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Supporting Information
for DOI: 10.1055/s-0030-1260553

Thieme

Nano Copper Oxide Catalyzed Synthesis of Symmetrical Diaryl Selenides via Cascade Reaction of KSeCN with Aryl Halides

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Contents:

General Information:

CuO nano particles (mean particle size, 33 nm, surface area, 29 m^2/g and purity, 99.99%) were purchased from Sigma Aldrich. Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F_{254} pre-coated plates. Visualization was accomplished with UV lamp or I_2 stain. All products were characterized by their NMR and MS spectra. ^{1}H and ^{13}C NMR was recorded on 100, 200 and 300 MHz, in $CDCl_3$ using TMS as the internal standard, Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane.

General procedure for synthesis of symmetrical diaryl selenides:

To a stirred solution of aryl halides (2.0 mmol) and potassium selenocyanate (1.2 equiv) in dry DMSO (2.0 mL) at rt was added nano CuO (5.0 mol %) followed by KOH (2.0 equiv) and heated at 110 ^{0}C for 15 h. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was allowed to cool, and a 1:1 mixture of ethyl acetate/water (20 mL) was added. The combined organic extracts were washed with brain and water and dried with anhydrous Na_2SO_4. The solvent and volatiles were completely removed under vacuum to give the crude product, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding coupling product in excellent yields.

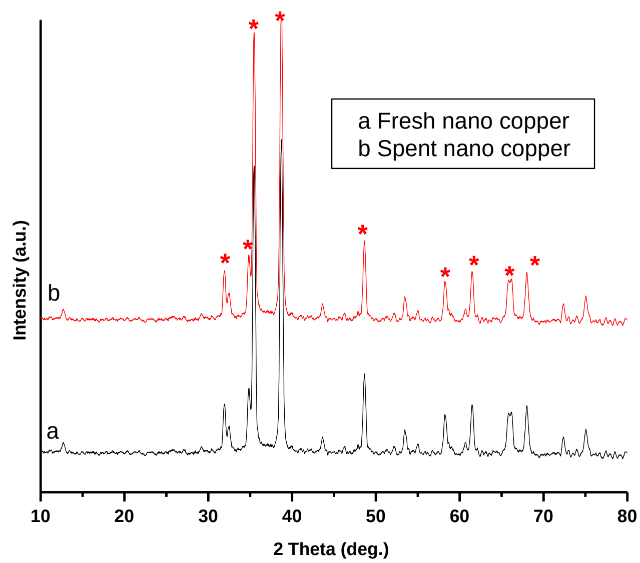
Recycling of the catalyst:

After the reaction was complete, the reaction mixture was allowed to cool, and a 1:1 mixture of ethyl acetate/water (2.0 mL) was added and CuO was removed by centrifugation. After each cycle, the catalyst was recovered by simple centrifugation, washing with deionized water and ethyl acetate and then drying in vacuo. The recovered nano-CuO was used directly in the next cycle.

Demonstration of heterogeneous catalysis

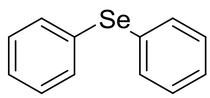
To a stirred solution of iodo benzene (2.0 mmol) and potassium selenocyanate (1.0 mmol) in dry DMSO (2.0 mL) at rt was added CuO nanoparticles (5.0 mol %) followed by KOH (2.0equiv) and heated at 110 ^{0}C for 15 h. The reaction mixture was allowed to cool and the catalyst was separated via centrifugation and 0.5 mL of the reaction mixture was worked out. The ^{1}H NMR spectrum of the reaction mass indicated 50% of product formation. This filtrate obtained after the catalyst separation was further stirred for 7 h at 110 ^{0}C and the reaction mixture was worked out. No further progress of the reaction was observed as seen by ^{1}H NMR spectroscopy and the product remained at 50% only. This experiment clearly demonstrated that no leaching of the catalyst is taking place and that the reaction is heterogeneous.

Powder X-ray diffraction analysis :



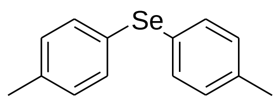
CuO remains CuO under the reaction conditions. This was confirmed by the powder X-ray diffraction analysis exhibited identical peaks for both the fresh and recovered CuO nanoparticles. It is observed that the shape and size of the particles remain unchanged and supports the assumption that the morphology of the catalyst remains the same even after recycling.

Spectroscopic Data:



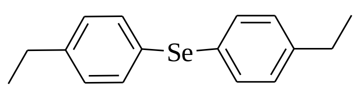
diphenylselane (Table 2, entry 1)[1]

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.40-7.38 (m, 4H), 7.20-7.18 (m, 6H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ = 132.6, 131.1, 129.5, 127.7; **Mass** (ESI): *m/z* 251 [M+18].



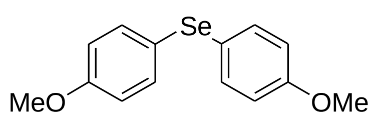
dip-tolylselane (Table 2, entry 4):[2]

^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ = 7.28 (d, 4H, J = 8.12 Hz), 7.01 (d, 4H, J = 8.12 Hz), 2.31 (s, 6H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ = 136.5, 132.83, 131.6, 129.4, 21.19; **Mass** (ESI): *m/z* 263 [M+1].



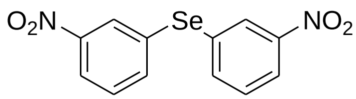
bis (4-ethylphenyl) selane (Table 2, entry 6):[2]

^{1}H-NMR (200 MHz, $CDCl_3$, TMS): δ = 7.34 (d, 4H, J = 8.12 Hz), 7.06 (d, 4H, J = 8.12 Hz), 2.59 (q, 4H, J = 7.54 Hz), 1.22 (t, 6H, J = 7.54 Hz). **^{13}C-NMR** (50 MHz, $CDCl_3$, TMS): δ =133.5, 132.8 128.4, 127.7, 28.2, 15.7. **Mass** (ESI): *m/z* 291 [M+1].



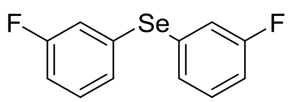
bis(4-methoxyphenyl) selane(Table 2, entry 7):[1]

Yellow solid; **^{1}H NMR** (200 MHz, $CDCl_3$, TMS): δ = 7.38 (d, 4H, J = 8.30 Hz), 6.75 (d, 4H, J = 8.30 Hz), 3.74 (s, 6H); **^{13}C-NMR** (50 MHz, $CDCl_3$, TMS): δ = 159.2, 132.6, 114.8, 114.6, 55.4; **Mass** (ESI): *m/z* 295 [M+1].



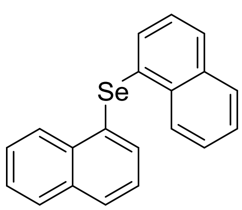
bis (3-nitrophenyl)selane (Table 2, entry 9):[2]

Yellow solid; m. p.: 92-94 ^{0}C; ^{1}**H NMR** (200 MHz, $CDCl_3$, TMS): δ = 8.33 (s, 2H), 8.22-8.16 (m, 2H), 7.77-7.74 (m, 2H), 7.50 (t, 2H, *J* = 7.55 Hz); ^{13}**C NMR** (50 MHz, $CDCl_3$, TMS): δ = 148.6, 138.8, 131.7, 130.4, 127.7, 123.0; **Mass** (ESI): *m/z* 325 [M+1].



