Supplementary Information (SI) for Organic Chemistry Frontiers.

Total synthesis of (-)-rhynchine A, (+)-rhynchine C and (+)-rhynchine E

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Supporting Information Available

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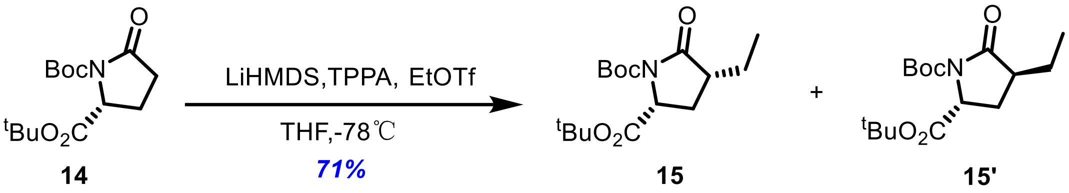
I) Experimental Procedures and Spectroscopic Data of Compounds

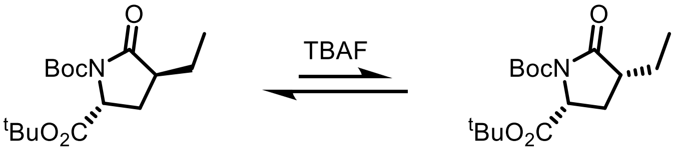
General Procedures: All solvents and reagents employed were obtained from commercial sources and without further purification. Reactions that required heating were operated on a magnetic stirrer with an oil bath. Solvent degassing was conducted by bubbling with a stream of argon for 15-30 min. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (0.4-0.5 mm), using UV light as visualizing agent and an ethanolic solution of sodium phosphomolybdate as developing agents. All the ^{1}H NMR and ^{13}C NMR spectra data were obtained on Bruker AVANC Ⅲ 600M spectrometer (Bruker Instruments, Inc.). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, td = triplet of doublets, tt = triplet of triplets, tdd = triplet of doublet of doublets, m = multiplet. Optical rotation data were obtained on Shanghai Yice WZZ-3A Automatic Polarimeter. Melting points (m.p.) were acquired on a Buchi B–540 melting point apparatus. High resolution mass spectra (HRMS) were perfomed on Agilent 6546 LC/Q-TOF.

Preparation of 15 and 15':



To a stirred solution of **14** (40.00 g, 140.35 mmol, 1.0 equiv) in THF (400 mL) at -78 °C was added LiHMDS (168.40 mL, 1.0 M in THF, 1.2 equiv). The resulting mixture was stirred at -78 °C for 1 h before it was added TPPA (45.75 g, 140.35 mmol, 1.0 equiv) and subsequently the EtOTf (20.00 mL, 154.39 mmol, 1.1 equiv). The reaction was stirred at -78 °C for 2 h before it was added NH_4Cl (200 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with brine (200 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 15:1) afforded **15** (20.65 g, 47%) as a colorless oil, along with **15'** (10.54 g, 24%) as a white soild. **15**: R_f = 0.30 (silica gel, PE/EtOAc = 4:1). $[\alpha]_D^{25}$ = +29.22 (c = 0.3, $CHCl_3$). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 4.37 (dd, *J* = 8.8, 6.1 Hz, 1H), 2.60-2.28 (m, 2H), 2.02-1.76 (m, 1H), 1.65 (dd, *J* = 12.5, 6.4 Hz, 1H), 1.50 (s, 9H), 1.48-1.43 (m, 1H), 1.47 (s, 9H), 0.96 ppm (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 175.4, 170.7, 149.7, 83.4, 82.2, 58.2, 44.2, 28.1 (3C)， 28.0 (3C), 27.2, 24.4, 11.6 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{27}NNaO_5^+$ 336.1781, found 336.1783.

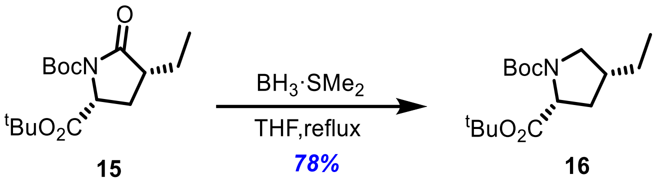
15': m.p. 64-66 °C (PE/EtOAc); R_f = 0.30 (silica gel, PE/EtOAc = 4:1). $[\alpha]_D^{25}$ = +26.13 (c = 0.8, $CHCl_3$). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 4.42 (dd, *J* = 9.6, 1.6 Hz, 1H), 2.57-2.48 (m, 1H), 2.16 (ddd, *J* = 13.2, 8.7, 1.6 Hz, 1H), 1.98-1.85 (m, 2H), 1.50 (s, 9H), 1.47 (s, 9H), 1.45-1.36 (m, 1H), 0.95 ppm (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 175.3, 170.6, 149.7, 83.3, 82.3, 57.9, 43.1, 28.2, 28.1(6C), 23.6, 11.3 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{27}NNaO_5^+$ 336.1781, found 336.1786.



15' **15**

To a stirred solution of **15'** (6.00 g, 19.17 mmol, 1.0 equiv) in THF (80 mL) at room temperature was added TBAF (20.32 mL, 1.0 M in THF, 1.06 equiv) under an argon atmosphere. The resulting mixture was stirred under reflux for 1.5 h before it was cooled to room temperature and added NH_4Cl (100 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 15:1) afforded **15** (1.80 g, 30%) as a colorless oil, along with **15'** (2.70 g, 45%) as a white soild.

Preparation of 16:

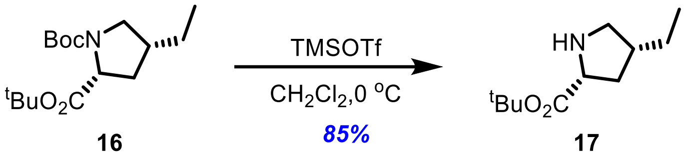


15 **16**

To a stirred solution of **15** (47.50 g, 151.75 mmol, 1.0 equiv) in THF (500 mL) at room temperature was added $BH_3{\cdot}SMe_2$ (151.75 mL, 2.0 M in THF, 2.0 equiv) under an argon atmosphere. The resulting mixture was stirred under reflux for 7 h before it was cooled to room temperature and added water (200 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 17:1) afforded **16** (35.39 g, 78%) as a colorless oil. **16**: R_f = 0.60 (silica gel, PE/EtOAc = 4:1). $[\alpha]_D^{25}$ = +81.57 (c = 0.3,

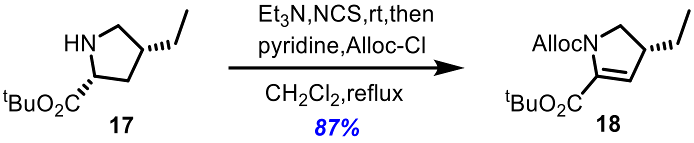
$CHCl_3$). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 4.14-4.03 (m, 1H), 3.81-3.59 (m, 1H), 2.94 (td, *J* = 10.1, 6.7 Hz, 1H), 2.44-2.32 (m, 1H), 2.06-1.94 (m, 1H), 1.51-1.33 (m, 21H), 0.90 ppm (td, *J* = 7.5, 3.4 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 172.5, 154.0, 80.9, 79.8, 60.0, 52.1, 39.7, 37.1, 28.5 (3C), 28.2 (3C), 26.0, 12.7 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{29}NNaO_4^+$ 322.1989 , found 322.1990.

<u>Preparation of 17:</u>



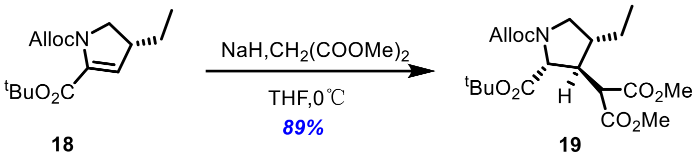
To a stirred solution of **16** (29.69 g, 99.30 mmol, 1.0 equiv) in CH_2Cl_2 (230 mL) at 0 °C was added TMSOTf (9.00 mL, 49.65 mmol, 0.5 equiv). The resulting mixture was stirred at 0 °C for 5 min before it was added $NaHCO_3$ (100 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 1:1) afforded **17** (16.80 g, 85%) as a colorless oil. **17**: R_f = 0.20 (silica gel, PE/EtOAc = 1:3). $[\alpha]_D^{25}$ = +52.25 (c = 0.2, MeOH). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 3.65 (t, *J* = 8.0 Hz, 1H), 3.05 (dd, *J* = 9.8, 7.0 Hz, 1H), 2.64 (t, *J* = 9.1 Hz, 1H), 2.29 (dd, *J* = 12.8, 7.7 Hz, 1H), 2.25 (s, 1H), 2.01 (p, *J* = 7.6 Hz, 1H), 1.45 (s, 9H), 1.39-1.31 (m, 3H), 0.89 ppm (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 175.0, 81.1, 60.6, 52.8, 41.9, 37.0, 28.2 (3C), 26.8, 13.0 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_{21}NNaO_2^+$ 222.1465, found 222.1463.

Preparation of 18:



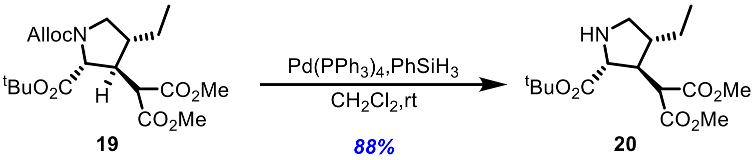
To a stirred solution of **17** (14.12 g, 70.96 mmol, 1.0 equiv) in CH_2Cl_2 (160 mL) at 0 °C were sequentially added Et_3N (24.61 mL, 177.40 mmol, 2.5 equiv) and NCS (11.32 g, 85.15 mmol, 1.2 eq). The resulting mixture was stirred at room temperature for 1.5h before it was added pyridine (12.94 mL, 160.21 mmol, 2.3 equiv) and subsequently the AllocCl (16.95 mL, 160.21 mmol, 2.3 equiv) at -20℃. The reaction was stirred under reflux for 2 h before it was cooled to room temperature and added NH_4Cl (200 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 15:1) afforded **18** (17.35 g, 87%) as a colorless oil. **18**: R_f = 0.60 (silica gel, PE/EtOAc = 6:1). $[\alpha]_D^{25}$ = -80.13 (c = 0.23, $CHCl_3$). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.09-5.83 (m, 1H), 5.71 (d, *J* = 2.8 Hz, 1H), 5.46-5.23 (m, 1H), 5.20 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.78-4.40 (m, 2H), 4.04 (dd, *J* = 11.3, 9.8 Hz, 1H), 3.57 (dd, *J* = 11.3, 6.7 Hz, 1H), 2.98-2.67 (m, 1H), 1.50 (s, 9H), 1.49-1.39 (m, 2H), 0.91 ppm (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 161.2, 153.5, 137.3, 132.7, 122.9, 118.0, 82.1, 66.5, 54.5, 43.1, 28.1, 27.3 (3C), 11.5 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{23}NNaO_4^+$ 304.1519 , found 304.1516.

Preparation of 19:



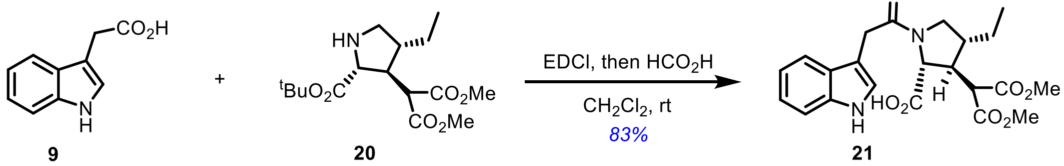
To a stirred solution of NaH (3.20 g, 60% in mineral oil, 80.04 mmol, 1.5 equiv) in THF (160 mL) at 0°C was added $CH_2(COOMe)_2$ (9.12 mL, 80.04 mmol, 1.5 equiv) in THF (40 mL) under an argon atmosphere. The resulting mixture was stirred at 0°C for 30 min before it was added a solution of **18** (14.99 g, 53.36 mmol, 1.0 equiv) in THF (40 mL). The reaction was stirred at room temperature for 7 h before it was added NH_4Cl (200 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 5:1) afforded **19** (19.61 g, 89%) as a colorless oil. **19**: R_f = 0.40 (silica gel, PE/EtOAc = 3:1). $[\alpha]_D^{25}$ = +10.83 (c = 0.28, $CHCl_3$). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.12-5.61 (m, 1H), 5.28 (ddd, *J* = 19.0, 17.2, 1.8 Hz, 1H), 5.21-5.10 (m, 1H), 4.62-4.49 (m, 2H), 4.19 (dd, *J* = 12.4, 4.6 Hz, 1H), 3.84-3.71 (m, 7H), 3.57 (dd, *J* = 7.1, 3.2 Hz, 1H), 3.19 (dt, *J* = 11.2, 6.1 Hz, 1H), 2.71 (dt, *J* = 6.5, 5.0 Hz, 1H), 2.00 (ddt, *J* = 34.4, 15.2, 6.4 Hz, 1H), 1.58-1.49 (m, 1H), 1.44 (d, *J* = 13.5 Hz, 9H), 1.33 (ddd, *J* = 13.7, 9.3, 7.1 Hz, 1H), 0.88 ppm (q, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 170.9, 168.3, 168.2, 154.3, 132.8, 117.4, 81.8, 66.1, 62.7, 53.8, 52.8 (2C), 51.4, 48.5, 42.6, 28.0 (3C), 26.4, 12.4 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{31}NNaO_8^+$ 436.1942 , found 436.1942.

Preparation of 20:



To a stirred solution of **19** (18.03 g, 43.66 mmol, 1.0 equiv) in CH_2Cl_2 (160 mL) at room temperature were sequentially added $PhSiH_3$ (26.88 mL,218.30 mmol, 5.0 equiv) and $Pd(PPh_3)_4$ (2.52 g, 2.18 mmol, 0.05 equiv). The resulting mixture was stirred at room temperature for 30 min before it was added water (100 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 1:2) afforded **20** (12.64 g, 88%) as a colorless oil. **20**: R_f = 0.40 (silica gel, PE/EtOAc = 1:3). $[\alpha]_D^{25}$ = -9.58 (c = 0.32, $CHCl_3$). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 3.74-3.69 (m, 6H), 3.60-3.53 (m, 2H), 3.04 (dd, *J* = 10.8, 7.0 Hz, 1H), 2.72 (dd, *J* = 10.8, 6.0 Hz, 1H), 2.51 (dt, *J* = 7.6, 5.0 Hz, 1H), 2.26 (s, 1H), 1.86-1.77 (m, 1H), 1.51-1.41 (m, 10H), 1.29-1.20 (m, 1H), 0.84 ppm (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 173.4, 168.9, 168.8, 81.5, 64.5, 54.8, 52.6, 52.5, 51.9, 48.6, 45.5, 28.1 (3C), 27.0, 12.5 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{27}NNaO_6^+$ 352.1731 , found 352.1736.

