

## Supporting Information

### Biomimetic Synthesis of *ent*-(-)-Azonazine and Stereochemical Reassignment of Natural Product

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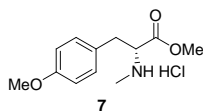
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## 1. Experimental procedures and characterizations of new compounds

**General:** All reactions were carried out in flame-dried glassware with magnetic stirring and monitored by thin-layer chromatography (TLC). THF was distilled from sodium; dichloromethane was distilled from  $\text{CaH}_2$ ; and ethyl acetate was dried over  $\text{K}_2\text{CO}_3$  and distilled. All melting points were uncorrected.  $^1\text{H}$  NMR was recorded on a Varian instrument (300 or 500 MHz) and a Bruker instrument (400 or 600 MHz);  $^{13}\text{C}$  NMR were recorded on a Varian instrument (75 or 125 MHz) and a Bruker instrument (100 or 150 MHz). IR spectra were recorded on Nicolet 380 FT-IR instrument. Optical rotations were measured on a Jasco P-1030 digital polarimeter. High resolution mass spectra (HRMS) were measured on an IonSpec 4.7 Tesla FTMS spectrometer. Flash column chromatographies were performed on silica gel H (10-40  $\mu\text{m}$ ). MPLC purification was performed using a Biotage Isolera system and KP-SIL SNAP flash cartridge column packed with silica gel (particle size 50-60 micron, 50-52 Å pore size). Microwave reactions were run on a CEM Discover S Microwave Synthesizer. X-ray intensity data were collected on a Bruker APEX-II CCD area detector employing graphite-monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at a temperature of 296(2) K.

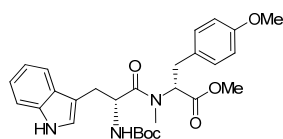
### 1.1 D-N-Me-Tyr(OMe)-OMe HCl (**7**)



To a solution of D-Boc-Tyr-OH (**5**) (50.0 g, 178 mmol) in 500 mL of dry THF under  $\text{N}_2$  atmosphere at 0 °C was added sodium hydride (60% oil dispersion, 35.6 g, 890 mmol, 5 eq) in portions. The resulting reaction mixture was stirred at 0 °C for 15 min, and methyl iodide (44.3 mL, 712 mmol, 4 eq) was then added. The reaction was stirred overnight at room temperature. The excess sodium hydride was quenched by the careful addition of water, and the solvents were removed *in vacuo*. The residue was diluted with 300 mL of water and washed with  $\text{Et}_2\text{O}$ . The aqueous phase was then acidified with  $\text{KHSO}_4$  (to pH 3) and was extracted with  $\text{EtOAc}$ . The combined extracts were successively washed with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  and brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. The resulting crude compound **6** was used directly for the next step.

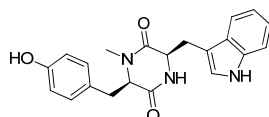
The above crude product was dissolved in methanol (400 mL) and cooled down to 0 °C under  $\text{N}_2$  atmosphere. Thionyl chloride (14.3 mL, 196 mmol, 1.1 eq) was slowly added to the reaction system. The resulting mixture was stirred at 0 °C for 0.5 h, and then refluxed for 2 h. The solvents were removed *in vacuo* to give **7** as white solid (45.3 g, 174 mmol, 98 % for two steps). Mp: 152-155°C.  $[\alpha]_{\text{D}}^{25.2} -31.3$  (c 1.0, MeOH); IR (KBr): 3417, 2954, 2834, 2691, 2433, 1745, 1612, 1514, 1249, 1029, 835  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  9.88 (brs, 2H), 7.22 and 7.16 (two d, 8.5 Hz, 2H), 6.87 (d,  $J = 8.5$  Hz, 2H), 4.22 and 4.08 (two dd,  $J = 7.5, 4.8$  Hz, 1H), 3.71 (s, 3H), 3.63 (s, 3H), 3.27 (m, 1H), 3.14 (m, 1H), 2.54 and 2.52 (two s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-d}_6$ )  $\delta$  169.45 and 168.62 (1C), 158.48 and 158.44 (1C), 130.61 and 130.47 (2C), 126.55 and 126.18 (1C), 114.00 and 113.91 (2C), 61.39 and 61.20 (1C), 55.07, 52.59, 33.91 and 33.84 (1C), 31.79 and 31.52 (1C); ESI-MS ( $m/z$ ): 224 ( $\text{M-HCl}+\text{H}^+$ ); HRMS (ESI) calcd. for  $\text{C}_{12}\text{H}_{18}\text{NO}_3$  ( $\text{M-HCl}+\text{H}^+$ ) 224.1287, found 224.1281.

## 1.2 Dipeptide **9**



To a solution of **7** (12.7 g, 49.0 mmol, 1.05 eq), N-Boc-D-Trp-OH (**8**) (14.2 g, 46.7 mmol, 1 eq) and BEP (16.6 g, 60.6 mmol, 1.3 eq) in dry CH<sub>2</sub>Cl<sub>2</sub> (500 ml) under N<sub>2</sub> atmosphere at 0 °C was added *N*-ethyl-diisopropylamine (24.3 ml, 140 mmol, 3 eq) slowly via a syringe pump (flow rate 25 ml/h). The resulting mixture was stirred at 0 °C for 0.5 h and then stirred at room temperature overnight. The organic solvent was removed *in vacuo*, and the resulting mixture was diluted with EtOAc. The organic layer was washed with H<sub>2</sub>O, brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude residue was purified by MPLC on silica gel (MeOH in CH<sub>2</sub>Cl<sub>2</sub>: 0 ~5 %) to give **9** (18.0 g, 76%) as a white foam.  $[\alpha]_D^{25.8} +48.0$  (*c* 1.02, CHCl<sub>3</sub>). IR (KBr): 3337, 3005, 2976, 2952, 2834, 1738, 1701, 1641, 1513, 1247, 1032, 747 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.34 – 8.20 (m, 1H), 7.68 – 7.50 (m, 1H), 7.34 – 7.27 (m, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.12 – 7.08 (m, 1H), 7.03 (d, *J* = 1.8 Hz, 1H), 6.94 – 6.76 (m, 2H), 6.72 – 6.62 (m, 2H), 5.16 (d, *J* = 9.0 Hz, 1H), 5.02 (dd, *J* = 9.9, 5.7 Hz, 1H), 4.92 – 4.78 (m, 1H), 3.73 – 3.59 (m, 6H), 3.29 – 3.13 (m, 2H), 3.09 – 3.03 (m, 1H), 2.87 – 2.81 (m, 1H), 2.88 and 2.66 (two s, 3H), 1.43 – 1.33 (d, *J* = 21.6 Hz, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.17 and 172.75 (1C), 171.10 and 170.57 (1C), 158.63 and 158.48 (1C), 155.30 and 155.12 (1C), 136.28, 130.15 and 129.97 (2C), 128.97, 127.93, 123.44 and 122.67 (1C), 122.12 and 122.09 (1C), 119.69 and 119.60 (1C), 119.03 and 118.93 (1C), 114.25 and 114.03 (2C), 111.28 and 111.06 (1C), 110.52 and 110.15 (1C), 79.73, 61.19 and 59.64 (1C), 55.31, 52.56 and 52.32 (1C), 50.90 and 50.47 (1C), 34.61 and 33.92 (1C), 33.39, 29.18 and 29.11 (1C), 28.49 and 28.41 (3C); ESI-MS (*m/z*): 532 (M+Na<sup>+</sup>); HRMS (ESI) calcd. for C<sub>28</sub>H<sub>35</sub>N<sub>3</sub>O<sub>6</sub> (M+Na<sup>+</sup>) 532.2427, found 532.2418.

## 1.3 Diketopiperazine **4**

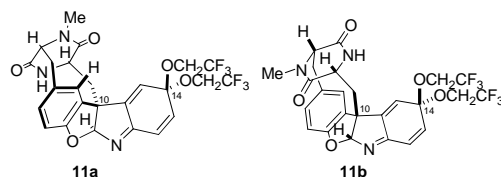


To a solution of 3 M HCl in EtOAc (100 mL) was added **9** (17.9 g, 35.1 mmol) at rt. The mixture was stirred at rt for 2 h. The solvent was removed *in vacuo*. The resulting residue was diluted with EtOAc, and the organic layer was successively washed with aqueous NaHCO<sub>3</sub>, water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude product **10** was used directly for the next step without further purification.

To a solution of crude **10** (13.0 g, 34.4 mmol, 1eq) in dry CH<sub>2</sub>Cl<sub>2</sub> (400 ml) was added BBr<sub>3</sub> (1.9 M in CH<sub>2</sub>Cl<sub>2</sub>, 90 mL, 171 mmol, 5 eq) at 0 °C. The resulting mixture was stirred at room temperature overnight. Water was slowly added at 0 °C to quench the reaction. The resulting solution was filtered, and the solid was washed with CH<sub>2</sub>Cl<sub>2</sub>. The organic phases were concentrated (to remove CH<sub>2</sub>Cl<sub>2</sub>), and then diluted with EtOAc. The organic layer was washed with aqueous NaHCO<sub>3</sub>, water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue combined with the previously filtered solid was purified by MPLC on silica gel (MeOH in CH<sub>2</sub>Cl<sub>2</sub>: 0 ~5 %) to give **4** (11.3 g, 90 % for two steps) as a white solid. Mp: 128-132 °C.  $[\alpha]_D^{25} +157.1$  (*c* 0.65, CH<sub>3</sub>CN); IR (KBr): 3291, 2926, 2685, 2600, 2261, 1664, 1632, 1516, 1458, 1233, 1100, 746

cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ 9.15 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.96 – 6.84 (m, 4H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.19 (s, 1H), 4.02 (t, *J* = 4.5 Hz, 1H), 3.92 (d, *J* = 9.6 Hz, 1H), 2.95 – 2.81 (m, 5H), 2.73 (dd, *J* = 14.3, 4.3 Hz, 1H), 1.56 (dd, *J* = 14.3, 9.7 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN) δ 167.00, 166.96, 157.28, 137.63, 132.25 (2C), 128.14, 128.05, 125.12, 122.51, 119.89, 119.50, 116.41 (2C), 112.35, 110.48, 64.09, 56.45, 36.91, 33.41, 31.75; ESI-MS (*m/z*): 364 (M+H<sup>+</sup>); HRMS (ESI) calcd. for C<sub>21</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub> (M+H<sup>+</sup>) 364.1648, found 364.1656.

#### 1.4 Ketals **11a** and **11b**

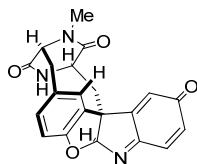


To a solution of PhI(OAc)<sub>2</sub> (3.86 g, 12.0 mmol, 2 eq) and LiOAc (2.38 g, 6 eq) in CF<sub>3</sub>CH<sub>2</sub>OH (550 mL) was added **4** (2.18 g, 6.0 mmol) in 50 mL CF<sub>3</sub>CH<sub>2</sub>OH slowly at -15°C. The reaction mixture was stirred for 30 min and quenched with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10 mL). The solvents were removed, and MeOH/CH<sub>2</sub>Cl<sub>2</sub> (1:20) was added. The sediment was filtered and washed three times with MeOH/CH<sub>2</sub>Cl<sub>2</sub> (1:20). The filtrates were concentrated *in vacuo*. The resulting residue was purified by MPLC on silica gel (MeOH in CH<sub>2</sub>Cl<sub>2</sub>: 0 ~5 %) to give a mixture of **11a/b**, which was further purified by preparative TLC (EtOAc) to give **11a** (535 mg, 16%) and **11b** (401 mg, 12%) as slightly yellow solids.

**11a**: Single crystal for X-ray analysis was prepared by slow evaporation from DMSO. Mp: >270 °C (decomposition); [α]<sub>D</sub><sup>28.0</sup> – 56.0 (*c* 1.0, THF). IR (KBr): 3445, 3218, 2945, 1678, 1621, 1580, 1483, 1282, 1170, 1107, 992 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN) δ 7.05 (s, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.89 (s, 1H), 6.85 (d, *J* = 10.2 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.58 (dd, *J* = 10.2, 2.4 Hz, 1H), 6.11 (s, 1H), 5.47 (s, 1H), 4.19 – 4.00 (m, 6H), 3.30 (d, *J* = 14.0 Hz, 1H), 3.06 (s, 3H), 2.89 (dd, *J* = 14.1, 4.3 Hz, 1H), 2.81 (dd, *J* = 16.1, 3.2 Hz, 1H), 2.00 (dd, *J* = 16.2, 3.8 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN) δ 168.76, 165.87, 164.86, 158.89, 148.41, 139.26, 133.55, 133.25, 128.13, 127.52, 126.05, 125.33(q, *J* = 275 Hz, 1C), 125.28 (q, *J* = 275 Hz, 1C), 122.28, 116.86, 111.37, 98.84, 66.32, 62.08 (q, *J* = 34.6 Hz, 2C), 57.42, 56.12, 38.38, 37.60, 33.86; ESI-MS (*m/z*): 558 (M+H<sup>+</sup>); HRMS (ESI) calcd. for C<sub>25</sub>H<sub>22</sub>N<sub>3</sub>O<sub>5</sub>F<sub>6</sub> (M+H<sup>+</sup>) 558.1469, found 558.1458.

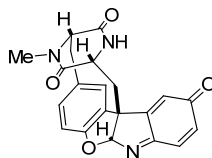
**11b**: Single crystals for X-ray analysis was prepared by vapor diffusion (THF/hexanes). Mp: >250 °C (decomposition); [α]<sub>D</sub><sup>25.1</sup> – 20.4 (*c* 1.02, THF). IR (KBr): 3260, 2933, 1682, 1655, 1579, 1484, 1287, 1155, 1112, 988, 752 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN) δ 7.32 (s, 1H), 6.97 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.94 (s, 1H), 6.87 (d, *J* = 10.2 Hz, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 6.58 (dd, *J* = 10.2, 2.4 Hz, 1H), 6.46 (d, *J* = 2.4 Hz, 1H), 6.25 (s, 1H), 4.17 – 3.99 (m, 6H), 3.48 (d, *J* = 14.0 Hz, 1H), 3.05 (dd, *J* = 14.1, 6.4 Hz, 1H), 2.71 (dd, *J* = 16.4, 3.9 Hz, 1H), 2.44 (s, 3H), 2.28 (dd, *J* = 16.4, 3.6 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN) δ 169.87, 165.19, 164.78, 159.56, 149.67, 139.18, 132.92, 132.31, 129.16, 127.40, 126.46, 125.37 (q, *J* = 275 Hz, 1C), 125.23 (q, *J* = 275 Hz, 1C), 121.23, 110.86, 118.18, 98.71, 66.84, 62.25 (q, *J* = 35 Hz, 1C), 62.10(q, *J* = 35 Hz, 1C), 57.17, 55.62, 39.29, 38.66, 32.93; ESI-MS (*m/z*): 558 (M+H<sup>+</sup>). HRMS (ESI) calcd. for C<sub>25</sub>H<sub>22</sub>N<sub>3</sub>O<sub>5</sub>F<sub>6</sub> (M + H<sup>+</sup>) 558.1472, found 558.1458.

### 1.5 Quinone **12a**



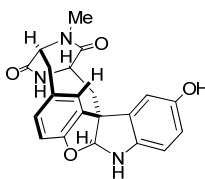
Ketal **11a** (60 mg, 0.108 mmol), HOAc (4.5 mL) and water (0.03 mL) were introduced into an oven-dried 20 mL CEM® vial. The vial was then sealed with a Teflon-lined septum. The resulting mixture was irradiated by microwave (50W) at 50 °C for 15 min. Solvents were removed *in vacuo*, and the residue was diluted with EtOAc. The organic layer was washed by aqueous NaHCO<sub>3</sub>, water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude residue was purified by MPLC on silica gel (MeOH in CH<sub>2</sub>Cl<sub>2</sub>: 0 ~5 %) to give **12a** (24 mg, 59 %) as a yellow solid. Mp: 135~137 °C; [ $\alpha$ ]<sub>D</sub><sup>24.8</sup> – 197.3 (*c* 0.50, THF); IR (KBr): 3244, 3062, 2922, 2851, 1679, 1638, 1481, 1235, 1030, 733 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (d, *J* = 10.0 Hz, 1H), 7.32 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.88 (s, 1H), 6.67 (d, *J* = 9.9 Hz, 1H), 6.17 (s, 1H), 5.39 (s, 1H), 4.24 (s, 1H), 4.20 (d, *J* = 3.7 Hz, 1H), 3.29 (d, *J* = 13.9 Hz, 1H), 3.13 (s, 3H), 3.10 – 3.01 (m, 2H), 1.99 (d, *J* = 15.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  187.94, 166.97, 166.32, 165.74, 157.75, 154.02, 137.33, 133.39, 133.15, 131.76, 125.79, 125.17, 123.85, 115.62, 111.61, 65.35, 57.18, 54.95, 37.69, 36.08, 33.83; ESI-MS (*m/z*): 376 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>21</sub>H<sub>18</sub>N<sub>3</sub>O<sub>4</sub> (M+H<sup>+</sup>) 376.1298; Found 376.1292.

