

## Supporting Information

# Palladium-catalyzed *C*-glycosylation and annulation of *o*-alkynylanilines with 1-iodoglycals: convenient access to 3-indolyl-*C*-glycosides

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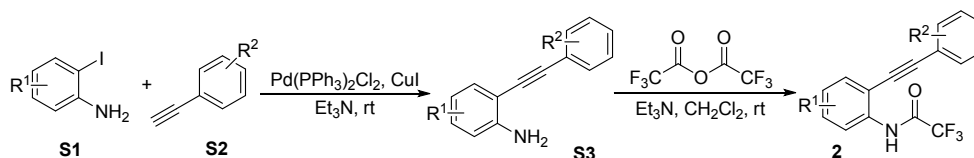
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**General Information.**  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (101 MHz) NMR spectra were recorded using  $\text{CDCl}_3$  (with TMS as internal standard),  $\text{DMSO}-d_6$  or  $\text{CD}_3\text{OD}$  as a solvent. Coupling constants are reported and expressed in Hz; splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), dt (double triplet), dq (double quartet), br (broad). Mass spectra were obtained from high resolution ESI mass spectrometer. All reactions were carried out using freshly distilled and dry solvents. Column chromatography was performed over silica gel (200-300 Mesh).

## Synthesis of substrates 1

The 1-iodoglycols **1a** and **1b** were prepared following the reported procedures.<sup>1</sup>

## General Procedure for the Preparation of 2a-e, 2g, 2j-m, 2o-v<sup>2</sup>

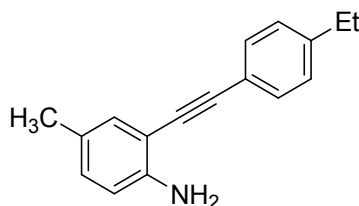


To a solution of **S1** (3 mmol, 1.0 equiv),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.06 mmol, 2 mol%), and  $\text{CuI}$  (0.12 mmol, 4 mol%) in anhydrous  $\text{Et}_3\text{N}$  (9 mL) under nitrogen atmosphere was added aryl alkynes **S2** (4.5 mmol, 1.5 equiv), the resulting solution was stirred at room temperature until the disappearance of the starting material according to the TLC, the reaction mixture was filtered through a pad of celite, eluting with  $\text{EtOAc}$  ( $3 \times 5$  mL). The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified by flash chromatography on a silica gel (using petroleum ether/ethyl acetate = 40:1 as the eluent) to give **S3a-e**, **S3g**, **S3j-m**, **S3o-v**.

To a solution of **S3** (1 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (10 mL) at 0 °C, was added  $\text{Et}_3\text{N}$  (2 mmol, 2.0 equiv), trifluoroacetic anhydride (1.5 mmol, 1.5 equiv). The reaction mixture was warmed up to room temperature and then stirred at this temperature until the disappearance of the starting material according to the TLC.  $\text{H}_2\text{O}$  (5 mL) was added to the reaction mixture and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic extracts were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified by flash chromatography on a silica gel (using petroleum ether/ethyl acetate = 60:1 as the eluent) to give **2a-e**, **2g**, **2j-m**, **2o-v**.

The following is the characterization data for the new compounds

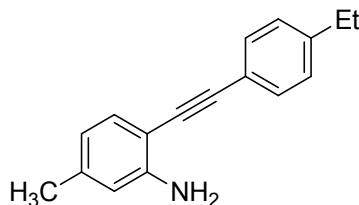
### 2-((4-ethylphenyl)ethynyl)-4-methylaniline (**S3q**)



Colorless solid (599 mg, 85%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 8.0$  Hz, 2H), 7.17 (s, 2H), 7.15 (s, 1H), 6.93 (d,  $J = 8.1$  Hz, 1H), 6.63 (d,  $J = 8.2$  Hz, 1H), 3.85 (br, 2H), 2.65 (q,  $J = 7.6$  Hz, 2H),

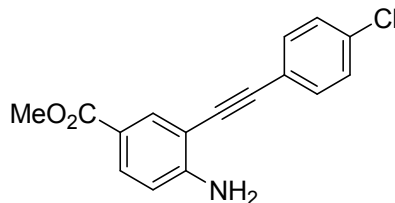
2.22 (s, 3H), 1.23 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.29, 144.62, 132.22, 131.48, 130.43, 127.97, 127.32, 120.60, 114.63, 108.37, 94.69, 85.42, 28.86, 20.31, 15.39; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{18}\text{N}$   $[\text{M} + \text{H}]^+$ : 236.1434; Found: 236.1437.

**2-((4-ethylphenyl)ethynyl)-5-methylaniline (S3s)**



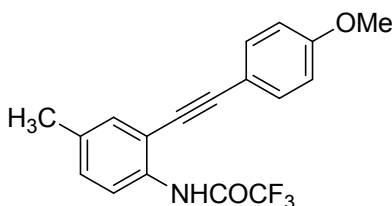
Yellow solid (620 mg, 88%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 8.1$  Hz, 2H), 7.23 (d,  $J = 7.9$  Hz, 1H), 7.14 (d,  $J = 8.2$  Hz, 2H), 6.52 (d,  $J = 7.6$  Hz, 2H), 4.07 (br, 2H), 2.63 (q,  $J = 7.6$  Hz, 2H), 2.24 (s, 3H), 1.22 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.70, 144.52, 139.94, 131.95, 131.46, 127.99, 120.76, 119.21, 115.06, 105.48, 94.37, 85.49, 28.88, 21.67, 15.44; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{18}\text{N}$   $[\text{M} + \text{H}]^+$ : 236.1434; Found: 236.1432.

**methyl 4-amino-3-((4-chlorophenyl)ethynyl)benzoate (S3v)**



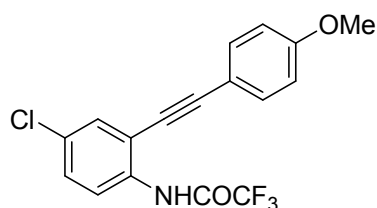
Colorless solid (701mg, 82%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 1.8$  Hz, 1H), 7.82 (dd,  $J = 8.6, 1.9$  Hz, 1H), 7.44 (d,  $J = 8.5$  Hz, 2H), 7.33 (d,  $J = 8.5$  Hz, 2H), 6.70 (d,  $J = 8.6$  Hz, 1H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.55, 151.45, 134.55, 134.51, 132.70, 131.65, 128.81, 121.39, 119.55, 113.40, 106.83, 93.95, 85.76, 51.78; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{13}\text{ClNO}_2$   $[\text{M} + \text{H}]^+$ : 286.0629; Found: 286.0628.

**2,2,2-trifluoro-N-(2-((4-methoxyphenyl)ethynyl)-4-methylphenyl)acetamide (2k)**



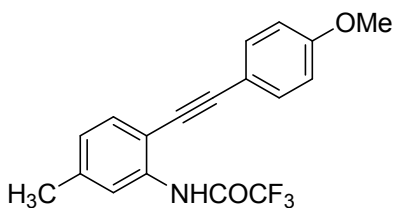
Colorless solid (306 mg, 92%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.81 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.34 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 2.33 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.39, 154.23 (q, *J* = 37.3 Hz), 135.37, 133.52, 133.00, 131.74, 130.16, 119.48, 115.85 (q, *J* = 290.1 Hz), 114.36, 113.83, 113.78, 97.81, 81.95, 55.36, 20.80; HRMS (ESI) *m/z* calcd for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 334.1049; Found: 334.1048.

**N-(4-chloro-2-((4-methoxyphenyl)ethynyl)phenyl)-2,2,2-trifluoroacetamide (2l)**



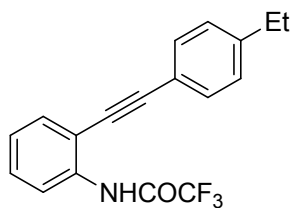
Colorless solid (332 mg, 94%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.82 (s, 1H), 8.30 (d, *J* = 8.9 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.33 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.73, 154.38 (q, *J* = 37.3 Hz), 134.41, 133.16, 130.97, 130.70, 129.42, 120.66, 115.69 (q, *J* = 290.0 Hz), 115.53, 114.46, 113.12, 99.46, 80.66, 55.39; HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>12</sub>ClF<sub>3</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 354.0503; Found: 354.0501.

**2,2,2-trifluoro-N-(2-((4-methoxyphenyl)ethynyl)-5-methylphenyl)acetamide (2o)**



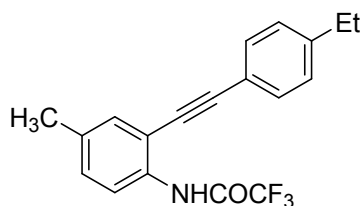
Colorless solid (320 mg, 96%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.85 (s, 1H), 8.19 (s, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 2.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.30, 154.35 (q, *J* = 37.3 Hz), 140.17, 135.78, 132.92, 131.16, 126.37, 120.14, 115.81 (q, *J* = 290.1 Hz), 114.34, 113.94, 110.97, 97.55, 81.88, 55.35, 21.88; HRMS (ESI) *m/z* calcd for C<sub>18</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>2</sub>K [M + K]<sup>+</sup>: 372.0608; Found: 372.0631.

**N-(2-((4-ethylphenyl)ethynyl)phenyl)-2,2,2-trifluoroacetamide (2p)**



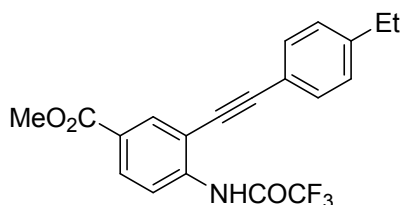
White solid (298 mg, 94%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (s, 1H), 8.36 (d,  $J = 8.3$  Hz, 1H), 7.54 (dd,  $J = 7.7, 1.0$  Hz, 1H), 7.44 (d,  $J = 8.1$  Hz, 2H), 7.42 – 7.37 (m, 1H), 7.24 – 7.18 (m, 3H), 2.68 (q,  $J = 7.6$  Hz, 2H), 1.25 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.4 (q,  $J = 37.4$  Hz), 145.99, 136.03, 131.59, 131.50, 129.66, 128.30, 125.51, 119.56, 118.84, 115.78 (q,  $J = 290.1$  Hz), 113.72, 98.42, 82.29, 28.92, 15.28; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NONa}$  [ $\text{M} + \text{Na}$ ] $^+$ : 340.0920; Found: 340.0926.

**N-(2-((4-ethylphenyl)ethynyl)-4-methylphenyl)-2,2,2-trifluoroacetamide (2q)**



Colorless solid (308 mg, 93%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (s, 1H), 8.22 (d,  $J = 8.4$  Hz, 1H), 7.43 (d,  $J = 8.1$  Hz, 2H), 7.35 (s, 1H), 7.23 – 7.17 (m, 3H), 2.68 (q,  $J = 7.6$  Hz, 2H), 2.33 (s, 3H), 1.25 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.27 (q,  $J = 37.3$  Hz), 145.87, 135.38, 133.66, 131.88, 131.47, 130.35, 128.27, 119.51, 118.97, 115.85 (q,  $J = 290.0$  Hz), 113.61, 97.96, 82.51, 28.90, 20.78, 15.24; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}\text{F}_3\text{NOK}$  [ $\text{M} + \text{K}$ ] $^+$ : 370.0816; Found: 370.0828.

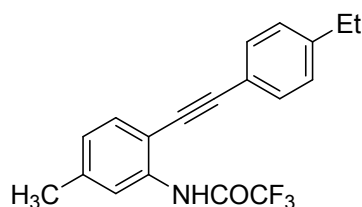
**methyl 3-((4-ethylphenyl)ethynyl)-4-(2,2,2-trifluoroacetamido)benzoate (2r)**



Yellow solid (345 mg, 92%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.02 (s, 1H), 8.45 (d,  $J = 8.7$  Hz, 1H), 8.22 (d,  $J = 1.8$  Hz, 1H), 8.04 (dd,  $J = 8.7, 1.7$  Hz, 1H), 7.45 (d,  $J = 8.1$  Hz, 2H), 7.24 (d,  $J = 8.0$  Hz, 2H), 3.93 (s, 3H), 2.69 (q,  $J = 7.6$  Hz, 2H), 1.26 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.58,

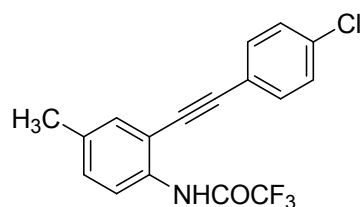
154.61 (q,  $J = 37.9$  Hz), 146.34, 139.38, 132.94, 131.57, 130.89, 128.34, 127.20, 118.99, 118.40, 115.60 (q,  $J = 290.19$  Hz), 113.80, 99.28, 81.42, 52.35, 28.91, 15.21; HRMS (ESI)  $m/z$  calcd for  $C_{20}H_{16}F_3NO_3K$   $[M + K]^+$ : 414.0714; Found: 414.0727.

**N-(2-((4-ethylphenyl)ethynyl)-5-methylphenyl)-2,2,2-trifluoroacetamide (2s)**



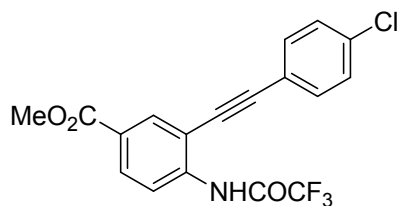
Colorless solid (314 mg, 95%);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.85 (s, 1H), 8.20 (s, 1H), 7.42 (d,  $J = 8.0$  Hz, 3H), 7.21 (d,  $J = 7.9$  Hz, 2H), 7.01 (d,  $J = 7.9$  Hz, 1H), 2.68 (q,  $J = 7.6$  Hz, 2H), 2.40 (s, 3H), 1.25 (t,  $J = 7.6$  Hz, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  154.38 (q,  $J = 37.4$  Hz), 145.73, 140.38, 135.91, 131.40, 131.30, 128.24, 126.37, 120.16, 119.08, 115.81 (q,  $J = 290.2$  Hz), 110.82, 97.73, 82.46, 28.88, 21.89, 15.25; HRMS (ESI)  $m/z$  calcd for  $C_{19}H_{16}F_3NOK$   $[M + K]^+$ : 370.0816; Found: 370.0818.

**N-(2-((4-chlorophenyl)ethynyl)-4-methylphenyl)-2,2,2-trifluoroacetamide (2u)**



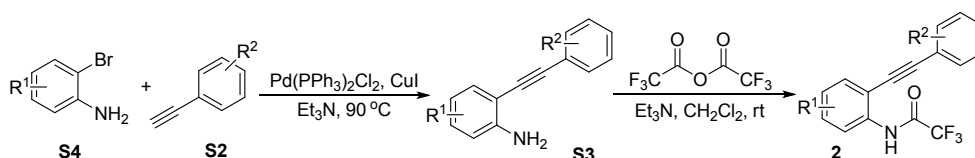
White solid (313 mg, 93%);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.73 (s, 1H), 8.21 (d,  $J = 8.5$  Hz, 1H), 7.45 – 7.41 (m, 2H), 7.36 (dd,  $J = 6.5, 2.0$  Hz, 3H), 7.22 (d,  $J = 8.4$  Hz, 1H), 2.34 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  154.25 (q,  $J = 37.3$  Hz), 135.54, 135.41, 133.69, 132.62, 132.03, 130.83, 129.09, 120.30, 119.71, 115.81 (q,  $J = 290.1$  Hz), 113.10, 96.37, 84.11, 20.78; HRMS (ESI)  $m/z$  calcd for  $C_{17}H_{11}ClF_3NOK$   $[M + K]^+$ : 376.0113; Found: 376.0107.

**methyl 3-((4-chlorophenyl)ethynyl)-4-(2,2,2-trifluoroacetamido)benzoate (2v)**



Yellow solid (351 mg, 92%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.93 (s, 1H), 8.44 (d,  $J = 8.7$  Hz, 1H), 8.22 (d,  $J = 1.7$  Hz, 1H), 8.06 (dd,  $J = 8.7, 1.7$  Hz, 1H), 7.45 (d,  $J = 8.5$  Hz, 2H), 7.38 (d,  $J = 8.5$  Hz, 2H), 3.93 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.43, 154.55 (q,  $J = 38.0$  Hz), 139.41, 135.88, 133.12, 132.70, 131.31, 129.18, 127.30, 119.72, 119.16, 115.57 (q,  $J = 290.2$  Hz), 113.24, 97.62, 82.94, 52.39; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{11}\text{ClF}_3\text{NO}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 404.0272; Found: 404.0274.

### General Procedure for the Preparation of **2f**, **2h**, **2i**, **2n**<sup>3</sup>



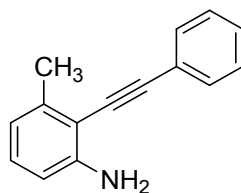
To a solution of **S4** (3 mmol, 1.0 equiv),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.06 mmol, 2 mol%), and  $\text{CuI}$  (0.12 mmol, 4 mol%) in anhydrous  $\text{Et}_3\text{N}$  (9 mL) under nitrogen atmosphere was added aryl alkynes **S2** (4.5 mmol, 1.5 equiv), the resulting solution was stirred at 90 °C until the disappearance of the starting material according to the TLC, the reaction mixture was filtered through a pad of celite, eluting with  $\text{EtOAc}$  ( $3 \times 5$  mL). The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified by flash chromatography on a silica gel (using petroleum ether/ethyl acetate = 40:1 as the eluent) to give **S3f**, **S3h**, **S3i**, **S3n**.

To a solution of **S3** (1 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (10 mL) at 0 °C, was added  $\text{Et}_3\text{N}$  (2 mmol, 2.0 equiv), trifluoroacetic anhydride (1.5 mmol, 1.5 equiv). The reaction mixture was warmed to room temperature and then stirred at this temperature until the disappearance of the starting material according to the TLC.  $\text{H}_2\text{O}$  (5 mL) was added to the reaction mixture and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic extracts were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified by flash chromatography on a silica gel (using petroleum ether/ethyl acetate = 60:1 as the eluent) to give product **2f**, **2h**, **2i**, **2n**.

**The following is the characterization data for the new compounds**

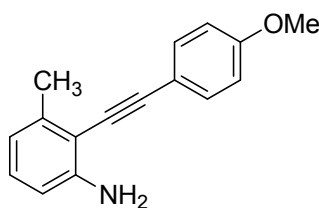


### 3-methyl-2-(phenylethynyl)aniline (S3f)



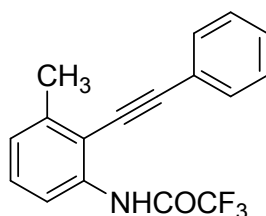
Yellow oil (279mg, 45%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (dd,  $J = 7.6, 1.7$  Hz, 2H), 7.34 (q,  $J = 5.2$  Hz, 3H), 7.02 (t,  $J = 7.8$  Hz, 1H), 6.62 (d,  $J = 7.5$  Hz, 1H), 6.58 (d,  $J = 8.1$  Hz, 1H), 3.77 (br, 2H), 2.45 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.73, 141.02, 131.40, 129.06, 128.41, 128.16, 123.61, 119.27, 111.78, 108.37, 98.90, 84.83, 21.04; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{13}\text{NK}$   $[\text{M} + \text{K}]^+$ : 246.0680; Found: 246.0678.

### 2-((4-methoxyphenyl)ethynyl)-3-methylaniline (S3n)



Yellow oil (299mg, 42%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 8.7$  Hz, 2H), 7.00 (t,  $J = 7.8$  Hz, 1H), 6.87 (d,  $J = 8.6$  Hz, 2H), 6.61 (d,  $J = 7.5$  Hz, 1H), 6.57 (d,  $J = 8.1$  Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.59, 147.63, 140.80, 132.83, 128.71, 119.19, 115.77, 114.06, 111.68, 108.70, 98.81, 83.41, 55.35, 21.04; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{NONa}$   $[\text{M} + \text{Na}]^+$ : 260.1046; Found: 260.1036.

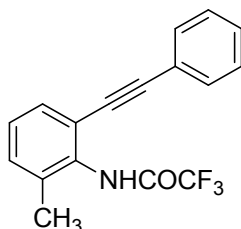
### 2,2,2-trifluoro-N-(3-methyl-2-(phenylethynyl)phenyl)acetamide (2f)



Colorless solid (267 mg, 88%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.93 (s, 1H), 8.20 (d,  $J = 8.3$  Hz, 1H), 7.56 – 7.50 (m, 2H), 7.40 (dd,  $J = 6.4, 3.6$  Hz, 3H), 7.29 (t,  $J = 8.0$  Hz, 1H), 7.10 (d,  $J = 7.7$  Hz, 1H),

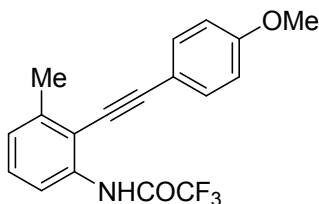
2.53 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.4 (q,  $J = 37.43$  Hz), 140.90, 136.10, 131.37, 129.26, 129.19, 128.72, 126.63, 121.96, 116.87, 115.83 (q,  $J = 290.1$  Hz), 113.45, 102.02, 81.95, 20.99; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}$   $[\text{M} + \text{H}]^+$ : 304.0944; Found: 304.0941.

**2,2,2-trifluoro-N-(2-methyl-6-(phenylethynyl)phenyl)acetamide (2i)**



Colorless solid (261 mg, 86%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (s, 1H), 7.47 (dd,  $J = 6.5, 2.8$  Hz, 2H), 7.42 (t,  $J = 4.6$  Hz, 1H), 7.37 – 7.33 (m, 3H), 7.23 (d,  $J = 4.8$  Hz, 2H), 2.26 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.27 (q,  $J = 37.2$  Hz), 135.70, 132.99, 131.55, 131.34, 130.07, 128.90, 128.52, 128.12, 122.40, 120.81, 116.13 (q,  $J = 289.9$  Hz), 95.76, 84.71, 18.39; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{12}\text{F}_3\text{NONa}$   $[\text{M} + \text{Na}]^+$ : 326.0763; Found: 326.0759.

**2,2,2-trifluoro-N-(2-((4-methoxyphenyl)ethynyl)-3-methylphenyl)acetamide (2n)**

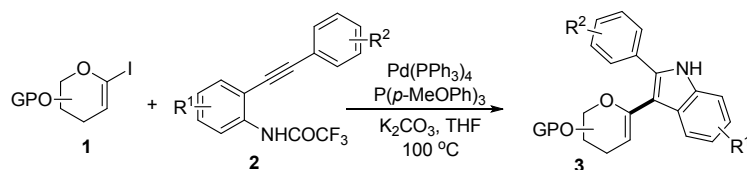


White solid (300 mg, 90%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (s, 1H), 8.12 (d,  $J = 8.3$  Hz, 1H), 7.40 (d,  $J = 8.8$  Hz, 2H), 7.20 (d,  $J = 7.9$  Hz, 1H), 7.03 (d,  $J = 7.6$  Hz, 1H), 6.85 (d,  $J = 8.8$  Hz, 2H), 3.78 (s, 3H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.36, 153.36 (q,  $J = 37.4$  Hz), 139.55, 134.85, 131.88, 127.75, 125.54, 115.78 (q,  $J = 290.1$  Hz), 115.74, 113.34, 112.93, 112.78, 101.13, 79.75, 54.37, 19.98; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_3\text{NO}_2$   $[\text{M} + \text{H}]^+$ : 334.1049; Found: 334.1075.

**Synthesis of substrates 4**

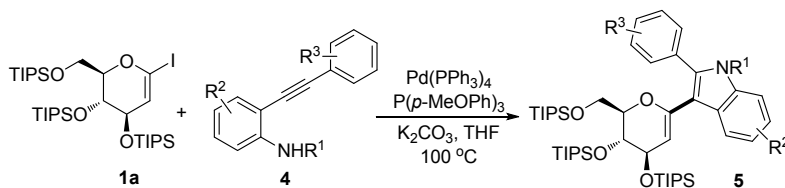
The *o*-alkynylanilines **4a**,<sup>4</sup> **4b-h**<sup>2a,5</sup> were prepared following the reported procedures.

### General procedure for the preparation of products 3



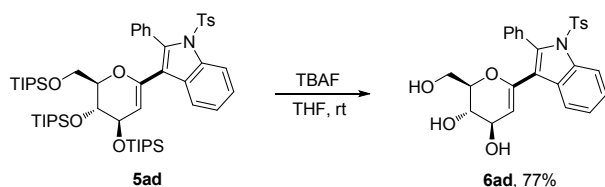
To the mixture of **2** (0.15 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.0075 mmol, 5 mol %),  $\text{K}_2\text{CO}_3$  (0.3 mmol), and  $\text{P}(p\text{-MeOPh})_3$  (0.015 mmol, 10 mol %) in a Schlenk flask was added a solution of **1** (0.18 mmol) in THF (2 mL) under nitrogen atmosphere. The reaction mixture was heated at  $100^\circ\text{C}$  for 6h.  $\text{H}_2\text{O}$  (5 mL) was added to the reaction mixture and the resulting mixture was extracted with ethyl acetate ( $3 \times 5$  mL). The combined organic extracts were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified by flash chromatography on a silica gel (using petroleum ether/ethyl acetate = 50:1 as the eluent) to give product **3**.

### General procedure for the preparation of products 5



To the mixture of **4** (0.15 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.0075 mmol, 5 mol %),  $\text{K}_2\text{CO}_3$  (0.3 mmol), and  $\text{P}(p\text{-MeOPh})_3$  (0.015 mmol, 10 mol %) in a Schlenk flask was added a solution of **1a** (0.18 mmol) in THF (2 mL) under nitrogen atmosphere. The reaction mixture was heated at  $100^\circ\text{C}$  for 6h.  $\text{H}_2\text{O}$  (5 mL) was added to the reaction mixture and the resulting mixture was extracted with ethyl acetate ( $3 \times 5$  mL). The combined organic extracts were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified by flash chromatography on a silica gel (using petroleum ether/ethyl acetate = 20:1 as the eluent) to give product **5**.

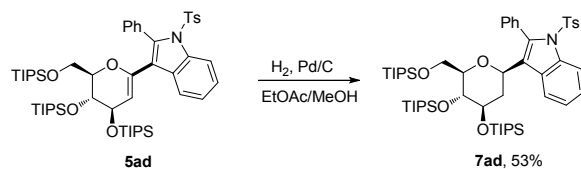
### Synthesis of product 6ad



To the solution of **5ad** (67.2 mg, 0.07 mmol) in THF (7 mL) was added tetrabutylammonium fluoride (TBAF) (126 mg, 0.48 mmol). The mixture was stirred at room temperature about 18 h.  $\text{H}_2\text{O}$  (5 mL) was added to the reaction mixture and THF was removed under reduced pressure. The resulting

mixture was extracted with ethyl acetate (3× 5 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography on a silica gel (using petroleum ether/ethyl acetate = 1:1 as the eluent) to give product **6ad** (26.6 mg, 77%).

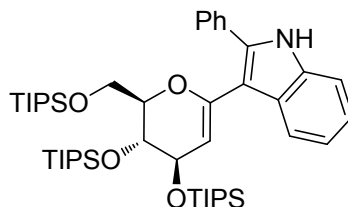
#### Synthesis of product **7ad**



A 25-mL oven-dried flask was charged with **5ad** (25 mg, 0.026 mmol), Pd/C (10 wt %, 50 mg), and EtOAc/MeOH (4 mL, v/v = 1/1). The flask was evacuated and refilled with H<sub>2</sub> (balloon). The mixture was stirred at room temperature about 17 h and filtered through a pad of celite, which was washed with ethyl acetate (3×5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>. The filtrate was concentrated, and the residue was purified by flash chromatography on a silica gel (using petroleum ether/dichloromethane = 2:1 as the eluent) to give product **7ad** (13.3 mg, 53%).

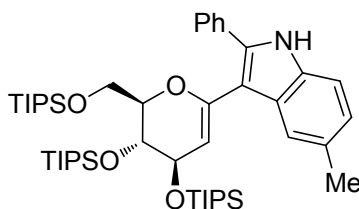
## Characterization of products

### 3-((2*R*,3*R*,4*R*)-3,4-bis((triisopropylsilyloxy)methyl)-2-(((triisopropylsilyloxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-phenyl-1H-indole (3aa)



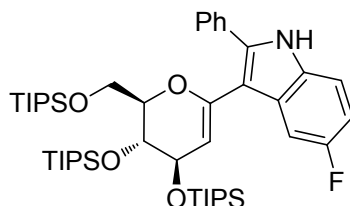
Colorless oil (109 mg, 90%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (s, 1H), 8.04 (d,  $J = 7.8$  Hz, 1H), 7.69 (d,  $J = 7.1$  Hz, 2H), 7.37 – 7.28 (m, 4H), 7.18 (t,  $J = 7.5$  Hz, 1H), 7.11 (t,  $J = 7.5$  Hz, 1H), 4.91 (d,  $J = 5.3$  Hz, 1H), 4.46 (dd,  $J = 6.7, 5.2$  Hz, 1H), 4.26 – 4.16 (m, 2H), 4.10 – 4.02 (m, 2H), 1.13 – 0.98 (m, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.92, 135.82, 135.47, 132.74, 128.82, 128.44, 128.29, 127.79, 122.53, 121.25, 120.42, 110.68, 110.50, 100.29, 81.45, 70.07, 66.85, 61.95, 18.25, 18.24, 18.19, 18.14, 18.12, 18.10, 18.02, 17.97, 17.73, 12.54, 12.36, 12.07;  $[\alpha]_{\text{D}}^{23} = +12.1$  ( $c = 0.54$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{47}\text{H}_{79}\text{NO}_4\text{Si}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 828.5214; Found: 828.5229.

### 3-((2*R*,3*R*,4*R*)-3,4-bis((triisopropylsilyloxy)methyl)-2-(((triisopropylsilyloxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-5-methyl-2-phenyl-1H-indole (3ab)



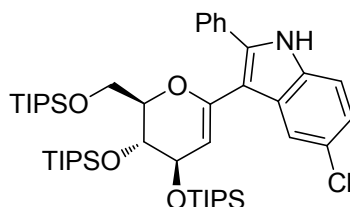
Colorless oil (106 mg, 86%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (s, 1H), 7.70 – 7.65 (m, 3H), 7.34 (t,  $J = 7.4$  Hz, 2H), 7.29 (d,  $J = 7.3$  Hz, 1H), 7.21 (d,  $J = 8.2$  Hz, 1H), 7.00 (d,  $J = 8.2$  Hz, 1H), 5.01 – 4.93 (m, 1H), 4.43 (t,  $J = 6.3$  Hz, 1H), 4.26 (d,  $J = 1.3$  Hz, 1H), 4.20 (dd,  $J = 10.7, 6.1$  Hz, 1H), 4.16 – 4.12 (m, 1H), 4.08 (dd,  $J = 10.7, 6.6$  Hz, 1H), 2.43 (s, 3H), 1.13 – 1.01 (m, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.08, 135.84, 133.81, 132.79, 129.63, 129.07, 128.43, 128.00, 127.66, 124.15, 120.21, 110.25, 100.58, 81.26, 69.70, 66.81, 62.07, 21.47, 18.27, 18.23, 18.18, 18.11, 18.09, 18.05, 18.01, 17.98, 17.74, 12.55, 12.38, 12.31, 12.03;  $[\alpha]_{\text{D}}^{23} = +7.6$  ( $c = 0.52$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{48}\text{H}_{81}\text{NO}_4\text{Si}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 842.5371; Found: 842.5376.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-5-fluoro-2-phenyl-1H-indole (3ac)**



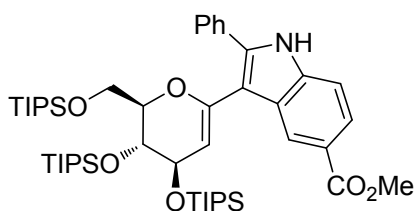
Colorless oil (101 mg, 82%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (s, 1H), 7.72 – 7.66 (m, 3H), 7.37 – 7.29 (m, 3H), 7.22 (dd, *J* = 8.8, 4.3 Hz, 1H), 7.12 – 6.86 (m, 1H), 4.88 (dd, *J* = 5.3, 1.3 Hz, 1H), 4.49 – 4.44 (m, 1H), 4.22 (dd, *J* = 11.2, 7.7 Hz, 1H), 4.15 (d, *J* = 1.6 Hz, 1H), 4.07 – 3.99 (m, 2H), 1.13 – 0.97 (m, 63H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.43 (d, *J*<sub>C-F</sub> = 236.0 Hz), 146.51, 137.53, 132.15 (d, *J*<sub>C-F</sub> = 44.4 Hz), 129.45 (d, *J*<sub>C-F</sub> = 30.0 Hz), 129.03 (d, *J*<sub>C-F</sub> = 35.4 Hz), 128.50, 128.25, 128.05, 111.22, 111.09 (d, *J*<sub>C-F</sub> = 7.5 Hz), 110.79, 106.10 (d, *J*<sub>C-F</sub> = 24.4 Hz), 100.34, 81.58, 69.99, 66.68, 61.86, 18.23, 18.22, 18.17, 18.12, 18.07, 18.02, 17.97, 17.73, 12.50, 12.32, 12.30, 11.98; [α]<sub>D</sub><sup>23</sup> = +8.6 (*c* = 0.75, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>47</sub>H<sub>78</sub>FNO<sub>4</sub>Si<sub>3</sub>Na [M + Na]<sup>+</sup>: 846.5120; Found: 846.5109.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-5-chloro-2-phenyl-1H-indole (3ad)**



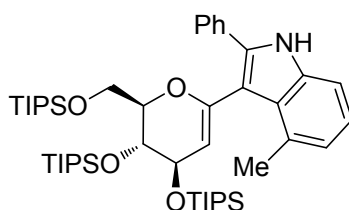
Colorless foam (107 mg, 85%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (s, 1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.35 (dd, *J* = 14.1, 6.6 Hz, 3H), 7.24 (s, 1H), 7.13 (dd, *J* = 8.6, 2.0 Hz, 1H), 4.93 (dd, *J* = 5.4, 1.4 Hz, 1H), 4.44 (dd, *J* = 6.8, 5.5 Hz, 1H), 4.20 (d, *J* = 1.7 Hz, 1H), 4.14 – 4.08 (m, 3H), 1.08 (dd, *J* = 29.3, 4.5 Hz, 63H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.43, 137.06, 133.76, 132.17, 129.79, 128.53, 128.20, 128.12, 126.18, 122.83, 120.17, 111.63, 110.25, 100.77, 81.55, 69.73, 66.61, 61.99, 18.25, 18.20, 18.14, 18.10, 17.99, 17.73, 12.51, 12.34, 12.30, 12.00; [α]<sub>D</sub><sup>23</sup> = +2.6 (*c* = 0.60, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>47</sub>H<sub>78</sub>ClNO<sub>4</sub>Si<sub>3</sub>Na [M + Na]<sup>+</sup>: 862.4825; Found: 862.4829.

**methyl 3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-phenyl-1H-indole-5-carboxylate (3ae)**



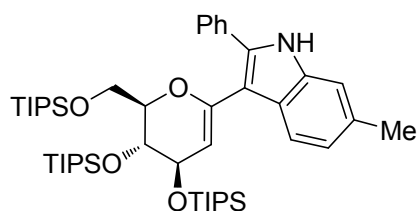
Colorless foam (118 mg, 91%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.60 (s, 1H), 8.48 (s, 1H), 7.91 (dd,  $J = 8.5, 1.5$  Hz, 1H), 7.68 (d,  $J = 6.8$  Hz, 2H), 7.52 – 7.45 (m, 1H), 7.34 (d,  $J = 8.0$  Hz, 2H), 7.21 (dd,  $J = 16.6, 8.2$  Hz, 1H), 5.10 (dd,  $J = 5.3, 1.0$  Hz, 1H), 4.40 (t,  $J = 6.6$  Hz, 1H), 4.34 – 4.26 (m, 2H), 4.24 – 4.20 (m, 1H), 3.99 (dd,  $J = 10.3, 6.1$  Hz, 1H), 3.90 (s, 3H), 1.13 – 0.99 (m, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.22, 146.50, 138.06, 137.06, 135.25, 132.15, 128.49, 128.11, 128.09, 124.14, 123.05, 122.45, 111.53, 110.50, 101.09, 81.12, 69.28, 66.58, 62.01, 51.71, 18.23, 18.18, 18.03, 18.02, 12.54, 12.38, 12.02;  $[\alpha]_{\text{D}}^{23} = +1.6$  ( $c = 0.52$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{49}\text{H}_{81}\text{NO}_6\text{Si}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 886.5264; Found: 886.5255.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-4-methyl-2-phenyl-1H-indole (3af)**



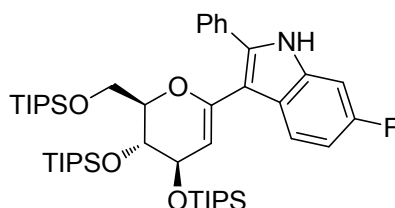
Colorless oil (88 mg, 72%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (s, 1H), 7.69 – 7.65 (m, 2H), 7.36 (t,  $J = 7.3$  Hz, 2H), 7.29 (t,  $J = 7.3$  Hz, 1H), 7.18 (d,  $J = 8.0$  Hz, 1H), 7.07 (t,  $J = 7.6$  Hz, 1H), 6.88 (d,  $J = 7.1$  Hz, 1H), 4.99 (dd,  $J = 5.2, 1.1$  Hz, 1H), 4.47 (dd,  $J = 7.5, 6.2$  Hz, 1H), 4.33 – 4.26 (m, 2H), 4.17 (dd,  $J = 3.3, 2.0$  Hz, 1H), 3.89 (dd,  $J = 10.0, 5.9$  Hz, 1H), 2.70 (s, 3H), 1.11 – 0.96 (m, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.51, 136.78, 135.36, 132.72, 132.00, 128.52, 128.14, 127.88, 127.18, 122.52, 121.69, 110.95, 108.30, 103.34, 81.31, 69.39, 66.82, 61.83, 20.02, 18.26, 18.22, 18.11, 18.09, 17.73, 12.49, 12.33, 12.31, 12.00;  $[\alpha]_{\text{D}}^{23} = +10.2$  ( $c = 0.62$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{48}\text{H}_{81}\text{NO}_4\text{Si}_3\text{K}$   $[\text{M} + \text{K}]^+$ : 858.5105; Found: 858.5107.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-6-methyl-2-phenyl-1H-indole (3ag)**



Colorless oil (102 mg, 83%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (s, 1H), 7.89 (d,  $J = 8.1$  Hz, 1H), 7.68 (d,  $J = 7.1$  Hz, 2H), 7.34 (t,  $J = 7.3$  Hz, 2H), 7.27 (t,  $J = 7.3$  Hz, 1H), 7.11 (s, 1H), 6.94 (d,  $J = 8.1$  Hz, 1H), 4.91 (dd,  $J = 5.2, 1.1$  Hz, 1H), 4.45 (dd,  $J = 6.8, 5.2$  Hz, 1H), 4.22 – 4.16 (m, 2H), 4.09 – 4.03 (m, 2H), 2.44 (s, 3H), 1.13 – 0.98 (m, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.05, 135.90, 135.11, 132.89, 132.35, 128.39, 128.16, 127.58, 126.69, 122.17, 120.82, 110.52, 110.43, 100.07, 81.35, 70.01, 66.85, 61.92, 21.79, 18.24, 18.24, 18.19, 18.14, 18.12, 18.10, 18.04, 17.99, 17.73, 12.53, 12.35, 12.31, 12.04;  $[\alpha]_{\text{D}}^{23} = +3.8$  ( $c = 0.45$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{48}\text{H}_{81}\text{NO}_4\text{Si}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 842.5366; Found: 842.5360.

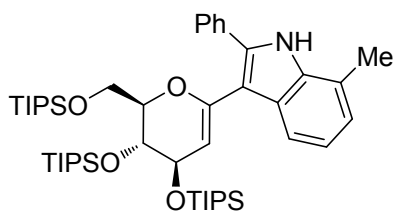
**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-6-fluoro-2-phenyl-1H-indole (3ah)**



Colorless foam (96 mg, 78%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (s, 1H), 8.00 (dd,  $J = 8.8, 5.5$  Hz, 1H), 7.69 – 7.64 (m, 2H), 7.35 – 7.28 (m, 3H), 6.98 (dd,  $J = 9.4, 2.2$  Hz, 1H), 6.86 (td,  $J = 9.7, 2.3$  Hz, 1H), 4.88 (dd,  $J = 5.3, 1.4$  Hz, 1H), 4.51 – 4.45 (m, 1H), 4.26 (dd,  $J = 11.3, 7.9$  Hz, 1H), 4.13 (d,  $J = 1.6$  Hz, 1H), 4.04 (dt,  $J = 5.1, 1.8$  Hz, 1H), 3.98 (dd,  $J = 11.3, 4.3$  Hz, 1H), 1.06 (ddd,  $J = 33.1, 20.2, 2.0$  Hz, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.22 (d,  $J_{\text{C-F}} = 239.1$  Hz), 146.56, 136.12 (d,  $J_{\text{C-F}} = 3.5$  Hz), 135.37 (d,  $J_{\text{C-F}} = 12.5$  Hz), 132.40, 128.50, 128.18, 127.88, 125.35, 122.30 (d,  $J_{\text{C-F}} = 9.8$  Hz), 110.52, 109.09 (d,  $J_{\text{C-F}} = 24.1$  Hz), 100.36, 96.87 (d,  $J_{\text{C-F}} = 26.3$  Hz), 81.57, 70.10, 66.70, 61.87, 18.24, 18.22, 18.17, 18.11, 18.09, 17.97, 17.73, 12.51, 12.32, 12.04;  $[\alpha]_{\text{D}}^{23} = +2.5$  ( $c = 0.56$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{47}\text{H}_{78}\text{FNO}_4\text{Si}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 846.5120; Found: 846.5121.

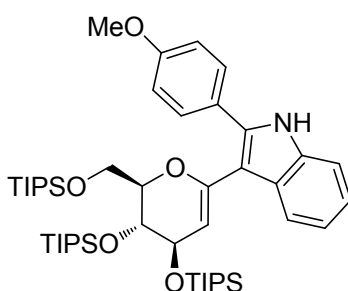
**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-7-methyl-2-phenyl-1H-indole (3ai)**





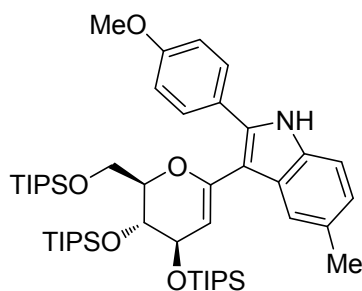
Colorless oil (93 mg, 76%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (s, 1H), 7.89 (d,  $J = 7.8$  Hz, 1H), 7.72 (d,  $J = 7.2$  Hz, 2H), 7.37 (t,  $J = 7.4$  Hz, 2H), 7.30 (t,  $J = 7.3$  Hz, 1H), 7.04 (t,  $J = 7.5$  Hz, 1H), 6.99 (d,  $J = 7.0$  Hz, 1H), 4.90 (d,  $J = 5.2$  Hz, 1H), 4.45 (t,  $J = 6.0$  Hz, 1H), 4.23 – 4.16 (m, 2H), 4.08 – 4.02 (m, 2H), 2.49 (s, 3H), 1.12 – 0.98 (m, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.01, 135.62, 134.98, 132.91, 128.44, 128.36, 128.31, 127.77, 123.06, 120.66, 119.60, 119.02, 111.20, 100.19, 81.36, 70.04, 66.84, 61.89, 18.24, 18.23, 18.19, 18.14, 18.12, 18.10, 18.05, 18.02, 17.98, 17.73, 16.62, 12.52, 12.34, 12.30, 12.05;  $[\alpha]_{\text{D}}^{23} = +0.86$  ( $c = 0.61$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{48}\text{H}_{82}\text{NO}_4\text{Si}_3$   $[\text{M} + \text{H}]^+$ : 820.5546; Found: 820.5531.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-methoxyphenyl)-1H-indole (3aj)**



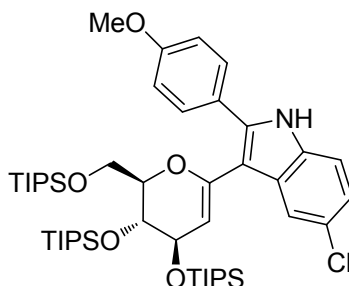
Colorless foam (108 mg, 86%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (s, 1H), 8.00 (d,  $J = 7.7$  Hz, 1H), 7.61 (d,  $J = 8.8$  Hz, 2H), 7.29 (d,  $J = 7.9$  Hz, 1H), 7.17 – 7.08 (m, 2H), 6.87 (d,  $J = 8.8$  Hz, 2H), 4.91 (dd,  $J = 5.3, 1.3$  Hz, 1H), 4.46 (dd,  $J = 7.0, 5.2$  Hz, 1H), 4.24 – 4.16 (m, 2H), 4.11 – 4.03 (m, 2H), 3.81 (s, 3H), 1.13 – 0.98 (m, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  154.00, 141.75, 130.50, 130.01, 124.19, 123.59, 119.94, 116.90, 115.62, 115.01, 108.59, 105.11, 104.54, 94.82, 76.09, 64.70, 61.51, 56.64, 49.92, 12.94, 12.90, 12.85, 12.80, 12.79, 12.43, 7.22, 7.05, 7.00, 6.73;  $[\alpha]_{\text{D}}^{23} = +1.5$  ( $c = 0.89$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{48}\text{H}_{82}\text{NO}_5\text{Si}_3$   $[\text{M} + \text{H}]^+$ : 836.5501; Found: 836.5497.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-methoxyphenyl)-5-methyl-1H-indole (3ak)**



Colorless oil (112 mg, 88%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (s, 1H), 7.62 (s, 1H), 7.60 (d,  $J = 8.8$  Hz, 2H), 7.18 (d,  $J = 8.2$  Hz, 1H), 6.99 – 6.96 (m, 1H), 6.87 (d,  $J = 8.8$  Hz, 2H), 4.97 (dd,  $J = 5.3, 1.2$  Hz, 1H), 4.42 (t,  $J = 6.3$  Hz, 1H), 4.26 (d,  $J = 1.5$  Hz, 1H), 4.20 (dd,  $J = 10.7, 6.2$  Hz, 1H), 4.15 (dd,  $J = 3.3, 2.1$  Hz, 1H), 4.07 (dd,  $J = 10.6, 6.6$  Hz, 1H), 3.81 (s, 3H), 2.42 (s, 3H), 1.13 – 1.02 (m, 63H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.23, 147.23, 135.85, 133.66, 129.49, 129.24, 129.15, 125.40, 123.77, 119.96, 113.88, 110.13, 109.43, 100.46, 81.21, 69.66, 66.83, 62.09, 55.23, 55.18, 21.45, 18.27, 18.24, 18.18, 18.08, 17.73, 12.55, 12.38, 12.31, 12.02;  $[\alpha]_{\text{D}}^{23} = +2.5$  ( $c = 0.38$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{49}\text{H}_{83}\text{NO}_5\text{Si}_3\text{K}$   $[\text{M} + \text{K}]^+$ : 888.5211; Found: 888.5207.

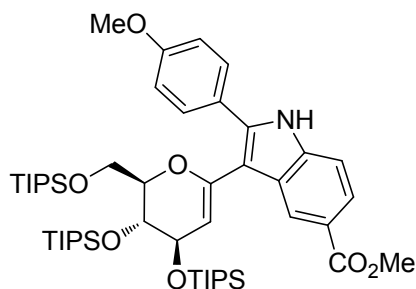
**3-((2R,3R,4R)-3,4-bis((triisopropylsilyloxy)methyl)-2-(((triisopropylsilyloxy)methyl)methyl)-3,4-dihydro-2H-pyran-6-yl)-5-chloro-2-(4-methoxyphenyl)-1H-indole (3a)**



Colorless oil (111 mg, 85%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (s, 1H), 7.82 (d,  $J = 1.4$  Hz, 1H), 7.51 (d,  $J = 8.7$  Hz, 2H), 7.11 (d,  $J = 8.5$  Hz, 1H), 7.04 (dd,  $J = 8.6, 1.9$  Hz, 1H), 6.78 (d,  $J = 8.7$  Hz, 2H), 4.97 (d,  $J = 5.3$  Hz, 1H), 4.42 (t,  $J = 6.2$  Hz, 1H), 4.22 (s, 1H), 4.16 – 4.06 (m, 3H), 3.79 (s, 3H), 1.12 – 1.01 (m, 63H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.55, 146.58, 137.07, 133.62, 129.93, 129.35, 126.08, 124.69, 122.46, 119.88, 113.97, 111.49, 109.47, 100.67, 81.51, 69.70, 66.62, 62.02, 55.21, 18.23, 18.23, 18.20, 18.14, 18.07, 18.05, 17.72, 12.52, 12.36, 11.99;  $[\alpha]_{\text{D}}^{23} = +2.8$  ( $c = 0.58$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{48}\text{H}_{80}\text{ClNO}_5\text{Si}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 892.4925; Found: 892.4929.

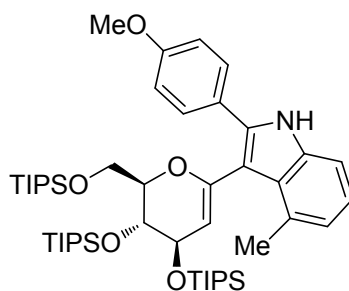
**methyl**

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-methoxyphenyl)-1H-indole-5-carboxylate (3am)**



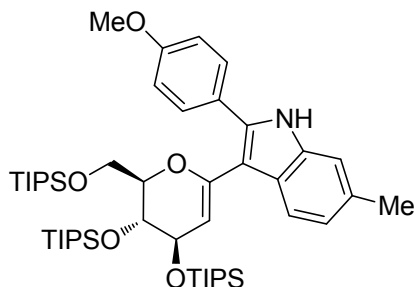
Colorless foam (123 mg, 92%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.61 (s, 1H), 8.45 (s, 1H), 7.85 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 2H), 5.11 (d, *J* = 4.6 Hz, 1H), 4.39 (t, *J* = 6.5 Hz, 1H), 4.33 – 4.23 (m, 3H), 3.98 (dd, *J* = 10.3, 6.1 Hz, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 1.12 – 0.98 (m, 63H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.25, 159.55, 146.59, 137.95, 137.06, 129.29, 128.20, 124.60, 123.82, 122.65, 122.28, 113.93, 110.54, 110.42, 101.05, 81.12, 69.22, 66.55, 62.01, 55.13, 51.69, 18.24, 18.23, 18.19, 18.01, 17.99, 17.72, 12.53, 12.38, 11.98; [α]<sub>D</sub><sup>23</sup> = +12.3 (*c* = 0.85, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>50</sub>H<sub>83</sub>NO<sub>7</sub>Si<sub>3</sub>Na [M + Na]<sup>+</sup>: 916.5370; Found: 916.5378.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-methoxyphenyl)-4-methyl-1H-indole (3an)**



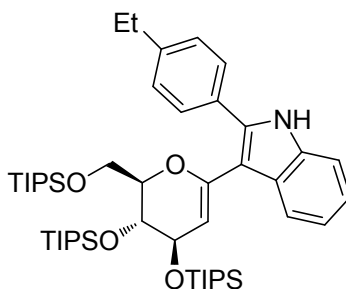
Colorless oil (87 mg, 68%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (s, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 7.2 Hz, 1H), 4.98 (dd, *J* = 5.3, 1.1 Hz, 1H), 4.47 (dd, *J* = 7.5, 6.2 Hz, 1H), 4.28 (dd, *J* = 9.9, 8.0 Hz, 2H), 4.17 (dd, *J* = 3.3, 2.0 Hz, 1H), 3.91 (dd, *J* = 10.1, 5.9 Hz, 1H), 3.81 (s, 3H), 2.69 (s, 3H), 1.11 – 1.08 (m, 19H), 1.07 – 1.03 (m, 23H), 1.00 – 0.96 (m, 21H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.44, 147.67, 136.81, 135.19, 131.74, 129.42, 127.23, 125.29, 122.22, 121.60, 113.95, 110.30, 108.18, 103.28, 81.30, 69.42, 66.84, 61.89, 55.12, 19.96, 18.25, 18.21, 18.09, 17.72, 12.49, 12.34, 12.01; [α]<sub>D</sub><sup>23</sup> = +6.8 (*c* = 0.68, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>49</sub>H<sub>83</sub>NO<sub>5</sub>Si<sub>3</sub>Na [M + Na]<sup>+</sup>: 872.5471; Found: 872.5480.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-methoxyphenyl)-6-methyl-1H-indole (3ao)**



Colorless foam (101 mg, 79%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (s, 1H), 7.85 (d,  $J = 8.1$  Hz, 1H), 7.59 (d,  $J = 8.7$  Hz, 2H), 7.07 (s, 1H), 6.92 (d,  $J = 8.1$  Hz, 1H), 6.86 (d,  $J = 8.7$  Hz, 2H), 4.93 – 4.90 (m, 1H), 4.43 (dd,  $J = 6.8, 5.4$  Hz, 1H), 4.17 (dd,  $J = 11.5, 6.5$  Hz, 2H), 4.11 – 4.04 (m, 2H), 3.81 (s, 3H), 2.43 (s, 3H), 1.13 – 0.99 (m, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.18, 147.22, 135.76, 135.10, 131.99, 129.39, 126.75, 125.48, 122.03, 120.53, 113.85, 110.36, 109.73, 99.91, 81.31, 69.98, 66.86, 61.96, 55.21, 21.76, 18.24, 18.20, 18.15, 18.10, 18.08, 18.01, 17.72, 12.53, 12.37, 12.31, 12.04;  $[\alpha]_{\text{D}}^{23} = +18.6$  ( $c = 0.92$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{49}\text{H}_{84}\text{NO}_5\text{Si}_3$   $[\text{M} + \text{H}]^+$ : 850.5652; Found: 850.5652.