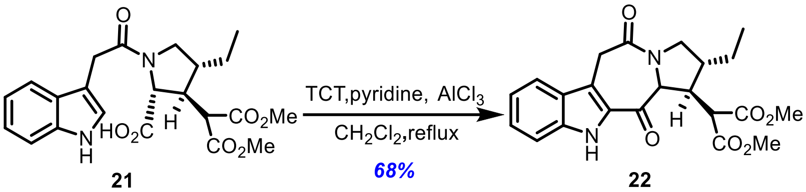
Preparation of 21:



To a stirred solution of **20** (10.97 g, 33.34 mmol, 1.0 equiv) in CH_2Cl_2 (240mL) at room temperature was added **9** (5.83 g, 33.34 mmol, 1.0 equiv) and 1-(3-

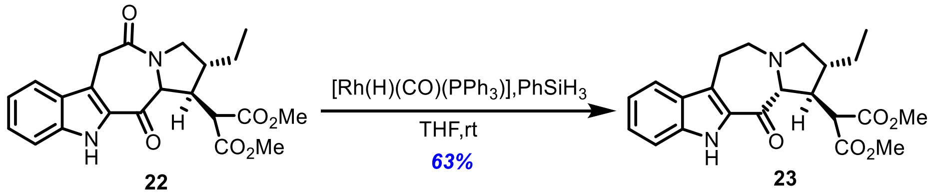
Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (9.55 g, 50.01 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 1 h before it was added Formic acid (75 mL). The reaction was stirred at room temperature for 5 h before it was concentrated *in vacuo*. Flash column chromatography (silica gel, CH_2Cl_2/MeOH = 20:1) afforded **21** (11.90 g, 83%) as an amorphous solid. **21**: R_f = 0.50 (silica gel, CH_2Cl_2/MeOH = 10:1). $[\alpha]_D^{25}$ = +8.57 (c = 0.21, $CHCl_3$). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.19-7.13 (m, 1H), 7.12-7.08 (m, 2H), 4.75 (d, *J* = 5.9 Hz, 1H), 3.90-3.75 (m, 3H), 3.69 (s, 6H), 3.65-3.59 (m, 1H), 3.17 (dd, *J* = 10.7, 7.9 Hz, 1H), 2.90 (t, *J* = 6.5 Hz, 1H), 2.14-2.04 (m, 1H), 1.53 (ddd, *J* = 13.4, 7.5, 5.4 Hz, 1H), 1.25-1.21 (m, 1H), 0.80 ppm (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 172.8, 172.6, 168.4, 168.3, 136.3, 127.2, 123.3, 122.2, 119.6, 118.3, 111.6, 107.4, 62.6, 52.9 (2C), 52.7, 52.5, 45.6, 43.5, 31.9, 25.6, 12.3 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{26}N_2NaO_7^+$ 453.1632 , found 453.1631.

Preparation of 22:



To a stirred solution of **21** (6.46 g, 15.03 mmol, 1.0 equiv) in CH_2Cl_2 (500 mL) at room temperature was added cyanuric chloride (4.43 g, 24.05 mmol, 1.6 equiv) and pyridine (1.21 mL, 15.03 mmol, 1.0 equiv). The resulting mixture was stirred at room temperature for 30 min before it was added $AlCl_3$ (2.60 g, 19.54 mmol, 1.3 equiv). The reaction was stirred under reflux for 12 h before it was cooled to room temperature and added water (100 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 2:1) afforded **22** (4.21 g, 68%) as an amorphous solid. **22**: $R_f = 0.40$ (silica gel, PE/EtOAc = 1:1). $[\alpha]_D^{25} = -67.94$ (c = 0.21, $CHCl_3$). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 9.38 (s, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.45 (dt, J = 8.3, 0.9 Hz, 1H), 7.37 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.15 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 5.19 (d, *J* = 5.3 Hz, 1H), 4.14 (dd, *J* = 11.9, 7.5 Hz, 1H), 3.86 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 2.75H), 3.76 (s, 0.25H), 3.81-3.80 (m,1H), 3.79 (s,2.75H), 3.75 (s,0.25H), 3.60 (d, *J* = 16.0 Hz, 1H), 3.47 (dt, *J* = 7.8, 5.3 Hz, 1H), 2.80 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.07-1.99 (m, 1H), 1.66-1.58 (m, 1H), 1.35-1.26 (m, 1H), 0.94 ppm (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 185.7, 169.9, 169.4, 168.5, 137.1, 130.1, 127.5, 126.7, 121.1, 120.9, 120.3, 112.5, 65.8, 53.2, 52.9, 51.8, 50.5, 43.0, 42.3, 34.1, 25.8, 12.5 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{24}N_2NaO_6^+$ 435.1527 , found 435.1526.

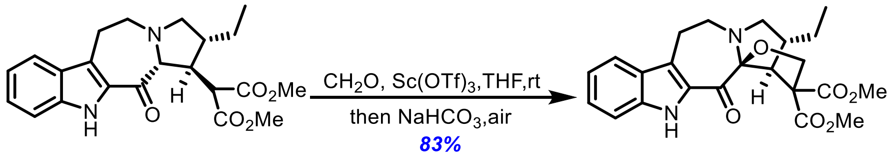
Preparation of 23:



To a stirred solution of **22** (3.76 g, 9.13 mmol, 1.0 equiv) in THF (180 mL) at room temperature was added sequentially $[Rh(H)(CO)(PPh_3)_3]$ (838 mg, 0.91 mmol, 0.1 equiv) and $PhSiH_3$ (5.62 ml, 45.65 mmol, 5.0 equiv) under an argon atmosphere. The resulting mixture was stirred at room temperature for 1 h before it was added NH_4Cl (100 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with

EtOAc (3 × 50 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 8:1) afforded **23** (2.29 g, 63%) as an amorphous solid. **23**: R_f= 0.40 (silica gel, PE/EtOAc = 3:1). $[\alpha]_D^{25}$ = +16.92 (c = 0.13, $CHCl_3$). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 7.63 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.39 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.34 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.12 (ddd, *J* = 8.0, 6.8, 1.0 Hz, 1H), 3.90 (d, *J* = 6.8 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.65 (d, *J* = 5.3 Hz, 1H), 3.43-3.22 (m, 2H), 3.17-3.04 (m, 2H), 3.04-2.95 (m, 2H), 2.83 (dd, J = 8.8, 2.8 Hz, 1H), 2.04-1.94 (m, 1H), 1.49 (ddd, *J* = 13.1, 7.5, 5.5 Hz, 1H), 1.37 (ddd, *J* = 13.7, 9.4, 7.2 Hz, 1H), 0.86 ppm (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 194.7, 169.4, 169.3, 136.9, 131.9, 127.9, 126.8, 123.9, 121.4, 120.2, 112.2, 74.8, 58.5, 55.4, 52.6, 52.4, 52.0, 47.6, 42.3, 28.4, 26.3, 12.7 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{26}N_2NaO_5^+$ 421.1734 , found 421.1732.

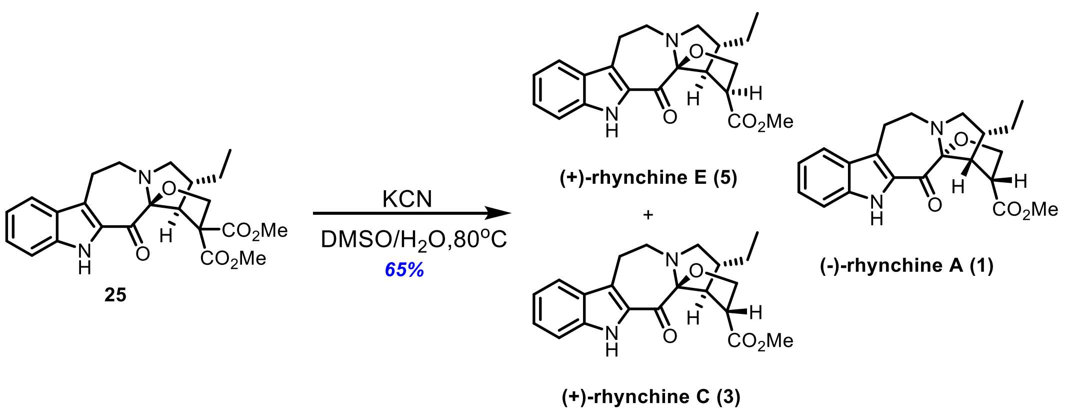
Preparation of 25:



23 **25**

To a stirred solution of **23** (1.56 g, 3.92 mmol, 1.0 equiv) in THF (45 mL) at room temperature was added sequentially $Sc(OTf)_3$ (3.86 g, 7.84 mmol, 2.0 equiv) and an aqueous solution of formaldehyde (1.58 g, 19.6 mmol, 5.0 equiv, 37% w/w) under an argon atmosphere. The resulting mixture was stirred at room temperature for 2 h before it was added $NaHCO_3$ (50 mL, sat. aq.). The reaction was exposed to the air and stirred at room temperature for 12 h before it was added water (100 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 5:1) afforded **25** (1.38 g, 83%) as an amorphous solid. **25**: R_f = 0.40 (silica gel, PE/EtOAc = 3:1). $[\alpha]_D^{25}$ = -41.33 (c = 0.1, $CHCl_3$). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 7.83-7.47 (m, 1H), 7.42-7.27 (m, 2H), 7.12 (ddd, *J* = 8.0, 6.4, 1.4 Hz, 1H), 4.54 (d, *J* = 9.4 Hz, 1H), 4.44 (d, *J* = 9.4 Hz, 1H), 3.88 (d, *J* = 4.7 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.60 (ddd, *J* = 13.0, 8.6, 4.2 Hz, 1H), 3.33 (dd, *J* = 8.7, 6.8 Hz, 1H), 3.27-3.15 (m, 2H), 3.01 (ddd, *J* = 13.2, 5.7, 4.2 Hz, 1H), 2.77 (dd, *J* = 8.8, 5.1 Hz, 1H), 1.99-1.71 (m, 1H), 1.54 (ddd, *J* = 13.5, 7.5, 5.9 Hz, 1H), 1.46-1.31 (m, 1H), 0.89 ppm (t, J = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 187.8, 169.9, 169.0, 137.1, 131.0, 127.6, 126.9, 125.4, 121.4, 120.4, 112.1, 107.3, 72.6, 65.6, 58.4, 57.0, 53.3, 52.7, 46.5, 40.0, 27.7, 25.2, 12.4 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{26}N_2NaO_6^+$ 449.1683 , found 449.1683.

Preparation of (-)-rhynchine A (1), (+)-rhynchine C (3) and (+)-rhynchine E (5):



To a stirred solution of **25** (1.20 g, 2.82 mmol, 1.0 equiv) in DMSO/H_2O (36 mL/1.8 mL) at room temperature was added and KCN (917 mg, 14.10mol, 5.0 equiv). The resulting mixture was warmed to 80°C and stirred for 4 h before it was cooled to room temperature and added water (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, PE/EtOAc = 12:1) afforded (+)-**5** (539 mg, 52%) as a pale-yellow solid, along with afford the mixture of compounds (-)-**1** and (+)-**3** (total 135mg, 0.366 mmol, 13%, (-)-**1**:(+)-**3** = 1:1.5) as pale-yellow solids.

NOTE: The mixture above was separated by reversed-phase semipreparative HPLC and obtained (+)-**3** (81mg, t_R 38.9 min) and (-)-**1** (54mg, t_R 42.8 min) [67% MeOH-H_2O, v/v, 3.5 mL/min, Agilent ZORBAX Eclipse XDB-C18 Prep. Column].

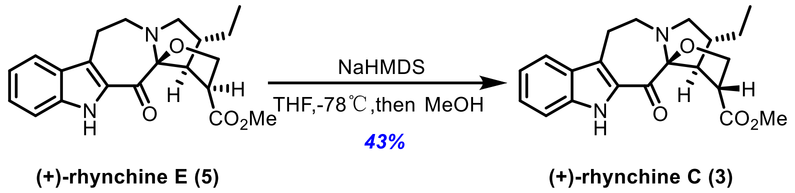
(-)-rhynchine A (1): m.p. 170-172 °C (PE/EtOAc) [Lit. m.p. 170-172 °C];[1] R_f = 0.42 (silica gel, PE/EtOAc = 4:1); $[\alpha]_D^{25}$ = -83.92 (c = 0.2, MeOH) [Lit. $[\alpha]_D^{24.3}$ = -82.5 (c = 0.16, MeOH)];[1] ^1H NMR (600 MHz, Chloroform-*d*) δ 8.87 (s, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.37-7.34 (m, 1H), 7.33-7.31 (m, 1H), 7.10 (ddd, *J* = 7.9, 6.7, 1.1 Hz, 1H), 4.18 (t, *J* = 8.1 Hz, 1H), 4.03 (t, *J* = 8.7 Hz, 1H), 3.85 (t, *J* = 7.9 Hz, 1H), 3.77 (s, 3H), 3.64 (dt, *J* = 13.0, 7.2 Hz, 1H), 3.25 (dd, *J* = 8.3, 6.2 Hz, 1H), 3.22-3.18 (m, 2H), 3.15 (q, *J* = 7.9 Hz, 1H), 3.02 (dt, *J* = 13.2, 5.0 Hz, 1H), 2.86 (dd, *J* = 11.2, 8.3 Hz, 1H), 2.25-2.14 (m, 1H), 1.57-1.51 (m, 1H), 1.45-1.36 (m, 1H), 0.93 ppm (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 187.7, 172.6, 137.1, 130.6, 128.0, 126.7, 123.3, 121.4, 120.2, 112.0, 106.5, 71.0, 59.0, 52.4 (2C), 45.3, 44.0, 40.6, 26.5, 21.3, 13.2 ppm. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{24}N_2NaO_4^+$ 391.1628 , found 391.1610.

(+)-rhynchine C (3): m.p. 112-114 °C (PE/EtOAc) [Lit. m.p. 112-114 °C];[1] R_f = 0.42 (silica gel, PE/EtOAc = 4:1); $[\alpha]_D^{25}$ = +95.28 (c = 0.2, MeOH) [Lit. $[\alpha]_D^{24.3}$ = +91.50

(c = 0.16, MeOH)];[1] ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.88 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.39-7.32 (m, 2H), 7.12 (ddd, *J* = 8.1, 6.2, 1.7 Hz, 1H), 4.23 (t, *J* = 8.1 Hz, 1H), 4.18 (dd, *J* = 10.9, 8.7 Hz, 1H), 3.73 (s, 3H), 3.72-3.68 (m, 1H) 3.68-3.62 (m, 1H), 3.33 (t, *J* = 8.1 Hz, 1H), 3.27-3.19 (m, 1H), 3.18-3.12 (m, 1H), 3.10-3.02 (m, 2H), 2.91 (dd, *J* = 9.1, 3.8 Hz, 1H), 1.92-1.82 (m, 1H), 1.51-1.43 (m, 1H), 1.42-1.32 (m, 1H), 0.86 ppm (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 189.5, 171.6, 137.3, 130.9, 127.9, 127.1, 125.3, 121.6, 120.4, 112.0, 106.9, 70.3, 59.7, 55.5, 51.7, 49.3, 45.5, 38.8, 28.3, 26.4, 12.3 ppm. **HRMS** (ESI) m/z: [M + Na]$^+$ calcd for $C_{21}H_{24}N_2NaO_4^+$ 391.1628 , found 391.1622.

