Supplementary Information

Synthesis of Chiral Germanium Center Enabled by Poly-Deborylative Alkylation and Desymmetrization

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1) General information and standard reaction setup

Commercial reagents were used without further purification unless otherwise indicated. All organic reaction solvents were purified according to the method of Grubbs¹. Unless otherwise indicated, filtrations of heterogeneous mixtures were performed using ChemRus 20 mL or 60 mL disposable filters. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath.

¹H and ¹³C NMR spectra were recorded on a Bruker NanoBay Avance III HD NMR 400 MHz instrument, and are internally referenced to residual proteo-solvent signals (note: CDCl₃ referenced at 7.26 ppm and 77.16 ppm). ¹⁹F NMR spectra were recorded on a Bruker NanoBay Avance III HD NMR 400 MHz and are reported unreferenced. Data for ¹H and ¹⁹F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, hept = heptet, m = multiplet, br = broad), coupling constant (Hz), and integration. Data for ¹³C NMR are reported in terms of chemical shifts; multiplicity and coupling constants are included only when coupling with ¹⁹F nuclei. ¹¹B NMR spectra were recorded on a Bruker NanoBay Avance III HD NMR 400 MHz. Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system.

IR spectra were collected using Bruker-TENSOR 27 spectrometer and Agilent Technologies Cary 630 FTIR, and only major peaks were reported in cm⁻¹. HRMS was performed on Bruker Apex II FT-ICR mass instrument (ESI) and waters GCT Premier TOFMS (EI). GC-MS data was collected on Agilent 8890-5977B. The some compounds was purified by an automated Combiflash NextGen 300⁺ system using RediSep Rf Gold silica gel columns (20 to 40 microns). Thin layer chromatography was carried out using XINNUO SGF254 TLC plates. Flash chromatography was performed using XINNUO silica gel (200-300 mesh).

2) Preliminary investigation of the reaction mechanism.

2.1 Kinetic monitoring of the desymmetrized product 80

This compound was prepared according to General procedure E from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 228.0 mg, 1.0 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 324 mg, 3.0 mmol, 1.5 equiv), Cu(OTf)2 (36 mg, 0.1 mmol), **L8** (61 mg, 0.1 mmol), DIPEA (155 mg, 1.2 mmol, 1.2 equiv). The reaction mixture was monitored by 1H NMR and chiral HPLC in the absence (Supplementary Figure S1), or presence of catalyst and chiral ligand. As the followings: using catalyst and ligand, the desired product **80** was rapidly produced in a short time (2 h), 60% yield and 96% e.e. were obtained. The yield of the desired product **80** steadily increased to 87% until the reaction completion after 18 h, and the corresponding enantioselctivity of the desired product **80** remains unchanged after 2 h. The formation of racemic compound **80** could slowly took place under the conditions without chiral ligand and without catalyst.

Based on the related diol-desymmetrization reaction, we wanted to ensure the excellent enantiomeric excess indeed originated from the diols **65** to mono-ester **80** step instead of secondary kinetic resolution of the mono-ester **80** to the corresponding bis-esters. So we have conducted the kinetic monitoring of the ee of **80**. We found that the ee of **80** was constantly as high as 97% through the whole process ignoring the yield of **80** and the formation of bis-esters. So, based on this observation, we believe that the observed 97% ee all came from the diols to mono-ester step. There was with no further kinetic resolution involved in this process.

The absolute configuration of **91** was assigned to be (*S*) by chiral HPLC comparison with that reported in the ref. 27 (**Supplementary Figure S10**), and the configuration of all other chiral products including product **80** were assigned by analogy. The X-Ray Structure of **73'** is consistent with the absolute configuration of **91**.



Supplementary Figure S1. | Kinetic monitoring for the formation and enantiomeric excess of product 80.

2.2 Uncatalyzed esterification reaction as the racemic background reaction.

In an argon-filled glovebox, (methyl(phenyl)germanediyl)dimethanol (65, 228.0 mg, 1.0 mmol), aryl acyl chloride (1.5 mmol, 1.5 equiv), and DIPEA (157.5 mg, 1.2 mmol, 1.2 equiv) were added to a 50 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, along with freshly distilled chloroform (10.0 mL), hexane (5.0 mL), and DCM (5.0 mL). The reaction mixture yield was determined by ¹H NMR using dibromomethane as the internal standard.



Supplementary Figure S2. | Background experiments on product yield.

The prochiral diol **65** can react with benzoyl chlorides in the absence of the copper catalysis, which would generate the racemic **80** to diminish the enantioselectivity of the product **80**. We were wondering whether this background reaction rate had a direct connection with benzoyl chloride's different electronic properties. As expected, we indeed observed a faster background rate and higher racemic product yield with more electronic-deficient benzoyl chloride. For example, the *para*-cyano benzoyl chloride's background rate was almost twice as fast than the *para*-OMe, the *para*-F and *ortho*-phenyl analog. This significant rate difference in the background rate perfect explained the observed trend between ee value and the benzoyl chloride's electronic nature.

2.3 Non-linear effect study on the formation of product 80

This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EA described in the general procedure E. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), and enantioselctivity were determined by chiral HPLC.



Supplementary Figure S3. | Non-linear effect study of 80

To further probe what is the real active catalyst, we have conducted non-linear effect study of new synthesized pyridine-bisimidazoline ligand. Since the non-linear effect can be observed for Cu-PyBox system, we want to know how many ligands are bonded to the active copper catalyst. Sur-

prisingly, we found that our copper (II) triflate/pyridine-bisimidazoline ligand system did not exhibit a non-linear effect under our standard conditions. This suggests that copper (II) triflate and pyridine-bisimidazoline ligand were likely to form 1:1 ratio complex as the active catalyst, which was opposite to the Cu-PyBox system.

0 e.e.% of L8



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Typ	e Width	Area	Height	Area
# [min]	[min]	[mAU*s]	[mAU]	%
	-			<mark>-</mark>
1 13.067 BB	0.3737	9871.93848	408.90643	50.0030
2 24.483 BB	0.7714	9870.76465	198.08116	49.9970
Totals :		1.97427e4	606.98759	

20 e.e.% of L8



Signal 3: DAD1 C, Sig=210,4 Ref=off Peak RetTime Type Width Area Height Area [min] [min] [mAU*s] [mAU] # % 1 13.053 BB 0.3802 2264.87720 92.96453 40.0735 2 24.081 MM R 0.7970 3386.93237 70.82430 59.9265 Totals : 5651.80957 163.78883

40 e.e.% of L8



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1 2	13.067 24.090	 MM R MM R	0.4122 0.7826	533.98334 1250.34473	21.59171 26.62883	29.9263 70.0737
Total	ls :			1784.32806	48.22053	

60 e.e.% of L8





80 e.e.% of L8



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.922	MM R	0.3816	582.09241	25.42074	12.0539
2	23.712	BB	0.6952	4246.99219	87.98407	87.9461
Total	ls :			4829.08459	113.40481	

> 99 e.e.% of **L8**



Signal 3: DAD1 C, Sig=210,4 Ref=off Peak RetTime Type Width Height Area Area # [min] [min] [mAU*s] [mAU] % 1 12.949 MM R 0.3741 112.54356 5.01389 1.6491 2 24.275 BB 0.7651 6712.06494 136.64398 98.3509 Totals : 6824.60851 141.65788

2.4 Hammett free liner energy analysis for enantiomeric ratio of desymmetrization products

This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), aryl acyl chloride (0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EA described in the general procedure E. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), and enantioselctivity were determined by chiral HPLC.



Supplementary Figure S4. | Hammett plot for enantiomeric ratio of desymmetrization products

To gain more mechanistic insights of the copper(II) catalyzed diol de-symmetrization reactions; we have tested benzoyl chloride with different electronic properties at the para position of the arene. We found that more electron- rich benzoyl chloride gave a higher ee compared to the electron-deficient one; the desymmetrization product's enantiomeric ratio had a linear relationship with the traditional Hammett substituent constants. The negative slope of this linear free energy relationship indicates that reaction was likely involving the cationic intermediate. Based on this

mechanism evidence, we propose that copper catalyzed esterification went through an ionic pathway instead of the open-shell radical pathway.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), 4-fluorobenzoyl chloride (**66n**, 47.4 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **67a** as a colorless oil (57.4 mg, 82% yield, 90% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 18.29 min, $t_{\rm R}$ (minor) = 12.41 min. $[\alpha]_{\rm D}^{25}$ = +0.86 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl 4-fluorobenzoate (67a)



¹**H NMR (400 MHz, CDCl₃)** δ 8.03-7.98 (m, 2H), 7.54-7.51 (m, 2H), 7.38-7.35 (m, 3H), 7.13-7.08 (m, 2H), 4.56 (q, *J* = 12.4 Hz, 2H), 3.99 (q, *J* = 12.8 Hz, 2H), 2.26 (s, 1H), 0.54 (s, 3H). ¹³**C** NMR (101 MHz, CDCl₃) δ 166.94, 165.96 (d, $J_{C-F} = 253.0$ Hz), 136.52, 133.86, 132.23 (d, $J_{C-F} = 9.0$ Hz), 129.39, 128.50, 126.23 (d, $J_{C-F} = 3.0$ Hz), 115.73 (d, $J_{C-F} = 21.0$ Hz), 57.79, 54.81, -7.44.

¹⁹F NMR (376 MHz, CDCl₃): δ -105.30.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₆H₁₇FGeNaO₃ ([M+Na]⁺) 373.0266, found 373.0266.

IR (film) v_{max} 2927, 2360, 2341, 1723, 1602, 1431, 1311, 1292, 1090, 1013 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), 4-bromobenzoyl chloride (**660**, 65.4 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **67b** as a colorless oil (68.9 mg, 84% yield, 88% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 16.51 min, $t_{\rm R}$ (minor) = 9.73 min. $[\alpha]_{\rm D}^{25}$ = +0.60 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl 4-bromobenzoate (67b)



¹H NMR (400 MHz, CDCl₃) δ 7.94-7.91 (m, 2H), 7.55-7.50 (m, 2H), 7.42-7.35 (m, 5H), 4.56 (q, J = 12.4 Hz, 2H), 3.99 (q, J = 12.4 Hz, 2H), 2.23 (s, 1H), 0.54 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.02, 139.67, 136.44, 133.85, 131.03, 129.40, 128.90, 128.49, 128.41, 57.87, 54.79, -7.43.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₆H₁₇BrGeNaO₃ ([M+Na]⁺) 432.9465, found 432.9460.

IR (film) v_{max} 2927, 2360, 2341, 1698, 1594, 1487, 1315, 1172, 1090, 1014 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), 4-cyanobenzoyl chloride (**66p**, 49.5 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **67c** as a colorless oil (70.2 mg, 81% yield, 81% e.e.). HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 26.28 min, $t_{\rm R}$ (minor) = 20.26 min. [α]_D²⁵ = -0.70 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl 4-cyanobenzoate (67c)



¹**H NMR (400 MHz, CDCl₃)** δ 8.07-8.04 (m, 2H), 7.73-7.70 (m, 2H), 7.54-7.49 (m, 2H), 7.37-7.34 (m, 3H), 4.0 (q, *J* = 12.4 Hz, 2H), 4.00 (q, *J* = 12.4 Hz, 2H), 2.01 (s, 1H), 0.55 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.14, 136.09, 133.84, 133.82, 132.36, 130.10, 129.48, 128.52, 118.03, 116.53, 58.41, 54.77, -7.36.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₇H₁₇GeNNaO₃ ([M+Na]⁺) 380.0312, found 380.0311.

IR (film) v_{max} 2927, 2361, 2341, 1722, 1431, 1315, 1234, 1176, 1105, 1018 cm⁻¹.

2.5 Proposed mechanism of copper catalyzed 1,3-diol desymmetrization reactions.



Supplementary Figure S5. | Proposed mechanism of copper catalyzed 1,3-diol desymmetrization reactions based on all previous mechanism study.

Based on all these mechanism information, we have proposed the following reaction mechanism: The symmetrical diol **65** ligates with copper(II) triflate and ligand **L8** to form the deprotonated neutral complex **Int-1** with the help of the mild base. The C-2 symmetrical chiral pocket would recognize the pro-chiral diol, the phenyl substitution would point to the empty quadrant. The benzoyl chloride's carbonyl oxygen atom would coordinate to the copper from the last empty quadrant to form **Int-2**. By forming that key intermediate, one of the diol's oxygen atom is positioned close to the benzoyl chloride, allowing the standard ester formation pathway could happen to give the desired mono-ester **80** with high enantiomeric excess.

3) Extended reaction scopes

All products, as indicated, were isolated and fully characterized in the experimental procedure section of this supplementary information. The majority of the reaction scope were all disclosed in the manuscript itself, here listed some additional examples for polyalkylation reactions.



Supplementary Figure S6. | Extended scope of borylative alkylation reaction of MCl₄^a. All yields are isolated. Standard conditions: ^aMCl₄ (2.0 mmol), bis(4,4,5,5-tetramethyl-1,3,2-diox-aborolan-2-yl)methane (**2**, 12.0 mmol, 6.0 equiv), 'BuOK (13.0 mmol, 6.5 equiv) in THF (0.10 M), 48 h, at 60 °C under Ar.

4) Reaction optimization and control experiments

Borylative alkylation reaction of chlorogermanane optimization and control experiments were performed on 0.2 mmol scale with exactly same experiments procedure as described in the isolation part.

Supplementary Table S1. Control experiments for borylative alkylation reaction of monochlorogermanene^a.

Bpin Bpin + Bpin	Et CI-Ge-Et Et LIHMDS (1.5 equi THF (0.2 M) 25°C, 12h	V) Bpin Ge~Et Et ()
2a , 1.0 equiv	1z , 1.5 equiv	36 ^{Lt} Et
Entry	Change of conditions	Yield ^b (%)
1	none	96 (99 ^c)
2	Without of LiHMDS	0
3	^t BuOK instead of LiHMDS	80
4	^t BuOLi instead of LiHMDS	74
5	^t BuONa instead of LiHMDS	64
6	LiTMP instead of LiHMDS	67
7	NaOMe instead of LiHMDS	59
8	CH ₃ CN as the solvent	0
9	1,4-Dioxane as the solvent	89
10	toluene as the solvent	trace
11	at 60 °C	81
12	1z (1.2 equiv)	81

^a2a (0.2 mmol), 1z (0.3 mmol), LiHMDS (1.5 equiv) in THF (2 mL), 12 h, at 25 °C under Ar.
^bYield was isolated. ^cThe yields were determined by NMR.

Supplementary Table S2. Control experiments for borylative alkylation reaction of dichlorogermanene^a.

Me, CI Ge +		^t BuOK (4.5 equiv)	Me,Bpin
Me	орин орин	THF (0.1 M) 60 °C, 48 h	Me ^{-Ge} _Bpin
1e , 1.0 equiv	2, 4.0 equiv		15
Entry	Change	of conditions	Yield ^b (%)
1	r	82 (88 ^c)	
2	Withou	0	
3	KOMe ins	64	
4	^t BuOLi inst	66	
5	^t BuONa ins	69	
6	KHMDS ins	0	
7	^{<i>n</i>} BuLi inst	27	
8	CH ₃ CN a	s the solvent	0
9	DMF as	the solvent	0
10	toluene as	11	
11	at 2	25 °C	21
12	2	4 h	61

^a 1e (0.2 mmol), 2 (0.8 mmol), ^tBuOK (0.9 mmol) in THF (0.10 M), 48 h, at 60 °C under Ar.
^b Yield was isolated. ^cThe yields were determined by NMR.

Supplementary Table S3. Control experiments for borylative alkylation reaction of trichlorogermanene^a.

ÇI Ge ^{-CI} CI	+ Bpin Bpin -	BuOK (4.5 equiv) THF (0.1 M)	Bpin Ge Bpin	
1 , 1.0 equiv	2 , 4.0 equiv	00 0,4011	3	
Entry	Change of co	Change of conditions		
1	none	none		
2	Without of ^t E	0		
3	KOMe instead	52		
4	^t BuOLi instead c	48		
5	^t BuONa instead	60		
6	KHMDS instead	0		
7	ⁿ BuLi instead o	67		
8	CH ₃ CN as the	0		
9	DMF as the so	0		
10	toluene as the s	9		
11	at 25 °C	13		
12	24 h		43	

^a **1** (0.2 mmol), **2** (0.8 mmol), ^{*t*}BuOK (0.9 mmol) in THF (0.10 M), 48 h, at 60 °C under Ar. ^{*b*} Yield was isolated. ^{*c*}The yields were determined by NMR.

Supplementary Table S4. Control experiments for borylative alkylation reaction of trichlorogermanene^{*a*}.

CI CI ← ^{Ge −CI} CI 4, 1.0 equiv	+ Bpin Bpin HB (6.5 equiv) THF (0.1 M) 60 °C, 48 h 2, 6.0 equiv	Bpin Bpin Bpin Bpin 5
Entry	Change of conditions	Yield ^b (%)
1	none	76 (80 ^c)
2	Without of ^t BuOK	0
3	KOMe instead of ^t BuOK	22
4	^t BuOLi instead of ^t BuOK	29
5	^t BuONa instead of ^t BuOK	51
6	KHMDS instead of ^t BuOK	0
7	ⁿ BuLi instead of ^t BuOK	0
8	CH ₃ CN as the solvent	0
9	1,4-Dioxane as the solvent	66
10	toluene as the solvent	9
11	2 (5.0 equiv), [/] BuOK (5.5 equiv)	69
12	20 °C	18

^a **4** (0.2 mmol), **2** (1.2 mmol), ^tBuOK (1.3 mmol) in THF (0.10 M), 48 h, at 60 °C under Ar.

^b Yield was isolated. ^cThe yields were determined by NMR.

The reaction of desymmetrization of germanium containing 1,3-diols enabled copper catalysis. optimization and control experiments were performed on 0.1 mmol scale with exactly same experiments procedure as described in the isolation part.

Supplementary Table S5. Control experiments for the reaction of desymmetrization of germanium containing 1,3-diols enabled copper catalysis^{*a*}.

Ме		Cu(OTf) ₂ (10 mol %) L8 (10 mol %) DIPEA (1.2 equiv)	
ОН +		► CM : ^{<i>n</i>} Hexane = 2 : 1 : 1 (0.025 M) -80 °C, 16 h	OH
65 , 1.0 equiv	66, 1.5 equiv		67
Entry	Change of condition	ns Yield ^b (%)	e.e. (%)
1	none	87 (90 [°])	91
2	CuBr ₂	85	88
3	CuCl ₂	72	85
4	CuBr	29	0
5	Et ₃ N	81	89
6	2,6-di- <i>tert</i> -butyl-4-methylp	byridine 54	69
7	2,4,6-tri- <i>tert</i> -butylpyric	dine 45	37
8	K ₂ CO ₃	67	70
9	Hexane as the solve	nt 40	10
10	DCM as the solvent	t 82	80
11	CHCl ₃ (-60 °C)	71	90
12	CHCl ₃ : ⁿ Hexane as the solve	ent (-70 °C) 76	90
13	no Cu no Ligand	35	0

^a **65** (0.1 mmol), **66** (0.15 mmol), Cu(OTf)₂ (10 mol %), DIPEA (0.12 mmol), CHCl₃ : DCM : ^{*n*}Hexane = 2 : 1 : 1 (0.025 M), 16 h, at -80 °C, under Ar. ^{*b*} Yield was isolated. ^cThe yields were determined by NMR.

Supplementary Table S6. Evaluation of Ligand effect for the reaction of desymmetrization of germanium containing 1,3-diols enabled copper catalysis.



5) Experimental procedure for substrates and ligands synthesis

Preparation of starting materials

Chlorogermanes



Supplementary Figure S7. | Overview of chlorogermanes

Chlorogermanes 1, 1a-1h, 1z, 1y-1ae, 1ag, 1ai, 1am, 1an, 4, 1ao, 1ay, 1az are commercially available. 1i³, 1j-1l⁴, 1r-1s⁵, 1t⁶, 1u⁷, 1v⁸, 1w⁹, 1x¹⁰, 1af¹¹, 1ah⁷, 1aj-1al¹², 1ap¹³, 1aq¹⁴, 1ar¹⁵, 1as¹⁶, 1at¹⁷, 1au¹⁸, 1av¹⁵, 1aw¹⁹, 1ax²⁰ are known compound. 1m-1q were synthesized according to the literature Procedure³, which were used directly without further purification.

Alkyl borate esters



Supplementary Figure S8. | Overview of alkyl borate esters

Alkyl borate ester 2, 2b are commercially available. $2a^{21}$, $2c^{22}$, $2d^{23}$, $2e-2h^{21}$, $2i^{24}$, $2j-2k^{21}$, $2l^{23}$

Aryl/alkylacyl acid chlorides



Supplementary Figure S9. | Overview of Aryl/alkylacyl acid chlorides

Aryl/alkylacyl acid chlorides 66-66p are commercially available.

General Procedure 1 for the preparation of chiral bis(imidazoline) ligands L8-L12:



L8-L12 was synthesized according to the literature procedure.²⁵ To a solution of pyridine-2,6dicarbonyl dichloride (1.02 g, 5.0 mmol) in DCM (6.25 mL) was added dropwise at 0 °C to a

stirred solution of (*S*)-2-amino-2-phenylethanol (**II**, 1.38 g, 10 mmol) and triethylamine (1.39 mL, 10 mmol) in DCM (18.75 mL). The reaction mixture was then allowed to warm to room temperature and stirring was continued for 12 h. The reaction was quenched with water (20.0 mL) and the aqueous layer was extracted with DCM (3×20.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give a white solid, which was recrystallized from DCM to afford **III**.

To a solution of **III** (1.0 equiv) in CHCl₃ (0.2 M) was added dropwise SOCl₂ (5.75 equiv) at 0 °C, which was then stirred at reflux for 5 h. PCl₅ (2.1 equiv) was then added, the mixture was stirred at reflux for a further 6 h, and volatiles were removed under reduced pressure to afford **IV**. CHCl₃ (0.2 M), Et₃N (7.0 equiv), and arylamine (2.1 equiv) were added to the residue at 0 °C and the resulting mixture was stirred at room temperature for 2 h, followed by heating at reflux for 24 h. The solution was then washed with NaOH (20 %) and the aqueous layer was extracted with DCM ($3 \times 20.0 \text{ mL}$). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford corresponding bis(imidazoline) ligand (**L8-L12**).

L8 was obtained in 1.15 g, 38% yield as brown solid according to General Procedure 1

2,6-bis((S)-1-mesityl-4-phenyl-4,5-dihydro-1H-imidazol-2-yl)pyridine (L8)



¹**H NMR (400 MHz, CDCl₃)** δ 7.46-7.40 (m, 10H), 7.33-7.29 (m, 2H), 6.84 (s, 2H), 6.66 (s, 1.2H), 5.41-5.38 (m, 2H), 4.23 (dd, *J* = 11.6, 9.6 Hz, 2H), 3.50 (t, *J* = 10.0 Hz, 2H), 2.32 (s, 3H), 2.20 (s, 3H), 1.83 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 163.43, 149.69, 144.62, 137.30, 136.86, 136.43, 136.19, 136.07, 129.46, 129.24, 128.60, 127.09, 127.05, 123.94, 77.48, 77.16, 76.84, 68.40, 60.05, 21.02, 18.57, 18.15.

HRMS (ESI-TOF) m/z calcd. for C₄₁H₄₂N₅ ([M+H]⁺) 604.3535, found 604.3530.

IR (film) v_{max} 3028, 2922, 2850, 1598, 1475, 1383, 1275, 1160, 1078, 1025 cm⁻¹.

