Arylseleninic Acid as a Green, Bench-Stable Selenylating Agent: Synthesis of Selanylanilines and 3-Selanylindoles

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CONTENT:

EXPERIMENTAL SECTION

General Information: The reactions were monitored by TLC carried out on pre-coated TLC sheets ALUGRAM® Xtra SIL G/UV_{254} by using UV light as visualization agent and the mixture of 5% vanillin in 10% H_2SO_4 under heating conditions as developing agent. Merck silica gel (particle size 63-200 μm) was used to flash chromatography, and PTLC Glass Plates L × W 20 cm × 20 cm, silica gel 60 F_{254}, 1 mm, was used in the preparative thin layer chromatography. Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 400 MHz on A Bruker Ascend 400 spectrometer. The spectra were recorded in $CDCl_3$ solutions. The chemical shifts are reported in ppm, referenced to tetramethysilane (TMS) as the external reference. Hydrogen coupling patterns are described as singlet (s), doublet (d), triplet (t), doublet of doublets (dd), doublet of doublet of doublets (ddd) and multiplet (m). Coupling constants (*J*) are reported in Hertz. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHz on Bruker Nuclear Ascend 400 spectrometer. The chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Selenium-77 nuclear magnetic resonance spectra (^{77}Se NMR) were obtained at 76 MHz on Bruker Nuclear Ascend 400 spectrometer. The chemical shifts are reported in ppm, referenced to diphenyl diselenide as the external reference. The HRMS analyses were performed in a Bruker micrOTOF-QII spectrometer equipped with an APCI source operating in positive mode. The samples were solubilized in acetonitrile and analyzed by direct infusion at a constant flow rate of 180 μL/min. The acquisition parameters were capillary: 4000 V, end plate offset: -500 V, nebulizer: 1.5 bar, dry gas: 1.5 L min^{-1}, and dry heater: 180 °C. The collision cell energy was set to 5.0 eV. The mass-to-charge ratio (m/z) data were processed and analyzed using Bruker Daltonics softwares: Compass Data Analysis and Isotope Pattern.

General procedure for the synthesis of the arylseleninic acids 1a-f[1]

In a round-bottomed flask were added diselenide (0.5 mmol) and DCM (3 mL) and the system was cooled with an ice bath (0 °C). Thus, H2O2 (3.0 equiv) was added dropwise. The result mixture was stirred at 0 °C until the formation of a white suspension and the disappearance of the yellow solution. After, the solvent was evaporated, removing DCM and residual water, being the precipitate washed several times with hexanes and dried at the vacuum pump. The freshly dried white solid was directly employed in the next reaction step as substrate.

^{77}Se NMR studies on the electrophilic selenium species

Aiming to check the equilibrium between $PhSeO_2H$ **1a** and PhSeOH **8** (and/or $(PhSe)_2O$ **9**) in the presence of PhSeSePh **7**, several ^{77}Se-NMR spectra were collected, both at 25 ^{o}C and at 50 ^{o}C (a temperature close to the experimental one), Figures S1-S4.

It is possible to verify the presence of a second peak (1020 ppm) in the freshly prepared $PhSeO_2H$ (DMF solution), which could be attributed both to PhSeOH and/or PhSeOSePh, once it is not possible to detect such equilibrium at the working temperature (Fig. S1). After 24 h, the intensity of the signal at 1020 ppm increases, meanwhile a new peak, due to PhSeSePh (455 ppm) appears in the spectrum (Fig. S2).

The presence of PhSeSePh is mandatory to the conversion of the Se(IV) species benzeneseleninic acid **1a** to the actual Se(II) electrophiles PhSeOH **8** and/or PhSeOSePh **9**, as proposed in the literature.[2-4] To verify the comproportionation of $PhSeO_2H$ and PhSeSePh, a mixture of equimolar amounts of these compounds (0.1 mmol in DMF) was prepared and the ^{77}Se NMR spectra were collected at different times at 50 ^{o}C. Immediately after the preparation of the mixture, it was possible to observe three peaks in the spectrum, with an increase in the intensity of the peak at 1020 ppm, indicating that it's forming at a higher rate in the presence of PhSeSePh (Figure S3). The amount of PhSeOH/PhSeOSePh (peak at 1020 ppm) is even larger after 24 h at 50 ^{o}C, and did not increase substantially after 48 h, as observed by NMR.

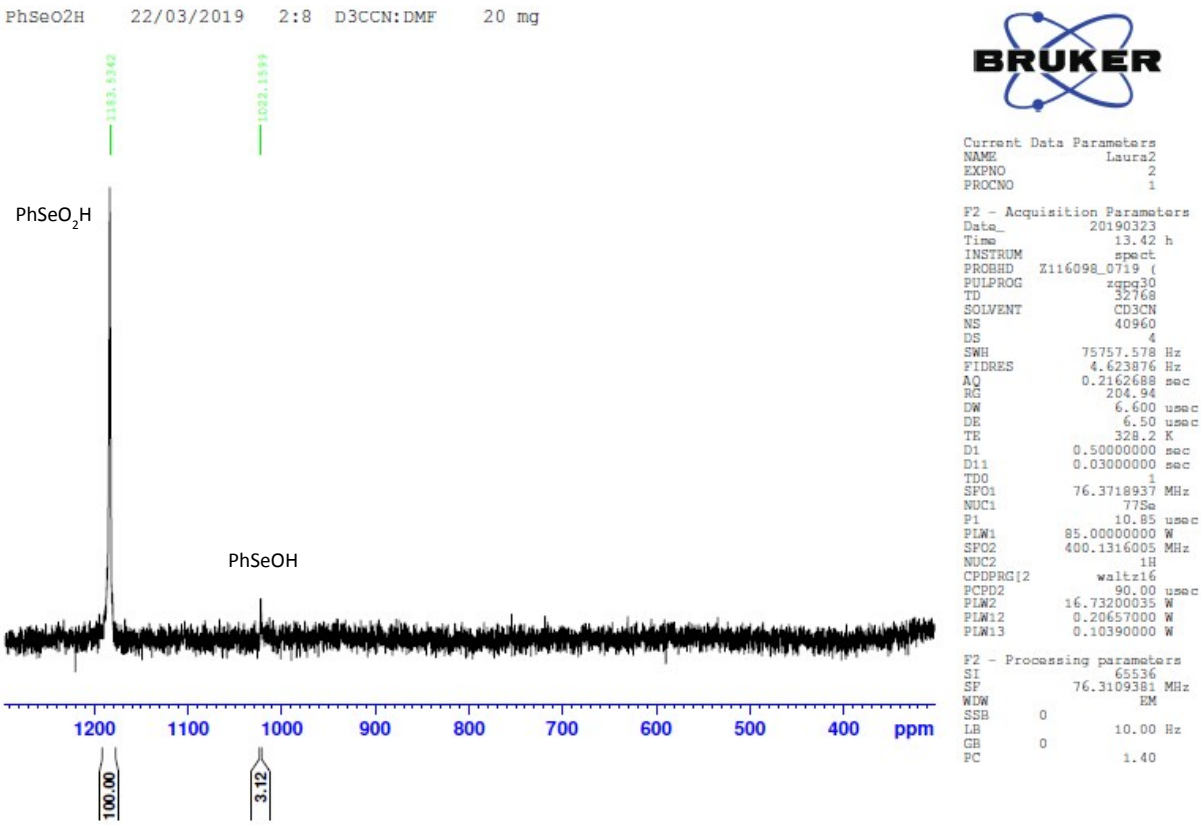

Figure S1. ^{77}Se NMR (76 MHz) spectrum, solution in DMF of $PhSeO_2H$ **1a**, freshly prepared (64K data points and 20,0 exponential apodization).

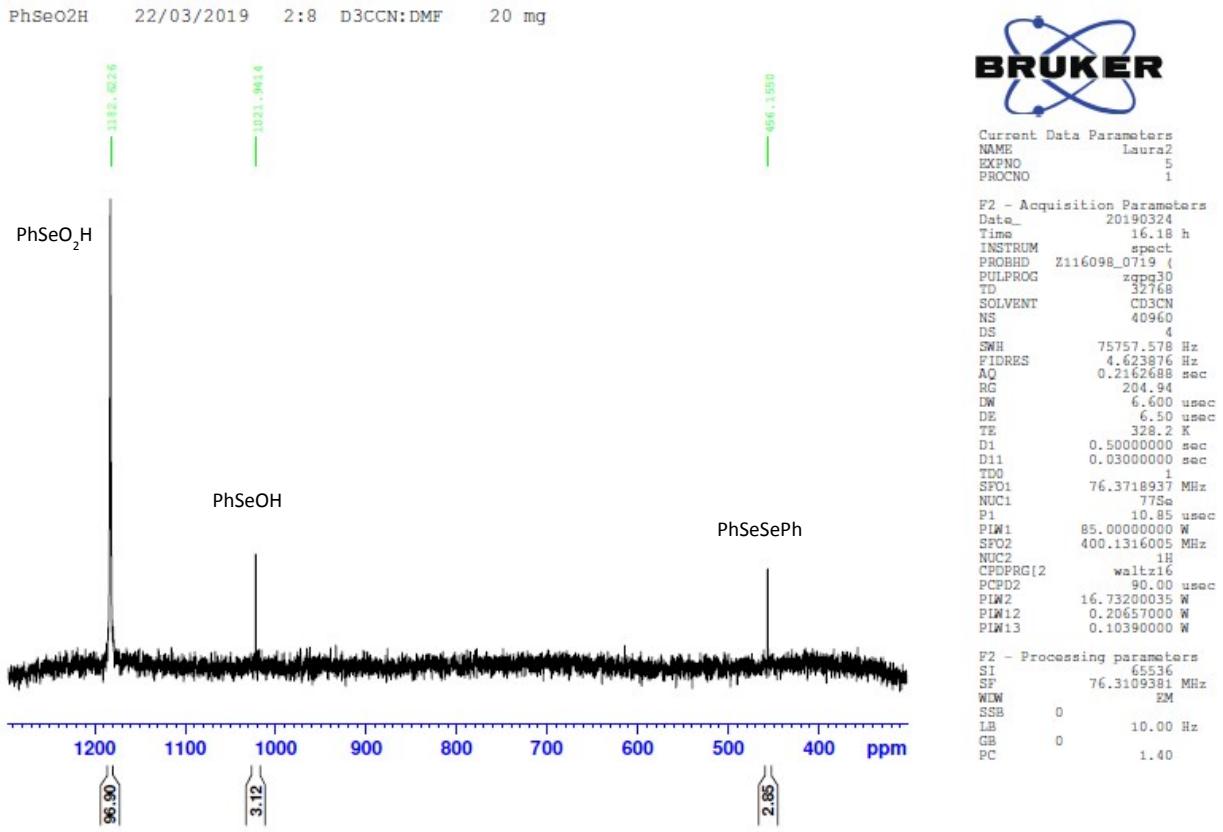

Figure S2: ^{77}Se NMR (76 MHz) spectrum, solution in DMF of $PhSeO_2H$ **1a** after 24 h at 25 °C (64K data points and 20,0 exponential apodization).

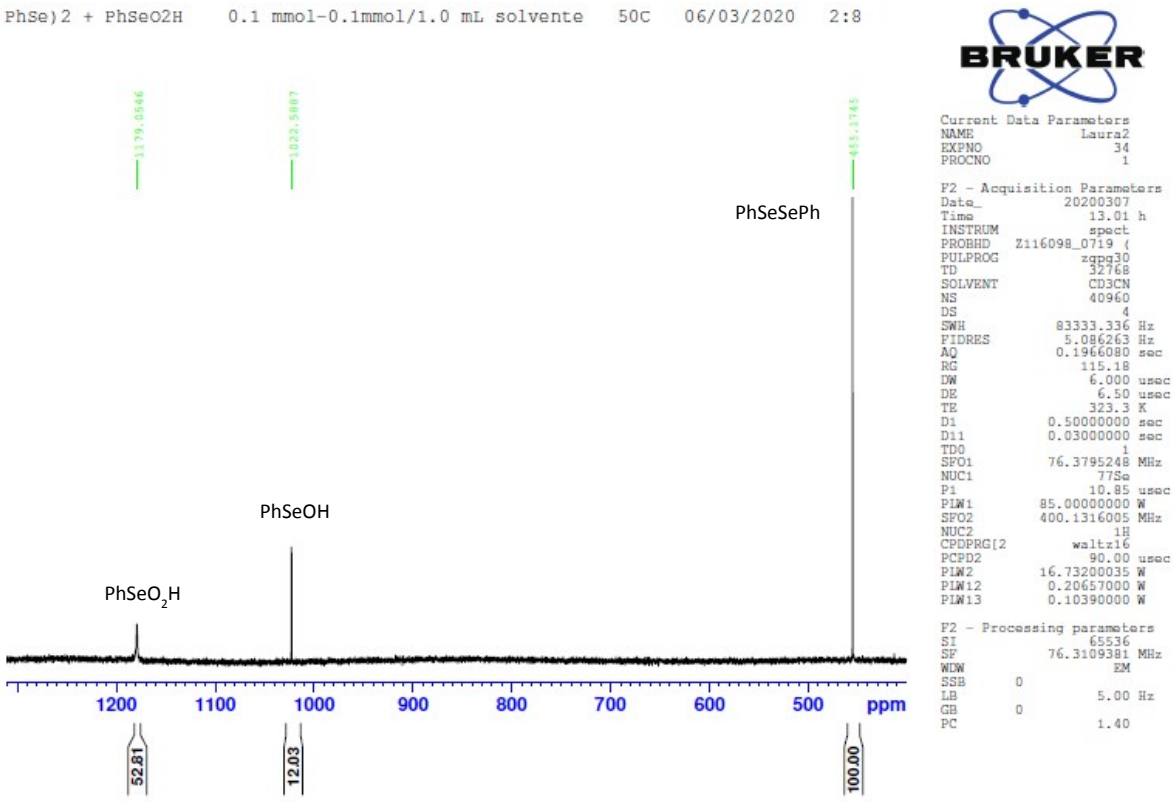

Figure S3. ^{77}Se NMR (76 MHz) spectrum, solution in DMF, of a freshly prepared mixture of $PhSeO_2H$ **1a** (0.1 mmol) and PhSeSePh **7** (0.1 mmol) at 50 °C.

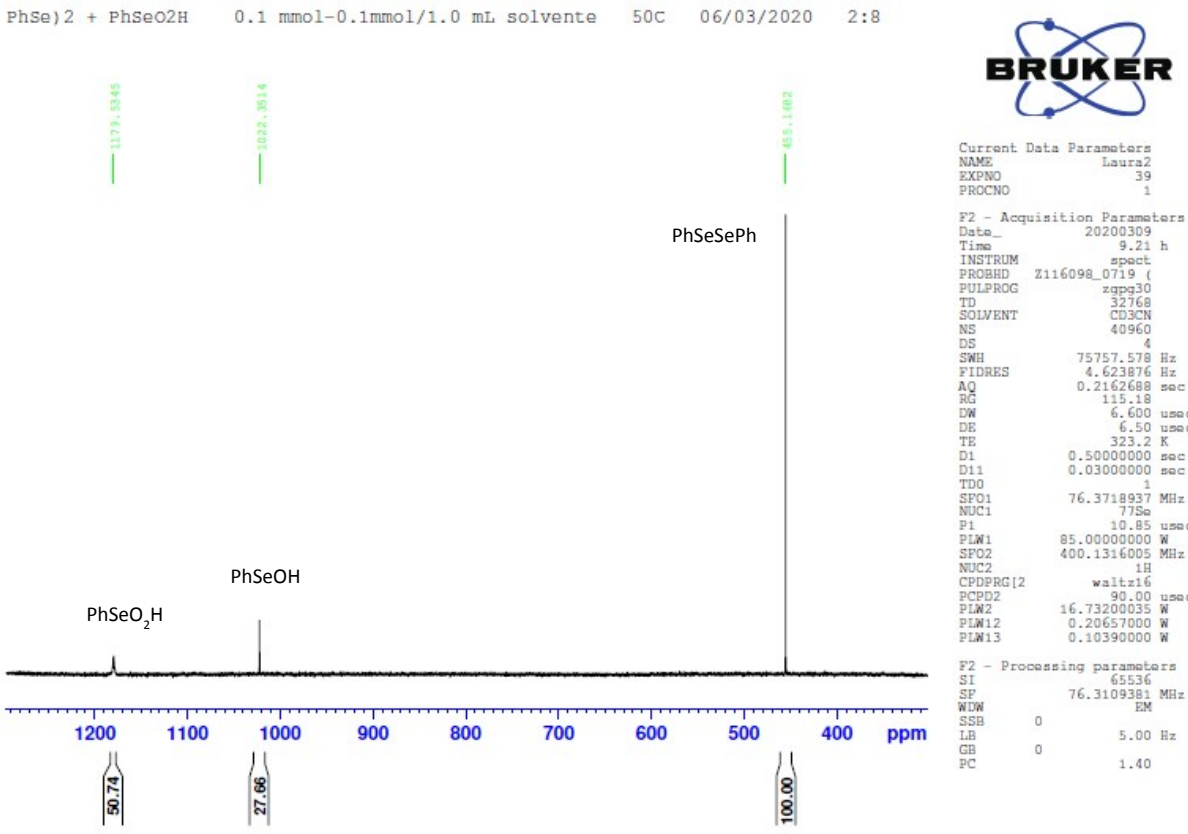

Figure S4. ^{77}Se NMR (76 MHz) spectrum, solution in DMF, of a mixture of $PhSeO_2H$ **1a** (0.1 mmol) and PhSeSePh **7** (0.1 mmol) after 24 h at 50 °C.

General procedure for the synthesis of the products 3a-n: In a round-bottomed flask were added phenylseleninc acid **1a-f** (0.3 mmol), aniline **2a-c** (0.25 mmol), DMF (2 mL) and the mixture was stirring at 70 °C for a specific time for each starting material. After this time, the reaction was extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$ and concentrated under vacuum. Then, the crude was purified by preparative thin layer chromatography in a mixture of hexanes/ethyl acetate (97:3) as the eluent.

*N,N-dimethyl-4-(phenylselanyl)aniline (**3a**).*[5] Yield: 0.065 g (94%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.51 – 7.45 (m, 2H), 7.30 – 7.24 (m, 2H), 7.22 – 7.09 (m, 3H), 6.69 – 6.64 (m, 2H), 2.97 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 150.5, 137.1, 134.6, 129.8, 129.0, 125.8, 113.7, 113.2, 40.3.

*N,N-diethyl-4-(phenylselanyl)aniline (**3b**).*[5] Yield: 0.087 g (95%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.48 – 7.42 (m, 2H), 7.31 – 7.26 (m, 2H), 7.21 – 7.09 (m, 3H), 3.36 (q, J = 7.0 Hz, 4H), 1.17 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 147.9, 137.5, 134.8, 129.6, 128.9, 125.7, 112.4, 112.1, 44.3, 12.5.

*N,N-dibutyl-4-(phenylselanyl)aniline (**3c**).*[5] Yield: 0.107 g (99%); brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.43 (d, J = 8.9 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.21 – 7.08 (m, 3H), 6.57 (d, J = 8.9 Hz, 2H), 3.26 (t, J = 7.7 Hz, 4H), 1.62 – 1.51 (m, 4H), 1.35 (h, J = 7.4 Hz, 4H), 0.96 (t, J = 7.3 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 148.3, 137.4, 134.8, 129.6, 128.9, 125.7, 112.4, 111.9, 50.7, 29.3, 20.3, 14.0.

*4-((4-chlorophenyl)selanyl)-N,N-dimethylaniline (**3d**).*[5] Yield: 0.056 g (60%); white solid, mp: 111 – 113 ºC (Lit.:[5] 111 – 116 ºC). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.46 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 2.98 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 150.6, 137.1, 133.0, 131.8, 131.0, 129.0, 113.2, 40.2.

*4-((4-chlorophenyl)selanyl)-N,N-diethylaniline (**3e**).* Yield: 0.062 g (61%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.42 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 3.35 (q, J = 7.0 Hz, 2H), 1.17 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 148.1, 137.5, 133.2, 131.6, 130.8, 129.0, 112.4, 111.7, 44.3, 12.5. HRMS (APCI-QTOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{19}ClNS$, 340.0364; found, 340.0352.

*N,N-dibutyl-4-((4-chlorophenyl)selanyl)aniline (**3f**).* Yield: 0.054 g (55%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.41 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 6.57 (d, J = 8.4 Hz, 2H), 3.26 (t, J = 7.7 Hz, 4H), 1.63 – 1.51 (m, 4H), 1.35 (sex, J = 7.4 Hz, 4H), 0.96 (t, J = 7.4 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)

δ (ppm) 148.5, 137.4, 133.2, 131.6, 130.9, 129.0, 112.4, 111.5, 50.7, 29.3, 20.3, 14.0. HRMS (APCI-QTOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{27}ClNSe$, 396.0990; found, 396.0998.

*4-((4-fluorophenyl)selanyl)-N,N-dimethylaniline (**3g**).*[4] Yield: 0.064 g (88%); white solid, mp: 50 – 55 ºC (Lit.:[4] 49 – 52 ºC). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.45 (d, J = 8.8 Hz, 2H), 7.31 – 7.23 (m, 2H), 6.93 – 6.86 (m, 2H), 6.65 (d, J = 8.8 Hz, 2H), 2.96 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 161.7 (d, J = 245,1 Hz), 150.5, 136.6, 132.1 (d, J = 7.5 Hz,), 128.6 (d, J = 3.2 Hz), 116.1 (d, J = 21.5 Hz), 114.3, 113.2, 40.3.

