

Exploration of Chromophores for VCD Couplet in Biomolecularly Transparent Infrared Region

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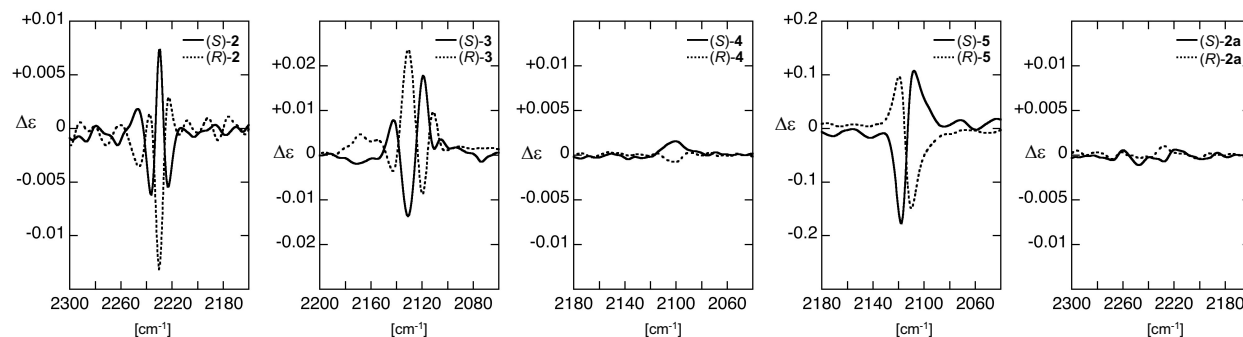


Fig. S1 VCD spectra of enantiomeric pairs of **2-5** without “enantiomer correction” in the 2300-2000 cm^{-1} region. Measurement conditions are described in the caption of Figures 2 and 3.

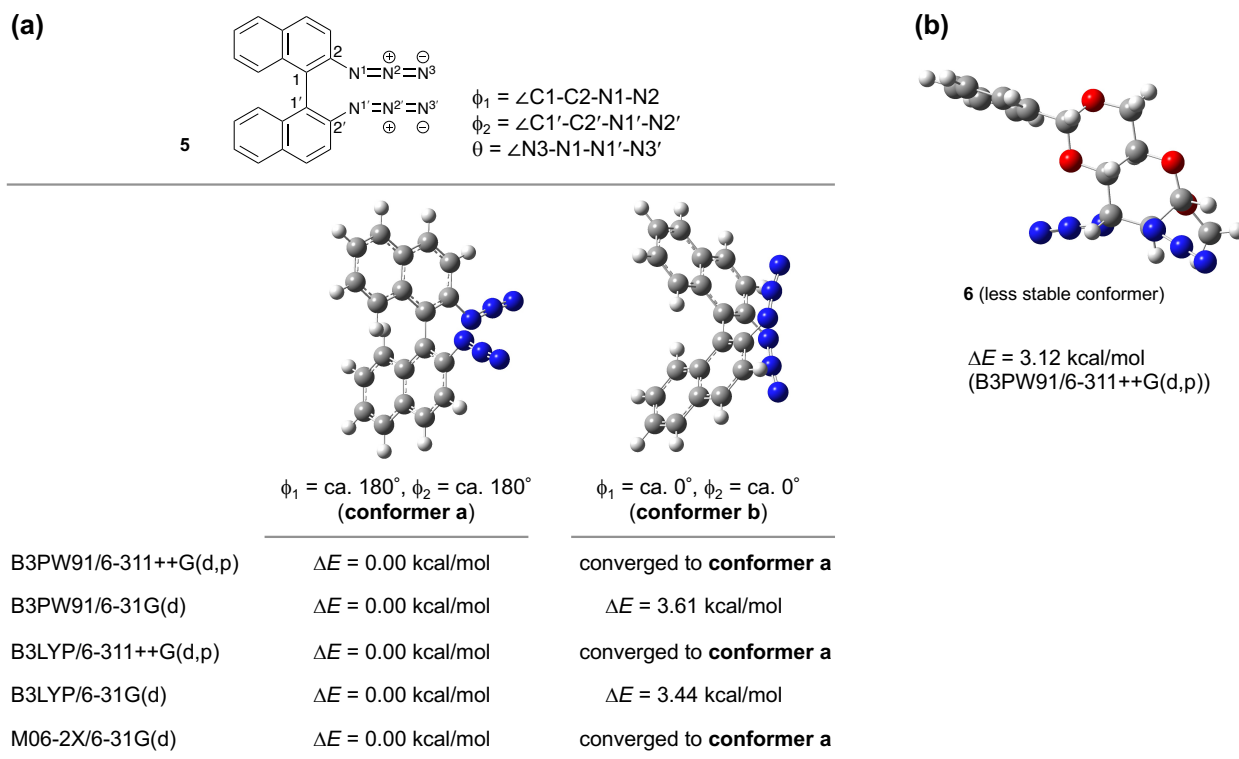


Fig. S2 Less stable conformers of **5** and **6**. (a) Three geometries with $(\phi_1, \phi_2) = (0^\circ, 0^\circ)$, $(0^\circ, 180^\circ)$, and $(180^\circ, 180^\circ)$ were submitted to DFT optimization. With B3PW91/6-311++G(d,p) level of optimization, all geometries were converged to a conformer with angles ϕ_1 and ϕ_2 of approximately 180° and 180° ($\theta = -23^\circ$). Some of different DFT levels yielded the second most stable conformer with ϕ_1 and ϕ_2 of approximately 0° and 0° with ΔE of higher than 3.0 kcal/mol. Conformers with $(\phi_1, \phi_2) = (0^\circ, 180^\circ)$ could not be obtained by all the tested calculation conditions. (b) The second most stable conformer of **6** predicted at DFT/B3PW91/6-311++G(d,p).

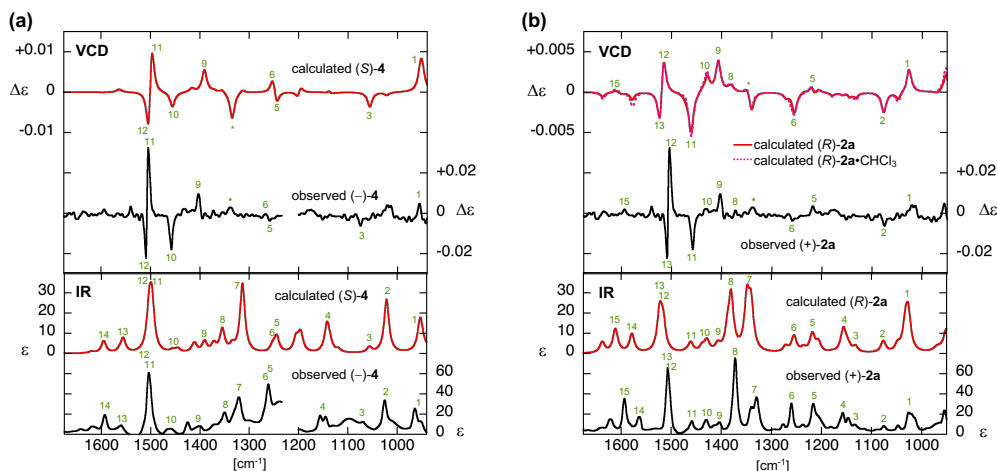


Fig. S3 Assignment of the chirality of (a) (-)-**4** and (b) (+)-**2a** by comparison of calculated and observed VCD (top) and IR (bottom) spectra. Theoretical VCD spectrum for (*R*)-**2a** was almost superimposable to that for (*R*)-**2a**•CHCl₃. Part of corresponding VCD and IR peaks are labelled, while nonmatching peaks are indicated by asterisks. Measurement conditions: *c* 0.6 M in CHCl₃ (for (-)-**4**) or 0.3 M in CDCl₃ (for (+)-**2a**), *l* 50 μm (for (-)-**4**) or 100 μm (for (+)-**2a**), corrected by solvent spectra. Calculation conditions: B3PW91/6-311++G(d,p). Frequency scaling factor: 0.97 (for (*S*)-**4**) or 0.98 (for (*R*)-**2a**). Part of observed spectra are omitted due to strong solvent absorption.

