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Functional Paracyclophanes: Synthesis of [2.2]Paracyclophanemethyldithiocarbonates Using Thione–Thiol Rearrangement of *S,O*-Dithiocarbonates (Benzyl Schönberg Rearrangement) at Mild Conditions

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Abstract: A pathway to benzylic [2.2]paracyclophane thiol derivatives was investigated using the benzyl Schönberg rearrangement.

Keywords: [2.2]paracyclophane · *S*-ligand · solid phase catalysis · sulfur · thione–thiol rearrangement

1. Introduction

[2.2]Paracyclophanes and their derivatives build an exciting class of molecules, which is of great interest for the areas of polymer science,[1] advanced materials[2,3] and catalysis.[4]

Recently, we embarked on the exploration of functionalized paracyclophanes for the generation of soft-matter surfaces suitable for reaction at biological interfaces.[5,6] The versatility of [2.2]paracyclophane chemistry, combined with the processibility of [2.2]paracyclophanes via chemical vapor deposition polymerization,[2] makes them ideal precursors for reactive polymer coatings useful in a wide range of biomedical and biotechnological applications. Due to their planar chirality, benzylic functionalized [2.2]paracyclophanes play an important role as ligands in asymmetric synthesis, for example, the addition of diethyl zinc to ketones and aldehydes.[7] Although this substance class is well-explored, there exist only a few examples of thiol-containing derivatives of [2.2]paracyclophanes.[8]

A straightforward approach towards [2.2]paracyclophanemethylthiols could be based on a thione–thiol rearrangement (benzyl Schönberg rearrangement), but this rearrangement has only been reported for alkyl and aryl xanthates under high temperatures and harsh conditions.[9,10]

Here, we report a convenient route for the preparation of (*rac*)-4-thiomethyl[2.2]paracyclophane derivatives under unusually mild reaction conditions.

The introduction of a carbonyl function to [2.2]paracyclophane can easily be achieved via electrophilic substitution using a Lewis acid, for example, aluminum trichloride. For representing investigations, the four different carbonyl compounds **1a–d** were synthesized.[11]

The corresponding alcohols **2a–d** were synthesized from **1a–d** in good yields using sodium boronhydride in ethanol or lithium aluminum hydride in dry THF.[13] The diastereomeric ratio of the resulting products can be varied by the choice of the reducing agent. The diastereomers were separated using flash chromatography.

However, the diastereomers of **2c** could not be separated with common techniques. 4-Formyl[2.2]paracyclophane (**1a**) showed an unexpected low reactivity towards sodium boronhydride, hence lithium aluminum hydride was used according to literature.[13]

The synthesized alcohols (**2b**: 2nd eluted diastereomer; **2c**: mixture; **2d**: 1st eluted diastereomer) were treated with sodium hydride, carbon disulfide, and methyl iodide

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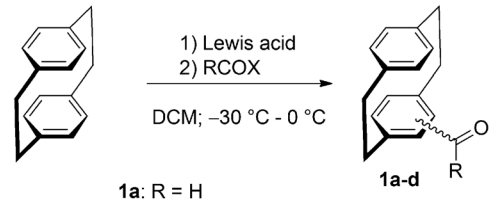
Table 1. Used substrates for the electrophilic substitution.



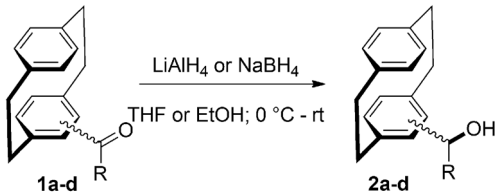
1a-d

1a: R = H
1b: R = Me
1c: R = CF_3
1d: R = Ph

Entry	Lewis acid	RCOX	Yield (%)	Product
1	$TiCl_4$	Cl_2CHOMe	96	**1a**
2	$AlCl_3$	CH_3COCl	56[a]	**1b**
3	$AlCl_3$	TFAA	92	**1c**
4	$AlCl_3$	BzCl	75	**1d**

[a] Cram et al.[12]

Table 2. Used substrates for the reduction.



