Supporting Information

Synthesis, Chiral Resolution, and Absolute Configuration of Dissymmetric 4,15-Difunctionalized [2.2]Paracyclophanes

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1. NMR spectra of new compounds

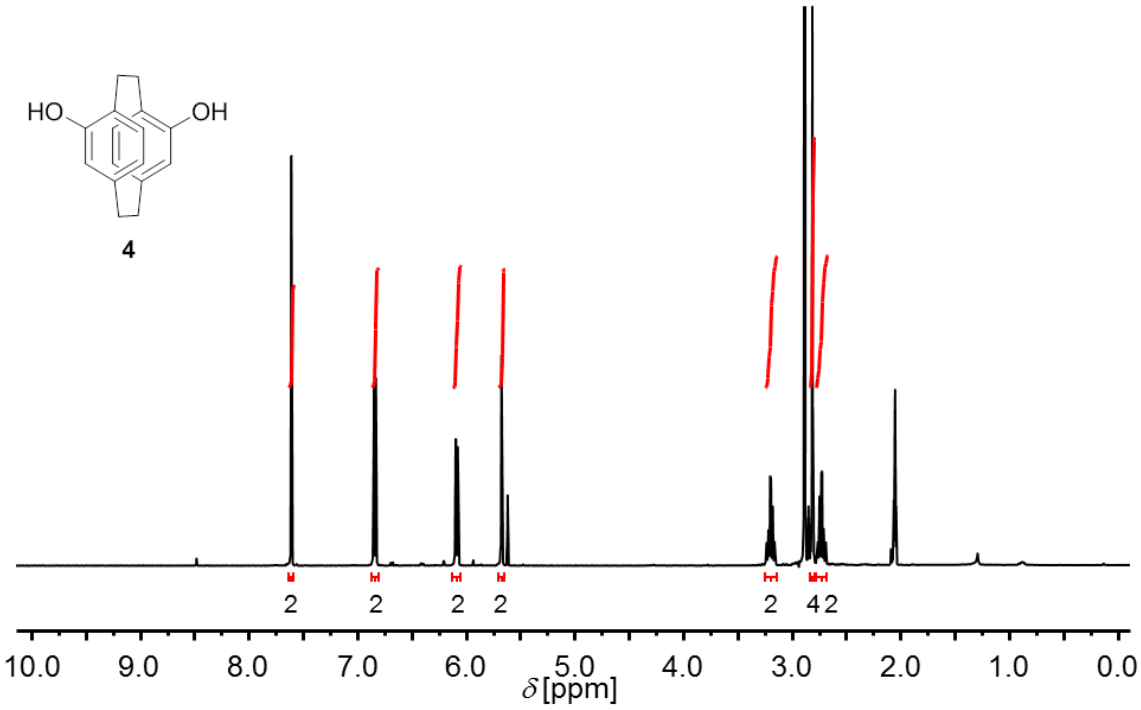

Figure S1: ^{1}H NMR spectrum of **4** (500.1 MHz, acetone-d_6, 298 K)

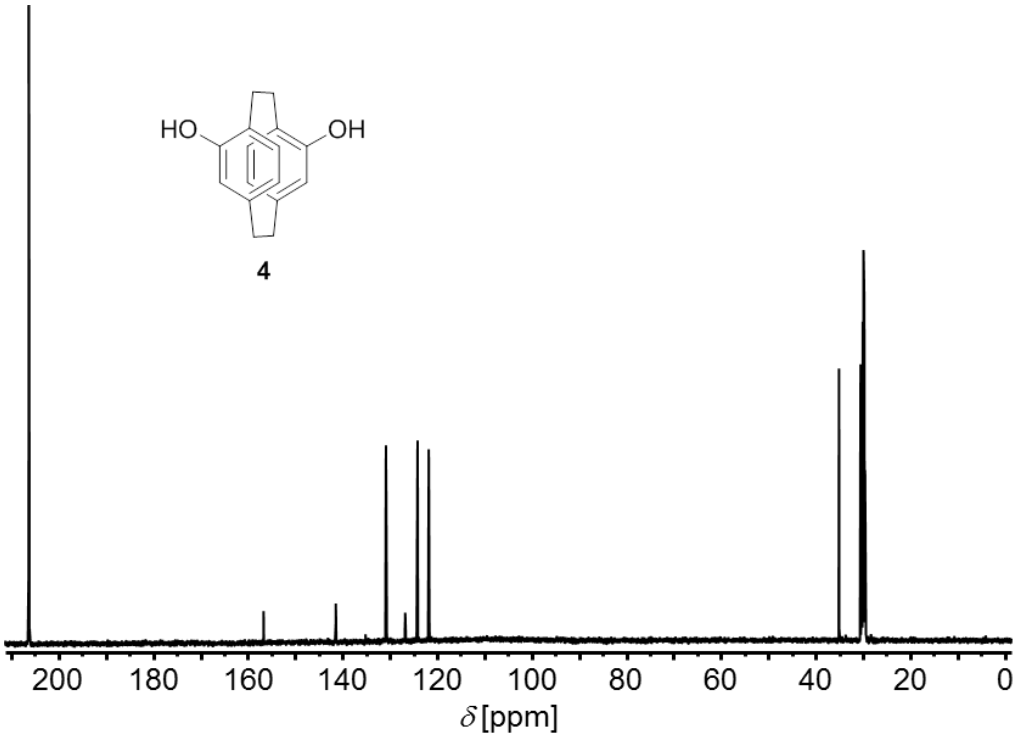

Figure S2: ^{13}C {^{1}H} NMR spectrum of **4** (125.8 MHz, acetone-d_6, 298 K)

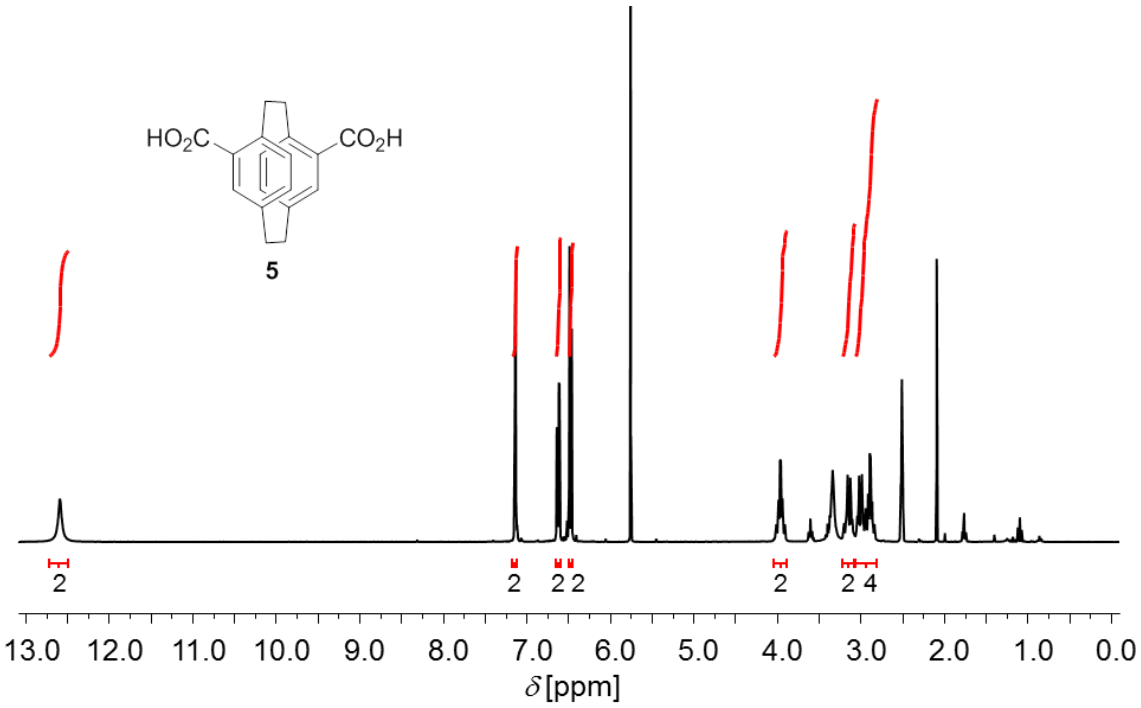

Figure S3: ^{1}H NMR spectrum of **5** (400.1 MHz, DMSO-d_6, 293 K)

