Supporting Information

Green Synthesis of selenol esters from diorganyl diselenides and acyl chlorides under solvent-free conditions and microwave irradiation

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Table of Contents

Materials and Methods

Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 400 MHz or 200 MHz. Spectra were recorded in $CDCl_3$ solutions. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant *(J)* in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHz or 75 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to the TMS (^{1}H NMR) and to the solvent (^{13}C NMR). Thin layer chromatography (TLC) was performed using Merck Silica Gel GF_{254}, 0.25 mm thickness. Most reactions were monitored by TLC for disappearance of starting material. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin.

All reactions under microwave irradiation were performed in 10 mL sealed tube in a commercially available monomode reactor (CEM Discover) with IR monitoring and non-invasive pressure transducer.

General procedure for the synthesis of selenol esters under microwave irradiation

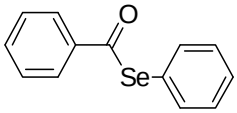
Acyl chloride (0.5 mmol) and Zn dust (0.25 mmol) were placed into a dry tube followed by diorganyl chalcogenide **(**0.25 mmol). The tube was sealed and placed into a CEM Discover microwave apparatus. Initially, an irradiation power of 100 W was applied. After the temperature reached 80 °C, the instrument was automatically adjusted to maintain a constant temperature. After stirring for 2 min the reaction was quenched with water and the aqueous layer was extracted with ethyl acetate. The organic phase was dried over $MgSO_4$, filtered, and the solvent and volatiles were completely removed under vacuum to give the crude product. Purification by either crystallization with a mixture of hexane/ethyl acetate or flash chromatography on silica eluting with a mixture of hexane/ethyl acetate (90:10) afforded the desired selenol ester.

General procedure for the synthesis of selenol esters under conventional heating

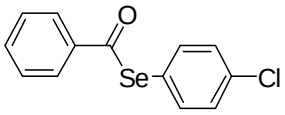
Acyl chloride (0.5 mmol) and Zn dust (0.25 mmol) were placed into a dry round flask, followed by diorganyl chalcogenide **(**0.25 mmol). The reaction was stirred at 80 °C in an oil bath for 90 min. The reaction was then cooled to room temperature, quenched with water and the aqueous layer was extracted with ethyl acetate. The organic phase was dried over $MgSO_4$, filtered, and the solvent and volatiles were completely removed under vacuum to give the crude product. Purification by crystallization with a mixture of hexane/ethyl acetate afforded the selenol ester.

General procedure for the synthesis of selenocarbonates under microwave irradiation

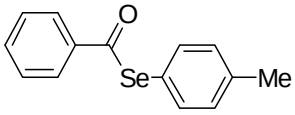
Alkyl carbonochloridate (0.5 mmol) and Zn dust (0.25 mmol) were placed into a dry tube followed by phenyl diselenide **(**0.25 mmol). The tube was sealed and placed into a CEM Discover microwave apparatus. Initially, an irradiation power of 100 W was applied. After the temperature reached 80 °C, the instrument was automatically adjusted to maintain a constant temperature. After stirring for 2 min the reaction was quenched with water and the aqueous layer was extracted with ethyl acetate. The organic phase was dried over $MgSO_4$, filtered, and the solvent and volatiles were completely removed under vacuum to give the crude product. Purification by either crystallization with a mixture of hexane/ethyl acetate or flash chromatography on silica eluting with a mixture of hexane/ethyl acetate (90:10) afforded the desired selenol ester.



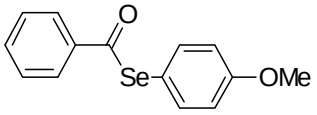
***Se*-phenyl selenobenzoate 3a:** Yield: 88%; yellow solid, mp 37.5-38.5 °C (lit.[1] 37-38 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.94 - 7.92 (m, 2H), 7.63 - 7.58 (m, 3H) 7.50 - 7.42 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 193.70; 138.90; 138.40; 136.70; 134.20; 129.70; 129.40; 129.30; 127.70; 126.10.



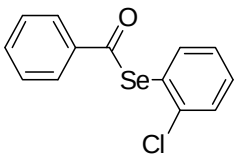
***Se*-4-chlorophenyl selenobenzoate 3b:** Yield: 90%; yellow solid, mp 84-85 °C (lit.[1] 84-85 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.91 - 7.89 (m, 5H); 7.61 - 7.59 (m, 2H); 7.50 - 7.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 192.45; 138.22; 137.91; 136.45; 133.73; 129.27; 128.67; 127.03; 123.61.



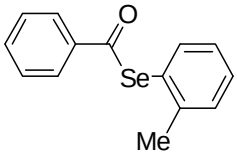
Se-4-tolyl selenobenzoate 3c: Yield: 66%; yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 - 7.80 (m, 2H), 7.54 - 7.38 (m, 5H), 7.18 (d, J= 8.0 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 192.7, 142.5, 138.6, 137.7, 133.7, 130.4, 129.8, 128.8, 127.2, 127.2, 126.5, 22.9.



Se-4-methoxyphenyl selenobenzoate 3d: Yield: 61%; White solid; mp 61-62 °C (lit.[1] 60-62 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.93 - 7.90 (m, 2H); 7.59 - 7.37 (m, 3H); 6.96 - 6.94 (m, 2H); 6.80 - 6.78 (m, 2H); 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.25; 160.45; 137.84; 135.42; 134.57; 133.78; 128.90; 127.30; 114.30; 55.77.

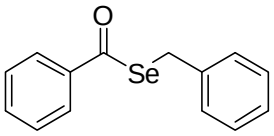


***Se*-2-chlorophenyl selenobenzoate 3e:** Yield: 92%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.93 - 7.24 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.47; 138.75; 137.84; 133.62; 130.82; 130.35; 129.90; 129.38; 129.18; 128.98; 127.40.

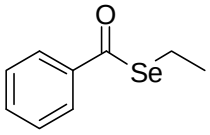


***Se-o*-tolyl selenobenzoate 3f:** Yield: 70%; yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 - 7.80 (m, 2H); 7.50 - 7.20 (m, 7H); 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 192.77; 142.54; 138.63; 137.75; 133.70; 130.40; 129.82; 128.83; 127.29; 127.20; 126.57; 22.91.

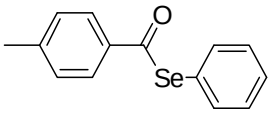
[1] G. Marin, A. L. Braga, A. S. Rosa, F. Z. Galetto, R. A. Burrow, H. Gallardo and M. W. Paixao, *Tetrahedron*, 2009, **65** , 4614.



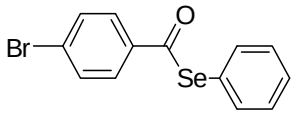
***Se*-benzyl selenobenzoate 3g:** Yield: 71%; yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87 - 7.84 (m, 2H); 7.49 - 7.32 (m, 3H); 7.24 - 7.17 (m, 5H); 4.30 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 194.50; 138.93; 138.71; 133.60; 128.94; 128.90; 128.72; 127.15; 126.92; 29.12.



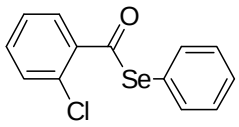
***Se*-ethyl selenobenzoate 3h:** Yield: 70%; brown liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.90 - 7.40 (m, 5H); 3.08 (q, 2H); 1.50 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 195.00; 138.88; 133.27; 130.20; 127.07; 19.45; 15.84.



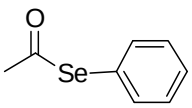
***Se*-phenyl 4-methylselenobenzoate 3i:** Yield: 80%; Light yellow solid; mp 92.5-93.5 °C (lit.[2] 93-94 °C).
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (d, J= 8.4 Hz, 2H), 7.58 – 7.55 (m, 2H), 7.38 - 7.36 (m, 3H), 7.20 (d, J= 8.0 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 192.4, 144.7, 136.1, 135.8, 129.4, 129.1, 128.7, 127.2, 125.8, 21.5.



***Se*- phenyl 4-bromoselenobenzoate 3j:** Yield: 96%; yellow solid; mp 54.5 °C (lit.[3] 55 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.81 (d, J= 8.7 Hz, 2H), 7.58 – 7.64 (d, J= 8.7 Hz, 2H), 7.61 - 7.57 (m, 3H), 7.46 - 7.43 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 192.53, 137.31, 136.28, 132.25, 129.46, 129.25, 128.98, 128.70, 125.40.

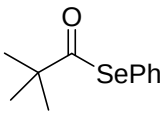


***Se*- phenyl 2-chlorobenzoselenoate 3l:** Yield: 64%; yellow solid; mp 59.5 °C (lit.[1] 59 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.65 - 7.59 (m, 4H); 7.37 - 7.18 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.19; 136.32; 135.70; 135.00; 132.30; 131.51; 130.90; 129.17; 128.61; 127.71; 126.50.

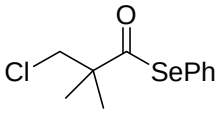


***Se*-phenyl ethaneselenoate 3m:** Yield: 86%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.54 – 7.25 (m, 5H); 2.46 (s, 3H).^{13}C NMR ($CDCl_3$, 50 MHz) δ = 196.4; 135.7; 131.4; 129.1; 127.7; 33.9.

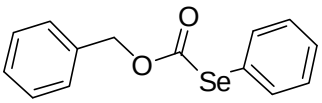
[2] H. Ishihara, N. Matsunami and Y. Yamada, *Synthesis* **1987**, 371.
[3] I. P. Beletskaya, A. S. Sigeev, A. S. Peregudov, and P. V. Petrovskii, *Russ. J. Org. Chem.*, 2001, **37**, 1703.



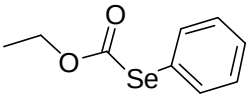
***Se*-phenyl 2,2-dimethylpropaneselenoate 3n:** Yield: 40%; brown oil, ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49 - 7.46 (m, 2H); 7.37 - 7.33 (m, 3H); 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 207.98; 136.48; 129.15; 128.81; 126.41; 50.03; 27.22.



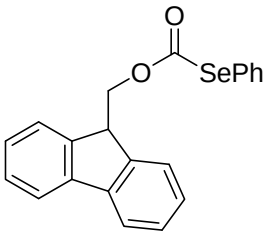
***Se*-phenyl 3-chloro-2,2-dimethylpropaneselenoate 3o:** Yield: 41%; yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49 - 7.35 (m, 5H); 3.64 (s, 2H); 1.38 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 204.84; 135.84; 128.90; 128.57; 125.23; 53.93; 51.03; 22.81.



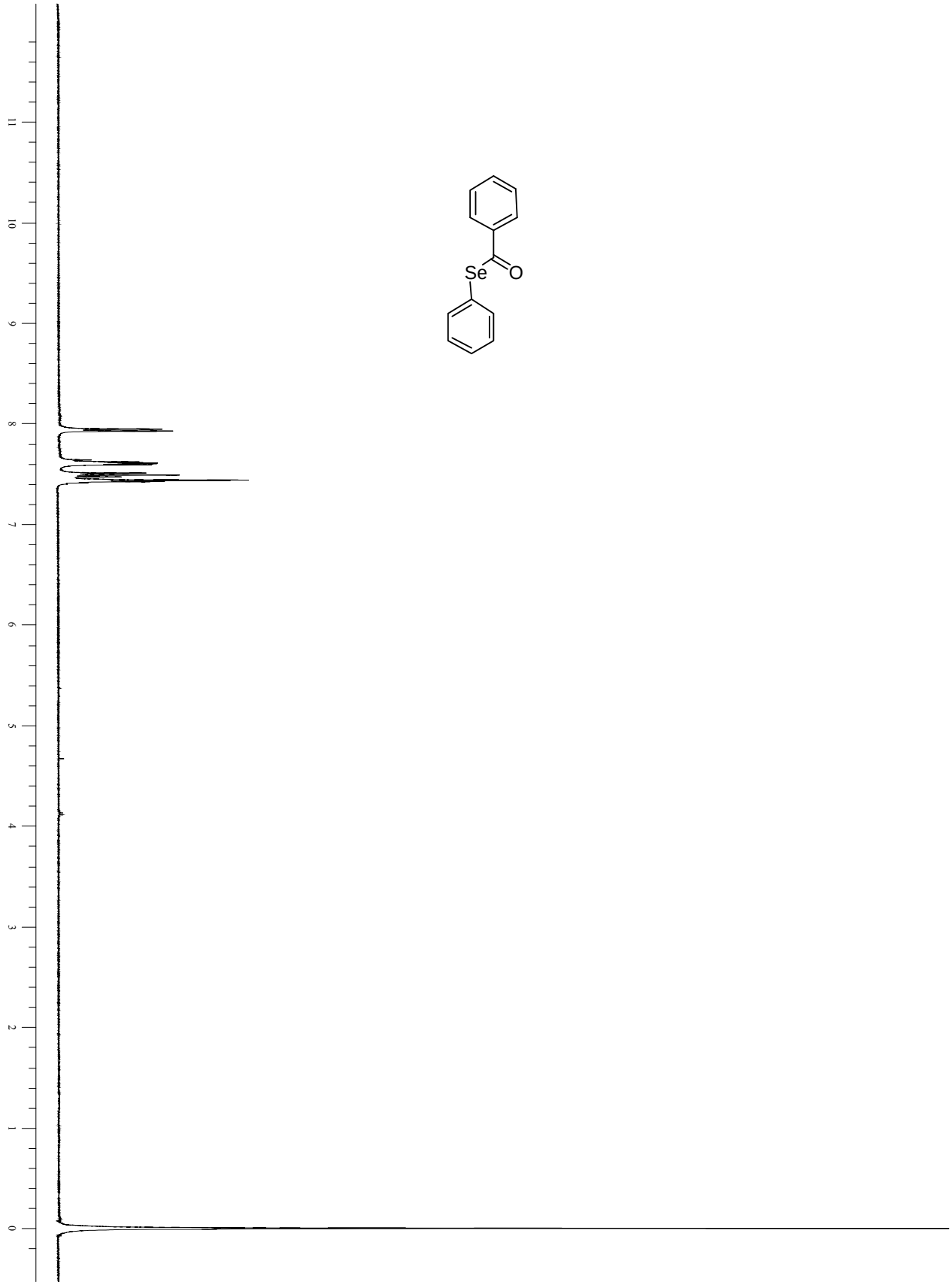
***O*-benzyl *Se*-phenyl carbonoselenoate 3p:** Yield: 62%; yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.63 - 7.28 (m, 5H); 4.29 (q, J = 7.0 Hz, 2H); 1.29 (t, J = 6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.73; 135.67; 131.40; 128.90; 125.70; 64.35; 14.25.



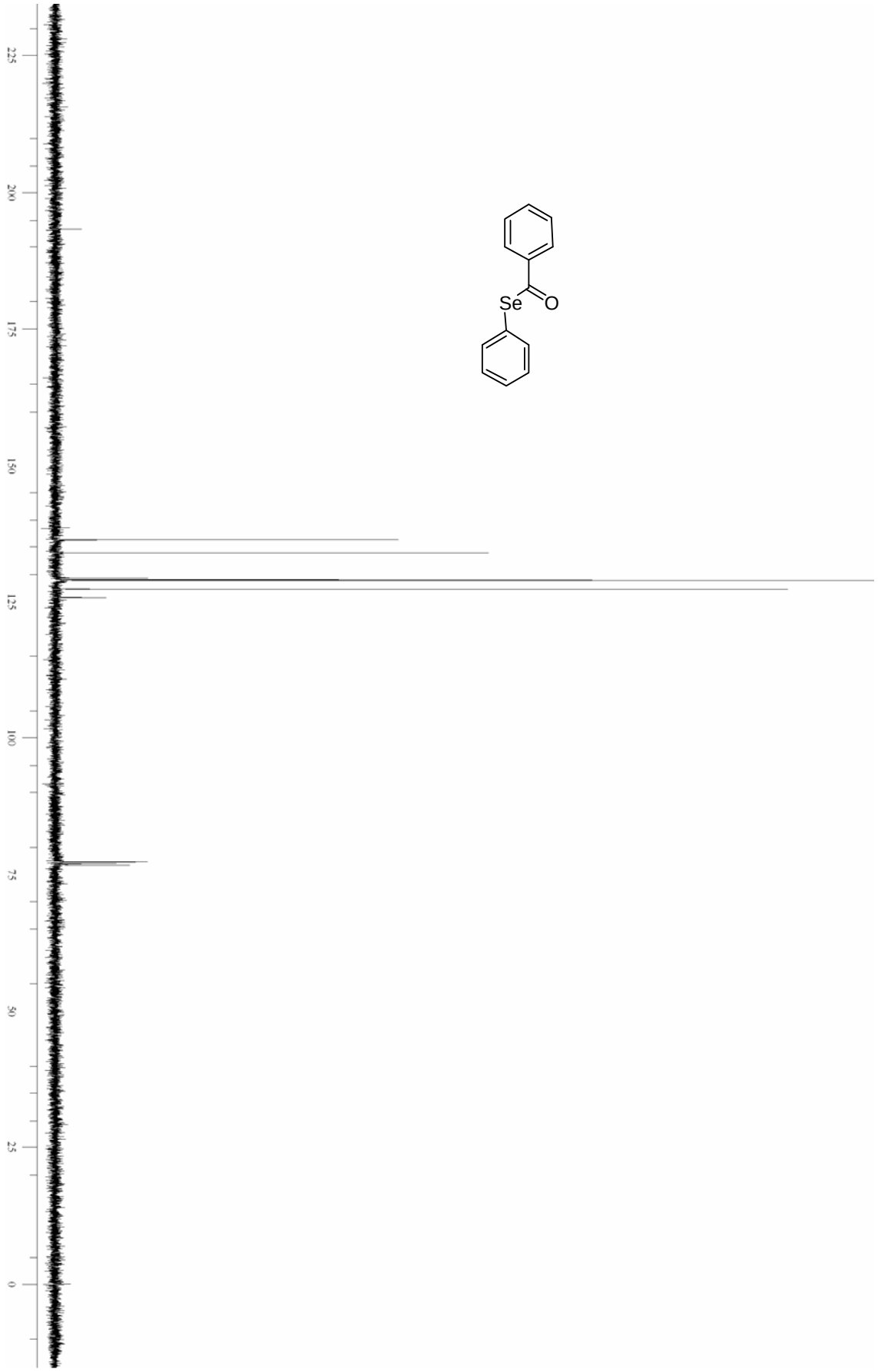
***O*-ethyl *Se*-phenyl carbonoselenoate 3q**: Yield: 53%; yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.63 - 7.28 (m, 5H); 4.29 (q, J = 7.0 Hz, 2H); 1.29 (t, J = 6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.73; 135.67; 131.40; 128.90; 125.70; 64.35; 14.25.