1a-d **2a-d**

Starting material	Reducing agent	Reaction Time	Product	Yield (%)
1a	$LiAlH_4$	3 d	**2a**	80
1b	$LiAlH_4$	3 h	**2b**	quant.[a]
1c	$NaBH_4$	20 min	**2c**	quant.[b]
1d	$LiAlH_4$	12 h	**2d**	92[c]

[a] diastereomeric ratio = 7:10; [b] diastereomeric ratio = 7:10; [c] diastereomeric ratio = 4:3.

or benzyl bromide to give the desired *S,O*-dithiocarbonates in moderate to excellent yields.[14]

The aqueous work-up had no effect on the dithiocarbonate functionality of compounds **3a-Me** and **3a-Bn**. However, a partially rearrangement could be observed during purification (vide infra).

Moreover, the dithiocarbonate **3b-Me** already rearranged during work-up: it reacted immediately with water or semi-saturated ammonium chloride solution, which resulted in 30% loss of the product due to a Chugaev-like elimination of the dithiocarbonate. The formed 4-vinyl[2.2]paracyclophane is known in literature.[15,16]

In contrast to all other investigated substances, **3c-Me** did not rearrange, either during work-up or during purification, and could be obtained as a pure yellow solid.

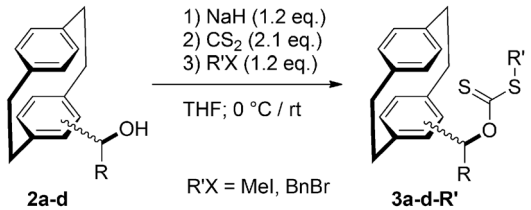
The dithiocarbonate **3d-Bn** rearranged under the influence of water or aqueous solutions, which resulted in quantitative conversion into the corresponding *S,S*-dithiocarbonates. A S_N1 mechanism, according to the strong mesomeric stabilization and size of the formed cation, can be expected. After crystallization from dichloromethane and hexane, crystals were obtained for X-ray diffraction that corroborate the postulated *S,S*-carbonate structure (Figure 1).

To ensure that the conditions for the rearrangement were comparable to the conditions during chromatographical separation, a suspension of silica gel in various solvents was chosen. To compare this method with another set of conditions, the substrates were also added to a solution acidified with acetic acid or trifluoroacetic acid, as shown in Table 4.

The diastereomeric ratio of **3c-Me** changed during the rearrangement from 7:10 to 2:13, while the diastereomeric ratio of **4c-Me** was 3:10.

The results show that silica gel can be used as an efficient catalyst for the thione–thiol rearrangement in nonpolar and aprotic solvents. In a simple work-up proce-

Table 3. Used substrates for the *S,O*-dithiocarbonate formation.



2a-d **3a-d-R'**

Starting material	R'X	Stability towards aqueous solutions	Product [a]	Yield (%)	Product [b]	Yield (%)
2a	MeI	Stable	**3a-Me**	quant.	**4a-Me**	–
2a	BnBr	Stable	**3a-Bn**	78	**4a-Bn**	–
2b	MeI	Unstable	**3b-Me**	22	**4b-Me**	43[c]
2b	MeI	–[d]	**3b-Me**	37	**4b-Me**	14[e]
2c	MeI	Stable	**3c-Me**	91	**4c-Me**	–
2d	BnBr	Unstable	**3d-Bn**	–	**4d-Bn**	87[f]

[a] *S,O*-dithiocarbonate; [b] *S,S*-dithiocarbonate; [c] diastereomeric ratio 2:11; [d] no aqueous work-up, 65% conversion of the alcohol; [e] diastereomeric ratio 1:4; [f] diastereomeric ratio 11:20.