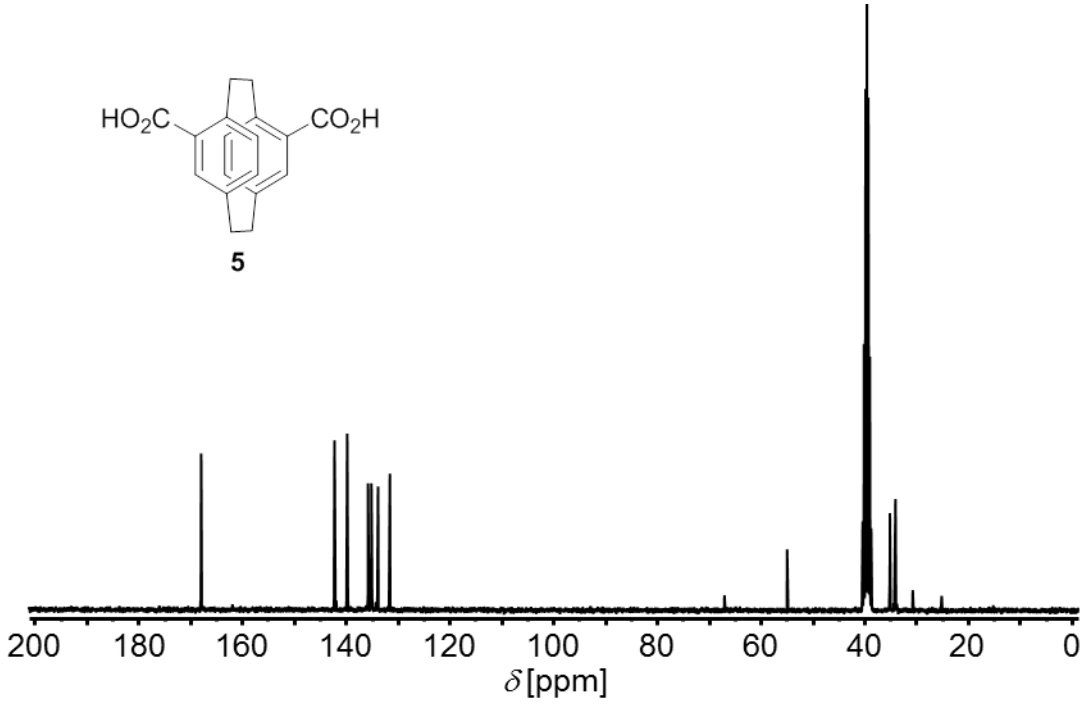

Figure S4: ^{13}C {^{1}H} NMR spectrum of **5** (100.6 MHz, DMSO-d_6, 293 K)

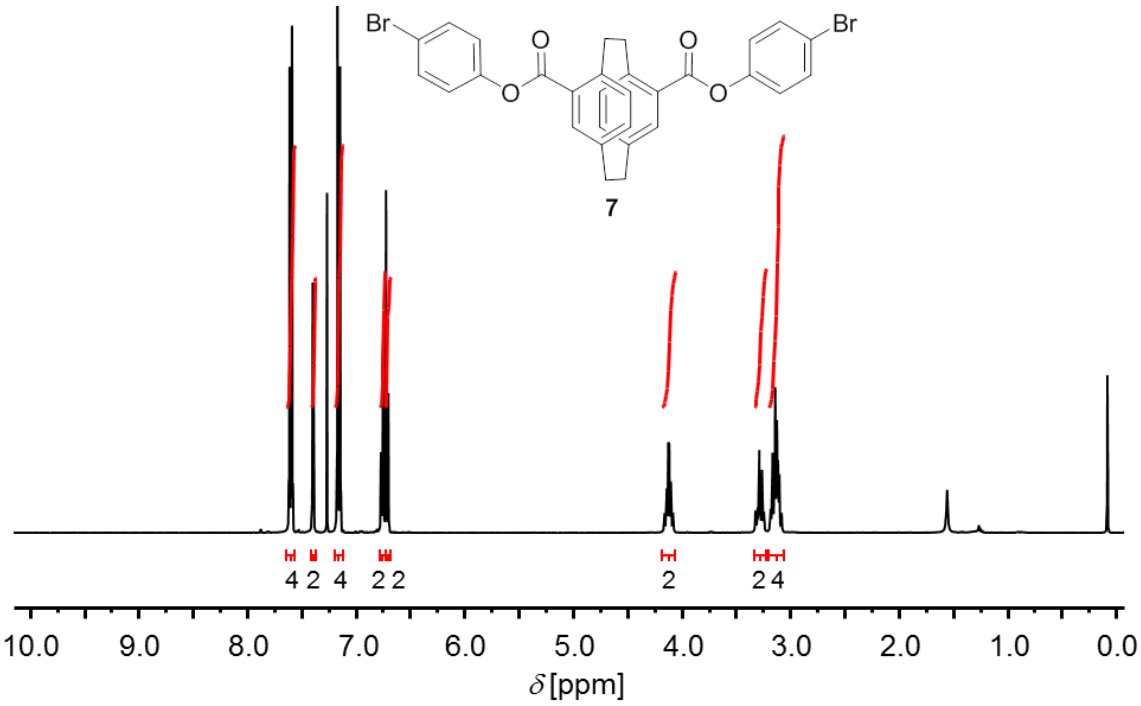

Figure S5: ^{1}H NMR spectrum of **7** (400.1 MHz, $CDCl_3$, 293 K)

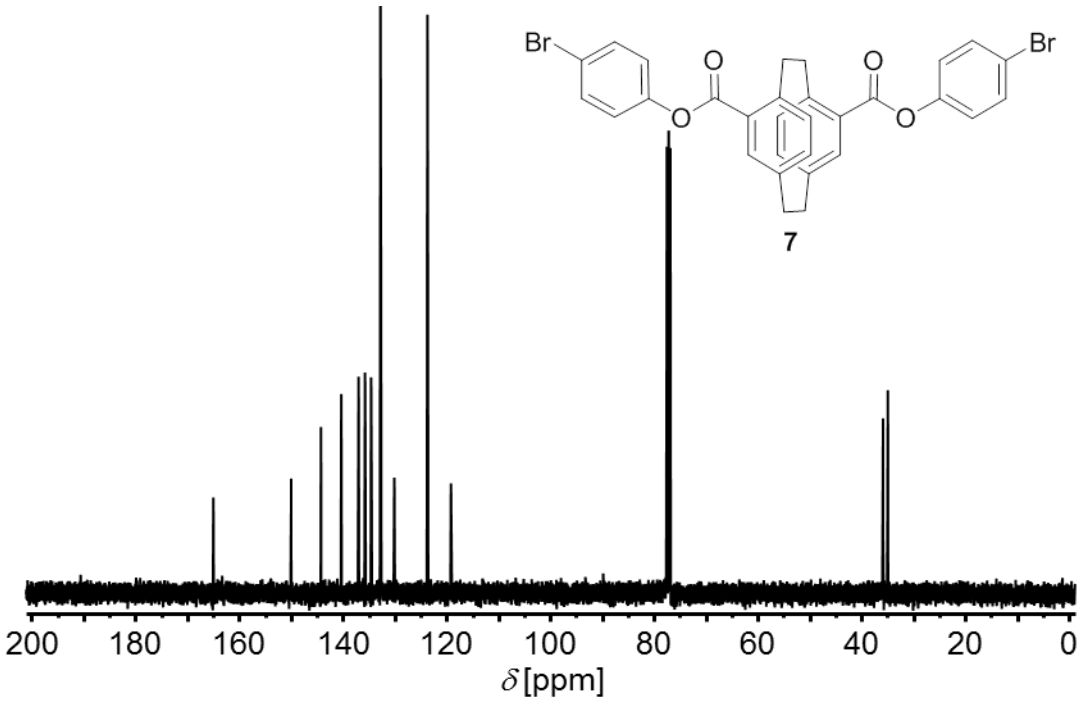

Figure S6: ^{13}C {^{1}H} NMR spectrum of **7** (100.6 MHz, $CDCl_3$, 293 K)

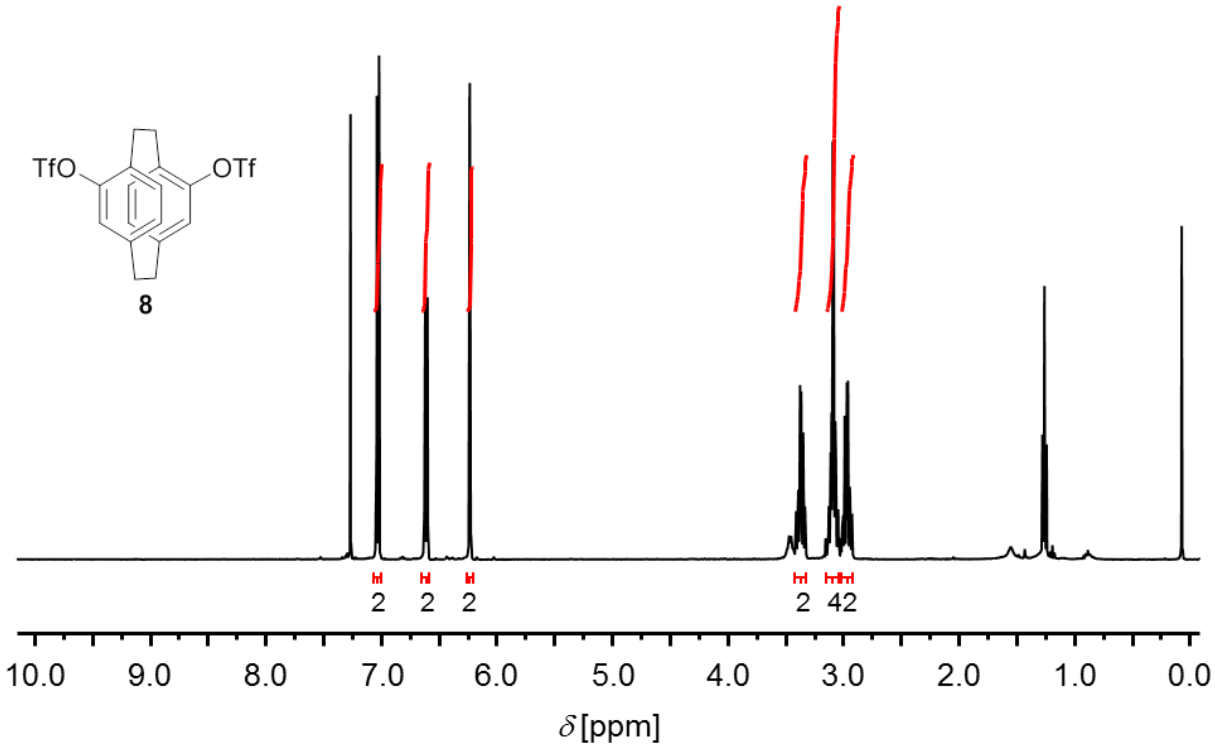

Figure S7: ^{1}H NMR spectrum of **8** (400.1 MHz, $CDCl_3$, 293 K)

