Electronic Supplemmentary Information

Hydrogen Bonding to Carbonyl Oxygen of Nitrogen-Pyramidalized Amide – Detection of Pyramidalization Direction Preference by Vibrational Circular Dichroism Spectroscopy

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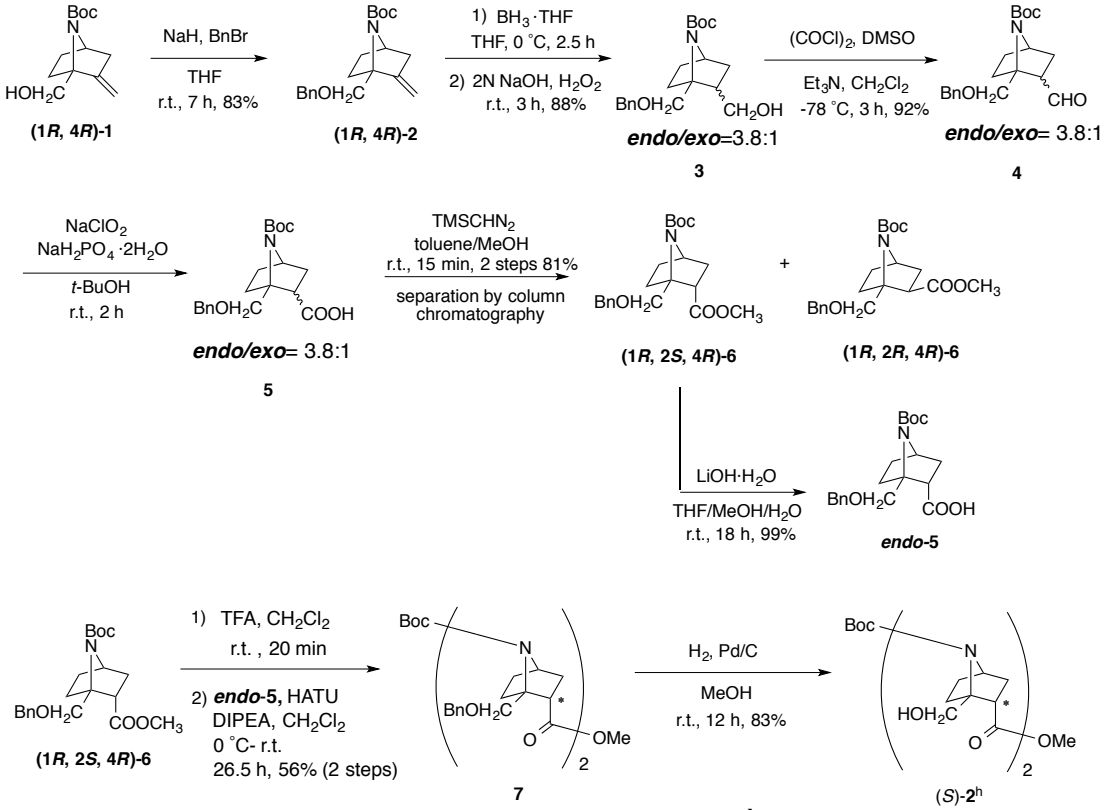
General Methods.

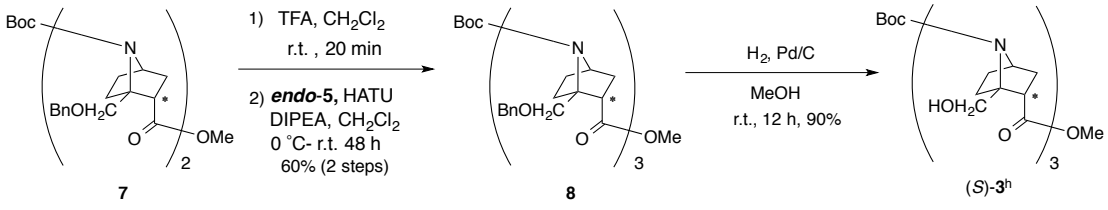
Open column chromatography was carried out using Kanto chemical silica gel (silica gel 60 N (100-210 μm)). Thin-layer chromatography was carried out using Merck Kieselgel 60 F254 fluorescent silica. Visualization of the developed chromatogram was performed by UV absorbance, ninhydrin spray. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded on a Bruker AV 400 NMR spectrometer running Topspin at 25°C. ^{1}H-NMR and ^{13}C-NMR chemical shifts (δ) are given in parts per million (ppm) and coupling constants are given in hertz (Hz). Mass spectra were recorded on a Bruker micrOTOF-05. The combustion analysis was carried out in the microanalytical laboratory of the University of Tokyo. All of the melting points were measured with a Yanaco Micro Melting Point Apparatus without correction. Unless stated otherwise, commercial grade reagents were used without further purification.

Synthetic Procedures

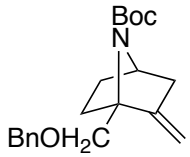
Compounds (***S***)-**2**, (***S***)-**3** and (1*R*, 4*R*)-**1** were produced according to the previously reported methods.[1]



Scheme S1. Synthesis of **(*S*)-2**^{h}



Scheme S2. Synthesis of **(*S*)-3**^{h}



(1*R*, 4*R*)-2

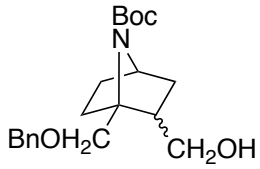
To a solution of compound (1*R*, 4*R*)-**1** (771.2 mg, 3.23 mmol) in THF (40 mL) was added NaH (193.6 mg, 4.84 mmol) at 0 °C. 10 min later, BnBr (0.8 mL, 6.46 mmol) was added dropwise at 0 °C. Then the ice bath was withdrawn, and the mixture was stirred at room temperature for 7 hr. The reaction mixture was poured into water. The mixture was extracted with Et_2O. The combined organic phase was washed with brine, dried over Na_2SO_4, and the solvent was evaporated. Open column chromatography (solvent system: *n*-hexane/EtOAc= 7/1 v/v) gave compound (1*R*, 4*R*)-**2** (880.5 mg, 83% yield) as a colorless oil.

TLC: R_f=0.47 (*n*-hexane/EtOAc 7:1 v/v, UV)

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.390-7.276 (m, 5H), 4.977-4.965 (m, 1H), 4.798-4.787 (m, 1H), 4.649 (s, 2H), 4.334-4.309 (m, 1H), 4.165 (s, 2H), 2.537-2.480 (m, 1H), 2.181-2.132 (m, 1H), 2.088-2.016 (m, 1H), 1.905-1.815 (m, 1H), 1.687-1.623 (m, 1H), 1.427 (s, 9H), 1.412-1.377 (m, 1H).

^{13}C-NMR (100MHz, $CDCl_3$): δ 155.57, 150.65, 138.61, 128.27, 127.70, 127.46, 103.18, 79.77, 73.48, 69.98, 69.85, 58.12, 38.58, 33.84, 28.34, 27.50.

HRMS (ESI-TOF, $[M+Na]^+$): Calcd. For $C_{20}H_{27}NO_3Na$: 352.1883; Found: 352.1880.



***endo/exo*=3.8:1**

3

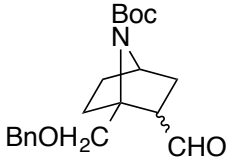
To a solution of **2** (625.0 mg, 1.90 mmol) in anhydrous THF (60 mL) was added BH_3·THF (1.0 M in THF, 5.7 mL, 5.7 mmol) at 0 °C, and the reaction mixture was stirred for 2.5 hours at room temperature. To the reaction mixture were added 2 N NaOH aq (2.3 mL) and 30% H_2O_2 (1.6 mL) at 0 °C, and the reaction mixture was stirred for 3 hours at room temperature. The reaction mixture was poured into water, and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, and the solvent was evaporated. Open column chromatography

(solvent system: *n*-hexane/ EtOAc= 10:1-5:1 v/v) gave compound *endo/exo* **3** (580.3 mg, 88% yield) as a colorless oil.

TLC: R_f=0.27 (*n*-hexane/EtOAc 3:1 v/v, UV)

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.354-7.299 (m, 5H), 4.676 (d, *J*=11.6 Hz, 1H), 4.588 (d, *J*=11.6 Hz, 1H), 3.683-3.614 (m, 0.8H), 3.575-3.459 (m, 0.79H), 3.340-3.285 (m, 0.21H), 3.049-3.022 (m, 0.17H), 2.353-2.310 (m ,0.77H), 2.157-2.034 (m, 1.78H), 1.830-1.741 (m, 1.2H), 1.654-1.573 (m, 1H), 1.416 (s, 9H), 1.289-1.224 (m, 1H), 0.836-0.793 (m, 0.78H).

HRMS (ESI-TOF, $[M+Na]^+$): Calcd. For $C_{20}H_{29}NO_4Na$: 370.1989; Found: 370.2000.



4

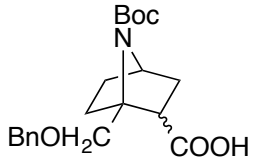
To a solution of oxalyl chloride (0.3 mL, 3.34 mmol) in anhydrous CH_2Cl_2 (10 mL) was added DMSO (0.4 mL, 5.01 mmol) at -78 °C. The reaction mixture was stirred for 20 min and a solution of *endo/exo* **3** (580.3 mg, 1.67 mmol) in anhydrous CH_2Cl_2 (8.0 mL) was added at -78 °C. The reaction mixture was stirred for 40 min at -78 °C, then Et_3N (1.4 mL, 10.02 mmol) was added. The solution was allowed to warm to room temperature. After 1 h stirring, the reaction mixture was quenched by addition of water. The mixture was extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, and the solvent was evaporated. Open column chromatograph (solvent system: *n*-hexane/EtOAc= 6/1 v/v) gave compound *endo/exo* **4** (530.7 mg, 92% yield) as a colorless oil. During the column chromatography process, we obtained some pure compound *endo* **4**, so the pure *endo* compound was used to measure the ^{1}H-NMR and ^{13}C-NMR.

TLC: R_f=0.33 (*n*-hexane/EtOAc 7:1 v/v, UV)

^{1}H-NMR (400MHz, $CDCl_3$): δ 9.826 (s, 1H), 7.356-7.276 (m, 5H), 4.656 (d, *J*=12.4 Hz, 1H), 4.599 (d, *J*=12.0 Hz, 1H), 4.371 (d, *J*=9.6 Hz, 1H), 4.297-4.273 (m, 1H), 4.139 (d, *J*=9.6 Hz, 1H), 3.093-3.043 (m, 1H), 1.938-1.778 (m, 4H), 1.698-1.638 (m, 1H), 1.472-1.407 (m, 1H), 1.426 (s, 9H).

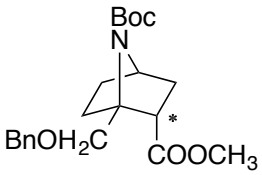
^{13}C-NMR (100MHz, $CDCl_3$): δ 202.34, 155.09, 138.26, 128.54, 127.75, 80.36, 73.80, 72.81, 69.70, 59.29, 57.97, 30.57, 30.45, 28.51, 28.43.

HRMS (ESI-TOF, $[M+Na]^+$): Calcd. For $C_{20}H_{27}NO_4Na$: 368.1832; Found: 368.1841.



5

To a solution of *endo/exo* **4** (360.1 mg, 1.04 mmol) in *t*-BuOH (20 mL) were added 2-methyl-2-butene (2.3 mL, 21.43 mmol) and a solution of $NaClO_2$ (874.6 mg, 9.67 mmol) and $NaH_2PO_4 \cdot 2H_2O$ (1.1529 g, 7.39 mmol) in H_2O (20 mL) at room temperature, and the reaction mixture was stirred for 2 hr at room temperature. *t*-BuOH was evaporated and the aqueous residue was poured into 5% aqueous solution of $KHSO_4$, and extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, and the solvent was evaporated, gave compound *endo/exo* **5** (375.8 mg) as a colorless oil without further purification directly to the next step.



(1*R*, 2*S*, 4*R*)-6

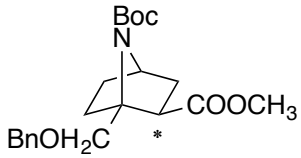
To a solution of compound *endo/exo* **5** (184.4 mg, 0.51 mmol) in anhydrous toluene/MeOH (4 mL/1 mL) was added $TMSCHN_2$ (0.51 mL, 1.02 mmol) at 0 °C. The reaction mixture was stirred for 15 min at room temperature under Ar atmosphere and the solvent was evaporated. Open column chromatography (solvent system: *n*-hexane/EtOAc= 5/1 v/v) gave compound (1*R*, 2*S*, 4*R*)-**6** (122.6 mg) as a colorless oil and (1*R*, 2*R*, 4*R*)-**6** (32.1 mg) as a colorless oil (81% in 2 steps' yields).

TLC: R_f=0.36 (*n*-hexane/EtOAc 7:1 v/v, UV)

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.352-7.253 (m, 5H), 4.657 (d, *J*=12.4 Hz, 1H), 4.582 (d, *J*=12.0 Hz, 1H), 4.299-4.274 (m, 1H), 4.215 (d, *J*=9.6 Hz, 1H), 4.083 (d, *J*=9.6 Hz, 1H), 3.554 (s, 3H), 3.132-3.085 (m, 1H), 2.058-1.998 (m, 1H), 1.964-1.901 (m, 1H), 1.830-1.775 (m, 2H), 1.709-1.661 (m, 1H), 1.580-1.517 (m, 1H), 1.438 (s, 9H).

^{13}C-NMR (100MHz, $CDCl_3$): δ 173.55, 155.15, 138.60, 128.17, 127.59, 127.36, 79.93, 73.28, 70.45, 70.24, 59.09, 51.65, 48.24, 33.38, 28.77, 28.38, 28.31.

