Stereoselective Functionalization of Cyclopropane Derivatives Using Bromine/Magnesium and Sulfoxide/Magnesium Exchange Reactions

Supporting Information

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General: All reactions were carried out under an argon atmosphere in dried glassware using Schlenk techniques. All starting materials were purchased from commercial sources and used without further purification. 2,2-dibromo-1-methylcyclopropanecarbonitrile¹ (see also procedure below), *N*-(1*H*-1,2,3-benzotriazol-1-ylmethyl)-*N,N*-diethylamine² *S*-phenyl benzenesulfonothioate³ and CuCN·2LiCl in THF⁴ were prepared according to literature procedures. Bromoform was washed with water, dried (K₂CO₃) and distilled under reduced pressure; it was stored under an argon atmosphere over silver wool and under exclusion of light. Benzaldehyde was distilled under reduced pressure before use. Dichloromethane was pre-dried over calcium hydride and afterwards distilled from fresh calcium hydride. *i*-PrMgCl in Et₂O was prepared using the standard procedure for insertion of magnesium. Yields refer to isolated yields of compounds estimated to be >95 % pure by GC/NMR.

¹Dehmlow, E. V.; Lissel, M.; Heider, J. *Tetrahedron* **1977**, 33, 363.

²Katritzky, A.R.; Yannakopoulou, K.; Kuzmierkiewicz, W.; Aurecochea, J. M.; Palenik, G. J.; Koziol A. E.; Szczesniak, M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2673.

³Fujili, K.; Tanifuji, N.; Sasaki, Y.; Yokoyama, T. *Synthesis* **2002**, 343.

1. Preparation of the functionalized cyclopropanes of type 3

Preparation of the starting material, 2,2-dibromo-1-methylcyclopropanecarbonitrile (1) (according to Lit 1):

To a solution of methacrylnitrile (2.01 g, 30.0 mmol) and benzyltriethylammonium chloride (68 mg, 3.0 mmol, 1 mol%) in bromoform (5.20 mL, 60.0 mmol, 2.00 equiv) an aqueous solution of sodium hydroxide (12.0 g, 150 mmol, 5.00 equiv 50 % w/w) was added slowly under vigorous stirring. The flask was covered with aluminum foil to prevent eventual decomposition by sunlight. Then, the solution was stirred for 12 h at room temperature. The crude mixture was extracted with dichloromethane (3 x 40 mL) and the combined organic layers were washed with a saturated aqueous solution of NH_4Cl . After drying (Na_2SO_4) the solvent was removed *in vacuo* and the crude product was subsequently purified by distillation (78-80 °C /1.0 mbar) to give 2,2-dibromo-1-methylcyclo-propanecarbonitrile as colorless oil (6.34 g, 88%).

$^1\text{H-NMR}$ (CDCl_3 , 200 MHz): δ [ppm] = 2.23 (d, 1 H, J = 8.00 Hz); 1.77 (d, 1 H, J = 8.00 Hz); 1.68 (s, 3H).

MS (EI): m/z (%) = 239 ($\text{M}^+ [^{81}\text{Br}]$, 4); 237 ($\text{M}^+ [^{79}\text{Br}]$, 2); 225 (18); 224 (36); 222 (18); 186 (3); 172 (5); 160 (98); 158 (100); 133 (30); 131 (30); 107 (5); 105 (5); 93 (3); 78 (16); 51 (12).

Typical procedure for the preparation of functionalized cyclopropane carbonitriles of type 3 (TP1):

i-PrMgCl (2.20 mmol, 1.10 equiv; 2.56 M solution in Et_2O) was added dropwise to a solution of 2,2-dibromo-1-methylcyclopropanecarbonitrile (2.00 mmol) in dichloromethane (4 mL) at -50 °C and stirred for 5 min at this temperature (To our experience, the exchange reaction is practically finished when the complete amount of *i*-PrMgCl is added. A reaction time of more than 10 min should be avoided, as by time obviously the decomposition of the carbenoid begins, which can result in lower yields). Then, the electrophile (1.20 equiv) was added neat and the reaction mixture

⁴ Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. J. *Org. Chem.* **1988**, 53, 2390.

was allowed to warm up to r.t. The reaction was followed by GCMS-analysis of reaction aliquots. After the conversion was complete, a saturated aqueous solution of ammonium chloride (10 mL) was added, and the resulting mixture was extracted with dichloromethane (4 x 15 mL). The combined organic layers were dried (Na₂SO₄) and evaporated *in vacuo*. The crude residue was purified by flash column chromatography.

Preparation of 2-bromo-1-methylcyclopropanecarbonitrile (3a): According to **TP 1** the magnesium carbenoid **2** was prepared from 2,2-dibromo-1-methylcyclopropanecarbonitrile (**1**) (478 mg, 2.00 mmol) and at -50 °C quenched by addition of sat. aq. NH₄Cl (2 mL, then workup as described in **TP1**). Flash column chromatography (silica; CH₂Cl₂) afforded **3a** as a colorless oil (243 mg, 1.52 mmol, 76 %).

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 3.45 (dd, 1 H, ³J = 5.71 Hz, ³J = 8.38 Hz); 1.86 (dd, 1 H, ²J = 6.90 Hz, ³J = 8.38 Hz); 1.53 (s, 1H); 1.09 (dd, 1 H, ²J = 6.90 Hz, ³J = 5.71 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 121.4; 25.6; 23.6; 18.4; 9.7.

IR (KBr): ν [cm⁻¹] = 3452 (w); 3093 (m); 3065 (m); 2979 (m); 2939 (m); 2876 (w); 2239 (vs); 1725 (m); 1600 (w); 1458 (s); 1434 (s); 1386 (m); 1310 (s); 1273 (m); 1212 (s); 1087 (m); 1052 (m); 958 (m); 936 (m); 893 (m); 832 (m); 665 (m); 639 (s); 536 (m).

MS (EI): m/z (%) = 162 ([M+1H]⁺ [⁸¹Br], 1); 160 ([M+1H]⁺ [⁷⁹Br], 1); 146 (5); 144 (5); 108 (2); 106 (2); 95 (2); 93 (2); 81 (6); 80 (100); 64 (4); 53 (76); 52 (5); 51 (6).

HR-MS: (C₅H₇BrN, [M+1H]⁺) calculated: 159.9762 found: 159.9756.

