**Supporting information**
for

# Molecular Iodine Catalyzed Selective C-3 Benzylation of Indoles with Benzylic Alcohols: A Greener Approach towards Benzylated Indoles

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## 1. $^1$H and $^{13}$C{$^1$H} NMR spectra of all compounds

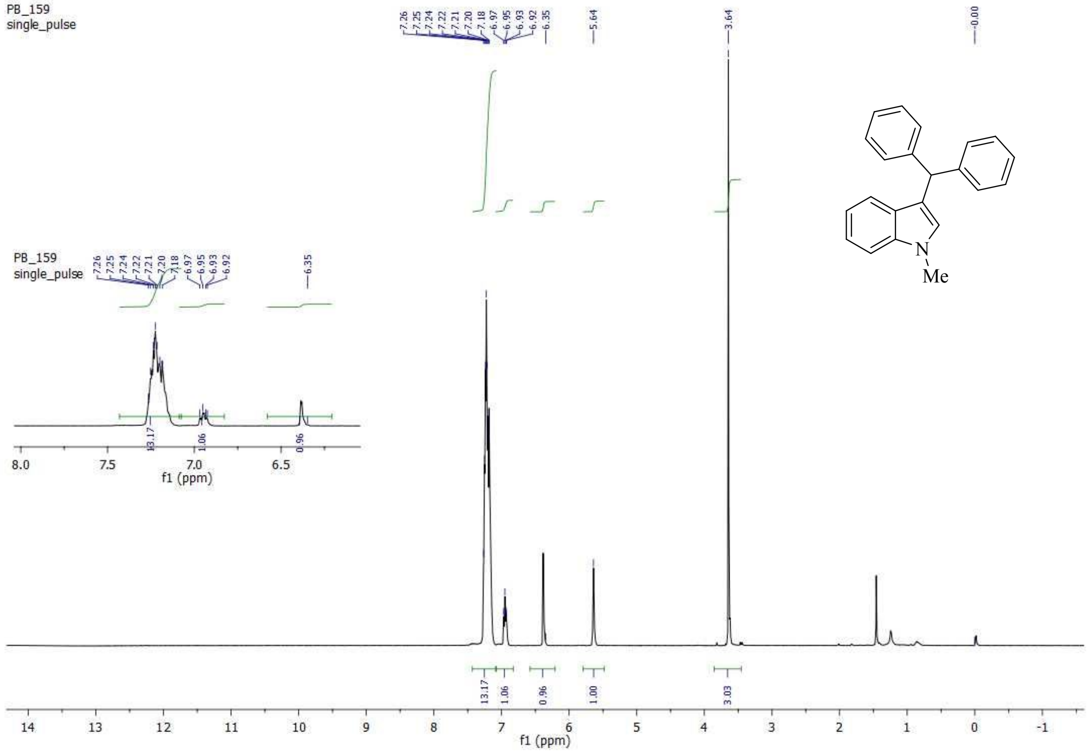


**Figure S1.** 400 MHz $^1$H NMR spectrum of **3a**$^1$ in CDCl$_3$

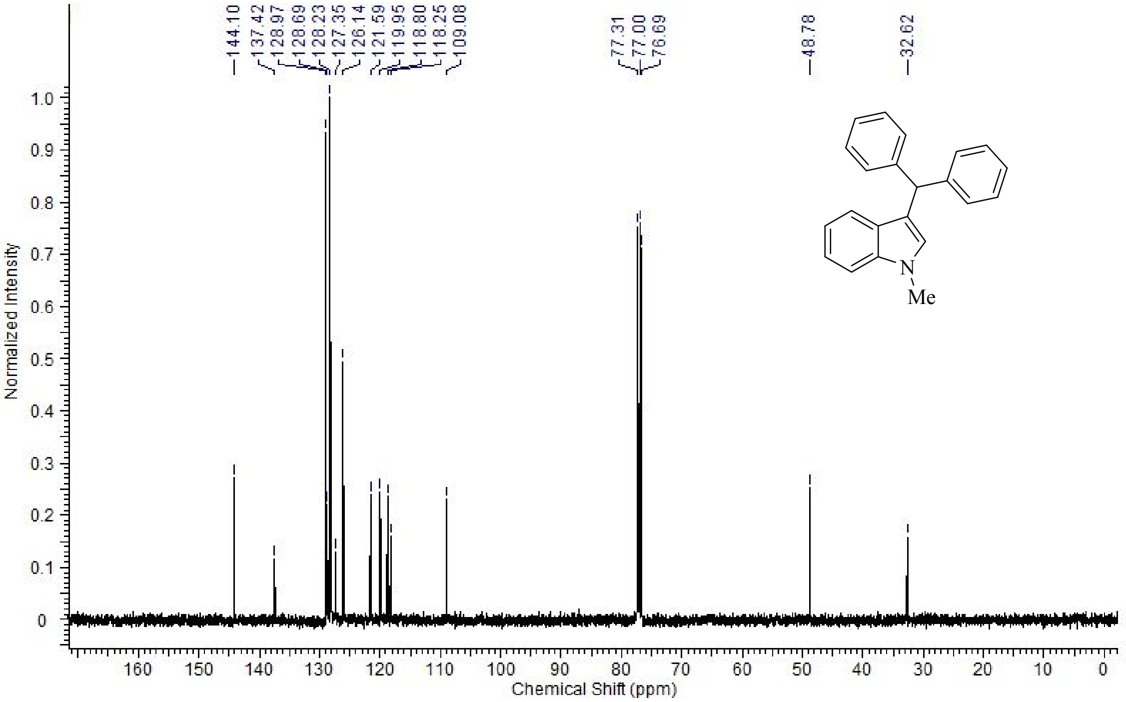


**Figure S2.** 100 MHz $^{13}$C{$^1$H} NMR spectrum of **3a** in CDCl$_3$

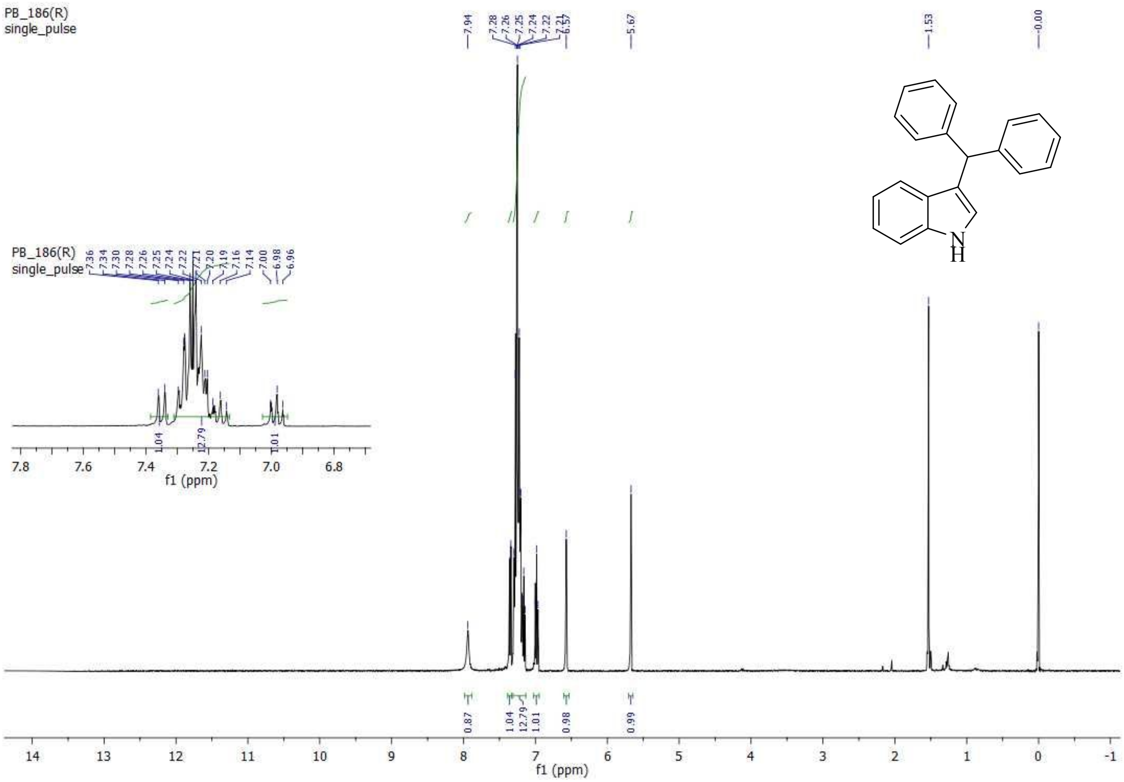


**Figure S3.** 400 MHz $^{1}$H NMR spectrum of **3b$^{2}$** in $CDCl_3$

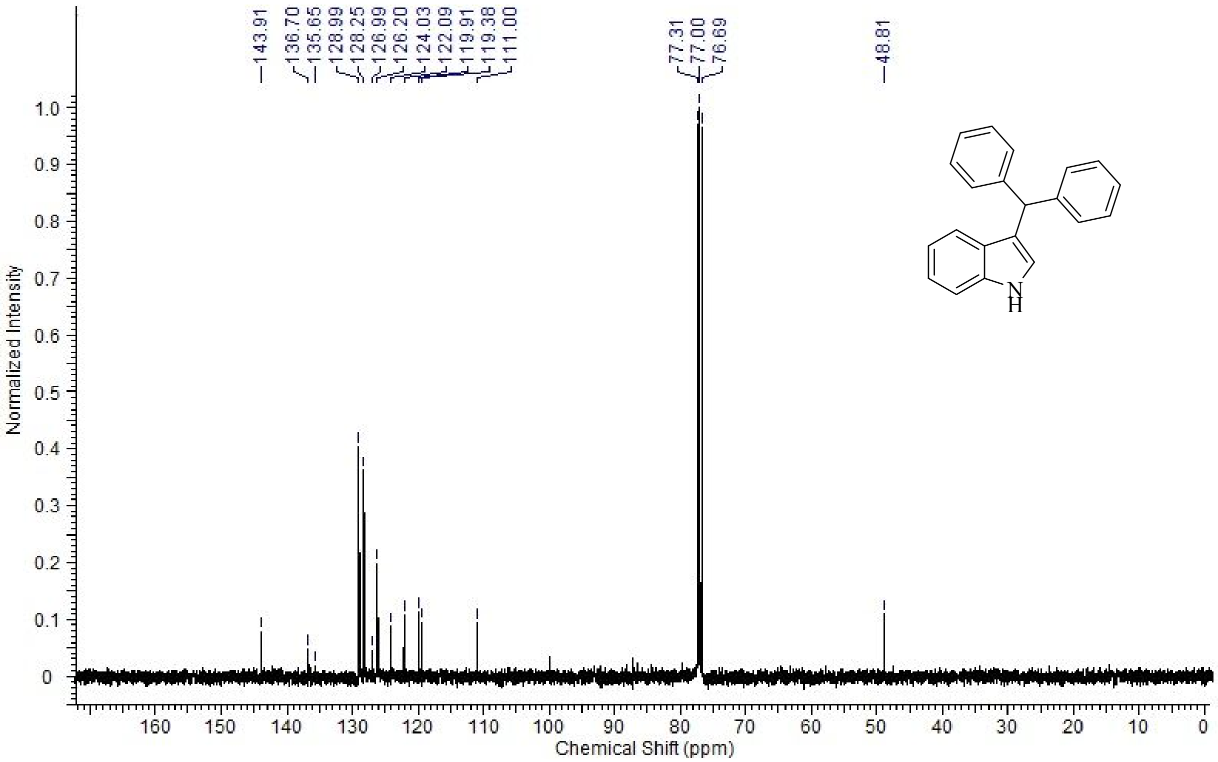


**Figure S4.** 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$

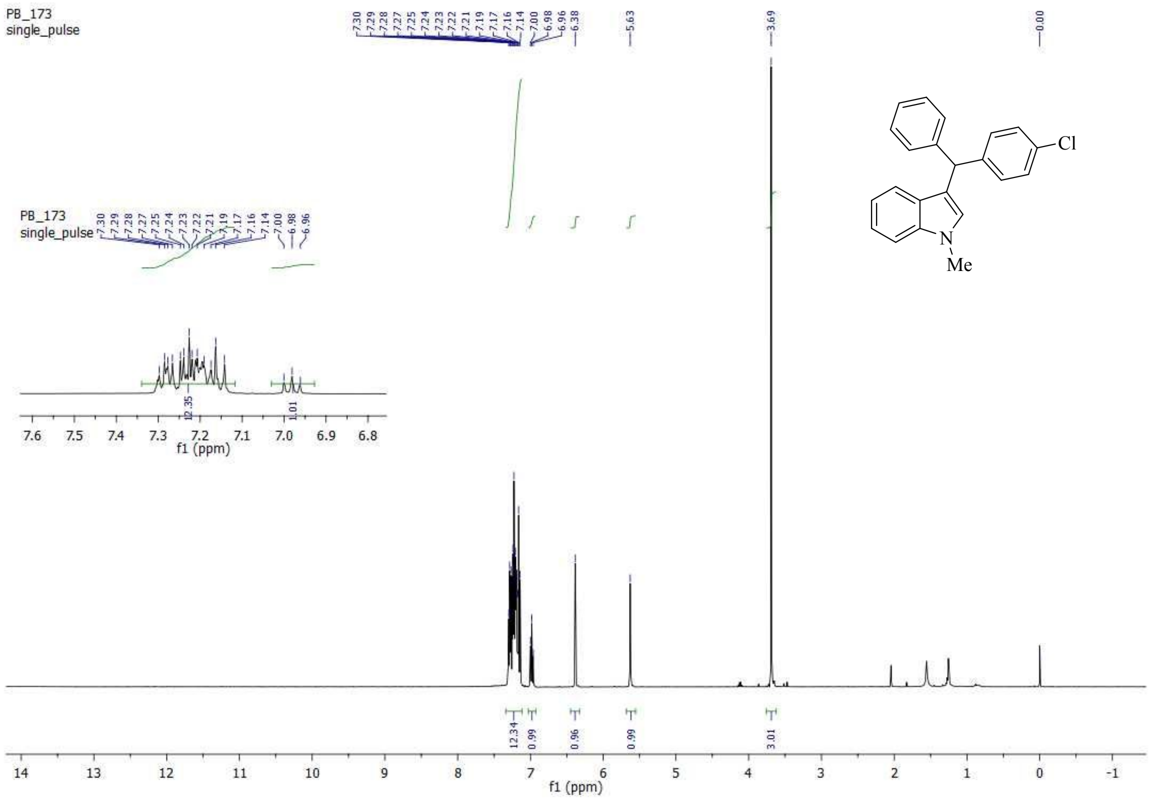


**Figure S5.** 400 MHz $^1$H NMR spectrum of **3c**[1] in $CDCl_3$

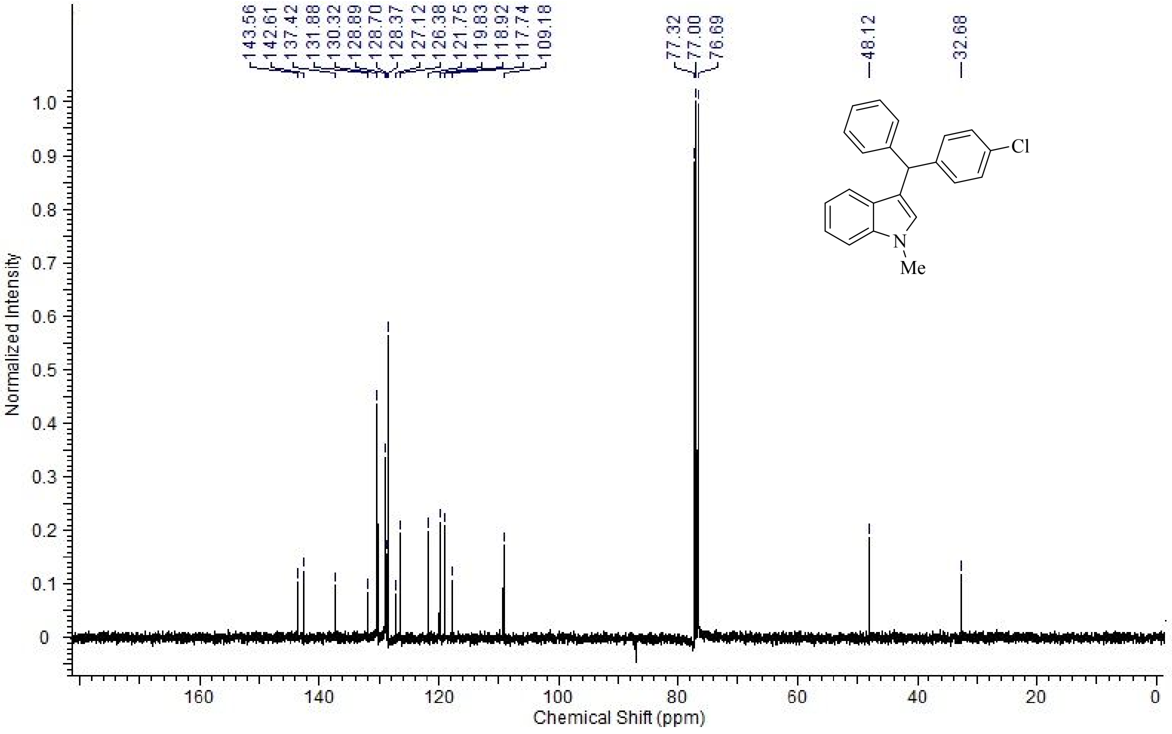


**Figure S6.** 100 MHz $^{13}C\{^1H\}$ NMR spectrum of **3c** in $CDCl_3$

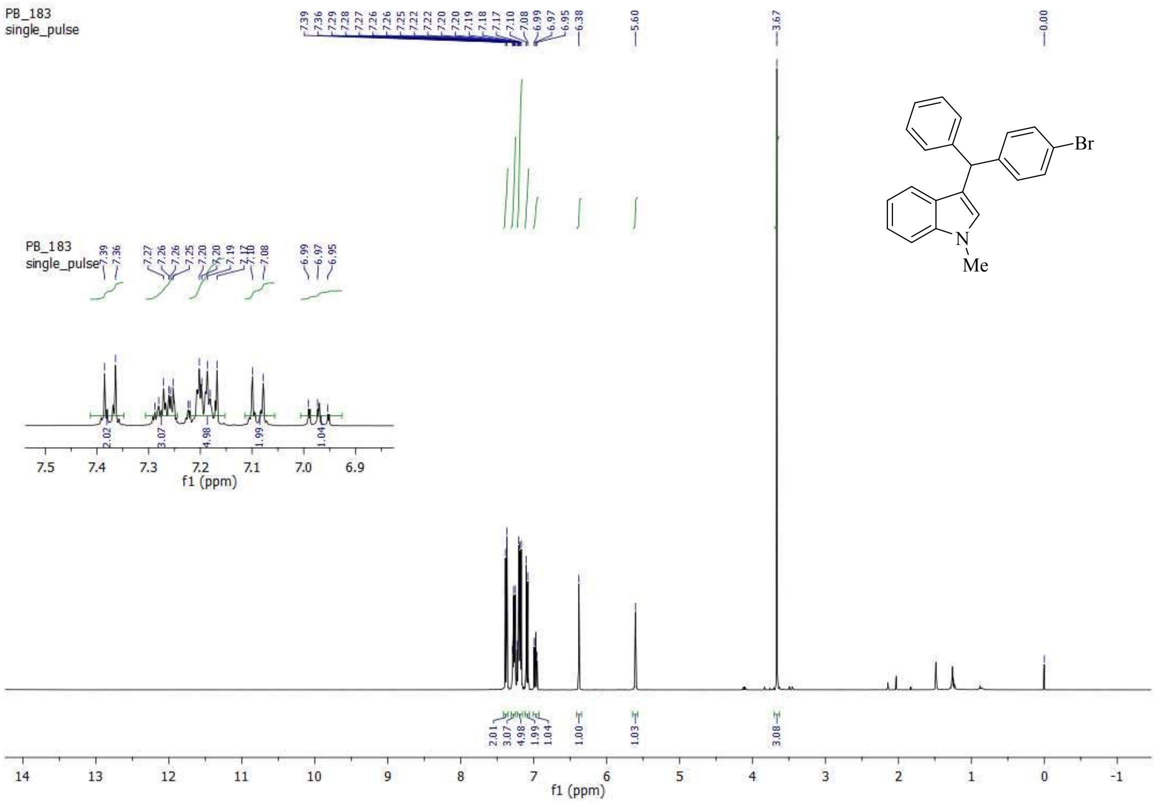


**Figure S7.** 400 MHz $^1$H NMR spectrum of **3d$^1$** in CDCl$_3$

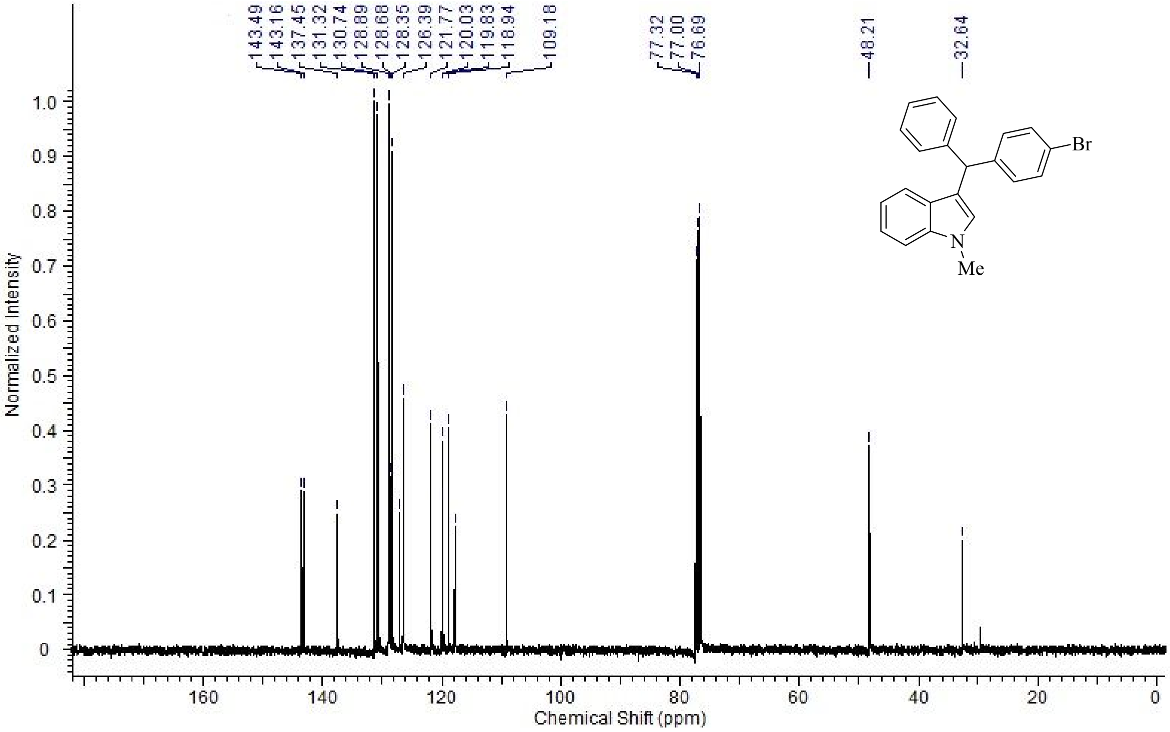


