Supporting Information

Modular Generation of (Iodinated) Polyarenes Using Triethylgermane as Orthogonal Masking Group

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1. General Experimental Details

Reagents and Starting Materials

All reagents and starting materials were commercially available and used as received. Methyl 3-bromo-4-(((trifluoromethyl)sulfonyl)oxy)benzoate\textsuperscript{[1]} and 2-bromo-4-chlorophenyl fluorosulfate\textsuperscript{[2]} were synthesized as previously reported. [Pd(μ-I)(PtBu\textsubscript{3})\textsubscript{2}] was prepared according to the literature procedure.\textsuperscript{[3]} Anhydrous solvents were dried using an Innovative Technology PS-MD-5 solvent purification system. Solvents used in work up and purification were received in technical grade and distilled prior to use. Thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F\textsubscript{254} aluminium plates with unmodified silica and visualized under UV light. Flash column chromatography was performed with Merck silica gel 60 (35 – 70 mesh).

Experimental Techniques

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in dried glassware under an argon atmosphere and were performed either in an argon-filled glovebox or by using standard Schlenk techniques unless otherwise stated. Kugelrohr distillation was performed using a Büchi Glass Oven B-585 Kugelrohr apparatus.

Characterization

All \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{19}F NMR spectra were recorded on Bruker Avance Neo 600, Varian VNMRS 600, Varian VNMRS 400 or Varian Mercury 300 spectrometers at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) and were referenced to residual solvent peak (for \textsuperscript{1}H and \textsuperscript{13}C) or by the instrument internally after locking and shimming to the deuterated solvent (for \textsuperscript{19}F). Coupling constants (J) are given in Hertz (Hz).

Gas chromatography coupled with mass spectrometry (GC-MS) was performed on an Agilent Technologies 5975 series MSD mass spectrometer under electrospray ionization (EI) mode coupled with an Agilent Technologies 7820A gas chromatograph employing an Agilent 19091s-433 HP-5MS column (30 m x 0.25 μm x 0.25 μm). High-resolution mass spectrometry (HRMS) was performed using a Thermo Scientific LTQ Orbitrap XL spectrometer (ESI), Finnigan MAT 95 (EI) or Bruker Maxis II LC-MS-System (APCI). Low-resolution masses of known compounds were extracted from their GC-MS chromatograms. Melting points were measured with a Coesfeld melting point meter (MPM-H2) with visual detection and temperature increase of 1 °C/min.
2. General procedures

2.1. General procedure A – Double sequential coupling (0.2 mmol scale without purification of intermediates)

1st Coupling: The appropriate aryl bromide (0.2 mmol, 1.0 equiv.) and [Pd(μ-I)(P^t^Bu^3^)]_2 (0.005 mmol, 2.5 mol%) were placed into a vial. The vial was evacuated and backfilled with argon three times before dry toluene (1 mL) was added. A freshly prepared solution of appropriate organozinc (0.3 mmol, 1.5 equiv.) was added in one portion. The reaction mixture was stirred for 5 min before the reaction was quenched with pentane or hexane (1 mL). The mixture was filtered through a plug of silica eluting with hexane/DCM (1:1, 10 mL) and the obtained filtrate was concentrated under reduced pressure.

Bromination: The crude was dissolved in MeCN (2 mL), NBS (0.3 mmol, 1.5 equiv.) was added and the mixture was stirred at 60 °C for 1 hour. Volatiles were removed under reduced pressure and the residue was filtered through a short pad of silica gel eluting with hexane. Volatiles were removed under reduced pressure to give the crude bromoarene.

2nd Coupling: The crude bromoarene was transferred into a vial, which was then evacuated and backfilled with argon three times. Dry toluene (0.1 M, 2 mL) was added, followed by the addition of freshly prepared organozinc reagent (0.5 equiv.; to quench excess brominating agent, alternatively the crude bromoarene can be purified by column chromatography prior to the second coupling) and [Pd(μ-I)(P^t^Bu^3^)]_2 (0.006 mmol, 3.0 mol%; added as a solid under a stream of argon). More of the organozinc reagent (1.5 equiv.) was then added dropwise over 10 min via syringe pump. The reaction mixture was stirred for additional 5 min before the reaction was quenched with hexane (1 mL) and a spatula tip of ammonium pyrrolidine-1-dithiocarboxilic acid was added to precipitate palladium.[4] The mixture was filtered through a plug of silica eluting with hexane/DCM (1:1, 10 mL). After evaporation of all volatiles the product was purified by column chromatography on silica gel.

Amination: In an argon-filled glovebox, a 4 mL glass-vial was charged with KOEt (0.8 mmol, 4.0 equiv.), [Pd(μ-I)(P^t^Bu^3^)]_2 (0.01 mmol, 5 mol%), amine (0.3 mmol, 1.5 equiv.), bromoarene (0.2 mmol, 1.0 equiv.) and dry THF (1 mL). If the amine and/or the bromoarene were a liquid, they
were added as a solution in THF. The vial was sealed, and the mixture was stirred for 1.5 hours at 50 °C. The solution was filtered through a plug of silica gel, eluting with EtOAc (10 mL). The solvent was removed under reduced pressure and the crude purified by column chromatography on silica gel.

2.2. General procedure B – Sequential synthesis (1 mmol scale)

*C-C Coupling*: The appropriate aryl bromide (1.0 equiv., 1 mmol) and [Pd(μ-I)(P̃Bu₃)]₂ (2.5 mol%) were placed into 25 mL round bottom flask. The flask was evacuated and backfilled with argon three times before dry toluene (0.2 M, 5 mL) was added. A freshly prepared solution of organozinc reagent (1.5 equiv.) was added slowly to the reaction mixture via syringe pump over 15 min while the mixture was stirred gently. The reaction mixture was stirred for additional 5 min before the reaction was quenched with pentane or hexane and a spatula tip ammonium pyrrolidine-1-dithiocarboxilic acid was added to precipitate palladium. The mixture was filtered through a plug of silica gel eluting with Et₂O, the filtrate was concentrated under reduced pressure.

*Bromination*: The crude aryl germane was dissolved in MeCN (0.2 M) or HFIP (0.2 M, for electron deficient or sterically hindered aryl germanes) and NBS (2.0 equiv.) was added. The reaction was stirred at 60 °C for 1.5 hours. After that time, the mixture was allowed to cool to room temperature, filtered through a plug of silica gel, eluting with Et₂O. Volatiles were removed under reduced pressure and the crude material was purified by column chromatography on silica gel.

For sequential coupling the C-C coupling and bromination steps were repeated, followed by a final iodination.

*Iodination*: The crude obtained from cross-coupling was dissolved in HFIP (0.2 M) and NIS (2.0 equiv.) was added. The reaction was stirred at 60 °C for 24 hours. After that time, the mixture was allowed to cool to room temperature, filtered through a plug of silica, concentrated under reduced pressure and the crude material was purified by column chromatography on silica gel.
2.3. General procedure C – Iodination of Germanes in DMF

According to Fricke et al.\textsuperscript{[5]}, to a solution of aryl germane (1.0 equiv.) in DMF (0.1 M) was added NIS (2.0 equiv.) and the reaction mixture was stirred at 60 °C, until the starting material was fully consumed (monitored via GC-MS). After cooling to ambient temperature, H\textsubscript{2}O (10 mL) and DCM (15 mL) were added and the aqueous layer was extracted with DCM (10 mL). The combined organic layers were washed with saturated aq. Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (25 mL) and 10% w/w aq. LiCl (25 mL), dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure. The product was purified by chromatography on silica gel.

2.4. General procedure D – Iodination of Germanes in HFIP

To a solution of aryl germane (1.0 equiv.) in HFIP (0.1 M) was added NIS (2.0 equiv.) and the reaction mixture was stirred at 60 °C, until the starting material was fully consumed (monitored via GC-MS). After cooling to ambient temperature, the reaction mixture was diluted with DCM (20 mL). The organic layer was washed with saturated aq. Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (25 mL), dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure. The product was purified by chromatography on silica gel.

*Note:* During the course of this investigation direct C-H germylations have become available,\textsuperscript{[6]} which offer alternatives to the general procedures E and F presented herein.

2.5. General procedure E – Synthesis of aryl germanes with \textsuperscript{t}PrMgCl-LiCl

According to Fricke et al.\textsuperscript{[5]} the appropriate aryl halide was weighed into an oven dried Schlenk flask and dissolved in dry THF (0.2 M). The solution was cooled to 0 °C and a solution of \textsuperscript{t}PrMgCl-LiCl (1.2 equiv., 1.3 M in THF) was added dropwise to the stirred solution. After the addition was complete, GeEt\textsubscript{3}Cl (1.0 equiv.) was added and the reaction mixture stirred at ambient temperature. After full
conversion was observed (monitored via GC-MS), saturated aq. NH₄Cl was added and the aqueous layer was extracted with DCM (3x). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. The product was purified by column chromatography on silica gel.

2.6. General procedure F – Synthesis of aryl germanes with nBuLi

\[
\text{R-Br/I} \xrightarrow{\text{nBuLi (1.0 equiv.), Et₃GeCl (1.0 equiv.)}} \text{R-GeEt₃}
\]

THF, -78°C to r.t.

According to Fricke et al.[5] the appropriate aryl halide (1.0 equiv.) was placed to an oven dried Schlenk flask and dissolved in THF (0.25 M). The solution was then cooled to -78 °C and nBuLi (2.5 M in hexane, 1.0 equiv.) was added dropwise stirred for 30 min at the same temperature. Et₃GeCl (1.0 equiv.) was added and the reaction was stirred overnight, while warming up to ambient temperature. The reaction was quenched with saturated aq. NH₄Cl and the aqueous layer was extracted with DCM (3x). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The product was purified by column chromatography on silica gel.

2.7. General procedure G – Preparation of organomagnesium and -zinc reagents

\[
\text{Et₃Ge} \xrightarrow{\text{Mg (1.5 equiv.), LiCl (1.1 equiv.)}} \text{Et₃Ge} \xrightarrow{\text{ZnCl₂ (1.1 equiv.)}} \text{Et₃Ge}
\]

\(X = \text{Br, I}\)

Organomagnesium Reagents: In an oven dried flask magnesium powder (1.5 equiv.) and dry LiCl (1.1 equiv.; previously dried under high vacuum using a Bunsen burner and allowing to cool under high vacuum) were suspended in dry THF (1 M). A solution of aryl bromide or iodide in THF (1 M) was added and the mixture was stirred overnight. The obtained mixture was filtered through a syringe filter and stored at ambient temperature in the glovebox (no decomposition was observed for months). The organomagnesium reagent was titrated following Knochel’s protocol.[7]
Organozinc Reagents: Solutions of ZnCl$_2$ (1M in THF, 1.1 equiv.) and LiCl (0.5M in THF, 1.1 equiv.; only added if a commercial organomagnesium reagent was employed) were added to a solution of aryl magnesium halide (in THF, 1.0 equiv.) in a 16 mL vial under argon atmosphere and stirred for 10 min. The organometallic species was then used without further analysis.