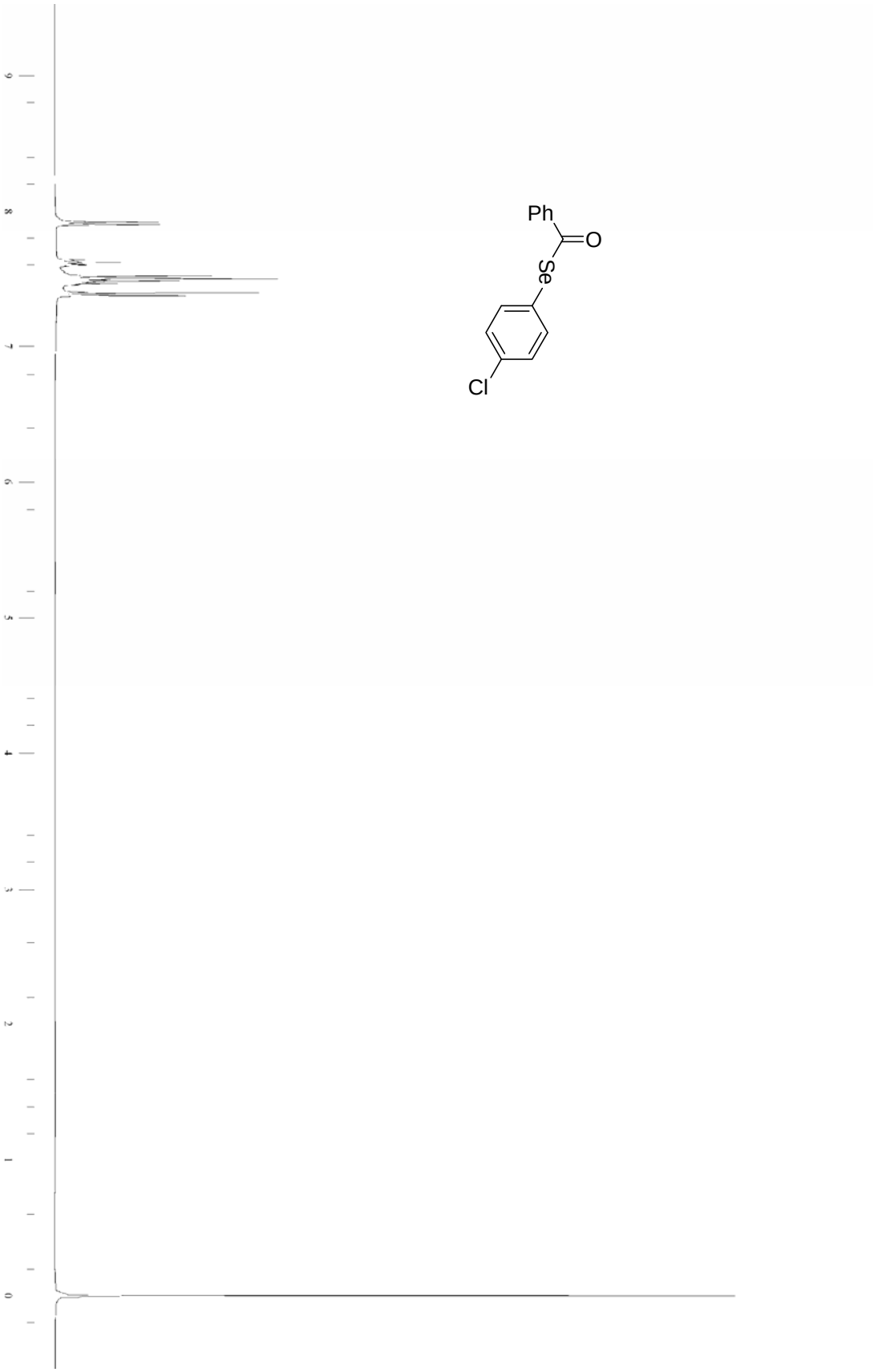
***O*-(9H-fluoren-9-yl)methyl *Se*-phenyl carbonoselenoate 3r:** Yield: 60%; yellow solid; mp 113.1-114.6°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78 - 7.26 (m, 13H); 4.53 (d, J = 7.6 Hz, 2H); 4.12 (t, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.50; 134.85; 129.30; 128.10; 127.44; 126.90; 124.92; 119.92; 64.99; 50.23.



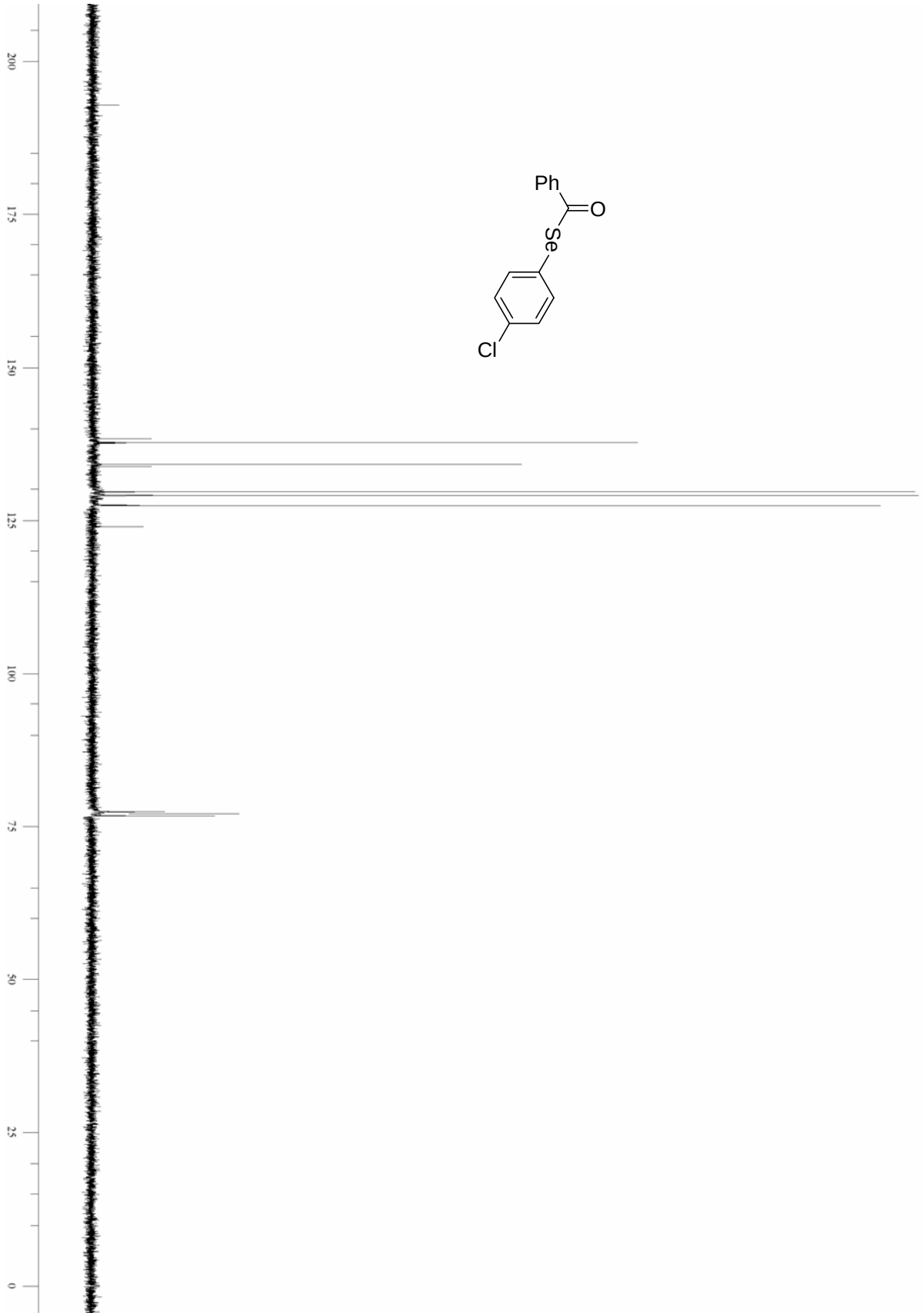
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Se-phenyl selenobenzoate **3a**.



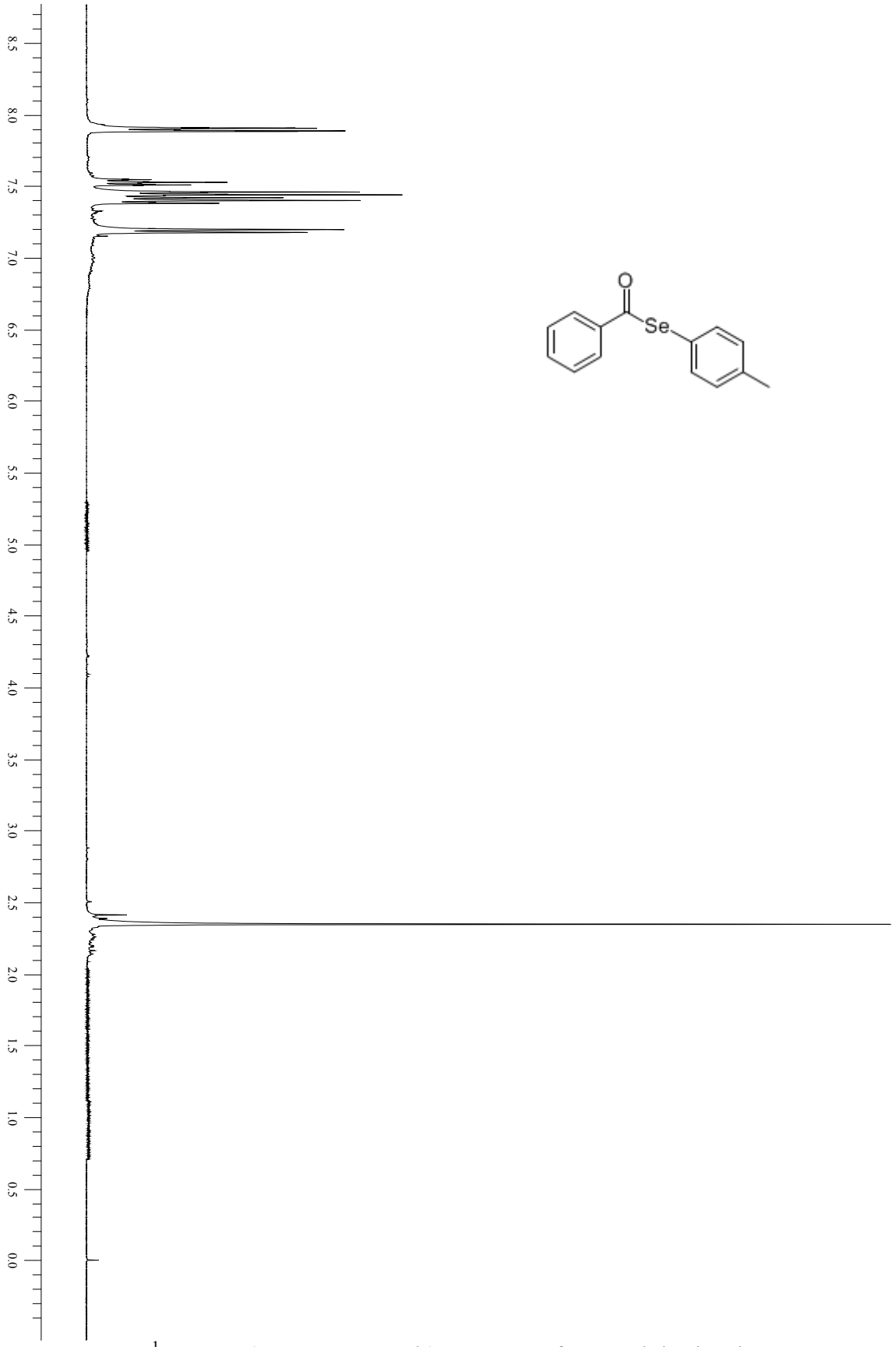
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *Se*-phenyl selenobenzoate **3a**



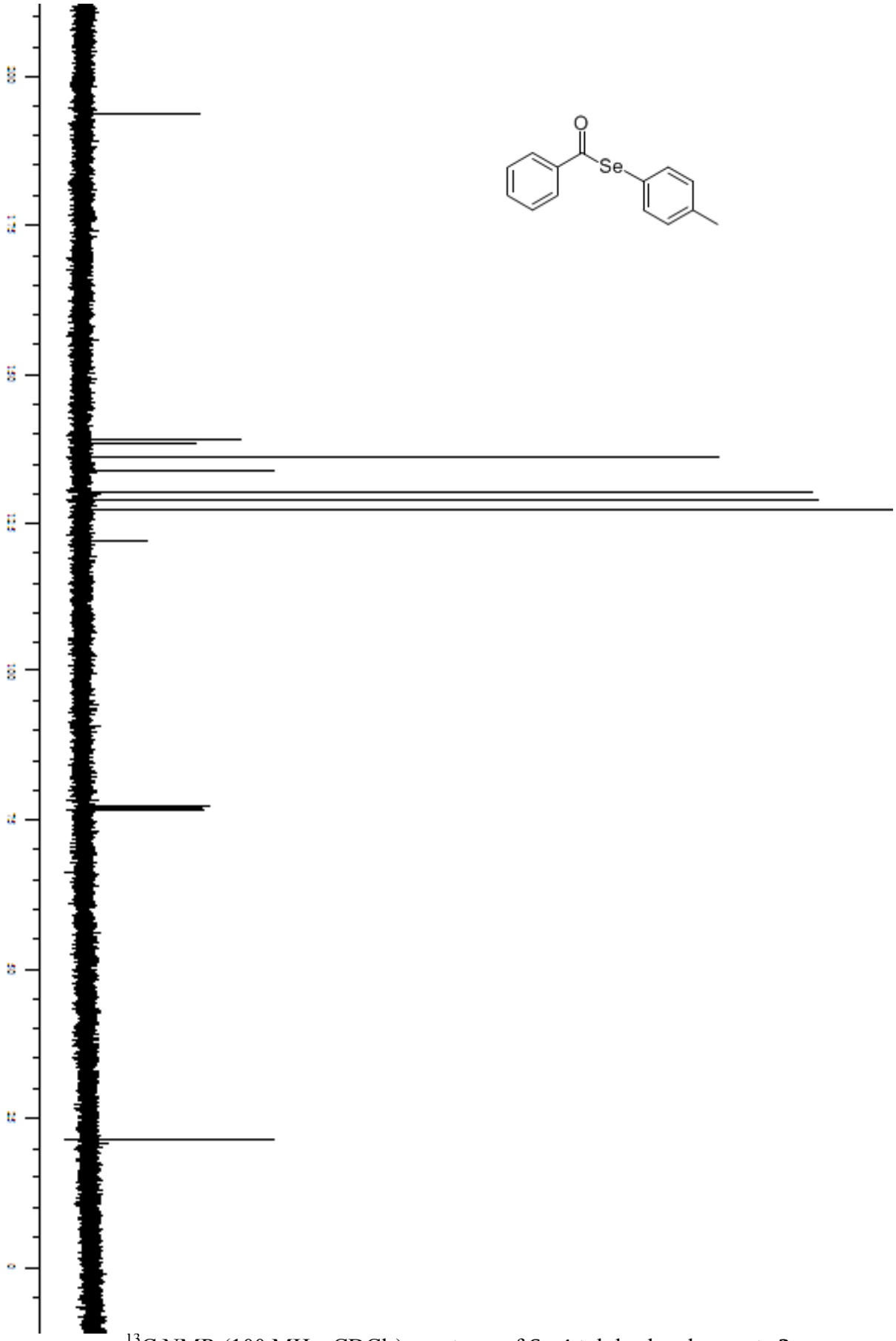
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *Se*-4-chlorophenyl selenobenzoate **3b**.