**Figure S8.** 100 MHz $^{13}$C{$^1$H} NMR spectrum of **3d** in CDCl$_3$

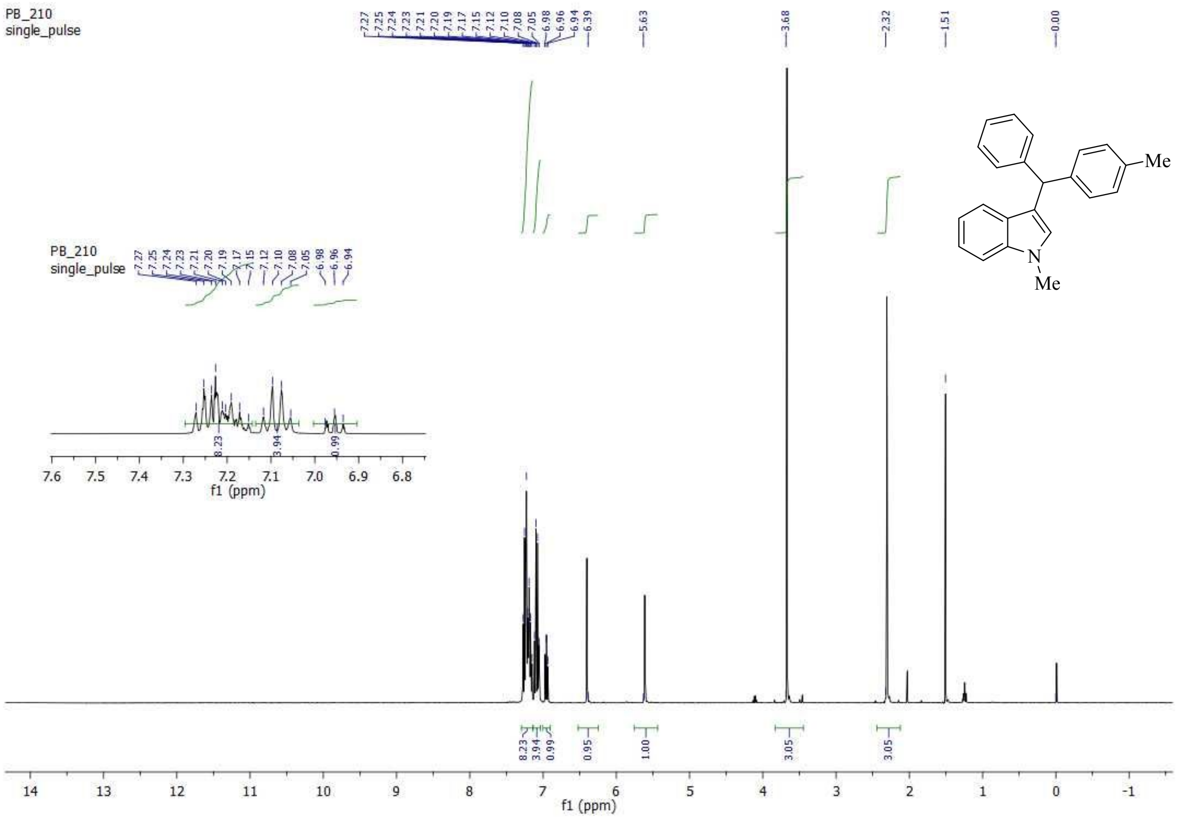


**Figure S9.** 400 MHz $^{1}$H NMR spectrum of **3e**[1] in CDCl$_3$

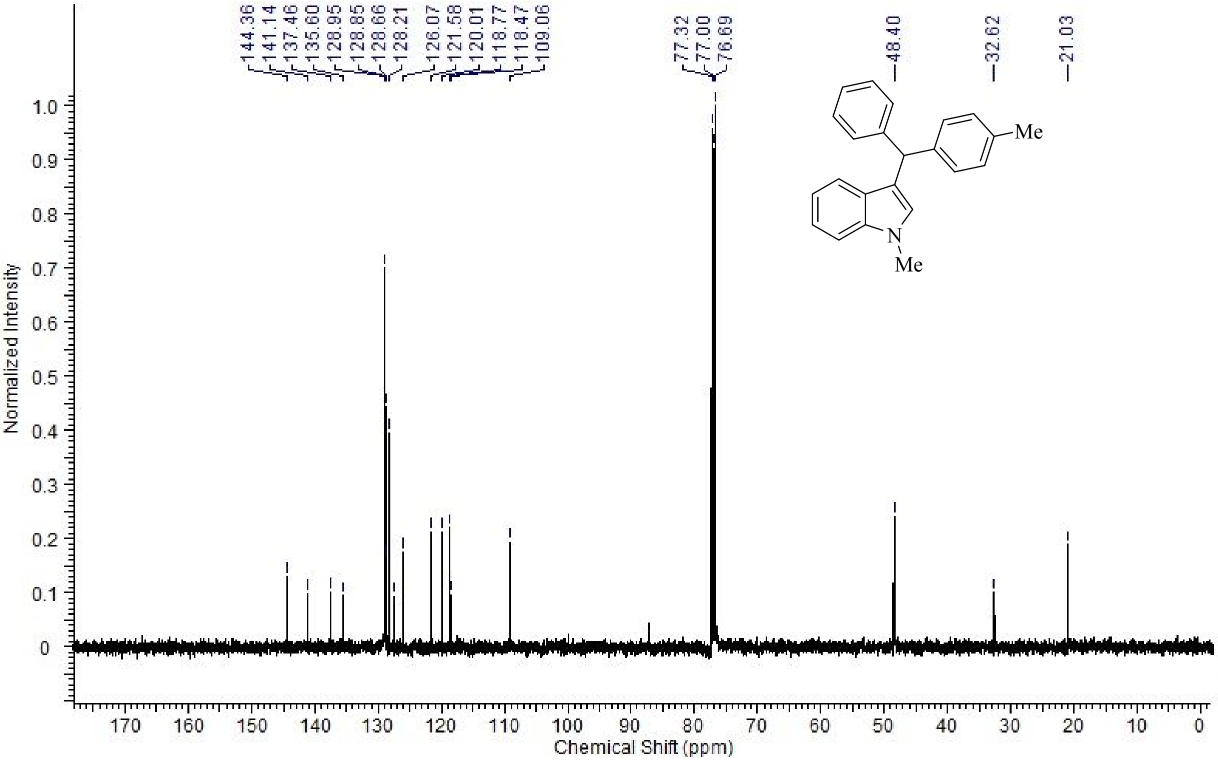


**Figure S10.** 100 MHz $^{13}$C{$^{1}$H} NMR spectrum of **3e** in CDCl$_3$

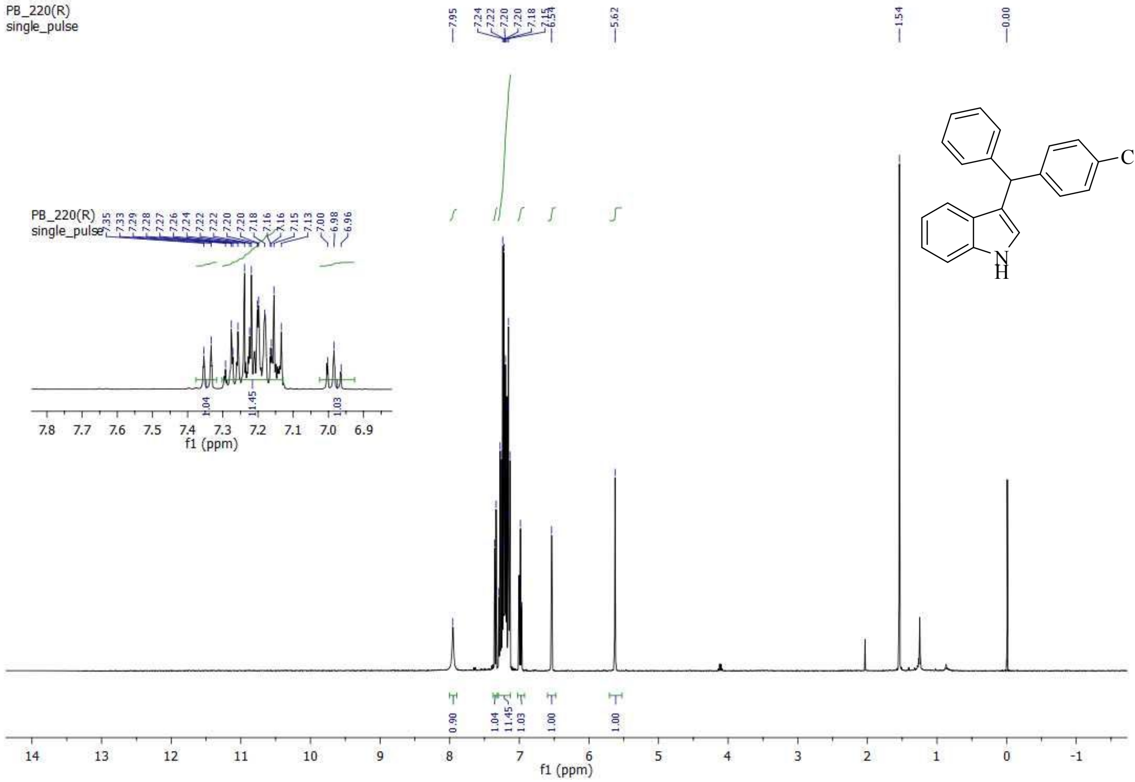


**Figure S11.** 400 MHz $^{1}$H NMR spectrum of **3f**[3] in CDCl$_3$

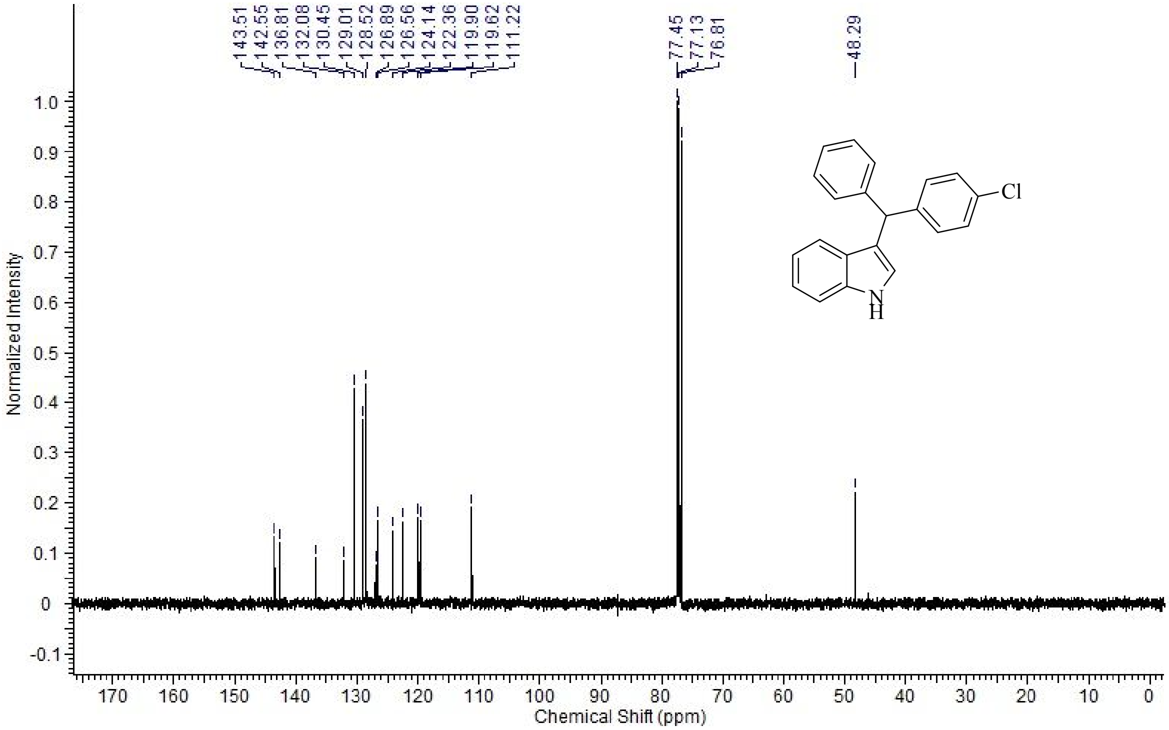


**Figure S12.** 100 MHz $^{13}$C{$^{1}$H} NMR spectrum of **3f** in CDCl$_3$

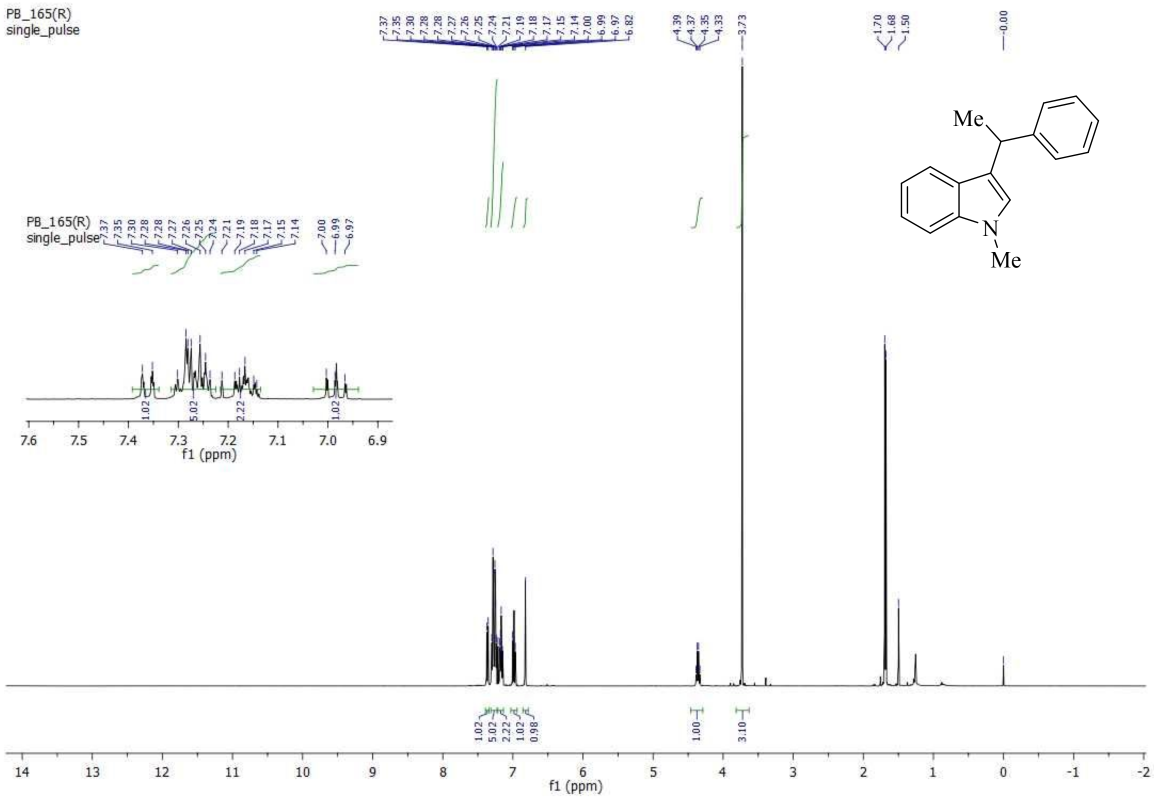


**Figure S13.** 400 MHz $^1$H NMR spectrum of **3g**[1] in $CDCl_3$

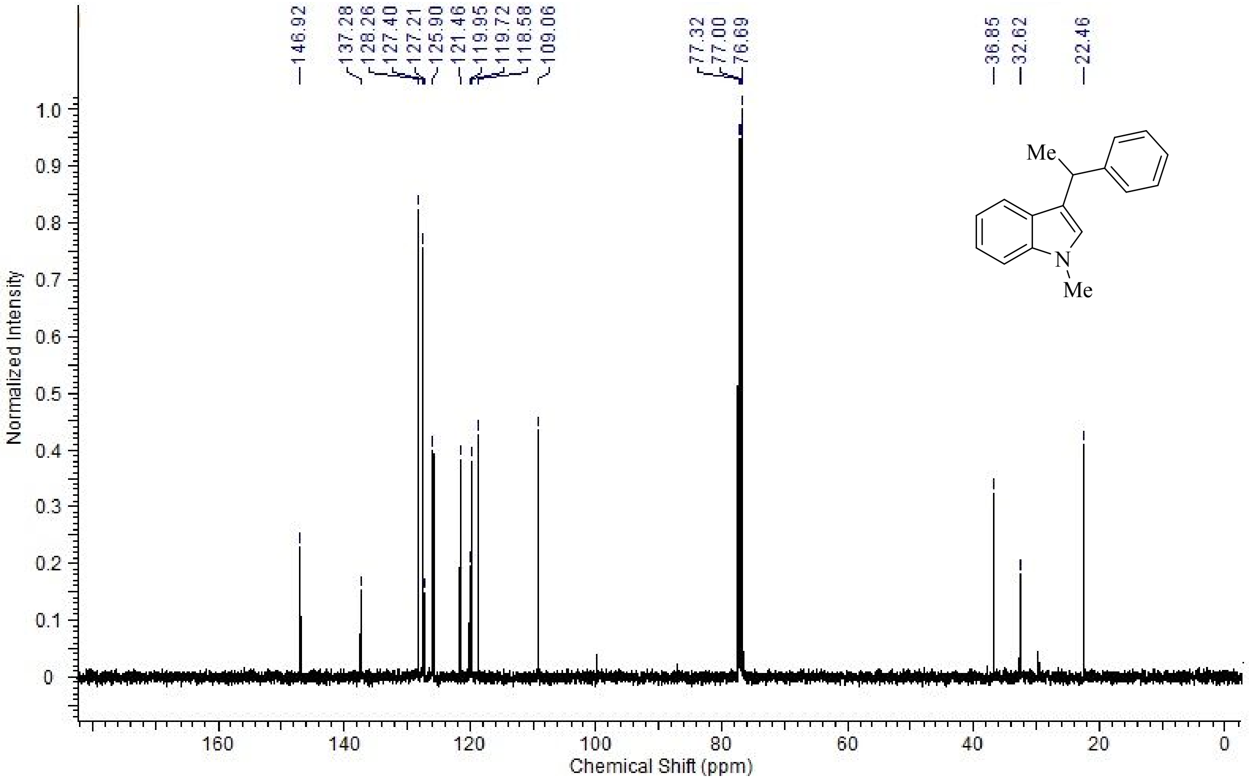


**Figure S14.** 100 MHz $^{13}C\{^1H\}$ NMR spectrum of **3g** in $CDCl_3$

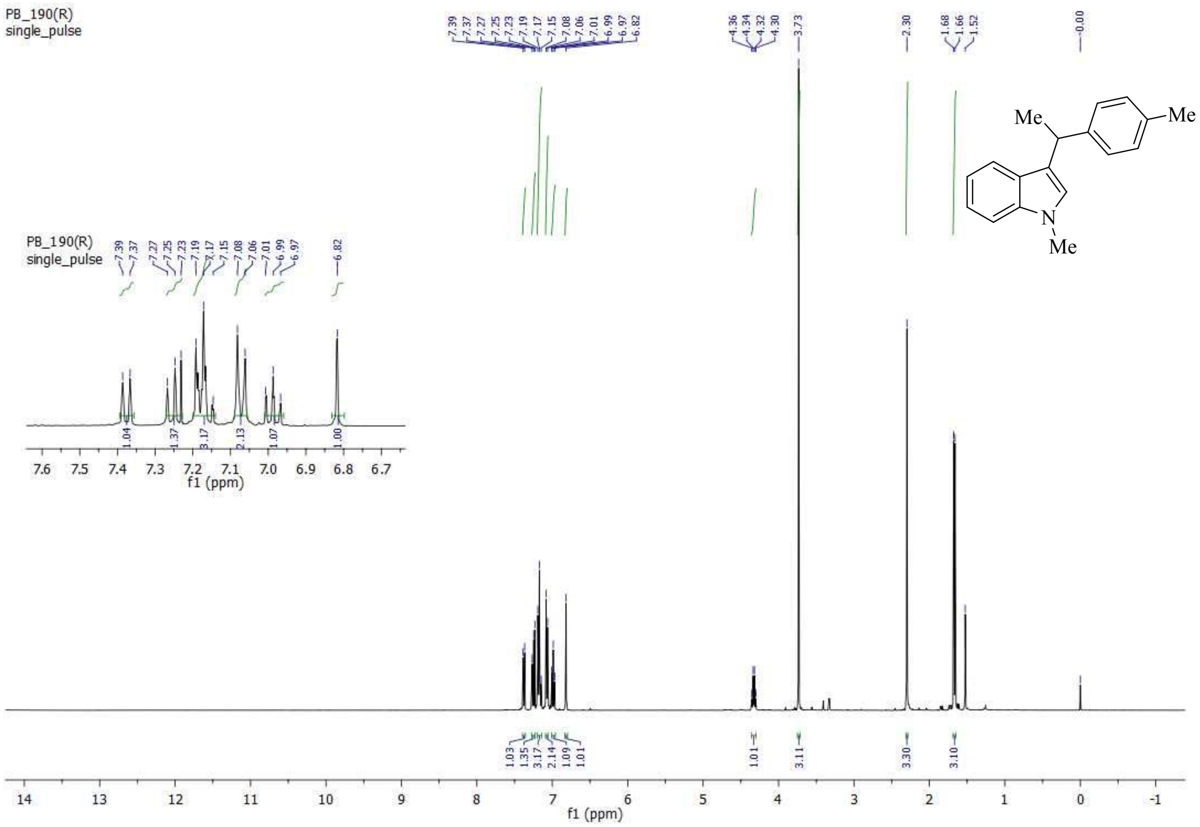


**Figure S15.** 400 MHz $^{1}$H NMR spectrum of **3h**$^{4}$ in CDCl$_3$

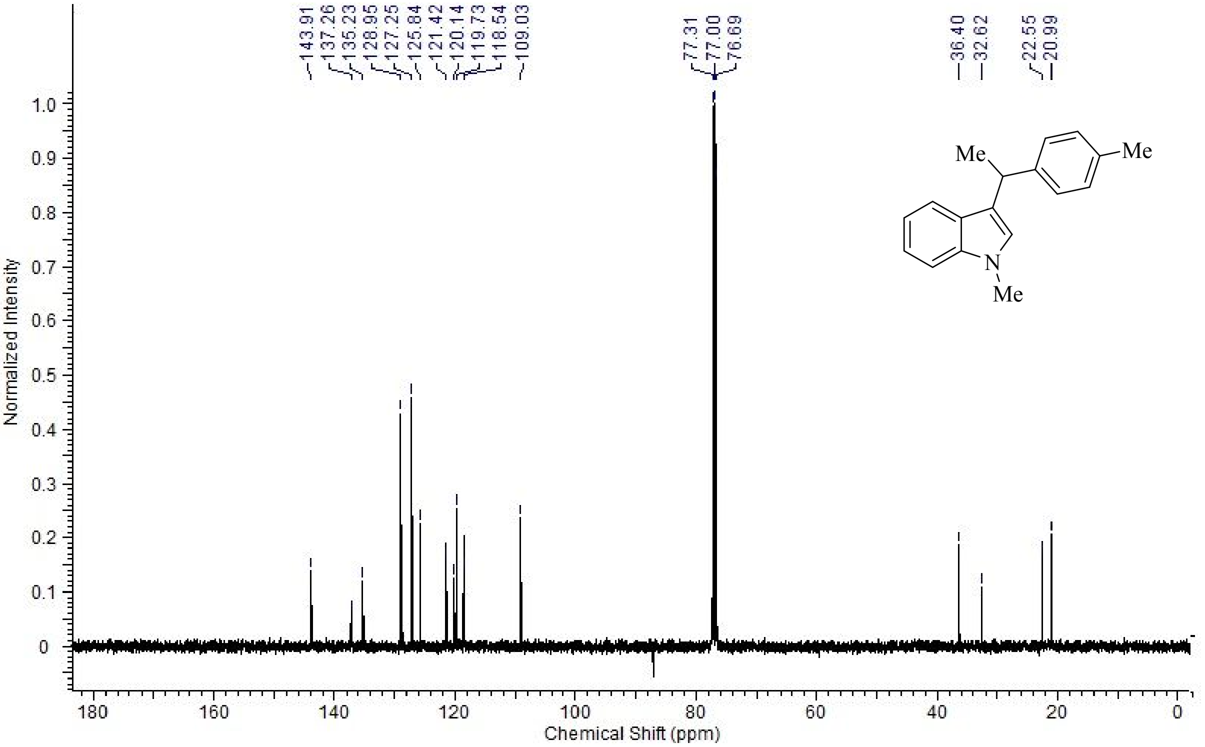


**Figure S16.** 100 MHz $^{13}$C{$^{1}$H} NMR spectrum of **3h** in CDCl$_3$

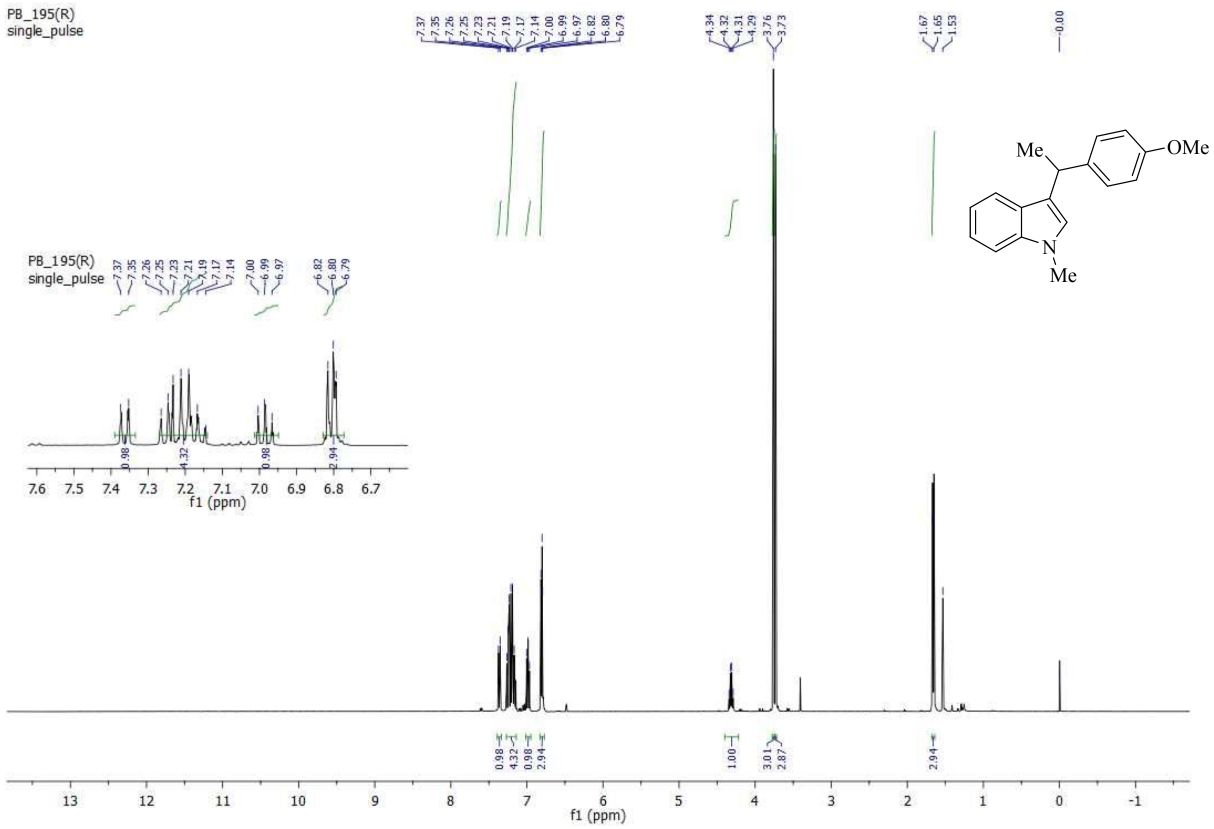


**Figure S17.** 400 MHz $^{1}$H NMR spectrum of **3i**[1] in CDCl$_3$

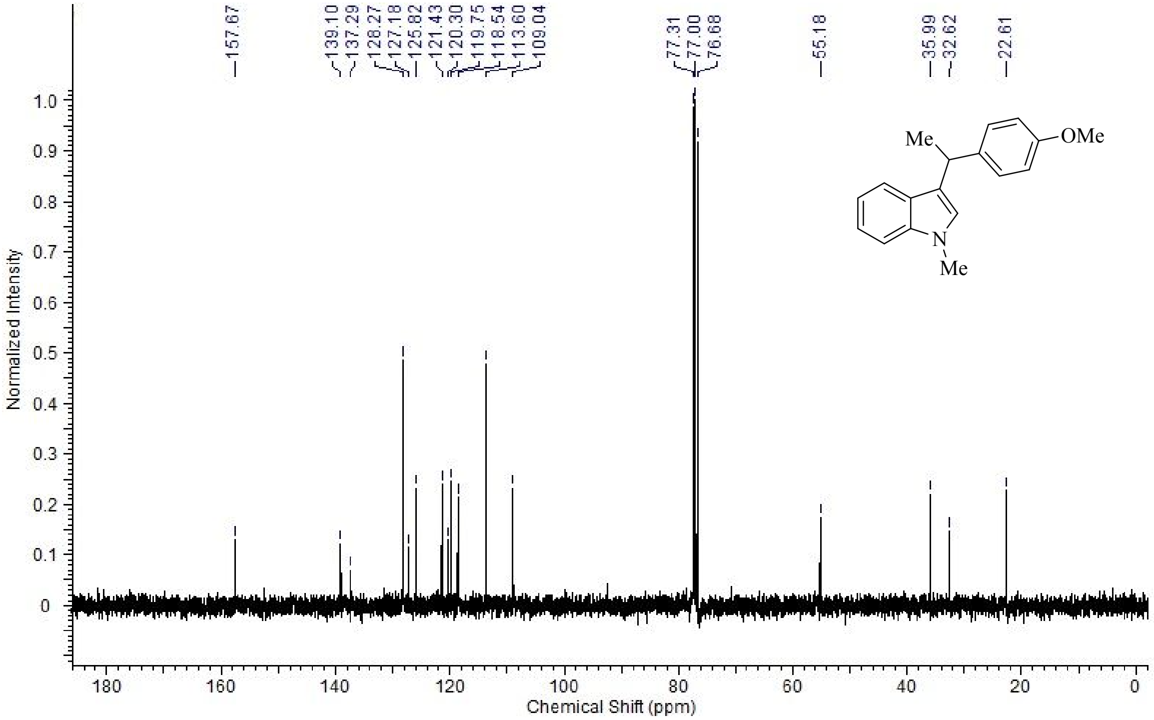


