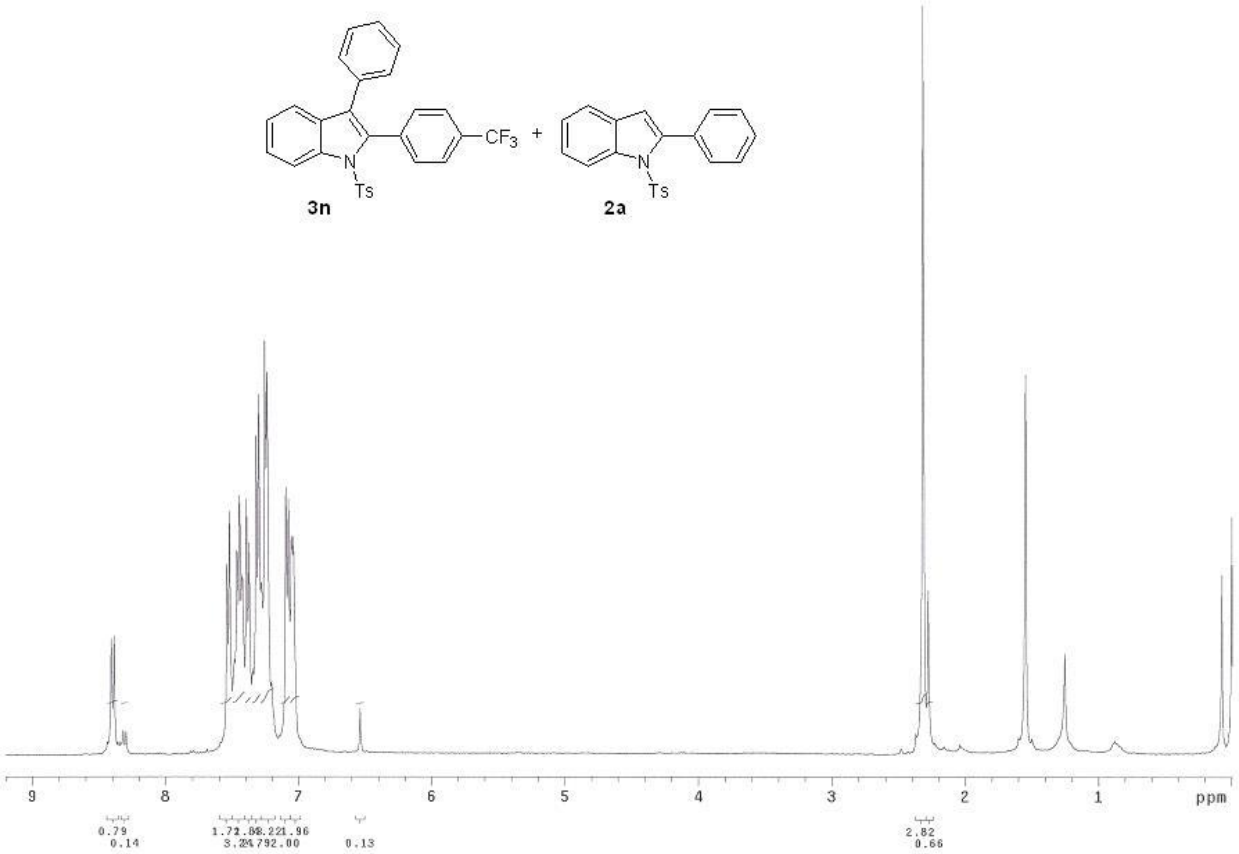


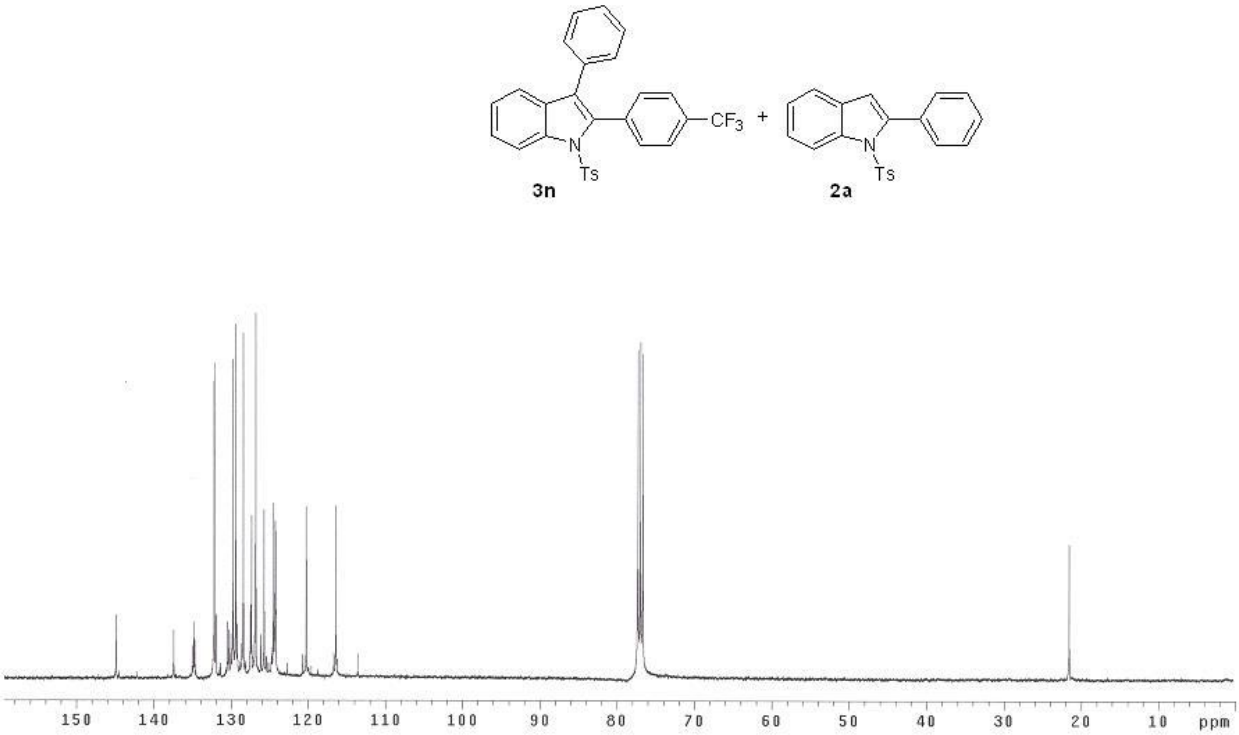




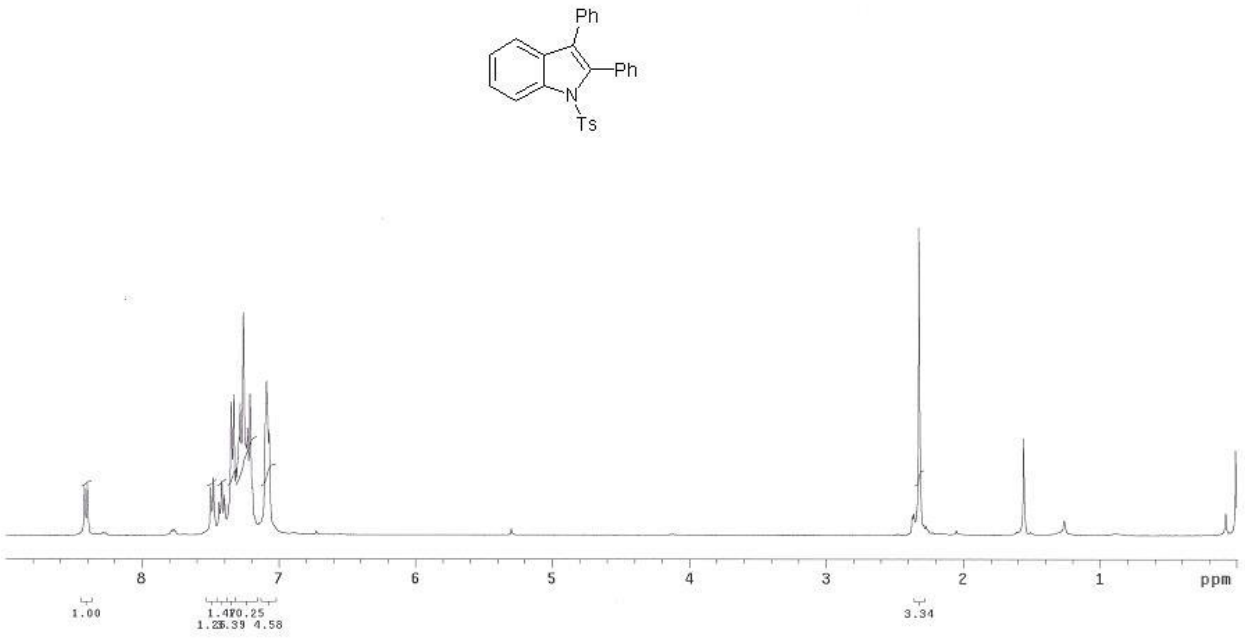