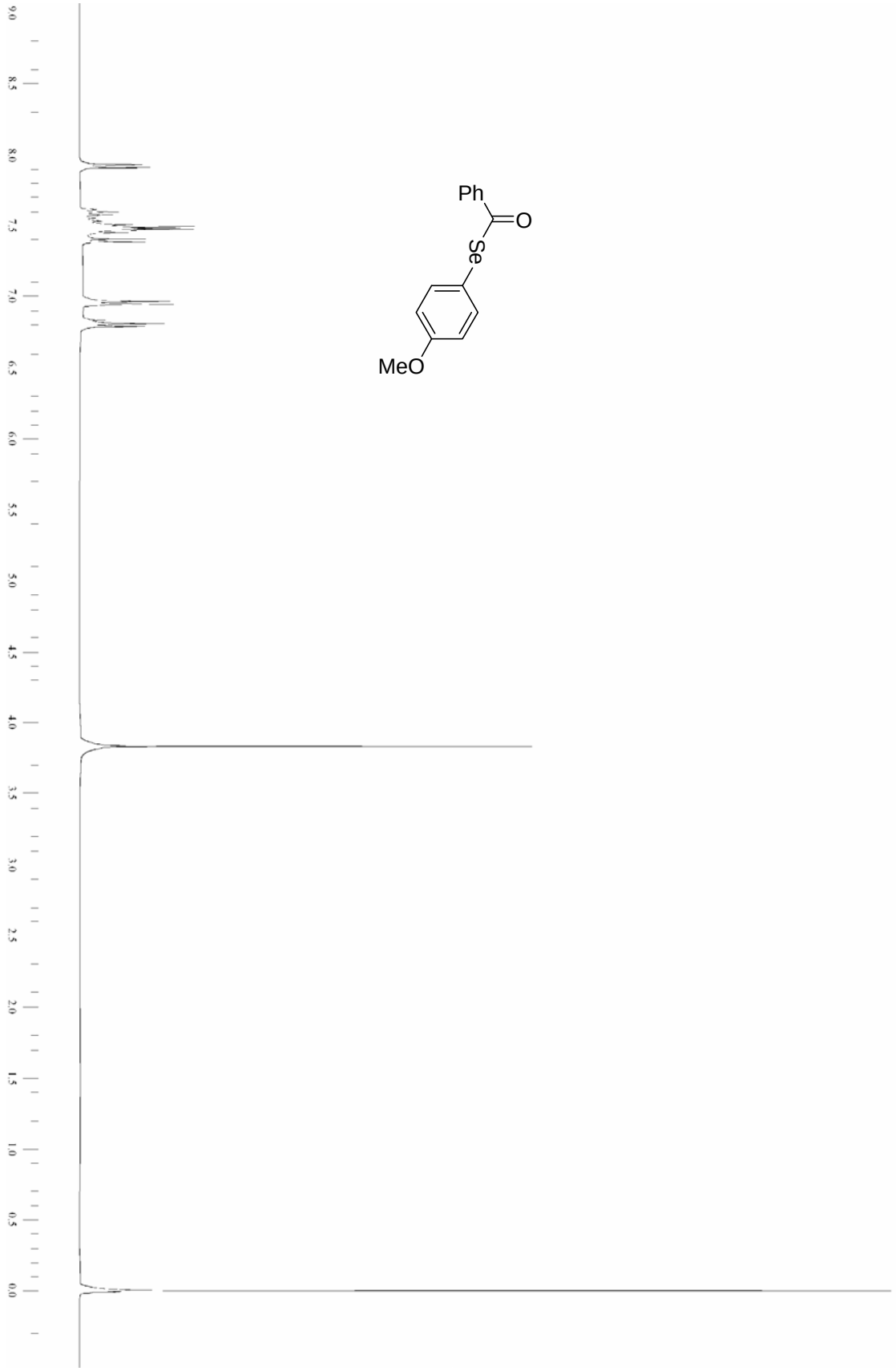
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *Se*-4-chlorophenyl selenobenzoate **3b**



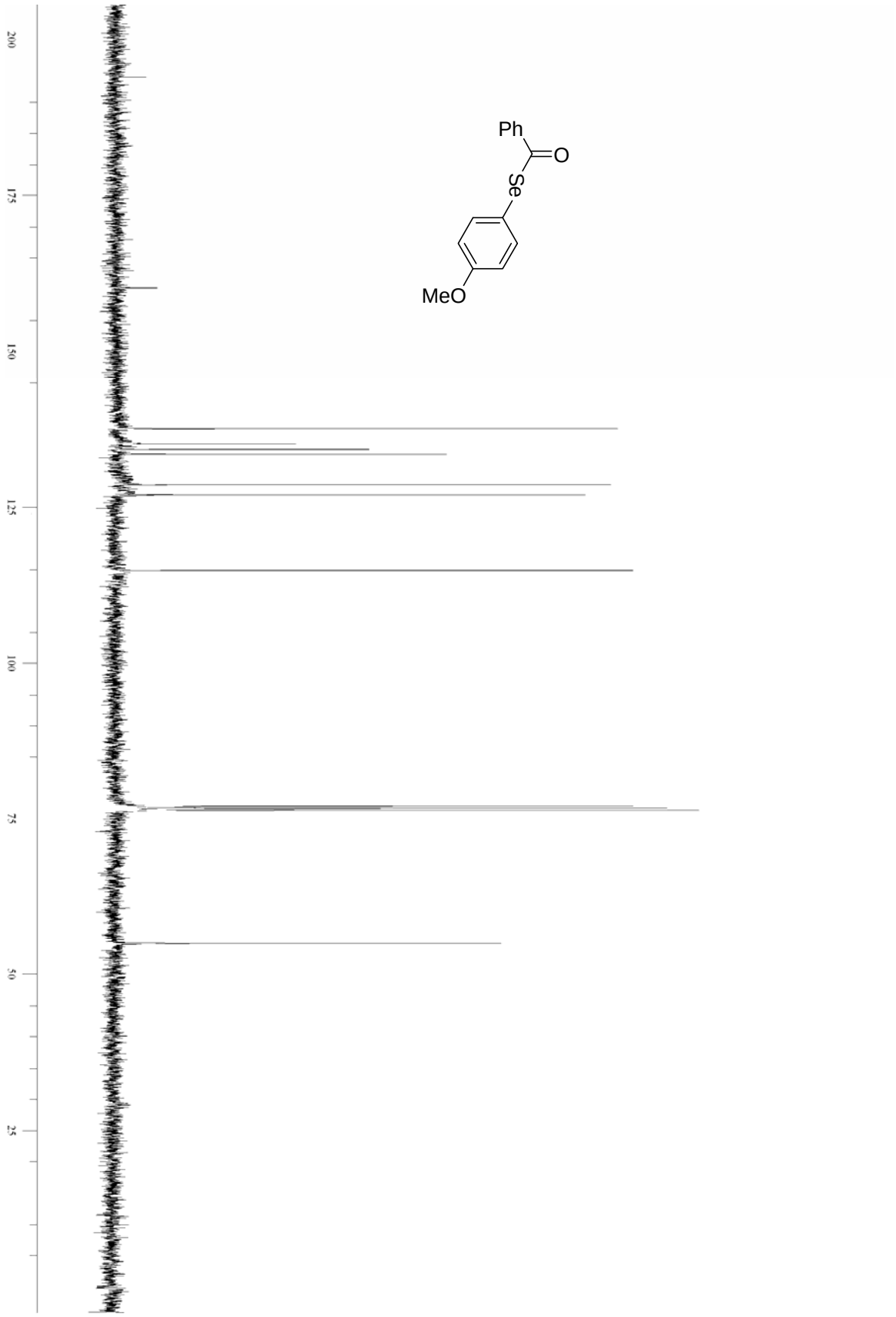
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se-4*-tolyl selenobenzoate **3c**.



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-*4*-tolyl selenobenzoate **3c**.



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *Se*-4-methoxyphenyl selenobenzoate **3d**.



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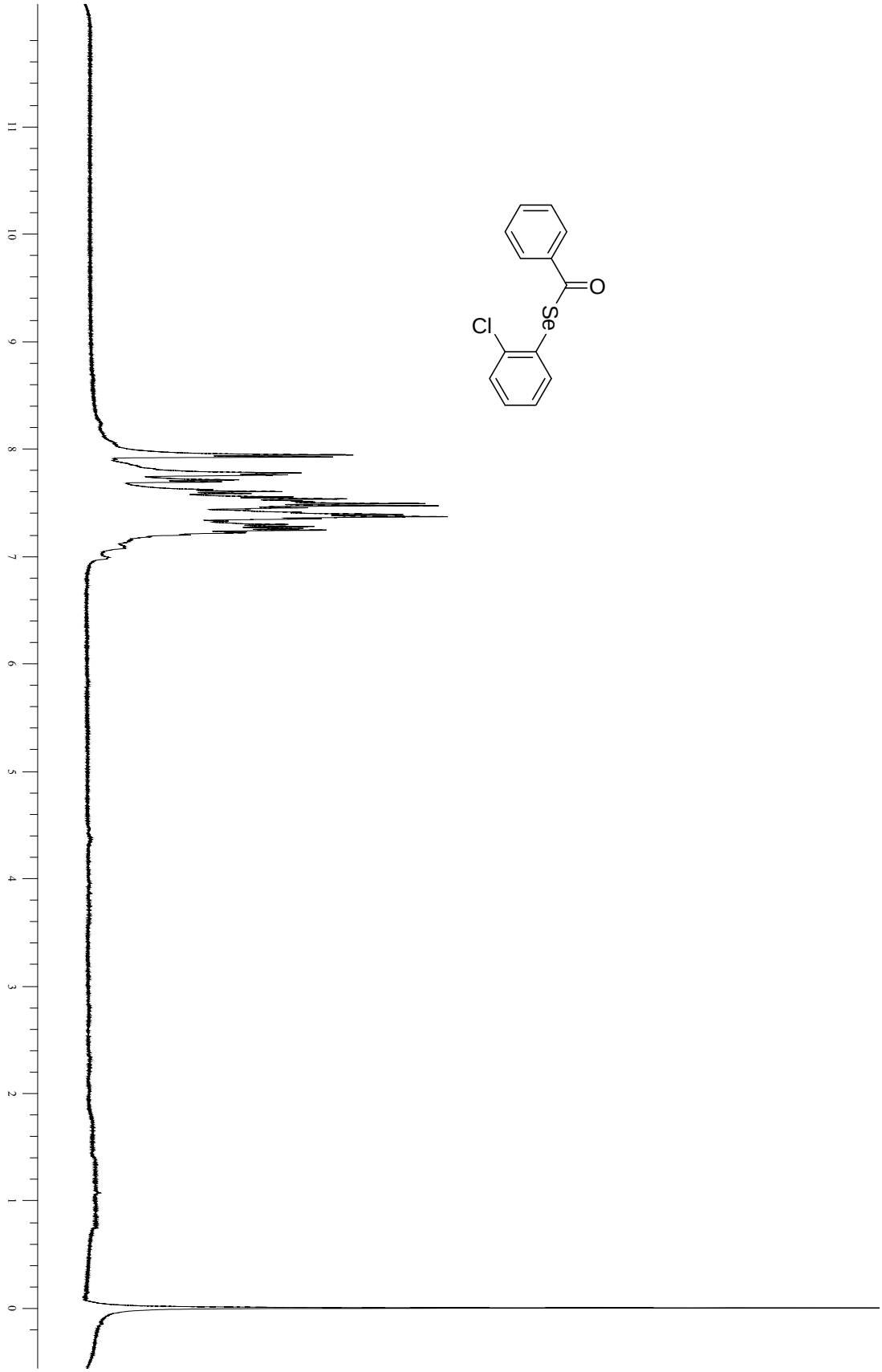

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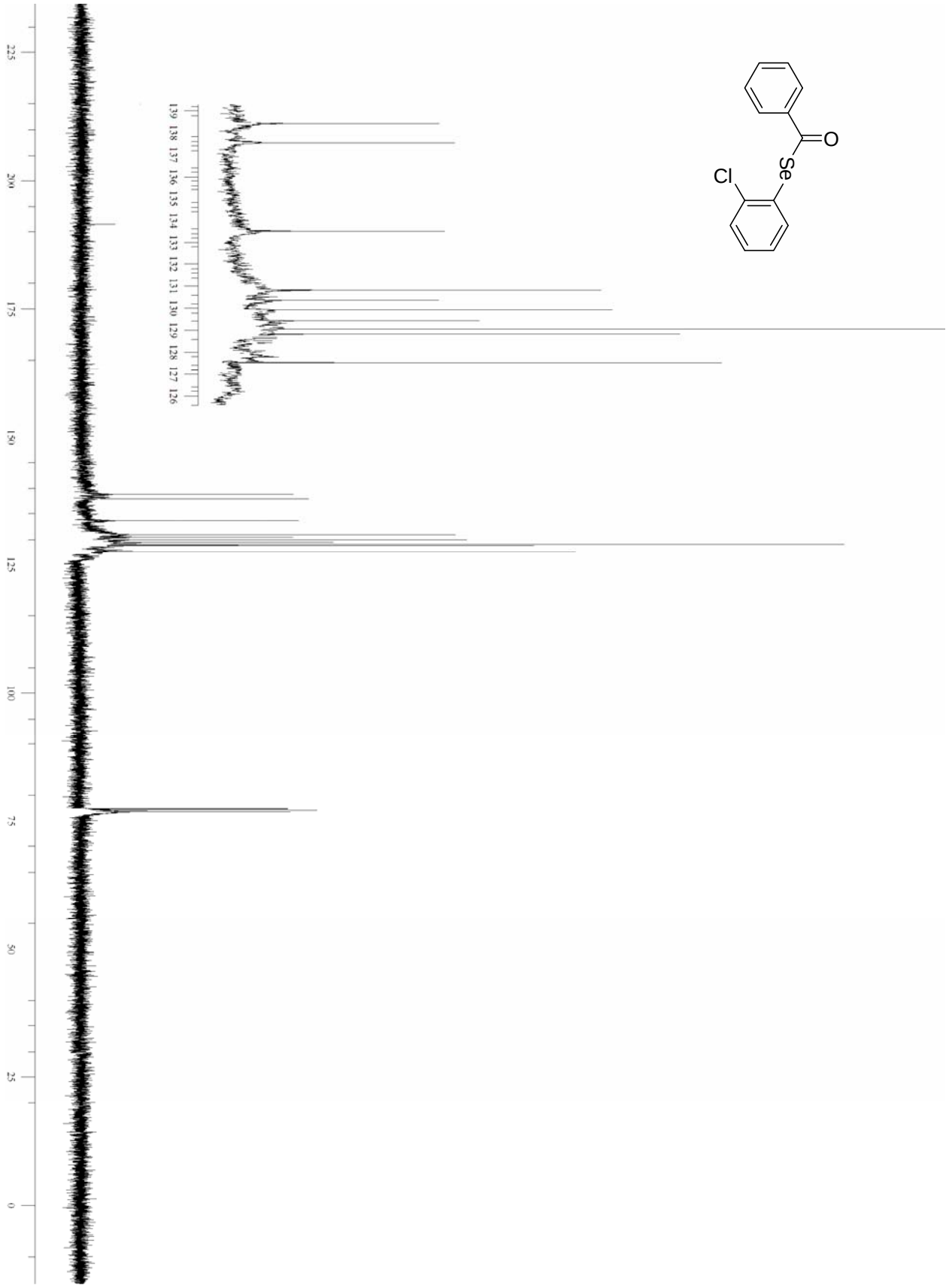