L9 was obtained in 0.94 g, 36% yield as slight yellow solid according to General Procedure 1

2,6-bis((S)-1,4-diphenyl-4,5-dihydro-1H-imidazol-2-yl)pyridine (L9)



¹**H NMR (400 MHz, CDCl₃)** δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.88 (t, *J* = 8.0 Hz, 1H), 7.40-7.28 (m, 16H), 6.58 (d, *J* = 8.0 Hz, 4H), 5.34-5.29 (m, 2H), 4.30 (t, *J* = 9.6 Hz, 2H), 3.89 (t, *J* = 9.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 160.87, 149.62, 143.73, 142.52, 137.10, 128.71, 128.54, 127.37, 126.92, 125.08, 123.75, 123.08, 77.48, 77.16, 76.84, 67.84, 61.62.

HRMS (ESI-TOF) m/z calcd. for C₃₅H₃₀N₅ ([M+H]⁺) 520.2501, found 520.2495.

IR (film) v_{max} 3028, 2924, 2361, 1595, 1452, 1378, 1245, 1153, 1079, 1029 cm⁻¹.

L10 was obtained in 0.68 g, 25% yield as slight yellow solid according to General Procedure 1

2,6-bis((S)-4-phenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)pyridine (L10)



¹**H NMR (400 MHz, CDCl₃)** δ 7.72-7.66 (m, 3H), 7.40-7.26 (m, 10H), 6.98 (d, *J* = 8.0 Hz, 4H), 6.62 (d, *J* = 8.4 Hz, 4H), 5.34 (dd, *J* = 11.2, 8.4 Hz, 2H), 3.84 (t, *J* = 8.8 Hz, 2H), 2.28 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 161.29, 149.85, 143.93, 140.20, 136.90, 133.48, 129.14, 128.68, 127.29, 126.91, 124.97, 123.28, 77.48, 77.16, 76.84, 67.93, 61.90, 21.00.

HRMS (ESI-TOF) m/z calcd. for C₃₇H₃₄N₅ ([M+H]⁺) 548.2814, found 548.2808.

IR (film) v_{max} 3028, 2922, 2856, 1601, 1477, 1431, 1385, 1277, 1081, 1030 cm⁻¹.

L11 was obtained in 0.66 g, 20% yield as slight yellow solid according to General Procedure 1

2,6-bis((S)-4-phenyl-1-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-imidazol-2-yl)pyridine (L11)



¹**H NMR (400 MHz, CDCl₃)** δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.88 (t, *J* = 8.0 Hz, 1H), 7.40-7.28 (m, 15H), 6.58 (d, *J* = 8.4 Hz, 3H), 5.33 (dd, *J* = 10.8, 8.8 Hz, 2H), 4.31 (dd, J = 10.4, 9.2 Hz, 2H), 3.89 (t, *J* = 9.2 Hz, 2H).

¹³**C NMR (101 MHz, CDCl₃)** δ 158.98, 148.67, 145.05 (d, $J_{C-F} = 1.0$ Hz), 142.79, 137.78, 128.92, 127.77, 126.89, 125.78, 125.74 (q, $J_{C-F} = 272.8$ Hz), 125.35 (q, $J_{C-F} = 3.0$ Hz), 124.74 (q, $J_{C-F} = 32.4$ Hz), 121.56, 6.84, 60.86.

¹⁹F NMR (**376** MHz, CDCl₃): δ -61.75.

HRMS (ESI-TOF) m/z calcd. for C₃₇H₂₈F₆N₅ ([M+H]⁺) 656.2249, found 656.2239.

IR (film) v_{max} 3026, 2928, 2850, 1607, 1470, 1430, 1383, 1274, 1080, 1029 cm⁻¹.

L12 was obtained in 0.94 g, 36% yield as slight yellow solid according to General Procedure 1

4-chloro-2,6-bis((S)-1,4-diphenyl-4,5-dihydro-1H-imidazol-2-yl)pyridine (L12)



¹**H NMR (400 MHz, CDCl₃)** δ 7.86 (s, 2H), 7.40 (m, 5H), 7.31-7.26 (m, 5H), 7.20-7.16 (m, 4H), 7.08-7.04 (m, 2H), 6.67-6.65 (m, 3H), 5.31-5.26 (m, 2H), 4.34-4.29 (m, 2H), 3.88-3.84 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 159.99, 150.73, 145.07, 143.53, 142.34, 128.78, 128.61, 127.51, 126.90, 125.30, 124.09, 123.33, 77.48, 77.16, 76.84, 67.98, 61.82.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₅H₂₉ClN₅ ([M+H]⁺) 554.2111, found 554.2107.

IR (film) v_{max} 3028, 2927, 1595, 1454, 1421, 1394, 1248, 1178, 1156, 1079, 1029 cm⁻¹.

6) General procedure for alkyl germanium and germanium stereoscopic compounds synthesis.

General procedure A of deborylative alkylation reaction of chlorogermanane:



In an argon-filled glovebox, alkyl borate ester (0.5 mmol, 1.0 equiv), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv) in THF (5.0 mL) were added to a 20 mL vial equipped with a magnetic stirring bar. The reaction mixture was stirred at 25 °C for 1 h. Chlorogermanane (0.70 mmol, 1.4 equiv)

was added and The reaction mixture was stirred at 25 °C for 12 h. The reaction was quenched with water (20.0 mL) and, the solution was extracted with ethyl acetate (3×15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford corresponding alkyl germanium compound.

General procedure B of deborylative alkylation reaction of chlorogermanane:



In an argon-filled glovebox, alkyl borate ester (2.0 mmol or 3.0 mmol, 4.0 equiv or 6.0 equiv), 'BuOK (252.5 mg or 336.6 mg, 2.25 mmol or 3.0 mmol, 4.5 equiv or 6.0 equiv) in THF (5.0 mL) were added to a 20 mL vial equipped with a magnetic stirring bar. The reaction mixture was stirred at 60 °C for 1 h. Chlorogermanane (0.50 mmol, 1.0 equiv) was added and The reaction mixture was stirred at 60 °C for 48 h. The reaction was quenched with water (20.0 mL) and, the solution was extracted with ethyl acetate (3×15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford corresponding alkyl germanium compound.

General procedure C of deborylative alkylation reaction of chlorogermanane:



In an argon-filled glovebox, alkyl borate ester (0.5 mmol, 1.0 equiv), 'BuOK (84.2 mg, 0.75 mmol, 1.5 equiv) in THF (5.0 mL) were added to a 20 mL vial equipped with a magnetic stirring bar. The reaction mixture was stirred at 25 °C for 1 h. Chlorogermanane (0.70 mmol, 1.4 equiv) was added and The reaction mixture was stirred at 25 °C for 12 h. The reaction was quenched with water (20.0 mL) and, the solution was extracted with ethyl acetate (3×15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford corresponding alkyl germanium compound.

General procedure D of deborylative alkylation of dichlorogermanane:



In an argon-filled glovebox, **2** (536.0 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv) in THF (5.0 mL) were added to a 20 mL vial equipped with a magnetic stirring bar. The reaction mixture was stirred at 60 °C for 1 h. Chlorogermanane (0.50 mmol, 1.0 equiv) was added and The reaction mixture was stirred at 60 °C for 48 h. The reaction was quenched with water (20.0 mL) and, the solution was extracted with ethyl acetate (3×15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford corresponding alkyl germanium compound. The alkyl germanium compounds was transferred to a 25 mL round bottom flask and cooled to 0 °C (ice/water) and charged with 5 M sodium hydroxide (8.5 equiv), and 30% hydrogen peroxide (0.85 mL) and THF (5.0 mL). The reaction was gradually

warmed to room temperature and allowed to stir for 4 h at which time the vial was cooled to 0 °C and saturated aqueous sodium thiosulfate was added dropwise over 5 min. The reaction mixture was diluted with ethyl acetate and the aqueous and organic layers were separated. The aqueous layer was extracted with ethyl acetate ($3 \times 20.0 \text{ mL}$) and the combined organics were dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatog-raphy on silica gel to afford corresponding prochiral bis(hydroxymethyl)germane.

General procedure E of desymmetrization of germanium containing 1,3-diols enabled copper catalysis:



In an argon-filled glovebox, $Cu(OTf)_2$ (7.2 mg, 0.02 mmol), L8 (12.1 mg, 0.02 mmol) in freshly distilled chloroform (2.0 mL) were added to a 20 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, and then the mixture was stirred at 25 °C for 3 h. To the generated catalyst solution, A solution of the corresponding bis(hydroxymethyl)germane (0.2 mmol, 1.0 equiv) in distilled dichloromethane (2.0 mL) and distilled n-hexane (2.0 mL) was added to the above generated catalyst solution, and the mixture was stirred at 25 °C for 10 min. After cooling down the above reaction mixture to -80 °C, a solution of aryl/alkyl acyl chloride (0.3 mmol, 1.5 equiv) and DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv) in distilled choroform (2.0 mL) was finally added dropwise at -80 °C. The reaction mixture was then allowed to stir at -80 °C for 16 h. The reaction was quenched with water (20.0 mL) and, the solution was extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and

concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford corresponding germanium stereoscopic compound.

7) Experimental data for products



This compound was prepared according to **General procedure B** from the reaction of trichloro(phenyl)germane (1, 127.9 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (2, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 30/1), to yield the product **3** as a colorless oil (229.7 mg, 80% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.61-7.59 (m, 2H), 7.28-7.23 (m, 3H), 1.11 (s, 36H), 0.54 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 141.72, 134.03, 128.27, 127.51, 82.80, 25.03. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 33.50.
HRMS (ESI-TOF) *m*/*z* calcd. for C₂₇H₄₇B₃GeNaO₆ ([M+Na]⁺) 597.2756, found 597.2762.

IR (film) v_{max} 2976, 2361, 1372, 1300, 1267, 1214, 1142, 1092, 1004, 962 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of Germanium tetrachloride (4, 427.6 mg, 2.0 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (2, 3.2g, 12.0 mmol, 6.0 equiv), 'BuOK (1.45g, 13.0 mmol, 6.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **5** as a colorless oil (970.3 mg, 76% yield). The Germanium tetrachloride (4, 5.4 g, 25.0 mmol) was used and, **5** was isolated using the same procedure (11.0 g, 69% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.21 (s, 48H), 0.34 (s, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 82.62, 25.13. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B** NMR (128 MHz, CDCl₃) δ 33.45.

HRMS (ESI-TOF) m/z calcd. for C₂₈H₅₇B₄GeO₈ ([M+H]⁺) 639.3639, found 639.3644.

IR (film) v_{max} 2978, 2361, 1468, 1379, 1300, 1267, 1215, 1143, 1005, 969 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of Tin tetrachloride (**1az**, 521.0 mg, 2.0 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 3.2g, 12.0 mmol, 6.0 equiv), 'BuOK (1.45g, 13.0 mmol, 6.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **5c** as a colorless oil (904.7 mg, 66% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.15 (s, 48H), 0.28 (s, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 82.62, 25.07. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B** NMR (128 MHz, CDCl₃) δ 33.19.

HRMS (ESI-TOF) m/z calcd. for C₂₈H₅₇B₄O₈Sn ([M+H]⁺) 685.3447, found 685.3442.

IR (film) v_{max} 2976, 2930, 1468, 1371, 1296, 1264, 1214, 1166, 1068, 997 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of trichloro(methyl)germane (**1a**, 96.9 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **11** as a colorless oil (153.7 mg, 60% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.20 (s, 36H), 0.30 (s, 3H), 0.27 (s, 6H).
¹³C NMR (101 MHz, CDCl₃) δ 82.77, 25.12, 0.22. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 34.63.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₂H₄₅B₃GeNaO₆ ([M+Na]⁺) 535.2599, found 535.2594.

IR (film) v_{max} 2977, 1389, 1371, 1341, 1269, 1215, 1166, 1114, 1003, 969 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of trichloro(ethyl)germane (**1b**, 103.9 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **12** as a colorless oil (184.0 mg, 70% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.21 (s, 36H), 1.09-1.05 (m, 3H), 0.89-0.83 (m, 2H), 0.26 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 82.73, 25.15, 10.38, 8.91. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 34.66.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₃H₄₇B₃GeNaO₆ ([M+Na]⁺) 549.2756, found 549.2751.

IR (film) v_{max} 2977, 1389, 1372, 1341, 1268, 1215, 1166, 1004, 970, 846 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of butyltrichlorogermane (**1c**, 117.9 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **13** as a colorless oil (158.0 mg, 57% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.42-1.27 (m, 4H), 1.20 (s, 36H), 0.88-0.84 (m, 5H), 0.25 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 82.71, 27.02, 26.54, 17.96, 13.84. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 34.16.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₅H₅₁B₃GeNaO₆ ([M+Na]⁺) 577.3069, found 577.3065.

IR (film) v_{max} 2977, 2930, 1477, 1389, 1371, 1341, 1267, 1215, 1166, 969 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of trichloro(vinyl)germane (1d, 102.9 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (2, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product 14 as a colorless oil (154.7 mg, 59% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 6.37 (dd, *J* = 20.0, 13.6 Hz, 1H), 5.93 (dd, *J* = 13.6, 3.0 Hz, 1H), 5.74 (dd, *J* = 20.0, 3.0 Hz, 1H), 1.20 (s, 36H), 0.35 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 140.10, 130.31, 82.86, 25.14. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B** NMR (128 MHz, CDCl₃) δ 34.00.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₃H₄₅B₃GeNaO₆ ([M+Na]⁺) 547.2599, found 547.2593.

IR (film) v_{max} 2978, 2359, 2224, 1389, 1373, 1340, 1270, 1216, 1004, 970 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of dichlorodimethylgermane (**1e**, 87.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **15** as a colorless oil (158.3 mg, 82% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.21 (s, 24H), 0.25 (s, 6H), 0.21 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 82.81, 25.11, 0.11. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 34.08.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₆H₃₄B₂GeNaO₄ ([M+Na]⁺) 409.1747, found 407.1751.

IR (film) v_{max} 2977, 1390, 1371, 1341, 1269, 1235, 1215, 1169, 1114, 1003 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of dichlorodiethylgermane (**1f**, 101.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)methane (536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **16** as a colorless oil (134.6 mg, 65% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.20 (s, 24H), 1.05-1.01 (m, 6H), 0.83-0.77 (m, 4H), 0.16 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 82.72, 25.10, 8.87, 8.07. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B** NMR (128 MHz, CDCl₃) δ 34.52.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₈H₃₈B₂GeNaO₄ ([M+Na]⁺) 437.2060, found 437.2054.

IR (film) v_{max} 2978, 1389, 1371, 1340, 1268, 1215, 1166, 1114, 1058, 1003 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of dibutyldichlorogermane (**1g**, 129.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **17** as a colorless oil (141.1 mg, 60% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 1.40-1.36 (m, 8H), 1.21 (s, 24H), 0.87 (t, *J* = 6.8 Hz, 6H), 0.82-0.78 (m, 4H), 0.16 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 82.69, 27.15, 26.57, 25.13, 16.15, 13.85. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 34.65.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₂H₄₆B₂GeNaO₄ ([M+Na]⁺) 493.2686, found 493.2681.

IR (film) v_{max} 2978, 2955, 2927, 2360, 1399, 1374, 1340, 1269, 1215, 1083 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of dichlorodiphenylgermane (**1h**, 149.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **18** as a colorless oil (204.1 mg, 80% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.60-7.56 (m, 4H), 7.33-7.29 (m, 6H), 1.04 (s, 24H), 0.76 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 139.81, 134.50, 128.60, 127.80, 82.93, 24.92. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 33.88.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₆H₃₈B₂GeNaO₄ ([M+Na]⁺) 533.2060, found 533.2055.

IR (film) v_{max} 2977, 2927, 1484, 1431, 1389, 1371, 1268, 1214, 1166, 1092 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(methyl)(phenyl)germane (**1i**, 118.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **19** as a colorless oil (74.1 mg, 65% yield). The dichloro(methyl)(phenyl)germane (**1i**, 18.9 g, 80.0 mmol) was used and, **19** was isolated using the same procedure (10.8 g, 60% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.55-7.52 (m, 2H), 7.39-7.36 (m, 3H), 4.12-4.00 (m, 4H), 2.09 (s, 2H), 0.52 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 137.20, 133.92, 129.26, 128.46, 56.38, -7.57.

HRMS (ESI-TOF) *m*/*z* calcd. for C₉H₁₄GeNaO₂ ([M+Na]⁺) 251.0103, found 251.0100.

IR (film) v_{max} 3047, 2911, 1486, 1430, 1263, 1239, 1186, 1093, 1065, 949 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(ethyl)(phenyl)germane (**1j**, 125.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **20** as a colorless oil (77.5 mg, 64% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.52-7.48 (m, 2H), 7.38-7.34 (m, 3H), 4.12-4.05 (m, 4H), 2.79 (s, 2H), 1.16-1.14 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 136.60, 134.15, 129.10, 128.38, 54.87, 9.02, 3.91.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₀H₁₆GeNaO₂ ([M+Na]⁺) 265.0260, found 265.0257.

IR (film) v_{max} 3048, 2989, 2957, 1486, 1450, 1378, 1262, 1227, 1092, 1066 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(phenyl)(propyl)germane (**1k**, 132.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **21** as a colorless oil (76.8 mg, 60% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.54-7.49 (m, 2H), 7.40-7.35 (m, 3H), 4.14-4.07 (m, 4H), 2.21 (s, 2H), 1.59-1.50 (m, 2H), 1.19-1.14 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 136.86, 134.15, 129.14, 128.44, 55.55, 18.64, 18.04, 14.31.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₁H₁₈GeNaO₂ ([M+Na]⁺) 279.0416, found 279.0412.



IR (film) v_{max} 3070, 3048, 2980, 1486, 1463, 1431, 1371, 1183, 1156, 1071, 950 cm⁻¹.

This compound was prepared according to **General procedure D** from the reaction of butyldichloro(phenyl)germane (**11**, 139.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **22** as a colorless oil (78.3 mg, 58% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.54-7.50 (m, 2H), 7.38-7.35 (m, 3H), 4.14-4.06 (m, 4H), 2.32 (s, 2H), 1.50-1.44 (m, 2H), 1.40-1.32 (m, 2H), 1.18-1.14 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 136.88, 134.16, 129.14, 128.44, 55.50, 27.26, 26.46, 13.81, 11.53.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₂H₂₀GeNaO₂ ([M+Na]⁺) 293.0573, found 293.0570.

IR (film) v_{max} 3069, 3049, 2982, 1486, 1465, 1431, 1375, 1182, 1156, 1093, 950 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(phenethyl)(phenyl)germane (**1m**, 163.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H_2O_2 was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **23** as a colorless oil (100.2 mg, 63% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.53-7.49 (m, 2H), 7.41-7.37 (m, 3H), 7.31-7.27 (m, 2H), 7.22-7.18 (m, 3H), 4.06-3.96 (m, 4H), 2.85 (t, *J* = 8.4 Hz, 2H), 2.59 (s, 2H), 1.56-1.52 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 144.14, 136.40, 134.13, 129.18, 128.55, 128.45, 127.96, 126.06, 55.12, 30.93, 13.64.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₆H₂₀GeNaO₂ ([M+Na]⁺) 341.0573, found 341.0576.

IR (film) v_{max} 3068, 3048, 2980, 1482, 1462, 1433, 1380, 1180, 1152, 1091, 951 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(4-fluorophenyl)(methyl)germane (**1n**, 127.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-diox-aborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5

equiv), then NaOH and H_2O_2 was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **24** as a colorless oil (81.2 mg, 66% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.60-7.46 (m, 2H), 7.14-7.03 (m, 2H), 4.05-3.93 (m, 4H), 2.87 (s, 2H), 0.47 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 163.82 (d, J_{C-F} = 249.4 Hz), 135.64 (d, J_{C-F} = 7.0 Hz), 132.51 (d, J_{C-F} = 4.0 Hz), 115.58 (d, J_{C-F} = 19.0 Hz), 56.10, -7.45.

¹⁹F NMR (376 MHz, CDCl₃): δ -111.89.

HRMS (ESI-TOF) *m*/*z* calcd. for C₉H₁₃FGeNaO₂ ([M+Na]⁺) 269.0009, found 269.0006.

IR (film) v_{max} 3033, 2911, 2846, 1558, 1541, 1388, 1266, 1163, 1186, 939 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(methyl)(o-tolyl)germane (**1o**, 125.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H_2O_2 was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **25** as a colorless oil (79.9 mg, 66% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.42-7.40 (m, 1H), 7.29-7.25 (m, 1H), 7.20-7.15 (m, 2H), 4.19-4.16 (m, 2H), 4.03-4.00 (m, 2H), 2.84 (s, 2H), 2.41 (s, 3H), 0.56 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.23, 136.46, 134.34, 129.86, 129.41, 125.41, 56.58, 23.38, -6.01.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₀H₁₆GeNaO₂ ([M+Na]⁺) 265.0260, found 265.0255.

IR (film) v_{max} 3035, 2915, 2850, 1567, 1565, 1390, 1271, 1166, 1183, 950 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(methyl)(o-tolyl)germane (**1p**, 125.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H_2O_2 was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **26** as a colorless oil (84.7 mg, 66% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.33-7.31 (m, 2H), 7.29-7.25 (m, 1H), 7.20-7.17 (m, 1H), 4.10-3.97 (m, 4H), 2.68 (s, 2H), 2.36 (s, 3H), 0.51 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 137.88, 137.01, 134.50, 130.84, 130.01, 128.29, 56.17, 21.57, -7.58.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₀H₁₆GeNaO₂ ([M+Na]⁺) 265.0260, found 265.0256.

IR (film) v_{max} 3033, 2917, 2854, 1568, 1562, 1392, 1273, 1165, 1180, 952 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(methyl)(p-tolyl)germane (**1q**, 125.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **27** as a colorless oil (70.2 mg, 58% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.43-7.41 (m, 2H), 7.21-7.19 (m, 2H), 4.08-3.95 (m, 4H), 2.82 (s, 2H), 2.35 (s, 3H), 0.50 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 139.05, 133.84, 133.41, 129.22, 56.12, 21.50, -7.58.

HRMS (ESI-TOF) m/z calcd. for C₁₀H₁₆GeNaO₂ ([M+Na]⁺) 265.0260, found 265.0253.

IR (film) v_{max} 3033, 2915, 2851, 1569, 1560, 1390, 1272, 1166, 1182, 950 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(phenyl)(vinyl)germane (**1r**, 124.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **28** as a colorless oil (61.2 mg, 51% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.56-7.52 (m, 2H), 7.40-7.36 (m, 3H), 6.43-6.34 (m, 1H), 6.21 (dd, J = 13.6, 2.8 Hz, 1H), 5.86 (dd, J = 20.0, 3.2 Hz, 1H), 4.15 (s, 4H), 2.31 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 135.48, 134.49, 134.35, 132.73, 129.42, 128.52, 55.32, 24.94.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₀H₁₄GeNaO₂ ([M+Na]⁺) 263.0103, found 263.0100.

IR (film) v_{max} 3567, 2958, 1700, 1685, 1671, 1651, 1574, 1558, 1459, 997 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of dichloro(methyl)(vinyl)germane (**1s**, 93.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **29** as a colorless oil (111.5 mg, 56% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 6.39-6.30 (m, 1H), 5.95-5.90 (m, 1H), 5.69-5.63 (m, 1H), 1.21 (s, 24H), 0.32 (s, 3H), 0.28 (d, *J* = 4.4 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 140.40, 129.93, 82.91, 25.13, 25.10, -1.78. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 33.97.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₇H₃₄B₂GeNaO₄ ([M+Na]⁺) 421.1747, found 421.1744.

IR (film) v_{max} 2978, 1467, 1389, 1371, 1341, 1269, 1166, 1114, 1004, 969 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of dichlorodivinylgermane (**1t**, 99.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **30** as a colorless oil (106.6 mg, 52% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 6.37-6.29 (m, 2H), 5.99 (dd, *J* = 13.6, 3.2 Hz, 2H), 5.73 (dd, *J* = 19.6, 2.8 Hz, 2H), 1.21 (s, 24H), 0.35 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 138.18, 131.25, 83.00, 25.12. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 34.26.