### 1.6 Quinone **12b**



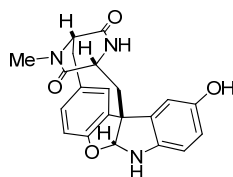
Ketal **11b** (40 mg, 0.072 mmol), HOAc (1 mL) and dioxane (1 mL), water (0.1 mL) were introduced into an oven-dried 10 mL CEM® vial. The vial was then sealed with a Teflon-lined septum. The resulting mixture was irradiated by microwave (50W) at 65 °C for 1.2 h. Solvent was removed *in vacuo*, and the residue was diluted with EtOAc. The organic layer was washed by aqueous NaHCO<sub>3</sub>, water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude residue was purified by MPLC on silica gel (MeOH in CH<sub>2</sub>Cl<sub>2</sub>: 0~5 %) to give **12b** (13 mg, 48 %) as a yellow solid. Mp: 160~165 °C; [ $\alpha$ ]<sub>D</sub><sup>25.6</sup> – 1.72 (*c* 0.275, CHCl<sub>3</sub>); IR (KBr): 3473, 3223, 2928, 1672, 1637, 1483, 1274, 1027, 753 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.95 (s, 1H), 7.46 (d, *J* = 9.9 Hz, 1H), 7.36 (s, 1H), 7.08 (s, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.63 (d, *J* = 9.9 Hz, 1H), 6.40 (s, 1H), 4.28 (s, 1H), 4.16 (d, *J* = 6.1 Hz, 1H), 3.90 (d, *J* = 14.3 Hz, 1H), 3.06 (dd, *J* = 14.4, 6.3 Hz, 1H), 2.97 (dd, *J* = 16.4, 3.7 Hz, 1H), 2.56 (s, 3H), 2.48 (dd, *J* = 16.3, 3.4 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  187.77, 170.58, 165.65, 163.93, 158.51, 155.48, 136.79, 133.65, 131.31, 131.28, 126.34, 125.12, 122.11, 116.32, 110.58, 65.84, 56.86, 54.34, 38.54, 36.19, 32.62; ESI-MS (*m/z*): 376 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>21</sub>H<sub>18</sub>N<sub>3</sub>O<sub>4</sub> (M+H<sup>+</sup>) 376.1295; Found 376.1292.

### 1.7 Phenol **13a**



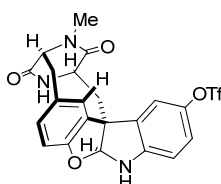
To a solution of **12a** (86 mg, 0.23 mmol) in MeOH (5 mL) was added NaBH<sub>4</sub> (10 mg, 0.26 mmol, 1.14 eq) at 0°C. The reaction was monitored by TLC until the starting material was consumed. Silica gel was added and the solvent was removed *in vacuo*. The residue was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 100:1~20:1) to give **13a** (58 mg, 67%) as a white solid. Mp: >240 °C (decomposition); [ $\alpha$ ]<sub>D</sub><sup>29</sup> + 193.7 (*c* 0.108, MeOH); IR (KBr): 3350, 2970, 2937, 2835, 1661, 1635, 1481, 1236, 1058, 925 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  7.52 (d, *J* = 2.6 Hz, 1H), 6.93 (d, *J* = 1.6 Hz, 1H), 6.85 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.53 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.49 – 6.44 (m, 2H), 6.08 (d, *J* = 5.3 Hz, 1H), 5.50 (s, 1H), 5.27 (d, *J* = 5.3 Hz, 1H), 4.10 (d, *J* = 4.2 Hz, 2H), 3.26 (d, *J* = 14.0 Hz, 1H), 3.08 (s, 3H), 2.96 (dd, *J* = 16.1, 3.2 Hz, 1H), 2.86 (dd, *J* = 14.0, 4.6 Hz, 1H), 1.91 (d, *J* = 4.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN)  $\delta$  168.18, 165.84, 158.50, 151.61, 142.54, 133.81, 132.57, 132.46, 130.61, 125.53, 115.18, 113.25, 110.87, 110.73, 110.32, 65.97, 59.95, 56.18, 41.15, 38.15, 33.86; ESI-MS (*m/z*): 378 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>21</sub>H<sub>20</sub>N<sub>3</sub>O<sub>4</sub> (M+H<sup>+</sup>) 378.1459; Found 378.1448.

#### 1.8 Phenol **13b**



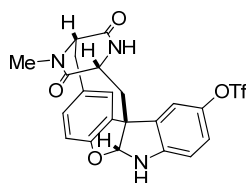
To a solution of **12b** (110 mg, 0.29 mmol) in MeOH (5 mL) was added NaBH<sub>4</sub> (12 mg, 0.32 mmol, 1.1 eq) at 0°C. The reaction was monitored by TLC until consumption of the starting material. Silica gel was added and the solvent was removed *in vacuo*. The residue was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 100:1~20:1) to give **13b** (88 mg, 80 %) as a white solid. Mp: >220 °C (decomposition); [ $\alpha$ ]<sub>D</sub><sup>24</sup> – 253.6 (*c* 0.33, MeOH); IR (KBr): 3336, 2935, 2852, 1662, 1632, 1482, 1454, 1200, 1019, 819 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  7.33 (d, *J* = 1.5 Hz, 1H), 7.00 (s, 1H), 6.96 (d, *J* = 2.3 Hz, 1H), 6.89 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.62 – 6.48 (m, 4H), 6.17 (d, *J* = 4.6 Hz, 1H), 5.40 (d, *J* = 4.1 Hz, 1H), 4.12 (s, 1H), 4.07 (d, *J* = 6.5 Hz, 1H), 3.46 (d, *J* = 14.0 Hz, 1H), 3.02 (dd, *J* = 14.1, 6.6 Hz, 1H), 2.62 (dd, *J* = 16.3, 4.5 Hz, 1H), 2.43 – 2.38 (m, 4H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN)  $\delta$  169.94, 165.32, 159.23, 151.88, 142.32, 134.20, 132.19, 131.81, 130.82, 126.00, 115.60, 111.53, 111.00, 110.74, 110.12, 66.52, 59.88, 55.18, 42.19, 38.92, 32.76; ESI-MS (*m/z*): 378 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>21</sub>H<sub>20</sub>N<sub>3</sub>O<sub>4</sub> (M+H<sup>+</sup>) 378.1455; Found 378.1448.

#### 1.9 Triflate **14a**



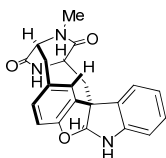
To a solution of **13a** (50 mg, 0.13 mmol) in dry EtOAc (8 mL) under N<sub>2</sub> atmosphere was added triethylamine (0.3 mL). The solution was cooled down to -15 °C for 10 min, and Tf<sub>2</sub>O (48 µl, 0.28 mmol, 2.15 eq) was slowly added. The solution was stirred for 3 h at -15 °C until aqueous NH<sub>4</sub>Cl solution was added. The resulting mixture was diluted with EtOAc and washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude residue was purified by flash column chromatograph (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 100:1~20:1) to give **14a** (36 mg, 53 %) as a white solid. Mp: >270 °C (decomposition); [α]<sub>D</sub><sup>28</sup> +217.0 (c 0.16, MeOH); IR (KBr): 3285, 3053, 2928, 2845, 1673, 1654, 1488, 1418, 1213, 1060, 893 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-d<sup>6</sup>) δ 8.03 (d, *J* = 2.7 Hz, 1H), 7.36 (d, *J* = 3.7 Hz, 1H), 7.26 (d, *J* = 1.6 Hz, 1H), 7.12 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.75 (dd, *J* = 6.1, 4.8 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 1H), 6.20 (d, *J* = 3.8 Hz, 1H), 4.18 (d, *J* = 4.2 Hz, 1H), 4.14 (s, 1H), 3.26 (d, *J* = 13.8 Hz, 1H), 3.03 (s, 3H), 2.79 (dd, *J* = 14.0, 4.6 Hz, 1H), 2.74 (dd, *J* = 15.9, 3.6 Hz, 1H), 1.94 (dd, *J* = 16.1, 3.9 Hz, 1H); <sup>13</sup>C NMR (125 MHz, DMSO-d<sup>6</sup>) δ 167.41, 164.24, 156.49, 148.89, 141.32, 132.82, 131.60, 131.50, 128.47, 123.91, 121.09, 118.38 (q, *J* = 319 Hz, 1C), 117.26, 109.93, 108.68, 107.95, 64.43, 58.13, 54.20, 39.09, 36.71, 32.67; ESI-MS (*m/z*): 510 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>22</sub>H<sub>19</sub>N<sub>3</sub>O<sub>6</sub>F<sub>3</sub>S (M+H<sup>+</sup>) 510.0957; Found 510.0941.

#### 1.10 Triflate **14b**



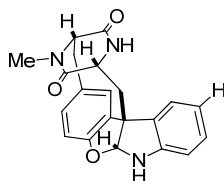
To a solution of **13b** (28 mg, 0.074 mmol) in dry EtOAc (2 mL) under N<sub>2</sub> atmosphere was added triethylamine (0.05 mL). The solution was cooled down to -15 °C for 10 min, and Tf<sub>2</sub>O (25 µl, 0.15 mmol, 2 eq) was slowly added. The solution was stirred for 1 h at -15 °C until aqueous NH<sub>4</sub>Cl solution was added. The resulting mixture was diluted with EtOAc and washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude residue was purified by flash column chromatograph (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 100:1~20:1) to give **14b** (26.5 mg, 70 %) as a white solid. Mp: >250 °C (decomposition); [α]<sub>D</sub><sup>25</sup> -368.4 (c 0.115, MeOH); IR (KBr): 3444, 2934, 2848, 1673, 1636, 1490, 1419, 1217, 1137, 884 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-d<sup>6</sup>) δ 8.83 (s, 1H), 7.58 (d, *J* = 2.6 Hz, 1H), 7.52 (d, *J* = 3.1 Hz, 1H), 7.22 (d, *J* = 1.5 Hz, 1H), 7.10 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.93 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.63 (d, *J* = 3.7 Hz, 1H), 6.62 (d, *J* = 3.1 Hz, 1H), 6.28 (d, *J* = 3.2 Hz, 1H), 4.12 (d, *J* = 6.5 Hz, 2H), 3.35 (d, *J* = 13.7 Hz, 1H), 3.02 (dd, *J* = 13.9, 6.4 Hz, 1H), 2.55 (dd, *J* = 16.2, 4.5 Hz, 1H), 2.39 – 2.32 (m, 4H); <sup>13</sup>C NMR (125 MHz, DMSO-d<sup>6</sup>) δ 168.19, 164.00, 157.60, 148.64, 141.29, 133.21, 130.74, 130.15, 129.93, 124.52, 120.89, 118.28 (q, *J* = 319 Hz, 1C), 116.78, 109.16, 108.58, 108.01, 64.83, 58.04, 53.41, 39.59 (DEPT, HMQC), 37.55, 31.62; ESI-MS (*m/z*): 510 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>22</sub>H<sub>18</sub>N<sub>3</sub>O<sub>6</sub>F<sub>3</sub>SN<sub>a</sub> (M+Na<sup>+</sup>) 532.0760; Found 532.0761.

#### 1.11 Compound **15a**



A mixture of **14a** (35 mg, 0.069 mmol), triethylamine (30  $\mu$ L, 0.22 mmol) and 15 mg Pd(OH)<sub>2</sub>/C (20% Pd) in MeOH (1.5 mL) and EtOAc (1.5 mL) was stirred at room temperature under hydrogen atmosphere (1 atm) at rt for 2 h. The reaction mixture was filtered through a pad of Celite. The solid was washed with 5% MeOH/CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were concentrated *in vacuo*. The residue was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 100:1~20:1) to afford **15a** (20 mg, 80 %) as a white solid. Mp: >300 °C (decomposition); [ $\alpha$ ]<sub>D</sub><sup>29</sup> + 154.8 (*c* 0.14, CHCl<sub>3</sub>); IR (KBr): 3330, 2925, 2848, 1670, 1650, 1485, 1316, 1233, 1057, 944, 752 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.97 – 6.89 (m, 3H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.14 (d, *J* = 3.6 Hz, 1H), 5.44 (s, 1H), 4.91 (d, *J* = 3.6 Hz, 1H), 4.22 (s, 1H), 4.17 (d, *J* = 4.5 Hz, 1H), 3.29 – 3.24 (m, 2H), 3.16 (s, 3H), 3.02 (dd, *J* = 14.0, 4.6 Hz, 1H), 1.89 (dd, *J* = 16.2, 4.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  166.95, 165.57, 156.95, 147.47, 131.93, 131.39, 130.82, 129.55, 128.51, 124.82, 124.75, 120.59, 110.94, 109.20, 109.07, 65.35, 58.93, 55.48, 40.58, 37.61, 33.84; ESI-MS (*m/z*): 362 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>21</sub>H<sub>20</sub>N<sub>3</sub>O<sub>3</sub> (M+H<sup>+</sup>) 362.1496; Found 362.1499.

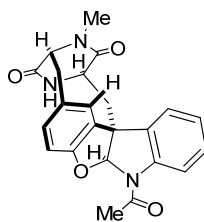
#### 1.12 Compound **15b**



A mixture of **14b** (62.6 mg, 0.123 mmol), triethylamine (34  $\mu$ L, 0.246 mmol) and 15 mg Pd(OH)<sub>2</sub>/C (20% Pd) in MeOH (3 mL) and EtOAc (1 mL) was stirred at room temperature under hydrogen atmosphere (1 bar) at rt for 2 h. The reaction mixture was filtered through a pad of Celite. The solid was rinsed with 5% methanol/dichloromethane. The combined filtrates were concentrated *in vacuo*. The residue was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 100:1~20:1) to afford **15b** (43.0 mg, 96 %) as a white solid. Mp: >300 °C (dec.); [ $\alpha$ ]<sub>D</sub><sup>28.7</sup> – 416.2 (*c* 0.125, MeOH); IR (KBr): 3430, 2979, 2858, 1664, 1634, 1479, 1055, 1012, 810, 744 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.78 (s, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 1.4 Hz, 1H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.03 (td, *J* = 7.7, 1.2 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.73 (td, *J* = 7.4, 0.8 Hz, 1H), 6.60 – 6.54 (m, 2H), 6.19 (d, *J* = 3.6 Hz, 1H), 4.12 (m, 2H), 3.36 (m, 1H), 2.99 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.55 (m, 1H), 2.41 – 2.34 (m, 4H); <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  168.28, 164.18, 157.70, 148.45, 131.67, 131.11, 130.30, 129.66, 127.96, 124.51, 122.92, 118.20, 108.87, 108.58, 108.06, 64.92, 58.02, 53.60, 40.47, 37.49, 31.63; ESI-MS (*m/z*): 362 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>21</sub>H<sub>20</sub>N<sub>3</sub>O<sub>3</sub> (M+H<sup>+</sup>) 362.1504; Found 362.1499.

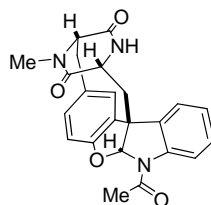
#### 1.13 Azonazine diastereomer **1a** (The originally proposed structure)





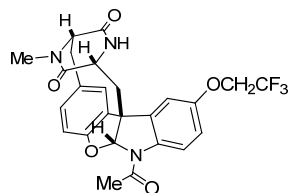
To a solution of **15a** (14 mg, 0.039 mmol) in HOAc (2 mL) was added Ac<sub>2</sub>O (0.01 mL, 0.106 mmol) at rt. The resulting mixture was stirred at rt for 6 h. The solvent was removed, and the residue was diluted by EtOAc. The organic layer was washed with aqueous NaHCO<sub>3</sub>, water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude residue was purified by preparative TLC (EtOAc/MeOH, 50:1) to afford **1a** (10.5 mg, 67 %) as a white solid. Mp: >300 °C (dec.); [ $\alpha$ ]<sub>D</sub><sup>28.2</sup> + 342.7 (*c* 0.175, MeOH); IR (KBr): 3518, 3232, 3012, 2928, 2848, 1677, 1649, 1485, 1391, 1241, 971, 756 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  8.10 (s, 1H), 8.06 (d, *J* = 7.1 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.01 (s, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.46 (s, 1H), 5.61 (s, 1H), 4.18 (s, 1H), 4.14 (d, *J* = 4.5 Hz, 1H), 3.29 (d, *J* = 14.1 Hz, 1H), 3.13 (dd, *J* = 16.3, 2.8 Hz, 1H), 3.09 (s, 3H), 2.89 (dd, *J* = 14.1, 4.7 Hz, 1H), 2.41 (s, 3H), 2.18 (dd, *J* = 16.3, 4.8 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN)  $\delta$  171.74, 168.24, 165.77, 157.67, 142.95, 134.78, 133.77, 132.82, 130.35, 129.28, 125.35 (2C), 124.95, 116.52, 111.25, 107.01, 65.97, 58.79, 56.18, 40.98, 38.20, 33.94, 24.37; ESI-MS (*m/z*): 404 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>Na (M+Na<sup>+</sup>) 426.1429; Found 426.1424.