*N,N-dimethyl-4-((3-(trifluoromethyl)phenyl)selanyl)aniline (**3h**).*[5] Yield: 0.076 g (88%); light yellow solid, mp: 45 – 47 ºC (Lit.:[5] 48 – 52 ºC). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.52 (s, 1H), 7.48 (d, J = 8.8 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.28 – 7.21 (m, 1H), 6.67 (d, J = 8.8 Hz, 2H), 2.98 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 150.8, 137.5, 136.3, 132.5, 131.1 (q, $J_{C\text{-}F}$ = 32.2 Hz), 129.1, 125.8 (q, $J_{C\text{-}F}$ = 3.9 Hz), 125.2, 122.4 (q, $J_{C\text{-}F}$ = 3.9 Hz), 113.2, 112.2, 40.2.

*N,N-diethyl-4-((3-(trifluoromethyl)phenyl)selanyl)aniline (**3i**).* Yield: 0.075 g (79%); yellow solid, mp: 47 – 50 ºC. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.53 (s, 1H), 7.45 (d, J = 8.7 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.29 – 7.22 (m, 1H), 6.63 (d, J = 8.7 Hz, 2H), 3.37 (q, J = 7.1 Hz, 4H), 1.18 (t, J = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 148.3, 137.8, 136.5, 132.4, 131.1 (q, $J_{C\text{-}F}$ = 32.0 Hz), 129.1, 125.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.8 (q, $J_{C\text{-}F}$ = 270.9 Hz), 122.3 (q, $J_{C\text{-}F}$ = 3.7 Hz), 112.5, 110.7, 44.3, 12.5. HRMS (APCI-QTOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{19}F_3NSe$, 374.0630; found, 374.0627.

*N,N-dimethyl-4-(p-tolylselanyl)aniline (**3j**).*[6] Yield: 0.058 g (80%); brown solid, mp: 60 – 65 ºC (Lit.:[6] 67 – 69 ºC). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.45 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 2.95 (s, 6H), 2.27 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 150.3, 136.5, 135.8, 130.5, 130.3, 129.8, 114.6, 113.1, 40.3, 20.9.

*N,N-diethyl-4-(p-tolylselanyl)aniline (**3k**).* Yield: 0.056 g (71%); green oil. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.42 (d, J = 8.9 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 7.8 Hz, 2H), 6.60 (d, J = 8.9 Hz, 2H), 3.35 (q, J = 7.0 Hz, 4H), 2.27 (s, 3H), 1.16 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 147.8, 136.9, 135.7, 130.4, 129.8, 129.2, 113.0, 112.4, 44.3, 21.0, 12.5. HRMS (APCI-QTOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{22}NSe$, 320.0823; found, 320.0828.

*N,N-dibutyl-4-(p-tolylselanyl)aniline (**3l**).* Yield: 0.062 g (67%); brown oil. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.42 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 8.9 Hz, 2H), 3.29 – 3.21 (m, 4H), 2.27 (s, 3H), 1.61 – 1.50 (m,

6H), 1.40 – 1.29 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) *δ* (ppm) 148.2, 136.8, 135.7, 130.4, 129.8, 112.8, 112.4, 50.7, 29.3, 21.0, 20.3, 14.0. HRMS (APCI-QTOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{30}NSe$, 376.1469; found, 376.1472.

*4-(mesitylselanyl)-N,N-dimethylaniline (**3m**).*[5] Yield: 0.049 g (60%); brown solid, mp: 57-60 C (Lit.:[5] 56 – 59 ºC). ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) 7.06 (d, *J* = 8.8 Hz, 2H), 6.94 (s, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 2.88 (s, 6H), 2.46 (s, 6H), 2.27 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) *δ* (ppm) 149.1, 143.1, 138.3, 131.2, 128.6, 118.1, 113.6, 40.5, 24.4, 21.0.

*N,N-diethyl-4-(mesitylselanyl)aniline (**3n**).* Yield: 0.049 g (57%); green oil. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) 7.05 (d, *J* = 8.8 Hz, 2H), 6.93 (s, 2H), 6.50 (d, *J* = 8.8 Hz, 2H), 3.26 (q, *J* = 7.1 Hz, 4H), 2.47 (s, 6H), 2.26 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) *δ* (ppm) 146.4, 143.1, 138.2, 131.8, 128.6, 116.4, 112.9, 44.3, 24.4, 21.0, 12.5. HRMS (APCI-QTOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{26}NSe$, 348.1156; found, 348.1160.

General procedure for the synthesis of the products 5a-e: In a round-bottomed flask were added arylseleninc acid **1a,c-f** (0.3 mmol), indole **4a** (0.25 mmol), DMF (2 mL) and the mixture was stirring at 70 °C for a specific time for each starting material. After this time, the reaction was extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$ and concentrated under vacuum. Then, the crude was purified by preparative thin layer chromatography in a mixture of hexanes/ethyl acetate (90:10) as the eluent.

*3-(phenylselanyl)-1H-indole (**5a**).*[7] Yield: 0.041 g (60%); white solid, mp: 149 – 151 °C (Lit.:[3] 150 – 151 ºC). ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) 8.42 (br, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.30 – 7.04 (m, 7H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) *δ* (ppm) 136.4, 133.8, 131.2, 130.0, 128.9, 128.6, 125.6, 122.9, 120.8, 120.4, 111.3, 98.2.

*3-((4-fluorophenyl)selanyl)-1H-indole (**5b**).*[7] Yield: 0.044 g (61%); white solid, mp: 130-132 (Lit.:[7] 134 – 137 ºC). °C. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) 8.40 (br, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.29 – 7.14 (m, 4H), 6.87 – 6.79 (m, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) *δ* (ppm) 161.5 (d, $J_{C\text{-}F}$ = 244.6 Hz), 136.4, 131.0, 130.7 (d, $J_{C\text{-}F}$ = 7.6 Hz), 129.7, 127.9 (d, $J_{C\text{-}F}$ = 3.1 Hz), 123.0, 120.9, 120.2, 116.0 (d, $J_{C\text{-}F}$ = 21.5 Hz), 111.4, 98.6.

*3-((3-(trifluoromethyl)phenyl)selanyl)-1H-indole (**5c**).*[7] Yield: 0.062 g (73%), white solid, mp: 75 – 80 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) 8.46 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.53 (s, 1H), 7.48 (d, *J* = 2.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.14 (m, 5H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) *δ* (ppm) 136.4, 135.2, 131.7, 131.5, 131.3, 130.9,

130.6, 130.9, 130.6, 129.6, 129.2, 125.1 (d, $J_{C\text{-}F}$ = 4.0 Hz), 123.2, 124.4 (d, $J_{C\text{-}F}$ = 4.0 Hz), 121.1, 120.1, 111.5, 97.2.

*3-(p-tolylselanyl)-1H-indole (**5d**).*[8] Yield: 0.040 g (56%); white solid, mp: 122 – 126 °C (Lit.:[8] 124 – 126 ºC). ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) 8.32 (br, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.27 – 7.20 (m, 1H), 7.19 – 7.12 (m, 3H), 6.94 (d, *J* = 7.9 Hz, 2H), 2.22 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) *δ* (ppm) 136.3, 135.5, 130.9, 129.9, 129.7, 129.0, 122.8, 120.7, 120.3, 111.3, 98.6, 20.9.

*3-(mesitylselanyl)-1H-indole (**5e**).*[8] Yield: 0.031 g (40%); white solid, mp: 135 – 140 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) 8.17 (br, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.13 – 7.07 (m, 1H), 6.87 (s, 2H), 2.56 (s, 6H), 2.22 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) *δ* (ppm) 142.5, 137.8, 136.1, 129.6, 128.7, 128.6, 127.9, 122.4, 120.2, 120.2, 111.1, 101.1, 24.5, 20.9.

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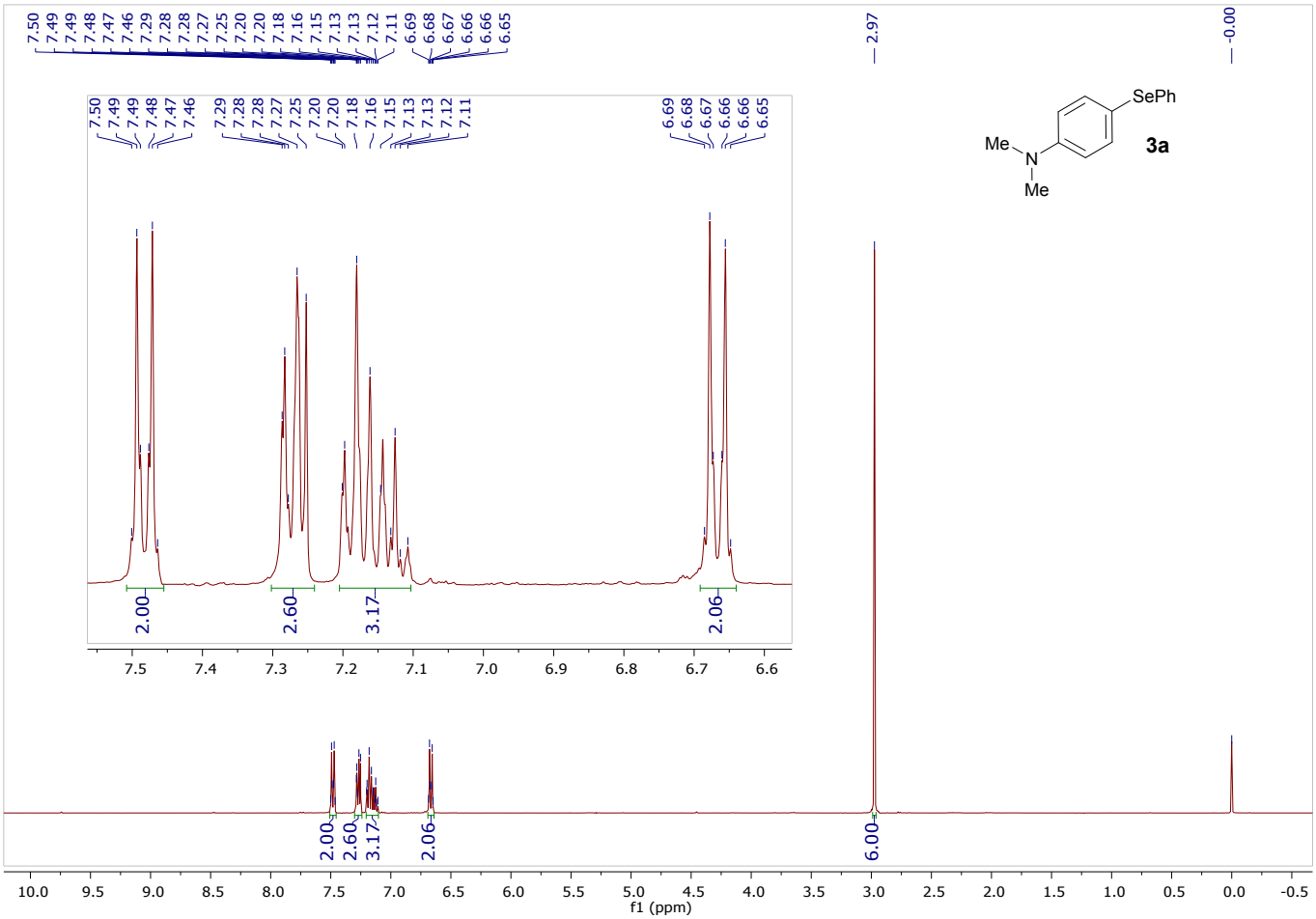
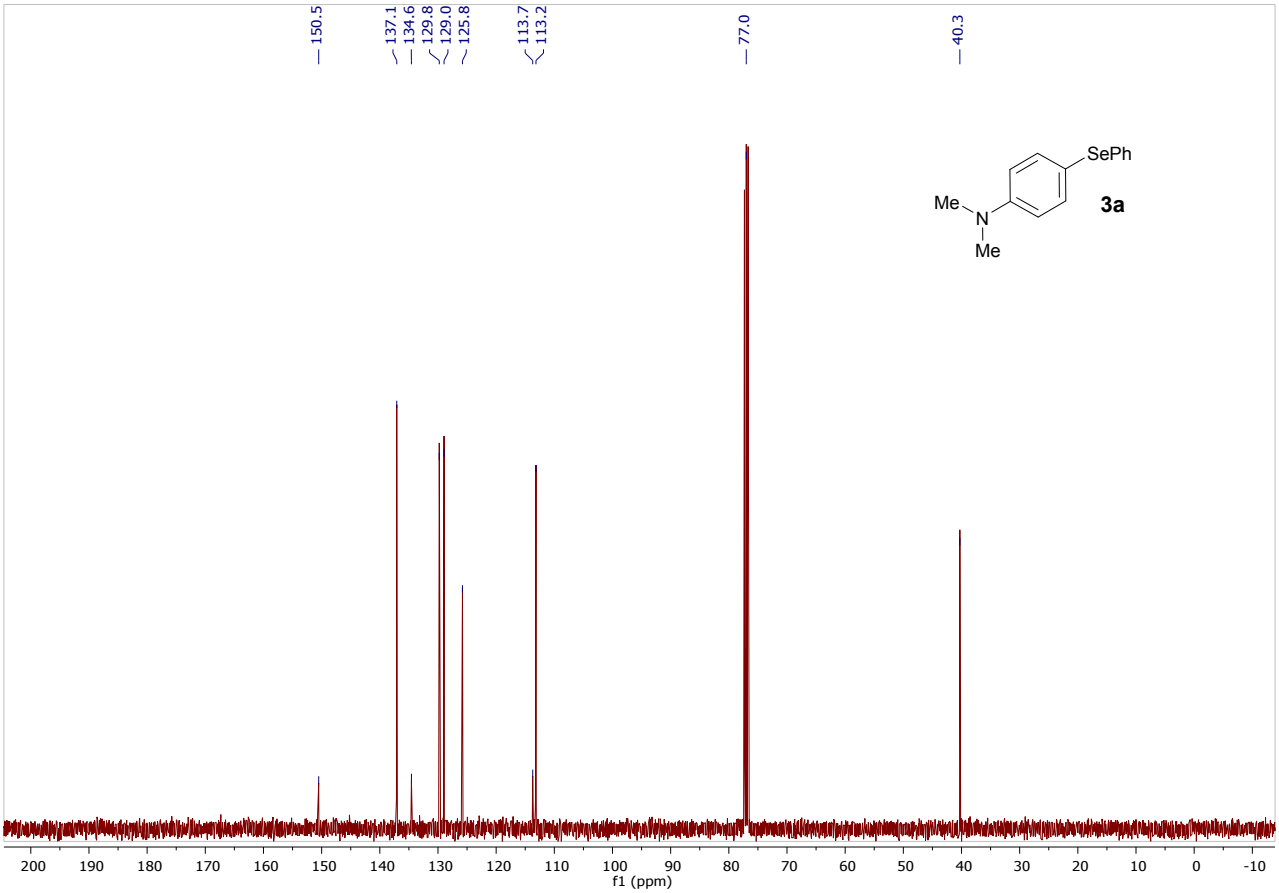
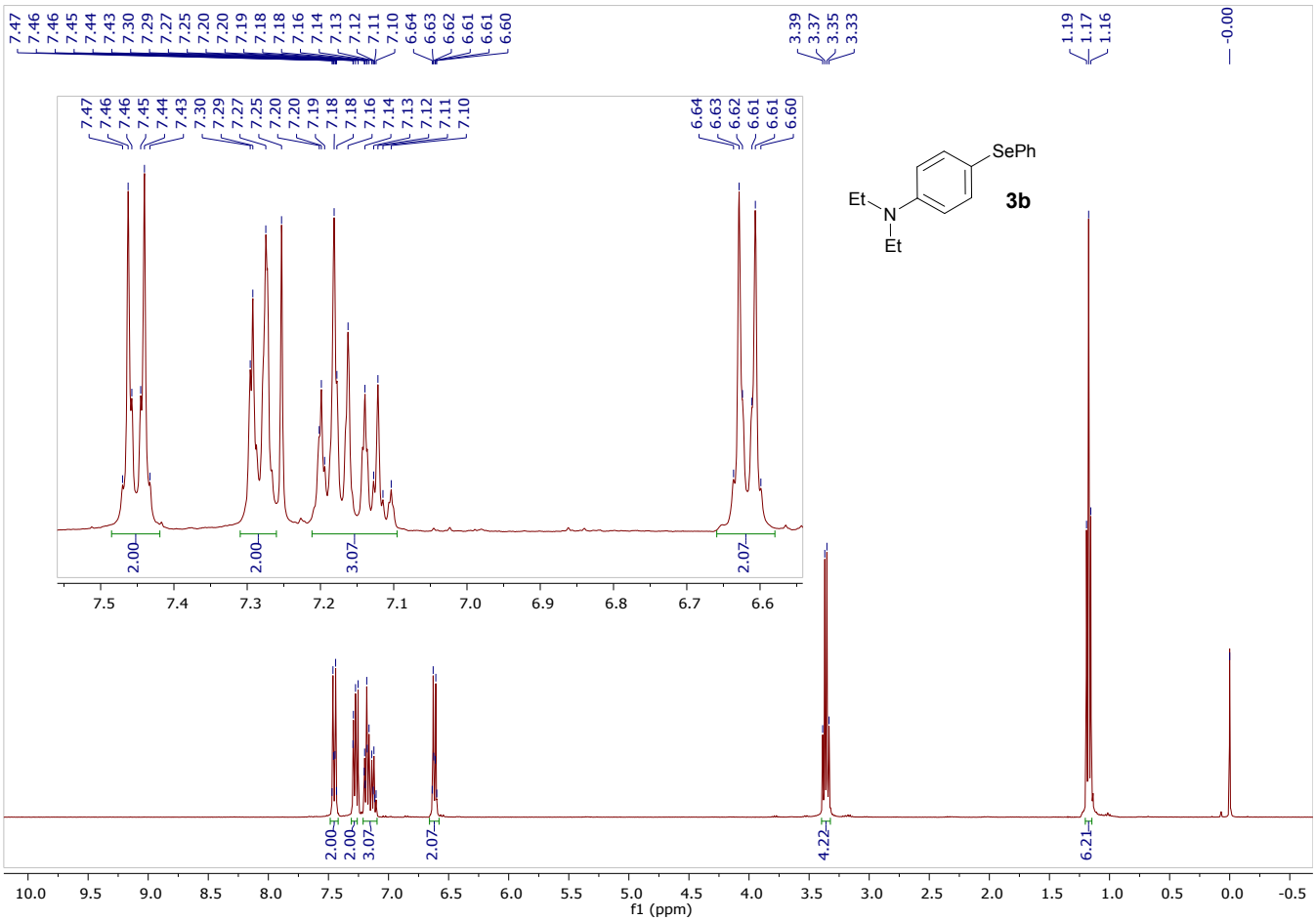
SELECTED SPECTRA



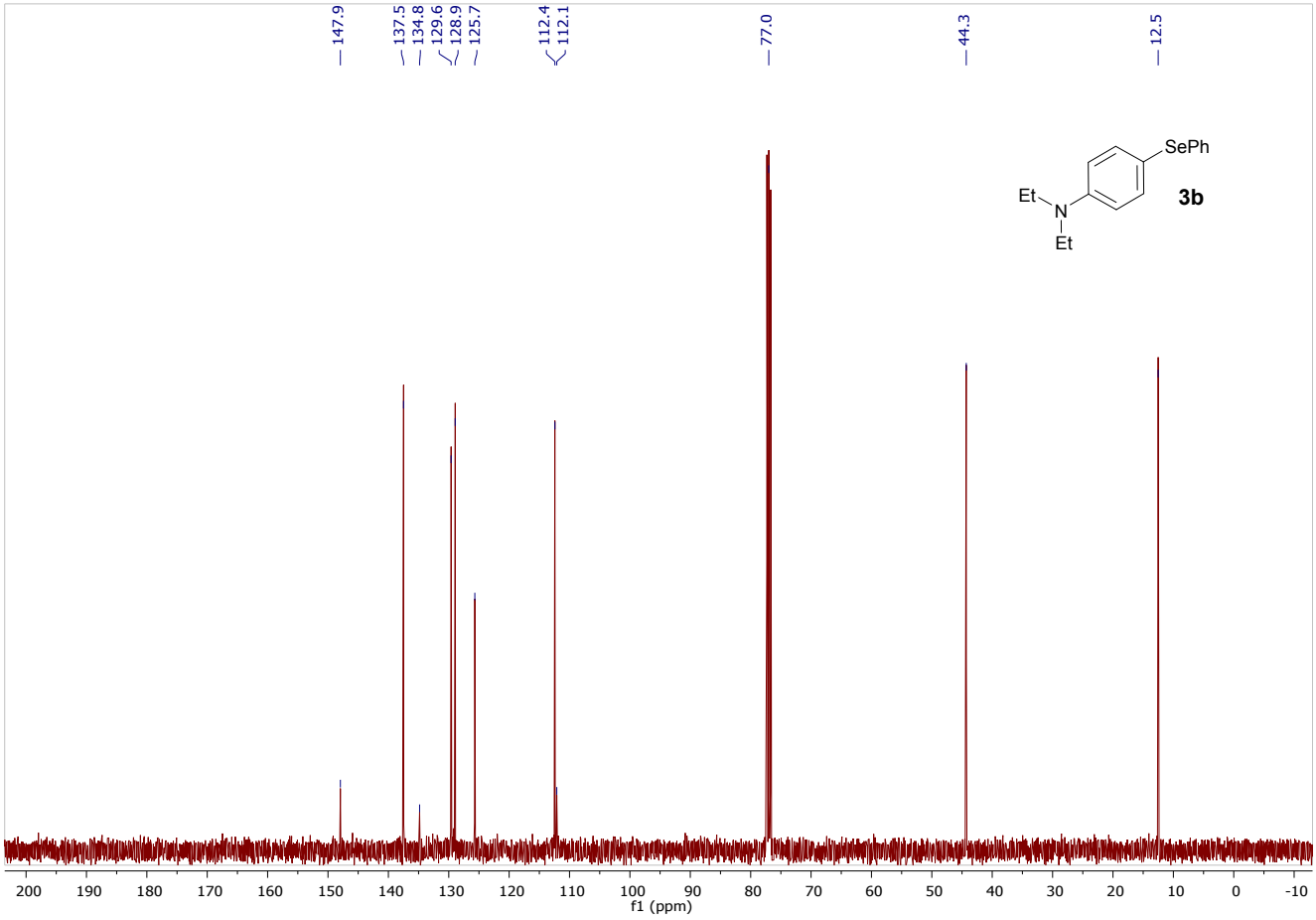
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3a**.