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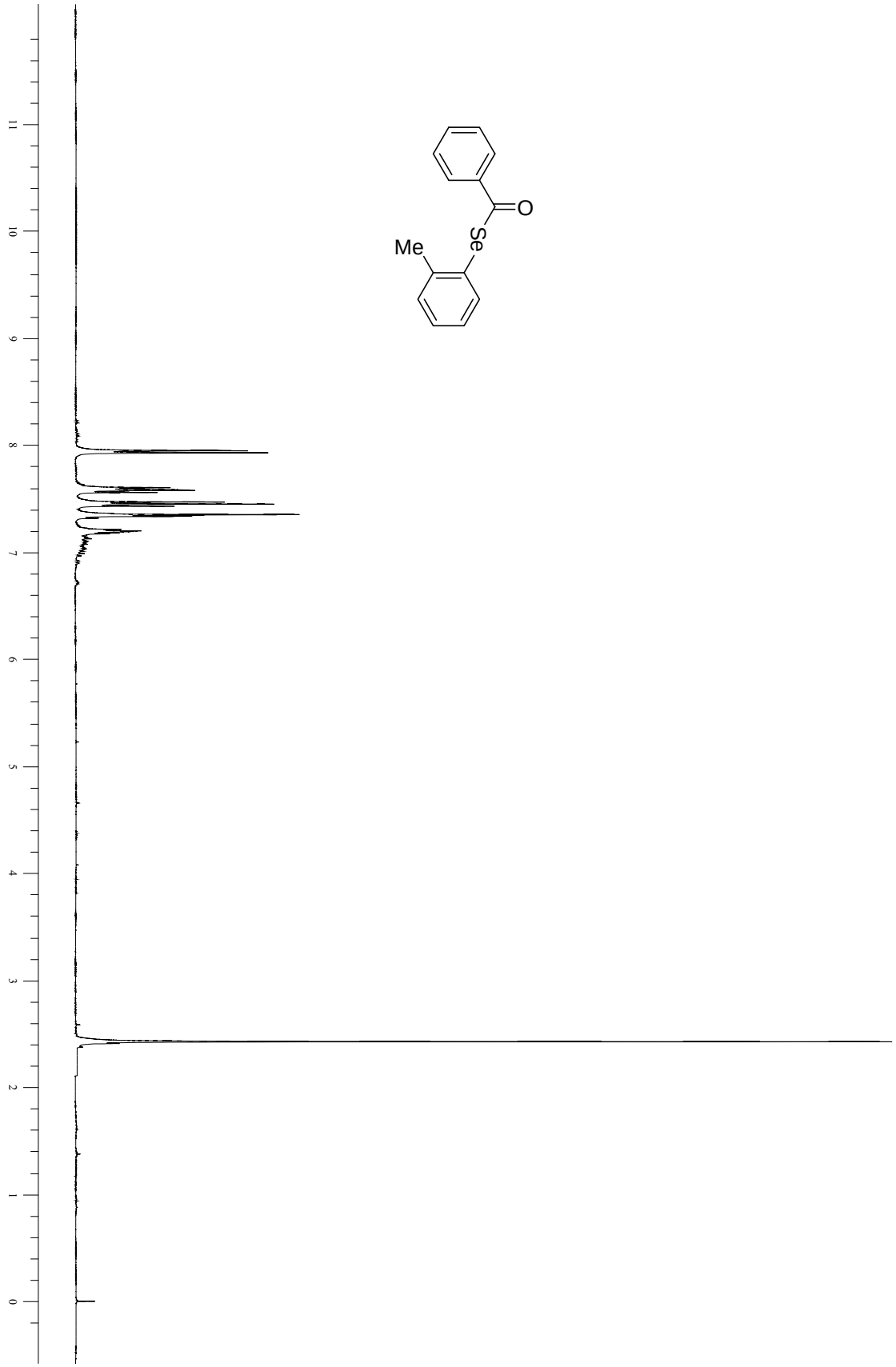
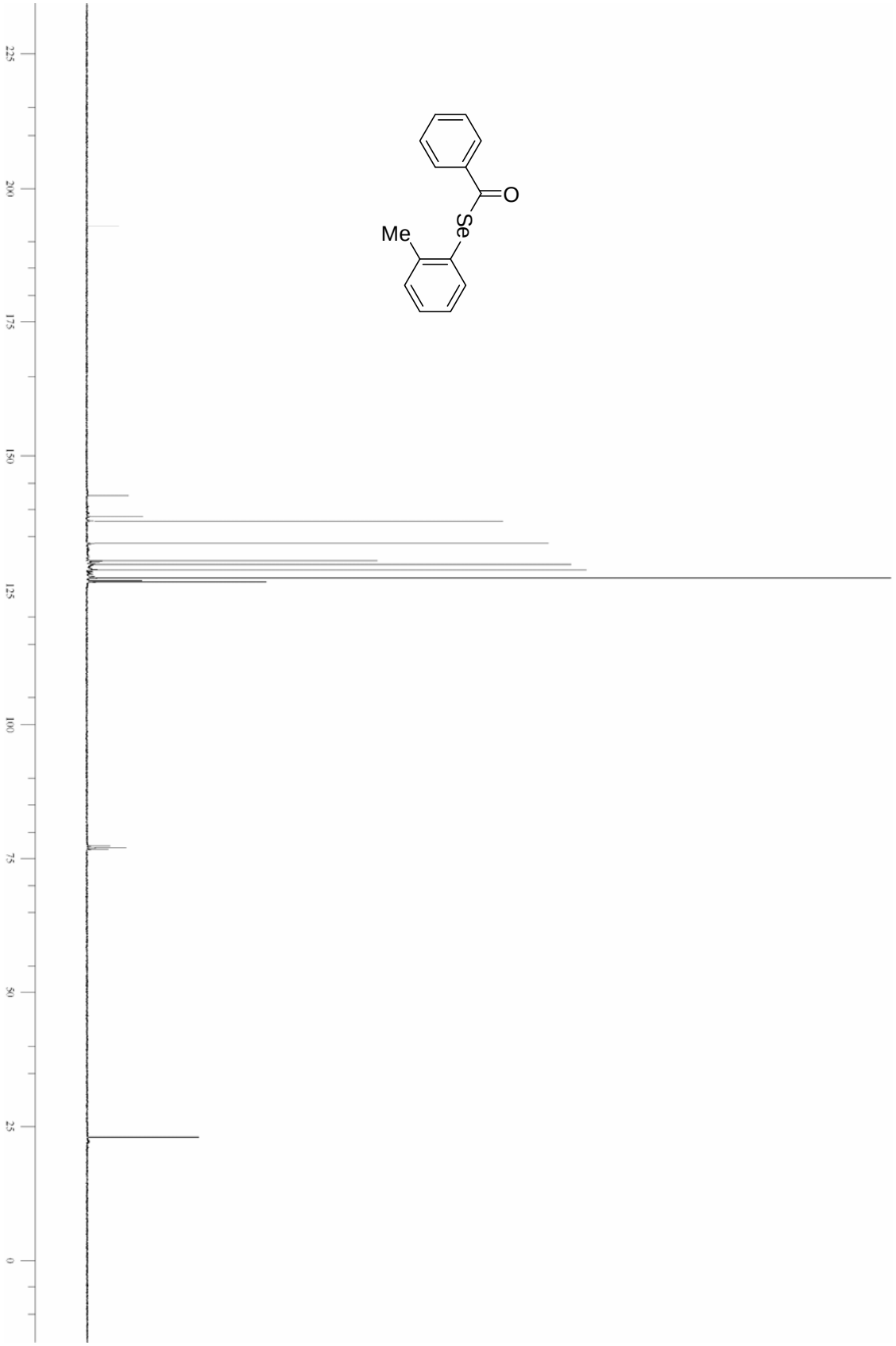
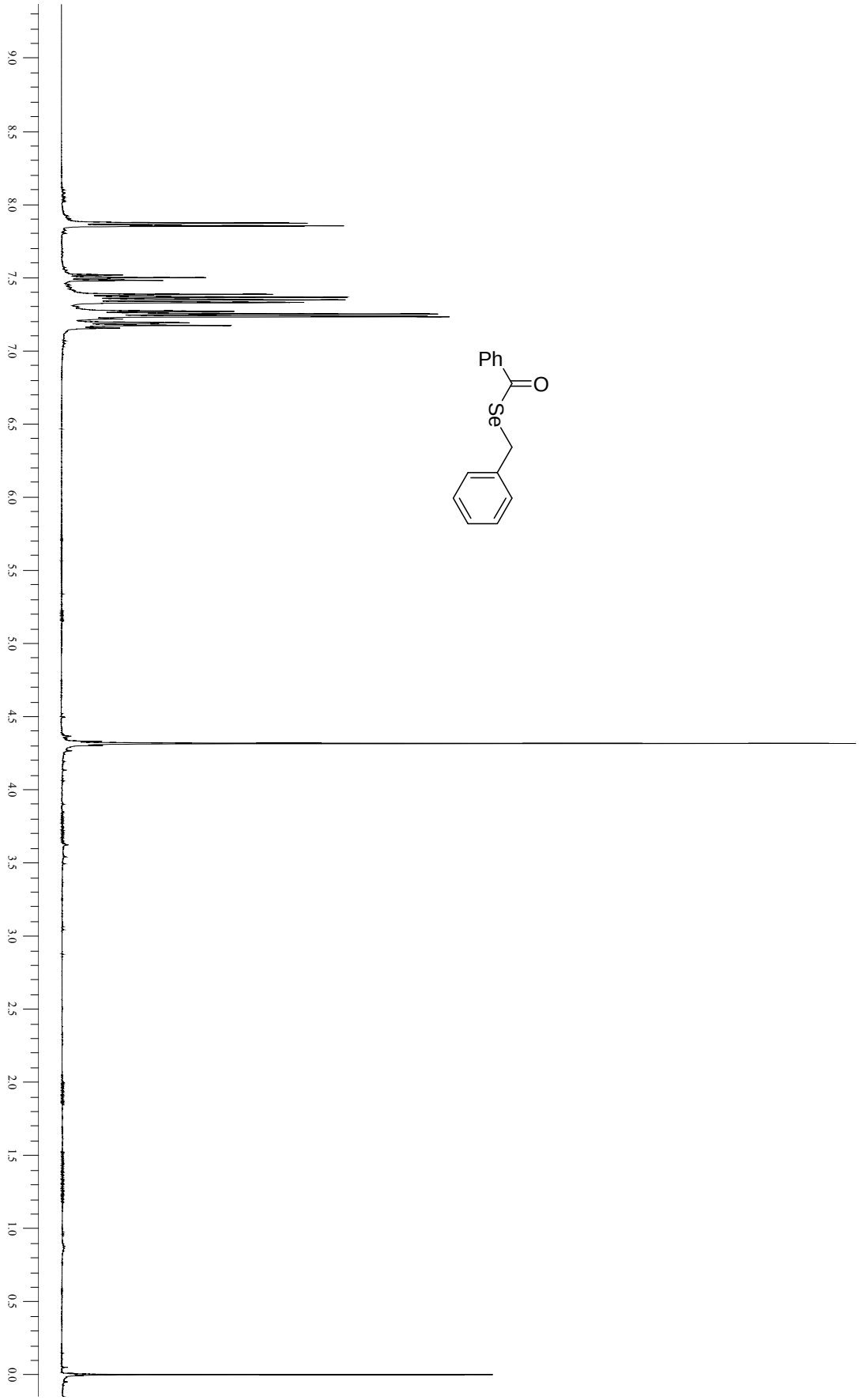


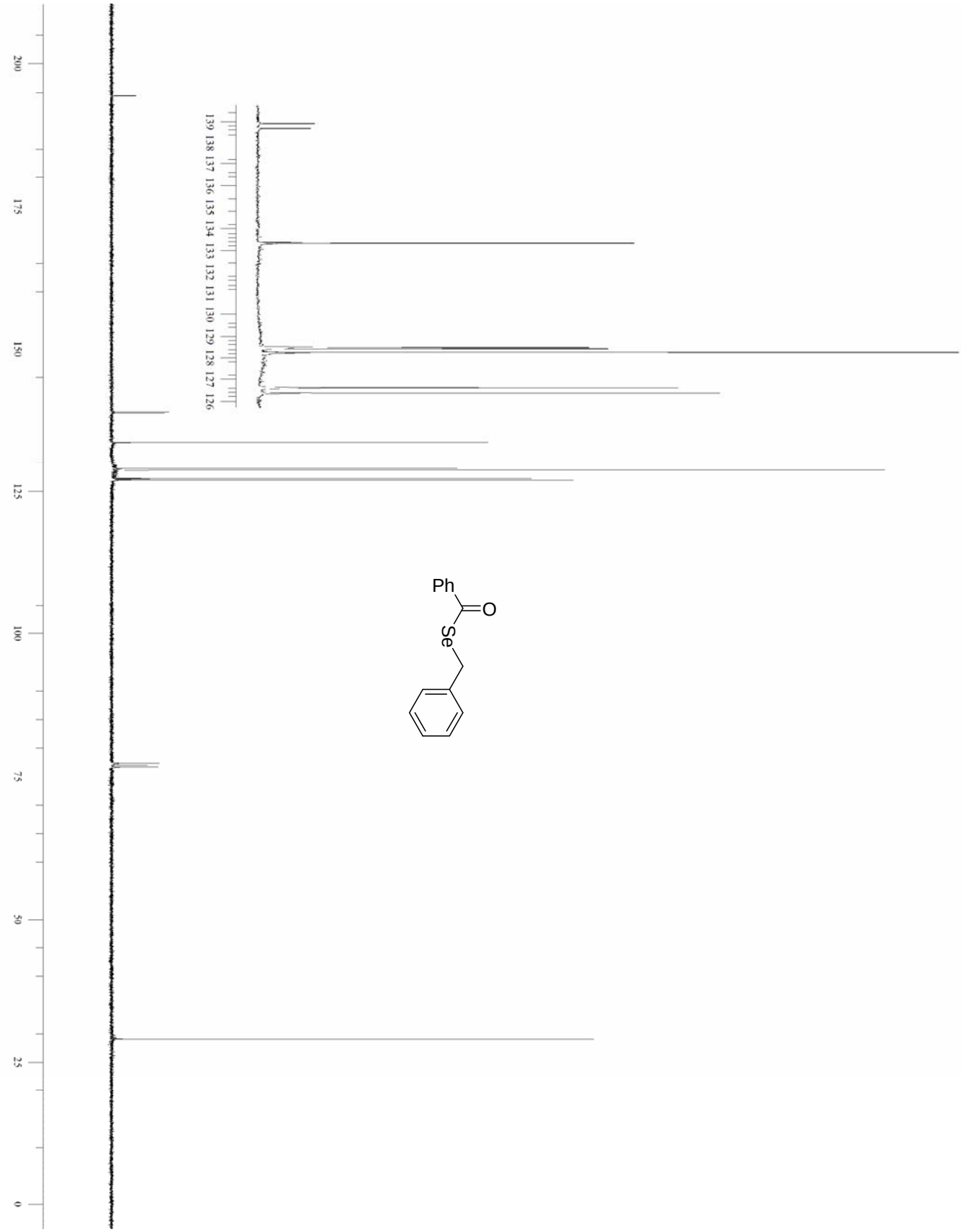
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *Se*-*o*-tolyl selenobenzoate **3f**.



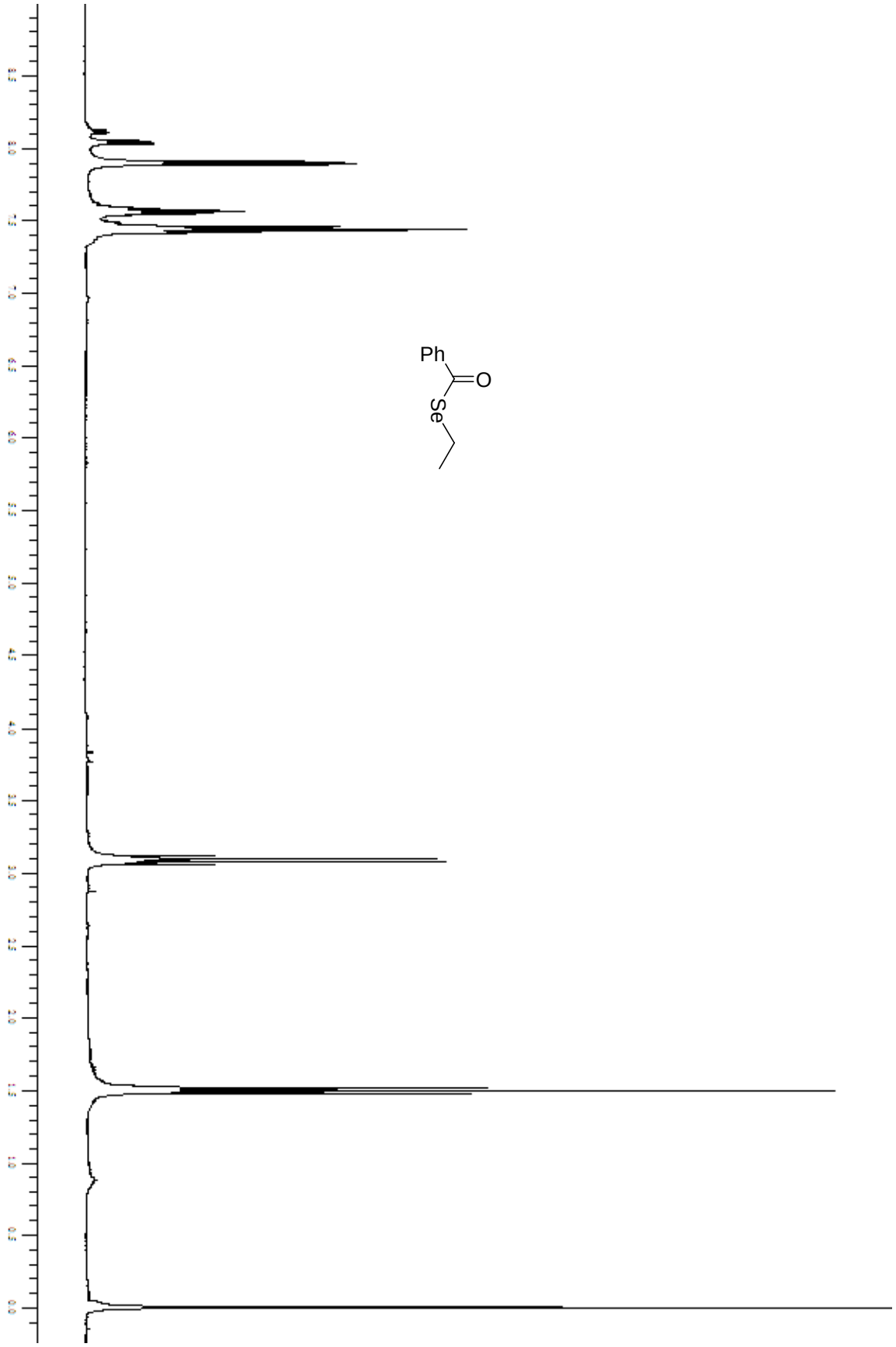
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *Se*-*o*-tolyl selenobenzoate **3f**.