#### 1.14 *ent*-(-)- Azonazine (**1b**)



To a solution of **15b** (13 mg, 0.036 mmol) in HOAc (1.5 mL) was added Ac<sub>2</sub>O (0.01 mL, 0.106 mmol) at rt. The resulting mixture was stirred at rt for 4 h. The solvent was removed and the residue was diluted by EtOAc. The organic layer was washed with aqueous NaHCO<sub>3</sub>, water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude residue was purified by preparative TLC (EtOAc/MeOH, 50:1) to afford **1b** (13 mg, 89 %). The single crystal for X-ray analysis was prepared by slow evaporation from CH<sub>3</sub>CN. Mp: >350 °C (dec.); [ $\alpha$ ]<sub>D</sub><sup>26.5</sup> – 299.3 (*c* 0.11, MeOH); IR (KBr): 3430, 3219, 2926, 2849, 1661, 1626, 1485, 1394, 1283, 1027, 740 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN)  $\delta$  8.13 (s, 1H), 7.60 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.29 (td, *J* = 7.8, 1.3 Hz, 1H), 7.19 (td, *J* = 7.5, 1.1 Hz, 1H), 6.96 (m, 2H), 6.67 (d, *J* = 8.1 Hz, 1H), 6.59 (s, 1H), 4.27 (d, *J* = 5.1 Hz, 1H), 4.09 (d, *J* = 6.5 Hz, 1H), 3.50 (d, *J* = 14.2 Hz, 1H), 3.08 (dd, *J* = 14.2, 6.9 Hz, 1H), 2.84 (dd, *J* = 16.5, 5.8 Hz, 1H), 2.49 (dd, *J* = 16.5, 2.2 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H); <sup>13</sup>C NMR (150 MHz, CD<sub>3</sub>CN)  $\delta$  171.29, 169.43, 165.49, 159.05, 142.52, 135.37, 133.22, 132.02, 131.51, 129.62, 126.46, 125.71, 124.15, 117.31, 110.84, 106.98, 66.32, 59.08, 54.84, 43.41, 39.24, 32.83, 24.17; ESI-MS (*m/z*): 404 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>O<sub>4</sub> (M+H<sup>+</sup>) 404.1610; Found 404.1605.

### 1.15 *ent*-Azonazine analogue **16**

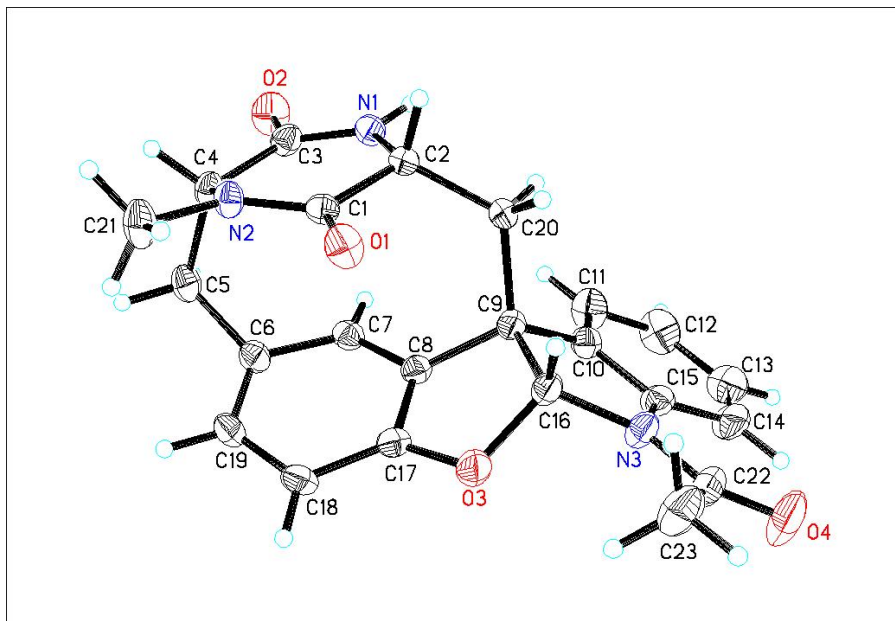


To a solution of **11b** (26 mg, 0.047 mmol) in THF (3 mL) was added Zn powder (9.0 mg, 0.14 mmol), Et<sub>3</sub>SiH (29  $\mu$ l, 0.19 mmol) and AcOH (30  $\mu$ l, 0.52 mmol) at rt under N<sub>2</sub> atmosphere. The reaction mixture was stirred at rt until consumption of the starting material (monitored by TLC). The reaction mixture was diluted with EtOAc and filtered through a pad of Celite. The solid was washed with EtOAc. The organic layers were washed with aqueous NaHCO<sub>3</sub>, water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude residue was directly used for the next step without further purification.

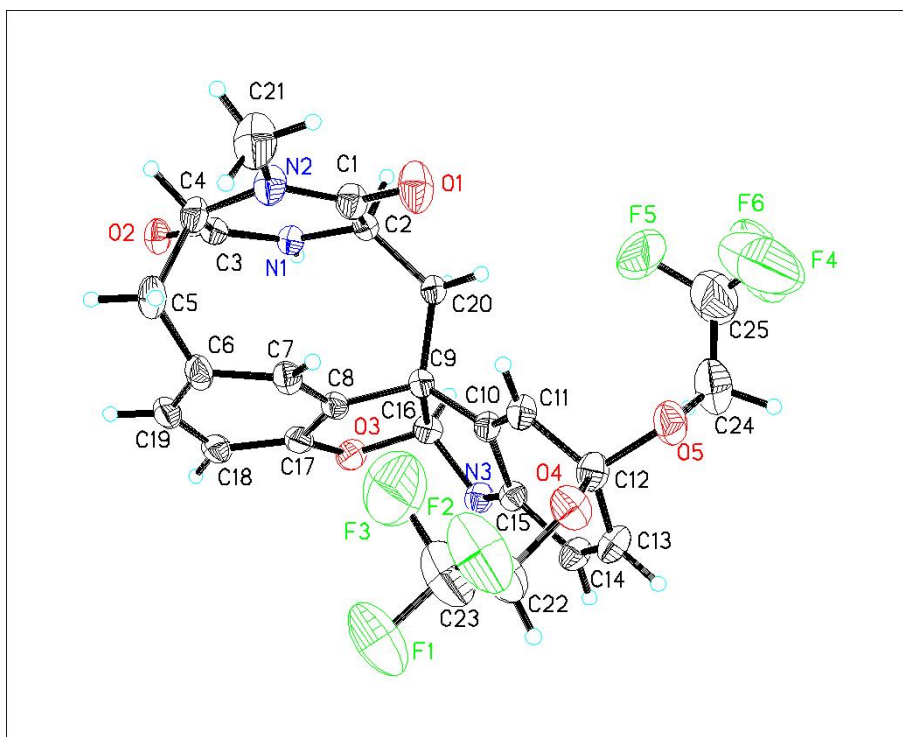
The above crude product was treated with HOAc (1.5 mL) and Ac<sub>2</sub>O (0.01 mL, 0.106 mmol), and the resulting mixture was stirred at rt for 10 h. The mixture was concentrated *in vacuo*, and the residue was then diluted by EtOAc. The solution was washed with aqueous NaHCO<sub>3</sub>, water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude residue was purified by preparative TLC (EtOAc/MeOH, 50:1) to afford **16** (16 mg, 68 % for two steps) as a white solid. Mp: >270 °C (dec.); [ $\alpha$ ]<sub>D</sub><sup>26</sup> – 251.4 (c 0.725, THF); IR (KBr): 3451, 2964, 2917, 2844, 1673, 1656, 1492, 1391, 1259, 1154, 1077, 1018, 797 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.82 (s, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.39 (s, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 6.99 (s, 1H), 6.97 (d, *J* = 1.8 Hz, 1H), 6.74 – 6.68 (d, *J* = 8.5 Hz, 2H), 4.87 – 4.71 (m, 2H), 4.25 (s, 1H), 4.16 (d, *J* = 6.3 Hz, 1H), 3.40 (d, *J* = 13.9 Hz, 1H), 3.06 (dd, *J* = 14.0, 6.6 Hz, 1H), 2.80 (dd, *J* = 16.2, 5.1 Hz, 1H), 2.50 – 2.43 (m, 1H), 2.38 (s, 3H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  169.64, 168.07, 164.17, 157.14, 153.98, 135.95, 135.82, 131.76, 130.44, 129.98, 124.92, 124.02 (q, *J* = 277 Hz, 1C), 116.20, 113.55, 110.82, 109.49, 105.49, 65.13 (q, *J* = 34 Hz, 1C), 64.73, 57.37, 53.33, 40.64, 37.73, 31.67, 23.36; ESI-MS (*m/z*): 502 (M+H<sup>+</sup>); HRMS (ESI): calc'd for C<sub>25</sub>H<sub>23</sub>N<sub>3</sub>O<sub>5</sub>F<sub>3</sub> (M+H<sup>+</sup>) 502.1576; Found 502.1584.

## 2. X-ray single crystal structures of compounds 1b, 11a and 11b.<sup>1</sup>

### 2-1. XRD structure of 1b

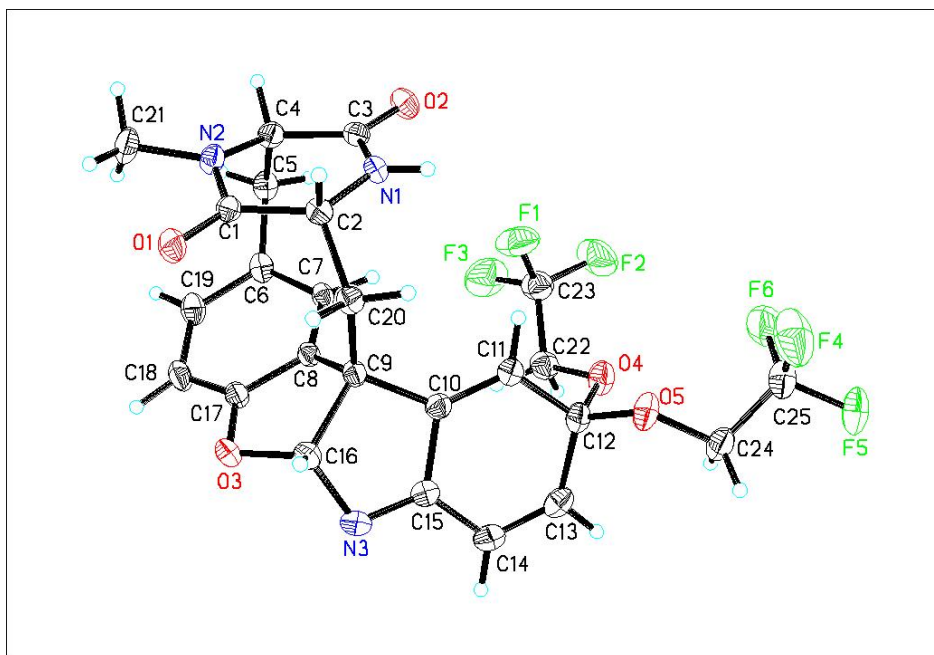


### 2-2. XRD structure of 11a

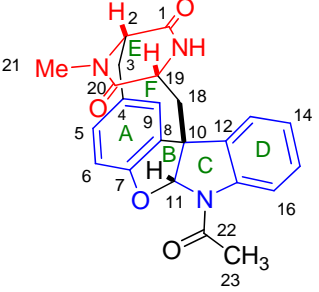


### 2-3. XRD structure of 11b

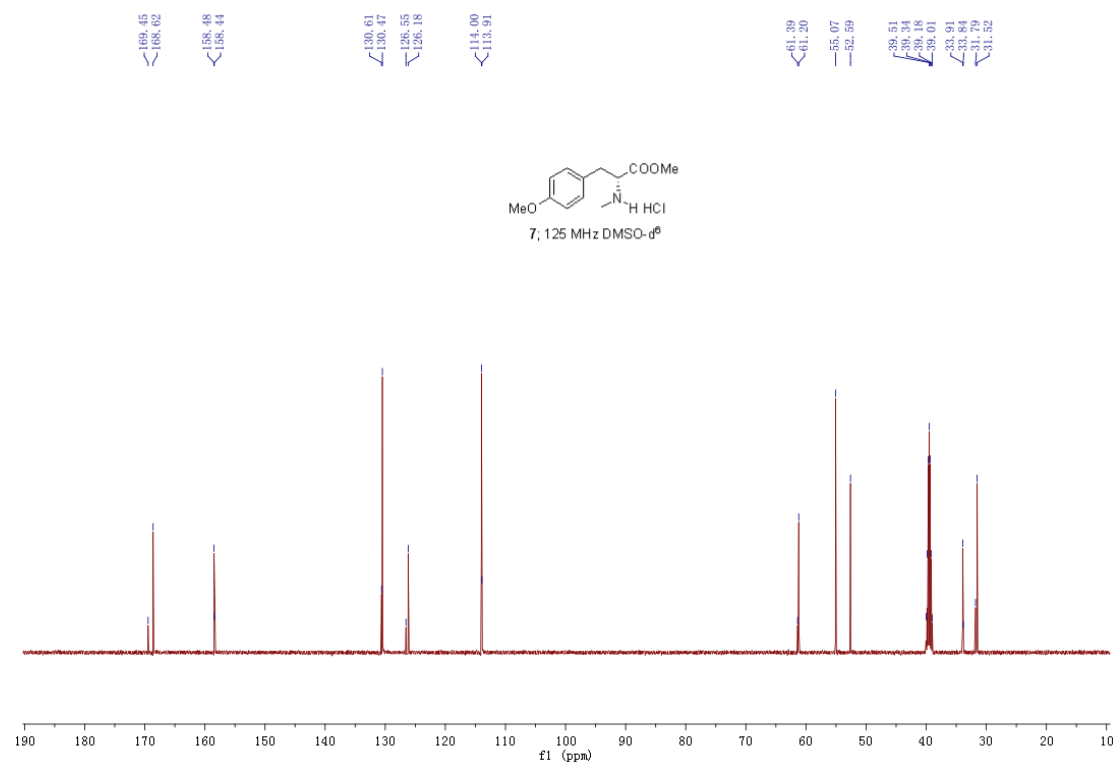
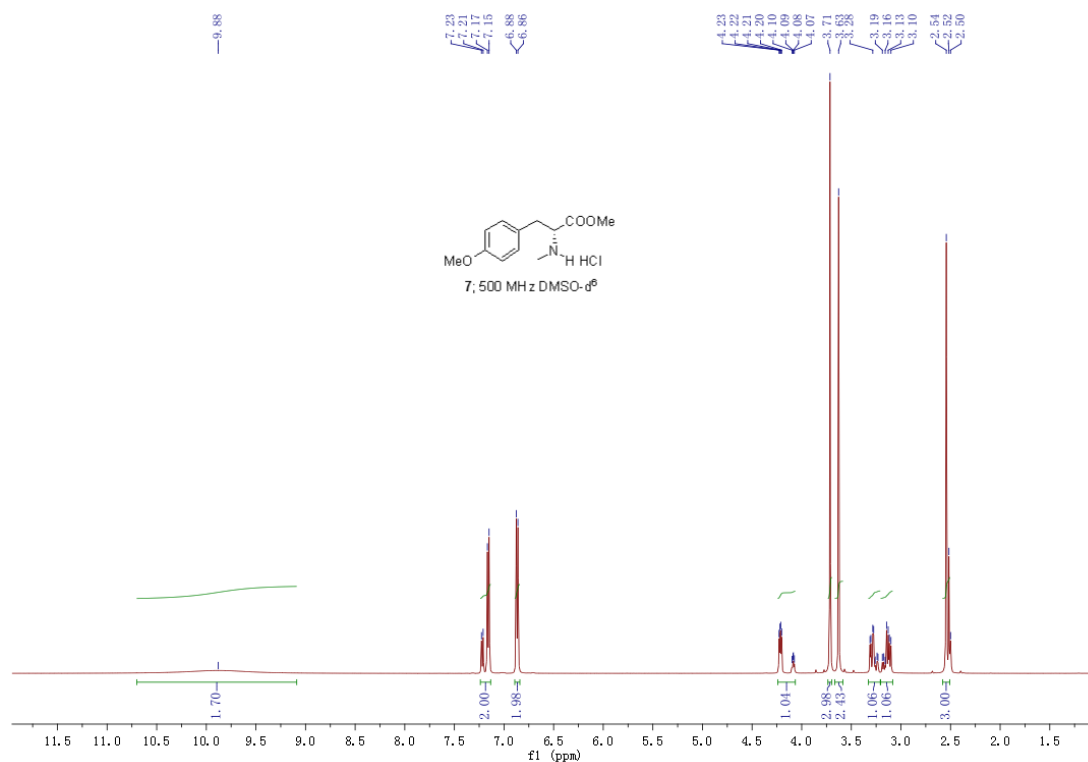
<sup>1</sup> The CIF files were provided as separated files in the Supporting Information.