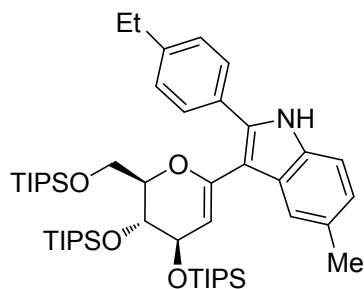
**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-ethylphenyl)-1H-indole (3ap)**



Colorless foam (110 mg, 88%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (s, 1H), 8.01 (d,  $J = 7.8$  Hz, 1H), 7.60 (d,  $J = 8.1$  Hz, 2H), 7.31 (d,  $J = 7.9$  Hz, 1H), 7.17 – 7.09 (m, 4H), 4.91 (dd,  $J = 5.2, 1.1$  Hz, 1H), 4.46 (dd,  $J = 6.8, 5.3$  Hz, 1H), 4.22 – 4.17 (m, 2H), 4.07 (dd,  $J = 11.2, 5.2$  Hz, 2H), 2.66 (q,  $J = 7.6$  Hz, 2H), 1.25 (t,  $J = 7.6$  Hz, 3H), 1.13 – 0.98 (m, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.99, 143.95, 136.06, 135.37, 130.06, 128.85, 128.24, 127.94, 122.32, 121.07, 120.32, 110.46, 110.27, 100.19, 81.34, 69.99, 66.85, 61.88, 28.71, 18.25, 18.20, 18.15, 18.11, 18.10, 17.74, 15.47, 12.54, 12.36, 12.31, 12.05;

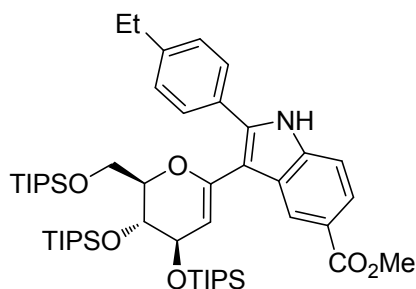
$[\alpha]_D^{23} = +12.5$  ( $c = 0.80$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{49}\text{H}_{83}\text{NO}_4\text{Si}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 856.5527;  
Found: 856.5508.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-ethylphenyl)-5-methyl-1H-indole (3aq)**



Colorless foam (114 mg, 90%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (s, 1H), 7.64 (s, 1H), 7.59 (d,  $J = 8.1$  Hz, 2H), 7.21 – 7.17 (m, 3H), 6.99 (d,  $J = 7.5$  Hz, 1H), 4.97 (d,  $J = 4.2$  Hz, 1H), 4.42 (t,  $J = 6.3$  Hz, 1H), 4.28 – 4.20 (m, 2H), 4.15 (dd,  $J = 3.3, 2.0$  Hz, 1H), 4.06 (dd,  $J = 10.5, 6.5$  Hz, 1H), 2.65 (q,  $J = 7.6$  Hz, 2H), 2.42 (s, 3H), 1.25 (t,  $J = 7.6$  Hz, 3H), 1.13 – 1.01 (m, 63H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.17, 143.78, 136.06, 133.71, 130.14, 129.53, 129.13, 127.95, 127.94, 123.92, 120.09, 110.16, 109.88, 100.50, 81.15, 69.64, 66.84, 62.01, 28.69, 21.46, 18.27, 18.23, 18.18, 18.10, 18.08, 17.73, 15.43, 12.55, 12.38, 12.31, 12.02;  $[\alpha]_D^{23} = +6.8$  ( $c = 0.55$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{50}\text{H}_{85}\text{NO}_4\text{Si}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 870.5684; Found: 870.5703.

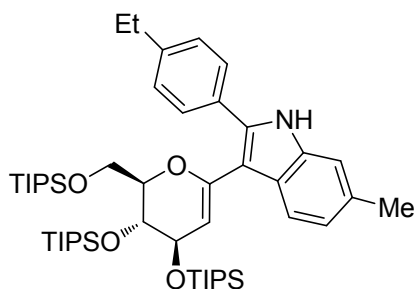
**methyl 3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-ethylphenyl)-1H-indole-5-carboxylate (3ar)**



Colorless foam (115 mg, 86%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (s, 1H), 8.46 (s, 1H), 7.91 (dd,  $J = 8.5, 1.4$  Hz, 1H), 7.60 (d,  $J = 8.1$  Hz, 2H), 7.34 (d,  $J = 8.5$  Hz, 1H), 7.19 (d,  $J = 8.1$  Hz, 2H), 5.08 (dd,  $J = 5.3, 1.0$  Hz, 1H), 4.39 (t,  $J = 6.6$  Hz, 1H), 4.31 (dd,  $J = 10.5, 8.0$  Hz, 2H), 4.24 – 4.21 (m, 1H), 3.97 (dd,  $J = 5.9, 4.2$  Hz, 1H), 3.90 (s, 3H), 2.66 (q,  $J = 7.6$  Hz, 2H), 1.26 (t,  $J = 7.6$  Hz, 3H), 1.12 – 1.01 (m,

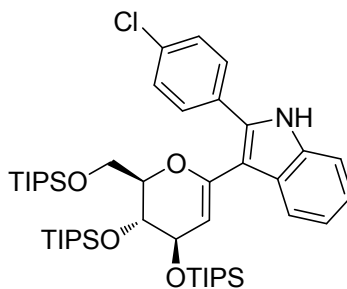
63H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.19, 146.51, 144.33, 137.92, 137.24, 129.45, 128.23, 128.02, 128.01, 124.02, 122.94, 122.43, 111.21, 110.36, 101.05, 81.01, 69.19, 66.58, 61.90, 51.69, 28.67, 18.23, 18.18, 18.03, 18.01, 17.98, 17.72, 15.29, 12.52, 12.37, 12.00;  $[\alpha]_{\text{D}}^{23} = +1.2$  ( $c = 0.66$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{51}\text{H}_{85}\text{NO}_6\text{Si}_3\text{K}$   $[\text{M} + \text{K}]^+$ : 930.5316; Found: 930.5333.

**3-((2*R*,3*R*,4*R*)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-ethylphenyl)-6-methyl-1H-indole (3as)**



Colorless foam (108 mg, 85%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (s, 1H), 7.86 (d,  $J = 8.1$  Hz, 1H), 7.59 (d,  $J = 8.1$  Hz, 2H), 7.17 (d,  $J = 8.0$  Hz, 2H), 7.11 (s, 1H), 6.93 (d,  $J = 8.1$  Hz, 1H), 4.90 (d,  $J = 4.2$  Hz, 1H), 4.43 (dd,  $J = 6.7, 5.6$  Hz, 1H), 4.16 (dd,  $J = 11.2, 7.4$  Hz, 2H), 4.09 (dd,  $J = 7.2, 3.4$  Hz, 2H), 2.65 (q,  $J = 7.6$  Hz, 2H), 2.44 (s, 3H), 1.25 (t,  $J = 7.6$  Hz, 3H), 1.12 – 0.99 (m, 63H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.13, 143.73, 135.79, 135.33, 132.14, 130.24, 128.12, 127.89, 126.72, 122.07, 120.66, 110.37, 110.15, 99.98, 81.25, 69.94, 66.87, 61.88, 28.69, 21.79, 18.24, 18.20, 18.15, 18.11, 18.09, 17.98, 17.73, 15.47, 12.53, 12.36, 12.04;  $[\alpha]_{\text{D}}^{23} = +0.89$  ( $c = 0.35$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{50}\text{H}_{86}\text{NO}_4\text{Si}_3$   $[\text{M} + \text{H}]^+$ : 848.5859; Found: 848.5868.

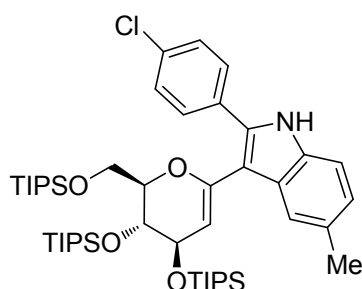
**3-((2*R*,3*R*,4*R*)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-chlorophenyl)-1H-indole (3at)**



Colorless oil (103 mg, 82%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (s, 1H), 8.01 (d,  $J = 7.9$  Hz, 1H), 7.62 (d,  $J = 8.5$  Hz, 2H), 7.33 – 7.29 (m, 3H), 7.18 (dd,  $J = 11.1, 4.0$  Hz, 1H), 7.12 (t,  $J = 7.4$  Hz, 1H), 4.93

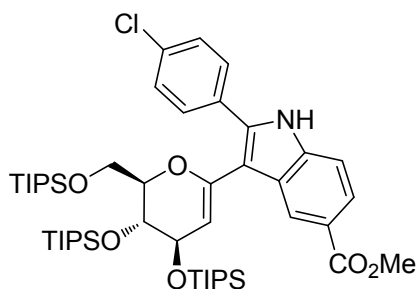
(dd,  $J = 5.2, 1.1$  Hz, 1H), 4.44 (dd,  $J = 6.9, 5.1$  Hz, 1H), 4.19 (dd,  $J = 11.2, 7.6$  Hz, 2H), 4.10 – 4.07 (m, 1H), 4.03 (dd,  $J = 11.1, 4.8$  Hz, 1H), 1.12 – 1.00 (m, 63H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.69, 135.54, 134.53, 133.69, 131.22, 129.53, 128.67, 122.81, 121.15, 120.58, 111.10, 110.61, 100.51, 81.50, 69.94, 66.70, 61.92, 18.23, 18.21, 18.18, 18.13, 18.08, 18.06, 18.02, 17.97, 17.73, 12.51, 12.34, 12.30, 12.03;  $[\alpha]_{\text{D}}^{23} = +2.9$  ( $c = 0.74$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{47}\text{H}_{78}\text{ClNO}_4\text{Si}_3\text{K}$   $[\text{M} + \text{K}]^+$ : 878.4559; Found: 878.4538.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-chlorophenyl)-5-methyl-1H-indole (3au)**



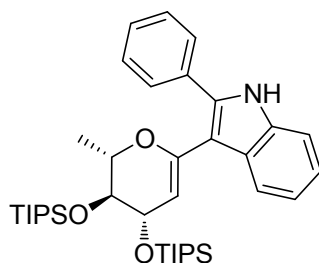
Colorless foam (102 mg, 80%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (s, 1H), 7.63 (s, 1H), 7.57 (d,  $J = 8.5$  Hz, 2H), 7.27 (d,  $J = 8.5$  Hz, 2H), 7.18 (d,  $J = 8.2$  Hz, 1H), 7.00 (d,  $J = 7.7$  Hz, 1H), 4.99 (d,  $J = 4.3$  Hz, 1H), 4.40 (t,  $J = 6.3$  Hz, 1H), 4.25 (d,  $J = 1.3$  Hz, 1H), 4.17 (dd,  $J = 11.0, 6.0$  Hz, 2H), 4.05 (dd,  $J = 10.7, 6.7$  Hz, 1H), 2.42 (s, 3H), 1.02 – 1.01 (m, 63H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.85, 134.56, 133.90, 133.55, 131.30, 129.80, 129.25, 128.90, 128.64, 124.43, 120.13, 110.68, 110.37, 100.80, 81.36, 69.61, 66.68, 62.09, 21.46, 18.25, 18.22, 18.17, 18.07, 18.04, 17.73, 12.54, 12.39, 12.31, 12.02;  $[\alpha]_{\text{D}}^{23} = +10.5$  ( $c = 0.48$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{48}\text{H}_{80}\text{ClNO}_4\text{Si}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 876.4976; Found: 876.4992.

**methyl 3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-chlorophenyl)-1H-indole-5-carboxylate (3av)**



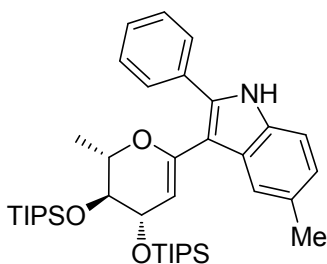
Colorless foam (109 mg, 81%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.75 (s, 1H), 8.41 (s, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.12 (d, *J* = 5.4 Hz, 1H), 4.40 (t, *J* = 6.4 Hz, 1H), 4.29 (s, 1H), 4.25 – 4.19 (m, 2H), 4.07 – 4.01 (m, 1H), 3.91 (s, 3H), 1.12 – 1.00 (m, 63H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.17, 146.22, 138.11, 135.73, 134.01, 130.61, 129.37, 128.58, 127.78, 124.26, 122.90, 122.42, 111.65, 110.55, 101.20, 81.39, 69.26, 66.33, 62.26, 51.77, 18.21, 18.19, 17.99, 17.72, 12.53, 12.37, 12.30, 12.00; [α]<sub>D</sub><sup>23</sup> = +3.2 (*c* = 0.63, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>49</sub>H<sub>80</sub>ClNO<sub>6</sub>Si<sub>3</sub>Na [M + Na]<sup>+</sup>: 920.4874; Found: 920.4883.

**3-((2*S*,3*S*,4*S*)-2-methyl-3,4-bis((triisopropylsilyloxy)-3,4-dihydro-2H-pyran-6-yl)-2-phenyl-1H-indole(3ba)**



Colorless foam (85 mg, 89%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.38 – 7.30 (m, 4H), 7.19 – 7.11 (m, 2H), 5.01 (dd, *J* = 5.1, 1.2 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 1H), 4.18 (dd, *J* = 3.1, 2.1 Hz, 1H), 4.00 (d, *J* = 1.5 Hz, 1H), 1.54 (d, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 4.6 Hz, 21H), 1.02 (s, 21H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.11, 135.68, 135.51, 132.59, 128.85, 128.45, 128.13, 127.80, 122.51, 120.43, 120.35, 110.83, 110.68, 100.66, 75.42, 73.13, 67.42, 18.24, 18.21, 18.19, 18.14, 17.73, 16.30, 12.57, 12.45, 12.31; [α]<sub>D</sub><sup>23</sup> = +12.8 (*c* = 0.68, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>38</sub>H<sub>60</sub>NO<sub>3</sub>Si<sub>2</sub> [M + H]<sup>+</sup>: 634.4106; Found: 634.4120.

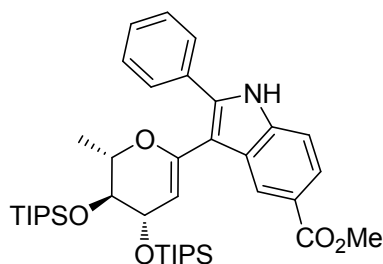
**5-methyl-3-((2*S*,3*S*,4*S*)-2-methyl-3,4-bis((triisopropylsilyloxy)-3,4-dihydro-2H-pyran-6-yl)-2-phenyl-1H-indole (3bb)**





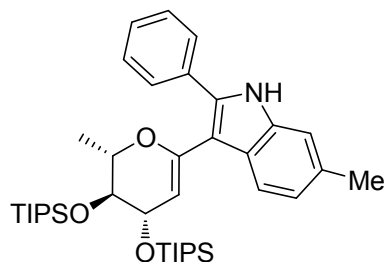
Colorless foam (81 mg, 83%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (s, 1H), 7.71 – 7.68 (m, 2H), 7.60 (s, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.00 (dd, *J* = 8.2, 1.0 Hz, 1H), 5.01 (dd, *J* = 5.2, 1.2 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 1H), 4.19 (dd, *J* = 3.1, 2.1 Hz, 1H), 4.00 (d, *J* = 1.6 Hz, 1H), 2.43 (s, 3H), 1.53 (d, *J* = 7.1 Hz, 3H), 1.11 (d, *J* = 4.7 Hz, 21H), 1.03 (s, 21H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.28, 135.65, 133.85, 132.70, 129.59, 129.11, 128.42, 127.96, 127.66, 124.12, 120.03, 110.49, 110.30, 100.61, 75.40, 73.07, 67.40, 21.49, 18.25, 18.23, 18.19, 18.14, 17.72, 16.34, 12.58, 12.45; [α]<sub>D</sub><sup>23</sup> = +8.8 (*c* = 0.75, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>39</sub>H<sub>62</sub>NO<sub>3</sub>Si<sub>2</sub> [M + H]<sup>+</sup>: 648.4263; Found: 648.4271.

**methyl 3-((2*S*,3*S*,4*S*)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-2-phenyl-1H-indole-5-carboxylate (3be)**



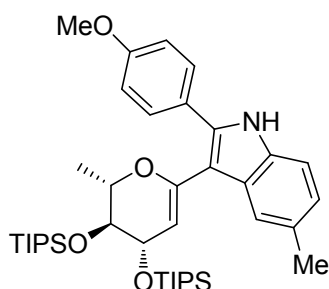
Colorless foam (95 mg, 92%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.55 (s, 1H), 8.51 (s, 1H), 7.90 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.69 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.32 (m, 4H), 5.06 – 5.02 (m, 1H), 4.48 (q, *J* = 7.0 Hz, 1H), 4.22 – 4.18 (m, 1H), 4.01 (d, *J* = 1.4 Hz, 1H), 3.91 (s, 3H), 1.55 (d, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 4.9 Hz, 21H), 1.03 (s, 21H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.17, 145.58, 138.07, 136.94, 132.03, 128.53, 128.30, 128.18, 128.16, 124.07, 123.34, 122.49, 111.86, 110.45, 101.08, 75.56, 72.96, 67.20, 51.75, 18.20, 18.18, 18.17, 18.11, 17.71, 16.28, 12.55, 12.40, 12.31; [α]<sub>D</sub><sup>23</sup> = +8.1 (*c* = 0.68, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>40</sub>H<sub>62</sub>NO<sub>5</sub>Si<sub>2</sub> [M + H]<sup>+</sup>: 692.4161; Found: 692.4171.

**6-methyl-3-((2*S*,3*S*,4*S*)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-2-phenyl-1H-indole (3bg)**



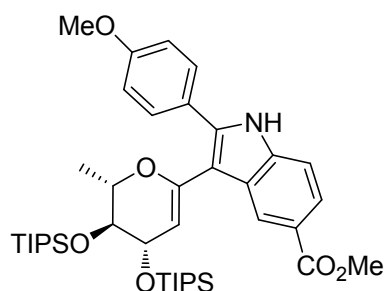
Colorless oil (80 mg, 82%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (s, 1H), 7.69 – 7.65 (m, 3H), 7.35 (t,  $J$  = 7.4 Hz, 2H), 7.29 (d,  $J$  = 7.3 Hz, 1H), 7.10 (s, 1H), 6.96 (d,  $J$  = 8.1 Hz, 1H), 5.01 (dd,  $J$  = 5.1, 1.1 Hz, 1H), 4.45 (q,  $J$  = 7.0 Hz, 1H), 4.21 – 4.16 (m, 1H), 3.99 (d,  $J$  = 1.5 Hz, 1H), 2.44 (s, 3H), 1.52 (d,  $J$  = 7.1 Hz, 3H), 1.09 (d,  $J$  = 4.6 Hz, 21H), 1.02 (s, 21H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.27, 135.95, 134.96, 132.78, 132.36, 128.39, 128.01, 127.58, 126.74, 122.11, 120.06, 110.71, 110.59, 100.44, 75.37, 73.14, 67.46, 21.73, 18.23, 18.20, 18.18, 18.14, 17.72, 16.28, 12.57, 12.46;  $[\alpha]_{\text{D}}^{23}$  = +2.9 ( $c$  = 0.62,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{39}\text{H}_{62}\text{NO}_3\text{Si}_2$   $[\text{M} + \text{H}]^+$ : 648.4263; Found: 648.4269.

**2-(4-methoxyphenyl)-5-methyl-3-((2S,3S,4S)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-1H-indole (3bk)**



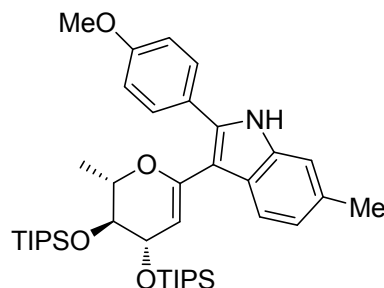
Colorless foam (85 mg, 84%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (s, 1H), 7.60 – 7.56 (m, 3H), 7.14 (d,  $J$  = 8.2 Hz, 1H), 6.96 (d,  $J$  = 8.2 Hz, 1H), 6.85 (d,  $J$  = 8.7 Hz, 2H), 5.03 – 4.98 (m, 1H), 4.46 (q,  $J$  = 7.0 Hz, 1H), 4.22 – 4.18 (m, 1H), 4.00 (d,  $J$  = 1.5 Hz, 1H), 3.80 (s, 3H), 2.43 (s, 3H), 1.53 (d,  $J$  = 7.1 Hz, 3H), 1.10 (d,  $J$  = 4.6 Hz, 21H), 1.04 (s, 21H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.23, 146.43, 135.66, 133.71, 129.43, 129.20, 129.17, 125.29, 123.72, 119.77, 113.89, 110.26, 109.56, 100.48, 75.40, 73.06, 67.40, 55.25, 21.53, 18.27, 18.24, 18.22, 18.18, 16.43, 12.58, 12.47;  $[\alpha]_{\text{D}}^{23}$  = +3.5 ( $c$  = 0.65,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{40}\text{H}_{64}\text{NO}_4\text{Si}_2$   $[\text{M} + \text{H}]^+$ : 678.4368; Found: 678.4386.

**methyl 2-(4-methoxyphenyl)-3-((2S,3S,4S)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-1H-indole-5-carboxylate (3bm)**



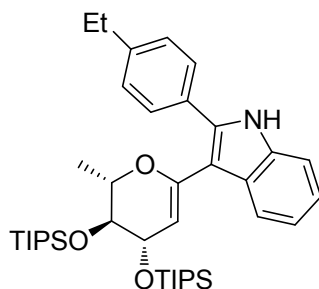
Colorless foam (101 mg, 93%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62 (s, 1H), 8.52 (s, 1H), 7.82 (dd,  $J = 8.5, 1.5$  Hz, 1H), 7.50 (d,  $J = 8.7$  Hz, 2H), 7.17 (d,  $J = 8.5$  Hz, 1H), 6.76 (d,  $J = 8.7$  Hz, 2H), 5.09 – 5.07 (m, 1H), 4.46 (q,  $J = 7.0$  Hz, 1H), 4.22 (dd,  $J = 3.1, 2.1$  Hz, 1H), 4.00 (d,  $J = 1.4$  Hz, 1H), 3.91 (s, 3H), 3.77 (s, 3H), 1.53 (d,  $J = 7.1$  Hz, 3H), 1.08 (d,  $J = 4.8$  Hz, 21H), 1.04 (s, 21H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.28, 159.55, 145.69, 138.04, 137.01, 129.36, 128.35, 124.43, 123.69, 122.86, 122.23, 113.94, 110.69, 110.52, 101.03, 75.64, 72.89, 67.16, 55.20, 51.77, 18.20, 18.15, 16.40, 12.52, 12.42;  $[\alpha]_{\text{D}}^{23} = +0.56$  ( $c = 0.92$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{41}\text{H}_{64}\text{NO}_6\text{Si}_2$   $[\text{M} + \text{H}]^+$ : 722.4267; Found: 722.4287.

**2-(4-methoxyphenyl)-6-methyl-3-((2S,3S,4S)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-1H-indole (3bo)**



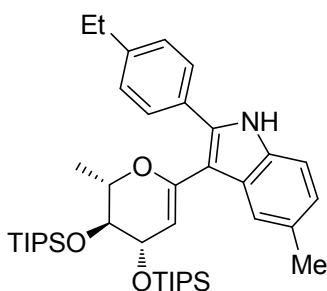
Colorless foam (83 mg, 82%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (s, 1H), 7.65 (d,  $J = 8.1$  Hz, 1H), 7.54 (d,  $J = 8.7$  Hz, 2H), 7.01 (s, 1H), 6.95 (d,  $J = 8.1$  Hz, 1H), 6.82 (d,  $J = 8.7$  Hz, 2H), 5.02 (dd,  $J = 5.2, 1.3$  Hz, 1H), 4.43 (q,  $J = 7.0$  Hz, 1H), 4.19 (dd,  $J = 3.1, 2.1$  Hz, 1H), 3.98 (d,  $J = 1.6$  Hz, 1H), 3.79 (s, 3H), 2.41 (s, 3H), 1.51 (d,  $J = 7.1$  Hz, 3H), 1.08 (d,  $J = 4.4$  Hz, 21H), 1.03 (d,  $J = 2.5$  Hz, 21H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.15, 146.41, 135.83, 134.97, 131.93, 129.23, 126.78, 125.34, 121.93, 119.73, 113.84, 110.60, 109.71, 100.28, 75.36, 73.11, 67.45, 55.22, 21.68, 18.23, 18.20, 18.16, 18.01, 17.73, 16.35, 12.56, 12.47;  $[\alpha]_{\text{D}}^{23} = +9.6$  ( $c = 0.92$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{40}\text{H}_{64}\text{NO}_4\text{Si}_2$   $[\text{M} + \text{H}]^+$ : 678.4368; Found: 678.4385.

**2-(4-ethylphenyl)-3-((2*S*,3*S*,4*S*)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-1H-indole (3bp)**



Colorless oil (79 mg, 80%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.09 (m, 2H), 4.99 (d, *J* = 5.1 Hz, 1H), 4.47 (q, *J* = 7.0 Hz, 1H), 4.20 – 4.16 (m, 1H), 4.00 (d, *J* = 1.4 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.54 (d, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.6 Hz, 3H), 1.10 (d, *J* = 4.7 Hz, 21H), 1.02 (s, 21H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.23, 143.97, 135.89, 135.42, 129.95, 128.90, 128.09, 127.96, 122.31, 120.36, 120.26, 110.58, 110.47, 100.55, 75.38, 73.17, 67.45, 28.69, 18.23, 18.21, 18.18, 18.14, 17.72, 16.30, 15.45, 12.58, 12.46; [α]<sub>D</sub><sup>23</sup> = +2.4 (*c* = 0.75, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>40</sub>H<sub>64</sub>NO<sub>3</sub>Si<sub>2</sub> [M + H]<sup>+</sup>: 662.4419; Found: 662.4422.

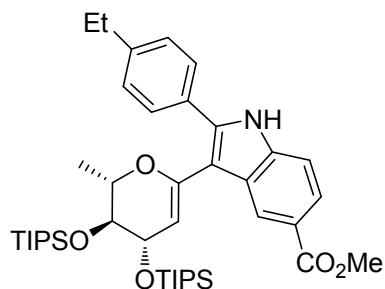
**2-(4-ethylphenyl)-5-methyl-3-((2*S*,3*S*,4*S*)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-1H-indole (3bq)**



Colorless foam (79 mg, 78%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 3H), 7.19 (dd, *J* = 7.9, 5.5 Hz, 3H), 6.99 (d, *J* = 8.2 Hz, 1H), 4.99 (d, *J* = 4.3 Hz, 1H), 4.47 (q, *J* = 7.0 Hz, 1H), 4.21 – 4.15 (m, 1H), 4.00 (d, *J* = 1.3 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.54 (d, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.6 Hz, 3H), 1.11 (d, *J* = 4.6 Hz, 21H), 1.03 (s, 21H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.37, 143.82, 135.87, 133.74, 130.02, 129.50, 129.15, 127.96, 127.92, 123.90, 119.93, 110.24, 110.07, 100.51, 75.37, 73.07, 67.40, 28.70, 21.51, 18.27, 18.24, 18.20, 18.16, 16.36, 15.50,

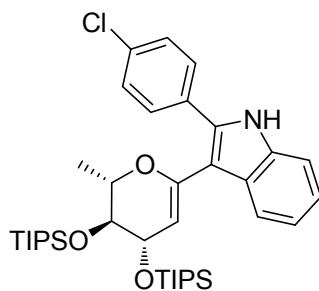
12.58, 12.45;  $[\alpha]_{\text{D}}^{23} = +5.3$  ( $c = 0.46$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{41}\text{H}_{66}\text{NO}_3\text{Si}_2$   $[\text{M} + \text{H}]^+$ : 676.4575; Found: 676.4596.

**methyl 2-(4-ethylphenyl)-3-((2*S*,3*S*,4*S*)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-1H-indole-5-carboxylate (3br)**



Colorless foam (93 mg, 86%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (s, 1H), 8.50 (s, 1H), 7.88 (dd,  $J = 8.5, 1.6$  Hz, 1H), 7.58 (d,  $J = 8.1$  Hz, 2H), 7.28 (d,  $J = 8.5$  Hz, 1H), 7.18 (d,  $J = 8.1$  Hz, 2H), 5.03 (dd,  $J = 5.2, 1.3$  Hz, 1H), 4.48 (q,  $J = 7.0$  Hz, 1H), 4.19 (dt,  $J = 5.0, 1.8$  Hz, 1H), 4.01 (d,  $J = 1.6$  Hz, 1H), 3.91 (s, 3H), 2.66 (q,  $J = 7.6$  Hz, 2H), 1.55 (d,  $J = 7.1$  Hz, 3H), 1.25 (t,  $J = 7.6$  Hz, 3H), 1.10 (d,  $J = 4.9$  Hz, 21H), 1.03 (s, 21H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.25, 145.67, 144.40, 138.02, 137.18, 129.31, 128.34, 128.10, 128.05, 123.90, 123.19, 122.35, 111.38, 110.41, 100.97, 75.54, 72.92, 67.19, 51.74, 28.70, 18.19, 18.13, 16.30, 15.41, 12.54, 12.41;  $[\alpha]_{\text{D}}^{23} = +10.5$  ( $c = 0.76$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{42}\text{H}_{65}\text{NO}_5\text{Si}_2\text{Na}$   $[\text{M} + \text{Na}]^+$ : 742.4294; Found: 742.4278.

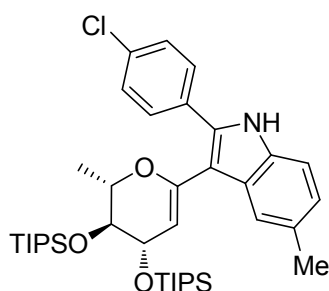
**2-(4-chlorophenyl)-3-((2*S*,3*S*,4*S*)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-1H-indole (3bt)**



Colorless foam (81 mg, 81%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (s, 1H), 7.80 (d,  $J = 7.5$  Hz, 1H), 7.57 (d,  $J = 8.5$  Hz, 2H), 7.29 (d,  $J = 8.5$  Hz, 2H), 7.26 (d,  $J = 8.4$  Hz, 1H), 7.19 – 7.11 (m, 2H), 5.01

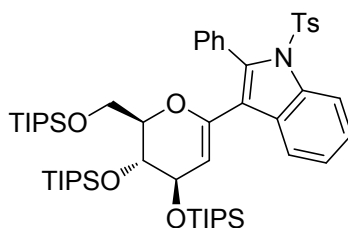
(dd,  $J = 5.1, 1.1$  Hz, 1H), 4.46 (q,  $J = 7.0$  Hz, 1H), 4.19 (dd,  $J = 3.1, 2.1$  Hz, 1H), 4.00 (d,  $J = 1.4$  Hz, 1H), 1.53 (d,  $J = 7.1$  Hz, 3H), 1.09 (d,  $J = 4.4$  Hz, 21H), 1.03 (s, 21H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.89, 135.61, 134.39, 133.71, 131.07, 129.36, 128.70, 128.67, 122.80, 120.52, 120.42, 111.27, 110.79, 100.92, 75.51, 73.02, 67.30, 18.21, 18.18, 18.18, 18.13, 17.72, 16.32, 12.56, 12.46;  $[\alpha]_{\text{D}}^{23} = +9.6$  ( $c = 0.52$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{38}\text{H}_{59}\text{ClNO}_3\text{Si}_2$   $[\text{M} + \text{H}]^+$ : 668.3717; Found: 668.3726.

**2-(4-chlorophenyl)-5-methyl-3-((2S,3S,4S)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-1H-indole (3bu)**



Colorless oil (81 mg, 79%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (s, 1H), 7.57 (d,  $J = 7.1$  Hz, 3H), 7.28 (d,  $J = 8.5$  Hz, 2H), 7.17 (d,  $J = 8.2$  Hz, 1H), 7.00 (d,  $J = 8.3$  Hz, 1H), 5.03 – 4.99 (m, 1H), 4.46 (q,  $J = 7.0$  Hz, 1H), 4.21 – 4.17 (m, 1H), 4.00 (d,  $J = 1.5$  Hz, 1H), 2.43 (s, 3H), 1.52 (d,  $J = 7.1$  Hz, 3H), 1.10 (d,  $J = 4.4$  Hz, 21H), 1.04 (s, 21H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.00, 134.35, 133.91, 133.53, 131.14, 129.81, 129.18, 128.94, 128.65, 124.43, 119.98, 110.88, 110.43, 100.86, 75.49, 72.92, 67.23, 21.50, 18.24, 18.21, 18.19, 18.14, 17.73, 16.38, 12.55, 12.44;  $[\alpha]_{\text{D}}^{23} = +6.6$  ( $c = 0.58$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{39}\text{H}_{60}\text{ClNO}_3\text{Si}_2\text{K}$   $[\text{M} + \text{K}]^+$ : 720.3432; Found: 720.3453.

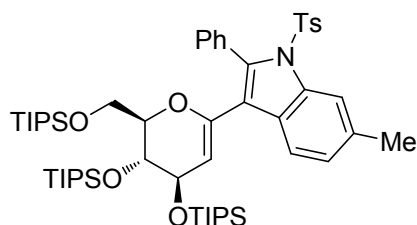
**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-phenyl-1-tosyl-1H-indole (5ad)**



Colorless foam (124 mg, 86%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 (d,  $J = 8.4$  Hz, 1H), 8.06 (d,  $J = 7.5$  Hz, 1H), 7.37 – 7.29 (m, 8H), 7.26 – 7.23 (m, 1H), 7.06 (d,  $J = 8.1$  Hz, 2H), 4.45 (dd,  $J = 5.3, 1.3$  Hz,

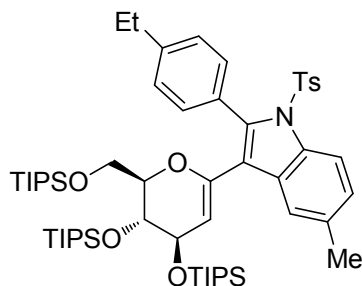
1H), 4.36 – 4.31 (m, 1H), 4.03 – 3.96 (m, 2H), 3.77 – 3.73 (m, 2H), 2.31 (s, 3H), 1.07 – 1.02 (m, 43H), 0.93 – 0.88 (m, 20H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.72, 144.58, 138.15, 136.64, 135.60, 131.68, 131.13, 129.59, 129.35, 128.55, 127.24, 126.95, 124.94, 124.07, 121.82, 120.12, 115.44, 102.28, 81.59, 69.94, 66.02, 61.49, 21.54, 18.13, 18.10, 18.06, 18.05, 18.04, 17.72, 12.42, 12.30, 12.18, 11.98; [α]<sub>D</sub><sup>23</sup> = +32.8 (c = 0.17, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>54</sub>H<sub>85</sub>NO<sub>6</sub>SSi<sub>3</sub>K [M + K]<sup>+</sup>: 998.5037; Found: 998.5046.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-6-methyl-2-phenyl-1-tosyl-1H-indole (5ae)**



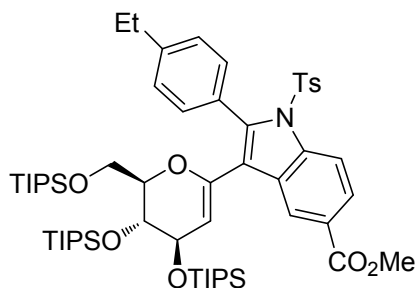
Colorless foam (108 mg, 74%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.26 (m, 7H), 7.08 – 7.04 (m, 3H), 4.43 (dd, *J* = 5.3, 1.3 Hz, 1H), 4.34 – 4.29 (m, 1H), 4.00 – 3.93 (m, 2H), 3.77 – 3.73 (m, 2H), 2.52 (s, 3H), 2.31 (s, 3H), 1.07 – 1.01 (m, 43H), 0.92 – 0.86 (m, 20H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.85, 144.46, 137.45, 137.08, 135.73, 134.98, 131.71, 131.27, 129.32, 128.42, 127.34, 127.19, 126.91, 125.52, 121.35, 120.08, 115.52, 102.08, 81.50, 69.91, 66.03, 61.50, 29.72, 22.14, 21.55, 18.13, 18.10, 18.07, 18.05, 18.04, 17.72, 12.42, 12.30, 12.18, 11.97; [α]<sub>D</sub><sup>23</sup> = +9.6 (c = 0.25, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>55</sub>H<sub>87</sub>NO<sub>6</sub>SSi<sub>3</sub>K [M + K]<sup>+</sup>: 1012.5193; Found: 1012.5197.

**3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-ethylphenyl)-5-methyl-1-tosyl-1H-indole (5af)**



Colorless foam (108 mg, 72%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.60 (s, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 5.1 Hz, 2H), 7.16 – 7.11 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 2H), 4.51 (dd, *J* = 5.4, 1.3 Hz, 1H), 4.32 (t, *J* = 6.0 Hz, 1H), 4.07 (d, *J* = 1.6 Hz, 1H), 3.91 – 3.82 (m, 3H), 2.69 (q, *J* = 7.6 Hz, 2H), 2.39 (s, 3H), 2.30 (s, 3H), 1.29 (t, *J* = 7.6 Hz, 3H), 1.07 – 1.02 (m, 43H), 0.93 – 0.89 (m, 20H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.14, 144.39, 144.36, 138.77, 135.48, 134.90, 133.68, 131.49, 130.04, 129.25, 128.32, 126.96, 126.66, 126.24, 120.85, 120.03, 115.37, 102.10, 81.47, 69.67, 66.07, 61.75, 29.72, 28.68, 21.53, 21.23, 18.18, 18.12, 18.06, 17.72, 15.05, 12.45, 12.19, 11.98; [α]<sub>D</sub><sup>23</sup> = +15.6 (*c* = 0.37, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>57</sub>H<sub>92</sub>NO<sub>6</sub>SSi<sub>3</sub> [M + H]<sup>+</sup>: 1002.5947; Found: 1002.5971.

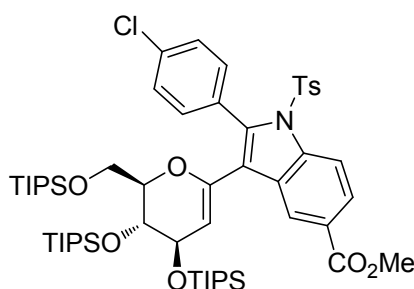
**methyl 3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-ethylphenyl)-1-tosyl-1H-indole-5-carboxylate (5ag)**



Colorless foam (129 mg, 82%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36 (d, *J* = 8.9 Hz, 2H), 8.06 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 4.66 (dd, *J* = 5.4, 1.3 Hz, 1H), 4.29 (t, *J* = 6.6 Hz, 1H), 4.16 (d, *J* = 1.5 Hz, 1H), 3.99 (dd, *J* = 10.5, 7.1 Hz, 1H), 3.96 – 3.94 (m, 1H), 3.90 (s, 3H), 3.69 (dd, *J* = 10.5, 6.3 Hz, 1H), 2.70 (q, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H), 1.07 – 1.04 (m, 26H), 1.02 – 0.99 (m, 20H), 0.95 – 0.92 (m, 17H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.29, 144.87, 144.78, 144.73, 139.68, 139.20, 135.43, 131.51, 129.68, 129.41, 129.21, 127.67, 127.12, 127.02, 126.71, 126.23, 125.96, 122.87, 120.03, 115.31, 102.41, 80.92, 69.07, 65.99, 61.42, 51.92, 28.66, 21.58, 18.15, 18.11, 18.01, 17.92, 17.72, 14.98, 12.41, 12.37, 12.30, 12.19, 12.02, 11.96; [α]<sub>D</sub><sup>23</sup> = +12.9 (*c* = 0.25, CHCl<sub>3</sub>); HRMS (ESI) *m/z* calcd for C<sub>58</sub>H<sub>92</sub>NO<sub>8</sub>SSi<sub>3</sub> [M + H]<sup>+</sup>: 1046.5846; Found: 1046.5866.

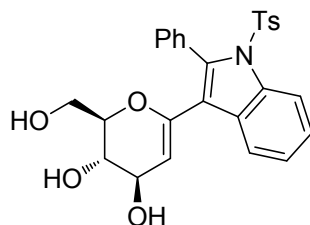
**methyl 3-((2R,3R,4R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-2-(4-chlorophenyl)-1-tosyl-1H-indole-5-carboxylate (5ah)**





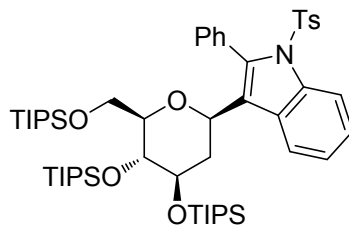
Colorless foam (102 mg, 65%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (d,  $J = 6.4$  Hz, 1H), 8.36 (s, 1H), 8.09 (dd,  $J = 9.0, 1.5$  Hz, 1H), 7.28 (dd,  $J = 14.3, 6.5$  Hz, 6H), 7.10 (d,  $J = 8.2$  Hz, 2H), 4.72 (dd,  $J = 5.5, 1.2$  Hz, 1H), 4.26 (t,  $J = 6.5$  Hz, 1H), 4.14 (d,  $J = 1.5$  Hz, 1H), 4.02 – 3.97 (m, 1H), 3.96 – 3.92 (m, 1H), 3.91 (s, 3H), 3.63 (dd,  $J = 10.6, 6.5$  Hz, 1H), 2.33 (s, 3H), 1.07 – 1.04 (m, 23H), 1.01 – 0.95 (m, 40H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.14, 145.22, 144.41, 139.22, 137.96, 135.30, 135.24, 132.86, 129.58, 129.09, 129.02, 127.60, 126.89, 126.60, 126.20, 122.88, 120.81, 115.34, 102.71, 81.10, 68.97, 65.82, 61.45, 51.98, 21.60, 18.12, 18.08, 17.97, 12.39, 12.21, 11.94;  $[\alpha]_{\text{D}}^{23} = +5.8$  ( $c = 0.31$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{56}\text{H}_{87}\text{ClNO}_8\text{SSi}_3$   $[\text{M} + \text{H}]^+$ : 1052.5143; Found: 1052.5140.

**(2R,3S,4R)-2-(hydroxymethyl)-6-(2-phenyl-1-tosyl-1H-indol-3-yl)-3,4-dihydro-2H-pyran-3,4-diol (6ad)**



Colorless oil (26.6 mg, 77%);  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  8.17 (d,  $J = 8.4$  Hz, 1H), 7.65 (d,  $J = 7.6$  Hz, 1H), 7.34 – 7.23 (m, 6H), 7.22 – 7.16 (m, 3H), 7.04 (d,  $J = 8.1$  Hz, 2H), 4.56 (d,  $J = 2.6$  Hz, 1H), 3.97 (dd,  $J = 6.8, 2.6$  Hz, 1H), 3.56 – 3.42 (m, 4H), 2.18 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  146.53, 145.29, 138.52, 136.80, 135.14, 131.45, 131.24, 129.21, 129.01, 128.41, 126.90, 126.53, 124.85, 124.00, 120.47, 119.00, 115.43, 105.16, 79.30, 70.07, 69.01, 60.43, 20.10;  $[\alpha]_{\text{D}}^{23} = +28.8$  ( $c = 0.17$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{25}\text{NO}_6\text{SK}$   $[\text{M} + \text{K}]^+$ : 530.1034; Found: 530.1031.

**3-((2R,4R,5R,6R)-4,5-bis((triisopropylsilyl)oxy)-6-(((triisopropylsilyl)oxy)methyl)tetrahydro-2H-pyran-2-yl)-2-phenyl-1-tosyl-1H-indole (7ad)**



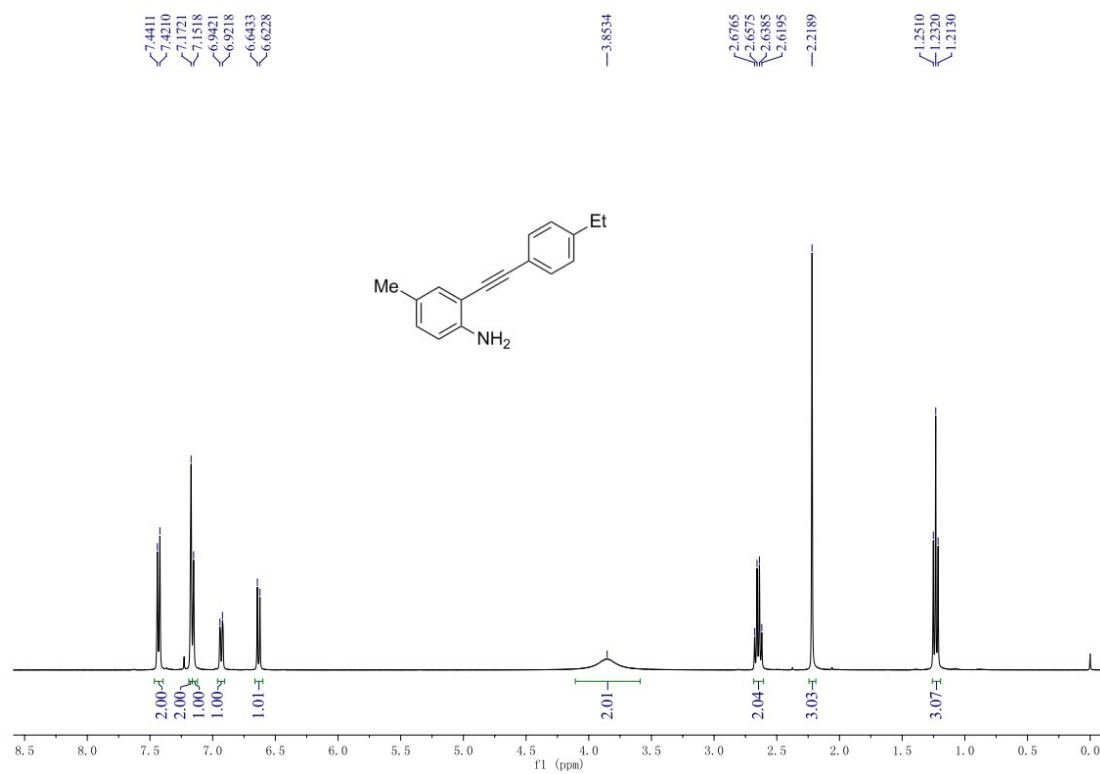
Colorless oil (13.3 mg, 53%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (d,  $J = 8.4$  Hz, 1H), 7.96 (d,  $J = 7.8$  Hz, 1H), 7.46 – 7.27 (m, 7H), 7.24 – 7.18 (m, 2H), 7.07 (d,  $J = 8.2$  Hz, 2H), 4.51 (dd,  $J = 10.9, 4.0$  Hz, 1H), 4.04 – 3.89 (m, 3H), 3.81 (dd,  $J = 10.1, 5.1$  Hz, 1H), 3.51 (dd,  $J = 9.8, 5.1$  Hz, 1H), 2.31 (s, 3H), 2.10 – 2.02 (m, 1H), 1.99 – 1.91 (m, 1H), 1.04 – 0.94 (m, 63H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.42, 137.38, 136.23, 135.73, 131.29, 130.83, 129.25, 128.79, 128.42, 127.48, 126.87, 124.76, 123.81, 123.34, 122.34, 115.44, 82.66, 72.69, 71.20, 68.64, 64.35, 38.63, 29.71, 21.54, 18.35, 18.28, 18.20, 17.96, 17.94, 13.00, 12.96, 11.98;  $[\alpha]_{\text{D}}^{23} = +21.1$  ( $c = 0.071$ ,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{54}\text{H}_{87}\text{NO}_6\text{SSi}_3\text{Na}$   $[\text{M} + \text{Na}]^+$ : 984.5454; Found: 984.5441.

## References

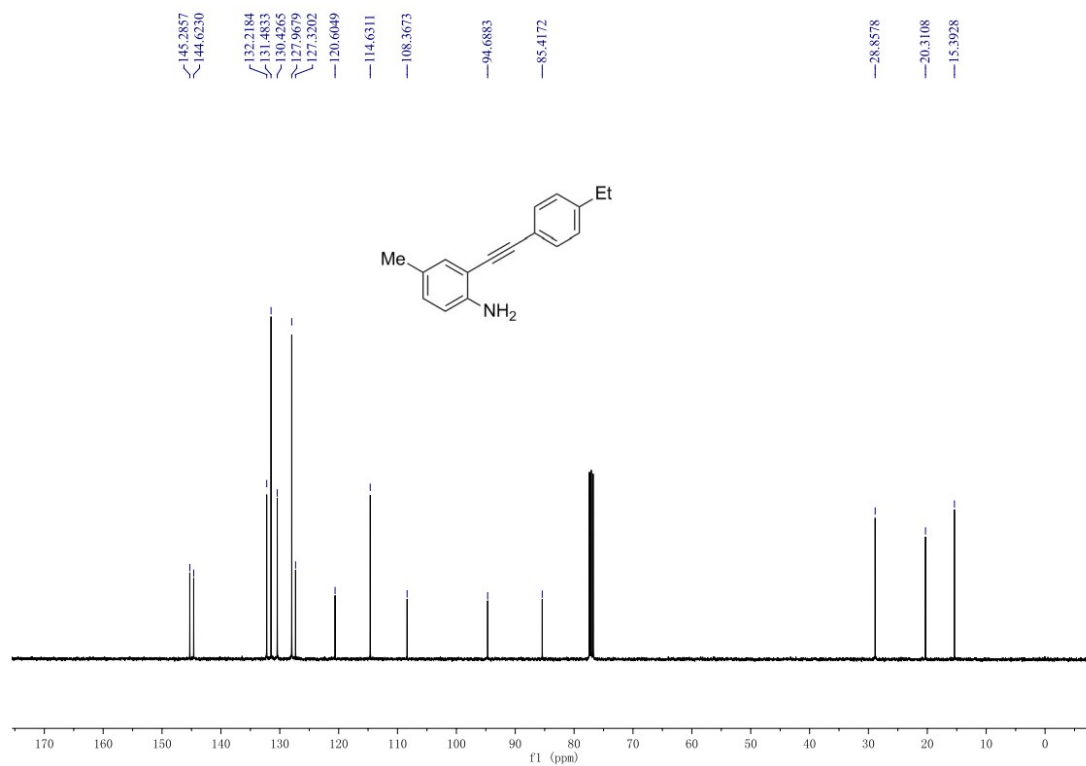
1. (a) M. Liu, Y. Niu, Y.-F. Wu and X.-S. Ye, *Org. Lett.* 2016, **18**, 1836; (b) S. Zhang, Y.-H. Niu and X.-S. Ye, *Org. Lett.* 2017, **19**, 3608.
2. (a) N. K. Swamy, A. Yazici and S. G. Pyne, *J. Org. Chem.* 2010, **75**, 3412; (b) Y. Yang, J.-X. Yu, X.-H. Ouyang and J.-H. Li, *Org. Lett.* 2017, **19**, 3982; (c) B. Miao, Y. Zheng, P. Wu, S. Li and S. Ma, *Adv. Synth. Catal.* 2017, **359**, 1691.