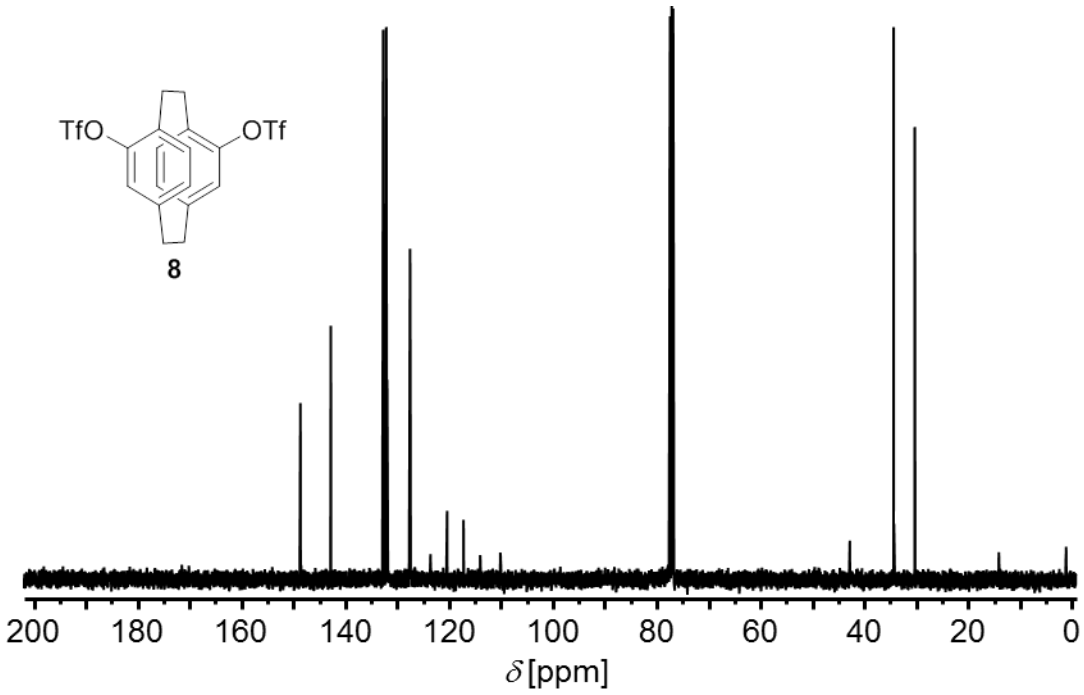

Figure S8: ^{13}C {^{1}H} NMR spectrum of **8** (100.6 MHz, $CDCl_3$, 293 K)

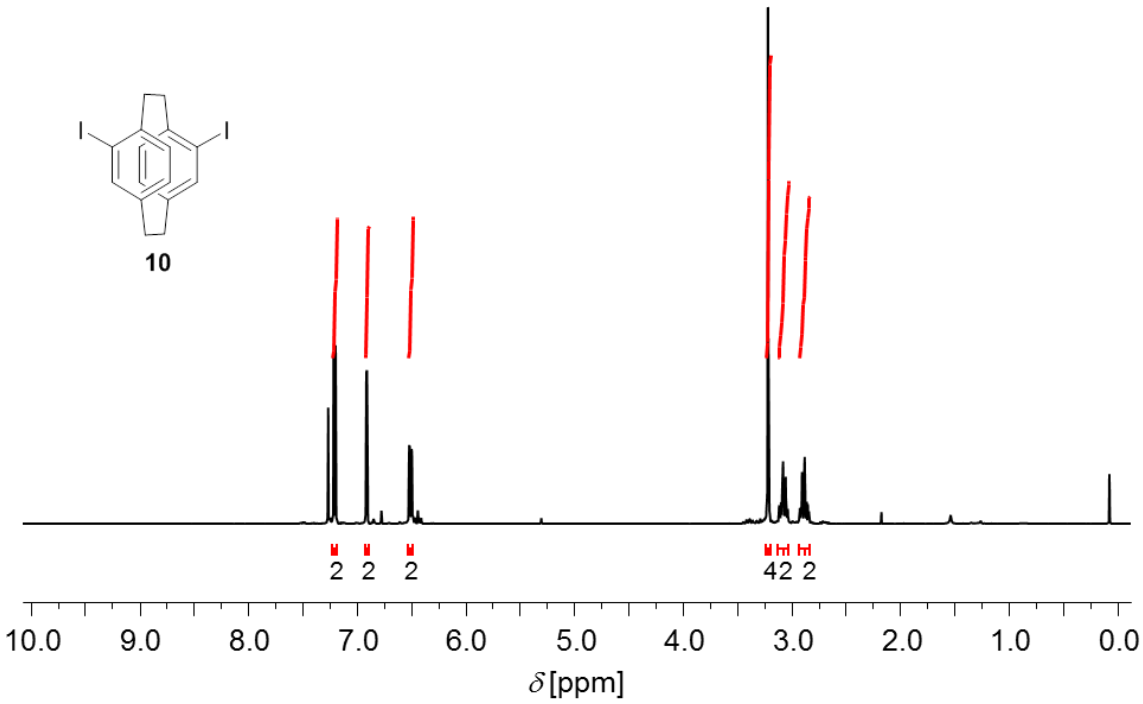

Figure S9: ^{1}H NMR spectrum of **10** (400.1 MHz, $CDCl_3$, 293 K)

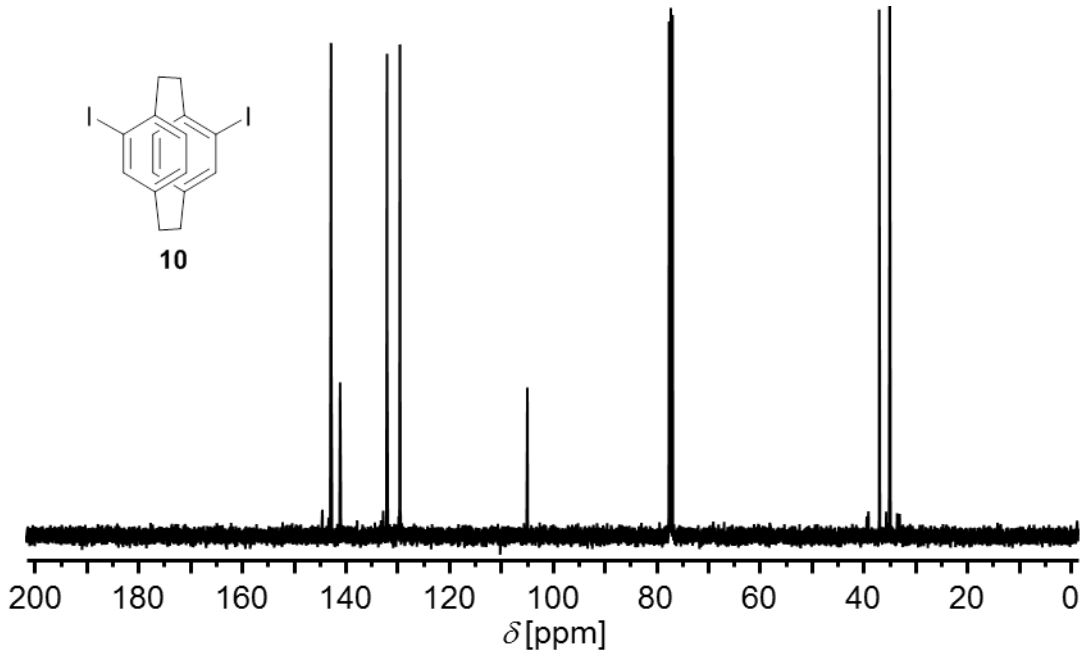

Figure S10: ^{13}C {^{1}H} NMR spectrum of **10** (100.6 MHz, $CDCl_3$, 293 K)

