Towards a General Solid Phase Approach for the Iterative Synthesis of Conjugated Oligomers Using a Germanium Based Linker – First Solid Phase Synthesis of an Oligo-(triarylamine)

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SUPPORTING INFORMATION

Supplementary Experimental Section – for general directions see main manuscript**.**

2-Bromo-3-(*n*-hexyl)thiophene 6.[1] To a solution of 3-(*n*-hexyl)thiophene (**11**, 2.97 g, 17.6 mmol) in glacial acetic acid (8.7 mL) was added *N*-bromosuccinimide (3.11 g, 17.6 mmol) under N_2. The mixture was left to stir at RT for 24 h before partitioning between sat. $NaHCO_3$ (aq) (50 mL) and ether (50 mL). After evolution of gas ceased the aqueous layer was extracted with ether (2×50 mL), the organic fractions were combined, dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by FC (pentane) to afford bromide **6** as a colourless oil (4.37 g, 99%). R_f (pentane) 0.80; ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6, 3H), 1.20-1.40 (6H), 1.57 (m, 2H), 2.55 (t, *J* = 7.5, 2H), 6.78 (d, *J* = 5.5, 1H), 7.17 (d, *J* = 5.5, 1H); MS (EI+) *m/z* 246 (M^+); HRMS (EI+) calcd. for $C_{10}H_{15}BrS$ (M^+) 246.0078, found 246.0077.

Triethyl-[3-(*n*-hexyl)thiophen-2-yl]silane 1b. According to general procedure A, bromide **6** (275 mg, 1.11 mmol), *n*-BuLi (1.04 mL, 1.17 M, 1.22 mmol) in hexanes, and triethylchlorosilane (373 μL, 2.22 mmol) gave silylthiophene **1b** as a colourless oil (260 mg, 83%). R_f 0.70 (pentane); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.78-1.01 (18H), 1.22-1.41 (6H), 1.59 (m, 2H), 2.64 (t, *J* = 7.5, 2H), 7.05 (d, *J* = 4.5, 1H), 7.47 (d, *J* = 4.5, 1H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 4.7 (t, 3C), 7.5 (q, 3C), 14.1 (q), 22.7 (t), 29.5 (t), 31.4 (t), 31.8 (t), 31.8 (t), 129.4 (s), 129.7 (d), 130.1 (d), 150.7 (s); IR (neat) 2955-2875 (C-H), 1512, 1458, 1416, 1402, 1378, 1238, cm^{-1}; MS (EI+) *m/z* 282 (M^+); HRMS calcd. for $C_{16}H_{30}SSi$ (M^+) 282.1838, found 282.1837; Anal. calcd. for $C_{16}H_{30}SSi$: C 68.0, H 10.7, S 11.4, found C 68.2, H 10.8, S 11.5.

***tert*-Butyl-[3-(*n*-hexyl)thiophen-2-yl]dimethylsilane 1c.** According to general procedure A, bromide **6** (275 mg, 1.11 mmol), *n*-BuLi (1.04 mL, 1.17 M, 1.22 mmol) in hexanes, and *tert*-butylchlorodimethylsilane (335 mg, 2.22 mmol) gave silylthiophene **1c** as a colourless oil (238 mg, 76%). R_f 0.75 (pentane); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.33 (s, 6H), 0.85-0.92 (12H), 1.23-1.38 (6H), 1.57 (m, 2H), 2.66 (t, *J* = 8, 2H), 7.05 (d, *J* = 5, 1H), 7.47 (d, *J* = 5, 1H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ -3.6 (q, 2C), 14.1 (q), 17.9 (s), 22.6 (t), 26.8 (q, 2C), 29.6 (t), 31.8 (t, 2C), 31.9 (t), 118.9 (s), 129.8 (d), 130.1 (d), 151.1 (s); IR (neat) 2960-2855 (C-H), 1513, 1464, 1403, 1362, 1250 [$Si(CH_3)_n$] cm^{-1}; MS (EI+) *m/z* 282 (M^+); HRMS calcd. for $C_{16}H_{30}SSi$ (M^+) 282.1838, found 282.1833; Anal. calcd. for $C_{16}H_{30}SSi$: C 68.0, H 10.7, S 11.4, found C 68.0, H 10.8, S 11.4.

4-{2-[Diethyl-(4-methoxyphenyl)germanyl]ethyl}phenol 8b. According to general procedure B, *4-{2-dichloro-(4-methoxyphenyl)germanyl]ethyl}phenol* (**7**)[2] (272 mg, 730 μmol) and EtMgBr (3.63 mL, 2.0 M, 7.26 mmol) in THF gave diethylgermane **8b** as a pale yellow oil (195 mg, 74%). R_f 0.55 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.82-1.15 (10H); 1.20 (m, 2H), 2.54 (m, 2H), 3.74 (s, 3H), 4.57 (broad s, 1H), 6.66 (d, *J* = 8.5, 2H), 6.85 (d, *J* = 8.5, 2H), 6.97 (d, *J* = 8.5, 2H), 7.29 (d, *J* = 8.5, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 4.8 (t, 2C), 9.0 (q, 2C), 14.5 (t), 30.3 (t), 55.1 (q), 113.9 (d, 2C), 115.2 (d, 2C), 128.9 (d, 2C), 130.2 (s), 135.2 (d, 2C), 137.4 (s), 153.5 (s), 159.8 (s); IR (neat) 3402 (broad, O-H), 3020-2835 (C-H), 1612, 1593, 1568, 1512, 1499, 1461, 1337, 1279, 1246 cm^{-1}; MS (EI+) *m/z* 360 (M^+); HRMS calcd. for $C_{19}H_{26}Ge^{74}O_2$ (M^+) 360.1145, found 360.1147.

4-{2-[Diisopropyl-(4-methoxyphenyl)germanyl]ethyl}phenol 8c. According to general procedure B, *4-{2-dichloro-(4-methoxyphenyl)germanyl]ethyl}phenol* (**7**)[2] (272 mg, 730 μmol) and isopropyl magnesium chloride (3.63 mL, 2.0 M, 7.26 mmol) in THF gave di-*iso*-propylgermane **8c** as a pale yellow oil (150 mg, 53%). R_f 0.55 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.5, 6H), 1.07 (d, *J* = 7.5, 6H), 1.25 (m, 2H), 1.46 (sept, *J* = 7.5, 2H), 2.62 (m,

2H), 3.74 (s, 3H), 4.71 (broad s, 1H), 6.68 (d, *J* = 8.5, 2H), 6.85 (d, *J* = 9, 2H), 7.01 (d, *J* = 8.5, 2H), 7.29 (d, *J* = 9, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 12.5 (t), 14.2 (d, 2C), 19.5 (q, 2C), 19.6 (q, 2C), 30.7 (t), 55.0 (q), 113.7 (d, 2C), 115.3 (d, 2C), 128.5 (s), 128.8 (d, 2C), 135.8 (d, 2C), 137.8 (s), 153.5 (s), 159.7 (s); IR (neat) 3402 (broad, O-H), 3020-2861 (C-H), 1612, 1592, 1568, 1513, 1499, 1463, 1365, 1278, 1246 cm^{-1}; MS (ES-) *m/z* 387 ((M-H)$^-$); HRMS (EI+) calcd. for $C_{21}H_{30}Ge^{74}O_2$ (M^+) 388.1458, found 388.1466.

4-{2-[(4-Methoxyphenyl)diphenylgermanyl]ethyl}phenol 8d. According to general procedure B, *4-{2-dichloro-(4-methoxyphenyl)germanyl]ethyl}phenol* (**7**)[2] (275 mg, 738 μmol) and phenyl magnesium bromide (2.47 mL, 3.0 M, 7.41 mmol) in Et_2O gave diphenylgermane **8d** as a pale yellow oil (310 mg, 92%). R_f 0.30 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.79 (m, 2H), 2.79 (m, 2H), 3.84 (s, 3H), 5.00 (broad s, 1H), 6.74 (d, *J* = 8.5, 2H), 6.97 (d, *J* = 8.5, 2H), 7.07 (d, *J* = 8.5, 2H), 7.37-7.55 (12H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 16.5 (t), 21.6 (q, 2C), 30.3 (t), 55.2 (q), 114.2 (d, 2C), 115.3 (d, 2C), 127.6 (s), 128.3 (d, 4C), 129.0 (d, 2C), 135.0 (d, 4C), 136.3 (d, 2C), 137.0 (s, 2C), 137.3 (s), 153.6 (s), 160.4 (s); IR (neat) 3407 (broad, O-H), 3020-2835 (C-H), 1611, 1592, 1567, 1513, 1500, 1442, 1430, 1337, 1281, 1247 cm^{-1}; MS (EI+) *m/z* 456 (M^+); HRMS (EI+) calcd. for $C_{27}H_{26}Ge^{74}O_2$ (M^+) 456.1143, found 456.1145.

4-{2-[(4-Methoxyphenyl)-di-*para*-tolylgermanyl]ethyl}phenol 8e. According to general procedure B, *4-{2-dichloro-(4-methoxyphenyl)germanyl]ethyl}phenol* (**7**)[2] (186 mg, 499 μmol) and the Grignard reagent formed between Mg (120 mg, 5.00 mmol) and 4-bromotoluene (855 mg, 5.00 mmol) gave di-*para*-tolylgermane **8e** as a yellow oil (222 mg, 92%). R_f 0.40 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.76 (m, 2H), 2.36 (s, 6H), 2.74 (m, 2H), 3.81 (s, 3H), 4.64 (broad s, 1H), 6.71 (d, *J* = 8.5, 2H), 6.92 (d, *J* = 8.5, 2H), 7.04 (d, *J* = 8.5, 2H), 7.19 (d, *J* = 8, 4H), 7.38 (d, *J* = 8, 4H), 7.40 (d, *J* = 8.5, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 16.6 (t), 21.6 (q, 2C), 30.4 (t), 55.2 (q), 114.2 (d, 2C), 115.3 (d, 2C), 128.2 (s), 129.0 (d, 2C), 129.2 (d, 4C), 133.8 (s, 2C), 135.0 (d, 4C), 136.3 (d, 2C), 137.1 (s), 138.8 (s, 2C), 153.6 (s), 160.3 (s); IR (neat) 3409 (broad, O-H), 3015-2860 (C-H), 1593, 1568, 1512, 1442, 1392, 1281, 1247 cm^{-1}; MS (EI+) *m/z* 484 (M^+); HRMS (EI+) calcd. for $C_{29}H_{30}Ge^{74}O_2$ (M^+) 484.1458, found 484.1446; Anal. calcd. for $C_{29}H_{30}GeO_2$: C 72.1, H 6.3, found C 72.6, H 6.1.

{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}diethyl-(4-methoxyphenyl)germane 9b. According to general procedure C, phenol **8b** (150 mg, 41.8 μmol), 2-chlorodiethyl ether (100 μL, 911 μmol), TBAI (15.5 mg, 42.0 μmol) and caesium carbonate (222 mg, 629 μmol) gave ether **9b** as a pale yellow oil (163 mg, 90%). R_f 0.30 (petrol/EtOAc, 9/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.91-1.11 (10H), 1.22-1.32 (5H), 2.64 (m, 2H), 3.61 (q, *J* = 7, 2H), 3.79 (t, *J* = 4.5, 2H), 3.82 (s, 3H), 4.10 (t, *J* = 4.5, 2H), 6.85 [d, *J* = 8.5, 2H], 6.93 [d, *J* = 8.5, 2H], 7.10 [d, *J* = 8.5, 2H], 7.37 [d, *J* = 8.5, 2H]; ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 4.8 (t, 2C), 9.0 (q, 1C), 14.4 (t, 1C), 15.2 (q, 1C), 30.3 (t, 1C), 55.0 (q, 1C), 66.9 (t, 1C), 67.6 (t, 1C), 69.1 (t, 1C), 113.8 (d, , 2C), 114.6 (d, 2C), 128.7 (d, 2C), 130.0 (s, 1C), 135.1 (d, 2C), 137.4 (s, 1C), 157.0 (s, 1C), 159.8 (s, 1C); IR (neat) 3030-2870 (C-H), 1611, 1593, 1568, 1511, 1500, 1456, 1374, 1279, 1246 cm^{-1}; MS (EI+) *m/z* 432 (M^+); HRMS calcd. for $C_{23}H_{34}Ge^{74}O_3$ (M^+) 432.1720, found 432.1722.

{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}diisopropyl-(4-methoxyphenyl)germane 9c. According to general procedure C, phenol **8c** (115 mg, 297 μmol), 2-chlorodiethyl ether (71.0 μL, 647 μmol), TBAI (11.0 mg, 29.7 μmol) and caesium carbonate (159 mg, 451 μmol) gave ether **9c** as a pale yellow oil (105 mg, 77%). R_f 0.30 (petrol/EtOAc, 9/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.12 (d, *J* = 7.5, 6H), 1.16 (d, *J* = 7.5, 6H), 1.25 (t, *J* = 7, 3H), 1.34 (m, 2H), 1.54 (sept, *J* = 7.5, 2H), 2.70 (m, 2H), 3.61 (q, *J* = 7, 2H), 3.79 (t, *J* = 4.5, 2H), 3.82 (s, O$\underline{C}H_3$, 3H), 4.11 (t, *J* = 4.5, 2H), 6.87 (d, *J* = 8.5, 2H), 6.93 (d, *J* = 9, 2H), 7.13 (d, *J* = 8.5, 2H), 7.37 (d, *J* = 9, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 12.5 (t, 1C), 14.2 (d,

2C), 15.2 (q, 1C), 19.6 (q, 2C), 19.6 (q, 2C), 30.7 (t, 1C), 55.0 (q, 1C), 66.9 (t, 1C), 67.6 (t, 1C), 69.1 (t, 1C), 113.7 (d, 2C), 114.6 (d, 2C), 128.4 (s, 1C), 128.6 (d, 2C), 135.8 (d, 2C), 137.9 (s, 1C), 157.0 (s, 1C), 159.8 (s, 1C); IR (neat) 3025-2860 (C-H), 1610, 1593, 1567, 1510, 1500, 1461, 1372, 1298, 1279, 1247 cm^{-1}; MS (EI+) *m/z* 459 ($(M-H)^+$); HRMS calcd. for $C_{25}H_{38}Ge^{74}O_3$ (M^+) 460.2033, found 460.2023.

{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(4-methoxyphenyl)diphenylgermane 9d. According to general procedure C. phenol **8d** (124 mg, 272 μmol), 2-chlorodiethyl ether (65.0 μL, 592 μmol), TBAI (10.0 mg, 27.1 μmol) and caesium carbonate (143 mg, 405 μmol) gave ether **9d** as a pale yellow oil (115 mg, 80%). R_f 0.75 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7, 3H), 1.82 (m, 2H), 2.77 (m, 2H), 3.60 (q, *J* = 7, 2H), 3.78 (t, *J* = 5.5, 2H), 3.82 (s, 3H), 4.10 (t, *J* = 5.5, 2H), 6.83 (d, *J* = 8.5, 2H), 6.94 (d, *J* = 8.5, 2H), 7.08 (d, *J* = 8.5, 2H), 7.34-7.52 ($CH_3OC(=C\underline{H})C\underline{H}$, 2×$C\underline{H}$=$C\underline{H}C\underline{H}$=$C\underline{H}C\underline{H}$, m, 12H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 15.3 (q, 1C), 16.4 (t, 1C), 30.3 (t, 1C), 55.1 (q 1C), 66.8 (t, 1C), 67.6 (t, 1C), 69.1 (t, 1C), 114.1 (d, 2C), 114.7 (d, 2C), 127.5 (s, 1C), 128.3 (d, 4C), 128.7 (d, 2C), 135.0 (d, 4C), 128.9 (d, 2C), 136.3 (d, 2C), 137.0 (s, 2C), 137.3 (s, 1C), 157.1 (s, 1C), 160.4 (s, 1C); IR (neat) 3010-2870 (C-H), 1610, 1593, 1567, 1510, 1456, 1430, 1372, 1281, 1247 cm^{-1}; MS (EI+) *m/z* 528 (M^+); HRMS (EI+) calcd. for $C_{31}H_{34}Ge^{74}O_3$ (M^+) 528.1720, found 528.1717.

{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(4-methoxyphenyl)di-*para*-tolylgermane 9e. According to general procedure C. phenol **8e** (9.57 g, 19.8 mmol), 2-chlorodiethyl ether (4.56 mL, 41.5 mmol), TBAI (739 mg, 2.00 mmol) and caesium carbonate (14.1 g, 40.0 mmol) gave:

Ether **9e** as a colourless oil (7.81 g, 71%): R_f 0.55 (petrol/EtOAc, 9/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7, 3H), 1.76 (m, 2H), 2.36 (s, 6H), 2.74 (m, 2H), 3.59 (q, J = 7, 2H), 3.77 (t, *J* = 5.5, 2H), 3.81 (s, 3H), 4.09 (q, *J* = 5.5, 2H), 6.82 (d, *J* = 8.5, 2H), 6.92 (d, *J* = 8.5, 2H), 7.07 (d, *J* = 8.5, 2H), 7.18 (d, *J* = 8, 4H), 7.38 (d, *J* = 8, 4H), 7.40 (d, *J* = 8.5, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 15.3 (q), 16.6 (t), 21.6 (q, 2C), 30.4 (t), 55.1 (q), 66.9 (t), 67.6 (t), 69.1 (t), 114.1 (d, 2C), 114.7 (d, 2C), 128.0 (s), 128.8 (d, 2C), 129.1 (d, 4C), 133.8 (s, 2C), 135.0 (d, 4C), 136.3 (d, 2C), 137.2 (s), 138.7 (s, 2C), 157.0 (s), 160.4 (s); IR (neat) 3010-2925 (C-H), 1593, 1567, 1510, 1454, 1392, 1281, 1247 cm^{-1}; MS (EI+) *m/z* 556 (M^+); HRMS (EI+) calcd. for $C_{33}H_{38}Ge^{74}O_3$ (M^+) 556.2033, found 556.2042.

Bis-(4-{2-[(4-methoxyphenyl)-di-para-tolylgermanyl]ethyl}phenoxy)methane[§] as white needles (1.94 g, 20%). Mp 43.0-44.5 °C; R_f 0.50 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.77 (m, 4H), 2.37 (s, 12H), 2.76 (m, 4H), 3.82 (s, 6H), 5.66 (s, 2H), 6.93 (d, *J* = 9, 4H), 7.00 (d, *J* = 8.5, 4H), 7.10 (d, *J* = 8.5, 4H), 7.20 (d, *J* = 8, 8H), 7.36-7.42 (12H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 16.7 (t, 2C), 21.7 (q, 4C), 30.7 (t, 2C), 55.2 (q, 2C), 91.7 (t), 114.3 (d, 4C), 116.7 (d, 4C), 128.0 (s, 2C), 128.8 (d, 4C), 129.0 (d, 8C), 133.9 (s, 4C), 135.1 (d, 8C), 136.4 (d, 4C), 138.8 (s, 4C), 139.0 (s, 2C), 155.4 (s, 2C), 160.5 (s, 2C); IR (CH_2Cl_2 cell) 3015-2920 (C-H), 1593, 1568, 1509, 1464, 1442, 1281, 1247, 1209 cm^{-1}; MS (EI+) *m/z* 978 ($M-2H^+$); HRMS calcd. for $C_{59}H_{60}Ge^{74}{}_2O_4$ (M^+) 980.2915, found 980.2919; Anal. calcd. for $C_{59}H_{60}Ge_2O_4$: C 72.4, H 6.4, found C 72.5, H 6.4.

{2-[4-(2-Ethoxy)phenyl]ethyl}diethyl-[4-(*n*-hexyl)thiophen-2-yl]germane 10b. To germyl-*p*-anisole **9b** (161 mg, 374 μmol) was added HCl (5.00 mL, 1.0 M, 5.00 mmol) in Et_2O and the reaction mixture left to stir for 1.5 h. The solvent was then removed *in vacuo* to give the crude germyl chloride as a brown oil. In a separate flask, a solution of LDA (925

[§] This acetal dimer is formed readily under the Williamson etherification reactions conditions if CH_2Cl_2 is carried through from the previous step (as happened in this reaction). The reaction of phenolates with CH_2Cl_2 in this fashion has been reported previously. See ref 3 (pp47).

μL, 2.0 M, 1.85 mmol) in hexanes/THF/ethylbenzene (6/5/3) was added dropwise to a degassed solution of 3-(*n*-hexyl)thiophene (311 mg, 1.85 mmol) in THF (3 mL) at -50 °C. This solution was warmed to -40 °C, stirred for 40 min at this temperature and recooled to -50 °C before being transferred by cannula to a degassed solution of the crude germyl chloride in THF (2mL) at -50 °C. The resulting mixture was stirred for 1 h at -40 °C, warmed to RT and stirred for a further 1 h. After quenching with sat. NH_4Cl (aq) (100 mL), the mixture was extracted with Et_2O (3 × 100 mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by FC (petrol/EtOAc, 19/1) to give diethylgermylthiophene **10b** as a yellow oil (132 mg, 72%). R_f 0.40 (petrol/EtOAc, 9/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7, 3H), 0.90–1.37 (21H), 1.62 (t, *J* = 7.5, 2H), 2.59-2.72 (4H), 3.59 (q, *J* = 7, 2H), 3.78 (t, *J* = 5, 2H), 4.09 (t, *J* = 5, 2H), 6.83 (d, *J* = 8.5, 2H), 6.96 (s, 1H), 7.06 (s, 1H), 7.11 (d, *J* = 8.5, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 6.0 (t, 2C), 8.9 (q, 2C), 14.1 (q), 15.2 (q), 15.5 (t), 22.7 (t), 29.2 (t), 30.1 (t), 30.2 (t), 30.7 (t), 31.7 (t), 66.8 (t), 67.5 (t), 69.1 (t), 114.6 (d, 2C), 124.5 (d), 128.7 (d, 2C), 134.5 (d), 136.8 (s), 139.6 (s), 144.5 (s), 157.0 (s); IR (neat) 2930-2870 (C-H), 1611, 1584, 1511, 1456, 1425, 1377, 1298, 1246 cm^{-1}; MS (EI+) *m/z* 492 (M^+); HRMS (EI+) calcd. for $C_{26}H_{42}Ge^{74}O_2S$ (M^+) 492.2117, found 492.2103.

