Supporting information

Divergent Enantioselective Total Synthesis of Hapalindole-Type Alkaloids Using Catalytic Asymmetric Hydrogenation of a Ketone to Construct the Chiral Core Structure

Yang Liu,[a,†] Li-Jie Cheng,[a,†] Hai-Tao Yue,[a] Wen Che,[a] Jian-Hua Xie*[,a] and Qi-Lin Zhou[a,b]

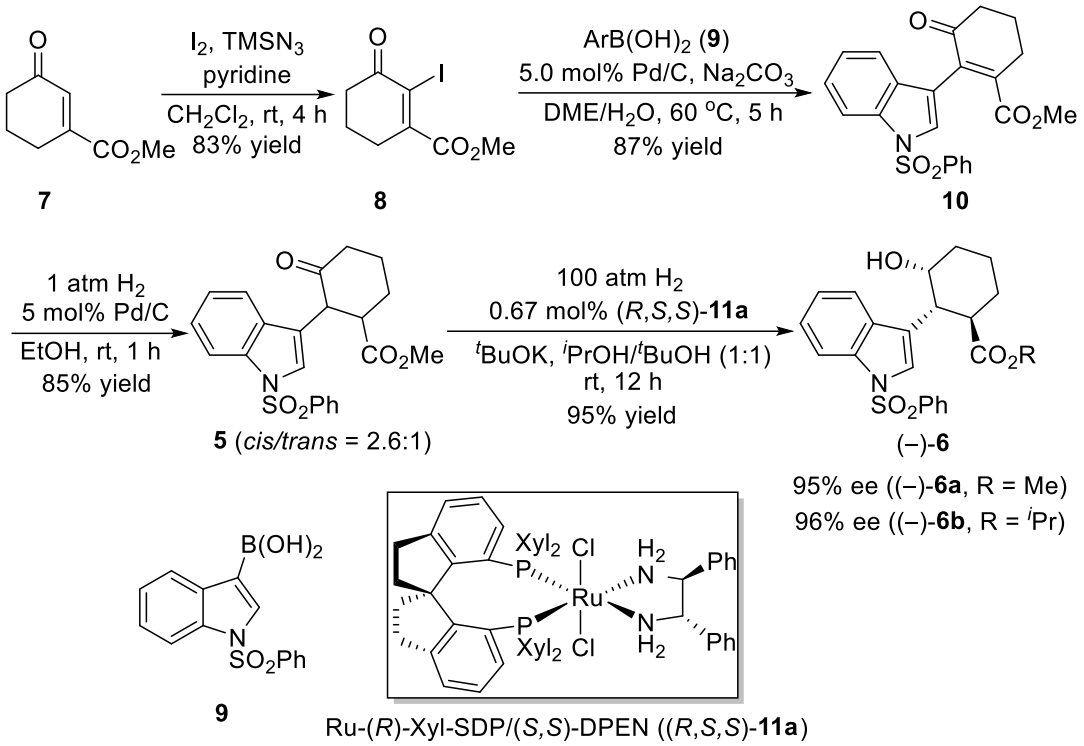
[a] *State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China.*
[b] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China.*

Contents:

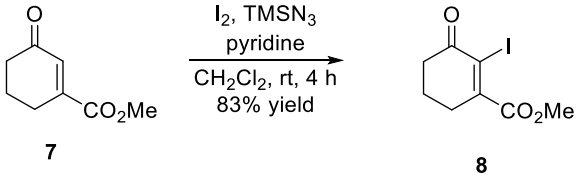
General: All reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glove box (VAC DRI-LAB HE 493) or using standard Schlenk techniques. Hydrogen gas (99.999%) was purchased from Boc Gas Inc., Tianjin. Chemical reagents such as Pd/C (10% wt), KO^{t}Bu and CH_3MgBr were purchased from Alfa Aesar company. Anhydrous THF and benzene was distilled from sodium benzophenone ketyl. Anhydrous DMF, *i*-PrOH, Et_3N and CH_2Cl_2 were freshly distilled from calcium hydride. Melting points were measured on a RY-I apparatus and uncorrected. NMR spectra were recorded with a Bruker AV 400 spectrometer at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). Chemical shifts were reported in ppm down field from internal Me_4Si. Optical rotations were determined using a Perkin Elmer 341 MC polarimeter. IR spectra were obtained with a Perkin-Elmer spectrometer in KBr disks. High Resolution Mass Spectra (HRMS) were recorded on an Ion Spec FT-ICR mass spectrometer with Electron Spray Ionization (ESI) resource. HPLC analyses were determined using a Hewlett Packard Model HP 1100 Series chromatography.

(A) Asymmetric Synthesis of Chiral Alcohol (–)/(+)-6

The route for the synthesis of chiral alcohol (–)/(+)-**6** is outlined below:

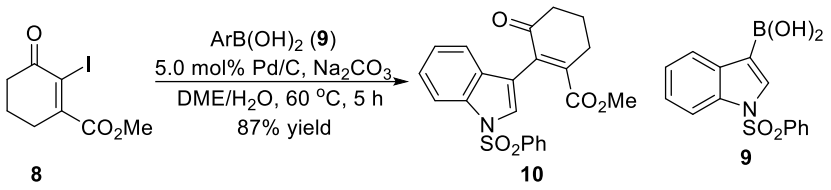


Methyl 2-iodo-3-oxocyclohex-1-enecarboxylate (8)[1]



To solution of methyl 3-oxocyclohex-1-enecarboxylate (**7**, 10.0 g, 66.0 mmol) in CH_2Cl_2 (100 mL) was added freshly distilled trimethylsilyl azide (22.3 mL, 165 mmol) at 0 °C. After the mixture was stirred at 0 °C for 2 h, a solution of iodine (42.0 g, 165 mmol) in CH_2Cl_2 (100 mL) and pyridine (100 mL) was added slowly at 0 °C. The mixture was allowed to warm to room temperature and stirred for 4 h. The mixture was then diluted with Et_2O (300 mL) and H_2O (300 mL). The organic layer was washed successively with water, aqueous HCl (1 M), saturated $NaHCO_3$, $Na_2S_2O_3$ and brine, and dried over anhydrous $MgSO_4$ and concentrated in *vacuo* to yield a residue. The residue was purified by chromatography on silica gel column (petroleum ether/ethyl acetate = 4:1) to afford iodide **8** as a white solid (15.3 g, 83% yield). R_f = 0.41 (silica gel, petroleum ether/ethyl acetate = 5:1). mp 68–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 2.67–2.63 (m, 4H), 2.15–2.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 167.8, 157.6, 104.6, 52.7, 36.4, 30.3, 22.2. IR (KBr): ν_{max} 2949, 1730, 1689, 1431, 1291, 1227, 1179 cm^{-1}. HRMS (ESI) Calcd for $C_8H_9IO_3Na$ ([M+Na]$^+$): 302.9489, found: 302.9491.

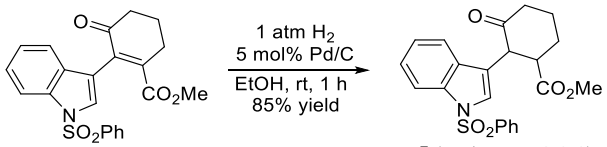
Methyl 3-oxo-2-(1-(phenylsulfonyl)-1*H*-indol-3-yl)cyclohex-1-enecarboxylate (10)



8 10 9

To a solution of iodide **8** (14.0 g, 50.0 mmol), arylboronic acid **9** (19.6 g, 65.0 mmol), and Na_2CO_3 (10.6 g, 100 mmol) in 1,2-dimethoxyethane (140 mL) and H_2O (140 mL) was added a catalytic amount of Pd/C (10% wt, 2.6 g, 2.5 mmol). The reaction mixture was then heated to 60 °C with vigorous stirring for 5 h. After cooling to room temperature and diluted with water (200 mL), the reaction mixture was extracted with ethyl acetate (3 × 200 mL). The combined organic solutions were washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The residue was purified by chromatography on silica gel column (petroleum ether/ethyl acetate = 3:1) to afford enone **10** as a yellow oil (17.9 g, 87% yield). R_f = 0.32 (silica gel, petroleum ether/ethyl acetate = 3:1). mp 116–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.92–7.86 (m, 2H), 7.54 (s, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.44–7.40 (m, 2H), 7.28 (m, 1H), 7.22–7.14 (m, 2H), 3.25 (s, 3H), 2.78 (t, *J* = 6.0 Hz, 2H), 2.70–2.60 (m, 2H), 2.25–2.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 168.6, 149.0, 138.0, 134.4, 133.8, 131.2, 130.1, 129.2, 126.7, 126.0, 124.6, 123.3, 120.1, 115.9, 113.5, 51.9, 38.0, 27.8, 22.1. IR (KBr): ν_{max} 2951, 1737, 1682, 1448, 1367, 1275, 1228, 1175, 1125, 728, 596 cm^{-1}. HRMS (ESI) Calcd for $C_{22}H_{19}NO_5SNa$ ([M+Na]$^+$): 432.0876, found: 432.0880.

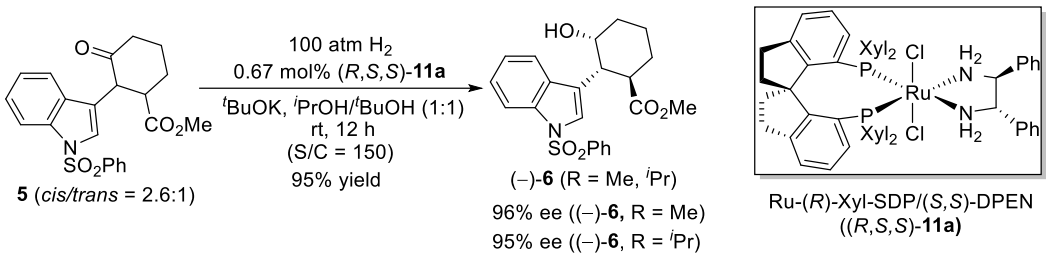
Methyl 3-oxo-2-(1-(phenylsulfonyl)-1*H*-indol-3-yl)cyclohexanecarboxylate (5)



10 5 (*cis/trans* = 2.6:1)

To a solution of enone **10** (12.0 g, 29.3 mmol) in ethanol (600 mL) was added Pd/C (10% wt, 1.56 g, 1.47 mmol). The mixture was stirred under atmospheric pressure of H_2 for 12 h and was then filtered through a pad of Florisil. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel column (toluene/ethyl acetate = 6:1) to afford ketone **5** as a white solid (10.2 g, 85% yield, *cis/trans* ≈ 3:1). R_f = 0.58 (silica, toluene/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 0.75H), 7.48 (d, *J* = 8.0 Hz, 0.25H), 7.85–7.80 (m, 2H), 7.73 (s, 0.75H), 7.47–7.41 (m, 2H), 7.41–7.33 (m, 2H), 7.31–7.23 (m, 1.25H), 7.20–7.16 (m, 1H), 4.13 (d, *J* = 12.0 Hz, 0.25H), 4.03 (d, *J* = 5.2 Hz, 0.75H), 3.44 (s, 2.25H), 3.37 (q, *J* = 4.8 Hz, 0.75H), 3.33 (s, 0.75H), 3.11 (td, *J* = 11.6, 3.6 Hz, 1H), 2.60–2.52 (m, 1.25H), 2.45–2.35 (m, 0.75H), 2.25–2.15 (m, 2H), 2.14–2.02 (m, 1H), 1.98–1.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 205.3, 173.1, 172.8, 137.8, 134.3, 133.6, 130.2, 129.0, 126.5, 126.4, 125.3, 124.6, 124.6, 124.4, 123.1, 123.0, 119.9, 118.9, 116.6, 113.4, 113.4, 51.7, 51.5, 50.0, 49.5, 48.1, 48.0, 41.1, 39.7, 28.8, 26.6, 25.4, 22.9. HRMS (ESI) Calcd for $C_{22}H_{21}NO_5SNa$ ([M+Na]$^+$): 434.1033, found: 434.1035.

Asymmetric Synthesis of (–)/(+)-6

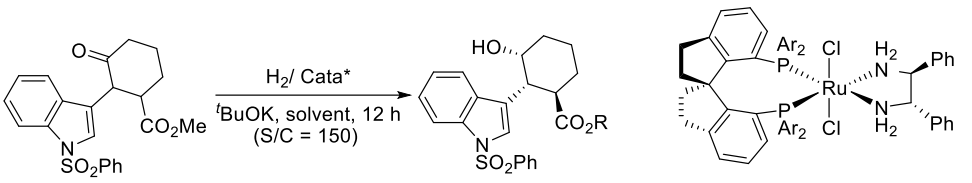


The catalyst [$RuCl_2$-(*R*)-Xyl-SDP/(*S*,*S*)-DPEN] (18 mg, 0.018 mmol) was placed in a hydrogenation vessel in a glove box under argon atmosphere. A mixture solvent (20.0 mL, ^{i}PrOH/^{t}BuOH = 1:1) was introduced with a syringe, and the vessel was purged with hydrogen and pressurized to 20 atm for 5 min. After releasing the pressure, a solution of ketone **5** (1.13 g, 2.75 mmol) in the mixture solvent (10.0 mL, ^{i}PrOH/^{t}BuOH = 1:1) and a solution of ^{t}BuOK (0.2 mmol/mL, 0.8 mmol) also in the mixture solvent (4 mL, ^{i}PrOH/^{t}BuOH = 1:1) were added sequentially into the vessel. The vessel was then purged with hydrogen and pressurized to 100 atm. After stirring at room temperature for 12 h, the reaction was stopped. The reaction mixture was concentrated in *vacuo* and the residue was purified through a short silica gel column (petroleum ether/ethyl acetate = 4:1) to afford alcohol (–)-**6** (1.08 g, 95% yield) as a mixture of methyl ester ((–)-**6a**, 0.80 g, 70.4% yield) and isopropyl ester ((–)-**6b**, 0.28 g, 24.6% yield) in a ratio around 3:1. (–)-**6a**: white solid. R_f = 0.52 (silica, petroleum ether/ethyl acetate = 3:1). 96% ee. mp 60–62 °C. $[\alpha]_D^{20}$ –87.2 (*c* 1.06, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.86–7.79 (m, 2H), 7.52–7.49 (m, 3H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 4.03 (s, 1H), 3.36 (s, 3H), 3.29 (dd, *J* = 12.0, 1.2 Hz, 1H), 3.14 (td, *J* = 11.8, 3.5 Hz, 1H), 2.04 (t, *J* = 13.5 Hz, 2H), 1.90–1.77 (m, 1H), 1.73–1.56 (m, 3H), 1.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 135.4, 133.7, 129.9, 129.2, 126.6, 125.2, 123.6, 123.4, 123.0, 119.5, 113.9, 66.9, 51.5, 42.2, 41.2, 31.6, 29.9, 18.7. IR (KBr): ν_{max} 3473, 2937, 1728, 1447, 1367, 1175, 725, 598 cm^{-1}. HRMS (ESI) Calcd for $C_{22}H_{23}NO_5SNa$ ([M+Na]$^+$): 436.1189, found: 436.1191. (–)-**6b**: white solid. R_f = 0.55 (silica, petroleum ether/ethyl acetate = 3:1). 95% ee. mp 114–116 °C. $[\alpha]_D^{20}$ –74.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.87–7.81 (m, 2H), 7.55–7.47 (m, 3H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* =8.0 Hz, 1H), 4.66 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.02 (s, 1H), 3.28 (dd, *J* = 12.0, 1.8 Hz, 1H), 3.08 (td, *J* = 12.0, 3.5 Hz, 1H), 2.10–1.95 (m, 2H), 1.87–1.79 (m, 1H), 1.64 (m, 3H), 1.38 (s, 1H), 0.91 (d, *J* = 6.3 Hz, 3H), 0.76 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 138.1, 135.3, 133.1, 130.1, 129.2, 126.7, 125.1, 123.6, 123.2, 123.0, 119.6, 113.8, 67.3, 67.1, 42.6, 41.2, 31.7, 29.9, 21.4, 21.2, 18.8. IR (KBr): ν_{max} 3478, 2923, 1704, 1448, 1367, 1177, 598 cm^{-1}. HRMS (ESI) Calcd for $C_{24}H_{27}NO_5SNa$ ([M+Na]$^+$): 464.1502, found: 464.1501.

With the same procedure chiral alcohol (+)-**6** was also obtained as a mixture of methyl ester and isopropyl ester by using [$RuCl_2$-(*S*)-Xyl-SDP/(*R*,*R*)-DPEN] as the catalyst. 95% yield. (+)-**6a**: white solid, mp 60–62 °C, 96% ee, $[\alpha]_D^{20}$ +85.5 (*c* 1.0, $CHCl_3$). (+)-**6b**: white solid, mp 113–115 °C. 95% ee, $[\alpha]_D^{20}$ –73.4 (*c* 1.0, $CHCl_3$).

The experiment data of optimizing the hydrogenation conditions see below.[a]

Table S1 Optimizing the hydrogenation conditions



5 (*cis/trans* = 2.6:1)

(–)-**6a** (R = Me)
(–)-**6b** (R = ^{i}Pr)

Ru-(*R*)-Xyl-SDP/(*S*,*S*)-DPEN
((*R*,*S*,*S*)-**11a**, Ar = 3,5-(Me)$_2$-C$_6$H$_3$)
Ru-(*R*)-SDP/(*S*,*S*)-DPEN
((*R*,*S*,*S*)-**11b**, Ar = C$_6$H$_5$)

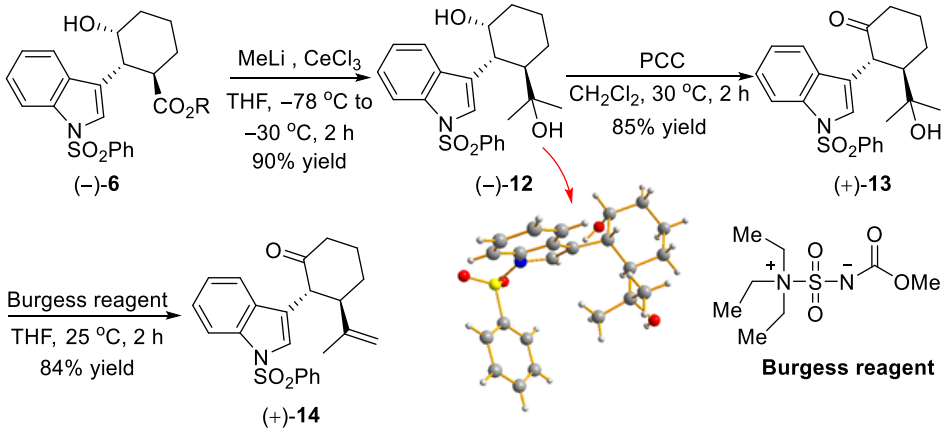
Entry	Catalyst	Solvent	Conv. (%)[b]	Yield (%)[c]	Ee (%)[d]	
					(–)-**6a**	(–)-**6b**
1	(*R*,*S*,*S*)-**11a**	^{i}PrOH	100	75	87	84
2	(*R*,*S*,*S*)-**11b**	^{i}PrOH	100	55	77	0
3	(*R*,*S*,*S*)-**11a**	^{t}BuOH	60	38	97	–
4[e]	(*R*,*S*,*S*)-**11a**	^{t}BuOH	60	34	71	–
5	(*R*,*S*,*S*)-**11a**	Toluene	15	11	98	–
6	(*R*,*S*,*S*)-**11a**	THF	70	28	99	–
7	(*R*,*S*,*S*)-**11a**	^{i}PrOH/^{t}BuOH (2:1)	100	62	95	85
8	(*R*,*S*,*S*)-**11a**	^{i}PrOH/^{t}BuOH (1:1)	100	56	97	93
9[f]	(*R*,*S*,*S*)-**11a**	^{i}PrOH/^{t}BuOH (1:1)	100	95	96	95

Notes: [a] Reaction conditions: 0.5 mmol scale, [**5**] = 0.08 M, [KO^{t}Bu] = 0.02 M, 25–30 °C, 50 atm H_2, 12 h. [b] Determined by ^{1}H NMR. [c] Isolated yield. The ratio of (–)-**6a** to (–)-**6b** from 3:1 to 1:1 determined by ^{1}H NMR, and the low yield (compare to the conversion) is due to the substrate and the product are prone to hydrolysis by water, which is inevitably coming from the solvents used). [d] Determined by HPLC on chiral OD-H column. [e] at 60 °C; [f] 100 atm H_2, 4 Å MS.

HPLC conditions: For (–)-**6a**: Chiralcel OD-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 85:15; temp, rt; flow rate = 1.0 mL/min; 220 nm UV detector; t_R (1*S*,2*S*,3*S*) = 5.95 min and t_R (1*R*,2*R*,3*R*) = 12.68 min. For (–)-**6b**: Chiralcel OD-H column (25 cm × 0.46 cm ID); *n*-hexane/2-propanol = 85:15; temp, rt; flow rate = 1.0 mL/min; 220 nm UV detector; t_R (1*S*,2*S*,3*S*) = 4.73 min and t_R (1*R*,2*R*,3*R*) = 10.55 min.

(B) Synthesis of Ketone (–)/(+)-14

The route for the synthesis of chiral ketone (–)/(+)-**14** is outlined below.



(–)-**6**

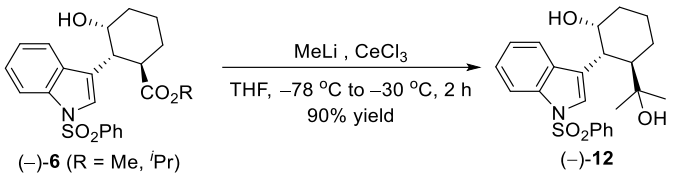
(–)-**12**

(+)-**13**

(+)-**14**

Burgess reagent

Alcohol (–)-12



A suspension of $CeCl_3$ (26.4 g, 107 mmol) and chiral alcohol (–)-**6** (7.6 g, 17.8 mmol, (–)-**6a**/(–)-**6b** = 3:1) in THF (30 mL) was stirred at room temperature for 2 h. Then the mixture cooled to –78 °C, and a solution of MeLi (1.0 M, 107 mL, 107 mmol) in THF was added. After completion of the addition, the temperature was allowed to –30 °C for 2 h. The mixture was quenched with aqueous HCl (1 M, 200 mL) and extracted with ethyl acetate. The combined organic solutions were washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The residue was purified by chromatography on silica gel column (petroleum ether/ethyl acetate = 2:1) to afford the product (–)-**12** as a white solid (6.6 g, 90% yield). R_f = 0.43 (silica gel, petroleum ether/ethyl acetate = 2:1). mp 138–140 °C, $[\alpha]_D^{20}$ –55.1 (*c* 1.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.93–7.87 (m, 2H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.63 (s, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 8.0Hz, 1H), 3.73 (s, 1H), 2.95 (dd, *J* = 11.6, 2.1 Hz, 1H), 2.37 (td, *J* = 11.8, 3.6 Hz, 1H), 2.11–2.01 (m, 1H), 1.97–1.86 (m , 2H), 1.76–1.54 (m, 3H), 1.18–1.14 (m, 1H), 1.08 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 135.2, 133.8, 130.3, 129.3, 126.6, 125.2, 125.1, 124.4, 123.4, 120.3, 113.9, 73.9, 70.2, 45.4, 41.7, 32.7, 28.8, 28.4, 26.7, 19.5. IR (KBr): ν_{max} 3372, 2922, 1447, 1370, 1180, 1098, 725, 600, 553 cm^{-1}. HRMS (ESI) Calcd for $C_{23}H_{27}NO_4SNa$ ($[M+Na]^+$): 436.1553, found: 436.1550.

Crystals of **(–)-12** suitable for X-ray analysis were grown from diethyl ether/hexane. Crystallographic data for **(–)-12** are given in Table S2.

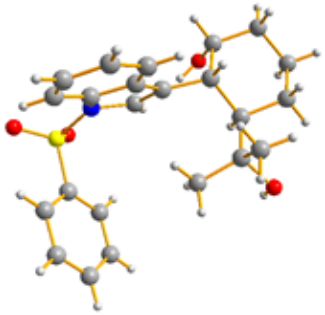
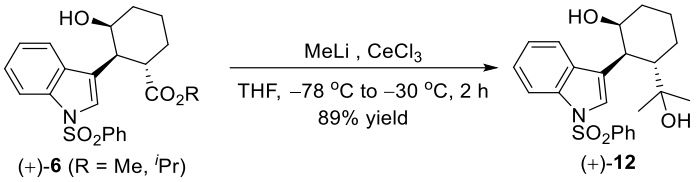


Table S2. Crystallographic data and structure refinement for (–)-**12**

Empirical Formula	$C_{26}H_{33}NO_5S$
Formula weight	471.59
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 7.8163(16) Å α = 90° b = 11.555(2) Å β = 90° c = 26.919(5) Å γ = 90°
Volume	2431.2(8) $Å^3$
Z, Calculated density	4, 1.288 Mg/m^3
Absorption coefficient	0.170 mm^{-1}
F(000)	1008

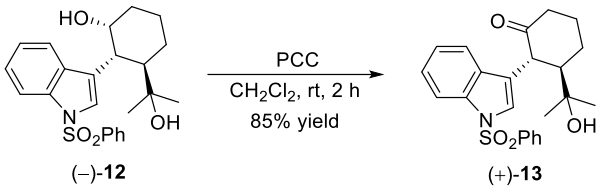
Crystal size	0.20 × 0.18 × 0.12 mm
Theta range for data collection	1.51 to 24.99 deg
Limiting indices	-9<=h<=9, -13<=k<=13, -31<=l<=31
Reflections collected / unique	19854 / 4263 [R(int) = 0.1047]
Completeness to theta = 24.99	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9799 and 0.9668
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4263 / 24 / 304
Goodness-of-fit on F^2	1.121
Final R indices [I>2sigma(I)]	R1 = 0.0842, wR2 = 0.1925
R indices (all data)	R1 = 0.1155, wR2 = 0.2088
Absolute structure parameter	-0.09 (18)
Largest diff. peak and hole	0.299 and -0.488 e.Å^{-3}

Alcohol (+)-12



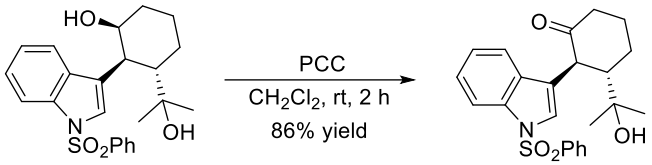
With the same procedure the chiral alcohol (+)-**12** was synthesized from the chiral alcohol (+)-**6**: 89% yield, white solid. mp 139–141 ºC. $[\alpha]_D^{20}$ +57.2 (*c* 1.0, $CHCl_3$).

Ketone (+)-13



Pyridinium chlorochromate (10.0 g, 46.5 mmol) was added in small portions to a vigorously stirred solution of alcohol (–)-**12** (6.4 g, 15.5 mmol) in DCM (200 mL). After completing the addition, the mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with ether and filtered through a pad of Florisil. The filtrate was concentrated in *vacuo* and the residue was purified through a short silica gel column (petroleum ether/ethyl acetate = 2:2) to afford compound (+)-**13** as a white solid (5.4 g, 85% yield). R_f = 0.37 (silica gel, petroleum ether/ethyl acetate = 2:1). mp 126–128 ºC. $[\alpha]_D^{20}$ +103.2 (*c* 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.52 (dd, *J* = 14.1, 7.5 Hz, 2H), 7.46 (s, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 3.92 (d, *J* = 6.2 Hz, 1H), 2.55–2.28 (m, 3H), 2.16 (d, *J* = 6.8 Hz, 2H), 1.90 (brs, 1H), 1.76–1.68 (m, 1H), 1.28–1.26 (m, 1H), 1.19 (s, 3H), 1.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 138.0, 135.2, 133.8, 130.3, 129.2, 126.6, 125.0, 124.0, 123.5, 121.5, 120.7, 113.7, 51.7, 49.6, 39.3, 29.0, 27.2, 25.1, 23.2. IR (KBr): ν_{max} 3449, 2962, 1690, 1639, 1450, 1369, 1175, 750, 595, 570 cm^{-1}. HRMS (ESI) Calcd for $C_{23}H_{25}NO_4SNa$ ($[M+Na]^+$): 434.1397, found: 434.1399.

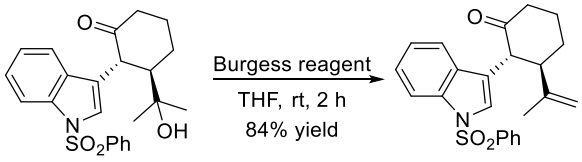
Ketone (–)-13



(+)-**12** (–)-**13**

With the same procedure the chiral ketone (–)-**13** was synthesized from the chiral alcohol (+)-**12**: 86% yield. mp 125–127 °C. $[\alpha]_D^{20}$ –98.5 (*c* 1.0, $CHCl_3$).

