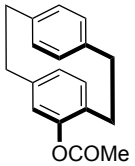
1. Asymmetric *O*-Acylation Reactions:

General procedure for the screening of different acyl-transfer reagents 4:

Racemic 4-hydroxy[2.2]paracyclophane (**2**, 0.1 mmol) and catalyst **ITU 2** (10 mol%) were dissolved in dry toluene (1.5 mL) in a Schlenkflask under argon, before adding Hünig's base (diisopropylethylamine, DIPEA; 0.06 mmol) as a solution in toluene (0.15 mL). This solution was then cooled to -40°C and a solution of acylating agent **4** (0.6 mmol) in 0.15 mL toluene was added (resulting in a concentration of 0.055 M with respect to **2**) and the mixture stirred for 4 h. The reaction was quenched with MeOH in the cold and allowed to reach room temperature. The crude product was filtered over Na_2SO_4 and the solvents removed in vacuum, before the desired product was purified by column chromatography.

***Analytical data for other O*-acylated paracyclophanes 3**

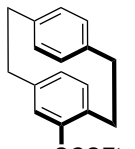
3b: Following the general procedure using anhydride **4d**, a conversion of 45% of *rac*-**2** was achieved.



3b

Ester **3b** was obtained as a white solid after silica gel column chromatography using heptanes/ethyl acetate (10:1); ***e.r.*** = 68:32 (s = 2.5); TLC (heptanes/ethyl acetate = 10/1): R_f = 0.21 (UV). Analytical data are in accordance with those reported in literature[1]. $[\alpha]_D^{22}$ = 14.1 (c 0.62, CH_2Cl_2, *e.r.* = 68:32); **m.p.** = 125-130°C; **^{1}H-NMR** (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 6.91 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.56 - 6.43 (m, 5H), 6.01 (d, *J* = 1.7 Hz, 1H), 3.20 - 2.96 (m, 7H), 2.76 - 2.67 (m, 1H), 2.34 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$, 298.0 K): δ / ppm = 169.0 (1C, C=O), 149.0 (1C, C_{Ar}), 141.7 (1C, C_{Ar}), 139.6 (1C, C_{Ar}), 139.3 (1C, C_{Ar}), 135.4 (1C, C_{Ar}), 133.5 (1C, C_{Ar}) 133.0 (1C, C_{Ar}), 132.3 (1C, C_{Ar}), 131.2 (1C, C_{Ar}), 130.4 (1C, C_{Ar}), 129.6 (1C, C_{Ar}), 128.0 (1C, C_{Ar}), 35.4 (1C, -CH_2), 35.0 (1C, -CH_2), 34.4 (1C, -CH2), 31.8 (1C, -CH2), 21.3 (1C, -CH_3); **HRMS** (ESI) *m*/*z*: calculated for [$C_{18}H_{18}O_2$ + H] $^+$: 267.1380; found: 267.1389, **HPLC:** YMC Chiral ART Cellulose-SB, *n*-hexane/*i*-PrOH 3:1, 1 mL/min, 10 °C; t_R = 9.2 min [minor], 11.1 min [major].

3c: Following the general procedure using **4e**, a conversion of 38% of *rac*-**2** was achieved. Ester **3c** was

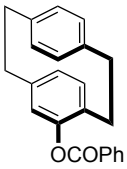


3c

obtained as a white solid after silica gel column chromatography using heptanes/ethyl acetate (10:1); ***e.r.*** = 77:23 (s = 4.5); TLC (heptanes/ethyl acetate = 10/1): R_f = 0.27 (UV). $[\alpha]_D^{22}$ = 12.5 (c 0.75, CH_2Cl_2, *e.r.* = 77:23); **m.p.** = 68-70°C; **^{1}H-NMR** (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 6.91 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.55 - 6.42 (m, 5H), 6.01 (d, *J* = 1.7 Hz, 1H), 3.17 - 2.96 (m, 7H), 2.74 - 2.67 (m, 2H), 2.64 (q, 1H, *J* = 7.5 Hz) 1.35 (t, *J* = 7.5 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$, 298.0 K): δ / ppm = 172.3 (1C, C=O), 149.0 (1C, C_{Ar}), 141.7 (1C, C_{Ar}), 139.6 (1C, C_{Ar}), 139.3 (1C, C_{Ar}), 135.4 (1C, C_{Ar}), 133.5 (1C, C_{Ar}), 133.0 (1C, C_{Ar}), 132.4 (1C, C_{Ar}), 131.1 (1C, C_{Ar}), 130.2 (1C, C_{Ar}), 129.6 (1C, C_{Ar}), 128.1 (1C, C_{Ar}), 35.4 (1C, -CH_2), 35.0 (1C, -CH_2), 34.4 (1C, -CH_2), 31.8 (1C, -CH_2), 28.1 (1C, -CH_2), 9.5 (1C, -CH_2); **HRMS** (ESI) *m*/*z*: calculated for [$C_{19}H_{20}O_2$ + H] $^+$: 281.1536; found: 281.1541, **HPLC:** YMC Chiral ART Cellulose-SB, *n*-hexane/*i*-PrOH 3:1, 1 mL/min, 10 °C; t_R = 8.7 min [minor], 10.4 min [major].

[1] a) Cipiciani, A.; Fringuelli, F.; Mancini, V.; Piermatti, O.; Pizzo, F. *J. Org. Chem*. **1997**, *62*, 3744-3747; b) Rozenberg, V.; Danilova, T.; Sergeeva, E.; Vorontsov, E.; Starikova, Z.; Lysenko, K.; Belokon, Y. *Eur. J. Org. Chem.* **2000**, 3295–3303; c) Cipiciani, A.; Fringuelli, F.; Mancini, V.; Piermatti, O.; Scappini, A. M.; Ruzziconi, R. *Tetrahedron* **1997**, *53*, 11853–11858.