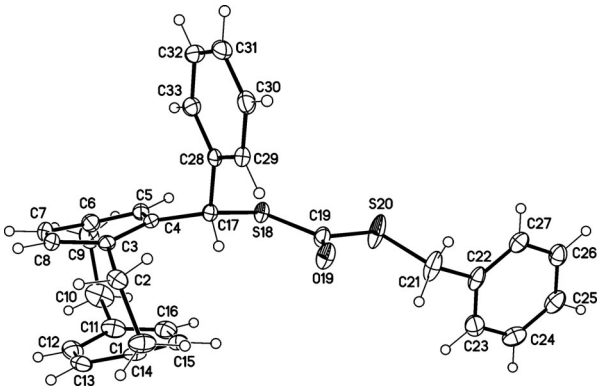


Figure 1. X-ray structure of racemic *S*-benzyl-*S*-(S_p/*S*)-([2.2]paracyclophan-4-yl)phenylmethyl dithiocarbonate (**4d-Bn**).

dure, the suspension can be filtered off with the product remaining in solution.

The rearrangement can also be catalyzed using a strong acid in low-polar solvents, but this method might not be as tolerant to acid-sensitive groups as the method mentioned above.

2. Representative Experimental Procedures

Solvents and chemicals used for reactions were ordered from VWR and used without further purification. The reactions were carried out under argon. Thin-layer chromatography (TLC) was carried out on silica gel plates (Kieselgel 60, F254, Merck) with detection by UV light.

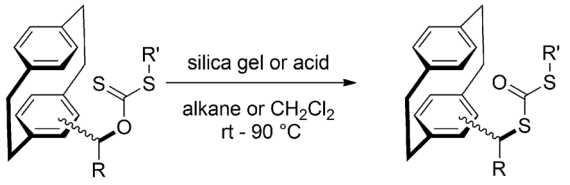
The compounds **1a-d** were synthesized according to literature.[11]

The compounds **2a–b** and **2d** were synthesized according to literature.[13]

(S_p/*R*)/(R_p/*S*) and (S_p/*S*)/(R_p/*R*)-(*rac*)-[2.2]Paracyclophan-4-yl-(trifluormethyl)methanol (2c)

(*rac*)-4-Trifluoracetyl[2.2]paracyclophane (2.40 g, 7.89 mmol, 1.00 equiv) was dissolved in 200 mL ethanol and cooled down to 0 °C. Then sodium boronhydride (310 mg, 8.19 mmol, 1.04 equiv) was added and the solution was stirred 10 min at 0 °C afterwards 10 min at room temperature. The conversion was monitored by TLC. The reaction mixture was quenched with saturated ammonium chloride solution and extracted twice with diethyl ether. The combined organic phases were washed with brine and dried over magnesium sulfate. After removal of the solvent under reduced pressure the crude product was purified using column chromatography (hexane : ethyl acetate 4 : 1) yielding 2.42 g (7.84 mmol, quant.) of a yellow, crystalline solid. Mp: 86 °C. Diastereomeric ratio 10 : 7. - Diastereomer A: ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 2.57 (d, J = 4.6 Hz, 1H, O*H*), 2.89–3.25 (m, 7H, H_{Pc}), 3.41 (ddd, J = 13.9 Hz, 9.9 Hz, 1.9 Hz, 1H, H_{Pc}), 5.43–5.50 (m, 1H, C*H*OH), 6.45–6.60 (m, 6H, H_{Ar}), 6.77 (bs, 1H, H_{Ar}). – ^{19}F NMR (500 MHz, $CDCl_3$): δ [ppm] = −78.36 (d, J = 6.8 Hz, CF_3). – Diastereomer B: ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 2.20 (d, J = 6.9 Hz, 1H, O*H*), 2.89–3.25 (m, 7H, H_{Pc}), 3.60 (ddd, J = 13.2 Hz, 9.9 Hz, 3.2 Hz, 1H, H_{Pc}), 4.97 (quint., J = 7.1 Hz, 1H, C*H*OH), 6.39 (d, J = 8.1 Hz, 1H, H_{Ar}), 6.45–6.60 (m, 6H, H_{Ar}). – ^{19}F NMR (500 MHz, $CDCl_3$): δ [ppm] = −74.99 (d, J = 7.3 Hz, CF_3). ^{13}C NMR (500 MHz, $CDCl_3$): δ [ppm] = 33.3 (−), 33.6 (−), 34.5 (−), 35.1 (−), 35.2 (−), 35.2 (−), 35.3 (−), 69.7 (+, q, J = 31.4 Hz, *C*HOH), 72.5 (+, q, J = 31.4 Hz, *C*HOH), 124.3 (q, J = 282.3 Hz, *C*F_3), 124.8 (q, J = 283.0 Hz, *C*F_3), 131.3 (+), 131.3 (+), 132.5 (+), 132.6 (+), 132.6 (+), 132.7 (+), 133.0 (+), 133.5 (+), 133.9 (+), 134.3 (+), 135.3 (+), 136.5 (+), 137.7 ($C_{quart.}$), 138.9 ($C_{quart.}$), 139.3 ($C_{quart.}$), 139.5 ($C_{quart.}$), 139.6 ($C_{quart.}$), 139.8 ($C_{quart.}$), 140.3 ($C_{quart.}$), 140.3 ($C_{quart.}$). – IR (KBr): ν [cm^{-1}] = 3545 (vw), 2925 (vw), 2852 (vw), 2349 (vw), 2330 (vw), 2325 (vw), 2161 (vw), 1986 (vw), 1594 (vw), 1498 (vw), 1346 (vw), 1261 (vw), 1166 (vw), 1120 (vw), 1051 (vw), 945 (vw), 903 (vw), 879 (vw), 837 (vw), 798 (vw), 778 (vw), 739 (vw), 718 (vw), 701 (vw), 670 (vw), 665 (vw), 641 (vw), 627 (vw), 599 (vw), 512 (vw),