HRMS (ESI-TOF, $[M+Na]^+$): Calcd. For $C_{21}H_{29}NO_5Na$: 398.1938; Found: 398.1933.



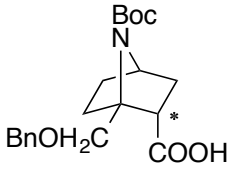
(1*R*, 2*R*, 4*R*)-6

TLC: R_f=0.25 (*n*-hexane/EtOAc 7:1 v/v, UV)

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.339-7.257 (m, 5H), 4.584 (d, *J*=12.0 Hz, 1H), 4.548 (d, *J*=12.0 Hz, 1H), 4.386-4.375 (m, 1H), 4.067-4.035 (m, 2H), 3.605 (s, 3H), 2.877-2.842 (m, 1H), 2.167-2.110 (m, 1H), 1.853-1.682 (m, 4H), 1.438 (s, 9H), 1.426-1.373 (m, 1H).

^{13}C-NMR (100MHz, $CDCl_3$): δ 174.05, 154.04, 138.48, 128.28, 127.68, 127.50, 79.71, 73.60, 70.72, 68.84, 57.20, 51.59, 49.46, 35.95, 34.53, 28.33, 28.06.

HRMS (ESI-TOF, $[M+Na]^+$): Calcd. For $C_{21}H_{29}NO_5Na$: 398.1938; Found: 398.1955.



***endo*-5**

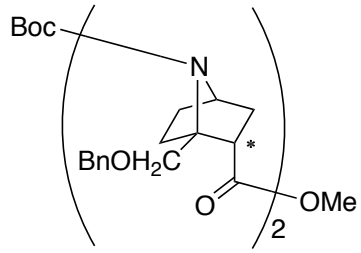
To a solution of (1*R*, 2*S*, 4*R*)-**6** (500.0 mg, 1.33 mmol) in THF (15 mL) was added a solution of $LiOH·H_2O$ (111.8 mg, 2.66 mmol) in H_2O (4 mL) at room temperature. MeOH (8 mL) was added to the reaction mixture and the mixture was stirred at room temperature for 18 hr. The reaction mixture was poured into 5% aqueous solution of $KHSO_4$, and the whole was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and then evaporated. Open column chromatography (solvent system: *n*-hexane/EtOAc/AcOH= 50/50/0.5 v/v/v) gave compound ***endo*-5** (479.0 mg, 99% yield) as a colorless oil.

TLC: R_f=0.22 (*n*-hexane/EtOAc 1:1 v/v, UV)

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.345-7.273 (m, 5H), 4.678 (quartet, *J*=12.0 Hz, 2H), 4.403 (d, *J*=10.0 Hz, 1H), 4.285-4.261 (m, 1H), 4.197 (d, *J*=10.0 Hz, 1H), 3.156-3.122 (m, 1H), 2.112-1.938 (m, 3H), 1.886-1.805 (m, 1H), 1.796-1.646 (m, 1H), 1.552-1.490 (m, 1H), 1.427 (s, 9H).

^{13}C-NMR (100MHz, $CDCl_3$): δ 175.23, 155.15, 137.17, 128.61, 128.12, 128.04, 80.40, 73.99, 71.72, 69.11, 58.80, 50.05, 33.95, 30.20, 28.39, 28.24.

HRMS (ESI-TOF, $[M-H]^-$): Calcd. For $C_{20}H_{26}NO_5$: 360.1816; Found: 360.1840.



7

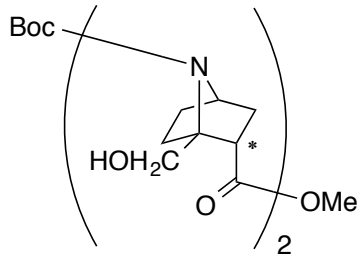
To a solution of compound (1*R*, 2*S*, 4*R*)-**6** (60.0 mg, 0.16 mmol) in anhydrous CH_2Cl_2 (3.0 mL) was added TFA (0.5 mL) at 0 °C. The reaction mixture was stirred for 20 min at room temperature. The reaction mixture was evaporated. The residue was washed with 10% Na_2CO_3 aqueous solution and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. To a solution of *endo/exo* **5** (57.8 mg, 0.16 mmol) in anhydrous CH_2Cl_2 (3.0 mL), HATU (79.9 mg, 0.21 mmol) and DIPEA (75 μL, 0.42 mmol) were added at 0 °C, and the reaction mixture was allowed to increase to ambiente temperature for 26.5 hr under Ar atmosphere. The reaction mixture was washed with water and extracted with CH_2Cl_2. The organic phase was dried, and the solvent was evaporated. Open column chromatography (solvent system: *n*-hexane/EtOAc= 6/1 v/v) gave compound **7** (55.2 mg, 56% yield) as a colorless oil.

TLC: R_f=0.59 (*n*-hexane/EtOAc 2:1 v/v, ninhydrin stain)

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.346-7.230 (m, 10H), 4.687-4.512 (m, 4H), 4.458-4.419 (m, 2H), 4.306-4.263 (m, 2H), 4.139 (d, *J*=9.6 Hz, 1H), 3.939 (d, *J*=10.4 Hz, 1H), 3.529 (s, 3H), 3.263-3.219 (m, 1H), 3.058-3.021 (m, 1H), 2.159-2.116 (m, 1H), 2.035-1.994 (m, 1H), 1.950-1.879 (m, 1H), 1.816-1.721 (m, 4H), 1.663-1.543 (m, 4H), 1.453 (s, 9H), 1.426-1.373 (m, 1H).

^{13}C-NMR (100MHz, $CDCl_3$): δ 173.46, 170.67, 155.23, 138.79, 138.39, 128.31, 128.13, 127.92, 127.59, 127.43, 127.28, 79.60, 73.49, 73.10, 70.89, 70.87, 69.46, 59.42, 58.82, 51.66, 47.76, 46.48, 33.47, 33.15, 30.25, 28.96, 28.40, 27.90, 27.46.

HRMS (ESI-TOF, $[M+Na]^+$): Calcd. For $C_{36}H_{46}N_2O_7Na$: 641.3197; Found: 641.3173.



(*S*)-**2**[h]

To a solution of **7** (43.1 mg, 0.07 mmol) in metanol (3 mL) was added 10% palladium on activated carbon catalyst (20.0 mg). After stirring under an atmosphere of hydrogen for 12 hr, the reaction mixture was filtered through a pad of Celite and concentrated. Open column chromatography (solvent system: *n*-hexane/EtOAc= 4/1 v/v) gave (*S*)-**2**[h] (25.2 mg, 83% yield) as a white solid.

TLC: R_f=0.24 (*n*-hexane/EtOAc 2:1 v/v, ninhydrin stain)

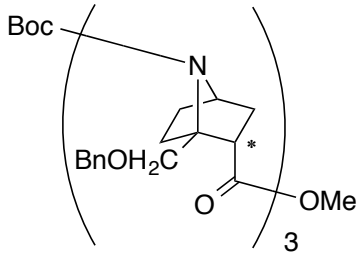
M.p.: 142.0-143.0 °C (colorless crystal, recrystallized from *n*-hexane/Et_2O)

^{1}H-NMR (400MHz, $CDCl_3$): δ 5.228 (br, 1H), 5.080-5.042 (m, 1H), 4.899-4.876 (m, 1H), 4.267-4.242 (m, 1H), 4.123-4.073 (m, 2H), 4.024-3.970 (m, 1H), 3.711 (s, 3H), 3.583-3.521 (m, 1H), 3.355-3.310 (m, 1H), 3.205-3.163 (m, 1H), 2.104-1.875 (m, 5H), 1.793-1.610 (m, 6H), 1.448 (s, 9H), 1.407-1.359 (m, 1H).

^{13}C-NMR (100MHz, $CDCl_3$): δ 172.58, 168.30, 154.50, 80.70, 73.40, 72.21, 60.96, 60.63, 58.74, 58.35, 52.10, 46.17, 44.41, 34.92, 33.45, 29.58, 28.89, 28.37, 26.58.

HRMS (ESI-TOF, $[M+Na]^+$): Calcd. For $C_{22}H_{34}N_2O_7Na$: 461.2258; Found: 461.2261.

Anal. Calcd for $C_{22}H_{34}N_2O_7$: C, 60.26; H, 7.82; N, 6.39. Found: C, 60.17; H, 7.57; N, 6.38.



8

To a solution of compound **7** (105.5 mg, 0.17 mmol) in anhydrous CH_2Cl_2 (5.0 mL) was added TFA (0.9 mL) at 0 °C. The reaction mixture was stirred for 20 min at room temperature. The reaction mixture was evaporated. The residue was washed with 10% Na_2CO_3 aqueous solution and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. To a solution of *endo*-**5** (54.2 mg, 0.15 mmol)

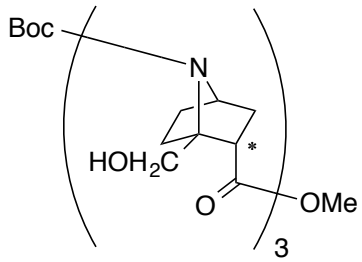
in anhydrous CH_2Cl_2 (5.0 mL), HATU (72.3 mg, 0.19 mmol) and DIPEA (70 μL, 0.39 mmol) were added at 0 °C, and the reaction mixture was allowed to increase to ambiente temperature for 48 hr under Ar atmosphere. The reaction mixture was washed with water and extracted with CH_2Cl_2. The organic phase was dried, and the solvent was evaporated. Open column chromatography (solvent system: *n*-hexane/EtOAc= 4/1-2/1 v/v) gave compound **8** (77.6 mg, 60% yield) as a colorless oil.

TLC: R_f=0.30 (*n*-hexane/EtOAc 3:1 v/v, UV)

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.326-7.207 (m, 15H), 4.674-4.386 (m, 10H), 4.306-4.281 (m, 2H), 4.096 (d, *J*=10.8 Hz, 1H), 3.967 (d, *J*=10.4 Hz, 1H), 3.843 (d, *J*=10.0 Hz, 1H), 3.539 (s, 3H), 3.293-3.256 (m, 1H), 3.191-3.166 (m, 1H), 3.115-3.073 (m, 1H), 2.114-1.355 (m, 18H), 1.459 (s, 9H).

^{13}C-NMR (100MHz, $CDCl_3$): δ 173.54, 170.76, 170.35, 155.42, 138.88, 138.64, 138.57, 128.39, 128.34, 128.27, 128.23, 127.80, 127.73, 127.52, 127.39, 79.65, 73.47, 73.18, 71.51, 71.09, 70.96, 69.60, 59.62, 59.34, 58.86, 51.79, 47.75, 46.93, 46.00, 33.47, 33.02, 30.61, 29.39, 28.86, 28.51, 28.07.

HRMS (ESI-TOF, $[M+Na]^+$): Calcd. For $C_{51}H_{63}N_3O_9Na$: 884.4457; Found: 884.4478.



(*S*)-**3**^{h}

To a solution of compound **8** (41.1 mg, 0.05 mmol) in metanol (3 mL) was added 10% palladium on activated carbon catalyst (20.0 mg). After stirring under an atmosphere of hydrogen for 12 hr, the reaction mixture was filtered through a pad of Celite and concentrated. Open column chromatography (solvent system: *n*-hexane/EtOAc= 1/1 v/v) gave (*S*)-**3**^{h} (25.2 mg, 90% yield) as a white solid.

TLC: R_f=0.19 (*n*-hexane: EtOAc 1:1 v/v, ninhydrin stain)

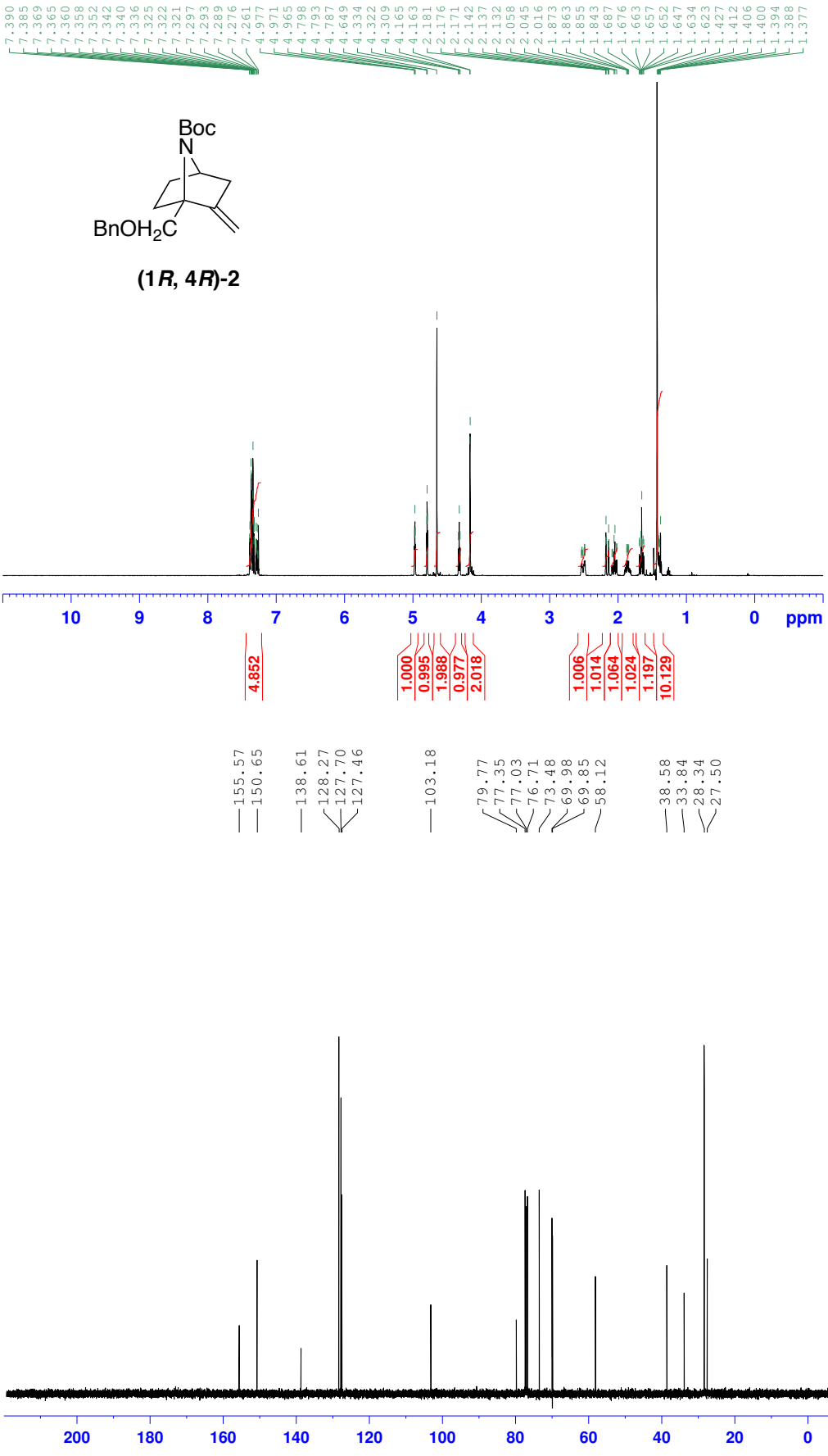
M.p.: 175.0-176.0 °C (needle crystal, recrystallized from MeOH/H_2O)