**Figure S18.** 100 MHz $^{13}$C{$^{1}$H} NMR spectrum of **3i** in CDCl$_3$

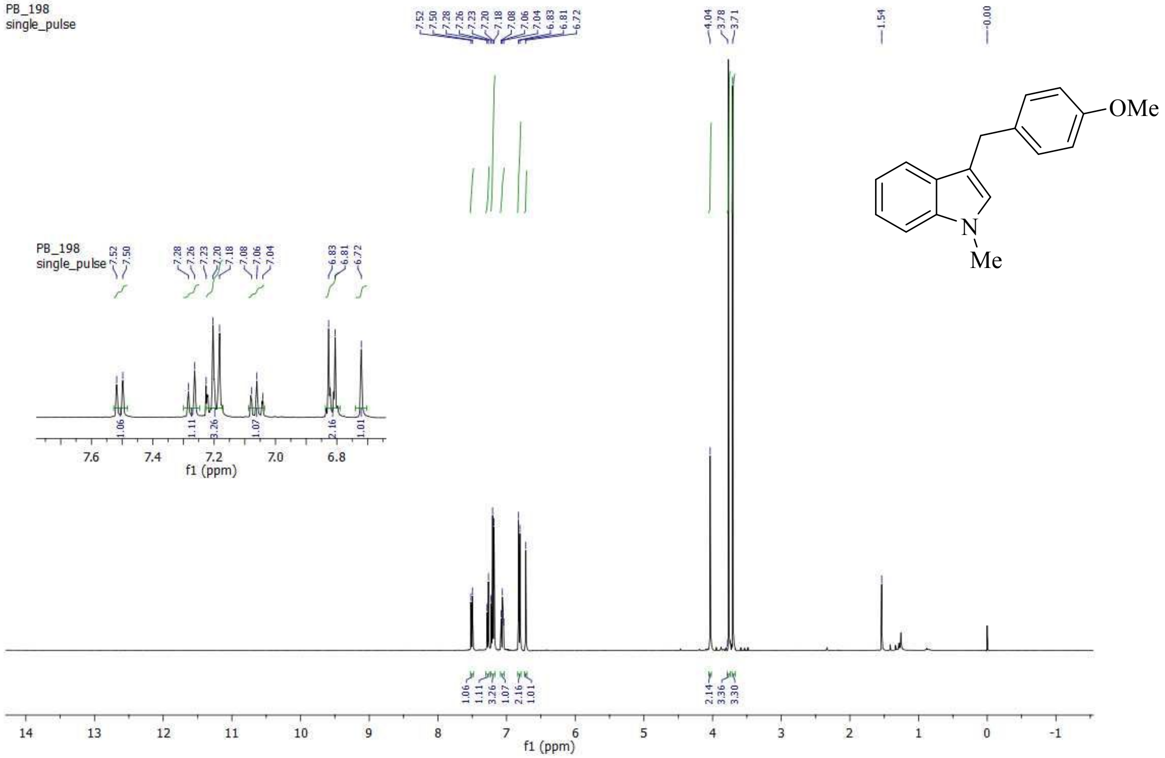


Figure S19. 400 MHz $^1$H NMR spectrum of **3j**[1] in CDCl$_3$

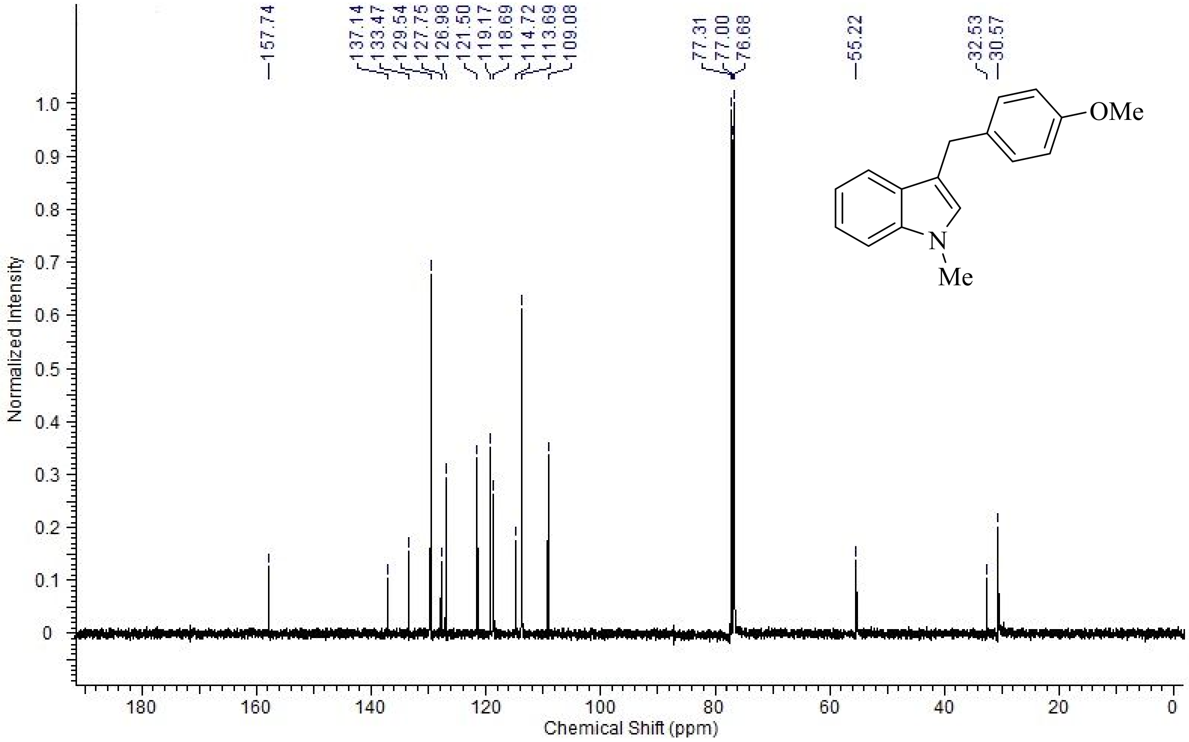


**Figure S20.** 100 MHz $^{13}$C{$^1$H} NMR spectrum of **3j** in CDCl$_3$

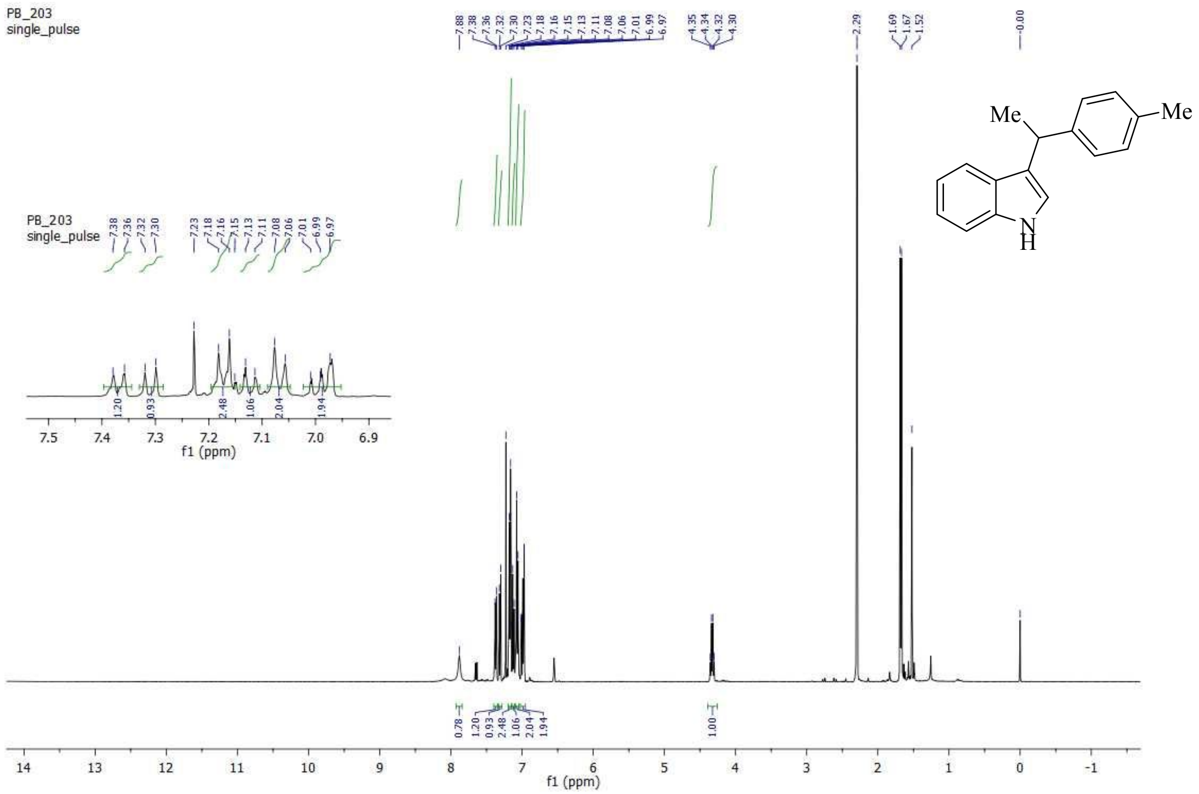


**Figure S21.** 400 MHz $^{1}$H NMR spectrum of **3k**$^{5}$ in $CDCl_3$

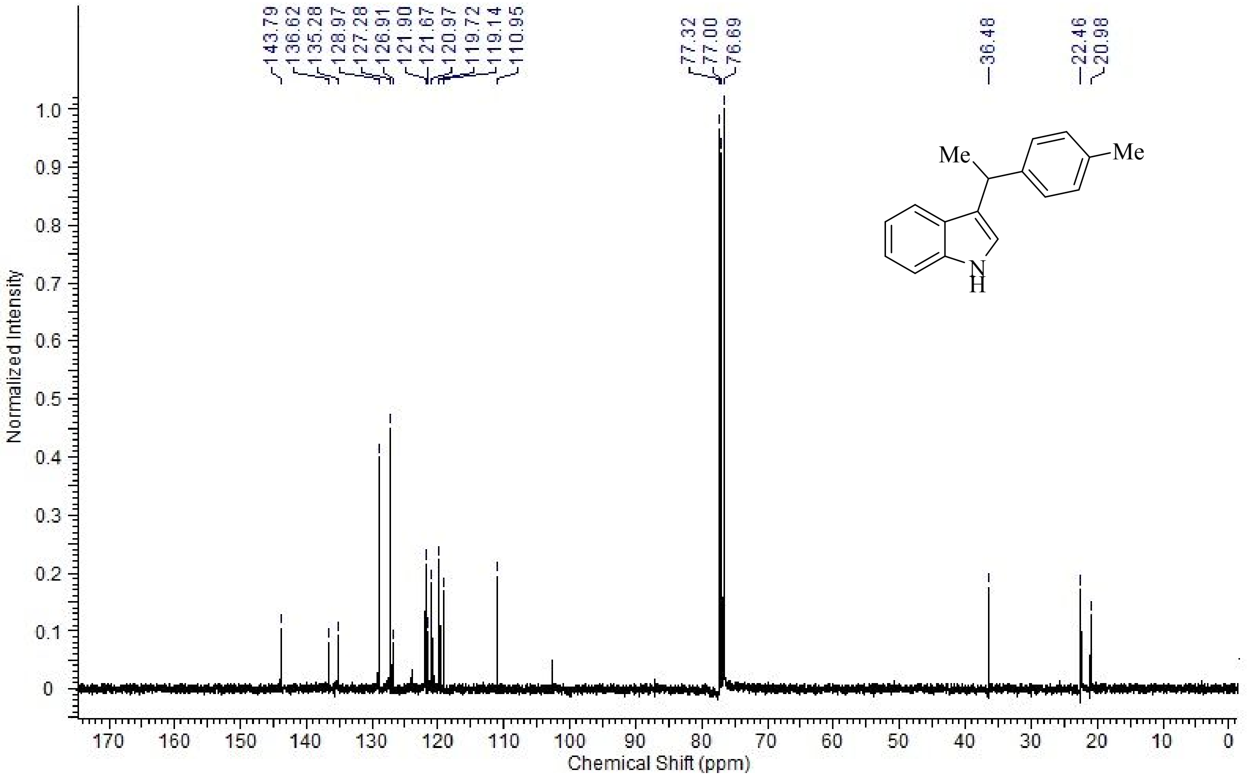


**Figure S22.** 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **3k** in $CDCl_3$

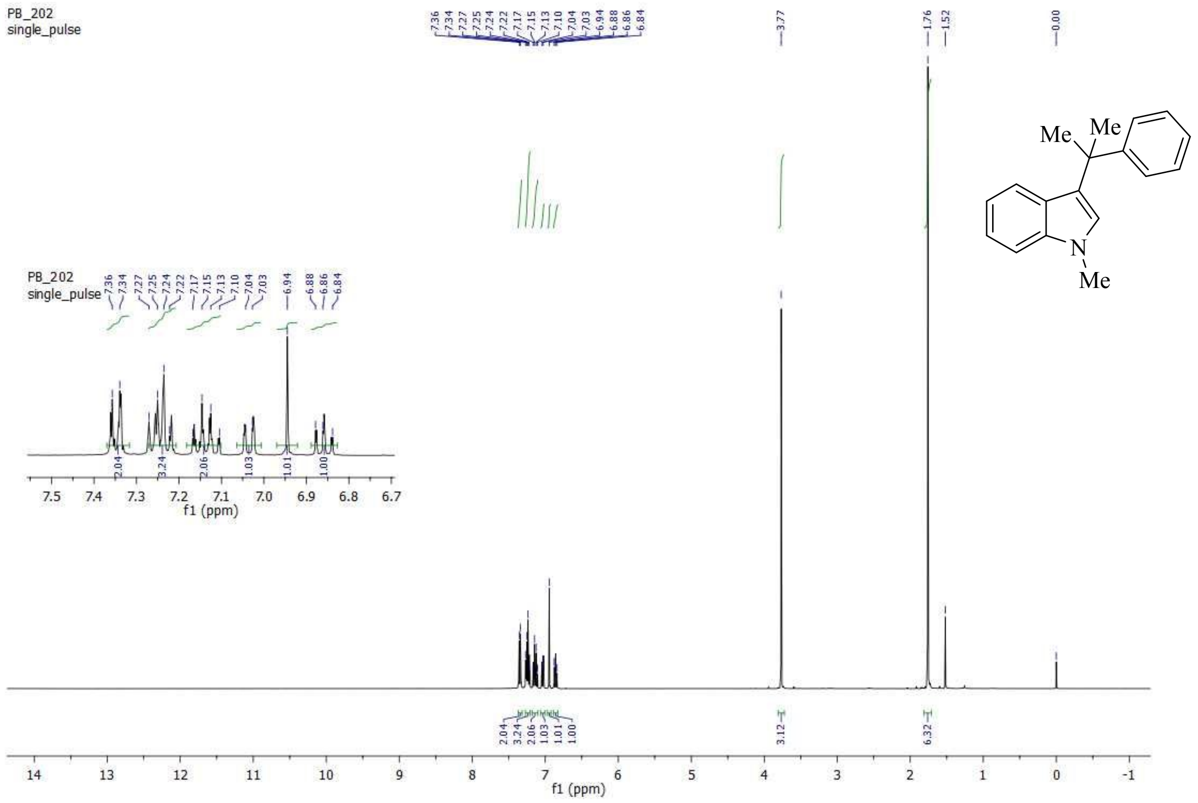


**Figure S23.** 400 MHz $^1$H NMR spectrum of **3l**$^{\mathbf{6}}$ in CDCl$_3$

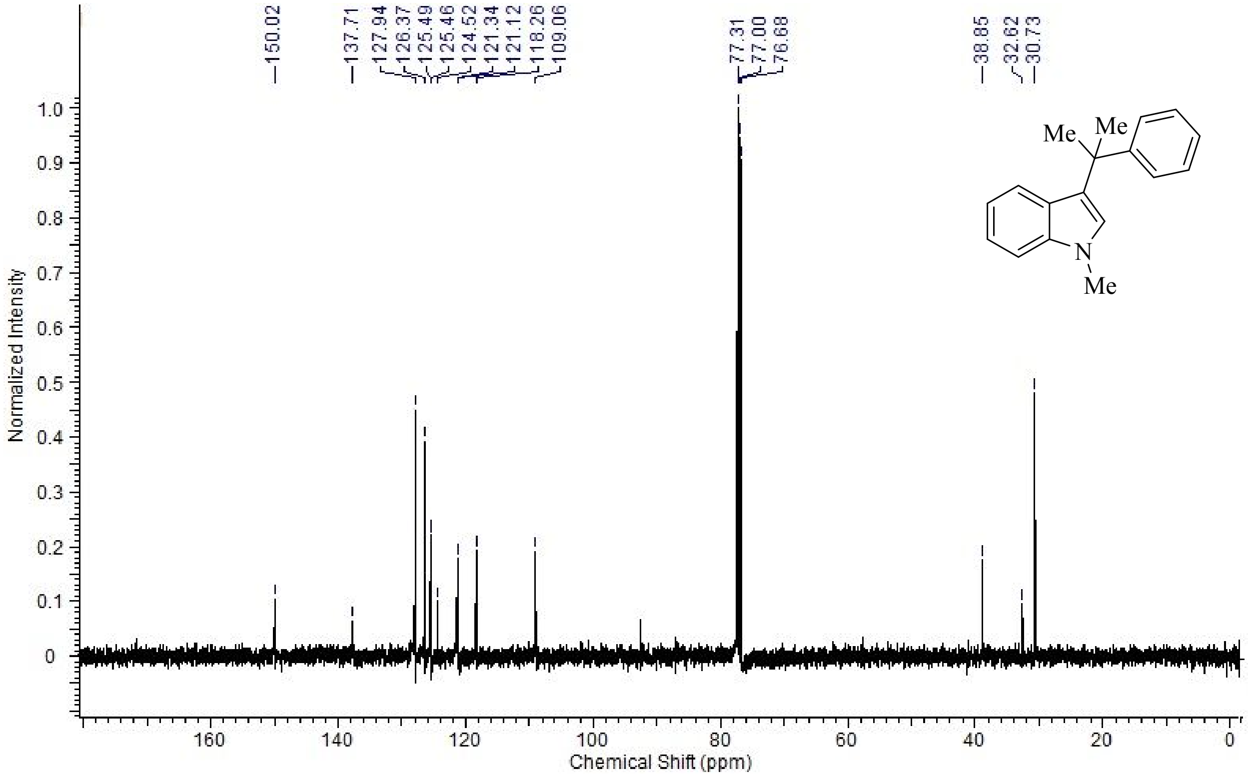


**Figure S24.** 100 MHz $^{13}$C{$^1$H} NMR spectrum of **3l** in CDCl$_3$

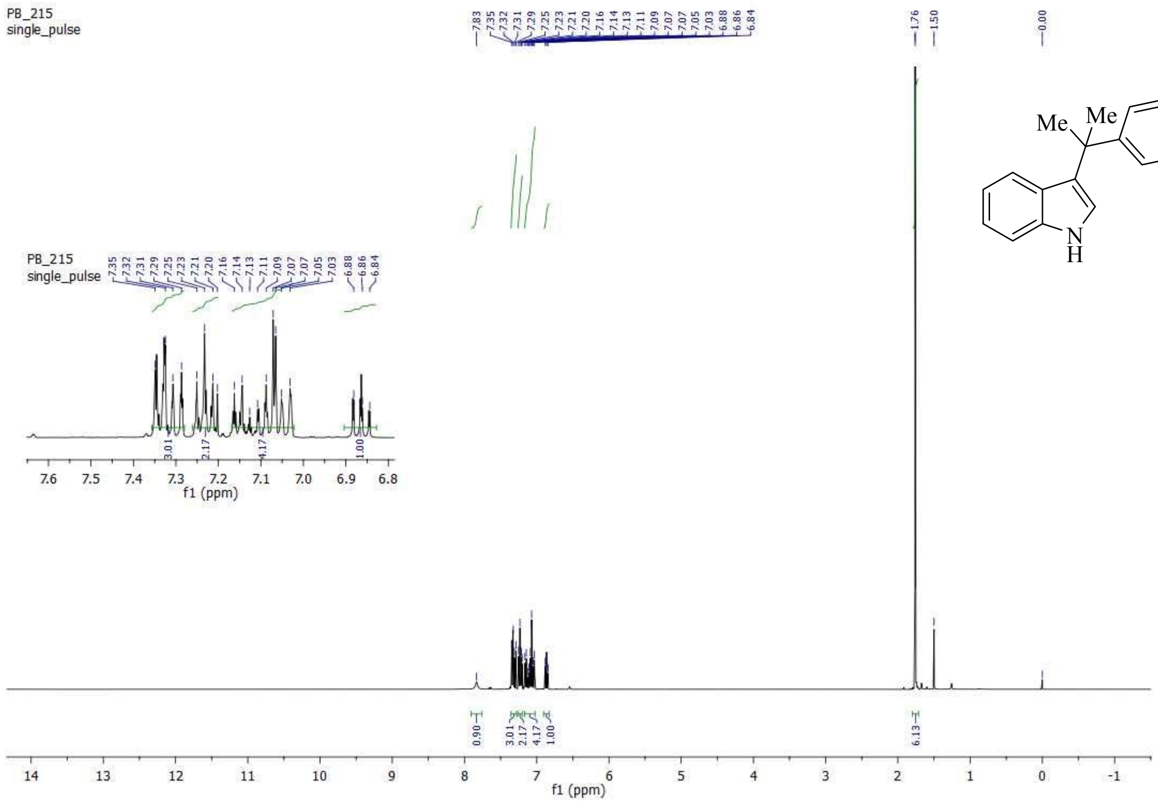


**Figure S25.** 400 MHz $^1$H NMR spectrum of **3m**[7] in CDCl$_3$

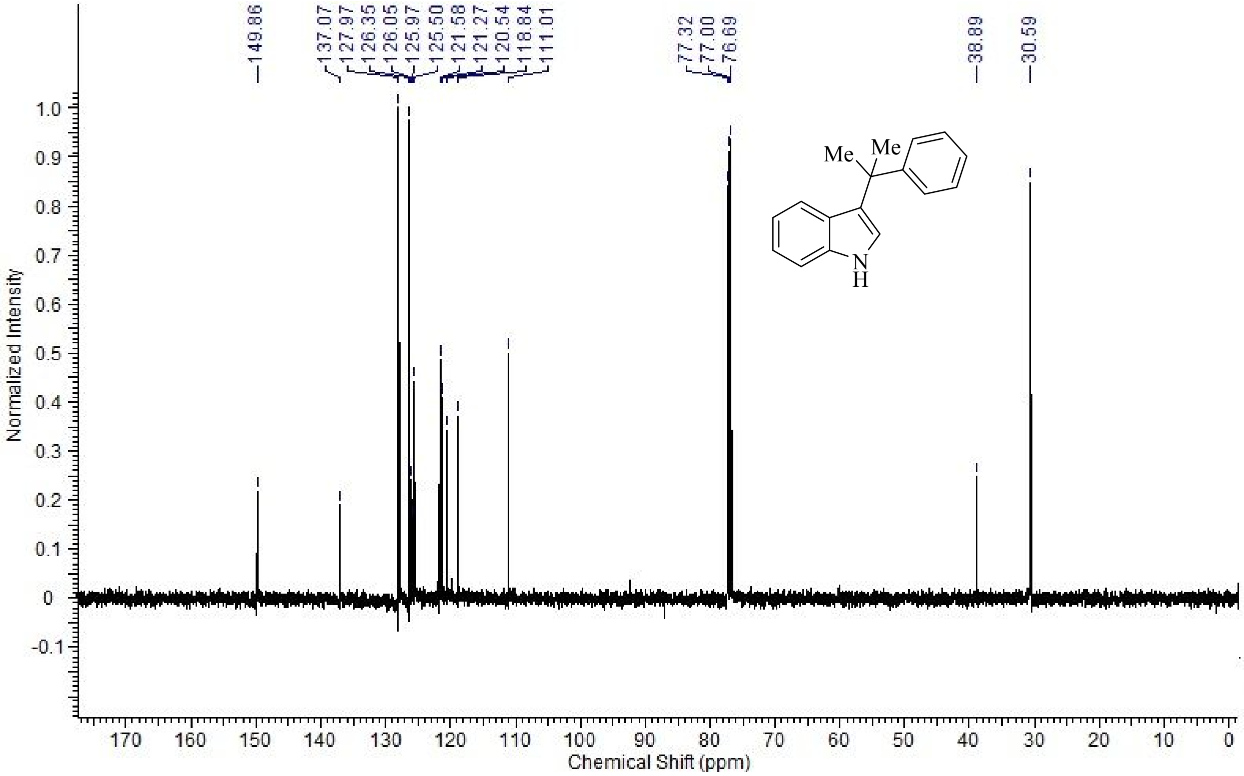


**Figure S26.** 100 MHz $^{13}C\{^1H\}$ NMR spectrum of **3m** in $CDCl_3$

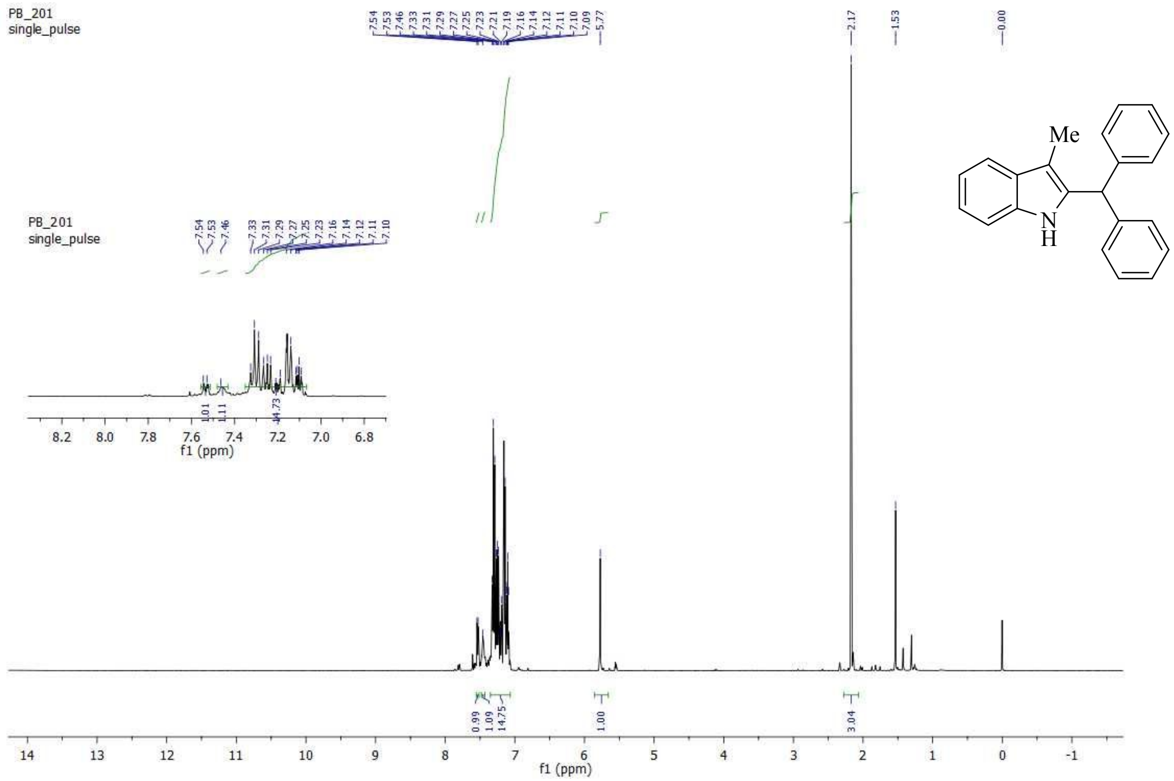


