

Supporting Information

**Synthesis of C3-functionalized indole derivatives *via* Brønsted acid-catalyzed regioselective arylation of 2-indolylmethanols with guaiazulene**

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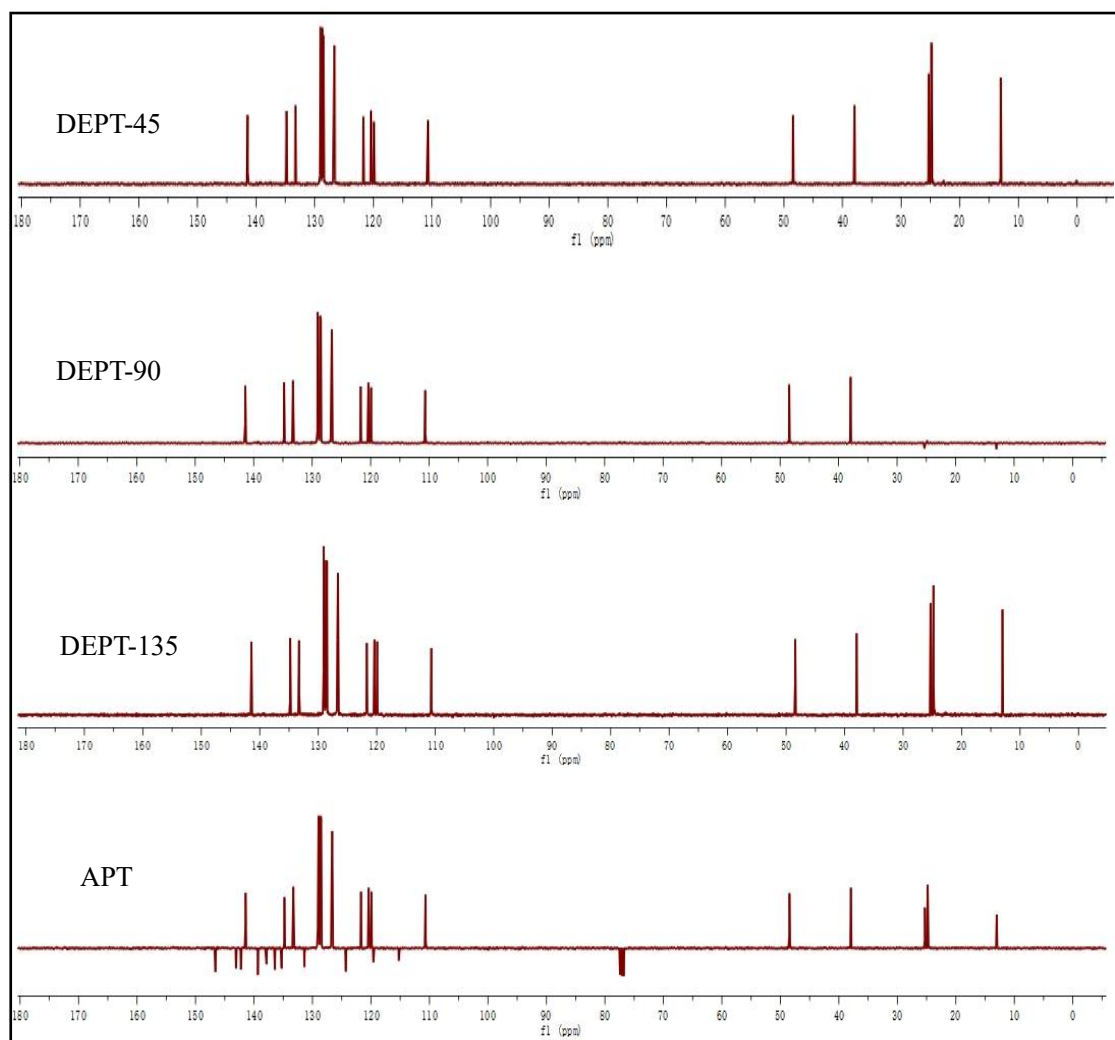
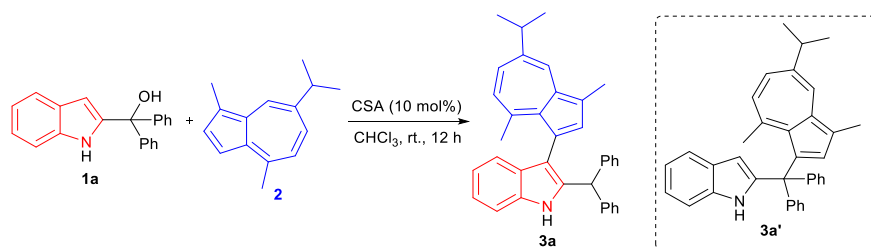
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**The APT (attached proton test) spectrum and DEPT (distortionless enhancement by polarization transfer) spectra of 3a**

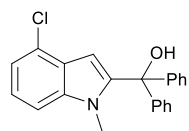
The reaction of 2-indolylmethanol **1a** and guaiazulene **2** may lead to two products, which are C3-functionalized indole **3a** or/and benzylic site functionalized indole **3a'**. The APT spectrum and DEPT spectra of product were performed to ensure this product is C3-functionalized indole derivative **3a** rather than the benzylic substituted product **3a'**.



**Fig. 1** APT spectrum and DEPT spectra of **3a**

## The spectra data of new substrates 1

### (4-chloro-1-methyl-1*H*-indol-2-yl)diphenylmethanol (1s)



Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (95:5-80:20). White solid, m.p. 115-116 °C.

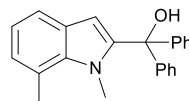
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35-7.26 (m, 10H, ArH), 7.16-7.05 (m, 3H, ArH), 5.96 (s, 1H, ArH), 3.49 (s, 3H,  $\text{CH}_3$ ), 3.06 (s, 1H, OH).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.9, 144.3, 139.6, 128.3, 127.9, 127.2, 126.2, 125.1, 122.8, 119.4, 108.0, 103.5, 79.1, 32.5.

HRMS-ESI:  $m/z$  calcd for  $\text{C}_{22}\text{H}_{19}\text{ClNO}^+$  ( $[\text{M}+\text{H}]^+$ ) 348.1155; found 348.1148.

IR (KBr): 3543, 3059, 3026, 2939, 1608, 1565, 1491, 1452, 1339, 1278, 1197, 1120, 1032, 1002, 921, 797, 767, 734, 700, 633  $\text{cm}^{-1}$ .

### (1,7-dimethyl-1*H*-indol-2-yl)diphenylmethanol (1t)



Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (95:5-80:20). White solid, m.p. 131-133 °C.

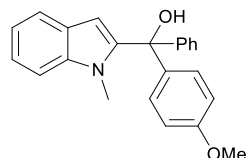
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35-7.28 (m, 11H, ArH), 6.94-6.90 (m, 2H, ArH), 5.78 (s, 1H, ArH), 3.82 (s, 3H,  $\text{NCH}_3$ ), 3.04 (s, 1H, OH), 2.73 (s, 1H,  $\text{CH}_3$ ).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.5, 143.6, 137.8, 128.2, 127.7, 127.2, 125.6, 121.5, 119.8, 119.2, 106.1, 79.2, 35.5, 20.8.

HRMS-ESI:  $m/z$  calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}^+$  ( $[\text{M}+\text{H}]^+$ ) 328.1702; found 328.1693.

IR (KBr): 3527, 3057, 2960, 2928, 1598, 1490, 1447, 1404, 1374, 1160, 1114, 1001, 905, 801, 760, 745, 700, 686  $\text{cm}^{-1}$ .

### (4-methoxyphenyl)(1-methyl-1*H*-indol-2-yl)(phenyl)methanol (1u)



Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (95:5-80:20). White solid, m.p. 120-122 °C.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47 (d,  $J = 7.8$  Hz, 1H, ArH), 7.34-7.26 (m, 6H, ArH), 7.21-7.17 (m, 3H, ArH), 7.06 (td,  $J = 7.4, 0.8$  Hz, 1H, ArH), 6.83 (dt,  $J = 8.8, 2.6$  Hz, 2H, ArH), 5.84 (s, 1H, ArH), 3.79 (s, 3H,  $\text{OCH}_3$ ), 3.52 (s, 3H,  $\text{NCH}_3$ ), 3.00 (s, 1H, OH).

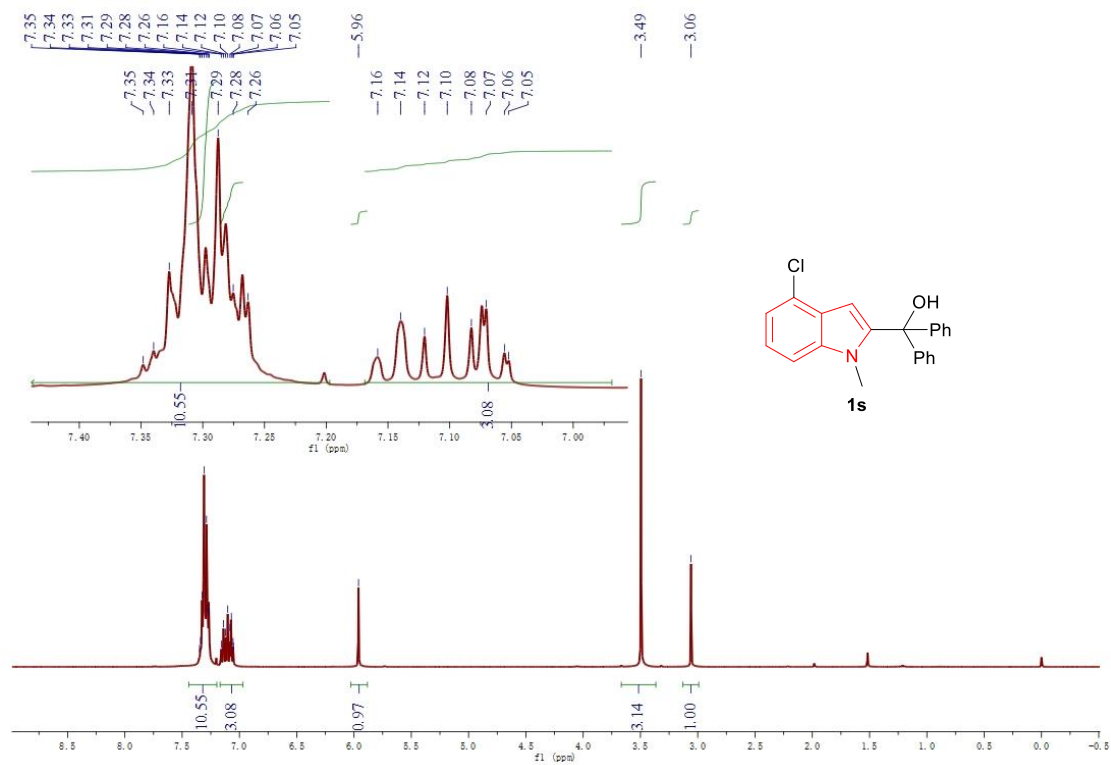
$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.0, 145.5, 143.8, 138.9, 137.7, 128.5, 128.1, 127.6, 127.2, 126.4, 122.2, 120.9, 119.6, 113.4, 109.3, 105.1, 78.9, 55.4, 32.0.

HRMS-ESI:  $m/z$  calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 344.1651; found 344.1643.

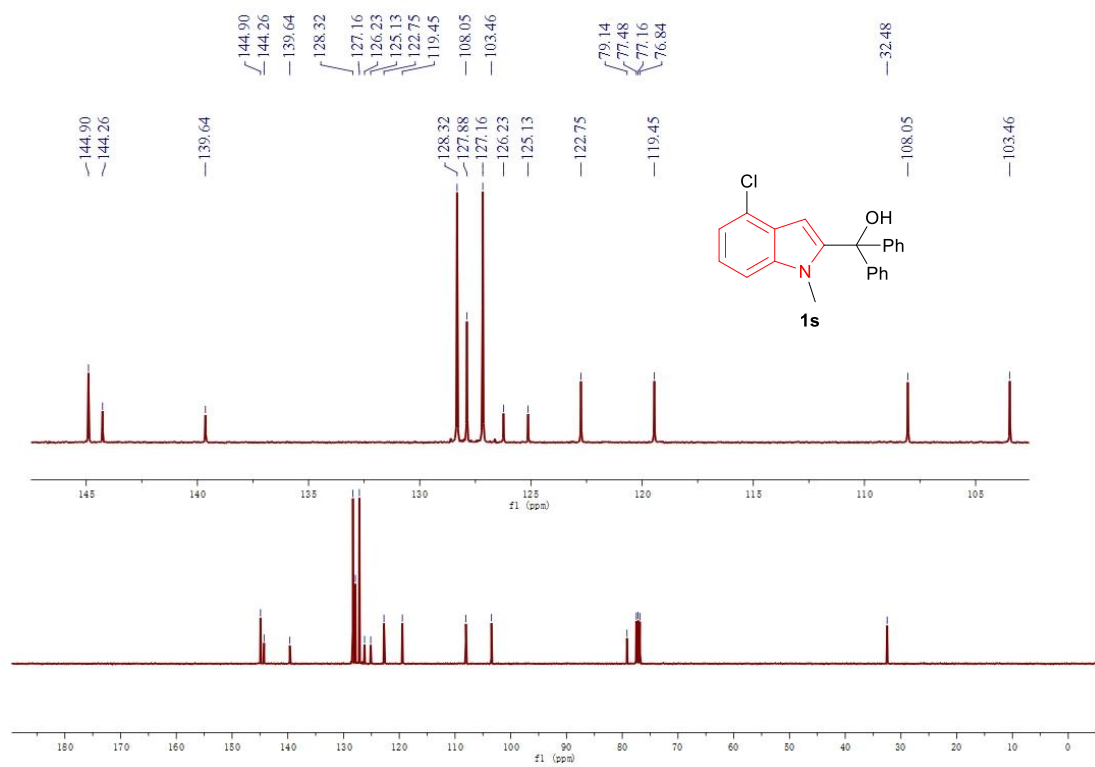
IR (KBr): 3474, 3056, 2933, 2835, 1607, 1467, 1446, 1313, 1179, 1033, 916, 831, 752, 737, 701  $\text{cm}^{-1}$ .

### NMR Spectra of new substrates **1** and products **3**

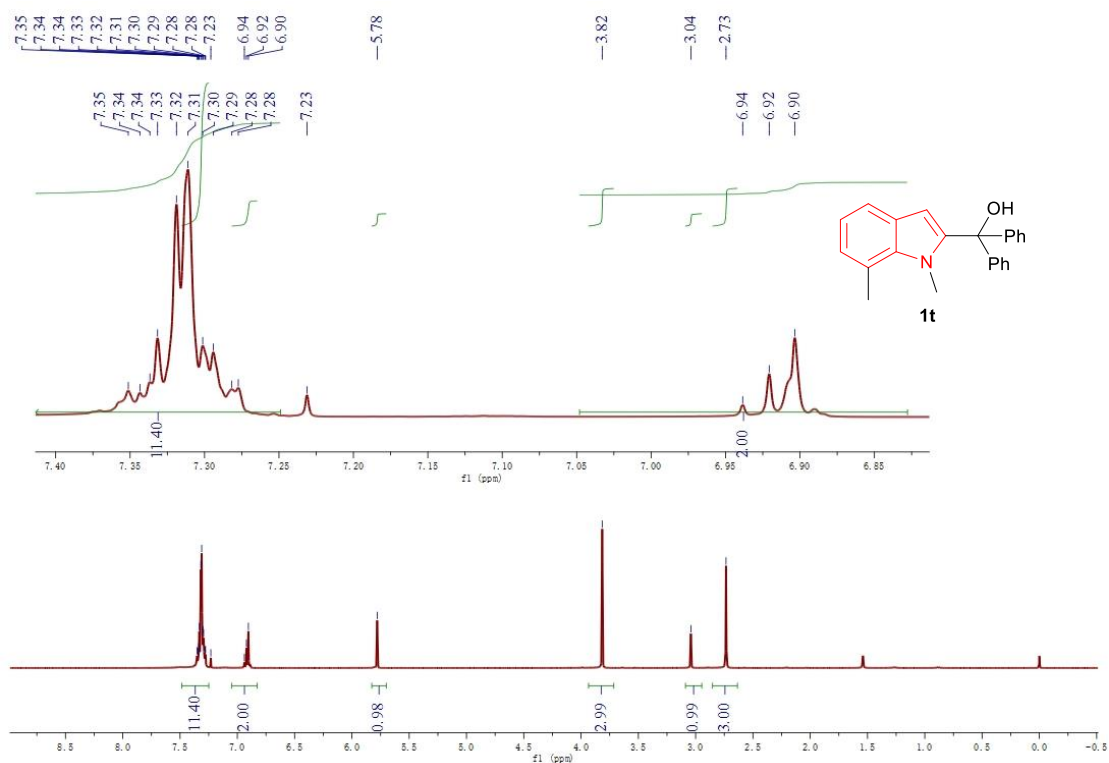
#### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ ) (**1s**)