Table 4. Conversion of *S,O*-dithiocarbonates into the corresponding xanthates in various solvents.



3a-Me **4a-Me**
3a-Bn **4a-Bn**
3c-Me **4c-Me**

Starting material	Solvent/Catalyst	t, T	Yield (%)	Product
3a-Me	CH_2Cl_2/TFA[a]	12 h, rt	50	**4a-Me**
3a-Me	CH_2Cl_2/AcOH[a]	16 h, rt	-	**4a-Me**
3a-Me	EtOAc/SiO_2[b]	12 h, rt	-	**4a-Me**
3a-Me	*n*-Hexane, EtOAc 15:1/SiO_2[c]	24 h, rt	67	**4a-Me**
3a-Me	*n*-Hexane/SiO_2[b]	12 h, rt	90[d]	**4a-Me**
3a-Bn	CH_2Cl_2/TFA[a]	12 h, rt	75	**4a-Bn**
3a-Bn	*n*-Hexane/SiO_2[b]	12 h, rt	quant.	**4a-Bn**
3c-Me	*n*-Hexane/SiO_2[b]	48 h, 40 °C	traces	**4c-Me**
3c-Me	*n*-Heptane	24 h, 90 °C	16	**4c-Me**

[a] Two drops of acid in 5 mL dichloromethane; [b] 2.2 g silica gel and 5 mL of solvent; [c] 1.61 g silica gel and 3.2 mL solvent; [d] 10% hydrolysis of the *S,O*-dithiocarbonate.

442 (vw), 401 (vw). – MS (70 eV, EI), *m/z* (%): 306 [M^+] (38), 202 [$C_{10}H_9F_3O^+$] (14), 104 [$C_8H_8^+$] (100). – EA $C_{18}H_{17}F_3O$ (306.12): calcd: C 70.57, H 5.59, F 18.61, O 5.22, found: C 70.52, H 5.43.