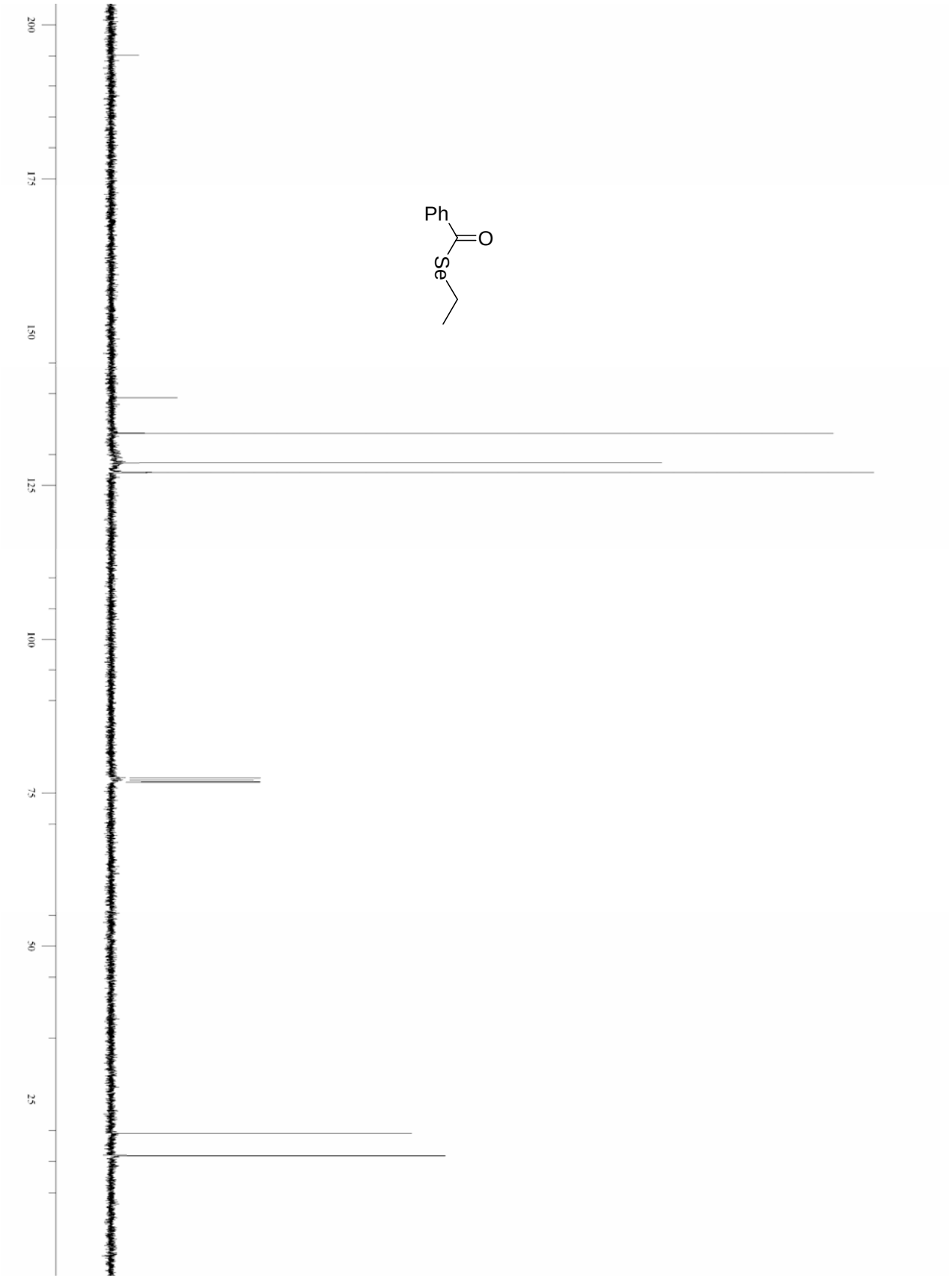
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *Se*-benzyl selenobenzoate **3g**.



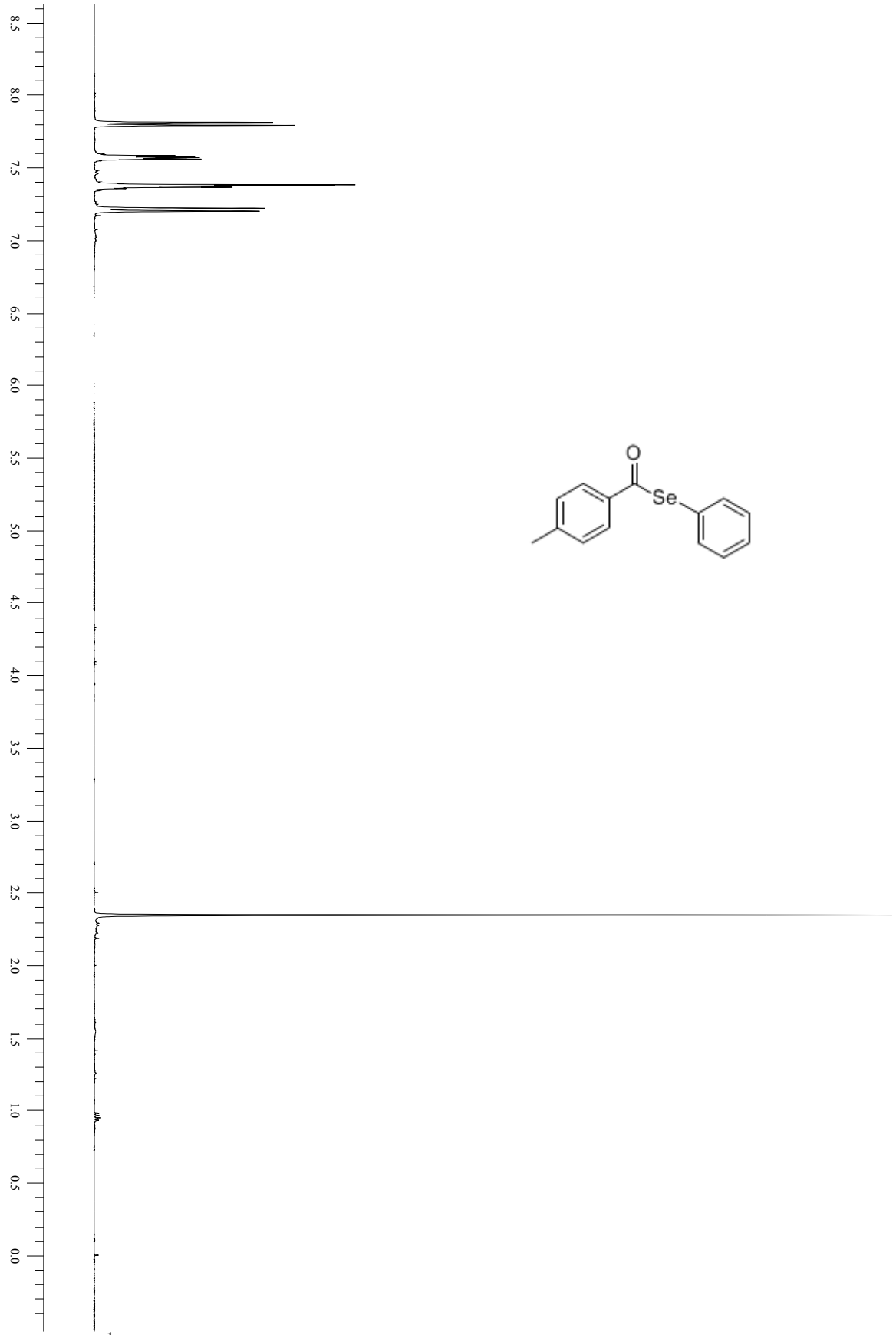
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *Se*-benzyl selenobenzoate **3g**.



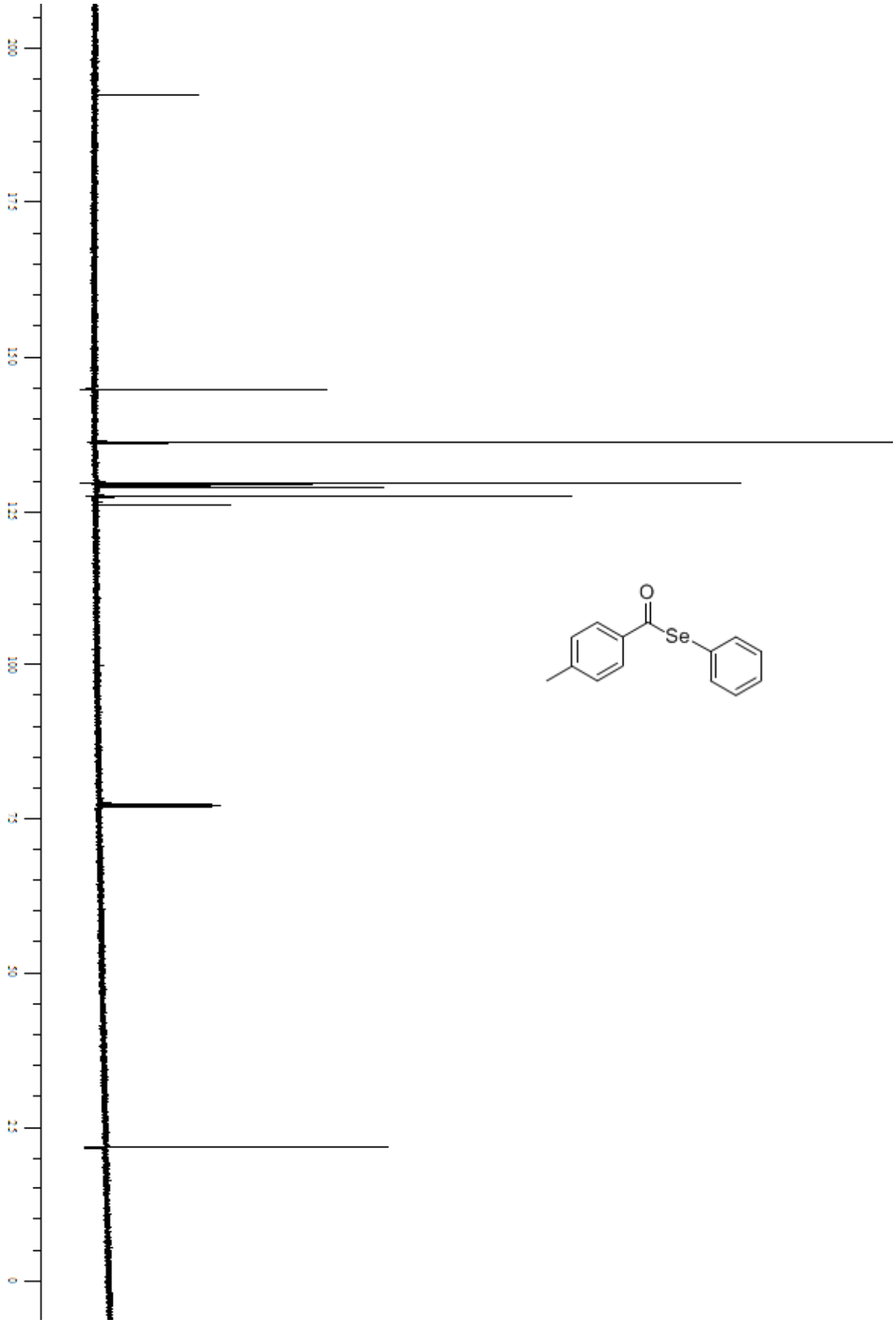
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *Se*-ethyl selenobenzoate **3h**.



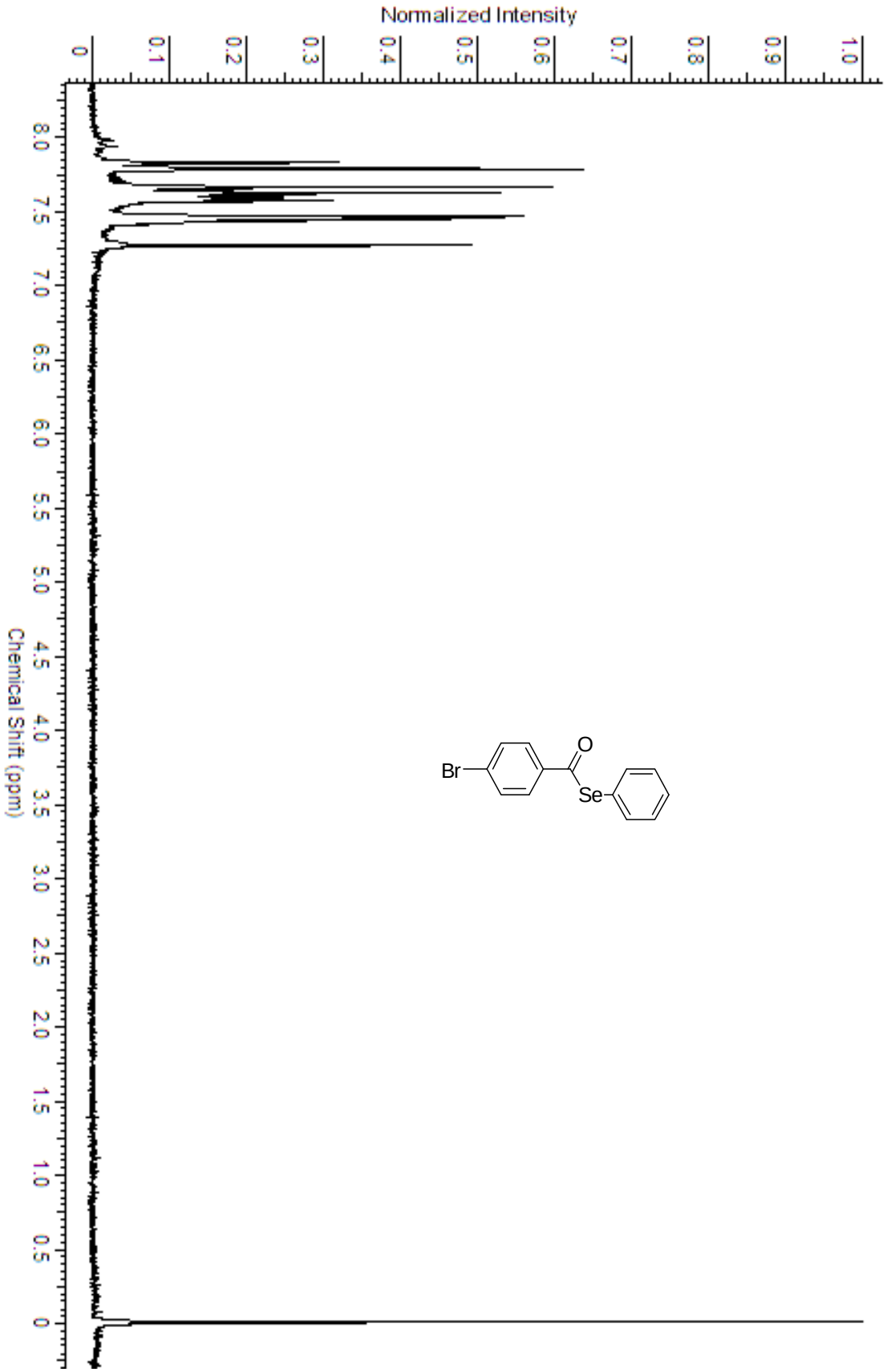
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *Se*-ethyl selenobenzoate **3h**.



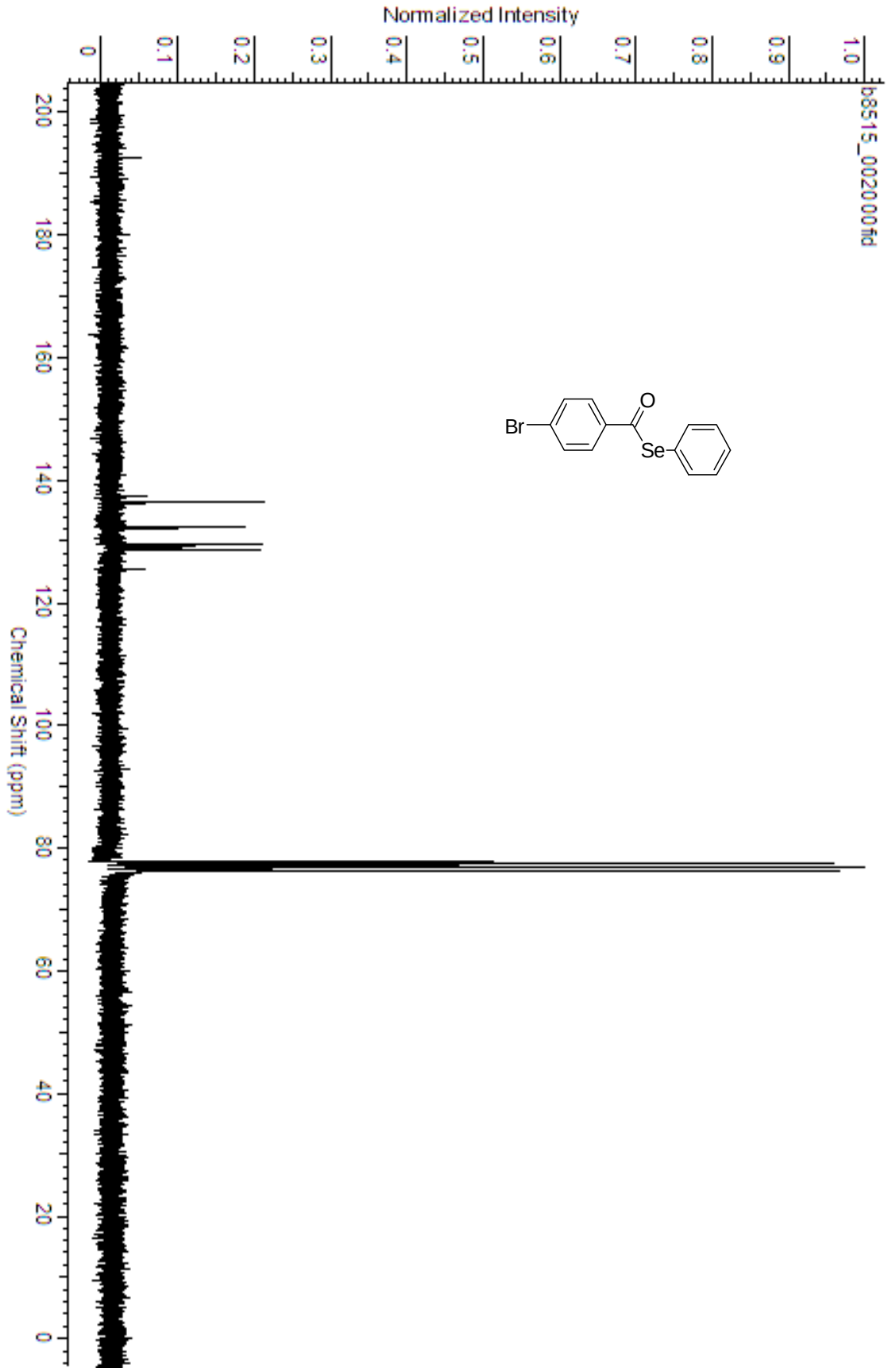
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-phenyl 4-methylselenobenzoate **3i**.