^{1}H-NMR (400MHz, $CDCl_3$): δ 5.206-5.168 (m, 2H), 5.027-4,990 (m, 1H), 4.882-4.841 (m, 1H), 4.827-4.803 (m, 1H), 4.292-4.268 (m, 1H), 4.158-4.098 (m, 2H), 4.039-3.984 (m, 1H), 3.728 (s, 3H), 3.678-3.542 (m, 2H), 3.381-3.291 (m, 2H), 3.241-3.200 (m, 1H), 2.131-1.627 (m, 16H), 1.465 (s, 9H), 1.451-1.365 (m, 2H).

^{13}C-NMR (100MHz, $CDCl_3$): δ 172.68, 167.98, 167.83, 80.88, 74.34, 73.57, 72.33, 61.26, 60.91, 60.72, 58.89, 58.83, 58.55, 52.28, 46.16, 44.58, 35.21, 34.78, 33.56, 29.69, 28.91, 28.66, 28.51, 27.27, 26.84.

HRMS (ESI-TOF, $[M+Na]^+$): Calcd. For $C_{30}H_{45}N_3O_9Na$: 614.3048; Found: 614.3049.

NMR Spectra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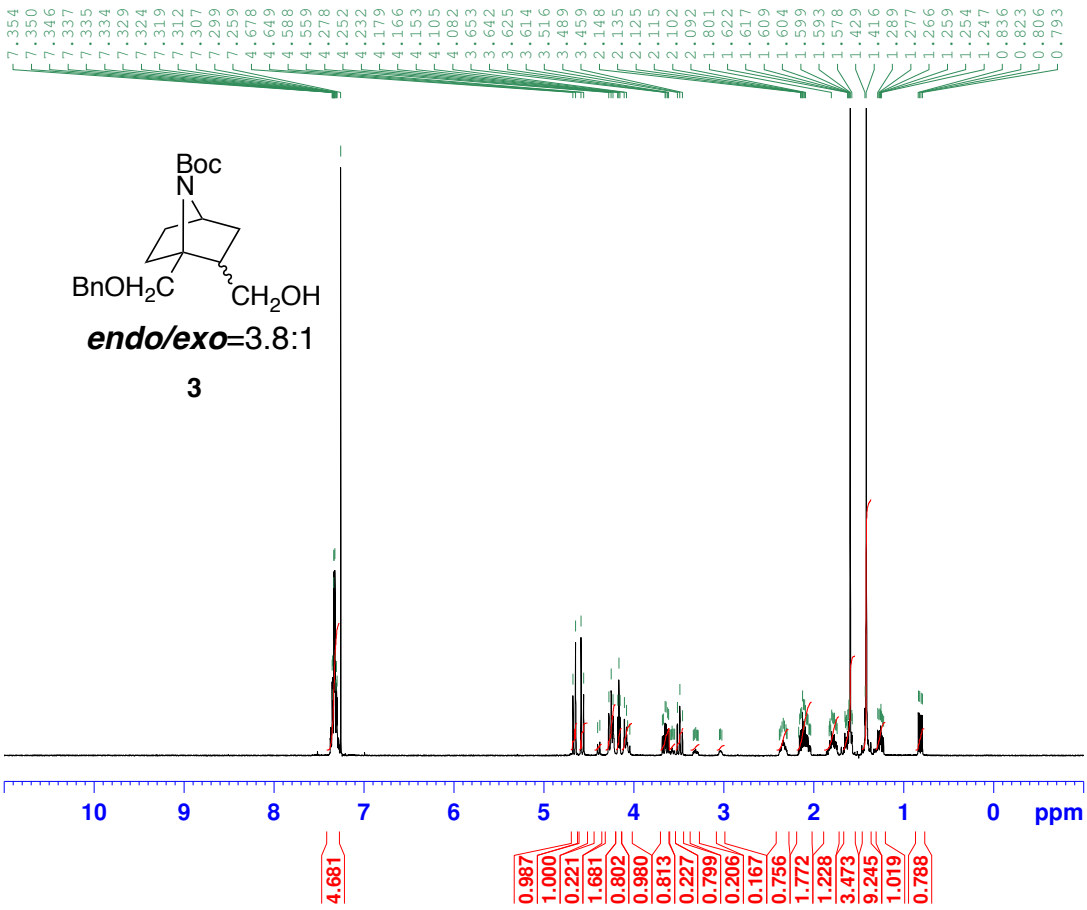
27.50