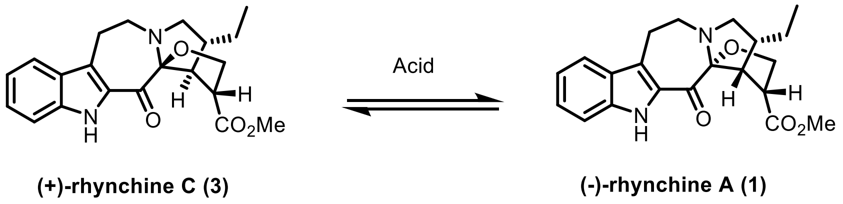
(+)-rhynchine E (5): m.p. 153-155 °C (PE/EtOAc) [Lit. m.p. 152-154 °C];[1] R_f = 0.40 (silica gel, PE/EtOAc = 4:1); $[\alpha]_D^{25}$ = +25.55 (c = 0.2, MeOH) [Lit. $[\alpha]_D^{24.3}$ = +21.54 (c = 0.083, MeOH)];[1] **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.99 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.36-7.31 (m, 2H), 7.11 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 4.22 (dd, *J* = 9.0, 7.1 Hz, 1H), 4.15 (dd, *J* = 9.0, 7.6 Hz, 1H), 3.77 (s, 3H), 3.62 (ddd, J = 13.7, 9.9, 4.1 Hz, 1H), 3.41 (dd, *J* = 6.3, 2.8 Hz, 1H), 3.36 (dd, *J* = 8.8, 6.1 Hz, 1H), 3.26-3.13 (m, 2H), 3.04 (dt, *J* = 13.4, 4.7 Hz, 1H), 2.98-2.91 (m, 2H), 1.91-1.83 (m, 1H), 1.47-1.41 (m, 2H), 0.93 ppm (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 188.5, 172.4, 137.1, 130.7, 127.8, 126.8, 124.4, 121.4, 120.3, 112.1, 105.9, 69.6, 58.0, 55.4, 52.2, 51.2, 45.0, 44.0, 26.8, 26.0, 12.4 ppm. **HRMS** (ESI) m/z: [M + Na]$^+$ calcd for $C_{21}H_{24}N_2NaO_4^+$ 391.1628 , found 391.1627.

Preparation of (+)-rhynchine C (3)



To a stirred solution of (+)-**5** (50 mg, 0.136 mmol, 1.0 equiv) in THF (5 mL) at -78 °C was added NaHMDS (0.20 mL, 1.0 M in THF, 1.5 equiv). The resulting mixture was stirred at -78 °C for 1h before it was added MeOH (0.2 mL). The reaction was warmed to room temperature before it was added water (0.5 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by reversed-phase semi-preparative HPLC (67% MeOH-H_2O, v/v, 3.5 mL/min, Agilent ZORBAX Eclipse XDB-C18 Prep. Column, t_R 38.9 min) to afford product **3** (21.5 mg, 43%) as a pale-yellow solid.

Tautomerization of (+)-rhynchine C (3) to (-)-rhynchine A (1)

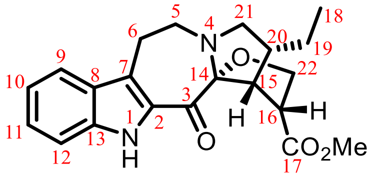


1. To a stirred solution of (+)-**3** (10 mg, 0.027 mmol, 1.0 equiv) in THF (1 mL) at room temperature was added $Sc(OTf)_3$ (40 mg, 0.081 mmol, 3 equiv) under an argon atmosphere. The resulting mixture was stirred at room temperature for 4h before it was added $NaHCO_3$ (2 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (2 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by

reversed-phase semi-preparative HPLC (67% MeOH-H_2O, v/v, 3.5 mL/min, Agilent ZORBAX Eclipse XDB-C18 Prep. Column, t_R 38.9 min and t_R 42.8 min) to afford product (+)-**3** (5.28 mg, 52.8%) as a pale-yellow solid, along with product (-)-**1** (4.40 mg, 44%) as a pale-yellow solid.

2. To a stirred solution of (+)-**3** (10 mg, 0.027 mmol, 1.0 equiv) in THF (1 mL) at room temperature was added HCl (0.14 mL ,0.27 mmol, 2.0 M aq) under an argon atmosphere. The resulting mixture was stirred at room temperature for 3h before it was added $NaHCO_3$ (2 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (2 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by reversed-phase semi-preparative HPLC (67% MeOH-H_2O, v/v, 3.5 mL/min, Agilent ZORBAX Eclipse XDB-C18 Prep. Column, t_R 38.9 min and t_R 42.8 min) to afford product (+)-**3** (4.80 mg, 48%) as a pale-yellow solid, along with product (-)-**1** (4.80 mg, 48%) as a pale-yellow solid.

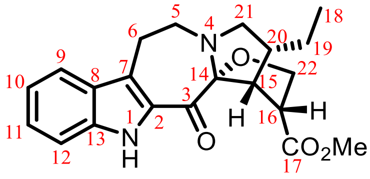
Table S1. ^{1}H NMR Spectroscopic (Chloroform-*d*, 25 °C) Comparison of Natural[1] and Synthetic **(-)-rhynchine A (1)**.



(-)-rhynchine A (1)

No.	**Natural** δ ^{1}H [ppm, mult, *J* (Hz)]	**Ours** δ ^{1}H [ppm, mult, *J* (Hz)]
N1	9.02 s, 1H	8.87, s, 1H
2		
3		
N4		
5	3.64, dt (*J* = 13.1, 7.4, 1H) 3.02, dt (*J* = 13.1, 5.0, 1H)	3.64, dt (*J* = 13.0, 7.2, 1H) 3.02, dt (*J* =13.2, 5.0, 1H)
6	3.20, m, 2H	3.20, m, 2H
7		
8		
9	7.62, dd (*J* = 8.1, 1.0,1H)	7.62, d (*J* = 8.1, 1H)
10	7.10, ddd (*J* = 8.1, 6.8, 1.0, 1H)	7.10, ddd (*J* = 7.9, 6.7, 1.1, 1H)
11	7.32, ddd (*J* = 8.2, 6.8, 1.0, 1H)	7.32, m, 1H
12	7.37, dd (*J* = 8.2, 1.0, 1H)	7.35, m, 1H
13		
14		
15	3.87, t (*J* = 7.8, 1H)	3.85, t (*J* = 7.9, 1H)
16	3.16 dt (*J* = 8.8, 7.8, 1H)	3.15, q (*J* = 7.9, 1H)
17		
18	0.93, t (*J* = 7.4, 3H)	0.93, t (*J* = 7.4, 3H)
19	1.56, m, 1H 1.40, m, 1H	1.55, m, 1H 1.40, m, 1H
20	2.19, m, 1H	2.19, m, 1H
21α	2.86, dd (*J* = 11.4, 8.4, 1H)	2.86, dd, (*J* = 11.2, 8.3, 1H)
21β	3.25, dd (*J* = 8.4, 6.2, 1H)	3.25, dd (*J* = 8.3, 6.2, 1H)
22α	4.03, t (*J* = 8.8, 1H)	4.03, t (*J* = 8.7, 1H)
22β	4.18, t (*J* = 8.8, 1H)	4.18, t (*J* = 8.1, 1H)
OMe	3.77, s, 3H	3.77, s, 3H

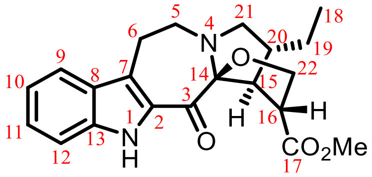
Table S2. ^{13}C NMR Spectroscopic (Chloroform-*d*, 25 °C) Comparison of Natural[1] and Synthetic **(-)-rhynchine A (1)**.



(-)-rhynchine A (1)

No.	**Natural** δ ^{13}C (ppm)	**Ours** δ ^{13}C (ppm)
N1		
2	130.6	130.6
3	187.8	187.7
N4		
5	44.0	44.0
6	26.6	26.5
7	123.4	123.3
8	128.0	128.0
9	121.5	121.4
10	120.3	120.2
11	126.8	126.7
12	112.1	112.0
13	137.2	137.1
14	106.5	106.5
15	52.4	52.4
16	45.3	45.3
17	172.7	172.6
18	13.2	13.2
19	21.3	21.3
20	40.7	40.6
21	59.0	59.0
22	71.0	71.0
OMe	52.4	52.4

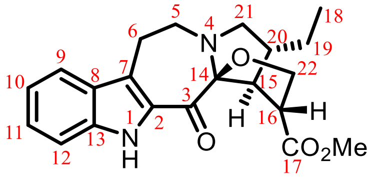
Table S3. ^{1}H NMR Spectroscopic (Chloroform-*d*, 25 °C) Comparison of Natural[1] and Synthetic **(+)-rhynchine C (3)**.



(+)-rhynchine C (3)

No.	**Natural** δ ^{1}H [ppm, mult, *J* (Hz)]	**Ours** δ ^{1}H [ppm, mult, *J* (Hz)]
N1	9.02 s, 1H	8.88, s, 1H
2		
3		
N4		
5	3.65, ddd (*J* = 14.0, 11.3, 3.2, 1H) 3.04, dt (*J* = 14.0, 4.2, 1H)	3.66, ddd (*J* = 14.1, 11.4, 3.0, 1H) 3.04, m, 1H
6	3.21, ddd (*J* = 17.2, 11.3, 4.2, 1H) 3.14, ddd (*J* = 17.2, 4.2, 3.2, 1H)	3.22, m, 1H 3.15, m, 1H
7		
8		
9	7.63, dd (*J* = 8.2, 1.0,1H)	7.63, d (*J* = 8.1, 1H)
10	7.12, ddd (*J* = 8.2, 6.6, 1.2, 1H)	7.12, ddd (*J* = 8.1, 6.2, 1.7, 1H)
11	7.34, m, 1H	7.34, m, 1H
12	7.36, m, 1H	7.36, m, 1H
13		
14		
15	3.06, dd (*J* = 8.2, 4.6, 1H)	3.06, m, 1H
16	3.72 (overlapped)	3.70, m, 1H
17		
18	0.86, t (*J* = 7.4, 3H)	0.86, t (*J* = 7.4, 3H)
19	1.46, m, 1H 1.36, m, 1H	1.46, m, 1H 1.36, m, 1H
20	1.86, m, 1H	1.87, m, 1H
21α	2.90, dd (*J* = 8.8, 3.8, 1H)	2.91, dd, (*J* = 9.1, 3.8, 1H)
21β	3.32, dd (*J* = 8.8, 7.2, 1H)	3.33, t (*J* = 8.1, 1H)
22α	4.17, dd (*J* = 8.6, 7.6, 1H)	4.18, dd (*J* = 10.9, 8.7, 1H)
22β	4.23, dd (*J* = 10.8, 8.6, 1H)	4.23, t (*J* = 8.1, 1H)
OMe	3.73, s, 3H	3.73, s, 3H

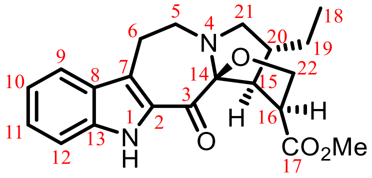
Table S4. ^{13}C NMR Spectroscopic (Chloroform-*d*, 25 °C) Comparison of Natural[1] and Synthetic **(+)-rhynchine (3)**.



(+)-rhynchine C (3)

No.	**Natural** δ ^{13}C (ppm)	**Ours** δ ^{13}C (ppm)
N1		
2	130.9	130.9
3	189.6	189.5
N4		
5	45.6	45.5
6	26.4	26.4
7	125.5	125.3
8	127.9	127.9
9	121.7	121.6
10	120.4	120.4
11	127.1	127.1
12	112.1	112.0
13	137.4	137.3
14	106.9	106.9
15	55.6	55.5
16	49.3	49.3
17	171.7	171.6
18	12.4	12.3
19	28.4	28.3
20	38.8	38.8
21	59.7	59.7
22	70.4	70.3
OMe	51.8	51.7

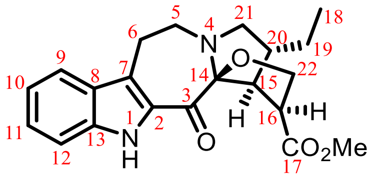
Table S5. ^{1}H NMR Spectroscopic (Chloroform-*d*, 25 °C) Comparison of Natural[1] and Synthetic **(+)-rhynchine E (5)**.



(+)-rhynchine E (5)

No.	**Natural** δ ^{1}H [ppm, mult, *J* (Hz)]	**Ours** δ ^{1}H [ppm, mult, *J* (Hz)]
N1	8.82, s, 1H	8.99, s, 1H
2		
3		
N4		
5	3.62, ddd (*J* = 13.8, 10.4, 3.6, 1H)	3.62, ddd (*J* = 13.7, 9.9, 4.1, 1H)
	3.04, dt (*J* = 13.8, 4.2, 1H)	3.04, dt (*J* = 13.4, 4.7, 1H)
6	3.21, m, 1H	3.21, m, 1H
	3.17, m, 1H	3.15, m, 1H
7		
8		
9	7.63, d (*J* = 8.2, 1H)	7.63, d (*J* = 8.1, 1H)
10	7.12, ddd (*J* = 8.2, 6.6, 1.2, 1H)	7.11, ddd (*J* = 8.0, 6.8, 1.1, 1H)
11	7.33, m, 1H	7.33, m, 1H
12	7.35, m, 1H	7.35, m, 1H
13		
14		
15	3.39, dd (*J* = 6.2, 2.8, 1H)	3.41, dd (*J* = 6.3, 2.8, 1H)
16	2.94, m, 1H	2.94, m, 1H
17		
18	0.93, t (*J* = 7.4, 3H)	0.93, t (*J* = 7.4, 3H)
19	1.45, m, 2H	1.44, m, 2H
20	1.86, m, 1H	1.86, m, 1H
21α	2.94, m, 1H	2.94, m, 1H
21β	3.36, dd (*J* = 8.8, 6.2, 1H)	3.36, dd (*J* = 8.8, 6.1, 1H)
22α	4.22, dd (*J* = 9.0, 7.6, 1H)	4.22, dd (*J* = 9.0, 7.1, 1H)
22β	4.15, dd (*J* = 9.0, 7.0, 1H)	4.15, dd (*J* = 9.0, 7.6, 1H)
OMe	3.78, s, 3H	3.77, s, 3H

Table S6. ^{13}C NMR Spectroscopic (Chloroform-*d*, 25 °C) Comparison of Natural[1] and Synthetic **(+)-rhynchine E (5)**.