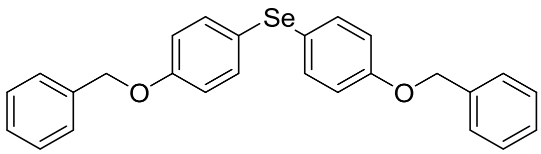
bis(3-fluorophenyl)selane (Table 2, entry 10):

Colorless oil; ^{1}**H NMR** (200 MHz, $CDCl_3$, TMS): δ = 7.32-7.12 (m, 6H), 7.02-6.93 (m, 2H); ^{13}**C NMR** (50 MHz, $CDCl_3$, TMS): δ = 164.6, 161.2, 130.6, 128.6, 119.9, 114.7 **Mass** (ESI): *m/z* 271 [M+1]. **Anal calcd for**: $C_{12}H_8F_2Se$ (269) C, 53.55; H, 3.00; **Found:** C, 53.49; H, 2.92%.



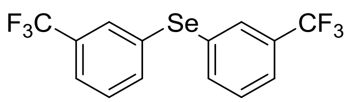
dinaphthalen-1-ylselane (Table 2, entry 11):

yello liquid; **IR** (Neat): ν 3091, 2928, 1588, 1390, 1077, 968, 848 $cm^{-1;}$ ^{1}**H-NMR** (200 MHz, $CDCl_3$, TMS): δ = 8.05- 8.02 (m, 4H), 7.79- 7.65 (m, 4H), 7.55- 7.40 (m, 4H), 7.15 (t, 2H, *J* = 7.93Hz); ^{13}**C NMR** (50 MHz, $CDCl_3$, TMS): δ = 137.2, 133.9, 131.9, 128.8, 128.3, 127.5, 126.6, 125.6; **Mass** (ESI): *m/z* 335[M+1]; **Anal calcd for**: $C_{20}H_{14}Se$ (334) C, 72.07; H, 4.23%; **Found:** C, 72.01; H, 4.18%.



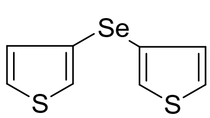
bis(4-(benzyloxy)phenyl)selane (Table 2, entry 13):

Colorless oil; **IR** (Neat): ν 3099, 2923, 1598, 1397, 1081, 961, 842 cm^{-1}; ^{1}**H-NMR** (200 MHz, $CDCl_3$, TMS): δ = 7.51 (d, 4H, *J* = 9.16 Hz), 7.39- 7.25 (m, 10H), 6.70 (d, 4H, *J* = 9.16 Hz), 5.02 (s, 4H); ^{13}**C NMR** (50 MHz, $CDCl_3$, TMS): δ = 158.63, 138.35, 136.35, 128.52, 128.11, 127.30, 117.53, 69.87; **Mass** (ESI): *m/z* 447 [M+1]; **Anal calcd for**: $C_{26}H_{22}O_2Se$ (446) C, 70.11; H, 4.98%; **Found:** C, 70.04; H, 4.91%.



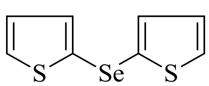
bis(3-(trifluoromethyl)phenyl)selane(Table 2, entry 14):

Colorless oil; **IR** (Neat): ν 3099, 2926, 1580, 1446, 1067, 858, 740 cm^{-1}; ^{1}**H-NMR** (200 MHz, $CDCl_3$, TMS): δ = 7.87- 7.69(m, 2H), 7.62-7.15(m, 6H); ^{13}**C NMR** (50 MHz, $CDCl_3$, TMS): δ = 136.24, 134.86, 129.86, 129.55, 128.27, 124.63; **Mass** (ESI): *m/z* 371 [M+1]; **Anal calcd for** $C_{14}H_8F_6Se$ (370) C, 45.55; H, 2.18%; **Found:** C, 45.48; H, 2.13%.



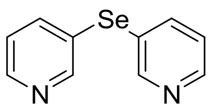
Dithiophen-3-ylselane (Table 2, entry 15):[2]

Colorless oil; ^{1}**H-NMR** (200 MHz, $CDCl_3$, TMS): δ = 7.32-7.21 (m, 4H), 7.07-6.96 (m, 2H); ^{13}**C NMR** (50 MHz, $CDCl_3$, TMS): δ = 131.7, 126.8, 126.3, 123.7; **Mass** (ESI): *m/z* 247 [M+1]; **Anal calcd for** $C_8H_6S_2Se$(246) C, 39.18; H, 2.47; S, 26.15%; **Found:** C, 39.29; H, 2.51%.



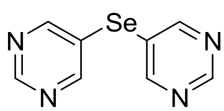
Dithiophen-2-ylselane (Table 2, entry 16):[2]

Colorless oil; ^{1}**H-NMR** (200 MHz, $CDCl_3$, TMS): δ = 7.30-7.28 (m, 2H), 7.21-7.19 (m, 2H), 6.87 (dd, 2H, *J* = 3.58 Hz); ^{13}**C NMR** (50 MHz, $CDCl_3$, TMS): δ = 134.9, 131.1, 127.5, 126.2; **Mass** (ESI): *m/z*247 [M+1]; **Anal calcd for** $C_8H_6S_2Se$(246) C, 39.18; H, 2.47; S, 26.15%; **Found:** C, 39.26; H, 2.53%.



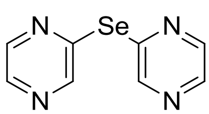
Dipyridin-3-ylselane (Table 2, entry 18):[2]

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.69 (s, 2H), 8.58-8.52 (m, 2H), 7.73 (d, 2H, *J* = 7.93 Hz), 7.25-7.19 (m, 2H); **^{13}C NMR** (50 MHz, $CDCl_3$, TMS): δ = 153.3, 148.9, 140.6, 124.4; **Mass** (ESI): *m/z* 237 [M+1]; **Anal calcd for**: $C_{10}H_8N_2Se$ (236) C, 51.08; H, 3.43; N, 11.91; C, 51.14; H, 3.46; N, 11.95.



dipyrimidin-5-ylselane (Table 2, entry 20):

Colorless oil;**IR** (neat): ν 3092, 2960, 1597, 1444, 1068, 865, 738 cm^{-1}; **^{1}H-NMR** (200 MHz, $CDCl_3$, TMS): δ = 7.51(s, 2H), 7.25(s, 4H); **^{13}C NMR** (50 MHz, $CDCl_3$, TMS): δ = 132.9, 129.0, 127.5; **Mass** (ESI): *m/z* 239 [M+1]; **Anal calcd for**: $C_8H_6N_4Se$ (238) C, 40.52; H, 2.55; N, 23.63%; **Found:** C, 40.46; H, 2.45; N, 23.57%.



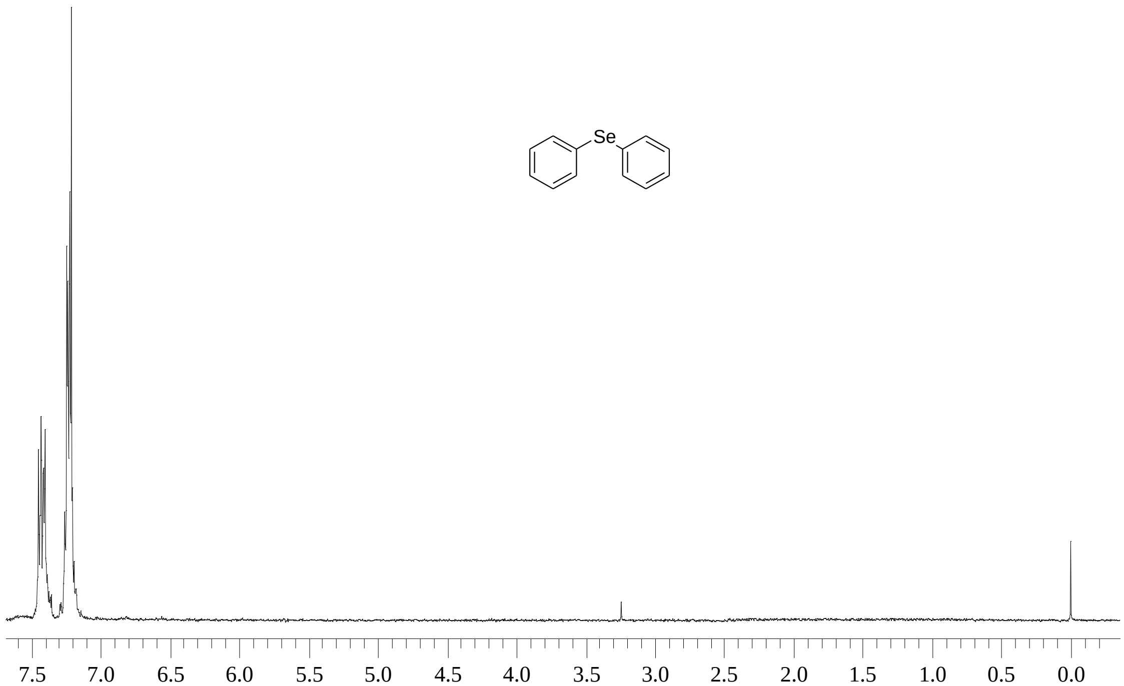
Dipyrazin-2-ylselane (Table 2, entry 21):[2]