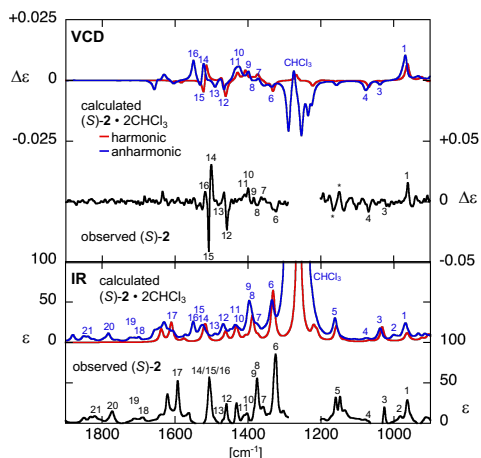


Fig. S4 VCD (top) and IR (bottom) of measured (black) for (*S*)-**2** and calculated (red for harmonic DFT and blue for anharmonic DFT) spectra (*S*)-**2**•2CHCl₃. Part of corresponding VCD and IR peaks of observed spectra and anharmonically calculated spectra are labelled, while nonmatching peaks are indicated by asterisks. Both the anharmonic and harmonic VCD spectra were qualitatively similar to observed one, whereas only anharmonically calculated IR spectrum well reproduced the observed anharmonic signals in the region above 1600 cm^{-1} (peaks 18-21). Measurement conditions: *c* 0.3 M in CHCl₃, *l* 50 μm , corrected by solvent spectra. Calculation conditions: B3PW91/6-311++G(d,p). Harmonic calculated spectra are scaled by a factor of 0.98, while anharmonic ones are unscaled. Part of observed spectra are omitted due to strong solvent absorption.

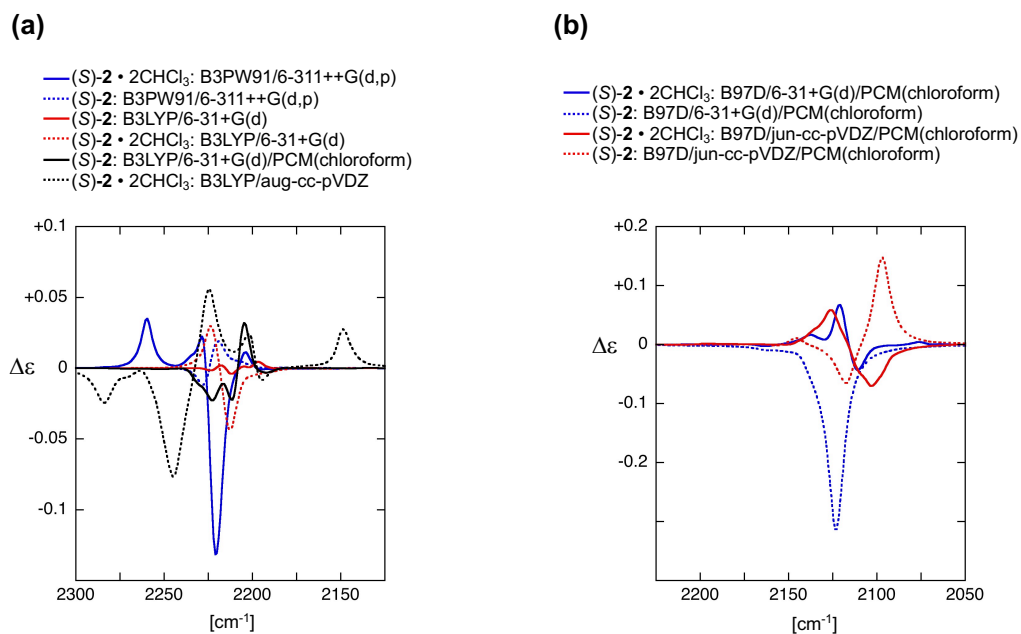


Fig. S5 Predicted VCD patterns of (S)-2 by anharmonic DFT using (a) B3PW91 or B3LYP, or (b) B97D functionals. All spectra were scaled by a factor of 0.967.

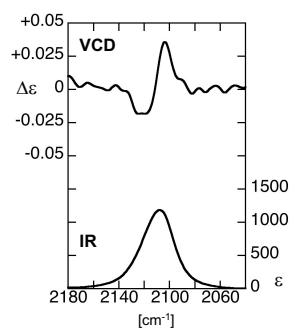


Fig. S6 Observed VCD and IR spectra of **6** in DMSO-*h*₆ – H₂O (9:1) mixed solvent. Measurement conditions: *c* 0.04 M, *l* 50 μm, corrected by solvent spectra.

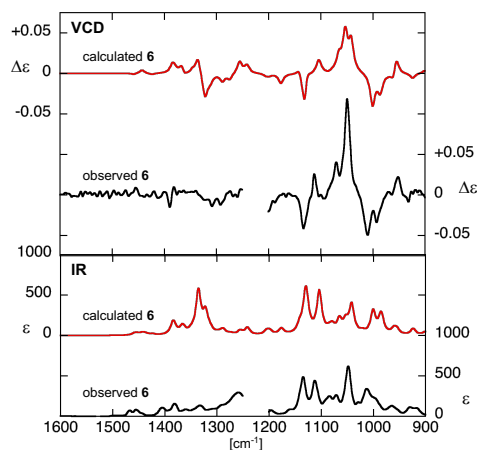


Fig. S7 VCD (top) and IR (bottom) of measured and calculated spectra for **6**. Agreement between the experimental and theoretical spectra supported the validity of the molecular geometry used for spectral calculations. Measurement conditions: c 0.3 M in CHCl_3 , l 50 μm , corrected by solvent spectra. Calculation conditions: harmonic DFT at B3PW91/6-311++G(d,p). Frequency scaling factor: 0.97.