ppm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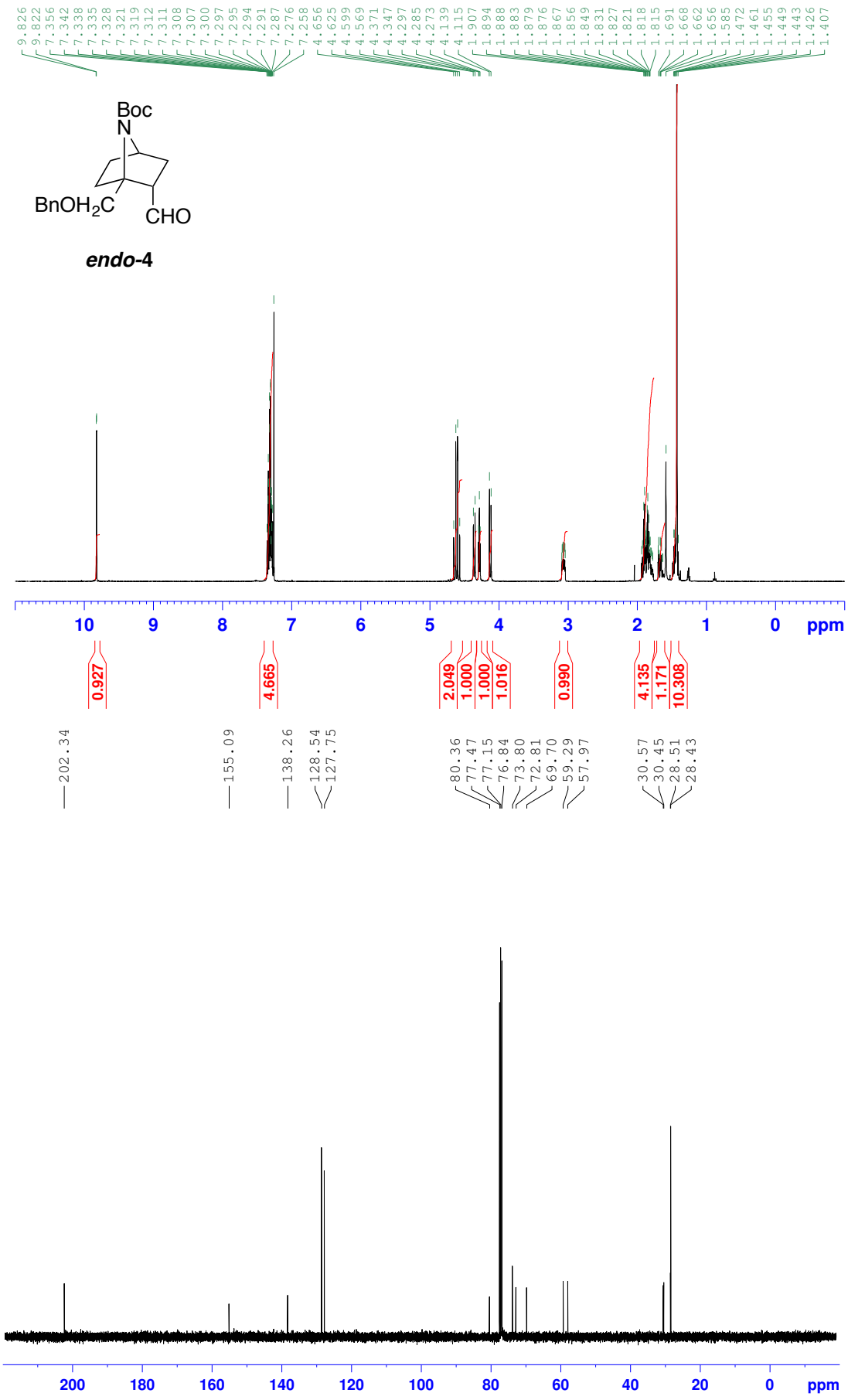
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7.300
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80.36
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77.15
76.84
73.80
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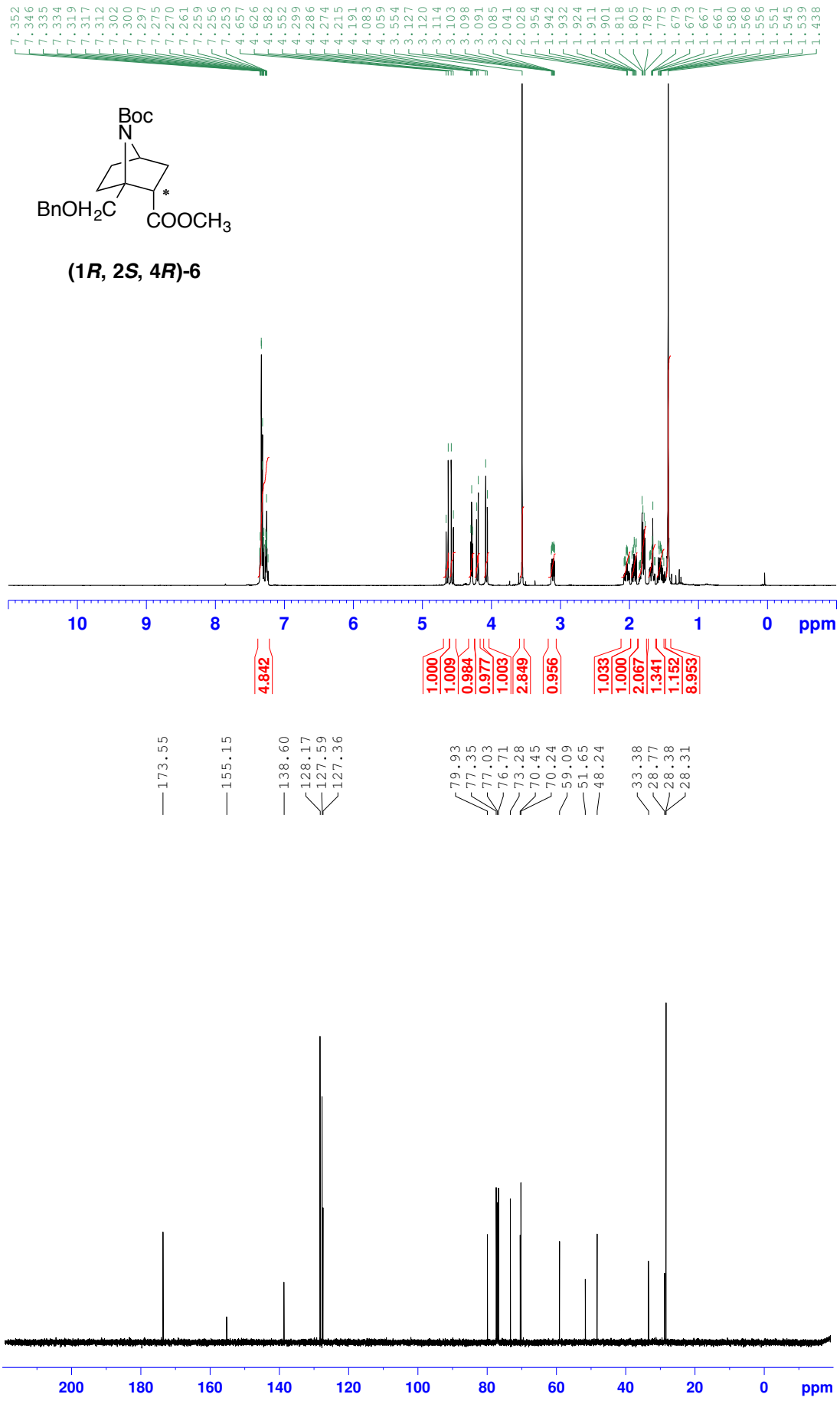
ppm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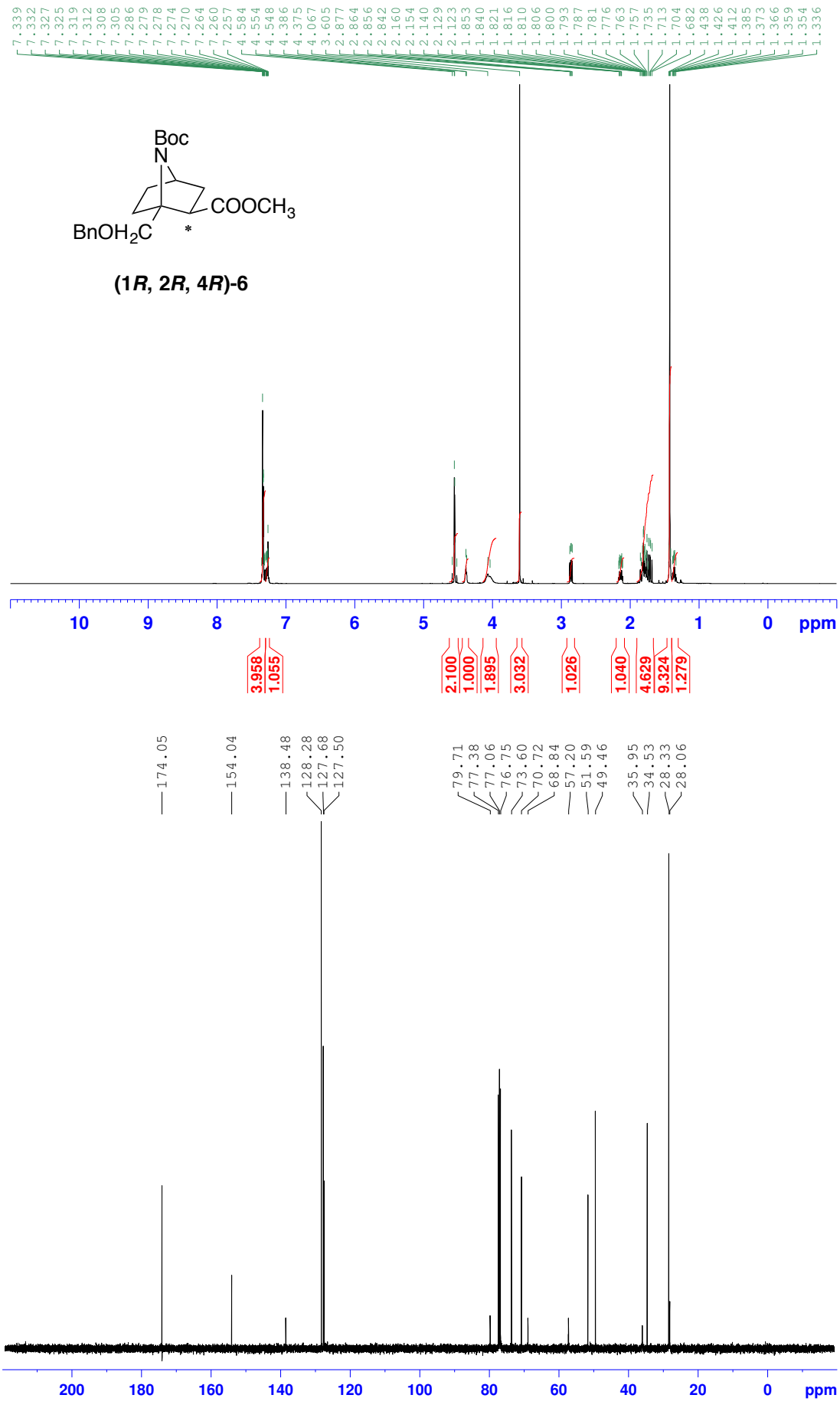
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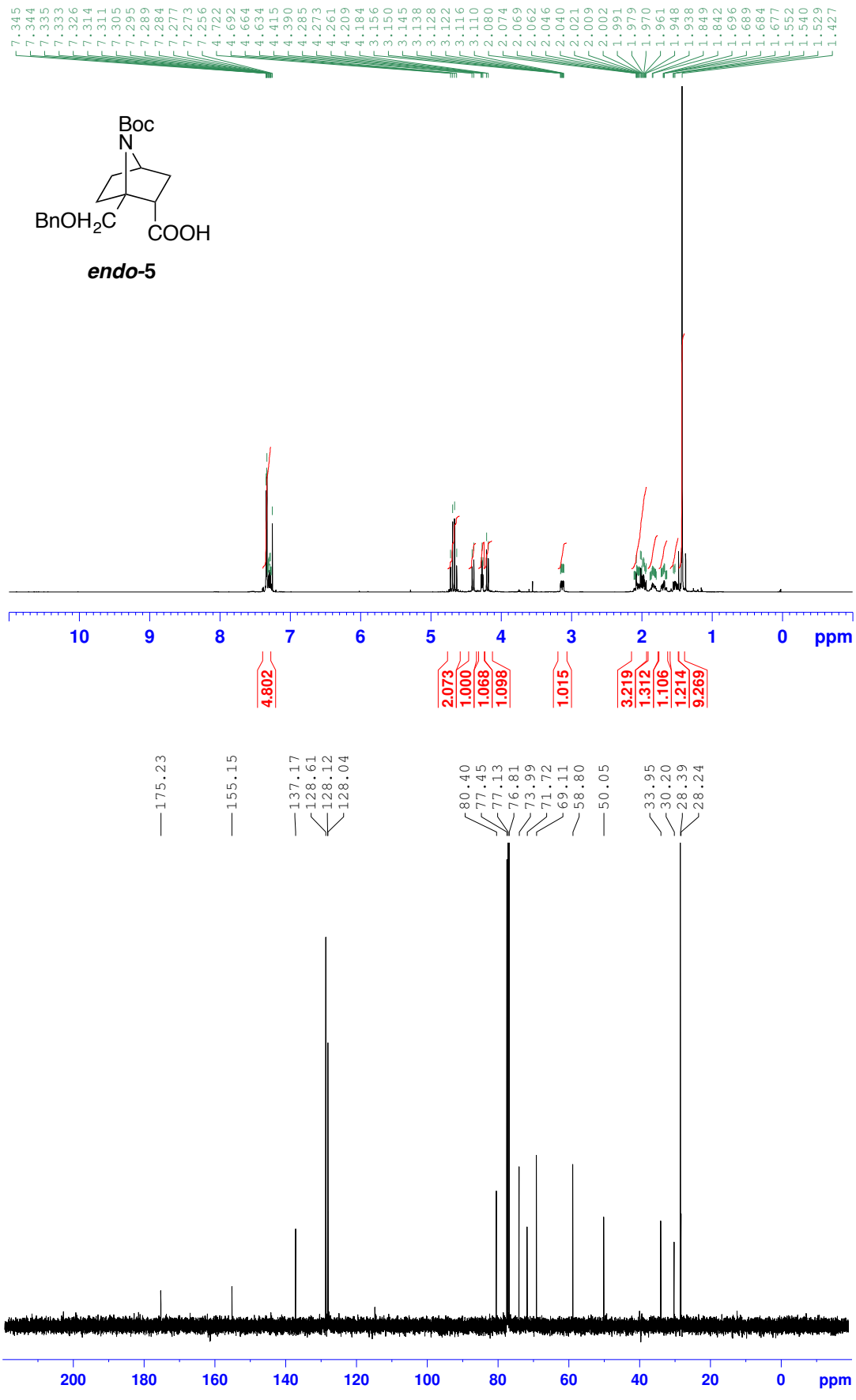
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77.45
77.13
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71.72
69.11
58.80
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120