3. (a) C. M. Le, T. Sperger, R. Fu, X. Hou, Y. H. Lim, F. Schoenebeck and M. Lautens, *J. Am. Chem. Soc.* 2016, **138**, 14441. (b) M. Li, J. Zheng, W. Hu, C. Li, J. Li, S. Fang, H. Jiang and W. Wu, *Org. Lett.* 2018, **20**, 7245.
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5. J. Liu, X. Xie and Y. Liu, *Chem. Commun.*, 2013, **49**, 11794.

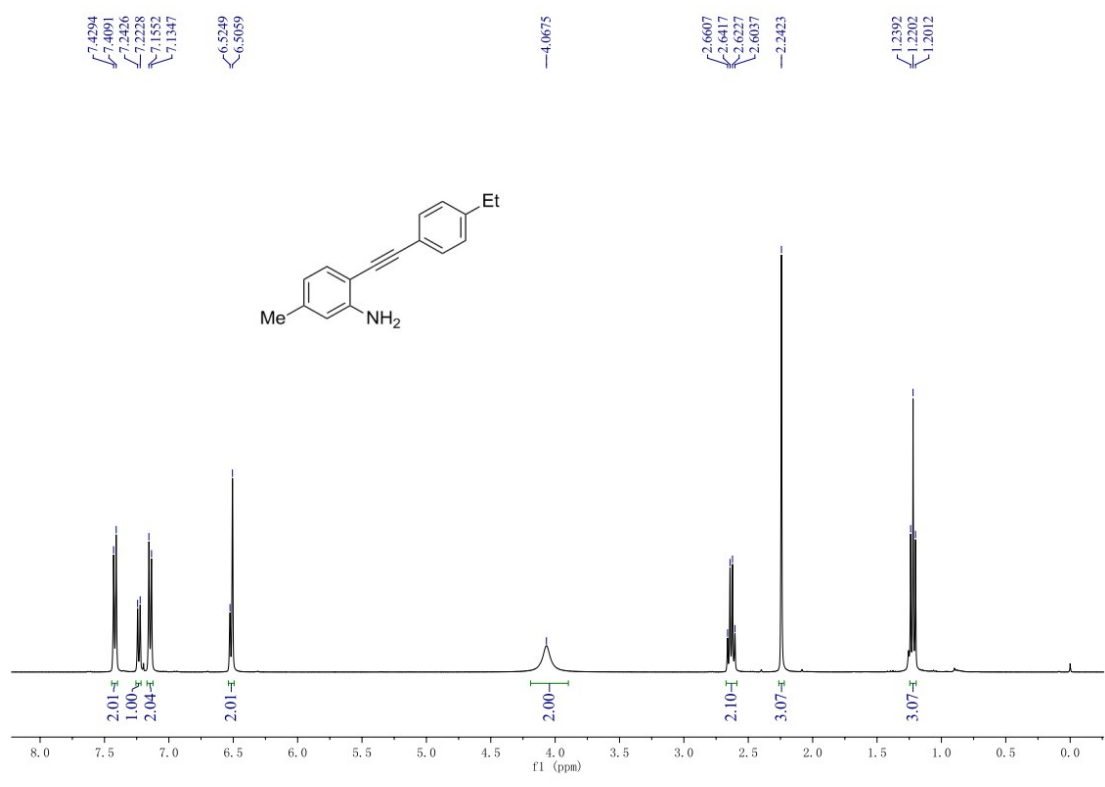
### Copies of 1D and 2D NMR spectra



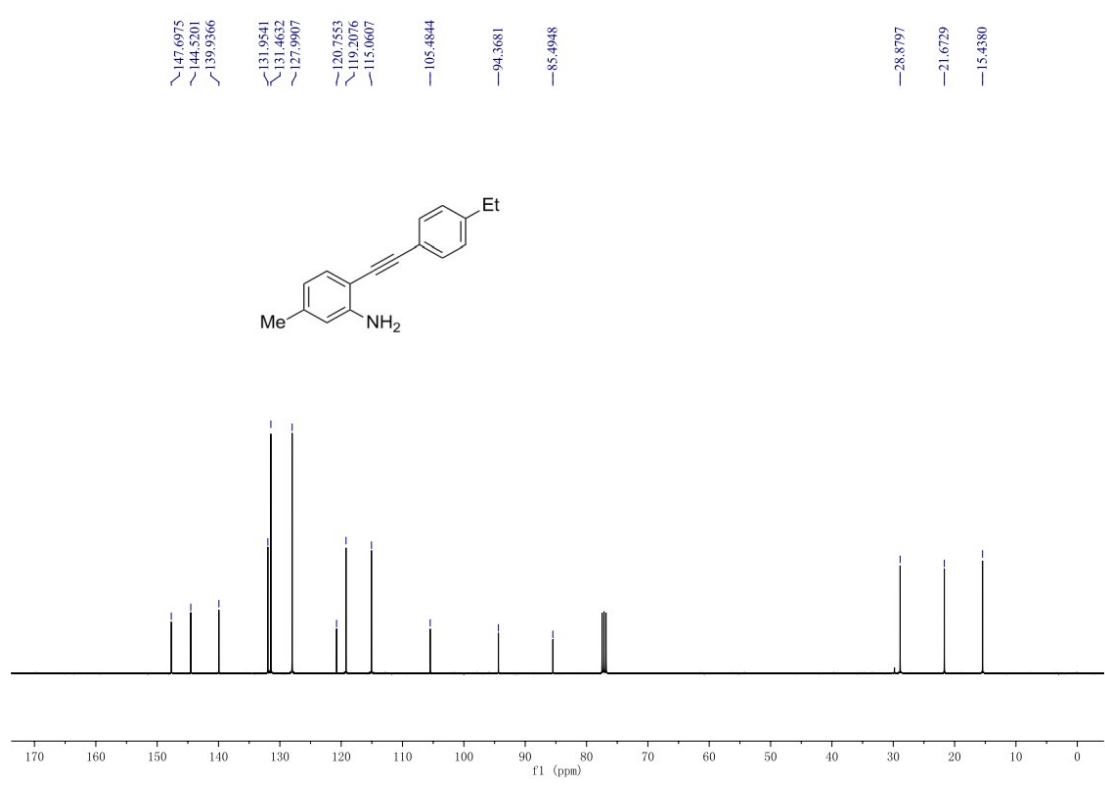
<sup>1</sup>H NMR spectrum of S3q



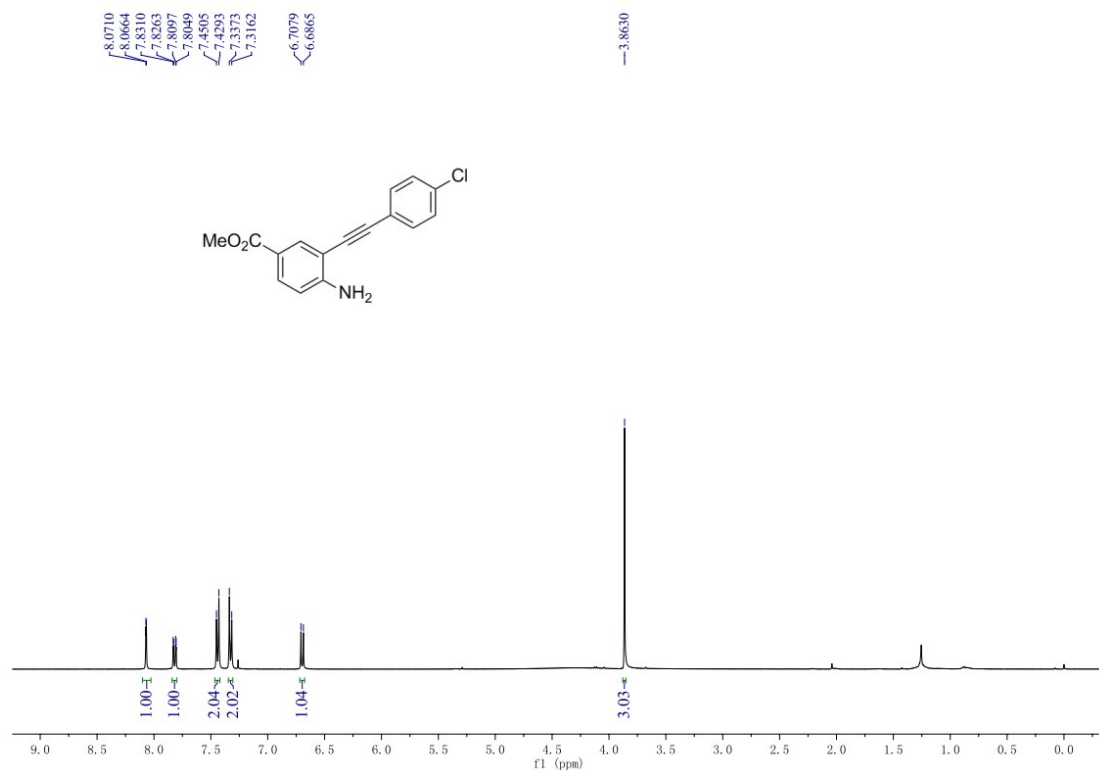
<sup>13</sup>C NMR spectrum of S3q



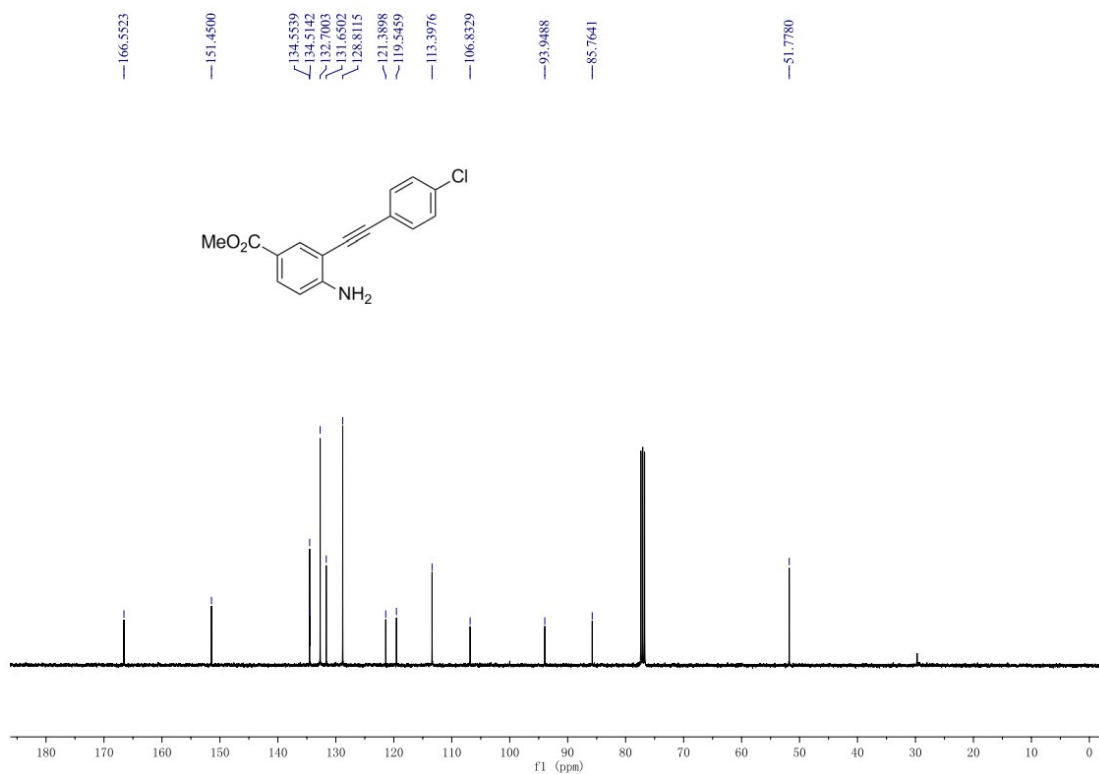
<sup>1</sup>H NMR spectrum of S3s



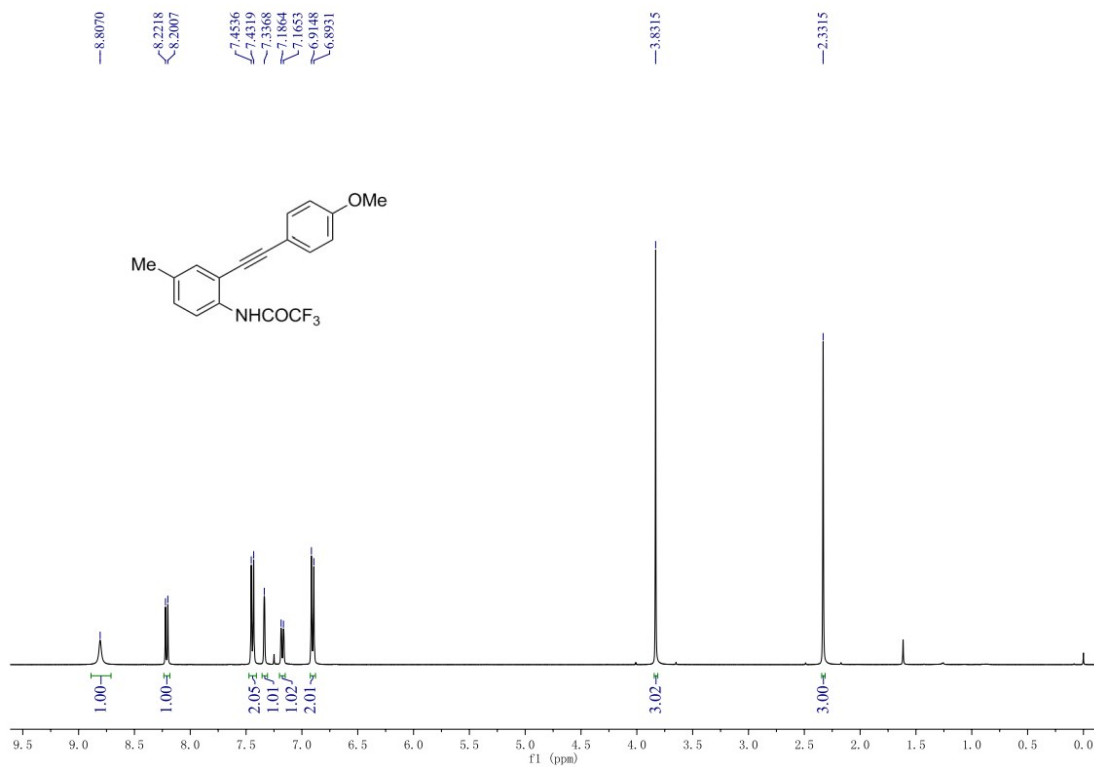
<sup>13</sup>C NMR spectrum of S3s



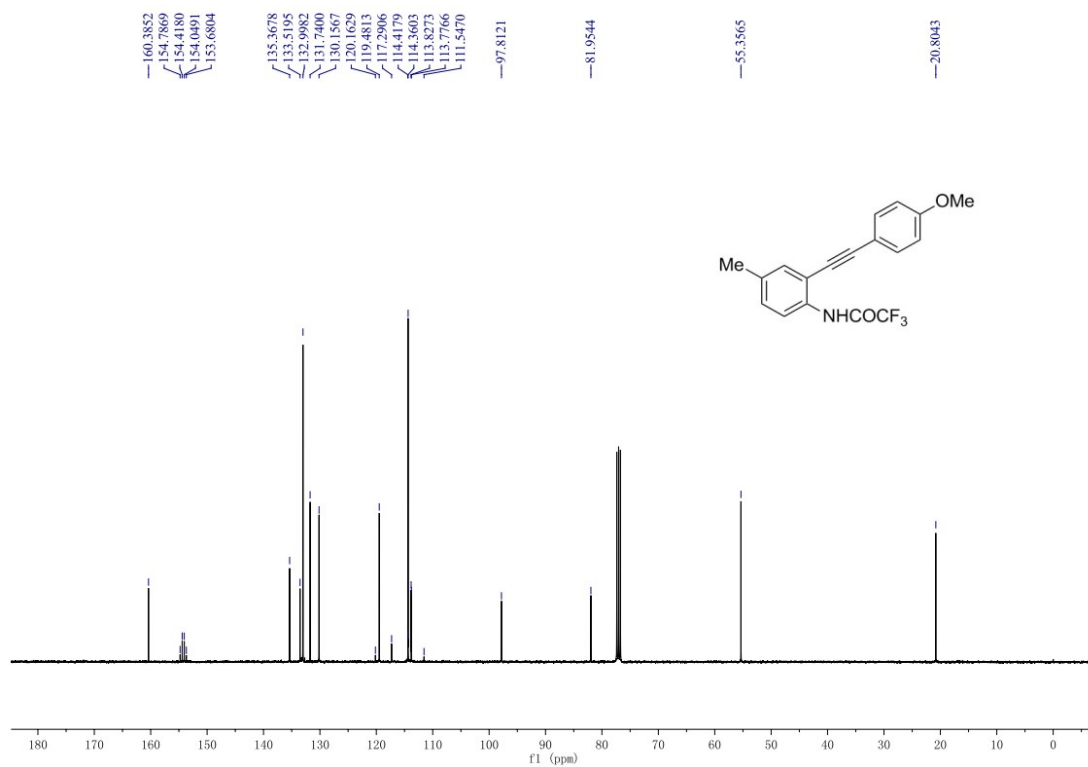
$^1\text{H}$  NMR spectrum of S3v



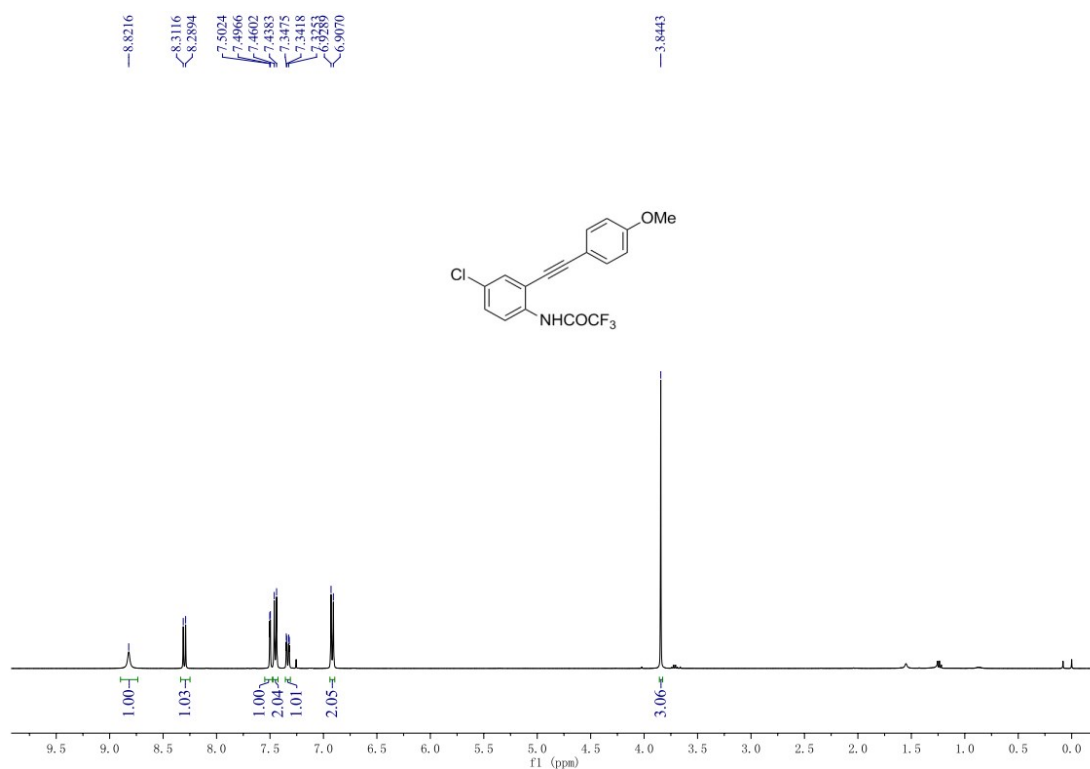
$^{13}\text{C}$  NMR spectrum of S3v



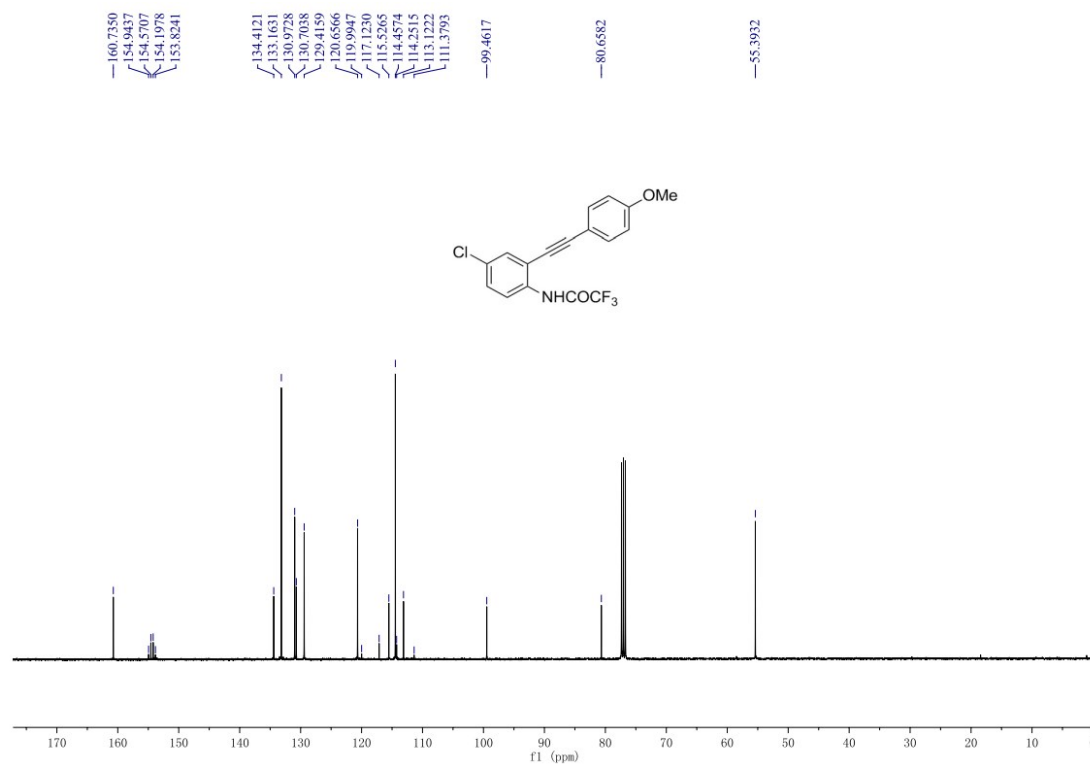
<sup>1</sup>H NMR spectrum of 2k



<sup>13</sup>C NMR spectrum of 2k

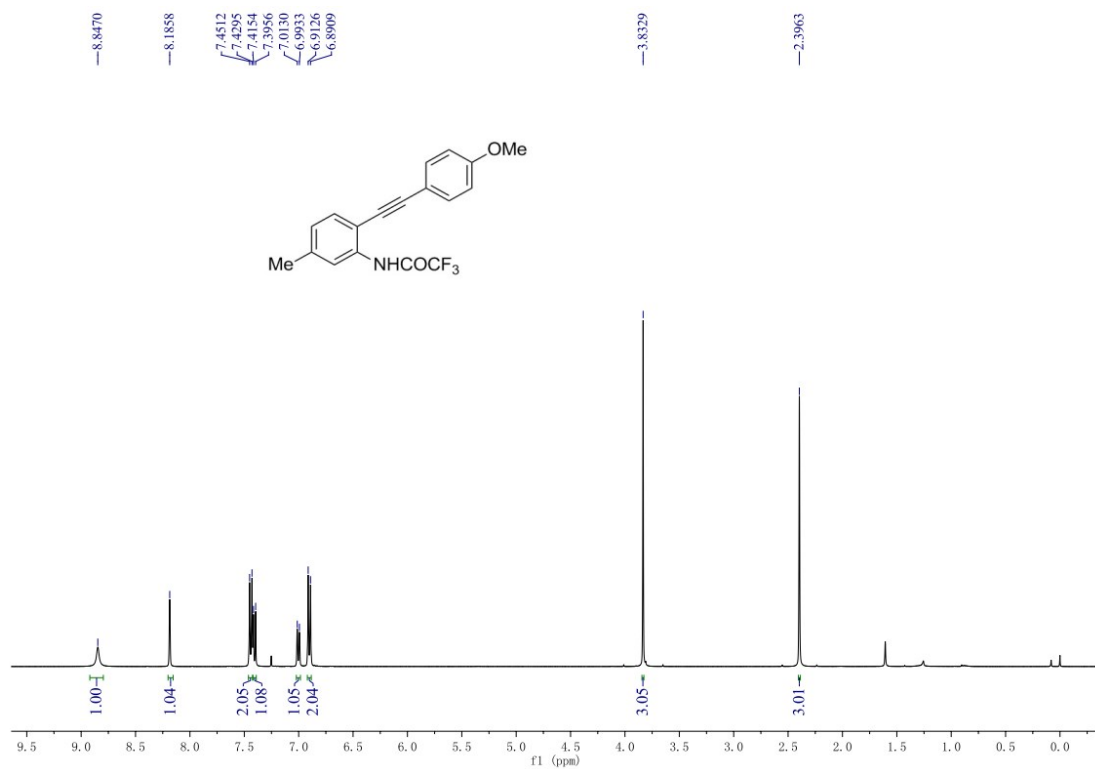


<sup>1</sup>H NMR spectrum of **21**

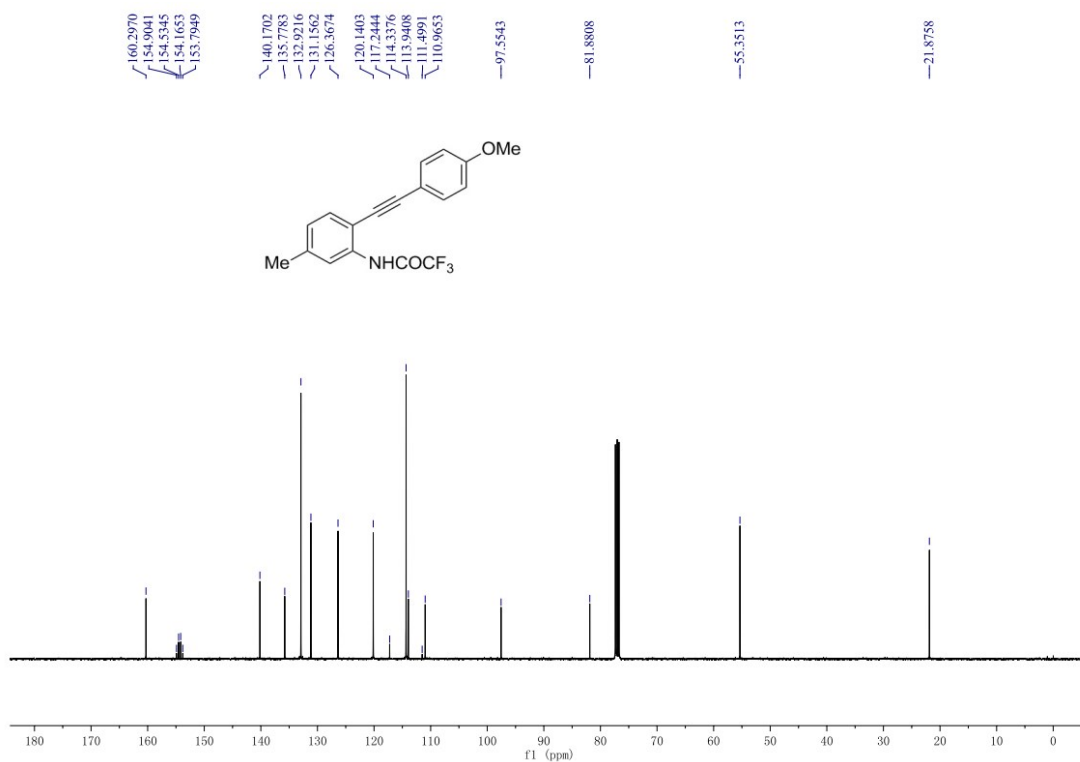


<sup>13</sup>C NMR spectrum of **21**

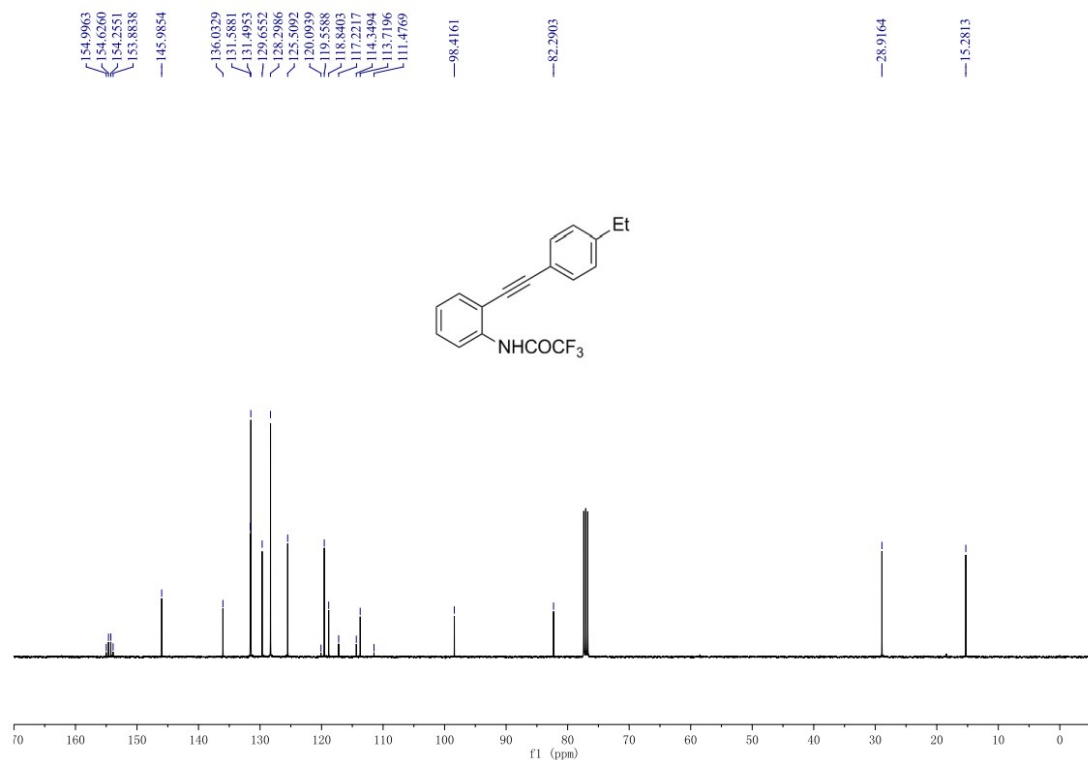
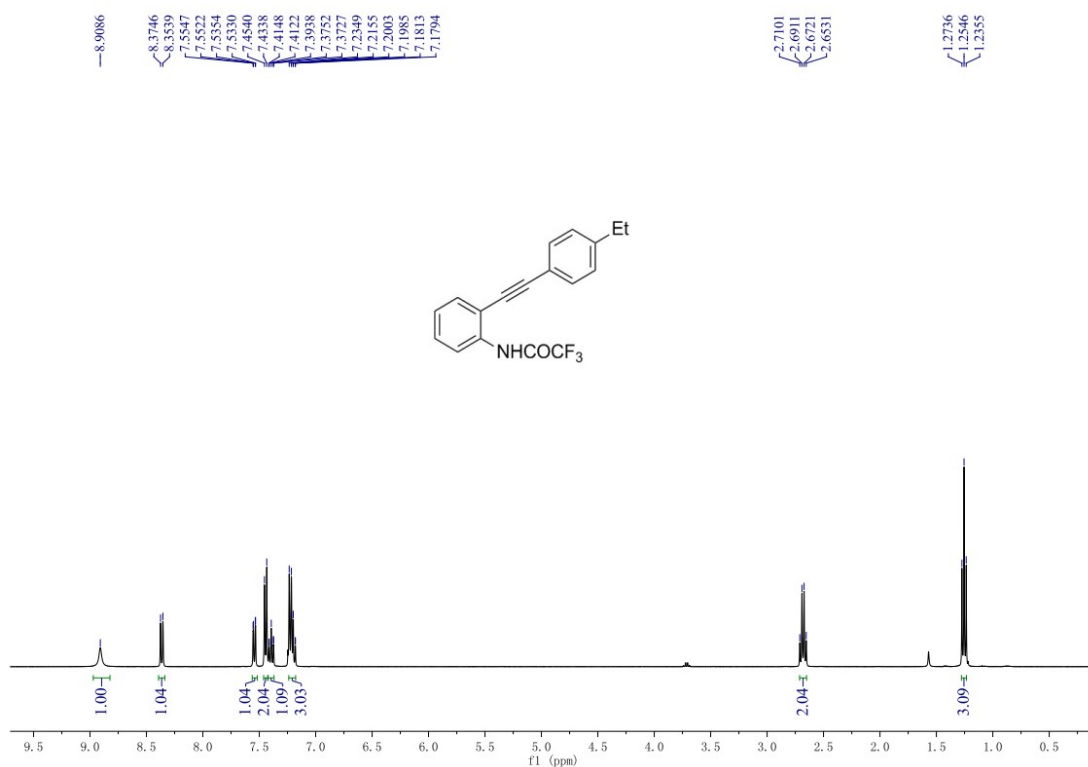


