Supporting Information

Orthogonal Stability and Reactivity of Aryl Germanes Enables Rapid and Selective (Multi)Halogenations
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General Information

Reagents and Solvents

Unless otherwise stated, all reagents and starting materials were commercially available and used as received. Solvents used in work up and purification were distilled prior to use. Anhydrous and degassed dimethylformamide (DMF) and acetone were purchased from Sigma Aldrich. Dry and anhydrous THF was obtained from an SP-105 solvent drying system from LC Technology Solutions Inc.

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. Column chromatography was carried out using silica gel (35–70 mesh; 60 Å). Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 aluminum plates; detection either under UV light or by dipping into a solution of KMnO₄ (1.5 g) and NaHCO₃ (5.0 g) in H₂O (400 mL) followed by heating. Preparative HPLC was performed on a Gilson-Abimed HPLC (employing UV detector model 117) using a Merck LiChrosorb Si60 column (porosity 7 μm, 250 x 25 mm).

All ¹H, ¹³C and ¹⁹F NMR spectra were recorded at ambient temperature on a Varian V NMRS 600 or a Varian V NMRS 400 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to SiMe₄ and referenced to either the residual solvent peak for ¹H (7.26 ppm for CDCl₃ and 2.92 ppm for DMF-d₇) and ¹³C NMR spectra (77.2 ppm for CDCl₃ and 163.2 ppm for DMF-d₇) or internally by the instrument after locking and shimming to the deuterated solvent (for ¹⁹F). Coupling constants (J) are given in Hertz (Hz). High-resolution mass spectrometry (HRMS) was performed using a Thermo Scientific LTQ Orbitrap XL (ESI) or an Finnigan MAT 95 (EI, 70 eV). IR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer with an UATR Diamond/KRS-5 crystal with attenuated total reflectance (ATR). Relative intensities are given in parentheses (w = weak, m = medium, s = strong).

Low-resolution mass spectrometry and reaction monitoring were performed with an Agilent Technologies 5975 series MSD mass spectrometer under electron ionization (EI) mode coupled with an Agilent Technologies 7820A gas chromatograph employing an Agilent HP-5MS column (30 m × 0.25 mm inner diameter × 0.25 μm (5% phenyl)-methylpolysiloxane film) or an Agilent CP-Sil8-CB column (30 m × 0.25 mm inner diameter × 1.00 μm (5% phenyl)-
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methyldiphenyldimethylpolysiloxane film). Operating with a constant He-flow of 1.2 mL min$^{-1}$, injector temperature 250 °C, detector-line temperature 280 °C.

EPR analysis was performed with a Miniscope MS400 spectrometer from Freiberg Instruments with a FC 400 frequency generator.
Bromination

General Procedure 1 (GP 1)

Aryl germane (1.0 equiv.) and N-bromosuccinimide (NBS; 2.0 equiv.) were added to the reaction vial in air, dissolved in DMF (0.3 M) and stirred at room temperature for 4 h. After completion of reaction, the reaction was quenched by addition of aqueous solution of Na$_2$S$_2$O$_3$ (sat.), the organic phase was separated and the aqueous phase was extracted with DCM (3x). The combined organic phases were dried over MgSO$_4$, the solvent was removed under reduced pressure and the crude product mixture was purified by silica column chromatography. Some of the brominated compounds are not isolable due to their high volatility. In these cases, the yield was determined by $^1$H NMR (quant., ethylene carbonate as internal standard) or $^{19}$F NMR (quant., 1,4-difluorobiphenyl as internal standard) and the further analysis for unambiguous characterization was performed using the crude reaction mixture.

**Bromobenzene**

Prepared according to GP 1. The yield was determined by quantitative $^1$H NMR (94%).

$^1$H NMR (600 MHz, DMF-d$_7$) δ/ ppm = 7.64 – 7.59 (m, 2H), 7.45 – 7.41 (m, 1H), 7.41 – 7.36 (m, 2H). $^{13}$C NMR (151 MHz, DMF-d$_7$) δ/ ppm = 132.5, 131.7, 128.5, 123.1. MS (70 eV, EI): m/z (%): 158.0 (62) [M]$^+$ ($^{81}$Br), 156.0 (64) [M]$^+$ ($^{79}$Br), 77.0 (100), 74.0 (21), 51.0 (42).

Due to its high volatility, the title compound was not isolated.

**1-Bromo-4-methylbenzene**

Prepared according to GP 1. The yield was determined by quantitative $^1$H NMR (96%).

$^1$H NMR (600 MHz, DMF-d$_7$) δ/ ppm = 7.47 (d, $J$ = 8.3 Hz, 2H), 7.20 (d, $J$ = 8.3 Hz, 2H), 2.30 (s, 3H). $^{13}$C NMR (151 MHz, DMF-d$_7$) δ/ ppm = 138.3, 132.3, 132.2, 119.6, 21.2. MS (70 eV, EI): m/z (%): 172.0 (36) [M]$^+$ ($^{81}$Br), 170.0 (63) [M]$^+$ ($^{79}$Br), 91.1 (100), 89.1 (18), 65.0 (20), 63.0 (20).

Due to its high volatility, the title compound was not isolated.
5-Bromo-1,2,3-trimethoxybenzene

Prepared according to GP 1. The title product was obtained after purification by column chromatography (n-pentane/Et₂O, 5:1) as a white solid (68.4 mg, 0.277 mmol, 91%).

Rᵣ = 0.51 (n-pentane/Et₂O, 5:1). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 6.71 (s, 2H), 3.84 (s, 6H), 3.81 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 154.0, 137.4, 116.3, 109.0, 61.0, 56.4. HRMS (EI) calculated for C₉H₁₁O₃Br: 268.9784 [M+Na]⁺, found: 268.9784.

These data are in agreement with those reported previously in the literature.[1]

1-Bromonaphthalene

Prepared according to GP 1. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (62.0 mg, 0.300 mmol, 99%).

Rᵣ = 0.80 (n-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 8.25 (d, J = 8.5 Hz, 1H), 7.86 – 7.78 (m, 3H), 7.61 (dd, J = 8.5, 6.8 Hz, 1H), 7.54 (dd, J = 8.0, 6.8 Hz, 1H), 7.33 (dd, J = 8.0, 7.4 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 134.7, 132.1, 130.0, 128.4, 128.1, 127.5, 127.2, 126.8, 126.3, 123.0. HRMS (EI) calculated for C₁₀H₇OBr: 205.9726 [M]⁺, found: 205.9728.

These data are in agreement with those reported previously in the literature.[2]

1-Bromo-4-methoxybenzene

Prepared according to GP 1. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (48.4 mg, 0.259 mmol, 85%).

Rᵣ = 0.90 (n-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 7.38 (d, J = 8.9 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 3.78 (d, J = 1.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 158.8, 132.4, 115.8, 112.9, 55.6. HRMS (EI) calculated for C₇H₇OBr: 185.9675 [M]⁺, found: 185.9670.

These data are in agreement with those reported previously in the literature.[3]

1-Bromo-2-methoxybenzene

Prepared according to GP 1. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (42.4 mg, 0.227 mmol, 75%).

Rᵣ = 0.68 (n-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 7.54 (dd, J = 7.9, 1.6 Hz, 1H), 7.32 – 7.25 (m, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.87 – 6.80 (m, 1H), 3.90 (s, 3H). ¹³C NMR (151 MHz, CDCl₃)
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δ/ppm = 156.0, 133.5, 128.6, 121.9, 112.1, 111.8, 56.3. **HRMS** (EI) calculated for C₇H₇O⁷Br: 185.9675 [M]+, found: 185.9674.
These data are in agreement with those reported previously in the literature.[⁴]

**2-Bromo-1,3,5-trimethylbenzene**

Prepared according to GP 1. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (48.4 mg, 0.243 mmol, 80%).

Rᵣ = 0.90 (n-pentane). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 6.90 (s, 2H), 2.38 (s, 6H), 2.24 (s, 3H).

**¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 138.0, 136.4, 129.2, 124.3, 23.9, 20.8. **HRMS** (EI) calculated for C₉H₁₁O⁷⁷Br: 198.0039 [M]+, found: 198.0034.
These data are in agreement with those reported previously in the literature.[³]

**2-Bromo-1,3-dimethoxybenzene**

Prepared according to GP 1. The title product was obtained after purification by column chromatography (pentane/Et₂O, 5:1) as a white solid (67.0 mg, 0.309 mmol, 99%).

Rᵣ = 0.65 (pentane/Et₂O, 8:1). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.23 (t, J = 8.3 Hz, 1H), 6.58 (d, J = 8.3 Hz, 2H), 3.90 (s, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 157.3, 128.4, 104.8, 101.0, 56.6. **HRMS** (EI) calculated for C₈H₉O₂⁷⁷Br: 215.9780 [M]+, found: 215.9782.
These data are in agreement with those reported previously in the literature.[⁵]

**1-Bromo-4-iodobenzene**

Prepared according to GP 1. The title product was obtained after purification by column chromatography (n-pentane) as a white solid (83.4 mg, 0.295 mmol, 96%).

Rᵣ = 0.90 (n-pentane). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.54 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 139.2, 133.6, 122.3, 92.2. **HRMS** (EI) calculated for C₆H₄I⁷⁷Br: 281.8536 [M]+, found: 281.8523.
These data are in agreement with those reported previously in the literature.[⁶]
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1,4-Dibromobenzene

\[
\text{Br} \quad \text{Br}
\]
Prepared according to GP 1. The title product was obtained after purification by column chromatography (n-pentane) as a white solid (64.8 mg, 0.275 mmol, 92%).

\[ R_f = 0.90 \text{ (n-pentane).} \]

\[ ^1H \text{ NMR (600 MHz, CDCl}_3\text{) } \delta/ \text{ppm} = 7.36 \text{ (s, 4H).} \]

\[ ^13C \text{ NMR (151 MHz, CDCl}_3\text{) } \delta/ \text{ppm} = 133.3, 121.2. \]

HRMS (EI) calculated for C\textsubscript{6}H\textsubscript{4}79Br\textsubscript{2}: 233.8674 [M]+, found: 233.8673.

These data are in agreement with those reported previously in the literature.[7]

1-Bromo-4-chlorobenzene

\[
\text{Cl} \quad \text{Br}
\]
Prepared according to GP 1. The yield was determined by quantitative \(^1H\) NMR (99%). The title product was obtained after purification by column chromatography (n-pentane) as a white solid.

\[ R_f = 0.87 \text{ (n-pentane).} \]

\[ ^1H \text{ NMR (600 MHz, CDCl}_3\text{) } \delta/ \text{ppm} = 7.42 \text{ (d, } J = 8.7 \text{ Hz, 2H), 7.21 \text{ (d, } J = 8.7 \text{ Hz, 2H).} \]

\[ ^13C \text{ NMR (151 MHz, CDCl}_3\text{) } \delta/ \text{ppm} = 133.4, 132.9, 130.3, 120.4. \]

HRMS (EI) calculated for C\textsubscript{6}H\textsubscript{4}79Br\textsubscript{35}Cl: 289.9179 [M]+, found: 289.9181.

Due to its high volatility, the title compound was not isolated in a representative yield. These data are in agreement with those reported previously in the literature.[7]

1-Bromo-4-fluorobenzene

\[
\text{F} \quad \text{Br}
\]
Prepared according to GP 1. The yield was determined by quantitative \(^1H\) NMR (82%).

\[ ^1H \text{ NMR (600 MHz, DMF-d}_7\text{) } \delta/ \text{ppm} = 7.69 - 7.62 \text{ (m, 2H), 7.28 - 7.22 \text{ (m, 2H).} } \]

\[ ^19F \text{ NMR (564 MHz, DMF-d}_7\text{) } \delta/ \text{ppm} = -116.06 - -116.34 \text{ (m).} \]

MS (70 eV, EI): \( m/z \) (%): 176.0 (90) [M]+ (81Br), 174.0 (91) [M]+ (79Br), 95.0 (100), 94 (11), 75 (46), 74 (15).

Due to its high volatility, the title compound was not isolated. The resolution of the NMR made it impossible to assign the correct \(^13C\) NMR shifts.

4-Bromo-3,5-dimethylisoxazole

\[
\text{O} \quad \text{Br} \quad \text{Me}
\]
Prepared according to GP 1. The yield was determined by quantitative \(^1H\) NMR (98%).

\[ ^1H \text{ NMR (600 MHz, DMF-d}_7\text{) } \delta/ \text{ppm} = 2.43 \text{ (s, 3H), 2.24 \text{ (s, 3H).} } \]

\[ ^13C \text{ NMR (151 MHz, DMF-d}_7\text{) } \delta/ \text{ppm} = 167.9, 160.2, 93.2, 11.6, 10.9. \]

MS (70 eV, EI): \( m/z \) (%): 177.0 (21) [M]+ (81Br),
Due to its high volatility, the title compound was not isolated.

3-Bromobenzo[b]thiophene

Prepared according to GP 1. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (62.5 mg, 0.293 mmol, 96%).

\[ R_f = 0.82 \text{ (pentane)}. \]

\[ ^1H \text{ NMR (600 MHz, CDCl}_3\text{)} \delta/\text{ppm} = 7.85 \text{ (dd, } J = 7.3, 7.3 \text{ Hz, 2H), } 7.51 - 7.39 \text{ (m, 3H).} \]

\[ ^{13}C \text{ NMR (151 MHz, CDCl}_3\text{)} \delta/\text{ppm} = 138.7, 137.6, 125.4, 125.1, 123.6, 123.2, 122.8, 107.8. \]

HRMS (EI) calculated for C\textsubscript{8}H\textsubscript{5}79\textsubscript{Br}S: 211.9290 [M]+, found: 211.9282.

These data are in agreement with those reported previously in the literature.\cite{8}

2-Bromothiophene

Prepared according to GP 1. The yield was determined by quantitative \(^1H\) NMR (99%).

\[ ^1H \text{ NMR (400 MHz, DMF-d}_7\text{)} \delta/\text{ppm} = 7.66 - 7.59 \text{ (m, 1H), } 7.29 - 7.22 \text{ (m, 1H), } 7.06 - 6.99 \text{ (m, 1H).} \]

\[ ^{13}C \text{ NMR (151 MHz, DMF-d}_7\text{)} \delta/\text{ppm} = 156.0, 130.7, 128.5, 111.4. \]

MS (70 eV, EI): m/z (%): 163.9 (84) [M]+ (\textsuperscript{81}Br), 161.9 (79) [M]+ (\textsuperscript{79}Br), 117.0 (12), 83.0 (100), 82.0 (30), 81.0 (49), 78.9 (25), 58.0 (13), 57.0 (54).

