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

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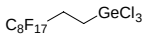
General directions

Solvents and reagents: Solvents were distilled as follows: THF and Et_2O over Na-benzophenone ketyl, toluene over Na, CH_2Cl_2 and DMF over CaH_2; 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 F_{254}) which were developed with UV fluorescence (254 nm and 365 nm) and $KMnO_4$(aq)/Δ. **^{1}H 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_H) are given in parts per million (ppm) as referenced to the appropriate residual solvent peak. Broad signals are assigned as b. **^{13}C 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_C) are given in parts per million (ppm) as referenced to $CHCl_3$, and are assigned as s, d, t, and q, for C, CH, CH_2, and CH_3 respectively; The chemical shift of carbons on the fluorous-tag were recorded by applying fluorine-decoupling at δ -125.1 ppm during ^{13}C NMR acquisition. **^{19}F NMR spectra:** These were recorded at 367 MHz on a Bruker AM-400 instrument. Chemical shifts (δ_F) are given in parts per million (ppm) as referenced to $CFCl_3$. **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 ^{74}Ge, ^{35}Cl and ^{79}Br isotopes. HRMS values are valid to ±5 ppm. **GC-MS**: Analyses were carried out using a Finnigan Trio-1000 EI^+ 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

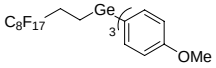
Trichloro-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)germane



1H,2H-Perfluorodecyl iodide (12.5 g, 41.56 mmol) and germanium(II) chloride dioxane complex[2] (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 CH_2Cl_2 (500 mL) and added dropwise to H_2O (500 mL). The resulting white precipitate was collected by filtration, washed with H_2O (300 mL) then CH_2Cl_2 (300 mL) and dried under suction. The dried precipitate was stirred in conc. HCl (37% w/v) for 16 h and then extracted with CH_2Cl_2 (5 × 100 mL). The combined organic extracts were dried over $MgSO_4$ 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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.20 (m, 2H, CH_2CH_2Ge), 2.47 (m, 2H, CH_2CH_2Ge); ^{13}C NMR (100 MHz; $CDCl_3$): δ 22.1 (t),

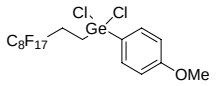
25.0 (t, J_{CF} 23.0), 108.6 (m), 110.5 (m), 113.5 (m), 114.4 (m), 115.7 (m), 116.9 (t), 117.3 (m), 118.6 (m); ^{19}F NMR (376 MHz; $CDCl_3$): δ - 126.5 [s, 2F,$CF_2(CH_2)_2$], -123.2 (s, 2F), -122.6 (s, 2F), -121.8 (s, 4F, 4 × CF_2), -121.6 (s, 2F), -115.3 (s, 2F), -80.7 [s, 3F, $CF_3(CF_2)_7(CH_2)_2$]; IR υ_{max} (neat) 1442 (C-F), 1367, 1243, 906, 826 cm^{-1}; *m/z* (CI^+) (rel. intensity) 606 [$(M-F)^+$, 41), 590 (4), 464 (33), 158 (23), 109 (20); Analysis for $C_{10}H_4GeCl_3F_{17}$ expected C 19.18%, H 0.64%, found C 19.19%, H 0.54%.

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)tris-(4-methoxyphenyl)germane



To a solution of *trichloro-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-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 Et_2O (20.0 mL) and washed with water (2 × 20.0 mL). The combined organic extracts were dried over $MgSO_4$ 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/CH_2Cl_2 50/50 → CH_2Cl_2) and drying under high vacuum gave *(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)tris-(4-methoxyphenyl)germane* as a white amorphous solid (2.84 g, 85%). mp 55-57 °C; R_f 0.35 (petrol/CH_2Cl_2, 70/30); ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.63 (m, 2H, CH_2CH_2Ge), 2.19 (m, 2H, CH_2CH_2Ge), 3.81 (s, 9H, 3 × $ArOCH_3$), 6.94 (d, *J* = 8.5 Hz, 6H, ArH), 7.37 (d, *J* = 8.5 Hz, 6H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 3.7 (t), 27.0 (t, J_{CF} 23.0), 55.0 (3q), 114.0 (6d), 118.9 (3s), 126 (6d), 160.6 (3s), eight carbons not observed; ^{19}F NMR (376 MHz; $CDCl_3$): δ - 126.3 (s, 2F), -123.2 (s, 2F), -122.7 (s, 2F), -122.1 (s, 4F, 2 × CF_2), -121.9 (s, 2F), -115.3 (s, 2F), -80.8 [s, 3F, $CF_3(CF_2)_7(CH_2)_2$]; IR υ_{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 $C_{31}H_{24}{}^{74}GeO_3F_{17}$ (M^+) 841.0666, found 841.0705, Δ -4.6 ppm; Analysis for $C_{31}H_{24}GeO_3F_{17}$ expected C 44.27%, H 3.00%, found C 44.21%, H 2.95%.

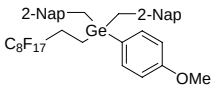
Dichloro-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)(4-methoxyphenyl)germane



To a solution of *(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)tris-(4-methoxyphenyl)germane* (2.84 g, 3.377 mmol) in CH_2Cl_2 (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-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)(4-methoxyphenyl)germane* as a white amorphous solid (2.32 g, 98%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.95 (m, 2H, CH_2CH_2Ge), 2.45 (m, 2H, CH_2CH_2Ge), 3.81 (s, 3H, 3 × $ArOCH_3$), 6.92 (d, *J* = 8.5 Hz, 2H, ArH), 7.35 (d, *J* = 8.5 Hz, 2H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 15.3 (t), 25.4 (t, J_{CF} = 23.0 Hz), 55.3 (q), 114.8 (2d), 125.1 (s), 133.7 (2d) 162.7 (s), eight carbons not observed; ^{19}F NMR (376 MHz; $CDCl_3$): δ - 126.2 (s, 2F), -123.3 (s, 2F), -122.7 (s, 2F), -122.1 (s, 4F, 2 × CF_2), -121.9 (s, 2F), -115.4 $(CF_2)_6CF_2CF_3$], -80.8 (t, 3F, $(CF_2)_6CF_2CF_3$); IR υ_{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 [$M(^{35}Cl_2)^+$, 47], 663 (4), 295 (12), 251

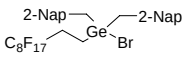
(100), 235 (16); HRMS (EI^+) calc'd. for $C_{17}H_{11}{}^{74}GeO^{35}Cl_2F_{17}$ (M^+) 697.9127, found 697.9125, Δ 0.3 ppm; Analysis for $C_{17}H_{11}GeCl_2F_{17}O$ expected C 29.26%, H 1.59%, found C 29.27%, H 1.64%.

(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, I_2 (0.01 g , 0.04 mmol) activated magnesium turnings (0.42 g, 17.3 mmol) in Et_2O (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 Et_2O (5.0 mL) dropwise and the resulting mixture stirred for 2.5 h. A sat. solution NH_4Cl was added to the reaction mixture until no effervescence occurred and the solvent was then removed *in vacuo*. The residue taken up in Et_2O (30.0 mL) and washed with water (2 × 10.0 mL) and was dried over $MgSO_4$. 2-Methylnaphthalene was sublimed from the residue (60 °C/0.1mmHg using a Kugelrohr) then 1,2-bis-(2-naphthyl)ethylene was removed from the residue by recrystalisation with Et_2O (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/CH_2Cl_2, 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); ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.16 (m, 2H, CH_2CH_2Ge), 1.87 (m, 2H, CH_2CH_2Ge), 2.73 (s, 4H, 2 × $GeCH_2Nap$), 3.85 (s, 3H, OCH_3), 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 2.2 (t), 22.8 (t, J_{CF} = 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); ^{19}F NMR (376 MHz; $CDCl_3$): 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, $(CF_2)_6CF_2CF_3$], -79.8 (t, J = 10.0 Hz, 3F, $(CF_2)_6CF_2CF_3$); IR υ_{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^+) (rel. intensity) 910 (M^+, 9), 769 (89), 436 (3), 341 (52), 141 (100); HRMS (EI^+) calc'd. for $C_{39}H_{29}{}^{74}GeF_{17}O$ (M^+) 910.1159, found 910.1145, Δ 1.6 ppm; Analysis for $C_{39}H_{29}GeF_{17}O$ expected C 51.52%, H 3.21%, found C 51.68%, H 3.11%.

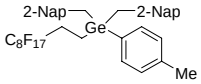
Bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)bis-(naphthalen-2-ylmethyl)germane



To a solution of *4-anisyl germane* **1a** (0.102 g, 0.112 mmol) in CH_2Cl_2 (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 Et_2O (3 × 20.0 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated *in vacuo* to give *bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)bis-(naphthalen-2-ylmethyl)germane* as a brown amorphous solid (0.087 g, 88%). mp 172-174 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.38 (m, 2H, $C_8F_{17}CH_2CH_2Ge$), 1.93 (m, 2H, $C_8F_{17}CH_2CH_2Ge$), 2.99 (dd, J = 12.6, 5.6 Hz, 4H, 2 × $GeCH_2Nap$), 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,

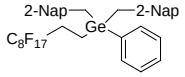
ArH), 7.81 (dd, *J* = 6.6, 1.8 Hz, 2H ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 7.5 (t), 26.4 (t, J_{CF} 23.0 Hz), 28.3 (2t), 110.2 (s), 110.6 (2s), 110.7 (s), 110.9 (3s), 117.1 (s), 125.4 (2d), 126.3 (2d), 126.4 (2d), 126.9 (2d), 127.1 (2d), 127.7 (2d), 128.5 (2d), 131.7 (2s), 133.6 (2s), 133.7 (2s); ^{19}F NMR (376 MHz; $CDCl_3$) δ -125.2 (s, 2F), -122.6 (s, 2F), -121.8 (s, 2F), -121.0 (m, 6F), -115.0 [quintet, *J* = 15.1 Hz, 2F, $(CF_2)_6CF_2CF_3$], -79.8 [t, *J* = 9.4 Hz, 3F, $(CF_2)_6CF_2CF_3$]; IR υ_{max} (neat) 3054 (C-H), 2987 (C-H) 1601 (C=C), 1422 (C-F), 1265, 896, 748 cm^{-1}; *m/z* (FAB$^+$) (rel. intensity) 882 [M(^{79}Br)$^+$, 1], 803 (1), 141 (100); HRMS (ESI$^+$) calc'd. for $C_{32}H_{23}{}^{79}BrF_{17}{}^{74}Ge$ (MH^+) 882.9924, found 882.9932, Δ 1.0 ppm.

(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 Et_2O (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 Et_2O (20.0 mL) and a solution of 1.0 M NH_4Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et_2O, the combined organic extracts were dried over $MgSO_4$ 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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.20 (m, 2H, CH_2CH_2Ge), 1.89 (m, 2H, CH_2CH_2Ge), 2.45 (s, 3H, $GeC_6H_4CH_3$), 2.76 (s, 4H, 2 × $GeCH_2Nap$), 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 1.9 (t), 21.4 (q), 22.5 (2t), 26.3 (t, J_{CF} 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), 132.7 (s), 133.8 (2d+s), 136.7 (3s), 139.2 (s); ^{19}F NMR (376 MHz; $CDCl_3$): δ -126.6 (s, 2F), -123.9 (s, 2F), -123.1 (s, 2F), -122.3 (m, 6F), -116.7 [quintet, *J* = 15 Hz, 2F, $(CF_2)_6CF_2CF_3$], -81.2 [t, *J* = 10 Hz, 3F, $(CF_2)_6CF_2CF_3$]; IR υ_{max} (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 $C_{39}H_{29}{}^{74}GeF_{17}$ (M^+) 894.1209, found 894.1244, Δ 3.8 ppm; Analysis for $C_{39}H_{29}GeF_{17}$ expected C 52.44%, H 3.27%, found C 52.53%, H 3.36%.

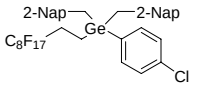
(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)bis-(naphthalen-2-ylmethyl)phenylgermane 1c



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 Et_2O (20.0 mL) and a solution of 1.0 M NH_4Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0

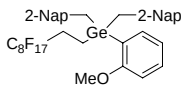
mL) of Et_2O, the combined organic extracts were dried over $MgSO_4$ and evaporated *in vacuo* to give green oily residue which was purified by FC (hexane/EtOAc, 97/3) to give phenylgermane **1c** as a pale yellow oil (0.4122 g, 83%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.19 (m, 2H, CH_2CH_2Ge), 1.89 (m, 2H, CH_2CH_2Ge), 2.76 (s, 4H, 2 × $GeCH_2Nap$), 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 1.9 (t), 22.5 (2t), 26.3 (t, J_{CF} 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+s), 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); ^{19}F NMR (376 MHz; $CDCl_3$): δ -125.2 (s, 2F), -122.6 (s, 2F), -121.8 (s, 2F), -121.0 (m, 6F), -115.4 [quintet, *J* = 14.7 Hz, 2F, $(CF_2)_6CF_2CF_3$], -79.8 [t, *J* = 9.7 Hz, 3F, $(CF_2)_6CF_2CF_3$]; IR υ_{max} (neat) 3032 (C-H), 2985 (C-H) 1598 (C=C), 1415 (C-F), 1265, 896, 749 cm^{-1}; *m/z* (FAB$^+$) (rel. intensity) 739 [(M-$NapCH_2$)$^+$, 2], 459 (1), 141 (100); HRMS (FAB$^+$) calc'd. for $C_{27}H_{19}F_{17}{}^{74}Ge$ [(M-$NapCH_2$)$^+$] 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



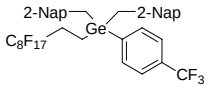
To a solution of *4-chloro-1-bromoenzene* (0.4038 g, 2.10 mmol) in THF (10.0 mL) at -78 °C was added ^{t}BuLi (3.3 mL, 4.62 mmol, 1.4M) dropwise resulting in a yellow solution. The solution was stirred at -78 °C for 30 min to achieve lithium-halogen exchange. The resulting solution mixture was added *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 Et_2O (20.0 mL) and a solution of 1.0 M NH_4Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et_2O, the combined organic extracts were dried over $MgSO_4$ and evaporated *in vacuo* to give green oily residue which was purified by FC (hexane/EtOAc, 97/3) to give (4-chlorophenyl)germane **1d** as a pale yellow oil (0.5168 g, 80%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.20 (m, 2H, CH_2CH_2Ge), 1.84 (m, 2H, CH_2CH_2Ge), 2.74 (s, 4H, 2 × $GeCH_2Nap$), 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), 7.81 (d, *J* = 7.7 Hz, 2H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 1.8 (t), 22.4 (2t), 26.2 (t, J_{CF} 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), 135.1 (2d), 135.7 (s), 136.1 (2s); ^{19}F NMR (376 MHz; $CDCl_3$): δ -125.2 (s, 2F), -122.5 (s, 2F), -121.8 (s, 2F), -121.0 (m, 6F), -115.4 [quintet, *J* = 15 Hz, 2F, $(CF_2)_6CF_2CF_3$], -79.8 [t, *J* = 10 Hz, 3F, $(CF_2)_6CF_2CF_3$]; IR υ_{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(^{35}Cl)-$NapCH_2$]$^+$, 1}, 429 (1), 401 (2), 141 (100); HRMS (FAB$^+$) calc'd. for $C_{27}H_{17}{}^{35}ClF_{17}{}^{74}Ge$ [M-($NapCH_2$)$^+$] 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 ^{o}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 ^{o}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 ^{o}C and stirred for 1 h than warmed up to rt for 16 h. The reaction mixture was diluted with Et_2O (20.0 mL) and a solution of 1.0 M NH_4Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et_2O, the combined organic extracts were dried over $MgSO_4$ 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%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.19 (m, 2H, CH_2CH_2Ge), 1.89 (m, 2H, CH_2CH_2Ge), 2.78 (s, 4H, 2 × $GeCH_2Nap$), 3.69 (s, 3H, OCH_3), 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 (d, *J* = 8.0 Hz, 2H, ArH), 7.68 (d, *J* = 8.4 Hz, 2H, ArH), 7.79 (d, *J* = 7.7 Hz, 2H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 2.7 (t), 22.7 (2t), 26.6 (t, J_{CF} 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); ^{19}F NMR (376 MHz; $CDCl_3$): 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, $(CF_2)_6CF_2CF_3$], -79.8 [t, *J* = 9.8 Hz, 3F, $(CF_2)_6CF_2CF_3$]; 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 [$(M\text{-}NapCH_2)^{+}$, 1], 463 (1), 341 (5), 141 (100); HRMS (FAB^{+}) calc'd. for $C_{28}H_{20}F_{17}O^{70}Ge$ [$M\text{-}(NapCH_2)^{+}$] 765.0480, found 765.0480, Δ 0.0 ppm.

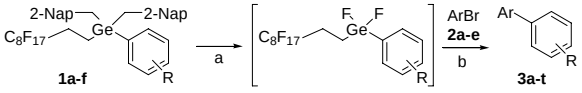
(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(4-trifluoromethylphenyl)bis-(naphthalen-2-ylmethyl)germane 1f



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 NH_4Cl was added to the reaction mixture until no effervescence occurred and the reaction mixture was partitioned between Et_2O (40.0 mL) and water (10.0 mL), extracted with CH_2Cl_2 (2 × 10.0 mL) and dried over $MgSO_4$. Purification by FC (petrol → petrol/EtOAc, 95/5) gave (4-trifluoromethylphenyl)germane **1f** as a colourless oil (0.474 g, 84%). R_f 0.31 (petrol/ EtOAc, 95/5); ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.21 (m, 2H, CH_2CH_2Ge), 1.83 (m, 2H, CH_2CH_2Ge), 2.76 (s, 4H, 2 × $GeCH_2Nap$), 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); ^{13}C NMR (101 MHz; $CDCl_3$) 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), 127.0 (2d), 127.1 (2d), 127.6 (2d), 128.2 (2d), 131.3 (2s), 133.7 (2s), 134.2 (2d), 135.8 (3s); ^{19}F NMR (376 MHz; $CDCl_3$): 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, $(CF_2)_6CF_2CF_3$], -79.8 [t, *J* = 10.0 Hz, 3F, $(CF_2)_6CF_2CF_3$], -62.0 (s, 3F, $ArCF_3$); IR υ_{max} (neat) 3020 (C-H), 2985 (C-H) 1593 (C=C), 1421 (C-F),

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 $C_{39}H_{26}{}^{74}GeF_{20}$ (M^+) 948.0927, found 948.0962, Δ 3.7 ppm; Analysis for $C_{39}H_{29}GeF_{20}$ expected C 50.49%, H 3.10%, found C 50.54%, H 2.99%.

Photoactivation/cross-coupling reactions (Table 1):



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 $Cu(BF_4)_2{\cdot}nH_2O$ (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 $Cu(BF_4)_2{\cdot}nH_2O$ (0.084 g) was then added and the solution irradiated for a furter 1 h. After this time, the solvent was removed *in vacuo*, the residue was taken up in CH_2Cl_2 (20.0 mL), washed with water (2 × 8.00 mL) and dried over $MgSO_4$ to give the crude *difluoroarylgermane*.

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

The ^{19}F NMR after <2 h displays a singlet at δ_F -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_f 0.40 (CH_2Cl_2); ^1H NMR (400 MHz; $CDCl_3$): δ 1.43 (m, 2H, CH_2CH_2Ge), 2.11 (m, 2H, CH_2CH_2Ge), 3.03 (m, 2H, $GeCH_2Nap$), 3.84 (s, 3H, OCH_3), 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), 7.40-7.52 (m, 2H, ArH), 7.59 (s, 1H, ArH), 7.72-7.85 (m, 3H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 6.1 (t), 25.1 (t), 26.3 (t), 55.1 (q), 108.7 (s), 110.6 (s), 111.1 (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; ^{19}F NMR (376 MHz; $CDCl_3$): 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, $(CF_2)_6CF_2CF_3$], -79.8 (t, *J* = 10.0 Hz, 3F, $(CF_2)_6CF_2CF_3$); *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 ^{19}F NMR displays three singlets at δ_F -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 $C_{17}H_{11}{}^{74}GeF_{19}O$ (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; $CDCl_3$): δ 3.41 (s, 3H, OMe), 4.62 (s, 2H, $ArCH_2$), 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; $CDCl_3$): 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**[3]

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. $PdCl_2(MeCN)_2$ (1.2 mg, 0.0046 mmol) and P(2-Tol)$_3$ (2.2 mg, 0.007 mmol) were dissolved 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 ^oC for 16 h under nitrogen atmosphere. The crude reaction mixture was diluted with Et_2O (20.0 mL) and washed with water (3 × 10.0 mL), the combined organic extracts were dried over $MgSO_4$ and evaporated *in vacuo*. Purification by FC (hexane/EtOAc, 97/3) gave *biphenyl* **3a** as a clear liquid (14.0 mg, 96%). R_f 0.22 (cyclohexane); ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.88 (s, 3H, OC*H*$_3$), 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). ^{19}F NMR (376 MHz; $CDCl_3$): δ -62.8 (s, 6F, 2 × CF_3). ^{13}C NMR ($CDCl_3$, 67 MHz) δ 55.4 (q), 114.7 (d), 120.2 (d), 126.6 (d), 128.4 (d), 5 quaternary carbons not seen; IR υ_{max} (neat) 2940, 2842, 1610, 1521, 1383, 1279, 1185, 1132, 1061, 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 $C_{15}H_{10}F_6O$ 320.0636, found 320.0625, Δ 3.4 ppm.

Entry 2: **4-Chloro-4'-methoxybiphenyl 3b**[4]

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), $PdCl_2(MeCN)_2$ (1.8 mg, 0.007 mmol), P(2-Tol)$_3$ (3.2 mg, 0.0105mmol), *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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.85 (s, 3H, OC*H*$_3$), 6.96-6.99 (m, 2H, ArH), 7.37-7.39 (m, 2H, ArH), 7.46-7.51 (m, 4H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) 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 $C_{13}H_{11}{}^{35}ClO$ (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), $PdCl_2(MeCN)_2$ (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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.85 (s, 3H, OC*H*$_3$), 5.11 (s, 2H, ArOC*H*$_2$Ph), 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); ^{13}C NMR (100 MHz; $CDCl_3$) 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 $C_{20}H_{18}O_2$ (M^+) 290.1307, found 290.1303, Δ -1.3 ppm.

Entry 4: **1-(4-Methoxyphenyl)naphthalene 3d**[5, 6]

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), $PdCl_2(MeCN)_2$ (1.8 mg, 0.007 mmol), $P(2\text{-Tol})_3$ (3.2 mg, 0.0105 mmol), *1-bromonaphthalene* (29.8 mg, 0.143 mmol, 20 μL) and CuI (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%). R_f 0.16 (cyclohexane); mp. 110.4-116.2 °C (*cf.* 114-115 °C[7]).^{1}H NMR (400 MHz; $CDCl_3$): δ 3.90 (s, 3H, OCH_3), 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); ^{13}C NMR (100 MHz; $CDCl_3$) 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 $C_{17}H_{14}O$ (M^+) 234.1045, found 234.1041, Δ −1.6 ppm.

Entry 5: **4-Methyl-3',5'-bis-(trifluoromethyl)biphenyl 3e**[8, 9]

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), $PdCl_2(MeCN)_2$ (2.2 mg, 0.0085 mmol), $P(2\text{-Tol})_3$ (3.9 mg, 0.0128 mmol), *3,5-bis-(trifluoromethyl)bromobenzene* (49.8 mg, 0.17 mmol, 29.3 μL) and CuI (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%). R_f 0.65 (cyclohexane); ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.43 (s, 3H, $ArCH_3$), 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 21.2 (q), 120.6 (2s), 122.1 (d), 126.9 (2d), 127.0 (2d), 130.0 (2d), 131.8 (s), 132.2 (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 $C_{15}H_{10}F_6$ (M^+) 304.0687, found 304.0681, Δ −1.9 ppm.

Entry 6: **4-Chloro-4'-methylbiphenyl 3f**[10]

Using the *typical method*, the crude difluoroarylgermane from the photolysis of *arylgermane* **1b** (55.2mg, 0.085 mmol), TBAF (80.0 mg, 0.254 mmol), $PdCl_2(MeCN)_2$ (2.2 mg, 0.0085 mmol), $P(2\text{-Tol})_3$ (3.9 mg, 0.0128 mmol), *4-chloro-bromobenzene* (32.6mg, 0.170 mmol) and CuI (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 %). ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.40 (s, 3H, $ArCH_3$), 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 21.1 (q), 126.8 (2d), 128.17 (2d), 128.21 (d), 128.8 (d), 129.0 (d), 129.6 (d), 133.0 (s), 137.1 (s), 137.4 (s), 139.6 (s); *m/z* (EI^+) (rel. intensity) 202 [$M(^{35}Cl)^+$, 100), 165 (65), 82 (40); HRMS (EI^+) calc'd. for $C_{13}H_{11}{}^{35}Cl$ (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** (55.2mg, 0.085 mmol), TBAF (80.0 mg, 0.254 mmol), $PdCl_2(MeCN)_2$ (2.2 mg, 0.0085 mmol), $P(2\text{-Tol})_3$ (3.9 mg, 0.0128 mmol), *4-(phenylmethoxy)bromobenzene* (44.8 mg, 0.17 mmol) and CuI (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 %). ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.38 (s, 3H, $ArCH_3$), 5.11 (s, 2H, $ArOCH_2Ph$), 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 21.1 (q), 70.1 (t), 115.1 (2d), 126.6 (2d), 127.5 (2d), 128.0 (3d), 128.6

(2d), 129.4 (2d), 134.0 (s), 136.4 (s), 137.0 (s), 137.9 (s), 158.1 (s); IR υ_{max} (neat) 3026 (C-H), 2852 (C-H) 1532 (C=C), 900, 750, 670 cm^{-1}; *m/z* (EI^+) (rel. intensity) 274 (M^+, 30), 183 (20), 141 (25), 91 (100); HRMS (EI^+) calc'd. for (M^+) $C_{20}H_{18}O$ 274.1358, found 274.1359, Δ 0.5 ppm.

Entry 8: **1-(4-Methylphenyl)naphthalene 3h**[11]

Using the *typical method*, the crude difluoroarylgermane from the photolysis of *arylgermane* **1b** (55.2mg, 0.085 mmol), TBAF (80.0 mg, 0.254 mmol), $PdCl_2(MeCN)_2$ (2.2 mg, 0.0085 mmol), $P(2\text{-Tol})_3$ (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 %). ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.47 (s, 3H, ArC*H*$_3$), 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); ^{13}C NMR (100 MHz; $CDCl_3$) 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), 203 970), 202 (85), 108 (50); HRMS (EI^+) calc'd. for $C_{17}H_{14}$ (M^+) 218.1096, found 218.1098, Δ 1.1 ppm.

Entry 9: **3',5'-bis-(Trifluoromethyl)biphenyl 3i**[8]

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), $PdCl_2(MeCN)_2$ (2.1 mg, 0.0081 mmol), $P(2\text{-Tol})_3$ (3.7 mg, 0.088 mmol), *3,5-bis-(trifluoromethyl)bromobenzen*e (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 %). ^{1}H NMR (400 MHz; $CDCl_3$): 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 $C_{14}H_8F_6$ (M^+) 290.0530, found 290.0523, Δ -2.5 ppm.

Entry 10: **4-Chlorobiphenyl 3j**[12]

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), $PdCl_2(MeCN)_2$ (2.1 mg, 0.0081 mmol), $P(2\text{-Tol})_3$ (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 %). ^{1}H NMR (400 MHz; $CDCl_3$): 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); ^{13}C NMR (100 MHz; $CDCl_3$) 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(^{35}Cl)$^+$, 80], 152 (100); HRMS (EI^+) calc'd. for $C_{12}H_9{}^{35}Cl$ (M^+)188.0393, found 188.0385, Δ -4.1 ppm.

Entry 11: **4-(Phenylmethoxy)biphenyl 3k**[5]

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), $PdCl_2(MeCN)_2$ (2.1 mg, 0.0081 mmol), $P(2\text{-Tol})_3$ (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%). ^{1}H NMR (400 MHz; $CDCl_3$): 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 70.1 (t), 115.1

(2d), 126.67 (d), 126.73 (2d), 127.5 (2d), 128.0 (d), 128.2 (2d), 128.6 (2d), 128.7 (2d), 134.2 (s), 135.7 (s), 140.1 (s), 158.3 (s); *m/z* (EI^+) (rel. intensity) 260 (M^+, 40), 91 (100); HRMS (EI^+) calc'd. for $C_{19}H_{16}O$ (M^+) 260.1601, found 260.1190, Δ -4.3 ppm.

Entry 12: **1-Phenylnaphthalene 3l**[11]

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), $PdCl_2(MeCN)_2$ (2.1 mg, 0.0081 mmol), $P(2\text{-Tol})_3$ (3.7 mg, 0.088 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%). ^{1}H NMR (400 MHz; $CDCl_3$): 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); ^{13}C NMR (100 MHz; $CDCl_3$) 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 $C_{16}H_{12}$ (M^+) 204.0903, found 204.0903, Δ 0.0 ppm.

Entry 13: **4-Chloro-3',5'-bis-(trifluoromethyl)biphenyl 3m**[8]

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), $PdCl_2(MeCN)_2$ (2.1 mg, 0.008 mmol), $P(2\text{-Tol})_3$ (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%). ^{1}H NMR (400 MHz; $CDCl_3$): 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 [$M(^{35}Cl)^+$, 35], 149 (50), 83 (90), 41 (100); HRMS (EI^+) calc'd. for $C_{14}H_7{}^{35}ClF_6$ (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), $PdCl_2(MeCN)_2$ (2.1 mg, 0.008 mmol), $P(2\text{-Tol})_3$ (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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 5.14 (s, 2H, ArOC*H*$_2$Ph), 7.05 (d, *J* = 8.7 Hz, 2H, ArH), 7.31-7.42 (m, 5H, ArH), 7.44-7.50 (m, 6H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) 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), 128.8 (d), 128.9 (d), 129.1 (d), 132.6 (s), 132.7 (s), 136.8 (s), 139.2 (s), 158.5 (s); IR υ_{max} (neat) 3035 (C-H), 2893 (C-H) 1547 (C=C), 870, 738, 665 cm^{-1}; *m/z* (EI^+) (rel. intensity) 296 [$M(^{37}Cl)^+$, 30], 294 [$M(^{35}Cl)^+$, 88], 139 (30), 84 (60), 49 (100); HRMS (EI^+) calc'd. for $C_{19}H_{15}{}^{35}ClO$ (M^+) 294.0811, found 294.0807, Δ -1.5 ppm.

Entry 15: **1-(4-Chlorophenyl)naphthalene 3o**[13]

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), $PdCl_2(MeCN)_2$ (2.1 mg, 0.008 mmol), $P(2\text{-Tol})_3$ (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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.39-7.41 (m, 5H, ArH), 7.49-7.55 (m, 3H, ArH), 7.85 (d, *J* = 8.5 Hz, 1H,

ArH), 7.88 (d, *J* = 8.3 Hz, 1H, ArH), 7.92 (d, *J* = 7.9 Hz, 1H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) 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 [$M(^{35}Cl)^+$, 35], 203 (35), 202 (35), 84 (100); HRMS (EI^+) calc'd. for $C_{16}H_{11}{}^{35}Cl$ (M^+) 238.0549, found 238.0541, Δ -3.9 ppm.

Entry 16: **4-Chloro-2'-nitrobiphenyl 3p**[14, 15]

Using the *typical method*, the crude difluoroarylgermane from the photolysis of *arylgermane* **1d** (37.7 mg, 0.056 mmol), TBAF (53.3 mg, 0.169 mmol), $PdCl_2(MeCN)_2$ (1.5 mg, 0.006 mmol), $P(2\text{-Tol})_3$ (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%). ^{1}H NMR (400 MHz; $CDCl_3$): 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 124.3 (d), 128.5 (d), 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 [$M(^{37}Cl)^+$, 15], 233 [$M(^{35}Cl)^+$, 45], 199 (70), 156 (80), 141 (100); HRMS (EI^+) calc'd. for $C_{12}H_8{}^{35}ClNO_2$ (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 *arylgermane* **1e** (61.5 mg, 0.092 mmol), TBAF (87.4 mg, 0.277 mmol), $PdCl_2(MeCN)_2$ (2.4 mg, 0.0093 mmol), $P(2\text{-Tol})_3$ (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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.82 (s, 3H, OC*H*$_3$), 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); ^{13}C NMR (100 MHz; $CDCl_3$) 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} (CH_2Cl_2) 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 $C_{15}H_{10}F_6O$ (M^+) 320.0636, found 320.0632, Δ -1.2 ppm.

Entry 18: **2-Methoxy-4'-chloro-1,1'-biphenyl 3r**[12]

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), $PdCl_2(MeCN)_2$ (2.4 mg, 0.0093 mmol), $P(2\text{-Tol})_3$ (4.2 mg, 0.0139 mmol), *4-chlorobromobenzen*e (35.2 mg, 0.185 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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.85 (s, 3H, OCH_3), 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); ^{13}C NMR (100 MHz; $CDCl_3$) 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 [$M(^{35}Cl)^+$, 75), 168 (100), 49 (45); HRMS (EI^+) calc'd. for $C_{13}H_{11}{}^{35}ClO$ (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), $PdCl_2(MeCN)_2$ (2.4 mg, 0.0093 mmol), $P(2\text{-Tol})_3$ (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 over12 min]. A yield of 11% for *biphenyl* **3s** was deduced from the ratio of peak intensities for 2-naphthylmethyl methyl ether (R_t 8.1 min, *m/z* 172) *vs*. *biphenyl* **3s** (R_t 13.3 min, *m/z* 290). *m/z* (EI^+) (rel. intensity) 290 (M^+, 20), 91 (100); HRMS (EI^+) calc'd. for $C_{20}H_{18}O$ 290.1307, found 290.1301, Δ -2.0 ppm.

Entry 20: **1-(2-Methoxyphenyl)naphthalene 3t**[12]

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), $PdCl_2(MeCN)_2$ (2.4 mg, 0.0093 mmol), $P(2\text{-Tol})_3$ (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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.70 (s, 3H, OC*H*$_3$), 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); ^{13}C NMR (100 MHz; $CDCl_3$) 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 $C_{17}H_{14}O$ (M^+) 234.1045, found 234.1045, Δ 0.0 ppm.

Entry 21: **4-Trifluoromethyl-3',5'-bis-(trifluoromethyl)biphenyl 3u**[8]

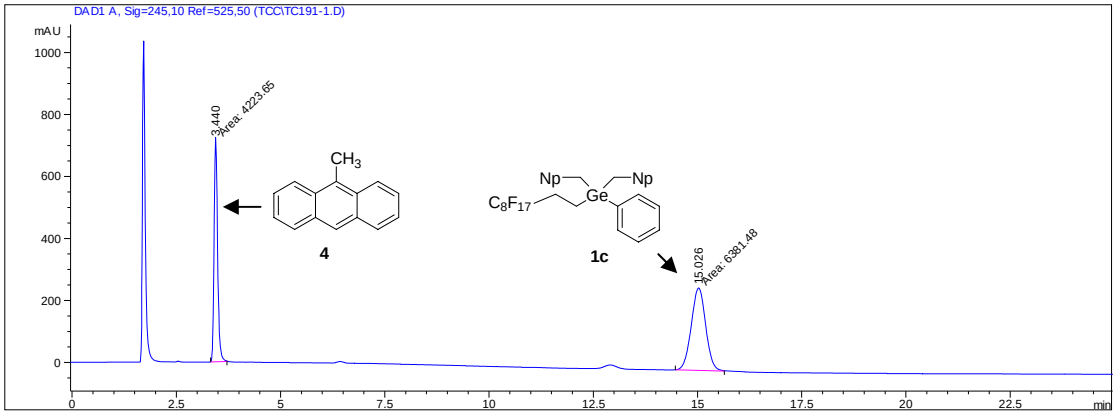
Using the *typical method*, the crude difluoroarylgermane from the photolysis of *arylgermane* **1f** (46.1 mg, 0.066 mmol), TBAF (62 mg, 0.197 mmol), $PdCl_2(MeCN)_2$ (1.7 mg, 0.0066 mmol), $P(2\text{-Tol})_3$ (3 mg, 0.0099 mmol), *3,5-bis-(trifluoromethyl)bromobenzene* (38.4 mg, 0.131 mmol, 22.6 μL) 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 over12 min]. A yield of 26% for *biphenyl* **3u** was deduced from the ratio of peak intensities for 2-naphthylmethyl methyl ether (R_t 8.0 min, *m/z* 172) *vs*. *biphenyl* **3u** (R_t 6.6 min, *m/z* 358). *m/z* (EI^+) (rel. intensity) 358 (M^+, 25), 84 (70), 49 (100); HRMS (EI^+) calc'd. for $C_{15}H_7F_9$ (M^+) 358.0404, found 358.0386, Δ -5.0 ppm.

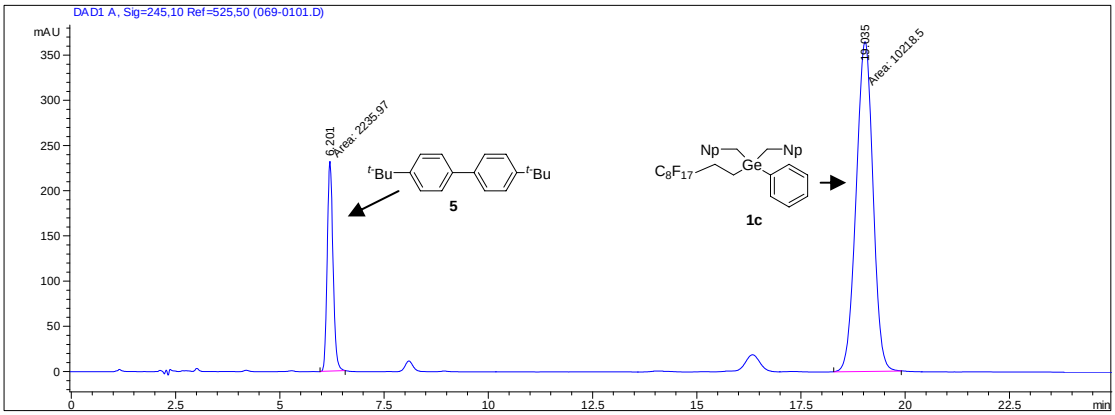
Entry 22: **4-Trifluoromethyl-4'-chloro-1,1'-biphenyl 3v**[16]

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), $PdCl_2(MeCN)_2$ (1.7 mg, 0.0066 mmol), $P(2\text{-Tol})_3$ (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 over12 min]. A yield of 11% for *biphenyl* **3v** was deduced from the ratio of peak intensities for 2-naphthylmethyl methyl ether (R_t 8.0 min, *m/z* 172) *vs*. *biphenyl* **3v** (R_t 10.2 min, *m/z* 256). *m/z* (EI^+) (rel. intensity) 256 (M^+, 50), 141 (100), 115 (45); HRMS (EI^+) calc'd. for $C_{13}H_8{}^{35}ClF_3$ (M^+) 256.0267, found 256.0265, Δ -0.6 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-methylanthrance (**4**) or 4,4'-di-*tert*-butyl-1,1'-biphenyl (**5**) as the internal standard.[17, 18] 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 Et_2O (5 mL) before being extracted with Et_2O (5 × 10 mL). The organic layer was evapourated to dryness under a stream of N_2 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/H_2O = 80:20*; Flow rate:* 1 mLmin^{-1}; *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.





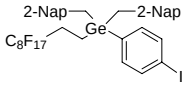
#	Conditions[a]	Ref.	Rec. 1c/% (Run 1)[a]	Rec. 1c/% (Run 2)[a]	Rec. 1c/% (Mean)[a]
1	$NaBH_4$, THF	**4**	106	107	107
2	$LiAlH_4$, THF	**5**	97	110	104
3	Hydrazine/DMF (2% v/v)	**4**	114	93	104
4	$HS(CH_2)_2OH$, DBU, DMF	**4**	109	95	102
5	Piperidine/DMF (20% v/v)	**4**	111	91	101
6	TBAF, THF	**4**	101	103	102
7	*m*-CPBA, CH_2Cl_2	**4**	75	76	76
8	TFA/CH_2Cl_2 (50% v/v)	**4**	18	22	20

[a]% recovery of **1c** by HPLC *vs*. the internal standard.

Table Showing stability profile of fluorous-tagged phenylgermane **1c**.

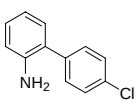
Synthesis of Boscalid® (16) and its alkynyl derivatives 17 and 18 (Scheme 1)

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



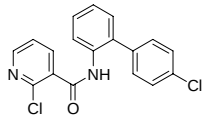
To a solution of *1,4-diiodobenzene* (0.1258 g, 0.382 mmol) in THF (10.0 mL) at -78 °C was added ^{t}BuLi (0.546mL, 0.764 mmol, 1.4M) dropwise resulting in a dark red solution. The solution was stirred at -78 °C for 30 min to achieve lithium-halogen exchange. The resulting solution mixture was added *bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-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 Et_2O (20.0 mL) and a solution of 1.0 M NH_4Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et_2O, the combined organic extracts were dried over $MgSO_4$ 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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.20 (m, 2H, CH_2CH_2Ge), 1.87 (m, 2H, CH_2CH_2Ge), 2.77 (s, 4H, 2 × $GeCH_2Nap$), 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), 7.65 (d, *J* = 7.7 Hz, 2H, ArH), 7.70 (d, *J* = 8.2 Hz, 2H, ArH), 7.79 (d, *J* = 7.7 Hz, 2H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 1.8 (t), 22.4 (2t), 26.2 (t, J_{CF} 23.0 Hz), 96.2 (s), 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), 135.1 (2d), 135.7 (s), 136.1 (2s); ^{19}F NMR (376 MHz; $CDCl_3$): 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, $(CF_2)_6CF_2CF_3$], -80.7 [t, *J* = 10 Hz, 3F, $(CF_2)_6CF_2CF_3$]; IR υ_{max} (neat) 3035 (C-H), 2988 (C-H) 1549 (C=C), 1421 (C-F), 1265, 1050 (C-I), 896, 740 cm^{-1}; *m/z* (FAB^+) (rel. intensity) 864 [$(M\text{-}NapCH_2)^+$, 2], 803 (1), 709 (5), 141 (100); HRMS (FAB^+) calc'd. for $C_{27}H_{17}F_{17}{}^{74}GeI$ [$M\text{-}(NapCH_2)^+$] 864.9310, found 864.9307, Δ -0.3 ppm.

4-Chloro-2'-aminobiphenyl 11[14]



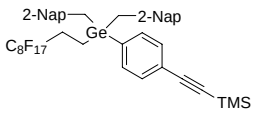
To a solution of *4-chloro-2'-nitrobiphenyl* (**3p**, 15 mg, 0.064 mmol) in THF-EtOH (1:1, 10 mL) was added tin(II) chloride (122 mg, 0.64 mmol) and conc. HC (1 mL) and the reaction mixture was stirred for 16 h. A sat. solution of K_2CO_3 was added and the reaction mixture was partitioned between Et_2O (40.0 mL) and water (10.0 mL). The phases were separated, the aqueous phase extracted with CH_2Cl_2 (2 × 10.0 mL) and the combined organic extracts were dried over $MgSO_4$. Purification by FC (hexane/EtOAc, 90/10) gave *4-chloro-2'-aminobiphenyl* **11** as a colourless oil (10.3 mg, 88%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.73 (brs, 2H, NH_2), 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 115.7 (d), 118.7 (d), 126.3 (s), 128.8 (d), 129.0 (2d), 130.3 (d), 130.5 (2d), 133.1 (s), 137.9 (s), 143.4 (s); IR υ_{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(^{37}Cl)$^+$, 9], 203 [M(^{35}Cl)$^+$, 25], 167 (25), 49 (30), 84 (90), 49 (100); HRMS (EI$^+$) calc'd. for $C_{12}H_{10}{}^{35}ClN$ (M^+) 203.0502, found 203.0501, Δ -0.4 ppm.

Boscalid® 16[19, 20]



To a solution of *4-chloro-2'-aminobiphenyl* (**11**, 20.0 mg, 0.098 mmol) in CH_2Cl_2 (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 K_2CO_3 was added to the reaction mixture and the reaction mixture was partitioned between Et_2O (40.0 mL) and water (10.0 mL), extracted with CH_2Cl_2 (2 × 10.0 mL) and dried over $MgSO_4$. Purification by FC (hexane/EtOAc, 75/25) gave *Boscalid®* (**16**) as a colourless oil (22.1 mg, 65%). ^{1}H NMR (400 MHz; $CDCl_3$): 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); ^{13}C NMR (100 MHz; $CDCl_3$) 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 υ_{max} (neat) 3338 (N-H), 3084 (C-H), 2935 (C-H), 1887 (comb), 1656 (C=O), 1580 (C=C), 1472, 810 cm^{-1}; *m/z* (EI$^+$) (rel. intensity) 347 [M(^{37}Cl^{37}Cl)H$^+$, 10], 345 [M(^{37}Cl^{35}Cl)H$^+$, 35], 343 [M(^{35}Cl^{35}Cl)H$^+$, 40], 309 (15), 225 (100); HRMS (CI$^+$) calc'd. for $C_{18}H_{13}{}^{35}Cl_2N_2O$ (MH^+) 343.0405, found 343.0409, Δ 1.1 ppm.

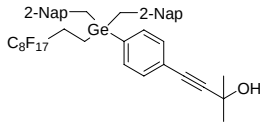
(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)bis(naphthalen-2-ylmethyl)(4-trimethylsilylethynylphenyl)germane 6



Using conditions adapted from those of Menchi,[21] $Pd(OAc)_2$ (1.0 mg, 0.0045 mmol) and PPh_3 (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). *Trimethylsilylacetylene* (4.9 mg, 0.05 mmol, 7 μL), CuI (2 mg, 0.01 mmol) and ^{n}BuNH$_2$ (5 mL) were then added to the reaction mixture and the resulting reaction mixture was stirred at 55 ^{o}C for 16 h. The reaction mixture was then diluted with Et_2O (20.0 mL), washed with water (3 × 10.0 mL), the organic phase

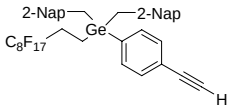
dried over $MgSO_4$ and evaporated *in vacuo*. Purification by FC (hexane/EtOAc, 95/5) gave *alkynylgermane* **6** as a pale yellow oil (12.6 mg, 52%). ^{1}H NMR (400 MHz; C_6D_6): δ 0.27 (s, 9H, Si(CH_3)$_3$), 1.02 (m, 2H, CH_2CH_2Ge), 1.71 (m, 2H, CH_2CH_2Ge), 2.36 (s, 4H, 2 × GeCH_2Nap), 6.86 (dd, *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, *J* = 6.8, 1.4 Hz, 1H, ArH), 7.25 (dd, *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); ^{13}C NMR (100 MHz; C_6D_6) δ 0.07 (3s), 2.1 (t), 22.5 (2t), 26.6 (t, J_{CF} 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); ^{19}F NMR (376 MHz; C_6D_6): 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, $(CF_2)_6CF_2CF_3$], -79.9 [t, *J* = 9.8 Hz, 3F, $(CF_2)_6CF_2CF_3$]; IR υ_{max} (neat) 3052 (C-H), 2982 (C-H), 2360 (CC), 1592 (C=C), 1421 (C-F), 1260 (C-Si), 897, 740 cm^{-1}; *m/z* (FAB$^+$) (rel. intensity) 835 [(M-NapCH_2)$^+$, 60], 709 (55), 313 (80), 141 (100); HRMS (FAB$^+$) calc'd. for $C_{32}H_{26}F_{17}{}^{74}$GeSi [M-(Nap$CH_2$)$^+$] 835.0739, found 835.0734, Δ -0.6 ppm.

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-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 PPh_3 (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 ^{n}BuNH$_2$ (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 Et_2O (20.0 mL), washed with water (3 × 10.0 mL), the organic phase dried over $MgSO_4$ and evaporated *in vacuo*. Purification by FC (hexane/EtOAc, 85/15) gave *alkynylgermane* **8** as a pale yellow oil (83.6 mg , 68%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.15 (m, 2H, CH_2CH_2Ge), 1.65 (s, 6H, C$C(CH_3)_2$OH), 1.81 (m, 2H, CH_2CH_2Ge), 2.07 (brs, 1H, O*H*), 2.72 (s, 4H, 2 × GeCH_2Nap), 7.04 (dd, *J* = 8.4, 1.7 Hz, 2H, ArH), 7.27 (d, *J* = 7.8 Hz, 2H, ArH), 7.34 (s, 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 1.8 (t), 22.4 (2t), 26.2 (t, J_{CF} 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); ^{19}F NMR (376 MHz; $CDCl_3$): 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, $(CF_2)_6CF_2CF_3$], -79.8 [t, *J* = 9.8 Hz, 3F, $(CF_2)_6CF_2CF_3$]; IR υ_{max} (neat) 3320 (OH, br), 3054 (C-H), 2985 (C-H), 2354 (CC), 1595 (C=C), 1421 (C-F), 895, 740 cm^{-1}; *m/z* (FAB$^+$) (rel. intensity) 821 [(M-NapCH_2)$^+$, 55], 551 (50), 279 (45), 141 (100); HRMS (FAB$^+$) calc'd. for $C_{32}H_{24}F_{17}O^{74}$Ge [M-(NapCH_2)$^+$] 821.0762, found 821.0762, Δ -0.2 ppm.

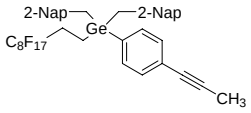
(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)bis(naphthalen-2-ylmethyl)(4-phenylethynyl)germane 7



Method A: Using conditions adapted from those of Vasella,[22] a mixture of K_2CO_3 and KF (1:1 w/w, 100 mg) was added to a solution of *(4-trimethylsilylethynylphenyl)germane* **6** (115.6 mg, 0.118 mmol) in MeOH-THF (1:1 v/v, 10 mL) and the resulting reaction mixture stirred at 80 ^oC for 8 h. The resulting reaction mixture was the diluted with Et_2O (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* **7** as pale yellow oil (69.7 mg, 67%). ^1H NMR (400 MHz; $CDCl_3$): δ 1.14 (m, 2H, CH_2CH_2Ge), 1.81 (m, 2H, CH_2CH_2Ge), 2.72 (s, 4H, 2 × $GeCH_2Nap$), 3.15 (s, 1H, C_6H_4CCH), 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 (s), 110.9 (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), 132.0 (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, $(CF_2)_6CF_2CF_3$], -79.8 [t, *J* = 9.9 Hz, 3F, $(CF_2)_6CF_2CF_3$]; IR υ_{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 [$(M\text{-}NapCH_2)^+$, 40], 549 (15), 279 (45), 141 (100); HRMS (FAB^+) calc'd. for $C_{29}H_{18}F_{17}{}^{74}Ge$ [$M\text{-}(NapCH_2)^+$] 763.0343, found 763.0350, Δ 0.9 ppm.

Method B: Using conditions adapted from those of Walton,[23] powdered KOH (50 mg, 0.893 mmol) was added to a solution of *4-[(3-methyl-3-hydroxybutynyl)phenyl]germane* **8** (80.0 mg, 0.083 mmol) in THF (10 mL). The reaction mixture was then stirred at 80 ^oC for 1 h. The resulting reaction mixture was diluted with Et_2O (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, 90/10) gave *(4-phenylethynyl)germane* **7** as a pale yellow oil (73.8 mg, 98%). Analytical data as above.

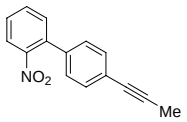
(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)bis(naphthalen-2-ylmethyl)(4-propynylphenyl)germane 10



Using conditions adapted from those of Feldman,[24] 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* **7** (73.8 mg, 0.082 mmol) and DMPU (10 μL, 0.083 mmol) in THF (10 mL) at -40 ^oC. 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_2O (10.0 mL) and a solution of 1.0 M NH_4Cl was added to the reaction mixture until no effervescence occurred. Following extraction with (2 × 20.0 mL) of Et_2O, 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* **10** as pale yellow oil (65.4 mg,

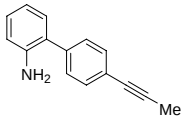
87%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.21 (m, 2H, CH_2CH_2Ge), 1.80 (m, 2H, CH_2CH_2Ge), 2.08 (s, 3H, $CCCH_3$), 2.71 (s, 4H, 2 × $GeCH_2Nap$), 7.03 (dd, *J* = 8.4, 1.6 Hz, 2H, ArH), 7.23 (d, *J* = 8.2 Hz, 2H, ArH), 7.33 (s, 2H, ArH), 7.35-7.42 (m, 6H, ArH), 7.60 (d, *J* = 7.8 Hz, 2H, ArH), 7.66 (d, *J* = 8.4 Hz, 2H, ArH), 7.76 (d, *J* = 7.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 2.1 (t), 3.2 (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), 125.3 (2d), 126.1 (2d), 126.5 (2d), 127.4 (2d), 127.4 (2d), 128.2 (2d), 128.3 (2d), 131.8 (2d), 132.0 (2s), 134.6 (2d), 134.8 (2s), 136.9 (2s), 137.7 (s); ^{19}F NMR (376 MHz; $CDCl_3$): δ -126.1 (s, 2F), -123.5 (s, 2F), -122.7 (s, 2F), -121.9 (m, 6F), -116.3 [quintet, *J* = 15.2 Hz, 2F, $(CF_2)_6CF_2CF_3$], -80.7 [t, *J* = 9.7 Hz, 3F, $(CF_2)_6CF_2CF_3$]; IR υ_{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 [$(M\text{-}NapCH_2)^+$, 30], 549 (15), 279 (55), 141 (100); HRMS (FAB^+) calc'd. for $C_{30}H_{20}F_{17}{}^{74}Ge$ [$M\text{-}(NapCH_2)^+$] 777.0500, found 777.0498, Δ -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), $P(2\text{-}Tol)_3$ (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; $CDCl_3$): δ 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; $CDCl_3$) δ 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 υ_{max} (neat) 3054 (C-H), 2987 (C-H), 2360 (CC), 1588 (C=C), 1537 (N=O), 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, Δ –2.4 ppm.

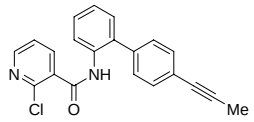
4-Propynyl-2'-aminobiphenyl 13[19]



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_2CO_3 was added and the reaction mixture was partitioned between Et_2O (40.0 mL) and water (10.0 mL). The phases were separated, the aqueous phase extracted with CH_2Cl_2 (2 × 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; $CDCl_3$): δ 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; $CDCl_3$) δ 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 υ_{max} (neat) 3475 (N-H), 3384 (N-H), 3052 (C-H), 2984 (C-H), 2359 (CC), 1888 (comb),

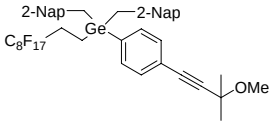
1616 (C=C), 1472, 817, 738, 704 cm^{-1}; *m/z* (EI^+) (rel. intensity) 207 (M^+, 100), 167 (40), 149 (85), 57 (65); HRMS (EI^+) calc'd. for $C_{15}H_{13}N$ (M^+) 207.1048, found 207.1050, Δ -1.0 ppm.

2-Chloro-*N*-(4'-prop-1-ynylbiphenyl-2-yl)nicotinamide 17[19]



To a solution of *biphenylamine* **13** (4.5 mg, 0.022 mmol) in CH_2Cl_2 (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 K_2CO_3 was added and the reaction mixture was partitioned between Et_2O (40.0 mL) and water (10.0 mL). The phases were separated, the aqueous phase extracted with CH_2Cl_2 (2 × 10.0 mL) and the combined organic extracts were dried over $MgSO_4$. Purification by FC (hexane/EtOAc, 70/30) gave *biarylalkyne* **17** as a colourless oil (4.4 mg, 59%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.07 (s, 3H, CH_3), 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 4.3 (q), 86.2 (s), 93.1 (s), 121.6 (d), 122.8 (d), 122.9 (s), 125.0 (d), 128.0 (d), 129.2 (2d), 130.1 (d), 131.0 (s), 132.2 (2d), 132.4 (s), 134.3 (s), 137.4 (s), 140.0 (d), 146.5 (s), 151.1 (d), 162.3 (s); IR υ_{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* (CI^+) (rel. intensity) 349 [M(^{37}Cl)H^+, 5], 347 [M(^{35}Cl)H^+, 15], 328 (40), 225 (100); HRMS (CI^+) calc'd. for $C_{21}H_{16}{}^{35}ClN_2O$ (MH^+) 347.0951, found 347.0952, Δ 1.3 ppm.

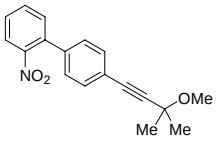
(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)bis(naphthalen-2-ylmethyl){4-[(3-methyl-3-methoxybutynyl)phenyl]}germane 9



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 resultingreaction mixture was then diluted with Et_2O (20.0 mL), washed with water (3 × 10.0 mL) and the organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by FC (hexane/EtOAc, 95/5) gave *alkynylgermane* **9** as pale yellow oil (28.3 mg, 87%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.16 (m, 2H, CH_2CH_2Ge), 1.59 (s, 6H, $CC(CH_3)_2OCH_3$), 1.83 (m, 2H, CH_2CH_2Ge), 2.73 (s, 4H, 2 × $GeCH_2Nap$), 3.47 (s, 3H, $CC(CH_3)_2OCH_3$), 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 1.8 (t), 22.4 (2t), 26.2 (t, J_{CF} 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); ^{19}F NMR (376 MHz; C_6D_6): 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, $(CF_2)_6CF_2CF_3$], -79.8 [t, *J* = 9.9 Hz, 3F, $(CF_2)_6CF_2CF_3$]; IR υ_{max} (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 [$(M\text{-}NapCH_2)^+$, 60], 551 (60), 537 (50),

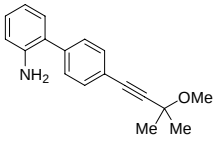
279 (60), 141 (100); HRMS (FAB$^+$) calc'd. for $C_{33}H_{26}F_{17}O^{74}Ge$ [M-(NapCH$_2$)$^+$] 835.0918, found 835.0913, Δ -0.7 ppm.

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



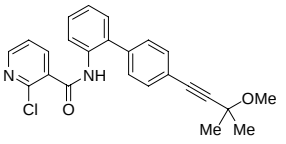
Using the *typical method*, the crude difluoroarylgermane from the photolysis of *arylgermane* **9** (48.9 mg, 0.067 mmol), TBAF (63.0 mg, 0.2 mmol), $PdCl_2(MeCN)_2$ (2 mg, 0.0077 mmol), P(2-Tol)$_3$ (3.5 mg, 0.012 mmol), *2-bromonitrobenzene* (27 mg, 0.134 mmol) and CuI (13.3 mg, 0.067 mmol) were employed. Purification by FC (hexane/EtOAc, 90/10) gave *nitrobiphenyl* **14** as a yellow oil (9.9 mg, 50%). ^{1}H 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); ^{13}C 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 (CC), 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_2CO_3 was added and the reaction mixture was partitioned between Et_2O (40.0 mL) and water (10.0 mL). The phases were separated, the aqueous phase extracted with CH_2Cl_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%). ^{1}H 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); ^{13}C 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), 2280 (CC), 1887 (comb), 1617 (C=C), 1472, 810, 743 cm^{-1}; *m/z* (EI$^+$) (rel. intensity) 265 (M$^+$, 85), 250 (100), 234 (50), 220 (40), 125 (30); HRMS (EI$^+$) calc'd. for $C_{18}H_{19}NO$ (M$^+$) 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_2Cl_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_2CO_3 was added to the reaction mixture and the reaction mixture was partitioned between Et_2O (40.0 mL) and water (10.0 mL). The phases were separated, the aqueous phase extracted with CH_2Cl_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%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.56 (s, 6H, 2 × 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); ^{13}C NMR (100 MHz; $CDCl_3$) δ 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), 151.3 (d), 162.5 (s); IR υ_{max} (neat) 3325 (N-H), 3053 (C-H), 2931 (C-H), 2341 (CC), 1654 (C=O), 1578 (C=C), 1070, 734 cm^{-1}; *m/z* (CI$^+$) (rel. intensity) 424 [M(^{37}Cl)NH_4^+, 1], 422 [M(^{35}Cl)NH_4^+, 3], 390 (40), 373 (100), 339 (20), 225 (50); HRMS (CI$^+$) calc'd. for $C_{24}H_{25}{}^{35}ClN_3O_2$ (MNH_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.

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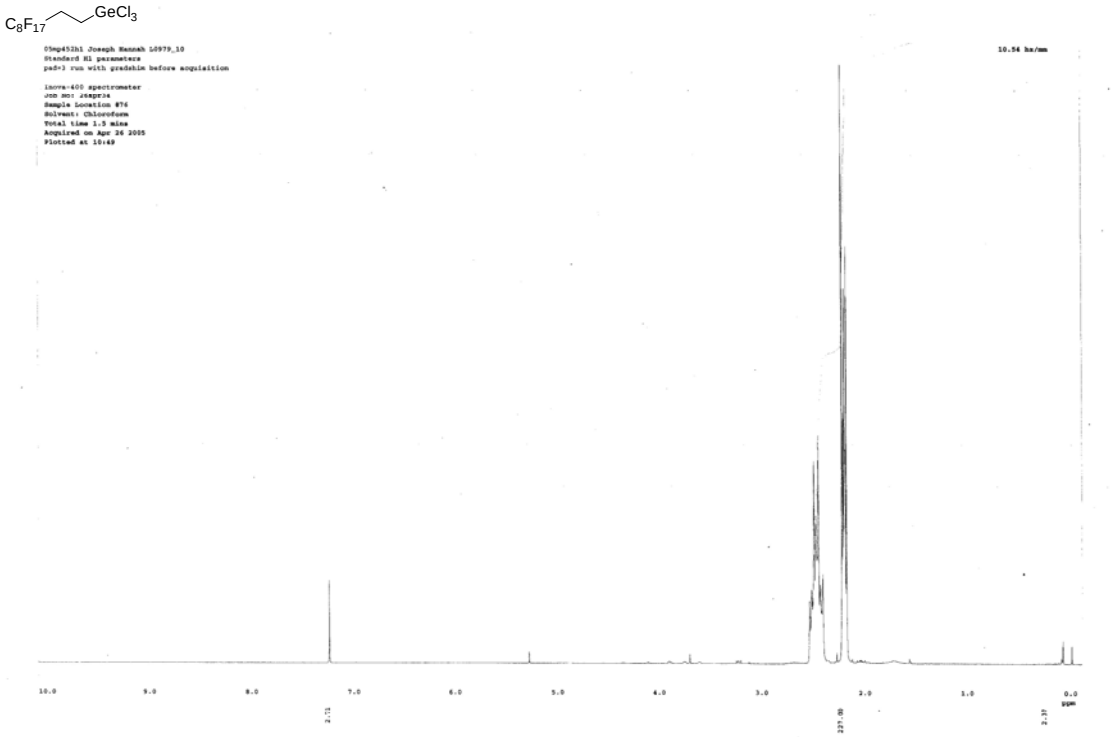
^{1}H NMR, 400 MHz, $CDCl_3$



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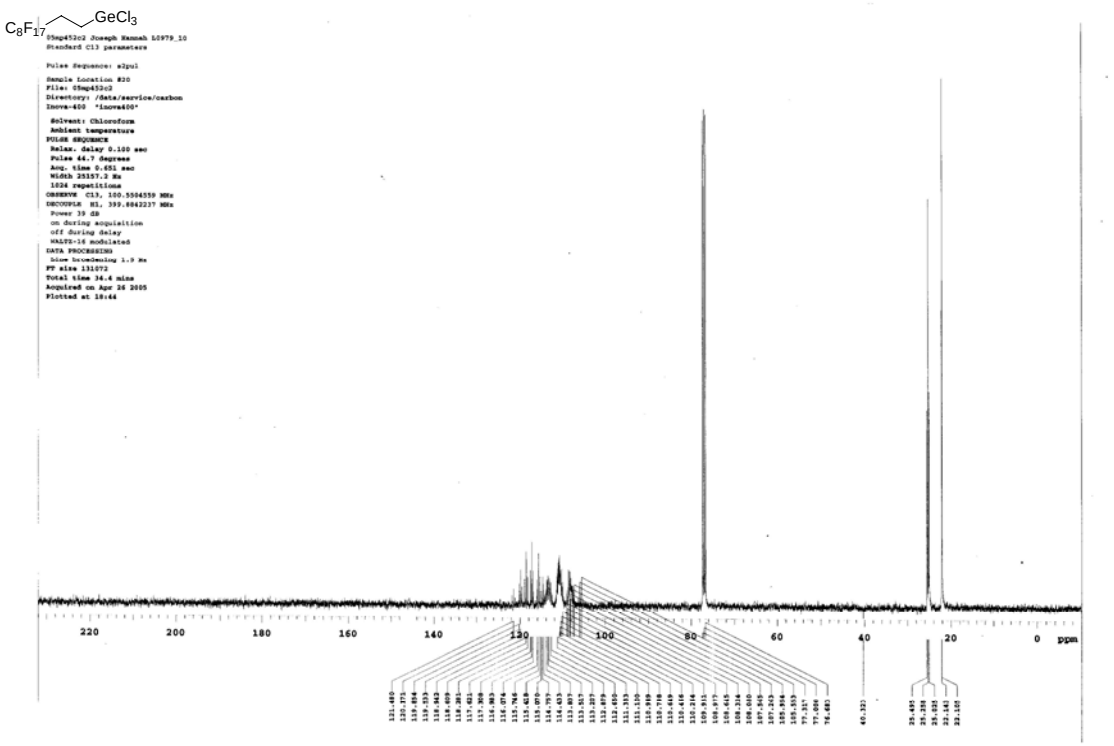

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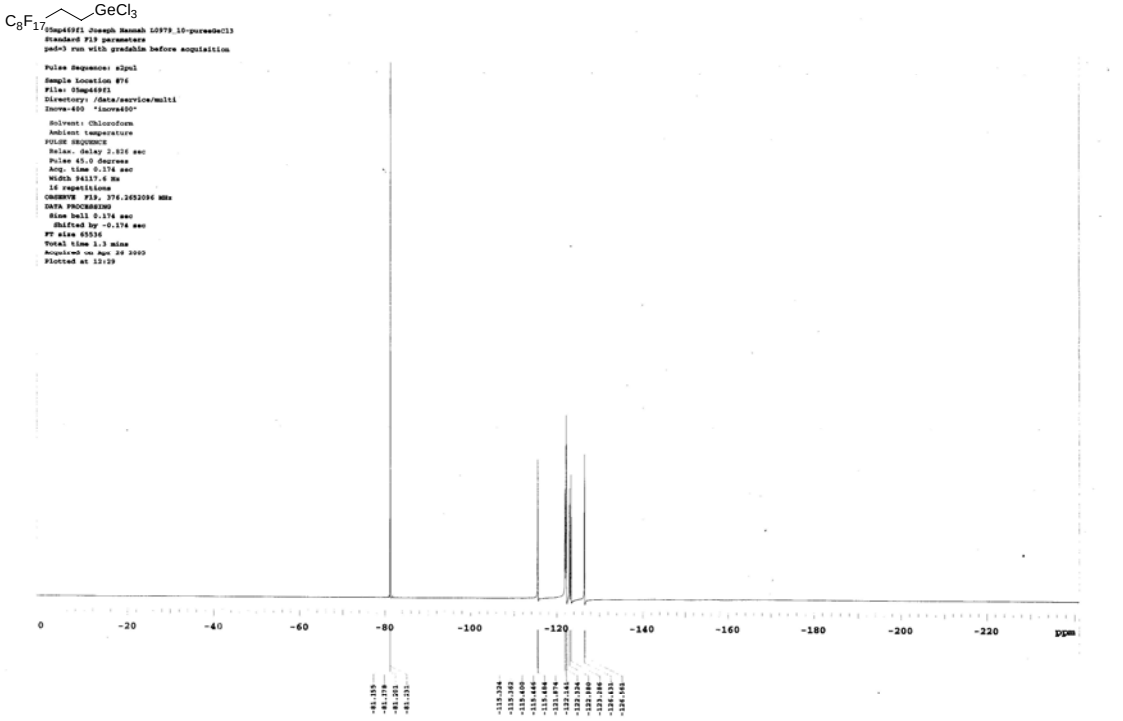

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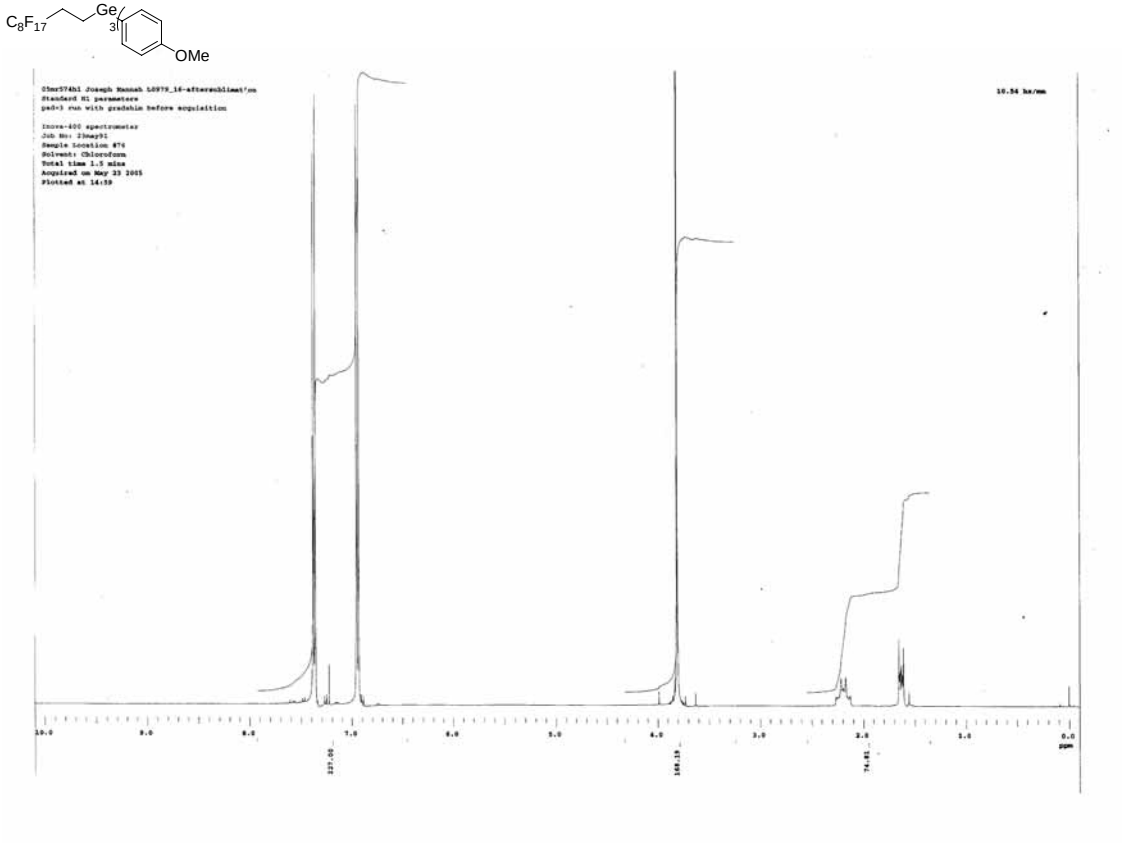

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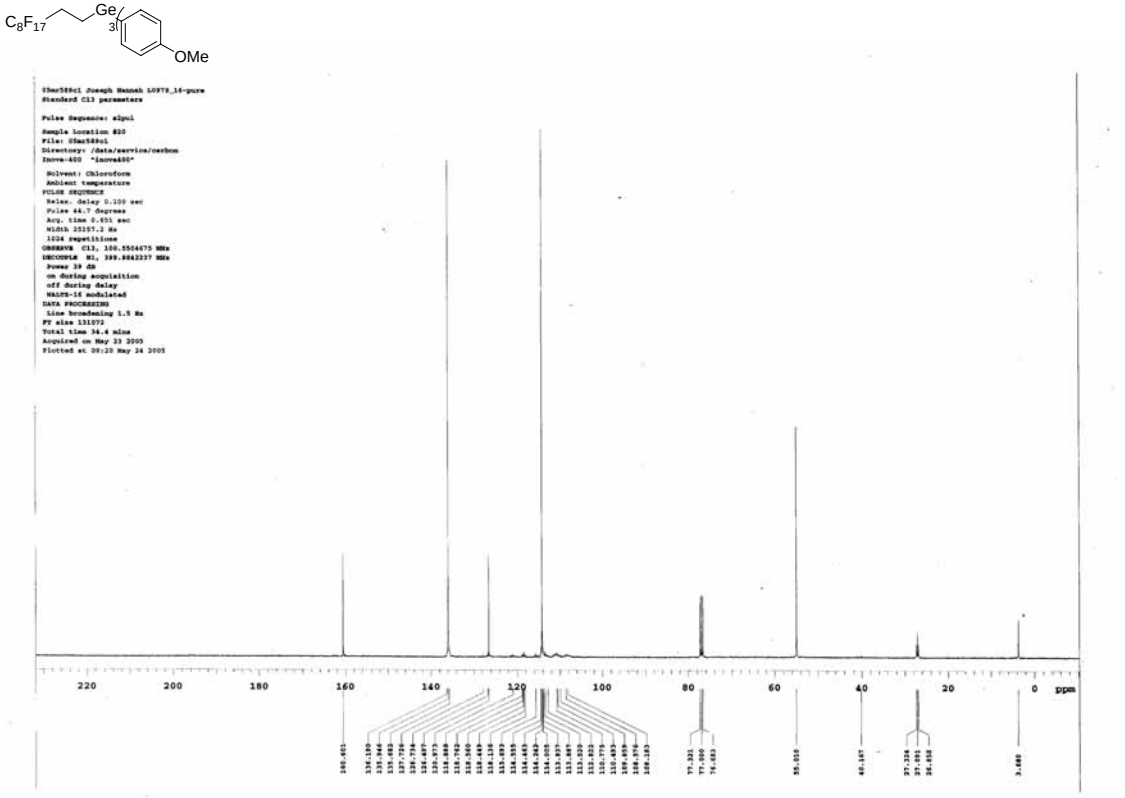

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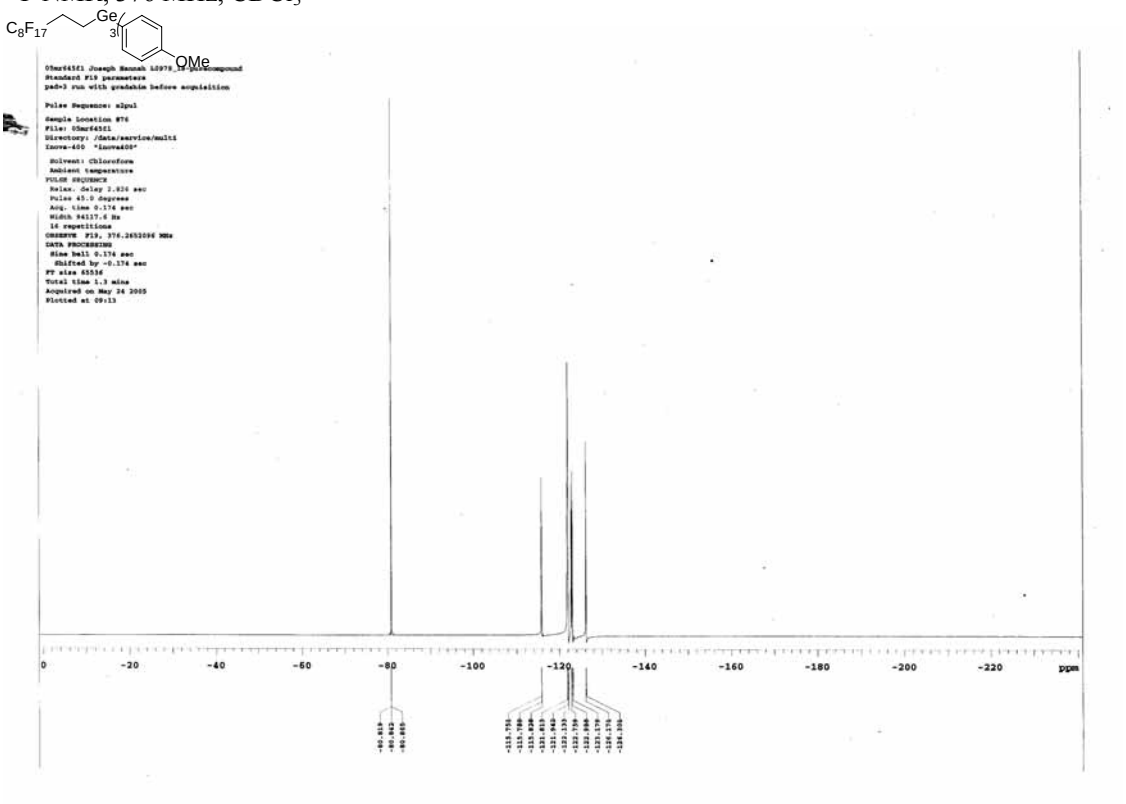

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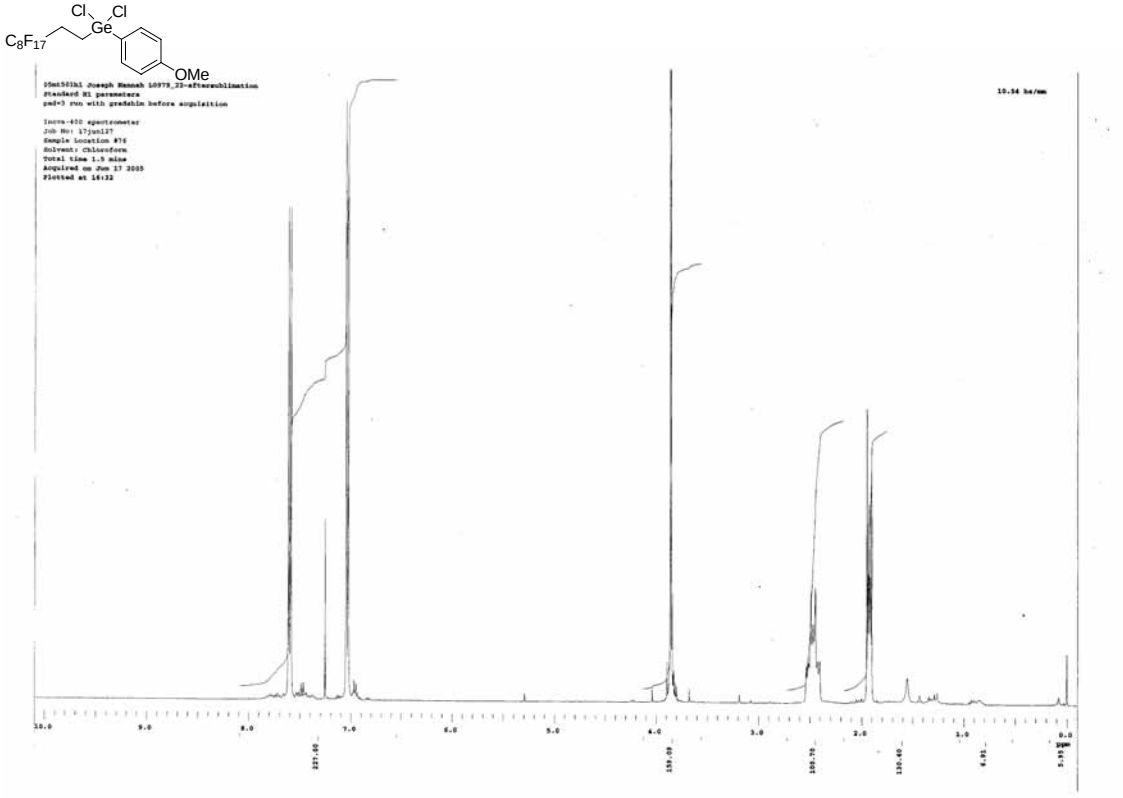

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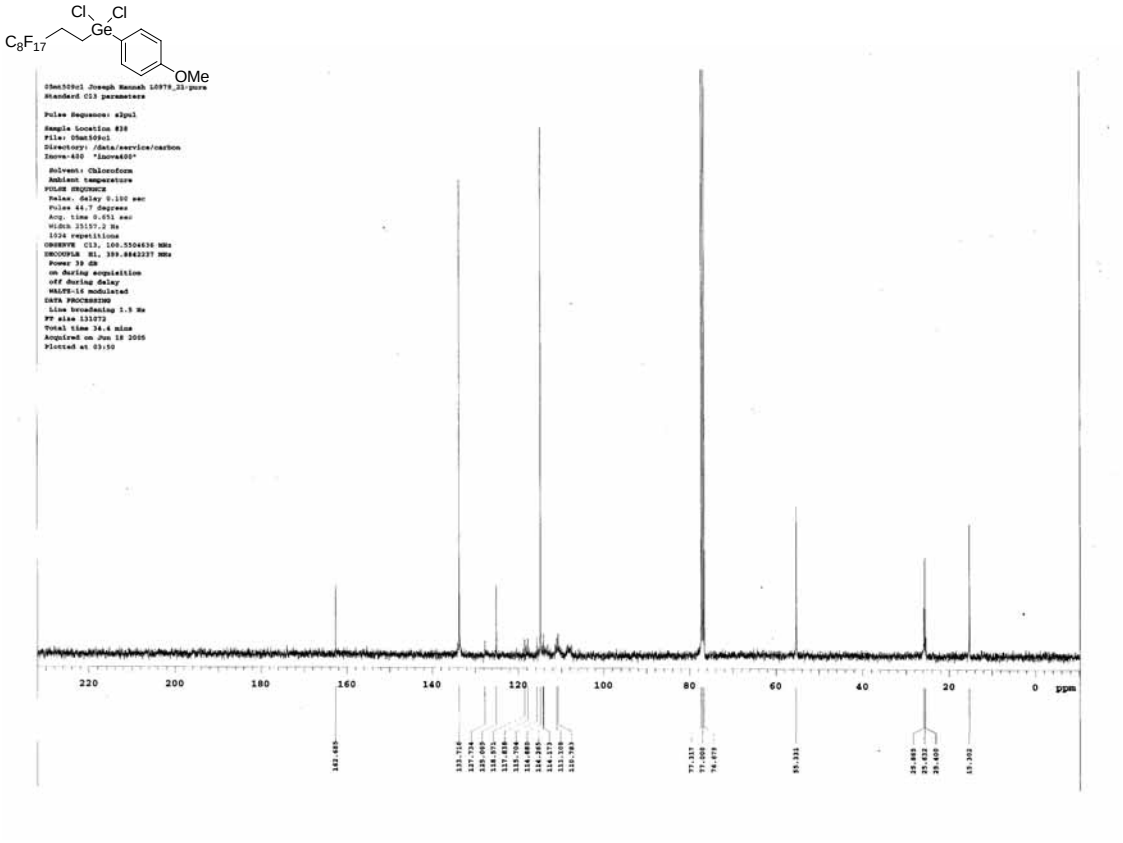

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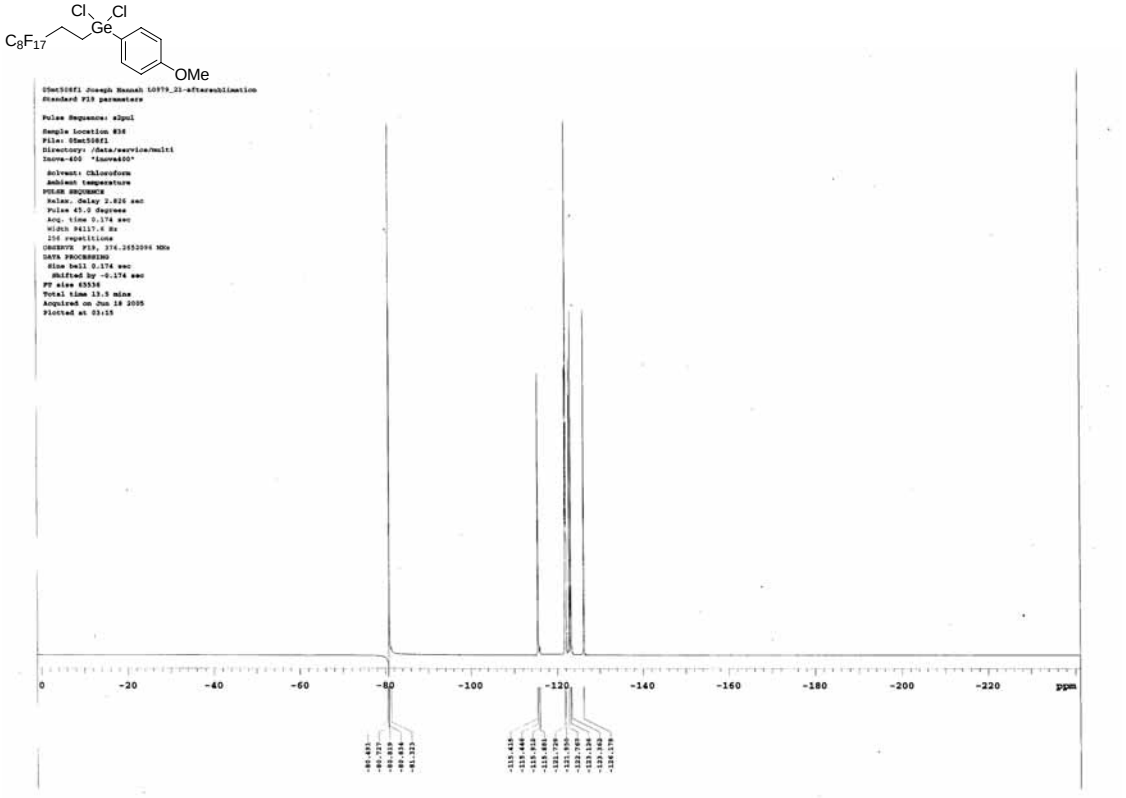

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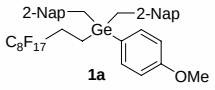

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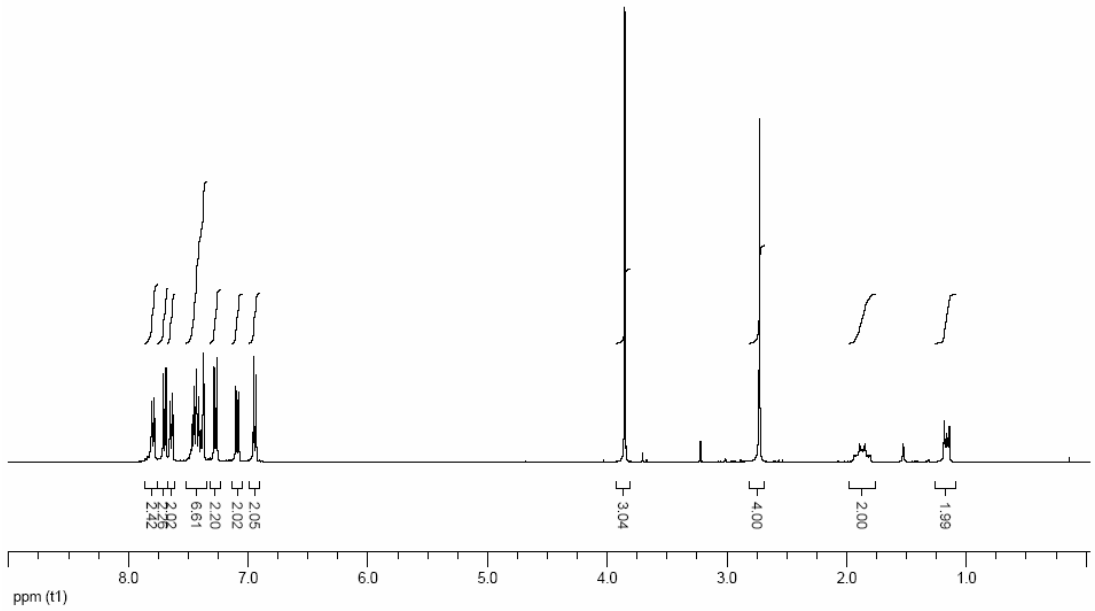

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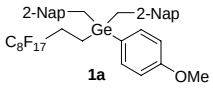
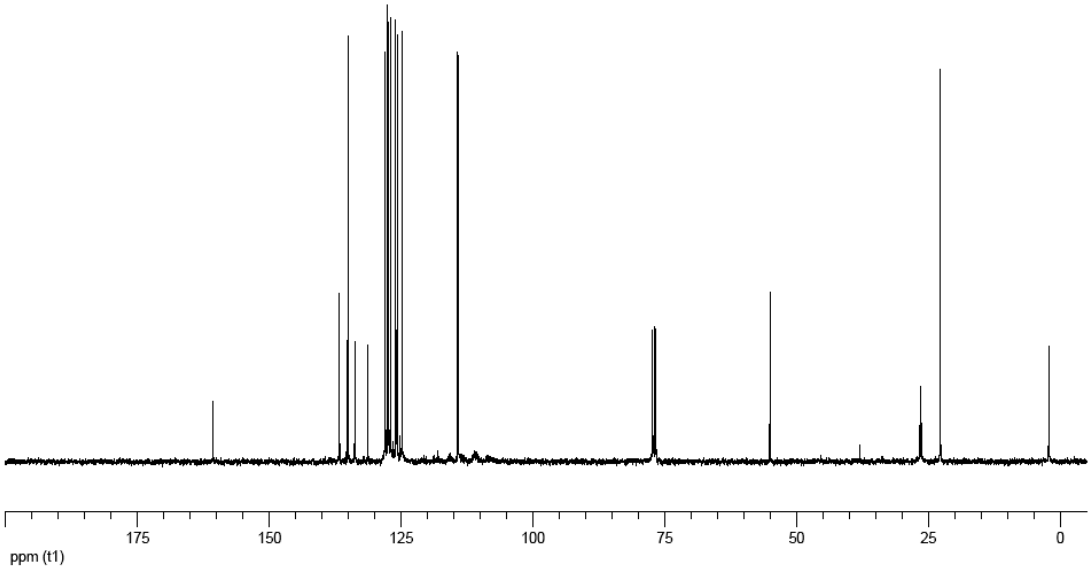
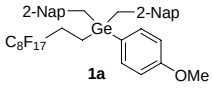
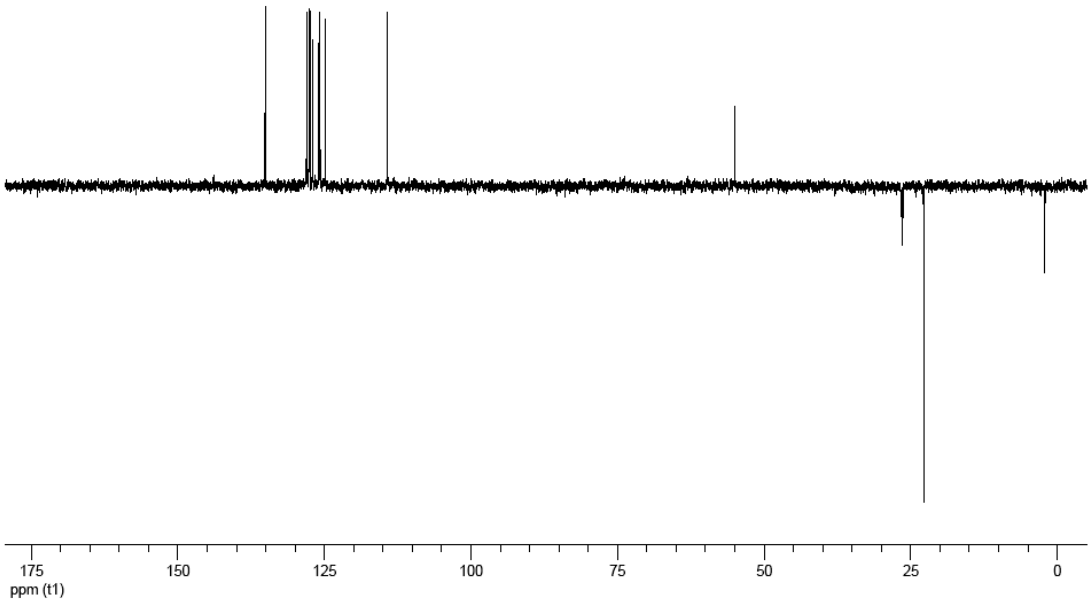




DEPT 135 100 MHz, $CDCl_3$





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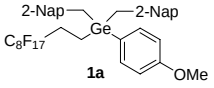

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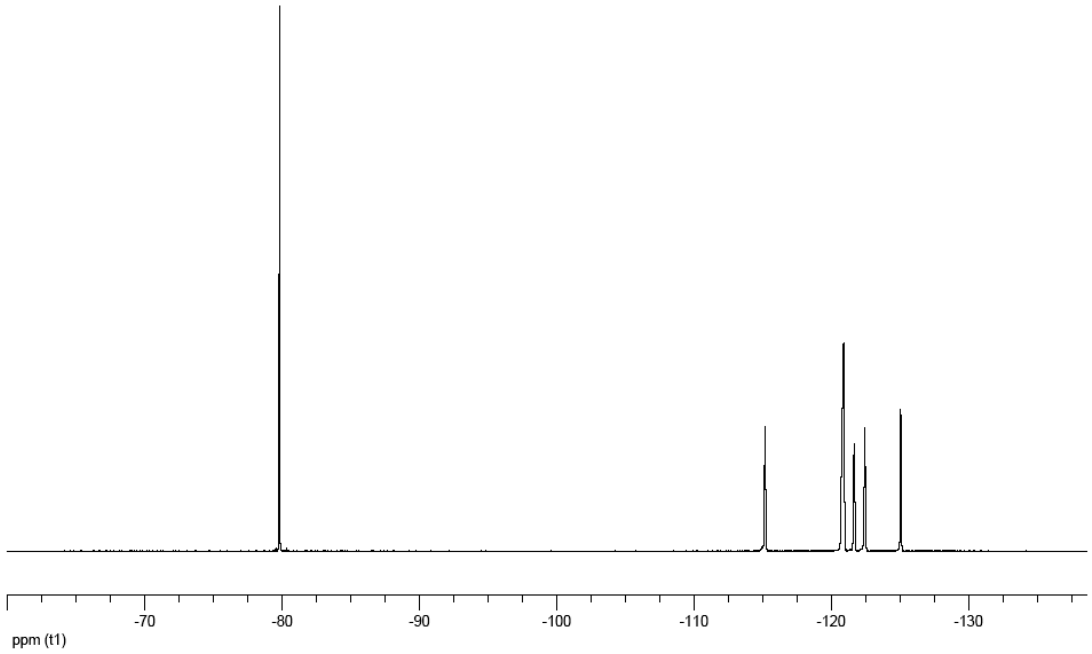

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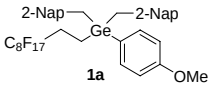

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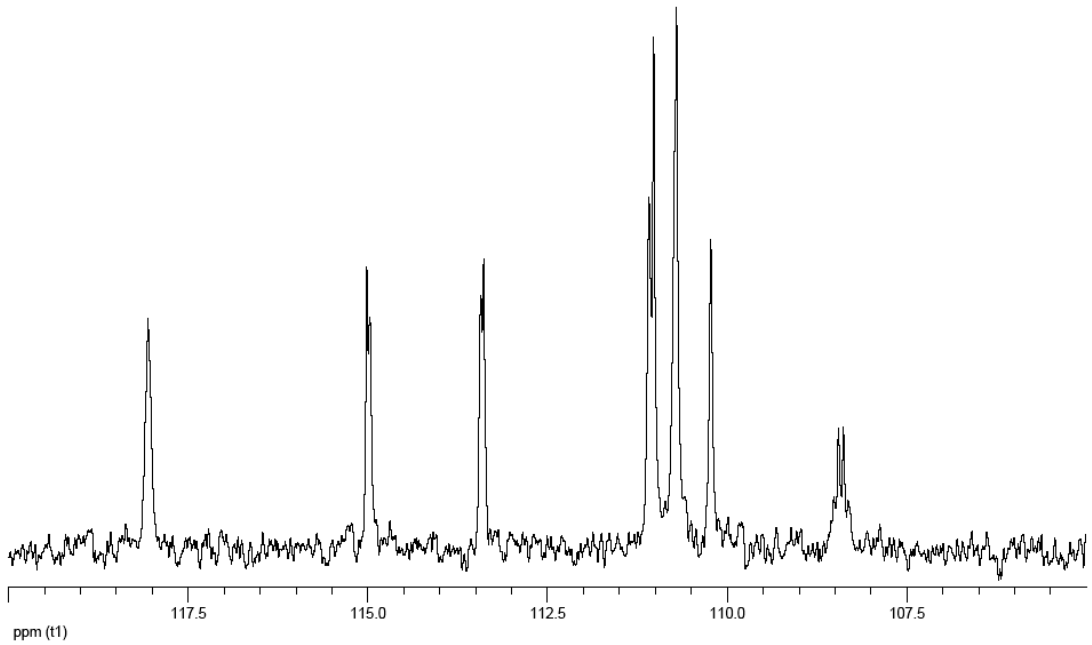

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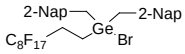

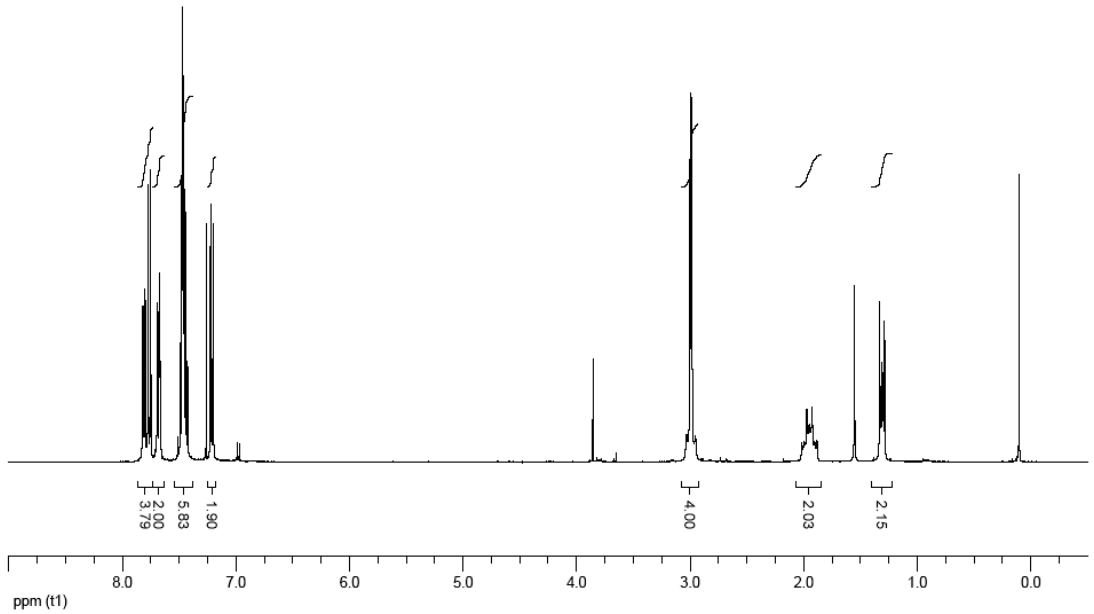

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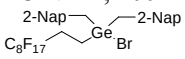
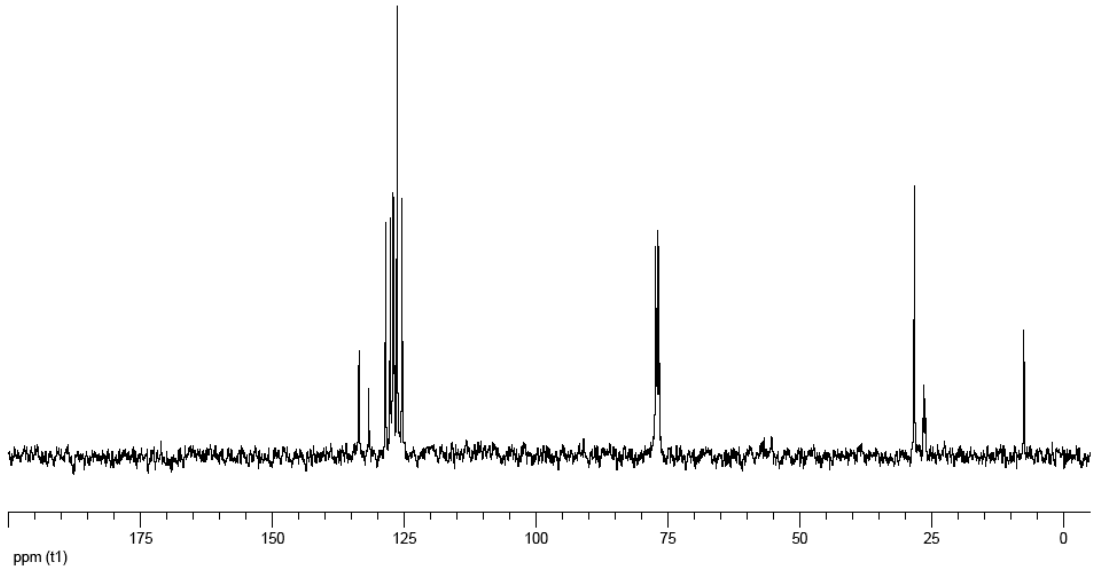
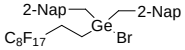
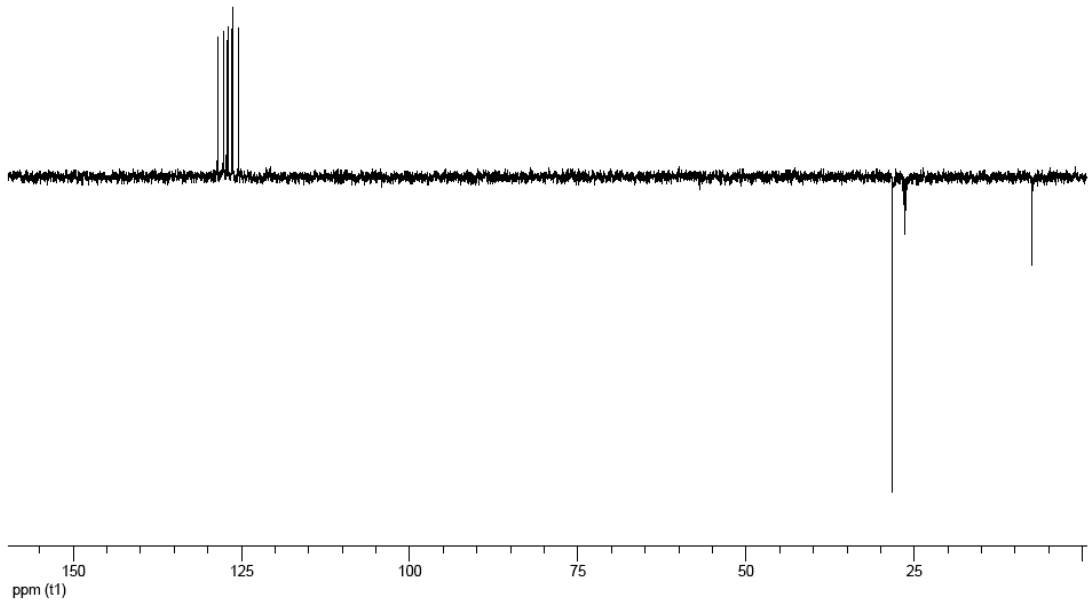




DEPT 135 100 MHz, $CDCl_3$





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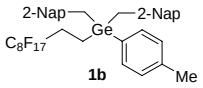

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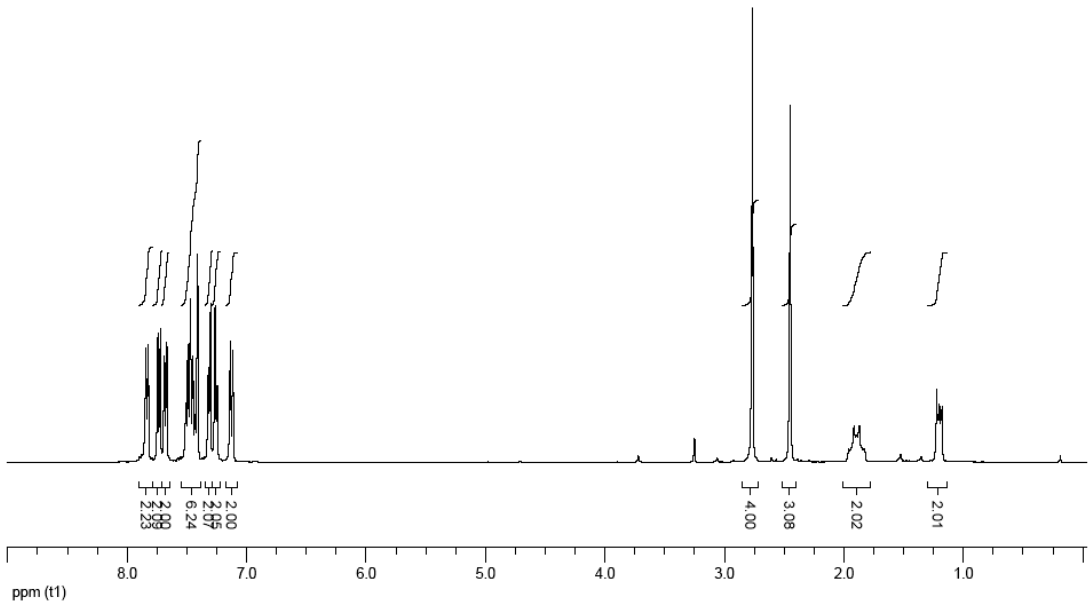

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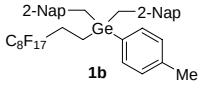

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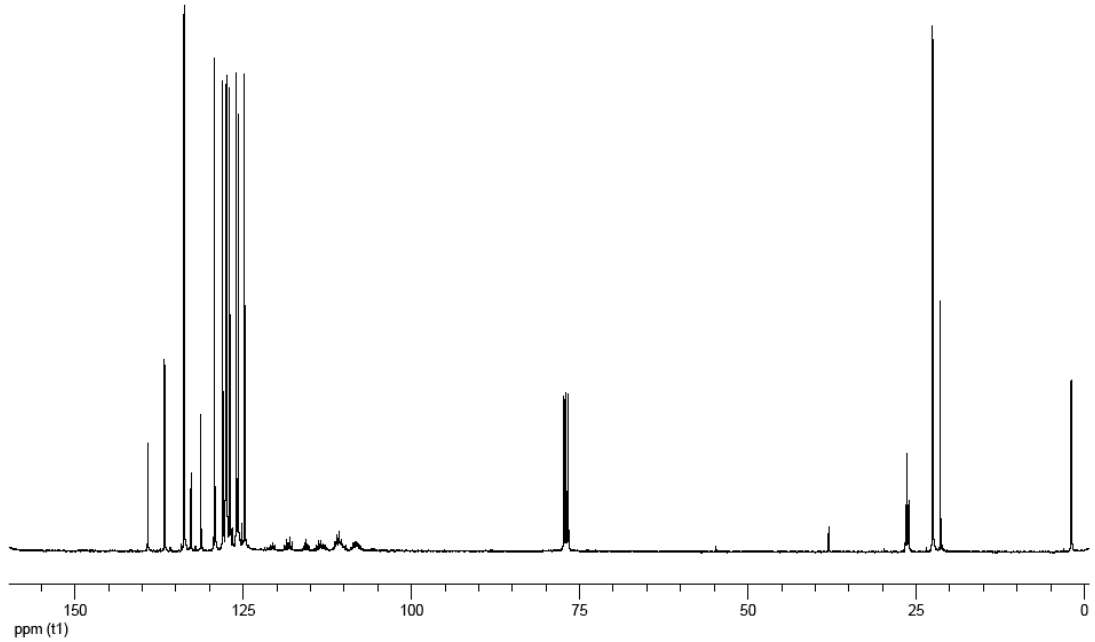

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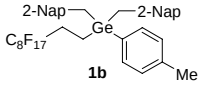

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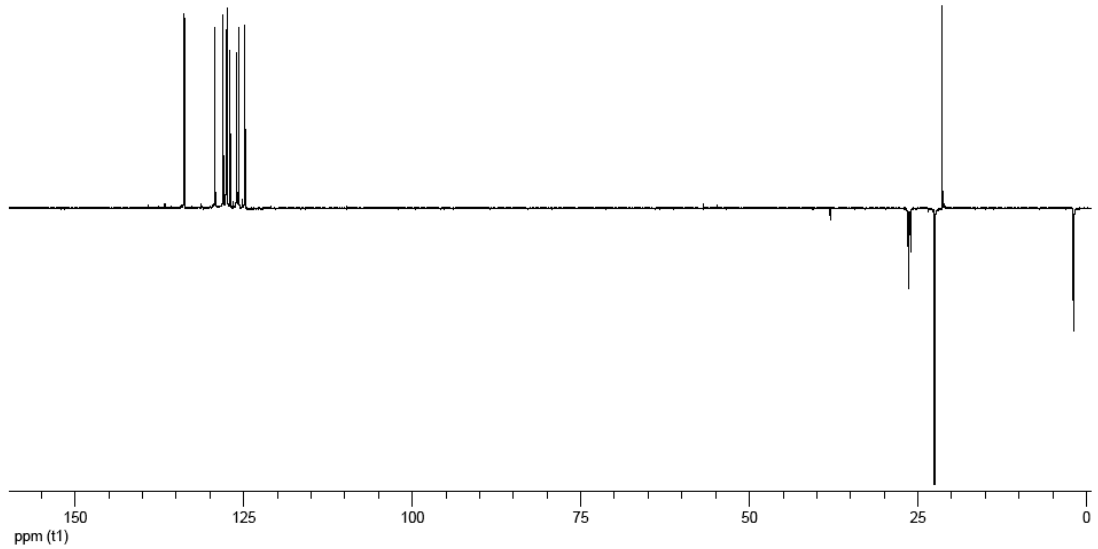

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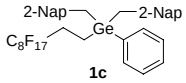

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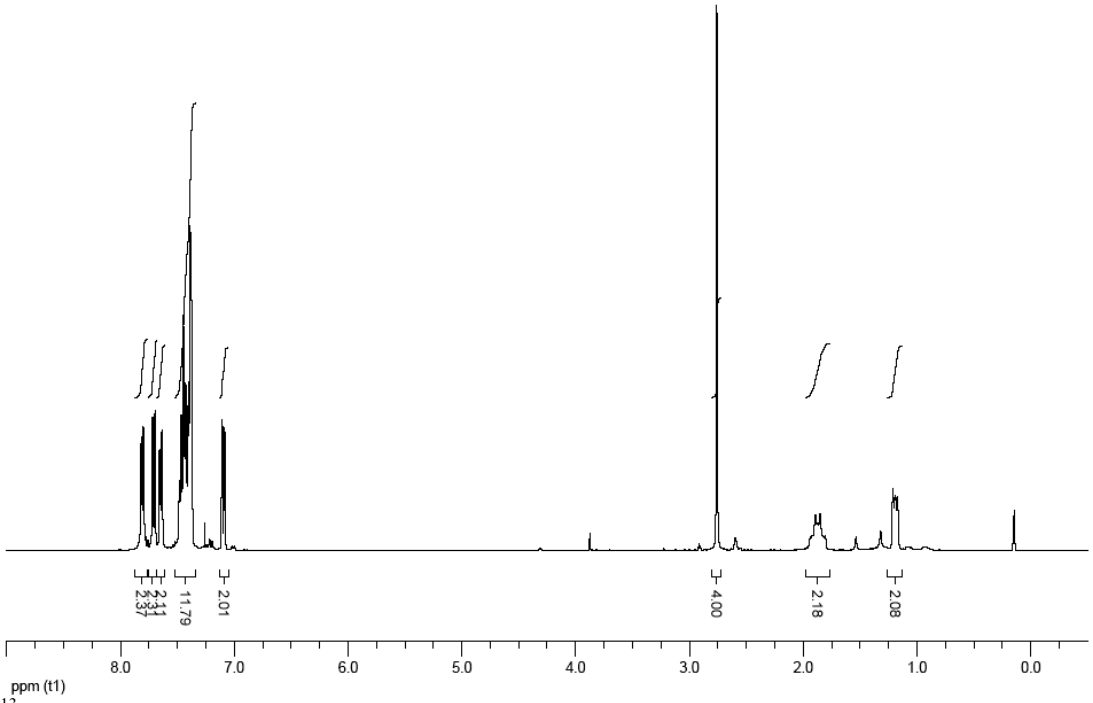

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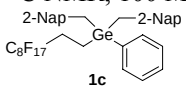

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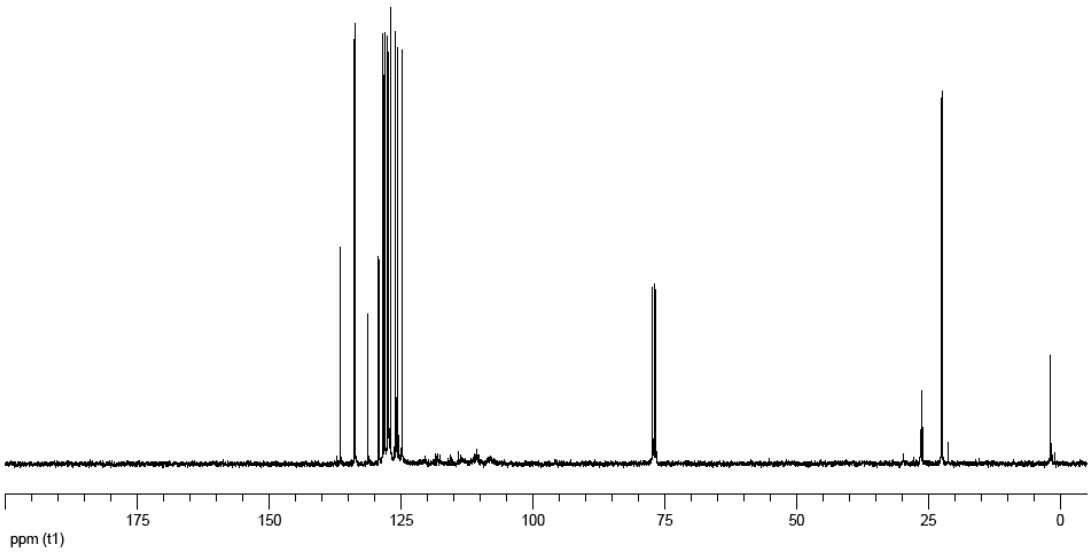

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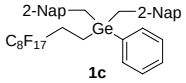

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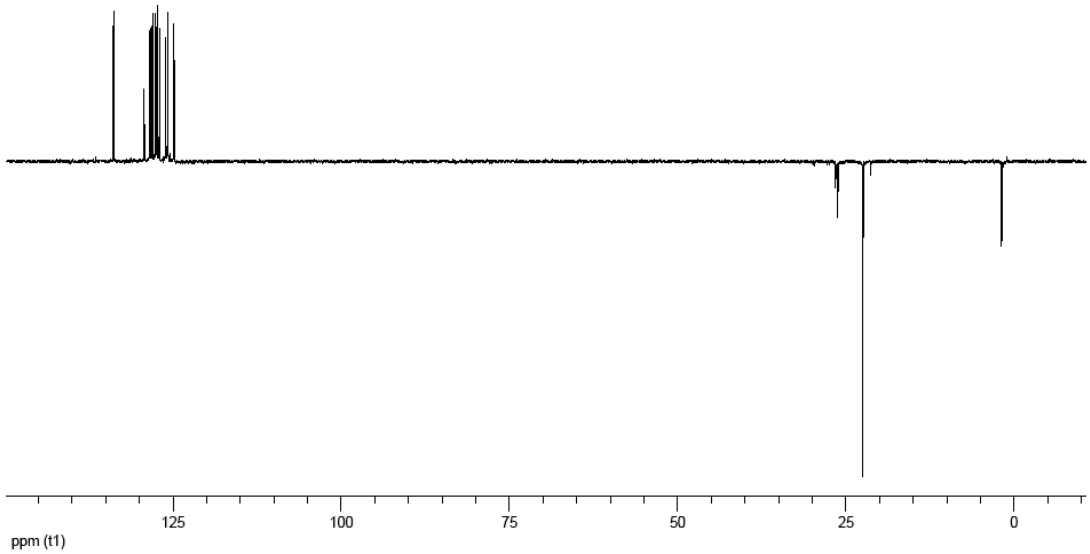
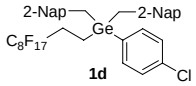


^1H NMR, 400 MHz, $CDCl_3$



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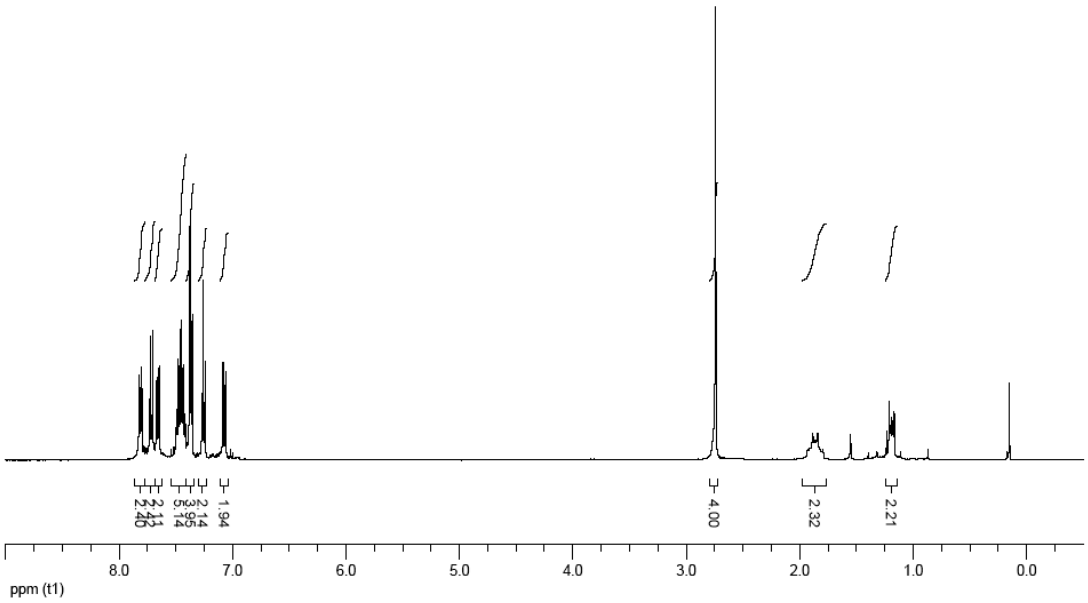
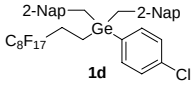


^{13}C NMR, 100 MHz, $CDCl_3$



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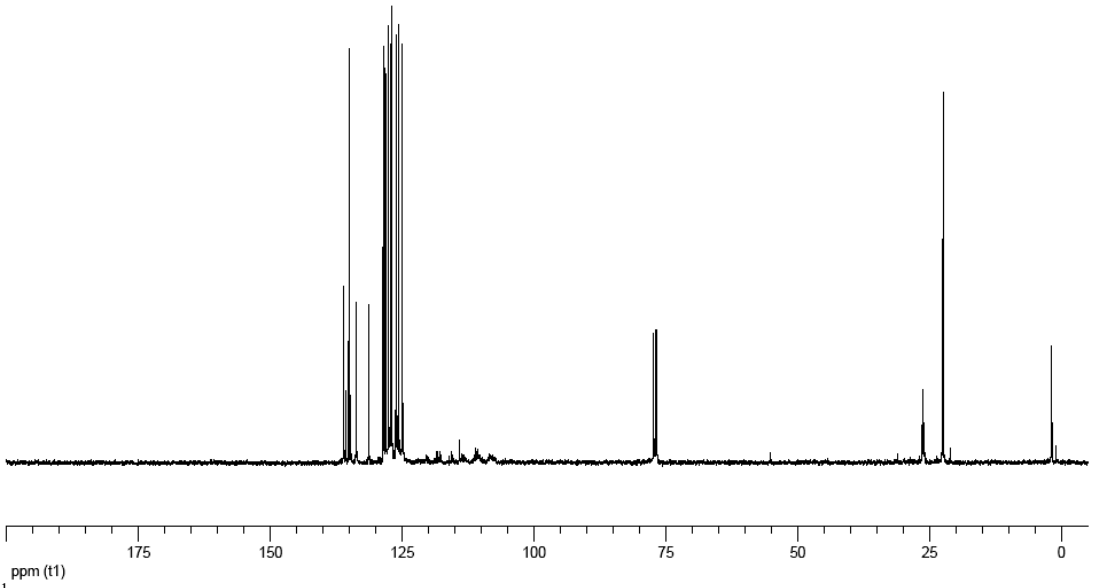
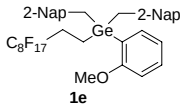


^{1}H NMR, 400 MHz, $CDCl_3$



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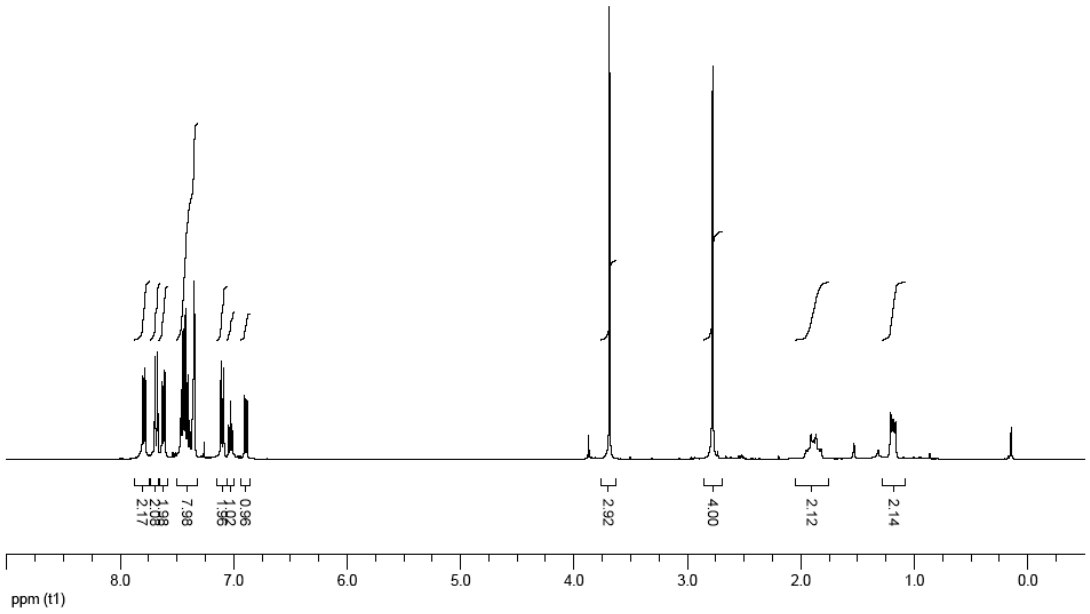
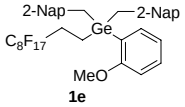


^{13}C NMR, 100 MHz, $CDCl_3$



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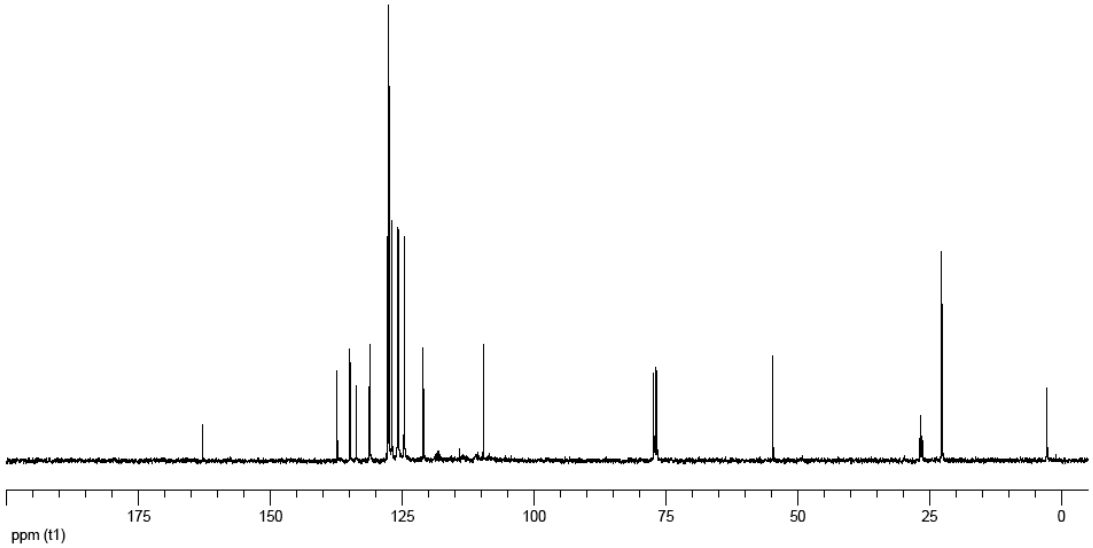
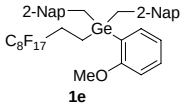


DEPT 135 100 MHz, $CDCl_3$



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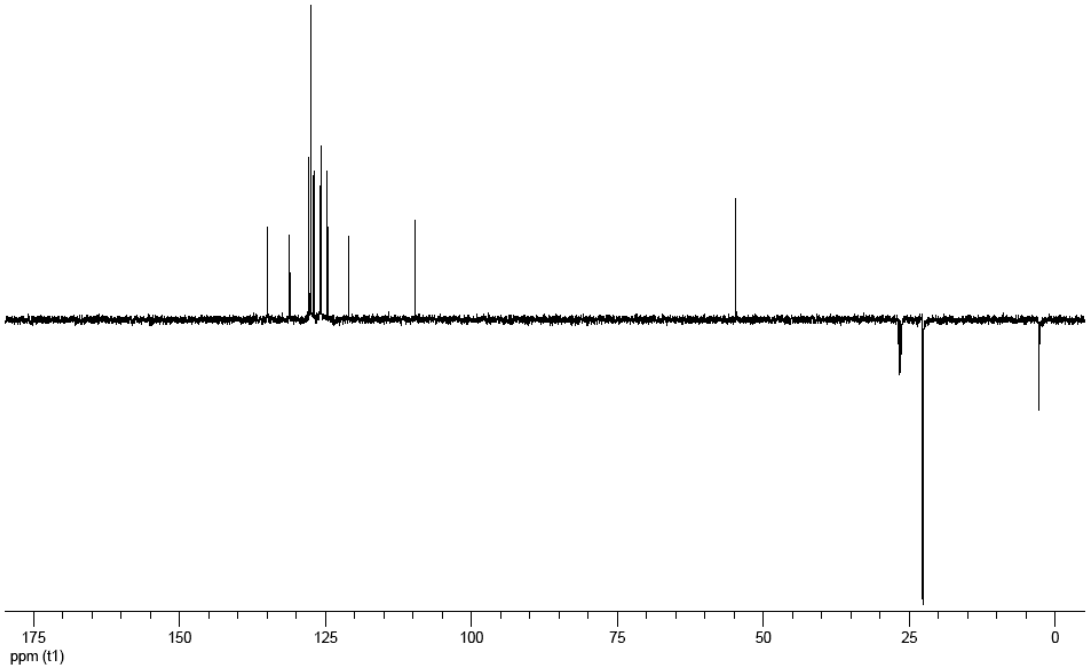
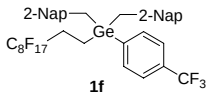


^{1}H NMR, 400 MHz, $CDCl_3$



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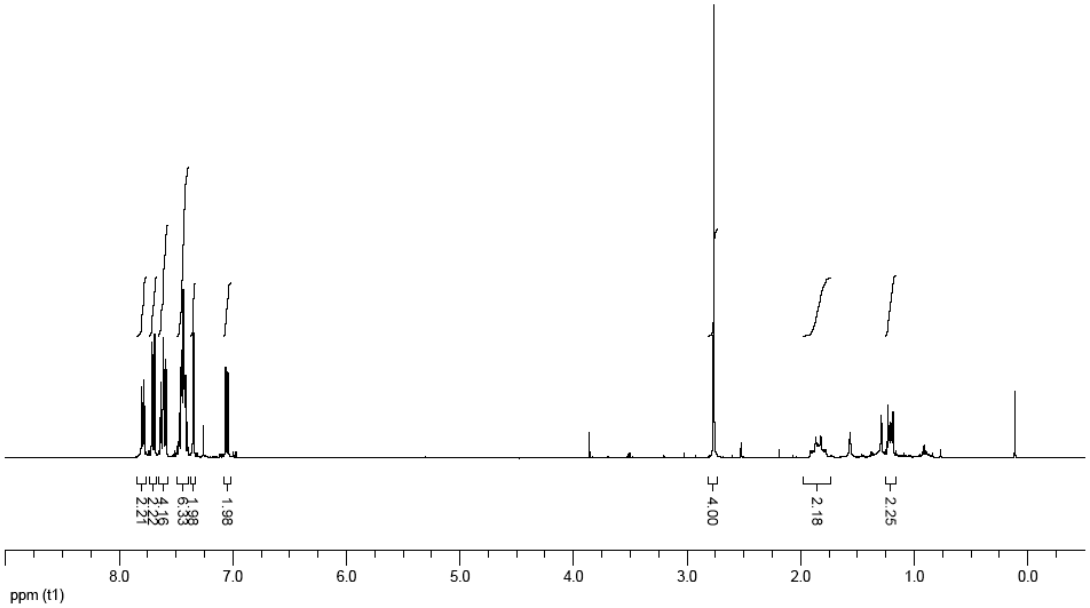
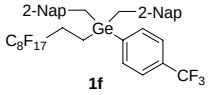


^{13}C NMR, 100 MHz, $CDCl_3$



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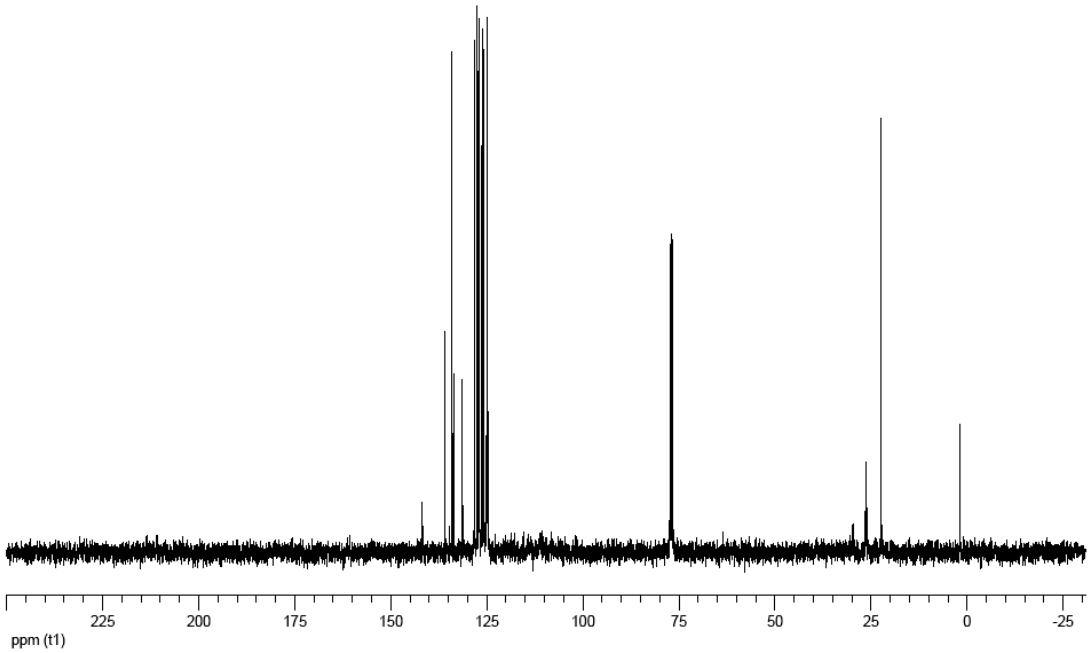
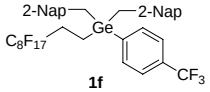


DEPT 135 100 MHz, $CDCl_3$



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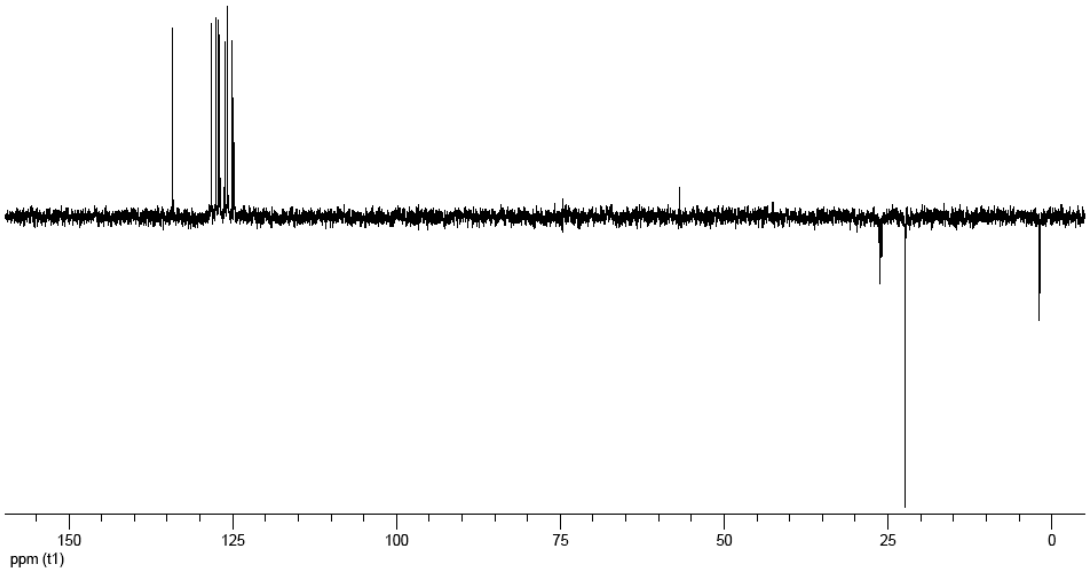
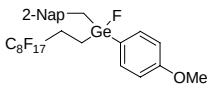
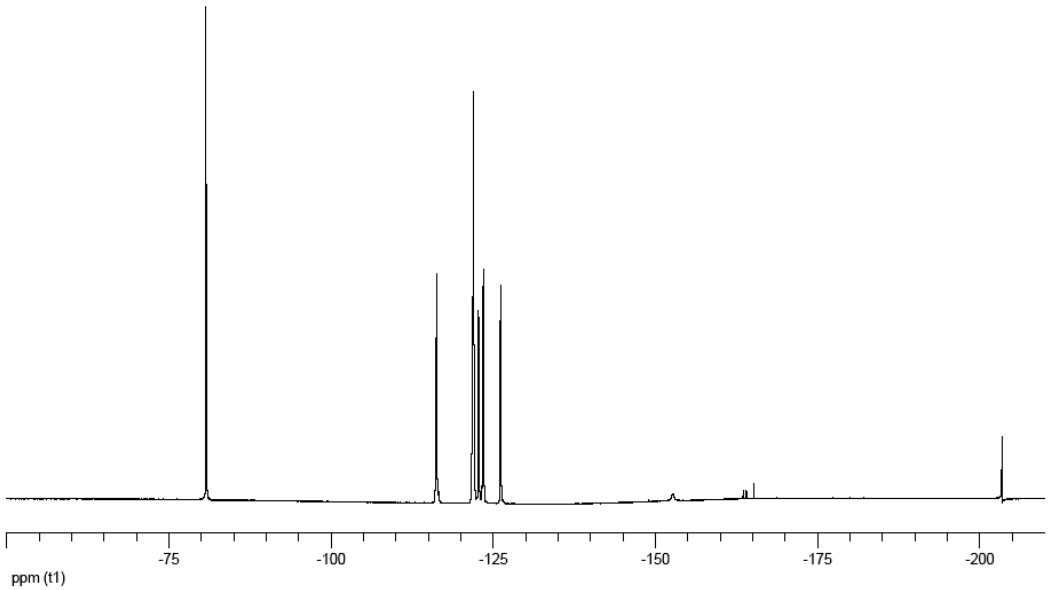
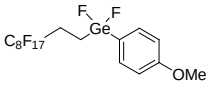


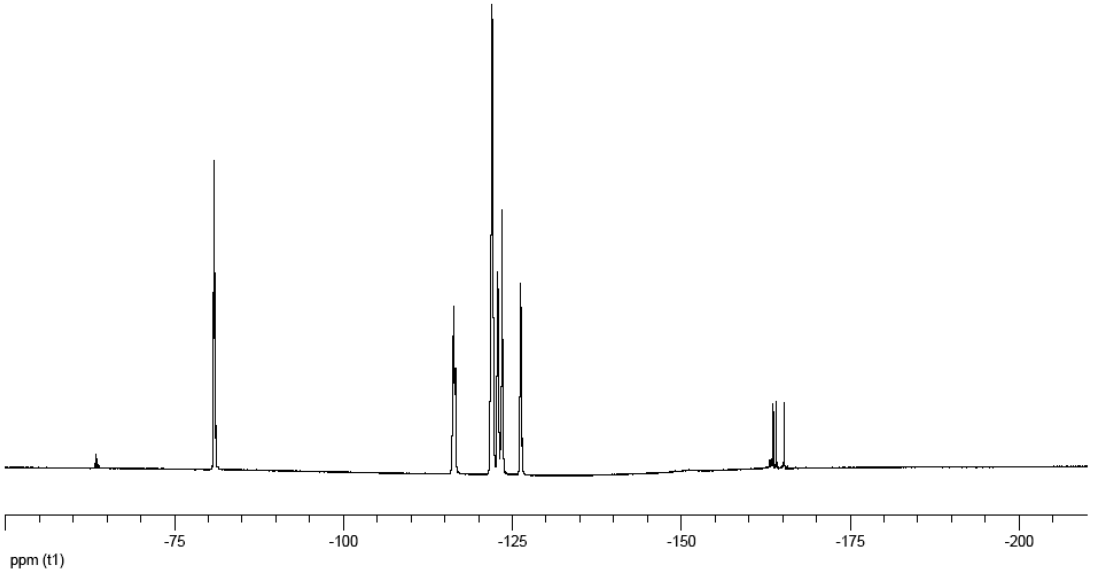
^{19}F NMR, 376 MHz, $CDCl_3$



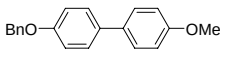


^{19}F NMR, 376 MHz, $CDCl_3$





^{1}H NMR, 400 MHz, $CDCl_3$



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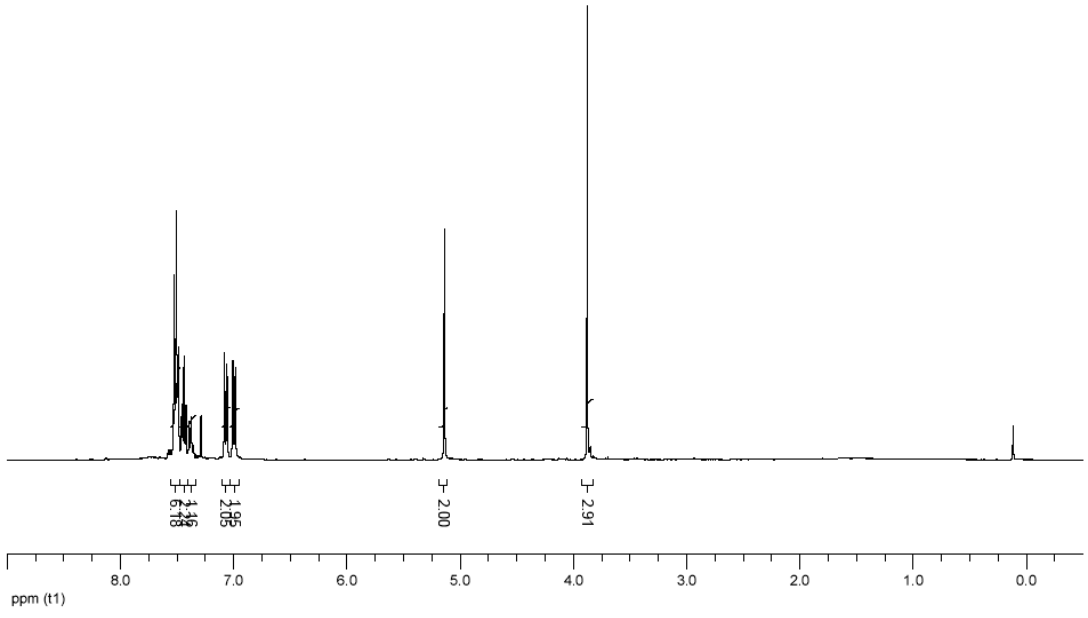
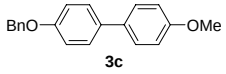


^{13}C NMR, 100 MHz, $CDCl_3$



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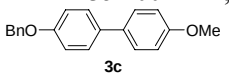
DEPT 135 100 MHz, $CDCl_3$



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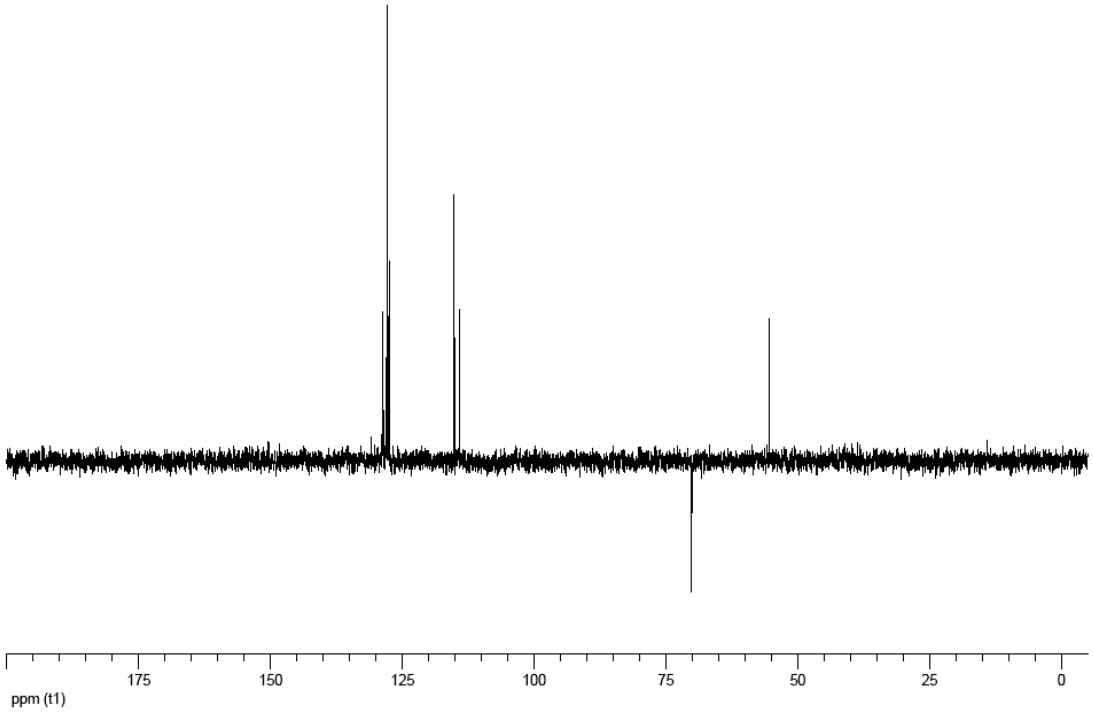
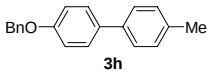


^{1}H NMR, 400 MHz, $CDCl_3$



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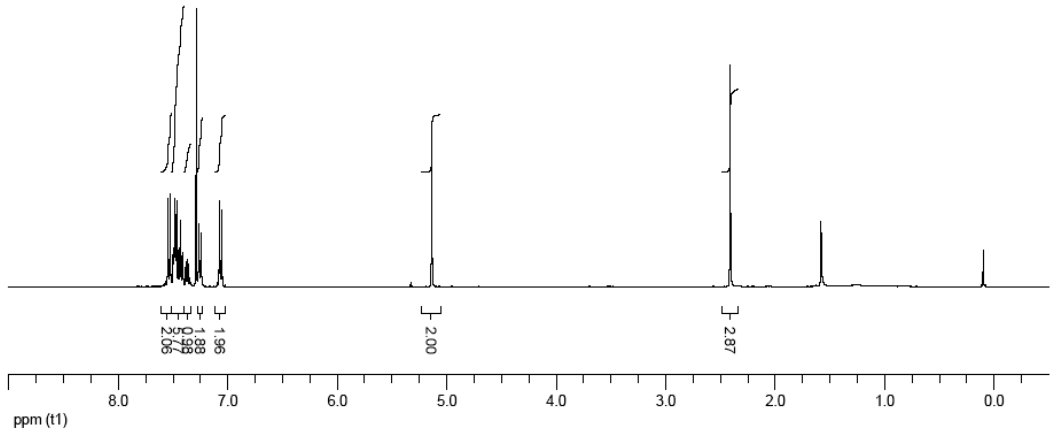
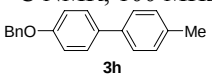


^{13}C NMR, 100 MHz, $CDCl_3$



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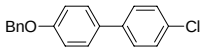
^{1}H NMR, 400 MHz, $CDCl_3$



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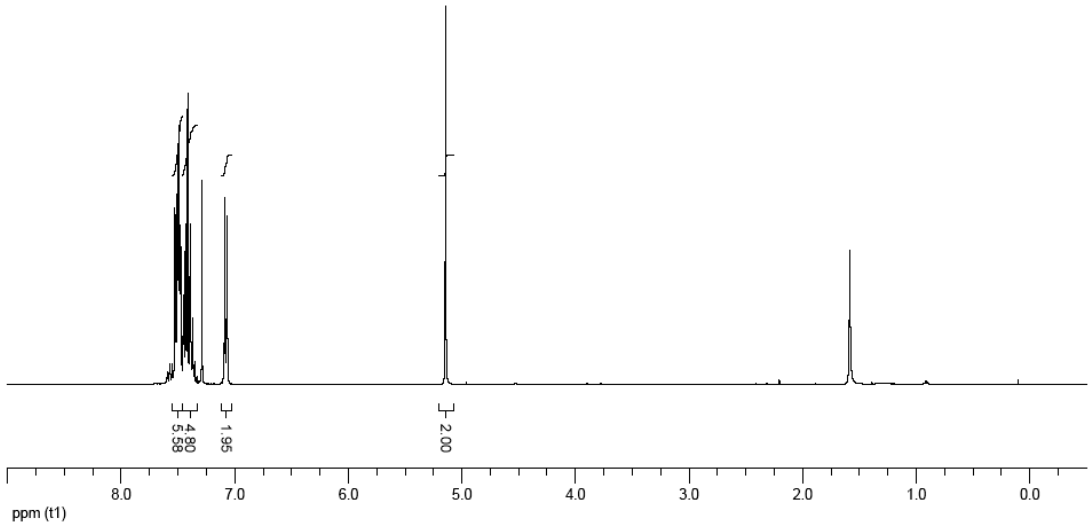
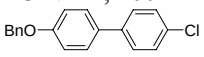


^{13}C NMR, 100 MHz, $CDCl_3$



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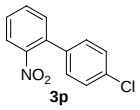
^{1}H NMR, 400 MHz, $CDCl_3$



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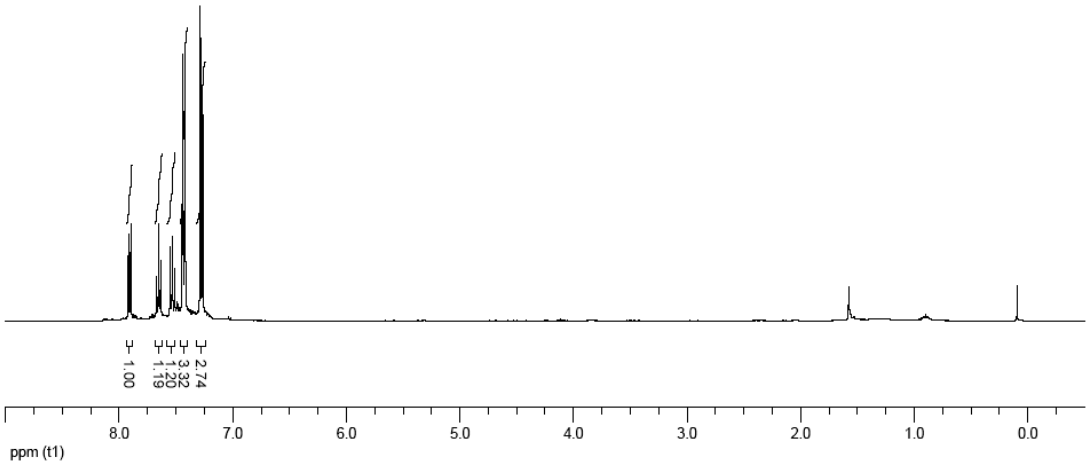
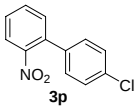


^{13}C NMR, 100 MHz, $CDCl_3$



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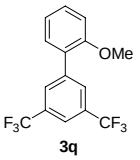
^{1}H NMR, 400 MHz, $CDCl_3$



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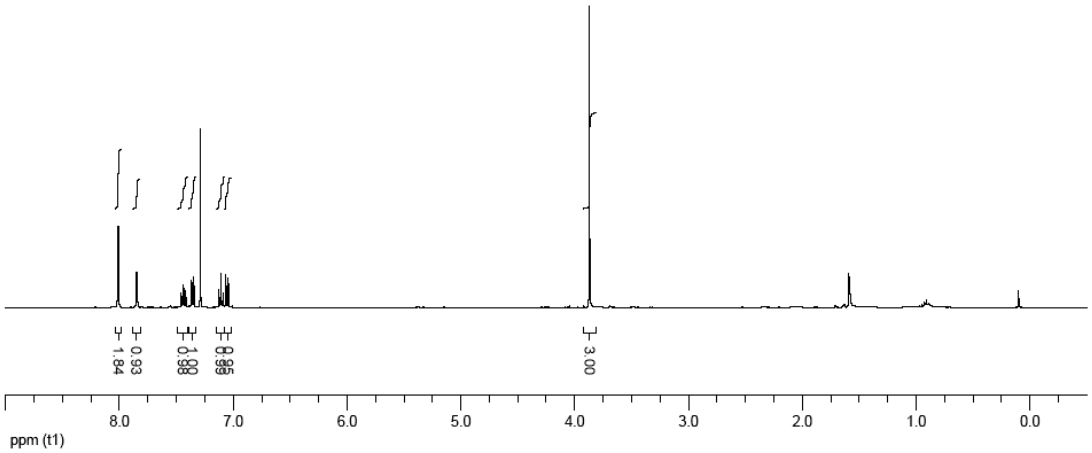
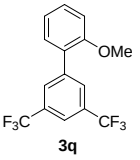


^{13}C NMR, 100 MHz, $CDCl_3$



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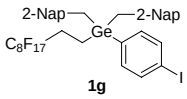
^{1}H NMR, 400 MHz, $CDCl_3$



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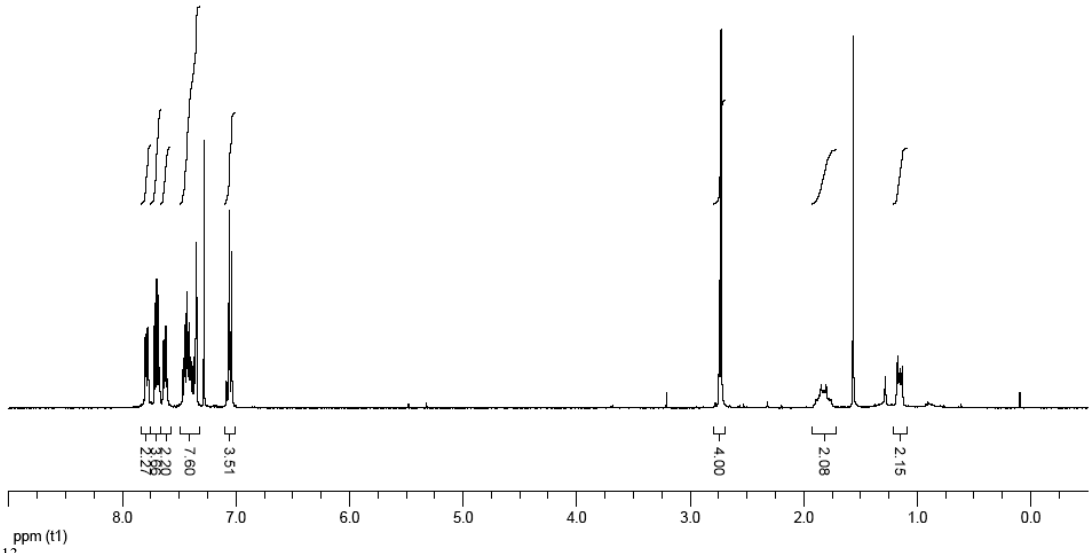
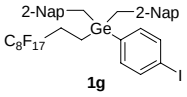


^{13}C NMR, 100 MHz, $CDCl_3$



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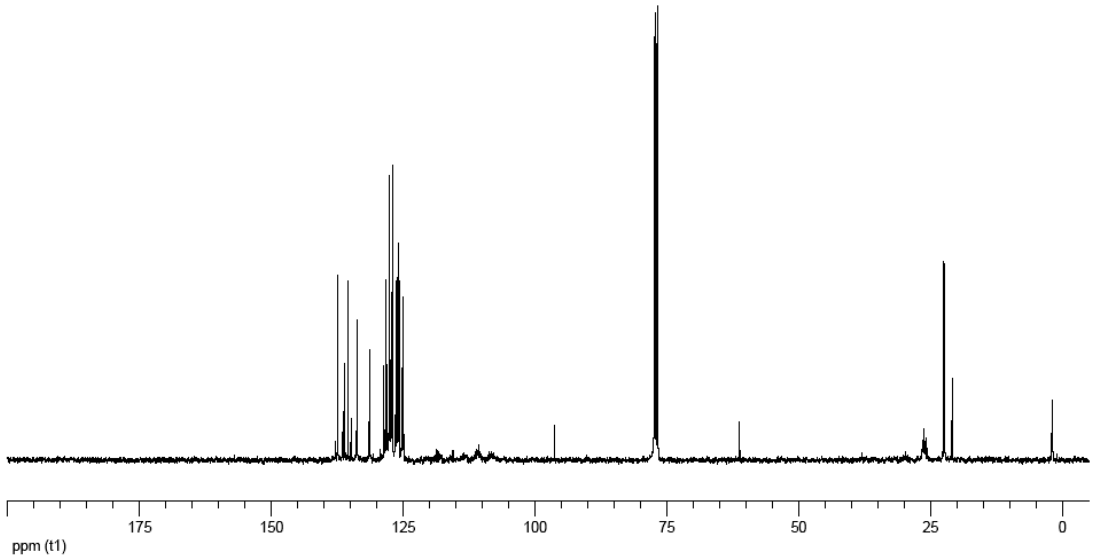
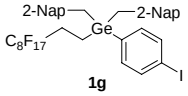


DEPT 135 100 MHz, $CDCl_3$



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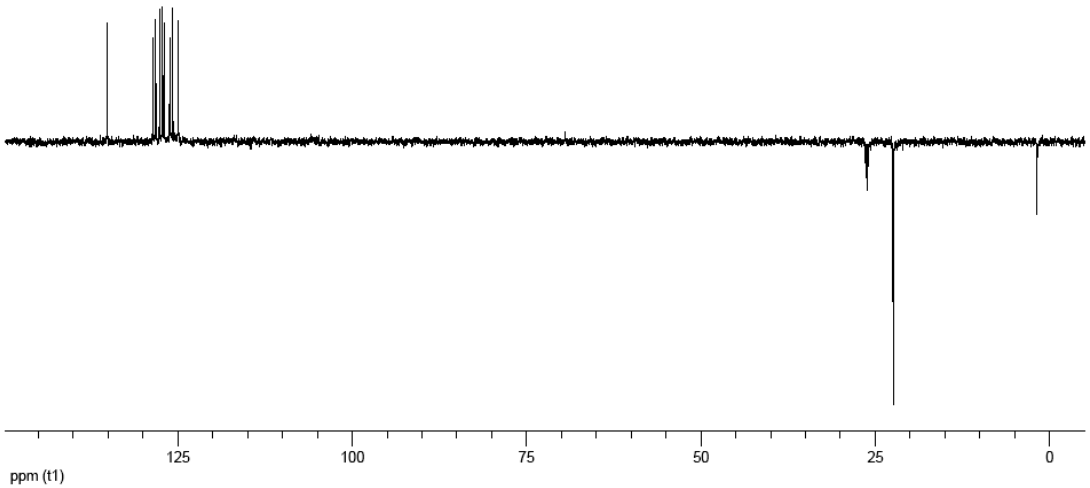
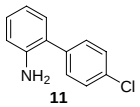


^1H NMR, 400 MHz, $CDCl_3$



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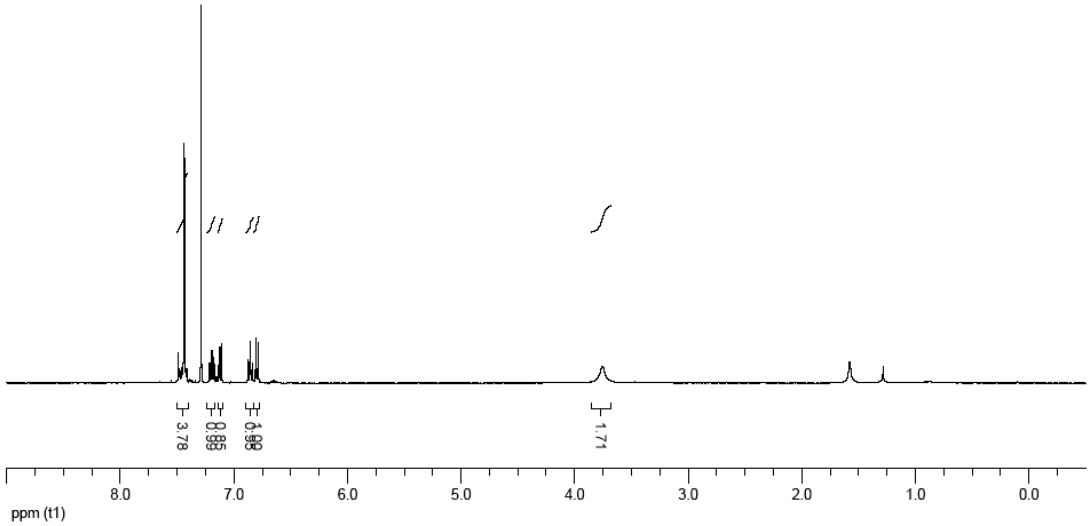
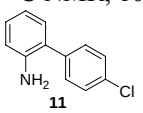


^{13}C NMR, 100 MHz, $CDCl_3$



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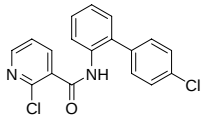
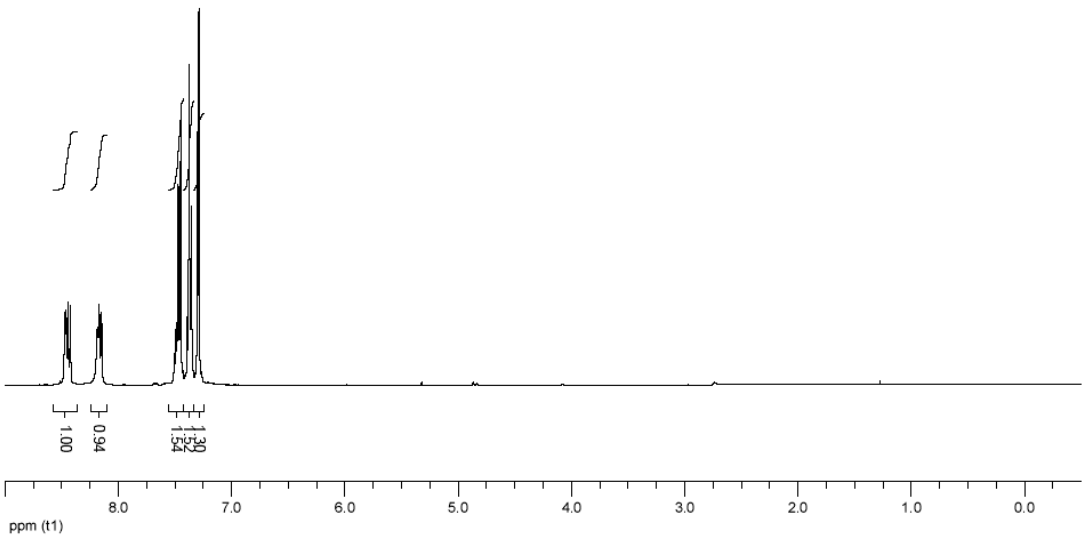
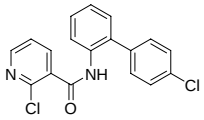
^{1}H NMR, 400 MHz, $CDCl_3$



Boscalid 17



^{13}C NMR, 100 MHz, $CDCl_3$



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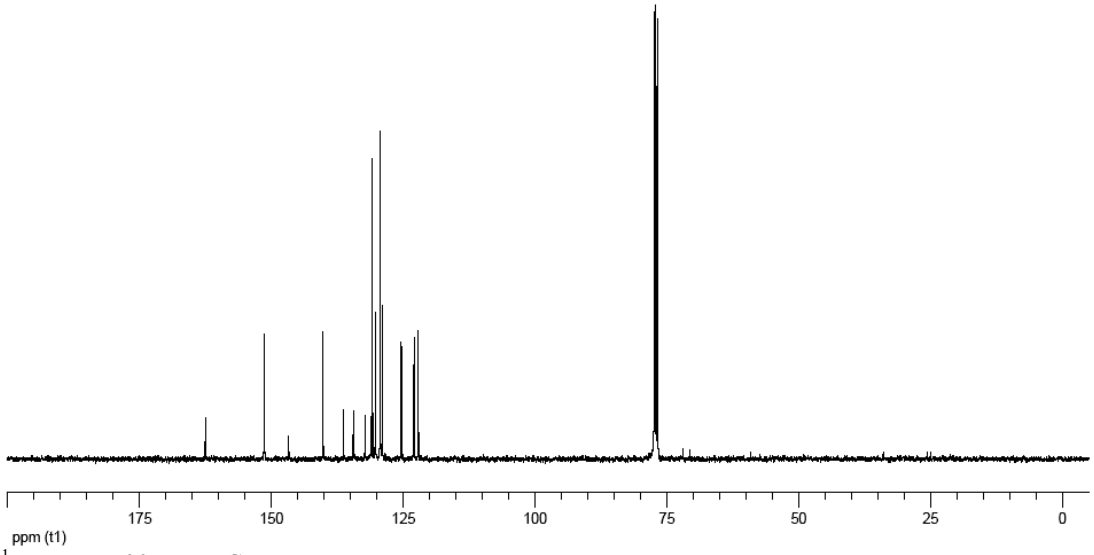
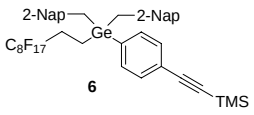