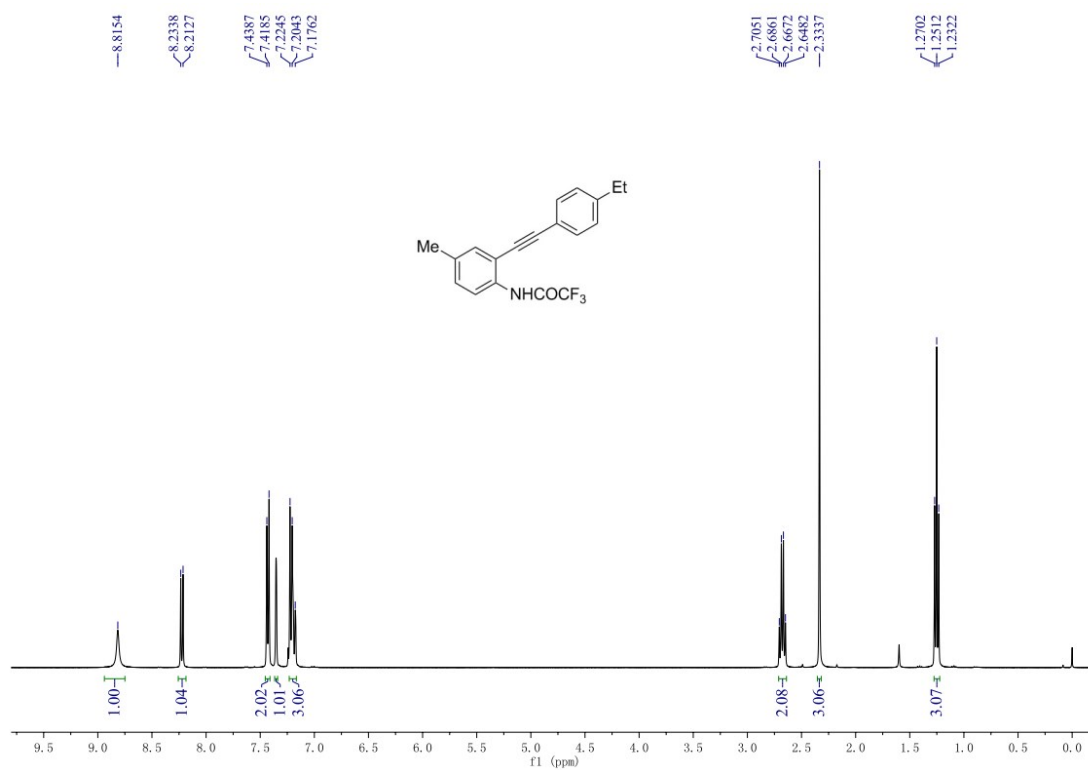


$^1\text{H}$  NMR spectrum of **2o**

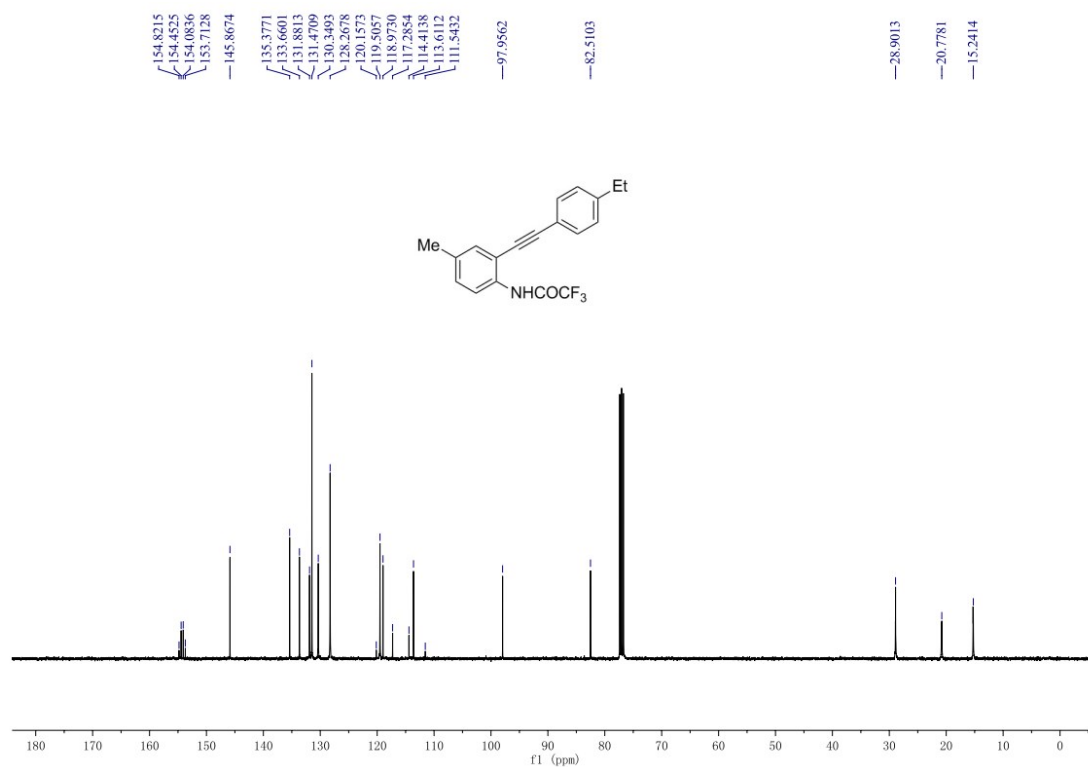


$^{13}\text{C}$  NMR spectrum of **2o**

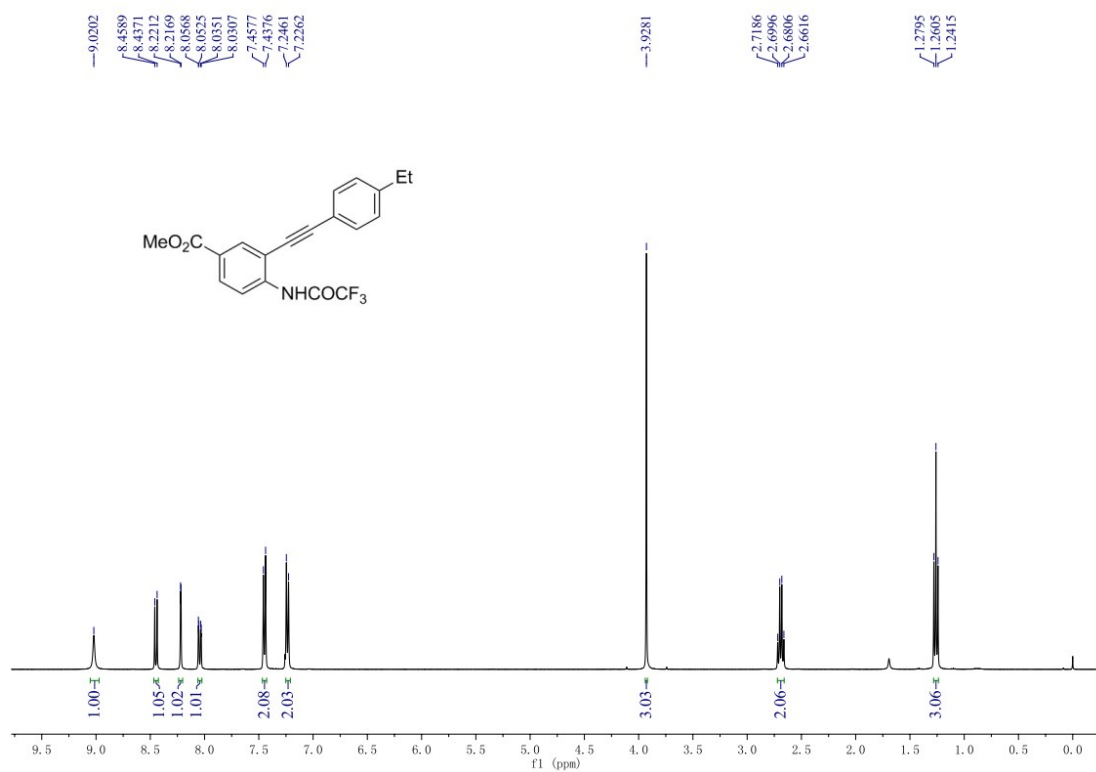




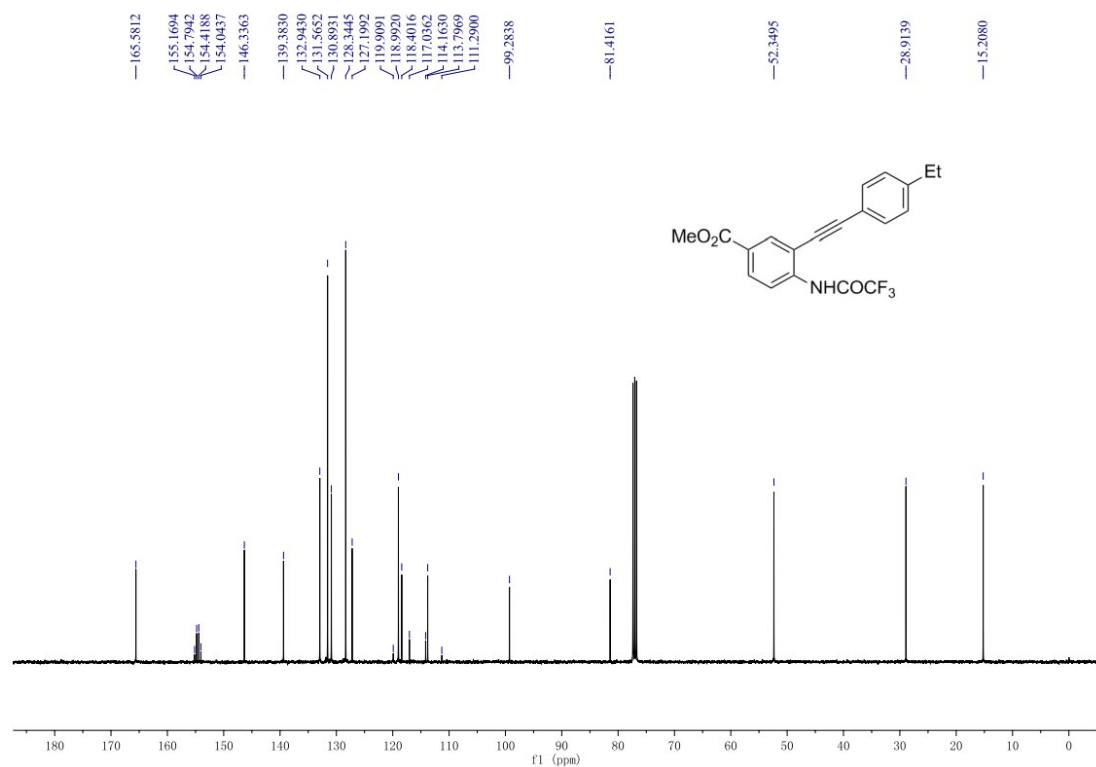
<sup>1</sup>H NMR spectrum of **2q**



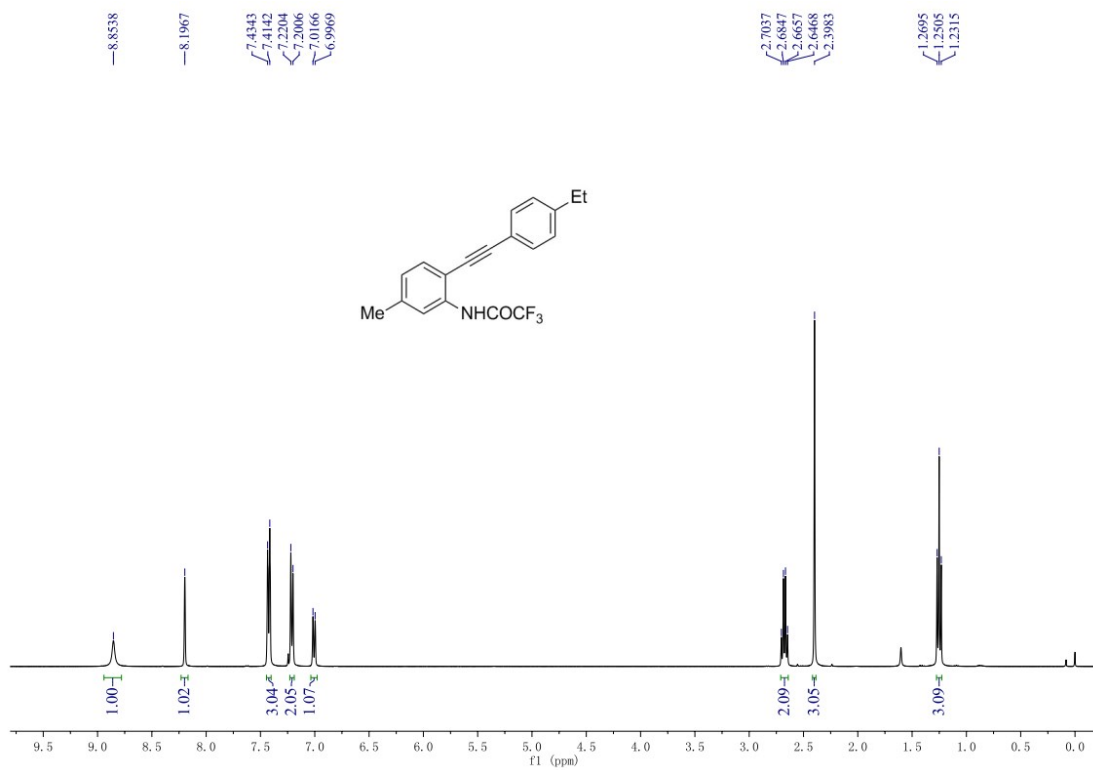
<sup>13</sup>C NMR spectrum of **2q**



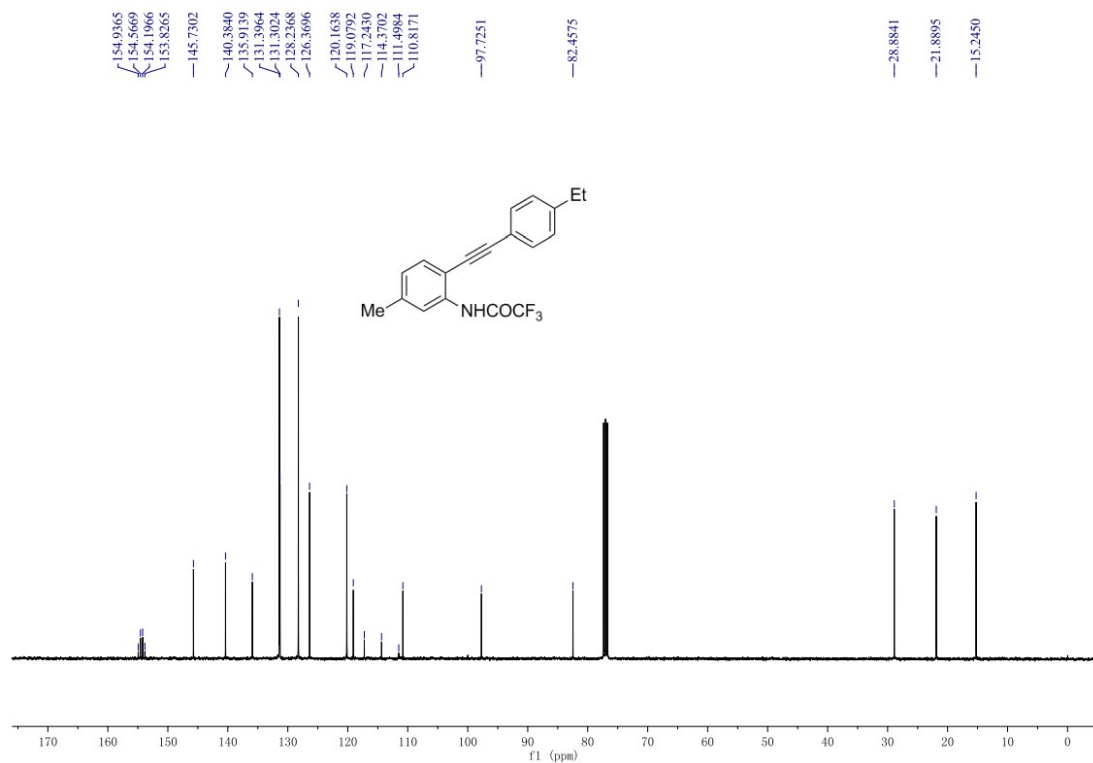
<sup>1</sup>H NMR spectrum of **2r**



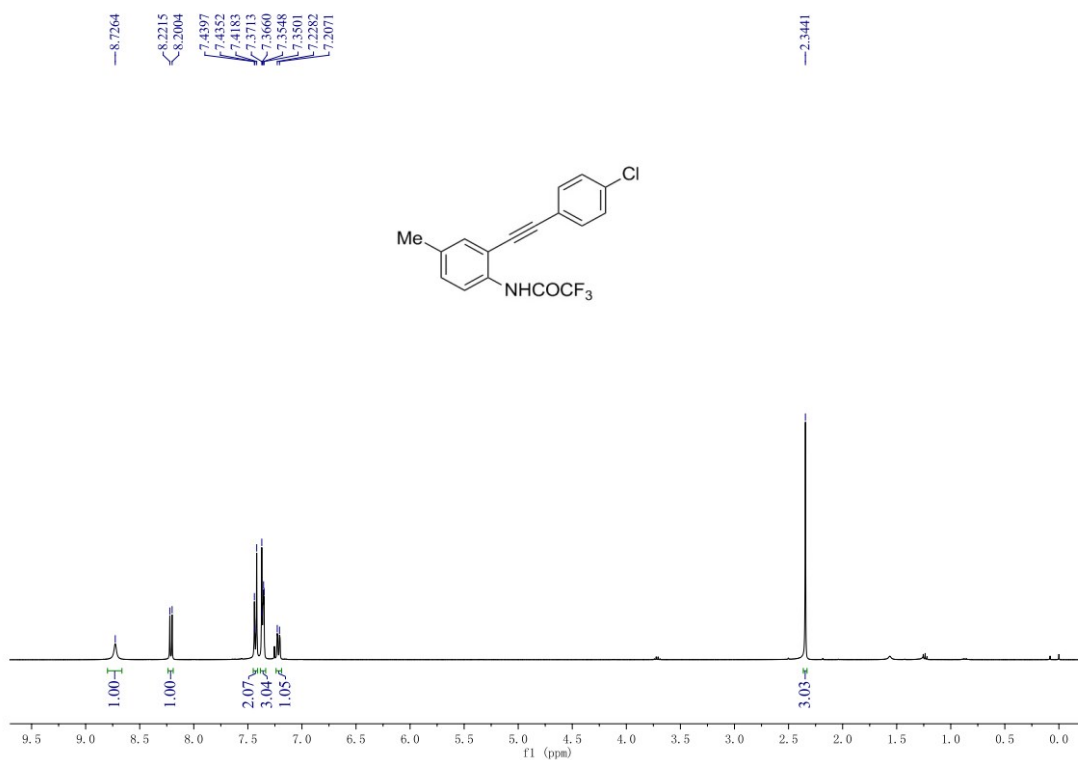
<sup>13</sup>C NMR spectrum of **2r**



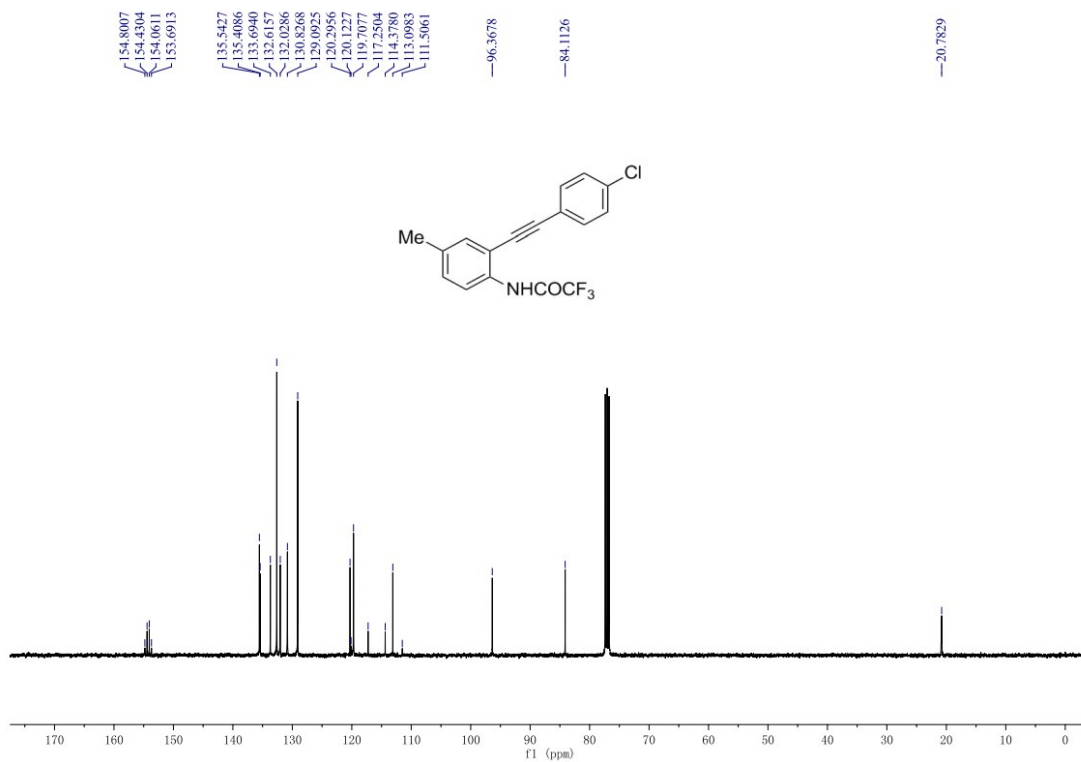
<sup>1</sup>H NMR spectrum of **2s**



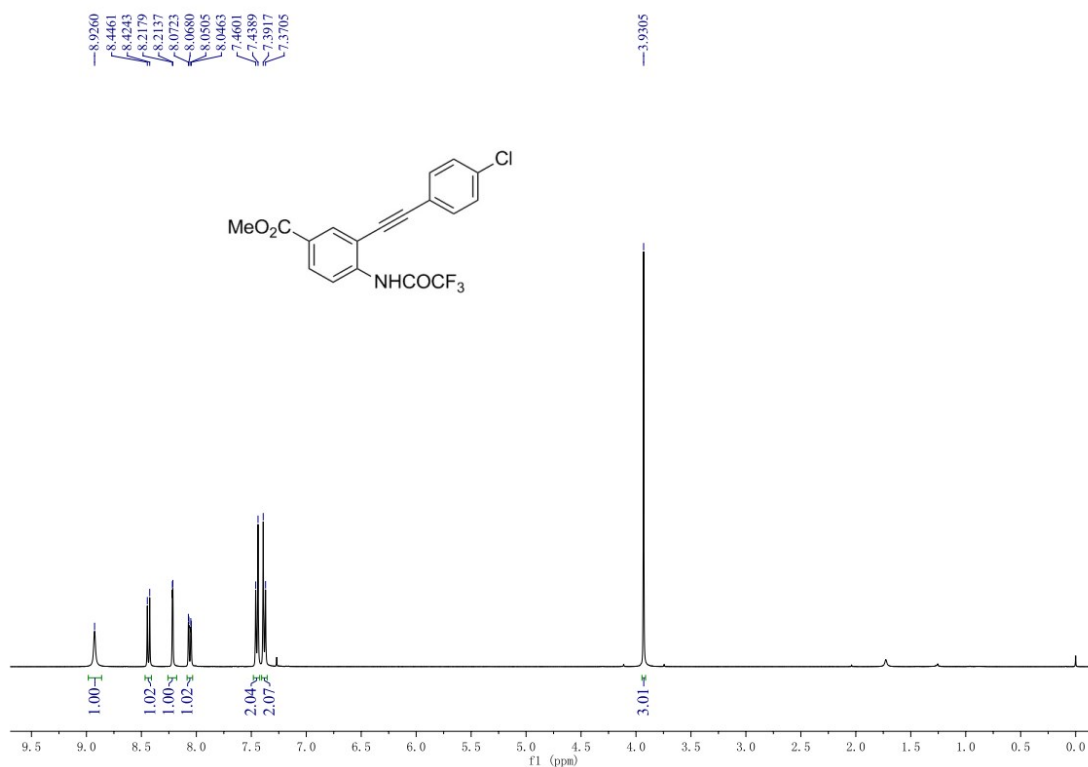
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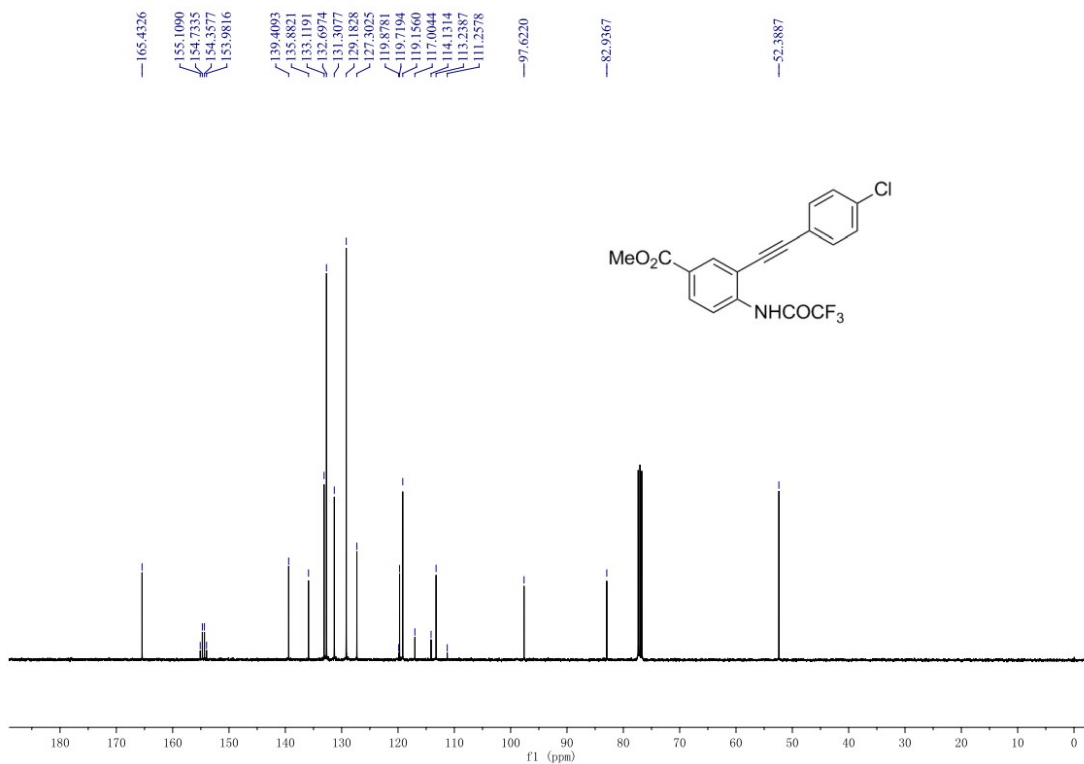
<sup>1</sup>H NMR spectrum of **2u**



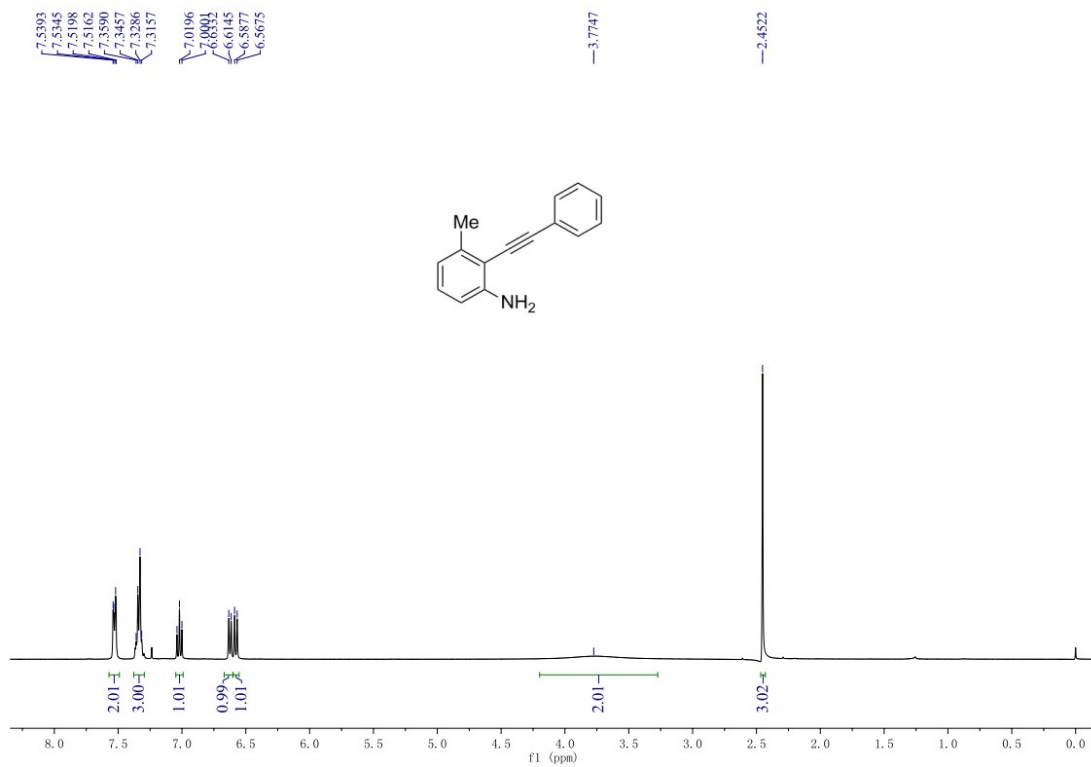
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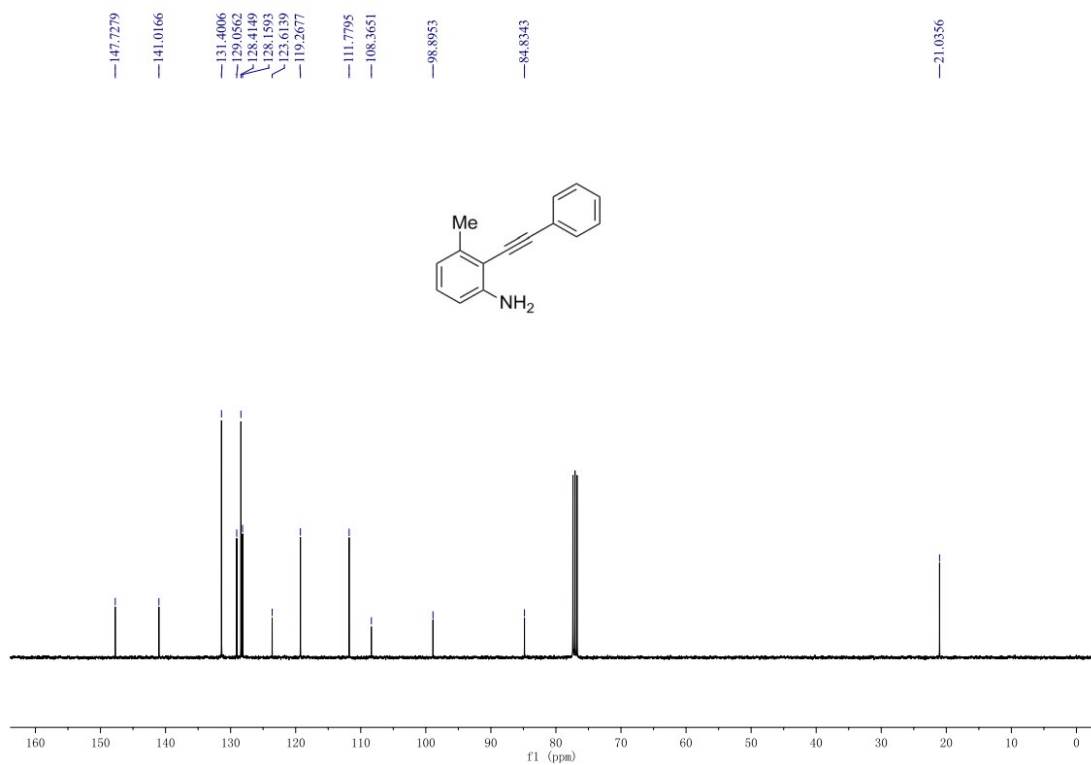
<sup>1</sup>H NMR spectrum of **2v**



<sup>13</sup>C NMR spectrum of **2v**

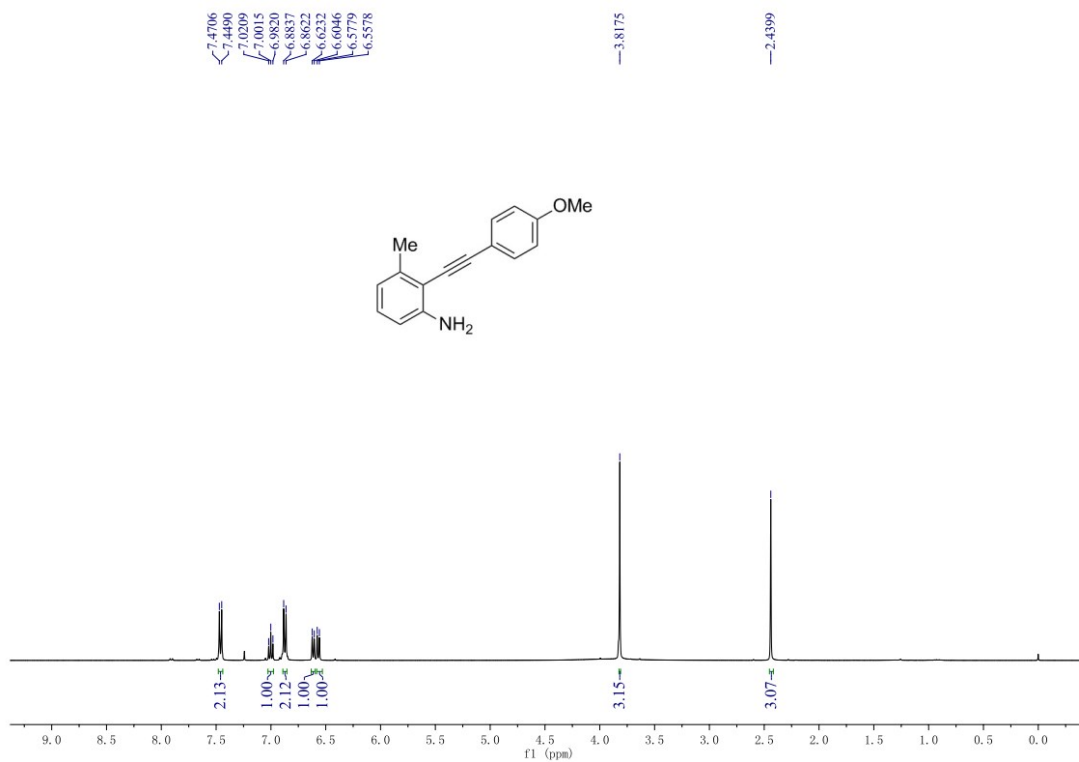


<sup>1</sup>H NMR spectrum of S3f

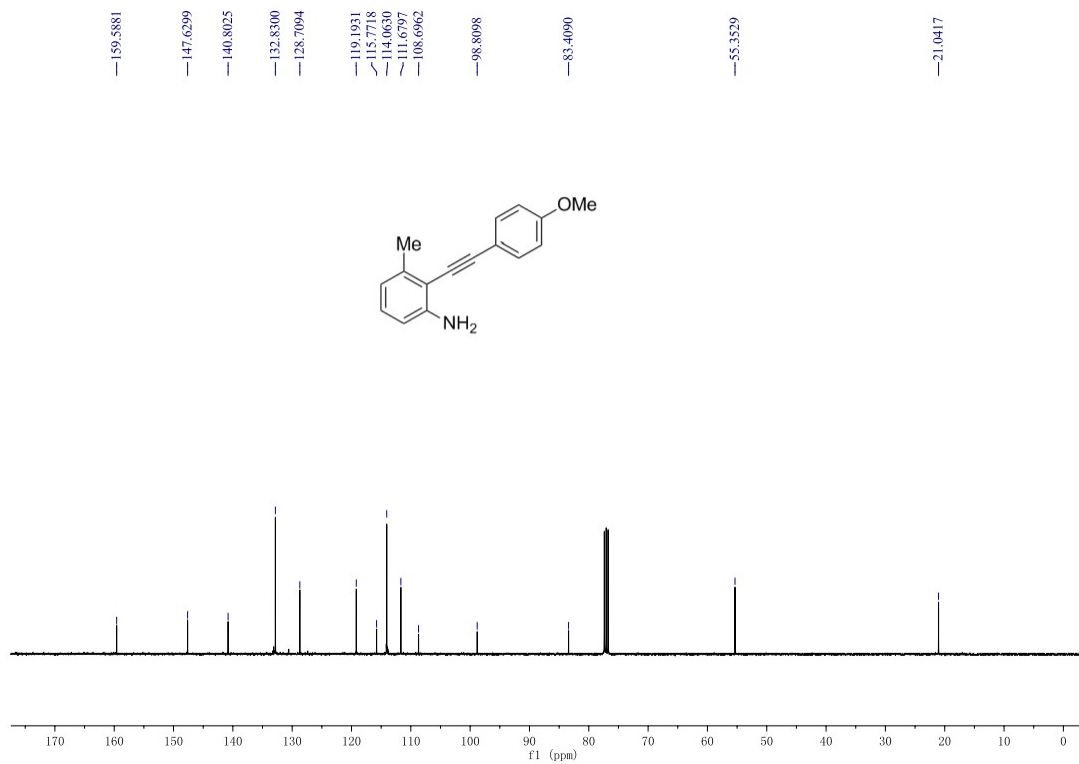


<sup>13</sup>C NMR spectrum of S3f

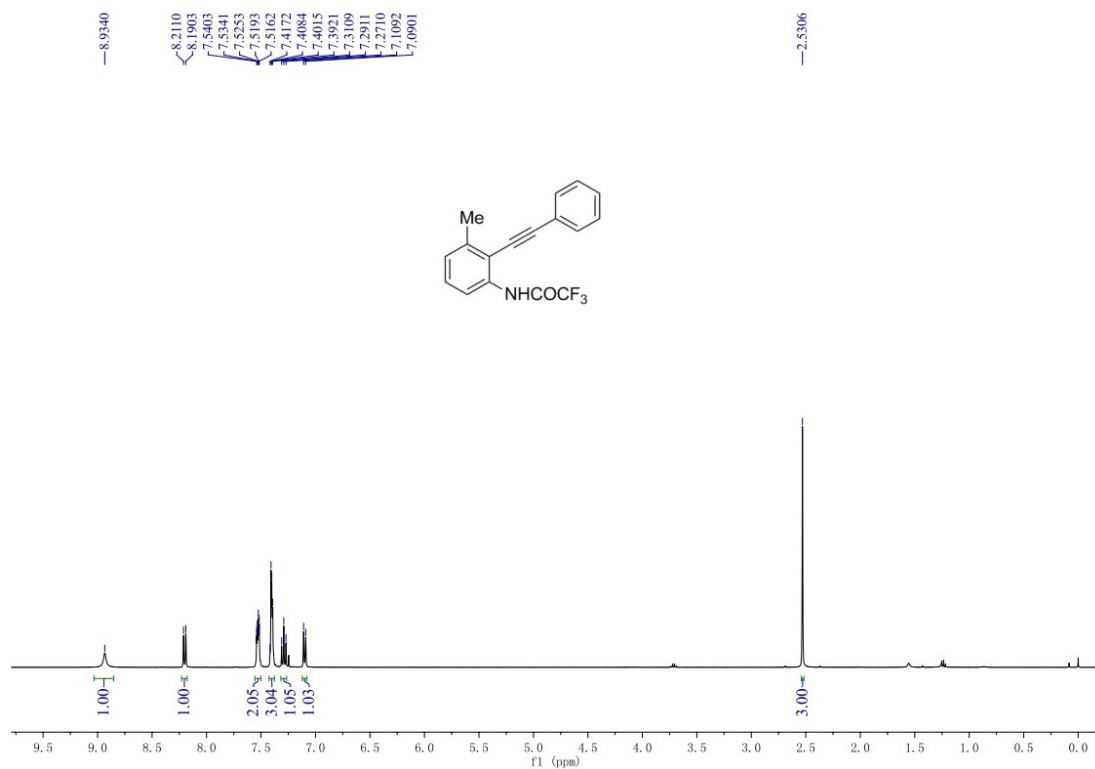




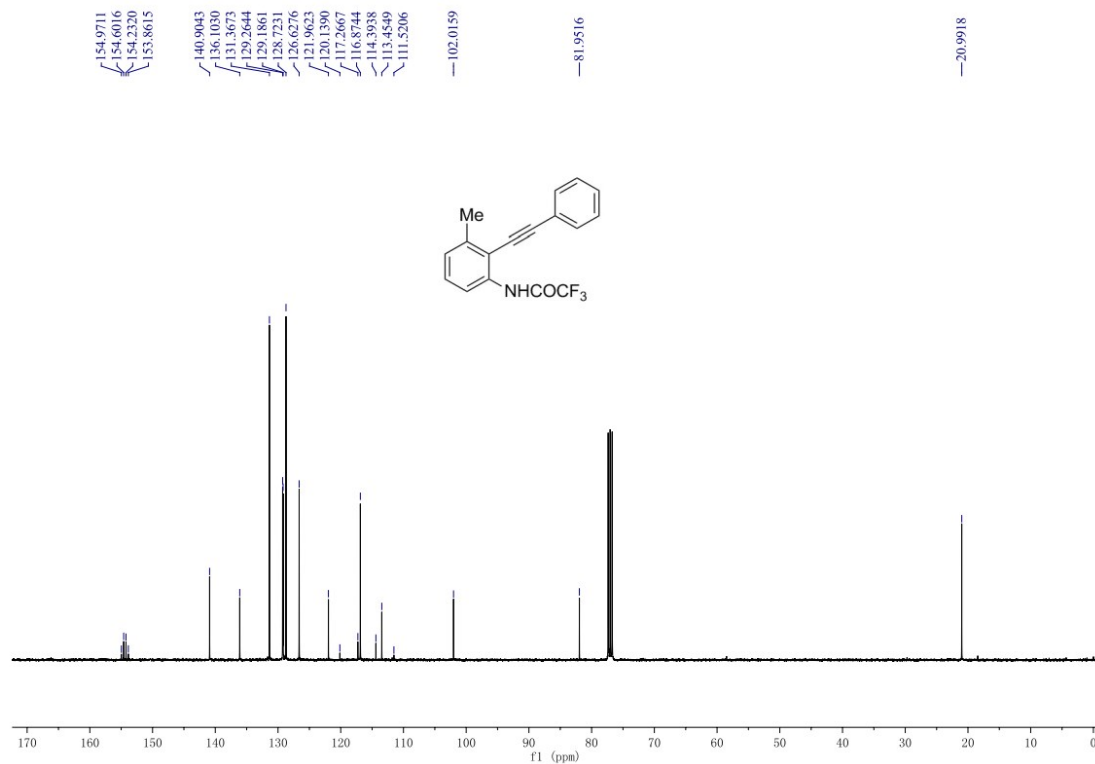
<sup>1</sup>H NMR spectrum of **S3n**



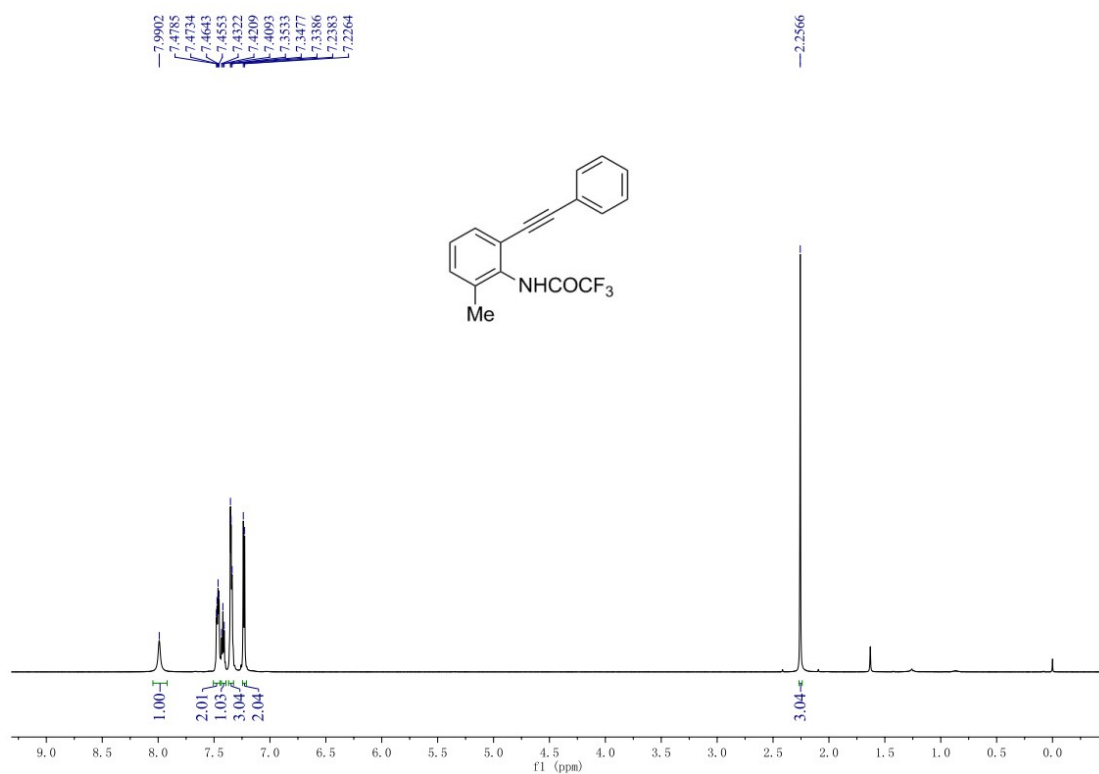
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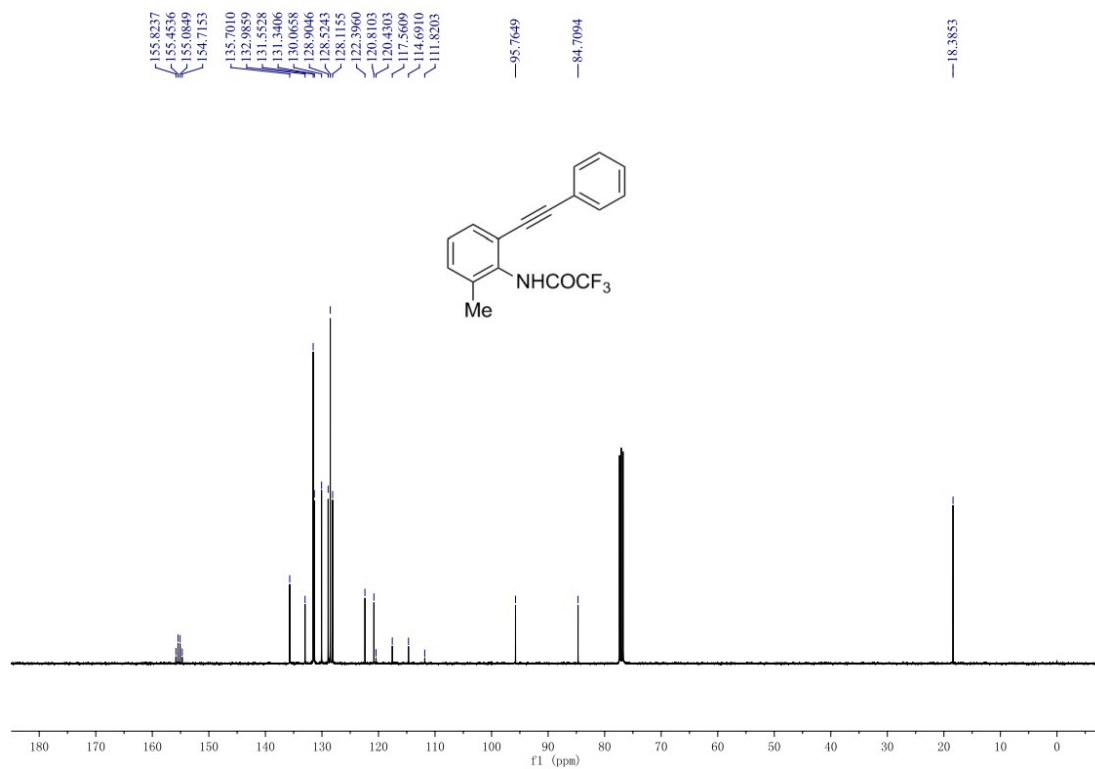
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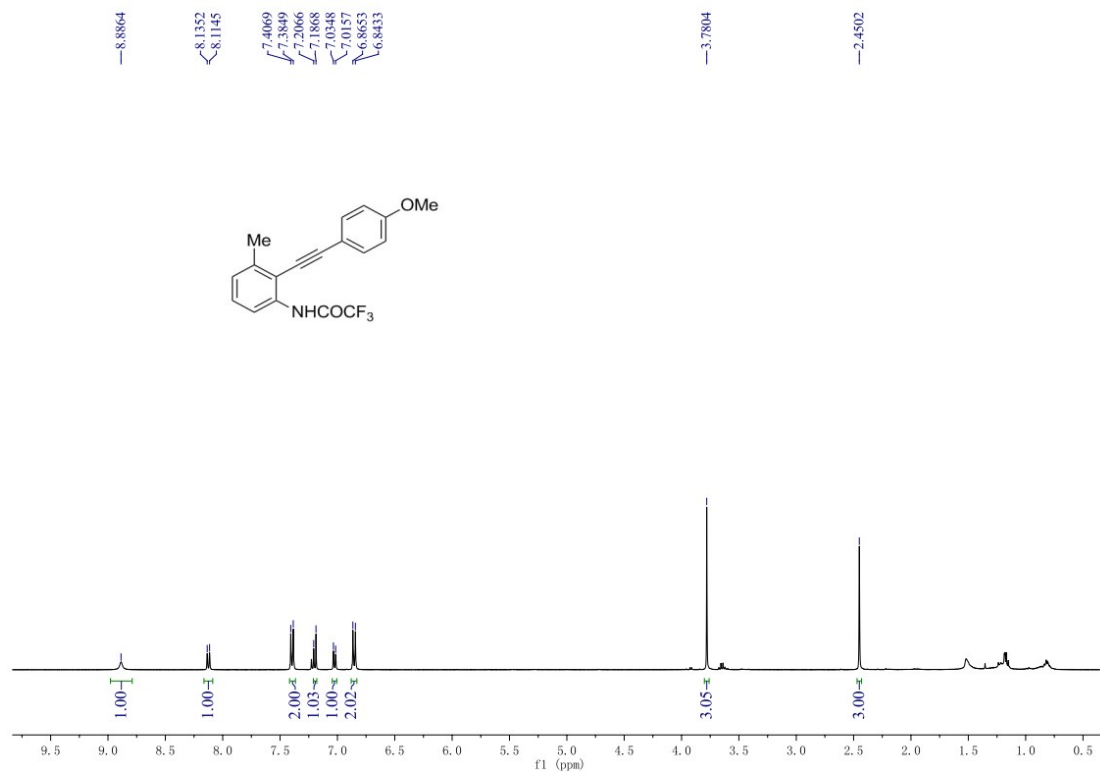
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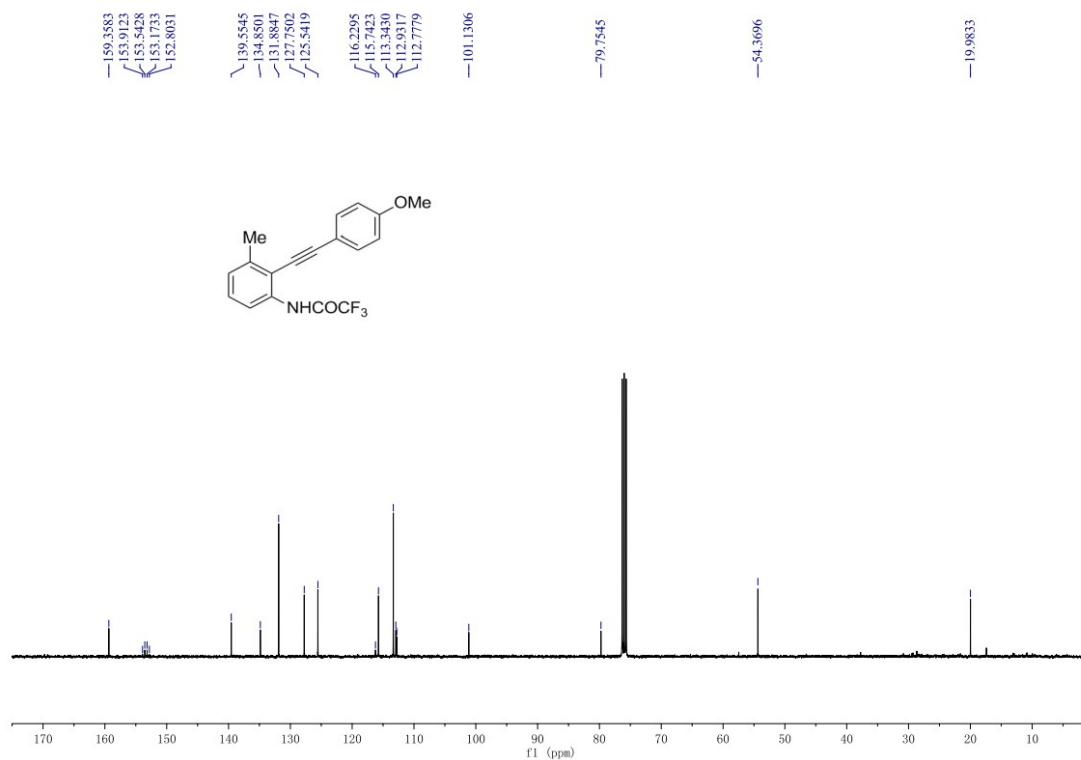
<sup>1</sup>H NMR spectrum of **2i**



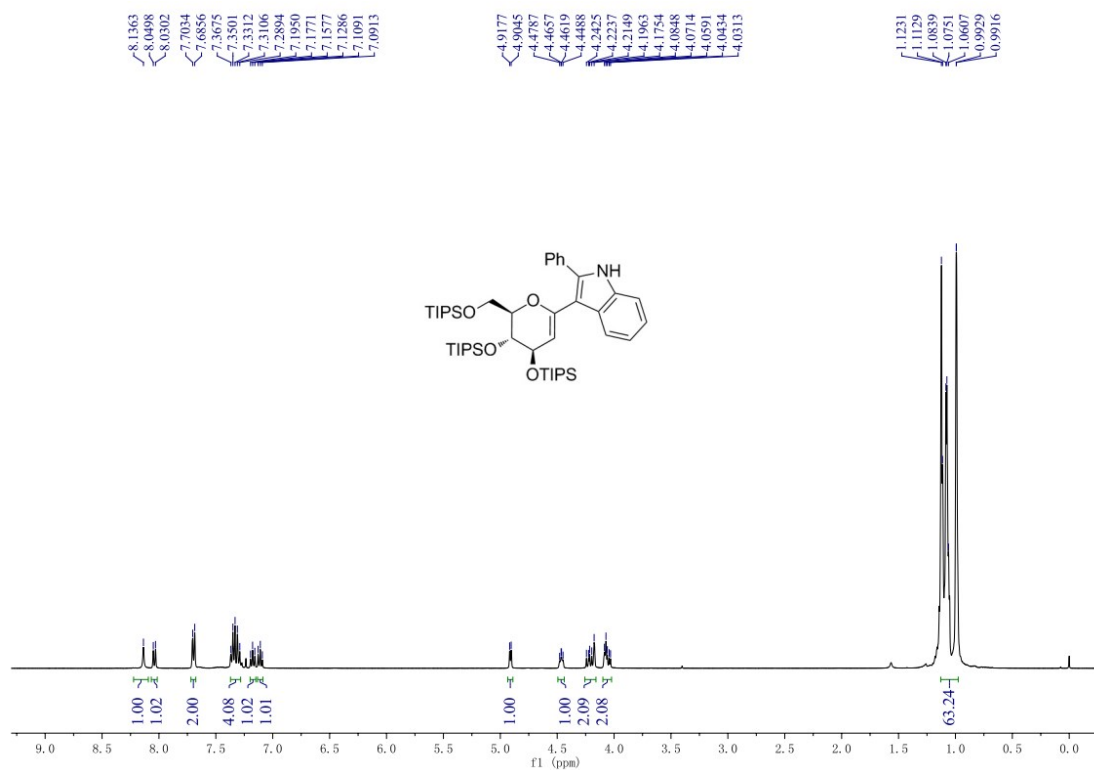
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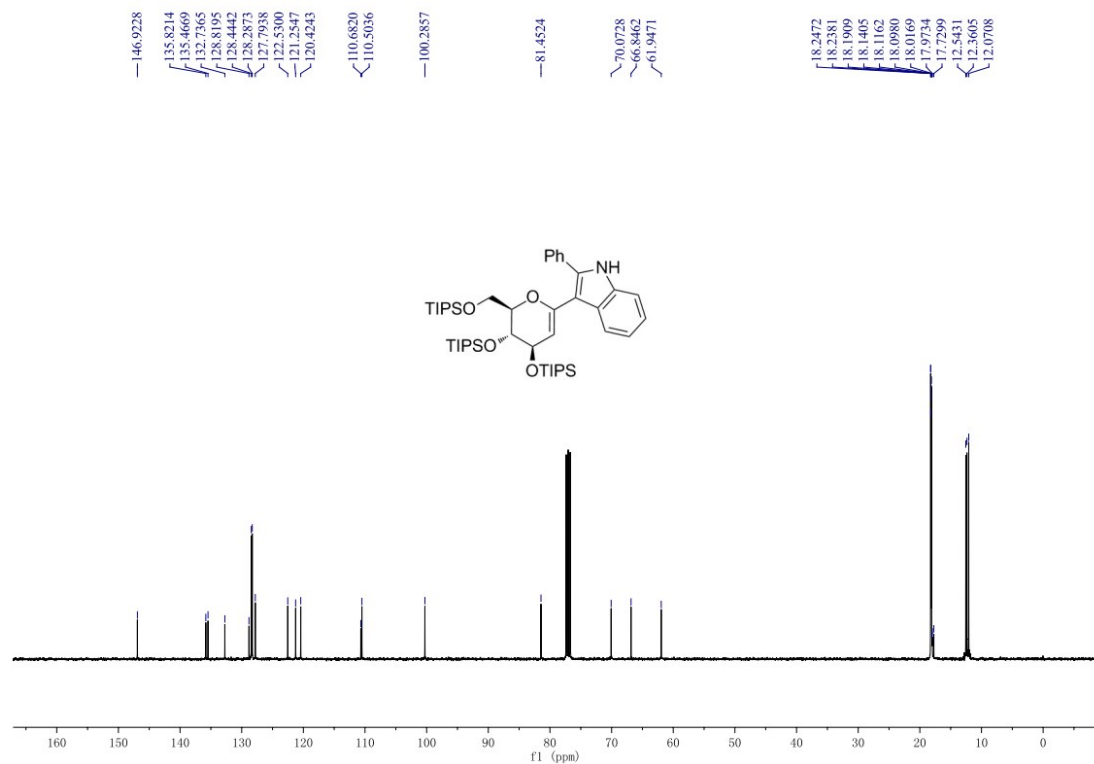
$^1\text{H}$  NMR spectrum of **2n**



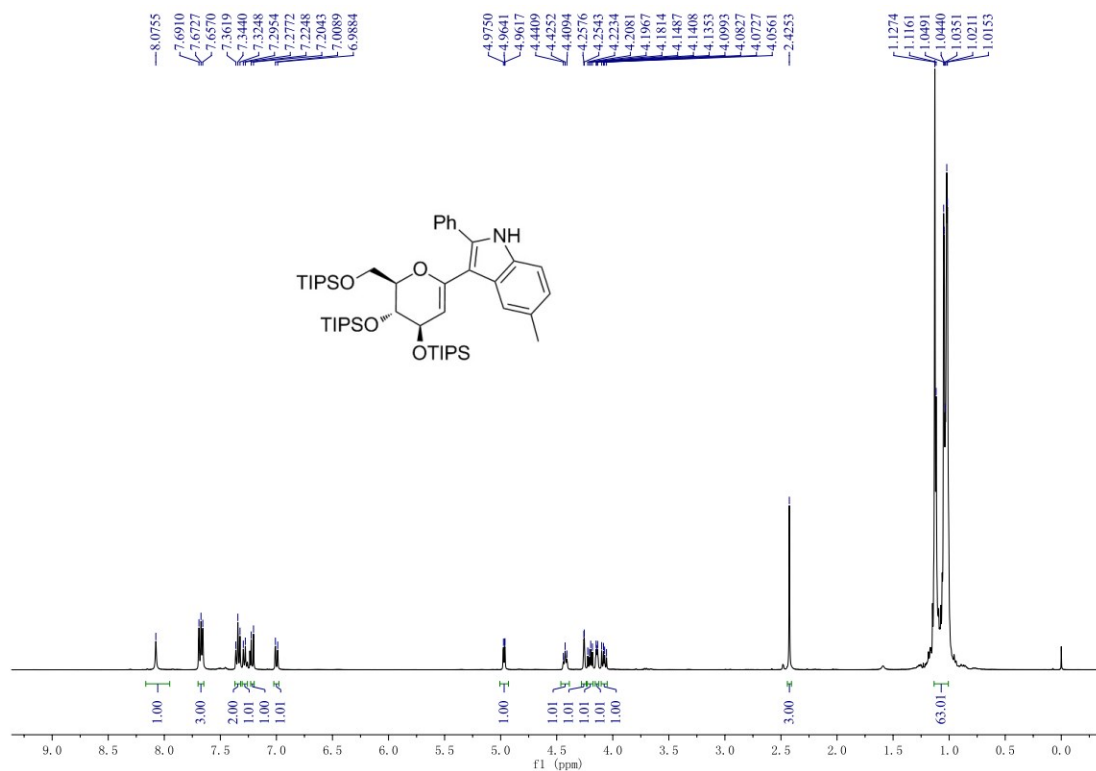
$^{13}\text{C}$  NMR spectrum of **2n**



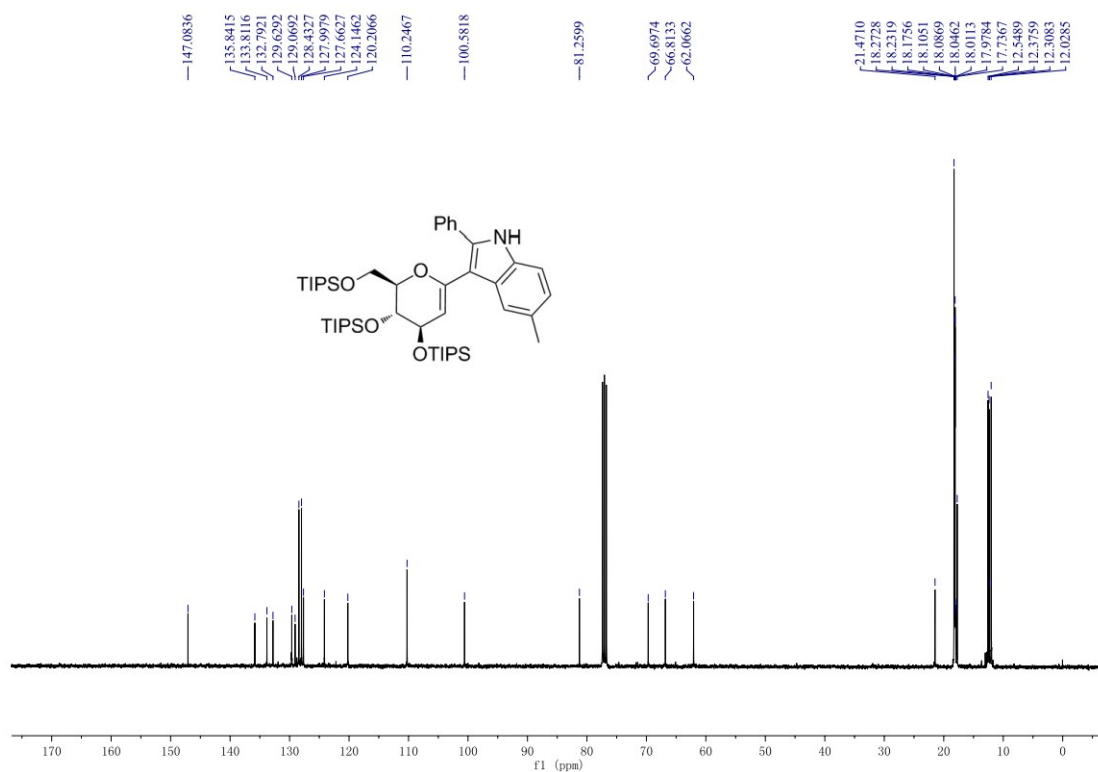
<sup>1</sup>H NMR spectrum of **3aa**



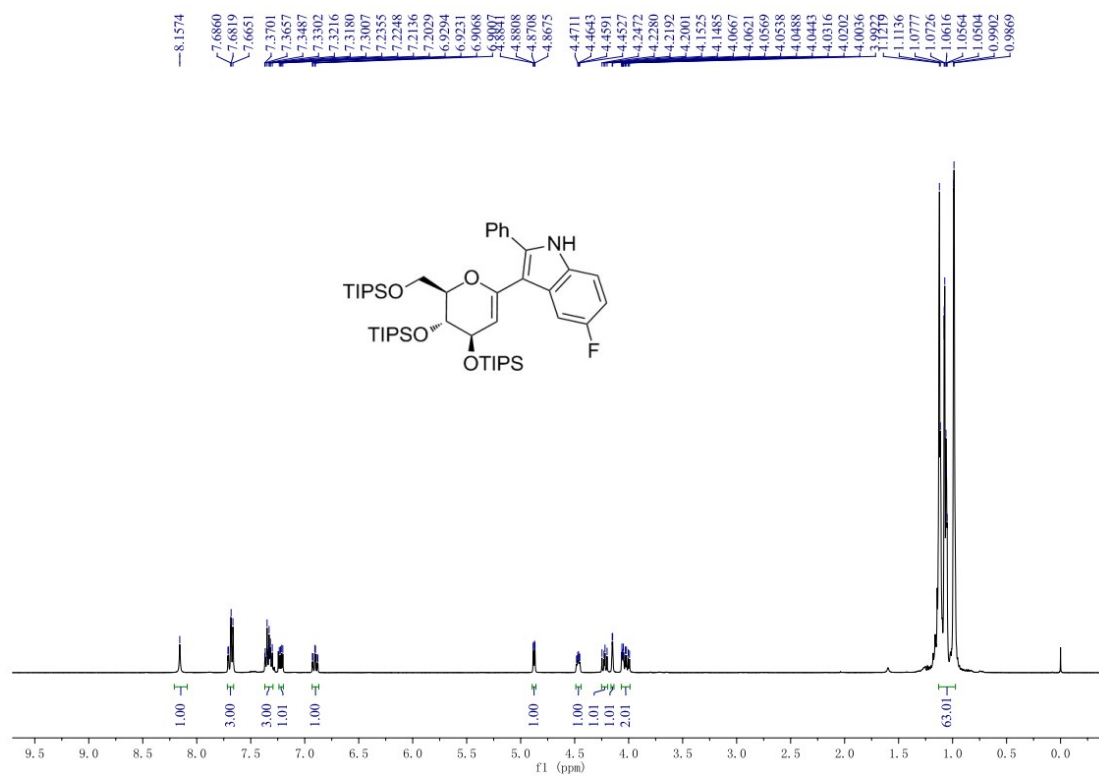
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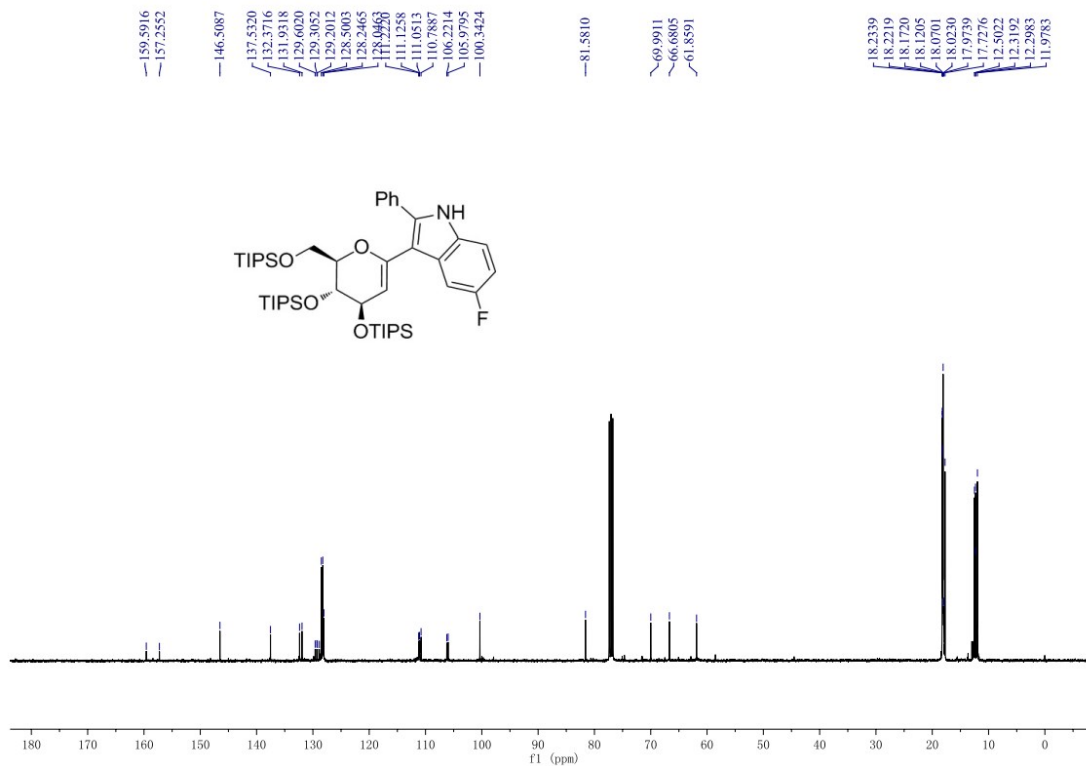
**<sup>1</sup>H NMR spectrum of **3ab****