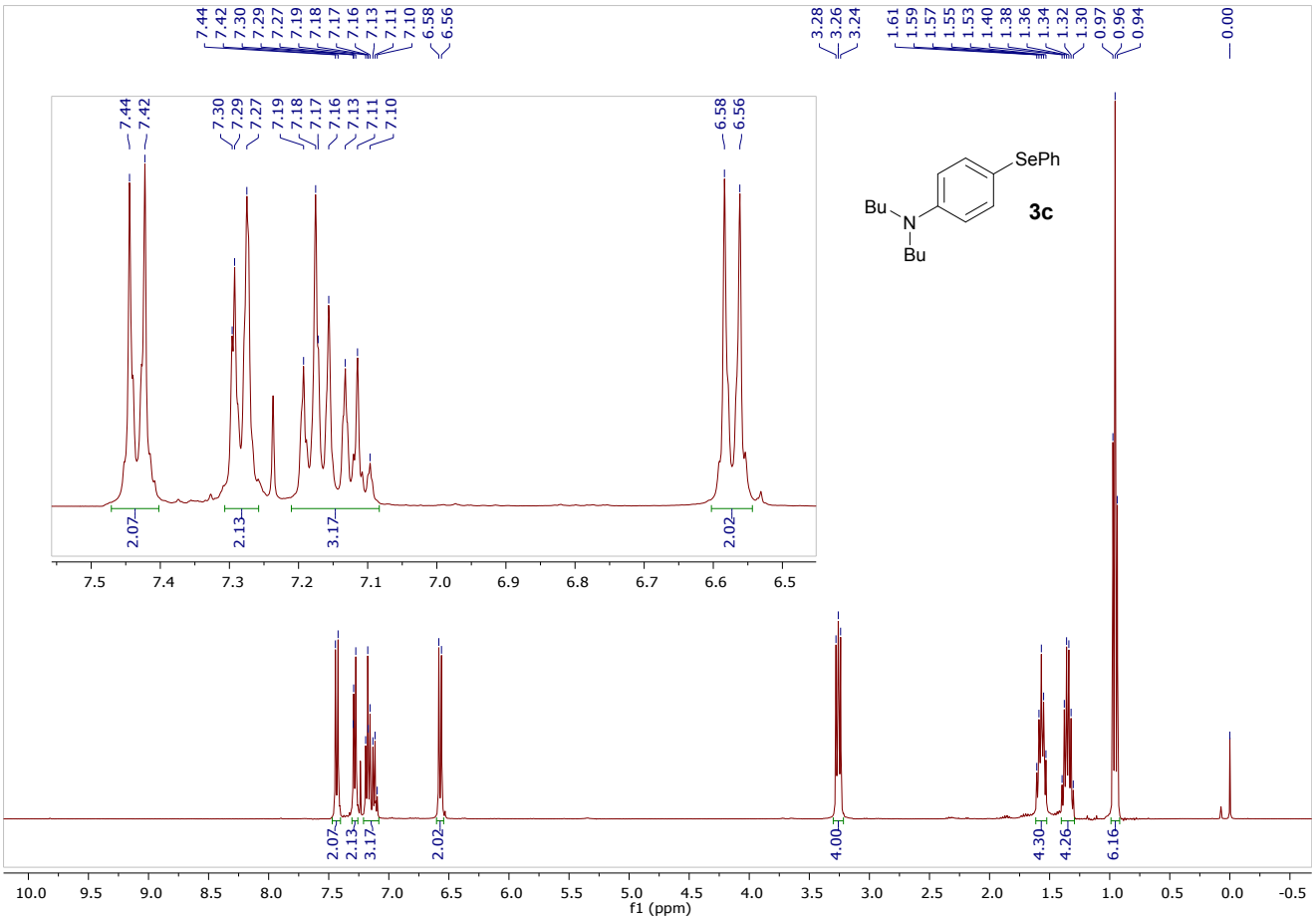
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3a**.



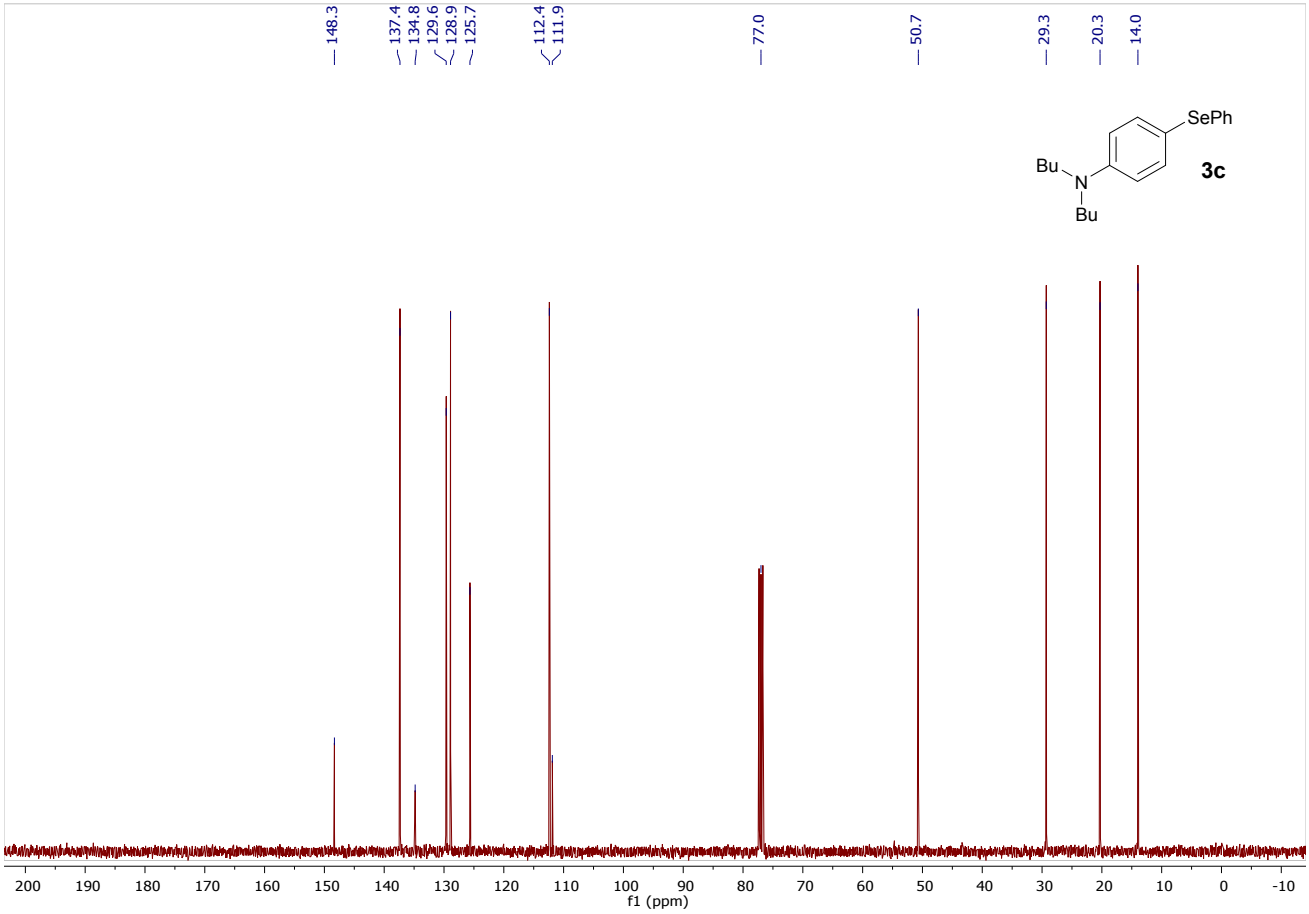
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3b**.



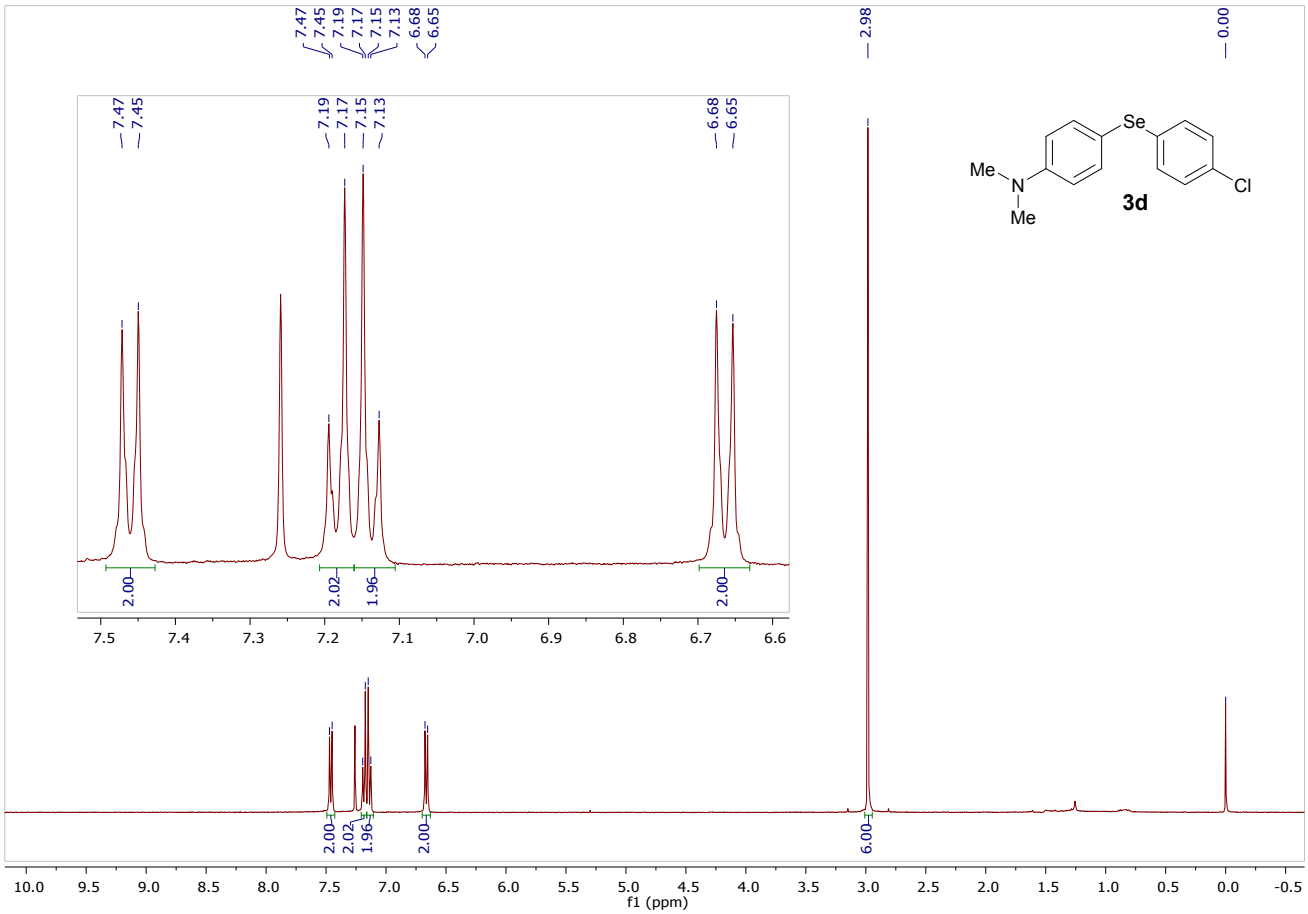
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3b**.



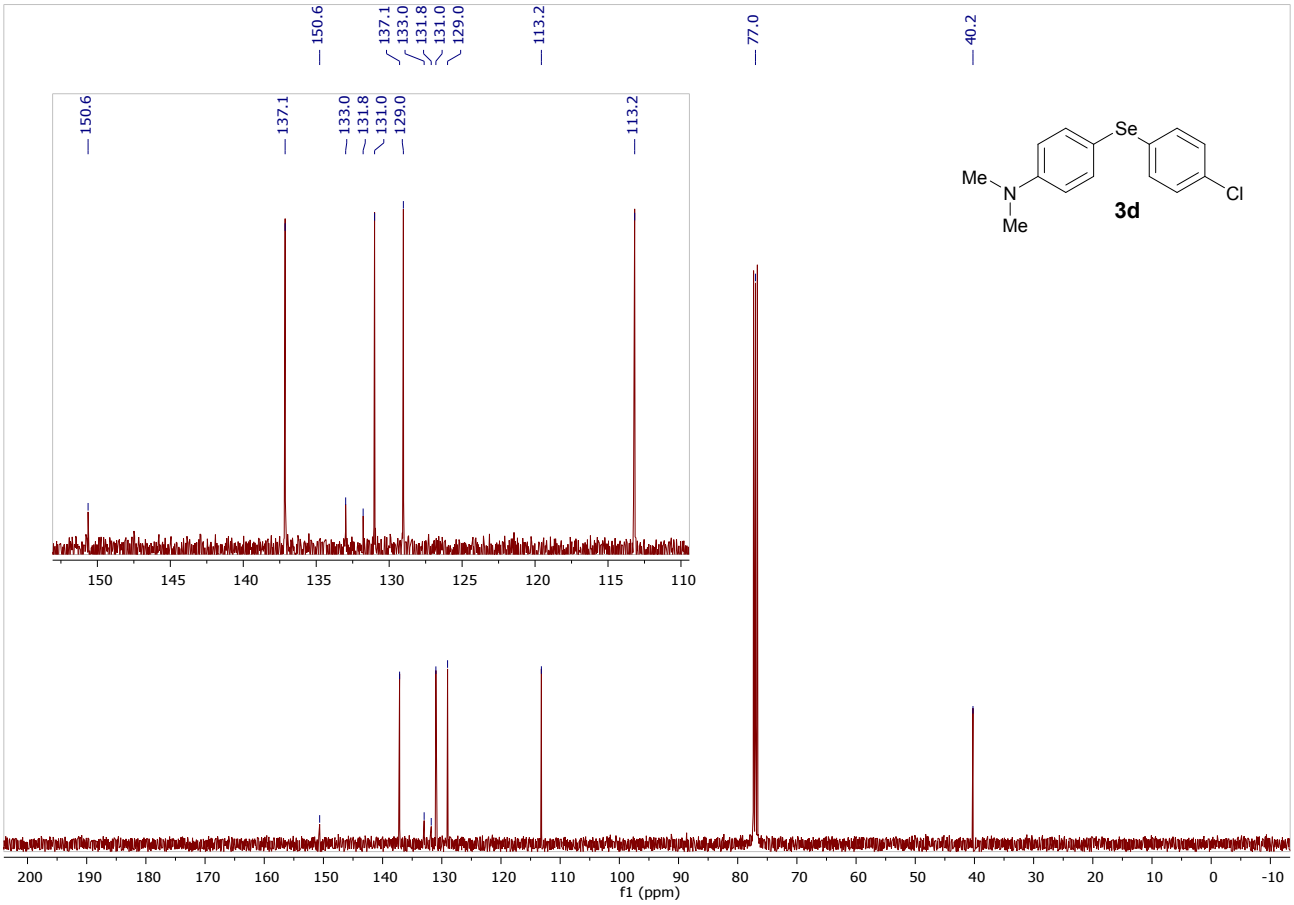
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3c**.



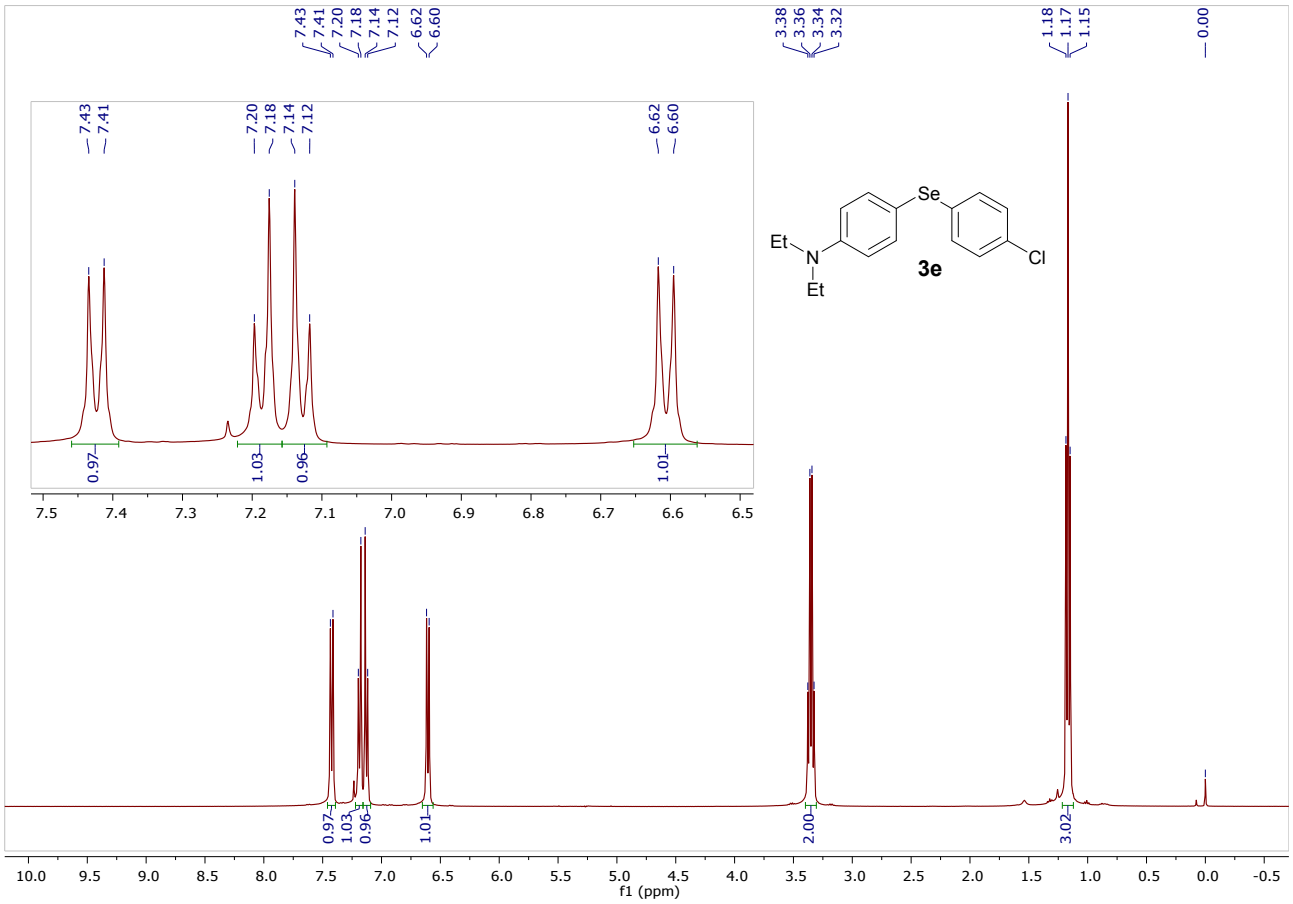
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3c**.