Preparation of the ZnCl$_2$ solution:[8] To an oven dried Schlenk tube equipped with a stir-bar was added anhydrous ZnCl$_2$ (1.36 g, 10 mmol) under argon atmosphere. Upon melting under high vacuum using a Bunsen burner, the tube was allowed to cool to room temperature and was then refilled with argon. Subsequently, anhydrous THF (10 mL) was added and the mixture was stirred vigorously until a clear solution resulted.
3. Compound characterization data

3.1. Products of double sequential coupling

2-Butyl-3,4'-dichloro-1,1'-biphenyl (6): Prepared, following the general procedure A from (2-bromo-6-chlorophenyl)triethylgermane, 4-chlorophenylzinc chloride and n-butylzinc chloride. Bromination of arylgermane was performed at 60 °C for 6 h. The title product was obtained after purification by column chromatography (hexane) as a colorless oil (96.0 mg, 0.344 mmol, 86%). Rf (Hexane): 0.5. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 7.41 – 7.34\) (m, 3H), 7.21 (d, \(J = 8.3\) Hz, 2H), 7.14 (dd, \(J = 7.8\) Hz, 1H), 7.05 (dd, \(J = 7.6, 1.3\) Hz, 1H), 2.63 (m, 2H), 1.43 (tt, \(J = 7.9, 6.3\) Hz, 2H), 1.22 (h, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta 142.8, 140.0, 138.6, 135.0, 133.3, 130.5, 129.2, 128.6, 128.3, 126.5, 31.8, 30.6, 22.8, 13.8\).

HRMS (APCI): \(m/z\) [M+H]\(^+\) calcd for C\(_{16}\)H\(_{17}\)Cl\(_2\): 279.07018; found: 279.06909.

\(((4'-Fluoro-2,5-dimethyl-[1,1'-biphenyl]-4-yl)methyl)trimethylsilane (7): Prepared, following the general procedure A from (4-bromo-2,5-dimethylphenyl)triethylgermane, 4-fluorophenylzinc chloride and (trimethylsilyl)methylzinc chloride. The title product was obtained after purification by column chromatography (pentane) as a colorless oil (40.0 mg, 0.14 mmol, 70%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.30\) (dd, \(J = 8.8, 5.5\) Hz, 2H), 7.09 (dd, \(J = 8.8\) Hz, 2H), 6.97 (s, 1H), 6.88 (s, 1H), 2.23 (s, 3H), 2.12 (s, 2H), 0.07 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 161.8\) (d, \(J = 244.8\) Hz), 138.2, 138.2 (d, \(J = 3.4\) Hz), 136.7, 132.2, 132.1, 131.6, 131.0, 130.9, 114.9 (d, \(J = 21.1\) Hz), 23.5, 20.1, 19.9, -1.2. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta -116.83 – 116.91\) (m). HRMS (APCI): \(m/z\) [M+H]\(^+\) calcd for C\(_{18}\)H\(_{24}\)FSi: 287.1626; found: 287.1620.

4'-Chloro-5-ethyl-[1,1'-biphenyl]-3-carbonitrile (8): Prepared, following the general procedure A from 3-bromo-5-(triethylgermyl)benzonitrile, 4-chlorophenylzinc chloride and ethylzinc chloride. The title product was obtained after purification by column chromatography (hexane/EtOAc 20:1) as a brown oil (32.5 mg, 0.13 mmol, 67%). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 7.64\) (s, 1H), 7.59 (s, 1H), 7.50 – 7.42 (m, 5H), 2.75 (q, \(J = 7.6\) Hz, 2H), 1.30 (t, \(J = 7.6\) Hz, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta 146.3, 141.4, 137.8, 134.7, 131.3, 130.5, 129.4, 128.5, 128.1, 119.0, 113.2, 28.8, 15.4\). HRMS (APCI): \(m/z\) [M+H]\(^+\) calcd for C\(_{15}\)H\(_{13}\)Cl: 242.0731; found: 242.0740.
2-(4-Cyclopentylphenyl)thiophene (9): Prepared, following the general procedure A from (4-bromophenyl)triethylgermane, cyclopentylzinc chloride and 2-thienylzinc chloride. The title product was obtained after purification by column chromatography (hexane) as a brown solid (28.6 mg, 0.13 mmol, 63%). M.p.: 57 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.53 (d, \(J = 8.2\) Hz, 2H), 7.38 – 7.23 (m, 4H), 7.06 (dd, \(J = 5.0, 3.6\) Hz, 1H), 3.06 – 2.97 (m, 1H), 2.09 (q, \(J = 10.4, 9.4\) Hz, 2H), 1.86 – 1.79 (m, 2H), 1.75 – 1.66 (m, 2H), 1.65 – 1.57 (m, 2H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 146.2, 144.8, 132.1, 128.0, 127.7, 126.0, 124.4, 122.7, 45.8, 34.7, 25.7. HRMS (EI): m/z [M]\(^{+}\) calcd for C\(_{15}\)H\(_{16}\)S: 228.0967; found: 228.0972.

2’-Methyl-5-{2-methyl-2-phenylpropyl}-[1,1’-biphenyl]-3-carbonitrile (10): Prepared, following the general procedure A from 3-bromo-5-{(triethylgermyl)benzonitrile, 2-phenyl-2-methylpropyl zinc chloride and 2-tolyllzinc chloride. The title product was obtained after purification by column chromatography (hexane/EtOAc 20:1) as a pale-yellow oil (55.7 mg, 0.17 mmol, 86%). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.38 (s, 1H), 7.32 – 7.29 (m, 2H), 7.27 (s, 2H), 7.24 – 7.18 (m, 4H), 7.05 (s, 1H), 6.95 (d, \(J = 7.5\) Hz, 1H), 6.91 (s, 1H), 2.93 (s, 2H), 2.09 (s, 3H), 1.38 (s, 6H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 147.6, 142.4, 140.2, 139.7, 135.9, 135.3, 132.2, 130.6, 130.4, 129.7, 128.4, 128.1, 126.3, 126.2, 126.0, 119.2, 111.5, 50.9, 39.1, 28.4, 20.4. HRMS (APCI): m/z [M+H]\(^{+}\) calcd for C\(_{24}\)H\(_{24}\)N: 326.1903; found: 326.1907.

(4-{Sec-butyl}-2,5-dimethylbenzyl)trimethylsilane (11): Prepared, following the general procedure A from (4-bromo-2,5-dimethylphenyl)triethylgermane, (trimethylsilyl)methylzinc chloride and sec-butylzinc chloride. The title product was obtained as an 88:12 mixture of sec-Bu and n-Bu (branched and linear) isomers after purification by column chromatography (pentane) as a colorless oil (29.2 mg, 0.12 mmol, 59%). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 6.89 (s, 1H), 6.72 (s, 1H), 2.79 (h, \(J = 7.0\) Hz, 1H), 2.24 (s, 3H), 2.19 (s, 3H), 2.02 (s, 2H), 1.63 – 1.52 (m, 2H), 1.18 (d, \(J = 6.9\) Hz, 3H), 0.86 (t, \(J = 7.4\) Hz, 3H), 0.01 (s, 9H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 141.5, 135.6, 132.5, 132.1, 130.6, 127.1, 35.9, 30.9, 23.1, 21.3, 20.2, 19.2, 12.5, -1.2. Note: signals from minor linear product isomer could not be assigned. HRMS (APCI): m/z [M+H]\(^{+}\) calcd for C\(_{16}\)H\(_{29}\)Si: 249.2033; found: 249.2027.

4’-Chloro-N-(2-methoxy-5-methylphenyl)-[1,1’-biphenyl]-3-amine (12): Prepared, following the general procedure A from (3-bromophenyl)triethylgermane, 4-chlorophenylzinc chloride and 2-methoxy-5-methylaniline. The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) as a yellow liquid (57.4 mg, 0.177 mmol, 89%). R\(_f\) = 0.35 (hexane/EtOAc 10:1). \(^1\)H NMR (600 MHz, CDCl\(_3\)):...
δ 7.52 (dd, J = 8.4, 1.5 Hz, 2H), 7.41 (dd, J = 8.4, 1.5 Hz, 2H), 7.36 (ddd, J = 7.9, 7.9, 1.4 Hz, 2H), 7.32 (dd, J = 1.9, 1.9 Hz, 1H), 7.18 (m, 2H), 7.13 (m, 1H), 6.82 (dd, J = 8.1, 1.4 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 5.83 (brs, 1H), 3.88 (s, 3H), 2.29 (s, 3H). \(^{13}C\) NMR (151 MHz, CDCl\(_3\)): δ 146.6, 143.5, 141.3, 139.8, 133.5, 132.4, 130.4, 129.9, 129.0, 128.5, 120.8, 119.9, 117.6, 117.2, 116.2, 110.8, 55.9, 21.2. HRMS (ESI): m/z [M+H]\(^+\) calcd for C\(_{20}\)H\(_{19}\)NO\(_3\)Cl: 324.1150; found: 324.1152.

\(N\)-(3-benzyl-5-(trimethylsilyl)phenyl)-3-chloro-4-methoxyaniline (13): Prepared, following the general procedure A from (3-bromo-5-(triethylgermyl)phenyl)trimethylsilane, benzylzinc chloride and 3-chloro-4-methoxyaniline. The title product was obtained after purification by column chromatography (hexane/EtOAc 8:1) as a light orange liquid (65.3 mg, 0.165 mmol, 81%). \(R_f\) = 0.34 (hexane/EtOAc 8:1). \(^1H\) NMR (600 MHz, CDCl\(_3\)): δ 7.31 (ddd, J = 7.6, 7.6, 1.4 Hz, 2H), 7.22 (m, 3H), 7.13 (d, J = 2.7 Hz, 1H), 6.97 (d, J = 15.8 Hz, 2H), 6.93 (dd, J = 8.7, 2.7 Hz, 1H), 6.85 (d, J = 8.8 Hz, 1H), 6.78 (s, 1H), 5.66 (brs, 1H), 3.95 (s, 2H), 3.88 (s, 3H), 0.26 (m, 9H). \(^{13}C\) NMR (151 MHz, CDCl\(_3\)): δ 150.2, 143.2, 142.1, 141.8, 141.1, 137.1, 129.0, 128.6, 126.5, 126.2, 123.1, 121.4, 119.7, 118.5, 118.0, 113.3, 56.7, 42.1, -1.0. HRMS (ESI): m/z [M+Na]\(^+\) calcd for C\(_{23}\)H\(_{26}\)ON\(_3\)ClNaSi: 418.1364; found: 418.1360.