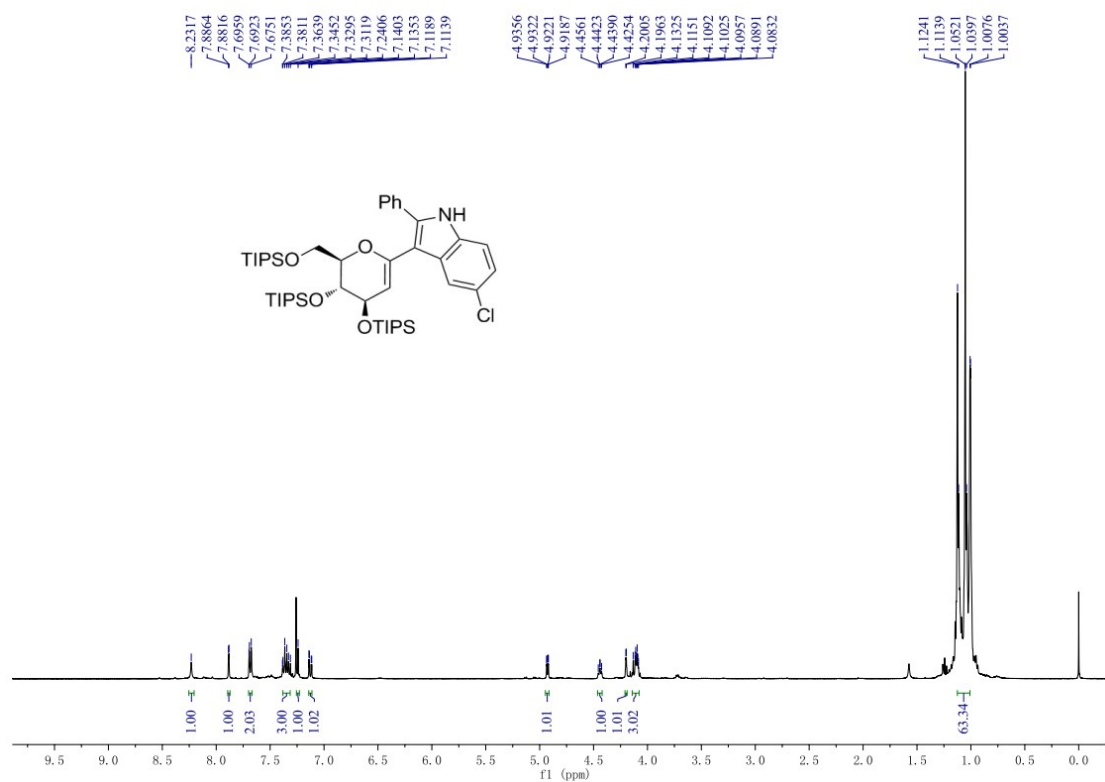
**<sup>13</sup>C NMR spectrum of **3ab****