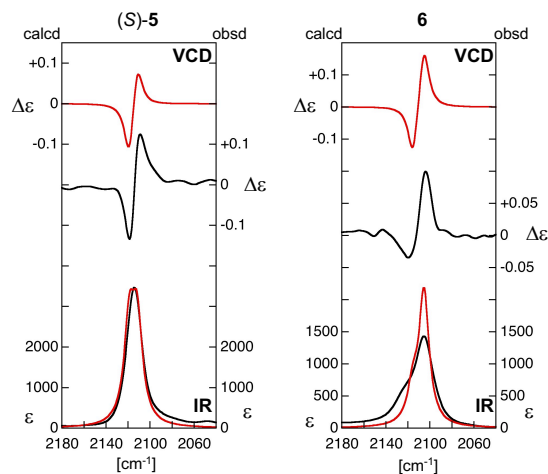


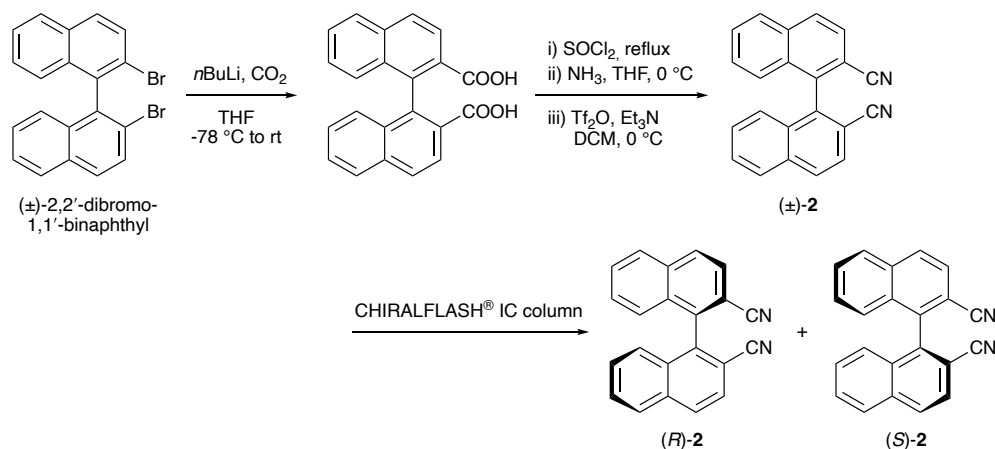
Fig. S8 Comparison of the VCD and IR (bottom) spectra observed for *(S)*-**5** and **6** and those calculated using harmonic DFT at B3PW91/6-31G(d). The observed spectra are the same as those shown in Figure 2 and 4. Frequency scaling factor: 0.936 (for *(S)*-**5**) and 0.931 (for **6**).

Synthesis of 2, 3, 4, 5, 2a, and 6

General Procedures

¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded on a Varian Inova instrument at 25 °C. Chemical shift values (δ) are reported in ppm relative to tetramethylsilane. The following abbreviations were used for signal multiplicities: s = singlet; d = doublet; m = multiplet. Optical rotations were measured on a JASCO P-1020 polarimeter at the sodium D-line under ambient temperature, and reported as $[\alpha]_D$ (concentration in grams/100 mL solvent). Enantioseparation of **2** and **4** was performed by using a uf-3020SZB2 pump (Denso Sangyo, Japan) equipped with a Shimamura (Japan) YRU-880 midiget UV-RI detector, using a Daicel CHIRALFLASH[®] IC column (3.0 cm ϕ \times 10 cm). Enantioseparation of **2a** was conducted on two JASCO PU-2086 intelligent pumps equipped with a JASCO MX-2080-31 solvent mixing module on a PU-2075 intelligent UV/Vis detector, using a Daicel CHIRALPAK[®] IB column (1.0 cm ϕ \times 25 cm). Spectroscopic grade CHCl₃ and CDCl₃ were purchased from Wako Pure Chemical Industries and Cambridge Isotope Laboratories, respectively. Purchased chemicals were used without further purification. Synthesis of (*S*)-**1** and (*R*)-**1** is reported previously.^[1]

Synthesis of (*S*)-**2** and (*R*)-**2**



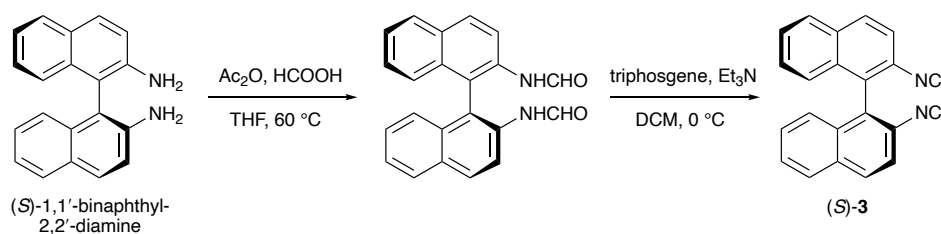
Conversion from (±)-2,2'-dibromo-1,1'-binaphthyl to (±)-**2** was carried out in a similar manner to a reported procedure.^[2] (±)-2,2'-dibromo-1,1'-binaphthyl (206 mg, 499 μ mol) in THF (10 mL) was added *n*-butyllithium in hexane (2.5 M, 0.48 mL) dropwise under N₂ at -78 °C. After 30 mins, N₂ was replaced with CO₂, and the mixture was stirred at -78 °C for 1.5 h and then gradually brought to rt overnight. The reaction was quenched with 2 M HCl aq and then extracted using Et₂O. The organic layer was washed with brine, and then dried over MgSO₄. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc-AcOH = 95:5:1 to 80:20:1), which afforded (±)-1,1'-binaphthyl-2,2'-dicarboxylic acid^[3] (105 mg, 61%).

The diacid (105 mg) was added SOCl₂ (2 mL) and the mixture was refluxed. After 15 mins, the mixture was dried under reduced pressure. The residue was dissolved in THF (1 mL) and then bubbled with NH₃

gas at 0 °C for 10 mins. After removal of the solvent, the residue was dissolved in DCM (1 mL) and added Tf₂O (0.25 mL) and Et₃N (0.5 mL) and the mixture was stirred at 0 °C. After 40 mins, the mixture was diluted with EtOAc, washed sequentially with 2 M HCl aq and brine, and then dried over MgSO₄. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 8:1 to 1:1), which afforded (±)-**2**^[3] (34 mg, 37% from diacid).

Enantioseparation of (±)-**2** was carried out on a CHIRALFLASH[®] IC column (3.0 cm ϕ × 10 cm) using hexane-EtOAc = 4:1, which led to the first-eluted (*R*)-(-)-**2** and the second-eluted (*S*)-(+)-**2**. (*R*)-(-)-**2**: [α]_D -43.8 (c 1.0, CHCl₃); lit^[4] [α]_D -70.5 (c 1, CHCl₃). (*S*)-(+)-**2**: [α]_D +44.3 (c 1.0, CHCl₃); lit^[4] [α]_D +68.6 (c 1.54, CHCl₃).