GCMS of crude reaction mixture:

Abundance

Time-->

Abundance

m/z-->

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. %	% of max.	% of total	
1	2.753	282	291	339	BV	2449224	76691912	100.00%	90.656%		} product, isomer 1
2	3.033	339	340	396	VV	72112	6184811	8.06%	7.311%		
3	3.673	438	452	460	BV 2	14616	478290	0.62%	0.565%		product, isomer 2

^1H -NMR of pure product:

^{13}C -NMR of pure product:

HSQC experiment:

NOESY NMR experiment:

Preparation of 2-bromo-2-iodo-1-methylcyclopropanecarbonitrile (3b):

According to **TP 1** the magnesium carbenoid **2** was prepared from 2,2-dibromo-1-methylcyclopropanecarbonitrile (**1**) (478 mg, 2.00 mmol) and at -50 °C reacted with iodine (610 mg, 2.40 mmol, 1.20 equiv). In this case, the diastereoisomers were separable neither on GC nor on preparative column. After workup and gel filtration (silica; CH₂Cl₂) **3b** was isolated as a yellowish oil (441 mg, 1.54 mmol, 77 %), consisting of 2 diastereoisomers. The diastereomeric ratio was determined from the ¹H-NMR (see below).

¹H-NMR (CDCl₃, 300 MHz) (main diastereoisomer): δ [ppm] = 2.18 (d, 1 H, *J* = 8.13 Hz); 1.88 (d, 1 H, *J* = 8.13 Hz); 1.67 (s, 3 H).

¹³C-NMR (CDCl₃, 75 MHz) (main diastereoisomer): δ [ppm] = 121.2; 37.3; 25.7; 22.1; 20.6.

IR (KBr): ν [cm⁻¹] = 3082 (w); 3000 (w); 2934 (w); 2239 (vs); 1637 (m); 1446 (m); 1428 (m); 1383 (w); 1240 (w); 1085 (m); 1060 (m); 1023 (s); 945 (m); 894 (w); 819 (w); 693 (s); 668 (m); 576 (m).

MS (EI): *m/z* (%) = 287 (M⁺[⁸¹Br], 66); 285 (M⁺[⁷⁹Br], 68); 272 (13); 270 (13); 220 (8); 218 (8); 208 (4); 206 (10); 179 (12); 160 (97); 158 (100); 133 (55); 131 (56); 128 (4); 127 (43); 107 (8); 105 (8); 95 (4); 93 (5); 79 (11); 78 (49); 64 (10); 63 (5); 52 (32); 51 (43); 50 (13).

HR-MS: (C₅H₅BrIN) calculated: 284.8650 found: 284.8654.

^1H -NMR of pure product:

Zoom on aliphatic region:

^{13}C -NMR of pure product:

Preparation of 2-bromo-1-methyl-2-(methylsulfonyl)cyclopropanecarbonitrile (3c):

According to **TP 1** the magnesium carbenoid **2** was prepared from 2,2-dibromo-1-methylcyclopropanecarbonitrile (**1**) (478 mg, 2.00 mmol) and at -50 °C reacted with MeSSO₂Me (302 mg, 2.40 mmol, 1.20 equiv). Column chromatography (silica; gradient pentane/Et₂O 50:1 to 30:1) afforded **3c** as yellow oil (297 mg, 1.44 mmol, 72 %).

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 2.41 (s, 3H); 1.97 (d, 1 H, *J* = 6.98 Hz); 1.67 (s, 3H); 1.59 (d, 1 H, *J* = 6.98 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 119.5; 45.2; 33.2; 22.7; 22.4; 16.3.

IR (KBr): ν [cm⁻¹] = 3087 (m); 2976 (m); 2923 (s); 2854 (m); 2283 (vs); 1729 (w); 1424 (vs); 1384 (m); 1319 (w); 1246 (w); 1088 (m); 1044 (s); 976 (m); 946 (m); 896 (w); 832 (m); 739 (s); 708 (m); 676 (m); 602 (w).

MS (EI): *m/z* (%) = 207 (M⁺[⁸¹Br], 28); 205 (M⁺[⁷⁹Br], 27); 192 (32); 190 (31); 140 (5); 138 (5); 127 (7); 126 (100); 125 (19); 123 (19); 111 (7); 110 (12); 99 (20); 96 (9); 84 (5); 80 (12); 78 (14); 65 (9); 58 (8); 51 (5).

HR-MS: (C₆H₈BrNS) calculated: 204.9561 found: 204.9564.

GCMS of crude reaction mixture:

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. %	% of max.	% of total	
3	3.388	400	404	527	VV	1458150	105175417	18.85%	12.985%		electrophile xs
4	4.406	575	582	682	PV 2	12656282	557842438	100.00%	68.871%		product, isomer 1
5	5.006	682	687	787	VB 4	349853	40783922	7.31%	5.035%		product, isomer 2

^1H -NMR of pure product:

^{13}C -NMR of pure product:

Preparation of 2-bromo-1-methyl-2-(phenylsulfanyl)cyclopropane-carbonitrile (3d):

According to **TP 1** the magnesium carbenoid **2** was prepared from 2,2-dibromo-1-methylcyclopropanecarbonitrile (**1**) (478 mg, 2.00 mmol) and at -50 °C reacted with PhSSO₂Ph (600 mg, 2.40 mmol, 1.20 equiv). Column chromatography (silica; CH₂Cl₂/pentane 1:1) afforded **3d** as colorless, crystalline solid (461 mg, 1.72 mmol, 86 %).

mp: 65.0-66.0 °C.

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 7.57 (m, 5 H); 2.07 (d, 1 H, *J* = 7.03 Hz); 1.71 (s, 3H); 1.65 (d, 1 H, *J* = 7.03 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 132.0; 130.9; 129.1; 128.2; 119.4; 42.9; 32.7; 23.0; 22.1.

IR (KBr): ν [cm⁻¹] = 3131 (w); 3080 (m); 3066 (w); 3001 (w); 2981 (w); 2934 (w); 2234 (s); 1949 (w); 1884 (w); 1866 (w); 1799 (w); 1733 (w); 1642 (w); 1584 (s); 1483 (s); 1450 (m); 1441 (m); 1430 (m); 1384 (m); 1302 (w); 1249 (w); 1185 (w); 1159 (w); 1087 (m); 1075 (m); 1048 (m); 1025 (m); 998 (w); 986 (m); 967 (m); 952 (m); 899 (w); 831 (w); 742 (vs); 699 (m); 690 (s); 673 (m); 616 (w); 608 (w); 480 (w); 460 (w).

MS (EI): *m/z* (%) = 269 (M⁺[⁸¹Br], 6); 267 (M⁺[⁷⁹Br], 5); 189 (14); 188 (100); 173 (5); 172 (5); 161 (33); 154 (6); 135 (7); 134 (31); 131 (8); 130 (70); 129 (4); 128 (12); 121 (42); 111 (5); 110 (20); 109 (32); 91 (12); 78 (7); 77 (20); 69 (11).

HR-MS: (C₁₁H₁₀BrNS) calculated: 266.9717 found: 266.9745.