{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-[4-(*n*-hexyl)thiophen-2-yl]di-*iso*-propylgermane 10c. To germyl-*p*-anisole **9c** (110 mg, 239 μmol) was added HCl (5.0 mL, 1.0 M, 5.0 mmol) in Et_2O and the reaction left to stir for 2.5 h. The solvent was then removed *in vacuo* to give crude germyl chloride as a brown oil. In a separate flask, a solution of LDA (600 μL, 2.0 M, 1.20 mmol) in hexanes/THF/ethylbenzene (6/5/3) was added dropwise to a degassed solution of 3-(*n*-hexyl)thiophene (202 mg, 1.20 mmol) in THF (2.5 mL) at -50 °C. This solution was warmed to -40 °C, stirred for 40 min at this temperature and recooled to -50 °C before being transferred by cannula to a degassed solution of the crude germyl chloride in THF (2 mL) at -50 °C. The resulting mixture was stirred for 1 hr at -40 °C, warmed to RT and stirred for a further 1 h. After quenching with sat. NH_4Cl (aq) (100 mL), the reaction mixture was extracted with Et_2O (3×100 mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification by FC (petrol/EtOAc, 19/1) gave di-*iso*-propylgermylthiophene **10c** as a colourless oil (97.0 mg, 78%). R_f 0.40 (petrol/EtOAc, 9/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7, 3H), 1.13-1.56 (27H), 2.60-2.74 (4H), 3.59 (q, *J* = 7, 2H), 3.77 (t, *J* = 4.5, 2H), 4.10 (t, *J* = 4.5, 2H), 6.84 (d, *J* = 8.5, 2H), 6.96 (d, *J* = 1, 1H), 7.11 (d, *J* = 8.5, 2H), 7.14 (d, *J* = 1, 1H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 13.7 (t, 2C), 14.1 (q, 2C), 15.2 (q, 2C), 19.5 (q, 2C), 19.5 (q), 22.7 (t), 29.1 (t), 30.1 (t), 30.7 (t, 2C), 31.7 (t), 66.9 (t), 67.5 (t), 69.1 (t), 114.6 (d, 2C), 124.5 (d), 128.6 (d, 2C), 135.1 (s), 135.6 (d), 137.6 (s), 144.3 (s), 157.0 (s); IR (neat) 2930-2860 (C-H), 1611, 1510, 1458, 1383, 1299, 1246 cm^{-1}; MS (EI+) *m/z* 520 (M^+); HRMS (EI+) calcd. for $C_{28}H_{46}Ge^{74}O_2S$ (M^+) 520.2430, found 520.2423.

{2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-[4-(*n*-hexyl)thiophen-2-yl]diphenylgermane 10d. To germyl-*p*-anisole **9d** (114 mg, 196 μmol) was added HCl in Et_2O (5.00 mL, 1.0 M, 5.00 mmol) and the reaction mixture left to stir for 16 h. The solvent was then removed *in vacuo* to give the crude germyl chloride as a colourless oil [^{1}H NMR (250 MHz, $CDCl_3$): δ 1.28 (t, *J* = 7, 3H), 1.98 (m, 2H), 2.91 (m, 2H), 3.63 (q, *J* = 7, 2H), 3.80 (t, *J* = 5, 2H), 4.11 (q, *J* = 5, 2H), 6.85 (d, *J* = 8.5, 2H), 7.11 (d, *J* = 8.5, 2H), 7.40-7.64 (10H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 15.2 (q), 21.1 (t), 29.2 (t), 66.9 (t), 67.6 (t), 69.1 (t), 114.8 (d, 2C), 128.6 (d, 4C), 128.9 (d, 2C), 130.3 (d, 2C), 133.5 (d, 4C), 135.4 (s, 2C), 135.7 (s), 157.3 (s); IR (neat) 3070-2870 (C-H), 1611, 1584, 1511, 1485, 1455, 1433, 1373, 1301, 1246 cm^{-1}; MS (EI+) *m/z* 456 (M^+); HRMS (EI+) calcd. for $C_{24}H_{27}ClGe^{74}O_2$ (M^+) 456.0911, found 456.0894.]. In a separate flask, a solution of LDA (595 μL, 1.8 M, 1.07 mmol) in hexanes/THF/ethylbenzene (6/5/3) was added dropwise to a degassed solution of 3-(*n*-hexyl)thiophene (180 mg, 1.07 mmol) in THF (5 mL) at -50 °C. This solution was stirred for 40 min at -40 °C, and then

transferred by cannula to a degassed solution of the crude germylchloride (98.0 mg) in THF (5 mL) at -50 °C. The resulting mixture was stirred for 1 h at -40 °C, warmed to RT and stirred for a further 1 h. After quenching with sat. NH_4Cl (aq) (100 mL), the mixture was extracted with Et_2O (3 × 100 mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by FC (petrol/EtOAc, 9/1) to give diphenylgermylthiophene **10d** as a yellow oil (72.1 mg, 57%). R_f 0.30 (9/1, petrol/EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.5, 3H), 1.25 (t, *J* = 7, 3H), 1.24-1.37 (6H), 1.62 (m, 2H), 1.79 (m, 2H), 2.64 (t, *J* = 8, 2H), 2.80 (m, 2H), 3.60 (q, *J* = 7, 2H), 3.78 (t, *J* = 5, 2H), 4.09 (t, *J* = 5, 2H), 6.83 (d, *J* = 8.5, 2H), 7.04 (d, *J* = 1, 1H), 7.08 (d, *J* = 8.5, 2H), 7.23 (d, *J* = 1, 1H), 7.33-7.46 (6H), 7.51-7.57 (4H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 14.1 (q), 15.2 (q, 2C), 17.4 (t), 22.6 (t), 29.1 (t), 30.1 (t), 30.1 (t), 30.6 (t), 31.7 (t), 66.8 (t), 67.5 (t), 69.0 (t), 114.6 (d, 2C), 125.8 (d), 128.3 (d, 4C), 128.7 (d, 2C), 129.1 (d, 2C), 134.5 (s, 2C), 134.6 (d, 4C), 136.8 (s), 137.0 (d), 144.7 (s), 157.0 (s); IR (neat) 2930-2855 (C-H), 1611, 1584, 1510, 1485, 1455, 1431, 1373, 1300, 1246 cm^{-1}; MS (EI+) *m/z* 588 (M^+). HRMS (EI+) calcd. for $C_{34}H_{42}Ge^{74}O_2S$ (M^+) 588.2117, found 588.2091.

{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-[4-(*n*-hexyl)thiophen-2-yl]di-*para*-tolylgermane 10e. To germyl-*p*-anisole **9e** (100 mg, 180 μmol) was added HCl in Et_2O (7.0 mL, 1.0 M, 7.0 mmol) and the reaction mixture left to stir for 16 h. The solvent was then removed *in vacuo* to give the crude germyl chloride as a colourless oil [^{1}H NMR (250 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7, 3H), 1.89 (m, 2H), 2.37 (s, 6H), 2.84 (m, 2H), 3.60 (q, *J* = 7, 2H), 3.77 (t, *J* = 5, 2H), 4.08 (q, *J* = 5, 2H), 6.81 (d, *J* = 8.5, 2H), 7.07 (d, *J* = 8.5, 2H), 7.23 (d, *J* = 8, 4H), 7.45 (d, *J* = 8, 4H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 15.3 (q), 21.6 (t), 21.6 (q, 2C), 29.2 (t), 66.9 (t), 67.6 (t), 69.1 (t), 114.7 (d, 2C), 128.9 (d, 2C), 129.4 (d, 4C), 132.3 (s, 2C), 133.5 (d, 4C), 135.6 (s), 140.4 (s, 2C), 157.3 (s); IR (neat) 2975-2865 (C-H), 1610, 1584, 1511, 1453, 1393, 1300, 1247 cm^{-1}; MS (EI+) *m/z* 483 (M^+); HRMS (EI+) calcd. for $C_{26}H_{31}ClGe^{74}O_2$ (M^+) 484.1224, found 484.1207; Anal. calcd. for $C_{26}H_{31}ClGe^{74}O_2$: C 64.6, H 6.5, Cl 7.3, found C 64.1, H 6.6, Cl 7.7]. In a separate flask, a solution of LDA (3.71 mL, 2.0 M, 742 μmol) in hexanes/THF/ethylbenzene (6/5/3) was added dropwise to a degassed solution of 3-(*n*-hexyl)thiophene (124 mg, 737 μmol) in THF (5 mL) at -50 °C. This solution was stirred for 40 min at -40 °C, and then transferred by cannula to a degassed solution of the crude germylchloride (82.2 mg) in THF (5 mL) at -50 °C. The resulting mixture was stirred for 1 h at -40 °C, warmed to RT and stirred for a further 1 h. After quenching with sat. NH_4Cl (aq) (100 mL), the mixture was extracted with Et_2O (3 × 100 mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by FC (petrol/EtOAc, 9/1) to give di-*para*-tolylgermylthiophene **10e** as a a pale yellow oil (56.0 mg, 61%). R_f 0.60 (3/1, petrol/EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7, 3H), 1.21-1.63 (11H), 1.78 (m, 2H), 2.36 (s, 6H), 2.62 (t, *J* = 8, 2H), 2.77 (m, 2H), 3.59 (q, *J* = 7, 2H), 3.77 (t, *J* = 5, 2H), 4.09 (t, *J* = 5, 2H), 6.82 (d, *J* = 8.5, 2H), 7.01 (d, *J* = 1, 1H), 7.08 (d, *J* = 8.5, 2H), 7.17-7.21 (5H), 7.42 (d, *J* = 8, 4H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 14.1 (q), 15.2 (q), 17.5 (t), 21.5 (q, 2C), 22.7 (t), 29.1 (t), 30.1 (t), 30.2 (t), 30.6 (t), 31.7 (t), 66.9 (t), 67.5 (t), 69.0 (t), 114.6 (d, 2C), 125.7 (d), 128.7 (d, 2C), 129.1 (d, 4C), 133.2 (s, 2C), 134.6 (d, 4C), 135.0 (s), 136.8 (s), 136.9 (d), 138.9 (s, 2C), 144.6 (s), 157.0 (s); IR (neat) 2926-2857 (C-H), 1686, 1610, 1584, 1510, 1485, 1455, 1392, 1299, 1246 cm^{-1}; MS (EI+) *m/z* 616 (M^+); HRMS (EI+) calcd. for $C_{36}H_{46}Ge^{74}O_2S$ (M^+) 616.2430, found 616.2428.

***tert*-Butyl-[4-(*n*-hexyl)thophen-2-yl]dimethylsilane 12.** A solution of LDA (3.12 mL, 2.0 M, 6.24 mmol) in hexanes/ethylbenzene/THF (6/5/3) was added dropwise to a degassed solution of 3-(*n*-hexyl)thiophene (**7**) (1.00 g, 5.94 mmol) in THF (10 mL) at -50 °C to give an orange solution. After stirring for 40 min at -40 °C, a degassed solution of *tert*-butyldimethylsilyl chloride (1.34 g, 8.89 mmol) in THF (5 mL) was added by cannula at -50 °C. The resulting mixture was warmed to -40 °C, stirred for 30 min at this temperature, warmed to RT and stirred for a further 40 min to

give a yellow solution. After quenching with sat. NH_4Cl (aq) (50 mL), the mixture was extracted with Et_2O (3×50 mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification by vacuum distillation (105 °C, 10^{-3} Torr) removed starting material. Further purification by HPLC (Jupiter ODS-C18 column, UV 254 nm detection, 1 mLmin^{-1}, 5→100% MeCN in H_2O + 0.1% formic acid, R_t = 14.2 min) gave silylthiophene **12** as a colourless oil (1.05 g, 62%). R_f (pentane) 0.85; ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.27 (s, 6H), 0.87 (t, *J* = 7.5, 3H), 0.90 (s, 9H), 1.24-1.30 (6H), 1.61 (t, *J* = 8, 2H), 2.62 (t, *J* = 8, 2H), 7.15 (s, 1H), 7.25 (s, 1H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ -4.9 (q, 2C), 14.2 (q), 16.9 (s), 22.7 (t), 26.4 (q, 3C), 29.1 (t), 30.0 (t), 30.7 (t), 31.7 (t), 125.4 (d), 136.6 (d), 136.9 (s), 144.5 (s); IR (neat) 2955-2855 (C-H), 1462, 1406, 1361, 1249 [$Si(CH_3)_n$] cm^{-1}; MS (EI+) *m/z* 282 (M^+); HRMS (EI+) calcd. for $C_{16}H_{30}SSi$ (M^+) 282.1838, found 282.1827; Anal. calcd. for $C_{16}H_{30}SSi$: C 68.0, H 10.7, S 11.4, found C 68.5, H 11.0, S 11.5.

***tert*-Butyl-5-({2-[4-(2-ethoxyethoxy)phenyl]ethyl}di-*para*-tolylgermanyl)-[4-(*n*-hexyl)thiophen-2-yl]dimethylsilane 13.** A solution of LDA (730 μL, 2.0 M, 1.46 mmol) in hexanes/THF/ethylbenzene (6/5/3) was added dropwise to a degassed solution of silylthiophene **12** (360 mg, 1.27 mmol) in THF (40 mL) at -50 °C. This solution was warmed to -40 °C, stirred for 40 min at this temperature and recooled to -50 °C before being transferred by cannula to a degassed solution of the germylchloride obtained from treatment of *p*-anisylgermane **9e** with HCl in Et_2O (as described in the preparation of **10e**, above) (411 mg, 848 μmol) in THF (40 mL) at -50 °C. The resulting mixture was stirred for 1 h at -40 °C, warmed to RT and stirred for a further 1 h. After quenching with sat. NH_4Cl (aq) (100 mL), the mixture was extracted with Et_2O (3×100 mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by FC (petrol/EtOAc, 9/1) to give germylthiophene **13** as a pale yellow oil (456 mg, 73%). R_f 0.30 (9/1, petrol/EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.27 (s, 6H], 0.78 (t, *J* = 7.5, 3H), 0.80-1.26 (m, 20H), 1.80 (m, 2H), 2.35 (s, 8H), 2.71 (m, 2H), 3.59 (q, *J* = 7, 2H), 3.76 (t, *J* = 5, 2H), 4.08 (q, *J* = 5, 2H), 6.81 (d, *J* = 8.5, 2H), 7.05 (d, *J* = 8.5, 2H), 7.17 (d, *J* = 8, 4H), 7.18 (s, 1H), 7.39 (d, *J* = 8, 4H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ -4.6 (q, 2C), 14.2 (q, 1C), 15.4 (q, 1C), 17.1 [s, 1C), 18.4/ 22.7/ 29.4/ 30.5/ 31.4/ 31.7/ 31.8 (t, 14H), 21.6 (q, 2C), 26.6 (q, 3C), 66.9 (t, 1C), 67.6 (t, 1C), 69.2 (t, 1C), 114.7 (d, 2C), 128.9 (d, 2C), 129.2 (d, 4C), 133.6 (s, 2C), 134.6 (s, 1C), 134.9 (d, 4C), 137.2 (s, 1C), 138.1 (d, 1C), 138.8 (s, 22C), 142.4 (s, 1C), 151.7 (s, 1C), 157.([s, 1C); IR (neat) 2955-2855 (C-H), 1610, 1509, 1457, 1391, 1300, 1278, 1250 [$Si(CH_3)_n$] cm^{-1}; MS (EI+) *m/z* 730 (M^+). HRMS (EI+) calcd. for $C_{42}H_{60}Ge^{74}O_2SSi$ (M^+) 730.3295, found 730.3298.

{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-[3-(*n*-hexyl)thiophen-2-yl]di-*para*-tolylgermane 14. To silylthiophene **13** (225 mg, 308 μmol) in DMF (3 mL) was added caesium fluoride (234 mg, 1.54 mmol) and the mixture left to stir for 24 h at 110 °C. The reaction mixture was partitioned between Et_2O (40 mL) and H_2O (75 mL) and the Et_2O layer extracted with H_2O (3 × 40 mL). The organic layer was dried ($MgSO_4$), the solvent removed *in vacuo* and the residue purified by FC (petrol/EtOAc, 9/1) to give germylthiophene **14** as a pale yellow oil (182 mg, 95%). R_f 0.30 (petrol/EtOAc, 9/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.81 (t, *J* = 7.5, 3H), 0.83-1.37 (11H), 1.84 (m, 2H), 2.35 (s, 6H), 2.44 (t, *J* = 8, 2H), 2.78 (m, 2H), 3.61 (q, *J* = 7, 2H), 3.79 (t, *J* = 5, 2H), 4.10 (q, *J* = 5, 2H), 6.84 (d, *J* = 8.5, 2H), 7.09 (d, *J* = 8.5, 2H), 7.12 (d, *J* = 5, 1H), 7.20 (d, *J* = 8, 4H), 7.43 (d, *J* = 8, 4H), 7.54 (d, *J* = 5, 1H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 14.3 (q), 15.4 (q), 18.4 (t), 21.6 (q, 2C), 22.7 (t), 29.4 (t), 30.6 (t), 31.6 (t), 31.8 (t), 31.8 (t), 67.0 (t), 67.7 (t), 69.2 (t), 114.8 (d, 2C), 128.9 (d, 2C), 129.2 (d, 4C), 130.1 (d), 130.3 (d), 133.5 (s, 2C), 134.9 (d, 4C; s), 137.1 (s), 139.0 (s, 2C), 150.8 (s), 157.2 (s); IR (neat) 2930-2860 (C-H), 1610, 1510, 1457, 1392, 1300, 1258, 1245 cm^{-1}; MS (EI+) *m/z* 616 (M^+); HRMS (EI+) calcd. for $C_{36}H_{46}Ge^{74}O_2S$ (M^+) 616.2430, found 616.2435.

{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-[3-(*n*-hexyl)-5-iodothiophen-2-yl]di-*para*-tolylgermane 15. A solution of LDA (545 μL, 2.0 M, 1.09 mmol) in hexanes/THF/ethylbenzene (6/5/3) was added dropwise to a solution of germylthiophene **14** (224 mg, 36.4 μmol) in THF (3 mL) at -50 °C. After stirring for 40 min at -40 °C, a solution of degassed 1,2-diiodoethane (1.56 g, 5.53 mmol) in THF (2 mL) was added by cannula at -50 °C. The resulting mixture was stirred in the dark for 1 h at –40 °C, warmed to RT and stirred for a further 1 h. The reaction mixture was partitioned between sat. $Na_2S_2O_3$ (aq) (200 mL) and Et_2O (100 mL), extracted with Et_2O (2 × 100 mL), the organic fractions combined and then dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purified by FC (petrol/EtOAc, 9/1) to give iodide **15** as a pale yellow oil (251 mg, 90%). R_f 0.50 (petrol/EtOAc, 9/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.79 (t, *J* = 7, 3H), 0.87-1.30 (11H), 1.80 (m, 2H), 2.34-2.41 (8H), 2.75 (m, 2H), 3.60 (q, *J* = 7, 2H), 3.78 (t, *J* = 5, 2H), 4.09 (q, *J* = 5, 2H), 6.82 (d, *J* = 8.5, 2H), 7.06 (d, *J* = 8.5, 2H), 7.17 (s, 1H), 7.19 (d, *J* = 8, 4H), 7.38 (d, *J* = 8, 4H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 14.2 (q), 15.3 (q), 18.2 (t), 21.6 (q, 2C), 22.6 (t), 29.2 (t), 30.4 (t), 31.3 (t), 31.5 (t), 31.7 (t), 66.9 (t), 67.6 (t), 69.1 (t), 77.7 (s), 114.7 (d, 2C), 128.8 (d, 2C), 129.2 (d, 4C), 132.8 (s, 2C), 134.7 (d, 4C; s), 136.7 (s), 139.2 (s, 2C), 139.8 (d), 152.7 (s), 157.1 (s); IR (neat) 2925-2855 (C-H), 1610, 1510, 1454, 1393, 1299, 1246 cm^{-1}; MS (ES+) *m/z* 765 (MNa^+); HRMS (ES+) calcd. for $C_{36}H_{45}Ge^{74}INaO_2S$ (MNa^+) 765.1295, found 765.1266.

2-[5-(*tert*-Butyldimethylsilanyl)-[3-(*n*-hexyl)thiophen-2-yl]-4,4,5,5-tetramethyl-[1,2,3]dioxaborolane 16. A solution of LDA (1.33 mL, 2.0 M, 2.66 mmol) in hexanes/ethylbenzene/THF (6/5/3) was added dropwise to a solution of silylthiophene **12** (501 mg, 1.77 mmol) in THF (5 mL) at -50 °C and then warmed to -40 °C give an orange solution. After stirring for 40 min at this temperature the reaction mixture was cooled to -50 °C and a solution of *2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane* (162 mg, 871 μmol) in THF (1 mL) was added dropwise by cannula. The resulting mixture was stirred for 30min at -40 °C, warmed to RT and stirred for a further 15 min. The reaction mixture was then cooled to 0 °C and anhydrous HCl (710 μL, 1.0 M, 710 μmol) in Et_2O added. The mixture was left to stir at this temperature for 15 min and then allowed to warm to RT. The solvent was removed *in vacuo* and the residue dissolved in dry Et_2O (50 mL). The solution was passed through a pad of dry Celite^{TM}, dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by FC (petrol/ CH_2Cl_2, 3/1) to give boronic ester **16** as a pale yellow oil (371 mg, 51%). R_f 0.40 (3:1, petrol/ CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.26 (s, 6H), 0.87 (t, *J* = 7, 3H), 0.90 (s, 9H), 1.27-1.32 (18H), 1.57 (t, *J* = 8, 2H), 2.87 (t, *J* = 8, 2H), 7.12 (s, 1H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ -4.8 (q, 2C), 14.2 (q), 16.9 (s), 22.7 (t), 24.9 (q, 4C), 26.4 (q, 3C), 29.1 (t), 30.0 (t), 31.7 (t), 32.0 (t), 83.4 (s, 2C), 138.4 (d), 144.9 (s), 155.3 (s), (absent: CB); IR (neat) 2955-2855 (C-H), 1525, 1470, 1435, 1370, 1332, 1298, 1271, 1250 [$Si(CH_3)n$], 1214 cm^{-1}; MS (ES+) *m/z* 409 (MH^+); HRMS (ES+) calcd. for $C_{22}H_{42}BO_2SSi$ (MH^+) 409.2768, found 409.2770.