Due to its high volatility, the title compound was not isolated.

3-Bromothiophene

Prepared according to GP 1. The yield was determined by quantitative \(^1H\) NMR (63%).

\[ ^1H \text{ NMR (600 MHz, DMF-d}_7\text{)} \delta/\text{ppm} = 7.81 \text{ (d, } J = 5.7 \text{ Hz, 1H), } 7.72 - 7.68 \text{ (m, 1H), } 7.20 - 7.15 \text{ (m, 1H).} \]

MS (70 eV, EI): m/z (%): 163.9 (100) [M]+ (\textsuperscript{81}Br), 161.9 (94) [M]+ (\textsuperscript{79}Br), 118.9 (12), 116.9 (12), 83.0 (90), 82.0 (40), 81.0 (61), 80.0 (11), 78.9 (27), 57.0 (30), 57.0 (54).

Due to its high volatility, the title compound was not isolated. The resolution of the NMR spectrum made it impossible to assign the correct \(^{13}C\) NMR shifts.
Iodination

General Procedure 2 (GP 2)

Aryl germane (1.0 equiv.) and N-iodosuccinimide (NIS; 1.0 equiv.) were added to the reaction vial in air, dissolved in DMF (0.3 M) and stirred at room temperature or at 50 °C for 4 h. After completion of reaction (monitored by GC-MS or TLC), the reaction was quenched by addition of aqueous solution of Na₂S₂O₃ (sat.), the organic phase was separated and the aqueous phase was extracted with DCM (3x). The combined organic phases were dried with MgSO₄, the solvent was removed under reduced pressure and the crude product mixture was purified over silica column chromatography. Some of the iodinated compounds are not isolable due to their high volatility. An ¹H NMR (quant.) or ¹⁹F NMR (quant.) yield is given in those cases and the further analysis was performed using the crude reaction mixture.

1-Iodo-4-methylbenzene

Prepared according to GP 2 at room temperature. The yield was determined by quantitative ¹H NMR (96%).

¹H NMR (600 MHz, DMF-d₇) δ/ ppm = 7.64 (d, J = 7.9 Hz, 2H), 7.06 (d, J = 7.9 Hz, 2H). ¹³C NMR (151 MHz, DMF-d₇) δ/ ppm = 156.9, 138.8, 138.3, 132.6, 66.3. MS (70 eV, EI): m/z (%): 218.0 (100) [M]+, 126.9 (19), 91.1 (73), 89.1 (14), 65.1 (29), 63 (13).

Due to its high volatility, the title compound was not isolated.

5-Iodo-1,2,3-trimethoxybenzene

Prepared according to GP 2 at room temperature. The title product was obtained after purification by column chromatography (n-pentane/Et₂O, 5:1) as a white solid (85.4 mg, 0.290 mmol, 97%).

Rf = 0.40 (n-pentane/Et₂O, 7:1). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 6.88 (d, J = 1.3 Hz, 2H), 3.83 (d, J = 1.5 Hz, 6H), 3.81 (d, J = 1.3 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 154.1, 138.3, 115.1, 86.3, 61.0, 56.4. HRMS (EI) calculated for C₉H₁₁O₃I: 293.9748 [M]+, found: 293.9749.

These data are in agreement with those reported previously in the literature.⁹
1-Iodonaphthalene

Prepared according to GP 2 at room temperature. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (77.4 mg, 0.305 mmol, 99%).

Rf = 0.62 (n-pentane). 1H NMR (600 MHz, CDCl3) δ/ ppm = 8.10 (d, J = 7.3, 7.3, 1.6 Hz, 2H), 7.84 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.59 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.53 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.22 - 7.14 (m, 1H). 13C NMR (151 MHz, CDCl3) δ/ ppm = 137.6, 134.5, 134.3, 132.3, 129.1, 128.7, 127.9, 127.0, 126.9, 99.7. HRMS (EI) calculated for C10H7I: 253.9587 [M]+, found: 253.9580.

These data are in agreement with those reported previously in the literature.[10]

1-Iodo-4-methoxybenzene

Prepared according to GP 2 at room temperature. The title product was obtained after purification by column chromatography (n-pentane) as a white solid (59.0 mg, 0.252 mmol, 84%).

Rf = 0.30 (n-pentane). 1H NMR (600 MHz, CDCl3) δ/ ppm = 7.56 (d, J = 9.0 Hz, 2H), 6.68 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H). 13C NMR (151 MHz, CDCl3) δ/ ppm = 159.6, 138.3, 116.5, 82.8, 55.4. HRMS (EI) calculated for C7H7OI: 233.9536 [M]+, found: 233.9544.

These data are in agreement with those reported previously in the literature.[6]

1-Iodo-2-methoxybenzene

Prepared according to GP 2 at room temperature. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (66.2 mg, 0.283 mmol, 94%).

Rf = 0.46 (n-pentane). 1H NMR (600 MHz, CDCl3) δ/ ppm = 7.77 (dd, J = 7.8, 1.6 Hz, 1H), 7.31 (ddd, J = 8.7, 7.4, 1.6 Hz, 1H), 6.83 (dd, J = 8.1, 1.3 Hz, 1H), 6.71 (ddd, J = 7.4, 7.4, 1.3 Hz, 1H), 3.88 (s, 3H). 13C NMR (151 MHz, CDCl3) δ/ ppm = 158.2, 139.6, 129.7, 122.6, 111.1, 86.1, 56.4. HRMS (EI) calculated for C7H7OI: 233.9536 [M]+, found: 233.9530.

These data are in agreement with those reported previously in the literature.[3]
2-Iodo-1,3,5-trimethylbenzene

Prepared according to GP 2 at room temperature. The title product was obtained after purification by column chromatography (n-pentane) as a white solid (54.4 mg, 0.221 mmol, 72%).

Rf = 0.77 (n-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 6.89 (s, 2H), 2.43 (s, 6H), 2.24 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 141.9, 137.5, 128.1, 104.4, 29.6, 20.8. HRMS (EI) calculated for C₉H₁₁I: 245.9900 [M]+, found: 245.9900.

These data are in agreement with those reported previously in the literature.[³]

2-Iodo-1,3-dimethoxybenzene

Prepared according to GP 2 at room temperature. The title product was obtained after purification by column chromatography (n-pentane/Et₂O, 7:1) as a yellow solid (74.7 mg, 0.283 mmol, 93%).

Rf = 0.61 (n-pentane/Et₂O, 7:1). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 7.27 (td, J = 8.1, 1.4 Hz, 1H), 6.52 (dd, J = 8.1, 1.4 Hz, 2H), 3.90 (d, J = 1.4 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 159.7, 130.0, 104.2, 77.8, 56.7. HRMS (EI) calculated for C₇H₆O₂I: 248.9407 [M-Me]+, found: 248.9403.

These data are in agreement with those reported previously in the literature.[⁵]

1,4-Diiodobenzene

Prepared according to GP 2 at 50 °C; reaction time 24 h. The title product was obtained after purification by column chromatography (n-pentane) as a white solid (94.3 mg, 0.286 mmol, 96%).

Rf = 0.76 (n-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 7.41 (s, 4H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 139.5, 93.5. HRMS (EI) calculated for C₆H₄I₂: 329.8397 [M]+, found: 329.8398.

These data are in agreement with those reported previously in the literature.[¹¹]

1-Iodo-4-bromobenzene

Prepared according to GP 2 at 50 °C; reaction time 24 h. The title product was obtained after purification by column chromatography (pentane) as a white solid (81.3 mg, 0.287 mmol, 96%).

Rf = 0.90 (n-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 7.54 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 139.2, 133.6, 122.3, 92.2. HRMS (EI) calculated for C₆H₄BrI: 281.8536 [M]+, found: 281.8522.
These data are in agreement with those reported previously in the literature.\textsuperscript{[11]}

1-Iodo-4-chlorobenzene

\[
\begin{align*}
\text{Cl} & \quad \text{I} \\
\end{align*}
\]
Prepared according to GP 2 at 50 °C; reaction time 24 h. The title product was obtained after purification by column chromatography (n-pentane) as a white solid (52.0 mg, 0.218 mmol, 73%).

\( R_f = 0.79 \) (pentane). \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \( \delta \) ppm = 7.61 (d, \( J = 8.6 \) Hz, 2H), 7.09 (d, \( J = 8.6 \) Hz, 2H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \( \delta \) ppm = 138.9, 134.4, 130.7, 91.3. HRMS (EI) calculated for C\textsubscript{6}H\textsubscript{4}I:\textsubscript{35}Cl: 237.9041 \([M]+\), found: 237.9044.

These data are in agreement with those reported previously in the literature.\textsuperscript{[11]}

1-Iodo-4-fluorobenzene

\[
\begin{align*}
\text{F} & \quad \text{I} \\
\end{align*}
\]
Prepared according to GP 2 at 50 °C; reaction time 24 h. The yield was determined by quantitative \textsuperscript{1}H NMR (79%).

\textsuperscript{1}H NMR (600 MHz, DMF-d\textsubscript{7}) \( \delta \) ppm = 7.85 – 7.79 (m, 2H), 7.11 (dd, \( J = 8.3 \) Hz, 2H). \textsuperscript{13}C NMR (151 MHz, DMF-d\textsubscript{7}) \( \delta \) ppm = 163.02 (d), 139.60 (d, \( J = 8.0 \) Hz), 127.20, 118.19 (d, \( J = 22.2 \) Hz). \textsuperscript{19}F NMR (564 MHz, DMF-d\textsubscript{7}) \( \delta \) ppm = -115.6. MS (70 eV, EI): \( m/z \) (%): 221.9 (100), 126.9 (19), 95.0 (58), 75.0 (35), 74.0 (10).

Due to its high volatility, the title compound was not isolated.

4-Iodo-3,5-dimethylisoxazole

\[
\begin{align*}
\text{Me} & \quad \text{N} & \quad \text{I} \\
\end{align*}
\]
Prepared according to GP 2 at 50 °C; reaction time 24 h. The yield was determined by quantitative \textsuperscript{1}H NMR (97%).

\textsuperscript{1}H NMR (600 MHz, DMF-d\textsubscript{7}) \( \delta \) ppm = 2.45 (s, 3H), 2.22 (s, 3H). MS (70 eV, EI): \( m/z \) (%): 223.0 (100) \([M]+\), 207.9 (20), 180.9 (31), 179.98 (14), 153.9 (11), 126.9 (37), 96.0 (25), 81.0 (14), 63.0 (12), 54.0 (44), 52.0 (15).

Due to its high volatility, the title compound was not isolated. The resolution of the NMR made it impossible to assign the correct \textsuperscript{13}C NMR shifts.
**3-Iodobenzo[b]thiophene**

Prepared according to GP 2 at room temperature. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (70.8 mg, 0.272 mmol, 91%).

$R_f = 0.80$ (n-pentane). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$/ ppm = 7.86 (d, $J = 8.2$ Hz, 1H), 7.77 (dd, $J = 8.2$ Hz, 1H), 7.62 (s, 1H), 7.48 (dd, $J = 7.2$ Hz, 1H), 7.40 (dd, $J = 7.2$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$/ ppm = 140.4, 138.5, 129.3, 125.4, 125.3, 122.6, 78.4. HRMS (EI) calculated for C$_8$H$_5$I:S: 259.9151 [M]$^+$, found: 259.9149.

These data are in agreement with those reported previously in the literature.$^{[10]}$ 1 C atom missing in the $^{13}$C NMR. This is in line with literature reports.

**2-Iodothiophene**

Prepared according to GP 2 at room temperature. The yield was determined by quantitative $^1$H NMR (97%).

$^1$H NMR (600 MHz, DMF-d$_7$) $\delta$/ ppm = 7.71 (dd, $J = 5.4$, 1.2 Hz, 1H), 7.39 (dd, $J = 3.6$, 1.2 Hz, 1H), 6.92 (dd, $J = 5.4$, 3.6 Hz, 1H). $^{13}$C NMR (151 MHz, DMF-d$_7$) $\delta$/ ppm = 156.9, 138.3, 133.4, 130.4. MS (70 eV, EI): m/z (%): 209.9 (100) [M]$^+$, 126.9 (21), 83.0 (27), 57 (12).

Due to its high volatility, the title compound was not isolated.

**3-Iodothiophene**

Prepared according to GP 2 at room temperature. The yield was determined by quantitative $^1$H NMR (97%).

$^1$H NMR (600 MHz, DMF-d$_7$) $\delta$/ ppm = 7.86 – 7.80 (m, 1H), 7.61 – 7.55 (m, 1H), 7.23 (dd, $J = 5.0$, 1.2 Hz, 1H). $^{13}$C NMR (151 MHz, DMF-d$_7$) $\delta$/ ppm = 156.9, 135.9, 130.5, 129.6. MS (70 eV, EI): m/z (%): 209.9 (100) [M]$^+$, 126.9 (10), 83.0 (21).

Due to its high volatility, the title compound was not isolated.
Supporting Information

Synthesis of Aryl Germanes

**General Procedure 3 (GP 3)**

Triethylgermanium chloride (1.05 equiv.) and the corresponding aryl iodide or aryl bromide (1.0 equiv.) were dissolved in anhydrous and degassed THF (0.2 M) under argon, iPrMgCl (1.2 M in THF; 1.2 equiv.) was added slowly and the reaction was stirred for 3 h at room temperature (ArI) or for 12 h at 60 °C (ArBr). The reaction was quenched by addition of aqueous solution of NH₄Cl (sat.), the organic phase was separated and the aqueous phase was extracted with DCM (3x). The combined organic phases were dried over MgSO₄, the solvent was removed under reduced pressure and the crude product mixture was purified by silica column chromatography.

**General Procedure 4 (GP 4)**

Triethylgermanium chloride (1.0 equiv.) and the corresponding aryl Grignard reagent (1.1 equiv.) were dissolved in anhydrous and degassed THF (0.2 M) under argon and stirred for 3 h at room temperature. The reaction was quenched by addition of aqueous solution of NH₄Cl (sat.), the organic phase was separated and the aqueous phase was extracted with DCM (3x). The combined organic phases were dried over MgSO₄, the solvent was removed under reduced pressure and the crude product mixture was purified by silica column chromatography.

