Supporting Information

Asymmetric Total Synthesis of (+)-Tubingensin A

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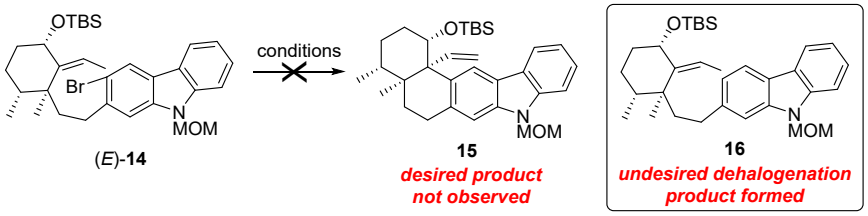
I. Attempts for Intramolecular Heck Reaction

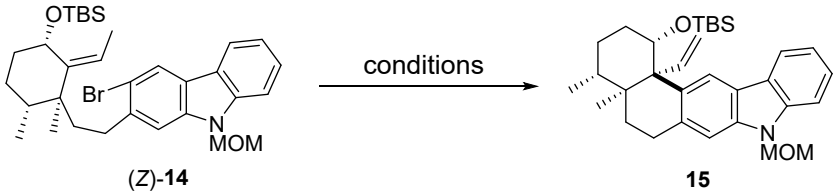
Table S1 Attempts for Intramolecular Heck Reaction with (*E*)-**14**[a]



Entry	[Pd]	Ligand	Base	Solvent	*T* (°C)	t (h)	Result
1	$Pd(OAc)_2$	PPh_3	Et_3N	DMF	90	12	NR
2	$Pd(OAc)_2$	PPh_3	Et_3N	DMF	100	12	**16**
3	$Pd(OAc)_2$	PPh_3	Et_3N	PhMe	100	12	**16**
4	$Pd(OAc)_2$	PPh_3	Et_3N	dioxane	100	12	NR
5	$Pd(OAc)_2$	PPh_3	Et_3N	DMF	120	12	**16**
6	$Pd(OAc)_2$	PPh_3	Pyridine	DMF	100	12	**16**
7	$Pd(OAc)_2$	PPh_3	DIPEA	DMF	100	12	**16**
8[b]	$Pd(OAc)_2$	PPh_3	Ag_3PO_4	DMF	100	12	NR
9[b]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	DMF	100	12	NR
10[b]	$Pd(OAc)_2$	PPh_3	AcONa	DMF	100	12	NR
11	$Pd(OAc)_2$	P(*o*-tol)$_3$	Et_3N	DMF	100	12	**16**
12	$Pd(TFA)_2$	PPh_3	Et_3N	DMF	100	12	**16**
13	$Pd(TFA)_2$	P(*o*-tol)$_3$	Et_3N	DMF	100	12	**16**
14	$Pd(dba)_2$	P(*o*-tol)$_3$	Et_3N	DMF	100	12	**16**
15	$Pd(dba)_2$	dppf	Et_3N	DMF	100	12	**16**
16	$Pd_2(dba)_3$	PPh_3	Et_3N	DMF	100	12	**16**
17	$Pd_2(dba)_3$	dppf	Et_3N	DMF	100	12	**16**
18	$Pd_2(dba)_3$	P(*o*-tol)$_3$	Et_3N	DMF	100	12	**16**
19	$Pd(PPh_3)_2Cl_2$	PPh_3	Et_3N	DMF	100	12	**16**
20	$Pd(PPh_3)_4$	/	Et_3N	DMF	100	12	**16**
21	$Pd(PPh_3)_4$	/	Et_3N	DMF	100	24	**16**

[a]Reaction conditions: (*E*)-**14** (0.01 mmol), [Pd] catalyst (10 mol%), ligand (20 mol%), base (5 equiv), solvent (1 mL), Ar, *T*, 12 h. [b]TBAI was added. DIPEA = N,N-diisopropylethylamine. dppf = 1,1'-Bis(diphenylphosphino)ferrocene

Table S2 Optimization of the Intramolecular Heck Reaction with (*Z*)-**14**[a]



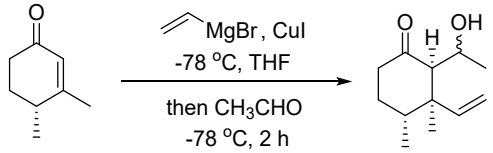
(*Z*)-**14** **15**

Entry	[Pd]	Ligand	Base	Solvent	*T* (°C)	t (h)	Yield (%)[b]
1	$Pd(OAc)_2$	PPh_3	Et_3N	MeCN	80	12	0
2	$Pd(OAc)_2$	PPh_3	Et_3N	DMF	90	12	trace
3	$Pd(OAc)_2$	PPh_3	Et_3N	DMF	100	12	15
4	$Pd(OAc)_2$	PPh_3	Et_3N	PhMe	100	12	12
5	$Pd(OAc)_2$	P(*o*-tol)$_3$	Et_3N	DMF	100	12	16
6	$Pd(Ph_3P)_2Cl_2$	PPh_3	Et_3N	DMF	100	12	36
7	$Pd(TFA)_2$	PPh_3	Et_3N	DMF	100	12	19
8	$Pd(dba)_2$	PPh_3	Et_3N	DMF	100	12	16
9	$Pd_2(dba)_3$	PPh_3	Et_3N	DMF	100	12	23
10	$Pd_2(dba)_3$	P(*o*-tol)$_3$	Et_3N	DMF	100	24	20
11	$Pd(Ph_3P)_4$	/	Et_3N	DMF	100	12	60
12	$Pd(Ph_3P)_4$	/	PMP	DMF	100	12	54
13	$Pd(Ph_3P)_4$	/	DIPEA	DMF	100	12	41
14[c]	$Pd(Ph_3P)_4$	/	Ag_3PO_4	DMF	110	12	37
15[c]	$Pd(Ph_3P)_4$	/	Cs_2CO_3	DMF	100	12	35
16	$Pd(Ph_3P)_4$		K_2CO_3	DMF/H_2O[d]	100	12	29
17	$Pd(Ph_3P)_4$	/	Et_3N	DMF/H_2O[d]	100	12	58
18	$Pd(Ph_3P)_4$[e]	/	Et_3N	DMF	100	12	66
19	$Pd(Ph_3P)_4$[e]	/	Et_3N	DMF	100	24	75
20	$Pd(Ph_3P)_4$[e]	/	Et_3N	DMF	90	24	10
21	$Pd(Ph_3P)_4$[e]	/	Et_3N	DMF	120	24	70

[a]Reaction conditions: (*Z*)-**14** (0.01 mmol), [Pd] catalyst (10 mol%), ligand (20 mol%), base (5 equiv), solvent (1 mL), Ar, *T*, 12 h. [b]Isolated yields. [c]TBAI was added. [d]DMF/H_2O (10:1), [e]20 mol% of $Pd(PPh_3)_4$ was used. PMP = 1,2,2,6,6-pentamethylenepiperidine, DIPEA = N,N-diisopropylethylamine.

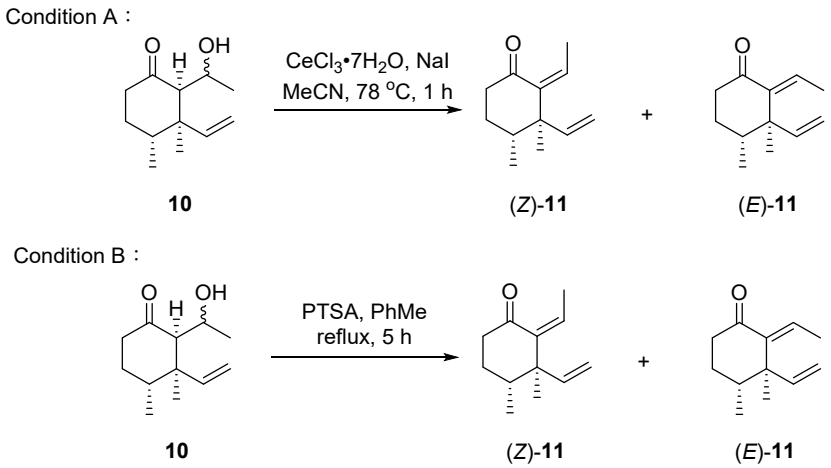
II. Experimental Procedures and Spectroscopic Data

General Information. All reactions involving air or moisture sensitive reagents or intermediates were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D. Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to isolated compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (60F-254) using Tsingdao silica gel (60, particle size 0.040-0.063 mm). And the silica gel from the same company was also used for flash column chromatography. NMR spectra were recorded on a Brüker AVANCE 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or a Brüker AVANCE 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) instrument. Chemical shifts were reported in parts per million (ppm) with respect to the residual solvent signal $CDCl_3$ (^{1}H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.00$). Peak multiplicities were reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet, br = broad signal. High resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). X-ray diffraction data were collected by using a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer.



(+)-**8** **10**

Compound 10. To a mixture of CuI (3.80 g, 20.0 mmol) in dry THF (100 mL), vinylmagnesium bromide (1.0 M in THF, 40 mL, 40.0 mmol) was added at –78 °C over 10 min. The mixture was then warmed to –15 °C and stirred at this temperature for 30 min. The reaction mixture was cooled to –78 °C and a solution of enone (+)-**8** (2.1 g, 17 mmol) in THF (20 mL) was added dropwise. After stirring for 1 h at this temperature, a solution of acetaldehyde (5.0 M in THF, 4 mL, 20.0 mmol) in THF (20 mL) was added dropwise and stirred at –78 °C for 2 h. The reaction mixture was quenched with saturated aqueous ammonium chloride (100 mL) and extracted with diethyl ether (3 x 100 mL) The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude product was used for dehydration without further purification.

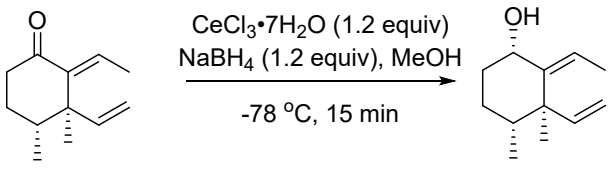


Compounds (*Z*)-**11 and** (*E*)-**11**. Condition A: A suspension of $CeCl_3•7H_2O$ (5.96 g, 16 mmol) and NaI (2.4 g, 16 mmol) in acetonitrile (20 mL) was stirred at refluxing temperature for 24 h. After being cooled to room temperature, this mixture was treated with **10** (981 mg, 5 mmol), and the resulting mixture was refluxed for 1 h. The reaction mixture was then diluted with ether (20 mL) and treated with 0.5 N HCl (50 mL). The organic layer was separated and the aqueous layer was extracted with ether (3 x 30 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (silica, ethyl acetate/hexane = 1:10) to give (*Z*)-**11** (715 mg, 80%) as a yellow oil and (*E*)-**11** (146 mg, 16%) as a yellow oil.

Condition B: To a solution of alcohol **10** (981 mg, 5 mmol) in toluene (30 mL) was added PTSA (172 mg, 1 mmol). The reaction mixture was allowed to be heated to reflux for 5 h. Then the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:10) to afford (*Z*)-**11** (45 mg, 5%) as a yellow oil and (*E*)-**11** (712 mg, 80%) as a yellow oil.

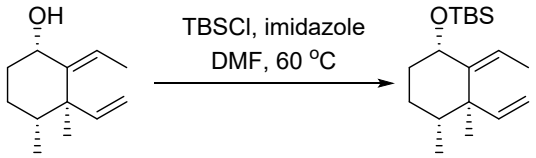
(*Z*)-**11**, TLC: R_f = 0.75 (ethyl acetate/hexane = 1:10). $[\alpha]^{26}_D$ -5.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 – 5.64 (m, 2H), 5.12 (dd, *J* = 10.7, 1.2 Hz, 1H), 4.95 (dd, *J* = 17.5, 1.2 Hz, 1H), 2.47 (m, 1H), 2.36 (m, 1H), 1.96 (m, 1H), 1.89 – 1.83 (m, 1H), 1.82 (d, *J* = 7.2 Hz, 3H), 1.69 – 1.63 (m, 1H), 1.01 (s, 3H), 0.92 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 205.0, 145.9, 144.7, 130.4, 114.2, 49.5, 40.8, 38.5, 28.6, 19.2, 15.6, 15.3. HRMS (ESI-TOF) calculated for $C_{12}H_{19}O$ ($[M + H]^+$) 179.1430, found 179.1428.

(*E*)-**11**, TLC: R_f = 0.68 (ethyl acetate/hexane = 1:10). $[\alpha]^{26}_D$ -5.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (q, *J* = 7.3, 4.9, 2.3 Hz, 1H), 5.74 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.04 – 4.92 (m, 2H), 2.64 (m, 1H), 2.38 (d, *J* = 17.0 Hz, 1H), 2.27 (d, *J* = 16.9 Hz, 1H), 2.17 – 2.09 (m, 1H), 1.88 – 1.81 (m, 1H), 1.73 (d, *J* = 7.3 Hz, 3H), 0.97 – 0.93 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) 200.3, 146.6, 135.5, 134.8, 112.1, 51.0, 40.7, 36.5, 31.3, 17.7, 16.0, 13.7. HRMS (ESI-TOF) calculated for $C_{12}H_{19}O$ ($[M + H]^+$) 179.1430, found 179.1425.



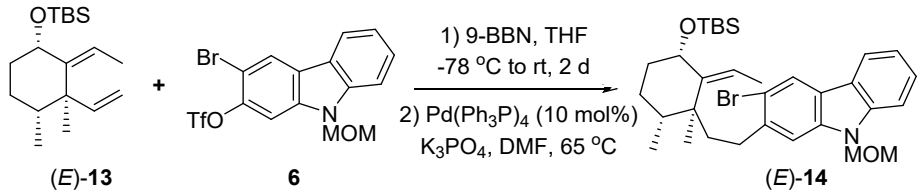
(*E*)-**11** (*E*)-**12**

Compound (*E*)-**12**. $CeCl_3$•$7H_2O$ (2.24 g, 6 mmol) was added to the solution of ketone (*E*)-**11** (890 mg, 5 mmol) in MeOH (30 mL) at -78 °C. Then $NaBH_4$ (227 mg, 6 mmol) was added to the solution in portions. After addition, the resultant yellow-colored solution was then stirred at -78 °C for 15 min. Then the reaction mixture was warmed to 0 °C and quenched with water (30 mL), extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (silica, ethyl acetate/hexane = 1:6) to give (*E*)-**12** (829 mg, 92%) as a colorless liquid. TLC: R_f = 0.38 (ethyl acetate/hexane = 1:10). $[\alpha]^{26}_D$ -4.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (dd, *J* = 17.8, 10.6 Hz, 1H), 5.44 (q, *J* = 6.7, 3.7 Hz, 1H), 4.95 (dq, *J* = 13.9, 1.6 Hz, 2H), 4.25 – 4.06 (m, 1H), 2.50 (dd, *J* = 14.4, 4.1 Hz, 1H), 1.87 (s, 1H), 1.75 (dd, *J* = 12.2, 4.1 Hz, 1H), 1.69 – 1.64 (m, 1H), 1.63 (dt, *J* = 6.7, 1.6 Hz, 3H), 1.45 – 1.35 (m, 1H), 1.30 (d, *J* = 11.9 Hz, 1H), 1.00 (s, 3H), 0.79 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 141.2, 111.8, 111.2, 69.6, 49.4, 40.8, 39.8, 31.2, 16.0, 15.8, 12.2. HRMS (ESI-TOF) calculated for $C_{12}H_{20}NaO$ ($[M + Na]^+$) 203.1403, found 203.1399.