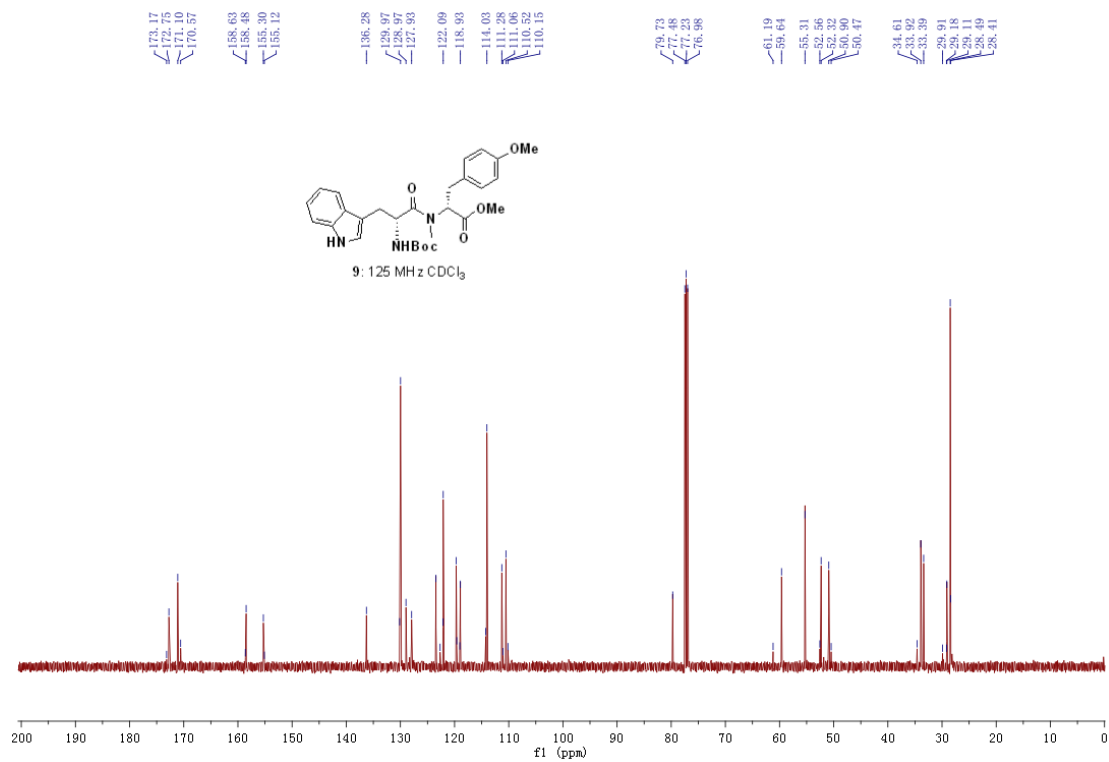
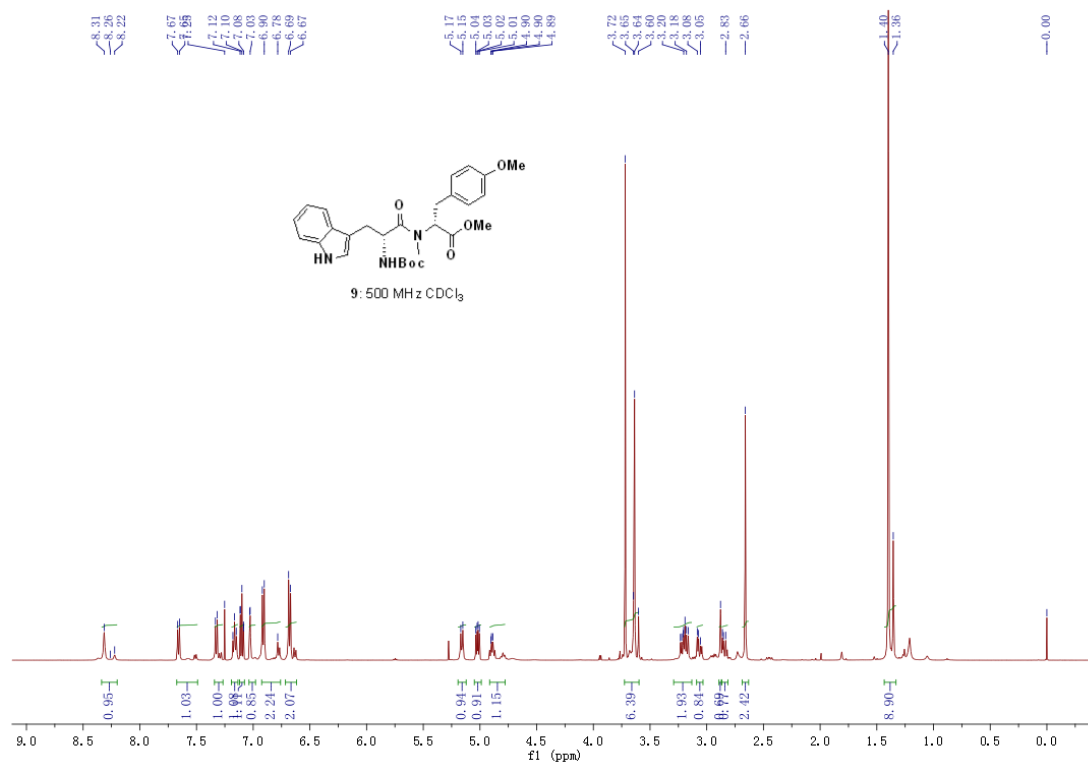


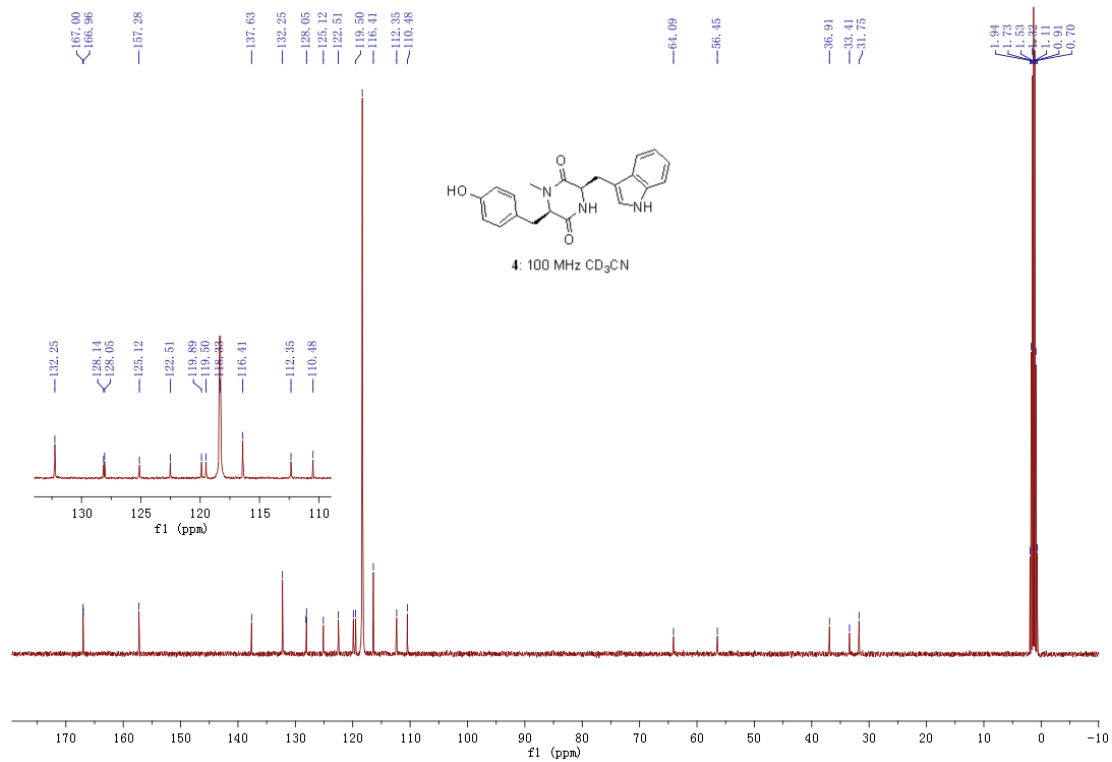
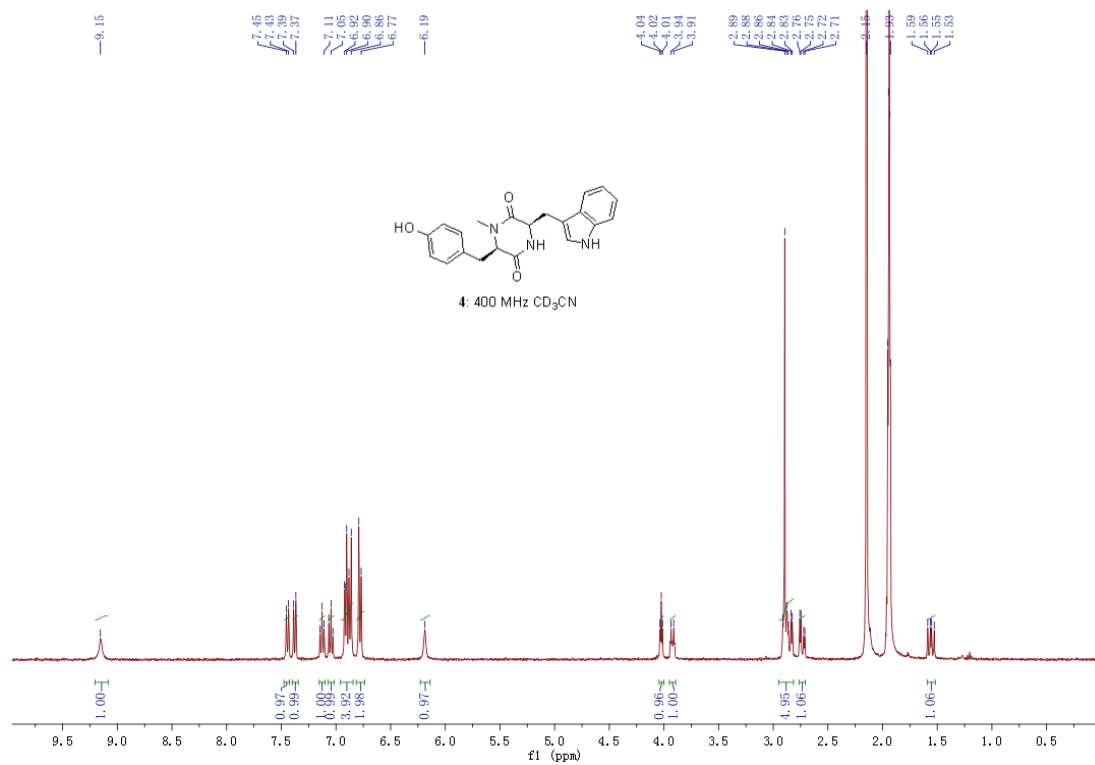
2-4. Table S1. Representative *unusual* structural factors of compound **1b**.

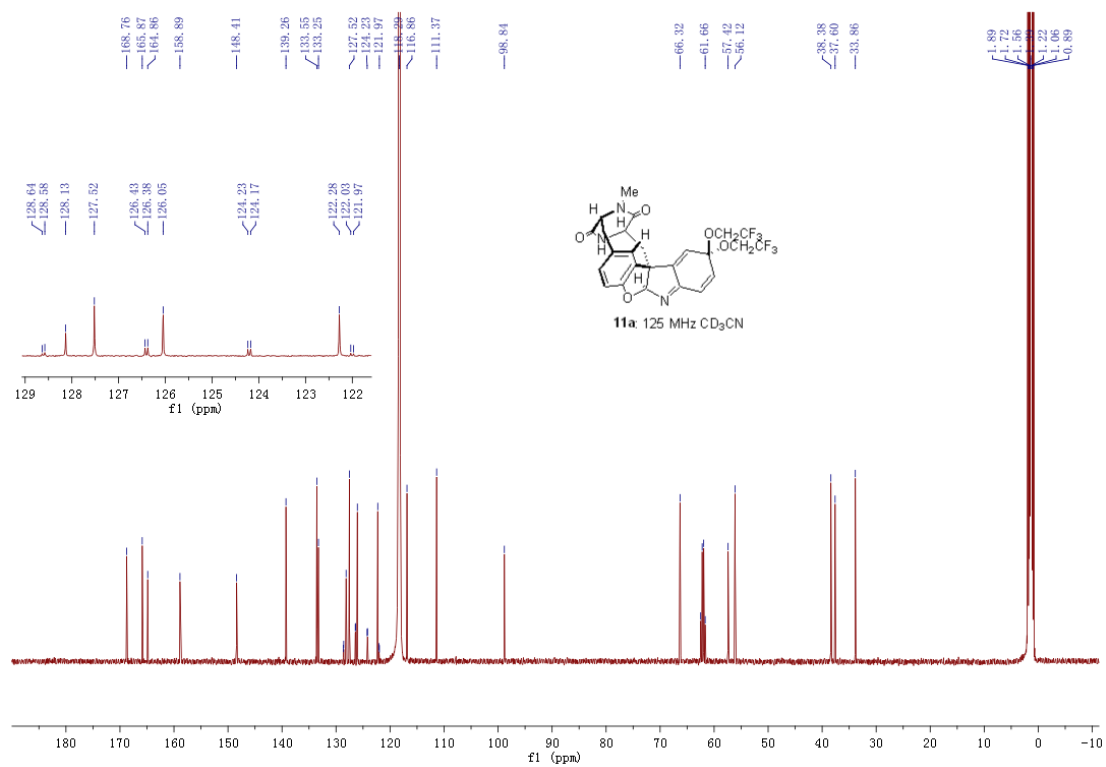
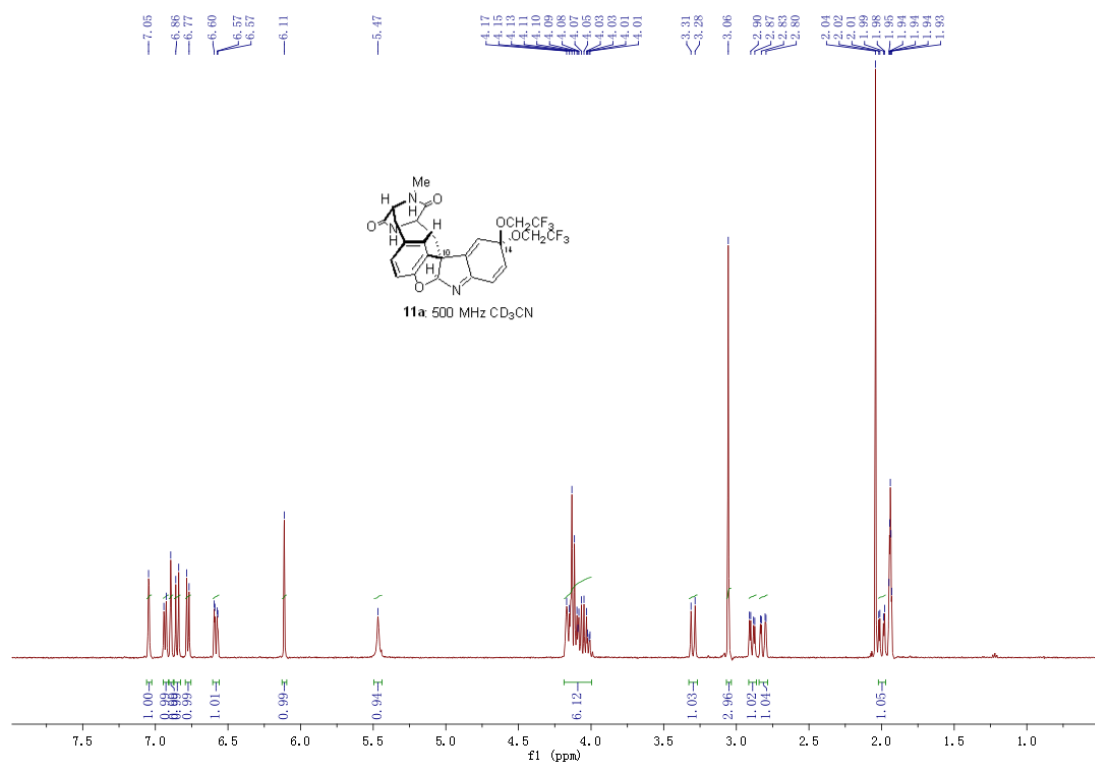
					
Bond angles	Observed	Normal	Dihedral angles	Observed	Normal
$\angle C5-C6-C7$	117.2°	120°	$\angle C3-C4C9-C8$	145.6°	180°
$\angle C8-C7-O$	112.5°	108°	$\angle C3-C4C5-C6$	154.3°	180°
$\angle C12-C10-C11$	102.7°	108°	$\angle C2-N(CH_3)C20-O$	160.1°	180°
$\angle C19-C18-C10$	122.6°	109.5°	$\angle C6-C7C8-C10$	163.6°	180°
$\angle C1-NH-C19$	127.1°	120°	$\angle C21-N(CH_3)C20-C19$	165.0°	180°
$\angle NH-C19-C20$	113.4°	109.5°	$\angle C20-C19NH-C18$	136.5°	120°
			$\angle C8-C10C18-C12$	132.5°	120°