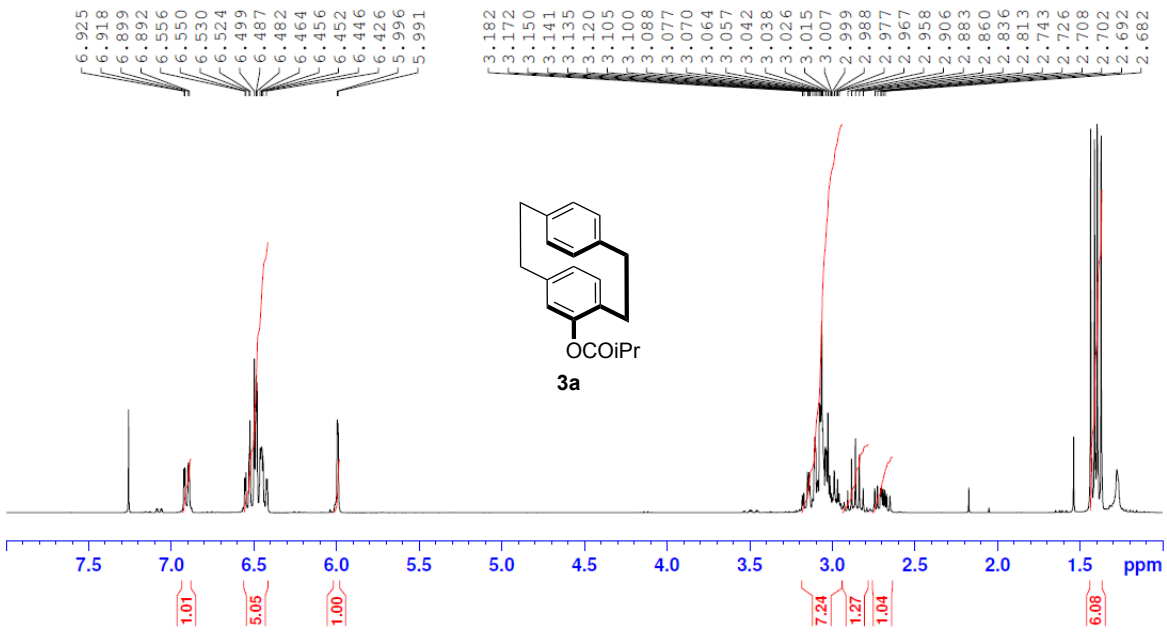
3d: Following the general procedure, a conversion of 30 % of rac-2 was achieved. Ester **3d** was obtained as a white solid after silica gel column chromatography using heptanes/ethyl acetate (10:1). ***rac***; TLC (heptanes/ethyl acetate = 10/1): R_f = 0.30 (UV). **m.p.** = 135-139°C; **^{1}H-NMR** (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 8.32-8.27 (m, 2H), 7.71-7.66 (m, 1H), 7.61-7.56(m, 2H), 7.04 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.58 - 6.45 (m, 5H), 6.16 (d, *J* = 1.7 Hz, 1H), 3.28 - 3.18 (m, 1H), 3.15 - 2.97 (m, 6H), 2.79 - 2.69 (m, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$, 298.0 K): δ / ppm = 164.5 (1C, C=O), 149.2 (1C, C_{Ar}), 141.9 (1C, C_{Ar}), ,139.7 (1C, C_{Ar}), 139.4 (1C, C_{Ar}), 135.5 (1C, C_{Ar}), 133.7 (1C, C_{Ar}), 133.6 (1C, C_{Ar}), 133.2 (1C, C_{Ar}), 132.4 (1C, C_{Ar}), 131.3 (1C, C_{Ar}), 130.3 (1C, C_{Ar}), 130.2 (2C, C_{Ar}), 130.0 (1C, C_{Ar}), 129.7 (1C, C_{Ar}), 128.9 (2C, C_{Ar}), 128.3 (1C, C_{Ar}), 35.4 (1C, -CH_2), 35.0 (1C, -CH_2), 34.7 (1C, -CH_2), 32.0 (1C, -CH_2); **MS** (ESI) *m*/*z*: calculated for $[C_{23}H_{20}O_2 + H]^+$: 329.1536; found: 329.1531, **HPLC:** YMC Chiral ART Cellulose-SB, *n*-hexane/*i*-PrOH 3:1, 1 mL/min, 10 °C; t_R = 9.0, 9.7 min;