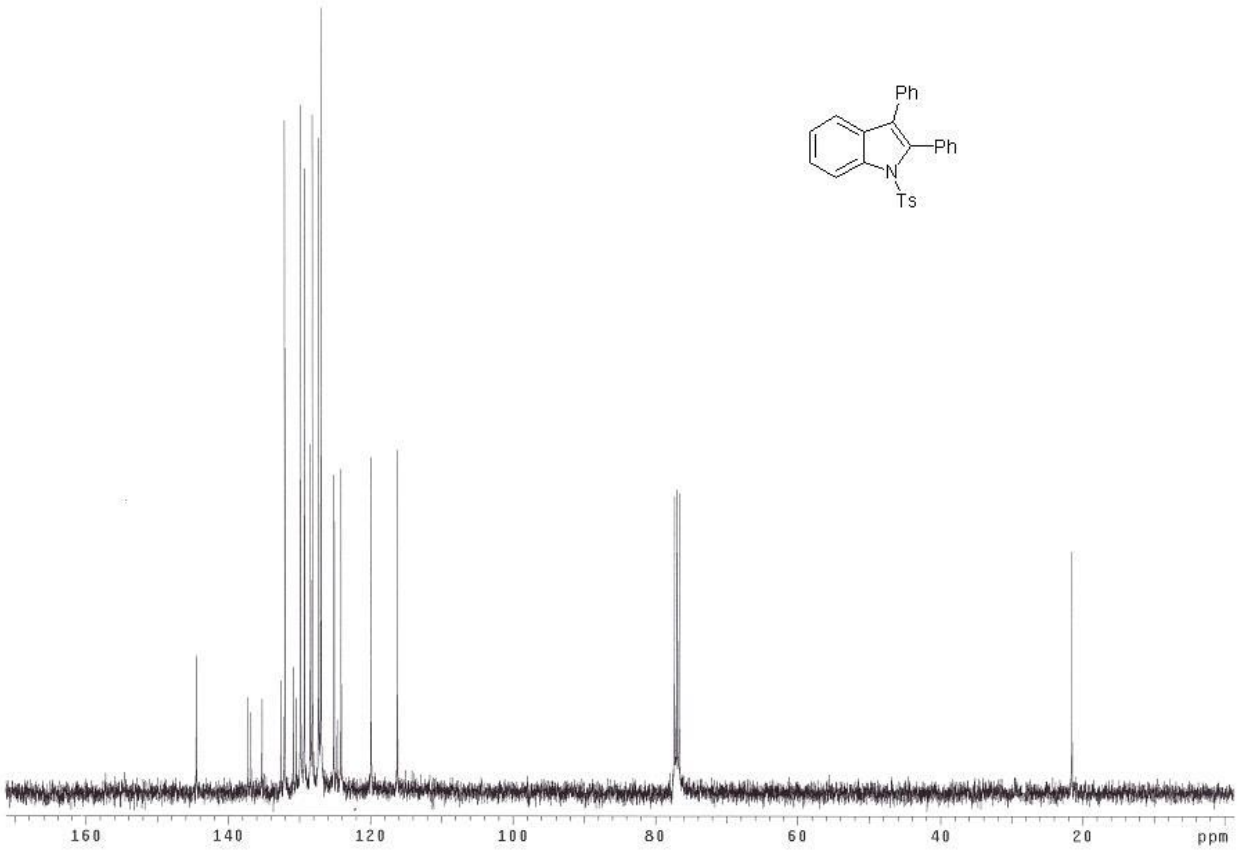
_N_-Ts-3-Phenyl-2-(4-(trifluoromethyl)phenyl)indole (3n) & _N_-Ts-2-Phenylindole (2a)