***tert*-Butyl-[5'-({2-[4-(2-ethoxyethoxy)phenyl]ethyl}-di-*para*-tolylgermanyl)-3,4'-dihexithiophenyl-5-yl]dimethylsilane 17.** To a degassed solution of boronic ester **16** (256 mg, 627 μmol), K_3PO_4 (427mg, 3.14mmol) and iodide **15** (155 mg, 203 μmol) in DMF (1 mL) was added [$Pd(PPh_3)_4$] (23.1 mg, 20.0 μmol) and the resulting mixture stirred at 60 ^{o}C for 24 h. The reaction mixture was partitioned between H_2O (100 mL) and Et_2O (50 mL), extracted with Et_2O (2 × 50 mL) and the organic fractions combined and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purified by FC (petrol/CH_2Cl_2, 2/1) to give germylbithiophene **17** as a yellow oil (112 mg, 60%). R_f 0.50 (petrol/ CH_2Cl_2, 2/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.27 (s, 6H), 0.75-1.36 (34H), 1.80 (m, 2H), 2.32-2.39 (8H), 2.71-2.80 (4H), 3.59 (q, *J* = 7, 2H), 3.76 (t, *J* = 5, 2H), 4.08 (q, *J* = 5, 2H), 6.82 (d, *J* = 8.5, 2H), 6.99 (s, 1H), 7.07 (d, *J* = 8.5, 2H), 7.11 (s, 1H), 7.18 (d, *J* = 8, 4H), 7.42 (d, *J* = 8, 4H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ -5.0 (q, 2C), 14.1 (q, 2C), 15.2 (q), 16.9 (s), 18.2 (t), 21.5 (q, 2C), 22.6 (t), 22.7 (t), 26.4 (q, 3C), 29.3 (t), 29.3 (t, 2C), 30.4 (t), 30.7 (t), 31.3 (t), 31.7 (t, 2C),

31.8 (t), 66.8 (t), 67.5 (t), 69.1 (t), 114.6 (d, 2C), 128.4 (d), 128.7 (d, 2C), 129.0 (s), 129.1 (d, 4C), 133.3 (s, 2C), 134.7 (d, 4C), 135.1 (s), 136.5 (s), 137.0 (s), 138.3 (d), 138.9 (s, 2C), 140.2 (s), 141.1 (s), 151.0 (s), 157.0 (s); IR (neat) 2924-2854 (C-H), 1610, 1509, 1455, 1390, 1246 [$Si(CH_3)_n$] cm^{-1}; MS (EI+) *m/z* 896 (M^+). HRMS (ES+) calcd. for $C_{52}H_{74}Ge^{74}NaO_2S_2Si$ (MNa^+) 919.4009, found 919.4001.

[4,3'-Di-(*n*-hexyl)-[2,2']bithiophenyl-5-yl]-{2-[4-(2-ethoxyethoxy)phenyl]ethyl}di-*para*-tolylgermane 18. To silylthiophene **17** (60.0 mg, 86.0 μmol) in DMF (1 mL) was added caesium fluoride (63.4 mg, 0.42 mmol) and the mixture left to stir for 24 hrs at 110 °C. The reaction mixture was partitioned between Et_2O (50 mL) and H_2O (100 mL) and the Et_2O layer extracted with H_2O (3 × 50 mL). The organic layer was dried ($MgSO_4$), the solvent removed *in vacuo* and the residue purified by FC (petrol/EtOAc, 9/1) to give germylbithiophene **18** as a brown oil (54.0 mg, 99%). R_f 0.30 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.75-1.65 (25H), 1.82 (m, 2H), 2.40-2.55 (8H), 2.70-2.81 (4H), 3.59 (q, *J* = 7, 2H), 3.76 (t, *J* = 5, 2H), 4.08 (q, *J* = 5, 2H), 6.82 (d, *J* = 8.5, 2H), 6.89 (d, *J* = 5, 1H), 7.05-7.20 (8H), 7.43 (d, *J* = 8.5, 4H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 14.1 (q, 2C), 15.2 (q), 18.2 (t), 21.5 (q, 2C), 22.6 (t), 22.7 (t), 29.2 (t, 2C), 29.3 (t), 30.4 (t), 30.7 (t), 31.3 (t), 31.7 (t, 2C), 31.8 (t), 66.8 (t), 67.5 (t), 69.1 (t), 98.3 (s), 114.6 (d, 2C), 123.3 (d), 128.7 (d, 2C), 129.1 (d, 4C), 130.0 (d), 131.1 (s), 132.0 (d) 133.2 (s, 2C), 134.7 (d, 4C), 137.0 (s), 138.9 (s, 2C), 139.2 (s), 140.9 (s), 151.0 (s), 157.0 (s); IR (neat) 2925-2850, 1609, 1509, 1454, 1391, 1244 cm^{-1}; MS (ES+) *m/z* 805 (MNa^+). HRMS (ES+) calcd. for $C_{46}H_{60}Ge^{74}NaO_2S_2$ (MNa^+) 805.3144, found 805.3174.

3,4'-Di-(*n*-hexyl)-[2,2']bithiophene 19.[4] *Method 2:* To germylthiophene **18** (20.1 mg, 25.7 μmol) was added a solution of TFA in CH_2Cl_2 (33% v/v, 1.5 mL) and the mixture left to stir at RT for 1 h. The solvent was then removed *in vacuo* and the residue purified by FC (pentane) to give bithiophene **19** as a yellow oil (8.3 mg, 97%). Spectroscopic data as in main manuscript.

2-[3-(*n*-Hexyl)thiophen-2-yl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 20. To a solution of germylthiophene **14** (28.2 mg, 45.7 μmol) and propylene oxide (1.00 mL, 990 μmol) in CH_2Cl_2 (1 mL) at -78 °C was added boron trichloride (99.0 μL, 1.0 M, 14.3 mmol) in heptane. After stirring for 40 min at this temperature, anhydrous pinacol (41.0 mg, 347 μmol) was added and the reaction mixture allowed to warm to RT. The solvent was then removed *in vacuo* and the residue purified by FC (petrol/EtOAc, 19/1) to give boronic ester **20** as a yellow oil (4.1 mg, 30%). R_f 0.50 (9/1, petrol/EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.5, 3H), 1.23-1.30 (6H), 1.32 (s, 12H), 1.55 (m, 2H), 2.87 (t, *J* = 8, 2H), 7.00 (d, *J* = 4.5, 1H), 7.47 (d, *J* = 4.5, 1H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 14.3 (q), 22.7 (t), 24.9 (q, 4C), 29.1 (t), 30.2 (t), 31.8 (t), 31.9 (t), 83.6 (s, 2C), 130.4 (d), 131.4 (d), 154.8 (s), (absent: CB); IR (neat) 2930-2855 (C-H), 1530, 1435, 1373, 1337, 1272, 1215 cm^{-1}; MS (EI+) *m/z* 294 (M^+); HRMS calcd. for $C_{16}H_{27}BO_2S$ (M^+) 294.1825, found 294.1811.

2-[2-(2-*para*-Tolyloxyethoxy)ethoxy]ethanol 23. To a solution of *p*-cresol (**21**, 1.28 g, 11.8 mmol) in acetonitrile (12 mL) was added 2-[2-(2-chloroethoxy)ethoxy]ethanol (**22**, 862 μL, 5.93 mmol), TBAI (438 mg, 1.19 mmol) and caesium carbonate (4.06 g, 11.5 mmol). The mixture was refluxed at 85 °C for 17 h then cooled and filtered. The solvent was removed *in vacuo* and the residue purified by FC (petrol/EtOAc, 9/1) to give alcohol **23** as a colourless oil (2.16 g, 76%). R_f 0.55 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.62 (m, 2H), 3.67-3.76 (6H), 3.85 (t, *J* = 4.5, 2H), 4.10 (t, *J* = 4.5, 2H), 6.81 (d, *J* = 8.5, 2H), 7.07 (d, *J* = 8.5, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 20.5 (q), 61.7 (t), 67.4 (t), 69.8 (t), 70.3 (t), 70.8 (t), 72.6 (t), 114.5 (d, 2C), 129.9 (d, 2C), 130.1 (s), 156.6 (s); IR (neat) 3436 (broad, O-H), 2925-2870 (C-H), 1614, 1586, 1512, 1456, 1245 cm^{-1}; MS (EI+) *m/z* 240 (M^+); HRMS calcd. for $C_{13}H_{20}O_4$ (M^+) 240.1362, found 240.1368.

1-{2-[2-(2-Chloroethoxy)ethoxy]ethoxy}-4-methylbenzene 24 and **formic acid 2-[2-(2-*para*-tolyloxyethoxy)ethoxy]ethyl ester 25.** To a solution of the alcohol **23** (100 mg, 416 μmol) in CH_2Cl_2 (5 mL) at RT was added thionyl chloride (152 μL, 2.08 mmol) and DMF (6.2 μL, 80.0 mmol) and the mixture left to stir for 24 h. The solvent was removed *in vacuo* and the residue purified by FC (petrol/EtOAc, 4/1) to give:

Chloride **24** as a colourless oil (95.8 mg, 89%): R_f 0.55 (petrol/EtOAc, 1/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.46 (t, *J* = 6.5, 2H), 3.67-3.77 (4H), 3.77-3.87 (4H), 4.10 (t, *J* = 4.5, 2H), 6.81 (d, *J* = 8.5, 2H), 7.07 (d, *J* = 8.5, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 20.5 (q), 30.4 (t), 67.5 (t), 69.9 (t), 70.6 (t), 70.8 (t), 71.3 (t), 114.5 (d, 2C), 129.9 (d, 2C), 130.1 (s), 156.6 (s); IR (neat) 2925-2870 (C-H), 1614, 1586, 1512, 1456, 1245 cm^{-1}; MS (EI+) *m/z* 302 (M^+); HRMS calcd. for $C_{13}H_{19}BrO_3$ (M^+) 302.0518, found 302.0503.

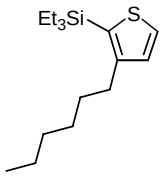
Formate ester **25** as a colourless oil (10.0 mg, 9%): R_f 0.70 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.26 (s, 3H), 3.65-3.75 (6H), 3.83 (t, *J* = 5, 2H), 4.10 (t, *J* = 5, 2H), 4.31 (t, *J* = 5, 2H), 6.80 (d, *J* = 8.5, 2H), 7.06 (d, *J* = 8.5, 2H), 8.06 (s, 1H); MS (EI+) *m/z* 268 (M^+); HRMS calcd. for $C_{14}H_{20}O_5$ (M^+) 268.1311, found 268.1315.

1-{2-[2-(2-Bromoethoxy)ethoxy]ethoxy}-4-methylbenzene 26. To a solution of the alcohol **23** (98.0 mg, 408 μmol) in CH_2Cl_2 (5 mL) at 0 °C was added triphenylphosphine (214 mg, 817 μmol) and carbon tetrabromide (542 mg, 1.63 mmol). The yellow solution was warmed to RT and left to stir for 24 h. The solvent was then removed *in vacuo* and the residue purified by FC (petrol/EtOAc, 4/1) to give bromide **26** as a colourless oil (120 mg, 97%). R_f 0.35 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.46 (t, *J* = 6.5, 2H), 3.67-3.77 (4H), 3.77-3.87 (4H), 4.10 (t, *J* = 4.5, 2H), 6.81 (d, *J* = 8.5, 2H), 7.07 (d, *J* = 8.5, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 20.5 (q), 30.4 (t), 67.5 (t), 69.9 (t), 70.6 (t), 70.8 (t), 71.3 (t), 114.5 (d, 2C), 129.9 (d, 2C), 130.1 (s), 156.6 (s); IR (neat) 2925-2870 (C-H), 1614, 1586, 1512, 1456, 1245 cm^{-1}; MS (EI+) *m/z* 302 (M^+); HRMS calcd. for $C_{13}H_{19}BrO_3$ (M) 302.0518, found 302.0503.

Trimethyl-[2-(4-{2-[2-(2-*para*-tolyloxyethoxy)ethoxy]ethoxy}phenyl)ethyl]germane 28. *Method 1:* To a solution of *4-(2-trimethylgermanylethyl)phenol* **27**[5] (105 mg, 298 μmol) in acetonitrile (2 mL) was added chloride **24** (77.2 mg, 321 μmol), TBAI (15.5 mg, 42.0 μmol) and caesium carbonate (145 mg, 411 μmol). The reaction mixture was refluxed at 85 °C for 17 h then cooled and filtered. The solvent was removed *in vacuo* and the residue purified by FC (petrol/EtOAc, 9/1) to give ether **28** as a colourless oil (119 mg, 87%). R_f 0.30 (petrol/EtOAc, 3/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.00 (s, 9H), 0.91 (m, 2H), 2.17 (s, 3H), 4.00 (m, 2H), 3.65 (s, 4H), 3.75 (t, *J* = 5, 4H), 4.00 (t, *J* = 5, 4H), 6.71 (d, *J* = 8.5, 2H), 6.72 (d, *J* = 8.5, 2H), 6.96 (d, *J* = 8.5, 2H), 6.99 (d, *J* = 8.5, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ -2.4 (q, 3C), 18.8 (t), 20.5 (q), 30.3 (t), 67.5 (t, 2C), 69.9 (t, 2C), 70.9 (t, 2C), 114.5 (d, 4C), 128.7 (d, 2C), 129.9 (d, 2C), 130.0 (s), 137.4 (s), 156.7 (s), 156.8 (s); IR (neat) 2920-2870 (C-H), 1612, 1585, 1511, 1455, 1246 cm^{-1}; MS (EI+) *m/z* 462 (M^+); HRMS calcd. for $C_{24}H_{36}Ge^{74}O_4$ (M^+) 462.1825, found 462.1807.

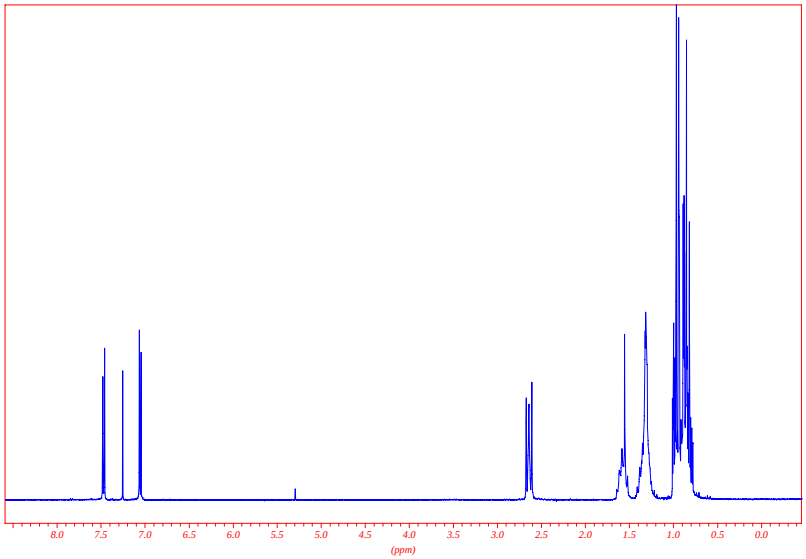
Method 2: To a solution of *4-(2-trimethylgermanylethyl)phenol* **27**[5] (54.0 mg, 178 μmol) in acetonitrile (2 mL) was added bromide **26** (54.0 mg, 178 μmol), TBAI (9.2 mg, 24.9 μmol) and caesium carbonate (87.3 mg, 247 μmol). The mixture was refluxed at 85 °C for 17 h then cooled and filtered. The solvent was removed *in vacuo* and the residue purified by FC (petrol/EtOAc, 9/1) to give the ether **28** as a colourless oil (70.1 mg, 84%) Spectroscopic data as above.

Triethyl-[3-(*n*-hexyl)thiophen-2-yl]silane 1b.

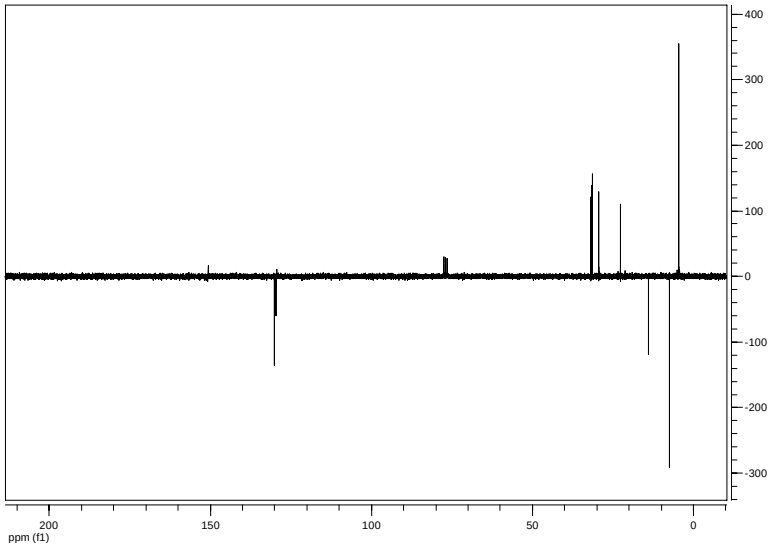


$C_{16}H_{30}SSi$
Mol. Wt.: 282.56

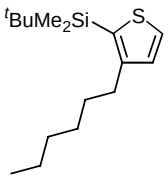
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

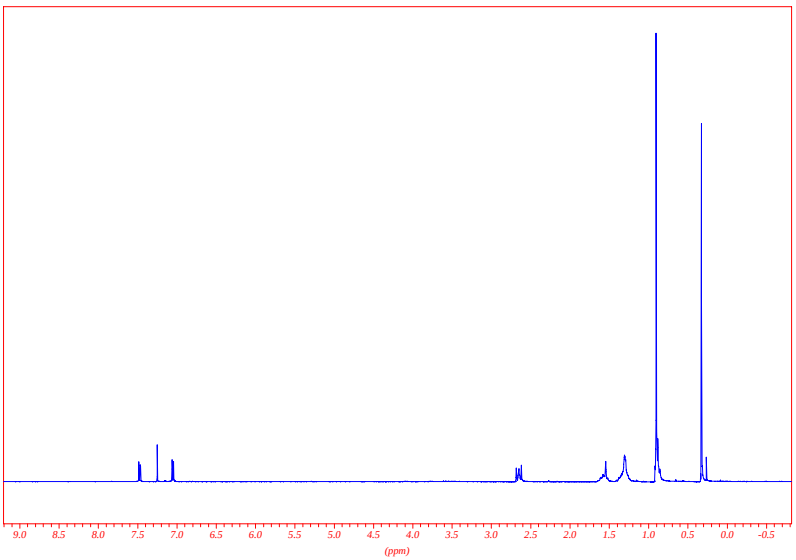


tert-Butyl-[3-(*n*-hexyl)thiophen-2-yl]dimethylsilane 1c.

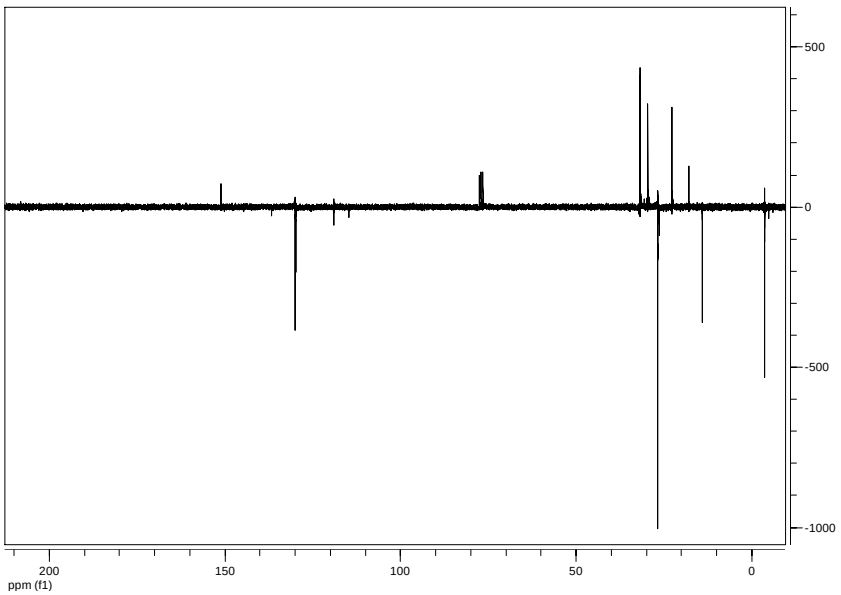


$C_{16}H_{30}SSi$
Mol. Wt.: 282.56

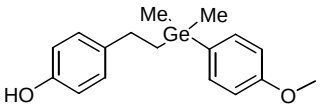
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

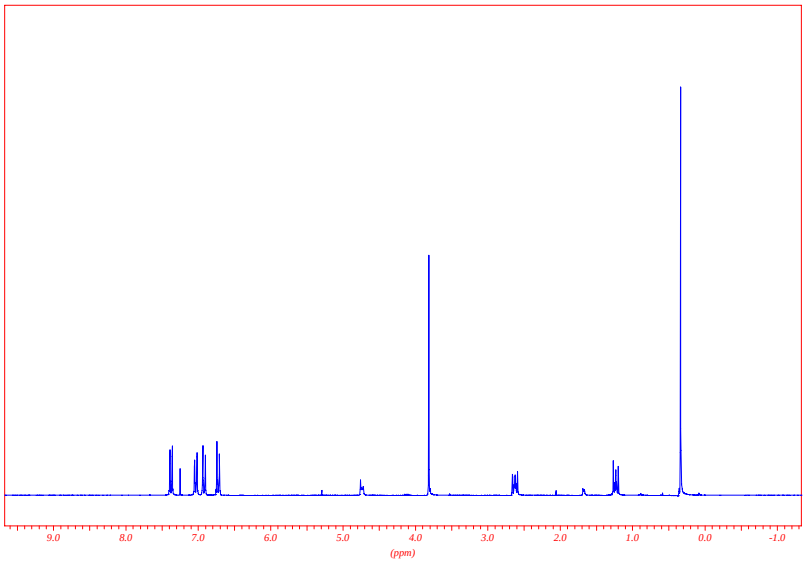


4-{2-[(4-Methoxyphenyl)dimethylgermanyl]ethyl}phenol 8a.