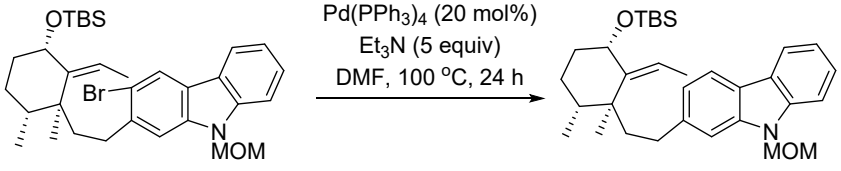
(*E*)-**12** (*E*)-**13**

Compound (*E*)-**13**. To a solution of alcohol (*E*)-**12** (630 mg, 3.5 mmol) in DMF (25 mL) were added imidazole (721 mg, 10.6 mmol) and TBSCl (790 mg, 5.3 mmol). The reaction mixture was allowed to stir at 60 °C for 12 h. Then the mixture was diluted with water (25 mL) and extracted with diethyl ether (3 x 20 mL). The combined organic extracts were washed with brine for three times, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane) to afford (*E*)-**13** (979 mg, 95%) as a colorless liquid. TLC: R_f = 0.95 (hexane). $[\alpha]^{26}_D$ -1.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (dd, *J* = 17.8, 10.5 Hz, 1H), 5.51 (td, *J* = 7.1, 5.2, 2.1 Hz, 1H), 5.01 – 4.88 (m, 2H), 4.18 (m, *J* = 11.7, 4.6, 2.4 Hz, 1H), 2.51 (dd, *J* = 14.3, 3.9 Hz, 1H), 1.69 – 1.58 (m, 5H), 1.44 – 1.33 (m, 2H), 1.02 (s, 3H), 0.92 (s, 9H), 0.80 (d, *J* = 6.8 Hz, 3H), 0.07 (d, *J* = 5.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8, 140.7, 112.5, 111.0, 70.3, 50.2, 41.0, 39.9, 31.5, 26.0, 16.2, 15.5, 12.3, -4.9, -4.9. HRMS (ESI-TOF) calculated for $C_{18}H_{34}NaOSi$ ($[M + Na]^+$) 317.2271, found 317.2275.



(*E*)-**13** **6** (*E*)-**14**

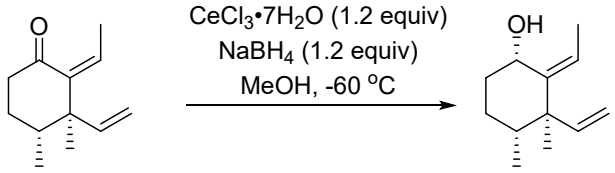
Compound (*E*)-**14**. To a solution of (*E*)-**13** (294.6 mg, 1 mmol) in dry THF (0.5 mL) was added 9-BBN (0.5 M in THF, 2.4 mL, 1.2 mmol) dropwise at -78 °C. The reaction was then allowed to warm to room temperature and stirred for 2 days. To a separate vial was added $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol), K_3PO_4 (159 mg, 0.75 mmol) and carbozole **6** (219 mg, 0.5 mmol) in the glovebox. Then the vial was removed, DMF (2 mL) was added and the solution was sparged with nitrogen for 15 min. The THF solution was then added to the DMF mixture and the reaction was heated at 65 °C for 12 h. The reaction was quenched with water (5 mL) and extracted with diethyl ether (3 x 10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica, ethyl acetate/hexane = 1:50) to give to obtain (*E*)-**14** as a white solid (219 mg, 75%). TLC: R_f= 0.70 (ethyl acetate/hexane = 1:10), mp 96 – 98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.98 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.35 (s, 1H), 7.29 – 7.23 (m, 1H), 5.65 (s, 2H), 5.52 (m, 1H), 4.25 – 4.18 (m, 1H), 3.29 (s, 3H), 2.84 (dd, *J* = 9.5, 8.1 Hz, 2H), 2.50 (dd, *J* = 13.9, 3.8 Hz, 1H), 1.84 (dd, *J* = 12.2, 4.7 Hz, 1H), 1.69 (d, *J* = 13.2 Hz, 1H), 1.65 (dt, *J* = 6.9, 1.5 Hz, 3H), 1.63 – 1.58 (m, 2H), 1.54 – 1.46 (m, 2H), 1.01 (s, 3H), 0.96 (s, 9H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.11 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.02, 140.97, 140.2, 140.1, 126.3, 124.2, 123.4, 122.5, 120.3, 120.3, 115.4, 112.3, 110.4, 109.3, 74.2, 70.8, 56.2, 48.6, 43.4, 39.0, 37.3, 31.8, 31.4, 26.0, 18.8, 15.7, 12.4, -4.7, -4.8. HRMS (ESI-TOF) calculated for $C_{32}H_{46}BrNaNO_2Si$ ($[M + Na]^+$) 606.2373, found 606.2371.



(*E*)-**14** **16** (major byproduct)

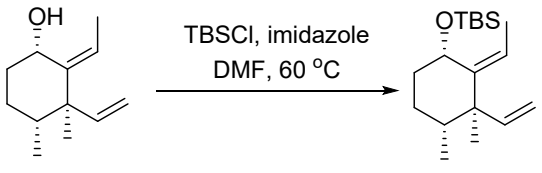
Compound 16. To a vial in the glovebox was added (*E*)-**14** (17.5 mg, 0.03 mmol) and $Pd(PPh_3)_4$ (7 mg, 0.006 mmol). The vial was removed from the glovebox and DMF (3.4 mL) was added, followed by Et_3N (21 µL, 0.15 mmol). The vial was heated to 100 °C and stirred for 24 h. After completion, the reaction was cooled to room temperature and quenched with water (5 mL), extracted with diethyl ether (3 x 10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica, ethyl acetate/hexane = 1:50) to give **16** (12.9 mg, 85%) as a pale yellow liquid. TLC: R_f= 0.70 (ethyl acetate/hexane = 1:10). $[\alpha]^{26}_D$ +4.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ

8.03 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.43 (m, 1H), 7.32 (s, 1H), 7.26 – 7.23 (m, 1H), 7.09 (dd, *J* = 8.0, 1.4 Hz, 1H), 5.68 (s, 2H), 5.54 – 5.48 (m, 1H), 4.20 (d, *J* = 11.3 Hz, 1H), 3.31 (s, 3H), 2.72 (dd, *J* = 10.1, 7.5 Hz, 2H), 2.48 (dd, *J* = 14.0, 3.9 Hz, 1H), 1.78 (dd, *J* = 12.2, 4.7 Hz, 1H), 1.71 – 1.59 (m, 6H), 1.52 – 1.44 (m, 2H), 0.98 (s, 3H), 0.94 (s, 9H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.10 (d, *J* = 2.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 141.0, 140.8, 132.8, 125.5, 121.4, 120.9, 120.2, 120.1, 119.9, 112.3, 109.1, 108.8, 100.0, 74.2, 70.8, 56.1, 48.6, 45.2, 38.9, 37.1, 31.8, 30.6, 26.0, 19.0, 15.6, 12.4, -4.8, -4.8. HRMS (ESI-TOF) calculated for $C_{32}H_{47}NaNO_2Si$ ($[M + Na]^+$) 528.3268, found 528.3270.



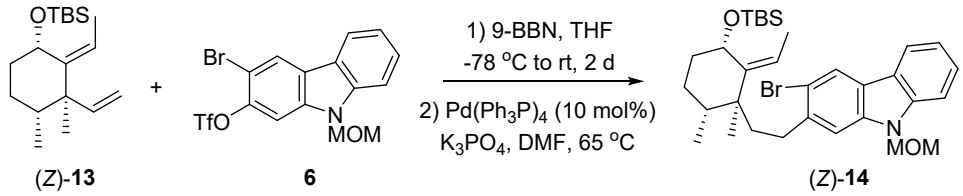
(*Z*)-**11** (*Z*)-**12**

Compound (*Z*)-**12**. $CeCl_3$•$7H_2O$ (2.68 g, 7.2 mmol) was added to the solution of ketone (*Z*)-**11** (1.07g, 6 mmol) in MeOH (35 mL) at -78 °C. Then $NaBH_4$ (272 mg, 7.2 mmol) was added to the solution in portions. After addition, the resultant yellow-colored solution was then stirred at -78 °C for 15 min. Then the reaction mixture was warmed to 0 °C and quenched with water, extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (silica, ethyl acetate/hexane = 1:6) to give (*Z*)-**12** (995 mg, 92%) as a colorless liquid. TLC: R_f = 0.40 (ethyl acetate/hexane = 1:10). $[\alpha]^{26}_D$ -3.9 (*c* 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.50 (q, *J* = 6.9 Hz, 1H), 5.14 (dd, *J* = 10.8, 1.5 Hz, 2H), 4.99 (dd, *J* = 17.6, 1.5 Hz, 1H), 4.87 (t, *J* = 3.0 Hz, 1H), 1.96 (ddd, *J* = 14.0, 5.9, 2.9 Hz, 1H), 1.82 – 1.71 (m, 1H), 1.68 (d, *J* = 6.9 Hz, 3H), 1.56 – 1.46 (m, 1H), 1.42 – 1.31 (m, 2H), 1.25 (s, 1H), 1.16 (s, 3H), 0.78 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 145.7, 123.6, 112.8, 64.4, 46.5, 39.7, 32.8, 24.3, 18.1, 16.9, 13.0. HRMS (ESI-TOF) calculated for $C_{12}H_{20}NaO$ ($[M + Na]^+$) 203.1403, found 203.1402.



(*Z*)-**12** (*Z*)-**13**

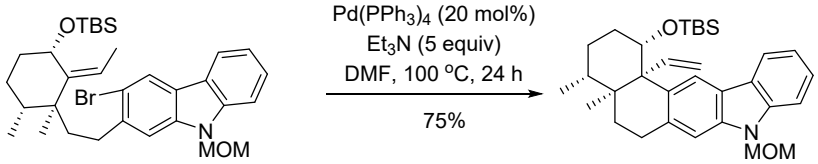
Compound (*Z*)-13. To a solution of alcohol (*Z*)-**12** (720 mg, 4 mmol) in DMF (30 mL) were added imidazole (817 mg, 12 mmol) and TBSCl (904 mg, 30 mmol). The reaction mixture was allowed to stir at 60 °C for 12 h. Then the mixture was diluted with water (30 mL) and extracted with diethyl ether (3 x 30 mL). The combined organic extracts were washed with brine for three times, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane) to afford (*E*)-**13** (1.13 mg, 96%) as a colorless liquid. TLC: R_f = 0.95 (hexane). $[\alpha]^{26}_D$ -1.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (dd, *J* = 17.7, 10.8 Hz, 1H), 5.32 (q, *J* = 7.0 Hz, 1H), 4.94 – 4.83 (m, 2H), 4.72 (t, *J* = 3.8 Hz, 1H), 2.14 (m, 1H), 1.89 (m, 1H), 1.71 (d, *J* = 7.0 Hz, 3H), 1.67 – 1.58 (m, 2H), 1.22 – 1.16 (m, 1H), 1.01 (s, 3H), 0.88 (s, 9H), 0.87 (d, *J* = 1.8 Hz, 3H), 0.78 (d, *J* = 7.0 Hz, 3H), 0.06 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 143.8, 119.9, 108.6, 66.2, 45.6, 36.7, 30.2, 25.7, 24.9, 22.1, 15.7, 13.4, -4.7, -4.8. HRMS (ESI-TOF) calculated for $C_{18}H_{34}NaOSi$ ($[M + Na]^+$) 317.2271, found 317.2266.



(*Z*)-**13** **6** (*Z*)-**14**

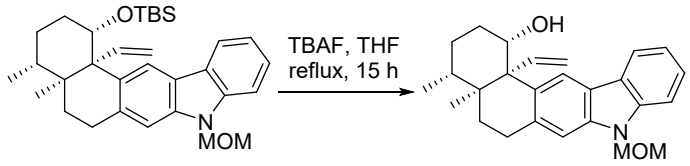
Compound (*Z*)-**14**. To a solution of (*Z*)-**13** (588.5 mg, 2 mmol) in dry THF (1 mL) was added 9-BBN (0.5 M in THF, 4.8 mL, 2.4 mmol) dropwise at -78 °C. The reaction was then allowed to warm to room temperature for 2 days. To a separate vial was added $Pd(PPh_3)_4$ (231 mg, 0.2 mmol), K_3PO_4 (318 mg, 1.5 mmol) and carbozole **6** (438 mg, 1 mmol) in the glovebox. Then the vial was removed, DMF (4 mL) was added and the solution was sparged with nitrogen for 15 min. The THF solution was then added to the DMF mixture and the reaction was heated to 65 °C for 12 h. Then it was quenched with water (10 mL) and extracted with diethyl ether (3 x 15 mL). Then the combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (silica, ethyl acetate/hexane = 1:80) to give (*Z*)-**14** as a white solid (444 mg, 76%). TLC: R_f = 0.65 (ethylacetate/hexane = 1:20). mp 96 – 97.5 °C. $[\alpha]^{26}_D$ +4.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.99 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.52 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.45 (m, 1H), 7.37 (s, 1H), 7.24 – 7.28 (m, 1H), 5.64 (s, 2H), 5.42 (q, *J* = 6.9 Hz, 1H), 4.78 (t, *J* = 3.0 Hz, 1H), 3.26 (s, 3H), 2.80 (m, 2H), 2.42 (tt, *J* = 13.3, 4.6 Hz, 1H), 2.11 (dd, *J* = 9.4, 7.6 Hz, 2H), 1.93 (dt, *J* = 7.4, 3.9 Hz, 1H), 1.74 (d, *J* = 6.9 Hz, 3H), 1.73 – 1.66 (m, 1H), 1.62 (m, 2H), 1.09 (s, 3H), 0.86 (d, *J* = 6.9 Hz, 3H), 0.68 (d, *J* = 0.6 Hz, 9H), 0.06 (s, 3H), -0.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 140.8, 140.6, 140.0, 125.9, 123.8, 122.7, 122.5, 120.8, 120.1, 120.0, 115.6,

109.8, 109.2, 74.0, 65.3, 55.9, 42.6, 40.9, 36.6, 32.3, 29.2, 25.6, 23.9, 17.8, 15.6, 13.3, -4.4, -4.9. HRMS (ESI-TOF) calculated for $C_{32}H_{46}BrNaNO_2Si$ ([M + Na]$^+$) 606.2373, found 606.2375.