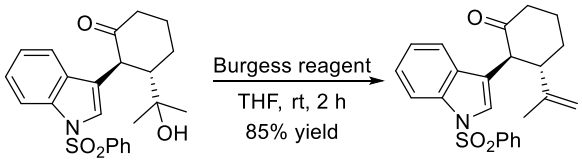
Ketone (+)-**15**[2]



(+)-**13** (+)-**14**

To a solution of alcohol (+)-**13** (4.6 g, 11.2 mmol) in THF (100 mL) was added Burgess reagent (8.6 g, 33.6 mmol mmol) at room temperature under an argon atmosphere. After stirring at room temperature for 2 h, H_2O (80 mL) was added to the mixture and the resulting mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic solutions were washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The residue was purified by chromatography on silica gel column (petroleum ether/ethyl acetate = 5:1) to afford the ketone (+)-**14** as a light yellow solid (3.7 g, 84% yield). R_f = 0.71 (silica gel, petroleum ether/ethyl acetate = 3:1). mp 132–134°C. $[\alpha]_D^{20}$ +45.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.80–7.73 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.32 (s, 1H), 7.28–7.23 (m, 2H), 7.20–7.12 (m, 1H), 4.51 (s, 1H), 4.47–4.42 (m, 1H), 3.78 (d, *J* = 12.1 Hz, 1H), 2.86 (td, *J* = 11.6, 4.0 Hz, 1H), 2.61–2.45 (m, 2H), 2.23–2.14 (m, 1H), 2.00–1.81 (m, 3H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 145.4, 138.1, 135.2, 133.5, 130.6, 129.0, 126.5, 125.0, 124.4, 123.1, 120.0, 119.0, 113.8, 112.6, 52.1, 52.1, 41.7, 31.5, 25.9, 18.4. IR (KBr): ν_{max} 2937, 1711, 1448, 1366, 1175, 725, 599 cm^{-1}. HRMS (ESI) Calcd for $C_{23}H_{23}NO_3SNa$ ($[M+Na]^+$): 416.1291, found:416.1294.

Ketone (–)-**14**

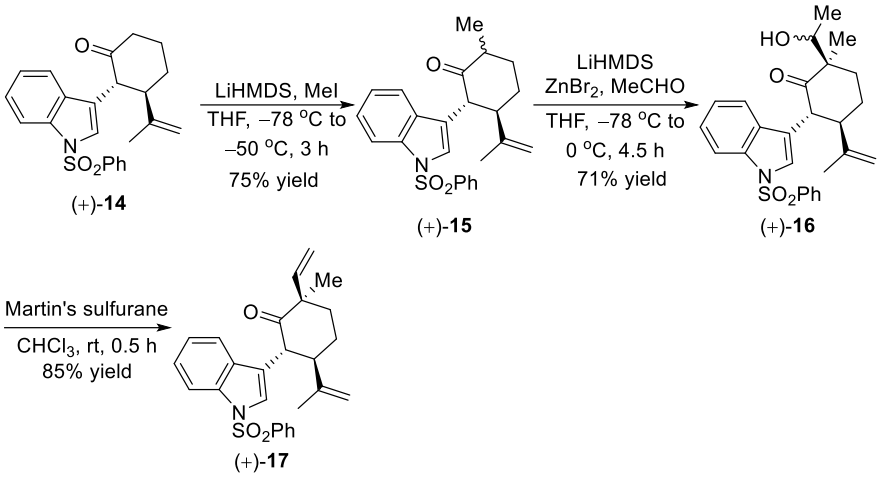


(+)-**13** (+)-**14**

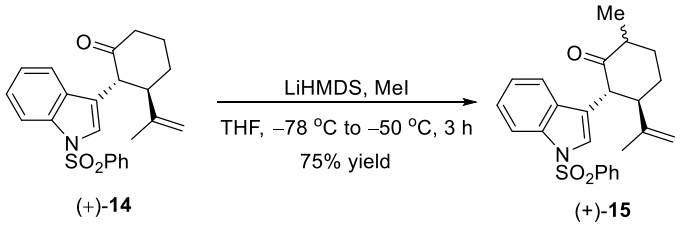
With the same procedure the ketone (–)-**14** was synthesized from the ketone (–)-**13**: 85% yield. mp 133–134 °C, $[\alpha]_D^{20}$ +46.1 (*c* 1.1, $CHCl_3$).

(C) Synthesis of Ketone (–)/(+)-17

The route for the synthesis of chiral ketone (–)/(+)-**17** is outlined below.

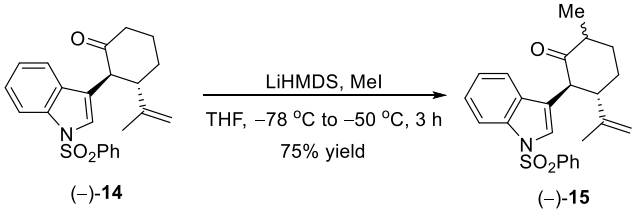


Ketone (+)-**15**



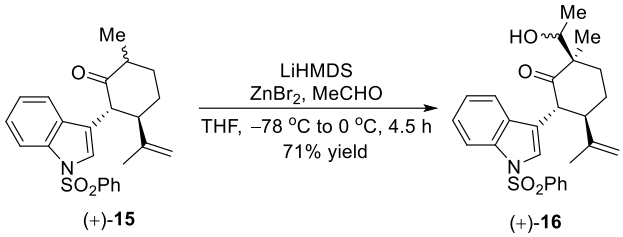
To a solution of ketone (+)-**14** (1.7 g, 4.3 mmol) in THF (10 mL) at –78 °C was slowly added a solution of LiHMDS (1.0 M, 8.6 mL, 8.6 mmol) in THF and the resulting solution was stirred at the same temperature for 1 h. Then iodomethane (0.31 mL, 4.95 mmol) was added to the reaction mixture and the resulting solution was again allowed to warm to –20 °C for 3 h. The mixture was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3 × 50 mL). The combined organic solutions were washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The residue was purified by chromatography on silica gel column (petroleum ether/ethyl acetate = 6:1) to afford the ketone (+)-**15** as a light semi-oil solid (1.32 g, 75% yield, *dr* = 5:1). R_f = 0.56 (silica gel, petroleum ether/ethyl acetate = 5:1). $[\alpha]_D^{20}$ +23.5 (*c* 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.84–7.76 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.43–7.36 (m, 4H), 7.32–7.28 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 4.64 (s, 2H), 4.00 (d, *J* = 9.2 Hz, 1H), 2.99–2.93 (m, 1H), 2.75–2.68 (m, 1H), 2.08–1.90 (m, 3H), 1.83–1.78 (m, 1H), 1.59 (s, 3H), 1.23 (d, *J* = 7.2 Hz, 2.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.8, 145.8, 138.1, 135.2, 133.7, 130.5, 129.1, 129.0, 126.6, 124.7, 124.3, 123.2, 120.2, 119.7, 113.7, 112.7, 50.1, 48.8, 43.3, 31.1, 25.7, 19.7, 16.3. HRMS (ESI) Calcd for $C_{24}H_{25}NO_3SNa$ ($[M+Na]^+$): 430.1447, found: 430.1447.

Ketone (–)-**15**



With the same procedure the ketone (–)-**15** was synthesized from the ketone (–)-**14**. 75% yield. $[\alpha]_D^{20}$ –24.3 (*c* 0.6, $CHCl_3$).

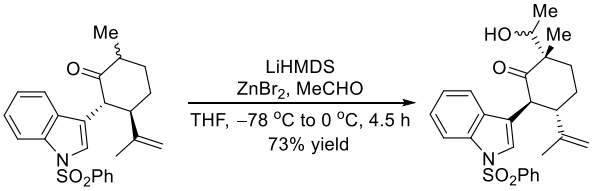
Alcohol (+)-**16**[3]



(+)-**15** (+)-**16**

To a solution of ketone (+)-**15** (2.21 g, 5.4 mmol) in THF (20 mL) was added a solution of LiHMDS (1.0 M, 10.8 mL, 10.8 mmol) in THF at –78 °C. After being stirred at 0 °C for 1 h, the mixture was cooled to –78 °C again, and a solution of $ZnBr_2$ (2.43 g, 10.8 mmol) in THF (12 mL) was added. After the addition, the reaction mixture was slowly warm to 0 °C and stirred at the same temperature for 0.5 h. Then, acetaldehyde (1.21 mL, 21.6 mmol) was added. The mixture continued to stir at 0 °C for 0.5 h, and then aqueous H_2O_2 (30 wt.%, 12 mL) and aqueous NaOH (3 M, 36 mL) was added dropwise to the reaction. The reaction mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic solutions were washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The residue was purified by chromatography on silica gel column (petroleum ether/ethyl acetate = 2:1) to afford the alcohol (+)-**16** as a white solid (1.72 g, 71% yield, *dr* = 10:1). R_f = 0.31 (silica gel, petroleum ether/ethyl acetate = 2:1). mp 78–80 °C. $[\alpha]_D^{20}$ +8.4 (*c* 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.41–7.33 (m, 4H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 4.70 (s, 1H), 4.61 (s, 1H), 4.57–4.58 (m, 1H), 4.25 (d, *J* = 12.4 Hz, 1H), 2.93 (td, *J* = 11.9, 4.3 Hz, 1H), 2.05–2.04 (m, 1H), 2.00 (dt, *J* = 14.3, 3.6 Hz, 1H), 1.80–1.63 (m, 3H), 1.49 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H), 0.99 (d, *J* = 9.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 146.0, 138.1, 135.0, 133.5, 131.2, 129.0, 126.5, 125.0, 124.4, 123.2, 120.1, 119.4, 113.6, 112.8, 70.3, 53.3, 51.4, 47.6, 36.0, 27.2, 18.2, 17.9, 16.3. IR (KBr): ν_{max} 3543, 2975, 2937, 1711, 1447, 1366, 1175, 745, 571 cm^{-1}. HRMS (ESI) Calcd for $C_{26}H_{29}NO_4SNa$ ($[M+Na]^+$): 474.1710, found: 474.1712.

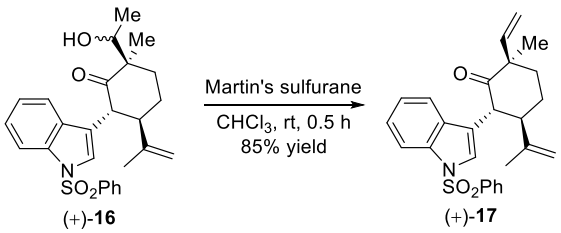
Alcohol (–)-**16**[4]



(–)-**15** (–)-**16**

With the same procedure the alcohol (–)-**16** was synthesized from the ketone (–)-**15**: 73% yield. $[\alpha]_D^{20}$ –10.1 (*c* 0.5, $CHCl_3$).

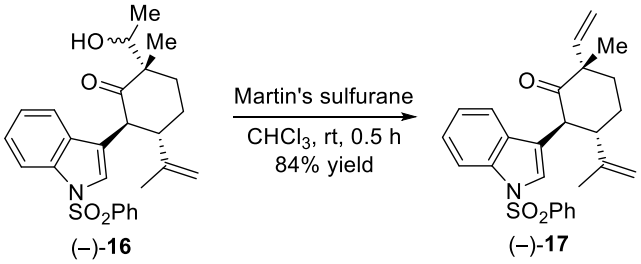
Ketone (+)-**17**



(+)-**16** (+)-**17**

To a solution of alcohol (+)-**16** (1.6 g, 3.5 mmol) in $CHCl_3$ (16 mL) was added Martin Sulfurane (9.5 g, 14.2 mmol), and the obtained reaction mixture was stirred at room temperature for 0.5 h. The solvent was removed in *vacuo* and the residue was purified by chromatography on silica gel column (petroleum ether/ethyl acetate = 8:1) to afford ketone (+)-**17** as a white solid (1.3 g, 85% yield). R_f = 0.67 (silica gel, petroleum ether/ethyl acetate = 6:1). mp 148–150 °C. $[\alpha]_D^{20}$ +89.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.34 (s, 1H), 7.30–7.16 (m, 3H), 6.14 (dd, *J* = 17.7, 10.7 Hz, 1H), 5.36 (d, *J* = 10.7 Hz, 1H), 5.17 (d, *J* = 17.7 Hz, 1H), 4.59 (s, 1H), 4.51 (s, 1H), 4.18 (d, *J* = 12.5 Hz, 1H), 2.96–2.85 (m, 1H), 2.26–2.08 (m, 2H), 1.89–1.77 (m, 2H), 1.47 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 145.7, 142.6, 138.2, 135.1, 133.5, 131.0, 129.0, 126.5, 125.2, 124.4, 123.1, 119.6, 119.1, 116.3, 113.8, 112.6, 52.8, 52.2, 48.4, 38.9, 28.2, 24.7, 18.2. IR (KBr): ν_{max} 2926, 1709, 1608, 1448, 1365, 1176, 725, 598 cm^{-1}. HRMS (ESI) Calcd for $C_{26}H_{27}NO_3SNa$ ([M+Na]$^+$): 456.1604, found:456.1599.

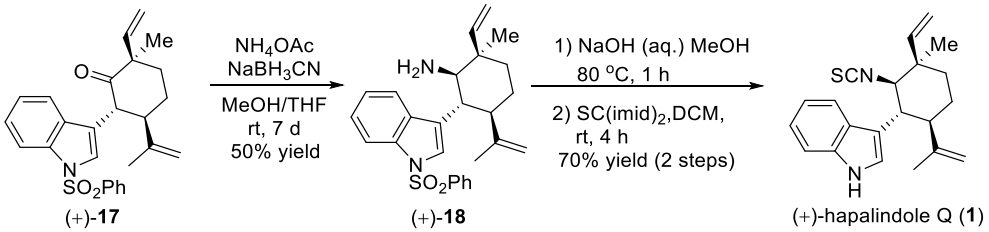
Ketone (–)-**17**



With the same procedure the ketone (–)-**17** was synthesized from the alcohol (–)-**16**: 84% yield. $[\alpha]_D^{20}$ –85.3 (*c* 0.4, $CHCl_3$).

(D) Total Synthesis of (+)-Hapalindole Q (1)[5]

The route for the synthesis of (+)-Hapalindole Q (**1**) is outlined below.

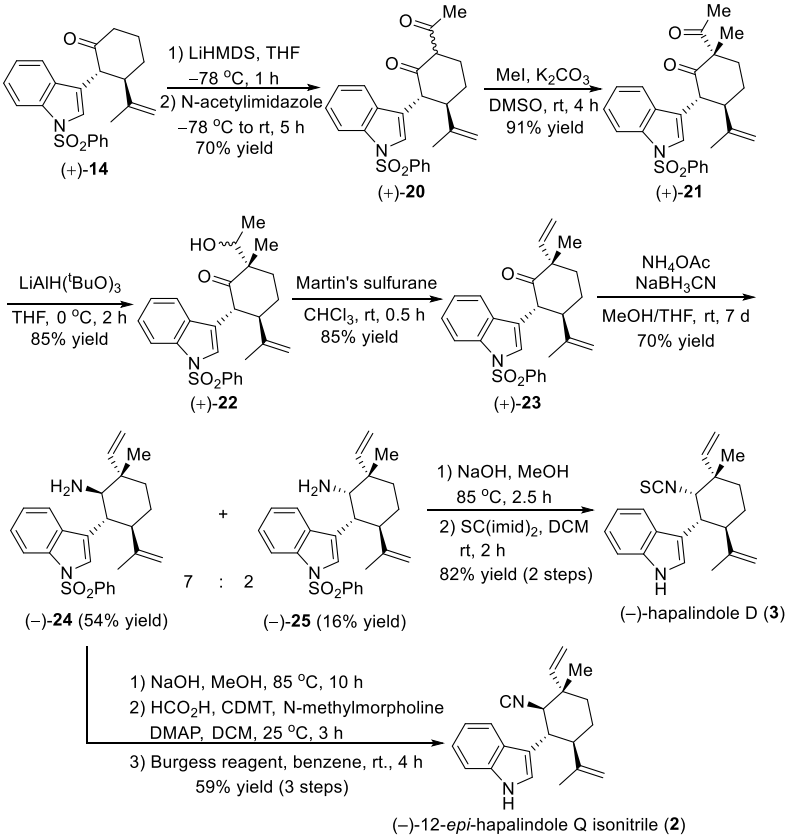


To a solution of ammonium acetate (249 mg, 3.23 mmol) and $NaBH_3CN$ (50 mg, 0.80 mmol) in MeOH (4.0 mL) was added a solution of ketone (+)-**17** (70 mg, 0.16 mmol) in THF (1.0 mL). The reaction mixture was stirred for 7 d at room temperature, and then quenched with aqueous $NaHCO_3$ (1 M, 3 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic solutions were washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The residue was purified by chromatography on silica gel column (petroleum ether/ethyl acetate/methol = 50:25:1) to afford the amine **18** as a white solid (35 mg, 50% yield) and recovered ketone (+)-**17** (32.9 mg, 47%). To a solution of amine (+)-**18** (35 mg, 0.08 mmol) in methol (5 mL) was added aqueous NaOH (3 N, 2.7 mL). The mixture was heated to 80 °C for 1 h, then cooled to room temperature. The solvent was removed in *vacuo* and the residue was diluted by ethyl acetate (15 mL) and H_2O (10 mL). After extracted with ethyl acetate (3 × 15 mL), the combined organic solutions were washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The residue

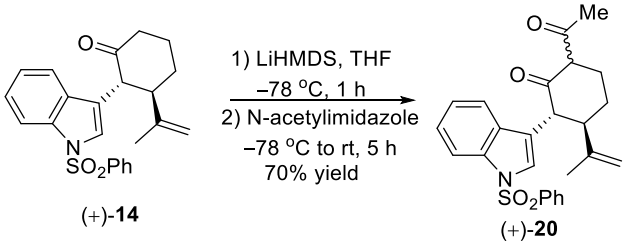
was then dissolved in DCM (8 mL) and $CS(imid)_2$ (17.2 mg, 0.167 mmol) added. The solution was allowed to stir at room temperature for 4 h and then concentrated in *vacuo*. The residue was purified by chromatography on silica gel column (hexane/CH_2Cl_2 = 2:1) to afford (+)-hapalindole Q (**1**) as a colorless oil (18.8 mg, 70% yield). R_f = 0.43 (silica gel, hexane/CH_2Cl_2 = 2:1). $[\alpha]_D^{25}$ + 27.8 (*c* 1.1, CH_2Cl_2) [lit: $[\alpha]_D^{25}$ + 24.1 (*c* 1.1, CH_2Cl_2)[6]]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 2.3 Hz, 1H), 6.24 (dd, *J* = 17.6, 11.1 Hz, 1H), 5.39 (d, *J* = 11.1 Hz, 1H), 5.29 (d, *J* = 17.6 Hz, 1H), 4.52 (s, 1H), 4.46 (s, 1H), 3.88 (s, 1H), 3.14 (s, 1H), 2.78 (s, 1H), 2.04–1.97 (m, 1H), 1.83 (m, 1H), 1.59 (d, *J* = 10.7 Hz, 2H), 1.51 (s, al3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 138.9, 136.7, 131.1, 123.5, 121.9, 119.3, 116.3, 115.0, 111.8, 111.5, 70.7, 50.0, 42.1, 36.4, 28.3, 27.4, 19.0. HRMS (ESI) calcd for $C_{21}H_{24}N_2SNa$ ($[M+Na]^+$): 359.1552, found: 359.1549.

(E) Total Synthesis of (–)-12-*epi*-Hapalindole Q Isonitrile (2) and (–)-Hapalindole D (3)

The route for the synthesis of (–)-12-*epi*-Hapalindole Q Isonitrile (**2**) and (–)-Hapalindole D (**3**) is outlined below.



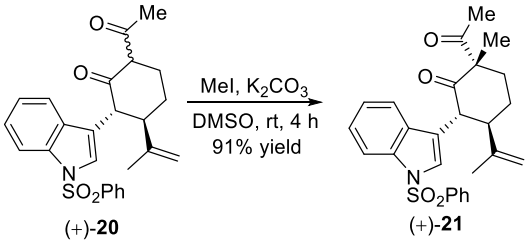
Diketone (+)-20[7]



To a stirred solution of (+)-**14** (4.0 g, 10.1 mmol) in 15 mL of THF was added a solution of LiHMDS

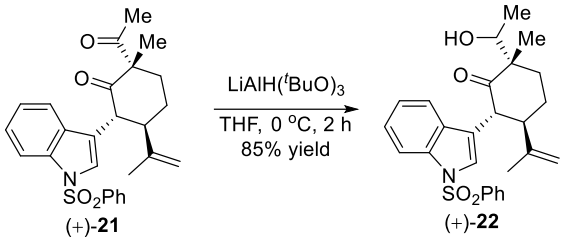
(1.0 mol/L, 30.3 mL, 30.3 mmol) in THF at −78 °C under nitrogen atmosphere. After the addition, the reaction mixture was stirred at the same temperature for 1 h, and then a solution of *N*-acetylimidazole (3.34 g, 30.3 mmol) in dry THF (15 mL) was added slowly at −78 °C. The resulting mixture was warmed to room temperature naturally and stirred at room temperature for 5 h. The reaction was quenched with 20 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (30 mL) and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in *vacuo*, the residue was purified by flash column chromatography on silica gel with ethyl acetate /petroleum ether (10:1) as a eluent to afford diketone (+)-**20** (3.15 g, 70% yield) as colorless semi-oil solid. R_f = 0.51 (silica gel, petroleum ether/ethyl acetate = 4:1). $[\alpha]_D^{20}$ +13.2 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.95 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.83–7.77 (m, 2H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.43–7.33 (m, 4H), 7.30–7.26 (m, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 4.63 (d, *J* = 1.2 Hz, 1H), 4.46 (s, 1H), 3.82 (d, *J* = 8.8 Hz, 1H), 2.59 (td, *J* = 10.0, 2.8 Hz, 1H), 2.50 (t, *J* = 5.6 Hz, 2H), 2.23 (s, 3H), 1.94–1.86 (m, 1H), 1.78–1.69 (m, 1H), 1.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 180.6, 145.6, 138.1, 135.3, 133.6, 129.9, 129.1, 126.6, 124.9, 124.7, 123.3, 121.8, 119.7, 113.9, 111.9, 107.0, 46.3, 42.8, 26.6, 25.3, 23.4, 19.9. IR (KBr): ν_{max} 3371, 2927, 1696, 1448, 1369, 1177, 908, 746 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{25}NO_4SNa^+$[M + Na^+]: 458.1402, found: 458.1403.

Diketone (+)-21[8]



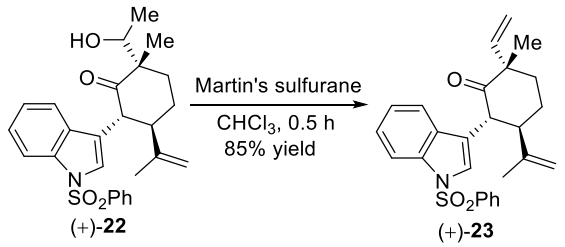
To a stirred solution of diketone (+)-**20** (2.96g, 6.8 mmol) in 10 mL of DMSO was added K_2CO_3 (5.64 g, 40.8 mmol) and MeI (5.80 g, 40.8 mmol) at room temperature. The resulting mixture was stirred at that temperature for 4 h. After quenched with H_2O (25 mL), the mixture was extracted with Et_2O (3 × 30 mL). The organic phase was washed with brine and dried over $MgSO_4$. After filtration and removal of the solvent in *vacuo*, the residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 20:1) to afford diketone (+)-**21** (2.8 g, 91% yield, *dr* = 10:1) as light orange semi-oil solid. R_f = 0.54 (silica gel, petroleum ether/ethyl acetate = 4:1). $[\alpha]_D^{20}$ +40.1 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.83–7.77 (m, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.36 (s, 1H), 7.29 (dd, *J* = 14.4, 6.8 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 4.56 (d, *J* = 8.4 Hz, 2H), 4.04 (d, *J* = 11.2 Hz, 1H), 2.97 (td, *J* = 10.8, 5.2 Hz, 1H), 2.50–2.40 (m, 1H), 2.02 (s, 5H), 1.87–1.79 (m, 1H), 1.54 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.8, 207.2, 145.2, 138.1, 135.1, 133.7, 130.3, 129.1, 129.0, 126.7, 126.6, 125.3, 124.7, 123.3, 119.9, 118.0, 113.8, 113.0, 61.8, 51.0, 48.8, 32.8, 27.0, 26.3, 20.3, 18.8. IR (KBr): ν_{max} 3363, 2936, 1707, 1448, 1366, 1264, 898, 746 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{27}NO_4SNa^+$[M + Na^+]: 472.1558, found: 472.1558.

Alcohol (+)-22[9]



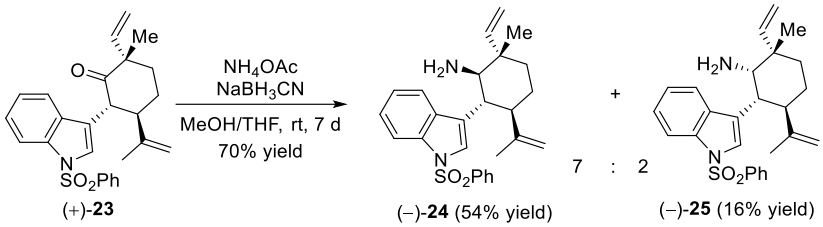
To a stirred solution of diketone (+)-**21** (2.5 g, 5.56 mmol) in THF (15 mL) was added a solution of $LiAlH(^tBuO)_3$ (1.0 M, 8.35 mL, 8.35 mmol) in THF slowly at 0 °C. The resulting reaction mixture was stirred at the same temperature for 2 h. The reaction was then quenched with aqueous HCl (1 M, 5 mL) and extracted with ethyl acetate (3 × 5 mL). The organic phase was washed with saturated $NaHCO_3$ solution, brine and dried over $MgSO_4$. After filtration and removal of the solvent in *vacuo*, the residue was purified by flash column chromatography on silica gel (ethyl acetate /petroleum ether = 10:1) to afford alcohol (+)-**22** (2.15 g, 85%, *dr* = 6:1) as a colorless solid. R_f = 0.27 (silica gel, petroleum ether/ethyl acetate =1:1). $[\alpha]_D^{20}$ +39.4 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.32 (s, 1H), 7.29–7.24 (m, 1H), 7.22–7.17 (m, 2H), 4.56 (s, 1H), 4.50 (s, 1H), 4.09 (d, *J* = 12.6 Hz, 1H), 4.03–3.96 (m, 1H), 3.48 (d, *J* = 3.2 Hz, 1H), 2.85 (td, *J* = 12.4, 3.2 Hz, 1H), 2.20–2.07 (m, 1H), 1.88–1.80 (m, 2H), 1.71 (td, *J* = 13.6, 3.6 Hz, 1H), 1.49 (s, 3H), 1.40 (s, 3H), 1.11 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.6, 145.2, 138.2, 135.2, 133.6, 130.5, 129.1, 126.6, 125.4, 124.6, 123.2, 119.6, 118.5, 114.0, 112.9, 71.5, 52.3, 52.2, 48.1, 35.3, 27.2, 18.2, 16.0, 15.9. IR (KBr): ν_{max} 3366, 2974, 2938, 1638, 1449, 1370, 1269, 1099, 975, 748 cm^{-1}. HRMS (ESI) Calcd. for $C_{26}H_{29}NO_4SNa^+$ [M + Na^+]: 474.1715, found: 474.1712.

Ketone (+)-23[10]



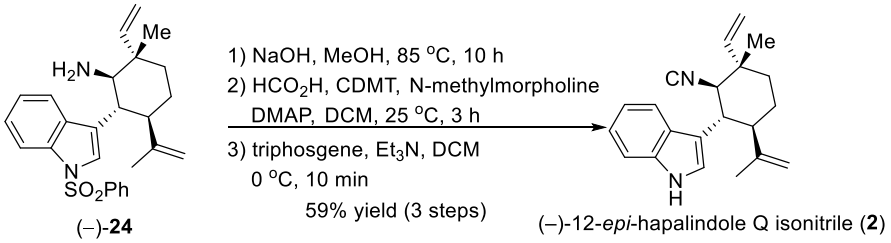
To a solution of alcohol (+)-**22** (1.67 g, 3.64 mmol) in $CHCl_3$ (16 mL) was added Martin Sulfurane (9.78 g, 14.5 mmol), and the obtained reaction mixture was stirred at room temperature for 0.5 h. The solvent was removed in *vacuo* and the residue was purified by chromatography on silica gel column (petroleum ether/ethyl acetate = 20:1 to 10:1) to afford ketone (+)-**23** (1.34 g, 85%) as a white solid. R_f = 0.71 (silica gel, petroleum ether/ethyl acetate = 4:1). mp. 148–150 °C. $[\alpha]_D^{20}$ +32.0 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.77 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.52–7.46 (m, 1H), 7.42–7.36 (m, 2H), 7.32 (s, 1H), 7.25 (td, *J* = 6.8, 1.2 Hz, 1H), 7.23–7.20 (m, 1H), 7.18–7.13 (m, 1H), 6.22 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.12 (dd, *J* = 11.2, 0.8 Hz, 1H), 5.06 (dd, *J* = 17.6, 0.8 Hz, 1H), 4.56 (m, 1H), 4.53–4.49 (m, 1H), 4.10 (d, *J* = 12.4 Hz, 1H), 2.88 (td, *J* = 12.0, 4.0 Hz, 1H), 2.15 (m, 1H), 2.07–1.85 (m, 3H), 1.51 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209. 9, 145.6, 142.5, 138.3, 135.2, 133.5, 130.7, 129.0, 126.6, 125.2, 124.5, 123.1, 119.9, 119.1, 113.8, 112.7, 112.6, 51.9, 50.6, 47.8, 36.6, 27.2, 22.8, 18.5. IR (KBr): ν_{max} 3366, 2974, 2938, 1639, 1449, 1370, 1268, 749 cm^{-1}. HRMS (ESI) Calcd. for $C_{26}H_{27}NO_3SNa^+$ [M + Na^+]: 456.1609, found: 456.1608.