(+)-rhynchine E (5)

No.	**Natural** δ ^{13}C (ppm)	**Ours** δ ^{13}C (ppm)
N1		
2	130.8	130.7
3	188.6	188.5
N4		
5	45.1	45.0
6	26.2	26.0
7	124.5	124.4
8	127.9	127.8
9	121.6	121.4
10	120.4	120.3
11	126.9	126.8
12	112.1	112.1
13	137.1	137.1
14	105.9	105.9
15	55.5	55.4
16	51.3	51.2
17	172.5	172.4
18	12.5	12.4
19	26.9	26.8
20	44.1	44.0
21	58.0	58.0
22	69.7	69.6
OMe	52.4	52.2

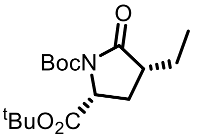
II) Abbreviations

Ac	acetyl
AllocCl	Allyl chloroformate
DMSO	Dimethyl sulfoxide
EDCI	1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
LiHMDS	Lithium hexamethyldisilazide
NaHMDS	Sodium hexamethyldisilazide
NCS	N-Chlorosuccinimide
PE	petroleum ether
py	pyridine
r.t.	room temperature
THF	tetrahydrofuran
TCT	Cyanuric chloride
Tf	trifluoromethanesulfonyl
TMSOTf	trimethylsilyl trifluoromethanesulfonate
TPPA	triphenyl phosphate

III) References

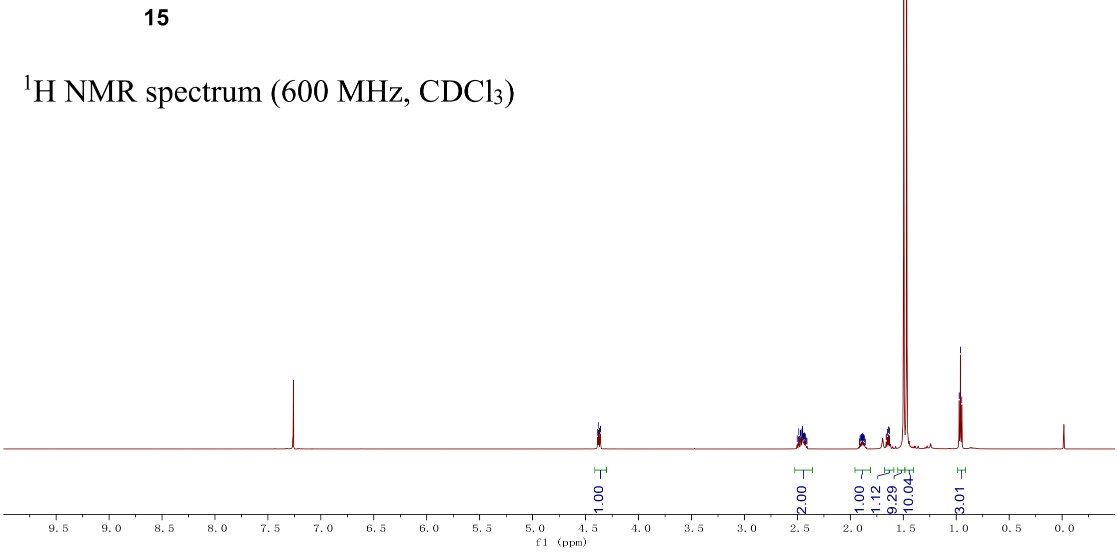
[1] Zhou, H. -F.; Li, W. -Y.; Peng, L. -Y.; Li, X. -N.; Zuo, Z. -L.; Zhao, Q. -S. Rhynchines A–E: $Ca_v3.1$ Calcium Channel Blockers from *Uncaria rhynchophylla*. *Org. Lett.* **2021**, *23*, 9463.

IV) ^{1}H and ^{13}C NMR Spectra of Compounds

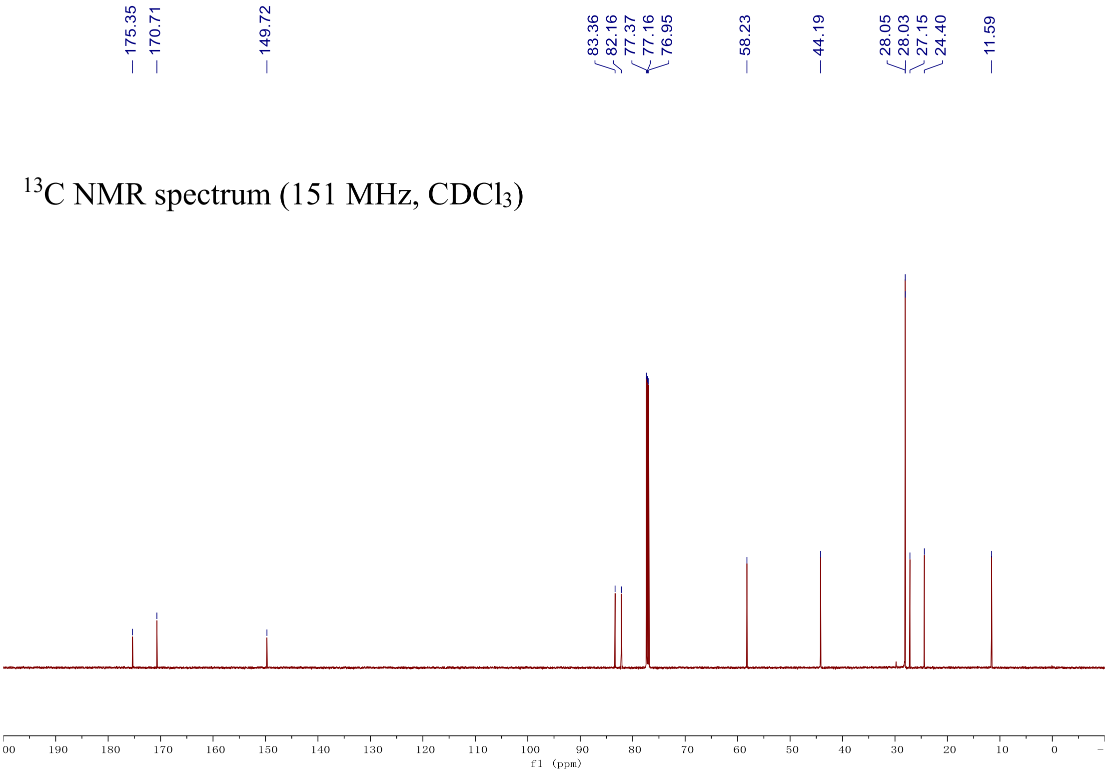


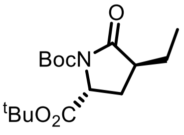
15

^{1}H NMR spectrum (600 MHz, CDCl$_3$)



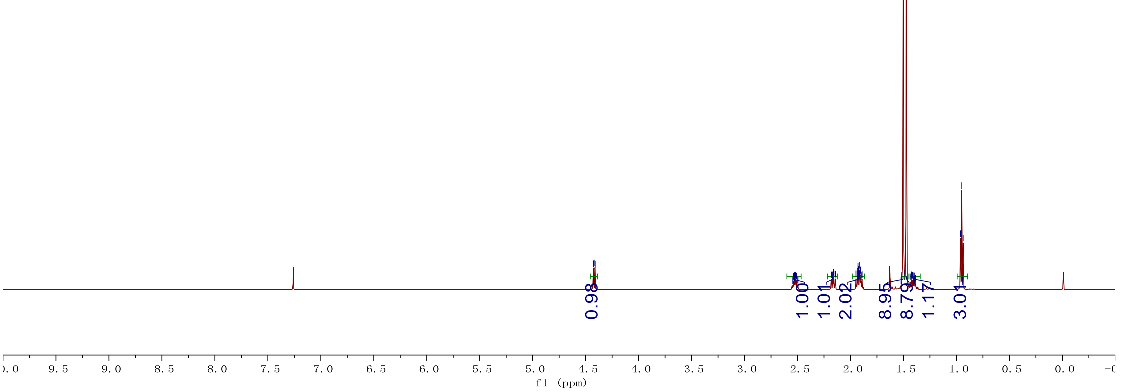
^{13}C NMR spectrum (151 MHz, CDCl$_3$)



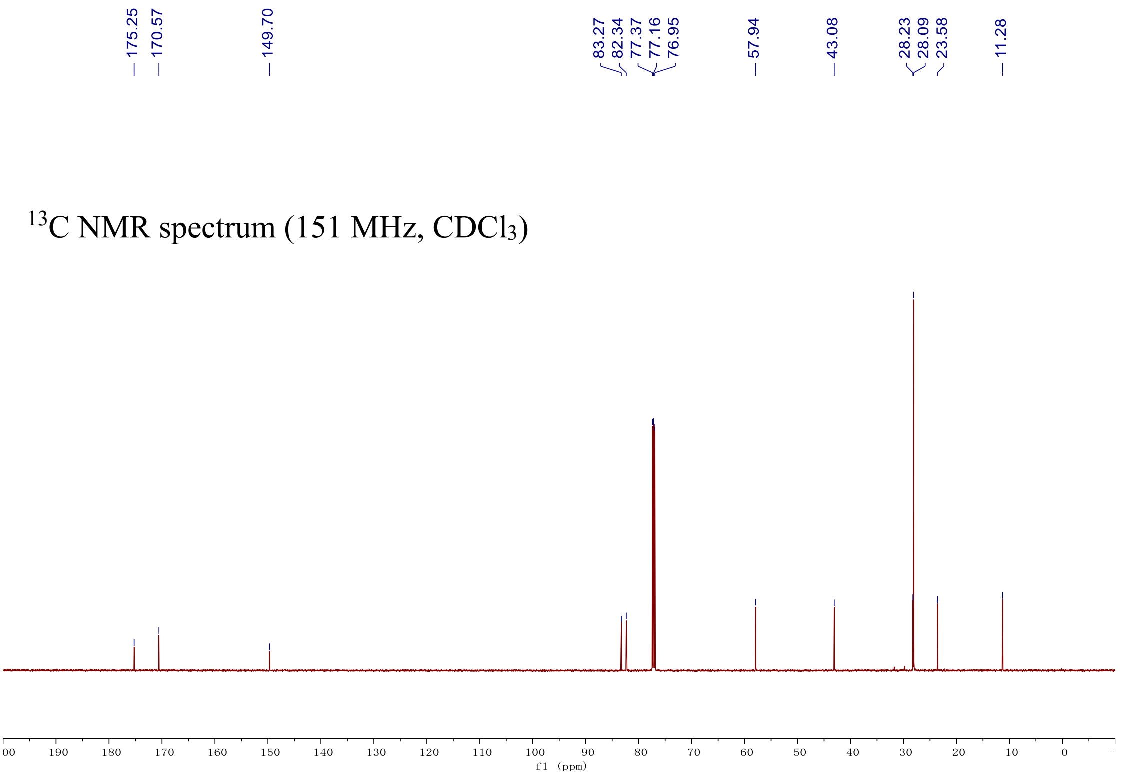


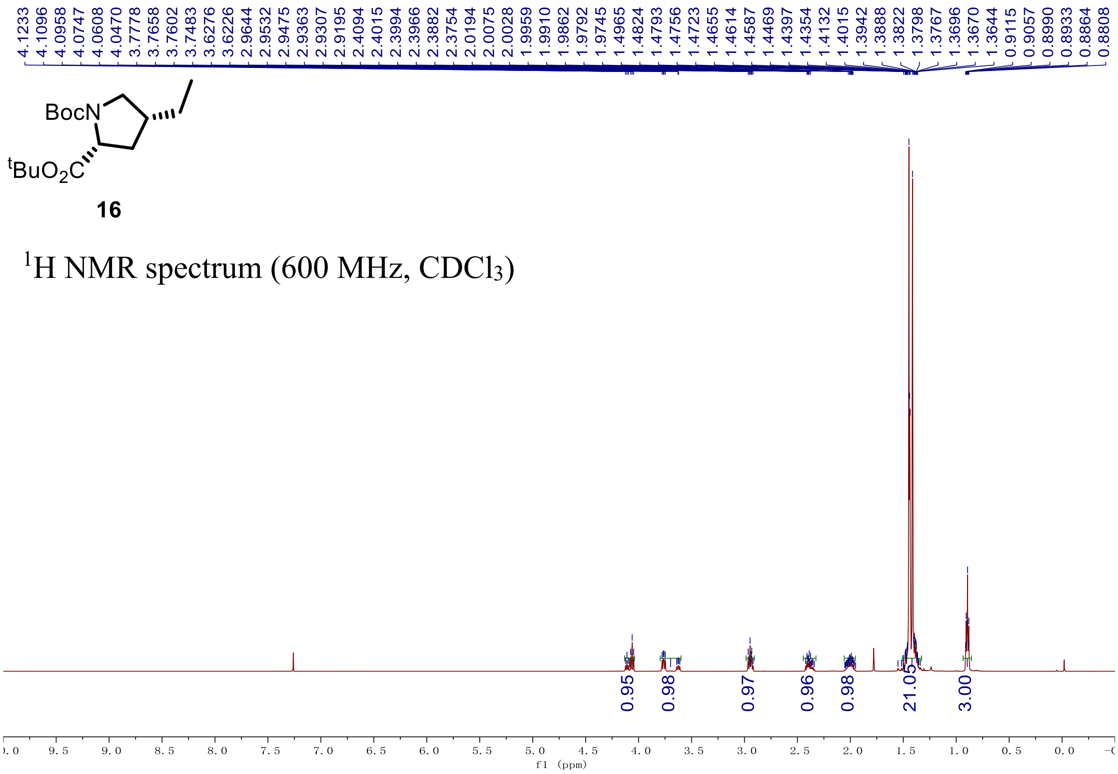
15'

¹H NMR spectrum (600 MHz, CDCl₃)



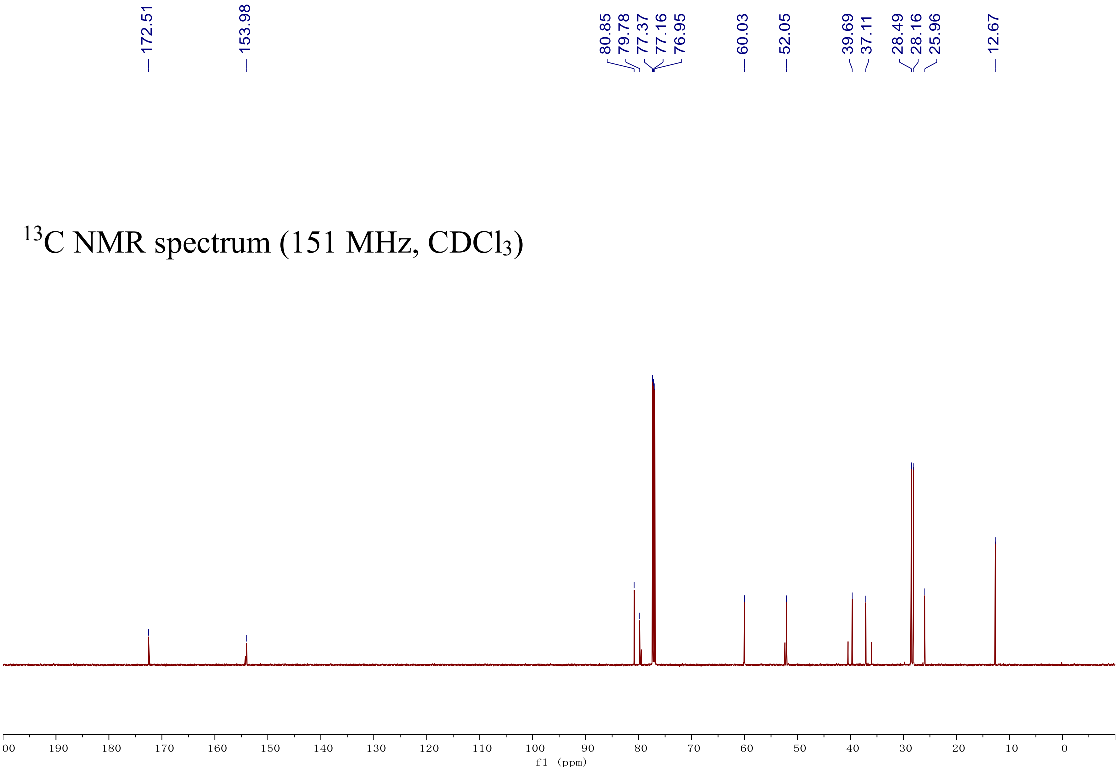
¹³C NMR spectrum (151 MHz, CDCl₃)