*Note: Our group meanwhile developed a formal C-H germylation strategy. Synthesis from pre-functionalized arenes (as followed herein) is hence not strictly necessary.*
Triethyl(phenyl)germane

Prepared according to GP 2. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (629 mg, 2.65 mmol, 89%).

\( R_f = 0.90 \) (n-pentane). \( ^1H \text{ NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) ppm = 7.45 (dd, \( J = 7.6, 1.8 \) Hz, 2H), 7.37 - 7.30 (m, 3H), 1.12 - 1.03 (m, 9H), 1.03 - 0.95 (m, 6H). \( ^{13}C \text{ NMR} \) (151 MHz, CDCl\(_3\)) \( \delta \) ppm = 140.0, 134.1, 128.2, 128.0, 9.1, 4.3. \( \text{HRMS (EI)} \) calculated for C\(_{12}\)H\(_{20}\)Ge: 238.0771 [M]+, found: 238.0772.

IR (neat): \( \nu /\text{cm}^{-1} = 3061 \) (m), 2948 (s), 2873 (m), 2332 (w), 1458 (m), 1429 (m), 1378 (w), 1304 (w), 1230 (w), 1091 (m), 1014 (s), 966 (m), 695 (s).

These data are in agreement with those reported previously in the literature.[12]

Triethyl(p-tolyl)germane

Prepared according to GP 4. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (575 mg, 2.29 mmol, 76%).

\( R_f = 0.85 \) (pentane). \( ^1H \text{ NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) ppm = 7.35 (d, \( J = 7.6 \) Hz, 2H), 7.18 (d, \( J = 7.6 \) Hz, 2H), 2.36 (s, 3H), 2.36 (s, 3H), 1.11 - 1.03 (m, 9H), 1.01 - 0.95 (m, 6H). \( ^{13}C \text{ NMR} \) (151 MHz, CDCl\(_3\)) \( \delta \) ppm = 137.8, 136.0, 133.9, 128.7, 21.4, 8.9, 4.2. \( \text{HRMS (EI)} \) calculated for C\(_{12}\)H\(_{22}\)Ge: 252.0933 [M]+, found: 252.0926.

IR (neat): \( \nu /\text{cm}^{-1} = 3016 \) (m), 2945 (s), 2732 (w), 2328 (m), 2087 (w), 1897 (m), 1738 (w), 1599 (w), 1455 (s), 1384 (m), 1228 (w), 1188 (w), 1086 (m), 1014 (s), 965 (m), 794 (s), 697 (s).

These data are in agreement with those reported previously in the literature.[12]

Triethyl(4-fluorophenyl)germane

Prepared according to GP 4. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (732 mg, 2.87 mmol, 96%).

\( R_f = 0.85 \) (n-pentane). \( ^1H \text{ NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) ppm = 7.39 (dd, \( J = 7.9, 1.6 \) Hz, 2H), 7.05 (dd, \( J = 8.8, 8.8 \) Hz, 2H), 1.12 - 1.01 (m, 9H), 1.01 - 0.92 (m, 6H). \( ^{13}C \text{ NMR} \) (151 MHz, CDCl\(_3\)) \( \delta \) ppm = 163.4 (d, \( J = 246.4 \) Hz), 135.7 (d, \( J = 6.9 \) Hz), 135.0 (d, \( J = 3.7 \) Hz), 115.1 (d, \( J = 19.1 \) Hz), 9.6, 4.4. \( ^{19}F \text{ NMR} \) (564 MHz, CDCl\(_3\)) \( \delta \) ppm = -113.75 - -113.84 (m). \( \text{HRMS (EI)} \) calculated for C\(_{12}\)H\(_{19}\)F\(_7\)Ge: 256.0683 [M]+, found: 256.0673. IR (neat): \( \nu /\text{cm}^{-1} = 3029 \) (m), 2949 (s), 2875 (m), 2332 (w), 2162 (w), 2092 (w), 1890 (w), 1752 (w), 1636 (w), 1584 (s), 1495 (s), 1459 (m), 1380 (w), 1304 (w), 1226 (s), 1160 (s), 1082 (m), 1014 (s), 965 (m), 816 (s), 698 (s).

These data are in agreement with those reported previously in the literature.[12]
Triethyl(4-methoxyphenyl)germane

Prepared according to GP 4. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (785 mg, 2.94 mmol, 98%).

R_f = 0.42 (n-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 7.36 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 3.81 (s, 3H), 1.10 – 1.02 (m, 9H), 1.00 – 0.93 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 159.9, 135.2, 130.5, 113.8, 55.1, 9.1, 4.4. HRMS (EI) calculated for C₁₃H₂₂⁷⁴GeO: 268.0882 [M]+, found: 268.0890. IR (neat): ν/ cm⁻¹ = 2946 (s), 2326 (w), 2073 (w), 1887 (w), 1731 (w), 1590 (s), 1497 (s), 1457 (s), 1387 (w), 1276 (s), 1243 (s), 1178 (s), 1091 (s), 1024 (s), 964 (m), 810 (m), 697 (s).

These data are in agreement with those reported previously in the literature.[¹²]

Triethyl(thiophen-2-yl)germane

Prepared according to GP 4. The title product was obtained after purification by column chromatography (n-hexane/EtOAc, 5:1) as a colorless oil (589 mg, 2.43 mmol, 81%).

R_f = 0.91 (n-hexane/EtOAc, 5:1). ¹H NMR (400 MHz, CDCl₃) δ/ ppm = 7.59 (dd, J = 4.6, 0.9 Hz, 1H), 7.22 (dd, J = 4.6, 3.3 Hz, 1H), 7.18 (dd, J = 3.3, 0.9 Hz, 1H), 1.14 – 0.99 (m, 15H).

¹³C NMR (101 MHz, CDCl₃) δ/ ppm = 137.6, 133.4, 129.7, 127.9, 9.0, 5.7. HRMS (EI) calculated for C₁₀H₁₈⁷⁴GeS: 244.0336 [M]+, found: 244.0342. IR (neat): ν/ cm⁻¹ = 3070 (w), 2951 (s), 2907 (s), 2872 (s), 2330 (w), 2101 (w), 1593 (w), 1497 (w), 1458 (m), 1425 (m), 1404 (w), 1379 (w), 1323 (m), 1212 (m), 1078 (w), 1016 (s), 965 (s), 846 (m), 823 (m), 746 (w), 698 (s).

These data are in agreement with those reported previously in the literature.[¹²]

Triethyl(4-iodophenyl)germane

Prepared according to GP 3. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (963 mg, 2.65 mmol, 88%).

R_f = 0.90 (n-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 7.67 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 1.09 – 1.01 (m, 9H), 1.01 – 0.93 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 139.4, 137.0, 135.9, 95.0, 9.0, 4.2. HRMS (EI) calculated for C₁₂H₁₉⁷⁴GeI: 363.9738 [M]+, found: 363.9744. IR (neat): ν/ cm⁻¹ = 3060 (w), 2948 (s), 2872 (s), 2734 (w), 2329 (w), 2097 (w), 1900 (w), 1741 (w), 1631 (w), 1561 (m), 1463 (m), 1426 (m), 1372 (m), 1228 (w), 1051 (w), 1014 (s), 966 (m), 797 (s), 696 (s).
These data are in agreement with those reported previously in the literature.[13]

**Triethyl(4-bromophenyl)germane**

Prepared according to GP 3. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (820 mg, 2.61 mmol, 87%).

\[ R_f = 0.90 \text{ (n-pentane).} \]

\[ {^1}H \text{ NMR (600 MHz, CDCl}_3\text{)} \delta/\text{ppm} = 7.47 \text{ (d, } J = 8.1 \text{ Hz, 2H), 7.29 (d, } J = 8.1 \text{ Hz, 2H), 1.09 - 1.01 \text{ (m, 9H), 1.01 - 0.94 \text{ (m, 6H).}} \]

\[ {^{13}}C \text{ NMR (151 MHz, CDCl}_3\text{)} \delta/\text{ppm} = 138.8, 135.7, 131.1, 123.0, 9.0, 4.3. \]

HRMS (EI) calculated for C\(_{12}\)H\(_{19}\)Br\(_7\)Ge: 315.9882 \([M]^+\), found: 315.9867.

IR (neat): \(\nu/\text{cm}^{-1} = 3068 \text{ (w), 2949 \text{ (s), 2872 \text{ (s), 2328 \text{ (w), 2113 \text{ (w), 1993 \text{ (w), 1900 \text{ (w), 1742 \text{ (w), 1633 \text{ (w), 1566 \text{ (m), 1464 \text{ (s), 1427 \text{ (m), 1374 \text{ (m), 1228 \text{ (w), 1091 \text{ (w), 866 \text{ (m), 801 \text{ (s), 701 \text{ (s).}}} \]

These data are in agreement with those reported previously in the literature.[13]

**3,5-Dimethyl-4-(triethylgermyl)isoxazole**

Prepared according to GP 3. The title product was obtained after purification by column chromatography (DCM) as a colorless oil (638 mg, 2.49 mmol, 83%).

\[ R_f = 0.83 \text{ (DCM).} \]

\[ {^1}H \text{ NMR (400 MHz, CDCl}_3\text{)} \delta/\text{ppm} = 2.36 \text{ (s, 3H), 2.23 \text{ (s, 3H), 1.08 - 0.94 \text{ (m, 15H).}} \]

\[ {^{13}}C \text{ NMR (101 MHz, CDCl}_3\text{)} \delta/\text{ppm} = 173.0, 163.8, 105.2, 13.2, 12.8, 8.9, 4.7. \]

HRMS (EI) calculated for C\(_{11}\)H\(_{21}\)GeNO\(_2\)Na: 280.0727 \([M+Na]^+\), found: 280.0725.

IR (neat): \(\nu/\text{cm}^{-1} = 3467 \text{ (w), 2953 \text{ (s), 2873 \text{ (s), 2735 \text{ (w), 2184 \text{ (w), 1578 \text{ (s), 1457 \text{ (s), 1397 \text{ (s), 1351 \text{ (s), 1239 \text{ (m), 1093 \text{ (m), 1014 \text{ (s), 971 \text{ (m), 901 \text{ (w), 803 \text{ (w), 754 \text{ (m), 705 \text{ (s), 579 \text{ (s).}}} \]

**Triethyl(4-chlorophenyl)germane**

Prepared according to GP 3. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (797 mg, 2.94 mmol, 98%).

\[ R_f = 0.87 \text{ (n-pentane).} \]

\[ {^1}H \text{ NMR (600 MHz, CDCl}_3\text{)} \delta/\text{ppm} = 7.36 \text{ (d, } J = 8.2 \text{ Hz, 2H), 7.31 (d, } J = 8.2 \text{ Hz, 2H), 1.08 - 1.02 \text{ (m, 9H), 1.01 - 0.94 \text{ (m, 6H).}} \]

\[ {^{13}}C \text{ NMR (151 MHz, CDCl}_3\text{)} \delta/\text{ppm} = 138.2, 135.4, 134.5, 128.2, 9.0, 4.3. \]

HRMS (EI) calculated for C\(_{12}\)H\(_{19}\)Cl\(_3\)Ge: 272.0387 \([M]^+\), found: 272.0385.

IR (neat): \(\nu/\text{cm}^{-1} = 3070 \text{ (w), 2949 \text{ (s), 2873 \text{ (s), 2332 \text{ (w), 2150 \text{ (w), 2091 \text{ (w), 2030 \text{ (w), 1900 \text{ (w), 1637 \text{ (w), 1572 \text{ (m), 1468 \text{ (s), 1428 \text{ (m), 1378 \text{ (m), 1304 \text{ (w), 1229 \text{ (w), 1075 \text{ (s), 1012 \text{ (s), 966 \text{ (m), 806 \text{ (s), 699 \text{ (s).}}} \]

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These data are in agreement with those reported previously in the literature.[13]

**Triethyl(2-methoxyphenyl)germane**

Prepared according to GP 3. The title product was obtained after purification by column chromatography (n-pentane) as a colorless oil (689 mg, 2.58 mmol, 86%).

$R_f = 0.68$ (n-pentane). \( ^1H \text{ NMR} \) (600 MHz, CDCl\(_3\)) $\delta$/ ppm = 7.34 – 7.29 (m, 2H), 6.95 (dd, $J = 7.2, 7.2$ Hz, 1H), 6.83 (d, $J = 8.4$ Hz, 1H), 3.79 (s, 3H), 1.09 – 0.97 (m, 15H). \( ^{13}C \text{ NMR} \) (151 MHz, CDCl\(_3\)) $\delta$/ ppm = 163.6, 135.3, 129.9, 127.7, 120.6, 109.5, 55.1, 9.2, 4.7. \( \text{HRMS (EI)} \) calculated for $C_{13}H_{22}74GeO$: 268.0882 [M]+, found: 268.0873. \( \text{IR (neat)} \): $\nu$/ cm\(^{-1}\) = 2945 (s), 2871 (m), 2834 (m), 2331 (w), 2159 (w), 1739 (w), 1578 (s), 1458 (s), 1427 (s), 1235 (s), 1169 (w), 1014 (m), 966 (w), 840 (w), 769 (s), 707 (s). These data are in agreement with those reported previously in the literature.[14]

**Triethyl(mesityl)germane**

Prepared according to GP 3. The title product was obtained after purification by column chromatography (DCM) as a colorless oil (839 mg, 3.00 mmol, 99%).

$R_f = 0.99$ (DCM). \( ^1H \text{ NMR} \) (600 MHz, CDCl\(_3\)) $\delta$/ ppm = 6.81 (s, 2H), 2.38 (s, 6H), 2.25 (s, 3H), 1.14 – 1.07 (m, 6H), 1.07 – 1.02 (m, 9H). \( ^{13}C \text{ NMR} \) (151 MHz, CDCl\(_3\)) $\delta$/ ppm = 144.4, 137.8, 134.2, 128.8, 24.5, 21.0, 9.4, 8.0. \( \text{HRMS (EI)} \) calculated for $C_{15}H_{26}74Ge$: 280.1241 [M]+, found: 280.1241. \( \text{IR (neat)} \): $\nu$/ cm\(^{-1}\) = 3468 (w), 2952 (s), 2871 (s), 2730 (w), 2395 (w), 2182 (w), 1720 (w), 1603 (m), 1550 (m), 1456 (s), 1381 (s), 1288 (w), 1236 (w), 1011 (s), 970 (m), 846 (m), 706 (s), 569 (s).