Amine (–)-24 and (–)-25[11]



To a solution of ketone (+)-**23** (1.10 g, 2.53 mmol) in THF (8 mL) was added to a solution of ammonium acetate (7.80 g, 101 mmol) and $NaBH_3CN$ (1.52 g, 25.3 mmol) in MeOH (40 mL). The reaction mixture was allowed to stir at room temperature for 7 d and then quenched with saturated $NaHCO_3$ solution and extracted with diethyl ether (3 × 50 mL). which were subsequently washed with brine, dried over $MgSO_4$. After removed the solvents and the residue was purified by flash column chromatography on silica gel column (petroleum ether/ethyl acetate = 1:2) to afford amine (–)-**24** (597 mg, 54%) and (–)-**25** (171 mg, 16%) as semi-oil solids. (–)-**24**. R_f = 0.25 (silica gel, petroleum ether/ethyl acetate = 1:2). $[\alpha]_D^{20}$ –3.2 (*c* 0.81, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (brs, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.74 (brs, 0.5H), 7.57 (brs, 0.5H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 3H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 5.79 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.10 (d, *J* = 17.2 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 4.58–4.14 (m, 2H), 3.19 –2.40 (m, 3H), 1.78–1.54 (m, 4H), 1.43 (m, 3H), 1.17 (s, 3H), 0.84 (brs, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 147.0, 138.2, 133.5, 129.0, 126.5, 125.6, 124.7, 123.1, 120.8, 119.7, 114.1, 112.6, 111.4, 62.9, 56.7, 51.9, 48.8, 44.0, 41.1, 39.3, 37.8, 27.9, 26.9, 18.5, 14.5. IR (KBr): ν_{max} 3340, 2974, 2928, 1636, 1447, 1369, 1269,745 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{31}NO_3S^+$ [M + H$^+$]: 435.2106, found: 435.2102. (–)-**25**: R_f = 0.37, silica gel, petroleum ether/ethyl acetate = 1:2). $[\alpha]_D^{20}$ –47.1 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38–7.33 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 5.78 (dd, *J* = 16.8, 11.2 Hz, 1H), 5.22 (d, *J* = 9.6 Hz, 1H), 5.06 (d, *J* = 3.6 Hz, 1H), 4.86 (s, 1H), 3.37 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.07–2.98 (m, 1H), 2.89 (d, *J* = 2.0 Hz, 1H), 2.17–2.07 (m, 1H), 1.86–1.68 (m, 3H), 1.41 (s, 3H), 1.39–1.33 (m, 2H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 147.5, 137.8, 135.35, 133.5, 133.2, 130.6, 129.3, 129.970, 127.6, 126.6, 125.1, 124.8, 123.4, 123.3, 118.9, 114.2, 112.3, 112.1, 68.0, 55.9, 41.4, 40.4, 36.4, 28.3, 27.6, 23.6, 18.6. IR (KBr): ν_{max} 3327, 2972, 2932, 1639, 1446, 1369, 1176 cm^{-1}. HRMS (ESI) Calcd. for $C_{26}H_{31}NO_3S^+$ [M + H$^+$]: 435.2106, found: 435.2105.

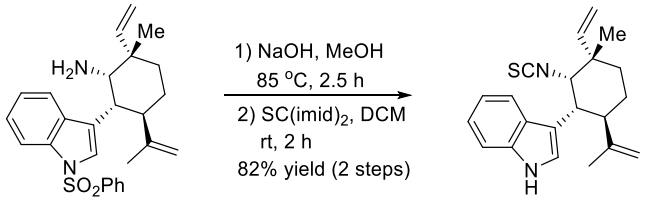
(–)-12-*epi*-Hapalindole Q isonitrile (2)[4]



To a solution of amine (–)-**24** (74 mg, 0.17 mmol) in MeOH (15 mL) was added aqueous NaOH (2 M, 2 mL, 4 mmol) at room temperature. Then the mixture was then warmed to 85 °C and kept at the same temperature for 10 h. After removal of the solvent in *vacuo*, the residue was extracted with ethyl acetate (3 × 5 mL). The organic phase was washed with brine and dried over $MgSO_4$. The solvent removed in *vacuo* to give a semi-oil solid. The semi-oil solid was redissoved in DCM (3 mL) and then added to a solution of formic acid (14.9 μL, 0.38 mmol), 2-chloro-4,6-dimethoxy-1,3,5-triazine (66.4 mg, 0.38

mmol), DMAP (1.0 mg, 11.8 μmol), *N*-methylmorpholine (40.7 μL, 0.38 mmol) in DCM (3 mL). The reaction mixture was stirred for 3 h at room temperature, after which the reaction was diluted with DCM (10 mL) and washed sequentially with aqueous HCl (1 M, 15 mL), saturated $NaHCO_3$ (15 mL), and brine (5 mL). The organic layer was dried over $MgSO_4$ and evaporated in *vacuo* and the residue was purified by flash column chromatography on silica gel column (hexane/ethyl acetate = 3:1) to afford an amide (44 mg, 80%) as an oil. Then the oil was redissolved in DCM (2 mL) to the obtained solution was added Et_3N (132.8 mg, 95 μL, 0.68 mmol) and a solution of triphosgene (40.3 mg, 0.137 mmol) in DCM (2 mL) at 0 ℃. The reaction mixture was allowed to stir at 0 °C for 10 min and quenched with saturated aq. $NaHCO_3$ (5 mL). The resulted mixture was extracted with DCM (3 × 5 mL), washed with brine (10 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent under vacuum, the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 6:1) to afford (–)-12-*epi*-hapalindole Q isonitrile (**2**, 31 mg, 74%) as a white foam. R_f = 0.65 (silica gel, hexane/ethyl acetate = 6:1). R_f = 0.65 (silica gel, hexane/ethyl acetate = 6:1). $[\alpha]_D^{20}$ –32.3 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.04 (s, 1H), 5.90 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.17 (d, *J* = 18.0 Hz, 1H), 5.13 (d, *J* = 11.2 Hz, 1H), 4.53 (s, 1H), 4.48 (s, 1H), 3.77 (brs, 1H), 3.14 (brs, 1H), 2.70 (brs, 1H), 1.54 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 146.6, 145.4, 138.3, 136.6, 130.9, 128.8, 121.7, 119.2, 116.2, 113.2, 111.9, 111.5, 65.6, 49.4, 40.4, 29.7, 27.0, 19.0, 16.5. IR (KBr): ν_{max} 3428, 2928, 2137, 1454, 1260, 1099, 749 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{25}N_2^+$ [M + H$^+$]: 305.2012, found: 305.2011.

(–)-**Hapalindole D (3)**

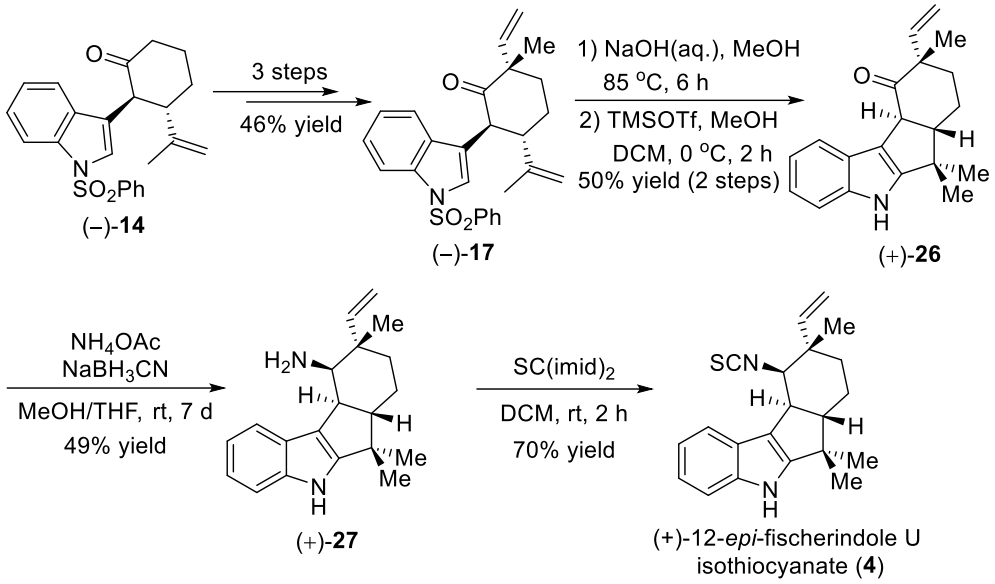


(–)-**25** (–)-hapalindole D (**3**)

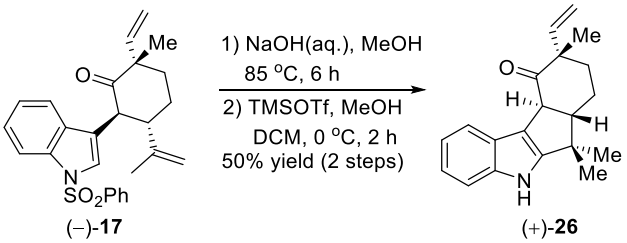
To a solution of (–)-**25** (30 mg, 69 μmol) in MeOH (6 mL) was added aqueous NaOH (3 M, 2 mL, 6.0 mmol) at room temperature. Then the mixture was allowed to be warmed to 85 °C and kept at the same temperature for 2.5 h. After removal of solvents, the residue was extracted with EtOAc (3 × 5 mL). The organic phase was washed with brine and dried over $MgSO_4$. After filtration and removal of the solvent under vacuum yielded a residue. The residue was then redissolved in DCM (3 mL), and to the solution was added $CS(imid)_2$ (15 mg, 77 μmol). The reaction mixture was allowed to stir at room temperature for 2 h. After removed the solvents and the residue was purified by flash column chromatography with hexane/dichloromethane (1:1) as an eluent to give (–)-hapalindole D (**3**) as a white foam (19 mg, 82%). R_f = 0.52 (silica gel, hexanes/ethyl acetate = 6:1). $[\alpha]_D^{25}$ –224 (*c* 3.1 CH_2Cl_2) [lit. (+)-hapalindole D, $[\alpha]_D^{25}$ +239 (*c* 3.1 CH_2Cl_2)[6]]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 5.87 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.12 (s, 1H), 5.08 (d, *J* = 6.4 Hz, 1H), 4.83 (s, 1H), 4.67 (s, 1H), 3.83 (s, 1H), 3.58 (d, *J* = 12.0 Hz, 1H), 2.88–2.78 (m, 1H), 2.04–1.95 (m, 1H), 1.90–1.76 (m, 2H), 1.64–1.52 (m, 2H), 1.54 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 145.6, 135.7, 126.5, 123.9, 122.0, 119.4, 117.3, 114.0, 113.0, 112.4, 111.5, 67.9, 44.0, 41.2, 36.7, 29.8, 28.0, 22.0, 18.8. IR (KBr): ν_{max} 3364, 2978, 2917, 1638, 1457, 1375, 742. HRMS (ESI) Calcd. for $C_{21}H_{25}N_2S^+$ [M + H$^+$]: 335.1733, found: 335.1735.

(F) Total Synthesis of (+)-12-*epi*-Fischerindole U Isothiocyanate (4).

The route for the synthesis of (+)-12-*epi*-fischerindole U isothiocyanate (**4**) is outlined below.

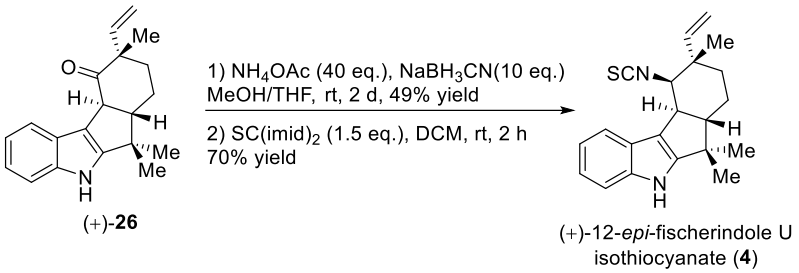


Ketone (+)-26



To a solution of (–)-**17** (1.0 g, 2.3 mmol) in MeOH (40 mL) was added aqueous NaOH (3 M, 15 mL, 45 mmol) at room temperature. Then the mixture was allowed to be warmed to 85 °C and kept at the same temperature for 6 h. After removal of solvents, the residue was extracted with ethyl acetate (3 × 30 mL). The organic phase was washed with brine and dried over $MgSO_4$. After filtration and removal of the solvent in *vacuo* the residue was then redissoved in DCM (25 mL), and the solution was cooled to 0 ℃ with ice-water bath. After the addition of TMSOTf (3.75 mL, 20.7 mmol) and MeOH (0.1 mL, 2.45 mmol) successively at 0 ℃. The obtained reaction mixture was stirred at 0 ℃ for 2 h. The reaction was then quenched with saturated aqueous $NaHCO_3$ (100 mL) and diluted with DCM (100 mL). The organic phase was separated and washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo to yield a residue. The residue was purified by flash column chromatography on silica gel column (petroleum ether/ethyl acetate = 6:1) to afford ketone (+)-**26** as semi-oil solid (338 mg, 50%). R_f = 0.66 (silica gel, petroleum ether/ethyl acetate = 3:1). $[\alpha]_D^{20}$ +34.1 (*c* 0.58, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.73–7.68 (m, 1H), 7.28–7.24 (m, 2H), 7.10 (m, 2H), 6.06 (dd, *J* = 17.6, 10.4 Hz, 1H), 5.23 (d, *J* = 11.6 Hz, 1 H), 5.19 (d, *J* = 4.4 Hz, 1 H), 4.03 (d, *J* = 12.0 Hz, 1 H), 2.40−2.27 (m, 2H), 2.03−1.91 (m, 1H), 1.80 –1.65 (m, 2H), 1.36 (s, 3H), 1.24 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 151.1, 142.9, 139.7, 124.4, 120.9, 120.1, 120.1, 115.1, 113.2, 111.4, 64.6, 52.6, 52.36, 41.2, 40.4, 25.1, 24.1, 22.2, 20.4. IR (KBr): ν_{max} 3408, 2928, 1705, 1637, 1452, 1296, 920, 744 cm^{-1}; HRMS (ESI) Calcd. for $C_{20}H_{24}NO^+$ [M + H$^+$]: 294.1858, found: 294.1857.

(+)-12-*epi*-Fischerindole U isothiocyanate (4)



(+)-**26**

(+)-12-*epi*-fischerindole U isothiocyanate (**4**)

Ketone (+)-**26** (100 mg, 0.34 mmol) was added to a solution of ammonium acetate (1.05 g, 13.7 mmol) and $NaBH_3CN$ (215 mg, 3.4 mmol) in a mixture solvent of MeOH (40 mL) and THF (10 mL). The reaction mixture was allowed to stir at room temperature for 2 d. The reaction mixture was then quenched with aqueous $NaHCO_3$ and extracted diethyl ether (3 × 20 mL). The organic layers was washed with brine and dried over $MgSO_4$. After filtration and removal of the solvent in *vacuo* the residue was purified by flash column chromatography on silica gel column (CH_2Cl_2/hexane = 40:1) to afford an amine (49 mg, 49%). The amine was then redissolved in DCM (2 mL), and to the solution was added $CS(imid)_2$ (50 mg, 0.25 mmol). The reaction mixture was allowed to stir at room temperature for 2 h. After removed the solvents and the residue was purified by flash chromatography on silica gel column (hexane/dichloromethane = 1:1) to afford (+)-12-*epi*-fischerindole U isothiocyanate (**4**) as a white foam (39 mg, 70%). R_f = 0.52 (silica gel, hexanes/dichloromethane = 1:1). $[\alpha]_D^{20}$ +217 (*c* 0.035, CH_2Cl_2) [lit: $[\alpha]_D^{20}$ +231 (*c* 0.035, CH_2Cl_2)[12]]. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 6.8 Hz, 1H), 7.12–6.89 (m, 2H), 5.91 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 5.19 (d, *J* = 2.4 Hz, 1H), 4.50 (s, 1H), 3.20 (d, *J* = 10.4 Hz, 1H), 2.23 (t, *J* = 10.4 Hz, 1H), 2.02–1.89 (m, 1H), 1.71–1.59 (m, 3H), 1.40 (s, 3H), 1.22 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 210.7, 151.1, 142.9, 139.7, 124.4, 120.9, 120.1, 120.1, 115.1, 113.2, 111.4, 64.6, 52.6, 52.4, 41.2, 40.4, 25.1, 24.1, 22.2, 20.4. IR (KBr): ν_{max} 3389, 2959, 2085, 1638, 1453, 1362, 742 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{25}N_2S^+$ [M + H$^+$]: 337.1733, found: 337.1733.

Reference:

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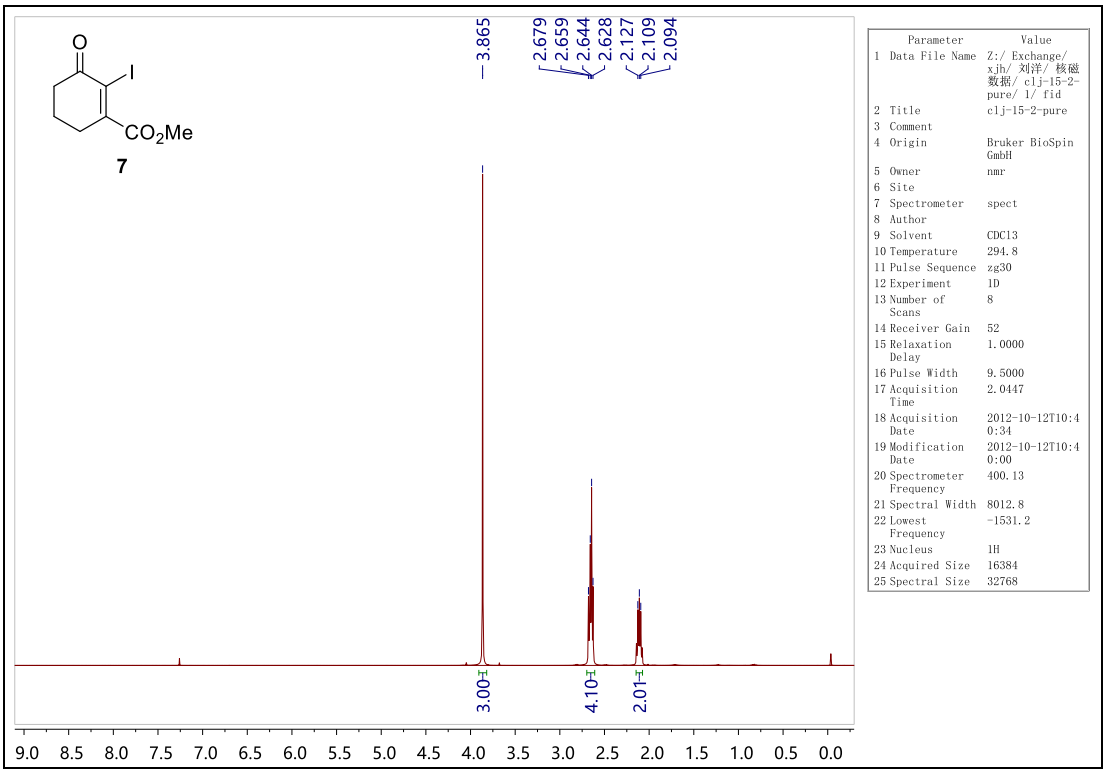
(G) NMR Spectra of New Compounds

Methyl 2-iodo-3-oxocyclohex-1-enecarboxylate (7)



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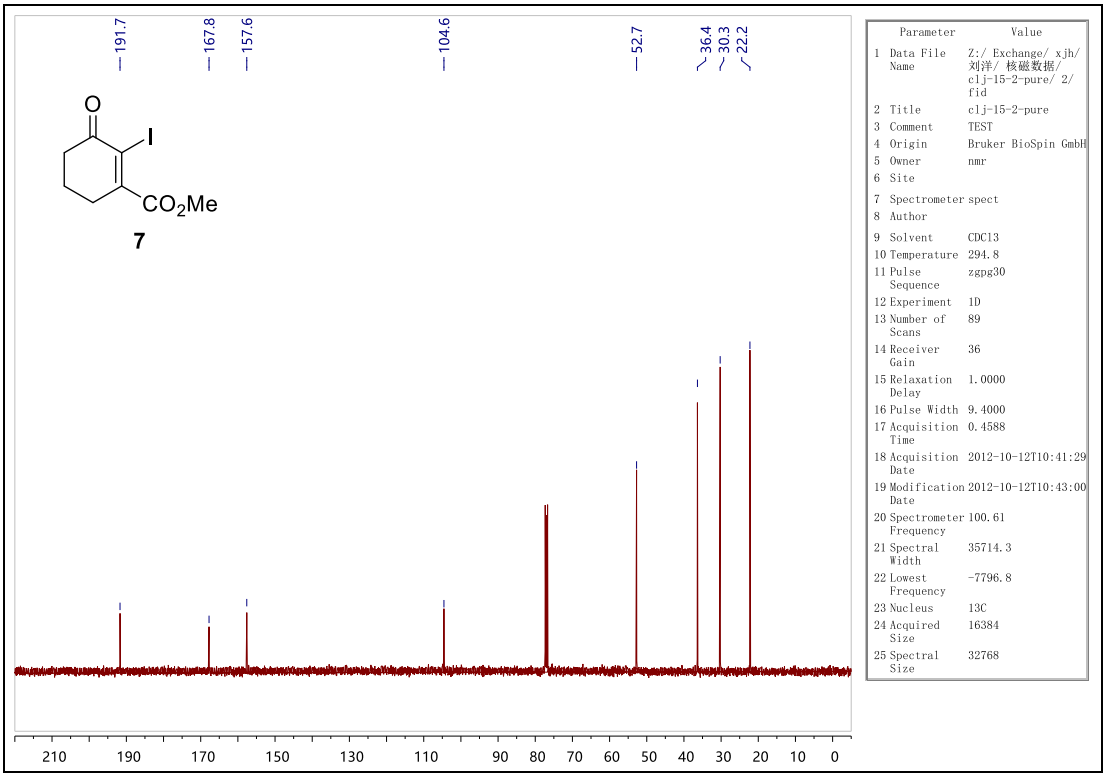
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.8
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	52
15	Relaxation Delay	1.0000
16	Pulse Width	9.5000
17	Acquisition Time	2.0447
18	Acquisition Date	2012-10-12T10:40:34
19	Modification Date	2012-10-12T10:40:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1531.2
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	32768



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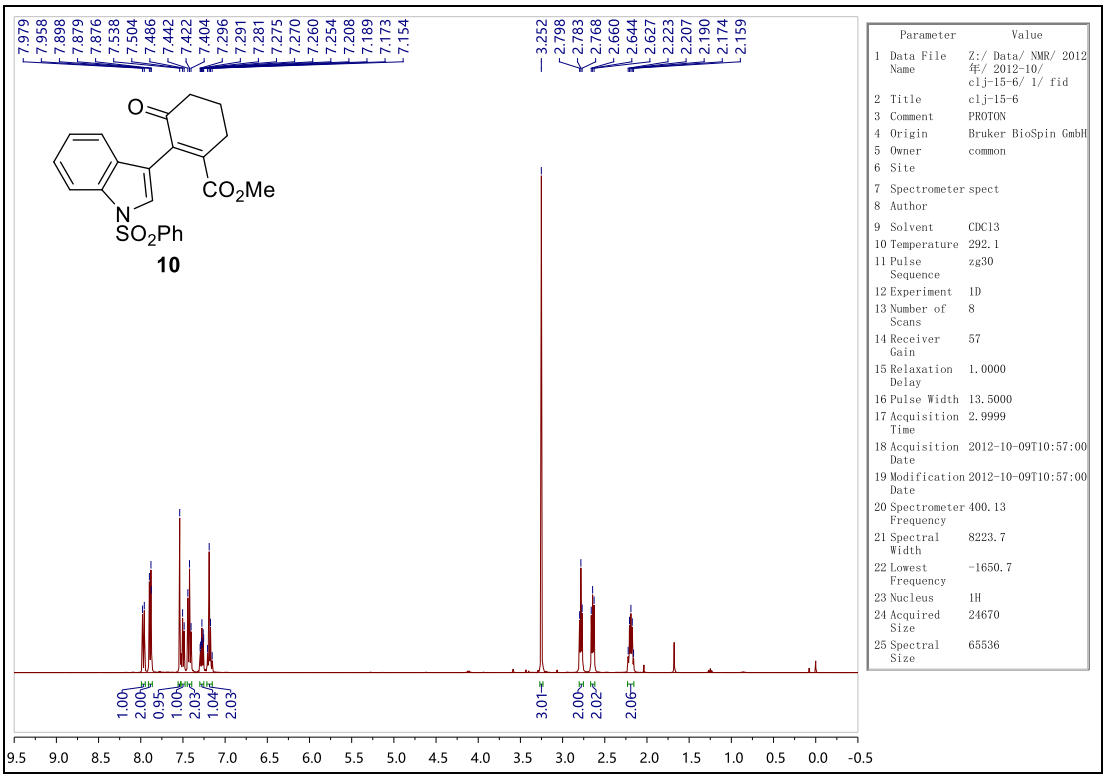
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.8
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	89
14	Receiver Gain	36
15	Relaxation Delay	1.0000
16	Pulse Width	9.4000
17	Acquisition Time	0.4588
18	Acquisition Date	2012-10-12T10:41:29
19	Modification Date	2012-10-12T10:43:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7796.8
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768

Methyl 3-oxo-2-(1-(phenylsulfonyl)-1*H*-indol-3-yl)cyclohex-1-enecarboxylate (10)



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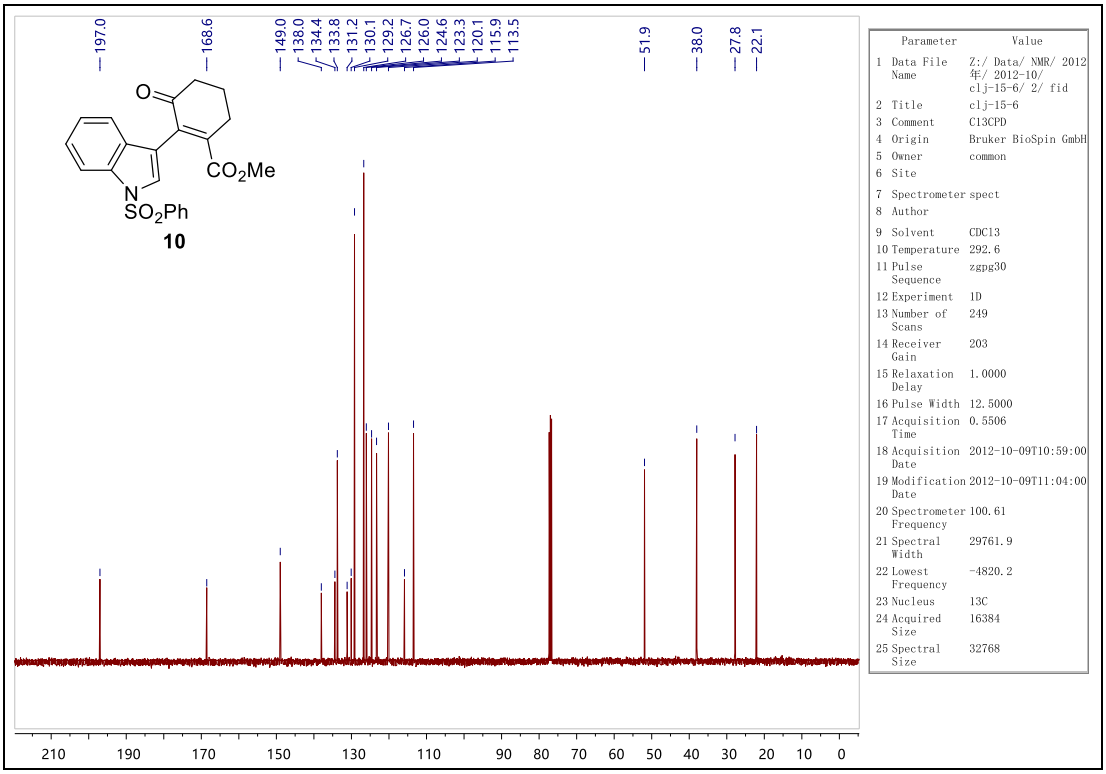
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.1
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	57
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	2.9999
18	Acquisition Date	2012-10-09T10:57:00
19	Modification Date	2012-10-09T10:57:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8223.7
22	Lowest Frequency	-1650.7
23	Nucleus	1H
24	Acquired Size	24670
25	Spectral Size	65536



