

## A Strategy for Isotope Containment During Radiosynthesis - Devolatilisation of Bromobenzene by Fluorous-tagging/Ir-Catalysed Borylation en route to the 4-Phenylpiperidine Pharmacophore

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**Experimental Procedures: General Directions:** All reactions were performed under anhydrous conditions and an atmosphere of nitrogen in flame-dried glassware. Yields refer to chromatographically and spectroscopically ( $^1\text{H-NMR}$ ) homogenous materials, unless otherwise indicated.

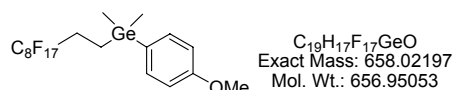
**Solvents and reagents:** All solvents were distilled before use. ‘Petrol’ refers to the fraction of light petroleum-ether boiling at 40-60 °C. Commercial grade solvents used for chromatography were distilled before use. Anhydrous THF and Et<sub>2</sub>O were distilled from sodium/benzophenone ketyl under nitrogen immediately prior to use. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> was distilled from CaH<sub>2</sub> immediately prior to use. Anhydrous DMF and octane were purchased from Sigma-Aldrich. All chemicals were handled in accordance with COSHH regulations. All reagents were used as commercially supplied. **Chromatography:** Flash chromatography (FC) was always performed on silica gel (Merck Kieselgel 60 F<sub>254</sub> 230-400 mesh) according to the method of W.C. Still.<sup>1</sup> Thin Layer Chromatography (TLC) was performed on Merck aluminium-backed plates pre-coated with silica (0.2 mm, 60 F<sub>254</sub>) which were visualized either by quenching of ultraviolet fluorescence ( $\lambda_{\text{max}} = 254$  and 366 nm) or by charring with 10% KMnO<sub>4</sub> in 1M H<sub>2</sub>SO<sub>4</sub> or by charring with 10% Ce(SO<sub>4</sub>)<sub>2</sub> and 15% H<sub>2</sub>SO<sub>4</sub>. **Melting points:** These were determined on a Kofler hot stage. **Infrared spectra:** These were recorded as thin films, on a Perkin-Elmer Paragon 1000 Fourier transform spectrometer. Only selected absorbances ( $\nu_{\text{max}}$ ) are reported.  **$^1\text{H NMR spectra}$ :** These were recorded at either 270, 300, 400 or 500 MHz on Jeol GSX-270, DRX-300, DRX-400, AMX-400 or AM-500 instruments respectively. Chemical shifts ( $\delta_{\text{H}}$ ) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak. Coupling constants ( $J$ ) are reported to the nearest 0.5 Hz. The abbreviation *app* = “apparent”, *p* = “para substituent”, *m* = “meta substituent”.  **$^{13}\text{C NMR spectra}$ :** These were recorded at 100 or 125 MHz on Bruker AMX-400 or AM-500 instruments respectively. Chemical shifts ( $\delta_{\text{C}}$ ) are quoted in ppm, referenced to the appropriate residual solvent peak. Degenerate peaks are suffixed by the number of carbons. **Mass spectra:** Low resolution mass spectra ( $m/z$ ) were recorded on either a VG platform II or

VG AutoSpec spectrometers, with only molecular ions ( $M^+$ ,  $MH^+$ ,  $MNH_4^+$ ) and major peaks being reported with intensities quoted as percentages of the base peak. High Resolution Mass Spectrometry (HRMS) measurements are valid to  $\pm 5$  ppm.

*General procedure for fluororous solid-phase extraction (F-SPE)*

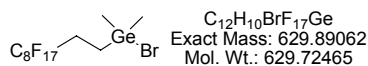
Pre-packed fluororous solid-phase extraction (F-SPE) cartridges were purchased from FLUOROUS Technologies Inc. and pre-conditioned with 50:50 MeCN- $H_2O$ . Crude reaction mixtures were loaded on the cartridge using  $CH_2Cl_2$  and eluted by 50:50 MeCN- $H_2O$  (10 ml), 70:30 MeCN: $H_2O$  (10 ml) as fluorophobic solvents followed by using MeCN as fluorophilic eluent. Compressed air flow was employed in a manner as described by Curran.<sup>2</sup>

**(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(4-methoxyphenyl)-  
dimethylgermane**



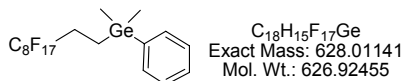
To a solution of *dichloro-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)(4-methoxyphenyl)germane*<sup>3</sup> (1.20 g, 1.72 mmol) in THF (20.0 mL) was added methylmagnesium chloride (2.86 ml, 8.6 mmol, 3M) dropwise. The reaction mixture was stirred at 0 °C for 1 h and then at rt for 16 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 ( $2 \times 20.0$  mL) of  $Et_2O$ , the combined organic extracts were dried over  $Na_2SO_4$  and evaporated *in vacuo* to give yellow oily residue which was purified by FC (hexane/ $EtOAc$ , 97/3) to give *3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)(4-methoxyphenyl)dimethylgermane* as a pale yellow oil (1.07 g, 95 %).  $\nu_{max}$  (neat)/ $cm^{-1}$  2905, 1592, 1511, 1246, 1180, 1035, 818;  $^1H$  NMR (400 MHz;  $CDCl_3$ ):  $\delta$  0.41 (s, 6H,  $2 \times CH_3Ge$ ), 1.07-1.21 (m, 2H,  $C_8F_{17}CH_2CH_2Ge$ ), 1.98-2.12 (m, 2H,  $C_8F_{17}CH_2CH_2Ge$ ), 3.82 (s, 3H,  $OCH_3$ ), 6.94 (d,  $J = 8.6$  Hz, 2H, ArH), 7.35 (d,  $J = 8.6$  Hz, 2H, ArH);  $^{13}C$  NMR (100 MHz;  $CDCl_3$ )  $\delta$  -4.0 (2q), 5.3 (t), 26.9 (t,  $J = 23.8$  Hz), 55.1 (q), 110.1 (s), 110.6 (s), 110.9 (s), 111.0 (2s), 111.1 (s), 111.3 (s), 114.0 (2d), 118.3 (s), 130.4 (s), 134.3 (2d), 160.2 (s);  $^{19}F$  NMR (376 MHz;  $CDCl_3$ ):  $\delta$  -125.0 (s, 2F), -122.1 (s, 2F), -121.7 (s, 2F), -120.8 (m, 6F), -115.0 (s, 2F), -79.9 (quintet,  $J = 9.7$  Hz, 3F); IR  $\nu_{max}$  (neat) 3024 (C-H), 2980 (C-H) 1598 (C=C), 1507, 1421 (C-F), 1265, 896, 744  $cm^{-1}$ ;  $m/z$  ( $EI^+$ ) (rel. intensity) 658 ( $M^+$ , 45), 643 (30), 409 (30), 389 (35), 211 (90), 86 (100); HRMS calc'd. for  $C_{19}H_{17}F_{17}GeO$  ( $M^+$ ) 658.0220, found 658.0228,  $\Delta$  1.3 ppm.

### Bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)dimethylgermane 3



To a solution of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl(4-methoxyphenyl)dimethylgermane (1.0 g, 1.52 mmol) in  $CH_2Cl_2$  (10.0 mL) was added a solution of conc. HBr (5.0 mL, 48% wt.). The resulting biphasic reaction mixture was stirred at rt for 12 h, extracted with  $CH_2Cl_2$  ( $3 \times 20.0$  mL). The combined organic extracts were dried over  $Na_2SO_4$  and evaporated *in vacuo* to give bromo-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)dimethylgermane **3** as a brown amorphous solid (0.957 g, 100 %).  $\nu_{max}$  (neat)/ $cm^{-1}$  2950, 1246, 1200, 1037, 818;  $^1H$  NMR (400 MHz;  $CDCl_3$ ):  $\delta$  0.87 (s, 6H,  $2 \times CH_3$ Ge), 1.37-1.45 (m, 2H,  $C_8F_{17}CH_2CH_2Ge$ ), 2.19-2.34 (m, 2H,  $C_8F_{17}CH_2CH_2Ge$ );  $^{13}C$  NMR (100 MHz;  $CDCl_3$ )  $\delta$  3.8 (2q), 11.1 (t), 29.7 (t);  $^{19}F$  NMR (376 MHz;  $CDCl_3$ ):  $\delta$  -126.1 (s, 2F), -123.2 (s, 2F), -122.7 (s, 2F), -121.9 (m, 4F), -121.7 (s, 2F), -115.5 (s, 2F), -80.7 (quintet,  $J = 9.5$  Hz, 3F);  $m/z$  ( $EI^+$ ) (rel. intensity) 615 [ $(M-CH_3)^+$ , 15], 551 (30), 389 (50), 243 (90), 214 (100); HRMS calc'd for  $C_{11}H_7BrF_{17}Ge$  614.8671 ( $M-CH_3$ ) $^+$ , found 614.8687,  $\Delta$  2.5 ppm.

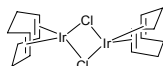
### (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptafluorodecyl)dimethylphenylgermane 4



To a solution of bromobenzene (50  $\mu$ L, 0.475 mmol, 74.55 mg) in THF (5 mL) was added *t*-BuLi (720  $\mu$ L, 1.045 mmol, 1.45 M) dropwise at  $-78$   $^{\circ}C$  for 30 min to achieve lithium-bromo exchange to generate phenyl lithium solution *in situ*. To a solution of bromodimethylgermane **3** (449 mg, 0.713 mmol) in THF (5 mL) was cooled at  $-78$   $^{\circ}C$  and cannulate into the phenyl lithium solution at this temperature and stirred for 16 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 ( $2 \times 20.0$  mL) of  $Et_2O$ , the combined organic extracts were dried over  $Na_2SO_4$  and evaporated *in vacuo* to give yellow oily residue which was purified by F-SPE cartridge to give (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)dimethylphenylgermane **4** as a yellow oil (288.8 mg, 97 %).  $\nu_{max}$  (neat)/ $cm^{-1}$  2904, 1511, 1245, 1038, 819;  $^1H$  NMR (400 MHz;  $CDCl_3$ ):  $\delta$  0.44 (s, 6H,  $2 \times CH_3$ Ge), 1.11-1.15 (m, 2H,  $C_8F_{17}CH_2CH_2Ge$ ), 2.00-2.13 (m, 2H,  $C_8F_{17}CH_2CH_2Ge$ ), 7.33-7.40 (m, 3H, ArH), 7.42-7.45 (m, 2H, ArH);  $^{13}C$  NMR (100 MHz;  $CDCl_3$ )  $\delta$  -4.1 (2q), 5.1 (t), 26.9 (t,  $J = 23.5$  Hz), 110.2 (s), 110.7 (s), 110.8 (s), 110.9 (2s), 111.2 (s), 111.3 (s), 118.4 (s), 128.3

(2d), 128.8 (d), 133.1 (2d), 139.5 (s);  $^{19}\text{F}$  NMR (376 MHz;  $\text{CDCl}_3$ ):  $\delta$  -125.2 (s, 2F), -122.2 (s, 2F), -121.8 (s, 2F), -120.8 (m, 6F), -115.0 (s, 2F), -79.8 (quintet,  $J = 9.8$  Hz, 3F);  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$  2904, 1511, 1245, 1038, 819;  $m/z$  ( $\text{EI}^+$ ) (rel. intensity) 613 [(M-CH $_3$ ) $^+$ , 50], 593 (20), 409 (30), 389 (25), 185 (100); HRMS calc'd for  $\text{C}_{18}\text{H}_{15}\text{F}_{17}\text{Ge}$  612.9879 (M-CH $_3$ ) $^+$ , found 612.9870,  $\Delta$  -1.5 ppm.

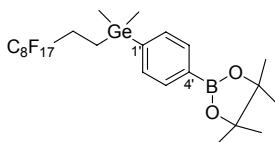
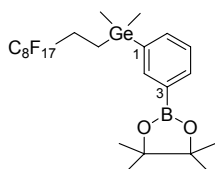
### Di- $\mu$ -chlorodi-( $\eta^4$ -1,5-cyclooctadiene)diiridium $^4$



$\text{C}_{16}\text{H}_{24}\text{Cl}_2\text{Ir}_2$   
Exact Mass: 672.05  
Mol. Wt.: 671.70

According to the method of Herde, a 250-mL, three-necked, round-bottomed flask containing a magnetic stirring bar was charged with 2.01 g of *iridium trichloride hydrate* ( $\text{IrCl}_3 \cdot \text{H}_2\text{O}$ , 57.0 mmol). One neck of the flask was equipped with an inlet for nitrogen, another neck was equipped with a water-jacketed condenser and the third neck was equipped with a nitrogen-bubbler. EtOH (96%, 34.0 mL), water (17.0 mL) and *cyclooctadiene* (6.0 mL, 48.9 mmol) were added and a stream of nitrogen was passed through the system for 15 min. The solution was then refluxed (90°C) with stirring for 24 h during which time the solution turned from brown to orange-red. The mixture was then left to cool to RT, the precipitate was filtered off, rinsed with ice cold MeOH (20 mL) and then dried *in vacuo* for 24 h to give *di- $\mu$ -chlorodi-( $\eta^4$ -1,5-cyclooctadiene)diiridium* as red-orange crystals (1.26 g, 66%).  $\nu_{\text{max}}$  (KBr disk)/ $\text{cm}^{-1}$  2978, 2934, 2878, 2829, 1472, 1447, 1322, 940, 831, 531 [lit. $^5$  (KBr disk) 2958, 2914, 2874, 2830, 1475, 1451, 1329, 972, 834]; MS ( $\text{EI}^+$ )  $m/z$  672 ( $\text{M}^+$ , 100), 632 (19), 590 (43), 486 (15), 295 (15).

### 2-{3-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptafluorodecyl)dimethylgermyl]-phenyl}-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **5m** and 2-{4-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptafluorodecyl)dimethylgermyl]-phenyl}-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **5p**

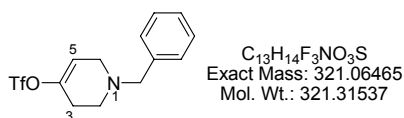


$\text{C}_{24}\text{H}_{26}\text{BF}_{17}\text{GeO}_2$   
Exact Mass: 754.09662  
Mol. Wt.: 752.88589

A sealed tube containing *dimethylphenylgermane* **4** (316 mg, 1.0 mmol),  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (1.5 mol%, 10 mg, 0.015 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy) (3 mol%, 8.0 mg, 0.03 mmol) and  $\text{B}_2\text{pin}_2$  (254 mg, 1.0 mmol) was flushed with nitrogen and then charged with

octane (1.9 mL). The mixture was then stirred at 125 °C for 48 h. The reaction residue was then concentrated *in vacuo* and the residue was purified by F-SPE to give a mixture of mono-borated arylgermanes **6**, diborated arylgermane **7** and unreacted starting material **5** (70:16:14 respectively, NMR ratio). The mixture was further purified by FC (EtOAc/hexane, 1:19) to give *m*- and *p*-perfluoroarylgermane boronic ester **5** as a colourless oil ( mg, 62 %, *m*:*p* ~ 2:1 by NMR).  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2978, 2932, 1590, 1512, 1355, 1245, 1145, 819, 710;  $^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  0.44 (s, 6 $H_p$ , 2 $\times\text{CH}_3\text{Ge}$ ), 0.45 (s, 6 $H_m$ , 2 $\times\text{CH}_3\text{Ge}$ ), 1.26-1.32 (m, 2 $H_m$ +2 $H_p$ ,  $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{Ge}$ ), 1.34 (s, 12 $H_p$ , Bpin), 1.35 (s, 12 $H_m$ , Bpin), 2.04-2.13 (m, 2 $H_p$ +2 $H_m$ ,  $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{Ge}$ ), 7.40 (t,  $J = 7.4$  Hz, 1 $H_m$ ,  $\text{C}^5\text{H}$ ), 7.48 (dd,  $J = 7.6, 2.6$  Hz, 2 $H_p$ ,  $\text{C}^{2'}\text{H}+\text{C}^{6'}\text{H}$ ), 7.51-7.55 (m, 2 $H_m$ ,  $\text{C}^4\text{H}+\text{C}^6\text{H}$ ), 7.78 (dd,  $J = 7.6, 2.6$  Hz, 2 $H_p$ ,  $\text{C}^{3'}\text{H}+\text{C}^{3'}\text{H}$ ), 7.89 (s, 1 $H_m$ ,  $\text{C}^2\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ )  $\delta$  -4.1 (2 $q_p$ ), -4.0 (2 $q_m$ ), 5.1 ( $t_p$ ), 5.2 ( $t_m$ ), 24.8 (4 $q_p$ +4 $q_m$ ), 26.9 (t,  $J = 23.9$  Hz,  $t_p+t_m$ ), 83.78 (2 $s_p$ ), 83.82 (2 $s_m$ ), 110.2 ( $s_p+s_m$ ), 110.6 ( $s_p+s_m$ ), 110.7 ( $s_p+s_m$ ), 110.8 (2 $s_p$ +2 $s_m$ ), 111.2 ( $s_p+s_m$ ), 111.3 ( $s_p+s_m$ ), 118.4 ( $s_p+s_m$ ), 127.5 ( $d_m$ ), 128.2 (2 $d_p$ ), 128.8 ( $d_m$ ), 133.1 (2 $d_p$ ), 135.3 ( $d_m$ ), 135.9 ( $d_p$ ), 136.0 (s), 138.6 (s), 139.4 (s), 142.2 (s);  $^{19}\text{F}$  NMR (376 MHz;  $\text{CDCl}_3$ ):  $\delta$  -126.1 (2 $s_p$ +2 $s_m$ , 4F), -123.2 (2 $s_p$ +2 $s_m$ , 4F), -122.7 (2 $s_p$ +2 $s_m$ , 4F), -121.8 (6 $s_p$ +6 $s_m$ , 12F), -115.9 (2 $s_p$ +2 $s_m$ , 4F), -80.7 (quintet,  $J = 9.6$  Hz, 6F, 3 $F_p$ +3 $F_m$ );  $m/z$  ( $\text{EI}^+$ ) (rel. intensity) 739 [(M- $\text{CH}_3$ ) $^+$ , 10], 433 (60), 307 (100), 207 (20); HRMS calc'd for  $\text{C}_{24}\text{H}_{26}\text{BF}_{17}\text{GeO}_2$  739.0731 (M- $\text{CH}_3$ ) $^+$ , found 739.0726,  $\Delta$  -0.7 ppm.

