

## Supporting Information

*for*

### **Palladium-catalysed annulative allylic alkylation for the synthesis of benzannulated heteroarenes**

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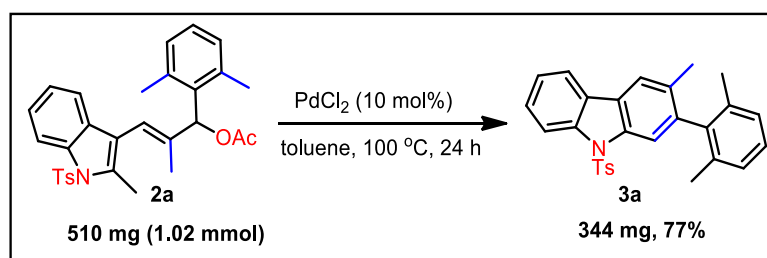
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**General experimental methods:** All the starting compounds and catalysts employed in this study were procured from Sigma-Aldrich and were used without further purification. For thin layer chromatography (TLC), silica aluminium foils/TLC plates with fluorescent indicator 254 nm (from Aldrich/Merck) were used and compounds were visualised by irradiation with UV light and/or by treatment with a solution of p-anisaldehyde (23 mL), conc. H<sub>2</sub>SO<sub>4</sub> (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Column chromatography was performed using SD Fine silica gel 100-200 mesh (approximately 15–20 g per 1 g of the crude product). Dry THF was obtained by distillation over sodium and stored over sodium wire. IR spectra were recorded on a Perkin–Elmer FT IR spectrometer using thin films or KBr pellet, as indicated, with  $\nu_{max}$  in inverse centimetres. Melting points were recorded on a digital melting point apparatus Stuart SMP30 and were uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III FT-NMR spectrometer. NMR shifts are reported as delta ( $\delta$ ) units in parts per million (ppm) and coupling constants ( $J$ ) are reported in Hertz (Hz). The following abbreviations are utilised to describe peak patterns where appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet. Proton chemical shifts are given in  $\delta$  relative to tetramethylsilane ( $\delta$  0.00 ppm) in CDCl<sub>3</sub> ( $\delta$  0.00 ppm) or in (CD<sub>3</sub>)<sub>2</sub>SO ( $\delta$  2.50 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in CDCl<sub>3</sub> ( $\delta$  77.1 ppm) or in (CD<sub>3</sub>)<sub>2</sub>SO ( $\delta$  39.5 ppm). Single crystal X-ray analysis was carried on a Rigaku XtaLAB mini diffractometer. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer.

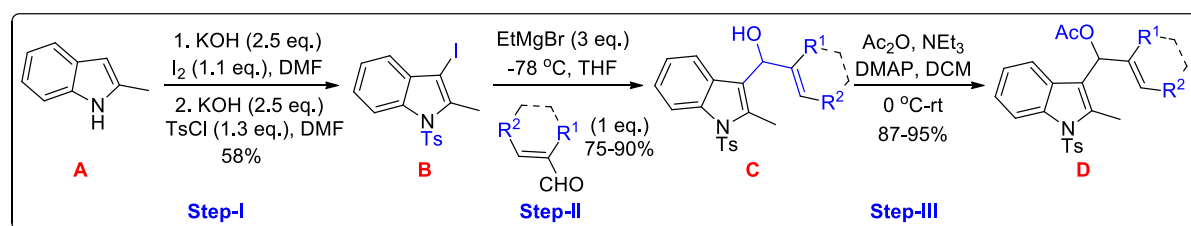
### Scale-up reaction of **2a**

A scale-up reaction with **2a** was performed on 1.02 mmol scale as shown below. The product **3a** was obtained in 77% yield, indicating that the reaction is practical and scalable.





## General procedure-1: Synthesis of allyl acetates 1



**Scheme 1S.** General approach for the synthesis of allyl acetates (**1a** and **1n-1p**).

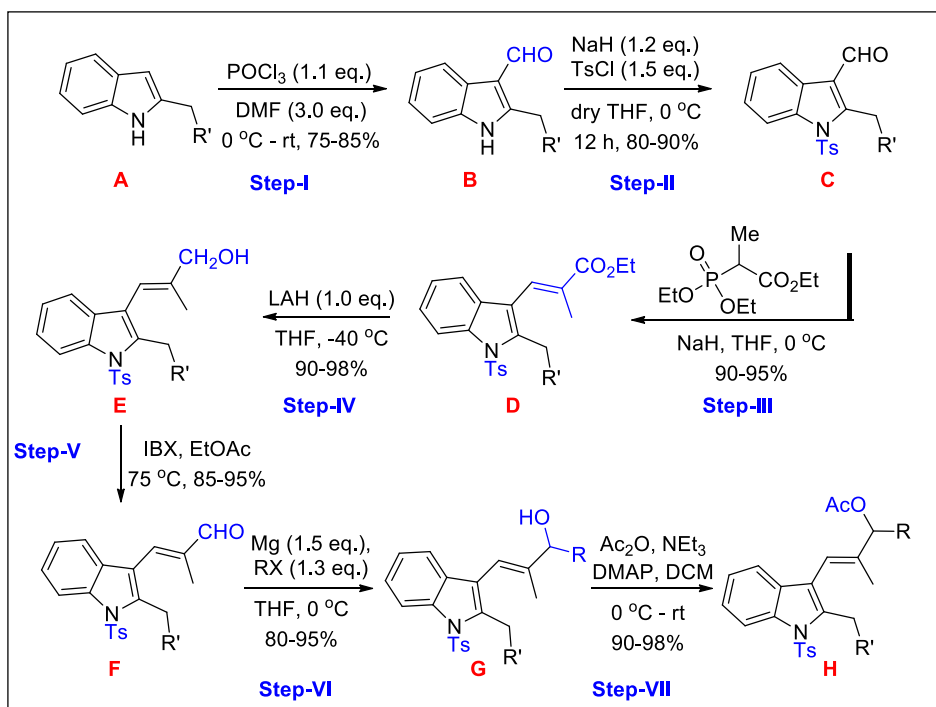
**A representative procedure for step-I:** 2-Methylindole (1 eq.) and KOH (2.5 eq.) were dissolved in DMF. A solution of I<sub>2</sub> (1.1 eq.) in DMF (5 mL) was then added dropwise at 0 °C. The brown coloured solution was stirred at room temperature for the next 30 min. Then, KOH (2.5 eq.) and tosylchloride (1.5 eq.) were added at 0 °C, and stirring was continued overnight at room temperature. The reaction mixture was then extracted with EtOAc several times. The organic layers were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was crystallized from hexanes to give a pale yellow solid **B** (58% yield).

**A representative procedure for step-II:** In an oven dried RB flask, compound **B** (3 eq.) was taken and dissolved in dried THF. EtMgBr (3M in diethylether, 3 eq.) was added to the solution at -78 °C. After stirring the reaction mixture for 1 h, appropriate enal (1 eq.) was added at the same temperature. The reaction mixture was then stirred at room temperature until the complete consumption of starting material (as detected by TLC). The reaction mixture was then quenched by adding saturated aq. NH<sub>4</sub>Cl solution and extracted with EtOAc. The organic layers were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude reaction mixture was purified by silica column chromatography using hexanes–ethyl acetate mixture (4:1) as eluent to obtain compound **C** (75-90% yield).

**A representative procedure for step-III:** Alcohol **C** (1.0 eq.) was dissolved in dry DCM and triethylamine (1.3 eq.), DMAP (0.1 eq.), acetic anhydride (1.3 eq.), were added sequentially at 0 °C. The reaction mixture was then stirred at room temperature, until the starting material was consumed (as detected by TLC). Upon completion, the reaction mixture was quenched by adding saturated aq. NH<sub>4</sub>Cl solution and extracted with DCM. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexanes–ethyl acetate mixture (9:1) as eluent to afford the **D** (87-95% yield).

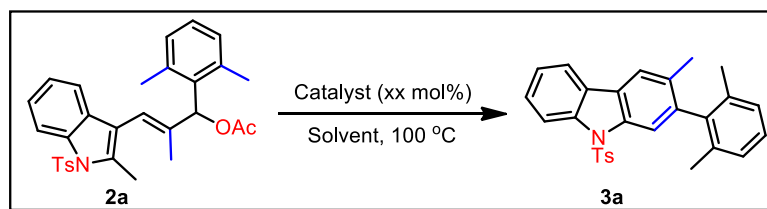
## General procedure-2: Synthesis of allyl acetates 2

Allyl acetates **2** were prepared as described in Scheme 2S.



**Scheme 2S.** General approach for the synthesis of allyl acetates **2**.

## General procedure-3: Screening of reaction parameters



**Scheme 3S.** Representative scheme for the optimization of the reaction conditions.

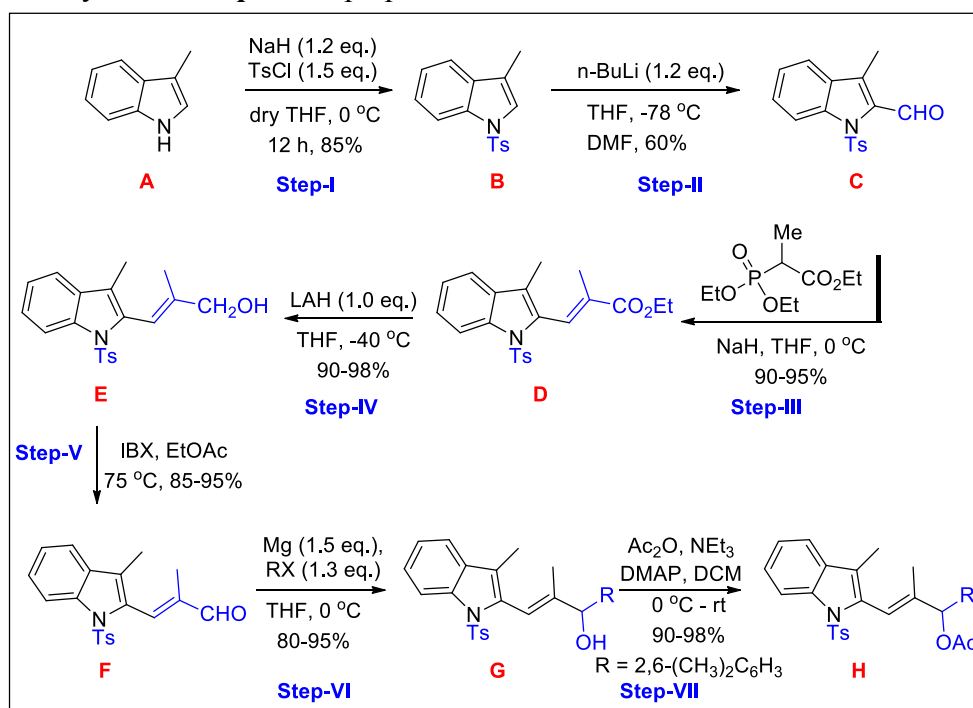
An oven dried 5 mL glass vial was charged with **2a** (0.1 mmol), an appropriate solvent (1.0 mL) and catalyst (as mentioned in Table 1) were introduced at room temperature. The reaction mixture was stirred at a temperature described in Table 1 until **2a** disappeared (as detected by TLC). Then the reaction was quenched with water and extracted with EtOAc (2x2 mL). The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel chromatography using hexanes/ethyl acetate (95:5) as eluent, to afford **3a**.

#### General procedure 4: Evaluating the substrate scope for the synthesis of 2,3-disubstitued carbazoles (**3** and **5**), and di- and tri- substituted dibenzothiophenes (**9**)

An oven dried 5 mL glass vial was charged with **1**, **2**, **4** or **8** (0.1 mmol), and PdCl<sub>2</sub> (0.01 mmol) and toluene (1.0 mL) were subsequently introduced. The reaction was allowed to stir at 100 °C until the starting material disappeared (as monitored by TLC). Then the reaction was quenched with water and extracted with EtOAc (2x2 mL). The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexanes/ethyl acetate (5-10%) as eluent, to afford **3**, **5** or **9** (43-83% yield).

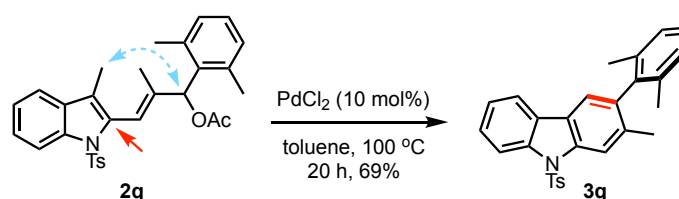
#### General procedure 5: Synthesis of allyl acetate **2q**

The allyl acetate **2q** can be prepared from the methods described in Scheme 4S.



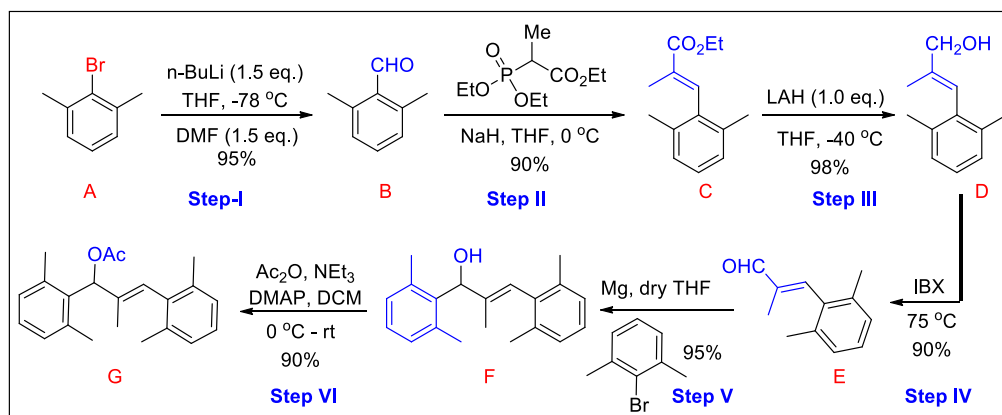
Scheme 4S. General approach for the synthesis of **2q**.

**Reaction with the allyl acetates appended to C-2:** The allyl acetates appended to C-2 position of indoles were also validated. For example, 3-(3-methylindol-2-yl)allyl acetate **2q** provided the respective carbazole **3q** in good yield. As it turns out, the benzenoids obtained by this means are positional isomers to those accessed in Tables 2 and 3.



### General procedure 6: Synthesis of allyl acetate 6

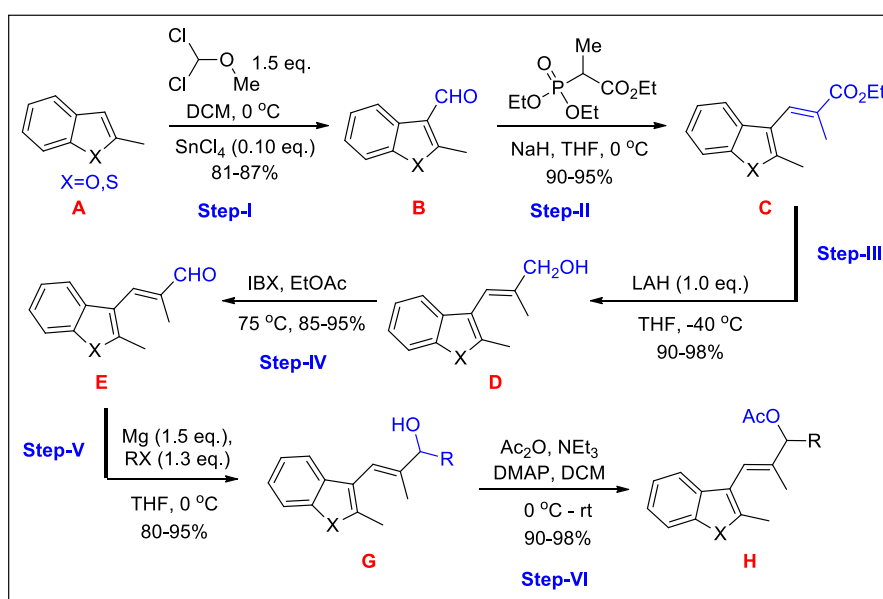
The allyl acetate 6 can be prepared from the methods described in Scheme 5S.



**Scheme 5S.** General approach for the synthesis of 6.

### General procedure 7: Synthesis of allyl acetates 7 and 8

Compounds 7 and 8 can be prepared from the methods described in Scheme 6S.

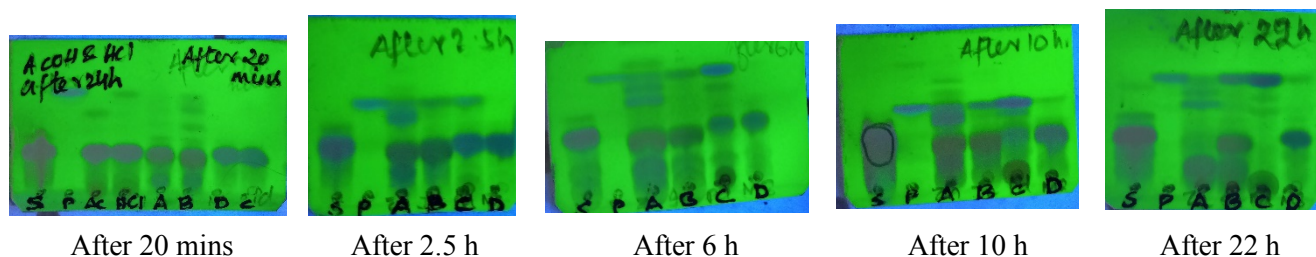


**Scheme 6S.** General approach for the synthesis of allyl acetates 7 and 8.

## Mechanistic Studies

### I. Lewis acid screening

In order to prove that palladium(II) chloride was behaving as a Lewis acid during this study, a brief screening of other well-known Lewis acids was undertaken. The reactions were done as described in the general procedure-4.



**Figure 1S.** Screening of Lewis acids (TLC profiles).

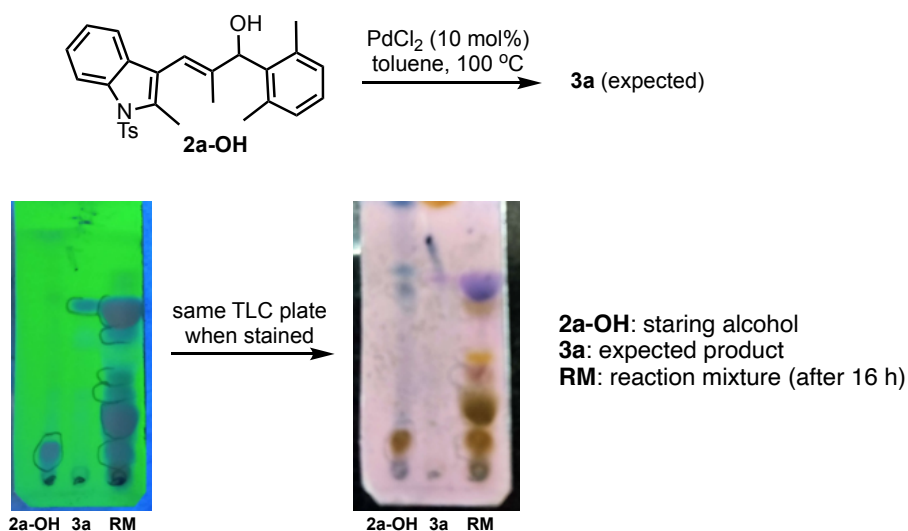
S – starting material (**2a**)

P – expected product (**3a**)

A – ZnCl<sub>2</sub> B - InCl<sub>3</sub> C – PdCl<sub>2</sub> D – MgBr<sub>2</sub>

It can be understood from the TLC patterns that only InCl<sub>3</sub> (**B**) formed the expected product **3a** in about 10%. No other Lewis acids could provide even traces of **3a**. This result indicates that PdCl<sub>2</sub> is not acting as a Lewis acid.

Further, an experiment under the optimized conditions was performed with the respective alcohol of **2a-OH**, Figure 2S. A mixture of several compounds was observed, with the expected product (**3a**) being minor. This result further supports the non-Lewis acidic nature of PdCl<sub>2</sub>.



**Figure 2S.** TLC profile of the reaction of **2a-OH** (the respective alcohol of **2a**).

## II. HRMS analysis of the crude reaction mixture of 2c

The HRMS analysis indicates the potential prevalence of 5- or 7-membered carbopalladated species (analogous to the species **M** and **N** described in Scheme 6). It can also represent the peak corresponding to the loss of the acetate counterion (analogous to **F** in Scheme 6).

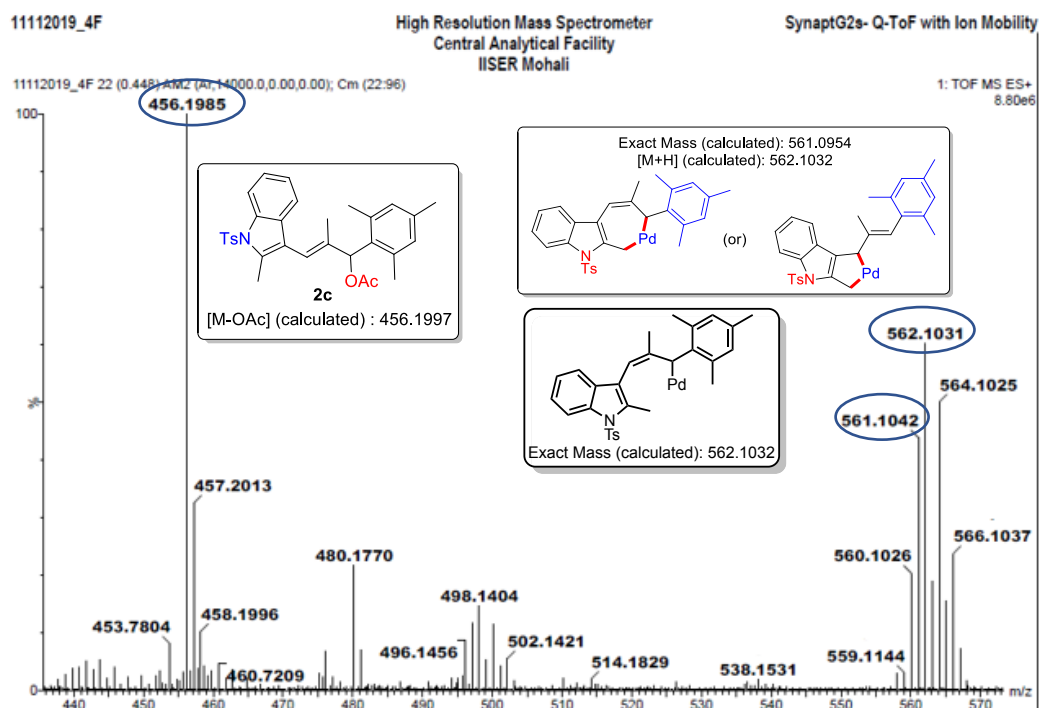
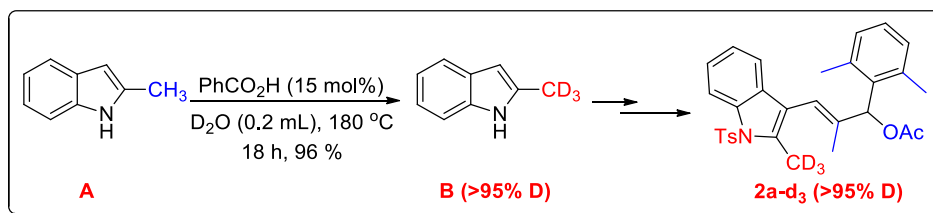


Figure 3S. HRMS data of the crude reaction mixture of 2c after 3 h of reaction.

### III. Calculation of Kinetic isotope effect (KIE)

#### Synthesis of the required starting compound (2a-d<sub>3</sub>):

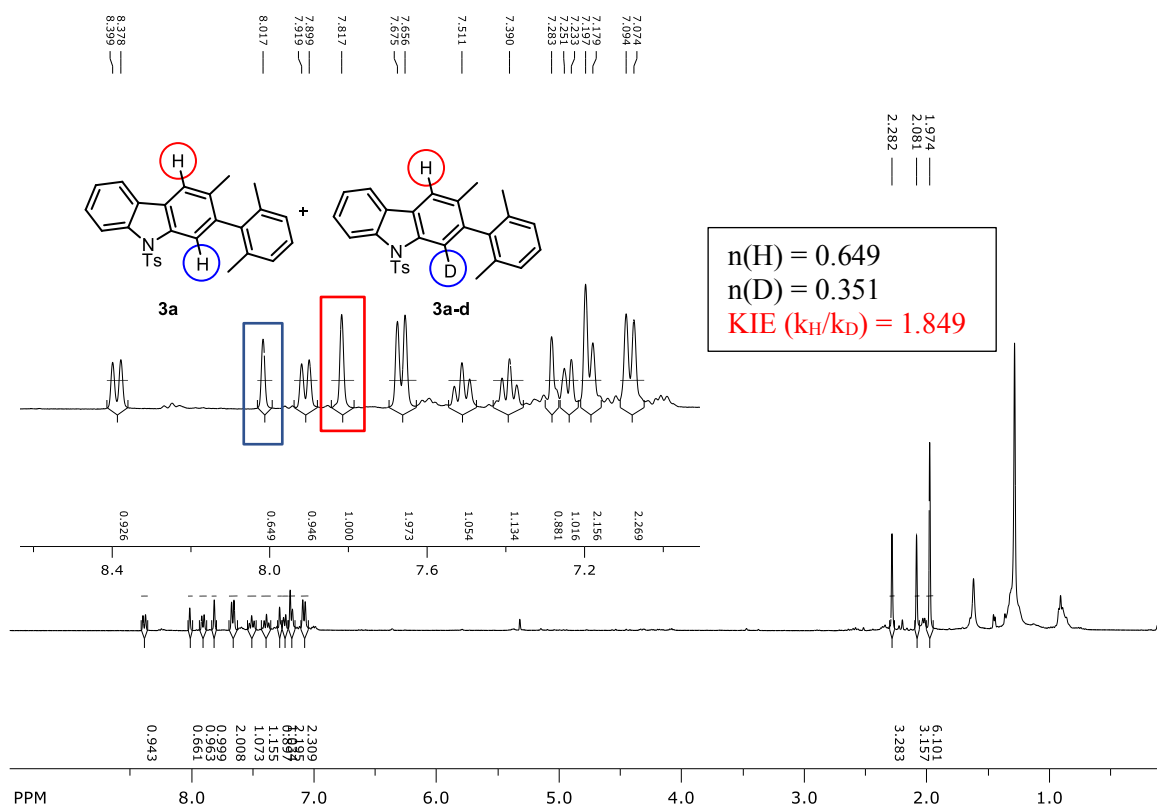


**Scheme 7S.** General approach for the synthesis of **2a-d<sub>3</sub>**.

Compound **B** can be prepared from **A** by following the literature procedure.<sup>1</sup> Further, by following the general procedure-2, compound **2a-d<sub>3</sub>** can be obtained with >95% deuterium incorporation (as indicated by the <sup>1</sup>H-NMR analysis).

#### Determination of the KIE:

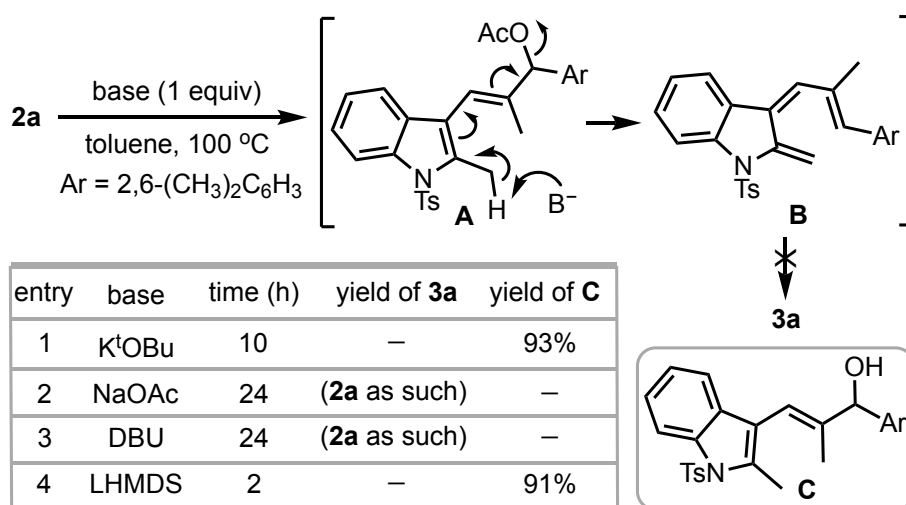
The reaction of **2a** (10 mg, 0.02 mmol) and **2a-d<sub>3</sub>** (10 mg, 0.02 mmol) was performed as described in the general procedure-4. The crude product was purified by silica gel column chromatography to give a mixture of **3a** and **3a-d** in 60% yield (10 mg). The KIE value ( $k_{\text{H}}/k_{\text{D}} \sim 1.85$ ) was determined on the basis of <sup>1</sup>H NMR analysis (see below).



<sup>1</sup> Liu, M.; Chen, X.; Chen, T. *Org. Biomol. Chem.* **2017**, *15*, 2507.

#### IV. The possibility of the formation of the triene **B** and subsequent $6\pi$ -electrocyclization

We intended to see whether the *in situ* generated acetate or chloride possibly acting as base facilitate the abstraction of the benzylic proton. So that the triene formation occurs and subsequently the  $6\pi$ -electrocyclization. For example, **3a** can also form via the  $6\pi$ -electrocyclization of the triene **B**. However, the reaction of **2a** with different bases only afforded the allyl alcohol **C**, suggesting that **2a** may not be amenable for the generation of trienes such as **B** (in a pathway shown in **A**), and thus questioning the  $6\pi$ -electrocyclization pathway during the formation of **3a**.

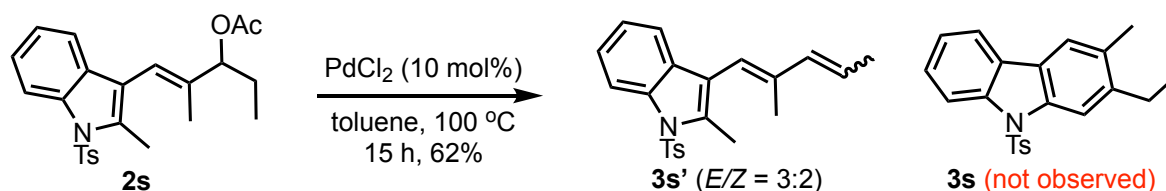


**Scheme 8S.** The reaction of **2a** under basic conditions



## V. The reaction of **2s**, possessing an aliphatic group at R<sup>1</sup>

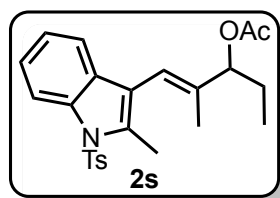
As part of the evaluation of the substrate scope, the reaction of the acetate **2s** with an aliphatic group at R<sup>1</sup> was considered, Scheme 9S. Against the expected carbazole **3s**, only the elimination product **3s'** was observed. This result indicates the significance of the nature of the substitution at R<sup>1</sup>. This method in the present form does not tolerate aliphatic groups at R<sup>1</sup>.



**Scheme 9S.** The reaction of the acetate **2s** with aliphatic group at R<sup>1</sup>.

### 2-Methyl-1-(2-methyl-1-tosyl-1H-indol-3-yl)pent-1-en-3-yl acetate (**2s**):

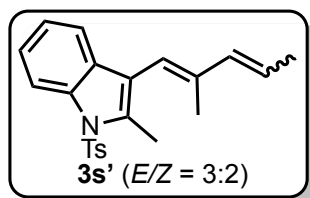
This compound was isolated as a pale yellow viscous liquid by following the general procedure



1. R<sub>f</sub> = 0.5 (Hexane/EtOAc = 8/2). **IR (thin film, neat):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2972, 2932, 1733, 1737, 1238, 1089. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.2 (d,  $J$  = 8.2 Hz, 1H), 7.66 (d,  $J$  = 7.9 Hz, 2H), 7.30-7.20 (m, 5H), 6.32 (s, 1H), 5.27 (t,  $J$  = 6.8 Hz, 1H), 2.46 (s, 3H), 2.34 (s, 3H), 2.12 (s, 3H), 1.79 (dq,  $J$  = 15 and 7.3 Hz, 2H), 1.51 (s, 3H), 0.99 (t,  $J$  = 7.4 Hz, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  170.40, 144.68, 140.10, 136.3, 136.18, 133.3, 130.01, 129.82 (2C), 126.3 (3C), 124.11, 123.4, 119.26, 118.2, 117.9, 114.5, 79.8, 25.7, 21.5, 21.3, 14.1, 9.8. **HRMS (ESI):**  $m/z$  calcd for C<sub>24</sub>H<sub>27</sub>NNaO<sub>4</sub>S (M+Na)<sup>+</sup>: 448.1558, Found: 448.1559.

### 2-Methyl-3-(2-methylpenta-1,3-dien-1-yl)-1-tosyl-1H-indole (**3s'**):

This compound was isolated as transparent liquid. Following the general procedure **4**, 30 mg

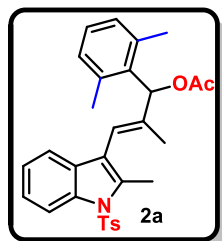


of **2s** afforded 16 mg of **3s'** (62% yield). R<sub>f</sub> = 0.5 (Hexane/EtOAc = 20/1). **IR (thin film, neat):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2932, 1455, 1175, 667, 541. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.24-8.20 (m, 1H), 7.68 (d,  $J$  = 8 Hz, 2H), 7.35-7.7.28 (m, 2H), 7.24-7.20 (m, 3H), 6.36 (d,  $J$  = 15.5 Hz, 1H), 6.21 (s, 1H), 5.88-5.80 (m, 1H), 2.48 (s, 3H), 2.36 (s, 3H), 1.87 (d,  $J$  = 6.6 Hz, 3H), 1.66 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  144.6, 139.49, 136.35, 135.30, 133.331, 130.32, 129.8 (2C), 127.13, 126.31 (2C), 125.36, 124.05, 123.38, 119.42, 119.25, 118.565, 114.56, 21.55, 18.36, 14.82, 14.25. **HRMS (ESI):**  $m/z$  calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>2</sub>S (M+H)<sup>+</sup>: 366.1528, Found: 366.1512.

## Spectral data of all the new compounds reported in this study

### 1-(2,6-Dimethylphenyl)-2-methyl-3-(2-methyl-1-tosyl-1*H*-indol-3-yl)allyl acetate (**2a**):

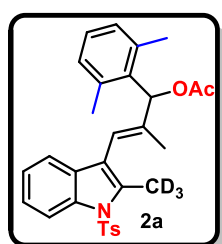
This compound was isolated as pale-yellow solid by following the general procedure **2**, M.P =



139 °C.  $R_f = 0.5$  (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2915, 1738, 1457, 1178.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.28 (d,  $J = 8.1$  Hz, 1H), 7.7 (d,  $J = 7.6$  Hz, 2H), 7.36-7.32 (m, 1H), 7.29 (brs, 2H), 7.22-7.16 (m, 3H), 7.12-7.10 (m, 2H), 6.96 (s, 1H), 6.16 (s, 1H), 2.6 (s, 6H), 2.53 (s, 3H), 2.35 (s, 3H), 2.21 (s, 3H), 1.62 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.1, 144.7, 139.4, 137.7 (2CH), 136.4, 136.1, 134.5, 133.2, 130.1, 129.8 (2CH), 129.1 (2CH), 128.2, 126.3 (2CH), 124.2, 123.5, 119.2, 118.5, 116.2, 114.7, 75.1, 21.5, 21.06, 20.8 (2CH), 16.1, 14.2. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{30}\text{H}_{31}\text{NO}_4\text{S}$  ( $\text{M}^+$ ): 501.1974, Found: 501.2003.

### 1-(2,6-Dimethylphenyl)-2-methyl-3-(2-deuterium-1-tosyl-1*H*-indol-3-yl)allyl acetate (**2a**):

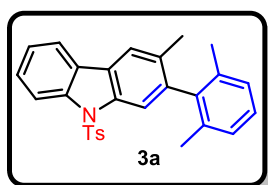
This compound was isolated as pale-yellow solid by following the procedure described in KIE



experiment. **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2924, 1738, 1451, 1022, 584.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.21 (d,  $J = 8.2$  Hz, 1H), 7.66 (d,  $J = 7.9$  Hz, 2H), 7.32-7.28 (m, 1H), 7.24-7.19 (m, 4H), 7.14 (d,  $J = 7.5$  Hz, 1H), 7.08-7.06 (m, 2H), 6.89 (s, 1H), 6.08 (s, 1H), 2.54 (s, 6H), 2.35 (s, 3H), 2.17 (s, 3H), 1.55 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.2, 144.7, 139.3, 137.7 (2CH), 136.3, 136.1, 134.4, 133.1, 130.06, 130.4, 129.8 (2CH), 129.1, 128.1, 126.2 (3CH), 124.1, 123.4, 119.1, 118.4, 116.1, 114.6, 75.1, 21.56, 21.04, 20.8 (2CH), 16.00. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{30}\text{H}_{28}\text{D}_3\text{NO}_4\text{S}$  ( $\text{M-OAc}$ ): 445.2029, Found: 445.2040.

### 2-(2,6-Dimethylphenyl)-3-methyl-9-tosyl-9*H*-carbazole (**3a**):

This compound was isolated as transparent liquid. Following the general procedure **4**, 50 mg

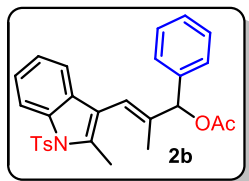


of **2a** afforded 35 mg of **3a** (81% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2356, 1369, 1173.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.39 (d,  $J = 8.4$  Hz, 1H), 8.02 (s, 1H), 7.91 (d,  $J = 7.8$  Hz, 1H), 7.82 (s, 1H), 7.67 (d,  $J = 7.8$  Hz, 2H), 7.52 (t,  $J = 7.6$  Hz, 1H), 7.41-7.38 (m, 1H), 7.25 (d,  $J = 7$  Hz, 1H), 7.20-7.18 (m, 2H), 7.12-7.08 (m, 2H), 2.29 (s, 3H), 2.09 (s, 3H), 1.98 (s, 6H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  144.7, 140.9, 140.4, 138.8, 137.1, 135.8 (2CH), 134.7, 131.9, 129.4 (2CH), 127.9 (2CH), 127.2, 127.1, 126.6, 126.5 (2CH),

125.7, 124.02, 121.03, 119.7, 115.5, 115.4, 21.5, 20.3 (2CH), 19.5. **HRMS (ESI):** m/z calcd for C<sub>28</sub>H<sub>26</sub>NO<sub>2</sub>S (M+H)<sup>+</sup>: 440.1684, Found: 440.1677.

### 2-Methyl-3-(2-methyl-1-tosyl-1H-indol-3-yl)-1-phenylallyl acetate (2b):

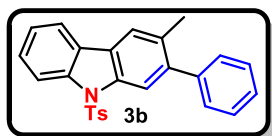
This compound was isolated as yellow viscous liquid by following the general procedure 2. R<sub>f</sub>



= 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2919, 1722, 1347, 1257, 1178. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.25 (d,  $J = 8.3$  Hz, 1H), 7.69 (d,  $J = 8.1$  Hz, 2H), 7.51-7.49 (m, 2H), 7.4 (t,  $J = 7.4$  Hz, 2H), 7.39-7.35 (m, 1H), 7.33-7.31 (m, 2H), 7.28-7.25 (m, 1H), 7.21-7.19 (m, 2H), 6.56 (s, 1H), 6.4 (s, 1H), 2.5 (s, 3H), 2.35 (s, 3H), 2.24 (s, 3H), 1.48 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  169.954, 144.776, 140.510, 138.596, 136.366, 136.136, 133.526, 130.025, 129.875 (2CH), 128.621 (2CH), 128.176, 126.907 (2CH), 126.331 (2CH), 124.229, 123.535, 119.292, 118.153, 117.466, 114.649, 79.396, 21.574, 21.341, 15.087, 14.215. **HRMS (ESI):** m/z calcd for C<sub>28</sub>H<sub>28</sub>NO<sub>4</sub>S (M+H)<sup>+</sup>: 474.1739, Found: 474.1760.

### 3-Methyl-2-phenyl-9-tosyl-9H-carbazole (3b):

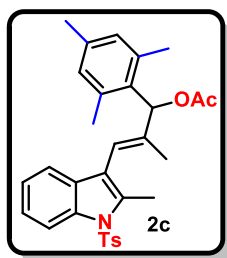
This compound was isolated as transparent liquid. Following the general procedure 4, 50 mg



of **2b** afforded 30 mg of **3b** (69% yield). R<sub>f</sub> = 0.5 (Hexane/EtOAc = 20/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2359, 1179, 1187, 667, 597. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.36 (d,  $J = 8.4$  Hz, 1H), 8.23 (s, 1H), 7.92 (d,  $J = 7.7$  Hz, 1H), 7.8 (s, 1H), 7.73 (d,  $J = 8$  Hz, 2H), 7.53-7.49 (m, 3H), 7.45-7.35 (4H), 7.13 (d,  $J = 7.9$  Hz, 2H), 2.4 (s, 3H), 2.28 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  144.8, 142.02, 141.7, 138.8, 136.8, 134.9, 131.5, 129.6 (2CH), 129.4 (2CH), 128.2 (2CH), 127.2, 127.09, 126.5 (2CH), 126.2, 125.5, 123.9, 121.1, 119.9, 116.1, 115.2, 21.5, 20.7. **HRMS (ESI):** m/z calcd for C<sub>26</sub>H<sub>22</sub>NO<sub>2</sub>S (M+H)<sup>+</sup>: 412.1371, Found: 412.1354.

### 1-Mesityl-2-methyl-3-(2-methyl-1-tosyl-1H-indol-3-yl)allyl acetate (2c):

This compound was isolated as yellow solid by following the general procedure 2. M.P = 119

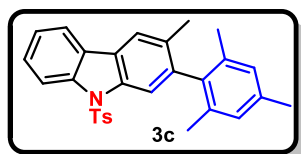


°C. R<sub>f</sub> = 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2977, 1737, 1372, 1175. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.25 (d,  $J = 8.3$  Hz, 1H), 7.6 (d,  $J = 8.3$  Hz, 2H), 7.35-7.31 (m, 1H), 7.27-7.25 (m, 2H), 7.21 (d,  $J = 8.1$  Hz, 2H), 6.92 (s, 2H), 6.9 (s, 1H), 6.14 (s, 1H), 2.54 (s, 6H), 2.50 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H), 2.18 (s, 3H), 1.58 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  170.2, 144.7, 139.6, 137.7, 137.6 (2CH), 136.4, 136.1, 133.1,

131.5, 130.1, 129.9 (2CH), 129.8 (2CH), 126.3 (2CH), 124.1, 123.4, 119.2, 118.5, 116.03, 114.6, 75.04, 21.5, 21.08, 20.9, 20.7 (2CH), 16.07, 14.19. **HRMS (ESI)**:  $m/z$  calcd for  $C_{29}H_{30}NO_2S$  (M-OAc)<sup>+</sup>: 456.1997, Found: 456.2009.

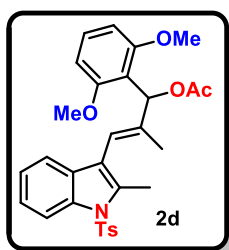
### 2-Mesityl-3-methyl-9-tosyl-9H-carbazole (3c):

This compound was isolated as transparent liquid. Following the general procedure 4, 50 mg of **2c** afforded 35 mg of **3c** (80% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR (thin film, neat)**:



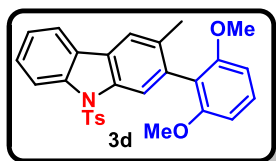
$\nu_{max}/cm^{-1}$  2344, 1422, 1342, 1182.  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**:  $\delta$  8.4 (d,  $J = 8.4$  Hz, 1H), 8.02 (s, 1H), 7.91 (d,  $J = 7.7$  Hz, 1H), 7.81 (s, 1H), 7.6 (d,  $J = 8.1$  Hz, 2H), 7.51 (d,  $J = 7.8$  Hz, 1H), 7.41-7.37 (m, 1H), 7.08 (d,  $J = 8.1$  Hz, 2H), 7.03 (s, 2H), 2.39 (s, 3H), 2.28 (s, 3H), 2.09 (s, 3H), 1.95 (s, 6H).  **$^{13}C$  NMR (100 MHz,  $CDCl_3$ )**:  $\delta$  144.7, 140.4, 138.8, 138.1, 137.1, 136.7, 135.6 (2CH), 134.7, 132.1, 129.4 (2CH), 128.1 (2CH), 127.1, 126.6, 126.5 (2CH), 125.6, 124.01, 120.9, 119.7, 115.7, 115.4, 21.5, 21.1, 20.2 (2CH), 19.6. **HRMS (ESI)**:  $m/z$  calcd for  $C_{29}H_{27}NO_2SNa$  (M+Na)<sup>+</sup>: 476.1660, Found: 476.1639.

### 1-(2,6-Dimethoxyphenyl)-2-methyl-3-(2-methyl-1-tosyl-1H-indol-3-yl)allyl acetate (2d):



This compound was isolated as yellow viscous liquid by following the general procedure 2.  $R_f = 0.5$  (Hexane/EtOAc = 8/2). **IR (thin film, neat)**:  $\nu_{max}/cm^{-1}$  2259, 1750, 1486, 901.  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**:  $\delta$  8.20-8.18 (m, 1H), 7.6 (d,  $J = 8.3$  Hz, 2H), 7.30-7.28 (m, 3H), 7.23 (d,  $J = 7.5$  Hz, 1H), 7.18 (d,  $J = 8.2$  Hz, 2H), 7.04 (s, 1H), 6.6 (d,  $J = 8.4$  Hz, 2H), 6.2 (s, 1H), 3.8 (s, 6H), 2.4 (s, 3H), 2.3 (s, 3H), 2.15 (s, 3H), 1.42 (s, 3H).  **$^{13}C$  NMR (100 MHz,  $CDCl_3$ )**:  $\delta$  170.51, 159.2 (2CH), 144.5, 139.8, 136.3, 136.1, 130.4, 129.9, 129.7 (3CH), 126.2 (3CH), 123.9, 123.3, 119.3, 119.2, 114.5, 113.3, 104.4 (2CH), 70.3, 55.9 (2CH), 21.5, 21.3, 15.8, 14.0. **HRMS (ESI)**:  $m/z$  calcd for  $C_{28}H_{28}NO_4S$  (M-OAc)<sup>+</sup>: 474.1739, Found: 474.1723.

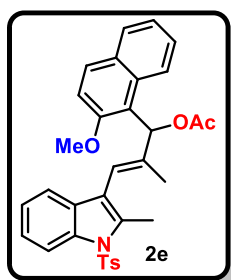
### 2-(2,6-Dimethoxyphenyl)-3-methyl-9-tosyl-9H-carbazole (3d):



This compound was isolated as white solid. Following the general procedure 4, 50 mg of **2d** afforded 35 mg of **3d** (79% yield). M.P = 160 °C.  $R_f = 0.5$  (Hexane/EtOAc = 9/1). **IR (thin film, neat)**:  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**:  $\delta$  8.35 (d,  $J = 8.3$  Hz, 1H), 8.18 (s, 1H), 7.8 (d,  $J = 7.6$  Hz, 1H), 7.8 (s, 1H), 7.7 (d,  $J = 7.6$  Hz, 2H), 7.4 (t,  $J = 7.8$  Hz, 1H), 7.41-7.34 (m, 2H), 7.1 (d,  $J = 7.8$  Hz, 2H), 6.7 (d,  $J = 8.3$  Hz, 2H), 3.8 (s, 6H), 2.28 (s, 3H), 2.21 (s, 3H).  **$^{13}C$  NMR (100**

**MHz, CDCl<sub>3</sub>**):  $\delta$  157.7 (2CH), 144.5, 138.7, 136.6, 134.9, 134.1, 133.6, 129.4 (2CH), 129.0, 126.96, 126.90, 126.6 (2CH), 125.8, 123.8, 120.4, 119.8, 118.9, 117.6, 115.3, 104.1 (2CH), 55.9 (2CH), 21.5, 19.8. **HRMS (ESI)**:  $m/z$  calcd for C<sub>28</sub>H<sub>25</sub>NO<sub>4</sub>SNa (M+Na)<sup>+</sup>: 494.1402, Found: 494.1381.