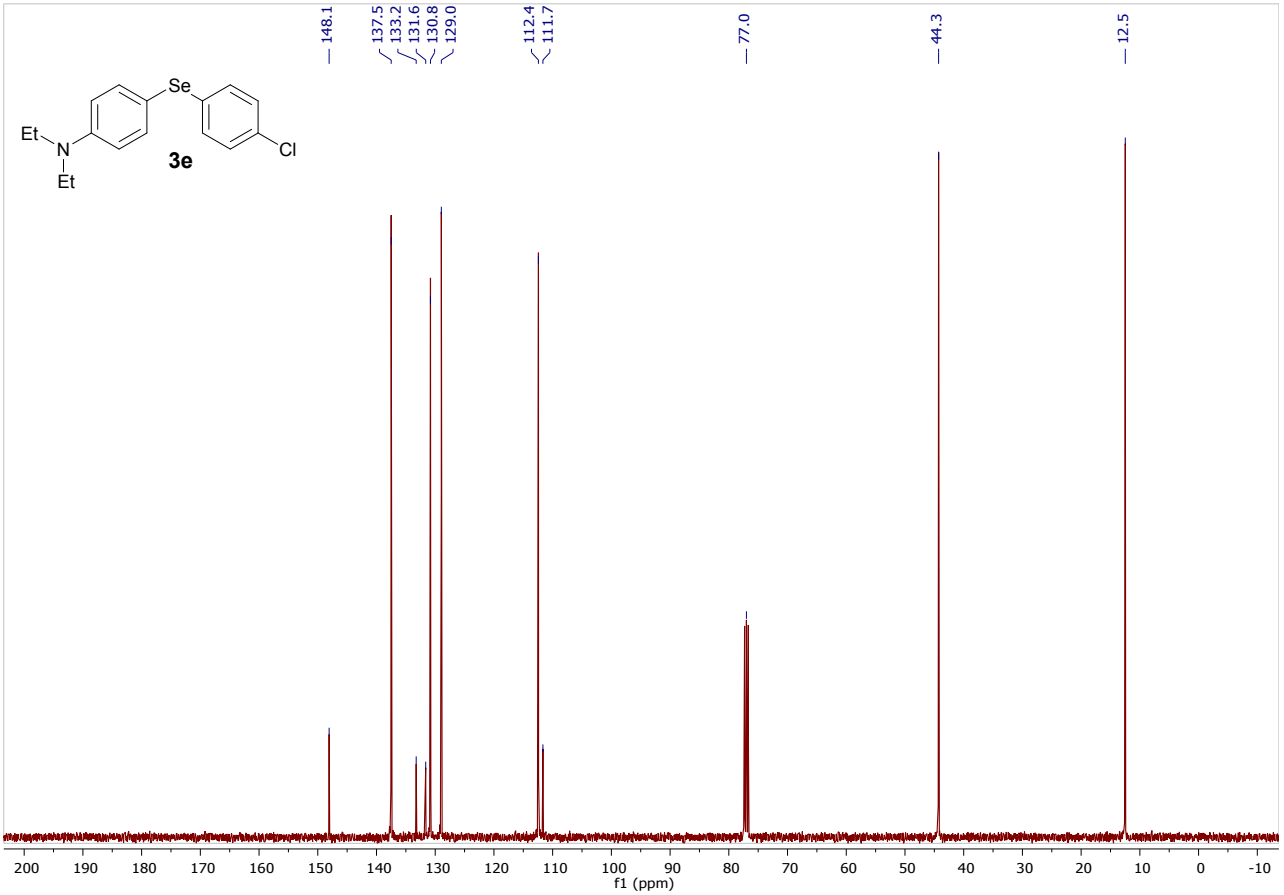
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3d**.



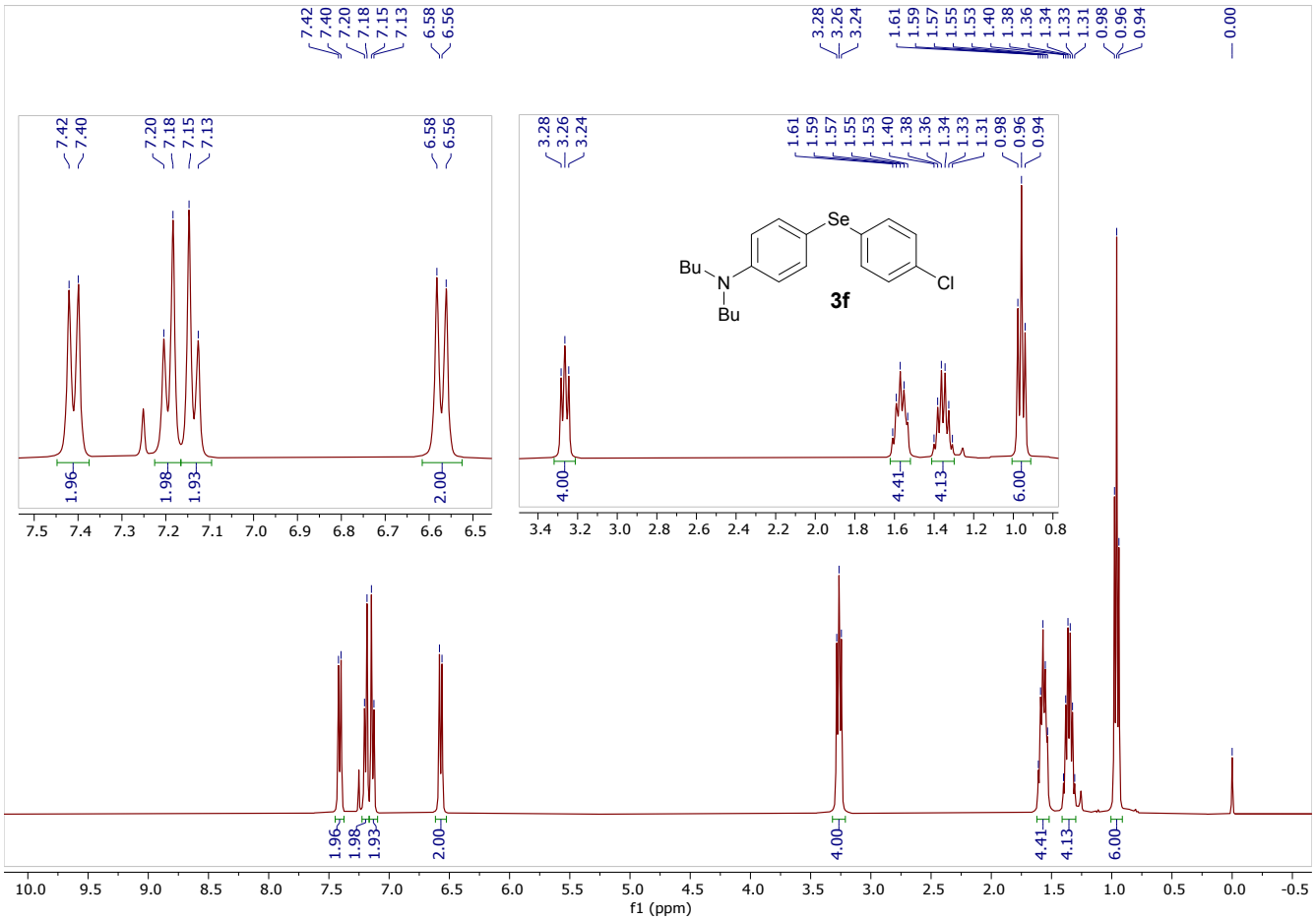
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3d**.



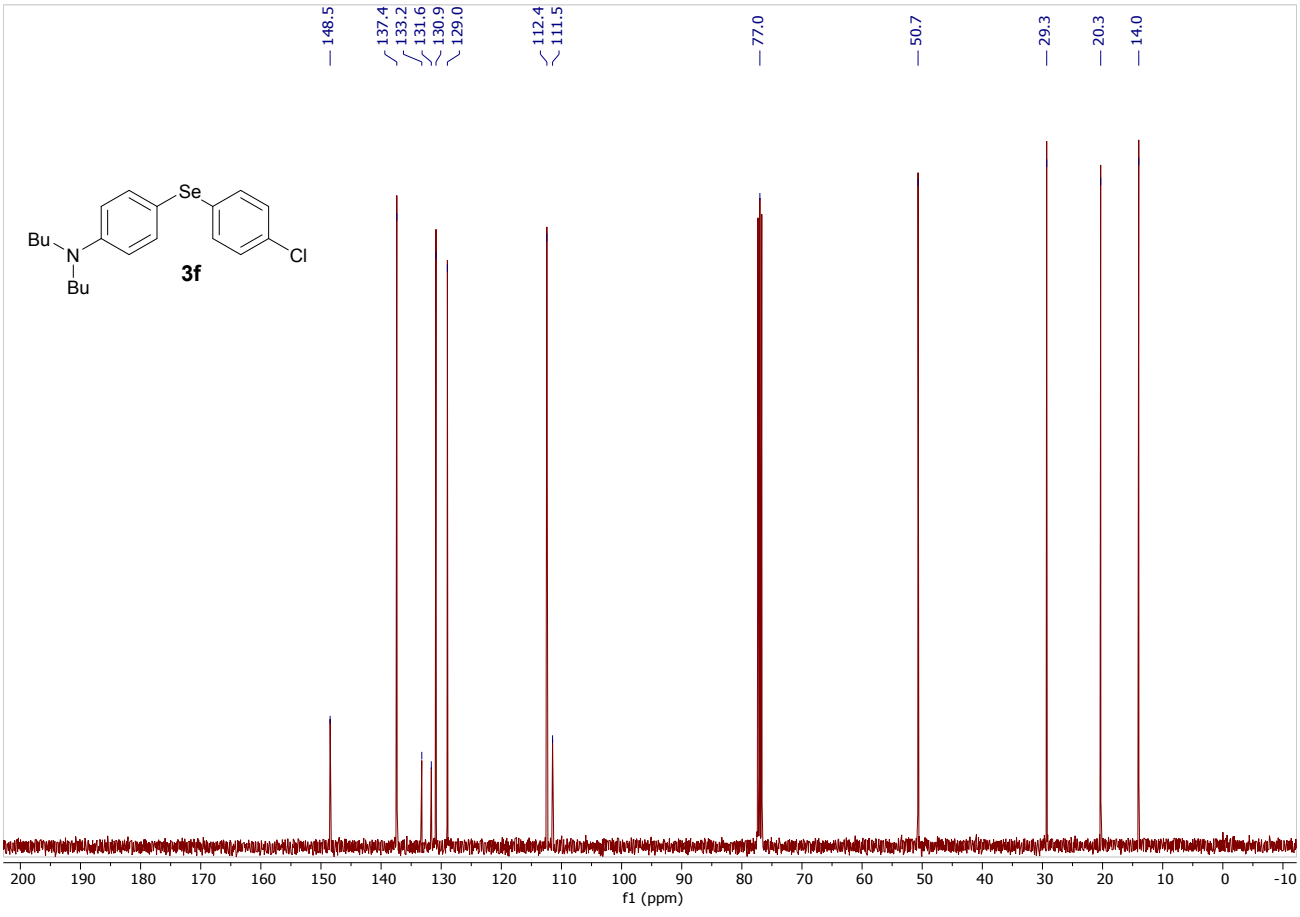
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3e**.



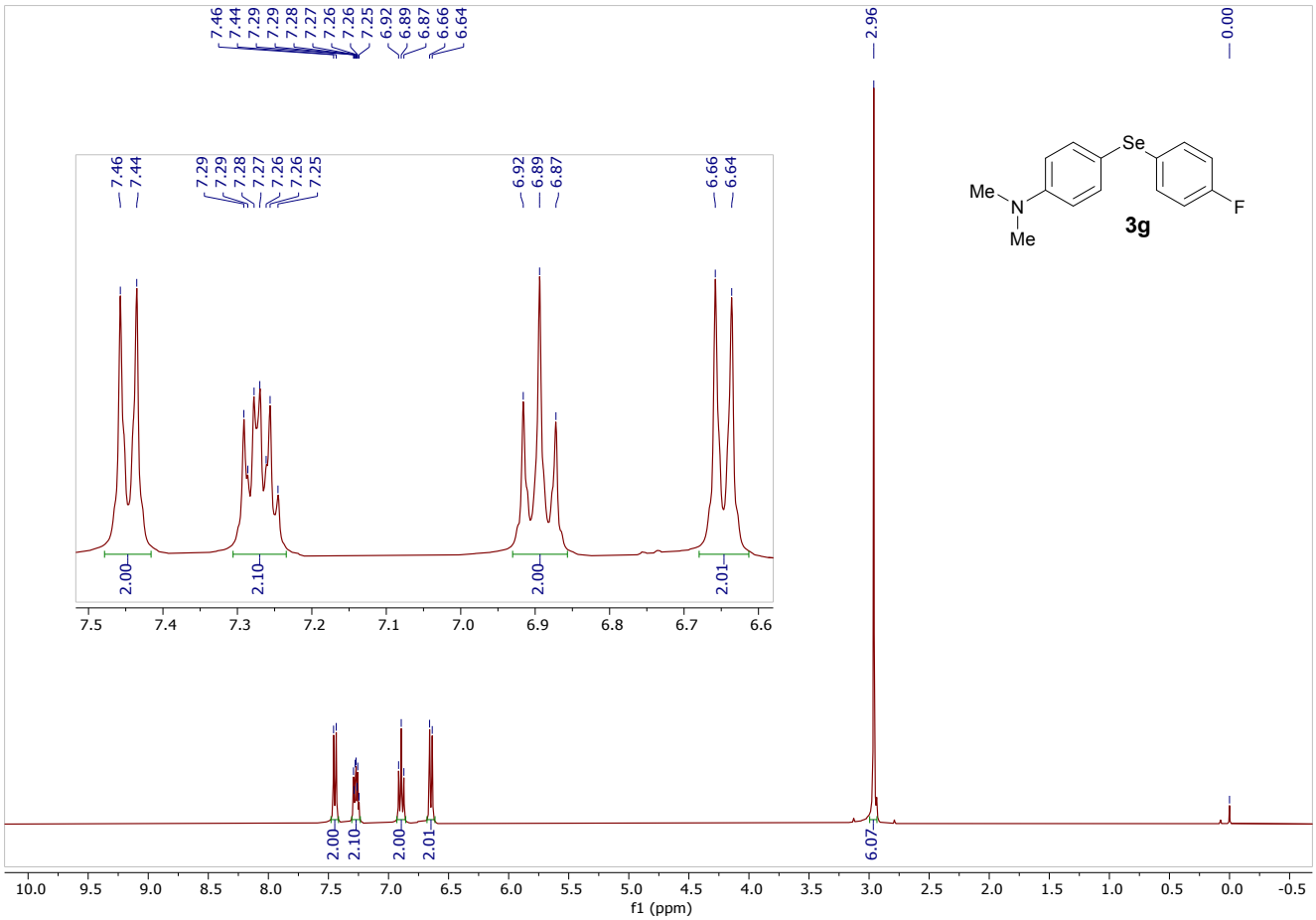
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3e**.



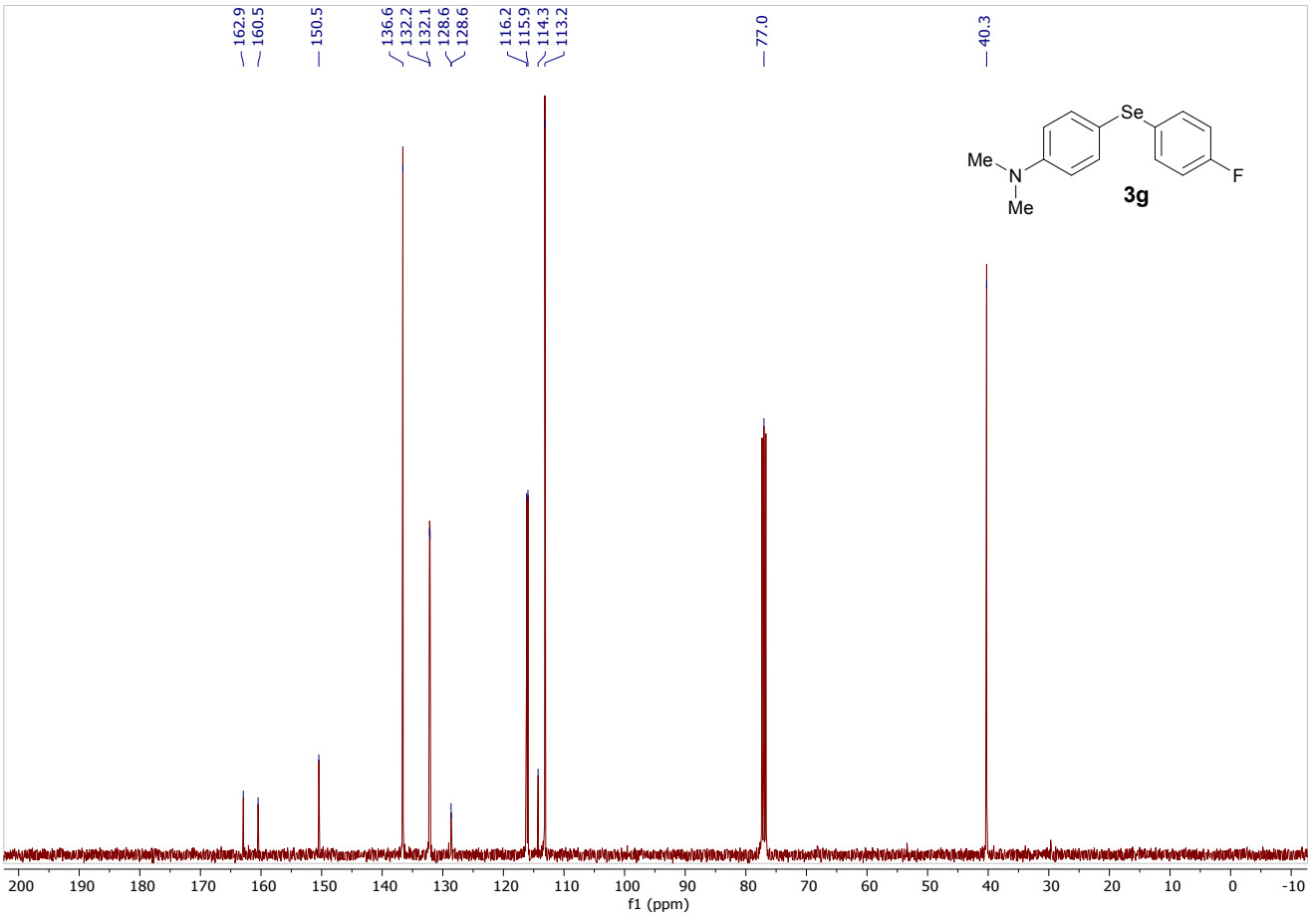
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3f**.



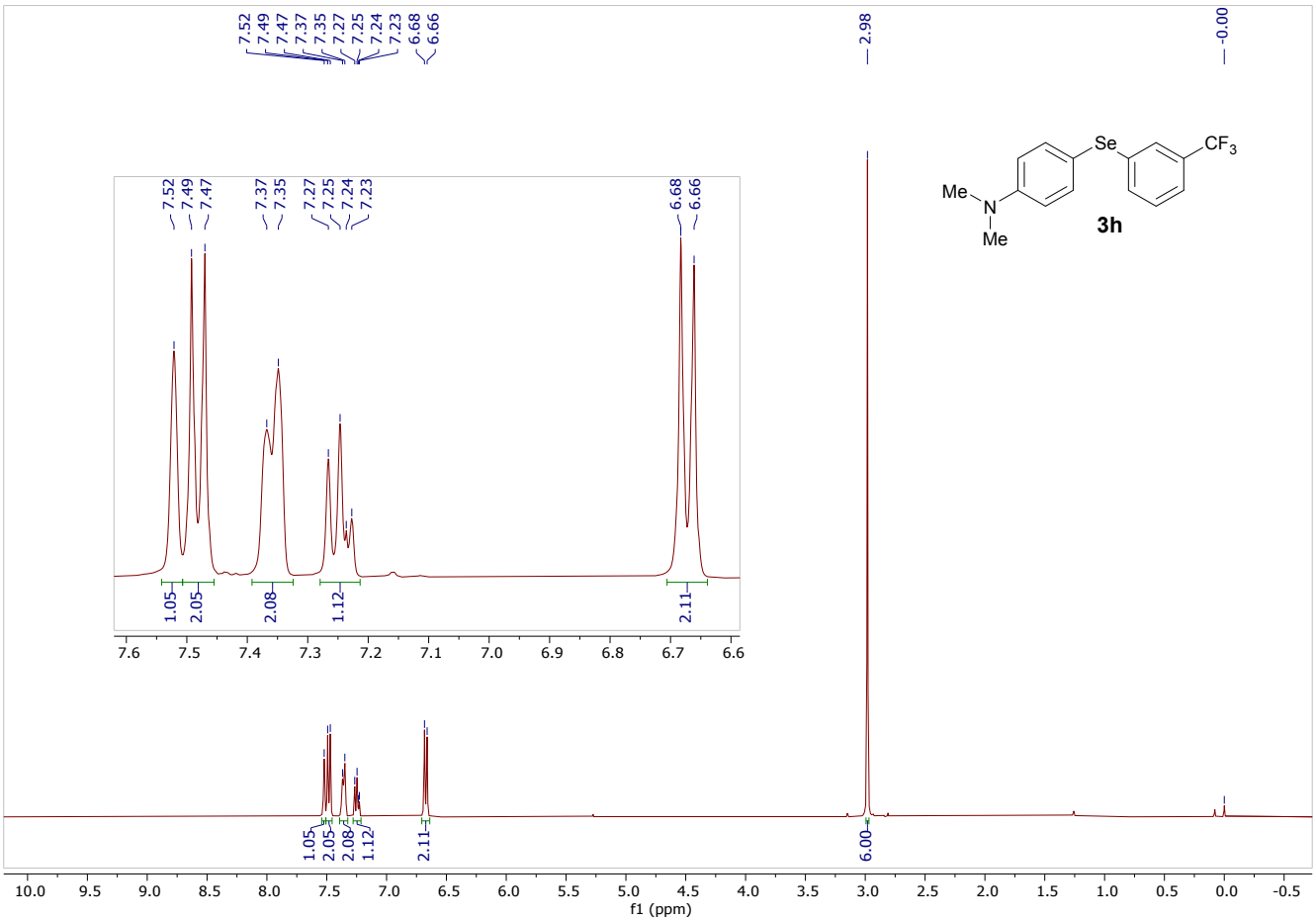
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3f**.