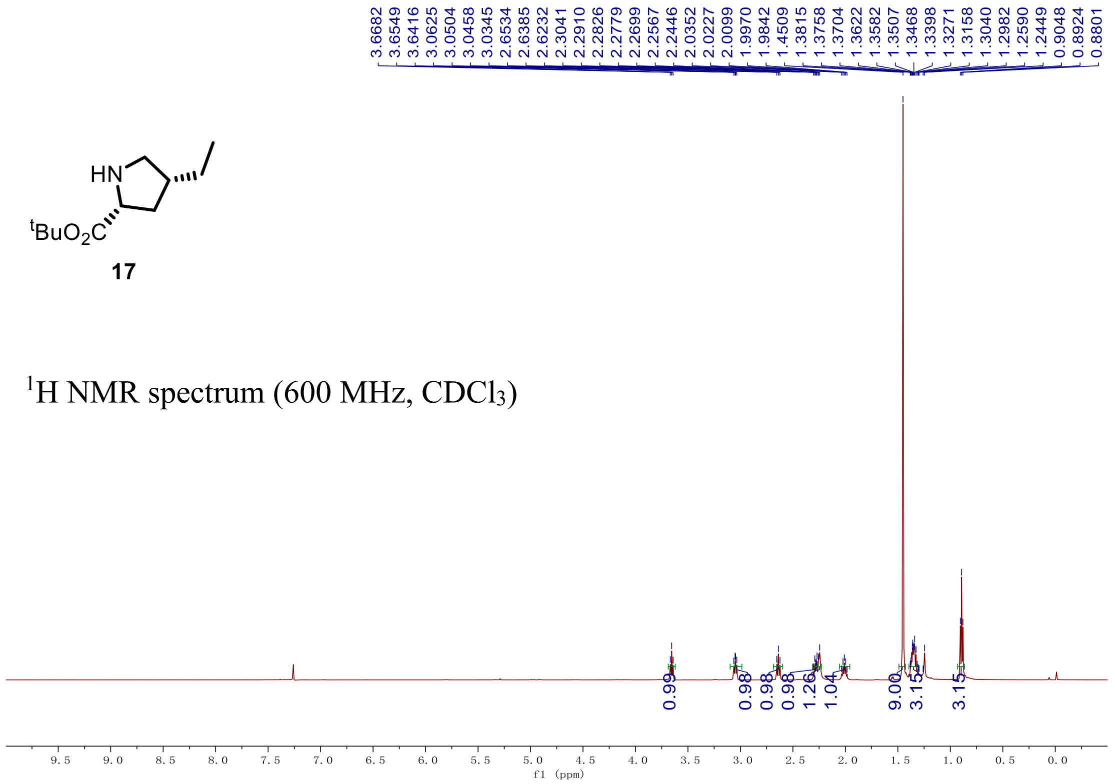
16

^{1}H NMR spectrum (600 MHz, CDCl$_3$)



^{13}C NMR spectrum (151 MHz, CDCl$_3$)

Note: The splitting of the carbon spectrum is due to atropisomer.



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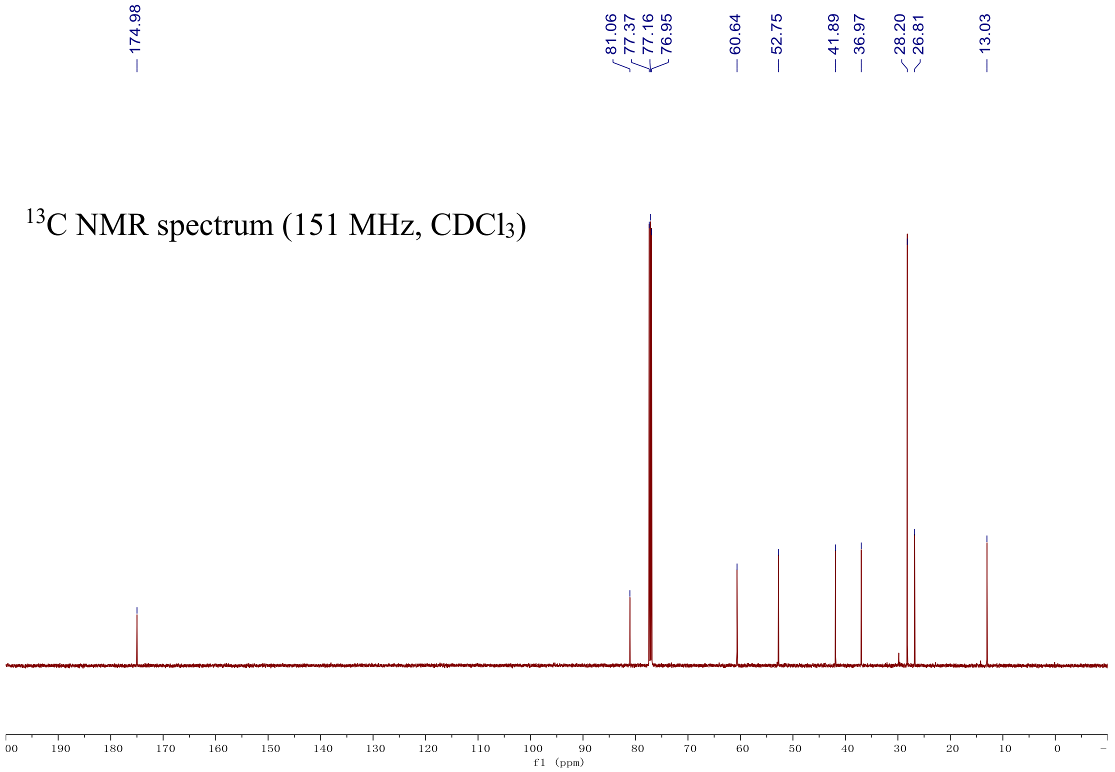
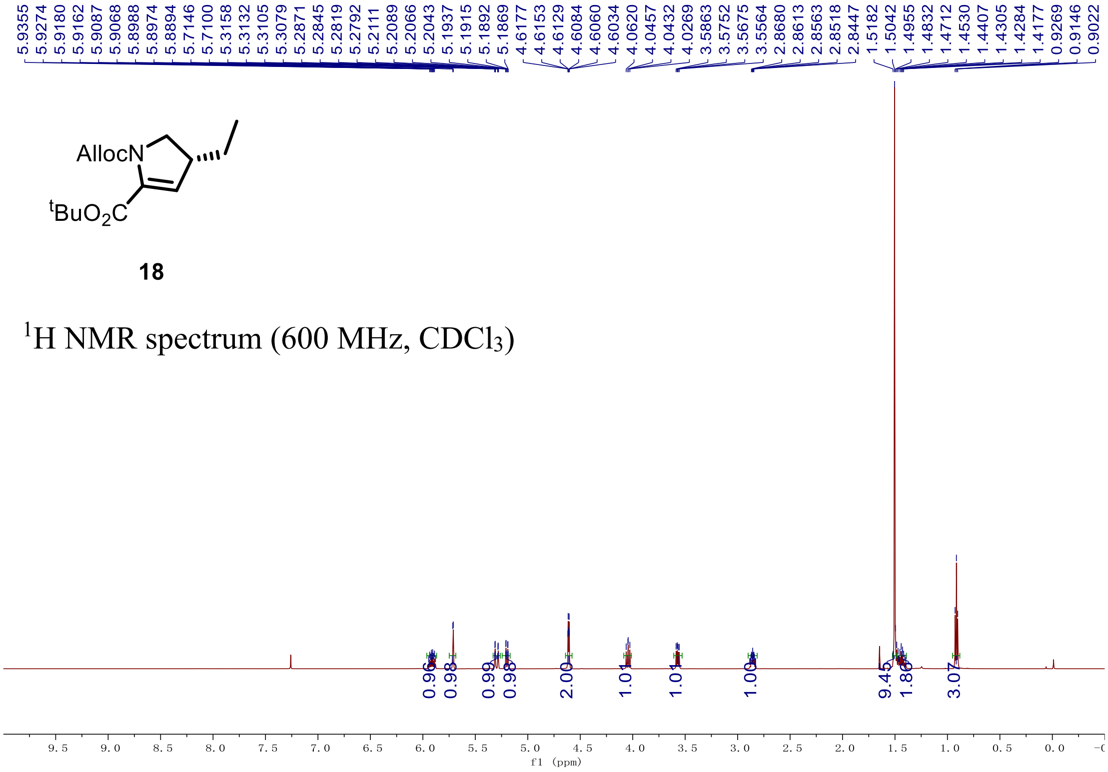
^{1}H NMR spectrum (600 MHz, CDCl$_3$)



^{13}C NMR spectrum (151 MHz, CDCl$_3$)



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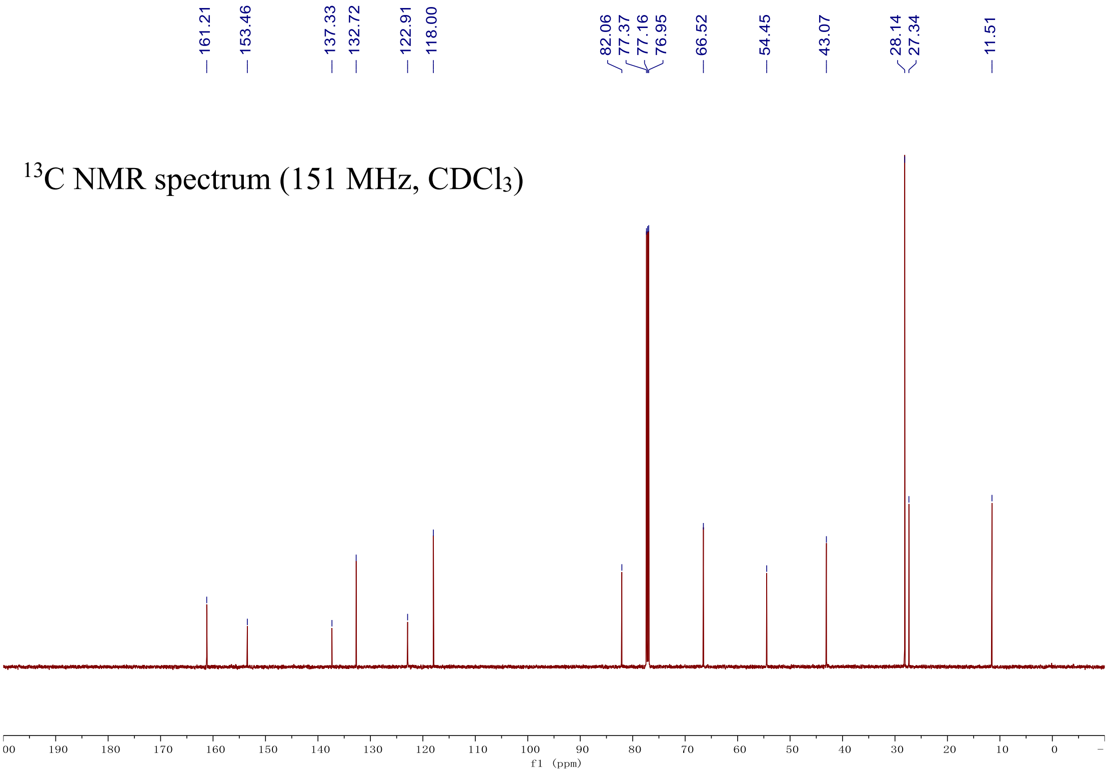
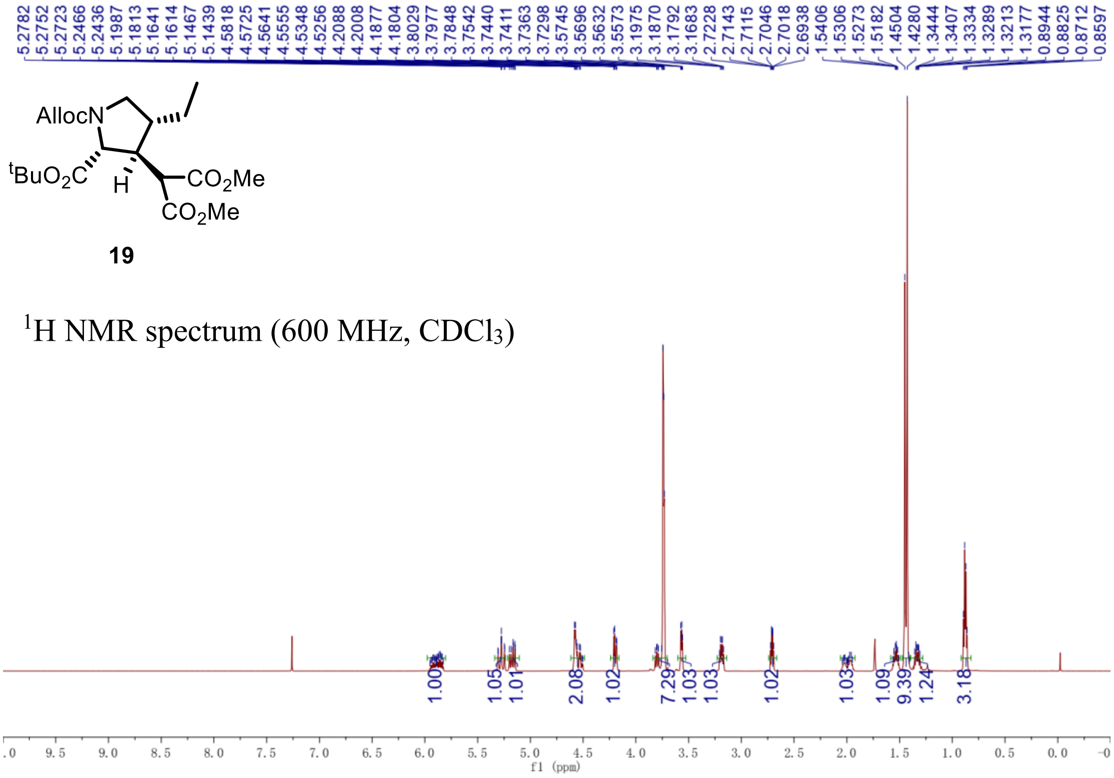
^{1}H NMR spectrum (600 MHz, CDCl$_3$)