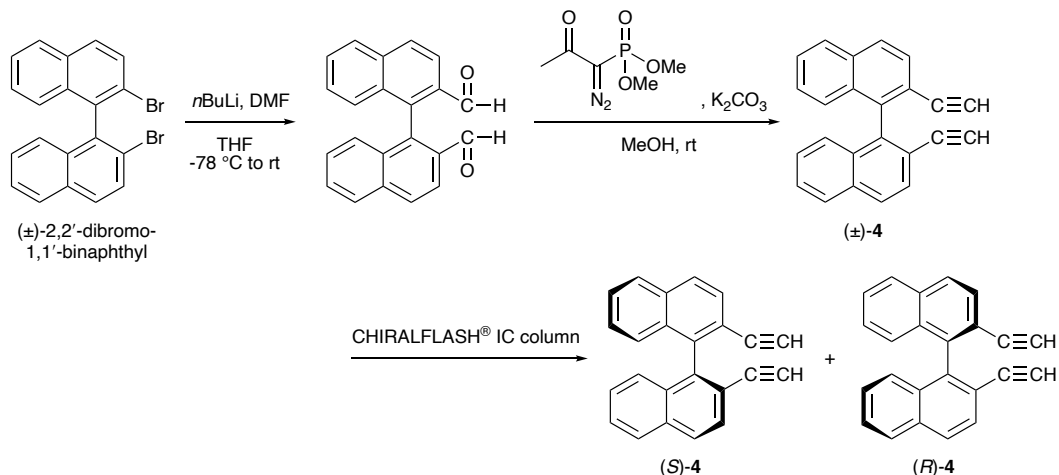
Synthesis of (*S*)-**3** and (*R*)-**3**



(*S*)-**3** was synthesized in a similar manner to a reported procedure.^[5] Formic acid (500 μ L) was added to Ac₂O (60 μ L) at 0 °C and the solution was stirred at 60 °C for 30 mins. To this solution, THF (0.5 mL) and (*S*)-1,1'-binaphthyl-2,2'-diamine (32 mg, 113 μ mol) in THF (0.5 mL) were successively added at 0 °C and the mixture was stirred at 60 °C. After 3 h, the mixture was diluted with EtOAc, washed sequentially with sat NaHCO₃ aq and brine, and then dried over MgSO₄. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 1:3 to 1:19), which afforded (*S*)-1,1'-binaphthyl-2,2'-diformamide containing some impurities (23 mg). Without further purification, the diformamide (23 mg) and Et₃N (150 μ L) in DCM (0.7 mL) was added a 0.3 mL DCM solution of triphosgene (33 mg) dropwise at 0 °C and stirred at rt. After 1.5 h, the solvent was removed and the residue was purified by silica-gel column chromatography (hexane-EtOAc = 3:1 to 1:3), which afforded (*S*)-**3**^[5] (10 mg, 29% from diamine).

(*R*)-**3**^[6] was prepared from (*R*)-1,1'-binaphthyl-2,2'-diamine using a similar procedure.

Synthesis of (*S*)-**4** and (*R*)-**4**

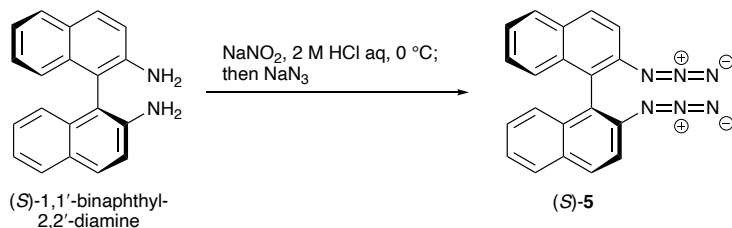


Conversion from (±)-2,2'-dibromo-1,1'-binaphthyl to (±)-**4** was carried out in a similar manner to a reported procedure.^[7] (±)-2,2'-dibromo-1,1'-binaphthyl (418 mg, 1.01 mmol) in THF (10 mL) was added *n*-butyllithium in hexane (2.5 M, 0.96 mL) dropwise under N₂ at -78 °C. After 30 mins, the mixture was added DMF (2.3 mL), stirred at -78 °C for 40 mins, and then gradually brought to rt overnight. The reaction mixture was diluted with Et₂O and the organic layer was washed with sat NH₄Cl aq. The aqueous layer was extracted with Et₂O. All organic layers were combined and dried over MgSO₄. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 10:1 to 4:1), which afforded (±)-2,2'-diformyl-1,1'-binaphthyl^[7] (85 mg, 27%).

The dialdehyde (85 mg, 274 μmol) and K₂CO₃ (85 mg) in MeOH (10 mL) was added Bestmann-Ohira reagent (165 μL) and stirred at rt for overnight. The reaction mixture was diluted with Et₂O and the organic layer was washed with sat NH₄Cl aq. The aqueous layer was extracted with Et₂O. All organic layers were combined and dried over MgSO₄. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 25:1 to 20:1), which afforded (±)-**4**^[7] (27 mg, 33%).

Enantioseparation of (±)-**4** was carried out on a CHIRALFLASH® IC column (3.0 cm ϕ × 10 cm) using hexane-EtOAc = 50:1, which led to the first-eluted (-)-**4** and the second-eluted (+)-**4**. The absolute configurations of these enantiomers were determined to be (*S*)-(-)-**4** and (*R*)-(+)-**4** by using VCD spectroscopy (Fig. S3a). (*S*)-(-)-**4**: [α]_D -28.4 (c 1.0, CHCl₃). (*R*)-(+)-**4**: [α]_D +27.2 (c 1.0, CHCl₃).

Synthesis of (*S*)-**5** and (*R*)-**5**

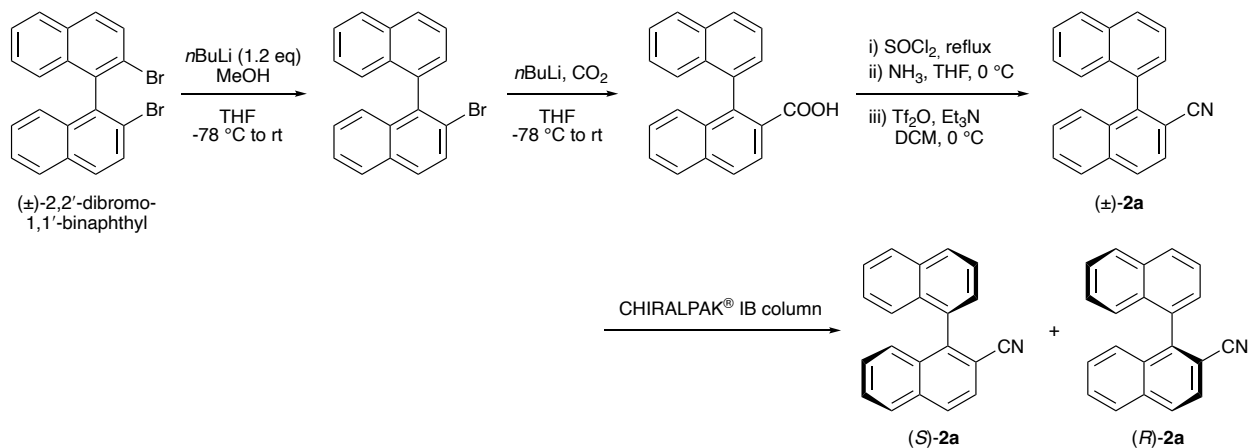


(*S*)-**5** was synthesized in a similar manner to a reported procedure.^[8] (*S*)-1,1'-binaphthyl-2,2'-diamine (142 mg, 499 μmol) in 2 M HCl aq (3.5 mL) was added NaNO₂ (105 mg) in H₂O (1 mL) and stirred at 0 °C.