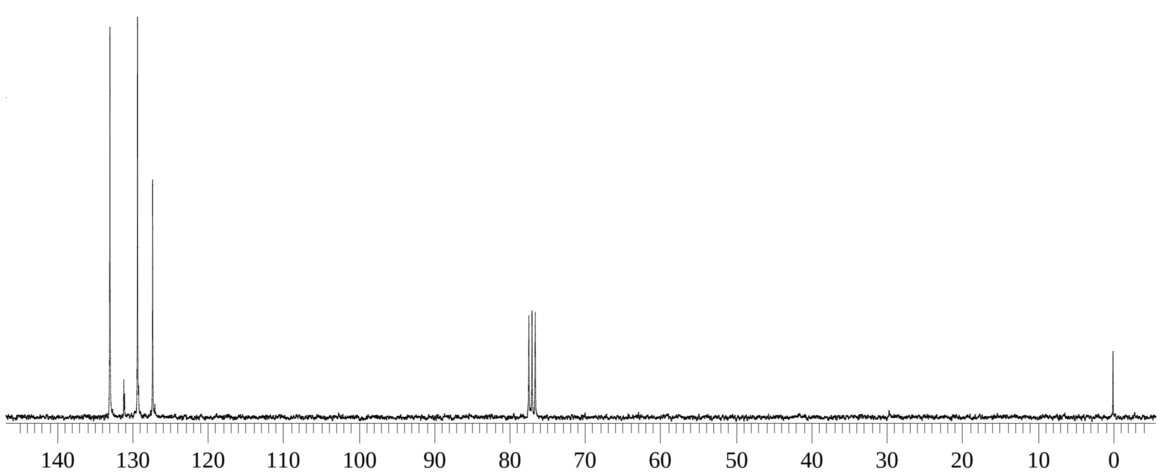
White solid; m. p.: 96-98 ^{0}C;**IR** (KBr): 3028, 2923, 1556, 1452, 1042, 833, 738 cm^{-1}; **^{1}H-NMR** (200 MHz, $CDCl_3$, TMS): δ = 8.75 (s, 2H), 8.45-8.42 (m, 4H); **^{13}C NMR** (50 MHz, $CDCl_3$, TMS): δ = 148.1, 145.1, 142.7; **Mass** (ESI): *m/z* 239 [M+1]; **Anal calcd for**: $C_8H_6N_4Se$ (238) C, 40.52; H, 2.55; N, 23.63%; **Found:** C, 40.45; H, 2.48; N, 23.59%.

References: (1) Alves, D.; Santos, C. G.; Paixao, M. W.; Soares, L. C.; de Souza, D.; Rodrigues, O. E. D.; Braga, A. L. *Tetrahedron Lett.* **2009**, *50*, 6635.
(2) Reddy, V. P.; K.; Kumar, A. V.; Rao, K. R. *J. Org. Chem.* 2**010**, *75*, 8720.

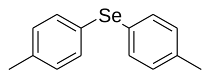
Copies of ^{1}H NMR and ^{13}C NMR of Compounds:

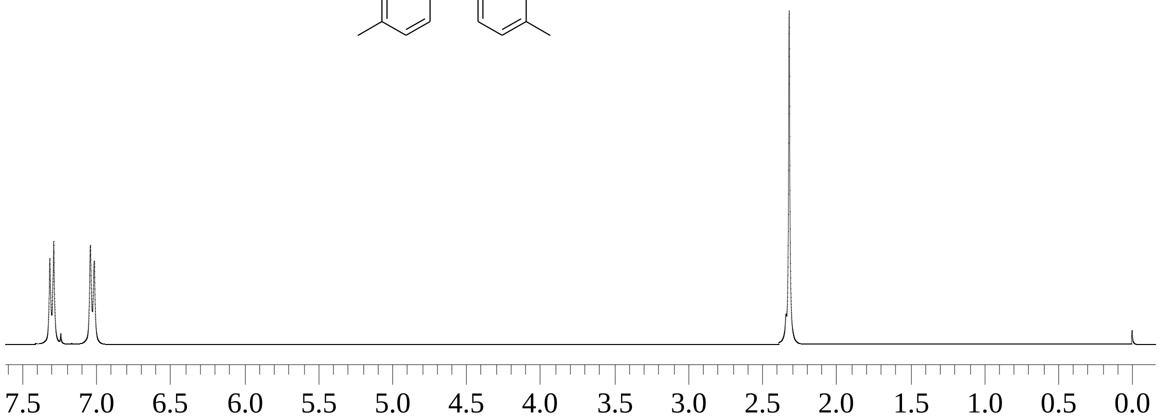
diphenylselane (Table 2, entry 1)