(*Z*)-**14** **15**

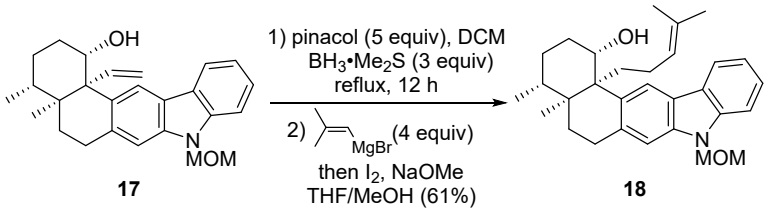
Compound 15. To a vial in the glovebox was added (*Z*)-**14** (25 mg, 0.043 mmol) and $Pd(PPh_3)_4$ (10 mg, 0.0086 mmol). The vial was removed from the glovebox and DMF (5 mL) was added, followed by Et_3N (30 µL, 0.22 mmol). The vial was heated to 100 °C and stirred for 24 h. After completion, the reaction was cooled to room temperature and quenched with water (5 mL), extracted with diethyl ether (3 x 10 mL). Then the combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (silica, ethyl acetate/hexane = 1:50) to give **15** (16 mg, 75%) as a pale yellow liquid. TLC: R_f = 0.6 (ethyl acetate/hexane = 1:20). $[\alpha]^{26}_D$ +4.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.21 – 7.17 (m, 2H), 6.12 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.62 (s, 2H), 5.10 (dd, *J* = 10.5, 2.0 Hz, 1H), 4.44 (dd, *J* = 12.0, 3.9 Hz, 1H), 4.10 (dd, *J* = 17.1, 2.0 Hz, 1H), 3.35 (s, 3H), 2.94 (dd, *J* = 12.7, 6.4 Hz, 1H), 2.90 – 2.84 (m, 1H), 2.03 – 1.84 (m, 3H), 1.73 (t, *J* = 3.7 Hz, 1H), 1.48 (d, *J* = 5.4 Hz, 1H), 1.45 – 1.40 (m, 2H), 1.06 (s, 9H), 0.99 (s, 3H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.18 (d, *J* = 9.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 141.0, 139.0, 137.0, 131.0, 125.1, 124.4, 123.6, 121.7, 120.0, 119.6, 118.3, 108.7, 107.8, 75.8, 74.2, 56.1, 55.2, 40.2, 31.4, 31.1, 30.2, 30.1, 26.7, 26.0, 16.4, 15.9, -4.0, -4.8. HRMS (ESI-TOF) calculated for $C_{32}H_{45}NaNO_2Si$ ([M + Na]$^+$) 526.3112, found 526.3109.



15 **17**

Compound 17. To a solution of **15** (20 mg, 0.04 mmol) in dry THF (3 mL) was added TBAF (1.0 M solution in THF, 0.2 mL, 0.2 mmol) at room temperature. Then the reaction mixture was heated to reflux at 65 °C for 15 h. After this period, the mixture was cooled to room temperature and quenched with water (5 mL). The aqueous phase was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (silica, ethyl acetate/hexane = 1:10) to give **17** (14 mg, 90%) as a colorless liquid. TLC: R_f = 0.2 (ethyl acetate/hexane = 1:20). $[\alpha]^{26}_D$ +6.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR

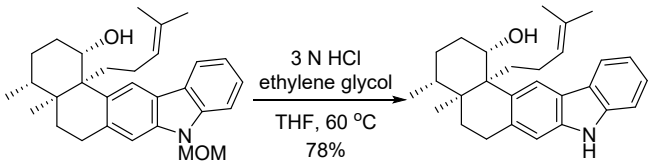
(500 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.04 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.48 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.40 (m, 1H), 7.24 (s, 1H), 7.21 (m, 1H), 6.24 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.62 (d, *J* = 0.8 Hz, 2H), 5.34 (dd, *J* = 10.6, 1.9 Hz, 1H), 4.49 – 4.38 (m, 2H), 3.36 (s, 3H), 3.03 – 2.87 (m, 2H), 2.13 (s, 1H), 1.90 (tt, *J* = 13.3, 7.0 Hz, 3H), 1.80 – 1.73 (m, 1H), 1.57 – 1.52 (m, 1H), 1.48 (td, *J* = 10.4, 9.9, 7.0 Hz, 2H), 1.03 (s, 3H), 0.83 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 141.1, 139.3, 136.8, 130.2, 125.4, 124.2, 122.8, 121,8, 121.1, 120.4, 119.8, 108.8, 108.6, 74.3, 74.2, 56.3, 55.4, 40.3, 31.2, 30.5, 29.9, 29.4, 26.8, 16.6, 16.0. HRMS (ESI-TOF) calculated for $C_{26}H_{31}NaNO_2$ ($[M + Na]^+$) 412.2247, found 412.2252.



Compound 18. To a stirred solution of alcohol **17** (15.6 mg, 0.04 mmol) and pinacol (23.6 mg, 0.2 mmol) in dry CH_2Cl_2 (0.4 mL) was added BH_3•Me_2S (0.12 mL, 1M in THF) dropwise at 0 °C. The solution was stirred at 0 °C for 1 h. Then toluene (0.4 mL) was added to the solution. The resultant mixture was heated to 80 °C and stirred for 5 h. The reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude product was used for the next step without further purification.

The crude product was dissolved in dry THF (0.5 mL). The solution was cooled to -78 °C and 2-methyl-1-propenylmagnesium bromide (0.2 mL, 0.2 mmol, 1 M in THF) was added. After being stirred at -78 °C for 1 h, the solution was allowed to warm up to -40 °C and stirred for 30 min. Then it was cooled to -78 °C again and a THF solution (0.1 mL) of iodine (50 mg, 0.2 mmol) was added. The mixture was stirred at -78 °C for 30 min and a MeOH solution of NaOMe (0.3 mmol, 1 M in MeOH) was added. The mixture was stirred at -78 °C for 10 min and it was allowed to warm up to room temperature for another 30 min. After completion, the reaction was quenched with saturated aqueous $Na_2S_2O_3$ (5 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:10) to afford **18** (10.9 mg, 61%) as a colorless oil. TLC: R_f = 0.36 (ethyl acetate/hexane = 1:10). $[\alpha]^{26}_D$ +6.4 (*c* 0.8, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.97 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.50 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.45 (m, 1H), 7.37 (s, 1H), 7.26 – 7.23 (m, 1H), 5.63 (s, 2H), 5.45 (t, *J* = 7.4 Hz, 1H), 4.85 (d, *J* = 3.1 Hz, 1H), 3.27 (s, 3H), 2.88 (td, *J* = 12.9, 4.9 Hz, 1H), 2.74 (td, *J* = 12.9, 4.4 Hz, 1H), 2.47 – 2.37 (m, 1H), 2.37 – 2.27 (m, 2H), 2.23 (m, 2H), 1.86 – 1.73 (m, 4H), 1.71 – 1.64 (m, 1H), 1.59 (d, *J* = 1.1 Hz, 6H), 1.56 – 1.52 (m, 2H), 1.13 (s, 3H), 0.88 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 138.7, 137.3, 134.4,

130.4, 126.3, 124.1, 123.3, 122.5, 120.30, 120.25, 115.5, 110.5, 109.3, 74.2, 65.4, 56.2, 42.4, 42.2, 39.9, 38.1, 32.7, 27.8, 25.4, 23.8, 23.6, 22.61, 22.58, 18.7, 15.5. HRMS (ESI-TOF) calculated for $C_{30}H_{39}NO_2Na$ ($[M + Na]^+$) 468.2873, found 468.2878.

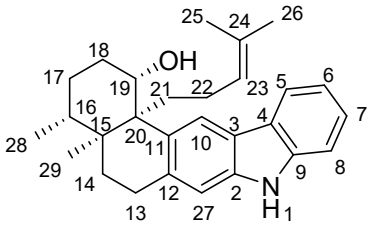


18 (+)-tubingensin A

(+)-Tubingensin A. To a stirred solution of compound **18** (4 mg, 0.009 mmol) in THF (1.5 mL) were added ethylene glycol (40µL, 0.72 mmol) and 3 N HCl (90µL, 0.27 mmol) at room temperature. The resultant mixture was heated to 60 °C and stirred for 15 h. Then the reaction was cooled to room temperature and quenched with saturated aqueous $NaHCO_3$ (2 mL). The mixture was extracted with diethyl ether (3 x 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (silica, ethyl acetate/hexane = 1:6) to give (+)-tubingensin A (2.8 mg, 78%) as a colorless oil. TLC: R_f = 0.40 (ethyl acetate/hexane = 1:5). $[\alpha]^{27}_D$ +10.5 (*c* 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.94 (s, 1H), 7.81 (s, 1H), 7.36 – 7.39 (m, 2H), 7.21 (ddd, *J* = 7.7, 5.8, 1.9 Hz, 1H), 7.14 (s, 1H), 5.04 (t, *J* = 6.9 Hz, 1H), 4.98 (s, 1H), 3.04 – 2.93 (m, 1H), 2.90 (dd, *J* = 17.5, 6.7 Hz, 1H), 2.13 – 1.97 (m, 3H), 1.84 – 1.65 (m, 5H), 1.60 (s, 3H), 1.59 – 1.51 (m, 3H), 1.44 (s, 3H), 1.23 (s, 3H), 1.21 – 1.18 (m, 1H), 0.86 (d, *J* = 5.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 138.0, 135.3, 132.7, 131.7, 125.5, 125.2, 124.0, 121.5, 120.0, 119.3, 118.7, 110.8, 110.6, 71.5, 47.4, 38.9, 35.1, 32.7, 29.8, 29.6, 27.2, 25.8, 25.5, 23.3, 18.5, 17.8, 16.4. HRMS (ESI-TOF) calculated for $C_{28}H_{35}NONa$ ($[M + Na]^+$) 424.2611, found 424.2613.

III. Comparison of the Spectra of Natural and Synthetic Products

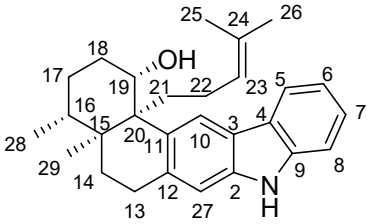
^{1}H NMR spectroscopic data of natural and synthetic (+)-tubingensin A (**1**)



(+)-tubingensin A (**1**)

Position	Natural (Ref.1) (360 MHz) δ_H (*J* in Hz)	Garg (Ref.2) (500 MHz) δ_H (*J* in Hz)	This work (500 MHz) δ_H (*J* in Hz)
NH	7.81, br s	7.81, s	7.81, s
5	7.98, br d (7.8)	8.00, d (7.8)	8.00, d (7.8)
6	7.18, dd (3.9, 7.6, 7.8)	7.19, ddd (7.7, 5.8, 1.8)	7.21, ddd (7.7, 5.8, 1.9)
7	7.34, m	7.39-7.44, m (α)	7.39-7.36, m
8	7.34, m	7.39-7.44, m (β)	7.39-7.36, m
10	7.92, s	7.94, s	7.94, s
13	2.99, ddd (7.3, 12.9, 17.6) 2.88, br dd (6.6, 17.6)	3.07-2.98, m 2.90, dd (17.5, 6.7)	3.04-2.93, m 2.90, dd (17.5, 6.7)
14	1.52, m 2.01, m	1.52, m 2.02, m	1.52, m 2.02, m
16	1.74, m	1.74, m	1.74, m
17	1.17, m 1.70, m	1.18, m 1.70, m	1.18, m 1.70, m
18	1.66, m 2.05, m	1.66, m 2.06, m	1.66, m 2.06, m
19	4.99, br s	4.98, s	4.98, s
21	1.71, m 2.08, m	1.72, m 2.08, m	1.73, m 2.08, m
22	1.76, m 2.06, m	1.77, m 2.06, m	1.77, m 2.06, m
23	5.03, dd (6.6, 5.9)	5.03, app t (6.9)	5.04, t (6.9)
25	1.43, br s	1.44, s	1.44, s
26	1.58, br s	1.59-1.50, m	1.59-1.51, m
27	7.11, s	7.14, s	7.14, s
28	0.85, d (5.6)	0.86, d (5.9)	0.86, d (5.9)
29	1.21, s	1.23, s	1.23, s

^{13}C NMR spectroscopic data of natural and synthetic arbophyllidine (**1**)



(+)-tubingensin A (**1**)

Position	Natural (Ref.1) (90.7 MHz) δ_c	Garg (Ref.2) (125 MHz) δ_c	This work (125 MHz) δ_c
2	137.8	138.0	138.0
3	121.3	121.5	121.5
4	123.8	123.9	124.0
5	119.8	119.9	120.0
6	119.1	119.3	119.3
7	125.3	125.5	125.5
8	110.4	110.6	110.6
9	140.0	140.1	140.2
10	118.5	118.6	118.7
11	132.4	132.6	132.7
12	135.1	135.3	135.5
13	27.1	27.2	27.2
14	29.4	29.5	29.6
15	38.8	38.9	38.9
16	32.6	32.7	32.7
17	25.4	25.5	25.5
18	29.6	29.7	29.8
19	71.4	71.5	71.5
20	47.2	47.4	47.4
21	34.9	35.0	35.1
22	23.1	23.2	23.3
23	125.0	125.2	125.2
24	131.5	131.7	131.7
25	17.6	17.8	17.8
26	25.6	25.8	25.8
27	110.7	110.8	110.8
28	16.2	16.4	16.4
29	18.4	18.5	18.5

IV. References

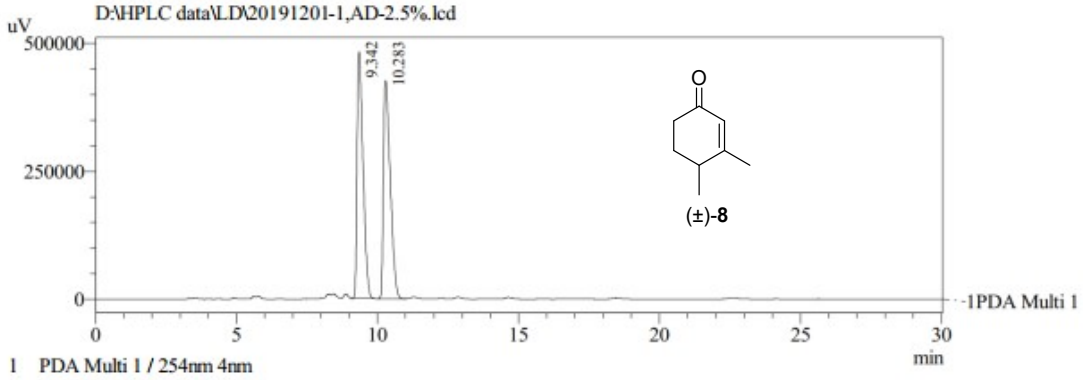
1 M. R. TePaske, J. B. Gloer, D. T. Wicklow and P. F. Dowd, Tubingensin A: An Antiviral Carbazole Alkaloid from the Sclerotia of Aspergillus tubingensis, *J. Org. Chem.*, 1989, **54**, 4743.

2 A. E. Goetz, A. L. Silberstein, M. A. Corsello and N. K. Garg, Concise enantiospecific total synthesis of tubingensin A, *J. Am. Chem. Soc.* 2014, **136**, 3036.