### 1-Benzyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **7**<sup>6</sup>



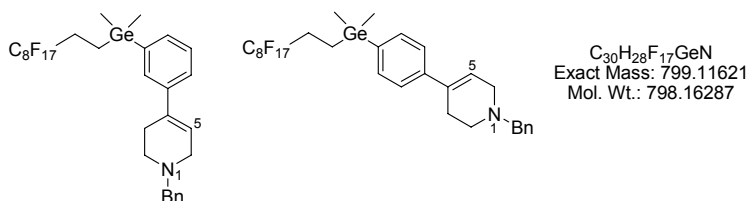
To a flask containing activated LiCl (896, 21.14 mmol) was added a solution of *l*-benzylpiperidin-4-one (1 g, 5.28 mmol) in THF (5 mL). The mixture was cooled to -78 °C and a solution of LHMDS (7.9 mL, 1M in hexane, 7.9 mmol) in THF (5 mL) was then added. The mixture was stirred for 50 min at -78 °C before adding a solution of *N*-phenyltrifluoromethane sulfonimide (2.25 g, 6.34 mmol) in THF (10 mL). The reaction was gradually allowed to warm to rt for 16 h (retaining the cooling bath). The reaction mixture was concentrated under reduced pressure. The residue was then dissolved in EtOAc and the organic layer was washed with brine (3  $\times$  10 mL), dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated *in vacuo* to give a pale yellow oil. This oil was absorbed onto a pad of neutral alumina, eluted with EtOAc/hexane, 1:9 and the eluant concentrated *in vacuo* to give vinyl triflate **7** as a clear pale yellow oil (1.44 g, 85 %).  $^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  2.34-2.47 (m, 2H,  $\text{C}^3\text{H}_2$ ), 2.72

(t,  $J = 5.7$  Hz, 2H, C<sup>2</sup>H<sub>2</sub>), 3.12 (d,  $J = 3.1$  Hz, 1H, C<sup>6</sup>H), 3.13 (d,  $J = 3.1$  Hz, 1H, C<sup>6</sup>H), 3.63 (s, 2H, NCH<sub>2</sub>Ph), 5.72-5.75 (m, 1H, C<sup>5</sup>H), 7.27-7.30 (m, 1H, ArH), 7.31-7.36 (m, 4H, ArH); <sup>19</sup>F NMR (376 MHz; CDCl<sub>3</sub>):  $\delta$  -73.9 (s).

### Thallium hydroxide<sup>7</sup>

According to the method of George, aqueous solution of 6 N thallium formate and 10 N sodium hydroxide were prepared using degassed water. To a solution of thallium formate (700  $\mu$ L, 6 N, 4.2 mmol) was added dropwise a solution of sodium hydroxide until the yellow precipitate was formed. The crystals were filtered and washed with cold degassed water. Thallium hydroxide was obtained as yellow needles (686 mg, 74%). A 10% aqueous solution was made up and used immediately.<sup>†</sup>

### 1-Benzyl-4-{3-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-dimethylgermanyl]phenyl}-1,2,3,6-tetrahydropyridine **8m** and 1-Benzyl-4-{4-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-dimethylgermanyl]phenyl}-1,2,3,6-tetrahydropyridine **8p**

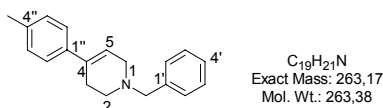


*Perfluoroarylgermane bronc esters* **5** (*m:p* ~2:1, 150 mg, 0.199 mmol), vinyl triflate **8** (221.9 mg, 0.597 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (34.4 mg, 0.0299 mmol) and anhydrous LiBr (34.5 mg, 0.398 mmol) were dissolved in freshly distilled THF (5 mL). The mixture was stirred for 10 min at rt before adding the freshly prepared solution of 10% (*w/w*) TIOH (1.32 mL, 0.597 mmol). The orange solution became cloudy. The mixture was stirred for 48 h at rt before adding CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and a saturated solution of NaHCO<sub>3</sub> (sat. aq., 10 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  10 mL), the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. The residue was then purified by FC (EtOAc/pentane, 1:19) to yield *perfluorogermyl styrene* **8** as a colourless oil (144.7 mg, 91 %, *m:p* ~2:1).  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2924, 2854, 1732, 1512, 1456, 1245, 799; <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  0.44 (s, 6H<sub>p</sub>, 2xCH<sub>3</sub>Ge), 0.45 (s, 6H<sub>m</sub>, 2xCH<sub>3</sub>Ge), 1.27-1.33 (m, 2H<sub>m</sub>+2H<sub>p</sub>, C<sub>8</sub>F<sub>17</sub>CH<sub>2</sub>CH<sub>2</sub>Ge), 2.00-2.04 (m, 2H<sub>p</sub>+2H<sub>m</sub>, C<sub>8</sub>F<sub>17</sub>CH<sub>2</sub>CH<sub>2</sub>Ge), 2.58-2.62 (m, 2H<sub>p</sub>+2H<sub>m</sub>, C<sup>3</sup>H<sub>2</sub>), 2.78-2.82 (m,

<sup>†</sup> The solution can be stored in the fridge, however a brown precipitate separates and the efficiency of the solution to promote the cross-coupling decreases with the age of the solution.

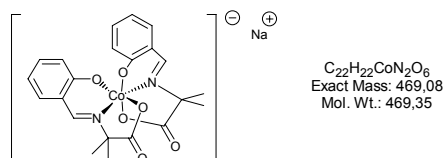
$2H_p+2H_m$ ,  $C^2H_2$ ), 3.23-3.26 (m,  $2H_p+2H_m$ ,  $C^6H_2$ ), 3.62 (s,  $2H_m$ ,  $NCH_2Ph$ ), 3.65 (s,  $2H_p$ ,  $NCH_2Ph$ ), 6.08 (m,  $1H_m$ ,  $C^5H$ ), 6.09 (m,  $1H_p$ ,  $C^5H$ ), 7.25-7.42 (m,  $9H_p+9H_m$ , ArH);  $^{13}C$  NMR (100 MHz;  $CDCl_3$ )  $\delta$  -4.1 (2 $q_p$ ), -4.06 (2 $q_m$ ), 5.1 ( $t_p$ ), 5.2 ( $t_m$ ), 26.9 (t,  $J = 23.9$  Hz,  $t_p+t_m$ ), 49.9 ( $t_p+t_m$ ), 53.3 ( $t_p+t_m$ ), 62.2 ( $t_p+t_m$ ), 68.0 ( $t_p+t_m$ ), 110.2 ( $s_p+s_m$ ), 110.6 ( $s_p+s_m$ ), 110.7 ( $s_p+s_m$ ), 110.8 (2 $s_p+2s_m$ ), 111.2 ( $s_p+s_m$ ), 111.3 ( $s_p+s_m$ ), 118.4 ( $s_p+s_m$ ), 122.2 (2d), 124.7 (2d), 127.2 (2d), 128.1 (2d), 128.3 (5d), 129.3 (3d), 129.8 (2d), 131.7 (2d), 133.1 (s), 135.2 (2s), 138.1 (s), 139.4 (s), 140.8 (2s), 144.9 (s);  $^{19}F$  NMR (376 MHz;  $CDCl_3$ ):  $\delta$  -126.2 (2 $s_p+2s_m$ , 4F), -123.3 (2 $s_p+2s_m$ , 4F), -122.6 (2 $s_p+2s_m$ , 4F), -121.7 (6 $s_p+6s_m$ , 12F), -115.8 (2 $s_p+2s_m$ , 4F), -80.6 (quintet,  $J = 9.3$  Hz, 6F, 3 $F_p+3F_m$ );  $m/z$  (EI $^+$ ) (rel. intensity) 799 (M $^+$ , 50), 708 (10), 352 (20), 233 (20), 91 (100); HRMS calc'd for  $C_{30}H_{28}F_{17}GeN$  799.1162, found 799.1146,  $\Delta$  -2.0 ppm.

### 1-Benzyl-4-(4-methylphenyl)-1,2,3,6-tetrahydropyridine 9



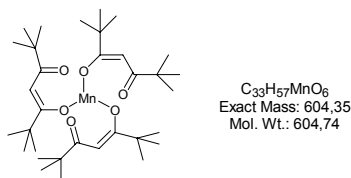
To a solution of pinacolato-4-tolylboronate (50.1 mg, 0.229 mmol),<sup>8</sup> vinyl triflate **7** (220.5 mg, 0.686 mmol),  $Pd(PPh_3)_4$  (39.7 mg, 0.0344 mmol) and anhydrous LiBr (39.8 mg, 0.458 mmol) were dissolved in freshly distilled THF (5 mL). The mixture was stirred for 10 min at rt before adding the freshly prepared solution of 10% (w/w) TIOH (1.52 mL, 0.687 mmol). The orange solution became cloudy. The mixture was stirred for 48 h at rt before adding  $CH_2Cl_2$  (5 mL) and a saturated solution of  $NaHCO_3$  (sat. aq., 10 mL). The aqueous phase was extracted with  $CH_2Cl_2$  ( $3 \times 10$  mL), the combined organic layers were dried ( $Na_2SO_4$ ), filtered and concentrated *in vacuo*. The residue was then purified by FC (EtOAc/pentane, 1:19) to yield *tetrahydropyridine 9* as a colourless oil (54.2 mg, 90 %).  $\nu_{max}$  (neat)/ $cm^{-1}$  3027, 2919, 2799, 1688, 1516, 1454, 1126, 798;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  2.34 (3H, s,  $CH_3$ ), 2.57 (2H, m,  $C^3H_2$ ), 2.74 (2H, t,  $J=6.0$ ,  $C^2H_2$ ), 3.19 (2H, dd,  $J=6.0$ , 3.0,  $C^6H_2$ ), 3.67 (2H, s,  $CH_2-Ph$ ), 6.04 (1H, m,  $C^5H$ ), 7.13 (2H, m,  $C^{3''}H + C^{5''}H$ ), 7.28-7.31 (3H,  $C^{2''}H + C^{6''}H + C^{4''}H$ ), 7.33-7.35 (2H,  $C^2H + C^6H$ ), 7.39-7.42 (2H,  $C^3H + C^5H$ );  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  21.0 (q), 27.3 (t), 49.9 (t), 53.2 (t), 62.6 (t), 120.9 (d), 124.8 (2d), 127.1 (d), 128.3 (2d), 128.9 (2d), 129.2 (2d), 134.8 (s), 136.6 (s), 138.0 (s), 138.1 (s); MS (CI $^+$ ):  $m/z$  264 (M+H $^+$ , 100), 186 (1), 172 (6), 145 (2), 108 (3), 91 (4); HRMS (CI $^+$ ): calc'd for  $C_{19}H_{22}N$  264.1752, found 264.1757,  $\Delta$  1.8 ppm.

### Sodium-bis[*N*-salicylidene-2-aminoisobutyrate]cobaltate(III): Co(sdmg)<sub>3</sub><sup>9</sup>



According to the method of Carreira,<sup>9</sup> NaOH (202 mg, 5.0 mmol) was dissolved in absolute EtOH (10 mL). Salicylaldehyde (1.1 mL, 10.0 mmol) was then added followed by 2-aminoisobutyric acid (1.037 mg, 10.1 mmol). The thick yellow suspension was cooled to 0 °C. A precooled solution (0 °C) of cobalt nitrate (1.47g, 5.0 mmol) in absolute EtOH (10 mL) was added to the suspension. The orange suspension was then stirred 20 min at 0 °C before adding hydrogen peroxide (35% solution, 7mL) dropwise over 20 min. The reaction turned dark brown and a gas was evolved. The reaction mixture was stirred at 0 °C for 2 h and then warmed to RT overnight. The resulting dark solution was filtered, the solvent was removed *in vacuo* and the residue was co-evaporated with MeOH (3 × 10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The resulting brown residue was triturated in Et<sub>2</sub>O (10 mL) for 3 h and the residue was dried *in vacuo* at 70 °C for 16 h to give the active catalyst *Co(sdmg)*<sub>3</sub> as a fine dark brown powder (2.49 g, 100%).

### Tris(dipivaloylmethanato)manganese (III): Mn(dpm)<sub>3</sub><sup>10</sup>

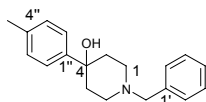


According to the method of Carreira,<sup>10</sup> 2,2,6,6-tetramethylhept-3,5-dione (1.3 mL, 6.1 mmol) was added to a solution of manganese(II) acetate tetrahydrate (500 mg, 2.0 mmol) in degassed MeOH (4.5 mL). The solution turned yellow. A solution of sodium hydroxide (245 mg in 1.25 mL of degassed water) was then added and a solid immediately precipitated. The solution was diluted with degassed MeOH (5.5 mL) and the mixture was stirred at RT for 20 h. A green-brown precipitate (1.72 g) was filtered off and dried *in vacuo* at 60 °C for 4 h. This was then dissolved in hot *i*-PrOH (15 mL) and upon cooling, followed by addition of water (3 mL), a precipitate was formed. The precipitate was filtered off, suspended in pentane (10 mL) and filtered to remove some brown-red impurities. The pentane was then removed *in vacuo* and the resulting olive-green solid was dried under high vacuum for 10 h to give *Mn(dpm)*<sub>3</sub> as a dark green powder (755 mg, 62%).  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2964, 2867, 1592, 1570, 1497, 1402, 1358, 1223, 1135, 872; MS (EI+): *m/z* 604 (M+H, 15), 421 (dimer+H, 100), 368 (63), 238



(22), 127 (31); HRMS (EI+): calculated for C<sub>22</sub>H<sub>38</sub>O<sub>4</sub>Mn 421. 2151 (dimer), found 421.2166  
Δ -3.6 ppm.