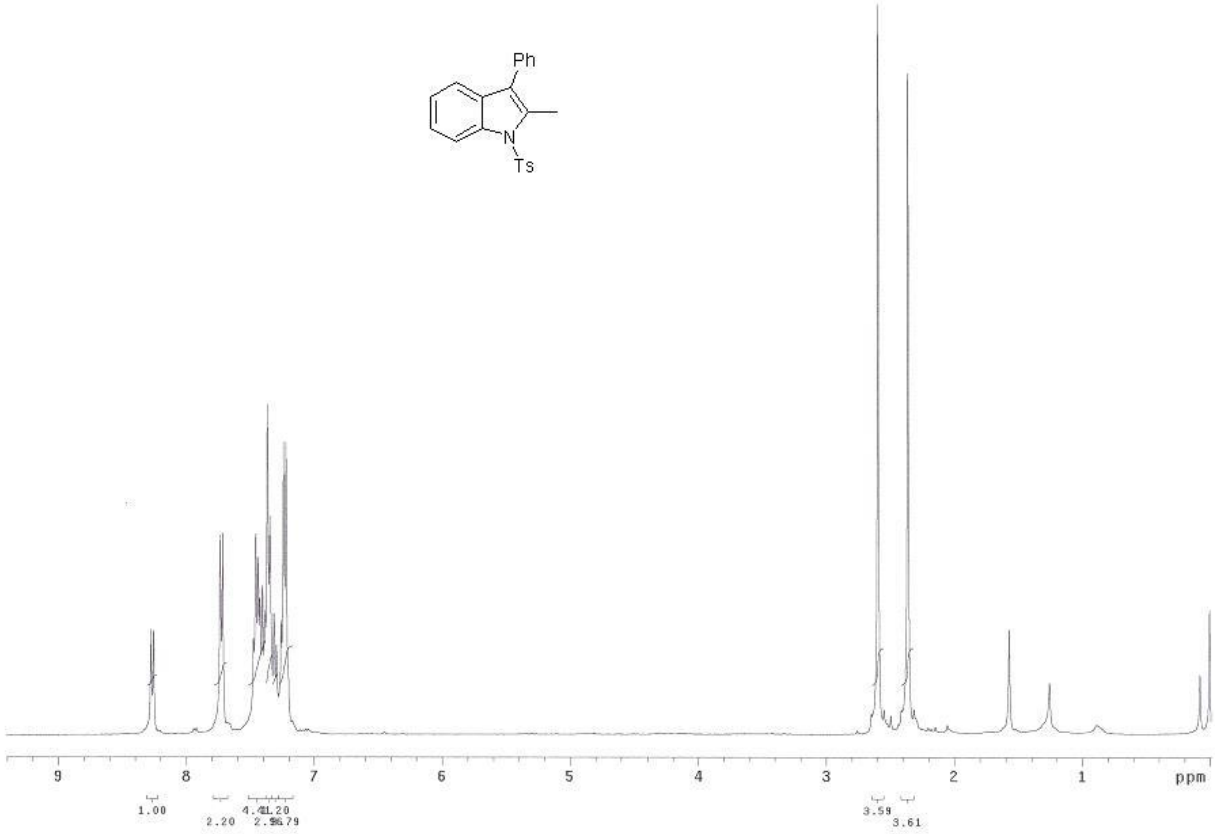


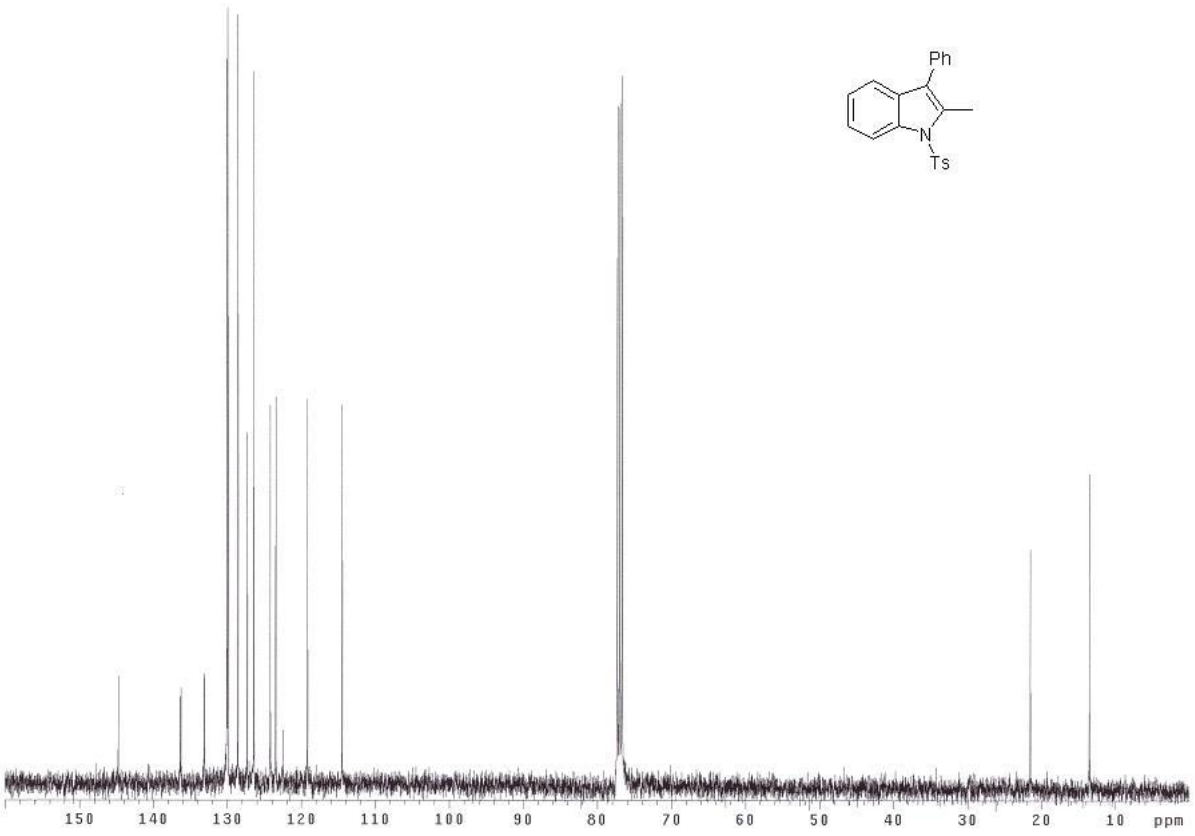
***N*-Ts-2,3-Diphenylindole**



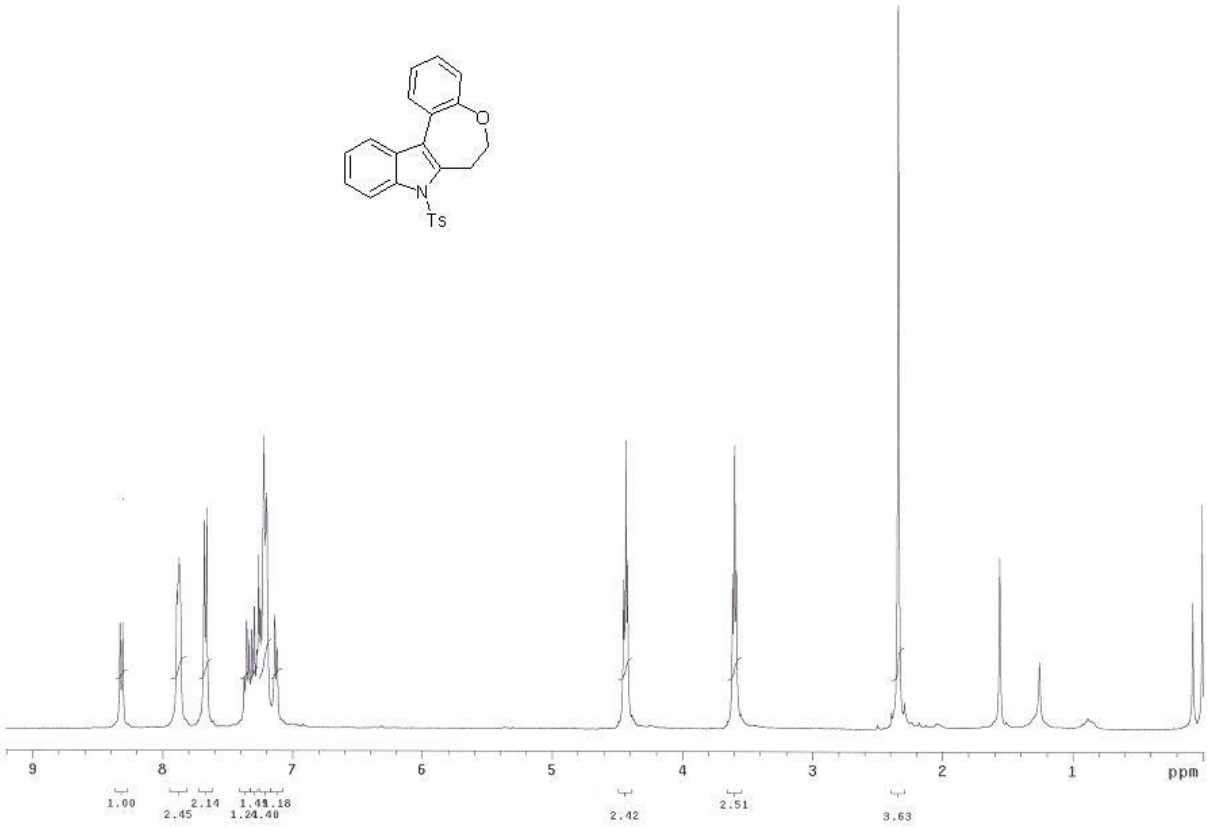


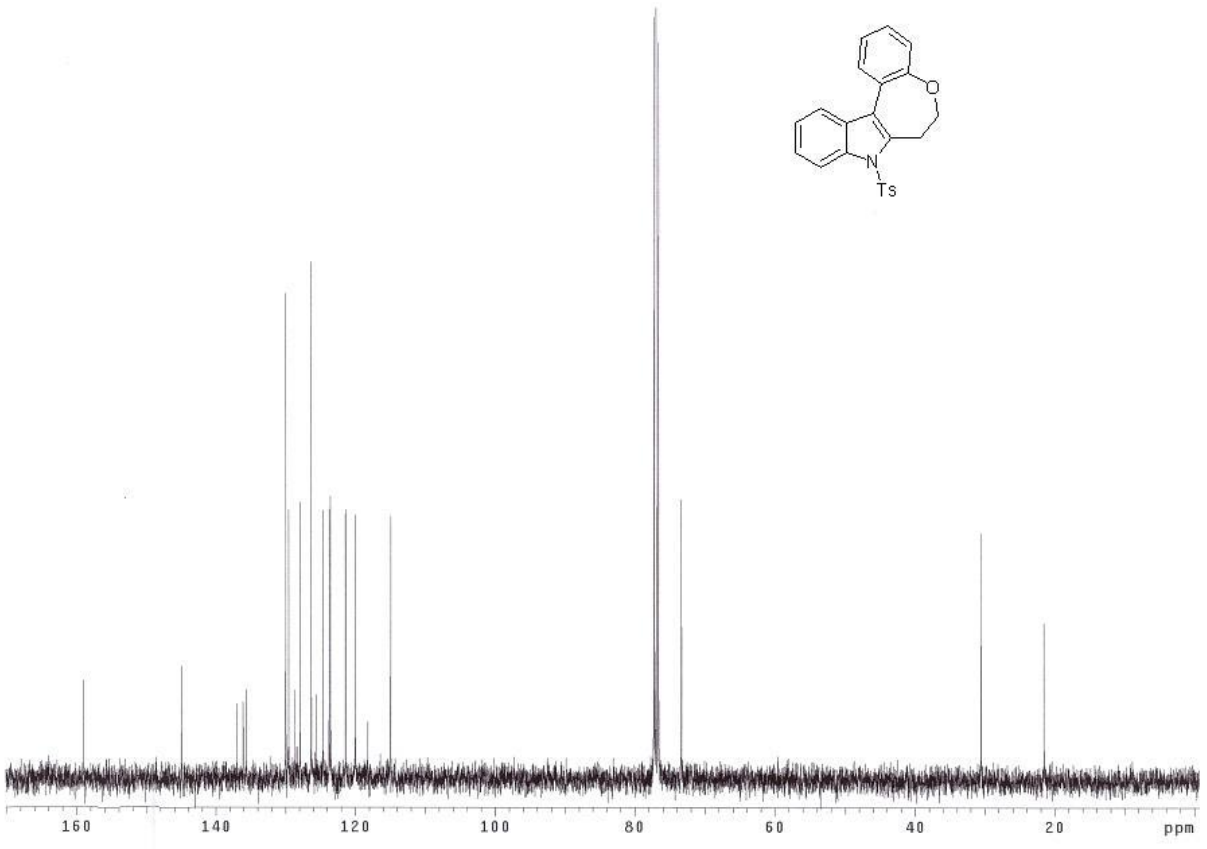