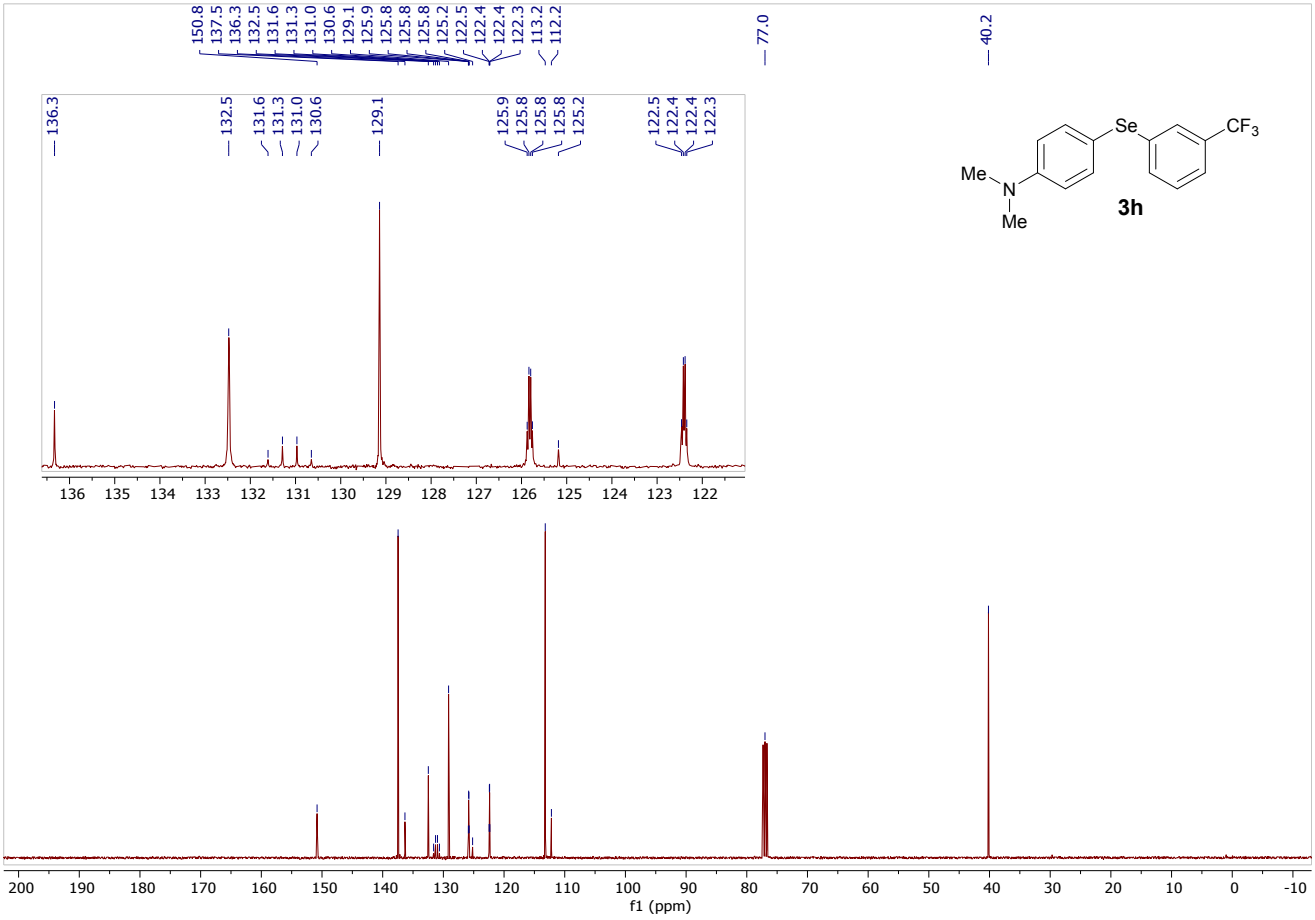
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3g**.



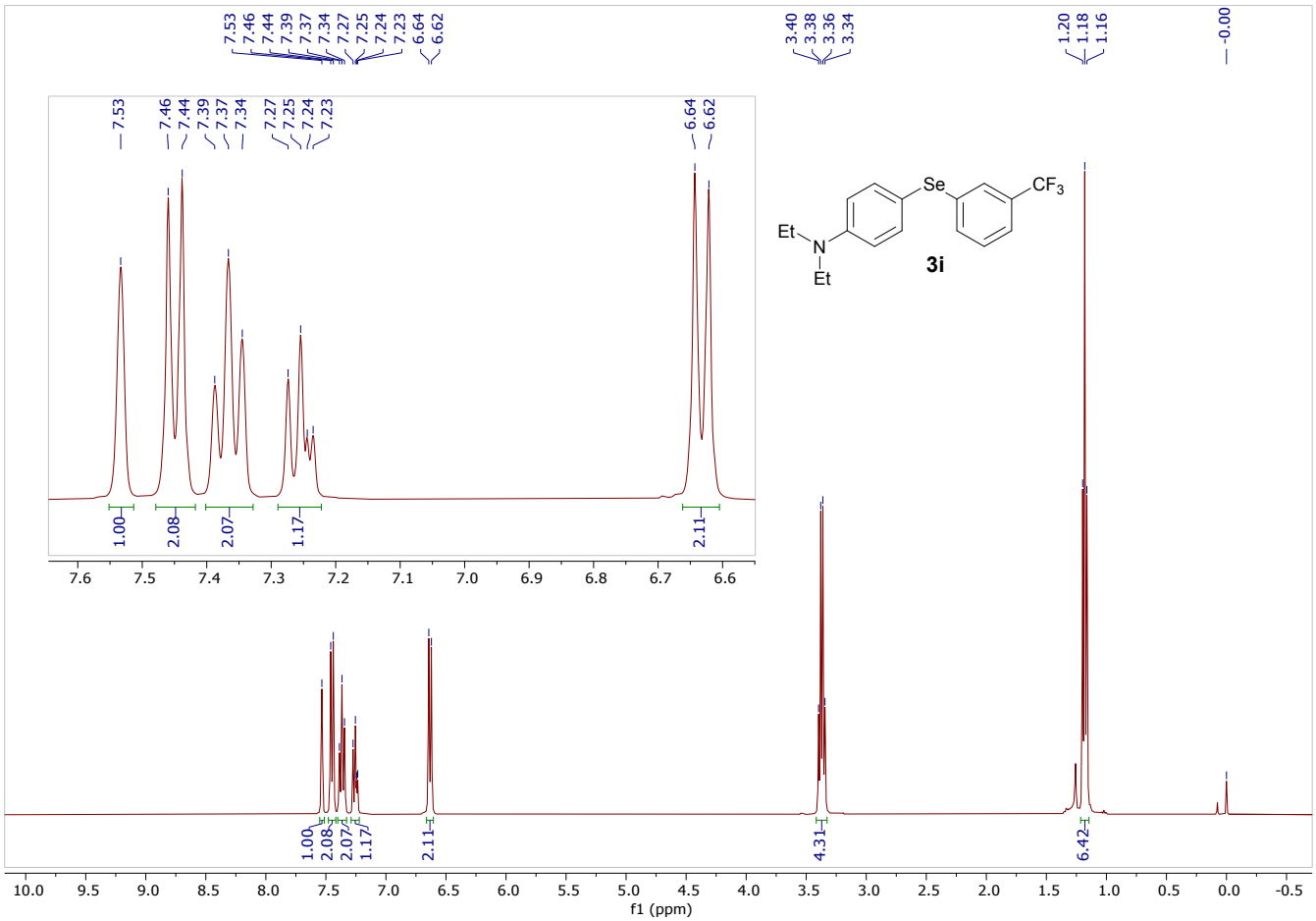
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3g**.



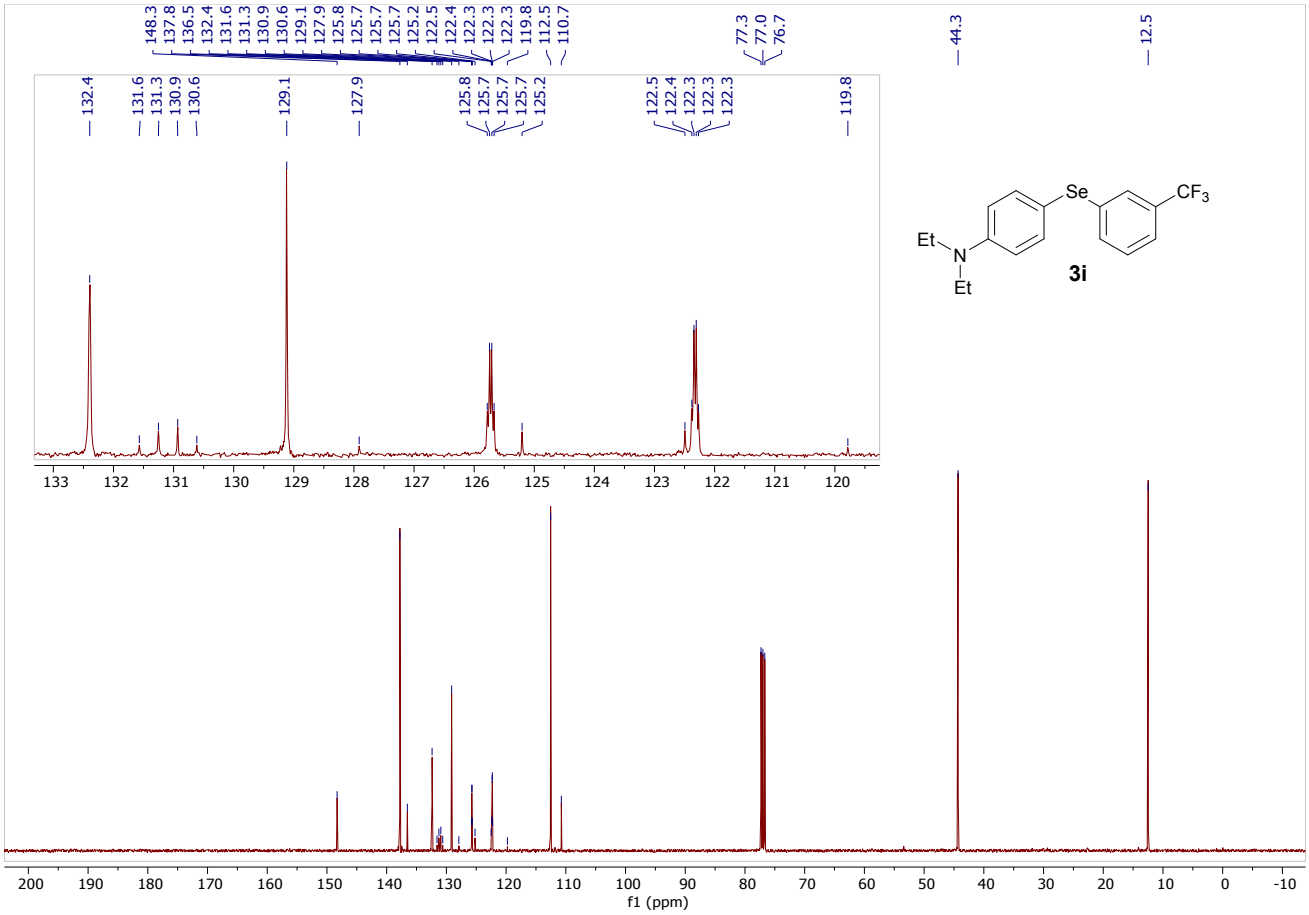
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3h**.



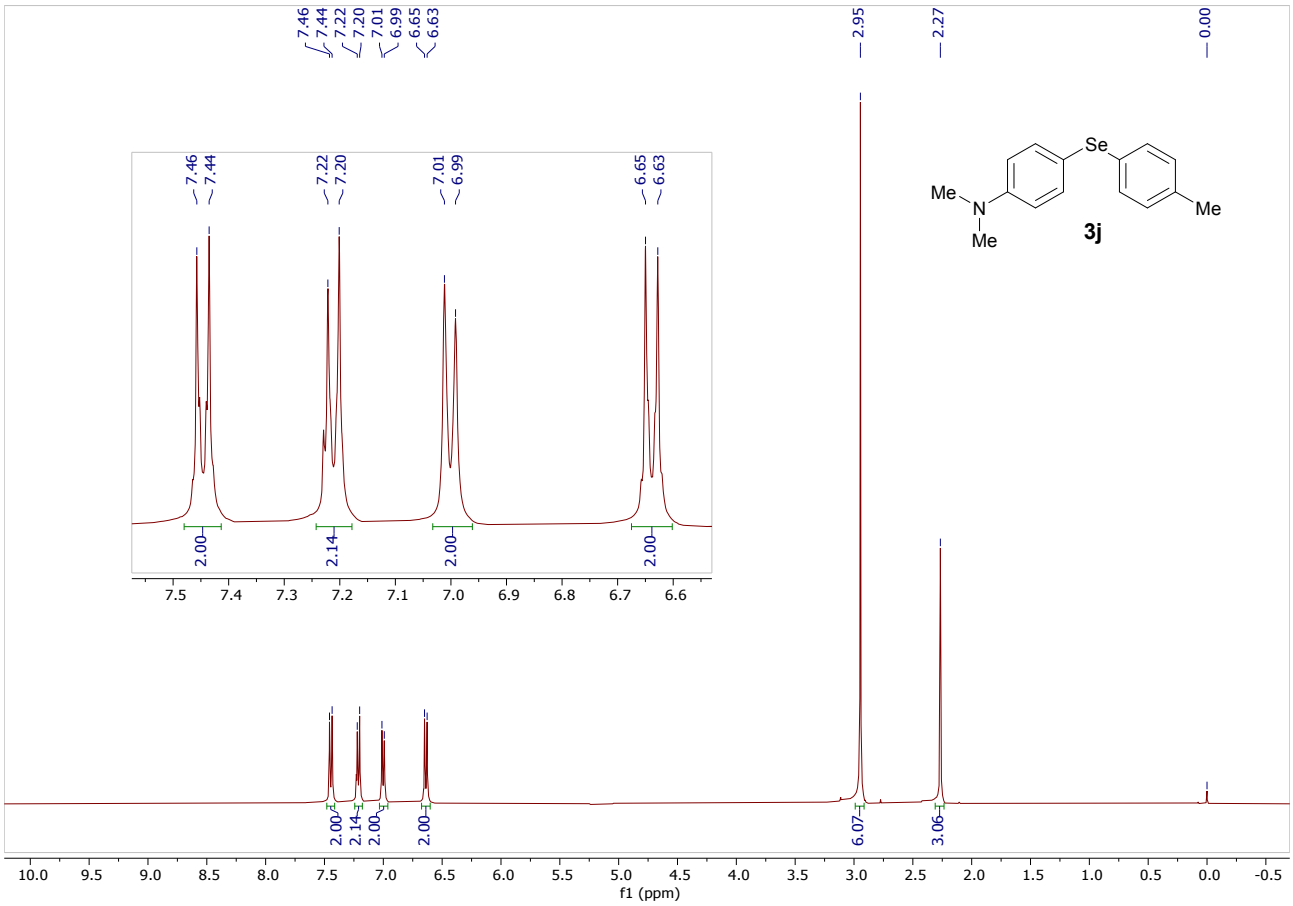
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3h**.



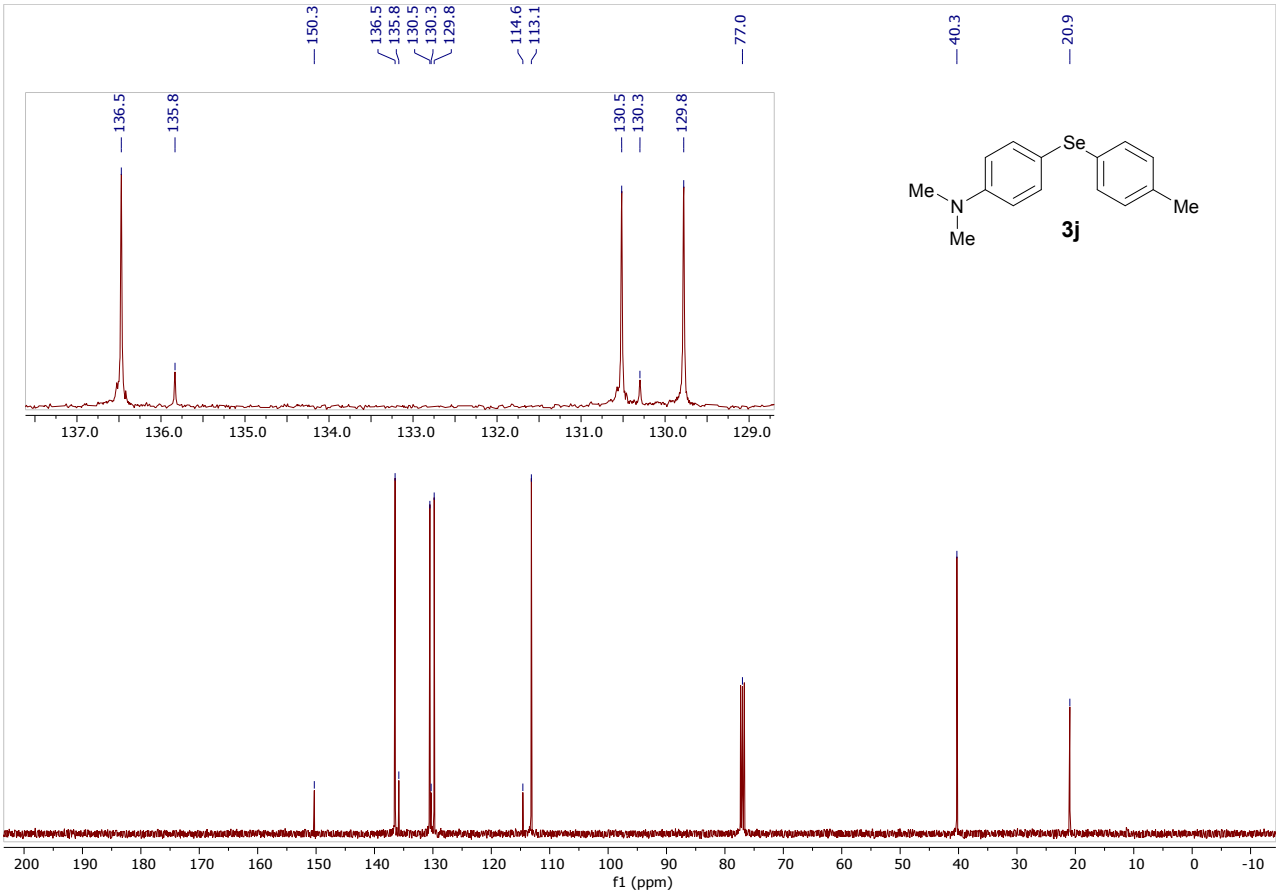
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3i**.



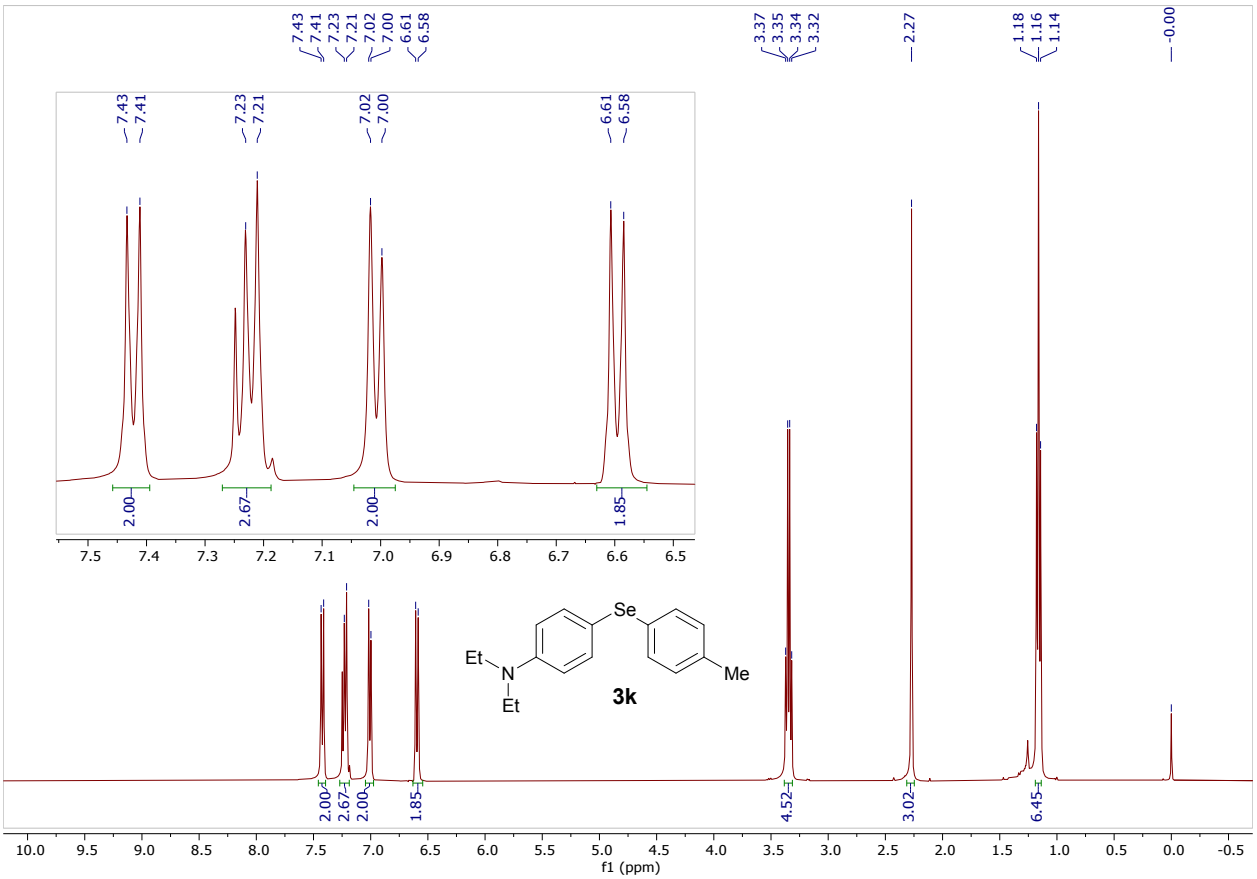
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3i**.



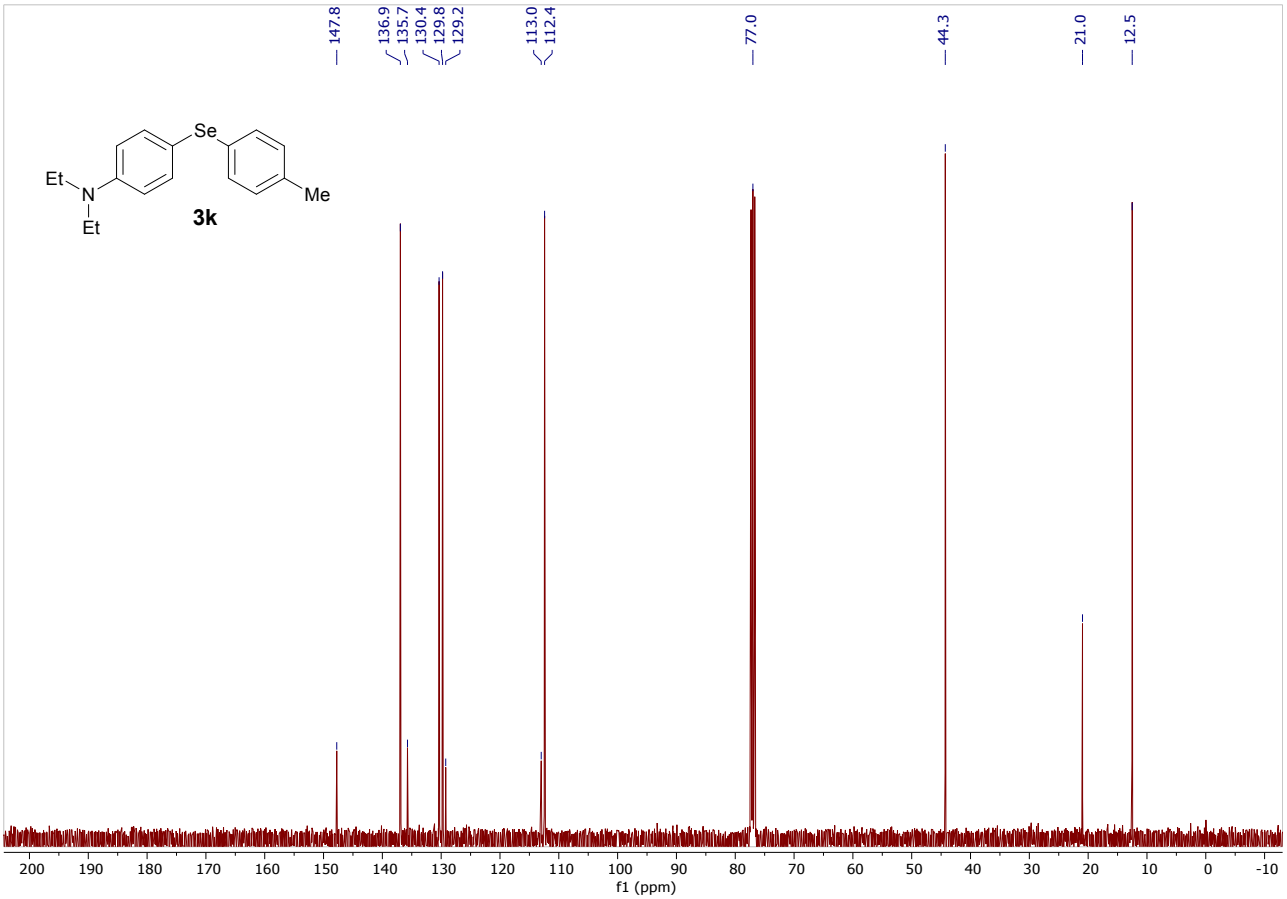
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3j**.



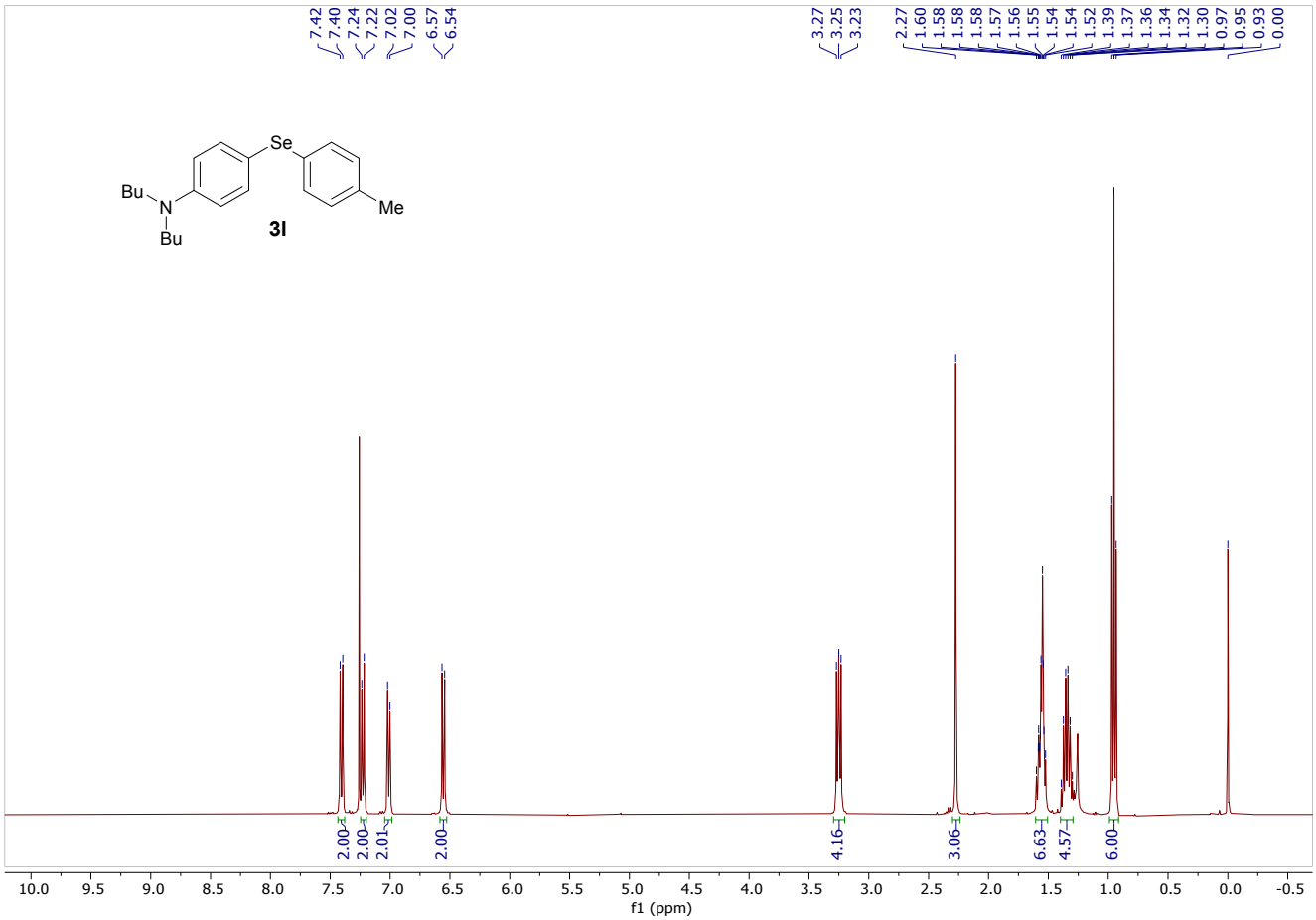
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3j**.



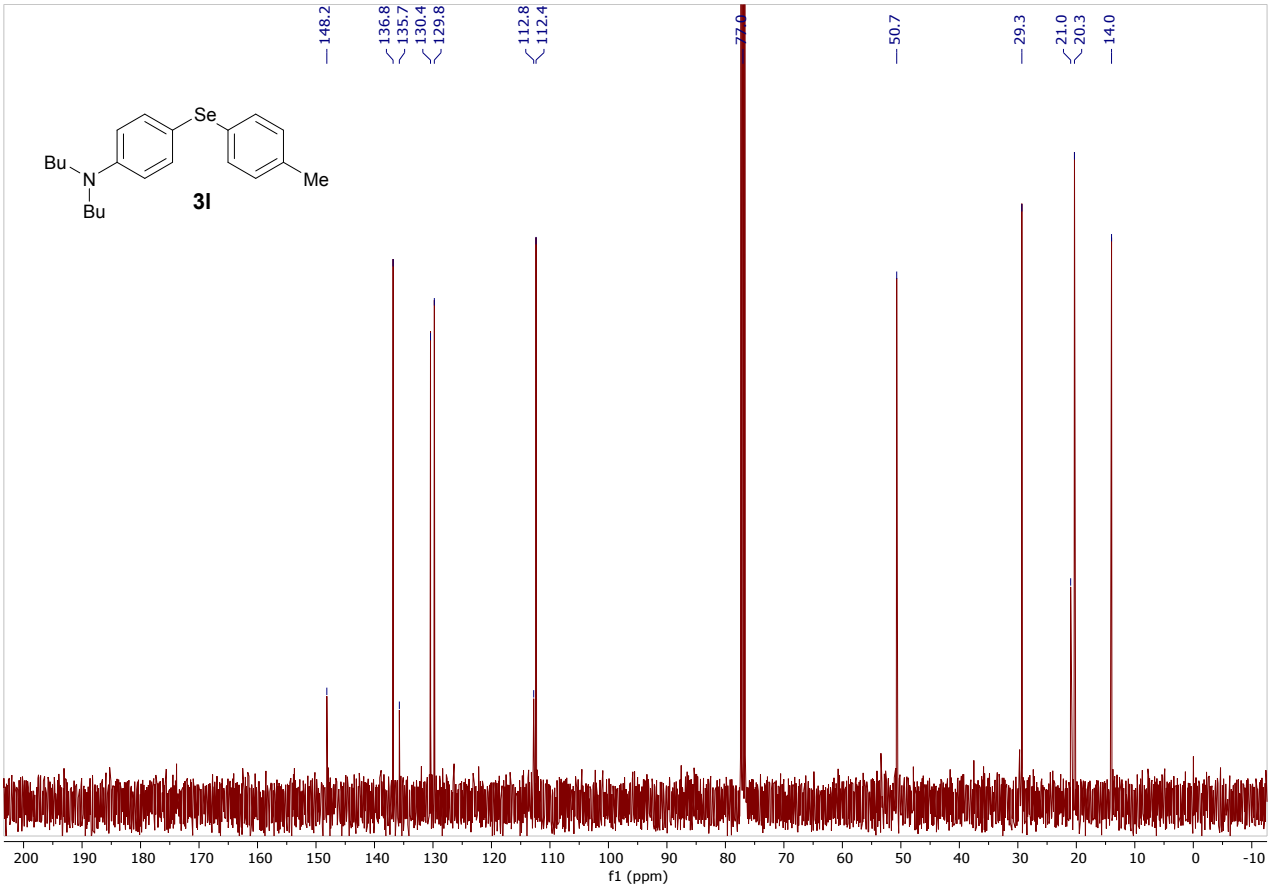
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3k**.



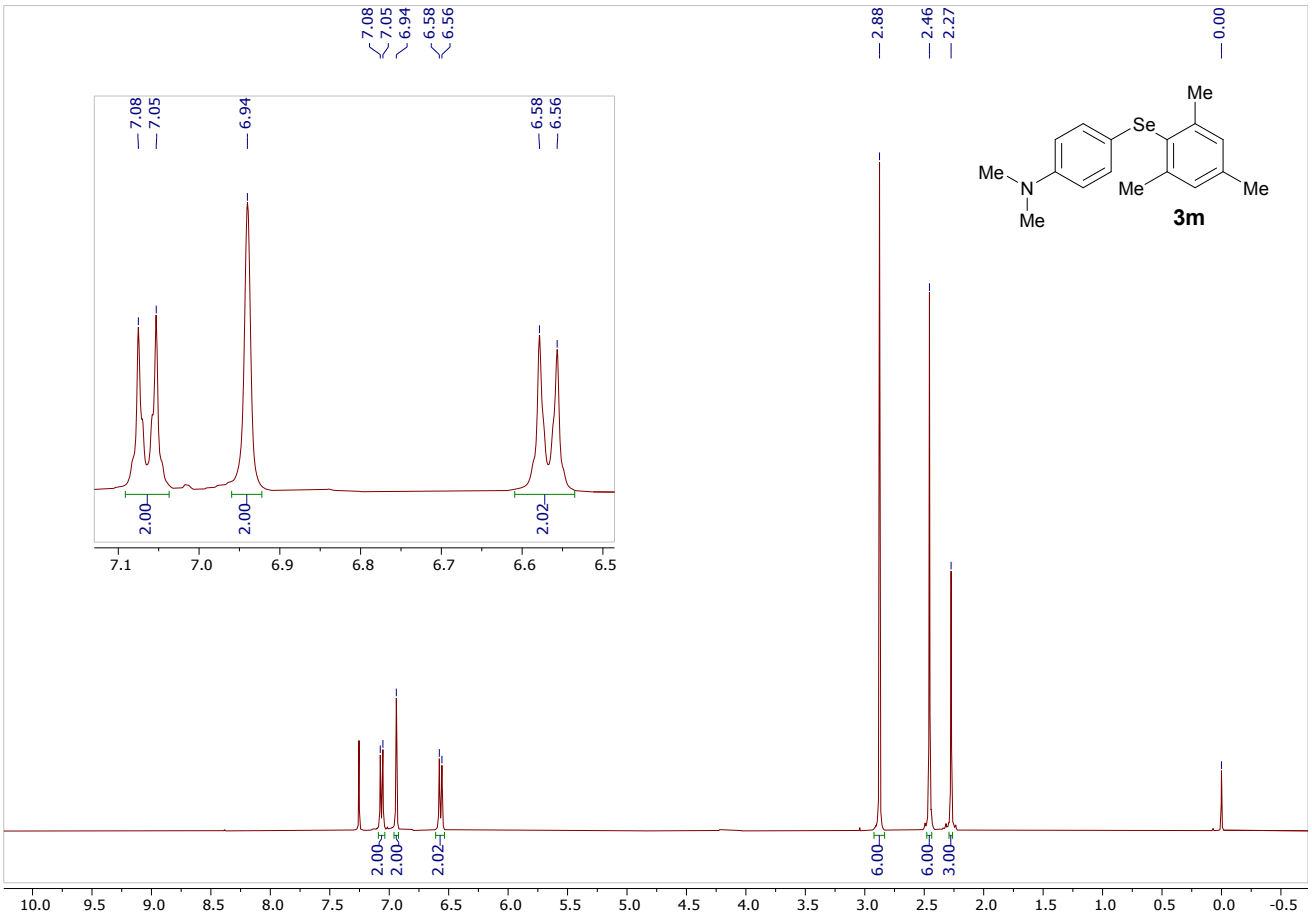
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3k**.



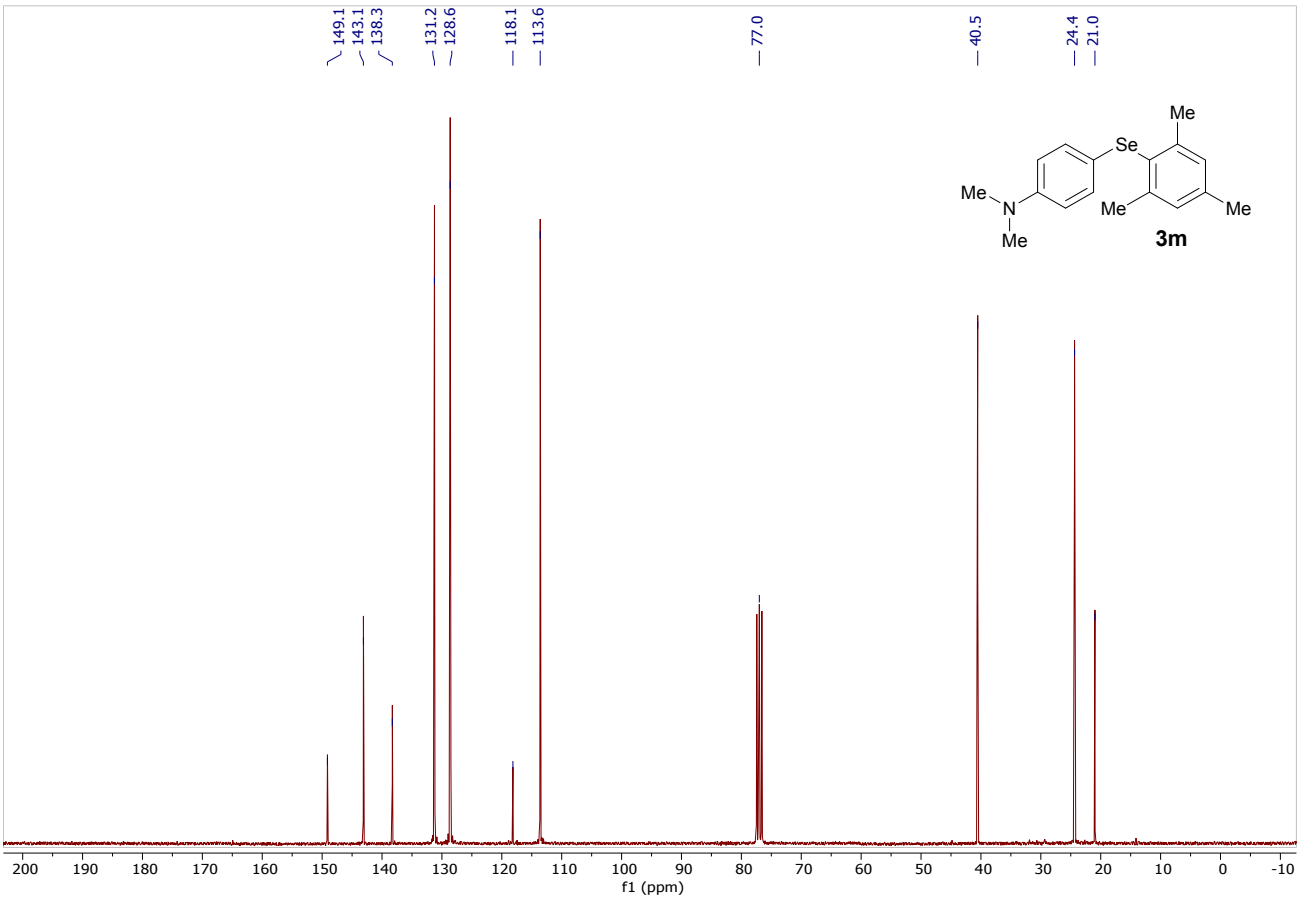
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3l**.



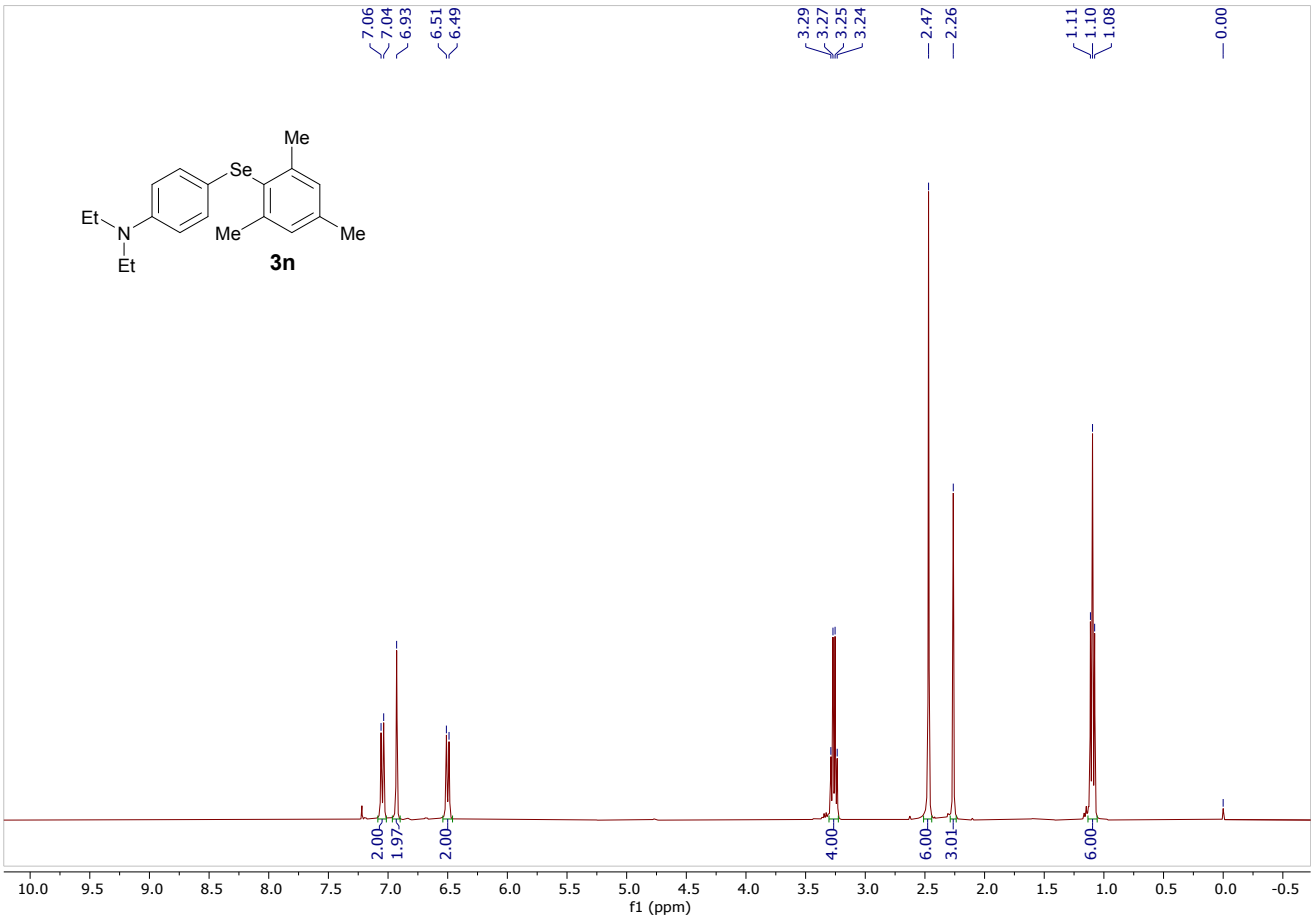
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3l**.