3-Cyclohexyl-N-(4-methoxyphenyl)-N-methylaniline (14): Prepared, following the general procedure A from (3-bromophenyl)triethylgermane, cyclohexylzinc chloride and 4-methoxy-N-methylaniline. The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) as a light orange liquid (47.4 mg, 0.160 mmol, 80%). \(R_f\) = 0.44 (hexane/EtOAc 10:1). \(^1H\) NMR (600 MHz, CDCl\(_3\)): δ 7.15 (dd, J = 8.1, 8.1 Hz, 1H), 7.10 (m, 2H), 6.91 (m, 2H), 6.70 (m, 1H), 6.66 (m, 1H), 3.83 (s, 3H), 3.28 (s, 3H), 2.42 (td, J = 9.8, 8.3, 3.3 Hz, 1H), 1.85 (m, 4H), 1.74 (m, 1H), 1.39 (m, 4H), 1.26 (m, 1H). \(^{13}C\) NMR (151 MHz, CDCl\(_3\)): δ 156.1, 149.7, 149.1, 142.5, 128.9, 125.8, 125.5, 117.4, 115.1, 114.8, 114.8, 114.0, 55.6, 45.0, 40.7, 34.6, 27.1, 26.3. HRMS (ESI): m/z [M+H]\(^+\) calcd for C\(_{20}\)H\(_{19}\)ON\(_3\): 296.2009; found: 296.2008.

4-(2'-Methyl-[1,1'-biphenyl]-4-yl)morpholine (15): Prepared, following the general procedure A from (4-bromophenyl)triethylgermane, 2-methylphenylzinc chloride and morpholine. The title product was obtained after purification by column chromatography (hexane/EtOAc 8:1) as a light yellow liquid (40.0 mg, 0.158 mmol, 79%). \(R_f\) = 0.22 (hexane/EtOAc 8:1). \(^1H\) NMR (600 MHz, CDCl\(_3\)): δ 7.27 (m, 3H), 7.24 (m, 3H), 6.99 (m, 2H), 3.91 (m, 4H), 3.24 (t, J = 4.3 Hz, 4H), 2.31 (s, 3H). \(^{13}C\) NMR (151 MHz, CDCl\(_3\)): δ 141.7, 135.6, 130.4, 130.2, 130.0 (br), 127.0, 125.9, 115.3 (br), 67.0, 49.4, 20.7. HRMS (ESI): m/z [M+H]\(^+\) calcd for C\(_{17}\)H\(_{20}\)ON: 254.1539; found: 254.1537.
**N-(4-chlorophenyl)-4′-fluoro-[1,1′-biphenyl]-4-amine (16):**
Prepared, following the general procedure A from (4-bromophenyl)triethylgermane, 4-fluorophenylzinc chloride and 4-chloroaniline. The title product was obtained after purification by column chromatography (hexane/EtOAc 8:1) as a red solid (38.4 mg, 0.129 mmol, 64%). \( R_f = 0.30 \) (hexane/EtOAc 8:1). **M.p.:** 113–115 °C. **\(^1\)H NMR** (600 MHz, CDCl\(_3\)): \( \delta \) 7.51 (ddd, \( J = 8.3, 5.2, 2.5 \) Hz, 2H), 7.48 – 7.45 (m, 2H), 7.26 – 7.23 (m, 2H), 7.14 – 7.08 (m, 4H), 7.04 (d, \( J = 8.7 \) Hz, 2H), 5.96 (br s, 1H). **\(^{13}\)C NMR** (151 MHz, CDCl\(_3\)): \( \delta \) 162.3 (d, \( J = 245.9 \) Hz), 142.1, 141.5, 136.9, 133.6, 129.5, 128.2 (d, \( J = 7.9 \) Hz), 128.1, 126.1, 119.4, 118.3, 115.7 (d, \( J = 21.4 \) Hz). **\(^{19}\)F NMR** (564 MHz, CDCl\(_3\)): \( \delta \) -116.43 – -116.58 (m, 1F). **HRMS** (ESI): \( m/z \) [M+H\(^+\)] calcd for C\(_{18}\)H\(_{14}\)ON\(_3\)ClF: 298.0793; found: 298.0794.

**N-(3,5-bis(trifluoromethyl)phenyl)-3-buty-5-chloroaniline (17):**
Prepared, following the general procedure A from (3-bromo-5-chlorophenyl)triethylgermane, \( n \)-butylzinc chloride and 3,5-bis(trifluoromethyl)aniline, but using HFIP instead of MeCN for the bromination. The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) as a yellow liquid (35.4 mg, 0.089 mmol, 44%). \( R_f = 0.40 \) (hexane/EtOAc 10:1). **\(^1\)H NMR** (600 MHz, CDCl\(_3\)): \( \delta \) 7.38 (s, 2H), 7.36 (s, 1H), 6.91 (ddd, \( J = 5.5, 1.8 \) Hz, 2H), 6.84 (dd, \( J = 1.6 \) Hz, 1H), 5.95 (brs, 1H), 2.57 (t, \( J = 7.7 \) Hz, 2H), 1.59 (m, 2H), 1.36 (dq, \( J = 14.7, 7.3 \) Hz, 2H), 0.93 (t, \( J = 7.4 \) Hz, 3H). **\(^{13}\)C NMR** (151 MHz, CDCl\(_3\)): \( \delta \) 146.5, 144.7, 141.7, 135.2, 133.0 (q, \( J = 32.2 \) Hz), 123.9, 123.4 (q, \( J = 272.6 \) Hz), 118.2, 117.4, 116.1 (m), 113.8 (m), 35.5, 33.3, 22.3, 14.0. **\(^{19}\)F NMR** (564 MHz, CDCl\(_3\)): \( \delta \) -63.27 (s, 6F). **HRMS** (APCI): \( m/z \) [M+H\(^+\)] calcd for C\(_{18}\)H\(_{17}\)N\(_3\)ClF\(_6\): 396.0948; found: 396.0956.

**Methyl 6-buty-3′-(triethylgerm)-1,1′-biphenyl-3-carboxylate (19):**[10] Under argon, to a solution of methyl 3-bromo-4-(((trifluoromethyl)sulfonyl)oxy)benzoate 18\(^{[1]}\) (72.6 mg, 0.2 mmol, 1.0 equiv.) and [Pd(\( \mu\)-I)(P\(_{Bu}\))\(_2\)]\(_2\) (4.4 mg, 0.005 mmol, 2.5 mol%) in dry THF (2.0 mL) was added (3-(triethylgermyl)phenyl)zinc chloride (0.25 M in THF, 1.2 mL, 0.3 mmol, 1.5 equiv.; prepared from (3-bromophenyl)triethylgermane according to general procedure G). The reaction was stirred for further 5 minutes at room temperature. Dry NMP (2.5 mL) was added, followed by the addition of \( n\)-
butylzinc chloride (0.67 M in THF, 0.45 mL, 0.3 mmol, 1.5 equiv.; prepared according to procedure C from n-butylmagnesium chloride). The reaction was stirred for 10 min at room temperature. The reaction mixture was then quenched by the addition of hexane (0.5 mL) and filtered through a pad of silica gel. Solvents were removed under reduced pressure. The title product was obtained after purification by column chromatography (hexane/EtOAc 100:1) as a colorless oil (77.9 mg, 0.18 mmol, 91%). 

1H NMR (600 MHz, CDCl₃): δ 7.95 (d, J = 8.0 Hz, 1H), 7.90 (s, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.40 – 7.38 (m, 1H), 7.37 – 7.33 (m, 2H), 7.24 (d, J = 7.4 Hz, 1H), 3.90 (s, 3H), 2.63 – 2.58 (m, 2H), 1.45 (p, J = 7.8 Hz, 2H), 1.23 – 1.17 (m, 2H), 1.08 – 1.05 (m, 9H), 0.77 (t, J = 7.4 Hz, 3H).

13C NMR (151 MHz, CDCl₃): δ 167.3, 146.2, 142.5, 140.4, 139.7, 134.7, 132.9, 131.3, 129.5, 129.1, 128.5, 127.7, 127.6, 52.1, 33.5, 33.2, 22.7, 13.9, 9.1, 4.3. HRMS (APCI): m/z [M+H]+ calcd for C₂₄H₃₅O₂⁺Ge: 429.1843; found: 429.1844.

Methyl 6-butyl-3'-iodo-[1,1'-biphenyl]-3-carboxylate (20): Prepared, following the general procedure C from methyl 6-butyl-3'-triethylgermyl-[1,1'-biphenyl]-3-carboxylate 17 (77.9 mg, 0.18 mmol, 1.0 equiv.). The title product was obtained after purification by column chromatography (hexane/EtOAc 100:1) as a colorless oil (56.2 mg, 0.14 mmol, 79%).

1H NMR (600 MHz, CDCl₃): δ 7.96 (dd, J = 8.0, 1.8 Hz, 1H), 7.84 (d, J = 1.8 Hz, 1H), 7.71 – 7.70 (m, 1H), 7.67 (m, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.16 – 7.14 (m, 1H), 3.90 (s, 3H), 2.61 – 2.55 (m, 2H), 1.46 (p, J = 7.6 Hz, 2H), 1.26 – 1.20 (m, 2H), 0.81 (t, J = 7.4 Hz, 3H).

13C NMR (151 MHz, CDCl₃): δ 167.0, 145.9, 143.2, 140.4, 138.1, 136.3, 131.1, 129.9, 129.6, 129.0, 128.6, 127.8, 94.2, 52.2, 33.3, 32.9, 22.5, 13.9. HRMS (APCI): m/z [M+H]+ calcd for C₁₈H₂₀O₂⁺: 395.0503; found: 395.0518.
3.2. Products of sequential coupling

\(\text{3-(5-(3',5'-dichloro-[1,1'-biphenyl]-4-yl)thiophen-2-yl)-5-iodophenyl} trimethylsilane (21):\) Prepared, following the general procedure B. The title product was obtained after purification by column chromatography (pentane/DCM 20:1) as a white solid (244 mg, 0.421 mmol, 42\%). \(R_f = 0.2\) (pentane/DCM 20:1). \(\text{M.p.: 55–64 °C.} \)\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.96 (dd, \(J = 1.7\) Hz, 1H), 7.74 – 7.70 (m, 3H), 7.68 (dd, \(J = 1.7, 0.9\) Hz, 1H), 7.57 (d, \(J = 8.4\) Hz, 2H), 7.49 (d, \(J = 1.8\) Hz, 2H), 7.37 – 7.34 (m, 2H), 7.30 (d, \(J = 3.8\) Hz, 1H), 0.32 (s, 9H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 144.8, 143.5, 142.6, 96.0, 141.5, 138.5, 136.4, 136.4, 135.5, 134.8, 129.6, 127.7, 127.4, 126.3, 125.5, 125.0, 124.6, 96.0, -1.1. \(^{19}\)F NMR \((600\) MHz, CDCl\(_3\)): \(\delta\) 40.64 (s, 3F). \(^{19}\)F NMR (156 MHz, CDCl\(_3\)): \(\delta\) 40.64 (s, 3F). HRMS (APCI): \(m/z [M+H]^+\) calculated for \(C_{25}H_{22}^{35}Cl_{2}SSi\): 578.9628, found 578.9629.