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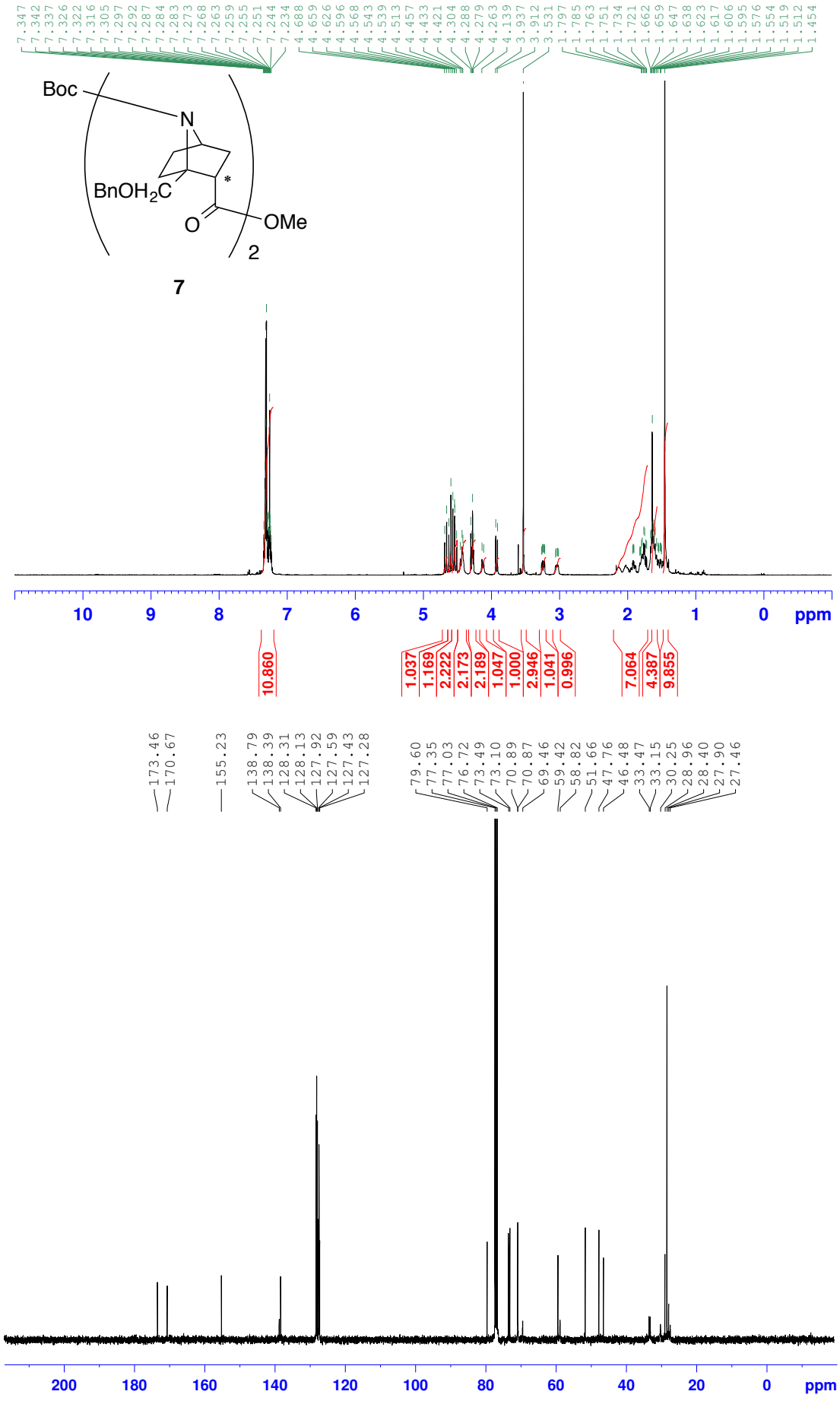
ppm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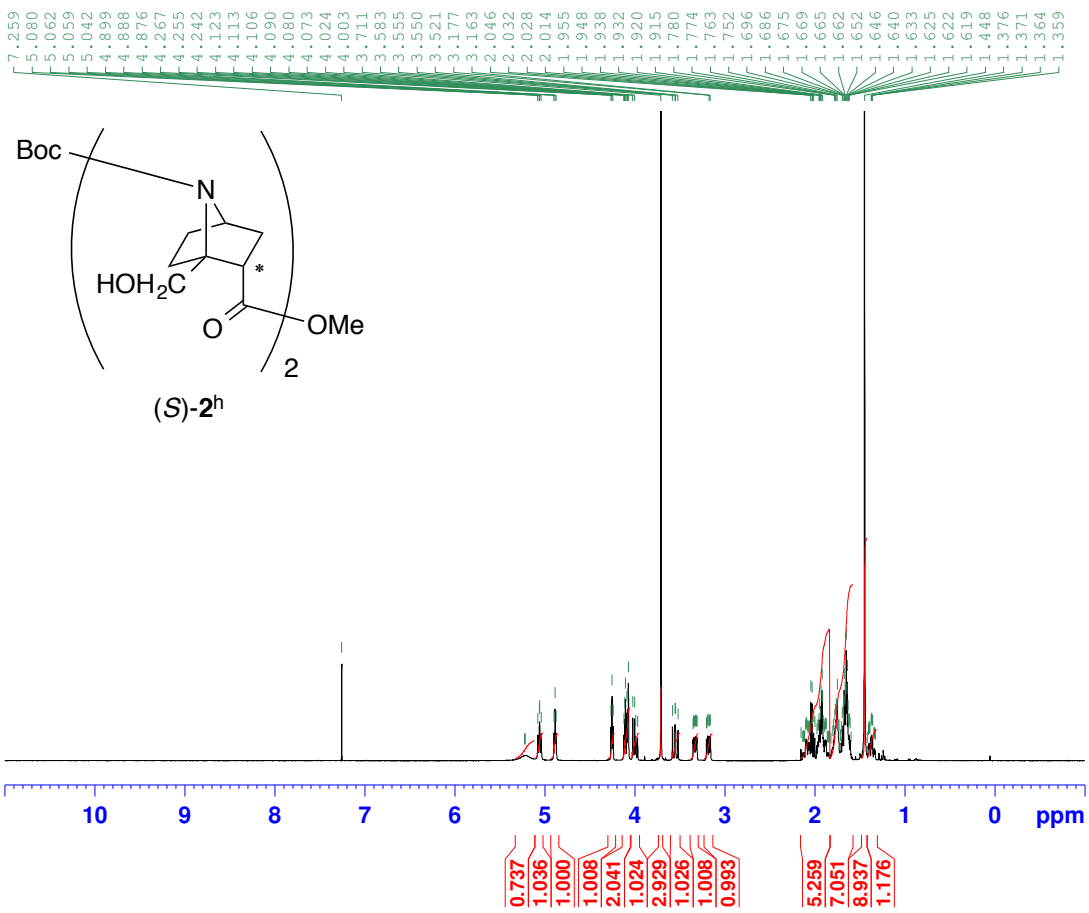
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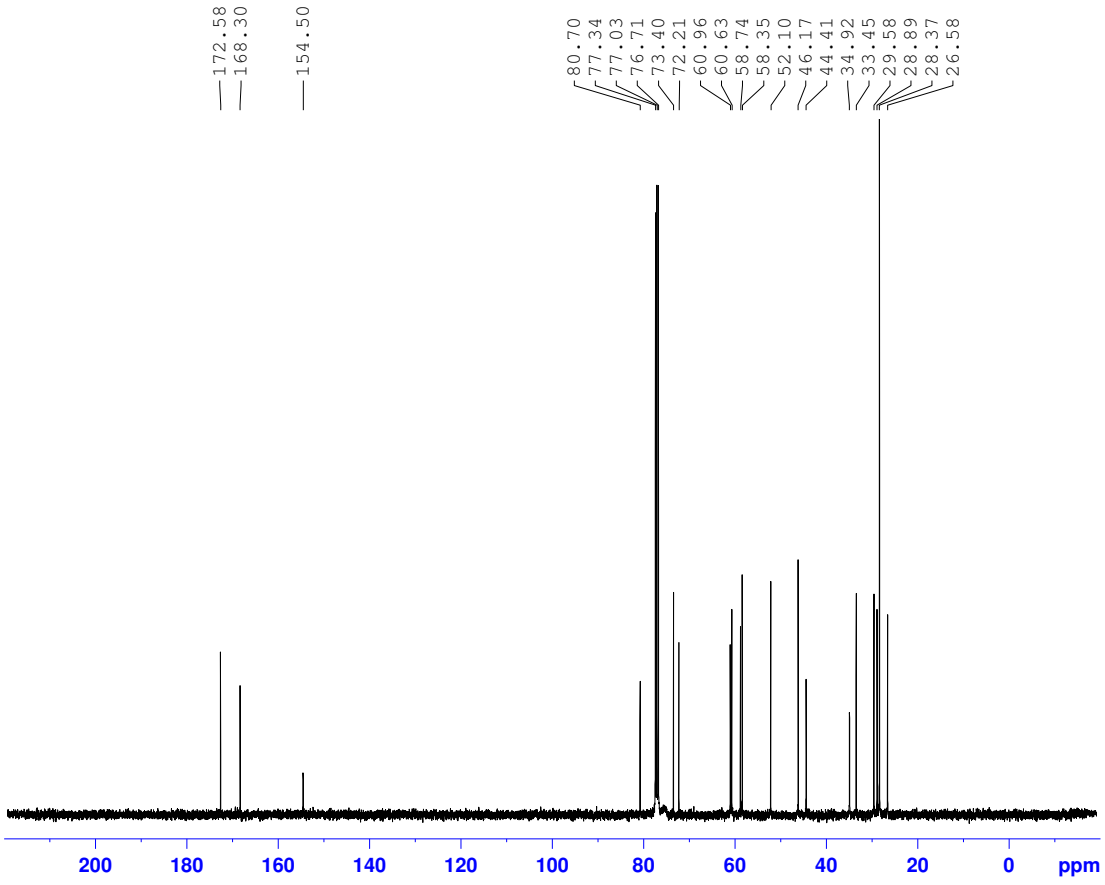
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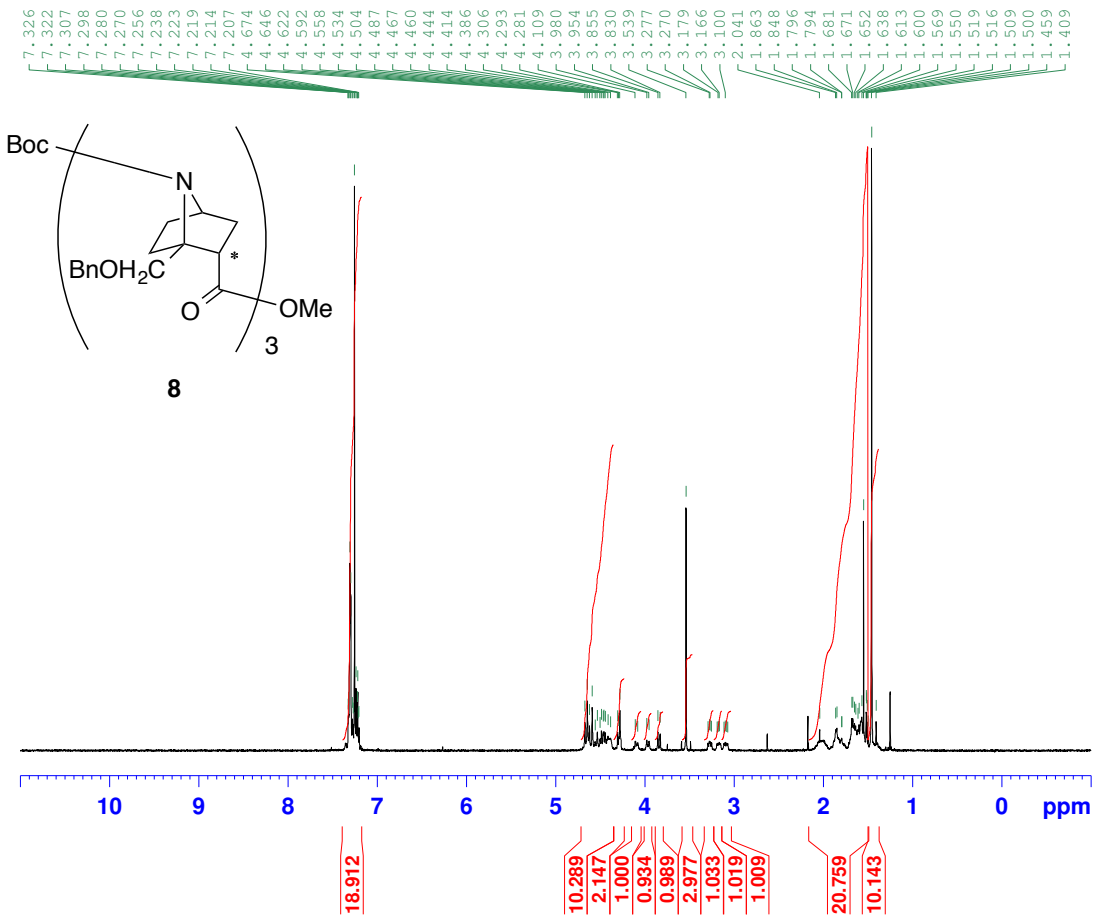
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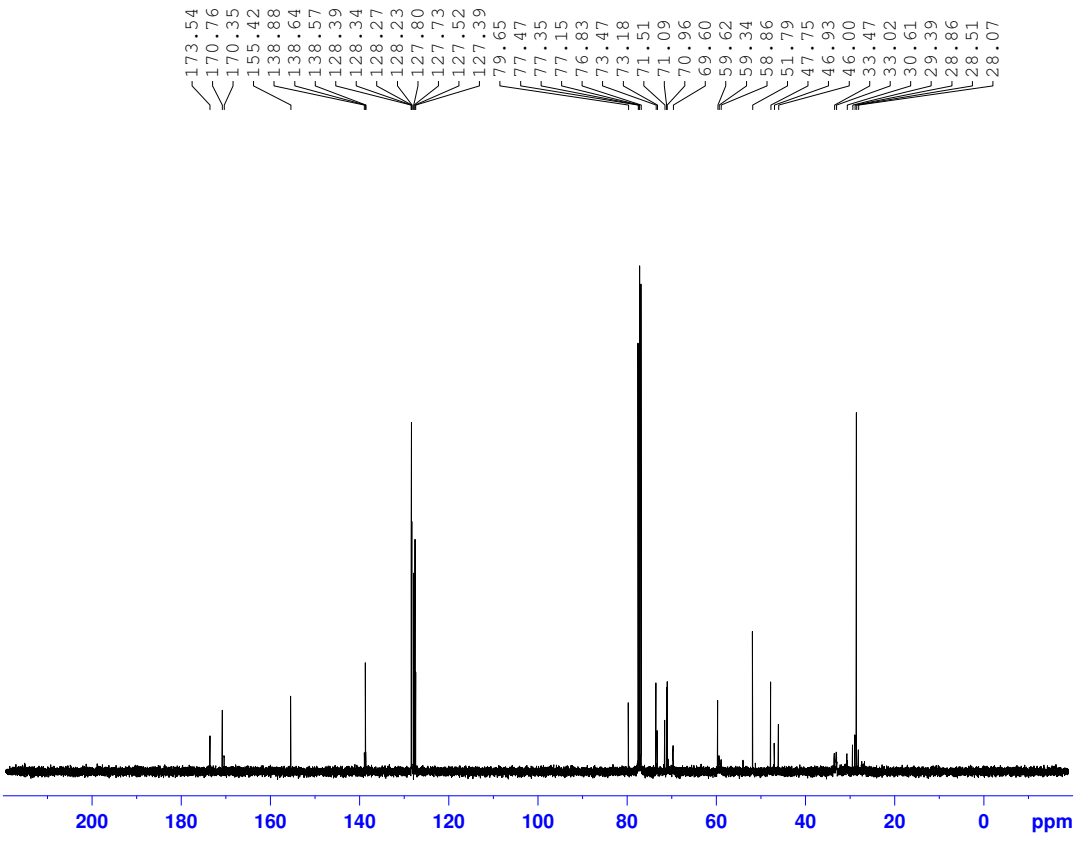
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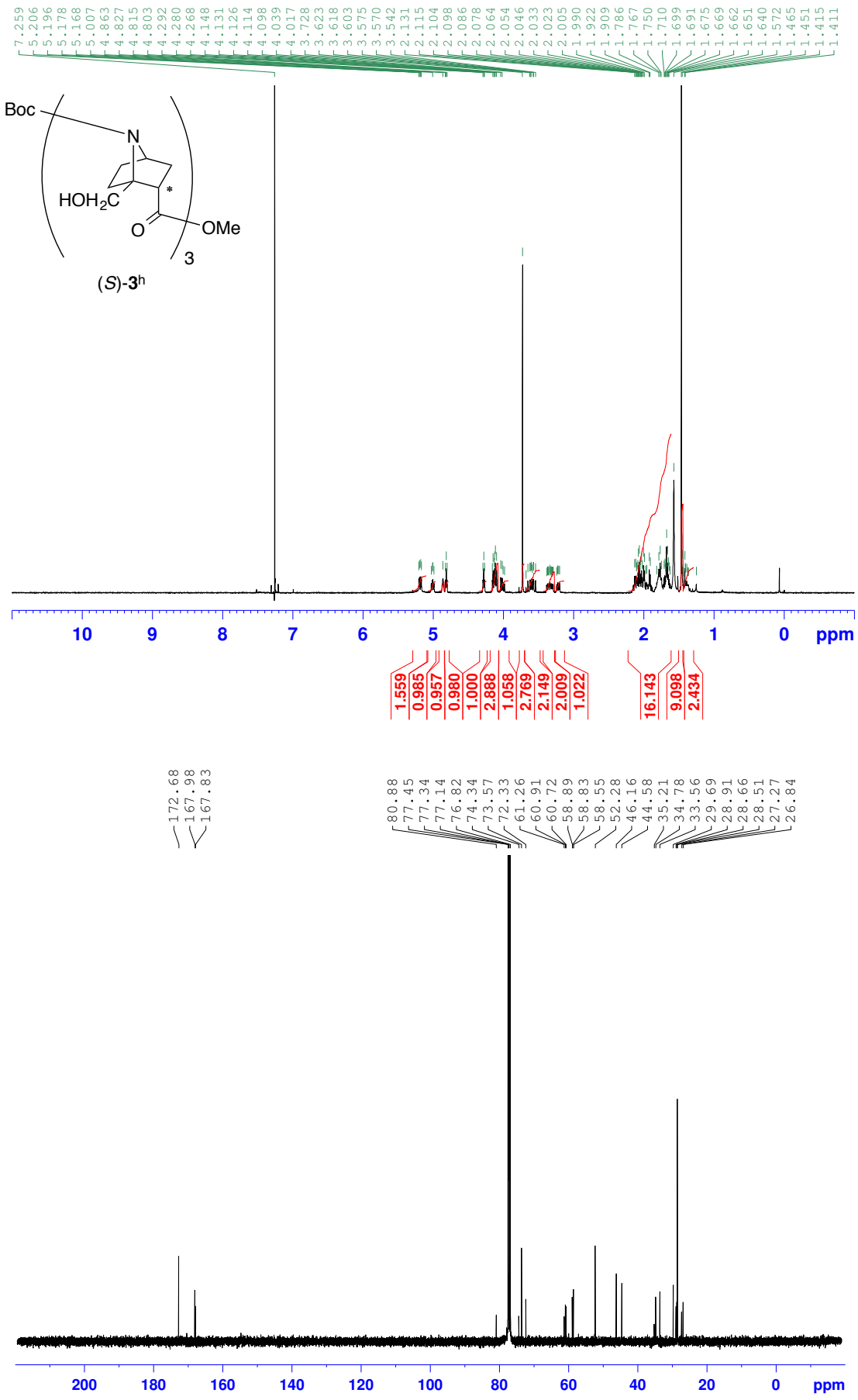
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28.51
27.27
26.84
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Single-crystal X-ray Diffraction Experiments