V. HPLC Data

Racemic compound **8**:

HPLC (DAICEL Chiralpak-AD column (0.46 cm × 25 cm); hexane/^{i}PrOH = 80:20; flow rate: 1.0 mL/min; λ = 210 nm)



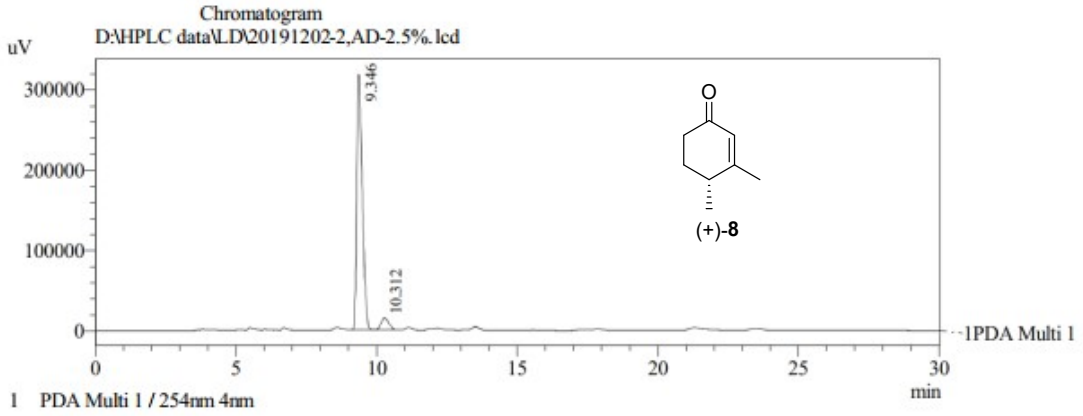
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.342	7106071	481837	49.720	53.099
2	10.283	7186228	425603	50.280	46.901
Total		14292299	907440	100.000	100.000

Optically active compound (+)-**8**:

HPLC (DAICEL Chiralpak-AD column (0.46 cm × 25 cm); hexane/^{i}PrOH = 80:20; flow rate: 1.0 mL/min; λ = 210 nm)



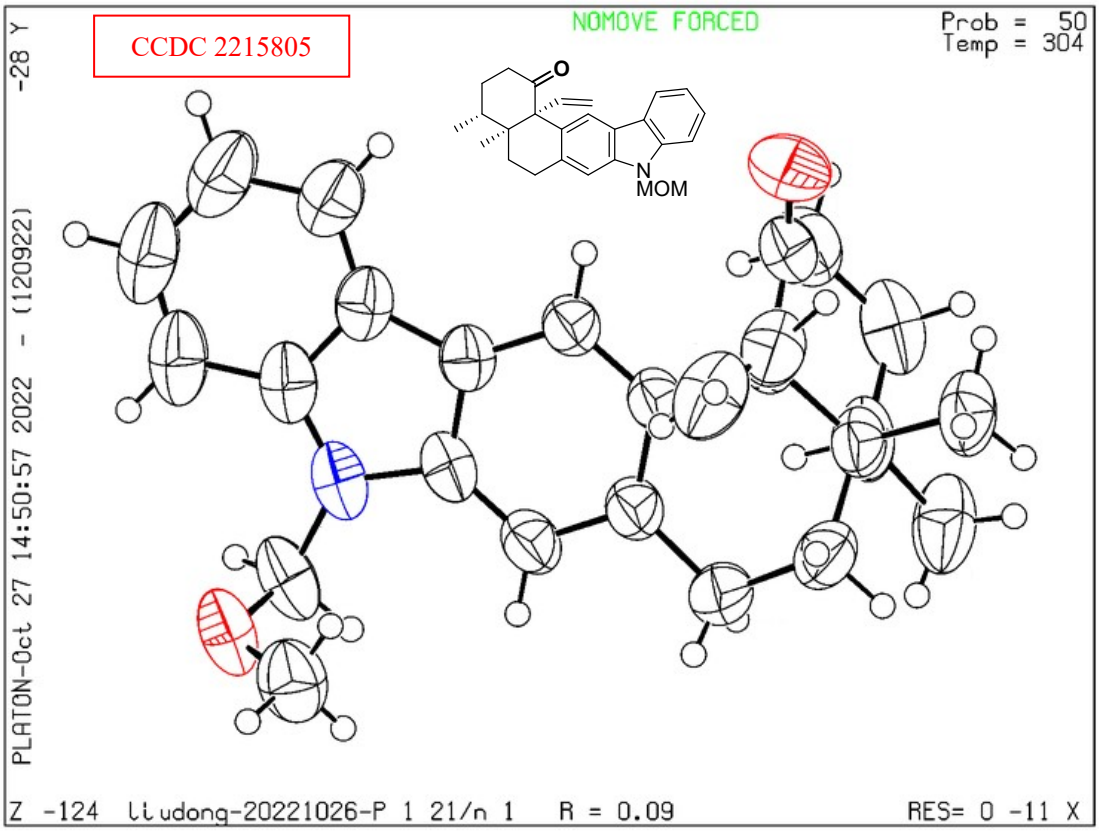
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.346	4568033	321589	95.535	94.442
2	10.312	213495	18926	4.465	5.558
Total		4781528	340515	100.000	100.000

Compound (+)-**8**: *ee* = 95.535% – 4.465% = 91.1%

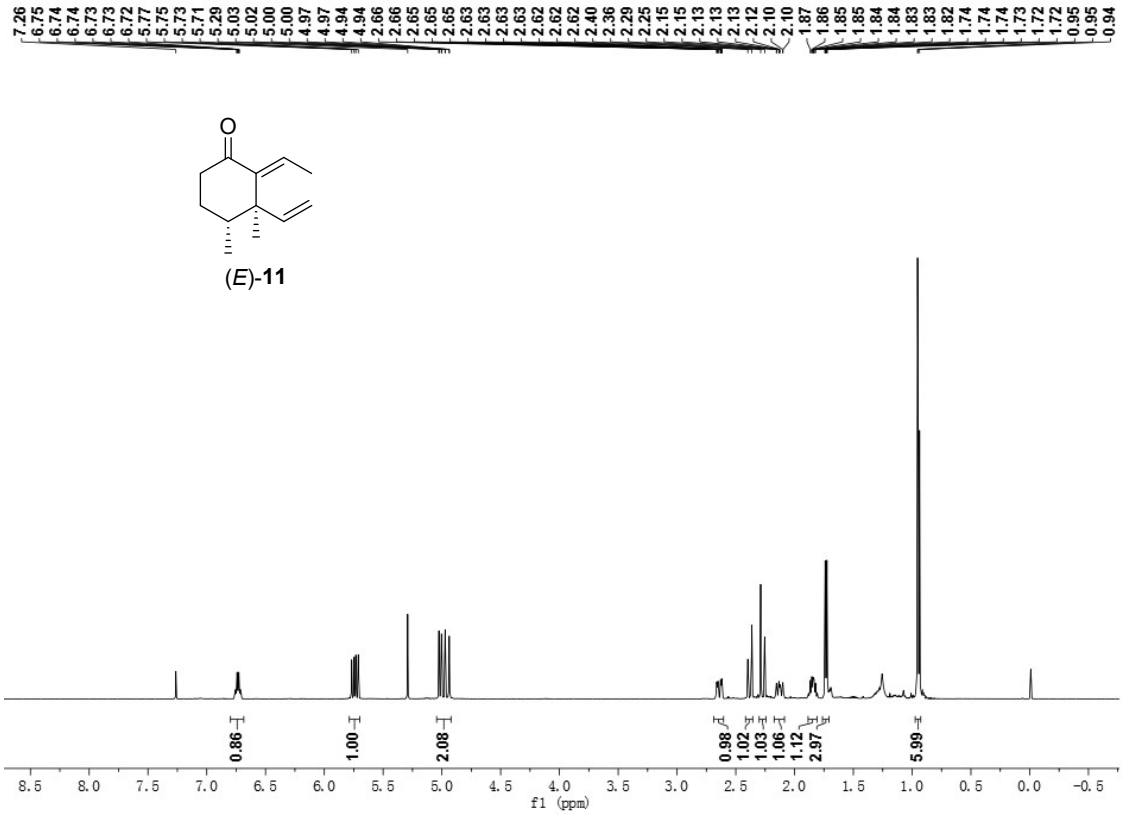
VI. X-Ray Structures of Derivative of 17

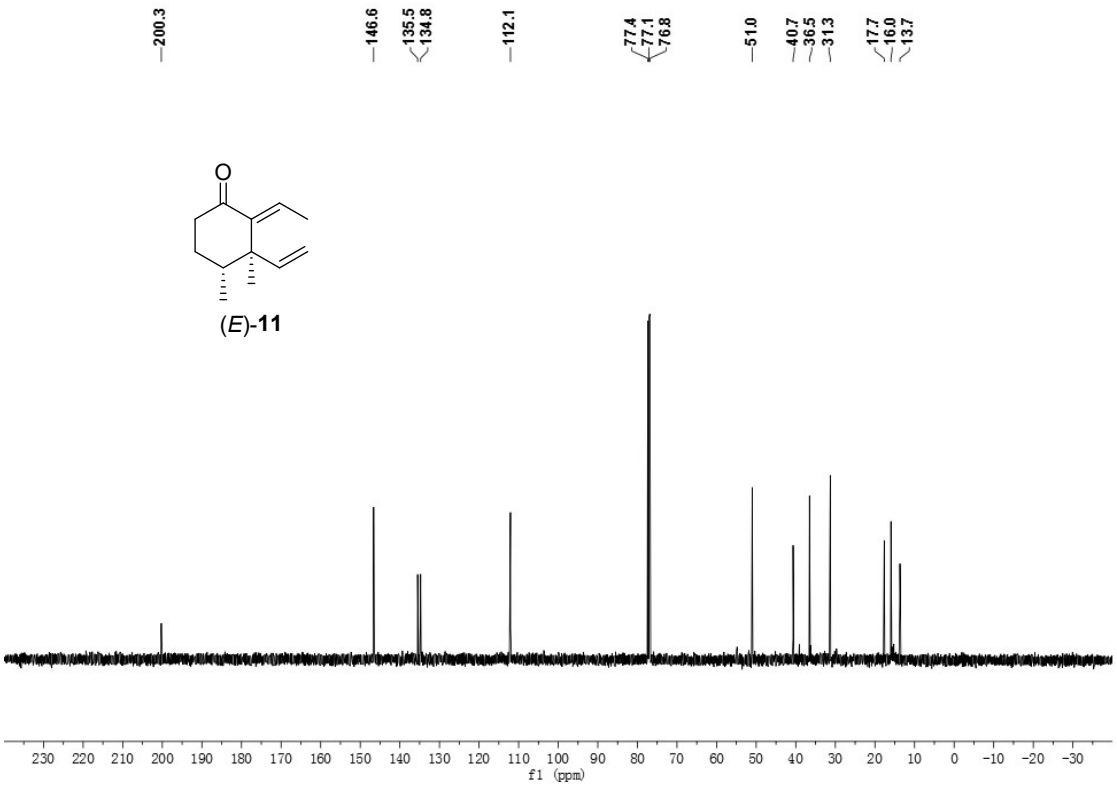


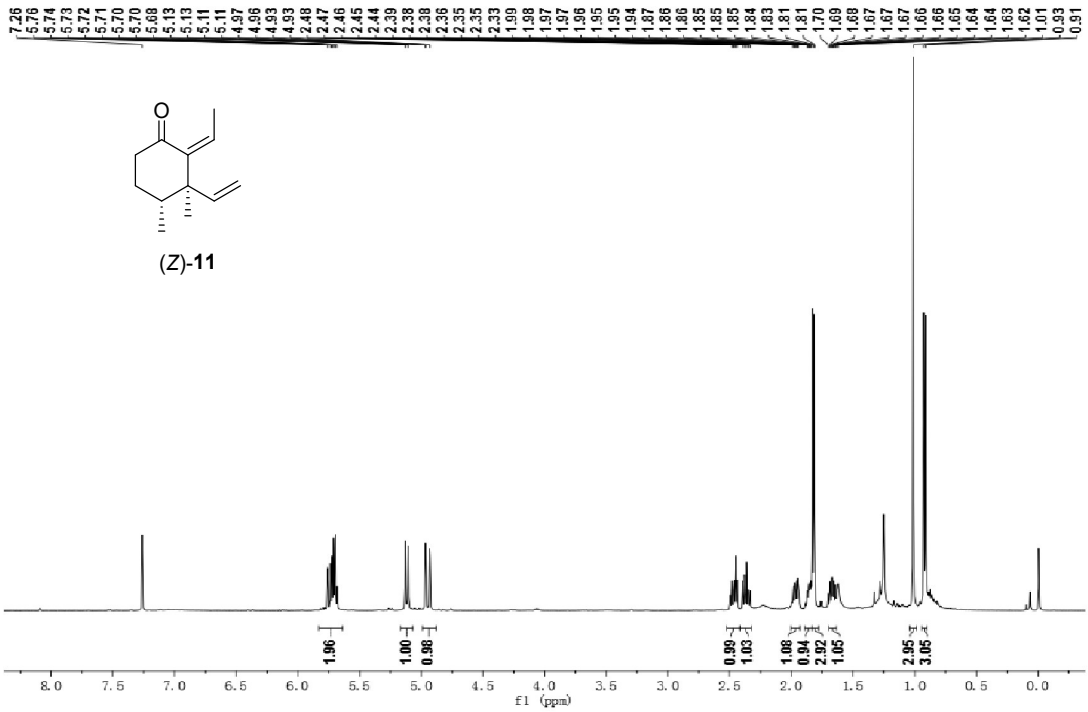
Crystal structure determination of

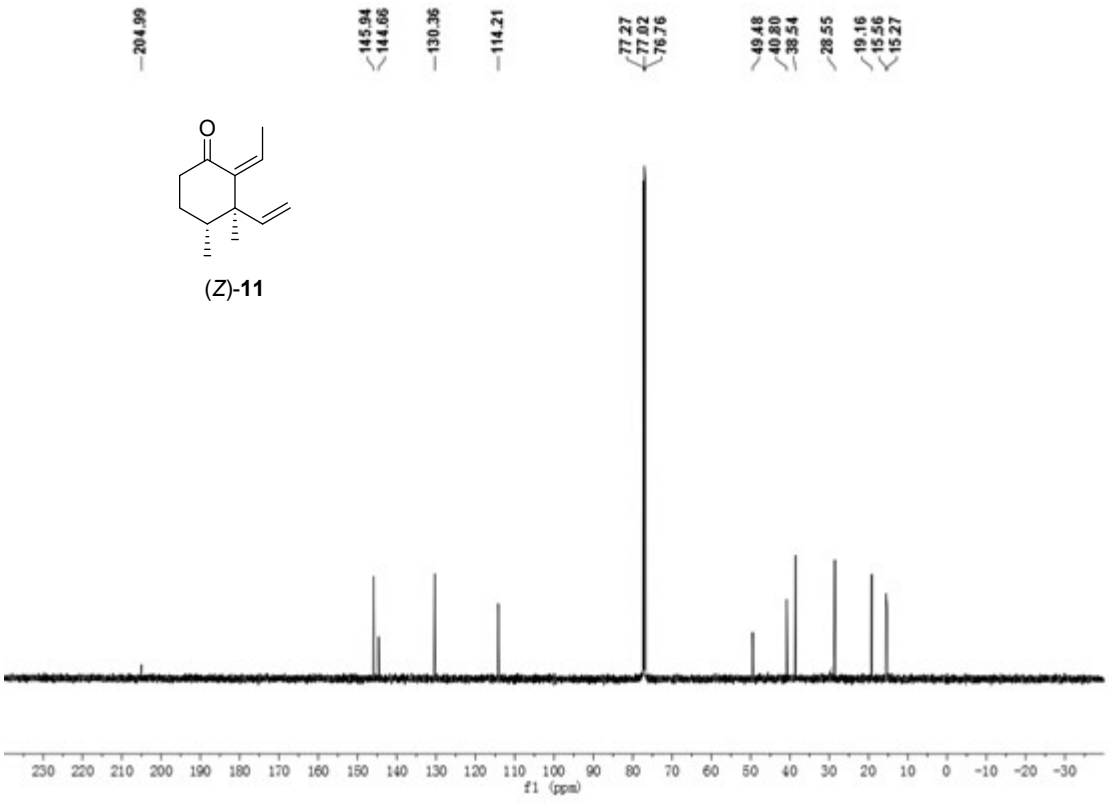
Crystal Data for $C_{26}H_{29}NO_2$ (M_r = 387.52 g/mol): monoclinic, $P2_1/n$ (No. 14), a = 8.0263(2) Å, b = 22.7764(4) Å, c = 11.9389(3) Å, b = 102.925(2)°, $a = g$ = 90°, V = 2127.26(9) Å^3, T = 304(2) K, Z = 4, Z' = 1, m(CuK$_a$) = 0.590, 52864 reflections measured, 4369 unique (R_{int} = 0.0946) which were used in all calculations. The final wR_2 was 0.2713 (all data) and R_1 was 0.0903 (I > 2(I)).