\(\text{3''',5-dichloro-5'''-iodo-3'''-methyl-[1,1':4',1''':4'',1'''''-quaterphenyl]-2-yl} \)fluorosulfate (22): Prepared, following the general procedure B. The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) and precipitation as a white solid (324 mg, 0.501 mmol, 50\%). \(R_f = 0.5\) (hexane/EtOAc 10:1). \(\text{M.p.: 55–59 °C.} \)\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.75 – 7.72 (m, 3H), 7.62 (d, \(J = 1.6\) Hz, 1H), 7.57 – 7.54 (m, 4H), 7.52 (dd, \(J = 7.7, 1.8\) Hz, 1H), 7.44 (d, \(J = 2.4\) Hz, 2H), 7.34 (dd, \(J = 1.7\) Hz, 1H), 7.28 (d, \(J = 7.8\) Hz, 1H), 2.36 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 145.5, 144.8, 141.0, 140.0, 138.5, 136.4, 136.4, 135.8, 135.5, 134.7, 134.6, 133.4, 131.8, 130.1, 129.4, 129.3, 129.1, 128.8, 127.5, 124.7, 123.0, 93.8, 20.5. \(^{19}\)F NMR (564 MHz, CDCl\(_3\)): \(\delta\) 40.64 (s, 3F). \(^{19}\)F NMR (564 MHz, CDCl\(_3\)): \(\delta\) 40.64 (s, 3F). HRMS (APCI): \(m/z [M+H]^+\) calculated for \(C_{25}H_{18}O_{3}^{35}Cl_{2}S\): 612.92987, found 612.93013.

\(\text{1-(5'-chloro-3-iodo-2''-methyl-[1,1':3',1''':4'',1'''''-quaterphenyl]-4'''-yl)-2,2,2-trifluoroethane-1-one (23):}\) Prepared, following the general procedure B. The title product was obtained after purification by column chromatography (pentane/DCM 4:1) and precipitation (dropwise addition of MeOH to a DCM solution of the product) as a white solid (277 mg, 0.480 mmol, 48\%). \(R_f = 0.6\) (pentane/DCM 4:1). \(\text{M.p.: 92–96 °C.} \)\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.18 (d, \(J = 8.0\) Hz, 2H), 7.95 (s, 1H), 7.82 (d, \(J = 8.4\) Hz, 2H), 7.73 (d, \(J = 7.8\) Hz, 1H), 7.59 – 7.55 (m, 4H), 7.41 (d, \(J = 1.7\) Hz, 1H), 7.38 (d, \(J = 7.9\) Hz, 1H), 7.36 (d, \(J = 1.8\) Hz, 1H), 7.20 (dd, \(J = 7.8\) Hz, 1H), 2.40 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 180.22 (q, \(J = 35.0\) Hz), 147.8, 143.6, 141.9, 141.5,
141.1, 138.9, 137.1, 136.4, 136.3, 134.8, 130.9 (d, J = 1.9 Hz), 130.7, 130.6, 129.6, 128.8, 128.5, 127.7, 126.6, 126.3, 126.1, 125.1, 116.9 (q, J = 291.8, 291.4 Hz), 95.0, 20.8. $^{19}$F NMR (565 MHz, CDCl$_3$): δ -71.30 (s, 3F). HRMS (APCI): m/z [M+H]$^+$ calculated for C$_{27}$H$_{18}$O$_3$ClF$_3$I: 577.00375, found 577.00411.

2-chloro-6-(5-chloro-3'-iodo-[1,1'-biphenyl]-3-yl)quinoline (24): Prepared, following the general procedure B. The title product was obtained after purification by column chromatography (pentane/DCM 1:2) as a white solid (178 mg, 0.374 mmol, 75%). R$_f$ = 0.3 (pentane/DCM 1:2). M.p.: 155–160 °C. $^1$H NMR (600 MHz, CDCl$_3$): δ 8.13 (d, J = 8.5 Hz, 1H), 8.09 (d, J = 8.7 Hz, 1H), 7.95 (m, 3H), 7.72 (ddd, J = 7.9, 1.7, 1.0 Hz, 1H), 7.65 (dd, J = 1.6, 1.6 Hz, 1H), 7.62 (dd, J = 1.8, 1.8 Hz, 1H), 7.55 (ddd, J = 7.8, 1.8, 1.0 Hz, 1H), 7.51 (dd, J = 1.8, 1.8 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.19 (dd, J = 7.8, 7.8 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$): 151.1, 147.5, 142.2, 142.1, 141.7, 139.1, 138.1, 137.1, 136.1, 135.5, 130.7, 129.9, 129.4, 127.0, 126.8, 126.6, 126.5, 125.7, 124.5, 123.1, 95.0. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{21}$H$_{13}$N$_3$Cl$_2$I: 475.9464; found: 475.9458.

3,5'-dichloro-3''-iodo-[1,1':3',1''-terphenyl]-4-yl trifluoromethanesulfonate (25): Prepared, following the general procedure B. The title product was obtained after purification by column chromatography (hexane/EtOAc 50:1) as a colorless oil (185 mg, 0.323 mmol, 65%). R$_f$ = 0.52 (hexane/EtOAc 50:1). $^1$H NMR (600 MHz, CDCl$_3$): δ 7.93 (dd, J = 1.6, 1.6 Hz, 1H), 7.74 (m, 2H), 7.55 (m, 2H), 7.54 (m, 2H), 7.51 (dd, J = 1.7, 1.7 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.21 (dd, J = 7.8 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$): δ 145.5, 142.4, 141.5, 141.2, 140.6, 137.4, 136.2, 135.7, 130.8, 130.0, 128.0, 127.3, 127.1, 126.6, 126.6, 124.3, 123.6, 118.8 (q, J = 320.7 Hz), 95.1. $^{19}$F NMR (564 MHz, CDCl$_3$) δ -73.26 (s, 3F). HRMS (APCI): m/z [M]$^+$ calculated for C$_{19}$H$_{10}$O$_3$Cl$_2$F$_3$S$I$: 571.87190, found 571.87226.
3.3. Derivatizations of aryl germanes

4-(Triethylgermyl)benzaldehyde (29)[11] Under argon, n-BuLi (2.5 M in hexane, 2.1 mL, 5.25 mmol, 1.05 equiv.) was added dropwise to a solution of (4-bromophenyl)triethylgermane (1.58 g, 5.00 mmol, 1.0 equiv.) in dry THF (30 mL) at -78 °C. After stirring for 15 min at -78 °C dry DMF (1.0 mL, 12.5 mmol, 2.5 equiv.) was added. The reaction was stirred overnight, while slowly allowing to warm up to ambient temperature. Saturated aq. NH₄Cl (50 mL) was added and the aqueous layer was extracted with Et₂O (3 x 50 mL). The combined organic layers were washed with brine (25 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The title product was obtained after purification by column chromatography (hexane/EtOAc 25:1→10:1) as a colorless oil (1.07 g, 4.03 mmol, 81%).

**1H NMR** (600 MHz, CDCl₃): δ 10.01 (s, 1H), 7.82 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H), 1.10 – 1.00 (m, 15H).

**13C NMR** (151 MHz, CDCl₃): δ 192.8, 149.7, 136.3, 134.7, 128.8, 9.0, 4.3.

**HRMS (EI):** m/z [M]+ calcd for C₁₃H₂₀O₇Ge: 266.0721; found: 266.0721.

4-(Triethylgermyl)benzoic acid (30)[12] To a solution of 4-(triethylgermyl)benzaldehyde 29 (79.5 mg, 0.3 mmol, 1.0 equiv.) in tBuOH (1.8 mL) was added 5% w/w aq. NaH₂PO₄ (1.2 mL). Then, an aqueous solution of KMnO₄ (1.0 M, 1.8 mL) was added dropwise under stirring and the reaction mixture was stirred for 20 min at room temperature. Saturated aq. Na₂SO₃ (5 mL) was added followed by 10% aq. HCl, until all solids had dissolved. The aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1→0:1) as a colorless oil (77.9 mg, 0.28 mmol, 92%).

**1H NMR** (600 MHz, CDCl₃): δ 8.07 (d, J = 7.7 Hz, 2H), 7.59 – 7.54 (m, 2H), 1.10 – 1.00 (m, 15H). **Note:** The proton of the carboxylic acid was not observed.

**13C NMR** (151 MHz, CDCl₃): δ 172.8, 148.4, 134.2, 129.2, 9.0, 4.3. **HRMS (EI):** m/z [M]+ calcd for C₁₃H₂₀O₂₇Ge: 282.0675; found: 282.0685.
**1-(4-(Triethylgermyl)phenyl)pentan-1-ol (31):**[13] Under argon, to a solution of 4-(triethylgermyl)benzaldehyde 29 (79.5 mg, 0.3 mmol, 1.0 equiv.) in dry THF (3.0 mL) was added LaCl₃•2LiCl (0.6 M in THF, 0.15 mL, 0.09 mmol, 30 mol%) and the reaction was stirred for 1 hour at room temperature. n-Butylmagnesium chloride (2.0 M in THF, 0.25 mL, 0.45 mmol, 1.5 equiv.) was added dropwise at 0 °C and the reaction was stirred for 2 hours at room temperature. The reaction was quenched with saturated aq. NH₄Cl (5 mL) and the aqueous layer was extracted with EtOAc (3x 10 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) as a colorless oil (81.4 mg, 0.25 mmol, 84%).

**1H NMR** (600 MHz, CDCl₃): δ 7.43 (d, J = 7.7 Hz, 2H), 7.32 (d, J = 7.7 Hz, 2H), 4.65 – 4.61 (m, 1H), 1.94 (s, 1H), 1.85 – 1.77 (m, 1H), 1.76 – 1.69 (m, 1H), 1.47 – 1.39 (m, 1H), 1.39 – 1.32 (m, 2H), 1.32 – 1.26 (m, 1H), 1.10 – 1.05 (m, 9H), 1.00 (q, J = 7.5 Hz, 6H), 0.91 (t, J = 7.2 Hz, 3H).