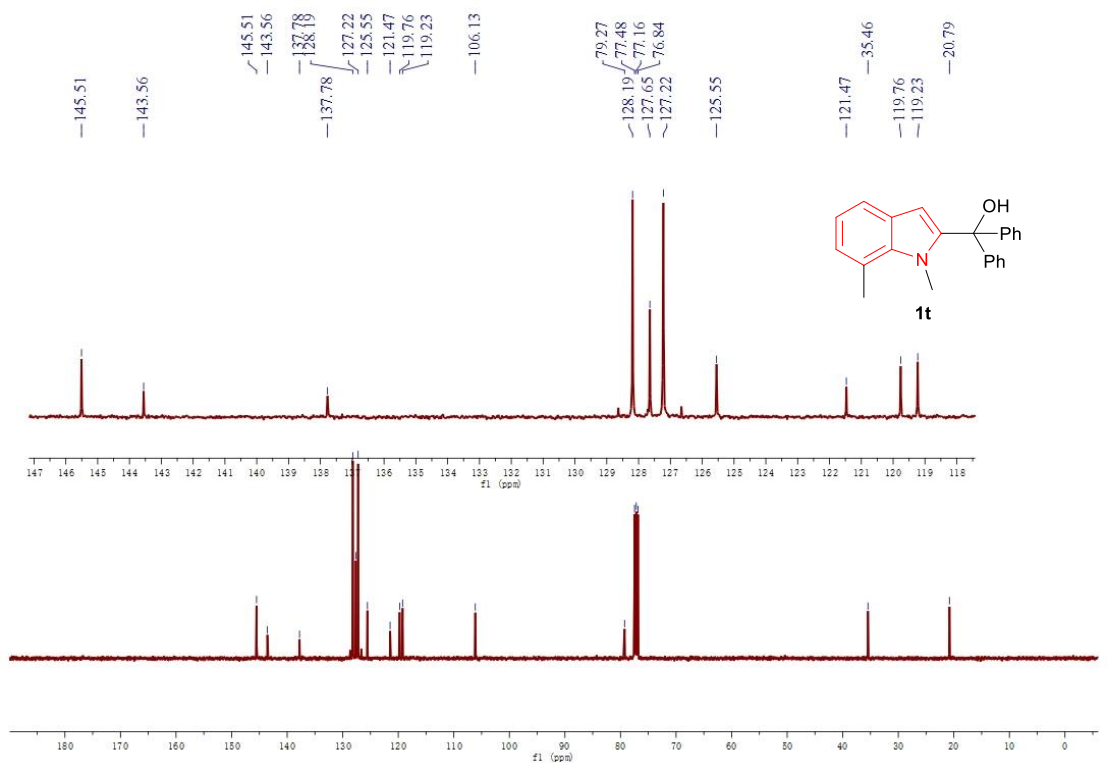
#### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ ) (**1s**)



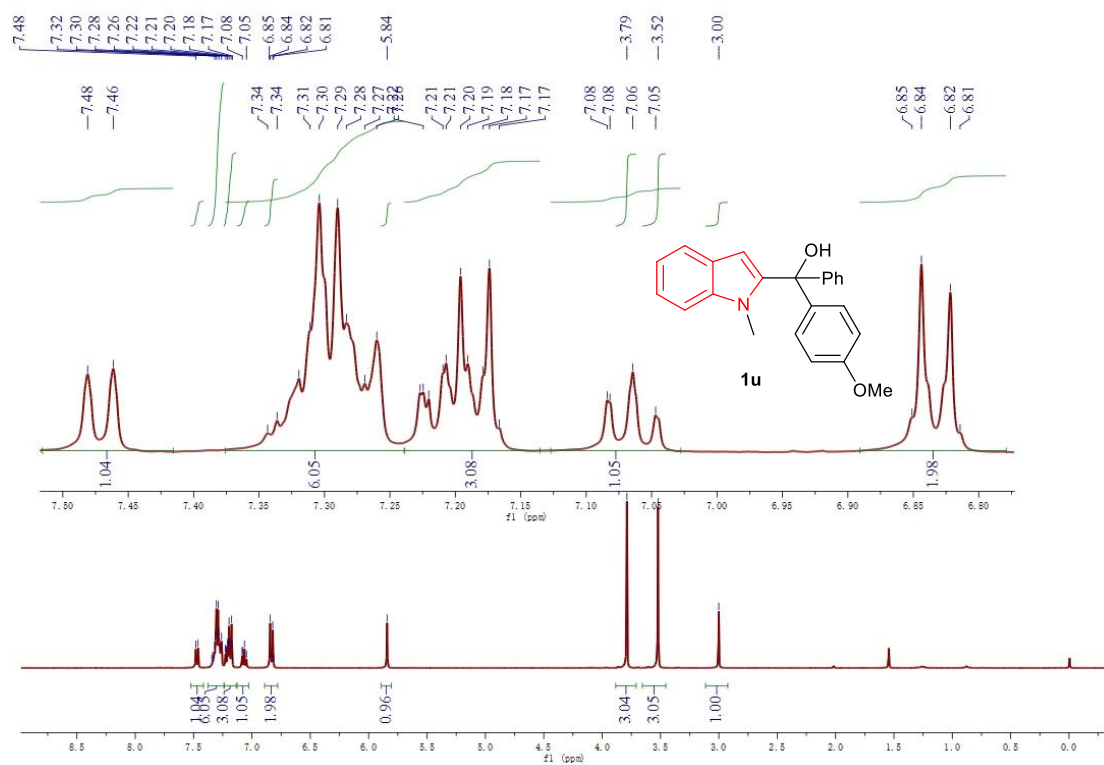
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**1t**)



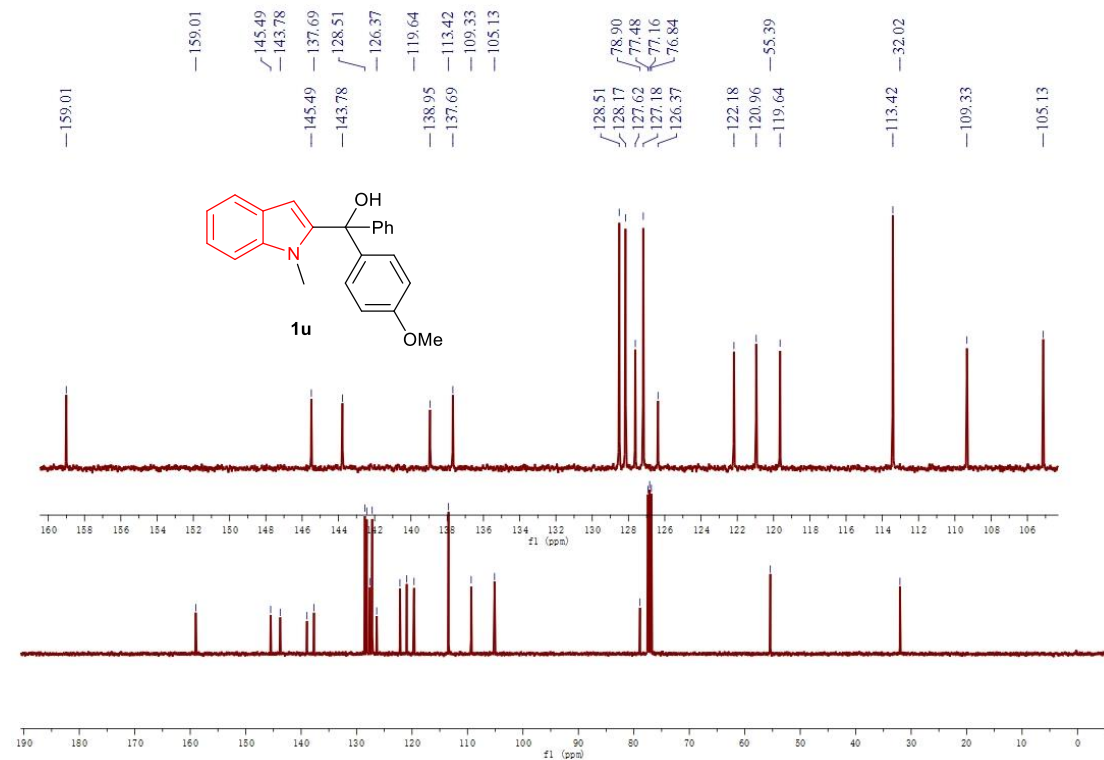
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**1t**)



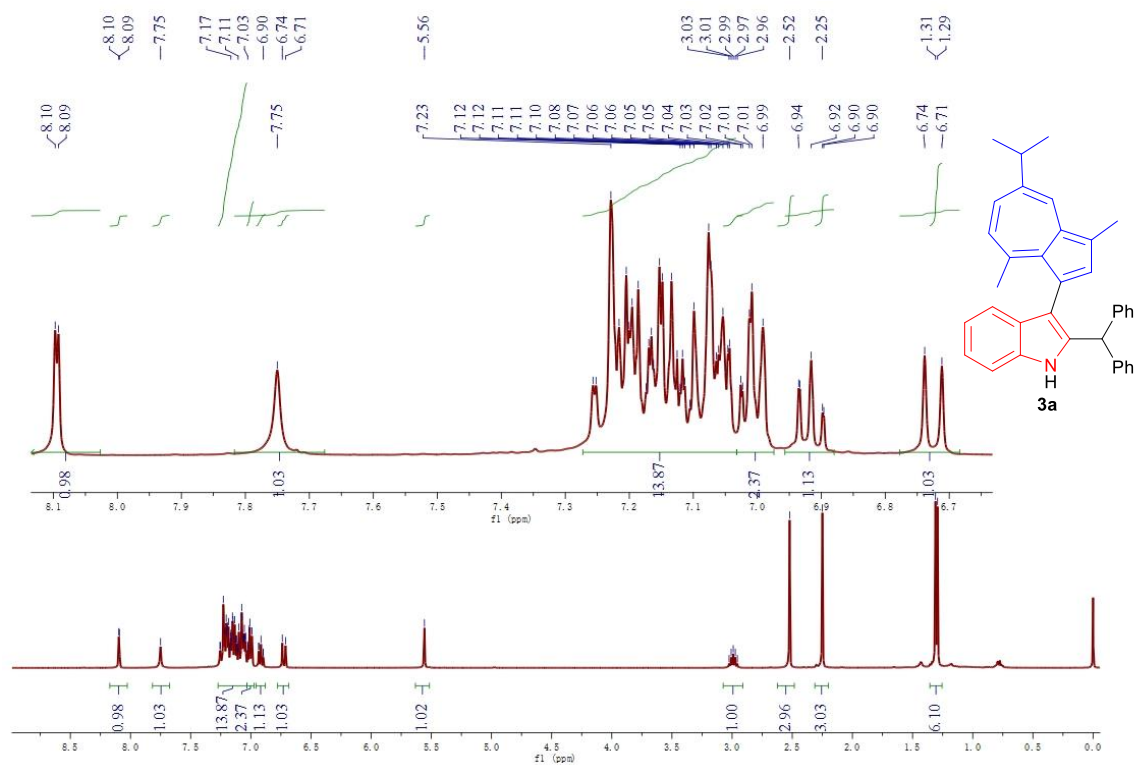
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**1u**)



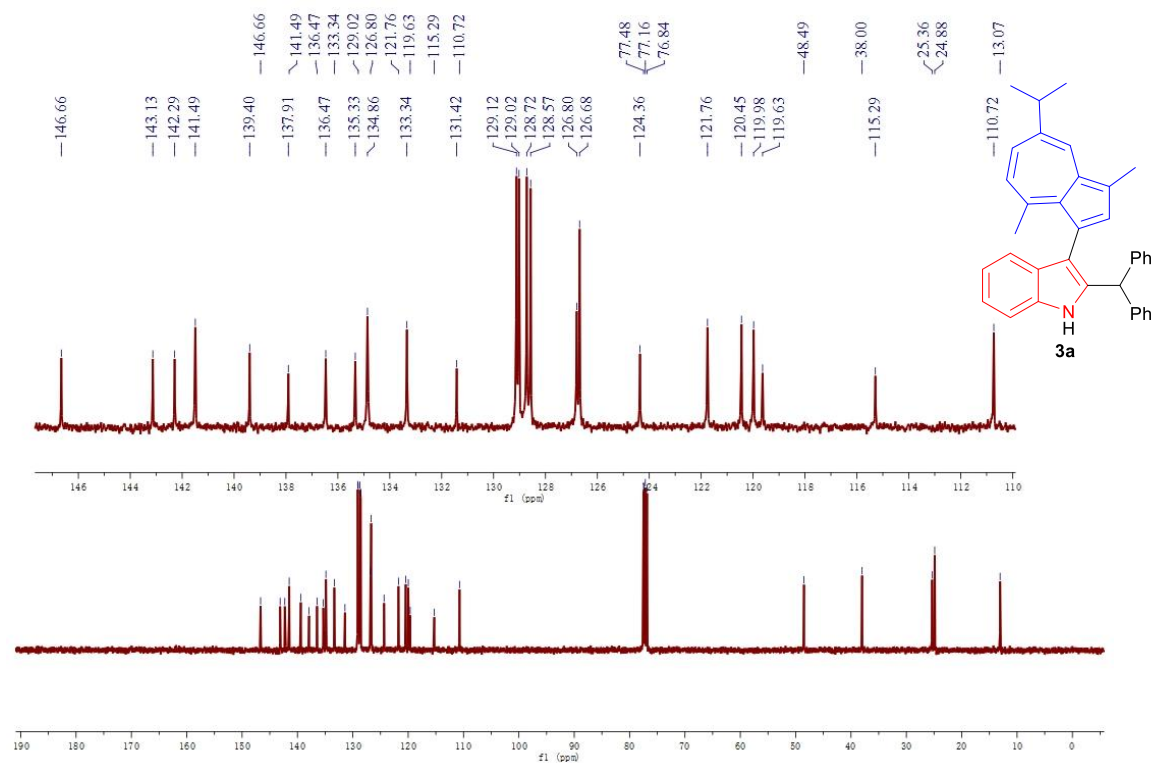
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**1u**)



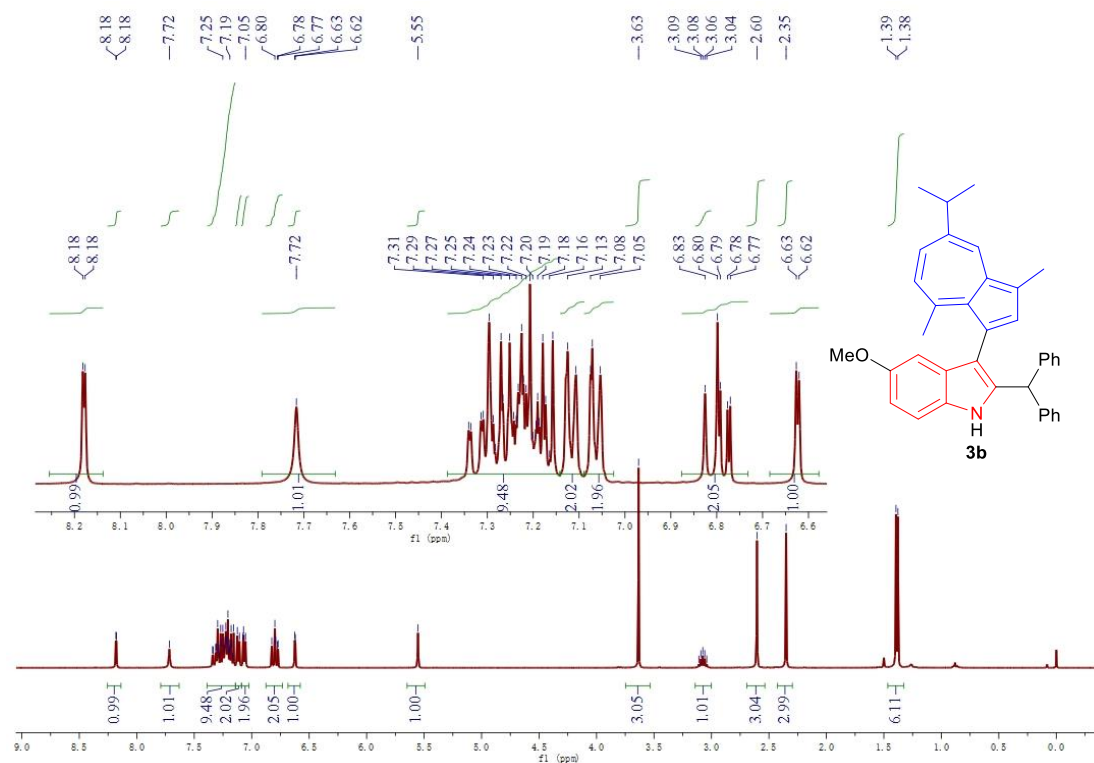
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**3a**)