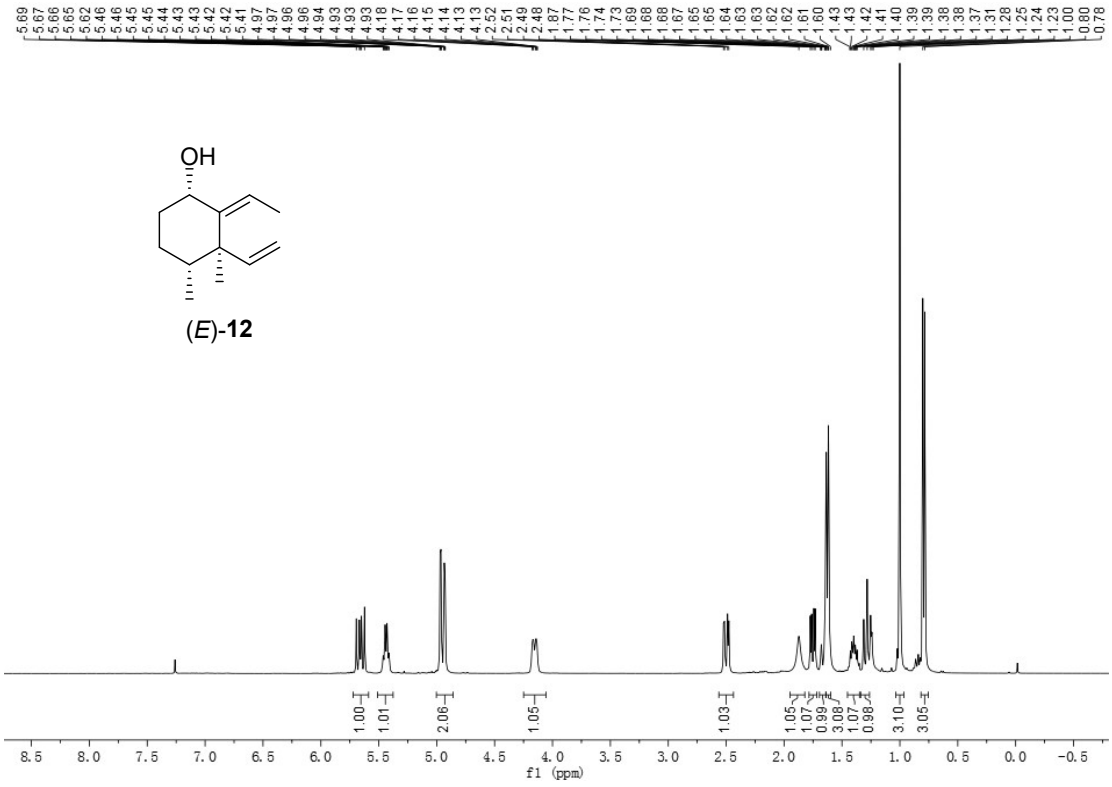
VII. ^{1}H and ^{13}C NMR Spectra of Compounds

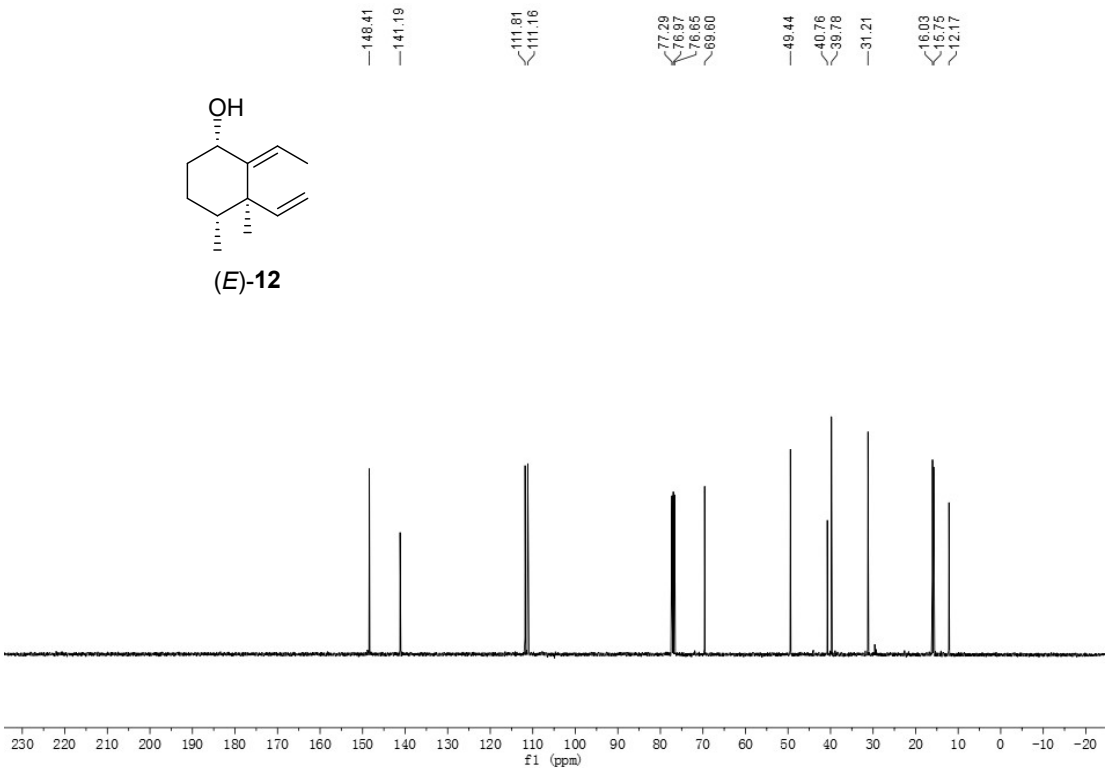


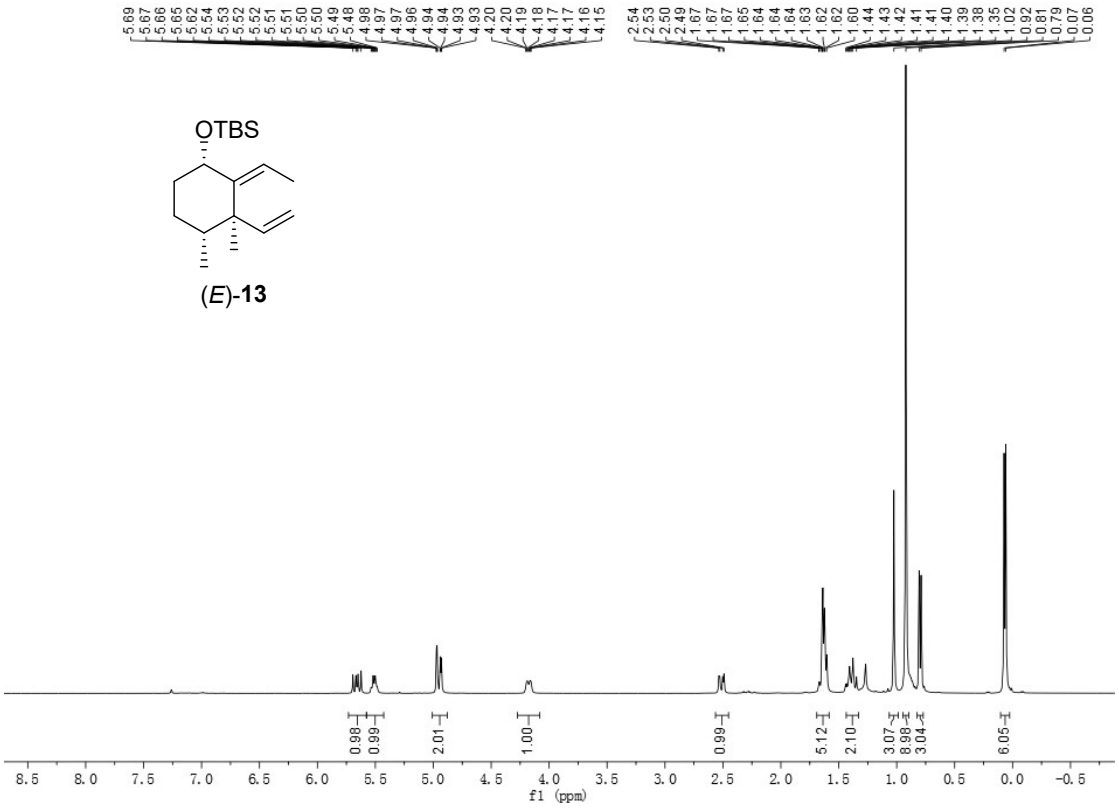


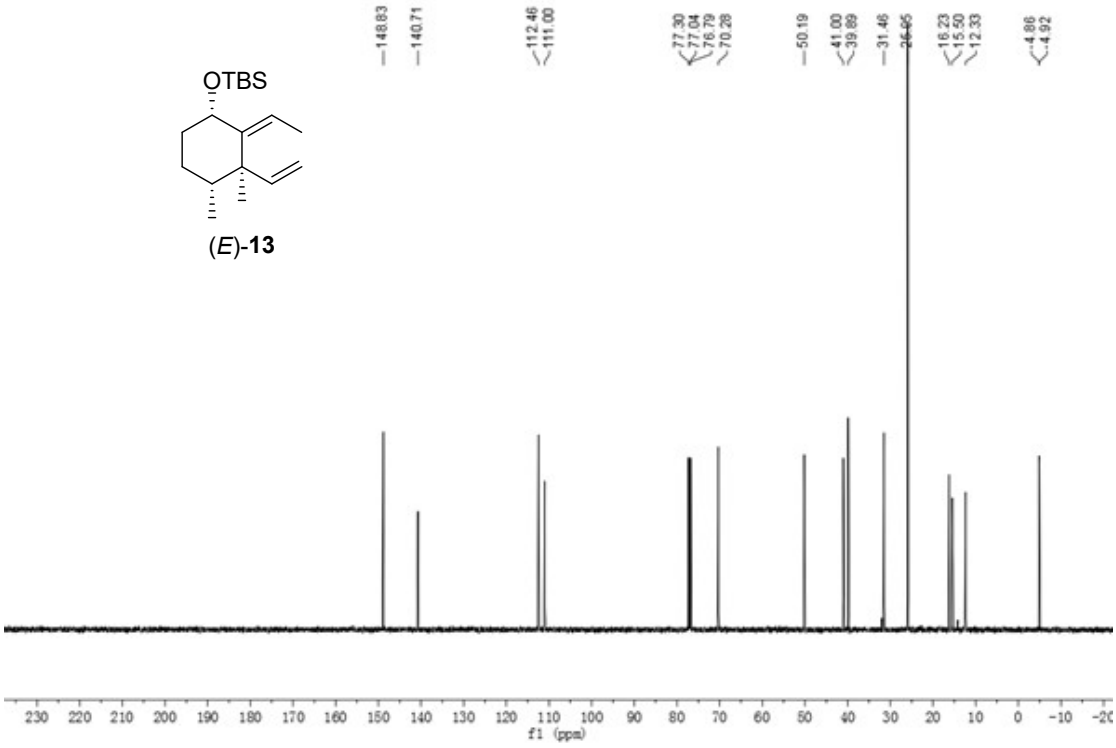

O
(Z)-11
1.96
1.00
0.98
0.99
1.03
1.08
0.94
2.92
1.05
2.95
3.05
f1 (ppm)

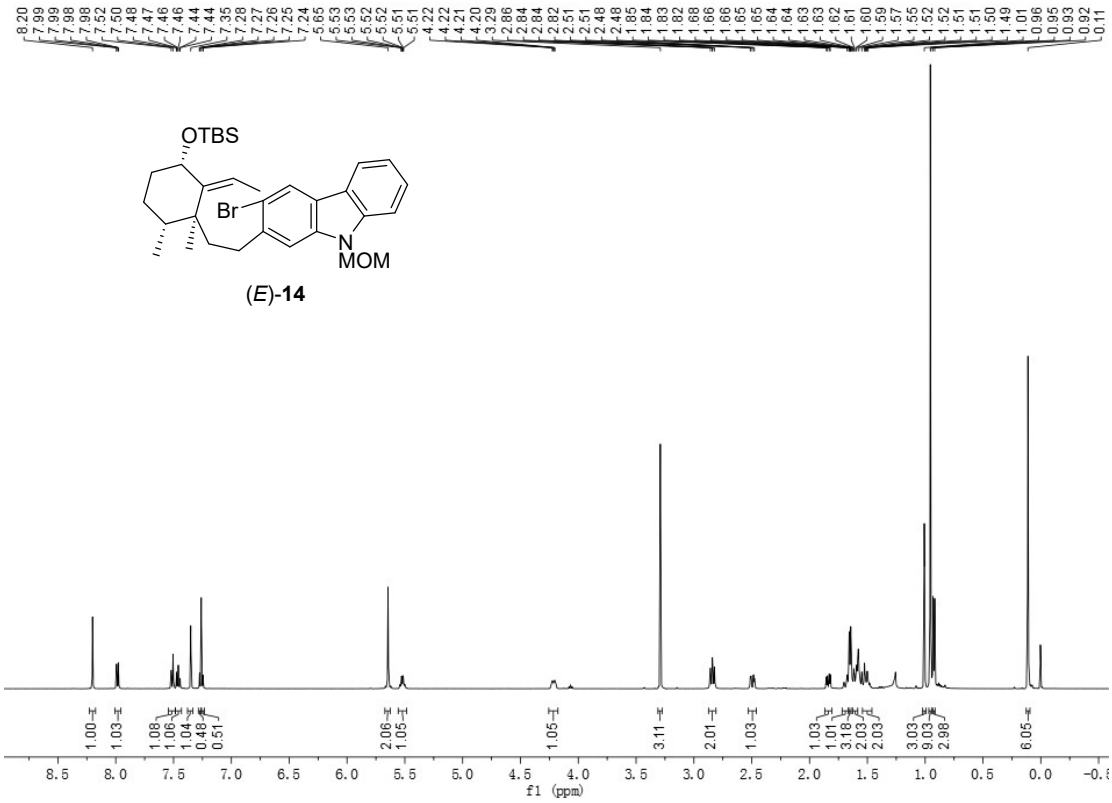

204.99
145.94
144.66
130.36
114.21
77.27
77.02
76.76
49.48
40.80
38.54
28.55
19.16
15.56
15.27
O
(Z)-11
f1 (ppm)


OH
(E)-12
f1 (ppm)