**13C NMR** (151 MHz, CDCl₃): δ 144.9, 139.1, 134.2, 125.5, 74.8, 38.9, 28.2, 22.8, 14.1, 9.1, 4.3.

**HRMS (EI):** m/z [M-H]⁺ calcd for C₁₇H₂₉O⁻Ge: 323.1436; found: 323.1428.

**1-(4-Iodophenyl)pentan-1-ol (32):**[14] Under argon, to a mixture of the alcohol 31 (41.1 mg, 0.127 mmol, 1.0 equiv.) and imidazole (26.6 mg, 0.39 mmol, 3.0 equiv.) in dry DMF (0.4 mL) was added TBDPSCI (0.04 mL, 0.14 mmol, 1.1 equiv.) dropwise and the reaction was heated at 70 °C for 3.5 hours. After cooling to room temperature, H₂O (10 mL) was added and the aqueous layer extracted with EtOAc (3x 10 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc 20:1→10:1) and directly used without further characterization. To the protected germane in HFIP (3.0 mL) was added NIS (135.0 mg, 0.6 mmol, 2.0 equiv.) and the reaction mixture was stirred at 60 °C for 16 hours. After cooling to room temperature, the mixture was diluted with DCM (20 mL). The organic layer was washed with saturated aq. Na₂S₂O₃ (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The flask containing the crude product was evacuated and backfilled with argon three times. Then dry THF (1.0 mL) and TBAF (1.0 M in THF, 0.25 mmol, 0.25 mL) were added consecutively. After stirring for 4 hours at room temperature, H₂O (10 mL) was added and the aqueous layer was extracted with DCM (3x 10 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The title product was obtained after
purification by column chromatography (hexane/EtOAc 10:1) as a colorless oil (24.3 mg, 0.084 mmol, 66%). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 7.67\) (d, \(J = 8.0\) Hz, 2H), \(7.09\) (d, \(J = 8.0\) Hz, 2H), \(4.62\) (t, \(J = 8.0\) Hz, 1H), \(1.82\) (d, \(J = 3.3\) Hz, 1H), \(1.80 - 1.72\) (m, 1H), \(1.71 - 1.63\) (m, 1H), \(1.40 - 1.25\) (m, 4H), \(0.88\) (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta 144.7, 137.6, 128.1, 92.9, 74.2, 39.0, 28.0, 22.7, 14.1\).

HRMS (ESI): \(m/z\) [M+Na]\(^+\) calc for C\(_{11}\)H\(_{15}\)OINa: 313.0060; found: 313.0058. The data are in agreement with those previously reported.\(^{[15]}\)

Methyl \((E)-3-\)\((4-\)\((\text{triethylgermyl})\)\)phenyl)acrylate \((33)\): Under argon, \(4-\)\((\text{triethylgermyl})\) benzaldehyde \(29\) (79.5 mg, 0.3 mmol, 1.0 equiv.) and methyl \((\text{triphenylphosphoranylidene})\)acetate (150.5 mg, 0.45 mmol, 1.5 equiv.) in dry THF (1.5 mL) were refluxed for 3 hours. After cooling to ambient temperature, H\(_2\)O (5 mL) was added and the aqueous layer extracted with DCM (3x 10 mL). The combined organic layers were dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) as a colorless oil (59.2 mg, 0.18 mmol, 61%). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 7.69\) (d, \(J = 16.0\) Hz, 1H), \(7.51 - 7.45\) (m, 4H), \(6.45\) (d, \(J = 15.9\) Hz, 1H), \(3.81\) (s, 3H), \(1.10 - 1.03\) (m, 9H), \(1.02 - 0.97\) (m, 6H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta 167.7, 145.3, 143.8, 134.7, 134.2, 127.4, 117.7, 51.8, 9.0, 4.3\).

HRMS (APCI): \(m/z\) [M+H]\(^+\) calc for C\(_{16}\)H\(_{25}\)O\(_2\)Ge: 323.1066; found: 323.1066.

Methyl \((E)-3-\)\((4-\)\((\text{iodophenyl})\)\)acrylate \((34)\): Prepared, following the general procedure D from methyl \((E)-3-\)\((4-\)\((\text{triethylgermyl})\)\)phenyl)acrylate \(35\). The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) as a white solid (38.6 mg, 0.13 mmol, 73%). M.p.: 127 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 7.72\) (d, \(J = 8.4\) Hz, 2H), \(7.60\) (d, \(J = 16.0\) Hz, 1H), \(7.24\) (d, \(J = 8.4\) Hz, 2H), \(6.43\) (d, \(J = 16.0\) Hz, 1H), \(3.80\) (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta 167.3, 143.8, 138.3, 134.0, 129.6, 118.7, 96.6, 51.9\).

HRMS (APCI): \(m/z\) [M+H]\(^+\) calc for C\(_{10}\)H\(_{10}\)O\(_2\)I: 288.9720; found: 288.9727. The data are in agreement with those previously reported.\(^{[17]}\)

2-\((4-\)\((\text{triethylgermyl})\)\)phenylbenzo[d]thiazole \((35)\): A mixture of \(4-\)\((\text{triethylgermyl})\) benzaldehyde \(29\) (103.3 mg, 0.39 mmol, 1.3 equiv.), 2-iodoaniline (65.7 mg, 0.3 mmol, 1.0 equiv.),
K₂CO₃ (82.9 mg, 0.6 mmol, 2.0 equiv.), sulfur (28.9 mg, 0.9 mmol, 3.0 equiv.), CuCl₂ (4.0 mg, 0.03 mmol, 10 mol%) and 1,10-phenanthroline (5.4 mg, 0.03 mmol, 10 mol%) in H₂O (3.0 mL) was heated at 100 °C for 48 hours. After cooling to room temperature, H₂O (5 mL) was added and the aqueous layer extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The title product was obtained after purification by column chromatography (hexane/EtOAc 25:1) as a yellow oil (74.1 mg, 0.20 mmol, 67%). ¹H NMR (600 MHz, CDCl₃): δ 8.08 (d, J = 8.1 Hz, 1H), 8.05 (d, J = 8.1 Hz, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.51 – 7.48 (m, 1H), 7.41 – 7.37 (m, 1H), 1.10 – 1.01 (m, 15H).

¹³C NMR (151 MHz, CDCl₃): δ 168.6, 154.3, 144.6, 135.1, 134.8, 133.4, 126.8, 126.4, 125.3, 123.3, 121.8, 9.1, 4.4.

HRMS (APCI): m/z [M+H]+ calcd for C₁₉H₂₄S₇GeN: 372.0836; found: 372.0840.

2-(4-Iodophenyl)benzo[d]thiazole (36): Prepared, following the general procedure D from 2-(4-((triethylgermyl)phenyl)benzo[d]thiazole 35. The title product was obtained after purification by column chromatography (hexane/EtOAc 20:1) as a white solid (51.1 mg, 0.15 mmol, 76%). M.p.: 154 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.07 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.86 – 7.77 (m, 4H), 7.52 – 7.49 (m, 1H), 7.41 – 7.39 (m, 1H).

¹³C NMR (151 MHz, CDCl₃): δ 167.0, 154.2, 138.3, 135.2, 133.3, 129.1, 126.6, 125.6, 123.5, 121.8, 97.6. HRMS (ESI): m/z [M+H]+ calcd for C₁₃H₉INS: 337.9495; found: 337.9494. The data are in agreement with those previously reported.[19]

3,4-Dipropyl-6-(triethylgermyl)-1H-isochromen-1-one (37): In an argon-filled glovebox, a pressure tube was charged with [RuCl₂(p-cumene)]₂ (2.5 mol%), KPF₆ (20 mol%), Cu(OAc)₂•H₂O (2.5 mol%), tAmOH (0.5 mL). The reaction was heated at 120 °C for 19 hours. After cooling to room temperature, saturated aq. NH₄Cl/25% aq. NH₃ (1:1, 20 mL) was added and the aqueous layer was extracted with EtOAc (3x 20 mL). The combined organic layers were washed with saturated aq. NH₄Cl/25% aq. NH₃ (1:1, 10 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The title product was obtained after purification by column chromatography (hexane/EtOAc 20:1) as a colorless oil (56.4 g, 0.15 mmol, 85%). ¹H NMR (600 MHz, CDCl₃): δ 8.24 (d, J = 7.7 Hz, 1H), 7.59 (s, 1H), 7.53 (dd, J = 7.7, 0.8 Hz, 1H), 2.64 – 2.59 (m, 2H), 2.59 – 2.55 (m, 2H), 1.74 (h, J = 7.4 Hz, 2H), 1.60 (h, J = 7.4 Hz, 2H), 1.09 – 1.03 (m, 18H), 0.99 (t, J = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃): δ 163.3, 154.1, 149.3,
3,4-Dipropyl-6-iodo-1H-isochromen-1-one (38): Prepared, following the general procedure D from 3,4-dipropyl-6-(triethylgermyl)-1H-isochromen-1-one 37. The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) as a yellow solid (49.3 mg, 0.14 mmol, 97%). M.p.: 137 °C. 1H NMR (600 MHz, CDCl3): δ 7.98 (d, J = 8.3 Hz, 1H), 7.87 (s, 1H), 7.79 (d, J = 8.2 Hz, 1H), 2.55 (q, J = 10.0, 9.2 Hz, 4H), 1.74 (m, 2H), 1.59 (m, 2H), 1.04 (t, J = 7.3 Hz, 3H), 0.99 (t, J = 7.3 Hz, 3H). 13C NMR (151 MHz, CDCl3): δ 162.6, 155.6, 139.5, 136.4, 132.1, 131.3, 120.2, 111.3, 103.5, 33.0, 28.2, 22.9, 21.3, 14.3, 14.0. HRMS (ESI): m/z [M+Na]+ calcd for C21H32O2GeNa: 413.1506; found: 413.1503.

N-Ethyl-4-(triethylgermyl)benzamide (39):[22] Under argon, 4-(triethylgermyl)benzoic acid 30 (84.3 mg, 0.30 mmol, 1.0 equiv.) in SOCl2 (1.0 mL) was refluxed for 3 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The flask containing the crude acid chloride was evacuated and backfilled with argon three times. Under argon, the acid chloride was dissolved in Et2O (0.6 mL), then NEt3 (0.08 mL, 0.6 mmol, 2.0 equiv.) and ethylamine (0.03 mL, 0.45 mmol, 1.5 equiv.) were added under stirring. The reaction mixture was stirred for 3 hours at room temperature. H2O was added (5 mL) and the aqueous layer was extracted with Et2O (3x 10 mL). The combined organic layers were dried over Na2SO4 and concentrated under reduced pressure. The title product was obtained after purification by column chromatography (hexane/EtOAc 3:1) as a colorless oil (87.2 mg, 0.28 mmol, 94%). 1H NMR (600 MHz, CDCl3): δ 7.70 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 6.08 (s, 1H), 3.50 (p, J = 7.2 Hz, 2H), 1.25 (t, J = 7.3 Hz, 3H), 1.07 – 0.97 (m, 15H). 13C NMR (151 MHz, CDCl3): δ 167.8, 144.7, 134.6, 134.3, 126.0, 35.0, 15.1, 9.0, 4.3. HRMS (ESI): m/z [M+H]+ calcd for C15H26O74GeN: 310.1221; found: 310.1217.