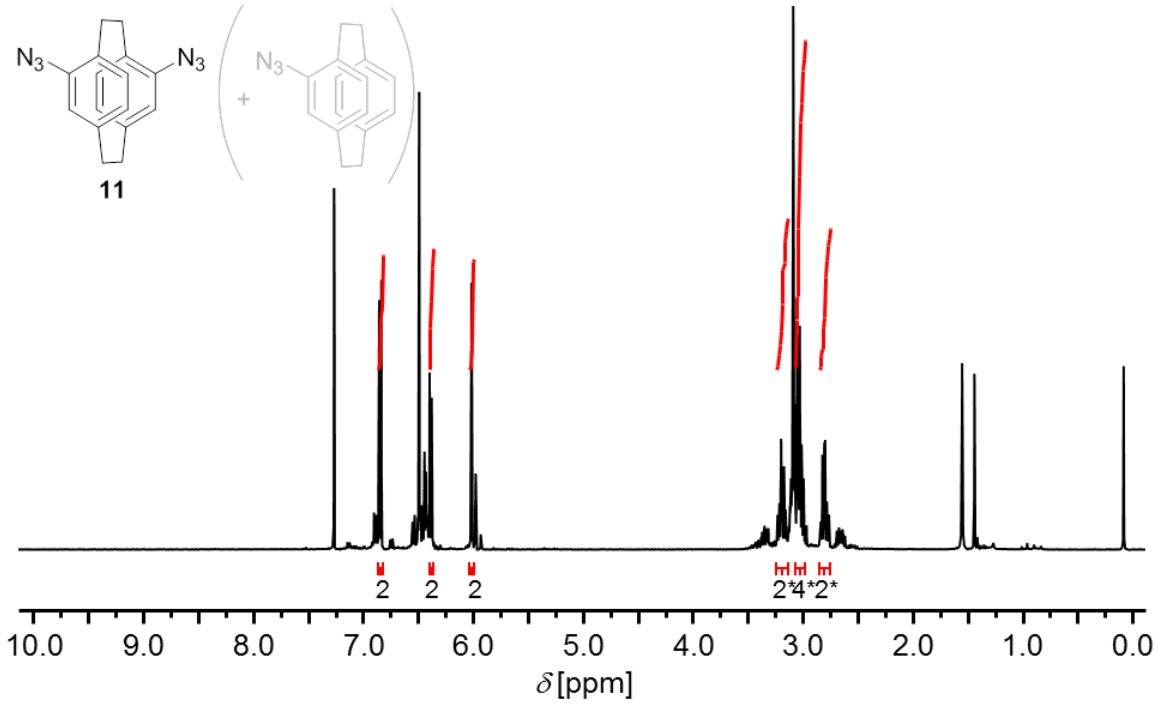

Figure S11: ^{1}H NMR spectrum of **11** (400.1 MHz, $CDCl_3$, 293 K, * signal overlap with the signals of the monoazide cause slightly larger integrals by a factor of 1.25)

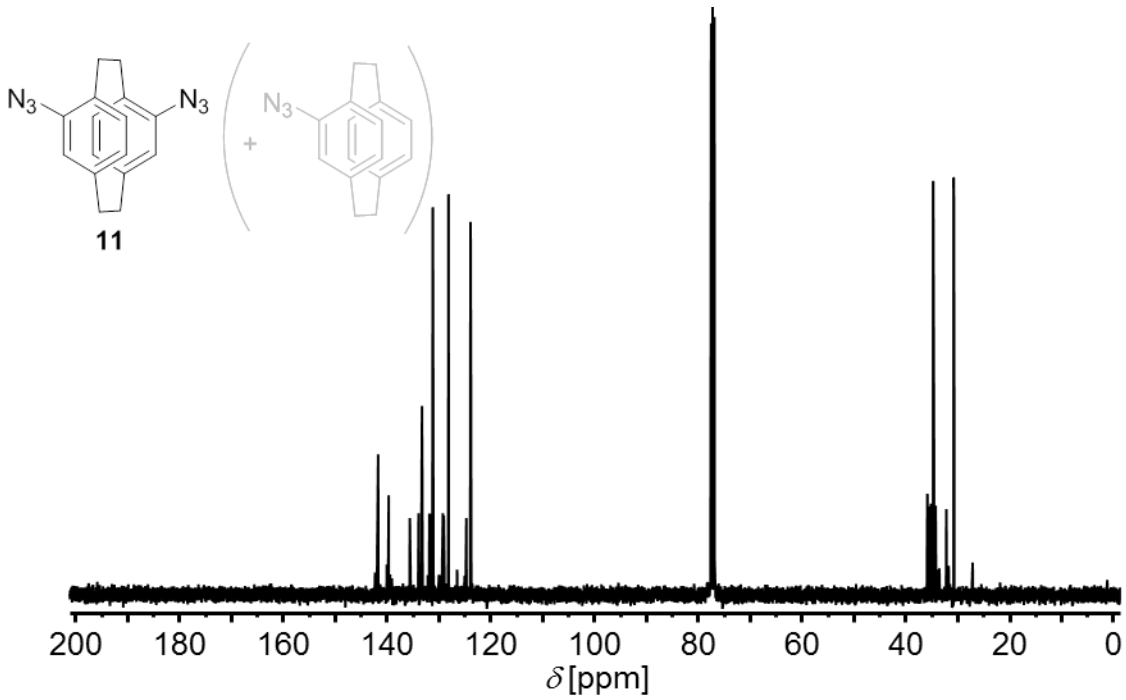

Figure S12: ^{13}C {^{1}H} NMR spectrum of **11** (100.6 MHz, $CDCl_3$, 293 K)

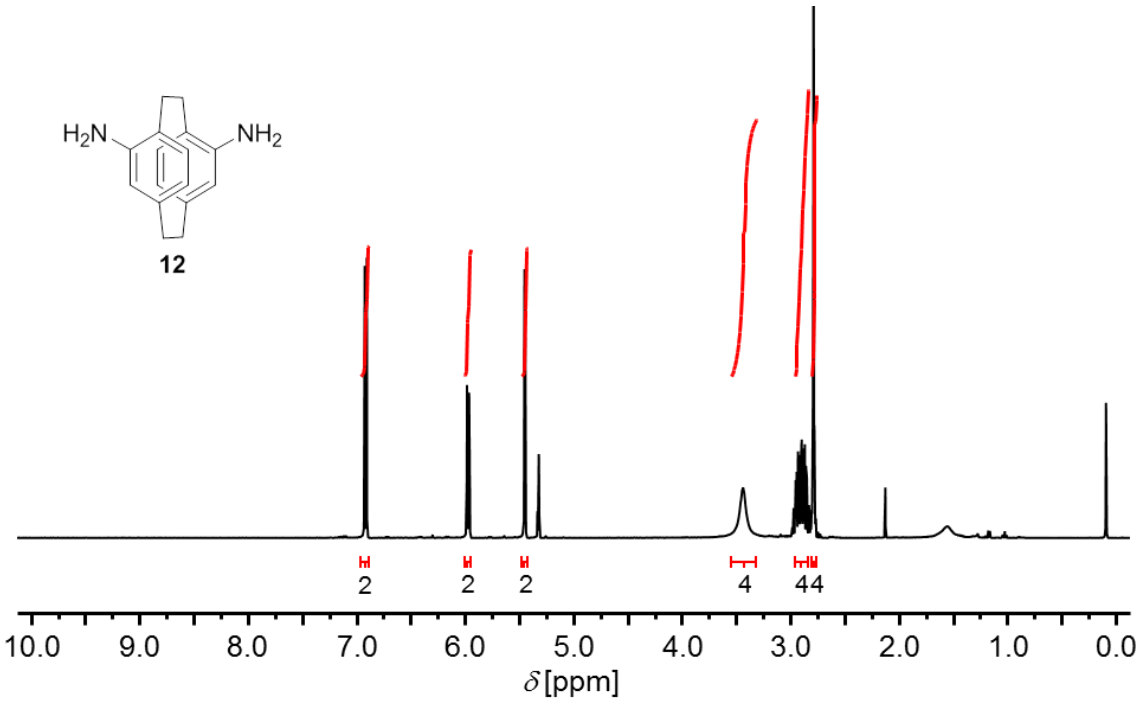

Figure S13: ^{1}H NMR spectrum of **12** (400.1 MHz, CD_2Cl_2, 293 K)