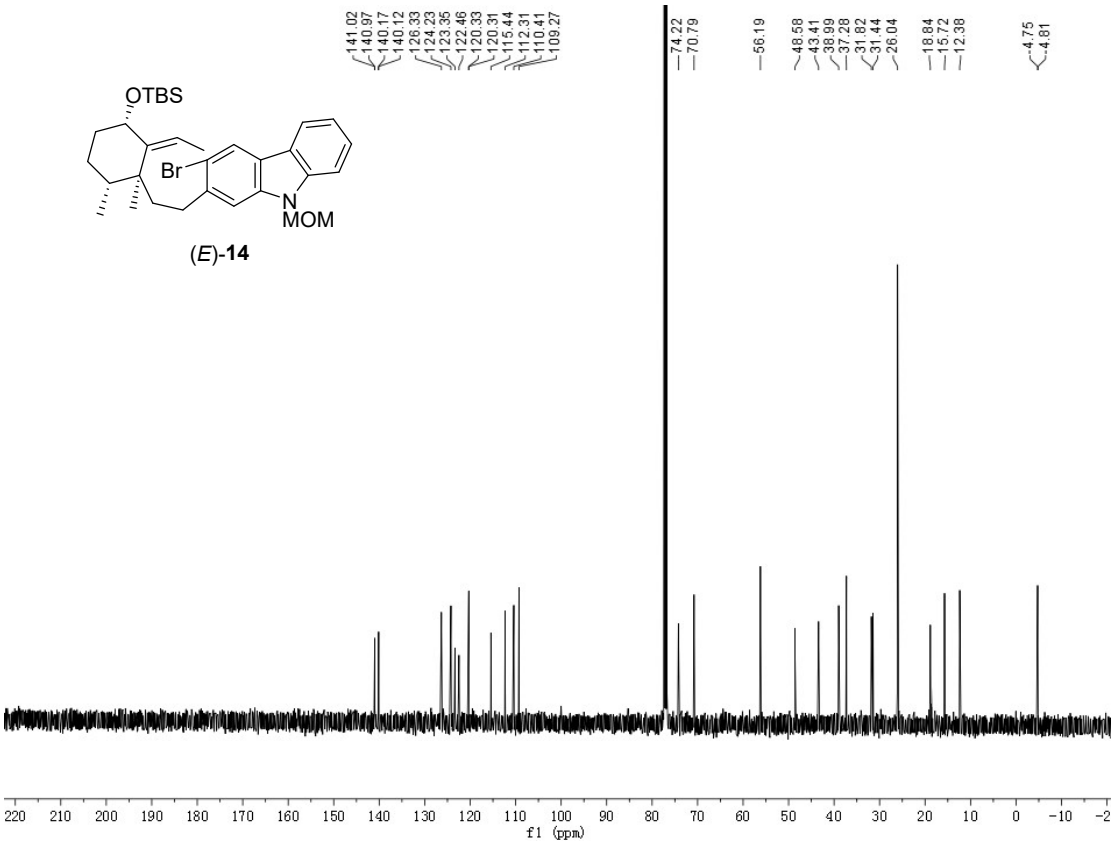

OH
(E)-12
f1 (ppm)


OTBS
(E)-13
f1 (ppm)

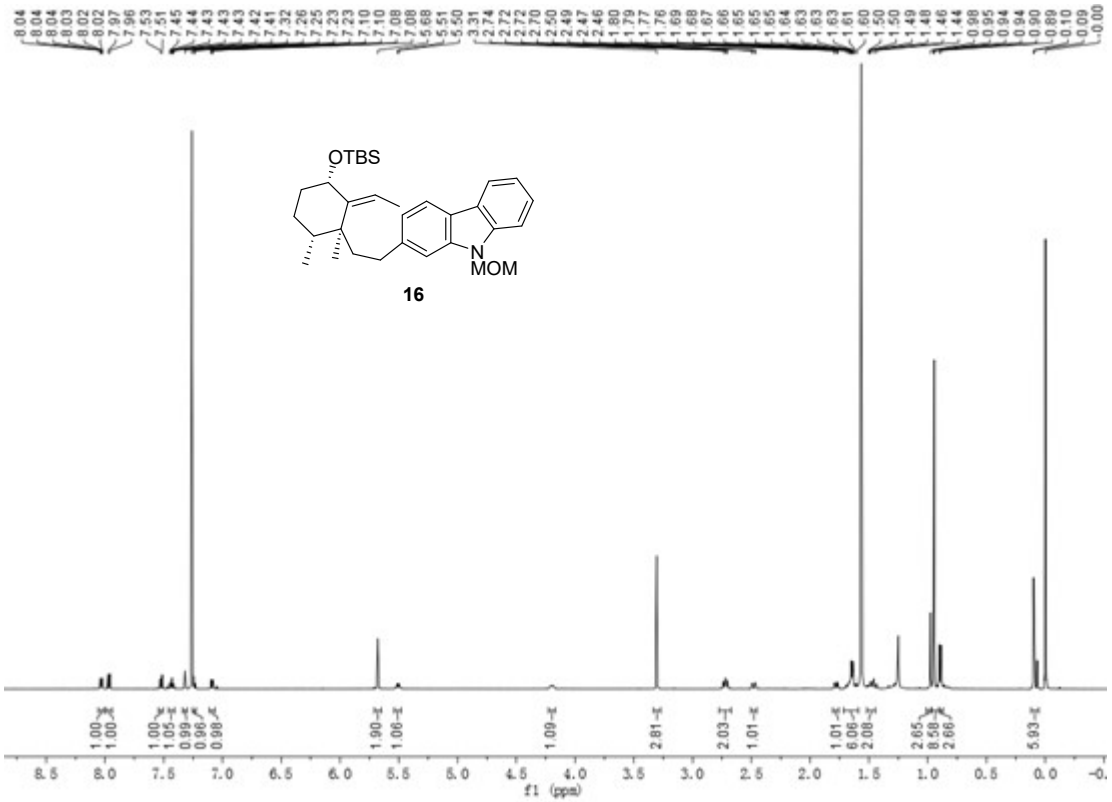

OTBS
(E)-13
f1 (ppm)

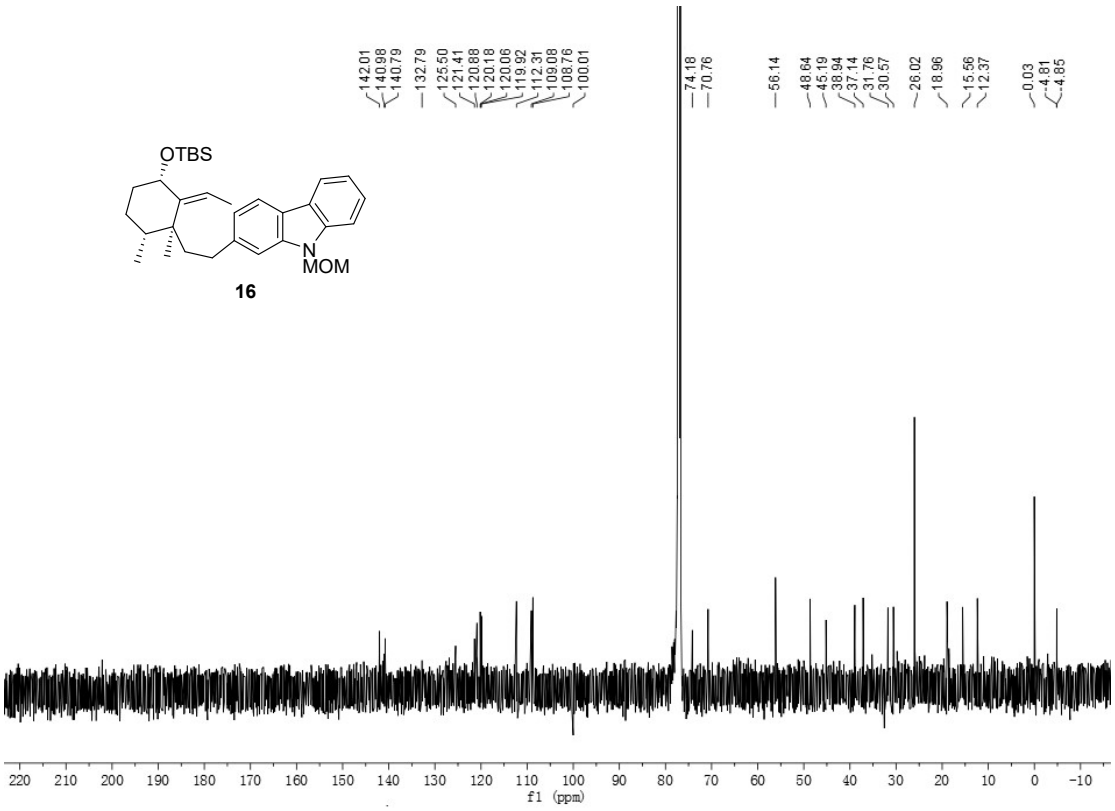


(*E*)-**14**

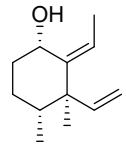


(*E*)-**14**

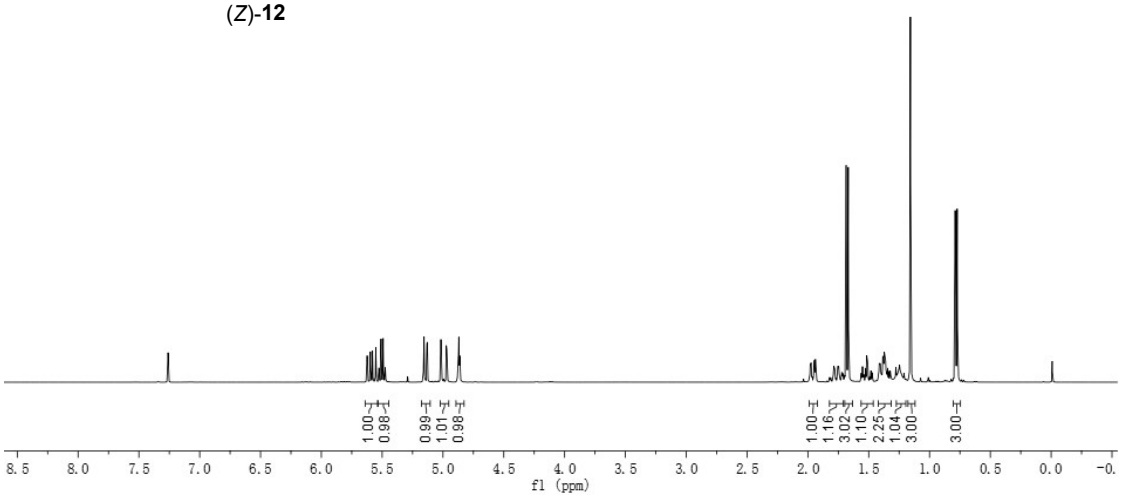

OTBS
N
MOM
16
f1 (ppm)


OTBS
N
MOM
16
f1 (ppm)

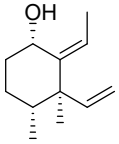

7.26
5.62
5.60
5.58
5.55
5.53
5.51
5.49
5.47
5.16
5.16
5.13
5.13
5.02
5.01
4.97
4.97
4.88
4.87
4.86
1.98
1.97
1.95
1.94
1.79
1.75
1.75
1.69
1.67
1.55
1.53
1.52
1.51
1.41
1.40
1.38
1.38
1.37
1.36
1.34
1.25
0.78
0.77


OH

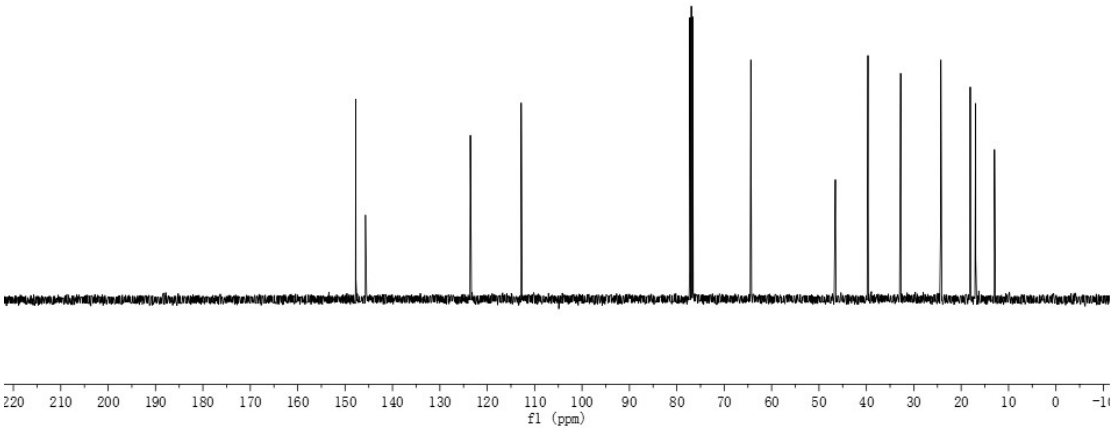
(*Z*)-**12**

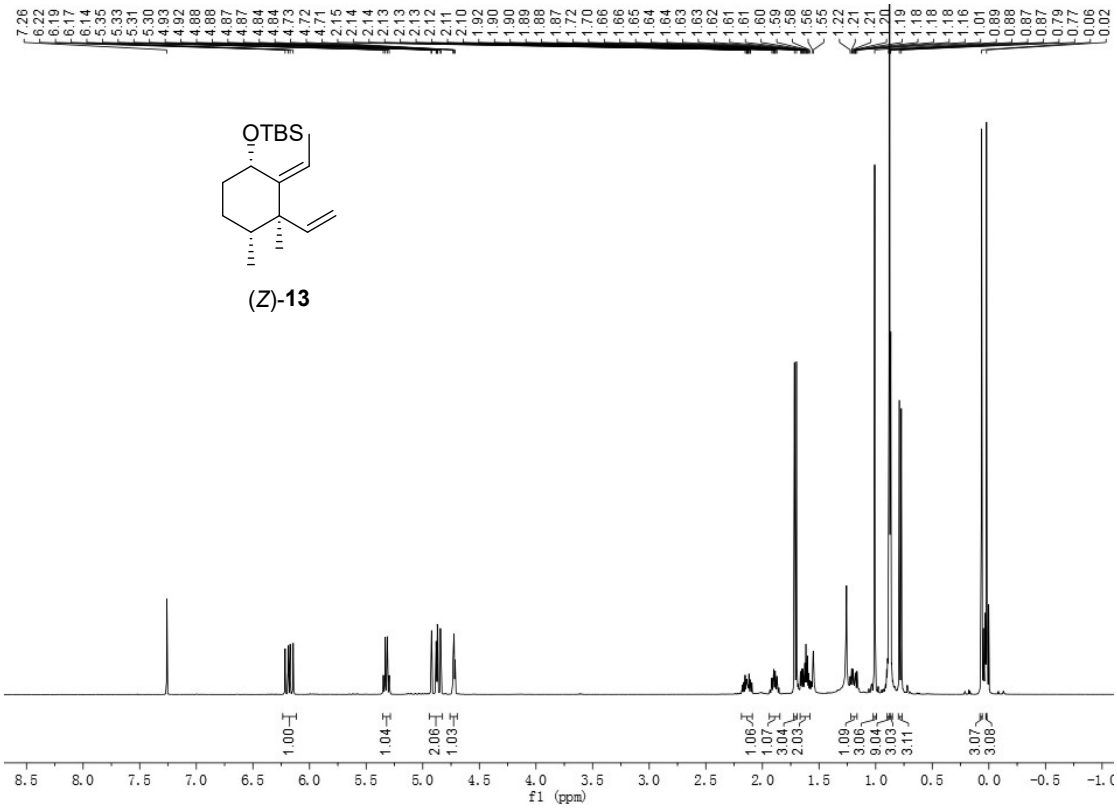

1.00
0.98
0.99
1.01
0.98
1.00
1.16
3.02
1.10
2.25
1.04
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