### 3. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of new compounds

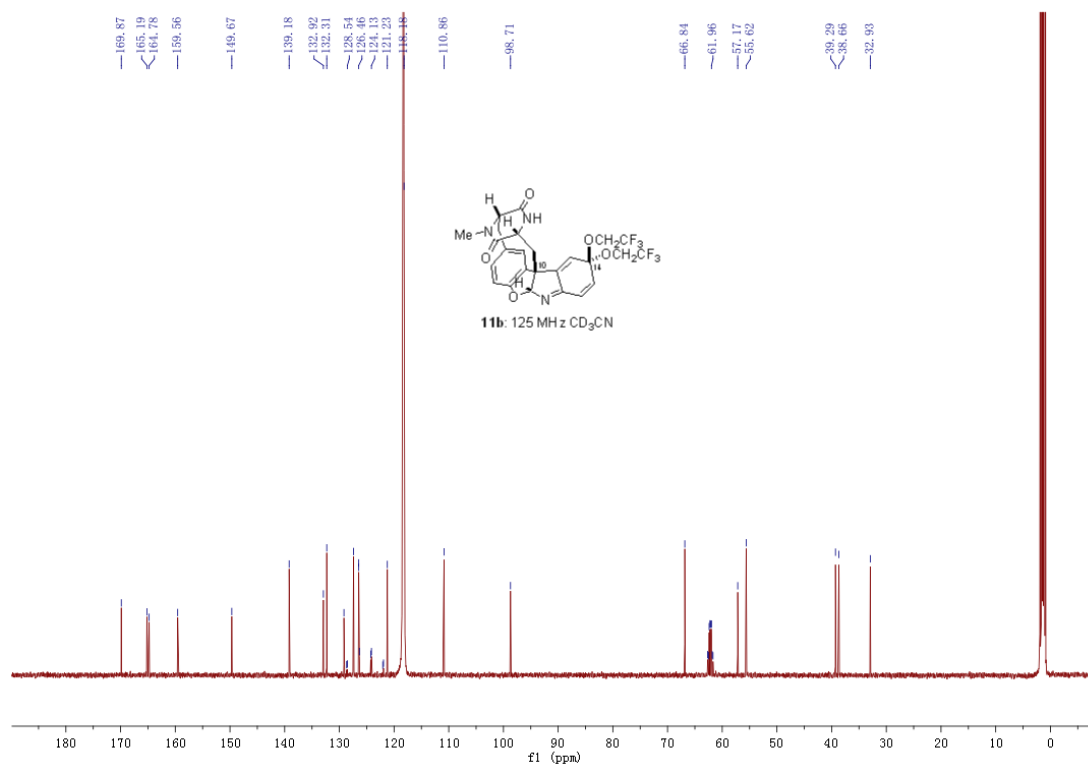
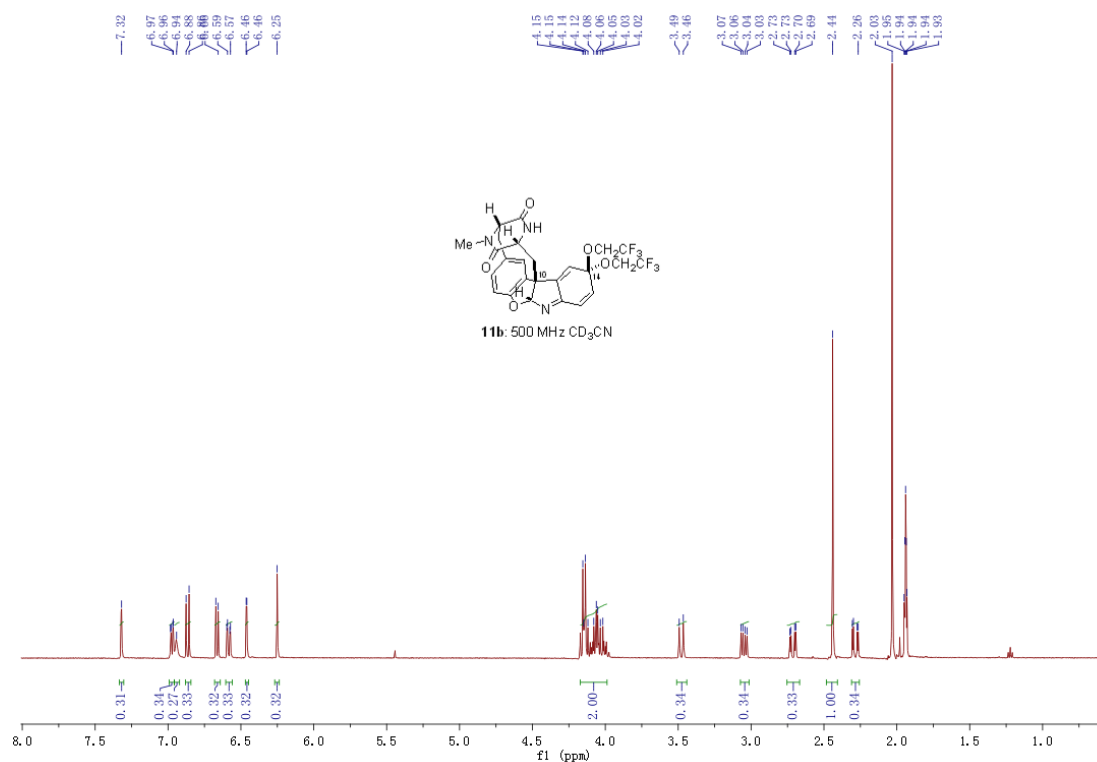


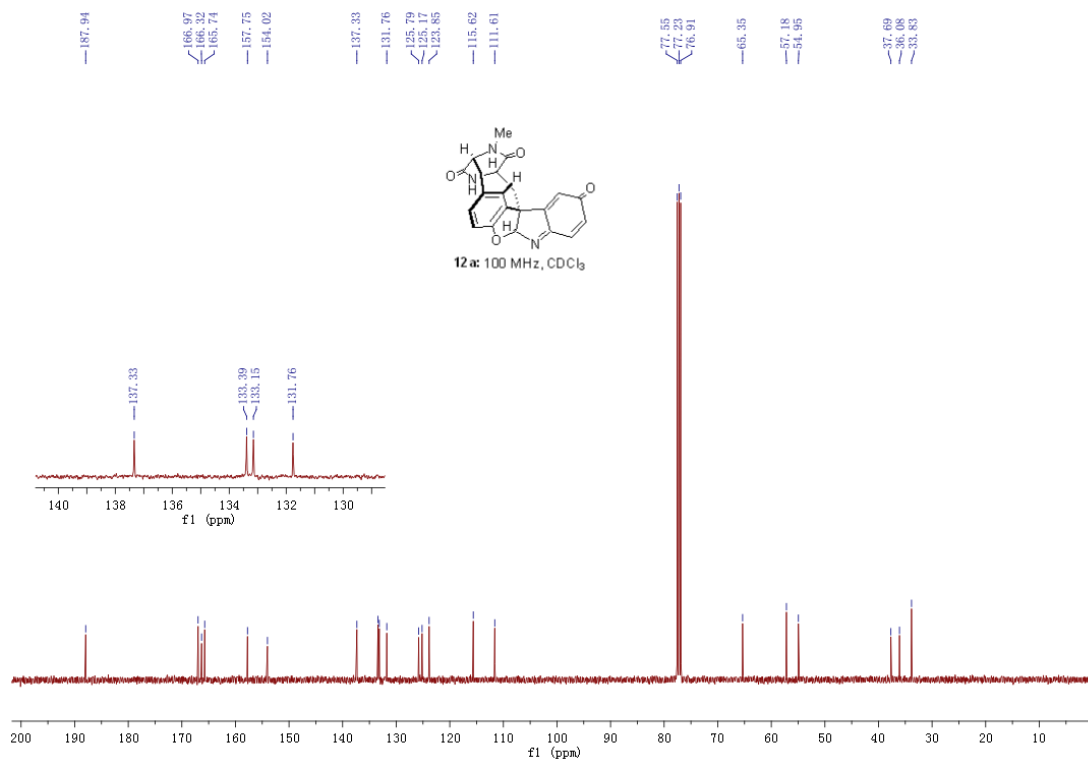
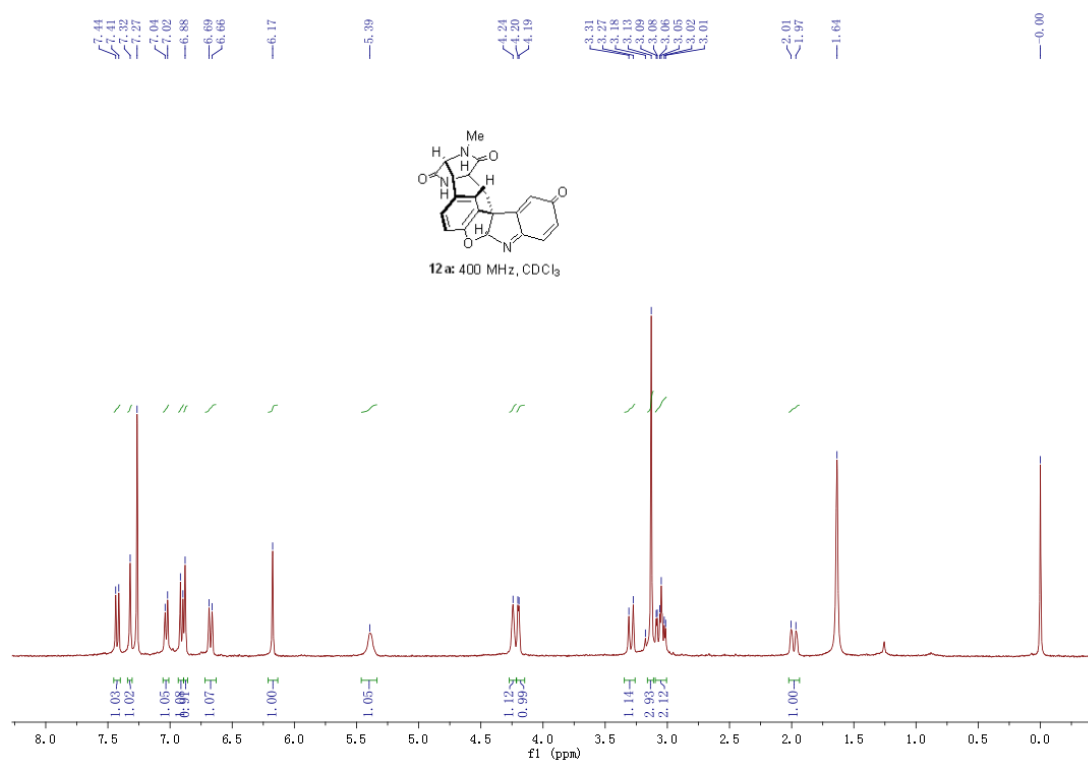


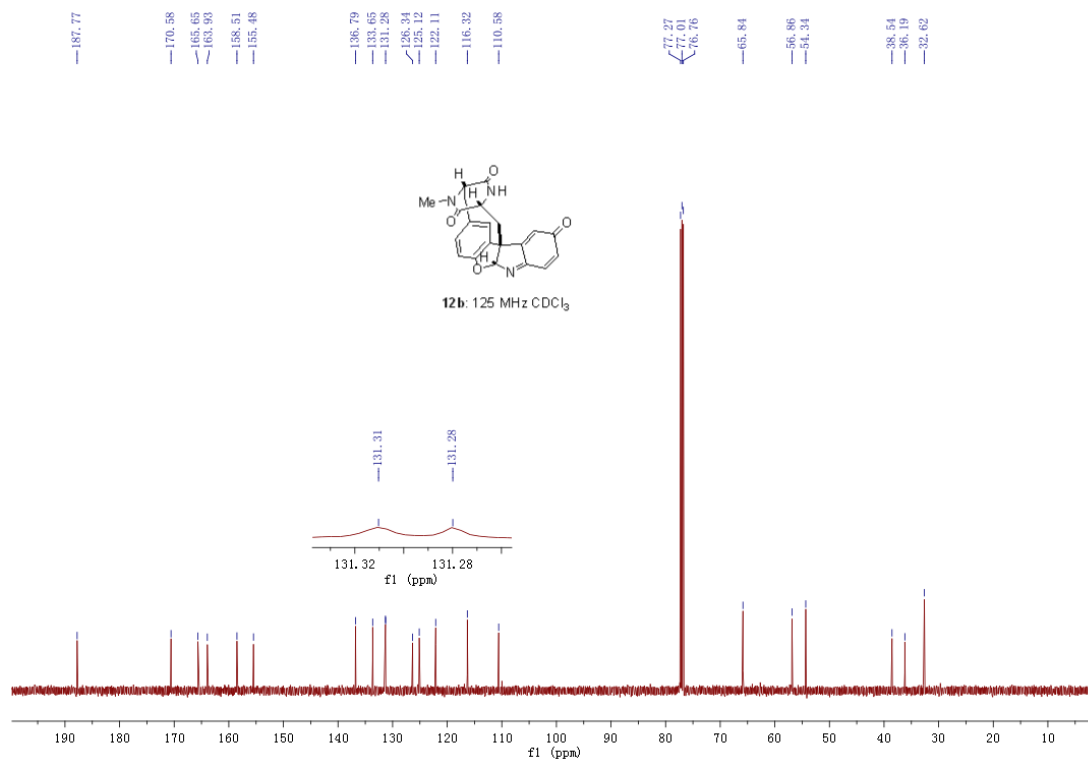
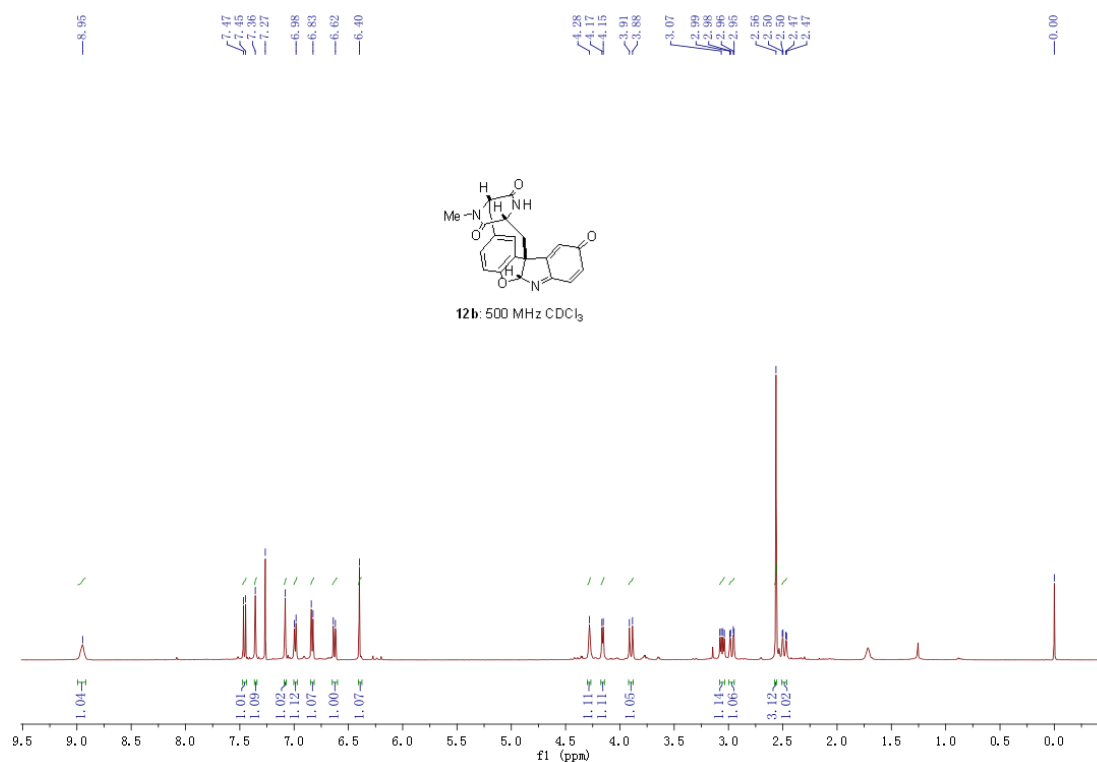