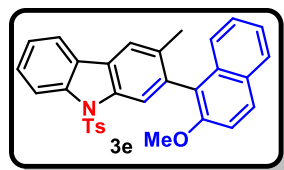
**1-(2-methoxynaphthalen-1-yl)-2-methyl-3-(2-methyl-1-tosyl-1H-indol-3-yl)allyl acetate (2e):**



This compound was isolated as colorless viscous liquid by following the general procedure 2.  $R_f$  = 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat)**:  $\nu_{\max}/\text{cm}^{-1}$  2261, 1738, 1511, 1373, 1226. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  8.49 (d,  $J$  = 8.7 Hz, 1H), 8.19 (d,  $J$  = 8.3 Hz, 1H), 7.88-7.79 (m, 2H), 7.66-7.62 (m, 2H), 7.55 (s, 1H), 7.52-7.48 (m, 1H), 7.41-7.37 (m, 1H), 7.3 (d,  $J$  = 9.1 Hz, 1H), 7.28-7.26 (m, 1H), 7.22-7.16 (m, 4H), 6.34 (s, 1H), 4.05 (s, 3H), 2.4 (s, 3H), 2.3 (s, 3H), 2.1 (s, 3H), 1.4 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  170.1, 155.5, 144.6, 140.5, 136.3, 136.1, 133.2, 132.5, 130.8, 130.2, 129.78 (2CH), 129.72, 128.5, 126.2 (2CH), 126.1, 125.4, 124.04, 123.6, 123.4, 119.3, 118.8, 118.7, 115.1, 114.5, 113.7, 71.7, 57.2, 21.5, 21.1, 15.9, 14.08. **HRMS (ESI)**:  $m/z$  calcd for C<sub>31</sub>H<sub>28</sub>NO<sub>3</sub>S (M-OAc)<sup>+</sup>: 494.1790, Found: 494.1769.

**2-(2-Methoxynaphthalen-1-yl)-3-methyl-9-tosyl-9H-carbazole (3e):**

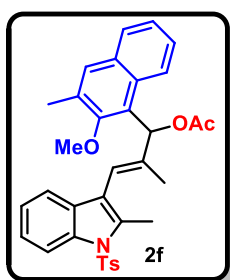
This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of **2e** afforded 34 mg of **3e** (77% yield).  $R_f$  = 0.5 (Hexane/EtOAc = 20/1). **IR (thin film, neat)**: 2523,



1369, 658, 590. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  8.4 (d,  $J$  = 8.3 Hz, 1H), 8.18 (s, 1H), 8.0-7.8 (m, 4H), 7.6 (d,  $J$  = 7.7 Hz, 2H), 7.5 (t,  $J$  = 7.8 Hz, 1H), 7.47-7.32 (m, 4H), 7.18 (d,  $J$  = 8.5 Hz, 1H), 7.11 (d,  $J$  = 7.8 Hz, 2H), 3.9 (s, 3H), 2.32 (s, 3H), 2.12 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  153.8, 144.6, 138.9, 136.7, 136.01, 134.7, 133.8, 133.6, 129.5 (2CH), 129.3, 129.05, 128.06, 127.1, 126.7, 126.6 (2CH), 126.3, 126.1, 124.8, 124.3, 124.02, 123.5, 120.8, 119.8, 117.6, 115.5, 113.5, 56.5, 21.5, 19.8. **HRMS (ESI)**:  $m/z$  calcd for C<sub>31</sub>H<sub>26</sub>NO<sub>3</sub>S (M+H)<sup>+</sup>: 492.1633, Found: 492.1647.

**1-(2-Methoxy-3-methylnaphthalen-1-yl)-2-methyl-3-(2-methyl-1-tosyl-1H-indol-3-yl)allyl acetate (2f):**

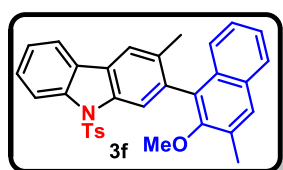
This compound was isolated as yellow viscous liquid by following the general procedure 2.  $R_f$



= 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2233, 1699, 1412, 1250.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.47 (d,  $J$  = 8.3 Hz, 1H), 8.19 (d,  $J$  = 8.3 Hz, 1H), 7.78-7.76 (m, 1H), 7.7 (s, 1H), 7.63 (d,  $J$  = 8.3 Hz, 2H), 7.51-7.41 (m, 3H), 7.30-7.26 (m, 1H), 7.20-7.16 (m, 4H), 6.24 (s, 1H), 3.97 (s, 3H), 2.53 (s, 3H), 2.4 (s, 3H), 2.34 (s, 3H), 2.17 (s, 3H), 1.52 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.216, 156.243, 144.653, 140.676, 136.350, 136.131, 132.236, 131.578, 131.270, 131.181, 130.122, 130.121, 129.796 (2C), 127.842, 126.272 (2C), 125.993, 125.121, 124.839, 124.175, 124.075, 123.421, 119.295, 118.587, 116.112, 114.589, 72.719, 61.349, 21.553, 21.225, 17.22, 16.157, 14.078. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{32}\text{H}_{30}\text{NO}_3\text{S}$  (M-OAc) $^+$ : 508.1946, Found: 508.1924.

### 2-(2-Methoxy-3-methylnaphthalen-1-yl)-3-methyl-9-tosyl-9H-carbazole (3f):

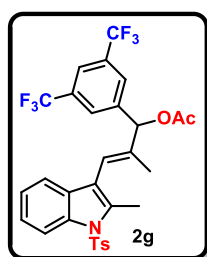
This compound was isolated as viscous transparent liquid. Following the general procedure 4,



50 mg of **2f** afforded 33 mg of **3f** (72% yield).  $R_f$  = 0.5 (Hexane/EtOAc = 20/1). **IR (thin film, neat):** 2523, 1330, 670, 549.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.45 (d,  $J$  = 8.4 Hz, 1H), 8.29 (s, 1H), 7.97 (d,  $J$  = 7.6 Hz, 1H), 7.9 (s, 1H), 7.86 (d,  $J$  = 8.1 Hz, 1H), 7.8 (s, 1H), 7.7 (d,  $J$  = 8.1 Hz, 2H), 7.56 (t,  $J$  = 7.8 Hz, 1H), 7.44 (q,  $J$  = 7.3 Hz, 2H), 7.34-7.28 (m, 1H), 7.23-7.21 (m, 1H), 7.11 (d,  $J$  = 8.1 Hz, 2H), 3.48 (s, 3H), 2.59 (s, 3H), 2.31 (s, 3H), 2.19 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  154.441, 144.785, 139.026, 136.561, 135.988, 134.753, 133.869, 132.426, 131.439, 130.917, 129.637, 129.545 (2C), 129.394, 127.380, 127.332, 126.682 (2C), 126.642, 126.282, 125.335, 125.191, 124.790, 124.135, 120.926, 119.987, 117.685, 115.561, 60.203, 21.568, 20.044, 17.272. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{32}\text{H}_{28}\text{NO}_3\text{S}$  (M+H) $^+$ : 506.1790, Found: 506.1779.

### 1-(3,5-Bis(trifluoromethyl)phenyl)-2-methyl-3-(2-methyl-1-tosyl-1H-indol-3-yl)allyl acetate (2g):

This compound was isolated as yellow viscous liquid by following the general procedure 2.  $R_f$

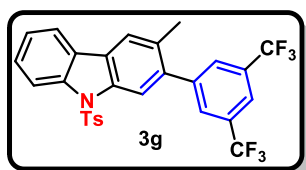


= 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2989, 1746, 1279, 1174, 1229, 577.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.24 (d,  $J$  = 8.3 Hz, 1H), 7.98 (s, 2H), 7.92 (s, 1H), 7.69 (d,  $J$  = 8.3 Hz, 2H), 7.34-7.28 (m, 1H), 7.27-7.26 (m, 2H), 7.21 (d,  $J$  = 8.3 Hz, 2H), 6.67 (s, 1H), 6.53 (s, 1H), 2.48 (s, 3H), 2.3 (s, 3H), 2.28 (s, 3H), 1.47 (s, 3H).  **$^{13}\text{C NMR}$  (100**

**MHz, CDCl<sub>3</sub>**):  $\delta$  169.582, 144.881, 141.623, 139.025, 136.315, 136.092, 133.732, 131.987 (q,  $J = 66.6$  Hz, 1C), 129.885 (2CH), 126.928, 126.323 (3C), 125.759 (q,  $J = 272.6$  Hz, 1C), 124.601, 123.601, 122.165, 122.131, 122.094, 122.059, 120.000, 119.035, 117.349, 114.657, 78.190, 21.458, 21.050, 14.551, 14.002. **<sup>19</sup>F NMR (374 MHz, CDCl<sub>3</sub>)**:  $\delta$  -62.838. **HRMS (ESI)**:  $m/z$  calcd for C<sub>28</sub>H<sub>22</sub>F<sub>6</sub>NO<sub>2</sub>S (M-OAc)<sup>+</sup>: 550.1275, Found: 550.1255.

### 2-(3,5-Bis(trifluoromethyl)phenyl)-3-methyl-9H-carbazole (3g):

This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of

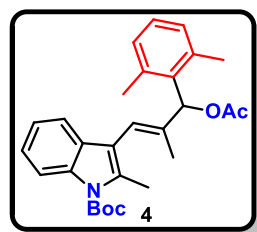


**2g** afforded 37 mg of **3g** (83% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR (thin film, neat)**: 2931, 1274, 686, 541. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  8.36 (d,  $J = 8.4$  Hz, 1H), 8.17 (s, 1H), 7.96-7.94 (m, 2H), 7.8 (d,  $J = 9.9$  Hz, 3H), 7.72-7.69 (m, 2H), 7.55 (dd,  $J =$

8.4, 7.3 and 1.3 Hz, 1H), 7.44-7.40 (m, 1H), 7.16 (d,  $J = 8.1$  Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  145.1401, 143.9855, 138.9822, 138.2161, 135.8333 (d,  $J = 245$  Hz, 1C), 131.6364 (d,  $J = 41$  Hz, 1CH), 131.1402, 130.3338 (d,  $J = 179.8$  Hz, 1C), 129.7745 (3CH), 127.8454 (2CH), 126.6327, 126.5452 (3CH), 125.7230, 124.7366, 124.1034, 122.0234, 121.7372, 121.1540, 120.2259, 115.9143, 115.2259, 21.5663, 20.5171. **<sup>19</sup>F NMR (374 MHz, CDCl<sub>3</sub>)**:  $\delta$  -62.843. **HRMS (ESI)**:  $m/z$  calcd for C<sub>28</sub>H<sub>19</sub>F<sub>6</sub>NO<sub>2</sub>S (M)<sup>+</sup>: 547.1041, Found: 547.1022.

### tert-Butyl 3-(3-acetoxy-3-(2,6-dimethylphenyl)-2-methylprop-1-en-1-yl)-2-methyl-1H-indole-1-carboxylate (4):

This compound was isolated as white solid by following the general procedure 2. M.P = 150



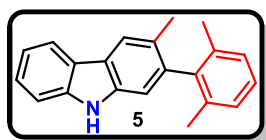
$^{\circ}\text{C}$ .  $R_f = 0.5$  (Hexane/EtOAc = 9/1). **IR (thin film, neat)**:  $\nu_{\text{max}}/\text{cm}^{-1}$  2253, 1725, 1456, 1253, 1119. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**:  $\delta$  8.09-8.08 (m, 1H), 7.24-7.21 (m, 2H), 7.19-7.16 (m, 1H), 7.13-7.103 (m, 1H), 7.04-7.03 (m, 2H), 6.8 (s, 1H), 6.1 (s, 1H), 2.5 (s, 6H), 2.4 (s, 3H), 2.1 (s, 3H), 1.67 (s, 9H), 1.63 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**:  $\delta$  170.2, 150.7,

138.4, 137.8, 135.7, 134.7, 133.7, 129.5, 129.1 (2CH), 128.6, 128.1, 123.5, 122.5, 118.7, 116.9, 116.5, 115.4, 83.6, 75.3, 28.3 (3CH), 21.09, 20.8 (2CH), 16.18, 15.4. **HRMS (ESI)**:  $m/z$  calcd for C<sub>26</sub>H<sub>30</sub>NO<sub>2</sub> (M-OAc)<sup>+</sup>: 388.2277, Found: 388.2262.

### 2-(2,6-Dimethylphenyl)-3-methyl-9H-carbazole (5):



This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of 4



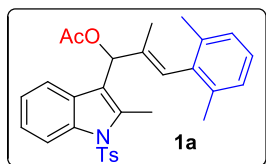
afforded 21 mg of 5 (65% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR**

(thin film, neat):  **$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.067 (d,  $J = 7.5$  Hz, 1H), 7.98 (s, 1H), 7.95 (brs, 1H), 7.40-7.39 (m, 2H), 7.24-7.18 (m, 2H),

7.15-7.13 (m, 2H), 7.08 (s, 1H), 2.09 (s, 3H), 1.97 (s, 6H).  **$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):**  $\delta$  141.7, 139.8, 138.9, 138.4, 136.1, 127.2 (3CH), 126.97, 126.93, 125.5, 123.2, 122.5, 121.1, 120.1, 119.3, 110.5, 110.47, 20.4 (2CH), 19.6. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{21}\text{H}_{20}\text{N}$  ( $\text{M}+\text{H}$ ) $^+$ : 286.1596, Found: 286.1586.

### 3-(2,6-Dimethylphenyl)-2-methyl-1-(2-methyl-1-tosyl-1H-indol-3-yl)allyl acetate (1a):

This compound was isolated as colorless liquid by following the general procedure 1.  $R_f = 0.5$



(Hexane/EtOAc = 9/1). **IR** (thin film, neat):  $\nu_{\text{max}}/\text{cm}^{-1}$  2264, 1715,

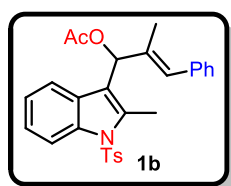
1340, 816, 514.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.33-8.31 (m, 1H), 7.94 (d,  $J = 6.4$  Hz, 1H), 7.82 (d,  $J = 7$  Hz, 1H), 7.71 (d,  $J = 8.3$  Hz,

2H), 7.37-7.33 (m, 4H), 7.12 (dd,  $J = 10.6$  Hz and 8.4 Hz, 2H), 6.75 (s, 1H), 6.62-6.56 (m, 1H), 2.82 (s, 3H), 2.27 (s, 3H), 2.21 (s, 6H), 2.14 (s, 3H), 1.36 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.186, 114.947, 137.155, 136.896, 135.944, 135.339, 133.415, 132.557, 129.842 (2C), 128.839, 128.581, 126.976, 126.273, 125.958, 125.239, 124.850, 124.339, 124.097, 123.628, 120.556, 117.873, 115.080, 72.652, 21.413, 21.128 (2C), 20.410, 15.169, 13.309.

**HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{30}\text{H}_{31}\text{NO}_4\text{S}$  (M): 501.1974, Found: 501.2003.

### 2-Methyl-1-(2-methyl-1-tosyl-1H-indol-3-yl)-3-phenylallyl acetate (1b):

This compound was isolated as colorless viscous liquid by following the general procedure 1.



$R_f = 0.5$  (Hexane/EtOAc = 9/1). **IR** (thin film, neat):  $\nu_{\text{max}}/\text{cm}^{-1}$  2269,

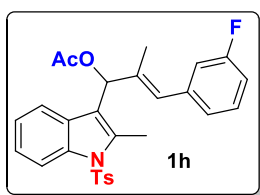
1732, 1454, 1250, 1091.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.31 (d,  $J = 8.3$  Hz, 1H), 7.81 (d,  $J = 7.7$  Hz, 1H), 7.72 (d,  $J = 8.1$  Hz, 2H), 7.39-7.33 (m,

3H), 7.28-7.22 (m, 6H), 6.65 (d,  $J = 11.1$  Hz, 2H), 2.8 (s, 3H), 2.36 (s, 3H), 2.15 (s, 3H), 1.79 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.04, 144.9, 137.1, 136.6, 136.07, 135.7, 134.5, 129.6 (2CH), 129.03 (2CH), 128.7, 128.2 (2CH), 126.7, 126.39 (2CH), 125.9, 124.2, 123.6, 120.2, 117.3, 114.8, 72.5, 21.5, 21.1, 15.4, 13.2. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{28}\text{H}_{27}\text{NNaO}_4\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 496.1558, Found: 496.1544.

### 3-(3-Fluorophenyl)-2-methyl-1-(2-methyl-1-tosyl-1H-indol-3-yl)allyl acetate (1h):



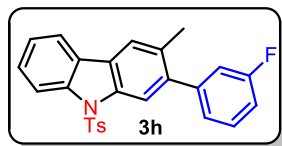
This compound was isolated as yellow viscous liquid by following the general procedure 1.  $R_f$



$R_f = 0.5$  (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2349, 1735, 885, 540.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  6.28 (d,  $J = 8.3$  Hz, 1H), 7.75-7.68 (m, 3H), 7.35-7.22 (m, 5H), 7.07-6.90 (m, 3H), 6.56 (s, 2H), 2.76 (d,  $J = 3.1$  Hz, 3H), 2.35 (s, 3H), 2.14 (s, 3H), 1.76 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  166.934, 162.6215 (d,  $J = 243.9$  Hz, 1C), 144.997, 139.369 (d,  $J = 7.6$  Hz, 1C), 136.641, 136.041, 135.845 (d,  $J = 9.4$  Hz, 1C), 129.948 (2C), 129.649 (d,  $J = 8.3$  Hz, 1C), 128.577, 126.368 (2C), 124.768, 124.237, 123.612, 120.123, 117.092, 115.794, 115.582, 114.829, 113.701, 113.491, 72.268, 21.543, 21.067, 15.432, 13.165.  **$^{19}\text{F NMR}$  (374 MHz,  $\text{CDCl}_3$ ):**  $\delta$  -112.464. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{26}\text{H}_{23}\text{FNO}_2\text{S}$  (M-OAc) $^+$ : 432.1434, Found: 432.1420.

### 2-(3-Fluorophenyl)-3-methyl-9-tosyl-9H-carbazole (3h).

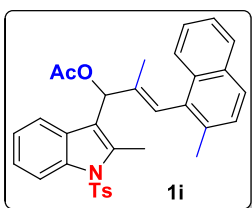
This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of



**1h** afforded 36 mg of **3h** (81% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR (thin film, neat):** 2933, 1368, 1274, 663.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.351 (d,  $J = 8.4$  Hz, 1H), 8.193 (m, 1H), 7.922 (d,  $J = 7.6$  Hz, 1H), 7.798 (s, 1H), 7.165 (d,  $J = 7.6$  Hz, 2H), 7.51-7.39 (m, 3H), 7.284 (s, 1H), 7.201 (d,  $J = 7.6$  Hz, 1H), 7.15-7.11 (m, 3H), 2.39 (s, 3H), 2.30 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  144.897, 144.1554 (d,  $J = 30.24$  Hz, 1C), 138.8441, 136.745, 134.918, 131.320, 129.694 (2CH), 127.416, 126.516 (2CH), 126.354, 126.1015, 125.867, 125.247 (d,  $J = 11.04$  Hz, 1C), 123.974, 121.315, 120.010, 116.563, 116.349, 115.981, 115.2301, 114.116, 113.906, 21.5, 20.65.  **$^{19}\text{F NMR}$  (374 MHz,  $\text{CDCl}_3$ ):**  $\delta$  -113.419. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{26}\text{H}_{21}\text{FNO}_2\text{S}$  (M+H) $^+$ : 430.1277, Found: 430.1263.

### 2-Methyl-1-(2-methyl-1-tosyl-1H-indol-3-yl)-3-(2-methylnaphthalen-1-yl)allyl acetate (1i):

This compound was isolated as colorless viscous liquid by following the general procedure 1.

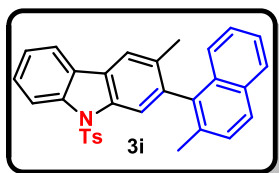


$R_f = 0.5$  (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2924, 1741, 1454, 1232, 542.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.31 (d,  $J = 7.6$  Hz, 1H), 7.93 (brs, 1H), 7.81 (d,  $J = 7.1$  Hz, 1H), 7.71-7.62 (m, 4H), 7.45-7.33 (m, 5H), 7.12 (dd,  $J = 10.2$  and 8.7 Hz, 2H), 6.74 (s, 1H), 6.61-6.56 (m, 1H), 2.82 (s, 3H), 2.27 (s, 3H), 2.12-2.153 (s, 6H), 1.37 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.185, 144.946 (2C), 137.156, 136.902, 135.947, 135.342, 133.412, 135.556,

131.942, 129.839 (3C), 128.843, 128.575, 128.127, 126.976, 126.267 (2C), 125.956, 125.237, 124.849, 124.340, 123.631, 120.555, 117.883, 115.082, 72.660, 21.400, 21.120, 20.401, 15.166, 13.303. **HRMS (ESI):** m/z calcd for C<sub>31</sub>H<sub>28</sub>NO<sub>2</sub>S (M-OAc)<sup>+</sup>: 478.1841, Found: 478.1830.

### 3-Methyl-2-(2-methylnaphthalen-1-yl)-9-tosyl-9H-carbazole (3i):

This compound was isolated as colorless viscous liquid. Following the general procedure 4, 50

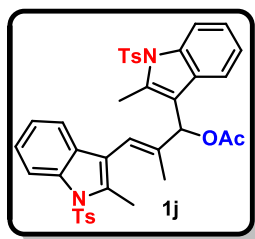


mg of **1i** afforded 32 mg of **3i** (73% yield). R<sub>f</sub> = 0.5 (Hexane/EtOAc = 20/1). **IR (thin film, neat):** 2934, 1187, 703, 542. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.4 (d, *J* = 8.4 Hz, 1H), 8.13 (s, 1H), 7.94 (dd, *J* = 11.7 and 7.9 Hz, 2H), 7.89-7.87 (m, 2H), 7.65 (d, *J* = 8.4 Hz, 2H),

7.57-7.41 (m, 4H), 7.33 (td, *J* = 7.6 Hz and 1.1 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.3 (s, 3H), 2.21 (s, 3H), 2.04 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 144.785, 139.003, 138.989, 137.306, 136.999, 134.565, 133.260, 133.067, 132.688, 132.092, 129.519 (2C), 128.662, 128.020, 127.471, 127.330, 126.643, 126.624 (2C), 126.153, 125.909, 125.572, 124.869, 124.125, 121.016, 119.890, 116.753, 115.622, 21.574, 20.353, 19.620. **HRMS (ESI):** m/z calcd for C<sub>31</sub>H<sub>26</sub>NO<sub>2</sub>S (M+H)<sup>+</sup>: 476.1684, Found: 476.1668.

### 2-Methyl-1,3-bis(2-methyl-1-tosyl-1H-indol-3-yl)allyl acetate (1j):

This compound was isolated as colorless viscous liquid by following the general procedure 1.

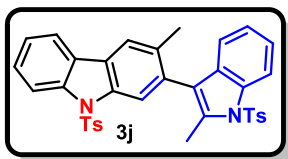


R<sub>f</sub> = 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat):** ν<sub>max</sub>/cm<sup>-1</sup> 2931, 1741, 1367, 1228, 661. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.26 (d, *J* = 8.3 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 4H), 7.35-7.26 (m, 3H), 7.21-7.18 (s, 5H), 7.15-7.13 (m, 1H), 6.6 (s, 1H), 6.36 (s, 1H), 2.7 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H), 2.29 (s,

3H), 2.14 (s, 3H), 1.4 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 169.9, 144.9, 144.7, 138.7, 136.6, 136.2, 136.1, 135.9, 135.5, 133.2, 129.9 (2CH), 129.8 (2CH), 129.8, 128.4, 126.3 (4CH), 124.2, 124.1, 123.48, 123.45, 120.1, 119.1, 118.06, 117.09, 116.3, 114.8, 114.5, 72.09, 21.58, 21.51, 21.09, 15.8, 14.08, 13.1. **HRMS (ESI):** m/z calcd for C<sub>36</sub>H<sub>33</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (M-OAc)<sup>+</sup>: 621.1882, Found: 621.1850.

### 3-Methyl-2-(2-methyl-1-tosyl-1H-indol-3-yl)-9-tosyl-9H-carbazole (3j):

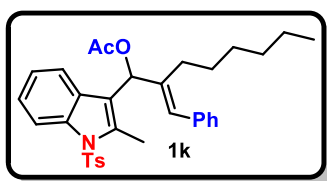
This compound was isolated as pale yellow solid. Following the general procedure 4, 50 mg



of **1j** afforded 32 mg of **3j** (71% yield). M. P = 210 °C. **IR (thin film, neat):** 2254, 1736, 1595, 1091. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.39 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.07 (s, 1H), 7.9 (d, *J* = 7.6 Hz, 1H), 7.8 (s, 1H), 7.7 (d, *J* = 7.9 Hz, 2H), 7.69-7.66 (m, 2H), 7.5 (t, *J* = 7.6 Hz, 1H), 7.43-7.35 (m, 2H), 7.32-7.30 (m, 2H), 7.26-7.23 (m, 1H), 7.1 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.3 Hz, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 2.3 (s, 3H), 2.12 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 144.9 (2CH), 138.9, 136.5, 136.3, 136.2, 134.7, 133.76, 133.72, 131.8, 130.5, 130.04 (2CH), 129.6 (2CH), 127.5, 126.5 (2CH), 126.43 (2CH), 126.41, 126.2, 124.2, 124.07, 123.5, 122.4, 121.1, 119.9, 119.2, 117.3, 115.3, 114.7, 21.6, 21.5, 19.8, 13.6. **HRMS (ESI):** *m/z* calcd for C<sub>36</sub>H<sub>31</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (M+H)<sup>+</sup>: 619.1725 Found: 619.1754.

### 2-Benzylidene-1-(2-methyl-1-tosyl-1H-indol-3-yl)octyl acetate (1k):

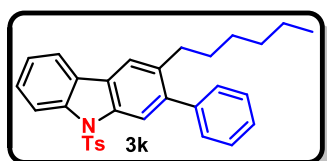
This compound was isolated as colorless viscous liquid by following the general procedure 1.



*R<sub>f</sub>* = 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat):** *v*<sub>max</sub>/cm<sup>-1</sup> 2261, 1763, 1453, 1091, 748. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.2 (d, *J* = 8.2 Hz, 1H), 7.7 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.38-7.31 (m, 3H), 7.29-7.26 (m, 2H), 7.22-7.20 (m, 4H), 6.72 (s, 1H), 6.61 (s, 1H), 2.7 (s, 3H), 2.36 (s, 3H), 2.12 (s, 3H), 1.93-1.86 (m, 1H), 1.46 (d, *J* = 14.5 Hz, 2H), 1.33-1.19 (m, 7H), 0.9 (t, *J* = 6.8 Hz, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.02, 144.9, 139.09, 137.3, 136.7, 136.1, 135.8, 129.9 (2CH), 128.8, 128.6 (2CH), 128.2 (2CH), 126.7, 126.3 (2CH), 126.1, 124.2, 123.5, 120.3, 117.4, 114.8, 70.5, 31.4, 29.3, 28.7, 28.4, 22.5, 21.5, 21.1, 14.1, 13.2. **HRMS (ESI):** *m/z* calcd for C<sub>33</sub>H<sub>37</sub>NO<sub>4</sub>SNa (M+Na)<sup>+</sup>: 566.2341, Found: 566.2330.

### 3-Hexyl-2-phenyl-9-tosyl-9H-carbazole (3k):

This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of **1k**

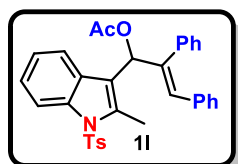


afforded 31 mg of **3k** (70% yield). *R<sub>f</sub>* = 0.5 (Hexane/EtOAc = 20/1). **IR (thin film, neat):** 3060, 1466, 1369, 1173, 703. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.3 (d, *J* = 8.2 Hz, 1H), 8.19 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.81 (s, 1H), 7.74-7.72 (m, 2H), 7.53-7.48 (m, 3H), 7.43-7.37 (m, 3H), 7.15-7.13 (m, 2H), 2.71-2.67 (m, 2H), 2.29 (s, 3H), 1.54-1.48 (m, 2H), 1.27-1.16 (m, 7H), 0.85-0.83 (m, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 144.7, 142.08, 141.07, 138.7, 136.6, 136.4, 135.02, 129.6 (2CH), 129.5 (2CH), 128.09 (2CH), 127.2, 127.01,

126.5 (2CH), 126.3, 125.5, 123.8, 120.1, 119.9, 116.2, 115.1, 33.1, 31.5 (2CH), 29.1, 22.5, 21.5, 14.06. **HRMS (ESI):** m/z calcd for C<sub>31</sub>H<sub>31</sub>NO<sub>2</sub>SNa (M+Na)<sup>+</sup>: 504.1973, Found: 504.1955.

### 1-(2-Methyl-1-tosyl-1H-indol-3-yl)-2,3-diphenylallyl acetate (**1l**):

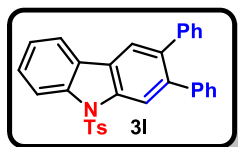
This compound was isolated as colorless viscous liquid by following the general procedure 1.



$R_f = 0.5$  (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2269, 1738, 1486, 901. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.22-8.20 (m, 1H), 7.79 (d,  $J = 7.6$  Hz, 1H), 7.5 (d,  $J = 8.3$  Hz, 2H), 7.32-7.23 (m, 2H), 7.21-7.19 (m, 3H), 7.15-7.09 (m, 5H), 6.93-6.89 (m, 4H), 6.84-6.80 (m, 2H), 2.38 (d,  $J = 3.9$  Hz, 6H), 2.12 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  169.8, 144.6, 139.01, 137.7, 136.4, 136.1, 135.9, 135.6, 129.8 (2CH), 129.2 (2CH), 128.9 (2CH), 128.47 (2CH), 128.40, 127.9 (2CH), 127.4, 127.07, 126.6, 126.3 (2CH), 124.04, 123.4, 120.2, 116.2, 114.6, 72.3, 21.6, 21.09, 12.7. **HRMS (ESI):** m/z calcd for C<sub>31</sub>H<sub>26</sub>NO<sub>2</sub>S (M-OAc)<sup>+</sup>: 476.1684, Found: 476.1672.

### 2,3-Diphenyl-9-tosyl-9H-carbazole (**3l**):

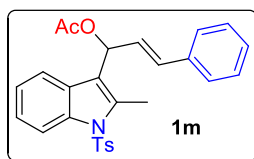
This compound was isolated as colorless viscous liquid. Following the general procedure 4,



50 mg of **1l** afforded 36 mg of **3l** (81% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2344, 560, 719, 589. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.42 (s, 1H), 8.39 (d,  $J = 8.4$  Hz, 1H), 7.96-7.94 (m, 2H), 7.8 (d,  $J = 7.8$  Hz, 2H), 7.5 (t,  $J = 7.8$  Hz, 1H), 7.43-7.39 (m, 1H), 7.31-7.26 (m, 8H), 7.22-7.15 (m, 4H), 2.31 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  144.9, 141.6, 141.4, 140.3, 138.9, 137.7, 137.01, 135.08, 130.2 (2CH), 130.01 (2CH), 129.8 (2CH), 127.9 (3CH), 127.5, 126.7, 126.6 (3CH), 126.5, 126.1, 125.5, 124.03, 121.8, 120.1, 116.6, 115.1, 21.5. **HRMS (ESI):** m/z calcd for C<sub>31</sub>H<sub>23</sub>NO<sub>2</sub>S (M)<sup>+</sup>: 473.1449, Found: 473.1409.

### 1-(2-Methyl-1-tosyl-1H-indol-3-yl)-3-phenylallyl acetate (**1m**):

This compound was isolated as yellow viscous liquid by following the general procedure 1.  $R_f$

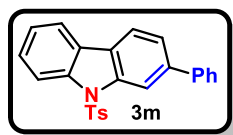


= 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2288, 1744, 1375, 761. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.27 (d,  $J = 8.2$  Hz, 1H), 7.75-7.69 (m, 2H), 7.32-7.21 (m, 10H), 6.72 (d,  $J = 2.5$  Hz, 1H), 6.53-6.49 (m, 2H), 2.71 (s, 3H), 2.38 (s, 3H), 2.11 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  170.159, 144.934, 136.563, 136.167, 136.013, 134.995, 132.528, 129.996 (2C), 128.607 (2C), 128.146, 126.693 (2C), 126.478 (2C), 126.401, 125.994, 124.199, 123.482, 120.149, 117.494,

114.692, 69.707, 21.613, 21.220, 13.098. **HRMS (ESI):**  $m/z$  calcd for  $C_{27}H_{25}NNaO_4S$  ( $M+Na$ )<sup>+</sup>: 482.1402, Found: 482.1420.

### 2-Phenyl-9-tosyl-9H-carbazole (**3m**):

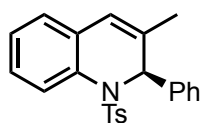
This compound was isolated as yellow viscous liquid. Following the general procedure **4**, 50



mg of **1m** afforded 18 mg of **3m** (43% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR (thin film, neat):** 2924, 1599, 1279, 980. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.62 (s, 1H), 8.38 (d,  $J = 8.4$  Hz, 1H), 7.97-7.93 (m, 2H), 7.77-

7.74 (m, 4H), 7.63 (d,  $J = 8.1$  Hz, 1H), 7.53 (q,  $J = 7.8$  Hz, 3H), 7.40-7.38 (m, 2H), 7.12 (d,  $J = 8.1$  Hz, 2H), 2.28 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  144.947, 141.176, 140.776, 139.057, 138.812, 135.007, 129.73 (2C), 128.94 (2C), 127.58 (3C), 127.391, 126.529 (2C), 126.172, 125.532, 124.021, 123.373, 120.211, 120.037, 115.218, 113.636, 21.531. **HRMS (ESI):**  $m/z$  calcd for  $C_{25}H_{20}NO_2S$  ( $M+H$ )<sup>+</sup>: 398.1215, Found: 398.1220.

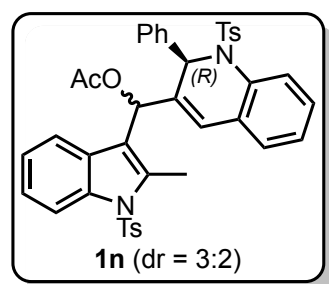
### Optical purity of the following aldehyde employed in the preparation of **1n**:



$[\alpha]^{25}_D = -295.2$  ( $c$  0.4,  $CHCl_3$ ),  $ee = 79\%$

### (2-Methyl-1-tosyl-1H-indol-3-yl)(2-phenyl-1-tosyl-1,2-dihydroquinolin-3-yl)methyl acetate (**1n**):

This compound was isolated as fluffy pale yellow solid by following the general procedure **1**.

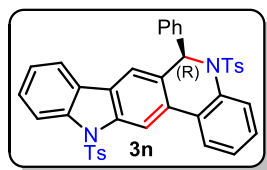


M.P = 115 °C.  $R_f = 0.5$  (Hexane/EtOAc = 4/1). **IR (thin film, neat):**  $\nu_{max}/cm^{-1}$  2256, 1736, 1475, 1175, 577. **Optical rotation**  $[\alpha]^{25}_D = -107.03$  ( $c$  0.05,  $CHCl_3$ ). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  8.403 (d,  $J = 8.5$  Hz, 1H), 7.89 (d,  $J = 8.5$  Hz, 2H), 7.845 (d,  $J = 8.5$  Hz, 1H), 7.515-7.482 (m, 3H), 7.39-7.28 (m, 8H), 7.02 (d,  $J = 8$  Hz, 2H), 6.82 (d,  $J = 8$  Hz, 2H), 6.47 (d,  $J = 1.5$  Hz, 1H), 6.41

(s, 1H), 6.03 (s, 1H), 2.68 (s, 3H), 2.45 (s, 3H), 2.41 (s, 3H), 2.00 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  167.824, 143.375, 141.368, 135.535, 134.610, 134.302, 134.068, 133.790, 133.010, 130.197, 128.363 (2C), 127.292, 127.214, 126.988 (3C), 126.770, 126.449, 126.197, 126.089 (2C), 125.361, 125.190, 124.917, 124.750 (2C), 124.715, 124.463, 122.493, 121.493, 120.301, 118.603, 113.962, 112.984, 67.609, 56.592, 19.899, 19.809, 18.873, 114.415. **HRMS (ESI):**  $m/z$  calcd for  $C_{39}H_{33}N_2O_4S_2$  ( $M-OAc$ )<sup>+</sup>: 657.1882, Found: 657.1904.

### 6-Phenyl-5,12-ditosyl-6,12-dihydro-5H-indolo[3,2-j]phenanthridine (3n):

This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of **1n**



afforded 34 mg of **3n** (74% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1).

**IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2367, 1340, 718, 535. **Optical rotation**

$[\alpha]^{25}_{\text{D}} = +63.61$  ( $c$  0.07,  $\text{CHCl}_3$ ).  **$^1\text{H NMR}$  (500 MHz, DMSO):**  $\delta$  8.275

(d,  $J = 4$  Hz, 2H), 8.09 (s, 2H), 7.912 (d,  $J = 8.5$  Hz, 3H), 7.638-7.605

(m, 2H), 7.491-7.461 (m, 1H), 7.437-7.416 (m, 2H), 7.387-7.370 (m, 2H), 7.200-7.139 (m,

3H), 7.063 (d,  $J = 7.5$  Hz, 2H), 7.021 (d,  $J = 8$  Hz, 2H), 6.591 (d,  $J = 8$  Hz, 2H), 6.55 (s, 1H),

2.281 (s, 3H), 1.64 (s, 3H).  **$^{13}\text{C NMR}$  (125 MHz, DMSO):**  $\delta$  146.327, 143.767, 139.129,

138.267, 137.845, 134.663, 134.375, 133.890, 130.814 (2C), 130.494, 129.909, 129.456,

129.362, 129.293, 128.966 (2C), 128.766 (2C), 128.690, 128.411, 128.014, 127.494 (2C),

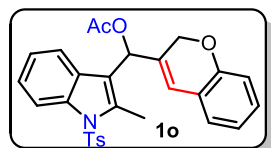
127.160 (2C), 126.994 (2C), 125.569, 125.487, 124.850, 124.662, 121.265, 121.048, 114.837,

109.590, 60.591, 21.472, 20.653. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{32}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$  (M-Ts) $^+$ :

499.1480, Found: 499.1492.

### (2H-Chromen-3-yl)(2-methyl-1-tosyl-1H-indol-3-yl)methyl acetate (1o):

This compound was isolated as colorless viscous liquid by following the general procedure 1.



$R_f = 0.5$  (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2931,

1747, 1367, 1177, 576.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.212 (d,  $J =$

8.5 Hz, 1H), 7.64-7.60 (m, 3H), 7.27-7.25 (m, 1H), 7.192 (d,  $J = 8.5$

Hz, 3H), 7.08-7.05 (m, 1H), 6.86-6.82 (m, 2H), 6.74 (d,  $J = 8$  Hz, 1H), 6.57 (s, 1H), 6.22 (s,

1H), 4.6 (d,  $J = 14.5$  Hz, 1H), 4.43 (d,  $J = 14.5$  Hz, 1H), 2.66 (s, 3H), 2.33 (s, 3H), 2.06 (s, 3H).

**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  169.910, 153.248, 145.09, 136.613, 136.058, 135.966,

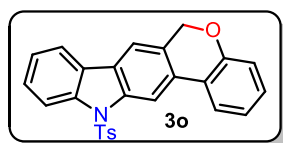
130.431, 130.009 (2C), 129.471, 128.314, 127.028, 126.380 (2C), 124.418, 123.759, 121.881,

121.544, 120.953, 119.944, 115.667, 115.611, 114.883, 68.520, 65.717, 21.606, 20.906,

13.109. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{26}\text{H}_{22}\text{NO}_3\text{S}$  (M-OAc) $^+$ : 428.1320, Found: 428.1302.

### 12-Tosyl-6,12-dihydrochromeno[4,3-b]carbazole (3o):

This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of **1o**



afforded 35 mg of **3o** (80% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1).

**IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2931, 1126, 708, 576.  **$^1\text{H NMR}$  (400**

**MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.715 (s, 1H), 8.344 (d,  $J = 10.5$  Hz, 1H), 8.019-

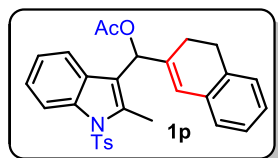
7.996 (m, 1H), 7.88 (d,  $J = 9.5$  Hz, 1H), 7.732-7.689 (m, 3H), 7.517-7.514 (m, 1H), 7.385-

7.332 (m, 2H), 7.215-7.194 (m, 1H), 7.127-7.064 (m, 3H), 5.25 (s, 2H), 2.27 (s, 3H).  **$^{13}\text{C NMR}$**

(100 MHz, CDCl<sub>3</sub>):  $\delta$  154.891, 145.052, 138.953, 138.822, 134.782, 129.898, 129.809, 129.778 (2C), 127.944, 127.581, 126.507 (2C), 126.119, 125.777, 124.136, 123.889, 123.407, 122.541, 119.953, 117.545, 116.125, 115.300, 108.782, 68.803, 21.555. **HRMS (ESI):** m/z calcd for C<sub>26</sub>H<sub>19</sub>NO<sub>3</sub>S (M)<sup>+</sup>: 425.1086, Found: 425.1071.

### (3,4-Dihydronaphthalen-2-yl)(2-methyl-1-tosyl-1H-indol-3-yl)methyl acetate (1p):

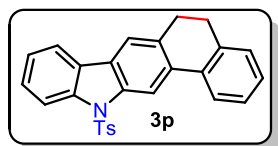
This compound was isolated as colorless viscous liquid by following the general procedure 1.



$R_f$  = 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2261, 1732, 1435, 1225. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  8.20-8.17 (m, 1H), 7.64-7.61 (m, 3H), 7.266-7.236 (m, 1H), 7.18 (d,  $J$  = 8 Hz, 2H), 7.16-7.08 (m, 3H), 7.05-7.03 (m, 1H), 6.95-6.94 (m, 1H), 6.59 (s, 1H), 6.40 (s, 1H), 2.755-2.709 (m, 1H), 2.67-2.62 (m, 4H), 2.341 (s, 3H), 2.15-2.09 (s, 1H), 2.09 (s, 3H), 1.95-1.91 (s, 1H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  170.102, 144.890, 137.035, 136.592, 136.065, 135.858, 134.735, 133.566, 129.919 (2C), 128.644, 127.320, 127.267, 126.566, 126.468, 126.383 (2C), 124.178, 123.554, 123.270, 120.161, 116.917, 114.742, 70.567, 27.789, 24.356, 21.614, 21.088, 13.183. **HRMS (ESI):** m/z calcd for C<sub>27</sub>H<sub>24</sub>NO<sub>2</sub>S (M-OAc)<sup>+</sup>: 426.1528, Found: 426.1517.

### 12-Tosyl-6,12-dihydro-5H-naphtho[1,2-b]carbazole (3p):

This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of **1p**

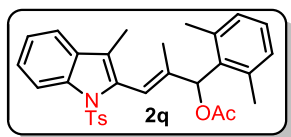


afforded 34 mg of **3p** (77% yield).  $R_f$  = 0.5 (Hexane/EtOAc = 20/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2926, 1450, 720. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  8.767 (s, 1H), 8.350 (d,  $J$  = 8.5 Hz, 1H), 8.017 (d,  $J$  = 7.5 Hz, 1H), 7.89 (d,  $J$  = 8.5 Hz, 1H), 7.75-7.73 (m, 3H), 7.51-7.48 (m, 1H), 7.45-7.42 (m, 1H), 7.39-7.36 (m, 1H), 7.33-7.31 (m, 2H), 7.11 (d,  $J$  = 8.5 Hz, 2H), 3.04-3.01 (m, 2H), 2.97-2.95 (m, 2H), 2.27 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  144.892, 138.950, 138.124, 137.656, 134.995, 134.852, 134.347, 133.782, 129.684 (2C), 128.220, 127.735, 127.275, 127.222, 126.54 (2C), 126.414, 125.578, 124.428, 123.968, 119.881, 119.053, 115.298, 110.470, 29.416, 29.299, 21.508. **HRMS (ESI):** m/z calcd for C<sub>27</sub>H<sub>21</sub>NO<sub>2</sub>S (M)<sup>+</sup>: 423.1293, Found: 423.1275.

### 1-(2,6-Dimethylphenyl)-2-methyl-3-(3-methyl-1-tosyl-1H-indol-2-yl)allyl acetate (2q):

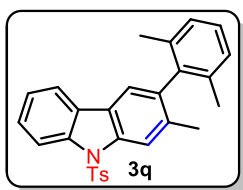


This compound was isolated as colorless viscous liquid by following the general procedure 5.



$R_f = 0.5$  (Hexane/EtOAc = 9/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2919, 1480, 570.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.302 (d,  $J = 10$  Hz, 1H), 7.55-7.53 (m, 2H), 7.45 (d,  $J = 10$  Hz, 1H), 7.389-7.350 (m, 1H), 7.314-7.277 (m, 1H), 7.217-7.200 (m, 1H), 7.15-7.12 (m, 4H), 6.99 (s, 1H), 6.42 (s, 1H), 2.62 (s, 6H), 2.34 (s, 3H), 2.25 (s, 3H), 2.06 (s, 3H), 1.509 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.347, 144.432, 139.423, 137.911, 136.682, 136.127, 134.334, 132.386, 131.213, 129.579 (3C), 129.203, 128.292, 126.600 (3C), 124.815, 123.418, 118.899, 118.176, 117.095, 114.799, 75.017, 21.57, 21.07, 20.89 (2C), 16.2, 10.14. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{30}\text{H}_{32}\text{NO}_4\text{S}$  ( $\text{M}+\text{H}^+$ ): 502.2052, Found: 502.2030.

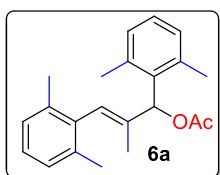
### 3-(2,6-Dimethylphenyl)-2-methyl-9-tosyl-9H-carbazole (3q):



This compound was isolated as viscous liquid. Following the general procedure 6, 50 mg of **2q** afforded 30 mg of **3q** (69% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2356, 1369, 1173, 667.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.34-8.30 (m, 2H), 7.83-7.79 (m, 3H), 7.59 (s, 1H), 7.50-7.46 (m, 1H), 7.37-7.33 (m, 1H), 7.28-7.21 (m, 2H), 7.18-7.16 (m, 3H), 2.3 (s, 3H), 2.19 (s, 3H), 1.97 (s, 6H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  144.829, 140.707, 138.427, 137.889, 136.82, 136.18 (2C), 135.88, 135.19, 129.68 (2C), 127.36 (2C), 127.21, 126.94, 126.58 (2C), 126.55, 124.72, 123.84, 120.01, 119.76, 116.07, 115.16, 21.5, 20.6, 20.4 (2C). **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{28}\text{H}_{25}\text{NO}_2\text{S}$  ( $\text{M}^+$ ): 439.1606, Found: 439.1602.

### 1,3-bis(2,6-Dimethylphenyl)-2-methylallyl acetate (6a):

This compound was isolated as colorless viscous liquid by following the general procedure 6.

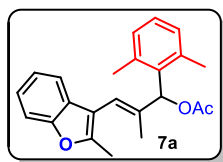


$R_f = 0.5$  (Hexane/EtOAc = 10/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2898, 11740, 546, 450.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.16-7.12 (m, 1H), 7.07-7.01 (m, 5H), 6.87 (s, 1H), 6.01 (s, 1H), 2.53 (s, 6H), 2.18-2.13 (m, 9H), 1.54 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.372, 137.597 (2C), 136.518, 135.765, 134.718, 128.934 (2C), 127.900 (2C), 127.131 (2C), 126.57 (2C), 125.360, 75.385, 21.00, 20.781 (2C), 20.32 (2C), 15.007. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{22}\text{H}_{26}\text{O}_2$  ( $\text{M}+\text{H}^+$ ): 323.2011, Found: 323.2036.

### 1-(2,6-Dimethylphenyl)-2-methyl-3-(2-methylbenzofuran-3-yl)allyl acetate (7a):



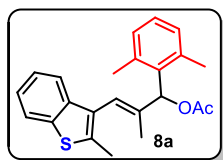
This compound was isolated as colorless viscous liquid by following the general procedure 7.