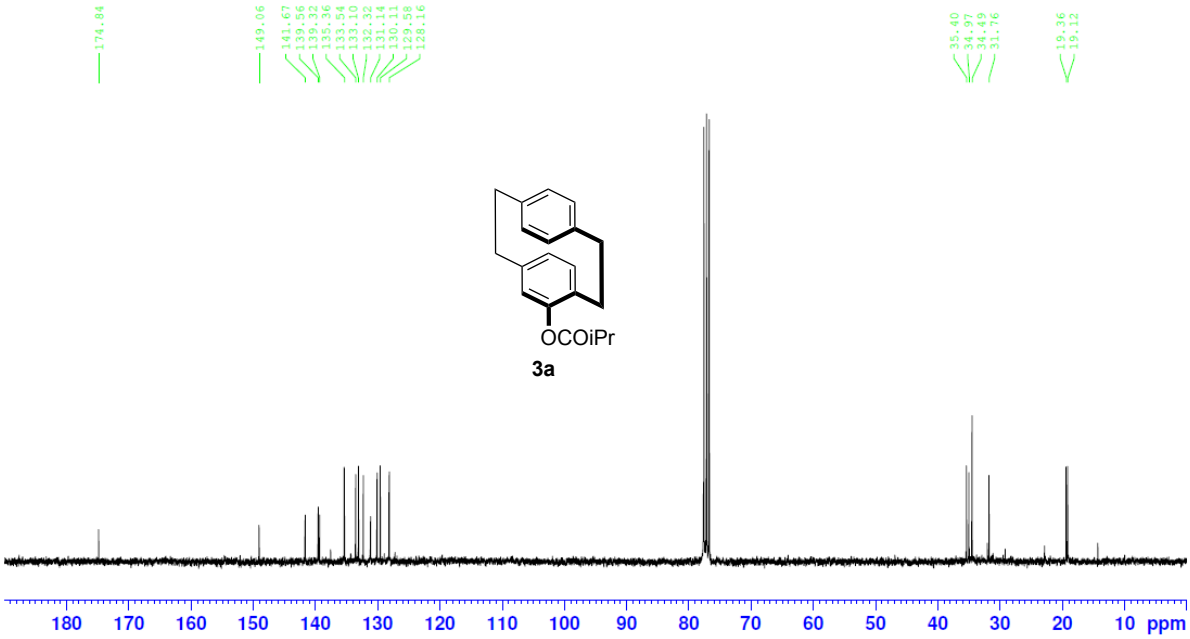


3d

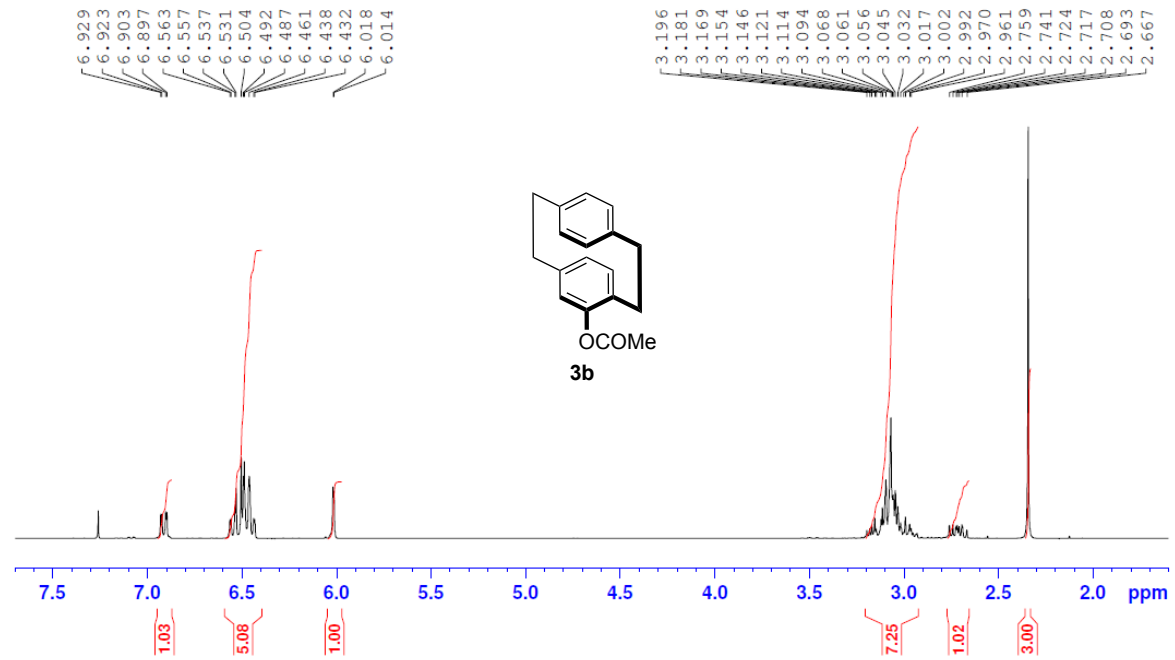
2. NMR spectra of products 3

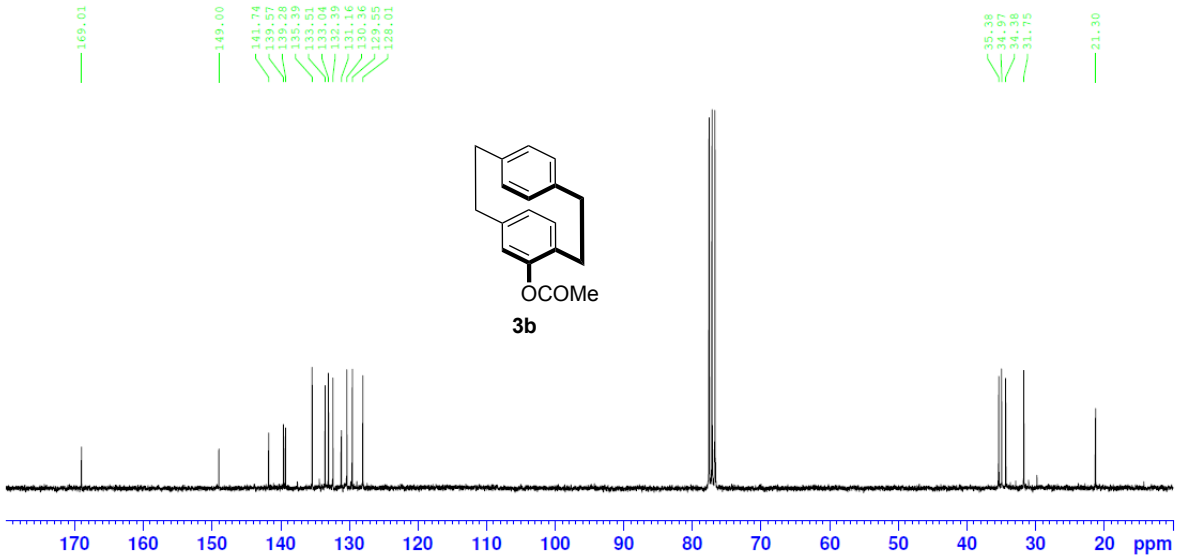
NMR-spectra of **3a**



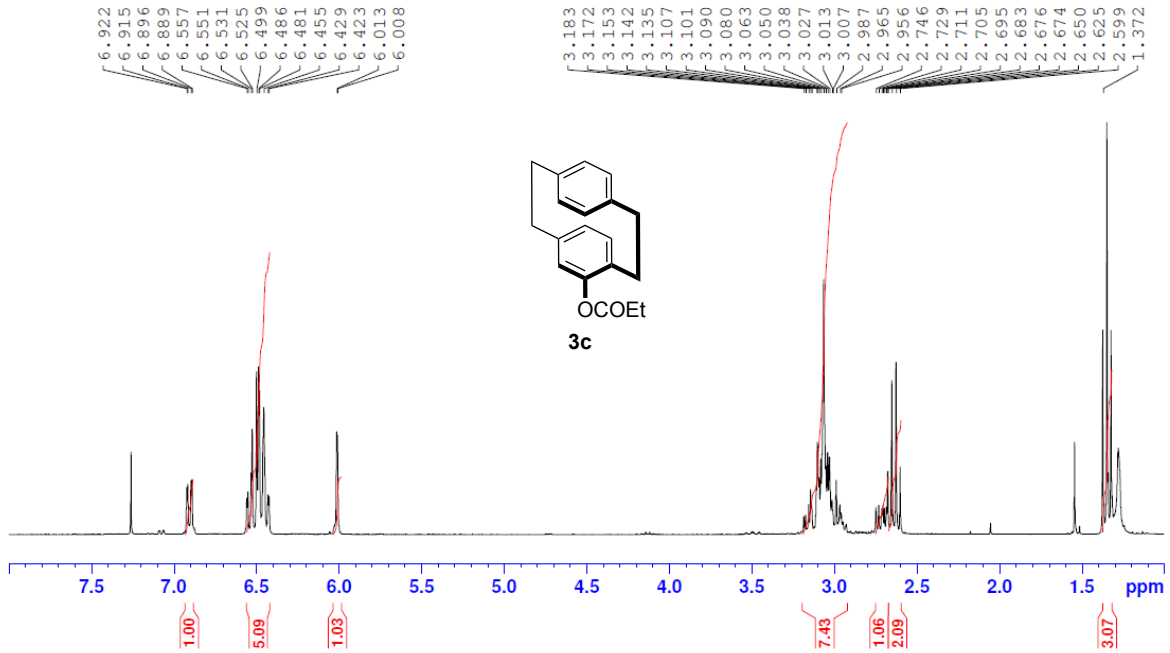


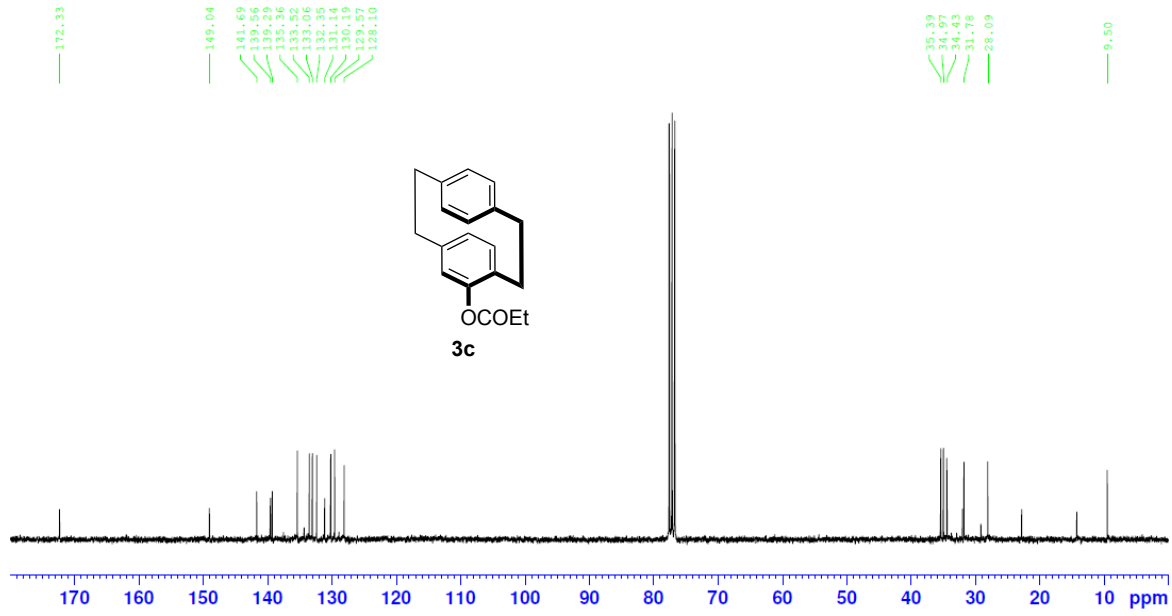
NMR-spectra of **3b**



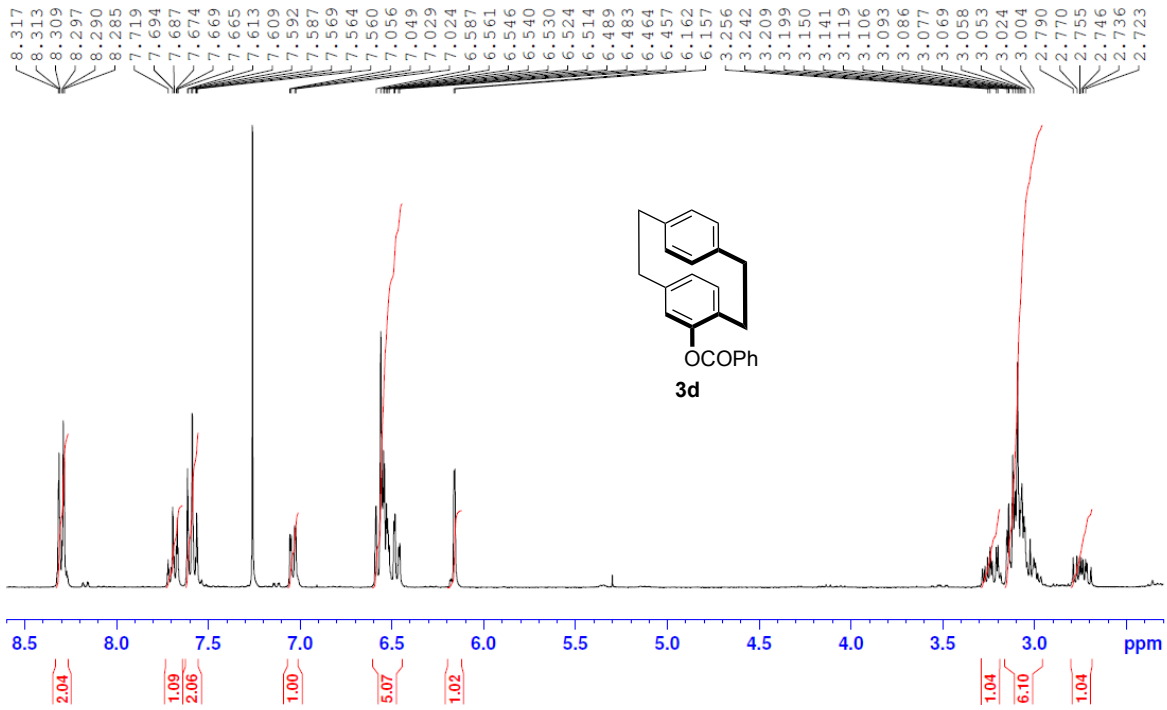