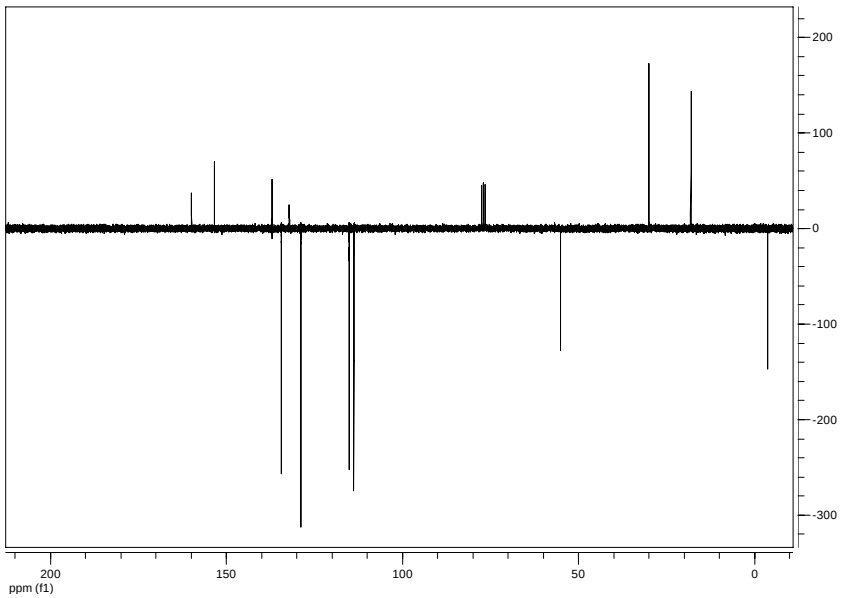


$C_{17}H_{22}GeO_2$
Mol. Wt.: 330.97

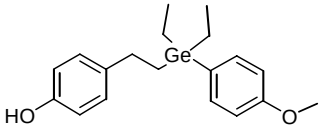
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

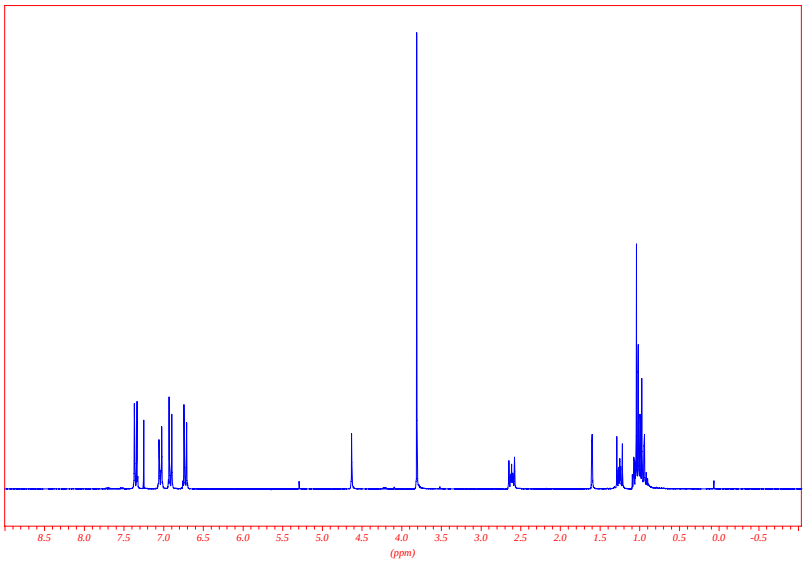


4-{2-[Diethyl-(4-methoxyphenyl)germanyl]ethyl}phenol 8b.

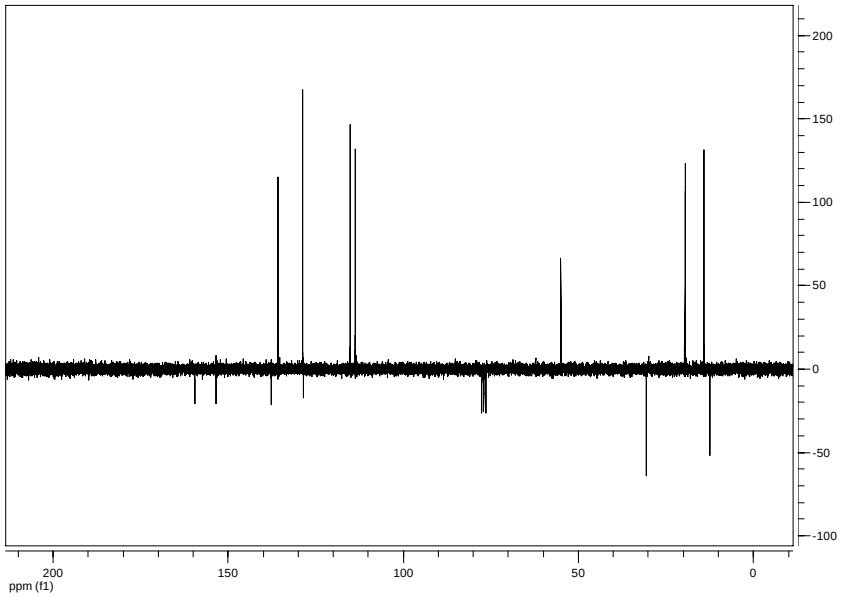


$C_{19}H_{26}GeO_2$
Mol. Wt.: 359.02

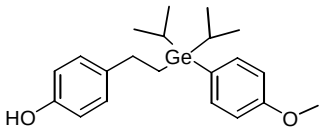
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

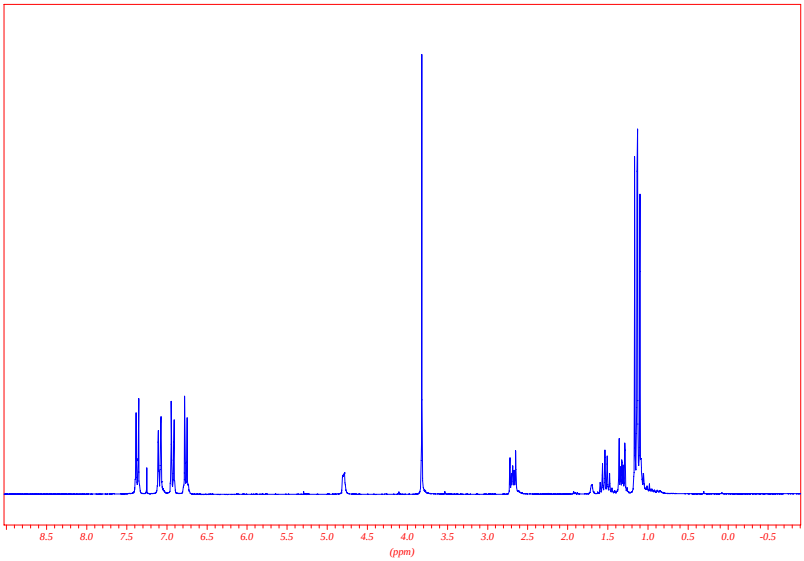


4-{2-[Diisopropyl-(4-methoxyphenyl)germanyl]ethyl}phenol 8c.

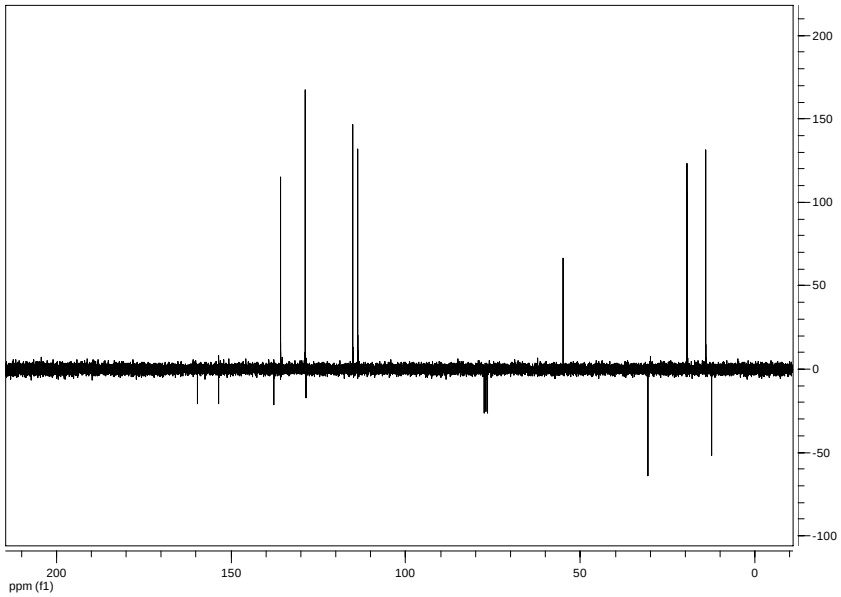


$C_{21}H_{30}GeO_2$
Mol. Wt.: 387.07

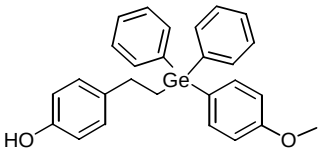
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

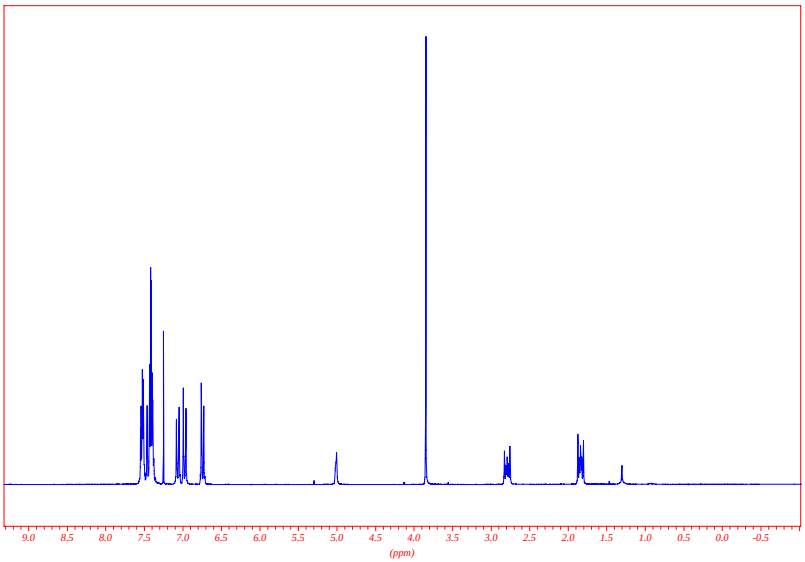


4-{2-[(4-Methoxyphenyl)diphenylgermanyl]ethyl}phenol 8d.

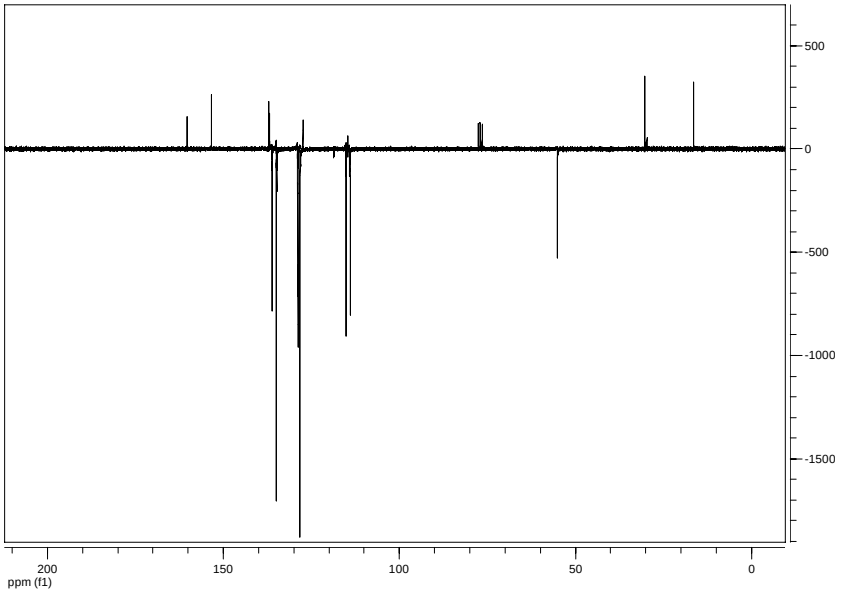


$C_{27}H_{26}GeO_2$
Mol. Wt.: 455.10

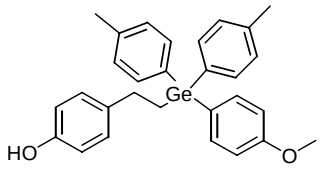
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

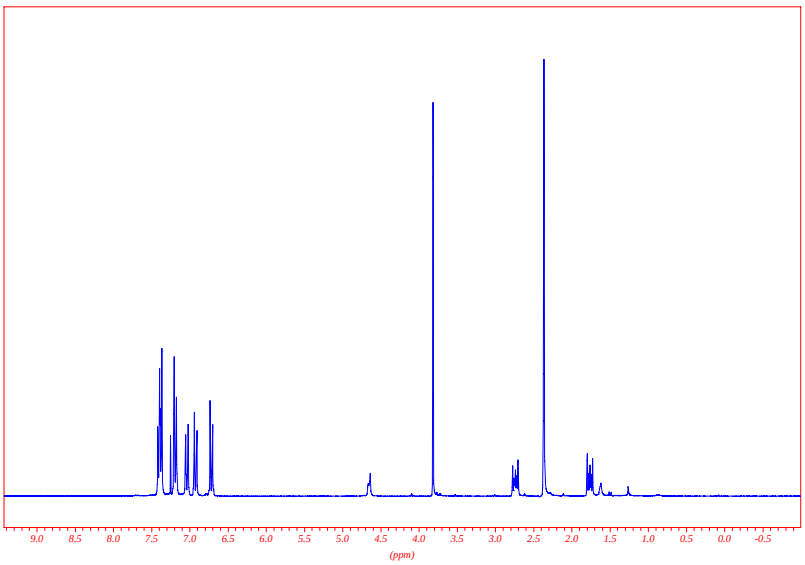


4-{2-[(4-Methoxyphenyl)-di-*para*-tolylgermanyl]ethyl}phenol 8e.

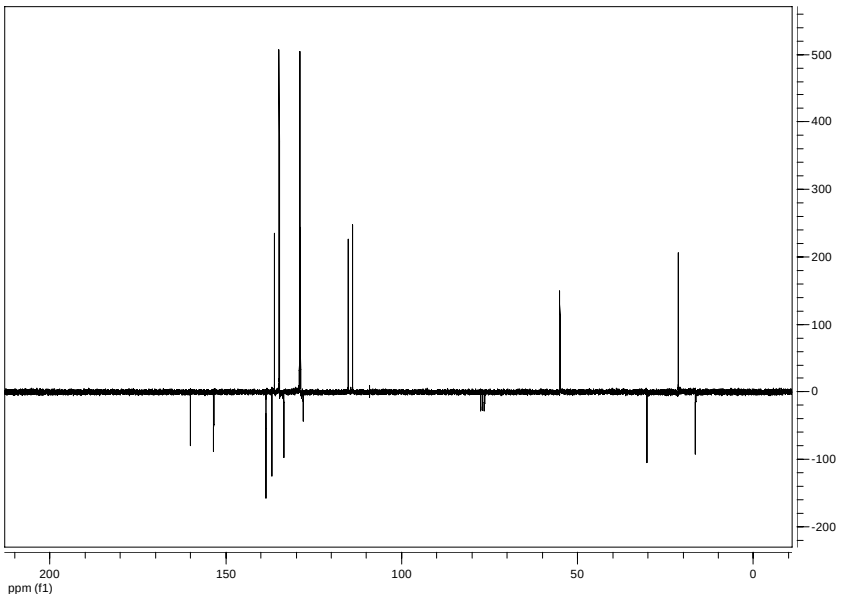


$C_{29}H_{30}GeO_2$
Mol. Wt.: 483.16

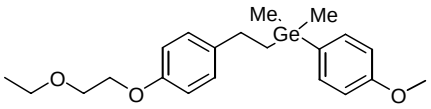
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

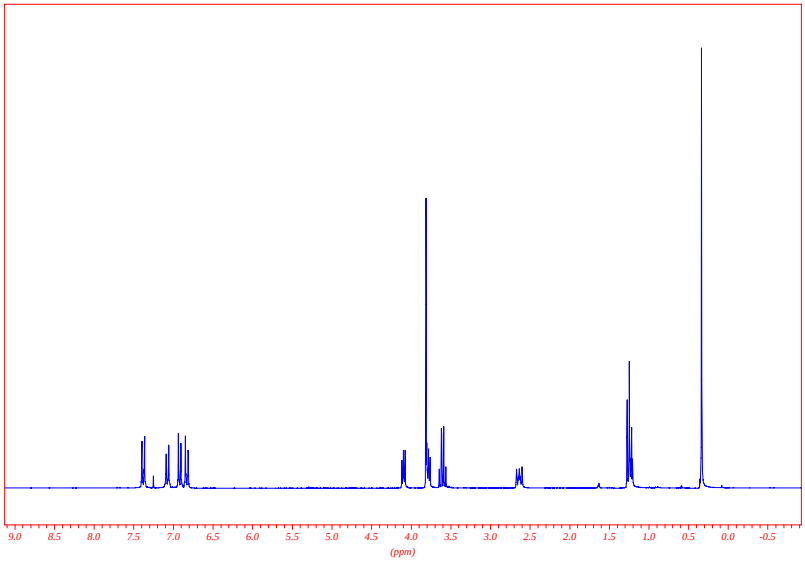


{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(4-methoxyphenyl)dimethylgermane 9a.

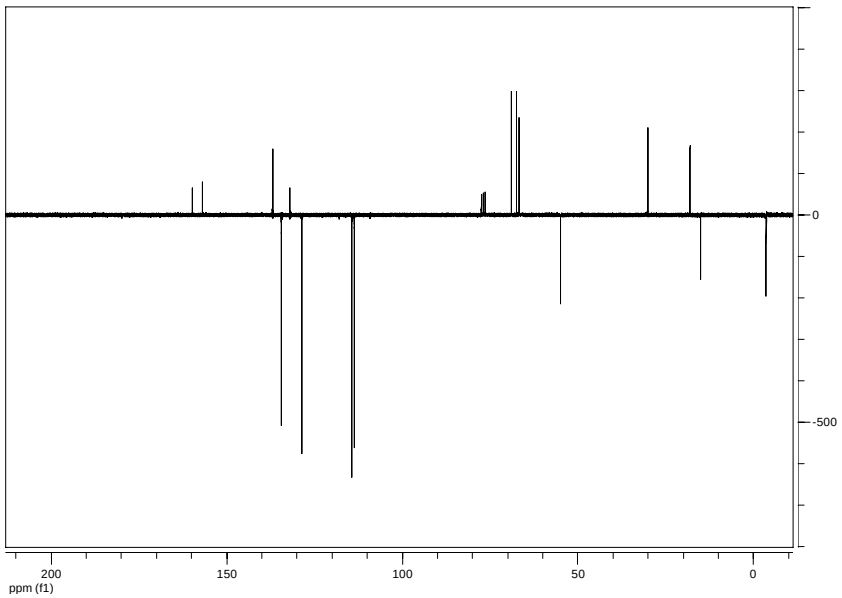


$C_{21}H_{30}GeO_3$
Mol. Wt.: 403.07

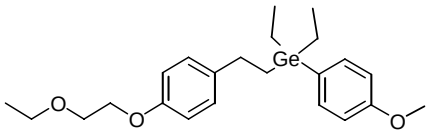
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

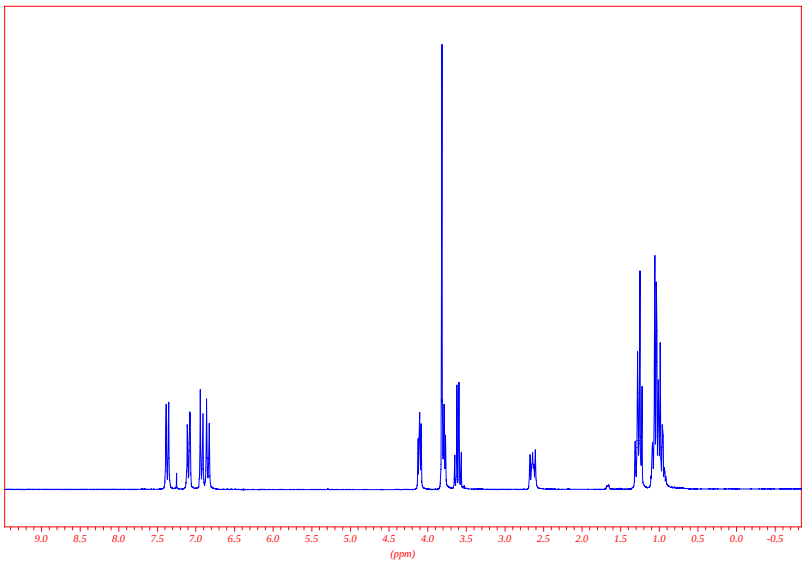


{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}diethyl-(4-methoxyphenyl)germane 9b.

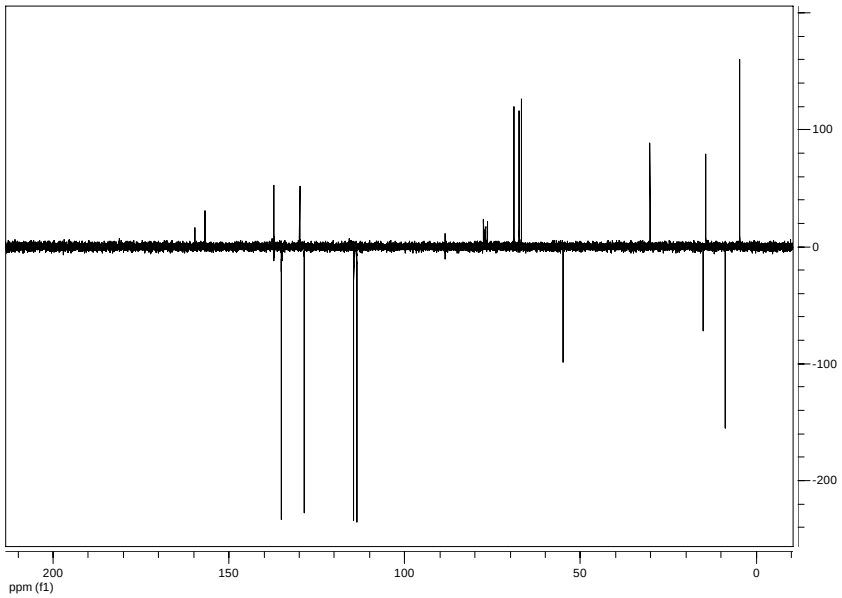


$C_{23}H_{34}GeO_3$
Mol. Wt.: 431.12

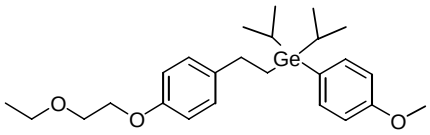
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

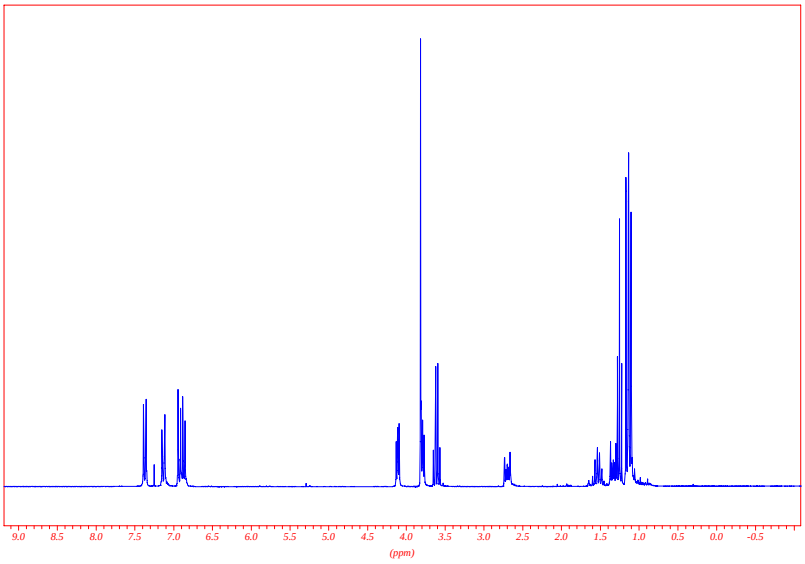


{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}diisopropyl-(4-methoxyphenyl)germane 9c.