$R_f = 0.5$  (Hexane/EtOAc = 10/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2985, 1733, 1187, 542, 590.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.51-7.49 (m, 1H), 7.44-7.42 (m, 1H), 7.33-7.27 (m, 2H), 7.24 (d,  $J = 7.2$  Hz, 1H), 7.17 (d,  $J = 7.8$  Hz, 2H), 7.05 (s, 1H), 6.29 (brs, 1H), 2.67 (s, 6H), 2.44 (s, 3H), 2.27 (s, 3H), 1.82 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.251, 154.097, 151.413, 138.093, 137.872 (2C), 134.739, 129.363, 129.235 (2C), 128.234, 123.427, 122.431, 119.540, 115.276, 112.779, 110.736, 75.250, 21.109, 20.881 (2C), 16.243, 13.243. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{21}\text{H}_{21}\text{O}$  (M-OAc) $^+$ : 289.1592, Found: 289.1574.

### 1-(2,6-Dimethylphenyl)-2-methyl-3-(2-methylbenzo[*b*]thiophen-3-yl)allyl acetate (8a):

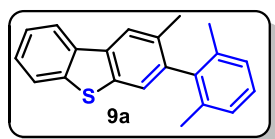
This compound was isolated as colorless viscous liquid by following the general procedure 7.



$R_f = 0.5$  (Hexane/EtOAc = 10/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2918, 1738, 1457, 1369, 763.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.84 (d,  $J = 7.7$  Hz, 1H), 7.57-7.51 (m, 1H), 7.46-7.37 (m, 2H), 7.26-7.20 (m, 3H), 7.11 (brs, 1H), 6.35 (brs, 1H), 2.71 (s, 6H), 2.54 (s, 3H), 2.28 (s, 3H), 1.76 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.297, 140.112, 139.100, 138.404, 137.834 (2C), 135.953, 134.757, 129.583, 129.279 (2C), 128.283, 124.127, 123.810, 122.138 (2C), 118.907, 75.288, 21.124, 21.010 (2C), 16.144, 14.995. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{21}\text{H}_{21}\text{S}$  (M-OAc) $^+$ : 305.1364, Found: 305.1355.

### 3-(2,6-Dimethylphenyl)-2-methyldibenzo[*b,d*]thiophene (9a):

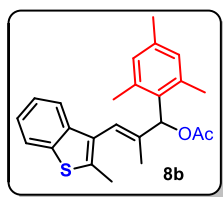
This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of **8a**



afforded 32 mg of **9a** (77% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2899, 1543, 1189, 516.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.21-8.10 (m, 1H), 8.13 (s, 1H), 7.93-7.88 (m, 1H), 7.55 (s, 1H), 7.50-7.48 (m, 2H), 7.27-7.13 (m, 3H), 2.18 (s, 3H), 2.03 (s, 6H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  140.744, 140.091, 139.697, 137.215, 136.015, 135.465, 134.797, 132.519, 127.360 (3C), 127.229, 126.507, 124.347, 122.901, 122.718, 122.643, 121.442, 20.461 (2C), 19.806. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{21}\text{H}_{18}\text{S}$  (M) $^+$ : 302.1129, Found: 302.1149.

### 1-Mesityl-2-methyl-3-(2-methylbenzo[*b*]thiophen-3-yl)allyl acetate (8b):

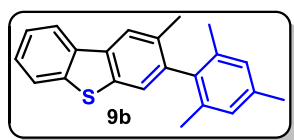
This compound was isolated as colorless viscous liquid by following the general procedure 7.



$R_f = 0.5$  (Hexane/EtOAc = 10/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2916, 1752, 1457, 1369, 1024.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.79 (d,  $J = 7.8$  Hz, 1H), 7.48 (d,  $J = 7.7$  Hz, 1H), 7.40-7.28 (m, 2H), 6.97-6.95 (m, 3H), 6.27 (brs, 1H), 2.61 (s, 6H), 2.46 (s, 3H), 2.36 (s, 3H), 2.23 (s, 3H), 1.69 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.303, 104.061, 139.224, 138.294, 137.755, 137.688 (2C), 135.831, 131.690, 129.965 (2C), 129.582, 124.014, 123.699, 122.088, 122.054, 118.609, 75.124, 21.129, 20.989, 20.802 (2C), 16.068, 14.940. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{22}\text{H}_{23}\text{S}$  (M-OAc) $^+$ : 319.1520, Found: 319.1525.

### 3-Mesityl-2-methyldibenzo[*b,d*]thiophene (9b):

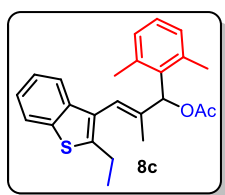
This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of **8b**



afforded 34 mg of **9b** (84% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2918, 1372, 748, 575.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.20-8.18 (m, 1H), 8.11 (s, 1H), 7.89-7.87 (m, 1H), 7.53 (s, 1H), 7.49-7.47 (m, 2H), 7.01 (s, 2H), 2.38 (s, 3H), 2.17 (s, 3H), 1.97 (s, 6H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  140.163, 139.676, 137.851, 137.159, 136.685, 123.847 (2C), 1235.489, 134.710, 132.769, 128.131 (2C), 126.452, 124.312, 122.926, 122.883, 122.625, 121.412, 21.148, 20.343 (2C), 19.865. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{22}\text{H}_{21}\text{S}$  (M+H) $^+$ : 317.1364, Found: 317.1346.

### 1-(2,6-Dimethylphenyl)-3-(2-ethylbenzo[*b*]thiophen-3-yl)-2-methylallyl acetate (8c):

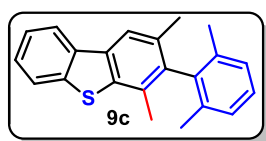
This compound was isolated as colorless viscous liquid by following the general procedure 7.



$R_f = 0.5$  (Hexane/EtOAc = 10/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2320, 1737, 1179, 448.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.8 (d,  $J = 7.8$  Hz, 1H), 7.46-7.43 (m, 1H), 7.37-7.28 (m, 2H), 7.19-7.17 (m, 1H), 7.12-7.10 (m, 2H), 6.9 (s, 1H), 6.2 (s, 1H), 2.82 (q,  $J = 7.5$  Hz, 2H), 2.61 (s, 6H), 2.12 (s, 3H), 1.64 (s, 3H), 1.34 (t,  $J = 7.5$  Hz, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.3, 143.5, 139.8, 138.9, 138.1, 137.7 (2C), 134.6, 129.1 (2C), 128.3, 128.1, 123.9, 123.6, 122.2, 122.1, 118.9, 75.1, 22.8, 21.09, 20.8 (2C), 16.01, 15.6. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{22}\text{H}_{23}\text{S}$  (M-OAc) $^+$ : 319.1520, Found: 319.1531.

### 3-(2,6-Dimethylphenyl)-2,4-dimethyldibenzo[*b,d*]thiophene (9c):

This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of **8c**



afforded 29 mg of **9c** (69% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1).

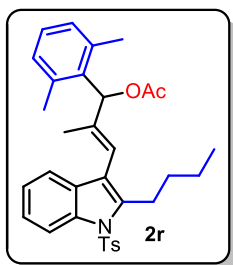
**IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2931, 1255, 1024, 566.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.19-8.17 (m, 1H), 7.99 (s, 1H), 7.92-7.90 (m, 1H),

7.49-7.47 (m, 2H), 7.27-7.23 (m, 1H), 7.20-7.17 (m, 2H), 2.18 (s, 3H), 2.11 (s, 3H), 1.94 (s, 6H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  139.5, 139.3, 138.7, 137.9, 136.3, 135.8, 134.1, 132.7, 129.3, 127.5 (2C), 127.1, 126.3, 125.3, 124.3, 122.8, 121.4, 120.3, 20.4, 20.01 (2C), 18.09.

**HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{22}\text{H}_{20}\text{S}$  (M)<sup>+</sup>: 316.1286, Found: 316.1269.

### 3-(2-Butyl-1-tosyl-1H-indol-3-yl)-1-(2,6-dimethylphenyl)-2-methylallyl acetate (**2r**):

This compound was isolated as colorless viscous liquid by following the general procedure 2.



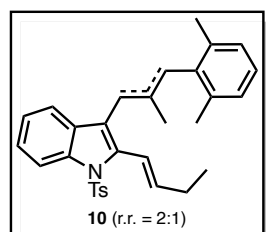
$R_f = 0.5$  (Hexane/EtOAc = 10/1). **IR (thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2261,

1761, 1453, 1186, 771.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.22-8.20 (m, 1H), 7.59 (d,  $J = 8.3$  Hz, 2H), 7.32-7.22 (m, 3H), 7.16 (d,  $J = 8$  Hz, 3H), 7.09-7.08 (m, 2H), 6.9 (s, 1H), 6.04 (brs, 1H), 2.88 (t,  $J = 7.3$  Hz, 2H), 2.54 (s, 6H), 2.3 (s, 3H), 2.18 (s, 3H), 1.71-1.66 (m, 2H), 1.55 (d,  $J = 0.9$

Hz, 3H), 1.38-1.31 (m, 2H), 0.94 (t,  $J = 7.3$  Hz, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.234, 144.556, 139.543, 138.714, 137.693 (2C), 136.833, 135.784, 134.518, 130.290, 129.662 (2C), 129.106 (2C), 128.143, 126.231 (2C), 124.133, 123.632, 119.429, 119.192, 116.553, 115.377, 75.171, 32.558, 27.505, 22.595, 21.543, 21.034, 20.795 (2C), 16.043, 13.875. **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{31}\text{H}_{34}\text{NO}_2\text{S}$  (M-OAc)<sup>+</sup>: 484.2310, Found: 484.2609.

### 2-((*E*-But-1-en-1-yl)-3-(3-(2,6-dimethylphenyl)-2-methylprop-1-en-1-yl)-1-tosyl-1H-indole (**10**):

This compound was isolated as viscous liquid. Following the general procedure 4, 50 mg of **2r**



afforded 32 mg of **10** (71% yield).  $R_f = 0.5$  (Hexane/EtOAc = 20/1). **IR**

**(thin film, neat):**  $\nu_{\max}/\text{cm}^{-1}$  2954, 1256, 715, 559.  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.29 (d,  $J = 8.3$  Hz, 1H), 7.48 (d,  $J = 8.3$  Hz, 2H), 7.33-7.27

(m, 1H), 7.11-7.08 (m, 3H), 6.99-6.97 (m, 2H), 6.92 (d,  $J = 8.2$  Hz, 2H), 6.84 (d,  $J = 16$  Hz, 1H), 5.98 (dt,  $J = 15.9$  and 6.7 Hz, 1H), 5.05 (s, 1H),

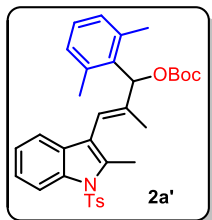
3.43 (s, 2H), 2.41-2.36 (m, 2H), 2.3 (s, 3H), 1.95 (s, 6H), 1.52 (s, 3H), 1.22-1.16 (m, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  144.766, 139.35, 138.28, 137.04, 136.55, 136.48, 136.366, 135.89, 134.64, 132.48, 128.95 (2C), 126.94 (2C), 126.64, 126.54 (2C), 124.78, 124.07,

123.75, 120.59, 119.79, 119.22, 116.23, 33.484, 26.52, 20.93, 20.419, 20.271 (2C), 13.77.

**HRMS (ESI):** m/z calcd for C<sub>31</sub>H<sub>34</sub>NO<sub>2</sub>S (M+H)<sup>+</sup>: 484.2310, Found: 484.2300.

**tert-Butyl (1-(2,6-dimethylphenyl)-2-methyl-3-(2-methyl-1-tosyl-1H-indol-3-yl)allyl) carbonate (2a')**:

This compound was isolated as colorless viscous liquid by following the general procedure 2.

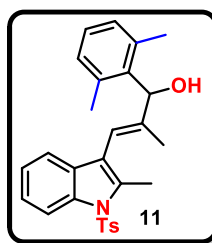


R<sub>f</sub> = 0.5 (Hexane/EtOAc = 10/1). **IR (thin film, neat):** ν<sub>max</sub>/cm<sup>-1</sup> 2868, 1746, 1257, 1379. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8 Hz, 2H), 7.28-7.27 (m, 1H), 7.22-7.16 (m, 4H), 7.15-7.12 (m, 1H), 7.07-7.05 (m, 2H), 6.64 (s, 1H), 6.08 (s, 1H), 2.5 (s, 6H), 2.44 (s, 3H),

2.35 (s, 3H), 1.57 (s, 3H), 1.48 (s, 9H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 153.422, 144.653, 139.237, 137.629 (2C), 136.365, 136.188, 134.356, 133.165, 130.070, 129.804 (2C), 129.078 (2C), 129.078, 128.038 (2C), 124.086, 123.407, 119.181, 118.508, 116.534, 114.630, 82.107, 78.012, 27.822 (3C), 21.536, 20.84 (2C), 16.03, 14.07. **HRMS (ESI):** m/z calcd for C<sub>28</sub>H<sub>28</sub>NO<sub>2</sub>S (M-Boc)<sup>+</sup>: 442.1841, Found: 442.1853.

**1-(2,6-Dimethylphenyl)-2-methyl-3-(2-methyl-1-tosyl-1H-indol-3-yl)prop-2-en-1-ol (11):**

This compound was isolated as colorless viscous liquid by following the protocol mentioned

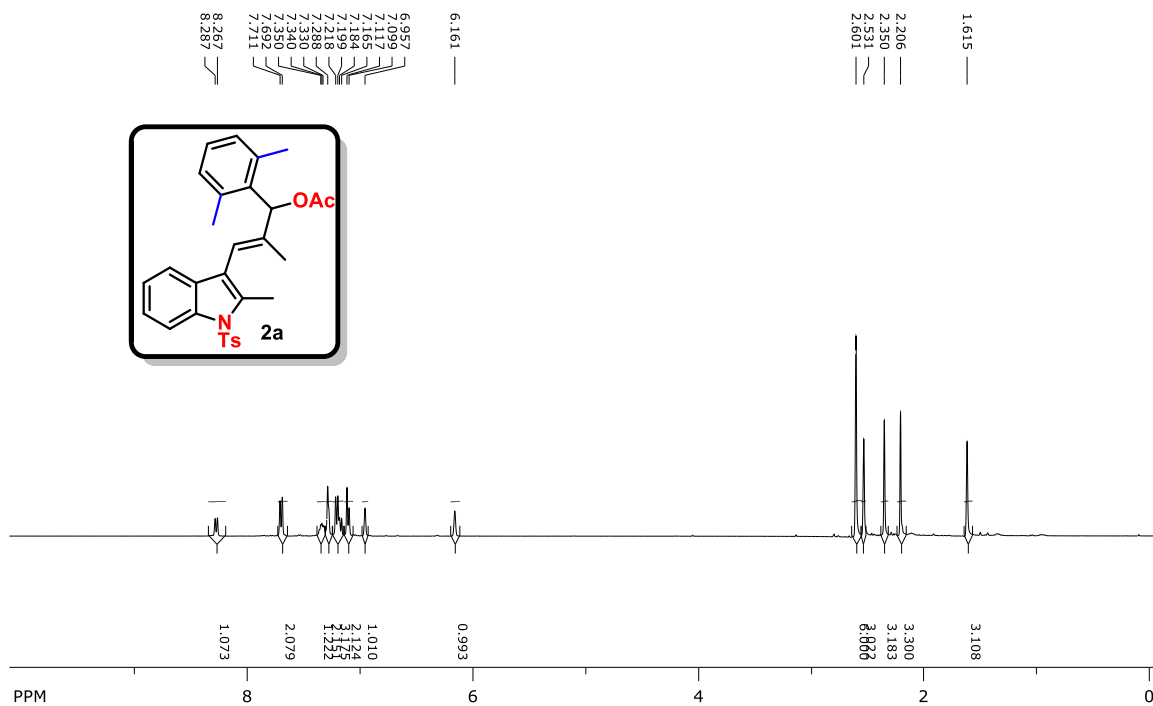


in controlled experiments. R<sub>f</sub> = 0.5 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν<sub>max</sub>/cm<sup>-1</sup> 3391, 2961, 1102, 1105, 516. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.2 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.33-7.22 (m, 3H), 7.22-7.18 (m, 2H), 7.15-7.14 (m, 1H), 7.07-7.05 (m, 2H), 6.42 (s, 1H), 5.81 (s, 1H), 2.54 (s, 6H), 2.49 (s, 3H), 2.35 (s, 3H), 1.51 (s, 3H). **<sup>13</sup>C**

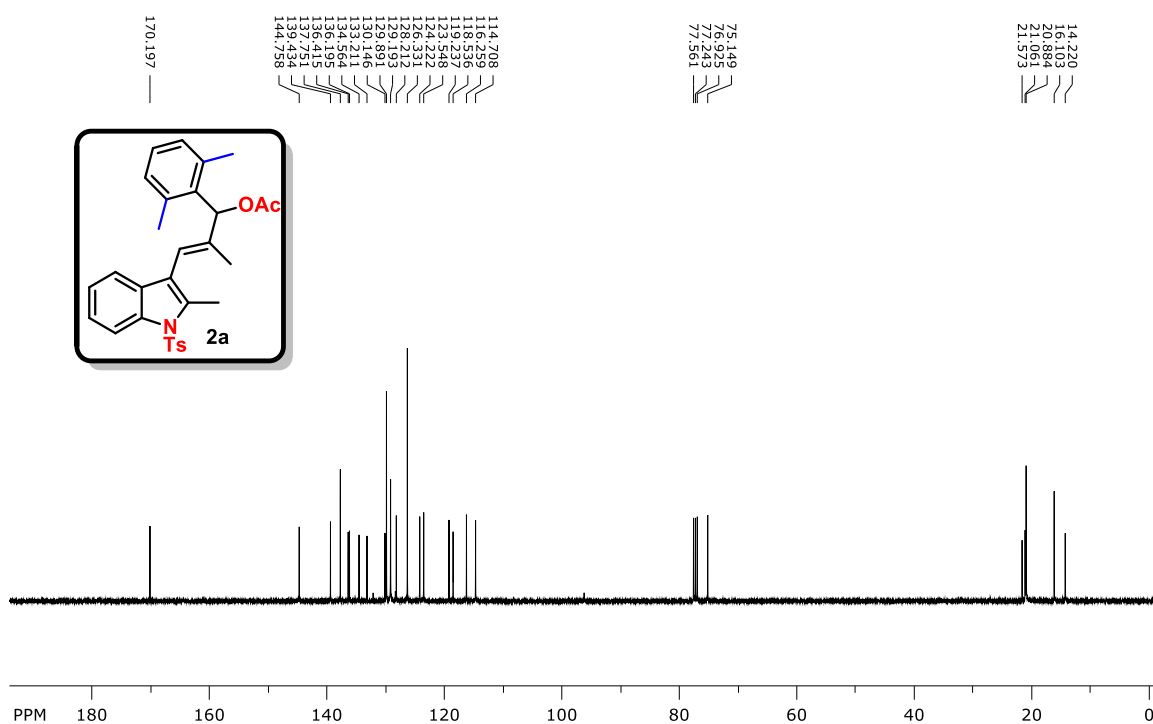
**NMR (100 MHz, CDCl<sub>3</sub>):** δ 144.650, 142.329, 137.700, 137.196, 136.417, 136.189, 132.986, 130.418, 129.825 (2C), 129.409 (2C), 127.700, 126.302 (3C), 124.041, 123.420, 119.341, 119.035, 114.682, 114.641, 73.835, 21.567, 20.809 (2C), 16.124, 14.194. **HRMS (ESI):** m/z calcd for C<sub>28</sub>H<sub>28</sub>NO<sub>2</sub>S (M-OH)<sup>+</sup>: 442.1841; Found: 442.1818.

# Copies of $^1\text{H}$ and $^{13}\text{C}$ -NMR spectra of all the compounds reported in this study

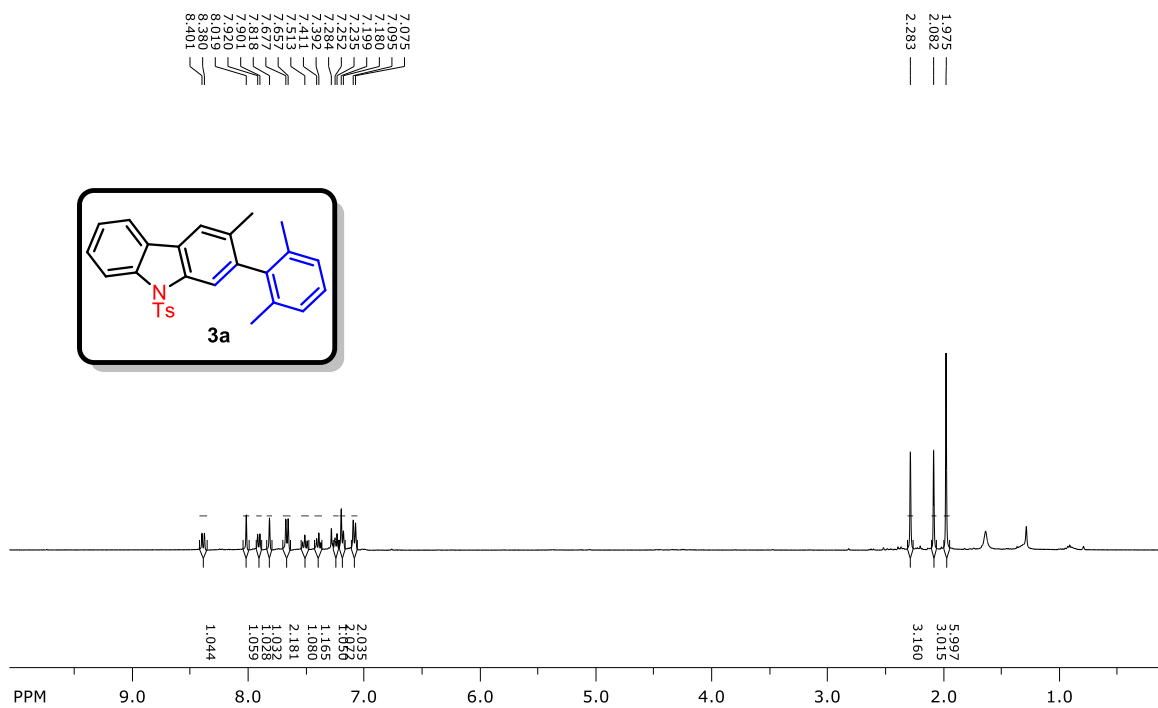
## $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



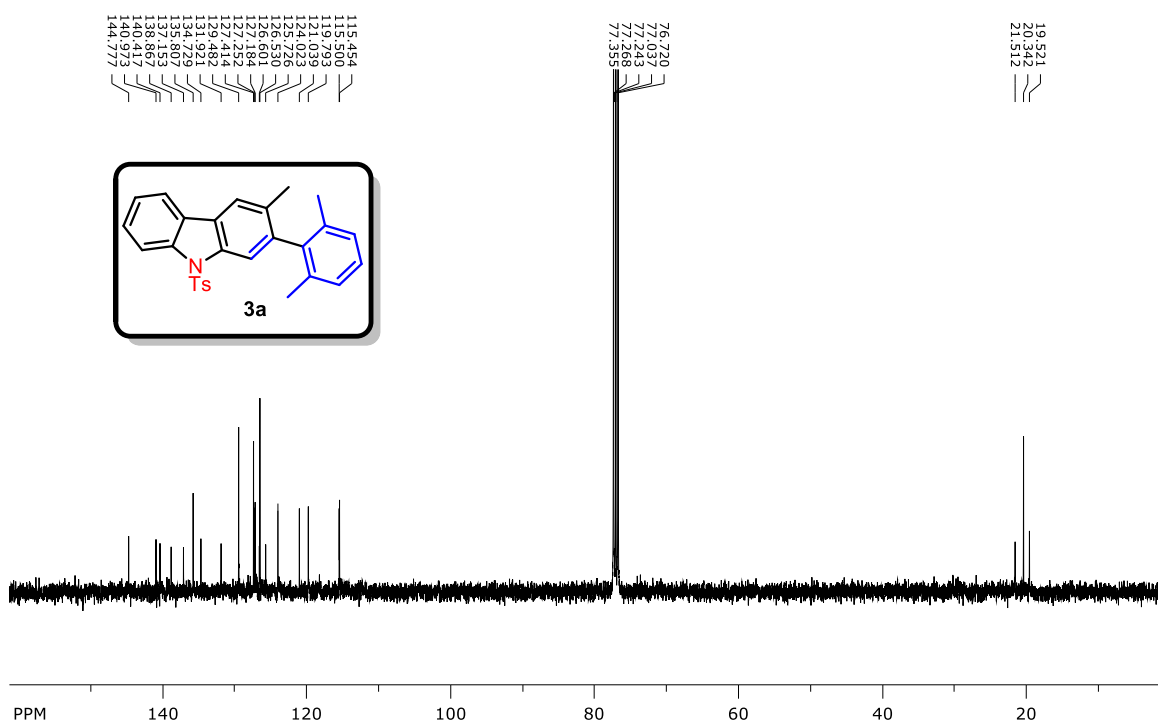
## $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



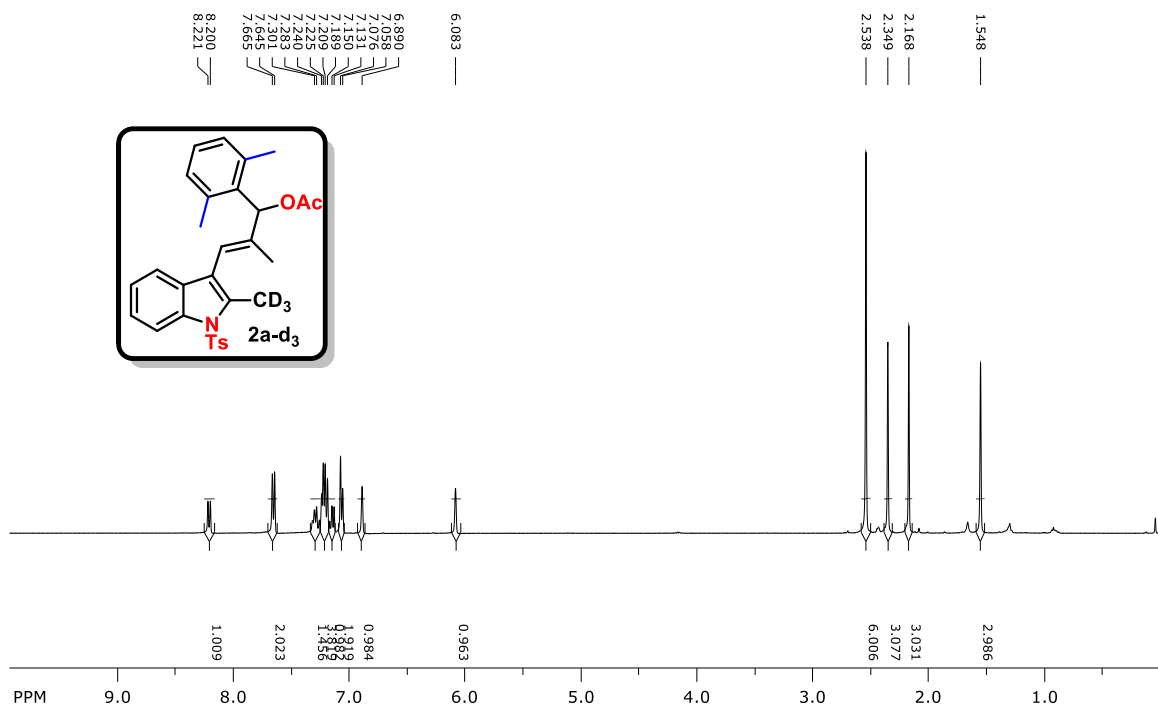
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



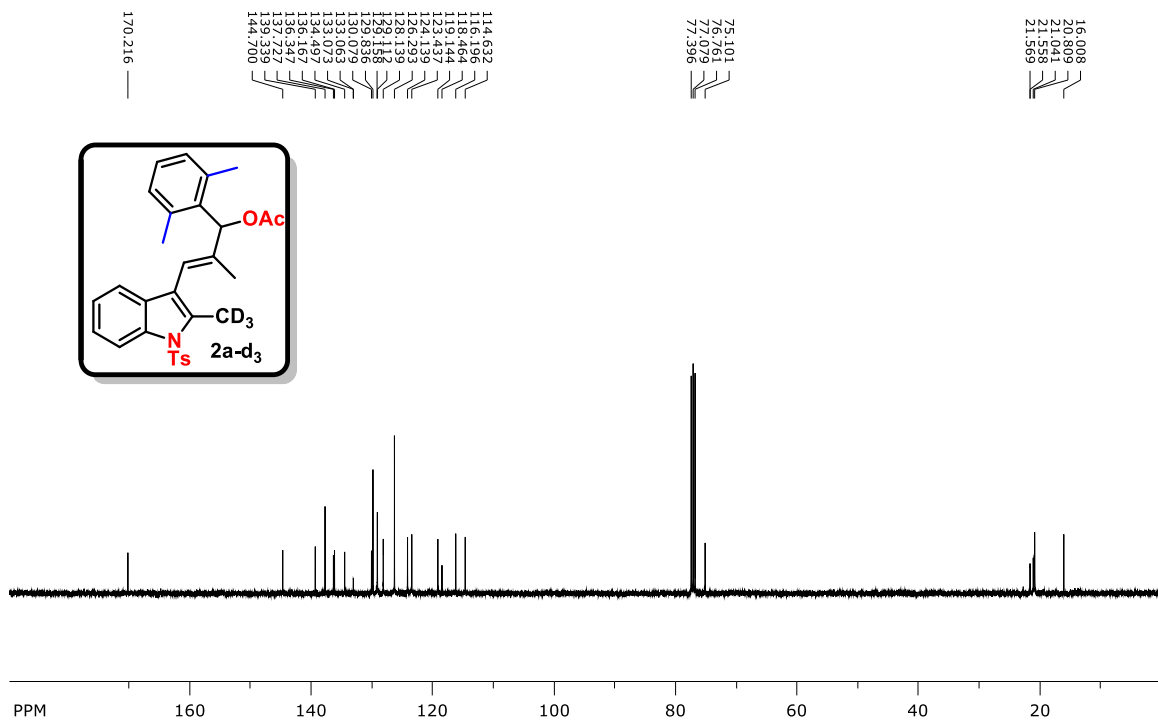
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



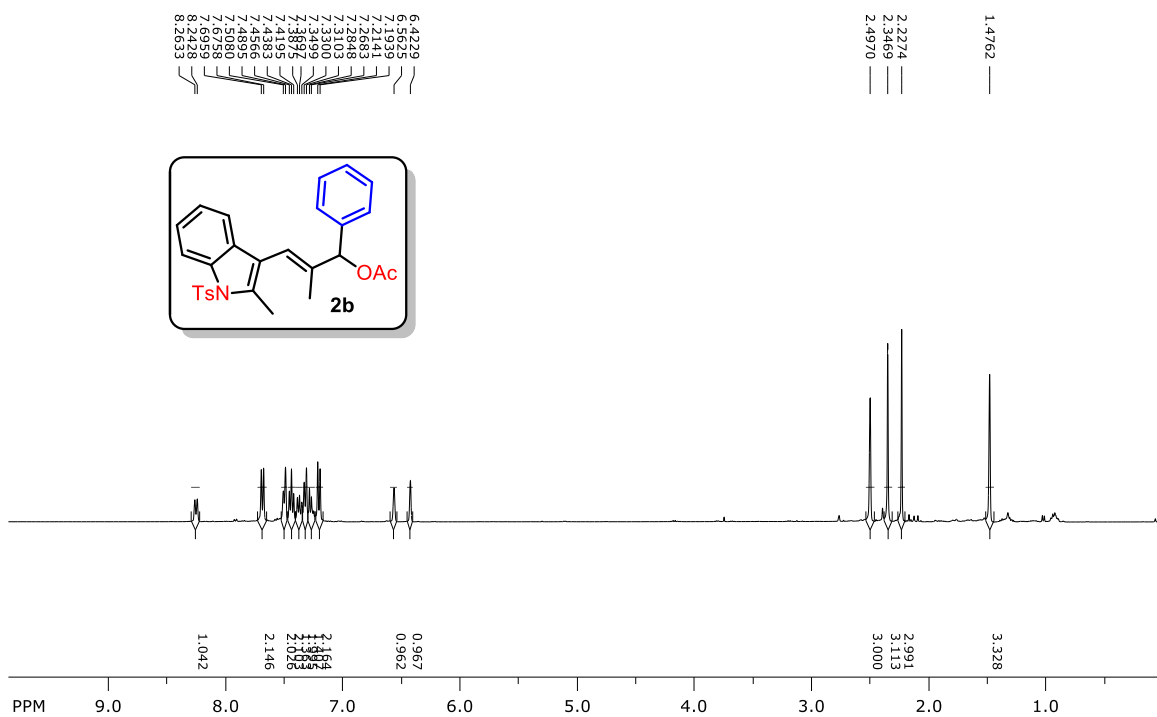
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



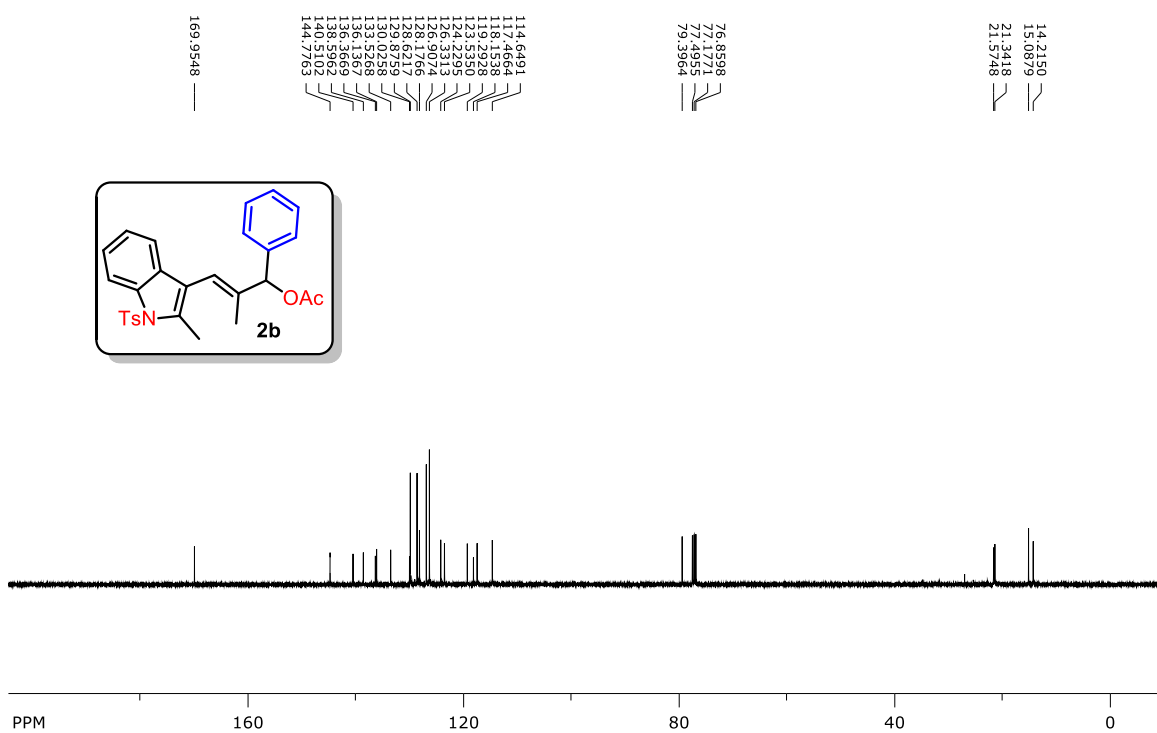
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

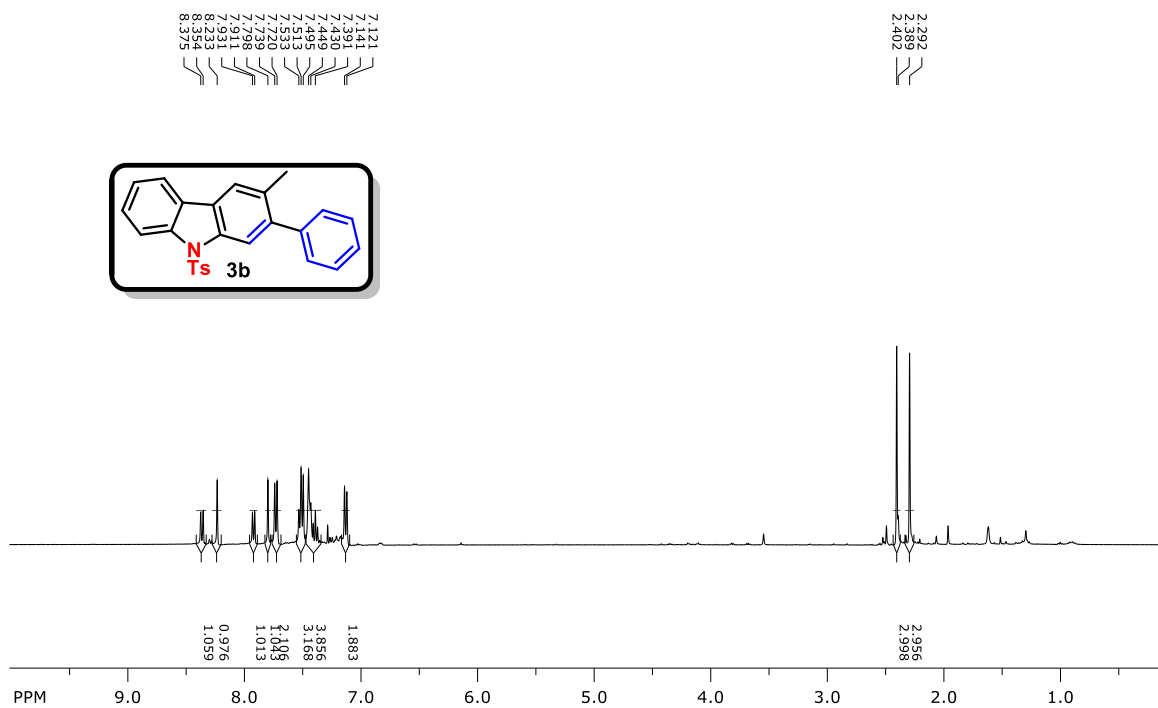


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

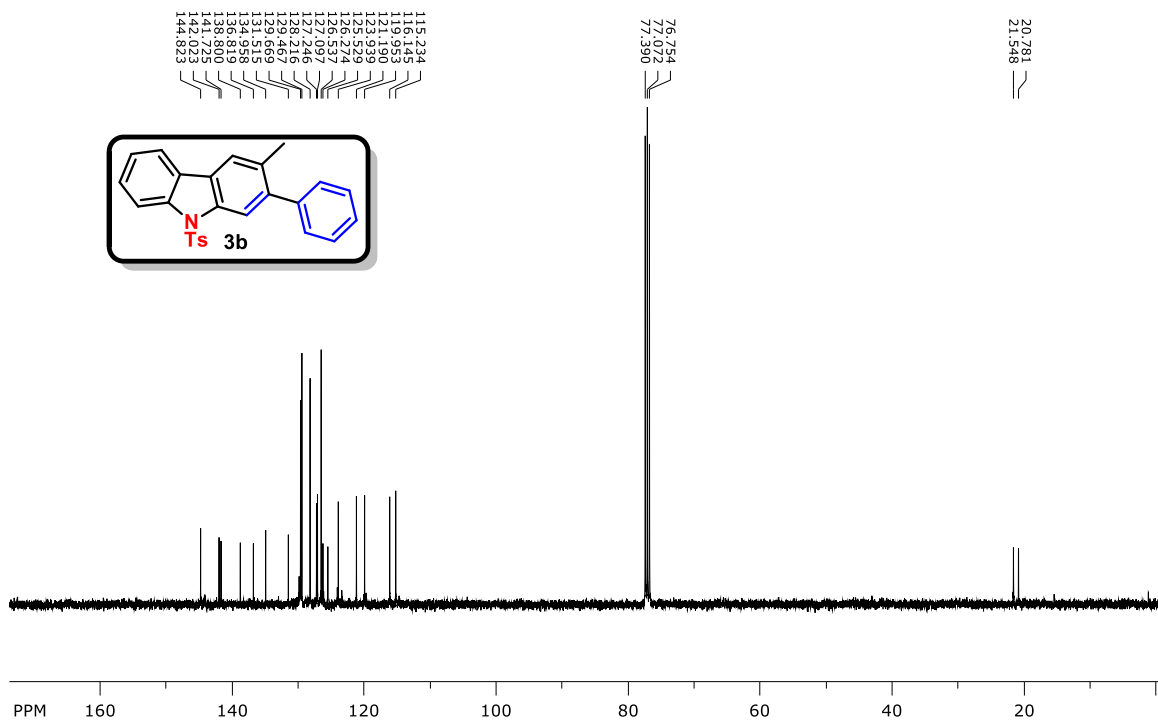




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

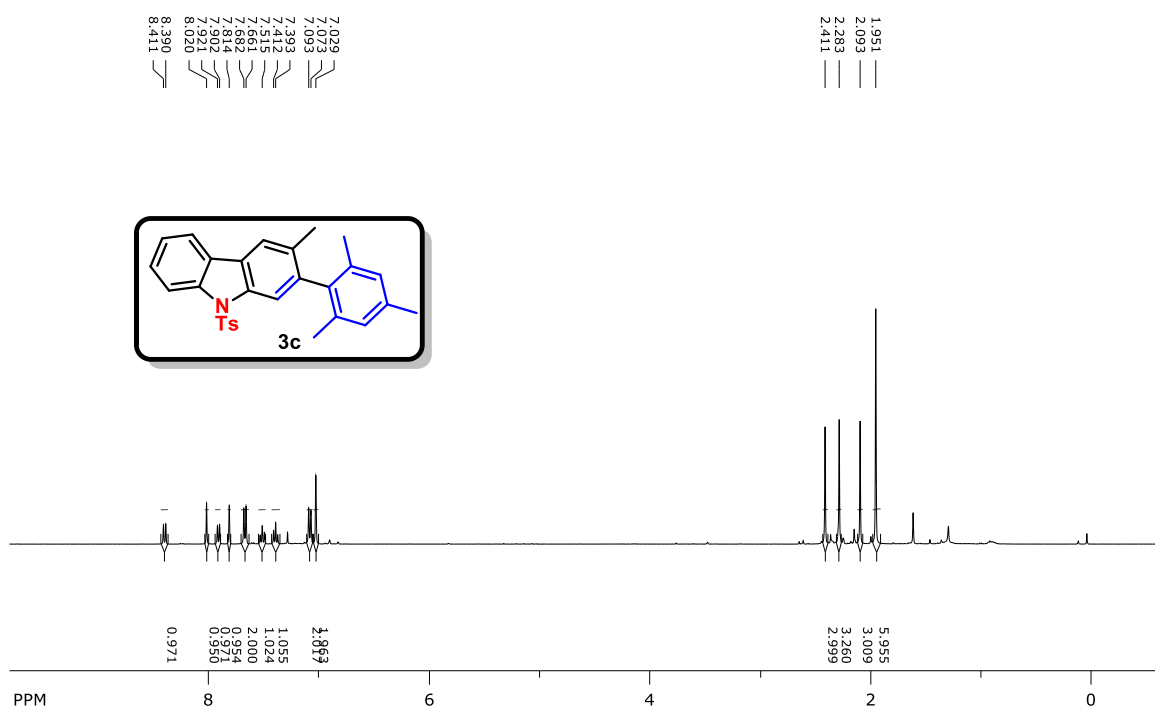


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

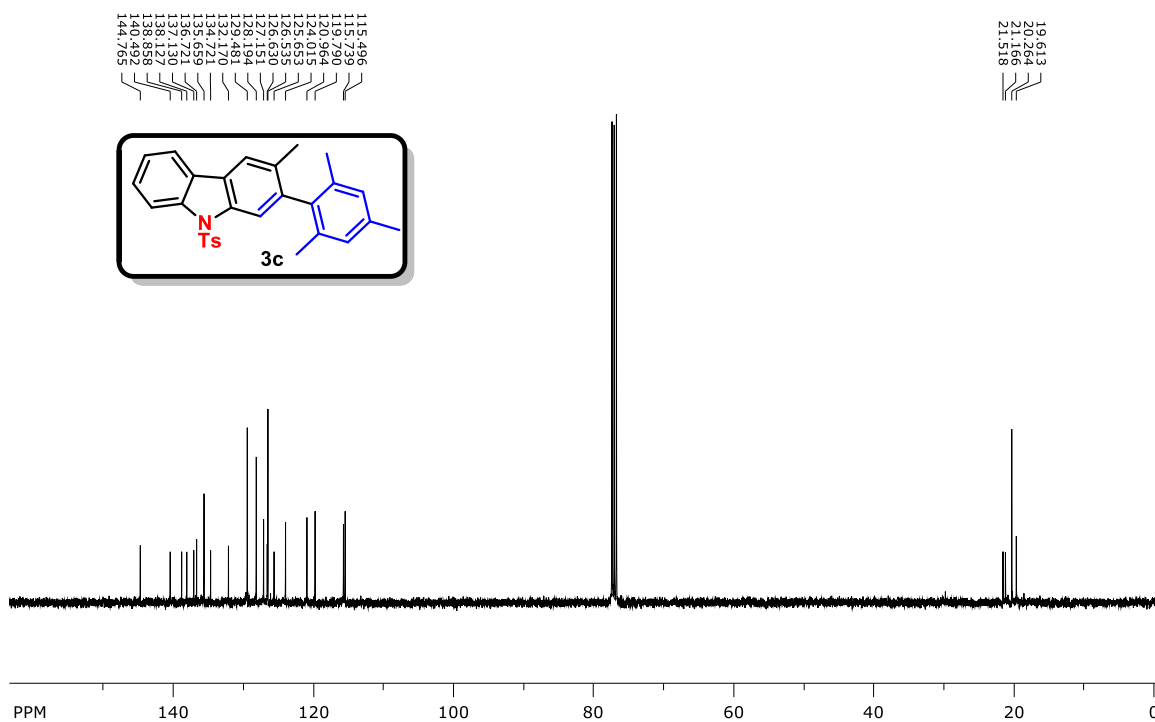




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

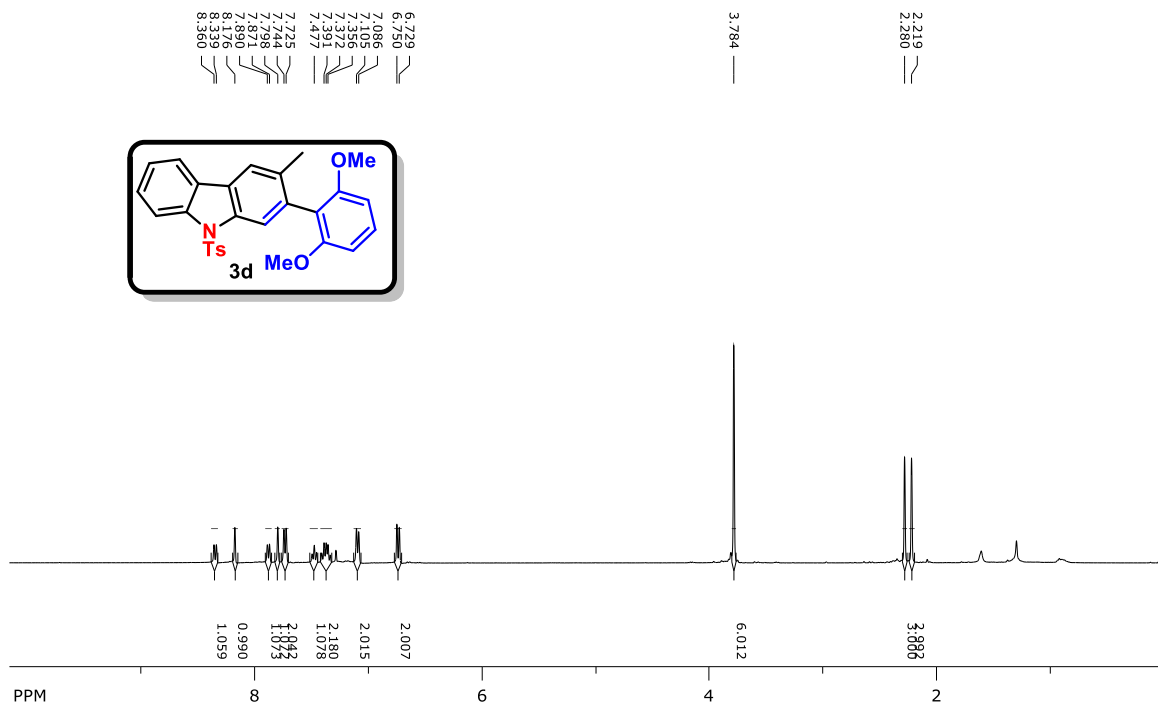


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

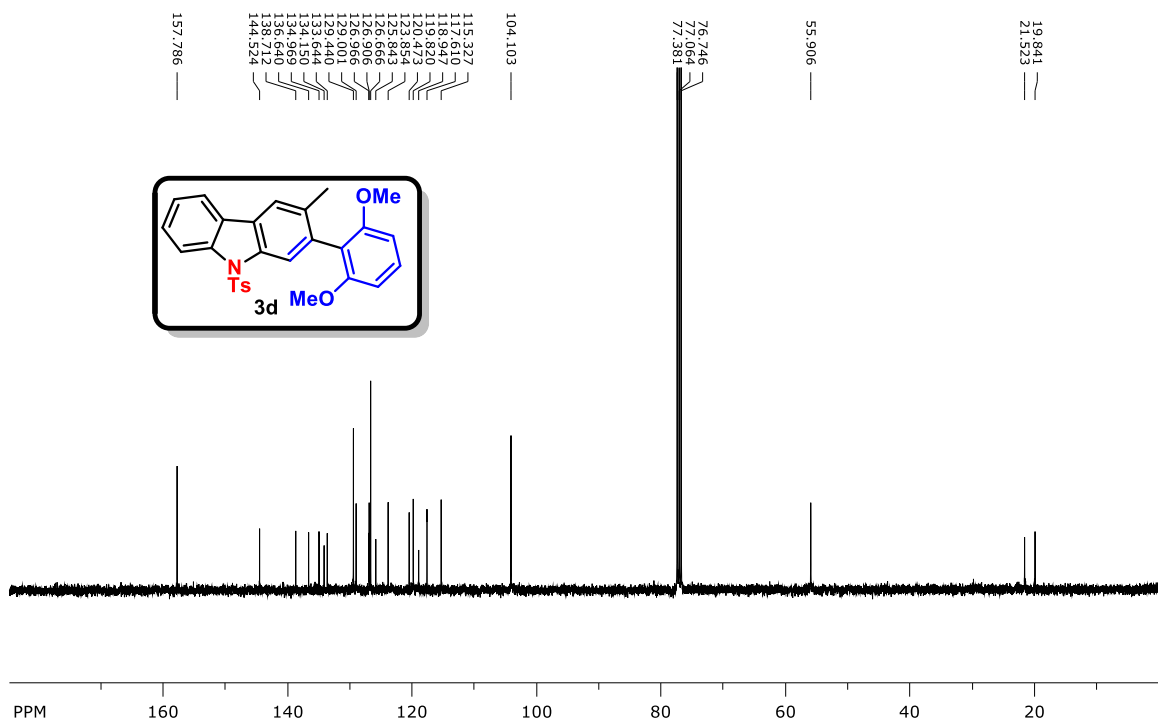




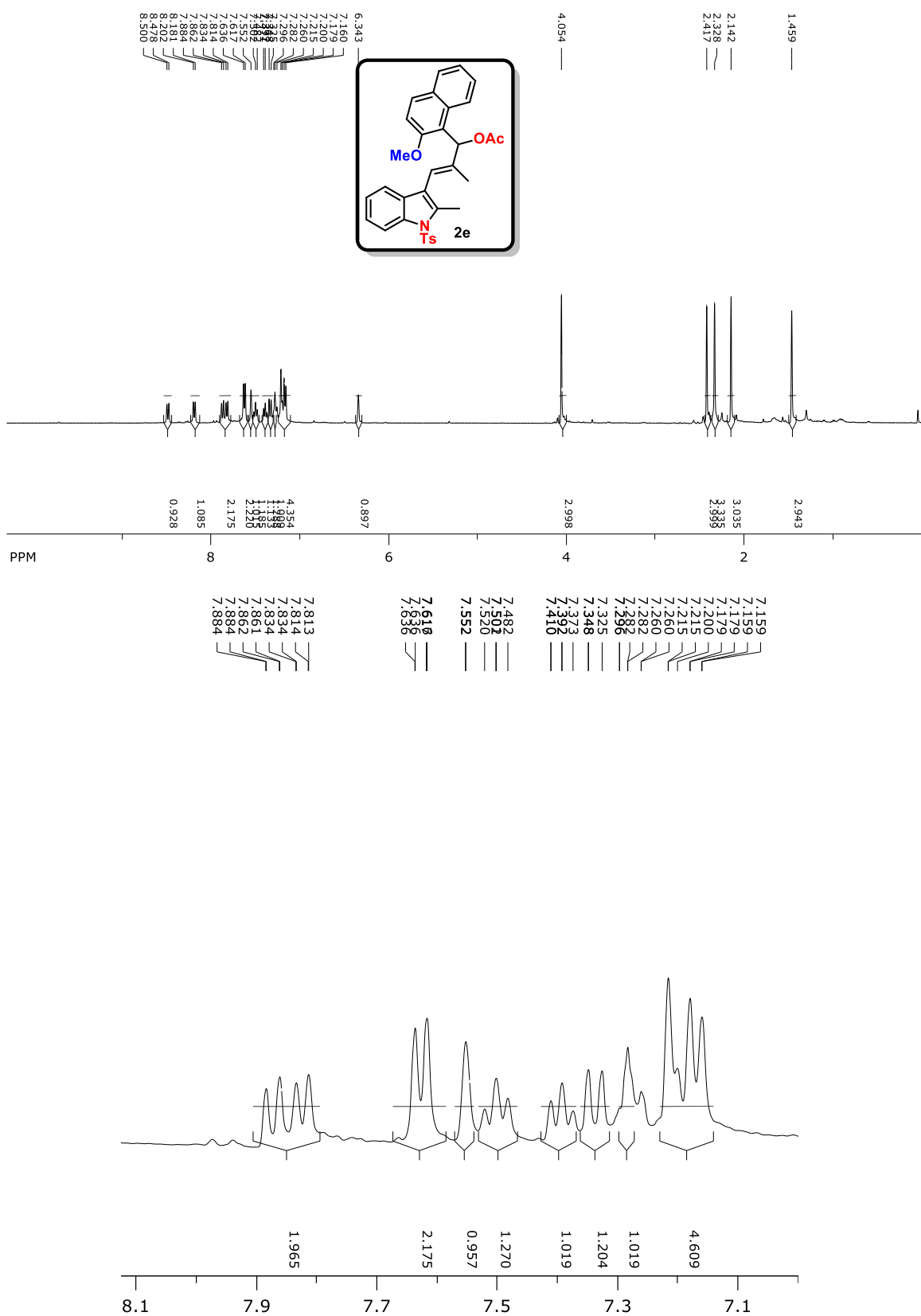
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