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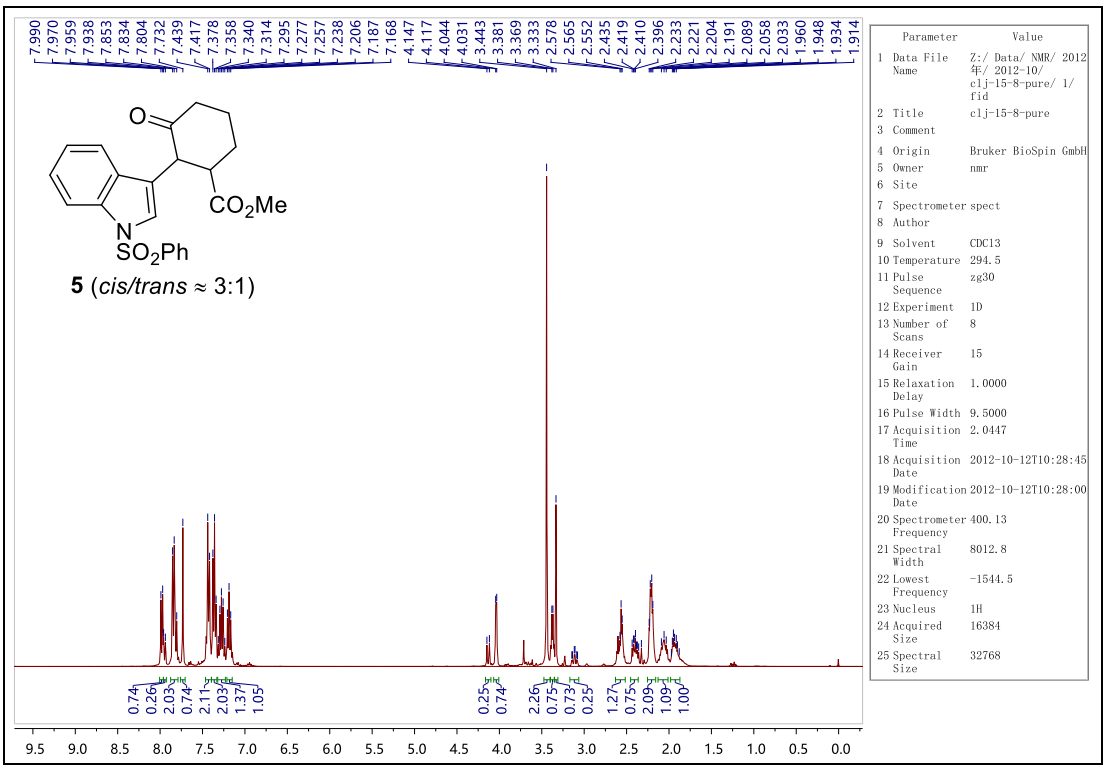
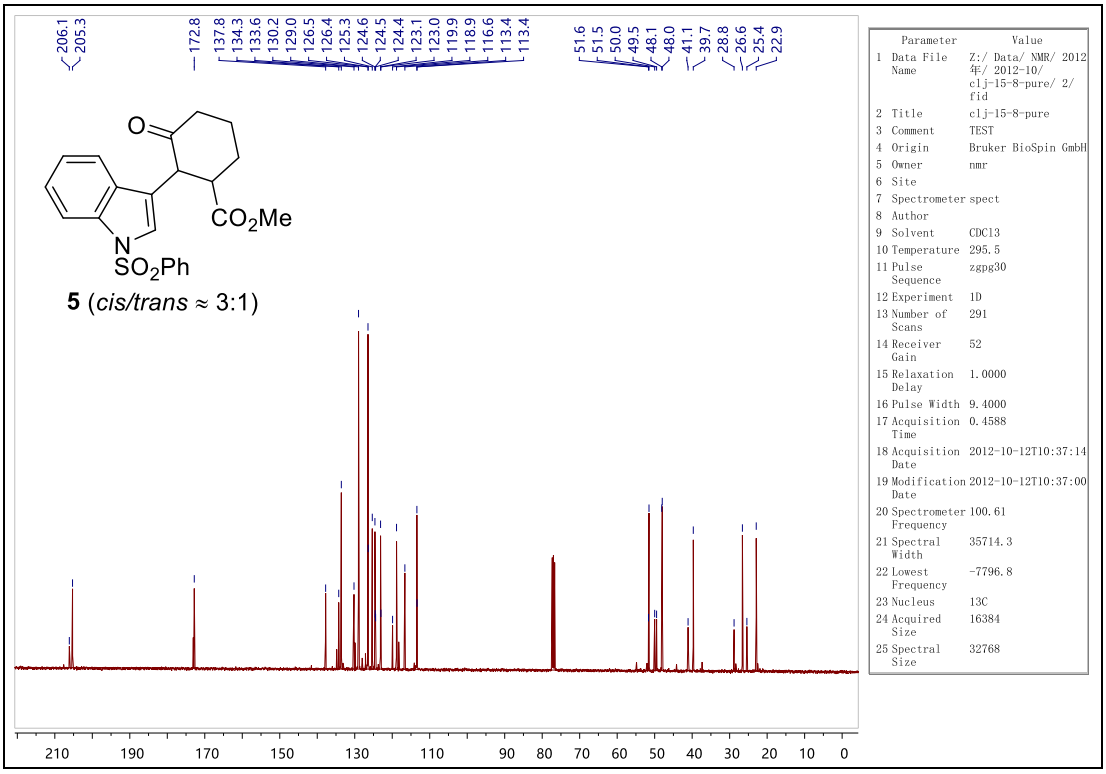
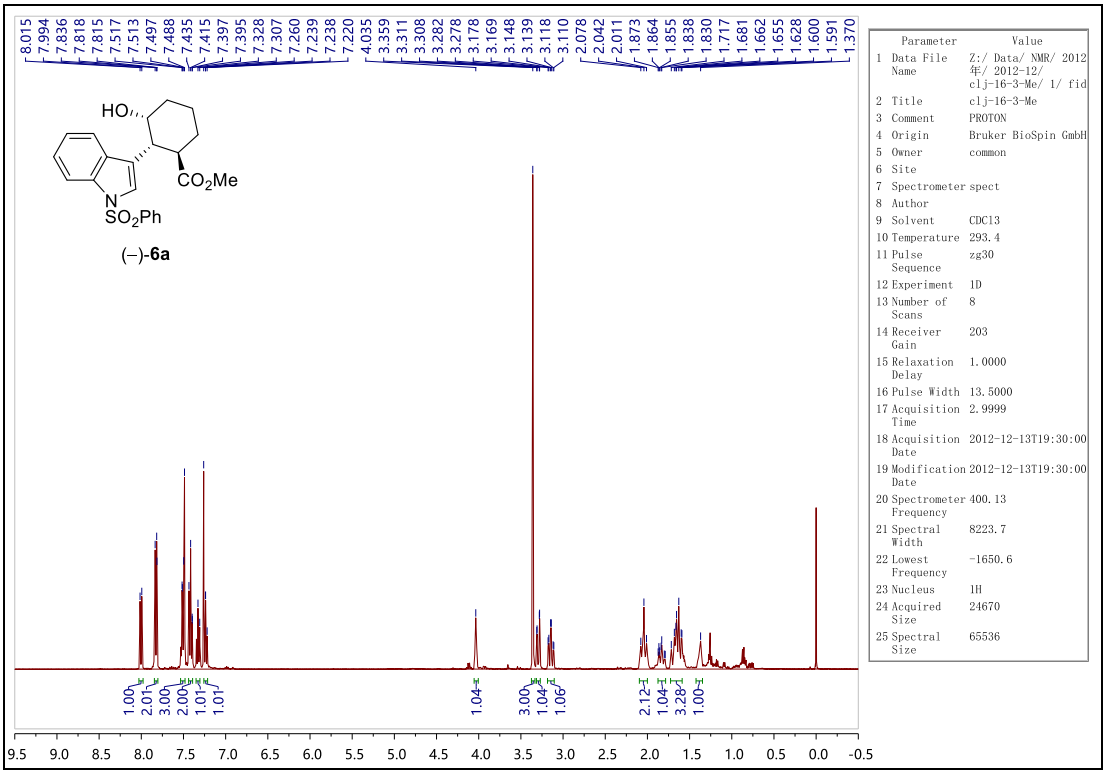
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.6
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	249
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.5000
17	Acquisition Time	0.5506
18	Acquisition Date	2012-10-09T10:59:00
19	Modification Date	2012-10-09T11:04:00
20	Spectrometer Frequency	100.61
21	Spectral Width	29761.9
22	Lowest Frequency	-4820.2
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768

Methyl 3-oxo-2-(1-(phenylsulfonyl)-1*H*-indol-3-yl)cyclohexanecarboxylate (5)





Alcohol (–)-6a



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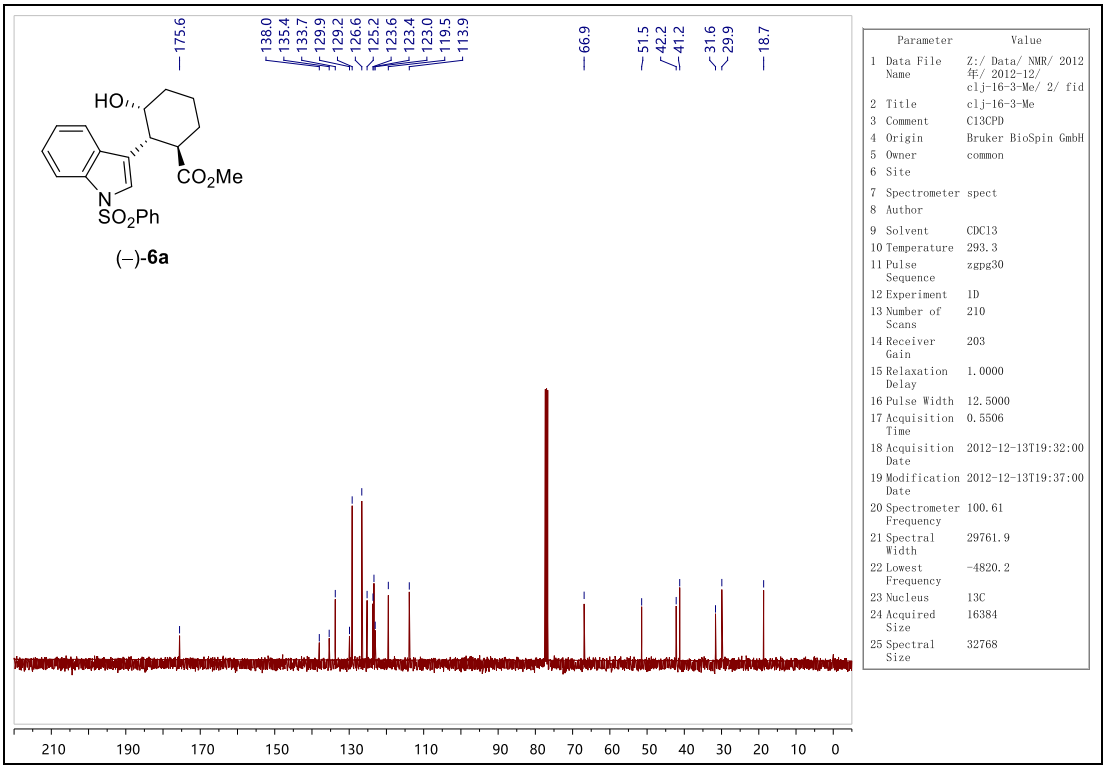
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.4
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	2.9999
18	Acquisition Date	2012-12-13T19:30:00
19	Modification Date	2012-12-13T19:30:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8223.7
22	Lowest Frequency	-1650.6
23	Nucleus	1H
24	Acquired Size	24670
25	Spectral Size	65536



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5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.3
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	210
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.5000
17	Acquisition Time	0.5506
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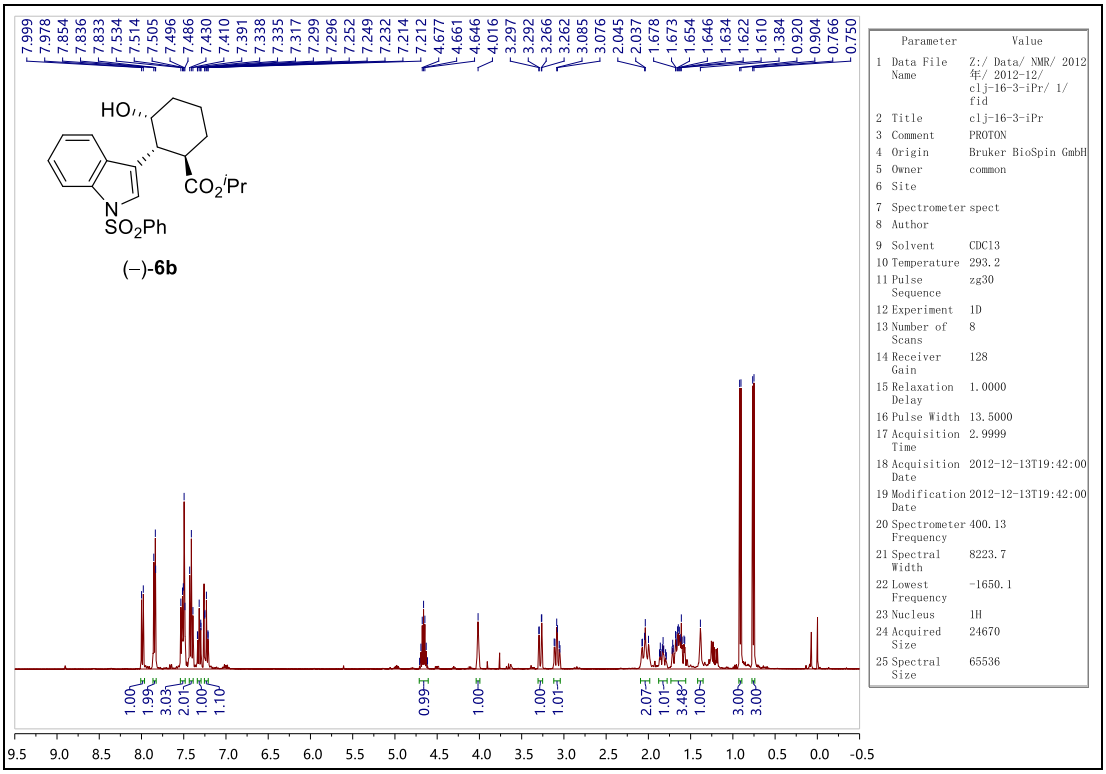
19	Modification Date	2012-12-13T19:37:00
20	Spectrometer Frequency	100.61
21	Spectral Width	29761.9
22	Lowest Frequency	-4820.2
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768

Alcohol (–)-6b


HO
CO2iPr
N
SO2Ph
(–)-6b
7.999 7.978 7.854 7.836 7.833 7.534 7.514 7.505 7.496 7.486 7.430 7.410 7.391 7.338 7.335 7.317 7.299 7.296 7.252 7.249 7.232 7.214 7.212 4.677 4.661 4.646 4.016 3.297 3.292 3.266 3.262 3.085 3.076 2.045 2.037 1.678 1.673 1.654 1.646 1.634 1.622 1.610 1.384 0.920 0.904 0.766 0.750
1.00 1.99 3.03 2.01 1.00 1.10 0.99 1.00 1.00 1.01 2.07 1.01 3.48 1.00 3.00 3.00
9.5 9.0 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 -0.5
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4 Origin Bruker BioSpin GmbH
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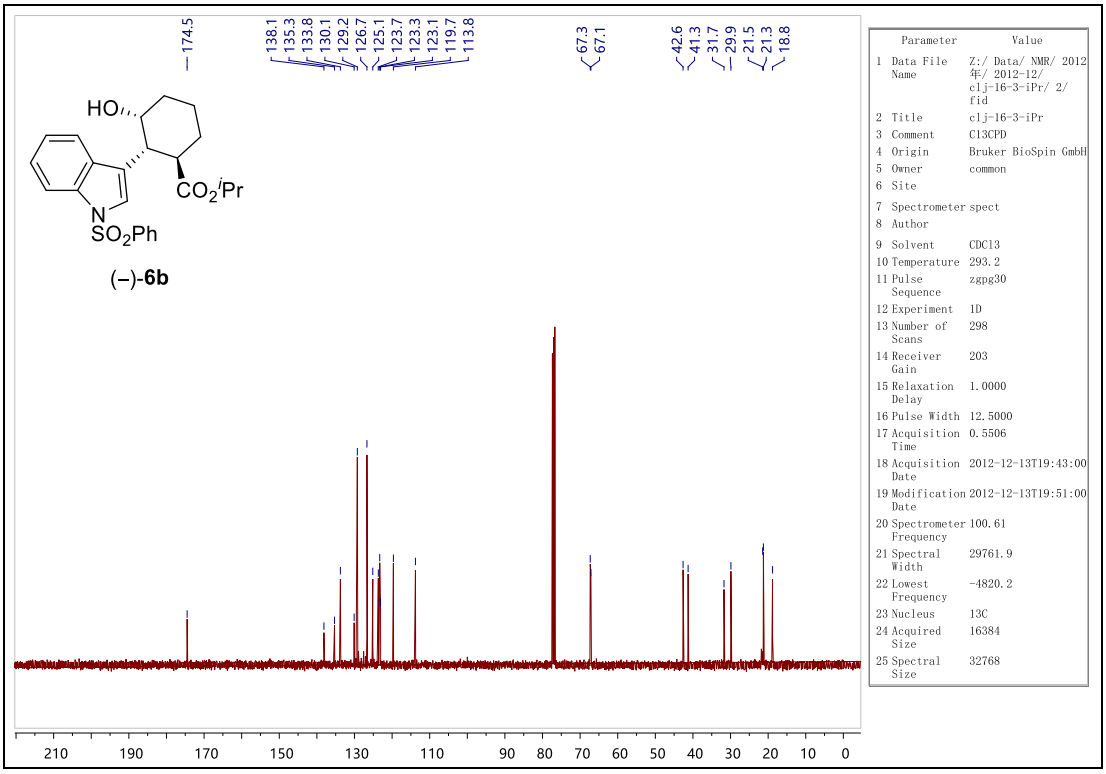
6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 293.2
11 Pulse Sequence zg30
12 Experiment 1D
13 Number of Scans 8
14 Receiver Gain 128
15 Relaxation Delay 1.0000
16 Pulse Width 13.5000
17 Acquisition Time 2.9999
18 Acquisition Date 2012-12-13T19:42:00
19 Modification Date 2012-12-13T19:42:00
20 Spectrometer Frequency 400.13
21 Spectral Width 8223.7
22 Lowest Frequency -1650.1
23 Nucleus 1H
24 Acquired Size 24670
25 Spectral Size 65536


HO
CO2iPr
N
SO2Ph
(–)-6b
174.5 138.1 135.3 133.8 130.1 129.2 126.7 125.1 123.7 123.3 123.1 119.7 113.8 67.3 67.1 42.6 41.3 31.7 29.9 21.5 21.3 18.8
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
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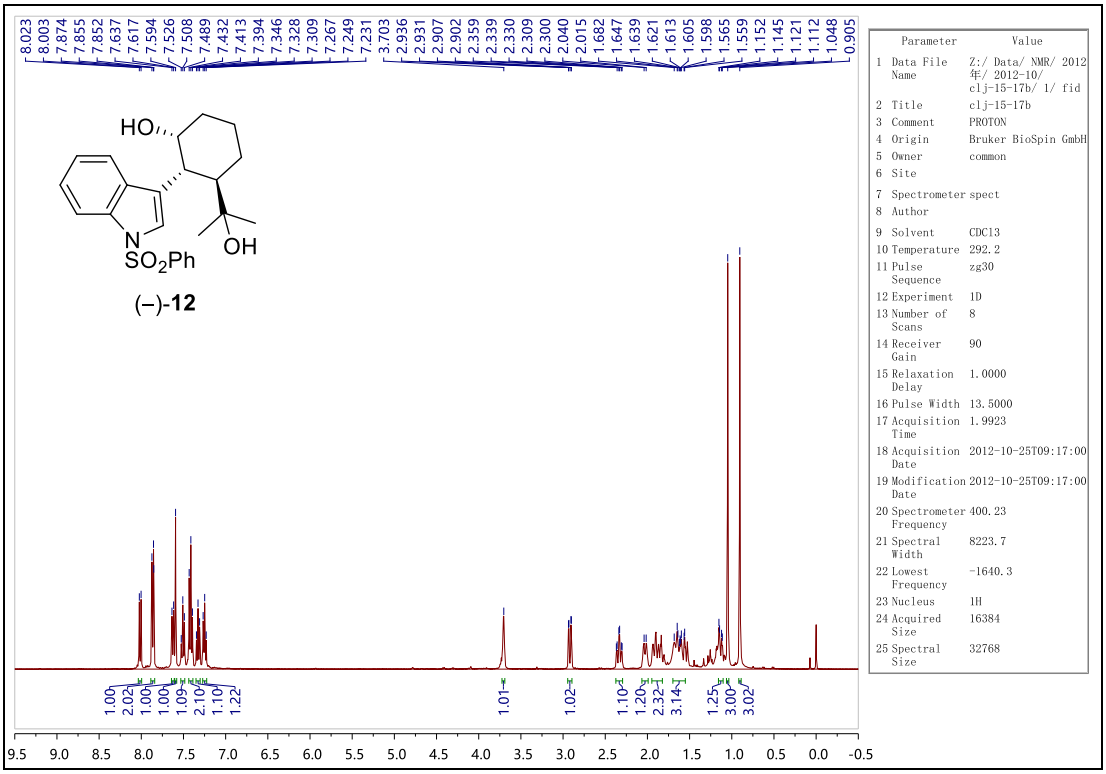
5 Owner common
6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 293.2
11 Pulse Sequence zgpg30
12 Experiment 1D
13 Number of Scans 298
14 Receiver Gain 203
15 Relaxation Delay 1.0000
16 Pulse Width 12.5000
17 Acquisition Time 0.5506
18 Acquisition Date 2012-12-13T19:43:00
19 Modification Date 2012-12-13T19:51:00
20 Spectrometer Frequency 100.61
21 Spectral Width 29761.9
22 Lowest Frequency -4820.2
23 Nucleus 13C
24 Acquired Size 16384
25 Spectral Size 32768

Alcohol (–)-12



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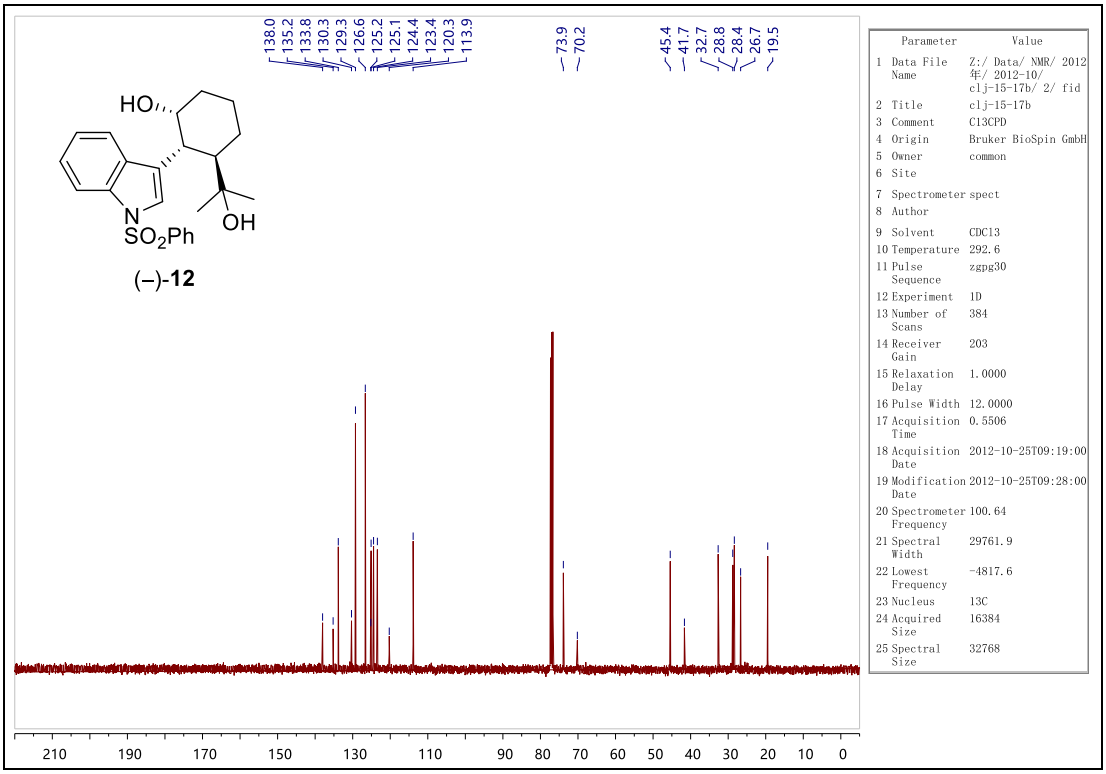
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.2
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	90
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	1.9923
18	Acquisition Date	2012-10-25T09:17:00
19	Modification Date	2012-10-25T09:17:00
20	Spectrometer Frequency	400.23
21	Spectral Width	8223.7
22	Lowest Frequency	-1640.3
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	32768



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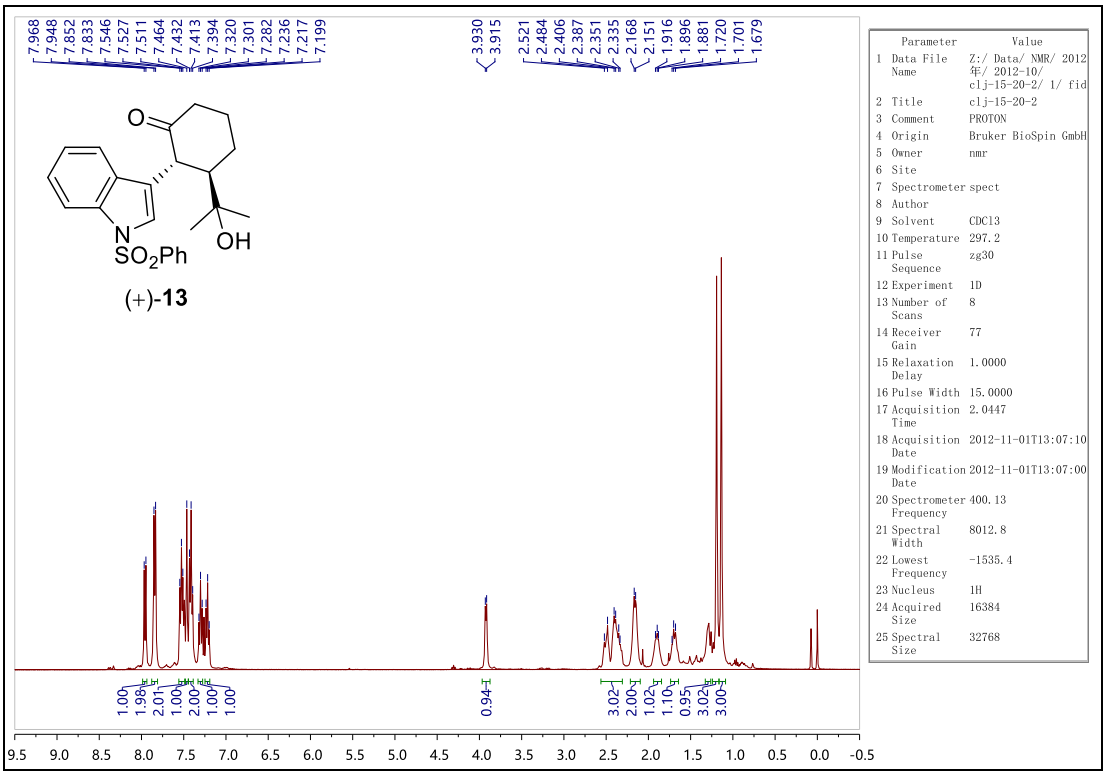
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.6
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	384
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.5506
18	Acquisition Date	2012-10-25T09:19:00
19	Modification Date	2012-10-25T09:28:00
20	Spectrometer Frequency	100.64
21	Spectral Width	29761.9
22	Lowest Frequency	-4817.6
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768