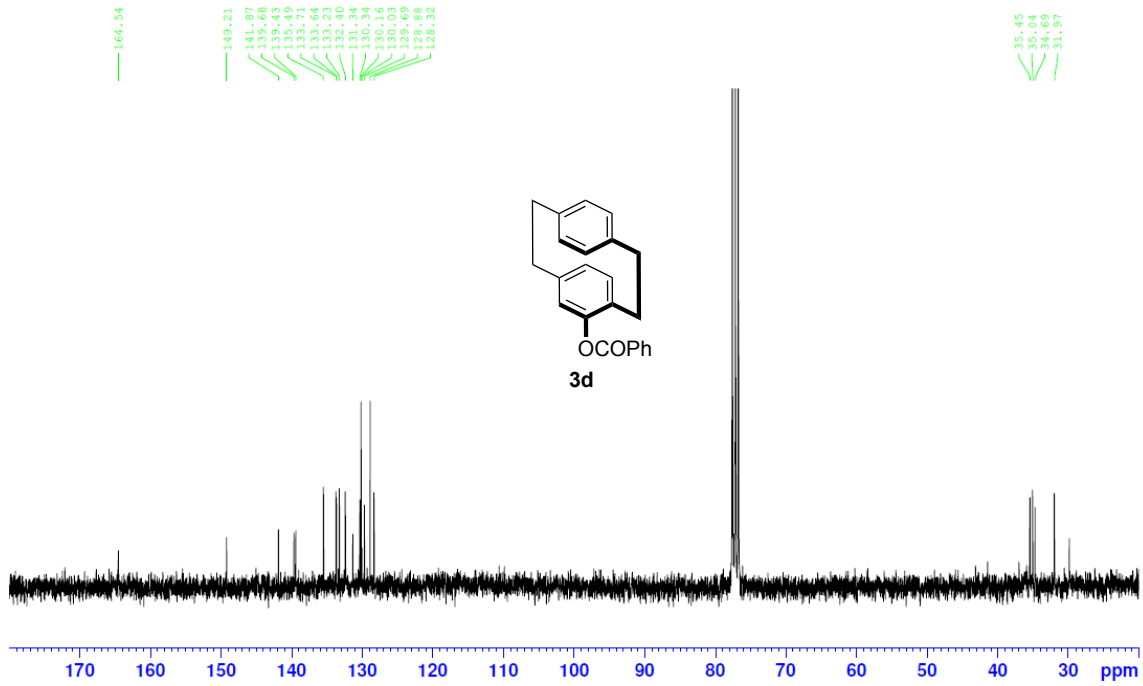
NMR-spectra of **3c**





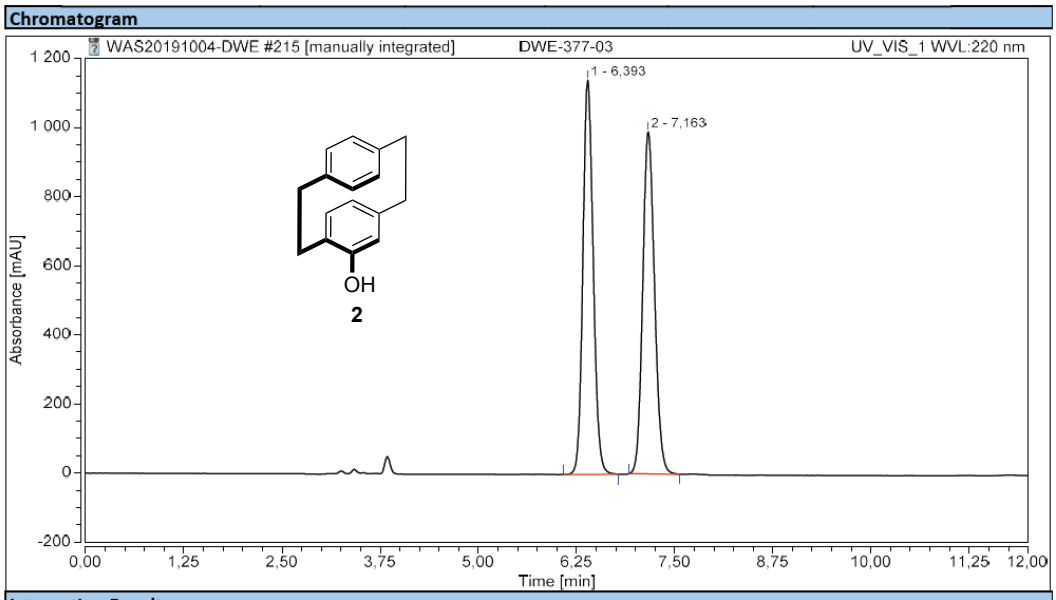
NMR-spectra of **3d**





3. HPLC Chromatograms

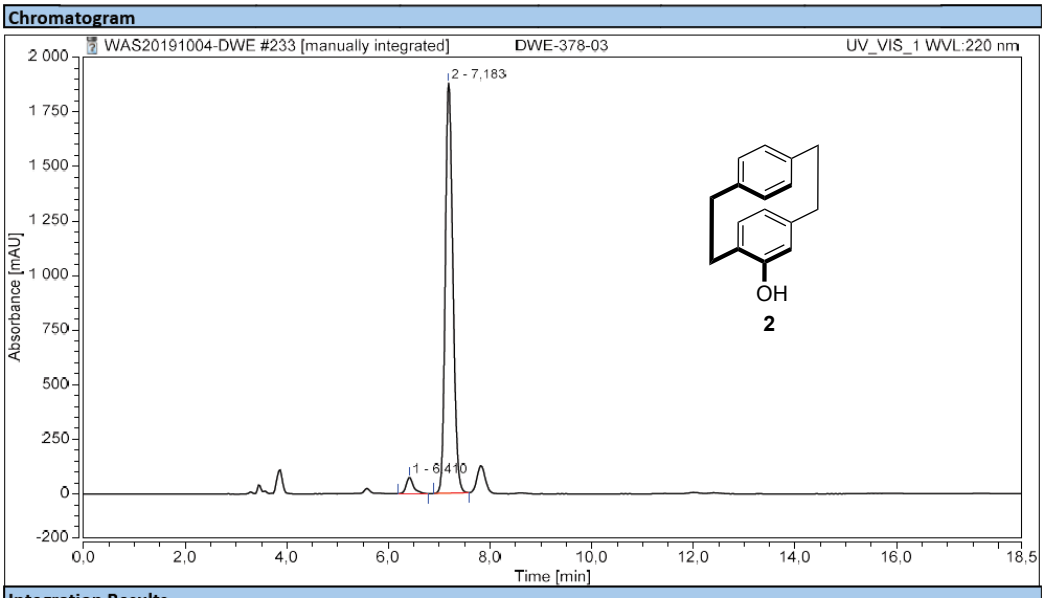
HPLC chromatogram of (*rac*)-**2**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6,393	173,282	1141,130	50,27	53,56	n.a.