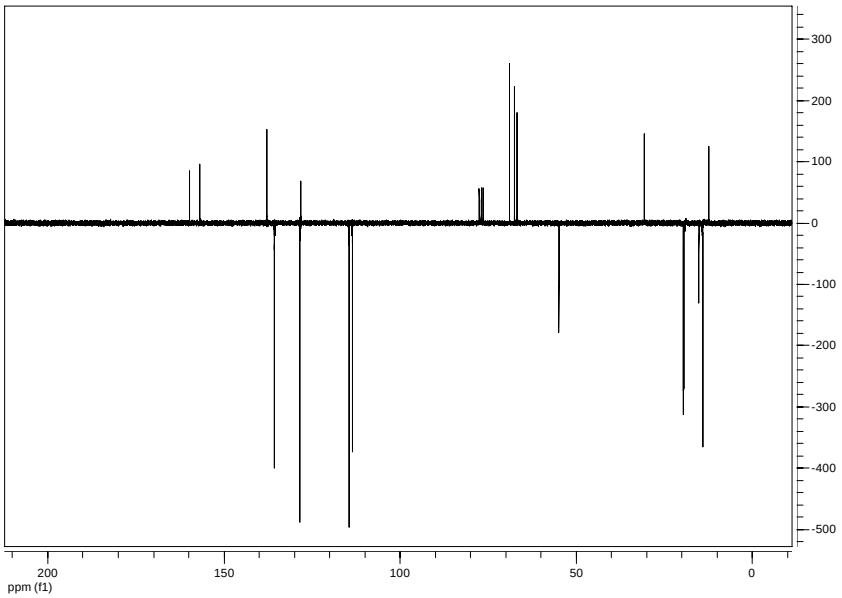


$C_{25}H_{38}GeO_3$
Mol. Wt.: 459.18

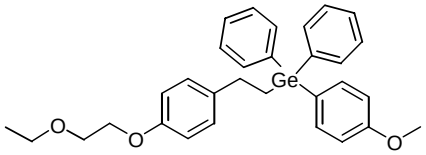
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

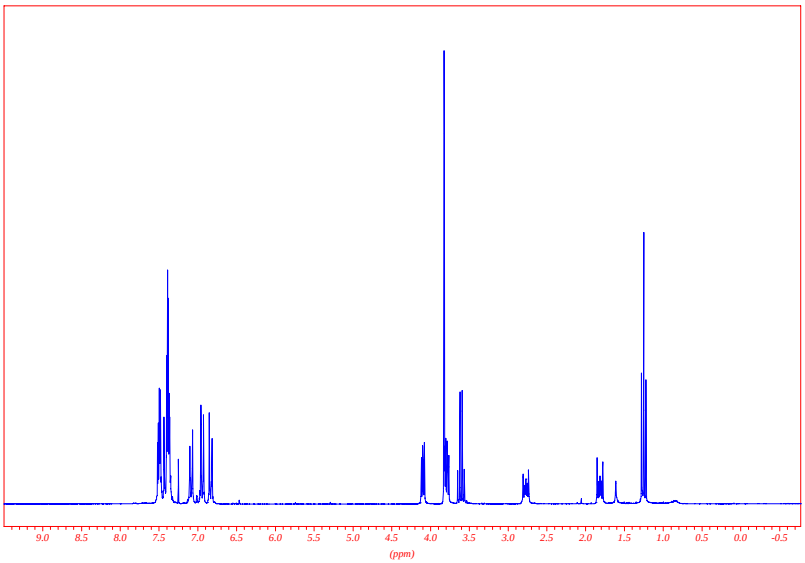


{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(4-methoxyphenyl)diphenylgermane 9d.

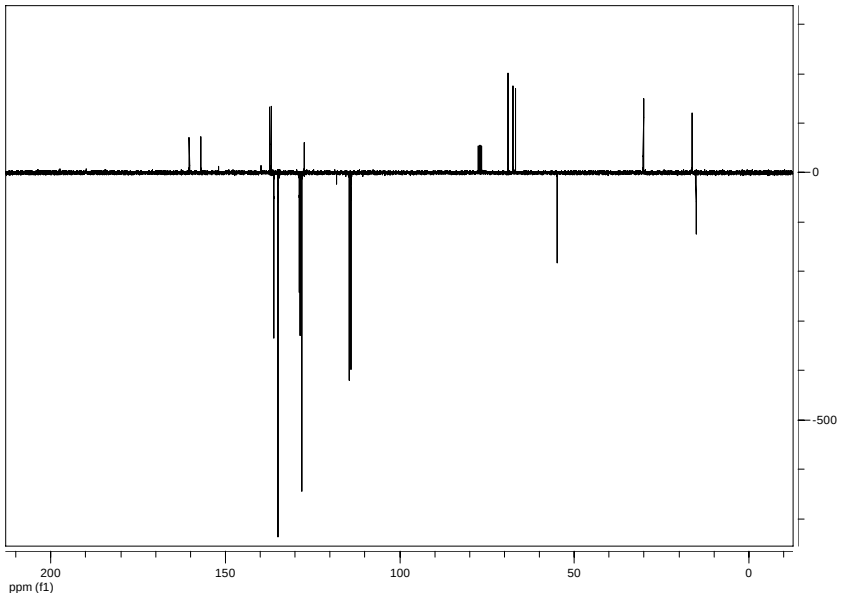


$C_{31}H_{34}GeO_3$
Mol. Wt.: 527.21

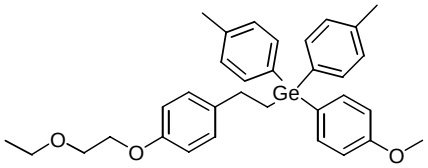
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

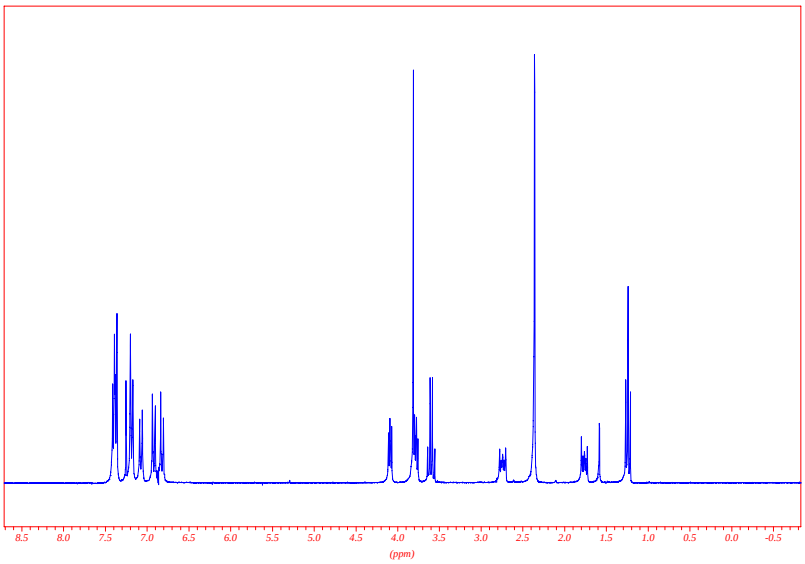


{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(4-methoxyphenyl)di-*para*-tolylgermane 9e.

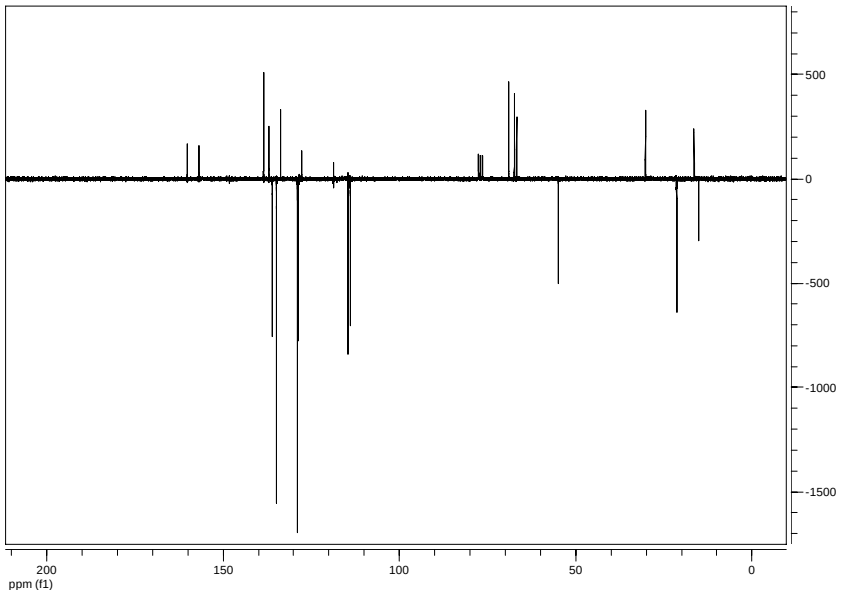


$C_{33}H_{38}GeO_3$
Mol. Wt.: 555.26

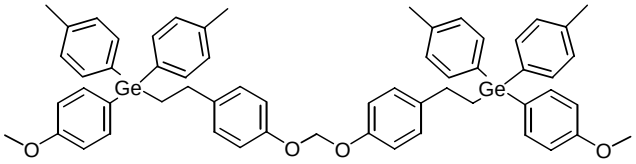
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

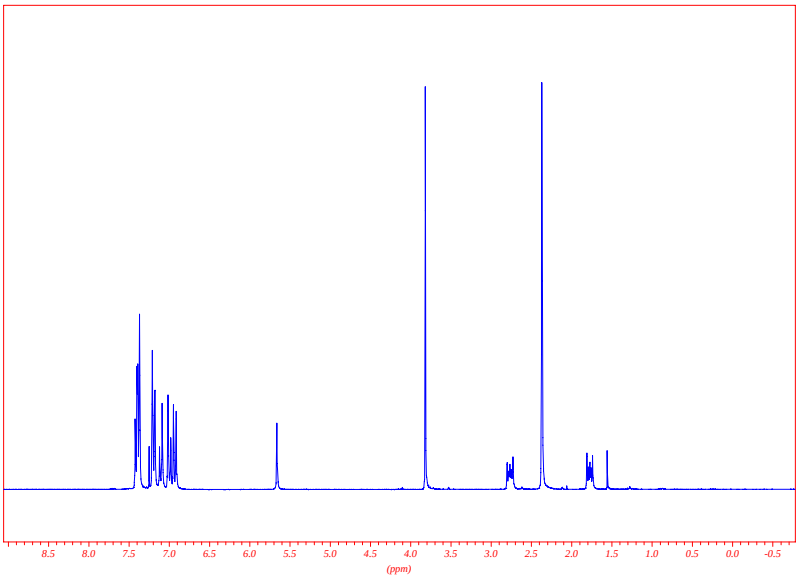


Bis-(4-{2-[(4-methoxyphenyl)-di-*para*-tolylgermanyl]ethyl}phenoxy)methane.

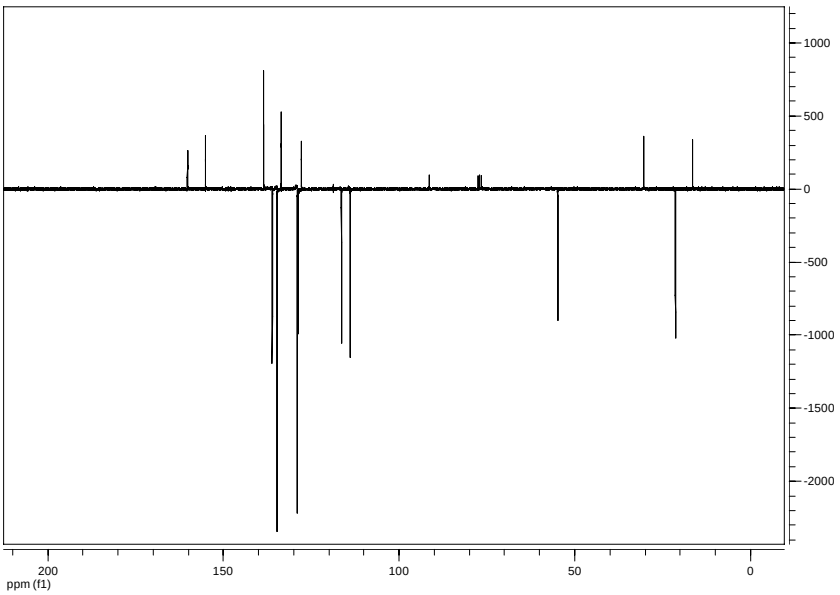


$C_{59}H_{60}Ge_2O_4$
Mol. Wt.: 978.33

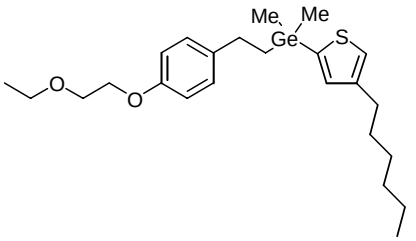
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

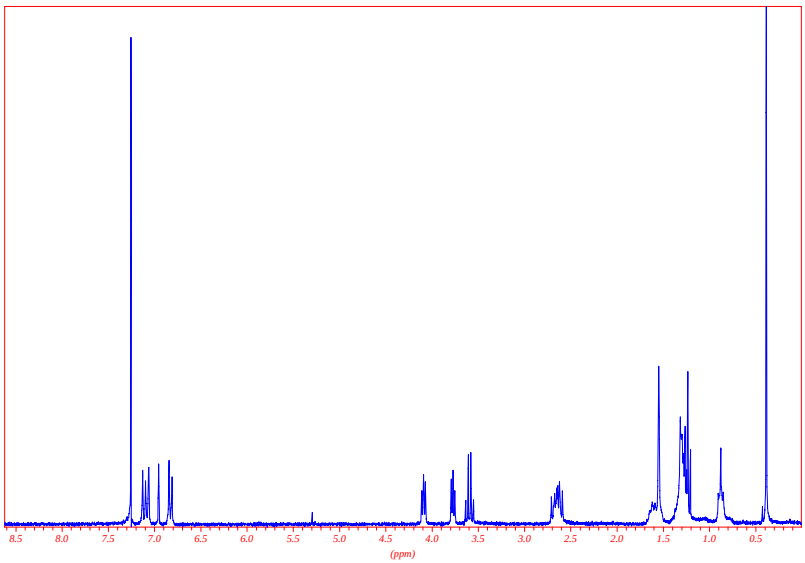


{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(4-hexylthiophen-2-yl)dimethylgermane 10a.

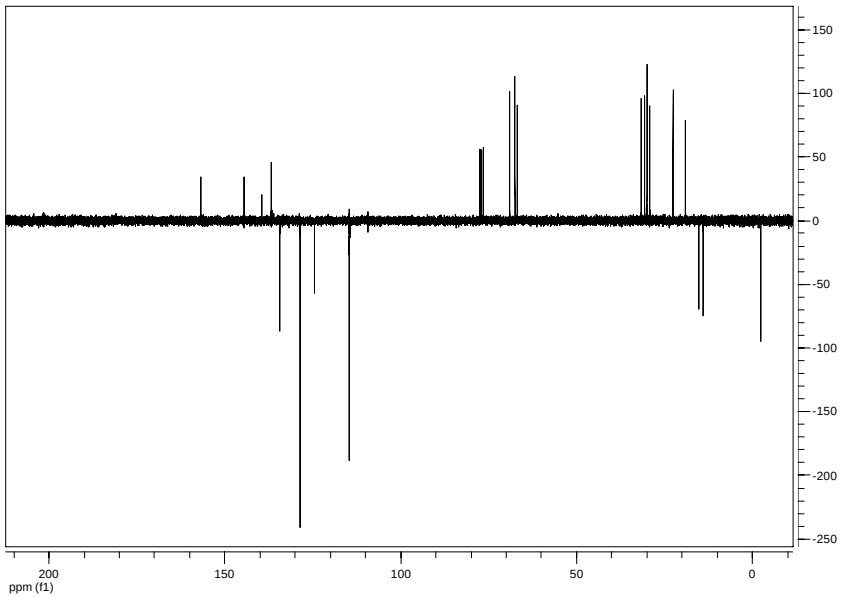


$C_{24}H_{38}GeO_2S$
Mol. Wt.: 463.23

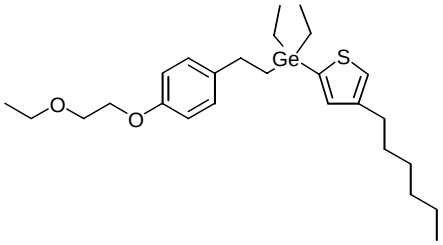
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

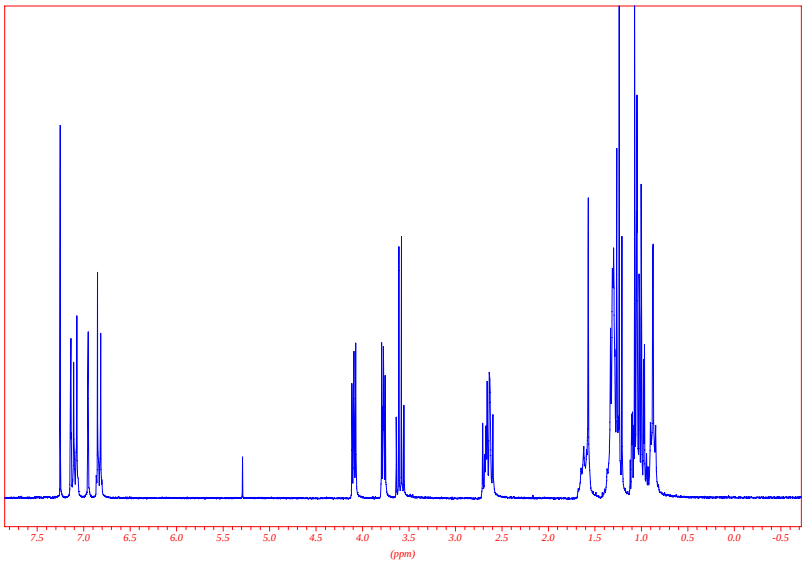


{2-[4-(2-Ethoxy)phenyl]ethyl}diethyl-(4-hexylthiophen-2-yl)germane 10b.

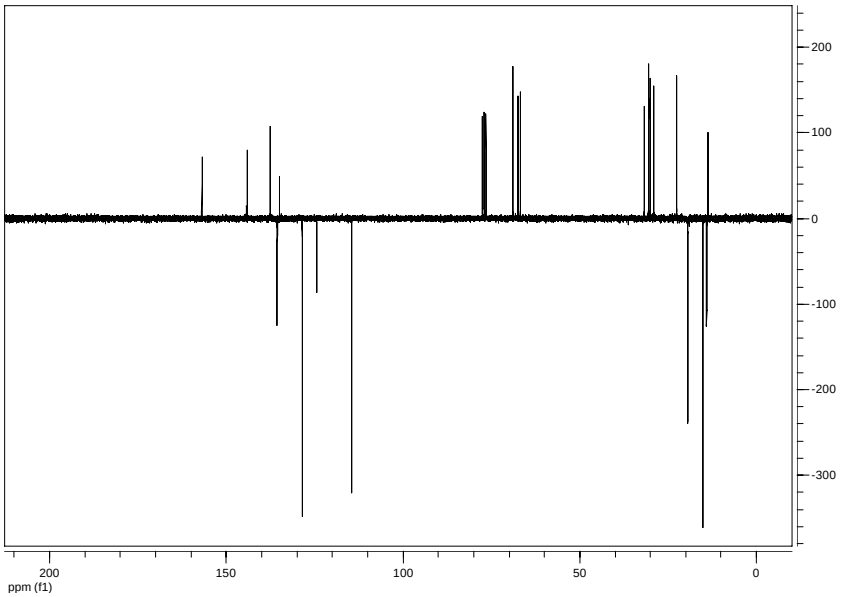


$C_{26}H_{42}GeO_2S$
Mol. Wt.: 491.29

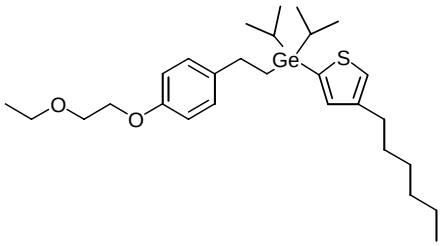
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

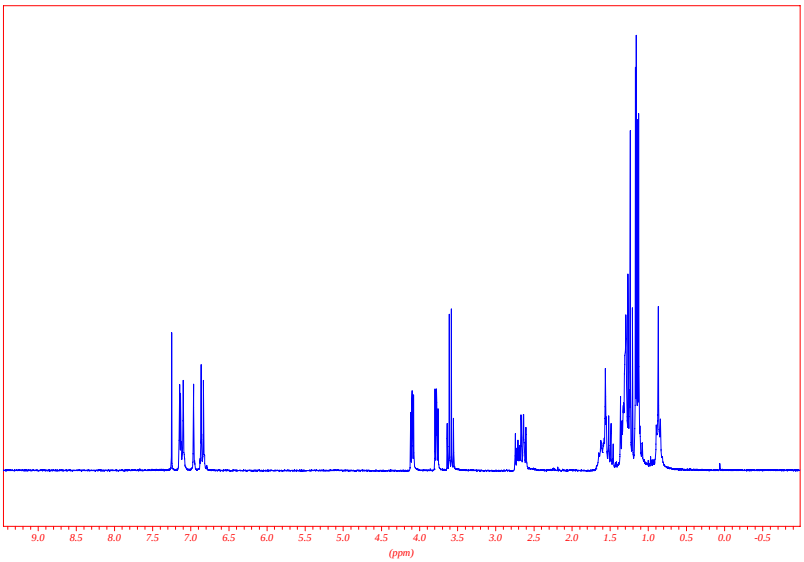


{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(4-hexylthiophen-2-yl)di-*iso*-propylgermane 10c.

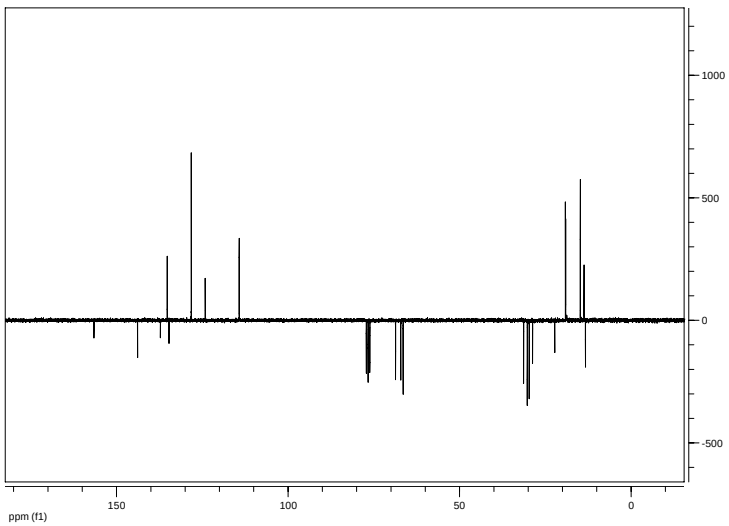


$C_{28}H_{46}GeO_2S$
Mol. Wt.: 519.34

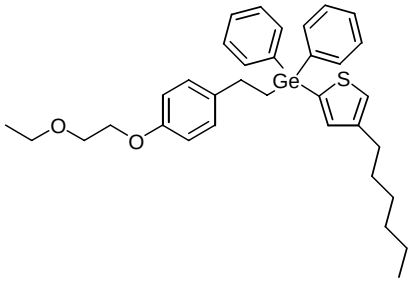
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

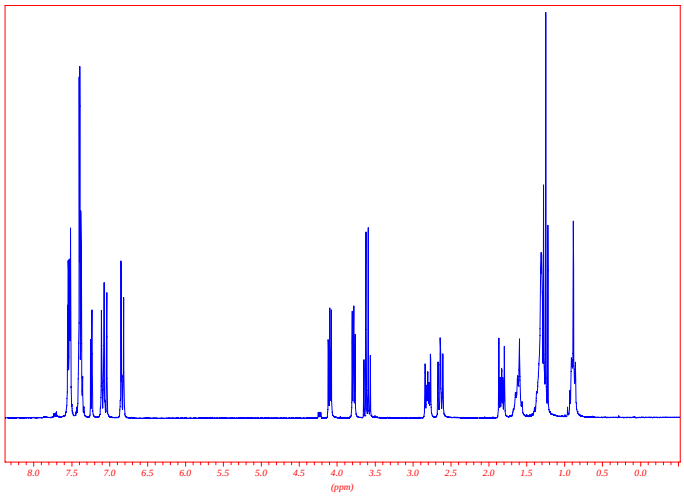


{2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-(4-hexyl-thiophen-2-yl)-diphenyl-germane 10d.

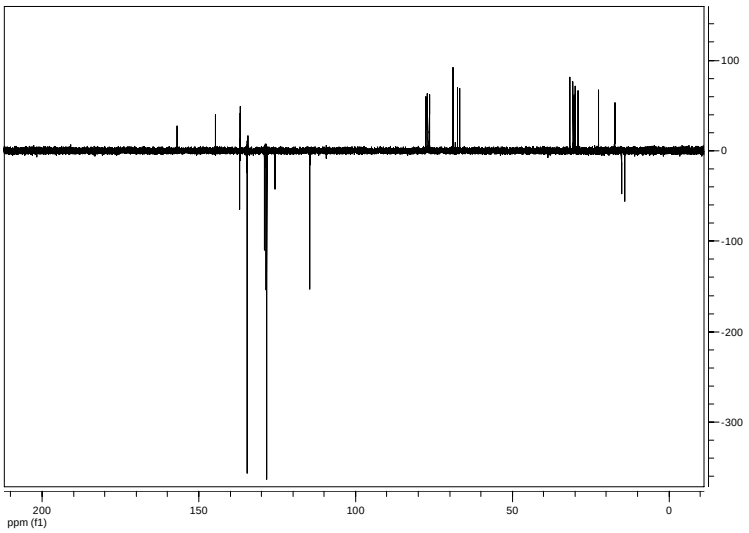


$C_{34}H_{42}GeO_2S$
Mol. Wt.: 587.37

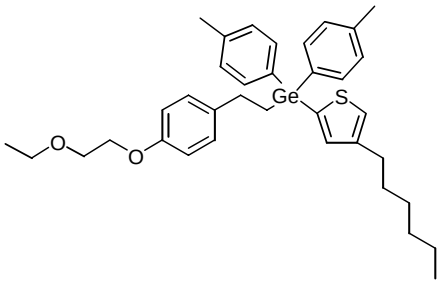
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

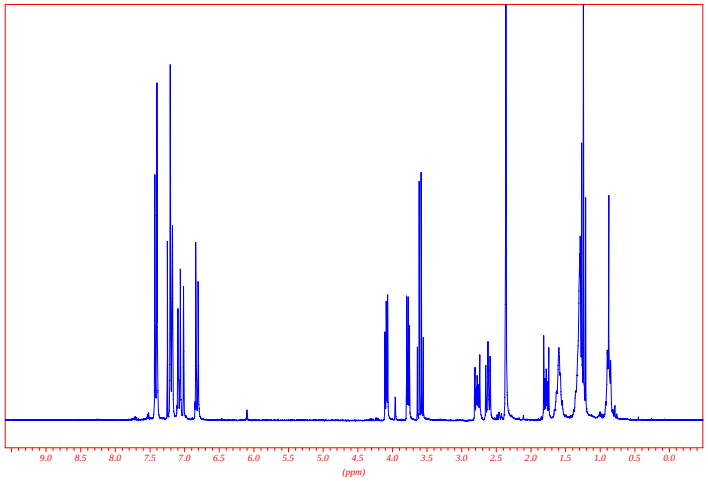


{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(4-hexylthiophen-2-yl)-di-*para*-tolylgermane 10e.

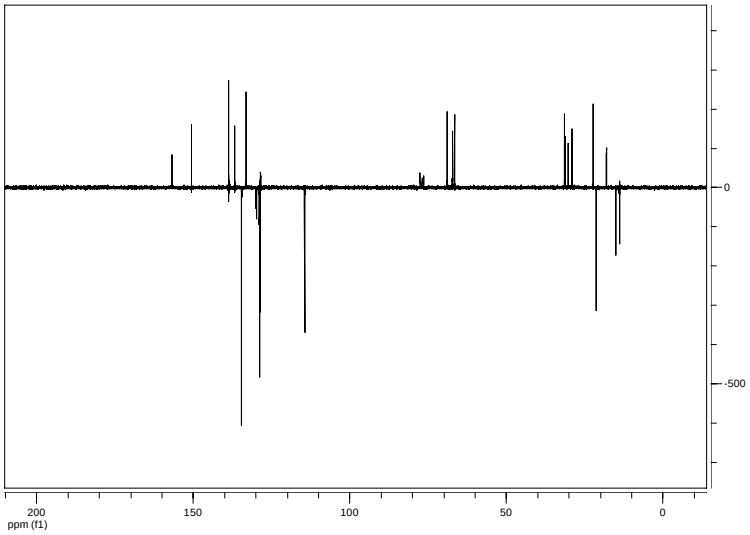


$C_{36}H_{46}GeO_2S$
Mol. Wt.: 615.43

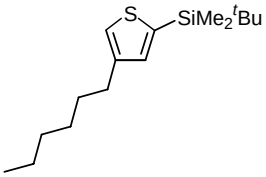
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

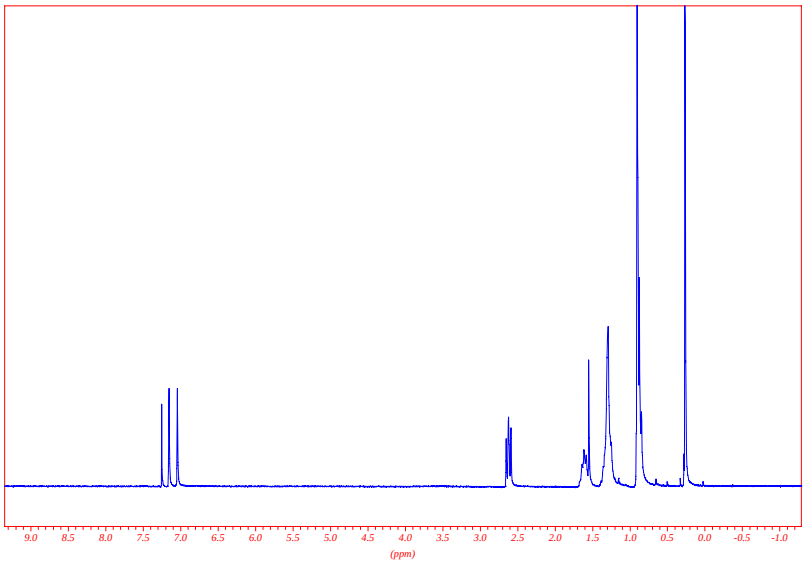


***tert*-Butyl-(4-hexylthophen-2-yl)dimethylsilane 12.**

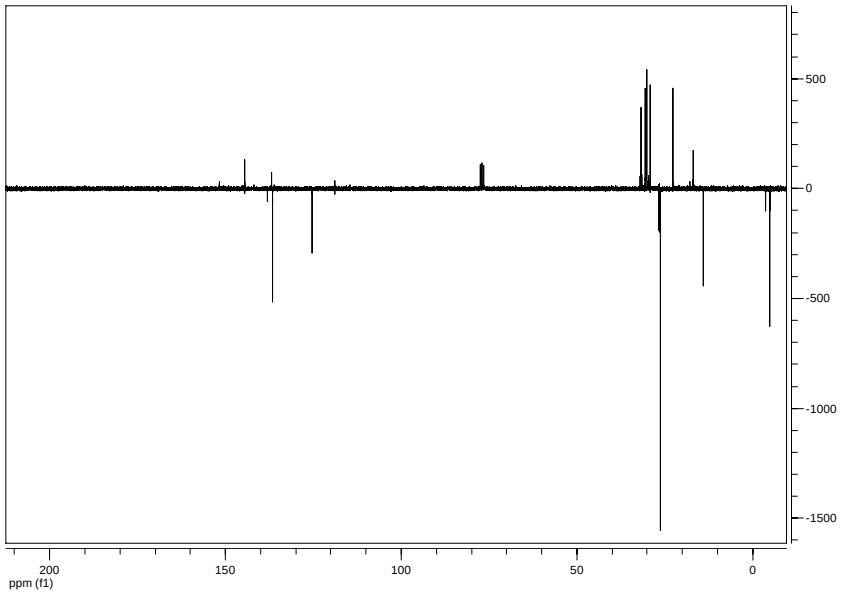


$C_{16}H_{30}SSi$
Mol. Wt.: 282.56

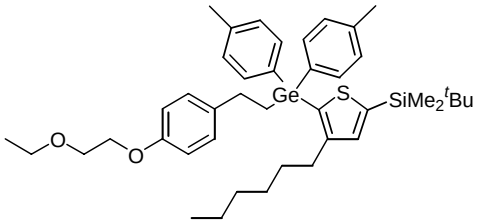
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

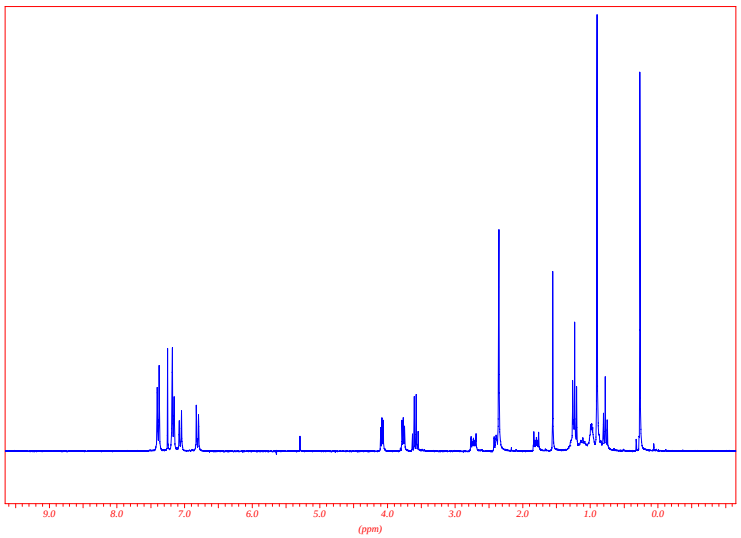


***tert*-Butyl-[5-({2-[4-(2-ethoxyethoxy)phenyl]ethyl}di-*para*-tolylgermanyl)-4-hexylthiophen-2-yl]dimethylsilane 13.**

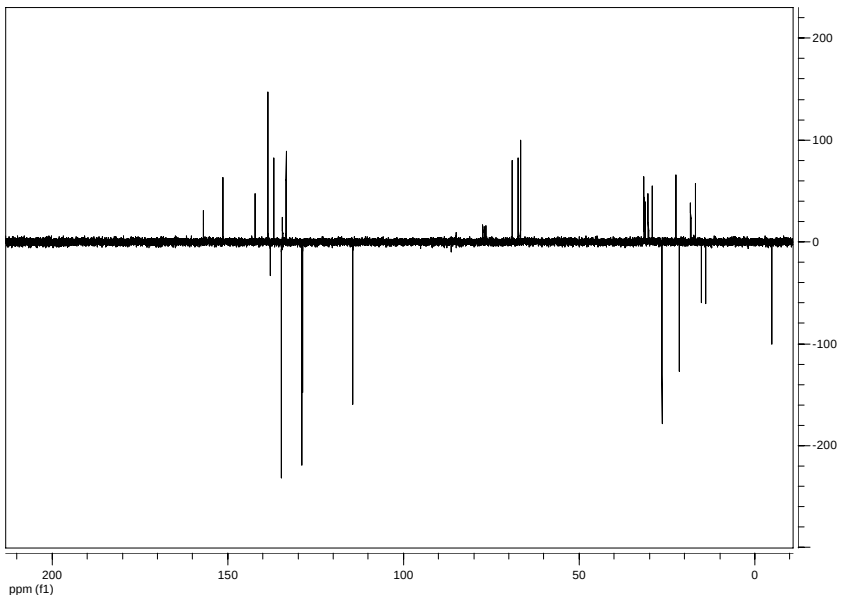


$C_{42}H_{60}GeO_2SSi$
Mol. Wt.: 729.69

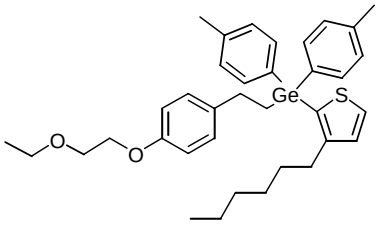
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

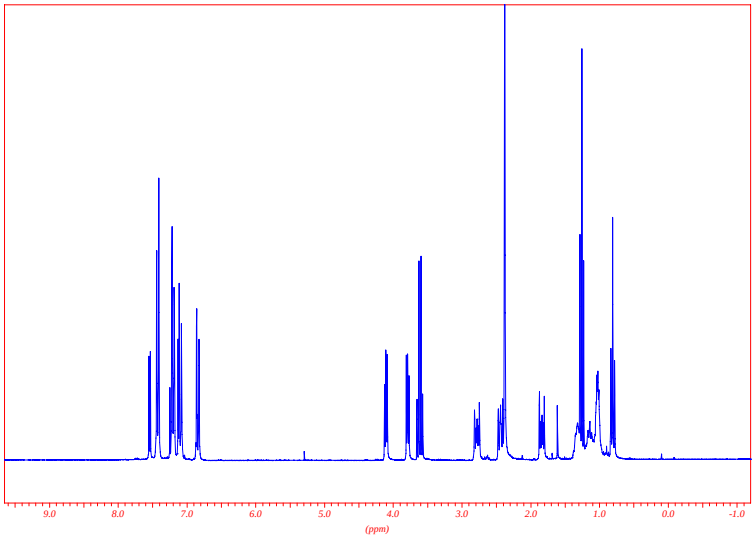


{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(3-*n*-hexylthiophen-2-yl)di-*para*-tolylgermane 14.

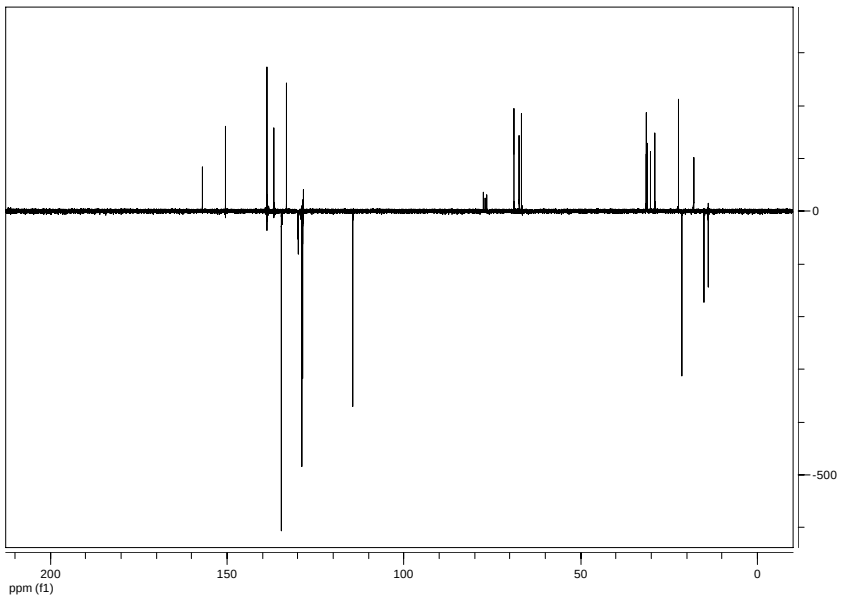


$C_{36}H_{46}GeO_2S$
Mol. Wt.: 615.43

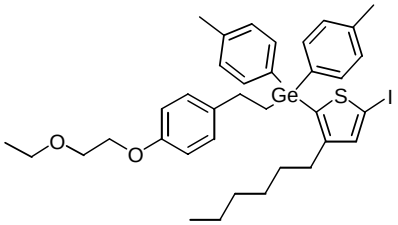
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

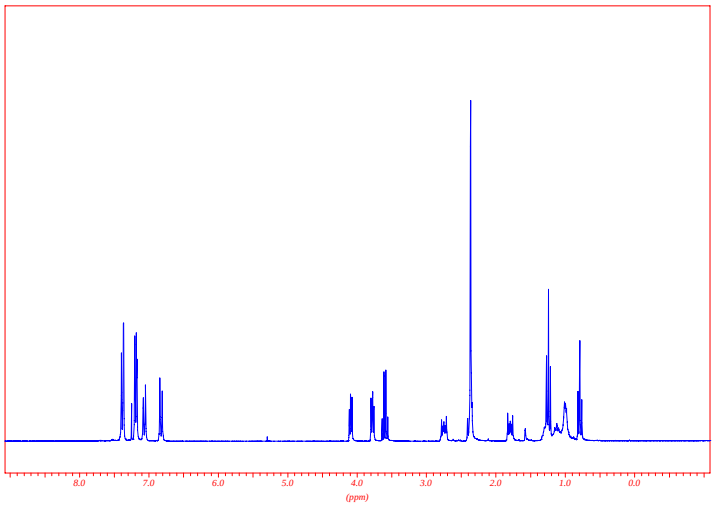


{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(3-*n*-hexyl-5-iodothiophen-2-yl)-di-*para*-tolylgermane 15.

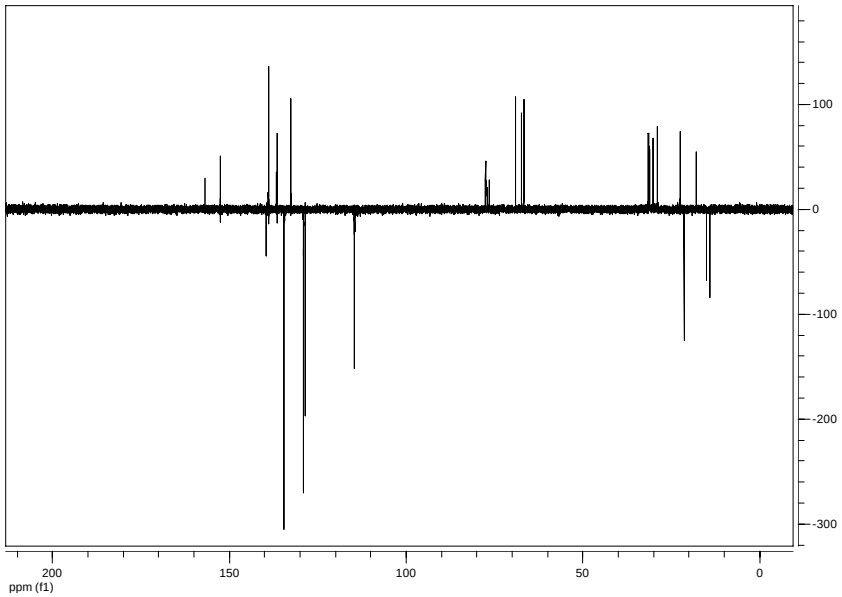


$C_{36}H_{45}GeIO_2S$
Mol. Wt.: 741.32

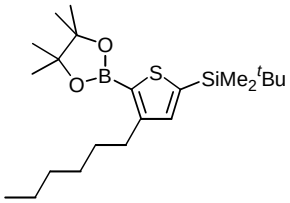
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

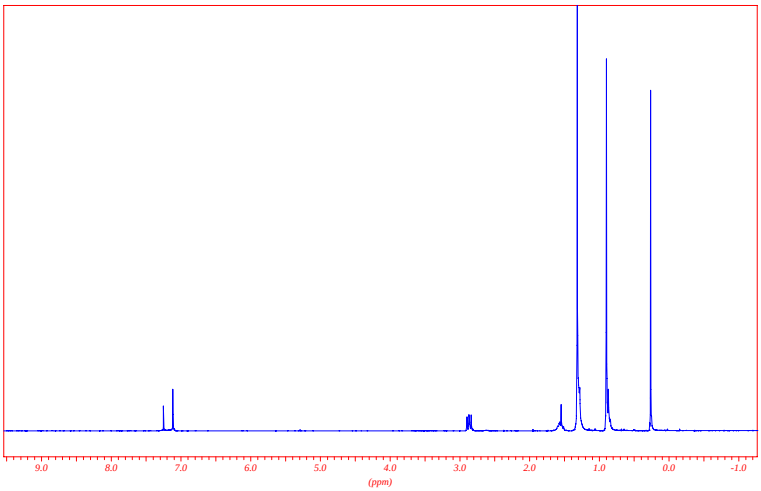


2-[5-(*tert*-Butyldimethylsilanyl)-3-*n*-hexylthophen-2-yl]-4,4,5,5-tetramethyl-[1,2,3]dioxaboralane 16.