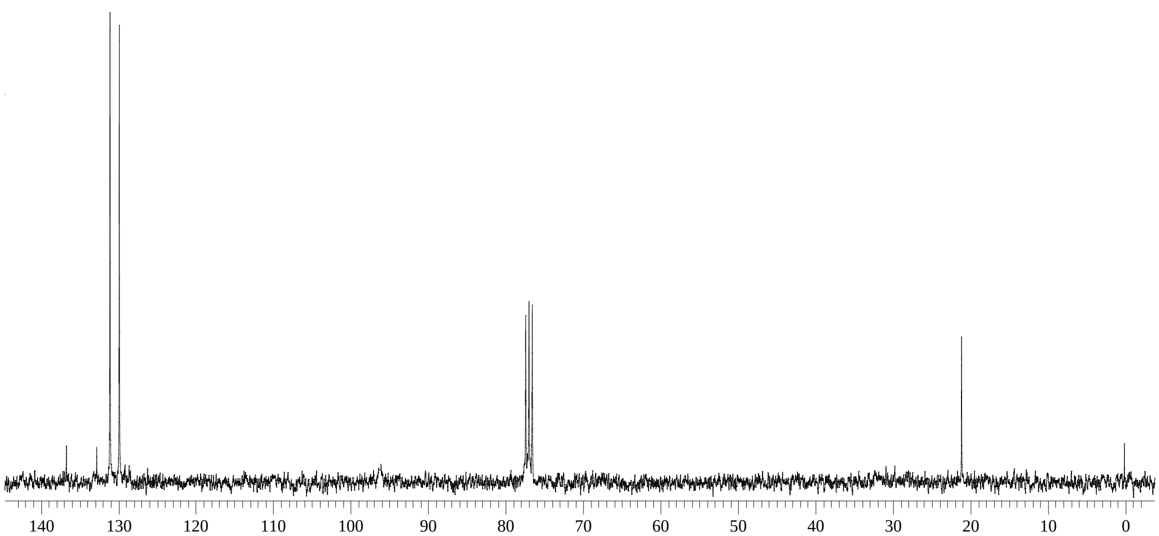




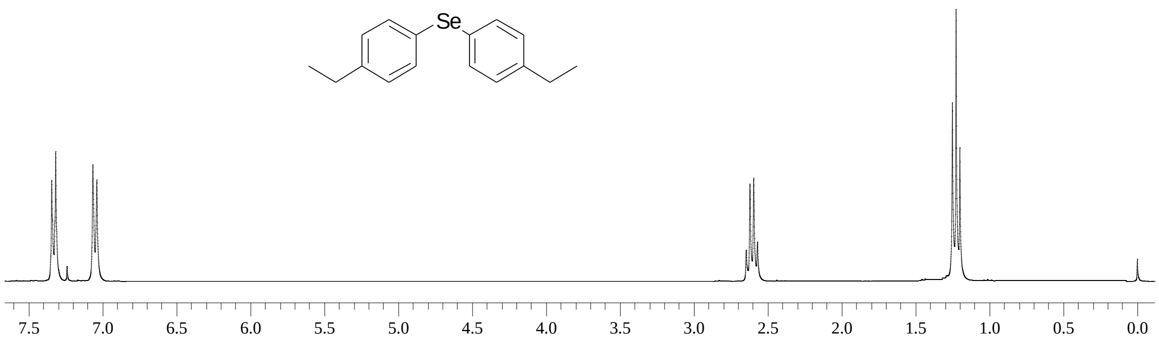
dip-tolylselane (Table 2, entry 4):

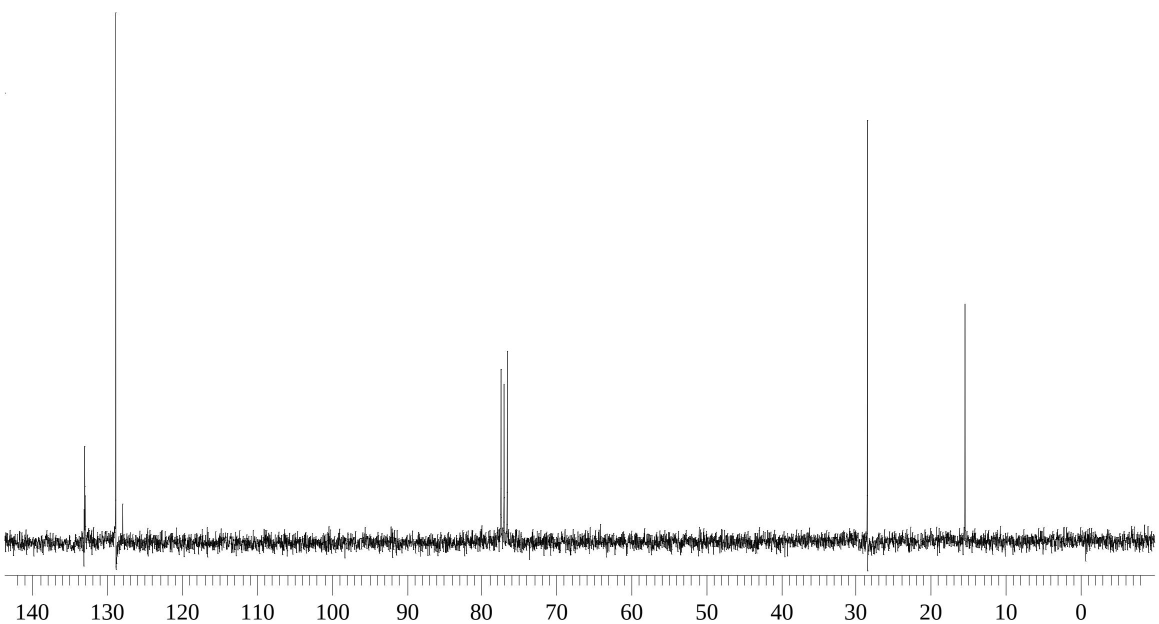




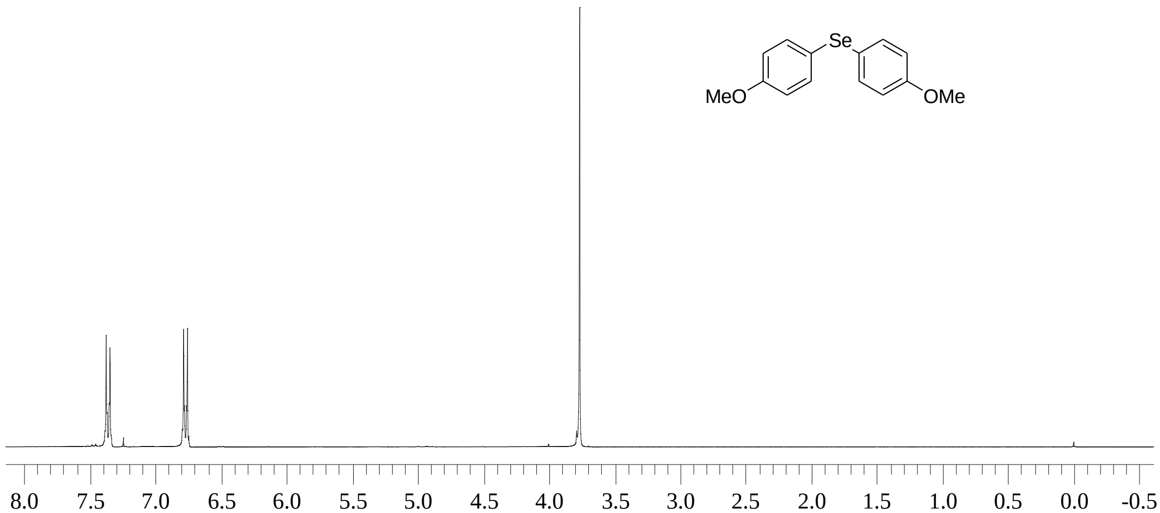


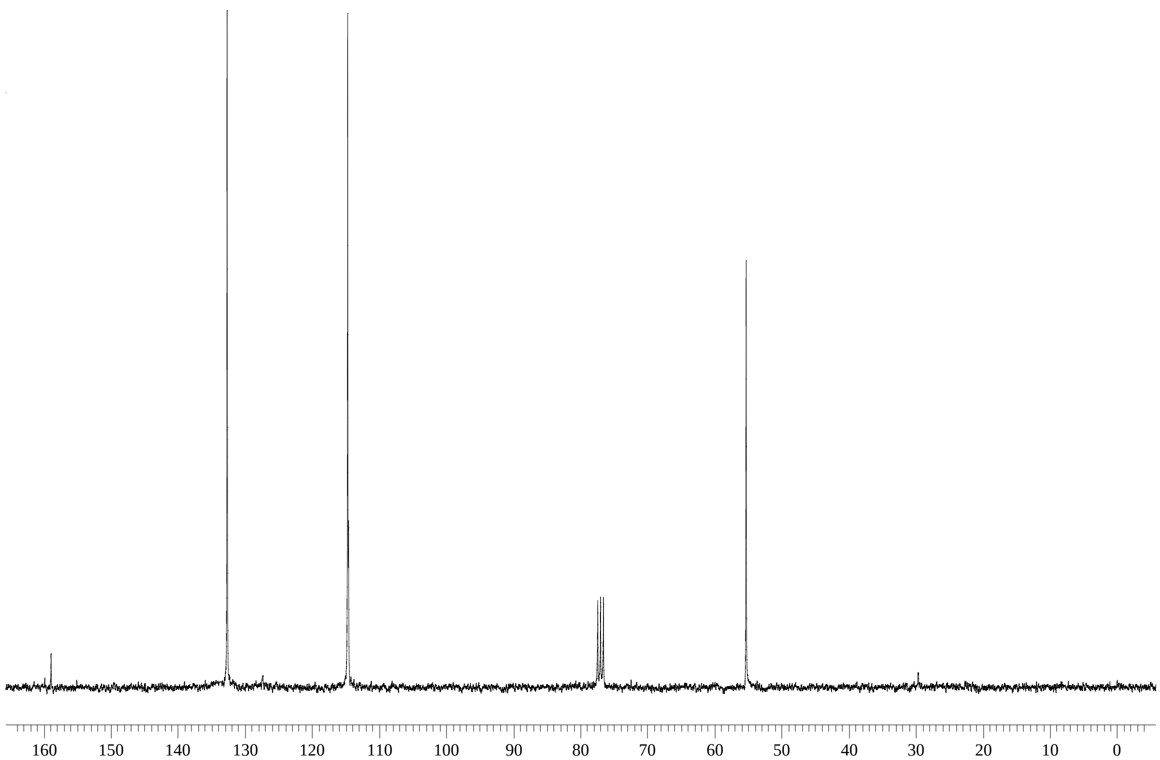
bis (4-ethylphenyl)selane (Table 2, entry 6):