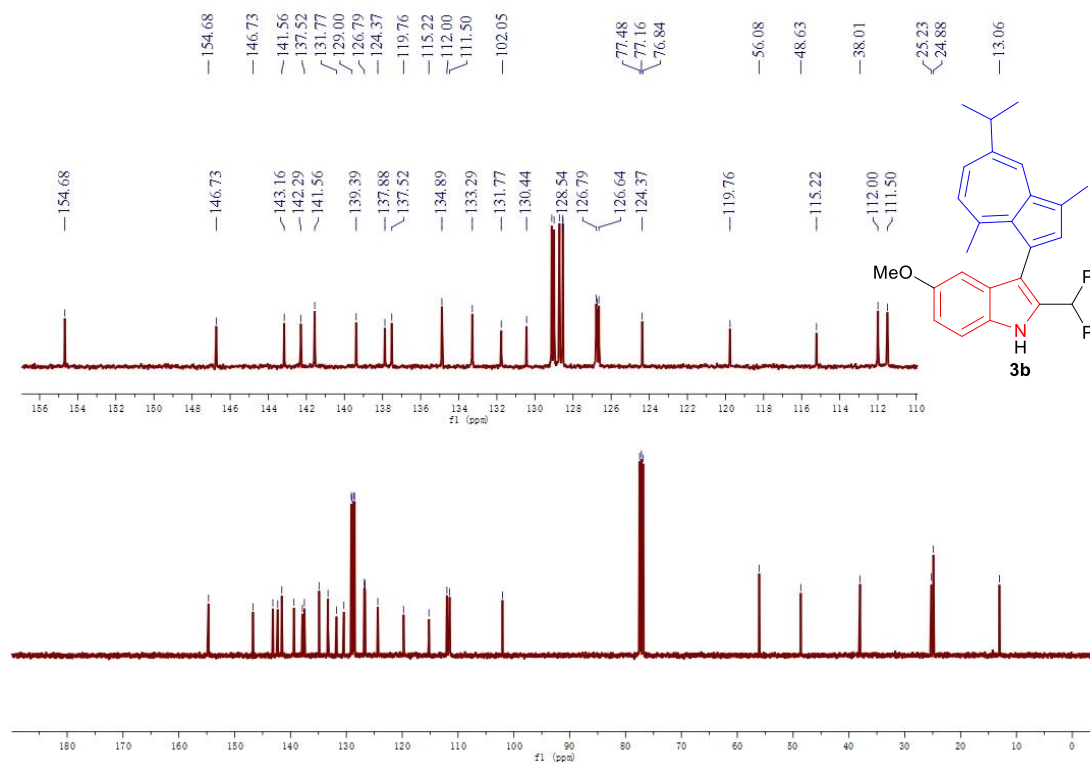
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3a**)



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

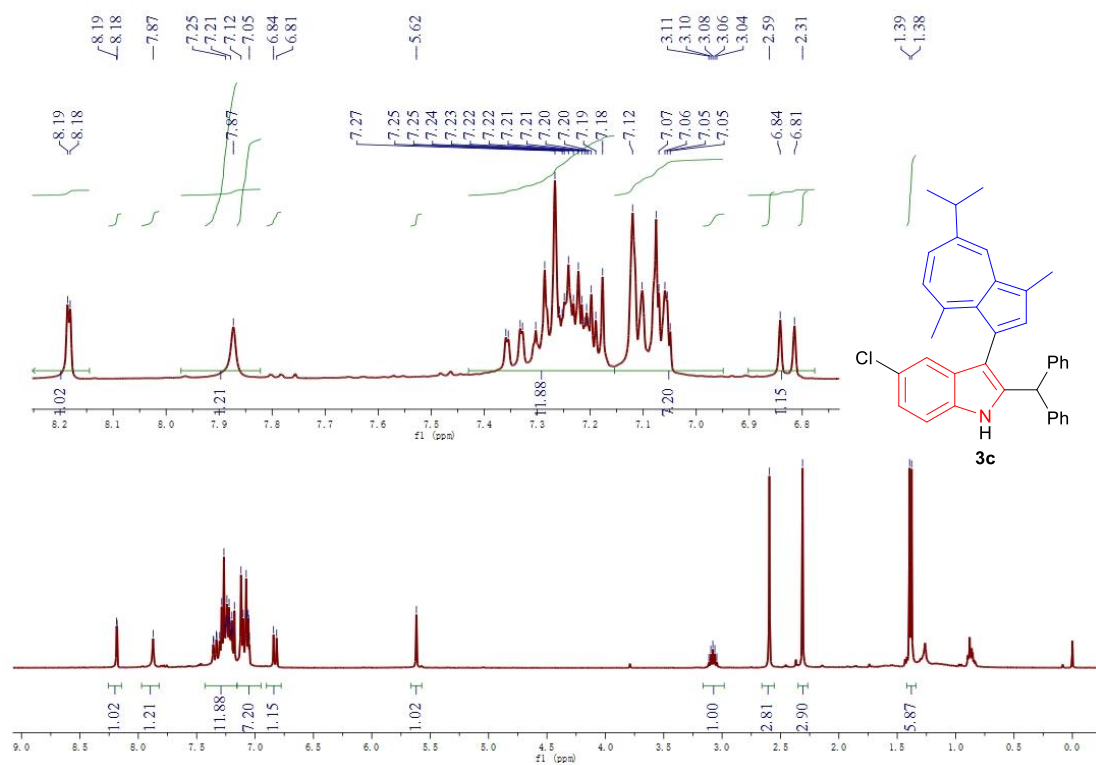


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3b**)

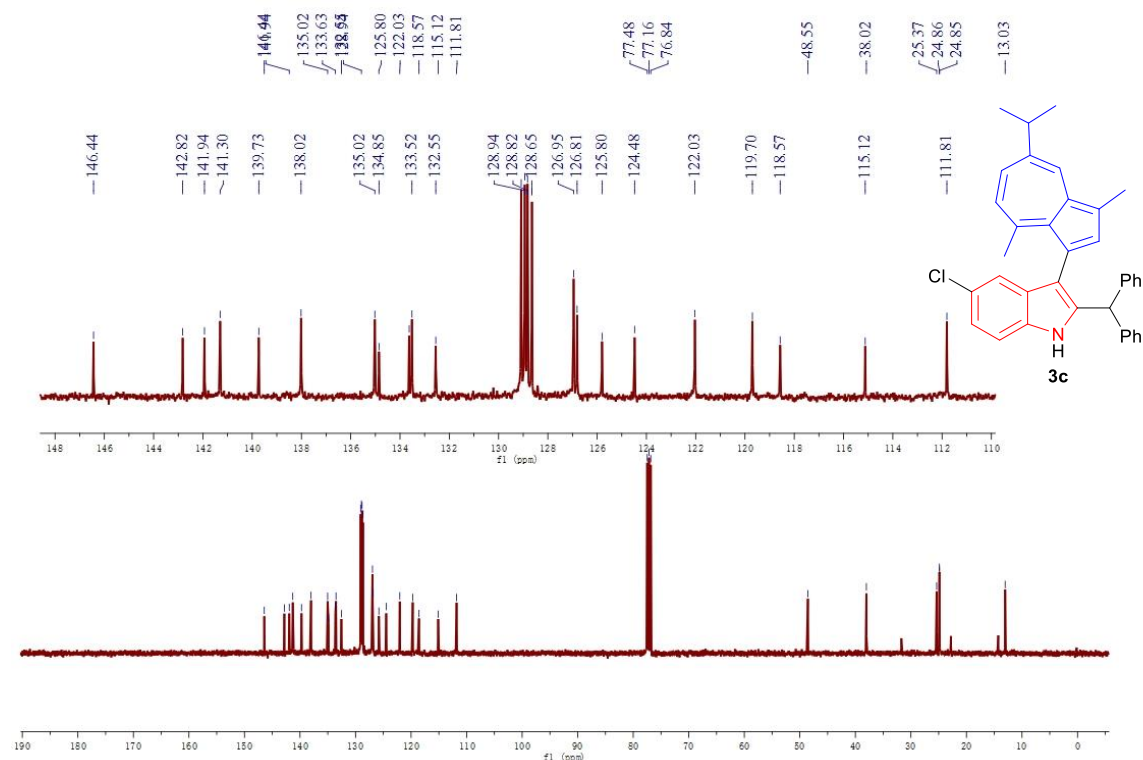




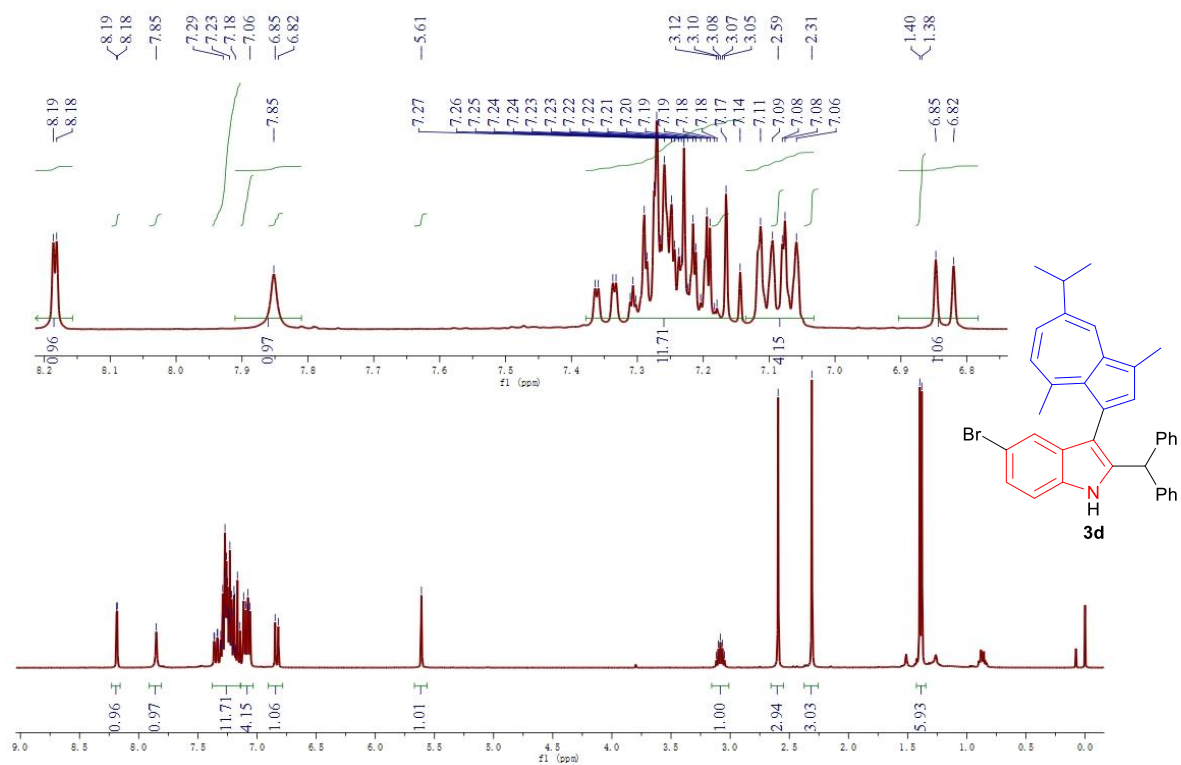
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (**3c**)



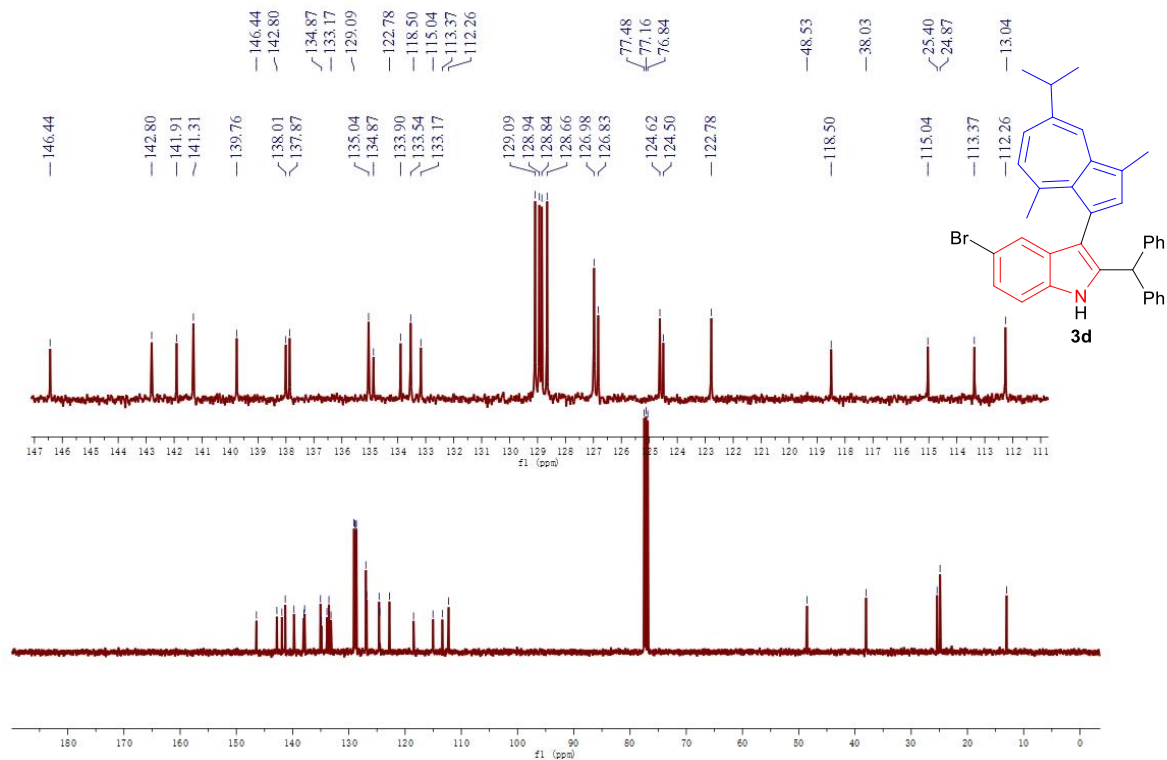
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) (**3c**)



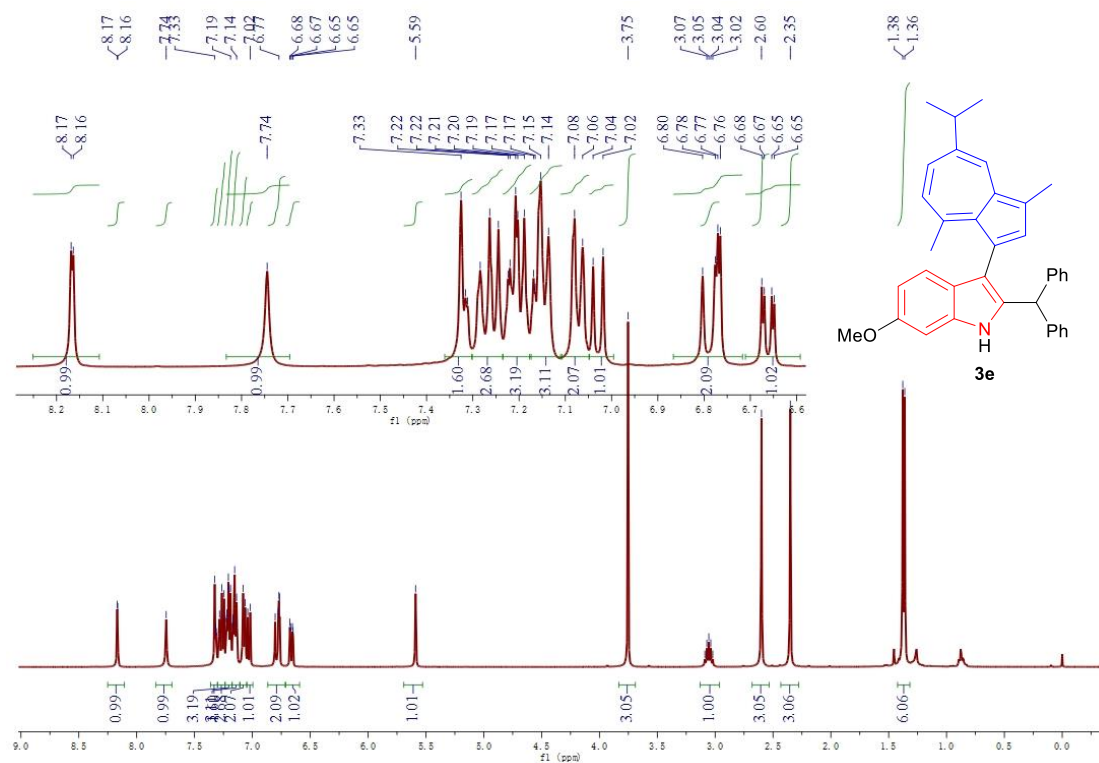
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**3d**)