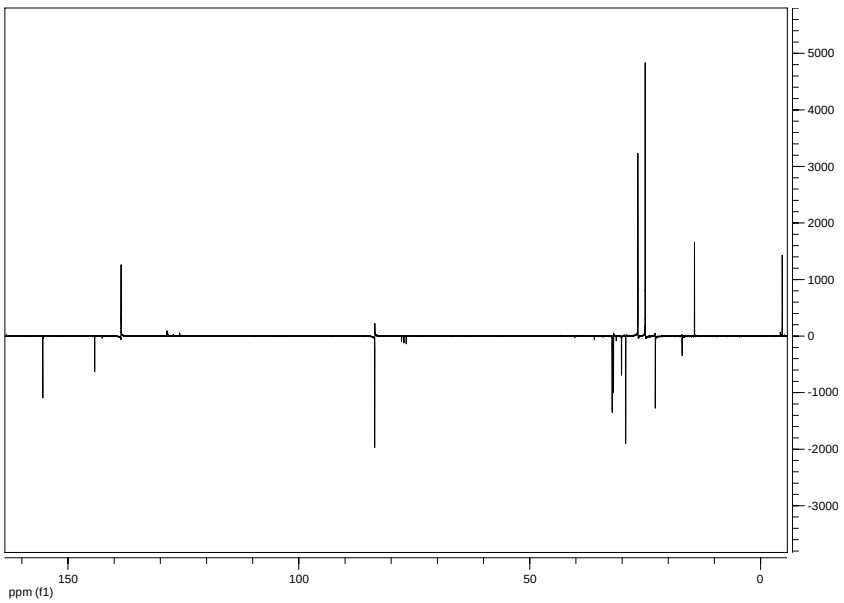


$C_{22}H_{41}BO_2SSi$
Mol. Wt.: 408.52

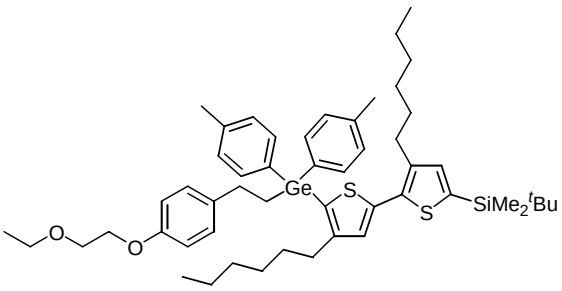
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

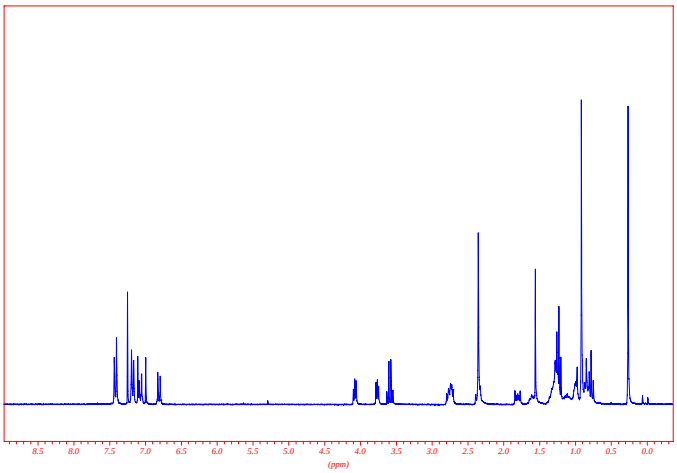


tert-Butyl-[5'-({2-[4-(2-ethoxyethoxy)phenyl]ethyl}-di-_para_-tolylgermanyl)-3,4'-dihexithiophenyl-5-yl]dimethylsilane 17.

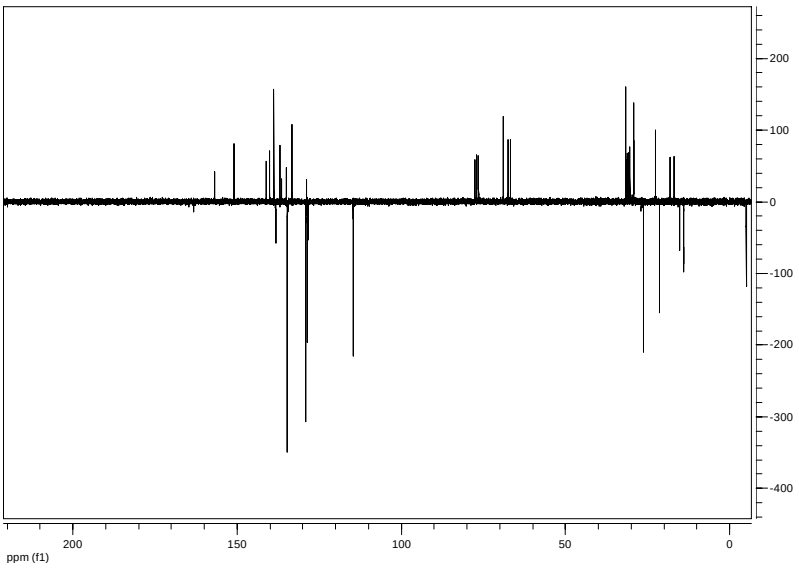


$C_{52}H_{74}GeO_2S_2Si$
Mol. Wt.: 895.97

^{1}H NMR (250 MHz, $CDCl_3$)

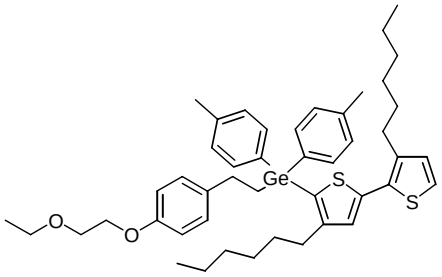


^{13}C NMR APT (62.8 MHz, $CDCl_3$)



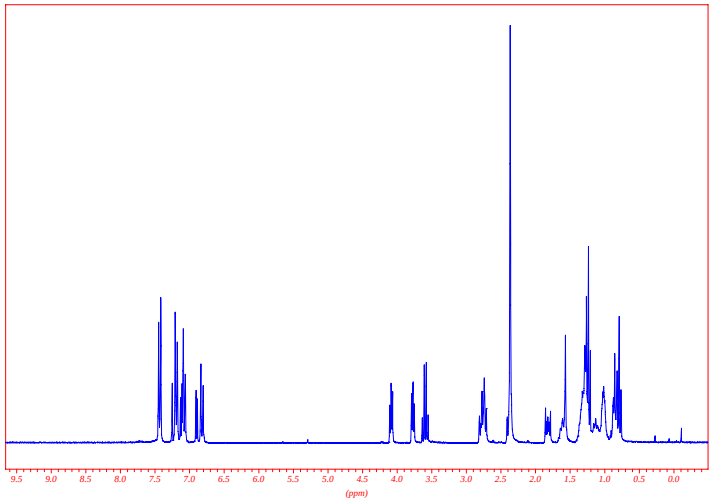
(4,3'-Dihexyl[2,2']bithiophenyl-5-yl)-{2-[4-(2-ethoxyethoxy)phenyl]ethyl}-di-*para*-tolylgermane

18.

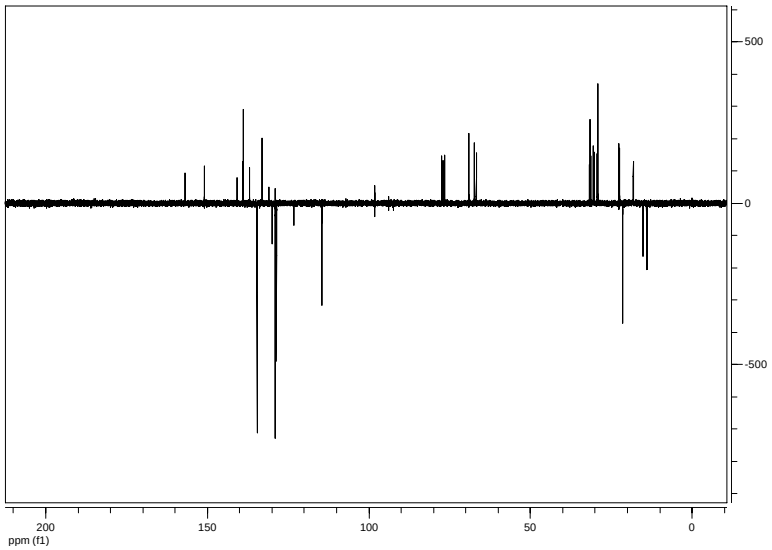


$C_{46}H_{60}GeO_2S_2$
Mol. Wt.: 781.71

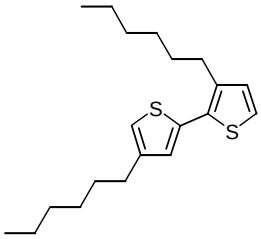
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)



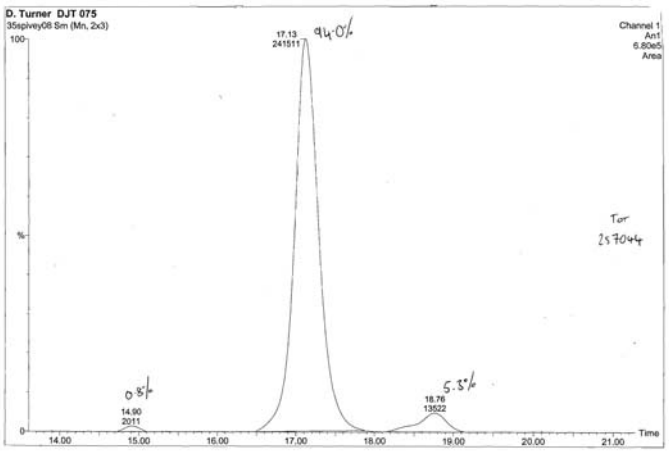
3,4'-Dihexyl-[2,2']bithiophene 19.



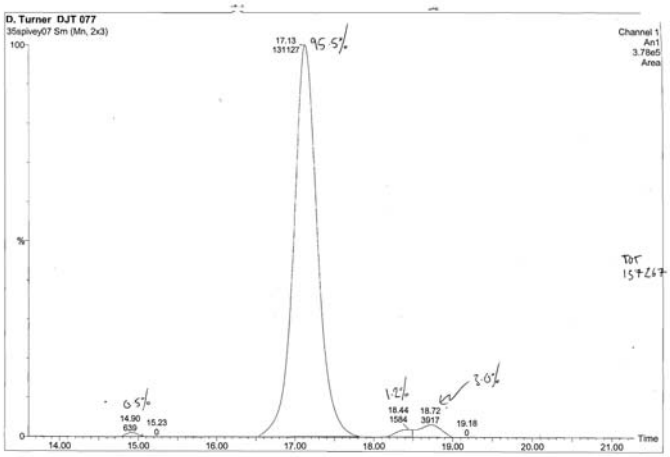
$C_{20}H_{30}S_2$
Mol. Wt.: 334.58

HPLC: Jupiter ODS-C18 column (250 × 0.46 cm), UV 254 nm detection, 1 mLmin^{-1}, 5→100% MeCN in H_2O + 0.1% formic acid, R_t = 17.1 min.

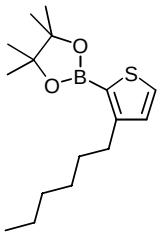
Before 'double coupling':



After 'double coupling':

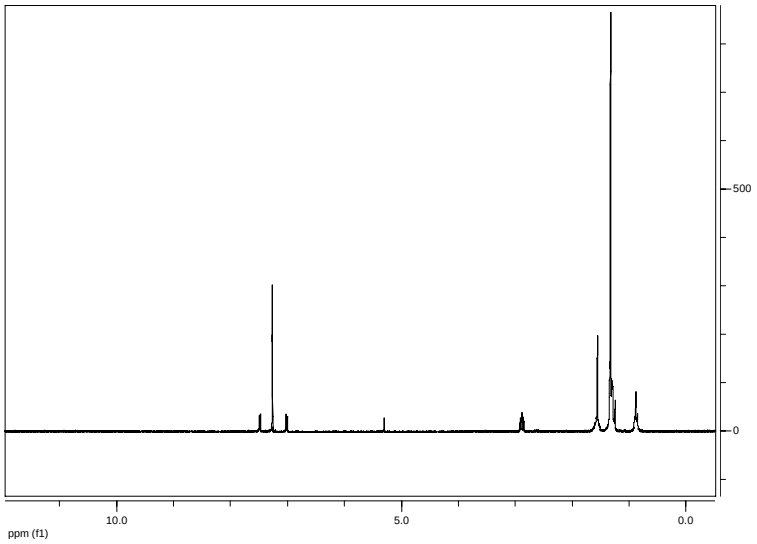


2-(3-*n*-Hexylthiophen-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 20.

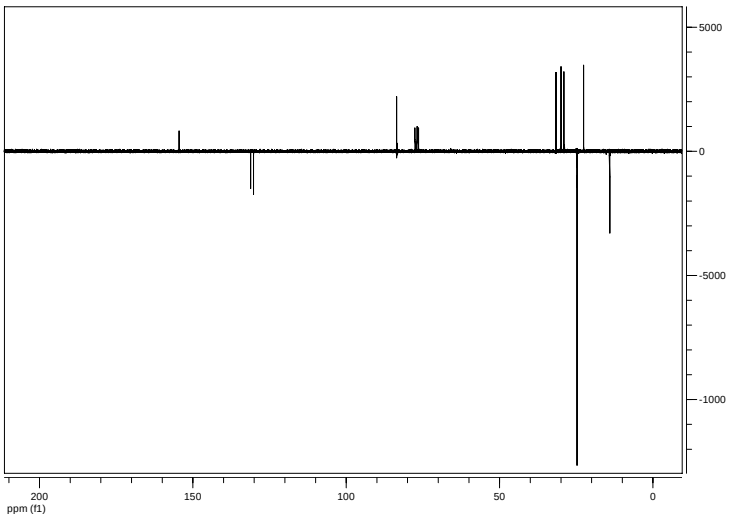


$C_{16}H_{27}BO_2S$
Mol. Wt.: 294.26

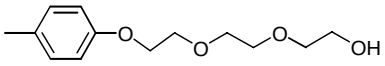
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

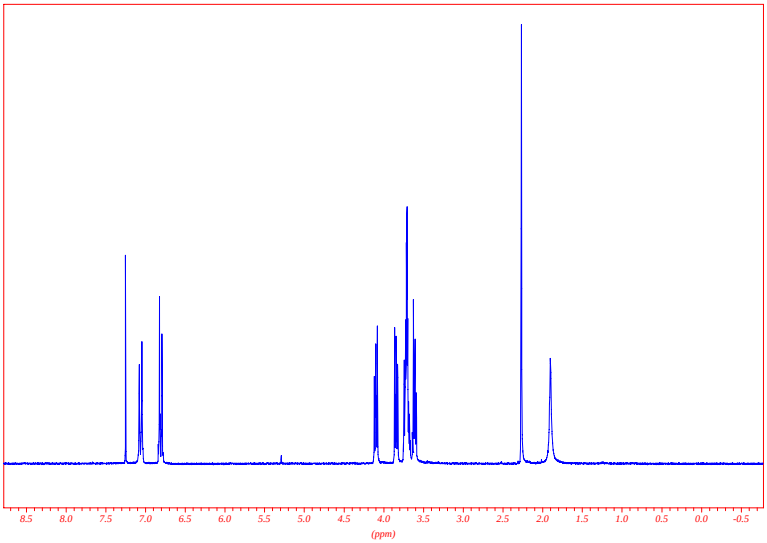


2-[2-(2-*para*-Tolyloxyethoxy)ethoxy]ethanol 23.

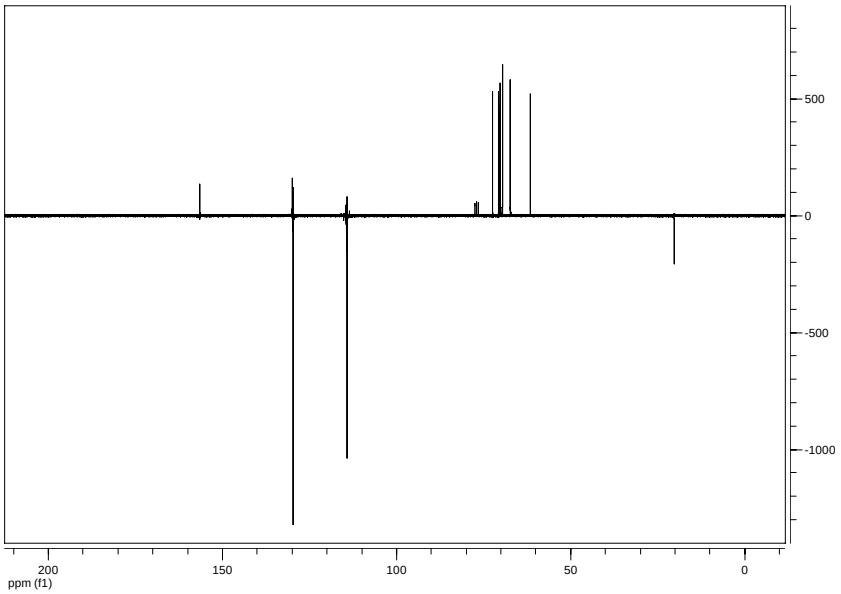


$C_{13}H_{20}O_4$
Mol. Wt.: 240.30

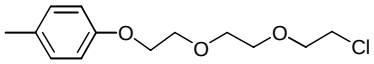
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

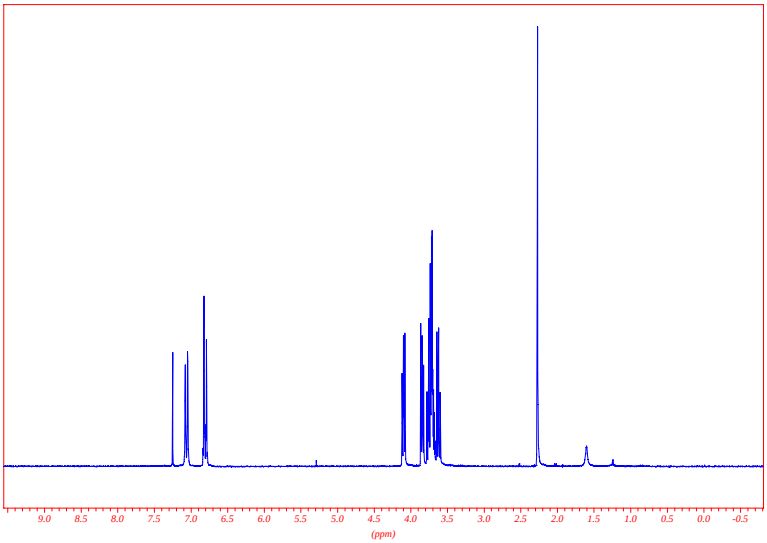


1-{2-[2-(2-Chloroethoxy)ethoxy]ethoxy}-4-methylbenzene 24

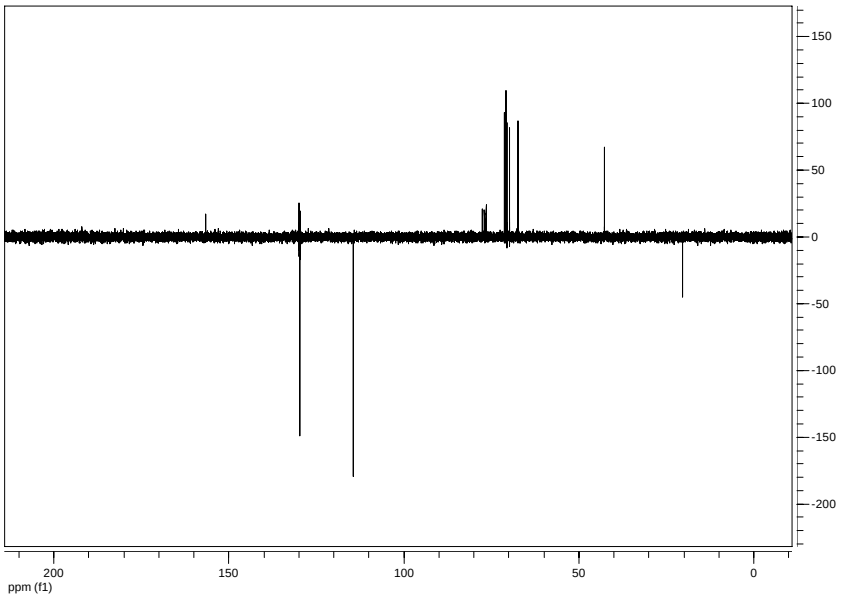


$C_{13}H_{19}ClO_3$
Mol. Wt.: 258.74

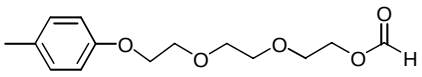
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

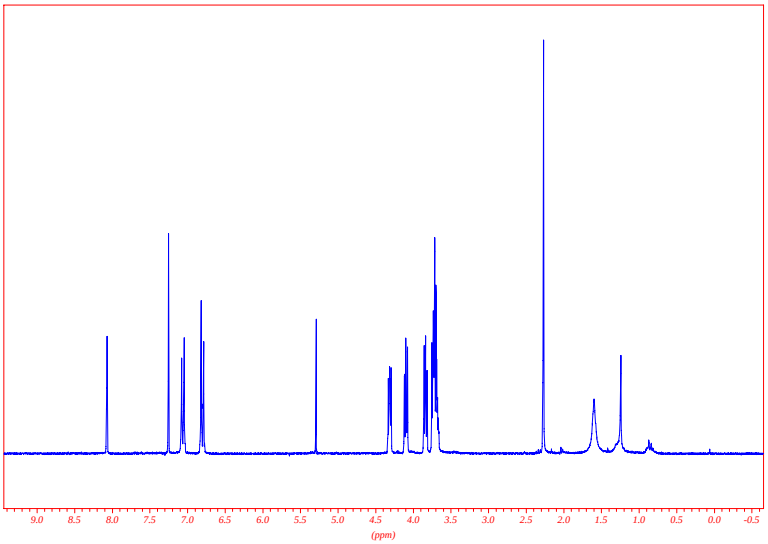


Formic acid 2-[2-(2-*para*-tolyloxyethoxy)ethoxy]ethyl ester 25.

