

## **Electronic Supplementary Information (ESI)**

### **Facile synthesis of 2-arylmethylindoles and 2-vinyl indoles through palladium-catalyzed heteroannulations of 2-(2-propynyl)aniline and 2-(2-propynyl)tosylanilide**

Bimolendu Das, Priyanka Kundu, and Chinmay Chowdhury\*

Chemistry Division, Indian Institute of Chemical Biology (CSIR), 4, Raja S. C. Mullick Road, Kolkata-700032, India  
*E-mail: chinmay@iicb.res.in*

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## 1. General:

All solvents were distilled prior to use. Petroleum ether refers to fraction boiling in the range 60-80 °C. DMF and DCM were dried over CaH<sub>2</sub>, distilled, and stored over 3 Å molecular sieves in sealed container. THF was distilled over sodium and benzophenone. All the reactions were carried out under argon atmosphere and anhydrous conditions unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on Silica gel 60 F<sub>254</sub> aluminium TLC sheets. Visualization of the developed chromatogram was performed by UV absorbance or iodine exposure. For purification, column chromatography was performed using 60-120 or 100-200 mesh silica gel.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 300, 500 or 600 MHz spectrometer using tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are given from TMS (δ = 0.00) in parts per million (ppm) with reference to the residual nuclei of the deuterated solvent used [CDCl<sub>3</sub>: <sup>1</sup>H NMR δ = 7.26 ppm (s); <sup>13</sup>C NMR δ = 77.0 ppm]. Coupling constants (*J*) are expressed in hertz (Hz) and spin multiplicities are given as s (singlet), d (doublet), dd (double doublet), dt (double triplet), t (triplet), m (multiplet), and br (broad). All <sup>13</sup>C NMR spectra were obtained with complete proton decoupling. Mass spectra were performed using ESI-TOF, EI or FAB ionization mode. Infrared spectra were obtained on FT/IR-4200 infrared spectrometer as neat sample or as KBr pellet.

## 2. X-Ray crystallographic informations of product **9c**:

Single crystals of products **9c** were obtained through slow evaporation (at room temperature) of a solution in dichloromethane-petroleum ether. A single crystal of **9c** was attached to a glass fiber with epoxy glue and transferred to a Brüker SHELXL-97 X-ray diffractometer, equipped with a graphite-monochromator. Diffraction data of product **9c** was measured with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 296(2)K. Computing cell refinement and data reduction was carried out at APEX 2 Brüker Kappa. The structure was solved by direct methods using the SHELXS-97 program.<sup>1</sup> Refinements were carried out with a full matrix least squares method against  $F^2$  using SHELXL-97.<sup>2</sup> The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The ORTEP diagram (Figure S1) and some important crystallographic data (Table S1) of compound **9c** are given below.

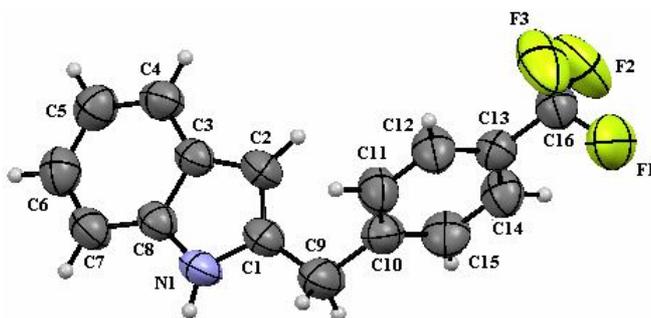


Figure S1 ORTEP diagram of product **9c**

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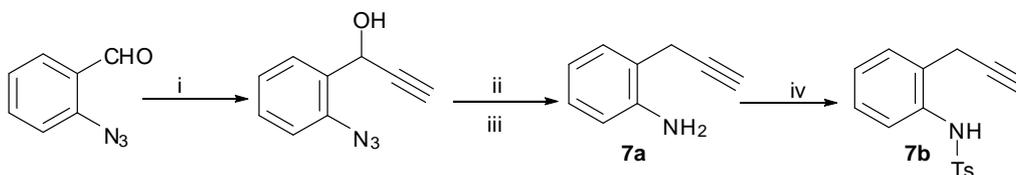
**Table S1: Important crystal data of product 9c:**

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Empirical formula	C <sub>16</sub> H <sub>12</sub> F <sub>3</sub> N
Formula weight	275.27
Temperature	296(2) K
Wavelength	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.5871 (16) Å α = 93.549° (9) b = 10.4916 (18) Å β = 109.310° (9) c = 14.112 (2) Å γ = 95.346° (10)
Volume	1327.3 (4) Å <sup>3</sup>
Z	4
Density (calculated)	1.378 g/m <sup>3</sup>
Absorption coefficient (Mu)	0.110 mm <sup>-1</sup>
F(000)	568.0
Theta range for data collection	1.54 to 23.72°
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflection collected	20553
Independent reflections	3977 [R(int) = 0.0451]
Completeness to theta = 25.44°	98.8%
Absorption correction	Multi-scan
Max. and min. transmission	0.991 and 0.977
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3977/0/361
Goodness-of-fit on F <sup>2</sup>	1.155
Final R indices [I > 2σ(I)]	R1 = 0.0579, wR2 = 0.1732
R indices (all data)	R1 = 0.0735, wR2 = 0.1944
Largest diff. peak and hole	0.408 & -0.269 e.Å <sup>-3</sup>
The crystal data of product 9c has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is 939088	

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### 3. Synthesis of starting substrates 7:



**Scheme S1** Reagent and conditions: (i) ethynylmagnesium bromide, THF, 0 °C, 0.75 h, 62%; (ii)  $E_t_3SiH$ , trifluoroacetic acid, DCM, 0 °C to rt, 2 h, 45%; (iii)  $LiAlH_4$ , THF, 0 °C, 2h, 75%; (iv)  $TsCl$ , pyridine, DCM, 0 °C to rt, 2h, 78%.

The starting substrates, i.e., 2-(prop-2-ynyl)aniline **7a** and 2-(2-propynyl)tosylanilide **7b** were prepared through a sequence of steps starting from *ortho*-azidobenzaldehyde (Scheme S1). The *ortho*-azidobenzaldehyde was first treated with ethynylmagnesium bromide, the resulting acetylenic carbinol was then underwent dehydroxylation followed by reduction to yield the product **7a**. Finally, tosylation of amine **7a** using tosyl chloride and pyridine in dry DCM led to the synthesis of compound **7b**.

#### Procedure for the synthesis of starting substrate 7a-b:

To a solution of *ortho*-azido benzaldehyde (3.0 g, 20.39 mmol) in dry THF (30 mL) was added 0.5 M ethynylmagnesium bromide solution in dry THF (41 mL) dropwise at 0 °C under argon atmosphere and stirred for 45 minutes at the same temperature. After completion of reaction (TLC), the reaction mixture was quenched with saturated  $NH_4Cl$  solution at 0 °C. THF was evaporated under reduced pressure, and the resulting residue was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with water (50 mL) and brine (50 mL), dried over anhydrous  $Na_2SO_4$ , filtered, and concentrated under reduced pressure. The crude product was purified through silica gel (100-200 mesh) column chromatography (ethyl acetate-petroleum ether) to afford the acetylenic carbinol (2.18 g, 62%).

To a solution of the acetylenic carbinol (3.0 g, 17.32 mmol) in dry DCM were added consecutively triethylsilane (5.53 mL, 34.64 mmol) and trifluoroacetic acid (5.3 mL, 69.28 mmol) at 0 °C under argon atmosphere and the reaction mixture was allowed to stir at room temperature. After completion of the reaction (TLC), the solvent was evaporated under reduced pressure; the resulting residue was dissolved in ethyl acetate (60 mL) and

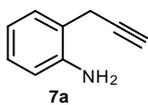
the pH of the solution was adjusted to 7 by dropwise addition of aqueous NaHCO<sub>3</sub> solution. The mixture was then washed with water (30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by silica gel (100–200 mesh) column chromatography (ethyl acetate-petroleum ether) to afford 2-(2-propynyl)azidobenzene (1.22 g, 45%).

To an ice cooled solution of 2-(2-propynyl)azidobenzene (2.0 g, 12.72 mmol) in dry THF (50 mL) was added slowly lithium aluminum hydride (0.96 g, 25.44 mmol) at 0 °C and the reaction mixture was allowed to stir at the same temperature until the completion of the reaction (TLC). It was then quenched with ethanol and water at 0 °C and the solvent was removed under reduced pressure. The residue was extracted with ethyl acetate (3 × 40 mL), and washed with water (30 mL) and brine (30 mL) successively. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The resulting crude product was purified through silica gel (100-200 mesh) column chromatography (ethyl acetate-petroleum ether) to afford 2-(2-propynyl)aniline **7a** (1.25 g, 75%).

To a solution of compound **7a** (1.0 g, 7.62 mmol) in dry DCM (30 mL) were added successively pyridine (0.92 mL, 11.43 mmol) and *p*-toluenesulfonyl chloride (1.74 g, 9.14 mmol) at 0 °C and the reaction mixture was then allowed to stir at room temperature for 2 h. After completion of the reaction (tlc), it was extracted with DCM (2 × 30 mL), washed with water (20 mL) and brine (20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The resulting residue was purified through silica gel (100-200 mess) column chromatography (ethyl acetate-petroleum ether) to afford the desired product **7b** (1.69 g, 78%).

#### 4. Spectral data of starting substrates 7a-b:

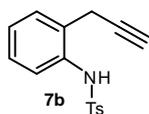
**2-(Prop-2-ynyl)aniline (7a):** Light yellow solid (1.25 g, 75% yield); mp 40-42 °C; <sup>1</sup>H



NMR (CDCl<sub>3</sub>, 300 MHz) δ<sub>H</sub> 7.18 (d, *J* = 7.5 Hz, 1H), 7.10 (td, *J* = 7.6, 1.2 Hz, 1H), 6.79-6.69 (m, 2H), 3.83 (brs, 2H), 3.44 (d, *J* = 2.7 Hz, 2H), 2.18 (t, *J* = 2.7 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ<sub>C</sub> 144.4, 129.3, 128.2,

120.8, 118.9, 116.0, 80.8, 70.7, 21.6; HRMS (EI+) calcd. for C<sub>9</sub>H<sub>9</sub>N [M]<sup>+</sup> 131.07350, found 131.07352.

**2-(2-Propynyl)tosylanilide (7b):**<sup>3</sup> Colorless solid (1.69 g, 78% yield); mp 118-120 °C;



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ<sub>H</sub> 7.61 (d, *J* = 8.4 Hz, 2H), 7.31-7.17 (m, 6H), 6.83 (brs, 1H), 3.19 (d, *J* = 2.4 Hz, 2H), 2.39 (s, 3H), 2.24 (t, *J* = 2.7 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ<sub>C</sub> 143.9, 136.6, 134.3, 130.6,

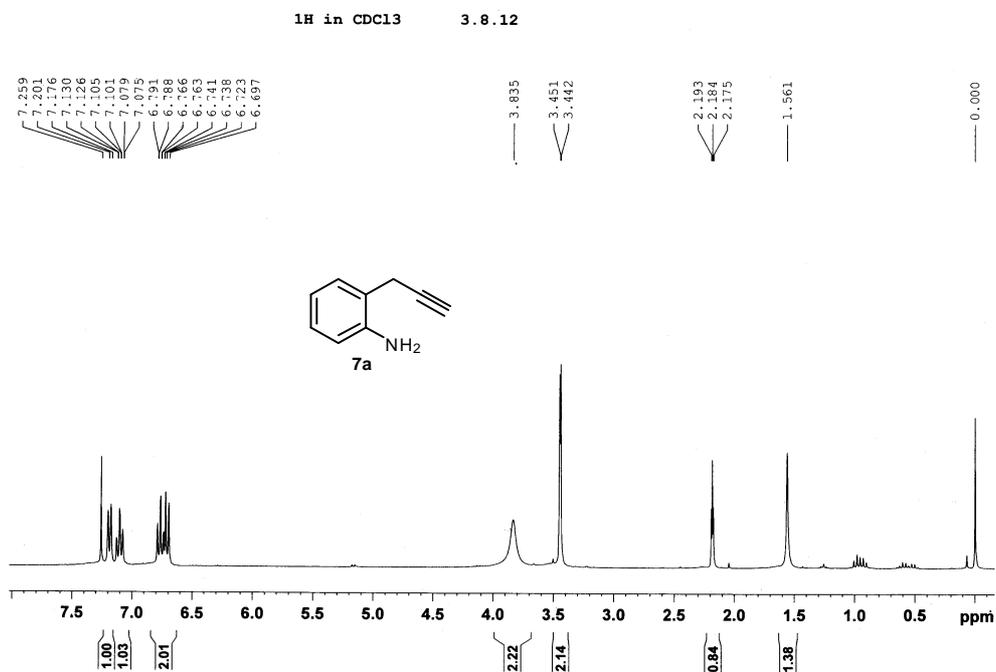
129.65, 129.62, 128.1, 127.1, 126.9, 125.9, 80.4, 71.9, 21.6, 21.5; HRMS (EI+) calcd. for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>S [M]<sup>+</sup> 285.08235, found 285.08261.