GCMS of reaction mixture:

Abundance

Time-->
Abundance

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	% of total
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5	6.636	965	971	995	VV	15011135	187123666	100.00%	68.397%
6	6.797	995	999	1004	VV	602084	9534299	5.10%	3.485%
7	6.848	1004	1008	1053	VB	497426	21575012	11.53%	7.886%

product, isomer 1
product, isomer 2

diphenyl disulfide

^1H -NMR of pure product:

^{13}C -NMR of pure product:

X-ray data (Crystal was obtained by crystallization from chloroform) :

M_r = 268.17, monoclinic, space group $P2_1/c$, $a = 10.1973(11)$ Å, $b = 15.796(2)$ Å, $c = 7.0016(14)$ Å, $V = 1122.4(3)$ Å³, $Z=4$, $\rho_{\text{calcd}} = 1.587$ g/cm³, $\text{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 3.808$ mm⁻¹. Data were collected on a NONIUS MACH3 system at 295 K. The structure was solved by direct methods (SHELXS-86, SHELXL-97). All non-hydrogen atoms were refined anisotropically. $R_1 = 0.0420$, $\omega R_2 = 0.1044$ for all data with $I > 2\sigma(I)$. CCDC 275462 contains the supplementary crystallographic data for this paper. These data can be [obtained online](#) free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Preparation of 2-bromo-2-[(diethylamino)methyl]-1-methylcyclopropanecarbonitrile (3e):

According to **TP 1** the magnesium carbenoid **2** was prepared from 2,2-dibromo-1-methylcyclopropanecarbonitrile (**1**) (478 mg, 2.00 mmol) and at -50 °C reacted with *N*-(1*H*-1,2,3-benzotriazol-1-ylmethyl)-*N,N*-diethylamine (490 mg, 2.40 mmol, 1.20 equiv). Column chromatography (silica; pentane/Et₂O 9:1) afforded **3e** as colorless oil (389 mg, 1.58 mmol, 79 %).

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 3.02 (d, 1 H, *J* = 14.71 Hz); 2.88 (d, 1 H, *J* = 14.71 Hz); 2.66 (q, 4 H, *J* = 7.16 Hz); 1.79 (d, 1 H, *J* = 6.75 Hz); 1.65 (s, 3 H); 1.29 (d, 1 H, *J* = 6.75 Hz); 1.02 (t, 6 H, *J* = 7.16 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 120.3; 60.9; 46.1; 42.9; 28.4; 21.4; 15.5; 11.1.

IR (KBr): ν [cm⁻¹] = 3086 (w); 271 (vs); 2936 (s); 2874 (m); 2812 (m); 2236 (m); 1455 (m); 1385 (m); 1344 (w); 1295 (w); 1207 (m); 1184 (m); 1145 (w); 1070 (s); 1004 (w); 955 (w); 898 (w); 771 (m); 680 (w); 663 (w); 575 (w).

MS (EI): *m/z* (%) = 246 (M⁺[⁸¹Br], 4); 244 (M⁺[⁷⁹Br], 3); 231 (21); 229 (24); 149 (3); 135 (7); 92 (3); 87 (4); 86 (100); 65 (3); 58 (12); 56 (5); 42 (5).

HR-MS: (C₁₀H₁₇BrN₂) calculated: 244.0575 found: 244.0574.

GCMS of crude reaction mixture:

Abundance

Abundance

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	% of total
2	2.969	327	329	366	rBV	417947	1207850	13.92%	10.593%
3	5.312	735	739	773	rBV	5532453	8676375	100.00%	76.093%
4	5.992	854	858	882	rBV	90870	373092	4.30%	3.272%

decane (int. standard)

product, isomer 1

product, isomer 2

^1H -NMR of pure product:

^{13}C -NMR of pure product:

Preparation of 2-allyl-2-bromo-1-methylcyclopropanecarbonitrile (3f):

According to **TP 1** the magnesium carbenoid **2** was prepared from 2,2-dibromo-1-methylcyclopropanecarbonitrile (**1**) (478 mg, 2.00 mmol). At -50 °C allyl bromide (290 mg, 2.40 mmol, 1.20 equiv) and subsequently CuCN·2LiCl (0.01 mL; 0.5 mol%; 1 M solution in THF) was added. After 5 min at -50 °C the solution was warmed up to r.t.; workup was done as described in **TP1**. Column chromatography (silica; pentane/CH₂Cl₂ 19:1) afforded **3f** as colorless oil (311 mg, 1.56 mmol, 78 %).

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 5.93 (m, 1 H); 5.25 (m, 2 H); 2.76 (d, 2 H, *J* = 6.70 Hz); 1.65 (s, 3H); 1.59 (d, 1 H, *J* = 6.95 Hz); 1.29 (d, 1 H, *J* = 6.95 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 133.3; 120.8; 119.5; 45.2; 43.4; 30.0; 21.8; 16.9.

IR (KBr): ν [cm⁻¹] = 3084 (m); 2981 (m); 2937 (s); 2237 (vs); 1644 (m); 1430 (s); 1385 (m); 1320 (w); 1290 (w); 1259 (w); 1146 (m); 1041 (m); 993 (s); 926 (s); 693 (w); 641 (w).

MS (EI): *m/z* (%) = 200 (M⁺, 3); 160 (5); 158 (5); 134 (91); 132 (100); 120 (9); 104 (5); 93 (19); 91 (11); 77 (12); 67 (7); 65 (7); 53 (15); 41 (7).

HR-MS: (C₈H₁₀BrN) calculated: 198.9997 found: 198.9984.

GCMS of crude reaction mixture:

Abundance

Time-->
Abundance

m/z-->

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	% of total
1	2.663	255	277	282	PV	2474256	46543969	8.33%	6.991%
2	2.697	282	283	310	VV	1533818	60637045	10.85%	9.107%
3	3.663	447	452	572	PV	10236491	558619665	100.00%	83.902%

decane (internal standard)

product, 2nd diastereomer not detected

^1H -NMR of pure product:

^{13}C -NMR of pure product:

2. Reactions of carbenoid 2 with different benzaldehydes (Scheme 2)

General: The ring closure in case of products of type **5** and the uncyclized alcohol in case of products of type **6** are clearly shown by ^{13}C NMR data (signal of the carbonyl group at around 174 ppm (**5**) compared to the nitrile signal at 113 ppm(**6**)) and high resolution mass spectra. In the IR experiments in both cases the nitrile function (expected at around 2200 cm^{-1}) is missing and the spectrum shows instead a strong bend in the carbonyl-region. Presumably, in case of the free alcohols, this is due to cyclization of the compound during preparation of the KBr pellet, induced by humidity in the KBr and mechanical energy.

For the reactions, it should be pointed out that vigorous stirring is essential as after addition of the aldehydes a slurry forms immediately and one may loose conversion if the reaction is not well mixed all the time.