^{1}H NMR, 500 MHz, C_6D_6



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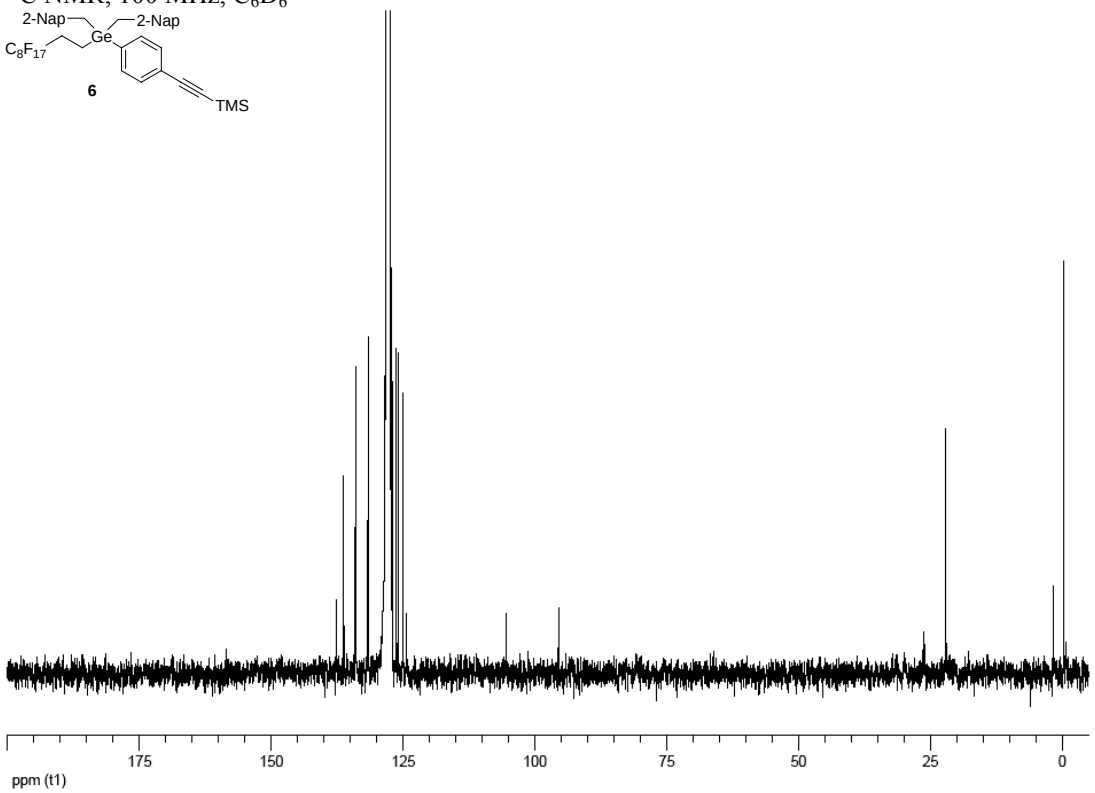
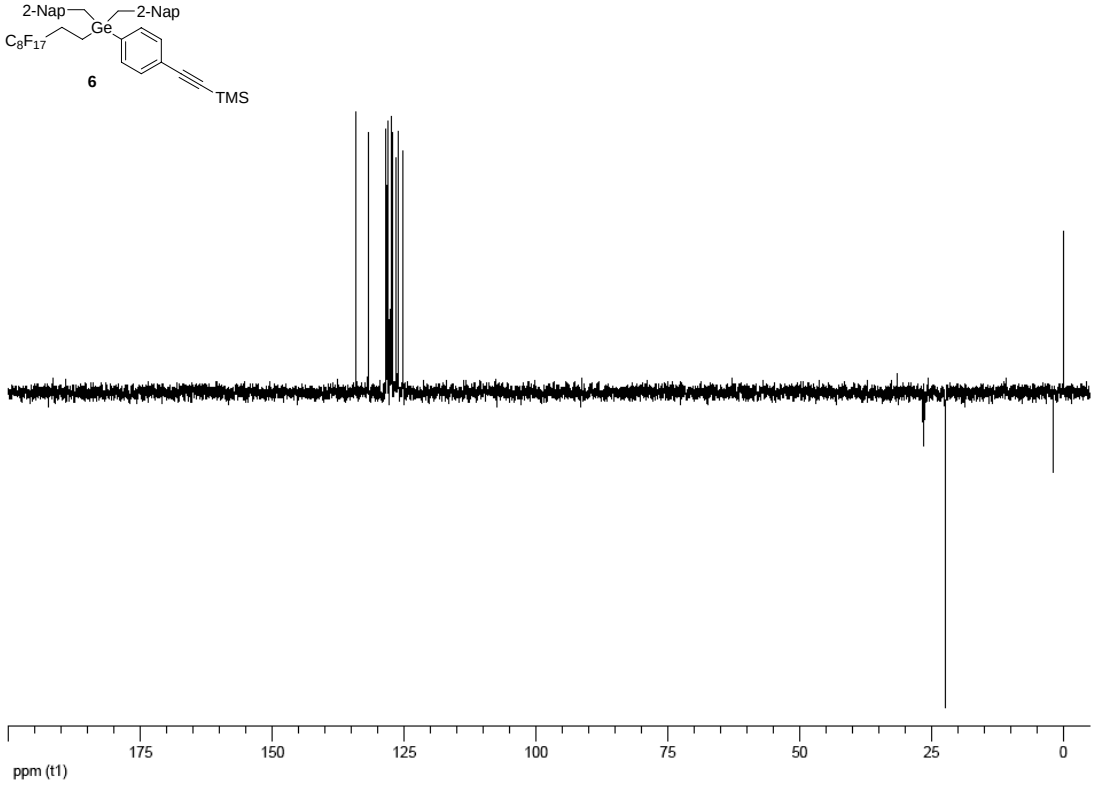
^{13}C NMR, 100 MHz, C_6D_6



6

DEPT 135 100 MHz, C_6D_6



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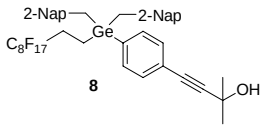
^{1}H NMR, 400 MHz, $CDCl_3$



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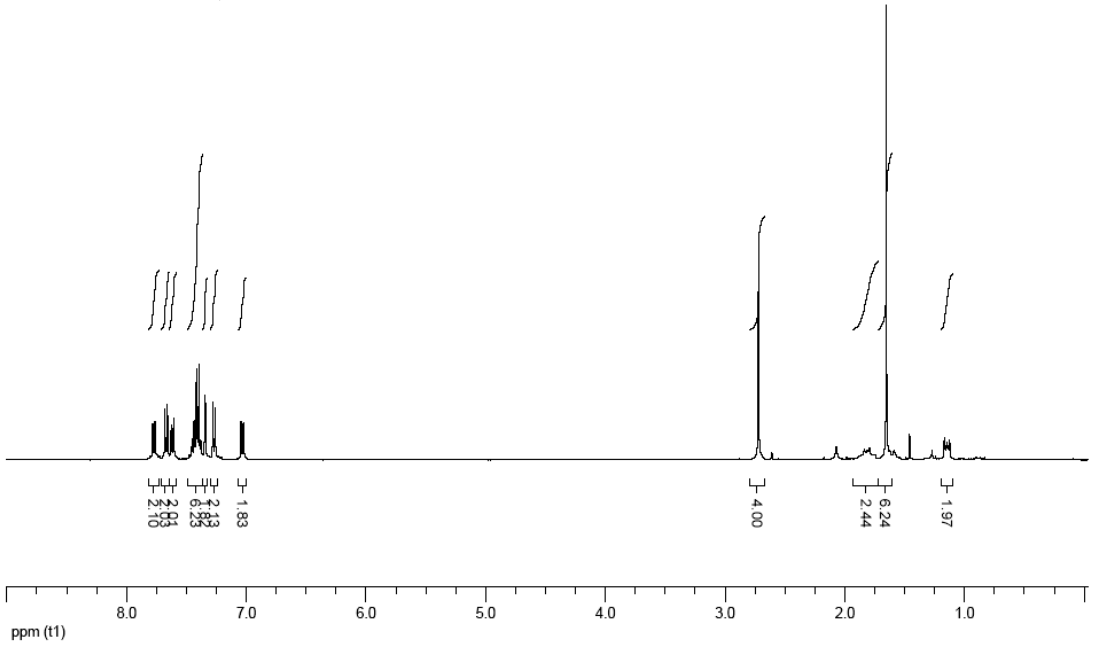
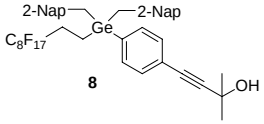


^{13}C NMR, 100 MHz, $CDCl_3$



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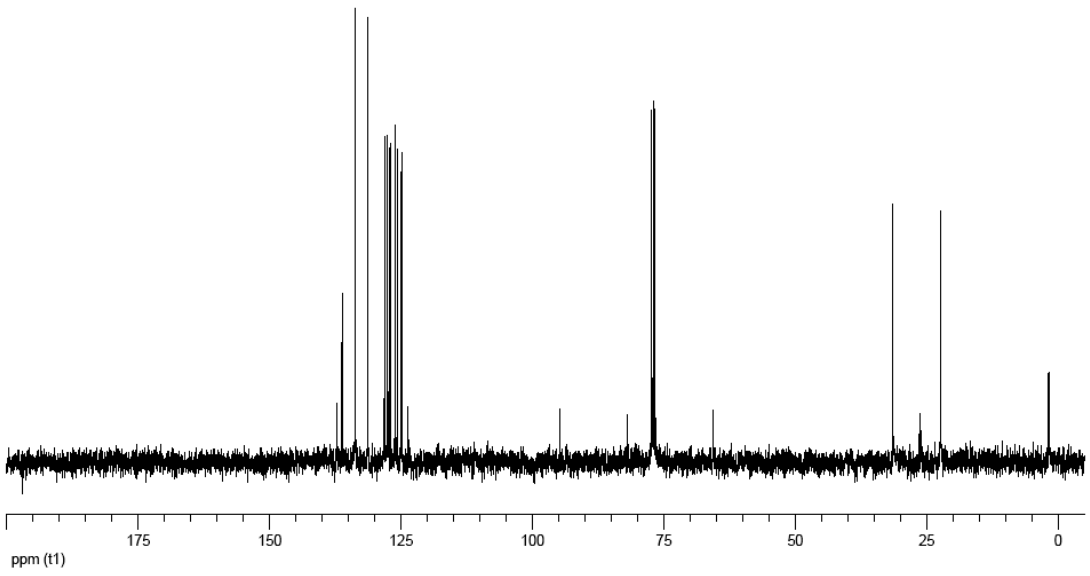
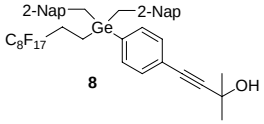


DEPT 135 100 MHz, $CDCl_3$



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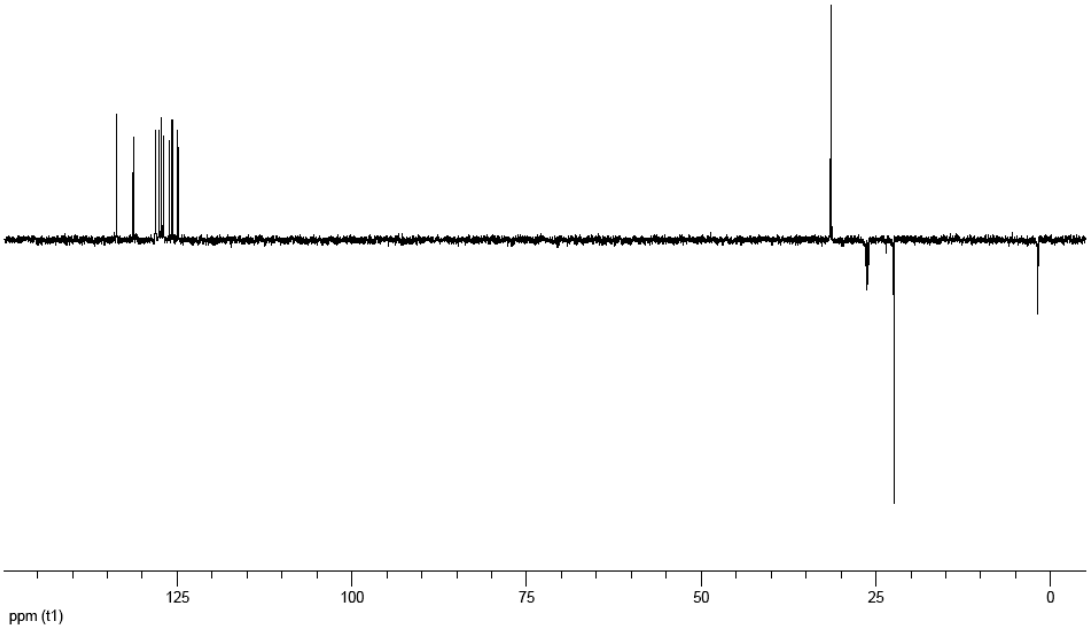
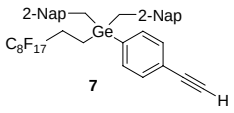


^1H NMR, 400 MHz, $CDCl_3$



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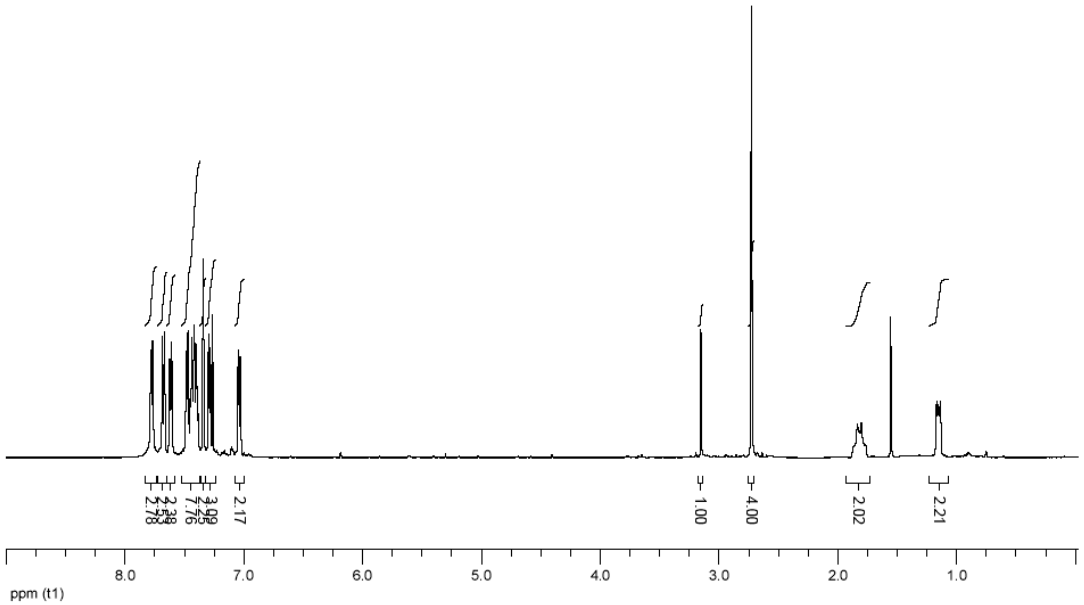
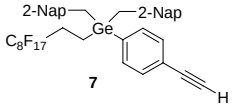


^{13}C NMR, 100 MHz, $CDCl_3$



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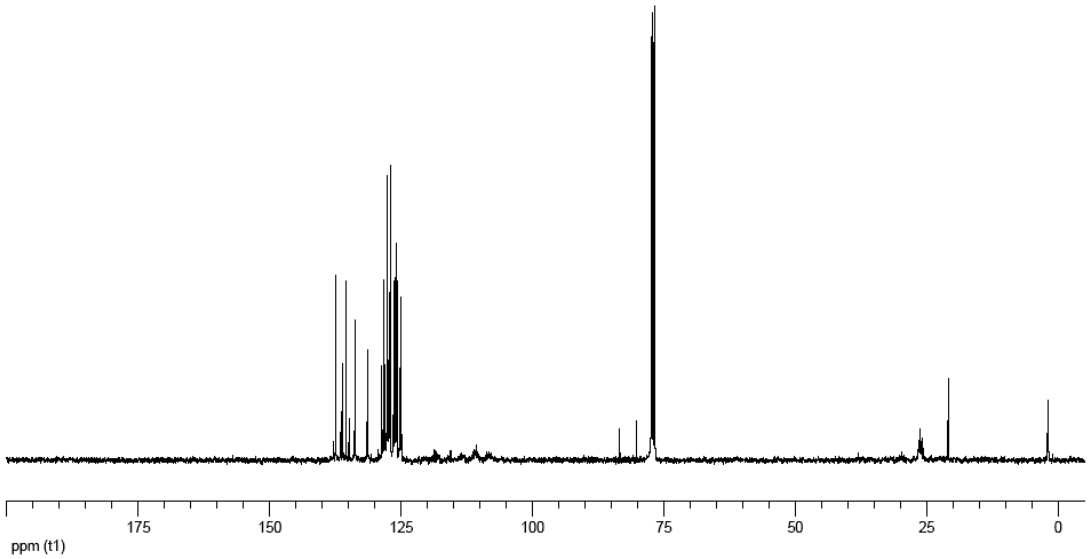
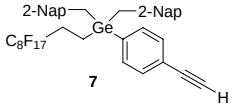


DEPT 135 100 MHz, $CDCl_3$



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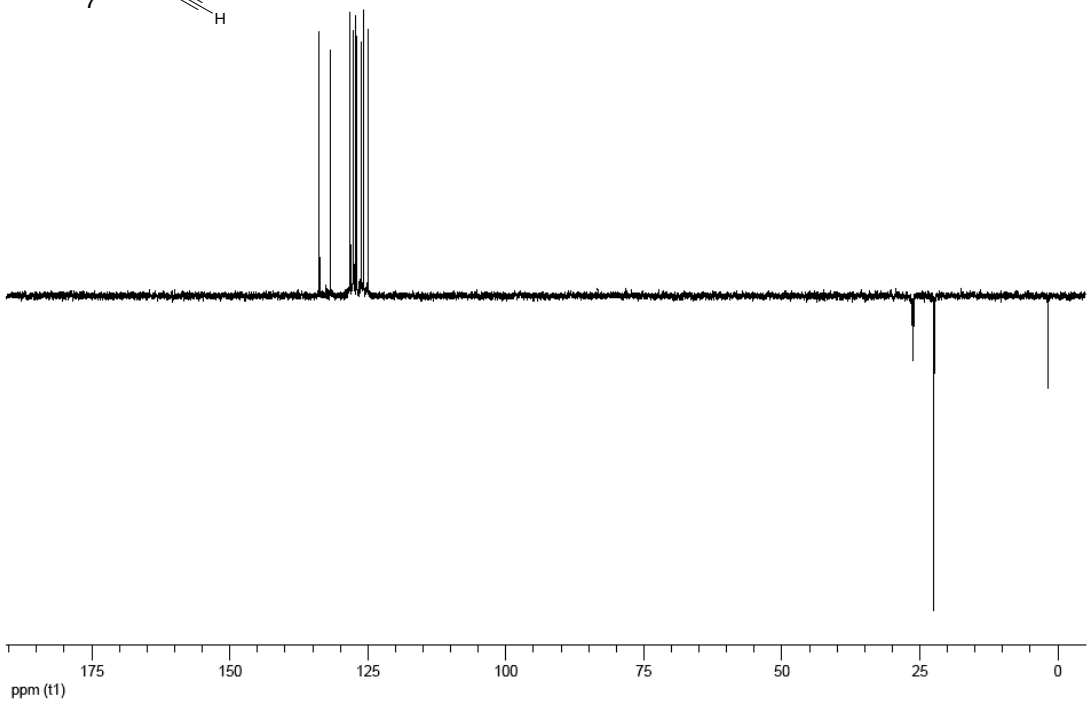
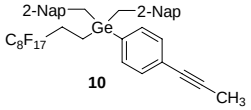


^{1}H NMR, 400 MHz, $CDCl_3$



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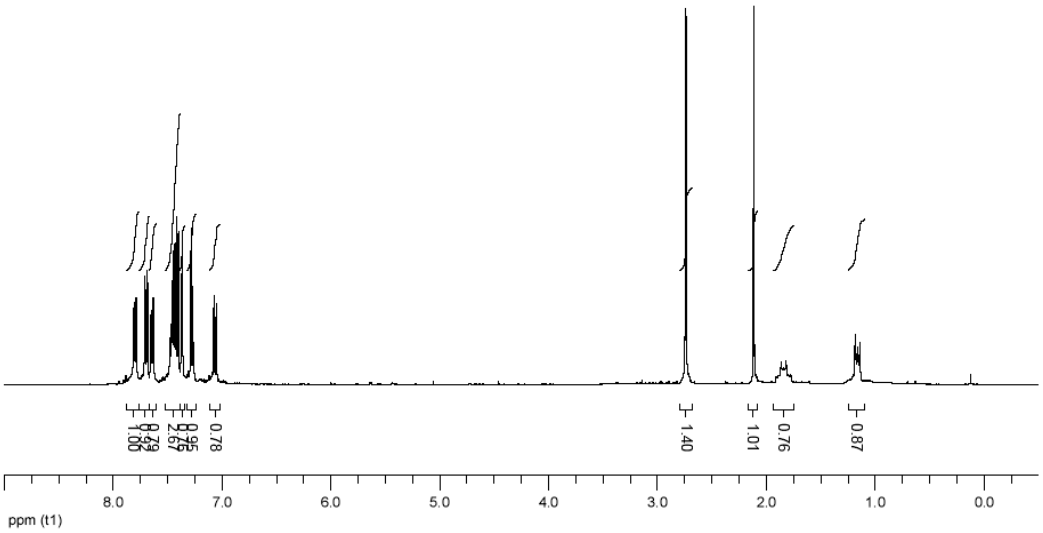
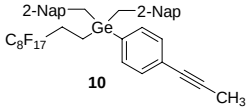


^{13}C NMR, 100 MHz, $CDCl_3$



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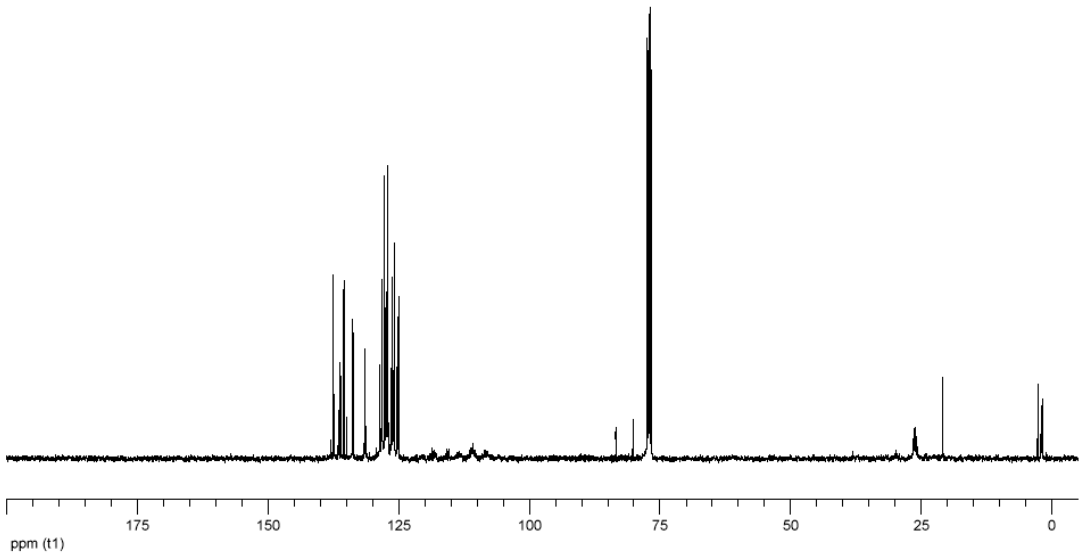
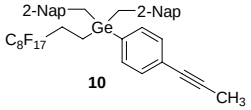


DEPT 135 100 MHz, $CDCl_3$



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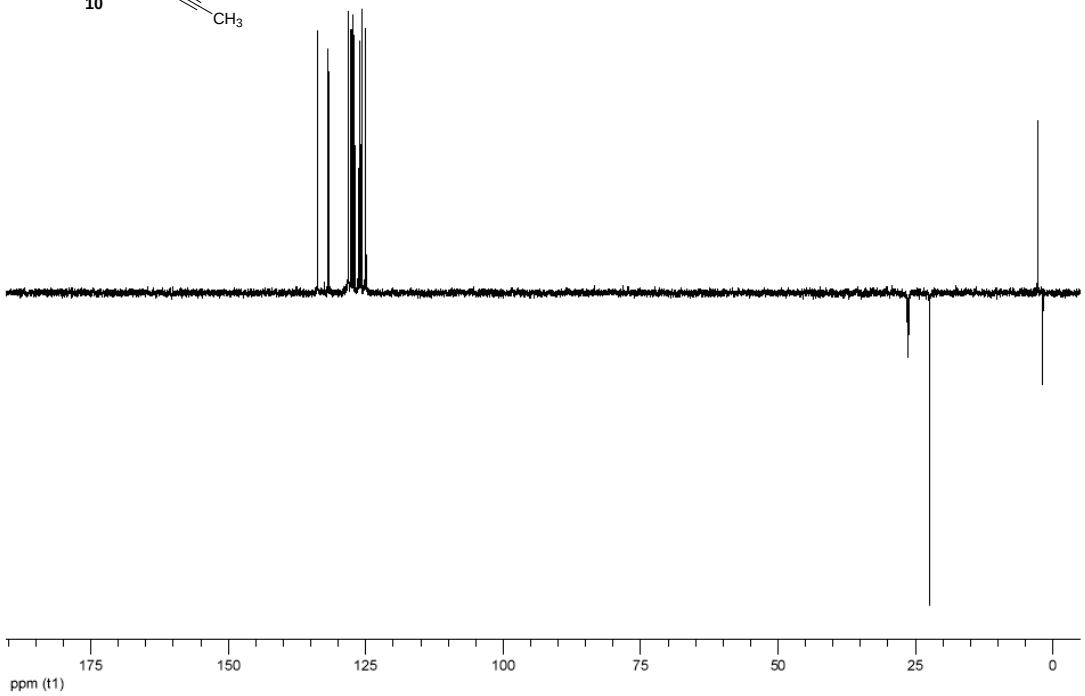
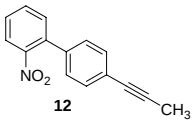