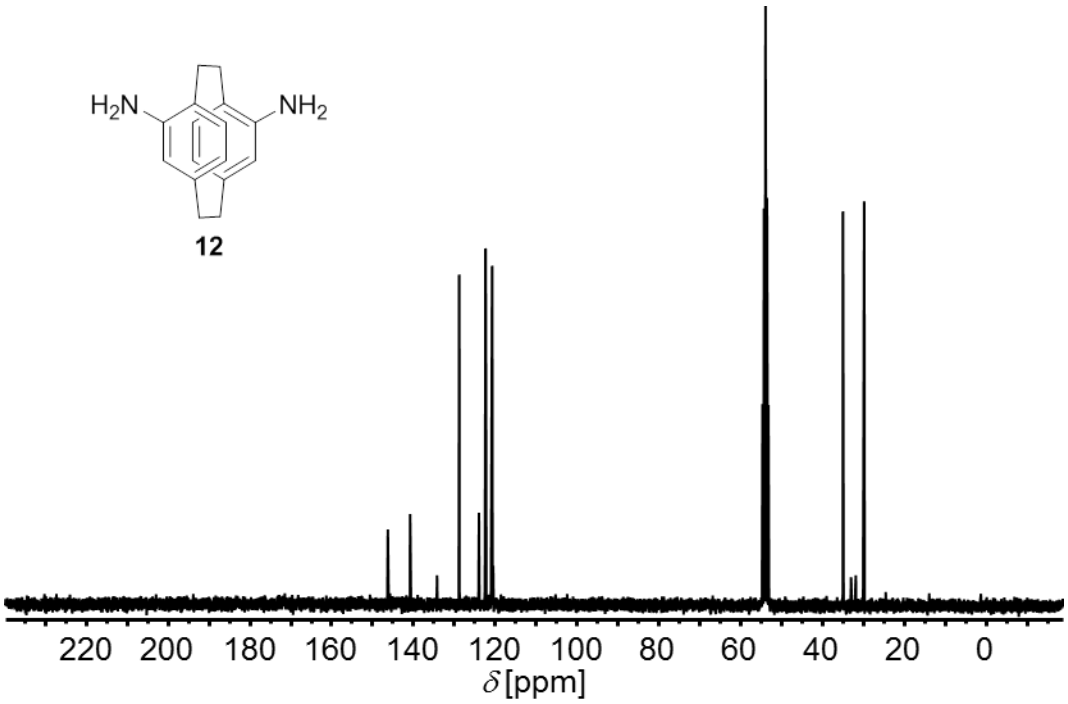

Figure S14: ^{13}C {^{1}H} NMR spectrum of **12** (100.6 MHz, CD_2Cl_2, 293 K)

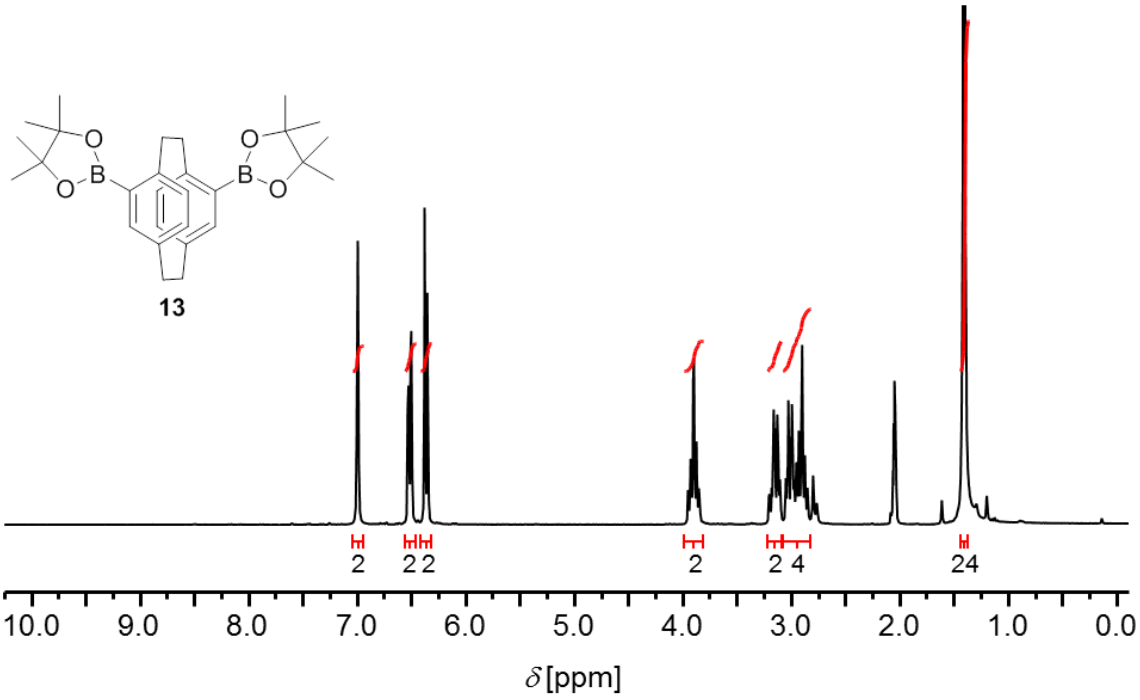

Figure S15: ^{1}H NMR spectrum of **13** (400.1 MHz, acetone-d_6, 293 K)

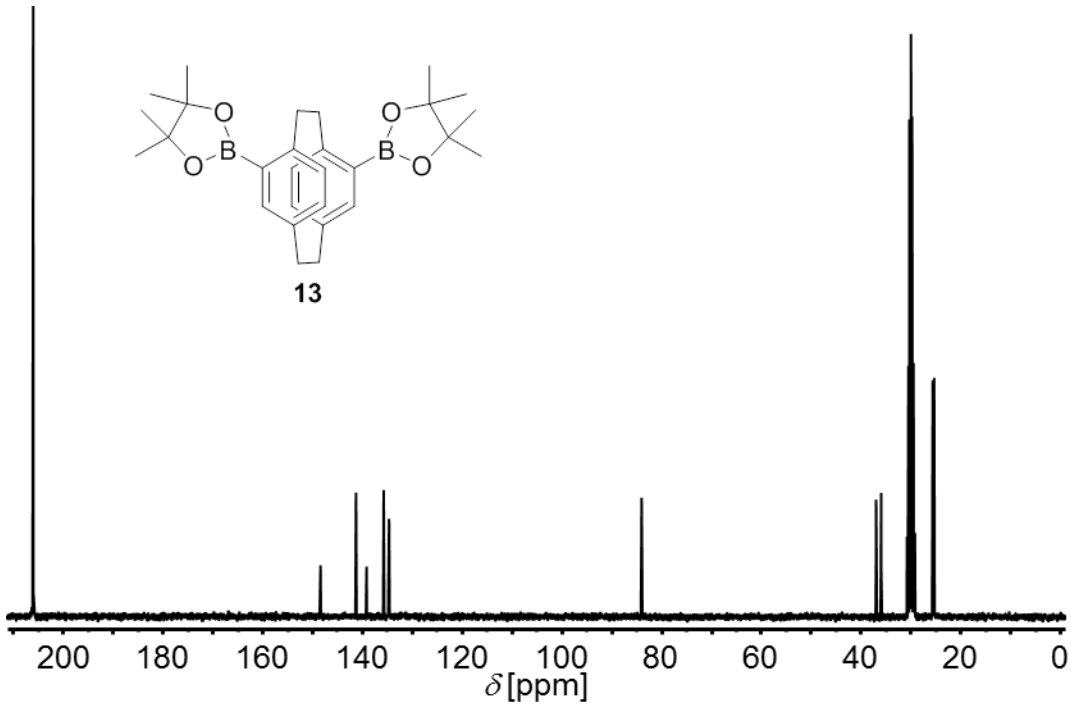

Figure S16: ^{13}C {^{1}H} NMR spectrum of **13** (100.6 MHz, acetone-d_6, 293 K)

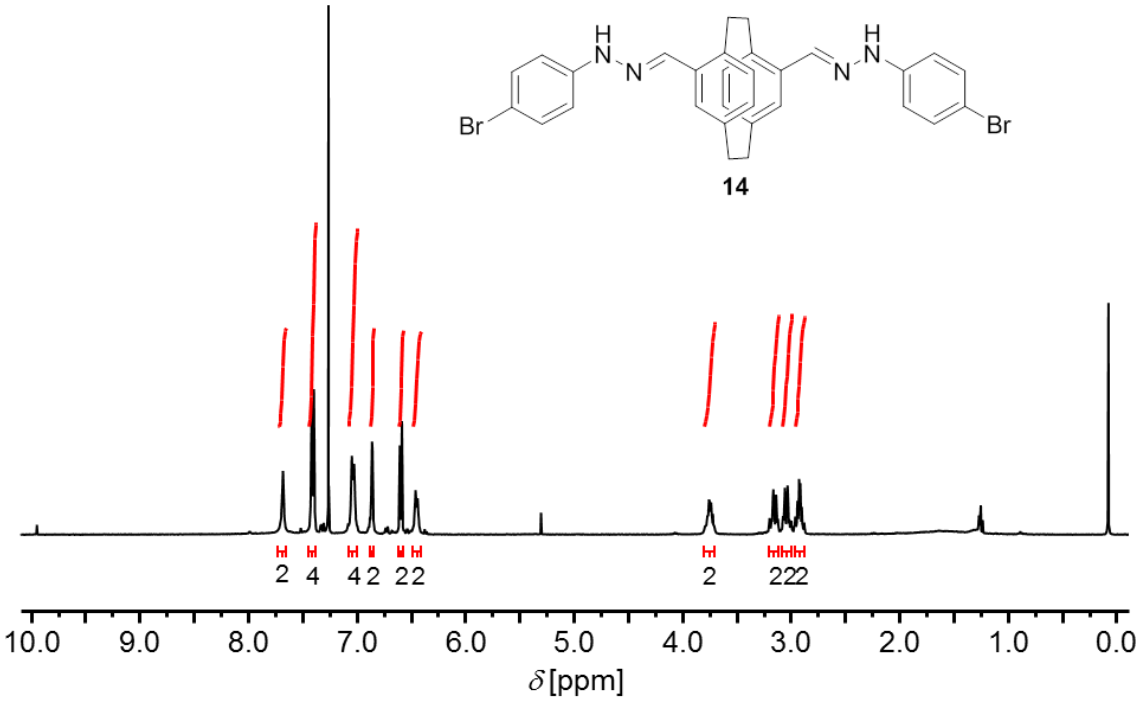

Figure S17: ^{1}H NMR spectrum of **14** (400.1 MHz, $CDCl_3$, 293 K)