### 1-Benzyl-4-(4-methylphenyl)piperidin-4-ol **11**



C<sub>19</sub>H<sub>23</sub>NO  
Exact Mass: 281.18  
Mol. Wt.: 281.39

*Method 1: manganese(III)-catalysed hydration (Table 1, entry 1):*

To a 2-neck flask containing *Mn(dpm)*<sub>3</sub> (1 mg, 0.0017 mmol) and *tetrahydropyridine 9* (20 mg, 0.076 mmol) under an oxygen atmosphere was added cold (0 °C) *i*-PrOH (350 μL), CH<sub>2</sub>Cl<sub>2</sub> (50 μL) and finally phenylsilane (19 μL, 0.153 mmol). The reaction mixture was stirred at 0 °C for 3 h. A saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (1 mL) was then added and the mixture was stirred at RT for 2 h. Brine (2 mL) was added and the mixture was extracted with EtOAc (3 × 2 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. The residue was then triturated with a saturated aqueous solution of sodium pyrophosphate for 14 h. Brine (2 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 2 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. The residue was purified by FC (EtOAc/pentane, 3:7) to give *alcohol 11* as a colourless oil (19 mg, 88 %). *R*<sub>f</sub> 0.36 (*i*-PrOH/CHCl<sub>3</sub>, 1:9). *v*<sub>max</sub> (neat)/cm<sup>-1</sup> 3361 (br), 2923, 2853, 1634, 1456, 1133, 698; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.77 (2H, dd, *J*<sub>app</sub>=14.0, 2.5, C<sup>3</sup>H<sub>eq2</sub>+ C<sup>5</sup>H<sub>eq2</sub>), 2.19 (2H, td, *J*<sub>app</sub>=13.5, 4.5, C<sup>3</sup>H<sub>ax2</sub>+ C<sup>5</sup>H<sub>ax2</sub>), 2.37 (3H, s, CH<sub>3</sub>), 2.51 (2H, td, *J*<sub>app</sub>=12.0, 2.0, C<sup>2</sup>H<sub>eq2</sub>+ C<sup>6</sup>H<sub>eq2</sub>), 2.81 (2H, m, C<sup>2</sup>H<sub>ax2</sub>+ C<sup>6</sup>H<sub>ax2</sub>), 3.62 (2H, s, CH<sub>2</sub>-Ph), 7.20 (2H, d, *J*=8.0, C<sup>3''</sup>H + C<sup>5''</sup>H), 7.27-7.32 (1H, C<sup>4'</sup>H), 7.34-7.48 (4H, C<sup>2'</sup>H + C<sup>3'</sup>H + C<sup>5'</sup>H + C<sup>6'</sup>H), 7.43 (2H, d, *J*=8.0, C<sup>2''</sup>H + C<sup>6''</sup>H), 1H missing (OH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 21.0 (q), 38.6 (2t), 49.6 (2t), 63.3 (t), 71.2 (s), 124.5 (2d), 127.0 (d), 128.2 (2d), 129.0 (2d), 129.2 (2d), 136.6 (s), 138.5 (s), 145.6 (s); MS (CI+): *m/z* 282 (M+H<sup>+</sup>, 100), 264 (22), 190 (12), 146 (5), 108 (5), 91 (6); HRMS (CI+): calculated for C<sub>19</sub>H<sub>24</sub>NO 282.1858, found 282.1859, Δ 0.4 ppm.

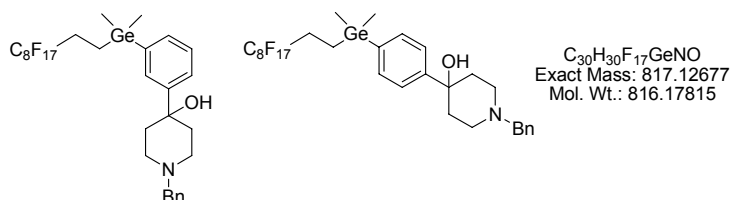
*Method 2: cobalt(III)-catalysed hydration (Table 1, entry 2):*

To a 2-neck flask containing *Co(sdmg)*<sub>3</sub> (2.7 mg, 0.0057 mmol) under an oxygen atmosphere was added EtOH (1.8 mL), then a solution of *tetrahydropyridine 9* (30mg, 0.114 mmol) in

EtOH/CH<sub>2</sub>Cl<sub>2</sub> (1:1, 480 μL) and finally phenylsilane (28 μL, 0.228 mmol). The reaction mixture was stirred at RT under an oxygen atmosphere for 3 d. A saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2 mL) was then added and the mixture was stirred at RT for 2 h. Brine (3 mL) was added and the mixture was extracted with EtOAc (3 × 3 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. The residue was purified by FC (EtOAc/pentane, 3:7) to give *alcohol 11* as a colourless oil (25 mg, 78 %). Spectroscopic data as described above.

**1-Benzyl-4-{3-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)-dimethylgermanyl]phenyl}-piperidin-4-ol 10m** and

**1-Benzyl-4-{4-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)-dimethylgermanyl]phenyl}-piperidin-4-ol 10p**

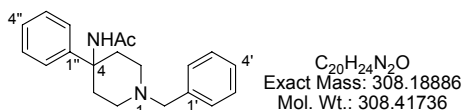


*Table 1, entry 3*

Using *method 2*, to a 2-neck flask containing *Co(sdmg)<sub>3</sub>* (1.5 mg, 0.0033 mmol) under an oxygen atmosphere was added EtOH (2 mL), then a solution of *perfluorogermyl styrene 8* (52.1 mg, 0.065 mmol) in EtOH/CH<sub>2</sub>Cl<sub>2</sub> (1:1, 500 μL) and finally phenylsilane (14.1 mg, 0.13 mmol, 9 μL). The reaction mixture was stirred at rt under an oxygen atmosphere for 24 h. A saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2 mL) was then added and the mixture was stirred at rt for 2 h. Brine (3 mL) was added and the mixture was extracted with EtOAc (3 × 3 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. The residue was purified by FC (EtOAc/pentane, 3:7) to give *alcohols 10* as a colourless oil (32.5 mg, 61 %, *m:p* ~2:1).  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 3436 (br), 3028, 2933, 2833, 1611, 1511, 1245, 1042, 818; <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  0.44 (s, 6H, 2xCH<sub>3</sub>Ge), 0.45 (s, 6H, 2xCH<sub>3</sub>Ge), 1.10-1.27 (*m*, 2H<sub>*m*</sub>+2H<sub>*p*</sub>, C<sub>8</sub>F<sub>17</sub>CH<sub>2</sub>CH<sub>2</sub>Ge), 1.74 (d, *J* = 12.0 Hz, 4H, C<sup>3</sup>H<sub>2eq</sub>+ C<sup>5</sup>H<sub>2eq</sub>), 2.00-2.14 (*m*, 2H<sub>*p*</sub>+2H<sub>*m*</sub>, C<sub>8</sub>F<sub>17</sub>CH<sub>2</sub>CH<sub>2</sub>Ge), 2.20 (td, *J* = 12.0, 4.4 Hz, 4H, C<sup>3</sup>H<sub>2ax</sub>+ C<sup>5</sup>H<sub>2ax</sub>), 2.51 (td, *J* = 11.1, 4.4 Hz, 4H, C<sup>2</sup>H<sub>2ax</sub>+ C<sup>6</sup>H<sub>2ax</sub>), 2.83 (d, *J* = 11.1 Hz, 4H, C<sup>2</sup>H<sub>2eq</sub>+ C<sup>6</sup>H<sub>2eq</sub>), 3.62 (s, 2H<sub>*p*</sub>+2H<sub>*m*</sub>, NCH<sub>2</sub>Ph), 7.28 (dd, *J* = 6.4, 2.0 Hz, 2H, ArH<sub>*p*</sub>), 7.31-7.39 (*m*, 12H, ArH), 7.45-7.51 (*m*, 2H, ArH), 7.58-7.61 (*m*, 2H, ArH); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>)  $\delta$  -4.02 (2q<sub>*p*</sub>), -4.0

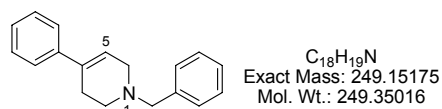
(2q<sub>m</sub>), 5.2 (t<sub>p</sub>+t<sub>m</sub>), 26.8 (t, *J* = 23.5 Hz, t<sub>p</sub>+t<sub>m</sub>), 38.4 (2t<sub>p</sub>+2t<sub>m</sub>), 49.4 (2t<sub>p</sub>+2t<sub>m</sub>), 63.2 (t<sub>p</sub>+t<sub>m</sub>), 71.4 (t<sub>p</sub>+t<sub>m</sub>), 110.2 (t<sub>p</sub>+t<sub>m</sub>), 110.6 (t<sub>p</sub>+t<sub>m</sub>), 110.7 (t<sub>p</sub>+t<sub>m</sub>), 110.8 (2t<sub>p</sub>+2t<sub>m</sub>), 111.2 (t<sub>p</sub>+t<sub>m</sub>), 111.3 (t<sub>p</sub>+t<sub>m</sub>), 118.4 (t<sub>p</sub>+t<sub>m</sub>), 125.2 (2d), 127.2 (2d), 127.7 (2d), 128.2 (4d), 129.0 (2d), 129.3 (4d), 131.7 (2d), 138.1 (2s), 139.6 (2s), 148.1 (2s); <sup>19</sup>F NMR (376 MHz; CDCl<sub>3</sub>): δ -126.2 (2s<sub>p</sub>+2s<sub>m</sub>, 4F), -123.3 (2s<sub>p</sub>+2s<sub>m</sub>, 4F), -122.7 (2s<sub>p</sub>+2s<sub>m</sub>, 4F), -121.9 (6s<sub>p</sub>+6s<sub>m</sub>, 12F), -115.8 (2s<sub>p</sub>+2s<sub>m</sub>, 4F), -80.8 (quintet, *J* = 9.6 Hz, 6F, 3F<sub>p</sub>+3F<sub>m</sub>); *m/z* (EI<sup>+</sup>) (rel. intensity) 817 (M<sup>+</sup>, 60), 799 (50), 726 (20), 370 (20), 146 (50), 91 (100), HRMS calc'd for C<sub>30</sub>H<sub>30</sub>F<sub>17</sub>GeNO 817.1268, found 817.1249, Δ -2.3 ppm.

### *N*-(1-Benzyl-4-phenylpiperidin-4-yl)acetamide **1**



To a suspension of *alcohol* **10** (20 mg, 0.0245 mmol) in acetonitrile (100 μL) at 0 °C was added *c.*H<sub>2</sub>SO<sub>4</sub> (25 μL) dropwise. The reaction mixture was warmed to rt over 19 h before being poured onto ice and basified with sat. aq. NH<sub>4</sub>OH until pH = 10 was attained. The mixture was extracted with EtOAc (3 × 2 mL) and the combined organic extracts were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. The residue was purified by FC (*i*-PrOH/CHCl<sub>3</sub>, 1:19) to give *acetamide* **1** as a white solid (7.5 mg, 100 %). R<sub>f</sub> 0.30 (*i*-PrOH/CHCl<sub>3</sub>, 1:19); ν<sub>max</sub> (neat)/cm<sup>-1</sup> 3294 (br), 3061, 2941, 2810, 1651, 1548, 1368, 1303, 738; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.03 (3H, s, CH<sub>3</sub>-CO), 2.11-2.39 (6H, C<sup>2</sup>H<sub>eq2</sub>+ C<sup>3</sup>H<sub>2</sub>+ C<sup>5</sup>H<sub>2</sub>+ C<sup>6</sup>H<sub>eq2</sub>), 2.81 (2H, m, C<sup>2</sup>H<sub>ax2</sub>+ C<sup>6</sup>H<sub>ax2</sub>), 3.57 (2H, s, CH<sub>2</sub>-Ph), 5.67 (1H, brs, NH), 7.21-7.45 (10H, C<sup>2'</sup> to 6'<sup>'</sup>H + C<sup>2''</sup> to 6''<sup>'</sup>H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 24.4 (q), 35.7 (2t), 49.7 (2t), 56.5 (s), 63.2 (t), 125.1 (2d), 126.7 (d), 127.1 (d), 128.3 (2d), 128.3 (2d), 129.1 (2d), 138.4 (s), 145.8 (s), 169.1 (s); MS (CI<sup>+</sup>): *m/z* 309 (M+H<sup>+</sup>, 100), 248 (6), 219 (10), 176 (4), 158 (8), 79 (9); HRMS (CI<sup>+</sup>): calculated for C<sub>20</sub>H<sub>25</sub>N<sub>2</sub>O 309.1967, found 309.1927, Δ 2.0 ppm; mp=172.9-173.7°C.

### 1-Benzyl-1,2,3,6-tetrahydro-4-phenylpyridine **2**<sup>11</sup>



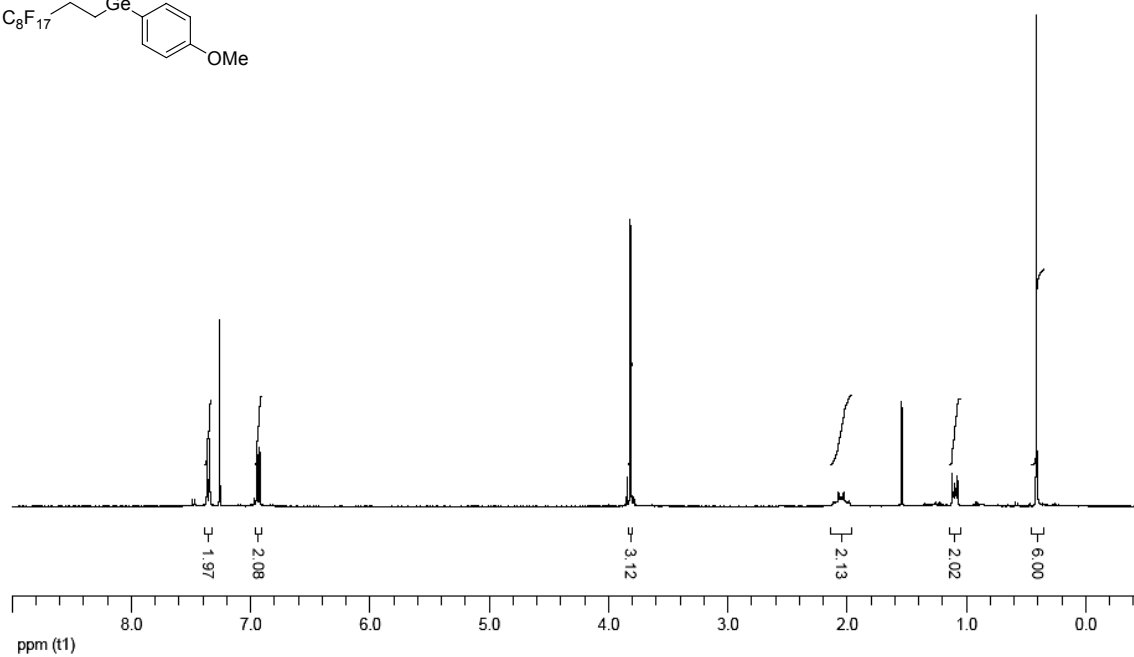
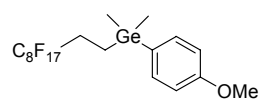
To a solution of *perfluorogermyl styrene* **8** (45 mg, 0.0564 mmol) in TFA (10 mL) was stirred at rt for 16 h. The reaction mixture was basified with sat. aq. NH<sub>4</sub>OH until pH = 10 and

extracted with EtOAc (3 × 2 mL) and the combined organic extracts were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. The residue was purified by FC (EtOAc/hexane, 1:6) to give *phenylpyridine 2* as a yellow oil (14.0 mg, 100 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.59 (m, 2H, CH<sub>2</sub>), 2.75 (m, 2H, CH<sub>2</sub>), 3.20 (m, CH<sub>2</sub>), 3.68 (s, 2H, NCH<sub>2</sub>Ph), 6.06 (m, 1H, CH), 7.20-7.41 (m, 10H, ArH); 28.0 (t), 50.1 (t), 53.4 (t), 62.7 (t), 122.1 (d), 124.9 (2d), 126.9 (2d), 127.0 (2d), 128.19 (d), 128.23 (d), 129.3 (2d), 134.9 (s), 138.3 (s), 141.2 (s); *m/z* (EI<sup>+</sup>) (rel. intensity) 249 (M<sup>+</sup>, 80), 172 (20), 158 (15), 91 (100); HRMS calc'd for C<sub>18</sub>H<sub>19</sub>N 249.1517, found 249.1511, Δ -2.6 ppm.