N-Ethyl-5-(triethylgermyl)-[1,1'-biphenyl]-2-carboxamide (40):[23] In an argon-filled glovebox, a pressure tube was charged with [RuCl2(p-cumene)]2 (4.9 mg, 0.008 mmol, 3 mol%), AgSbF6 (10.9 mg, 0.03 mmol, 1.5 mol%) and Ag2O (0.5 mg, 0.003 mmol, 0.02 mol%). 1H NMR (600 MHz, CDCl3): δ 7.66 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 6.06 (s, 1H), 3.70 (p, J = 7.2 Hz, 2H), 1.25 (t, J = 7.3 Hz, 3H), 1.07 – 0.97 (m, 15H). 13C NMR (151 MHz, CDCl3): δ 167.0, 144.7, 134.6, 134.3, 126.0, 35.0, 15.1, 9.0, 4.3. HRMS (ESI): m/z [M+H]+ calcd for C15H26O74GeN: 310.1221; found: 310.1217.
0.03 mmol, 12 mol%), Ag₂O (62.6 mg, 0.27 mmol, 1.0 equiv.), phenylboronic acid (48.4 mg, 0.4 mmol, 1.5 equiv.), N-ethyl-4-(triethylgermyl)benzamide 39 (81.6 mg, 0.27 mmol, 1.0 equiv.) and dry THF (0.8 mL). The reaction was heated at 110 °C for 20 hours. After cooling to room temperature, the reaction mixture was diluted with DCM and filtered through a pad of Celite and silica gel. Volatiles were removed under reduced pressure. The title product was obtained after purification by column chromatography (hexane/EtOAc 3:1) as a colorless oil (37.4 mg, 0.097 mmol, 37%). \( ^1\)H NMR (600 MHz, CDCl₃): \( \delta \) 7.67 (d, \( J = 7.5 \) Hz, 1H), 7.48 (d, \( J = 7.5 \) Hz, 1H), 7.42 (d, \( J = 4.3 \) Hz, 4H), 7.40 – 7.36 (m, 2H), 5.09 (s, 1H), 3.17 (p, \( J = 6.8 \) Hz, 2H), 1.08 – 1.00 (m, 15H), 0.79 (t, \( J = 7.3 \) Hz, 3H). \( ^{13}\)C NMR (151 MHz, CDCl₃): \( \delta \) 169.6, 143.1, 140.8, 138.6, 135.7, 135.6, 133.4, 129.0, 128.7, 128.0, 127.8, 34.7, 14.2, 9.1, 4.3. HRMS (ESI): \( m/z \) [M+H]+ calcd for C_{21}H_{30}O_{74}GeN: 386.1534; found: 386.1534.

**N-Ethyl-5-iodo-[1,1’-biphenyl]-2-carboxamide (41):** Prepared, following the general procedure D from N-ethyl-5-(triethylgermyl)-[1,1’-biphenyl]-2-carboxamide 40. The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) as a white solid (28.8 mg, 0.082 mmol, 84%). M.p.: 112 °C. \( ^1\)H NMR (600 MHz, CDCl₃): \( \delta \) 7.76 – 7.72 (m, 2H), 7.46 – 7.35 (m, 6H), 5.16 – 5.06 (m, 1H), 3.14 (q, \( J = 7.2 \) Hz, 2H), 0.78 (t, \( J = 7.3 \) Hz, 3H). \( ^{13}\)C NMR (151 MHz, CDCl₃): \( \delta \) 168.4, 141.4, 138.9, 138.8, 136.8, 135.3, 130.7, 128.9, 128.8, 128.4, 96.4, 34.8, 14.2. HRMS (ESI): \( m/z \) [M+H]+ calcd for C_{15}H_{15}OIN: 352.0193; found: 352.0192.

**Methyl 4-(triethylgermyl)benzoate (42):** To a solution of 4-(triethylgermyl)benzoic acid 30 (77.9 mg, 0.28 mmol, 1.0 equiv.) in MeOH (3.0 mL) was added SOCl₂ (0.3 mL, 4.11 mmol, 15 equiv.) dropwise and the mixture was stirred for 2 hours at ambient temperature. After evaporation of the volatiles, the title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) as a colorless oil (72.2 mg, 0.25 mmol, 88%). \( ^1\)H NMR (600 MHz, CDCl₃): \( \delta \) 7.98 (d, \( J = 8.1 \) Hz, 2H), 7.52 (d, \( J = 8.1 \) Hz, 2H), 3.91 (s, 3H), 1.09 – 0.98 (m, 15H). \( ^{13}\)C NMR (151 MHz, CDCl₃): \( \delta \) 167.6, 147.0, 134.1, 131.2, 129.9, 128.6, 52.2, 9.0, 4.3. HRMS (APCI): \( m/z \) [M+H]+ calcd for C_{14}H_{23}O_{2}Ge: 297.0904; found: 297.0910.

**Methyl 4-iodobenzoate (43):** Prepared, following the general procedure D from methyl 4-(triethylgermyl)benzoate 42. The title product was obtained after purification by column chromatography (hexane/EtOAc 10:1) as a white solid (53.1 mg, 0.20 mmol, 89%). M.p.: 115 °C. \( ^1\)H NMR (600 MHz, CDCl₃): \( \delta \) 7.81 – 7.78 (m, 2H), 7.75 – 7.72 (m, 2H), 3.90 (s, 3H). \( ^{13}\)C NMR (151 MHz, CDCl₃): \( \delta \) 166.7, 137.9, 131.2,
129.8, 100.8, 52.4. **HRMS (APCI):** m/z [M+H]+ calcd for C₈H₈O₂I: 262.9564; found: 262.9575. The data are in agreement with those previously reported.[24]
3.4. Aryl germane starting materials

*Note:* During the course of this investigation direct C-H germylations have become available,[6] which offer alternatives to the general procedures E and F presented herein.

**Aryl germane starting materials**

**Note:** During the course of this investigation direct C-H germylations have become available,[6] which offer alternatives to the general procedures E and F presented herein.

**4-Bromophenyl**triethylgermane: Prepared, following the general procedure E from 1-bromo-4-iodobenzene. The title product was obtained after purification by column chromatography (hexane) as a colorless oil (872.0 mg, 2.76 mmol, 97%). ¹H NMR (600 MHz, CDCl₃): δ 7.47 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 1.07 – 1.02 (m, 9H), 1.01 – 0.95 (m, 6H). ¹³C NMR (151 MHz, CDCl₃): δ 138.7, 135.7, 131.1, 123.0, 9.0, 4.3. HRMS (EI): m/z [M]+ calcd for C₁₁H₁₇Br₇Ge: 315.9876; found: 315.9882. The data are in agreement with those previously reported.[5]

**2-Bromo-6-chlorophenyl**triethylgermane: An oven dried round bottom flask equipped with a magnetic stirrer was evacuated and refilled with argon three times. Then, 2,2,6,6-tetramethylpiperidine (1.2 equiv., 12 mmol, 2.05 mL) was added and dissolved in dry THF (0.2 M, 50 mL). The solution was cooled to 0 °C and a hexane solution of n-butyllithium (1.0 equiv., 2.4 M, 4.2 mL) was added dropwise. After 15 minutes of stirring the solution was cooled to -78 °C and a solution of 1-bromo-3-chlorobenzene (1.0 equiv., 10 mmol, 1.2 mL) in THF (5 mL) was added dropwise. It was stirred for an additional 20 minutes before triethylgermanium chloride (1.5 equiv., 15 mmol, 2.5 mL) was added and the reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched by the addition of sat. aqueous NH₄Cl solution. The phases were separated and the aqueous phase was washed with DCM (2 × 50 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. The title product was obtained after purification by column chromatography (pentane) as a colorless oil (310 g, 8.85 mmol, 89%). Rₚ (Hexane): 0.8. ¹H NMR (600 MHz, CDCl₃): δ 7.43 (dd, J = 7.9, 1.2 Hz, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.04 (dd, J = 7.9 Hz, 1H), 1.30 (q, J = 7.9 Hz, 6H), 1.08 (t, J = 7.9 Hz, 9H). ¹³C NMR (151 MHz, CDCl₃): δ 142.4, 140.9, 132.0, 131.5, 130.5, 128.9, 9.3, 8.8. HRMS (APCI): m/z [M-Et]+ calcd for C₁₀H₁₃Br₇⁺: 320.90955; found: 320.90892.

**4-Bromo-2,5-dimethylphenyl**triethylgermane: Prepared, following the general procedure F from 2,5-dibromo-p-xylene. The title product was obtained after purification by column chromatography (hexane) as a colorless oil (460.3 mg, 1.34 mmol, 89%). ¹H NMR (600 MHz, CDCl₃): δ 7.34 (s, 1H), 7.15 (s, 1H), 2.34 (d, J = 12.5 Hz, 6H), 1.03 (s, 15H). ¹³C NMR (151 MHz, CDCl₃): δ 142.7, 137.6, 137.0, 134.0, 133.2, 125.5, 22.5, 22.2, 9.1, 5.1. HRMS (APCI): m/z [M-Et]+ calcd for C₁₂H₁₈Br₇⁺: 314.9798; found: 314.9795.
3-Bromo-5-(triethylgermyl)benzonitrile: Prepared, following the general procedure F from 3,5-dibromobenzonitrile. The title product was obtained after purification by column chromatography (hexane/EtOAc 25:1) as a yellow oil (1.25 g, 3.68 mmol, 74%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.74 (d, $J$ = 1.8 Hz, 1H), 7.72 (d, $J$ = 1.4 Hz, 1H), 7.60 (s, 1H), 1.08 – 0.99 (m, 15H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 145.4, 141.0, 135.9, 134.2, 123.1, 117.9, 113.9, 8.9, 4.3. HRMS (APCI): $m/z$ [M+H]$^+$ calcd for C$_{15}$H$_{19}$Br$_7$GeN: 341.9907; found: 341.9906.