***N*-Ts-2-Methyl-3-phenylindole (3o)**



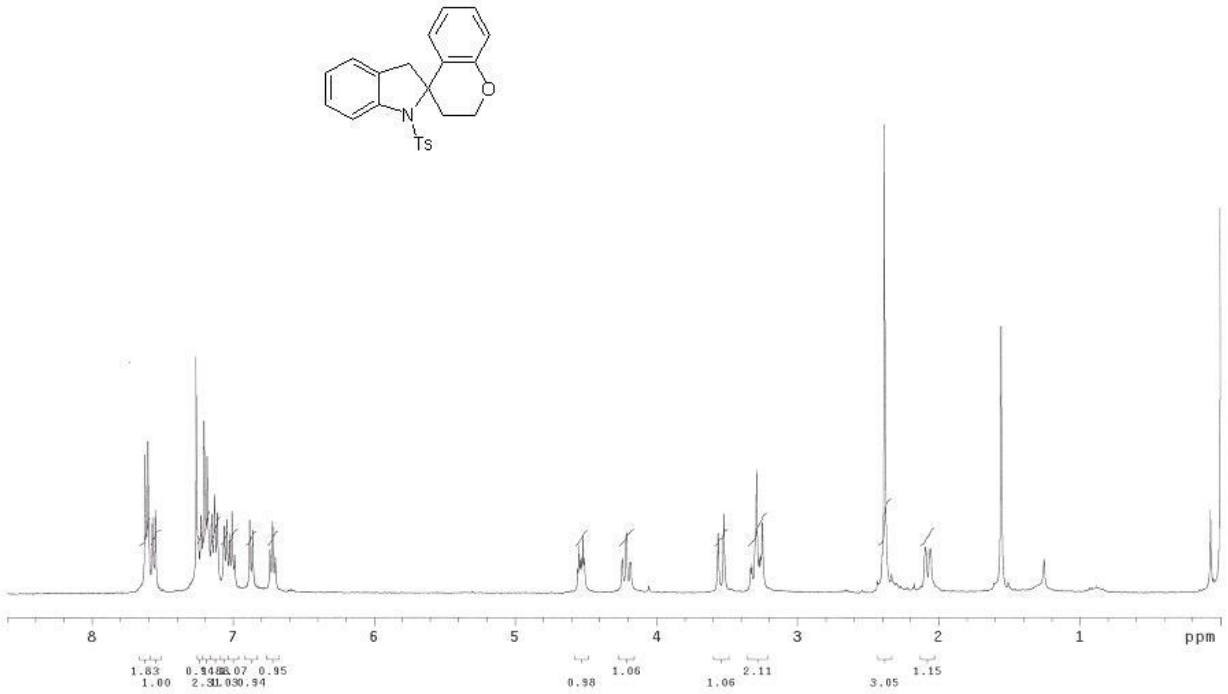


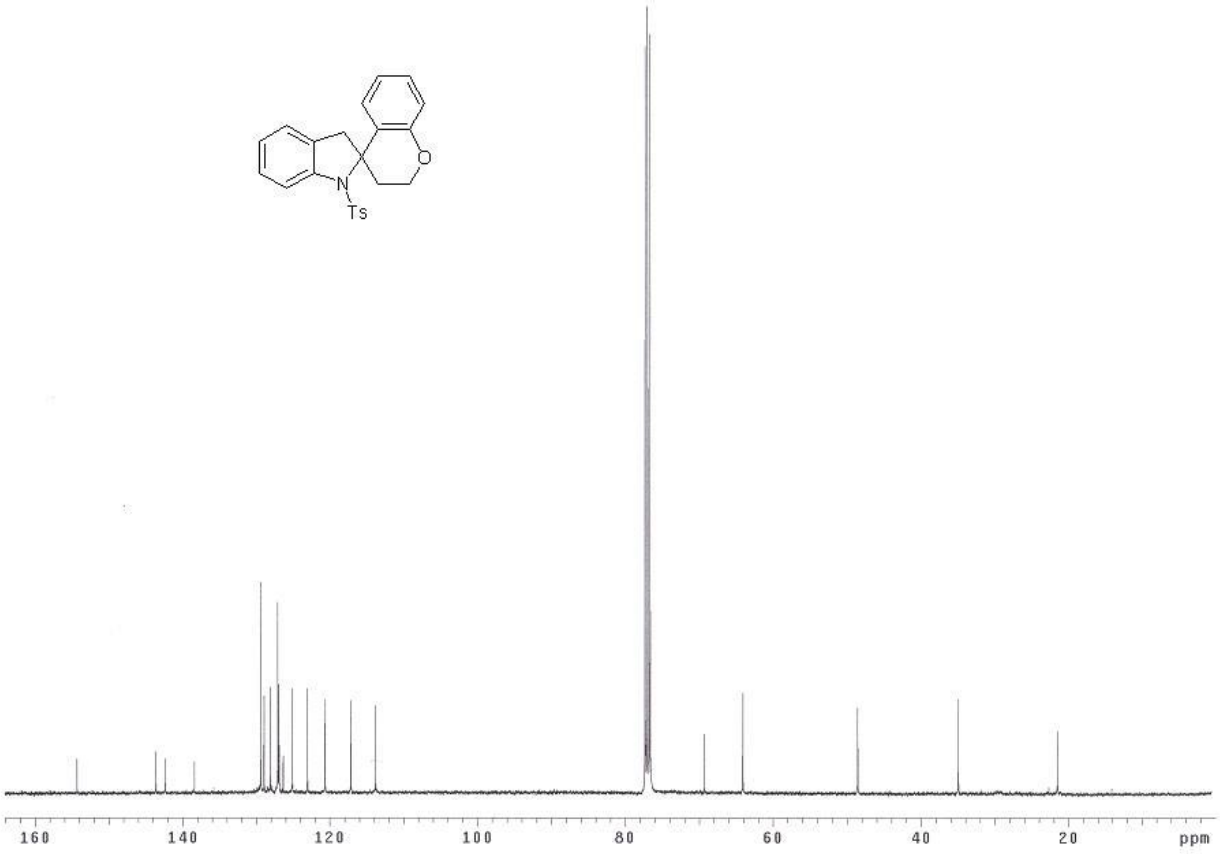
***N*-Ts-7,8-Dihydro-6*H*-benzo[6,7]oxepino[4,5-*b*]indole (3p)**





_N_-Ts-Spiro(chroman-4,2'-indoline) (4)