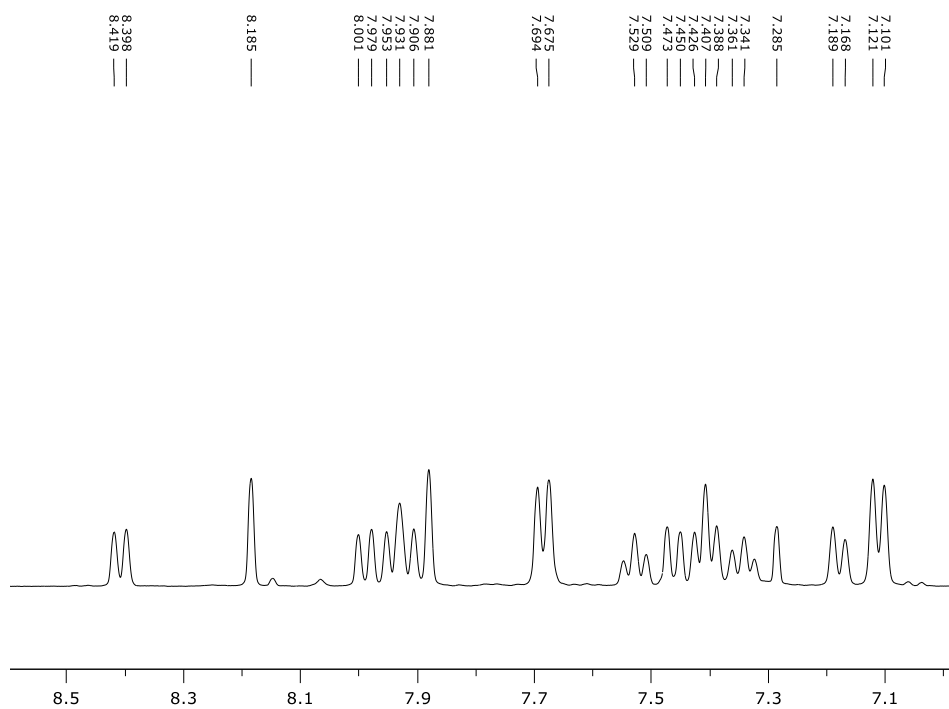
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



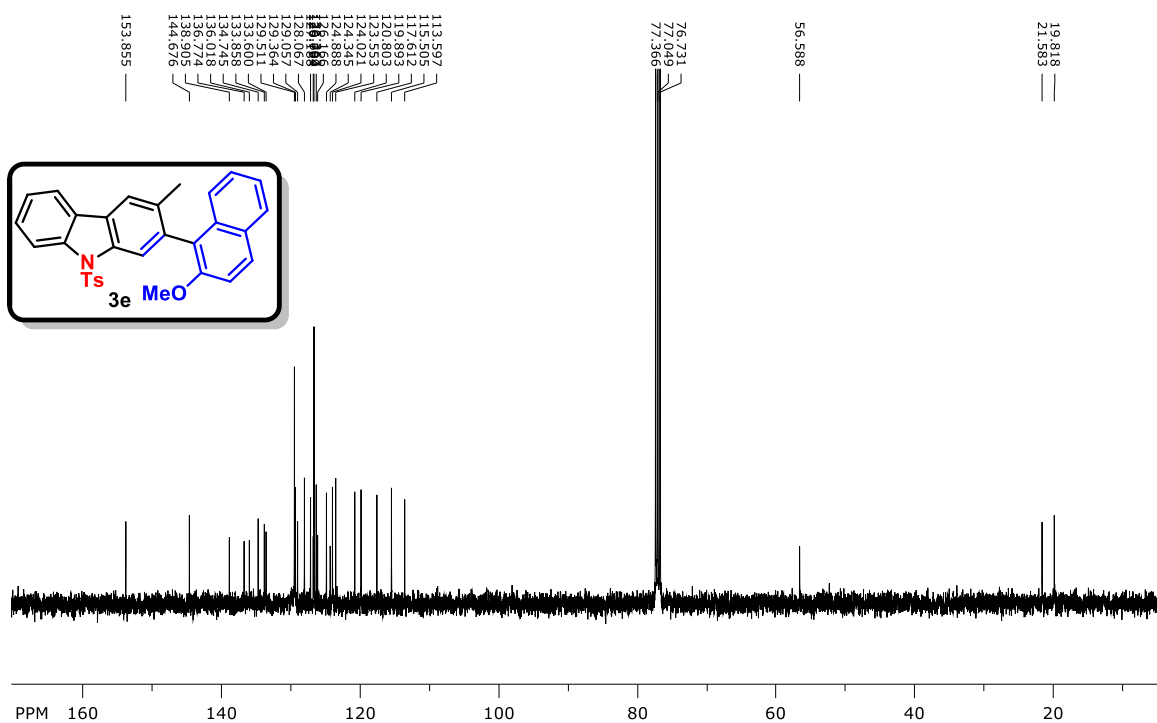
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



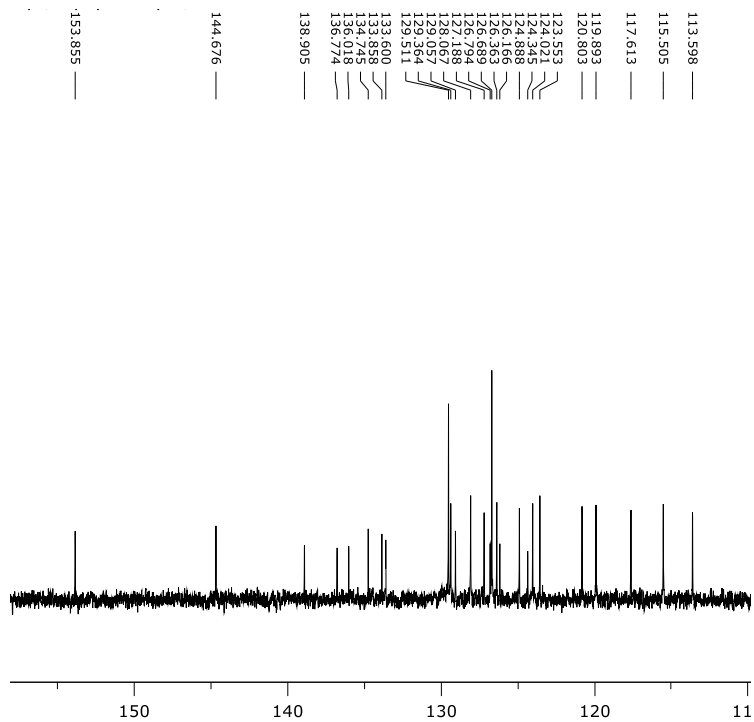




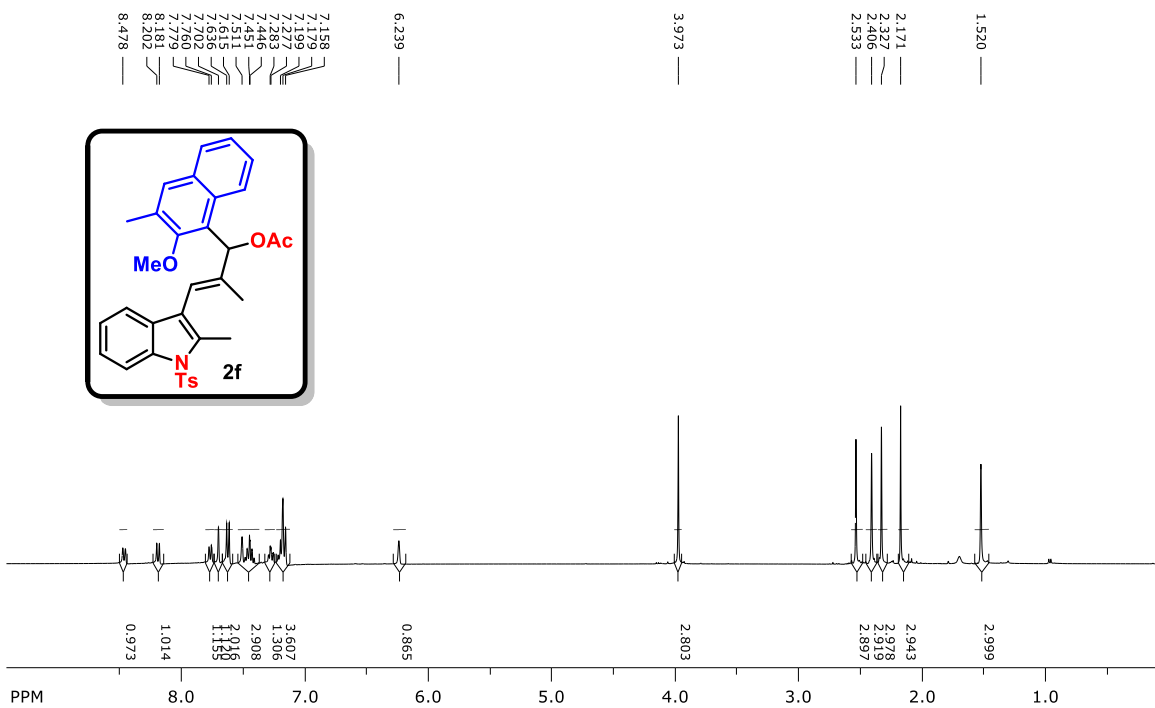
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



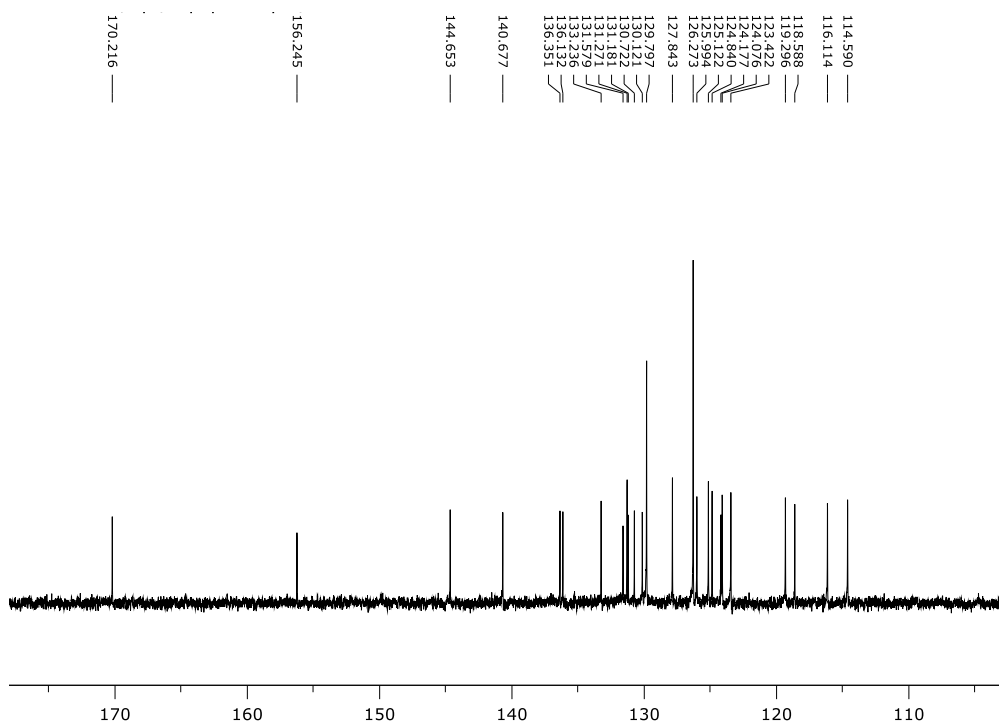
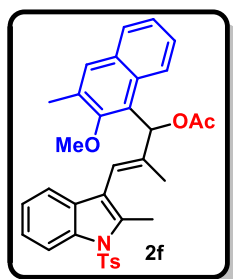
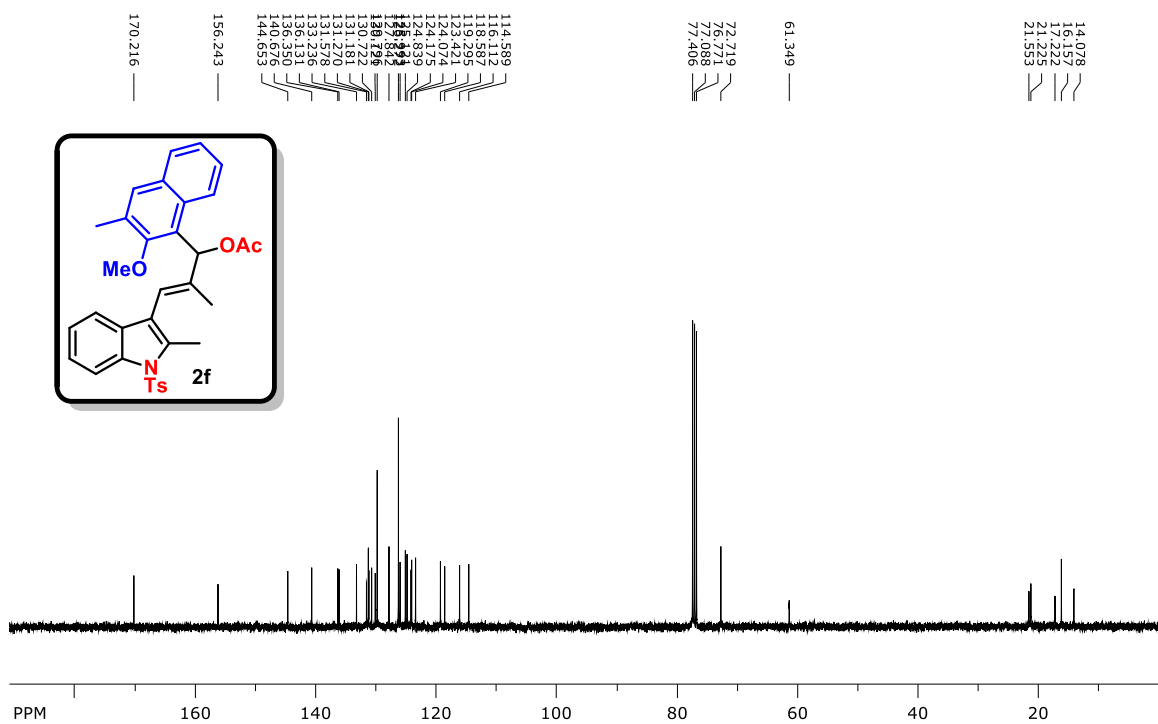




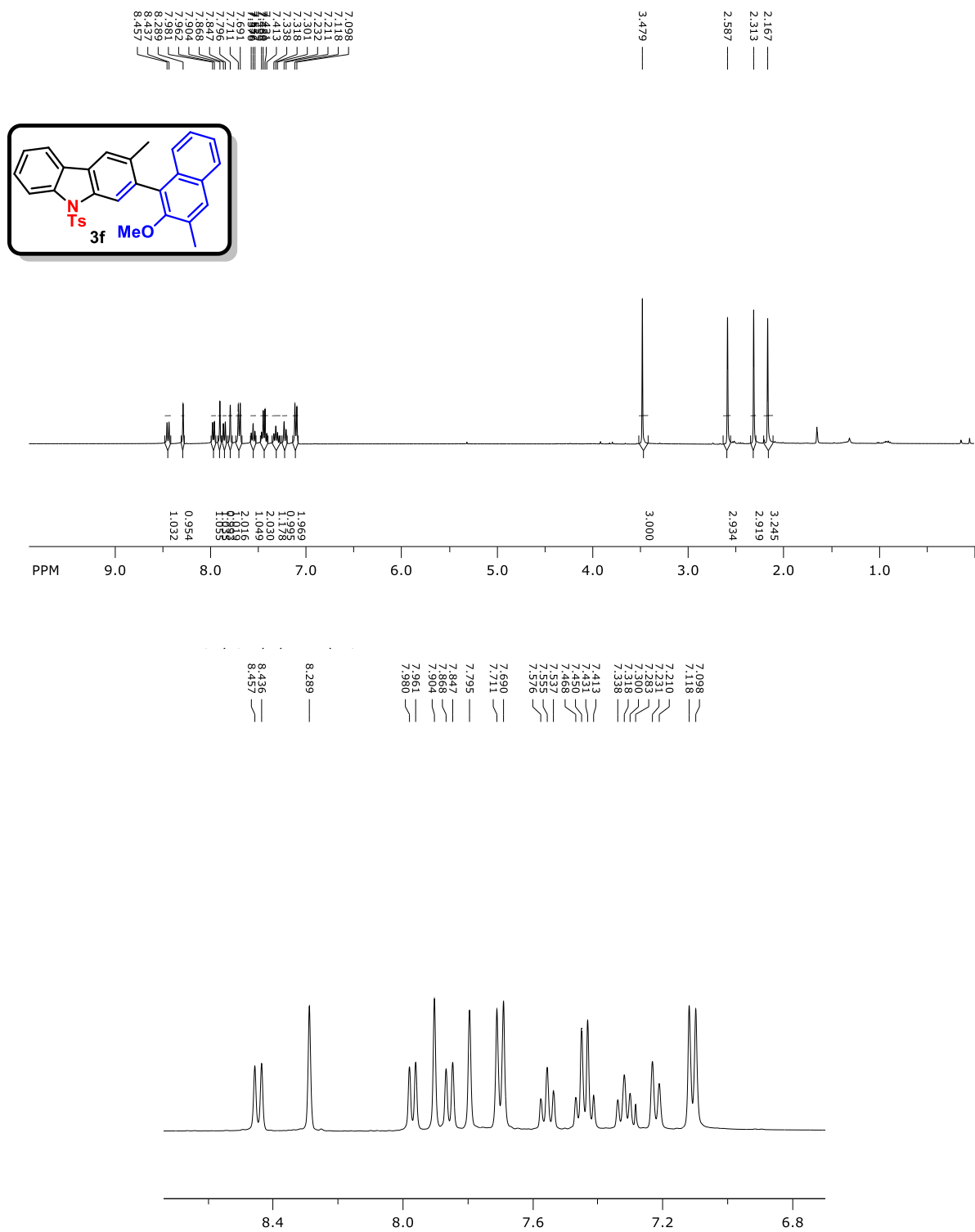
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



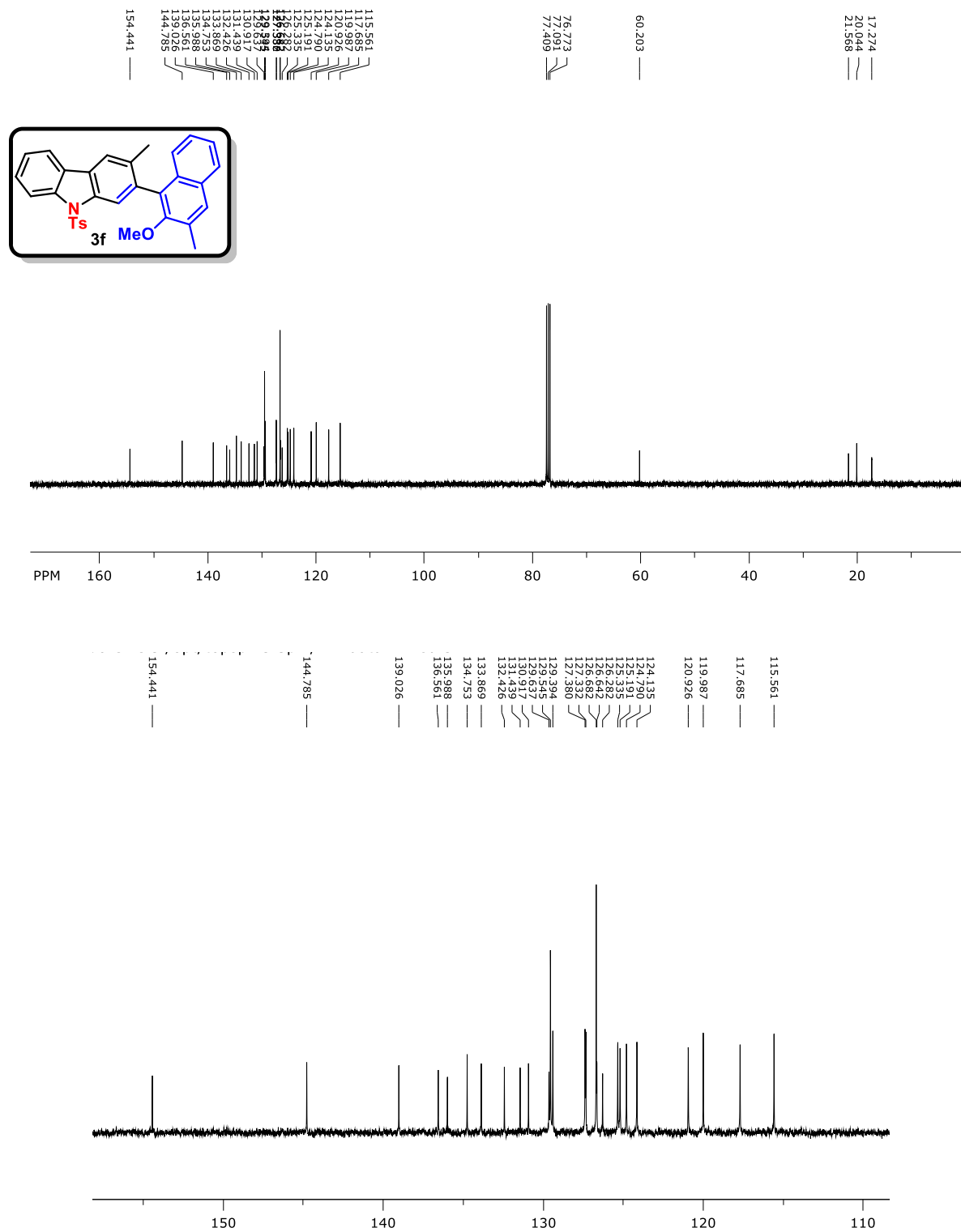
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**

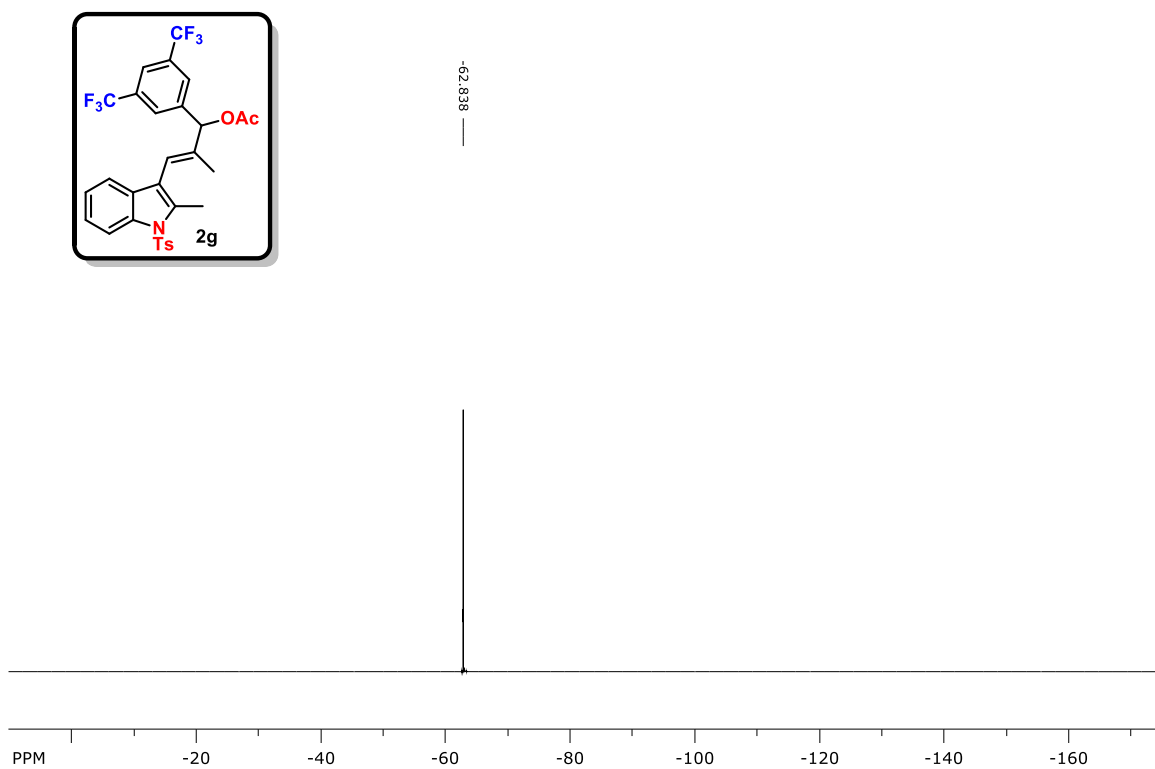


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**

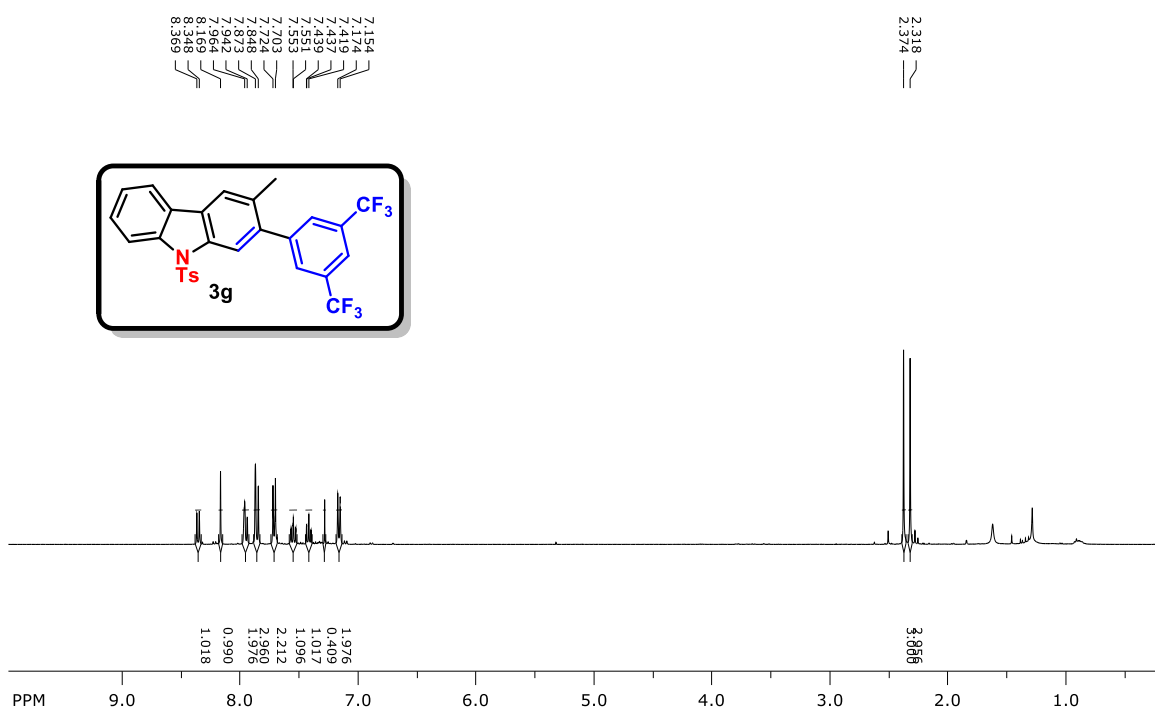




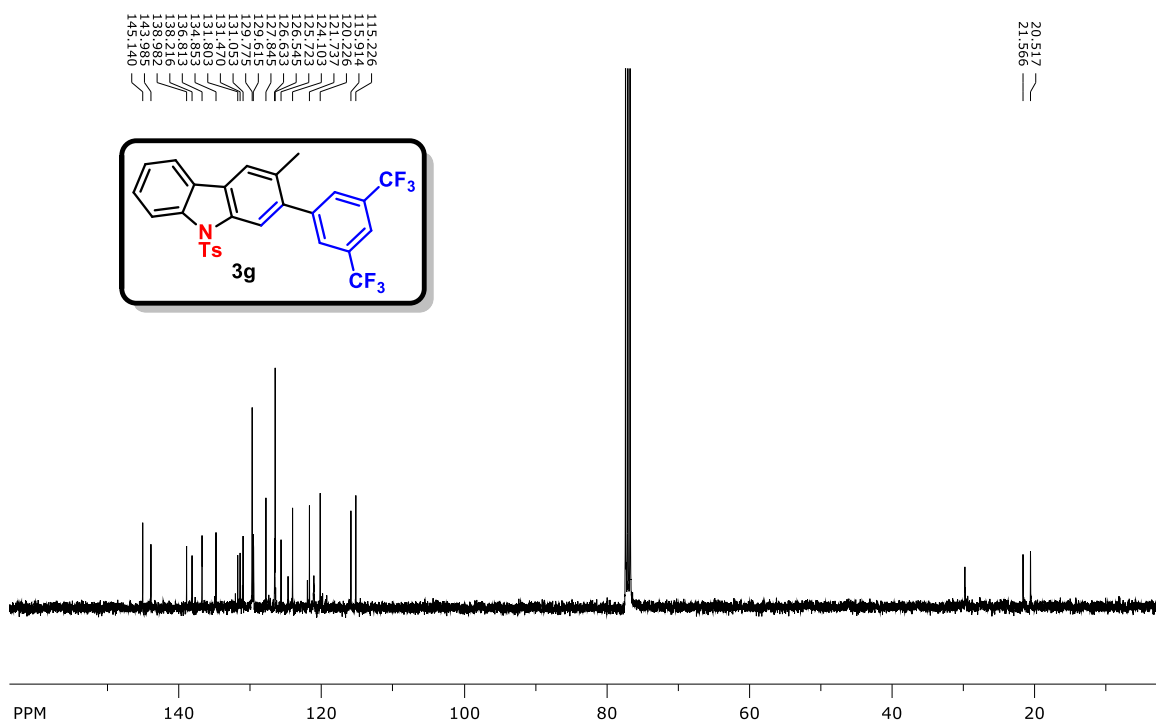
**<sup>19</sup>F NMR (374 MHz, CDCl<sub>3</sub>):**



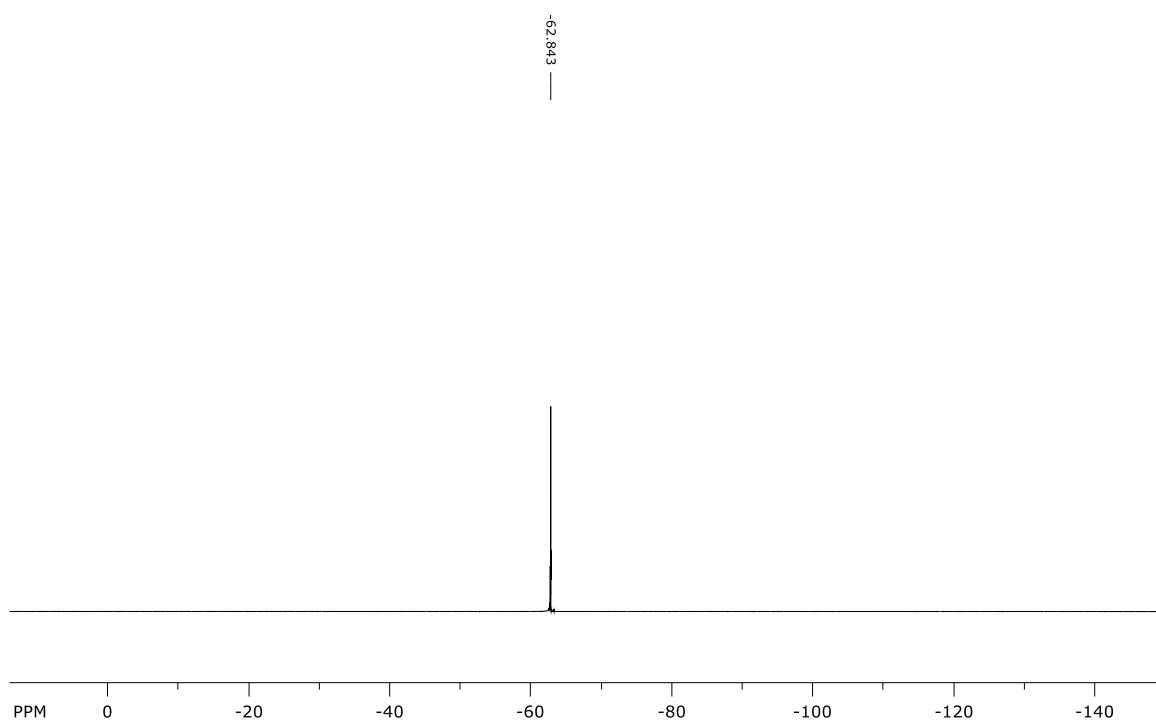
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



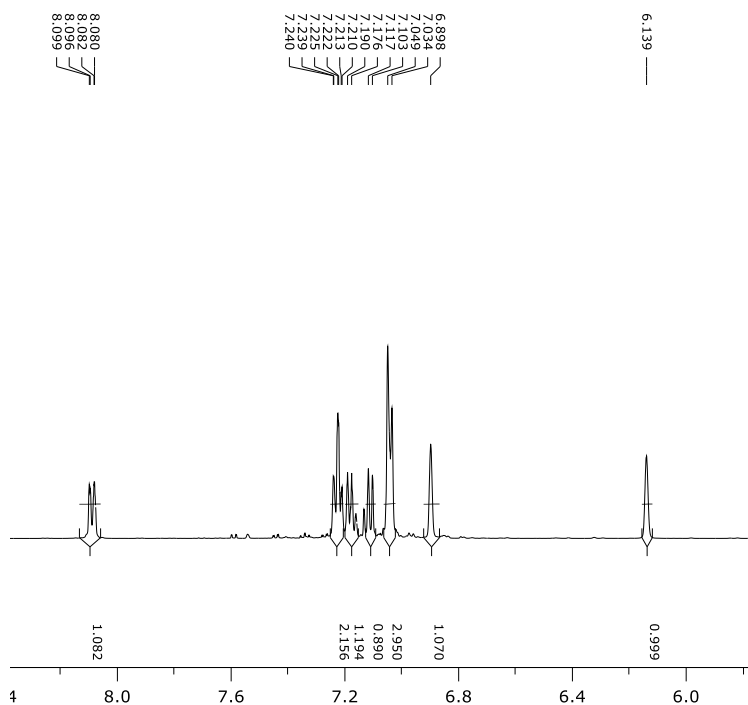
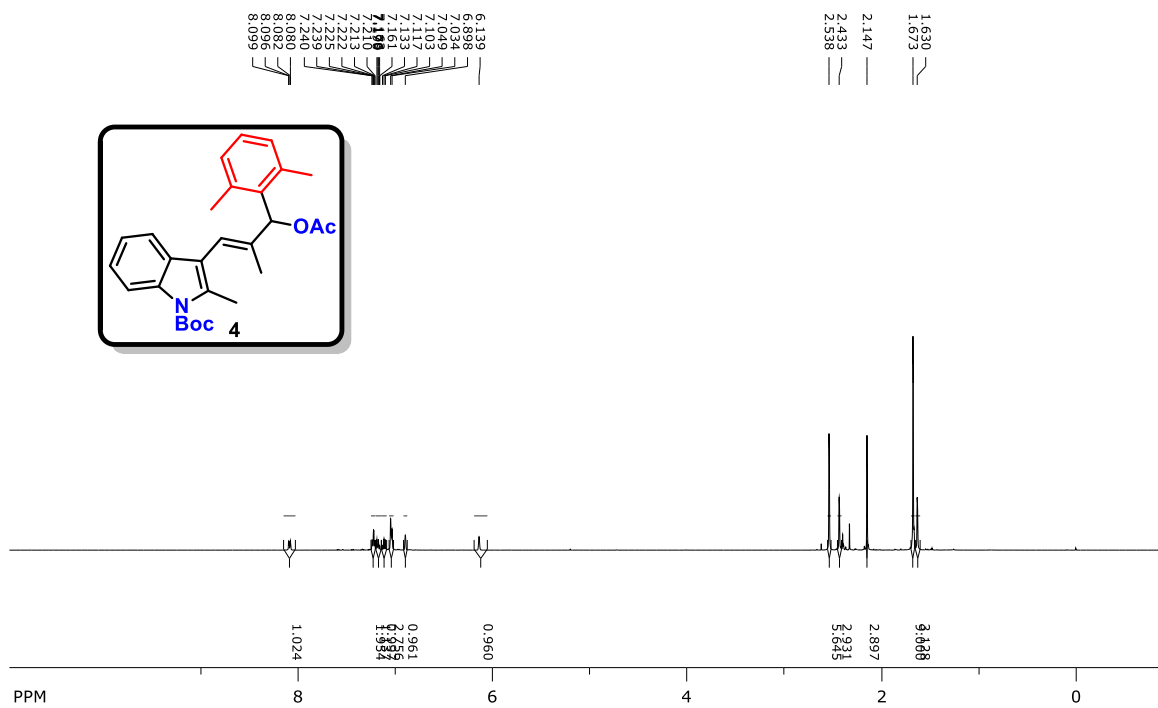
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



**<sup>19</sup>F NMR (374 MHz, CDCl<sub>3</sub>):**

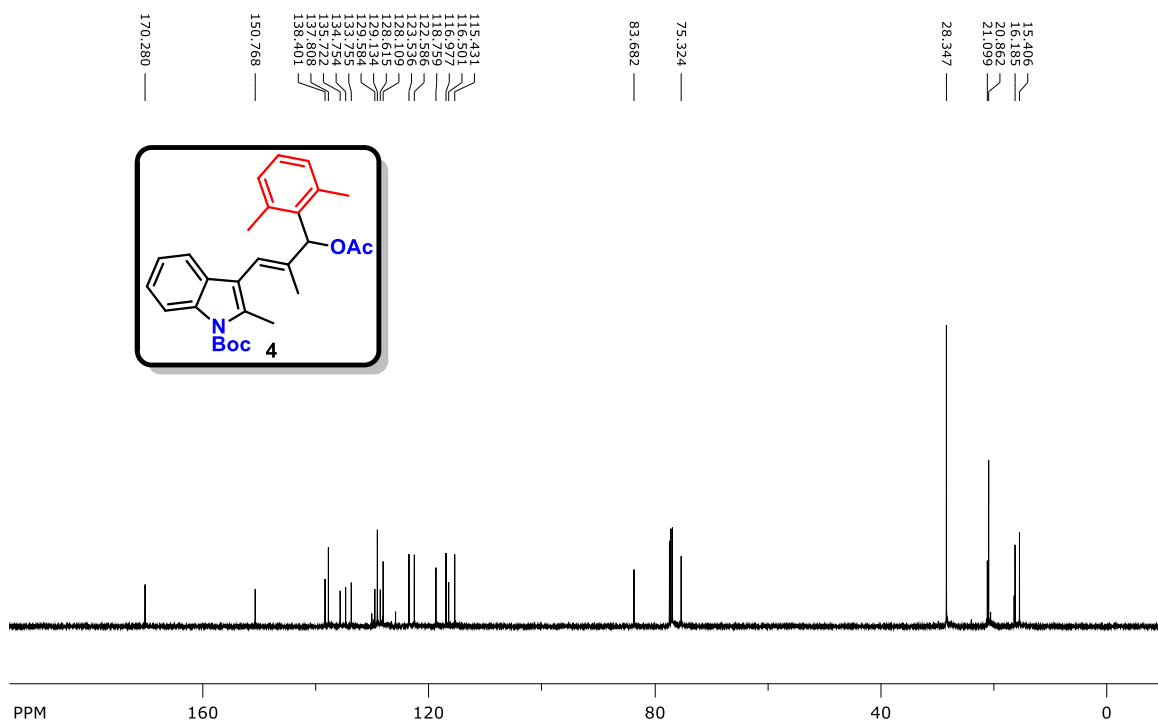


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**

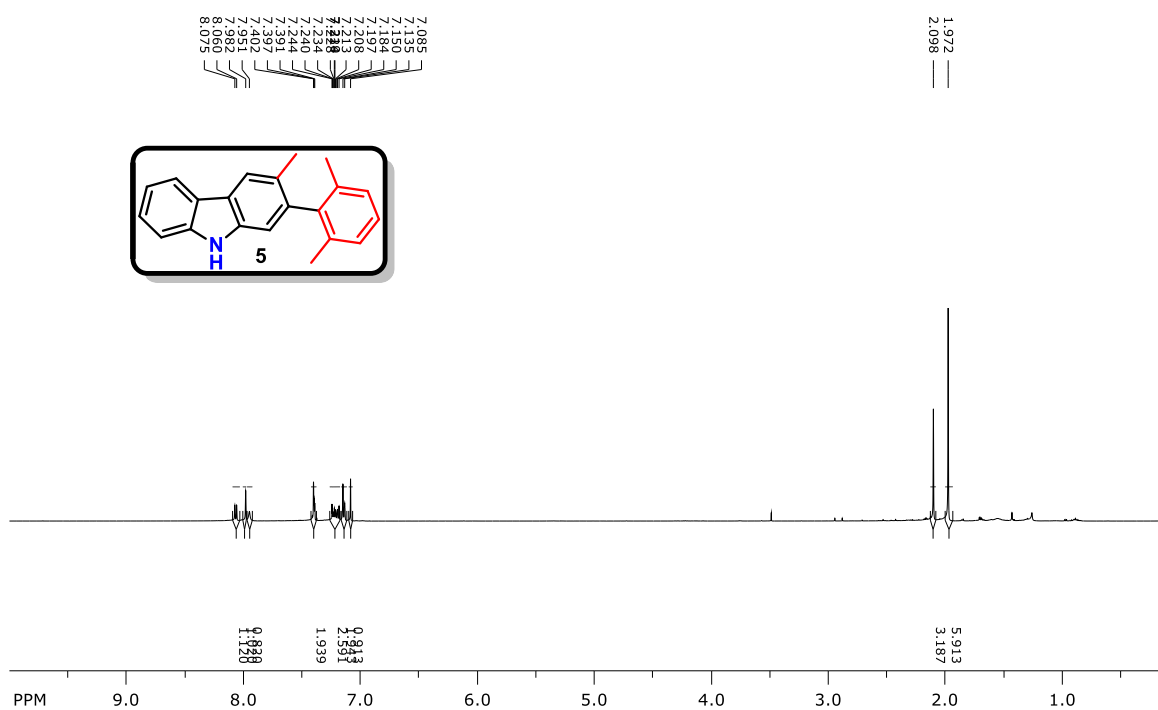




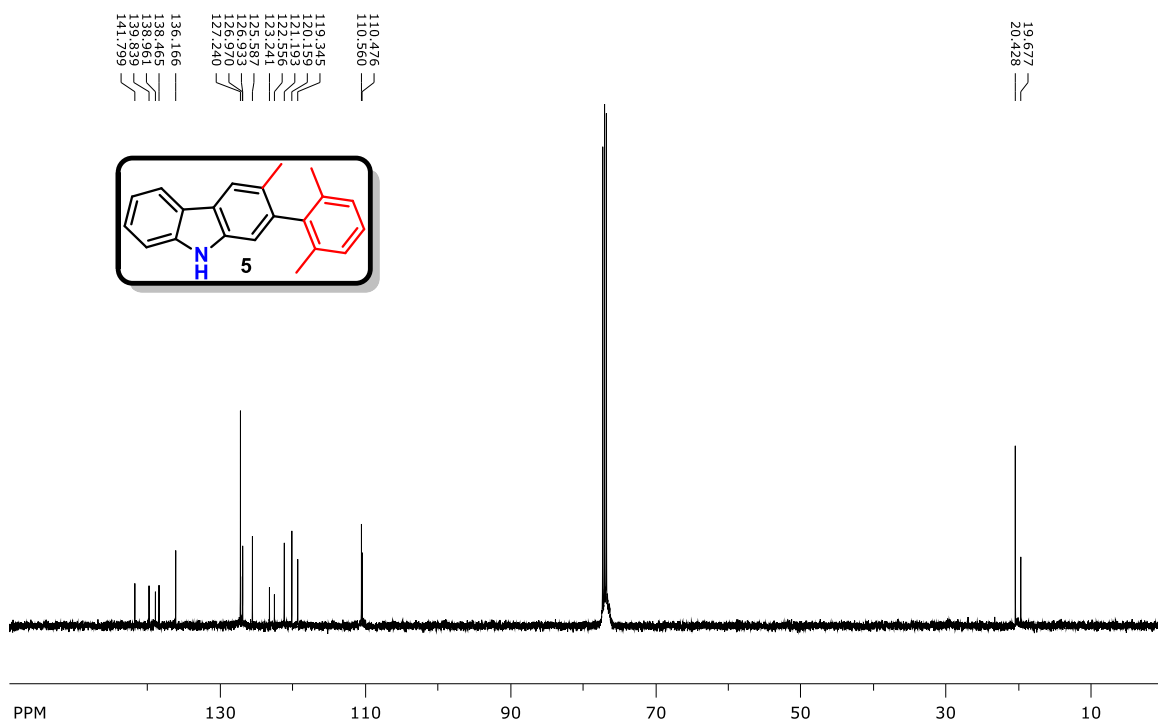
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**