HRMS (ESI-TOF) m/z calcd. for C₁₈H₃₄B₂GeNaO₄ ([M+Na]⁺) 433.1747, found 433.1743.

IR (film) v_{max} 3048, 2978, 1468, 1388, 1371, 1341, 1269, 1166, 1114, 1003 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of dichloro(3,3-dimethylbut-1-yn-1-yl)(phenyl)germane (**1u**, 151.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **31** as a colorless oil (221.1 mg, 86% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.67-7.65 (m, 2H), 7.33-7.29 (m, 3H), 1.25 (s, 9H), 1.16 (s, 12H), 1.15 (s, 12H), 0.62-0.55 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 139.57, 133.73, 128.69, 127.76, 116.43, 82.97, 79.01, 31.23, 28.36, 25.03, 25.02. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 34.14.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₆H₄₂B₂GeNaO₄ ([M+Na]⁺) 537.2373, found 537.2369.

IR (film) v_{max} 2975, 2928, 2868, 1433, 1388, 1374, 1270, 1252, 1166, 1094 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of 1,1-dichlorogermolane (**1v**, 100.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **32** as a colorless oil (206.1 mg, 70% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.56-1.53 (m, 4H), 1.20 (s, 24H), 0.82-0.77 (m, 4H), 0.31 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 82.84, 28.03, 25.10, 14.27. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 34.11.

HRMS (ESI-TOF) m/z calcd. for C₁₈H₃₆B₂GeNaO₄ ([M+Na]⁺) 435.1904, found 435.1909.

IR (film) v_{max} 2978, 2926, 1467, 1388, 1370, 1341, 1268, 1215, 1114, 969 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of 5,5-dichloro-5H-dibenzo[b,d]germole (**1w**, 148.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **33** as a colorless oil (165.2 mg, 65% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.76-7.74 (m, 2H), 7.40-7.36 (m, 2H), 7.29-7.25 (m, 2H), 1.07 (s, 24H), 0.67 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 146.18, 140.52, 133.78, 129.49, 127.43, 121.09, 83.07, 24.91. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 33.28.

HRMS (ESI-TOF) m/z calcd. for C₂₆H₃₆B₂GeNaO₄ ([M+Na]⁺) 531.1904, found 531.1906.

IR (film) v_{max} 2976, 1588, 1433, 1388, 1372, 1268, 1214, 1166, 1116, 968 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of 1,1-dichlorogerminane (**1x**, 107.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **34** as a colorless oil (140.7 mg, 66% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 1.73-1.67 (m, 4H), 1.38-1.32 (m, 2H), 1.21 (s, 24H), 0.94-0.91 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 82.80, 30.19, 25.76, 25.17, 16.02. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B** NMR (128 MHz, CDCl₃) δ 33.96.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₉H₃₈B₂GeNaO₄ ([M+Na]⁺) 449.2060, found 449.2053.

IR (film) v_{max} 2977, 2930, 2906, 1463, 1445, 1389, 1370, 1339, 1268, 1114 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorotrimethylgermane (**1y**, 115.5 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **35** as a colorless oil (228.6 mg, 96% yield). The 2,2',2"-(2-phenylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 2.4 g, 5.0 mmol) was used and, **35** was isolated using the same procedure (2.2 g, 94% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.23-7.07 (m, 3H), 3.02 (s, 2H), 1.18-1.14 (m, 24H), 0.21 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 144.57, 129.42, 127.48, 125.19, 82.61, 33.89, 25.01, 24.95, -1.01. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B** NMR (128 MHz, CDCl₃) δ 33.91.

HRMS (ESI-TOF) m/z calcd. for C₂₃H₄₁B₂GeO₄ ([M+H]⁺) 477.2397, found 477.2393.

IR (film) v_{max} 2978, 2907, 2871, 1496, 1458, 1370, 1332, 1290, 1110, 1015 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **36** as a colorless oil (248.8 mg, 96% yield). The 2,2',2"-(2-phe-nylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 2.4 g, 5.0 mmol) was used and, **36** was isolated using the same procedure (2.5 g, 95% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.37-7.35 (m, 2H), 7.19-7.15 (m, 2H), 7.10-7.06 (m, 1H), 3.06 (s, 2H), 1.67-1.14 (m, 24H), 1.11-1.06 (m, 9H), 0.99-0.92 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 144.80, 129.50, 127.34, 125.10, 82.51, 34.25, 25.19, 24.94, 9.76, 5.53. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 34.32.

HRMS (ESI-TOF) m/z calcd. for C₂₆H₄₇B₂GeO₄ ([M+H]⁺) 519.2867, found 519.2865.

IR (film) v_{max} 2977, 2905, 2871, 1457, 1368, 1330, 1288, 1165, 1109, 1014 cm⁻¹.



This compound was prepared according to General procedure A from the reaction of tributylchlorogermane (1aa', 210.1 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **37** as a colorless oil (298.2 mg, 99% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.37-7.35 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.10-7.06 (m, 1H), 3.05 (s, 2H), 1.42-1.30 (m, 12H), 1.17-1.14 (m, 24H), 1.01-0.84 (m, 15H).

¹³C NMR (101 MHz, CDCl₃) δ 144.82, 129.50, 127.33, 125.07, 82.47, 24.33, 27.93, 27.01, 25.24, 25.00, 13.94, 13.82. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 35.24.

HRMS (ESI-TOF) m/z calcd. for C₃₂H₅₉B₂GeO₄ ([M+H]⁺) 603.3806, found 603.3801.

IR (film) v_{max} 2978, 2955, 2926, 1457, 1374, 1319, 1288, 1260, 1109, 1079 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorotrihexylgermane (**1aa**, 273.1 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **38** as a colorless oil (329.5 mg, 96% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.36-7.34 (m, 2H), 7.18-7.14 (m, 1H), 7.10-7.05 (m, 2H), 3.04 (s, 2H), 1.42-1.27 (m, 24H), 1.16-1.13 (m, 24H), 0.92-0.88 (m, 15H).

¹³C NMR (101 MHz, CDCl₃) δ 144.86, 129.51, 127.33, 125.06, 82.46, 34.34, 33.76, 31.70, 25.62, 25.24, 25.00, 22.83, 14.32, 14.15. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B** NMR (128 MHz, CDCl₃) δ 35.12.

HRMS (ESI-TOF) m/z calcd. for C₃₈H₇₁B₂GeO₄ ([M+H]⁺) 687.4745, found 687.4739.

IR (film) v_{max} 2978, 2957, 2853, 1457, 1374, 1329, 1290, 1212, 1108, 1014 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chloro(ethyl)dimethylgermane (**1ab**, 126.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phe-nylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **39** as a colorless oil (232.9 mg, 95% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.37-7.35 (m, 2H), 7.20-7.16 (m, 1H), 7.14-7.07 (m, 2H), 3.04 (s, 2H), 1.19-1.15 (m, 24H), 1.02-0.98 (m, 3H), 0.87-0.81 (m, 2H), 0.19 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 144.64, 129.44, 127.43, 125.17, 82.55, 33.99, 25.05, 24.98, 9.08, 8.24, -3.83. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 33.75.

HRMS (ESI-TOF) m/z calcd. for C₂₄H₄₃B₂GeO₄ ([M+H]⁺) 491.2554, found 491.2550.

IR (film) v_{max} 2977, 1457, 1369, 1335, 1320, 1290, 1262, 1212, 1109, 1015 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chloro(cyclopropyl)diphenylgermane (**1ac**, 228.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **40** as a colorless oil (300.6 mg, 96% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.69-7.67 (m, 4H), 7.34-7.29 (m, 8H), 7.17-7.09 (m, 3H), 3.39 (s, 2H), 1.02-0.99 (m, 24H), 0.73-0.68 (m, 2H), 0.48-0.40 (m, 1H), 0.17-0.13 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 144.05, 137.29, 136.41, 129.99, 128.46, 127.47, 127.40, 125.33, 82.86, 34.91, 25.12, 24.78, 1.98, -3.78. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 34.52.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₅H₄₆B₂GeNaO₄ ([M+Na]⁺) 649.2686, found 649.2679.

IR (film) v_{max} 3567, 2995, 2975, 1558, 1457, 1375, 1320, 1262, 1089, 1035 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chloro(methyl)diphenylgermane (**1ad**, 208.5 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **41** as a colorless oil (282.1 mg, 94% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.75-7.72 (m, 4H), 7.39-7.36 (m, 6H), 7.27-7.24 (m, 2H), 7.19-7.13 (m, 3H), 3.33 (s, 2H), 1.13-1.11 (m, 24H), 0.70 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.61, 139.85, 135.49, 134.61, 129.86, 128.31, 127.55, 127.39, 125.39, 82.92, 34.65, 25.09, 24.86, -2.30. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 34.28.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₃H₄₄B₂GeNaO₄ ([M+Na]⁺) 623.2530, found 623.2522.

IR (film) v_{max} 2976, 1521, 1457, 1431, 1375, 1320, 1289, 1211, 1166, 1110 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorodiethyl(phenyl)germane (**1ae**, 183.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **42** as a colorless oil (277.5 mg, 98% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.63-7.60 (m, 2H), 7.35-7.28 (m, 5H), 7.16-7.07 (m, 3H), 3.15 (s, 2H), 1.25-1.09 (m, 34H).

¹³C NMR (101 MHz, CDCl₃) δ 144.10, 139.34, 135.29, 129.74, 128.00, 127.44, 127.31, 125.23, 82.74, 34.57, 25.27, 24.93, 9.71, 6.25. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 35.05.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₀H₄₆B₂GeNaO₄ ([M+Na]⁺) 589.2686, found 589.2680.

IR (film) v_{max} 2977, 2872, 1558, 1457, 1374, 1319, 1288, 1261, 1109, 1089 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorodiphenyl(vinyl)germane (**1af**, 217.5 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **43** as a colorless oil (297.0 mg, 97% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.71-7.63 (m, 4H), 7.36-7.30 (m, 8H), 7.19-7.09 (m, 3H), 6.68-6.58 (m, 1H), 6.23-6.18 (m, 1H), 5.63-5.55 (m, 1H), 3.34 (s, 2H), 1.02 (s, 24H).

¹³C NMR (101 MHz, CDCl₃) δ 143.92, 137.53, 137.43, 136.20, 133.17, 129.93, 128.55, 127.61, 127.45, 125.40, 82.92, 34.83, 25.08, 24.80. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B** NMR (128 MHz, CDCl₃) δ 32.56.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₄H₄₄B₂GeNaO₄ ([M+Na]⁺) 635.2530, found 635.2524.

IR (film) v_{max} 3557, 3483, 2977, 1558, 1457, 1433, 1323, 1262, 1090, 1013 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chloro(phenyl)divinylgermane (**1ag**, 180.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **44** as a colorless oil (267.1 mg, 95% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.66-7.63 (m, 2H), 7.34-7.30 (m, 5H), 7.17-7.09 (m, 3H), 6.48-6.40 (m, 2H), 6.12 (dd, *J* = 13.6, 3.6 Hz, 2H), 5.64 (dd, *J* = 20.4, 3.6 Hz, 2H), 3.22 (m, 2H), 1.12-1.10 (m, 24H).

¹³C NMR (101 MHz, CDCl₃) δ 143.92, 137.47, 136.78, 135.75, 132.65, 129.84, 127.58, 127.45, 125.40, 82.94, 34.36, 25.11, 24.93. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.
¹¹**B NMR (128 MHz, CDCl₃)** δ 34.36.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₀H₄₂B₂GeNaO₄ ([M+Na]⁺) 585.2373, found 585.2366.

IR (film) v_{max} 3047, 2977, 2942, 1496, 1431, 1393, 1328, 1291, 1262, 1110 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorobis(3,3-dimethylbut-1-yn-1-yl)(phenyl)germane (**1ah**, 261.1 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **45** as a colorless oil (301.7 mg, 90% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.85-7.81 (m, 2H), 7.49-7.46 (m, 2H), 7.31-7.27 (m, 3H), 7.16-7.08 (m, 3H), 3.29 (s, 2H), 1.28 (s, 18H), 1.31-1.11 (m, 24H). ¹³C NMR (101 MHz, CDCl₃) δ 143.18, 137.19, 135.15, 130.43, 128.61, 127.34, 127.12, 125.42, 115.89, 82.98, 77.48, 34.26, 31.09, 28.40, 25.14, 24.82. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B** NMR (128 MHz, CDCl₃) δ 34.14.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₈H₅₄B₂GeNaO₄ ([M+Na]⁺) 693.3312, found 693.3307.

IR (film) v_{max} 2972, 2928, 2868, 1477, 1455, 1376, 1332, 1292, 1251, 1111 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chloro(methyl)(phenyl)(vinyl)germane (**1ai**, 171.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **46** as a colorless oil (266.9 mg, 97% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.66-7.63 (m, 2H), 7.33-7.27 (m, 5H), 7.17-7.09 (m, 3H), 6.58-6.49 (m, 1H), 6.06 (dd, *J* = 13.6, 3.6 Hz, 1H), 5.65 (dd, *J* = 20.0, 2.8 Hz, 1H), 3.19 (s, 2H), 1.18-1.14 (m, 24H), 0.51 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.82, 139.89, 139.03, 135.00, 130.91, 129.78, 128.28, 127.55, 127.42, 125.38, 82.92, 82.87, 34.31, 25.12, 24.98, 24.93, -3.57. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 35.20.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₉H₄₂B₂GeNaO₄ ([M+Na]⁺) 573.2373, found 573.2369.

IR (film) v_{max} 2976, 1603, 1496, 1431, 1374, 1289, 1260, 1211, 1166, 1110 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of 1-chloro-1-phenylgermolane (**1aj**, 181.5 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **47** as a colorless oil (273.7 mg, 97% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.62-7.59 (m, 2H), 7.33-7.30 (m, 3H), 7.17-7.08 (m, 5H), 3.18 (s, 2H), 1.76-1.69 (m, 2H), 1.59-1.52 (m, 2H), 1.23-1.20 (m, 24H), 1.05-0.98 (m, 2H), 0.85-0.78 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 143.74, 141.76, 134.56, 129.72, 128.02, 127.66, 127.51, 125.46, 83.01, 34.49, 28.01, 25.04, 25.02, 14.08. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 34.90.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₀H₄₄B₂GeNaO₄ ([M+Na]⁺) 587.2530, found 587.2526.

IR (film) v_{max} 2977, 2929, 2850, 1430, 1375, 1329, 1300, 1261, 1166, 1075 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of 1-chloro-1-phenylgerminane (**1ak**, 192.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **48** as a colorless oil (268.9 mg, 93% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.60-7.56 (m, 2H), 7.33-7.32 (m, 3H), 7.21-7.20 (m, 2H), 7.14-7.06 (m, 2H), 3.06 (s, 2H), 2.01-1.96 (m, 2H), 1.64-1.58 (m, 1H), 1.36-1.15 (m, 31H).

¹³C NMR (101 MHz, CDCl₃) δ 143.88, 139.32, 134.97, 129.78, 128.10, 127.60, 127.35, 125.30, 82.84, 34.23, 29.90, 26.12, 25.27, 25.00, 13.96. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 33.94.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₁H₄₆B₂GeNaO₄ ([M+Na]⁺) 601.2686, found 601.2679.

IR (film) v_{max} 2976, 2911, 2846, 1496, 1444, 1328, 1286, 1259, 1212, 1108 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of 1-chloro-1-phenylgermepane (**1al**, 202.5 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **49** as a colorless oil (266.5 mg, 90% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.61-7.59 (m, 2H), 7.34-7.30 (m, 3H), 7.20-7.18 (m, 2H), 7.12-7.05 (m, 3H), 3.06 (s, 3H), 1.81-1.43 (m, 8H), 1.27-1.22 (m, 4H), 1.17-1.16 (m, 24H).

¹³C NMR (101 MHz, CDCl₃) δ 144.05, 140.90, 134.96, 129.83, 127.96, 127.53, 127.36, 125.27, 82.80, 34.46, 31.26, 25.28, 24.99, 24.75, 15.06. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B** NMR (128 MHz, CDCl₃) δ 33.66.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₂H₄₈B₂GeNaO₄ ([M+Na]⁺) 615.2843, found 615.2837.

IR (film) v_{max} 2976, 2852, 1496, 1455, 1374, 1329, 1287, 1258, 1165, 1109 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorodiphenylgermane (**1am**, 198.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **50** as a colorless oil (252.1 mg, 86% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.58-7.55 (m, 4H), 7.30-7.24 (m, 8H), 7.13-7.07 (m, 3H), .5.27 (s, 1H), 3.27 (s, 2H), 1.03-1.02 (m, 24H).

¹³C NMR (101 MHz, CDCl₃) δ 143.44, 137.20, 136.01, 129.94, 128.60, 127.72, 127.56, 125.54, 83.14, 35.43, 25.04, 24.67. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 33.87.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₂H₄₂B₂GeNaO₄ ([M+Na]⁺) 609.2373, found 609.2371.

IR (film) v_{max} 3054, 2977, 2930, 1432, 1375, 1331, 1288, 1261, 1166, 1090 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chloro(phenyl)germane (**1an**, 141.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-phenylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**, 242.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **51** as a colorless oil (211.7 mg, 83% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.49-7.46 (m, 2H), 7.30-7.21 (m, 5H), 7.18-7.11 (m, 3H), .4.56 (s, 2H), 3.18 (s, 2H), 1.164-1.157 (m, 24H).

¹³C NMR (101 MHz, CDCl₃) δ 143.03, 135.92, 135.61, 129.80, 128.59, 127.71, 127.65, 125.68, 83.28, 35.27, 24.98, 24.72. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 34.45.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₆H₃₈B₂GeNaO₄ ([M+Na]⁺) 533.2060, found 533.2055.

IR (film) v_{max} 2978, 2931, 1455, 1433, 1375, 1305, 1288, 1261, 1109, 1092 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(methyl)(phenyl)silane (**1ao**, 95.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **52** as a colorless oil (45.5 mg, 50% yield), the yield of 40 mmol scale is 60% (5.4g).



¹**H NMR (400 MHz, CDCl₃)** δ 7.59-7.57 (m, 2H), 7.42-7.36 (m, 3H), 3.83-3.71 (m, 4H), 2.84 (s, 2H), 0.39 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 134.27, 134.17, 129.96, 128.18, 54.36, -7.72.

HRMS (ESI-TOF) *m*/*z* calcd. for C₉H₁₄SiNaO₂ ([M+Na]⁺) 205.0655, found 205.0650.

IR (film) v_{max} 3043, 2909, 1483, 1426, 1260, 1243, 1182, 1096, 1066, 947 cm⁻¹.



This compound was prepared according to **General procedure C** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and 2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b**, 109.1 mg, 0.5 mmol), 'BuOK (84.2 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure C; the crude product was purified by column chromatography on silica gel (hexane), to yield the product **53** as a colorless oil (97.1 mg, 77% yield). ¹H NMR and ¹³C NMR data are consistent with those reported in ref. 26.



¹**H NMR (400 MHz, CDCl₃)** δ 7.22-7.18 (m, 2H), 7.07-7.01 (m, 3H), 2.23 (s, 2H), 1.00 (t, *J* = 8.0 Hz, 9H), 0.75-0.69 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 141.91, 128.28, 127.88, 123.72, 21.14, 8.95, 3.94.



This compound was prepared according to **General procedure C** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and 2,2'-(propane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2c**, 148.1 mg, 0.5 mmol), 'BuOK (84.2 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure C; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product 54 as a colorless oil (99.1 mg, 60% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.21 (s, 12H), 1.10-1.04 (m, 15H), 0.85-0.78 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 82.69, 25.11, 21.26, 9.66, 3.07.

¹¹B NMR (128 MHz, CDCl₃) δ 35.08.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₅H₃₃BGeNaO₂ ([M+Na]⁺) 353.1678, found 353.1672.

IR (film) v_{max} 2973, 1568, 1450, 1430, 1372, 1302, 1290, 1254, 1110, 1086 cm⁻¹.



This compound was prepared according to **General procedure C** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2d**, 197.1 mg, 0.5 mmol), 'BuOK (84.2 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure C; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **55** as a colorless oil (145.6 mg, 68% yield). The tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2d**, 2.0 g, 5.0 mmol) was used and, **55** was isolated using the same procedure (1.3 g, 63% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 1.16-1.14 (m, 24H), 0.99 (t, *J* = 5.6 Hz, 9H), 0.80 (q, *J* = 5.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 82.45, 25.07, 24.57, 8.99, 6.17. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 33.94.

HRMS (ESI-TOF) m/z calcd. for C₁₉H₄₁B₂GeO₄ ([M+H]⁺) 429.2397, found 429.2393.

IR (film) v_{max} 2978, 2908, 2872, 1462, 1375, 1318, 1296, 1268, 1215, 1068 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-(4-methoxyphenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2e**, 257.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hex-ane/EtOAc = 20/1), to yield the product **56** as a colorless oil (263.2 mg, 96% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.07 (t, *J* = 8.0 Hz, 1H), 6.98-6.92 (m, 2H), 6.66-6.63 (m, 1H), 3.78 (s, 3H), 3.03 (s, 2H), 1.16-1.13 (m, 24H), 1.11-1.07 (m, 9H), 0.99-0.92 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 159.13, 146.45, 128.17, 122.13, 114.97, 111.03, 82.48, 55.21, 34.36, 25.22, 24.96, 9.76, 5.56. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 33.73.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₇H₄₈B₂GeNaO₅ ([M+Na]⁺) 571.2792, found 571.2788.

IR (film) v_{max} 2977, 2871, 2833, 1599, 1582, 1466, 1341, 1314, 1258, 1110 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-(4-chlorophenyl)ethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2f**, 259.1 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **57** as a colorless oil (248.5 mg, 90% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.45-7.44 (m, 1H), 7.25-7.22 (m, 1H), 7.11-7.04 (m, 2H), 3.00 (s, 2H), 1.60-1.14 (m, 24H), 1.12-1.08 (m, 9H), 1.00-0.94 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 147.04, 133.15, 129.96, 128.46, 127.99, 125.11, 82.62, 33.96, 25.23, 24.91, 9.72, 5.48. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 33.71.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₆H₄₅B₂ClGeNaO₄ ([M+Na]⁺) 575.2296, found 575.2300.

IR (film) v_{max} 2978, 2872, 1596, 1479, 1368, 1339, 1288, 1264, 1212, 1110 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-(4-bromophenyl)ethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2g**, 281.1 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **58** as a colorless oil (259.3 mg, 87% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.61-7.60 (m, 1H), 7.30-7.27 (m, 1H), 7.23-7.20 (m, 12H), 7.03 (t, *J* = 8.0 Hz, 1H), 3.00 (s, 2H), 1.16-1.09 (m, 24H), 1.22-1.08 (m, 9H), 1.03-0.94 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 147.35, 132.50, 128.79, 128.48, 128.02, 121.60, 82.61, 33.94, 25.25, 24.91, 24.72, 9.72, 5.46. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 33.28.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₆H₄₆B₂BrGeO₄ ([M+H]⁺) 597.1976, found 597.1967.

IR (film) v_{max} 2978, 2930, 2872, 1593, 1567, 1478, 1368, 1338, 1212, 1110 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-(4-fluorophenyl)ethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2h**, 251.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **59** as a colorless oil (246.7 mg, 92% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.34-7.30 (m, 2H), 6.84 (t, *J* = 8.0 Hz, 2H), 2.98 (s, 2H), 1.14-1.13 (m, 24H), 1.08 (t, *J* = 8.0 Hz, 9H), 0.98-0.92 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 161.12 (d, J_{C-F} = 241.0 Hz), 140.50 (d, J_{C-F} = 3.0 Hz), 130.94 (d, J_{C-F} = 7.0 Hz), 115.58 (d, J_{C-F} = 20.0 Hz), 82.58, 33.45, 25.24, 24.93, 9.5, 5.54. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 34.44.