After 1 h, the mixture was added NaN₃ (135 mg) in H₂O (1 mL) dropwise at 0 °C and stirred at rt for overnight. The mixture was diluted with EtOAc, washed sequentially with sat NaHCO₃ aq and brine, and then dried over MgSO₄. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 99:1), which afforded (*S*)-**5** (146 mg, 87%). Its NMR data were virtually identical with those reported for (±)-**5**.^[8] (*S*)-(-)-**5**: [α]_D -42.1 (c 1.0, CHCl₃).

(*R*)-**5**^[9] was prepared from (*R*)-1,1'-binaphthyl-2,2'-diamine using a similar procedure.

Synthesis of (*S*)-**2a** and (*R*)-**2a**

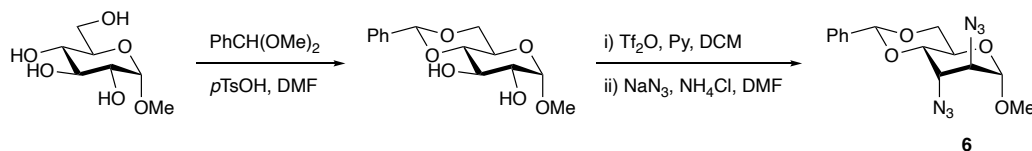


Conversion from (±)-2,2'-dibromo-1,1'-binaphthyl to (±)-1,1'-binaphthyl-2-carboxylic acid was carried out in a similar manner to a reported procedure.^[10] (±)-2,2'-dibromo-1,1'-binaphthyl (412 mg, 1.00 mmol) in THF (10 mL) was added *n*-butyllithium in hexane (2.6 M, 0.46 mL) dropwise under N₂ at -78 °C. After 1 h, the mixture was added MeOH (1 mL) and stirred for 10 mins at -78 °C. The mixture was diluted with CHCl₃, washed with brine, and then dried over MgSO₄. After removal of the solvent, the residue was dissolved in THF (10 mL) and added *n*-butyllithium in hexane (2.6 M, 0.58 mL) dropwise under N₂ at -78 °C. After 15 mins, N₂ was replaced with CO₂, and the mixture was gradually brought to rt over 1 h. The reaction mixture was diluted with CHCl₃, washed with 2 M HCl aq, and then dried over MgSO₄. After removal of the solvent, the mixture was purified by silica-gel column chromatography (CHCl₃-MeOH = 15:1), which afforded (±)-1,1'-binaphthyl-2-carboxylic acid^[10] (165 mg, 55% in 2 steps).

The following conversion from monoacid to (±)-**2a** was performed in a similar manner to the synthesis of (±)-**2**. The monoacid (160 mg) was added SOCl₂ (3 mL), and the mixture was refluxed. After 10 mins, the mixture was dried under reduced pressure. The residue was dissolved in THF (2 mL) and then bubbled with NH₃ gas at 0 °C for 10 mins. After removal of the solvent, the residue was dissolved in DCM (2 mL) and added Tf₂O (0.8 mL) and Et₃N (1 mL) and the mixture was stirred at 0 °C. After 40 mins, the mixture was diluted with EtOAc, washed sequentially with 2 M HCl aq, sat NaHCO₃ aq and brine, and then dried over MgSO₄. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 15:1), which afforded (±)-**2a**^[11] (80 mg, 54% from monoacid).

Enantioseparation of (\pm)-**2a** was carried out on a CHIRALPAK[®] IB column (1.0 cm ϕ \times 25 cm) using hexane-EtOH = 95:5, which led to the first-eluted (–)-**2** at $t_1 = 10.7$ min and the second-eluted (*S*)-(+)-**2** at $t_2 = 11.4$ min. The separation factor α was calculated as 1.1, where $t_0 = 4.0$ min was used. The absolute configurations of these enantiomers were determined to be (*S*)-(–)-**2a** and (*R*)-(+)-**2a** by using VCD spectroscopy (Fig. S3b). (*S*)-(–)-**2a**: $[\alpha]_D -112$ (*c* 1.0, CHCl₃). (*R*)-(+)-**2a**: $[\alpha]_D +106$ (*c* 1.0, CHCl₃); ; lit^[12] for (+)-**2a**: $[\alpha]_D +89.0$ (*c* 1.0, CHCl₃).