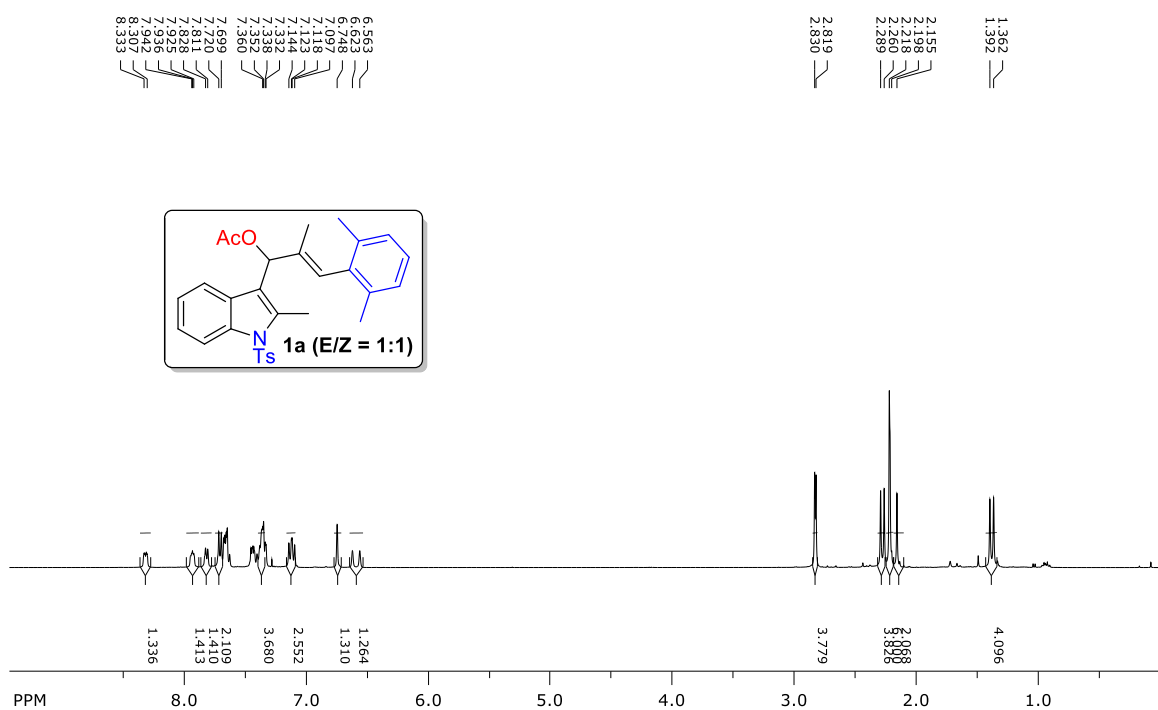
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



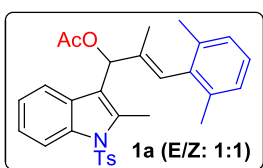
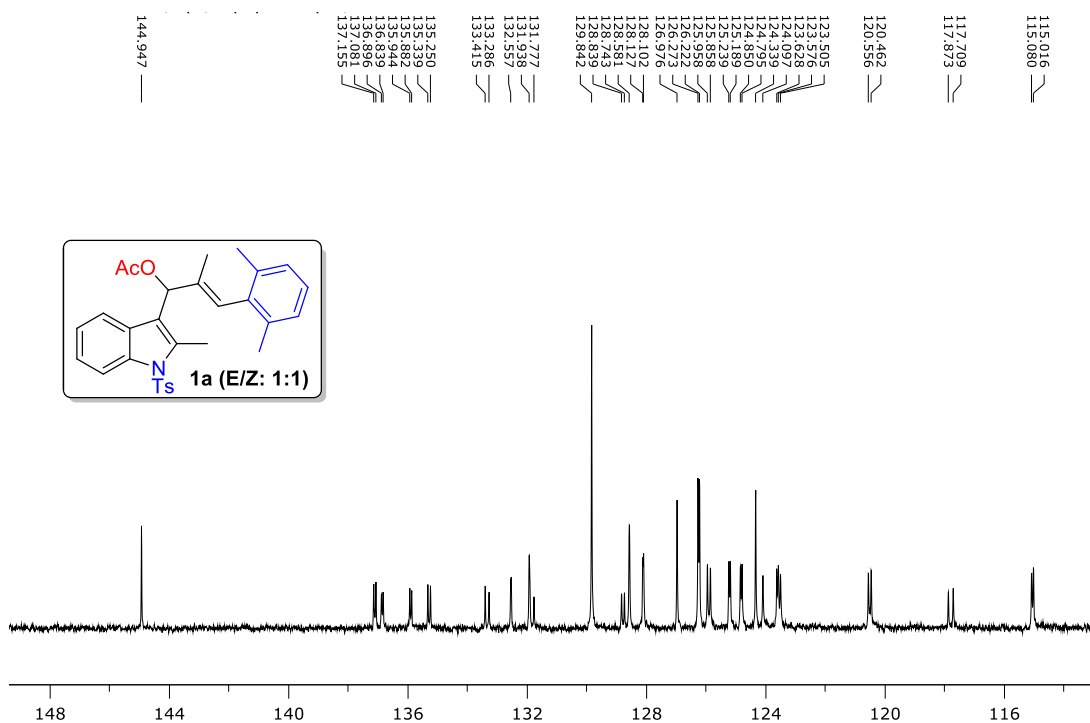
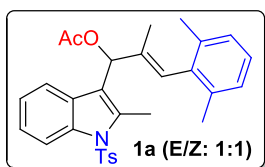
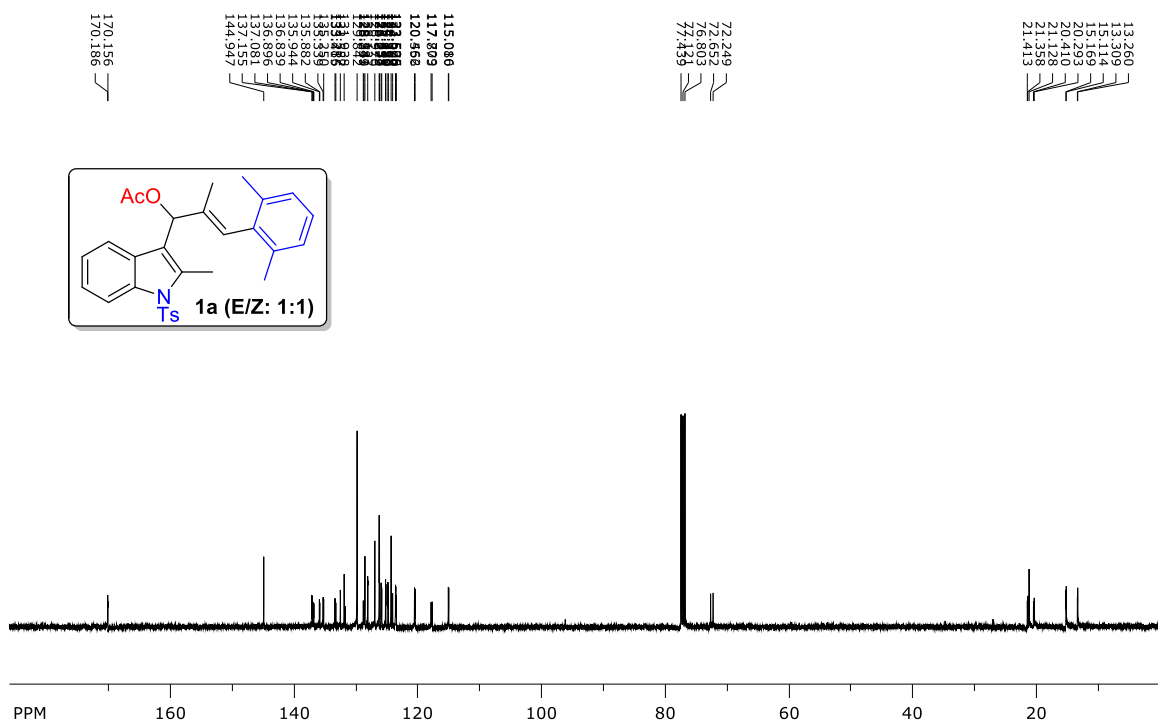
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**



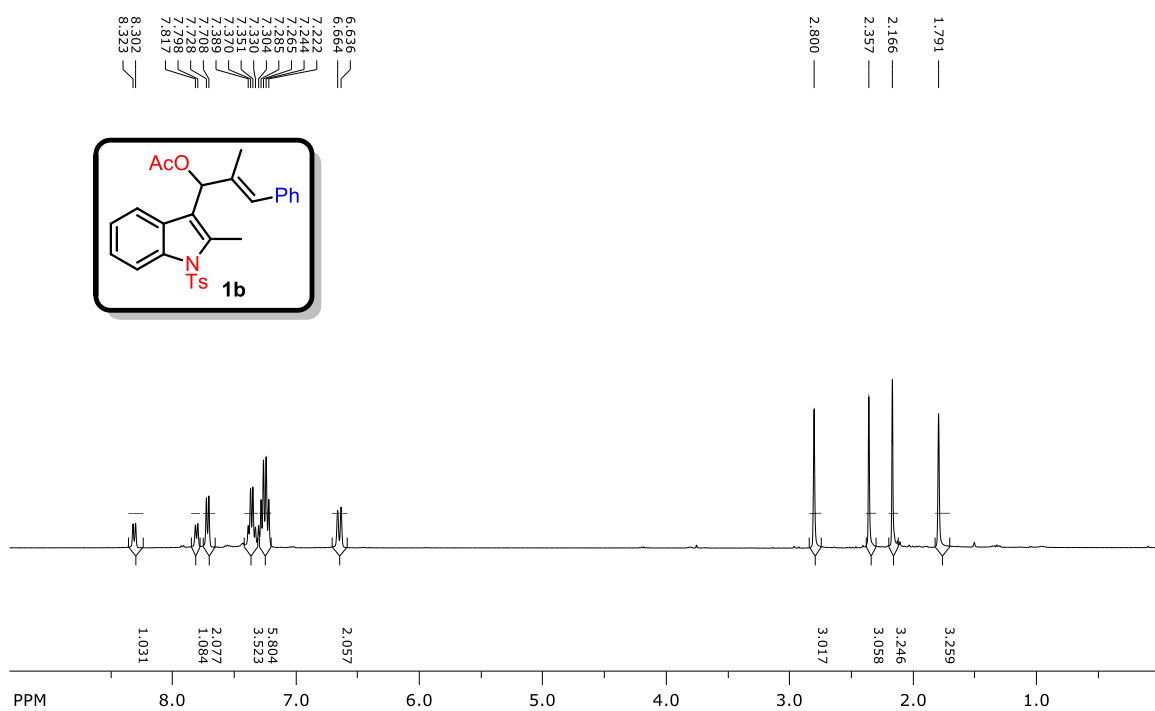
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



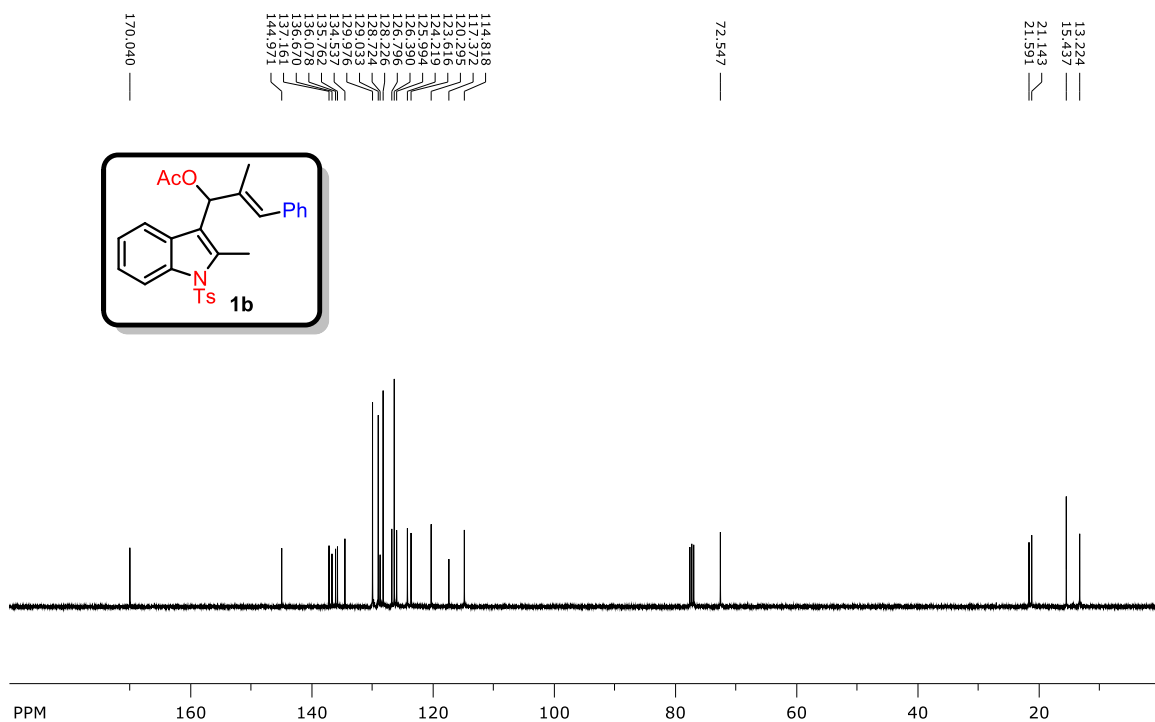
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



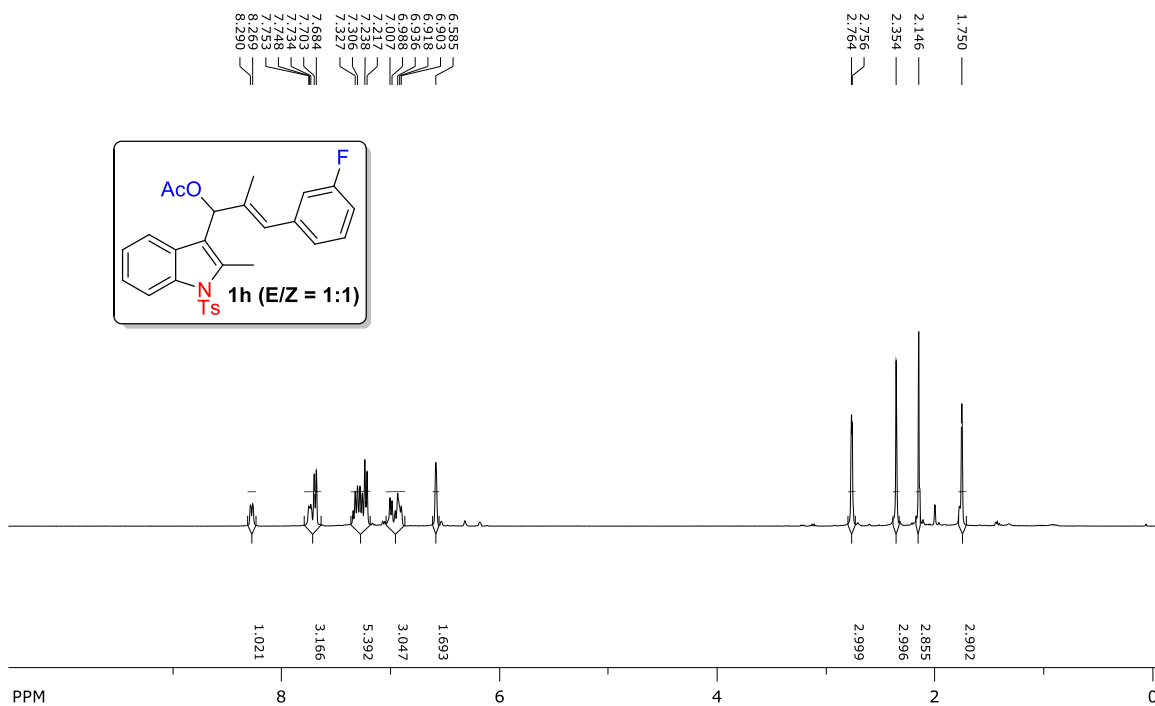
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



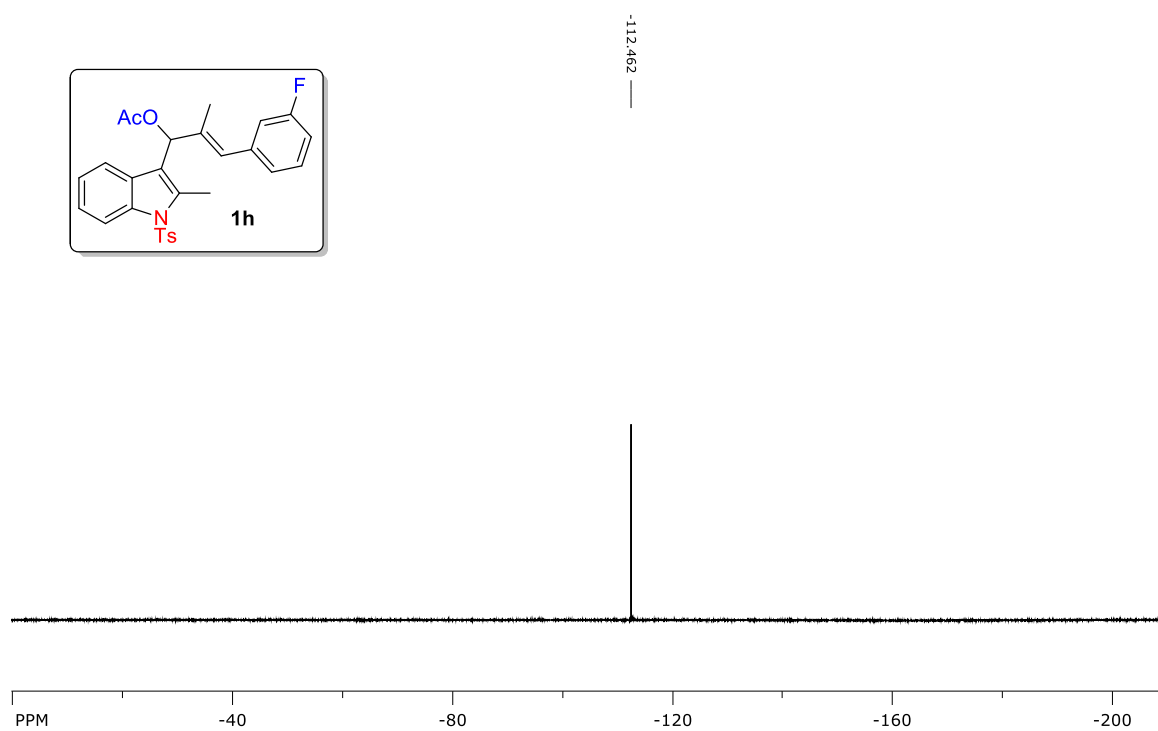
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



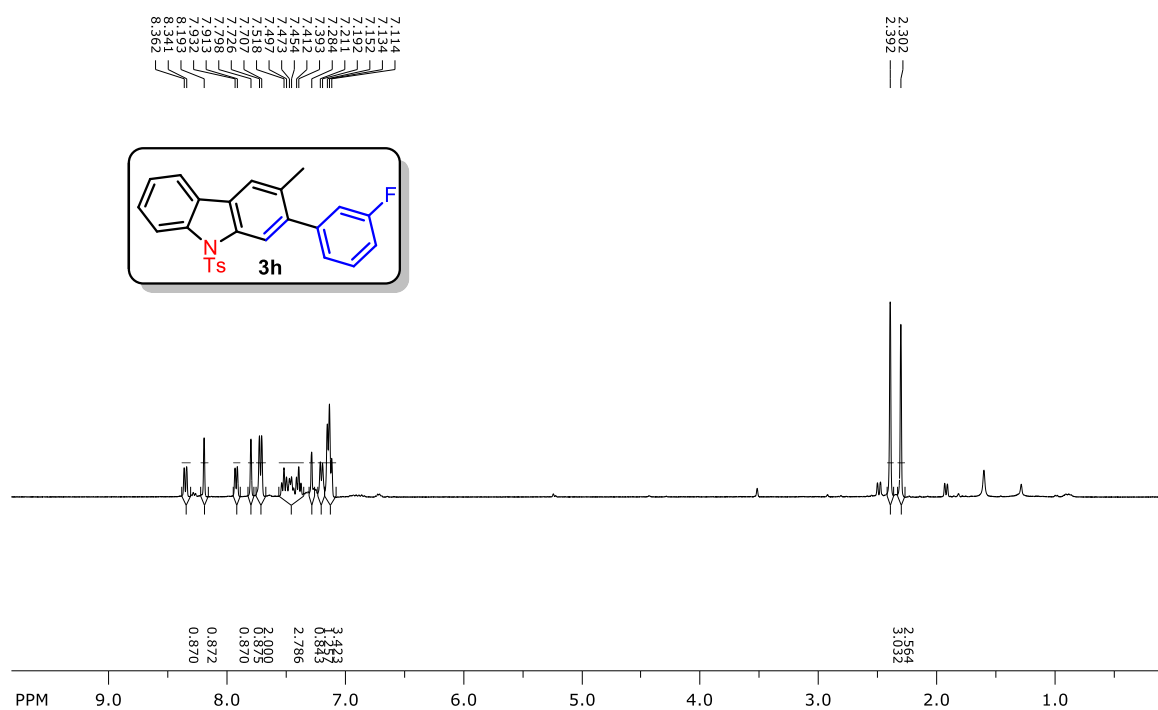
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



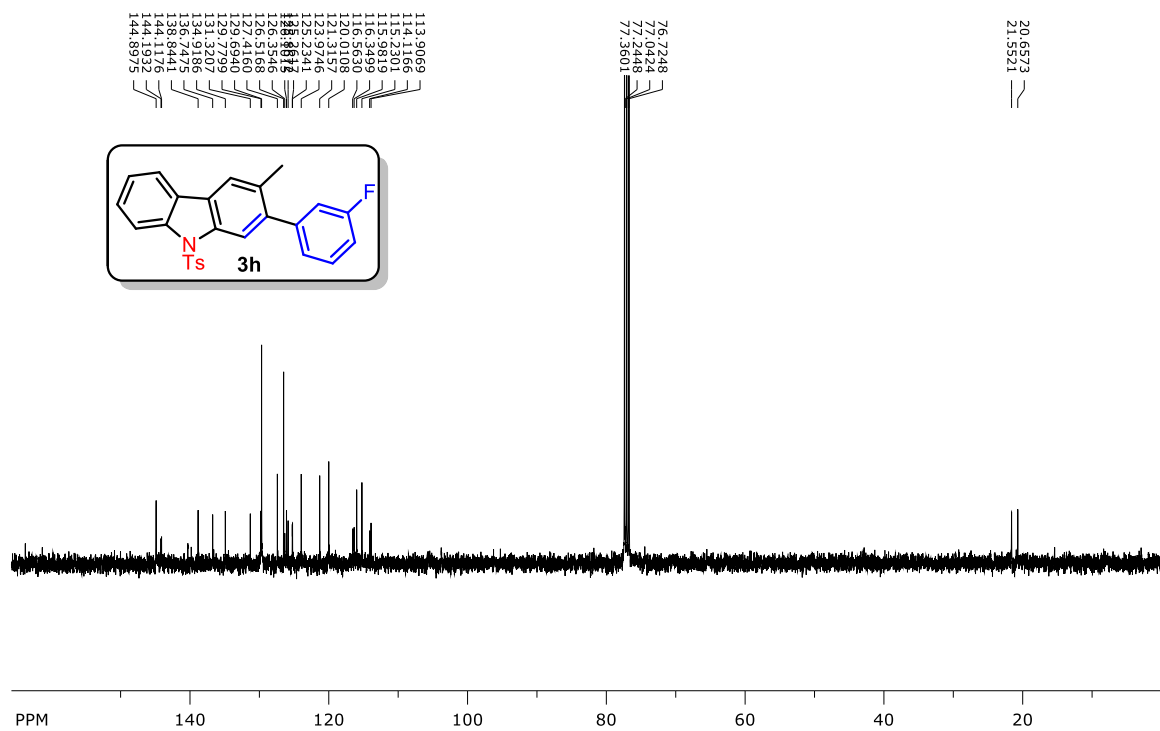
**<sup>19</sup>F NMR (374 MHz, CDCl<sub>3</sub>):**



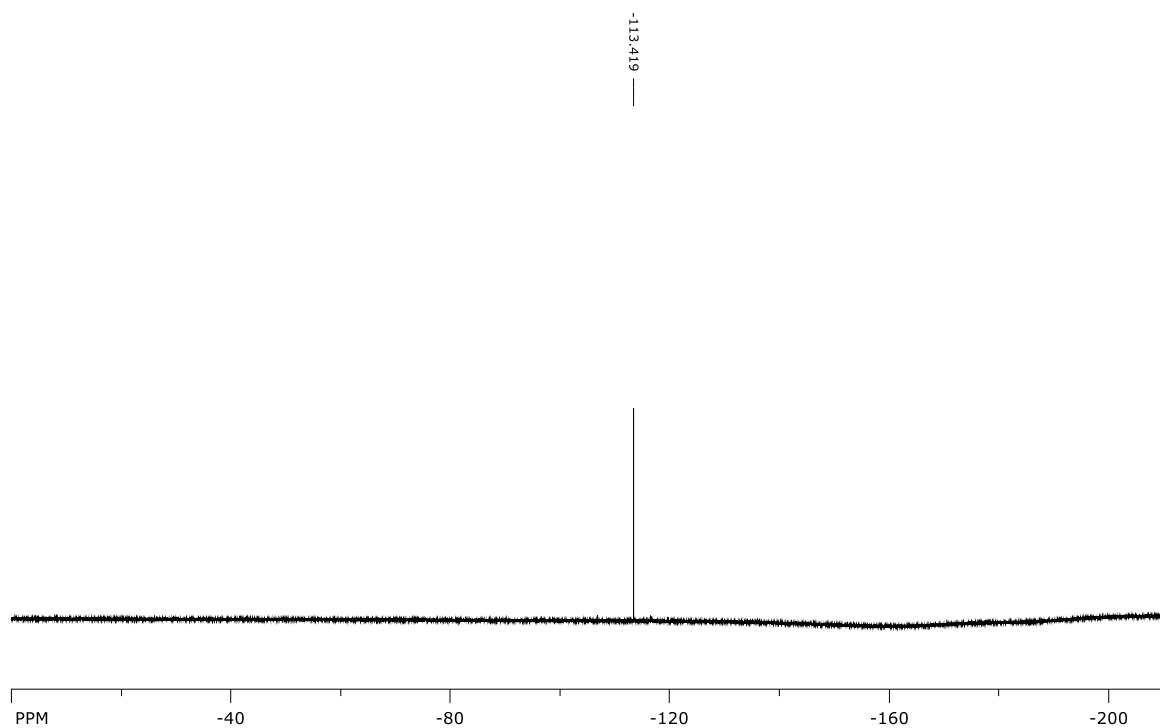
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



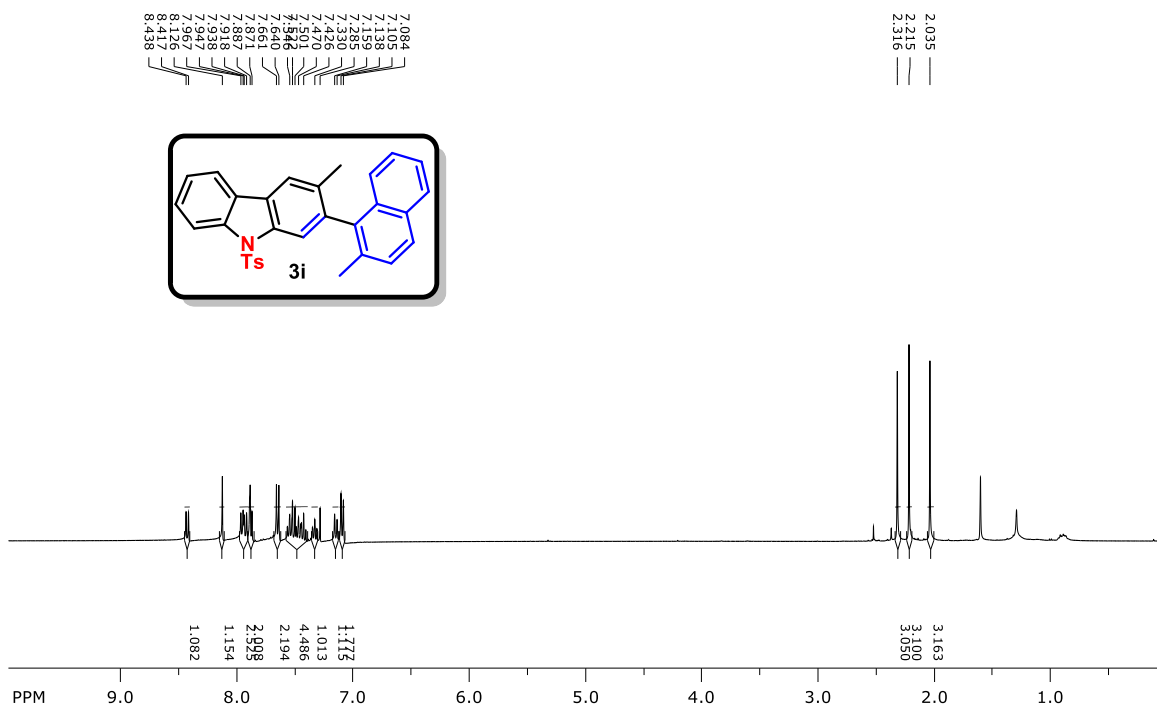
**<sup>19</sup>F NMR (374 MHz, CDCl<sub>3</sub>):**





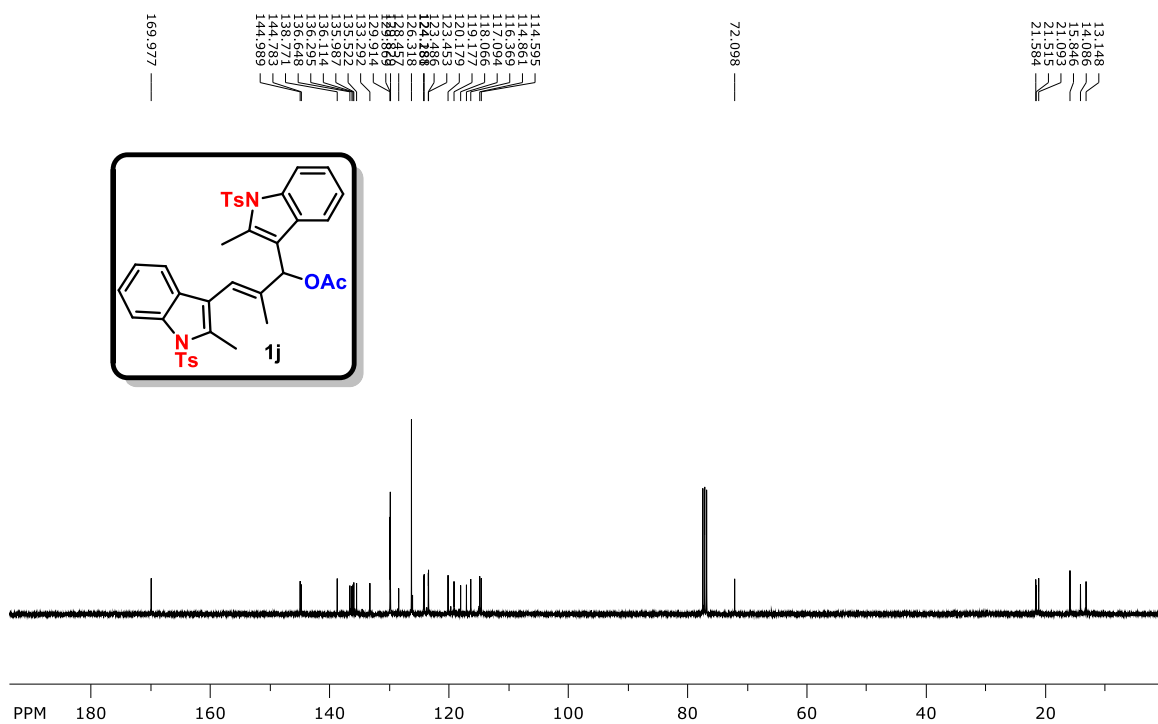


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

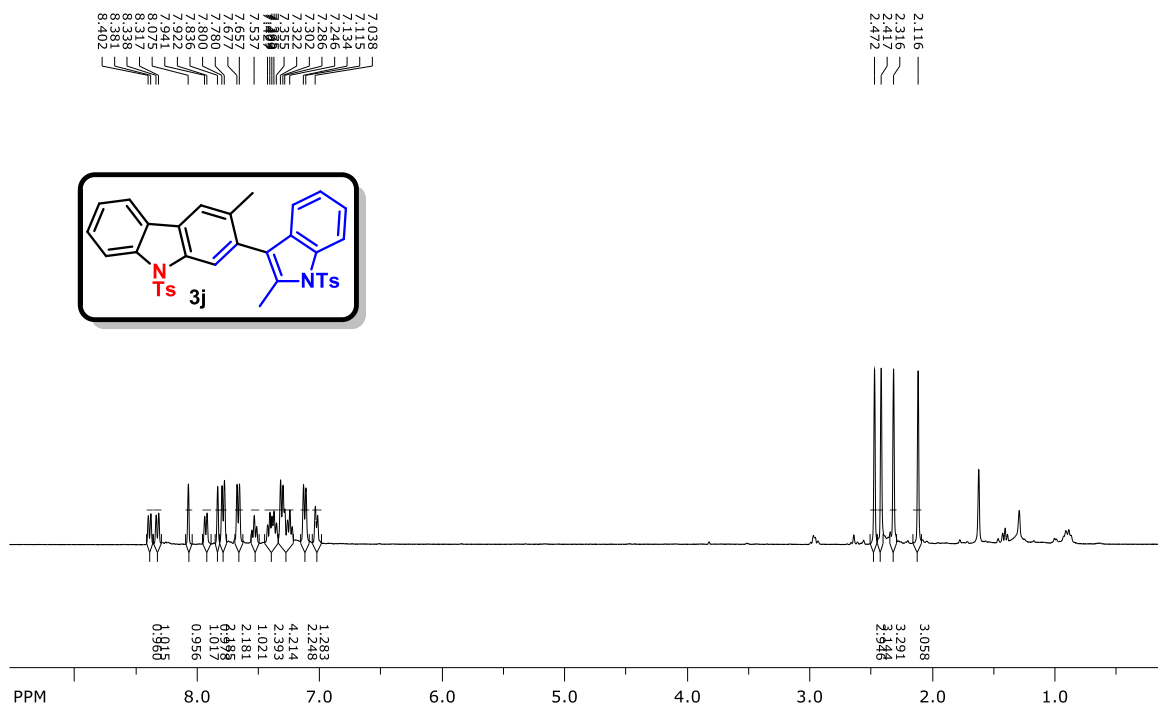


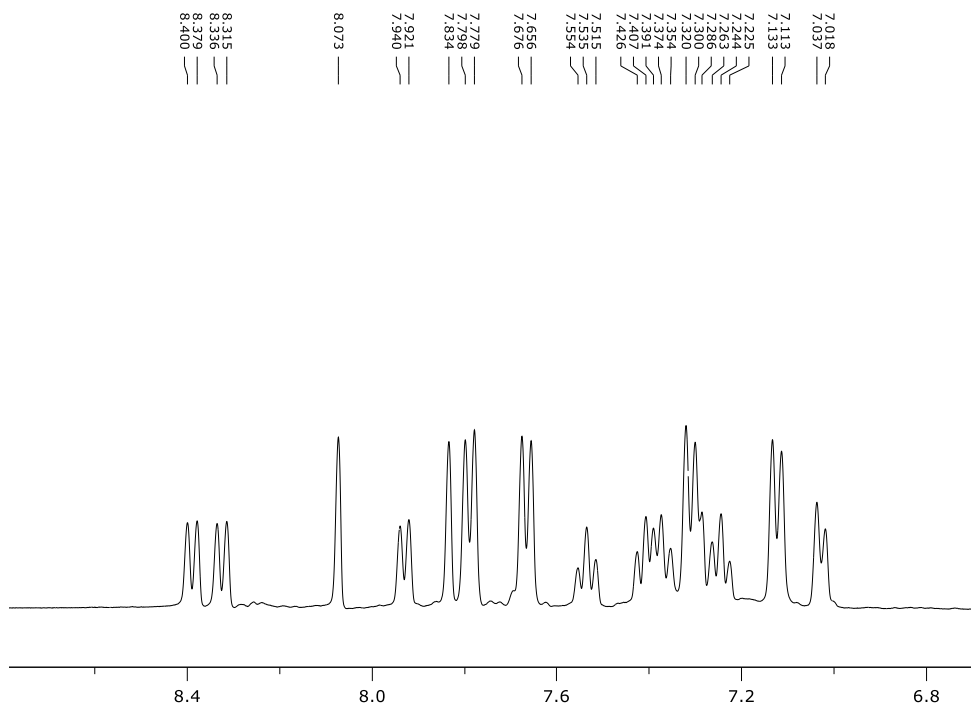


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

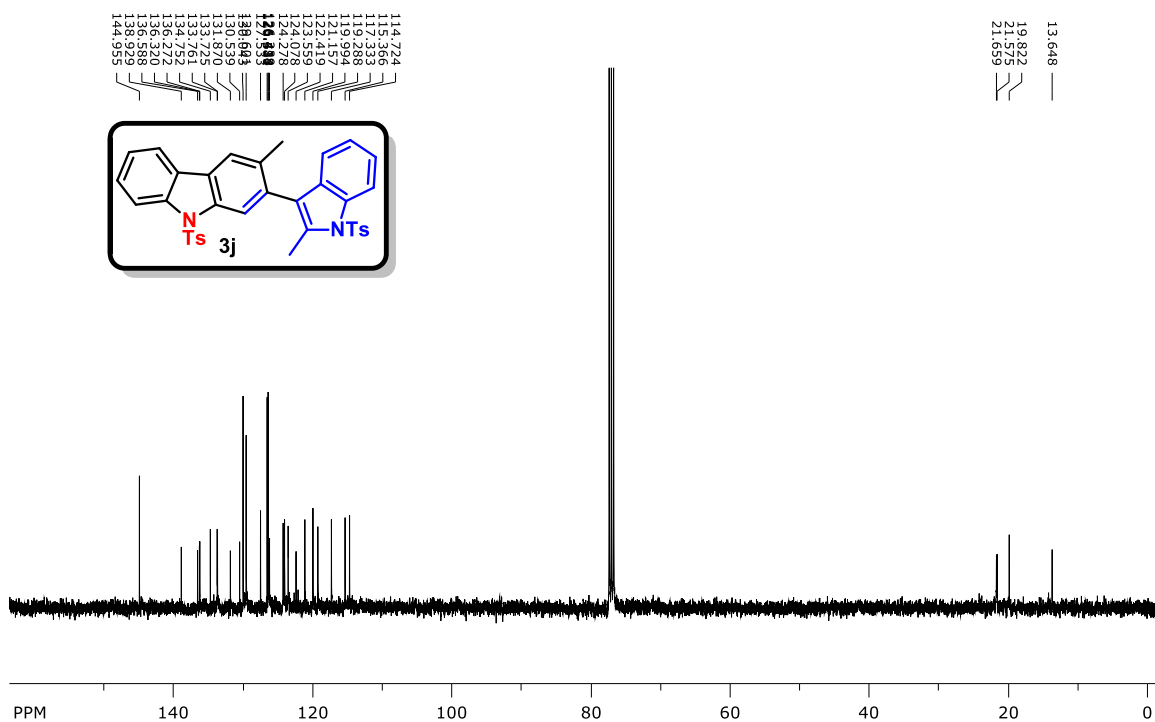


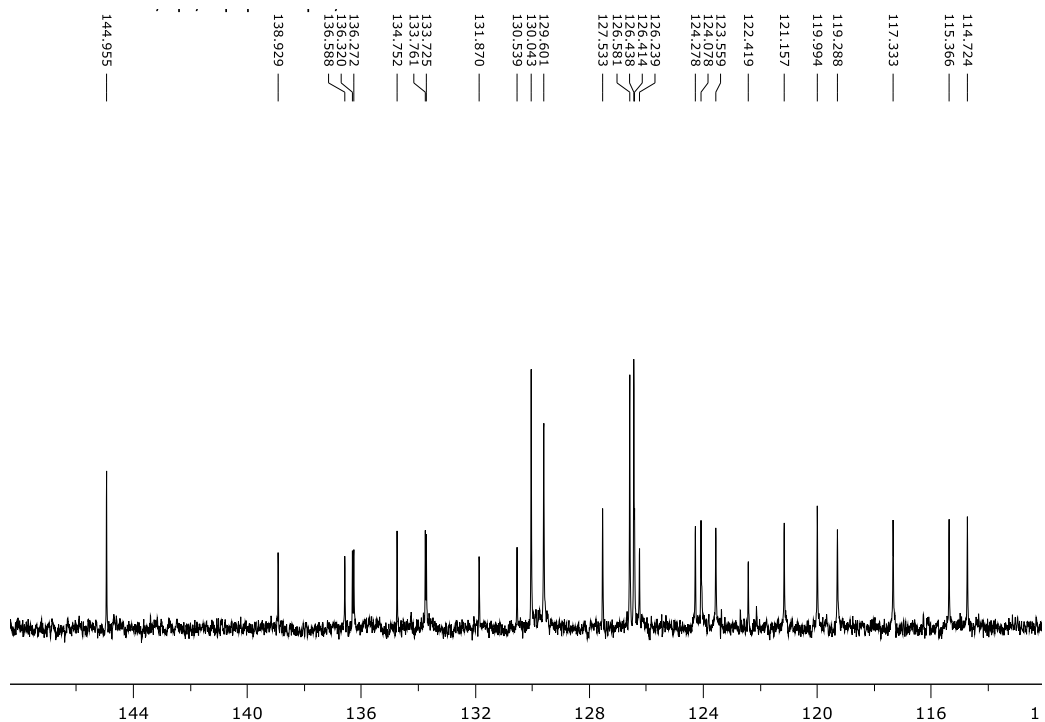
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



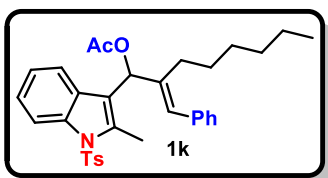
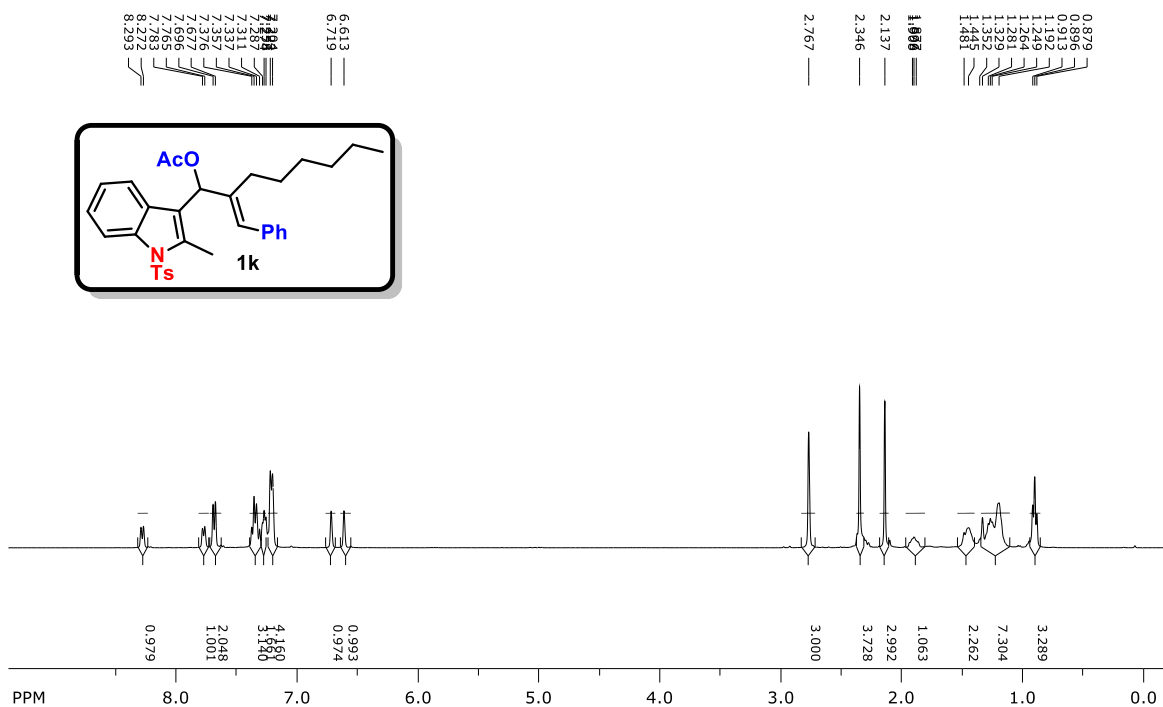