¹⁹F NMR (376 MHz, CDCl₃): δ -119.38.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₆H₄₅B₂FGeNaO₄ ([M+Na]⁺) 559.2592, found 559.2586.

IR (film) v_{max} 2977, 2929, 2870, 1586, 1496, 1475, 1366, 1334, 1210, 1109 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-(thiophen-2-yl)ethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2i**, 245.1 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **60** as a colorless oil (251.6 mg, 96% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.14-7.12 (m, 1H), 7.09-7.06 (m, 2H), 3.01 (s, 2H), 1.17-1.16 (m, 24H), 1.13-1.05 (m, 9H), 0.97-0.92 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 1145.45, 130.33, 123.16, 121.02, 82.50, 28.80, 25.25, 24.87, 9.73, 5.41. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 33.53.

HRMS (ESI-TOF) m/z calcd. for C₂₄H₄₅B₂GeO₄ ([M+H]⁺) 525.2431, found 525.2426.

IR (film) v_{max} 2977, 2872, 1462, 1442, 1368, 1333, 1309, 1245, 1109, 1015 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(2-cyclopropylethane-1,1,1triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2j**, 224.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **61** as a colorless oil (205.0 mg, 85% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 1.59 (d, *J* = 6.8 Hz, 2H), 1.20-1.19 (m, 24H), 1.07-1.03 (m, 9H), 0.95-0.89 (m, 6H), 0.33-0.29 (m, 2H), 0.18-0.14 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 82.33, 33.94, 25.26, 24.87, 12.70, 9.76, 5.89, 5.71. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 33.29.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₃H₄₆B₂GeNaO₄ ([M+Na]⁺) 505.2686, found 505.2683.

IR (film) v_{max} 3080, 2996, 2977, 1462, 1444, 1374, 1330, 1295, 1108, 1042 cm⁻¹.



This compound was prepared according to **General procedure A** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and 2,2',2"-(hexane-1,1,1-triyl)tris(4,4,5,5tetramethyl-1,3,2-dioxaborolane) (**2k**, 232.2 mg, 0.5 mmol), LiHMDS (125.5 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure A; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **62** as a colorless oil (219.3 mg, 88% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 1.60-1.56 (m, 2H), 1.40-1.23 (m, 6H), 1.19-1.18 (m, 24H), 1.06 (t, *J* = 8.0 Hz, 9H), 0.94-0.85 (m, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 82.29, 32.99, 31.19, 29.14, 25.18, 24.91, 22.78, 14.26, 9.74, 5.63. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 34.23.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₄H₅₀B₂GeNaO₄ ([M+Na]⁺) 521,2999, found 521.3004.

IR (film) v_{max} 3077, 2991, 2978, 1459, 1442, 1372, 1328, 1283, 1110, 1038 cm⁻¹.



This compound was prepared according to **General procedure C** from the reaction of chlorotriethylgermane (**1z**, 147.0 mg, 0.75 mmol, 1.5 equiv) and tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2l**, 260.2 mg, 0.5 mmol), 'BuOK (84.2 mg, 0.75 mmol, 1.5 equiv). The crude mixture was worked up using EA described in the general procedure C; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **63** as a colorless oil (133.0 mg, 48% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.18 (s, 36H), 1.08-1.04 (m, 9H), 0.97-0.92 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 82.37, 24.91, 9.77, 7.28. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹**B NMR (128 MHz, CDCl₃)** δ 33.77.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₅H₅₁B₃GeNaO₆ ([M+Na]⁺) 577.3069, found 577.3076.

IR (film) v_{max} 2977, 2912, 2862, 1465, 1378, 1316, 1299, 1263, 1212, 1086 cm⁻¹.



This compound was prepared according to **General procedure B** from the reaction of dichlorodiphenylgermane (**1h**, 149.0 mg, 0.5 mmol) and tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)methane (**2**, 788.6 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25mol, 4.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **64** as a colorless oil (125.8 mg, 33% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.80-7.79 (m, 4H), 7.26-7.22 (m, 6H), 1.23 (s, 2H), 1.014-1.007 (m, 48H).

¹³C NMR (101 MHz, CDCl₃) δ 139.98, 135.86, 127.87, 126.85, 82.53, 24.96, 24.60. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 34.45.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₈H₆₀B₄GeNaO₈ ([M+Na]⁺) 785.3764, found 785.3759.

IR (film) v_{max} 3048, 2976, 1484, 1468, 1375, 1265, 1214, 1166, 1091, 1076 cm⁻¹.



The absolute configuration of **91** was assigned to be (*S*) by chiral HPLC comparison with that reported in the ref. 27 (**Supplementary Figure 10**), and the configuration of all other products was assigned by analogy. The X-Ray Structure of **73'** is consistent with the absolute configuration of **91**.



Supplementary Figure S10. | The absolute configuration of 91 in reported literatures



Peak RetTime Type Width Area Height Area [mAU] [min] [min] [mAU*s] % # ----|-----|----|-----|-----|--------| ----10.598 BB 0.2667 6907.28369 1 405.55502 49.8192 13.552 BB 2 0.3076 6957.42822 350.50125 50.1808

Totals : 1.38647e4 756.05627



Signal 3: DAD1 C, Sig=210,4 Ref=off

Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.607	BB	0.2508	3999.94629	247.10660	99.3377
2	13.567	BB	0.2793	26.66715	1.40571	0.6623
Totals :			4026.61344	248.51231		

Supplementary Figure S11. | The chiral HPLC of 91 in this work

This compound was prepared according to **General procedure E** from the reaction of 2-methyl-2-phenylpropane-1,3-diol (33.2 mg, 0.2 mmol), benzoyl chloride (**66**, 42.0 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **91** as a colorless oil (53.5 mg, 99% yield, 99% e.e.). ¹H NMR and ¹³C NMR data are consistent with those reported in ref. 19.

HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 210$ nm), t_R (major) = 18.45 min, t_R (minor) = 22.17 min.

(S)-3-hydroxy-2-methyl-2-phenylpropyl benzoate (91)



¹H NMR (400 MHz, CDCl₃) δ 8.01-7.98 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.36 (m, 6H), 7.30-7.25 (m, 1H), 4.61 (s, 2H), 3.84 (s, 2H), 1.47 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.94, 142.70, 133.23, 129.98, 129.70, 128.70, 128.51, 126.94, 126.59, 69.03, 68.03, 20.84.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), benzoyl chloride (**66**, 42.0 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **67** as a colorless oil (57.8 mg, 87% yield, 91% e.e.). HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 18.99 min, $t_{\rm R}$ (minor) = 12.67 min. [α]_D²⁵ = +1.00 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl benzoate (67)



¹**H NMR (400 MHz, CDCl₃)** δ 8.03-8.00 (m, 2H), 7.59-7.52 (m, 3H), 7.46-7.42 (m, 2H), 7.39-7.35 (m, 3H), 4.57 (q, *J* = 12.4 Hz, 2H), 3.99 (q, *J* = 12.4 Hz, 2H), 2.14 (s, 1H), 0.54 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.95, 136.67, 133.87, 133.23, 129.96, 129.69, 129.37, 128.57, 128.50, 57.70, 54.86, -7.45.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₆H₁₈GeNaO₃ ([M+Na]⁺) 355.0360, found 355.0359.

IR (film) v_{max} 2360, 2341, 1716, 1601, 1451, 1431, 1318, 1295, 1111, 999 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), 2-methylbenzoyl chloride (**66b**, 46.2 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **68** as a colorless oil (60.9 mg, 88% yield, 95% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 210$ nm), $t_{\rm R}$ (major) = 17.32 min, $t_{\rm R}$ (minor) = 9.94 min. $[\alpha]_{\rm D}^{25} = +0.64$ (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl 2-methylbenzoate (68)



¹**H NMR (400 MHz, CDCl₃)** δ 7.84-7.82 (m, 1H), 7.56-7.51 (m, 2H), 7.42-7.35 (m, 4H), 7.25-7.20 (m, 2H), 4.54 (q, *J* = 12.4 Hz, 2H), 4.00 (q, *J* = 12.4 Hz, 2H), 2.56 (s, 3H), 0.55 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 168.98, 140.28, 136.69, 133.89, 132.24, 131.83, 130.70, 129.41, 129.35, 128.49, 125.86, 57.43, 54.89, 21.83, -7.31.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₆H₁₈GeNaO₃ ([M+Na]⁺) 355.0360, found 355.0359.

IR (film) v_{max} 2362, 2347, 1734, 1603, 1459, 1427, 1330, 1285, 1106, 996 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), 3-methylbenzoyl chloride (**66c**, 46.2 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **69** as a colorless oil (60.2 mg, 87% yield, 90% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 12.21 min, $t_{\rm R}$ (minor) = 9.91 min. $[\alpha]_{\rm D}^{25}$ = +1.82 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl 3-methylbenzoate (69)



¹**H NMR (400 MHz, CDCl₃)** δ 7.83-7.80 (m, 2H), 7.57-7.52 (m, 2H), 7.39-7.31 (m, 5H), 4.56 (q, *J* = 12.0 Hz, 2H), 3.99 (q, *J* = 12.4 Hz, 2H), 2.40 (s, 3H), 2.30 (s, 1H), 0.54 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 168.14, 138.35, 136.75, 133.99, 133.87, 130.24, 129.87, 129.32, 128.47, 128.44, 126.80, 57.64, 54.83, 21.38, -7.47.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₇H₂₀GeNaO₃ ([M+Na]⁺) 369.0516, found 369.0512.

IR (film) v_{max} 2363, 2339, 2162, 1719, 1424, 1310, 1264, 1197, 999, 896 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), 4-methoxybenzoyl chloride (**66d**, 51.0 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **70** as a colorless oil (58.7 mg, 81% yield, 93% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), $t_{\rm R}$ (major) = 34.10 min, $t_{\rm R}$ (minor) = 22.99 min. [α]_D²⁵ = +1.36 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl 4-methoxybenzoate (70)



¹**H NMR (400 MHz, CDCl₃)** δ 7.99-7.95 (m, 2H), 7.55-7.52 (m, 2H), 7.38-7.35 (m, 3H), 6.93-6.90 (m, 2H), 4.54 (q, *J* = 12.4 Hz, 2H), 3.99 (q, *J* = 12.8 Hz, 2H), 3.86 (s, 3H), 2.42 (s, 1H), 0.53 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.68, 163.60, 136.85, 133.85, 131.72, 129.27, 128.43, 122.32, 113.79, 57.34, 55.53, 54.77, -7.50.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₇H₂₀GeNaO₄ ([M+Na]⁺) 385.0466, found 385.0461.

IR (film) v_{max} 2361, 2341, 1710, 1607, 1512, 1299, 1277, 1260, 1169, 1101 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), 4-chlorobenzoyl chloride (**66e**, 52.2 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **71** as a colorless oil (60.8 mg, 83% yield, 85% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 210$ nm), $t_{\rm R}$ (major) = 19.24 min, $t_{\rm R}$ (minor) = 11.49 min. $[\alpha]_{\rm D}^{25} = +0.30$ (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl 4-chlorobenzoate (71)



¹**H NMR (400 MHz, CDCl₃)** δ 7.86-7.83 (m, 2H), 7.58-7.54 (m, 2H), 7.53-7.50 (m, 2H), 7.38-7.35 (m, 3H), 4.56 (q, *J* = 12.4 Hz, 2H), 3.99 (q, *J* = 12.4 Hz, 2H), 2.25 (s, 1H), 0.54 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.23, 136.52, 133.94, 131.98, 131.25, 129.49, 128.95, 128.58, 128.43, 57.98, 54.87, -7.34.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₆H₁₇ClGeNaO₃ ([M+Na]⁺) 388.9970, found 388.9963.

IR (film) v_{max} 2360, 2341, 1711, 1489, 1444, 1367, 1299, 1158, 1106, 1040 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), benzo[d][1,3]dioxole-5-carbonylchloride (**66f**, 55.2 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), L8 (12.1 mg, 0.02mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EAdescribed in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product 72 as a colorless oil (53.4 mg, 71% yield, 93% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 23.54 min, $t_{\rm R}$ (minor) = 17.81 min. [α]_D²⁵ = +0.52 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl benzo[d][1,3]dioxole-5-carboxylate (72)



¹**H NMR (400 MHz, CDCl₃)** δ 7.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.53-7.51 (m, 2H), 7.42 (d, *J* = 1.6 Hz, 1H), 7.38-7.35 (m, 3H), 6.83 (d, *J* = 8.0 Hz, 1H), 4.52 (q, *J* = 12.4 Hz, 2H), 3.97 (q, *J* = 12.8 Hz, 2H), 2.07 (s, 1H), 0.52 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.30, 151.90, 147.89, 136.73, 133.86, 129.35, 128.49, 125.56, 123.91, 109.57, 108.18, 101.97, 57.63, 54.84, -7.47.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₇H₁₈GeNaO₅ ([M+Na]⁺) 399.0258, found 399.0256.

IR (film) v_{max} 2361, 2341, 1711, 1691, 1489, 1444, 1298, 1277, 1260, 1039 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), Chlorocarbonyl ferrocene (**66g**, 71.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **73** as a brown oil (73.0 mg, 83% yield, 95% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 15.06 min, $t_{\rm R}$ (minor) = 10.54 min. $[\alpha]_{\rm D}^{25}$ = +1.20 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl ferrocene carboxylate (73)



¹**H NMR (400 MHz, CDCl₃)** δ 7.57-7.55 (m, 2H), 7.42-7.36 (m, 3H), 4.78 (s, 2H), 4.49-4.38 (m, 4H), 4.15 (s, 5H), 4.01 (q, *J* = 9.2 Hz, 2H), 2.48 (s, 1H), 0.55 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.38, 136.83, 133.94, 129.38, 128.51, 71.51, 71.02, 70.25, 70.21, 69.86, 56.98, 54.90, -7.27.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₀H₂₂FeGeNaO₃ ([M+Na]⁺) 463.0022, found 463.0019.

IR (film) v_{max} 3055, 2360, 2341, 1465, 1424, 1301, 1264, 1137, 1004, 896 cm⁻¹.

Absolute Stereochemistry: The absolute stereochemistry was determined via X-Ray diffractometry after product functionalization to the corresponding pyridine organosulfate salt (ref. 28), which yielded crystals of sufficient quality for X-Ray diffractometry (*vide infra*).



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), furan-2-carbonyl chloride (**66h**, 39.0 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **74** as a colorless oil (52.8 mg, 82% yield, 95% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 29.71 min, $t_{\rm R}$ (minor) = 20.49 min. [α]_D²⁵ = -0.92 (c = 0.1, CH₂Cl₂). (S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl furan-2-carboxylate (74)



¹**H NMR (400 MHz, CDCl₃)** δ 7.58-7.57 (m, 1H), 7.54-7.51 (m, 2H), 7.38-7.35 (m, 3H), 7.16-7.15 (m, 1H), 6.51-6.50 (m, 1H), 4.54 (q, *J* = 12.4 Hz, 2H), 4.00 (q, *J* = 12.8 Hz, 2H), 2.09 (s, 1H), 0.54 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.87, 146.62, 144.46, 136.43, 133.86, 129.38, 128.48, 118.30, 112.05, 57.68, 54.85, -7.47.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₄H₁₆GeNaO₄ ([M+Na]⁺) 345.0153, found 345.0150.

IR (film) v_{max} 2360, 2341, 1709, 1473, 1313, 1264, 1179, 1119, 1016, 897 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), thiophene-2-carbonyl chloride (**66i**, 43.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product 75 as a colorless oil (54.1 mg, 80% yield, 95% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 19.37 min, $t_{\rm R}$ (minor) = 13.30 min. [α]_D²⁵ = +1.06 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl thiophene-2-carboxylate (75)



¹**H NMR (400 MHz, CDCl₃)** δ 7.79-7.78 (m, 1H), 7.57-7.52 (m, 3H), 7.39-7.35 (m, 3H), 7.11-7.09 (m, 1H), 4.53 (q, *J* = 12.4 Hz, 2H), 4.00 (q, *J* = 12.8 Hz, 2H), 2.08 (s, 1H), 0.55 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 163.51, 136.51, 133.89, 133.75, 133.34, 132.75, 129.38, 128.49, 127.96, 57.77, 54.80, -7.50.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₄H₁₆GeNaO₃S ([M+Na]⁺) 360.9924, found 360.9919.

IR (film) v_{max} 2360, 1710, 1525, 1416, 1361, 1286, 1263, 1243, 1215, 1092 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), 5-chlorothiophene-2-carbonyl chloride (**66j**, 54.0 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **76** as a colorless oil (67.0 mg, 90% yield, 92% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 17.39 min, $t_{\rm R}$ (minor) = 12.05 min. [α]_D²⁵ = +0.58 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl 5-chlorothiophene-2-carboxylate (76)



¹**H NMR (400 MHz, CDCl₃)** δ 7.56 (d, *J* = 4.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.39-7.35 (m, 3H), 6.92 (d, *J* = 4.0 Hz, 1H), 4.51 (q, *J* = 12.4 Hz, 2H), 3.99 (q, *J* = 12.4 Hz, 2H), 2.10 (s, 1H), 0.54 (s, 3H).
¹³C NMR (101 MHz, CDCl₃) δ 162.40, 137.70, 136.27, 133.85, 133.28, 131.44, 129.42, 128.50, 127.46, 57.94, 54.72, -7.51.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₄H₁₅ClGeNaO₃S ([M+Na]⁺) 394.9534, found 394.9527.

IR (film) v_{max} 2360, 2341, 1710, 1534, 1425, 1338, 1264, 1092, 1061, 1003 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), 3-methylthiophene-2-carbonyl chloride (**66k**, 48.0 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), L8 (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **77** as a colorless oil (66.2 mg, 94% yield, 93% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm), $t_{\rm R}$ (major) = 19.74 min, $t_{\rm R}$ (minor) = 10.15 min. [α]_D²⁵ = -0.44 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl 3-methylthiophene-2-carboxylate (77)



¹**H NMR (400 MHz, CDCl₃)** δ 7.56-7.52 (m, 2H), 7.39-7.35 (m, 4H), 6.91 (d, *J* = 4.8 Hz, 1H), 4.51 (q, *J* = 12.4 Hz, 2H), 3.99 (q, *J* = 12.4 Hz, 2H), 2.58 (s, 1H), 2.53 (s, 3H), 0.55 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 164.12, 146.59, 136.60, 133.89, 131.88, 130.48, 129.33, 128.45, 126.41, 57.23, 54.29, 16.08, -7.49.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₅H₁₈GeNaO₃S ([M+Na]⁺) 375.0081, found 375.0077.

IR (film) v_{max} 2341, 2326, 1711, 1690, 1539, 1431, 1411, 1382, 1264, 1001 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), benzofuran-2-carbonyl chloride (**661**, 54.0 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **78** as a colorless oil (54.3 mg, 73% yield, 90% e.e.). HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 36.28 min, $t_{\rm R}$ (minor) = 18.91 min. [α]_D²⁵ = -1.36 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl benzofuran-2-carboxylate (78)



¹**H NMR (400 MHz, CDCl₃)** δ 7.70-7.67 (m, 1H), 7.61-7.58 (m, 1H), 7.57-7.53 (m, 2H), 7.51 (d, *J* = 1.2 Hz, 1H), 7.48-7.44 (m, 1H), 7.39-7.36 (m, 3H), 7.33-7.29 (m, 1H), 4.63 (q, *J* = 12.4 Hz, 2H), 4.04 (q, *J* = 12.4 Hz, 2H), 2.00 (s, 1H), 0.57 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 160.72, 155.89, 145.24, 136.30, 133.89, 129.46, 128.53, 127.92, 127.00, 124.00, 122.99, 114.28, 112.51, 77.48, 77.16, 76.84, 58.29, 54.93, -7.39.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₈H₁₈GeNaO₄ ([M+Na]⁺) 395.0309, found 395.0306.

IR (film) v_{max} 2360, 2341, 1727, 1563, 1431, 1303, 1264, 1175, 1145, 966 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), 1-Adamantanecarbonyl chloride (**66m**, 59.4 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **79** as a colorless oil (66.3 mg, 85% yield, 84% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 7.79 min, $t_{\rm R}$ (minor) = 5.05 min. $[\alpha]_{\rm D}^{25}$ = -36.20 (c = 0.1, CH₂Cl₂).

((S)-(hydroxymethyl)(methyl)(phenyl)germyl)methyl (3R,5R)-adamantane-1-carboxylate (79)



¹**H NMR (400 MHz, CDCl₃)** δ 7.51-7.47 (m, 2H), 7.38-7.35 (m, 3H), 4.29 (q, *J* = 12.4 Hz, 2H), 3.93 (q, *J* = 12.8 Hz, 2H), 2.27 (s, 1H), 2.00-1.97 (m, 3H), 1.82 (d, J = 2.8 Hz, 6H), 1.74-1.64 (m, 6H), 0.47 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 179.17, 136.77, 133.95, 129.27, 128.41, 56.98, 54.76, 41.02, 39.00, 36.54, 28.00, -7.32.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₀H₂₈GeNaO₃ ([M+Na]⁺) 413.1142, found 413.1138.

IR (film) v_{max} 3055, 2988, 2361, 2341, 2327, 1423, 1330, 1264, 1105, 1078 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **80** as a colorless oil (71.0 mg, 87% yield, 97% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 12.94 min, $t_{\rm R}$ (minor) = 24.27 min. $[\alpha]_{\rm D}^{25}$ = -2.50 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (80)



¹**H NMR (400 MHz, CDCl₃)** δ 7.76-7.74 (m, 1H), 7.56-7.52 (m, 1H), 7.44-7.33 (m, 10H), 7.31-7.29 (m, 2H), 4.29 (q, *J* = 12.4 Hz, 2H), 3.82 (q, *J* = 12.4 Hz, 2H), 1.08 (s, 1H), 0.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.00, 142.59, 141.36, 136.56, 133.87, 131.50, 130.98, 130.86, 130.01, 129.29, 128.48, 128.42, 128.25, 127.43, 127.32, 57.58, 54.75, -7.47.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₂H₂₂GeNaO₃ ([M+Na]⁺) 431.0673, found 431.0669.

IR (film) v_{max} 2360, 2341, 1725, 1704, 1598, 1478, 1451, 1263, 1092, 997 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)germanediyl)dimethanol (**65**, 45.6 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8**' (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **80**' as a colorless oil (73.5 mg, 90% yield, -95% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), t_R (major) = 12.93 min, t_R (minor) = 23.93 min.

(*R*)-((hydroxymethyl)(methyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (80')



This compound was prepared according to **General procedure E** from the reaction of (ethyl(phenyl)germanediyl)dimethanol (**20**, 48.4 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **81** as a colorless oil (71.8 mg, 85% yield, 97% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 16.49 min, $t_{\rm R}$ (minor) = 11.21 min. $[\alpha]_{\rm D}^{25}$ = -4.42 (c = 0.1, CH₂Cl₂).

(S)-(ethyl(hydroxymethyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (81)



¹**H NMR (400 MHz, CDCl₃)** δ 7.74-7.72 (m, 1H), 7.55-7.51 (m, 1H), 7.44-7.33 (m, 10H), 7.31-7.28 (m, 2H), 4.36 (q, *J* = 12.4 Hz, 2H), 3.88 (q, *J* = 12.4 Hz, 2H), 1.92 (s, 1H), 1.069-1.065 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 170.01, 142.56, 141.35, 135.67, 134.20, 131.46, 130.96, 130.70, 129.97, 129.22, 128.47, 128.41, 128.24, 127.40, 127.30, 56.47, 53.40, 8.87, 4.05.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₃H₂₄GeNaO₃ ([M+Na]⁺) 445.0829, found 445.0827.