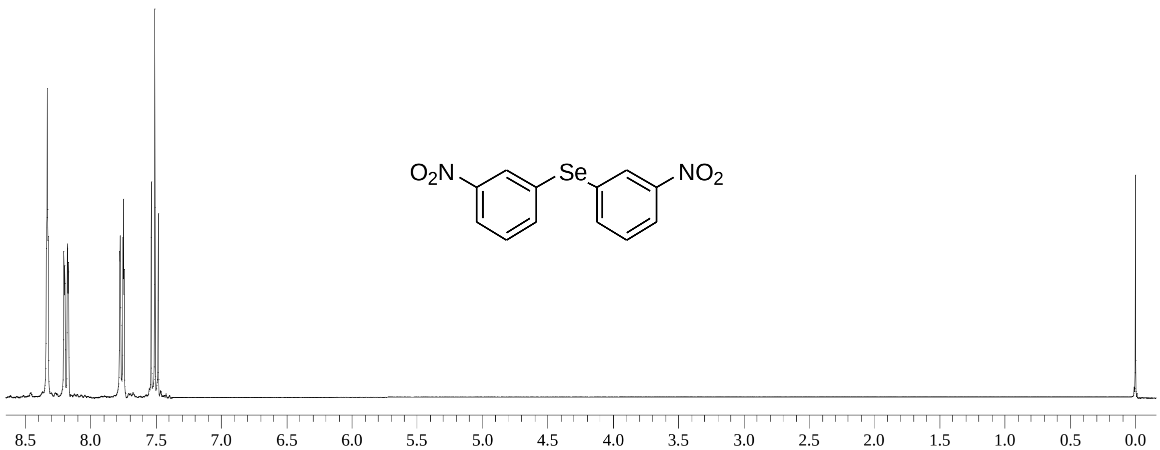


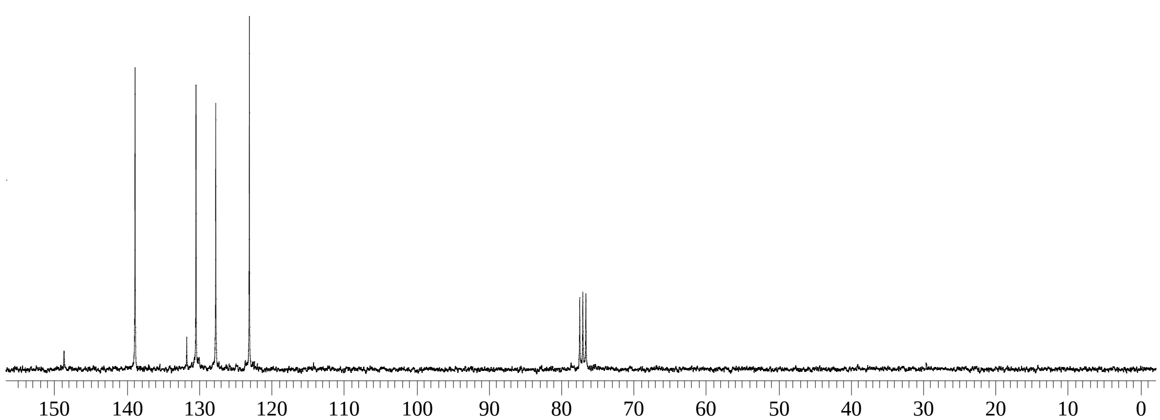
bis(4-methoxyphenyl) selane(Table 2, entry 7):



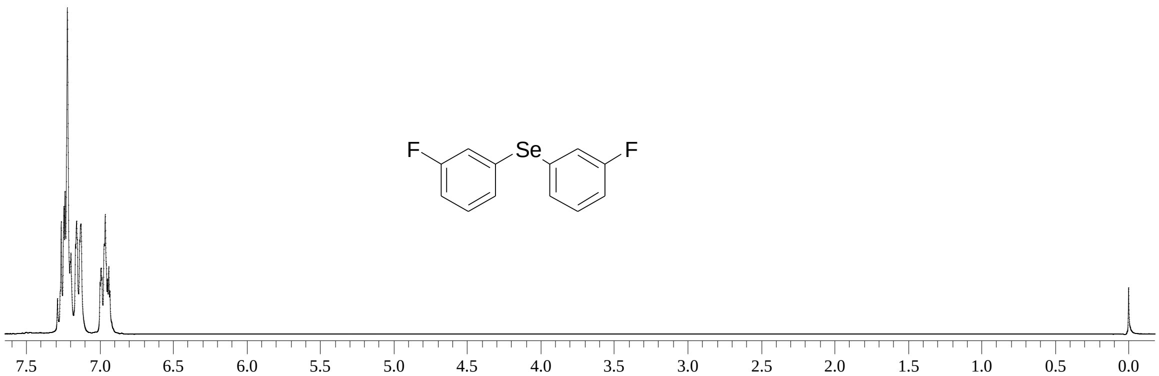


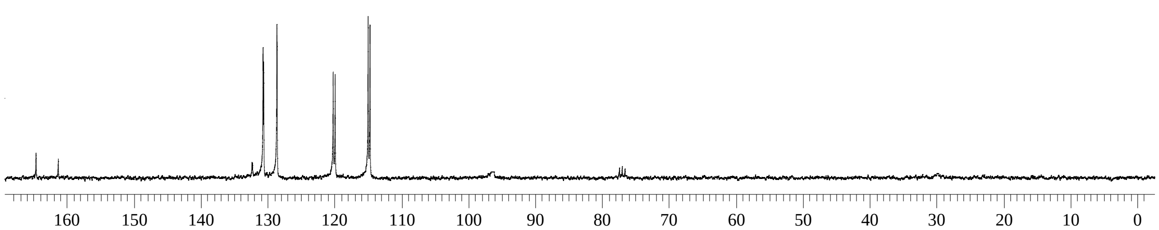
bis (3-nitrophenyl)selane (Table 2, entry 9):