#### 5. References:

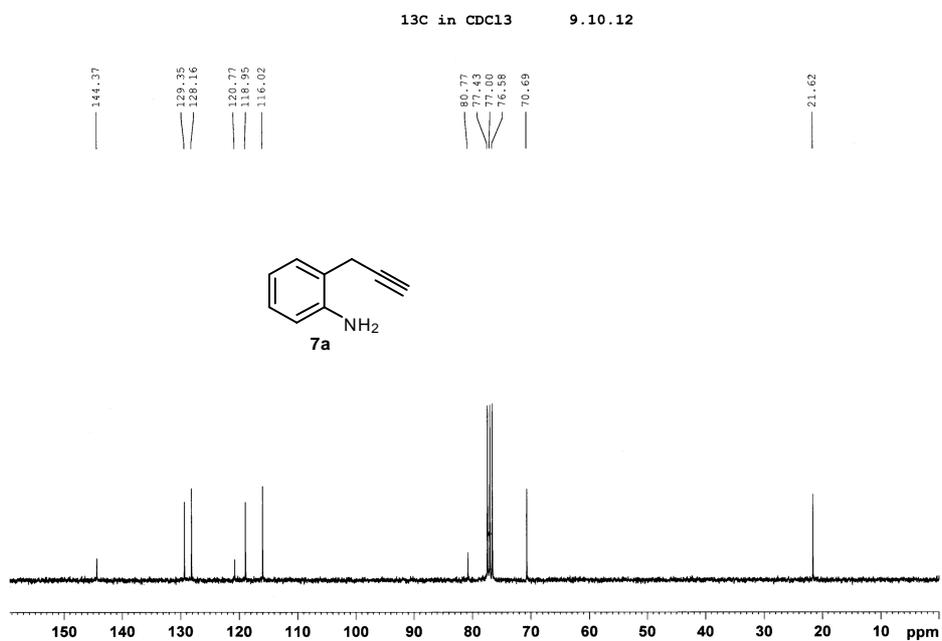
1. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
2. G. M. Sheldrick, *SHELX - 97, Program for Crystallography Refinement*, University of Gottingen: Gottingen, Germany, **1997**.
3. A. Varela-Fernandez, J. A. Varela, C. Saa, *Adv. Synth. Catal.* **2011**, *353*, 1933-1937.

## 6. NMR Spectra of compounds 7, 9 and 12:

### <sup>1</sup>H NMR (300 MHz) Spectrum of 7a:

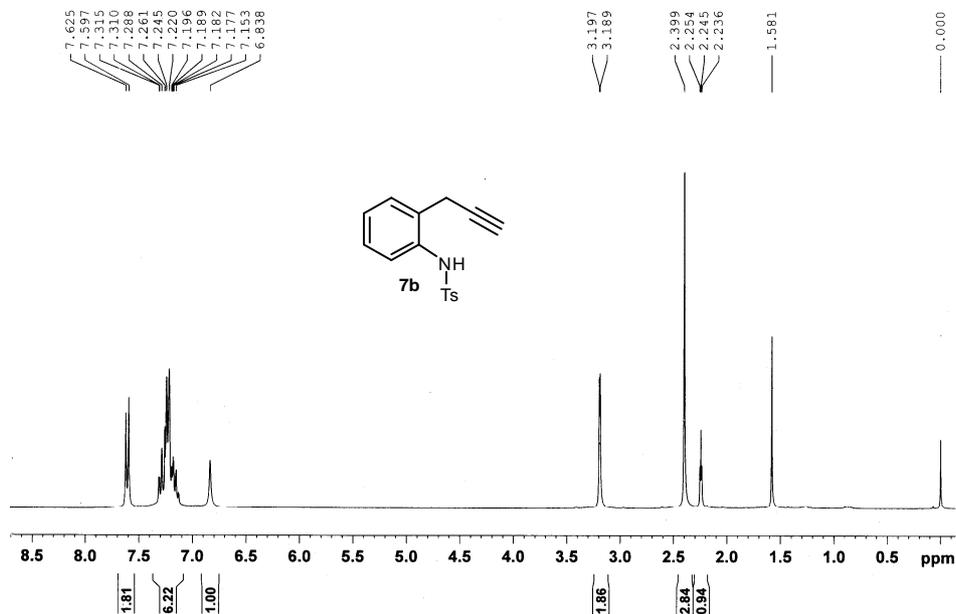


### <sup>13</sup>C NMR (75 MHz) Spectrum of 7a:



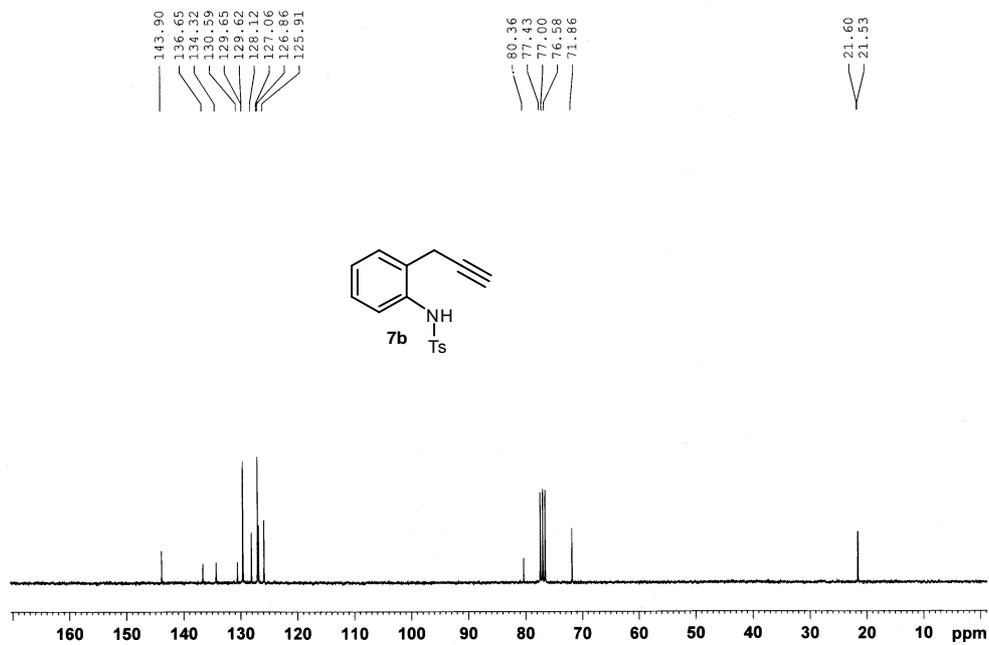
### $^1\text{H}$ NMR (300 MHz) Spectrum of 7b:

$^1\text{H}$  in  $\text{CDCl}_3$  3.12.12

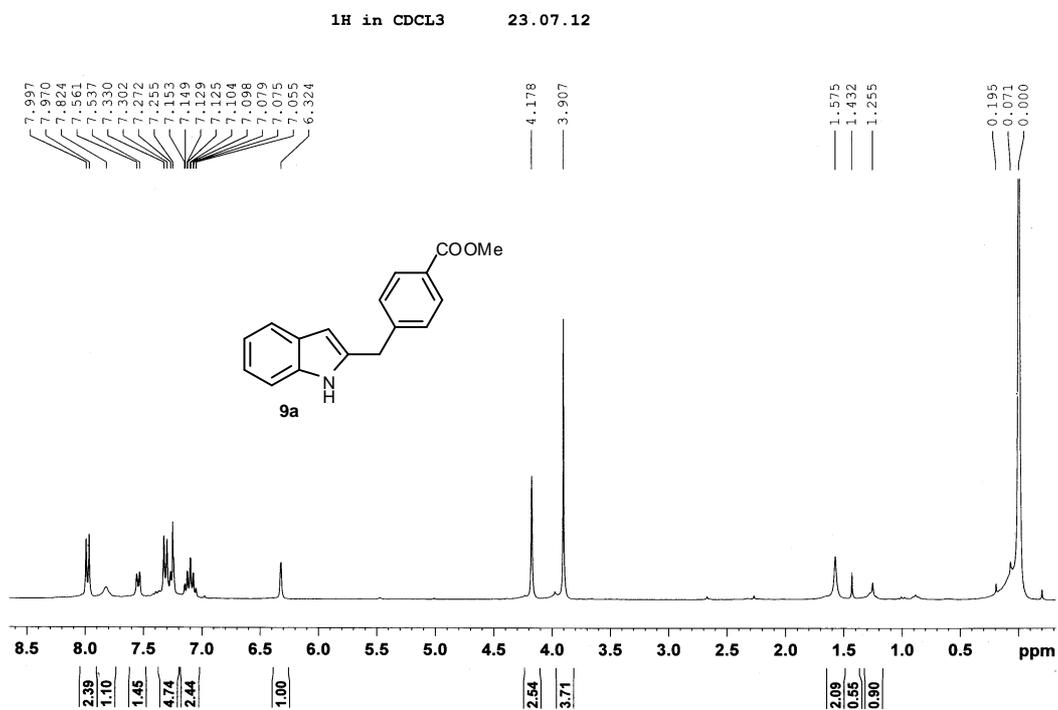


### $^{13}\text{C}$ NMR (75 MHz) Spectrum of 7b:

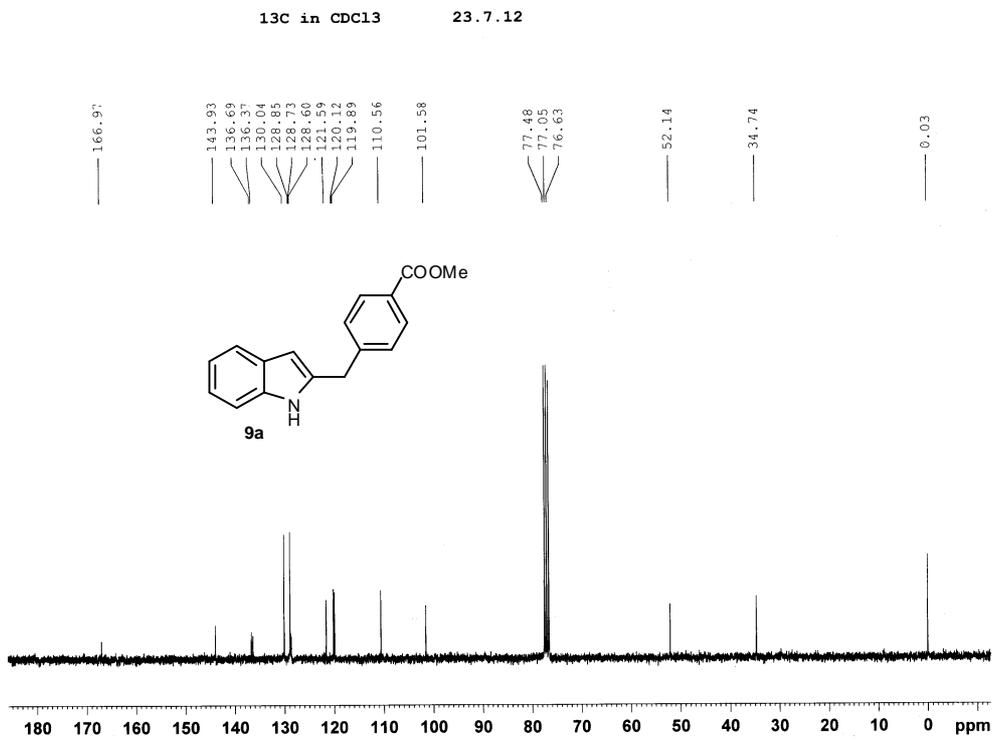
$^{13}\text{C}$  in  $\text{CDCl}_3$  18.09.12



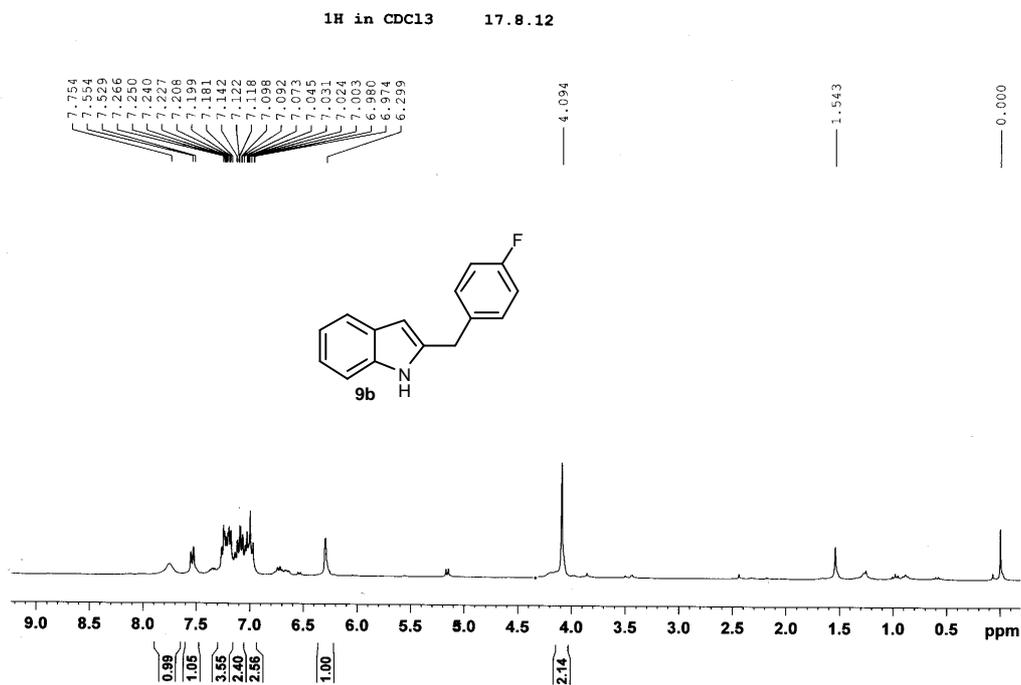
### <sup>1</sup>H NMR (300 MHz) Spectrum of 9a:



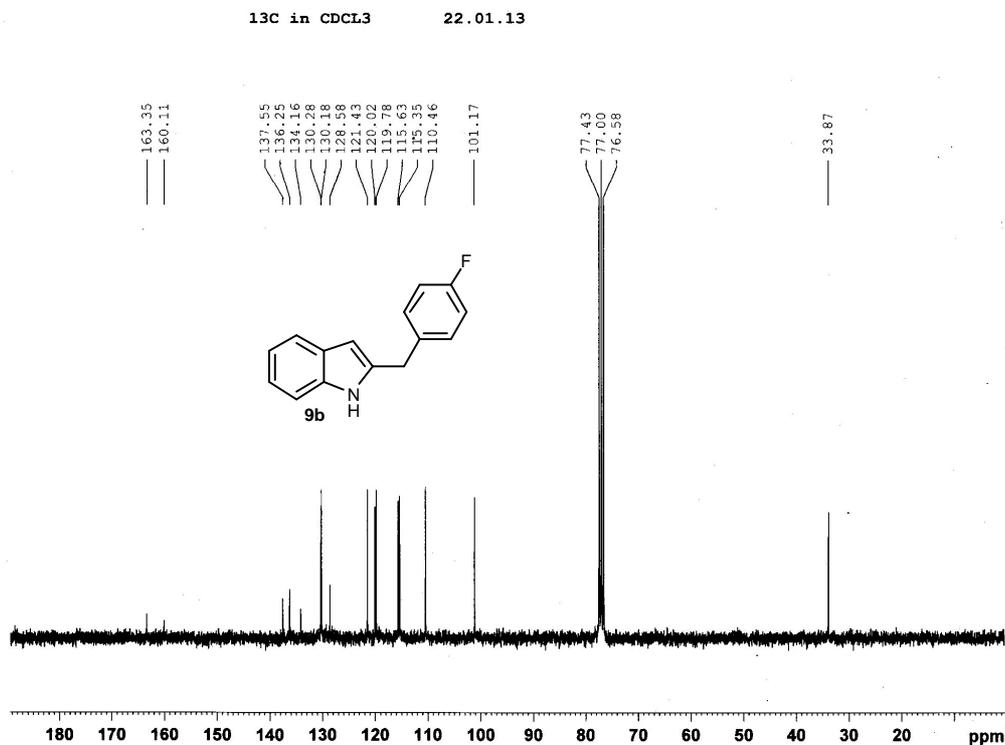
### <sup>13</sup>C NMR (75 MHz) Spectrum of 9a:



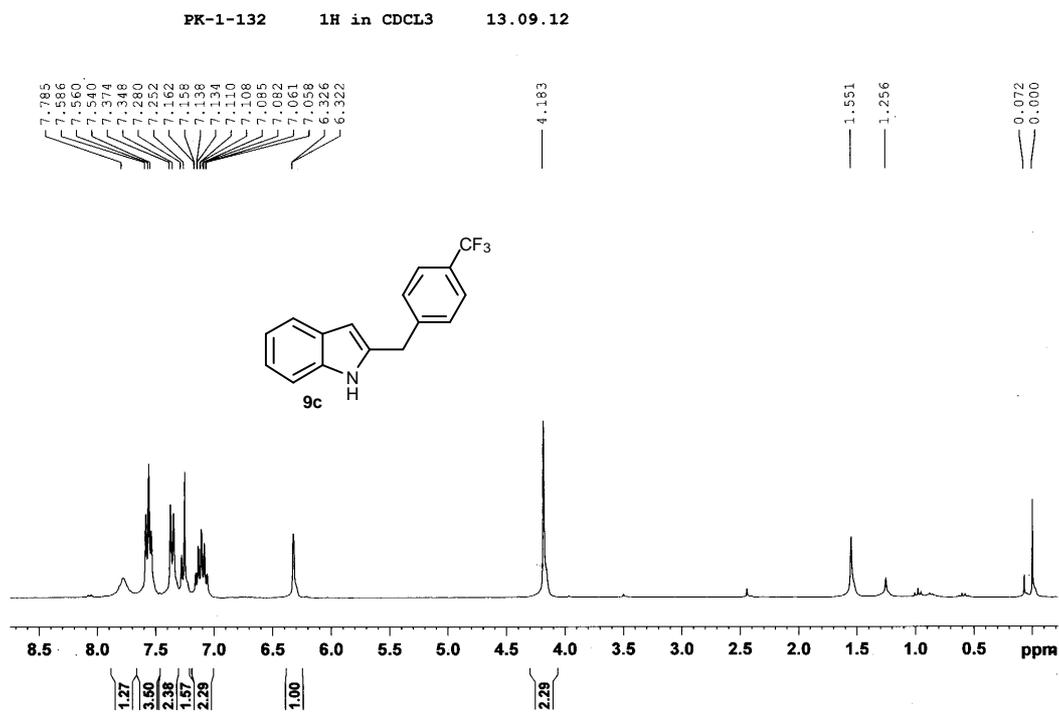
### $^1\text{H}$ NMR (300 MHz) Spectrum of 9b:



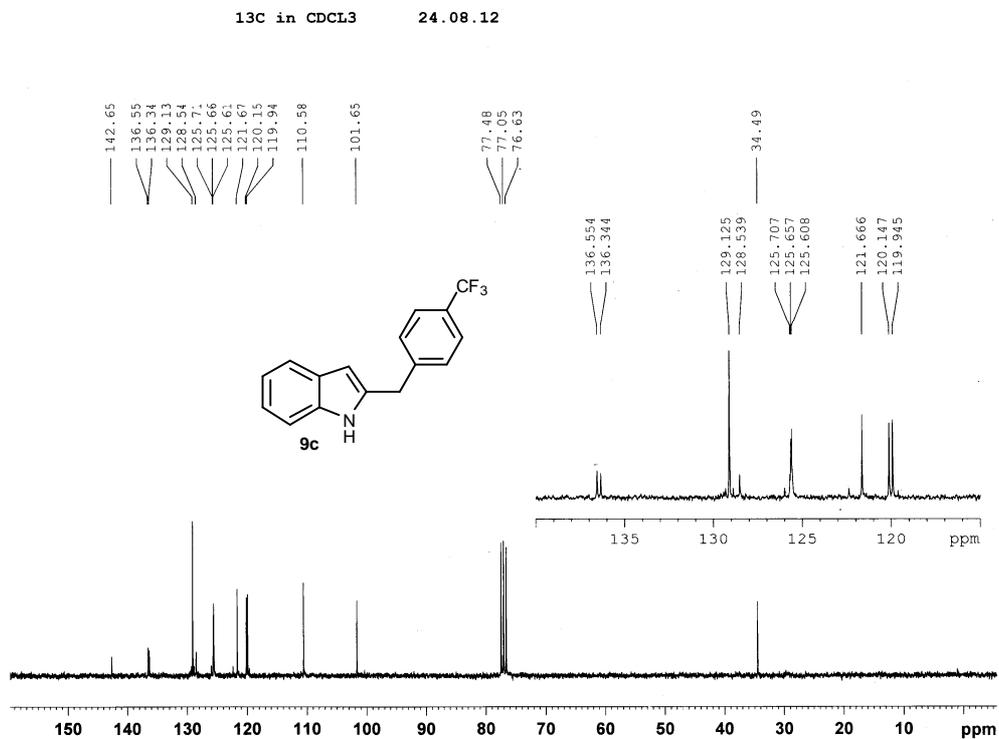
### $^{13}\text{C}$ NMR (75 MHz) Spectrum of 9b:



### $^1\text{H}$ NMR (300 MHz) Spectrum of 9c:

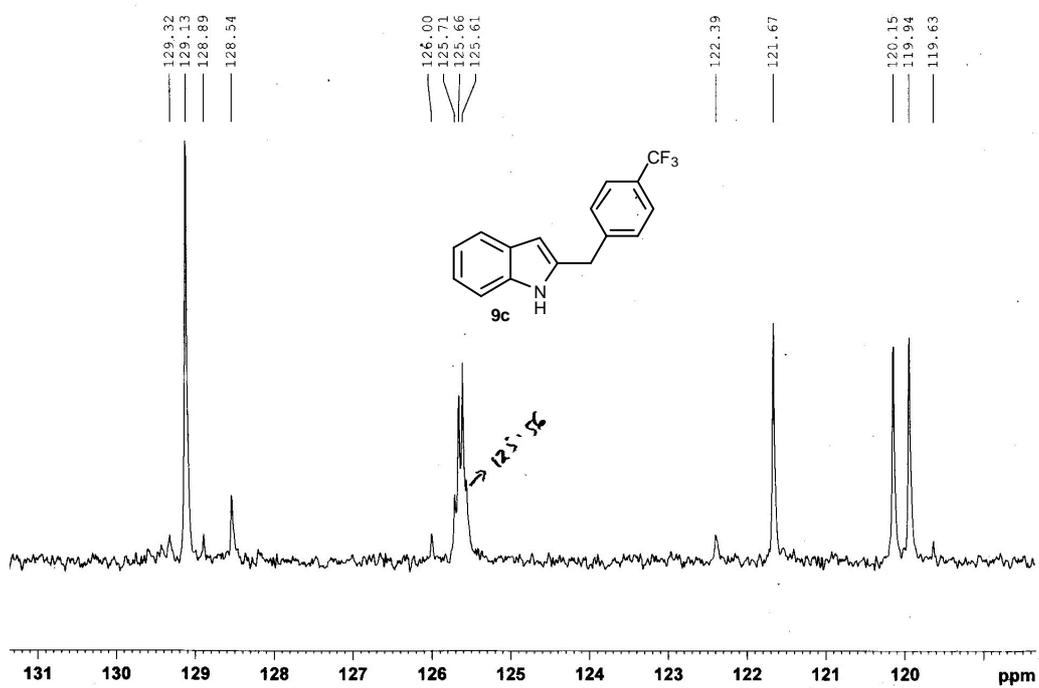


### $^{13}\text{C}$ NMR (75 MHz) Spectrum of 9c:

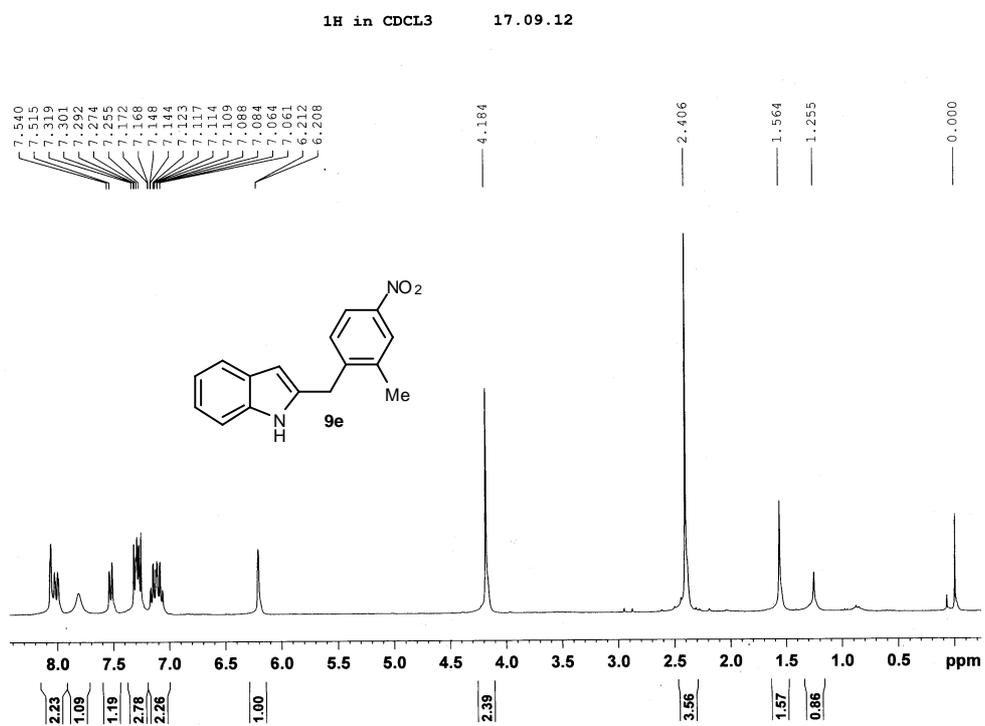


### <sup>13</sup>C NMR (75 MHz) Spectrum of 9c (Expansion):

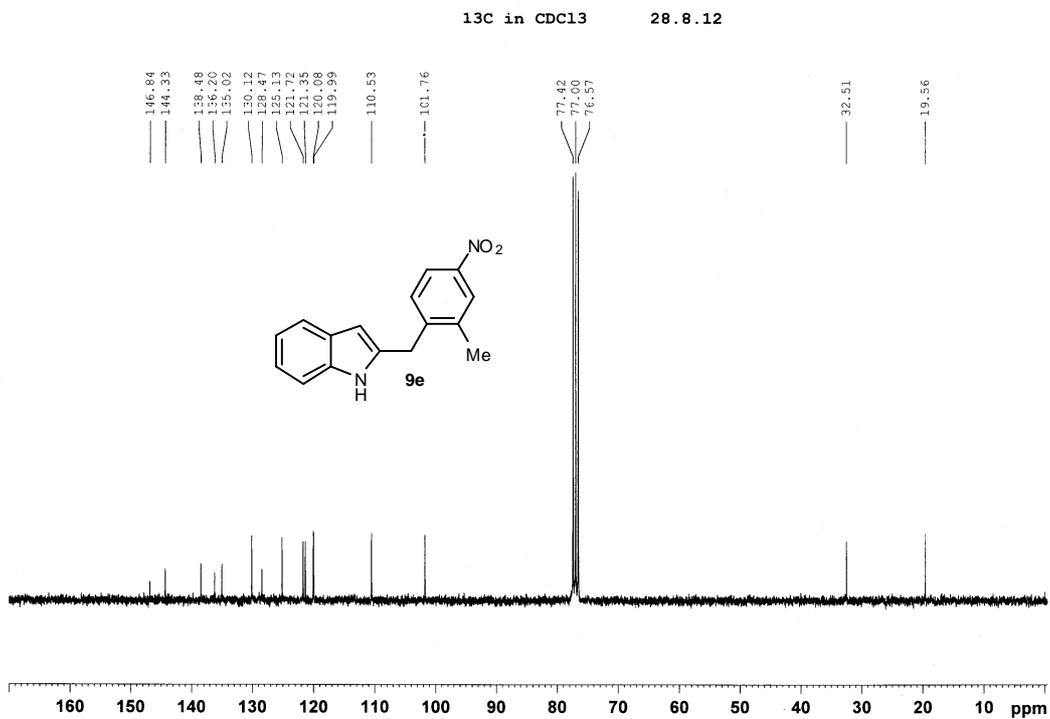
<sup>13</sup>C in CDCl<sub>3</sub>



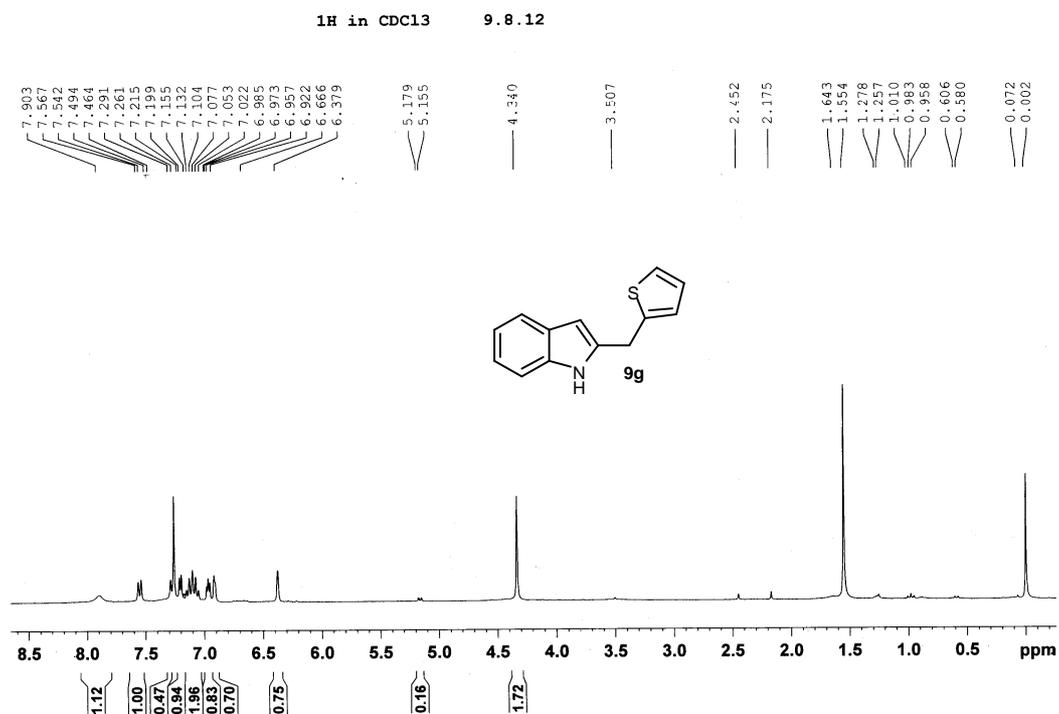
### <sup>1</sup>H NMR (300 MHz) Spectrum of 9e:



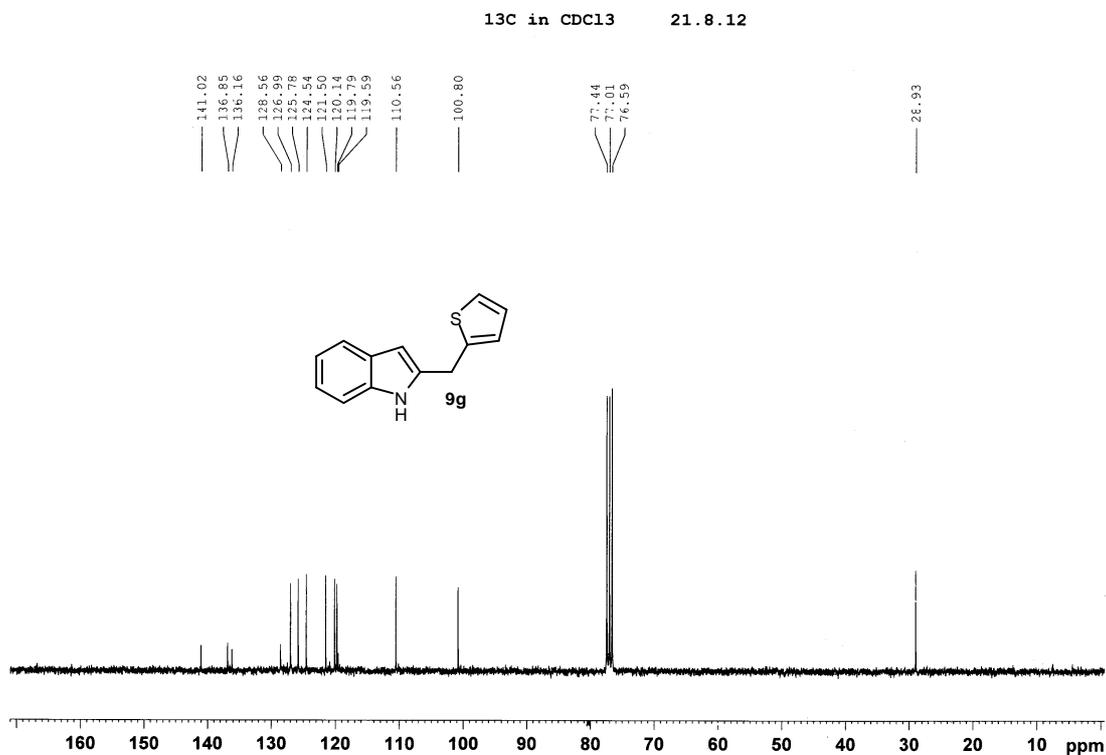
### <sup>13</sup>C NMR (75 MHz) Spectrum of 9e:



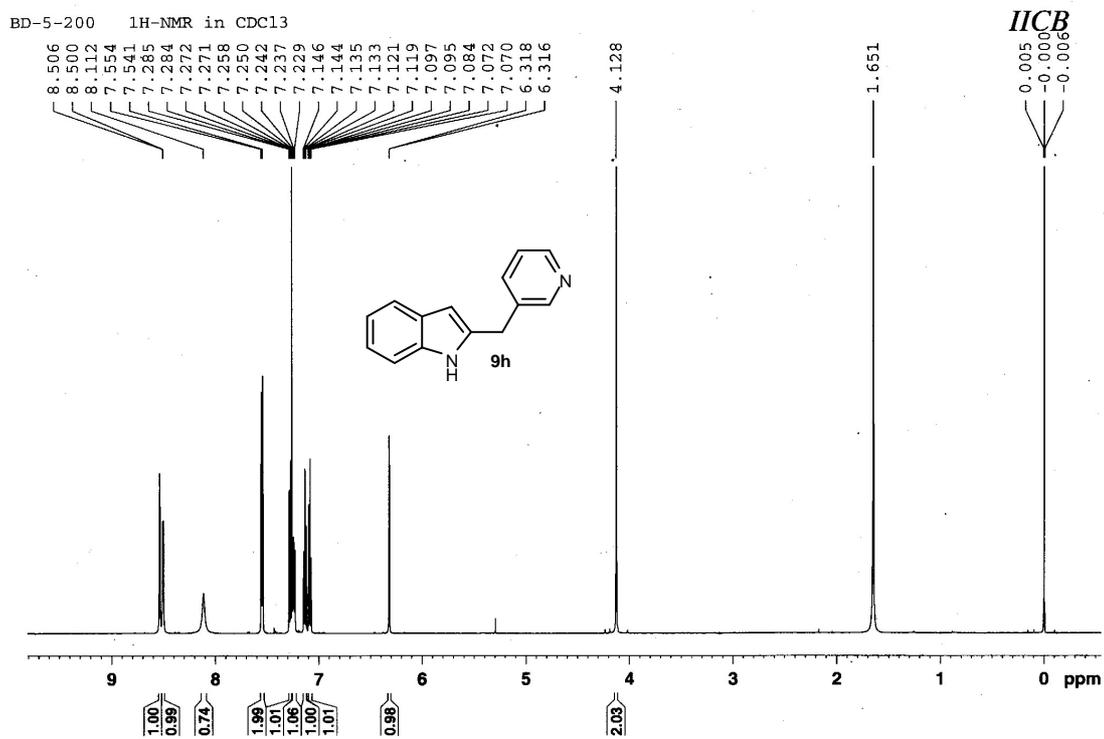
### <sup>1</sup>H NMR (300 MHz) Spectrum of 9g:



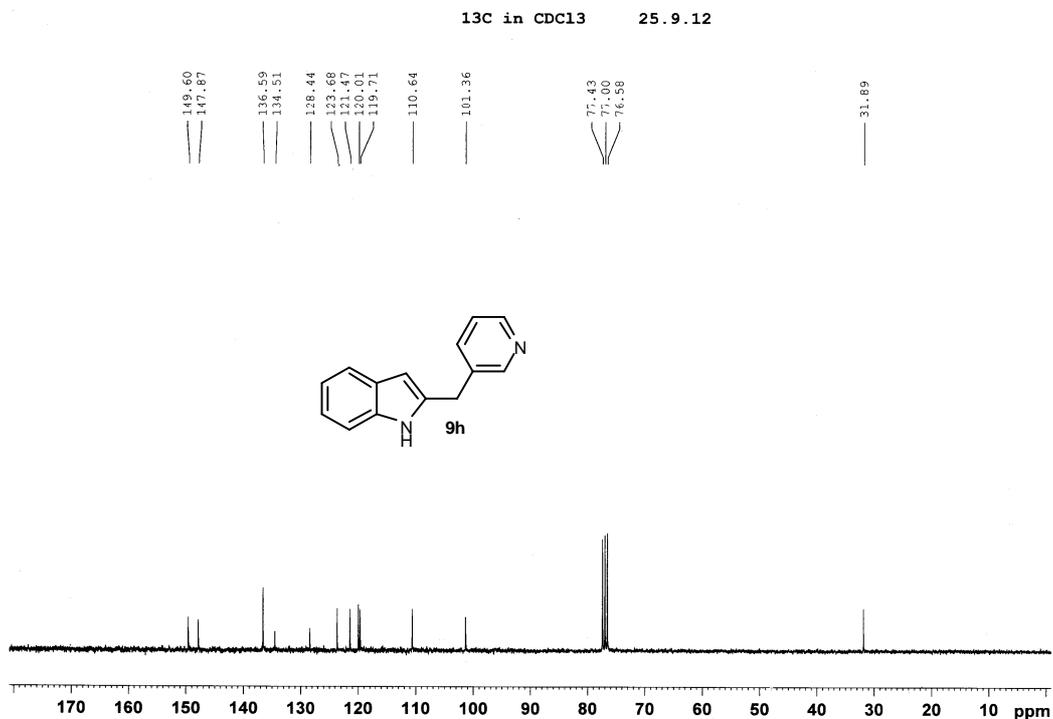
### <sup>13</sup>C NMR (75 MHz) Spectrum of 9g:



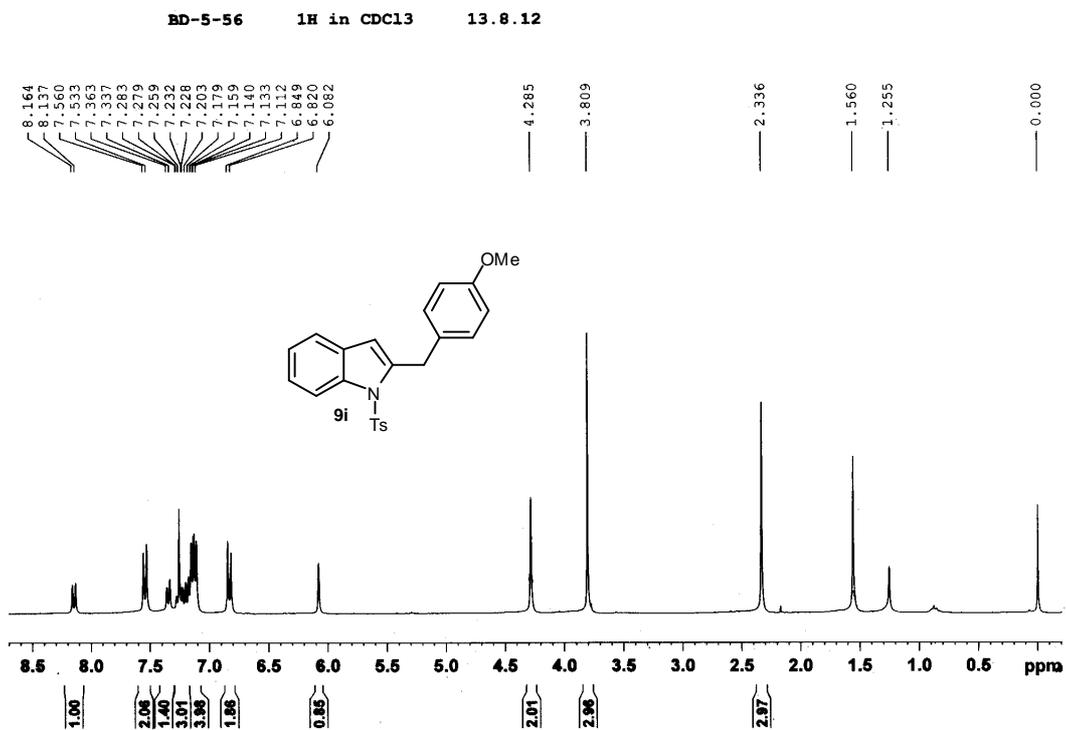
### $^1\text{H}$ NMR (600 MHz) Spectrum of 9h:



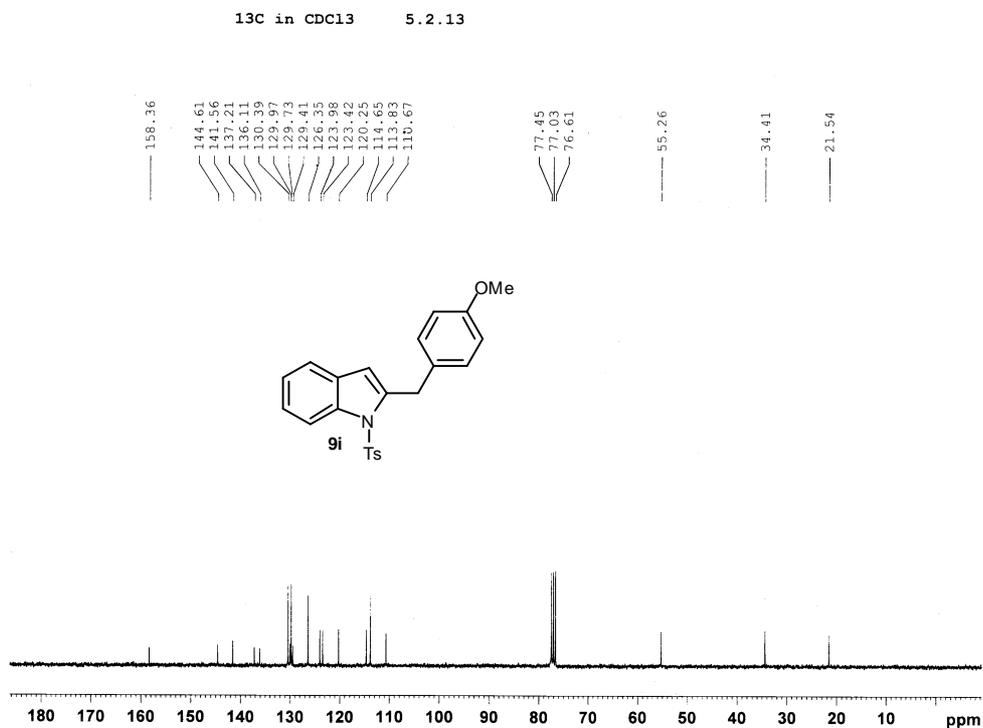
### $^{13}\text{C}$ NMR (75 MHz) Spectrum of 9h:



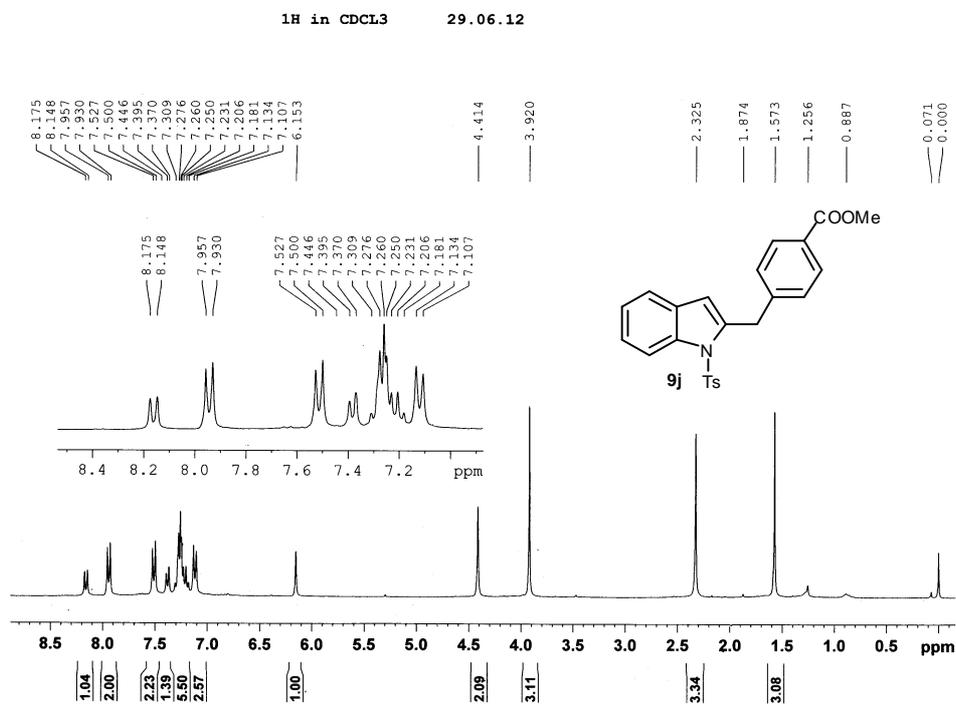
### $^1\text{H}$ NMR (300 MHz) Spectrum of 9i:



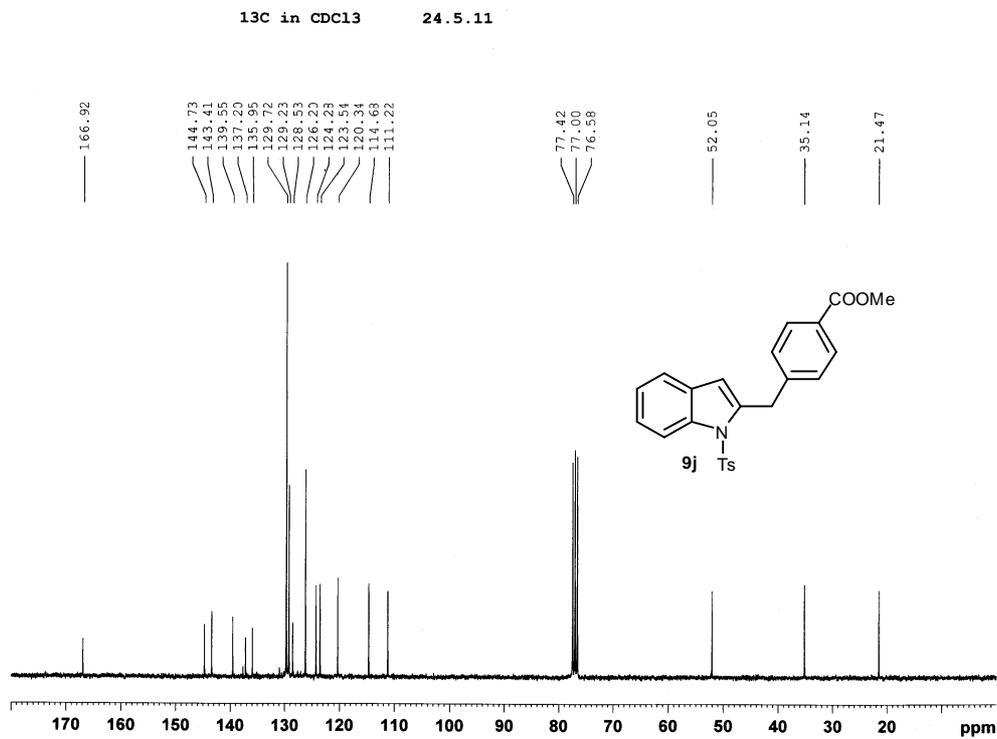
### $^{13}\text{C}$ NMR (75 MHz) Spectrum of 9i:



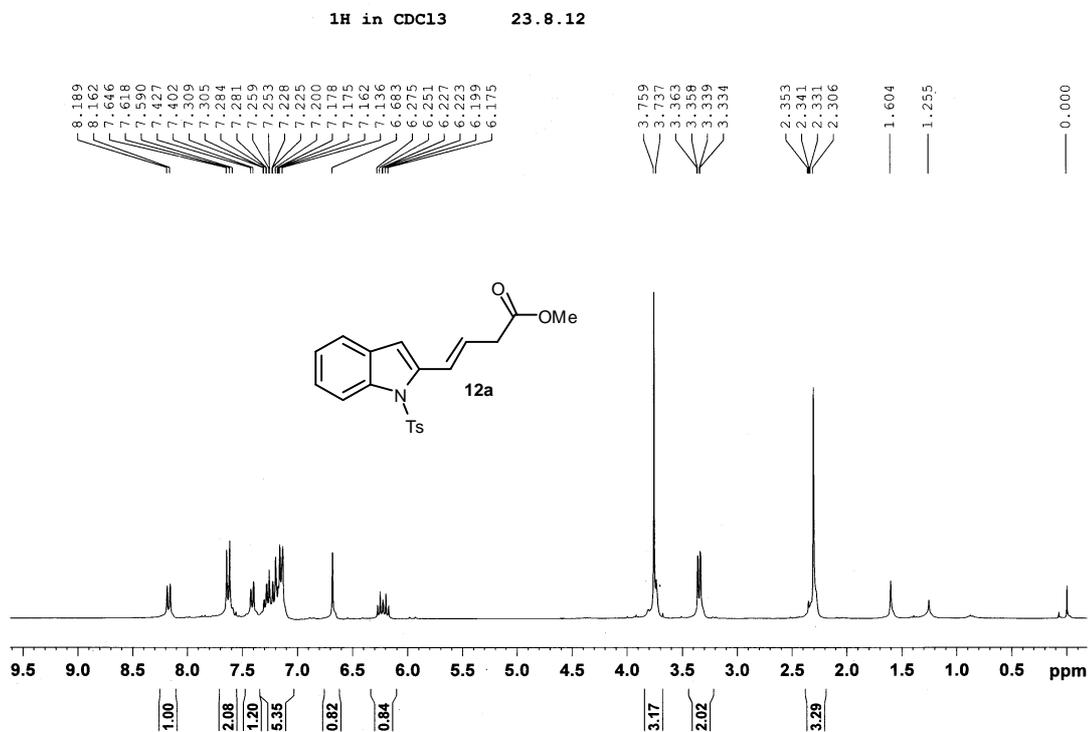
### <sup>1</sup>H NMR (300 MHz) Spectrum of 9j:



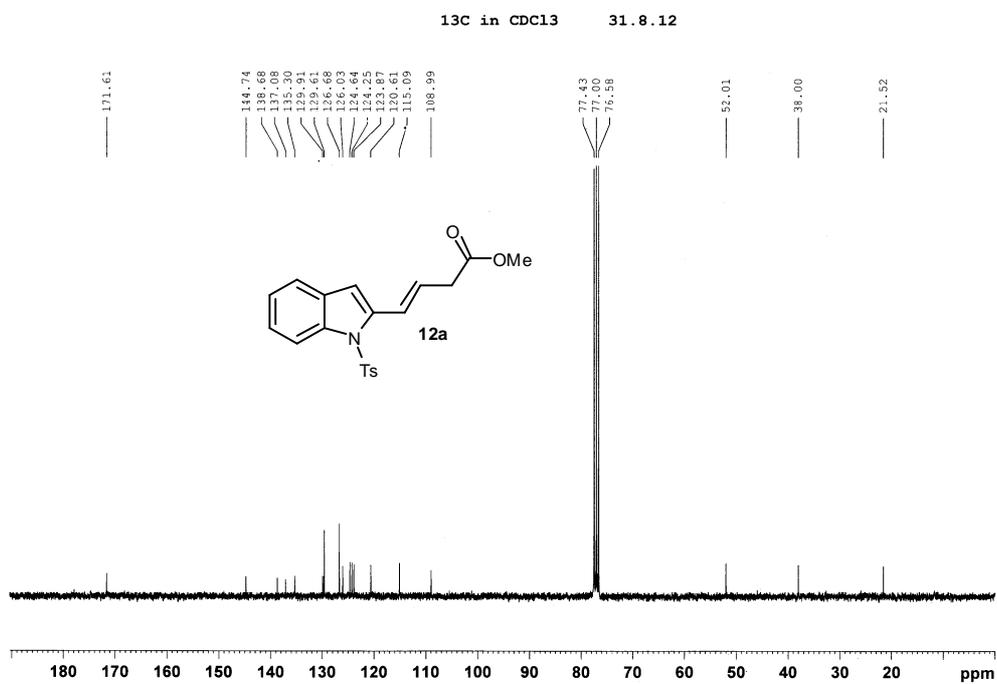
### <sup>13</sup>C NMR (75 MHz) Spectrum of 9j:



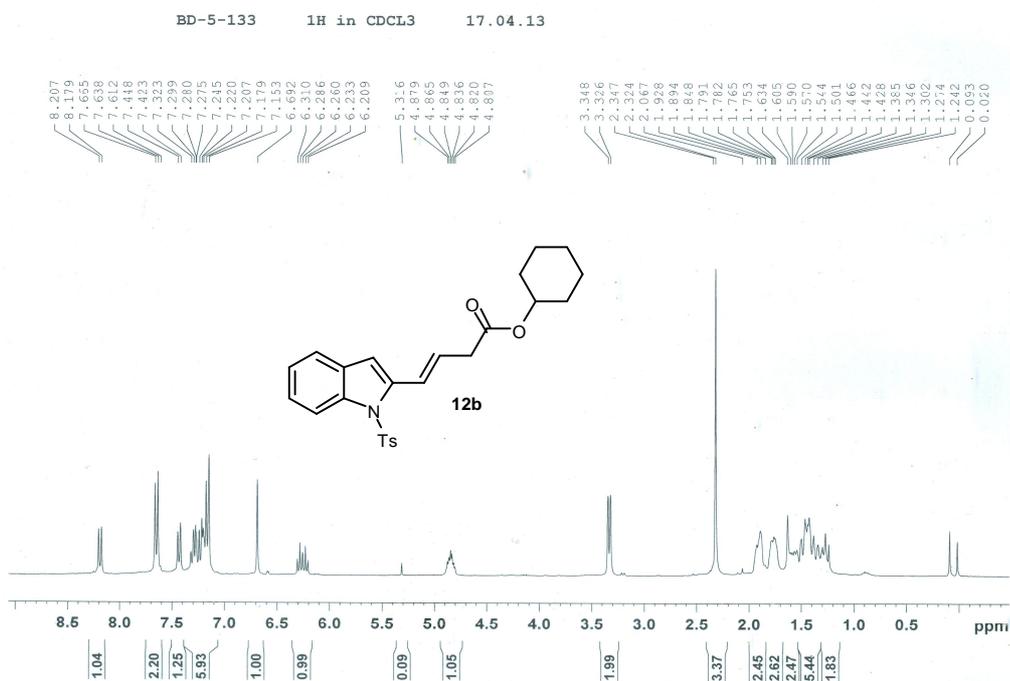
### <sup>1</sup>H NMR (300 MHz) Spectrum of 12a:



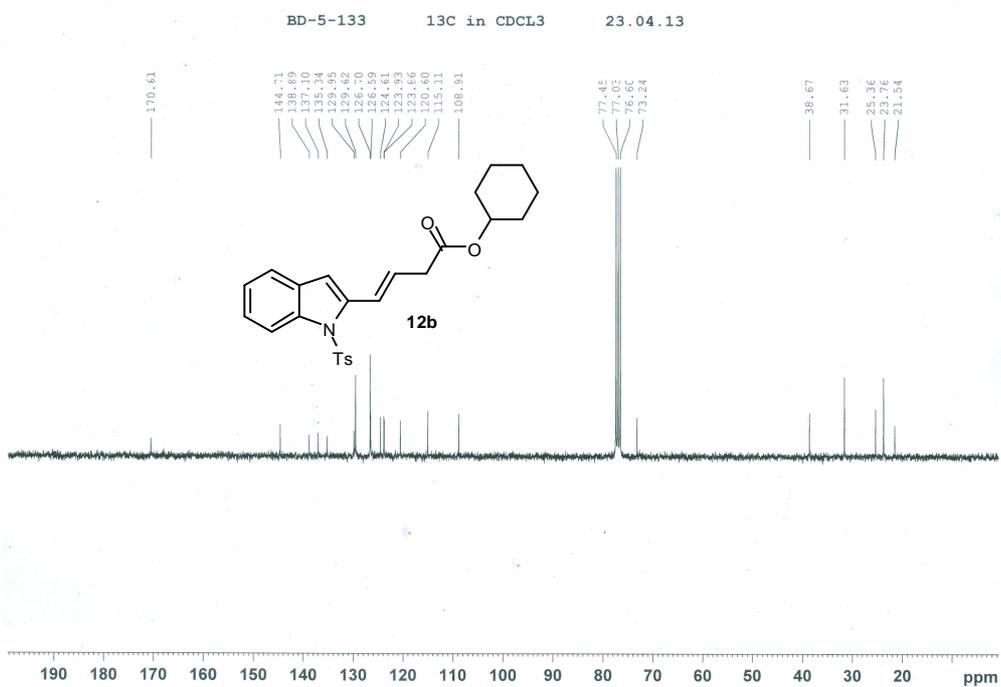
### <sup>13</sup>C NMR (75 MHz) Spectrum of 12a:



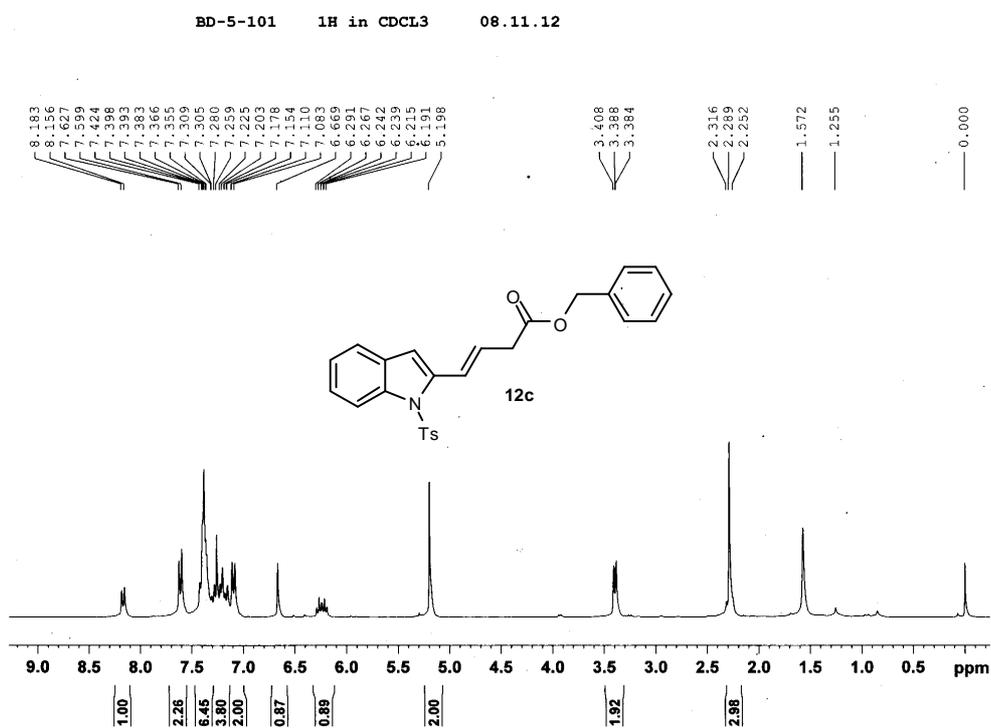
### $^1\text{H}$ NMR (300 MHz) Spectrum of 12b:



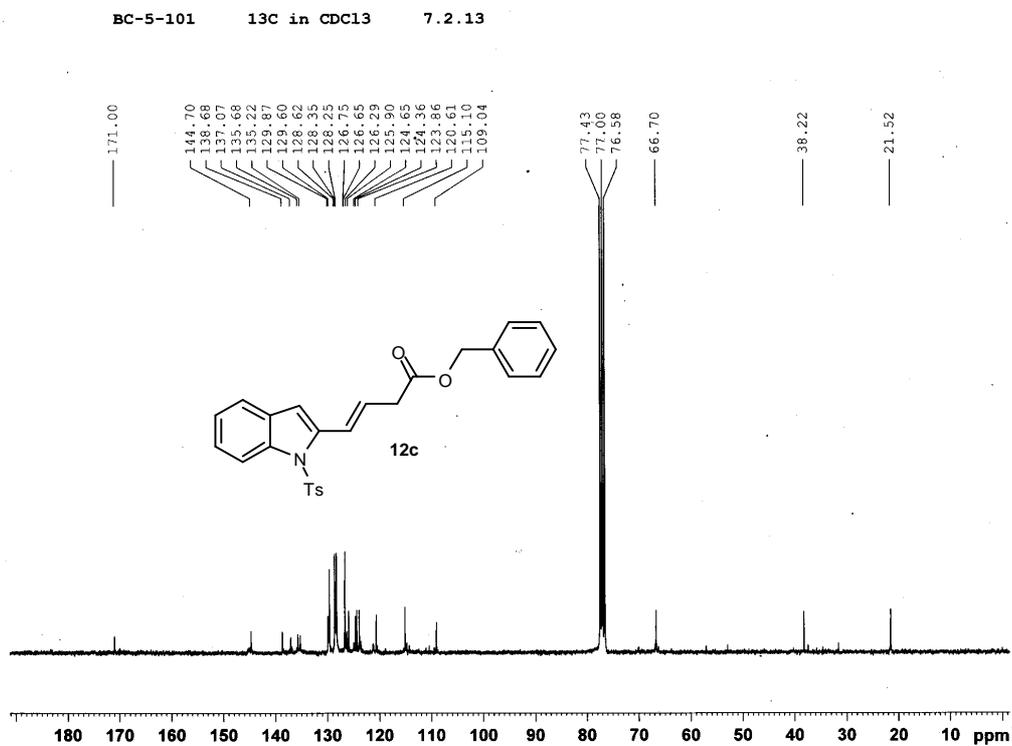
### $^{13}\text{C}$ NMR (75 MHz) Spectrum of 12b:



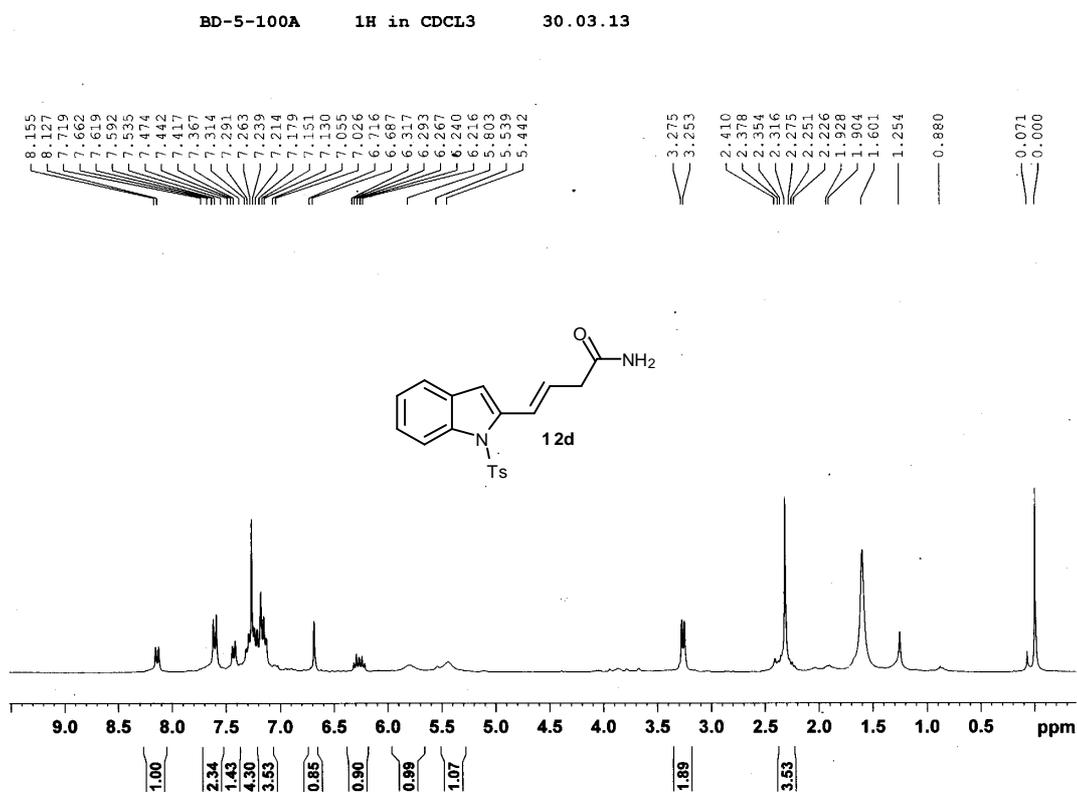
### $^1\text{H}$ NMR (300 MHz) Spectrum of 12c:



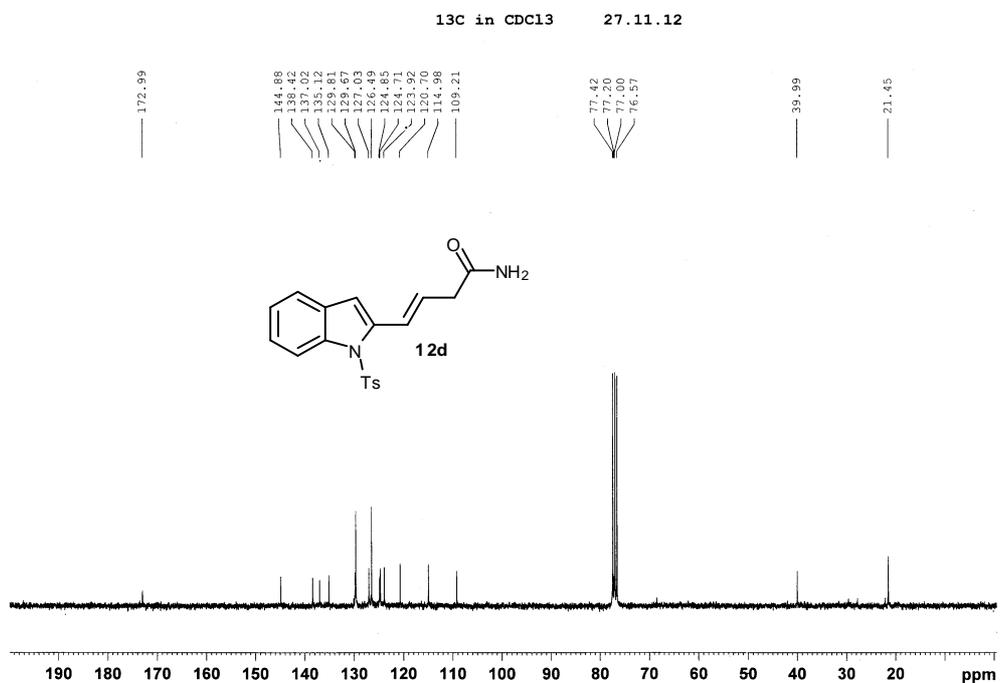
### $^{13}\text{C}$ NMR (75 MHz) Spectrum of 12c:



### $^1\text{H}$ NMR (300 MHz) Spectrum of 12d:



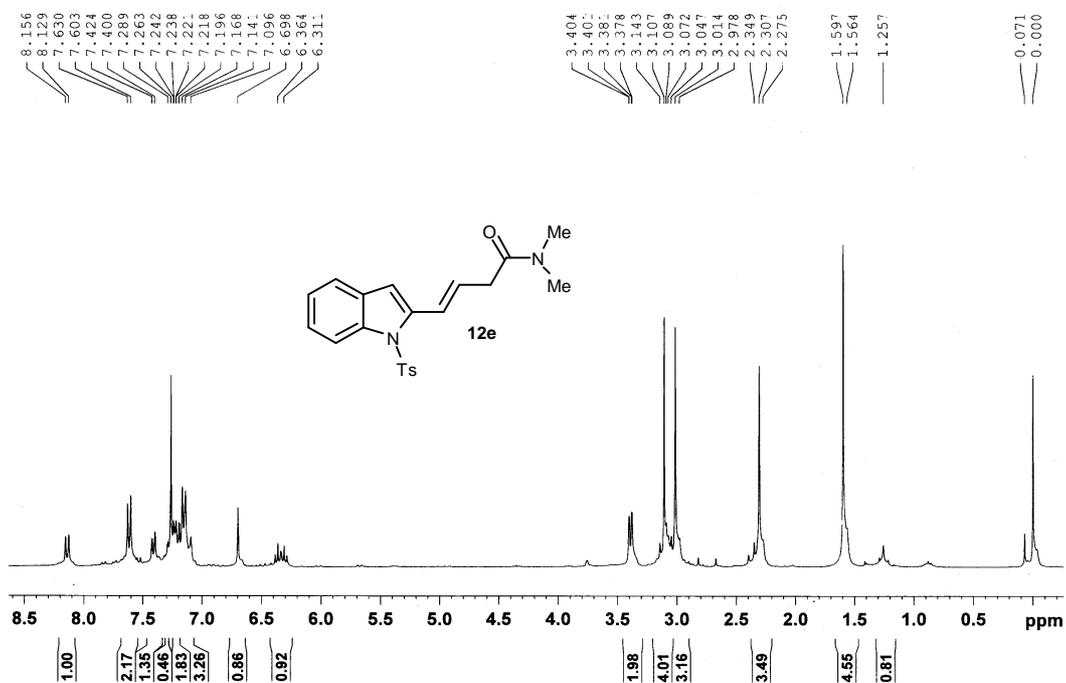
### $^{13}\text{C}$ NMR (75 MHz) Spectrum of 12d:



### $^1\text{H}$ NMR (300 MHz) Spectrum of 12e:

$^1\text{H}$  in  $\text{CDCl}_3$

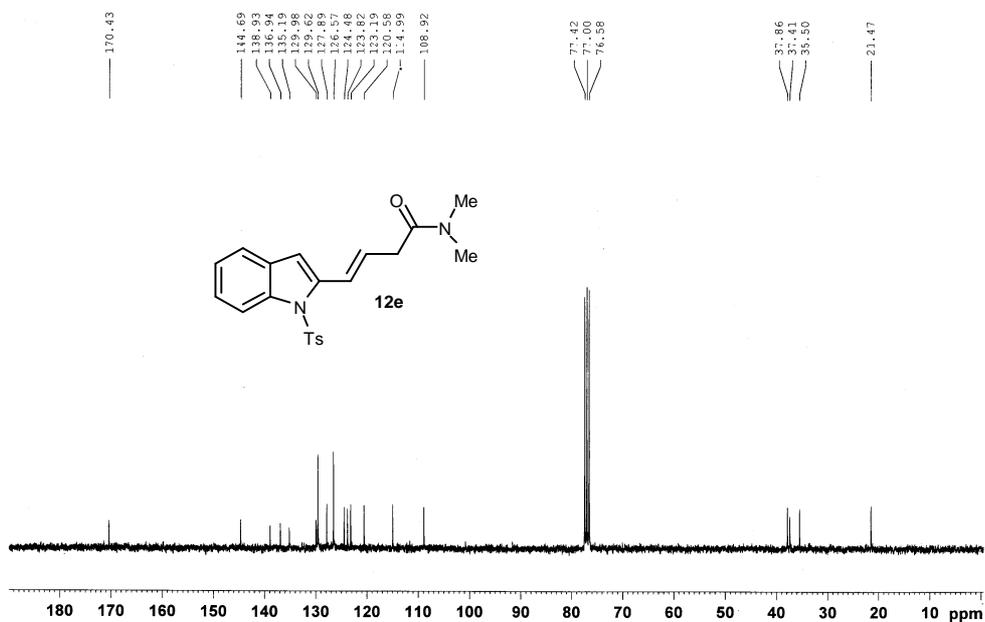
03.12.12



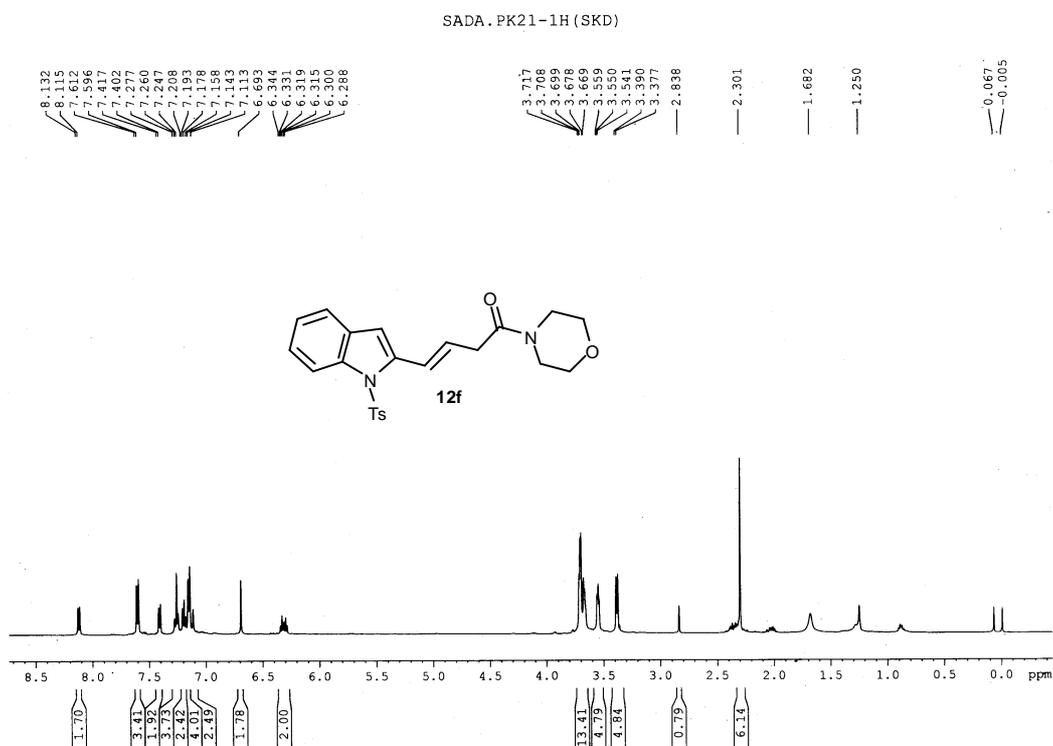
### $^{13}\text{C}$ NMR (75 MHz) Spectrum of 12e:

$^{13}\text{C}$  in  $\text{CDCl}_3$

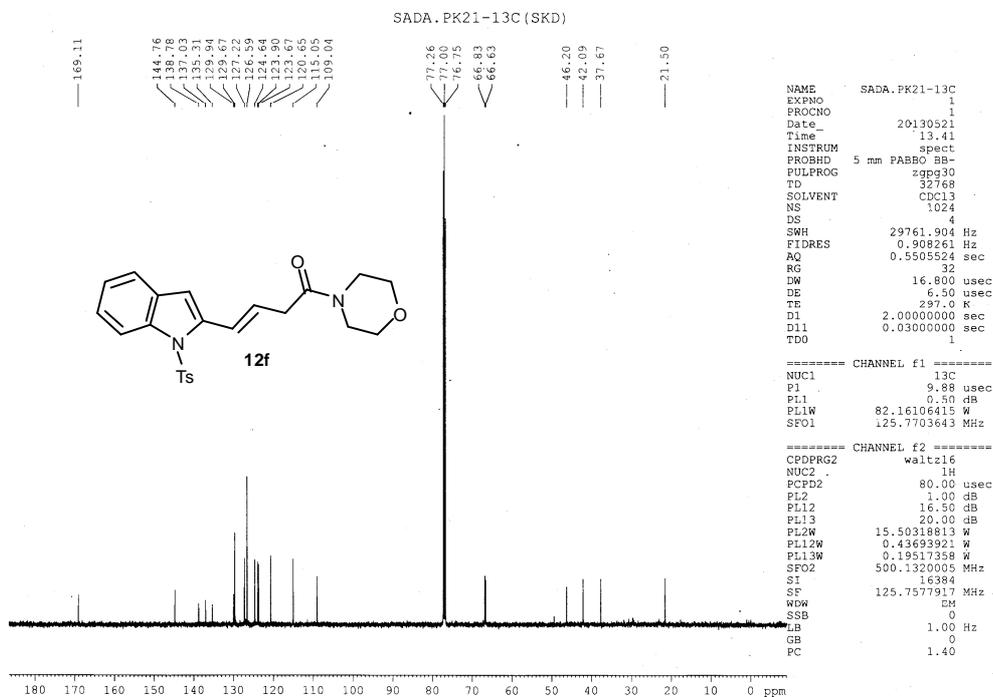
4.12.12



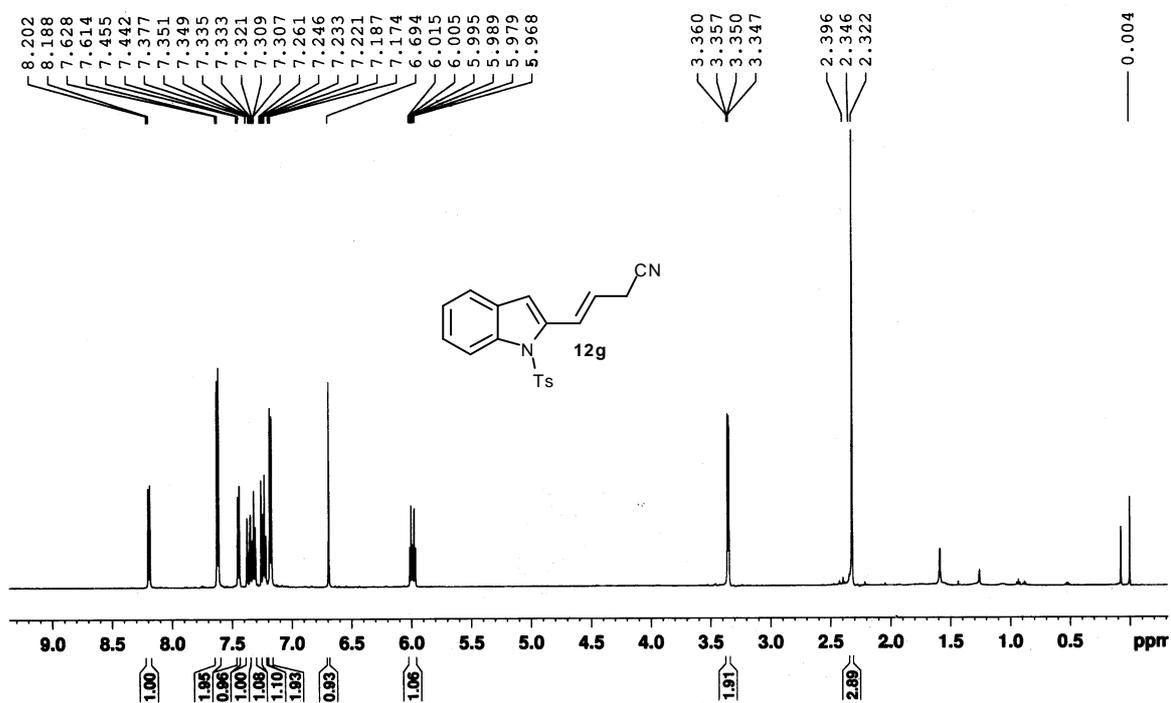
### <sup>1</sup>H NMR (500 MHz) Spectrum of 12f:



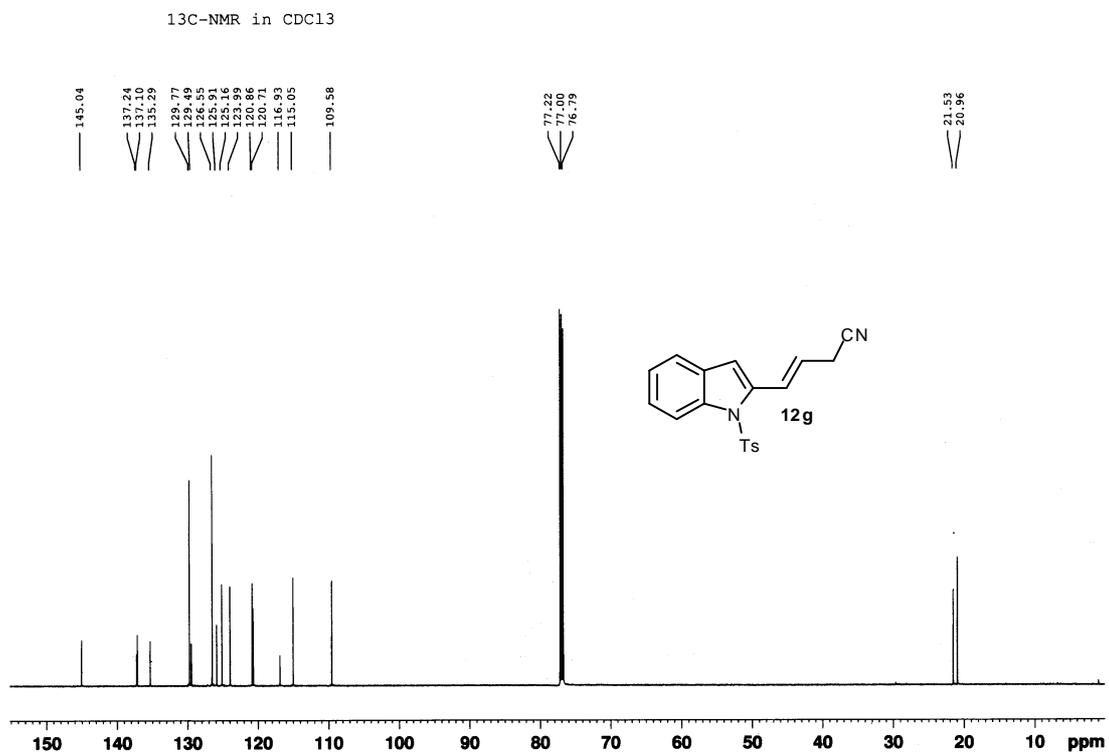
### <sup>13</sup>C NMR (125 MHz) Spectrum of 12f:



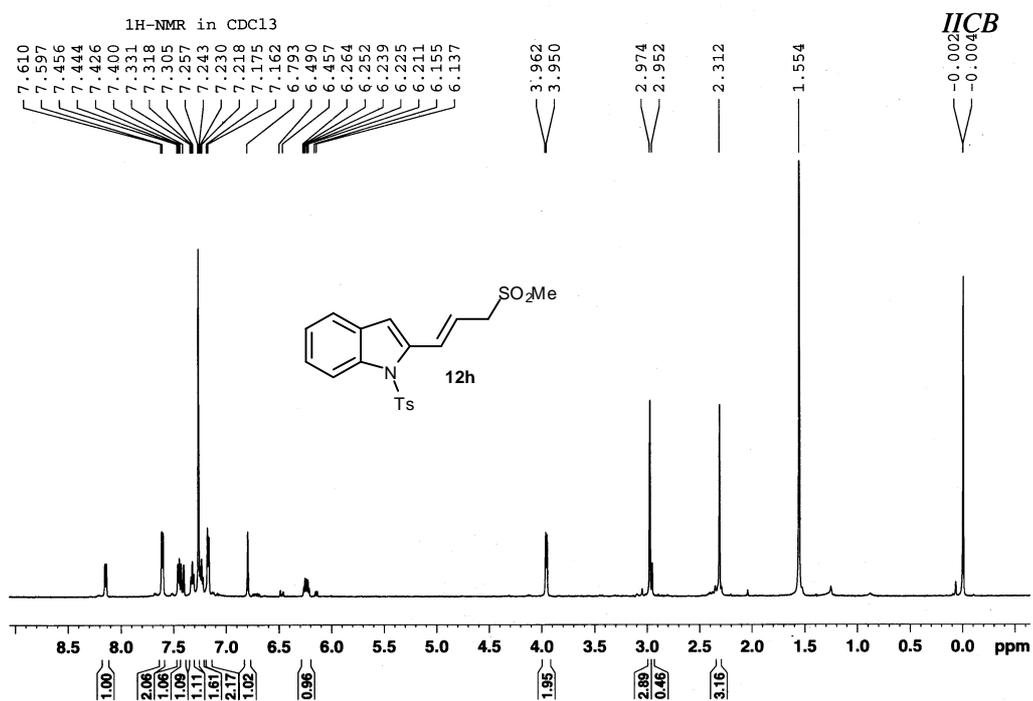
### <sup>1</sup>H NMR (600 MHz) Spectrum of 12g:



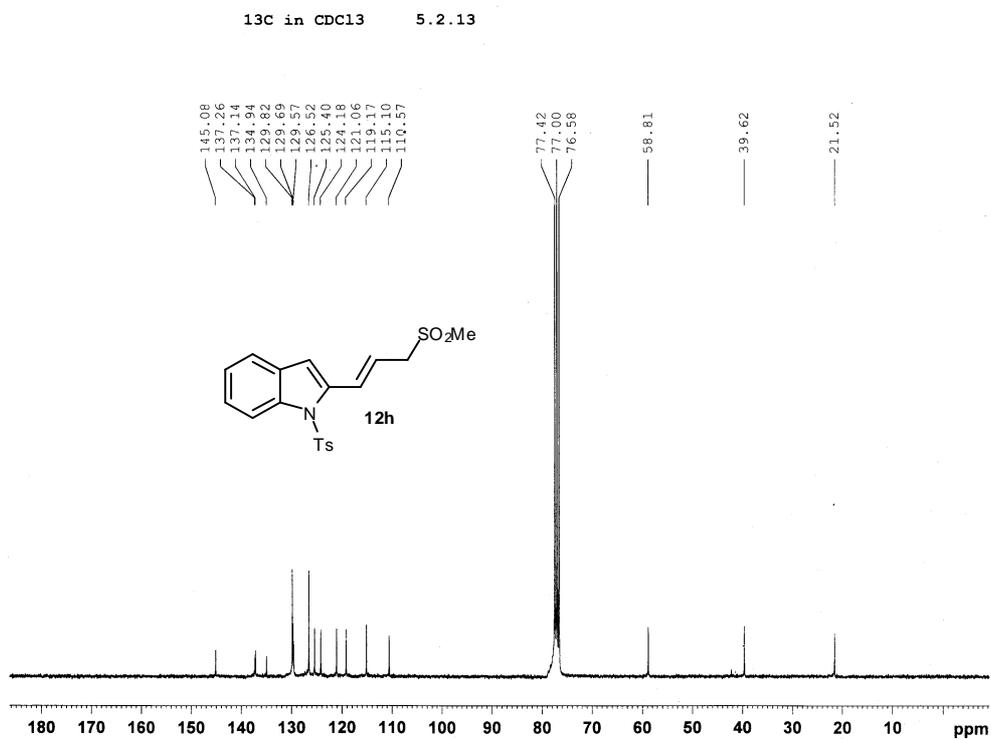
### <sup>13</sup>C NMR (150 MHz) Spectrum of 12g:



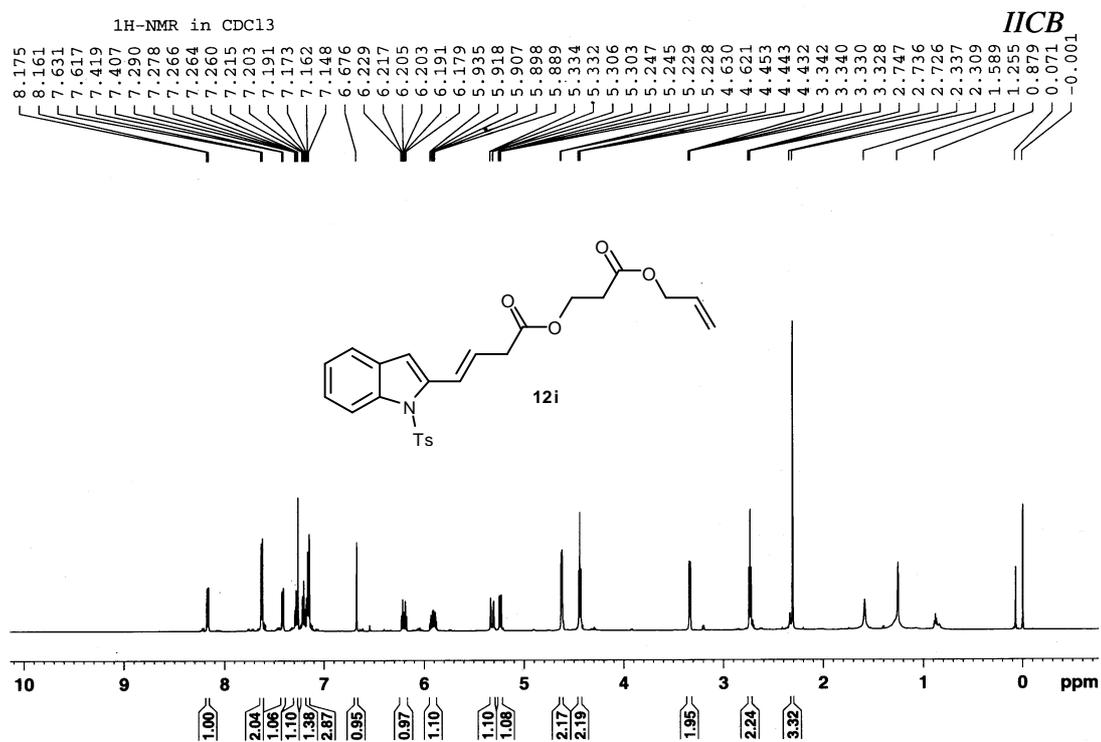
### <sup>1</sup>H NMR (600 MHz) Spectrum of 12h:



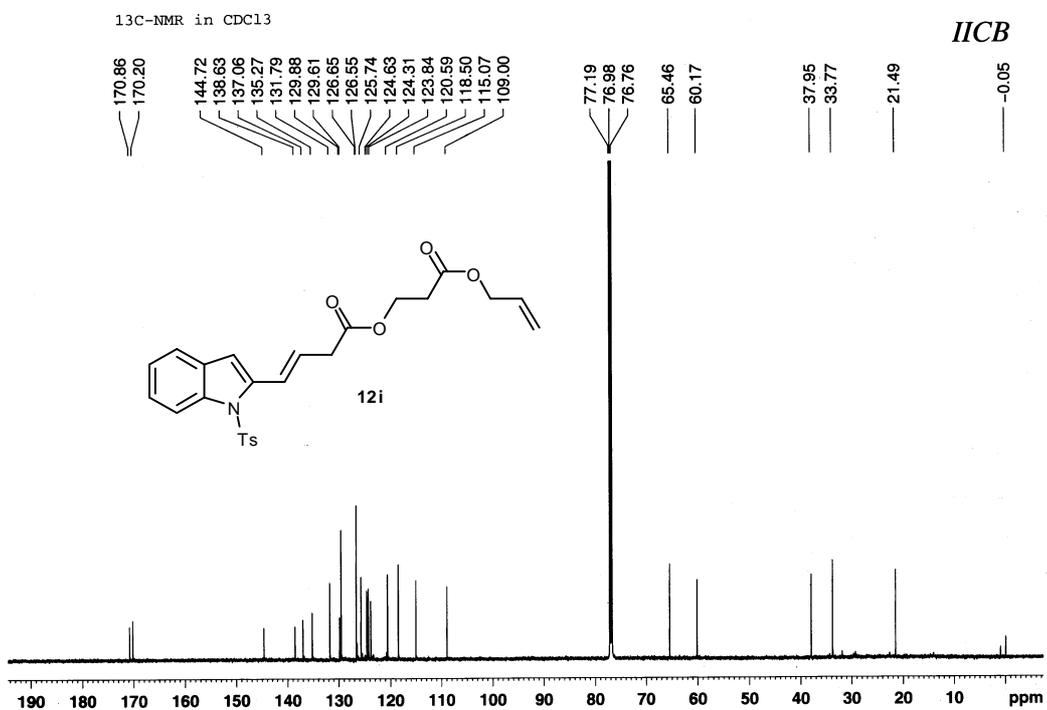
### <sup>13</sup>C NMR (75 MHz) Spectrum of 12h:



### <sup>1</sup>H NMR (600 MHz) Spectrum of 12i:



### <sup>13</sup>C NMR (150 MHz) Spectrum of 12i:



### ESI mass Spectrum of 12i:

