Light-fluorous Safety-catch Arylgermanes – Exceptionally Robust, Photochemically Activated Precursors for Biaryl Synthesis by Pd(0) Catalysed Cross-coupling

Alan C. Spivey,* Chih-Chung Tseng,* Joseph P. Hannah,* Christopher J.G. Gripton,† Paul de Fraine,* Nigel J. Parr,* and Jan J. Scicinski‡

*Department of Chemistry, South Kensington campus, Imperial College, London, London, SW7 2AZ, UK
†Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, S3 7HF, UK
‡Discovery Chemistry, Syngenta, Jealott's Hill, Bracknell, Berkshire, RG42 6EY, UK
§Medicinal Chemistry, GlaxoSmithKline, Gunnelswood Road, Stevenage, Hertfordshire, SG1 2NY, UK.

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General directions

Solvents and reagents: Solvents were distilled as follows: THF and Et₂O over Na-benzophenone ketyl, toluene over Na, CH₂Cl₂ and DMF over CaH₂; HPLC grade EtOAc and petrol were used as commercially supplied. Reagents were used as commercially supplied unless otherwise stated and handled in accordance with COSHH regulations. Chromatography: Flash chromatography (FC) was carried out on Silica gel (BDH Silica gel for FC) according to the method described by Still,¹ or by using either Isolute Flash Silica (1 g, 5 g, 50 g) or Varian Bond Elute Si (10 g) SPE cartridges in conjunction with a Varian Vac-Elut-20 vacuum manifold. Alumina was grade 1 basic supplied by BDH. TLC was performed on aluminium backed silica gel plates (Merck Silica gel 60 F₂₅₄) which were developed with UV fluorescence (254 nm and 365 nm) and KMnO₄(aq)/Δ.

¹H NMR spectra: These were recorded at 250 MHz on Bruker AC-250 instrument or at 400 MHz on a Bruker AM-400 instrument. Chemical shifts (δ) are given in parts per million (ppm) as referenced to the appropriate residual solvent peak. Broad signals are assigned as b.

¹³C NMR spectra: These were recorded at 63 MHz on a Bruker AC-250 instrument or at 101 MHz on a Bruker AM-400 instrument. Chemical shifts (δ) are given in parts per million (ppm) as referenced to CHCl₃, and are assigned as s, d, t, and q, for C, CH, CH₂, and CH₃ respectively; The chemical shift of carbons on the fluorous-tag were recorded by applying fluorine-decoupling at δ -125.1 ppm during ¹³C NMR acquisition.

¹⁹F NMR spectra: These were recorded at 367 MHz on a Bruker AM-400 instrument. Chemical shifts (δ) are given in parts per million (ppm) as referenced to CFCl₃.

Mass Spectra: Low resolution and high-resolution spectra were recorded on a VG Prospec spectrometer, with molecular ions and major peaks being reported. Intensities are given as percentages of the base peak. Molecular weights are calculated using ⁷⁴Ge, ³⁵Cl and ⁷⁹Br isotopes. HRMS values are valid to ±5 ppm. GC-MS: Analyses were carried out using a Finnigan Trio-1000 El⁺ mass spectrometer and HP-8590 gas chromatograph. GC retention times are given in minutes. MS data is reported as above. HPLC: Analyses were carried out using a HP-1100 liquid chromatograph. LC retention times are given in minutes. Elemental analysis: Analyses were carried out by Mr Steven Boyer of London Metropolitan University Services Ltd. Melting points: Analyses were carried out using a Khofler hot stage and are uncorrected. Photochemistry: Photolytic oxidation was carried out using a 125 Watt Cathodeon high pressure Hg vapour lamp (type HPK 125) cooled by a rotary fan.

Synthesis of substrates for Table 1

Trichloro-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)germane

\[
\text{C}_{8}\text{F}_{17}\text{GeCl}_3
\]

₁H₂,₂H₂-Perfluorodecyl iodide (12.5 g, 41.56 mmol) and germanium(II) chloride dioxane complex² (5.00 g, 41.56 mmol) were heated in a Carius tube at 150 °C for 24 h. After cooling to rt, the reaction mixture was diluted with CH₂Cl₂ (500 mL) and added dropwise to H₂O (500 mL). The resulting white precipitate was collected by filtration, washed with H₂O (300 mL) then CH₂Cl₂ (300 mL) and dried under suction. The dried precipitate was stirred in conc. HCl (37% w/v) for 16 h and then extracted with CH₂Cl₂ (5 × 100 mL). The combined organic extracts were dried over MgSO₄ and concentrated in vacuo to give trichloro-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)germane as a brown oil (9.70 g, 78%). ¹H NMR (400 MHz; CDCl₃): δ 2.20 (m, 2H, CH₂CH₂Ge), 2.47 (m, 2H, CH₂CH₂Ge); ¹³C NMR (100 MHz; CDCl₃): δ 22.1 (t),
To a solution of trichloro-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)germane (2.50 g, 3.987 mmol) in THF (15.0 mL) was added a solution of 4-methoxyphenylmagnesiumbromide (40.0 mL, 20.0 mmol, 0.5 M). The resulting reaction mixture was stirred at reflux for 3 h. The yellow reaction mixture was cooled to 0 °C before quenching dropwise with methanol until effervescence ceased. The reaction mixture was diluted with Et₂O (20.0 mL) and washed with water (2 × 20.0 mL). The combined organic extracts were dried over MgSO₄ and the solvent was removed in vacuo. Sublimation of 4,4'bismethoxybiphenyl from the residue (100 °C /0.1mmHg using a Kugelrohr) followed by purification by FC (petrol/CH₂Cl₂ 50/50 → CH₂Cl₂) and drying under high vacuum gave (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)tris-(4-methoxyphenyl)germane as a white amorphous solid (2.84 g, 85%). mp 55-57 °C; Rf 0.35 (petrol/CH₂Cl₂, 70/30); ¹H NMR (400 MHz; CDCl₃): δ 1.63 (m, 2H, CH₂CH₂Ge), 2.19 (m, 2H, CH₂CH₂Ge), 3.81 (s, 9H, 3 × ArOC₆H₃), 6.94 (d, J = 8.5 Hz, 6H, ArH), 7.37 (d, J = 8.5 Hz, 6H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 3.7 (t), 27.0 (t, JCF = 23.0), 55.0 (3q), 114.0 (6d), 118.9 (3s), 126 (6d), 160.6 (3s), eight carbons not observed; ¹⁹F NMR (376 MHz; CDCl₃): δ - 126.5 (s, 2F), -123.2 (s, 2F), -122.7 (s, 2F), -122.1 (s, 4F, 2 × CF₂), -121.9 (s, 2F), -115.3 (s, 2F), -80.8 [s, 3F, CF₃(CF₂)₇(CH₂)₂]; IR ν max (neat) 3020 (C-H), 1438 (C-F), 1365, 1243, 902, 836 cm⁻¹; m/z (EI⁺) (rel. intensity) 841 (M⁺, 9), 735 (42), 715 (24), 395 (100); HRMS (EI⁺) calc'd. for C₃₁H₂₄GeO₃F₁₇ (M⁺) 841.0666, found 841.0705, Δ -4.6 ppm; Analysis for C₃₁H₂₄GeO₃F₁₇ expected C 44.27%, H 3.00%, found C 44.21%, H 2.95%.

Dichloro-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)(4-methoxyphenyl)germane

To a solution of (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)tris-(4-methoxyphenyl)germane (2.84 g, 3.377 mmol) in CH₂Cl₂ (20.0 mL) was added conc. HCl (20.0 mL, 240 mmol, 12.0 M). The reaction mixture was stirred for 16 h and the solvent was then removed in vacuo to give dichloro-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)(4-methoxyphenyl)germane as a white amorphous solid (2.32 g, 98%). ¹H NMR (400 MHz; CDCl₃): δ 1.95 (m, 2H, CH₂CH₂Ge), 2.45 (m, 2H, CH₂CH₂Ge), 3.81 (s, 3H, 3 × ArOCH₃), 6.92 (d, J = 8.5 Hz, 2H, ArH), 7.35 (d, J = 8.5 Hz, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 15.3 (t), 25.4 (t, JCF = 23.0 Hz), 55.3 (q), 114.8 (2d), 125.1 (s), 133.7 (2d) 162.7 (s), eight carbons not observed; ¹⁹F NMR (376 MHz; CDCl₃): δ - 126.2 (s, 2F), -123.3 (s, 2F), -122.7 (s, 2F), -122.1 (s, 4F, 2 × CF₂), -121.9 (s, 2F), -115.4 (CF₂₃CF₂₃CF₂₃), -80.8 (t, 3F, (CF₂)₆CF₂CF₃); IR ν max (KBr) 3033 (C-H), 2975 (C-H) 1595 C=C, 1504, 1455 (C-F), 1201, 958, 826 cm⁻¹; m/z (EI⁺) (rel. intensity) 698 [M⁺(³⁵Cl₂)]⁺, 47), 663 (4), 295 (12), 251
(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(4-methoxyphenyl)bis(naphthalen-2-ylmethyl)germane 1a

To oven dried, I₂ (0.01 g, 0.04 mmol) activated magnesium turnings (0.42 g, 17.3 mmol) in Et₂O (25.0 mL) was added 2-bromomethylnaphthalene (3.68 g, 16.6 mmol) to initiate Grignard reagent formation. To this solution was added a solution of dichloro-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)(4-methoxyphenyl)germane (2.32 g, 3.33 mmol) in Et₂O (5.0 mL) dropwise and the resulting mixture stirred for 2.5 h. A sat. solution NH₄Cl was added to the reaction mixture until no effervescence occurred and the solvent was then removed in vacuo. The residue taken up in Et₂O (30.0 mL) and washed with water (2 × 10.0 mL) and was dried over MgSO₄. 2-Methylnaphthalene was sublimed from the residue (60 °C/0.1mmHg using a Kugelrohr) then 1,2-bis-(2-naphthylmethyl)germane was removed from the residue by recrystallisation with Et₂O (16.0 mL) at 0 °C, filtration through cotton plug and washed with hexane (2 × 10.0 mL). Solvents were then removed from the filtrate in vacuo and purification by FC (petrol/CH₂Cl₂, 95/5 → 80/20) gave bis-(2-naphthylmethyl)germane 1a as a yellow amorphous solid (2.59 g, 86%). mp 189-190 °C; R_f 0.30 (petrol:EtOAc, 95/5); ^1H NMR (400 MHz; CDCl₃): δ 1.16 (m, 2H, CH₂C₄H₂Ge), 1.87 (m, 2H, C₄H₂CH₂Ge), 2.73 (s, 4H, 2 × GeC₄H₂Nap), 3.85 (s, 3H, OCH₃), 6.95 (d, J = 6.7 Hz, 2H, ArH), 7.09 (dd, J = 6.7, 1.8 Hz, 2H, ArH), 7.27 (d, J = 6.7 Hz, 2H, ArH), 7.37 (s, 2H, ArH), 7.39-7.47 (m, 4H, ArH), 7.64 (d, J = 7.7 Hz, 2H, ArH), 7.70 (d, J = 8.4 Hz, 2H, ArH), 7.80 (d, J = 7.7 Hz, 2H, ArH); ^13C NMR (100 MHz; CDCl₃) δ 2.2 (t), 22.8 (t, JCF = 23.0 Hz), 26.4 (2t), 55.0 (q), 108.4 (s), 110.2 (s), 110.7 (2s), 111.02 (s), 113.4 (s), 114.2 (2d), 115.0 (s), 118.1 (s), 124.8 (2d), 125.8 (2d), 126.0 (2d), 127.0 (2d), 127.4 (2d), 127.6 (2d), 128.0 (2d), 131.3 (2s), 133.8 (2s), 135.1 (2d), 136.7 (3s), 160.6 (s); ^19F NMR (376 MHz; CDCl₃): δ -125.2 (s, 2F), -122.5 (s, 2F), -121.7 (s, 2F), -120.9 (m, 6F), -115.4 [quintet, J = 14.8 Hz, 2F, (CF₂)₂CF₂CF₃], -79.8 (t, J = 10.0 Hz, 3F, (CF₂)₂CF₂CF₃); IR ν_max (neat) 3031 (C-H), 2925 (C-H), 1628, 1590 (C=C), 1422 (C-F), 1282, 1245, 1201,1146, 820 cm⁻¹; m/z (EI⁺) calc’d. for C₃₉H₂₉GeF₁₇O (M⁺) 910.1159, found 910.1145, Δ 1.6 ppm; Analysis for C₃₉H₂₉GeF₁₇O expected C 51.52%, H 3.21%, found C 51.68%, H 3.11%.

Bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(4-methoxyphenyl)bis(naphthalen-2-ylmethyl)germane

To a solution of 4-anisyl germane 1a (0.102 g, 0.112 mmol) in CH₂Cl₂ (10.0 mL) was added a solution of conc. HBr (2.0 mL, 48% wt.). The resulting biphasic reaction mixture was stirred at rt for 12 h, extracted with Et₂O (3 × 20.0 mL). The combined organic extracts were dried over MgSO₄ and evaporated in vacuo to give bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Heptadecafluorodecyl)(4-methoxyphenyl)bis(naphthalen-2-ylmethyl)germane as a brown amorphous solid (0.087 g, 88%). mp 172-174 °C; ^1H NMR (400 MHz; CDCl₃): δ 1.38 (m, 2H, C₄H₁₀Ge), 1.93 (m, 2H, C₅F₁₇CH₂CH₂Ge), 2.99 (dd, J = 12.6, 5.6 Hz, 4H, 2 × GeCH₂Nap), 7.21 (dd, J = 6.6, 1.8 Hz, 2H, ArH), 7.42-7.49 (m, 6H, ArH), 7.68 (dd, J = 6.6, 1.8 Hz, 2H, ArH), 7.76 (d, J = 8.4 Hz, 2H, ArH); HRMS (EI⁺) calc’d. for C₁₇H₁₁GeCl₂F₁₇O (M⁺) 697.9127, found 697.9125, Δ 0.3 ppm; Analysis for C₁₇H₁₁GeCl₂F₁₇O expected C 29.26%, H 1.59%, found C 29.27%, H 1.64%.

(100), 235 (16); HRMS (EI⁺) calc’d. for C₁₇H₁₁GeO₃₅Cl₂F₁₇ (M⁺) 697.9127, found 697.9125, Δ 0.3 ppm; Analysis for C₁₇H₁₁GeCl₂F₁₇O expected C 29.26%, H 1.59%, found C 29.27%, H 1.64%. 

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(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(4-methylphenyl)bis-(naphthalen-2-ylmethyl)germane 1b

To a solution of bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)bis-(naphthalen-2-ylmethyl)germane (0.800 g, 0.955 mmol), in Et2O (10.0 mL) at 0 °C was added a solution of 4-tolylmagnesiumbromide (4.75 mL, 4.75 mmol, 1.0 M) dropwise. The reaction mixture was stirred at 0 °C for 1 h and then at rt for over 14 h. The resulting solution was diluted with Et2O (20.0 mL) and a solution of 1.0 M NH4Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et2O, the combined organic extracts were dried over MgSO4 and evaporated in vacuo to give green oily residue which was purified by FC (hexane/EtOAc, 97/3) to give 4-tolyl germane 1b as a brown oil (0.600 g, 71%). 1H NMR (400 MHz; CDCl3): δ 1.20 (m, 2H, CH2C6H2Ge), 1.89 (m, 2H, C6H2CH2Ge), 2.45 (s, 3H, GeC6H4C6H3), 2.76 (s, 4H, 2 × GeC6H2Nap), 7.13 (d, 2H, J = 8.4 Hz, ArH), 7.25 (d, 2H, J = 6.8 Hz, ArH), 7.31 (d, 2H, J = 7.6 Hz, ArH), 7.41–7.50 (m, 6H, ArH), 7.68 (d, 2H, J = 7.6 Hz, ArH), 7.73 (d, 2H, J = 8.4 Hz, ArH), 7.83 (d, 2H, J = 7.6 Hz, ArH); 13C NMR (100 MHz; CDCl3): δ 1.9 (t), 21.4 (q), 22.5 (2t), 26.3 (t, JCF 23.4 Hz), 108.5 (s), 110.2 (s), 110.69 (2s), 110.72 (s), 111.0 (s), 111.1 (s), 118.0 (s), 124.8 (2d), 125.7 (2d), 126.0 (2d), 127.0 (2d), 127.4 (2d), 127.6 (2d), 128.0 (2d), 129.2 (2d), 131.3 (2s), 133.7 (2d), 133.8 (2d+3s), 136.7 (3s), 139.2 (s); 19F NMR (376 MHz; CDCl3): δ -126.6 (s, 2F), -123.9 (s, 2F), -123.1 (s, 2F), -122.3 (m, 6F), -116.7 [quintet, J = 15 Hz, 2F, (CF2)6CF2CF3], -81.2 [t, J = 10 Hz, 3F, (CF2)6CF2CF3]; IR νmax (neat) 3024 (C-H), 2980 (C-H) 1598 (C=C), 1507 (C=C), 1421 (C-F), 1265, 896, 744 cm⁻¹; m/z (EI') (rel. intensity) 894 (M+, 25), 753 (44), 322 (43), 282 (47), 211 (66), 141 (100); HRMS calc’d. for C39H2979BrF17Ge (M+) 894.1209, found 894.1204, Δ 3.8 ppm; Analysis for C39H2979BrF17Ge expected C 52.44%, H 3.27%, found C 52.53%, H 3.36%.

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(phenyl)bis-(naphthalen-2-ylmethyl)phenylgermane 1c

To a solution of bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)bis-(naphthalen-2-ylmethyl)germane (0.50 g, 0.567 mmol), in THF (10.0 mL) at 0 °C was added a solution of phenylmagnesiumbromide (0.68 mL, 1.7 mmol, 2.5 M) dropwise. The reaction mixture was stirred at 0 °C for 1 h and then at rt for over 14 h. The resulting solution was diluted with Et2O (20.0 mL) and a solution of 1.0 M NH4Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et2O, the combined organic extracts were dried over MgSO4 and evaporated in vacuo to give green oily residue which was purified by FC (hexane/EtOAc, 97/3) to give phenyl germane 1c as a brown oil (0.550 g, 52.44%). 1H NMR (400 MHz; CDCl3): δ 1.20 (m, 2H, CH2C6H2Ge), 1.88 (m, 2H, C6H2CH2Ge), 2.45 (s, 3H, GeC6H4C6H3), 2.76 (s, 4H, 2 × GeC6H2Nap), 7.13 (d, 2H, J = 8.4 Hz, ArH), 7.25 (d, 2H, J = 6.8 Hz, ArH), 7.31 (d, 2H, J = 7.6 Hz, ArH), 7.41–7.50 (m, 6H, ArH), 7.68 (d, 2H, J = 7.6 Hz, ArH), 7.73 (d, 2H, J = 8.4 Hz, ArH), 7.83 (d, 2H, J = 7.6 Hz, ArH); 13C NMR (100 MHz; CDCl3): δ 1.9 (t), 21.4 (q), 22.5 (2t), 26.3 (t, JCF 23.4 Hz), 108.5 (s), 110.2 (s), 110.69 (2s), 110.72 (s), 111.0 (s), 111.1 (s), 118.0 (s), 124.8 (2d), 125.7 (2d), 126.0 (2d), 127.0 (2d), 127.4 (2d), 127.6 (2d), 128.0 (2d), 129.2 (2d), 131.3 (2s), 133.7 (2d), 133.8 (2d+3s), 136.7 (3s), 139.2 (s); 19F NMR (376 MHz; CDCl3): δ -126.6 (s, 2F), -123.9 (s, 2F), -123.1 (s, 2F), -122.3 (m, 6F), -116.7 [quintet, J = 15 Hz, 2F, (CF2)6CF2CF3], -81.2 [t, J = 10 Hz, 3F, (CF2)6CF2CF3]; IR νmax (neat) 3024 (C-H), 2980 (C-H) 1598 (C=C), 1507, 1421 (C-F), 1265, 896, 744 cm⁻¹; m/z (EI') (rel. intensity) 894 (M', 25), 753 (44), 322 (43), 282 (47), 211 (66), 141 (100); HRMS calc’d. for C39H2979BrF17Ge (M’) 894.1209, found 894.1244, Δ 3.8 ppm; Analysis for C39H2979BrF17Ge expected C 52.44%, H 3.27%, found C 52.53%, H 3.36%.
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6 mL of Et₂O, the combined organic extracts were dried over MgSO₄ and evaporated in vacuo to give green oily residue which was purified by FC (hexane/EtOAc, 97/3) to give phenylgermane 1c as a pale yellow oil (0.4122 g, 83%). ¹H NMR (400 MHz; CDCl₃): δ 1.19 (m, 2H, CH₂C₆H₄Ge), 1.89 (m, 2H, C₆H₄CH₂Ge), 2.76 (s, 4H, 2 × GeC₆H₂Nap), 7.09 (dd, J = 8.4, 1.2 Hz, 2H, ArH), 7.73–7.49 (m, 11H, ArH), 7.65 (d, J = 7.4 Hz, 2H, ArH), 7.71 (d, J = 8.4 Hz, 2H, ArH), 7.81 (d, J = 7.4 Hz, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 19.1 (t), 22.5 (2t), 26.2 (t, JCF = 23.4 Hz), 108.3 (s), 110.2 (2s), 110.7 (2s), 111.0 (2s), 111.1 (s), 118.0 (s), 124.8 (2d), 125.7 (2d), 126.1 (2d), 127.0 (2d), 127.4 (2d), 127.6 (2d), 128.1 (2d), 128.4 (2d), 129.3 (d), 131.3 (2s), 133.7 (2s), 133.8 (2d), 136.5 (2s); ¹⁹F NMR (376 MHz; CDCl₃): δ -125.2 (s, 2F), -122.5 (s, 2F), -121.8 (s, 2F), -121.0 (m, 6F), -115.4 [quintet, J = 15 Hz, 2F, (CF₃)₂CF₂CF₃], -79.8 [t, J = 10 Hz, 3F, (CF₃)₂CF₂CF₃]; IR ν max (neat) 3032 (C-H), 2985 (C-H) 1598 (C=C), 1415 (C-F), 1265, 1090 (C-Cl), 895, 749 cm⁻¹; m/z (FAB⁺) (rel. intensity) 739 [(M-NapCH₂)+, 2], 459 (1), 141 (100); HRMS (FAB⁺) calc’d. for C₂₇H₁₉F₁₇⁷⁴Ge [(M-NapCH₂)+] 739.0845, found 739.0870, Δ 3.4 ppm.

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(4-chlorophenyl)bis-(naphthalen-2-ylmethyl)germane 1d

To a solution of 4-chloro-1-bromoenzene (0.4038 g, 2.10 mmol) in THF (10.0 mL) at -78 °C was added 'BuLi (3.3 mL, 4.62 mmol, 1.4M) dropwise resulting in a yellow solution. The solution was stirred at -78 °C for 30 min to achieve lithium-halogen exchange. The resulting solution mixture was added bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)bis-(naphthalen-2-ylmethyl)germane (0.62 g, 0.756 mmol) at -78 °C and stirred for 1 h than warmed up to rt for 16 h. The reaction mixture was diluted with Et₂O (20.0 mL) and a solution of 1.0 M NH₄Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et₂O, the combined organic extracts were dried over MgSO₄ and evaporated in vacuo to give green oily residue which was purified by FC (hexane/EtOAc, 97/3) to give 4-chlorophenylgermane 1d as a pale yellow oil (0.5168 g, 80%). ¹H NMR (400 MHz; CDCl₃): δ 1.20 (m, 2H, CH₂C₆H₄Ge), 1.84 (m, 2H, C₆H₄CH₂Ge), 2.74 (s, 4H, 2 × GeC₆H₂Nap), 7.07 (dd, J = 6.7, 1.7 Hz, 2H, ArH), 7.25 (d, J = 8.2 Hz, 2H, ArH), 7.36 (d, J = 7.7 Hz, 2H, ArH), 7.42-7.49 (m, 6H, ArH), 7.66 (d, J = 7.7 Hz, 2H, ArH), 7.71 (d, J = 8.2 Hz, 2H, ArH), 8.18 (d, J = 7.7 Hz, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 18.0 (t), 22.4 (2t), 26.2 (t, JCF = 23.5 Hz), 108.3 (s), 110.2 (s), 110.7 (3s), 110.97 (s), 111.01 (s), 117.9 (s), 125.0 (2d), 125.7 (2d), 126.2 (2d), 127.0 (2d), 127.2 (2d), 127.6 (2d), 128.2 (2d), 128.6 (2d), 131.3 (2s), 133.7 (2s), 134.7 (s), 135.5 (2d), 135.7 (s), 136.1 (2s); ¹⁹F NMR (376 MHz; CDCl₃): δ -125.2 (s, 2F), -122.5 (s, 2F), -121.8 (s, 2F), -121.0 (m, 6F), -115.4 [quintet, J = 15 Hz, 2F, (CF₃)₂CF₂CF₃], -79.8 [t, J = 10 Hz, 3F, (CF₃)₂CF₂CF₃]; IR ν max (neat) 3048 (C-H), 2980 (C-H) 1596 (C=C), 1405 (C-F), 1264, 1090 (C-Cl), 895, 749 cm⁻¹; m/z (FAB⁺) (rel. intensity) 773 [(M(³⁵Cl)-NapCH₂)+, 1], 429 (1), 401 (2), 141 (100); HRMS (FAB⁺) calc’d. for C₇₂H₁₀F₁₇³⁵Cl⁷⁴Ge [M-(NapCH₂)+] 772.9954, found 772.9952, Δ -0.2 ppm.

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)bisnaphthalen-2-yl-(2-methoxyphenyl)germane 1e
To a solution of 2-methoxy-1-bromobenzene (0.3324 g, 1.78 mmol) in THF (10.0 mL) at -78 °C was added t-BuLi (2.6 mL, 3.64 mmol, 1.4M) dropwise resulting in a yellow solution. The solution was stirred at -78 °C for 30 min to achieve lithium-halogen exchange. The resulting solution mixture was added bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)bis-(naphthalen-2-ylmethyl)germane (0.5234 g, 0.593 mmol) at -78 °C and stirred for 1 h than warmed up to rt for 16 h. The reaction mixture was diluted with Et₂O (20.0 mL) and a solution of 1.0 M NH₄Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et₂O, the combined organic extracts were dried over MgSO₄ and evaporated in vacuo to give green oily residue which was purified by FC (hexane/EtOAc, 95/5) to give (2-methoxyphenyl)germane 1e as a pale yellow oil (0.4706 g, 87%); ¹H NMR (400 MHz; CDCl₃): δ 1.19 (m, 2H, CH₂C₆H₄Ge), 1.89 (m, 2H, C₆H₄CH₂Ge), 2.78 (s, 4H, 2 × GeC₆H₂Nap), 3.69 (s, 3H, OC₆H₃), 6.89 (d, J = 8.4 Hz, 1H, ArH), 7.02 (t, J = 7.2 Hz, 1H, ArH), 7.10 (d, J = 8.4 Hz, 2H, ArH), 7.34-7.39 (m, 3H, ArH), 7.40-7.46 (m, 5H, ArH), 7.62 (m, 2H, ArH), 7.68 (d, J = 8.4 Hz, 2H, ArH), 7.79 (d, J = 7.7 Hz, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 2.7 (t), 22.7 (2t), 26.6 (t, JCF = 23.2 Hz), 54.7 (q), 108.4 (s), 110.2 (s), 110.7 (2s), 109.6 (2d), 111.0 (2s), 111.1 (s), 118.2 (s), 121.0 (2d), 124.5 (s), 124.6 (2d), 125.7 (2d), 125.9 (2d), 127.0 (2d), 127.5 (2d+s), 127.8 (2d), 131.1 (d), 131.2 (s), 133.7 (2s), 134.9 (d), 137.3 (2s), 162.8 (s); ¹⁹F NMR (376 MHz; CDCl₃): δ -125.1 (s, 2F), -122.6 (s, 2F), -121.8 (s, 2F), -121.0 (m, 6F), -115.3 [quintet, J = 14.7 Hz, 2F, (CF₂)₆C₂F₂CF₃], -79.8 [t, J = 9.8 Hz, 3F, (CF₂)₆CF₂C₂F₃]; IR υ max (neat) 3032 (C-H), 2980 (C-H) 1595 (C=C), 1507, 1412 (C-F), 1265, 896, 748 cm⁻¹; m/z (FAB⁺) (rel. intensity) 769 [(M-NapCH₂)+, 1], 463 (1), 341 (5), 141 (100); HRMS (FAB⁺) calc’d. for C₂₈H₂₀F₁₇O₇₀Ge [M-(NapCH₂)+] 765.0480, found 765.0480, Δ 0.0 ppm.

To oven dried magnesium turnings (0.032 g, 1.34 mmol) in THF (33.0 mL) was added 4-trifluoromethylbromobenzene (1.23 g, 1.23 mL, 1.34 mmol) and the reaction mixture was stirred for 2 h to initiate Grignard reagent formation. To the resulting orange coloured reaction mixture was added a solution of bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)bis-(naphthalen-2-ylmethyl)germane (0.500 g, 0.600 mmol) in THF (2.00 mL) dropwise and the reaction mixture was stirred for 4 h. A sat. solution of NH₄Cl was added to the reaction mixture until no effervescence occurred and the reaction mixture was partitioned between Et₂O (40.0 mL) and water (10.0 mL), extracted with CH₂Cl₂ (2 × 10.0 mL) and dried over MgSO₄. Purification by FC (petrol → petrol/EtOAc, 95/5) gave (4-trifluoromethylphenyl)germane 1f as a pale yellow oil (0.474 g, 84%); ¹H NMR (400 MHz; CDCl₃): δ 1.21 (m, 2H, CH₂C₆H₄Ge), 1.83 (m, 2H, CH₂C₆H₄Ge), 2.76 (s, 4H, 2 × GeC₆H₂Nap), 7.06 (dd, J = 6.6, 1.8 Hz, 2H, ArH), 7.35 (s, 2H, ArH), 7.40-7.48 (m, 6H, ArH), 7.61 (t, J = 8.7 Hz, 4H, ArH), 7.70 (d, J = 8.4 Hz, 2H, ArH), 7.79 (d, J = 7.5 Hz, 2H, ArH); ¹³C NMR (101 MHz; CDCl₃) δ 1.9 (t), 22.4 (2t), 26.2 (t), 108.4 (s), 110.2 (s), 110.64 (2s), 110.67 (s), 110.95 (s), 110.99 (s), 117.9 (s), 124.77 (s), 124.81 (2d), 125.0 (2d), 125.8 (2d), 126.2 (2d), 126.2 (2d), 127.0 (2d), 127.1 (2d), 127.6 (2d), 128.2 (2d), 131.3 (2s), 133.7 (2s), 134.2 (2d), 135.8 (3s); ¹⁹F NMR (376 MHz; CDCl₃): δ -125.2 (s, 2F), -122.6 (s, 2F), -121.8 (s, 2F), -121.0 (m, 6F), -115.4 [quintet, J = 15.1 Hz, 2F, (CF₂)₆C₂F₂CF₃], -79.8 [t, J = 10.0 Hz, 3F, (CF₂)₆C₂F₂CF₃], -62.0 (s, 3F, ArCF₃); IR υ max (neat) 3020 (C-H), 2985 (C-H) 1595 (C=C), 1421 (C-F), 765.0480, found 765.0480, Δ 0.0 ppm.
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1265, 897, 740 cm⁻¹; m/z (EI⁺) (rel. intensity) 948 (M⁺, 55), 807 (71), 787 (16), 769 (20), 549 (23), 141 (100); HRMS (EI⁺) calc’d. for C₃₀H₂₆⁷⁴GeF₂₀ (M⁺) 948.0927, found 948.0962, Δ 3.7 ppm; Analysis for C₃₀H₂₉GeF₂₀ expected C 50.49%, H 3.10%, found C 50.54%, H 2.99%.

Photoactivation/cross-coupling reactions (Table 1):

![Photoactivation/cross-coupling reactions diagram]

**General method for photoactivation**

To a solution of the arylgermane (0.076 mmol) in MeCN/MeOH (3/1 v/v, 20 mL) in a Pyrex Schlenk tube (1 mm thick) was added powdered Cu(BF₄)₂·nH₂O (0.084 g). The resulting mixture was purged with argon for 30 min before irradiating using a 125 W high pressure Hg lamp for 1 h. A further portion of powdered Cu(BF₄)₂·nH₂O (0.084 g) was then added and the solution irradiated for a further 1 h. After this time, the solvent was removed in vacuo, the residue was taken up in CH₂Cl₂ (20.0 mL), washed with water (2 × 8.00 mL) and dried over MgSO₄ to give the crude difluoroarylgermane.

The progress of the photolysis can be conveniently monitored by ¹⁹F NMR. For example, for the photolysis of arylgermane 1a:

The ¹⁹F NMR after <2 h displays a singlet at δF -202.4 ppm which corresponds to the mono-germyl fluoride \{(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)(4-methoxyphenyl)(naphthalen-2-ylmethyl)germyl fluoride: R: 0.40 (CH₂Cl₂); ¹H NMR (400 MHz; CDCl₃): δ 1.43 (m, 2H, CH₂C₃H₂Ge), 2.11 (m, 2H, CH₂C₃H₂Ge), 3.03 (m, 2H, GeC₃H₂Nap), 3.84 (s, 3H, OC₃H₃), 6.99 (d, J = 6.7 Hz, 2H, ArH), 7.26 (d, J = 6.7 Hz, 1H, ArH), 7.40 (d, J = 6.7 Hz, 2H, ArH), 7.59 (s, 1H, ArH), 7.72-7.85 (m, 3H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 6.1 (t), 25.1 (t), 26.3 (t), 55.1 (q), 108.7 (s), 110.6 (s), 111.1 (s), 111.4 (3s), 114.5 (2d), 118.4 (s), 125.1 (d), 126.27 (d), 126.31 (d), 127.1 (2d), 127.6 (d), 128.5 (d), 131.6 (s), 133.1 (s), 133.7 (s), 134.3 (2d), 161.7 (s), 1 × (s) carbon signal absent; ¹⁹F NMR (376 MHz; CDCl₃): δ -202.4 (s, GeF), -125.2 (s, 2F), -122.5 (s, 2F), -121.8 (s, 2F), -120.9 (m, 6F), -115.3 [quintet, J = 14.8 Hz, 2F, (CF₃)CF₂CF₃], -79.8 (t, J = 10.0 Hz, 3F, (CF₃)CF₂CF₃); m/z (EI⁺) (rel. intensity) 788 (M⁺, 1), 530 (70), 281 (70), 57 (100).}

After 2 h the peak for this mono-germyl fluoride has disappeared and the ¹⁹F NMR displays three singlets at δF -163.6, -164.1 and -165.3 ppm which correspond to the difluorogermane and/or a derivative thereof \{m/z (EI⁺) (rel. intensity) 666 (M⁺, 1), 410 (25), 328 (30), 149 (60), 57 (100); HRMS (EI⁺) calc’d. for C₁₇H₁₁⁷⁴GeF₁₉O (M⁺) 665.9718, found 665.9701, Δ 2.7 ppm.}

The by-product of the photooxidation, 2-naphthylmethyl methyl ether, shows the following diagnostic ¹H NMR signals: ¹H NMR (400 MHz; CDCl₃): δ 3.41 (s, 3H, OMe), 4.62 (s, 2H, ArCH₂), 7.40-7.48 (m, 3H, ArH), 7.75-7.83 (m, 4H, ArH).

If the solution has not been efficiently deoxygenated, some 2-naphthaldehyde forms and shows the following diagnostic ¹H NMR signals: ¹H NMR (400 MHz; CDCl₃): δ 7.55-7.63 (m, 2H, ArH), 7.88-7.96 (m, 4H, ArH), 8.35 (s, 1H, ArH), 10.22 (s, 1H, ArCHO); m/z (EI⁺) (rel. intensity) 156 (M⁺, 100), 127 (90), 91 (20), 58 (50).

Typical method for cross-coupling of crude photoactivated germane
Entry 1: 4-Methoxy-3',5'-bis(trifluoromethyl)biphenyl 3a

The crude difluoroarylgermane from the photolysis of arylgermane 1a (31.1 mg, 0.047 mmol) and TBAF (44.2 mg, 0.14 mmol) was dissolved in degassed DMF (2 mL) and stirred for 30 min. PdCl2(MeCN)2 (1.2 mg, 0.0046 mmol) and P(2-Tol)3 (2.2 mg, 0.007 mmol) were dissolved in degased DMF (1 mL) for 30 min the active catalytic species. The catalyst solution was added to the difluoroarylgermane solution followed by adding 3,5-bis(trifluoromethyl)bromobenzene (27.2 mg, 0.093 mmol, 16 μL) and CuI (9.3 mg, 0.047 mmol). The resulting mixture heated at 120 °C for 16 h under nitrogen atmosphere. The crude reaction mixture was diluted with Et2O (20.0 mL) and washed with water (3 × 10.0 mL), the combined organic extracts were dried over MgSO4 and evaporated in vacuo. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3a as a clear liquid (14.0 mg, 96%). Rf 0.22 (cyclohexane); 1H NMR (400 MHz; CDCl3): δ 3.88 (s, 3H, OC6H3), 7.03 (d, J = 8.8 Hz, 2H, ArH), 7.55 (d, J = 8.8 Hz, 2H, ArH), 7.81 (s, 1H, ArH), 7.91 (s, 2H, ArH). 19F NMR (376 MHz; CDCl3): δ -62.8 (s, 6F, 2 × CF3). 13C NMR (CDCl3, 67 MHz) δ 55.4 (q), 114.7 (d), 120.2 (d), 126.6 (d), 128.4 (d), 132.4 (s), 132.6 (s), 139.2 (s), 159.2 (s); IR υ max (neat) 2940, 2842, 1610, 1521, 1383, 1279, 1185, 1132, 830, 682 cm−1; m/z (EI) (rel. intensity) 320 (M +, 100), 305 (16), 301 (20), 277 (60), 251 (9), 188 (13); HRMS calc’d for C15H10F6 O320.0636, found 320.0625, Δ 3.4 ppm.

Entry 2: 4-Chloro-4'-methoxybiphenyl 3b

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1a (48.3 mg, 0.07 mmol), TBAF (66.6 mg, 0.211 mmol), PdCl2(MeCN)2 (1.8 mg, 0.007 mmol), P(2-Tol)3 (3.2 mg, 0.0105 mmol), 4-chlorobromobenzene (27 mg, 0.141 mmol) and CuI (14 mg, 0.07 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3b as a colourless oil (13.1 mg, 85%). 1H NMR (400 MHz; CDCl3): δ 3.85 (s, 3H, OC6H3), 6.96-6.99 (m, 2H, ArH), 7.37-7.39 (m, 2H, ArH), 7.46-7.51 (m, 4H, ArH); 13C NMR (100 MHz; CDCl3) δ 55.3 (q), 114.3 (2d), 127.9 (2d), 128.0 (2d), 128.8 (2d), 132.4 (s), 132.6 (s), 139.2 (s), 159.2 (s); m/z (EI) (rel. intensity) 218 (M+, 100), 203 (40), 175 (30); HRMS (EI+) calc’d. for C13H1135ClO (M+) 218.0498, found 218.0499, Δ 0.3 ppm.

Entry 3: 4-Methoxy-4'-(phenylmethoxy)biphenyl 3c

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1a (48.3 mg, 0.07 mmol), TBAF (66.6 mg, 0.211 mmol), PdCl2(MeCN)2 (1.8 mg, 0.007 mmol), P(2-Tol)3 (3.2 mg, 0.0105 mmol), 4-(phenylmethoxy)bromobenzene (34.8 mg, 0.141 mmol) and CuI (14 mg, 0.07 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3c as a colourless oil (12.5 mg, 65%). 1H NMR (400 MHz; CDCl3): δ 3.85 (s, 3H, OC6H3), 5.11 (s, 2H, ArOC6H2Ph), 6.97 (d, J = 8.6 Hz, 2H, ArH), 7.04 (d, J = 8.6 Hz, 2H, ArH), 7.32-7.36 (m, 1H, ArH), 7.41 (t, J = 7.4 Hz, 2H, ArH), 7.46-7.50 (m, 6H, ArH); 13C NMR (100 MHz; CDCl3) δ 55.3 (q), 114.2 (t), 127.9 (2d), 128.0 (2d), 128.8 (2d), 132.4 (s), 132.6 (s), 139.2 (s), 159.2 (s); m/z (EI) (rel. intensity) 290 (M+, 60), 199 (100), 149 (35), 91 (60); HRMS (EI+) calc’d. for C20H18O2 (M+) 290.1307, found 290.1303, Δ -1.3 ppm.

Entry 4: 1-(4-Methoxyphenyl)naphthalene 3d

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1a (48.3 mg, 0.07 mmol), TBAF (66.6 mg, 0.211 mmol), PdCl2(MeCN)2 (1.8 mg, 0.007 mmol), P(2-Tol)3 (3.2 mg, 0.0105 mmol), 4-(phenylmethoxy)bromobenzene (34.8 mg, 0.141 mmol) and CuI (14 mg, 0.07 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3c as a colourless oil (12.5 mg, 65%). 1H NMR (400 MHz; CDCl3): δ 3.85 (s, 3H, OC6H3), 5.11 (s, 2H, ArOC6H2Ph), 6.97 (d, J = 8.6 Hz, 2H, ArH), 7.04 (d, J = 8.6 Hz, 2H, ArH), 7.32-7.36 (m, 1H, ArH), 7.41 (t, J = 7.4 Hz, 2H, ArH), 7.46-7.50 (m, 6H, ArH); 13C NMR (100 MHz; CDCl3) δ 55.3 (q), 70.1 (t), 114.2 (d), 115.1 (3d), 127.5 (2d), 127.8 (4d), 128.0 (d), 128.6 (2d), 133.4 (s), 133.7 (s), 137.0 (s) 157.9 (s), 158.7 (s); IR υ max (neat) 3027 (C-H), 2988 (C-H) 1567 (C=C), 980, 870 cm−1; m/z (EI) (rel. intensity) 290 (M+, 60), 199 (100), 149 (35), 91 (60); HRMS (EI+) calc’d. for C20H18O2 (M+) 290.1307, found 290.1303, Δ -1.3 ppm.
Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1a (48.3 mg, 0.07 mmol), TBAF (66.6 mg, 0.211 mmol), PdCl₂(MeCN)₂ (1.8 mg, 0.007 mmol), P(2-Tol)₃ (3.2 mg, 0.0105 mmol), 1-bromonaphthalene (29.8 mg, 0.143 mmol, 20 μL) and Cul (40.1 mg, 0.201 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave 1-(4-methoxyphenyl)naphthalene 3d as white plates (12.4 mg, 75%). Rₛ 0.16 (cyclohexane); mp. 110.4-116.2 °C (cf. 114-115 °C). ¹H NMR (400 MHz; CDCl₃): δ 3.90 (s, 3H, OCH₃), 7.04 (d, J = 8.6 Hz, 2H, ArH), 7.40-7.46 (m, 4H, ArH), 7.47-7.54 (m, 2H, ArH), 7.84 (d, J = 8.2 Hz, 1H, ArH), 7.92 (d, J = 9.2 Hz, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 55.3 (q), 113.7 (2d), 125.4 (d), 125.7 (d), 125.9 (d), 126.0 (d), 126.9 (d), 127.3 (d), 128.2 (d), 131.1 (2d), 131.8 (s), 133.1 (s), 133.8 (s), 139.9 (s), 158.9 (s); m/z (EI⁺) (rel. intensity) 234 (M⁺, 100%), 219 (38), 203 (14), 189 (55), 163 (9), 101 (23), 95 (29); HRMS (EI⁺) calc’d. for C₁₇H₁₄O (M⁺) 234.1045, found 234.1041, Δ −1.6 ppm.

**Entry 5:** 4-Methyl-3',5'-bis-(trifluoromethyl)biphenyl 3e

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1b (55.2 mg, 0.085 mmol), TBAF (80.0 mg, 0.254 mmol), PdCl₂(MeCN)₂ (2.2 mg, 0.0085 mmol), P(2-Tol)₃ (3.9 mg, 0.0128 mmol), 3,5-bis-(trifluoromethyl)bromobenzene (49.8 mg, 0.17 mmol, 29.3 μL) and Cul (17.5 mg, 0.088 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3e as a colourless oil (21.8 mg, 84%). Rₛ 0.65 (cyclohexane); ¹H NMR (400 MHz; CDCl₃): δ 2.43 (s, 3H, ArCH₃), 7.31 (d, J = 8.0 Hz, 2H, ArH), 7.51 (d, J = 8.0 Hz, 2H, ArH), 7.82 (s, 1H, ArH), 7.99 (s, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 21.2 (q), 120.6 (2s), 122.1 (d), 126.9 (2d), 130.0 (2d), 131.8 (s), 135.3 (s), 139.0 (s), 143.2 (s); m/z (EI⁺) (rel. intensity) 304 (M⁺, 91), 285 (19), 235 (66), 215 (39), 165 (100), 91 (66), 69 (25); HRMS (EI⁺) calc’d. for C₁₅H₁₀F₆ (M⁺) 304.0687, found 304.0681, Δ −1.9 ppm.

**Entry 6:** 4-Chloro-4'-methylbiphenyl 3f

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1b (55.2 mg, 0.085 mmol), TBAF (80.0 mg, 0.254 mmol), PdCl₂(MeCN)₂ (2.2 mg, 0.0085 mmol), P(2-Tol)₃ (3.9 mg, 0.0128 mmol), 4-chloro-bromobenzene (32.6 mg, 0.170 mmol) and Cul (17.5 mg, 0.088 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3f as a colourless oil (11.9 mg, 69 %). ¹H NMR (400 MHz; CDCl₃): δ 2.40 (s, 3H, ArCH₃), 7.24 (s, 1H, ArH), 7.37-7.40 (m, 2H, ArH), 7.41-7.48 (m, 3H, ArH), 7.49-7.52 (m, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 21.1 (q), 126.8 (2d), 129.6 (d), 133.0 (s), 137.1 (s), 137.4 (s), 139.6 (s); m/z (EI⁺) (rel. intensity) 202 [M(35Cl)+, 100), 165 (65), 82 (40); HRMS (EI⁺) calc’d. for C₁₃H₁₁Cl₃5Cl (M⁺) 202.0549, found 202.0557, Δ 3.8 ppm.

**Entry 7:** 4-Methyl-4'-((phenylmethoxy)biphenyl 3g

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1b (55.2 mg, 0.085 mmol), TBAF (80.0 mg, 0.254 mmol), PdCl₂(MeCN)₂ (2.2 mg, 0.0085 mmol), P(2-Tol)₃ (3.9 mg, 0.0128 mmol), 4-(phenylmethoxy)bromobenzene (44.8 mg, 0.170 mmol) and Cul (17.5 mg, 0.088 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3g as a colourless oil (11.2 mg, 48 %). ¹H NMR (400 MHz; CDCl₃): δ 2.38 (s, 3H, ArCH₃), 5.11 (s, 2H, ArOCH₂Ph), 7.04 (d, J = 8.7 Hz, 2H, ArH), 7.22 (d, J = 8.0 Hz, 2H, ArH), 7.30-7.36 (m, 1H, ArH), 7.38-7.42 (m, 2H, ArH), 7.43-7.47 (m, 4H, ArH), 7.51 (d, J = 8.7 Hz, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 21.1 (q), 70.1 (t), 115.1 (2d), 126.6 (2d), 127.5 (2d), 128.0 (3d), 128.6
Entry 8: 1-(4-Methylphenyl)naphthalene 3h

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1b (55.2 mg, 0.085 mmol), TBAF (80.0 mg, 0.254 mmol), PdCl₂(MeCN)₂ (2.2 mg, 0.0085 mmol), P(2-Tol)₃ (3.9 mg, 0.0128 mmol), 1-bromonaphthalene (35.4 mg, 0.171 mmol, 23.8 μL) and CuI (37.1 mg, 0.186 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave 1-(4-methylphenyl)naphthalene 3h as white plates (13.2 mg, 71%). ¹H NMR (400 MHz; CDCl₃): δ 2.47 (s, 3H, ArCH₃), 7.32 (d, J = 7.9 Hz, 2H, ArH), 7.40-7.48 (m, 4H, ArH), 7.49-7.55 (m, 2H, ArH), 7.86 (d, J = 8.2 Hz, 1H, ArH), 7.93 (t, J = 9.1 Hz), 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 21.2 (q), 125.4 (d), 125.7 (d), 125.9 (d), 126.1 (d), 126.9 (d), 127.4 (d), 128.2 (d), 129.0 (2d), 129.3 (2d), 131.7 (s), 133.8 (s), 136.9 (s), 137.8 (s), 140.2 (s); m/z (EI⁺) (rel. intensity) 218 (M⁺, 100), 203 (85), 108 (50); HRMS (EI⁺) calc'd. for C₁₇H₁₄ (M⁺) 218.1096, found 218.1098, Δ 1.1 ppm.

Entry 9: 3',5'-bis-(Trifluoromethyl)biphenyl 3i

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1c (50.6 mg, 0.08 mmol), TBAF (80.0 mg, 0.254 mmol), PdCl₂(MeCN)₂ (2.1 mg, 0.0081 mmol), P(2-Tol)₃ (3.7 mg, 0.088 mmol), 3,5-bis-(trifluoromethyl)bromobenzene (46.8 mg, 0.160 mmol, 27.5 μL) and CuI (17.5 mg, 0.0111 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3i as a colourless oil (17.1 mg, 74%). ¹H NMR (400 MHz; CDCl₃): δ 7.45-7.54 (m, 2H, ArH), 7.61-7.63 (m, 1H, ArH), 7.86 (s, 1H, ArH), 8.01 (d, J = 10.0 Hz, 2H, ArH), 8.03 (s, 2H, ArH); m/z (EI⁺) (rel. intensity) 290 (M⁺, 100); 57 (40); HRMS (EI⁺) calc'd. for C₁₄H₈F₆ (M⁺) 290.0530, found 290.0523, Δ -2.5 ppm.

Entry 10: 4-Chlorobiphenyl 3j

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1c (50.6 mg, 0.08 mmol), TBAF (80.0 mg, 0.254 mmol), PdCl₂(MeCN)₂ (2.1 mg, 0.0081 mmol), P(2-Tol)₃ (3.7 mg, 0.088 mmol), 4-chlorobromobenzene (30.5 mg, 0.159 mmol) and CuI (17.5 mg, 0.088 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3j as a colourless oil (9.5 mg, 63%). ¹H NMR (400 MHz; CDCl₃): δ 7.34-7.40 (m, 1H, ArH), 7.41-7.45 (m, 3H, ArH), 7.47-7.48 (m, 2H), 7.49-7.56 (m, 3H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 127.0 (d), 127.6 (d), 128.2 (2d), 128.4 (d), 128.9 (d), 129.0 (3d), 133.7 (s), 134.6 (s), 136.6 (s); m/z (EI⁺) (rel. intensity) 188 [M⁺(35Cl)+, 80], 152 (100); HRMS (EI⁺) calc'd. for C₁₂H₉Cl (M⁺) 188.0393, found 188.0385, Δ -0.1 ppm.

Entry 11: 4-(Phenylmethoxy)biphenyl 3k

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1c (50.6 mg, 0.08 mmol), TBAF (80.0 mg, 0.254 mmol), PdCl₂(MeCN)₂ (2.1 mg, 0.0081 mmol), P(2-Tol)₃ (3.7 mg, 0.088 mmol), 4-(phenylmethoxy)bromobenzene (41.9 mg, 0.159 mmol) and CuI (17.5 mg, 0.088 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3k as a colourless oil (8.3 mg, 40%). ¹H NMR (400 MHz; CDCl₃): δ 5.12 (s, 2H, ArH), 7.05 (d, J = 8.8 Hz, 2H, ArH), 7.30 (t, J = 7.3 Hz, 1H, ArH), 7.35 (d, J = 7.1 Hz, 1H, ArH), 7.38-7.48 (m, 6H, ArH), 7.51-7.56 (m, 4H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 70.1 (t), 115.1
Entry 12: 1-Phenylnaphthalene 3l

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1c (50.6 mg, 0.08 mmol), TBAF (80.0 mg, 0.254 mmol), PdCl₂(MeCN)₂ (3.7 mg, 0.0088 mmol), 1-bromonaphthalene (32.9 mg, 0.159 mmol, 22.1 μL) and CuI (17.5 mg, 0.088 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave 1-phenylnaphthalene 3l as white plates (9.8 mg, 60%). 1H NMR (400 MHz; CDCl₃): δ 7.41-7.45 (m, 3H, ArH), 7.47-7.55 (m, 6H, ArH), 7.86 (d, J = 8.0 Hz, 1H, ArH), 7.91 (dd, J = 8.0, 3.1 Hz, 2H, ArH); 13C NMR (100 MHz; CDCl₃) δ 125.4 (d), 125.8 (d), 126.0 (2d), 126.9 (d), 127.2 (d), 127.6 (d), 128.2 (3d), 130.1 (2d), 130.2 (s), 133.8 (s), 140.2 (s), 140.7 (s); m/z (EI⁺) (rel. intensity) 204 (M⁺, 100), 101 (20); HRMS (EI⁺) calc'd. for C₁₆H₁₂ (M⁺) 204.0903, found 204.0903, Δ 0.0 ppm.

Entry 13: 4-Chloro-3',5'-bis-(trifluoromethyl)biphenyl 3m

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1d (52.2 mg, 0.0782 mmol), TBAF (74 mg, 0.235 mmol), PdCl₂(MeCN)₂ (3.7 mg, 0.012 mmol), 3,5-bis-(trifluoromethyl)bromobenzene (45.9 mg, 0.157 mmol, 27 μL) and CuI (15.6 mg, 0.078 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3m as a colourless oil (17.9 mg, 71%). 1H NMR (400 MHz; CDCl₃): δ 7.47-7.50 (m, 2H, ArH), 7.51-7.57 (m, 2H, ArH), 7.87 (s, 2H, ArH); m/z (EI⁺) (rel. intensity) 324 [M(35Cl)+, 35], 149 (50), 83 (90), 41 (100); HRMS (EI⁺) calc'd. for C₁₄H₇₃₅ClF₆ (M⁺) 324.0140, found 324.0137, Δ -1.1 ppm.

Entry 14: 4-Chloro-4'-(phenylmethoxy)biphenyl 3n

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1d (52.2 mg, 0.0782 mmol), TBAF (74 mg, 0.235 mmol), PdCl₂(MeCN)₂ (3.7 mg, 0.012 mmol), 4-(phenylmethoxy)bromobenzene (41 mg, 0.156 mmol) and CuI (15.6 mg, 0.078 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3n as a colourless oil (9.7 mg, 42%). 1H NMR (400 MHz; CDCl₃): δ 5.14 (s, 2H, ArOC₆H₄Ph), 7.05 (d, J = 8.7 Hz, 2H, ArH), 7.31-7.42 (m, 5H, ArH), 7.44-7.50 (m, 6H, ArH); 13C NMR (100 MHz; CDCl₃) δ 70.1 (t), 115.1 (d), 126.7 (d), 127.5 (d), 127.7 (d), 127.9 (2d), 128.0 (2d), 128.3 (d), 128.6 (d), 128.9 (d), 129.1 (d), 132.6 (s), 132.7 (s), 136.8 (s), 139.2 (s), 158.5 (s); IR νₘₐₓ (neat) 3035 (C-H), 2893 (C-H), 1547 (C=C), 870, 738, 665 cm⁻¹; m/z (EI⁺) (rel. intensity) 296 [M(37Cl)+, 35], 294 [M(35Cl)+, 88], 139 (30), 84 (60), 49 (100); HRMS (EI⁺) calc'd. for C₁₉H₁₅₃₅ClO (M⁺) 294.0811, found 294.0807, Δ -0.5 ppm.

Entry 15: 1-(4-Chlorophenyl)naphthalene 3o

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1d (52.2 mg, 0.0782 mmol), TBAF (74 mg, 0.235 mmol), PdCl₂(MeCN)₂ (3.7 mg, 0.012 mmol), 1-bromonaphthalene (32.8 mg, 0.158 mmol, 22 μL) and CuI (15.6 mg, 0.078 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave 1-(4-chlorophenyl)naphthalene 3o as white plates (13.9 mg, 75%). 1H NMR (400 MHz; CDCl₃): δ 7.39-7.41 (m, 5H, ArH), 7.49-7.55 (m, 3H, ArH), 7.85 (d, J = 8.5 Hz, 1H,
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ArH), 7.88 (d, J = 8.3 Hz, 1H, ArH), 7.92 (d, J = 7.9 Hz, 1H, ArH); 13C NMR (100 MHz; CDCl3) δ 125.3 (d),
125.6 (d), 125.7 (d), 126.2 (d), 126.9 (d), 128.0 (d), 128.3 (d), 128.5 (2d), 130.1 (s), 131.3 (2d), 133.3 (s), 133.8 (s), 138.9 (s), 139.1 (s); m/z (EI') (rel. intensity) 238 [M(35Cl)+, 35], 203 (35), 202 (35), 84 (100); HRMS (EI')
calc'd. for C10H735Cl(M+) 238.0549, found 238.0541, Δ -3.9 ppm.

Entry 16: 4-Chloro-2'-nitrobiphenyl 3p14, 15
Using the typical method, the crude difluoroarylgermane from the photolysis of aryler°xane 1d (37.7 mg, 0.056 mmol), TBAF (53.3 mg, 0.169 mmol), PdCl2(MeCN)2 (1.5 mg, 0.006 mmol), P(2-Tol)3 (2.6 mg, 0.0087 mmol), 2-bromonitrobenzene (22.8 mg, 0.113 mmol) and CuI (11.2 mg, 0.056 mmol) were employed. Purification by FC (hexane/EtOAc, 94/6) to give biphenyl 3p as a pale yellow oil (8.1 mg, 61%). 1H NMR (400 MHz; CDCl3):
δ 7.27 (d, J = 7.0 Hz, 2H, ArH), 7.40-7.44 (m, 3H, ArH), 7.53 (td, J = 7.8, 1.3 Hz, 1H, ArH), 7.65 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.90 (dd, J = 8.2, 1.0 Hz, 1H, ArH); 13C NMR (100 MHz; CDCl3) δ 124.3 (d), 128.5 (2d), 128.9 (2d), 129.3 (2d), 131.8 (d), 132.5 (d), 134.5 (s), 135.2 (s), 135.9 (s), 149.0 (s); IR υ max (neat) 3054 (C-H), 2986 (C-H), 1588 (C=C), 1535 (N=O), 1472 (C-N), 1265 (N=O), 1009, 818, 738 cm−1; m/z (EI+) (rel. intensity) 235 [M(37Cl)+, 15], 233 [M(35Cl)+, 45], 199 (70), 156 (80), 141 (100); HRMS (EI+) calc'd. for C12H835ClNO2(M+) 233.0244, found 233.0241, Δ -1.1 ppm.

Entry 17: 2-Methoxy-3',5'-bis-(trifluoromethyl)biphenyl 3q
Using the typical method, the crude difluoroarylgermane from the photolysis of aryler°xane 1e (61.5 mg, 0.092 mmol), TBAF (87.4 mg, 0.277 mmol), PdCl2(MeCN)2 (2.4 mg, 0.0093 mmol), P(2-Tol)3 (4.2 mg, 0.0139 mmol), 3,5-bis-(trifluoromethyl)bromobenzene (53.9 mg, 0.184 mmol, 31.7 μL) and CuI (18.4 mg, 0.092 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3q as a colourless oil (19.2 mg, 65%). 1H NMR (400 MHz; CDCl3):
δ 3.82 (s, 3H, OC6H3), 7.02 (d, J = 8.3 Hz, 1H, ArH), 7.08 (t, J = 7.1 Hz, 1H, ArH), 7.33 (dd, J = 7.6, 1.7 Hz, 1H, ArH), 7.41 (td, J = 8.3, 1.7 Hz, 1H, ArH), 7.82 (s, 1H, ArH), 7.98 (s, 2H, ArH); 13C NMR (100 MHz; CDCl3) δ 55.6 (q), 111.3 (2d), 120.6 (2s), 121.2 (d), 127.5 (s), 129.7 (2d), 130.2 (d), 130.6 (d), 131.0 (2s), 140.5 (s), 156.0 (s); IR υ max (CH2Cl2) 3020 (C-H), 1605 (C=C), 1438 (C-F), 896, 738 cm−1; m/z (EI') (rel. intensity) 320 (M+, 70), 305 (20), 285 (30), 236 (40), 84 (70), 49 (100); HRMS (EI') calc'd. for C15H10F6O(M+) 320.0636, found 320.0632, Δ -1.2 ppm.

Entry 18: 2-Methoxy-4'-chloro-1,1'-biphenyl 3r12
Using the typical method, the crude difluoroarylgermane from the photolysis of aryler°xane 1e (61.5 mg, 0.092 mmol), TBAF (87.4 mg, 0.277 mmol), PdCl2(MeCN)2 (2.4 mg, 0.0093 mmol), P(2-Tol)3 (4.2 mg, 0.0139 mmol), 4-chlorobromobenzene (35.2 mg, 0.184 mmol) and CuI (18.4 mg, 0.092 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave biphenyl 3r as a colourless oil (9.9 mg, 49%). 1H NMR (400 MHz; CDCl3):
δ 3.85 (s, 3H, OCH3), 7.02 (d, J = 8.0 Hz, 1H, ArH), 7.08 (t, J = 7.5 Hz, 1H, ArH), 7.30-7.44 (m, 2H, ArH), 7.46 (d, J = 8.0 Hz, 2H, ArH), 7.52 (d, J = 8.0 Hz, 2H, ArH); 13C NMR (100 MHz; CDCl3) δ 55.5 (q), 111.2 (2d), 120.9 (2s), 121.2 (d), 127.4 (s), 129.6 (2d), 130.4 (d), 130.6 (d), 131.0 (2s), 140.2 (s), 156.3 (s); m/z (EI') (rel. intensity) 218 [M(35Cl)+, 75], 168 (100), 49 (45); HRMS (EI') calc'd. for C13H935ClO(M+) 218.0498, found 218.0496, Δ -0.9 ppm.

Entry 19: 2-Methoxy-4'-(phenylmethoxy)biphenyl 3s
Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1e (61.5 mg, 0.092 mmol), TBAF (87.4 mg, 0.277 mmol), PdCl₂(MeCN)₂ (2.4 mg, 0.0093 mmol), P(2-Tol)₃ (4.2 mg, 0.0139 mmol), 4-(phenylmethoxy)bromobenzene (48.4 mg, 0.184 mmol) and CuI (18.4 mg, 0.092 mmol) were employed. The crude mixture was analysed by GC-MS [Column: SGE25QC3/BP5 25 m × 0.25 mm; Carrier gas: He; Oven temp: 60 °C (3 min), 60 °C → 300 °C over 12 min]. A yield of 11% for biphenyl 3s was deduced from the ratio of peak intensities for 2-naphthylmethyl methyl ether (Rt 8.1 min, m/z 172) vs. biphenyl 3s (Rt 13.3 min, m/z 290). m/z (EI⁺) (rel. intensity) 290 (M⁺, 20), 91 (100); HRMS (EI⁺) calc’d. for C₂₀H₁₈O₂ 290.1307, found 290.1301, Δ -2.0 ppm.

Entry 20: 1-(2-Methoxyphenyl)naphthalene 3t¹²

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1e (61.5 mg, 0.092 mmol), TBAF (87.4 mg, 0.277 mmol), PdCl₂(MeCN)₂ (2.4 mg, 0.0093 mmol), P(2-Tol)₃ (4.2 mg, 0.0139 mmol), 1-bromonaphthalene (38.1 mg, 0.184 mmol, 25.6 μL) and CuI (18.4 mg, 0.092 mmol) were employed. Purification by FC (hexane/EtOAc, 97/3) gave 1-(2-methoxyphenyl)naphthalene 3t as white plates (5.8 mg, 27%). ¹H NMR (400 MHz; CDCl₃): δ 3.70 (s, 3H, OC₃H₃), 7.06 (t, J = 8.1 Hz, 1H, ArH), 7.09 (dd, J = 7.5, 1.0 Hz, 1H, ArH), 7.29 (dd, J = 7.5, 1.8 Hz, 1H, ArH), 7.37-7.46 (m, 4H, ArH), 7.53 (d, J = 8.1 Hz, 1H, ArH), 7.58 (d, J = 8.5 Hz, 1H, ArH), 7.87 (t, J = 9.1 Hz, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 55.6 (q), 110.9 (2d), 120.5 (2d), 125.3 (s), 125.5 (s), 125.6 (2d), 126.4 (d), 127.3 (s), 127.6 (d), 128.1 (d), 129.0 (s), 131.9 (2d), 153.2 (s); m/z (EI⁺) (rel. intensity) 234 (9M⁺, 100), 219 (35), 189 (40); HRMS (EI⁺) calc’d. for C₁₇H₁₄O (M⁺) 234.1045, found 234.1045, Δ 0.0 ppm.

Entry 21: 4-Trifluoromethyl-3',5'-bis-(trifluoromethyl)biphenyl 3u⁸

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1f (46.1 mg, 0.066 mmol), TBAF (62 mg, 0.197 mmol), PdCl₂(MeCN)₂ (1.7 mg, 0.0066 mmol), P(2-Tol)₃ (3 mg, 0.0099 mmol), 3,5-bis-(trifluoromethyl)bromobenzene (38.4 mg, 0.131 mmol, 22.6 μL) and CuI (13 mg, 0.066 mmol) were employed. The crude mixture was analysed by GC-MS [Column: SGE25QC3/BP5 25 m × 0.25 mm; Carrier gas: He; Oven temp: 60 °C (3 min), 60 °C → 300 °C over 12 min]. A yield of 26% for biphenyl 3u was deduced from the ratio of peak intensities for 2-naphthylmethyl methyl ether (Rt 8.0 min, m/z 172) vs. biphenyl 3u (Rt 6.6 min, m/z 358). m/z (EI⁺) (rel. intensity) 358 (M⁺, 100), 219 (35), 189 (40); HRMS (EI⁺) calc’d. for C₁₅H₇F₉ (M⁺) 358.0404, found 358.0386, Δ -5.0 ppm.

Entry 22: 4-Trifluoromethyl-4'-chloro-1,1'-biphenyl 3v¹⁶

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 1f (46.1 mg, 0.066 mmol), TBAF (62 mg, 0.197 mmol), PdCl₂(MeCN)₂ (1.7 mg, 0.0066 mmol), P(2-Tol)₃ (3 mg, 0.0099 mmol), 4-chlorobromobenzene (25.1 mg, 0.131 mmol) and CuI (13 mg, 0.066 mmol) were employed. The crude mixture was analysed by GC-MS [Column: SGE25QC3/BP5 25 m × 0.25 mm; Carrier gas: He; Oven temp: 60 °C (3 min), 60 °C → 300 °C over 12 min]. A yield of 26% for biphenyl 3v was deduced from the ratio of peak intensities for 2-naphthylmethyl methyl ether (Rt 8.0 min, m/z 172) vs. biphenyl 3v (Rt 6.6 min, m/z 358). m/z (EI⁺) (rel. intensity) 358 (M⁺, 100), 84 (70), 49 (100); HRMS (EI⁺) calc’d. for C₁₃H₈F₃Cl (M⁺) 358.0404, found 358.0386, Δ -5.0 ppm.
Stability profiling of fluorous-tagged phenylgermane 1c (Table 2)

Stability tests were carried out using 8 different conditions on fluorous-tagged aryl germane 1c using either 9-methylandanthrene (4) or 4,4'-di-tert-butyl-1,1'-biphenyl (5) as the internal standard. The tests were performed in duplicate in parallel against control runs containing no reagents. Thus, a solution of the fluorous-tagged arylgermane 1c (5 mg) and internal standard 4 or 5 (1 mg) in the appropriate reaction solvent (5 mL) was allowed to stir at RT for 3 h. The reaction mixtures were then quenched with water (5 mL) and diluted with Et2O (5 mL) before being extracted with Et2O (5 × 10 mL). The organic layer was evaporated to dryness under a stream of N2 and the residue was dissolved with acetonitrile (5 mL) for analysis by HPLC as follows: Column: XTerra RP8 4.6 mm × 150 mm, 5 μm; Mobile phase: MeCN/H2O = 80:20; Flow rate: 1 mL/min; Detection: UV diode array at 245 nm; Injection volume: 2 μL. The ratio of the peak areas was calculated for substrate 1c and internal standard 4 or 5. The mean percentage recovery of compound 1c over the two runs was compared to the reagentless control run in appropriate solvents for each of the 8 conditions. The chromatograms for representative control runs using internal standards 4 and 5 are shown below.
### Table Showing stability profile of fluorous-tagged phenylgermane 1c.

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<th>Conditions</th>
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*% recovery of 1c by HPLC vs. the internal standard.

**Synthesis of Boscalid® (16) and its alkynyl derivatives 17 and 18 (Scheme 1)**

(3,3,4,4,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(4-iodophenyl)bis-(naphthalen-2-ylmethyl)germane 1g

To a solution of 1,4-diiodobenzene (0.1258 g, 0.382 mmol) in THF (10.0 mL) at -78 °C was added 'BuLi (0.546mL, 0.764 mmol, 1.4M) dropwise resulting in a dark red solution. The solution was stirred at -78 °C for 30 min to achieve lithium-halogen exchange. The resulting solution mixture was added bromo-(3,3,4,4,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)bis-(naphthalen-2-ylmethyl)germane (0.281 g, 0.319 mmol) at -78 °C and stirred for 1 h than warmed up to rt for 16 h. The reaction mixture was diluted with Et₂O (20.0 mL) and a solution of 1.0 M NH₄Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et₂O, the combined organic extracts were dried over MgSO₄ and evaporated in vacuo to give green oily residue which was purified by FC (hexane/EtOAc, 97/3) to give (4-iodophenyl)germane 1f as a pale yellow oil (0.4706 g, 87%). ¹H NMR (400 MHz; CDCl₃): δ 1.20 (m, 2H, CH₂C₆H₄Ge), 1.87 (m, 2H, C₆H₄CH₂Ge), 2.77 (s, 4H, 2 × GeC₆H₂Nap), 7.07 (dd, J = 6.7, 1.7 Hz, 2H, ArH), 7.25 (d, J = 8.2 Hz, 2H, ArH), 7.35 (d, J = 7.7 Hz, 2H, ArH), 7.41-7.47 (m, 6H, ArH), 7.70 (d, J = 8.2 Hz, 2H, ArH), 7.79 (d, J = 7.7 Hz, 2H, ArH), ¹³C NMR (100 MHz; CDCl₃) δ 18 (t), 22.4 (2t), 26.2 (t, JCF = 23.0 Hz), 96.2 (s), 108.3 (s), 110.2 (s), 110.7 (3s), 110.97 (s), 117.9 (s), 125.0 (2d), 125.7 (2d), 126.2 (2d), 127.0 (2d), 127.2 (2d), 127.6 (2d), 128.2 (2d), 131.3 (2s), 133.7 (2s), 135.1 (2d), 135.7 (s), 136.1 (2s); ¹⁹F NMR (376 MHz; CDCl₃): δ -126.1 (s, 2F), -123.6 (s, 2F), -122.7 (s, 2F), -121.9 (m, 6F), -116.3 [quintet, J = 14.5 Hz, 2F, (CF₂)₂CF₂CF₃], -80.7 [t, J = 10 Hz, 3F, (CF₂)₃CF₂CF₃]; IR vmax (neat) 3035 (C-H), 2988 (C-H) 1549 (C=C), 1421 (C-F), 1050 (C-I), 896, 740 cm⁻¹; m/z (FAB⁺) (rel. intensity) 864 [(M-NapCH₂)+, 2], 803 (1), 709 (5), 141 (100); HRMS (FAB⁺) calc’d. for C₂₂H₁₁F₁₇Ge [M-(NapCH₂)⁺] 864.9310, found 864.9307, Δ -0.3 ppm.

**4-Chloro-2'-aminobiphenyl 11**

![Chemical structure of 4-Chloro-2'-aminobiphenyl 11](image-url)
To a solution of 4-chloro-2'-nitrobiphenyl (3p, 15 mg, 0.064 mmol) in THF-EtOH (1:1, 10 mL) was added tin(II) chloride (122 mg, 0.64 mmol) and conc. HC (1 mL) and the reaction mixture was stirred for 16 h. A sat. solution of K₂CO₃ was added and the reaction mixture was partitioned between Et₂O (40.0 mL) and water (10.0 mL). The phases were separated, the aqueous phase extracted with CH₂Cl₂ (2 × 10.0 mL) and the combined organic extracts were dried over MgSO₄. Purification by FC (hexane/EtOAc, 90/10) gave 4-chloro-2'-aminobiphenyl 11 as a colourless oil (10.3 mg, 88%). ¹H NMR (400 MHz; CDCl₃): δ 3.73 (brs, 2H, NH₂), 6.77 (dd, J = 7.9, 1.0 Hz, 1H, ArH), 6.83 (td, J = 7.6, 1.0 Hz, 1H, ArH), 7.09 (dd, J = 7.6, 1.5 Hz, 1H, ArH), 7.17 (td, J = 7.6, 1.5 Hz, 1H, ArH), 7.38-7.46 (m, 4H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 115.7 (d), 118.7 (d), 126.3 (s), 128.8 (d), 129.8 (d), 130.3 (d), 130.5 (2d), 133.1 (s), 137.9 (s), 143.4 (s); IR ν max (neat) 3475 (N-H), 3383 (N-H), 3083 (C-H), 1886 (comb), 1616 (C=C), 1472 (C-N), 1087, 1008, 810, 744 cm⁻¹; m/z (EI⁺) (rel. intensity) 205 [M(37Cl)+, 9], 203 [M(35Cl)+, 25], 167 (25), 49 (30), 84 (90), 49 (100); HRMS (EI⁺) calc’d. for C₁₂H₁₀₃₅ClN (M⁺) 203.0502, found 203.0501, Δ -0.4 ppm.

Boscalid® 16

To a solution of 4-chloro-2'-aminobiphenyl (11, 20.0 mg, 0.098 mmol) in CH₂Cl₂ (10 mL) was added 2-chloro-3-nicotinic acid (17.3 mg, 0.098 mmol), DMAP (0.5 mg, 0.004 mmol) and DCC (22.3 mg, 0.108 mmol) and the reaction mixture was stirred for 16 h. A sat. solution of K₂CO₃ was added to the reaction mixture and the reaction mixture was partitioned between Et₂O (40.0 mL) and water (10.0 mL), extracted with CH₂Cl₂ (2 × 10.0 mL) and dried over MgSO₄. Purification by FC (hexane/EtOAc, 75/25) gave Boscalid® (16) as a colourless oil (22.1 mg, 65%). ¹H NMR (400 MHz; CDCl₃): δ 7.27 (d, J = 4.8 Hz, 2H, ArH), 7.31-7.36 (m, 3H, ArH), 7.41-7.47 (m, 3H, ArH), 8.13 (dd, J = 7.7, 1.2 Hz, 1H, ArH), 8.16 (brs, 1H, NH), 8.41 (d, J = 8.2 Hz, 1H, ArH), 8.44 (dd, J = 4.6, 1.7 Hz, 1H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 122.1 (d), 122.9 (d), 125.3 (d), 128.9 (d), 129.3 (2d), 130.2 (d), 130.8 (2d), 131.0 (s), 132.2 (s), 134.3 (s), 134.4 (s), 136.2 (s), 140.1 (d), 146.6 (s), 151.3 (d), 162.5 (s); IR ν max (neat) 3338 (N-H), 3084 (C-H), 2935 (C-H), 1887 (comb), 1616 (C=C), 1472 (C-N), 1087, 1008, 810, 744 cm⁻¹; m/z (EI⁺) (rel. intensity) 347 [M(37Cl37Cl)H⁺, 10], 345 [M(37Cl35Cl)H⁺, 35], 343 [M(35Cl35Cl)H⁺, 40], 309 (15), 225 (100); HRMS (CI⁺) calc’d. for C₁₈H₁₃₃₅Cl₂N₂O (MH⁺) 343.0405, found 343.0409, Δ 1.1 ppm.

Using conditions adapted from those of Menchi, ²¹ Pd(OAc)₂ (1.0 mg, 0.0045 mmol) and PPh₃ (3.7 mg, 0.014 mmol) were dissolved in degased DMF (1 mL) and stirred for 30 min at RT to give a solution of the active Pd(0) catalyst. This solution was then added to a solution of (4-iodophenyl)germane 1g (25.1 mg, 0.025 mmol) in degassed DMF (2 mL). Trimethylisilylacetylene (4.9 mg, 0.05 mmol, 7 µL), CuI (2 mg, 0.01 mmol) and ⁷BuNH₂ (5 mL) were then added to the reaction mixture and the resulting reaction mixture was stirred at 55 °C for 16 h. The reaction mixture was then diluted with Et₂O (20.0 mL), washed with water (3 × 10.0 mL), the organic phase
dried over MgSO₄ and evaporated in vacuo. Purification by FC (hexane/EtOAc, 95/5) gave alkynylgermane 6 as a pale yellow oil (12.6 mg, 52%). ¹H NMR (400 MHz; CDCl₃): δ 0.27 (s, 9H, Si(CH₃)₃), 1.02 (m, 2H, CH₂CH₂Ge), 1.71 (m, 2H, CH₂CH₂Ge), 2.36 (s, 4H, 2 × GeCH₂Nap), 6.86 (dd, J = 8.4, 1.8 Hz, 2H, ArH), 6.93 (d, J = 8.1 Hz, 2H, ArH), 7.18-7.20 (m, 3H, ArH), 7.21 (dd, d, J = 6.8, 1.4 Hz, 1H, ArH), 7.27 (dd, J = 6.8, 1.4 Hz, 1H, ArH), 7.46 (d, J = 5.5 Hz, 2H, ArH), 7.53 (d, J = 8.1 Hz, 2H, ArH), 7.59 (d, J = 8.1 Hz, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 0.07 (3s), 2.1 (t), 22.5 (2t), 26.6 (t, JCF 23.0 Hz), 95.8 (s), 105.6 (s), 105.8 (s), 110.7 (s), 111.2 (s), 111.3 (s), 111.6 (3s), 118.6 (s), 124.7 (s), 125.3 (2d), 126.1 (2d), 126.5 (2d), 127.3 (2d), 127.5 (2d), 128.0 (2d), 128.4 (2d), 131.9 (2d), 132.0 (2s), 134.2 (2d), 134.4 (2s), 136.6 (2s), 138.0 (s); ¹⁹F NMR (376 MHz; CDCl₃): δ -125.1 (s, 2F), -122.3 (s, 2F), -121.7 (s, 2F), -120.8 (m, 4F), -120.3 (s, 2F), -114.9 [quintet, J = 15.0 Hz, 2F, (CF₃)₂CF₂CF₂], -79.9 [t, J = 9.8 Hz, 3F, (CF₃)₂CF₂CF₂]; IR νmax (neat) 3052 (C-H), 2982 (C-H), 2360 (C=C), 1592 (C=C), 1421 (C-F), 1260 (C-Si), 897, 740 cm⁻¹; m/z (FAB⁺) (rel. intensity) 835 [(M-NapCH₂)+, 60], 709 (55), 313 (80), 141 (100); HRMS (FAB⁺) calc’d. for C₃₂H₂₆F₁₇GeSi [M-(NapCH₂)+] 835.0739, found 835.0734, Δ -0.6 ppm.

(3,3,4,5,5,6,6,7,7,8,8,9,10,10-Heptadecafluorodecyl)bis(naphthalen-2-ylmethyl){4-[(3-methyl-3-hydroxybutynyl)phenyl]}germane 8

Using conditions adapted from those of Menchi,²¹ Pd(OAc)₂ (1.5 mg, 0.007 mmol) and PPh₃ (5.5 mg, 0.021 mmol) were dissolved in degased DMF (1 mL) and stirred for 30 min at RT to give a solution of the active Pd(0) catalyst. This solution was then added to a solution of (4-iodophenyl)germane 1g (128.6 mg, 0.128 mmol) in degassed DMF (2 mL). 2-Methylbut-3-yn-2-ol (21.5 mg, 0.256 mmol, 25 μL), CuI (2.8 mg, 0.014 mmol) and nBuNH₂ (5 mL) were then added to the reaction mixture and the resulting reaction mixture was stirred at 55 °C for 16 h. The reaction mixture was then diluted with Et₂O (20.0 mL), washed with water (3 × 10.0 mL), then diluted with Et₂O (20.0 mL), washed with water (3 × 10.0 mL), the organic phase dried over MgSO₄ and evaporated in vacuo. Purification by FC (hexane/EtOAc, 85/15) gave alkynylgermane 8 as a pale yellow oil (83.6 mg, 68%). ¹H NMR (400 MHz; CDCl₃): δ 1.15 (m, 2H, CH₂CH₂Ge), 1.65 (s, 6H, CC(CH₃)₂OH), 1.81 (m, 2H, CH₂CH₂Ge), 2.07 (brs, 1H, OH), 2.72 (s, 4H, 2 × GeCH₂Nap), 7.04 (dd, J = 8.4, 1.7 Hz, 2H, ArH), 7.27 (d, J = 7.8 Hz, 2H, ArH), 7.34 (s, 2H, 2H, ArH), 7.36-7.46 (m, 6H, ArH), 7.62 (d, J = 7.8 Hz, 2H, ArH), 7.67 (d, J = 8.4 Hz, 2H, ArH), 7.77 (d, J = 7.8 Hz, 2H, ArH); ¹³C NMR (100 MHz; CDCl₃) δ 1.8 (t), 22.4 (2t), 26.2 (t, JCF 23.0 Hz), 31.5 (2q), 65.7 (s), 81.9 (s), 94.8 (s), 110.2 (s), 110.6 (2s), 110.7 (s), 110.9 (2s), 111.0 (s), 117.9 (s), 123.6 (s), 124.9 (2d), 125.7 (2d), 126.1 (2d), 127.0 (2d), 127.3 (2d), 127.6 (2d), 128.1 (2d), 131.3 (2d+2s), 133.7 (2d+2s), 136.2 (2s), 137.1 (s); ¹⁹F NMR (376 MHz; CDCl₃): δ -125.2 (s, 2F), -122.6 (s, 2F), -121.8 (s, 2F), -121.0 (m, 6F), -115.4 [quintet, J = 14.3 Hz, 2F, (CF₃)₂CF₂CF₂], -79.8 [t, J = 9.8 Hz, 3F, (CF₃)₂CF₂CF₂]; IR νmax (neat) 3320 (OH, br), 3200 (OH, br), 2985 (C=H), 2354 (CC), 1595 (C=C), 1421 (C-F), 895, 740 cm⁻¹; m/z (FAB⁺) (rel. intensity) 821 [(M-NapCH₂)+, 55], 551 (50), 279 (45), 141 (100); HRMS (FAB⁺) calc’d. for C₃₂H₂₄F₁₇O²⁺Si [M-(NapCH₂)⁺] 821.0762, found 821.0762, Δ -0.2 ppm.
**Method A:** Using conditions adapted from those of Vasella, a mixture of K$_2$CO$_3$ and KF (1:1 w/w, 100 mg) was added to a solution of (4-trimethylsilylethynylphenyl)germane (115.6 mg, 0.118 mmol) in MeOH-THF (1:1 v/v, 10 mL) and the resulting reaction mixture stirred at 80 °C for 8 h. The resulting reaction mixture was diluted with Et$_2$O (20.0 mL), washed with water (3 × 10.0 mL) and the organic phase was dried over MgSO$_4$ and evaporated in vacuo. Purification by FC (hexane/EtOAc, 95/5) gave (4-phenylethynyl)germane as pale yellow oil (69.7 mg, 67%). $^1$H NMR (400 MHz; CDCl$_3$): δ 1.14 (m, 2H, CH$_2$C$_6$H$_2$Ge), 1.81 (m, 2H, C$_6$H$_2$CH$_2$Ge), 2.72 (s, 4H, 2×GeC$_6$H$_2$Nap), 3.15 (s, 1H, C$_6$H$_4$CC$_6$H$_4$), 7.04 (dd, $J$ = 8.4, 0.8 Hz, 2H, ArH), 7.29 (d, $J$ = 8.2 Hz, 2H, ArH), 7.34 (s, 2H, ArH), 7.37-7.48 (m, 6H, ArH), 7.61 (d, $J$ = 8.0 Hz, 2H, ArH), 7.68 (d, $J$ = 8.4 Hz, 2H, ArH), 7.77 (d, $J$ = 7.6 Hz, 2H, ArH); $^{13}$C NMR (100 MHz; CDCl$_3$): δ 2.1 (t), 22.5 (2t), 26.6 (t, $J_{CF}$ = 23.4 Hz), 78.2 (s), 83.4 (s), 108.3 (s), 110.2 (s), 110.6 (3s), 111.0 (s), 117.9 (s), 124.7 (s), 125.3 (2d), 126.1 (2d), 126.5 (2d), 127.4 (2d), 127.4 (2d), 128.0 (2d), 128.3 (2d), 131.8 (2d), 132.1 (2s), 134.3 (2d), 134.3 (2s), 136.5 (2s), 137.8 (s); $^{19}$F NMR (376 MHz; CDCl$_3$): δ -125.1 (s, 2F), -122.5 (s, 2F), -121.8 (s, 2F), -121.0 (m, 6F), -115.3 [quintet, $J$ = 14.8 Hz, 2F, (CF$_2$)$_6$CF$_2$CF$_3$], -79.8 [t, $J$ = 9.9 Hz, 3F, (CF$_2$)$_6$CF$_2$CF$_3$]; IR $\nu_{max}$ (neat) 3253 (CC-H), 3048 (C-H), 2984 (C-H), 2360 (CC), 1592 (C=C), 1420 (C-F), 910, 740 cm$^{-1}$; m/z (FAB$^+$) (rel. intensity) 763 [(M-NapCH$_2$)+, 40], 549 (15), 279 (45), 141 (100); HRMS (FAB$^+$) calc’d. for C$_{29}$H$_{18}$F$_{17}$Ge [M-(NapCH$_2$)$_2$] 763.0343, found 763.0350, Δ 0.9 ppm.

**Method B:** Using conditions adapted from those of Walton, powdered KOH (50 mg, 0.893 mmol) was added to a solution of 4-[(3-methyl-3-hydroxybutynyl)phenyl]germane (80.0 mg, 0.083 mmol) in THF (10 mL). The reaction mixture was then stirred at 80 °C for 1 h. The resulting reaction mixture was diluted with Et$_2$O (20.0 mL), washed with water (3 × 10.0 mL) and the organic phase was dried over MgSO$_4$ and evaporated in vacuo. Purification by FC (hexane/EtOAc, 95/5) gave (4-phenylethynyl)germane as a pale yellow oil (73.8 mg, 98%). Analytical data as above.

Using conditions adapted from those of Feldman, a solution of n-BuLi (50 μL, 0.09 mmol, 1.8 M in hexanes) was added dropwise to a solution of (4-phenylethynyl)germane (73.8 mg, 0.082 mmol) and DMPU (10 μL, 0.083 mmol) in THF (10 mL) at -40 °C. The resulting reaction mixture was stirred for 1 h at this temperature to give a brown solution. Methyltriflate (20.3 mg, 0.124 mmol, 14 μL) was then added and stirring continued for a further 16 h. The reaction mixture was diluted with Et$_2$O (10.0 mL) and a solution of 1.0 M NH$_4$Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et$_2$O, the combined organic extracts were dried over MgSO$_4$ and evaporated in vacuo to give a pale yellow residue which was purified by FC (hexane/EtOAc, 90/10) to give (4-propynylphenyl)germane as pale yellow oil (65.4 mg, 98%).
Supplementary Material (ESI) for Chemical Communications
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87%). $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 1.21 (m, 2H, CH$_2$C$_2$H$_2$Ge), 1.80 (m, 2H, C$_2$H$_2$CH$_2$Ge), 2.08 (s, 3H, CCCCH$_3$), 2.71 (s, 4H, 2 $\times$ GeCH$_2$Nap), 7.03 (dd, $J$ = 8.4, 1.6 Hz, 2H, ArH), 7.23 (d, $J$ = 8.2 Hz, 2H, ArH), 7.33 (s, 2H, ArH), 7.35-7.42 (m, 6H, ArH), 7.60 (d, $J$ = 7.8 Hz, 2H, ArH), 7.66 (d, $J$ = 8.4 Hz, 2H, ArH), 7.76 (d, $J$ = 7.8 Hz, 2H, ArH); $^{13}$C NMR (100 MHz; CDCl$_3$) $\delta$ 21.1 (t), 32.1 (q), 22.5 (2t), 26.3 (t, $J_{CF}$ 23.2 Hz), 78.3 (s), 83.5 (s), 108.1 (s), 110.2 (s), 110.6 (s), 110.8 (3s), 111.0 (s), 117.9 (s), 124.7 (s), 126.1 (2d), 126.5 (2d), 127.4 (2d), 127.4 (2d), 128.2 (2d), 128.3 (2d), 131.8 (2d), 132.0 (2d), 134.6 (2d), 134.8 (2s), 136.9 (2s), 137.7 (s); $^{19}$F NMR (376 MHz; CDCl$_3$): $\delta$ -126.1 (s, 2F), -123.5 (s, 2F), -122.7 (s, 2F), -121.9 (m, 6F), -116.3 [quintet, $J$ = 15.2 Hz, 2F, (CF$_2$)$_6$C$_2$F$_2$CF$_3$], -80.7 [t, $J$ = 9.7 Hz, 3F, (CF$_2$)$_6$CF$_2$C$_3$F$_3$]; IR $\nu_{\max}$ (neat) 3046 (C-H), 2975 (C-H), 2355 (CC), 1594 (C=C), 1419 (C-F), 913, 740 cm$^{-1}$; $m/z$ (FAB +) (rel. intensity) 777 [(M-NapCH$_2$)+, 30], 549 (15), 279 (55), 141 (100); HRMS (FAB +) calc’d. for C$_{30}$H$_{20}$F$_{17}$Ge [M-(NapCH$_2$)+] 777.0500, found 777.0498, $\Delta$ -0.2 ppm.

4-Propynyl-2’-nitrobiphenyl 12

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 10 (33.2 mg, 0.049 mmol), TBAF (46.6 mg, 0.148 mmol), PdCl$_2$(MeCN)$_2$ (1.5 mg, 0.0058 mmol), P(2-Tol)$_3$ (2.6 mg, 0.0087 mmol), 2-bromonitrobenzene (19.9 mg, 0.099 mmol) and CuI (9.8 mg, 0.049 mmol) were employed. Purification by FC (hexane/EtOAc, 90/10) gave biphenyl 12 as yellow oil (6.3 mg, 54%). $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 2.07 (s, 3H, CH$_3$), 7.24 (d, $J$ = 7.0, 2H, ArH), 7.41-7.48 (m, 3H, ArH), 7.48 (td, $J$ = 7.9, 1.4 Hz, 1H, ArH), 7.62 (td, $J$ = 7.5, 1.1 Hz, 1H, ArH), 7.86 (dd, $J$ = 8.1, 1.1 Hz, 1H, ArH); $^{13}$C NMR (100 MHz; CDCl$_3$) $\delta$ 4.4 (q), 79.2 (s), 87.1 (s), 124.1 (s), 124.2 (d), 127.8 (2d), 128.3 (d), 131.77 (2d), 131.8 (d), 132.3 (d), 135.8 (s), 136.4 (s), 149.1 (s); IR $\nu_{\max}$ (neat) 3054 (C-H), 2987 (C-H), 2360 (CC), 1888 (comb), 1588 (C=C), 1265 (N=O), 896, 738, 705 cm$^{-1}$; $m/z$ (EI +) (rel. intensity) 237 (M +, 20), 198 (100), 168 (50), 87 (70); HRMS (EI +) calc’d. for C$_{15}$H$_{11}$NO$_2$ (M+) 237.0790, found 237.0784, $\Delta$ -2.4 ppm.

4-Propynyl-2’-aminobiphenyl 13

To a solution of nitrobiphenyl 12 (6.3 mg, 0.027 mmol) in THF-EtOH (1:1, 10 mL) was added tin(II) chloride (50.1 mg, 0.27 mmol) and conc. HCl (1 mL) and the reaction mixture was stirred for 16 h. A sat. solution of K$_2$CO$_3$ was added and the reaction mixture was partitioned between Et$_2$O (40.0 mL) and water (10.0 mL). The phases were separated, the aqueous phase extracted with CH$_2$Cl$_2$ (2 $\times$ 10.0 mL) and the combined organic extracts were dried over MgSO$_4$. Purification by FC (hexane/EtOAc, 90/10) gave 4-propynyl-2’-aminobiphenyl 13 as a colourless oil (4.4 mg, 80%). $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 2.08 (s, 3H, CH$_3$), 3.76 (brs, 2H, NH$_2$), 6.76 (d, $J$ = 7.9 Hz, 1H, ArH), 6.82 (t, $J$ = 7.3 Hz, 1H, ArH), 7.11 (dd, $J$ = 7.5, 1.2 Hz, 1H, ArH), 7.16 (td, $J$ = 7.8, 1.4 Hz, 1H, ArH), 7.39 (d, $J$ = 8.2 Hz, 2H, ArH), 7.46 (d, $J$ = 8.2 Hz, 2H, ArH); $^{13}$C NMR (100 MHz; CDCl$_3$) $\delta$ 4.4 (q), 86.3 (s), 102.3 (s), 115.8 (d), 118.8 (d), 119.1 (s), 122.9 (s), 128.7 (d), 128.9 (2d), 130.3 (d), 131.9 (2d), 138.7 (s), 144.5 (s); IR $\nu_{\max}$ (neat) 3475 (N-H), 3384 (N-H), 3052 (C-H), 2984 (C-H), 2359 (CC), 1888 (comb),
2-Chloro-N-(4’-prop-1-ynylbiphenyl-2-yl)nicotinamide 17

To a solution of biphenylamine 13 (4.5 mg, 0.022 mmol) in CH2Cl2 (5 mL) was added 2-chloro-3-nicotinic acid (6.9 mg, 0.042 mmol), DMAP (0.5 mg, 0.004 mmol) and DCC (10.0 mg, 0.048 mmol) and the reaction mixture was stirred for 16 h. A sat. solution of K2CO3 was added and the reaction mixture was partitioned between Et2O (40.0 mL) and water (10.0 mL). The phases were separated, the aqueous phase extracted with CH2Cl2 (2 × 10.0 mL) and the combined organic extracts were dried over MgSO4. Purification by FC (hexane/EtOAc, 70/30) gave biarylalkyne 17 as a colourless oil (4.4 mg, 59%). 1H NMR (400 MHz; CDCl3): δ 2.07 (s, 3H, CH3), 7.27 (d, J = 6.5 Hz, 2H, ArH), 7.33-7.39 (m, 3H, ArH), 7.46 (td, J = 8.4, 1.6 Hz, 1H, ArH), 7.50 (d, J = 8.2 Hz, 2H, ArH), 8.12 (dd, J = 7.5, 1.9 Hz, 1H, ArH), 8.15 (brs, 1H, NH), 8.42-8.44 (m, 2H, ArH); IR ν max (neat) 3325 (N-H), 3053 (C-H), 2935 (C-H), 2305 (CC), 1654 (C=O), 1580 (C=C), 1265, 735 cm⁻¹; m/z (EI⁺) (rel. intensity) 349 [M(37Cl)H+, 5], 347 [M(35Cl)H+, 15], 225 (100); HRMS (Cl⁺) calc’d. for C21H1635ClN2O (MH⁺) 347.0951, found 347.0952, Δ 1.3 ppm.