S-Methyl-*O*-((*rac*)-[2.2]paracyclophan-4-yl)methyl dithiocarbonate (3 a-Me)

(*rac*)-4-Hydroxymethyl[2.2]paracyclophane (119 mg, 0.50 mmol, 1.00 equiv) (**2 a**) was dissolved in dry THF (10 mL) and cooled to 0 °C. Sodium hydride suspension (24 mg, 0.60 mmol, 1.20 equiv) was added and the suspension was stirred at room temperature for 1 h. The reaction mixture was cooled to 0 °C and carbon disulfide (64 μL, 1.05 mmol, 2.10 equiv) was added via cannula. The yellow solution was stirred for 12 h at room temperature, cooled down to 0 °C and methyl iodide (38 μL, 0.60 mmol, 1.20 equiv) was added. After stirring for further 6 h at room temperature, the reaction mixture was washed with semi-saturated ammonium chloride solution and brine. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The product was obtained (195 mg, quant.) as a colorless waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 2.57 (s, 3 H, CH_3), 2.92 (ddd, J = 13.7 Hz, 10.8 Hz, 5.7 Hz, 1 H, H_{Pc}), 2.97–3.20 (m, 6 H, H_{Pc}), 3.33 (ddd, J = 13.6 Hz, 10.2 Hz, 2.2 Hz, 1 H, H_{Pc}), 5.37 (d, J = 12.3 Hz, 1 H, CH_2O), 5.60 (d, J = 12.3 Hz, 1 H, CH_2O), 6.39–6.44 (m, 2 H, H_{Ar}), 6.49–6.58 (m, 4 H, H_{Ar}), 6.62–6.66 (m, 1 H, H_{Ar}). - ^{13}C NMR (500 MHz, $CDCl_3$): δ [ppm] = 19.1 (+, CH_3), 33.0 (−), 34.6 (−), 35.0 (−), 35.3 (−), 74.8 (–, CH_2O), 129.9 (+), 132.3 (+), 133.1 (+), 133.2 (C_{quart}), 133.3 (+), 133.4 (+), 134.1 (+), 135.2 (+), 138.8 ($C_{quart.}$), 139.2 ($C_{quart.}$), 139.5 ($C_{quart.}$), 140.2 ($C_{quart.}$), 216.0 ($C_{quart.}$). IR (ATR): ν [cm^{-1}] = 3005 (vw), 2922 (w), 2851 (w), 1640 (vw), 1592 (w), 1498 (w), 1438 (w), 1411 (w), 1318 (vw), 1226 (w), 1188 (m), 1052 (m), 961 (w), 935 (w), 894 (w), 863 (m), 795 (m), 773 (w), 716 (m), 643 (w), 622 (w), 588 (w), 571 (w), 509 (w), 492 (w), 447 (vw), 406 (vw) cm^{-1}.– m.p.: 48 °C. – EI-MS [70 eV, *m/z* (%)]: 328 (10) [M^+], 300 (15) [M^+ -C_2H_4], 221 (100) [$C_{17}H_{17}^+$], 208 (20) [$C_{16}H_{16}^+$], 164 (29) [$C_{10}H_{12}S^+$], 149 (18) [$C_9H_9S^+$], 117 (35) [$C_9H_9^+$], 104 (95) [$C_8H_8^+$], 91 (22) [$C_7H_7^+$]. – HR-MS (EI): 328.0956 (calculated for [M^+], $C_{19}H_{20}OS_2$), 328.0953 (observed).

S-methyl-*O*-((*rac*)-[2.2]paracyclophan-4-yl)(trifluormethyl)methyl dithiocarbonate (3 c-Me)

Sodium hydride suspension (48 mg, 1.2 mmol, 1.2 equiv) was added to a solution of (*rac*)-[2.2]paracyclophan-4-yl)(trifluoromethyl)methanol (306 mg, 1.0 mmol, 1.0 equiv) (**2 a**) in 20 mL dry THF at 0 °C. After stirring at room temperatue for 1 h the reaction mixture was cooled to 0 °C and carbon disulfide (0.13 mL, 2.1 mmol, 2.1 equiv) was added. The solution was warmed to room temperature and stirred for 12 h. Next methyl iodide (81 μL, 1.3 mmol, 1.3 equiv) was added at 0 °C. The solution was stirred for 3 h and quenched with diethyl ether and water. The organic layer was washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified using flash chromatography (hexane : ethyl acetate 15 : 1). A pale yellow solid was obtained in 91 % yield (360 mg, 0.91 mmol). Diastereomeric ratio 7:10. – ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 2.72 (s, 3 H, CH_3), 2.79 (s, 3 H, CH_3), 2.93–3.10 (m, 7 H, H_{Pc}), 3.11–3.23 (m, 7 H, H_{Pc}), 3.53 (ddd, J = 13.8 Hz, 6.8 Hz, 5.6 Hz, 1 H, H_{Pc}), 3.58–3.65 (m, 1 H, H_{Pc}), 6.25–6.29 (m, 2 H, H_{Ar}), 6.33–6.35 (m, 2 H, H_{Ar}), 6.48–6.11 (m, 9 H, H_{Ar}), 6.84 (s, 1 H, H_{Ar}), 7.15 (q, J = 7.3 Hz, 1 H, CH), 7.55 (q, J = 6.3 Hz, 1 H, CH). – ^{13}C NMR (500 MHz, $CDCl_3$): δ [ppm] = 19.9 (+, CH_3), 33.1 (−), 34.2 (−), 34.8 (−), 34.9 (−), 35.2 (−), 35.2 (−), 35.3 (−), 35.5 (−), 75.0 (+, q, J = 32.6 Hz, 1 H, CHO), 79.3 (+, q, J = 32.8 Hz, 1 H, CHO), 124.3 (d, J = 282.4 Hz, CF_3), 124.8 (d, J = 282.4 Hz, CF_3), 126.1 ($C_{quart.}$), 128.1($C_{quart.}$), 131.7 (+), 132.1 (+), 132.3 (+), 132.6 (+), 132.6 (+), 132.7 (+), 133.0 (+), 133.0 (+), 134.7 (+), 135.0 (+), 135.4 ($C_{quart.}$), 135.5 ($C_{quart.}$), 136.9 ($C_{quart.}$), 139.1 ($C_{quart.}$), 139.4 ($C_{quart.}$), 139.4 ($C_{quart.}$), 140.1 (+), 140.3 ($C_{quart.}$), 140.4 ($C_{quart.}$), 216.0 ($C_{quart.}$, COS_2), 216.3 ($C_{quart.}$, COS_2). – ^{19}F NMR (500 MHz, $CDCl_3$): δ [ppm] = −75.38 (d, J = 6.6 Hz, 3F, CF_3), −73.84 (d, J = 7.2 Hz, 3F, CF_3). – IR (KBr): ν [cm^{-1}] = 2956 (vw), 1594 (vw), 1497 (vw), 1412 (vw), 1361 (vw), 1270 (w), 1166 (w), 1128 (w), 1055 (w), 966 (vw), 859 (vw), 805 (w), 719 (vw), 707 (w), 691 (vw), 671 (vw), 631 (w), 588 (vw), 530 (vw), 513 (w), 496 (vw). – UV/VIS ($CHCl_3$): λ_{max} [nm] (A) = 235 (3.49), 277 (3.27), 280 (3.53), 282 (3.58), 289 (2.97). – MS (70 eV, EI), *m/z* (%): 396 [M^+] (2), 336 [$C_{19}H_{19}F_3S^+$] (37), 289 [$C_{18}H_{16}F_3^+$] (23), 185 [$C_{10}H_8F_3^+$] (24), 104 [$C_8H_8^+$] (100), 91 [$C_2H_3S_2^+$] (22). HR-MS (EI): 396.0829 (calculated for [M^+], $C_{20}H_{19}OS_2F_3$), 396.0832 (observed). – EA $C_{20}H_{19}F_3OS_2$ (396.10): calcd: C 60.58, H 4.83, S 16.17, found: C 61.52, H 4.92, S 16.82.

S-Methyl-*S*-((*rac*)-[2.2]paracyclophan-4-yl)methyl dithiocarbonate (4 a-Me)

S-Methyl-*O*-((*rac*)-[2.2]paracyclophan-4-yl)methyl dithiocarbonate (**3 a**) (40.0 mg, 0.12 mmol) was added to a suspension of 2.2 g silica gel in hexane (5 mL) and stirred for 12 h at room temperature. The reaction mixture was filtered and rinsed with 10 mL dichloromethane. After removal of the solvent a yellow solid was obtained (38 %, 90 %) and the yield was ascertained using NMR spectroscopy.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 2.44 (s, 3 H, CH_3), 2.85 (ddd, J = 13.8 Hz, 10.8 Hz, 6.1 Hz, 1 H, H_{Pc}), 2.94–3.11 (m, 4 H, H_{Pc}), 3.17 (ddd, J = 13.2 Hz, 10.8 Hz, 2.0 Hz, 1 H, H_{Pc}), 3.35 (ddd, J = 13.7 Hz, 10.3 Hz, 2.1 Hz, 1 H, H_{Pc}), 4.02 (d, J = 13.4 Hz, 1 H, CH_2S), 4.19 (d. J = 13.4 Hz, 1 H, CH_2S), 6.28 (m, 1 H, H_{Ar}), 6.41–6.46 (m, 2 H, H_{Ar}), 6.48 (cm, 2 H, H_{Ar}), 6.52 (dd, J = 7.8 Hz, 1.8 Hz, 1 H, H_{Ar}), 6.70 (dd, J = 1.9 Hz, 7.8 Hz, 1 H, H_{Ar}).– ^{13}C NMR (500 MHz, $CDCl_3$): δ [ppm] = 13.1 (+, CH_3), 33.3 (−), 33.7 (−), 34.3 (−), 34.9 (−), 35.3 (−), 129.0 (+), 132.2 (+), 132.2 (+), 133.2 (+), 133.4 (+),135.0 (+), 135.0 (+), 135.2 (+), 138.0 ($C_{quart.}$), 139.2 ($C_{quart.}$),139.5 ($C_{quart.}$), 140.3 ($C_{quart.}$), 189.9 ($C_{quart.}$, COS_2). – EI-MS [70 eV, *m/z* (%)]: 328 (5) [M^+], 268 (100) [M^+ -COS], 253 (70) [$C_{17}H_{17}S^+$], 221 (32) [$C_{17}H_{17}^+$], 220 (69) [$C_{17}H_{16}^+$], 207 (23) [$C_{16}H_{15}^+$], 164 (53) [$C_{10}H_{12}S^+$], 149 (71) [C_9H_9S], 118 (40) [$C_9H_{10}^+$], 117 (28) [$C_9H_9^+$], 104 (46) [$C_8H_8^+$], 91 (33) [$C_7H_7^+$]. – HR-MS (EI): 328.0956 (calculated for [M^+], $C_{19}H_{20}OS_2$), 328.0957 (observed). - IR (KBr): ν [cm^{-1}] = 2924 (w), 2850 (vw), 1700 (w), 1634 (m), 1592 (vw), 1498 (w), 1412 (w), 1309 (vw), 1179 (vw), 1132 (w), 1047 (vw), 971 (w), 944 (vw), 907 (w), 868 (w), 847 (m), 794 (w), 751 (vw), 716 (w), 694 (vw), 639 (w), 590 (w), 572 (vw), 511 (w), 486 (w), 411 (vw). - EA $C_{19}H_{20}OS_2$ (328.10): calcd: C 69.47, H 6.14, O 4.87, S 19.52, found: C 70.14, H 6.18, S 18.43.

(S_p/*R*)/(R_p/*S*) and (S_p/*S*)/(R_p/*R*)-*S*-Benzyl-*S*-(*rac*)-[2.2]paracyclophan-4-ylphenylmethyldithiocarbonate (4 d-Bn)

1.74 g (5.53 mmol, 1.00 equiv) (*rac*)-[2.2]Paracyclophan-4-ylphenylmethanol were dissolved in 50 mL dry THF and cooled down to 0 °C. After the addition of sodium hydride suspension (270 mg, 6.64 mmol, 1.20 equiv) in small portions, the reaction mixture was stirred for 1 h at room temperature. The suspension was cooled to 0 °C and carbon disulfide (0.75 mL, 11.7 mmol,