**Figure S27.** 400 MHz $^1H$ NMR spectrum of **3n**[8] in $CDCl_3$

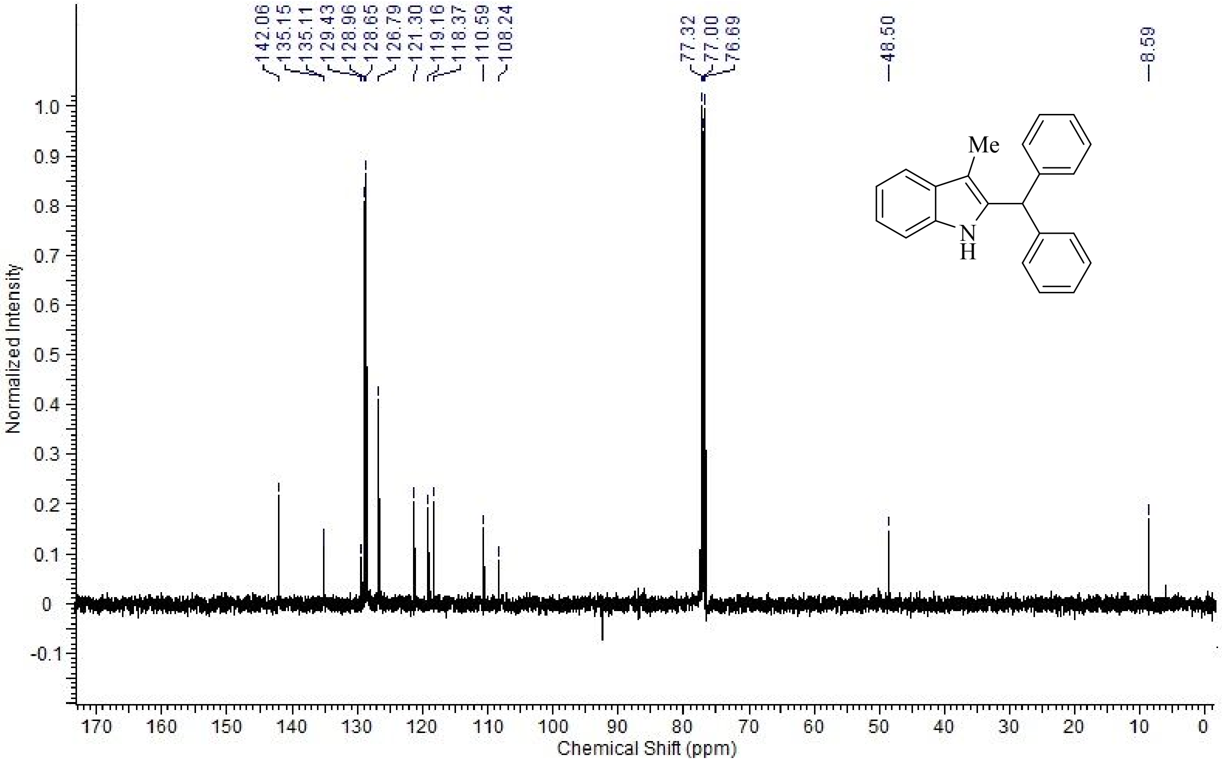


**Figure S28.** 100 MHz $^{13}C\{^1H\}$ NMR spectrum of **3n** in $CDCl_3$

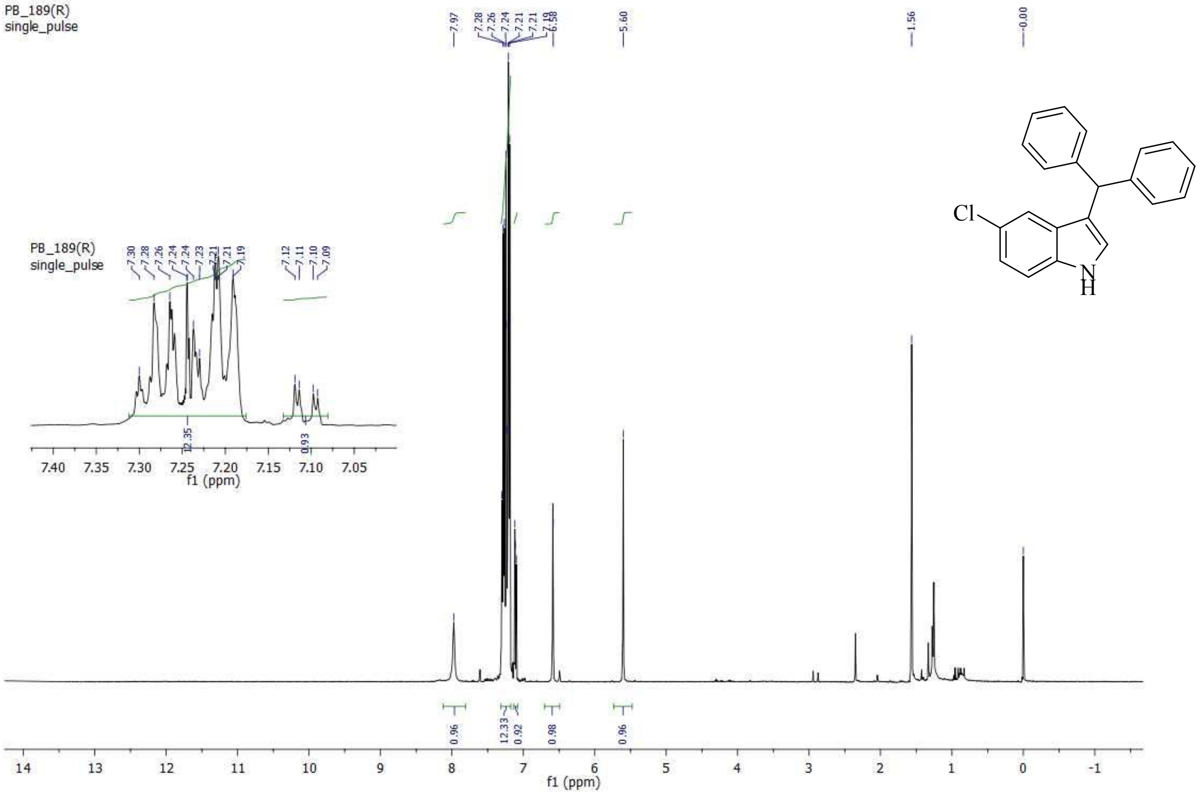


**Figure S29.** 400 MHz $^1H$ NMR spectrum of **3o** in $CDCl_3$

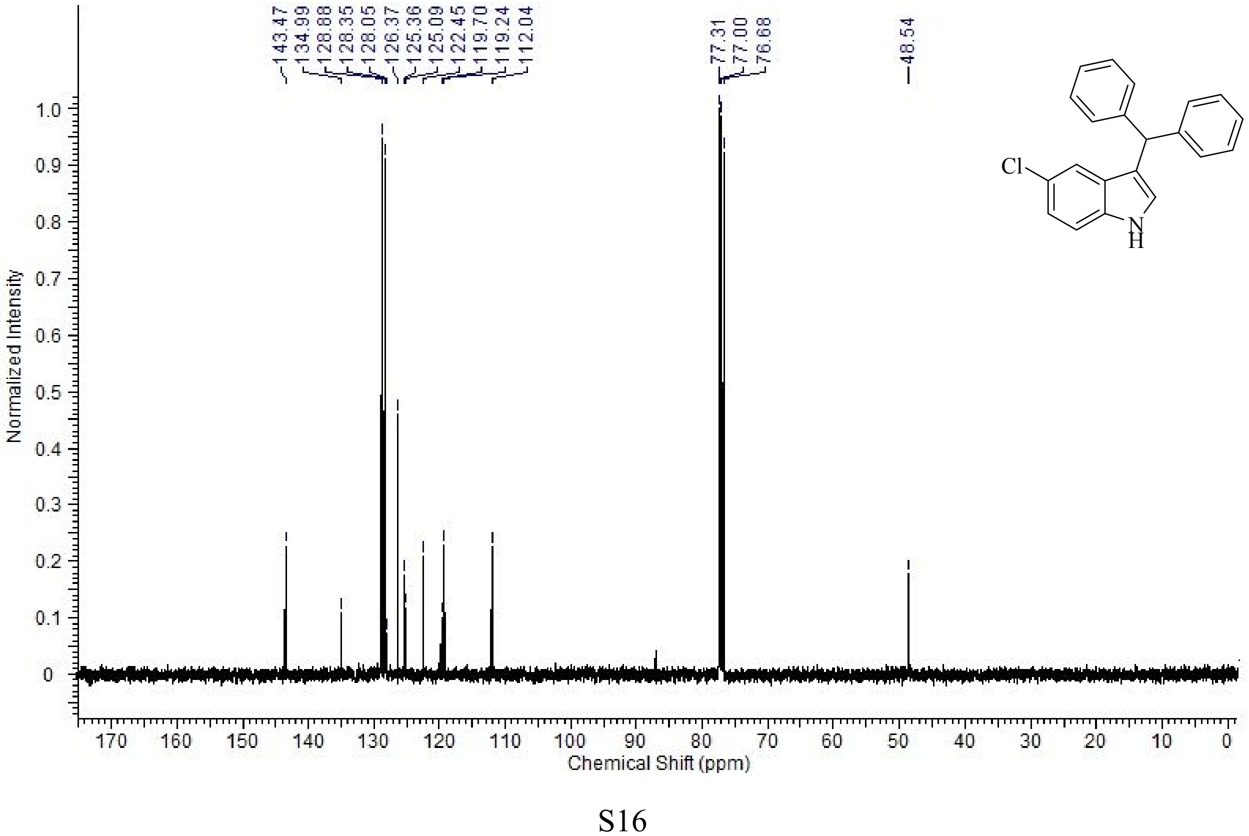


**Figure S30.** 100 MHz $^{13}C\{^1H\}$ NMR spectrum of **3o** in $CDCl_3$

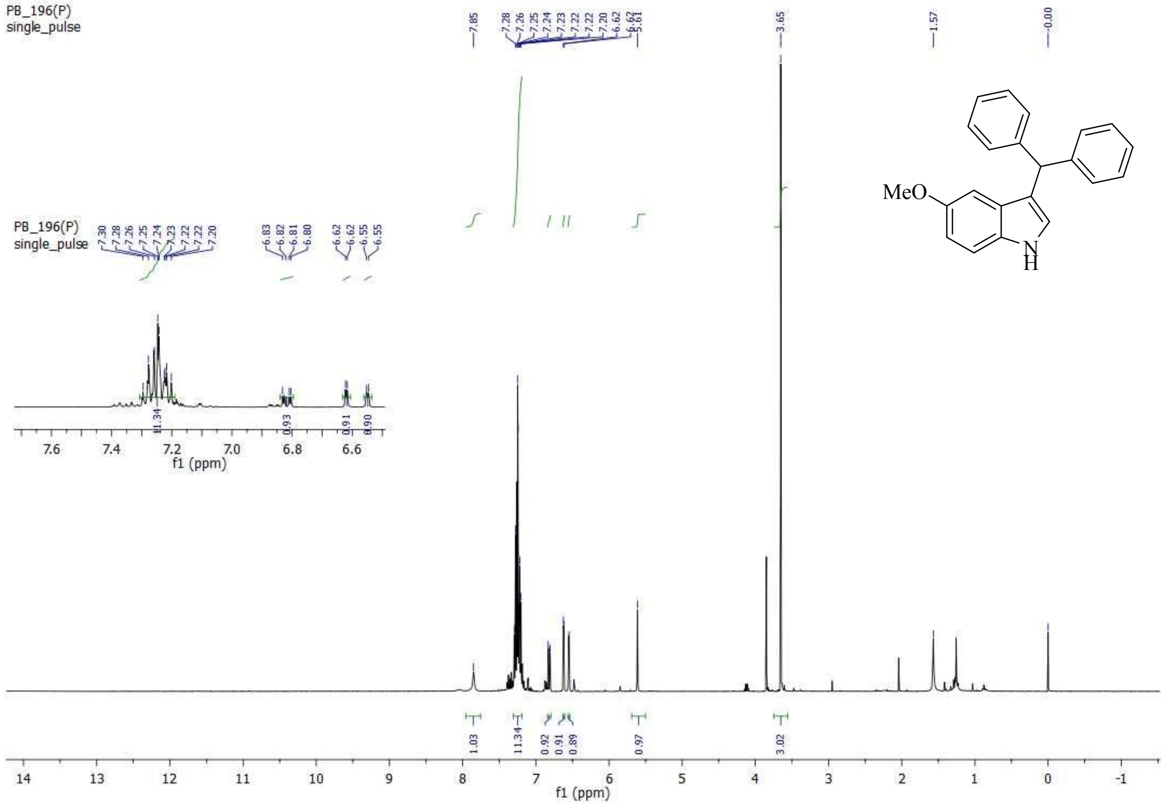


**Figure S31.** 400 MHz $^1H$ NMR spectrum of **3p** in $CDCl_3$

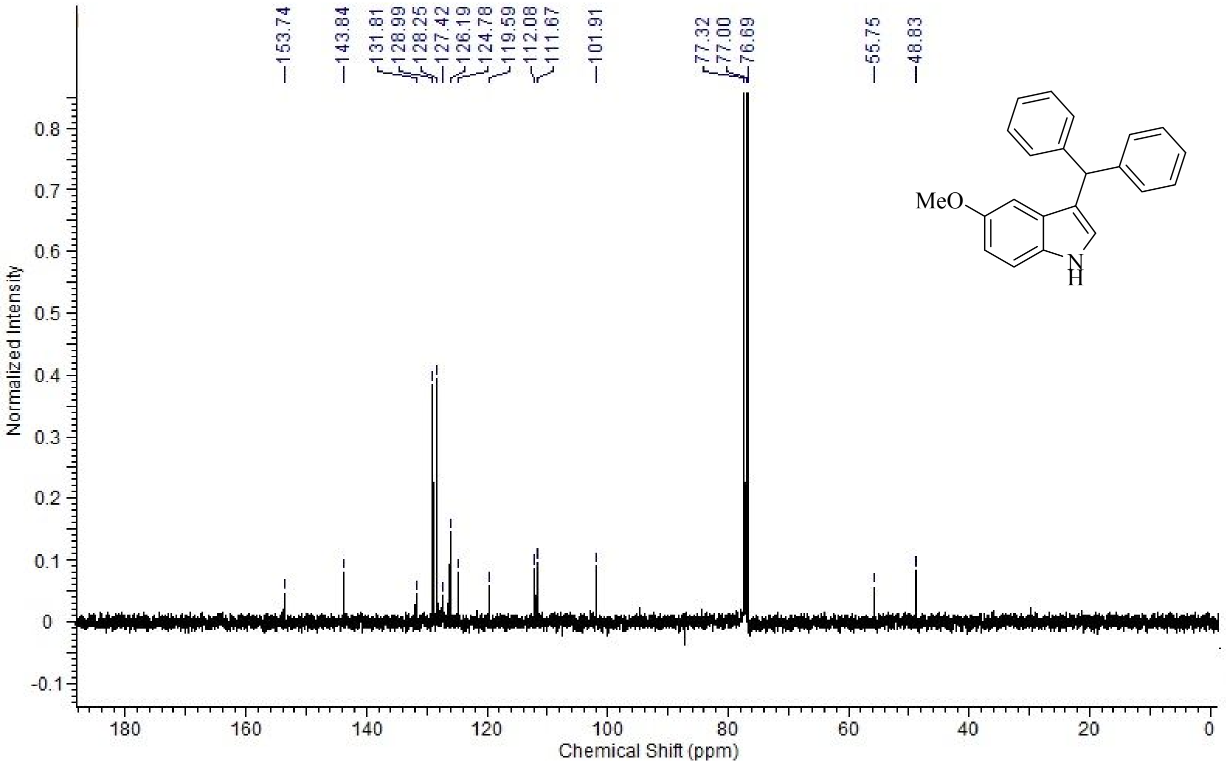


**Figure S32.** 100 MHz $^{13}C\{^1H\}$ NMR spectrum of **3p** in $CDCl_3$

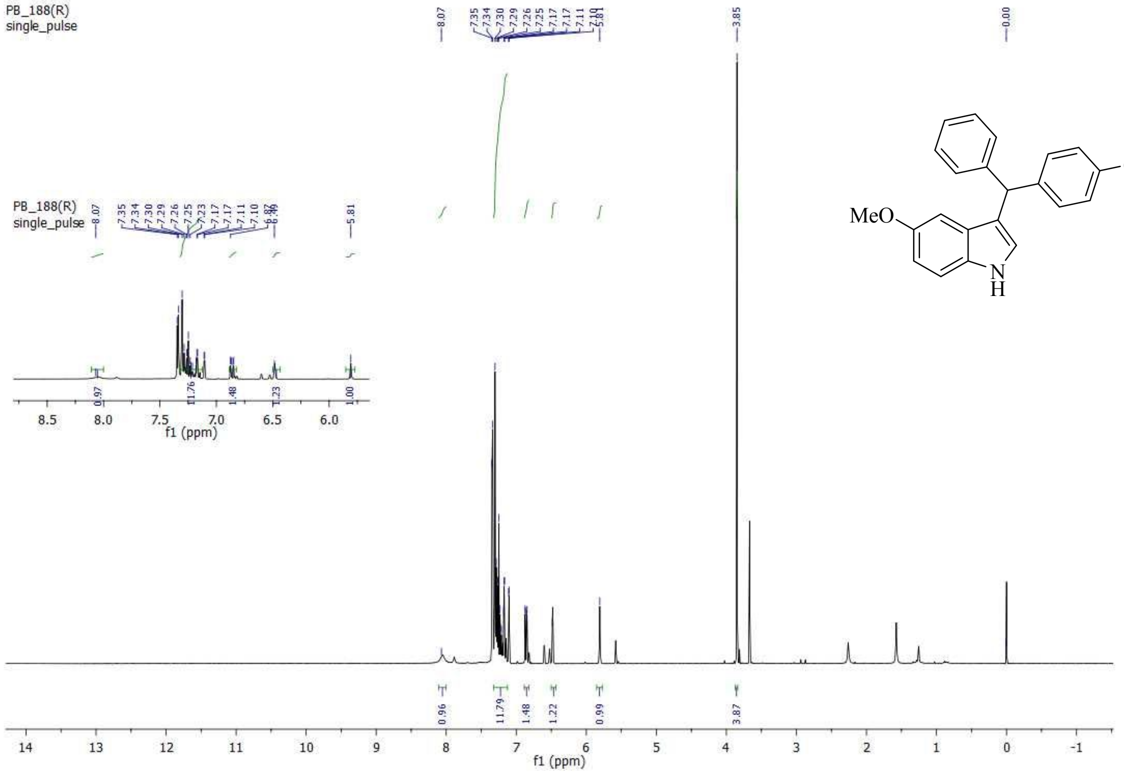


**Figure S33.** 400 MHz $^1H$ NMR spectrum of **3q** in $CDCl_3$

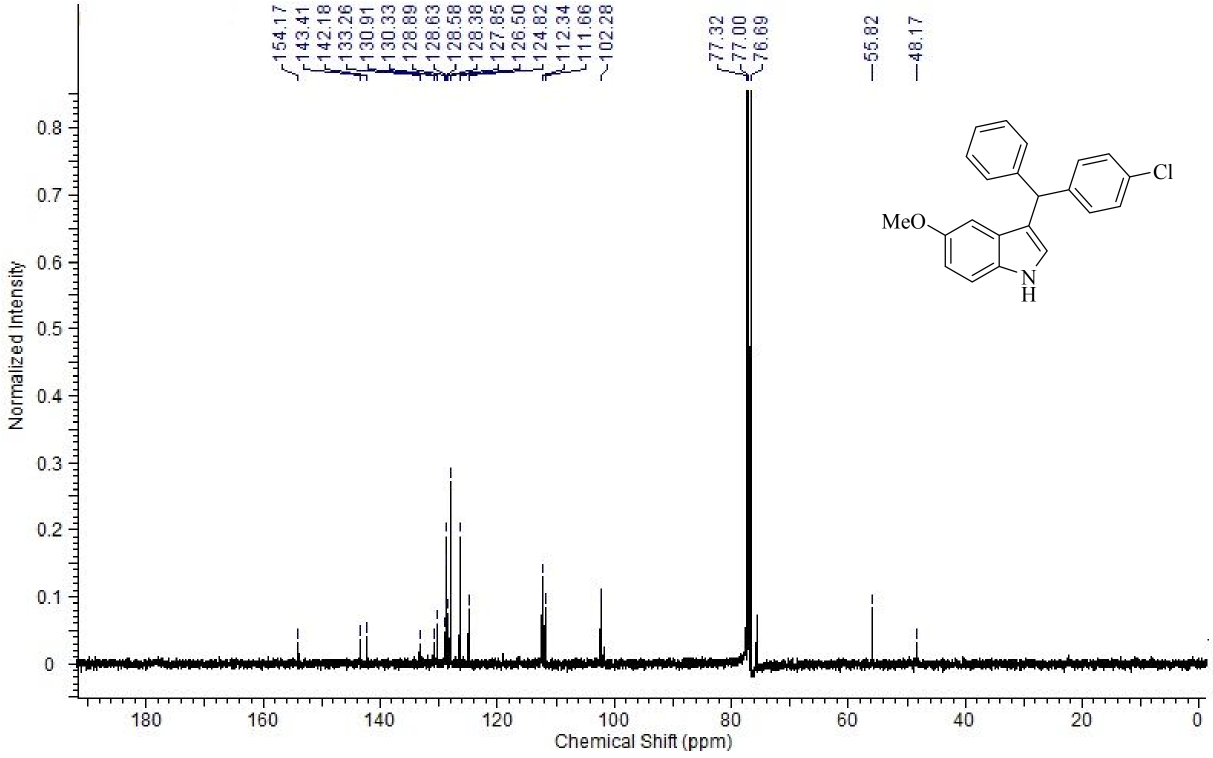


**Figure S34.** 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **3q** in $CDCl_3$

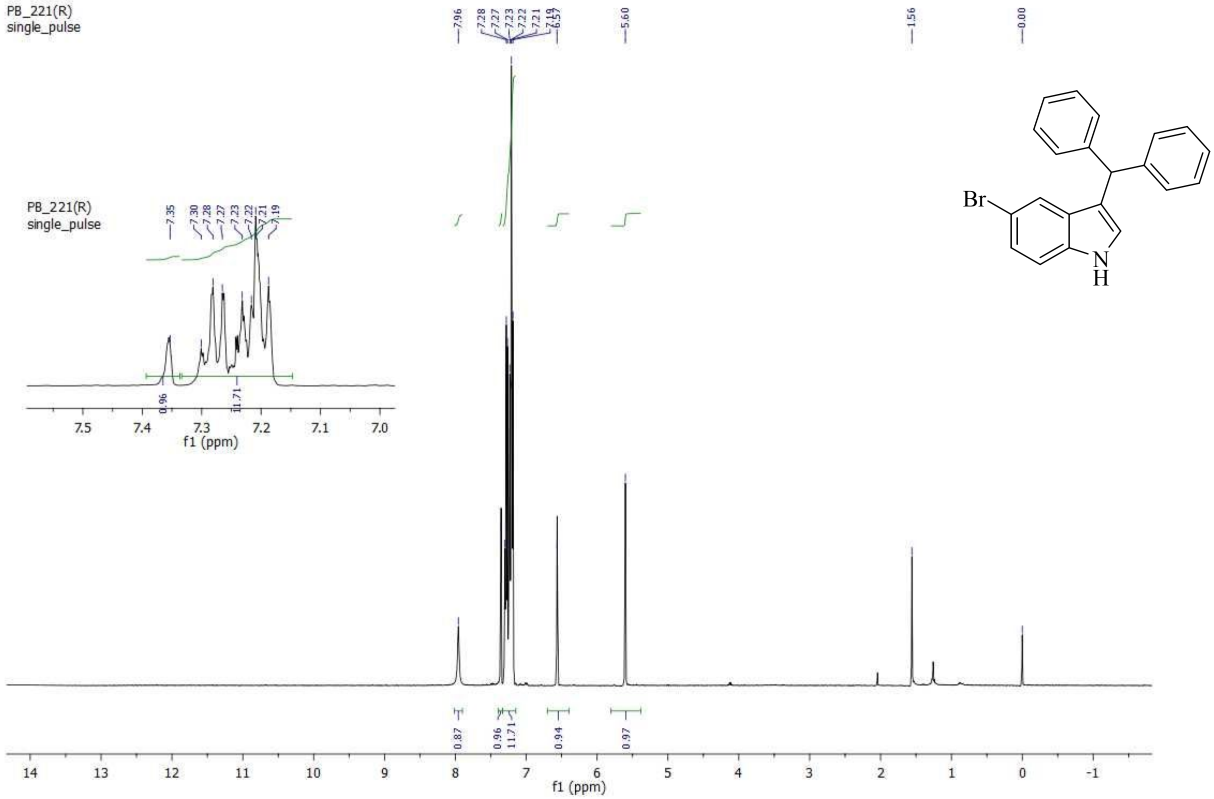


**Figure S35.** 400 MHz $^{1}H$ NMR spectrum of **3r**[7] in $CDCl_3$

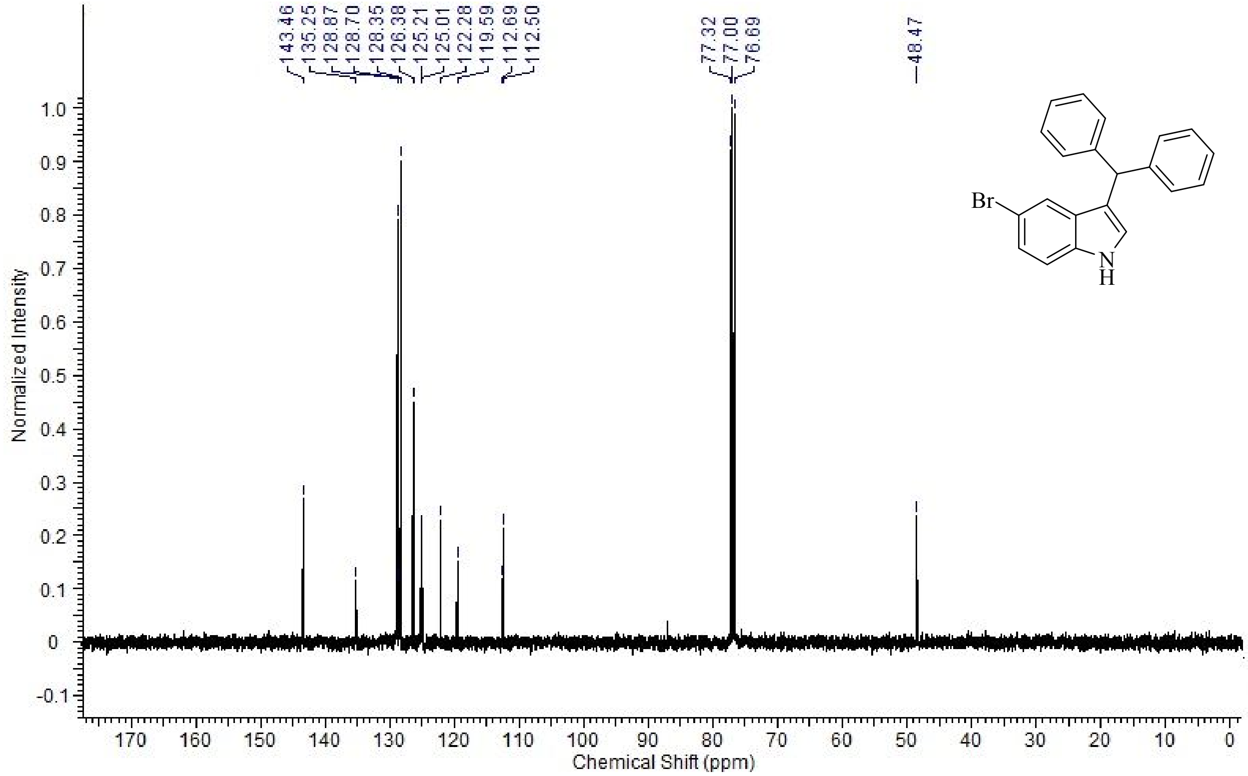


**Figure S36.** 100 MHz $^{13}C\{^1H\}$ NMR spectrum of **3r** in $CDCl_3$

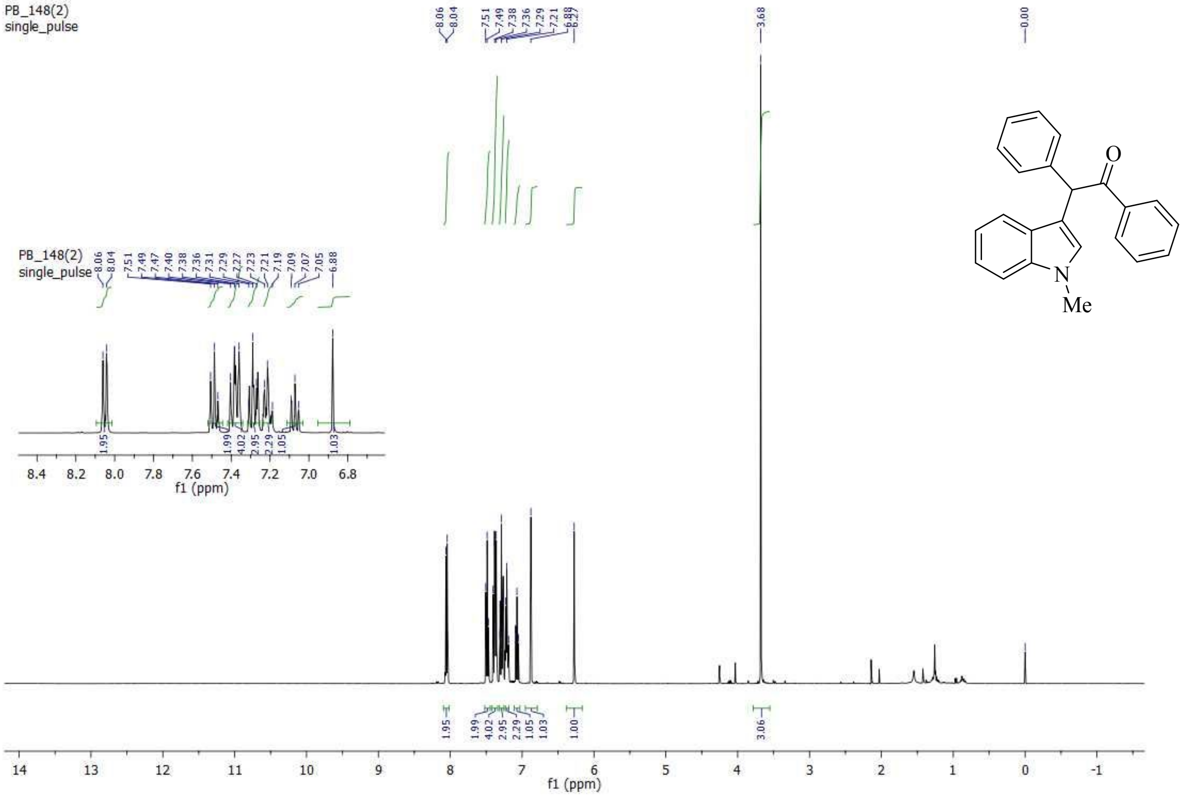