(3,3,4,5,5,6,6,7,7,8,8,9,9,10,10-Heptadecafluorodecyl)bis(naphthalen-2-ylmethyl){4-[(3-methyl-3-methoxybutynyl)phenyl]}germane 9

Using conditions adapted from those of Corey,25 NaH (4 mg, 0.1 mmol, 60% in mineral oil) was added to a solution of alkynylgermane 8 (32 mg, 0.0333 mmol) in THF (10 mL) and the reaction mixture stirred at RT for 1 h. Dimethylsulfate (9.5 μL, 0.1 mmol) was then added and the reaction mixture was stirred at RT for a further 16 h. The resulting reaction mixture was then diluted with Et2O (20.0 mL), washed with water (3 × 10.0 mL) and the organic phase was dried over MgSO4 and concentrated in vacuo. Purification by FC (hexane/EtOAc, 95/5) gave alkynylgermane 9 as pale yellow oil (28.3 mg, 87%). 1H NMR (400 MHz; CDCl3): δ 1.16 (m, 2H, CH2CF3Ge), 1.59 (s, 6H, CC(CH3)2OC), 1.83 (m, 2H, CH2CH2Ge), 2.73 (s, 4H, 2 × GeCH2Nap), 3.47 (s, 3H, CC(CH3)2OC)), 7.04 (dd, J = 8.4, 1.8 Hz, 2H, ArH), 7.25-7.29 (m, 2H, ArH), 7.34-7.50 (m, 8H, ArH), 7.63 (d, J = 7.7 Hz, 2H, ArH), 7.68 (d, J = 8.4 Hz, 2H, ArH), 7.78 (d, J = 7.7 Hz, 2H, ArH); 13C NMR (100 MHz; CDCl3) δ 1.8 (t), 22.4 (2t), 26.2 (t, JCF 23.0 Hz), 29.7 (2q), 51.7 (q), 70.9 (s), 83.9 (s), 92.1 (s), 108.2 (s), 110.2 (s), 110.6 (2s), 110.94 (2s), 110.98 (s), 117.9 (s), 123.7 (s), 124.9 (2d), 125.7 (2d), 125.8 (s), 126.1 (2d), 127.0 (2d), 127.3 (2d), 127.6 (2d), 128.1 (2d), 131.27 (2s), 131.35 (2d), 133.7 (2d+s), 136.2 (2s), 137.0 (s); 19F NMR (376 MHz; CδF) δ -125.1 (s, 2F), -122.6 (s, 2F), -121.8 (s, 2F), -121.0 (m, 6F), -115.4 [quintet, J = 14.6 Hz, 2F, (CF2)2CF(CF3)], -115.8 [t, J = 9.9 Hz, 3F, (CF3)2CF(CF3)]; IR νmax (neat) 3054 (C-H), 2985 (C-H), 2360 (CC), 1605 (C=C), 1420 (C-F), 912, 740 cm⁻¹; m/z (FAB⁺) (rel. intensity) 835 [(M-NapCH2)+, 60], 551 (60), 537 (50),
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2279 (60), 141 (100); HRMS (FAB') calc'd. for C_{33}H_{26}F_{17}O_{74}Ge [M-(NapCH2)+] 835.0918, found 835.0913, Δ -0.7 ppm.

4-(3-Methyl-3-methoxybutynyl)-2'-nitrobiphenyl 14

Using the typical method, the crude difluoroarylgermane from the photolysis of arylgermane 9 (48.9 mg, 0.067 mmol), TBAF (63.0 mg, 0.2 mmol), PdCl_{2}(MeCN)_{2} (2 mg, 0.0077 mmol), P(2-Tol)$_3$ (3.5 mg, 0.012 mmol), 2-bromonitrobenzene (27 mg, 0.134 mmol) and CuI (13.3 mg, 0.067 mmol) were employed. Purification by FC (hexane/EtOAc, 90/10) gave nitrobiphenyl 14 as a yellow oil (9.9 mg, 50%). 1H NMR (400 MHz; CDCl$_3$): δ 1.56 (s, 6H, 2 × CH$_3$), 3.44 (s, 3H, OCH$_3$), 7.27 (d, J = 6.8 Hz, 2H, ArH), 7.42 (dd, J = 7.7, 1.3 Hz, 1H, ArH), 7.48-7.50 (m, 3H, ArH), 7.63 (td, J = 7.5, 1.1 Hz, 1H, ArH), 7.88 (dd, J = 8.1, 1.0 Hz, 1H, ArH); 13C NMR (100 MHz; CDCl$_3$) δ 28.3 (2q), 51.8 (q), 70.9 (s), 83.7 (s), 92.2 (s), 122.9 (s), 124.2 (d), 127.8 (2d), 128.4 (d), 131.8 (d), 131.9 (2d), 132.0 (s), 132.4 (d), 135.7 (s), 137.2 (s); IR υ$_{max}$ (neat) 3055 (C-H), 2987 (C-H), 2360 (C=C), 1588 (C=C), 1537 (N=O), 1265 (N=O), 896, 738, 704 cm$^{-1}$; m/z (EI+) (rel. intensity) 295 (M$^+$, 20), 289 (50), 280 (100), 264 (30), 198 (30); HRMS (EI+) calc'd. for C$_{18}$H$_{17}$NO$_3$ (M$^+$) 295.1208, found 295.1207, Δ -0.5 ppm.

4-(3-Methyl-3-methoxybutynyl)-2'-aminobiphenyl 15

To a solution of nitrobiphenyl 14 (9.9 mg, 0.034 mmol) in THF-EtOH (1:1, 10 mL) was added tin(II) chloride (63.7 mg, 0.34 mmol) and conc. HC (1 mL) and the reaction mixture was stirred for 16 h. A sat. solution of K$_2$CO$_3$ was added and the reaction mixture was partitioned between Et$_2$O (40.0 mL) and water (10.0 mL). The phases were separated, the aqueous phase extracted with CH$_2$Cl$_2$ (2 × 10.0 mL) and the combined organic extracts were dried over MgSO$_4$. Purification by FC (hexane/EtOAc, 80/20) gave 4-(3-methyl-3-methoxybutynyl)-2'-aminobiphenyl 15 as a colourless oil (7.1 mg, 80%). 1H NMR (400 MHz; CDCl$_3$): δ 1.56 (s, 6H, 2 × CH$_3$), 3.45 (s, 3H, OCH$_3$), 3.75 (brs, 2H, NH$_2$), 6.77 (dd, J = 8.2, 0.7 Hz, 1H, ArH), 6.83 (td, J = 7.4, 1.0 Hz, 1H, ArH), 7.11 (dd, J = 7.6, 1.5 Hz, 1H, ArH), 7.16 (td, J = 7.6, 1.5 Hz, 1H, ArH), 7.42 (d, J = 8.3 Hz, 2H, ArH), 7.51 (d, J = 8.3 Hz, 2H, ArH); 13C NMR (100 MHz; CDCl$_3$) δ 28.4 (2q), 51.7 (q), 71.0 (s), 84.0 (s), 91.4 (s), 115.7 (d), 118.8 (d), 121.6 (s), 126.8 (s), 128.8 (d), 129.0 (2d), 130.3 (d), 132.1 (2d), 139.5 (s), 143.3 (s); IR υ$_{max}$ (neat) 3475 (N-H), 3382 (N-H), 3052 (C-H), 3021 (C-H), 1887 (comb), 1617 (C=C), 1472, 810, 743 cm$^{-1}$; m/z (EI') (rel. intensity) 265 (M$^{19+}$, 85), 250 (100), 234 (50), 220 (40), 125 (30); HRMS (EI') calc'd. for C$_{18}$H$_{19}$NO (M$^{19+}$) 265.1467, found 265.1464, Δ -1.0 ppm.

2-Chloro-N-[4'-(3-methoxy-3-methylbut-1-ynyl)biphenyl-2-yl]nicotinamide 18$^{19}$
To a solution of biphenylamine 15 (12 mg, 0.045 mmol) in CH$_2$Cl$_2$ (10 mL) was added 2-chloro-3-nicotinic acid (7.2 mg, 0.045 mmol), DMAP (0.6 mg, 0.0049 mmol) and DCC (10.3 mg, 0.050 mmol) and the reaction mixture was stirred for 16 h. A sat. solution of K$_2$CO$_3$ was added to the reaction mixture and the reaction mixture was partitioned between Et$_2$O (40.0 mL) and water (10.0 mL). The phases were separated, the aqueous phase extracted with CH$_2$Cl$_2$ (2 × 10.0 mL) and the combined organic extracts were dried over MgSO$_4$. Purification by FC (hexane/EtOAc, 70/30) gave biarylalkyne 18 as a colourless oil (12.5 mg, 68%).

**1H NMR (400 MHz; CDCl$_3$):**

\[
\delta = 1.56 (s, 6H, 2 \times CH$_3$), 3.44 (s, 3H, OCH$_3$), 7.27 (d, J = 6.3 Hz, 2H, ArH), 7.34-7.38 (m, 3H, ArH), 7.46 (td, J = 8.6, 2.8 Hz, 1H, ArH), 7.52 (d, J = 8.2 Hz, 2H, ArH), 8.14 (dd, J = 7.7, 1.9 Hz, 1H, ArH), 8.16 (brs, 1H, NH), 8.44-8.46 (m, 2H, ArH);
\]

**13C NMR (100 MHz; CDCl$_3$):**

\[
\delta = 28.3 (2q), 51.8 (q), 70.9 (s), 83.5 (s), 92.2 (s), 121.8 (d), 122.90 (d), 122.93 (s), 125.2 (d), 128.2 (d), 129.4 (2d), 130.1 (d), 131.1 (s), 132.4 (2d), 132.6 (s), 134.3 (s), 137.6 (s), 140.1 (d), 146.7 (s), 157.8 (C=O), 1654 (C=O), 2341 (CC), 1578 (C=C), 1070, 734 cm$^{-1}$; m/z (CI$^+$) (rel. intensity) 424 [M(37Cl)NH$_4^+$, 1], 422 [M(35Cl)NH$_4^+$, 3], 390 (40), 373 (100), 339 (20), 225 (50); HRMS (CI$^+$) calc'd. for C$_{24}$H$_{25}$ClN$_3$O$_2$ (M+NH$_4^+$) 422.1635, found 422.1633, Δ -0.5 ppm.

**Acknowledgement**

We thank the EPSRC National Mass Spectrometry Service Centre (Department of Chemistry, University of Wales Swansea, Swansea, Wales, UK) for some of the MS analyses.

**References**

$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^{19}$F NMR, 376 MHz, CDCl₃

$^1$H NMR, 400 MHz, CDCl₃
$^{13}$C NMR, 100 MHz, CDCl$_3$

![C-13 NMR spectrum](image1)

$^{19}$F NMR, 376 MHz, CDCl$_3$

![F-19 NMR spectrum](image2)
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^{19}$F NMR, 376 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 100 MHz, CDCl$_3$

DEPT 135 100 MHz, CDCl$_3$
$^{19}$F NMR, 376 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, decoupled at -125.1 ppm CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
DEPT 135 100 MHz, CDCl₃

$^{1}H$ NMR, 400 MHz, CDCl₃
$^{13}$C NMR, 100 MHz, CDCl$_3$

DEPT 135 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
DEPT 135 100 MHz, CDCl₃

C₈F₁₇Ge₂-Nap 2-Nap

C₈F₁₇Ge₂-Nap 2-Nap

Cl
$^{13}$C NMR, 100 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 100 MHz, CDCl$_3$

DEPT 135 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
DEPT 135 100 MHz, CDCl₃

\[^{19}F\text{ NMR 376 MHz, CDCl}_3\]

C₈F₁₇Ge

2-Nap

OMe

C₈F₁₇Ge

ppm (F)

ppm (F)
$^{19}$F NMR, 376 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
\[^{13}\text{C} \text{NMR, 100 MHz, CDCl}_3\]
$^1$H NMR, 400 MHz, CDCl$_3$

\[ \text{Me} - \text{BnO} - 3h \]

$^{13}$C NMR, 100 MHz, CDCl$_3$

\[ \text{BnO} - \text{Me} - 3h \]
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^{1}H$ NMR, 400 MHz, CDCl$_3$

$^{13}C$ NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^{13}$C NMR, 100 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$

Boscalid 17
$^{13}$C NMR, 100 MHz, CDCl$_3$

![Boscalid 17 NMR spectrum](image)

$^1$H NMR, 500 MHz, C$_6$D$_6$

![Chemical structure](image)

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$^{13}$C NMR, 100 MHz, C$_6$D$_6$

DEPT 135 100 MHz, C$_6$D$_6$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^{13}$C NMR, 100 MHz, CDCl$_3$

DEPT 135 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
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DEPT 135 100 MHz, CDCl₃

$^1$H NMR, 400 MHz, CDCl₃
$^{13}$C NMR, 100 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 100 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 100 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
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$^{13}$C NMR, 100 MHz, CDCl$_3$

DEPT 135 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$

ppm (11)

ppm (11)