Reaction of carbenoid 2 with benzaldehyde:

According to **TP 1** the magnesium carbenoid **2** was prepared from 2,2-dibromo-1-methylcyclopropanecarbonitrile (**1**) (478 mg, 2.00 mmol) and at $-50\text{ }^{\circ}\text{C}$ reacted with benzaldehyde (254 mg, 2.40 mmol, 1.20 equiv). Column chromatography (silica; $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ gradient 99:1 to 1:1) afforded the products **5a** and **6a** as colorless, crystalline solids (**5a**: 176 mg, 0.66 mmol, 33 %; **6a**: 186 mg, 0.70 mmol, 35 %).

Analytical data of compound **5a**:

mp: 98.3-98.8 $^{\circ}\text{C}$.

^1H -NMR (CDCl_3 , 300 MHz): δ [ppm] = 7.43 (m, 5 H); 5.76 (s, 1 H); 1.56 (m, 4 H); 1.27 (d, 1 H, $J = 6.38\text{ Hz}$).

^{13}C -NMR (CDCl_3 , 75 MHz): δ [ppm] = 174.5; 134.8; 128.9; 128.7; 125.7; 83.7; 41.3; 29.9; 24.6; 13.2.

IR (KBr): ν [cm^{-1}] = 3523 (w); 3079 (m); 3057 (m); 3033 (m); 2979 (m); 2938 (m); 1963 (w); 1889 (w); 1790 (vs); 1605 (w); 1585 (w);

1500 (m); 1451 (m); 1442 (m); 1386 (w); 1361 (w); 1350 (w); 1308 (s); 1294 (s); 1204 (w); 1162 (w); 1127 (s); 1084 (w); 1059 (w); 1043 (m); 1036 (m); 1020 (s); 972 (w); 920 (w); 885 (m); 865 (w); 830 (w); 780 (w); 770 (w); 762 (w); 745 (s); 702 (s); 678 (w); 632 (m); 618 (w); 600 (m); 481 (m).

MS (EI): m/z (%) = 268 ($M^+ [^{81}\text{Br}]$, 7); 266 ($M^+ [^{79}\text{Br}]$, 7); 187 (43); 160 (6); 159 (56); 141 (11); 131 (9); 129 (8); 128 (27); 127 (6); 118 (11); 115 (15); 105 (16); 91 (8); 81 (13); 77 (18); 69 (100); 53 (22); 51 (11); 41 (13).

HR-MS: ($\text{C}_{12}\text{H}_{11}\text{BrO}_2$) **calculated:** 265.9942 **found:** 265.9914.

X-ray data of 5a (The crystal was grown by sublimation of the clean product after column chromatography at 50 °C in high vacuum (10^{-2} mbar)):

M_r = 267.12, orthorhombic, space group $Pna2_1$, a = 7.0914(14) Å, b = 24.615(5) Å, c = 6.3857(13) Å, V = 1114.7(4) Å³, Z = 4, ρ_{calcd} = 1.592 g/cm³, $\text{MoK}\alpha$ radiation (λ = 0.71073 Å), μ = 3.664 mm⁻¹. Data were collected on a NONIUS MACH3 system at 295 K. The structure was solved by direct methods (SHELXS-90, SHELXL-97). All non-hydrogen atoms were refined anisotropically. R_1 = 0.0340, ωR_2 = 0.0780 for all data with $I > 2\sigma(I)$. CCDC 275461 contains the supplementary crystallographic data for this paper. These data can be [obtained online](#) free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Analytical data of compound **6a**:

mp: 110.0-111.5°C.

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 7.36 (m, 2 H); 7.17 (m, 3H); 5.32 (s, 1 H); 1.63 (d, 1 H, *J* = 5.84 Hz); 1.60 (s, 3H); 1.47 (d, 1 H, *J* = 5.84 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 138.6; 129.2; 128.5; 127.2; 112.6; 85.9; 43.3; 29.7; 28.3; 14.4.

IR (KBr): ν [cm⁻¹] = 3284 (m); 3060 (w); 3032 (w); 2968 (w); 2927 (w); 1783 (w); 1702 (vs); 1654 (w); 1496 (w); 1456 (m); 1441 (w); 1388 (w); 1366 (m); 1350 (m); 1322 (m); 1272 (w); 1194 (s); 1074 (w); 1052 (w); 1012 (s); 970 (m); 951 (s); 914 (m); 864 (m); 823 (w); 774 (m); 752 (m); 715 (m); 699 (m); 624 (w); 589 (w); 545 (w); 493 (w); 418 (w).

MS (EI): *m/z* (%) = 267 (M⁺[⁸¹Br], 14); 265 (M⁺[⁷⁹Br], 14); 200 (100); 198 (99); 186 (68); 158 (24); 143 (53); 142 (14); 141 (27); 133 (15); 128 (62); 118 (24); 115 (41); 105 (16); 91 (14); 80 (15); 77 (24); 68 (16); 53 (19); 51 (16).

HR-MS: (C₁₂H₁₂BrNO) **calculated**: 265.0102 **found**: 265.0097

GCMS of crude reaction mixture:

Abundance

peak R.T. first max last PK peak corr. corr. % of
min scan scan scan TY height area % max. total

6 3.920 494 497 509 VV 5029155 145138935 82.71% 39.221%

7 4.005 509 512 602 VV 4983499 175482879 100.00% 47.420%

8 4.651 621 625 664 VV 7 129402 7345094 4.19% 1.985%

product, major diastereomer 1

product, major diastereomer 2

product, minor diastereomers 1+2

^1H -NMR of pure product 5a:

^{13}C -NMR of pure product 5a:

^1H -NMR of pure product 6a:

^{13}C -NMR of pure product 6a:

Reaction of carbenoid 2 with 4-cyanobenzaldehyde:

According to **TP 1** the magnesium carbenoid **2** was prepared from 2,2-dibromo-1-methylcyclopropanecarbonitrile (**1**) (478 mg, 2.00 mmol) and at -50 °C reacted with *para*-cyanobenzaldehyde (314 mg, 2.40 mmol, 1.20 equiv). Column chromatography (silica; CH₂Cl₂/Et₂O gradient 39:1 to 1:1; afterwards washing with EtOAc) afforded **5b** as colorless, crystalline solid and **6b** as a very viscous, colorless resin (**5b**: 185 mg, 0.64 mmol, 32 %; **6b**: 204 mg, 0.70 mmol, 35 %).

Analytical data of compound **5b**:

mp: 130-132.5 °C.

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 7.72 (d, 2 H, *J* = 8.45 Hz); 7.59 (d, 2H, *J* = 8.45 Hz); 5.76 (s, 1 H); 1.55 (s, 3H); 1.44 (d, 1 H, *J* = 6.51 Hz); 1.27 (d, 1 H, *J* = 6.51 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 173.7; 140.1; 132.5; 126.4; 118.2; 113.0; 82.6; 40.5; 30.0; 24.4; 13.1.