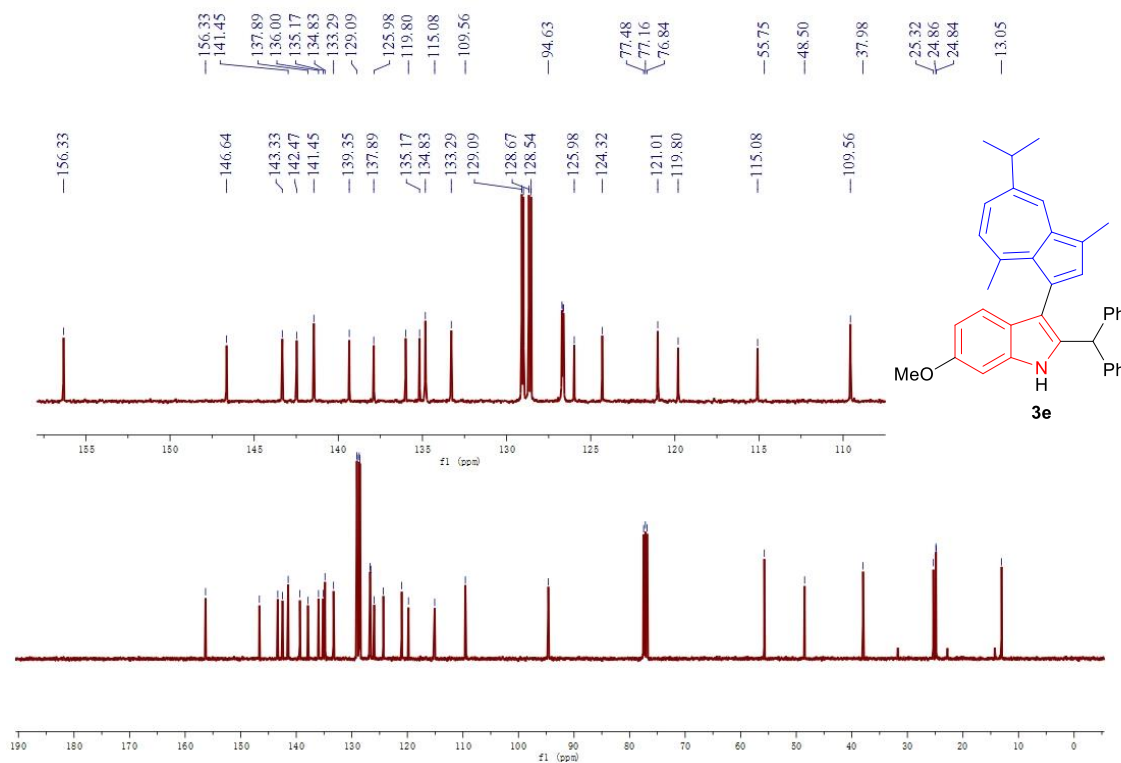
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3d**)



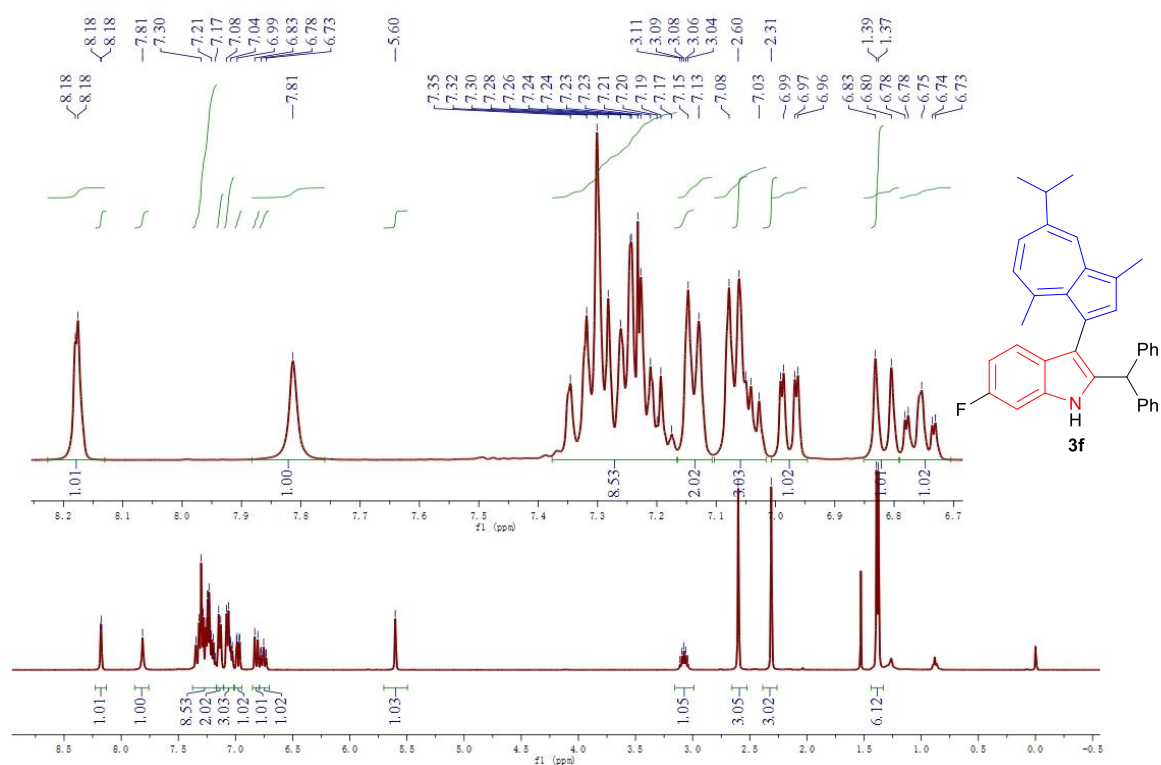
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**3e**)



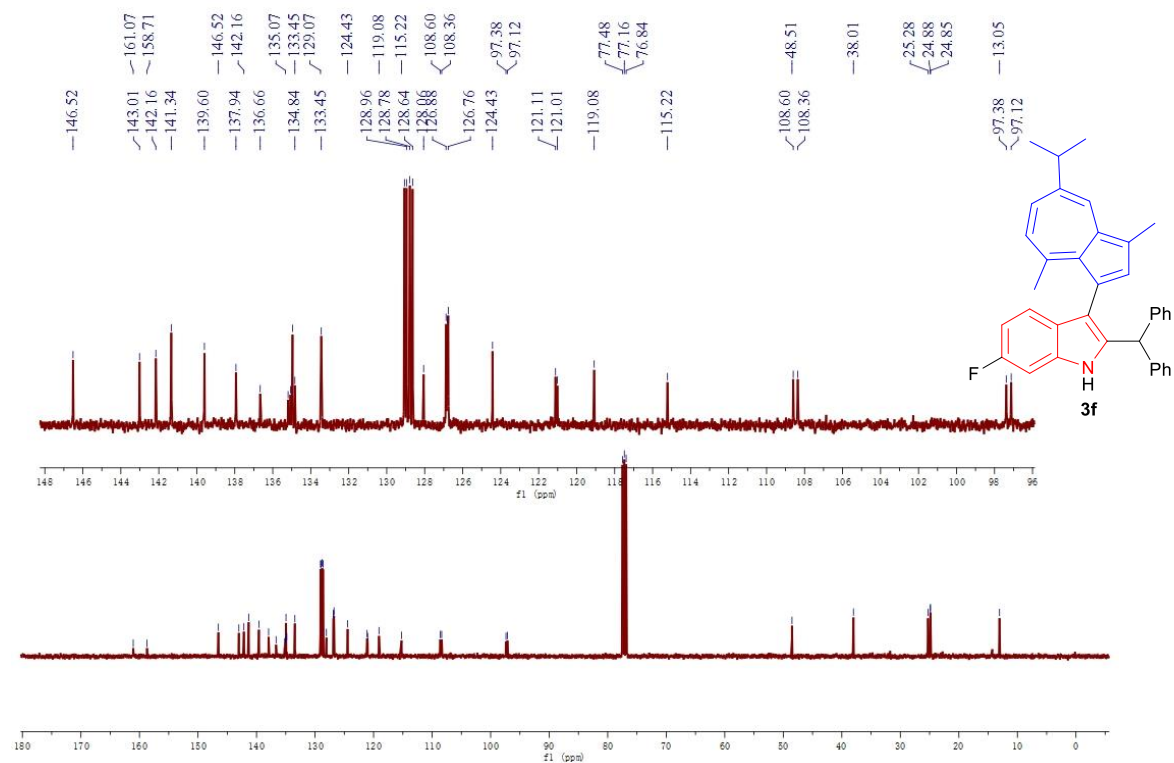
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3e**)



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

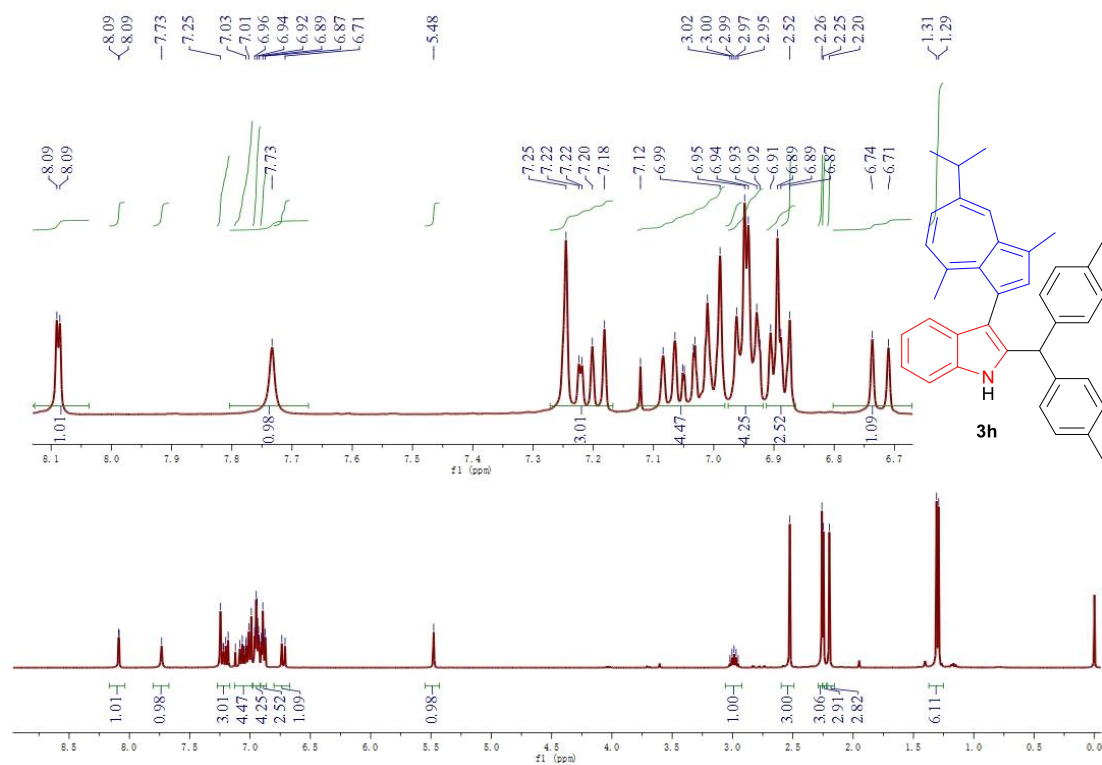


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3f**)

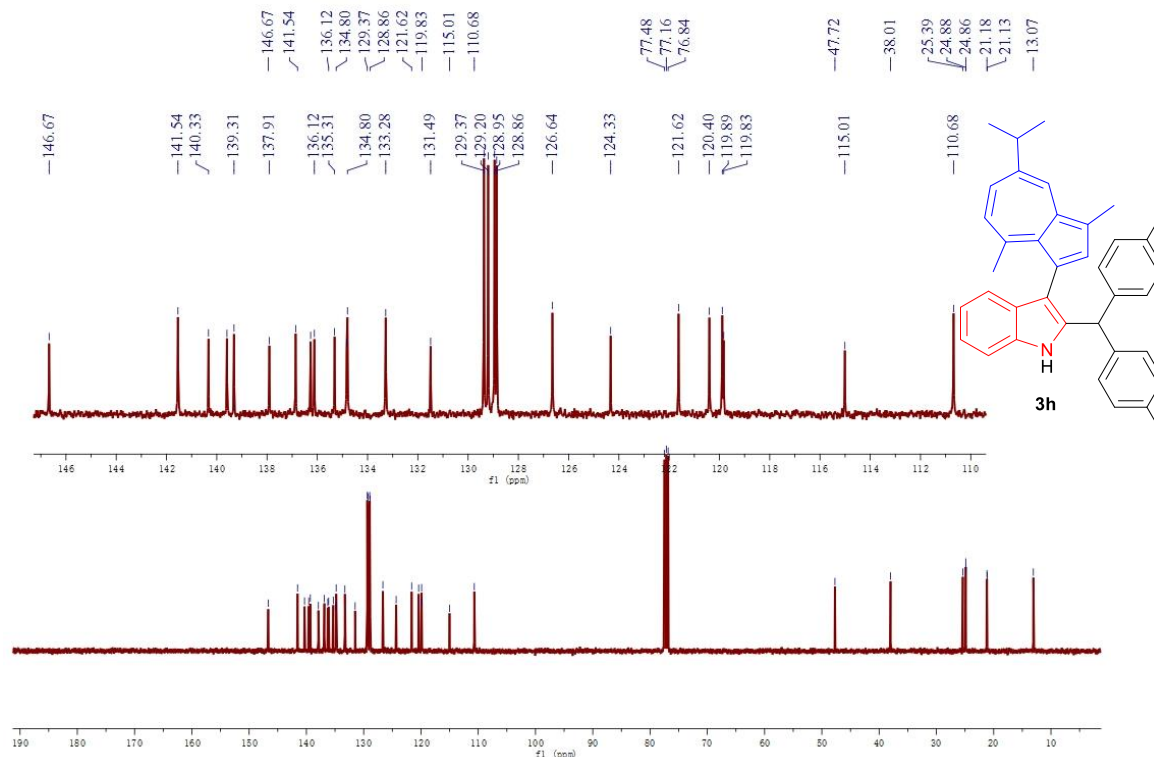




$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (**3h**)

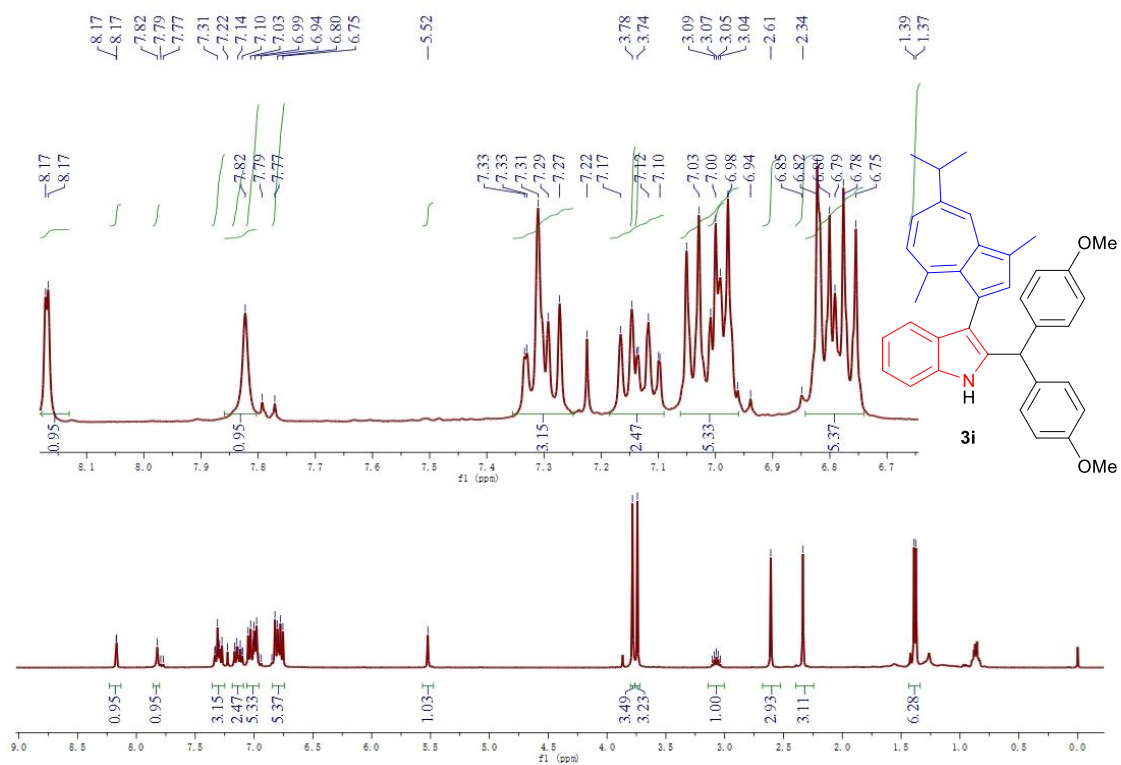


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) (**3h**)