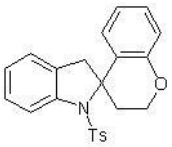


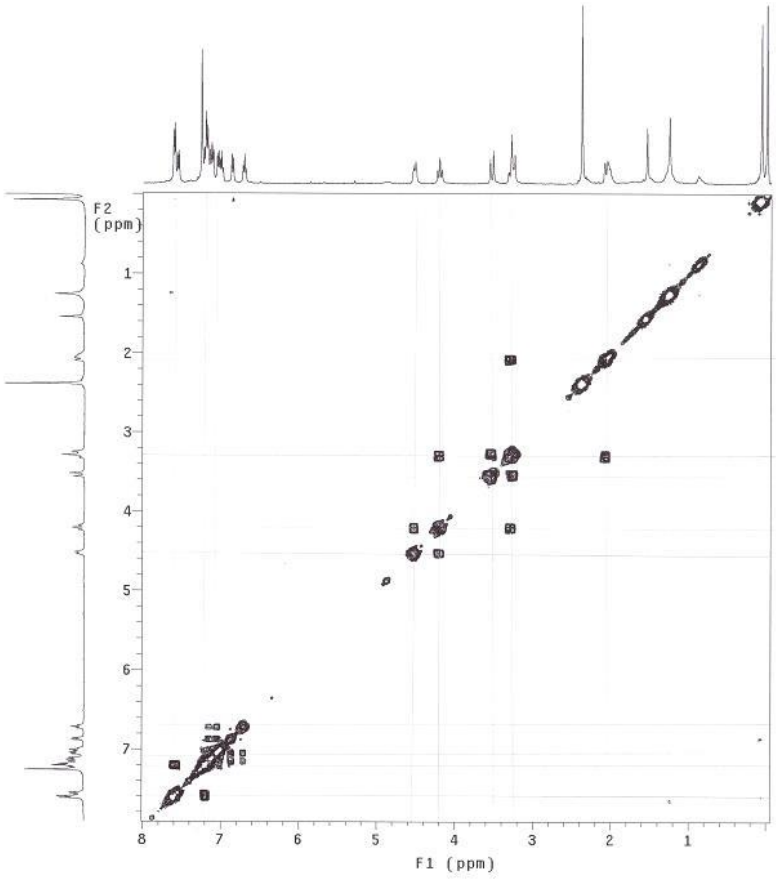
DEUTERIUM OBSERVE
STANDARD PARAMETERS

File: home/vnmr8/13.05-14.03/R222-2-cosy.fid

Pulse Sequence: COSY
 Solvent: cdcl3
 Ambient temperature
Operator: vnmr8
File: R222-2-cosy
Mercury-400BB "mercury"

 Relax. delay 1.301 sec
 Acq. time 0.160 sec
 Width 6398.0 Hz
 2D Width 6398.0 Hz
 2 repetitions
 128 increments
OBSERVE H1, 399.8053629 MHz
DATA PROCESSING
 Sine bell 0.080 sec
F1 DATA PROCESSING
 Sine bell 0.040 sec
FT size 2048 x 2048
Total time 7 min, 40 sec



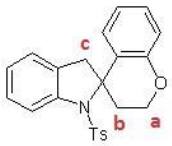


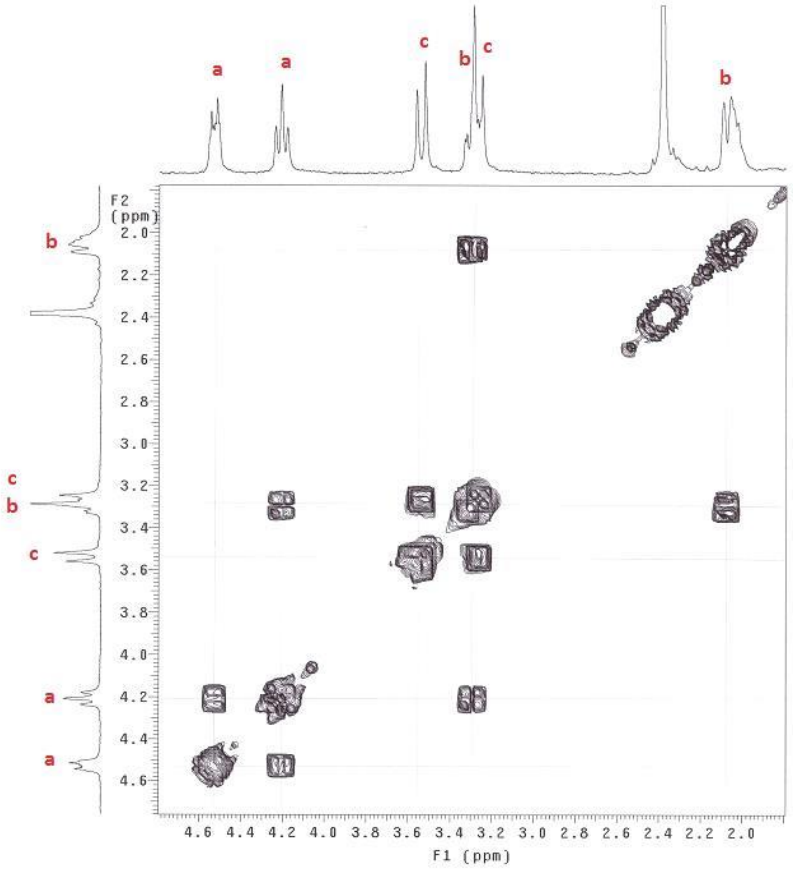
DEUTERIUM OBSERVE
STANDARD PARAMETERS

File: home/vnmr8/13.05-14.03/R222-2-cosy.fid

Pulse Sequence: COSY
 Solvent: cdcl3
 Ambient temperature
Operator: vnmr8
File: R222-2-cosy
Mercury-400BB "mercury"

 Relax. delay 1.301 sec
 Acq. time 0.160 sec
 Width 6398.0 Hz
 2D Width 6398.0 Hz
 2 repetitions
 128 increments
OBSERVE H1, 399.8053629 MHz
DATA PROCESSING
 Sine bell 0.080 sec
F1 DATA PROCESSING
 Sine bell 0.040 sec
FT size 2048 x 2048
Total time 7 min, 40 sec



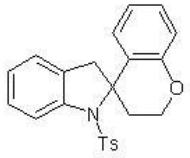


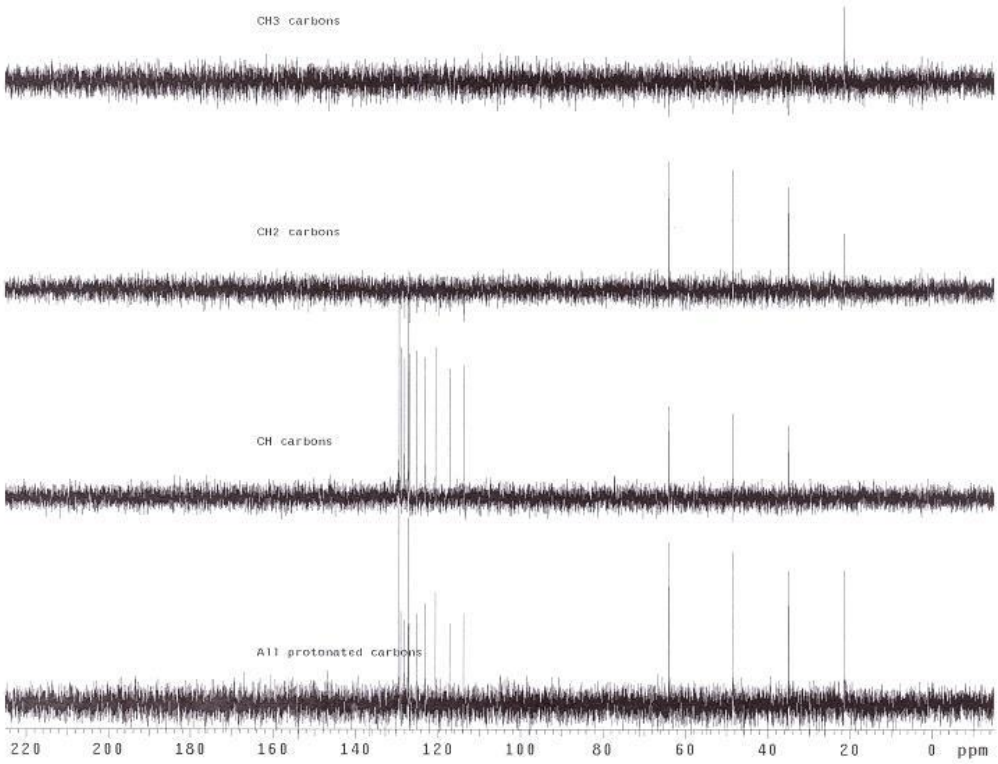
Heteronuclear polarization transfer experiment