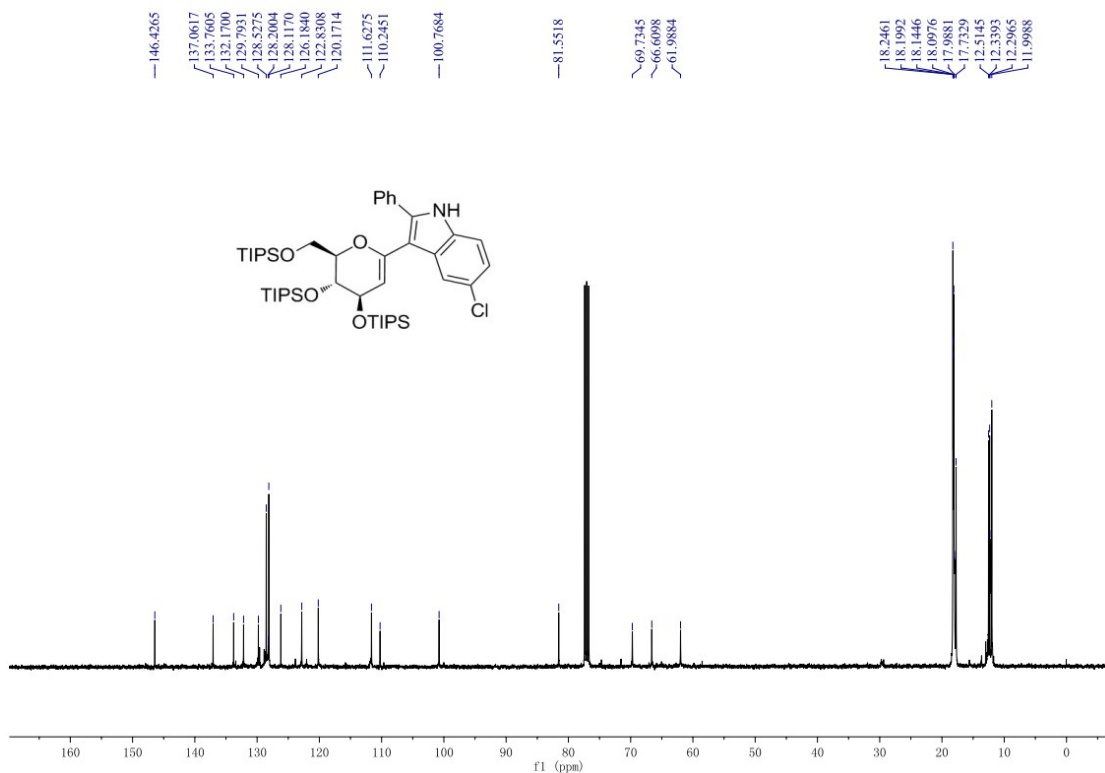
<sup>1</sup>H NMR spectrum of **3ac**



<sup>13</sup>C NMR spectrum of **3ac**

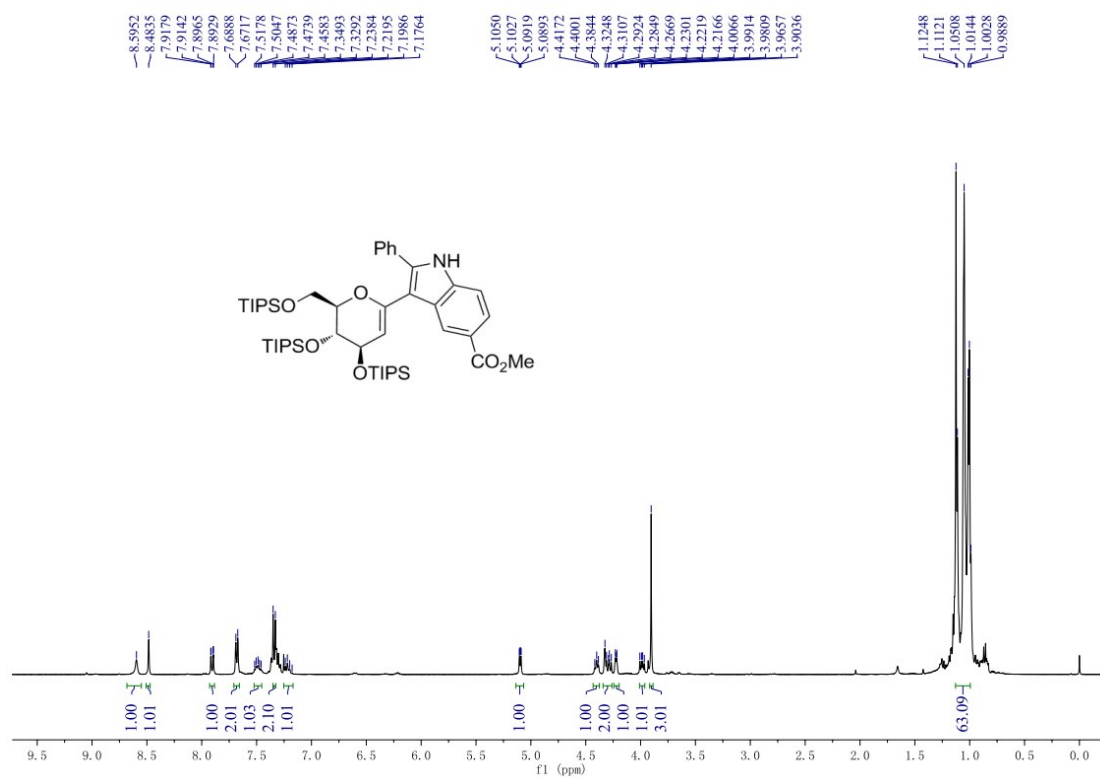


<sup>1</sup>H NMR spectrum of **3ad**

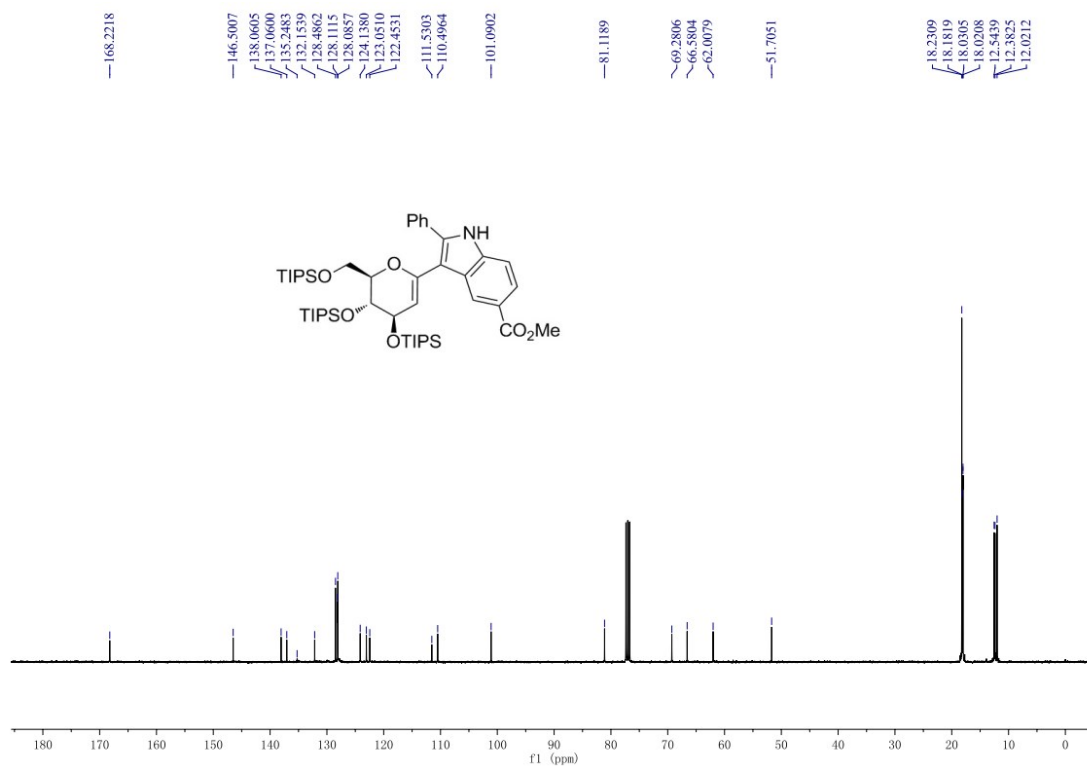


<sup>13</sup>C NMR spectrum of **3ad**

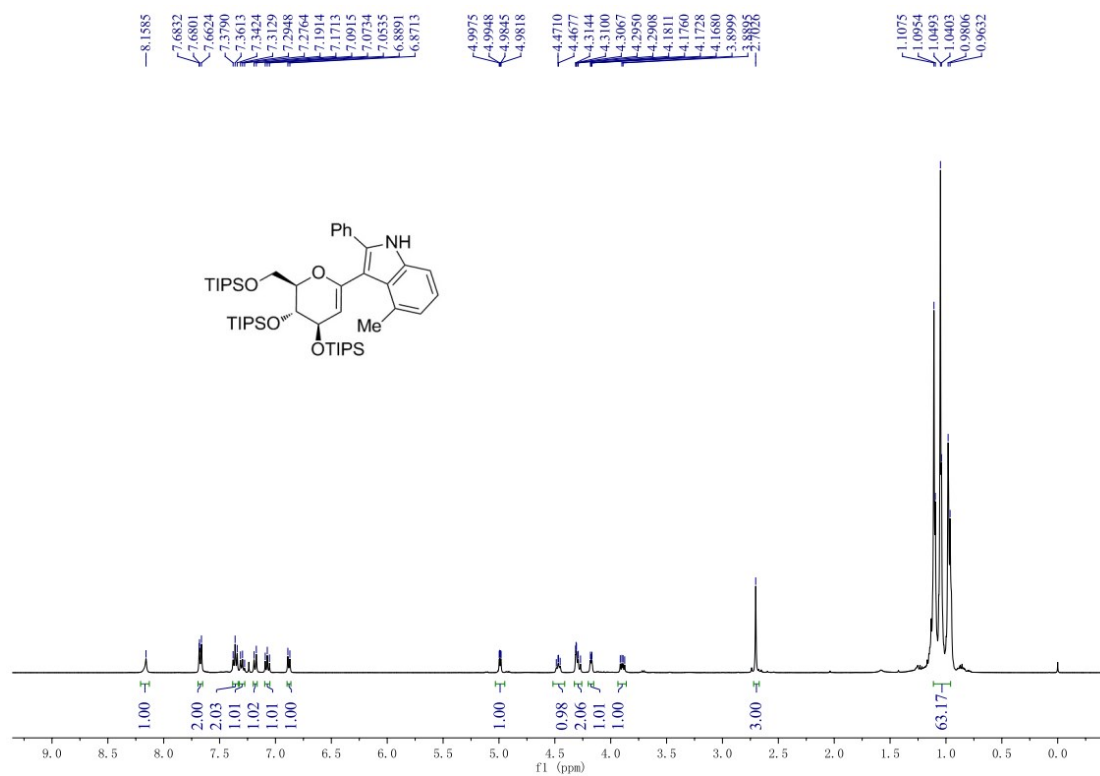




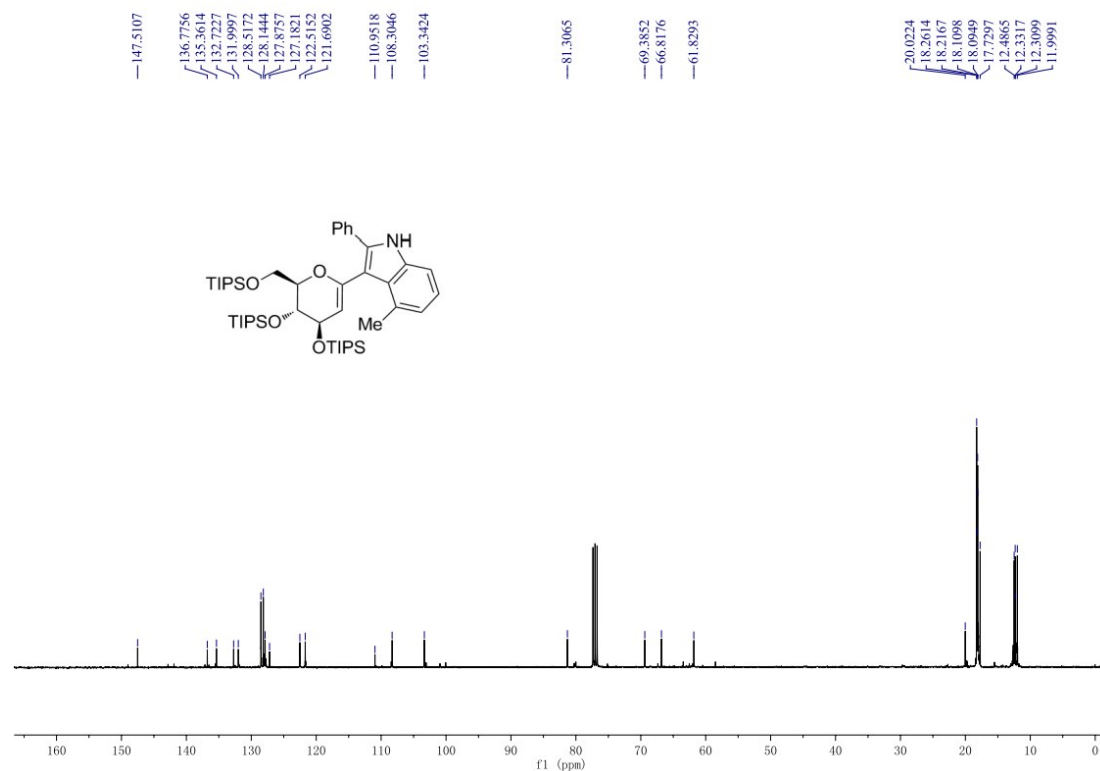
<sup>1</sup>H NMR spectrum of **3ae**



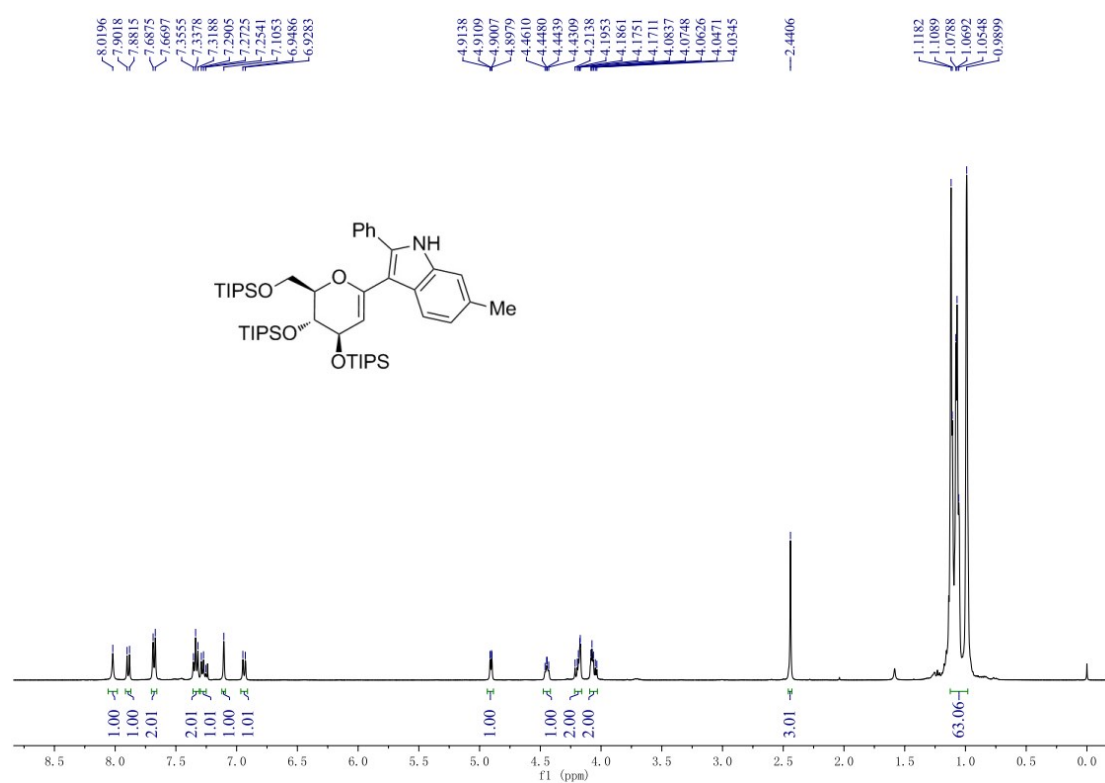
<sup>13</sup>C NMR spectrum of **3ae**



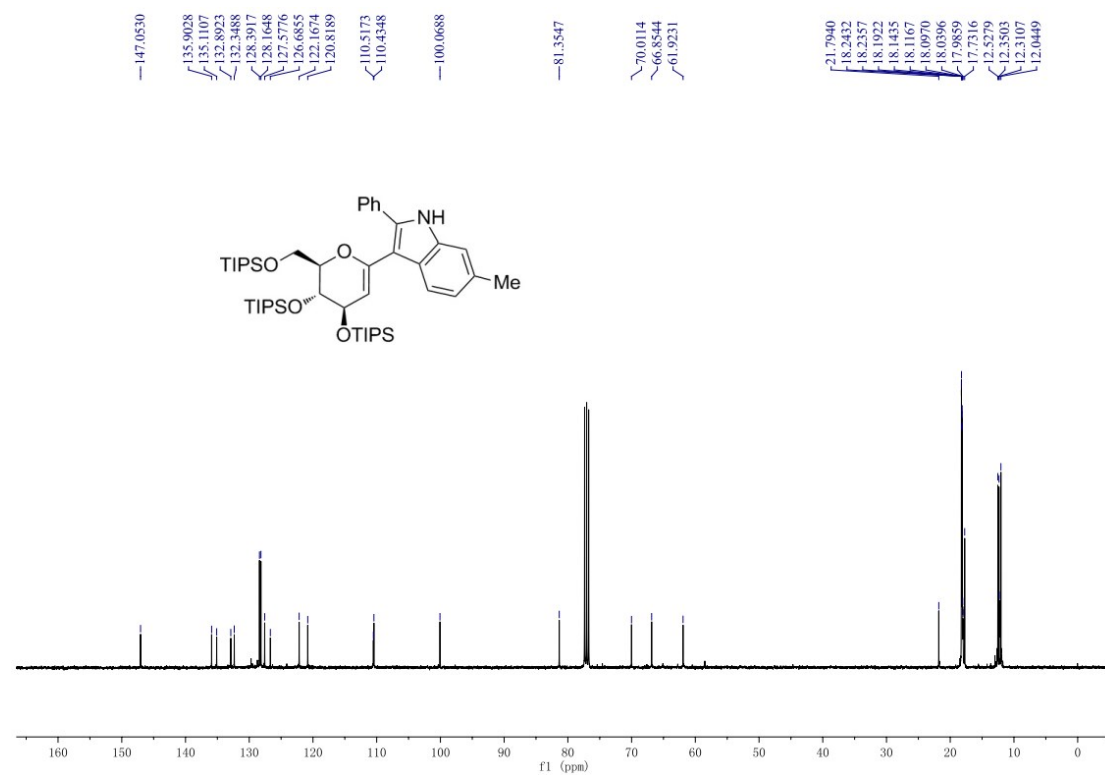
<sup>1</sup>H NMR spectrum of **3af**



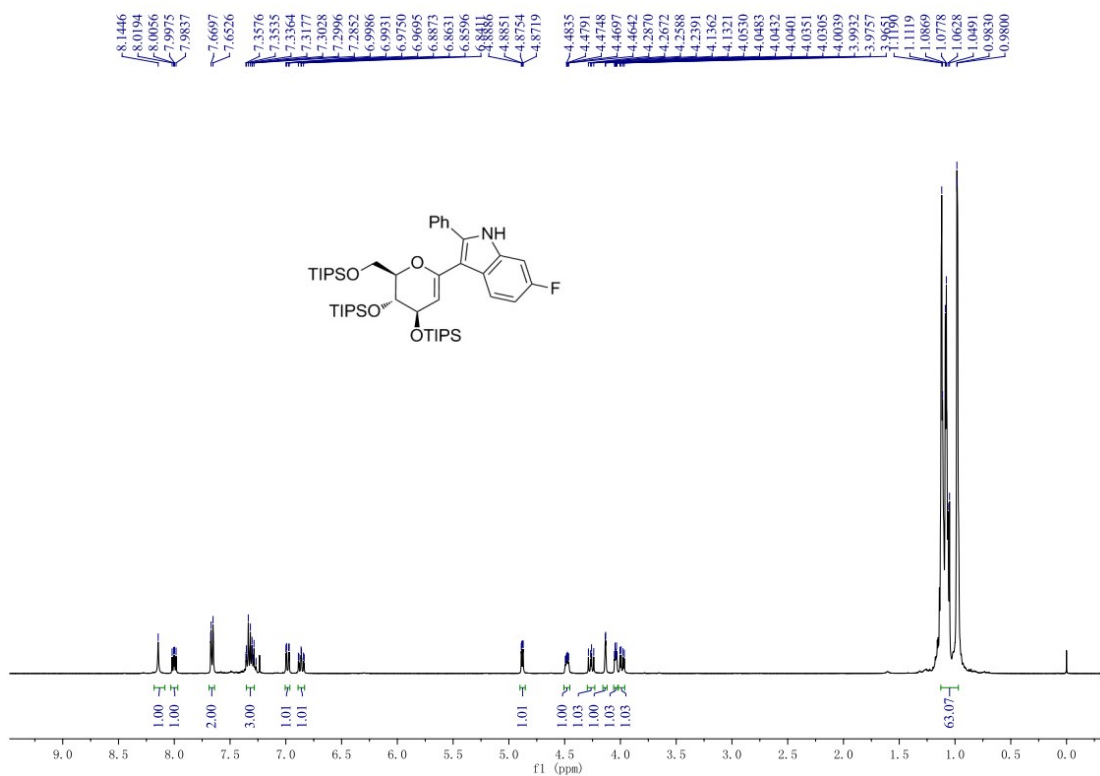
<sup>13</sup>C NMR spectrum of **3af**



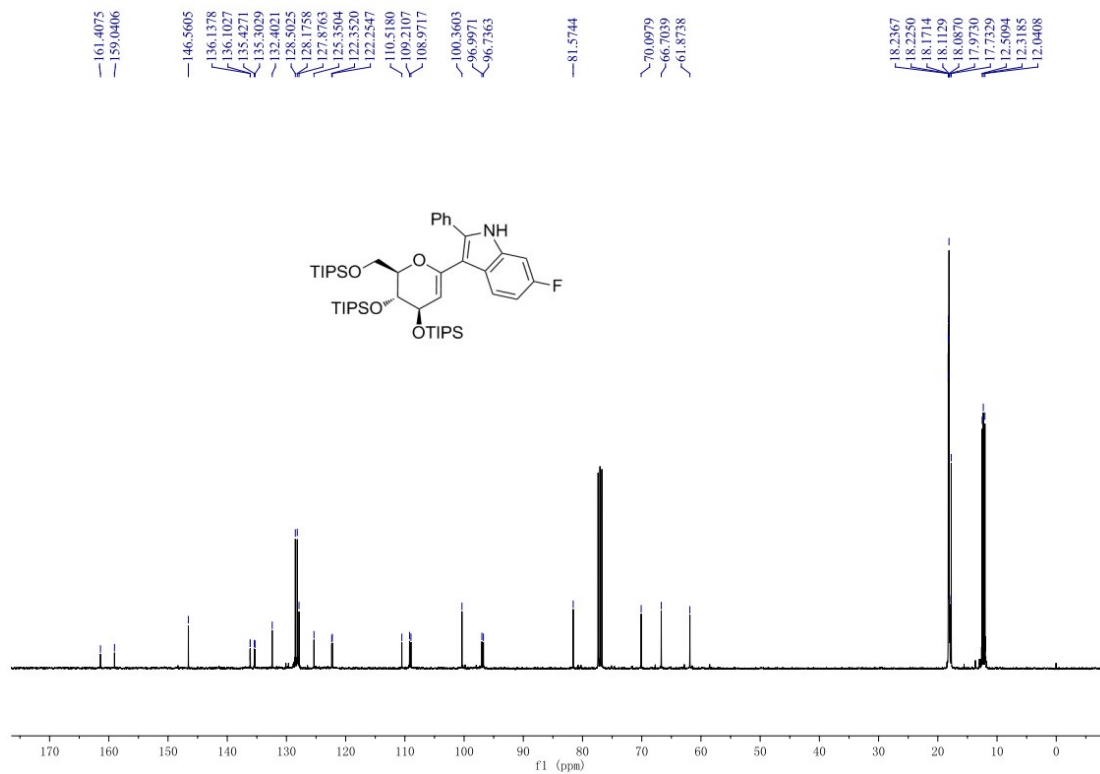
<sup>1</sup>H NMR spectrum of **3ag**



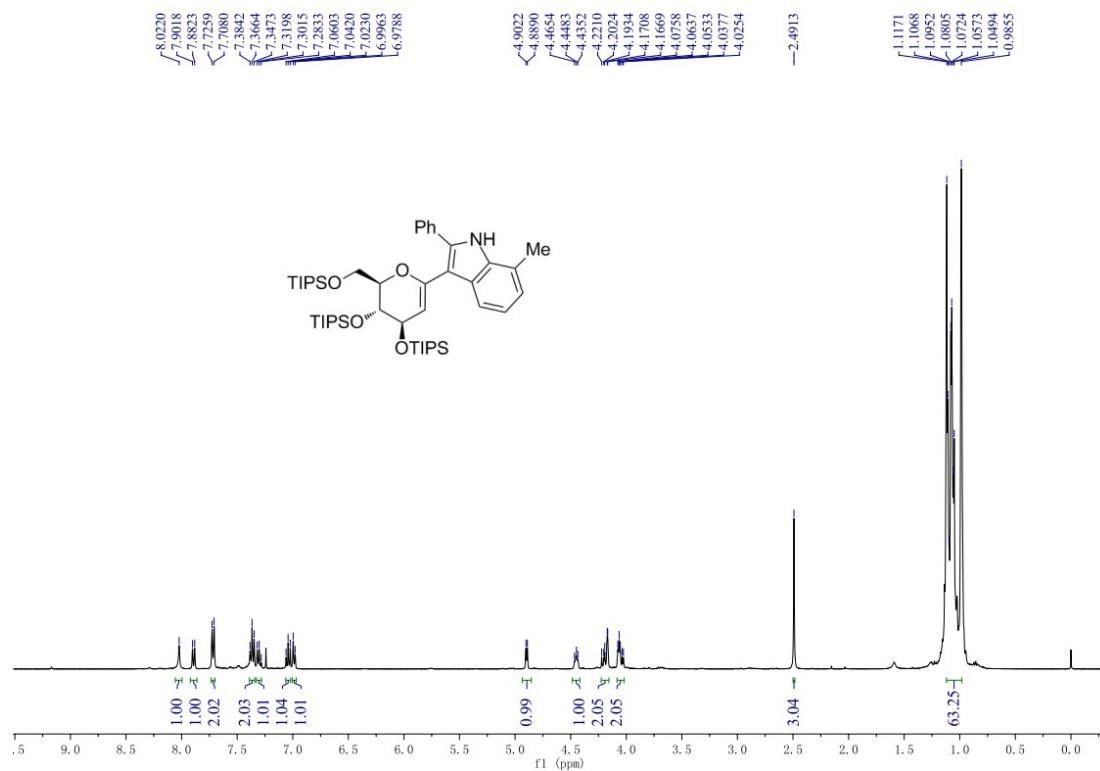
<sup>13</sup>C NMR spectrum of **3ag**



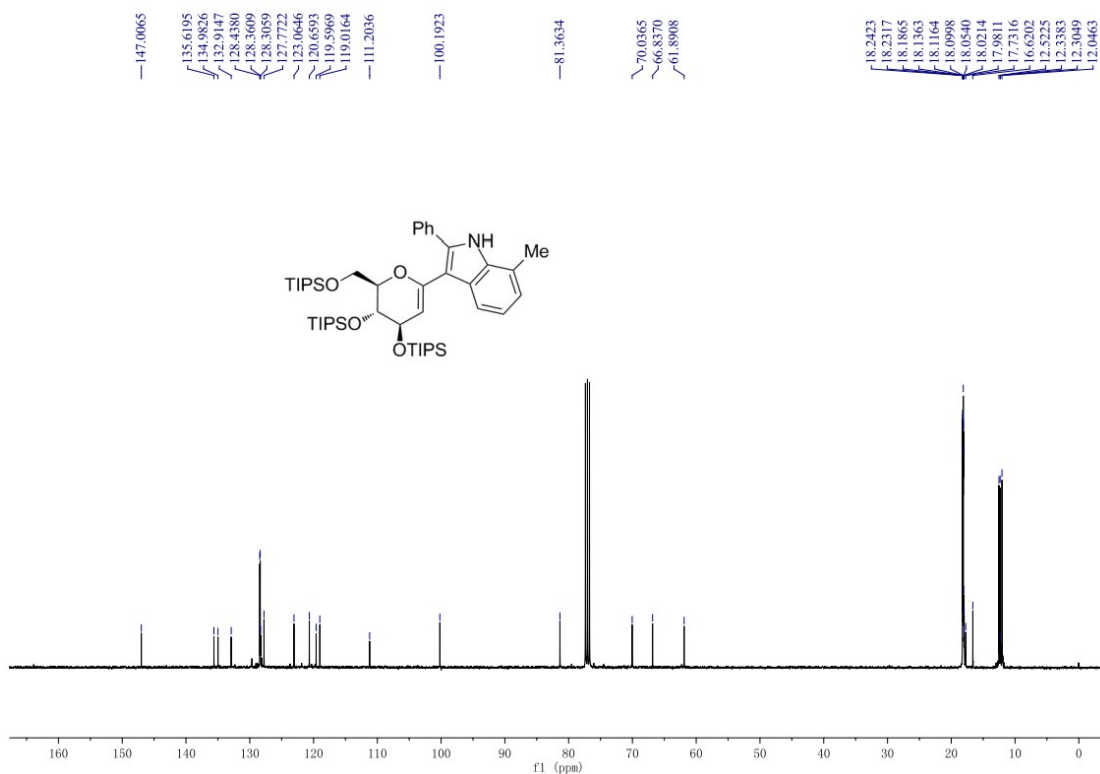
<sup>1</sup>H NMR spectrum of **3ah**



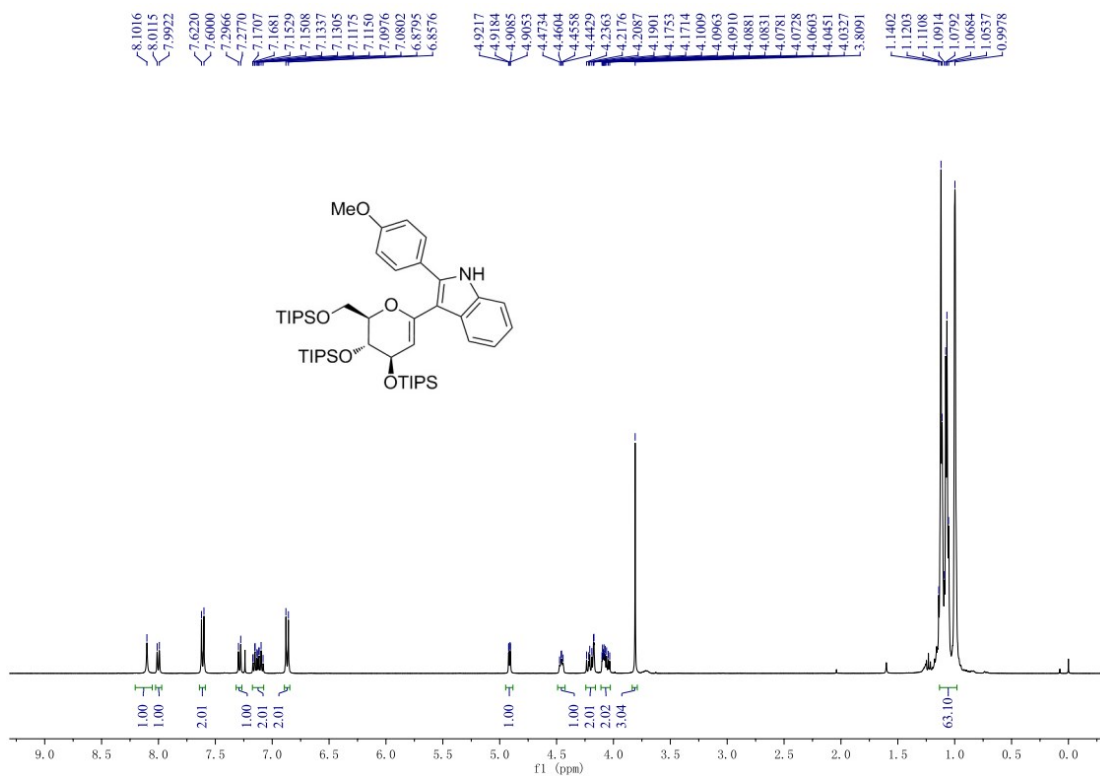
<sup>13</sup>C NMR spectrum of **3ah**



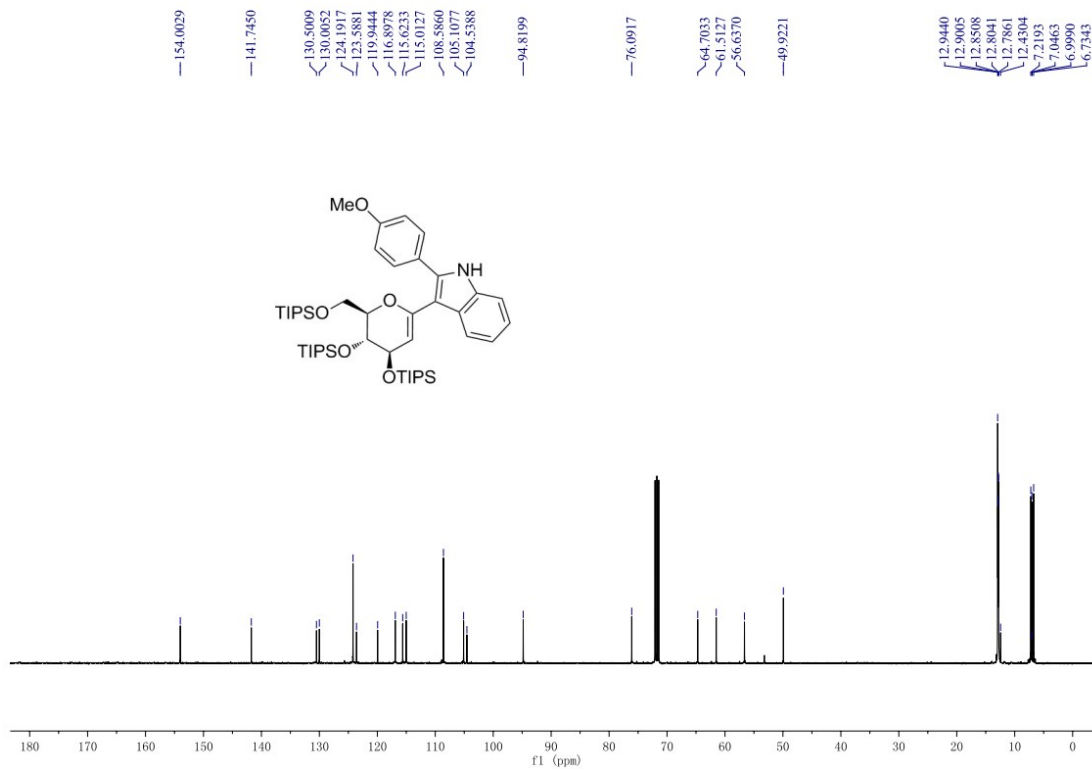
<sup>1</sup>H NMR spectrum of **3ai**



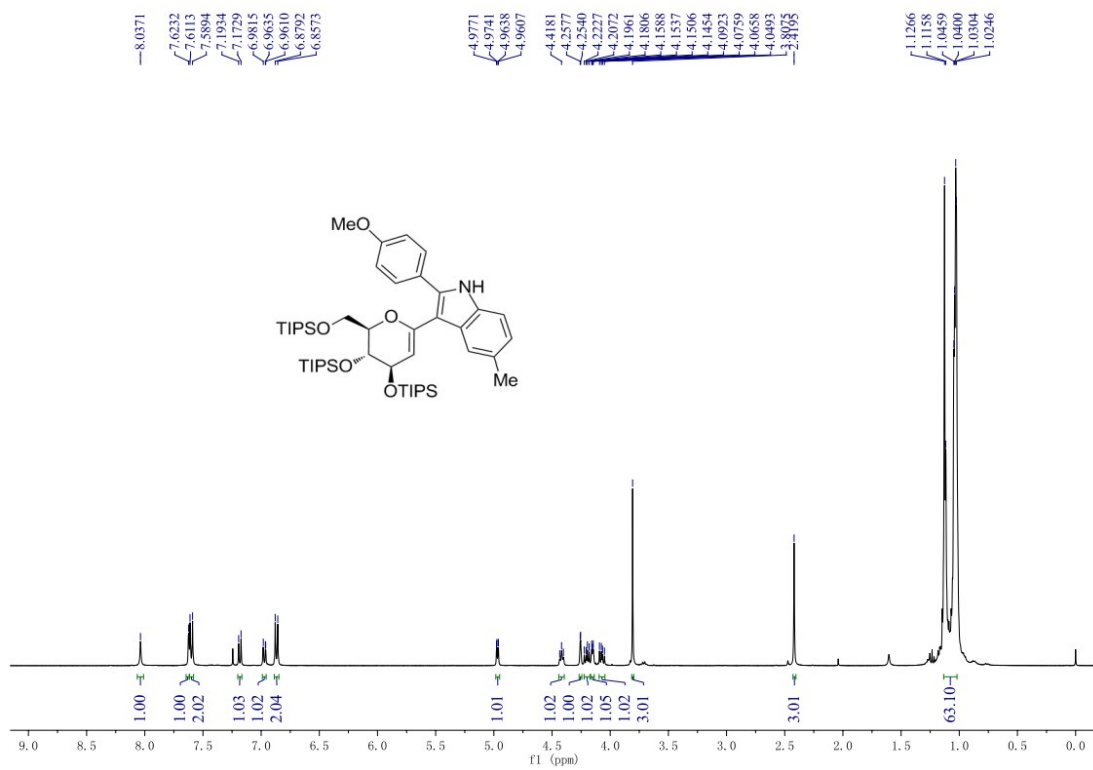
<sup>13</sup>C NMR spectrum of **3ai**



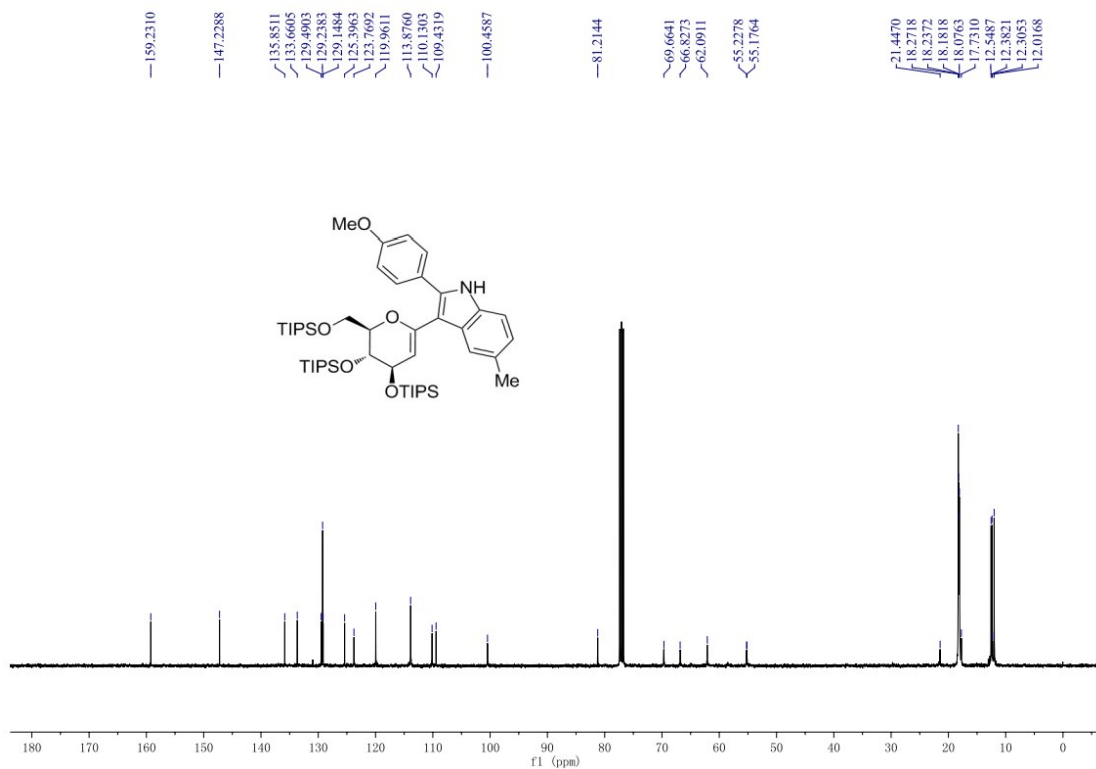
<sup>1</sup>H NMR spectrum of **3aj**



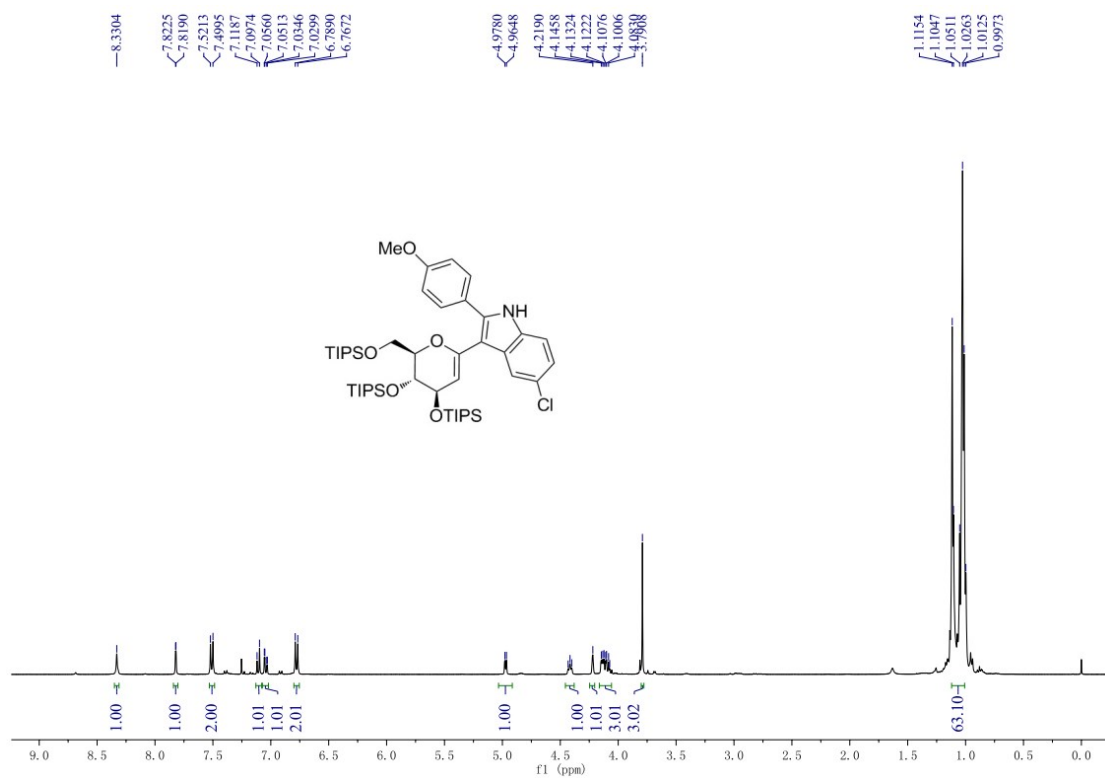
<sup>13</sup>C NMR spectrum of **3aj**



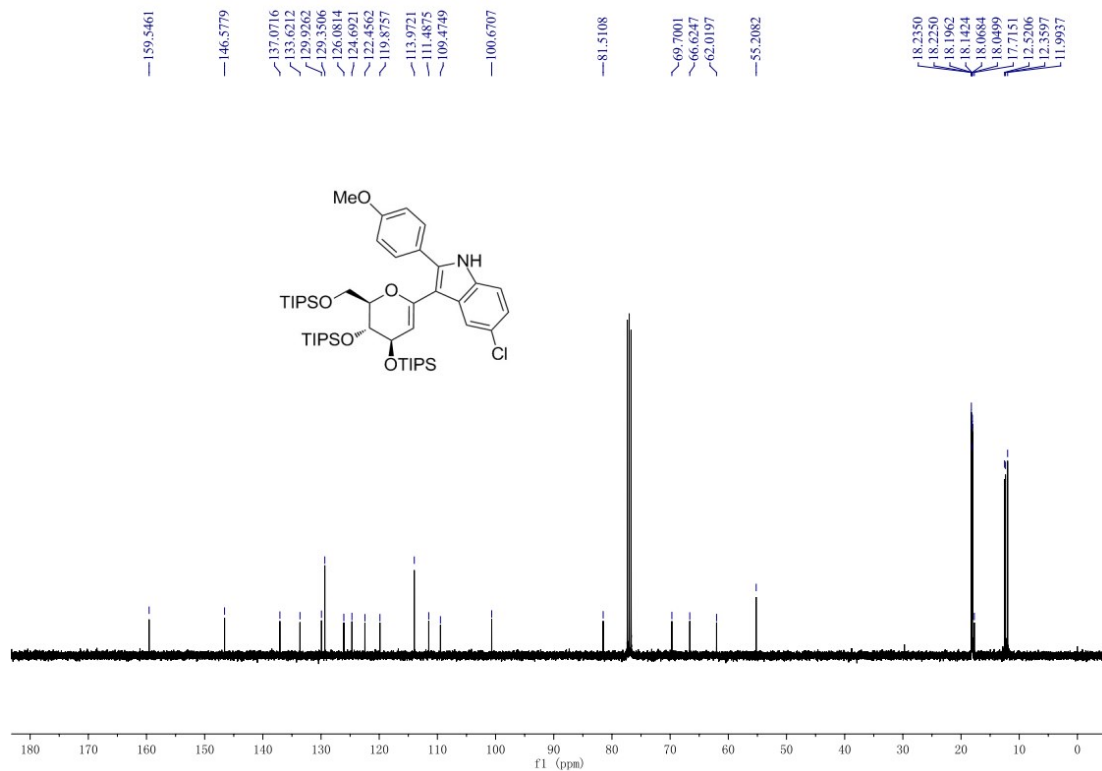
<sup>1</sup>H NMR spectrum of **3ak**



<sup>13</sup>C NMR spectrum of **3ak**

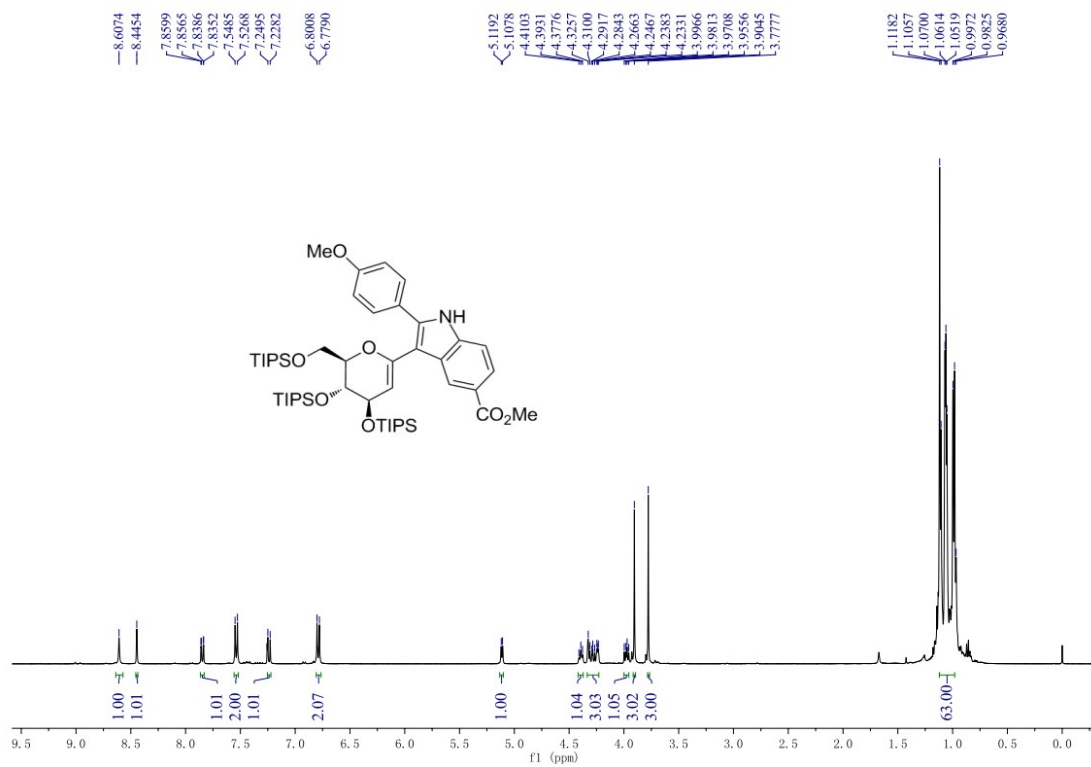


<sup>1</sup>H NMR spectrum of **3al**

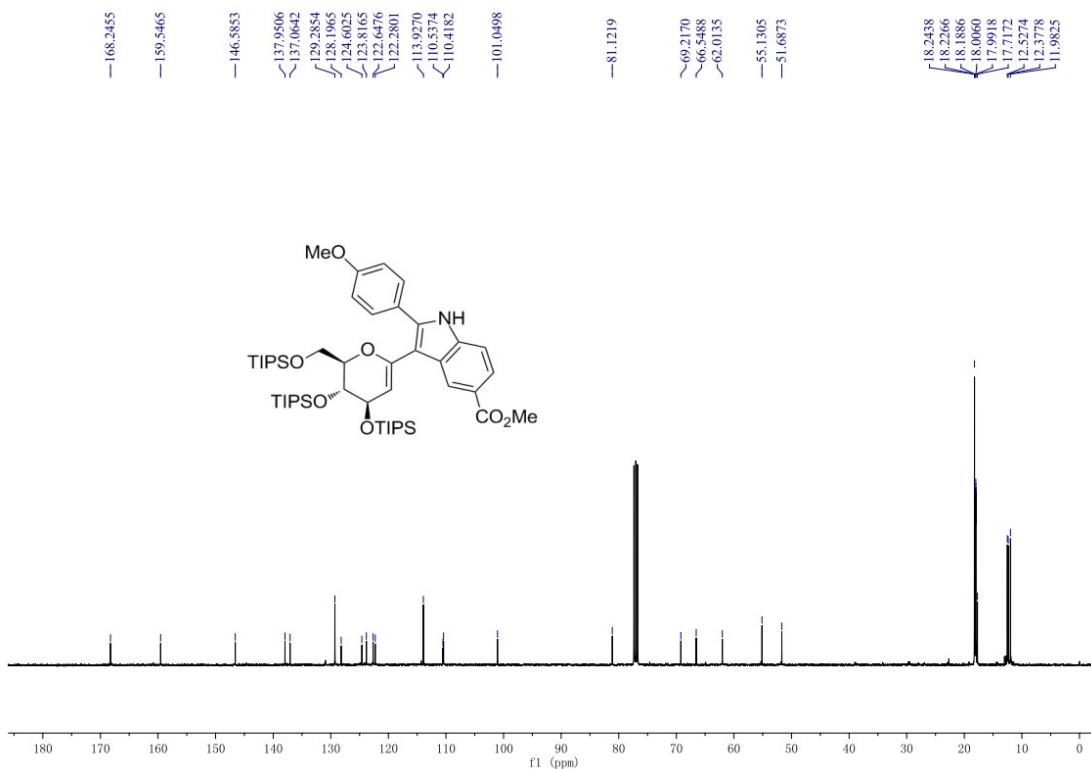


<sup>13</sup>C NMR spectrum of **3al**

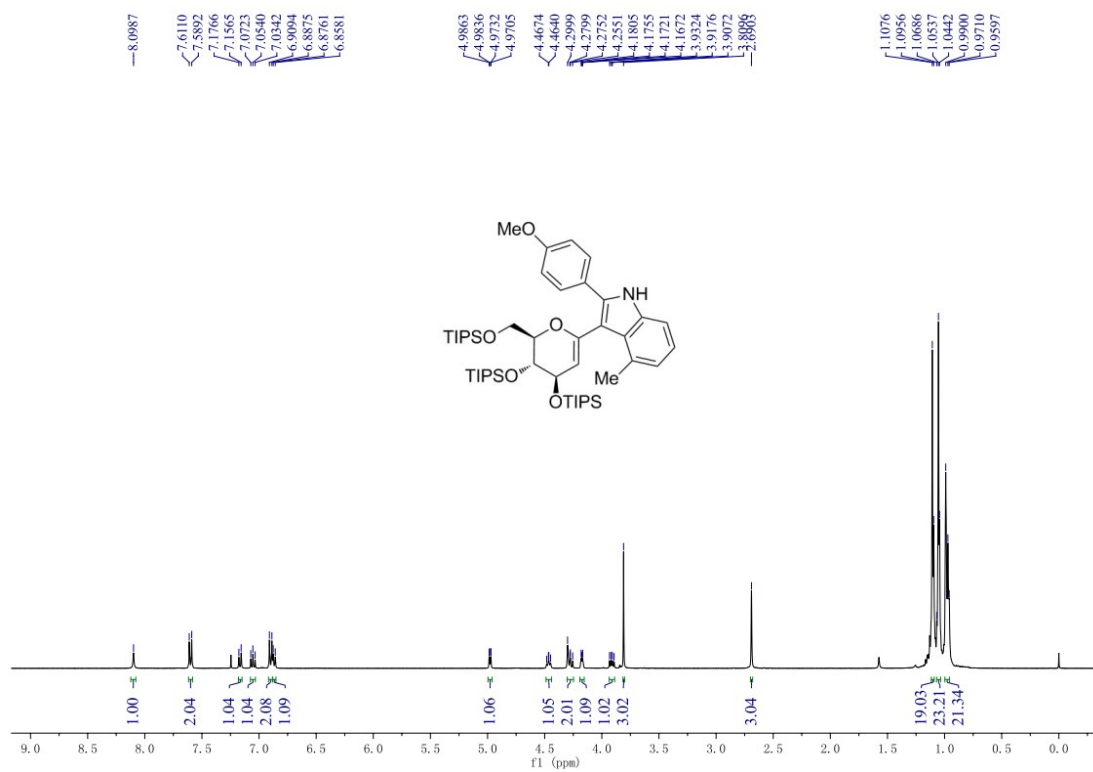




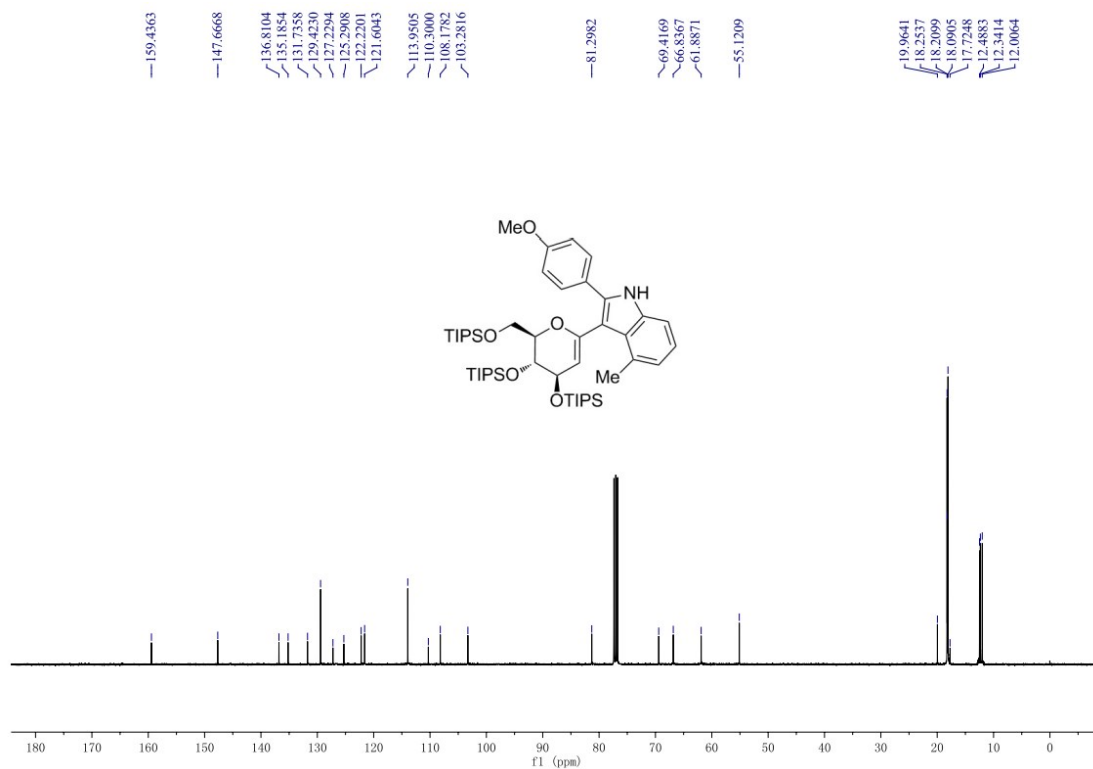
<sup>1</sup>H NMR spectrum of **3am**



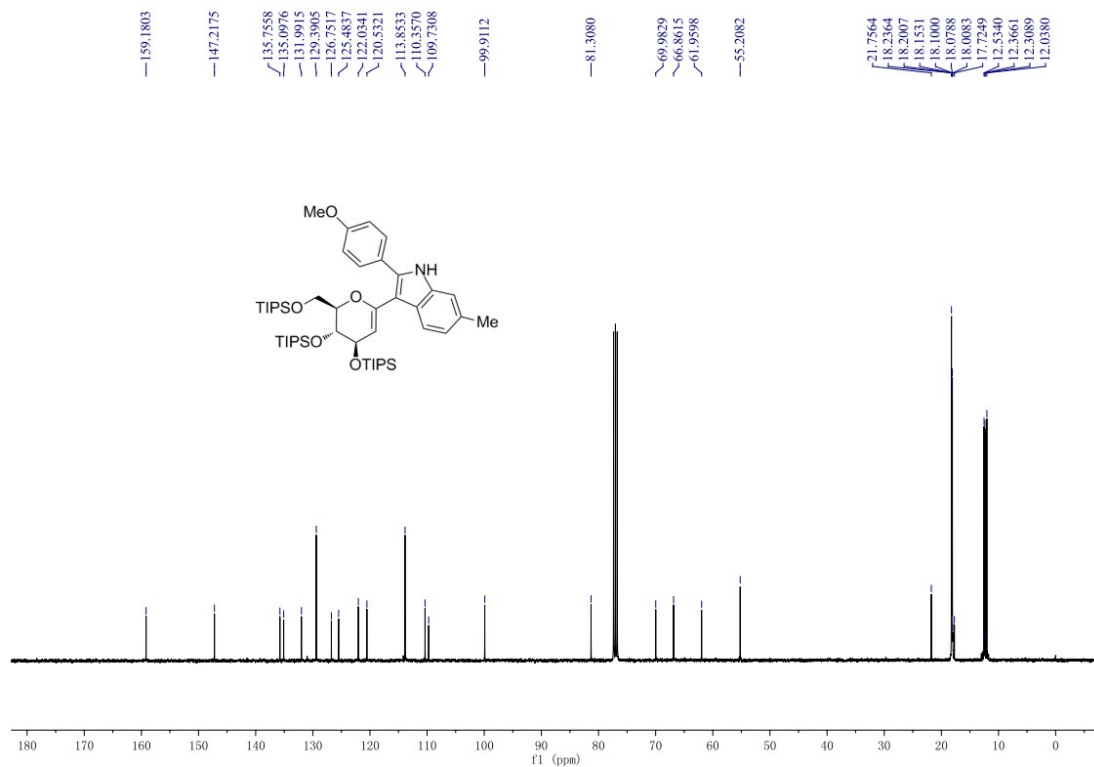
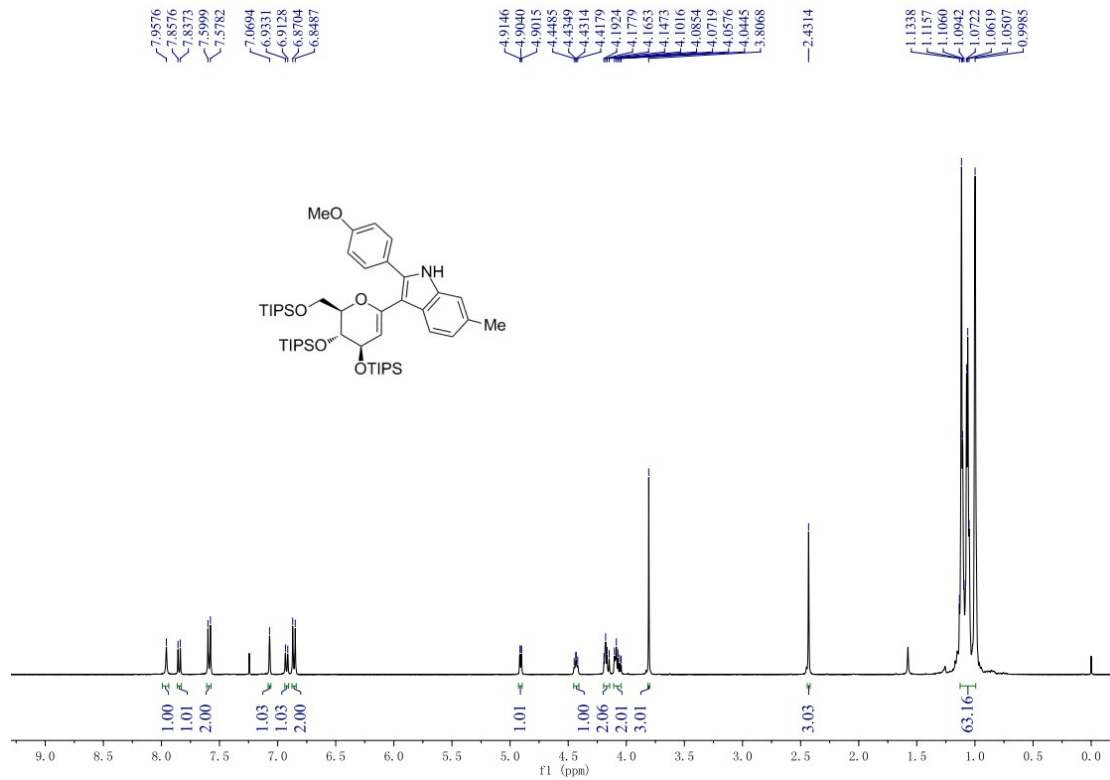
<sup>13</sup>C NMR spectrum of **3am**