The crystal data of **(*S*)-2** (CCDC 991065) was reported as earlier described by our group.[1]

The single-crystal XRD data collection of **(*S*)-2^{h}** was carried with a Bruker APEXII CCD area detector with MoKα radiation. The structure was solved by the direct methods and refined by full-matrix least-square procedures on F^2 using SHELXS-97 and SHELXL-97.

CCDC 1445081 contains supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.au.uk/data_request/cif.

Crystal Data for **(*S*)-2^{h}** $C_{22}H_{34}N_2O_7$, (M=438.51); monoclinic, $P2_1$, a = 6.582(4) Å, b = 10.854(6) Å, c = 15.521(8) Å, β = 94.787(5)°, V = 1104.9(10) Å^3, Z = 2, T = 100 K, μ(MoKα) = 0.098 mm^{-1}, D_{calc} = 1.318 mg/m^3, The final R_1 was 0.0267 ($I > 2\sigma(I)$) and wR_2 was 0.0811 (all data).

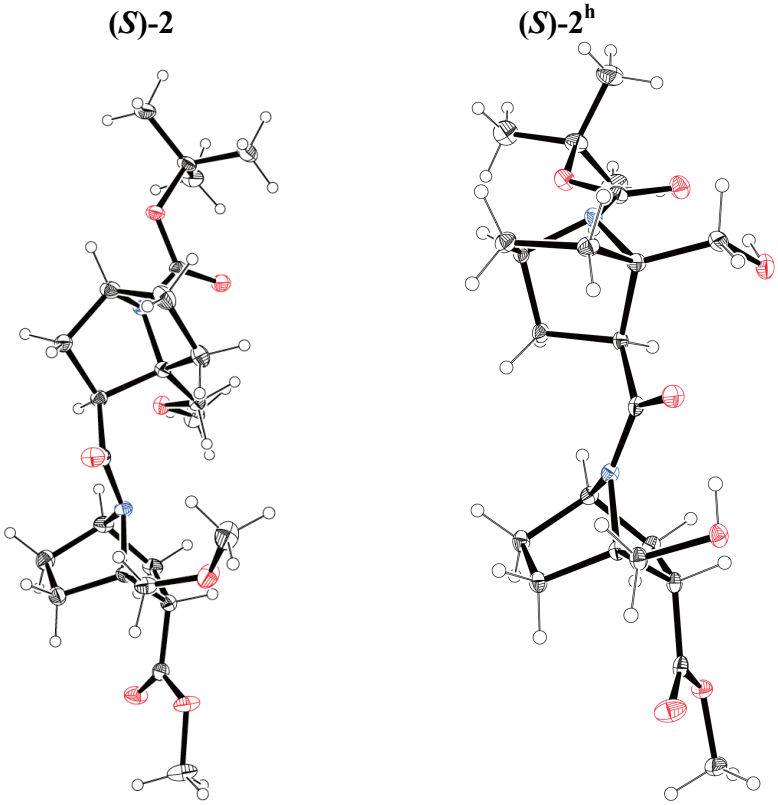
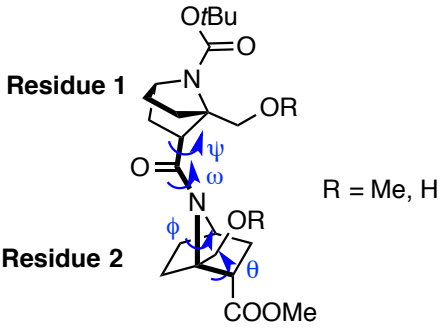


Figure S1. Enlarged versions of ORTEP drawing (50% probability) of the crystal structures of **(*S*)-2** and **(*S*)-2^{h}**.

Main Chain Torsional Angles

Table S1. Main Chain Torsional Angles in the Crystal Structures



Compound	Residue	ω (deg)	ϕ (deg)	θ (deg)	ψ (deg)
(*S*)-2	1	(-162.8)	(-166.7)	-160.1	-75.0
	2	-172.7	-162.9	-157.4	(-74.2)
(*S*)-2^{h}	1	160.07	(-86.53)	-161.51	166.98
	2	178.59	-106.44	-164.86	154.28

DMSO-d_6 into $CDCl_3$ Titration

Peptide **(*S*)-2^{h}** was dissolved to 15 mM in 590 μL of $CDCl_3$ and transferred to NMR tube by micropipette. DMSO-d_6 was added via micropipette. After that, the NMR tube was inverted several times to make sure the homogeneity.[2]

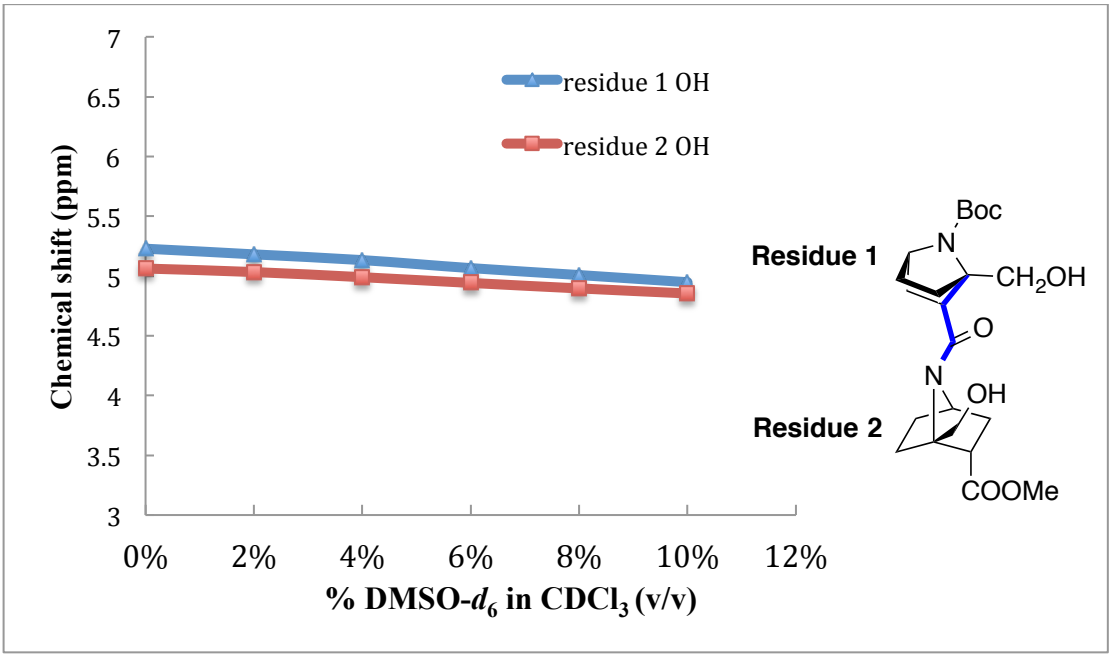


Fig. S2 Variation of OH proton chemical shift (ppm) of **(*S*)-2^{h}** as a function of mixed DMSO-d_6/ $CDCl_3$ solvent composition.

VCD Spectroscopy

VCD and IR spectra were recorded on a BioTools Chiral*ir* spectrometer equipped with a second photoelastic modulator at a resolution of 8 cm^{-1} under ambient temperature. All samples were measured in $CDCl_3$ using a 100 μm BaF_2 or CaF_2 cell. All spectral data were corrected by a solvent spectrum obtained under the same experimental condition, and presented as Δε and ε (both in M^{-1} cm^{-1}).

Prior to the theoretical calculations of IR and VCD spectra, preliminary conformational search was conducted using MMFF in SPARTAN'10 software. The resultant stable geometries were further optimized using DFT at the B3LYP/6-31G(d,p) or B3LYP/6-311+G(d,p) level of theory employing a PCM model for chloroform. The conformers within 2.0 kcal/mol from the most stable were taken into account for the following IR and VCD calculations. The IR and VCD spectra of each conformer were calculated at the same level of theory. The calculated frequencies ν were scaled with the equation of $0.9894\nu - 0.0000104\nu^2$. Final spectra were obtained based on the Boltzmann population average of each spectrum. All the DFT calculations were conducted on Gaussian 09 suites of program package. [3]

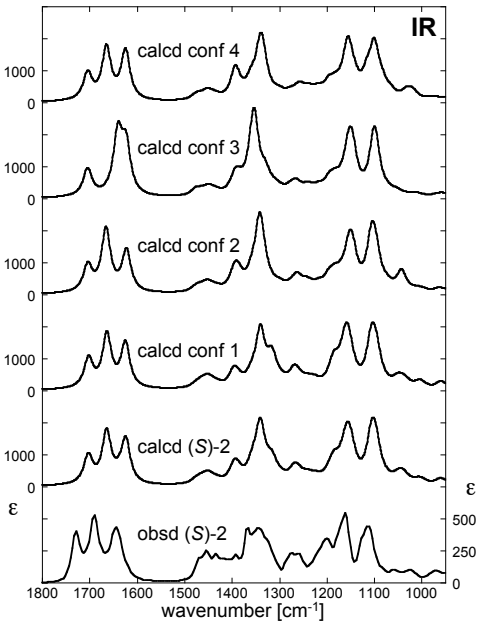


Fig. S3 Calculated IR spectra of each conformer, population-weighed calculated IR spectrum, and observed IR spectrum of **(*S*)-2**.

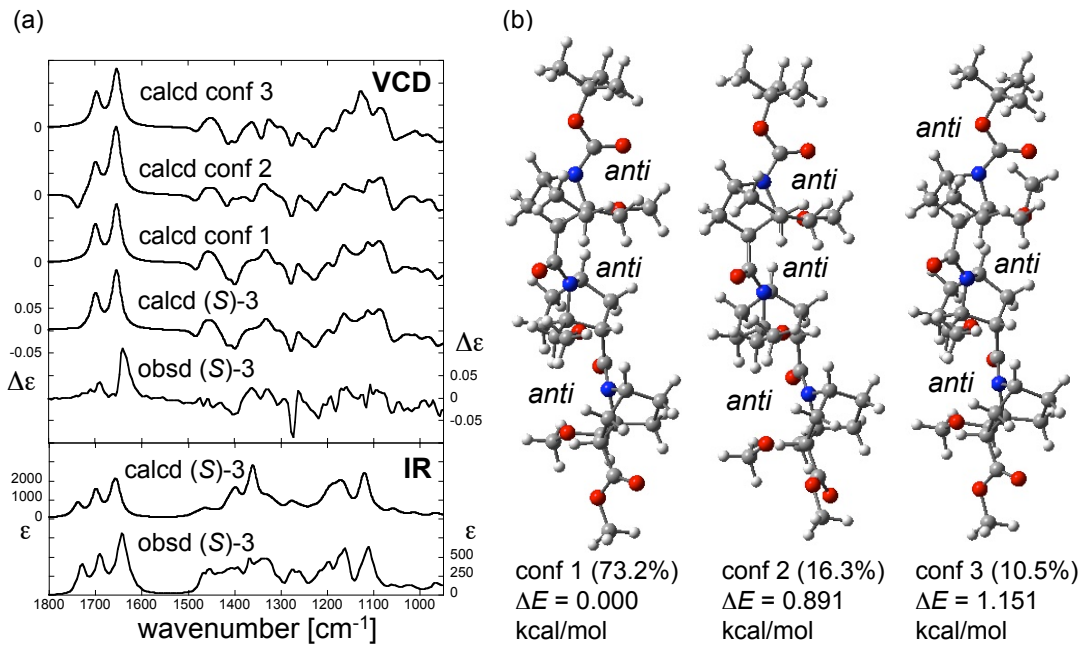


Fig. S4. (a) Calculated VCD spectra of each conformer, population-weighed calculated VCD spectrum, and observed VCD spectrum of **(*S*)-3** (top) and population-weighed calculated IR spectrum and observed IR spectrum (bottom). (b) Stable conformers of **(*S*)-3** and their relative energies. The Boltzmann populations of each conformer simulated at 298 K are shown in parenthesis. Measurement conditions: $CDCl_3$, l = 100 μm, c = 0.12 M, corrected by solvent spectra obtained under the same measurement conditions. Calculation condition: DFT/B3LYP/6-31G(d,p) using PCM for chloroform.