3-Bromophenyltriethylgermane: Prepared, following the general procedure E from 1-bromo-3-iodobenzene. The title product was obtained after purification by column chromatography (pentane) as a colorless oil (4.23 g, 13.4 mmol, 89%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.53 (dd, $J$ = 2.2, 1.0 Hz, 1H), 7.44 (ddd, $J$ = 7.9, 2.1, 1.2 Hz, 1H), 7.34 (ddd, $J$ = 7.2, 1.1 Hz, 1H), 7.20 (dd, $J$ = 7.6 Hz, 1H), 1.08 – 1.04 (m, 9H), 1.02 – 0.98 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.3, 136.5, 132.4, 132.2, 129.7, 123.1, 9.0, 4.3. The data are in agreement with those previously reported.[5]

3-Bromo-5-(triethylgermyl)phenyltrimethylsilane: Prepared, following the general procedure F from 3,5-dibromo-1-trimethylsilylbenzene. The title product was obtained after purification by column chromatography (hexane) as a colorless oil (163.0 mg, 0.42 mmol, 84%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.55 – 7.54 (m, 1H), 7.51 – 7.50 (m, 1H), 7.44 – 7.43 (m, 1H), 1.07 – 1.05 (m, 9H), 1.02 – 0.96 (m, 6H), 0.26 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 143.1, 142.6, 137.1, 136.8, 135.7, 123.6, 9.0, 4.4, -1.1. HRMS (EI): $m/z$ [M]$^+$ calcd for C$_{15}$H$_{27}$Br$_7$GeSi: 388.0272; found: 388.0261. The data are in agreement with those previously reported.[25]

5-Bromothiophen-2-yl)triethylgermane: Prepared, following the general procedure F from 2,5-dibromothiophene. The title product was obtained after purification by column chromatography (hexane) as a colorless oil (1.45 g, 4.51 mmol, 90%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.10 (d, $J$ = 3.5 Hz, 1H), 6.90 (d, $J$ = 3.5 Hz, 1H), 1.10 – 1.06 (m, 9H), 1.03 – 0.98 (m, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 140.8, 134.0, 131.0, 115.6, 8.9, 5.6. HRMS (APCI): $m/z$ [M+H]$^+$ calcd for C$_{10}$H$_{18}$Br$_7$GeS: 322.9519; found: 322.9517.

4-Bromo-2-methylphenyl)triethylgermane: Prepared, following the general procedure E from 5-bromo-2-iodotoluene. The title product was obtained after purification by column chromatography (hexane) as a colorless oil (1.09 g, 3.30 mmol, 66%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.32 (d, $J$ = 1.9 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.19 (d, $J$ = 7.9 Hz, 1H), 2.37 (d, $J$ = 0.6 Hz, 3H), 1.03 (s, 15H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 145.7, 137.2, 136.2, 132.5, 128.0, 123.1, 22.9, 9.1, 5.1. HRMS (APCI): $m/z$ [M-Et]$^+$ calcd for C$_{11}$H$_{16}$Br$_7$Ge: 300.9642; found: 300.9641.
**{(3-Bromo-5-chlorophenyl)triethylgermane}:** Prepared, following the general procedure from 1-bromo-3-chloro-5-iodobenzene. The title product was obtained after purification by column chromatography (pentane) as a colorless oil (4.41 g, 12.6 mmol, 84%). **$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.46 (dd, $J = 1.9, 1.9$ Hz, 1H), 7.39 (dd, $J = 1.8, 0.8$ Hz, 1H), 7.29 (dd, $J = 2.0, 0.8$ Hz, 1H), 1.08 – 0.96 (m, 15H). **$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$ 145.2, 135.0, 134.6, 132.3, 131.0, 123.1, 8.9, 4.4. **HRMS (APCI):** $m/z$ [M-Et]$^+$ calcd for C$_{10}$H$_{13}$Cl$_{57}$Br$_{74}$Ge: 320.90954, found 320.90925.
4. Comparison to BMIDA sequential coupling strategy

Adapted from Wang et al\(^\text{[26]}\). Under an argon atmosphere, di-iso-propylamine (0.294 mL, 2.1 mmol, 1.05 equiv.) was added to a three-necked flask, dissolved in MTBE (1 mL) and cooled to -55 °C. sec-Butyllithium (0.84 mL, 2.5 M in hexanes, 2.1 mmol, 1.05 equiv.) was then added dropwise and the reaction mixture stirred for 30 minutes at -55 °C. In a separate flask under argon, 3,5-difluorobromobenzene (383 mg, 2 mmol, 1 equiv.) was dissolved in MTBE (1 mL) and cooled to -78 °C. The prepared LDA solution was then added dropwise and the reaction mixture then stirred at -78 °C for 10 minutes. After this time, Et\(_3\)GeCl (508 mg, 2.6 mmol, 1.3 equiv.) was added dropwise and the solution warmed to -10 °C. After 2 hours of stirring at this temperature the reaction was then quenched with 10% aq. HCl, warmed to room temperature and extracted with MTBE (3x). The organic layers were dried over Na\(_2\)SO\(_4\) and concentrated in vacuo and the crude purified by column chromatography (hexane) to afford the product as a clear oil (588.4 mg, 1.68 mmol, 84%).

\[ \text{RF} = 0.88 \] (hexane). 1H NMR (600 MHz, CDCl\(_3\)): \( \delta \) 7.01 – 6.98 (m, 2H), 1.13 – 1.07 (m, 6H), 1.06 – 1.02 (m, 9H).

13C NMR (151 MHz, CDCl\(_3\)): \( \delta \) 166.8 (dd, \( J = 245.0, 18.7 \) Hz), 122.9 (t, \( J = 12.6 \) Hz), 116.1 – 113.5 (m), 112.1 (t, \( J = 40.4 \) Hz), 8.8, 5.6 (t, \( J = 2.6 \) Hz). 19F NMR (564 MHz, CDCl\(_3\)) \( \delta \) -95.60 (d, \( J = 6.6 \) Hz).

HRMS (APCI): \([M+H]^+\) calculated for C\(_{10}\)H\(_{12}\)BrF\(_2\)Ge: 322.92967, found 322.92846.

4-bromo-2,6-difluoro-4-methoxy-1,1'-biphenyl (4a): Coupling and bromination were performed according to general procedure A. The title product was obtained after purification by column chromatography (20:1 Hexane/EtOAc) as a white solid (42.8 mg, 0.143 mmol, 72%). \( R_f = 0.40 \) (20:1 Hexane/EtOAc). M.p.: 87 – 88 °C. 1H NMR (600 MHz, CDCl\(_3\)): \( \delta \) 7.50 – 7.44 (m, 2H), 7.07 – 7.00 (m, 2H), 6.99 – 6.95 (m, 2H), 3.85 (s, 3H).

13C NMR (151 MHz, CDCl\(_3\)): \( \delta \) 160.31, 160.30 (dd, \( J = 247.9, 5.1 \) Hz), 142.5 (t, \( J = 9.0 \) Hz), 130.7, 128.1, 114.7, 110.6 – 109.4 (m), 95.8 (t, \( J = 24.6 \) Hz), 55.6. 19F NMR (564 MHz, CDCl\(_3\)) \( \delta \) -105.63 – -105.68 (m, 2F). HRMS (APCI): \([M+H]^+\) calculated for C\(_{13}\)H\(_{12}\)BrF\(_2\): 298.98776, found 298.98629.

3,5-difluoro-4'-methoxy-4-methyl-1,1'-biphenyl (5a): The second coupling was performed from 4a (29.9 mg, 0.1 mmol) according to general procedure A. The title product was obtained after purification by column chromatography (50:1 Hexane/EtOAc) as a white solid (19.0 mg, 0.08 mmol, 81%). M.p. = 48 – 51 °C. \( R_f = 0.4 \) (50:1 Hexane/EtOAc). 1H NMR (600 MHz, CDCl\(_3\)): \( \delta \) 7.50 – 7.44 (m, 2H), 7.07 – 7.00 (m, 2H), 6.99 – 6.95 (m, 2H), 3.85 (s, 3H), 2.21 (d,
$J = 1.8 \text{ Hz}, 3\text{H})$. $^{13}\text{C NMR}$ (151 MHz, CDCl$_3$): δ 162.0 (dd, $J = 245.1$, 10.2 Hz), 159.9, 140.4 (t, $J = 10.0$ Hz), 131.7 (t, $J = 2.3$ Hz), 128.0, 114.5, 111.4 (t, $J = 21.6$ Hz), 108.9 (dd, $J = 20.8$, 6.1 Hz), 55.5, 7.1 (t, $J = 3.8$ Hz). $^{19}\text{F NMR}$ (564 MHz, CDCl$_3$): δ -115.09 (d, $J = 7.9$ Hz).

HRMS (APCI): m/z [M+H]$^+$ calculated for C$_{14}$H$_{13}$F$_2$O: 234.08507, found 234.08474.

Adapted from Wang et al.$^{[26]}$ Under an argon atmosphere, di-iso-propylamine (0.588 mL, 4.2 mmol, 1.05 equiv.) was added to a three-necked flask, dissolved in MTBE (2 mL) and cooled to -55 °C. sec-Butyllithium (1.68 mL, 2.5 M in hexanes, 4.2 mmol, 1.05 equiv.) was then added dropwise and the reaction mixture stirred for 30 minutes at -55 °C. In a separate flask under argon, 3,5-difluorobromobenzene (766 mg, 4 mmol, 1 equiv.) was dissolved in MTBE (2 mL) and cooled to -55 °C. The prepared LDA solution was then added dropwise and the reaction mixture then stirred at -55 °C for 10 minutes. After this time, B(O'Pr)$_3$ (1.2 mL, 5.2 mmol, 1.3 equiv) was added dropwise and the solution warmed to -10 °C. After 2 hours of stirring at this temperature the reaction was then quenched with 10% aq. HCl, warmed to room temperature and extracted with MTBE and EtOAc (3x). The organic layers were dried over Na$_2$SO$_4$ and concentrated in vacuo (bath kept below 55 °C) to afford the product as a white solid (425 mg, 1.8 mmol, 45%). $^1\text{H NMR}$ (400 MHz, DMSO-$d_6$): δ 8.78 (s, 2H), 7.36 (d, $J = 5.9$ Hz, 2H). $^{13}\text{C NMR}$ (100 MHz, DMSO-$d_6$): δ 164.2 (dd, $J = 246.0$, 16.8 Hz), 122.4 (t, $J = 12.7$ Hz), 115.0 (d, $J = 6.4$ Hz), 114.9 (d, $J = 6.4$ Hz). $^{19}\text{F NMR}$ (564 MHz, DMSO-$d_6$): δ -101.3 (s, 2F). HRMS (APCI): m/z [M+Na]$^+$ calculated for C$_6$H$_4$O$_2$B$^{79}$BrF$_2$Na: 258.93480, found 258.93441.