**Triethyl(3,4,5-trimethoxyphenyl)germane**

Prepared according to GP 3. The title product was obtained after purification by column chromatography (n-pentane/Et\(_2\)O 5:1) as a yellow oil (970 mg, 2.97 mmol, 99%).

$R_f = 0.64$ (n-pentane/Et\(_2\)O 5:1). \( ^1H \text{ NMR} \) (600 MHz, CDCl\(_3\)) $\delta$/ ppm = 6.61 (s, 2H), 3.88 (s, 6H), 3.86 (s, 3H), 1.08 (t, $J = 8.4$ Hz, 9H), 1.02 – 0.95 (m, 6H). \( ^{13}C \text{ NMR} \) (151 MHz, CDCl\(_3\)) $\delta$/ ppm = 153.1, 138.4, 135.1, 110.5, 60.9, 56.3, 9.1, 4.5. \( \text{HRMS (EI)} \) calculated for $C_{15}H_{32}74GeO_3$: 351.0986 [M+Na]+, found: 351.0996. \( \text{IR (neat)} \): $\nu$/ cm\(^{-1}\) = 2945 (s), 2833 (w), 1735 (w), 1570 (s), S19.
Triethyl(naphthalen-1-yl)germane

Prepared according to GP 3. The title product was obtained after purification by column chromatography (n-hexane) as a colorless oil (743 mg, 2.59 mmol, 86%). 

IR (neat): ν/cm⁻¹ = 3850 (w), 3052 (m), 2948 (s), 2872 (s), 2731 (w), 2660 (w), 2325 (m), 2103 (w), 1994 (w), 1930 (w), 1809 (w), 1588 (w), 1504 (m), 1457 (m), 1379 (m), 1322 (w), 1221 (w), 1138 (m), 1013 (s), 967 (s), 855 (w), 785 (s), 701 (s).

These data are in agreement with those reported previously in the literature.[12]

Triethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)germane

Triethyl(4-iodophenyl)germane (1.09 g, 3.0 mmol, 1.0 equiv.) was added to a round bottom flask and dissolved in anhydrous and degassed THF (20 mL) under argon. iPrMgCl (2.0 M in THF, 1.8 mL, 3.6 mmol, 1.2 equiv.) was added dropwise at 0 °C and the reaction was stirred for 30 min. Tris isoproplylborate (1.0 M in THF, 3.3 mL, 3.3 mmol, 1.2 equiv.) was added and the reaction was stirred at room temperature for 12 h. The solvent was removed in vacuo and anhydrous toluene (20 mL) and pinacol (1.42 g, 12.0 mmol, 4.0 equiv.) were added. The reaction was stirred for 8 h under reflux. It was quenched by addition of aqueous solution of NH₄Cl (sat.), the organic phase was separated and the aqueous phase was extracted with DCM (3x20 mL). The combined organic phases were dried over MgSO₄ and the solvent was removed under reduced pressure. The title product was obtained after purification by column chromatography (n-hexane/EtOAc, 50:1) as a white solid (496 mg, 1.34 mmol, 45%). 

IR (neat): ν/cm⁻¹ = 3057 (w), 2953 (m), 2875 (m), 1597 (m), 1503 (w), 1459 (w), 1355 (s), 1298 (m), 1270 (w), 1212 (w), 1143 (s), 1107 (w), 1064 (s), 1017 (m), 962 (m), 857 (s), 818 (m), 736 (w), 696 (s), 659 (m).
These data are in agreement with those reported previously in the literature.[12]

**Trimethyl(4-(triethylgermyl)phenyl)silane**

Triethyl(4-iodophenyl)germane (1.09 g, 3.0 mmol, 1.0 equiv.) was added to a round bottom flask and dissolved in anhydrous and degassed THF (20 mL) under argon. iPrMgCl (2.0 M in THF, 1.8 mL, 3.6 mmol, 1.2 equiv.) was added dropwise at 0 °C and the reaction was stirred for 30 min. Tetramethyl orthosilicate (899 μL, 6.0 mmol, 2.0 equiv.) was added and the mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of aqueous solution of NH₄Cl (sat.), the organic phase was separated and the aqueous phase was extracted with DCM (3x20 mL). The combined organic phases were dried over MgSO₄ and the solvent was removed under reduced pressure. The title product was obtained after purification by column chromatography (n-hexane) as a colorless oil (576 mg, 1.86 mmol, 62%).

Rᵣ = 0.89 (n-hexane). **¹H NMR** (600 MHz, CDCl₃) δ/ ppm = 7.49 (d, J = 7.7 Hz, 2H), 7.43 (d, J = 7.7 Hz, 2H), 1.10 – 1.04 (m, 9H), 1.02 – 0.94 (m, 6H), 0.26 (s, 9H). **¹³C NMR** (151 MHz, CDCl₃) δ/ ppm = 141.1, 137.9, 133.6, 133.5, 9.1, 4.3, -2.3. **HRMS (EI)** calculated for C₁₂H₂₈Si₇₄Ge: 310.1172 [M]⁺, found: 310.1180. **IR** (neat): ν/cm⁻¹ = 3048 (w), 2951 (s), 2873 (m), 2328 (w), 2113 (w), 1991 (w), 1914 (w), 1584 (w), 1458 (m), 1426 (w), 1377 (m), 1247 (s), 1122 (m), 1014 (m), 967 (m), 839 (s), 800 (m), 754 (m), 697 (s).

These data are in agreement with those reported previously in the literature.[12]

**Triethyl(4-(tributylstannyl)phenyl)germane**

Triethyl(4-iodophenyl)germane (276 mg, 0.76 mmol, 1.0 equiv.) was added to a round bottom flask and dissolved in anhydrous and degassed THF (3 mL) under argon. nBuLi (2.5 M in toluene, 0.46 mL, 1.14 mmol, 1.5 equiv.) was added dropwise at -78 °C and the reaction was stirred for 30 min. Tributyltin chloride (227 μL, 0.836 mmol, 1.1 equiv.) was added and the mixture was stirred while warming to room temperature for 12 h. The reaction was quenched by addition of aqueous solution of NH₄Cl (sat.), the organic phase was separated and the aqueous phase was extracted with DCM (3x20 mL). The combined organic phases were dried over MgSO₄ and the solvent was removed under reduced pressure. The title product was obtained after purification by column chromatography (n-hexane) as a colorless oil (132 mg, 0.251 mmol, 33%).

Rᵣ = 0.90 (n-hexane). **¹H NMR** (600 MHz, CDCl₃) δ/ ppm = 7.45 – 7.42 (m, 2H), 7.41 – 7.37 (m, 2H), 1.59 – 1.52 (m, 9H), 1.38 – 1.30 (m, 6H), 1.10 – 1.03 (m, 15H), 1.02 – 0.96 (m, 6H), 0.90 (t, J = 7.4 Hz,
9H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$/ ppm = 141.9, 139.5, 136.1, 133.6, 29.3, 27.6, 13.8, 9.7, 9.1, 4.3. MS (70 eV, EI): $m/\text{z}$ (%): 473.1 (14), 472.0 (10), 471.1 (40), 470.1 (25) [M-Et]+, 469.1 (50), 468.1 (27), 467.1 (46), 466.1 (16), 465.1 (22), 415.0 (11), 413.0 (13), 411.0 (12), 360.9 (13), 358.9 (36), 358 (19), 356.9 (48), 355.9 (24), 355 (50), 353.9 (14), 352.9 (26), 350.9 (11), 270.8 (12), 268.8 (13), 266.8 (12), 211.0 (12), 209.0 (54), 208.0 (28), 207.0 (100), 205.0 (26), 196.9 (12), 194.9 (10), 192.9 (19), 191.9 (131), 190.9 (18), 163.9 (12), 162.8 (15), 154.9 (12), 152.9 (59), 151.9 (19), 150.9 (79), 149.9 (24), 148.9 (66), 148.0 (11), 146.9 (29), 135.0 (11), 132.9 (10), 73.0 (15).

**Triethyl(thiophen-3-yl)germane**

Prepared according to GP 3. The title product was obtained after purification by column chromatography (DCM) as a colorless oil (625 mg, 2.57 mmol, 86%). $R_t = 0.95$ (DCM). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ ppm = 7.41 (dd, $J = 4.8$, 2.6 Hz, 1H), 7.33 (dd, $J = 2.6$, 1.1 Hz, 1H), 7.14 (dd, $J = 4.8$, 1.1 Hz, 1H), 1.12 – 1.03 (m, 9H), 1.03 – 0.93 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ ppm = 138.4, 131.7, 129.9, 125.2, 9.1, 5.0. HRMS (EI) calculated for C$_{19}$H$_{18}$GeS: 244.0336 [M]+; found: 244.0335. IR (neat): $\nu$/ cm$^{-1} = 3063$ (w), 2950 (s), 2907 (s), 2872 (s), 2829 (m), 2733 (w), 2327 (w), 2169 (w), 2099 (w), 1755 (w), 1570 (w), 1458 (s), 1426 (m), 1375 (m), 1337 (w), 1229 (w), 1199 (m), 1089 (s), 1015 (s), 967 (m), 846 (s), 798 (w), 765 (s), 695 (s).

These data are in agreement with those reported previously in the literature.\[12\]

**Benzo[b]thiophen-3-yltriethylgermane**

Prepared according to GP 3. The title product was obtained after purification by column chromatography (DCM) as a colorless oil (638 mg, 2.49 mmol, 83%). $R_t = 0.83$ (DCM). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ ppm = 7.98 – 7.92 (m, 1H), 7.89 – 7.84 (m, 1H), 7.42 (s, 1H), 7.40 – 7.30 (m, 2H), 1.20 – 1.05 (m, 15H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ ppm = 144.0, 141.4, 131.7, 125.4, 124.5, 124.0, 123.9, 122.8, 9.2, 5.1. HRMS (EI) calculated for C$_{21}$H$_{20}$GeS: 294.0497 [M]+; found: 294.0492. IR (neat): $\nu$/ cm$^{-1} = 3057$ (w), 2950 (s), 2907 (s), 2871 (s), 2828 (w), 2733 (w), 2329 (w), 2086 (w), 1571 (w), 1455 (s), 1415 (s), 1379 (m), 1307 (m), 1253 (m), 1172 (w), 1134 (w), 1062 (m), 1015 (s), 966 (m), 938 (m), 850 (w), 810 (m), 782 (m), 752 (s), 725 (s), 699 (s).
(2,6-Dimethoxyphenyl)triethylgermane

Prepared according to GP 3. The title product was obtained after purification by column chromatography (n-hexane) as a colorless oil (451 mg, 1.52 mmol, 51%).

Rf = 0.35 (n-hexane). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 7.24\) (t, \(J = 8.1\) Hz, 1H), 6.49 (d, \(J = 8.1\) Hz, 2H), 3.74 (s, 6H), 1.06 – 0.98 (m, 15H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 165.0, 130.6, 114.4, 103.4, 55.3, 9.4, 6.7\). HRMS (ESI) calculated for C\(_{14}\)H\(_{24}\)GeO\(_2\): 299.1061 [M+H]\(^+\), found: 299.1054. IR (neat): \(\nu/\text{cm}^{-1} = 3085\) (w), 2946 (m), 2870 (m), 2833 (w), 2329 (w), 1578 (s), 1458 (s), 1426 (s), 1376 (w), 1297 (w), 1236 (s), 1171 (w), 1020 (s), 1013 (m), 970 (w), 837 (w), 770 (s), 742 (m), 709 (s).
Supporting Information

Halolabeling of Physiologically Relevant Target Molecule

**tert-Butyl[(Z)-[(3-iodobenzyl)amino][(tert-butoxycarbonyl)amino]methylidene} carbamate**

3-Iodobenzylamine hydrochloride (472 mg, 1.75 mmol, 1.0 equiv.) and NEt₃ (0.97 mL, 7.00 mmol, 4.0 equiv.) were dissolved in DCM (17.5 mL) and stirred for 5 minutes. N,N'-bis(tert-butoxycarbonyl)-N''- triflylguanidine (685 mg, 1.75 mmol, 1.0 equiv.) was added and the reaction was stirred for further 30 minutes. The solvent was removed in vacuo, H₂O was added and the organic phase was separated. After extracting the aqueous phase with DCM (3x), the combined organic layers were washed with water and brine before drying over MgSO₄. The solvent was removed in vacuo to give the title product as a white solid (827 mg, 1.74 mmol, 99%).

**1H NMR** (600 MHz, CDCl₃) δ/ ppm = 11.53 (s, 1H), 8.58 (s, 1H), 7.66 (s, 1H), 7.64 – 7.59 (m, 1H), 7.30 – 7.24 (m, 1H), 7.08 (dd, J = 7.8 Hz, 1H), 4.57 (d, J = 5.3 Hz, 2H), 1.51 (s, 9H), 1.49 (s, 9H).

**13C NMR** (151 MHz, CDCl₃) δ/ ppm = 163.7, 156.3, 153.3, 139.9, 137.1, 136.9, 130.6, 127.2, 94.7, 83.5, 79.7, 44.2, 28.4, 28.2. **HRMS** (ESI) calculated for C₁₆H₂₆I₃O₄Na: 498.0860 [M+Na]⁺, found: 498.0852.

These data are in agreement with those reported previously in the literature.[15]

**tert-Butyl-N-[(1Z)-bis[(tert-butoxycarbonyl)amino][(tert-butoxycarbonyl)[(3-iodophenyl) methyl]amino}methylidene] carbamate**

Di-tert-butyl dicarbonate (1.50 g, 6.68 mmol, 4.0 equiv.), dimethyl amino pyridine (612 mg, 5.01 mmol, 3.0 equiv.), NEt₃ (0.93 mL, 6.68 mmol, 4.0 equiv.) and tert-butyl [(Z)-[(3-iodobenzyl) amino][[(tert-butoxy-carbonyl)amino} methylidene] carbamate (794 mg, 1.67 mmol, 1.0 equiv.) were dissolved in THF (25 mL) and stirred for 17 h at room temperature. The solvent was
removed in vacuo and the title product was purified by column chromatography (n-pentane/EtOAc 7:1 to 4:1) as a colorless oil (801 mg, 1.19 mmol, 71%).

\[ R_f = 0.13 \] (n-pentane/EtOAc 9:1). 1H NMR (600 MHz, CDCl₃) δ/ ppm = 7.74 (s, 1H), 7.58 (d, \( J = 7.9 \) Hz, 1H), 7.39 (d, \( J = 7.8 \) Hz, 1H), 7.02 (dd, \( J = 7.8 \) Hz, 1H), 4.96 (s, 2H), 1.49 (s, 9H), 1.46 (s, 18H), 1.41 (s, 9H). 13C NMR (151 MHz, CDCl₃) δ/ ppm = 157.4, 151.2, 147.4, 144.5, 140.0, 136.9, 136.4, 130.1, 127.4, 94.1, 84.2, 83.9, 82.2, 49.5, 28.1, 28.0, 71%.