**Figure S37.** 400 MHz $^1H$ NMR spectrum of **3s**[9] in $CDCl_3$

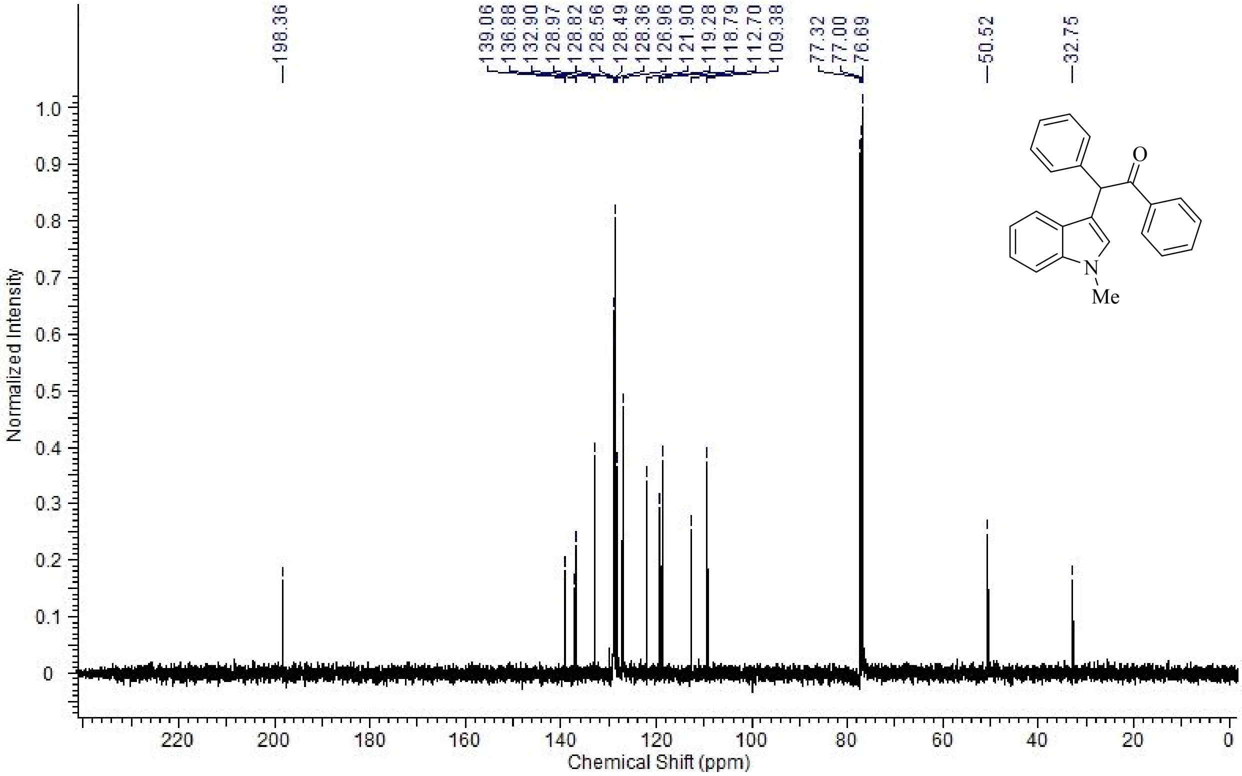


**Figure S38.** 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **3s** in $CDCl_3$

## 2. Copies of HRMS spectra

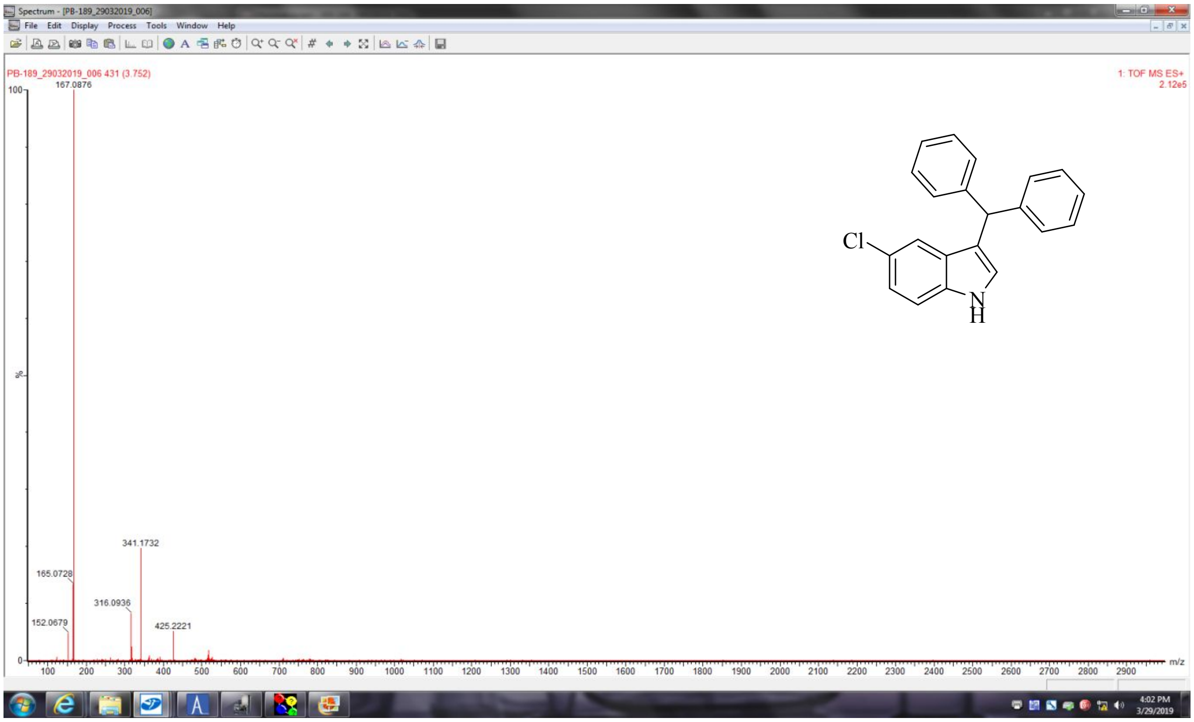
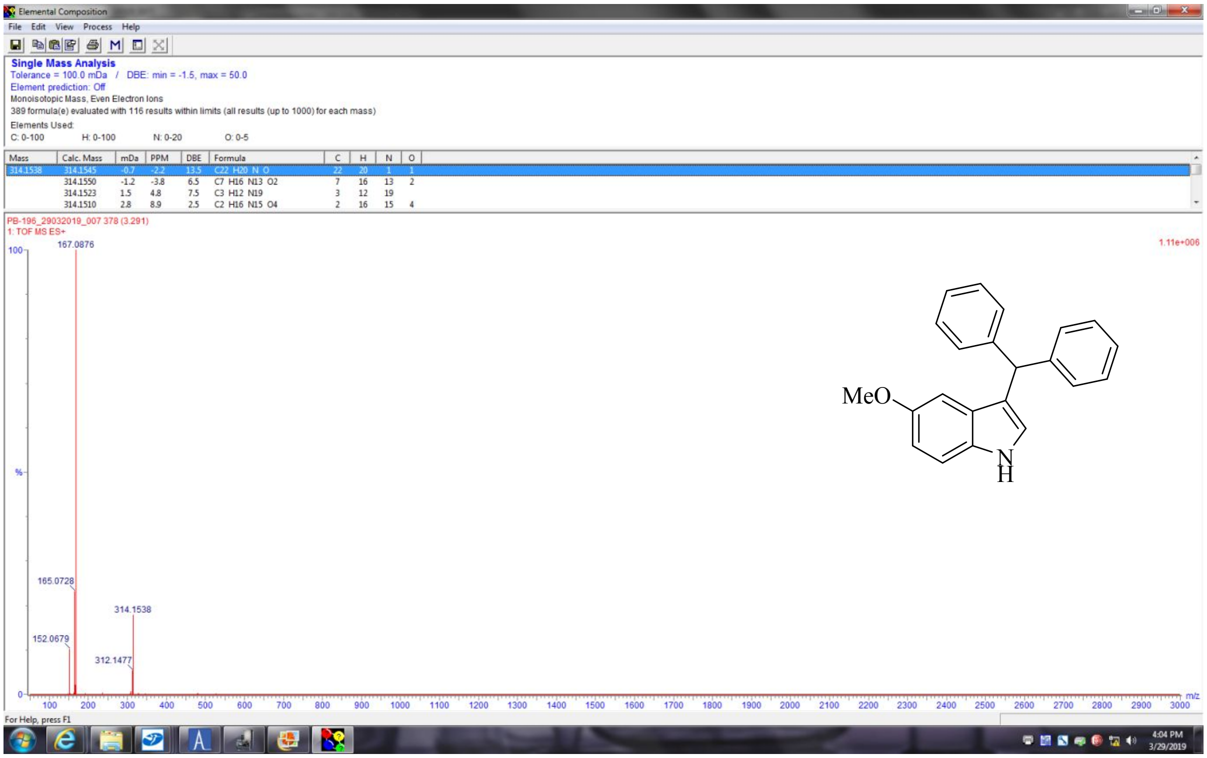


**Figure S39.** HRMS spectrum of **3o**



**Single Mass Analysis**
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Even Electron Ions
389 formula(e) evaluated with 116 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-20 O: 0-5

| Mass | Calc. Mass | mDa | PPM | DBE | Formula | C | H | N | O |
|---|---|---|---|---|---|---|---|---|---|
| 314.1538 | 314.1545 | -0.7 | -2.2 | 13.5 | C22 H20 N O | 22 | 20 | 1 | 1 |
|  | 314.1550 | -1.2 | -3.8 | 6.5 | C7 H16 N13 O2 | 7 | 16 | 13 | 2 |
|  | 314.1523 | 1.5 | 4.8 | 7.5 | C3 H12 N19 | 3 | 12 | 19 |  |
|  | 314.1510 | 2.8 | 8.9 | 2.5 | C2 H16 N15 O4 | 2 | 16 | 15 | 4 |

**Figure S40.** HRMS spectrum of **3p**

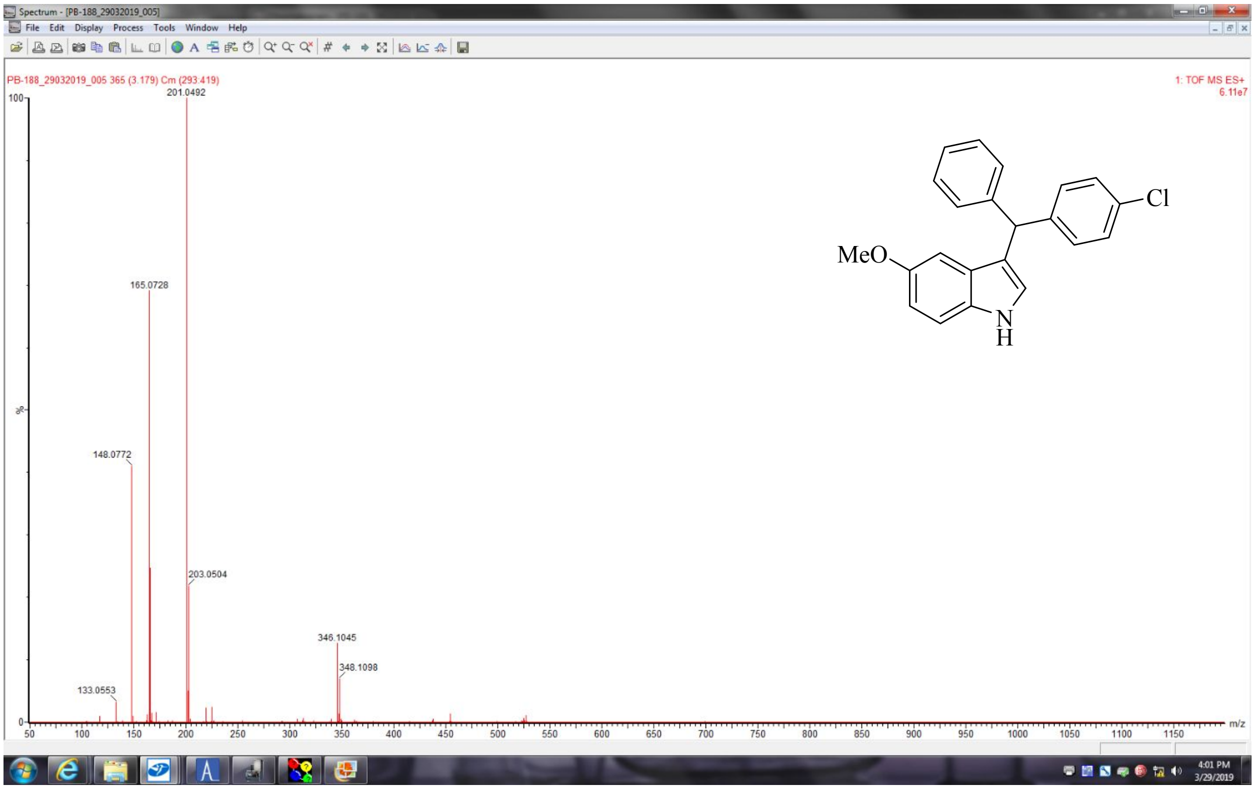


**Figure S41.** HRMS spectrum of **3q**

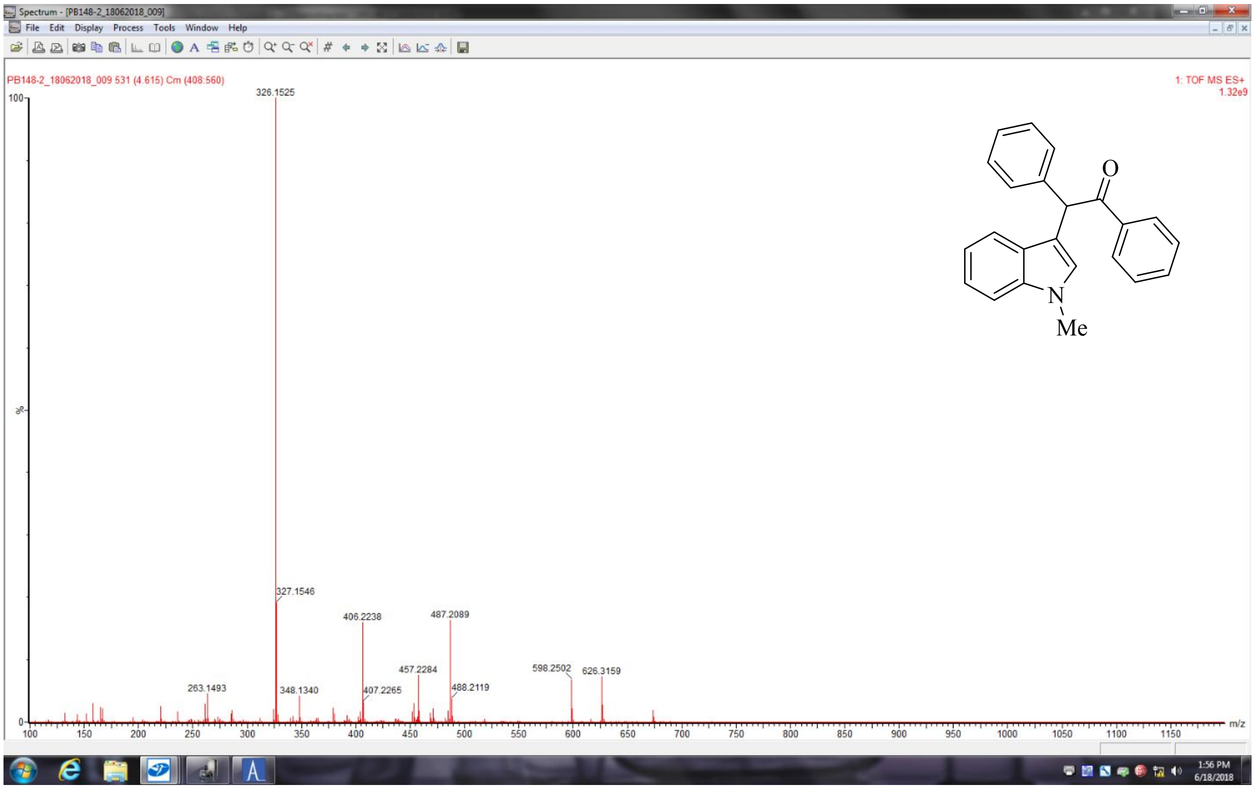