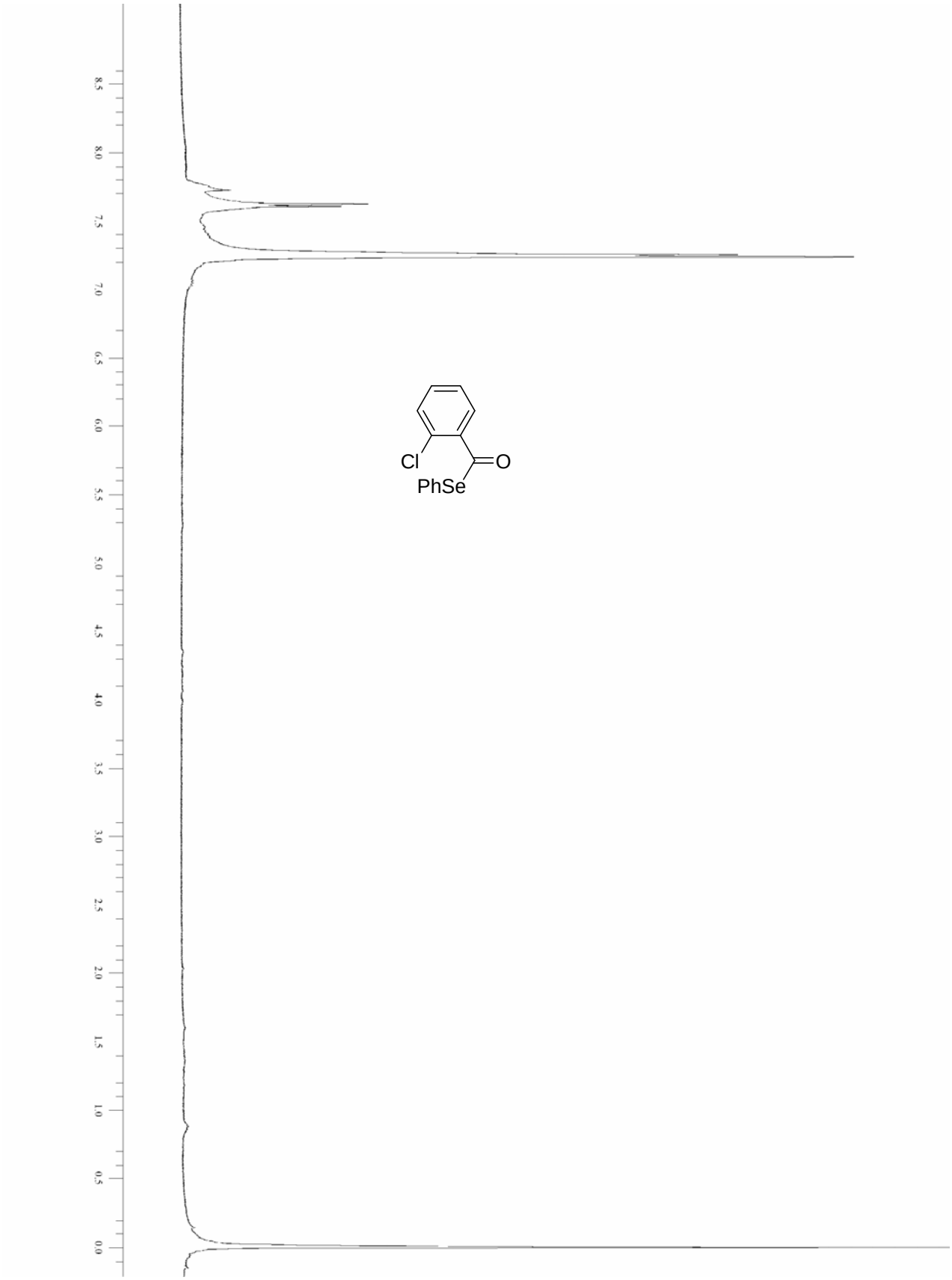
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-phenyl 4-methylselenobenzoate **3i**.



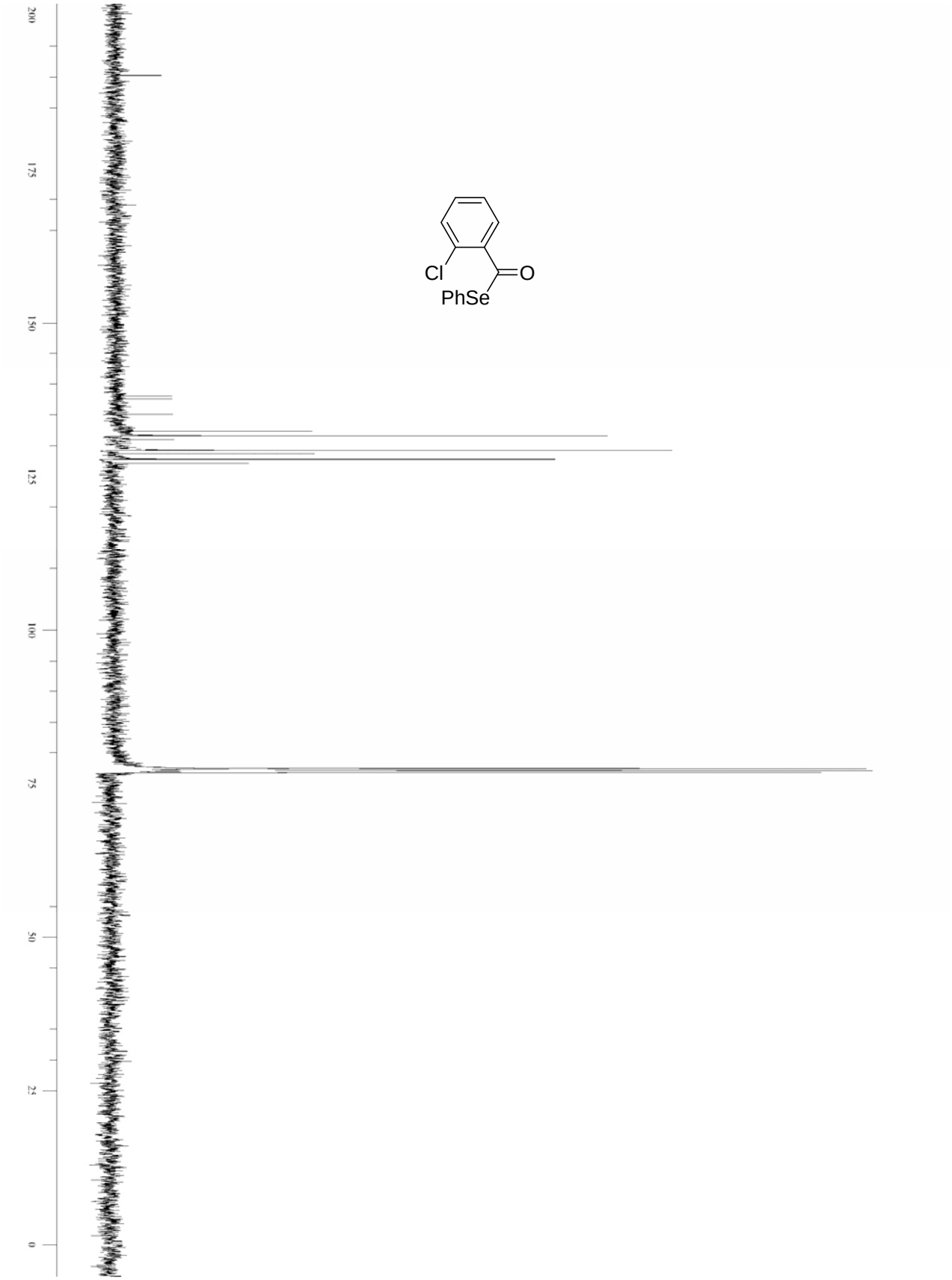
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of *Se*-*4*-bromo selenobenzoate **3j**.



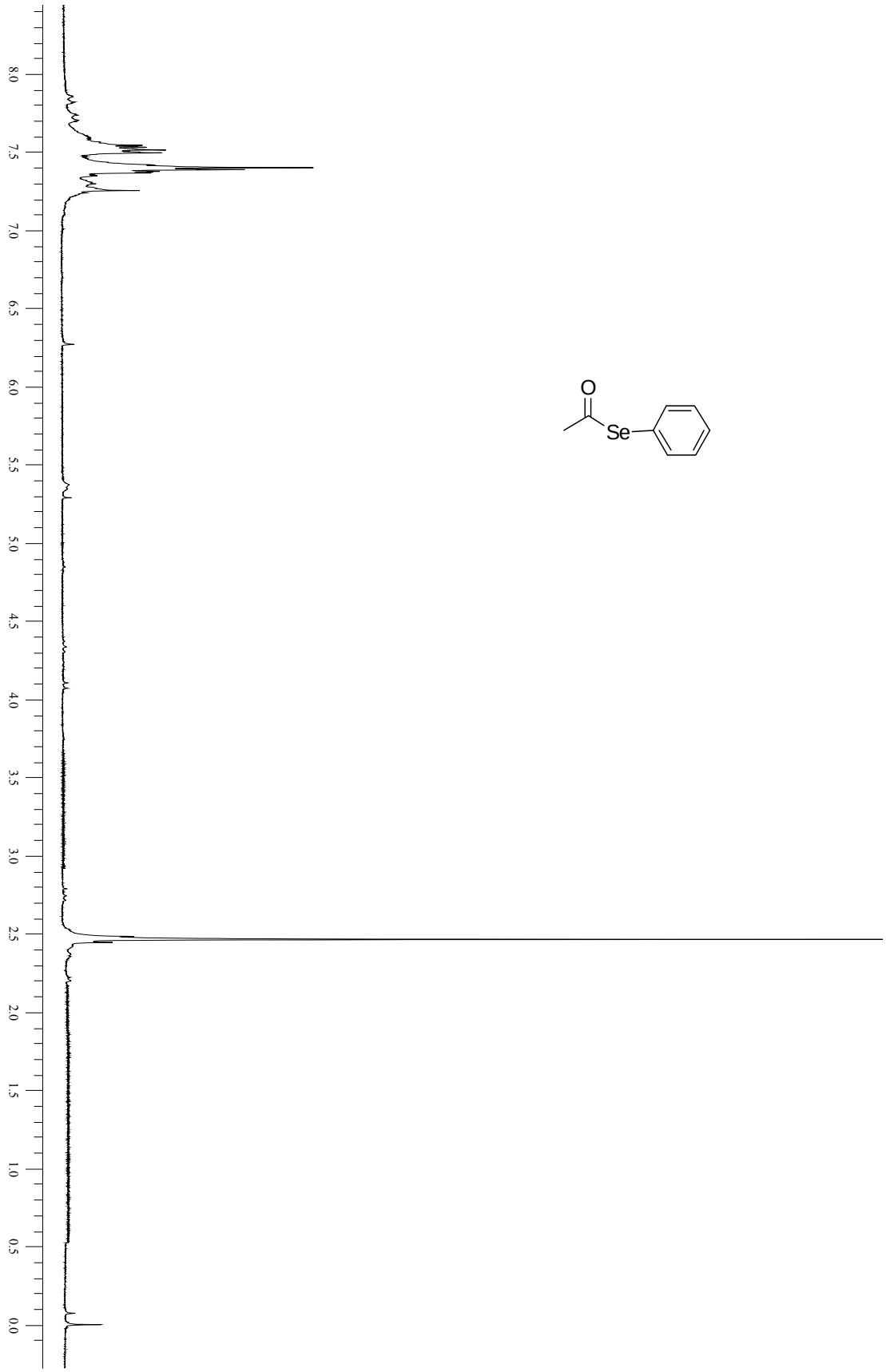
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of *Se*-*4*-bromo selenobenzoate **3j**.



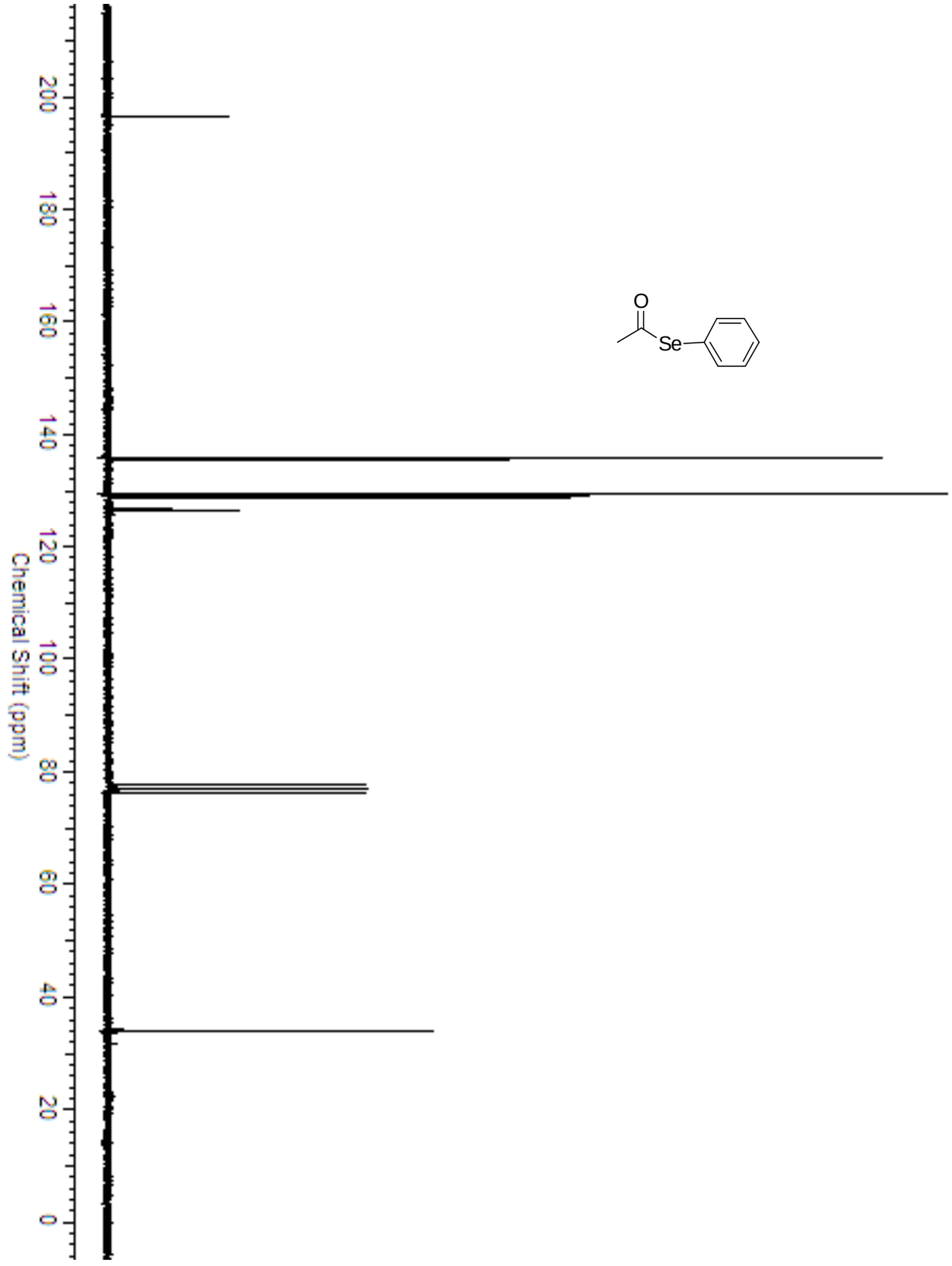
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *Se*-phenyl 2-chlorobenzoselenoate **3l**.