Ketone (+)-13



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6	Site	
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8	Author	
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10	Temperature	297.2
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	77
15	Relaxation Delay	1.0000
16	Pulse Width	15.0000
17	Acquisition Time	2.0447
18	Acquisition Date	2012-11-01T13:07:10
19	Modification Date	2012-11-01T13:07:00
20	Spectrometer Frequency	400.13
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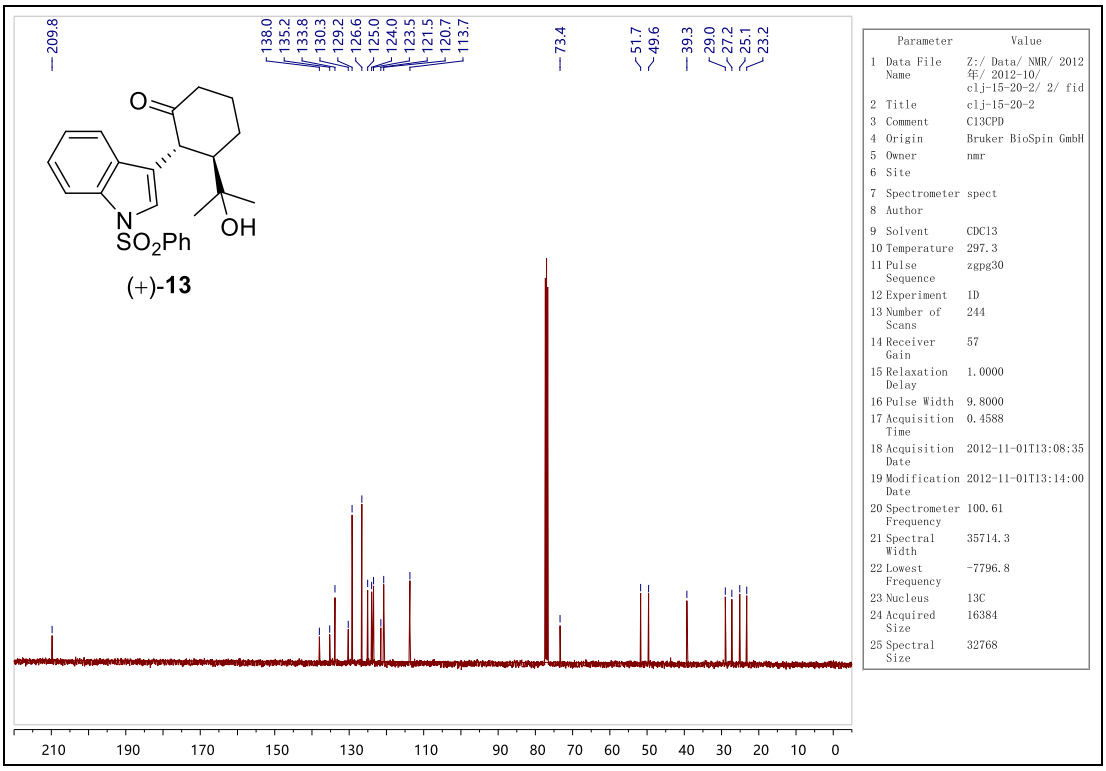
22	Lowest Frequency	-1535.4
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	32768



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5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.3
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	244
14	Receiver Gain	57
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.4588
18	Acquisition Date	2012-11-01T13:08:35
19	Modification Date	2012-11-01T13:14:00
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21	Spectral Width	35714.3
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23	Nucleus	13C
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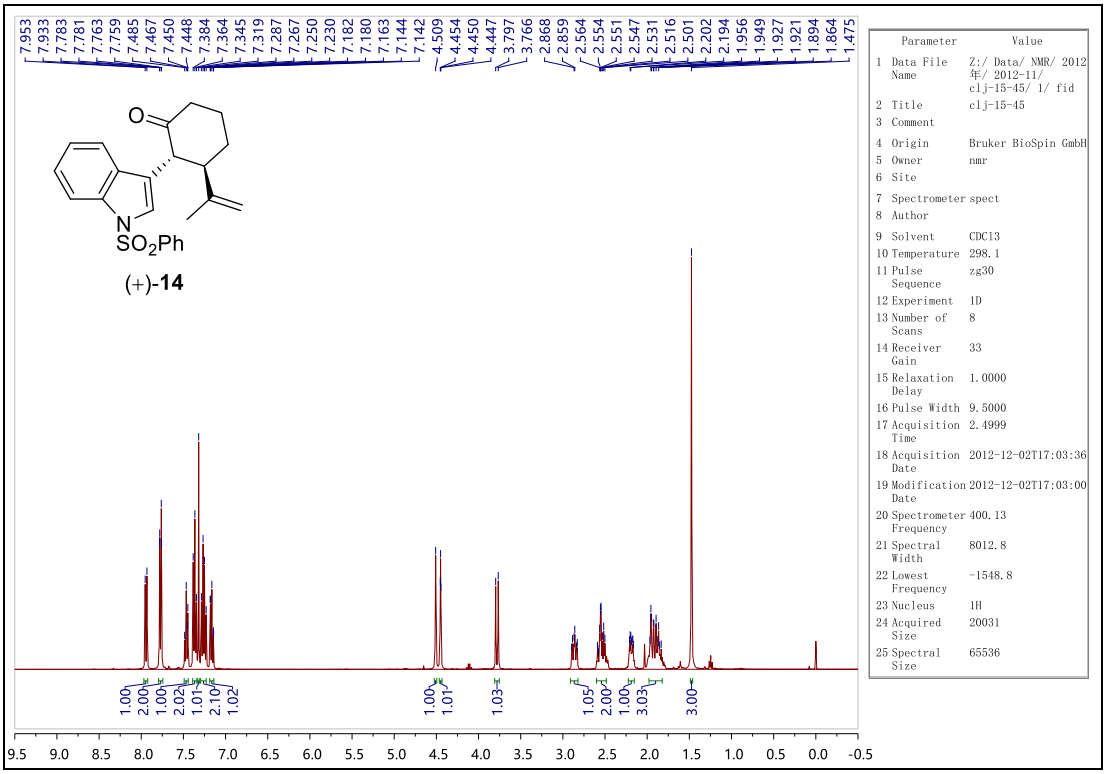
25	Spectral Size	32768

Ketone (+)-14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6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 298.1
11 Pulse Sequence zg30
12 Experiment 1D
13 Number of Scans 8
14 Receiver Gain 33
15 Relaxation Delay 1.0000
16 Pulse Width 9.5000
17 Acquisition Time 2.4999
18 Acquisition Date 2012-12-02T17:03:36
19 Modification Date 2012-12-02T17:03:00
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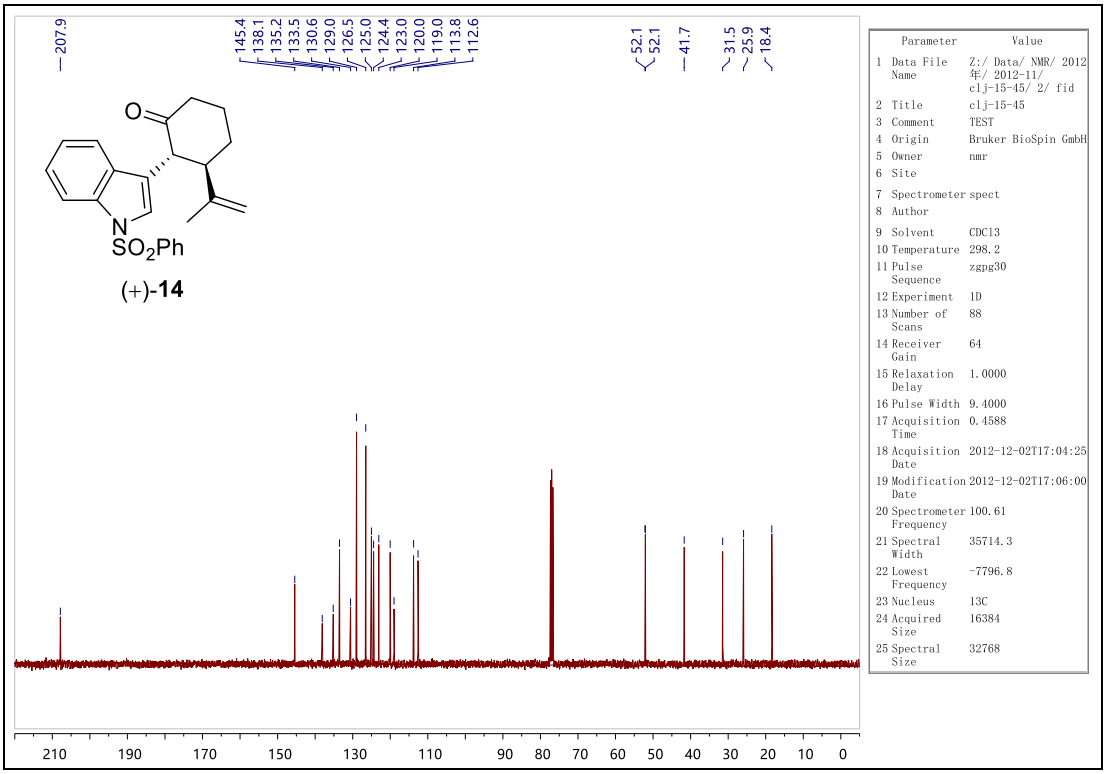
21 Spectral Width 8012.8
22 Lowest Frequency -1548.8
23 Nucleus 1H
24 Acquired Size 20031
25 Spectral Size 65536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6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 298.2
11 Pulse Sequence zgpg30
12 Experiment 1D
13 Number of Scans 88
14 Receiver Gain 64
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16 Pulse Width 9.4000
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18 Acquisition Date 2012-12-02T17:04:25
19 Modification Date 2012-12-02T17:06:00
20 Spectrometer Frequency 100.61
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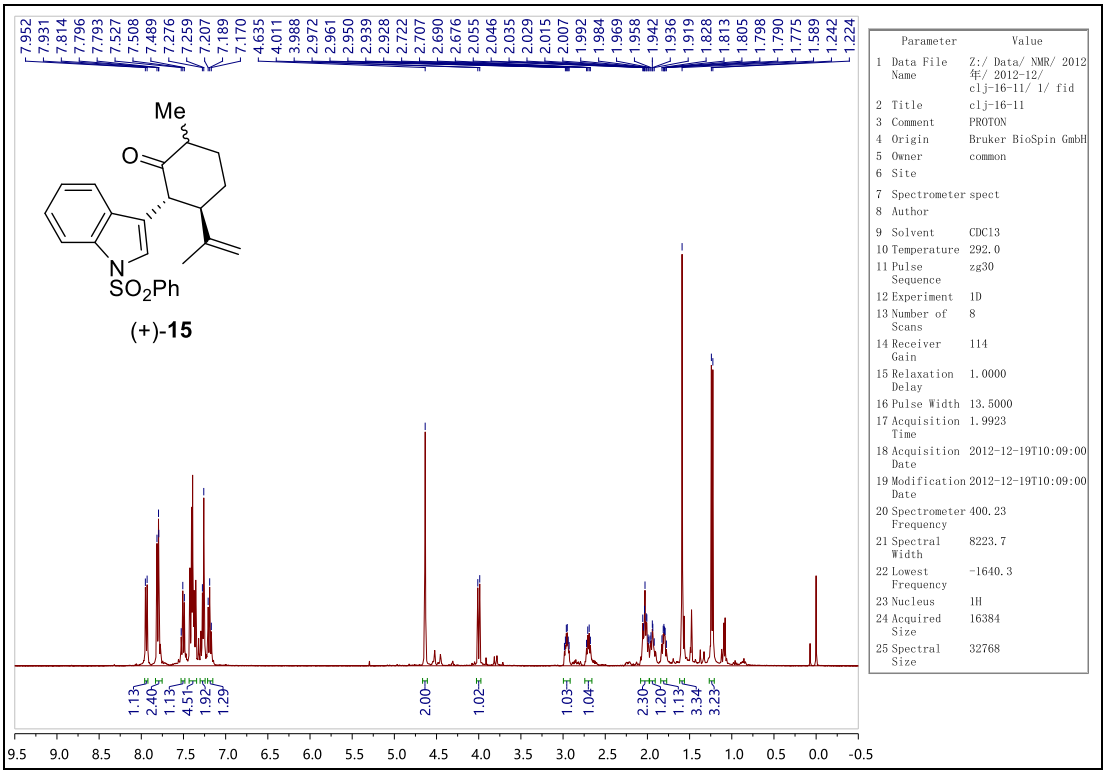
22 Lowest Frequency -7796.8
23 Nucleus 13C
24 Acquired Size 16384
25 Spectral Size 32768

Ketone (+)-15 (containing small isomers)



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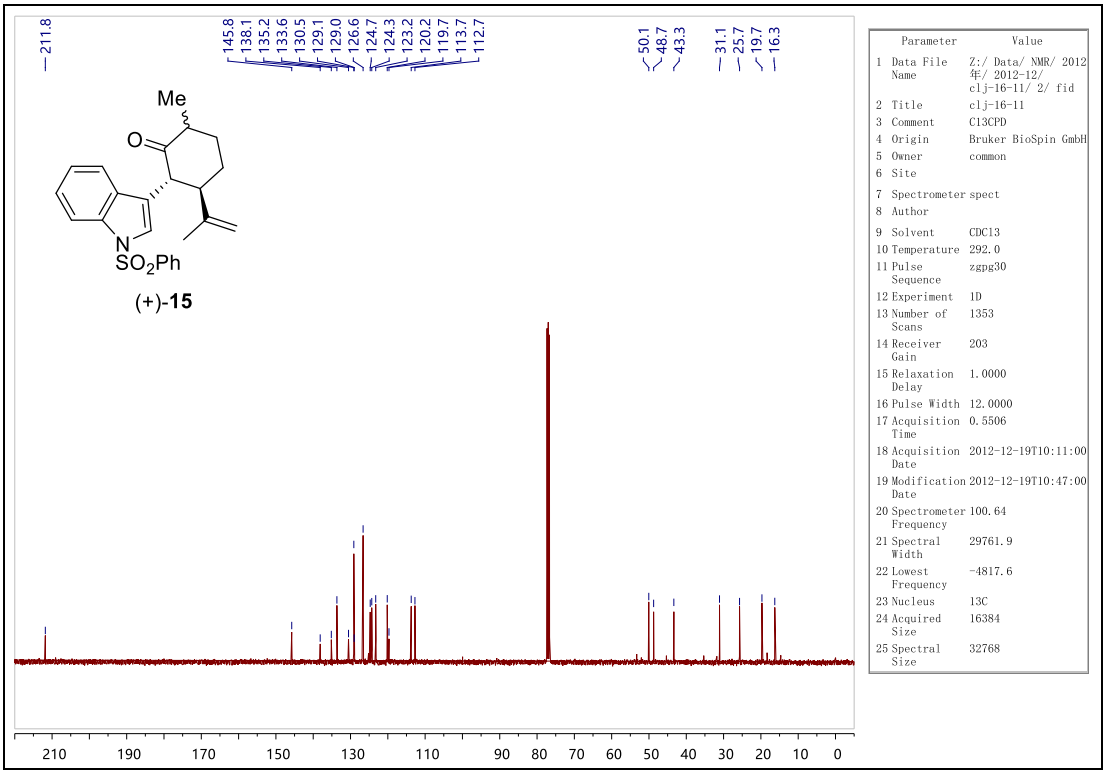
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	114
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	1.9923
18	Acquisition Date	2012-12-19T10:09:00
19	Modification Date	2012-12-19T10:09:00
20	Spectrometer Frequency	400.23
21	Spectral Width	8223.7
22	Lowest Frequency	-1640.3
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	32768



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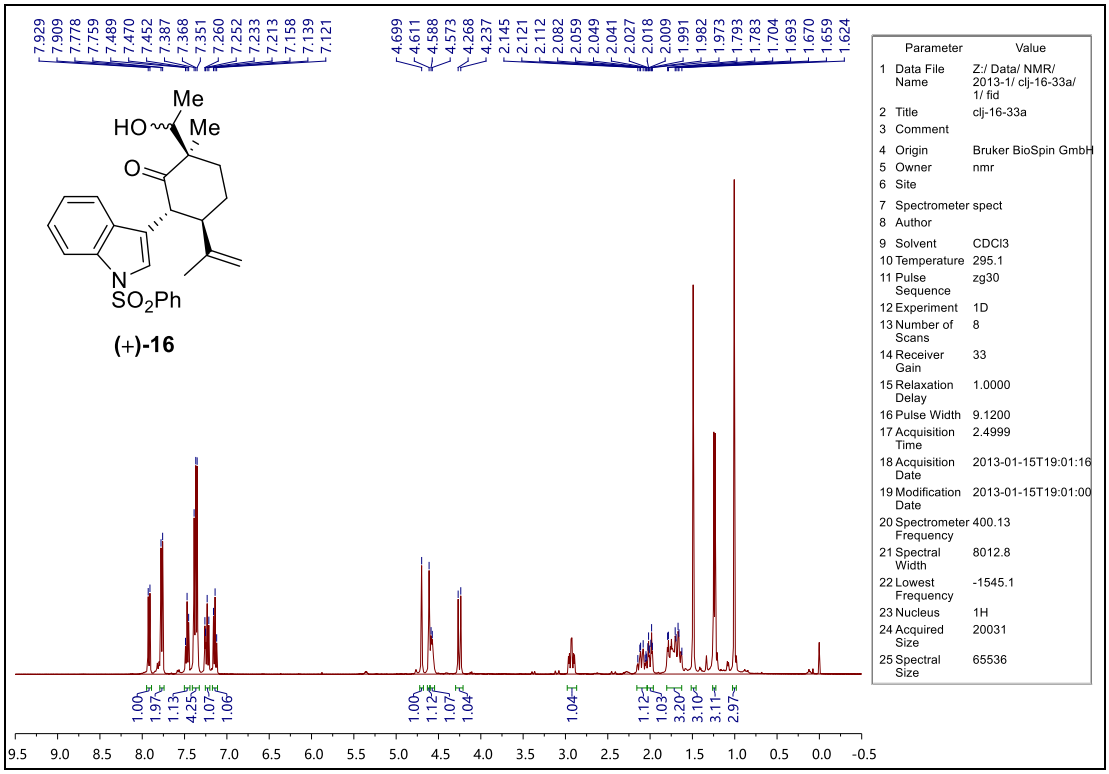
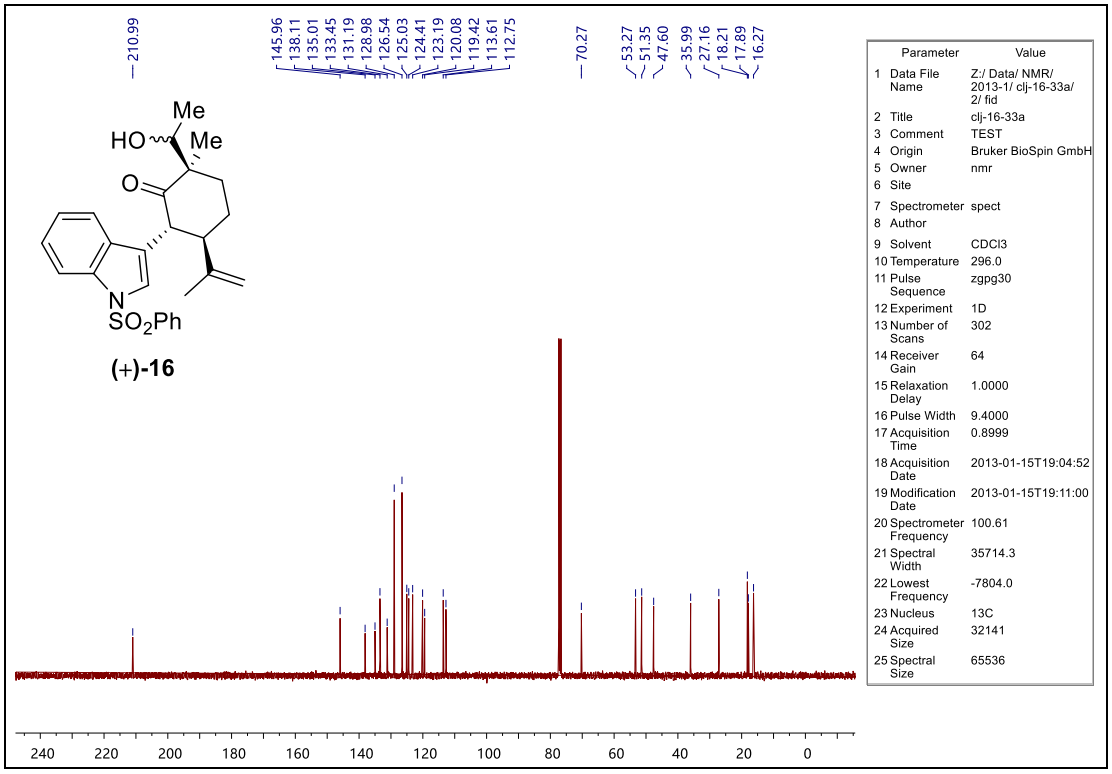
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	1353
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.5506
18	Acquisition Date	2012-12-19T10:11:00
19	Modification Date	2012-12-19T10:47:00
20	Spectrometer Frequency	100.64
21	Spectral Width	29761.9
22	Lowest Frequency	-4817.6
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768

Alcohol (+)-16



	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2013-1/ clj-16-33a/ 1/ fid
2	Title	clj-16-33a
3	Comment	
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.1
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	33
15	Relaxation Delay	1.0000
16	Pulse Width	9.1200
17	Acquisition Time	2.4999
18	Acquisition Date	2013-01-15T19:01:16
19	Modification Date	2013-01-15T19:01:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1545.1
23	Nucleus	1H
24	Acquired Size	20031
25	Spectral Size	65536



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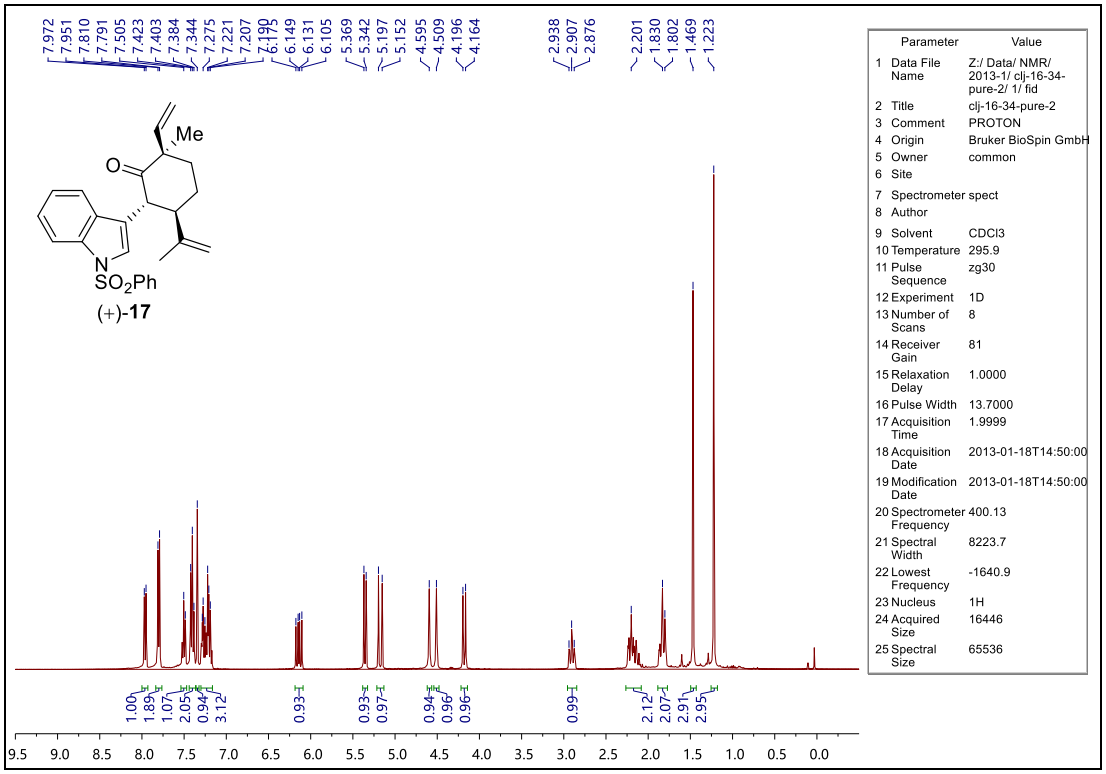
1	Data File Name	Z:/ Data/ NMR/ 2013-1/ clj-16-33a/ 2/ fid
2	Title	clj-16-33a
3	Comment	TEST
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	302
14	Receiver Gain	64
15	Relaxation Delay	1.0000
16	Pulse Width	9.4000
17	Acquisition Time	0.8999
18	Acquisition Date	2013-01-15T19:04:52
19	Modification Date	2013-01-15T19:11:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7804.0
23	Nucleus	13C
24	Acquired Size	32141
25	Spectral Size	65536

Ketone (+)-17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7.951
7.810
7.791
7.505
7.423
7.403
7.384
7.344
7.275
7.221
7.207
7.190
6.149
6.131
6.105
5.369
5.342
5.197
5.152
4.595
4.509
4.196
4.164
2.938
2.907
2.876
2.201
1.830
1.802
1.469
1.223
Me
O
N
SO2Ph
(+)-17
1.00
1.89
1.07
2.05
0.94
3.12
0.93
0.93
0.97
0.94
0.96
0.96
0.99
2.12
2.07
2.91
2.95
9.5 9.0 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
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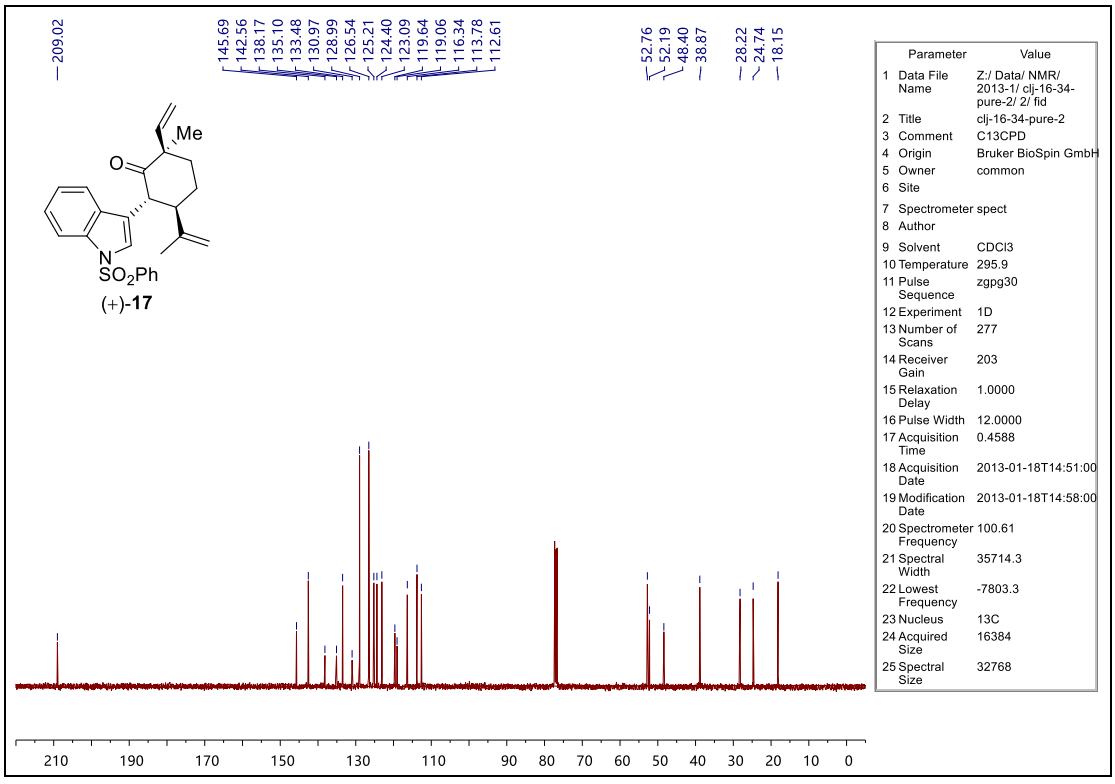
2 Title clj-16-34-pure-2
3 Comment PROTON
4 Origin Bruker BioSpin GmbH
5 Owner common
6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 295.9
11 Pulse Sequence zg30
12 Experiment 1D
13 Number of Scans 8
14 Receiver Gain 81
15 Relaxation Delay 1.0000
16 Pulse Width 13.7000
17 Acquisition Time 1.9999
18 Acquisition Date 2013-01-18T14:50:00
19 Modification Date 2013-01-18T14:50:00
20 Spectrometer Frequency 400.13
21 Spectral Width 8223.7
22 Lowest Frequency -1640.9
23 Nucleus 1H
24 Acquired Size 16446
25 Spectral Size 65536