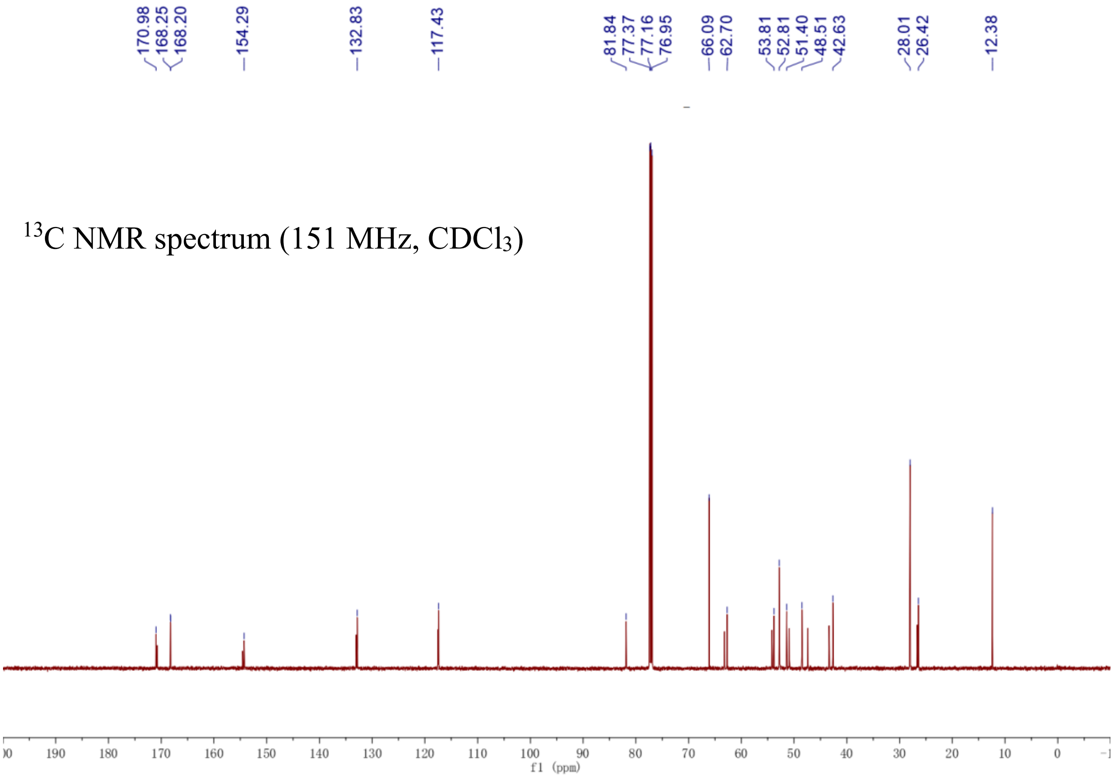


^{13}C NMR spectrum (151 MHz, CDCl$_3$)



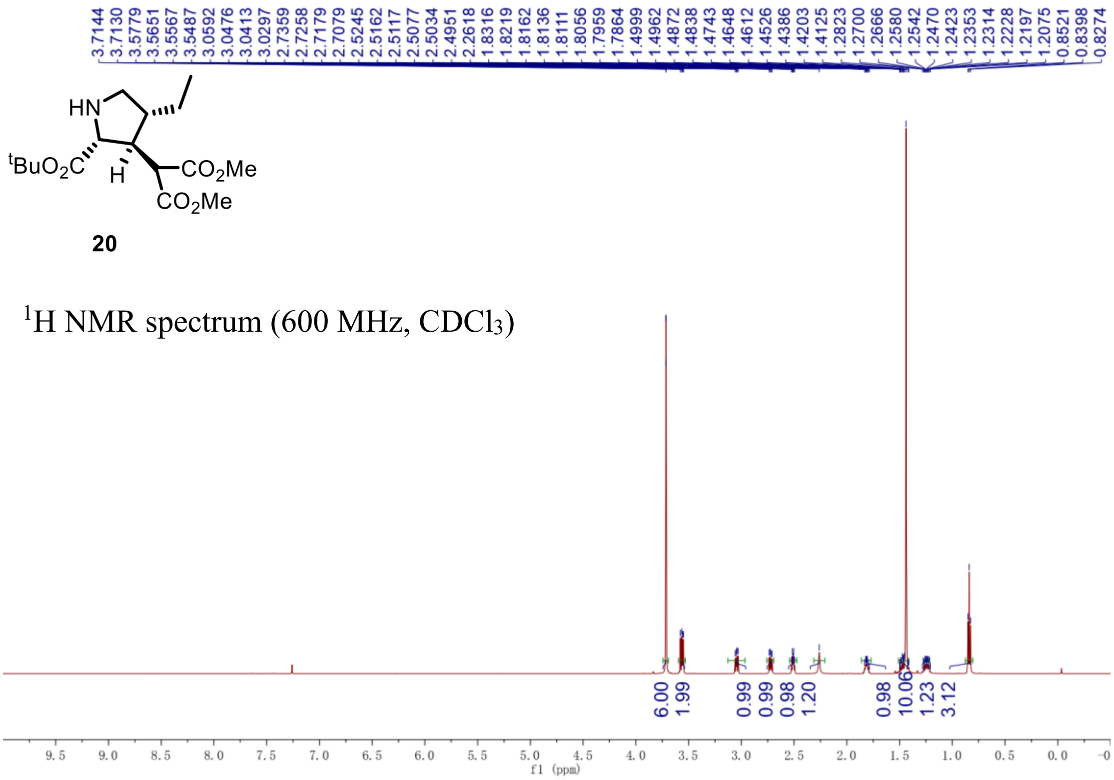
19

^{1}H NMR spectrum (600 MHz, CDCl$_3$)



^{13}C NMR spectrum (151 MHz, CDCl$_3$)

Note: The splitting of the carbon spectrum is due to atropisomer.



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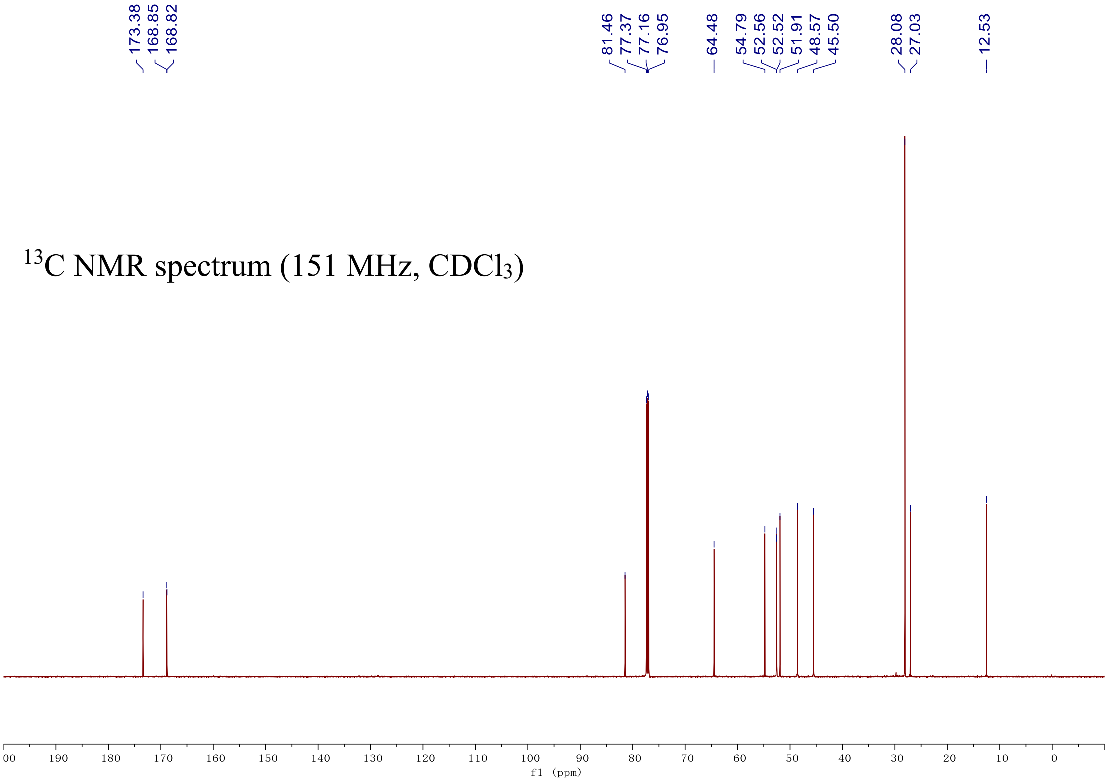
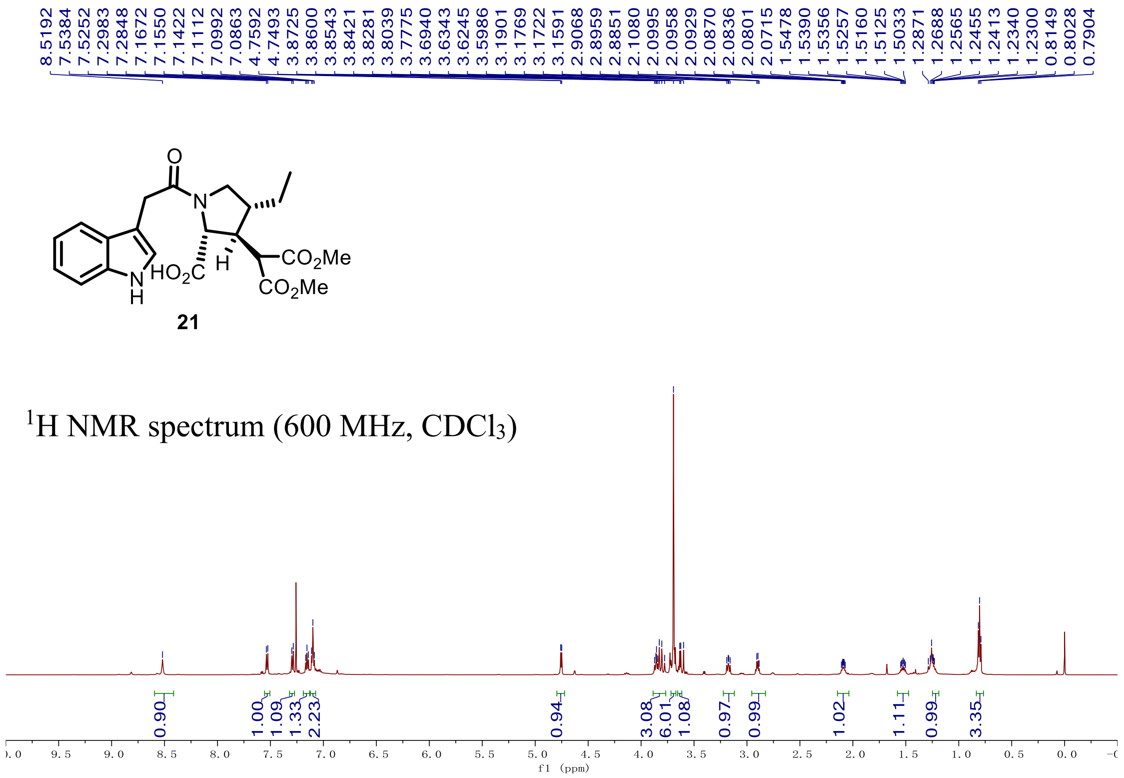
^{1}H NMR spectrum (600 MHz, $CDCl_3$)



^{13}C NMR spectrum (151 MHz, $CDCl_3$)



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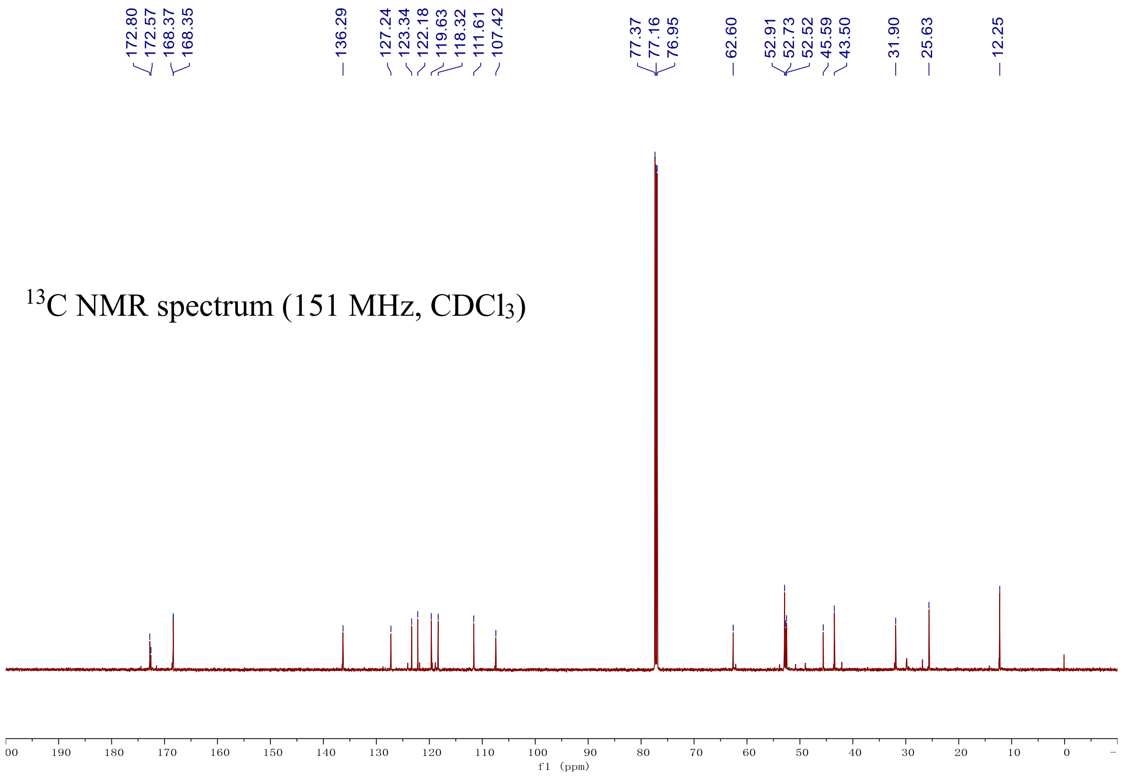
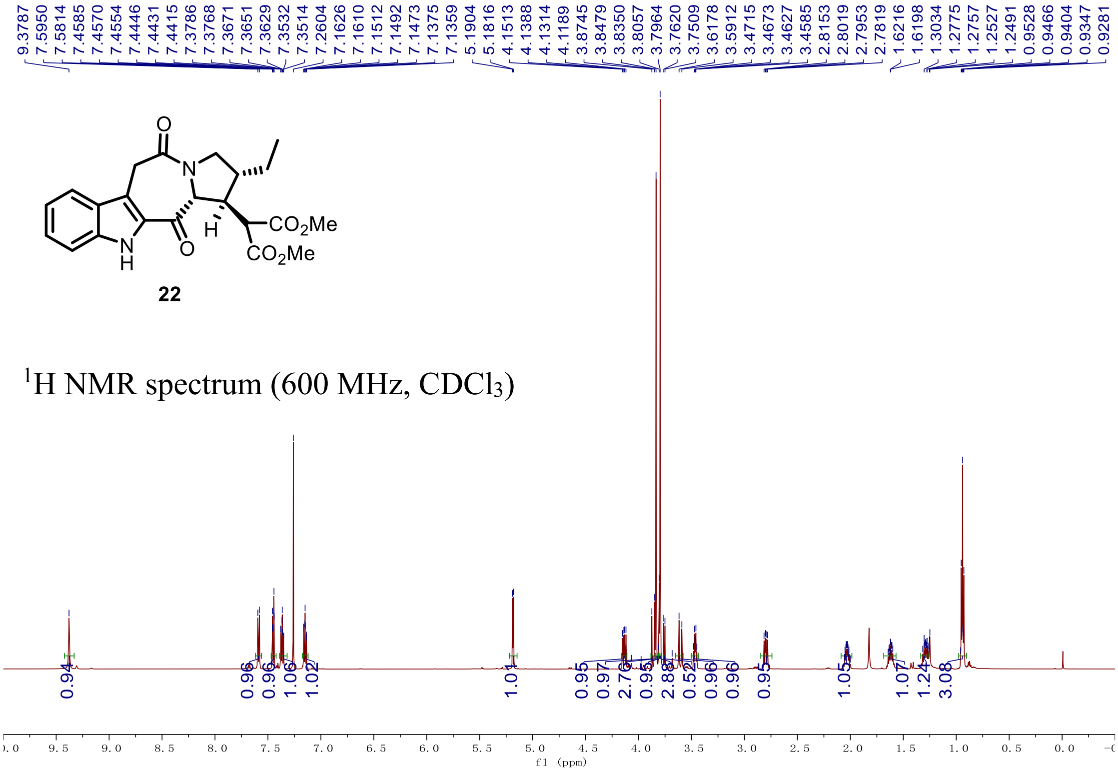