2. Chromatographic resolution

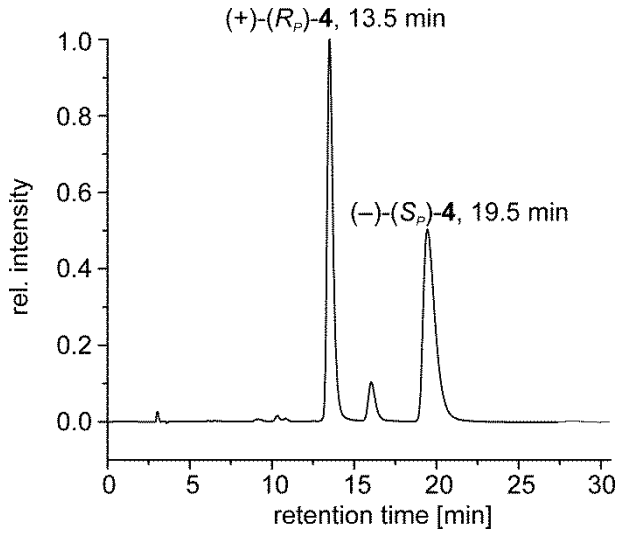

Figure S18: Chromatographic resolution of (*rac*)-**4** by analytical HPLC using a CHIRALPAK IA stationary phase with *n*-hexane/ethanol (90:10, v/v) as the eluent and a flow rate of f=1.0 mL/min, UV-detection at 220nm.

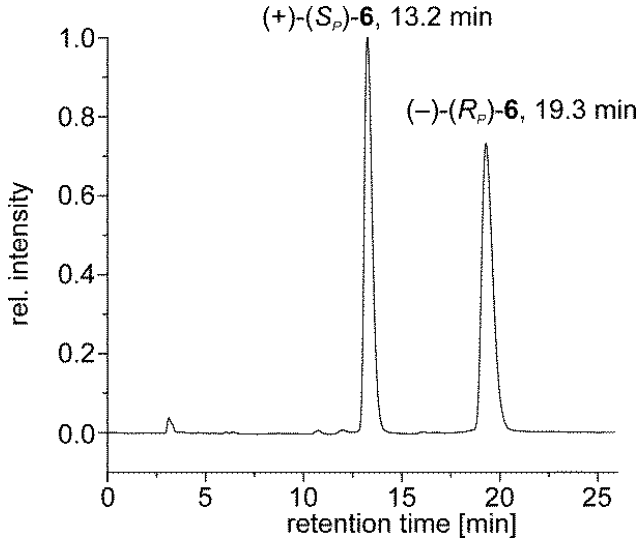

Figure S19. Chromatographic resolution of (*rac*)-**6** by analytical HPLC using a CHIRALPAK IA stationary phase with *n*-hexane/ethanol (90:10, v/v) as the eluent and a flow rate of f=1.0 mL/min, UV-detection at 220nm.

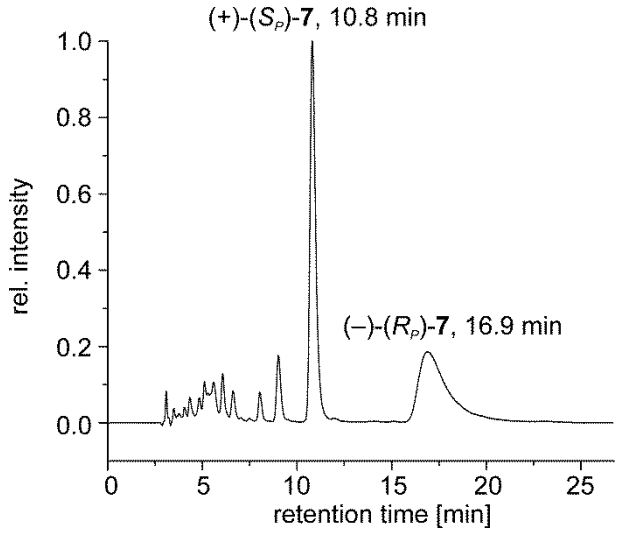

Figure S21: Chromatographic resolution of (*rac*)-**7** by analytical HPLC using a CHIRALPAK IA stationary phase with *n*-hexane/ethanol (80:20, v/v) as the eluent and a flow rate of *f*=1.0 mL/min, UV-detection at 220nm.

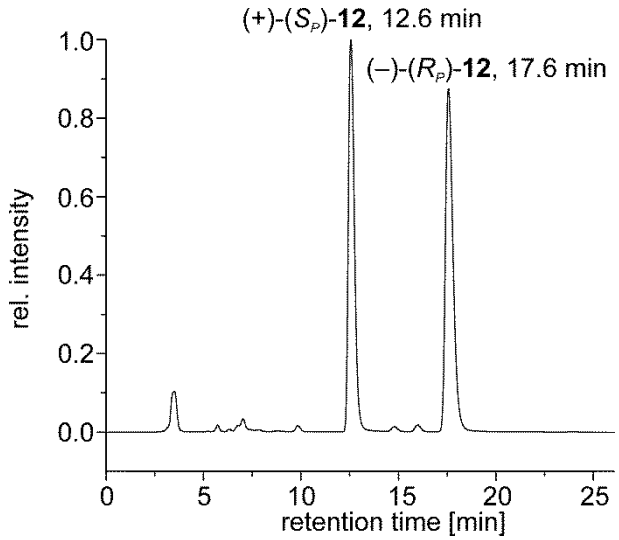

Figure S21: Chromatographic resolution of (*rac*)-**12** by analytical HPLC using a CHIRALPAK IB stationary phase with *n*-hexane/ethanol (70:30, v/v) as the eluent and a flow rate of *f*=1.0 mL/min, UV-detection at 220nm.

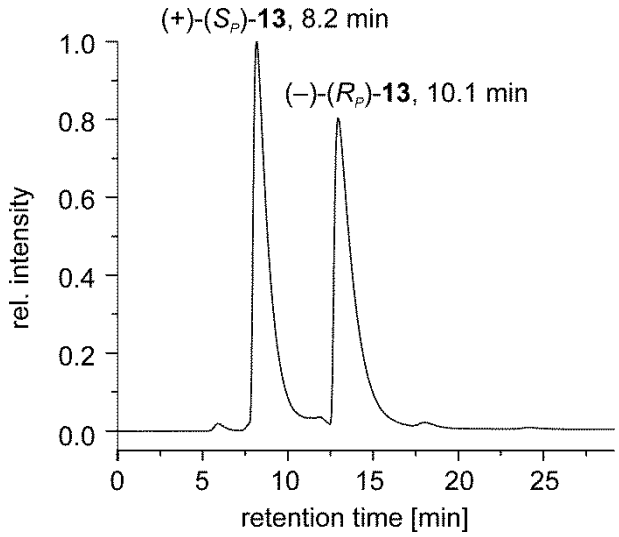

Figure S22: Chromatographic resolution of (*rac*)-**13** by analytical HPLC using a CHIRALPAK IB stationary phase with *n*-hexane/chloroform (98:2, v/v) as the eluent and a flow rate of f=1.0 mL/min, UV-detection at 220nm.