209.02
145.69
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138.17
135.10
133.48
130.97
128.99
126.54
125.21
124.40
123.09
119.64
119.06
116.34
113.78
112.61
52.76
52.19
48.40
38.87
28.22
24.74
18.15
Me
O
N
SO2Ph
(+)-17
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
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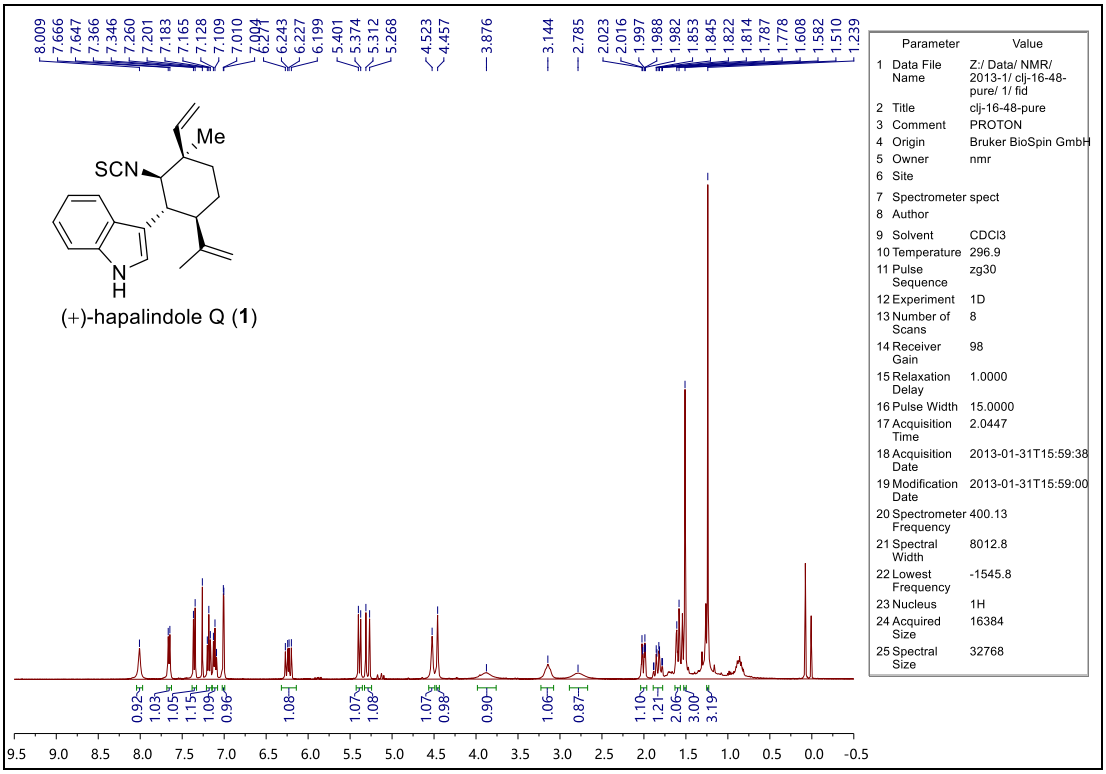
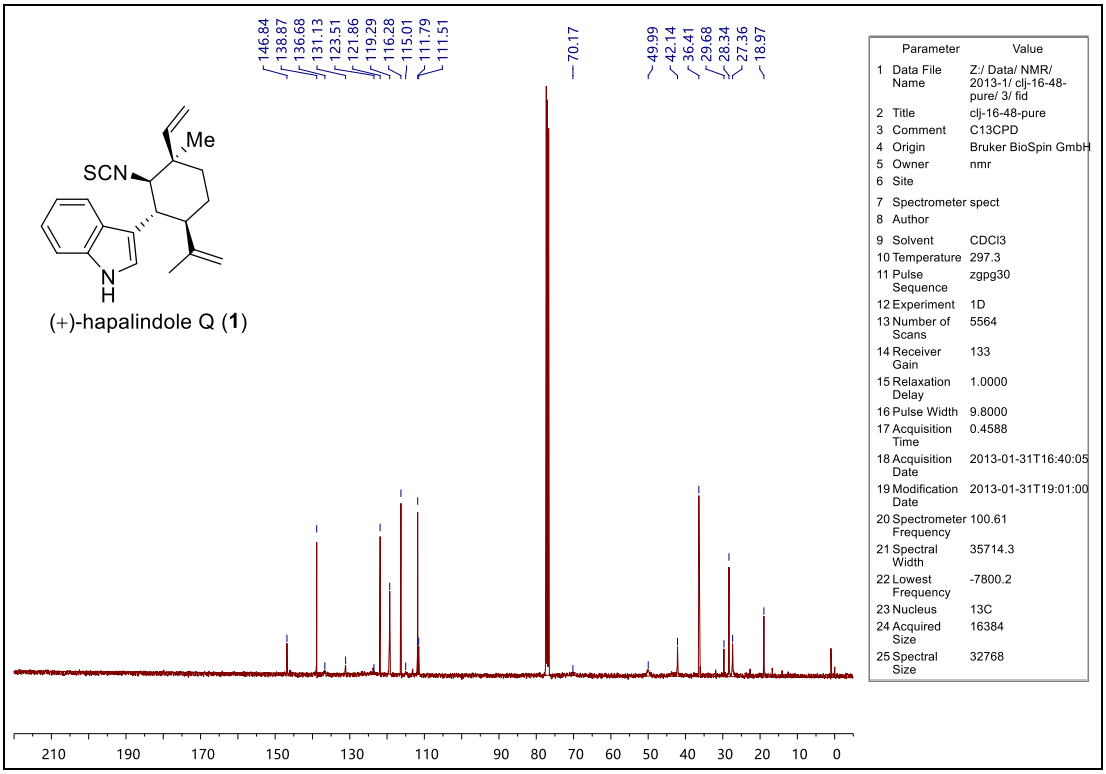
1 Data File Name Z:/ Data/ NMR/ 2013-1/ clj-16-34-pure-2/ 2/ fid
2 Title clj-16-34-pure-2
3 Comment C13CPD
4 Origin Bruker BioSpin GmbH
5 Owner common
6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 295.9
11 Pulse Sequence zgpg30
12 Experiment 1D
13 Number of Scans 277
14 Receiver Gain 203
15 Relaxation Delay 1.0000
16 Pulse Width 12.0000
17 Acquisition Time 0.4588
18 Acquisition Date 2013-01-18T14:51:00
19 Modification Date 2013-01-18T14:58:00
20 Spectrometer Frequency 100.61
21 Spectral Width 35714.3
22 Lowest Frequency -7803.3
23 Nucleus 13C
24 Acquired Size 16384
25 Spectral Size 32768

(+)-Hapalindole Q (1)

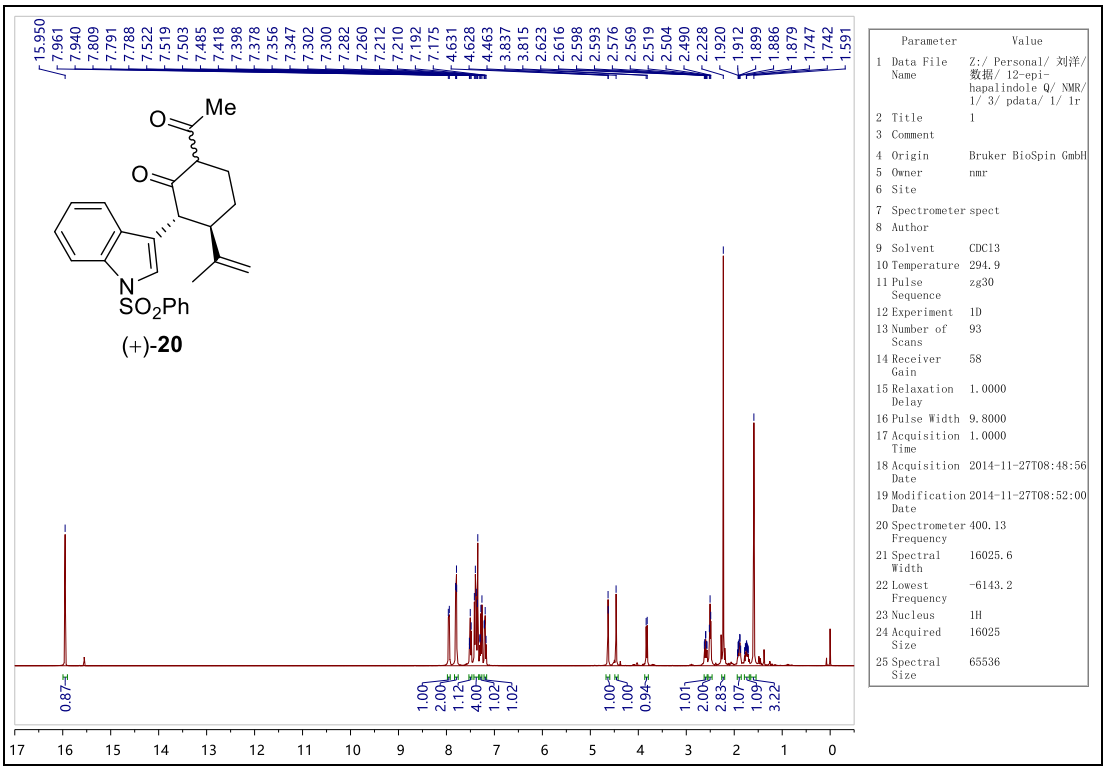


	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2013-1/ clj-16-48-pure/ 1/ fid
2	Title	clj-16-48-pure
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.9
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	98
15	Relaxation Delay	1.0000
16	Pulse Width	15.0000
17	Acquisition Time	2.0447
18	Acquisition Date	2013-01-31T15:59:38
19	Modification Date	2013-01-31T15:59:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1545.8
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	32768

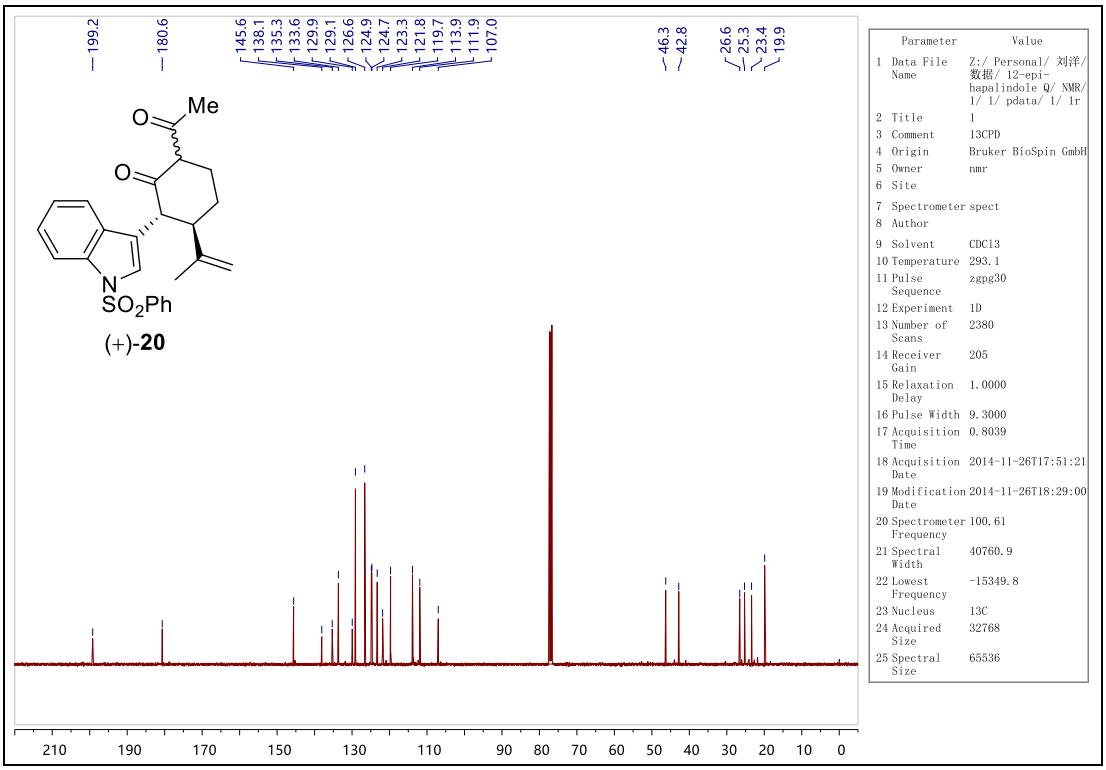


	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2013-1/ clj-16-48-pure/ 3/ fid
2	Title	clj-16-48-pure
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.3
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	5564
14	Receiver Gain	133
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.4588
18	Acquisition Date	2013-01-31T16:40:05
19	Modification Date	2013-01-31T19:01:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7800.2
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768

Diketone (+)-20

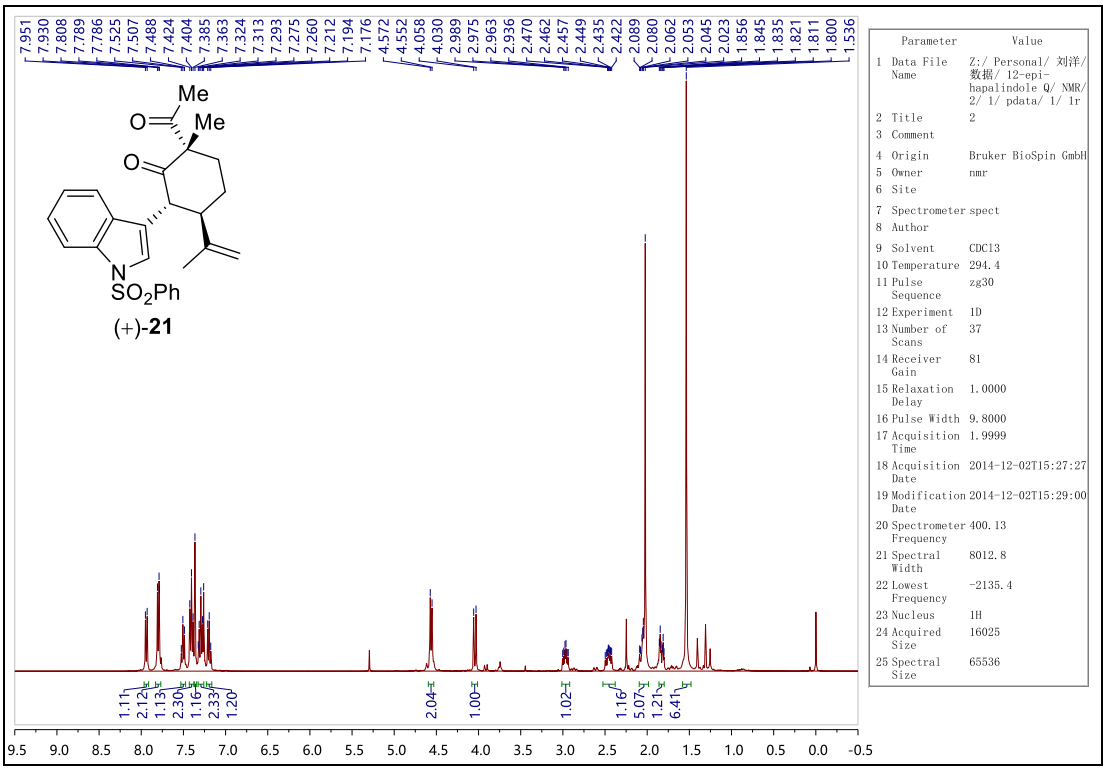


	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ 12-epi-hapalindole Q/ NMR/ 1/ 3/ pdata/ 1/ 1r
2	Title	1
3	Comment	
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.9
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	93
14	Receiver Gain	58
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	1.0000
18	Acquisition Date	2014-11-27T08:48:56
19	Modification Date	2014-11-27T08:52:00
20	Spectrometer Frequency	400.13
21	Spectral Width	16025.6
22	Lowest Frequency	-6143.2
23	Nucleus	1H
24	Acquired Size	16025
25	Spectral Size	65536



	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ 12-epi-hapalindole Q/ NMR/ 1/ 1/ pdata/ 1/ 1r
2	Title	1
3	Comment	13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.1
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	2380
14	Receiver Gain	205
15	Relaxation Delay	1.0000
16	Pulse Width	9.3000
17	Acquisition Time	0.8039
18	Acquisition Date	2014-11-26T17:51:21
19	Modification Date	2014-11-26T18:29:00
20	Spectrometer Frequency	100.61
21	Spectral Width	40760.9
22	Lowest Frequency	-15349.8
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	65536

Diketone (+)-21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Parameter Value
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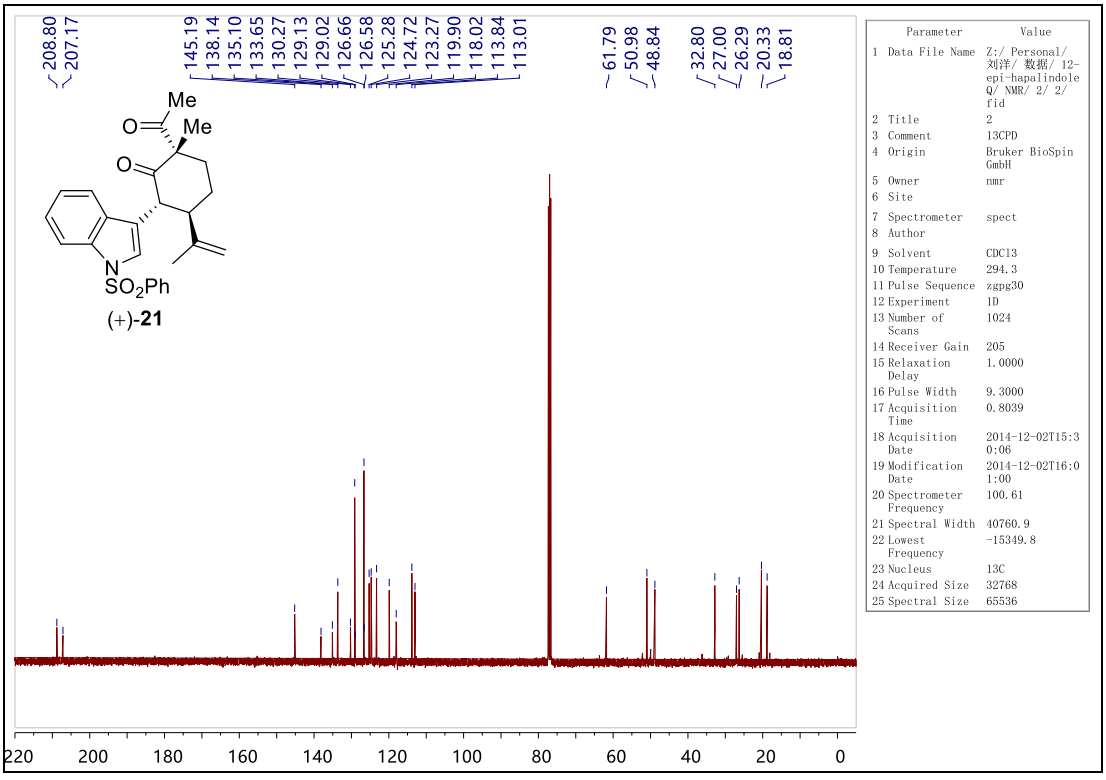
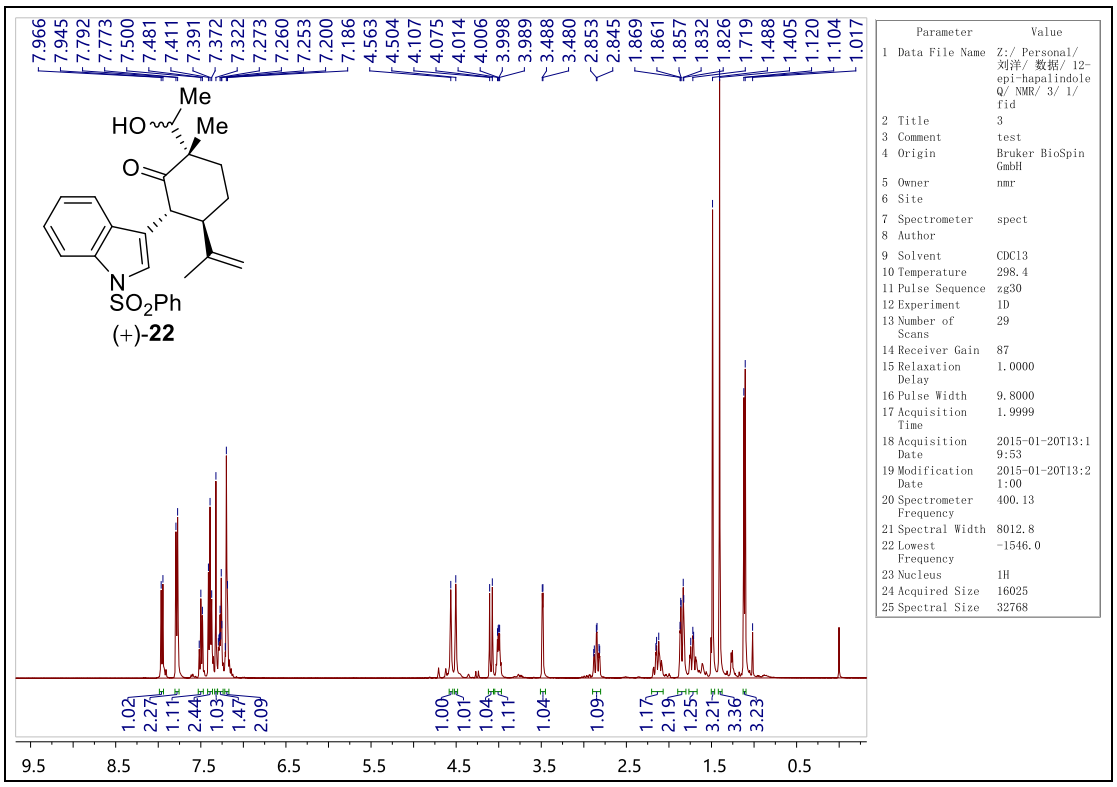
2 Title 2
3 Comment
4 Origin Bruker BioSpin GmbH
5 Owner nmr
6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 294.4
11 Pulse Sequence zg30
12 Experiment 1D
13 Number of Scans 37
14 Receiver Gain 81
15 Relaxation Delay 1.0000
16 Pulse Width 9.8000
17 Acquisition Time 1.9999
18 Acquisition Date 2014-12-02T15:27:27
19 Modification Date 2014-12-02T15:29:00
20 Spectrometer Frequency 400.13
21 Spectral Width 8012.8
22 Lowest Frequency -2135.4
23 Nucleus 1H
24 Acquired Size 16025
25 Spectral Size 65536


(+)-21
Parameter Value
1 Data File Name Z:/ Personal/ 刘洋/ 数据/ 12-epi-hapalindole Q/ NMR/ 2/ 2/ fid
2 Title 2
3 Comment 13CPD
4 Origin Bruker BioSpin GmbH
5 Owner nmr
6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 294.3
11 Pulse Sequence zgpg30
12 Experiment 1D
13 Number of Scans 1024
14 Receiver Gain 205
15 Relaxation Delay 1.0000
16 Pulse Width 9.3000
17 Acquisition Time 0.8039
18 Acquisition Date 2014-12-02T15:30:06
19 Modification Date 2014-12-02T16:01:00
20 Spectrometer Frequency 100.61
21 Spectral Width 40760.9
22 Lowest Frequency -15349.8
23 Nucleus 13C
24 Acquired Size 32768
25 Spectral Size 65536

Alcohol (+)-22



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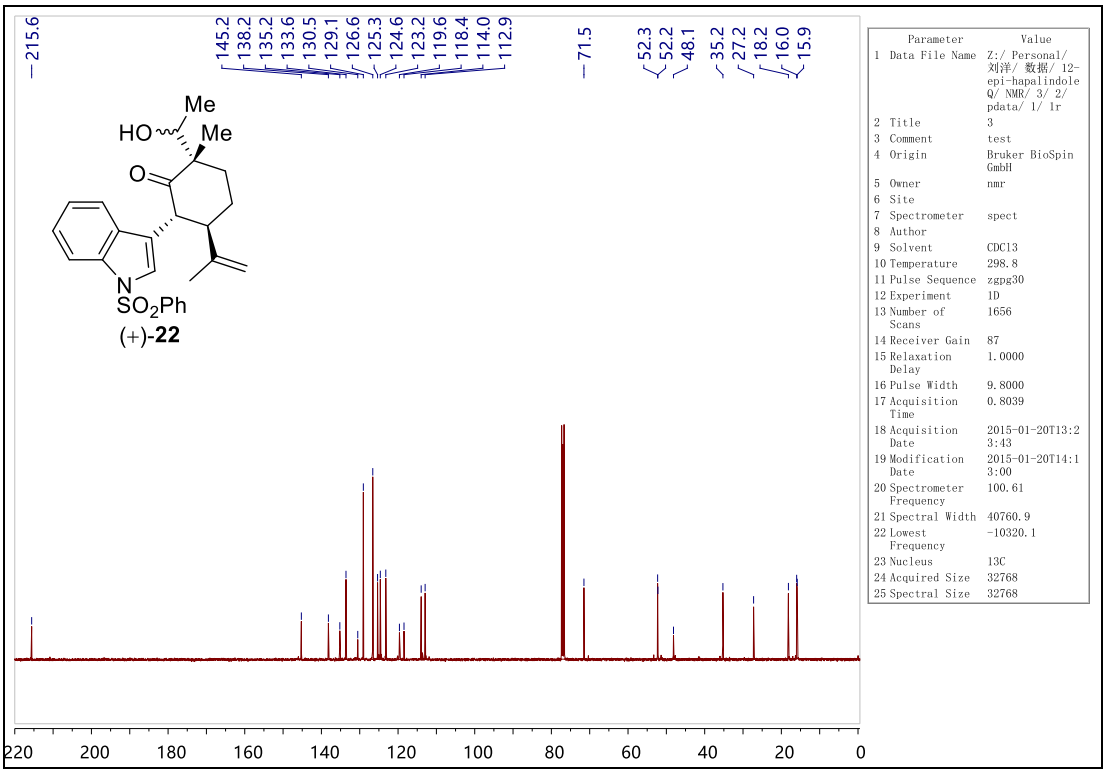
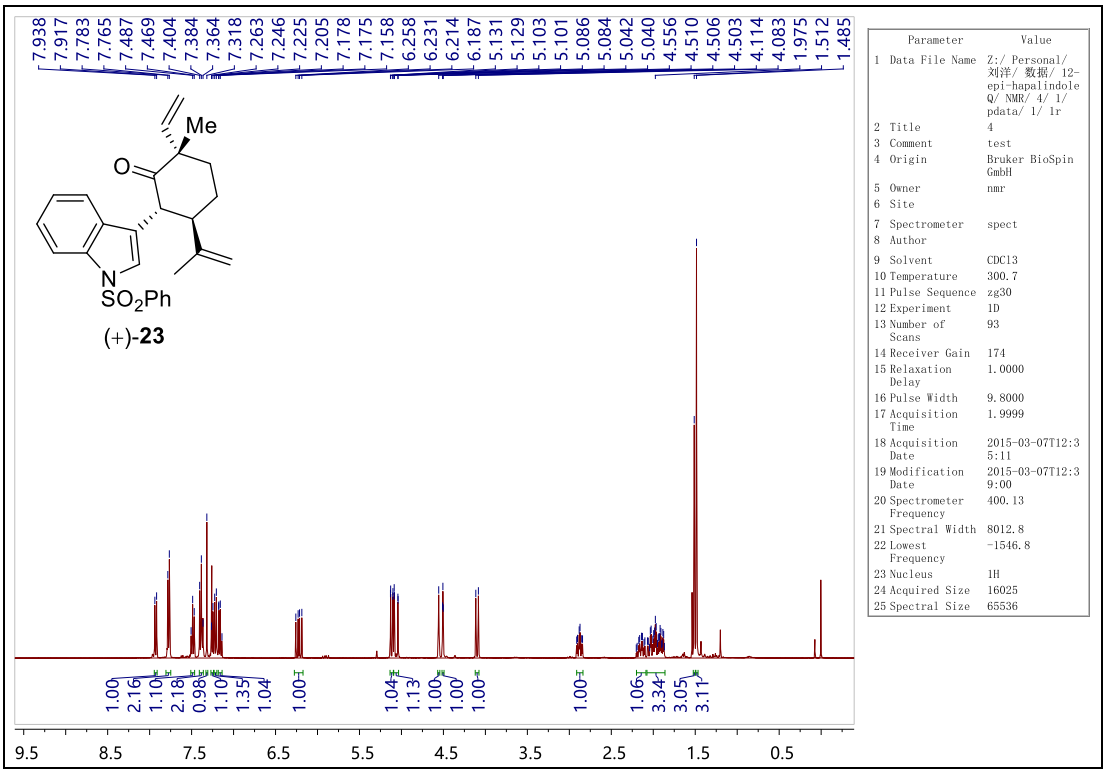
2	Title	3
3	Comment	test
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.4
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	29
14	Receiver Gain	87
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	1.9999
18	Acquisition Date	2015-01-20T13:19:53
19	Modification Date	2015-01-20T13:21:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1546.0
23	Nucleus	1H
24	Acquired Size	16025
25	Spectral Size	32768