2		7,163	171,449	989,582	49,73	46,44	n.a.
Total:			**344,731**	**2130,713**	**100,00**	**100,00**	

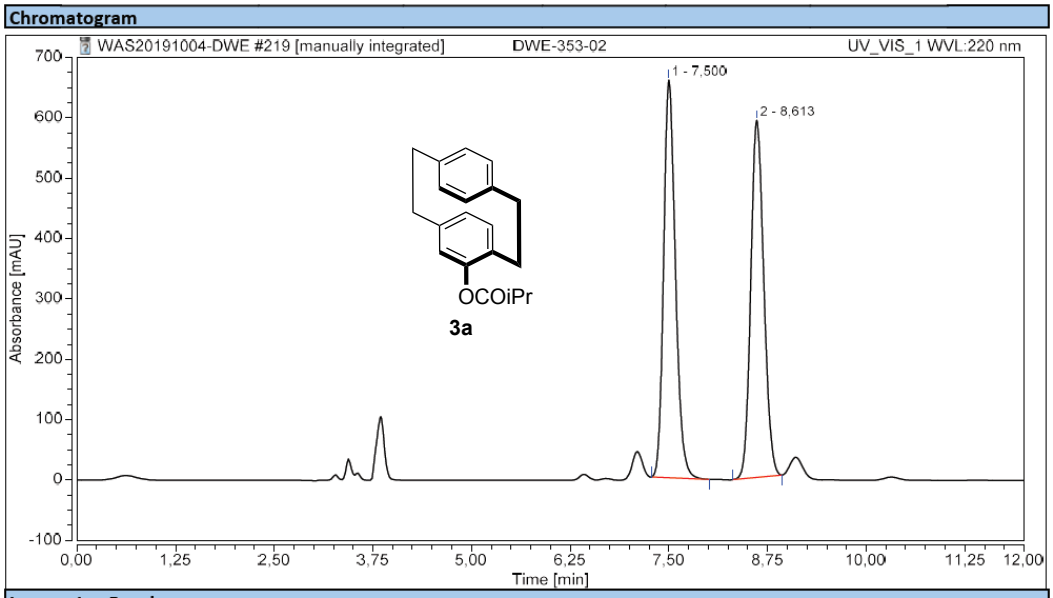
HPLC chromatogram of enantioenriched **2**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6,410	12,543	74,894	3,70	3,84	n.a.
2		7,183	326,521	1877,871	96,30	96,16	n.a.