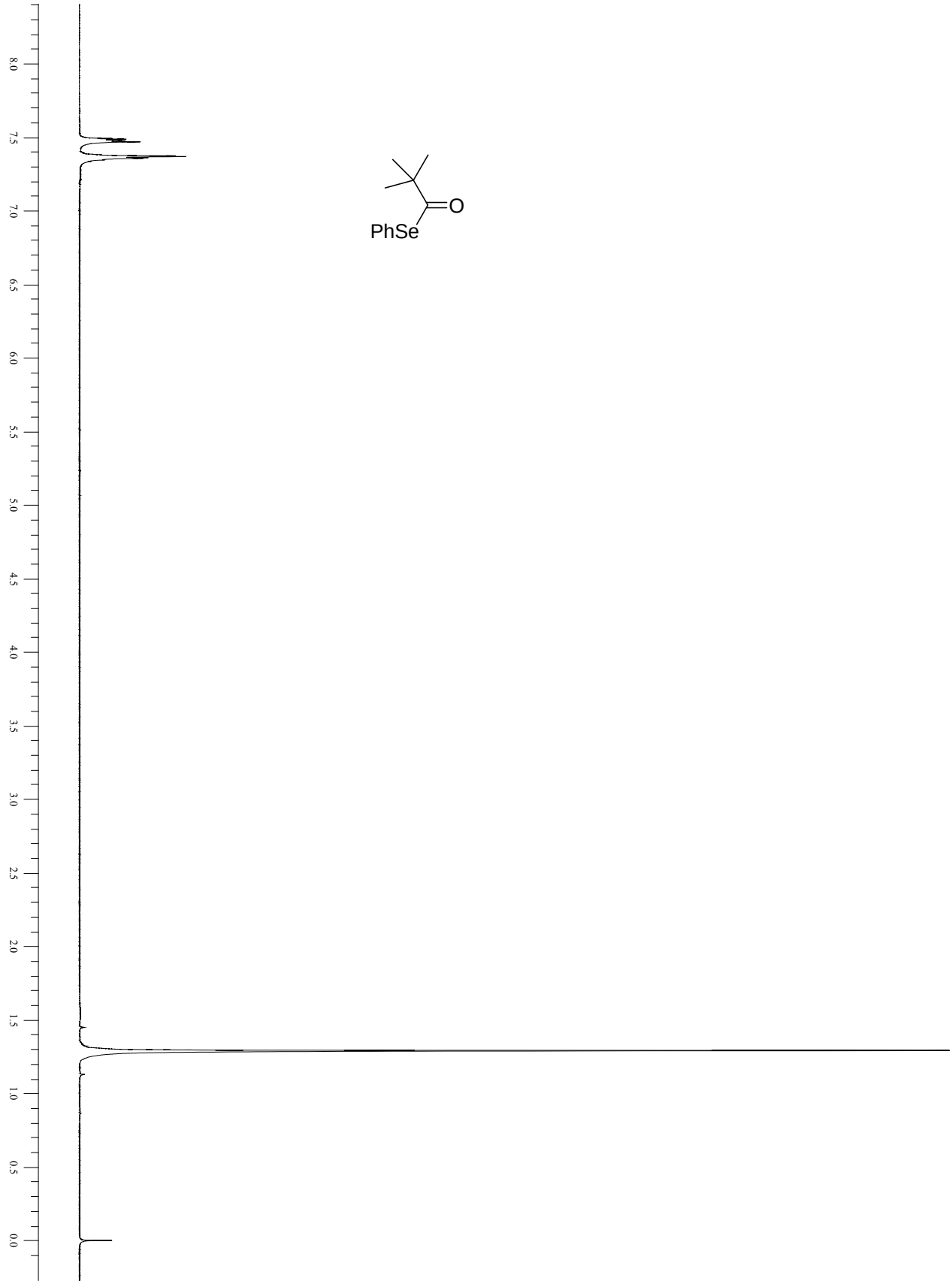
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *Se*-phenyl 2-chlorobenzoselenoate **3l**.



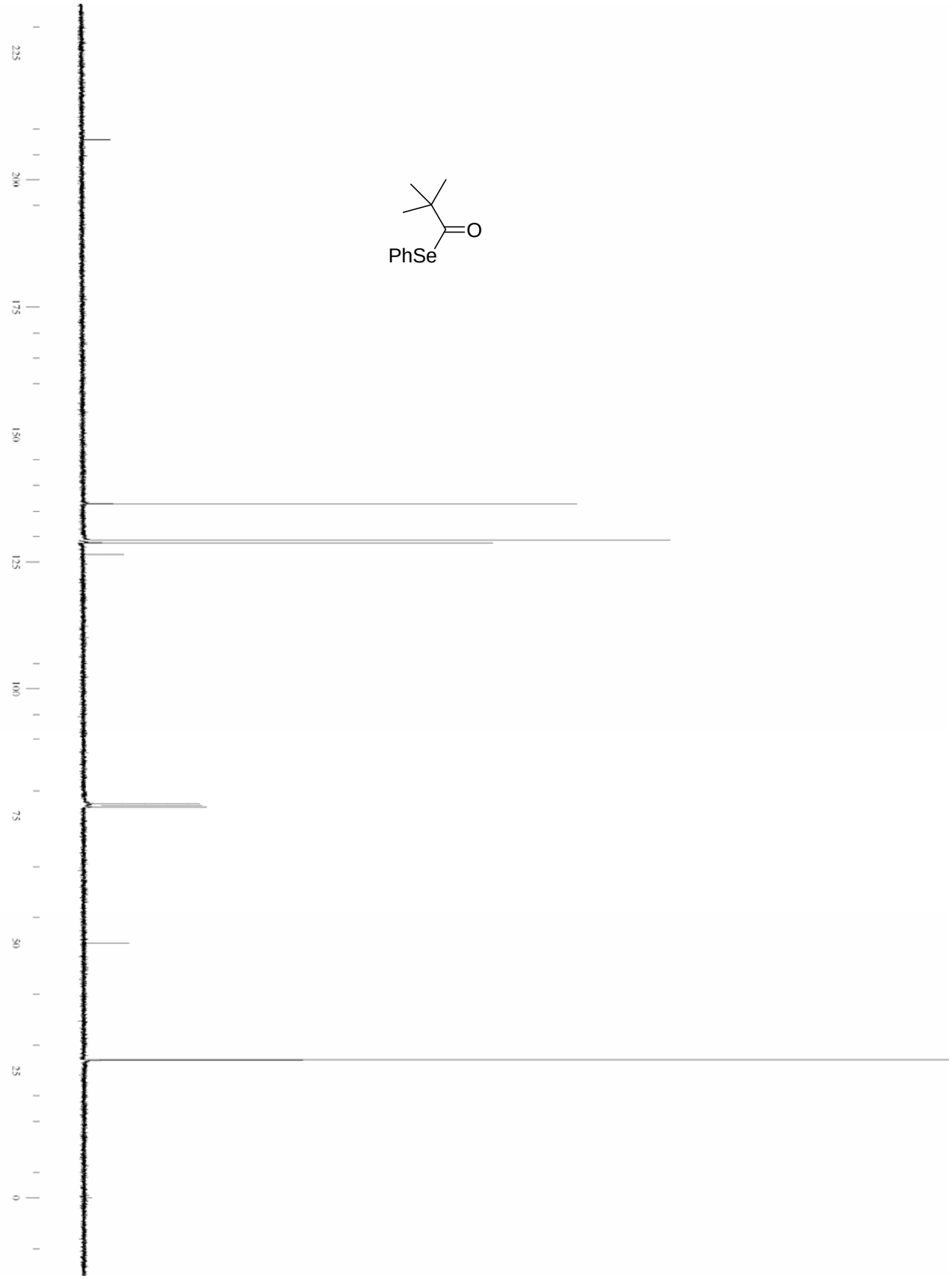
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *Se*-phenyl ethaneselenoate **3m**.



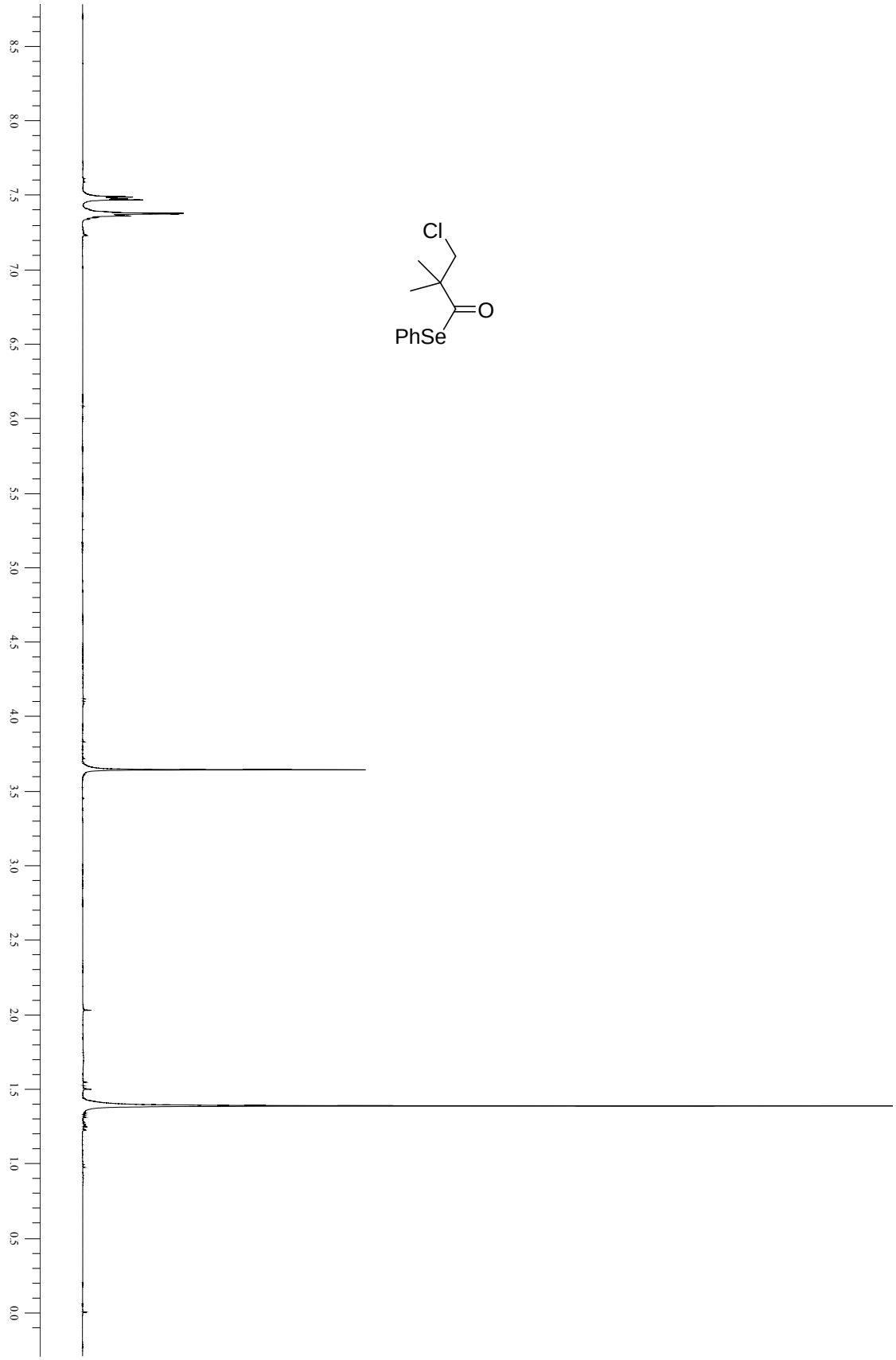
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *Se*-phenyl ethaneselenolate **3m**.



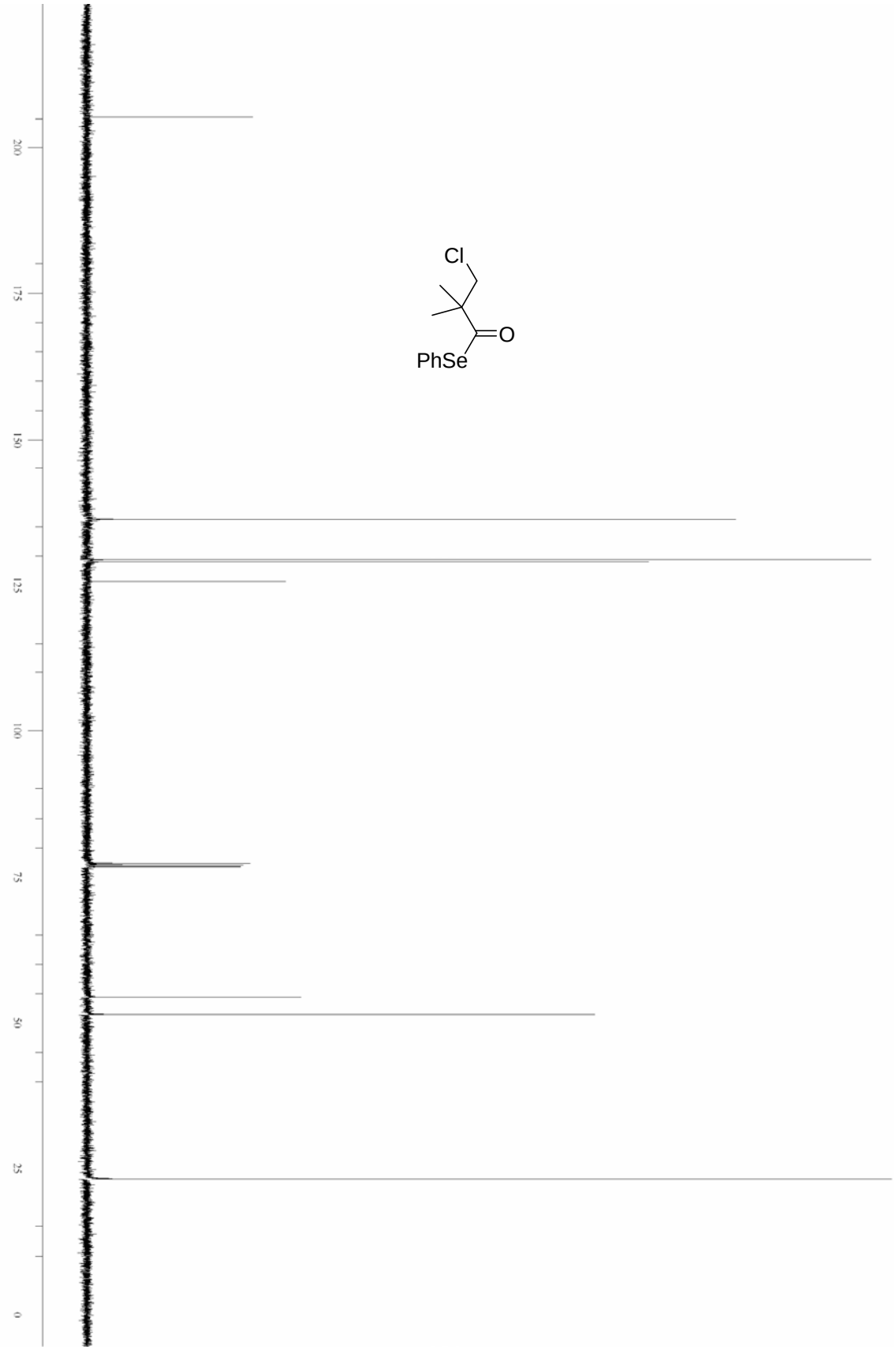
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *Se*-phenyl 2,2-dimethylpropaneselenoate **3n**.



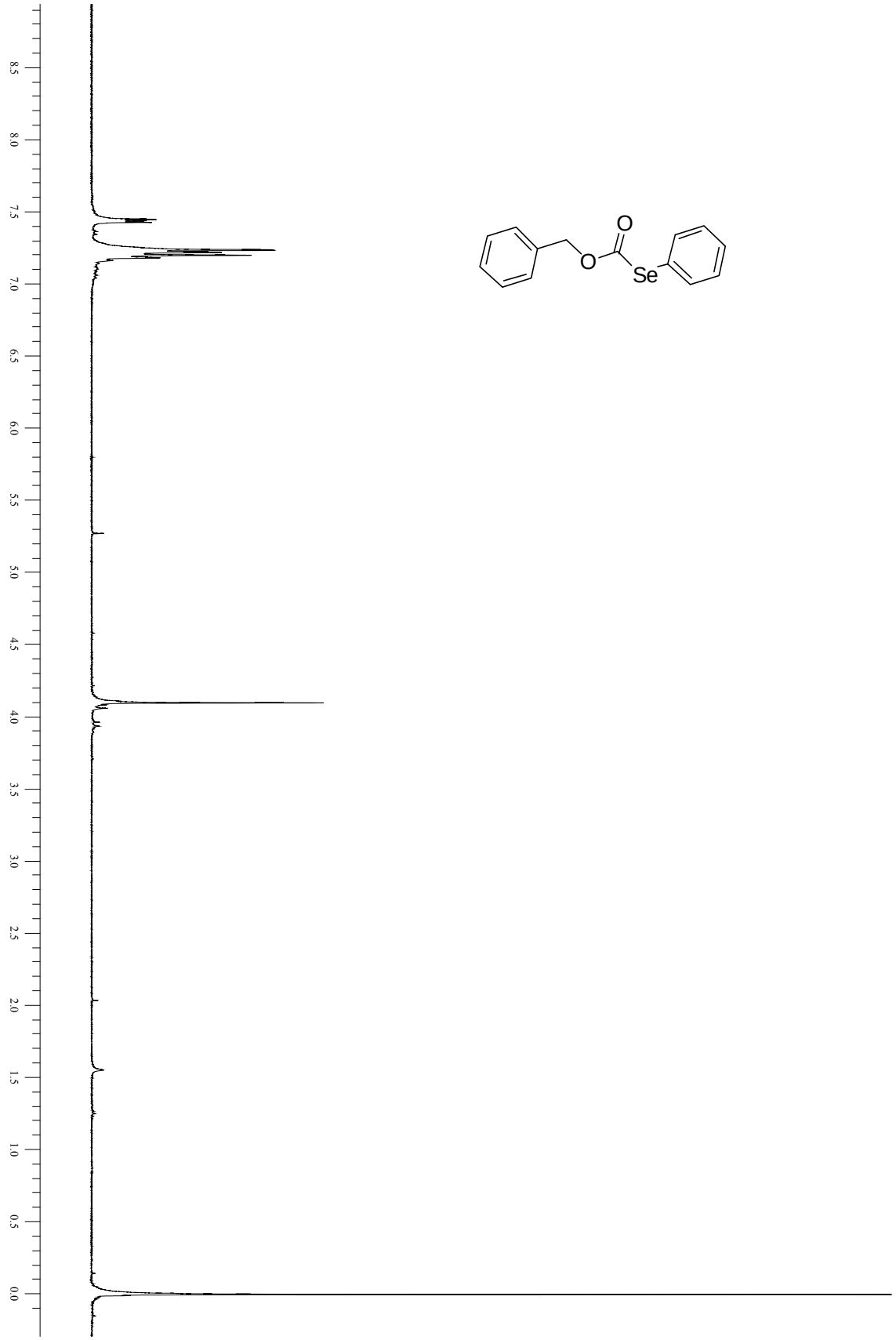
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *Se*-phenyl 2,2-dimethylpropaneselenoate **3n**.