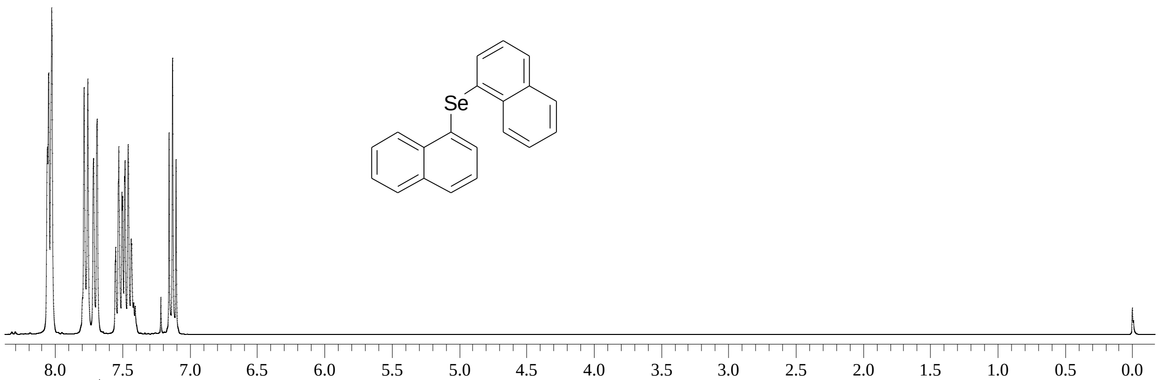


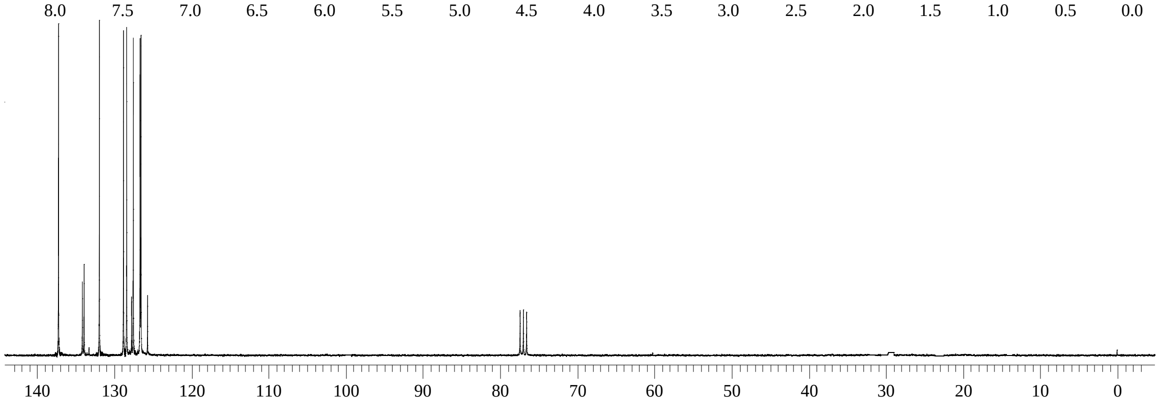
bis(3-fluorophenyl)selane (Table 2, entry 10):



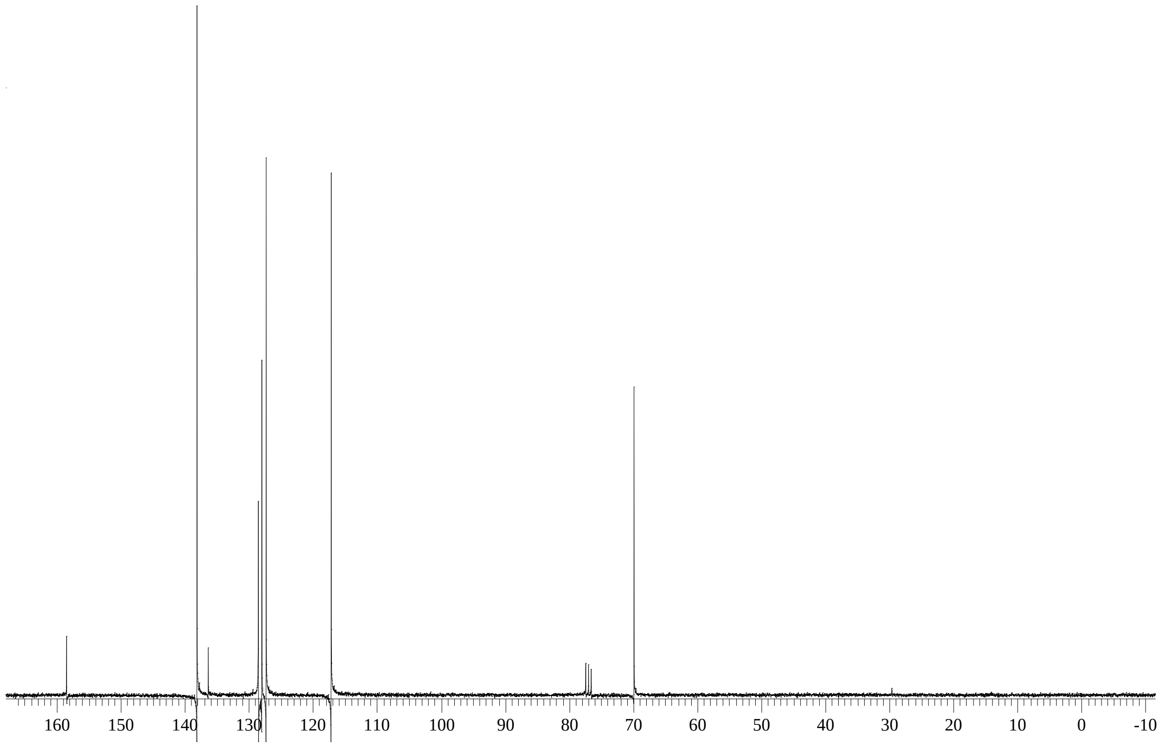


dinaphthalen-1-ylselane (Table 2, entry 11):

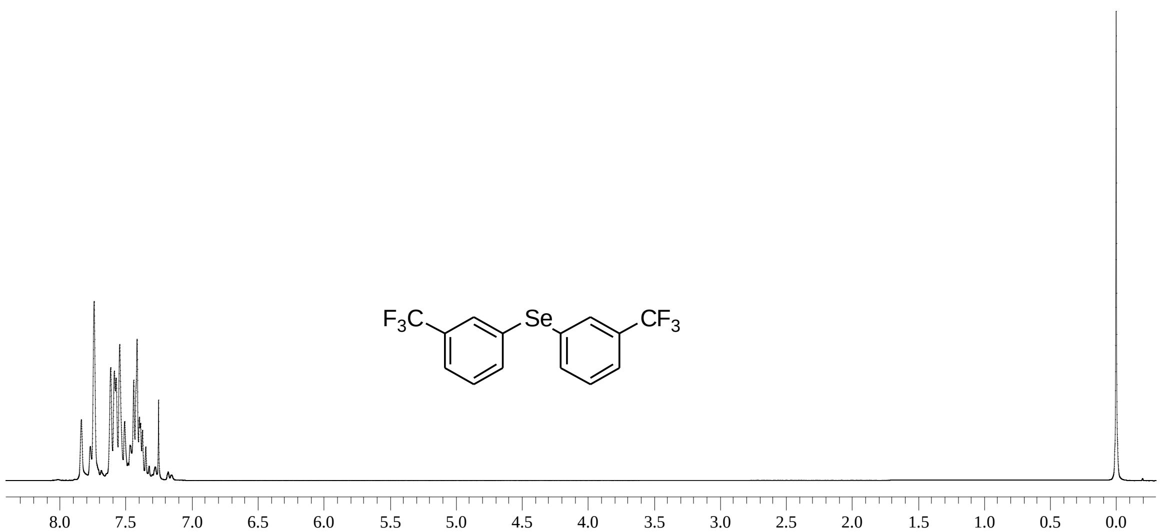


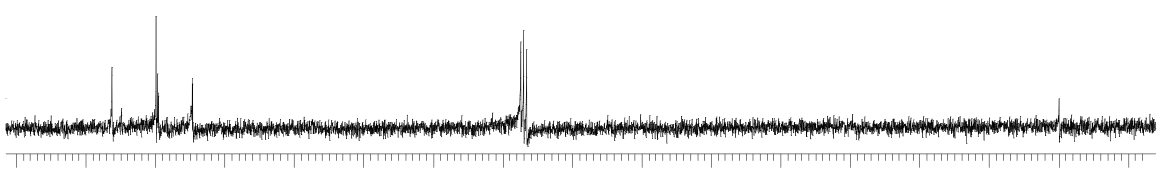


bis(4-(benzyloxy)phenyl)selane (Table 2, entry 13):