Total:			**339,065**	**1952,765**	**100,00**	**100,00**	

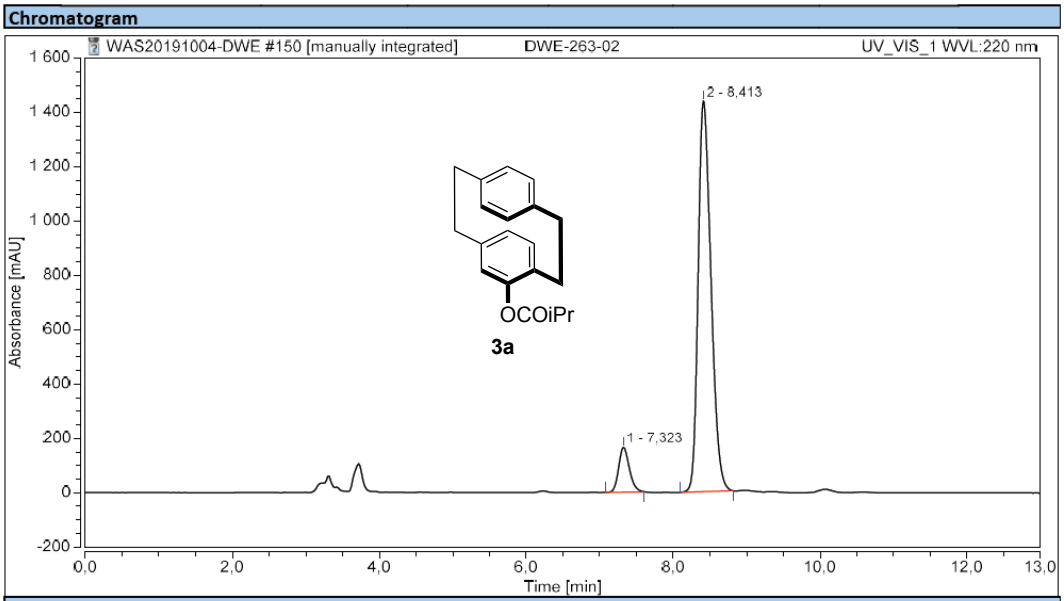
HPLC chromatogram of (*rac*)-**3a**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7,500	114,139	658,667	50,19	52,68	n.a.
2		8,613	113,277	591,646	49,81	47,32	n.a.
Total:			**227,415**	**1250,313**	**100,00**	**100,00**	