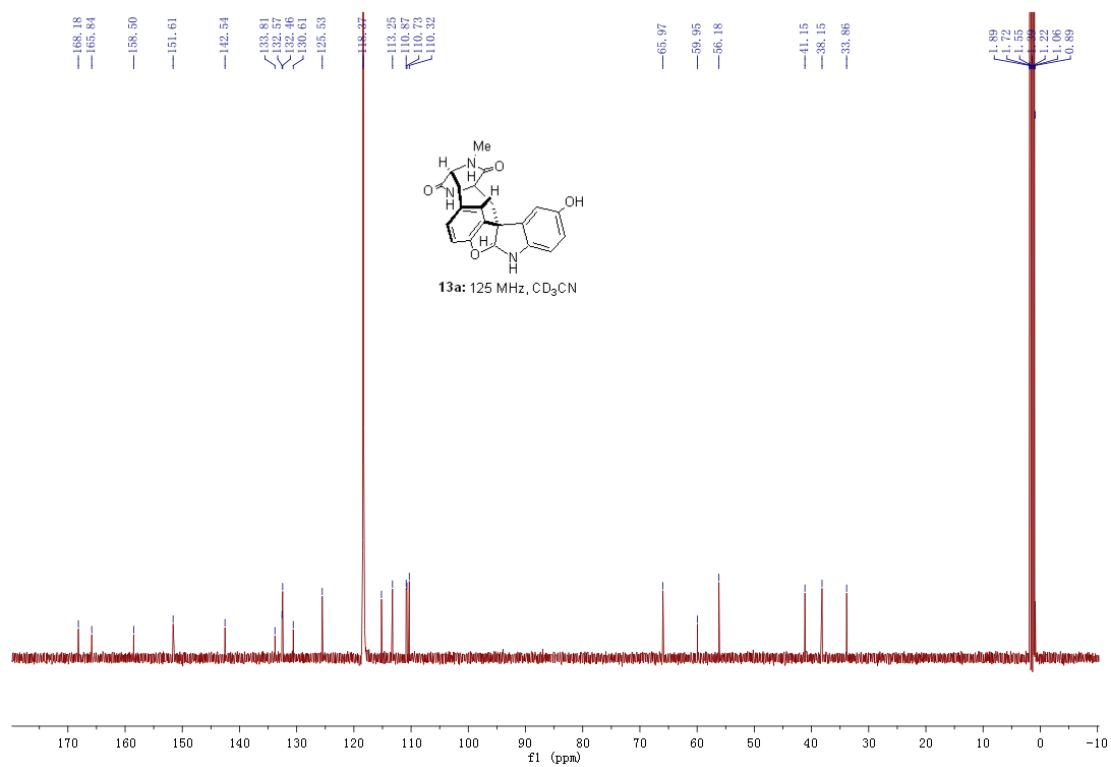
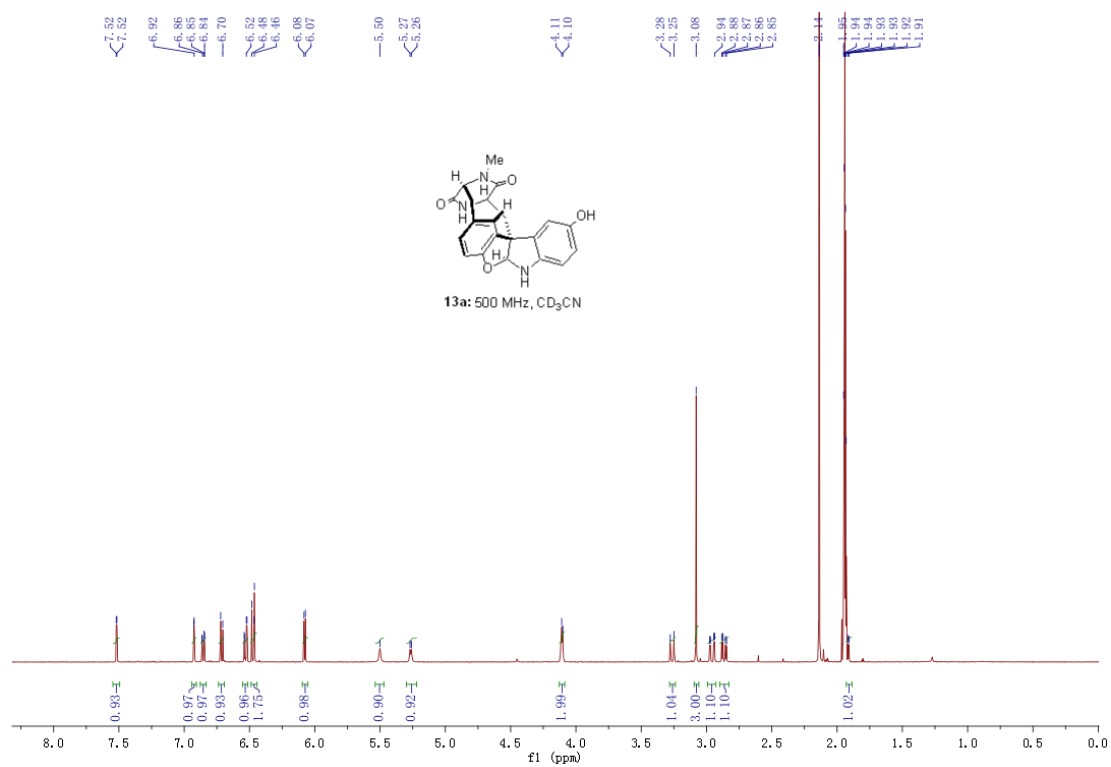


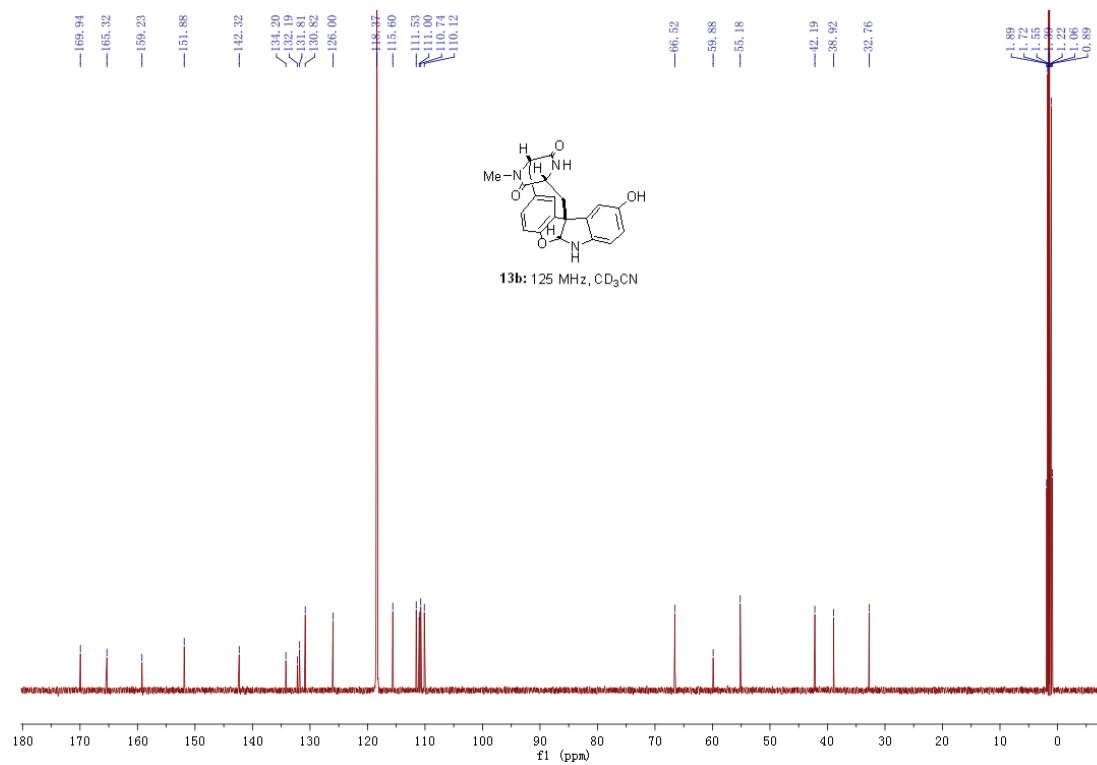
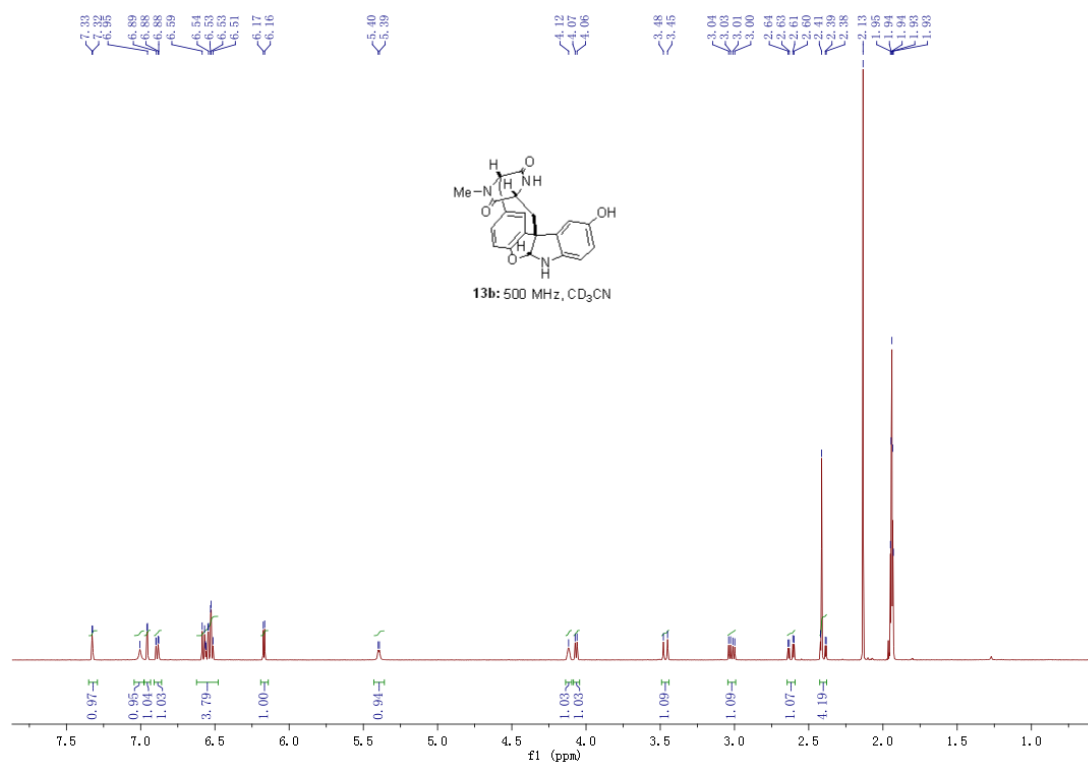


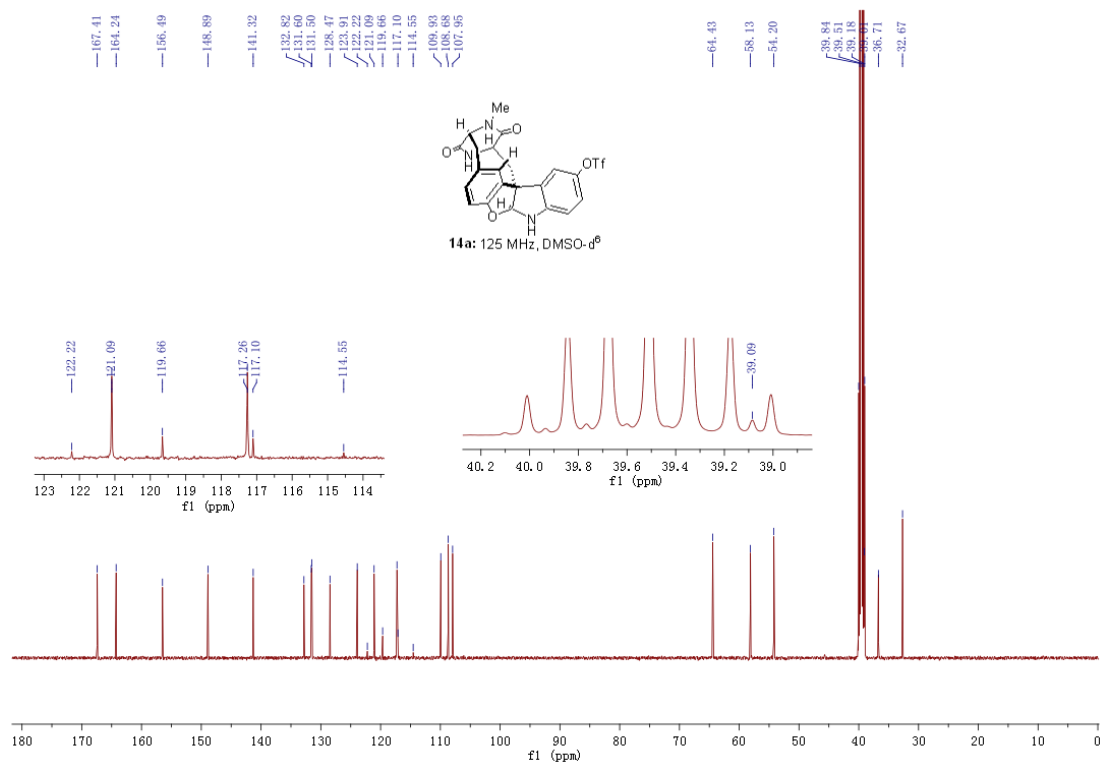
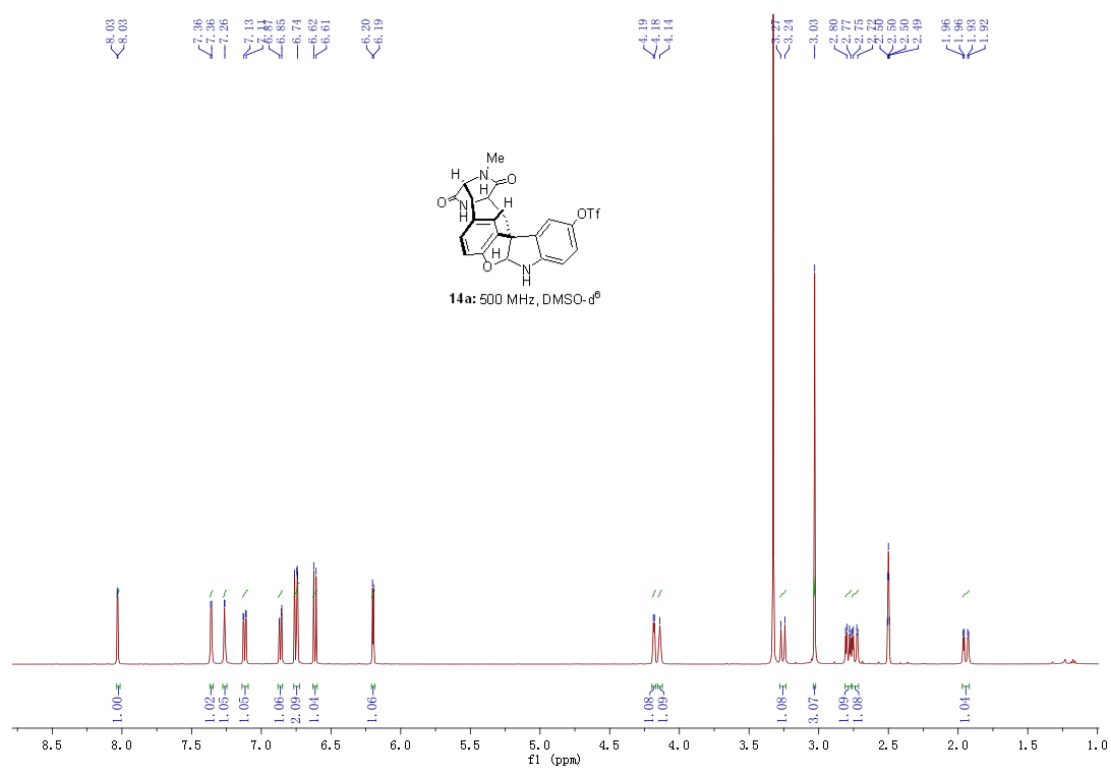