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

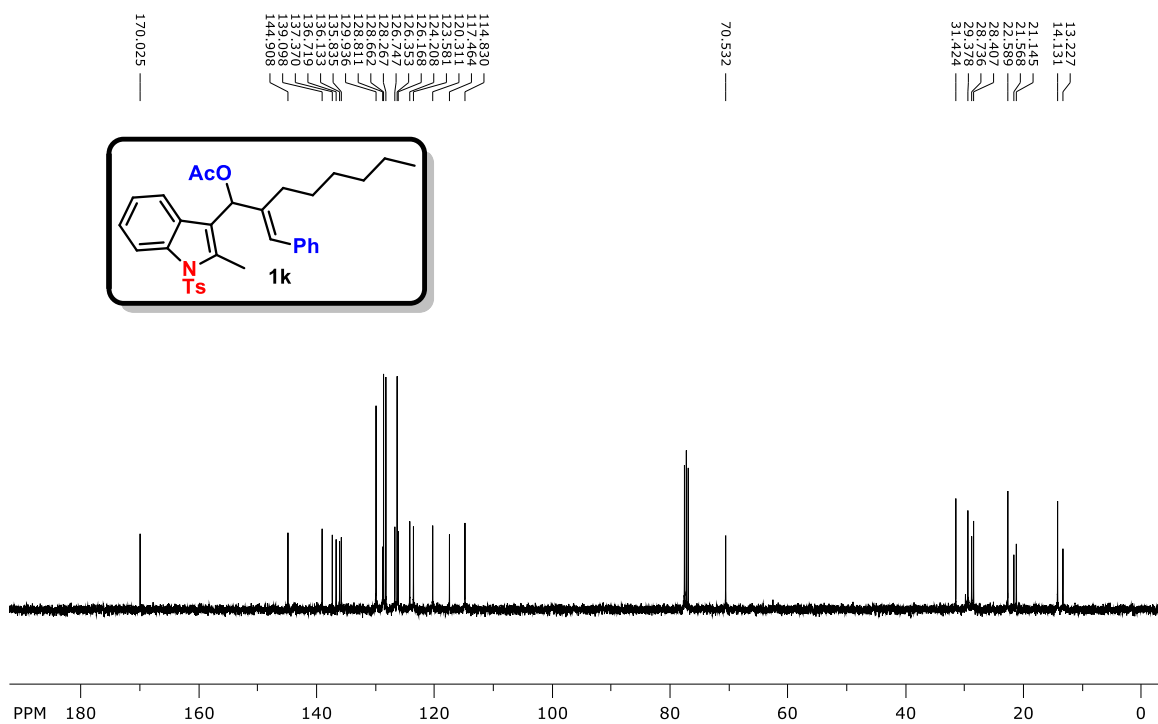




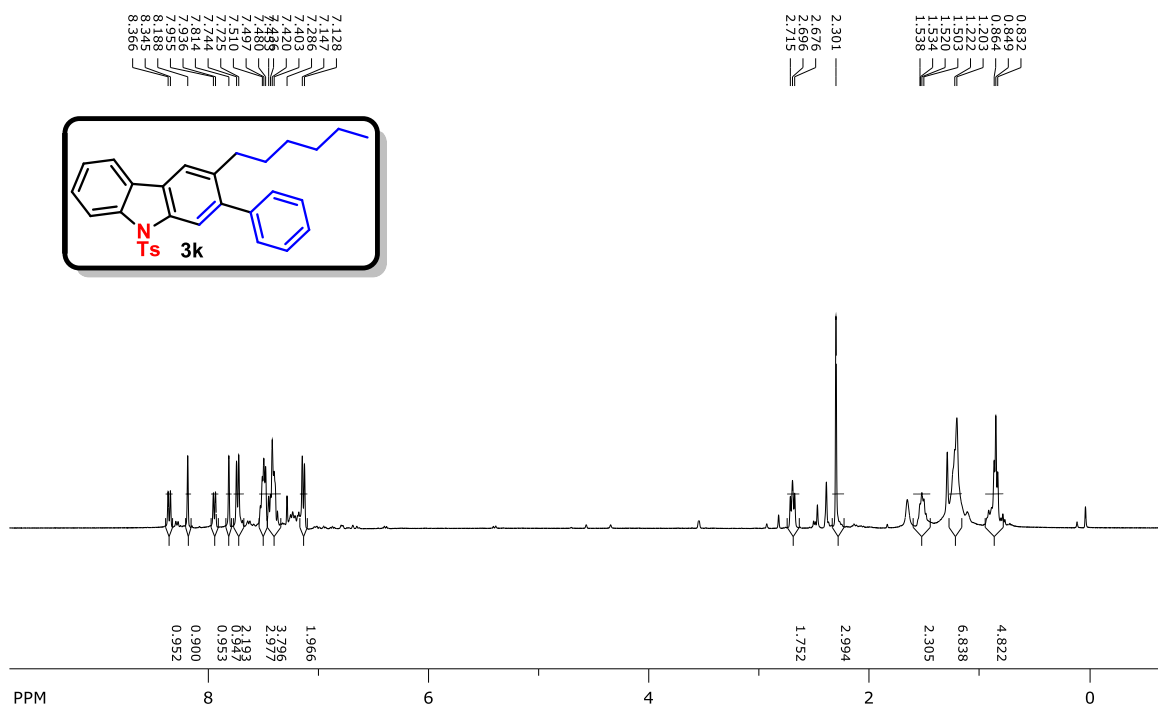
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



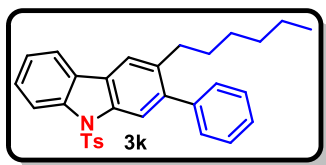
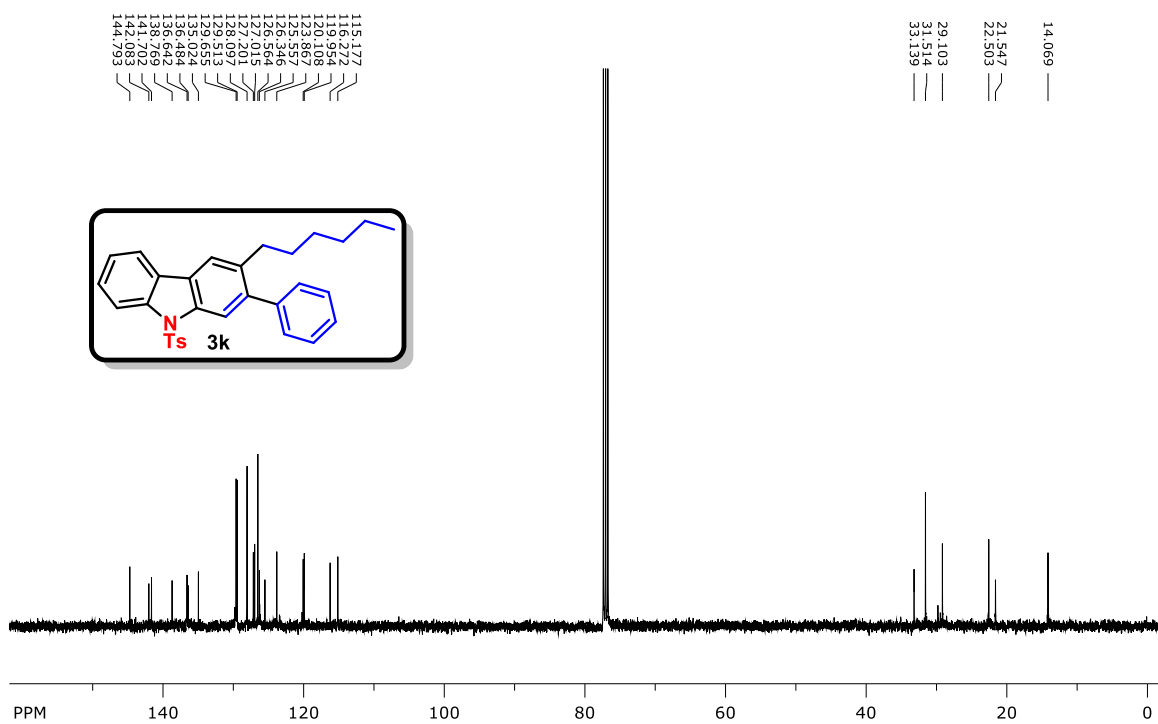
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



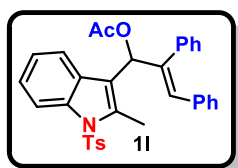
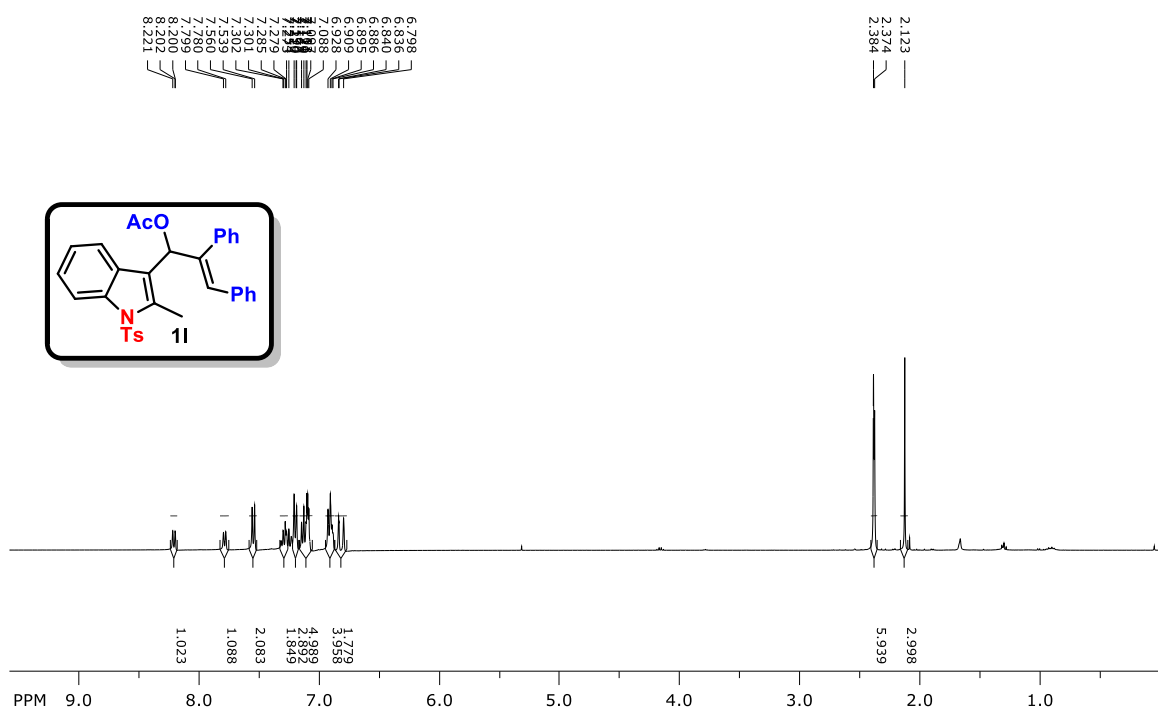
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

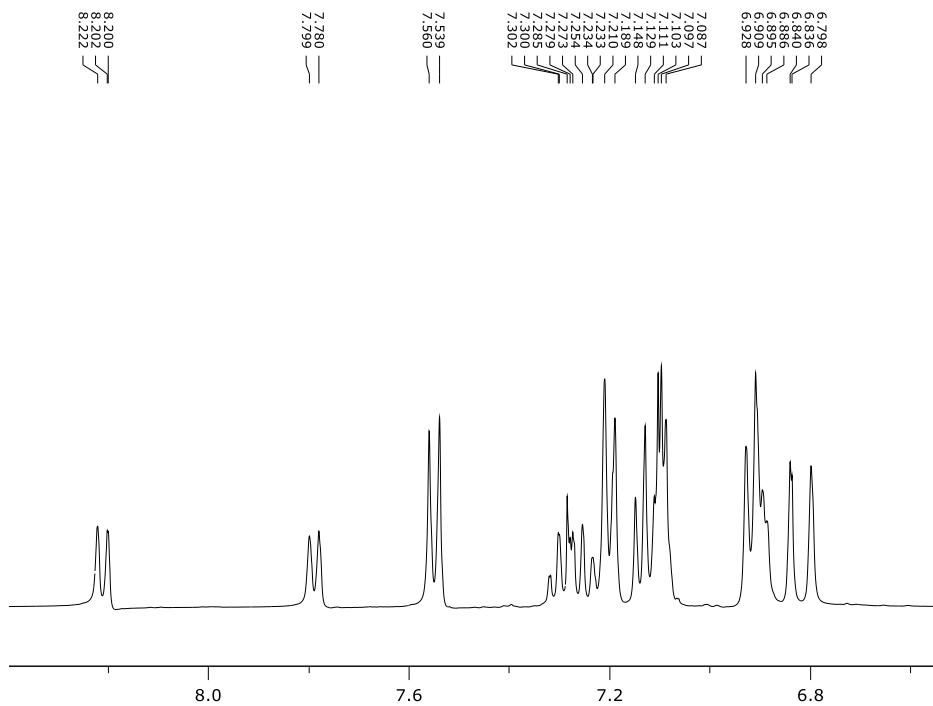


### <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

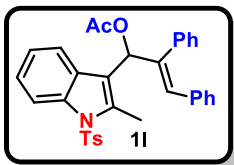
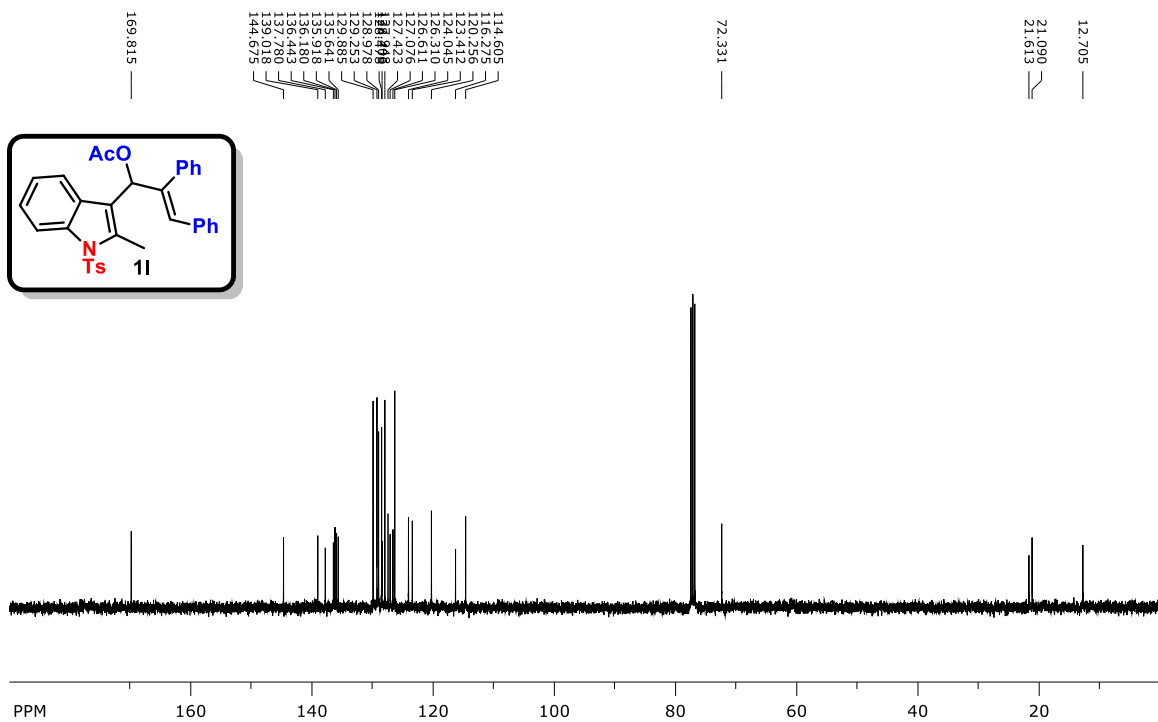


### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

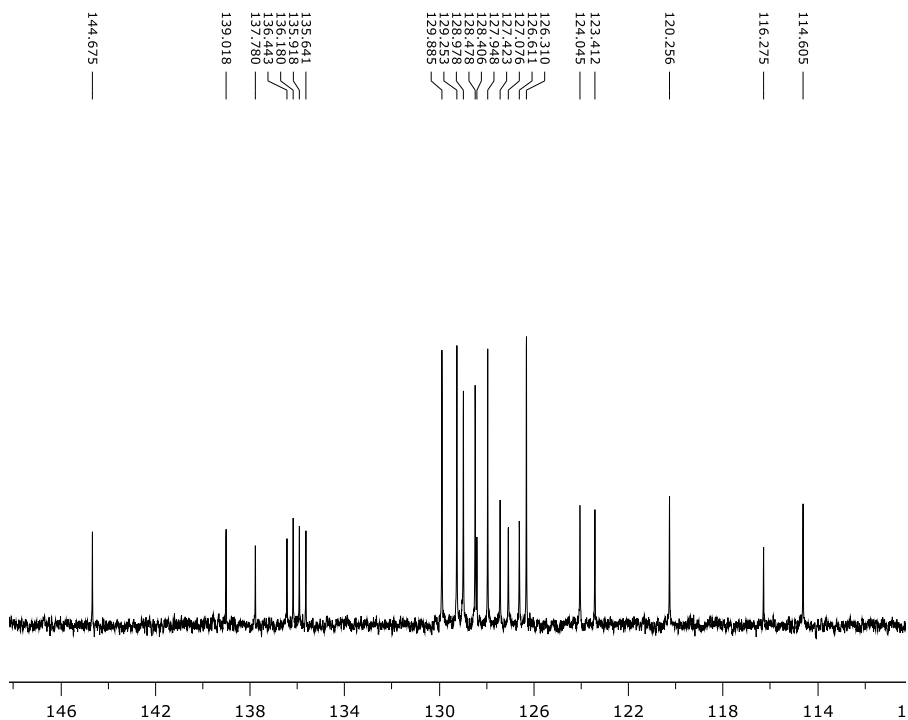




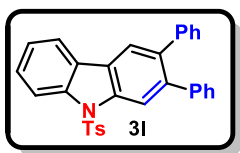
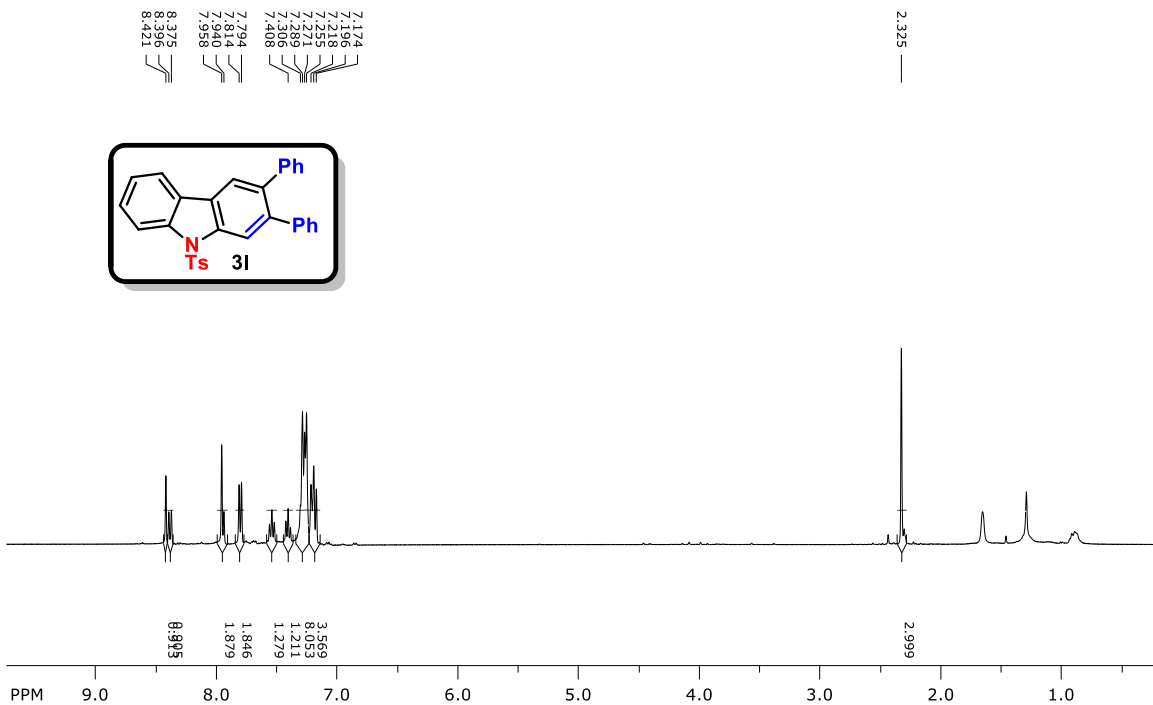
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



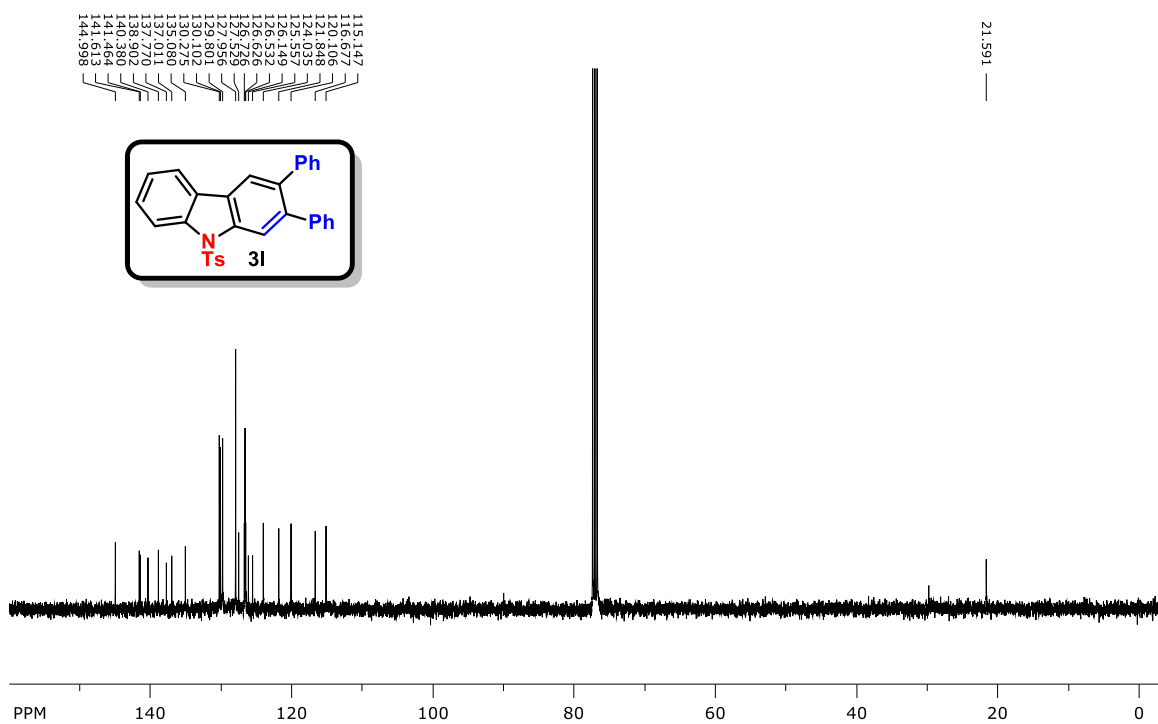




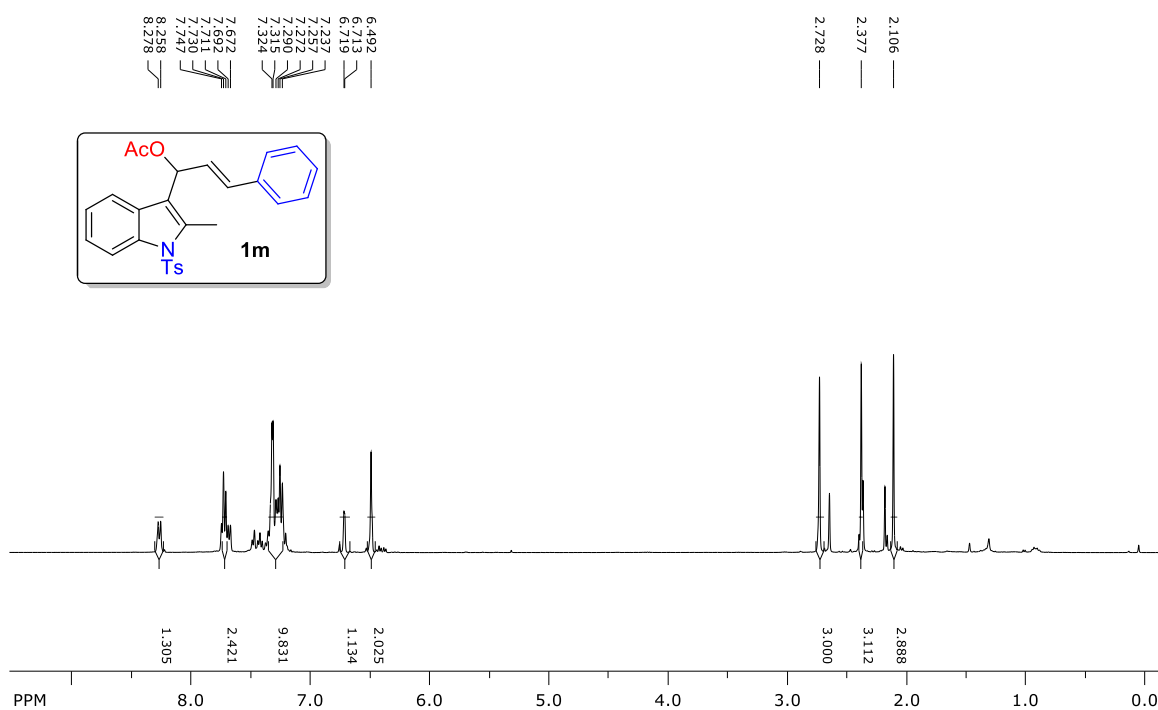
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

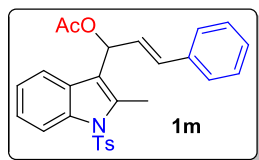
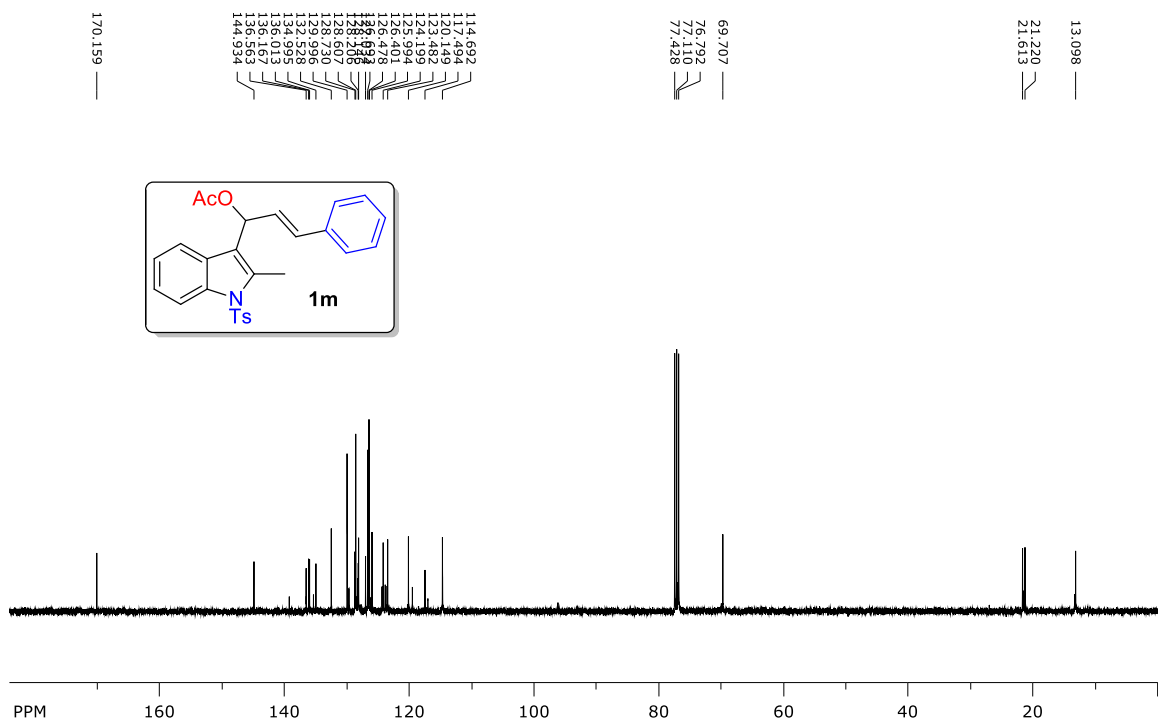


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

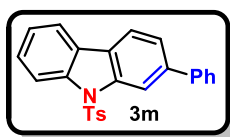
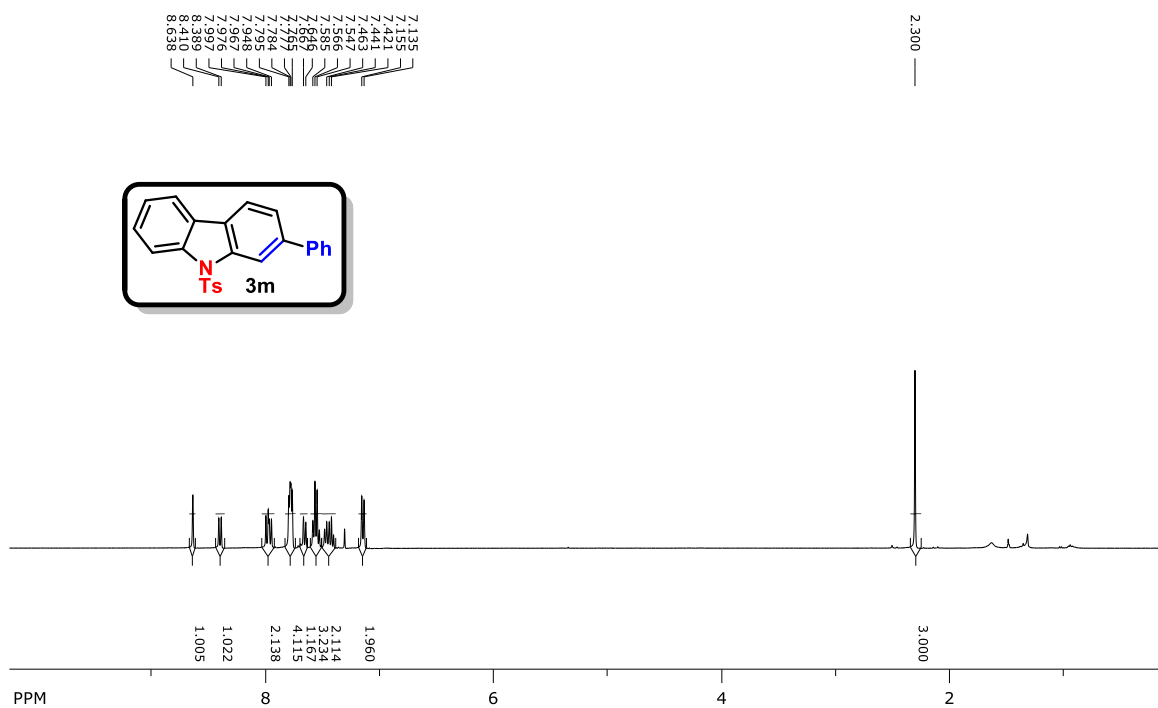


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**

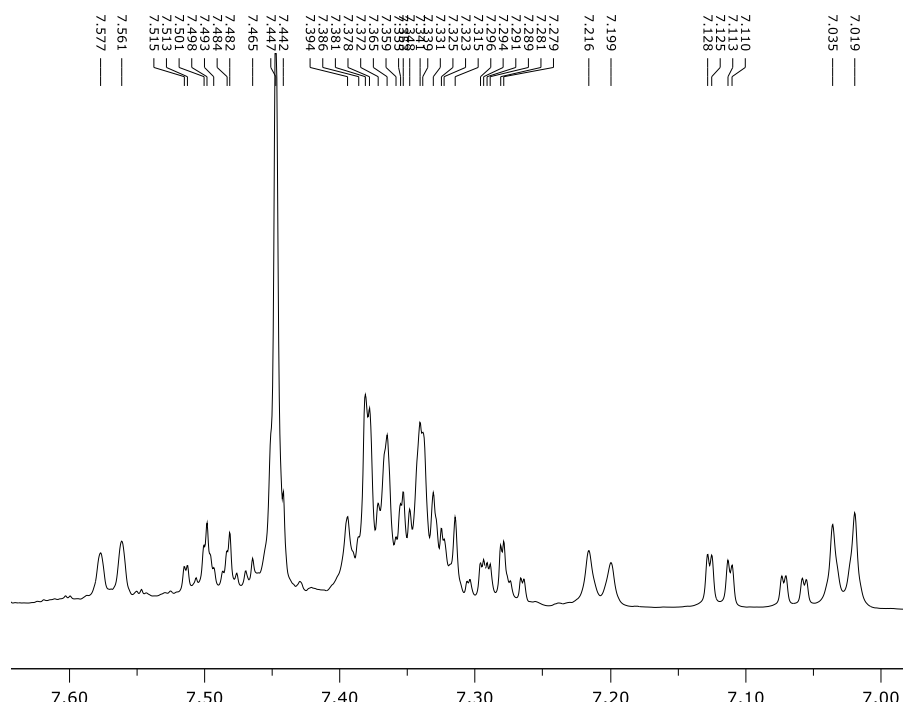




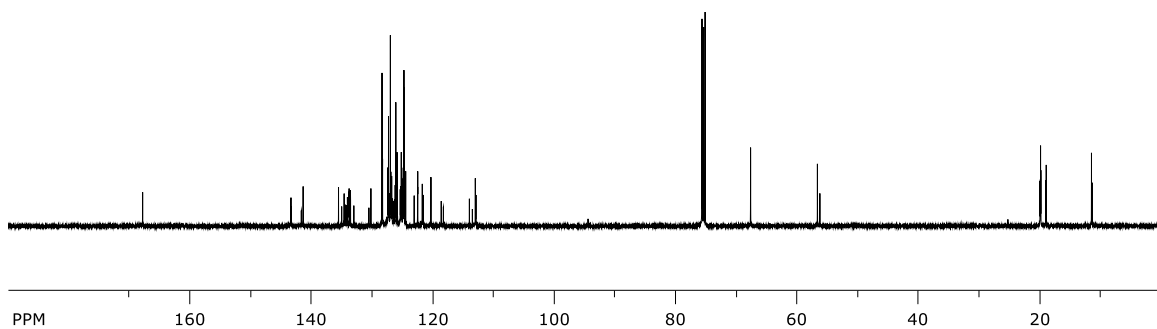
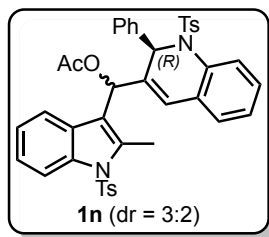
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**

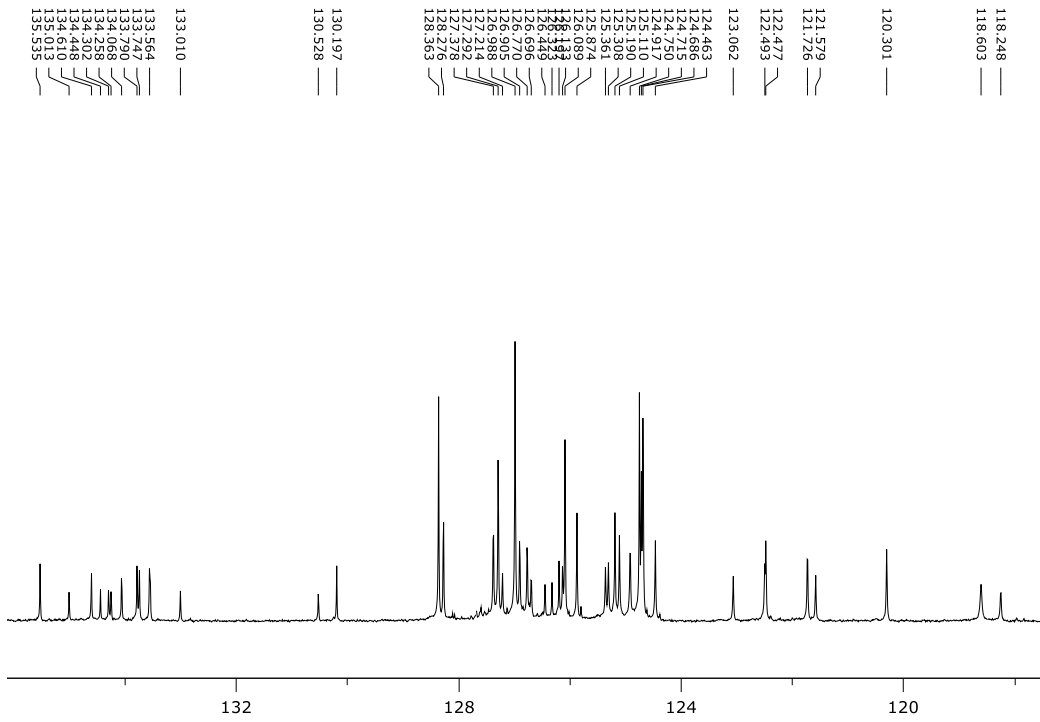




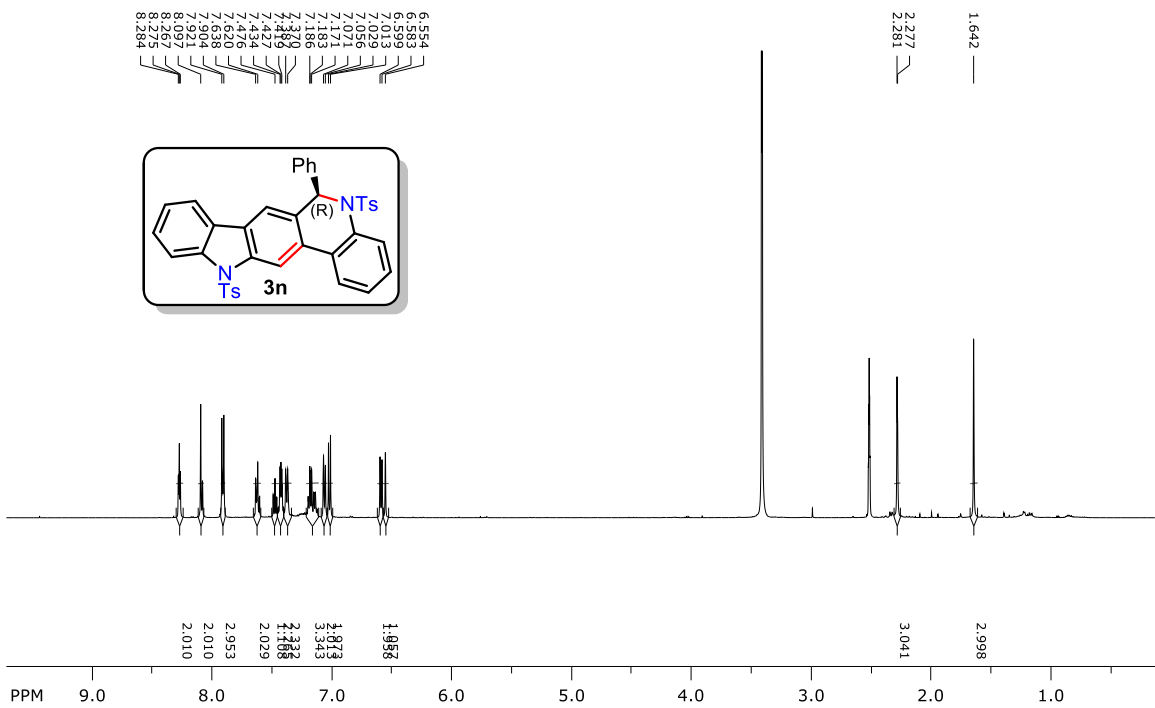


**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**

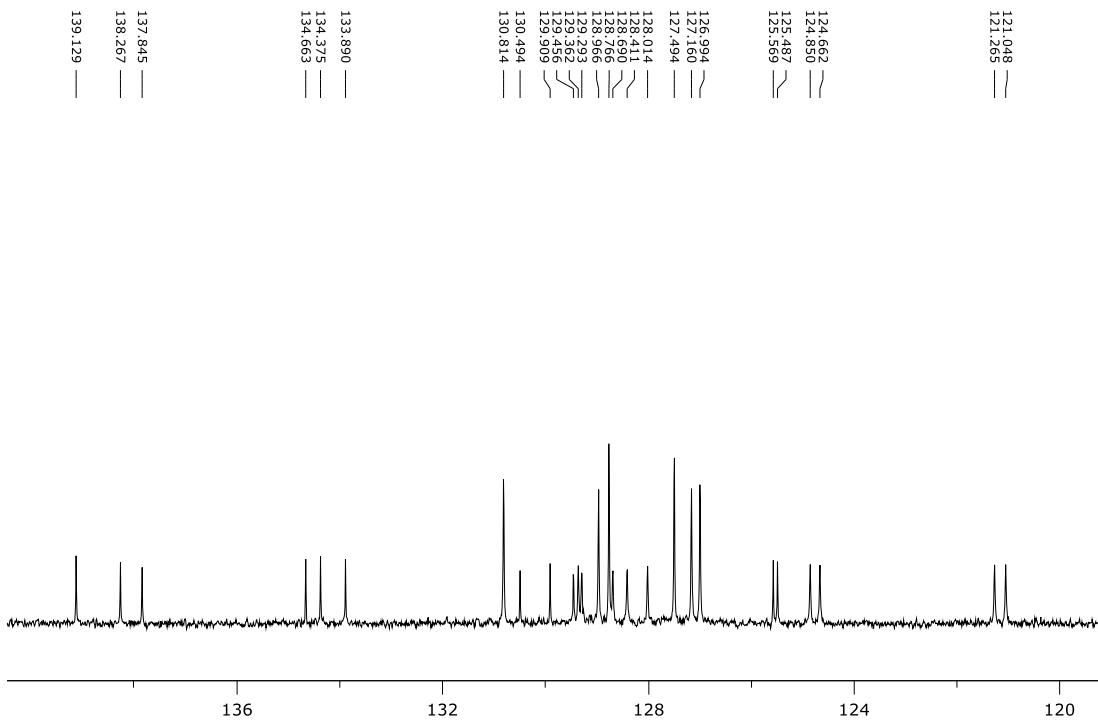
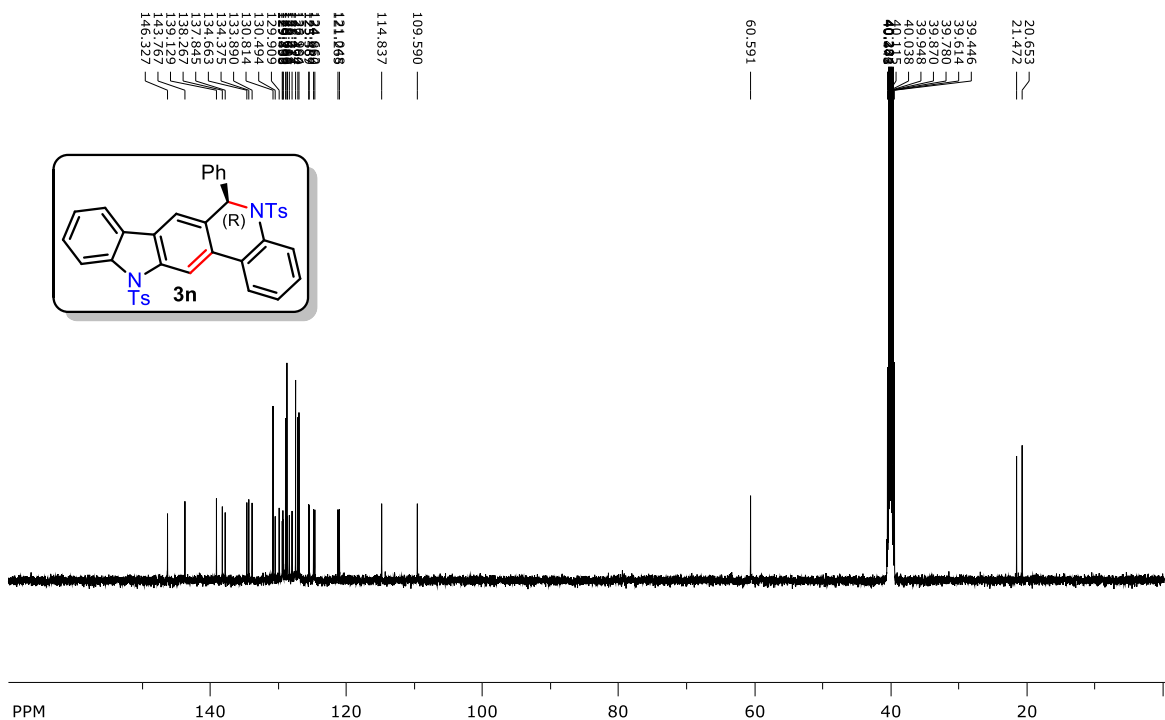