Adapted from Watson et al.$^{[27]}$ In an open flask, (4-bromo-2,6-difluorophenyl)boronic acid (425 mg, 1.8 mmol, 1 equiv.) and N-methyliminodiacetic acid (278 mg, 1.89 mmol, 10.5 equiv.) were dissolved in dry DMF (6 mL; containing molecular sieves). The reaction mixture was then heated at 40 °C for 72 h. After this time, the reaction mixture was allowed to cool to room temperature and concentrated in vacuo. EtOAc was added to the resulting sticky residue and the solid then collected by filtration, yielding the product as an off-white solid (437 mg, 1.26 mmol, 70%) which was used in cross-coupling without further purification.
In an argon filled glove box, ArBMIDA 2b (114.5 mg, 0.33 mmol, 3 equiv.), XPhosPd-G2 (4.4 mg, 5 mol%), K$_3$PO$_4$ (212 mg, 1 mmol, 9 equiv.) were dissolved in THF (3 mL). The reaction mixture was heated to 55 °C and a solution of 4-methoxyphenyl boronic acid (16.7 mg, 0.11 mmol, 1 equiv.) in THF (10 mL) added dropwise. The resulting suspension was stirred at this temperature for 24 hours. After this time, the reaction mixture was cooled to room temperature and directly filtered through a pad of silica washing with Et$_2$O, and then eluting with 10% MeOH/DCM. The solvent was removed in vacuo to afford the desired product as an off white solid (23.1 mg, 0.06 mmol, 56%).

$^1$H NMR (600 MHz, DMSO-$d_6$): δ 7.73 (d, $J$ = 8.8 Hz, 2H), 7.32 (d, $J$ = 9.5 Hz, 2H), 7.03 (d, $J$ = 8.5 Hz, 2H), 4.41 (d, $J$ = 17.3 Hz, 2H), 4.14 (d, $J$ = 17.3 Hz, 2H), 3.81 (s, 3H), 2.72 (s, 3H).

$^{13}$C NMR (151 MHz, DMSO-$d_6$): δ 168.7, 166.3 (dd, $J$ = 245.5, 14.7 Hz), 159.9, 144.1 (t, $J$ = 11.1 Hz), 135.8, 127.9, 114.4, 112.9, 108.9 (m), 62.1, 55.3, 47.3.

$^{19}$F NMR (565 MHz, DMSO-$d_6$): δ -101.47 (d, $J$ = 9.3 Hz).

According to Burke et al. ArBMIDA 3b (23.1 mg, 0.06 mmol, 1 equiv.) and NaOH (7.2 mg, 0.118 mmol, 3 equiv.) were dissolved in THF (0.72 mL), and water (0.18 mL) was added. The reaction mixture was stirred at room temperature for 20 min. After this time, potassium phosphate buffer (0.18 mL, pH=6, 0.5 M) was added and the mixture allowed to separate. The aqueous mixture was then washed with EtOAc, the organics dried over Na$_2$SO$_4$ and concentrated in vacuo. No desired ArB(OH)$_2$ 4b was observed, instead protodeboronation to 4b' had occurred.

$^1$H NMR (600 MHz, CDCl$_3$): δ 7.49 (d, $J$ = 8.8, 2H), 7.07–7.05 (m, 2H), 6.98 (d, $J$ = 8.8 Hz, 2H), 6.73 (tt, $J$ = 8.8, 2.3 Hz, 1H), 3.86 (s, 3H).
$^{1}H$ NMR
(600.44 MHz, CDCl₃)

- D (d) 7.49
  J(8.8)
- B (d) 6.98
  J(8.8)
- A (tt) 6.73
  J(8.8, 2.3)
- C (m) 7.06
- E (s) 3.86

4b'
5. Recycling of germanium masking group

During our investigation on the halogenation of arylgermanes with NBS as halogenating reagent we observed the formation of germanium containing by-products. The major by-product was identified as a succinimide-GeEt₃ species followed by low amounts of Et₃GeBr and Et₃GeCl. While the succinimide-GeEt₃ species is likely formed due to an excess of NBS, we assumed that the formation of the halogenated germanes Et₃GeX (X = Br, Cl) occurs due to the presence of the corresponding anions in solution (derived from ZnCl₂, organomagnesium bromide). Since isolation of the succinimide-GeEt₃ species proved difficult, we intended to increase the formation of Et₃GeBr by adding an excess of NH₄Br to the reaction mixture. Indeed, the succinimide-GeEt₃ formation was fully suppressed and high amounts of Et₃GeBr (and minor amounts of Et₃GeCl) were observed (Figure S1). The mixture of germanium halides (Et₃GeBr and Et₃GeCl) was then isolated by Kugelrohr distillation (see below).

Figure S1. GCMS analysis after bromination: a) under standard conditions and b) in presence of NH₄Br (5 equiv.).
(a) **C-C Coupling:** The coupling was performed according to general procedure B.

(b) **Halogenation:** The aryl germane obtained after cross-coupling was dissolved in MeCN (0.2 M). Subsequently, NBS (3 equiv.) and NH₄Br (5 equiv.) were added. The reaction was stirred at 60 °C for 1.5 hours. After that time, the mixture was allowed to cool to room temperature, filtered through a plug of silica gel, washed with Et₂O and concentrated under reduced pressure.

**Attention!** During the reaction Et₃GeCl and Et₃GeBr are formed, both are volatile, and one must make sure that the pressure is higher than 200 mbar and that the temperature remains below 40 °C.

(c) **Distillation:** The obtained crude mixture was subjected to Kugelrohr distillation (70 °C, 10 mbar, 2 hours, ice bath cooling). The distilled fractions were combined yielding a mixture of Et₃GeCl and Et₃GeBr, while the remainder of the distillation (i.e. the halogenated arene) was purified by column chromatography (pentane) and directly used for further coupling.

(d) **Germylation:** The obtained distillate (mixture of Et₃GeCl and Et₃GeBr) was placed into a 25 mL round bottom flask equipped with a magnetic stir bar. The flask was closed with a septum and gently purged with argon for 2 min. Subsequently, THF (1 M) was added followed by the appropriate organomagnesium reagent (2.0 equiv. with regard to [Ge]). After stirring overnight saturated aq. NH₄Cl (5 mL) was added and the aqueous phase was washed with DCM (3x 10 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. The aryl germanes (5-bromothiophen-2-yl)triethylgermane (27) and (4-bromophenyl)triethylgermane were obtained after purification by column chromatography (pentane) as colorless oils in 82% and 76% yield (based on employed [Ge]), respectively. Characterization data match those of the independently synthesized compounds (see 3.4).
2-bromo-5-(3’,5’-dichloro-[1,1’-biphenyl]-4-yl)thiophene (28): The title product was obtained after purification by column chromatography (hexane) as a pale yellow solid (248 mg, 0.645 mmol, 65%). M.p.: 128–131 °C. $^1$H NMR (600 MHz, CDCl$_3$): δ 7.62 – 7.56 (m, 2H), 7.56 – 7.53 (m, 2H), 7.47 (d, $J = 1.8$ Hz, 2H), 7.35 (dd, $J = 1.9, 1.9$ Hz, 1H), 7.11 (d, $J = 3.8$ Hz, 1H), 7.06 (d, $J = 3.9$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$): δ 145.0, 143.4, 137.9, 135.5, 133.9, 131.1, 127.7, 127.5, 126.2, 125.5, 123.8, 112.2. HRMS (APCI): $m/z$ [M+H]$^+$ calculated for C$_{16}$H$_{10}$Cl$_2$SBr: 383.89563, found: 383.89562.
6. NMR spectra

6.1. Products from double coupling

1H NMR (600.44 MHz, CDCl3)

13C NMR (151.00 MHz, CDCl3)
13C NMR
(150.85 MHz, CDCl3)

1H NMR
(599.86 MHz, CDCl3)
13C NMR
(150.85 MHz, CDCl3)

1H NMR
(599.86 MHz, CDCl3)
13C NMR
(150.85 MHz, CDCl3)

16

A (d) 162.26
J(245.9)

B (d) 128.19
J(7.9)

C (d) 115.73
J(21.4)

19F NMR
(564.38 MHz, CDCl3)

16

A (m) -116.50
6.2. Products from sequential coupling

1H NMR
(600.44 MHz, CDCl3)

13C NMR
(151.00 MHz, CDCl3)
19F NMR
(564.92 MHz, CDCl3)
19F NMR
(564.92 MHz, CDCl3)

A (s)
73.26

1H NMR
(600.44 MHz, CDCl3)

D (dd)
7.35
3(3.9)

E (d)
7.11
3(3.8)

25

28

B (m)
7.54

A (m)
7.59

C (d)
7.47
3(1.8)

F (d)
7.06
3(3.9)

Cl
Cl
Cl

Cl

Br

S

-SS4-
13C NMR (151.00 MHz, CDCl3)
6.3. Derivatized aryl germanes and corresponding iodides

1H NMR (600.44 MHz, CDCl3)

13C NMR (151.00 MHz, CDCl3)
1H NMR
(600.44 MHz, CDCl3)

Et₃Ge

OH
Me

31

B (d) 7.32 J(7.7)
A (d) 7.43 J(7.7)
C (m) 4.63

K (m) 1.35
E (m) 1.72
D (m) 1.81
G (m) 1.07
J (s) 1.94 J(7.2)
F (m) 1.43
I (t) 0.91 J(7.2)
L (m) 1.25

13C NMR
(151.00 MHz, CDCl3)

Et₃Ge

OH
Me

31
6.4. Aryl germene starting materials

1H NMR (600.44 MHz, CDCl3)

13C NMR (151.00 MHz, CDCl3)
1H NMR
(600.44 MHz, CDCl3)

13C NMR
(151.00 MHz, CDCl3)
1H NMR (399.97 MHz, CDCl3)

B (dd) 7.39
J(1.8, 0.8)

A (dd) 7.46
J(1.9)

C (dd) 7.29
J(2.0, 0.8)

13C NMR (100.58 MHz, CDCl3)

Cl
Br
GeEt3

-145.2
135.0
132.3
131.0
-8.9
-4.4
6.5. Comparison to BMIDA sequential coupling strategy

1H NMR
(599.86 MHz, CDCl3)

13C NMR
(150.85 MHz, CDCl3)
19F NMR
(564.92 MHz, CDCl3)

1H NMR
(600.44 MHz, DMSO)
13C NMR
(151.00 MHz, DMSO)

19F NMR
(564.92 MHz, DMSO)
19F NMR
(564.92 MHz, DMSO)

F
BMIDA
F
MeO
3b

A (d)
-101.47
J(9.3)
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