File: home/vnmr8/R222-2-dept.fid

Pulse Sequence: DEPT
 Solvent: cdcl3
 Ambient temperature
Operator: vnmr8
File: R222-2-dept
Mercury-400BB "mercury"

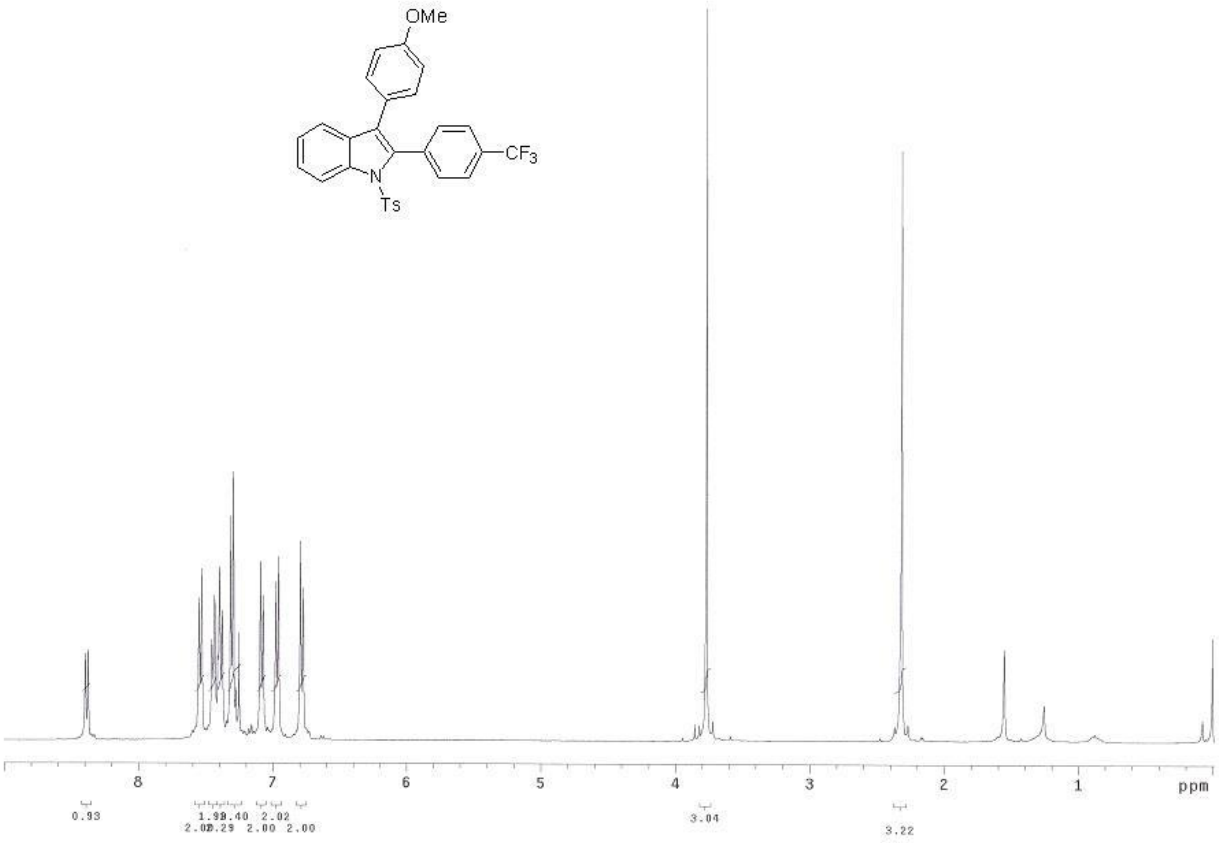
 Relax. delay 1.500 sec
 Pulse 90.0 degrees
 Acq. time 1.000 sec
 Width 24154.6 Hz
 200 repetitions
OBSERVE C13, 100.5311385 MHz
DECOUPLE H1, 399.8073989 MHz
 Power 46 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 30 sec