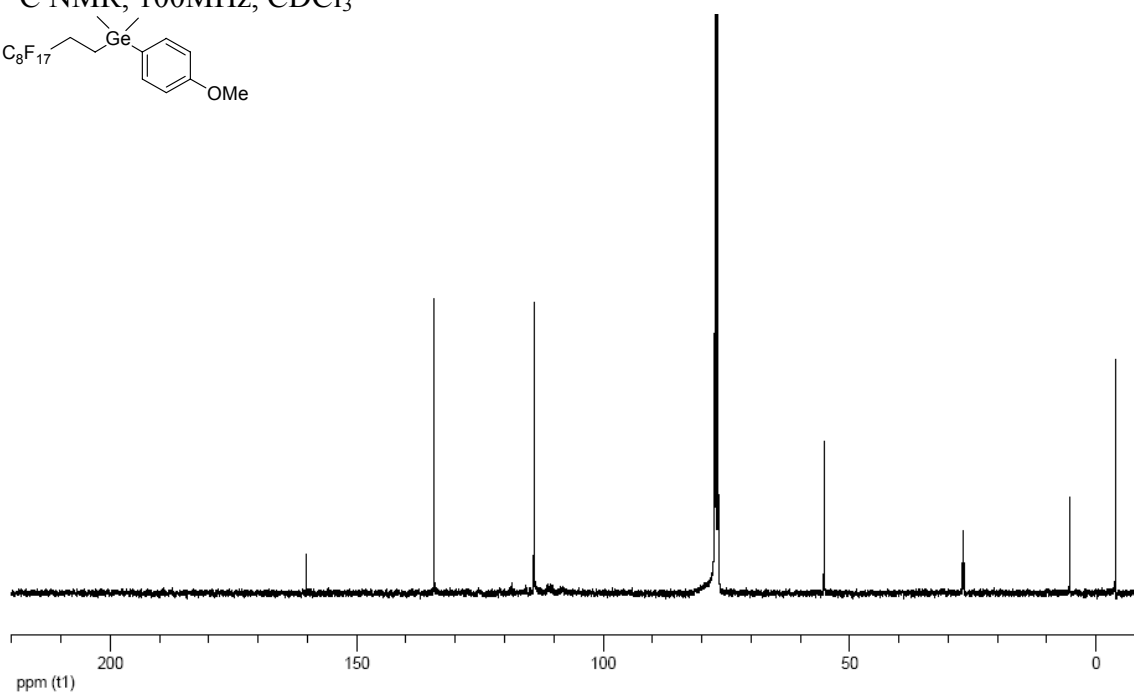
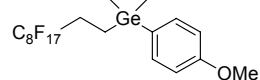
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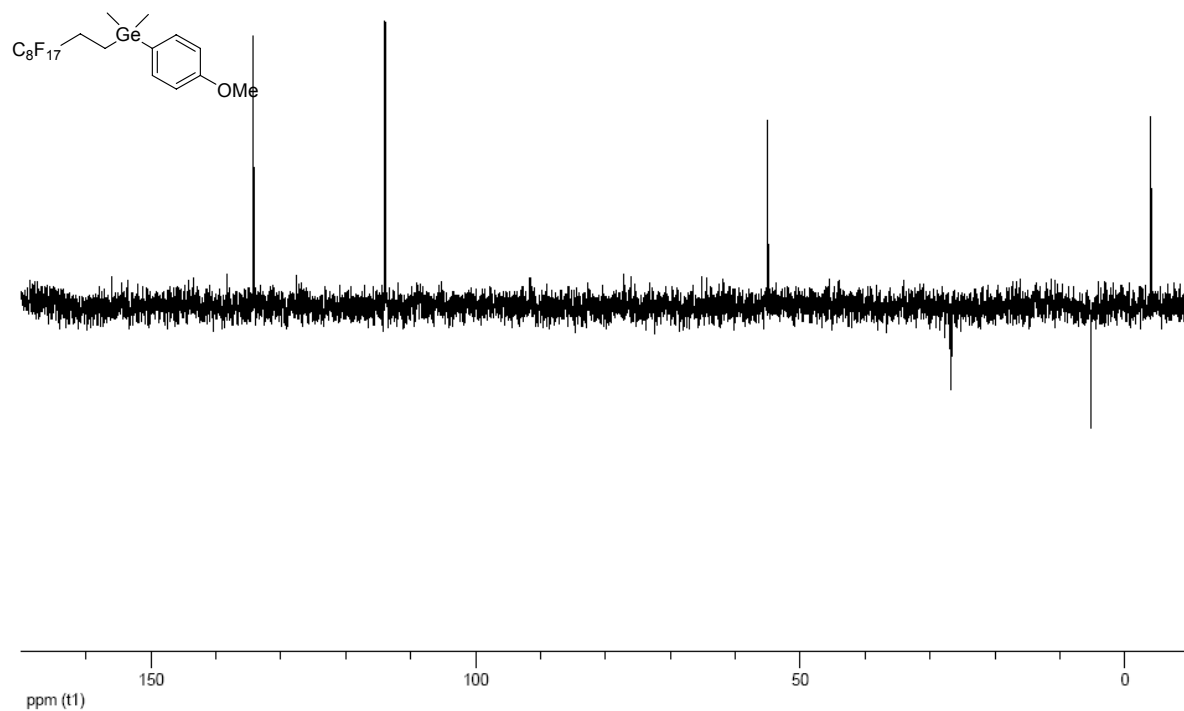
$^1\text{H}$  NMR, 400MHz,  $\text{CDCl}_3$



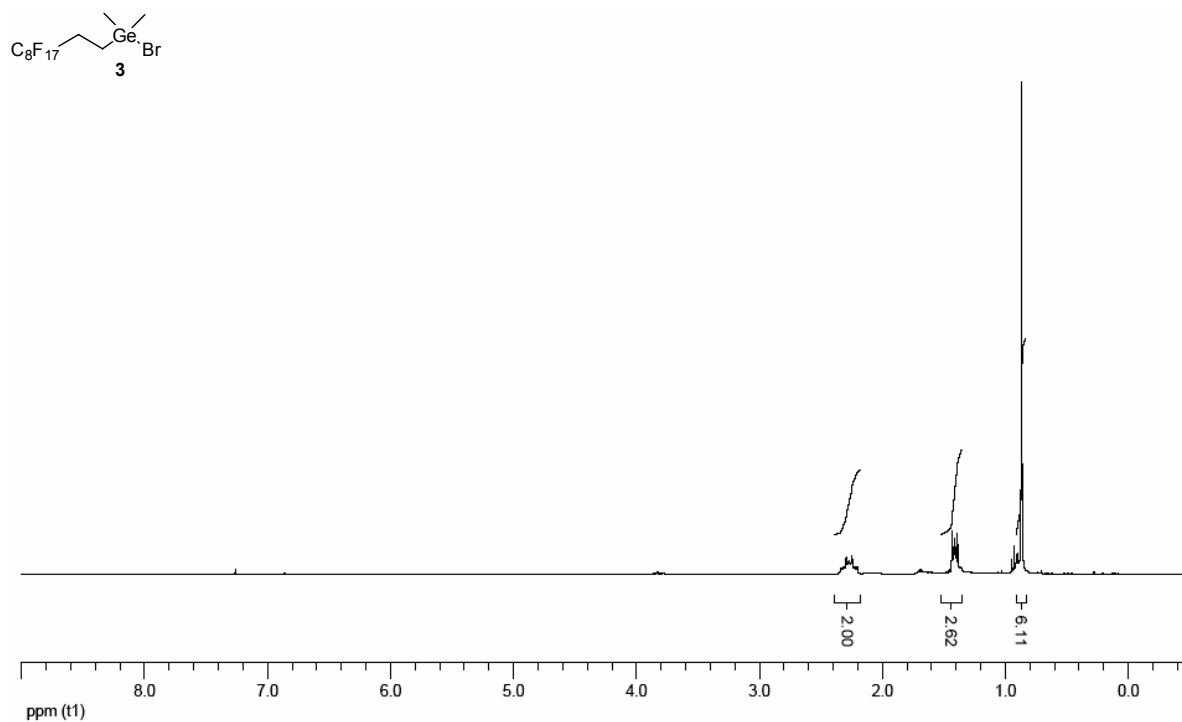
$^{13}\text{C}$  NMR, 100MHz,  $\text{CDCl}_3$



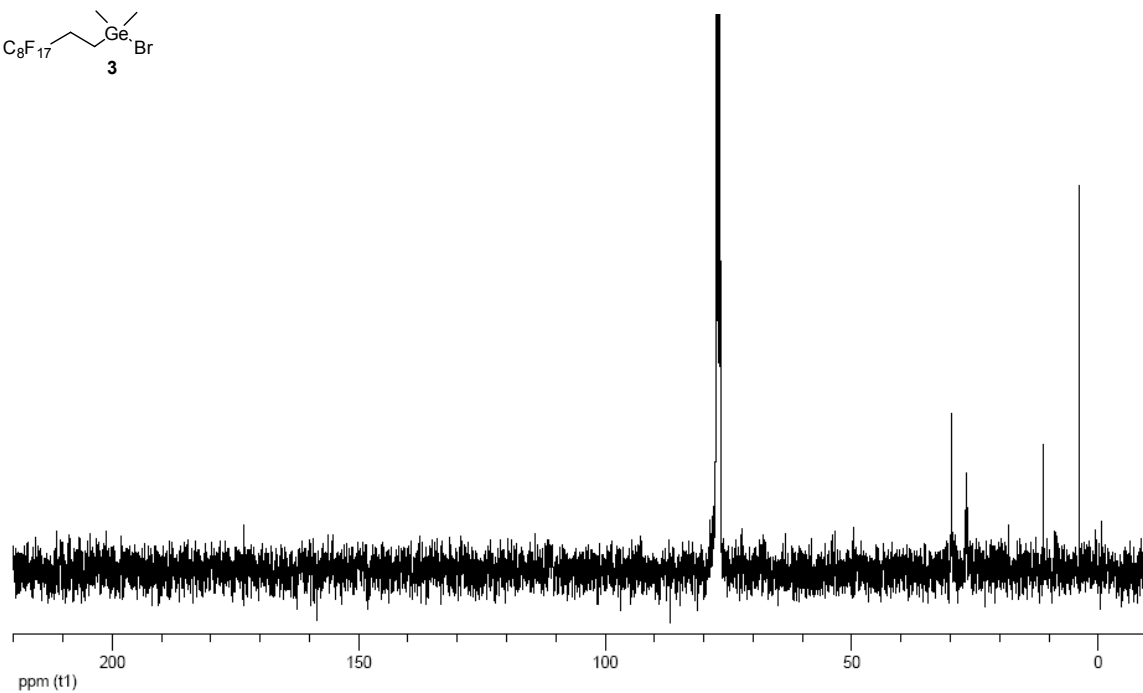
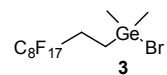
DEPT 135, 100MHz, CDCl<sub>3</sub>



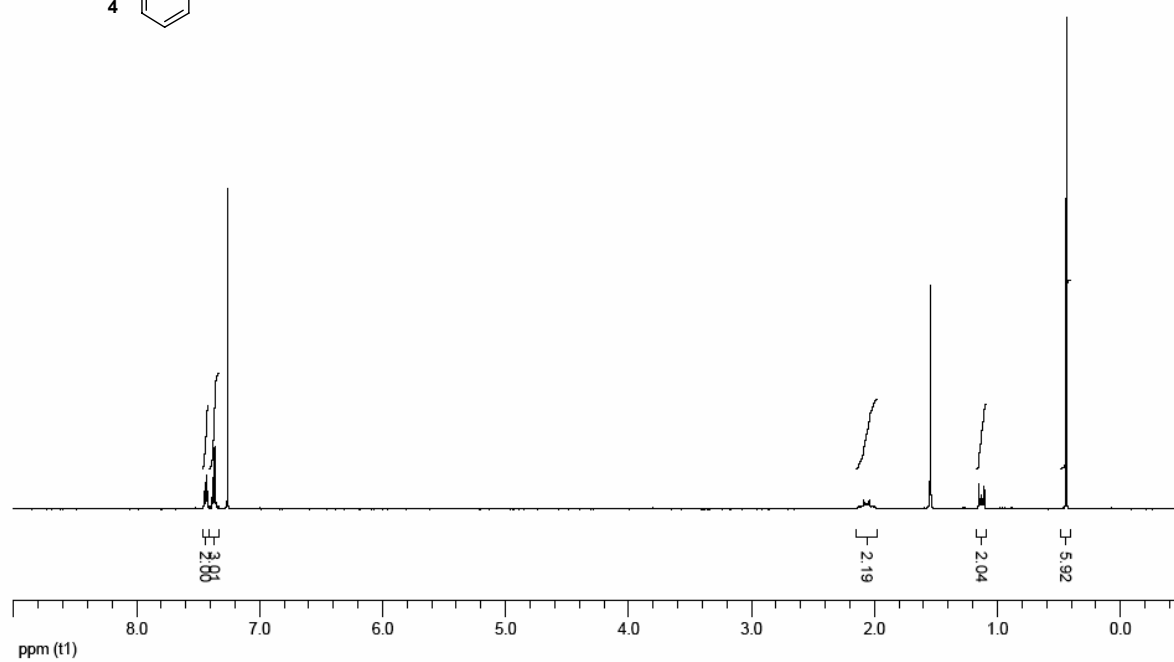
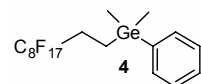
<sup>1</sup>H NMR, 400MHz, CDCl<sub>3</sub>



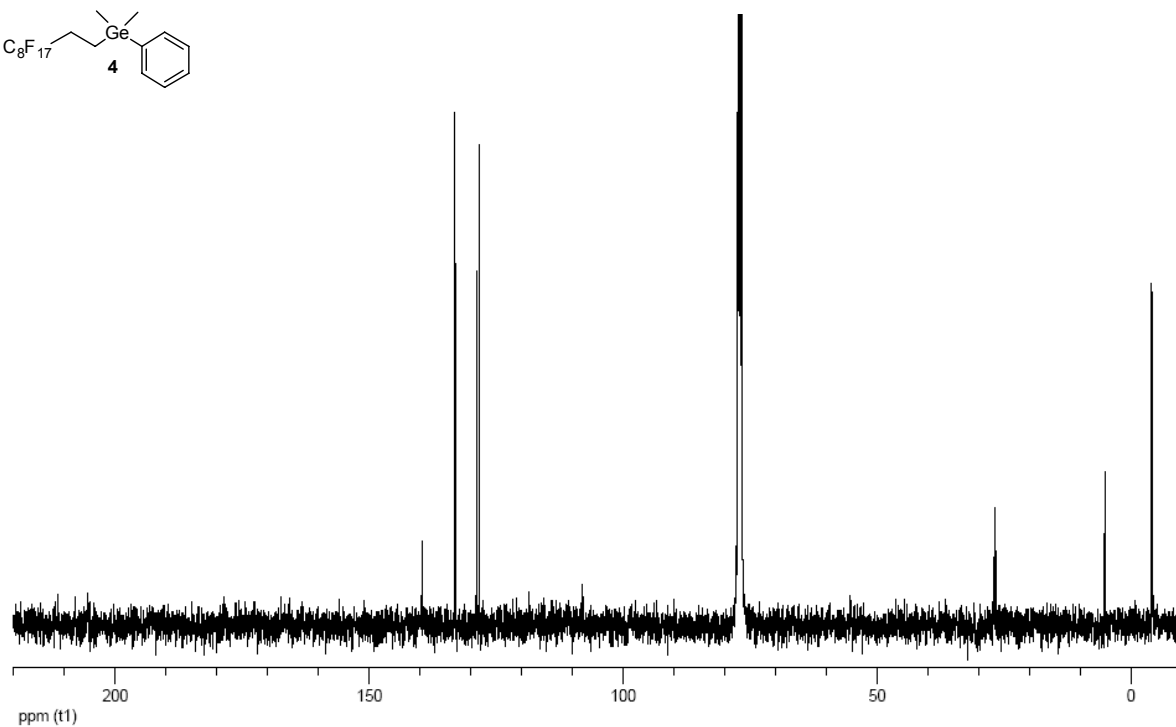
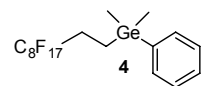
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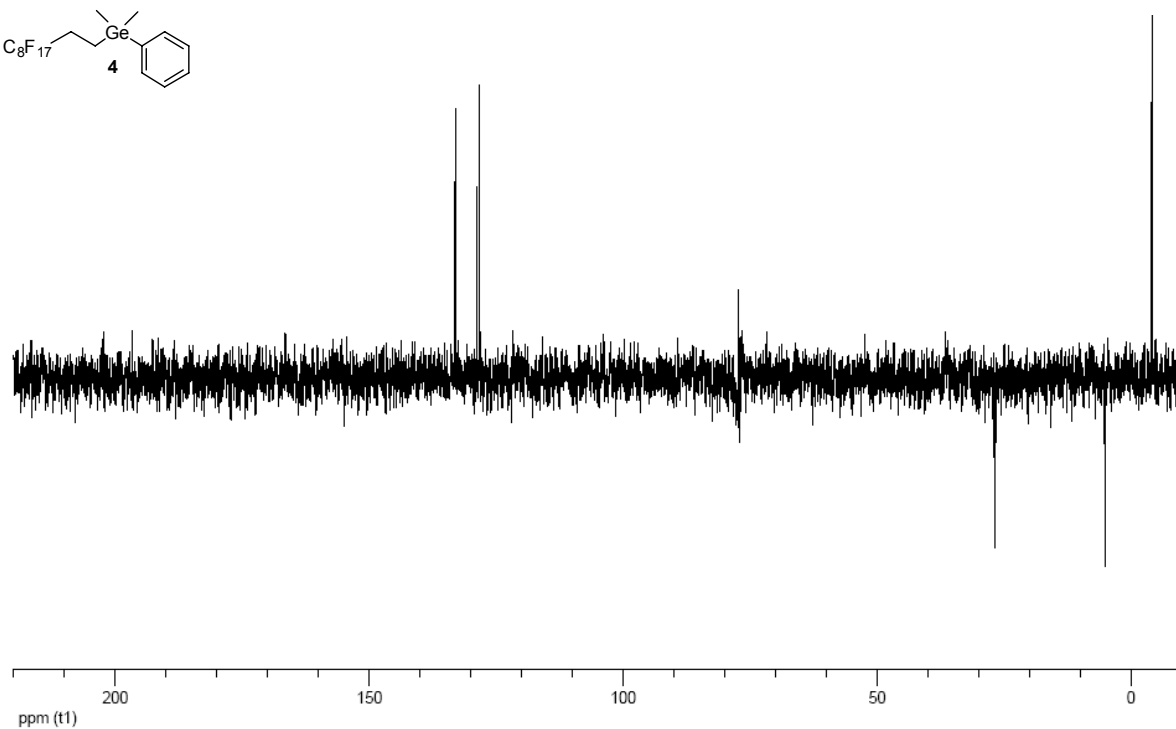
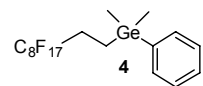
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$^{13}\text{C}$  NMR, 100MHz,  $\text{CDCl}_3$

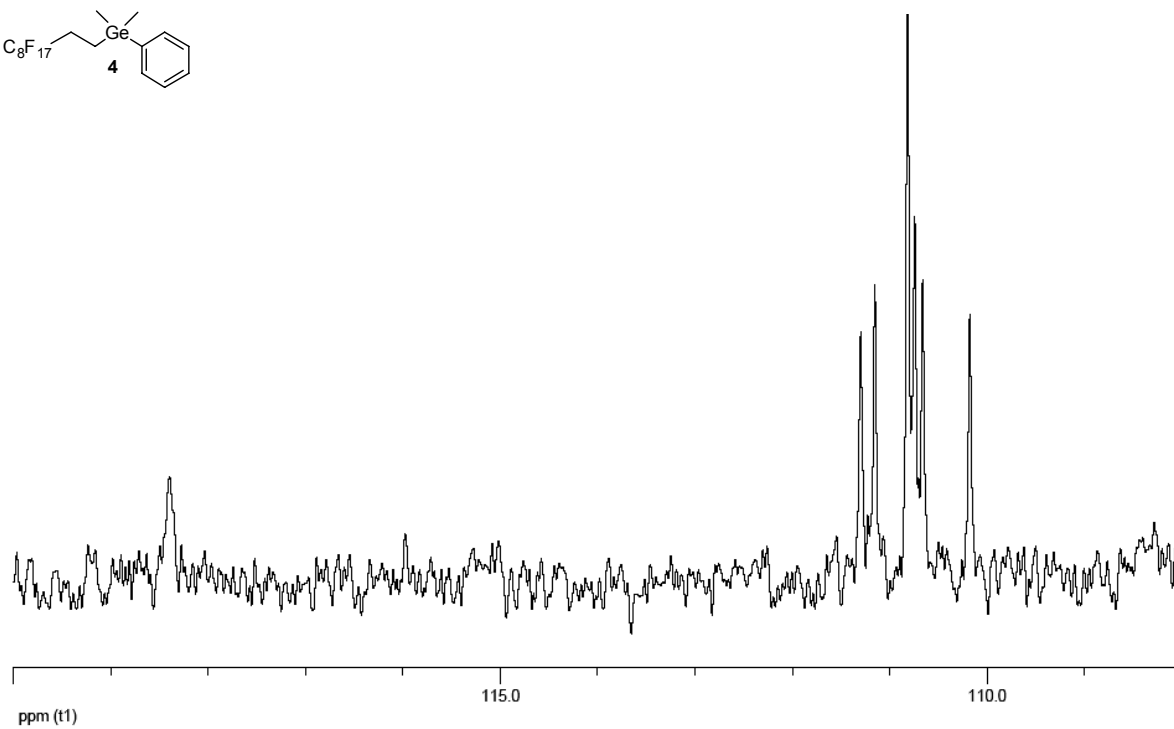
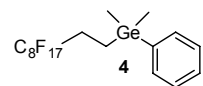


DEPT 135, 100MHz,  $\text{CDCl}_3$

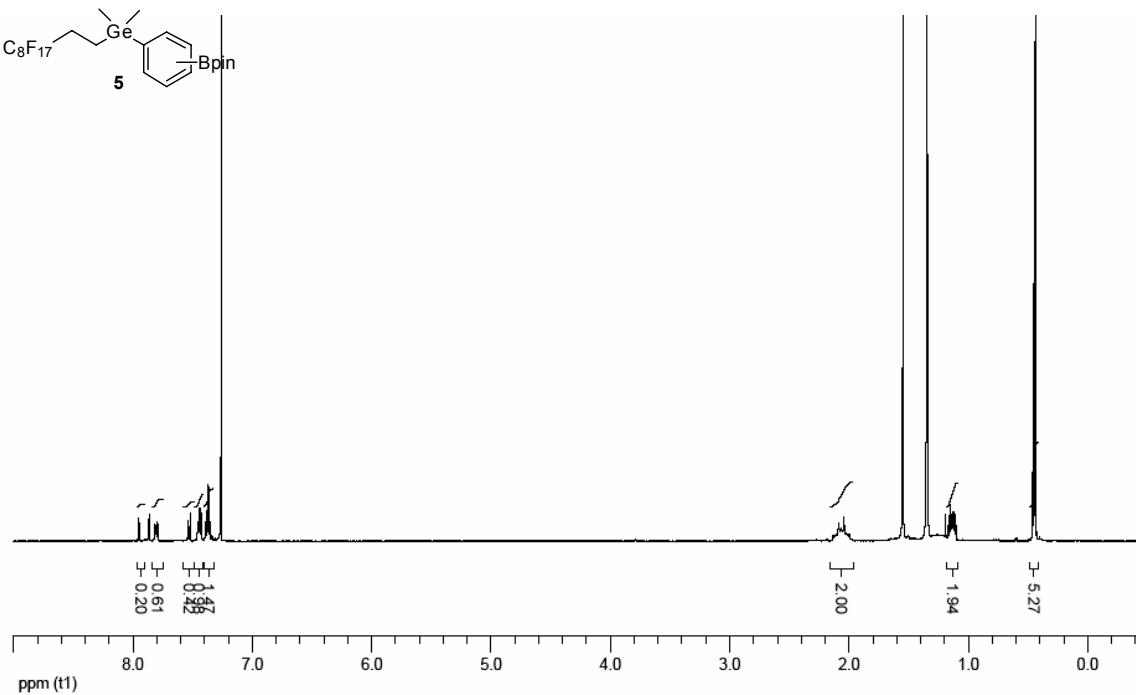
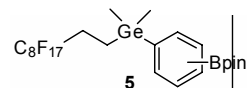




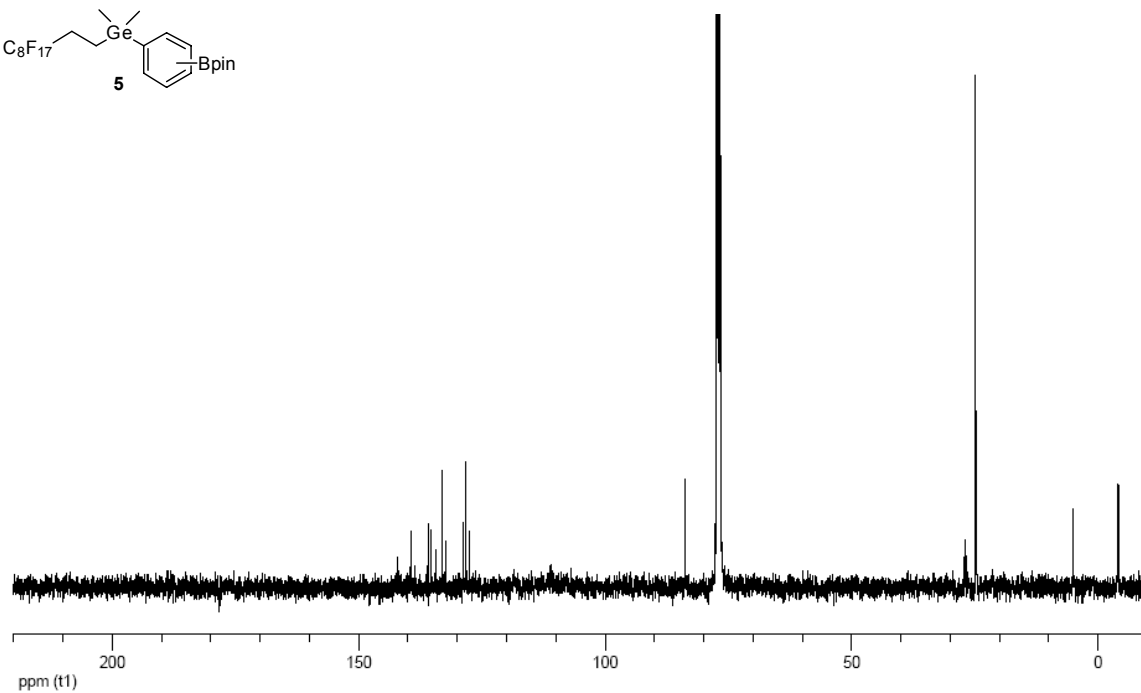
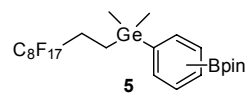
$^{13}\text{C}\{^{19}\text{F at -121 ppm}\}$  NMR, 100MHz,  $\text{CDCl}_3$