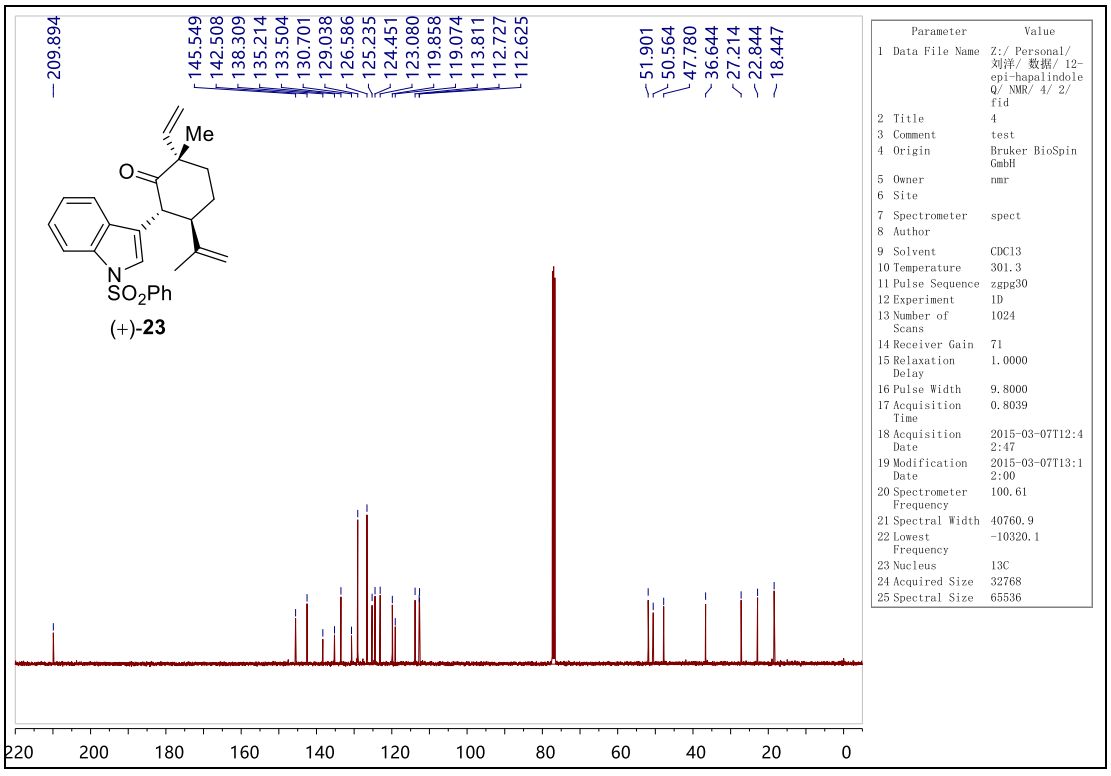


	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ 12-epi-hapalindole Q/ NMR/ 3/ 2/ pdata/ 1/ 1r
2	Title	3
3	Comment	test
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.8
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	1656
14	Receiver Gain	87
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.8039
18	Acquisition Date	2015-01-20T13:23:43
19	Modification Date	2015-01-20T14:13:00
20	Spectrometer Frequency	100.61
21	Spectral Width	40760.9
22	Lowest Frequency	-10320.1
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	32768

Ketone (+)-23

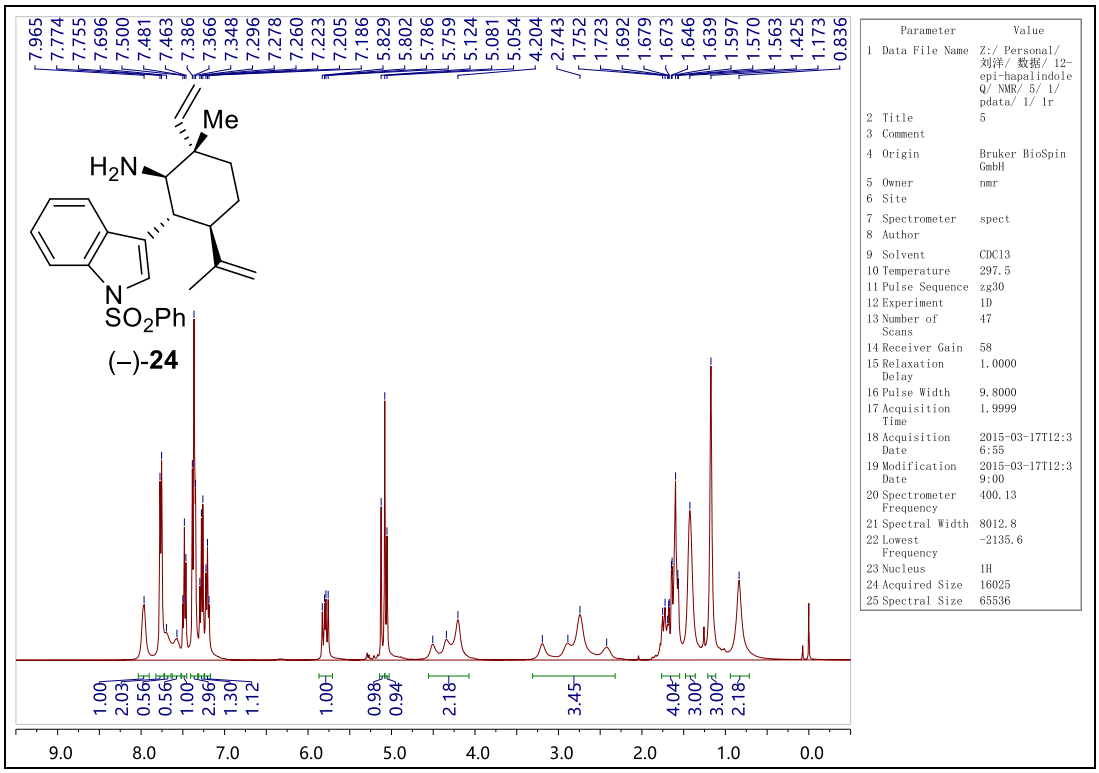


	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ 12-epi-hapalindole Q/ NMR/ 4/ 1/ pdata/ 1/ 1r
2	Title	4
3	Comment	test
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.7
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	93
14	Receiver Gain	174
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	1.9999
18	Acquisition Date	2015-03-07T12:35:11
19	Modification Date	2015-03-07T12:39:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1546.8
23	Nucleus	1H
24	Acquired Size	16025
25	Spectral Size	65536

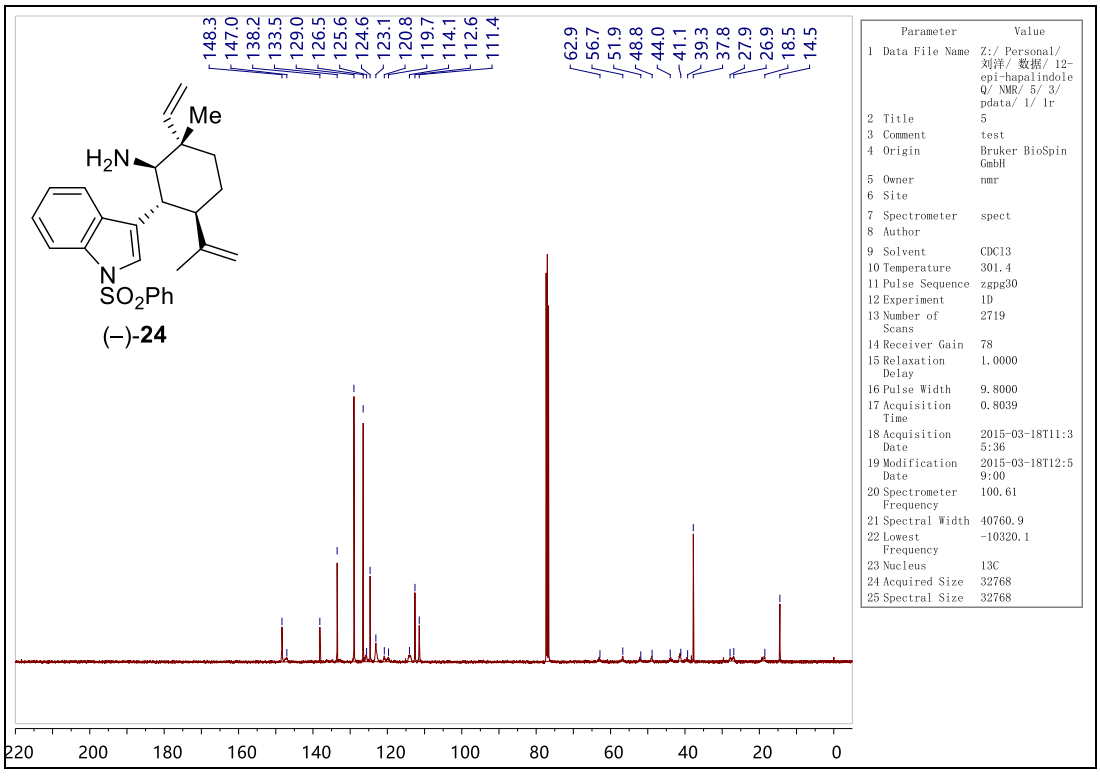


	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ 12-epi-hapalindole Q/ NMR/ 4/ 2/ fid
2	Title	4
3	Comment	test
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	301.3
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	1024
14	Receiver Gain	71
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.8039
18	Acquisition Date	2015-03-07T12:42:47
19	Modification Date	2015-03-07T13:12:00
20	Spectrometer Frequency	100.61
21	Spectral Width	40760.9
22	Lowest Frequency	-10320.1
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	65536

Amine (–)-24

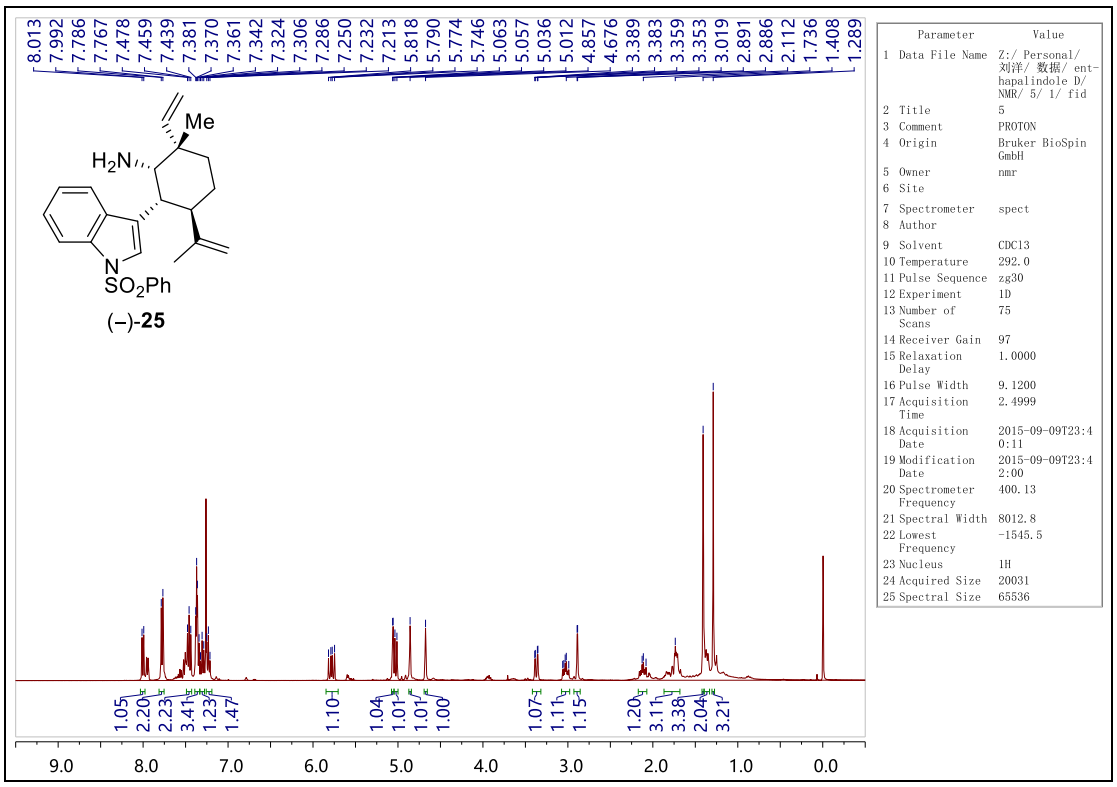


	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ 12-epi-hapalindole Q/ NMR/ 5/ 1/ pdata/ 1/ 1r
2	Title	5
3	Comment	
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.5
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	47
14	Receiver Gain	58
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	1.9999
18	Acquisition Date	2015-03-17T12:36:55
19	Modification Date	2015-03-17T12:39:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-2135.6
23	Nucleus	1H
24	Acquired Size	16025
25	Spectral Size	65536

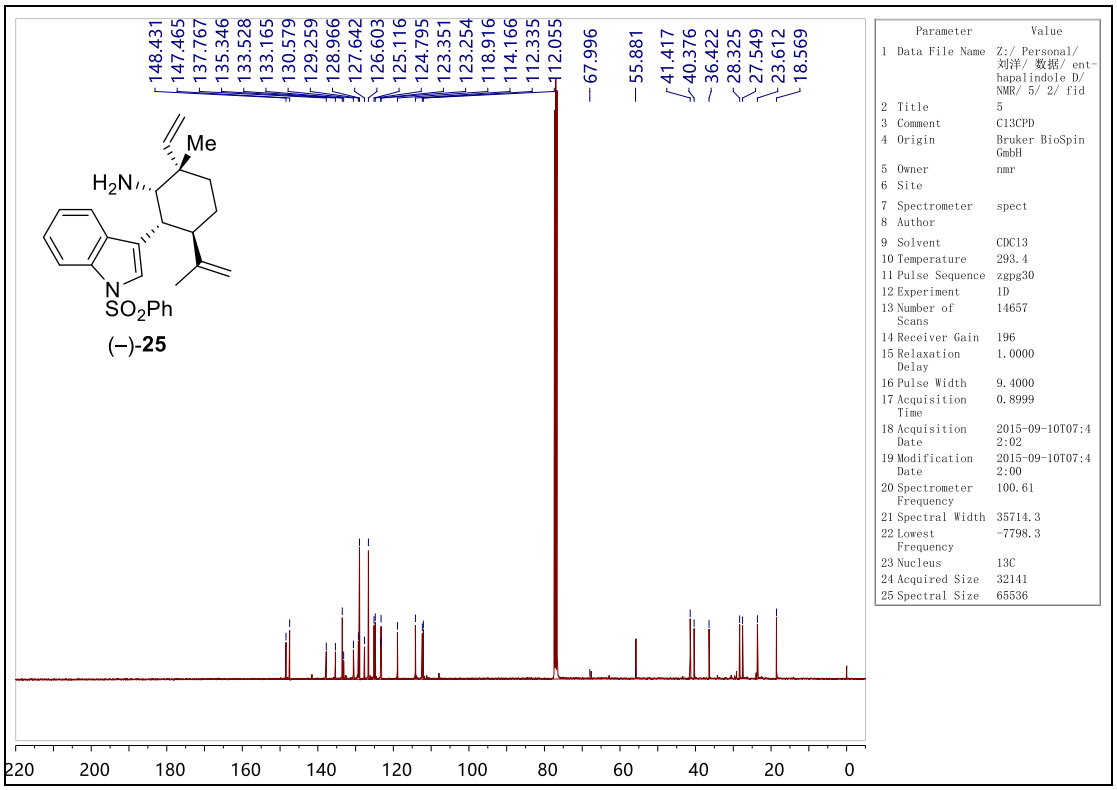


	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ 12-epi-hapalindole Q/ NMR/ 5/ 3/ pdata/ 1/ 1r
2	Title	5
3	Comment	test
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	301.4
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	2719
14	Receiver Gain	78
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.8039
18	Acquisition Date	2015-03-18T11:35:36
19	Modification Date	2015-03-18T12:59:00
20	Spectrometer Frequency	100.61
21	Spectral Width	40760.9
22	Lowest Frequency	-10320.1
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	32768

Amine (–)-25

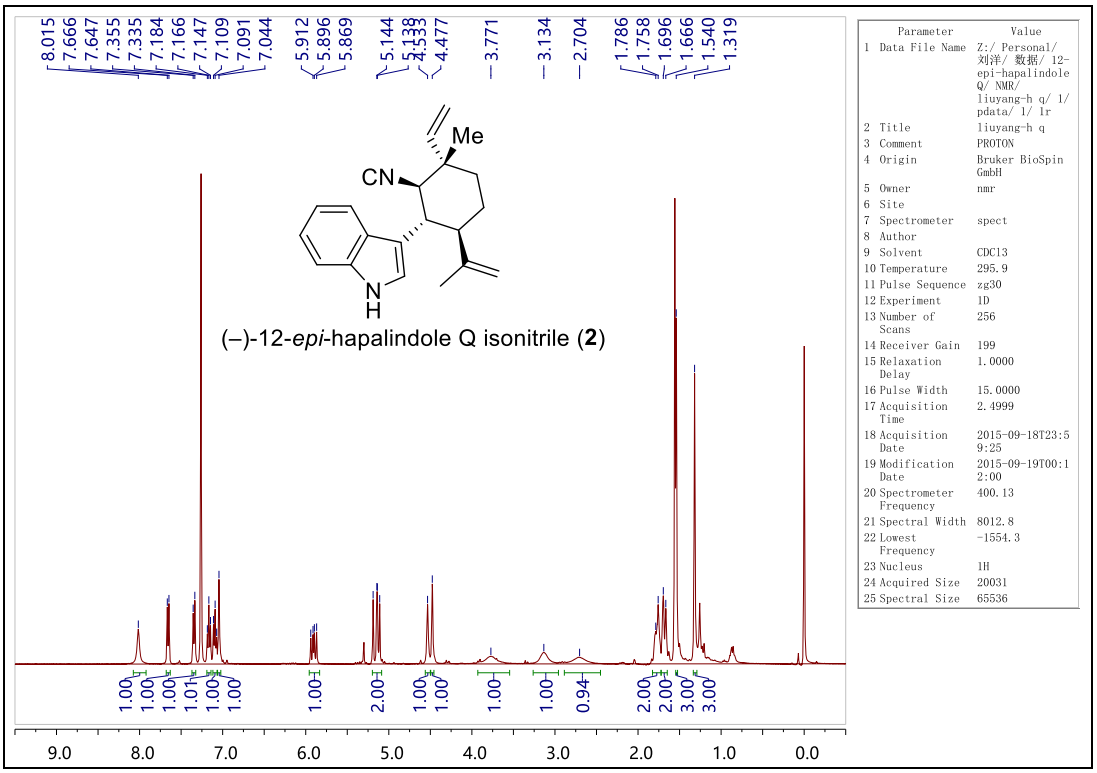


	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ ent-hapalindole D/ NMR/ 5/ 1/ fid
2	Title	5
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	75
14	Receiver Gain	97
15	Relaxation Delay	1.0000
16	Pulse Width	9.1200
17	Acquisition Time	2.4999
18	Acquisition Date	2015-09-09T23:40:11
19	Modification Date	2015-09-09T23:42:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1545.5
23	Nucleus	1H
24	Acquired Size	20031
25	Spectral Size	65536



	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ ent-hapalindole D/ NMR/ 5/ 2/ fid
2	Title	5
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.4
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	14657
14	Receiver Gain	196
15	Relaxation Delay	1.0000
16	Pulse Width	9.4000
17	Acquisition Time	0.8999
18	Acquisition Date	2015-09-10T07:42:02
19	Modification Date	2015-09-10T07:42:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7798.3
23	Nucleus	13C
24	Acquired Size	32141
25	Spectral Size	65536

(–)-**12-*epi*-Hapalindole Q isonitrile (2)**



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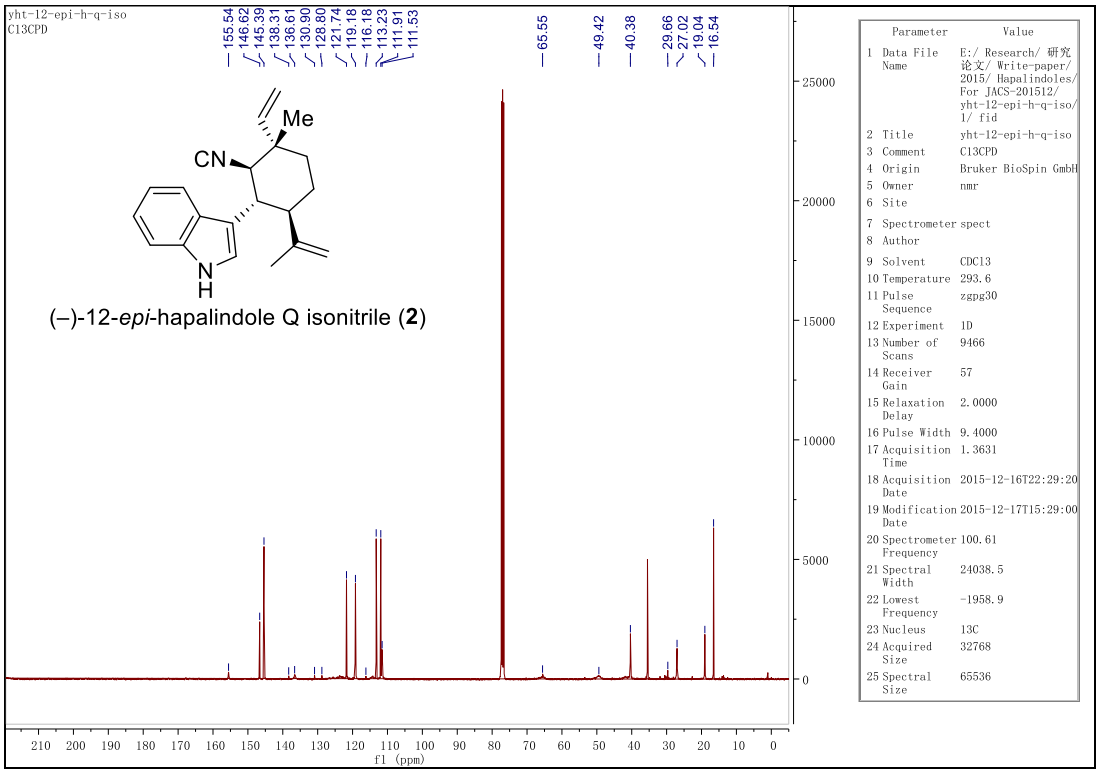
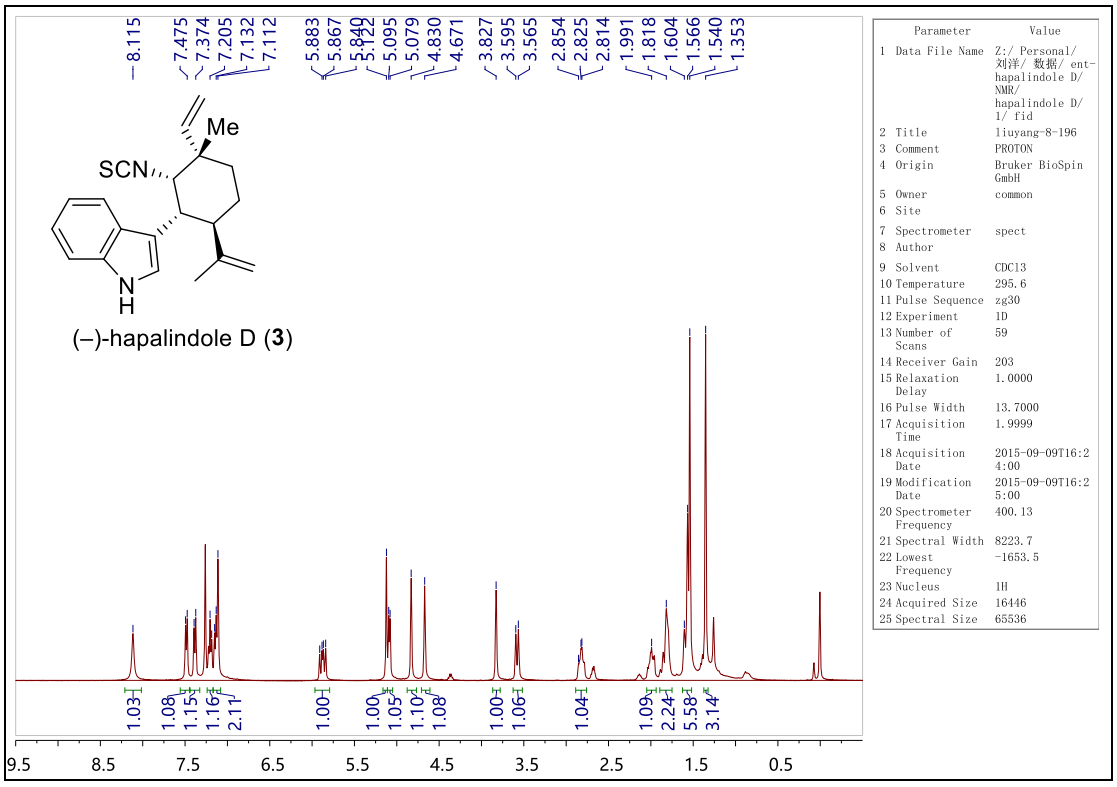
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ 12-epi-hapalindole Q/ NMR/ liuyang-h q/ 1/ pdata/ 1/ 1r
2	Title	liuyang-h q
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.9
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	256
14	Receiver Gain	199
15	Relaxation Delay	1.0000
16	Pulse Width	15.0000
17	Acquisition Time	2.4999
18	Acquisition Date	2015-09-18T23:59:25
19	Modification Date	2015-09-19T00:12:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1554.3
23	Nucleus	1H
24	Acquired Size	20031
25	Spectral Size	65536

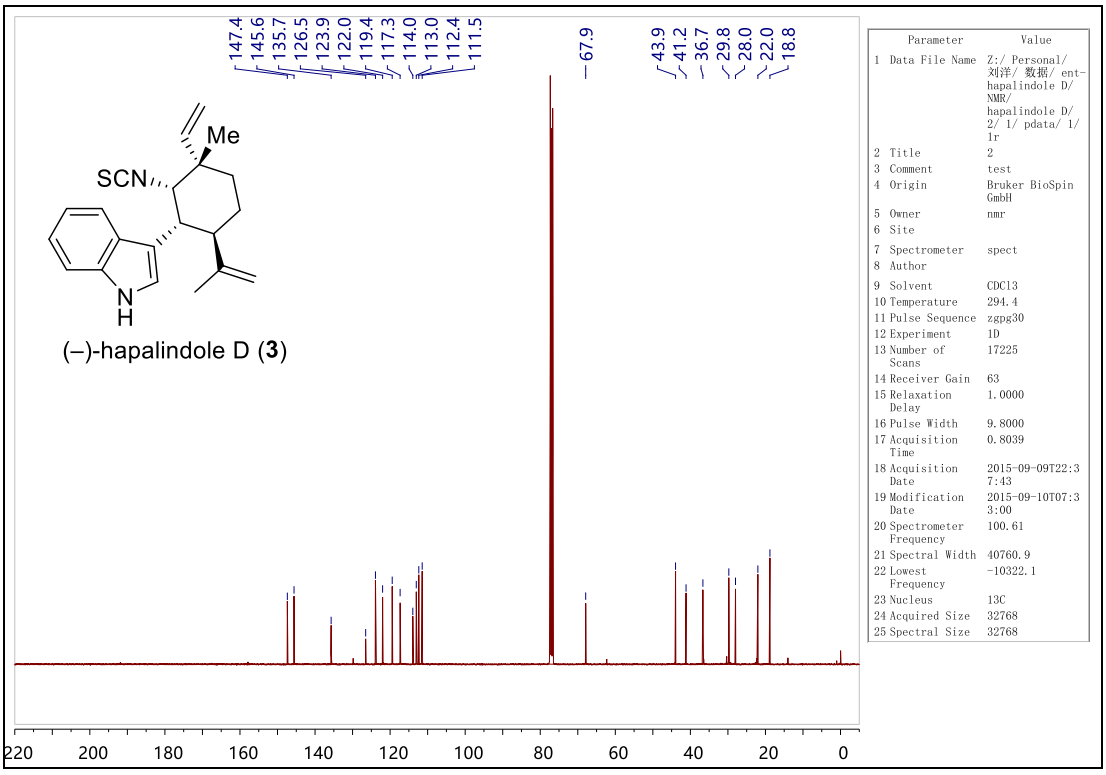


	Parameter	Value
1	Data File Name	E:/ Research/ 研究论文/ Write-paper/ 2015/ Hapalindoles/ For JACS-201512/ yht-12-epi-h-q-iso/ 1/ fid
2	Title	yht-12-epi-h-q-iso
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.6
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	9466
14	Receiver Gain	57
15	Relaxation Delay	2.0000
16	Pulse Width	9.4000
17	Acquisition Time	1.3631
18	Acquisition Date	2015-12-16T22:29:20
19	Modification Date	2015-12-17T15:29:00
20	Spectrometer Frequency	100.61
21	Spectral Width	24038.5
22	Lowest Frequency	-1958.9
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	65536