^{13}C NMR spectrum (151 MHz, $CDCl_3$)



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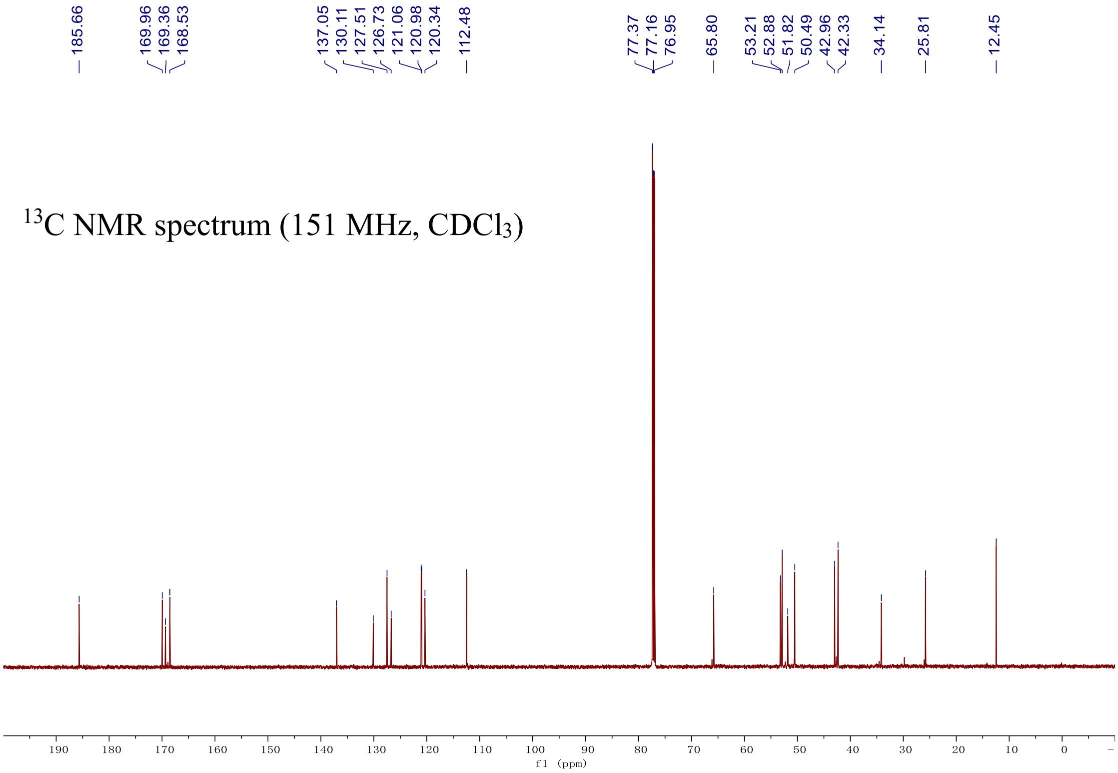
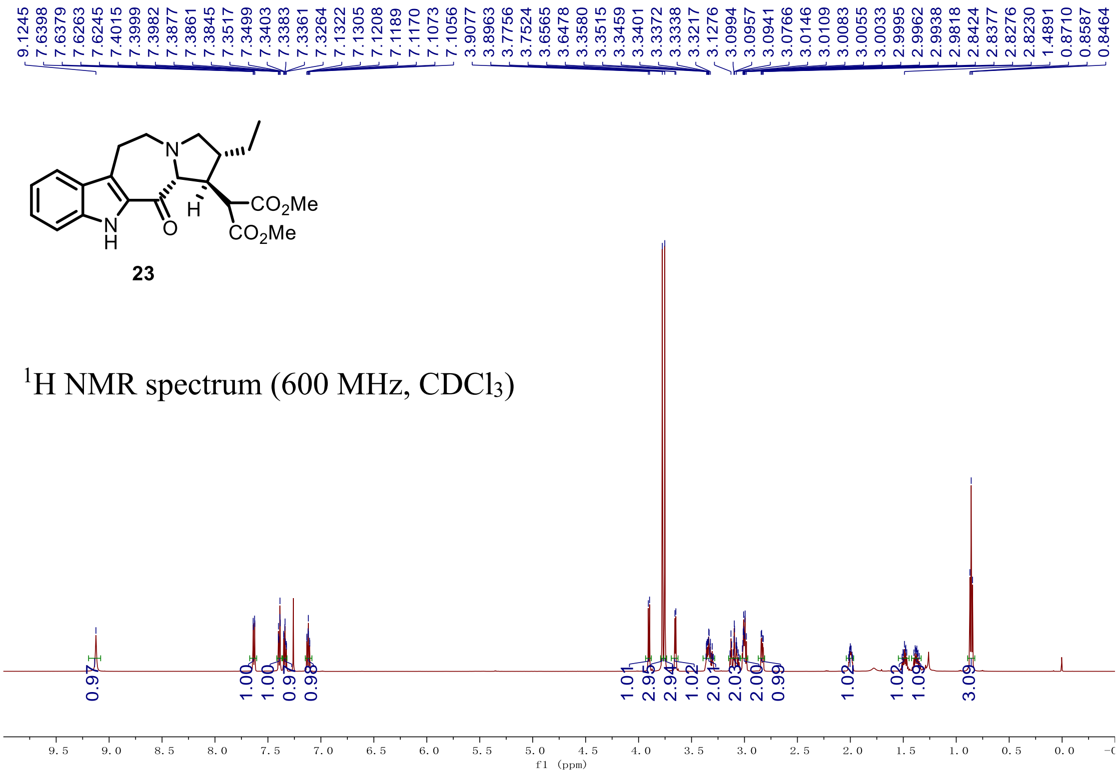
^{1}H NMR spectrum (600 MHz, CDCl$_3$)



^{13}C NMR spectrum (151 MHz, CDCl$_3$)



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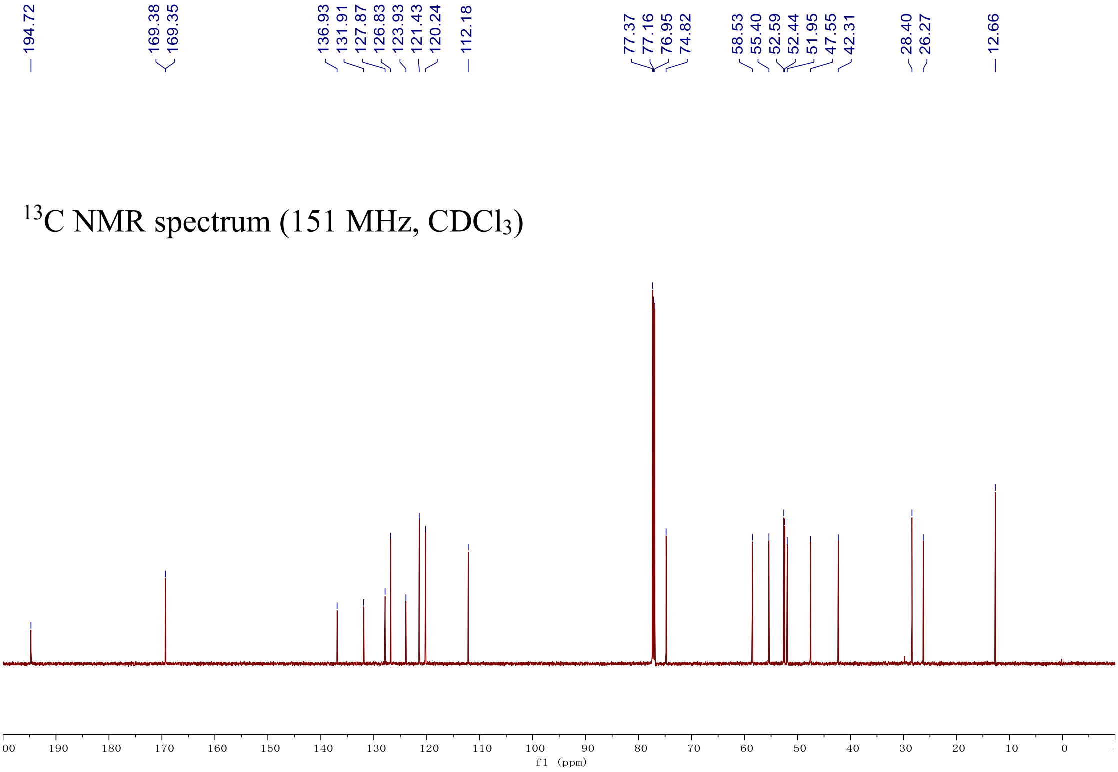
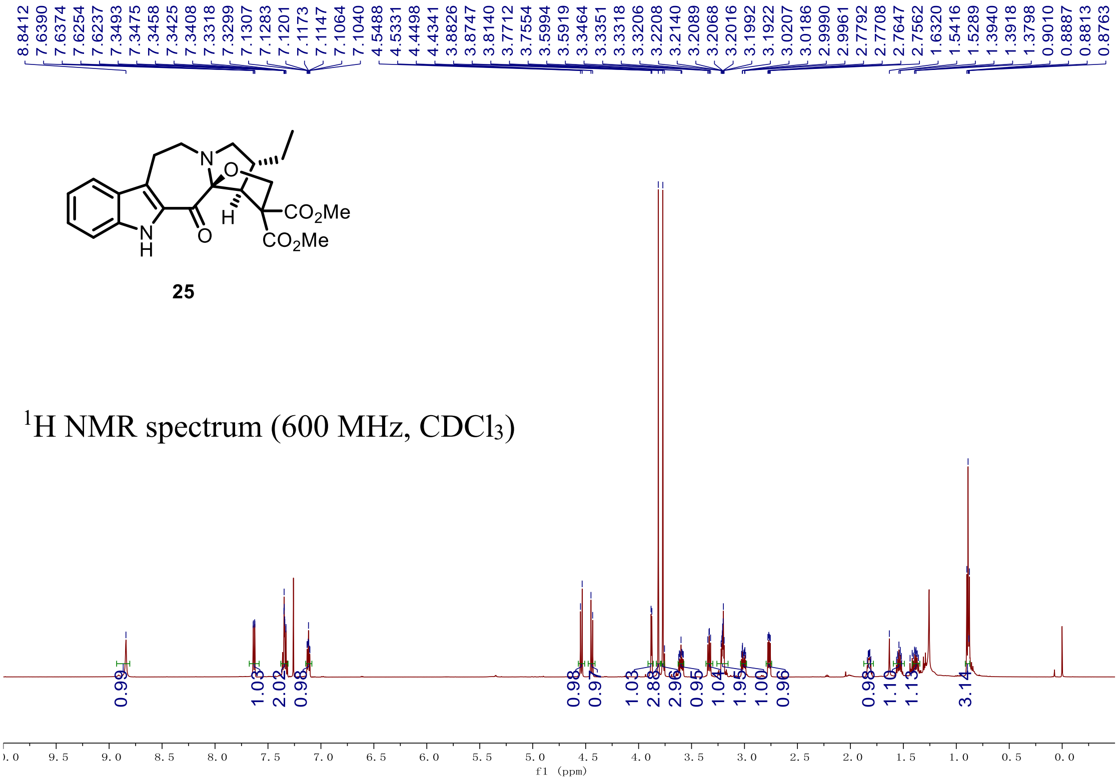
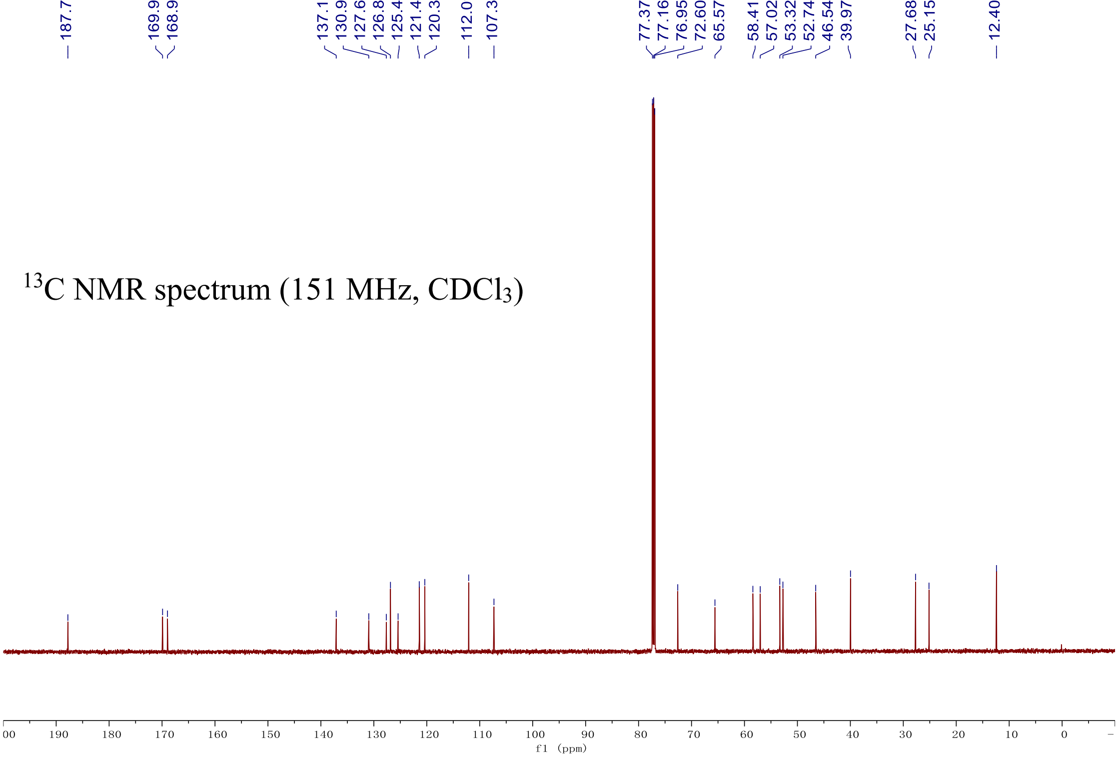


^{13}C NMR spectrum (151 MHz, CDCl$_3$)

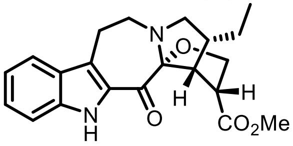


25

^{1}H NMR spectrum (600 MHz, CDCl$_3$)