HRMS (ESI) calculated for \( C_{28}H_{42}IN_3O_8Na \): 986.1909 \([M+Na]^+\), found: 698.1906.

These data are in agreement with those reported previously in the literature.[15]

**tert-Butyl-N-[[1Z]-[[[tert-butoxy)carbonyl]amino]([[tert-butoxy)carbonyl][3-(triethylgermanium)phenyl]methyl]amino)]methylidene]carbamate**

Prepared according to GP 3. The title product was obtained after purification by column chromatography (n-pentane/EtOAc 6:1 to 3:1) as a colorless oil (359 mg, 0.590 mmol, 50%).

\[ R_f = 0.45 \] (n-pentane/EtOAc 9:1). **M.p.** = 103-104 °C. 1H NMR (600 MHz, DMF-d7) δ/ ppm = 10.56 (s, 1H), 7.56 – 7.51 (m, 1H), 7.39 – 7.30 (m, 3H), 4.90 (s, 2H), 1.47 (s, 9H), 1.46 (s, 9H), 1.38 (s, 9H), 1.08 – 0.97 (m, 15H). 13C NMR (151 MHz, DMF-d7) δ/ ppm = 153.3, 150.9, 149.7, 139.4, 138.1, 133.4, 132.9, 128.0, 127.7, 82.9, 81.6, 79.5, 51.0, 27.9, 27.6, 8.8, 4.1. HRMS (ESI) calculated for \( C_{29}H_{49}O_6N_3GeK \): 648.2465 \([M+K]^+\), found: 648.2459.

**tert-Butyl{[Z][{3-bromobenzyl]amino}[[tert-butoxycarbonyl]amino]methylidene} carbamate ([Br]MIBG)**

Prepared according to GP 1 at 60°C for 2 h. The yield was determined by quantitative 1H NMR (95%). The title product was obtained by column chromatography (n-pentane/Et₂O 8:1 to 4:1) as a white solid (155 mg, 0.294 mmol, 81%).

\[ R_f = 0.31 \] (n-pentane/Et₂O 8:1 to 4:1). 1H NMR (600 MHz, CDCl₃) δ/ ppm = 10.67 (s, 1H), 7.54 (s, 1H), 7.36 (d, \( J = 8.0 \) Hz, 1H), 7.32 (d, \( J = 7.8 \) Hz, 1H), 7.16 (dd, \( J = 7.8 \) Hz, 1H), 4.97 (s, 2H), 1.50 (s, 18H), 1.37 (s, 9H). 13C NMR (151 MHz, CDCl₃) δ/ ppm = 153.3, 152.7, 140.4, 131.1, 130.3, 130.0, 126.6, 122.3, 84.0, 50.3, 28.2, 27.9. HRMS (ESI) calculated for \( C_{23}H_{34}BrN_3O_6Na \): 550.1523 [M+Na]^+, found: 550.1530.

Not all quaternary carbon atoms are fully visible in the 13C NMR analysis.
Performing the bromination according to GP 3 at 60 °C for 30 min yielded 95% of the title compound (quantified by 1H NMR analysis using ethylene carbonate as internal standard).
Performing the bromination according to GP 3 at 80 °C for 60 min with NaBr (10.3 mg, 0.1 mmol, 2.0 equiv.) and NCS (20.0 mg, 0.1 mmol, 2.0 equiv.) to form Br⁻ in situ yielded 78% of the title compound (quantified by 1H NMR analysis using ethylene carbonate as internal standard).

**tert-Butyl-N-[(1Z)-{bis-{(tert-butoxy)carbonyl}amino}{{(tert-butoxy)carbonyl}[(3-(triethylgermanium)-phenyl) methyl]amino}]methylidene]carbamate**

prepared according to GP 2 at 60°C for 1 h. The yield was determined by quantitative ¹H NMR (96%). The title product was obtained by column chromatography (n-pentane/EtOAc 7:1 to 4:1) as a colorless oil (57.2 mg, 0.085 mmol, 85%).

The characterization data matches the one previously reported in this manuscript (see S25).
Tolerance and Orthogonality of Halogenation Approaches

Tolerance of Aryl Iodides in Fluorination Approaches

![Chemical Reaction Diagram]

1-Iodo-4-methylbenzene (6.5 μL, 0.05 mmol, 1 equiv.), KF (5.8 mg, 0.10 mmol, 2 equiv.), copper(II) triflate (36.2 mg, 0.10 mmol, 2 equiv.) and 18-crown-6 (26.3 mg, 0.10 mmol, 2 equiv.) were dissolved in DMF (0.5 mL) and stirred for 12 h at 110 °C. The consumption of aryl iodide was determined by calibrated GC-MS analysis (using mesitylene as internal standard).

Compatibility of Functional Handles in Halogenation Approaches

To test the intermolecular tolerance of the SnBu$_3^-$- and B(OH)$_2$-site towards an established fluorination approach, tributyl(p-tolyl)stannane (19.1 mg, 0.05 mmol, 1 equiv.), p-tolylboronic acid (6.8 mg, 0.05 mmol, 1 equiv.), KF (2.9 mg, 0.05 mmol, 1 equiv.), cryptand[222] (18.8 mg, 0.05 mmol, 1 equiv.) and copper(II) triflate (8.5 mg, 0.0125 mmol, 0.25 equiv.) were dissolved in DMF-d$_7$ (0.3 mL) and stirred for 20 min at 110 °C. The reaction mixture was analyzed by quantitative $^1$H NMR (using 1,4-difluorobenzene as internal standard). The analysis revealed full consumption of both reaction partners.

To test the intermolecular tolerance of the SnBu$_3^-$- and B(OH)$_2$-site towards an established iodination approach, tributyl(p-tolyl)stannane (19.1 mg, 0.05 mmol, 1 equiv.), p-tolylboronic acid (6.8 mg, 0.05 mmol, 1 equiv.) and NIS (11.2 mg, 0.05 mmol, 1 equiv.) were dissolved in DMF-d$_7$ (0.3 mL) and stirred for 20 min at 110 °C. The reaction mixture was analyzed by quantitative $^1$H NMR (using 1,4-difluorobenzene as internal standard). The analysis revealed full consumption of aryl stannane and 38% consumption of aryl boronic acid.
Supporting Information

Tolerance of Functional Handles in Fluorination Approaches

To test the tolerance of the GeEt$_3$, SnBu$_3$, B(OH)$_2$, B(pin)- and SiMe$_3$-site towards established fluorination approaches, the corresponding starting materials (0.03 mmol, 1 equiv.) and the corresponding reagents (for details see Table S1) were dissolved in the DMF-$d_7$ and stirred under reaction conditions as specified. The procedures were adopted from literature.$^{[16]}$ The reaction mixtures were analyzed by calibrated GC-MS and quantitative $^1$H NMR (using mesitylene as internal standard). The results are shown in Table S1.

|                | GeEt$_3$ | SnBu$_3$ | B(OH)$_2$ | B(pin) | SiMe$_3$ |
|----------------|----------|-----------|-----------|--------|----------|
| **KF (2 equiv.)** |          |           |           |        |          |
| 18-crown-6 (2 equiv.) | 0%       | 100%      | 100%      | 20%    | 8%       |
| DMF-$d_7$; 110 °C, 1 h |          |           |           |        |          |
| **KF (2 equiv.)** |          |           |           |        |          |
| 18-crown-6 (2 equiv.) |         |           |           |        |          |
| [Cu(OTf)$_2$] (2 equiv.) | 1%       | 100%      | 100%      | 55%    | 12%      |
| DMF-$d_7$; 110 °C, 1 h |          |           |           |        |          |
| **Selectfluor (2 equiv.)** |          |           |           |        |          |
| DMF-$d_7$, 80 °C, 1 h | 2%       | 100%      | 100%      | 63%    | 22%      |
| **Selectfluor (2 equiv.)** |          |           |           |        |          |
| AgBF$_4$ (2 equiv.) |          |           |           |        |          |
| DMF-$d_7$, 80 °C, 1 h | 0%       | 100%      | 100%      | 82%    | 0%       |

Table S1: Consumption of functional handles in established fluorination approaches.

Consumption determined by calibrated GC-MS analysis or by quantitative $^1$H NMR analysis using mesitylene as internal standard.
Selective Fluorination of SnBu₃ vs. GeEt₃

Triethyl(4-(tributylstannyl)phenyl)germane (26.3 mg, 0.05 mmol, 1 equiv.), Selectfluor (17.7 mg, 0.05 mmol, 1 equiv.) and AgOTf (25.7 mg, 0.10 mmol, 2 equiv.) were dissolved in acetone (1 mL) and stirred for 20 min at rt. The solvent was removed in vacuo and the residue dissolved in hexane. The suspension was filtered over a plug of silica and concentrated in vacuo. The mixture was subsequently analyzed by quantitative ¹H and ¹⁹F NMR (using 1,4-difluorobenzene as internal standard). The analysis revealed full consumption of the starting material and 96% conversion to the desired fluorinated product. The analysis data matches the one previously reported in this manuscript (see S6).

Intermolecular Competition in Iodination

Aryl germane (25.1 mg, 0.1 mmol, 1.0 equiv.) and Ar-FG (0.1 mmol, 1.0 equiv.; FG = B(pin); FG = SiMe₃) were dissolved in DMF (1 mL) and NIS (17.8 mg, 0.1 mmol, 1.0 equiv.) was added in one portion. The reaction was stirred at room temperature and quenched after 2 h by dilution with EtOAc and subsequently analyzed by calibrated GC-MS (using mesitylene as internal standard) regarding consumption of starting material and formation of desired halogenated product.
Individual Bromination and Iodination

Ar-FG (0.1 mmol, 1.0 equiv.; (1) FG = GeEt₃; (2) FG = B(pin); (3) FG = SiMe₃) was dissolved in DMF (1 mL) and NXS (NBS or NIS; 0.1 mmol, 1.0 equiv.) was added in one portion. The reaction was stirred at room temperature and quenched after 1 h by dilution with EtOAc and subsequently analyzed by calibrated GC-MS (using mesitylene as internal standard) regarding consumption of starting material and formation of desired halogenated product. The results are shown in Table S2 and S3.

**Table S2:** Bromination of different functional handles.

| entry | FG     | product [%]ᵃ | recovered ArFG [%]ᵃ |
|-------|--------|--------------|---------------------|
| 1     | GeEt₃  | 96           | 0                   |
| 2     | B(pin) | 0            | > 99                |
| 3     | SiMe₃  | 0            | > 99                |

ᵃDetermined by calibrated GC-MS analysis using mesitylene as internal standard.

**Table S3:** Iodination of different functional handles.

| entry | FG     | product [%]ᵃ | recovered ArFG [%]ᵃ |
|-------|--------|--------------|---------------------|
| 1     | GeEt₃  | 62           | 30                  |
| 2     | B(pin) | 0            | > 99                |
| 3     | SiMe₃  | 0            | > 99                |

ᵃDetermined by calibrated GC-MS analysis using mesitylene as internal standard.
Intramolecular Competition

2-(4-Bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Prepared according to GP 1. The title product was obtained after purification by column chromatography (pentane/Et₂O, 7:1) as a colorless oil (41.3 mg, 0.282 mmol, 94%).

R_f = 0.73 (pentane/Et₂O, 9:1). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 7.66 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 1.34 (s, 12H).

13C NMR (151 MHz, CDCl₃) δ/ ppm = 136.4, 131.1, 126.4, 84.2, 25.0. C₁₂H₁₆O₂B: 282.0421 [M]+, found: 282.0422.

1 C atom missing in the ¹³C NMR. This is in line with literature reports.

These data are in agreement with those reported previously in the literature.¹⁷

(4-Bromophenyl)trimethylsilane

Prepared according to GP 1. The title product was obtained after purification by column chromatography (pentane) as a colorless oil (66.8 mg, 0.288 mmol, 96%).

R_f = 0.84 (pentane). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 7.66 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 0.26 (d, J = 0.8 Hz, 9H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 139.4, 135.1, 131.0, 123.7, -1.1.

MS (70 eV, EI): m/z (%): 230.0 (12) [M]+ (⁸¹Br), 228.0 (11) [M]+ (⁷⁹Br), 215.0 (100), 213.0 (99), 119.0 (11), 106.9 (10), 91.1 (20).

These data are in agreement with those reported previously in the literature.¹⁸

2-(4-Iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Prepared according to GP 2. The title product was obtained after purification by column chromatography (pentane/Et₂O, 7:1) as a yellow solid (38.7 mg, 0.231 mmol, 77%).

R_f = 0.72 (pentane/Et₂O, 9:1). ¹H NMR (600 MHz, CDCl₃) δ/ ppm = 7.72 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 1.33 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ/ ppm = 137.1, 136.4, 99.0, 84.2, 29.8, 25.0. HRMS (EI) calculated for C₁₂H₁₃O₂B: 315.0048 [M-Me]+, found: 315.0051.

These data are in agreement with those reported previously in the literature.¹⁹
Supporting Information

(4-Iodophenyl)trimethylsilane

Prepared according to GP 2. The title product was obtained after purification by column chromatography (pentane) as a colorless oil (40.6 mg, 0.279 mmol, 93%).

$R_f = 0.80$ (pentane). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$/ ppm = 7.70 (d, $J = 7.6$ Hz, 2H), 7.25 (d, $J = 7.6$ Hz, 2H), 0.26 (d, $J = 1.1$ Hz, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$/ ppm = 140.0, 136.9, 135.2, 95.8, -1.1.