IR (film) v_{max} 2361, 2341, 2327, 1725, 1479, 1432, 1308, 1264, 1091, 1008 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (phenyl(propyl)germanediyl)dimethanol (**21**, 51.2 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **82** as a colorless oil (61.9 mg, 71% yield, 98% e.e.).

HPLC analysis: Chiralcel AD-H (*n*-Hexane/*i*-PrOH = 92.5/7.5, flow rate 0.6 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 19.40 min, $t_{\rm R}$ (minor) = 20.55 min. $[\alpha]_{\rm D}^{25}$ = -3.92 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(phenyl)(propyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (82)



¹**H NMR (400 MHz, CDCl₃)** δ 7.73-7.71 (m, 1H), 7.55-7.51 (m, 1H), 7.43-7.33 (m, 10H), 7.30-7.28 (m, 2H), 4.34 (q, *J* = 12.4 Hz, 2H), 3.86 (q, *J* = 12.8 Hz, 2H), 1.90 (s, 1H), 1.49-1.40 (m, 2H), 1.08-1.03 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.02, 142.57, 141.37, 135.97, 134.18, 130.98, 130.72, 129.99, 129.20, 128.49, 128.41, 128.26, 127.42, 127.31, 56.79, 53.80, 18.41, 17.99, 14.33.

HRMS (ESI-TOF) *m/z* calcd. for C₂₄H₂₆GeNaO₃ ([M+Na]⁺) 459.0986, found 459.0984.

IR (film) v_{max} 2361, 2341, 2327, 1725, 1749, 1432, 1264, 1091, 1049, 1008 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (butyl(phenyl)germanediyl)dimethanol (**22**, 54.0 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **83** as a colorless oil (74.7 mg, 83% yield, 99% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 92.5/7.5, flow rate 0.6 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 18.23 min, $t_{\rm R}$ (minor) = 17.75. $[\alpha]_{\rm D}^{25}$ = -3.38 (c = 0.1, CH₂Cl₂).

(S)-(butyl(hydroxymethyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (83)



¹**H NMR (400 MHz, CDCl₃)** δ 7.73-7.71 (m, 1H), 7.55-7.51 (m, 1H), 7.43-7.33 (m, 10H), 7.30-7.28 (m, 2H), 4.35 (q, *J* = 12.4 Hz, 2H), 3.86 (q, *J* = 12.4 Hz, 2H), 1.88 (s, 1H), 1.43-1.26 (m, 4H), 1.08-1.034 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.01, 142.57, 141.36, 135.97, 134.18, 131.48, 130.97, 129.99, 129.20, 128.48, 128.41, 128.25, 127.42, 127.31, 56.76, 53.75, 27.01, 26.38, 13.76, 11.58.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₅H₂₈GeNaO₃ ([M+Na]⁺) 473.1142, found 473.1139.

IR (film) v_{max} 2360, 2341, 1727, 1598, 1477, 1431, 1306, 1260, 1121, 1007 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (phenethyl(phenyl)germanediyl)dimethanol (**23**, 63.6 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **84** as a colorless oil (84.7 mg, 85% yield, 96% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 69.96 min, $t_{\rm R}$ (minor) = 57.57. [α]_D²⁵ = -0.48 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(phenethyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (84)



¹**H NMR (400 MHz, CDCl₃)** δ 7.74-7.72 (m, 1 H), 7.56-7.52 (m, 1H), 7.43-7.33 (m, 10H), 7.30-7.24 (m, 4H), 7.21-7.16 (m, 1H), 7.13-7.10 (m, 2H), 4.31 (q, *J* = 12.4 Hz, 2H), 3.80 (q, *J* = 12.8 Hz, 2H). 2.76-2.72 (m, 2H), 1.75 (s, 1H), 1.44-1.40 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 169.95, 143.99, 142.58, 141.34, 135.51, 134.69, 134.18, 130.98, 130.63, 130.02, 129.29, 128.53, 128.46, 128.24, 127.94, 127.41, 127.31, 126.07, 56.59, 53.71, 30.76, 13.83.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₉H₂₈GeNaO₃ ([M+Na]⁺) 521.1142, found 521.1144.

IR (film) v_{max} 2926, 2361, 2341, 1726, 1567, 1306, 1263, 1234, 1121, 1008 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of ((4-fluor-ophenyl)(methyl)germanediyl)dimethanol (**24**, 49.2 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **85** as a colorless oil (75.0 mg, 88% yield, 94% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 23.09 min, $t_{\rm R}$ (minor) = 16.51. [α]_D²⁵ = -3.10 (c = 0.1, CH₂Cl₂).

(*S*)-((4-fluorophenyl)(hydroxymethyl)(methyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (85)



¹**H NMR (400 MHz, CDCl₃)** δ 7.75-7.73 (m, 1H), 7.56-7.52 (m, 1H), 7.42-7.35 (m, 7H), 7.31-7.28 (m, 2H), 4.26 (q, *J* = 12.4 Hz, 2H), 3.80 (q, *J* = 12.4 Hz, 2H), 1.92 (s, 1H), 0.39 (s, 3H).

¹³**C** NMR (101 MHz, CDCl₃) δ 169.99, 163.85 (d, $J_{C-F} = 246.0$ Hz), 141.98 (d, $J_{C-F} = 122.0$ Hz), 135.67 (d, $J_{C-F} = 7.0$ Hz), 131.85, 131.79, 131.56, 131.01, 130.58, 130.00, 128.46, 128.25, 127.43, 127.34, 115.60 (d, $J_{C-F} = 19.0$ Hz), 57.48, 54.75, -7.27.

¹⁹F NMR (376 MHz, CDCl₃): δ -111.68.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₂H₂₁FGeNaO₃ ([M+Na]⁺) 449.0579, found 449.0576.

IR (film) v_{max} 2927, 2854, 2360, 2341, 1726, 1586, 1496, 1307, 1262, 1008 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(o-tolyl)germanediyl)dimethanol (**25**, 48.4 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the

general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **86** as a colorless oil (59.9 mg, 71% yield, >99% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 14.29 min. [α]_D²⁵ = +1.64 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(o-tolyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (86)



¹**H NMR (400 MHz, CDCl₃)** δ 7.74-7.72 (m, 1H), 7.55-7.51 (m, 1H), 7.41-7.32 (m, 6H), 7.30-7.25 (m, 3H), 7.18-7.14 (m, 2H), 4.34 (q, *J* = 12.0 Hz, 2H), 3.86 (q, *J* = 12.8 Hz, 2H), 2.34 (s, 3H), 1.83 (s, 1H), 0.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.99, 143.09, 142.63, 141.38, 135.92, 134.39, 131.52, 131.00, 130.61, 130.02, 129.90, 129.53, 128.49, 128.25, 127.43, 127.33, 125.48, 57.95, 55.25, 23.40, - 6.35.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₃H₂₄GeNaO₃ ([M+Na]⁺) 445.0829, found 445.0826.

IR (film) v_{max} 2925, 2360, 2341, 1727, 1451, 1306, 1261, 1232, 1086, 1007 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(m-tolyl)germanediyl)dimethanol (**26**, 48.4 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **87** as a colorless oil (72.6 mg, 86% yield, 97% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 18.54 min, $t_{\rm R}$ (minor) = 13.46 min. $[\alpha]_{\rm D}^{25}$ = -1.74 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(m-tolyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (87)



¹**H NMR (400 MHz, CDCl₃)** δ 7.78-7.77 (m, 1H), 7.56-7.52 (m, 1H), 7.42-7.34 (m, 5H), 7.32-7.29 (m, 2H), 7.27-7.23 (m, 3H), 7.19-7.16 (m, 1H), 4.29 (q, *J* = 12.4 Hz, 2H), 3.82 (q, *J* = 12.8 Hz, 2H), 2.34 (s, 3H), 1.84 (s, 1H), 0.40 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.00, 142.61, 141.38, 137.88, 136.31, 134.47, 131.49, 130.98, 130.82, 130.69, 130.10, 130.02, 128.48, 128.31, 128.25, 127.42, 127.31, 57.63, 54.77, 21.56, -7.49.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₃H₂₄GeNaO₃ ([M+Na]⁺) 445.0829, found 445.0827.

IR (film) v_{max} 2923, 2360, 2341, 1727, 1568, 1477, 1451, 1261, 1233, 1008 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(p-tolyl)germanediyl)dimethanol (**27**, 48.4 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **87** as a colorless oil (65.0 mg, 77% yield, 96% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 31.80 min, $t_{\rm R}$ (minor) = 19.09 min. $[\alpha]_{\rm D}^{25}$ = -1.76 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(p-tolyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (88)



¹**H NMR (400 MHz, CDCl₃)** δ 7.77-7.74 (m, 1H), 7.56-7.52 (m, 1H), 7.42-7.34 (m, 5H), 7.35-7.29 (m, 4H), 7.19-7.17 (m, 2H), 4.28 (q, *J* = 12.4 Hz, 2H), 3.81 (q, *J* = 12.4 Hz, 2H), 2.35 (s, 3H), 2.06 (s, 1H), 0.39 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.01, 142.59, 141.37, 139.20, 133.82, 132.71, 131.48, 130.97, 130.71, 130.03, 129.25, 128.63, 128.49, 128.25, 128.17, 127.42, 127.31, 57.67, 54.78, 21.53, -7.46.

HRMS (ESI-TOF) *m/z* calcd. for C₂₃H₂₄GeNaO₃ ([M+Na]⁺) 445.0829, found 445.0828.

IR (film) v_{max} 2923, 2361, 2341, 1726, 1598, 1477, 1306, 1232, 1088, 1008 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (phenyl(vinyl)germanediyl)dimethanol (**28**, 48.0 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **89** as a colorless oil (74.8 mg, 89% yield, 82% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 17.83 min, $t_{\rm R}$ (minor) = 14.99 min. $[\alpha]_{\rm D}^{25}$ = -0.44 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(phenyl)(vinyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (89)



¹**H NMR (400 MHz, CDCl₃)** δ 7.73-7.71 (m, 1H), 7.55-7.51 (m, 1H), 7.47-7.44 (m, 2H), 7.41-7.33 (m, 8H), 7.30-7.27 (m, 2H), 6.30-6.12 (m, 2H), 5.77 (dd, *J* = 19.6, 2.8 Hz, 1H), 4.39 (q, *J* = 12.4 Hz, 2H), 3.93 (q, *J* = 12.8 Hz, 2H), 2.01 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.92, 142.63, 141.29, 134.81, 134.65, 132.17, 131.53, 130.97, 130.56, 130.04, 129.47, 128.49, 128.25, 127.43, 127.30, 56.61, 53.92.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₃H₂₂GeNaO₃ ([M+Na]⁺) 443.0673, found 443.0672.

IR (film) v_{max} 2924, 2361, 2341, 1727, 1598, 1478, 1432, 1306, 1233, 1006 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(vinyl)germanediyl)dimethanol (**29**, 35.6 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **90** as a colorless oil (66.6 mg, 93% yield, 70% e.e.). **HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 210 nm), *t*_R (major) = 18.95 min, *t*_R (minor) = 23.36 min. [α]p²⁵ = -6.7 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(vinyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (90)



¹**H NMR (400 MHz, CDCl₃)** δ 7.84-7.82 (m, 1H), 7.56-7.52 (m, 1H), 7.43-7.31 (m, 7H), 6.31-6.00 (m, 2H), 5.70-5.64 (m, 1H), 4.14 (q, *J* = 12.4 Hz, 2H), 3.66 (q, *J* = 12.4 Hz, 2H), 3.06 (s, 1H), 0.22 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.94, 142.53, 141.32, 134.37, 132.79, 131.43, 130.94, 130.68, 129.98, 128.45, 128.20, 127.37, 127.28, 57.40, 54.44, -7.67.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₈H₂₀GeNaO₃ ([M+Na]⁺) 381.0509, found 381.0516.

IR (film) v_{max} 3057, 3027, 2914, 1701, 1598, 1477, 1437, 1306, 1231, 948 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (methyl(phenyl)silanediyl)dimethanol (**52**, 36.4 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **92** as a colorless oil (65.9 mg, 91% yield, 97% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 30.38 min, $t_{\rm R}$ (minor) = 12.20 min. $[\alpha]_{\rm D}^{25}$ = -3.60 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(methyl)(phenyl)silyl)methyl [1,1'-biphenyl]-2-carboxylate (92)



¹**H NMR (400 MHz, CDCl₃)** δ 7.78-7.76 (m, 1H), 7.56-7.48 (m, 3H), 7.43-7.31 (m, 10H), 4.14 (q, *J* = 14.4 Hz, 2H), 3.53 (q, *J* = 14.8 Hz, 2H), 1.47 (s, 1H), 0.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.09, 142.36, 141.44, 134.28, 133.35, 131.37, 131.00, 130.92, 130.10, 129.97, 128.47, 128.31, 127.41, 127.31, 55.83, 52.84, -7.78.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₂H₂₂NaO₃Si ([M+Na]⁺) 385.1230, found 385.1225.

IR (film) v_{max} 2928, 2856, 2360, 1727, 1475, 1427, 1307, 1260, 1087, 1008 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of butyldichloro(phenyl)silane (**1ap**, 116.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **93'** as a colorless oil (71.7 mg, 64% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.59-7.56 (m, 2H), 7.42-7.35 (m, 3H), 3.84 (q, *J* = 14.0 Hz, 4H), 2.81 (s, 2H), 1.43-1.32 (m, 4H), 0.96-0.92 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 134.44, 133.63, 129.83, 128.16, 53.47, 26.66, 25.77, 13.76, 9.81.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₂H₂₀NaO₂Si ([M+Na]⁺) 247.1125, found 247.1121.

IR (film) v_{max} 2960, 2924, 2855, 1828, 1718, 1685, 1558, 1459, 1112, 998 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (butyl(phenyl)silanediyl)dimethanol (**93'**, 44.8 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **93** as a colorless oil (68.7 mg, 85% yield, 95% e.e.).

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 93/7, flow rate 0.8 mL/min, λ = 210 nm), t_R (major) = 21.30 min, t_R (minor) = 25.61 min. [α]_D²⁵ = -3.00 (c = 0.1, CH₂Cl₂).

(S)-(butyl(hydroxymethyl)(phenyl)silyl)methyl [1,1'-biphenyl]-2-carboxylate (93)



¹H NMR (400 MHz, CDCl₃) δ 7.77-7.75 (m, 1H), 7.55-7.48 (m, 3H), 7.43-7.30 (m, 10H), 4.19 (q, *J* = 14.4 Hz, 2H), 3.58 (q, *J* = 14.8 Hz, 2H), 1.50 (s, 1H), 1.36-1.26 (m, 4H), 0.93-0.81 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 170.04, 142.36, 141.42, 134.49, 132.72, 131.36, 131.00, 130.92, 130.00, 129.94, 128.46, 128.29, 128.20, 127.40, 127.29, 54.98, 51.87, 26.61, 25.60, 13.77, 9.74.

HRMS (ESI-TOF) *m/z* calcd. for C₂₅H₂₈NaO₃Si ([M+Na]⁺) 427.1700, found 427.1699.

IR (film) v_{max} 2958, 2925, 2361, 2341, 1711, 1598, 1472, 1261, 1113, 1008 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(cyclopropyl)(phenyl)silane (**1aq**, 108.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **94'** as a colorless oil (60.3 mg, 58% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.63-7.61 (m, 2H), 7.41-7.35 (m, 3H), 3.80 (q, *J* = 9.6 Hz, 4H), 2.07 (s, 2H), 0.74-0.71 (m, 2H), 0.44-0.42 (m, 2H), 0.13-0.19 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 134.68, 133.04, 129.92, 128.07, 52.95, 1.42, -9.79.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₁H₁₆NaO₂Si ([M+Na]⁺) 231.0812, found 231.0814.

IR (film) v_{max} 3070, 2997, 1772, 1651, 1558, 1541, 1458, 1428, 1113, 998 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (cyclopropyl(phenyl)silanediyl)dimethanol (**94'**, 41.6 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **94** as a colorless oil (76.1 mg, 98% yield, >99% e.e.).

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 93/7, flow rate 0.8 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 27.40 min. [α]_D²⁵ = -3.40 (c = 0.1, CH₂Cl₂).

(S)-(cyclopropyl(hydroxymethyl)(phenyl)silyl)methyl [1,1'-biphenyl]-2-carboxylate (94)



¹**H NMR (400 MHz, CDCl₃)** δ 7.77-7.75 (m, 1H), 7.55-7.51 (m, 3H), 7.43-7.29 (m, 10H), 4.19 (q, *J* = 14.4 Hz, 2H), 3.53 (s, 2H), 1.57 (s, 1H), 0.70-0.65 (m, 2H), 0.39-0.32 (m, 2H), -0.20--0.28 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.94, 142.39, 141.37, 134.75, 132.09, 131.35, 130.96, 130.91, 130.10, 129.91, 128.45, 128.25, 128.13, 127.35, 127.28, 54.62, 51.44, 1.52, 1.47, -9.82.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₄H₂₄NaO₃Si ([M+Na]⁺) 411.1387, found 411.1385.

IR (film) v_{max} 2925, 2361, 2341, 1712, 1599, 1493, 1428, 1306, 1206, 1008 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of benzyldichloro(phenyl)silane (**1ar**, 133.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H_2O_2 was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **95'** as a colorless oil (85.2 mg, 66% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.48-7.47 (m, 2H), 7.42-7.39 (m, 1H), 7.35 (t, *J* = 4.8 Hz, 2H), 3.79 (q, *J* = 9.6 Hz, 4H), 2.79 (s, 2H), 2.52 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 138.15, 134.53, 132.54, 130.03, 128.48, 128.43, 128.10, 124.64, 52.43, 20.00.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₅H₁₈NaO₂Si ([M+Na]⁺) 281.0968, found 281.0971.

IR (film) v_{max} 2952, 2834, 1717, 1651, 1579, 1558, 1460, 1296, 1210, 999 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (benzyl(phenyl)silanediyl)dimethanol (**95'**, 51.6 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **95** as a colorless oil (78.9 mg, 90% yield, >99% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 43.85 min. [α]_D²⁵ = -0.26 (c = 0.1, CH₂Cl₂).

(S)-(benzyl(hydroxymethyl)(phenyl)silyl)methyl [1,1'-biphenyl]-2-carboxylate (95)



¹**H NMR (400 MHz, CDCl₃)** δ 7.71-7.69 (m, 1H), 7.56-7.51 (m, 1H), 7.43-7.29 (m, 12H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.94-6.92 (m, 2H), 4.14 (s, 2H), 3.52 (s, 2H), 2.37 (s, 2H), 1.74 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.94, 142.39, 141.43, 137.65, 134.65, 131.69, 131.42, 130.94, 130.85, 130.23, 130.03, 128.55, 128.52, 128.48, 128.33, 128.17, 127.43, 127.30, 124.80, 54.18, 51.18, 20.03.

HRMS (ESI-TOF) m/z calcd. for C₂₈H₂₆NaO₃Si ([M+Na]⁺) 461.1543, found 461.1544.

IR (film) v_{max} 2962, 2925, 2360, 2341, 1713, 1577, 1451, 1259, 1083, 1013 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(phenyl)(3,3,3-trifluoropropyl)silane (**1as**, 136.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **96'** as a colorless oil (73.9mg, 56% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.53-7.49 (m, 2H), 7.44-7.35 (m, 3H), 3.84 (q, *J* = 14.4 Hz, 4H), 2.76 (s, 2H), 2.26-2.13 (m, 2H), 1.20-1.17 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 134.25, 131.77, 130.42, 128.98 (q, J_{C-F} = 275.0 Hz), 128.47, 52.62, 28.67 (q, J_{C-F} = 30.0 Hz), 2.48 (q, J_{C-F} = 3.0 Hz).

¹⁹F NMR (**376** MHz, CDCl₃): δ -68.79.

HRMS (ESI-TOF) m/z calcd. for C₁₁H₁₅F₃NaO₂Si ([M+Na]⁺) 287.0686, found 287.0688.

IR (film) v_{max} 3059, 3023, 2909, 2851, 1700, 1521, 1492, 1453, 1142, 998 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (phenyl(3,3,3-trifluoropropyl)silanediyl)dimethanol (**96'**, 52.8 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **96** as a colorless oil (72.8 mg, 82% yield, 90% e.e.).

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 210 nm), t_R (major) = 14.08 min, t_R (minor) = 16.78 min. $[\alpha]_D^{25}$ = -1.0 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(phenyl)(3,3,3-trifluoropropyl)silyl)methyl [1,1'-biphenyl]-2-carboxylate (96)



¹**H NMR (400 MHz, CDCl₃)** δ 7.78-7.76 (m, 1H), 7.57-7.53 (m, 1H), 7.46-7.30 (m, 12H), 4.18 (q, *J* = 14.8 Hz, 2H), 3.57 (s, 2H), 2.11-1.99 (m, 2H), 1.80 (s, 1H), 1.06-1.01 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 170.08, 142.36, 141.43, 134.32, 131.56, 130.97, 130.92, 130.69, 130.57, 130.00, 128.86 (q, *J*_{C-F} = 275.0 Hz), 128.51, 128.42, 128.36, 127.47, 127.39, 54.18, 51.41, 28.47 (q, *J*_{C-F} = 30.0 Hz), 2.39 (q, *J*_{C-F} = 2.0 Hz).

¹⁹F NMR (376 MHz, CDCl₃): δ -68.64.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₄H₂₃F₃NaO₃Si ([M+Na]⁺) 467.1261, found 467.1263.

IR (film) v_{max} 2926, 2360, 2341, 1717, 1598, 1429, 1367, 1236, 1115, 1009 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(phenyl)((trimethylsilyl)methyl)silane (**1at**, 131.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **97'** as a colorless oil (88.9 mg, 70% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.62-7.54 (m, 2H), 7.41-7.31 (m, 3H), 3.82 (q, *J* = 14.0 Hz, 4H), 2.69 (s, 2H), 0.07 (s, 2H), 0.04 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 134.86, 134.37, 129.78, 128.11, 55.01, 1.32, -2.79.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₂H₂₂NaO₂Si₂ ([M+Na]⁺) 277.1051, found 277.1054.

IR (film) v_{max} 2924, 2873, 2855, 1651, 1521, 1489, 1459, 1260, 1112, 998 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (phenyl((trimethylsilyl)methyl)silanediyl)dimethanol (**97'**, 50.8 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **97** as a colorless oil (60.8 mg, 70% yield, >99% e.e.).

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, $\lambda = 210$ nm), t_R (major) = 16.14 min, t_R (minor) = 19.28 min. $[\alpha]_D^{25} = -1.0$ (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(phenyl)((trimethylsilyl)methyl)silyl)methyl [1,1'-biphenyl]-2-carboxylate (97)



¹**H NMR (400 MHz, CDCl₃)** δ 7.74-7.72 (m, 1H), 7.54-7.46 (m, 3H), 7.41-7.29 (m, 11H), 4.15 (q, *J* = 14.4 Hz, 2H), 3.52 (q, *J* = 14.4 Hz, 2H), 1.77 (s, 1H), -0.03 (d, *J* = 2.4 Hz, 2H), -0.09 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 170.00, 142.20, 141.34, 134.25, 133.81, 131.24, 130.98, 130.80, 129.85, 129.82, 128.38, 128.02, 127.32, 127.20, 56.11, 52.99, 1.19, -3.08.

HRMS (ESI-TOF) *m/z* calcd. for C₂₅H₃₀NaO₃Si₂ ([M+Na]⁺) 457.1626, found 457.1623.

IR (film) v_{max} 2973, 2360, 1719, 1611, 1477, 1472, 1296, 1243, 1114, 1008 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of allyldichloro(phenyl)silane (**1au**, 108.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H_2O_2 was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **98'** as a colorless oil (55.1 mg, 53% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.60-7.56 (m, 2H), 7.43-7.34 (m, 3H), 5.91-5.79 (m, 1H), 5.01-4.89 (m, 2H), 3.87-3.79 (m, 4H), 2.63 (s, 1H), 1.97 (d, *J* = 8.0 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 134.48, 133.48, 132.73, 130.09, 128.20, 114.70, 52.85, 17.77.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₁H₁₆NaO₂Si ([M+Na]⁺) 231.0812, found 231.0815.