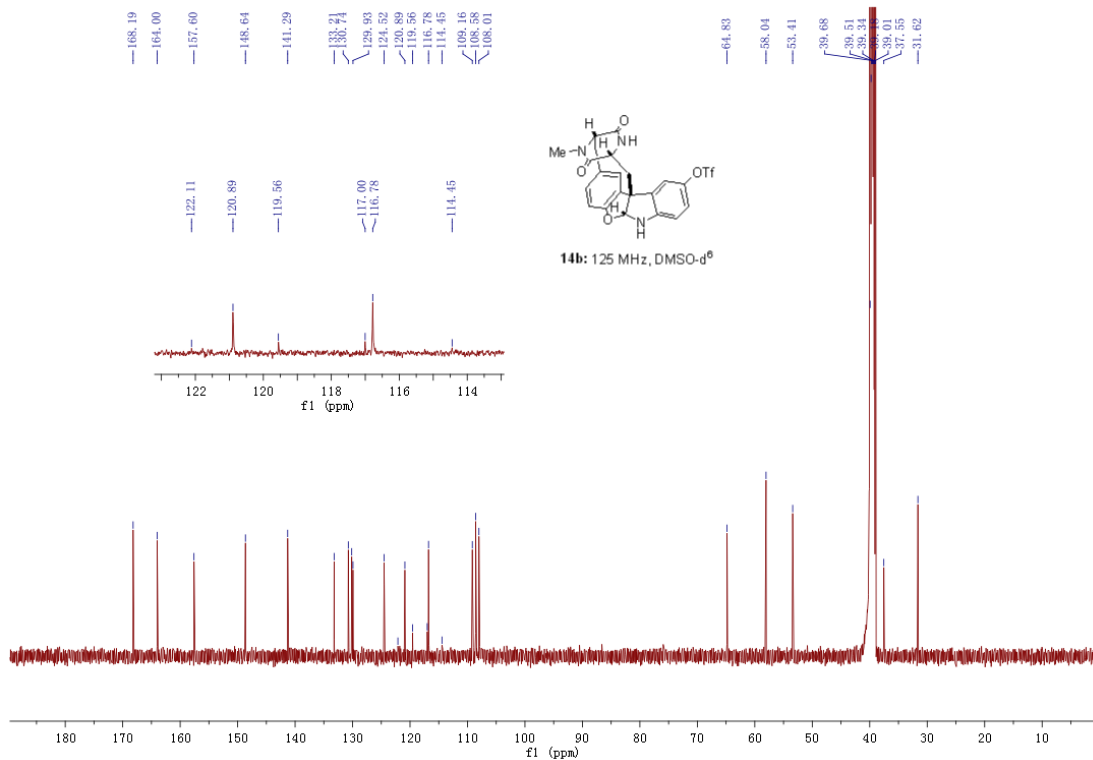
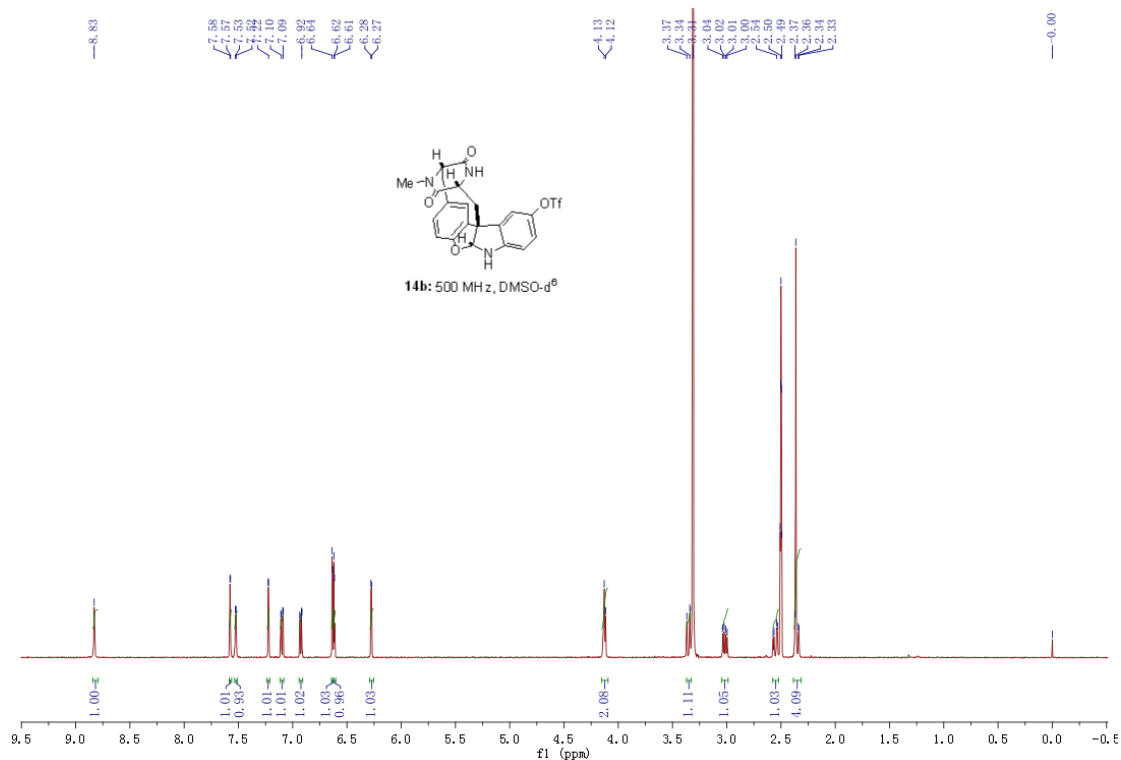


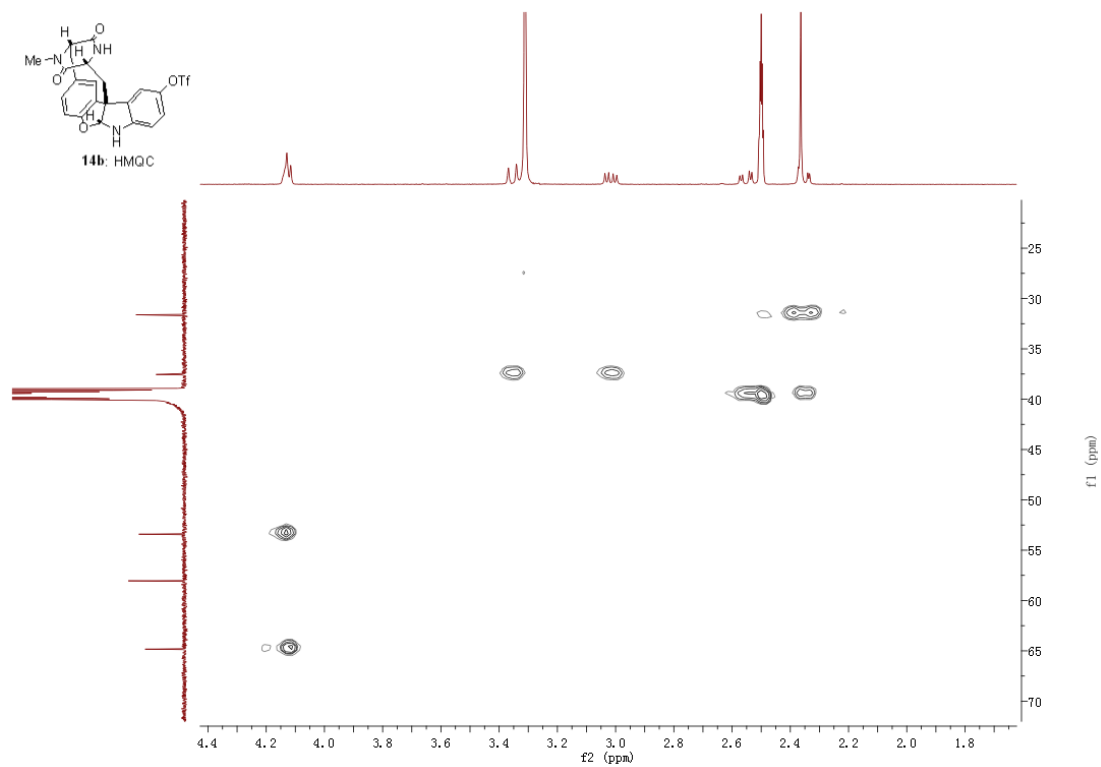
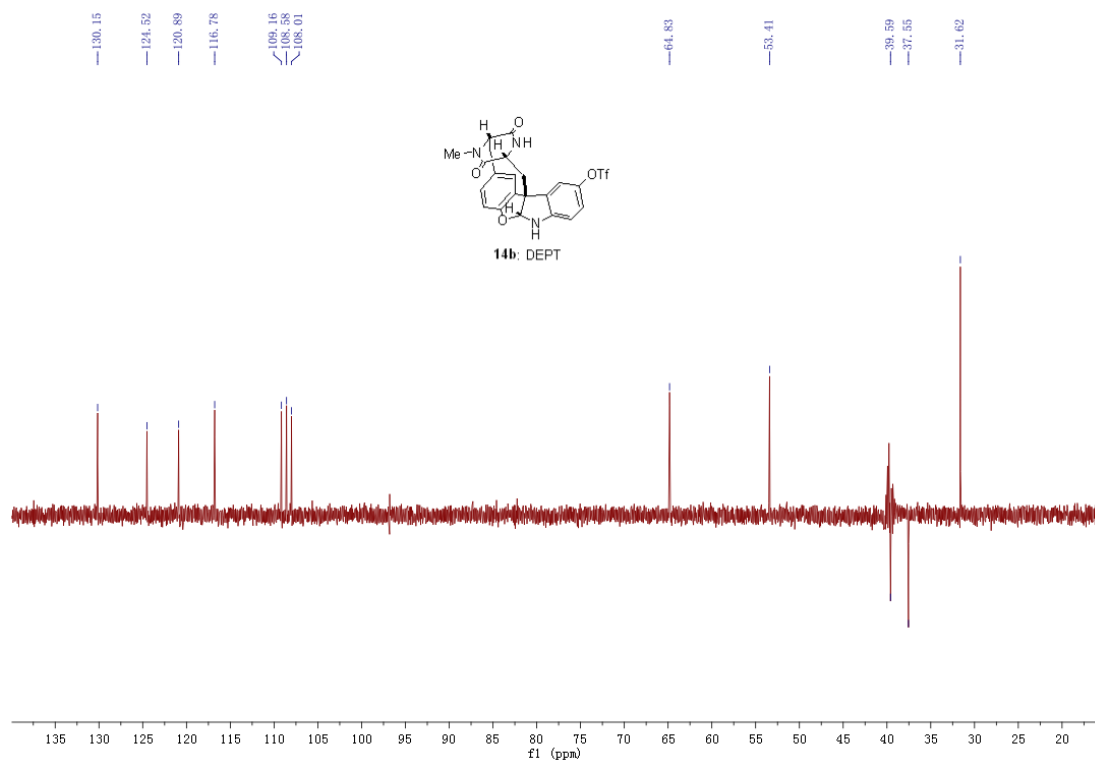




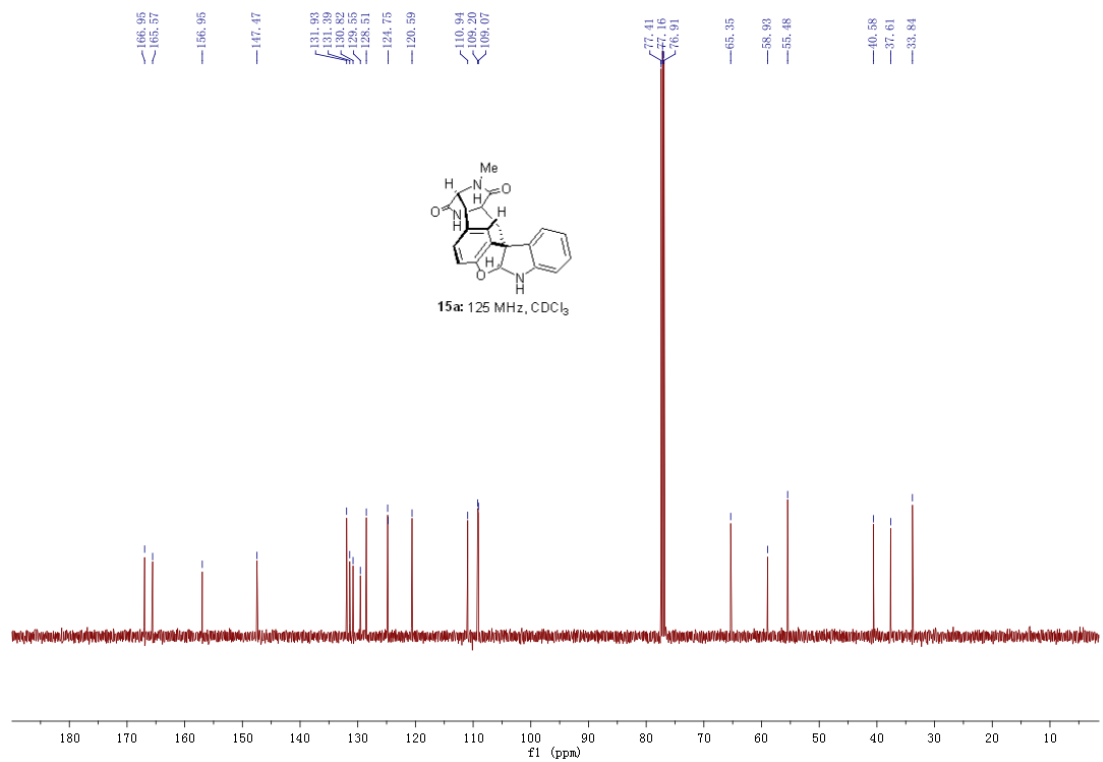
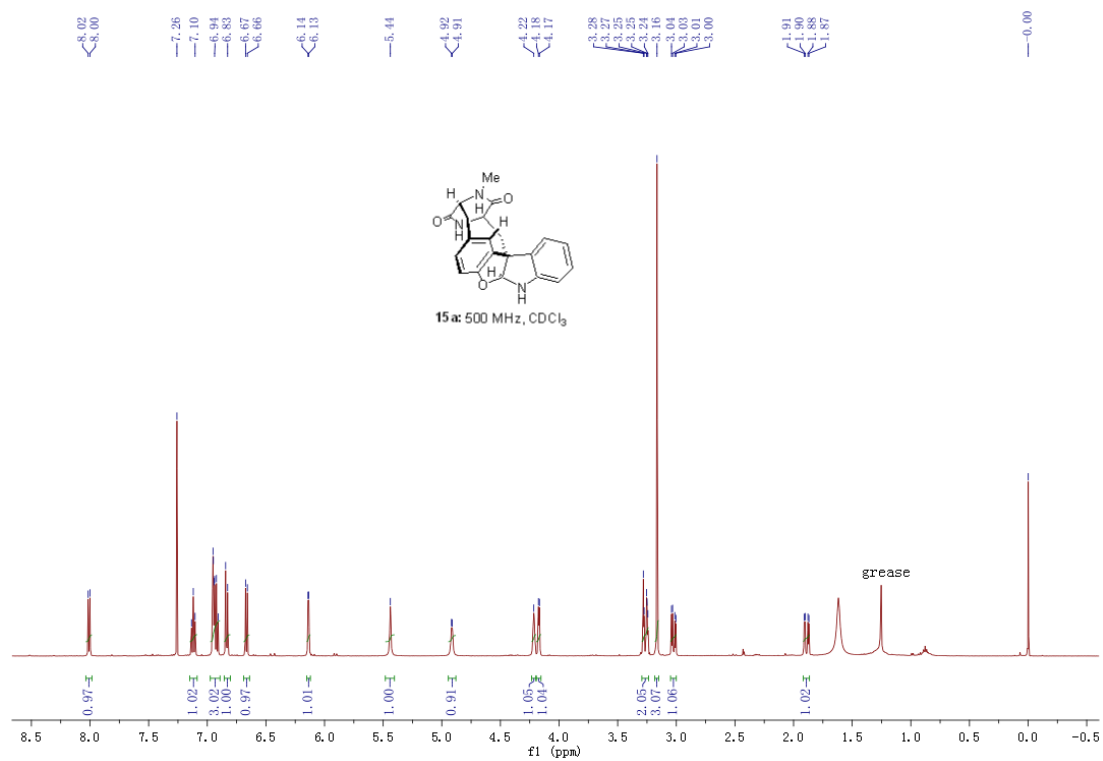