3. XRD analyses

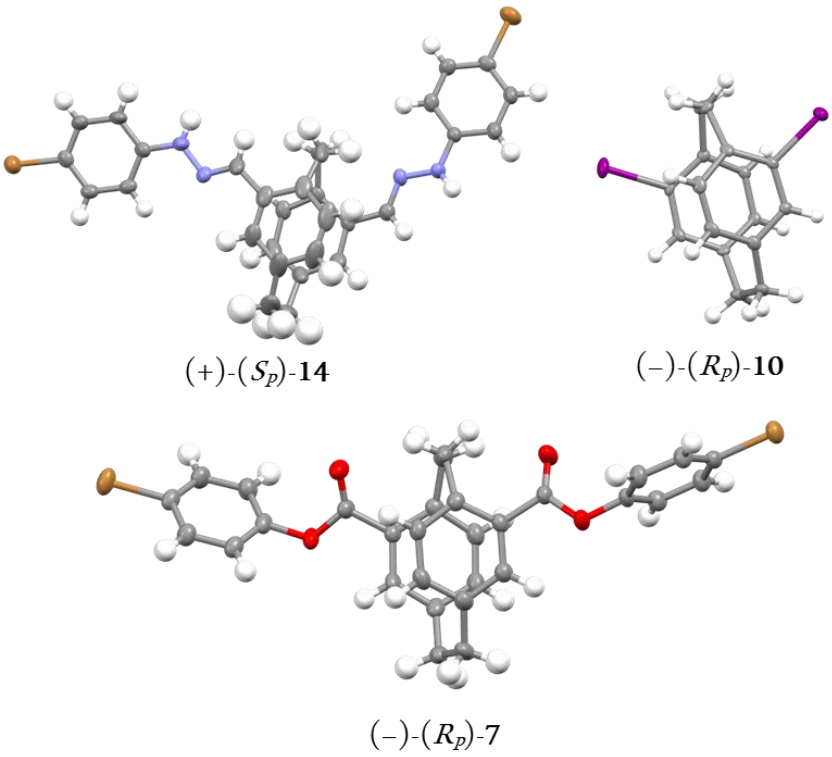

Figure S23. Molecular structures of (+)-(*S*P)-**14**, (–)-(*R*P)-**10**, and (–)-(*R*P)-**7** as determined by X-ray diffraction analysis (color code: grey: carbon; white: hydrogen; red: oxygen; blue: nitrogen; brown: bromine and purple iodine).

4. Theoretical simulation of CD spectra including the rotatory strength for CAM-B3LYP

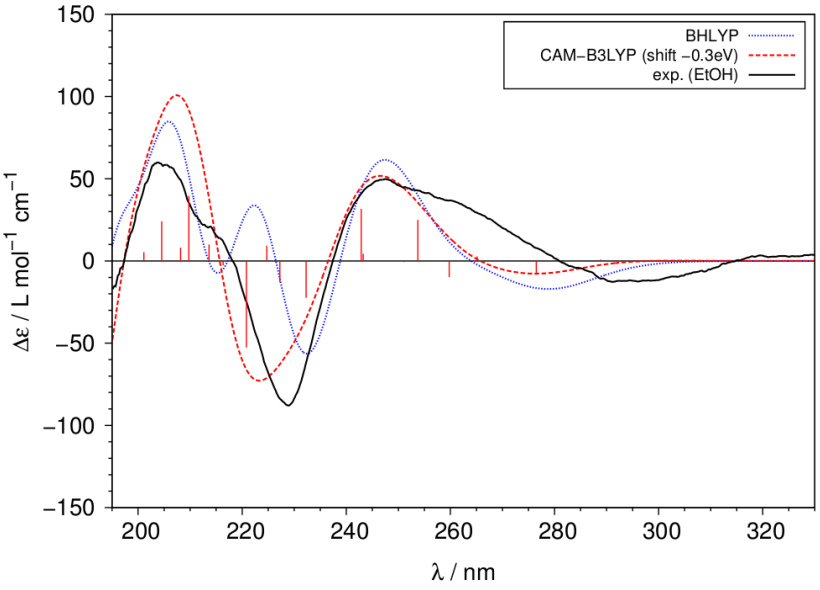

Figure S24: Experimental and simulated CD spectra of (–)-(S_P)-**4** including the rotator strengths for CAM-B3LYP.

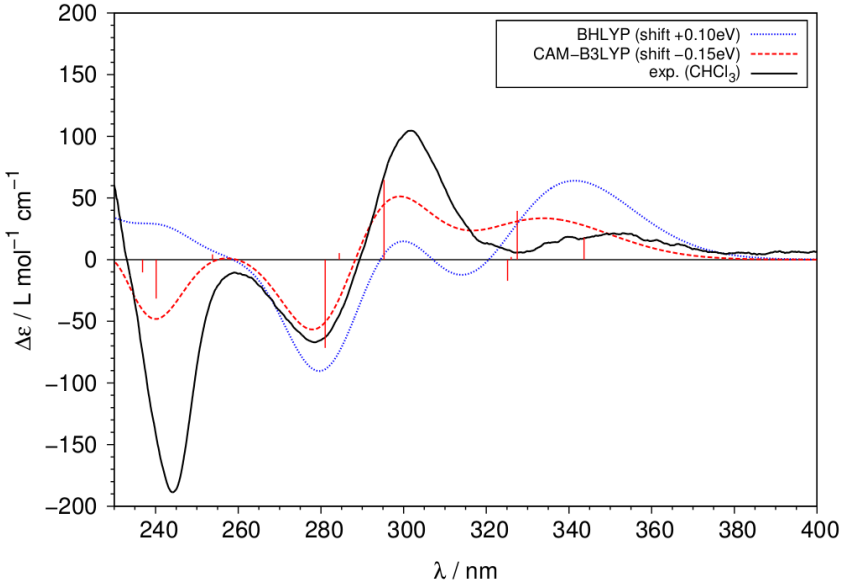

Figure S25: Experimental and simulated CD spectra of (+)-(S_P)-**6** including the rotator strengths for CAM-B3LYP.

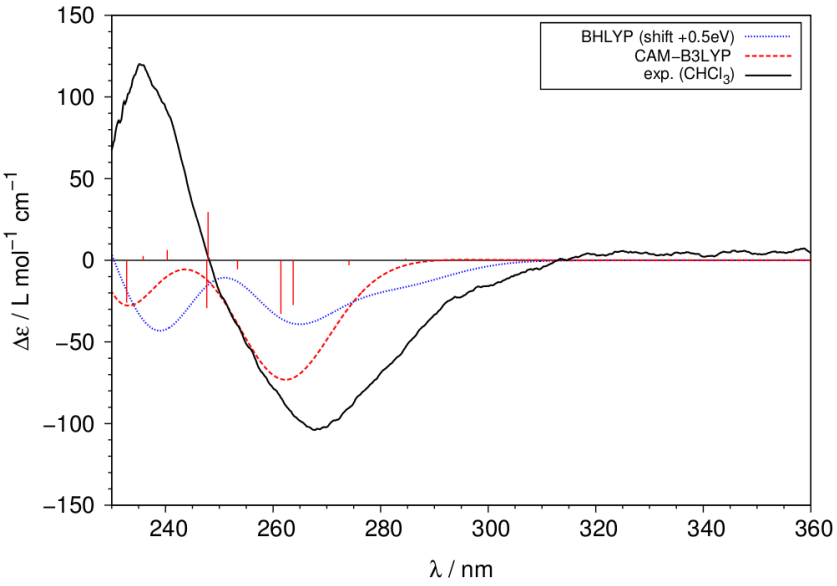

Figure S26: Experimental and simulated CD spectra of (–)-(R_P)-**10** including the rotator strengths for CAM-B3LYP.

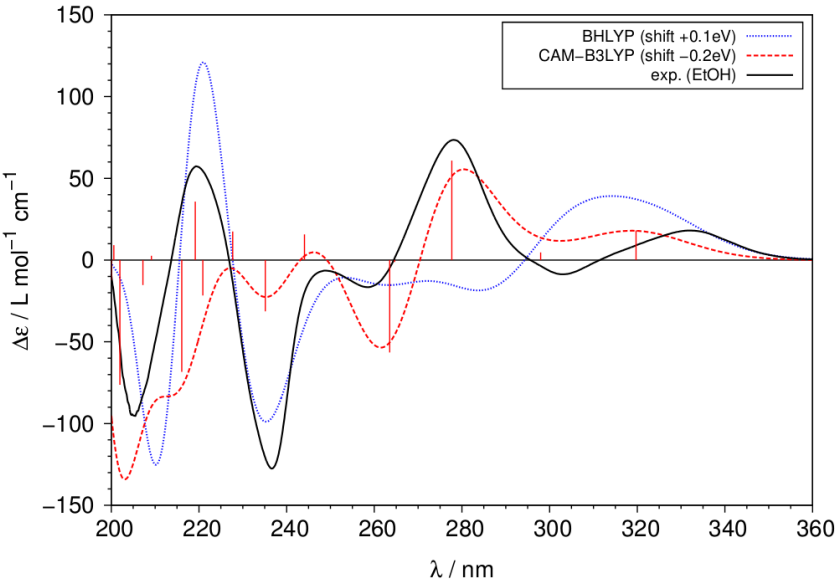

Figure S27: Experimental and simulated CD spectra of (+)-(S_P)-**13** including the rotator strengths for CAM-B3LYP.