IR (film) v_{max} 2929, 2856, 1869, 1772, 1717, 1685, 1620, 1574, 1428, 998 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (allyl(phenyl)silanediyl)dimethanol (**98'**, 41.6 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **98** as a colorless oil (69.9 mg, 90% yield, 94% e.e.). HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 210 nm), t_R (major) = 20.34 min, t_R (minor) = 24.36 min. $[\alpha]_D^{25}$ = -2.22 (c = 0.1, CH₂Cl₂).

(S)-(allyl(hydroxymethyl)(phenyl)silyl)methyl [1,1'-biphenyl]-2-carboxylate (98)



¹**H NMR (400 MHz, CDCl₃)** δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.56-7.49 (m, 3H), 7.43-7.30 (m, 12H), 5.79-5.69 (m, 1H), 4.95-4.87 (m, 2H), 4.18 (s, 2H), 3.58 (s, 2H), 2.74 (s, 1H), 1.83 (d, *J* = 8.0 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 170.01, 142.37, 141.41, 134.56, 132.96, 131.81, 131.41, 130.93, 130.22, 129.97, 128.59, 128.45, 128.31, 128.21, 127.42, 127.31, 115.03, 54.41, 51.50, 17.69.

HRMS (ESI-TOF) *m/z* calcd. for C₂₄H₂₄NaO₃Si ([M+Na]⁺) 411.1387, found 411.1386.

IR (film) v_{max} 3050, 2924, 2361, 2341, 1703, 1568, 1432, 1307, 1260, 1006 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(4methoxybenzyl)(phenyl)silane (**1av**, 148.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **99'** as a colorless oil (87.9 mg, 61% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.50-7.48 (m, 2H), 7.41-7.33 (m, 3H), 6.96-6.94 (m, 2H), 6.77-6.74 (m, 2H), 3.83-3.79 (m, 4H), 3.76 (s, 3H), 2.64 (s, 2H), 2.25 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.99, 134.53, 132.67, 130.02, 129.83, 129.28, 128.13, 114.02, 55.26, 52.74, 18.64.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₆H₂₀NaO₂Si ([M+Na]⁺) 311.1074, found 311.1069.

IR (film) v_{max} 2950, 2833, 1734, 1685, 1579, 1541, 1460, 1296, 1210, 999 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of ((4-meth-oxybenzyl)(phenyl)silanediyl)dimethanol (**99'**, 57.6 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **99** as a colorless oil (93.6 mg, 82% yield, 95% e.e.).

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, $\lambda = 210$ nm), t_R (major) = 22.64 min, t_R (minor) = 33.79 min. $[\alpha]_D^{25} = 0.99$ (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(4-methoxybenzyl)(phenyl)silyl)methyl [1,1'-biphenyl]-2-carboxylate (99)



¹**H NMR (400 MHz, CDCl₃)** δ 7.71-7.68 (m, 1H), 7.55-7.51 (m, 1H), 7.42-7.28 (m, 12H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 4.14 (s, 2H), 3.75 (s, 3H), 3.51 (s, 2H), 2.30 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 169.92, 157.10, 142.38, 141.42, 134.66, 131.87, 131.41, 130.94, 130.86, 130.18, 130.02, 129.38, 129.32, 128.47, 128.31, 128.16, 127.42, 127.29, 114.05, 55.31, 54.25, 51.22, 18.69.
HRMS (ESI-TOF) *m*/*z* calcd. for C₂₉H₂₈NaO₄Si ([M+Na]⁺) 491.1649, found 491.1648.

IR (film) v_{max} 3482, 2916, 2361, 2342, 1716, 1609, 1583, 1452, 1243, 1027 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of dichloro(4chlorophenyl)(methyl)silane (**1aw**, 112.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **100'** as a colorless oil (69.1 mg, 64% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.79 (q, *J* = 14.0 Hz, 4H), 2.28 (s, 2H), 0.37 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 136.45, 135.69, 132.50, 128.50, 54.46, -7.70.

HRMS (ESI-TOF) *m*/*z* calcd. for C₉H₁₃NaO₂Si ([M+Na]⁺) 239.0266, found 239.0268.

IR (film) v_{max} 3059, 2909, 2851, 1651, 1599, 1493, 1418, 1207, 1093, 999 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of ((4-chlo-rophenyl)(methyl)silanediyl)dimethanol (**100'**, 43.2 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **100** as a colorless oil (64.2 mg, 81% yield, 98% e.e.).

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 24.89 min, $t_{\rm R}$ (minor) = 28.25 min. [α]_D²⁵ = 0.99 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(4-methoxybenzyl)(phenyl)silyl)methyl [1,1'-biphenyl]-2-carboxylate (100)



¹**H NMR (400 MHz, CDCl₃)** δ 7.76-7.74 (m, 1H), 7.56-7.51 (m, 1H), 7.43-7.29 (m, 11H), 4.09 (q, *J* = 14.4 Hz, 2H), 3.49 (q, *J* = 14.4 Hz, 2H), 1.54 (s, 1H), 0.24 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.08, 142.38, 141.47, 136.55, 135.67, 131.71, 131.48, 130.99, 130.88, 129.99, 128.49, 128.47, 128.33, 127.45, 127.37, 55.60, 52.73, -7.71.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₂H₂₁NaO₃Si ([M+Na]⁺) 419.0841, found 419.0836.

IR (film) v_{max} 2962, 2925, 2360, 2341, 1713, 1577, 1451, 1259, 1083, 1013 cm⁻¹.



This compound was prepared according to **General procedure D** from the reaction of tert-butyldichloro(phenyl)silane (**1ax**, 116.0 mg, 0.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 536.4 mg, 2.0 mmol, 4.0 equiv), 'BuOK (252.5 mg, 2.25 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **101'** as a colorless oil (60.5 mg, 54% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.59-7.57 (m, 2H), 7.42-7.38 (m, 3H), 4.02 (s, 4H), 2.00 (s, 2H), 0.97 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 135.13, 132.18, 129.88, 128.19, 51.94, 27.22, 17.31.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₂H₂₀NaO₂Si ([M+Na]⁺) 247.1125, found 247.1127.

IR (film) v_{max} 3048, 2979, 2944, 1558, 1486, 1432, 1372, 1261, 1185, 949 cm⁻¹.



This compound was prepared according to **General procedure E** from the reaction of (tert-butyl(phenyl)silanediyl)dimethanol (**101'**, 44.8 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **101** as a colorless oil (74.4 mg, 92% yield, >99% e.e.).

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 13.71 min. $[\alpha]_{\rm D}^{25}$ = -9.99 (c = 0.1, CH₂Cl₂).

(S)-(tert-butyl(hydroxymethyl)(phenyl)silyl)methyl [1,1'-biphenyl]-2-carboxylate (101)



¹H NMR (400 MHz, CDCl₃) δ 7.72-7.68 (m, 1H), 7.54-7.46 (m, 3H), 7.43-7.30 (m, 8H), 7.28-7.25 (m, 3H), 4.35 (q, *J* = 14.8 Hz, 2H), 3.68 (s, 2H), 1.53 (s, 1H), 0.92 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 170.05, 142.38, 141.33, 135.11, 131.48, 131.39, 130.97, 130.91, 129.91, 129.89, 128.46, 128.31, 128.07, 127.42, 127.32, 53.22, 50.19, 27.19, 17.43.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₅H₂₈NaO₃Si ([M+Na]⁺) 427.1700, found 427.1699.

IR (film) v_{max} 2957, 2855, 2360, 2341, 1711, 1478, 1428, 1235, 1085, 996 cm⁻¹.

8) Synthetic applications



Step 1: This compound was synthesized according to the literature procedure.²⁹ To a solution of Mg (1.2 equiv) and I₂ (two crystals) in anhydrous THF was added Bromobenzene (1.0 equiv, 1.0 M in THF) under argon atmosphere at room temperature. The resulting mixture was stirred at 70 °C for 3h to afford Grignard reagent. Under argon atmosphere, a 50 mL Schlenk tube was charged with GeCl₄ (**4**, 427.6 mg, 2.0 mmol) and anhydrous Et₂O (0.4 - 0.5 M), and the resulting mixture was cooled to -78 °C. Then the Grignard reagent was added dropwise over 1h to the mixture at -78 °C. After 1 h, the reaction mixture was stirred at room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature, the reaction mixture was filtered off, and the filtrate was concentrated under vacuum. The resulting residue was used directly without further purification (the NMR yield is 75%).

Step 2: This compound was prepared according to **General procedure B** from the reaction of trichloro(phenyl)germane (382.4 mg, 1.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 1.61 g, 6.0 mmol, 4.0 equiv), 'BuOK (763.0 mg, 6.8 mmol, 4.5 equiv). The crude mixture is worked up using EA described in the general procedure B; the crude product is purified

by column chromatography on silica gel (hexane/EtOAc = 30/1), to yield the product **3** as a colorless oil (620.2 mg, 72% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.63-7.58 (m, 2H), 7.28-7.22 (m, 3H), 1.11 (s, 36H), 0.54 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 141.72, 134.03, 128.27, 127.51, 82.80, 25.03. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 33.50.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₇H₄₇B₃GeNaO₆ ([M+Na]⁺) 597.2756, found 597.2762.

IR (film) v_{max} 2976, 2361, 1372, 1300, 1267, 1214, 1142, 1092, 1004, 962 cm⁻¹.

Step 3: These compounds were synthesized according to the literature procedure.³⁰ In an argonfilled glovebox, **3** (564.4 mg, 1.0 mmol), ArBr (1.51 mmol, 1.5 equiv), solid potassium hydroxide (168.5 mg, 3.0 mmol, 3.0 equiv), Pd(OAc)₂ (2.4 mg, 0.01 mmol), RuPhos (4.7 mg, 0.01 mmol) in freshly distilled THF (9.0 mL, 0.1 M) were added to a 40 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, The oven-dried Schlenk tube was sealed, removed from the glovebox, and H₂O (sparged with N₂ for 30 min, 0.9 mL) was added. then the mixture was stirred at 70 °C for 12 h. The reaction was quenched with water (40.0 mL) and, the solution was extracted with ethyl acetate (3×20.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was transferred to a 25 mL round bottom flask and cooled to 0 °C (ice/water) and charged with 5 M sodium hydroxide (8.5 equiv), and 30% hydrogen peroxide (1.6 mL) and THF (9.0 mL). The reaction was gradually warmed to room temperature and allowed to stir for 4 h at which time the vial was cooled to 0 °C and saturated aqueous sodium thiosulfate was added dropwise over 5 min. The reaction mixture was diluted with ethyl acetate and the aqueous and organic layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 20.0 mL) and the combined organics were dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **102** as a colorless oil (134.0 mg, 42% yield) or **103** as a colorless oil (150.5 mg, 45% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.44-7.33 (m, 5H), 7.23-7.19 (m, 2H), 7.11-7.07 (m, 3H), 4.05-3.98 (m, 4H), 2.66 (s, 2H), 2.55 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 139.48, 135.99, 134.16, 129.29, 128.63, 128.39, 128.09, 124.65, 54.57, 24.85.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₅H₁₈GeNaO₂ ([M+Na]⁺) 327.0411, found 327.0404.

IR (film) v_{max} 3030, 2912, 2848, 1590, 1575, 1395, 1278, 1154, 1160, 980 cm⁻¹.



¹H NMR (400 MHz, CDCl₃) δ 7.45-7.41 (m, 2H), 7.39-7.32 (m, 3H), 7.01-6.97 (m, 2H), 6.79-6.75 (m, 2H), 4.06-3.98 (m, 4H), 3.76 (s, 3H), 2.60 (s, 2H), 2.38 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.98, 136.14, 134.18, 131.19, 129.25, 128.98, 128.39, 114.14, 55.34, 54.69, 19.45.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₆H₂₀GeNaO₃ ([M+Na]⁺) 357.0516, found 357.0510.

IR (film) v_{max} 3032, 2915, 2850, 1596, 1570, 1390, 1266, 1160, 1108, 1008 cm⁻¹.

Step 4: 104 and 105 were prepared according to General procedure E from the reaction of (benzyl(phenyl)germanediyl)dimethanol (102, 60.8 mg, 0.2 mmol) or ((4-methoxybenzyl)(phenyl)germanediyl)dimethanol (103, 66.8 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (66a, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), L8 (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product 104 as a colorless oil (90.0 mg, 93% yield, >99% e.e.) or 105 as a colorless oil (94.6 mg, 92% yield, >99% e.e.).

(S)-(benzyl(hydroxymethyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (104)



¹**H NMR (400 MHz, CDCl₃)** δ 7.68-7.66 (m, 1H), 7.56-7.52 (m, 1H), 7.41-7.32 (m, 10H), 7.29-7.27 (m, 2H), 7.19-7.15 (m, 2H), 7.09-7.05 (m, 1H), 7.0-6.97 (m, 2H), 4.34-4.26 (m, 2H), 3.84-3.77 (m, 2H), 2.54 (s, 2H), 1.77 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.90, 142.58, 141.32, 138.88, 135.03, 134.69, 134.27, 131.51, 130.97, 130.54, 130.05, 129.39, 128.59, 128.54, 128.47, 128.38, 128.26, 128.19, 127.43, 127.29, 124.73, 56.08, 53.28, 20.89.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₈H₂₆GeNaO₃ ([M+Na]⁺) 507.0986, found 507.0987.

IR (film) v_{max} 2962, 2360, 2341, 1703, 1598, 1493, 1431, 1306, 1091, 997 cm⁻¹.

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 210 nm), *t*_R (major) = 41.35 min. [α]_D²⁵ = -0.92 (c = 0.1, CH₂Cl₂).

(S)-((hydroxymethyl)(4-methoxybenzyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (105)



¹**H NMR (400 MHz, CDCl₃)** δ 7.68-7.65 (m, 1H), 7.55-7.51 (m, 1H), 7.40-7.29 (m, 10H), 7.28-7.25 (m, 2H), 6.91-6.87 (m, 2H), 6.73-6.70 (m, 2H), 4.33-4.25 (m, 2H), 3.83-3.75 (m, 5H), 2.48 (s, 2H), 1.74 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.89, 157.06, 142.57, 141.33, 135.21, 134.28, 131.50, 130.96, 130.57, 130.04, 129.35, 129.08, 128.47, 128.37, 128.26, 127.42, 127.28, 114.08, 56.15, 55.33, 53.31, 19.66.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₉H₂₈GeNaO₄ ([M+Na]⁺) 537.1092, found 537.1093.

IR (film) v_{max} 2929, 2360, 2341, 1725, 1704, 1610, 1478, 1296, 1243, 1090 cm⁻¹.

HPLC analysis: Chiralcel AD-H (*n*-Hexane/*i*-PrOH = 92.5/7.5, flow rate 0.6 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 39.45 min. $[\alpha]_{\rm D}^{25}$ = +0.36 (c = 0.1, CH₂Cl₂).



Step 1: This compound was prepared according to **General procedure B** from the reaction of GeCl₄ (**4**, 427.6 mg, 2.0 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 3.2g, 12.0 mmol, 6.0 equiv), 'BuOK (1.4g, 13.0 mmol, 6.5 equiv). The crude mixture was worked up using EA described in the general procedure B; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **5** as a colorless oil (970.3 mg, 76% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.21 (s, 48H), 0.34 (s, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 82.62, 25.13. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 33.45.

HRMS (ESI-TOF) m/z calcd. for C₂₈H₅₇B₄GeO₈ ([M+H]⁺) 639.3639, found 639.3644.

IR (film) v_{max} 2978, 2361, 1468, 1379, 1300, 1267, 1215, 1143, 1005, 969 cm⁻¹.

Step 2: This compound was synthesized according to the literature procedure.³¹ In an argon-filled glovebox, **5** (957.5 mg, 1.5 mmol, 1.0 equiv) in THF (7.5 mL) were added to a 20 mL vial equipped with a magnetic stirring bar. The vial was capped and sealed with Telfon tape, brought out of glovebox, and cooled to -78 °C. Tert-butyl lithium (1.2 mL, 1.3 M, 1.0 equiv) was added dropwise by a syringe and the reaction was allowed to warm to room temperature and further stir for 30 minutes. The reaction vial was transferred to the glovebox and was added Zn(OTf)₂ (575.7 mg, 1.58 mmol, 1.05 equiv) and the reaction was allowed to stir at room temperature for 12 h. Upon completion, [Pd-G3]₂ (5.6 mg, 0.075 mmol, 0.005 equiv) and CPhos (131.0 mg, 0.30 mmol, 0.02 equiv) was added as a THF solution (1.0 M, premixed for 10 min.), lithium chloride (66.8 mg, 1.58 mmol, 1.05 equiv) and toluene (7.5 mL). The vial was capped and sealed with Telfon tape, brought out of glovebox, and was allowed to stir at room temperature for 12 h. The reaction was quenched with water (20.0 mL) and, the solution was extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 20/1), to yield the product **9** as a colorless oil (407.3 mg, 53% yield).



¹H NMR (400 MHz, CDCl₃) δ 1.20 (s, 36H), 0.30 (s, 3H), 0.27 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 82.77, 25.12, 0.22. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃) δ 34.63.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₂H₄₅B₃GeNaO₆ ([M+Na]⁺) 535.2599, found 535.2594.

IR (film) v_{max} 2977, 1389, 1371, 1341, 1269, 1215, 1166, 1114, 1003, 969 cm⁻¹.

Step 3: These compounds were synthesized according to the literature procedure.³⁰ In an argonfilled glovebox, **9** (407.3 mg, 0.80 mmol), PhBr (189.6 mg, 1.2 mmol, 1.5 equiv), solid potassium hydroxide (134.7 mg, 2.4 mmol, 3.0 equiv), Pd(OAc)₂ (1.9 mg, 0.008 mmol), RuPhos (3.8 mg, 0.008 mmol) in freshly distilled THF (8.0 mL, 0.1 M) were added to a 20 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, The oven-dried Schlenk tube was sealed, removed from the glovebox, and H₂O (sparged with N₂ for 30 min, 0.75 mL) was added. then the mixture was stirred at 70 °C for 12 h. The reaction was quenched with water (20.0 mL) and, the solution was extracted with ethyl acetate (3×15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was transferred to a 25 mL round bottom flask and cooled to 0 °C (ice/water) and charged with 5 M sodium hydroxide (8.5 equiv), and 30% hydrogen peroxide (0.1.24 mL) and THF (7.5 mL). The reaction was gradually warmed to room temperature and allowed to stir for 4 h at which time the vial was cooled to 0 °C and saturated aqueous sodium thiosulfate was added dropwise over 5 min. The reaction mixture was diluted with ethyl acetate and the aqueous and organic layers were separated. The aqueous layer was extracted with ethyl acetate ($3 \times 20.0 \text{ mL}$) and the combined organics were dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **106** as a colorless oil (104.6 mg, 54% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.25-7.21 (m, 2H), 7.10-7.05 (m, 3H), 3.86-3.78 (m, 4H), 2.41 (s, 2H), 2.35 (s, 2H), 0.18 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 140.22, 128.67, 127.80, 124.47, 55.62, 21.36, -7.84.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₀H₁₆GeNaO₂ ([M+Na]⁺) 265.0254, found 265.0256.

IR (film) v_{max} 3049, 2980, 1651, 1558, 1486, 1431, 1398, 1262, 1093, 949 cm⁻¹.

Step 4: 97 was prepared according to **General procedure E** from the reaction of (benzyl(methyl)germanediyl)dimethanol (**106**, 48.4 mg, 0.2 mmol), benzoyl chloride (**66**, 42.0 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), L7 (8.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv).The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **107** as a colorless oil (59.5 mg, 86% yield, 80% e.e.). (S)-(benzyl(hydroxymethyl)(methyl)germyl)methyl benzoate (107)



¹**H NMR (400 MHz, CDCl₃)** δ 8.03-8.00 (m, 2H), 7.60-7.55 (m, 1H), 7.47-7.43 (m, 2H), 7.25-7.22 (m, 2H), 7.11-7.08 (m, 3H), 4.36 (q, *J* = 12.0 Hz, 2H), 3.76 (q, *J* = 12.4 Hz, 2H), 2.44 (s, 2H), 0.22 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.84, 139.64, 133.18, 129.91, 129.64, 128.65, 128.53, 127.87, 124.55, 57.11, 54.23, 21.52, -7.80.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₇H₂₀GeNaO₃ ([M+Na]⁺) 369.0516, found 369.0514.

IR (film) v_{max} 2926, 2853, 2361, 2341, 1719, 1590, 1484, 1296, 1099, 1011 cm⁻¹.

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 236 nm), *t*_R (major) = 20.85 min, *t*_R (minor) = 19.93. [α]_D²⁵ = -2.8 (c = 0.1, CH₂Cl₂).



Step 1: This compound was synthesized according to the literature procedure.²⁹ To a solution of Mg (1.2 equiv) and I₂ (two crystals) in anhydrous THF was added Bromobenzene (1.0 equiv, 1.0 M in THF) under argon atmosphere at room temperature. The resulting mixture was stirred at 70 °C for 3h to afford Grignard reagent. Under argon atmosphere, a 50 mL Schlenk tube was charged with GeCl₄ (**4**, 214.5 mg, 1.0 mmol) and anhydrous Et₂O (0.4 - 0.5 M), and the resulting mixture was cooled to -78 °C. Then the Grignard reagent was added dropwise over 1h to the mixture at -78 °C. After 1 h, the reaction mixture was stirred at room temperature, the reaction mixture was filtered off. Then the filtrate was added dropwise 'BuLi (1.0 equiv) under argon atmosphere at -78 °C. After 1 h, the reaction mixture for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature, the reaction mixture was filtered off, and the filtrate was concentrated under vacuum. The resulting residue was used directly without further purification (the NMR yield is 70%).

Step 2: This compound was prepared according to **General procedure D** from the reaction of tert-butyldichloro(phenyl)germane (194.6 mg, 0.7 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-diox-aborolan-2-yl)methane (**2**, 751.0 mg, 2.8 mmol, 4.0 equiv), 'BuOK (353.5 mg, 3.15 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **108** as a colorless oil (83.2 mg, 44% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.47-7.43 (m, 2H), 7.35-7.34 (m, 3H), 4.22-4.14 (m, 4H), 2.81 (s, 2H), 1.05 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 135.81, 134.63, 128.94, 128.26, 53.51, 28.19, 23.44.

HRMS (ESI-TOF) *m*/*z* calcd. for C₁₂H₂₀GeNaO₂ ([M+Na]⁺) 293.0567, found 293.0561.

IR (film) v_{max} 3032, 2922, 2850, 1588, 1570, 1398, 1266, 1150, 1163, 987 cm⁻¹.

Step 3: 109 was prepared according to **General procedure E** from the reaction of (tert-butyl(phenyl)germanediyl)dimethanol (**108**, 54.0 mg, 0.2 mmol), [1,1'-biphenyl]-2-carbonyl chloride (**66a**, 64.8 mg, 0.3 mmol, 1.5 equiv), Cu(OTf)₂ (7.2 mg, 0.02 mmol), **L8** (12.1 mg, 0.02 mmol), DIPEA (31.0 mg, 0.24 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **109** as a colorless oil (83.7 mg, 93% yield, >99% e.e.). (S)-(tert-butyl(hydroxymethyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (109)



¹H NMR (400 MHz, CDCl₃) δ 7.68-7.65 (m, 1H), 7.53-7.49 (m, 1H), 7.42-7.39 (m, 2H), 7.38-7.31 (m, 8H), 7.24-7.21 (m, 2H), 4.51-4.45 (m, 2H), 3.98-3.91 (m, 2H), 1.86 (s, 1H), 1.03 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 170.00, 142.56, 141.25, 134.81, 134.69, 131.46, 130.94, 130.68, 129.93, 129.11, 128.44, 128.29, 128.25, 127.40, 127.28, 54.99, 52.11, 28.19, 23.94.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₅H₂₈GeNaO₃ ([M+Na]⁺) 473.1142, found 473.1143.