**Figure S42.** HRMS spectrum of **3s**

## 3. Single crystal XRD data

### 3a (CCDC 1893717)

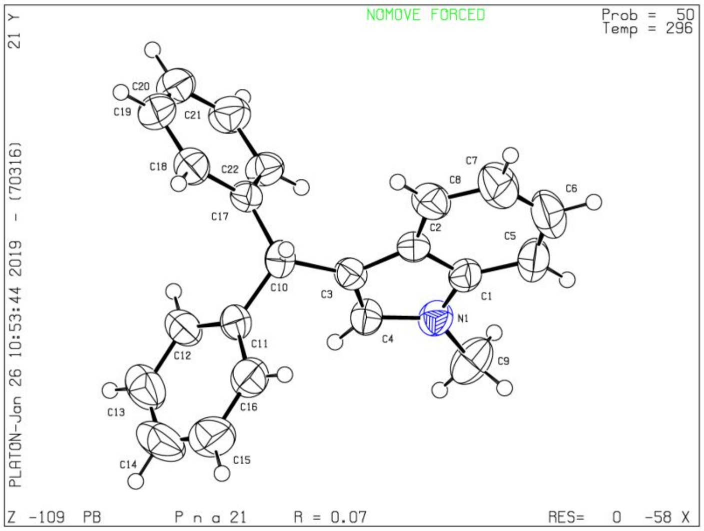


**Figure S43.** ORTEP diagram of **3a** with 50% probability ellipsoids

**Table S1.** Crystallographic parameters of structures **3a**

| **Crystal data** | **3a** |
|---|---|
| Formula unit | $C_{22}H_{19}N$ |
| Formula weight (gmol$^{-1}$) | 297.38 |
| Crystal system | orthorhombic |
| T [K] | 296 |
| *a* [Å] | 7.854(4) |
| *b* [Å] | 22.091(12) |
| *c* [Å] | 9.597(5) |
| *α* [°] | 90 |
| *β* [°] | 90 |
| *γ* [°] | 90 |
| Volume [Å$^3$] | 1665.0(15) |
| Space group | $Pna2_1$ |
| Z | 4 |
| $D_{cal}$ [g/cm$^3$] | 1.186 |
| $R_1$, *w*R2 | 0.0678, 0.1224 |
| Instrument | Bruker CCD Apex II |
| CCDC No | CCDC 1893717 |

**Single crystal X-ray diffraction**. Single crystal X-ray diffractions were collected on a Bruker SMART APEX-II CCD diffractometer using Mo Kα (λ =0.71073 Å) radiation. Bruker SAINT software has been employed for reducing the data and SADABS for correcting the intensities of absorption. Structure was solved and refined