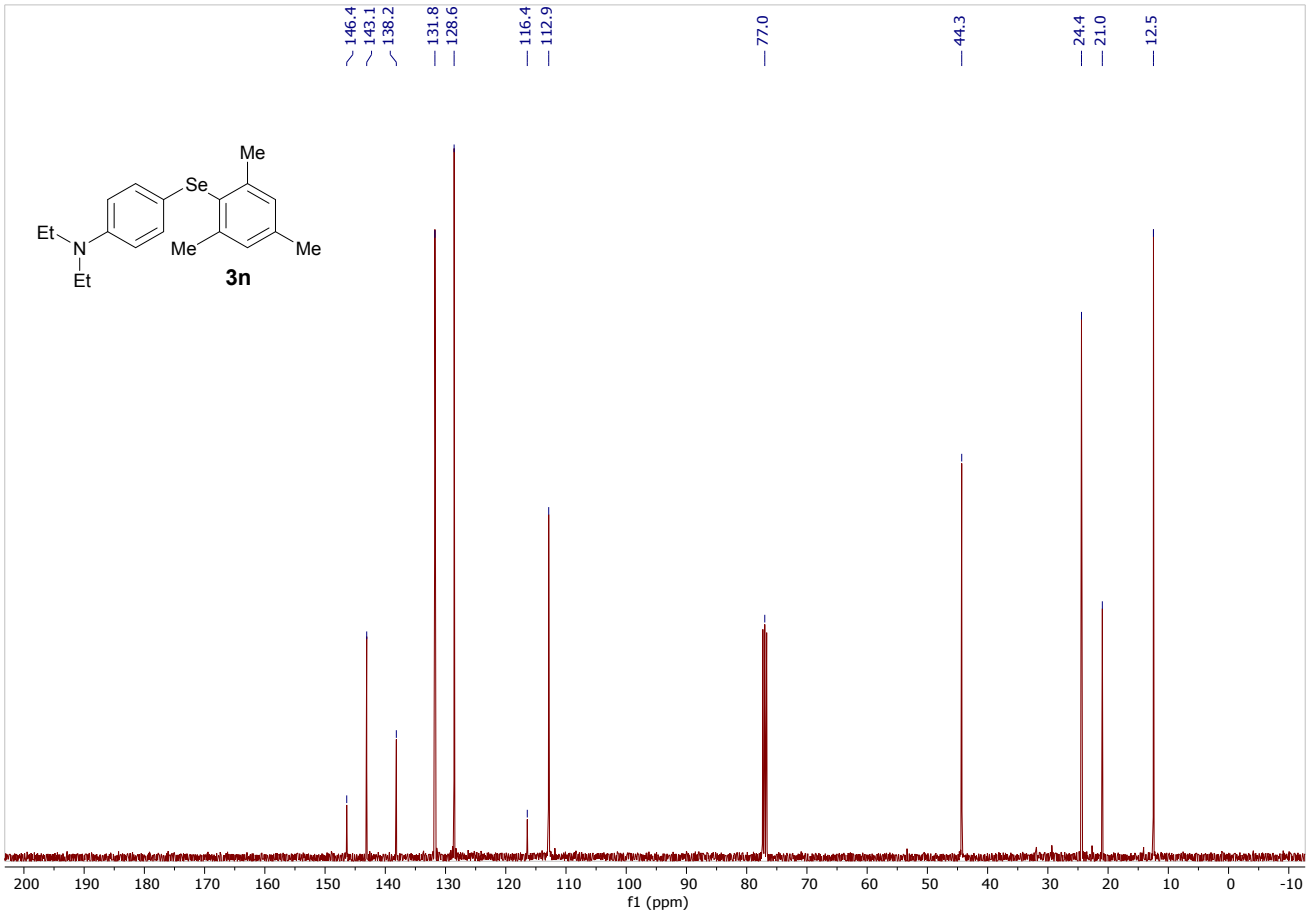
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3m**.



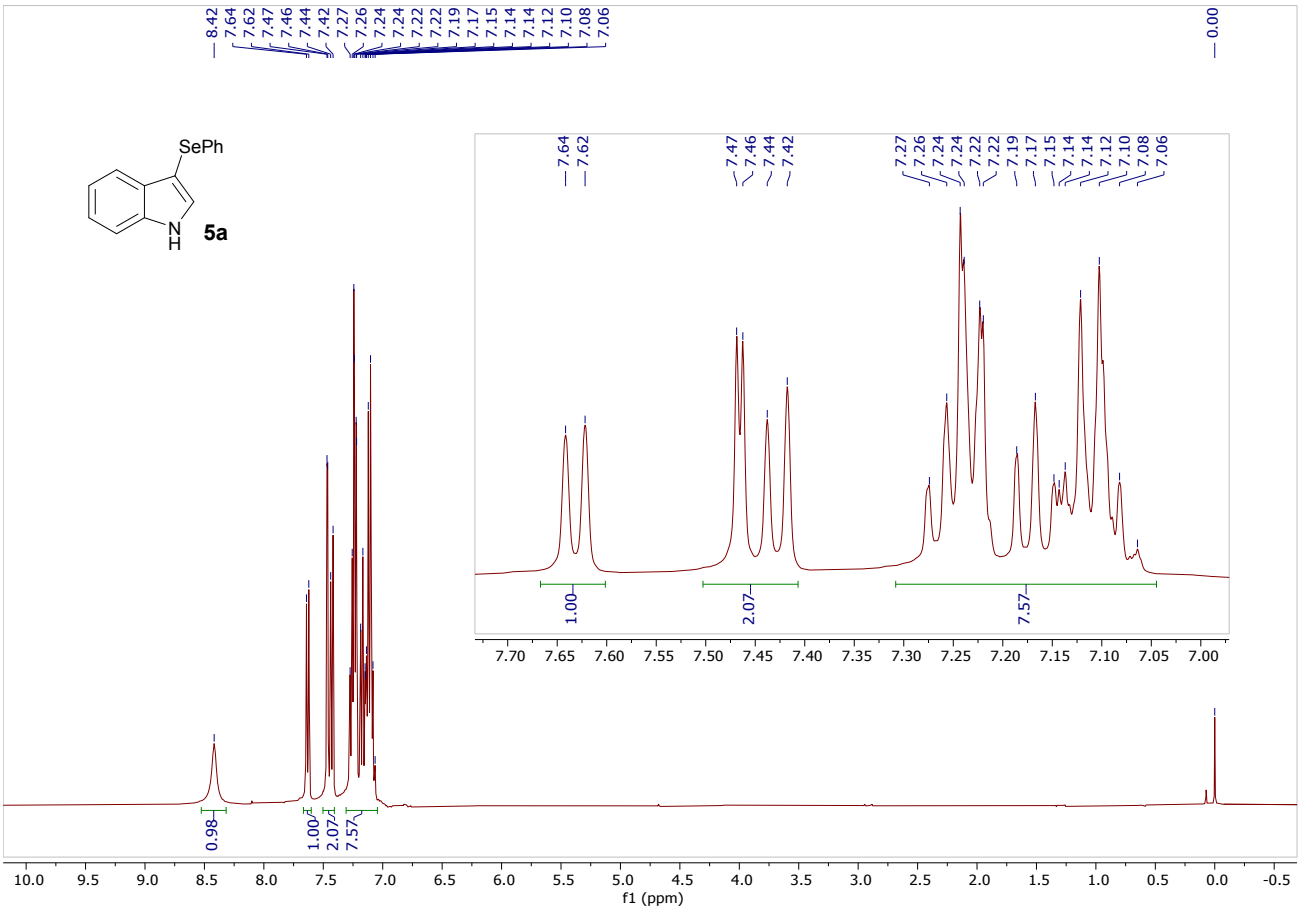
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3m**.



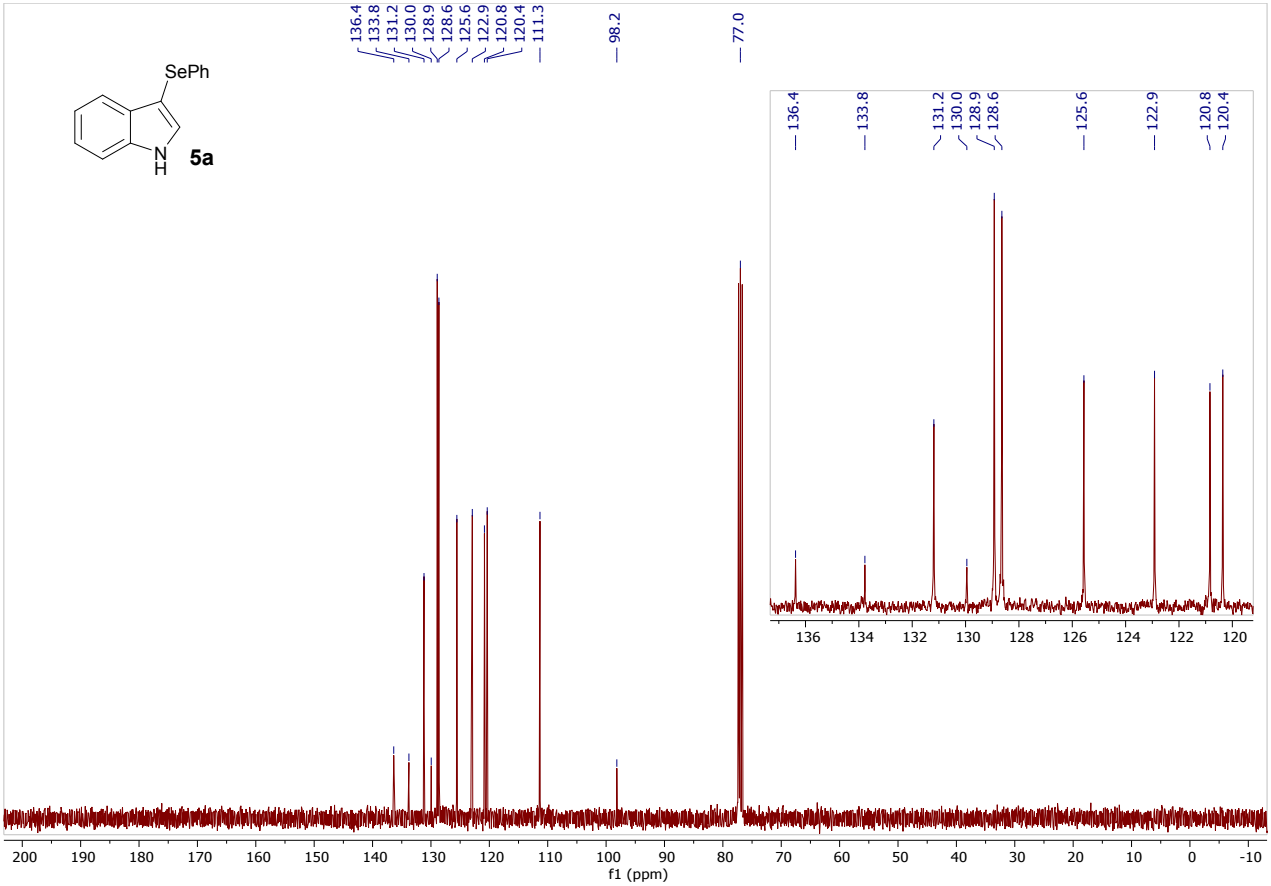
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **3n**.



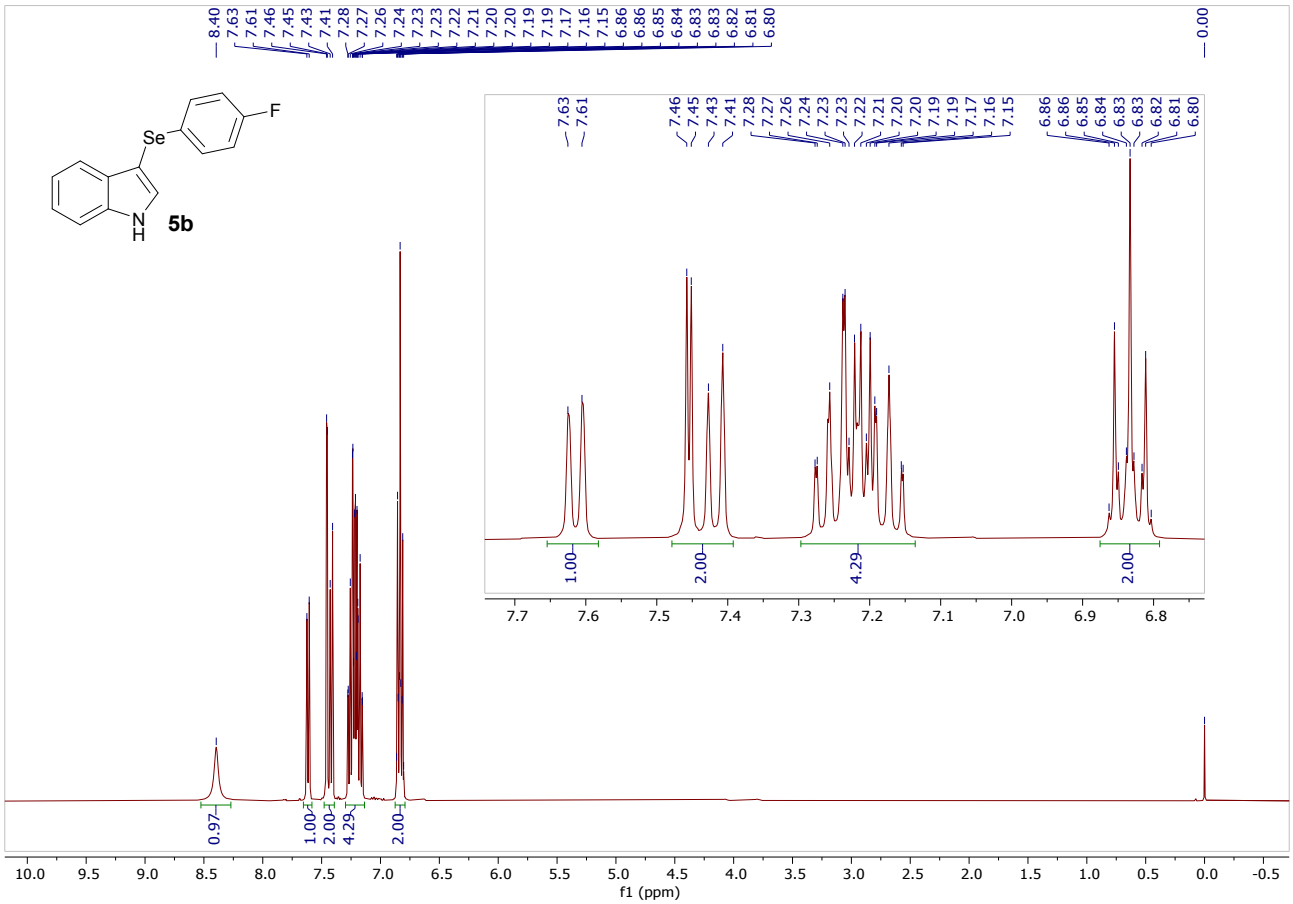
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **3n**.



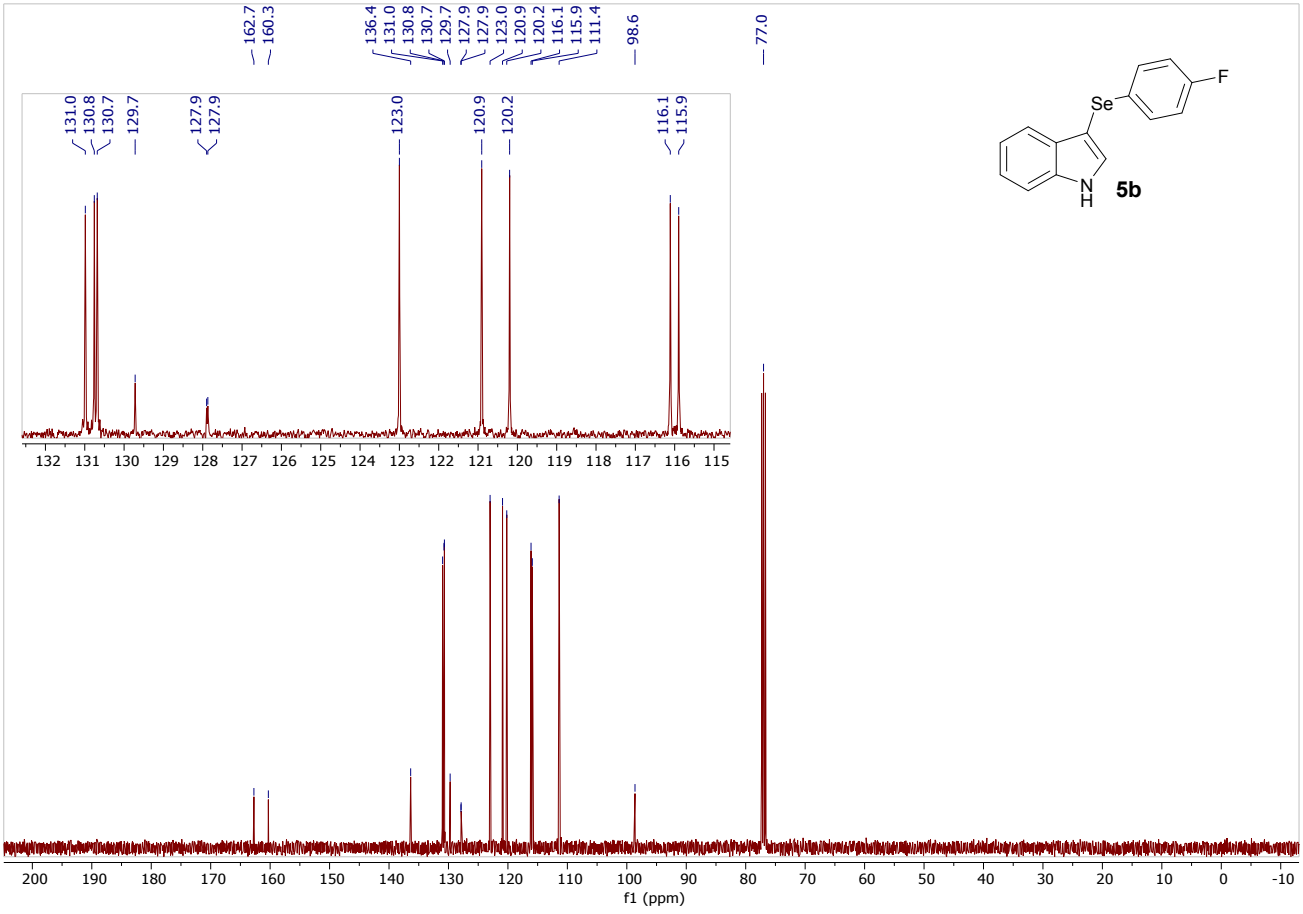
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **5a**.



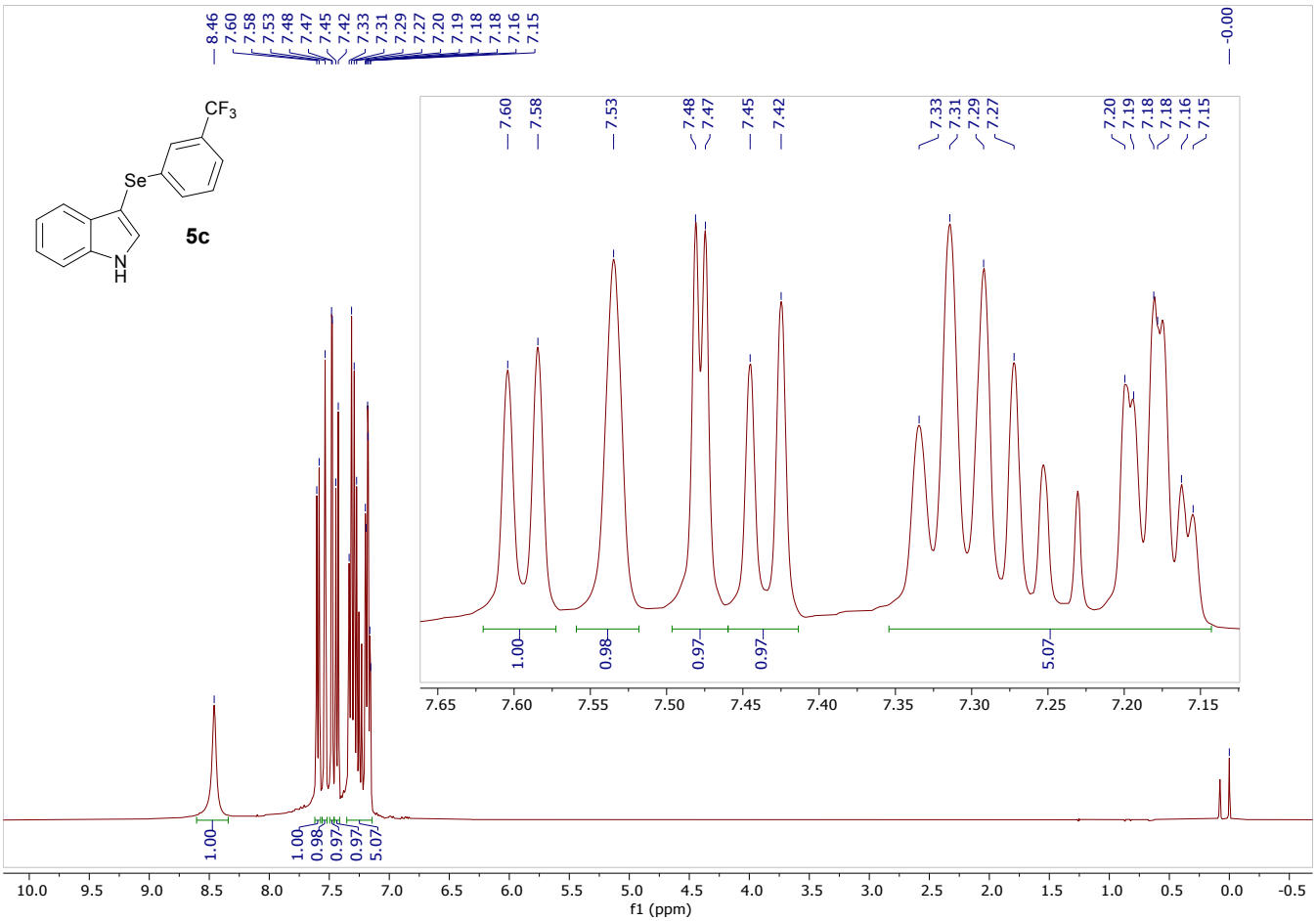
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **5a**.



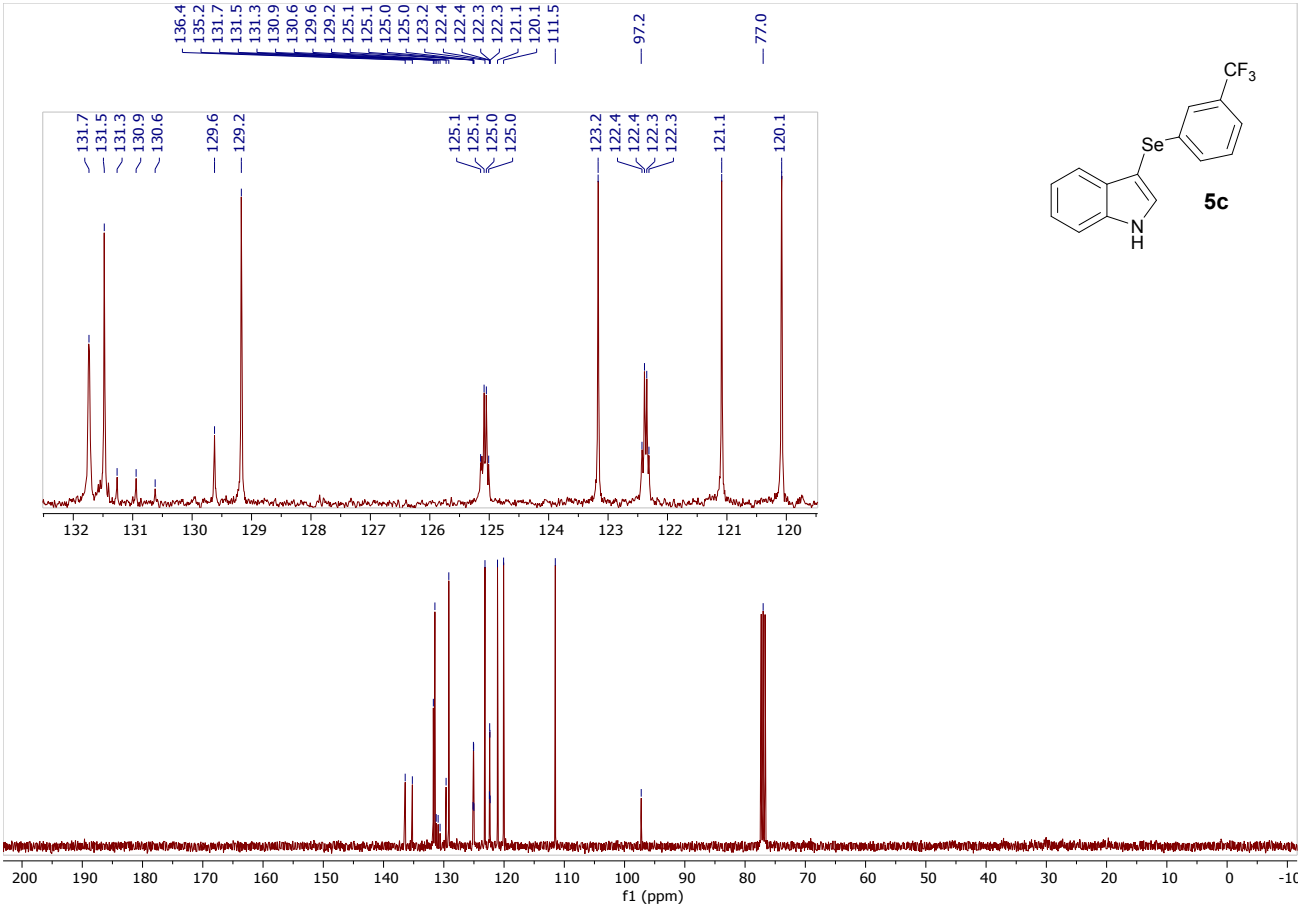
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **5b**.



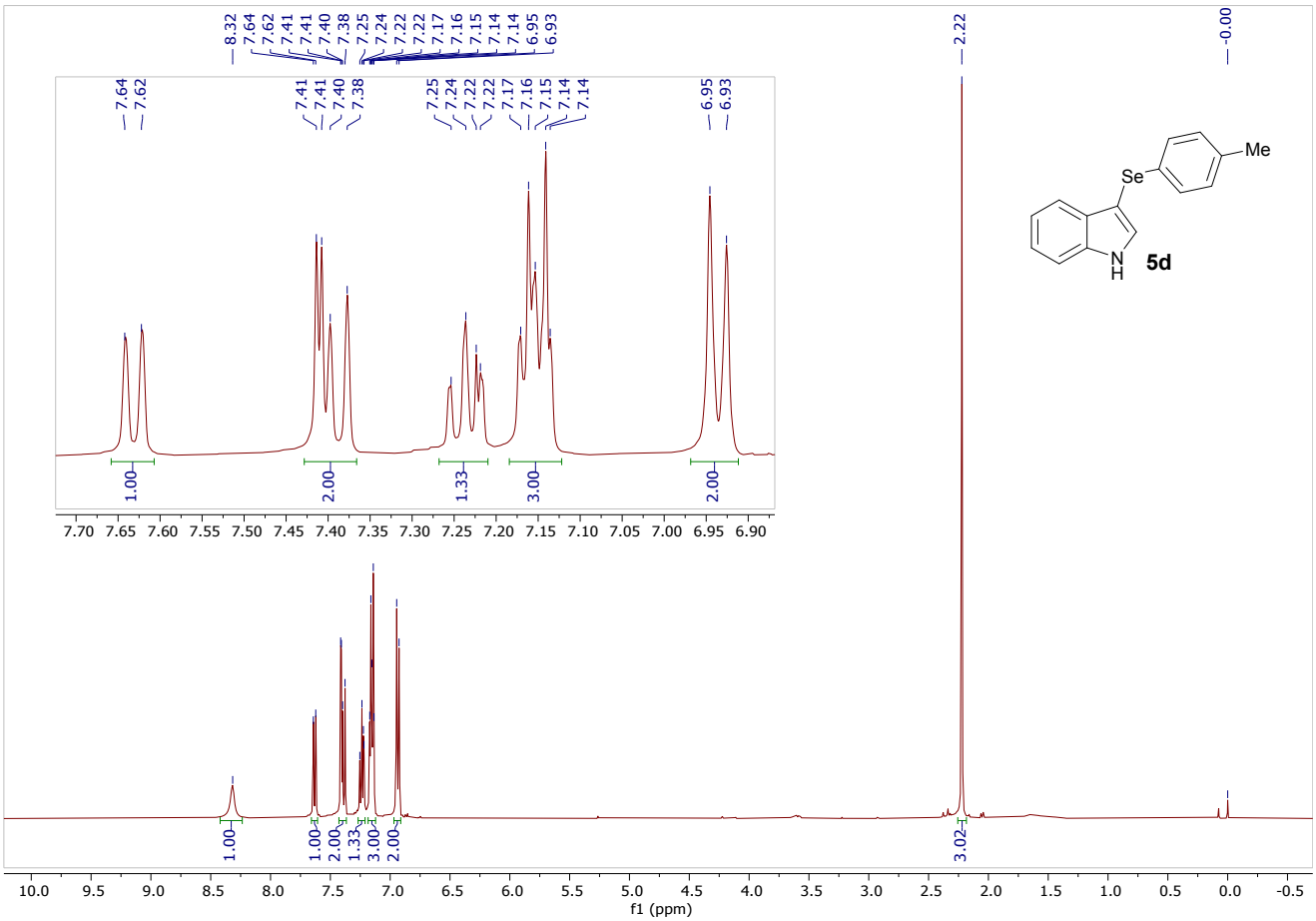
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **5b**.



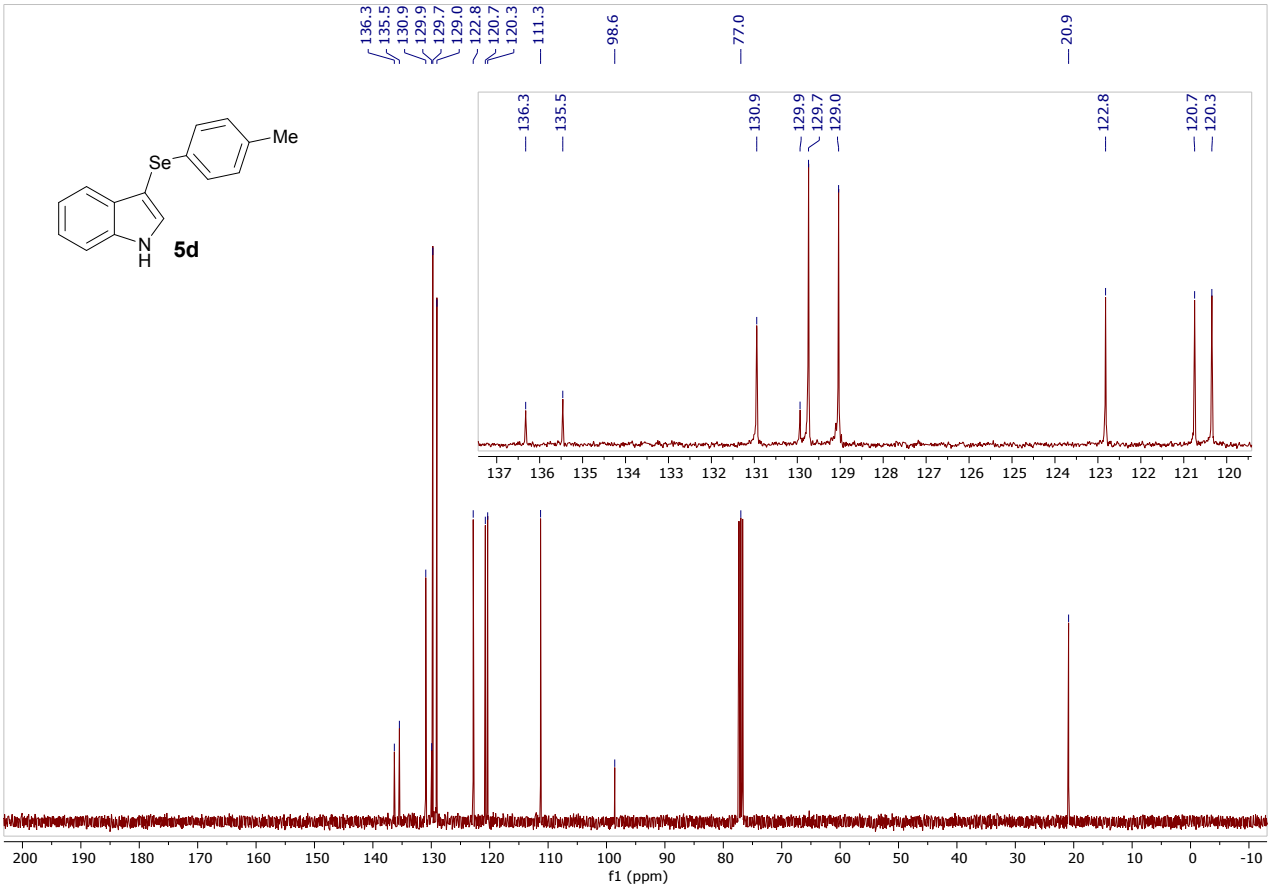
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **5c**.



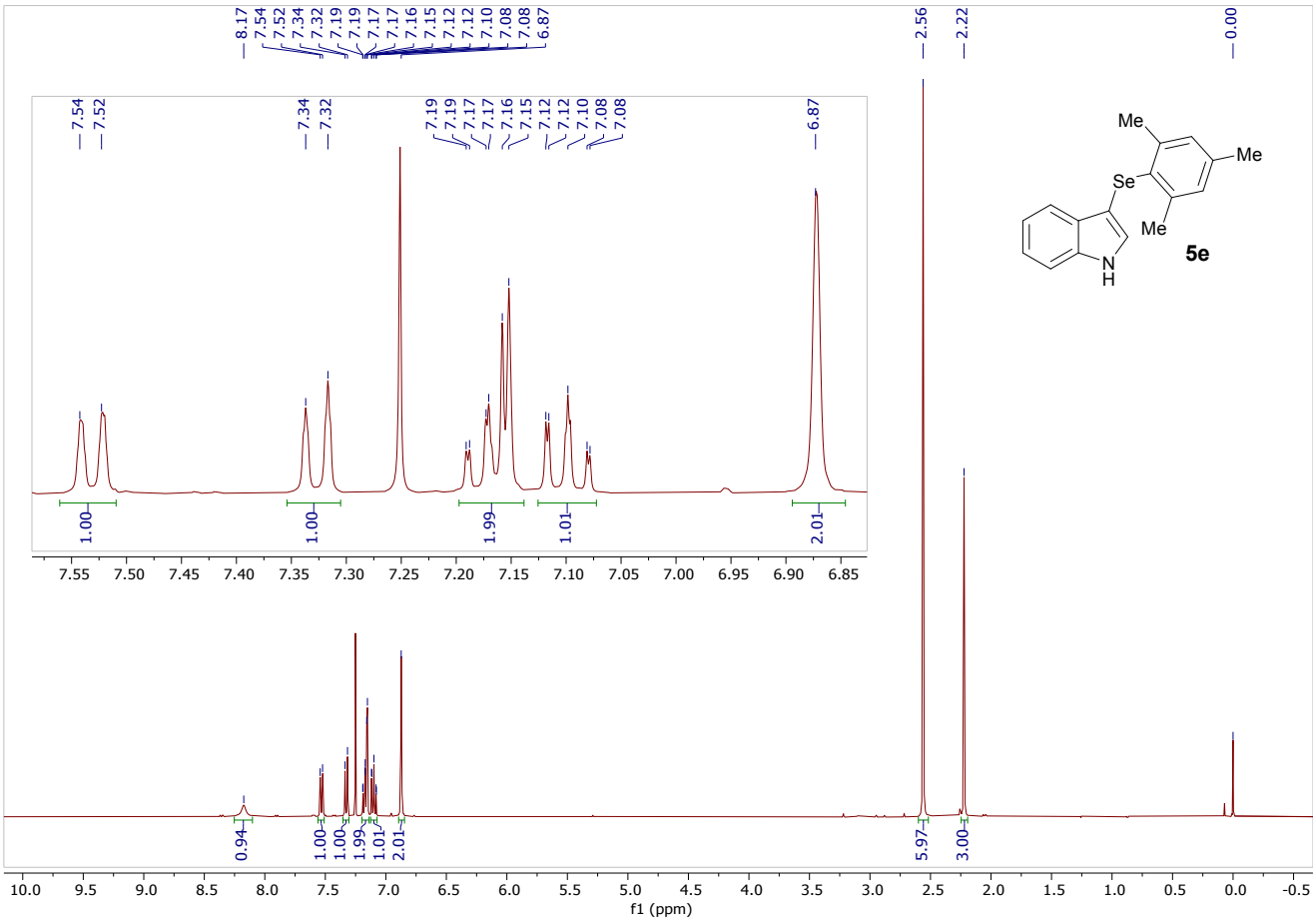
^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **5c**.



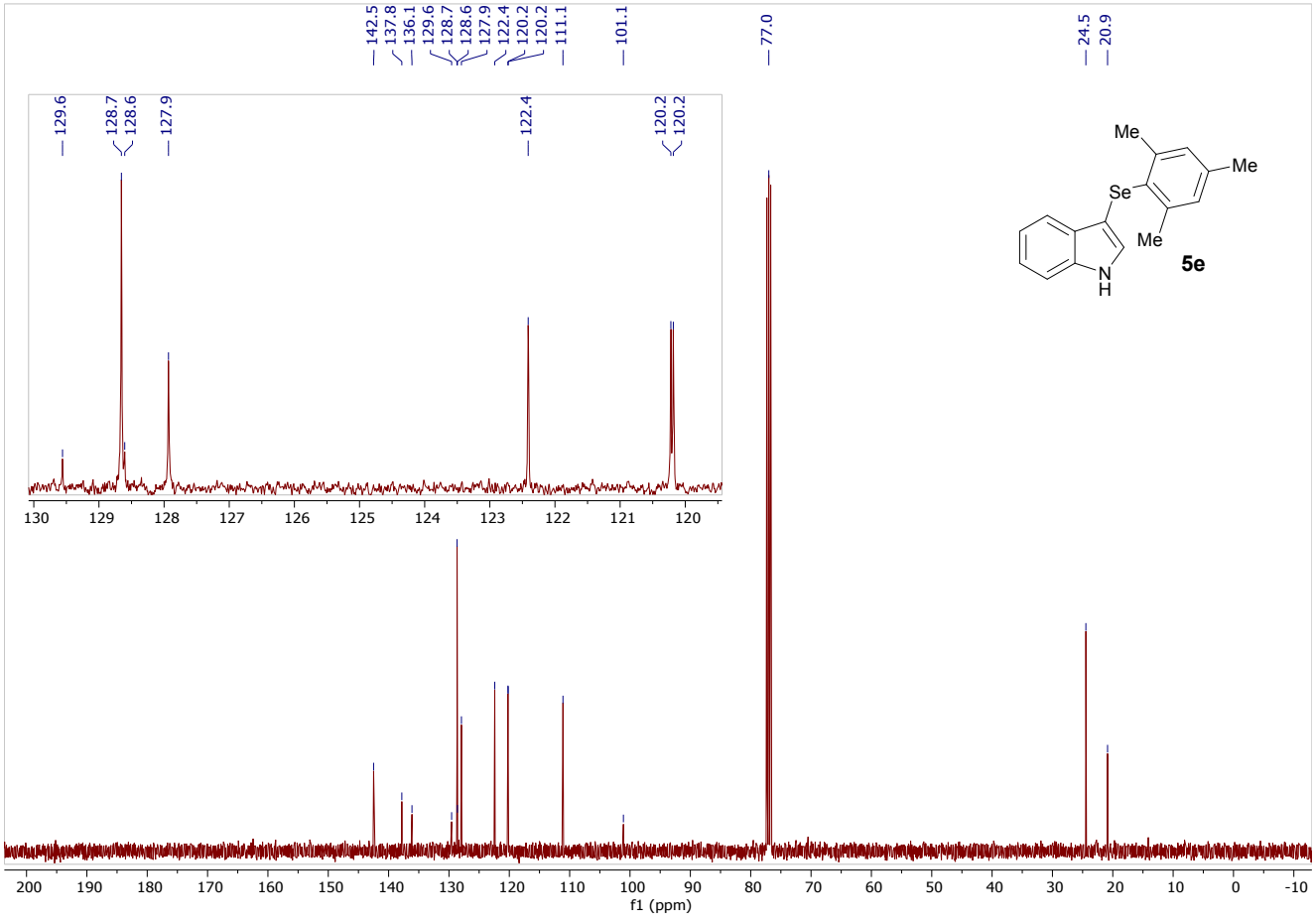
^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **5d**.



^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **5d**.



^{1}H NMR ($CDCl_3$, 400 MHz) of the compound **5e**.



^{13}C NMR ($CDCl_3$, 100 MHz) of the compound **5e**.