IR (KBr): ν [cm⁻¹] = 3094 (w); 3072 (w); 2980 (w); 2936 (w); 2230 (m); 1784 (vs); 1610 (m); 1544 (w); 1504 (w); 1460 (w); 1442 (w); 1413 (w); 1384 (w); 1358 (w); 1302 (m); 1207 (w); 1124 (s); 1066 (w); 1042 (w); 1026 (s); 1015 (s); 972 (w); 922 (w); 896 (m); 868 (w); 841 (w); 826 (m); 773 (m); 736 (w); 677 (w); 608 (w); 597 (w); 549 (m); 514 (w); 428 (w).

MS (EI): *m/z* (%) = 293 (M⁺[⁸¹Br], 15); 291 (M⁺[⁷⁹Br], 15); 212 (25); 184 (100); 168 (25); 166 (12); 153 (28); 143 (32); 140 (16); 130 (30); 102 (15); 81 (12); 69 (84); 53 (25); 41 (11).

HR-MS: (C₁₃H₁₀BrNO₂) **calculated: 290.9895 found: 290.9863.**

Analytical data of compound **6b**:

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 7.67 (d, 2 H, *J* = 8.67 Hz); 7.29 (d, 2H, *J* = 8.67 Hz); 5.35 (s, 1 H); 1.65 (d, 1 H, *J* = 5.97 Hz); 1.57 (s, 3H); 1.49 (d, 1 H, *J* = 5.97 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 143.6; 132.3; 127.8; 118.2; 113.0; 112.5; 84.5; 42.6; 29.5; 28.3; 14.3.

IR (KBr): ν [cm⁻¹] = 3289 (m); 2968 (w); 2931 (m); 2230 (s); 1928 (w); 1778 (s); 1694 (s, br); 1610 (m); 1529 (m); 1506 (m); 1446 (m); 1417 (w); 1369 (w); 1321 (m); 1271 (w); 1206 (m); 1059 (s); 1031 (s); 1018 (s); 979 (m); 942 (m); 912 (w); 873 (m); 845 (s); 761 (m); 642 (w); 600 (m); 565 (m); 504 (w).

MS (EI): *m/z* (%) = 293 ([M+1H]⁺[⁸¹Br], 4); 291 ([M+1H]⁺[⁷⁹Br], 4); 212 (13); 184 (51); 168 (18); 166 (12); 162 (7); 160 (7); 156 (7); 154 (7); 153 (23); 143 (24); 141 (10); 140 (16); 130 (23); 115 (8); 102 (18); 81 (17); 69 (100); 53 (38); 51 (10); 41 (21).

HR-MS: (C₁₃H₁₂BrN₂O, [M+1H]⁺) **calculated: 291.0133 found: 291.0109.**

GCMS of crude reaction mixture:

Abundance

m/z-->

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	% of total
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2	3.142	356	361	403	rBV3	254814	1955896	10.68%	5.919%	add. of <i>i</i> -PrMgCl to aldehyde
3	3.811	475	478	533	rVB2	349689	1943398	10.61%	5.881%	aldehyde xs
4	4.731	631	639	645	rBV	3528211	9636015	52.60%	29.160%	product, main diastereomers 1 & 2
5	4.783	645	648	725	rVB	4094237	18318634	100.00%	55.435%	

^1H -NMR of pure product 5b:

^{13}C -NMR of pure product 5b:

^1H -NMR of pure product 6b:

^{13}C -NMR of pure product 6b:

Reaction of carbenoid 2 with 4-bromobenzaldehyde:

According to **TP 1** the magnesium carbenoid **2** was prepared from 2,2-dibromo-1-methylcyclopropanecarbonitrile (**1**) (478 mg, 2.00 mmol) and at -50 °C reacted with para-bromobenzaldehyde (444 mg, 2.40 mmol, 1.20 equiv). Column chromatography (silica; CH₂Cl₂/Et₂O gradient 39:1 to 1:1) afforded the products **5c** and **6c** as colorless crystalline solids (**5c**: 222 mg, 0.64 mmol, 32 %; **6c**: 201 mg, 0.58 mmol, 35 %).

Analytical data of compound **5c**:

mp: 78.0-79.5 °C.

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 7.54 (d, 2 H, *J* = 8.45 Hz); 7.32 (d, 2H, *J* = 8.45 Hz); 5.69 (s, 1 H); 1.53 (s, 3H); 1.48 (d, 1 H, *J* = 6.77 Hz); 1.27 (d, 1 H, *J* = 6.77 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 174.1; 133.8; 131.9; 127.3; 123.0; 83.0; 40.9; 29.9; 24.4; 13.1.

IR (KBr): ν [cm⁻¹] = 2927 (w); 2854 (w); 1775 (vs); 1678 (br); 1593 (w); 1487 (m); 1444 (w); 1410 (w); 1365 (w); 1311 (m); 1279 (w); 1104 (s); 1072 (m); 1039 (m); 110 (s); 991 (s); 945 (w); 873 (w); 835 (m); 776 (w); 743 (w); 665 (w); 604 (w); 542 (w); 505 (w); 428 (w).

MS (EI): *m/z* (%) = 348 (M⁺[⁸¹Br], 41); 346 (M⁺, [⁷⁹Br/⁸¹Br], 89); 344 (M⁺[⁷⁹Br], 43); 280 (39); 278 (82); 276 (41); 266 (35); 264 (32); 239 (84); 237 (88); 196 (23); 185 (42); 183 (41); 158 (37), 142 (83); 141 (50); 115 (40); 69 (100); 53 (50).

HR-MS: (C₁₂H₁₀Br₂O₂) calculated: 343.9048 found: 343.9037.

Analytical data of compound **6c**:

mp: 80.0-81.0 °C.

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 7.54 (d, 2 H, *J* = 8.19 Hz); 7.08 (d, 2H, *J* = 8.19 Hz); 5.32 (s, 1 H); 1.66 (d, 1 H, *J* = 5.95 Hz); 1.61 (s, 3H); 1.50 (d, 1 H, *J* = 5.95 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 137.6; 131.7; 128.8; 123.3; 112.6; 85.11; 43.0; 29.7; 28.3; 14.4.

IR (KBr): ν [cm⁻¹] = 3282 (w); 1780 (w); 1694 (vs); 1591 (w); 1487 (m); 1442 (w); 1410 (w); 1364 (m); 1321 (m); 1196 (m); 1071 (m); 1025 (m); 1010 (s); 970 (m); 954 (m); 937 (m); 870 (m); 826 (s); 753 (w); 594 (w); 543 (w); 494 (w).