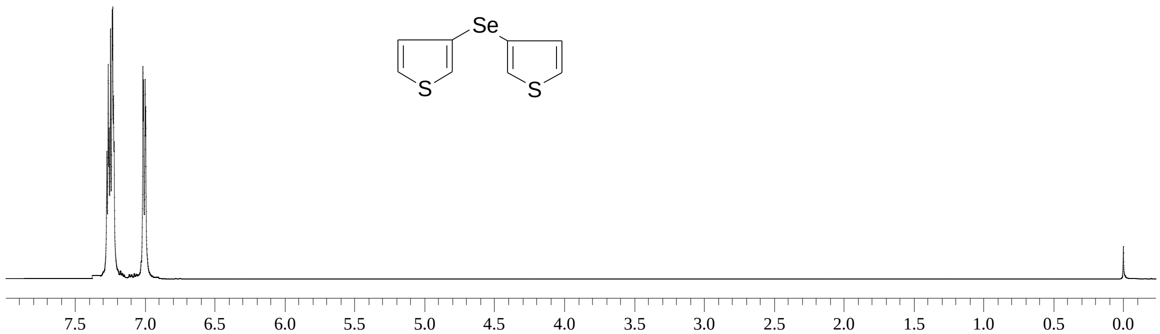


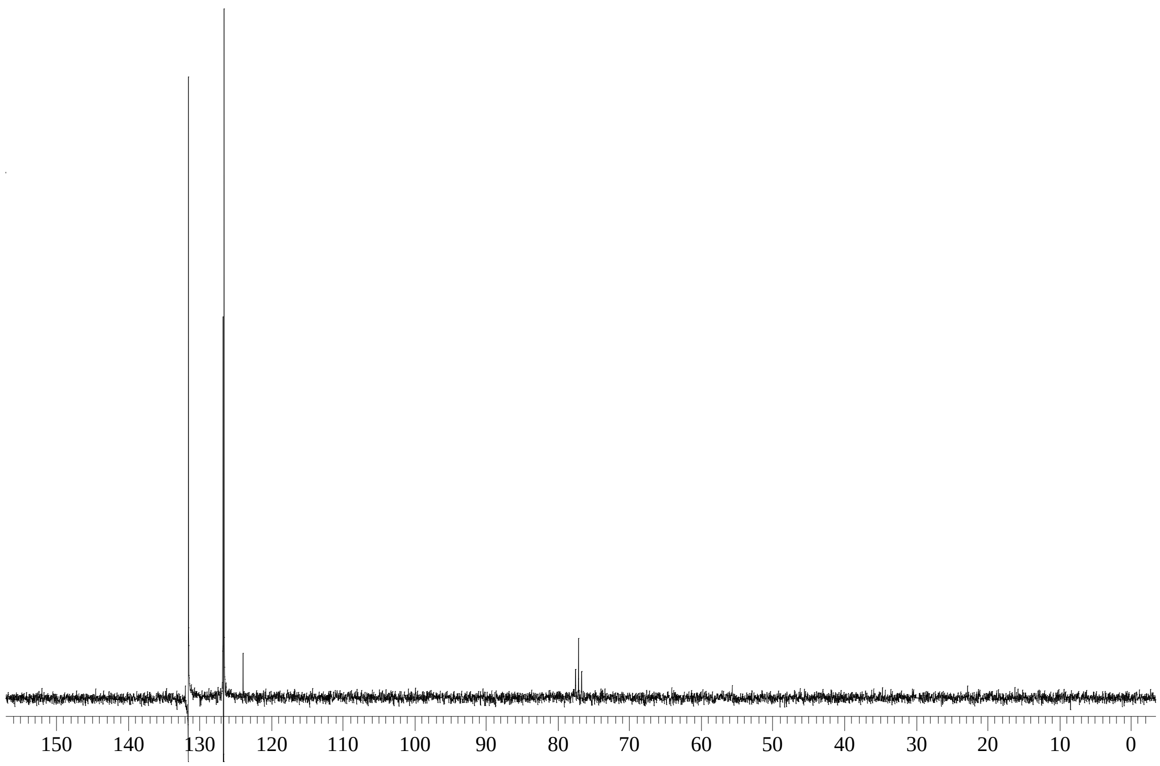
bis(3-(trifluoromethyl)phenyl)selane(Table 2, entry 14):



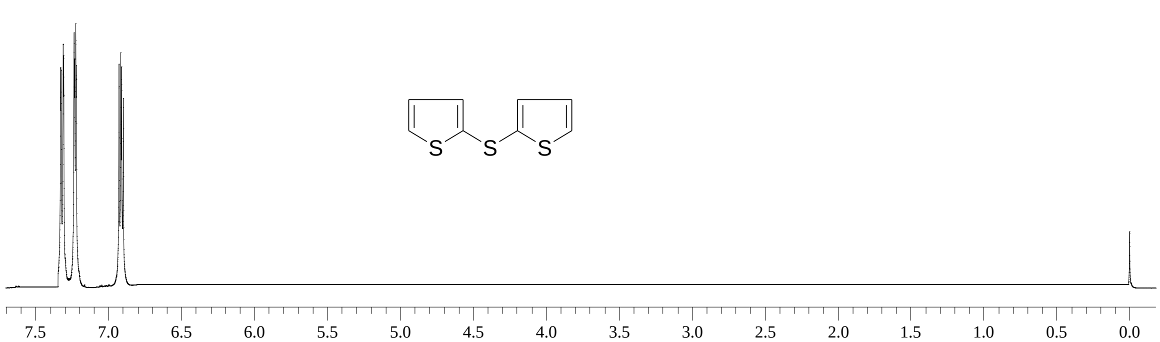


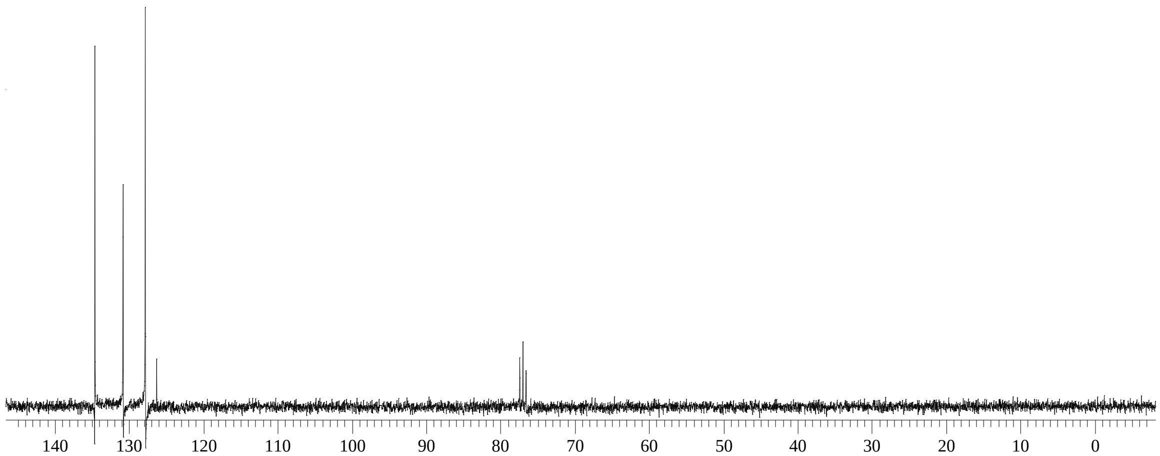
Dithiophen-3-ylselane (Table 2, entry 15):