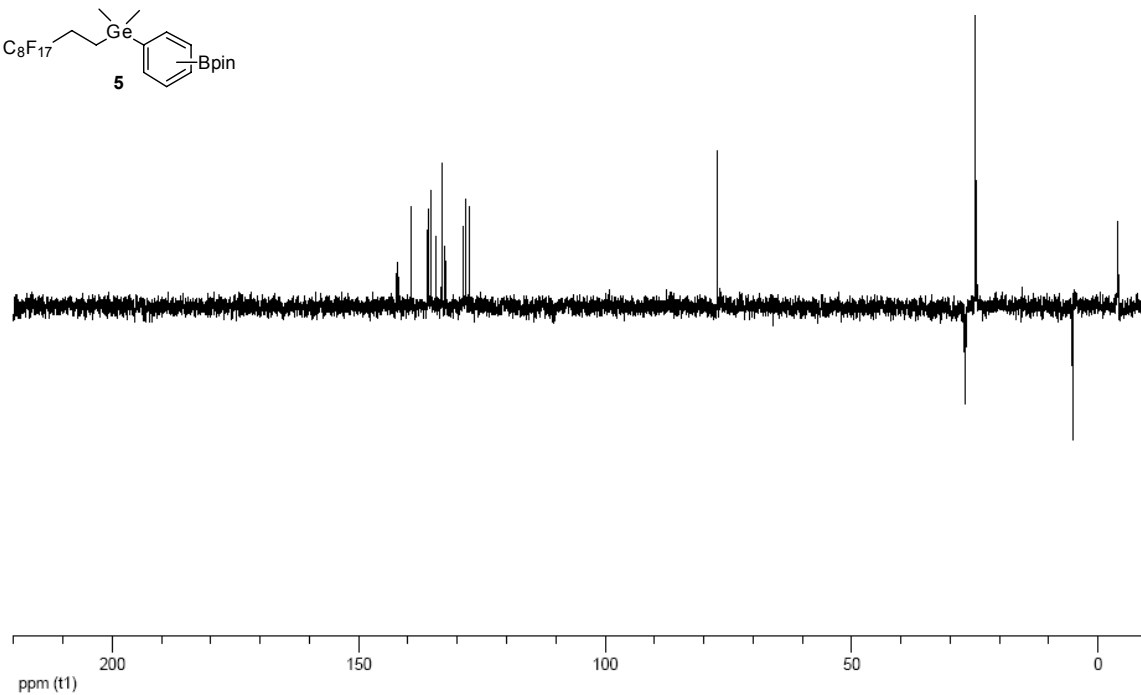
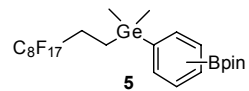
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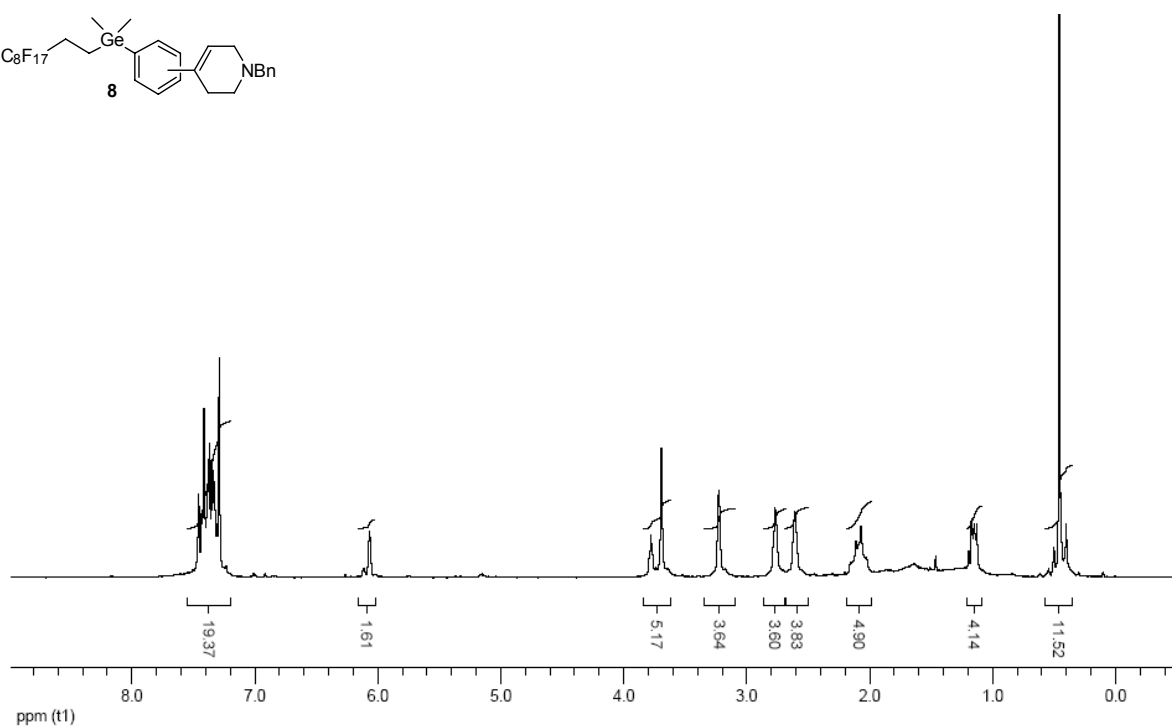
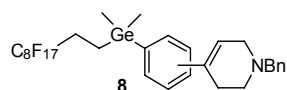
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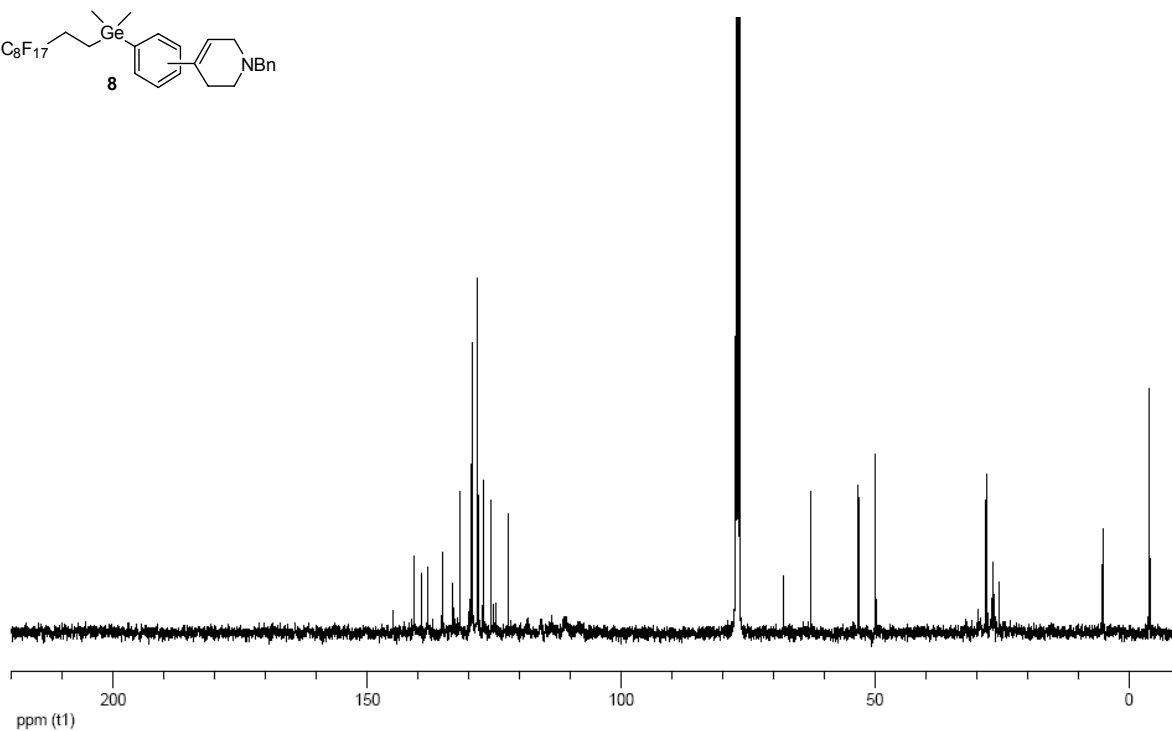
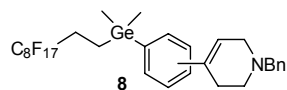
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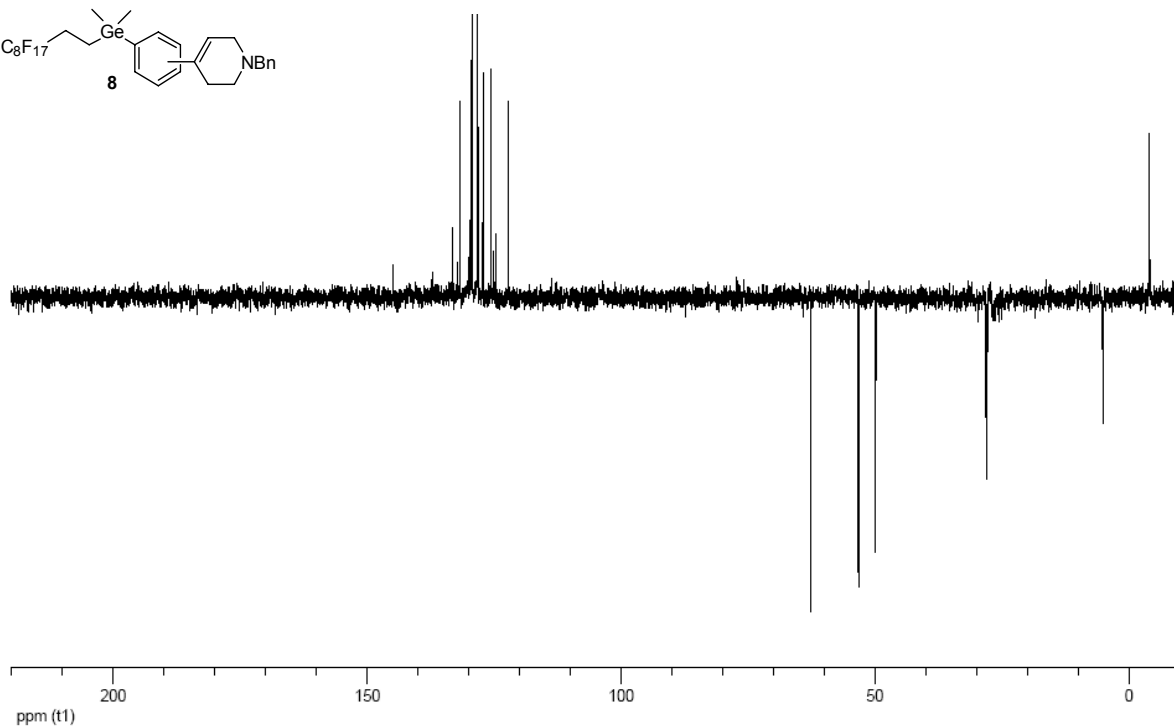
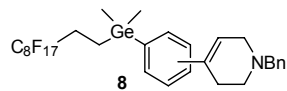
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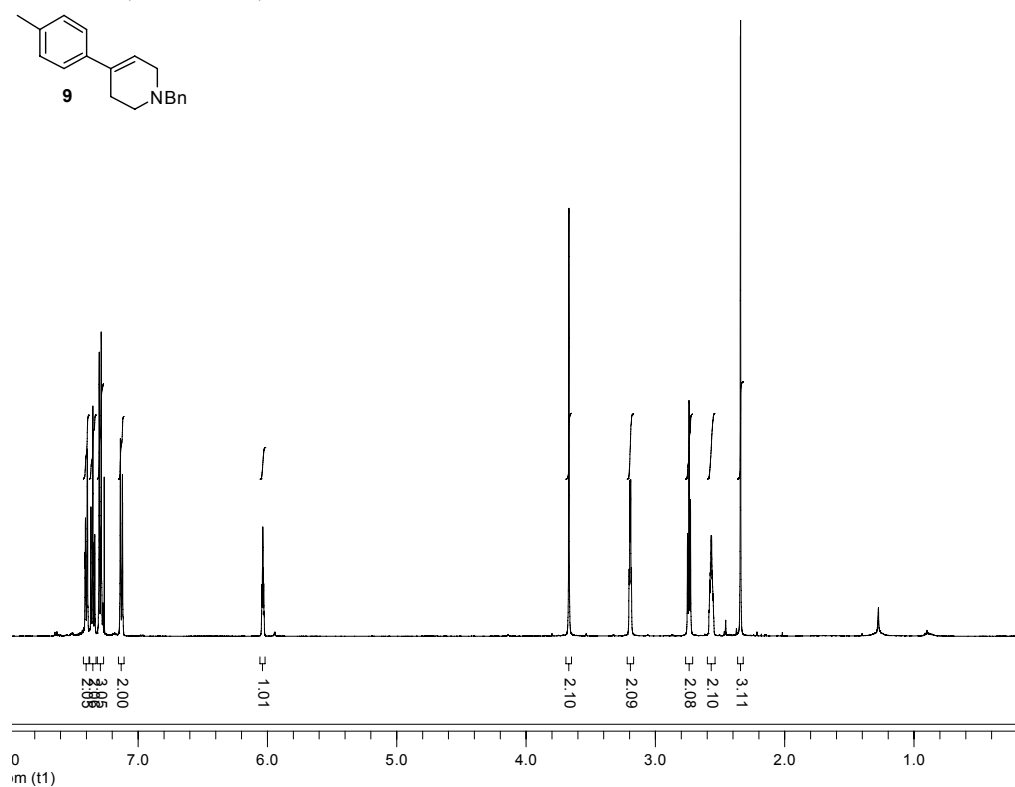
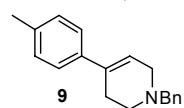
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DEPT 135, 100MHz, CDCl<sub>3</sub>

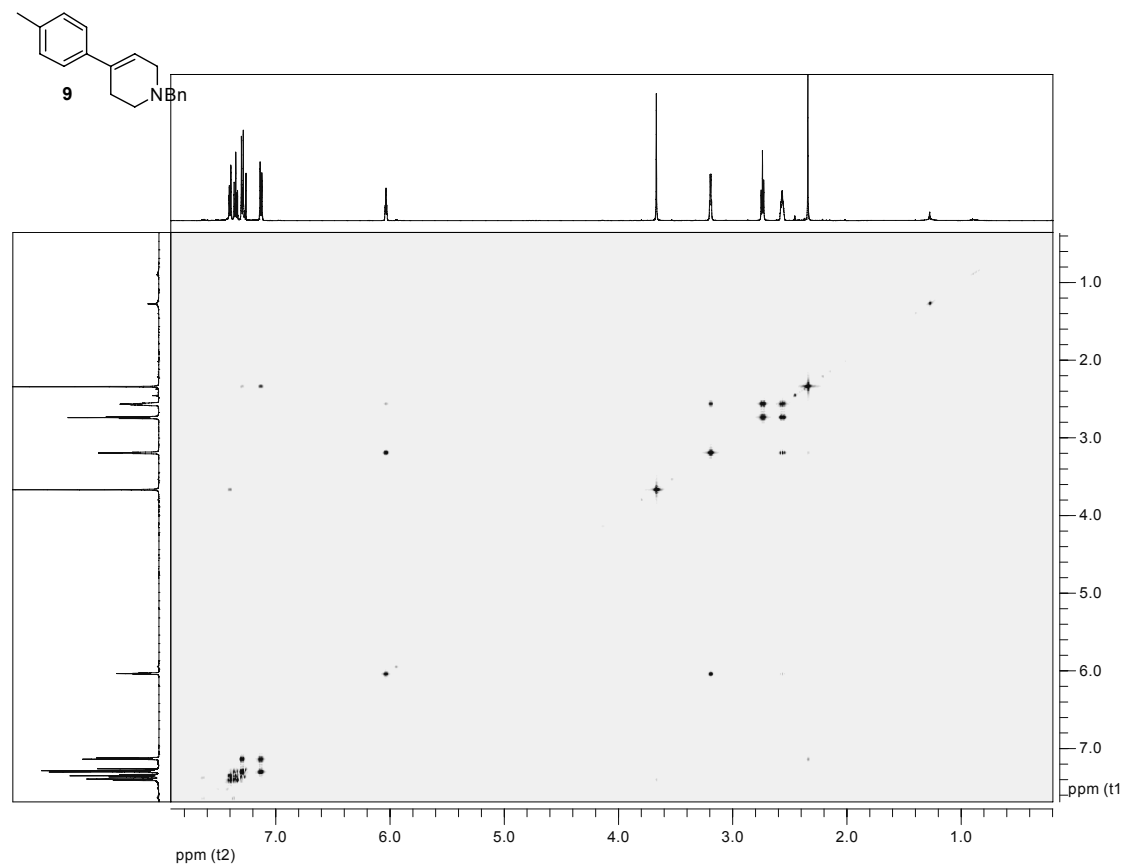


<sup>1</sup>H NMR, 500MHz, CDCl<sub>3</sub>

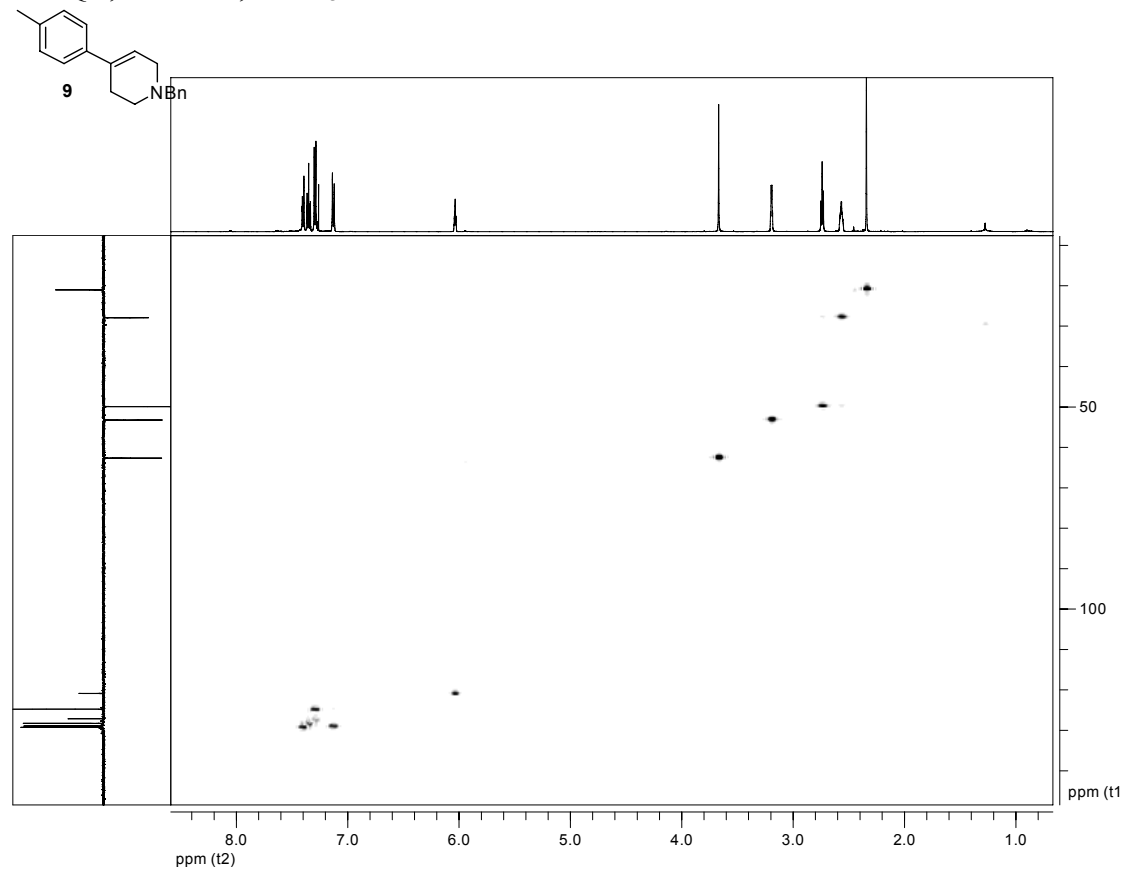




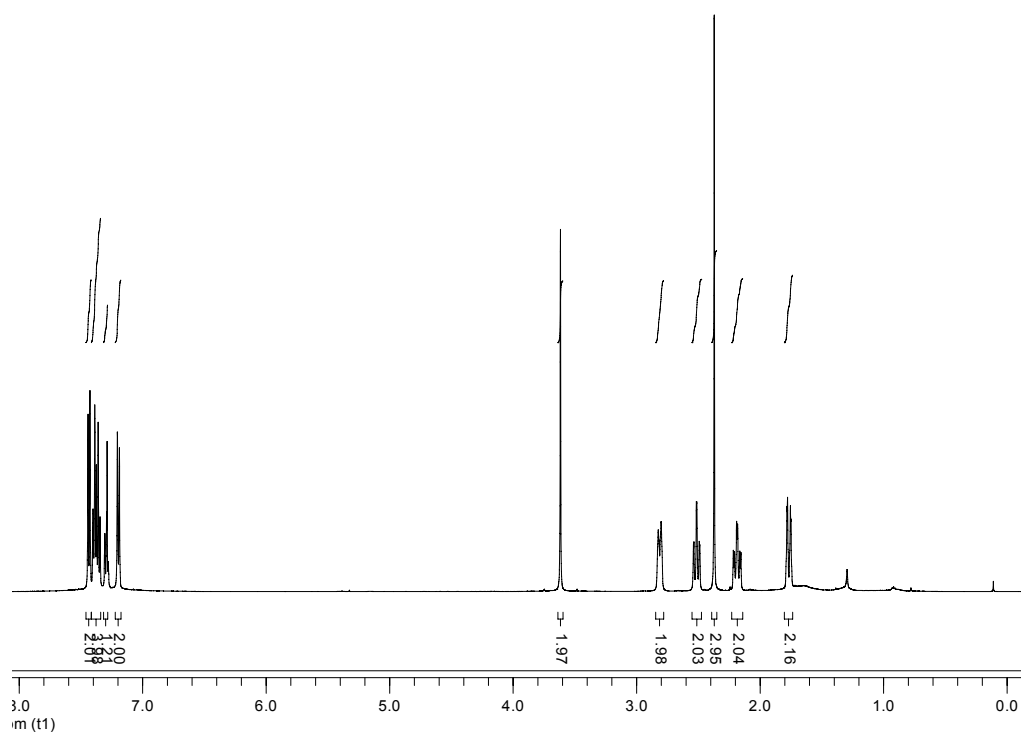
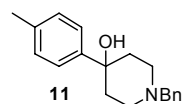
COSY, 500MHz, CDCl<sub>3</sub>