MS (EI): *m/z* (%) = 347 (M⁺[⁸¹Br], 13); 345 (M⁺, [⁷⁹Br/⁸¹Br], 26); 343 (M⁺[⁷⁹Br], 13); 280 (46); 278 (100); 276 (48); 266 (33); 264 (34); 236 (11); 198 (11); 196 (13); 185 (15); 157 (15), 142 (62); 141 (32); 115 (27); 80 (13); 68 (20); 53 (14).

HR-MS: (C₁₂H₁₁Br₂NO) **calculated: 342,9207** **found: 342.9197.**

GCMS of crude reaction mixture:

Abundance

Abundance

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	% of total	
2	1.936	144	148	202	rBV	497918	1742043	12.42%	5.320%	
4	3.714	456	459	525	rVB	777405	2742166	19.54%	8.374%	
6	4.817	649	652	664	rVV	4550481	13487518	96.13%	41.186%	product, main diastereomer 1
7	4.902	664	667	731	rVB	5245309	14030927	100.00%	42.845%	product, main diastereomer 2
8	5.760	811	817	818	rBV3	74267	133597	0.95%	0.408%	product, minor diastereomers

^1H -NMR of pure product 5c:

^{13}C -NMR of pure product 5c:

^1H -NMR of pure product 6c:

^{13}C -NMR of pure product 6c:

3. Preparation of the functionalized cyclopropanes of type 7 (Scheme3)

General procedure: *i*-PrMgCl (5.50 mmol, 1.10 equiv; 2.56 M solution in Et₂O) was added dropwise to a solution of 2-bromo-1-methyl-2-(phenylsulfanyl)cyclopropanecarbonitrile (**3d**) (1.34 g, 5.00 mmol) in dichloromethane (20 mL) at -50°C and stirred for 10 min at this temperature. Then, allyl bromide (726 mg, 6.00 mmol, 1.20 equiv) (or methallyl bromide, respectively) and subsequently CuCN·2LiCl (0.05 mL; 0.5 mol%; 1 M solution in THF) were added and the reaction mixture was allowed to warm up to r.t. The reaction was followed by GCMS-analysis of reaction aliquots. There could not be detected any isomerization during the reaction. After the conversion was complete, a saturated aqueous solution of ammonium chloride (20 mL) was added, and the resulting mixture was extracted with dichloromethane (4 x 25 mL). The combined organic layers were dried (Na₂SO₄) and evaporated *in vacuo*. The crude residue was purified by flash column chromatography.

allyl-1-methyl-2-(phenylsulfanyl)cyclopropanecarbonitrile (7a):

After flash column chromatography (silica; pentane/Et₂O 19:1), the product was isolated as colorless oil (813 mg; 3.55 mmol; 71 %).

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 7.47 (m, 2 H); 7.30 (m, 3 H); 5.93 (m, 1 H); 5.09 (m, 2 H); 2.39 (m, 1 H); 2.25 (m, 1H); 1.59 (d, 1 H, *J* = 6.07 Hz); 1.56 (s, 3 H); 1.06 (d, 1 H, *J* = 6.07 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 133.9; 132.9; 131.5; 129.1; 127.5; 122.2; 118.0; 36.5; 36.0; 27.3; 20.5; 17.9.

IR (KBr): ν [cm⁻¹] = 3436 (br); 3078 (m); 3003 (m); 2979 (m); 2938 (m); 2235 (s); 1738 (w); 1642 (m); 1584 (m); 1480 (s); 1458 (m); 1440 (s); 1386 (w); 1261 (w); 1158 (m); 1084 (m); 1025 (m); 995 (m); 964 (w); 919 (s); 742 (vs); 692 (vs); 568 (w).

MS (EI): *m/z* (%) = 229 (M⁺, 59); 214 (21); 196 (17); 188 (15); 175 (16); 161 (38); 149 (30); 147 (21); 135 (25); 134 (32); 131 (21);

130 (24); 129 (23); 128 (18); 120 (64); 110 (100); 109 (57); 104 (16); 99 (27); 93 (30); 91 (36); 85 (50), 77 (49); 65 (31); 51 (14); 41 (16).

HR-MS: ($C_{14}H_{15}NS$) calculated: 229.0925 found: 229.0900.

1H -NMR of pure product:

^{13}C -NMR of pure product:

COSY NMR experiment:

KOPP
 KOPP
 5010560
 Pulse Sequence: gDQCOSY
 Date: Jan 25 2005
 Solvent: CDCl3
 Temp: 24.0 C / 297.1 K
 INOVA-400 "sfgurd"
 Relax. delay 1.000 sec
 Acq. time 0.160 sec
 Width 3138.8 Hz
 2D Width 3138.8 Hz
 2 x 128 increments
 OBSERVE H1 399.9408614 MHz
 DATA PROCESSING
 Sg. sine bell 0.133 sec
 Shifted by -0.107 sec
 F1 DATA PROCESSING
 Sg. sine bell 0.107 sec
 Shifted by -0.107 sec
 F1 size 4096 x 4096
 Total time 21 min, 9 sec

NOE NMR experiment:

NOE NMR experiment 2:

1-methyl-2-(2-methyl-2-propenyl)-2-(phenylsulfanyl)cyclopropane-carbonitrile (7b):

After flash column chromatography (silica; pentane/Et₂O 19:1), the product was isolated as colorless oil (851 mg; 3.50 mmol; 70 %).

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 7.45 (m, 2 H); 7.29 (m, 3 H); 4.99 (s, 1 H); 4.66 (s, 1 H); 2.43 (d, 1 H, *J* = 16.20 Hz); 2.19 (d, 1 H, *J* = 16.20 Hz); 1.76 (s, 3 H); 1.64 (d, 1 H, *J* = 6.11 Hz); 1.55 (s, 3 H); 1.10 (d, 1 H, *J* = 6.11 Hz).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 141.1; 133.2; 131.4; 19.0; 127.4; 122.3; 114.2; 39.3; 35.0; 27.5; 22.5; 20.5; 18.1.

IR (KBr): ν [cm⁻¹] = 3077 (m); 2970 (m); 2938 (m); 2235 (s); 1953 (w); 1798 (w); 1731 (w); 1651 (m); 1584 (m); 1480 (s); 1440 (vs); 1375 (m); 1286 (w); 1260 (w); 1228 (w); 1156 (w); 1082 (m); 1025 (m); 959 (w); 895 (s); 741 (vs); 692 (vs); 610 (w); 566 (w).

MS (EI): *m/z* (%) = 243 (M⁺, 18); 229 (7); 228 (48); 201 (8); 188 (10); 161 (17); 147 (9); 135 (11); 134 (100); 133 (14); 130 (10); 118 (16); 113 (21); 111 (20); 110 (61); 109 (19); 107 (55); 99 (32); 91 (24); 79 (28), 77 (22); 65 (12).