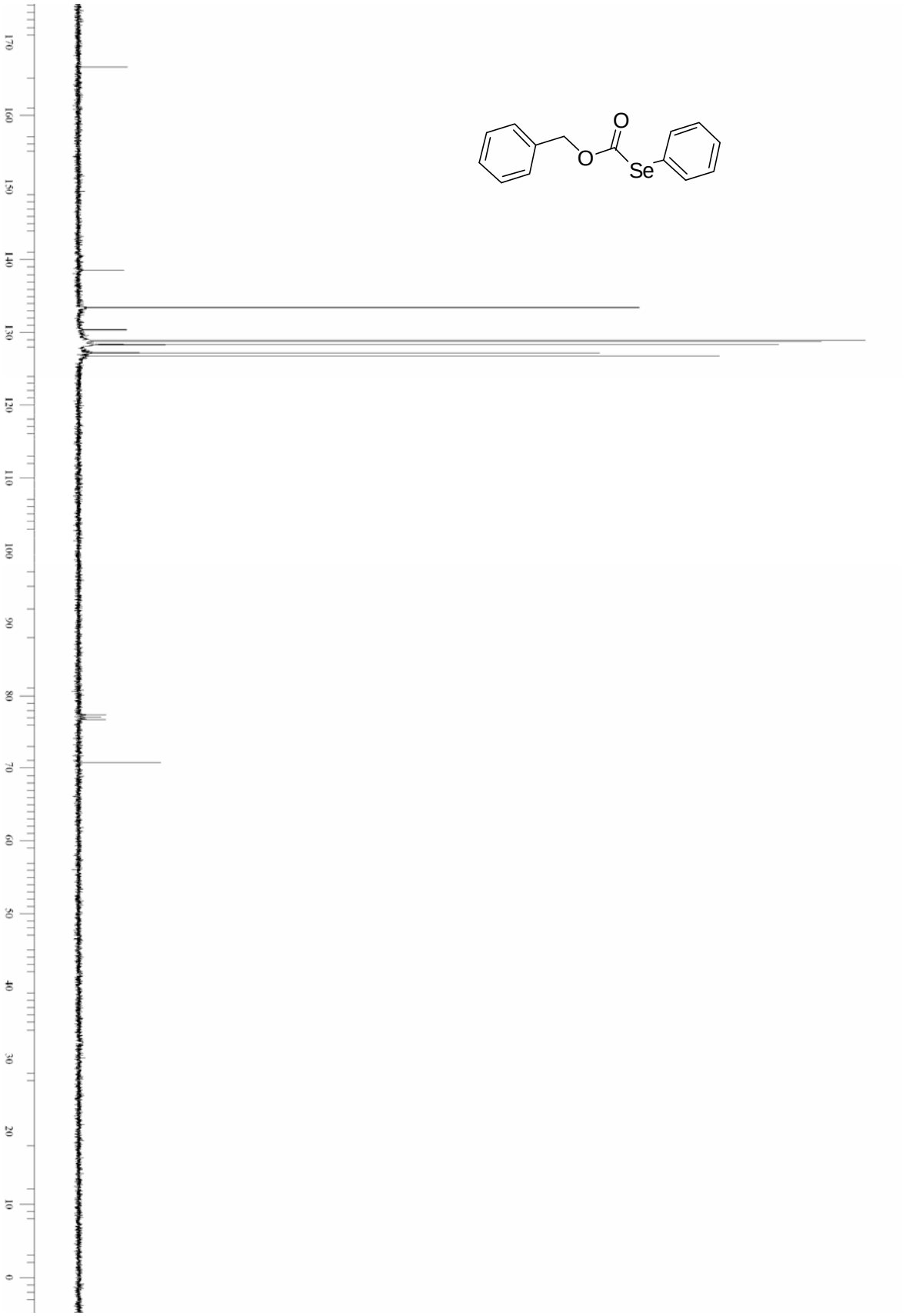
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *Se*-phenyl 3-chloro-2,2-dimethylpropaneselenoate **3o**.



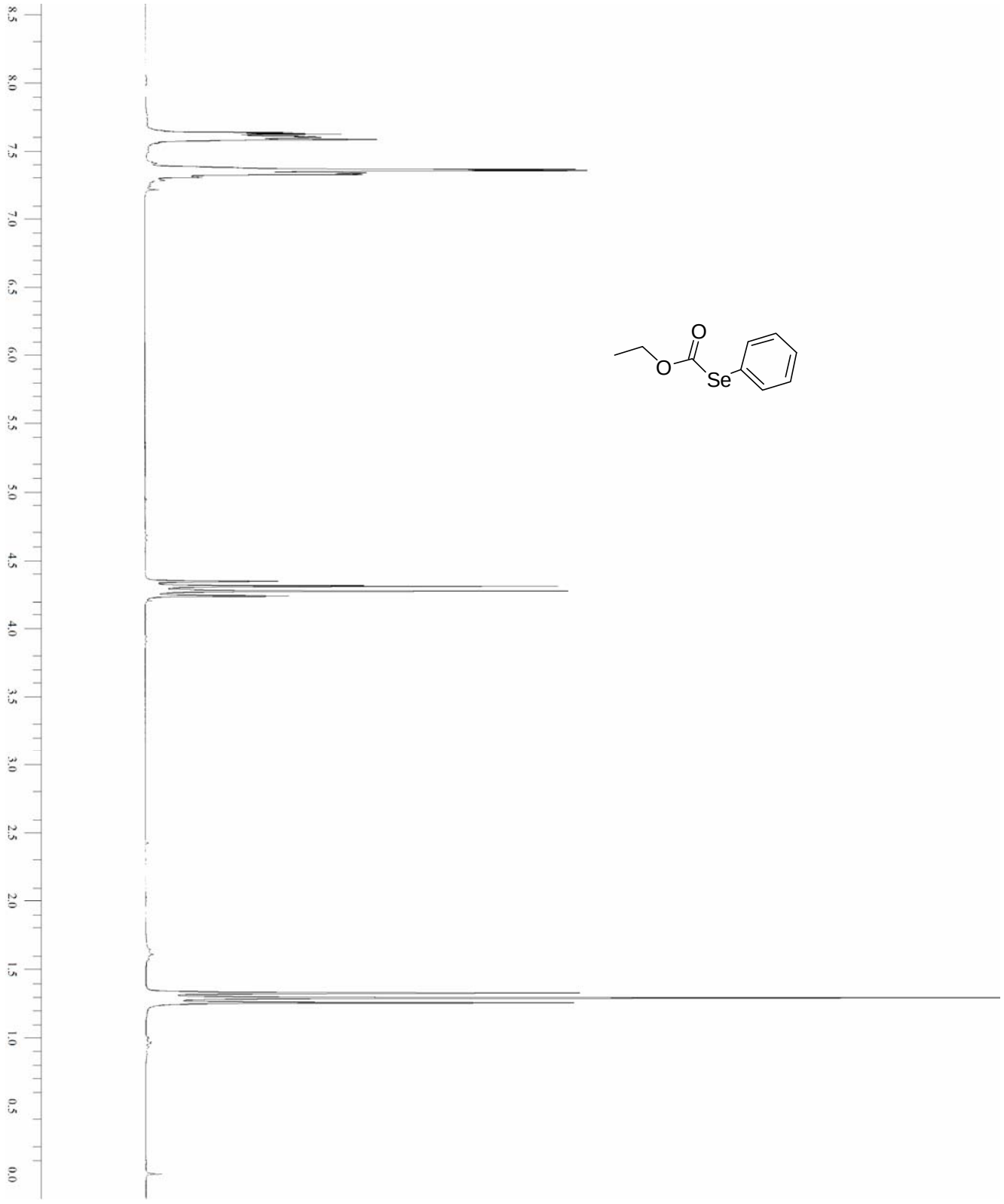
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *Se*-phenyl 3-chloro-2,2-dimethylpropaneselenoate **3o**.



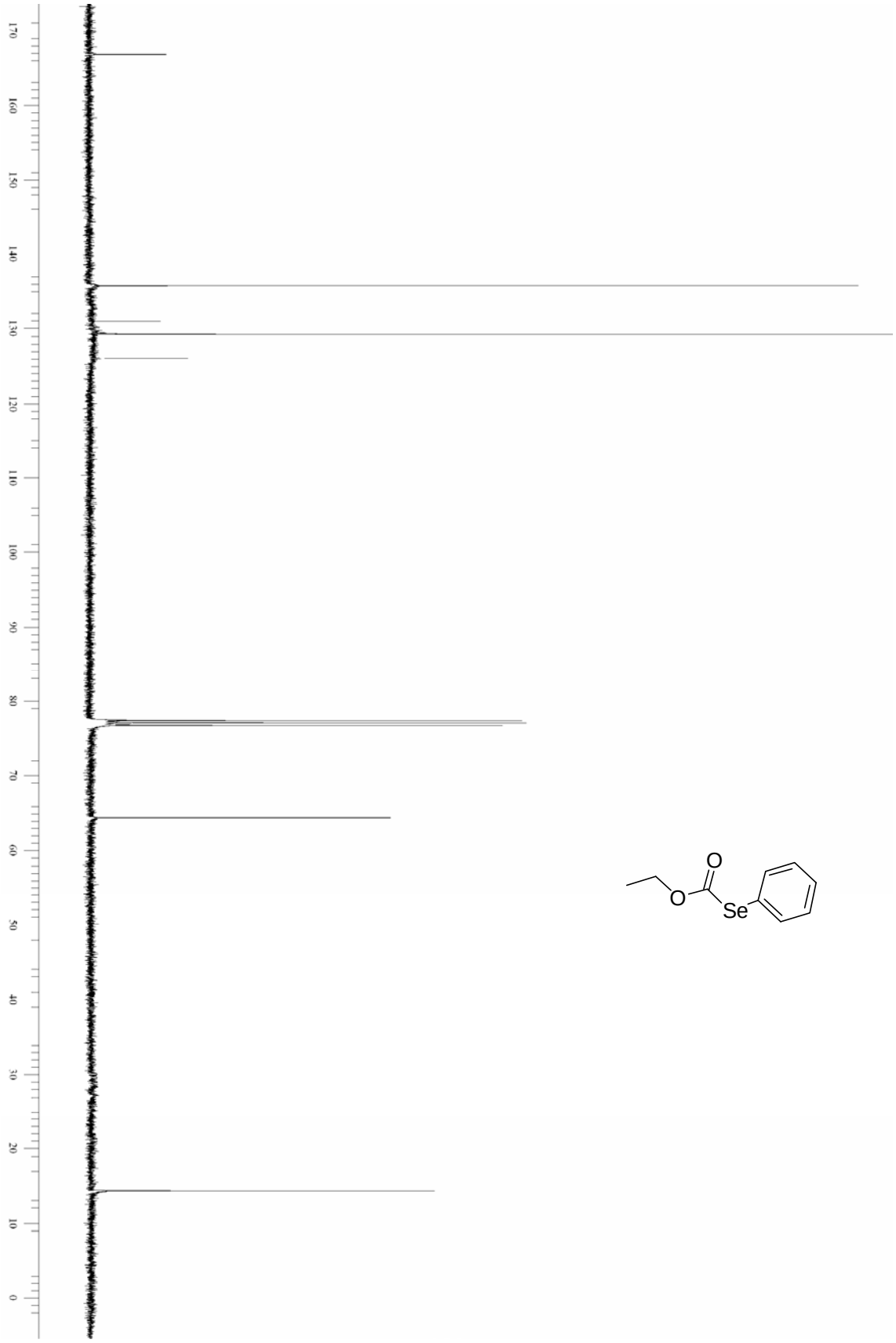
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *O*-benzyl *Se*-phenyl carbonoselenoate **3p**.



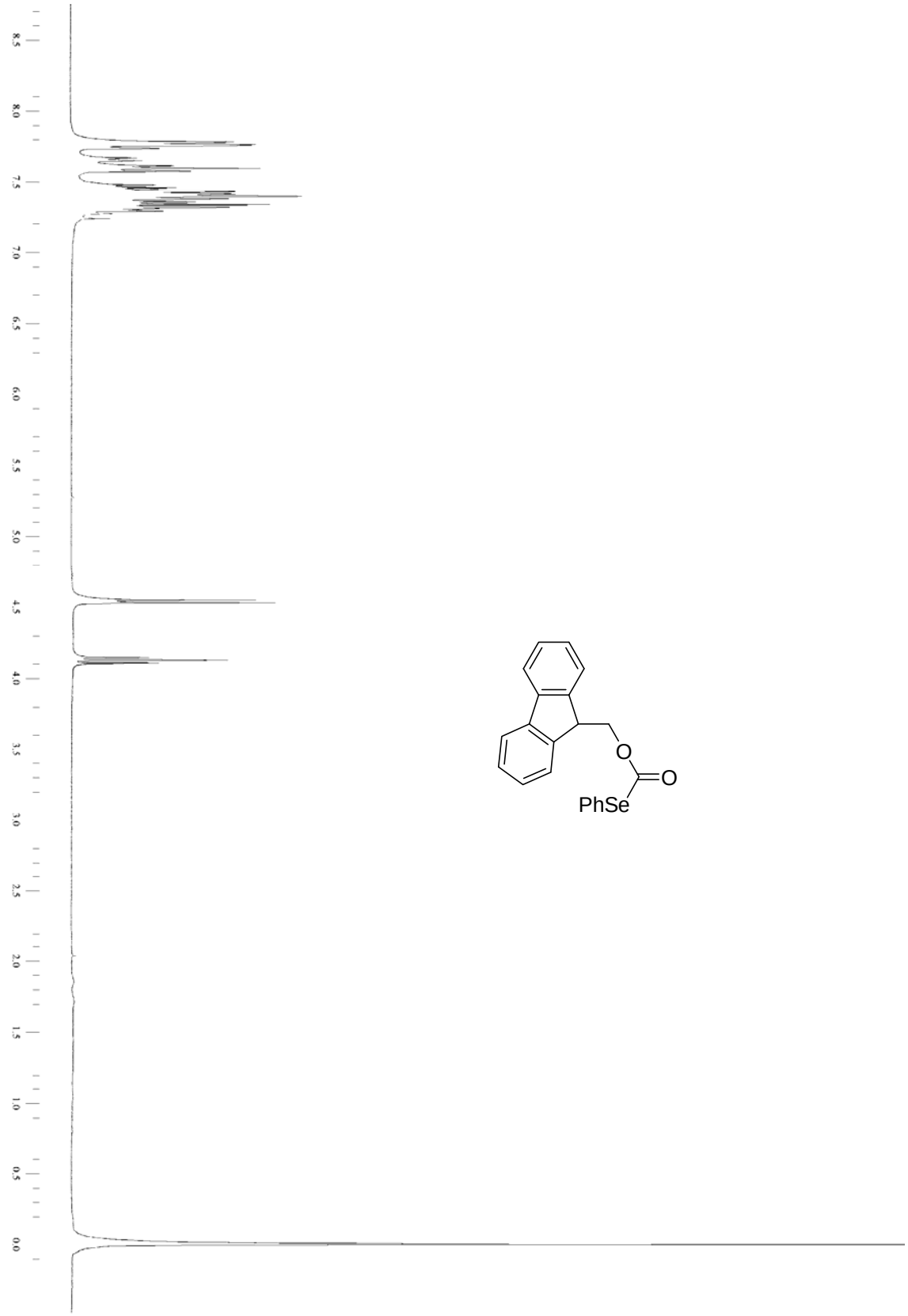
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *O*-benzyl *Se*-phenyl carbonoselenoate **3p**.



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *O*-ethyl *Se*-phenyl carbonoselenoate **3q**.



^{1}H NMR (100 MHz, $CDCl_3$) Spectrum of *O*-ethyl *Se*-phenyl carbonoselenoate **3q**.



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of *O*-(9H-fluoren-9-yl)methyl *Se*-phenyl carbonoselenoate **3r**.

^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of *O*-(9H-fluoren-9-yl)methyl *Se*-phenyl carbonoselenoate **3r**.