Synthesis of **6**

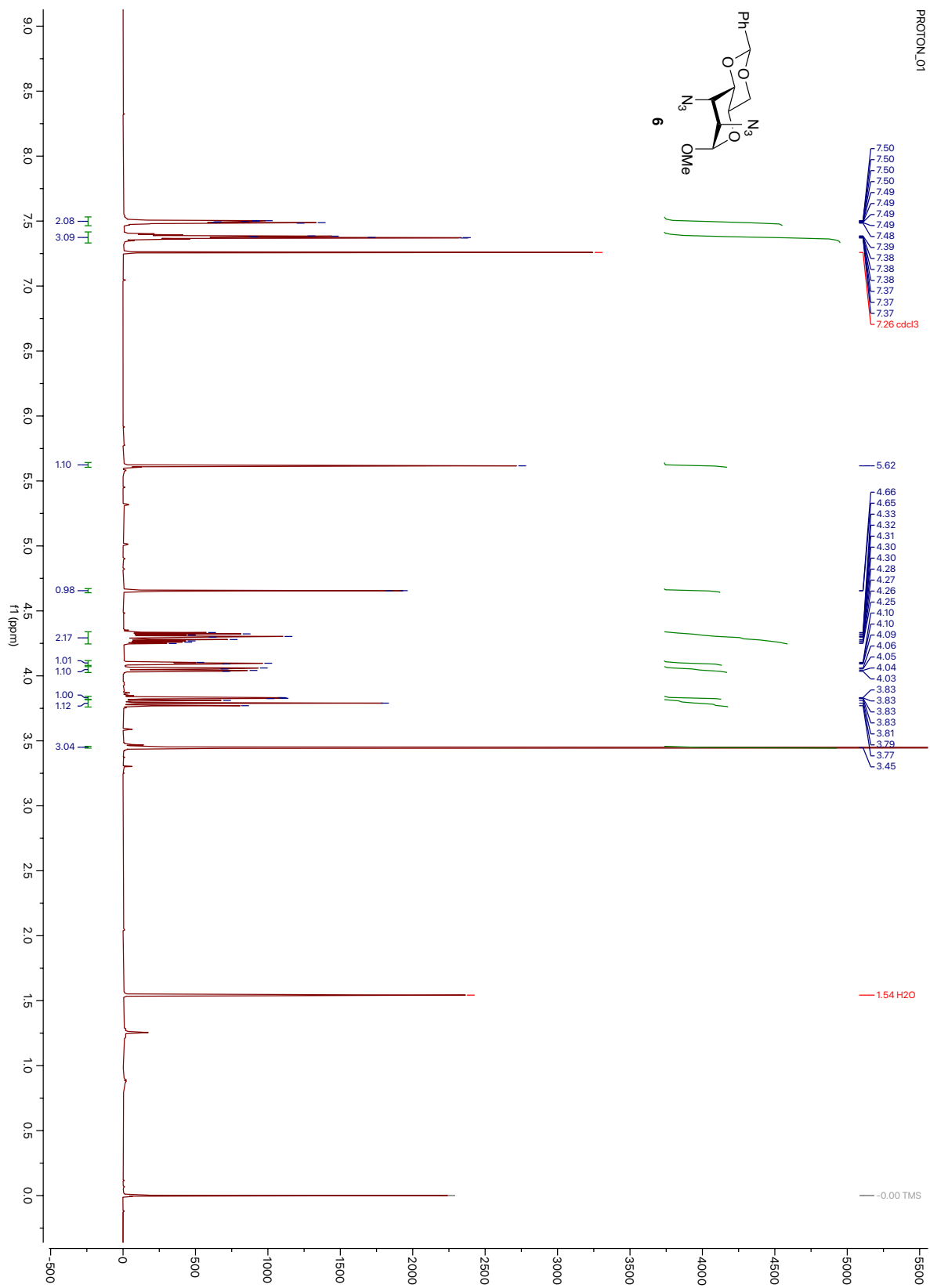


Methyl α -D-glucopyranoside (1.95 g, 10.0 mmol) in DMF (35 mL) was added benzaldehyde dimethoxy acetal (2 mL) and a catalytic amount of *p*-TsOH \cdot H₂O and stirred at rt overnight. The mixture was diluted with CHCl₃, washed sequentially with sat NaHCO₃ aq and brine, and dried over MgSO₄. After removal of the solvent, the mixture was purified by recrystallization with EtOH and hexane, which afforded methyl 4,6-*O*-benzylidene- α -D-glucopyranoside (2.14g, 76%). Its ¹H NMR spectrum was virtually identical with a reported one.^[13]

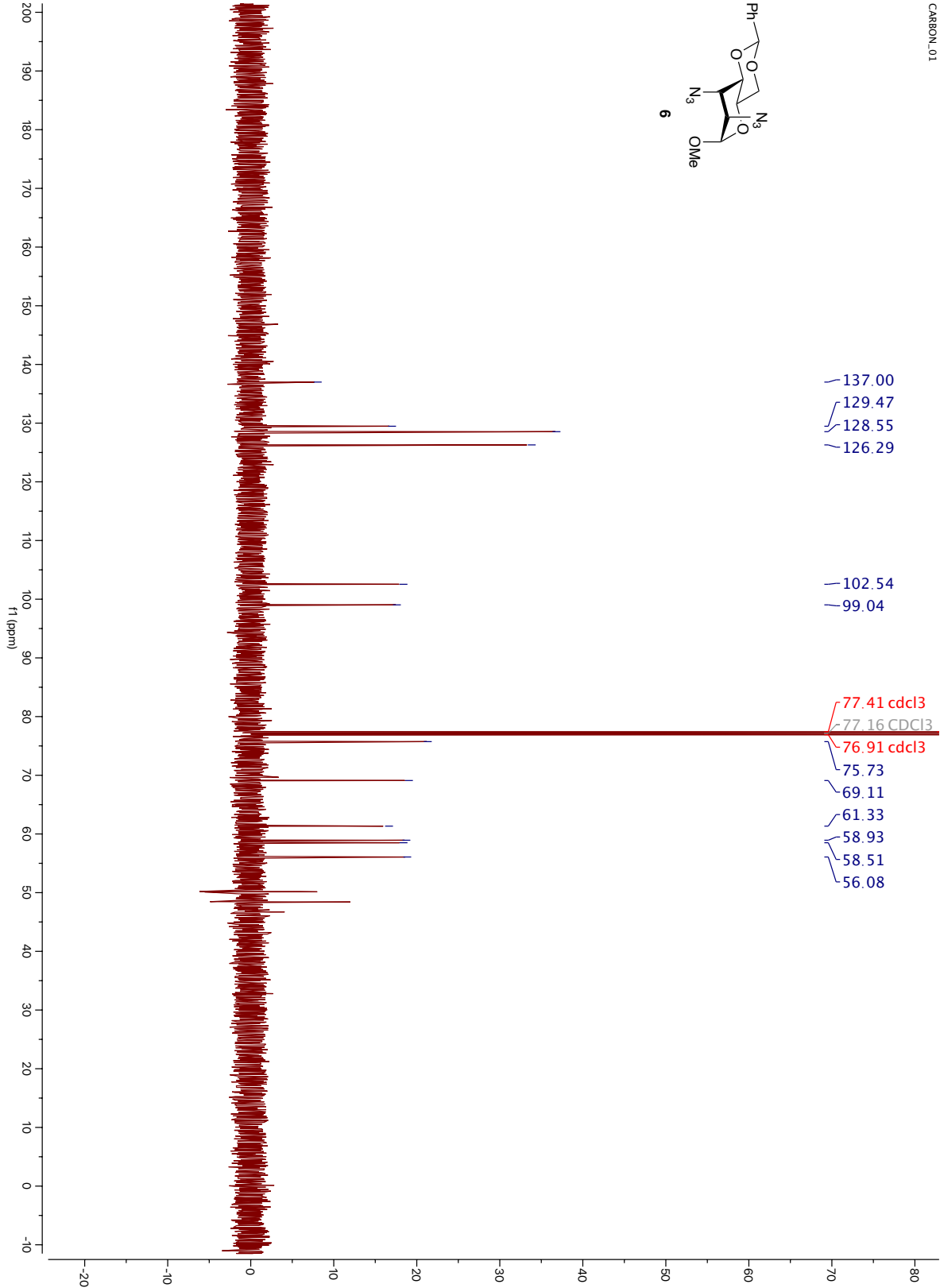
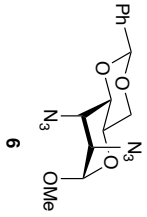
The 4,6-protected sugar (148 mg, 524 μ mol) in DCM (3 mL) was added pyridine (900 μ L) and trifluoromethanesulfonic anhydride (220 μ L) and stirred at rt. After 30 mins, the mixture was diluted with DCM, washed sequentially with water and brine, and then dried over MgSO₄. After removal of the solvent, the residue was dissolved in DMF (10 mL), added NaN₃ (374 mg) and NH₄Cl (18 mg) and stirred overnight at 80°C. The mixture was brought to rt, diluted with EtOAc, washed sequentially with water and brine, and then dried over MgSO₄. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 10:1 to 5:1), which afforded methyl 2,3-diazido-2,3-deoxy-4,6-*O*-benzylidene- α -D-glucopyranoside **6**^[14] (78 mg, 45% in 2 steps). ¹H NMR (CDCl₃) δ 7.51–7.47 (m, ArH, 2H), 7.41–7.34 (m, ArH, 3H), 5.62 (s, CHPh, 1H), 4.66 (d, H-1, *J* = 0.8 Hz, 1H), 4.34–4.25 (m, H-6a, H-5, 2H), 4.10 (dd, H-3, *J* = 3.0, 3.0 Hz, 1H), 4.05 (dd, H-4, *J* = 9.3, 3.5 Hz, 1H), 3.83 (dd, H-2, *J* = 2.6, 1.0 Hz, 1H), 3.79 (dd, H-6b, *J* = 10.1, 10.1 Hz, 1H), 3.45 (s, OMe, 3H); ¹³C NMR (CDCl₃) δ 137.0 (Ar), 129.5 (Ar), 128.6 (Ar), 126.3 (Ar), 102.5 (CHPh), 99.04 (C-1), 75.7 (C-4), 69.1 (C-6), 61.3 (C-2), 58.9 (C-5), 58.5 (C-3), 56.1 (OMe). $[\alpha]_D +20.8$ (*c* 1.0, CHCl₃).