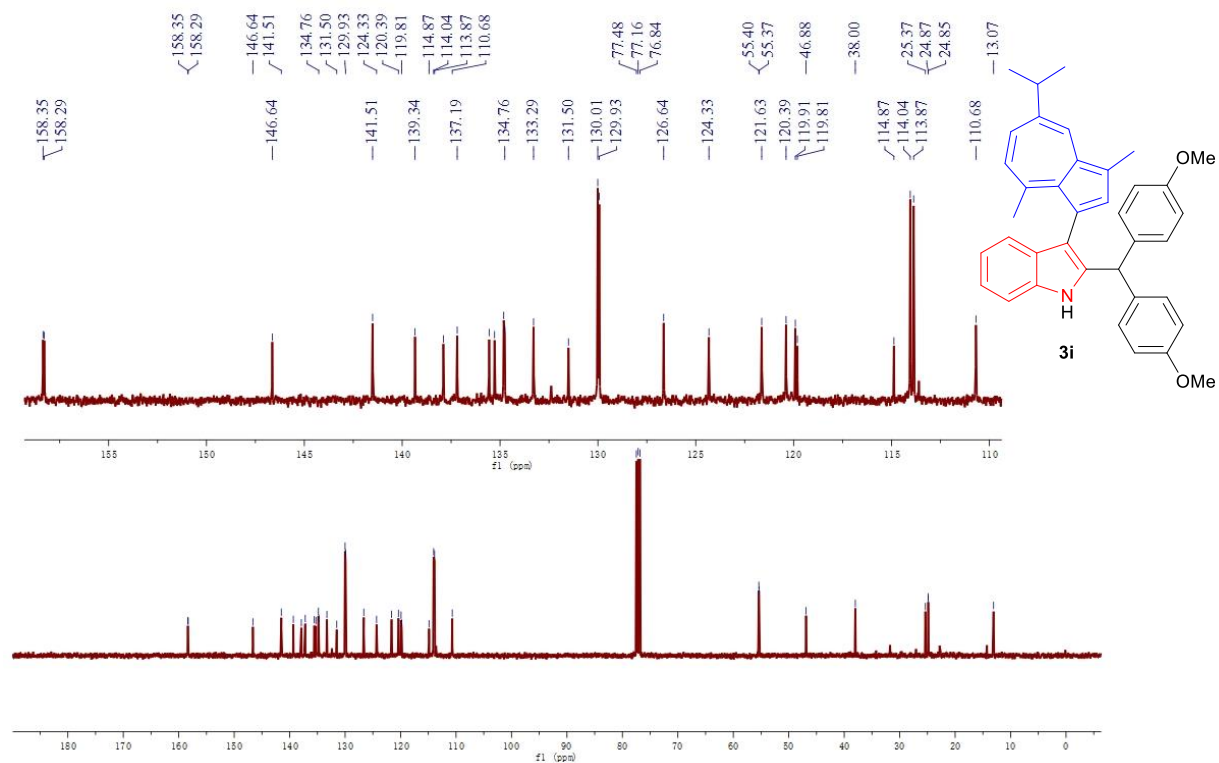




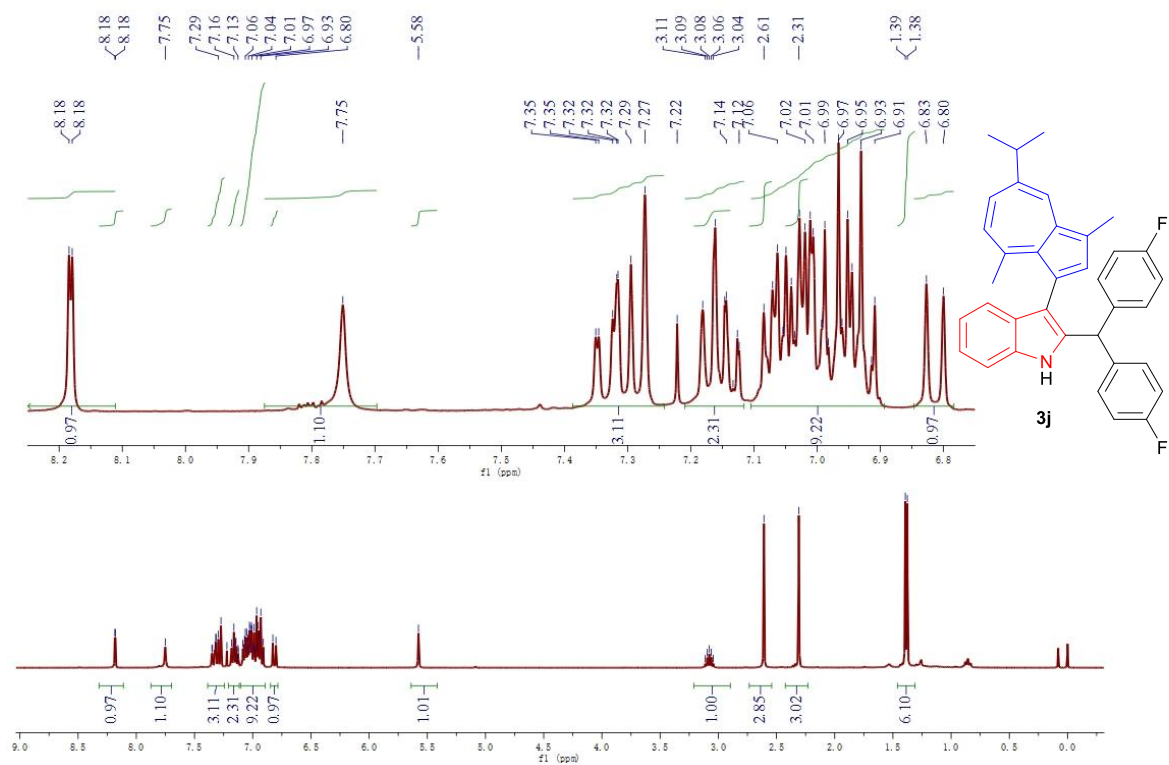
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**3i**)



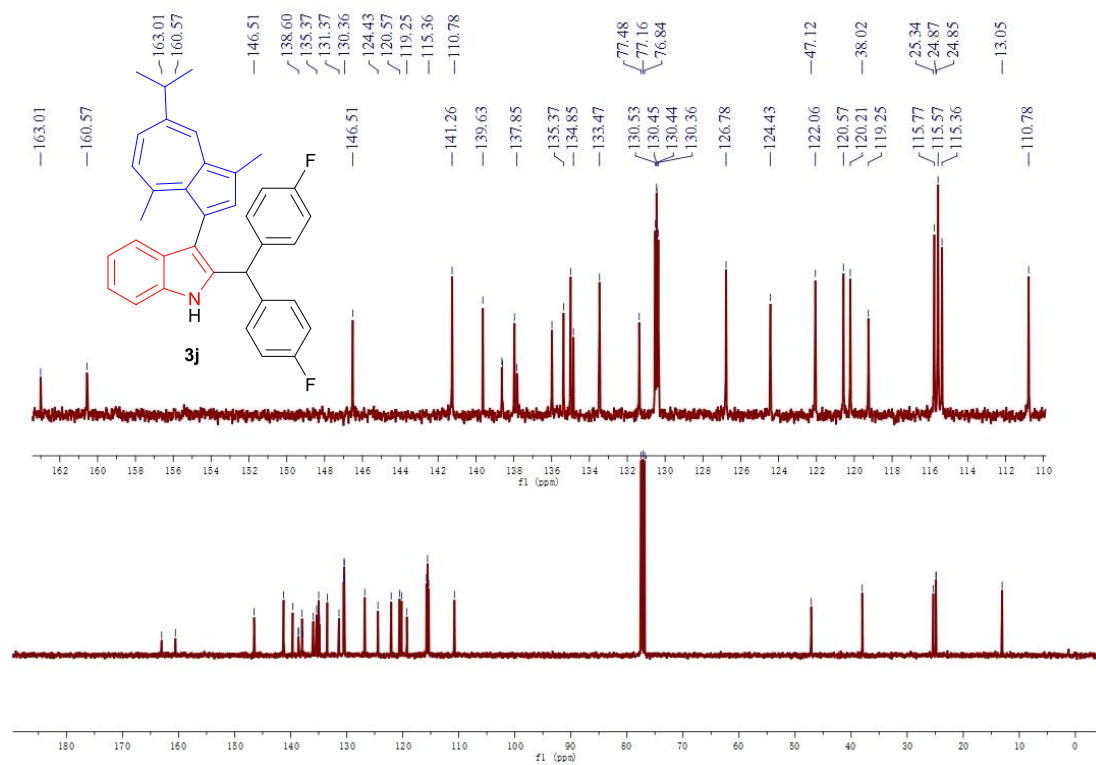
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3i**)



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

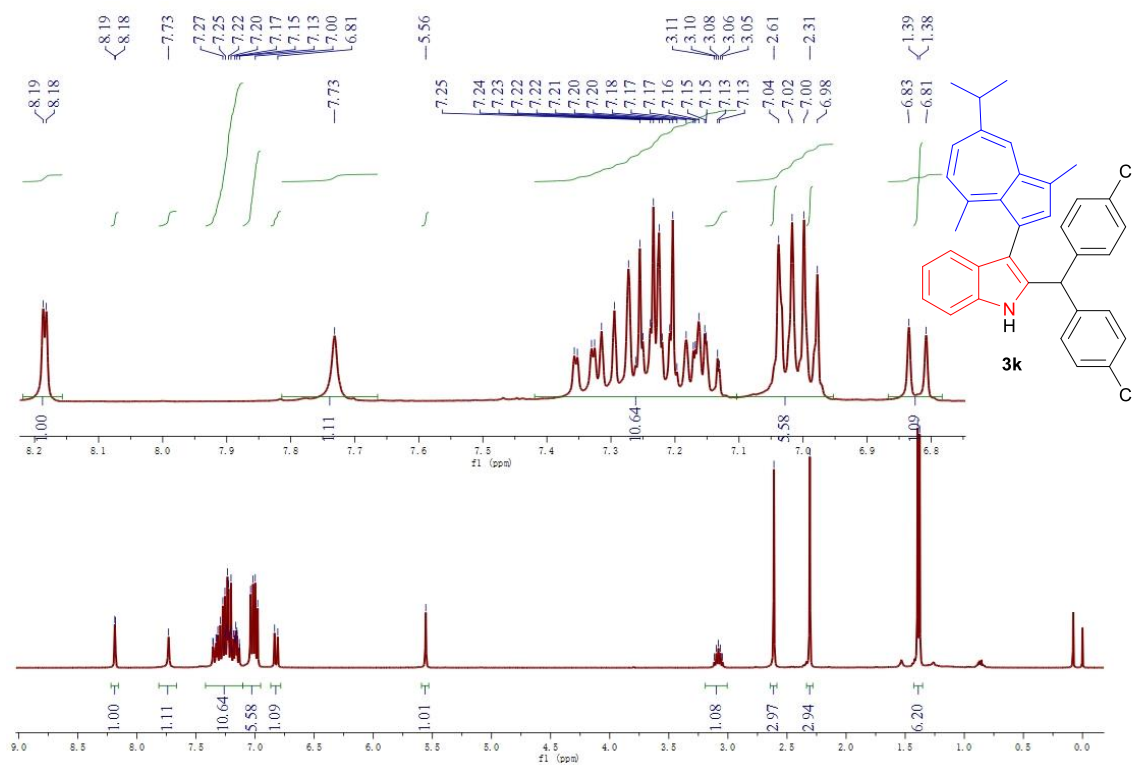


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3j**)

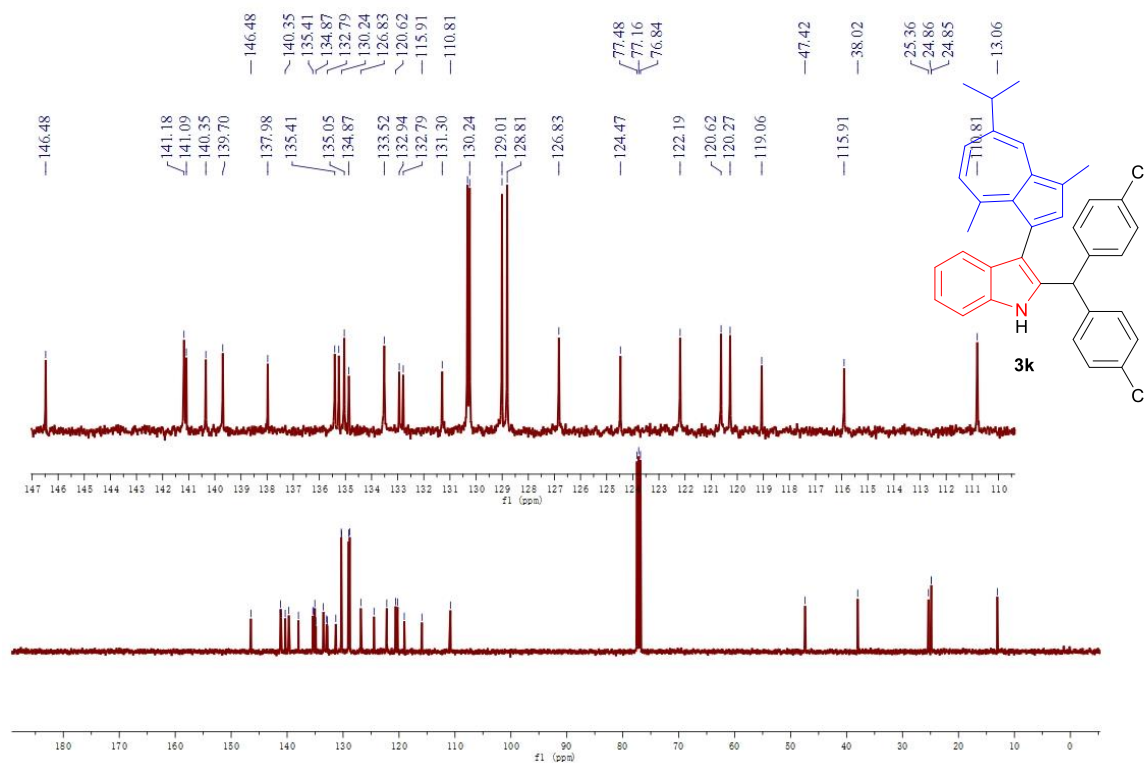




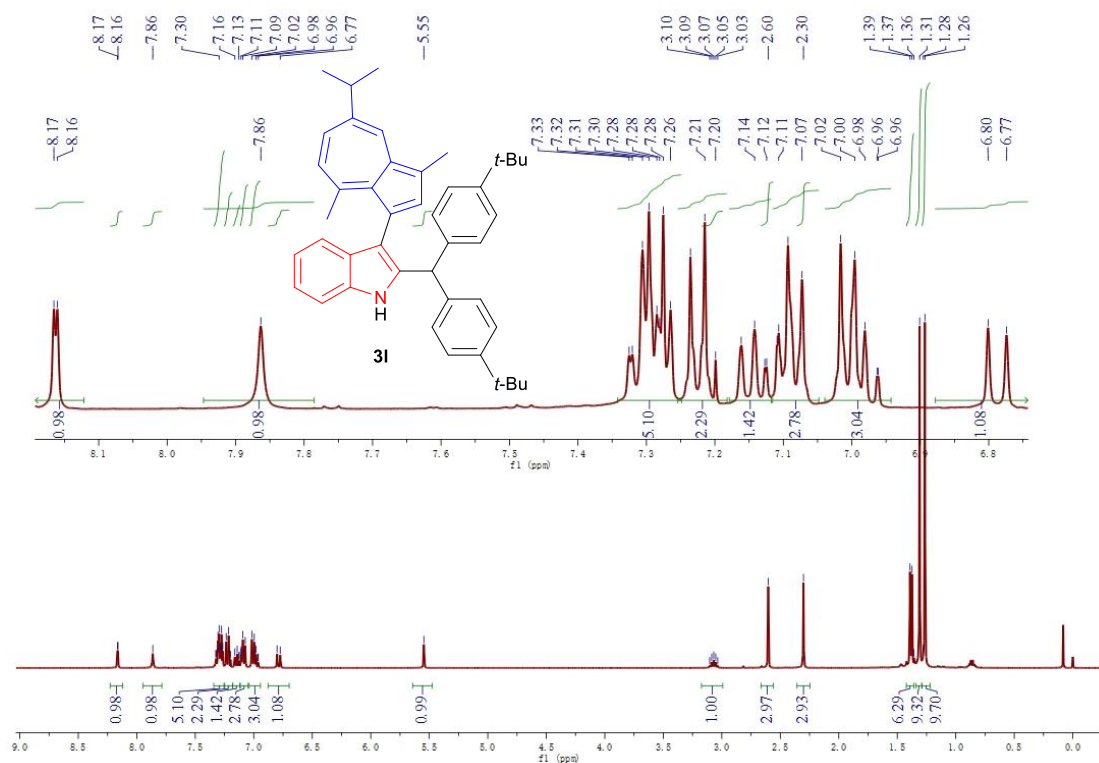
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**3k**)