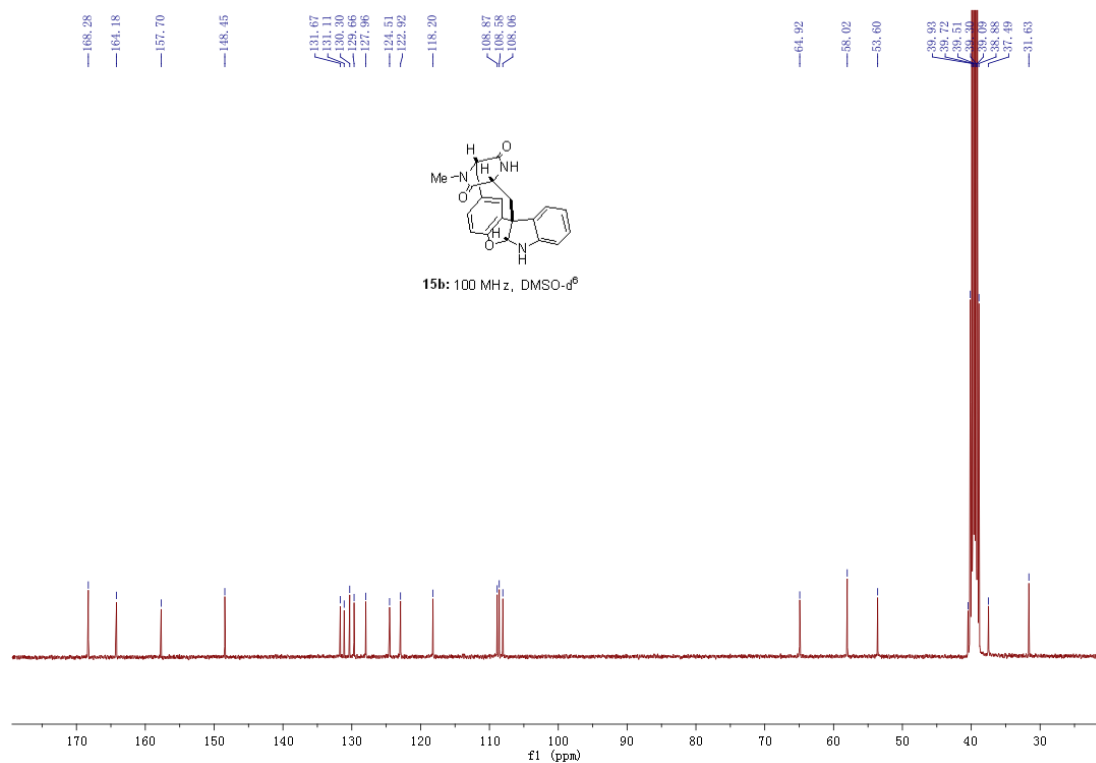
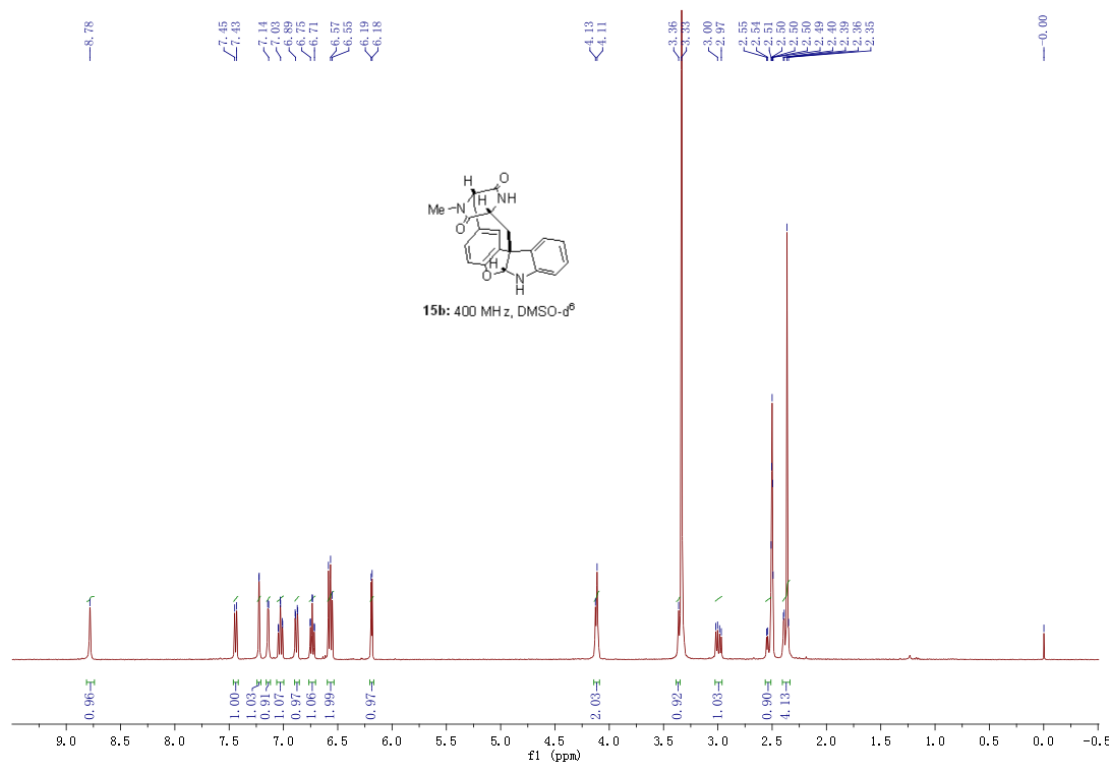


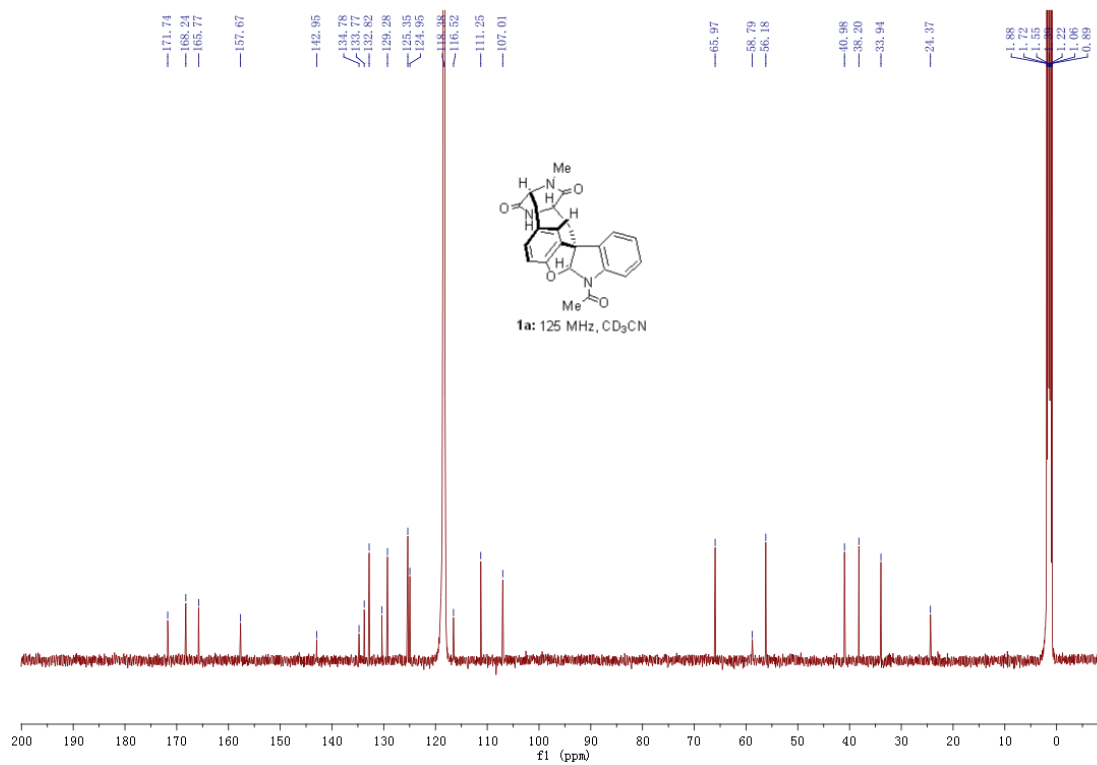
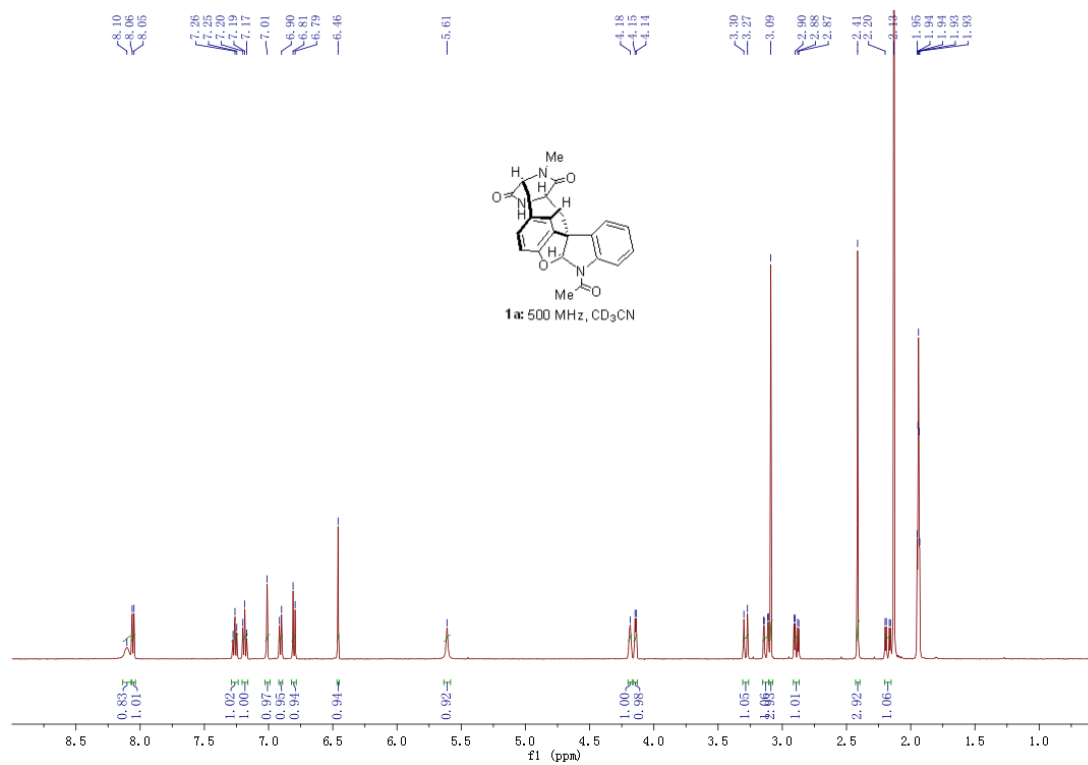


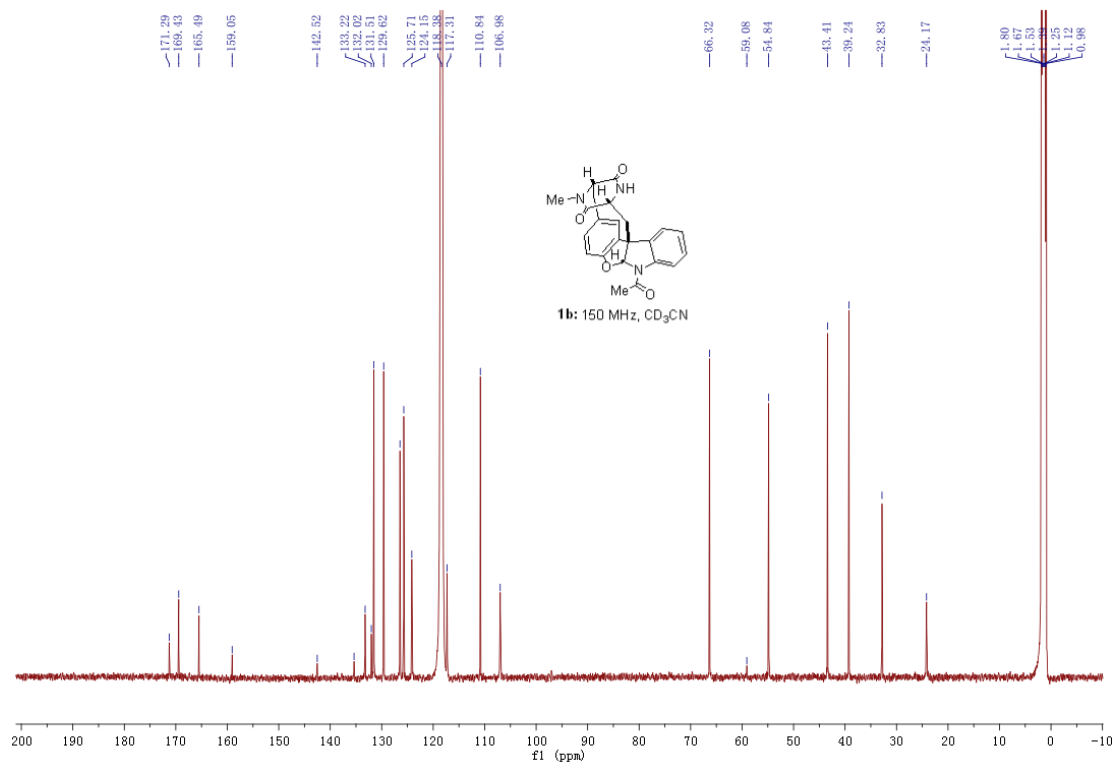
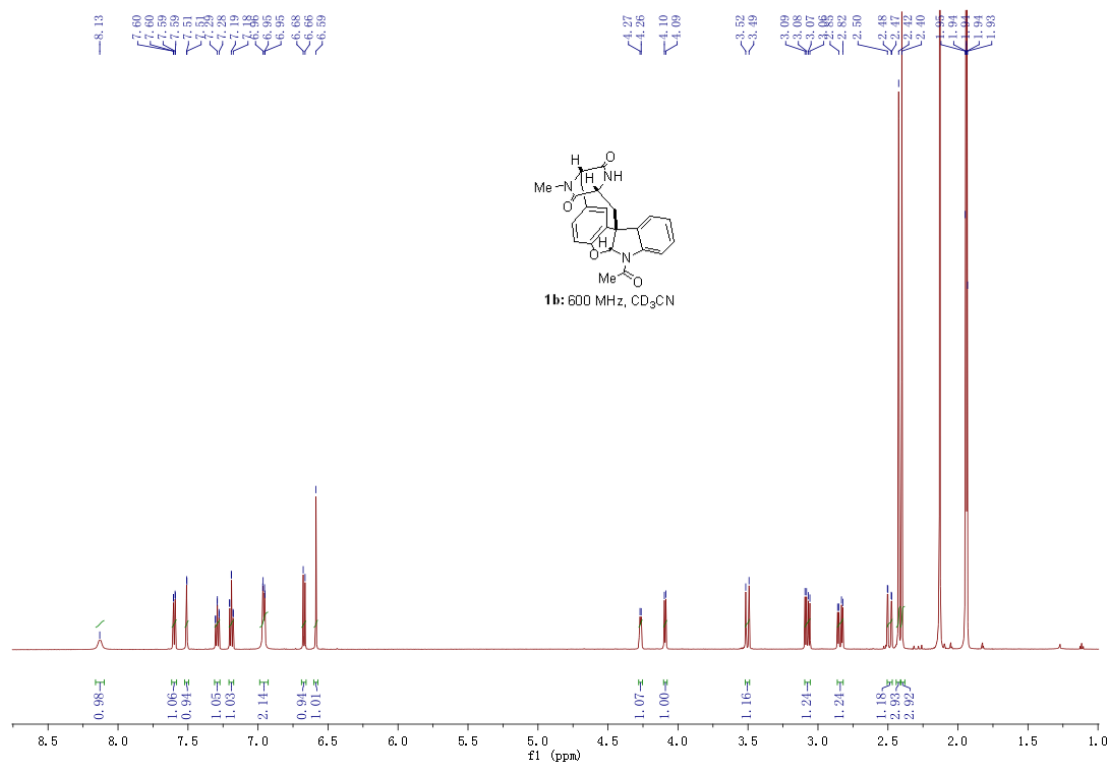


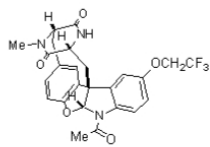
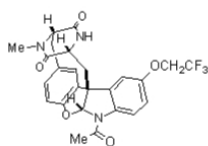




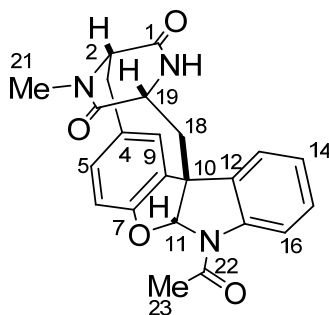








#### 4. NMR data comparison of synthetic **1b** with natural azonazine<sup>2</sup>



No.	$\delta_{\text{H}} (J)$		$\delta_{\text{C}} (J)$	
	Natural	Synthetic	Natural	Synthetic
1			169.49	169.43
2	4.09 d (7.2)	4.09 d (6.5)	66.26	66.32
3	a 3.08 dd (14.4, 7.2) b 3.49 d (14.4)	a 3.08 dd (14.2, 6.9) b 3.50 d (14.2)	39.21	39.24
4			133.20	133.22
5	6.95 dd (7.8, 1.2)	6.96 dd (7.8, 1.7)	131.51	131.51
6	6.67 d (8.4)	6.67 d (8.1)	110.83	110.84
7			158.99	159.05
8			131.98	132.02
9	7.50 s	7.51 d (1.6)	126.42	126.46
10			59.06	59.08
11	6.58 s	6.59 s	106.95	106.98
12			135.34	135.37
13	7.59 d (7.2)	7.60 dd (7.5, 0.8)	124.13	124.15
14	7.19 t (7.8)	7.19 td (7.5, 1.1)	125.72	125.71
15	7.29 t (7.8)	7.29 td (7.8, 1.3)	129.61	129.62
16	8.13 brs (w1/2 $\approx$ 7.8)	8.13 brs	117.29	117.31
17			142.48	142.52
18	a 2.49 dd (16.8, 1.8) b 2.84 dd (16.8, 5.4)	a 2.49 dd (16.5, 2.2 ) b 2.84 dd (16.5, 5.8)	43.35	43.41
19	4.26 d (5.4)	4.27 d (5.1)	54.80	54.84
20			165.51	165.49
21	2.40 s	2.40 s	32.83	32.83
22			171.34	171.29
23	2.42 s	2.42 s	24.16	24.17
NH	7.04 brs	6.96 br (overlapped with <b>H5</b> )		

<sup>2</sup> Wu, Q. X.; Crews, M. S.; Draskovic, M.; Sohn, J.; Johnson, T. A.; Tenney, K.; Valeriote, F. A.; Yao, X. J.; Bjeldanes, L. F.; Crews, P. *Org. Lett.* **2010**, *12*, 4458; and its Supporting Information.