HR-MS: (C₁₅H₁₇NS) **calculated:** 243.1082 **found:** 243.1059.

^1H -NMR of pure product:

^{13}C -NMR of pure product:

COSY NMR experiment:

NOE NMR experiment 1:

NOE NMR experiment 2:

4. Preparation of the sulfoxides of type 8 (scheme 3)

Typical procedure: Preparation of 2-allyl-1-methyl-2-(phenylsulfinyl)cyclopropanecarbonitrile (8a):

meta-chloroperbenzoic acid (1.124 g, 3.675 mmol, 1.050 equiv; wet, 75% w/w) was dissolved in dichloromethane (7 mL). The resulting solution was cooled to 0 °C and at this temperature dried 20 min over anhydrous sodium sulfate under vigorous stirring. The solution was filtered and subsequently added dropwise to a solution of allyl-1-methyl-2-(phenylsulfanyl)cyclopropanecarbonitrile (**7a**) (802 mg, 3.50 mmol) in dichloromethane (3.5 mL) at -50 °C. After addition, the reaction was allowed to warm up to room temperature. TLC monitoring showed complete conversion after 30 min. 2 N NaOH (10 mL) was added and the aqueous layer was extracted with ethyl acetate (4 x 10 mL). The combined organic layers were dried (Na₂SO₄) and evaporated in vacuo. The crude product was subsequently subjected to column chromatography (silica; gradient CHCl₂/EtOAc, 39:1 to 19:1).

The product was obtained as very viscous, colorless oil (660 mg, 2.70 mmol, 77 %)

¹H-NMR (CDCl₃, 300 MHz) (mixture of two diastereoisomers; the signals of these compounds are assigned as (d1) and (d2)) :
δ [ppm] = 7.83 (m, 2 H, (d1)); 7.66 (m, 2 H, (d2)); 7.54 (m, 3 H, (d1)+(d2)); 5.37 (m, 1 H, (d1)+(d2)); 4.90 (m, 2 H, (d1)); 4.74 (m, <2 H, (d2)); 2.89 (m, 1 H, (d2)); 2.53 (m, 1 H, (d1)); 2.15 (m, 2 H, (d1)+(d2)); 1.79 (d, 1 H, J = 6.72 Hz, (d1)); 1.51 (s, 3 H, (d2)); 1.45 (s, 3 H, (d1)); 1.29 (d, 1 H, J = 6.72 Hz, (d1)); 1.10 (d, 1 H, J = 6.72 Hz, (d2)).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 141.0 (d2); 140.0 (d1); 133.7 (d2); 133.7 (d1); 131.6 (d1); 131.6 (d2); 129.3 (d1); 129.2 (d2); 124.9 (d1); 124.8 (d2); 121.0 (d1); 120.0 (d2); 118.6 (d1); 118.2 (d2); 49.1 (d2); 48.9 (d1); 28.2 (d1); 25.9 (d2); 23.7 (d1); 21.5 (d2); 17.9 (d2); 17.6 (d2); 17.4 (d1); 14.8 (d1).

IR (KBr): ν [cm^{-1}] = 4057 (w); 3493 (br); 3079 (m); 2999 (m); 2980 (m); 2939 (m); 2603 (w); 2326 (w); 2234 (s); 2132 (w); 1979 (w); 1897 (w); 1834 (w); 1729 (w); 1640 (m); 1582 (m); 1478 (m); 1456 (m); 1444 (s); 1428 (m); 1387 (m); 1330 (w); 1307 (m); 1289 (w); 1260 (w); 1175 (w); 1159 (w); 1127 (w); 1987 (vs); 1049 (vs); 1022 (m); 999 (s); 968 (m); 922 (s); 866 (w); 785 (w); 752 (vs), 714 (m); 692 (s); 666 (w); 596 (m); 571 (m); 522 (m); 461 (m).

MS (EI): m/z (%) = 245 (M^+ , 1); 228 (2); 204 (2); 196 (3); 181 (1); 169 (6); 154 (14); 135 (7); 130 (12); 129 (9); 127 (14); 126 (100); 125 (97); 120 (10); 117 (12); 110 (13); 109 (14); 97 (21); 93 (37); 91 (33); 78 (64), 77 (65); 67 (11); 66 (18); 65 (20); 53 (17); 51 (26); 41 (44).

HR-MS: ($\text{C}_{14}\text{H}_{15}\text{NOS}$) **calculated:** 245.0874 **found:** 245.0858.

^1H -NMR of pure product (two diastereoisomers due to the unselective formation of the sulfoxide, both showing *cis*-configuration of the cyano- and the sulfur substituent; see also 2D-NMRs below):

^{13}C -NMR of pure product:

COSY NMR experiment:

NOESY NMR experiment (a):

NOESY NMR experiment (b) :

NOESY NMR experiment (c):

Preparation of 1-methyl-2-(2-methyl-2-propenyl)-2-(phenylsulfanyl)cyclopropanecarbonitrile (8b):

8b was prepared according to the oxidation procedure mentioned above starting from **7b** in a 2.5 mmol scale and was obtained as viscous, slightly yellow oil (571 mg, 2.20 mmol, 88 %).

¹H-NMR (CDCl₃, 300 MHz) (mixture of two diastereoisomers; the signals of these compounds are assigned as (d1) and (d2)) :
δ [ppm] = 7.80 (m, 2 H, (d1)); 7.69 (m, 2 H, (d2)); 7.53 (m, 3 H, (d1)+(d2)); 4.87 (brs, 1 H, (d1)); 4.71 (brs, 1 H, (d2)); 4.64 (brs, 1 H, (d1)); 4.52 (brs, 1 H, (d2)); 2.84 (d, 1 H, *J* = 16.60 Hz, (d2)); 2.84 (d, 1 H, *J* = 16.60 Hz, (d1)); 2.27 (m, 1 H, (d1)+(d2)); 1.86 (m, 1 H, (d1)+(d2)); 1.64 (s, 3 H, (d1)); 1.50 (s, 3 H, (d2)); 1.44 (s, 3 H, (d1)); 1.12 (d, 1 H, *J* = 6.76 Hz, (d1)); 1.03 (d, 1 H, *J* = 6.76 Hz, (d2)); 0.89 (s, 3 H, (d2)).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 141.8 (d1); 141.7 (d2); 141.4 (d1); 140.7 (d2); 132.2 (d2); 132.0 (d1); 129.7 (d1); 129.6 (d2); 125.7 (d2); 125.4 (d1); 121.4 (d1); 120.7 (d2); 116.5 (d2); 115.7 (d1); 48.1 (d1); 47.9 (d2); 32.4 (d1); 29.4 (d2); 23.2 (d1); 22.4 (d1); 22.0 (d2); 21.1 (d2); 18.1 (d2); 17.6 (d2); 17.4 (d1); 15.2 (d1).