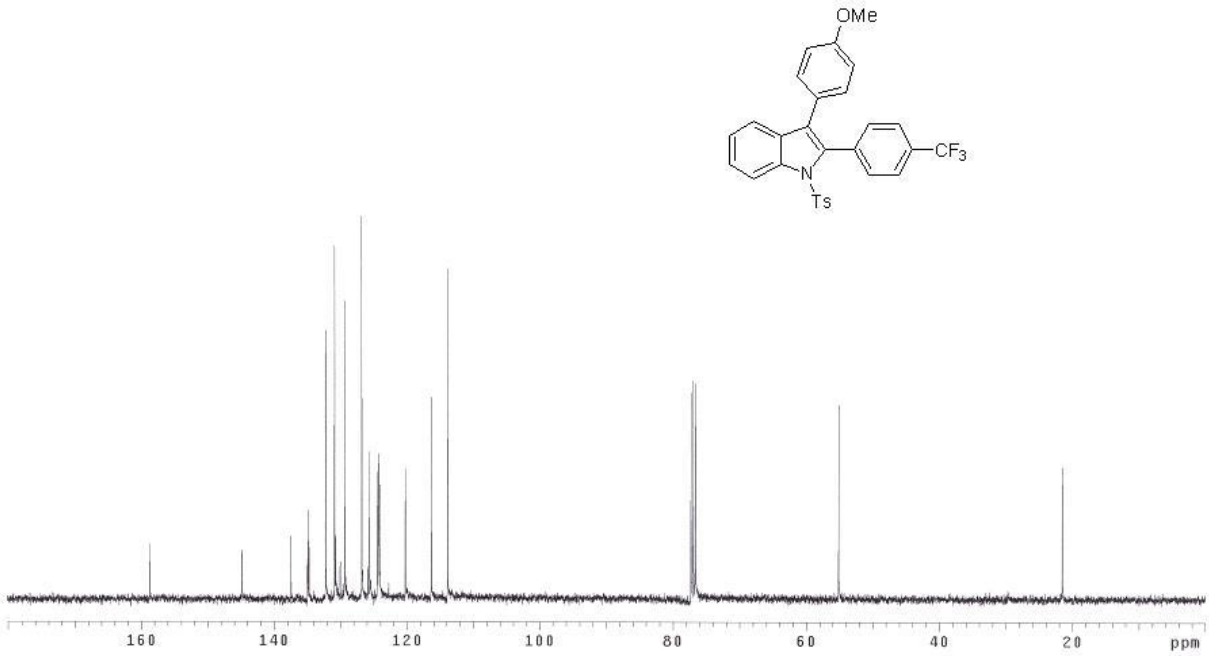




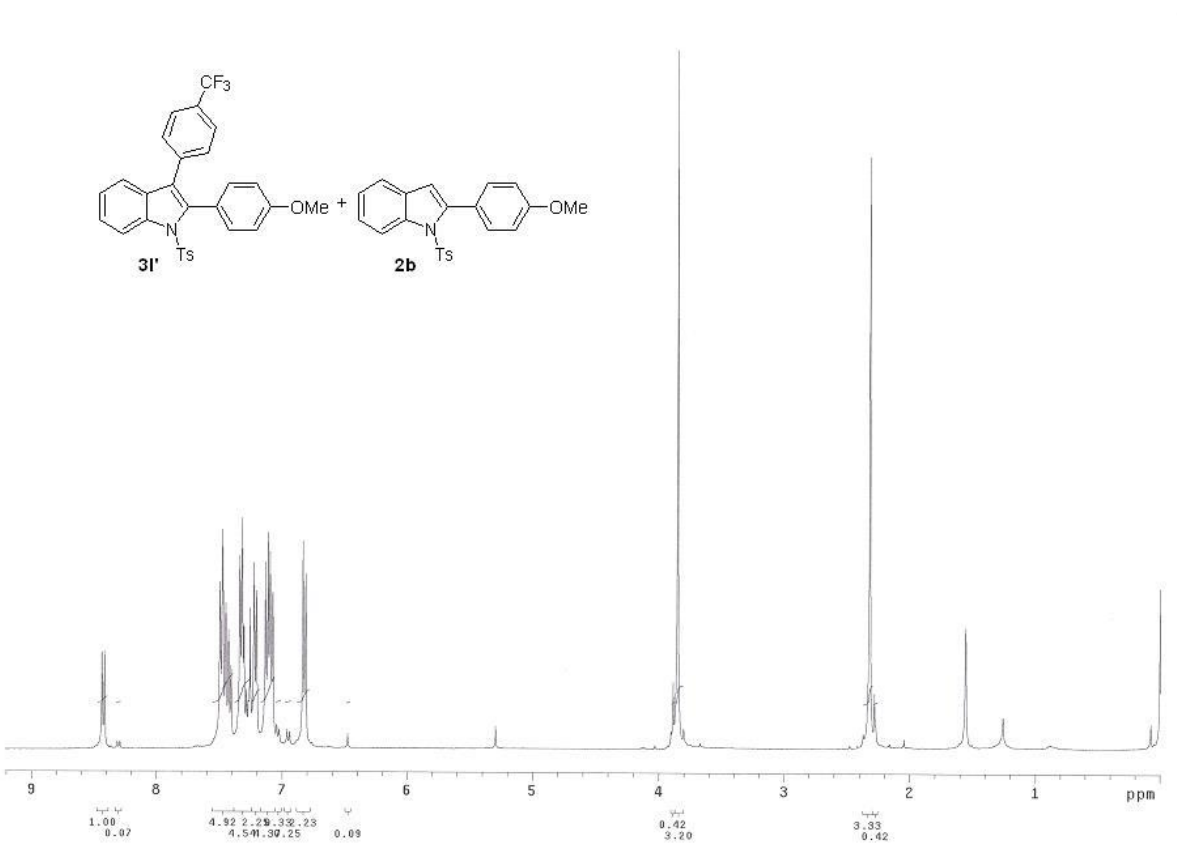
Authentic Samples of 2-Aryl-3-aryl'-substituted Indoles (3 and 3')

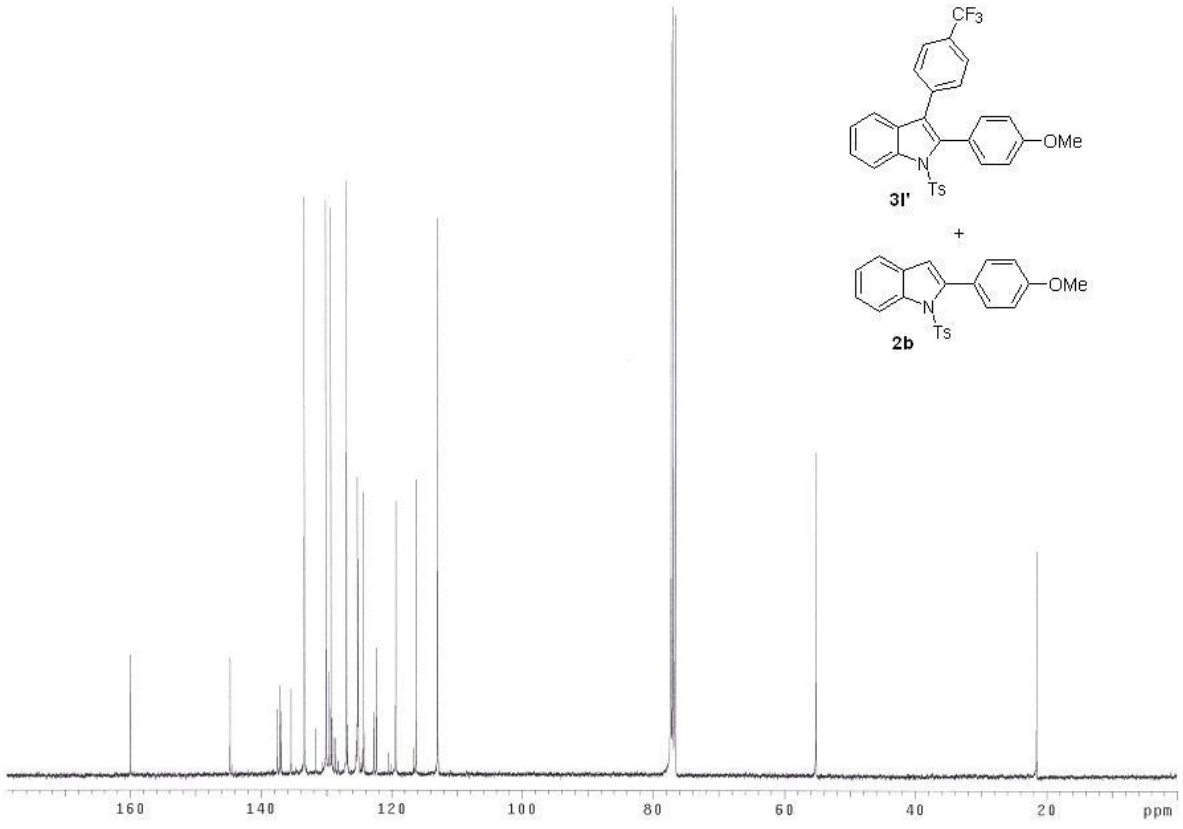
N-Ts-3-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)indole (3l)