0.89 g, 2.10 equiv) was added dropwise via cannula. The reaction mixture was vigorously stirred at room temperature for 12 h. After cooling to 0 °C benzyl bromide (0.85 mL, 7.19 mmol, 1.23 g, 1.30 equiv) was slowly added. The mixture was stirred for 3 h at room temperature and then quenched with water and diethyl ether. The aqueous phase was separated and extracted with dichloromethane. The combined organic layers were washed with brine and dried over magnesium sulfate. After removal of the solvent under reduced pressure a pale, yellow, slowly hardening solid remained. The residue was purified using column chromatography (hexane : ethyl acetate 15 : 1) yielding the product as a yellow solid (2.30 g, 4.81 mmol, 87 %). Diastereomeric ratio 20 : 11. A separate analysis of the two diastereomers was not possible. – ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 2.62–2.73 (m, 1 H, H_{Pc}), 2.77–3.28 (m, 6 H, H_{Pc}), 3.48 (ddd, J = 2.7 Hz, 10.3 Hz, 14.1 Hz, 1 H, H_{Pc}), 4.07 (d, J = 13.5 Hz, 1 H, CH_2Ph), 4.19 (d, J = 13.7 Hz, 1 H, CH_2Ph), 5.82 (s, 1 H, CH), 6.52 (dd, J = 1.6 Hz, 7.9 Hz, 1 H, H_{Ar}), 6.97–7.49 (m, 10 H, H_{Ar}); 2.62–2.73 (m, 1 H, H_{Pc}), 2.77–3.28 (m, 7 H, H_{Pc}), 4.23 (d, J = 13.5 Hz, 1 H, CH_2Ph), 4.33 (d, J = 13.7 Hz, 1 H, CH_2Ph), 5.89–5.92 (m, 1 H, CO), 6.14 (s, 1 H, H_{Ar}), 6.63 (dd, J = 1.3 Hz, 8.0 Hz, 1 H, H_{Ar}), 6.39–6.49 (m, 5 H, H_{Ar}), 6.97–7.49 (m, 10 H, H_{Ar}). – ^{13}C NMR (500 MHz, $CDCl_3$): δ [ppm] = 33.7 (–), 34.5 (–), 34.7 (–), 34.8 (–), 35.0 (–), 35.2 (–), 35.3 (–), 50.6 (–), 52.8 (–), 127.0 (+), 127.5 (+), 127.6 (+), 127.7 (+), 127.8 (+), 128.5 (+), 128.6 (+), 128.7 (+), 128.8 (+), 128.8 (+), 128.9 (+), 129.0 (+), 129.3 (+), 129.5 (+), 129.8 (+), 130.7 (+), 131.6 (+), 132.3 (+), 132.4 (+), 132.6 (+), 132.7 (+), 132.8 (+), 132.9 (+), 133.0 (+), 133.10 (+), 135.9 (+), 136.4 ($C_{quart.}$), 136.6 ($C_{quart.}$), 136.7 ($C_{quart.}$), 137.2 ($C_{quart.}$), 137.4 ($C_{quart.}$), 138.6 ($C_{quart.}$), 139.3 ($C_{quart.}$), 139.4 ($C_{quart.}$), 139.4 ($C_{quart.}$), 139.7 ($C_{quart.}$), 140.0 ($C_{quart.}$), 140.2 ($C_{quart.}$), 143.1 ($C_{quart.}$), 188.3 ($C_{quart.}$). - UV/VIS ($CHCl_3$): λ_{max} [nm] (A) = 227 (1.59), 232 (2.50). - MS (70 eV, EI), m/z: No M^+ peak could be detected. The structure was verified using X-ray diffraction (Figure 1; CCDC-830691).

3. Summary

A method for the synthesis of benzylic *S,S*-[2.2]paracyclophanemethyldithiocarbonates using *S,O*-dithiocarbonates was described. The precursors can be prepared in good yields. The thione–thiol rearrangement leading to the desired products can be catalyzed with silica gel and works even at room temperature.

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