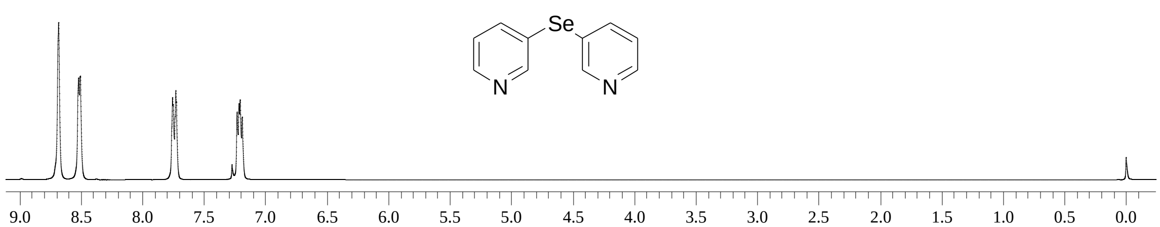


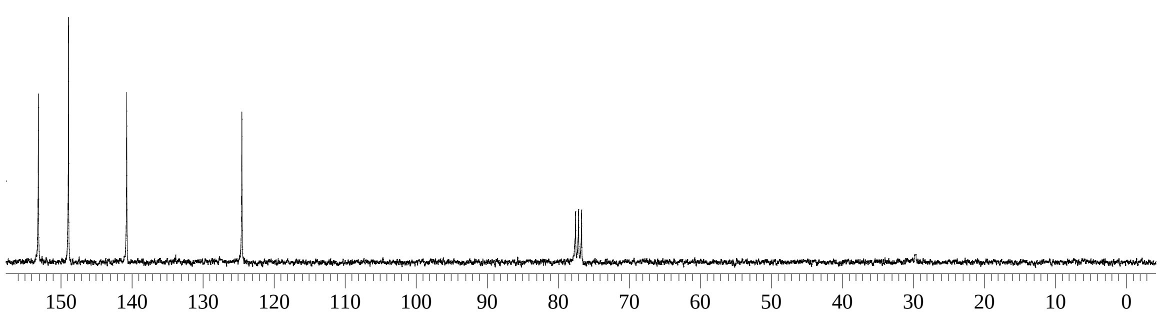
Dithiophen-2-ylselane (Table 2, entry 16):



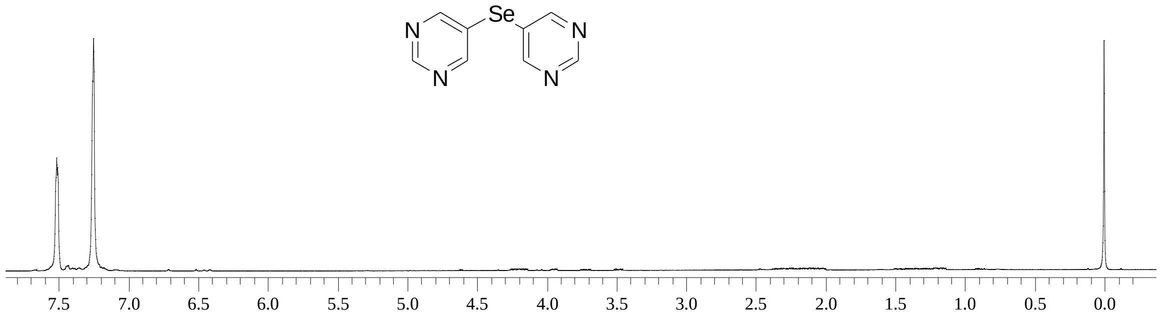


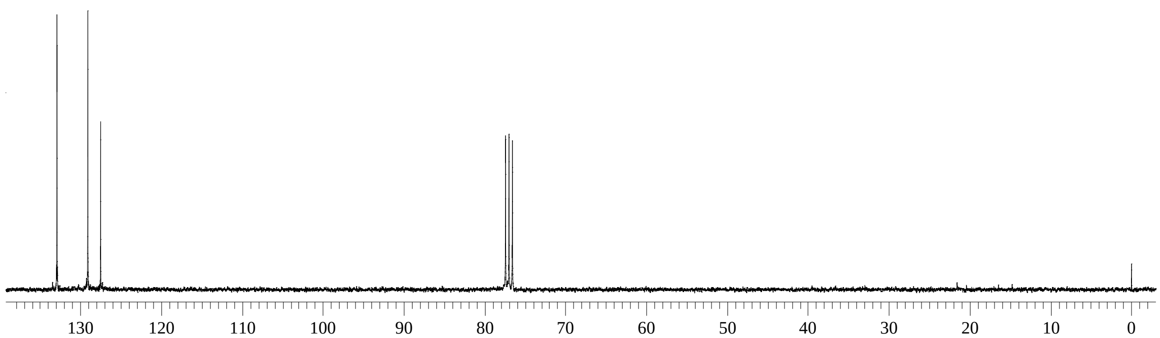
Dipyridin-3-ylselane (Table 2, entry 18):



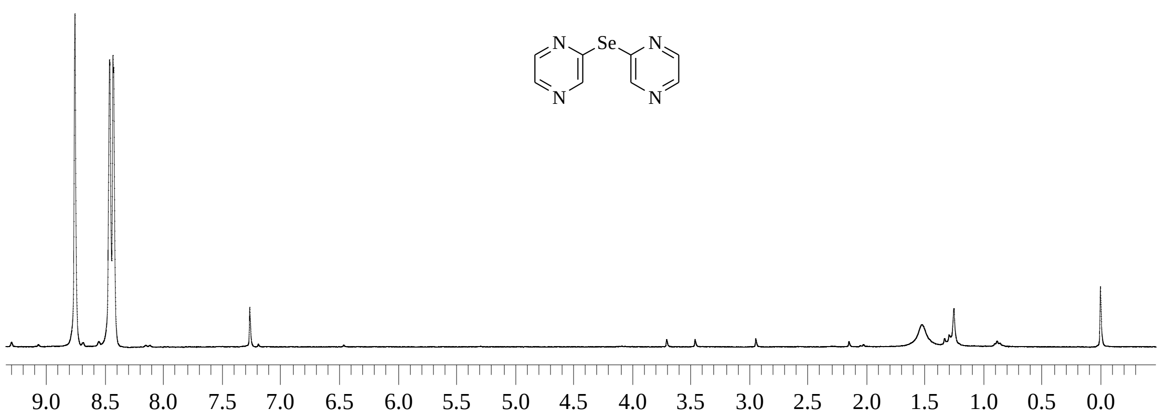


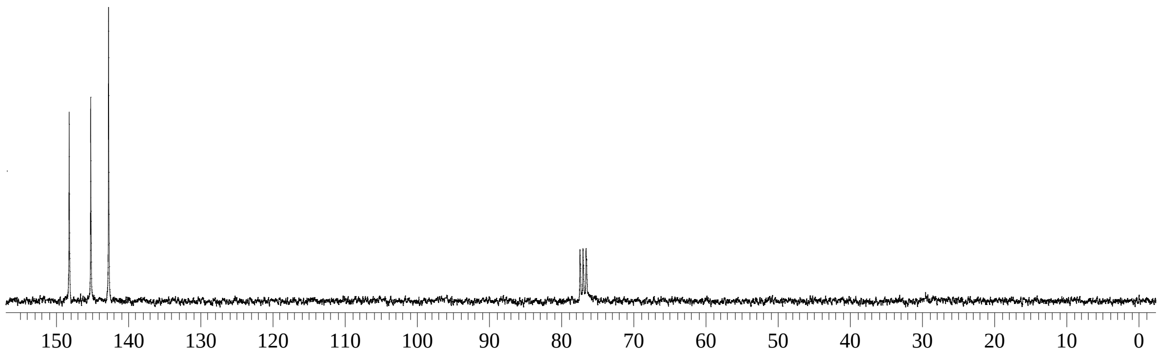
dipyrimidin-5-ylselane (Table 2, entry 20):





Dipyrazin-2-ylselane (Table 2, entry 21):

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