using SHELXL with anisotropic displacement parameters for non-H atoms. In the crystal structure H-atoms are located experimentally, whereas C–H atoms were fixed geometrically using the HFIX command in SHELX-TL. No any missed symmetry observed in the final check of CIF file using PLATON. Information of crystallographic parameters for all structures is furnished in **Table S1**.

## 4. References

(1) Hikawa, H.; Suzuki, H.; Azumaya, I. Au(III)/TPPMS-catalyzed benzylation of indoles with benzylic alcohols in water. *J. Org. Chem.* **2013**, *78*, 12128−12135.

(2) Di Gregorio, G.; Mari, M.; Bartoccini, F.; Piersanti, G. Iron-Catalyzed Direct C3-Benzylation of Indoles with Benzyl Alcohols through Borrowing Hydrogen. *J. Org. Chem.* **2017**, *82*, 8769−8775.

(3) Arulananda, B.; Baba, A.; Kono, T.; Sakamoto, T.; Tsukahara, Y.; Wada, Y.; Yamauchi, T.; Yasuda, M. Microwave-assisted preparation of indole derivatives. Jpn. Kokai Tokkyo Koho JP2009215223A, 2009.

(4) Kim, J.; Pannilawithana, N.; Yi, C. S. Catalytic Tandem and One-Pot Dehydrogenation–Alkylation and− Insertion Reactions of Saturated Hydrocarbons with Alcohols and Alkenes. *ACS Catal.* **2016**, *6*, 8395-8398.