^1H NMR, 400 MHz, $CDCl_3$



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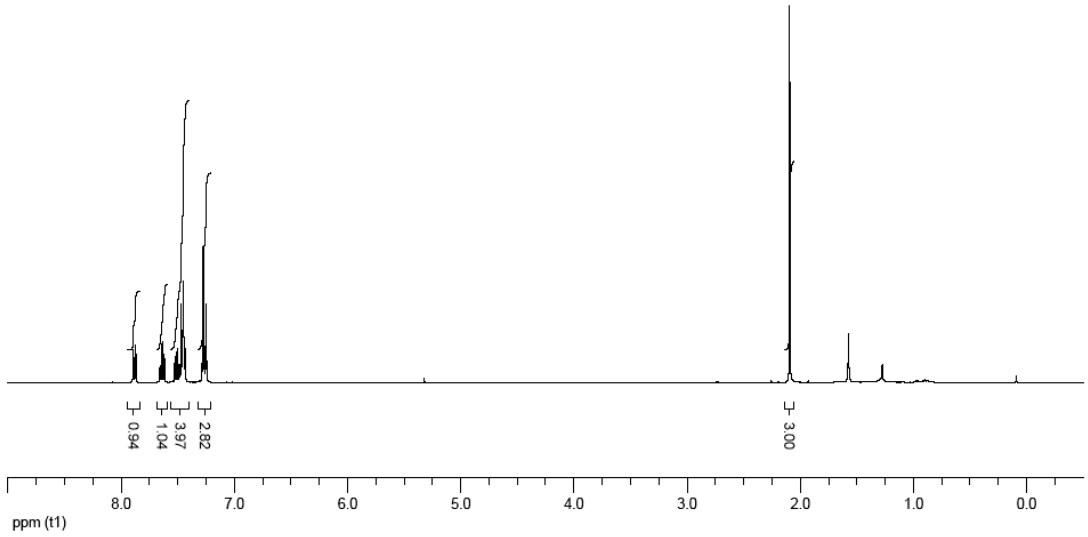
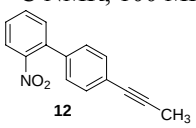


^{13}C NMR, 100 MHz, $CDCl_3$



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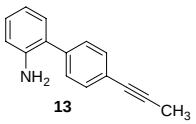
^{1}H NMR, 400 MHz, $CDCl_3$



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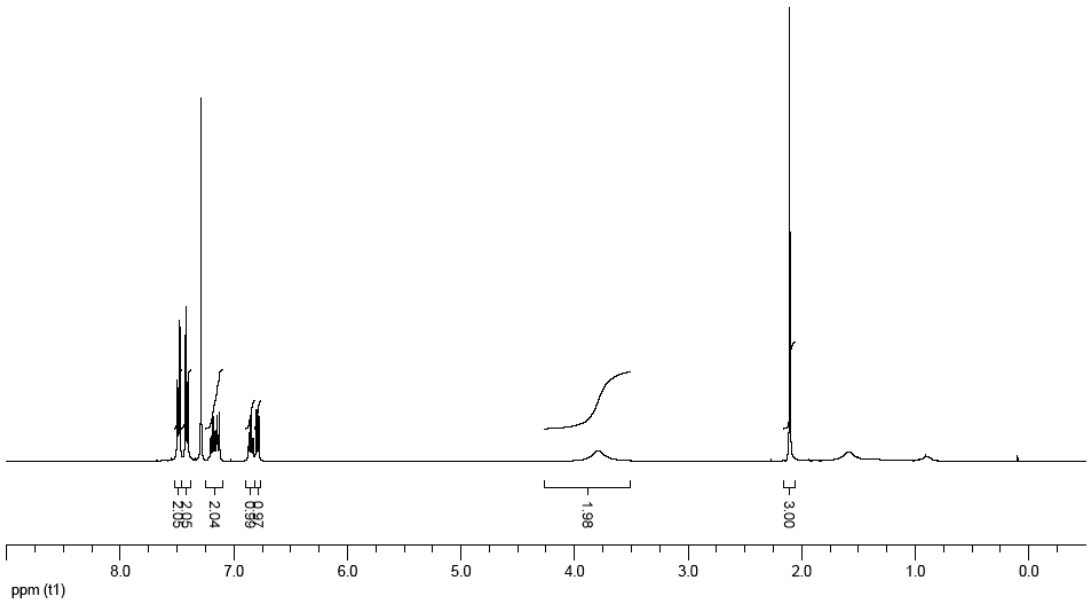
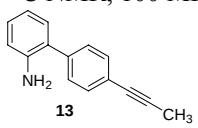


^{13}C NMR, 100 MHz, $CDCl_3$



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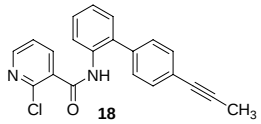
^{1}H NMR, 400 MHz, $CDCl_3$



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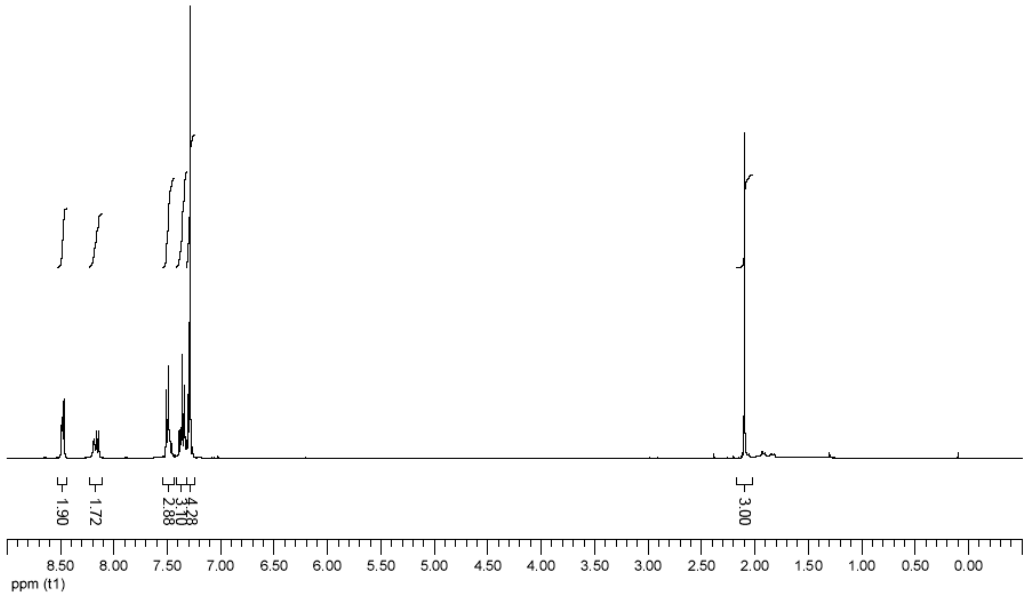
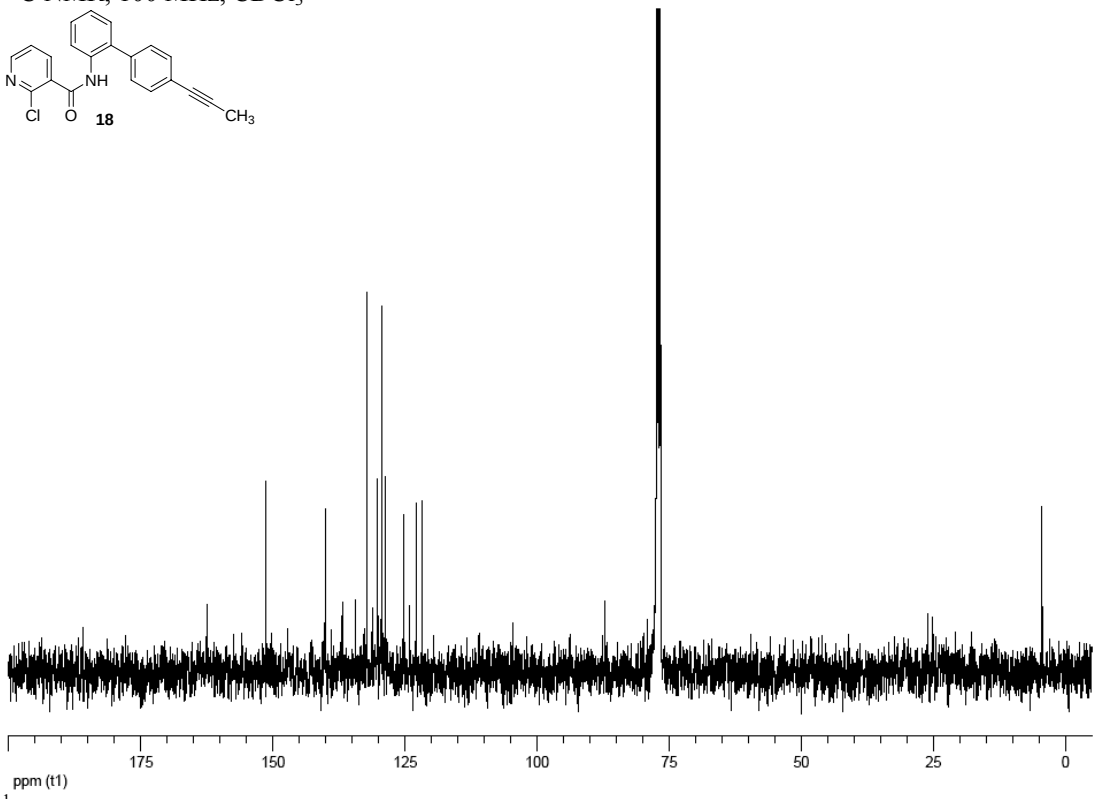
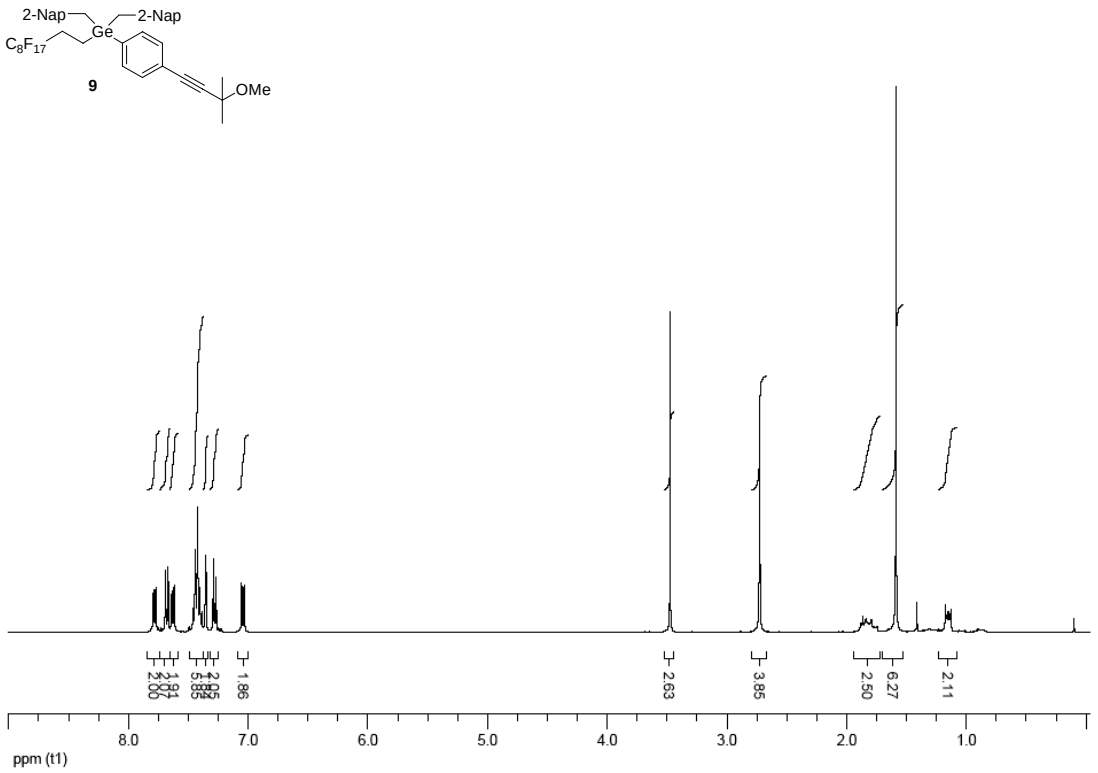


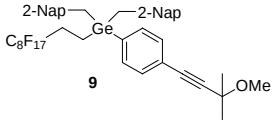
^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$



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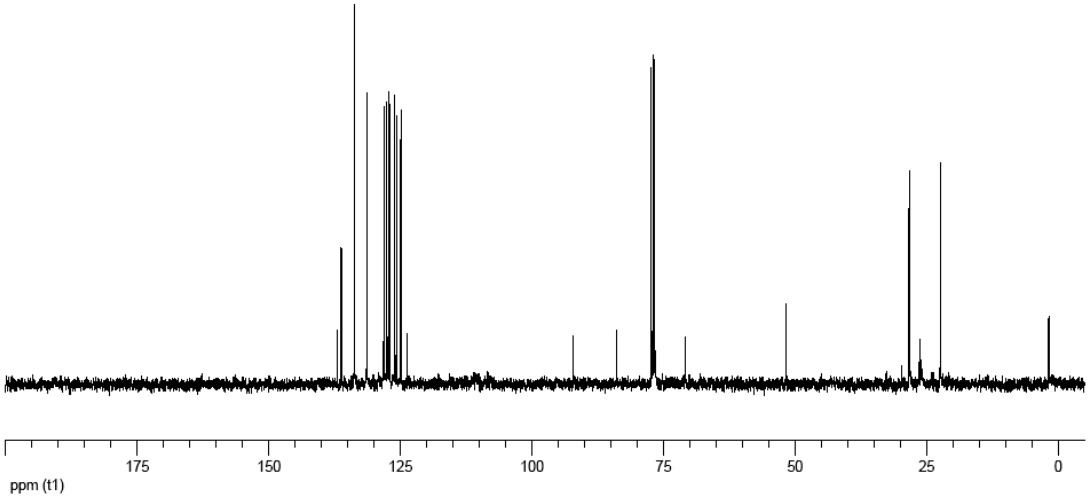
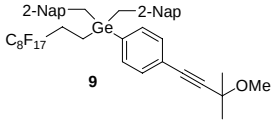


DEPT 135 100 MHz, $CDCl_3$



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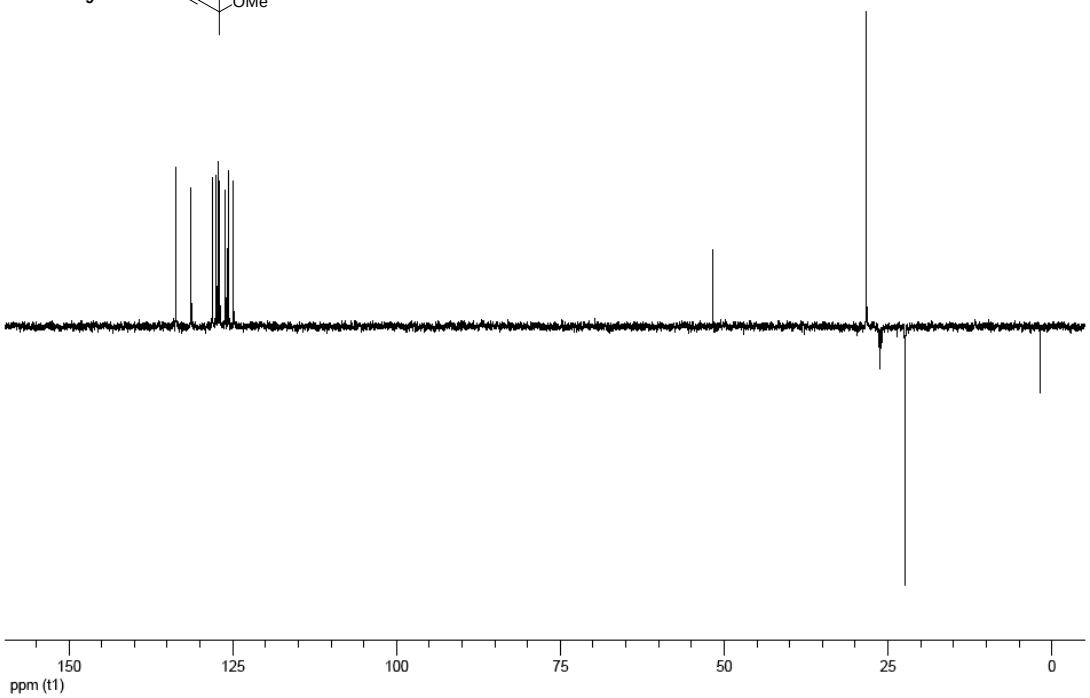
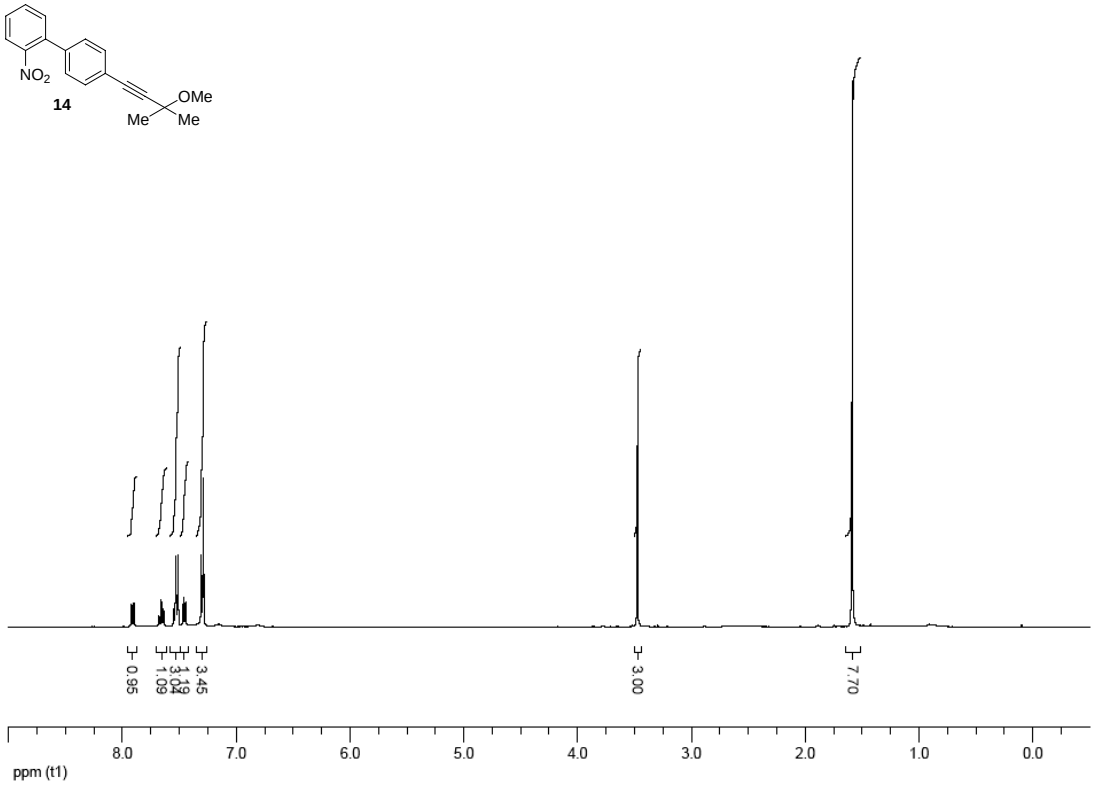
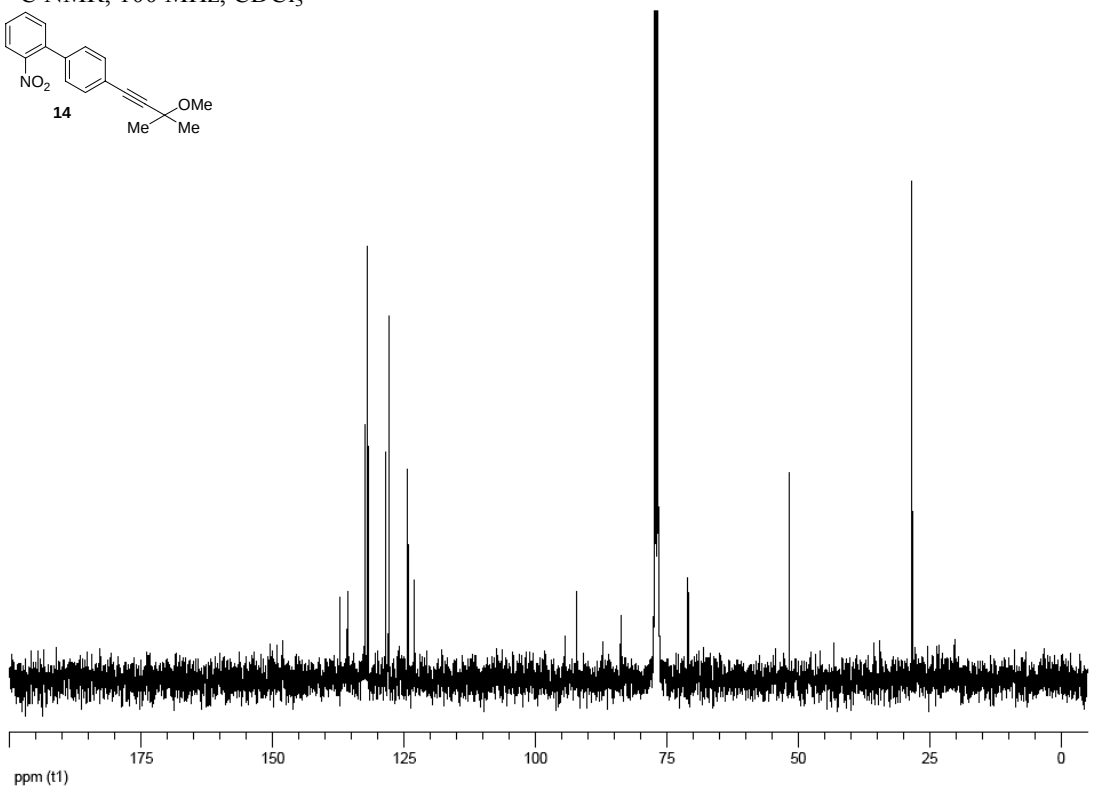


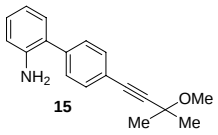
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



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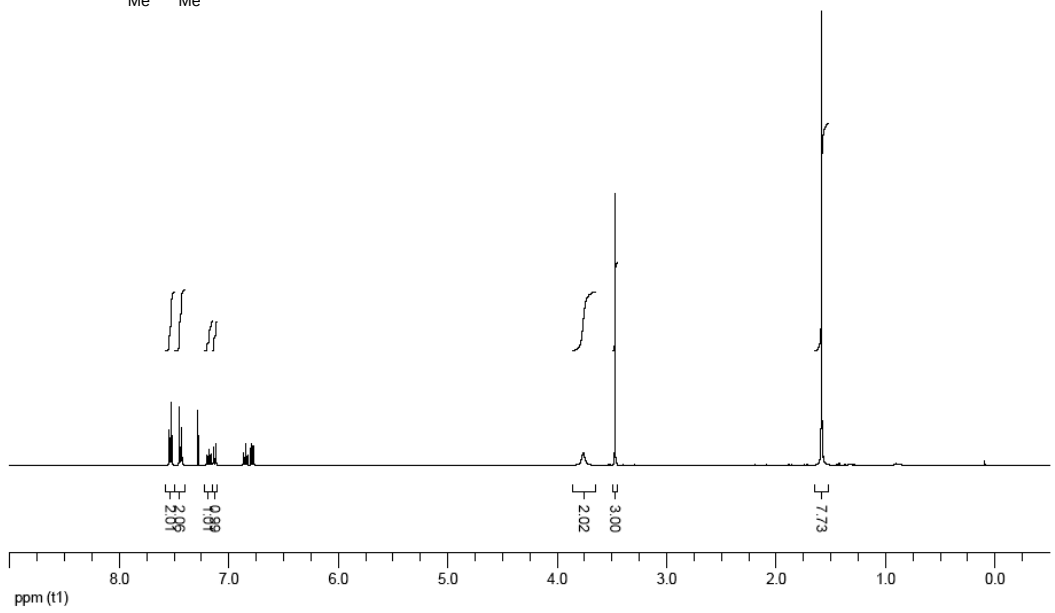
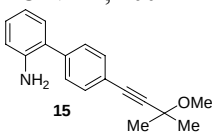


^{13}C NMR, 100 MHz, $CDCl_3$



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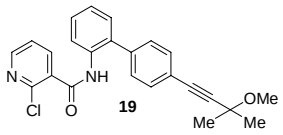
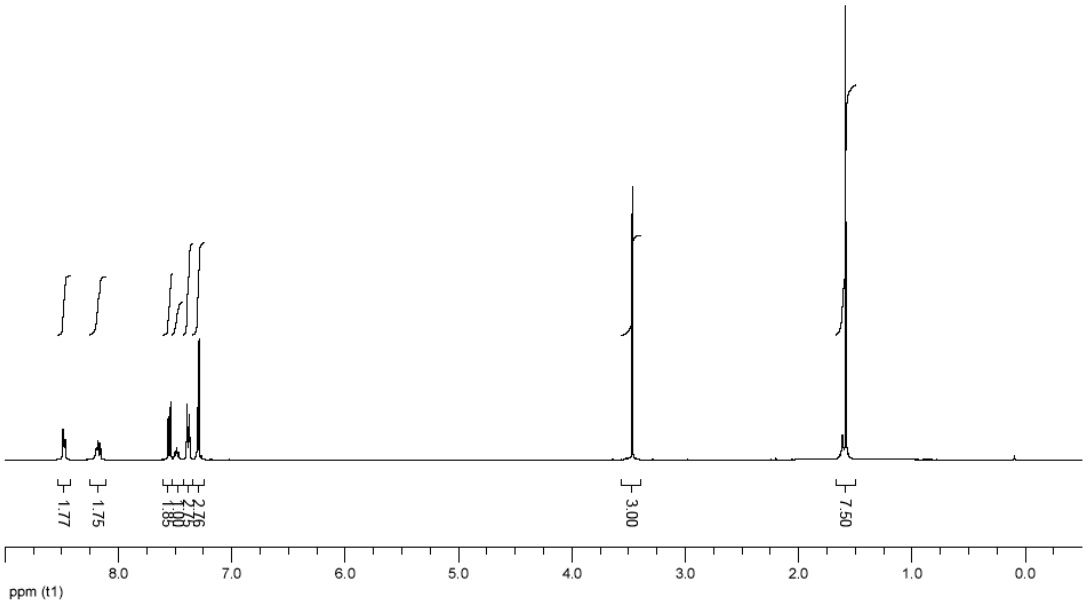
^{1}H NMR, 400 MHz, $CDCl_3$





^{13}C NMR, 100 MHz, $CDCl_3$