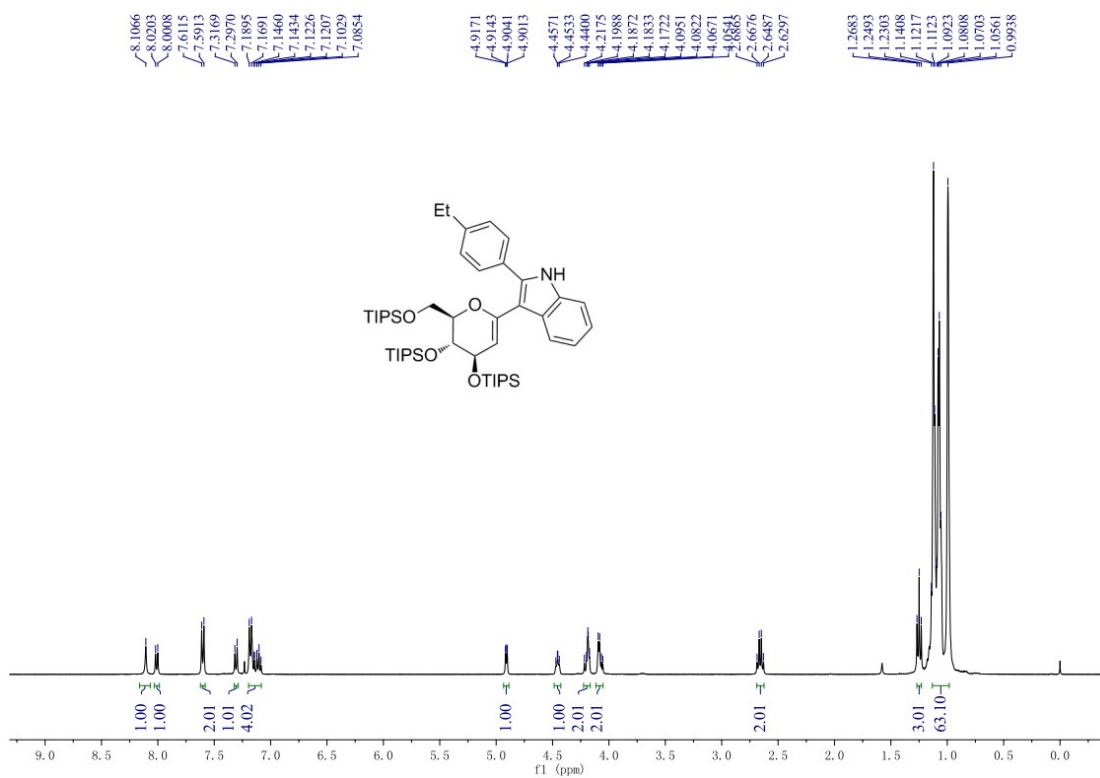


$^1\text{H}$  NMR spectrum of **3an**

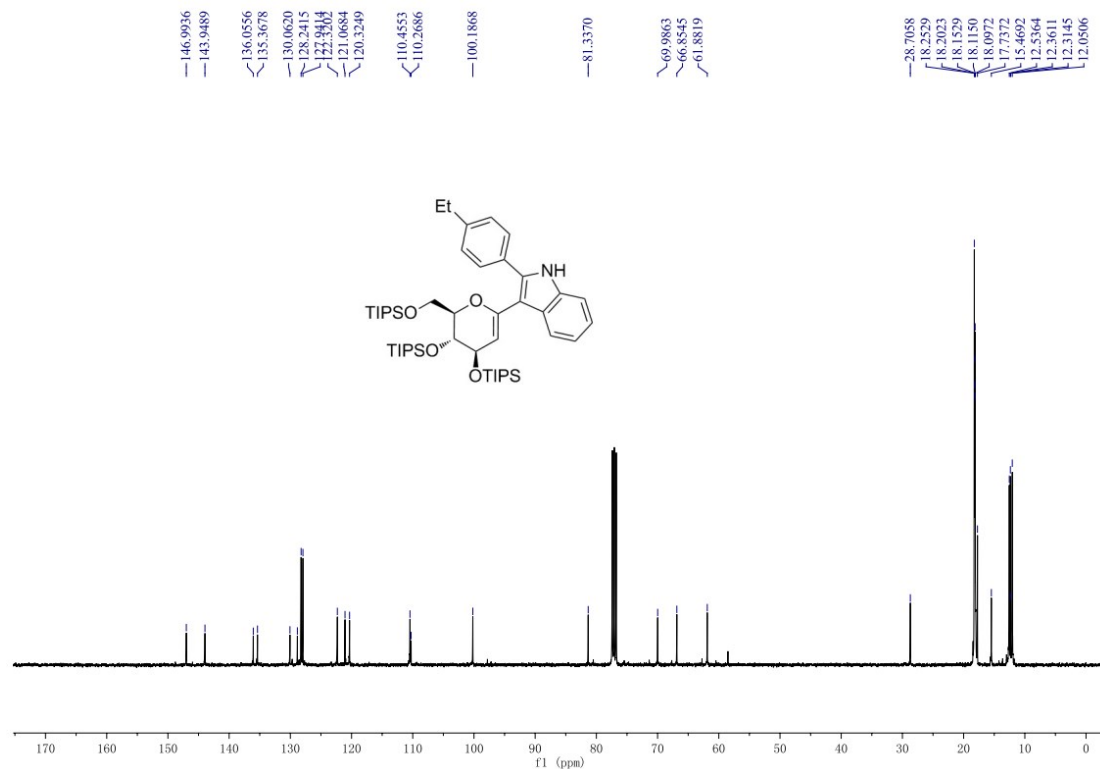


$^{13}\text{C}$  NMR spectrum of **3an**

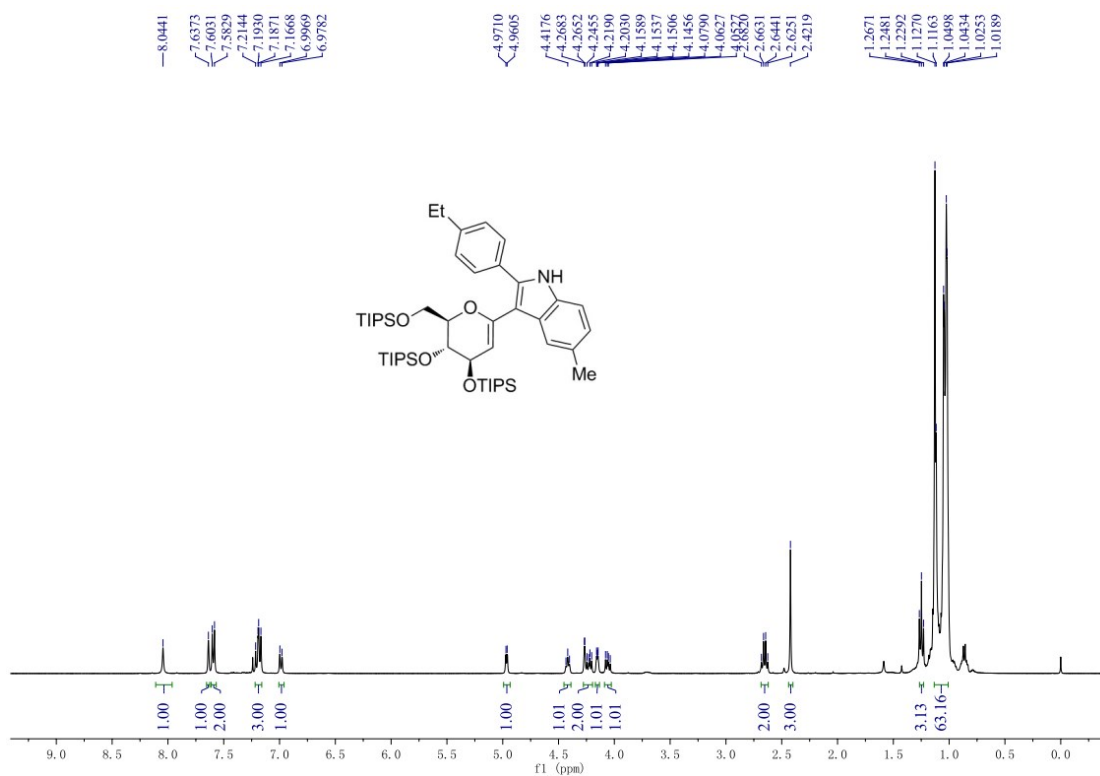




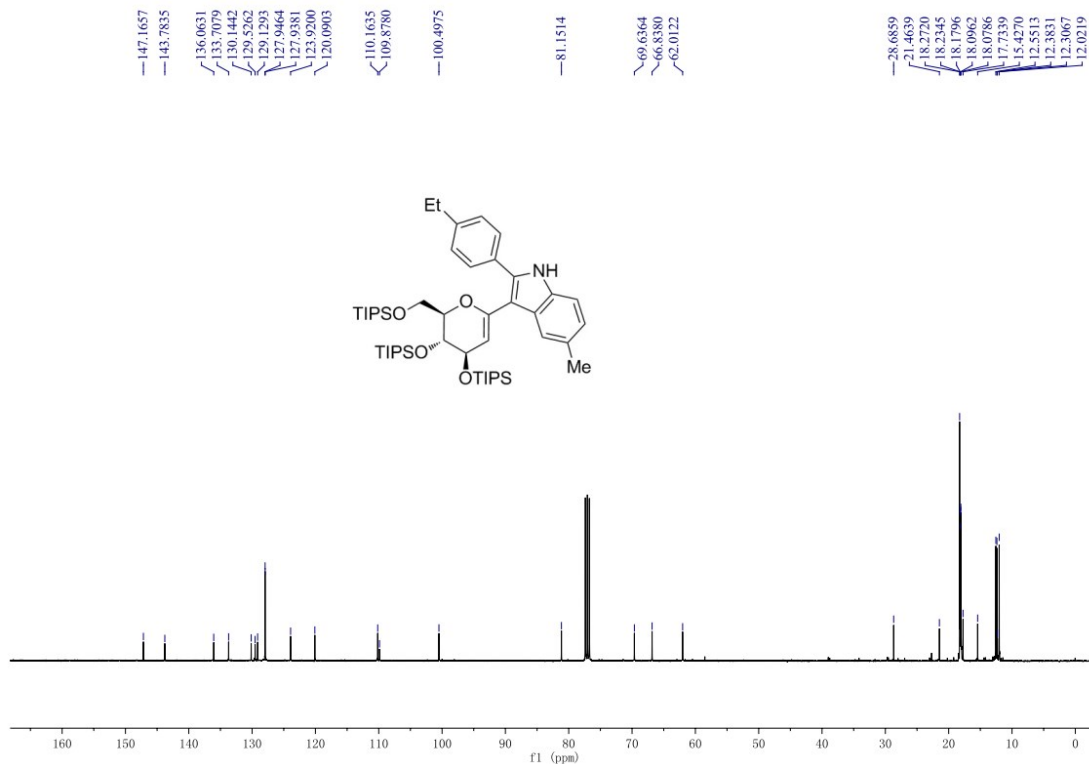
<sup>1</sup>H NMR spectrum of **3ap**



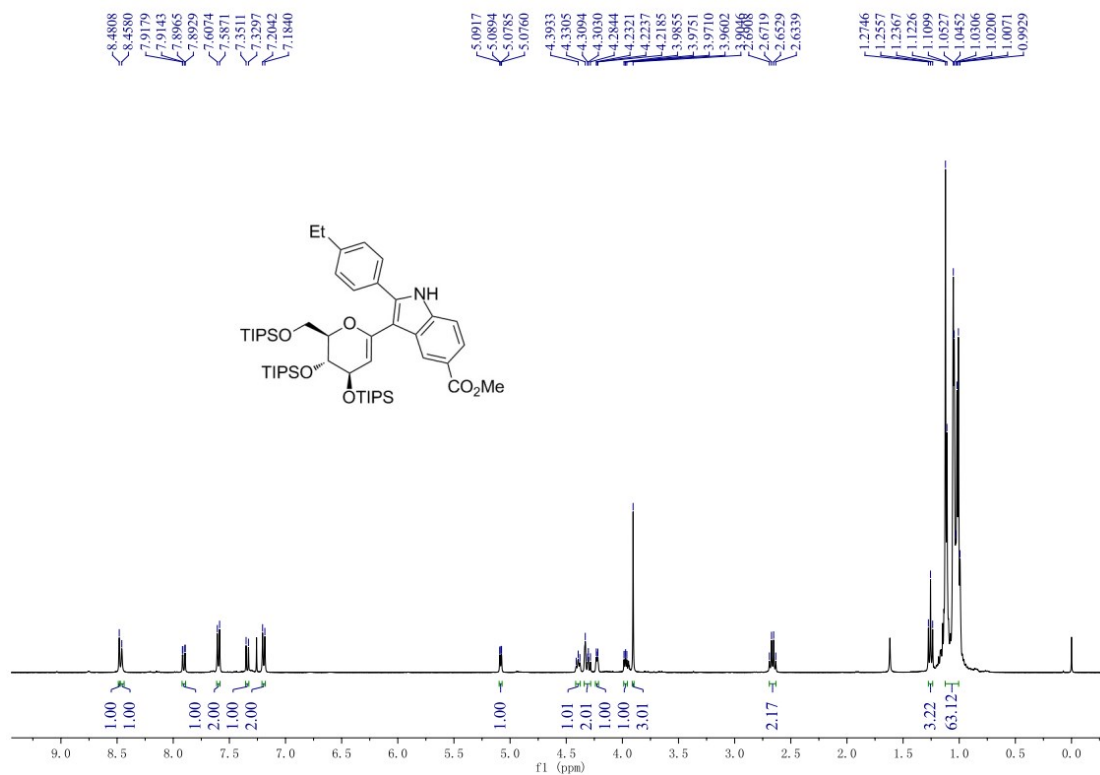
<sup>13</sup>C NMR spectrum of **3ap**



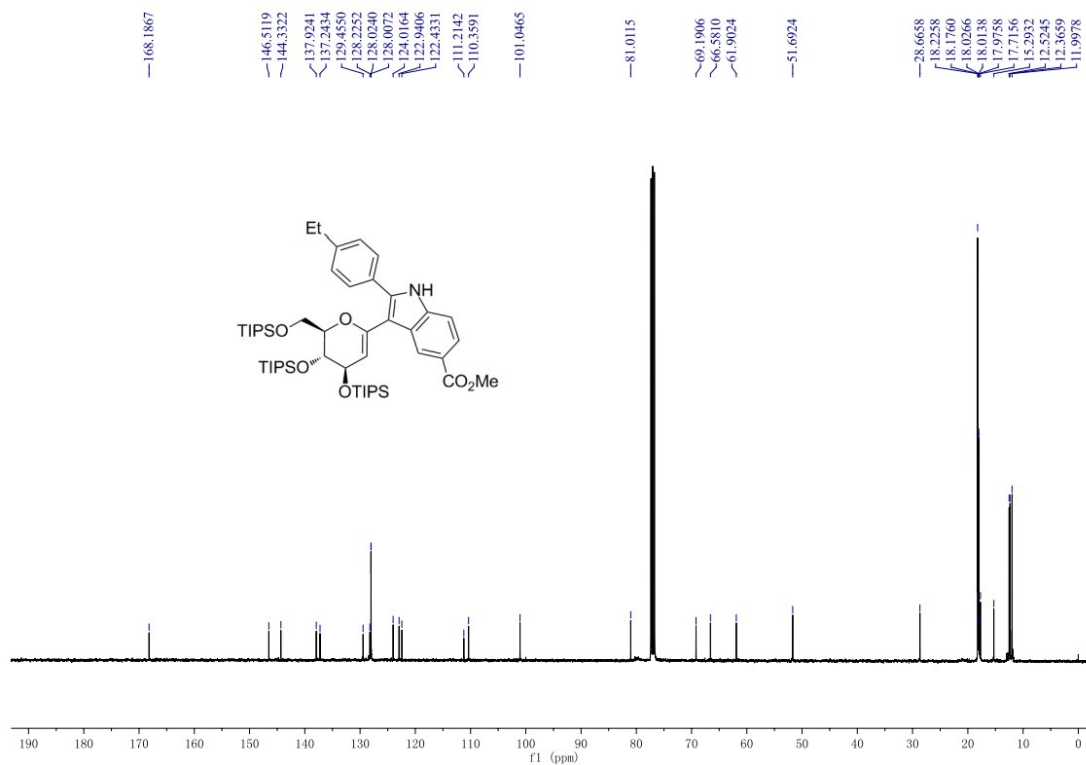
<sup>1</sup>H NMR spectrum of **3aq**



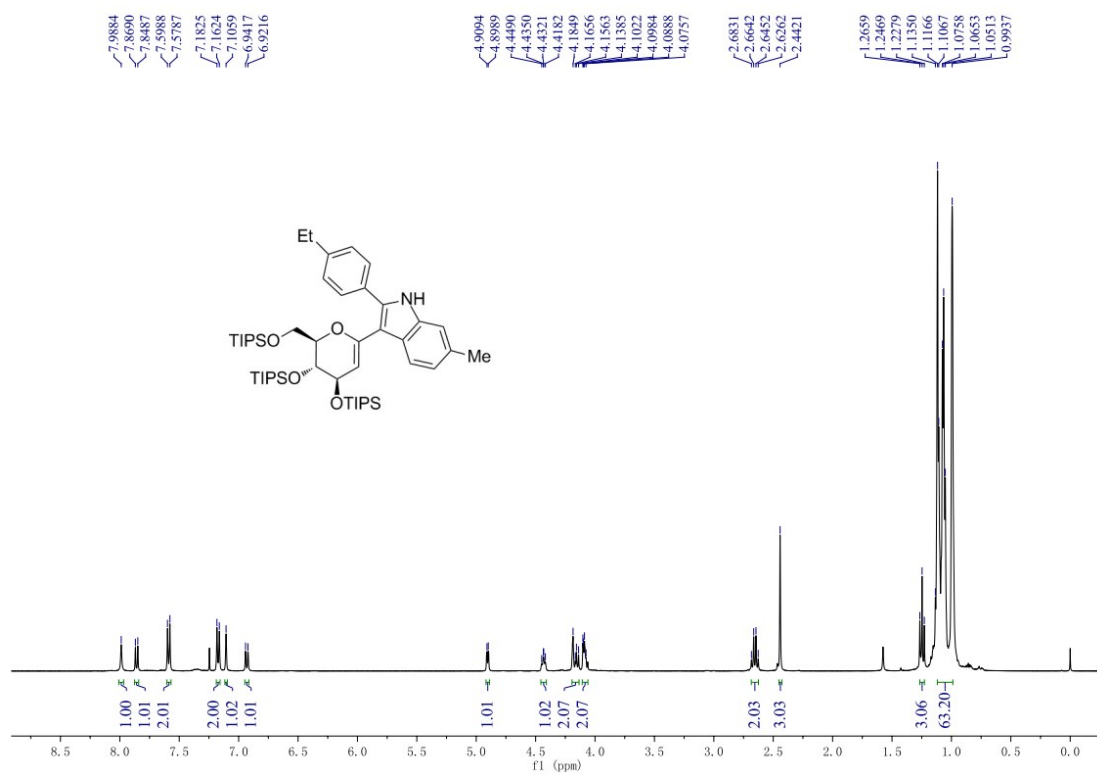
<sup>13</sup>C NMR spectrum of **3aq**



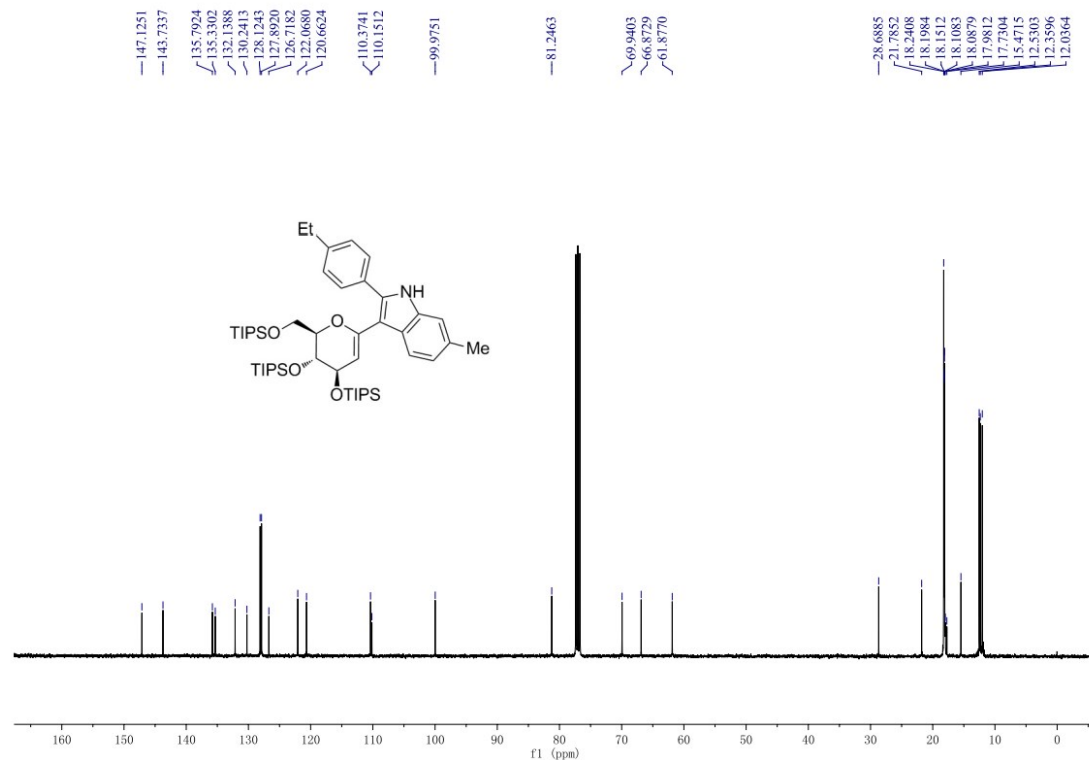
<sup>1</sup>H NMR spectrum of **3ar**



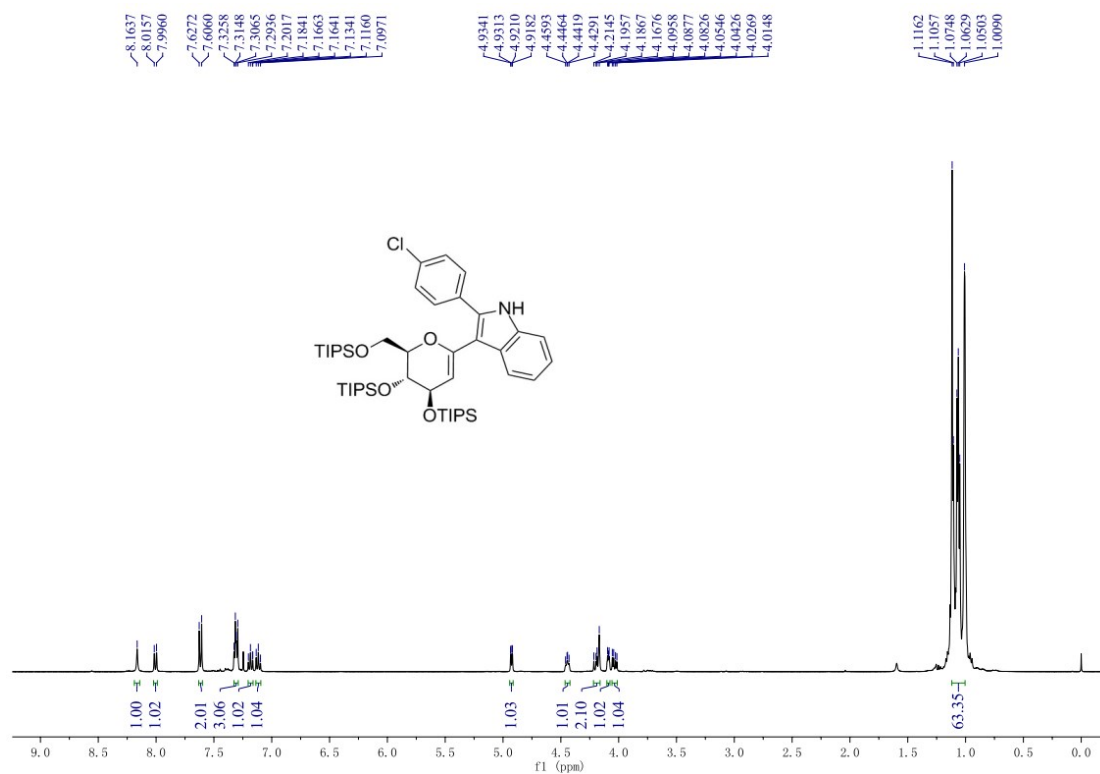
<sup>13</sup>C NMR spectrum of **3ar**



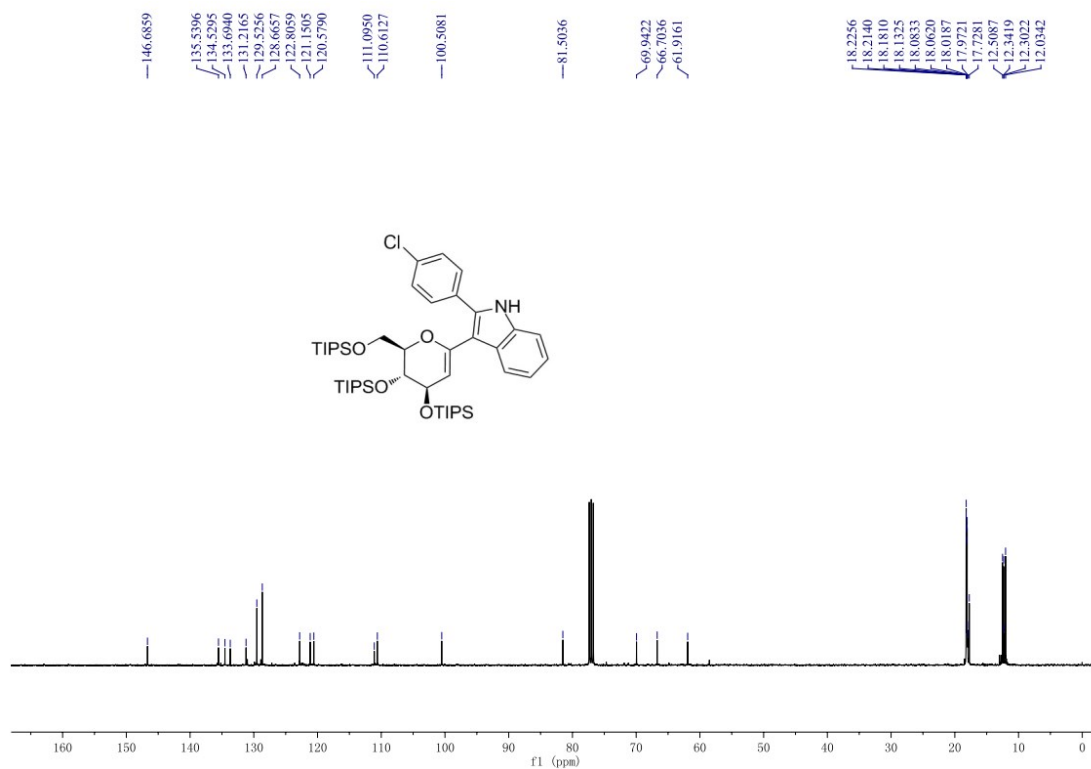
**<sup>1</sup>H NMR spectrum of 3as**



**<sup>13</sup>C NMR spectrum of 3as**

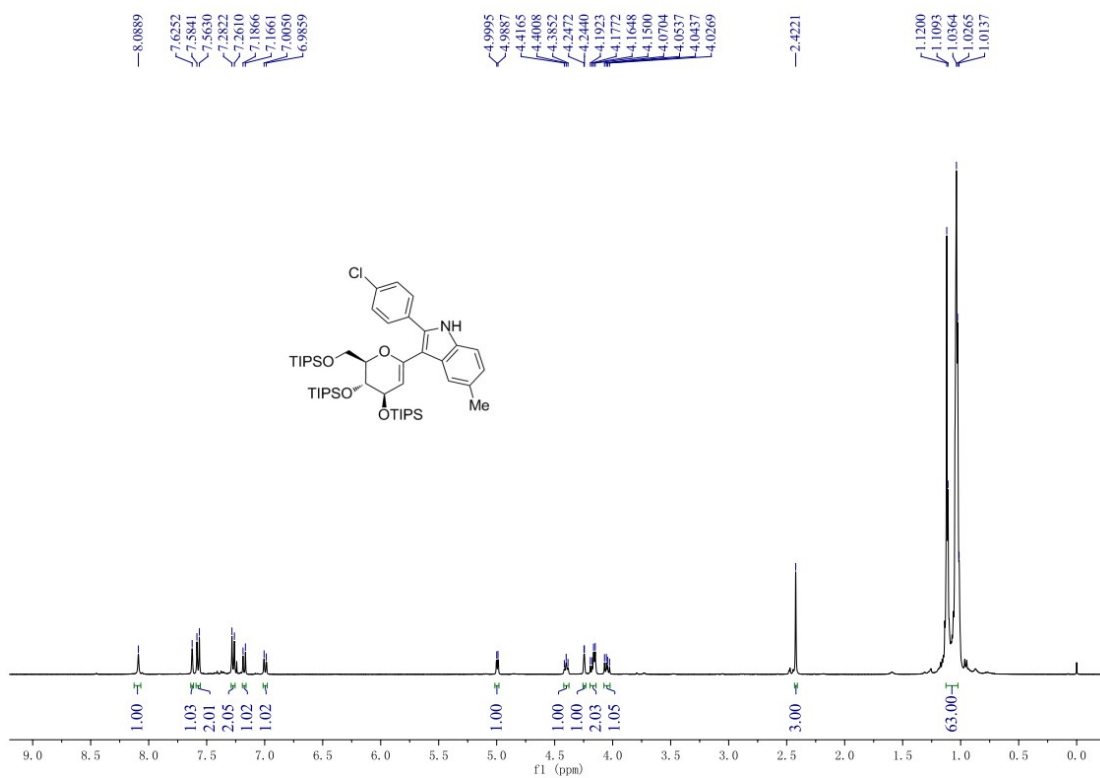


<sup>1</sup>H NMR spectrum of **3at**

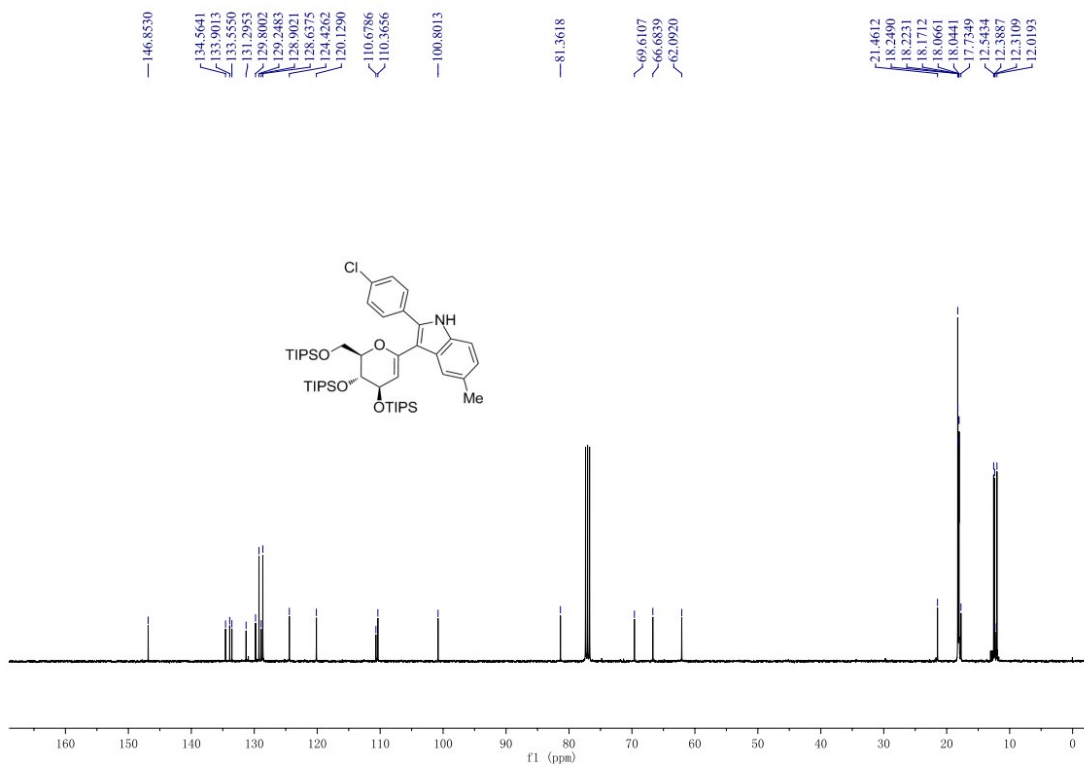


<sup>13</sup>C NMR spectrum of **3at**

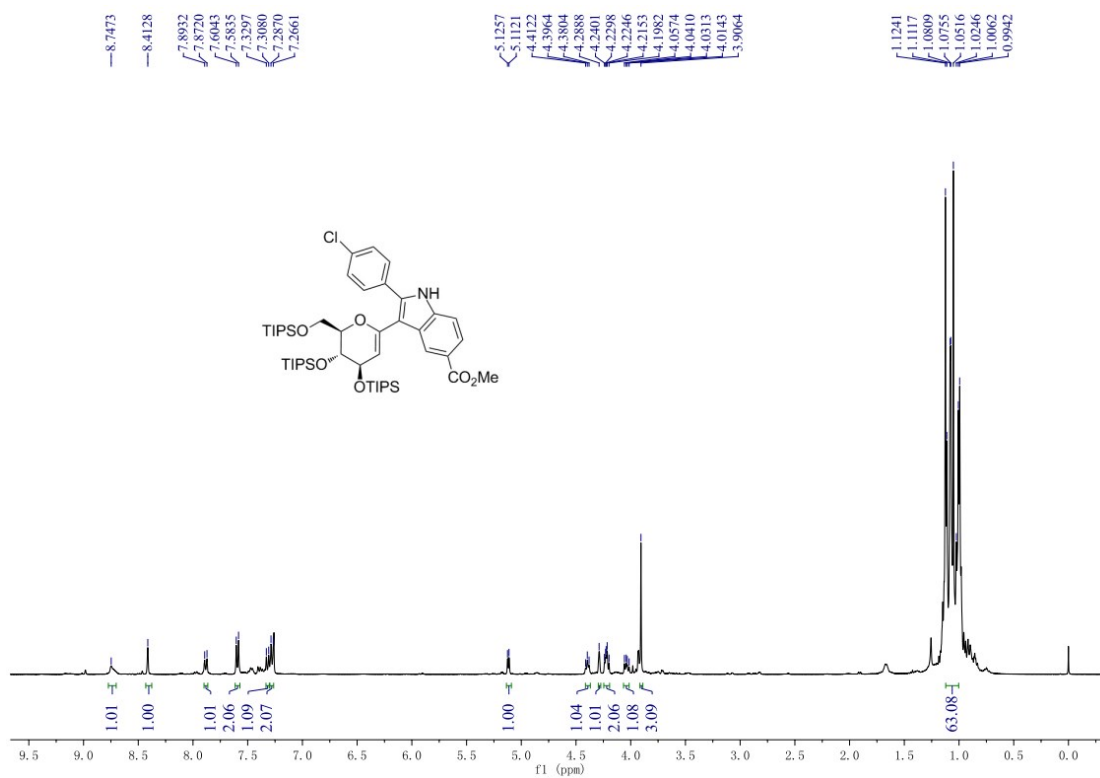




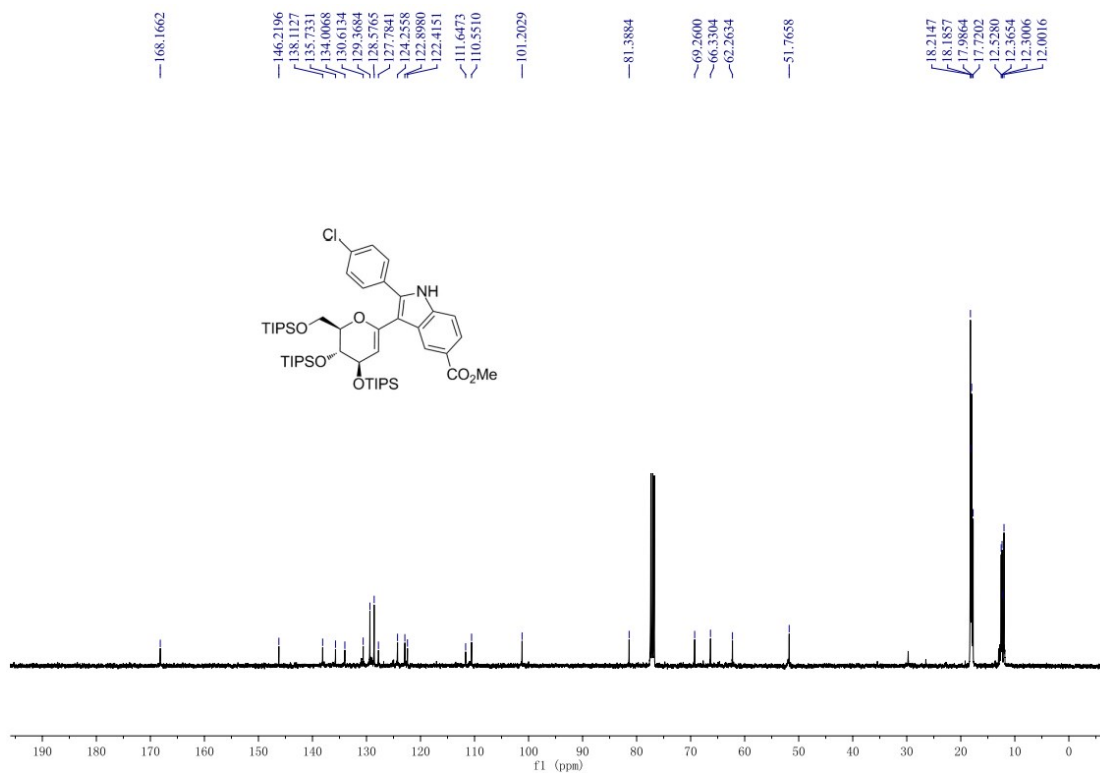
<sup>1</sup>H NMR spectrum of **3au**



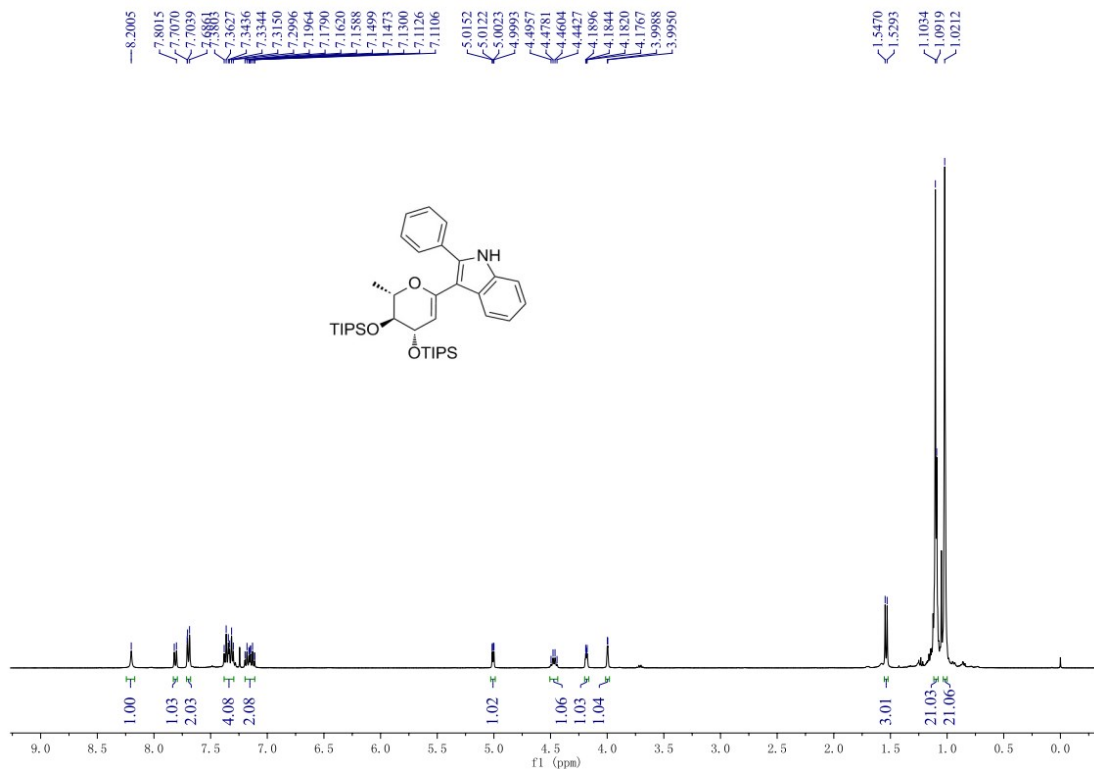
<sup>13</sup>C NMR spectrum of **3au**



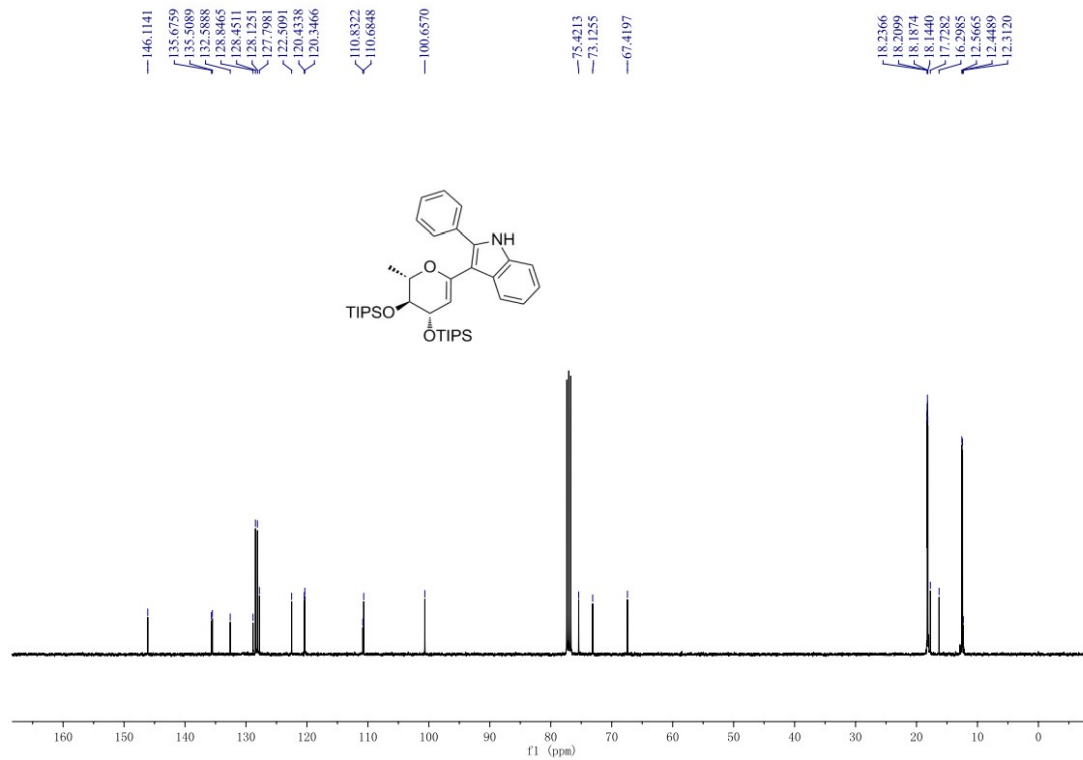
<sup>1</sup>H NMR spectrum of **3av**



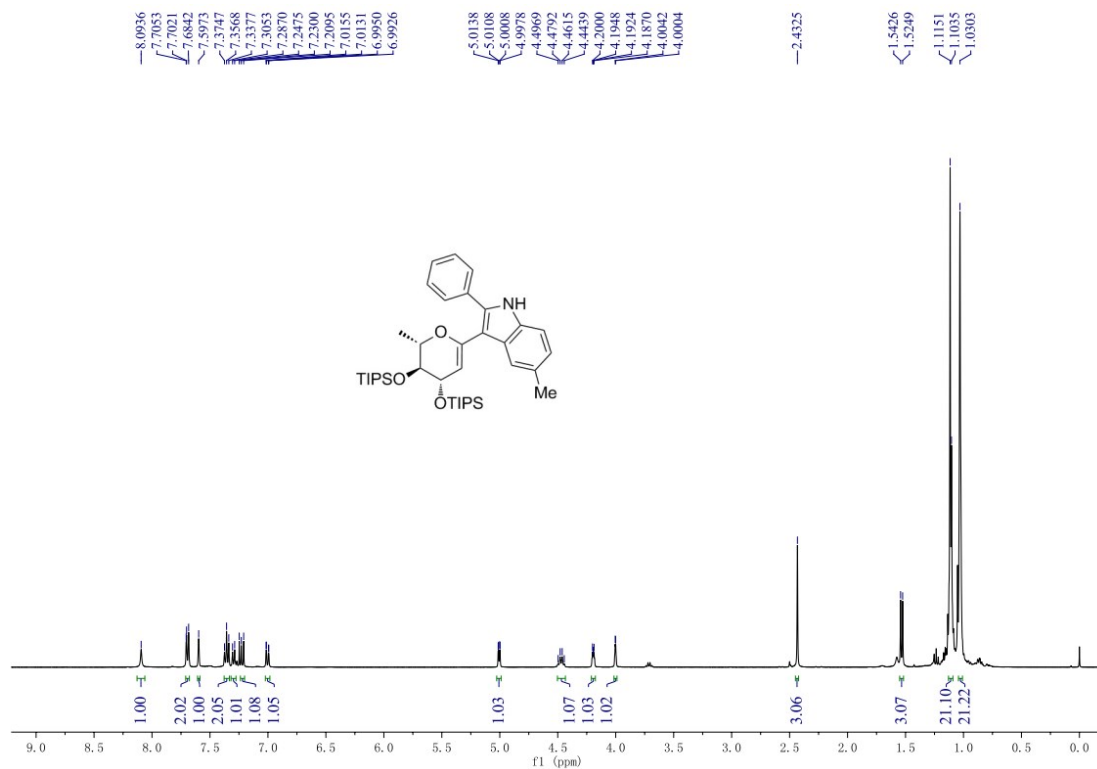
<sup>13</sup>C NMR spectrum of **3av**



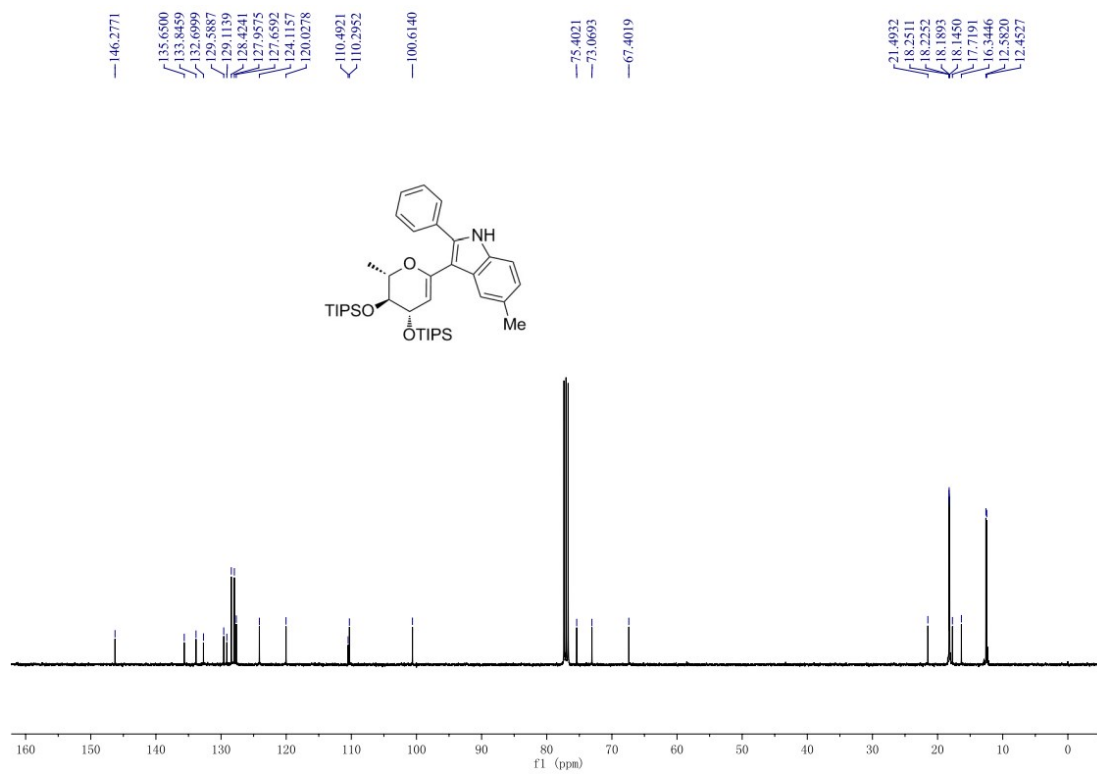
<sup>1</sup>H NMR spectrum of **3ba**



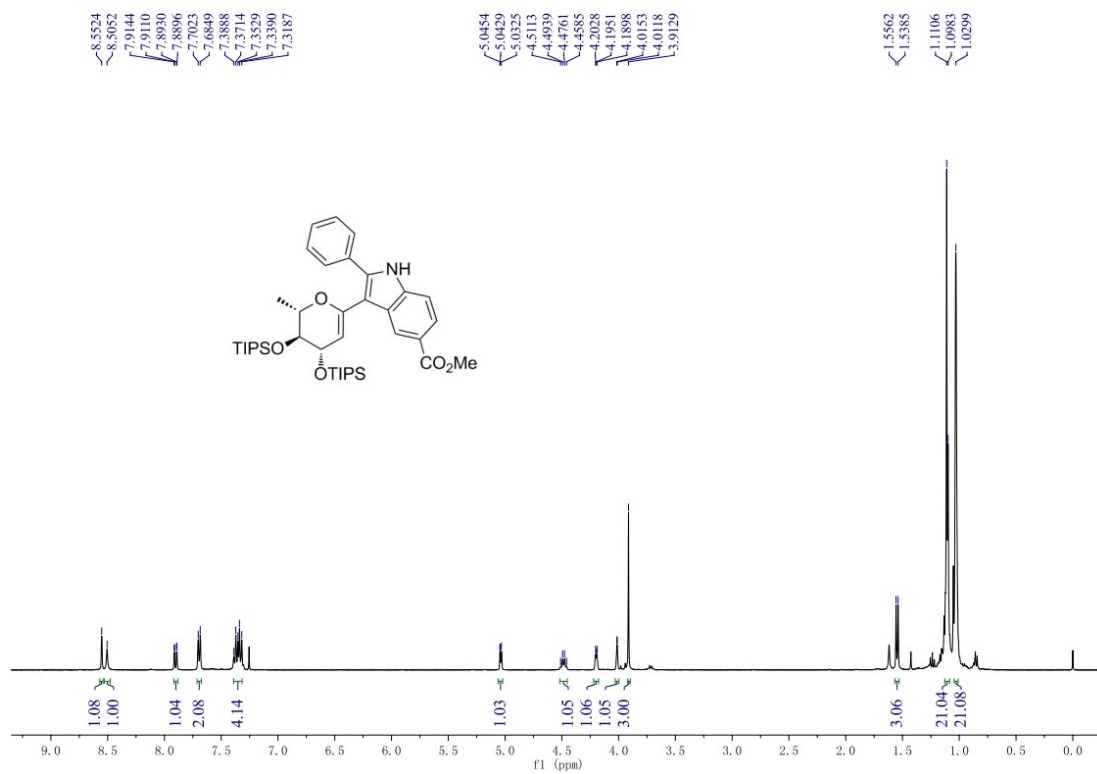
<sup>13</sup>C NMR spectrum of **3ba**



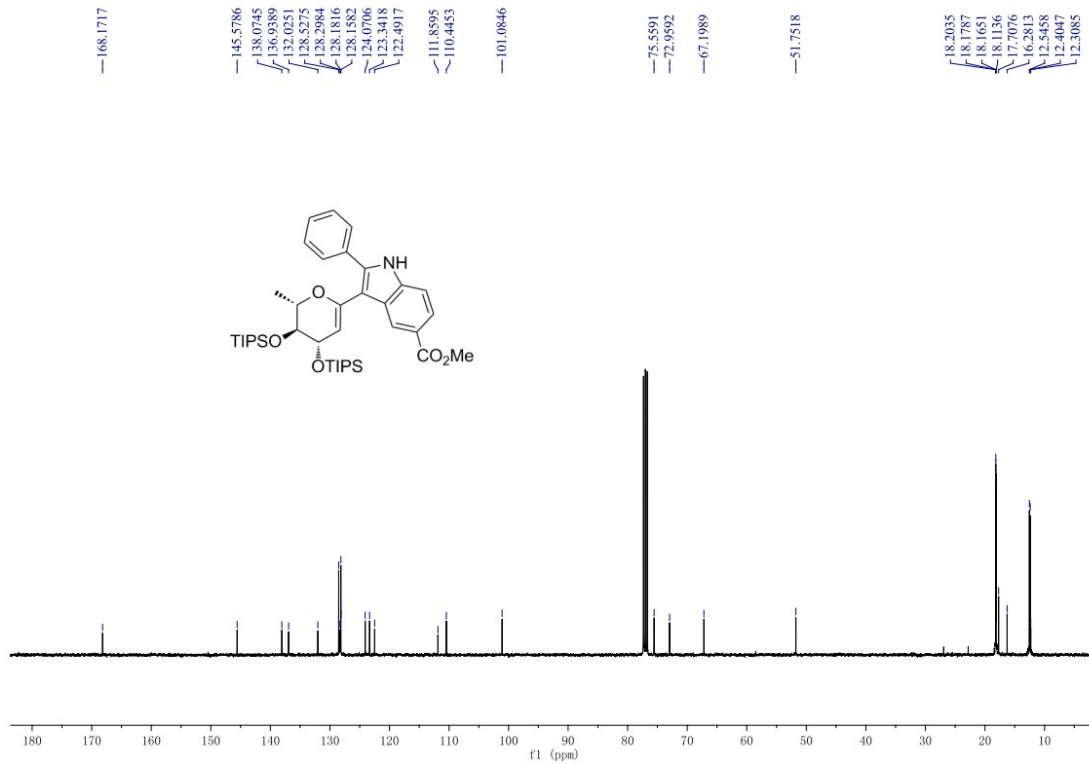
<sup>1</sup>H NMR spectrum of **3bb**



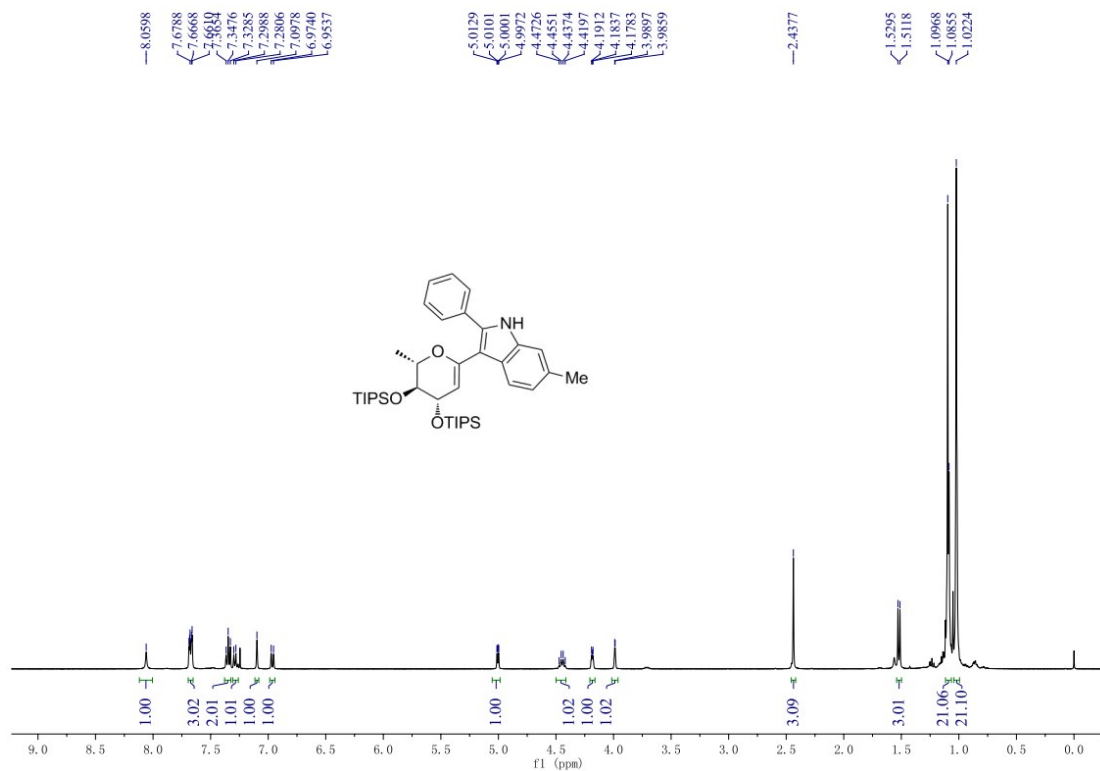
<sup>13</sup>C NMR spectrum of **3bb**



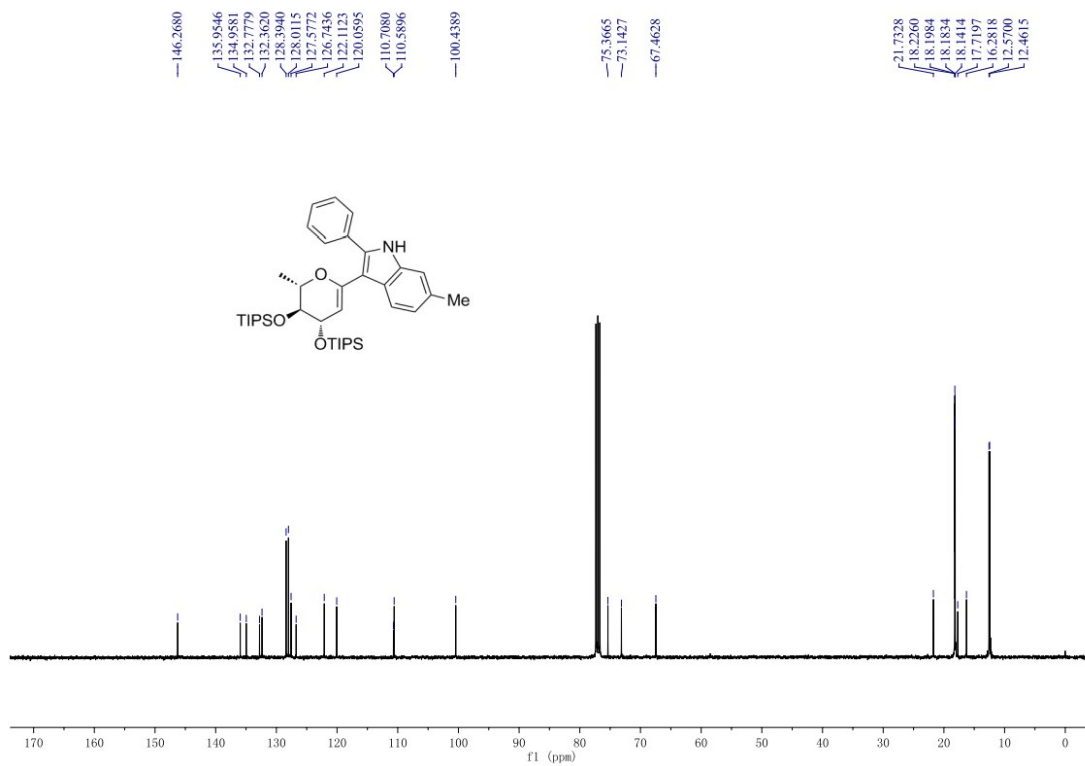
<sup>1</sup>H NMR spectrum of **3be**



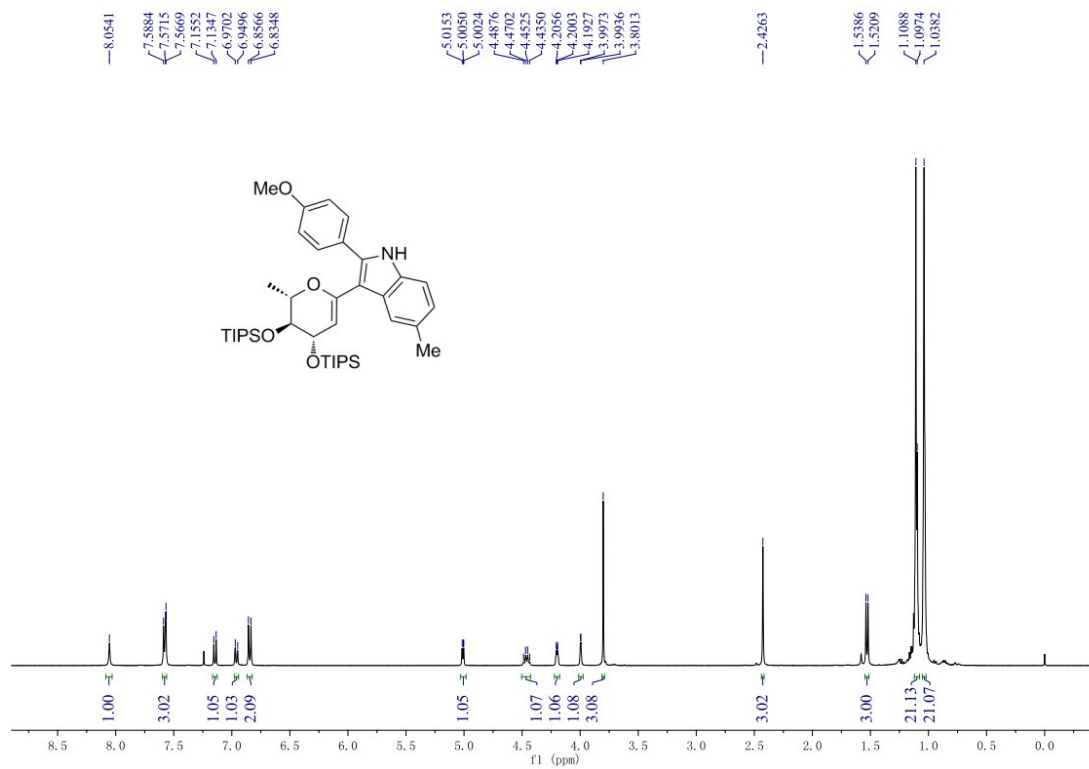
<sup>13</sup>C NMR spectrum of **3be**



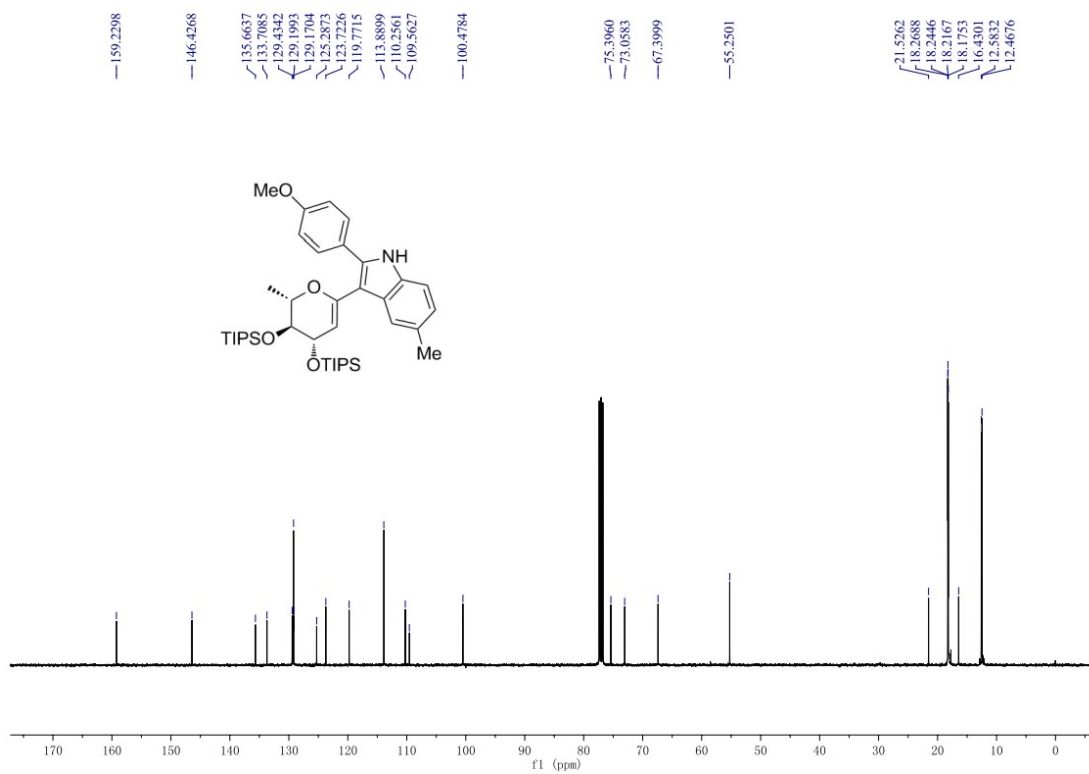
<sup>1</sup>H NMR spectrum of **3bg**



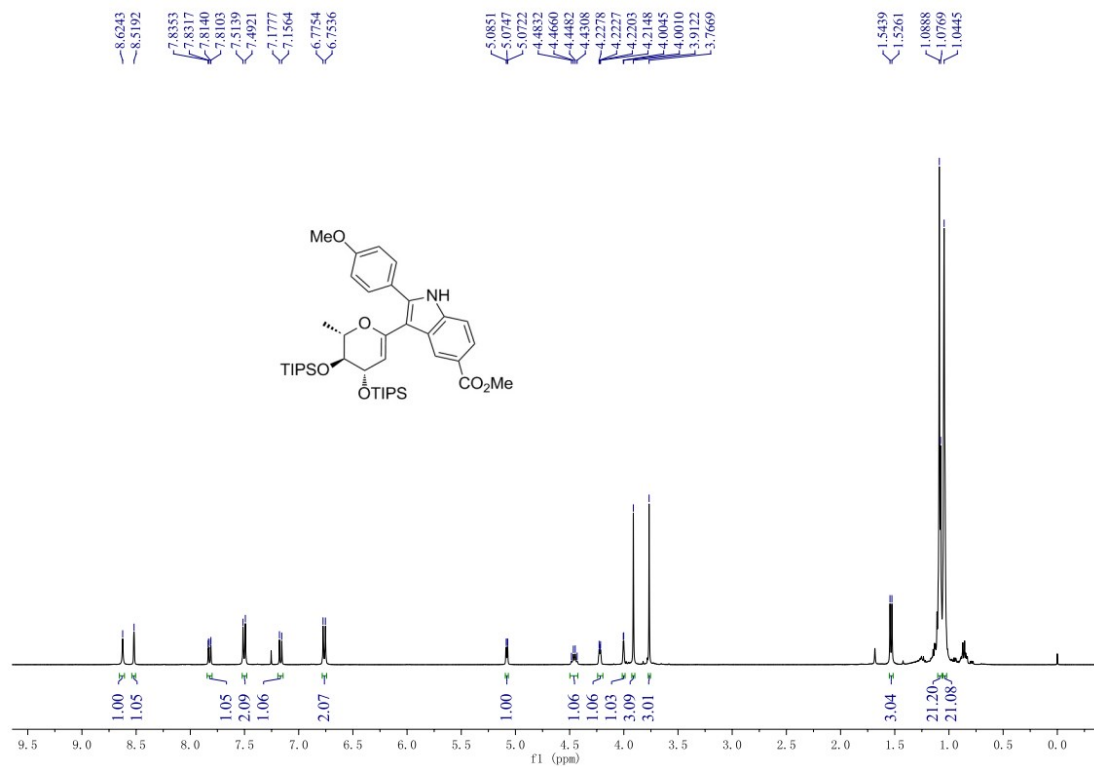
<sup>13</sup>C NMR spectrum of **3bg**



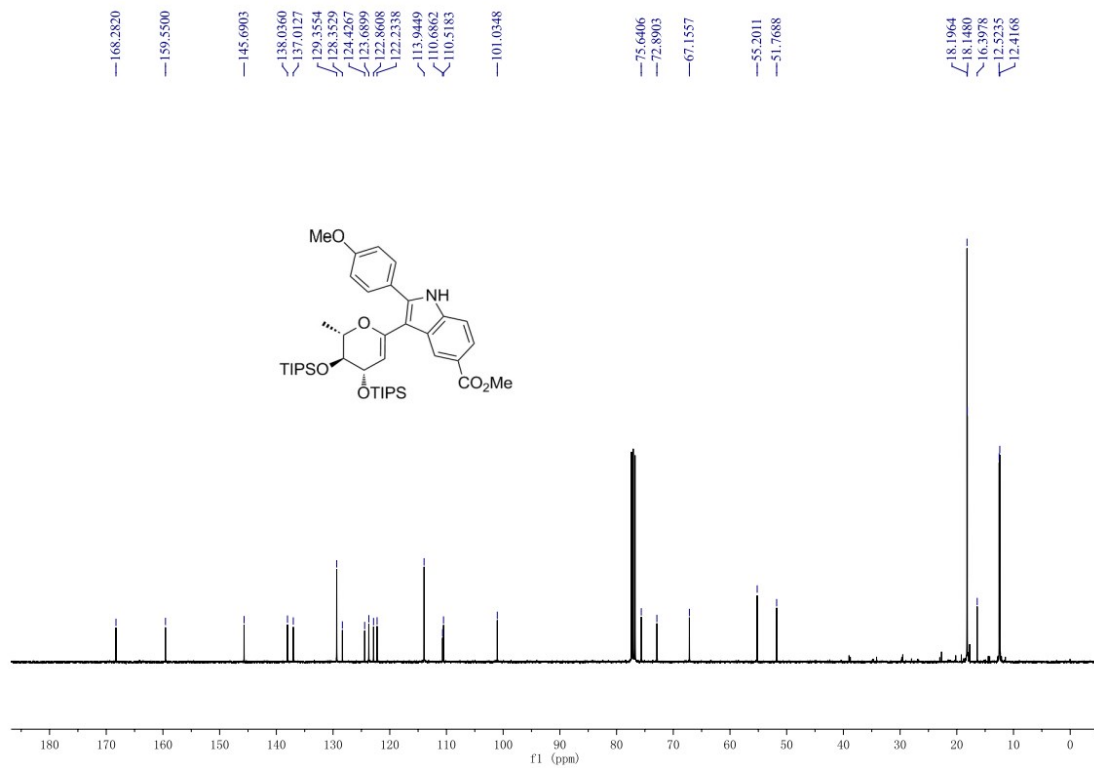
<sup>1</sup>H NMR spectrum of **3bk**



<sup>13</sup>C NMR spectrum of **3bk**