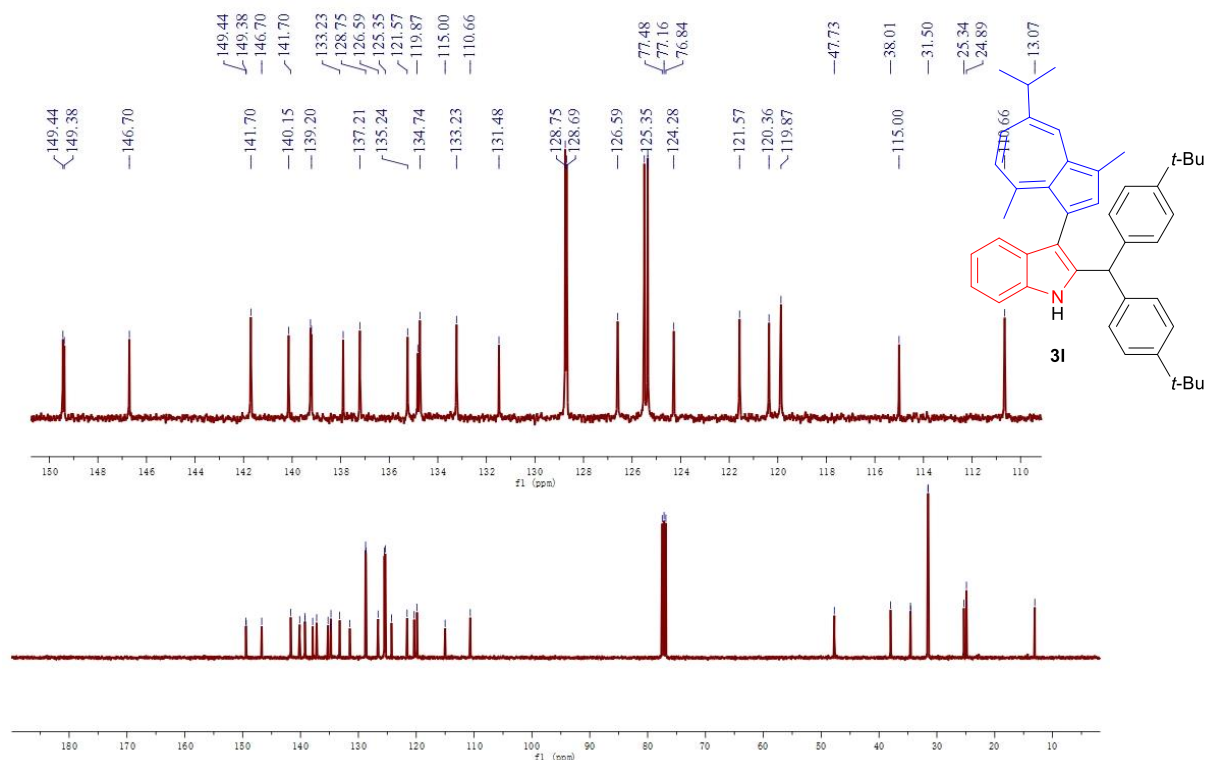
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3k**)



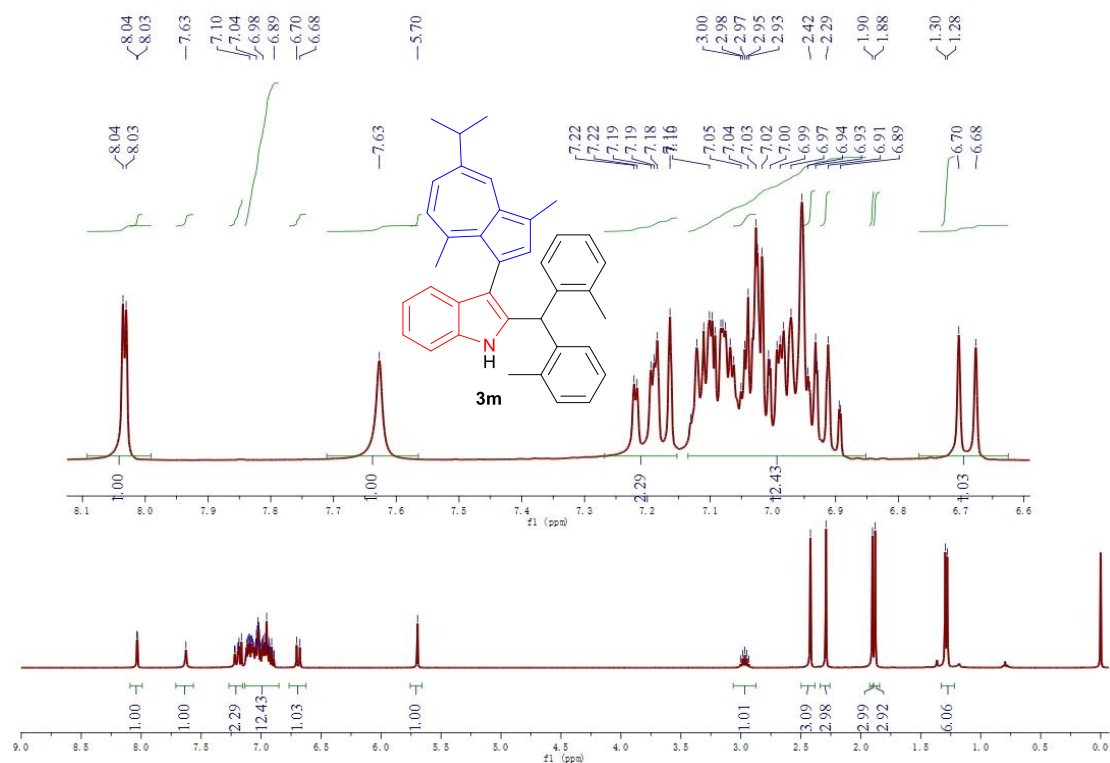
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (31)



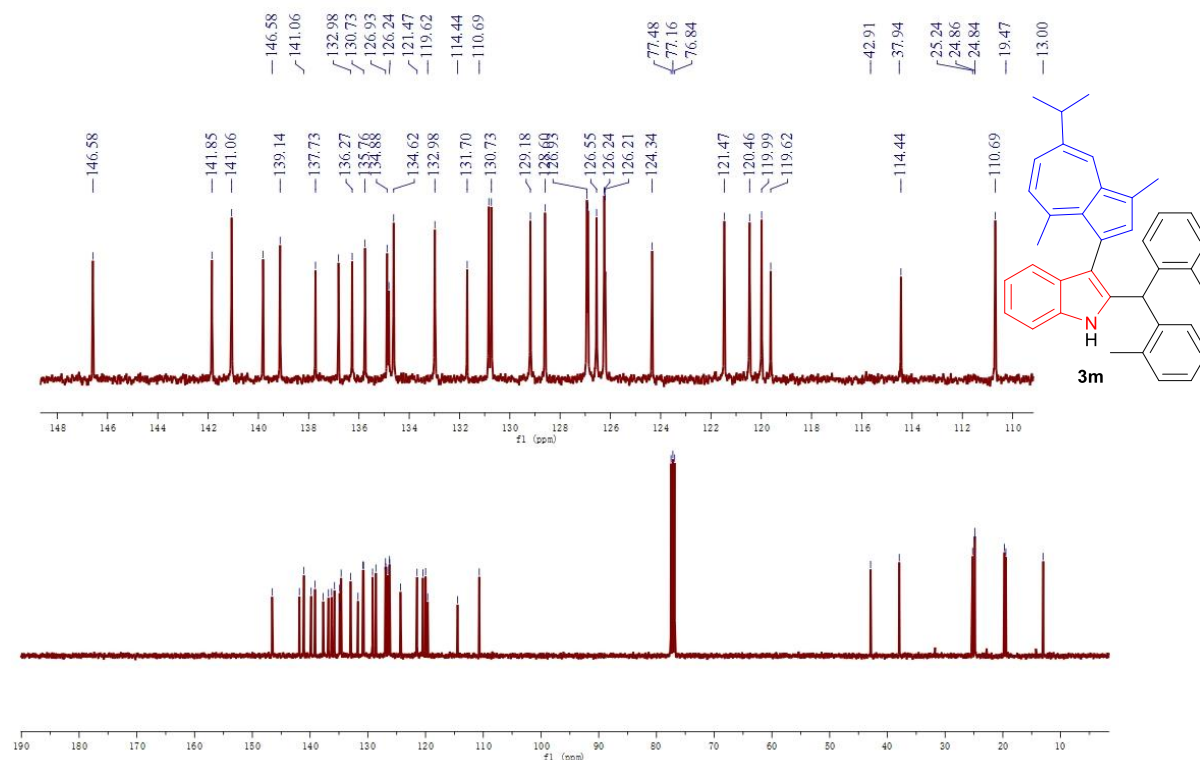
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (31)



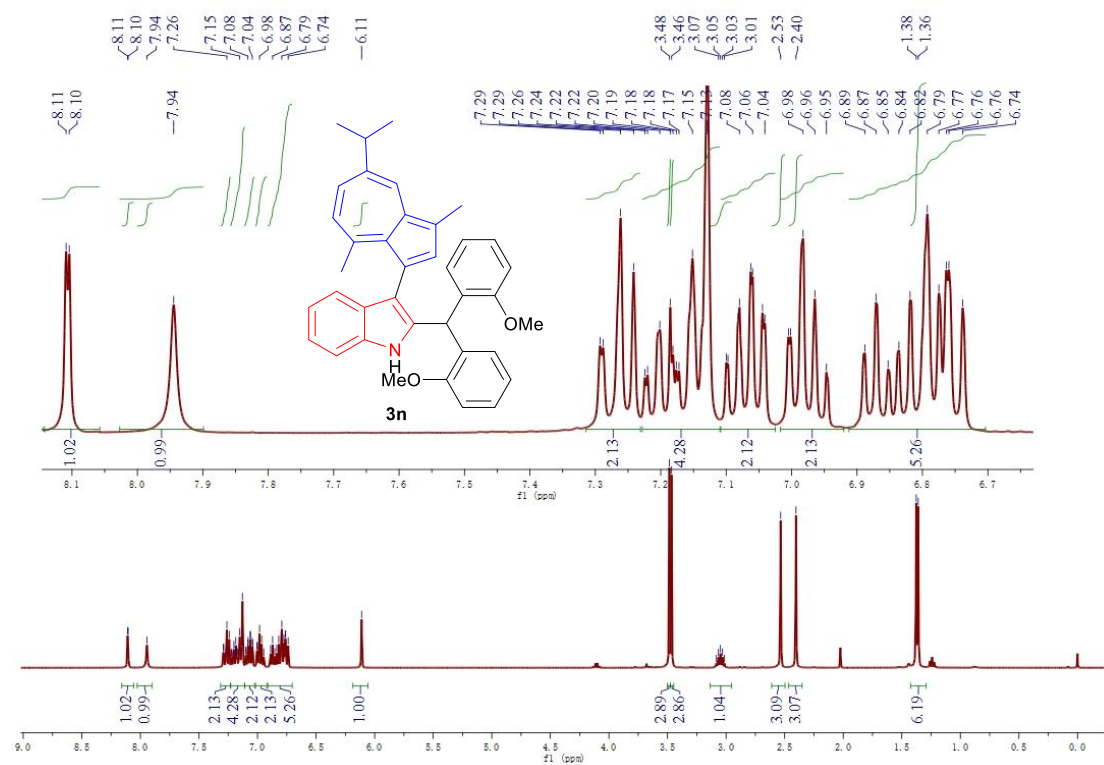
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (**3m**)



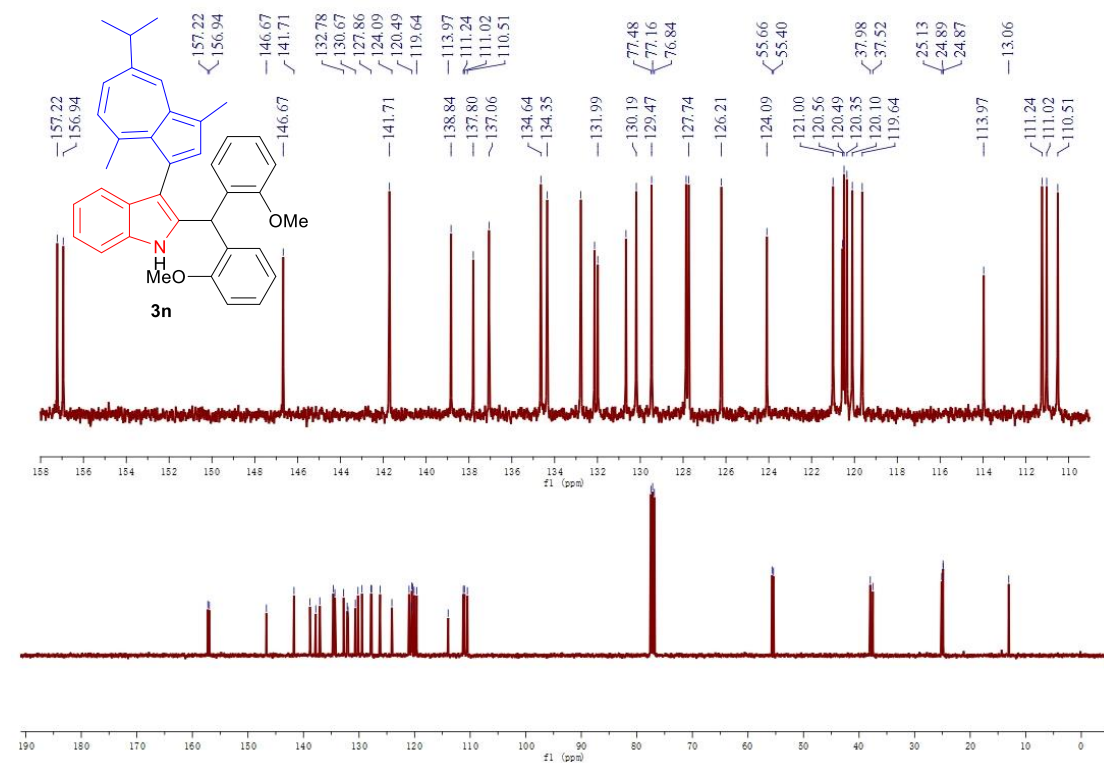
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) (**3m**)



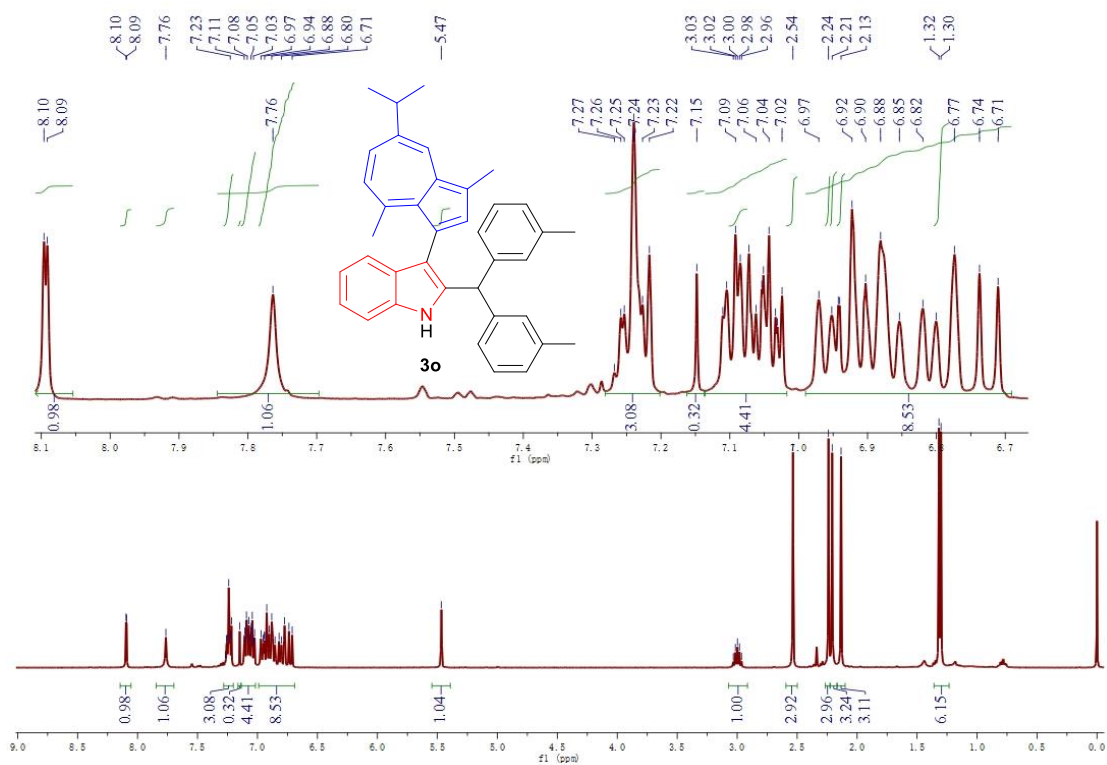
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**3n**)