References

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CARBON_01



Optimized Cartesian Coordinates

(S)-1 optimized at B3PW91/6-311++G(d,p)

1	H	3.056315	-1.811085	-1.809211
2	C	3.23911	-1.040381	-1.067836
3	C	3.647711	0.964473	0.874535
4	C	2.18821	-0.554295	-0.290983
5	C	4.502108	-0.503553	-0.868653
6	C	4.699983	0.492165	0.095888
7	C	2.37867	0.43011	0.675403
8	H	5.34191	-0.849747	-1.461827
9	H	5.694585	0.903688	0.237235
10	H	3.819538	1.735929	1.618788
11	C	0.775288	-0.96728	-0.314594
12	C	1.097099	0.745556	1.401669
13	H	1.146286	0.385347	2.435398
14	H	0.911197	1.822759	1.434209
15	C	-0.000004	-0.000085	0.620273
16	O	0.280272	-1.889203	-0.918533
17	C	-0.775253	0.967238	-0.314506
18	C	-1.097138	-0.745812	1.401538
19	H	-0.911278	-1.823029	1.433878
20	H	-1.14631	-0.385794	2.435334
21	C	-2.188194	0.554316	-0.290939
22	C	-4.700021	-0.492055	0.095824
23	C	-3.239074	1.040553	-1.067725
24	C	-2.378699	-0.430198	0.675327
25	C	-3.647768	-0.964516	0.874404
26	C	-4.502099	0.503769	-0.868598
27	H	-3.056242	1.811338	-1.809006
28	H	-3.819631	-1.736052	1.618565
29	H	-5.341887	0.850081	-1.461723
30	H	-5.694643	-0.90354	0.23713
31	O	-0.280199	1.889213	-0.918333

(S)-2•2CHCl₃ optimized at B3PW91/6-311++G(d,p)

1	H	0.743185	-0.082225	-3.601528
2	C	0.985076	0.615841	-2.808884
3	H	2.702848	1.411088	-3.78245
4	C	2.067292	1.44464	-2.903484
5	C	0.434867	1.528301	-0.605104
6	C	2.382031	2.353045	-1.86344
7	C	0.162792	0.659034	-1.653263
8	C	1.556577	2.399805	-0.697663
9	C	3.499451	3.217329	-1.9496
10	H	1.266062	3.355155	1.223065
11	C	3.791199	4.091212	-0.933008
12	H	4.125332	3.173842	-2.835421
13	H	4.65201	4.746992	-1.009697
14	C	2.976312	4.139421	0.217996
15	H	3.216903	4.83263	1.01698
16	C	1.88642	3.314413	0.334832
17	C	-0.162961	0.658372	1.652912
18	C	-0.435298	1.527944	0.605073
19	C	-2.067714	1.442924	2.90341
20	C	-1.55728	2.399064	0.697948
21	C	-0.985241	0.614497	2.808511
22	C	-2.382729	2.351615	1.863701
23	C	-1.887401	3.31395	-0.334212
24	H	-0.743138	-0.083788	3.600898
25	H	-4.126295	3.171507	2.835969
26	H	-2.703267	1.408847	3.782359
27	C	-2.977552	4.138574	-0.217081
28	H	-1.267049	3.355213	-1.222426
29	H	-3.218354	4.832002	-1.015811
30	C	-3.792433	4.089686	0.933899
31	H	-4.65345	4.745167	1.010823

32	C	-3.50042	3.215517	1.95017
33	C	0.96486	-0.213971	1.581117
34	C	-0.964759	-0.213683	-1.581781
35	N	-1.876001	-0.922825	-1.545631
36	N	1.876309	-0.922834	1.544739
37	H	3.745567	-1.983495	0.930791
38	H	-3.744991	-1.983752	-0.931355
39	C	4.662501	-2.435124	0.562457
40	C	-4.661792	-2.435415	-0.562732
41	Cl	5.841738	-1.129971	0.297551
42	Cl	4.285661	-3.270683	-0.960323
43	Cl	5.241645	-3.577752	1.792107
44	Cl	-4.284396	-3.271124	0.959828
45	Cl	-5.241385	-3.577922	-1.792282
46	Cl	-5.840929	-1.130284	-0.297269

(S)-**3** optimized at B3PW91/6-311++G(d,p)

1	H	-2.455887	2.013152	-2.737559
2	C	-2.271808	1.31614	-1.928835
3	H	-4.238795	0.504311	-1.912451
4	C	-3.249227	0.480235	-1.467331
5	C	-0.680588	0.421756	-0.300049
6	C	-2.99413	-0.42328	-0.406999
7	C	-0.984555	1.282117	-1.34086
8	C	-1.694857	-0.454611	0.185451
9	C	-3.996596	-1.29473	0.081719
10	H	-0.472949	-1.394509	1.703314
11	C	-3.732928	-2.163409	1.110666
12	H	-4.982165	-1.261866	-0.372546
13	H	-4.510014	-2.825374	1.477954
14	C	-2.450183	-2.196303	1.696374
15	H	-2.249562	-2.884462	2.510818
16	C	-1.455748	-1.363861	1.246595
17	C	0.984555	1.282107	1.34087
18	C	0.680591	0.421754	0.30005

19	C	3.249228	0.480228	1.467334
20	C	1.694861	-0.454606	-0.185456
21	C	2.271808	1.316127	1.928845
22	C	2.994134	-0.423278	0.406995
23	C	1.455754	-1.363848	-1.246609
24	H	2.455887	2.013131	2.737575
25	H	4.982171	-1.26186	0.372534
26	H	4.238796	0.504302	1.912455
27	C	2.45019	-2.196283	-1.696395
28	H	0.472955	-1.394492	-1.703328
29	H	2.249573	-2.884435	-2.510845
30	C	3.732936	-2.163392	-1.110686
31	H	4.510022	-2.825352	-1.477981
32	C	3.996603	-1.294722	-0.081732
33	N	-0.021469	2.138518	-1.836528
34	C	0.777508	2.875829	-2.282543
35	N	0.021466	2.138501	1.836545
36	C	-0.77755	2.875752	2.282587

(S)-4 optimized at B3PW91/6-311++G(d,p)

1	C	3.751591	-2.173134	-1.047506
2	C	3.990231	-1.320274	0.001142
3	C	2.978418	-0.451714	0.475706
4	C	1.695163	-0.467763	-0.150899
5	C	1.482495	-1.361302	-1.231855
6	C	2.484672	-2.191921	-1.667902
7	H	4.182318	0.445791	2.03169
8	H	4.535626	-2.83412	-1.402377
9	H	4.963024	-1.299446	0.483546
10	C	3.205378	0.433763	1.55786
11	C	0.671649	0.404279	0.322635
12	H	0.512154	-1.379511	-1.715082
13	H	2.302704	-2.867949	-2.497012
14	C	0.930926	1.25545	1.390622
15	C	2.214847	1.262065	2.003814
16	H	2.387866	1.939635	2.832199
17	C	-0.671654	0.404272	-0.322642