5. Cartesian coordinates and total electronic energies of the optimized molecules on the TPSS-D3/def2-TZVP level of theory

(–)-(*S*$_P$)-4

34

Energy = -770.2243962803

C	-1.5783407	0.8713979	0.5838496
C	-1.5792844	0.9159710	-0.8075353
C	-1.3600938	-0.2454935	-1.5515053
C	-1.4067285	-1.4748029	-0.8790856
C	-1.3951876	-1.5080095	0.5145192
C	-1.3433532	-0.3300850	1.2701579
C	1.3951876	1.5080095	0.5145192
C	1.4067285	1.4748029	-0.8790856
C	1.3600938	0.2454935	-1.5515053
C	1.5792844	-0.9159710	-0.8075353
C	1.5783407	-0.8713979	0.5838496
C	1.3433532	0.3300850	1.2701579
C	-0.7361762	-0.3140999	2.6564012
C	0.7361762	0.3140999	2.6564012
C	0.7963373	0.1265551	-2.9462656
C	-0.7963373	-0.1265551	-2.9462656
O	1.6331946	-2.0803399	1.2439949
O	-1.6331946	2.0803399	1.2439949
H	-1.5962121	1.8895769	-1.2890133
H	-1.3048522	-2.4018508	-1.4369342
H	-1.2678342	-2.4607070	1.0220820
H	1.2678342	2.4607070	1.0220820
H	1.3048522	2.4018508	-1.4369342
H	1.5962121	-1.8895769	-1.2890133
H	-1.3372101	0.2378027	3.3938368
H	-0.6927333	-1.3443053	3.0214985
H	1.3372101	-0.2378027	3.3938368
H	0.9968973	1.0365990	-3.5195625
H	1.2667924	-0.7077643	-3.4755272
H	-0.9968973	-1.0365990	-3.5195625
H	-1.2667924	0.7077643	-3.4755272
H	1.6854092	-1.9048896	2.1974938
H	-1.6854092	1.9048896	2.1974938
H	0.6927333	1.3443053	3.0214985

(+)-(*S*$_P$)-6

36

Energy = -846.4748508823

C	1.3682995	0.2672729	1.2361468
C	1.3616490	1.4299914	0.4562776
C	1.3686535	1.3651189	-0.9339081
C	1.3785878	0.1249253	-1.5927397
C	1.6870472	-0.9939765	-0.8229630
C	1.6912948	-0.9404471	0.5797835
C	0.8018626	-0.0335129	-2.9791500
C	-0.8018626	0.0335129	-2.9791500
C	-1.3785878	-0.1249253	-1.5927397
C	-1.6870472	0.9939765	-0.8229630
C	-1.6912948	0.9404471	0.5797835

C	-1.3682995	-0.2672729	1.2361468
C	-1.3616490	-1.4299914	0.4562776
C	-1.3686535	-1.3651189	-0.9339081
C	-1.8656030	2.1963434	1.3310352
C	-0.7332368	-0.3124315	2.6106566
C	0.7332368	0.3124315	2.6106566
C	1.8656030	-2.1963434	1.3310352
H	-1.8031746	1.9725874	-1.2825498
H	-1.2216203	-2.2793168	-1.5044273
H	-1.1929187	-2.3906762	0.9369327
H	1.1929187	2.3906762	0.9369327
H	1.2216203	2.2793168	-1.5044273
H	1.8031746	-1.9725874	-1.2825498
H	-1.3165323	0.2101885	3.3754299
H	-0.6631782	-1.3606080	2.9176514
H	1.3165323	-0.2101885	3.3754299
H	1.1669299	0.7425022	-3.6593478
H	1.1072713	-1.0012265	-3.3872365
H	-1.1669299	-0.7425022	-3.6593478
H	-1.1072713	1.0012265	-3.3872365
H	1.8556261	-2.0972430	2.4376469
H	-1.8556261	2.0972430	2.4376469
H	0.6631782	1.3606080	2.9176514
O	2.0235114	-3.2963723	0.8217214
O	-2.0235114	3.2963723	0.8217214

(–)-(R_P)-10

32

Energy = -1213.697923897

C	0.6496540	1.2247902	-1.3941382
C	-0.2643775	1.9612516	-0.6235681
C	-0.2335454	1.9409230	0.7678480
C	0.7287674	1.1800320	1.4412839
C	1.8105401	0.7014731	0.6905823
C	1.7675883	0.7411013	-0.7014074
C	0.4857032	0.6411655	2.8302353
C	-0.4857032	-0.6411655	2.8302353
C	-0.7287674	-1.1800320	1.4412839
C	-1.8105401	-0.7014731	0.6905823
C	-1.7675883	-0.7411013	-0.7014074
C	-0.6496540	-1.2247902	-1.3941382
C	0.2643775	-1.9612516	-0.6235681
C	0.2335454	-1.9409230	0.7678480
I	-3.3537908	0.1898415	-1.7564446
C	-0.2531420	-0.7587336	-2.7737468
C	0.2531420	0.7587336	-2.7737468
I	3.3537908	-0.1898415	-1.7564446
H	-2.6253521	-0.1844122	1.1880163
H	1.0461246	-2.4026471	1.3232885
H	1.1046130	-2.4295077	-1.1295525
H	-1.1046130	2.4295077	-1.1295525
H	-1.0461246	2.4026471	1.3232885
H	2.6253521	0.1844122	1.1880163
H	-1.0819758	-0.8302444	-3.4846565

H	0.5597885	-1.3939166	-3.1350287
H	1.0819758	0.8302444	-3.4846565
H	0.0347092	1.4018059	3.4750758
H	1.4377134	0.3475463	3.2822127
H	-0.0347092	-1.4018059	3.4750758
H	-1.4377134	-0.3475463	3.2822127
H	-0.5597885	1.3939166	-3.1350287

(+)-(S_P)-13

72

Energy = -1441.563724506

C	0.1015708	1.3836537	-0.1515561
C	-0.1174901	1.1356008	-2.9595127
C	1.2748955	1.3350399	-0.9422098
C	-1.1125335	1.6214222	-0.8070966
C	-1.2293191	1.4944246	-2.1887672
C	1.1310425	1.2158246	-2.3365163
H	-2.2175028	1.5298573	-2.6428637
H	2.0278267	1.0460639	-2.9287683
C	-0.1075645	-1.3775657	0.1132030
C	-0.5071407	-1.6026719	-2.6768828
C	0.9389294	-1.7464240	-0.7405188
C	-1.4249407	-1.4322113	-0.4014538
C	-1.5891245	-1.5483732	-1.7935096
C	0.7507317	-1.8531512	-2.1161914
H	-2.5956731	-1.4591541	-2.1971749
H	1.6161948	-1.9885574	-2.7618885
C	0.2401335	-0.6707388	1.4042592
H	1.2896756	-0.8671434	1.6396428
H	-0.3748149	-1.0068115	2.2420808
C	0.0564294	0.9114257	1.2846190
H	0.8315073	1.3741261	1.9002967
H	-0.9205000	1.1686956	1.7043674
C	-0.2667709	0.4208343	-4.2807691
H	0.6796844	0.4722407	-4.8281818
H	-1.0342524	0.8892937	-4.9061096
C	-0.6605392	-1.1270894	-4.1015288
H	-0.0381328	-1.7107033	-4.7882665
H	-1.7019082	-1.2533557	-4.4139918
B	2.7125125	1.2265417	-0.3723692
B	-2.7037653	-1.1938909	0.4424267
O	3.8282888	1.2581668	-1.1923947
O	3.0428932	1.0780633	0.9634942
O	-3.9561742	-1.0863231	-0.1397790
O	-2.7498592	-1.0739447	1.8202355
C	-4.9413003	-1.1403948	0.9411613
C	-4.1076638	-0.6514233	2.1753827
C	4.4958135	1.2398763	1.0718935
C	4.9790774	0.8753185	-0.3739476
C	5.0005518	0.3161713	2.1726753
H	6.0936526	0.3556072	2.2347435
H	4.6951624	-0.7172275	1.9958144
H	4.5915227	0.6362127	3.1355614
C	4.7441520	2.7055484	1.4352161
H	5.8091477	2.9008513	1.5964480

H	4.2039329	2.9372320	2.3575475
H	4.3792442	3.3691277	0.6455408
C	6.1974577	1.6504032	-0.8588196
H	7.0628267	1.4437311	-0.2194680
H	6.0086279	2.7257894	-0.8606236
H	6.4443438	1.3425640	-1.8791548
C	5.1785617	-0.6287801	-0.5772071
H	6.0662454	-0.9896923	-0.0481406
H	5.3041721	-0.8265866	-1.6454272
H	4.3073992	-1.1884024	-0.2237317
C	-4.4804260	-1.2982607	3.5028946
H	-3.8326040	-0.9094189	4.2941593
H	-4.3619162	-2.3828642	3.4631677
H	-5.5184455	-1.0648178	3.7642667
C	-4.0718837	0.8725280	2.3081230
H	-3.3120844	1.1467988	3.0455164
H	-5.0376837	1.2660114	2.6405329
H	-3.8126881	1.3411675	1.3541115
C	-5.3825014	-2.6013939	1.0586647
H	-4.5375384	-3.2425493	1.3272864
H	-5.7709859	-2.9312259	0.0910489
H	-6.1695523	-2.7212613	1.8101263
C	-6.1183871	-0.2491699	0.5664713
H	-5.7898335	0.7656353	0.3326885
H	-6.8433484	-0.2062147	1.3867693
H	-6.6219880	-0.6593788	-0.3138714
H	1.9491653	-1.7976238	-0.3402318
H	-2.0145361	1.7529466	-0.2135129