(5) Kong, C.; Jana, N.; Jones, C.; Driver, T. G. Control of the Chemoselectivity of Metal N-Aryl Nitrene Reactivity: C–H Bond Amination versus Electrocyclization. *J. Am. Chem. Soc.* **2016**, *138*, 13271-13280.

(6) Jana, U.; Maiti, S.; Biswas, S. An $FeCl_3$-catalyzed highly C3-selective Friedel–Crafts alkylation of indoles with alcohols. *Tetrahedron Lett.* **2007**, *48*, 7160–7163.

(7) Das, D.; Roy, S. Palladium (II)-Catalyzed Efficient C-3 Functionalization of Indoles with Benzylic and Allylic Alcohols under Co-Catalyst, Acid, Base, Additive and External Ligand-Free Conditions. *Adv. Synth. Catal.* **2013**, *355*, 1308-1314.

(8) Li, H.; Li, W.; Liu, W.; He, Z.; Li, Z. An Efficient and General Iron-Catalyzed C-C Bond Activation with 1, 3-Dicarbonyl Units as a Leaving Group. *Angew. Chem.* **2011**, *50*, 2975-2978.

(9) Liang, D.; Li, X.; Li, Y.; Yang, Y.; Gao, S.; Cheng, P. $Br_2$-Catalyzed regioselective dehydrative coupling of indoles with acyloins: direct synthesis of α-(3-indolyl) ketones. *RSC Adv.* **2016**, *6*, 29020–29025.