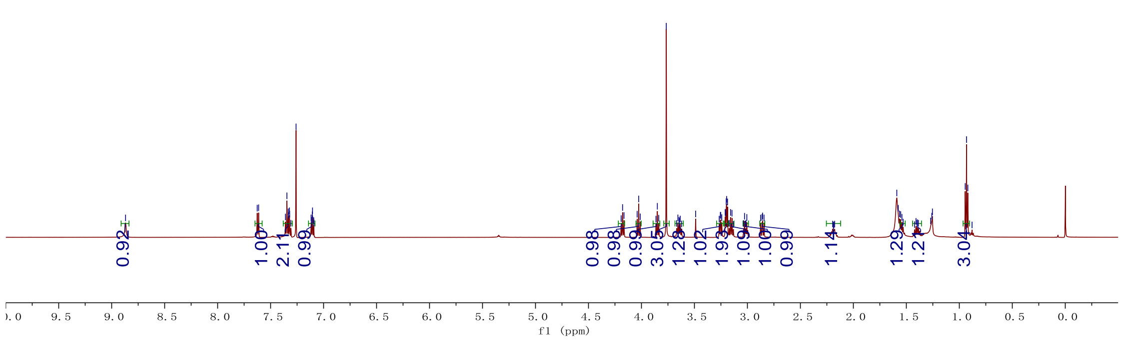


^{13}C NMR spectrum (151 MHz, CDCl$_3$)

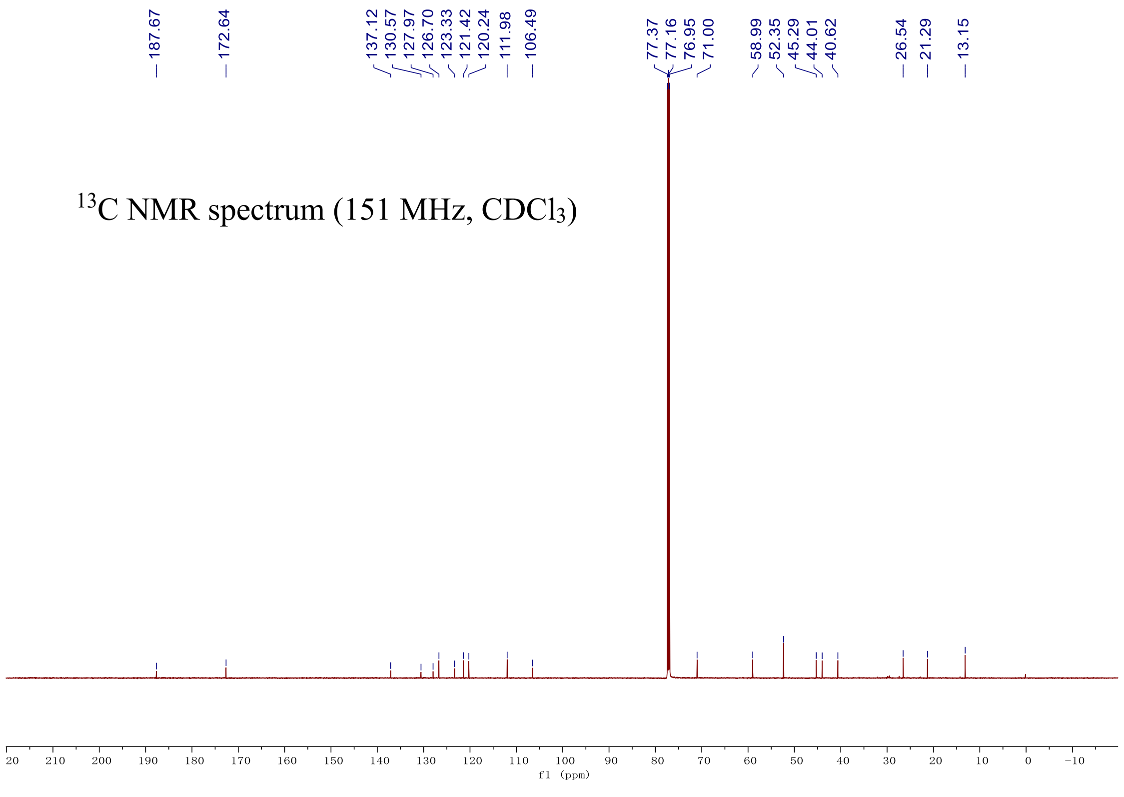


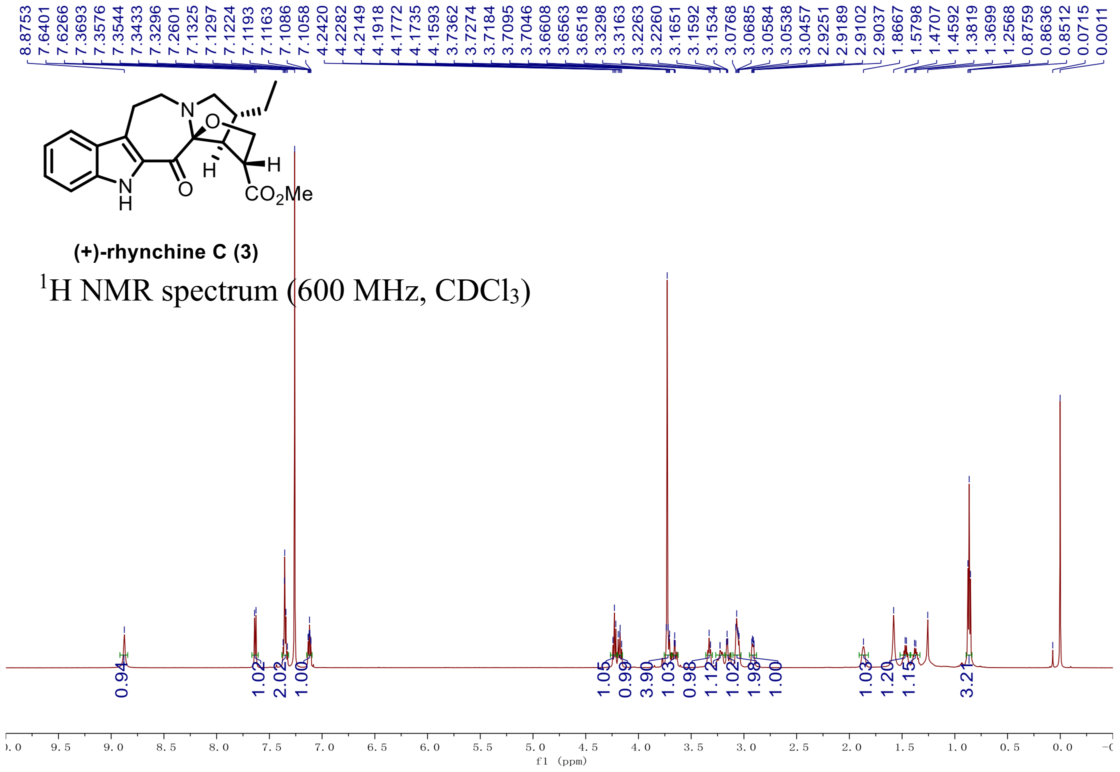
(-)-rhynchine A (1)

^{1}H NMR spectrum (600 MHz, CDCl$_3$)



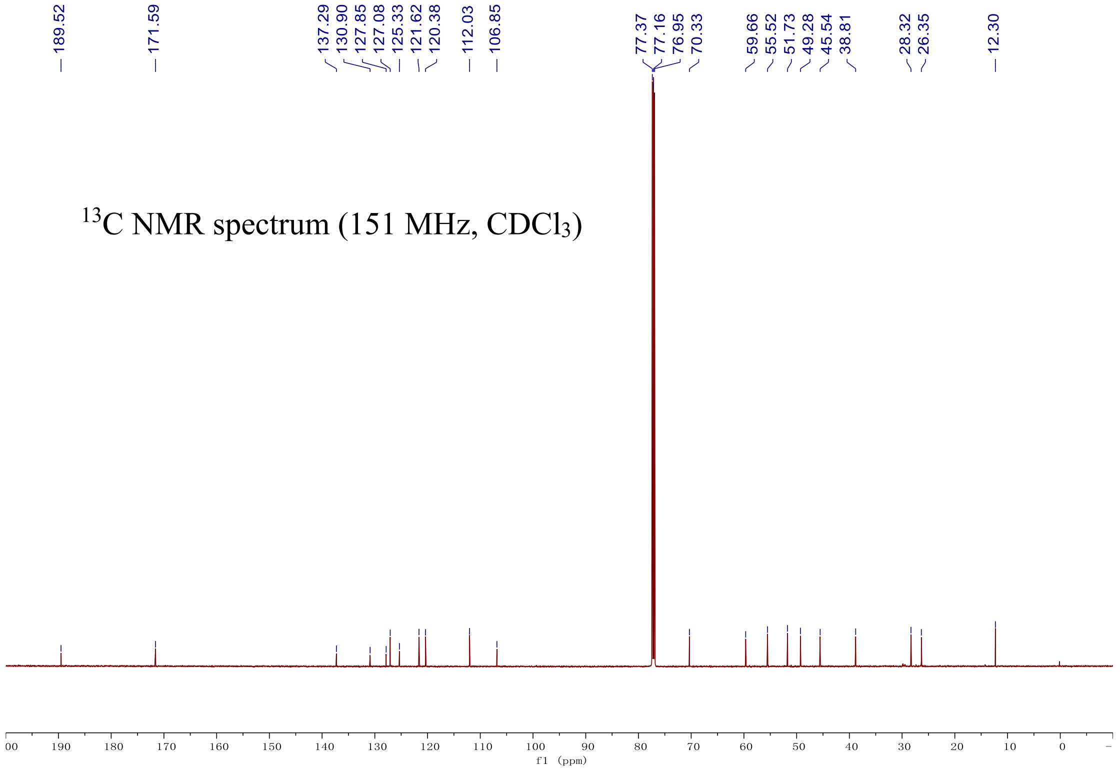
^{13}C NMR spectrum (151 MHz, CDCl$_3$)



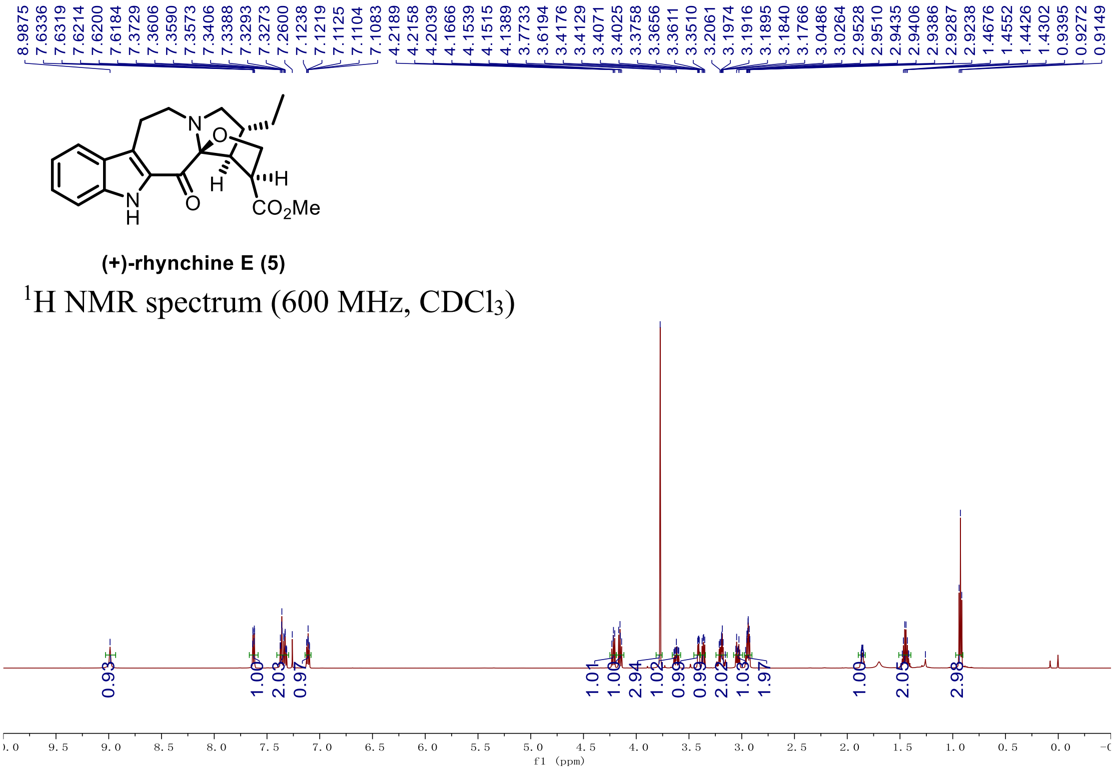


(+)-rhynchine C (3)

^{1}H NMR spectrum (600 MHz, $CDCl_3$)

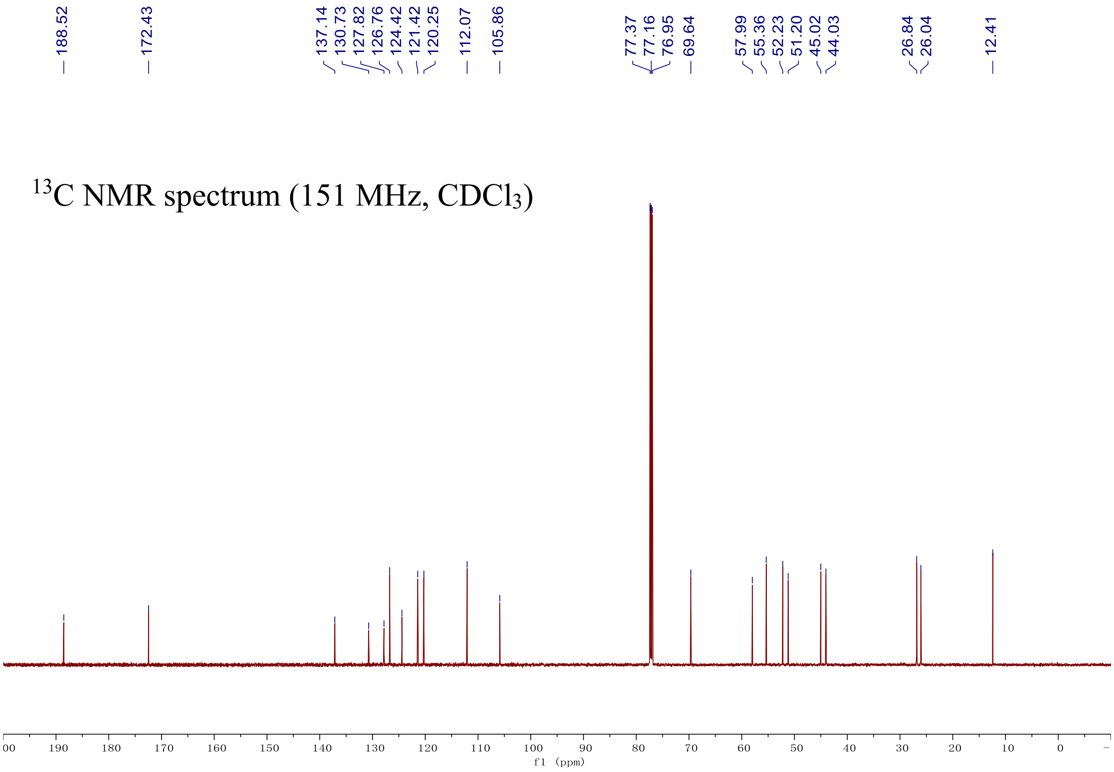


^{13}C NMR spectrum (151 MHz, $CDCl_3$)



(+)-rhynchine E (5)

^{1}H NMR spectrum (600 MHz, $CDCl_3$)



^{13}C NMR spectrum (151 MHz, $CDCl_3$)