HPLC chromatogram of enantioenriched **3a**:

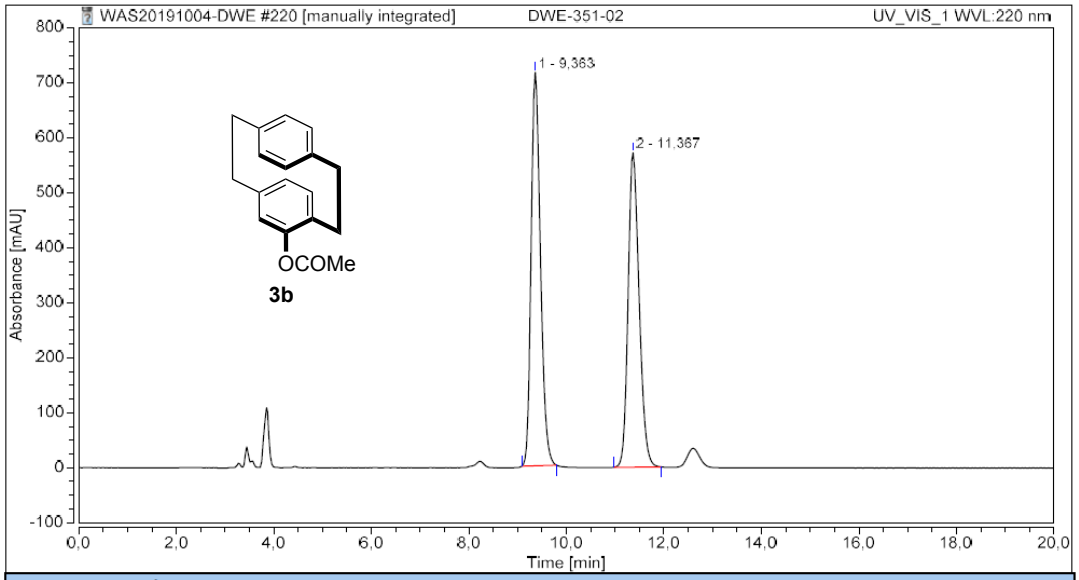


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7,323	28,033	165,559	8,84	10,32	n.a.
2		8,413	289,026	1438,841	91,16	89,68	n.a.
Total:			**317,059**	**1604,399**	**100,00**	**100,00**	

HPLC chromatogram of (*rac*)-**3b**:

Chromatogram

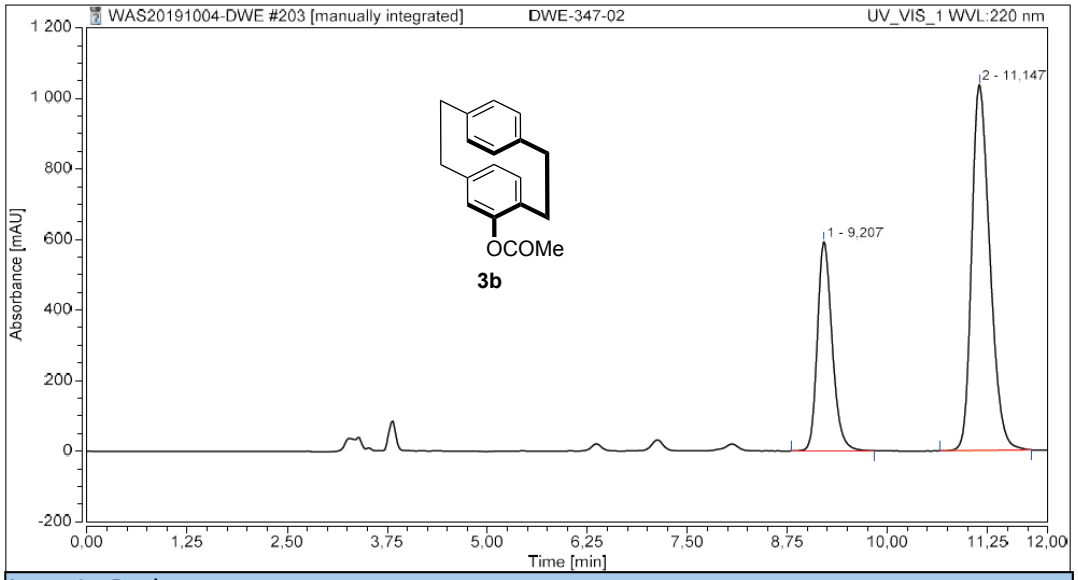


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9,363	157,712	715,335	51,05	55,55	n.a.
2		11,367	151,216	572,495	48,95	44,45	n.a.
Total:			**308,928**	**1287,830**	**100,00**	**100,00**	

HPLC chromatogram of enantioenriched **3b**:

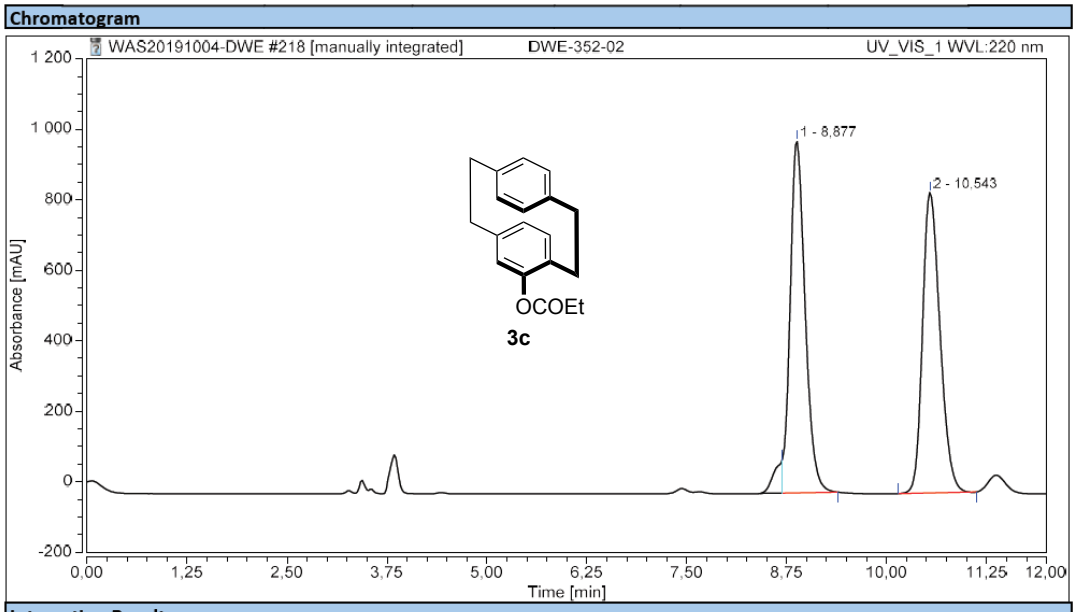
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9,207	126,281	592,306	31,64	36,36	n.a.
2		11,147	272,830	1036,724	68,36	63,64	n.a.
Total:			**399,111**	**1629,030**	**100,00**	**100,00**	

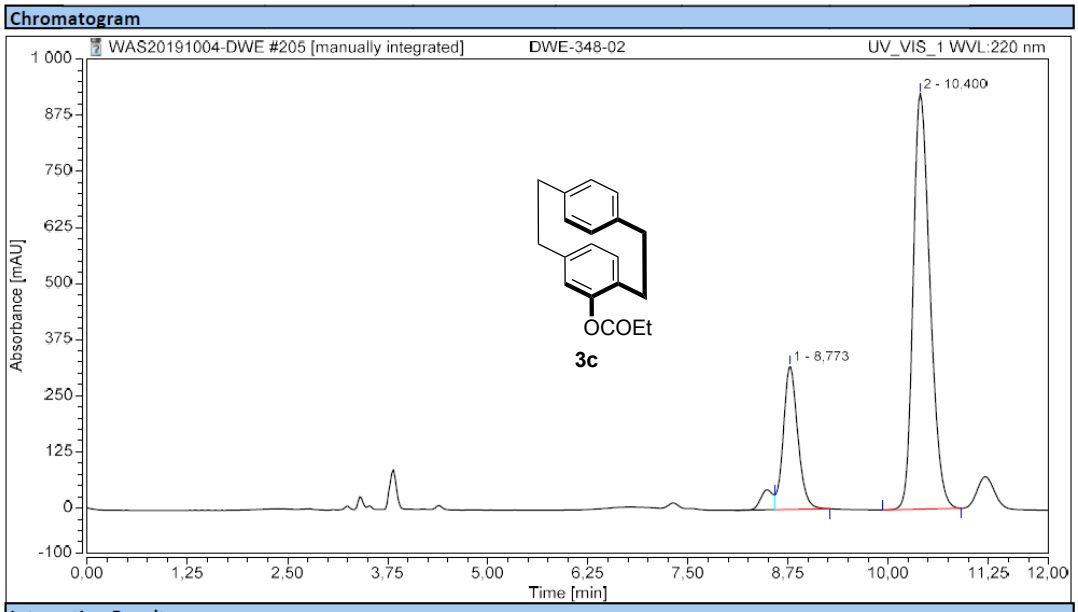
HPLC chromatogram of (*rac*)-**3c**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8,877	217,171	998,178	50,32	53,92	n.a.
2		10,543	214,397	853,039	49,68	46,08	n.a.
Total:			**431,568**	**1851,217**	**100,00**	**100,00**	

HPLC chromatogram of enantioenriched **3c**:

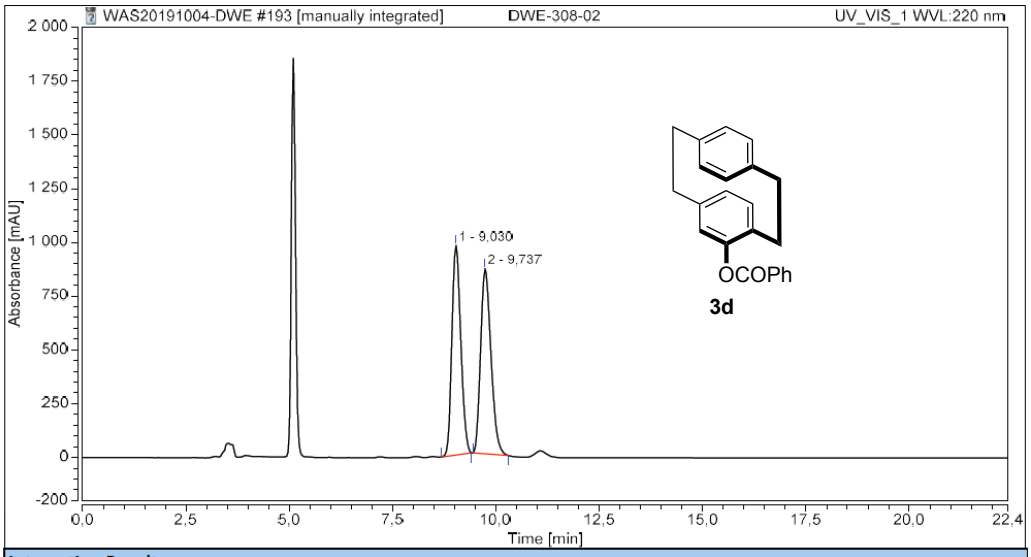


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8,773	66,695	319,623	22,78	25,65	n.a.
2		10,400	226,030	926,229	77,22	74,35	n.a.
Total:			**292,725**	**1245,852**	**100,00**	**100,00**	

HPLC chromatogram of (*rac*)-**3d**:

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9,030	243,577	975,083	49,32	53,09	n.a.
2		9,737	250,249	861,576	50,68	46,91	n.a.
Total:			**493,826**	**1836,659**	**100,00**	**100,00**	