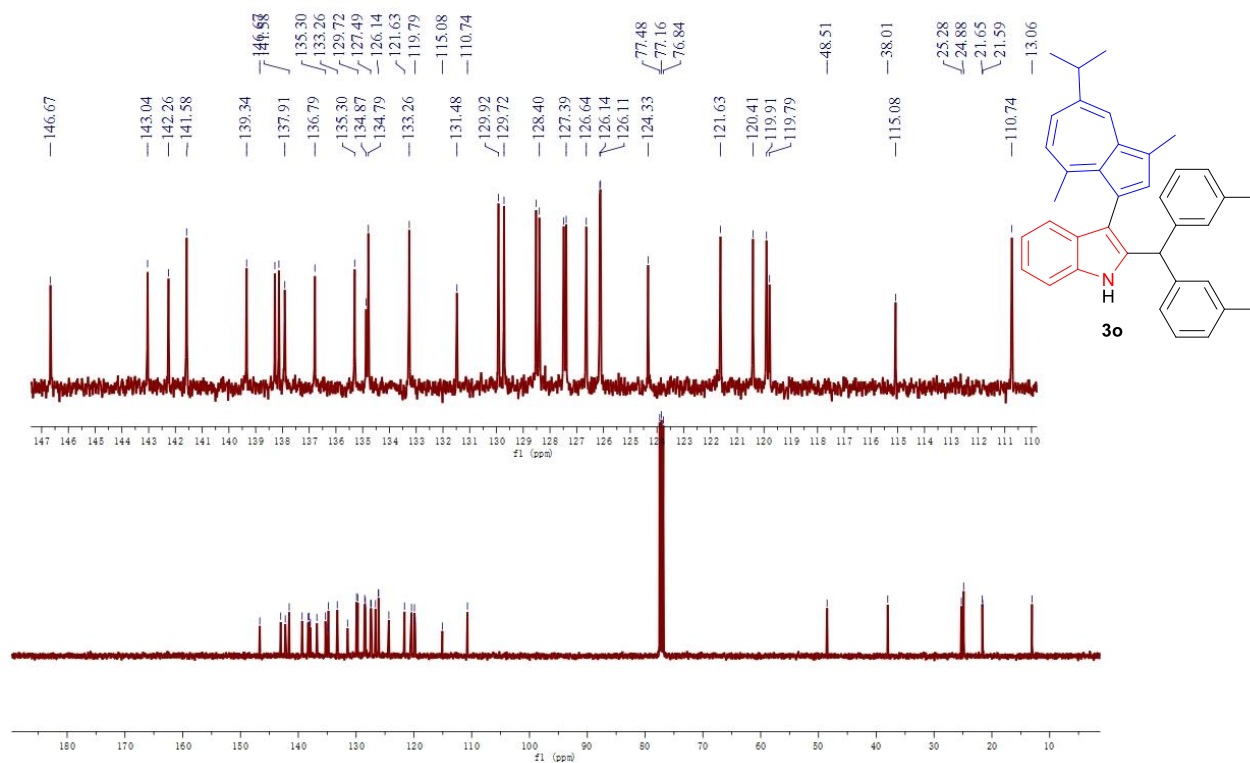
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3n**)



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

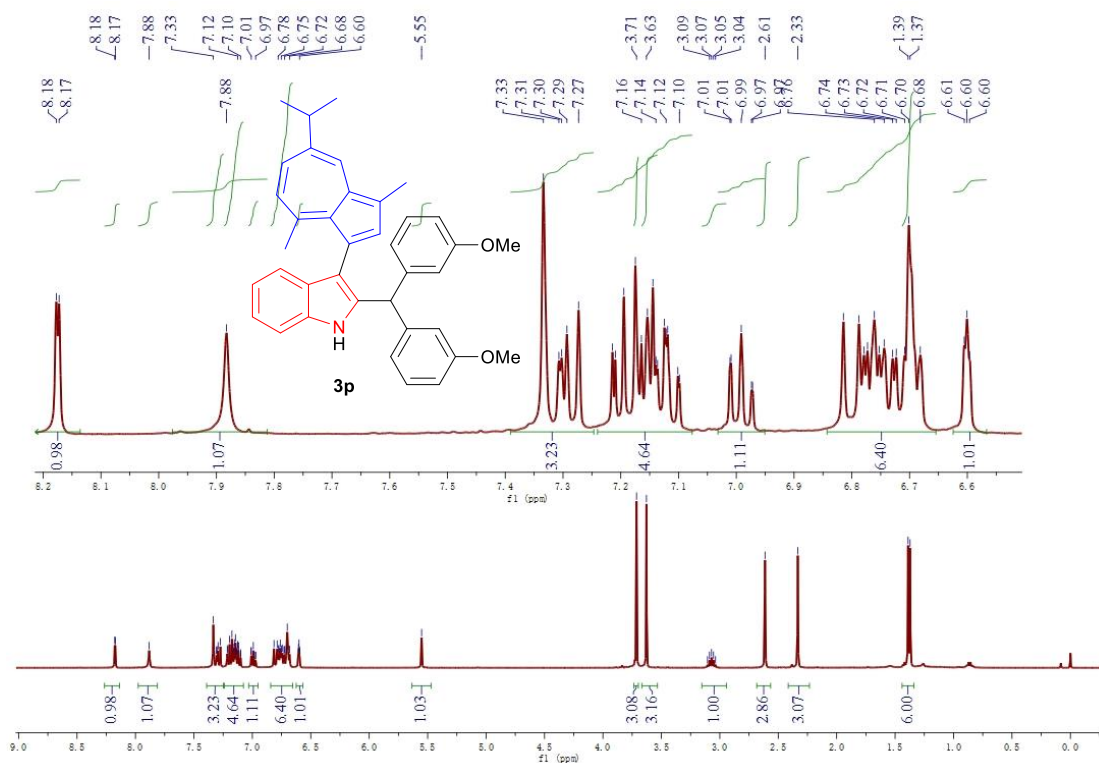


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3o**)

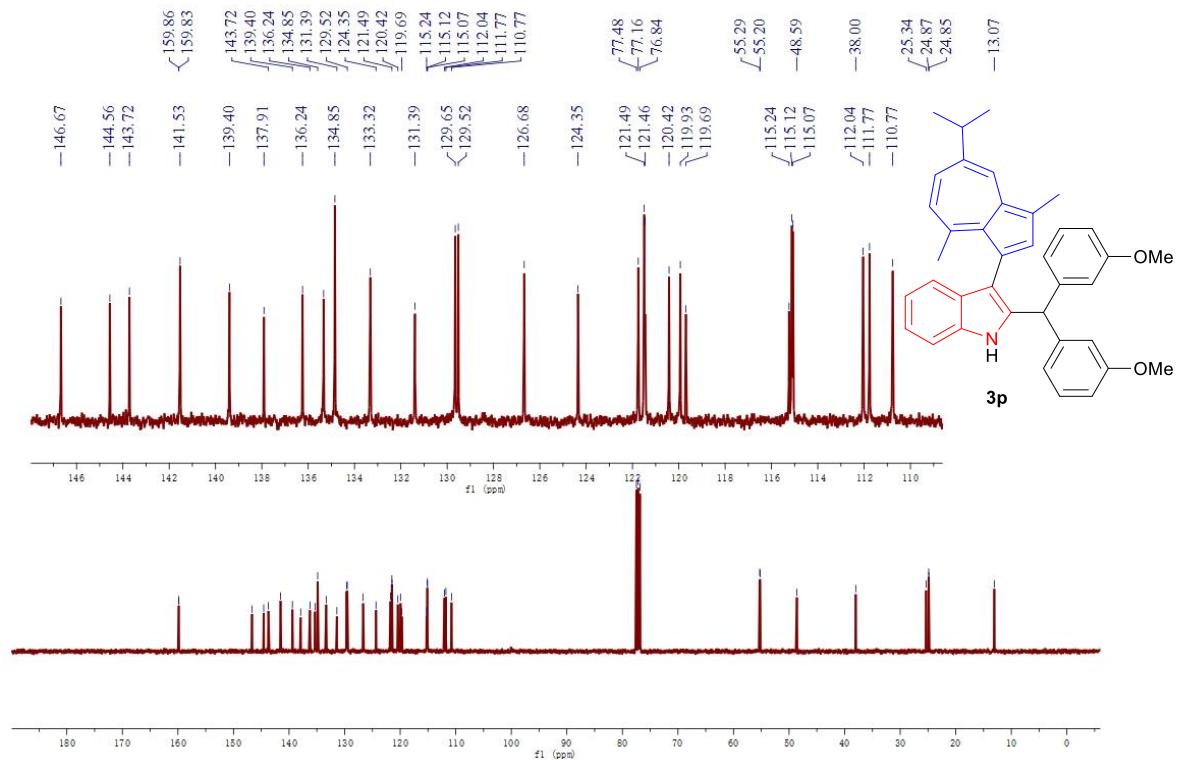




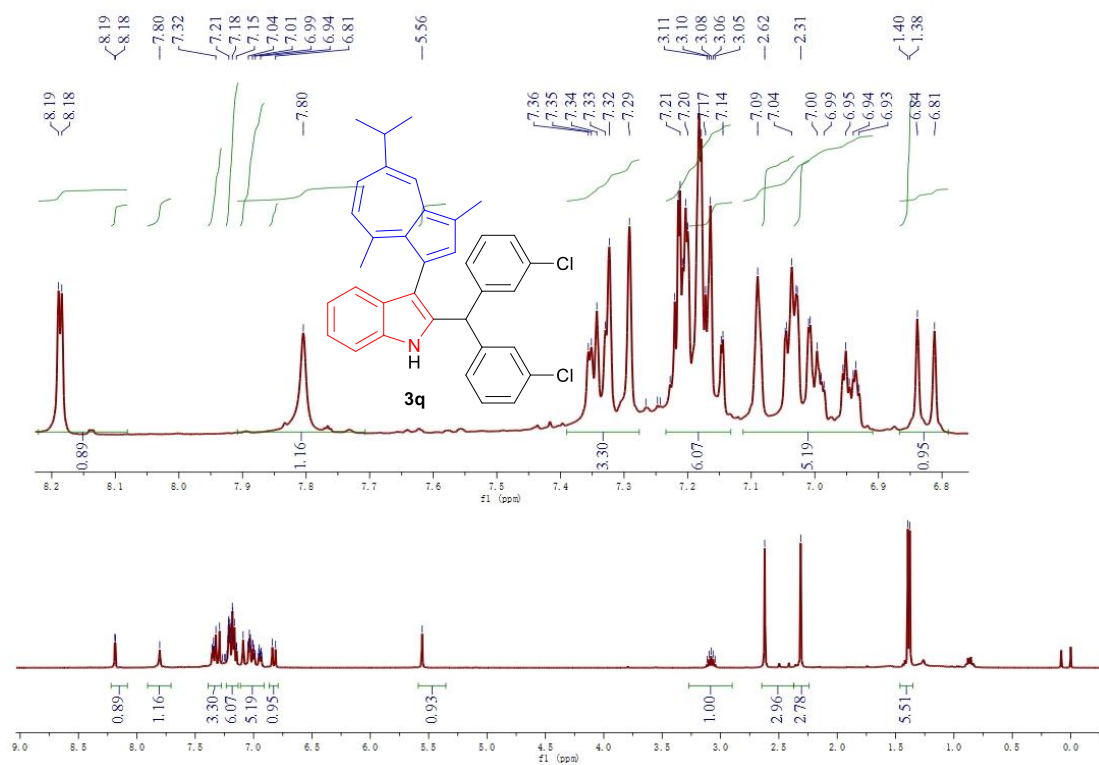
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**3p**)



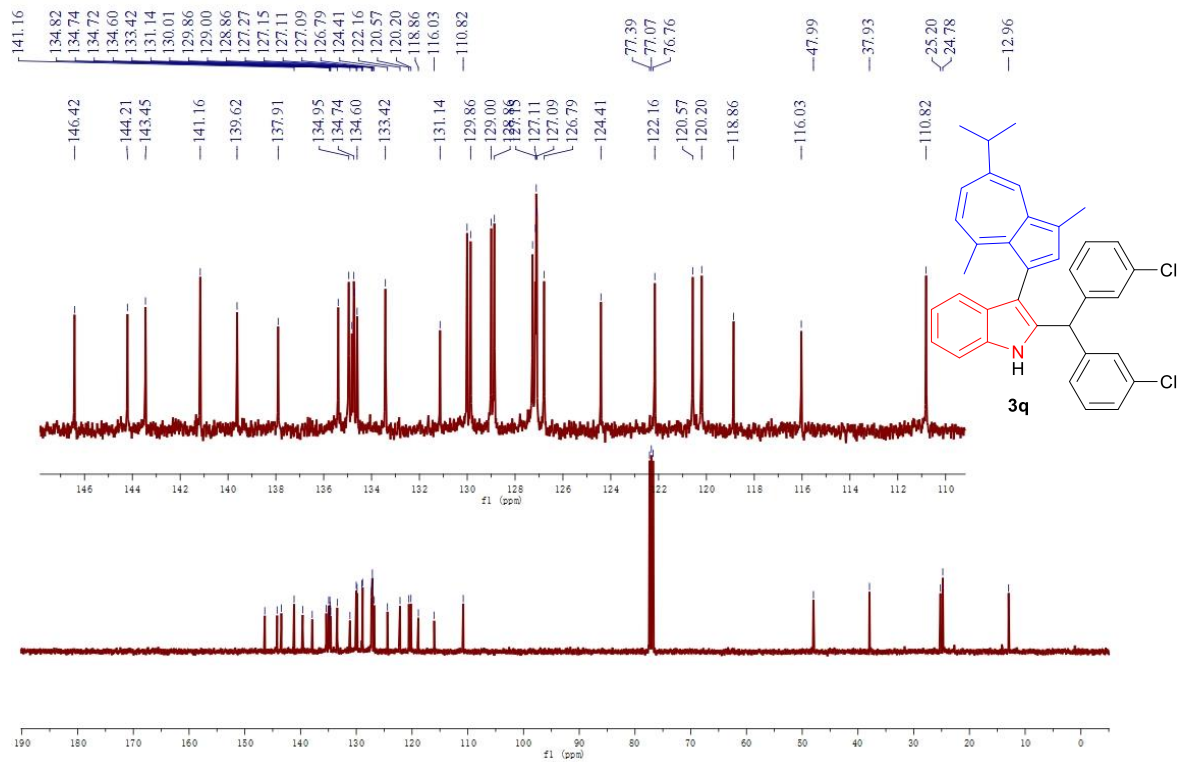
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3p**)



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



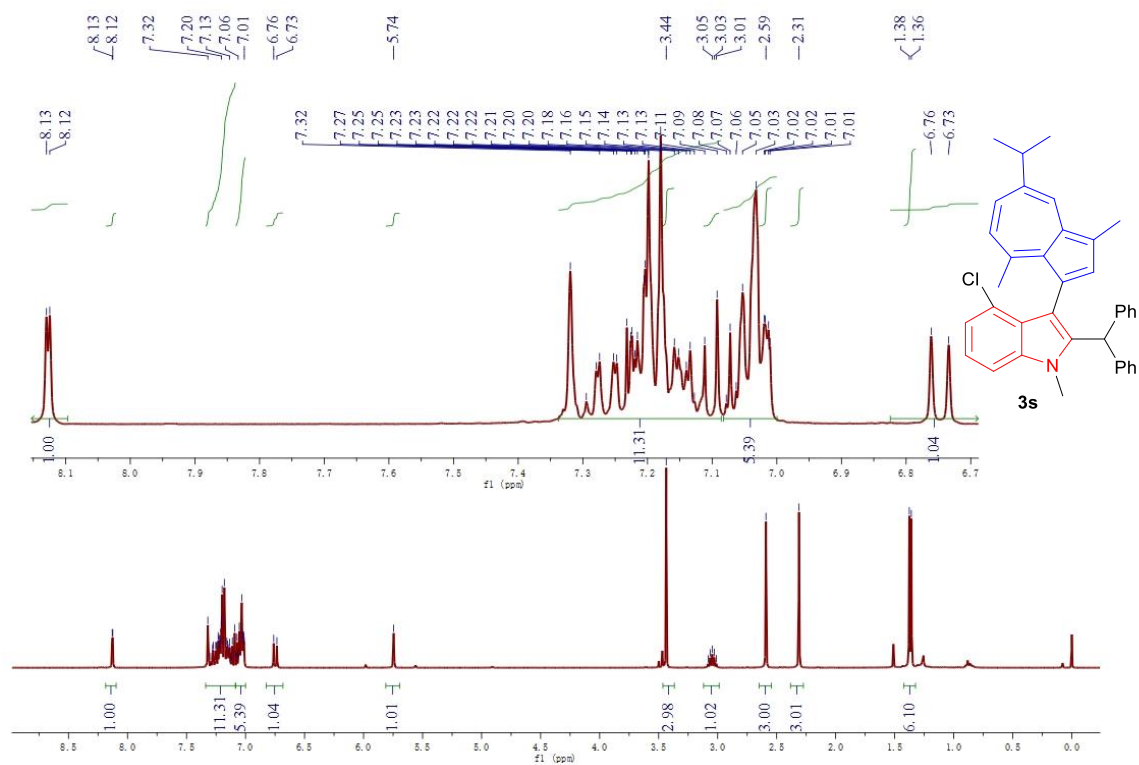
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3q**)