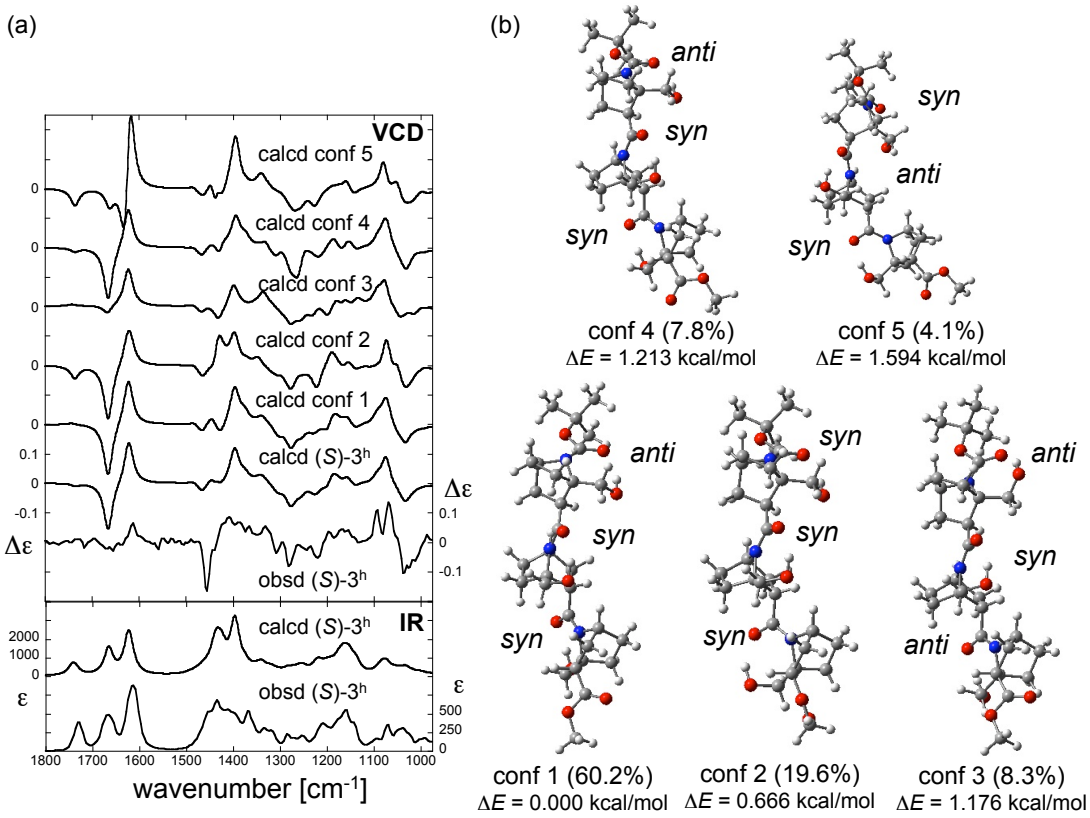


Fig. S5 (a) Calculated VCD spectra of each conformer, population-weighed calculated VCD spectrum, and observed VCD spectrum of **(*S*)-3^{h}** (top) and population-weighed calculated IR spectrum and observed IR spectrum (bottom). (b) Stable conformers of **(*S*)-3^{h}** and their relative energies. The Boltzmann populations of each conformer simulated at 298 K are shown in parenthesis. Measurement conditions: $CDCl_3$, l = 100 μm, c = 0.04 M, corrected by solvent spectra obtained under the same measurement conditions. Calculation condition: DFT/B3LYP/6-31G(d,p) using PCM for chloroform.

Cartesian Coordinates of Selected Calculated Conformers (PDB Format)

(*S*)-**2** conf 1

```
TITLE       Required
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HETATM    2  C           0       2.811  -1.967   0.033                      C
HETATM    3  C           0       3.279   0.380   0.537                      C
HETATM    4  C           0       2.676  -1.085   2.388                      C
HETATM    5  C           0       3.630   0.093   2.023                      C
HETATM    6  C           0       1.894  -1.303   1.070                      C
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HETATM    8  H           0       3.213  -1.984   2.693                      H
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HETATM   22  H           0       7.698  -1.562  -1.171                      H
HETATM   23  C           0       3.736   1.741   0.046                      C
HETATM   24  H           0       3.275   2.527   0.649                      H
HETATM   25  H           0       4.827   1.794   0.169                      H
HETATM   26  O           0       3.399   1.907  -1.321                      O
HETATM   27  C           0       3.748   3.191  -1.812                      C
HETATM   28  H           0       4.829   3.370  -1.727                      H
HETATM   29  H           0       3.464   3.223  -2.864                      H
HETATM   30  H           0       3.214   3.982  -1.271                      H
HETATM   31  C           0       0.798   0.986   0.721                      C
HETATM   32  O           0       0.975   2.201   0.657                      O
HETATM   33  C           0      -0.609   0.421   0.946                      C
HETATM   34  C           0      -2.763   1.525   0.968                      C
HETATM   35  C           0      -1.546   1.615  -1.123                      C
HETATM   36  C           0      -2.449   2.488  -0.202                      C
HETATM   37  C           0      -1.473   0.261  -0.361                      C
HETATM   38  C           0      -1.503   1.339   1.830                      C
HETATM   39  H           0      -2.010   1.454  -2.099                      H
HETATM   40  H           0      -1.947   3.394   0.142                      H
HETATM   41  H           0      -1.019   2.292   2.043                      H
HETATM   42  H           0      -0.556  -0.568   1.392                      H
HETATM   43  H           0      -3.668   1.749   1.522                      H
HETATM   44  H           0      -0.562   2.052  -1.281                      H
HETATM   45  H           0      -3.370   2.782  -0.711                      H
HETATM   46  H           0      -1.745   0.845   2.773                      H
HETATM   47  N           0      -2.826   0.213   0.278                      N
HETATM   48  C           0      -1.075  -0.905  -1.243                      C
HETATM   49  H           0      -1.804  -1.020  -2.049                      H
HETATM   50  H           0      -0.095  -0.678  -1.687                      H
HETATM   51  O           0      -0.995  -2.104  -0.484                      O
HETATM   52  C           0      -0.884  -3.258  -1.303                      C
HETATM   53  H           0      -0.815  -4.120  -0.640                      H
HETATM   54  H           0       0.015  -3.218  -1.933                      H
HETATM   55  H           0      -1.764  -3.369  -1.949                      H
HETATM   56  C           0      -3.958  -0.311  -0.287                      C
HETATM   57  O           0      -3.982  -1.145  -1.178                      O
HETATM   58  O           0      -5.059   0.192   0.325                      O
HETATM   59  C           0      -6.421  -0.286   0.001                      C
HETATM   60  C           0      -6.763   0.033  -1.456                      C
HETATM   61  H           0      -6.608   1.096  -1.659                      H
HETATM   62  H           0      -7.817  -0.195  -1.638                      H
HETATM   63  H           0      -6.155  -0.551  -2.145                      H
HETATM   64  C           0      -7.292   0.541   0.948                      C
HETATM   65  H           0      -7.168   1.609   0.753                      H
HETATM   66  H           0      -7.026   0.344   1.989                      H
HETATM   67  H           0      -8.344   0.285   0.806                      H
HETATM   68  C           0      -6.548  -1.778   0.319                      C
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HETATM   69  H           0      -7.591  -2.084   0.203                       H
HETATM   70  H           0      -6.250  -1.972   1.353                       H
HETATM   71  H           0      -5.931  -2.379  -0.346                       H
END
CONECT    1    2
CONECT    2    1    6    7   11
CONECT    3    5    7   15   23
CONECT    4    5    6    8   12
CONECT    5    3    4    9   13
CONECT    6    2    4   14   15
CONECT    7    2    3   10   16
CONECT    8    4
CONECT    9    5
CONECT   10    7
CONECT   11    2
CONECT   12    4
CONECT   13    5
CONECT   14    6
CONECT   15    6    3   31
CONECT   16    7   17   18
CONECT   17   16
CONECT   18   16   19
CONECT   19   18   20   21   22
CONECT   20   19
CONECT   21   19
CONECT   22   19
CONECT   23    3   24   25   26
CONECT   24   23
CONECT   25   23
CONECT   26   23   27
CONECT   27   26   28   29   30
CONECT   28   27
CONECT   29   27
CONECT   30   27
CONECT   31   15   32   33
CONECT   32   31
CONECT   33   31   37   38   42
CONECT   34   36   38   43   47
CONECT   35   36   37   39   44
CONECT   36   35   34   40   45
CONECT   37   35   33   47   48
CONECT   38   33   34   41   46
CONECT   39   35
CONECT   40   36
CONECT   41   38
CONECT   42   33
CONECT   43   34
CONECT   44   35
CONECT   45   36
CONECT   46   38
CONECT   47   37   34   56
CONECT   48   37   49   50   51
CONECT   49   48
CONECT   50   48
CONECT   51   48   52
CONECT   52   51   53   54   55
CONECT   53   52
CONECT   54   52
CONECT   55   52
CONECT   56   47   57   58
CONECT   57   56
CONECT   58   56   59
CONECT   59   58   60   64   68
CONECT   60   59   61   62   63
CONECT   61   60
CONECT   62   60
CONECT   63   60
CONECT   64   59   65   66   67
CONECT   65   64
CONECT   66   64
CONECT   67   64
CONECT   68   59   69   70   71
CONECT   69   68
CONECT   70   68
CONECT   71   68
```

(*S*)-**2** conf 2

```
TITLE       Required
REMARK   1 File created by GaussView 5.0.9
HETATM    1  H           0       2.033   1.783  -1.691                H
HETATM    2  C           0       2.658   0.901  -1.837                C
HETATM    3  C           0       3.256  -0.744  -0.132                C
HETATM    4  C           0       2.653  -1.564  -2.350                C
HETATM    5  C           0       3.670  -1.795  -1.197                C
HETATM    6  C           0       1.811  -0.396  -1.810                C
HETATM    7  C           0       3.621   0.711  -0.622                C
HETATM    8  H           0       3.135  -1.307  -3.295                H
HETATM    9  H           0       3.562  -2.793  -0.766                H
HETATM   10  H           0       3.349   1.392   0.185                H
HETATM   11  H           0       3.195   1.009  -2.779                H
HETATM   12  H           0       2.029  -2.444  -2.514                H
HETATM   13  H           0       4.703  -1.670  -1.508                H
HETATM   14  H           0       0.826  -0.298  -2.255                H
HETATM   15  N           0       1.783  -0.710  -0.361                N
HETATM   16  C           0       5.077   0.954  -0.955                C
HETATM   17  O           0       5.654   0.541  -1.938                O
HETATM   18  O           0       5.669   1.728  -0.027                O
HETATM   19  C           0       7.069   2.012  -0.225                C
HETATM   20  H           0       7.356   2.648   0.610                H
HETATM   21  H           0       7.222   2.531  -1.171                H
HETATM   22  H           0       7.647   1.088  -0.218                H
HETATM   23  C           0       3.722  -1.087   1.275                C
HETATM   24  H           0       3.499  -0.280   1.978                H
HETATM   25  H           0       3.212  -1.993   1.628                H
HETATM   26  O           0       5.127  -1.309   1.203                O
HETATM   27  C           0       5.703  -1.550   2.476                C
HETATM   28  H           0       5.557  -0.695   3.148                H
HETATM   29  H           0       6.771  -1.708   2.323                H
HETATM   30  H           0       5.271  -2.444   2.945                H
HETATM   31  C           0       0.800  -0.443   0.548                C
HETATM   32  O           0       1.025  -0.374   1.756                O
HETATM   33  C           0      -0.601  -0.285  -0.042                C
HETATM   34  C           0      -2.612  -1.623  -0.186                C
HETATM   35  C           0      -1.938  -0.978   2.042                C
HETATM   36  C           0      -2.564  -2.169   1.260                C
HETATM   37  C           0      -1.743   0.109   0.945                C
HETATM   38  C           0      -1.180  -1.556  -0.749                C
HETATM   39  H           0      -2.625  -0.600   2.804                H
HETATM   40  H           0      -1.972  -3.084   1.331                H
HETATM   41  H           0      -0.617  -2.461  -0.514                H
HETATM   42  H           0      -0.553   0.528  -0.768                H
HETATM   43  H           0      -3.336  -2.099  -0.839                H
HETATM   44  H           0      -0.996  -1.223   2.526                H
HETATM   45  H           0      -3.572  -2.394   1.615                H
HETATM   46  H           0      -1.189  -1.437  -1.834                H
HETATM   47  N           0      -2.901  -0.186   0.037                N
HETATM   48  C           0      -1.621   1.514   1.505                C
HETATM   49  H           0      -2.548   1.794   2.012                H
HETATM   50  H           0      -0.801   1.506   2.235                H
HETATM   51  O           0      -1.332   2.440   0.465                O
HETATM   52  C           0      -1.291   3.778   0.931                C
HETATM   53  H           0      -1.063   4.413   0.074                H
HETATM   54  H           0      -0.513   3.912   1.695                H
HETATM   55  H           0      -2.258   4.081   1.354                H
HETATM   56  C           0      -4.160   0.343   0.132                C
HETATM   57  O           0      -4.443   1.401   0.671                O
HETATM   58  O           0      -5.050  -0.456  -0.508                O
HETATM   59  C           0      -6.467  -0.067  -0.685                C
HETATM   60  C           0      -7.158   0.059   0.675                C
HETATM   61  H           0      -7.025  -0.858   1.255                H
HETATM   62  H           0      -8.230   0.209   0.521                H
HETATM   63  H           0      -6.764   0.899   1.244                H
HETATM   64  C           0      -7.036  -1.252  -1.468                C
HETATM   65  H           0      -6.936  -2.177  -0.896                H
HETATM   66  H           0      -6.514  -1.372  -2.420                H
HETATM   67  H           0      -8.096  -1.086  -1.673                H
HETATM   68  C           0      -6.561   1.218  -1.511                C
HETATM   69  H           0      -7.609   1.420  -1.747                H
HETATM   70  H           0      -6.017   1.105  -2.453                H
HETATM   71  H           0      -6.156   2.070  -0.968                H
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END
CONECT    1    2
CONECT    2    1    6    7   11
CONECT    3    5    7   15   23
CONECT    4    5    6    8   12
CONECT    5    4    3    9   13
CONECT    6    4    2   14   15
CONECT    7    3    2   10   16
CONECT    8    4
CONECT    9    5
CONECT   10    7
CONECT   11    2
CONECT   12    4
CONECT   13    5
CONECT   14    6
CONECT   15    6    3   31
CONECT   16    7   17   18
CONECT   17   16
CONECT   18   16   19
CONECT   19   18   20   21   22
CONECT   20   19
CONECT   21   19
CONECT   22   19
CONECT   23    3   24   25   26
CONECT   24   23
CONECT   25   23
CONECT   26   23   27
CONECT   27   26   28   29   30
CONECT   28   27
CONECT   29   27
CONECT   30   27
CONECT   31   15   32   33
CONECT   32   31
CONECT   33   31   37   38   42
CONECT   34   36   38   43   47
CONECT   35   36   37   39   44
CONECT   36   34   35   40   45
CONECT   37   33   35   47   48
CONECT   38   33   34   41   46
CONECT   39   35
CONECT   40   36
CONECT   41   38
CONECT   42   33
CONECT   43   34
CONECT   44   35
CONECT   45   36
CONECT   46   38
CONECT   47   34   37   56
CONECT   48   37   49   50   51
CONECT   49   48
CONECT   50   48
CONECT   51   48   52
CONECT   52   51   53   54   55
CONECT   53   52
CONECT   54   52
CONECT   55   52
CONECT   56   47   57   58
CONECT   57   56
CONECT   58   56   59
CONECT   59   58   60   64   68
CONECT   60   59   61   62   63
CONECT   61   60
CONECT   62   60
CONECT   63   60
CONECT   64   59   65   66   67
CONECT   65   64
CONECT   66   64
CONECT   67   64
CONECT   68   59   69   70   71
CONECT   69   68
CONECT   70   68
CONECT   71   68
```