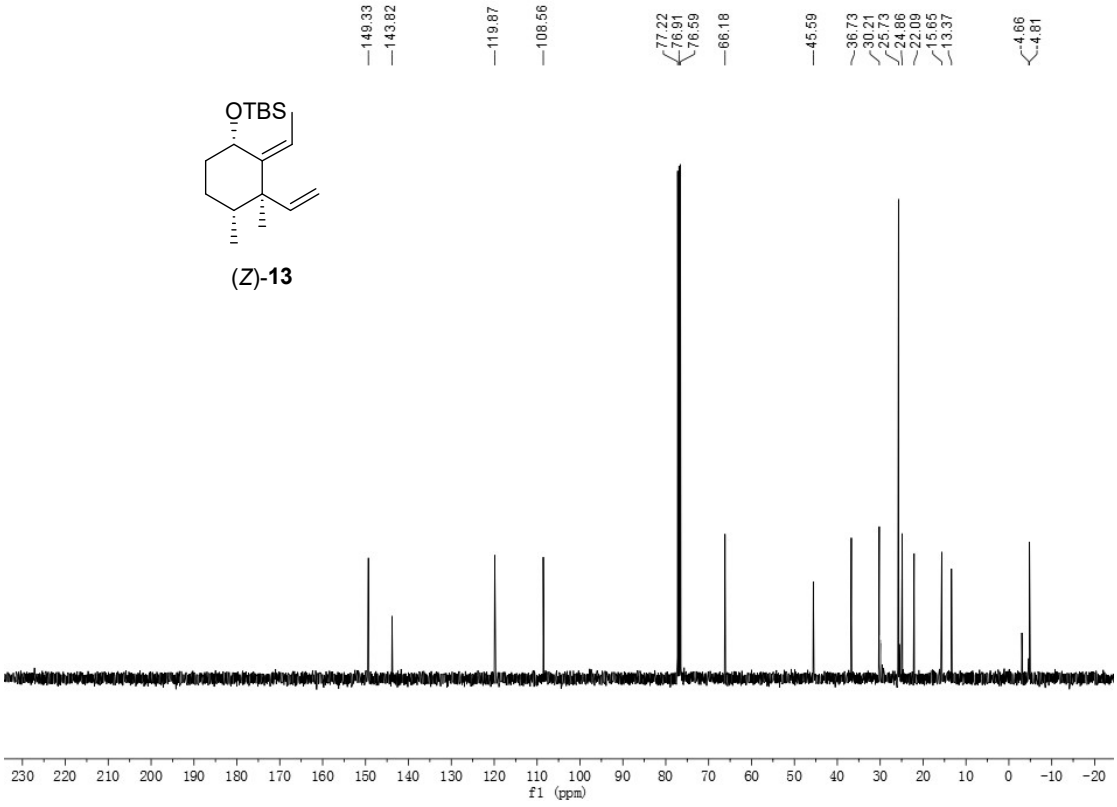

147.74
145.70
123.56
112.84
77.26
76.94
76.62
64.38
46.54
39.67
32.76
24.29
18.08
16.94
12.97

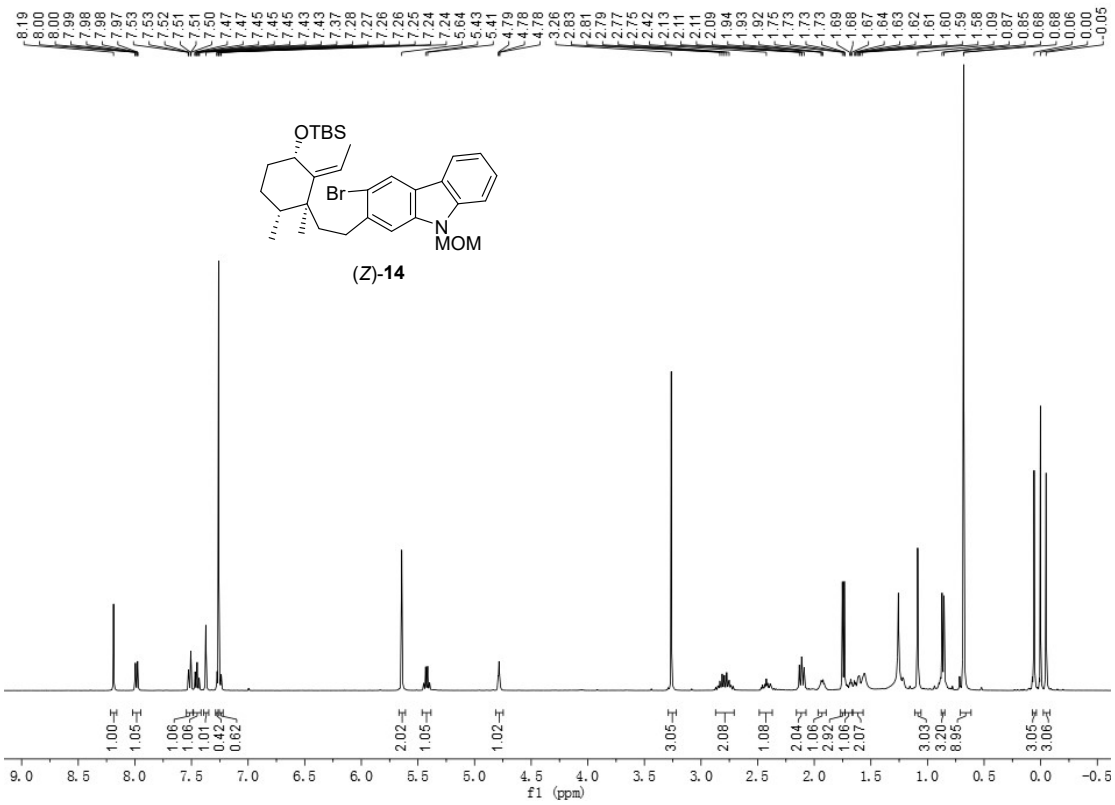

OH

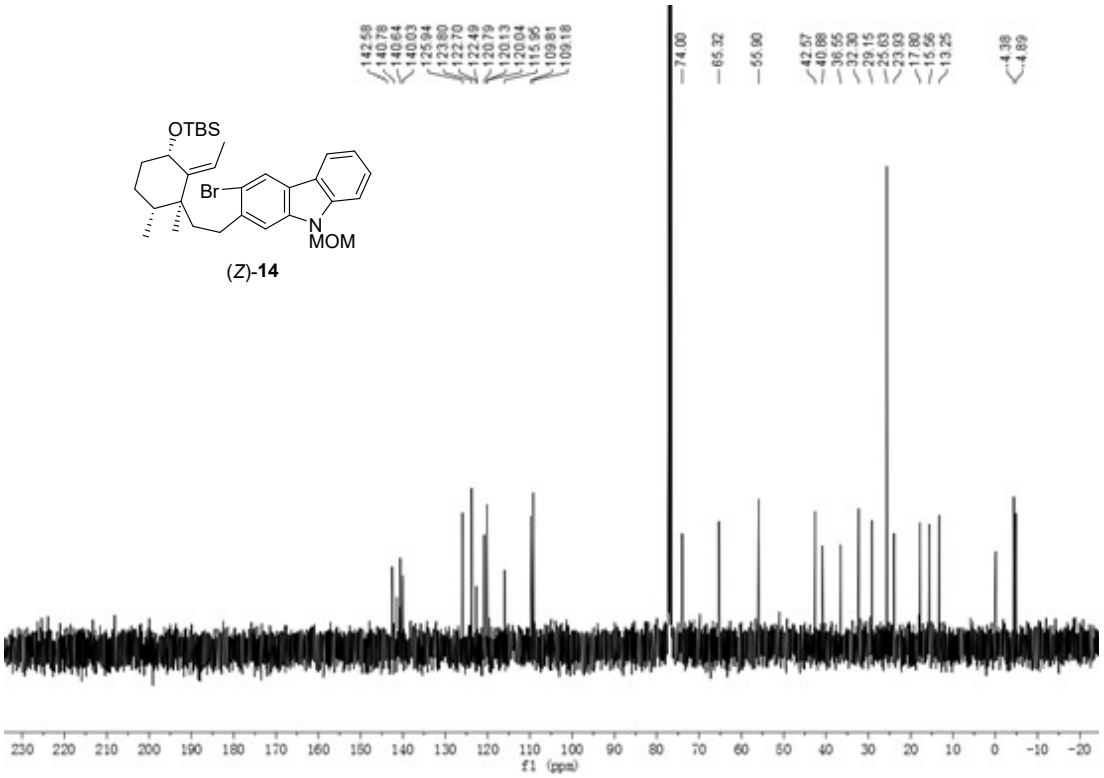
(*Z*)-**12**

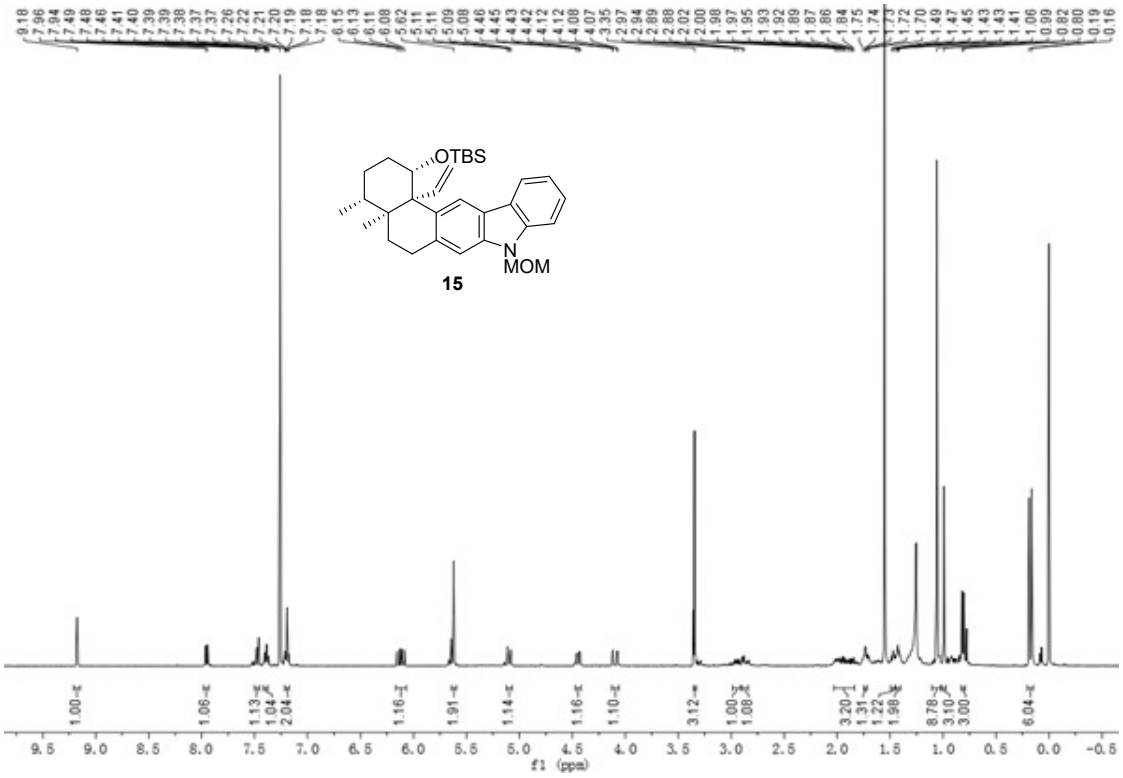

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

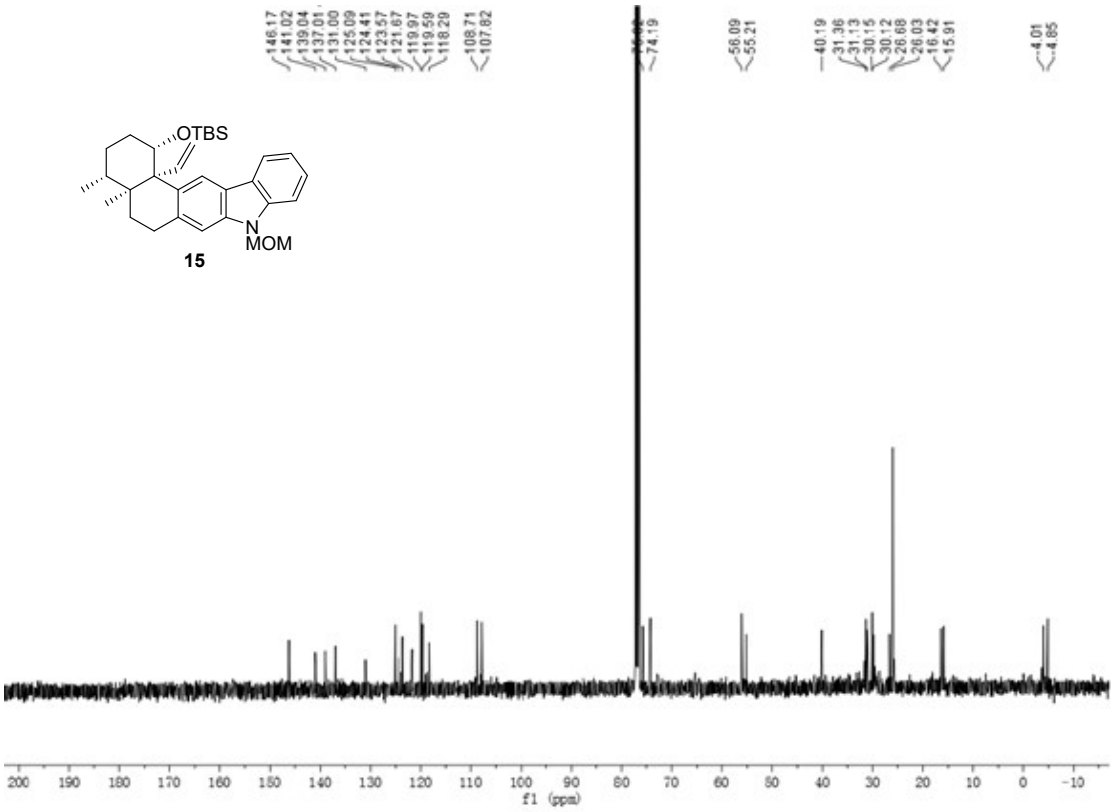

OTBS
(Z)-13
f1 (ppm)

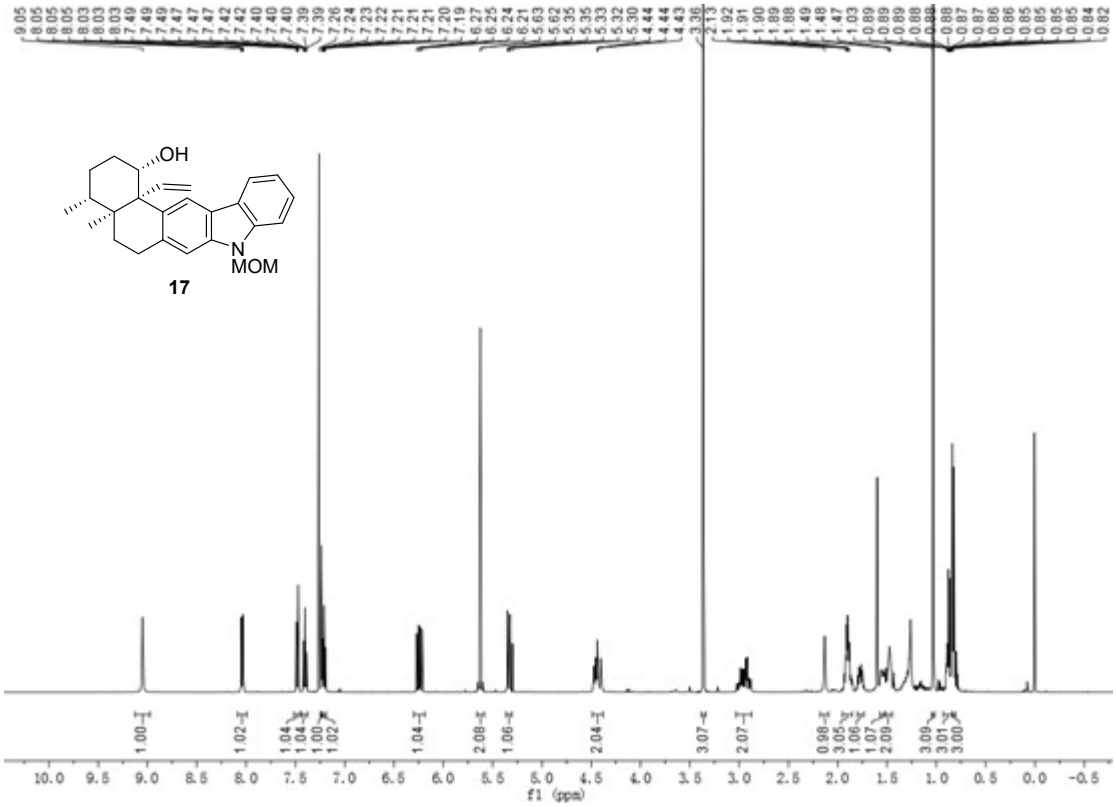

OTBS
(Z)-13
f1 (ppm)