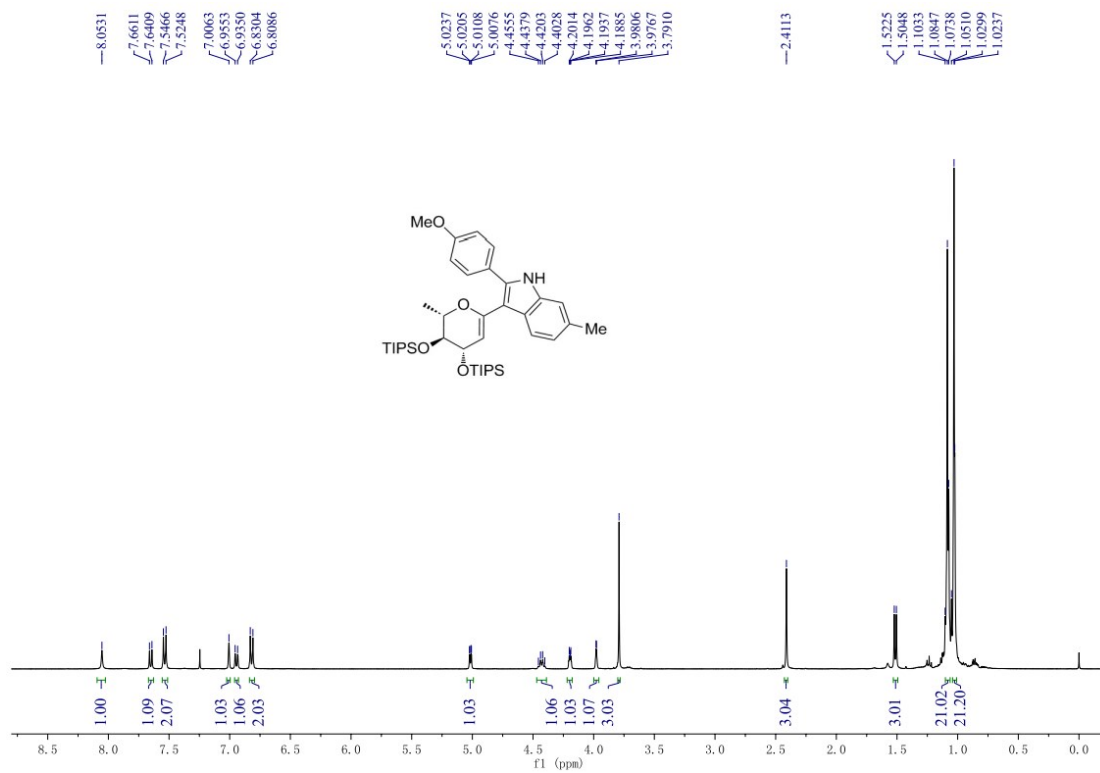


<sup>1</sup>H NMR spectrum of **3bm**

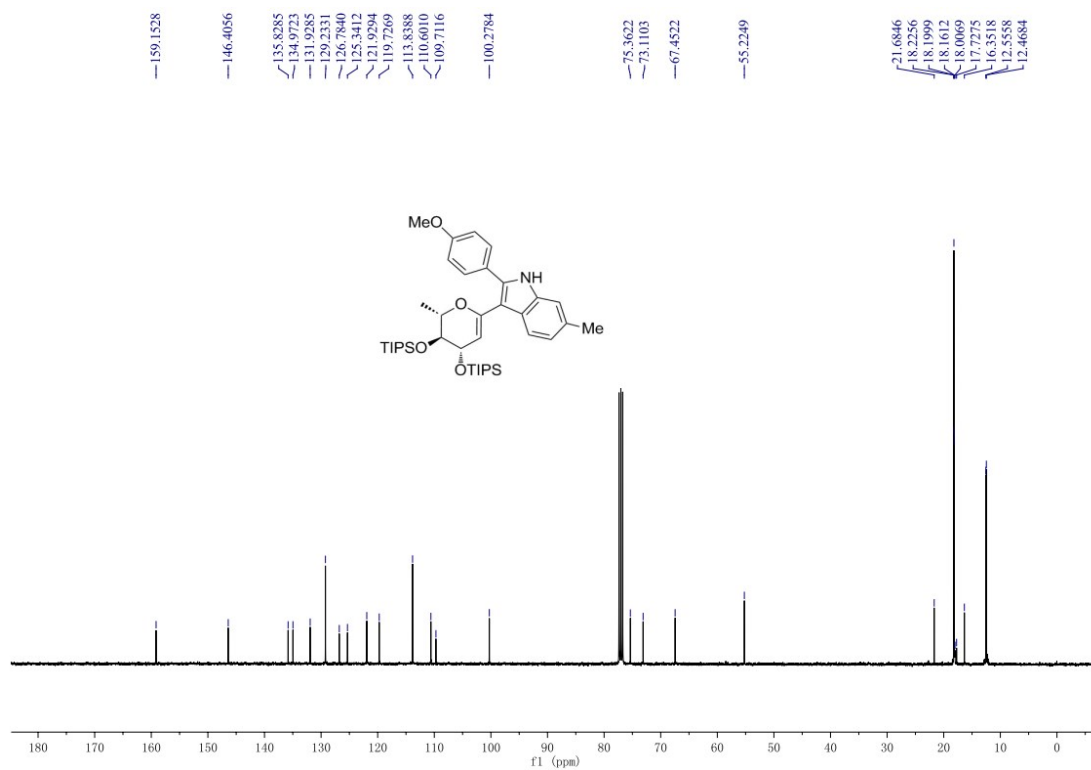


<sup>13</sup>C NMR spectrum of **3bm**

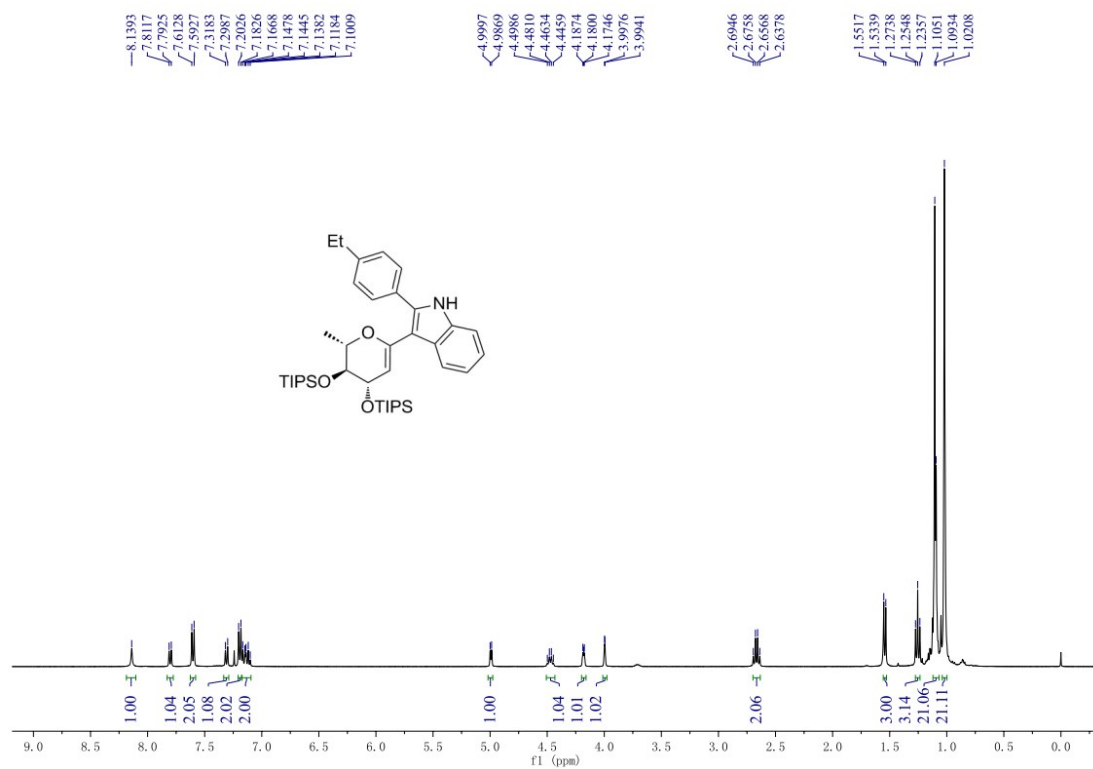




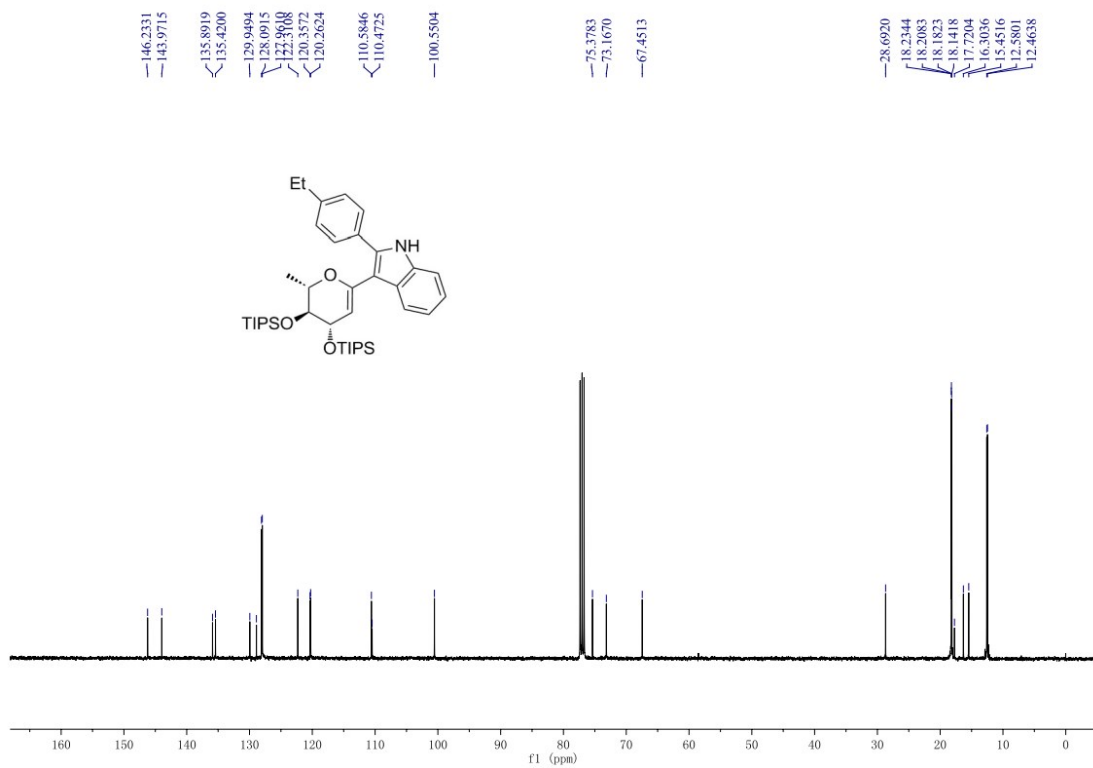
<sup>1</sup>H NMR spectrum of **3bo**



<sup>13</sup>C NMR spectrum of **3bo**

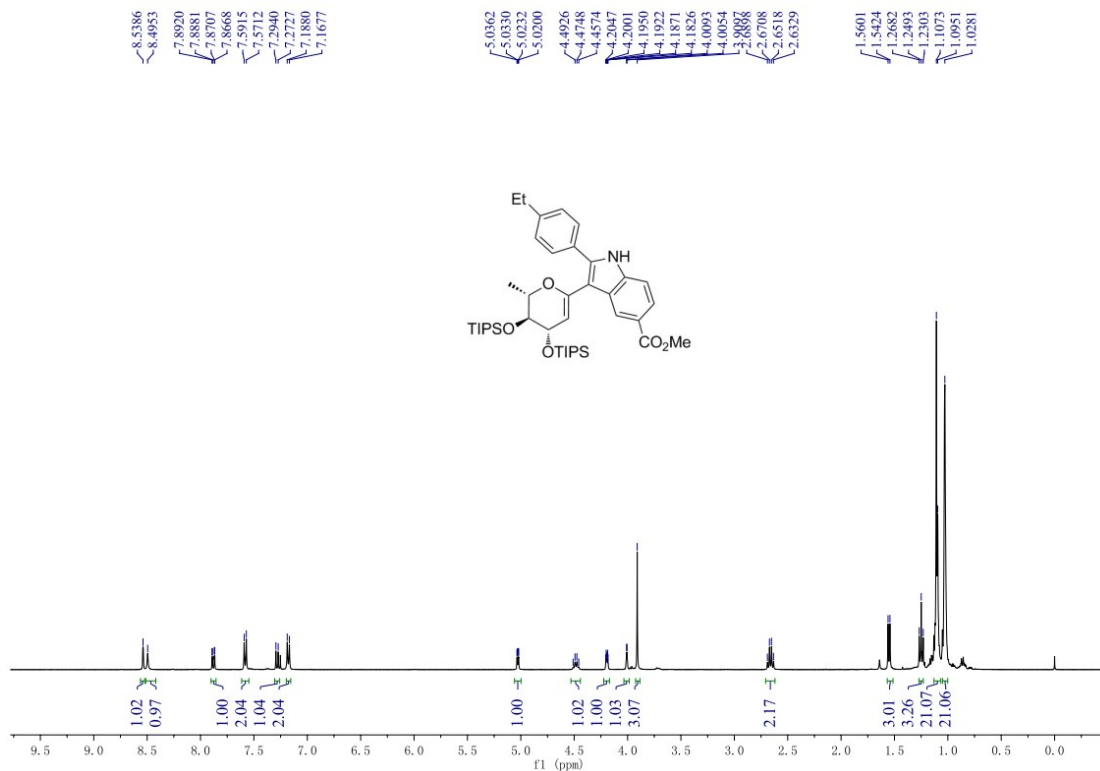


<sup>1</sup>H NMR spectrum of **3bp**

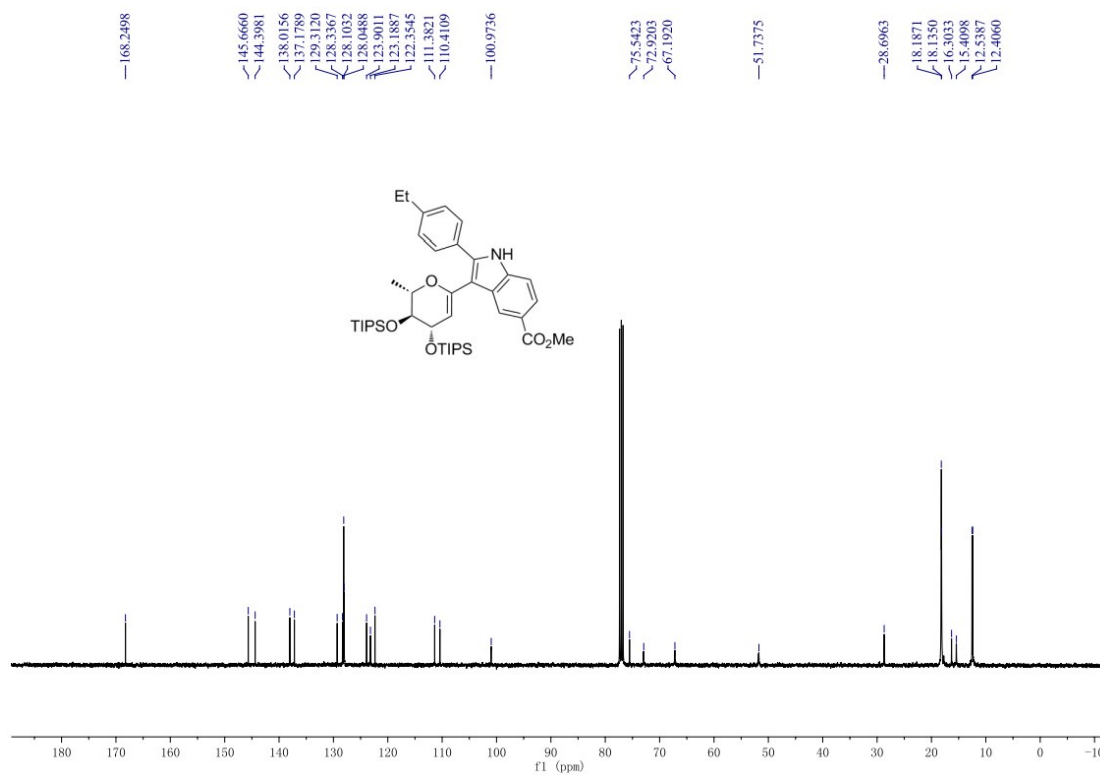


<sup>13</sup>C NMR spectrum of **3bp**

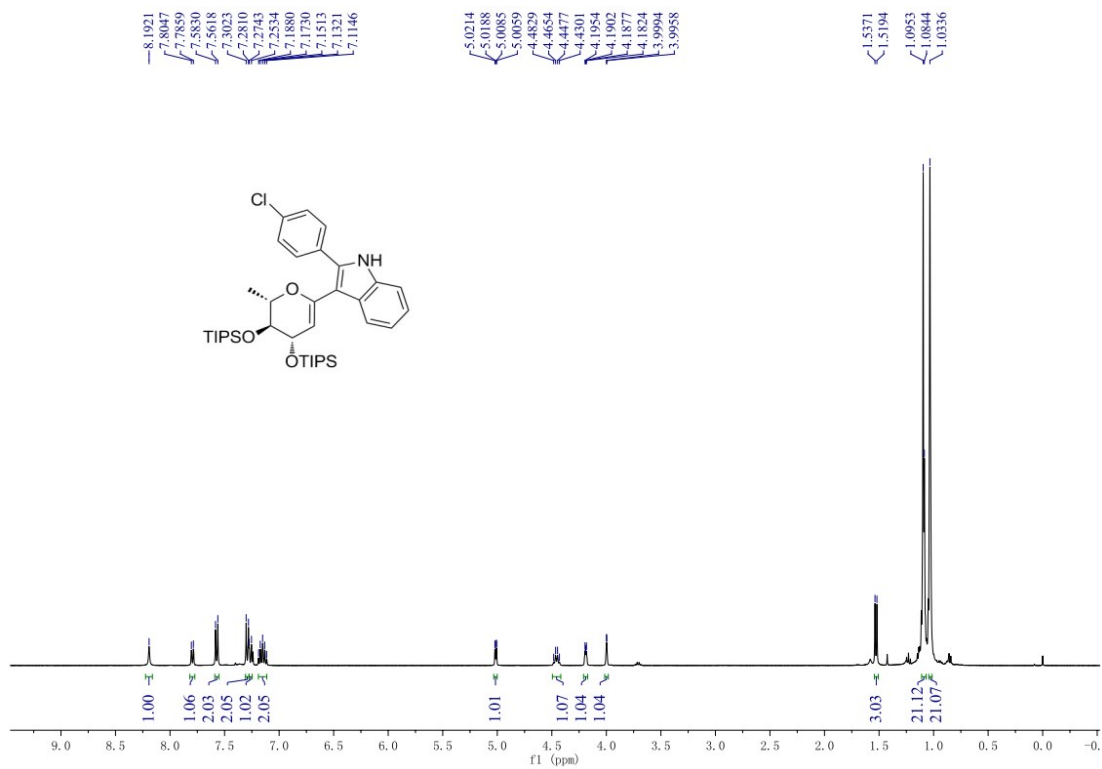




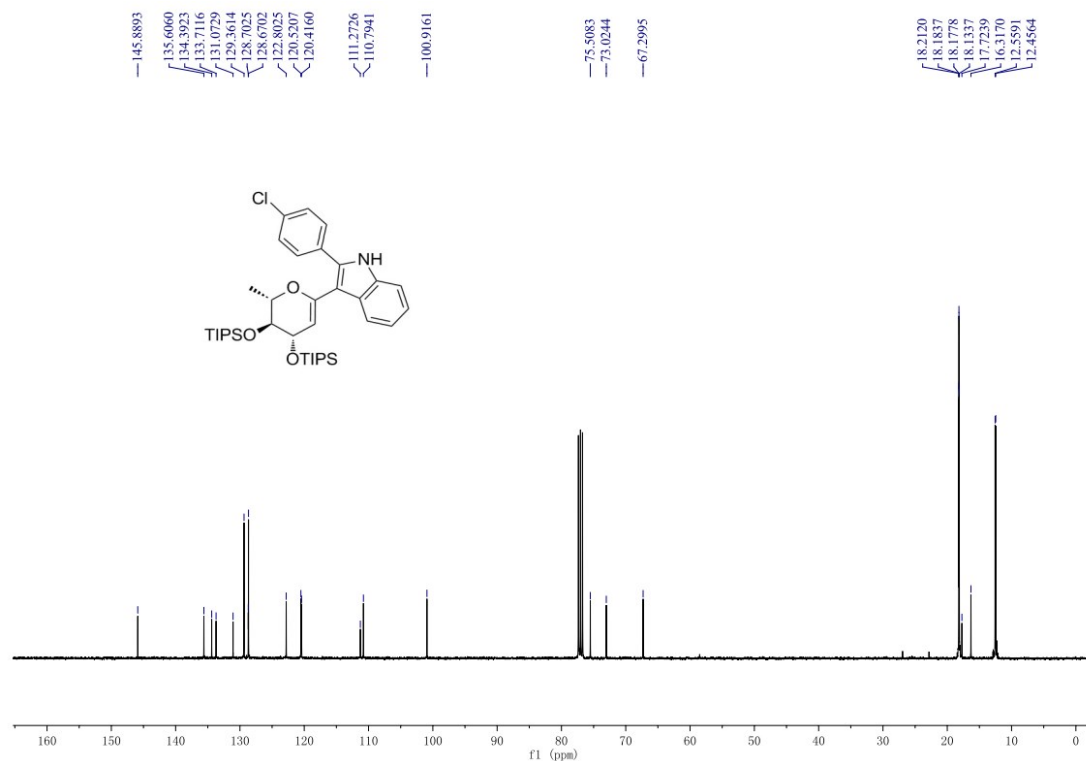
<sup>1</sup>H NMR spectrum of **3br**



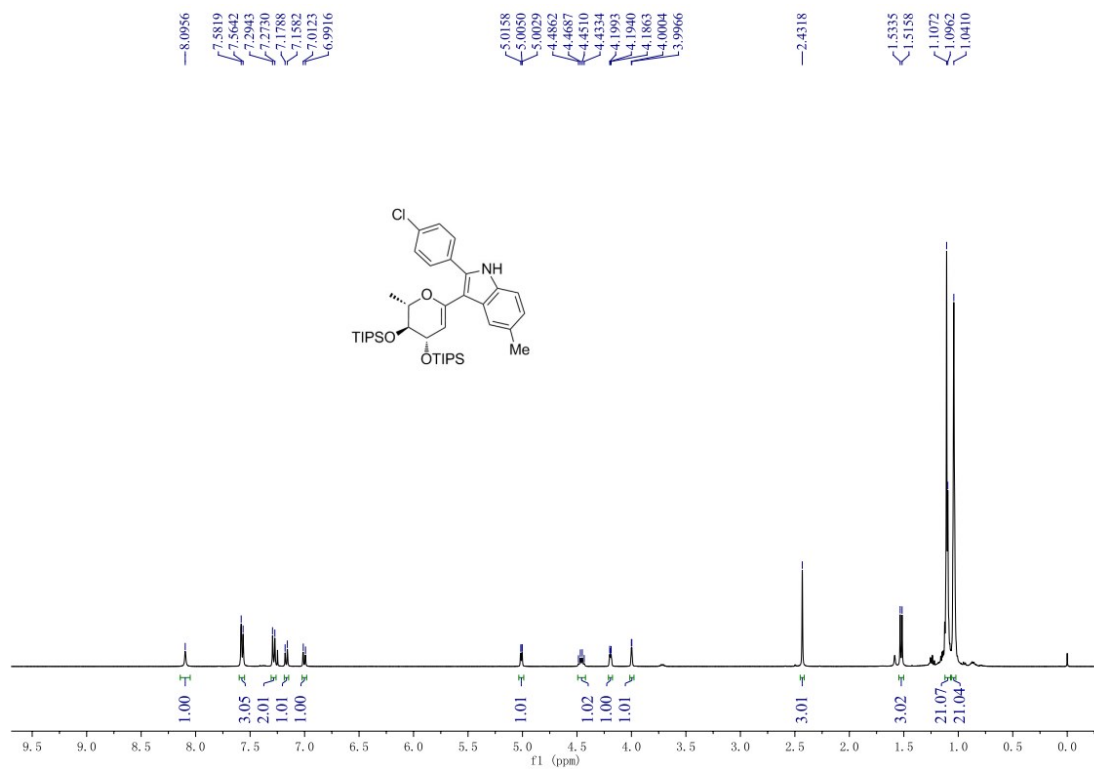
<sup>13</sup>C NMR spectrum of **3br**



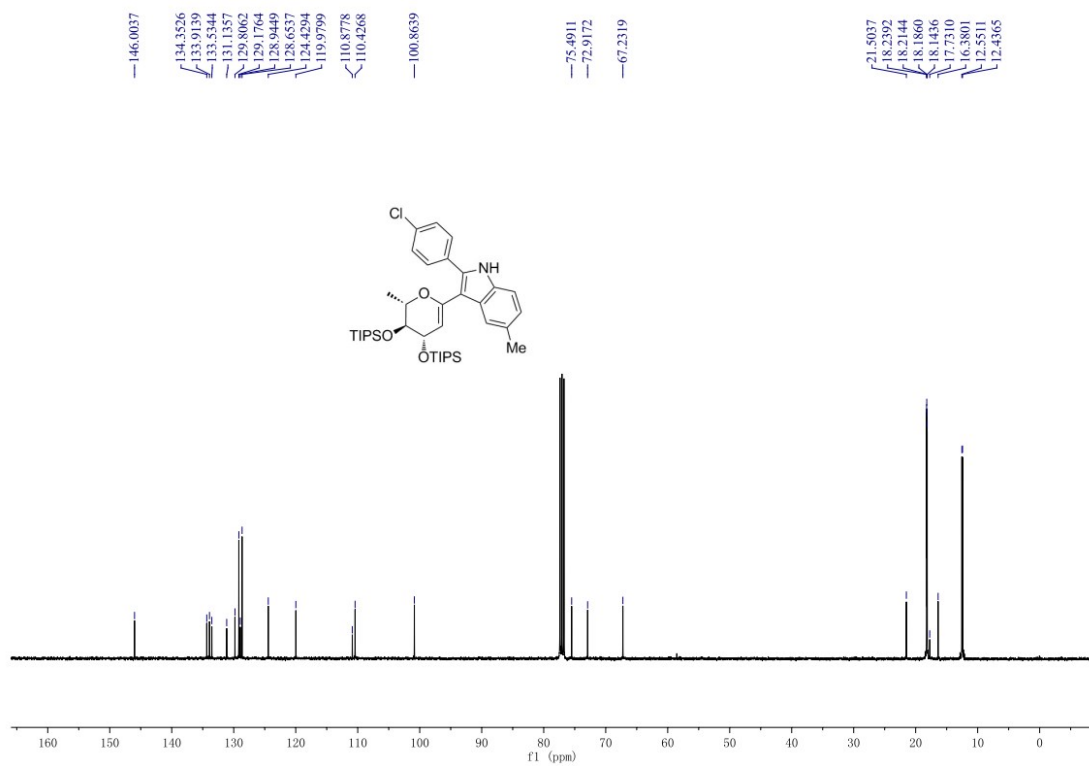
**<sup>1</sup>H NMR spectrum of 3bt**



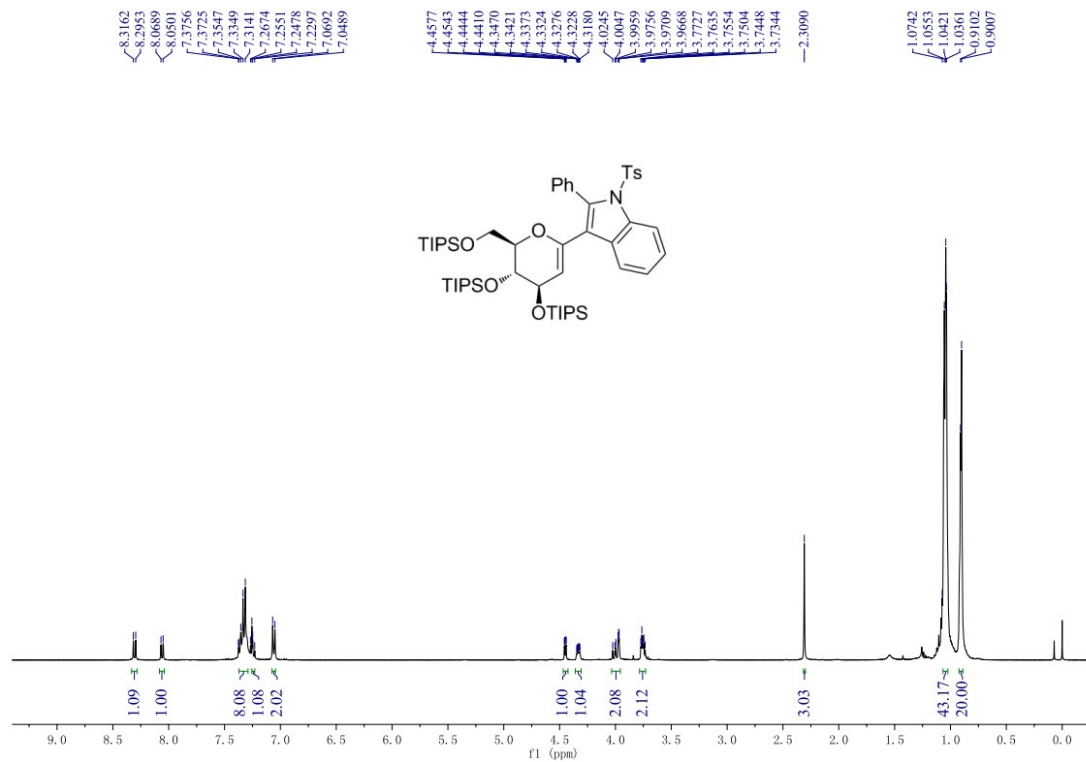
**<sup>13</sup>C NMR spectrum of 3bt**



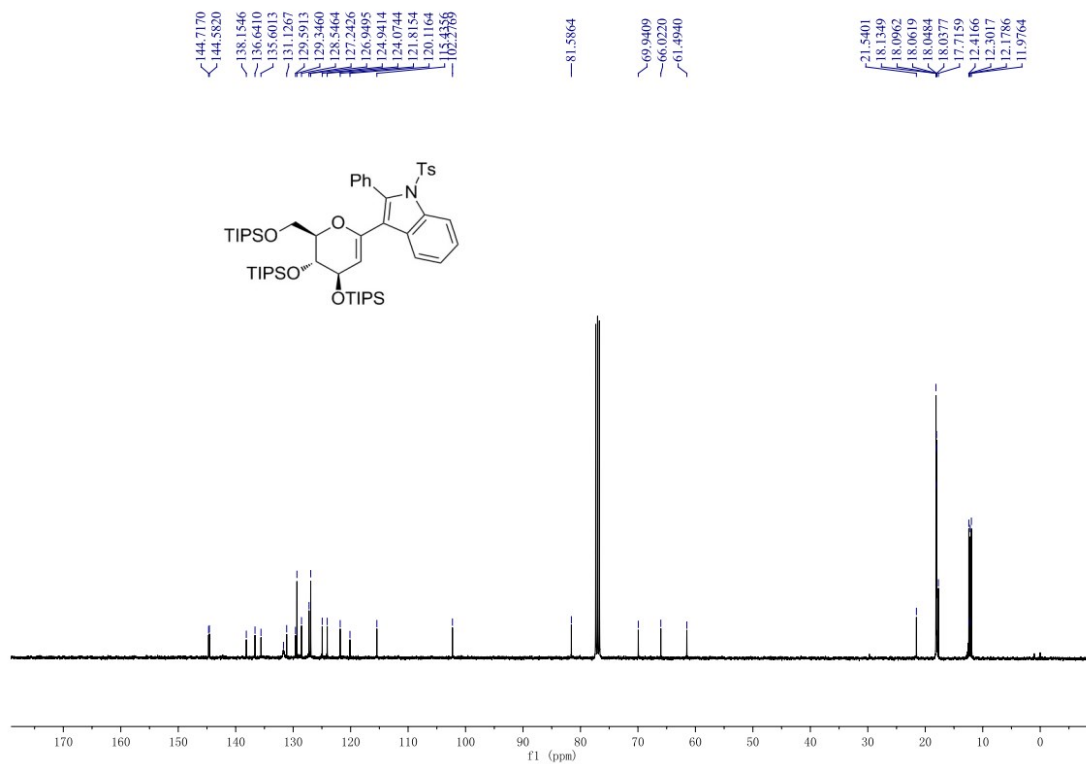
<sup>1</sup>H NMR spectrum of **3bu**



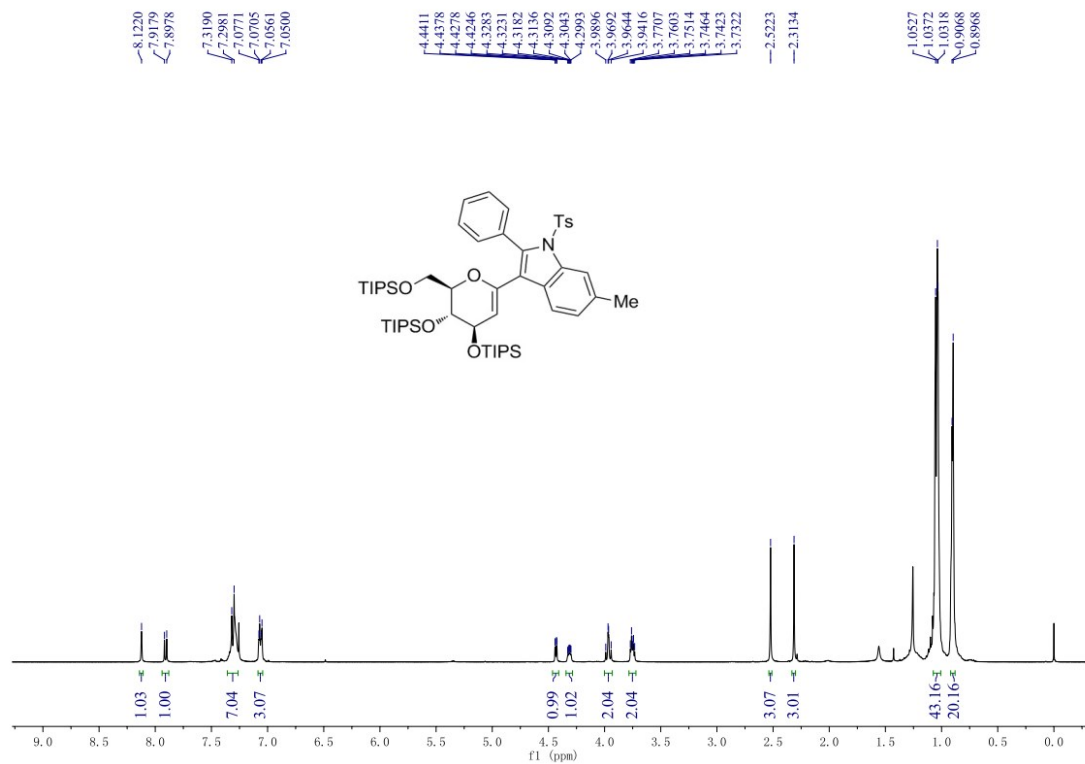
<sup>13</sup>C NMR spectrum of **3bu**



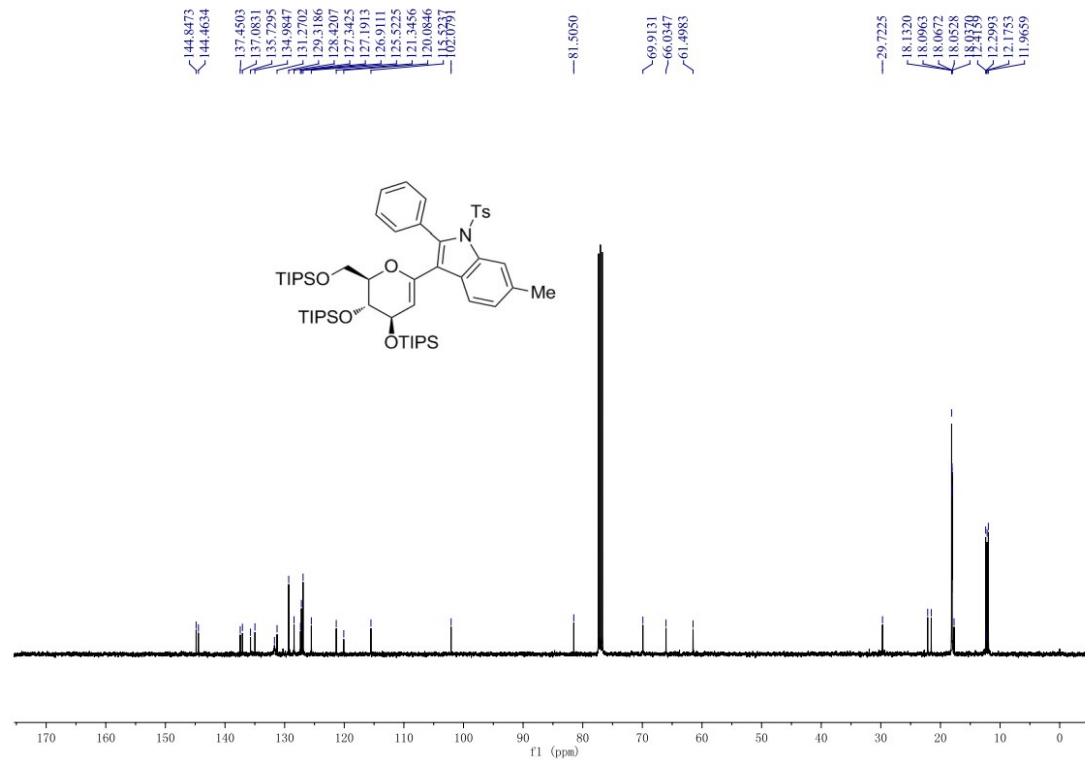
<sup>1</sup>H NMR spectrum of **5ad**



<sup>13</sup>C NMR spectrum of **5ad**

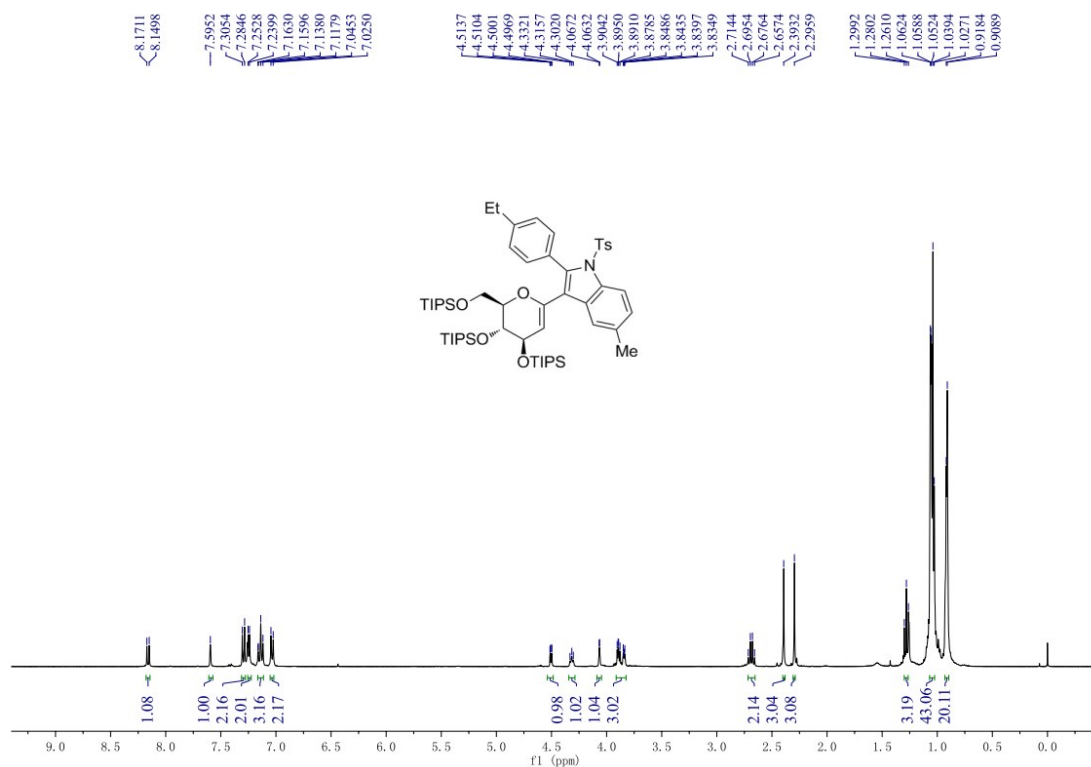


<sup>1</sup>H NMR spectrum of **5ae**

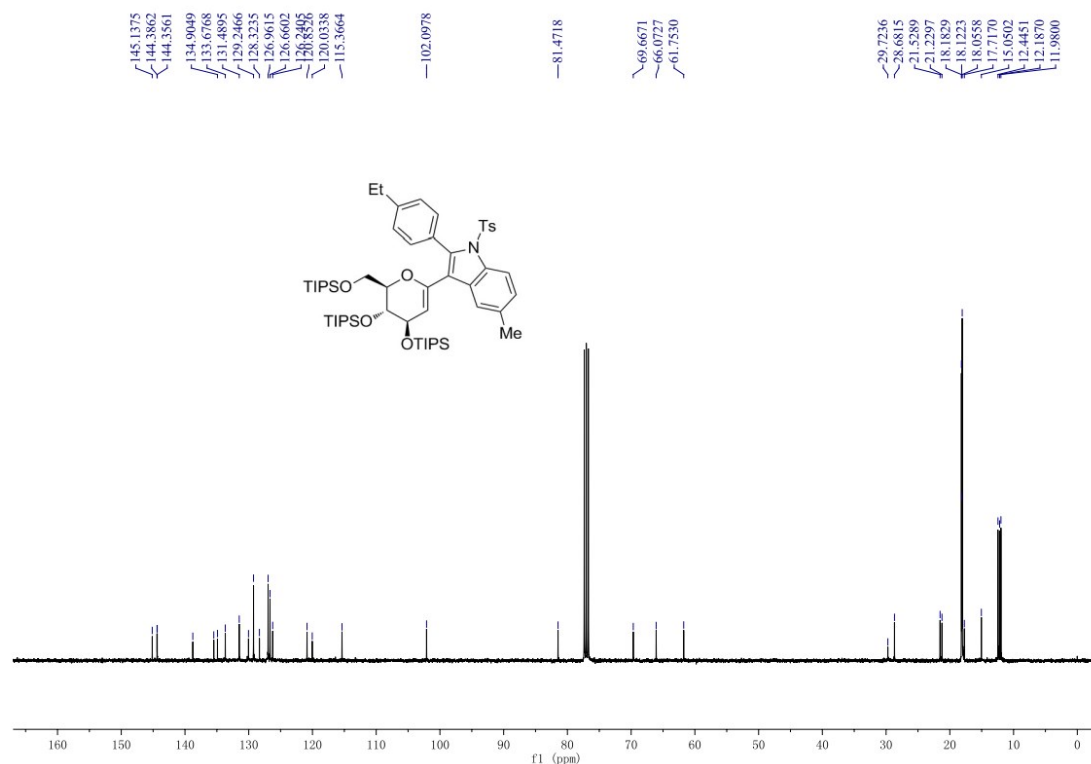


<sup>13</sup>C NMR spectrum of **5ae**

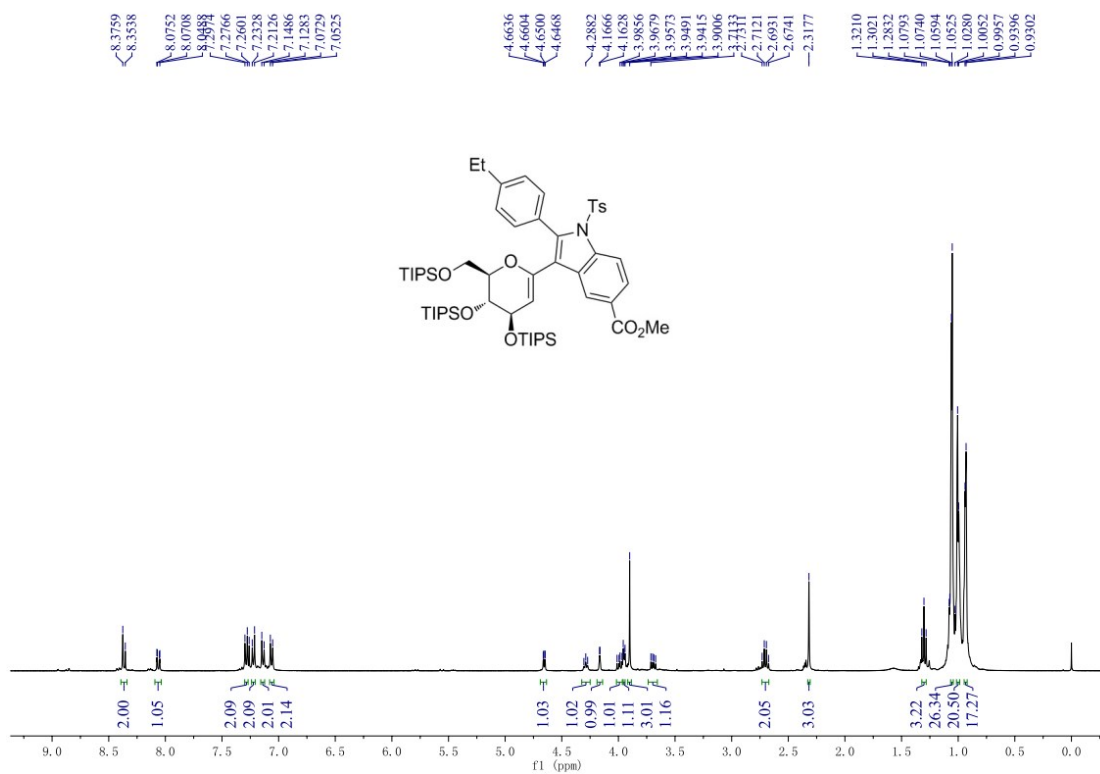




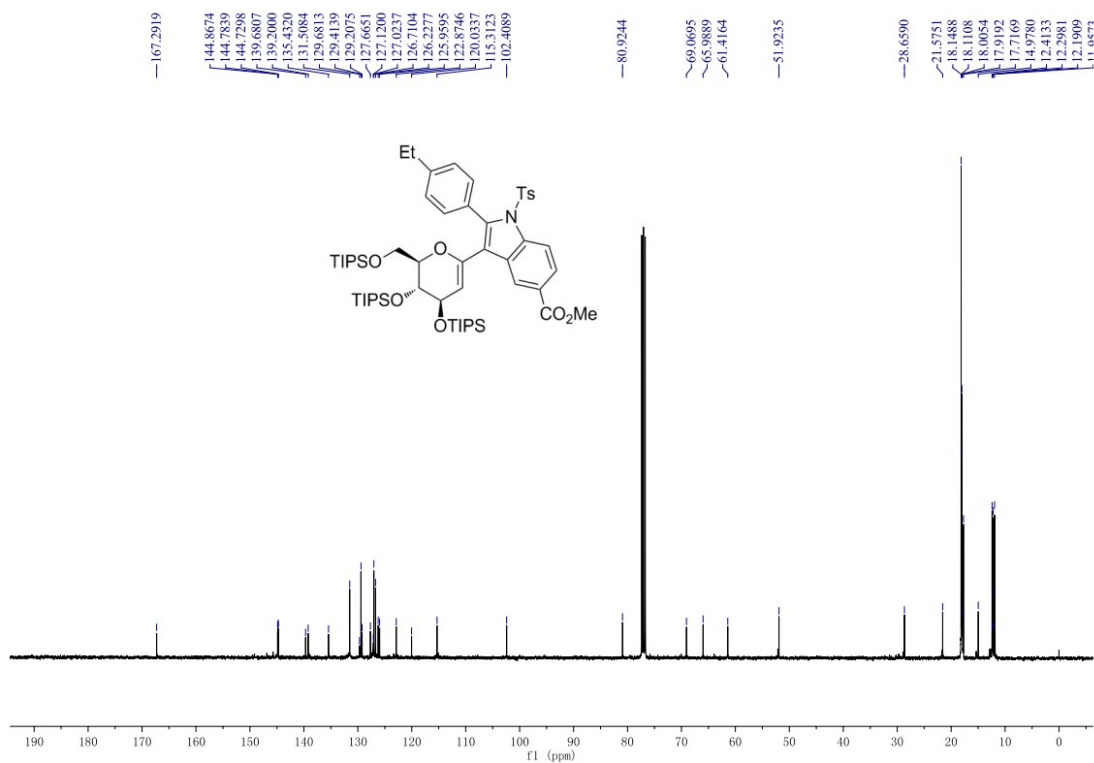
<sup>1</sup>H NMR spectrum of **5af**



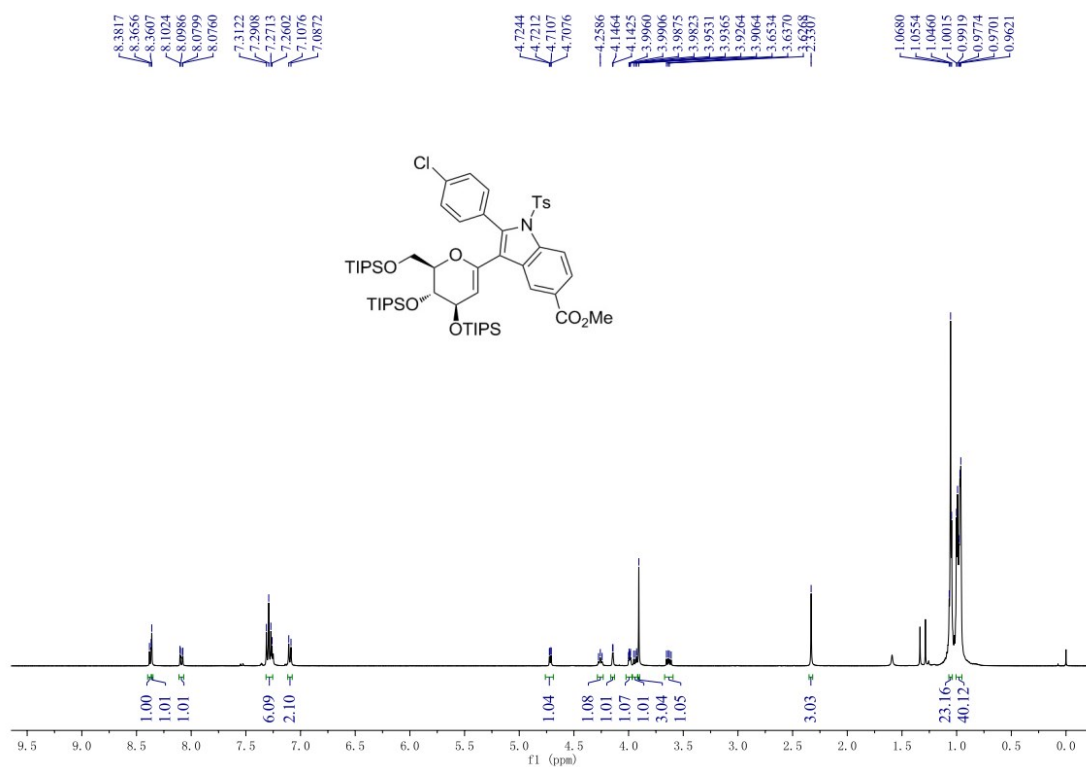
<sup>13</sup>C NMR spectrum of **5af**



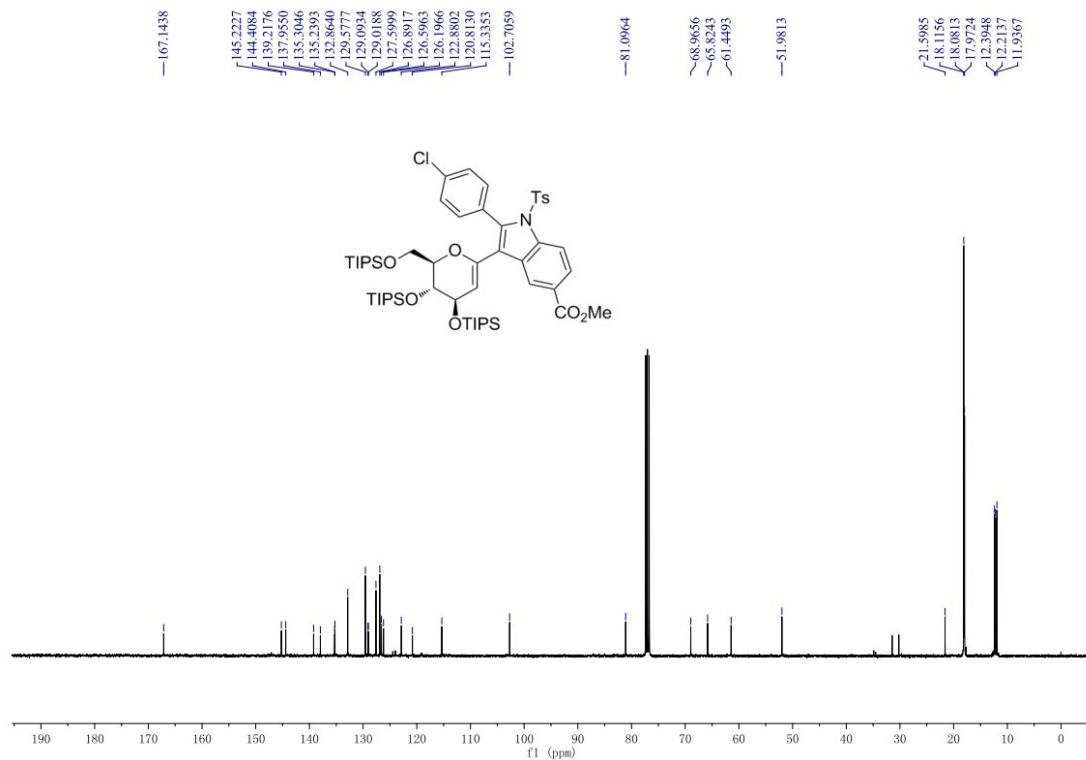
<sup>1</sup>H NMR spectrum of **5ag**



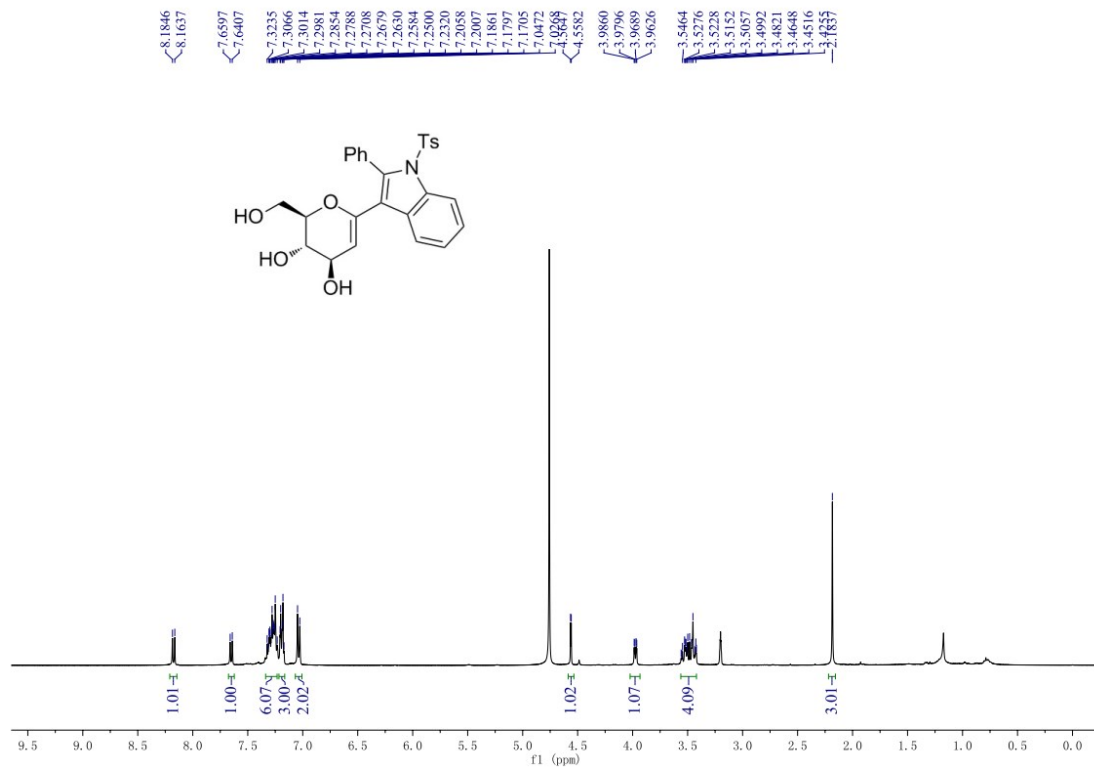
<sup>13</sup>C NMR spectrum of **5ag**



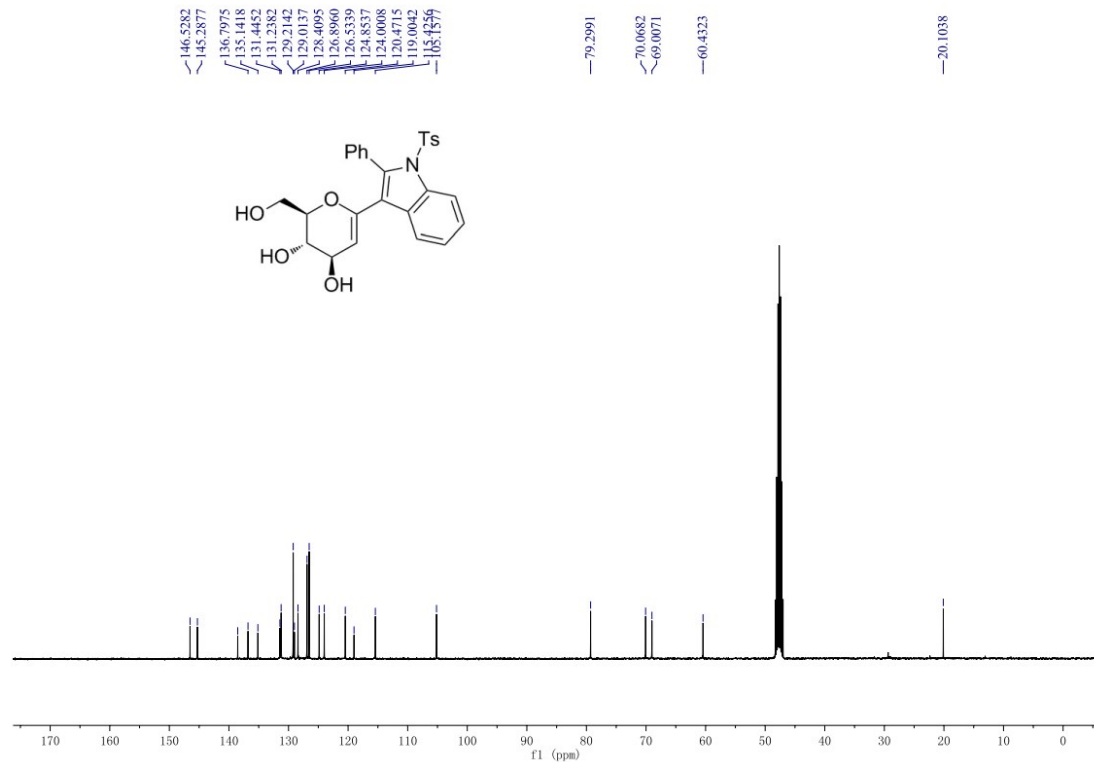
<sup>1</sup>H NMR spectrum of **5ah**



<sup>13</sup>C NMR spectrum of **5ah**



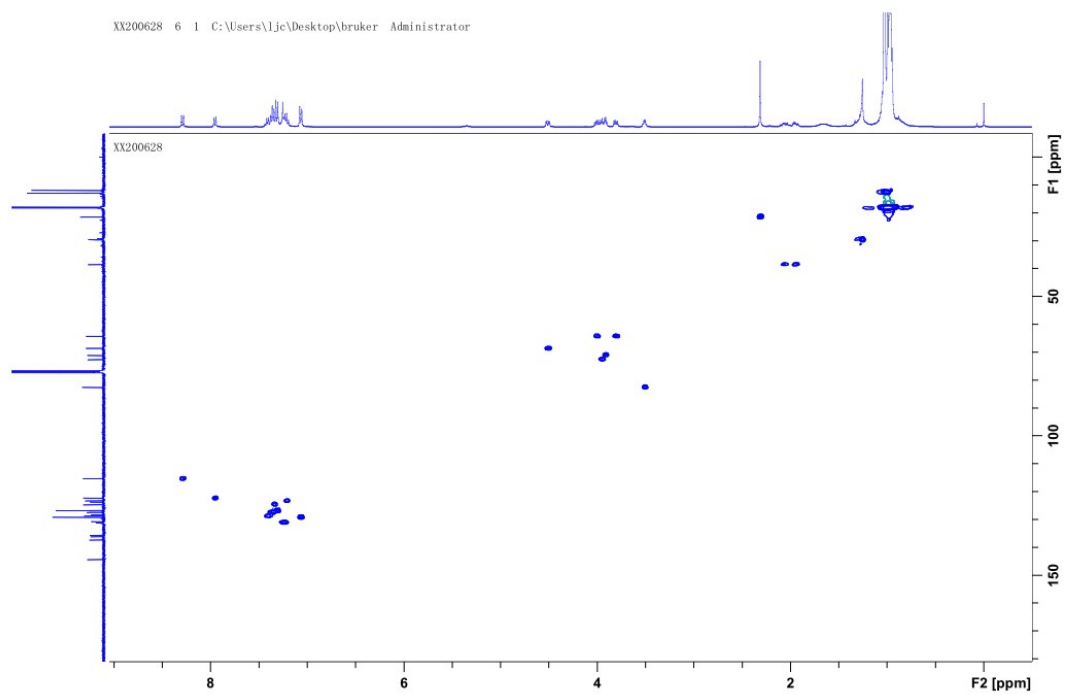
<sup>1</sup>H NMR spectrum of **6ad**



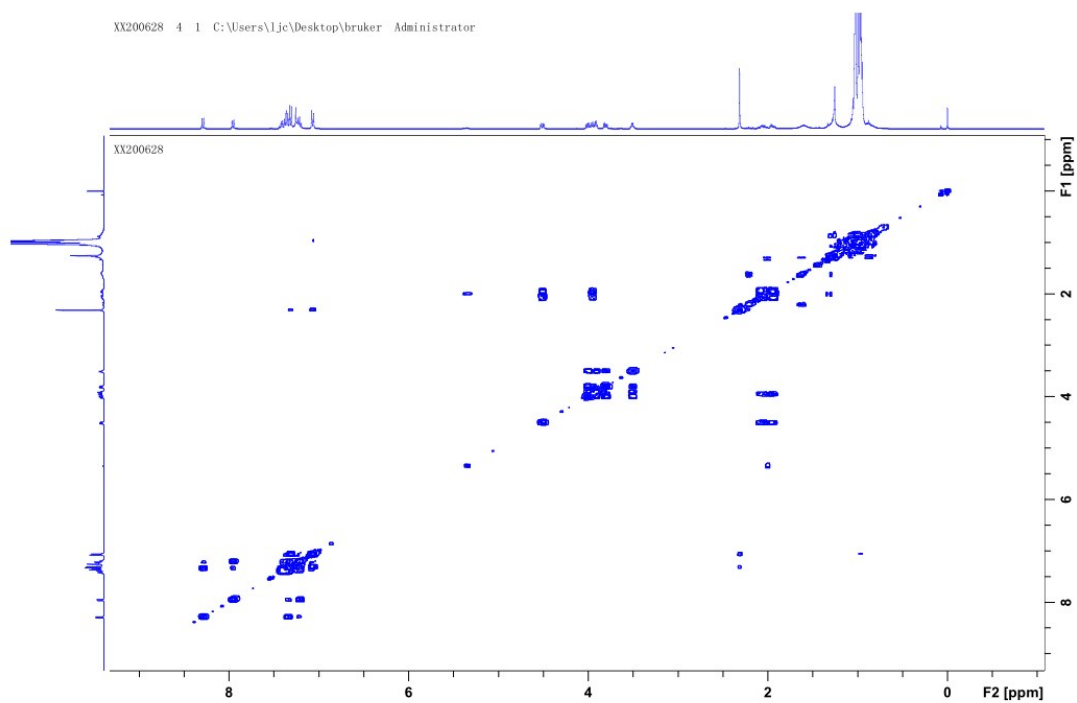
<sup>13</sup>C NMR spectrum of **6ad**



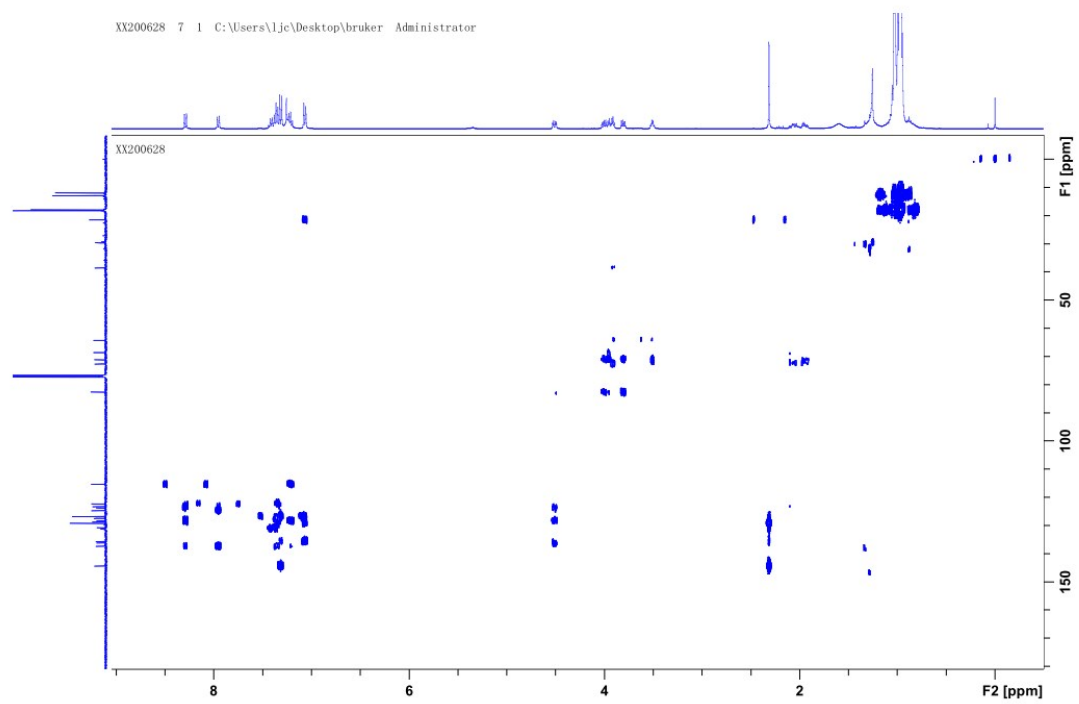
## HSQC of 7ad



## <sup>1</sup>H-<sup>1</sup>H COSY of 7ad



## HMBC of 7ad



## NOESY of 7ad