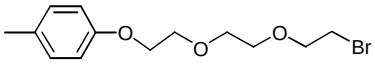


$C_{14}H_{20}O_5$
Mol. Wt.: 268.31

^{1}H NMR (250 MHz, $CDCl_3$)

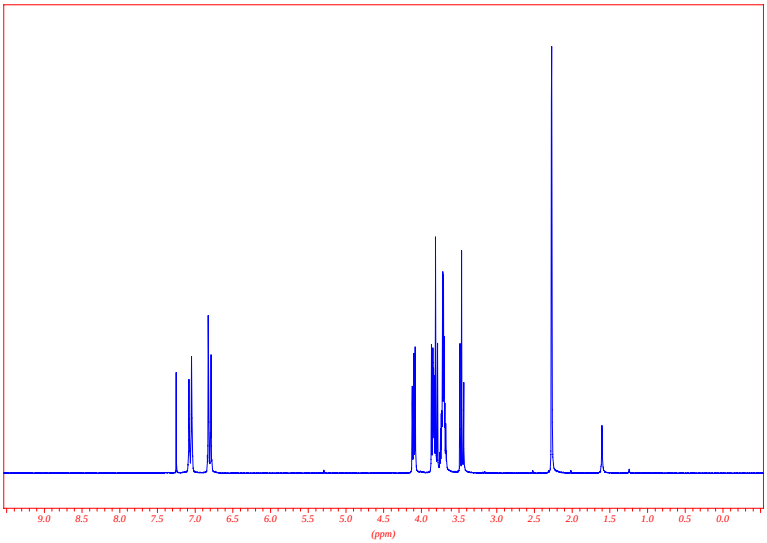


1-{2-[2-(2-Bromoethoxy)ethoxy]ethoxy}-4-methylbenzene 26.

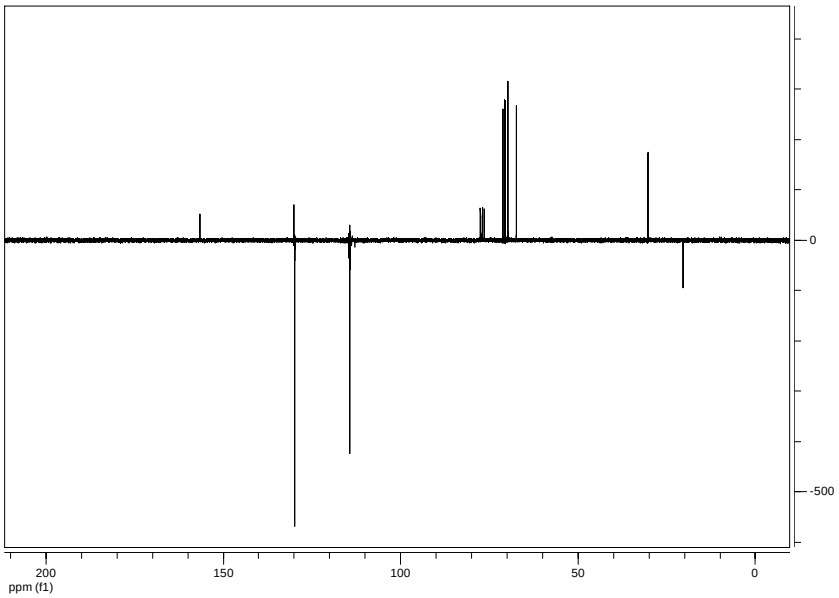


$C_{13}H_{19}BrO_3$
Mol. Wt.: 303.19

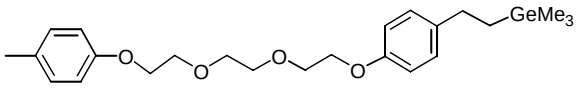
^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR APT (62.8 MHz, $CDCl_3$)

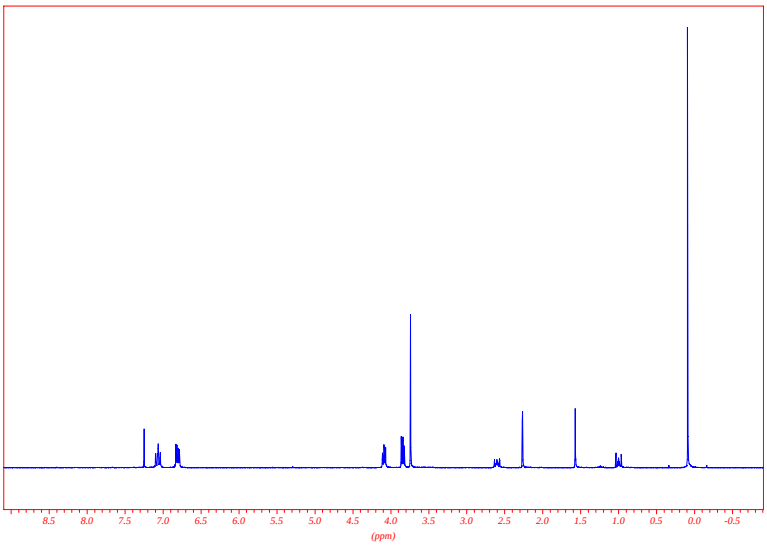


Trimethyl-[2-(4-{2-[2-(2-*para*-tolyloxyethoxy)ethoxy]ethoxy}phenyl)ethyl]germane 28.

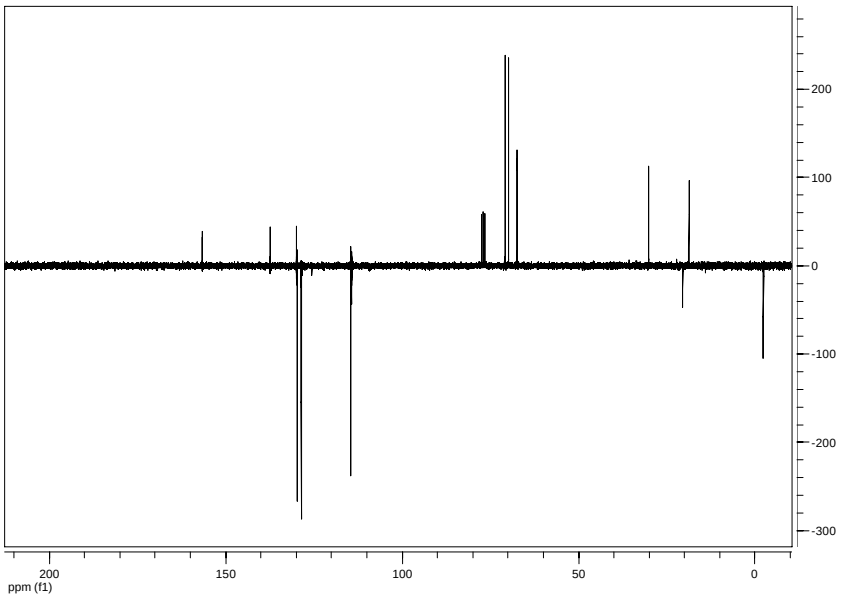


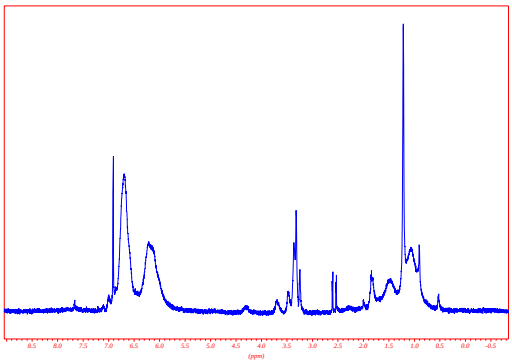
$C_{24}H_{36}GeO_4$
Mol. Wt.: 461.15

^{1}H NMR (250 MHz, $CDCl_3$)

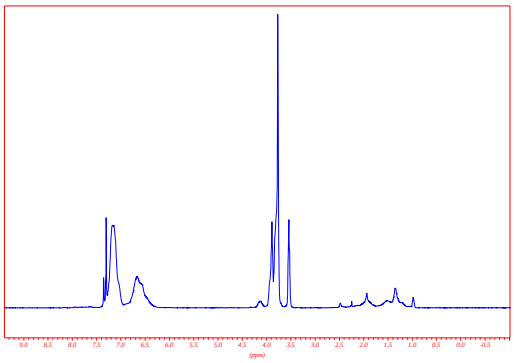


^{13}C NMR APT (62.8 MHz, $CDCl_3$)

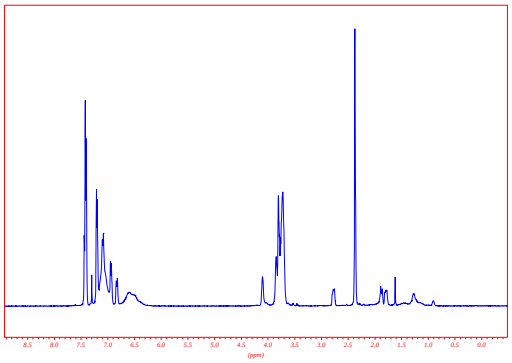




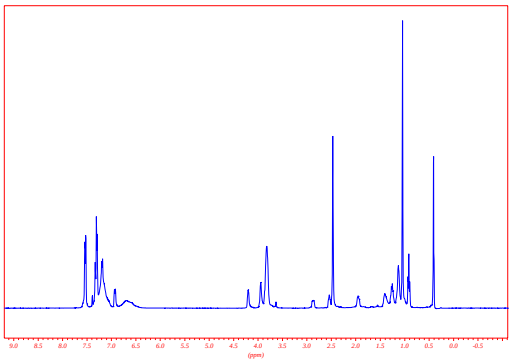
29



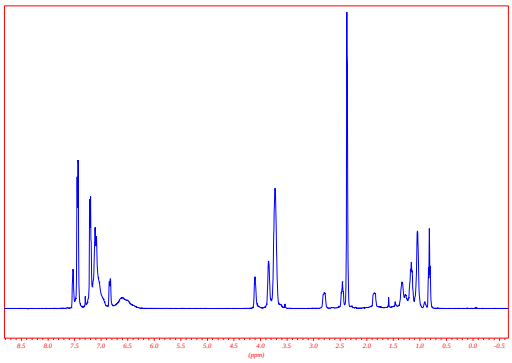
30



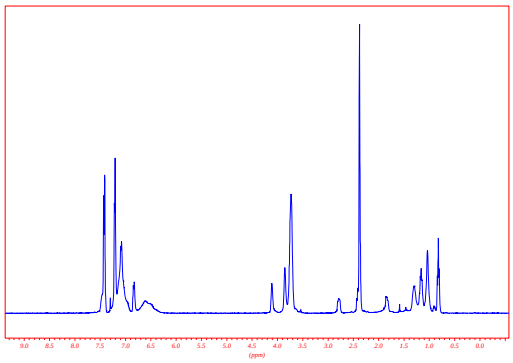
31



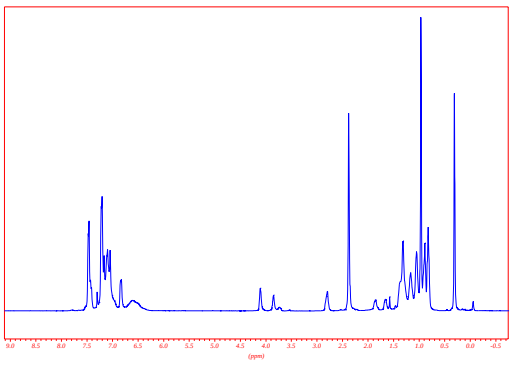
32



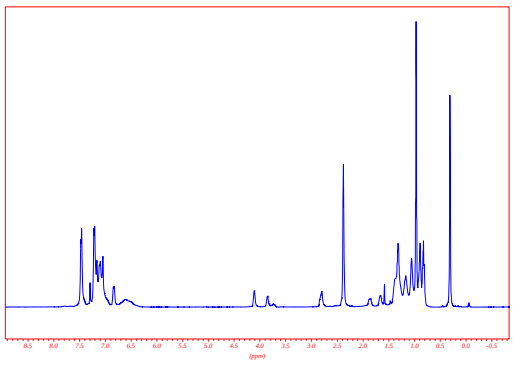
33



34



35



36

Figure 1. ^{1}H MAS NMR (400 MHz, $CDCl_3$) spectra for resins **30**-**36**. *NB.* All spectra except that for the initial resin **29** are Car-Purcell-Meiboon-Gill (CPMG) processed.[6, 7]

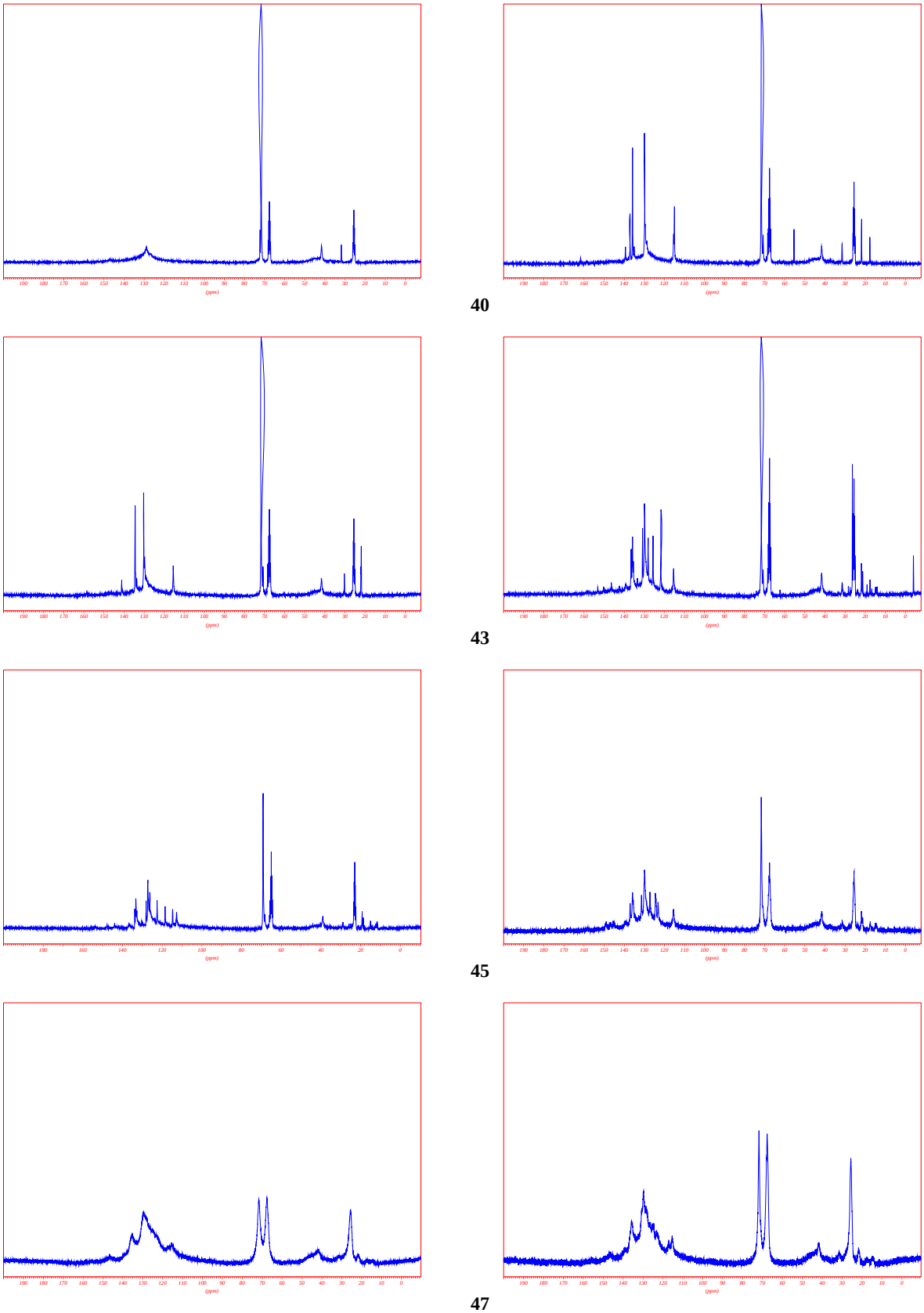
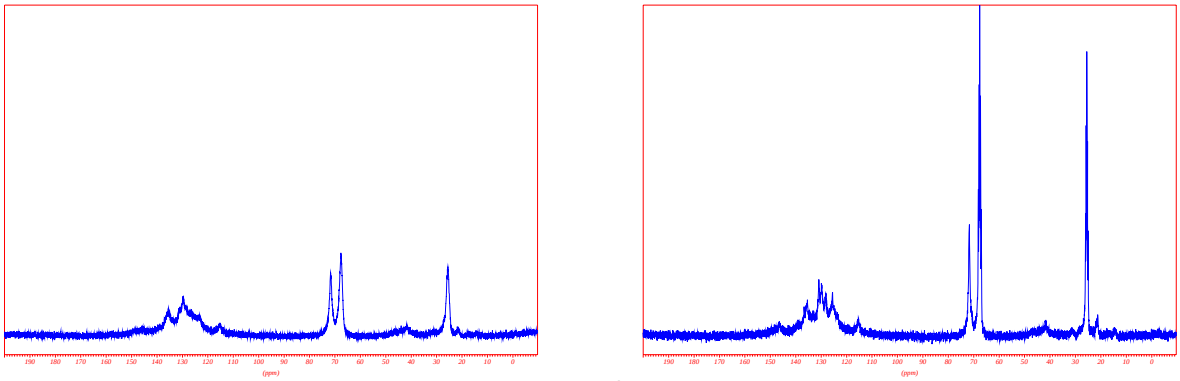


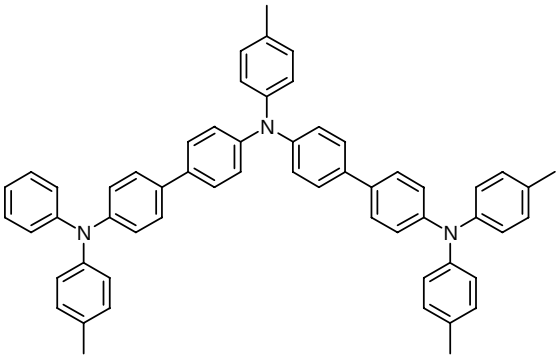
Figure 2. Gel phase ^{13}C NMR (75 MHz, d_8-THF) spectra for resins **39-41** & **43-47**.



48 **49**

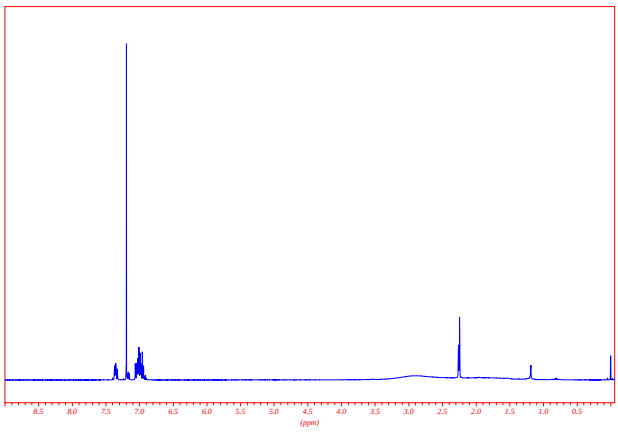
Figure 3. Gel phase ^{13}C NMR (75 MHz, d_8-THF) spectra for resins **48** & **49**.

***N*4'-[4'-(Di-*para*-tolylaminobiphenyl-4-yl]-*N*4-(4'-phenyl)-*N*4,*N*4'-di-*para*-tolyl-biphenyl-4,4'-diamine 50.**

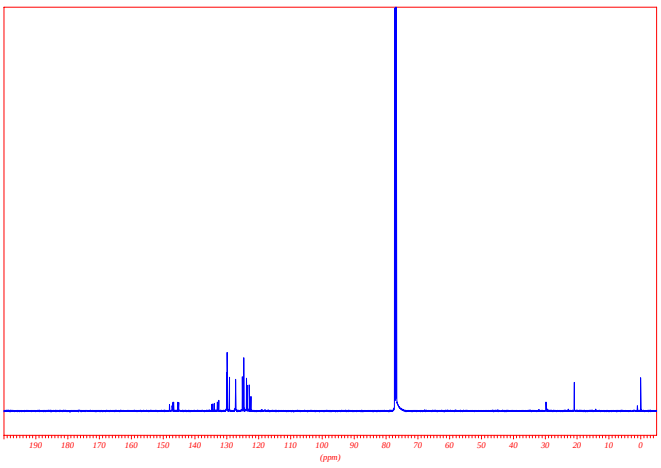


$C_{58}H_{49}N_3$
Mol. Wt.: 788.03
C, 88.40; H, 6.27; N, 5.33

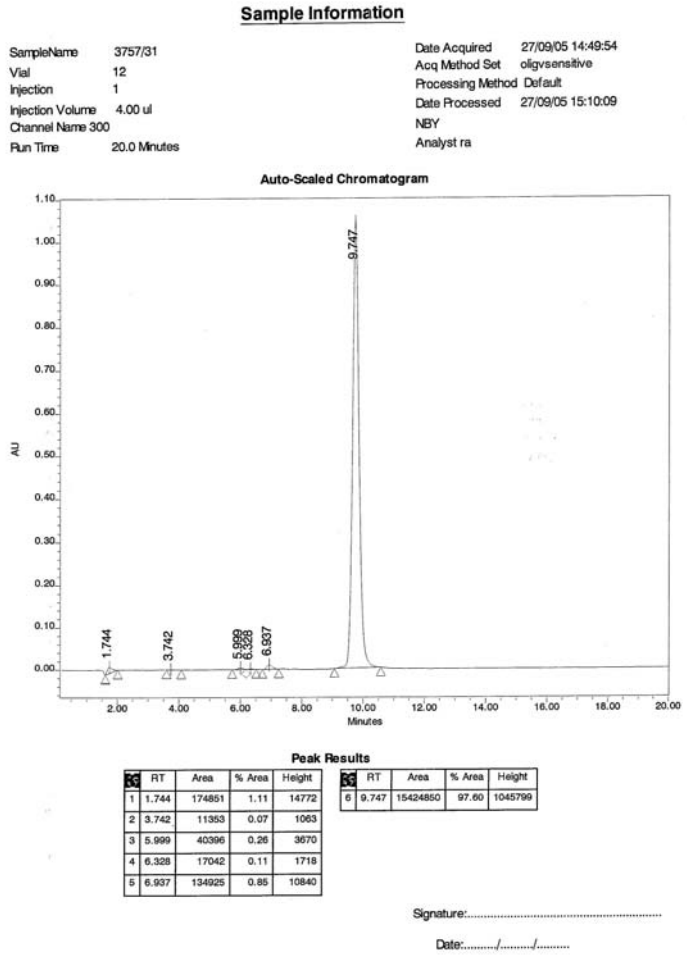
^{1}H NMR (400 MHz, $CDCl_3$)



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



HPLC: Jupiter ODS-C18 column (250 × 0.46 cm), UV 300 nm detection, 1 $mLmin^{-1}$, 5→100% MeCN in H_2O + 0.1% formic acid, R_t = 9.7 min.



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