HRMS (EI) calculated for C$_9$H$_{13}$Si: 275.9826 [M]$^+$, found: 275.9822. These data are in agreement with those reported previously in the literature.$^{[20]}$
Mechanistic Investigation

Linear Free Energy Relationship Analysis (Hammett Plot)

The reaction was performed according to GP 1. It was monitored using a Mettler Toledo ReactIR® 15 equipped with a 6.3 mm probe. The relative absorption data over time was normalized to yields obtained by calibrated GC-MS (using mesitylene as internal standard) or quantitative $^1$H or $^{19}$F NMR analysis (using mesitylene or 1,4-difluorobenzene as internal standard).

![Image of Hammett Plot]

**Figure S1:** Determination of initial reaction rates.

**Table S4:** Reaction rates for different substitution patterns.

| entry | RArGeEt$_3$ | $k$ [mol s$^{-1}$] | log($k/k_0$) | $\sigma_p$[21] | $\sigma_p^+$[21] |
|-------|-------------|-----------------|--------------|---------------|-----------------|
| 1     | 4-OMe       | 7.576           | 1.41         | -0.268        | -0.778          |
| 2     | 4-Me        | 0.568           | 0.29         | -0.17         | -0.311          |
| 3     | 4-H         | 0.294           | 0.00         | 0             | 0               |
| 4     | 4-F         | 0.058           | -0.70        | 0.062         | -0.073          |
| 5     | 4-I         | 0.039           | -0.87        | 0.18          | 0.135           |
**Supporting Information**

**Figure S2:** Hammett Plot $\sigma_p$.

**Figure S3:** Hammett Plot $\sigma_p^\prime$. 

$y = -4.8151x - 0.1636$

$R^2 = 0.902$

$y = -2.3867x - 0.4651$

$R^2 = 0.882$
Robustness Screen

The reaction was performed according to GP 1. In addition, an additive (1.0 equiv., for details see Table S5) was added to the reaction mixture. The tolerance of the reaction towards each additive was shown by quantification of yield of product (Y), remaining additive (A) and remaining starting material (SM) using calibrated GC-MS with mesitylene as internal standard. The results are shown in Table S5 (green: >66%; yellow 34-66%; red <34%).

Table S5: Robustness screen for aryl germanes.

| entry | additive | Y [%] | A [%] | SM [%] | entry | additive | Y [%] | A [%] | SM [%] |
|-------|----------|-------|-------|--------|-------|----------|-------|-------|--------|
| 1     | Boc     | 86    | 83    | 0      | 10    |          | 85    | n.d.  | 0      |
| 2     | Boc     | 51    | n.d.  | 33     | 11    | EtO      | 89    | 81    | 0      |
| 3     | Br      | 96    | 84    | 0      | 12    | MeO      | 95    | 74    | 0      |
| 4     | Me      | 57    | n.d.  | 30     | 13    | C3H7     | 85    | n.d.  | 0      |
| 5     |        | 83    | 99    | 0      | 14    | Ph--Me   | 79    | 99    | 0      |
| 6     |        | 84    | n.d.  | 0      | 15    | Me       | 15    | 0     | 36     |
| 7     | NCS     | 87    | n.d.  | 0      | 16    |          | 98    | 99    | 0      |
| 8     | NO2     | 88    | 48    | 0      | 17    |          | 86    | 48    | 0      |
| 9     | NH2     | 0     | n.d.  | 68     | 18    |          | 81    | n.d.  | 0      |
| entry | additive | Y [%] | A [%] | SM [%] | entry | additive | Y [%] | A [%] | SM [%] |
|-------|----------|-------|-------|--------|-------|----------|-------|-------|--------|
| 19    | PhI      | 84    | 99    | 0      | 32    | PhCHCH   | 84    | 95    | 0      |
| 20    | PhBr     | 87    | 99    | 0      | 33    | PhOTMS   | 92    | 51    | 0      |
| 21    | PhOH     | 63    | 0     | 26     | 34    | MeNCHTMS | 99    | n.d.  | 0      |
| 22    | PhOTf    | 80    | 99    | 0      | 35    | OTBDMS   | 94    | 48    | 0      |
| 23    | PhCl     | 97    | 29    | 0      | 36    | N-TMS    | 89    | 37    | 0      |
| 24    | PhPh     | 83    | 99    | 0      | 37    | N-CF3    | 99    | n.d.  | 0      |
| 25    | EtOMe    | 86    | n.d.  | 0      | 38    | N-N      | 92    | 21    | 0      |
| 26    | PhOTMS   | 87    | 99    | 0      | 39    | PhSiNp   | 99    | n.d.  | 0      |
| 27    | Ph       | 22    | 0     | 57     | 40    | Boc      | 99    | 90    | 0      |
| 28    | PhCHCH   | 18    | 0     | 61     | 41    | Ph        | 68    | 0     | 21     |
| 29    | PhCHMe   | 83    | n.d.  | 0      | 42    | PhH      | 99    | 99    | 0      |
| 30    | PhCH     | 58    | n.d.  | 0      | 43    | N-Me     | 83    | n.d.  | 0      |
| 31    | PhCHMe   | 87    | 99    | 0      | 44    | Ph        | 93    | 99    | 0      |
The vast majority of the additives is well tolerated. Due to their low molecular weight and resulting low boiling point, it was impossible to quantify some of the additives via GC-MS (marked in grey). However, also in those cases the reaction proceeded with high efficiency.

**Supporting Information**

| entry | additive | Y [%] | A [%] | SM [%] | entry | additive | Y [%] | A [%] | SM [%] |
|-------|----------|-------|-------|--------|-------|----------|-------|-------|--------|
| 45    | **[O]**  | 89    | n.d.  | 0      | 49    | **[N]Boc** | 99    | 99    | 0      |
| 46    | **[Me]** | 85    | n.d.  | 0      | 50    | **[Cl]**  | 95    | 0     | 0      |
| 47    | **[OH]** | 83    | n.d.  | 0      | 51    | **[Me]**  | 88    | 41    | 0      |
| 48    | **[NH2]**| 83    | n.d.  | 0      | 52    | **[O]**  | 83    | 91    | 0      |

![Figure S4: Yield of bromination.](image)

![Figure S5: Recovery of additive.](image)
Robustness Screen for ArB(pin) and ArSiMe$_3$

The reaction was performed according to GP 1 with ArFG (FG = GeEt$_3$, B(pin) or SiMe$_3$; 0.03 mmol, 1 equiv.). To investigate the tolerance of the reaction, different additives were added to the reaction mixture (see table below for details). The reaction was stirred for 1 h at rt and subsequently analyzed by calibrated GC-MS using mesitylene (1 equiv.) as internal standard. The results are shown in Table S6.

Table S6: Robustness screen comparing aryl germanes with aryl boronic esters and aryl silanes.

| entry | FG    | additive | recovery of additive [%]$^a$ | yield [%]$^a$ |
|-------|-------|----------|------------------------------|--------------|
| 1     | GeEt$_3$ | | 96 | 84 |
| 2     | SiMe$_3$ | | 0 | 0 |
| 3     | Bpin   | | 0 | 0 |
| 4     | GeEt$_3$ | Me$\equiv$Ph | >99 | 79 |
| 5     | SiMe$_3$ | Me$\equiv$Ph | 39$^b$ | 0 |
| 6     | Bpin   | Me$\equiv$Ph | 41$^b$ | 0 |

$^a$Determined by calibrated GC-MS analysis using mesitylene as internal standard. $^b$Brominated side products formed.
EPR Analysis

The reaction was performed according to GP 1. EPR measurements of the reaction mixture were performed every 20 min aiming to detect paramagnetic species which would indicate a SET type mechanism. No paramagnetic species were detected.

Additionally, the reaction was performed according to GP 1 with either 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) or N-tert-butyl-α-phenylnitrone (PBN) as spin probe/spin trap. After 2 h of reaction time, the reaction mixture was analyzed by EPR.

Table S7: TEMPO as spin probe.

| entry | equiv. TEMPO | yield [%]a |
|-------|-------------|------------|
| 1     | 0.5         | 99         |
| 2     | 1.0         | 99         |
| 3     | 2.0         | 99         |

a Determined by calibrated GC-MS analysis using mesitylene as internal standard.

In all experiments with various amounts of TEMPO as spin probe no TEMPO-related adducts were detected (GC-MS). Additionally, EPR measurements did not show any change in the TEMPO signal.

Table S8: PBN as spin trap.

| entry | equiv. PBN | yield [%]a |
|-------|------------|------------|
| 1     | 0.5        | 99         |
| 2     | 1.0        | 99         |
| 3     | 2.0        | 99         |

a Determined by calibrated GC-MS analysis using mesitylene as internal standard.
Supporting Information

In all experiments with various amounts of PBN as spin trap no (paramagnetic) PBN-related adducts of the aryl germane were detected (GC-MS and EPR analysis). Due to the excess of NBS, some paramagnetic N-O species were formed (EPR), which indicate reaction of an Br-radical with PBN (unambiguously confirmed by GC-MS analysis). This observation is in line with literature reports. [22] The quantitative yield confirmed that the aryl germane did not form significant amount of aryl radicals which might be trapped by the spin trap.
Reaction Monitoring

The reaction was performed according to GP 1. It was monitored using a Mettler Toledo ReactIR® equipped with a 6.3 mm probe. The relative absorption data over time was normalized to yields obtained by calibrated GC-MS (using mesitylene as internal standard).

**Figure S6**: Reaction monitoring (product formation) of bromination with NBS.
Supporting Information

Computational Details

DFT calculations were performed using the Gaussian software package (Gaussian16, revision A.03). Geometry optimization and frequency calculations were conducted with implicit solvation (CPCM model for DMF) at the ωB97XD/def2SVP level of theory. Calculated frequencies were used to verify the nature of all stationary points as either minima (no imaginary frequencies) or transition states (one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were performed to further confirm whether the transition state is connected to the corresponding intermediates. Single point energies were calculated at the M06/6-311++G(d,p) level of theory employing SDD as an ECP for Br, I and Ge and the CPCM solvation model for DMF. Energies of all structures were corrected to 1 m standard state (addition of 1.89 kcal/mol to every species). Images were created using the CYLview software.

Figure S7: Gibbs free energies computed at the CPCM (DMF) M06/6-311++G(d,p) (SDD)/ωB97XD/def2SVP level of theory. Energies are given relative to starting materials.
Supporting Information

Influence of para-Substituents on the Transition State Barrier (DFT)

Table S9: Transition state barriers.

| entry | R   | ΔG‡ [kcal/mol] | σ_p [21] |
|-------|-----|----------------|----------|
| 1     | OMe | 17.8           | -0.268   |
| 2     | Me  | 19.6           | -0.170   |
| 3     | H   | 21.9           | 0.000    |
| 4     | F   | 22.2           | 0.062    |
| 5     | I   | 23.8           | 0.180    |

Gibbs free energies computed at the CPCM (DMF) M06-6-311++G(d,p) (SDD)//ωB97XD/def2SVP level of theory. Energy barriers of transition states are relative to starting materials.

Figure S8: Transition state barriers for various substitution patterns plotted against σ_p value.
Comparison of Aryl Germanes with Aryl Silanes

Table S10: Transition state barriers.

| entry | FG     | $\Delta G^\ddagger$ [kcal mol$^{-1}$] |
|-------|--------|---------------------------------------|
| 1     | GeEt$_3$ | 21.9                                  |
| 2     | SiMe$_3$ | 25.2                                  |

Gibbs free energies computed at the CPCM (DMF) M06-6-311++G(d,p)(SDD)//ωB97XD/def2SVP level of theory. Energy barriers of transition states are relative to starting materials.
**Supporting Information**

**XYZ Coordinates and Energies**

### PhGeEt₃

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| Ge      | -0.69554700 | -0.09970800 | -0.07719500 |
| C       | 2.04998500  | 0.22669000  | -1.06593100 |
| C       | 3.44387200  | 0.18436900  | -1.00745200 |
| C       | 1.26342200  | -0.14021200 | 0.03751300  |
| C       | 4.08067900  | -0.22927500 | 0.16359800  |
| C       | 1.92278800  | -0.55163300 | 1.20568000  |
| C       | 3.31697300  | -0.59793700 | 1.27142900  |
| H       | 4.03579400  | 0.47633900  | -1.87836400 |
| H       | 5.17161700  | -0.26279400 | 0.21286700  |
| H       | 1.34374700  | -0.84236500 | 2.08742700  |
| C       | -1.43205600 | 0.00156700  | 1.74420700  |
| H       | -1.33732900 | -0.99493900 | 2.20866500  |
| H       | -0.78150500 | 0.67386300  | 2.32842600  |
| C       | -1.22716500 | 1.48972800  | -1.10174600 |
| H       | -0.85430700 | 1.37376300  | -2.13337000 |
| H       | -2.32742100 | 1.49094400  | -1.17699200 |
| C       | -1.27752500 | -1.72562400 | -1.01555800 |
| H       | -0.78530600 | -1.71614000 | -2.00301200 |
| H       | -0.85836500 | -2.59046600 | -0.47435500 |
| C       | 3.80898600  | -0.92170900 | 2.19187600  |
| C       | 1.57092200  | 0.55656400  | -1.03324800 |
| C       | -0.72959800 | 2.80203700  | -0.49534200 |
| H       | 0.37020400  | 2.82433100  | -0.43563700 |
| H       | -1.04542300 | 3.67478700  | -1.08902700 |
| H       | -1.11291000 | 2.94649000  | 0.52769200  |
| C       | -2.79061200 | -1.87886100 | -1.17599400 |
| H       | -3.23714200 | -1.01251700 | -1.68956500 |
| C       | -3.04821400 | -2.77483500 | -1.76294500 |
| H       | -3.29256300 | -1.97498100 | -0.20066100 |
| C       | -2.88169000 | 0.48714700  | 1.81459500  |
| H       | -2.99072000 | 1.49595800  | 1.38630900  |
| C       | -3.56435800 | -0.17455100 | 1.26021000  |
| H       | -3.24311700 | 0.53278300  | 2.85412500  |

Zero-point correction = 0.288402 (Hartree/Particle)
Thermal correction to Energy = 0.305101
Thermal correction to Enthalpy = 0.306046
Thermal correction to Gibbs Free Energy = 0.242248

### Sum of electronic and zero-point Energies = -2545.390337
Sum of electronic and thermal Energies = -2545.373637
Sum of electronic and thermal Enthalpies = -2545.372693
Sum of electronic and thermal Free Energies = -2545.436490
E(RM06) = -472.859048239