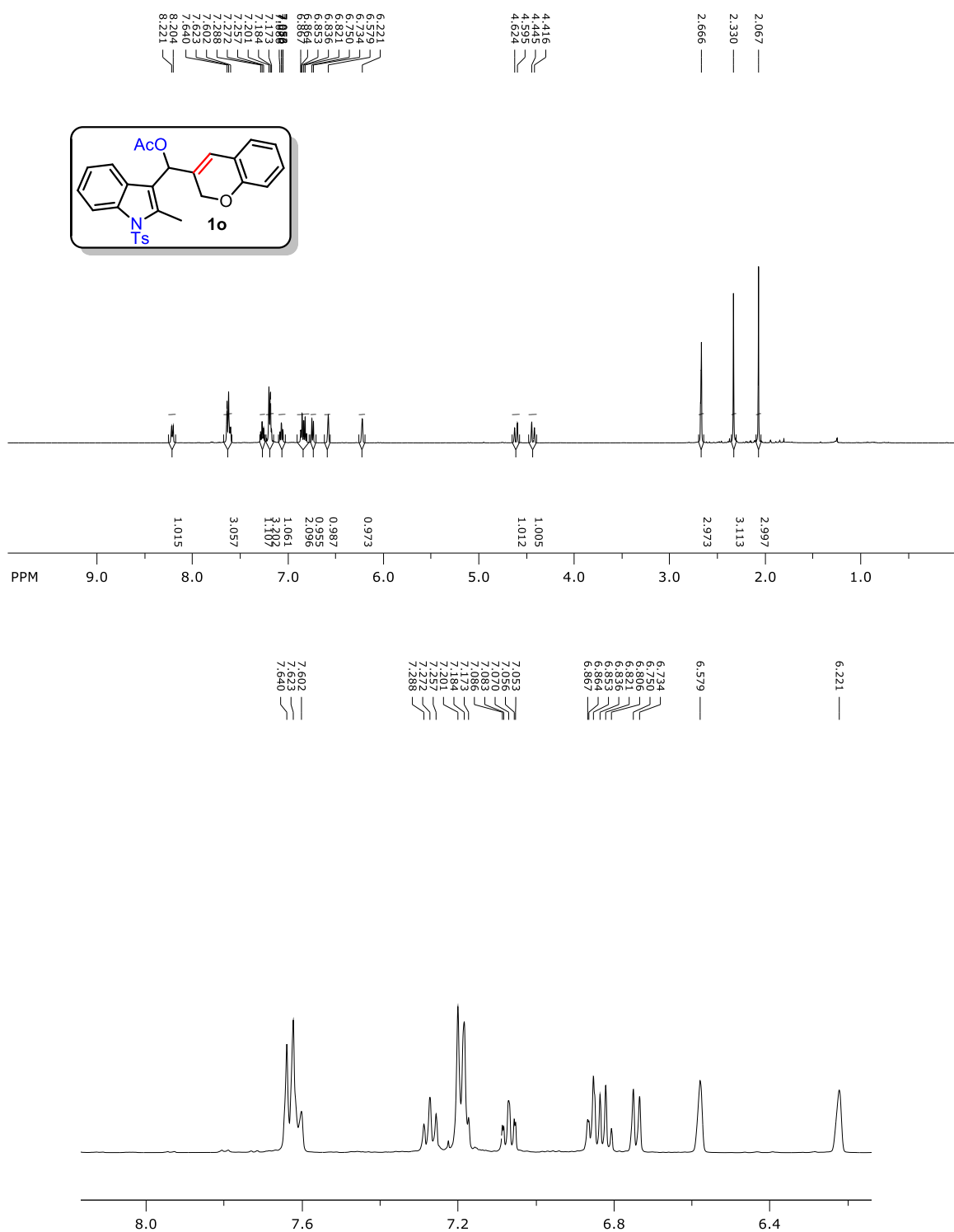
**<sup>1</sup>H NMR (500 MHz, DMSO)**



**<sup>13</sup>C NMR (125 MHz, DMSO)**

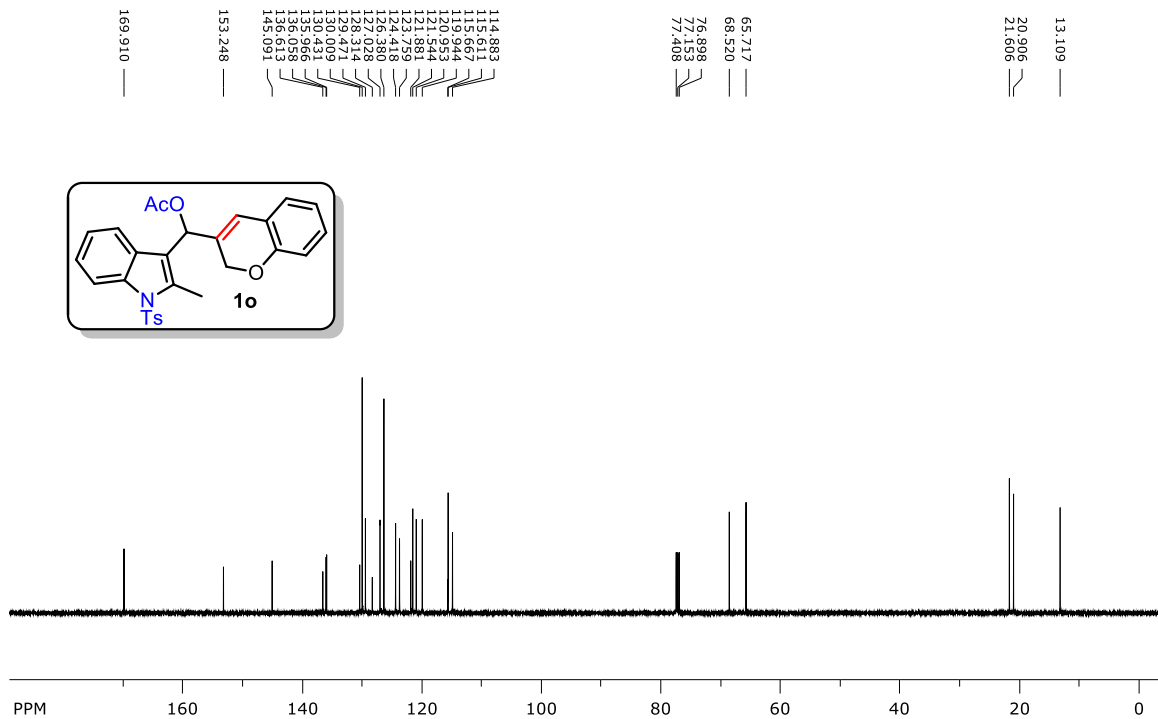


**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

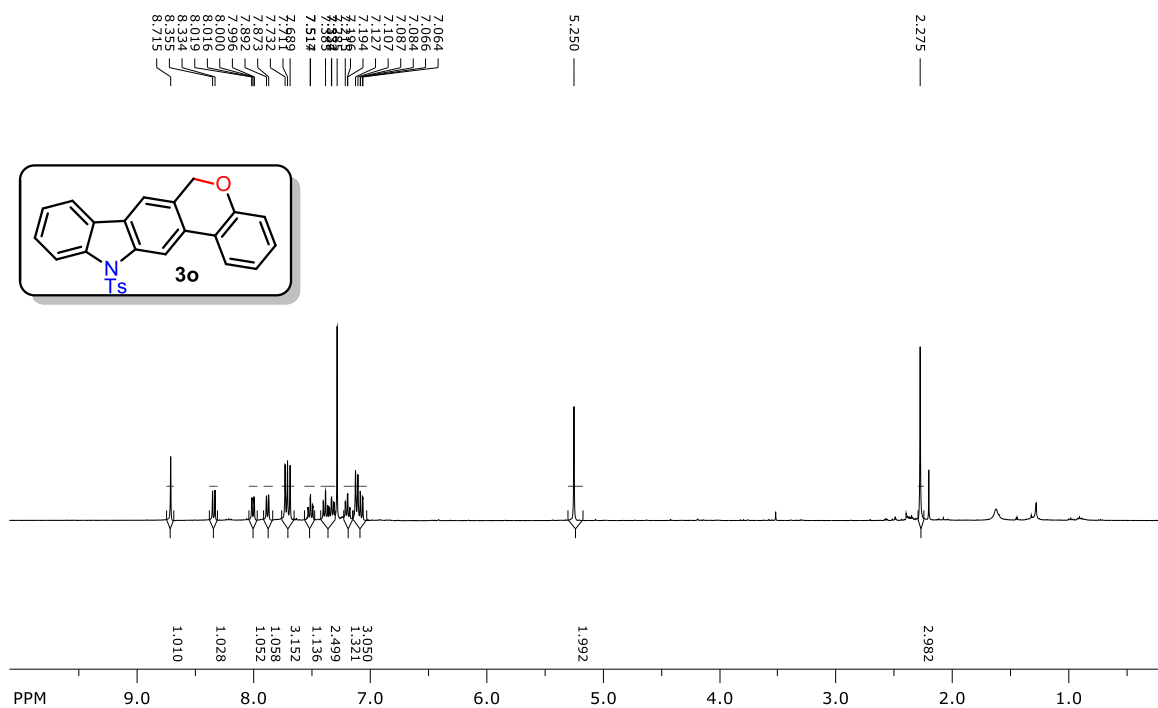




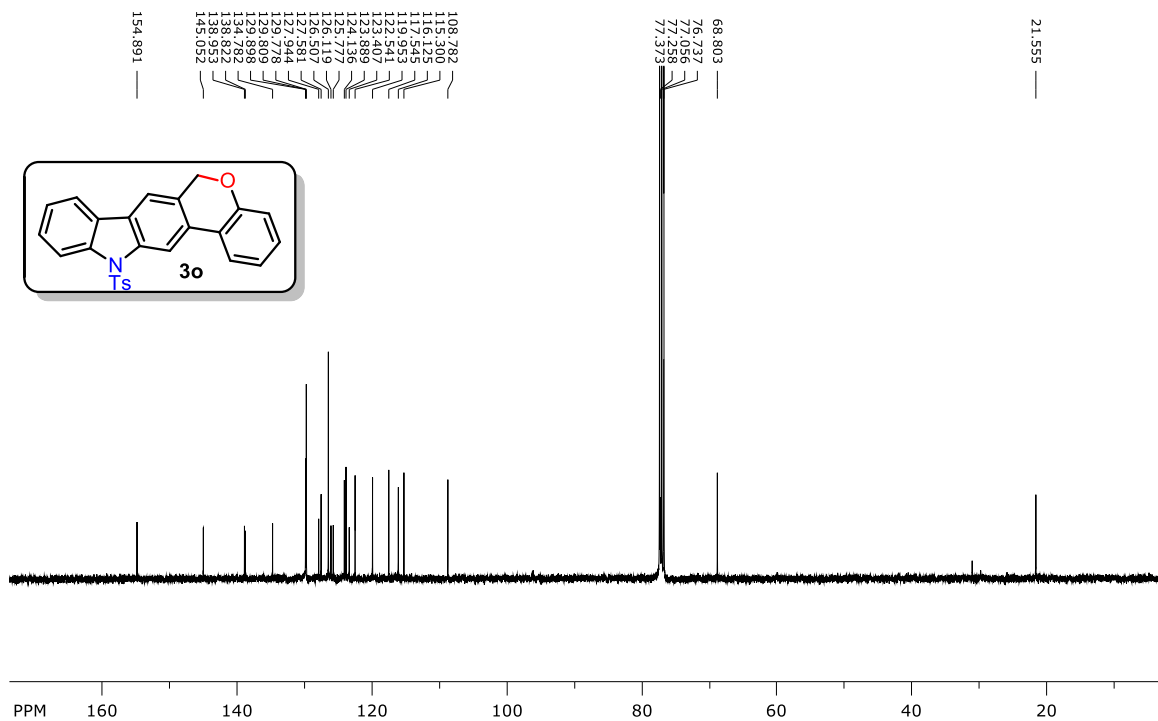
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



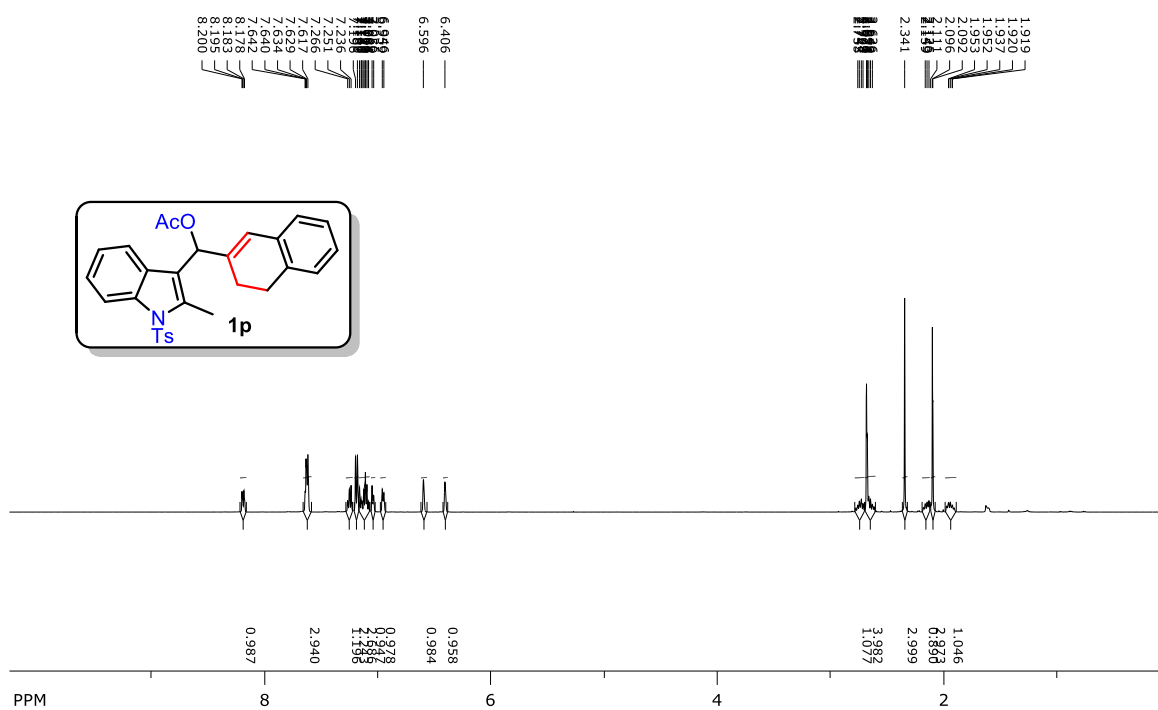
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

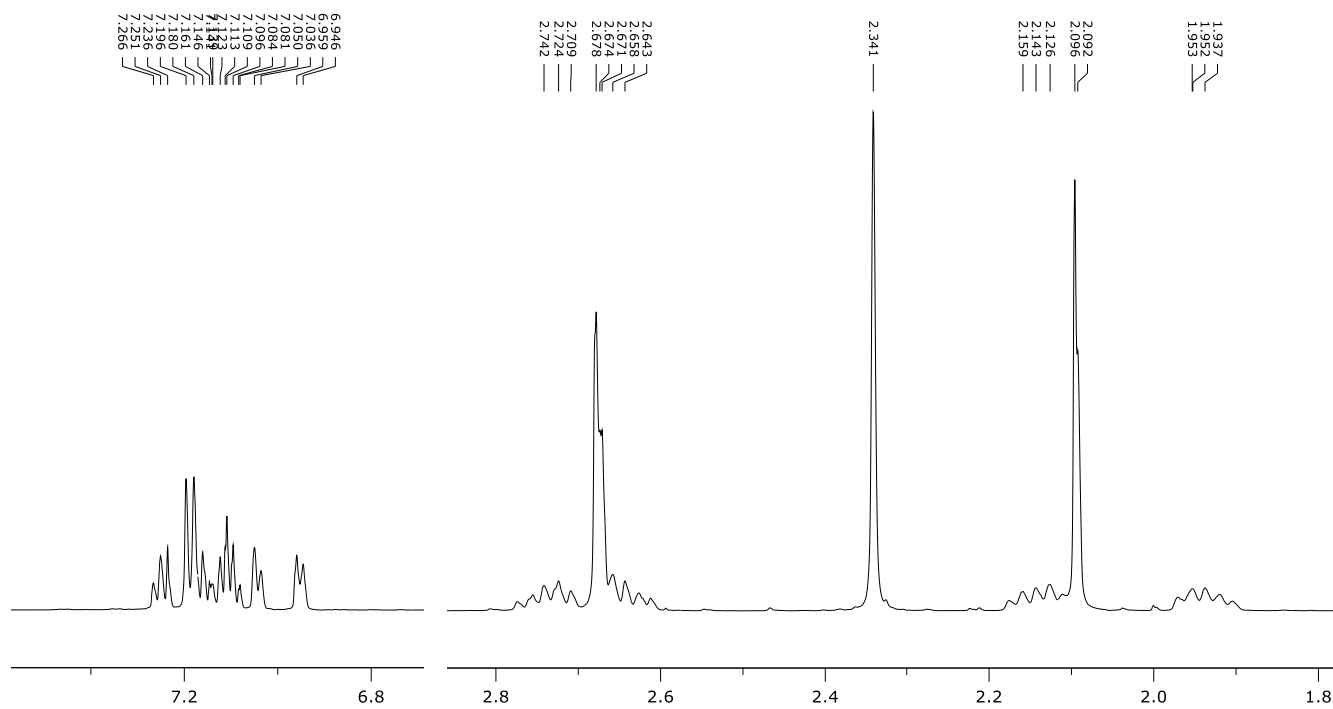


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

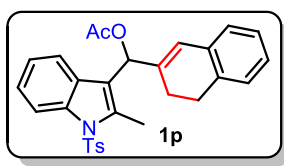
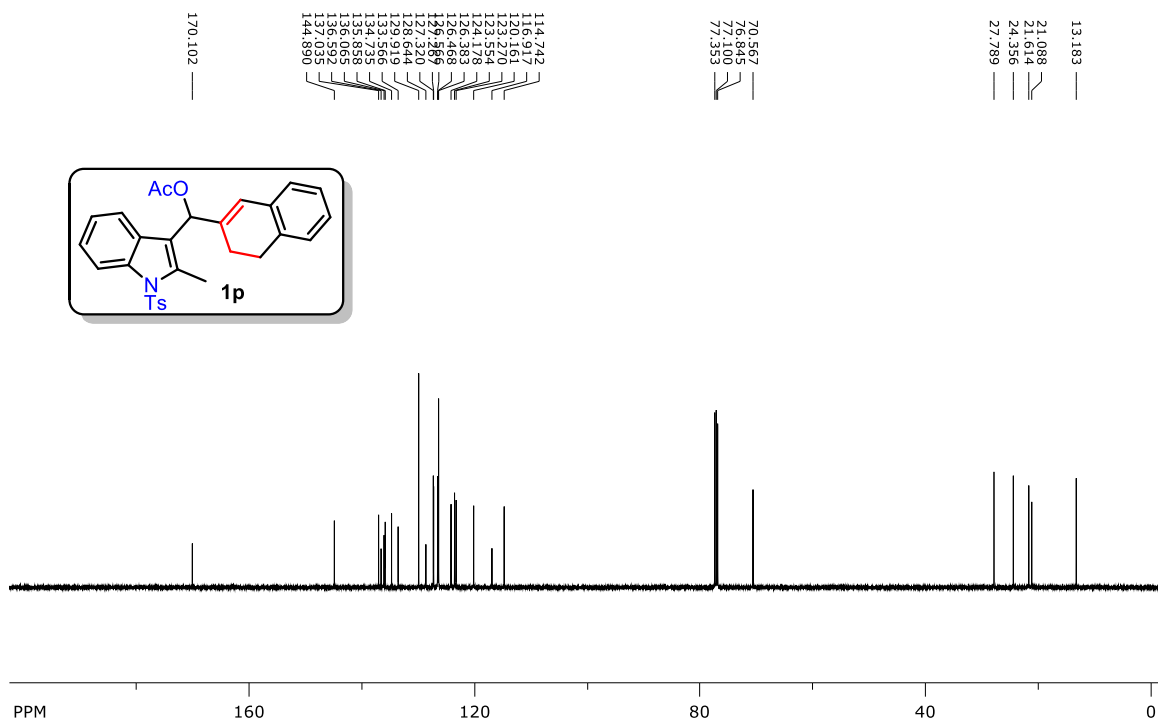


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

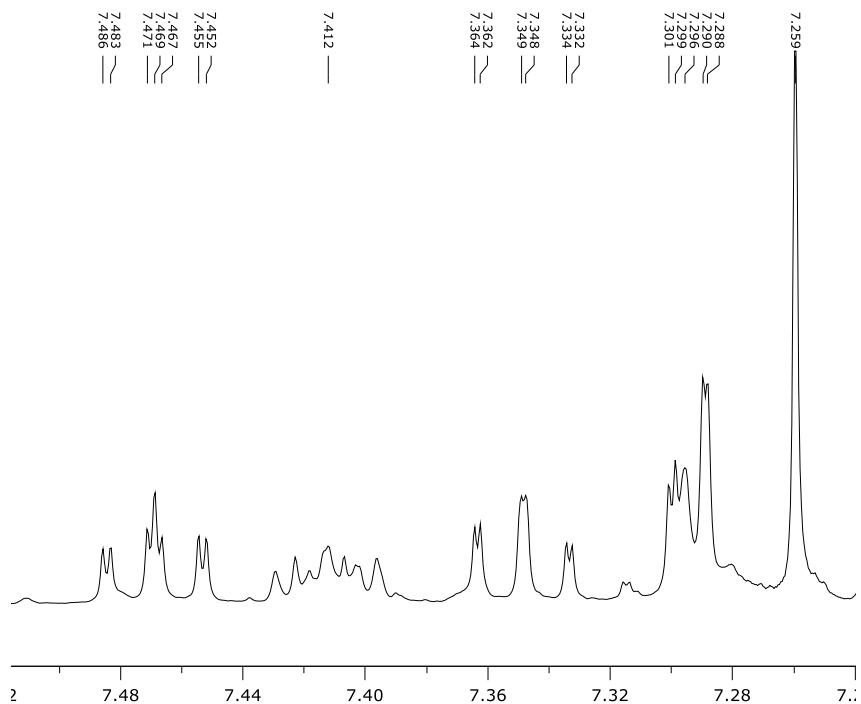
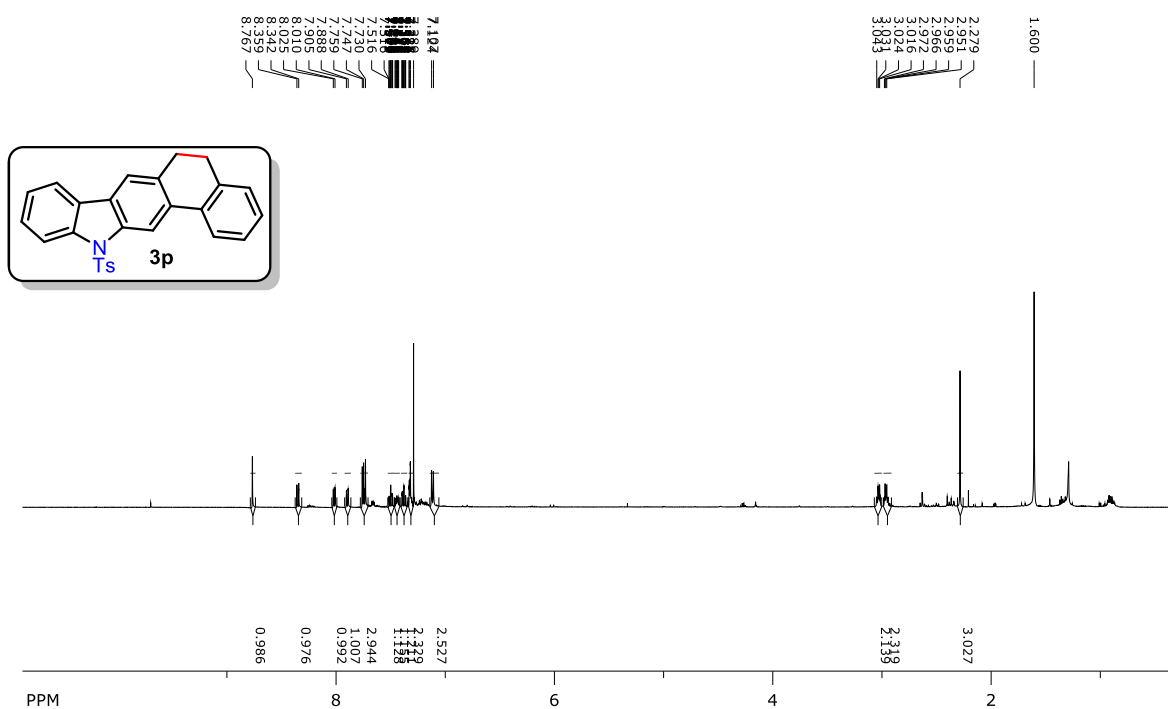




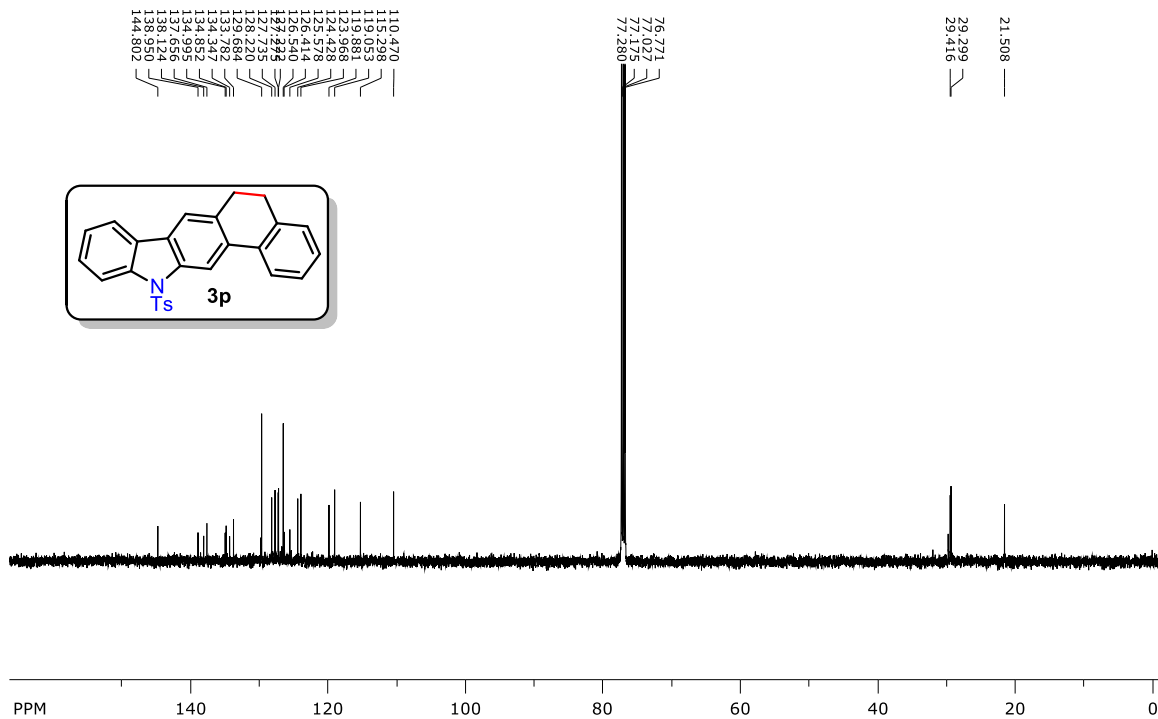
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



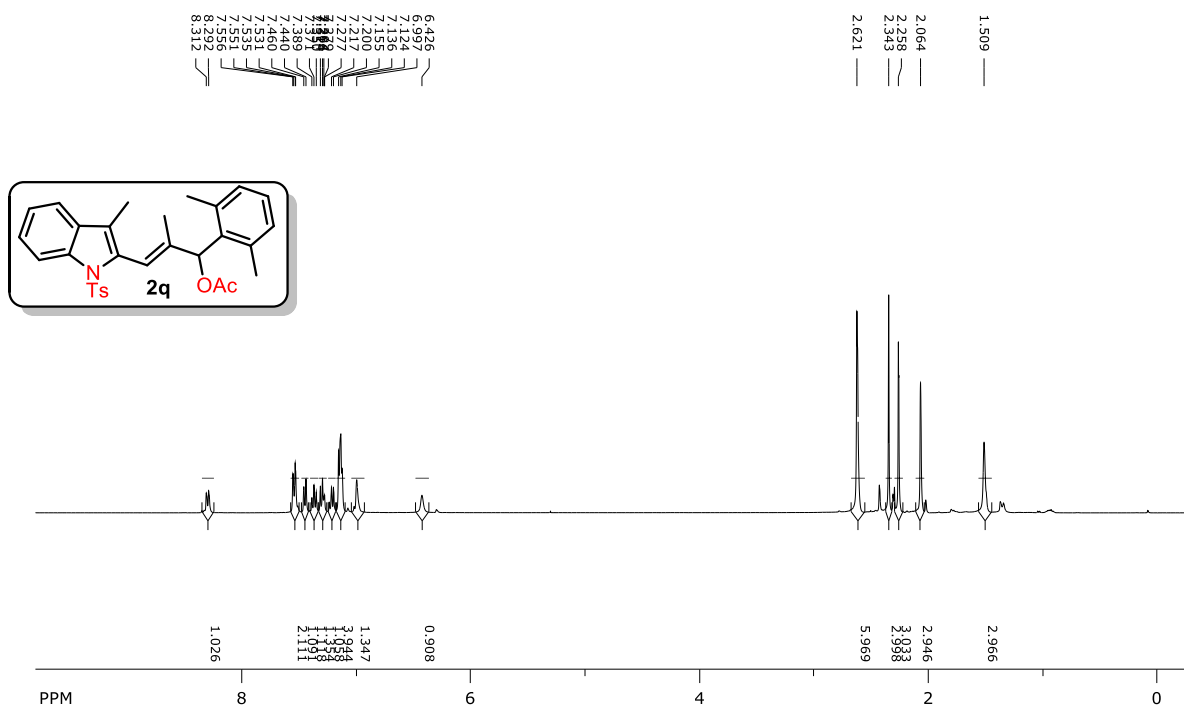
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

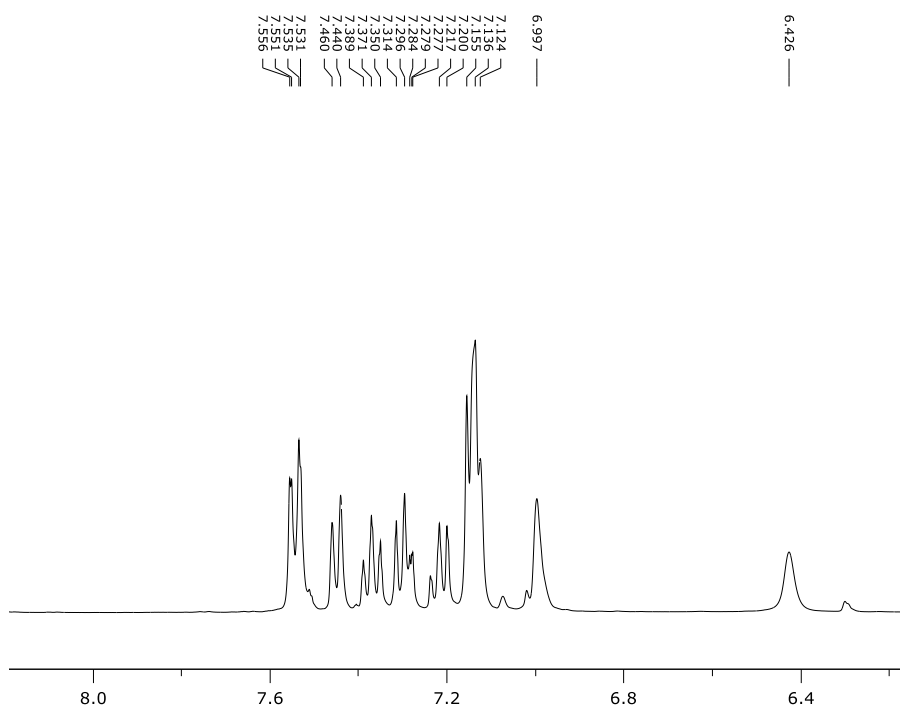


**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**

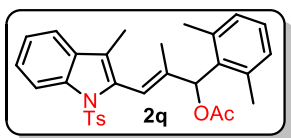
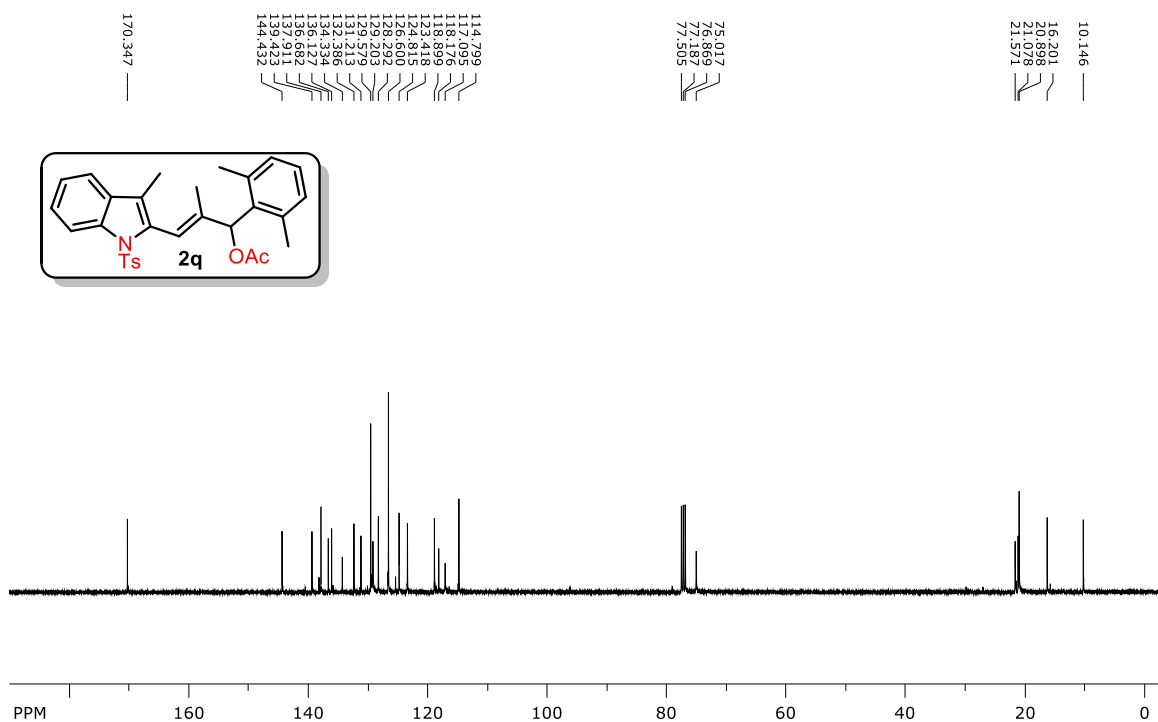


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

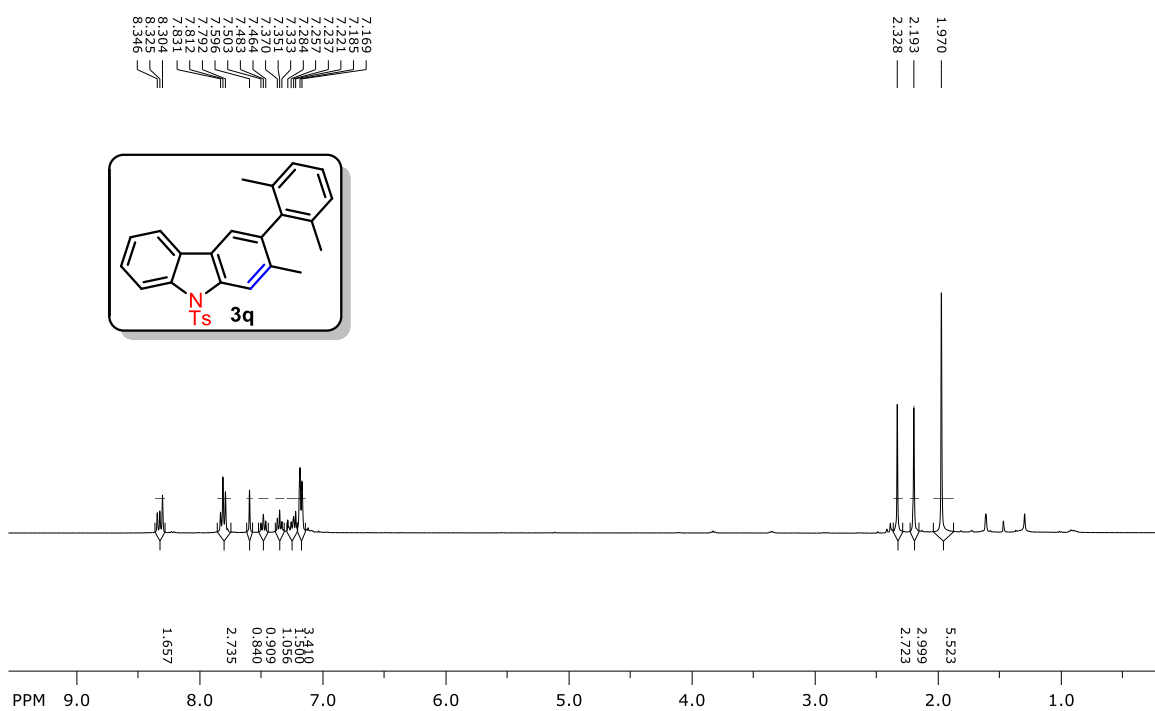




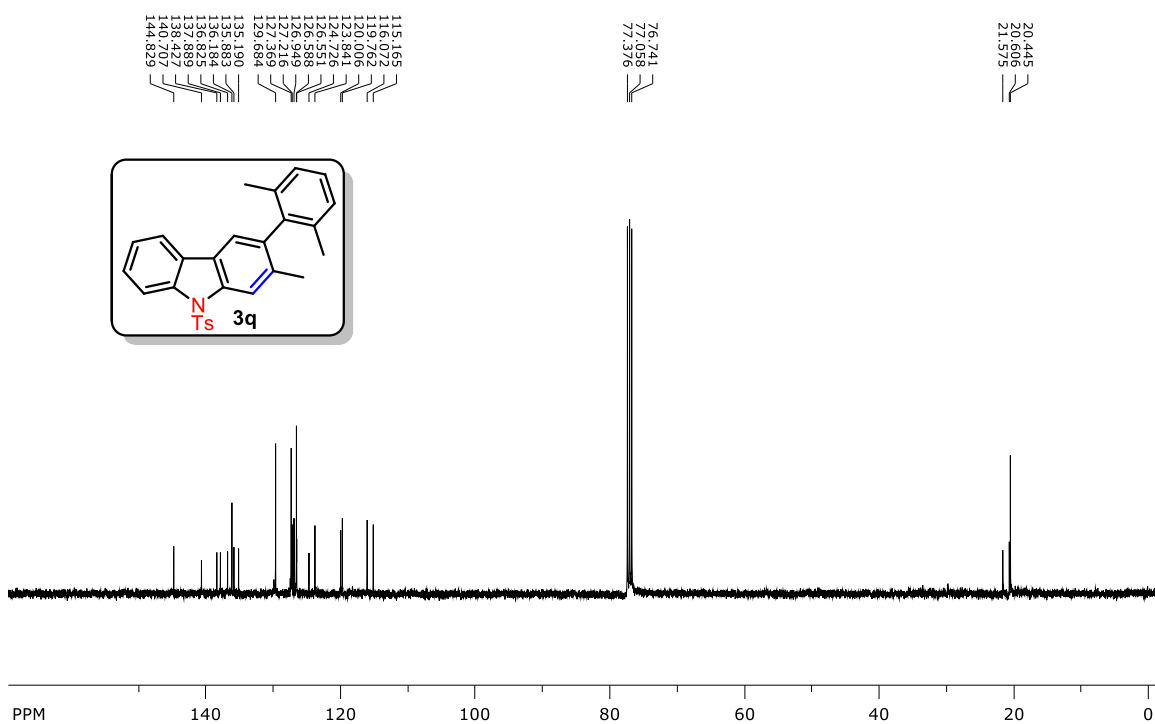
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



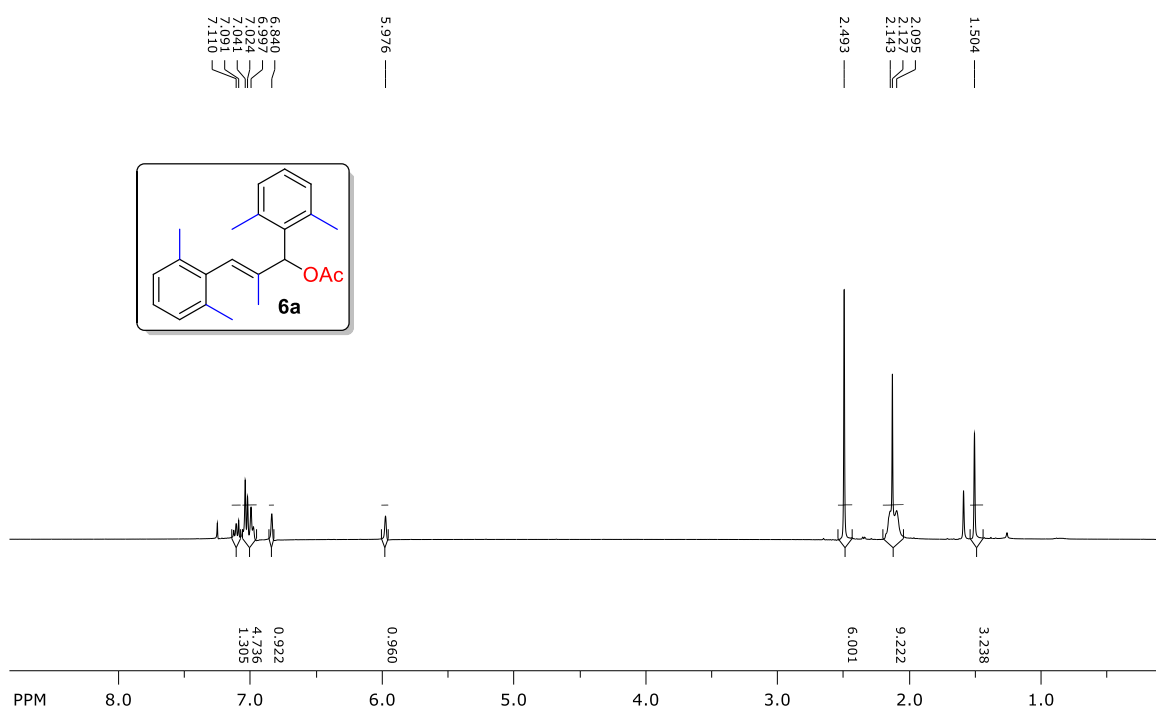
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



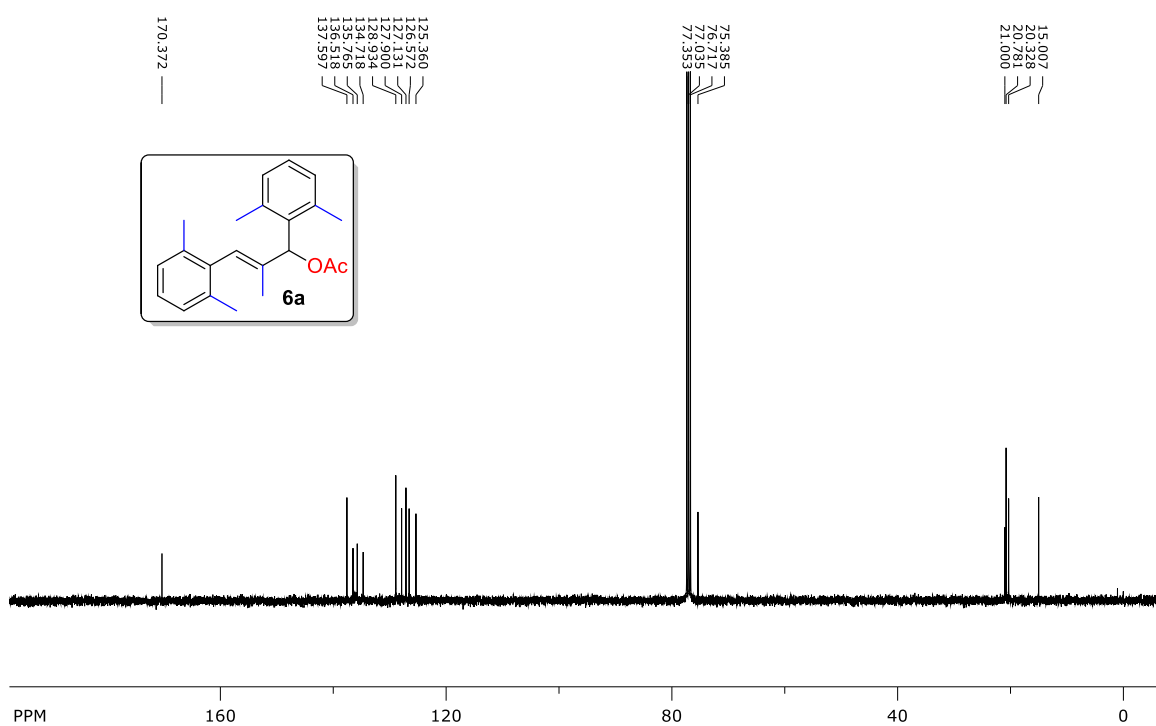
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

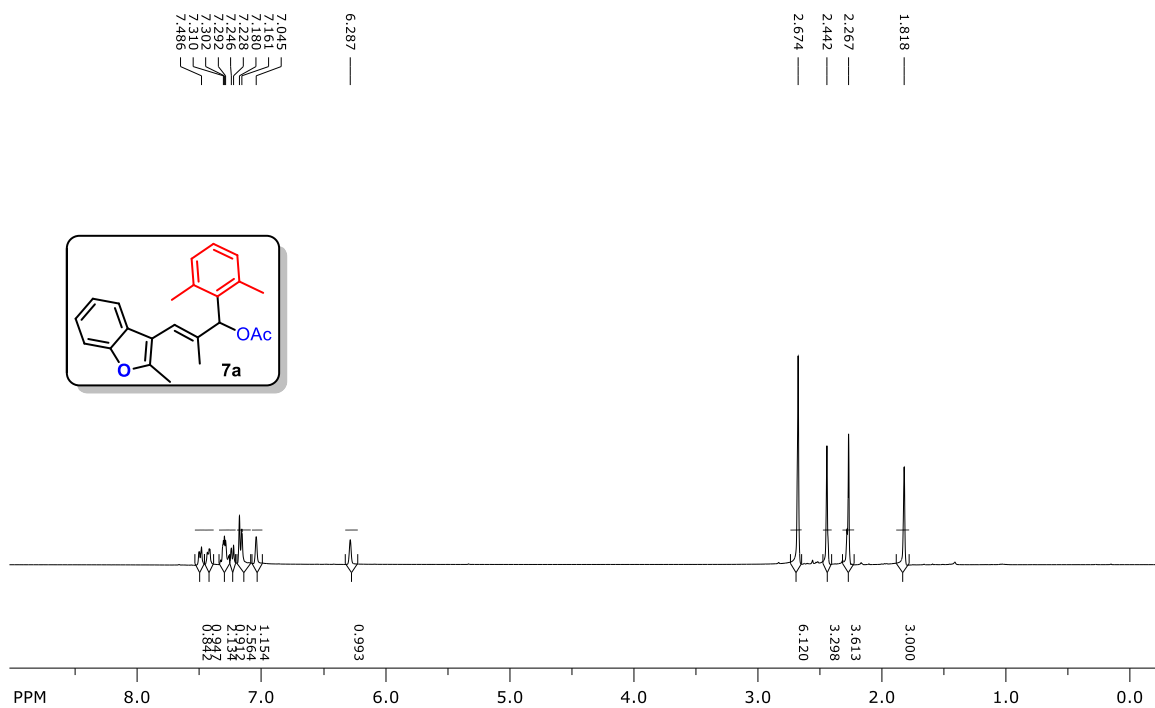


### <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

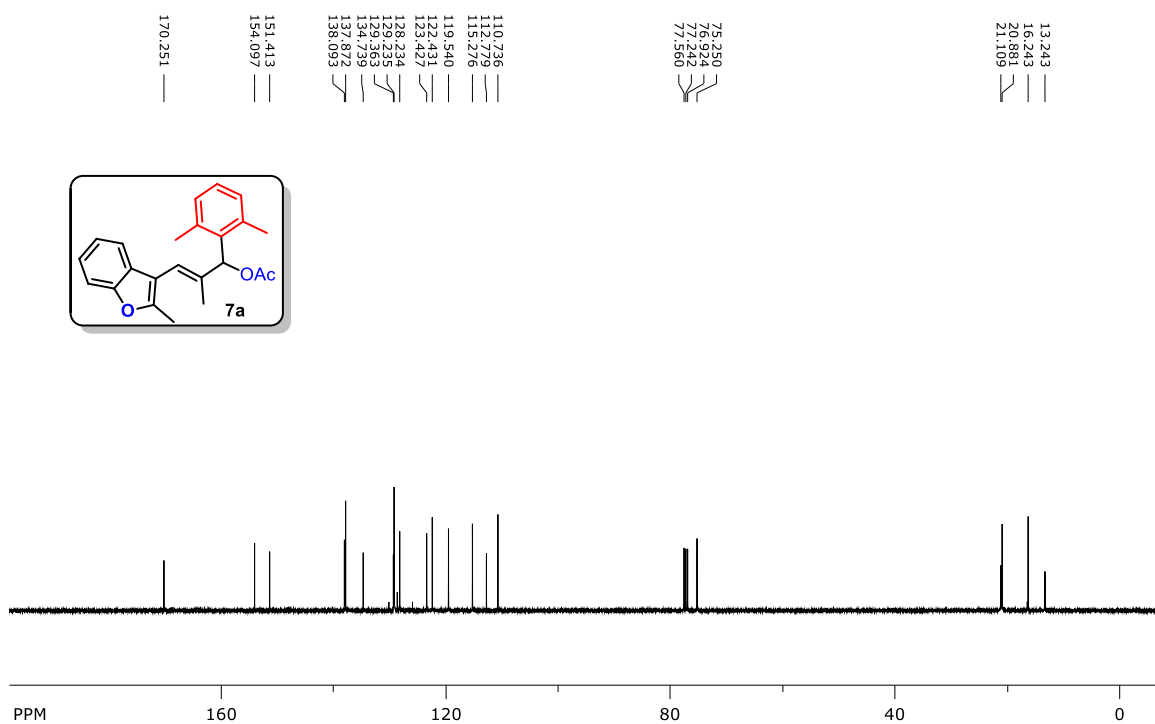




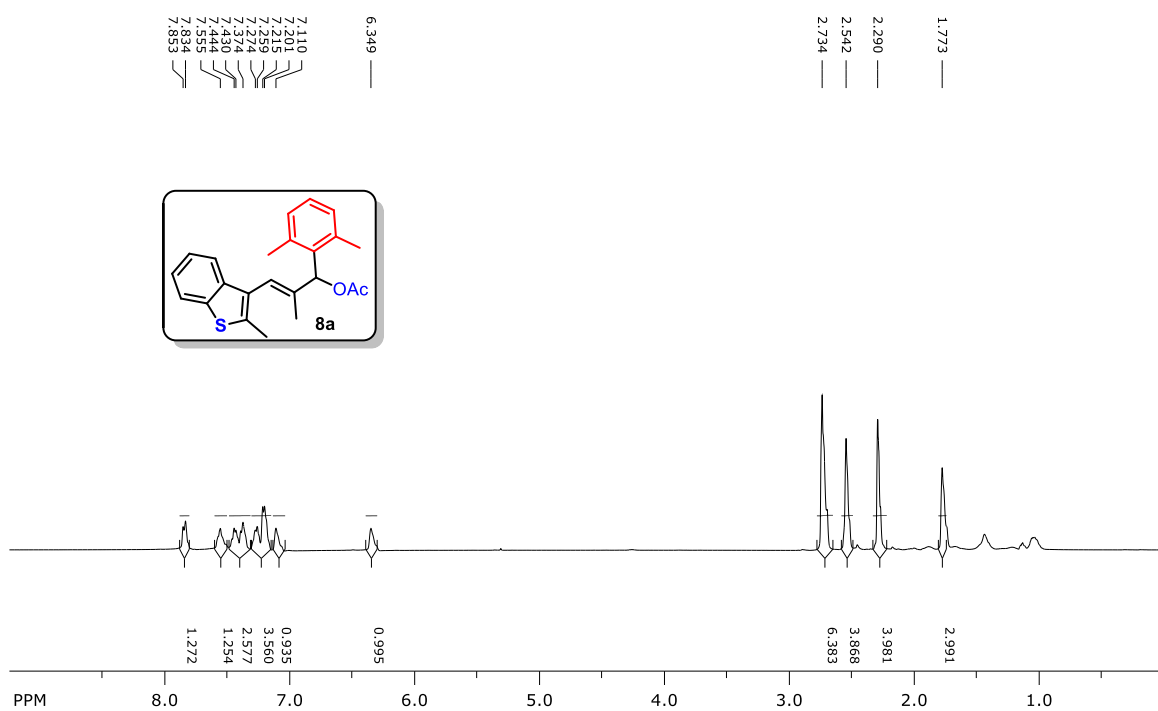
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