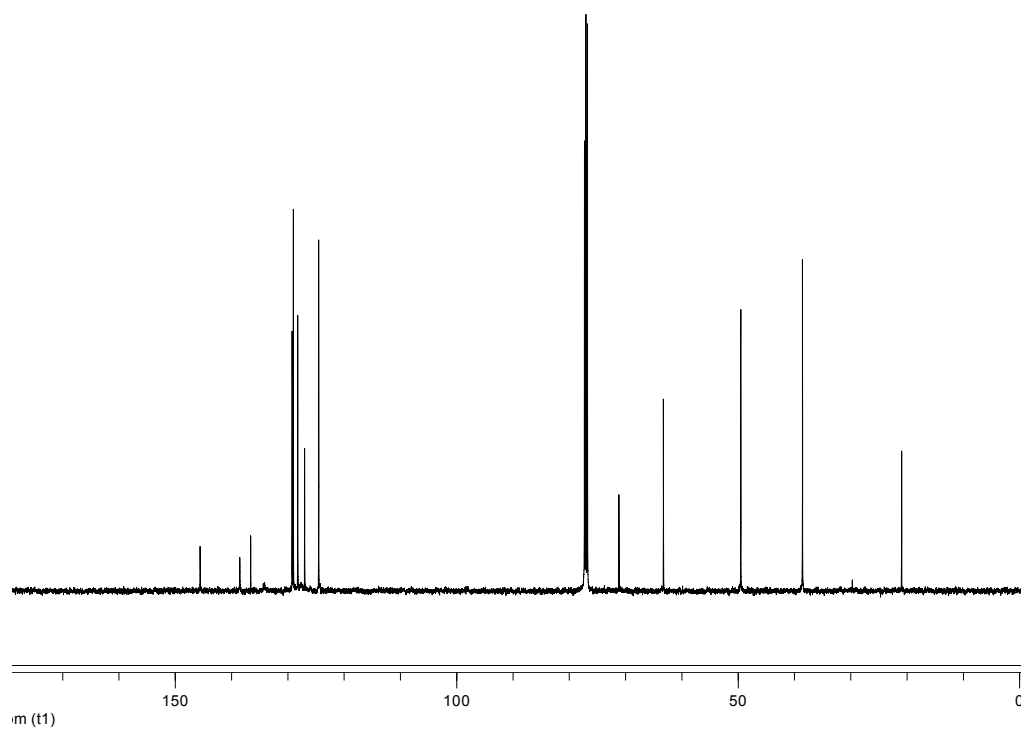
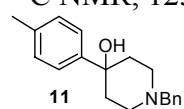
HMQC, 125MHz, CDCl<sub>3</sub>



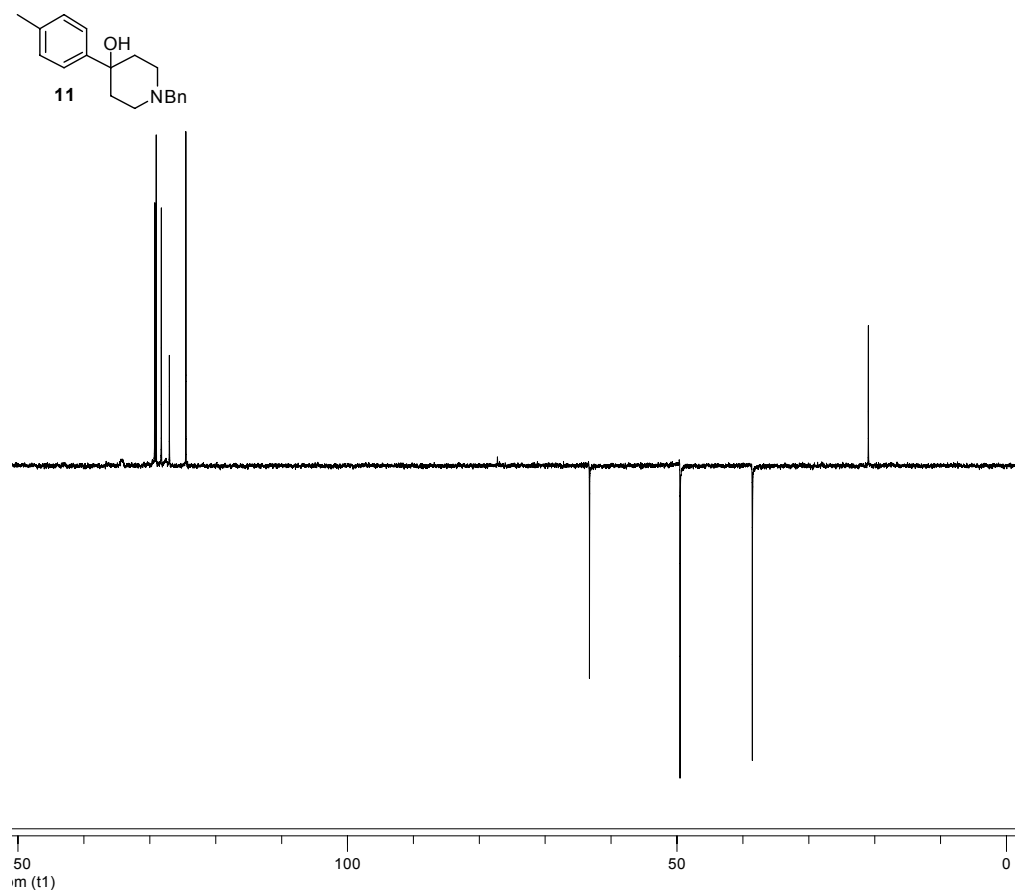
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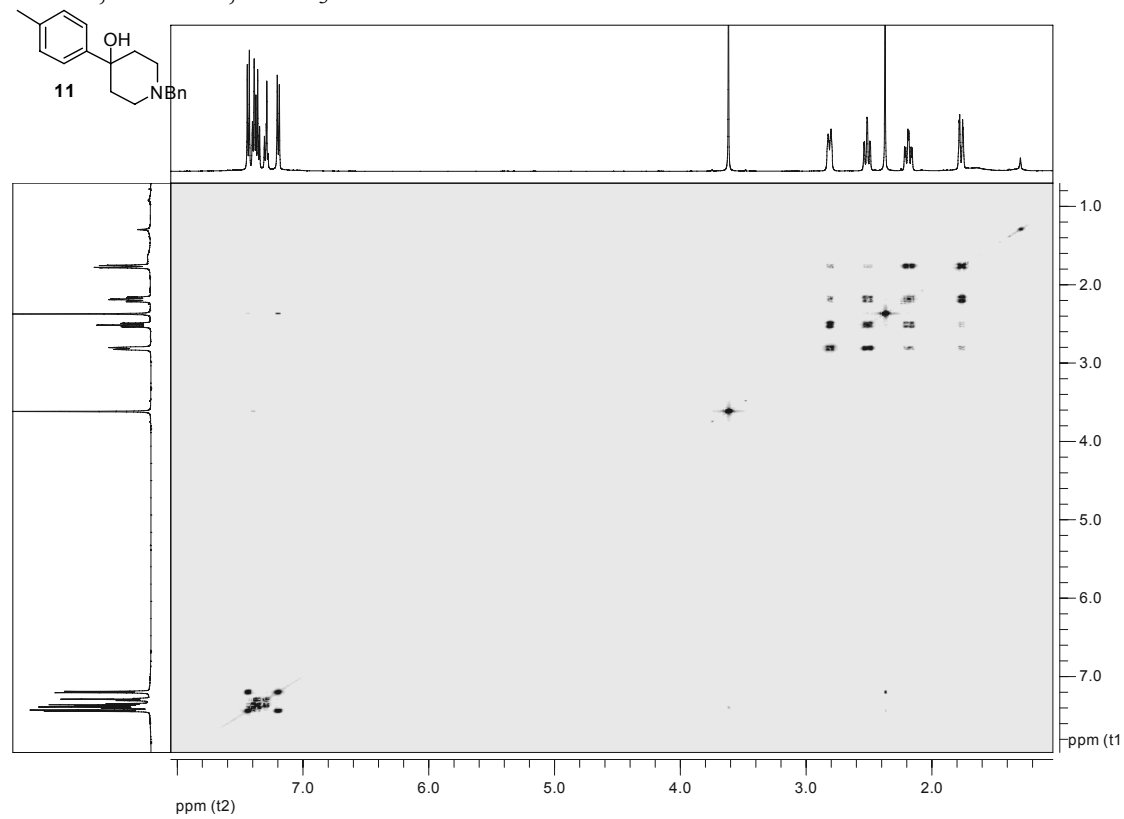
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DEPT 135, 125MHz, CDCl<sub>3</sub>

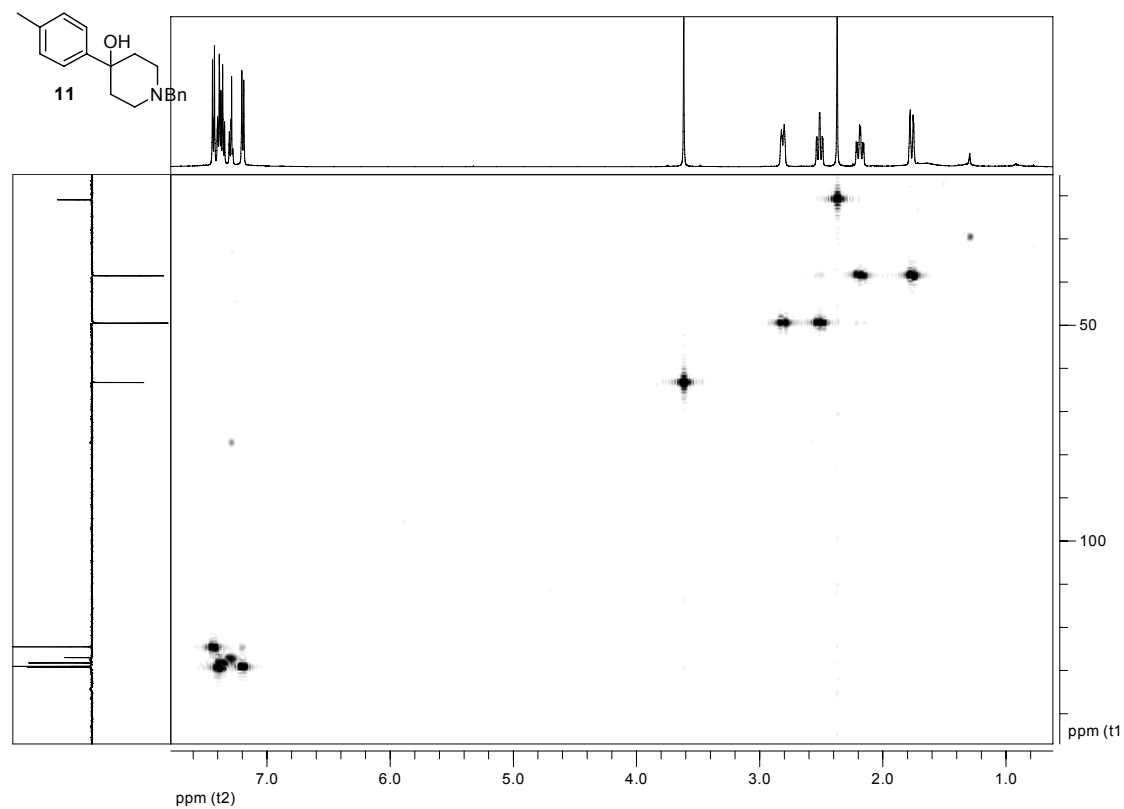


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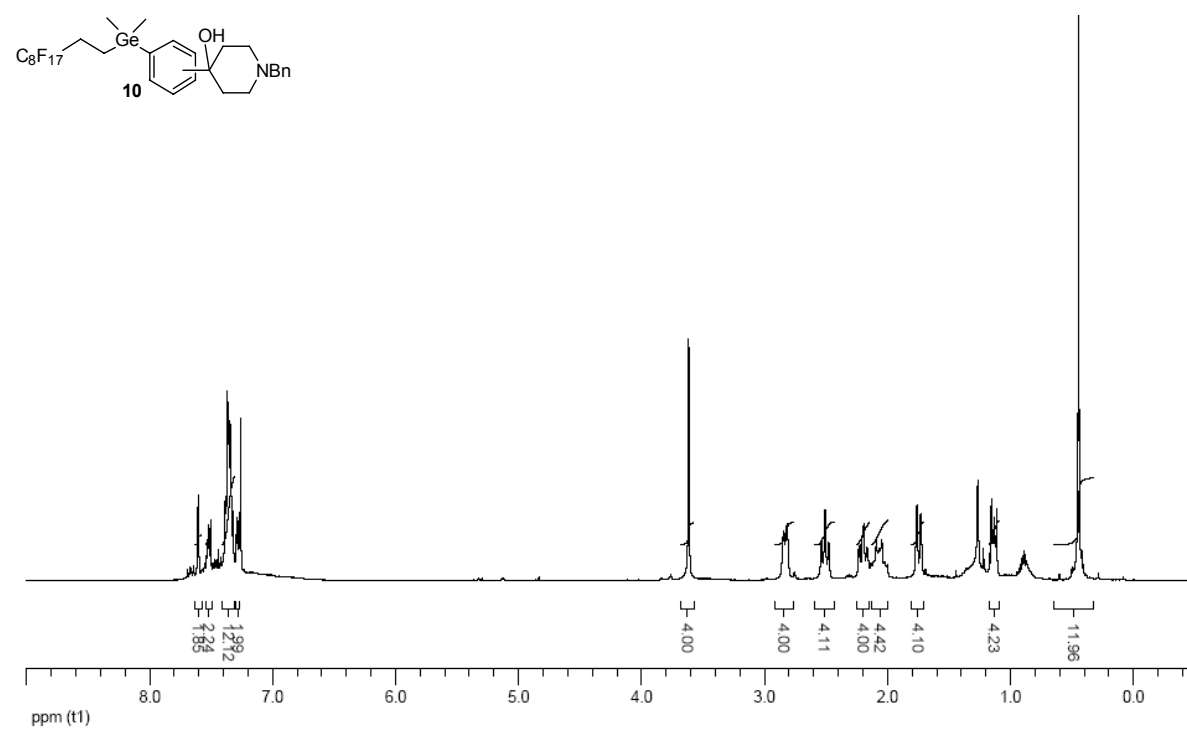