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### 4-Me-PhGeEt₃

| Element | X          | Y          | Z         |
|---------|------------|------------|-----------|
| Ge      | -1.04810500 | -0.10135100 | -0.07709100 |
| C       | 1.67850600  | 0.28066900  | -1.10172700 |
| C       | 3.07229600  | 0.25849000  | -1.06370700 |
| C       | 0.91046100  | -0.10993900 | 0.00574100 |
| C       | 3.75668800  | -0.15503000 | 0.08660800 |
| C       | 1.60073500  | -0.52455800 | 1.15362000 |
| C       | 2.99545200  | -0.54889200 | 1.19364500 |
| H       | 3.64130300  | 0.56782500  | -1.94528400 |
| H       | 1.04610100  | -0.83958800 | 2.04285800 |
| C       | -1.75789400 | -0.03529200 | 1.75692300 |
| H       | -1.64214000 | -1.03621400 | 2.20575700 |
| C       | -1.10722700 | 0.63762700  | 2.34036800 |
| C       | -1.62444800 | 1.49136900  | -1.07262600 |
| H       | -1.26706000 | 1.39423300  | -2.11169500 |
| H       | -2.72571000 | 1.47539000  | -1.12956900 |
| C       | -1.62388700 | -1.72372200 | -1.02626800 |
| H       | -1.15045700 | -1.69383400 | -2.02250700 |
| H       | -1.18145000 | -2.58909000 | -0.50472200 |
| C       | 3.50304500  | -0.88126700 | 2.10384700 |
| H       | 1.18483400  | 0.61211200  | -2.02093600 |
| C       | -1.13827500 | 2.80458500  | -0.45843700 |
| H       | -0.03813100 | 2.84368900  | -0.41648800 |
| H       | -1.47800400 | 3.67911000  | -1.03576200 |
| C       | -1.50666900 | 2.92991400  | 0.57256700 |
| C       | -3.13712900 | -1.89860500 | -1.16073100 |
| H       | -3.60654000 | -1.03264200 | -1.65419600 |
| H       | -3.39223600 | -2.79070100 | -1.75471200 |
| H       | -3.61913500 | -2.01522500 | -0.17785800 |
| C       | -3.21254300 | 0.42099000  | 1.85699000 |
| H       | -3.34194100 | 1.44232000  | 1.44507100 |
| H       | -3.89479300 | -0.23383800 | 1.30326300 |
Supporting Information

\[
E(\text{RM06}) = -512.15368994
\]

4-F-PhGeEt₃

4-I-PhGeEt₃
4-OMe-PhGeEt₃

C -0.344474000  0.505690000  -2.094355000
C -2.663805000  2.774034000  -0.584114000
H -1.563863000  2.830388000  -0.559672000
H -3.023546000  3.615234000  -1.197442000
H -3.020307000  2.942933000  0.447646000
C -4.587851000  -1.997232000  -1.044710000
H -5.077335000  -1.167598000  -1.579212000
H -4.827859000  -2.923863000  -1.589820000
H -5.061161000  -2.072299000  -0.053378000
C -4.672365000  0.470172000  1.873528000
H -4.832916000  1.457098000  1.411848000
H -5.347296000  -0.236970000  1.367657000
H -5.000862000  0.542628000  2.922329000
I  4.354148000  -0.045381000  0.043493000

Zero-point correction = 0.277783 (Hartree/Particle)
Thermal correction to Energy = 0.296141
Thermal correction to Enthalpy = 0.297085
Thermal correction to Gibbs Free Energy = 0.297418
Sum of electronic and zero-point Energies = -2842.574895
Sum of electronic and thermal Energies = -2842.555593
Sum of electronic and thermal Free Energies = -2842.556537
E(RM06) = -483.648464614

NBS

C -2.363631000  0.764556000  -0.00257000
C -0.905152000  1.180406000  -0.00021000
C -2.363629000  -0.764563000  0.000473000
N -0.154834000  0.000010000  0.00006600
C -0.905148000  -1.180408000  0.000114000
H -2.842827000  1.201616000  -0.885617000
H -2.842746000  -1.201622000  0.885878000
H -2.843677000  -1.202611000  -0.883923000
H -2.843598000  1.202605000  0.88418200

Supporting Information
**Supporting Information**

**pi_NBS_PhGeEt3**

| Atom | Ge | C  | N | Br |
|------|----|----|---|----|
|      | -2.10682800 | -1.73597000 | -1.10048100 | 1.53934700 |
|      | -0.67487400 | 1.25534400 | 3.33688700 | 0.81293700 |
|      | 0.07123100  | 0.11153300  | -0.99608000 | -0.22949000 |
|      | 0.22604000  | 0.83557400  | 1.36880500  | 0.15811400  |
|      | 0.22604000  | 0.83557400  | 1.36880500  | 0.15811400  |

**TS_H-PhGeEt3**

| Atom | Ge | C  | N | Br |
|------|----|----|---|----|
|      | 1.76493400 | 1.10673200 | -1.03193500 | 1.54273200 |
|      | 0.88437000 | -1.16648800 | -0.83943000 | -1.62138300 |
|      | -0.01728900 | 0.14317300 | 2.35854100 | 1.41678400 |
|      | 0.14317300 | 0.14317300 | 2.35854100 | 1.41678400 |

**E(RM06) = -373.274034339**

**Zero-point correction = 0.082115 (Hartree/Particle)**

**Thermal correction to Energy = 0.089457**

**Thermal correction to Enthalpy = 0.090401**

**Thermal correction to Gibbs Free Energy = 0.048021**

**Sum of electronic and zero-point Energies = -2933.483240**

**Sum of electronic and thermal Energies = -2933.475899**

**Sum of electronic and thermal Enthalpies = -2933.474954**

**Sum of electronic and thermal Free Energies = -2933.517335**

E(RM06) = -373.274034339
Supporting Information

TS_Me-PhGeEt₃

Zero-point correction = 0.370885 (Hartree/Particle)
Thermal correction to Energy = 0.396202
Thermal correction to Enthalpy = 0.397146
Thermal correction to Gibbs Free Energy = 0.312839

Sum of electronic and zero-point Energies = -5758.838808
Sum of electronic and thermal Energies = -5748.813491
Sum of electronic and thermal Enthalpies = -5478.812546
Sum of electronic and thermal Free Energies = -5478.896853

E(RM06) = -846.117757712
Supporting Information

E(RM06) = -885.416092283

TS_F-PhGeEt₃

Zero-point correction = 0.398110 (Hartree/Particle)
Thermal correction to Energy = 0.425339
Thermal correction to Enthalpy = 0.426283
Thermal correction to Gibbs Free Energy = 0.426283

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Supporting Information

TS_I-PhGeEt₃

Ge -0.179069000  1.935830000  -0.055096000  
C  0.298402000  -0.192950000  0.003431000  
C  1.038929000  -0.040829100  -1.185997000  
C  0.970910000  -0.395263000  1.236289000  
C  2.390604000  -0.721753000  -1.153215000  
C  2.319868000  -0.706393000  1.285240000  
C  3.028520000  -0.855056000  0.084917000  
H  0.545328000  -0.307910000  -2.156217000  
H  0.418832000  -0.287929000  2.173310000  
H  2.941962000  -0.858318000  -2.084267000  
H  2.811701000  -0.834839000  2.247338000  
C  1.595720000  2.763095000  -0.073729000  
H  1.476073000  3.729550000  0.444207000  
H  2.256833000  2.158931000  0.567937000  
C  -1.208060000  2.228032000  -1.696684000  
H  -1.124182000  1.330451000  -2.327535000  
H  -0.693224000  3.034489000  -2.243276000  
C  -1.181865000  2.287735000  1.585381000  
H  -2.176955000  1.834290000  1.461604000  
H  -0.692783000  1.771482000  2.425011000  
Br -1.734337000  -0.785746000  -0.015643000  
C  -6.201444000  -1.328873000  0.376474000  
C  -4.856110000  -0.603607000  0.424644000  
N  -3.863805000  -1.447957000  0.019864000  
C  -4.334941000  -2.688716000  -0.310722000  
C  -5.851691000  -2.727225000  -0.117767000  
H  -6.651114000  -1.310567000  1.380178000  
O  -4.708825000  0.556891000  0.772565000  
O  -3.658848000  -3.623359000  -0.699668000  
H  -6.324628000  -2.991745000  -1.074766000  
H  -6.878221000  -0.776417000  -0.291256000  
H  -6.097847000  -3.526257000  0.596866000  
C  -1.290457000  3.787258000  1.878180000  
H  -1.904639000  3.960854000  2.774735000  
H  -0.305989000  4.243261000  2.062482000  
H  -1.761395000  4.339498000  1.050213000  
C  -2.677445000  2.581948000  -1.463331000  
H  -2.783163000  3.531961000  -0.917590000  
H  -3.201950000  2.699320000  -2.424047000  
H  -3.320136000  1.807160000  -0.883329000  
C  2.216842000  2.975816000  -1.453073000  

Zero-point correction = 0.360623 (Hartree/Particle)
Thermal correction to Energy = 0.387428
Thermal correction to Enthalpy = 0.388372
Thermal correction to Gibbs Free Energy = 0.299156
Sum of electronic and zero-point Energies = -5776.020455
Sum of electronic and thermal Energies = -5775.993650
Sum of electronic and thermal Enthalpies = -5775.992706
Sum of electronic and thermal Free Energies = -5776.081922
E(RM06) = -856.905220923

TS_OMe-PhGeEt₃

Ge -1.163816000  -1.613070000  0.010859000  
C  -1.008623000  0.466931000  0.134238000  
C  -1.655673000  1.034936000  1.008733000  
C  -1.512454000  0.887475000  1.412649000  
C  -2.7546953000  1.869018000  -0.910483000  
C  -2.601124000  1.708777000  1.533311000  
C  -3.241772000  2.025283000  0.369393000  
H  -1.278528000  0.787971000  -2.004912000  
H  -1.017494000  0.552875400  2.318713000  
H  -3.214399000  2.257929000  -1.814030000  
H  -2.990857000  2.007713000  2.506916000  
C  -3.087343000  -1.978540000  0.098430000  
C  -3.180870000  -3.028876000  0.420848000  
C  -3.508186000  -1.370332000  0.914529000  
C  -0.367068000  -2.173100000  -1.693199000  
H  -0.289845000  -1.292911000  -2.350362000  
H  -1.102036000  -2.841809000  -2.170535000  
C  -0.227886000  -2.331622000  1.573638000  
H  0.849048000  -2.165212000  1.420977000  
H  -0.514706000  -1.747953000  2.461918000  
Br  1.094424000  0.640470000  0.022885000  
C  5.666867000  0.261974000  -0.001654000  
C  4.213915000  -0.218709000  -0.019226000  

SS1
### Supporting Information

| N | 3.369736000 | 0.851173000 | -0.049638000 | C | 1.621249000 | -1.603144000 | -1.239412000 |
|---|-------------|-------------|--------------|---|-------------|-------------|-------------|
| C | 4.043905000 | 2.039653000 | -0.049318000 | C | 1.996363000 | -2.060147000 | 1.124654000 |
| C | 5.552720000 | 1.780340000 | -0.032589000 | C | 2.979484000 | -1.823640000 | -1.488876000 |
| H | 6.159219000 | -0.129187000 | 0.909076700 | C | 3.346481000 | -2.260826000 | 0.859903000 |
| O | 3.882607000 | -1.393980000 | -0.007746000 | C | 3.838408000 | -2.154281000 | -0.445888000 |
| O | 5.352506000 | 3.146736000 | -0.060830000 | H | 0.939206000 | -1.388649000 | -2.064346000 |
| H | 6.001749000 | 2.241827000 | -0.924388000 | H | 1.607626000 | -2.170231000 | 2.138247000 |
| H | 6.193267000 | -0.164722000 | -0.867913000 | H | 3.354990000 | -1.743104000 | -2.510179000 |
| H | 5.989919000 | 2.279302000 | 0.844592000 | H | 4.020936000 | -2.514270000 | 1.679549000 |
| C | -0.522846000 | -3.816161000 | 1.804535000 | H | 4.897186000 | -2.327823000 | -0.644632000 |
| H | 0.060500000 | -4.204870000 | 2.653578000 | C | 3.336511000 | 1.310748000 | -0.171759000 |
| H | -1.585707000 | -3.991096000 | 2.030575000 | H | 3.567478000 | 2.141409000 | 0.517018000 |
| H | -0.268148000 | -4.430345000 | 0.926754000 | C | 3.846683000 | 0.432078000 | 0.254625000 |
| C | 0.990476000 | -2.867858000 | -1.574741000 | C | 0.256865000 | 1.467728000 | -1.435746000 |
| H | 0.921771000 | -3.790272000 | -0.977642000 | H | -0.520955000 | 0.690945000 | -1.482791000 |
| H | 1.366976000 | -3.154111000 | -2.563946000 | H | 0.841937000 | 1.423786000 | -2.365932000 |
| H | 1.748016000 | -2.224752000 | -1.102168000 | C | 0.733358000 | 1.214312000 | 1.846301000 |
| C | -3.865354000 | -1.760142000 | -1.200752000 | H | -0.356307000 | 1.069123000 | 1.777594000 |
| H | -4.930251000 | -2.007400000 | -1.070552000 | H | 1.169815000 | 0.420136000 | 2.469389000 |
| H | -3.812349000 | -0.715141000 | -1.540713000 | Br | -0.745342000 | -1.619886000 | 0.379391000 |
| H | -3.480643000 | -2.391610000 | -2.016252000 | C | -4.043466000 | 1.451512000 | -0.669290000 |
| O | -4.28391700 | 2.981397000 | 0.575446000 | O | -3.187535000 | 0.834390000 | 0.445680000 |
| C | -5.003632000 | 3.535310000 | -0.517929000 | N | -3.412541000 | -0.490692000 | 0.587013000 |
| H | -3.357933000 | 4.192353000 | -1.118334000 | C | -4.368204000 | -0.092237000 | -0.294399000 |
| H | -5.422792000 | 2.740243000 | -1.149963000 | C | -4.900183000 | 0.284830000 | -1.130383000 |
| H | -5.815514000 | 4.122701000 | -0.078161000 | H | -6.408163000 | 2.308399000 | -0.273056000 |
| O | -2.384357000 | 1.505456000 | 1.099258000 | O | -4.778873000 | -2.039258000 | -0.429462000 |