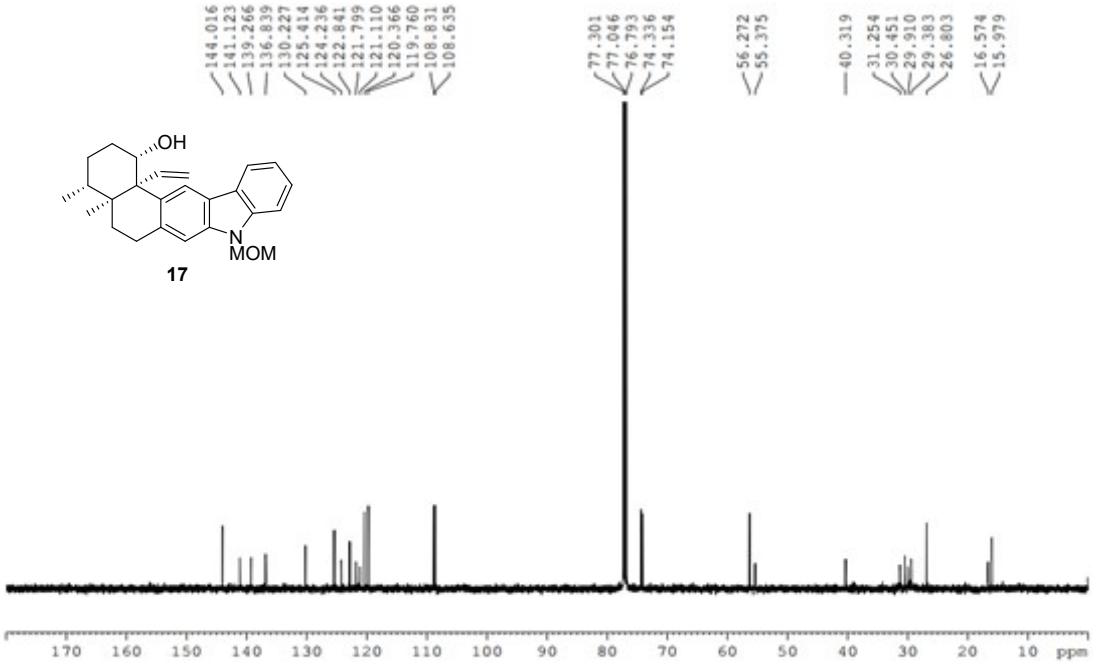

OTBS
Br
N
MOM
(Z)-14
f1 (ppm)

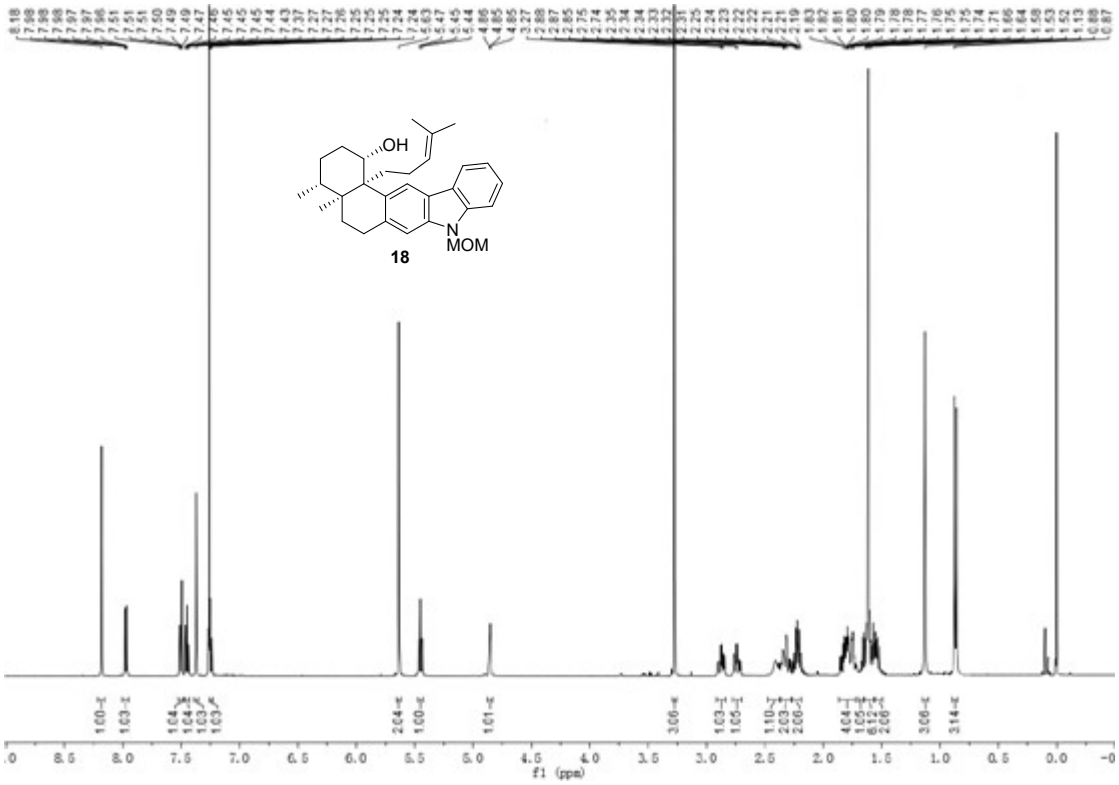

OTBS
Br
N
MOM
(Z)-14
f1 (ppm)

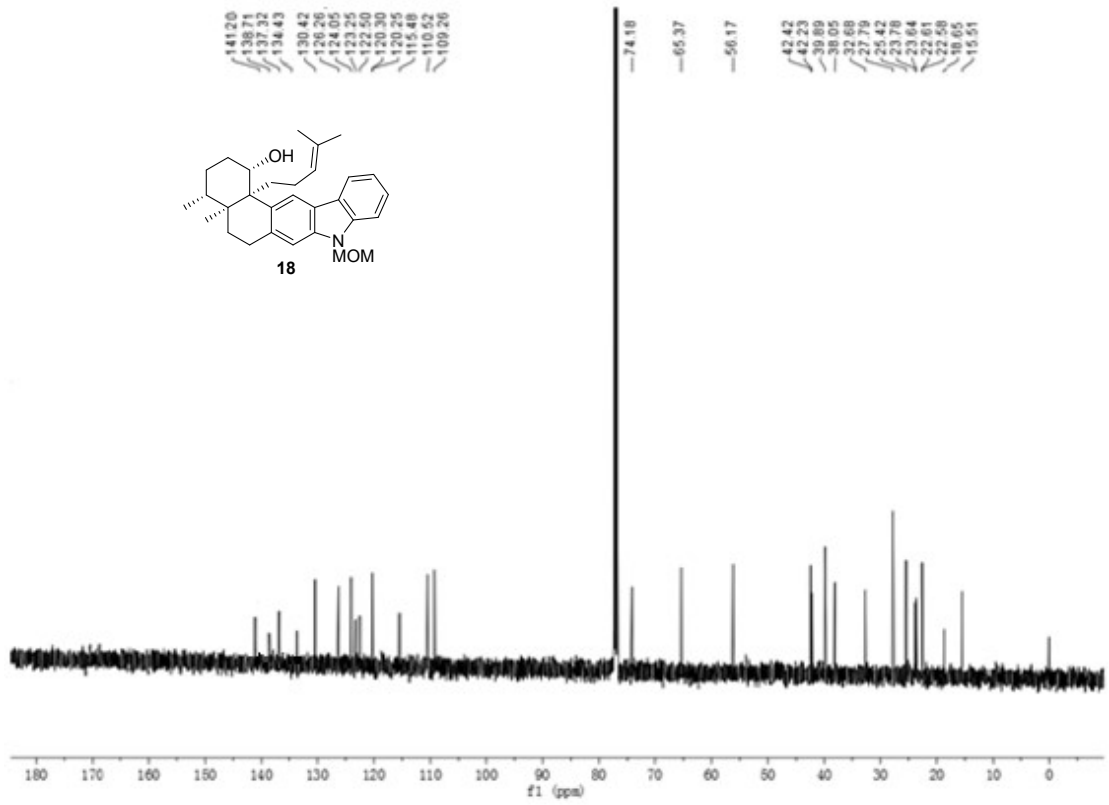

OTBS
N
MOM
15
f1 (ppm)

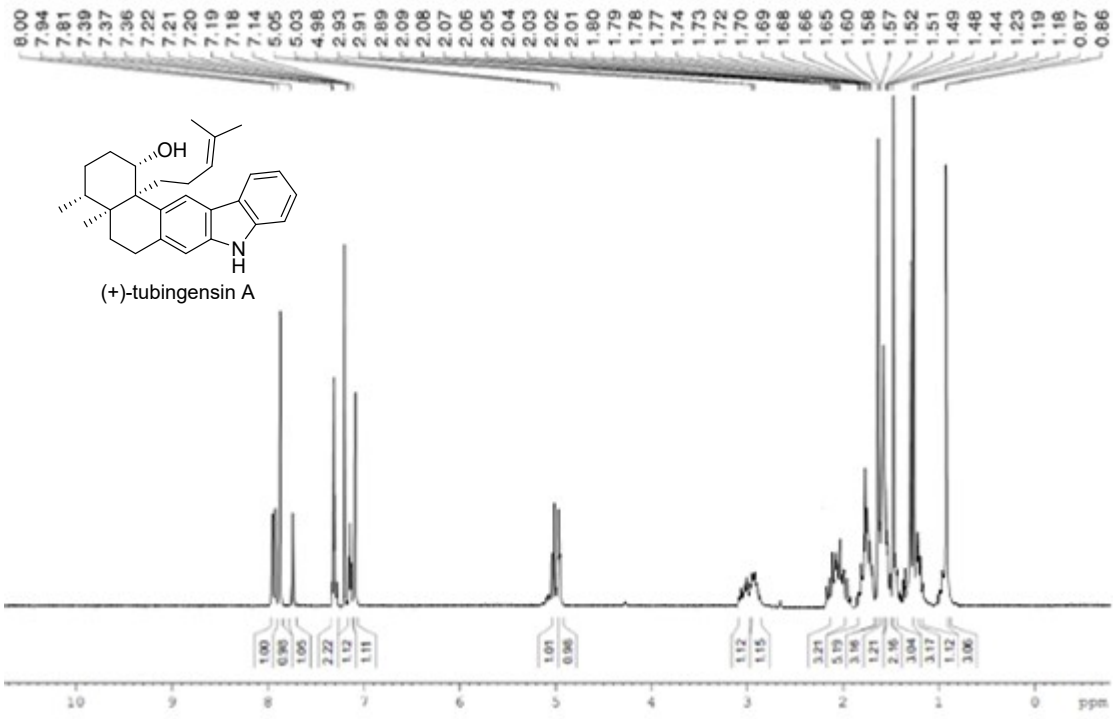

OTBS
N
MOM
15
f1 (ppm)

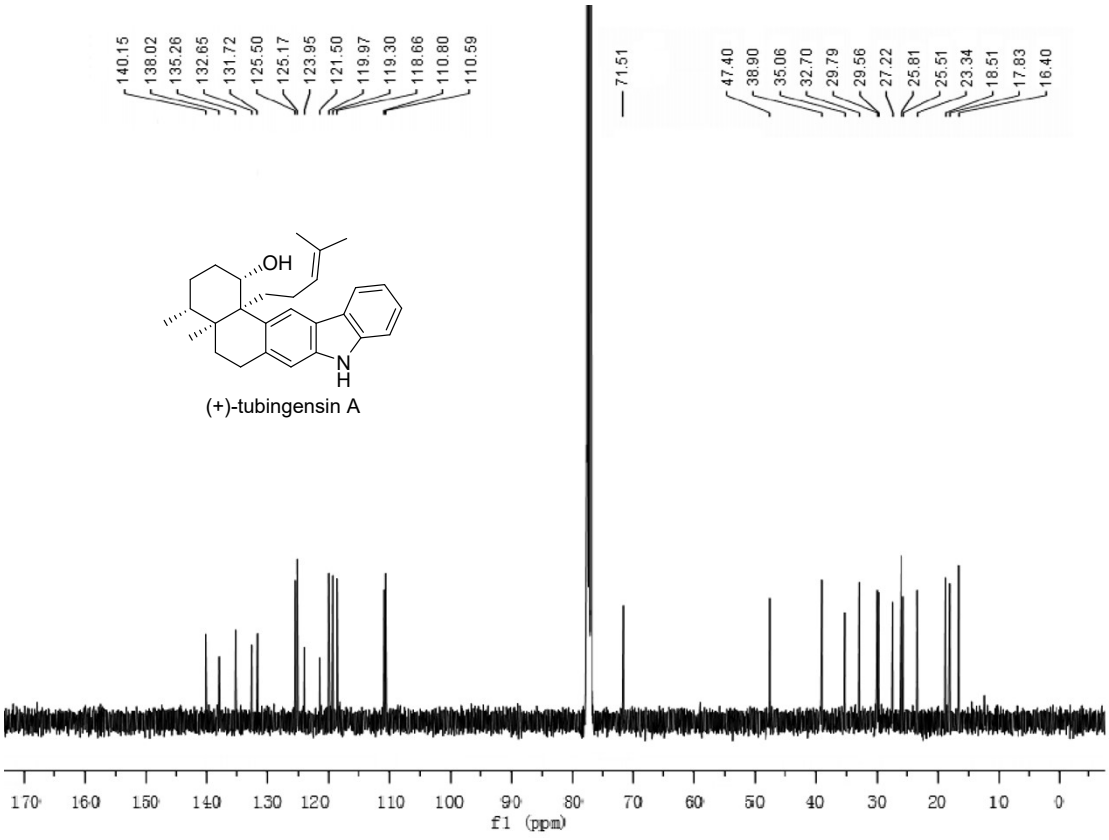

OH
N
MOM
17
f1 (ppm)


OH
N
MOM
17
ppm


OH
N
MOM
18
f1 (ppm)


OH
N
MOM
18
f1 (ppm)


8.00
7.94
7.81
7.39
7.37
7.36
7.22
7.21
7.20
7.19
7.18
7.14
5.05
5.03
4.98
2.93
2.91
2.89
2.09
2.08
2.07
2.06
2.05
2.04
2.03
2.02
2.01
1.80
1.79
1.78
1.77
1.74
1.73
1.72
1.70
1.69
1.68
1.66
1.65
1.60
1.58
1.57
1.52
1.51
1.49
1.48
1.44
1.23
1.19
1.18
0.87
0.86
OH
N
H
(+)-tubingensin A
1.00
0.90
1.05
2.22
1.12
1.11
1.01
0.98
1.12
1.15
3.21
5.19
3.16
1.21
2.16
3.04
3.17
1.12
3.06
10
9
8
7
6
5
4
3
2
1
0
ppm


140.15
138.02
135.26
132.65
131.72
125.50
125.17
123.95
121.50
119.97
119.30
118.66
110.80
110.59
71.51
47.40
38.90
35.06
32.70
29.79
29.56
27.22
25.81
25.51
23.34
18.51
17.83
16.40
OH
N
H
(+)-tubingensin A
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)