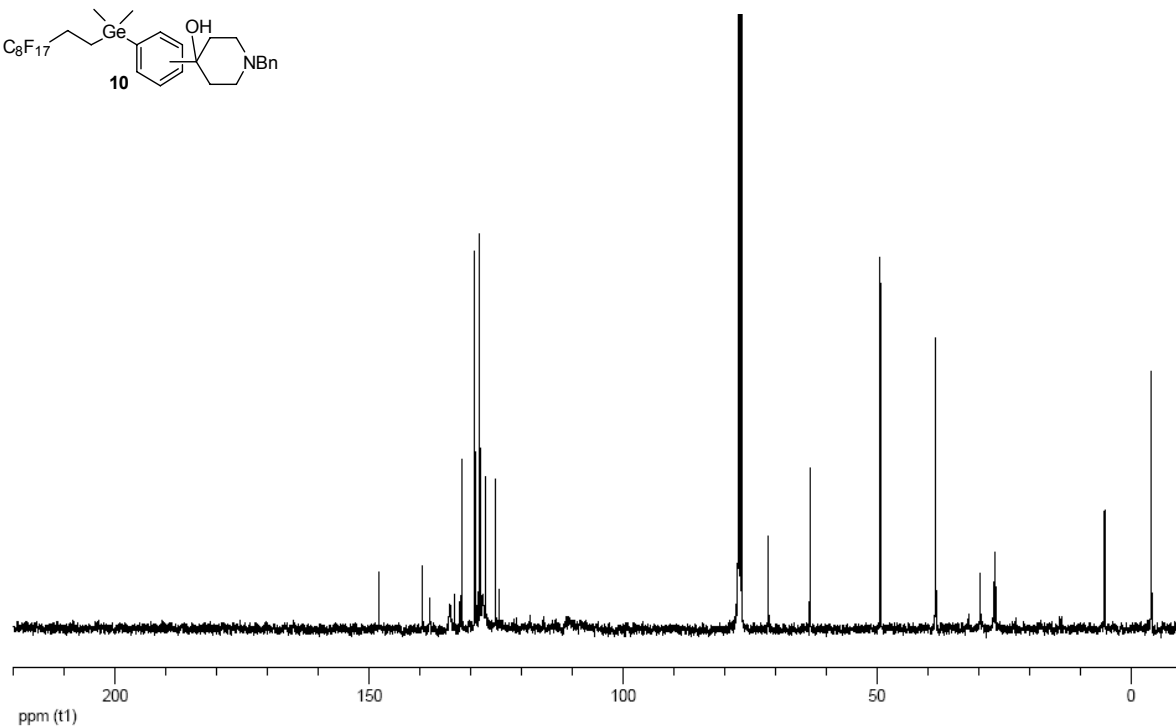
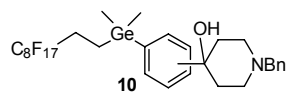
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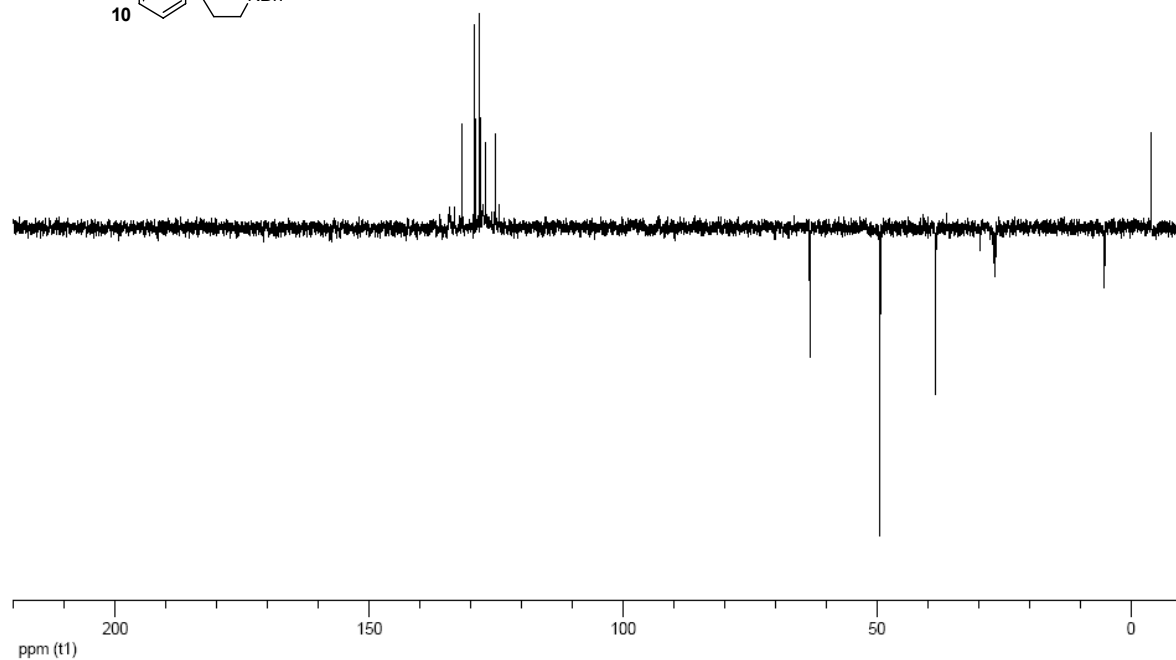
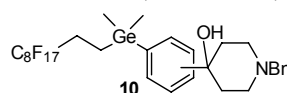
<sup>1</sup>H NMR, 400MHz, CDCl<sub>3</sub>



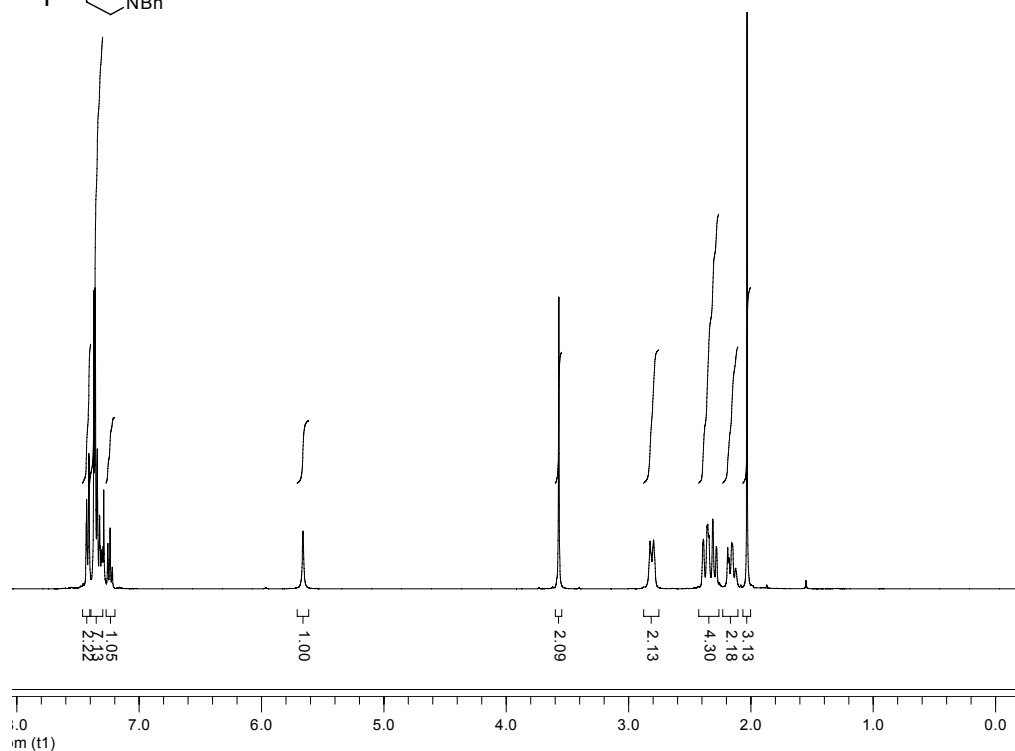
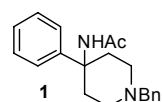
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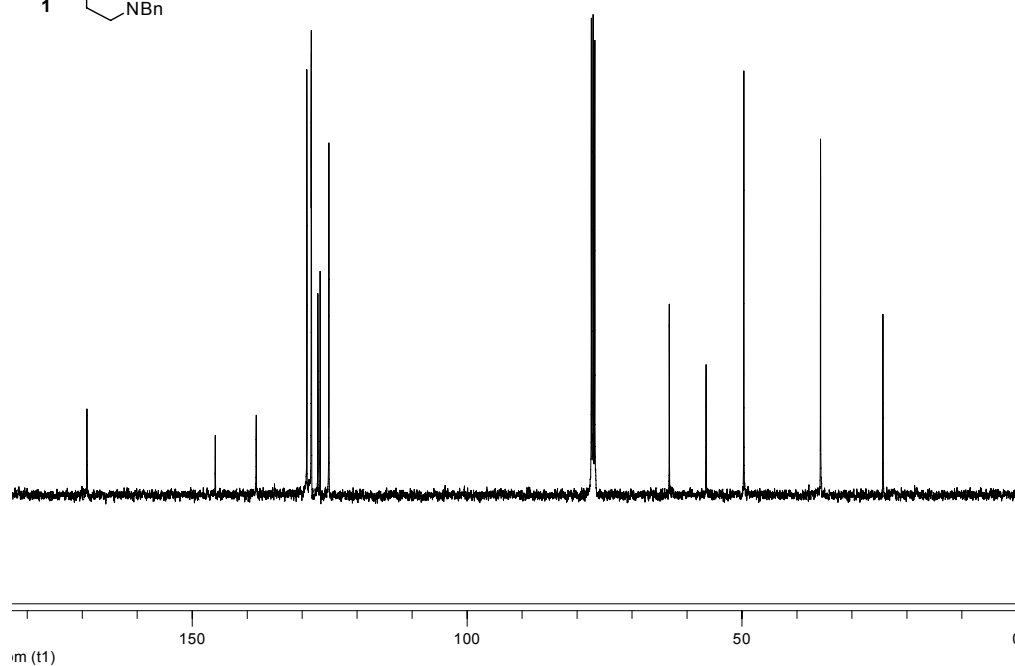
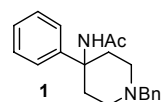
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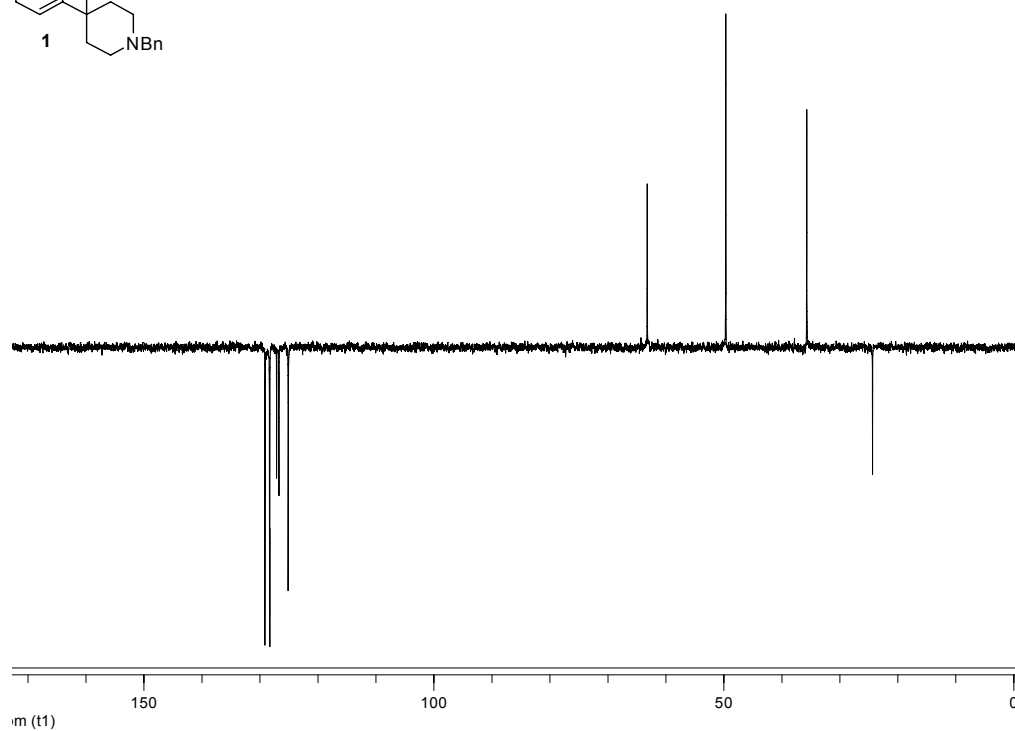
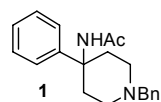
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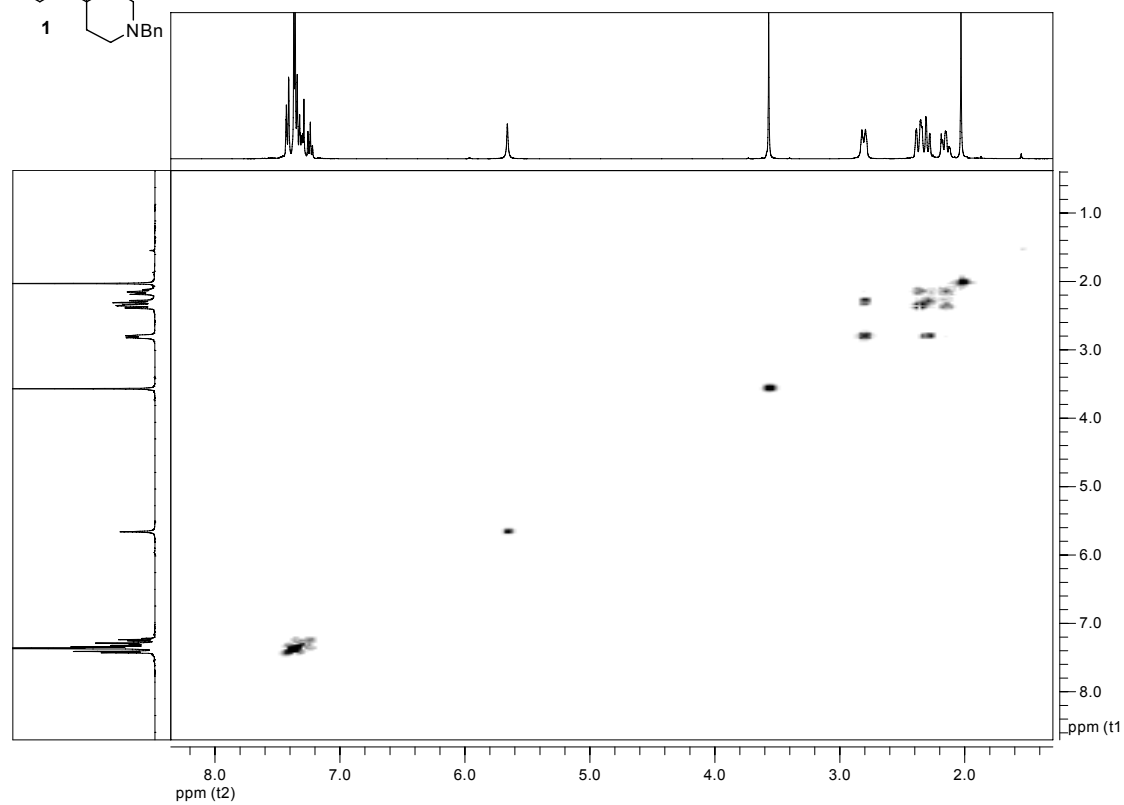
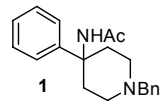
$^{13}\text{C}$  NMR, 100MHz,  $\text{CDCl}_3$



DEPT 135, 100MHz, CDCl<sub>3</sub>



COSY, 400MHz, CDCl<sub>3</sub>



$^1\text{H}$  NMR, 400MHz,  $\text{CDCl}_3$