(–)-**Hapalindole D (3)**

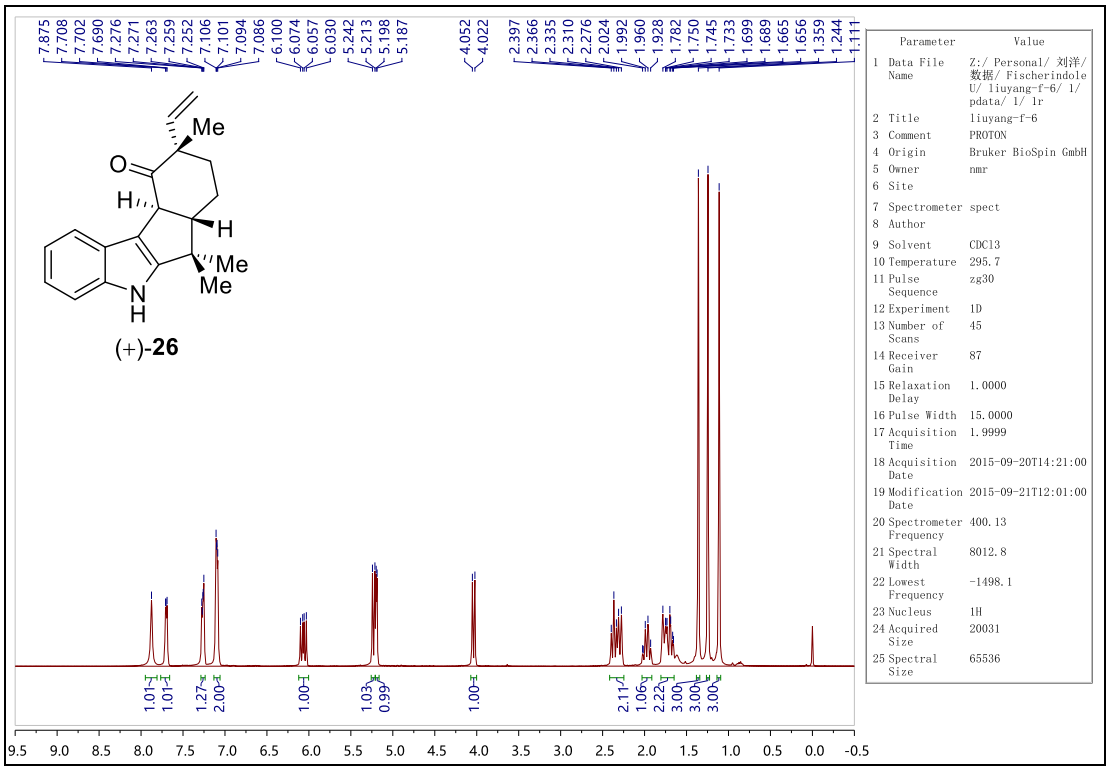


	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ ent-hapalindole D/ NMR/ hapalindole D/ 1/ fid
2	Title	liuyang-8-196
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.6
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	59
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	13.7000
17	Acquisition Time	1.9999
18	Acquisition Date	2015-09-09T16:24:00
19	Modification Date	2015-09-09T16:25:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8223.7
22	Lowest Frequency	-1653.5
23	Nucleus	1H
24	Acquired Size	16446
25	Spectral Size	65536



	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ ent-hapalindole D/ NMR/ hapalindole D/ 2/ 1/ pdata/ 1/ 1r
2	Title	2
3	Comment	test
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.4
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	17225
14	Receiver Gain	63
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.8039
18	Acquisition Date	2015-09-09T22:37:43
19	Modification Date	2015-09-10T07:33:00
20	Spectrometer Frequency	100.61
21	Spectral Width	40760.9
22	Lowest Frequency	-10322.1
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	32768

Ketone (+)-26



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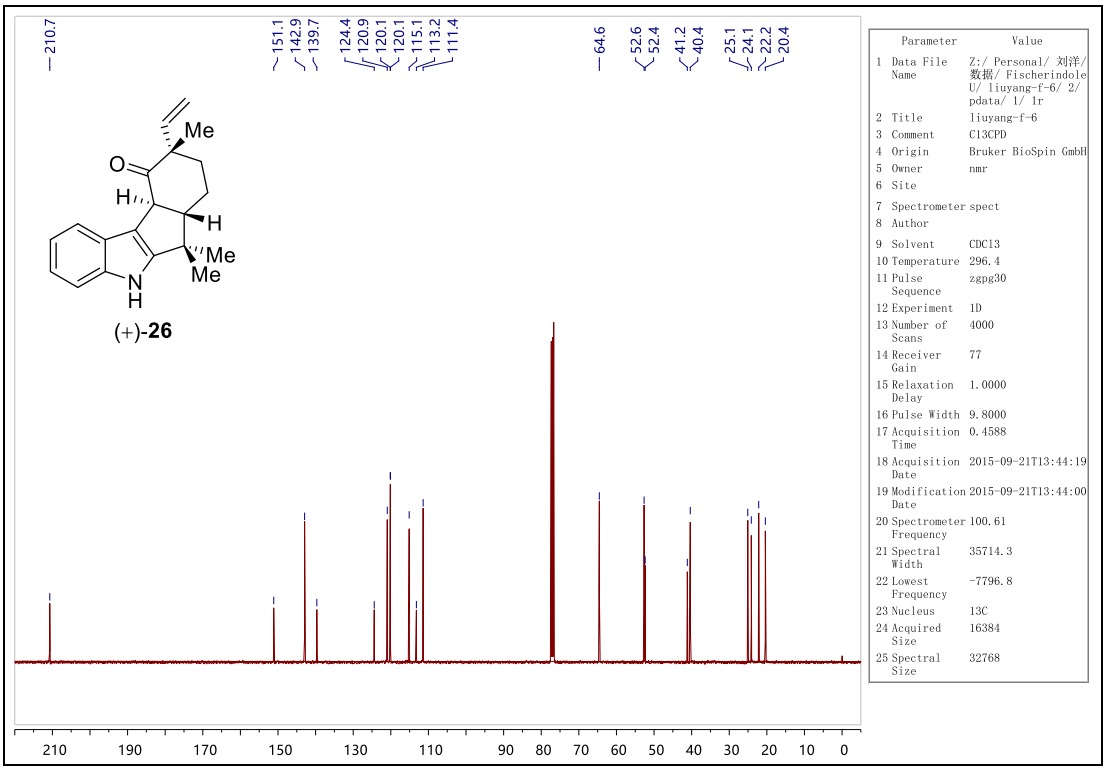
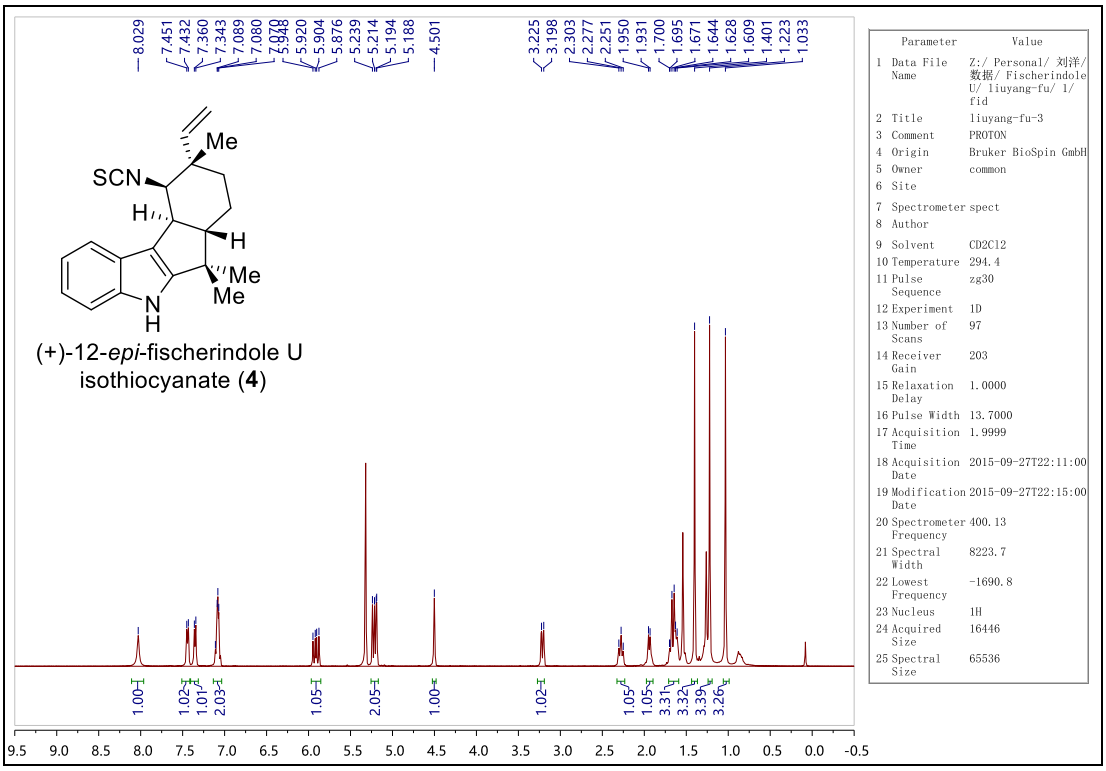
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ Fischerindole U/ liuyang-f-6/ 1/ pdata/ 1/ 1r
2	Title	liuyang-f-6
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.7
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	45
14	Receiver Gain	87
15	Relaxation Delay	1.0000
16	Pulse Width	15.0000
17	Acquisition Time	1.9999
18	Acquisition Date	2015-09-20T14:21:00
19	Modification Date	2015-09-21T12:01:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1498.1
23	Nucleus	1H
24	Acquired Size	20031
25	Spectral Size	65536

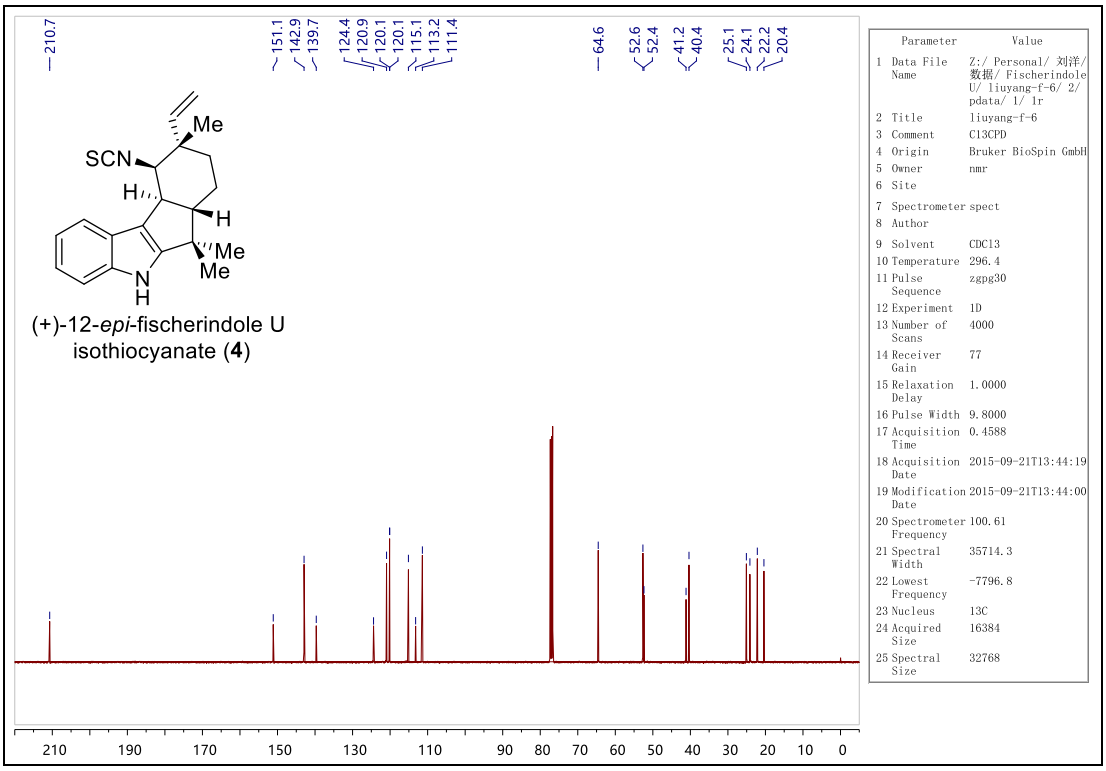


	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ Fischerindole U/ liuyang-f-6/ 2/ pdata/ 1/ 1r
2	Title	liuyang-f-6
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.4
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	4000
14	Receiver Gain	77
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.4588
18	Acquisition Date	2015-09-21T13:44:19
19	Modification Date	2015-09-21T13:44:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7796.8
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768

(+)-12-*epi*-Fischerindole U isothiocyanate (4)



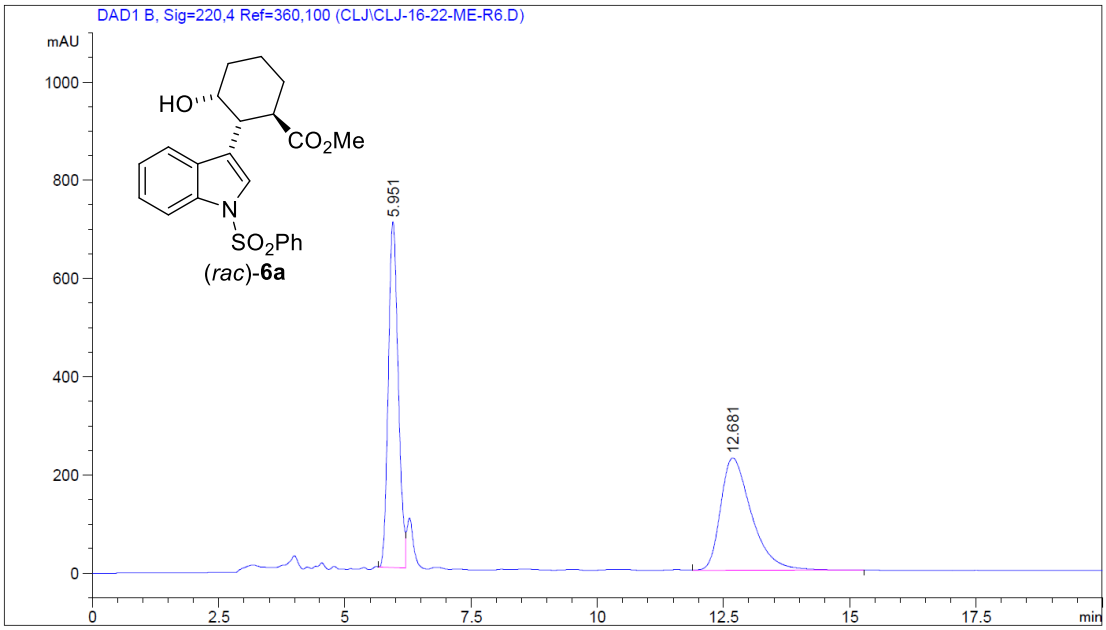
	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ Fischerindole U/ liuyang-fu/ 1/ fid
2	Title	liuyang-fu-3
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CD2Cl2
10	Temperature	294.4
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	97
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	13.7000
17	Acquisition Time	1.9999
18	Acquisition Date	2015-09-27T22:11:00
19	Modification Date	2015-09-27T22:15:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8223.7
22	Lowest Frequency	-1690.8
23	Nucleus	1H
24	Acquired Size	16446
25	Spectral Size	65536

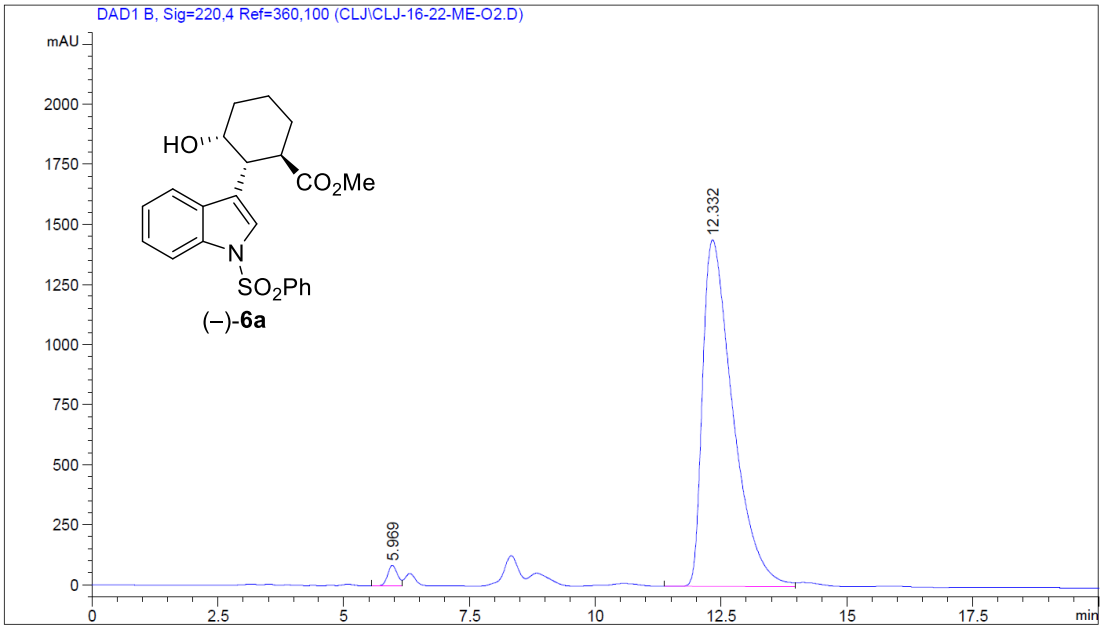


	Parameter	Value
1	Data File Name	Z:/ Personal/ 刘洋/ 数据/ Fischerindole U/ liuyang-f-6/ 2/ pdata/ 1/ 1r
2	Title	liuyang-f-6
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.4
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	4000
14	Receiver Gain	77
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.4588
18	Acquisition Date	2015-09-21T13:44:19
19	Modification Date	2015-09-21T13:44:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7796.8
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768

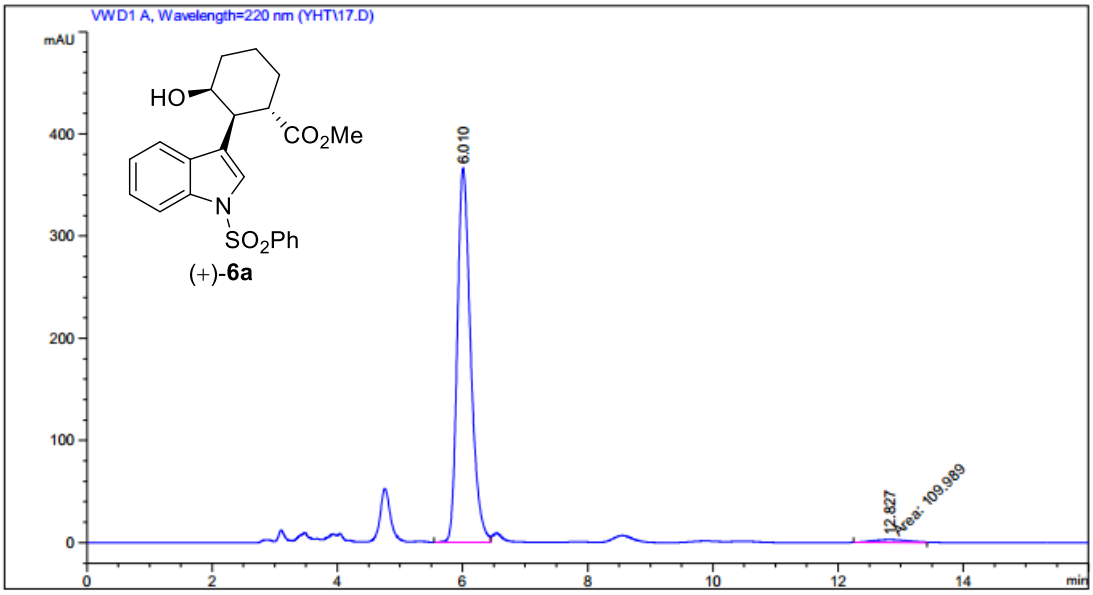
(H) HPLC Charts of (–)-6

For (–)- and (+)-6a



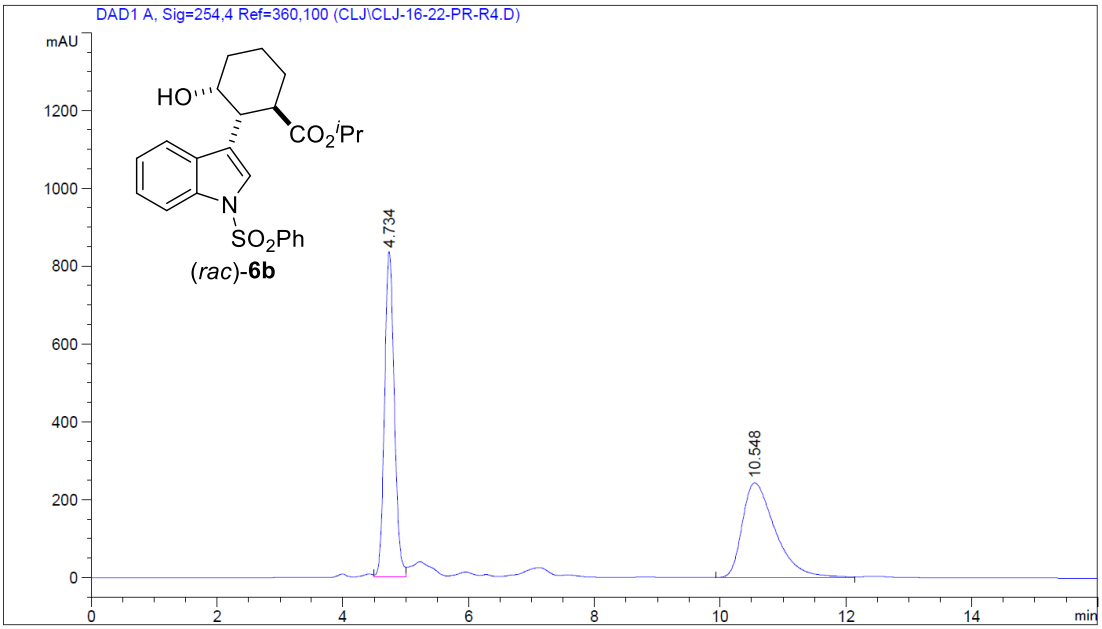


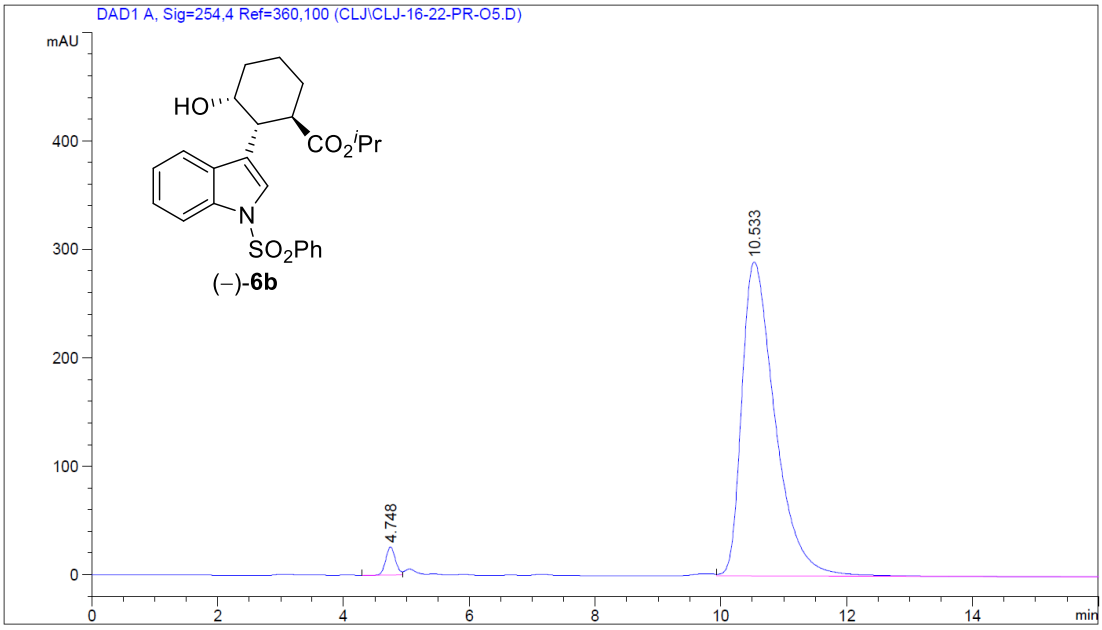
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.969	BV	0.2098	1150.23303	85.04601	1.8656
2	12.332	BV	0.6292	6.05045e4	1442.97424	98.1344



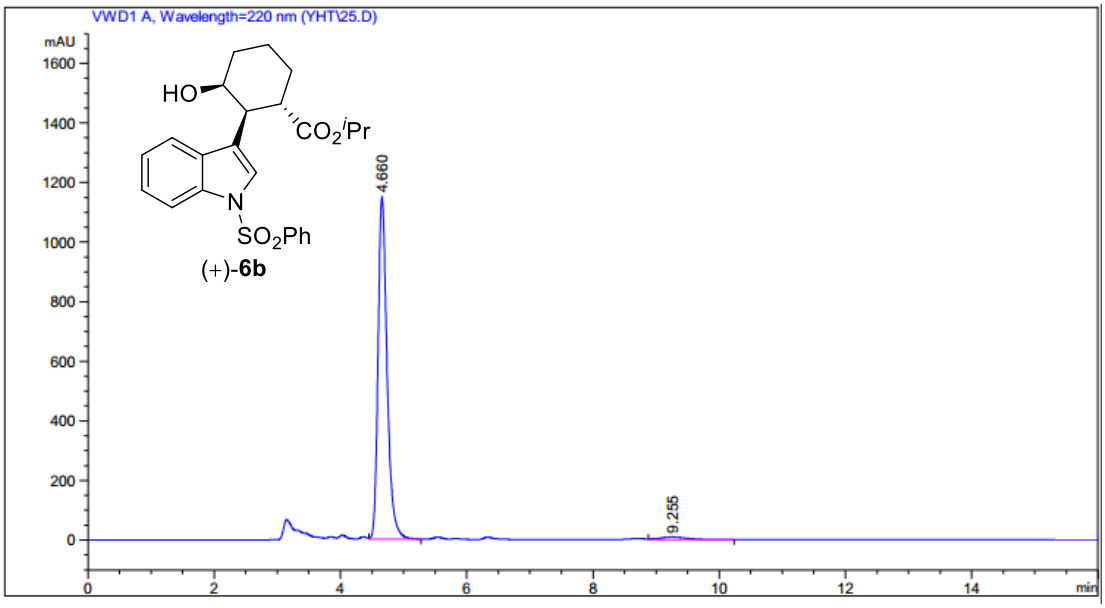
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.010	BV	0.2271	5431.11865	365.97589	98.0150
2	12.827	MM	0.6682	109.98916	2.74362	1.9850

For (–)- and (+)-6b





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.748	BV	0.1662	279.87994	25.87128	2.5576
2	10.533	VBA	0.5578	1.06633e4	289.44092	97.4424



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.660	VB	0.1505	1.13795e4	1149.24915	97.5877
2	9.255	VB	0.4624	281.29593	9.15712	2.4123