Zero-point correction = 0.403776 (Hartree/Particle)
Thermal correction to Energy = 0.431711
Thermal correction to Enthalpy = 0.432655
Thermal correction to Gibbs Free Energy = 0.341687

Sum of electronic and zero-point Energies = -5593.222083
Sum of electronic and thermal Energies = -5593.194147
Sum of electronic and thermal Enthalpies = -5593.193203
Sum of electronic and thermal Free Energies = -5593.284171

E(RM06) = -960.621798735

**pi_NBS-GeEt3_PbBr**

| Ge | 1.432773000 | 1.051361000 | 0.047577000 |
|---|-------------|-------------|--------------|
| C | 1.125429000 | -1.737479000 | 0.069925000 |

Zero-point correction = 0.371284 (Hartree/Particle)
Thermal correction to Energy = 0.397544
Thermal correction to Enthalpy = 0.398489
Thermal correction to Gibbs Free Energy = 0.310182

Sum of electronic and zero-point Energies = -5478.848753
Sum of electronic and thermal Energies = -5478.822492
Supporting Information

Sum of electronic and thermal Enthalpies = -5478.821548
Sum of electronic and thermal Free Energies = -5478.909854
$E(RM06) = -846.12962349$

PhBr

C 0.00000000 0.00000000 -0.09467600
C 0.00000000 1.21542900 -0.77948500
C 0.00000000 -1.21542900 -0.77948500
C 0.00000000 1.20724900 -2.17440500
C 0.00000000 -1.20724900 -2.17440500
Br 0.00000000 0.00000000 -3.96538900

Zero-point correction = 0.091414 (Hartree/Particle)
Thermal correction to Energy = 0.097052
Thermal correction to Enthalpy = 0.097996
Thermal correction to Gibbs Free Energy = 0.061238

Sum of electronic and zero-point Energies = -2805.214495
Sum of electronic and thermal Energies = -2805.208857
Sum of electronic and thermal Enthalpies = -2805.207912
Sum of electronic and thermal Free Energies = -2805.244671
$E(RM06) = -244.863206182$

NBS-GeEt3

Ge 0.82291600 0.02318000 -0.12062200
C 1.32065300 1.40430300 -1.41515900
H 2.22208500 1.03659800 -1.93324500
H 0.52445400 1.43677200 -2.17658000
C 1.23371000 0.47825400 1.73324500
H 0.78699600 1.46194000 1.94138200

PhSiMe3

Si 1.47234200 0.00722700 0.00000200
C -0.42173400 0.02345000 -0.00009100
### E(RM06)

**Sum of electronic and thermal Free Energies**

| Element | Electronic | Thermal | Total |
|---------|------------|---------|-------|
| C       | 1.36605000 | -1.18763100 | -0.00010400 |
| C       | -1.16305000 | 1.21573700 | -0.00040500 |
| C       | -2.53118900 | -1.20930300 | -0.00046000 |
| C       | -2.55983200 | 1.20320200 | 0.00011000 |
| C       | -3.24866200 | -0.01032000 | 0.00016000 |
| H       | -0.59691600 | -2.14443900 | -0.00015500 |
| H       | -0.64633700 | 2.17978300 | 0.00000000 |
| H       | -3.06291700 | -2.16390800 | -0.00005600 |
| H       | -3.11348600 | 2.14526900 | 0.00004500 |
| C       | 2.06859100 | -0.89957600 | 1.53787900 |
| H       | 3.16901800 | -0.95170500 | 1.55810900 |
| H       | 1.73305500 | -0.38571500 | 2.45266000 |
| H       | 1.68023600 | -1.93015600 | 1.56515300 |
| C       | 2.06885300 | -0.90237500 | -1.53610900 |
| H       | 1.73159600 | -0.39146700 | -2.45190400 |
| H       | 3.16936300 | -0.95245200 | -1.55710700 |
| H       | 1.68249100 | -1.93377700 | -1.56046600 |
| C       | 2.12014400 | 1.77177300 | -0.00159500 |
| H       | 3.22177600 | 1.76893000 | -0.00067800 |
| H       | 1.78511500 | 2.32311700 | -0.89453400 |
| H       | 1.78368500 | 2.32354500 | 0.88942400 |
| H       | -4.33937100 | -0.02333800 | 0.00006300 |

**Thermal correction to Enthalpy**

| Element | Electronic | Thermal |
|---------|------------|---------|
| C       | 2.60673800 | -0.97722100 |
| C       | 2.15996500 | -1.32901000 |
| C       | 2.43147700 | -2.33979700 |
| C       | 1.97917300 | -2.69515900 |
| C       | 2.11371800 | -3.20198900 |
| H       | 2.84857700 | -0.32007700 |
| H       | 2.05337100 | -0.95529900 |
| H       | 2.53855200 | -2.72984300 |
| H       | 1.73124400 | -3.36316100 |
| C       | 4.53883000 | 1.82248900 |
| H       | 4.72121200 | 2.89944900 |
| H       | 5.15412500 | 1.62947400 |
| C       | 1.69819400 | 2.37628600 |
| H       | 1.97833700 | 2.10210200 |
| H       | 1.87269600 | 3.45824100 |
| C       | 2.15561500 | 1.85068500 |
| H       | 1.09708600 | 1.58828800 |
| H       | 2.75589800 | 1.32715900 |
| Br      | -0.83718400 | -0.51600200 |
| C       | -4.35449700 | 1.48536900 |
| C       | -2.84626100 | 1.34698800 |
| N       | -2.55895800 | 0.00705640 |
| C       | -3.67766100 | -0.72003800 |
| H       | -4.66512400 | 2.30846100 |
| O       | -2.02378900 | 2.17232500 |
| O       | -3.63363000 | -1.84179600 |
| H       | -5.48016800 | -0.42420200 |
| H       | -4.63792400 | 1.69232300 |
| H       | -5.52015600 | 0.19630700 |
| H       | 1.97047200 | -4.26822100 |
| H       | 0.62061000 | 2.18644700 |
| H       | 4.88207600 | 1.55277900 |
| H       | 2.26527300 | 2.93318500 |

**Sum of electronic and thermal Free Energies**

-640.716740912

### Supporting Information

**pi_NBS_PhSiMe\(_3\)**

Zero-point correction = 0.202523 (Hartree/Particle)

Thermal correction to Energy = 0.214641

Thermal correction to Gibbs Free Energy = 0.164415

Sum of electronic and zero-point Energies = -640.269566

Sum of electronic and thermal Energies = -640.257448

Sum of electronic and thermal Enthalpies = -640.256503

Sum of electronic and thermal Free Energies = -640.307673

E(RM06) = -640.716740912

Zero-point correction = 0.285616 (Hartree/Particle)

Thermal correction to Energy = 0.307161

Thermal correction to Enthalpy = 0.308105

Thermal correction to Gibbs Free Energy = 0.230771

Sum of electronic and zero-point Energies = -357.761875

Sum of electronic and thermal Energies = -357.740331

Sum of electronic and thermal Enthalpies = -357.739387

Sum of electronic and thermal Free Energies = -357.816720

E(RM06) = -1013.99961232
Supporting Information

**TS_PhSiMe₃**

- Thermal correction to Enthalpy = 0.036492
- Thermal correction to Gibbs Free Energy = 0.233022
- Sum of electronic and zero-point Energies = -3573.711712
- Sum of electronic and thermal Energies = -3573.690986
- Sum of electronic and thermal Enthalpies = -3573.690042
- Sum of electronic and thermal Free Energies = -3573.763512
- E(RM06) = -1.01396822094

**pi_NBS-SiMe₃_PhBr**

- Zero-point correction = 0.284822 (Hartree/Particle)
- Thermal correction to Energy = 0.305548
### Supporting Information

| H   | -5.17753000 | 1.581352000 | -1.135771000                  | Thermal correction to Energy = 0.306504 |
| H   | -5.830333000 | -0.299787000 | 1.101800000                  | Thermal correction to Enthalpy = 0.307449 |
| H   | 5.363816000  | -1.871944000 | -0.408627000                 | Thermal correction to Gibbs Free Energy = 0.230888 |
| H   | -0.088130000 | 2.092805000  | -0.856942000                 | Sum of electronic and zero-point Energies = -3573.714058 |
| H   | 4.199425000  | 1.670787000  | -0.948386000                 | Sum of electronic and thermal Energies = -3573.692388 |
| H   | 1.363021000  | 2.751227000  | 2.192571000                  | Sum of electronic and thermal Enthalpies = -3573.691444 |

Zero-point correction = 0.284834 (Hartree/Particle)  
E(RM06) = -1013.96883132
NMR Spectra

Triethyl(phenyl)germane

**1H NMR**
(599.86 MHz, CDCl₃)

**13C NMR**
(150.85 MHz, CDCl₃)
Triethyl(4-fluorophenyl)germane

**1H NMR**
(599.86 MHz, CDCl3)

**13C NMR**
(150.85 MHz, CDCl3)
Supporting Information

Triethyl(4-methoxyphenyl)germane

$\text{MeO}$

$\text{GeEt}_3$

1H NMR (599.6 MHz, CDCl$_3$)

$\text{MeO}$

$\text{GeEt}_3$

13C NMR (150.85 MHz, CDCl$_3$)
Triethyl(mesityl)germane

**1H NMR**
(599.86 MHz, CDCl3)

**13C NMR**
(150.85 MHz, CDCl3)
Triethyl(4-chlorophenyl)germane

Supporting Information
Triethyl(4-bromophenyl)germane

**1H NMR**

(599.86 MHz, CDCl3)

**13C NMR**

(150.85 MHz, CDCl3)
Triethyl(4-iodophenyl)germane

1H NMR (599.86 MHz, CDCl3)

13C NMR (150.85 MHz, CDCl3)
Triethyl(thiophen-2-yl)germane

$\text{GeEt}_3$

$^1\text{H NMR}$

(599.86 MHz, CDCl$_3$)

$^13\text{C NMR}$

(150.85 MHz, CDCl$_3$)
Triethyl(\(p\)-tolyl)germane

**1H NMR**
(599.86 MHz, CDCl3)

**13C NMR**
(150.85 MHz, CDCl3)
Supporting Information

Triethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)germane

1H NMR (599.86 MHz, CDCl3)

13C NMR (150.85 MHz, CDCl3)
Triethyl(4-(tributylstannyl)phenyl)germane

1H NMR
(599.86 MHz, CDCl3)

13C NMR
(150.85 MHz, CDCl3)
Triethyl(thiophen-3-yl)germane

$\text{GeEt}_3$

**$^1$H NMR**

(599.86 MHz, CDCl$_3$)

- R (100) 7.33 (2H, d, $J_{2,3}$ = 2.5)
- A (AB) 7.41 (4H, 2J)
- C (AB) 7.14 (4H, 1J)

**$^{13}$C NMR**

(150.85 MHz, CDCl$_3$)

- C 100.00

S69
Supporting Information

Benzo[b]thiophen-3-yltriethylgermane

$^{13}$C NMR (150.85 MHz, CDCl$_3$)

12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Triethyl(naphthalen-1-yl)germane

$\text{GeEt}_3$

$\text{H NMR (599.86 MHz, CDCl}_3$)

$\text{C NMR (150.85 MHz, CDCl}_3$)
(2,6-Dimethoxyphenyl)triethylgermane

**1H NMR**
599.88 MHz, CDCl3

**13C NMR**
150.85 MHz, CDCl3
Triethyl(3,4,5-trimethoxyphenyl)germane

$^{1}H$ NMR (599.86 MHz, CDCl$_3$)

$^{13}C$ NMR (150.85 MHz, CDCl$_3$)
Triethyl(2-methoxyphenyl)germane

Supporting Information

1H NMR (599.86 MHz, CDCl3)

13C NMR (150.85 MHz, CDCl3)
Trimethyl(4-(triethylgermyl)phenyl)silane

**1H NMR** (599.86 MHz, CDCl3)

- 9.00 (s, 3H)
- 7.61 (d, 2H)
- 7.49 (d, 2H)
- 7.00 (m, 1H)
- 1.06 (s, 6H)
- 0.20 (s, 9H)

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

- 240
- 230
- 220
- 210
- 200
- 190
- 180
- 170
- 160
- 150
- 140
- 130
- 120
- 110
- 100
- 90
- 80
- 70
- 60
- 50
- 40
- 30
- 20
- 10
- 0
- -10
3,5-Dimethyl-4-(triethylgermyl)isoxazole

$^1$H NMR (599.86 MHz, CDCl₃)

$^{13}$C NMR (150.85 MHz, CDCl₃)
**Supporting Information**

**tert-Butyl[(Z)-[(3-iodobenzyl)amino][(tert-butoxycarbonyl)amino]methylidene} carbamate**

**1H NMR**

(595.86 MHz, CDCl3)

**13C NMR**

(150.85 MHz, CDCl3)

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**S77**
tert-Butyl-N-[(1Z)-{bis[(tert-butoxy)carbonyl]amino}{[[tert-butoxy]carbonyl]([3-iodophenyl]methyl)amino}}methylidene]carbamate
tert-Butyl-N-[(1Z)-{[(tert-butoxy)carbonyl]amino}{{[(tert-butoxy)carbonyl]((3-(triethylgermanium)phenyl)methyl)amino}}methylidene]carbamate

$^{1}H$ NMR
(599.86 MHz, DMF-$d_{7}$)

$I_{H}$ ppm

$^{13}C$ NMR
(150.85 MHz, DMF-$d_{7}$)

$I_{C}$ ppm
**Supporting Information**

**tert-Butyl[(Z)-[(3-bromobenzyl)amino]((tert-butoxycarbonyl)amino)methylidene} carbamate**

**1H NMR**

(599.86 MHz, CDCl3)

\[ \text{Proton Chemical Shifts (ppm)} \]

- 9.96 (s, 1H)
- 7.36 (br s, 2H)
- 7.29 (t, J = 7.5 Hz, 2H)
- 4.07 (br s, 2H)
- 3.67 (br s, 2H)
- 2.50 (s, 3H)
- 1.34 (s, 9H)

**13C NMR**

(150.85 MHz, CDCl3)

\[ \text{Carbon Chemical Shifts (ppm)} \]
tert-Butyl-N-[(1Z)-{bis- [ (tert-butoxy) carbonyl] amino} {([(tert-butoxy) carbonyl] [(3-(triethylgermanium)-phenyl) methyl]amino})methylidene]carbamate
Supporting Information

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