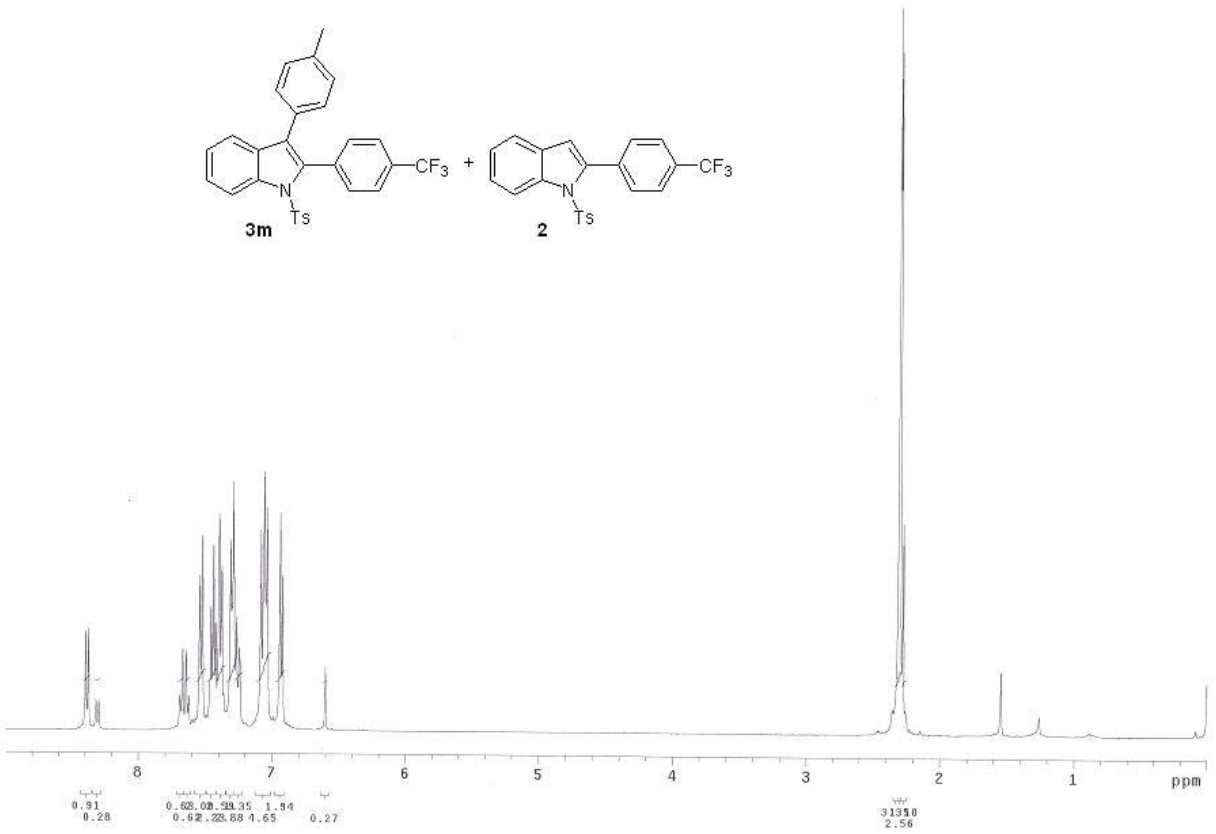


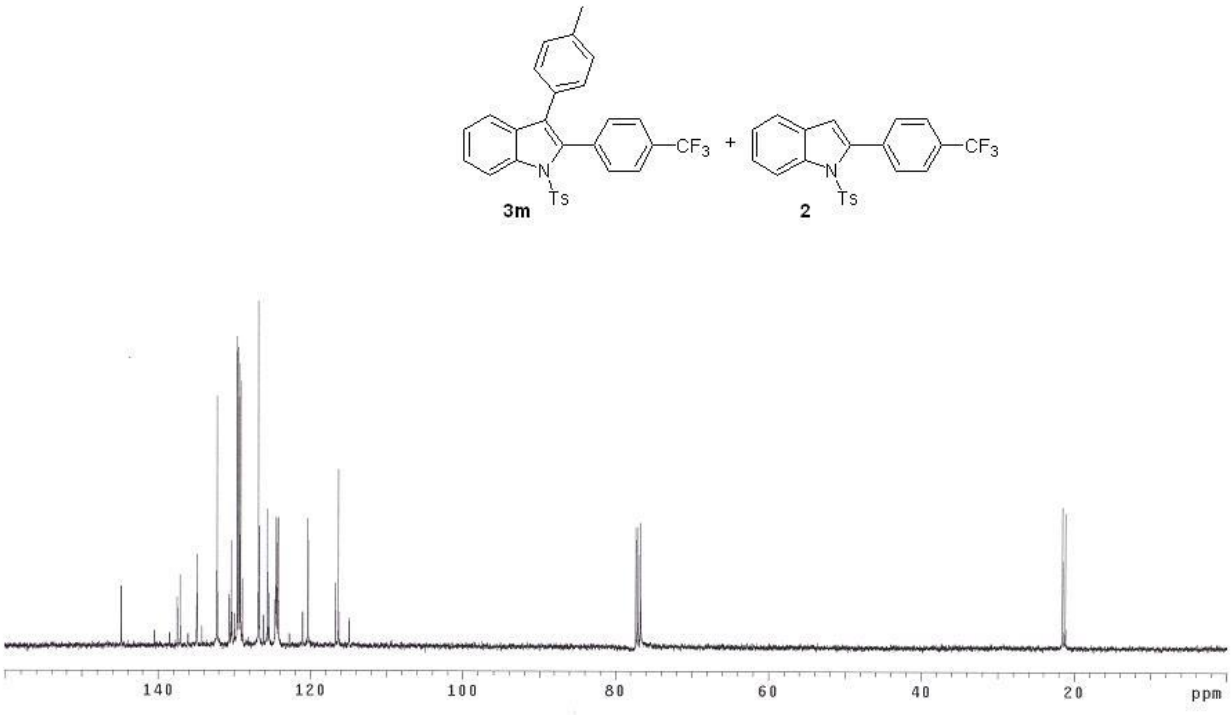
***N*-Ts-2-(4-Methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)indole (3l') & *N*-Ts-2-(4-Methoxyphenyl)indole (2b)**



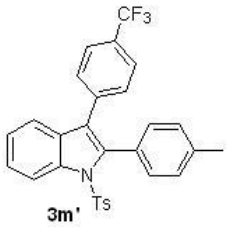


***N*-Ts-3-*p*-Tolyl-2-(4-(trifluoromethyl)phenyl)indole (3m) & *N*-Ts-2-(4-(Trifluoromethyl)phenyl)indole (2)**

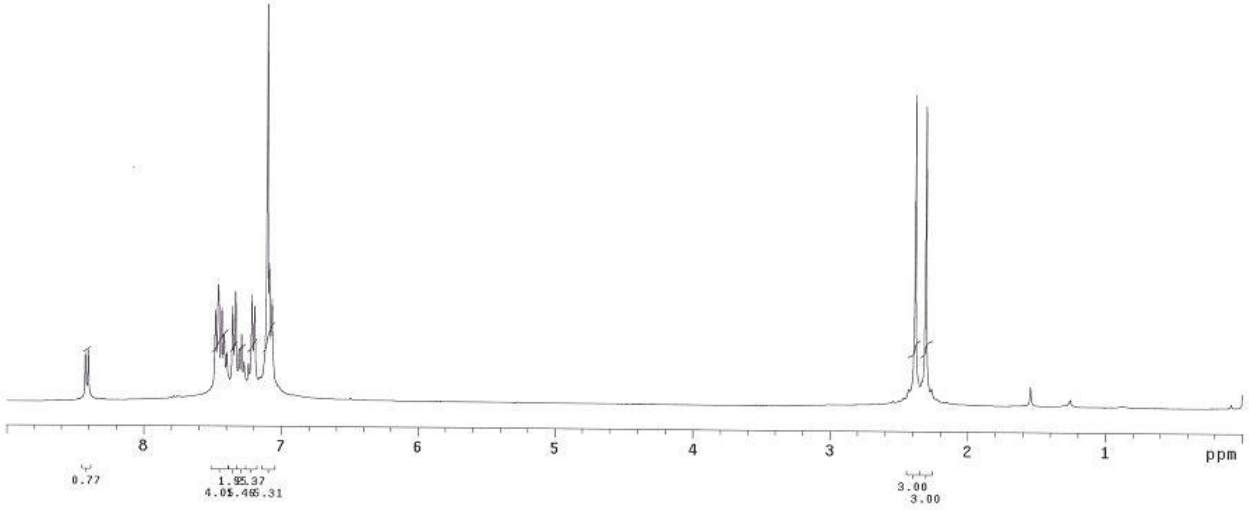


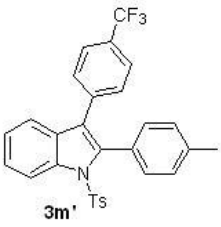


***N*-Ts-2-*p*-Tolyl-3-(4-(trifluoromethyl)phenyl)indole (3m')**

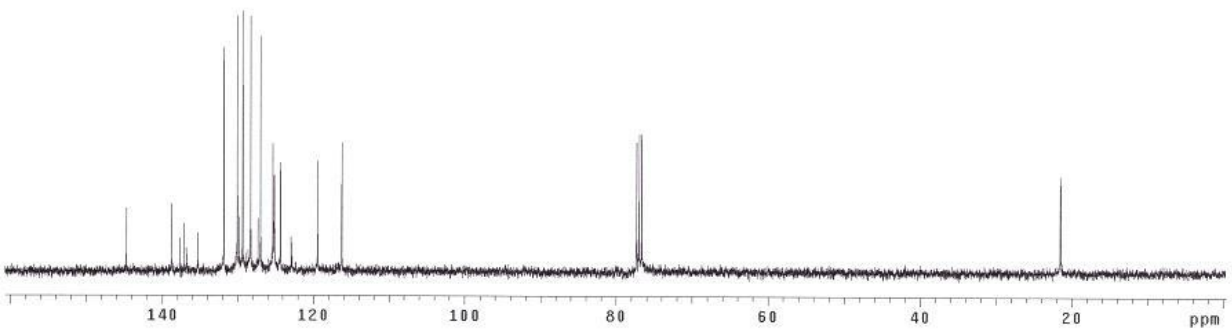


3m'





3m'



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