IR (KBr): ν [cm⁻¹] = 3488 (br); 3078 (m); 2974 (m); 2940 (m); 2916 (w); 2234 (m); 1899 (w); 1818 (w); 1652 (m); 1582 (w); 1478 (m); 1444 (s); 1380 (m); 1308 (w); 1260 (w); 1230 (w); 1158 (w); 1089 (vs); 1051 (vs); 1023 (w); 999 (w); 963 (w); 900 (s); 752 (s); 692 (s); 644 (w); 596 (w); 571 (w); 528 (m); 489 (w); 449 (w); 431 (w).

MS (EI): m/z (%) = 259 (M⁺, <1); 242 (37); 210 (29); 187 (16); 175 (26); 174 (11); 168 (28); 143 (13); 134 (27); 133 (18); 129 (10); 126 (100); 125 (70); 119 (14); 118 (26); 110 (13); 109 (20); 107 (39); 105 (11); 105 (15); 97 (21); 91 (62); 79 (70); 78 (75); 77 (56); 65 (29); 55 (36); 53 (21); 51 (29); 41 (29).

HR-MS: (C₁₅H₁₇NOS) calculated: 259.1031 found: 259.1047.

^1H -NMR of pure product (two diastereoisomers due to the unselective formation of the sulfoxide, both showing *cis*-configuration of the cyano- and the sulfur substituent; see also 2D-NMRs below):

^{13}C -NMR of pure product:

COSY NMR experiment (a):

COSY NMR experiment (b):

HSQC NMR experiment (a):

HSQC NMR experiment (b):

NOESY NMR experiment (a):

NOESY NMR experiment (b):

NOESY NMR experiment (c):

5. Sulfoxide-magnesium exchange and allylation on the sulfoxides of type 8 (Scheme 3)

Typical procedure: Preparation of 2-allyl-1-methyl-2-(2-methyl-2-propenyl)cyclopropanecarbonitrile 9a:

i-PrMgCl (0.55 mL, 1.43 mmol, 1.10 equiv; 2.56 M solution in Et₂O) was added dropwise to a solution of 2-allyl-1-methyl-2-(phenylsulfinyl)cyclopropanecarbonitrile (**8a**) (350 mg, 1.30 mmol) in dichloromethane (4 mL) at -50°C and stirred for 10 min at this temperature. Then, methallyl bromide (243 mg, 1.56 mmol, 1.20 equiv) and subsequently CuCN·2LiCl (0.005 mL; 0.5 mol%; 1 M solution in THF) were added and the reaction mixture was allowed to warm up to r.t.. The reaction was followed by GCMS-analysis of reaction aliquots. After the conversion was complete, a saturated aqueous solution of ammonium chloride (4 mL) was added, and the resulting mixture was extracted with dichloromethane (4 x 5 mL). The combined organic layers were dried (Na₂SO₄) and evaporated *in vacuo*. The crude residue was purified by flash column chromatography (silica; pentane/Et₂O 39:1).

The product was obtained as volatile, colorless oil (166 mg, 0.94 mmol, 73 %).

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 5.71 (m, 1 H); 5.08 (m, 2 H), 4.87 (s, 1H); 4.78 (s, 1 H); 2.47 (d, 1 H; *J* = 15.16 Hz); 2.20 (m, 2 H); 2.00 (m, 1 H); 1.75 (s, 3 H); 1.46 (s, 3 H); 1.18 (d, 1 H, *J* = 5.24 Hz); 0.75 (d, 1 H, *J* = 5.24 Hz).

¹³C-NMR (CDCl₃, 300 MHz): δ [ppm] = 141.9; 134.4; 123.3; 117.8; 113.5; 42.3; 34.4; 28.5; 26.7; 22.5; 17.2; 14.3.

IR (KBr): ν [cm⁻¹] = 3078 (m); 2972 (s); 2939 (s); 2231 (vs); 1738 (w); 1642 (m); 1440 (s); 1377 (m); 1288 (w); 1083 (m); 996 (m); 897 (vs); 620 (w); 567 (w).

MS (EI): *m/z* (%) = 174 ([M-1H]⁺, 2); 160 (5); 134 (7); 119 (5); 118 (5); 108 (19); 107 (11); 105 (4); 104 (6); 93 (100); 91 (27); 80 (16); 79 (31); 77 (17); 66 (5); 41 (8).

HR-MS: ($\text{C}_{12}\text{H}_{16}\text{N}$, $[\text{M}-1\text{H}]^+$) calculated: 174.1283 found: 174.1274.

^1H -NMR of pure product:

^{13}C -NMR of pure product:

COSY NMR experiment:

NOE NMR experiment:

Preparation of 2-allyl-1-methyl-2-(2-methyl-2-propenyl)cyclopropanecarbonitrile 9b:

9b was prepared starting from **8b** according to the method described above, using allyl bromide instead of methallyl bromide.

The product was received as volatile, colorless oil (157 mg, 0.90 mmol, 69 %).

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 5.82 (m, 1 H); 5.11 (m, 2 H), 4.88 (s, 1H); 4.78 (s, 1 H); 2.30 (brd, 1 H; *J* = 6.98 Hz); 2.16 (d, 1 H; *J* = 15.65 Hz); 2.03 (d, 1 H; *J* = 15.65 Hz); 1.70 (s, 3 H); 1.42 (s, 3 H); 1.19 (d, 1 H, *J* = 5.30 Hz); 0.72 (d, 1 H, *J* = 5.30 Hz).

¹³C-NMR (CDCl₃, 300 MHz): δ [ppm] = 141.9; 134.8; 123.8; 118.4; 113.8; 39.3; 38.2; 29.2; 27.2; 23.11; 17.9; 14.6.

IR (KBr): ν [cm⁻¹] = 3079 (m); 2972 (m); 2939 (s); 2917 (s); 2231 (vs); 1722 (w); 1643 (m); 1438 (s); 1376 (m); 1288 (w); 1231 (w); 1083 (m); 996 (m); 895 (vs) 918 (vs); 760 (w); 618 (w).

MS (EI): *m/z* (%) = 174 ([M-1H]⁺, 2); 160 (7); 134 (7); 119 (5); 118 (5); 108 (22); 107 (11); 105 (6); 104 (5); 93 (100); 91 (25); 80 (20); 79 (36); 77 (21); 66 (6); 55 (5); 41 (15).

HR-MS: (C₁₂H₁₆N, [M-1H]⁺) **calculated: 174.1283 found: 174.1271.**

^1H -NMR of pure product:

^{13}C -NMR of pure product:

COSY NMR experiment:

HSQC NMR experiment:

NOESY NMR experiment (a):

NOESY NMR experiment (b):