IR (film) v_{max} 2924, 2854, 2360, 2341, 1727, 1365, 1231, 1188, 1162, 1007 cm⁻¹.

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 210$ nm), $t_{\rm R}$ (major) = 7.63 min. $[\alpha]_{\rm D}^{25} = -13.5$ (c = 0.1, CH₂Cl₂).



Step 1: This compound was synthesized according to the literature procedure.²⁹ To a solution of Mg (1.2 equiv) and I₂ (two crystals) in anhydrous THF was added Bromobenzene (1.0 equiv, 1.0 M in THF) under argon atmosphere at room temperature. The resulting mixture was stirred at 70 °C for 3h to afford Grignard reagent. Under argon atmosphere, a 50 mL Schlenk tube was charged with GeCl₄ (**4**, 427.6 mg, 2.0 mmol) and anhydrous Et₂O (0.4 - 0.5 M), and the resulting mixture was cooled to -78 °C. Then the Grignard reagent was added dropwise over 1 h to the mixture at -78 °C. After 1 h, the reaction mixture was stirred at room temperature for 1 h, then refluxed at 46 °C for 16 h. After being cooled to room temperature, the reaction mixture was filtered off, and the filtrate was concentrated under vacuum. The resulting residue was used directly without further purification (the NMR yield is 75%).

Step 2: This compound was prepared according to **General procedure D** from the reaction of trichloro(phenyl)germane (383.8 mg, 1.5 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**2**, 1.61 g, 6.0 mmol, 4.0 equiv), 'BuOK (757.4 mg, 6.75 mmol, 4.5 equiv), then NaOH and H₂O₂ was added. The crude mixture was worked up using EA described in the general

procedure D; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 1/1), to yield the product **8'** as a colorless oil (190.3 mg, 52% yield, total yields of 2 steps is 39% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.45-7.43 (m, 2H), 7.34-7.31 (m, 3H), 4.12 (s, 6H), 3.60 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 135.16, 134.15, 129.52, 128.58, 54.07.

HRMS (ESI-TOF) *m*/*z* calcd. for C₉H₁₄GeNaO₃ ([M+Na]⁺) 267.0047, found 267.0045.

IR (film) v_{max} 3291, 2885, 2360, 1431, 1276, 1261, 1185, 1093, 1058, 994 cm⁻¹.

Step 3: This compound was synthesized according to the literature procedure.³² To a solution of **8'** (183.0 mg, 0.75 mmol) in dry DCM (0.3 M), imidazole (1.05 equiv.) was added followed by TBSCl (1.05 equiv.) at 0 °C. The reaction was stirred for 4 h, or until completion observed by TLC. The reaction was quenched with water (20.0 mL) and, the solution was extracted with DCM ($3 \times 15.0 \text{ mL}$). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 2/1), to yield the product **8** as a colorless oil (231.0 mg, 86% yield).



¹**H NMR (400 MHz, CDCl₃)** δ 7.53-7.51 (m, 2H), 7.38-7.36 (m, 3H), 4.18-4.13 (m, 6H), 2.22 (s, 2H), 0.90 (s, 9H), 0.08 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 125.49, 134.25, 129.48, 128.53, 55.06, 54.42, 26.00, 18.35, -5.79.

HRMS (ESI-TOF) *m/z* calcd. for C₁₅H₂₈GeNaO₃Si ([M+Na]⁺) 381.0912, found 381.0908.

IR (film) v_{max} 3350, 2928, 2856, 2361, 2342, 1725, 1471, 1256, 1065, 1004 cm⁻¹.

Step 4: 100' were prepared according to **General procedure E** from the reaction of (((((tert-bu-tyldimethylsilyl)oxy)methyl)(phenyl)germanediyl)dimethanol (**8**, 214.9 mg, 0.6 mmol), [1,1'-bi-phenyl]-2-carbonyl chloride (**66a**, 194.4 mg, 0.9 mmol, 1.5 equiv), Cu(OTf)₂ (21.6 mg, 0.06 mmol), **L8** (36.3 mg, 0.06 mmol), DIPEA (93.0 mg, 0.72 mmol, 1.2 equiv). The crude mixture was worked up using EA described in the general procedure E; the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **110'** as a colorless oil (264.8 mg, 82% yield, 97% e.e.).

(*S*)-((((tert-butyldimethylsilyl)oxy)methyl)(hydroxymethyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (110')



¹**H NMR (400 MHz, CDCl₃)** δ 7.70-7.69 (m, 1H), 7.55-7.52 (m, 1H), 7.50-7.48 (m, 2H), 7.40-7.34 (m, 8H), 7.29-7.27 (m, 2H), 4.38 (s, 2H), 3.99-3.98 (m, 4H), 0.88 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.87, 142.48, 141.30, 134.88, 134.36, 131.42, 130.89, 130.71, 129.99, 129.43, 128.48, 128.45, 128.41, 128.38, 128.26, 128.24, 127.38, 127.25, 55.65, 54.79, 53.86, 25.93, 18.27, -5.84.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₈H₃₆GeNaO₄Si ([M+Na]⁺) 561.1487, found 561.1483.

IR (film) v_{max} 3418, 2928, 2855, 2360, 1713, 1598, 1432, 1303, 1257, 1006 cm⁻¹.

HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 92.5/7.5, flow rate 0.7 mL/min, λ = 210 nm), $t_{\rm R}$ (major) = 10.22 min, $t_{\rm R}$ (minor) = 11.51. [α]_D²⁵ = -1.78 (c = 0.1, CH₂Cl₂).

Step 5: This compound was synthesized according to the literature procedure.³³ An oven-dried 10 mL vial was charged with (S)-((((tert-butyldimethylsilyl)oxy)methyl)(hydroxymethyl)(phe-nyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (**110'**, 188.4 mg, 0.35 mmol, 1.75 equiv), **NHC** (126.5 mg, 0.32 mmol, 1.6 equiv) and an magnetic stir bar. After the vial was vacuumed and refilled with nitrogen gas twice, methyl tert-butyl ether (1.6 mL) was added and the reaction stirred at r.t. for 5 min. Then, a pyridine solution (25.3 mg, 0.32 mmol, 1.6 equiv in 0.4 ml methyl tert-

butyl ether) was added dropwise at room temperature over the course of 2 min. The resulting solution stirred at r.t. for 10 min. A white solid precipitated out during this time. Another oven-dried 20 mL vial was charged with Ir[ppy]₂(dtbbpy)PF₆ (2.7 mg, 0.30 µmol, 0.015 equiv), NiBr₂(dtbbpy) (4.9 mg, 10 µmol, 0.05 equiv), quinuclidine (39.0 mg, 0.35 mmol, 1.75 equiv), 4-Bromobenzaldehyde (37.0 mg, 0.2 mmol, 1.0 equiv) and an magnetic stir bar. Dimethylacetamide (2.0 mL) was added to this vial under an atmosphere of nitrogen. The methyl tert-butyl ether suspension was transferred to a 5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl tert-butyl ether solution was injected through the syringe filter into the dimethylacetamide solution. The reaction mixture was sparged with nitrogen for 15 minutes before sealing with parafilm. The vial was stirred at 1500 rpm stir rate and irradiated under 450 nm LED modules at 100% light intensity with maxed fan speed of 1500 rpm stirring rate in a PennOC Integrated Photoreactor for 2 h. The reaction mixture was diluted with a 0.05 M KH₂PO₄/Na₂HPO₄ aqueous buffer solution (8 mL), water (25 mL) and EtOAc (15 mL). The aqueous layer was further extracted with EtOAc three times (15 mL \times 3). The combined organic layers was washed with water, brine and dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 10/1), to yield the product **110** as a colorless oil (71.4 mg, 57% yield, 99% e.e.).

(*S*)-((((tert-butyldimethylsilyl)oxy)methyl)(4-formylbenzyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (110)



¹**H NMR (400 MHz, CDCl₃)** δ 9.88 (s, 1H), 7.64-7.59 (m, 3H), 7.53-7.49 (m, 1H), 7.34-7.24 (m, 12H), 7.10-7.08 (m, 2H), 4.23 (s, 2H), 3.73 (q, *J* = 11.6 Hz, 2H), 2.60 (q, *J* = 12.4 Hz, 2H), 0.86 (s, 9H), -0.001 (s, 3H), -0.01 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 191.89, 169.54, 148.08, 142.37, 141.38, 135.08, 134.24, 133.33, 131.37, 130.92, 130.87, 130.06, 129.93, 129.42, 128.82, 128.48, 128.28, 128.26, 127.40, 127.23, 55.05, 52.91, 25.99, 21.79, -5.77.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₅H₄₀GeNaO₄Si ([M+Na]⁺) 649.1800, found 649.1805.

IR (film) v_{max} 2360, 2341, 1712, 1598, 1477, 1428, 1259, 1235, 1116, 996 cm⁻¹.

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 97.5/2.5, flow rate 0.4 mL/min, $\lambda = 210$ nm), $t_{\rm R}$ (major) = 32.50. [α]_D²⁵ = -6.58 (c = 0.1, CH₂Cl₂).



111 was synthesized according to the literature procedure.³⁴ To a solution of **80** (81.6 mg, 0.2 mmol, 1.0 equiv), Et₃N (30.4 mg, 0.3 mmol, 1.5 equiv) and DMAP (2.4 mg, 0.02 mmol, 0.1 equiv) in DCM (2 mL) was added by TsCl (42.0 mg, 0.22 mmol, 1.1 equiv). The reaction mixture was

stirred at room temperature for 12 h. The reaction was quenched with water (10.0 mL) and, the solution was extracted with DCM (3×15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 10/1), to yield the product **111** as a colorless oil (94.4 mg, 84% yield, 94% e.e.).

(S)-(methyl(phenyl)((tosyloxy)methyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (111)



¹**H NMR (400 MHz, CDCl₃)** δ 7.69-7.63 (m, 3H), 7.54-7.50 (m, 1H), 7.39-7.29 (m, 10H), 7.27-7.21 (m, 4H), 4.22 (q, *J* = 12.8 Hz, 2H), 4.00 (s, 2H), 2.42 (s, 3H), 0.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.47, 144.80, 142.46, 141.32, 134.54, 133.73, 132.21, 131.39, 130.89, .130.69, 129.96, 129.87, 129.66, 128.49, 128.42, 128.25, 127.43, 127.26, 61.49, 56.14, 21.77, -7.12.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₉H₂₈GeNaO₅S ([M+Na]⁺) 585.0761, found 585.0767.

IR (film) v_{max} 2921, 2361, 2341, 1726, 1560, 1432, 1361, 1174, 1095, 1009 cm⁻¹.

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 210 nm), t_R (major) = 105.34, t_R (minor) = 118.53. [α]_D²⁵ = -1.14 (c = 0.1, CH₂Cl₂).

112 was synthesized according to the literature procedure.¹⁶ A solution of oxalyl chloride (25.4 mg, 0.2 mmol, 1.0 equiv) in dry DCM (1 mL) was cooled to -78 °C under an atmosphere of Ar. A solution of DMSO (31.3 mg, 0.4 mmol, 1.0 equiv) in DCM (0.1 mL) was added at a rate such that the reaction temperature remained below -65 °C. After stirring for 5 min, a solution of 80 (81.6 mg, 0.2 mmol, 1.0 equiv) in DCM (0.2 mL) was added slowly, and the resulting mixture was stirred for 15 min. Next, Et₃N (101.2 mg, 1.0 mmol, 5.0 equiv) was added slowly. After stirring the reaction for 10 additional min at -70 °C, the cooling bath was removed and the reaction was allowed to warm for 45 min. Upon reaching room temperature, water (10 mL) was added and stirring continued for 15 min. The reaction mixture was transferred to a separatory funnel, washed successively with 5% HCl (0.5 mL), saturated NaHCO₃ solution (1 mL), and brine. dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to afford an oil. The resulting residue was used directly without further purification. A solution of the above residue and (2,4dinitrophenyl)hydrazine (43.6 mg, 0.22 mmol, 1.1 equiv) in EtOH (2 mL) was stirred at 25 °C for 12 h. the reaction mixture concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 2/1 to 4/1), to yield the product 112 as a colorless oil (93.8 mg, 80% yield, 94% e.e.).

(*S*,*E*)-(((2-(2,4-dinitrophenyl)hydrazineylidene)methyl)(methyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (112)



¹**H NMR (400 MHz, CDCl₃)** δ 11.06 (s, 1H), 9.12 (d, *J* = 2.4 Hz, 1H), 8.28 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.91 (d, *J* = 9.6 Hz, 1H), 7.82 (s, 1H), 7.70-7.68 (m, 1H), 7.54-7.50 (m, 1H), 7.48-7.43 (m, 2H), 7.42-7.32 (m, 9H), 7.31-7.27 (m, 2H), 4.41 (q, *J* = 12.4 Hz, 2H), 0.64 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.64, 157.43, 144.67, 142.37, 141.45, 138.58, 134.68, 133.89, 131.53, 131.02, 130.61, 130.11, 130.09, 129.99, 129.87, 129.16, 129.05, 128.66, 128.53, 128.29, 127.43, 127.31, 123.44, 116.97, 55.93, -5.87.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₉H₂₈GeN₄NaO₆ ([M+Na]⁺) 609.0800, found 609.0805.

IR (film) v_{max} 3301, 2924, 2360, 2341, 1725, 1617, 1593, 1502, 1313, 1029 cm⁻¹.

HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 210 nm), *t*_R (major) = 101.32, *t*_R (minor) = 122.93. [α]_D²⁵ = -16.4 (c = 0.1, CH₂Cl₂).

113 was synthesized according to the literature procedure.³⁵ To a solution of N-Boc p-toluenesulfonamide (81.4 mg, 0.3 mmol, 1.5 equiv) in dry THF (0.5 M), PPh₃ (157.4 mg, 0.6 mmol, 3.0 equiv) was added. The solution was stirred under nitrogen atmosphere and **80** (81.6 mg, 0.2 mmol, 1.0 equiv) was added followed by diethyl azodicarboxylate (87.1 mg, 0.5 mmol, 2.5 equiv). The mixture was stirred at room temperature for 3 h. The reaction mixture concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 4/1), to yield the product **113** as a colorless oil (129.6 mg, 98% yield, 95% e.e.).

(S)-((((N-(tert-butoxycarbonyl)-4-methylphenyl)sulfonamido)methyl)(methyl)(phenyl)germyl)methyl [1,1'-biphenyl]-2-carboxylate (113)



¹**H NMR (400 MHz, CDCl₃)** δ 7.67-7.64 (m, 3H), 7.51-7.48 (m, 3H), 7.37-7.27 (m, 10H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.40 (s, 2H), 3.70 (q, *J* = 14.4 Hz, 2H), 2.42 (s, 3H), 1.26 (s, 9H), 0.47 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.58, 151.43, 144.13, 142.31, 141.33, 137.33, 136.61, 134.09, 131.22, 131.09, 130.76, 129.92, 129.29, 129.13, 128.49, 128.23, 128.22, 127.73, 127.31, 127.14, 84.24, 58.01, 36.54, 27.86, 21.70, -5.78.

HRMS (ESI-TOF) *m*/*z* calcd. for C₃₄H₃₇GeNNaO₆S ([M+Na]⁺) 684.1446, found 684.1448.

IR (film) v_{max} 2922, 2851, 2360, 2341, 1712, 1477, 1369, 1307, 1153, 1008 cm⁻¹.

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 236 nm), t_R (major) = 68.42, t_R (minor) = 86.69. $[\alpha]_D^{25}$ = -0.4 (c = 0.1, CH₂Cl₂).

114 was synthesized according to the literature procedure.³³ An oven-dried 10 mL vial was charged with **80** (142.8 mg, 0.35 mmol, 1.75 equiv), **NHC** (126.5 mg, 0.32 mmol, 1.6 equiv) and an magnetic stir bar. After the vial was vacuumed and refilled with nitrogen gas twice, methyl tert-butyl ether (1.6 mL) was added and the reaction stirred at r.t. for 5 min. Then, a pyridine solution (25.3 mg, 0.32 mmol, 1.6 equiv in 0.4 ml methyl tert-butyl ether) was added dropwise at room temperature over the course of 2 min. The resulting solution stirred at r.t. for 10 min. A white solid precipitated out during this time. Another oven-dried 20 mL vial was charged with $Ir[ppy]_2(dtbbpy)PF_6$ (2.7 mg, 0.30 µmol, 0.015 equiv), NiBr₂(dtbbpy) (4.9 mg, 10 µmol, 0.05

equiv), quinuclidine (39.0 mg, 0.35 mmol, 1.75 equiv), methyl 5-bromopicolinate (43.2 mg, 0.2 mmol, 1.0 equiv) and an magnetic stir bar. Dimethylacetamide (2.0 mL) was added to this vial under an atmosphere of nitrogen. The methyl tert-butyl ether suspension was transferred to a 5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl tert-butyl ether solution was injected through the syringe filter into the dimethylacetamide solution. The reaction mixture was sparged with nitrogen for 15 minutes before sealing with parafilm. The vial was stirred at 1500 rpm stir rate and irradiated under 450 nm LED modules at 100% light intensity with maxed fan speed of 1500 rpm stirring rate in a PennOC Integrated Photoreactor for 2 h. The reaction mixture was diluted with a 0.05 M KH₂PO₄/Na₂HPO₄ aqueous buffer solution (8 mL), water (25 mL) and EtOAc (15 mL). The aqueous layer was further extracted with EtOAc three times (15 mL × 3). The combined organic layers was washed with water, brine and dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 10/1), to yield the product **114** as a colorless oil (77.0 mg, 73% yield, 96% e.e.).

methyl (S)-5-((((([1,1'-biphenyl]-2-carbonyl)oxy)methyl)(methyl)(phenyl)germyl)methyl)picolinate (114)



¹**H NMR (400 MHz, CDCl₃)** δ 8.27 (d, *J* = 2.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.70-7.68 (m, 1H), 7.55-7.51 (m, 1H), 7.41-7.28 (m, 10H), 7.23-7.20 (m, 3H), 4.21 (q, *J* = 12.4 Hz, 2H), 3.97 (s, 3H), 2.40 (q, *J* = 12.8 Hz, 2H), 0.26 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.65, 165.89, 149.18, 144.14, 142.25, 141.42, 140.29, 135.81, 135.75, 133.53, 131.39, 130.93, 130.79, 129.90, 129.51, 128.50, 128.46, 128.28, 127.42, 127.29, 124.83, 77.48, 77.16, 76.84, 56.72, 52.76, 20.73, -6.81.

HRMS (ESI-TOF) *m*/*z* calcd. for C₂₉H₂₇GeNO₄ ([M+H]⁺) 528.1225, found 528.1228.

IR (film) v_{max} 2921, 2851, 2361, 2341, 1742, 1586, 1392, 1256, 1120, 1024 cm⁻¹.

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 210 nm), t_R (major) = 74.16, t_R (minor) = 71.25. $[\alpha]_D^{25}$ = -3.62 (c = 0.1, CH₂Cl₂).



115 was synthesized according to the literature procedure.³⁶ To a solution of (11b*S*)-4-chlorodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (73.2 mg, 0.2 mmol, 1.0 equiv) in dry DCM (0.1 M), **80** (81.6 mg, 0.2 mmol) and Et₃N (30.4 mg, 0.3 mmol, 1.5 equiv) was added. The solution was stirred under nitrogen atmosphere for 24 h. The reaction mixture concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 5/1), to yield the product **115** as a colorless oil (96.0 mg, 65% yield, 10:1 d.r.).



¹**H NMR (400 MHz, CDCl₃)** δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.97-7.89 (m, 3H), 7.72-7.67 (m, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.53-7.47 (m, 3H), 7.42-7.15 (m, 17H), 4.52-4.40 (m, 2H), 4.30 (q, *J* = 12.4 Hz, 1H), 0.45 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.52, 147.50 (d, $J_{C-P} = 11.0$ Hz), 146.38 (d, $J_{C-P} = 8.0$ Hz), 141.80 (d, $J_{C-P} = 102.0$ Hz), 134.72, 133.78, 132.27, 131.89 (d, $J_{C-P} = 1.0$ Hz), 131.89 (d, $J_{C-P} = 1.0$ Hz), 131.62 ($J_{C-P} = 1.0$ Hz), 131.51, 131.29, 131.11, 130.81, 130.74, 129.89, 129.51, 128.54 (d, $J_{C-P} = 3.0$ Hz), 128.37 (d, $J_{C-P} = 4.0$ Hz), 128.24, 127.39, 127.20, 127.04, 126.82 (d, $J_{C-P} = 2.0$ Hz), 125.83 (d, $J_{C-P} = 4.0$ Hz), 121.48 (d, $J_{C-P} = 1.0$ Hz), 121.19 (d, $J_{C-P} = 2.0$ Hz), 120.21 (d, $J_{C-P} = 3.0$ Hz), 61.73 (d, $J_{C-P} = 1.0$ Hz), 56.21, -7.31.

³¹P NMR (162 MHz, CDCl₃) δ 4.40.

HRMS (ESI-TOF) *m*/*z* calcd. for C₄₂H₃₄GeO₆P ([M+H]⁺) 739.1294, found 739.1299.

IR (film) v_{max} 3058, 3024, 2963, 2920, 1719, 1508, 1433, 1203, 1121, 1037 cm⁻¹.

9) X-ray crystallographic data

X-Ray Structural Data for the pyridine sulfate salt of 73'

Crystals suitable for X-ray analysis were obtained via vapor diffusion (solvent: EtOH). CCDC Number: 2432397. Additional structural data can be found free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Representation of the solid state of 73' using 50% probability eliptoids.