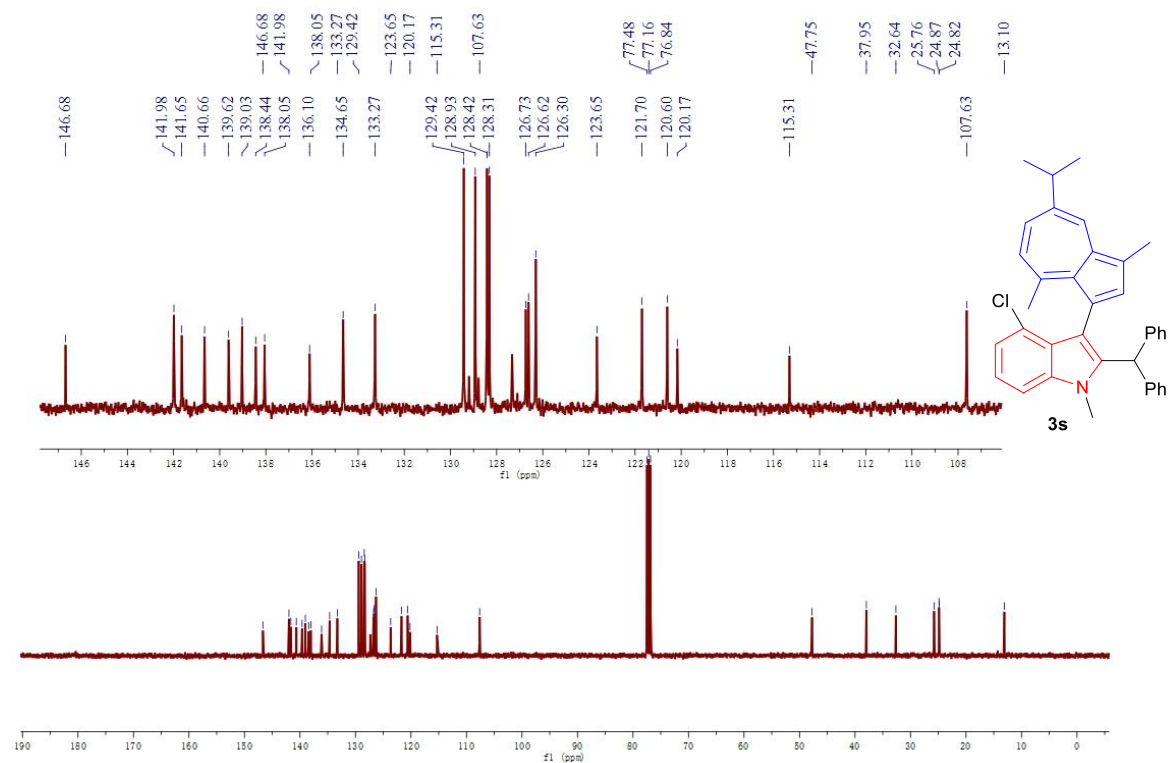




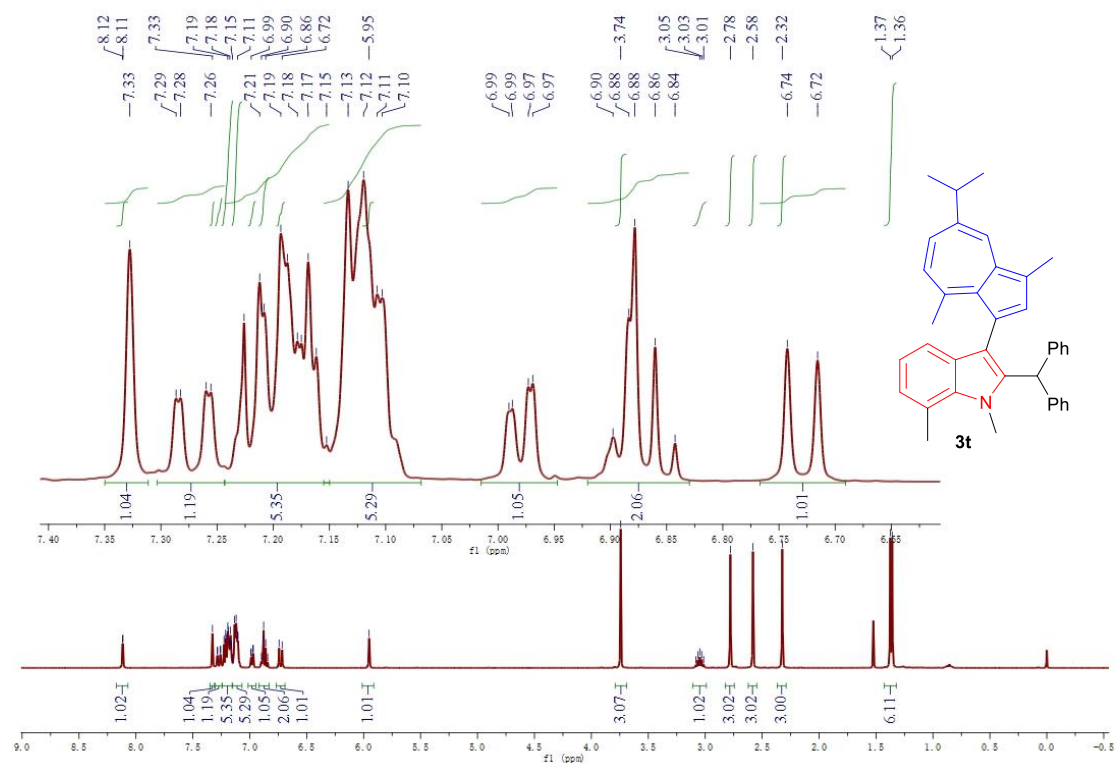
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**3s**)



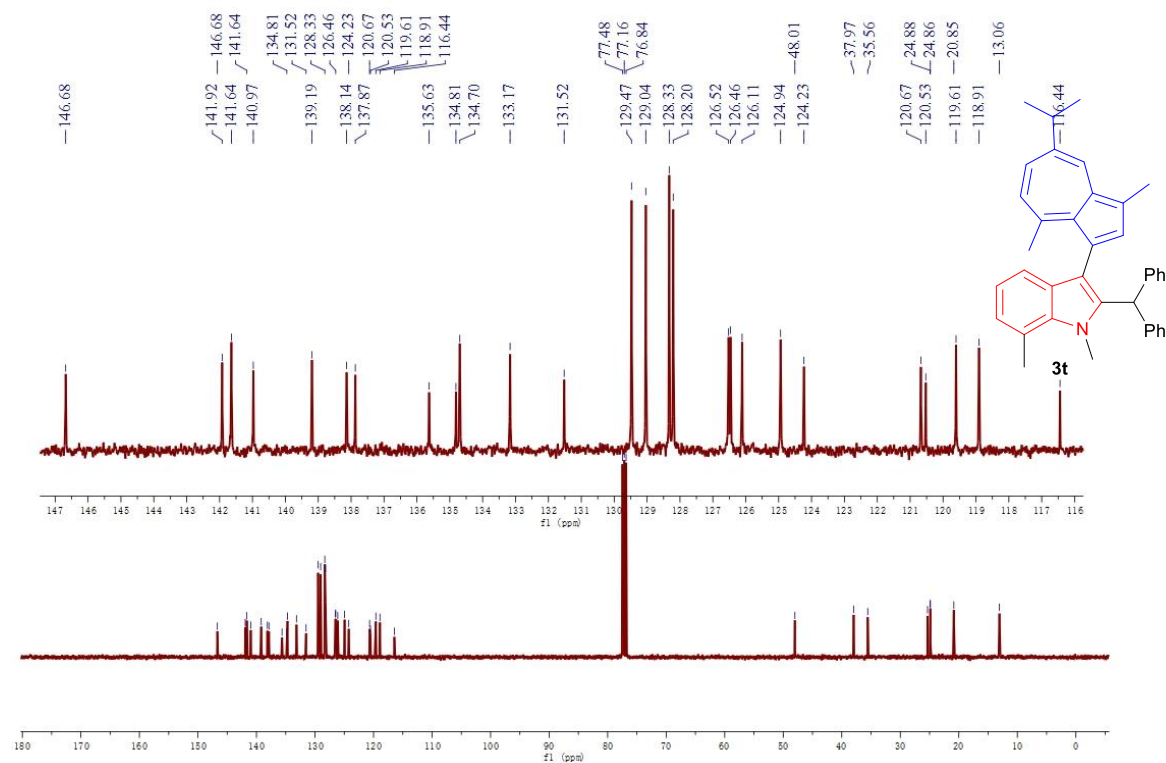
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (**3s**)



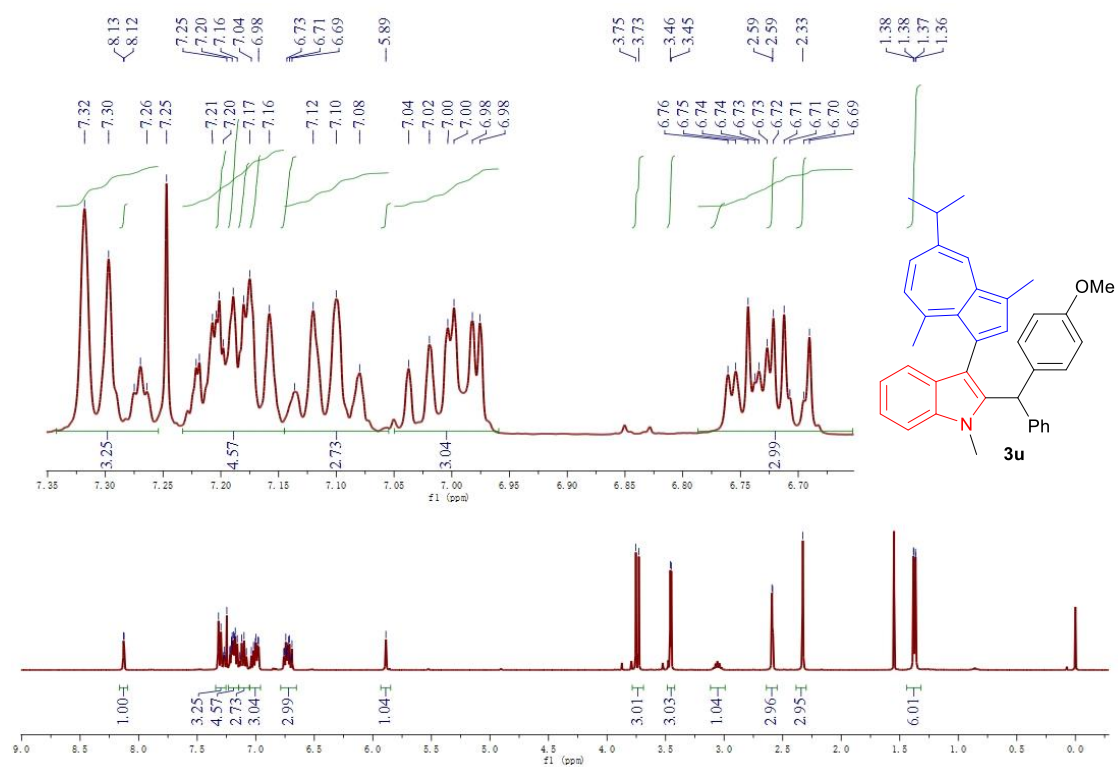
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (**3t**)



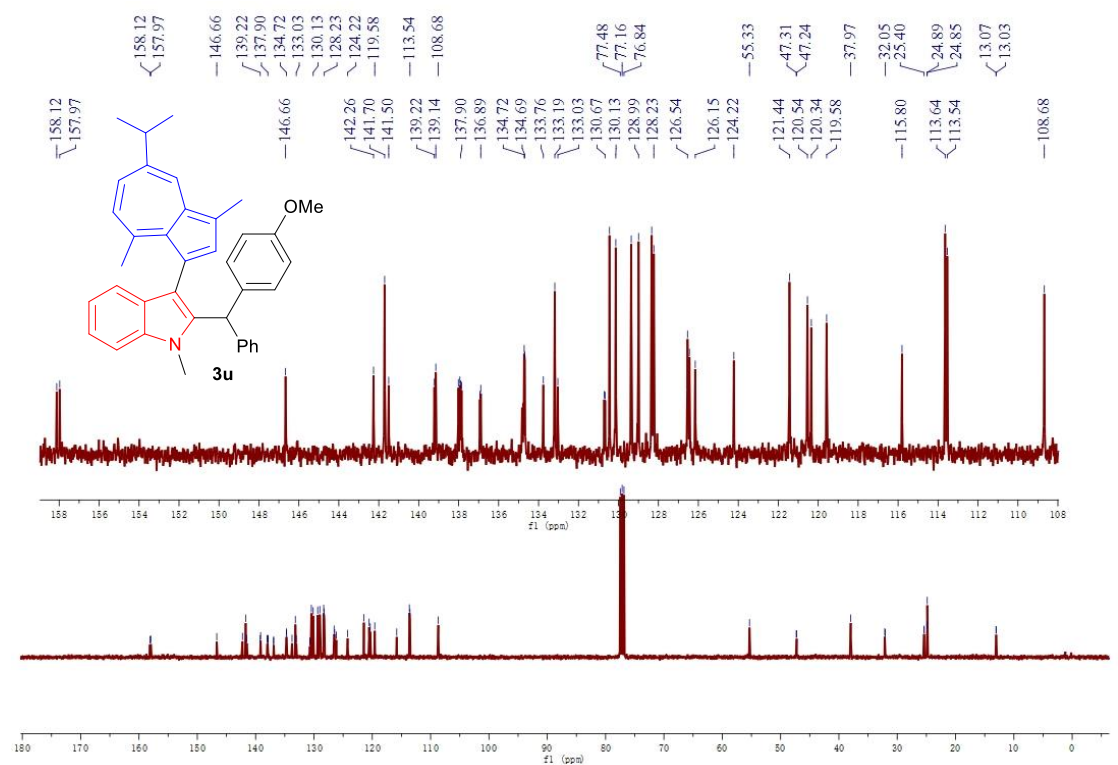
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) (**3t**)



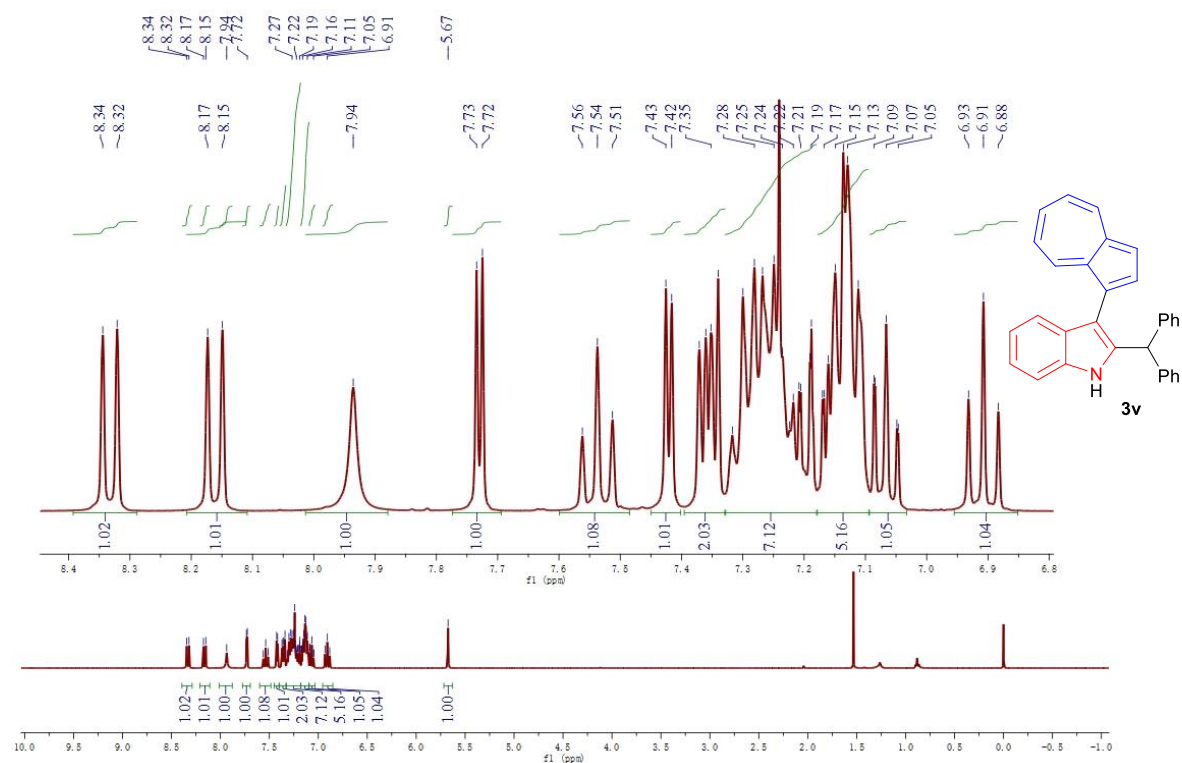
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (**3u**)



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



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



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