18	C	-1.695172	-0.467753	0.150916
19	C	-0.930927	1.255412	-1.390655
20	C	-1.482508	-1.361262	1.231897
21	C	-2.978426	-0.451718	-0.475691
22	C	-2.214847	1.262015	-2.003848
23	C	-2.484689	-2.191865	1.667967
24	H	-0.512168	-1.379461	1.715126
25	C	-3.990243	-1.32026	-0.001104
26	C	-3.205381	0.433729	-1.557871
27	H	-2.387862	1.939562	-2.832252
28	C	-3.751607	-2.173092	1.047568
29	H	-2.302725	-2.86787	2.497096
30	H	-4.963036	-1.299442	-0.48351
31	H	-4.182322	0.445748	-2.031703
32	H	-4.535645	-2.834065	1.402457
33	C	0.071188	2.133123	-1.895397
34	C	-0.071186	2.133177	1.895341
35	C	0.895113	2.885537	-2.352399
36	H	1.631808	3.546048	-2.74333
37	C	-0.89509	2.885617	2.352339
38	H	-1.63137	3.546797	2.74292

(S)-**5** (the most stable conformer) optimized at B3PW91/6-311++G(d,p)

1	C	1.120316	0.976708	1.211665
2	C	0.708671	0.094952	0.226666
3	C	3.382269	0.144423	1.116809
4	C	1.658588	-0.800971	-0.343645
5	C	2.464279	1.001424	1.657762
6	C	3.013525	-0.776929	0.107559
7	C	1.304097	-1.726425	-1.35824
8	H	2.763395	1.703016	2.430177
9	H	4.978771	-1.641205	-0.112231
10	H	4.411869	0.165848	1.46078
11	C	2.237946	-2.579915	-1.891669
12	H	0.278642	-1.752538	-1.709402
13	H	1.945899	-3.280492	-2.667325
14	C	3.575265	-2.554898	-1.442658

15	H	4.302658	-3.234654	-1.873872
16	C	3.951458	-1.669969	-0.463403
17	C	-1.120179	0.976669	-1.211774
18	C	-0.708705	0.095027	-0.226609
19	C	-3.382232	0.144738	-1.116931
20	C	-1.658796	-0.800647	0.343836
21	C	-2.464103	1.001535	-1.657969
22	C	-3.01369	-0.776479	-0.107466
23	C	-1.304505	-1.725965	1.358609
24	H	-2.763078	1.703034	-2.430521
25	H	-4.979093	-1.640386	0.112362
26	H	-4.411806	0.166229	-1.460977
27	C	-2.238522	-2.579227	1.892123
28	H	-0.279077	-1.752173	1.709846
29	H	-1.946626	-3.279717	2.667914
30	C	-3.575805	-2.554081	1.443028
31	H	-4.303332	-3.233645	1.874319
32	C	-3.951802	-1.669262	0.463591
33	N	0.137518	1.840016	1.740882
34	N	0.452245	2.643231	2.611955
35	N	0.601353	3.42842	3.415039
36	N	-0.137172	1.839875	-1.74084
37	N	-0.451534	2.642638	-2.612482
38	N	-0.600507	3.427595	-3.415805

(*R*)-**2a**•CHCl₃ optimized at B3PW91/6-311++G(d,p)

1	H	-0.102918	1.838565	3.509255
2	C	0.265621	1.812676	2.489345
3	H	-0.305248	3.826185	2.055794
4	C	0.153428	2.915322	1.683045
5	C	1.332928	0.558985	0.705397
6	C	0.624984	2.885678	0.348132
7	C	1.226295	1.692031	-0.156962
8	C	0.510421	4.011829	-0.504117
9	H	2.133086	0.774678	-1.895549
10	C	0.964959	3.966781	-1.797578
11	H	0.050121	4.914622	-0.113844

12	H	0.868417	4.835587	-2.440312
13	C	1.554655	2.786878	-2.298586
14	H	1.906892	2.756478	-3.324491
15	C	1.682075	1.678053	-1.499312
16	C	1.13531	-1.751927	-0.21914
17	C	1.942864	-0.711192	0.220557
18	C	3.040694	-3.155504	-0.686343
19	C	3.357337	-0.891119	0.214394
20	C	1.686159	-2.980107	-0.673595
21	C	3.909464	-2.126171	-0.246212
22	C	4.241188	0.123897	0.661972
23	H	1.01752	-3.764925	-1.007747
24	H	5.727792	-3.235208	-0.597438
25	H	3.466311	-4.091409	-1.034087
26	C	5.599467	-0.071744	0.648503
27	H	3.826612	1.059964	1.017977
28	H	6.261892	0.714822	0.994244
29	C	6.142723	-1.290295	0.189279
30	H	7.2185	-1.431652	0.184341
31	C	5.314942	-2.294328	-0.246646
32	C	-0.285039	-1.6047	-0.231459
33	N	-1.437456	-1.527226	-0.257667
34	H	-3.584155	-0.985488	-0.136351
35	C	-4.632656	-0.709299	-0.062533
36	Cl	-4.843826	0.858993	-0.870914
37	Cl	-5.046727	-0.598247	1.66315
38	Cl	-5.586595	-1.97549	-0.866271
39	C	0.85719	0.631713	1.996349
40	H	0.938846	-0.235727	2.643547

6 (the most stable conformer) optimized at B3PW91/6-311++G(d,p)

1	O	2.091929	-1.524906	0.424825
2	C	0.373087	-0.130032	-0.501439
3	C	2.721907	0.678207	-0.496892
4	C	1.247051	1.117718	-0.473777
5	C	3.046496	-0.488966	0.466762
6	C	0.7585	-1.070951	0.631142

7	H	0.559505	-0.647659	-1.456419
8	H	0.673657	-0.542915	1.587596
9	H	3.977255	-0.978686	0.144433
10	H	1.060945	1.716398	-1.372615
11	H	3.346542	1.529976	-0.209853
12	O	3.205436	0.056433	1.73727
13	C	3.741178	-0.851034	2.687709
14	H	3.070835	-1.699173	2.856979
15	H	3.86392	-0.292636	3.615401
16	H	4.719198	-1.228038	2.359584
17	N	2.989185	0.28094	-1.892114
18	N	4.16648	0.146599	-2.206053
19	N	5.210524	-0.002431	-2.619823
20	N	1.026959	1.92552	0.731634
21	N	0.091322	2.718589	0.696726
22	N	-0.716233	3.50418	0.800669
23	O	-0.990168	0.229994	-0.401908
24	C	-0.18787	-2.258439	0.609974
25	H	-0.018619	-2.851964	-0.301397
26	H	-0.051785	-2.905403	1.477731
27	O	-1.524464	-1.778549	0.654852
28	C	-1.820369	-0.922074	-0.423116
29	C	-3.254839	-0.490577	-0.33372
30	C	-5.920341	0.310166	-0.173882
31	C	-4.133079	-0.765191	-1.377986
32	C	-3.714886	0.187899	0.794915
33	C	-5.043059	0.586663	0.872924
34	C	-5.464718	-0.366328	-1.29988
35	H	-3.776741	-1.293737	-2.257537
36	H	-3.028846	0.400552	1.606751
37	H	-5.396668	1.115997	1.751719
38	H	-6.14368	-0.583955	-2.117818
39	H	-6.957534	0.623259	-0.110546
40	H	-1.631871	-1.461953	-1.367987