Table 1 Crystal data and structure refinement for 73	
Identification code	73' (CCDC:2432397)
Empirical formula	C ₂₅ H ₂₇ FeGeNO ₆ S

Formula weight	597.97
Temperature/K	150.02(10)
Crystal system	triclinic
Space group	P1
a/Å	12.63374(12)
b/Å	14.61502(14)
c/Å	15.17264(15)

α/°	102.2600(8)
β/°	113.5361(9)
γ/°	91.2681(7)
Volume/Å ³	2491.93(4)
Z	4
ρ _{calc} g/cm ³	1.594
μ/mm ⁻¹	7.291
F(000)	1224.0
Crystal size/mm ³	0.12 imes 0.1 imes 0.08
Radiation	Cu Ka ($\lambda = 1.54184$)
20 range for data collection /° 6.234 to 149.04	
Index ranges	$\text{-}15 \leq h \leq 14, \text{-}17 \leq k \leq 18, \text{-}18 \leq l \leq 18$
Reflections collected	54661
Independent reflections	16331 [$R_{int} = 0.0337$, $R_{sigma} = 0.0292$]
Data/restraints/parameters	16331/75/1320
Goodness-of-fit on F ²	1.074
Final R indexes [I>=2σ (I)]	$R_1 = 0.0282, wR_2 = 0.0680$
Final R indexes [all data]	$R_1 = 0.0307, wR_2 = 0.0687$
Largest diff. peak/hole / e $\rm \AA^{-3}$	0.47/-0.38
Flack/Hooft parameter	-0.003(2)/0.0017(15)

10) Spectral data for isolated products
















158.98 143.67 142.05 142.04 142.70 142.77 125.89 125.35 12









7,381 7,337 7,338 7,338 7,338 7,338 7,336 7,336 7,336 7,336 7,336 7,336 7,336 7,336 7,334 7,334 7,334 7,334 7,334 7,334 7,334 7,334 7,334 7,191 7,117 7,253 7,191 7,117 7,117 7,1191 7,1









5; ¹¹B NMR (128 MHz, CDCl₃)





5c; 11B NMR (128 MHz, CDCl₃)



-33.19



8; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



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9 and 11; ¹¹B NMR (128 MHz, CDCl₃)



-34.63









13; ¹¹B NMR (128 MHz, CDCl₃)





14; ¹¹B NMR (128 MHz, CDCl₃)









16; 11B NMR (128 MHz, CDCl₃)





17; ¹¹B NMR (128 MHz, CDCl₃)





18; ¹¹B NMR (128 MHz, CDCl₃)









21; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)









23; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



4.056 4.025 3.994 3.964

2.870 2.849 2.828 2.592 1.563 1.548 1.542 1.536 1.536 1.236

7.534 7.552 7.552 7.556 7.556 7.556 7.548 7.488 7.488 7.488 7.387 7.371 7.387 7.371 7.387 7.371 7.387 7.371 7.387 7.721 7.387 7.721 7.387 7.721 7.387 7.721 7.387 7.721 7.387 7.721 7.387 7.721 7.371 7.371 7.371 7.371 7.371 7.371 7.371 7.371 7.371 7.371 7.371 7.371 7.721

24; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)














29; 11B NMR (128 MHz, CDCl₃)





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1.250 1.158 1.151 0.623 0.591 0.579













-33.28





-33.96















-35.24





-35.12



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1(ppm)





-33.75















--35.05

43; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

7,7,7,7 7,7,69 7,7,7,68 7,7,7,68 7,7,7,68 7,7,58 7,7,73 7,7,58 7,7,73 7,7,58 7,7,73 7,73 7,





-32.56



44; 11B NMR (128 MHz, CDCl₃)



45; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)






46; 11B NMR (128 MHz, CDCl₃)









48; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

7,595 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,757 7,558 7,7577 7,7577 7,7577 7,7577 7,7577 7,7577 7,7577 7,7577 7,7577 7,7

3.0640





33.94















-34.45



S-267





























-34.44





-3.014 -3.014 -1.171 -1.162 -1.107 -1.107 -1.1085 -1.0085 -0.907















-34.23






1.014





-34.45





69; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

20 10

0 -10

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 f1 (ppm)





S-294









74; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)









78; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

7,685 7,575 7,575 7,575 7,575 7,575 7,575 7,5587 7,558 7,558 7,558 7,558 7,558 7,558 7,558 7,558 7,558























7.7.49 7.7.736 7.7.7355 7.7.555 7.7.555 7.7.555 7.7.555 7.7.551 7.7.551 7.7.413 7.7.413 7.7.413 7.7.413 7.7.413 7.7.413 7.7.305 7.7.30





10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

















92; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

7,783 7,759 7,759 7,757 7,757 7,759



93'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

7, 580 7, 7, 584 7, 7, 564 7, 7, 7, 564 7, 7, 7, 564 7, 7, 7, 564 7, 7, 7, 564 7, 7, 564 7, 7, 356 7, 7, 356 7, 35





94'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)





94'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

7,778 7,758 7,755 7,755 7,559 7,559 7,559 7,559 7,559 7,559 7,559 7,559 7,550 8 7,750 8 7,750 7,750 8 7,750 7,750 7,750 8 7,750 7,75



95'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)





95; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



96'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)





96'; ¹⁹F NMR (376 MHz, CDCl₃)



10 0 -10 -20 -30 -40 -50 -80 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)
7,775 7,775 7,775 7,550 7,755 550 7,755 550 7,755 7,550 7,755 7,550 7,7557 7,7557 7,7557 7,7557 7,75577 7,75



96; ¹⁹F NMR (376 MHz, CDCl₃)



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -116 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppn)

97'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)





97; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)





98'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



98; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



99'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



99; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)





100'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



100; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



101'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



101; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



102; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)









103; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



104; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

7, 682 7, 7, 682 7, 7, 534 7, 7, 554 7, 7, 554 7, 7, 554 7, 7, 554 7, 7, 554 7, 7, 554 7, 7, 554 7, 7, 354



105; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

7,677,7567 7,757,7567 1,7527 1,7557 1,7557 1,7557 1,7557 1,7557 1,7557 1,7557 1,7557





107; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



108; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



109; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



110'; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)





110; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



111; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)





112; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

11.063 9.121 9.121 9.121 9.121 9.121 9.9.121 9



113; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



114; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



115; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

8.064 8.064 8.064 8.064 8.042 8.0448 8.0448 8.0448 8.0448 8.0448 8.0448 8.0448 8.0448 8.0448 8.0448 8.0448 8.0448 8.0448



115; ³¹P NMR (162 MHz, CDCl₃)



67a; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)









10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



67b; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)

67c; ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃)



HPLC spectra



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.428	BB	0.2507	1127.74158	68.99631	49.8211
2	19.418	BB	0.4062	1135.84021	43.28333	50.1789

Totals :

2263.58179 112.27964



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.675	MM R	0.2582	160.76732	10.37543	4.6905
2	18.999	BB	0.3969	3266.75244	128.37416	95.3095

Totals : 3427.51976 138.74959



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.428	BB	0.2507	1127.74158	68.99631	49.8211
2	19.418	BB	0.4062	1135.84021	43.28333	50.1789

Totals :

2263.58179 112.27964



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.947	BB	0.2035	119.54751	9.20873	2.6056
2	17.323	BB	0.3763	4468.51172	184.65793	97.3944
Total	ls :			4588.05923	193.86666	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.962	BB	0.2157	4231.37793	301.57001	49.9789
2	12.432	BB	0.2760	4234.95850	237.49402	50.0211





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.913	MM R	0.2257	155.70616	11.49906	5.0958
2	12.212	BB	0.2615	2899.86914	171.26286	94.9042

Totals : 3055.57530 182.76193



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	23.019	BB	0.4848	3657.76074	116.97983	50.1013
2	35.410	BB	0.7893	3642.97485	70.68495	49.8987

Totals :

7300.73560 187.66478



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	22.996	BB	0.3888	99.48256	3.30852	3.6600
2	34.109	BB	0.7396	2618.63550	54.01187	96.3400
Total	ls :			2718.11806	57.32039	


Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak RetTin	ne Type	Width	Area	Height	Area
# [min]]	[min]	[mAU*s]	[mAU]	%
 1 11.56 2 19.39	 56 BB 94 BB	0.2465 0.4760	4466.19580 4479.47168	279.44977 147.63651	49.9258 50.0742





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.494	BB	0.2372	282.16589	18.37403	7.7324
2	19.243	BB	0.4598	3366.97070	114.25656	92.2676

Totals : 3649.13660 132.63059



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.746	BB	0.3778	4854.27734	199.58556	49.9647
2	23.431	BB	0.5075	4861.12695	147.88986	50.0353





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.811	 BB	0.3299	120.85316	5.07440	3.4184
2	23.544	BB	0.4989	3414.55078	105.12565	96.5816

Totals : 3535.40395 110.20005



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1 2	10.790 15.404	 BB BB	0.2710 0.4169	6085.95313 6113.14941	346.43320 227.94635	49.8885 50.1115





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1 2	10.540 15.065	BB BB BB	0.2596 0.4070	162.51932 6979.58301	9.40435 266.99094	2.2755 97.7245

Totals : 7142.10233 276.39529



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak RetTime	Туре	Width	Area	Height	Area
# [min]		[min]	[mAU*s]	[mAU]	%
1 20.572	BB	0.4387	2747.97266	96.95115	50.1253
2 29.555	BB	0.6323	2734.23877	66.69549	49.8747





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.493	BB	0.3354	91.12285	3.32861	2.4759
2	29.708	BB	0.6203	3589.33716	87.18079	97.5241

Totals : 3680.46001 90.50939



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.445	BB	0.2890	2826.06689	151.96370	49.9406
2	20.659	BB	0.4280	2832.79370	102.62971	50.0594

Totals : 5658.86060 254.59341



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.305	BB	0.2535	60.51562	3.50410	2.6276
2	19.372	BB	0.4076	2242.60376	85.05943	97.3724
Tota:	ls :			2303.11938	88.56353	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.723	BB	0.2667	3758.67578	218.53813	50.0629
2	19.099	BB	0.4289	3749.22754	137.16243	49.9371

7507.90332 355.70056



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.057	BB	0.2541	117.09351	7.11154	4.0600
2	17.394	BB	0.3859	2766.95850	110.57964	95.9400
Total	ls :			2884.05201	117.69119	



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.754	BB	0.2035	3988.45630	303.11700	49.9395
2	19.479	BB	0.4487	3998.12231	138.54698	50.0605





Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.154	MM R	0.2177	113.94485	8.72390	3.6558
2	19.742	BB	0.4494	3002.85083	103.81890	96.3442
Tota:	ls :			3116.79568	112.54280	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak R	etTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
-						<mark> </mark>
1	18.531	BB	0.4161	4948.70264	183.79019	50.0959
2	37.926	BB	0.9940	4929.74854	71.53825	49.9041





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
				<mark>-</mark>		
1	18.916	MM R	0.4323	95.40054	3.67813	5.1987
2	36.286	BB	0.8360	1739.68274	27.57512	94.8013
Total	s :			1835.08327	31.25325	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.822	BB	0.1375	2549.64673	287.43695	49.9522
2	8.855	BB	0.2009	2554.52393	197.48752	50.0478





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.052	BB	0.1199	165.20053 1870 99451	21.44344 131 47458	8.1132
2	/./50	00	0.2220	10/0.00401	1)1.4/4)0	51.0000
Total	s :			2036.19504	152.91802	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
	p					<mark></mark>]
1	13.067	BB	0.3737	9871.93848	408.90643	50.0030
2	24.483	BB	0.77 <mark>1</mark> 4	9870.76465	198.08116	49.9970
Tota	ls :			1.97427e4	606.98759	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
 1 2	12.949 24.275	 MM R BB	0.3741 0.7651	112.54356 6712.06494	5.01389 136.64398	 1.6491 98.3509
Total	ls :			6824.60851	141.65788	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
	<mark></mark>					
1	13.067	BB	0.3737	9871.93848	408.90643	50.0030
2	24.483	BB	0.7714	9870.76465	198.08116	49.9970

1.97427e4 606.98759



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.930	BB	0.3648	7655.39551	325.06021	97.6843
2	23.932	BB	0.5822	181.48087	3.97816	2.3157
Total	ls :			7836.87637	329.03837	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.059	BB	0.3653	6371.60986	269.98804	49.9302
2	16.376	BB	0.6269	6389.43359	159. <mark>6</mark> 4511	50.0698





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.212	BB	0.3319	132.09425	5.75171	1.7162
2	16.493	BB	0.6129	7564.65527	193.15788	98.2838

Totals :

7696.74953 198.90959



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
	18.414	 BV	0.4101	2781.55884	104.65986	 50.3796
2	19.527	VB	0.4344	2739.64258	97.91818	49.6204

Totals : 5521.20





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.405	BB	0.3989	2638.84644	102.99337	98.7459
2	20.550	BB	0.2687	33.51413	1.51112	1.2541
Tota]	ls :			2672.36057	104.50449	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.441	BV	0.5700	7381.57178	200.25714	49.7052
2	19.989	VB	0.6585	7469.13037	170.70865	50.2948





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.233	BB	0.5534	9522.12793	266.16122	99.3295
2	19.756	BB	0.3682	64.27994	2.12916	0.6705
Total	ls :			9586.40787	268.29039	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1 2	57.559 65.217	BB BB BB	1.5428 1.7304	3263.62305 3276.77441	24.90484 22.22087	49.8995 50.1005
Total	ls :			6540.39746	47.12571	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	57.573	MM R	1.9780	100.39644	8.45954e-1	2.0990
2	64.960	MM R	2.6147	4682.69043	29.84818	97.9010

Totals : 4783.08687 30.69413



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime	Туре	Width [min]	Area [mAU*s]	Height	Area %
			[]		[
1	14.688	BB	0.7370	977.04626	16.12277	50.7675
2	21.213	BB	0.6966	947.50269	17.14790	49.2325

Totals : 1924.54895 33.27067



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1 2	16.516 23.095	 BB BB	0.3563 0.6471	200.11945 6410.52832	6.82103 152.92770	3.0272 96.9728

Totals : 6610.64777 159.74874



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.644	BB	0.3329	2534.11255	116.89386	50.1547
2	14.380	BB	0.4343	2518.47754	90.04452	49.8453





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.291	BB	0.4163	2846.21289	105.66424	100.0000
Total	ls :			2846.21289	105.66424	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.226	BB	0.3926	3191.12622	125.54080	49.9963
2	18.376	BB	0.5663	3191.59229	86.53588	50.0037





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.467	MM R	0.4016	103.08246	4.27850	1.6144
2	18.541	BB	0.5813	6282.27100	167.58543	98.3856

Totals : 6385.35345 171.86393



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.853	BB	0.6057	2908.39575	73.17543	50.0969
2	31.661	BB	0.8771	2897.14868	41.36559	49.9031





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.097	MM R	0.6523	90.00508	2.29971	2.1182
2	31.808	BB	0.9282	4159.13574	59.30601	97.8818
Total	ls :			4249.14082	61.60572	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.267	BB	0.4696	6880.75537	228.31575	49.9630
2	18.148	BB	0.5715	6890.93896	188.07298	50.0370





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.992	BB	0.4504	588.27136	19.70136	9.2743
2	17.836	BB	0.5582	5754.76025	158.25435	90.7257

Totals : 6343.03162 177.95571



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.493	BB	0.3539	1693.29492	71.08002	49.9144
2	21.782	BB	0.7277	1699.10327	28.41139	50.0856





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.953	MM R	0.8625	5253.33838	101.51751	84.8761
2	23.365	MM R	0.7608	936.08228	20.50557	15.1239

Totals : 6189.42065 122.02308



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
 1 2	12.205	BB BB	0.3474	3622.77197	161.68567	50.0155





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.209	BB	0.2766	56.92482	2.52894	1.3961
2	30.388	BB	0.9464	4020.38257	61.85024	98.6039

Totals : 4077.30739 64.37918



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	22.366	BB	0.5050	9267.39844	286.80777	50.0892
2	26.851	BB	0.6023	9234.37402	236.09740	49.9108





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Type	Width	Area	Height	Area	
#	[min]		[min]	[mAU*s]	[mAU]	%	
				<mark> </mark>			
1	21.308	BB	0.4886	6973.55908	223.17183	97.4245	
2	25.618	BB	0.4624	184.35468	4.77585	2.5755	

Totals :

7157.91376 227.94768



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.109	BB	0.6460	1.45749e4	352.79327	50.0555
2	3 <mark>1.24</mark> 8	BB	0.7537	1.45425e4	297.81610	49.9445





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.407	BB	0.5976	1.07977e4	280.16235	100.0000
Total	ls :			1.07977e4	280.16235	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	39.601	BB	1.1564	1.44720e4	151.51035	49.7434
2	43.794	BB	1.1903	1.46214e4	151.18848	50.2566





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	43.859	BB	1.1693	1.11785e4	114.46992	100.0000
Tota:	ls :			1.11785e4	114.46992	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.001	BB	0.3020	2.05375e4	1069.54224	49.8196
2	16.771	VB	0.3623	2.06862e4	892.84760	50.1804





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.008	BB	0.2947	9993.49609	528.25940	94.7036
2	16.782	BB	0.3467	558.89716	24.63440	5.2964

Totals : 1.05524e4 552.89380



Signal 3: DAD1 C, Sig=210,4 Ref=off

 Peak RetTime Type Width
 Area
 Height
 Area

 # [min]
 [min]
 [mAU*s]
 [mAU]
 %

 ----|-----|-----|------|------|
 -----|------|------|
 -----|
 1

 1
 16.172
 MM
 R
 0.3456
 4542.67432
 219.04662
 50.4989

 2
 19.340
 BB
 0.4085
 4452.92090
 169.50548
 49.5011

```
Totals :
```

8995.59521 388.55209



Signal 3: DAD1 C, Sig=210,4 Ref=off

 Peak RetTime Type Width
 Area
 Height
 Area

 # [min]
 [min]
 [mAU*s]
 [mAU]
 %

 ----|-----|-----|------|-------|
 -----|------|-------|

 1
 16.140
 BB
 0.3332
 9678.46191
 453.08170
 99.5775

 2
 19.285
 BB
 0.2918
 41.06157
 1.72435
 0.4225

Totals : 9719.52349 454.80604



Signal 2: DAD1 B, Sig=236,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
 1 2	19.238 22.670	 BB BB	0.4767 0.5624	1641.45886 1637.09521	53.39032 44.58224	50.0665 49.9335



3278.55408 97.97255



Signal 2: DAD1 B, Sig=236,4 Ref=off

Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] % 1 20.341 BB 0.4422 2872.20825 101.47857 97.1507 2 24.375 BB 0.3761 84.23781 2.99520 2.8493 Totals : 2956.44606 104.47377



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	22.469	VB	0.5082	1.13131e4	343.53668	49.9979
2	33.251	BB	0.7553	1.13140e4	227.08241	50.0021



2.26270e4 570.61909



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	22.646	BB	0.5156	7714.45996	231.00505	97.7174
2	33.792	BB	0.5764	180.20053	3.69894	2.2826
Tota]	ls :			7894.66049	234.70399	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	24.957	BB	0.5083	1.32059e4	403.05029	49.8665
2	28.265	BB	0.5808	1.32766e4	354.62576	50.1335





Signal 3: DAD1 C, Sig=210,4 Ref=off

 Peak RetTime Type Width
 Area
 Height
 Area

 # [min]
 [min]
 [mAU*s]
 [mAU]
 %

 --- --- --- --- --- --- ---

 1
 24.896
 MM R
 0.5455
 6779.41113
 207.14902
 98.8043

 2
 28.259
 MM R
 0.5087
 82.03922
 2.68802
 1.1957

Totals : 6861.45035 209.83704



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.826	BB	0.5639	4852.68457	132.30676	49.6090
2	18.370	BB	0.8571	4929.17383	86.99128	50.3910

9781.85840 219.29804



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Type	Width	Area	Height	Area	
#	[min]		[min]	[mAU*s]	[mAU]	%	
				<mark> </mark>			
1	13.711	BB	0.5369	5268.11523	150.29396	100.0000	

Totals .	5268 11523	150 29396
IULAIS .	5200.11525	120.29390



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.328	BB	0.2521	3390.78027	208.07426	49.9822
2	18.897	BB	0.4015	3393.18945	130.44081	50.0178





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
 1 2	12.418 18.294	MM R BB	0.2535 0.3891	75.11997 1404.77747	4.93937 55.54346	5.0760 94.9240

Totals : 1479.89744 60.48283



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
	9.225	 BB	0.2297	 1917.39282	128.75606	50.1409
2	15.980	BB	0.4623	1906.61694	63.50765	49.8591





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
 1 2	9.736 16.511	BB BB BB	0.2052 0.4357	99.67409 1506.89392	7.49444 53.32681	6.2042 93.7958
Total	ls :			1606.56801	60.82124	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime Typ	e Width	Area	Height	Area
#	[min]	[min]	[mAU*s]	[mAU]	%
	<mark> </mark>				
1	20.748 BB	0.4536	1846.82922	63.07806	50.0074
2	27.521 BB	0.6014	1846.28223	46.88367	49.9926



3693.11145 109.96173



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.266	MM R	0.4815	230.74956	7.98671	9.4185
2	26.285	BB	0.5828	2219.22119	58.74152	90.5815
Tota]	ls :			2449.97075	66.72823	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	39.797	BV	1.0345	7680.83105	92.71399	50.2987
2	42.555	VB	1.2479	7589.61914	71.99591	49.7013



1.52705e4 164.70990



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime	Туре	Width	Area	Height	Area
# 	[min]			[mAU*S]	[mA0]	/0
1	41.353	BB	1.2364	8396.86426	96.00748	100.0000
Total	ls :			8396.86426	96.00748	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAll]	Area %
	[]					
1	36.917	BB	0.9396	6956.72510	106.01206	50.0552
2	45.511	BB	1.0822	6941.39160	89.56094	49.9448





Signal 3: DAD1 C, Sig=210,4 Ref=off


Signal 2: DAD1 B, Sig=236,4 Ref=off



6.59438e4 2440.77832



Signal 2: DAD1 B, Sig=236,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.938	MM R	0.3648	199.79793	9.12944	9.9985
2	20.855	MM R	0.4380	1798.48511	68.44227	90.0015
Tota]	ls :			1998.28304	77.57171	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %	
 1 2	6.578 7.814	BV BV VB	0.3050 0.4371	4491.65039 4469.43896	226.80603 158.46317	50.1239 49.8761	





Signal 3: DAD1 C, Sig=210,4 Ref=off

 Peak RetTime Type Width
 Area
 Height
 Area

 # [min]
 [min]
 [mAU*s]
 [mAU]
 %

----	-----
 -----|
 -----|

 1
 7.633
 BB
 0.3377
 3812.35645
 173.93721
 100.0000

Totals : 3812.35645 173.93721



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %	
 1 2	9.233 10.583	BB BB BB	0.2840 0.2929	4285.92383 4235.20361	233.70161 225.70644	50.2976 49.7024	

```
Totals :
```

8521.12744 459.40805



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type Width Height Area Area # [min] [min] % [mAU*s] [mAU] 1 10.221 BB 0.2202 8209.10938 583.10101 98.5099 2 11.511 BB 0.2258 124.17188 8.05508 1.4901 Totals : 8333.28125 591.15609



Signal 3: DAD1 C, Sig=210,4 Ref=off

 Peak RetTime Type Width
 Area
 Height
 Area

 # [min]
 [min]
 [mAU*s]
 [mAU]
 %

 ----|-----|----|-----|------|------|
 -----|-----|------|------|
 1
 35.572 BV
 0.7249
 6.29056e4
 1361.83838
 49.9409

 2
 37.362 VB
 0.7763
 6.30546e4
 1267.65613
 50.0591



1.25960e5 2629.49451



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type Width Area Height Area
[min] [min] [mAU*s] [mAU] %
----|-----|-----|------|------|
1 32.502 BB 0.9591 3.26808e4 525.84863 100.0000
Totals : 3.26808e4 525.84863



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime	Туре	Width [min]	Area	Height	Area %
	[""""]			[IIIAO 3]		
1	103.249	BV	1.6492	7510.28174	53.58205	49.8774
2	115.439	BV	1.8499	7547.19141	47.80338	50.1226





Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	105.340	VV	1.9422	1.59798e5	963.88885	96.7275
2	118.535	BB	1.8556	5406.33594	34.21198	3.2725
Total	ls :			1.65204e5	998.10084	



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	102.072	BB	1.6411	3822.96265	27.27808	50.1195
2	123.585	BV	1.9681	3804.72998	22.66892	49.8805



7627.69263 49.94700



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] % [mAU] 1 101.320 BB 1.6616 2.27547e4 160.34671 96.9796 2 122.938 MM R 2.4235 708.68054 4.87359 3.0204 Totals : 2.34634e4 165.22030



Signal 2: DAD1 B, Sig=236,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	71.834	MM R	1.9869	5207.97852	43.68579	50.4184
2	92.916	MM R	3.4237	5121.54004	24.93199	49.5816

```
Totals :
```

1.03295e4 68.61778



Signal 2: DAD1 B, Sig=236,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	68.425	BB BB	1.7207	5.97102e4	498.04886	97.4747
Z Total	86.692 ls :	БВ	1./19/	6.12572e4	508.61748	2.5255



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	70.741	VV	1.2924	7321.41504	66.71214	49.7396
2	74.070	VV	1.3847	7398.08301	63.24574	50.2604

Totals :

1.47195e4 129.95789



Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	71.256	BV	0.9661	568.25610	6.91929	1.9710
2	74.168	VB	1.3722	2.82632e4	246.04074	98.0290
Tota]	ls :			2.88314e4	252.96003	

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