(*S*)-**2**^{h} conf 1

```
TITLE       Required
REMARK   1 File created by GaussView 5.0.9
HETATM    1  H           0       2.099  -2.085  -1.162                      H
HETATM    2  C           0       2.638  -1.847  -0.244                      C
HETATM    3  C           0       3.252   0.396   0.520                      C
HETATM    4  C           0       2.397  -1.184   2.173                      C
HETATM    5  C           0       3.484  -0.086   1.976                      C
HETATM    6  C           0       1.698  -1.214   0.797                      C
HETATM    7  C           0       3.690  -0.731  -0.492                      C
HETATM    8  H           0       2.819  -2.158   2.429                      H
HETATM    9  H           0       3.335   0.756   2.652                      H
HETATM   10  H           0       3.589  -0.317  -1.497                      H
HETATM   11  H           0       3.096  -2.761   0.135                      H
HETATM   12  H           0       1.690  -0.904   2.956                      H
HETATM   13  H           0       4.496  -0.461   2.123                      H
HETATM   14  H           0       0.697  -1.628   0.777                      H
HETATM   15  N           0       1.762   0.220   0.409                      N
HETATM   16  C           0       5.128  -1.189  -0.336                      C
HETATM   17  O           0       5.506  -2.116   0.345                      O
HETATM   18  O           0       5.962  -0.422  -1.061                      O
HETATM   19  C           0       7.370  -0.740  -0.983                      C
HETATM   20  H           0       7.724  -0.639   0.043                      H
HETATM   21  H           0       7.864  -0.021  -1.631                      H
HETATM   22  H           0       7.546  -1.757  -1.333                      H
HETATM   23  C           0       3.854   1.756   0.169                      C
HETATM   24  H           0       4.939   1.645   0.193                      H
HETATM   25  H           0       3.574   2.021  -0.858                      H
HETATM   26  O           0       3.526   2.799   1.069                      O
HETATM   27  C           0       0.789   1.153   0.334                      C
HETATM   28  O           0       1.032   2.366   0.213                      O
HETATM   29  C           0      -0.664   0.677   0.363                      C
HETATM   30  C           0      -2.727   1.911  -0.019                      C
HETATM   31  C           0      -1.206   1.788  -1.885                      C
HETATM   32  C           0      -2.169   2.774  -1.166                      C
HETATM   33  C           0      -1.333   0.484  -1.055                      C
HETATM   34  C           0      -1.629   1.695   1.049                      C
HETATM   35  H           0      -1.532   1.592  -2.909                      H
HETATM   36  H           0      -1.656   3.659  -0.788                      H
HETATM   37  H           0      -1.126   2.627   1.304                      H
HETATM   38  H           0      -0.729  -0.285   0.867                      H
HETATM   39  H           0      -3.691   2.220   0.371                      H
HETATM   40  H           0      -0.179   2.149  -1.915                      H
HETATM   41  H           0      -2.974   3.098  -1.828                      H
HETATM   42  H           0      -2.053   1.265   1.958                      H
HETATM   43  N           0      -2.774   0.581  -0.672                      N
HETATM   44  C           0      -0.891  -0.744  -1.846                      C
HETATM   45  H           0      -1.527  -0.831  -2.736                      H
HETATM   46  H           0       0.130  -0.562  -2.190                      H
HETATM   47  O           0      -0.868  -1.960  -1.117                      O
HETATM   48  C           0      -3.654  -0.419  -0.409                      C
HETATM   49  O           0      -3.501  -1.596  -0.735                      O
HETATM   50  O           0      -4.748   0.052   0.219                      O
HETATM   51  C           0      -5.931  -0.802   0.500                      C
HETATM   52  C           0      -6.525  -1.321  -0.810                      C
HETATM   53  H           0      -5.853  -2.020  -1.304                      H
HETATM   54  H           0      -6.738  -0.490  -1.488                      H
HETATM   55  H           0      -7.467  -1.833  -0.598                      H
HETATM   56  C           0      -6.887   0.183   1.175                      C
HETATM   57  H           0      -7.127   1.010   0.503                      H
HETATM   58  H           0      -6.442   0.591   2.085                      H
HETATM   59  H           0      -7.815  -0.327   1.441                      H
HETATM   60  C           0      -5.552  -1.929   1.463                      C
HETATM   61  H           0      -4.878  -2.645   0.995                      H
HETATM   62  H           0      -6.459  -2.455   1.773                      H
HETATM   63  H           0      -5.075  -1.522   2.357                      H
HETATM   64  H           0       2.574   2.952   0.919                      H
HETATM   65  H           0      -1.805  -2.146  -0.914                      H
END
CONECT    1    2
CONECT    2    1    6    7   11
CONECT    3    5    7   15   23
CONECT    4    5    6    8   12
CONECT    5    4    3    9   13
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CONECT    6    2    4   14   15
CONECT    7    2    3   10   16
CONECT    8    4
CONECT    9    5
CONECT   10    7
CONECT   11    2
CONECT   12    4
CONECT   13    5
CONECT   14    6
CONECT   15    6    3   27
CONECT   16    7   17   18
CONECT   17   16
CONECT   18   16   19
CONECT   19   18   20   21   22
CONECT   20   19
CONECT   21   19
CONECT   22   19
CONECT   23    3   24   25   26
CONECT   24   23
CONECT   25   23
CONECT   26   23   64
CONECT   27   15   28   29
CONECT   28   27
CONECT   29   27   33   34   38
CONECT   30   32   34   39   43
CONECT   31   32   33   35   40
CONECT   32   30   31   36   41
CONECT   33   31   29   43   44
CONECT   34   30   29   37   42
CONECT   35   31
CONECT   36   32
CONECT   37   34
CONECT   38   29
CONECT   39   30
CONECT   40   31
CONECT   41   32
CONECT   42   34
CONECT   43   30   33   48
CONECT   44   33   45   46   47
CONECT   45   44
CONECT   46   44
CONECT   47   44   65
CONECT   48   43   49   50
CONECT   49   48
CONECT   50   48   51
CONECT   51   50   52   56   60
CONECT   52   51   53   54   55
CONECT   53   52
CONECT   54   52
CONECT   55   52
CONECT   56   51   57   58   59
CONECT   57   56
CONECT   58   56
CONECT   59   56
CONECT   60   51   61   62   63
CONECT   61   60
CONECT   62   60
CONECT   63   60
CONECT   64   26
CONECT   65   47
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(*S*)-**2**[h] conf 2

```
TITLE       Required
REMARK   1 File created by GaussView 5.0.9
HETATM    1  H           0       2.309  -1.766  -1.162                H
HETATM    2  C           0       2.774  -1.586  -0.193                C
HETATM    3  C           0       3.230   0.569   0.865                C
HETATM    4  C           0       2.347  -1.241   2.262                C
HETATM    5  C           0       3.404  -0.098   2.260                C
HETATM    6  C           0       1.735  -1.121   0.855                C
HETATM    7  C           0       3.761  -0.373  -0.254                C
HETATM    8  H           0       2.785  -2.227   2.429                H
HETATM    9  H           0       3.193   0.637   3.040                H
HETATM   10  H           0       3.628   0.150  -1.205                H
HETATM   11  H           0       3.261  -2.511   0.119                H
HETATM   12  H           0       1.585  -1.077   3.027                H
HETATM   13  H           0       4.424  -0.451   2.401                H
HETATM   14  H           0       0.758  -1.568   0.713                H
HETATM   15  N           0       1.756   0.350   0.658                N
HETATM   16  C           0       5.228  -0.740  -0.203                C
HETATM   17  O           0       6.051  -0.327   0.585                O
HETATM   18  O           0       5.531  -1.592  -1.200                O
HETATM   19  C           0       6.912  -1.999  -1.308                C
HETATM   20  H           0       6.949  -2.669  -2.163                H
HETATM   21  H           0       7.227  -2.517  -0.402                H
HETATM   22  H           0       7.551  -1.131  -1.474                H
HETATM   23  C           0       3.757   1.999   0.823                C
HETATM   24  H           0       3.265   2.585   1.608                H
HETATM   25  H           0       4.822   1.952   1.056                H
HETATM   26  O           0       3.628   2.635  -0.438                O
HETATM   27  C           0       0.776   1.224   0.353                C
HETATM   28  O           0       1.002   2.421   0.105                O
HETATM   29  C           0      -0.667   0.714   0.355                C
HETATM   30  C           0      -2.751   1.894  -0.093                C
HETATM   31  C           0      -1.208   1.735  -1.939                C
HETATM   32  C           0      -2.199   2.727  -1.265                C
HETATM   33  C           0      -1.316   0.461  -1.062                C
HETATM   34  C           0      -1.659   1.742   0.992                C
HETATM   35  H           0      -1.523   1.494  -2.957                H
HETATM   36  H           0      -1.708   3.635  -0.914                H
HETATM   37  H           0      -1.176   2.692   1.213                H
HETATM   38  H           0      -0.724  -0.228   0.895                H
HETATM   39  H           0      -3.725   2.198   0.277                H
HETATM   40  H           0      -0.190   2.117  -1.973                H
HETATM   41  H           0      -3.003   3.010  -1.946                H
HETATM   42  H           0      -2.082   1.339   1.914                H
HETATM   43  N           0      -2.763   0.541  -0.696                N
HETATM   44  C           0      -0.843  -0.784  -1.809                C
HETATM   45  H           0      -1.469  -0.912  -2.701                H
HETATM   46  H           0       0.177  -0.593  -2.151                H
HETATM   47  O           0      -0.804  -1.976  -1.042                O
HETATM   48  C           0      -3.624  -0.467  -0.400                C
HETATM   49  O           0      -3.442  -1.653  -0.675                O
HETATM   50  O           0      -4.735   0.005   0.195                O
HETATM   51  C           0      -5.898  -0.863   0.510                C
HETATM   52  C           0      -6.469  -1.463  -0.776                C
HETATM   53  H           0      -6.694  -0.674  -1.498                H
HETATM   54  H           0      -7.401  -1.985  -0.544                H
HETATM   55  H           0      -5.777  -2.172  -1.227                H
HETATM   56  C           0      -6.884   0.130   1.127                C
HETATM   57  H           0      -7.138   0.916   0.413                H
HETATM   58  H           0      -6.458   0.593   2.020                H
HETATM   59  H           0      -7.802  -0.390   1.411                H
HETATM   60  C           0      -5.498  -1.931   1.531                C
HETATM   61  H           0      -4.804  -2.652   1.104                H
HETATM   62  H           0      -6.394  -2.462   1.862                H
HETATM   63  H           0      -5.037  -1.467   2.407                H
HETATM   64  H           0       2.668   2.792  -0.523                H
HETATM   65  H           0      -1.738  -2.171  -0.835                H
END
CONECT    1    2
CONECT    2    1    6    7   11
CONECT    3    5    7   15   23
CONECT    4    5    6    8   12
CONECT    5    4    3    9   13
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CONECT    6    2    4   14   15
CONECT    7    2    3   10   16
CONECT    8    4
CONECT    9    5
CONECT   10    7
CONECT   11    2
CONECT   12    4
CONECT   13    5
CONECT   14    6
CONECT   15    6    3   27
CONECT   16    7   17   18
CONECT   17   16
CONECT   18   16   19
CONECT   19   18   20   21   22
CONECT   20   19
CONECT   21   19
CONECT   22   19
CONECT   23    3   24   25   26
CONECT   24   23
CONECT   25   23
CONECT   26   23   64
CONECT   27   15   28   29
CONECT   28   27
CONECT   29   27   33   34   38
CONECT   30   32   34   39   43
CONECT   31   32   33   35   40
CONECT   32   30   31   36   41
CONECT   33   31   29   43   44
CONECT   34   30   29   37   42
CONECT   35   31
CONECT   36   32
CONECT   37   34
CONECT   38   29
CONECT   39   30
CONECT   40   31
CONECT   41   32
CONECT   42   34
CONECT   43   30   33   48
CONECT   44   33   45   46   47
CONECT   45   44
CONECT   46   44
CONECT   47   44   65
CONECT   48   43   49   50
CONECT   49   48
CONECT   50   48   51
CONECT   51   50   52   56   60
CONECT   52   51   53   54   55
CONECT   53   52
CONECT   54   52
CONECT   55   52
CONECT   56   51   57   58   59
CONECT   57   56
CONECT   58   56
CONECT   59   56
CONECT   60   51   61   62   63
CONECT   61   60
CONECT   62   60
CONECT   63   60
CONECT   64   26
CONECT   65   47
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