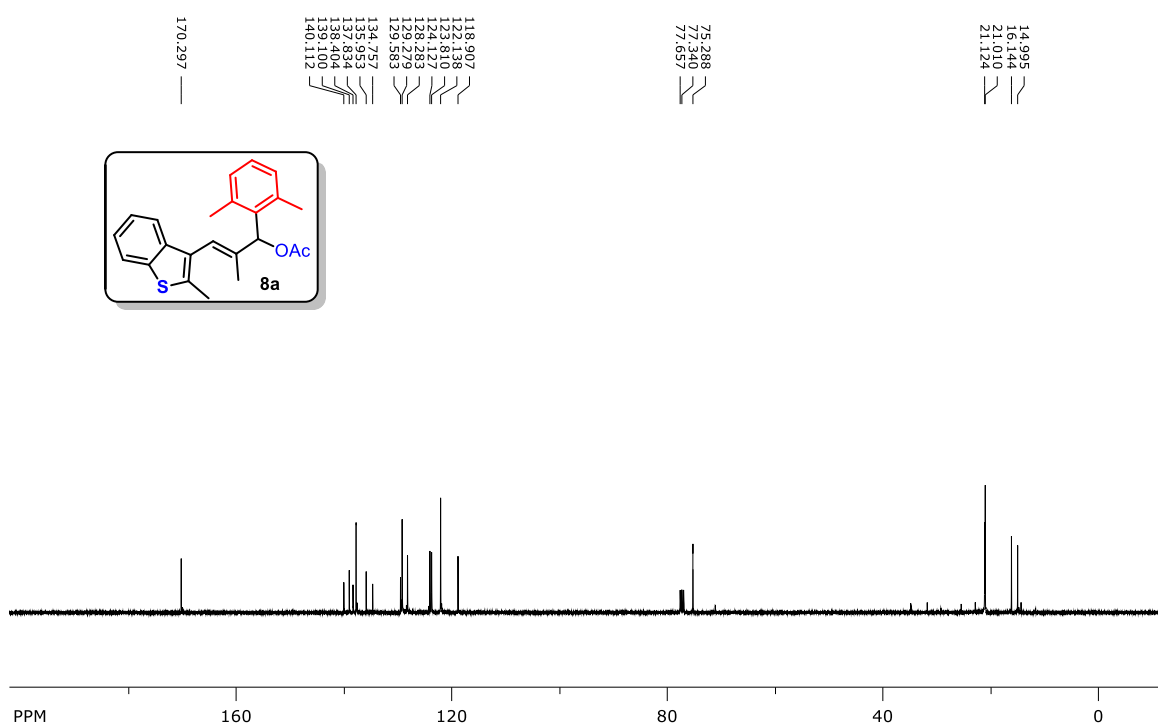
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



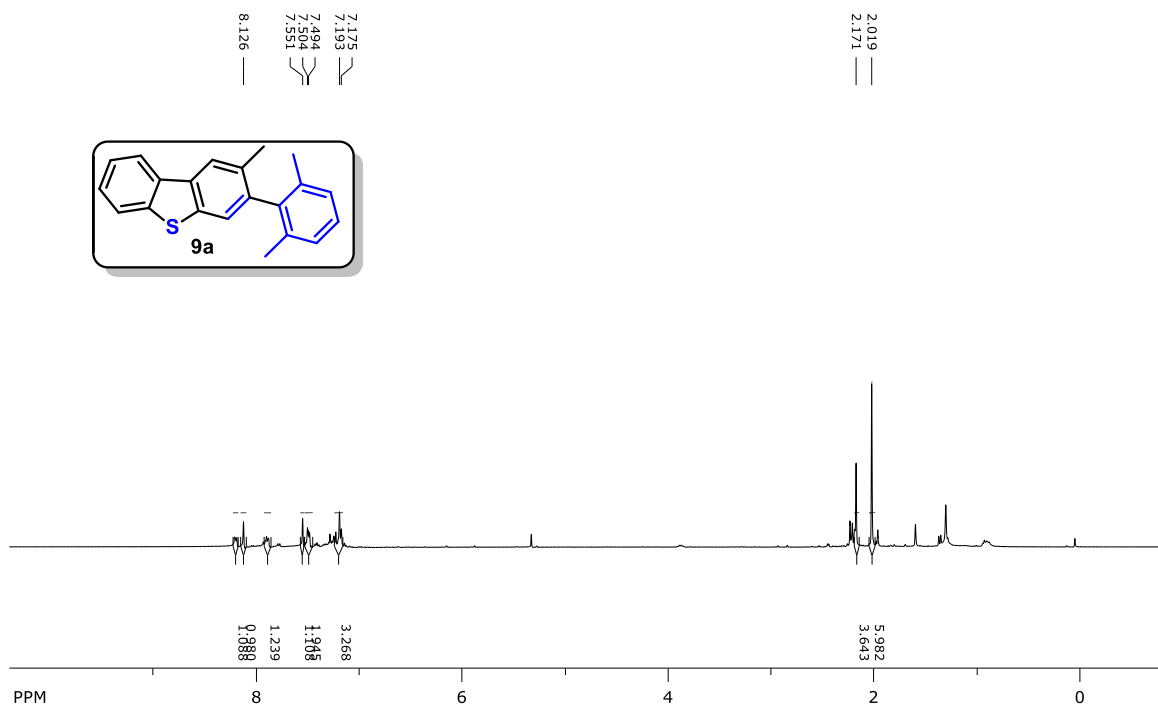
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



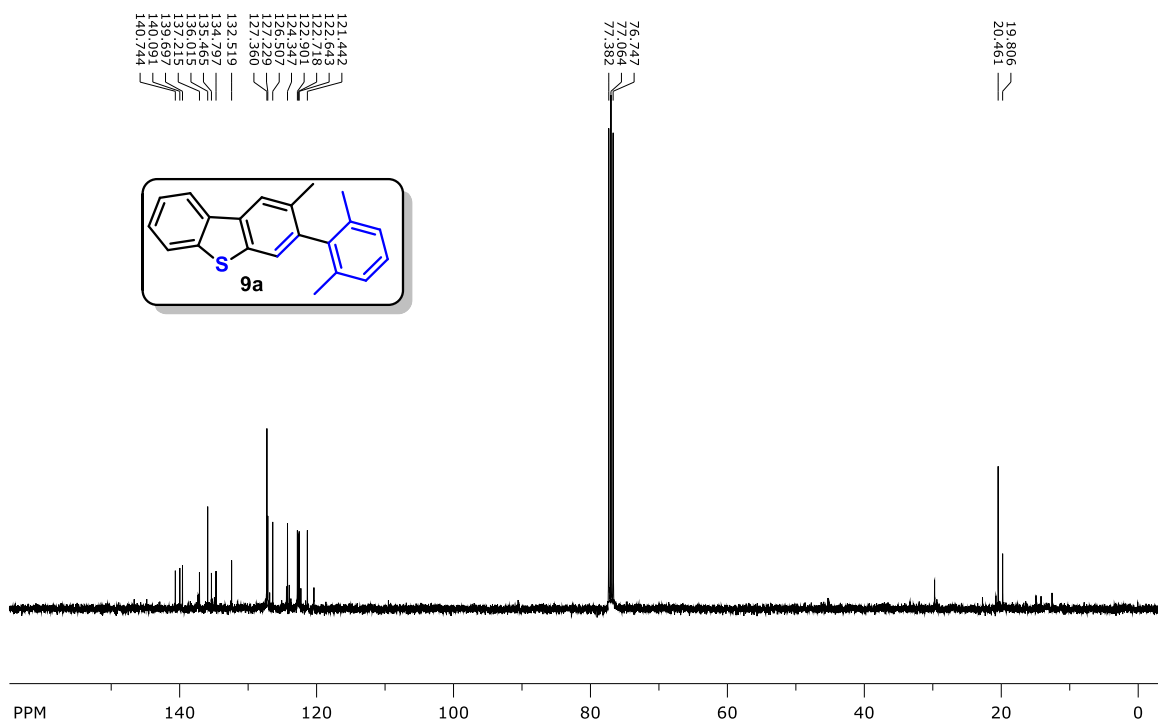
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



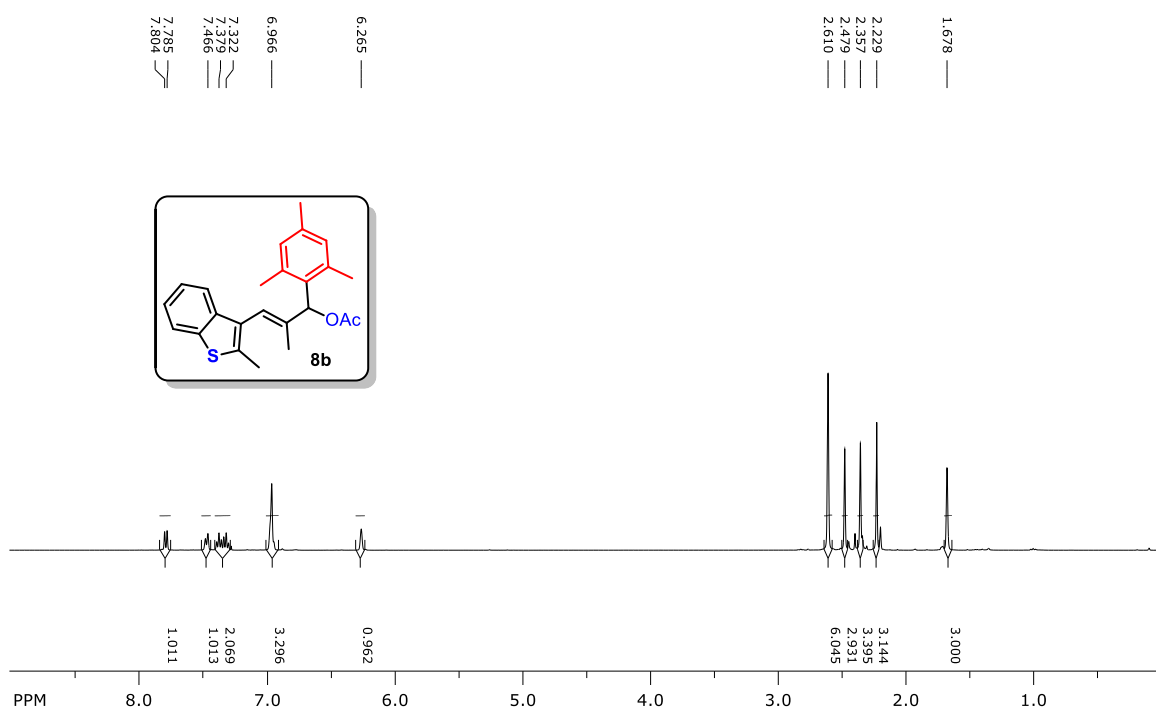
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



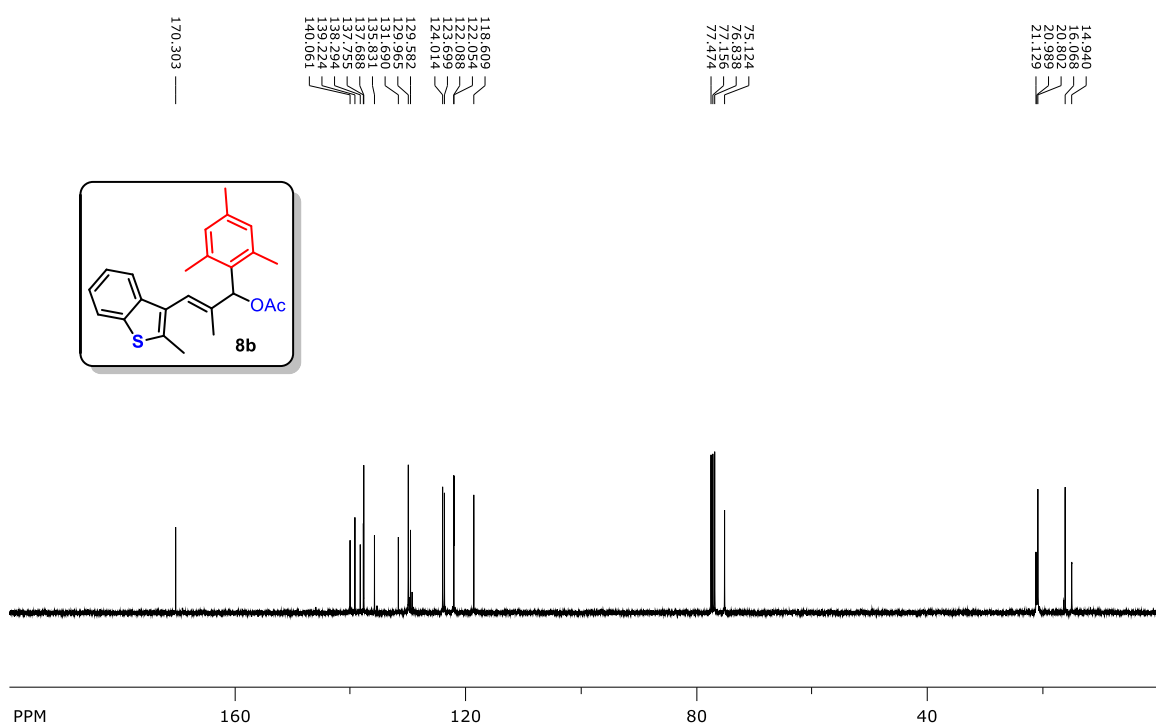
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



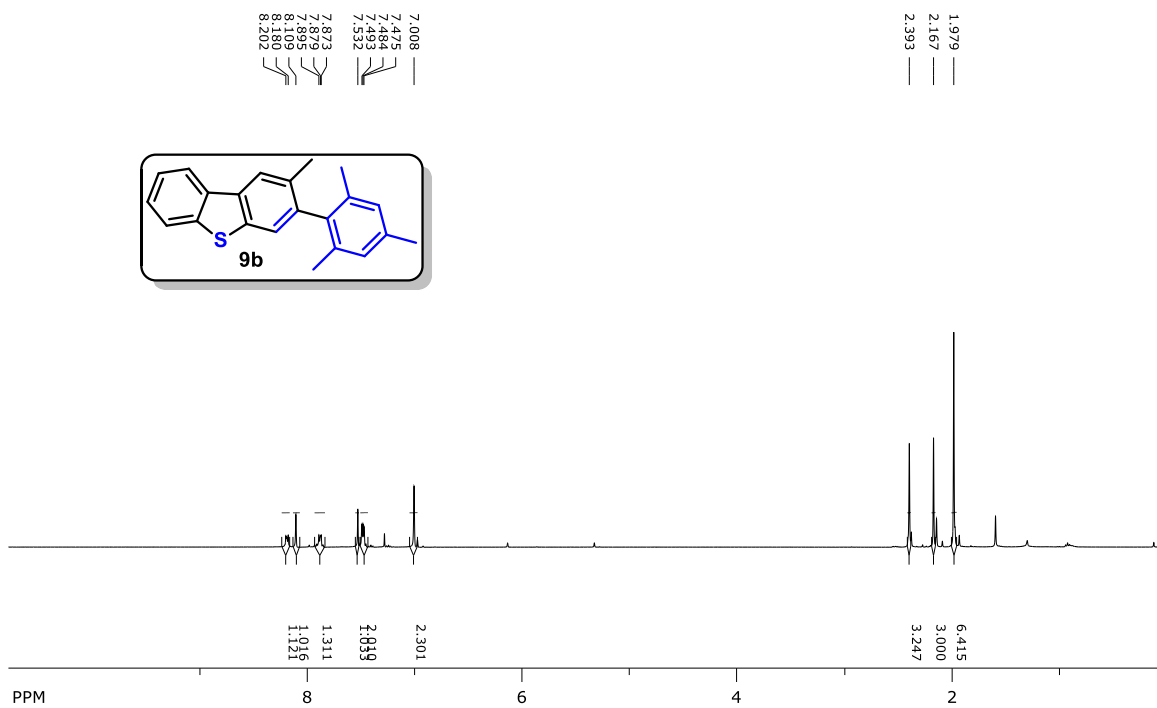
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



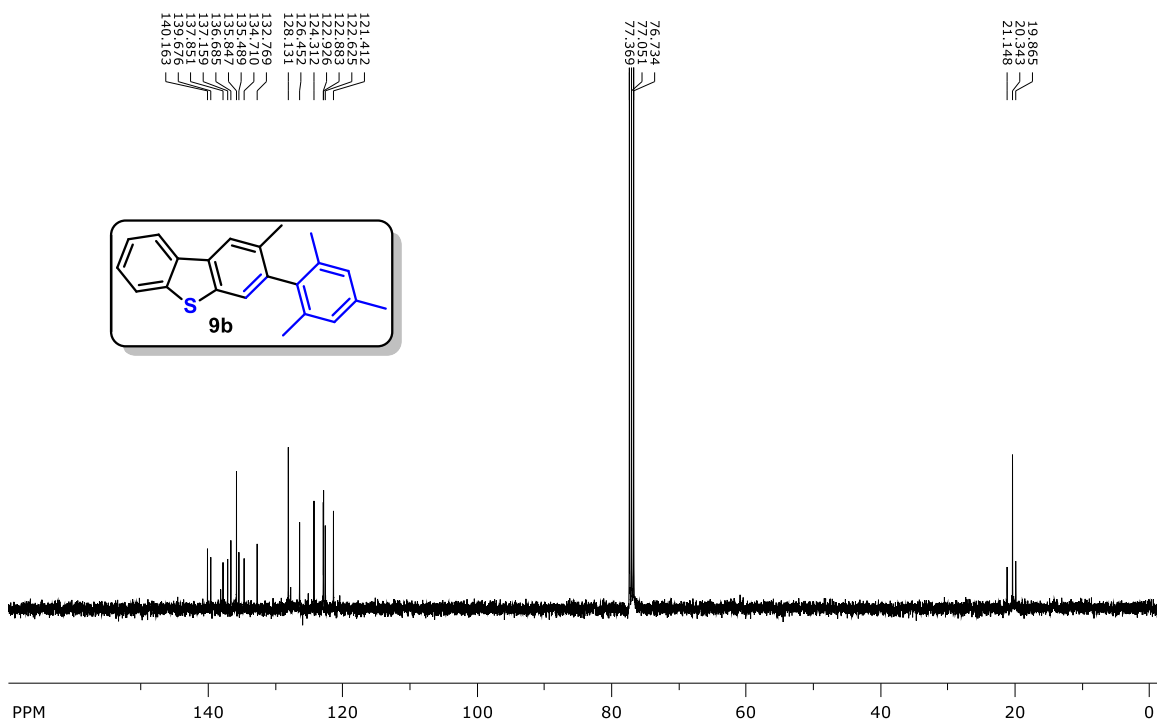
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



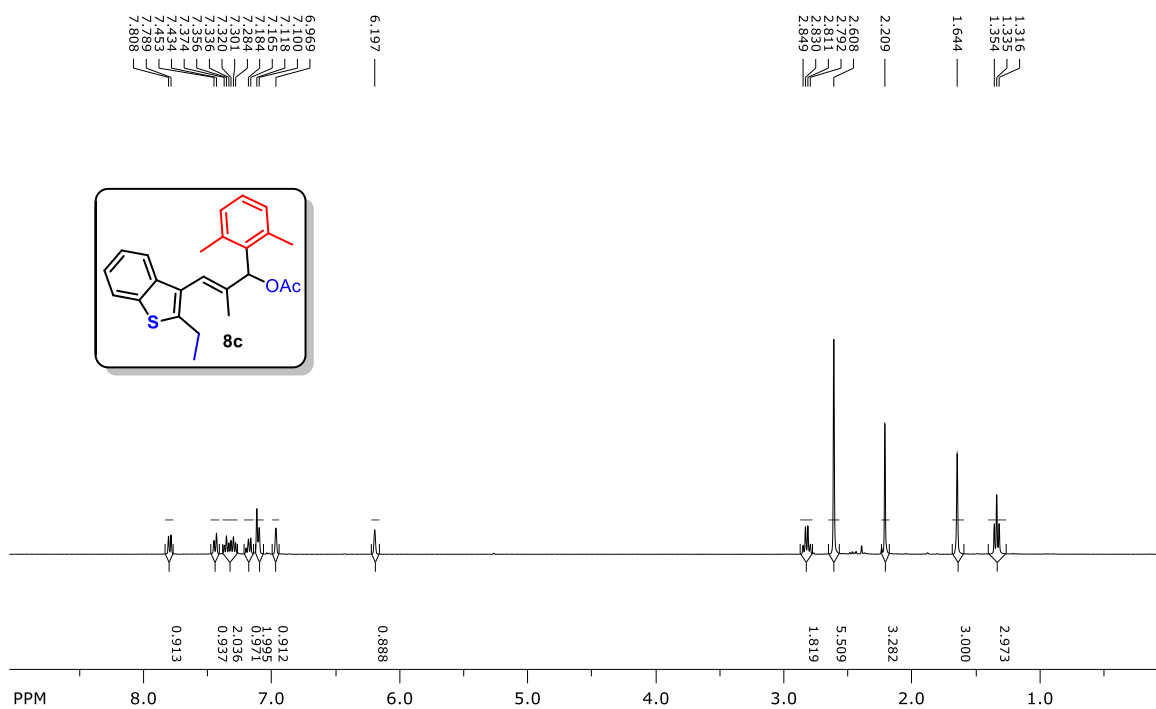
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



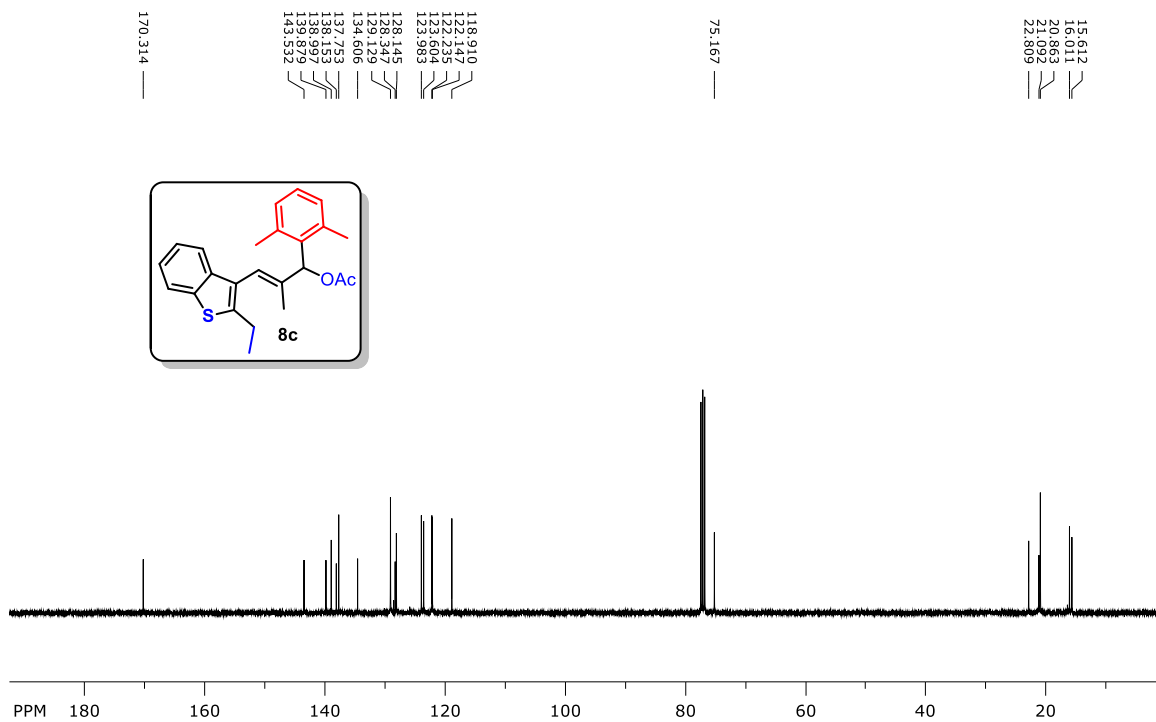
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



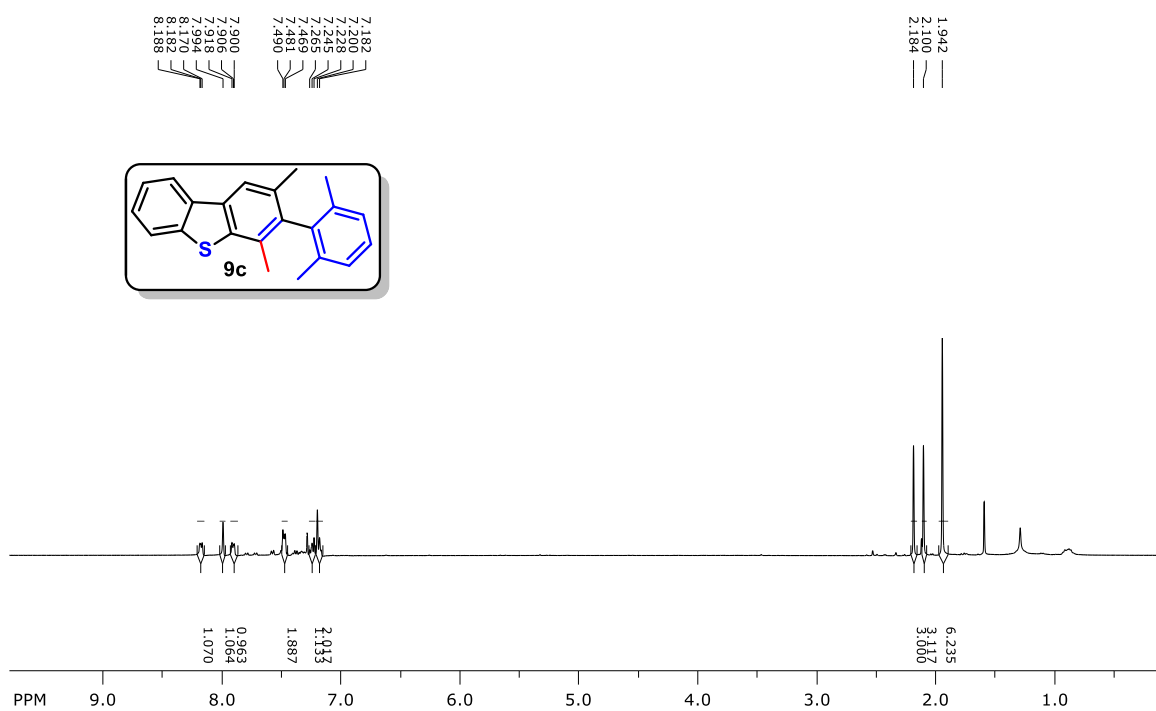
### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



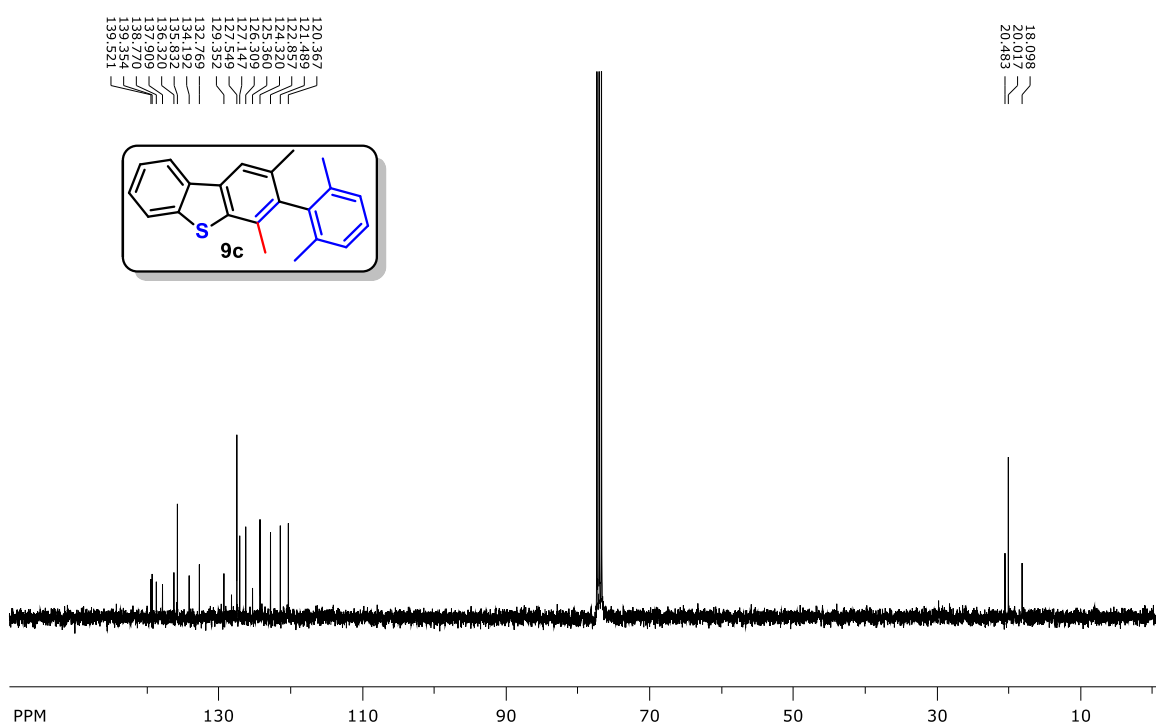
### <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



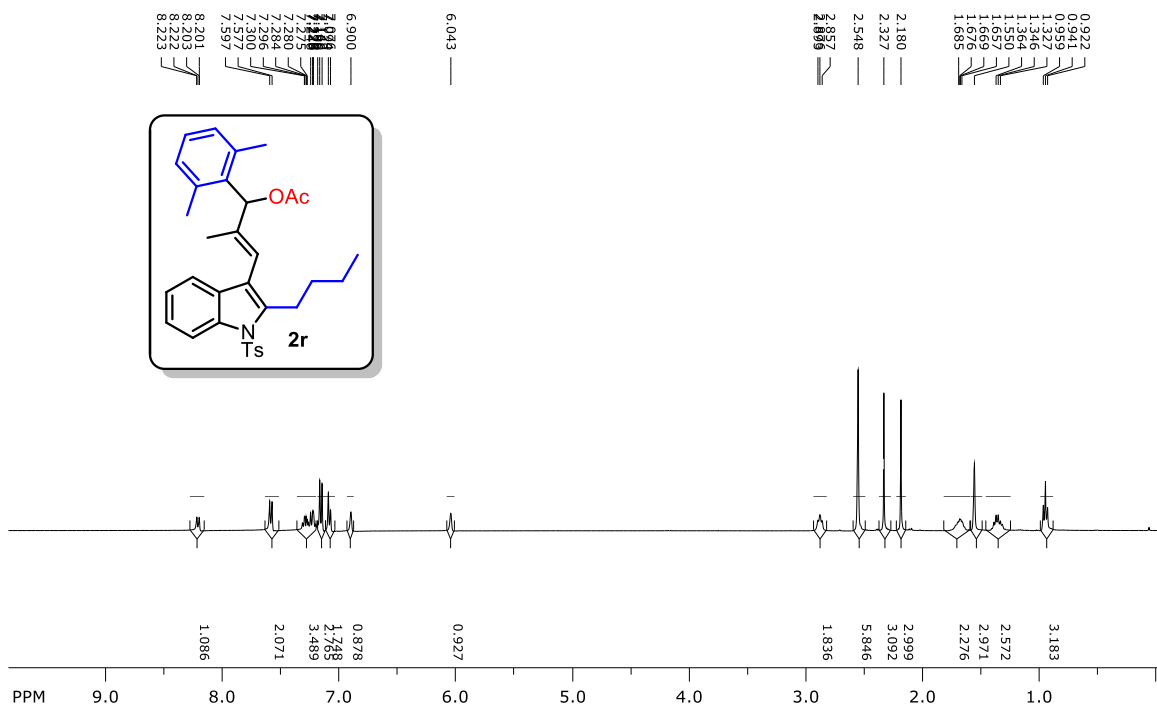
### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



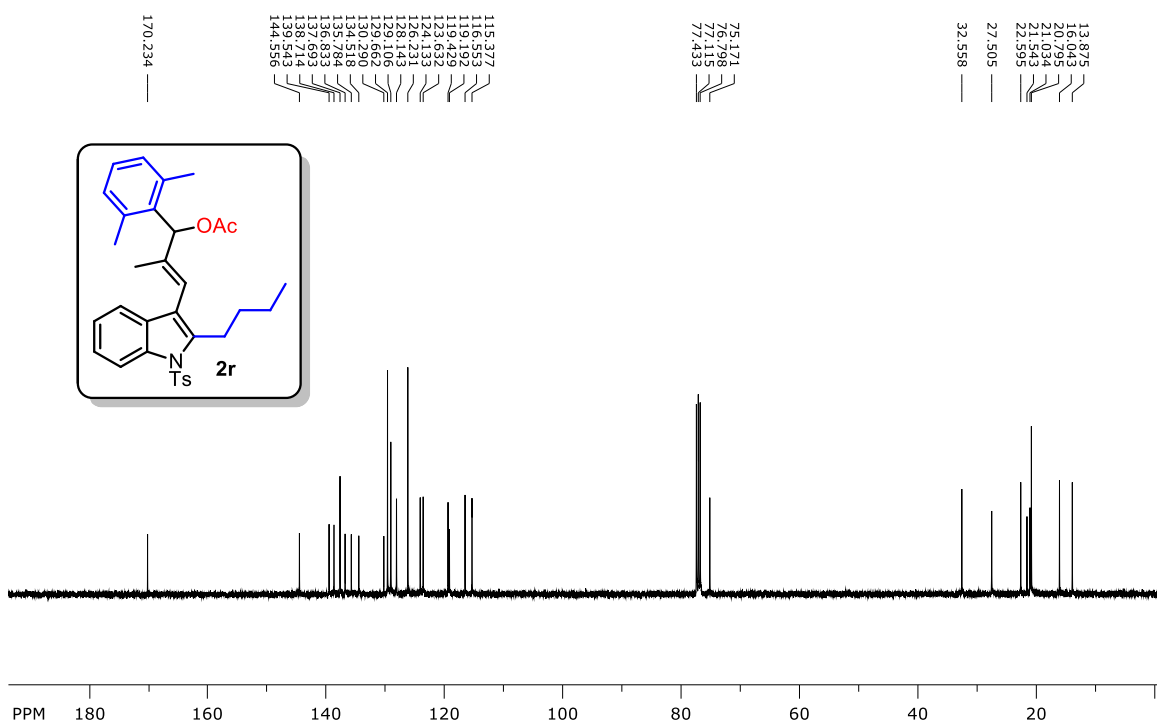
### <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**



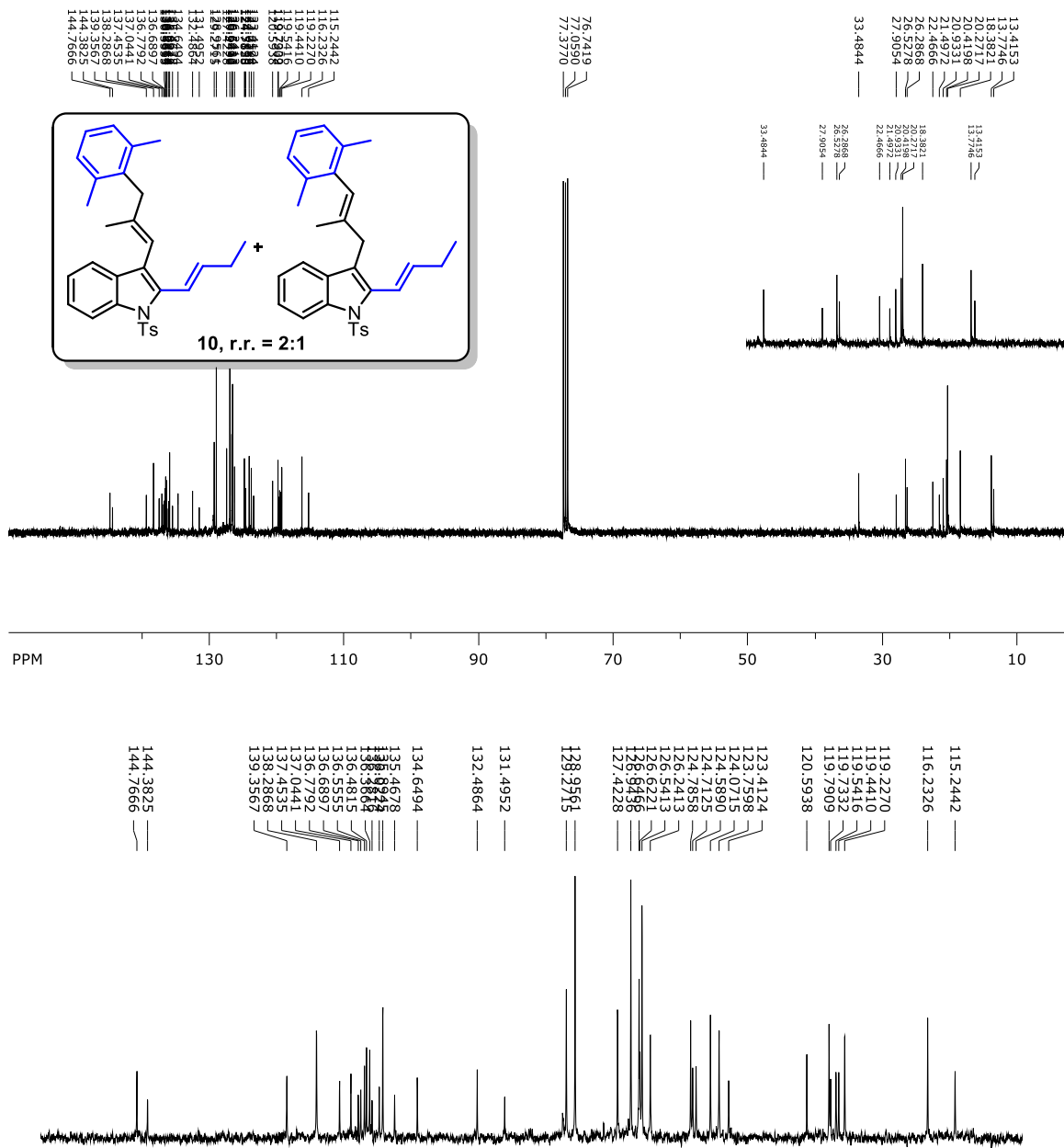
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



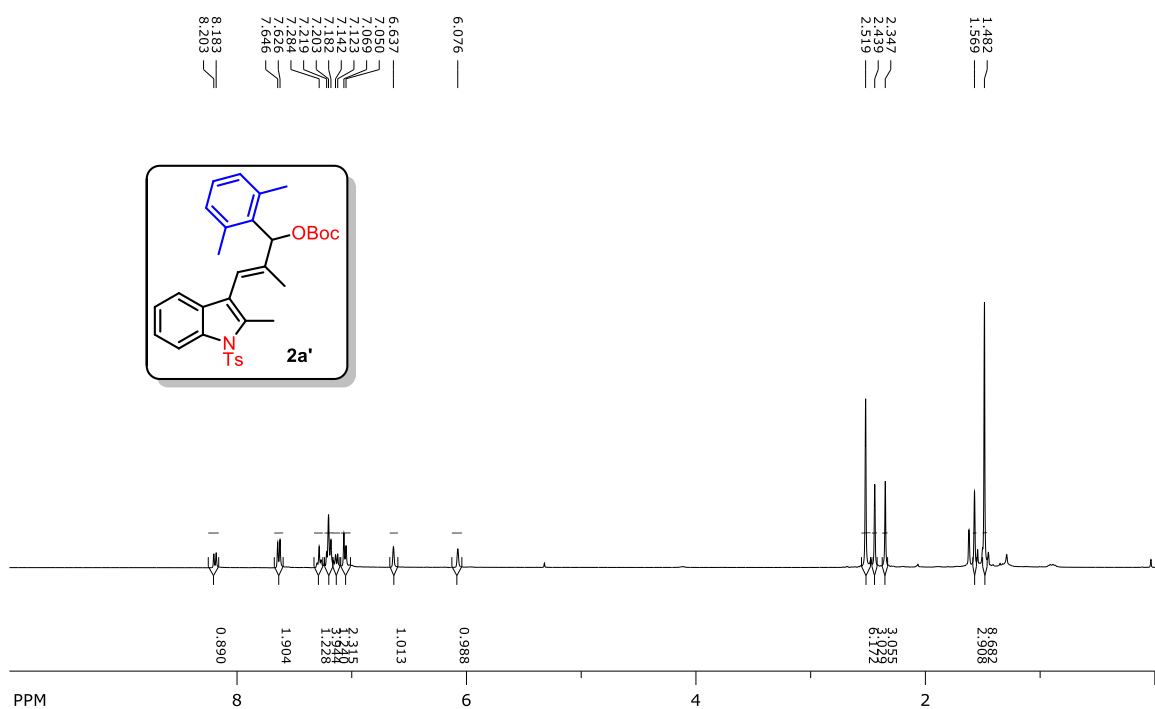




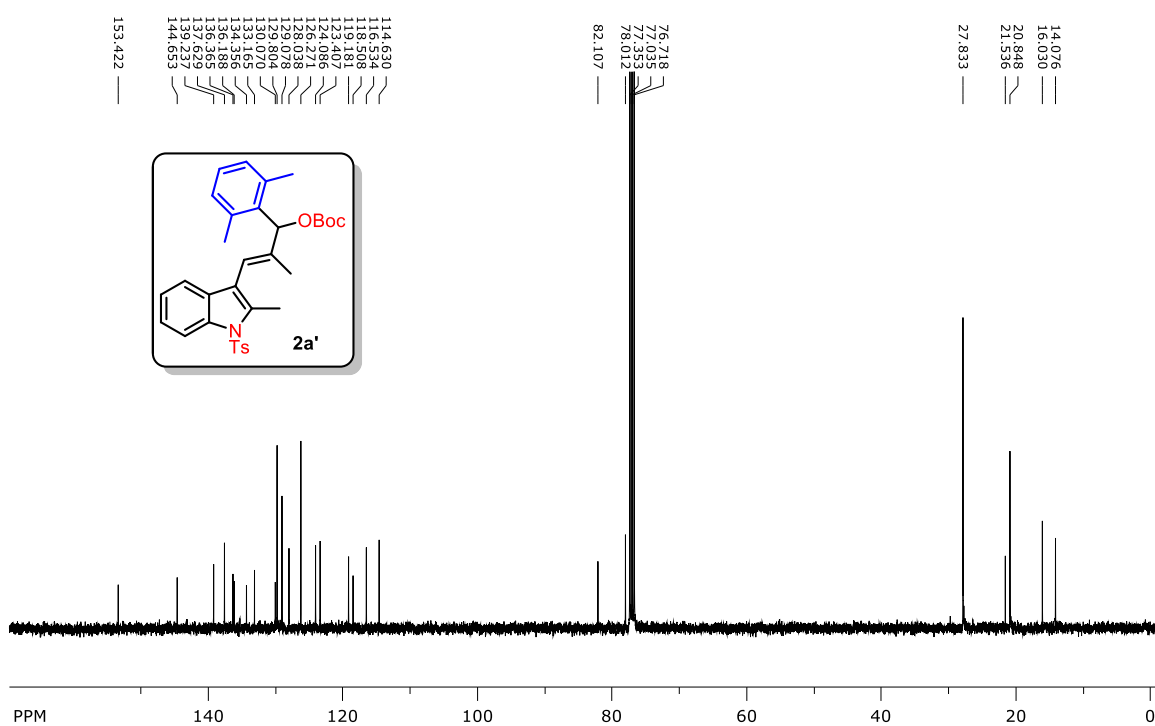
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):



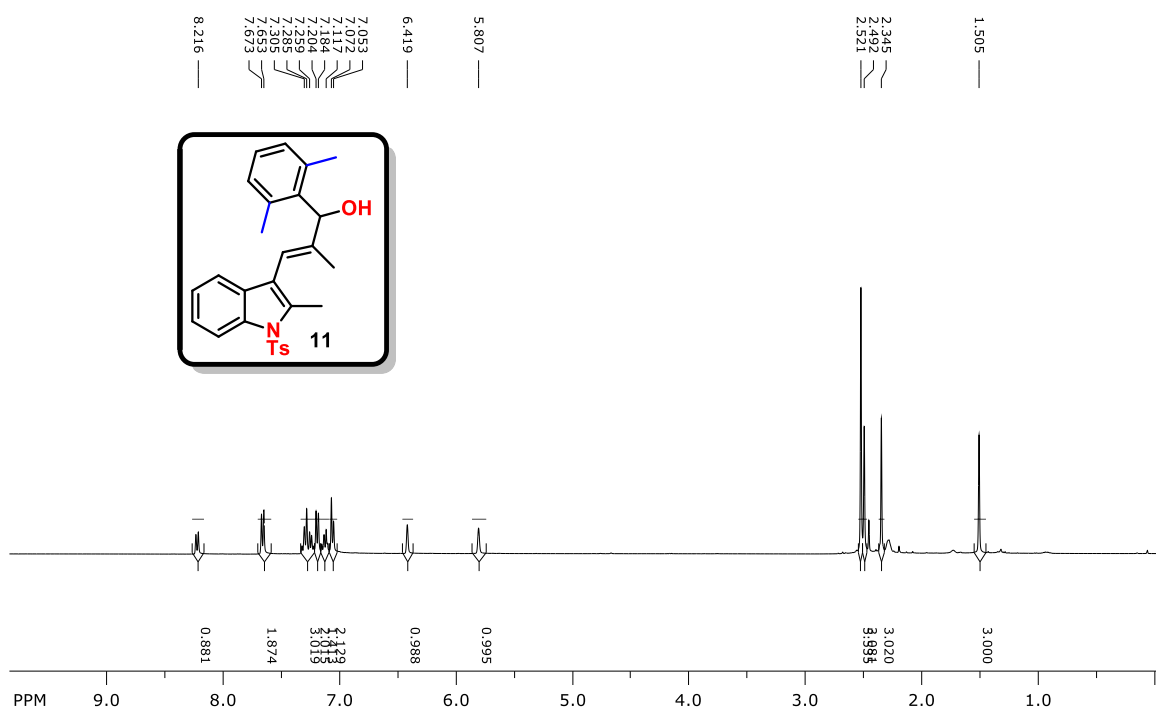
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**

