Supplementary Material

Rongalite®/PEG-400 as reducing system in the synthesis of new glycerol-derived selenol esters using anhydrides and bis-(2,2-dimethyl-1,3-dioxolanylmethyl)diselenide as substrates

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1. General Information

The reactions were monitored by thin layer chromatography (TLC) was performed using Merck silica gel (60 F_{254}), 0.25 mm thickness. For visualizing the spots, TLC plates were either exposed to UV light, or stained with iodine vapor, or 5% vanillin in 10% H_2SO_4 and heat. Column chromatography was performed using Merck Silica Gel (230-400 mesh). Low-resolution mass spectra (MS) were measured on a Shimadzu GC-MS-QP2010 mass spectrometer. High-resolution mass spectra (HRMS) were recorded in positive ion mode (ESI) using a Bruker micrOQTOF spectrometer. NMR spectra were recorded with Bruker DPX (^{1}H NMR = 400 MHz; ^{13}C NMR = 100 MHz) instruments using $CDCl_3$ as solvent and calibrated using tetramethylsilane (TMS) as internal standard. Coupling constants (*J*) are reported in Hertz and chemical shift (δ) in ppm. Optical rotations were measured with a JASCO P-2000 Polarimeter in CH_2Cl_2 solutions with percent concentrations.

2. General procedure for the synthesis of the selenol esters 3a-h

In a single-neck round-bottom flask equipped with a rubber septum and magnetic stirring containing a solution of the diselenide[1] **1** (0.194 g, 0.5 mmol), the apropriate anhydride **2a**-**h** (1.1 mmol) in PEG-400 (3.0 mL), Rongalite® (0.177 g, 1.5 mmol) and K_2CO_3 (0.069 g, 0.5 mmol) were added. The resulting mixture was stirred at room temperature and the reaction progress was followed by TLC. When the reaction was complete (the reaction time is indicated in Table 2), the mixture was received in water (50.0 mL) and extracted with ethyl acetate (3x 15.0 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated under vacuum. After that, the crude product was purified by column chromatography on silica gel eluting with hexanes yielding the products **3a-h**. All the compounds are not described in the literature and were properly characterized by MS, ^{1}H NMR, ^{13}C NMR and HRMS.

3. General Procedure for the synthesis of water-soluble selenol ester 4a using Dowex-(H^+) resin[2]

To a solution of **3a** (0.299 g, 1.0 mmol) in MeOH (2.3 mL) was added Dowex® acidic ion-exchange resin (50WX8 20-50 mesh, 1.122 g). The reaction mixture was stirred for 24 h at room temperature and then the resin was filtered off and washed with MeOH. The filtrate was concentrated under vacuum and the crude was purified by column chromatography (50% EtOAc/hexanes) to afford the product **4a** as yellowish oil.

4. Water solubility

A weighted amount (0.090 g) of the compound **4a** was stirred in a vial at 25 °C, and water was added by syringe in 0.25 mL portions until complete solubilization.

5. References

1. (a) Soares, K. L.; Silva, R. B.; Peglow, T. J.; Silva, M. S.; Jacob, R. G.; Alves, D.; Perin, G. *ChemistrySelect*. **2016**, *1*, 2009; (b) Borges, E. L.; Peglow, T. J.; Silva, M. S.; Jacoby, C. G.; Schneider, P. H.; Lenardão, E. J.; Jacob, R. G.; Perin, G. *New J. Chem*. **2016**, *40*, 2321.
2. Bergmeier, S. C.; Stanchina, D. M. *J. Org. Chem*. **1999**, *64*, 2852.

6. Selected spectra

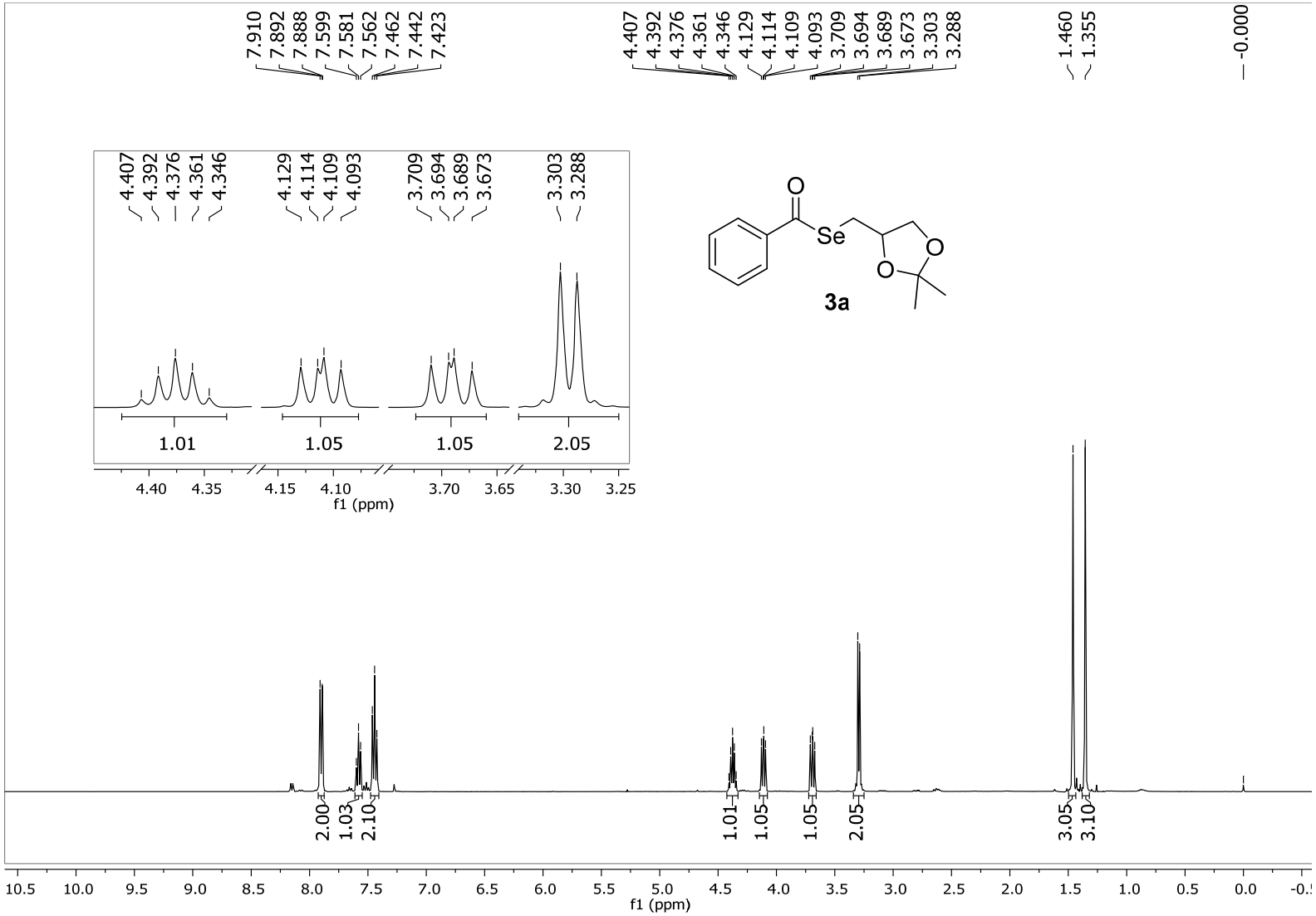

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzoselenoate **3a**.

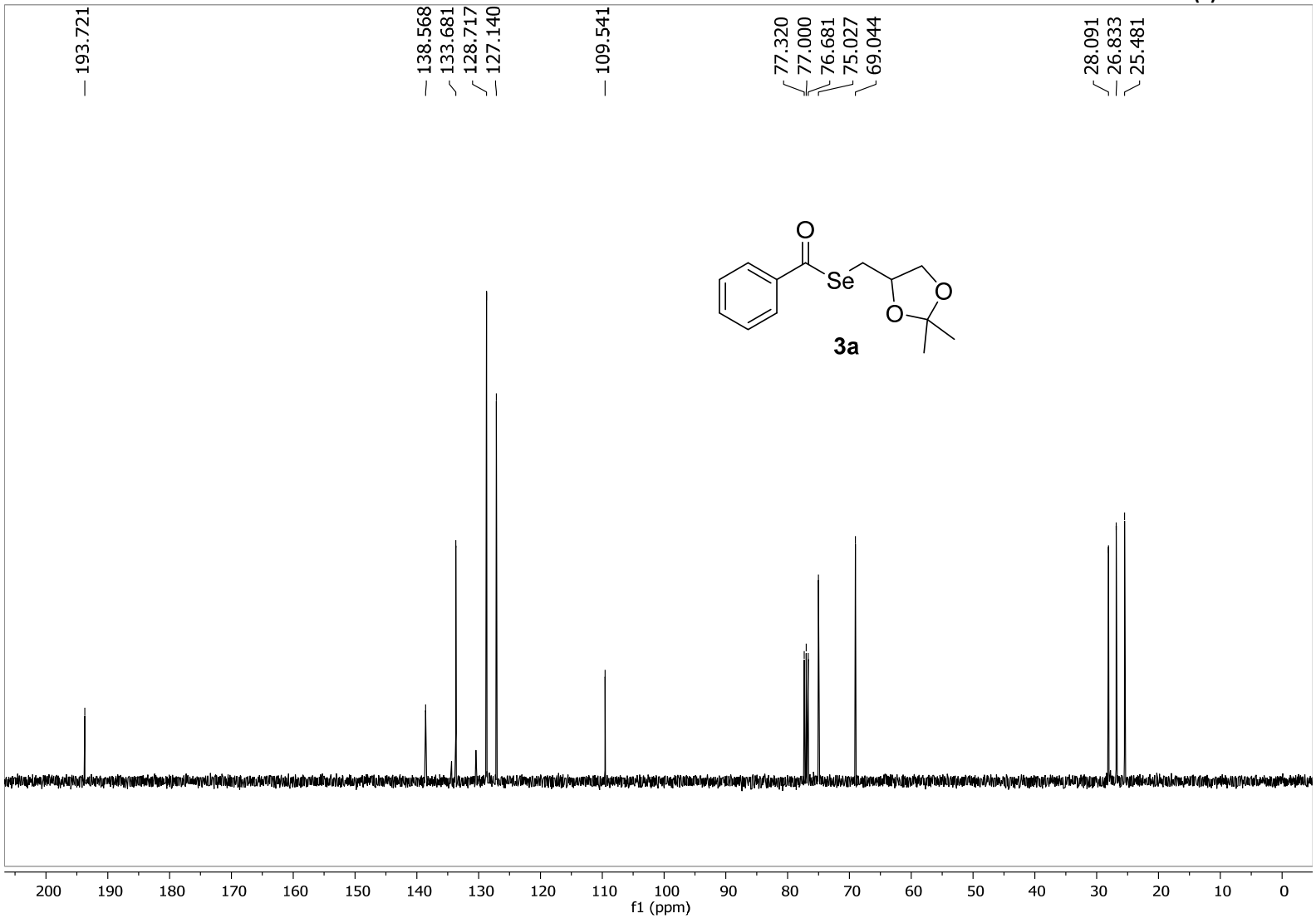

Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzoselenoate **3a**.

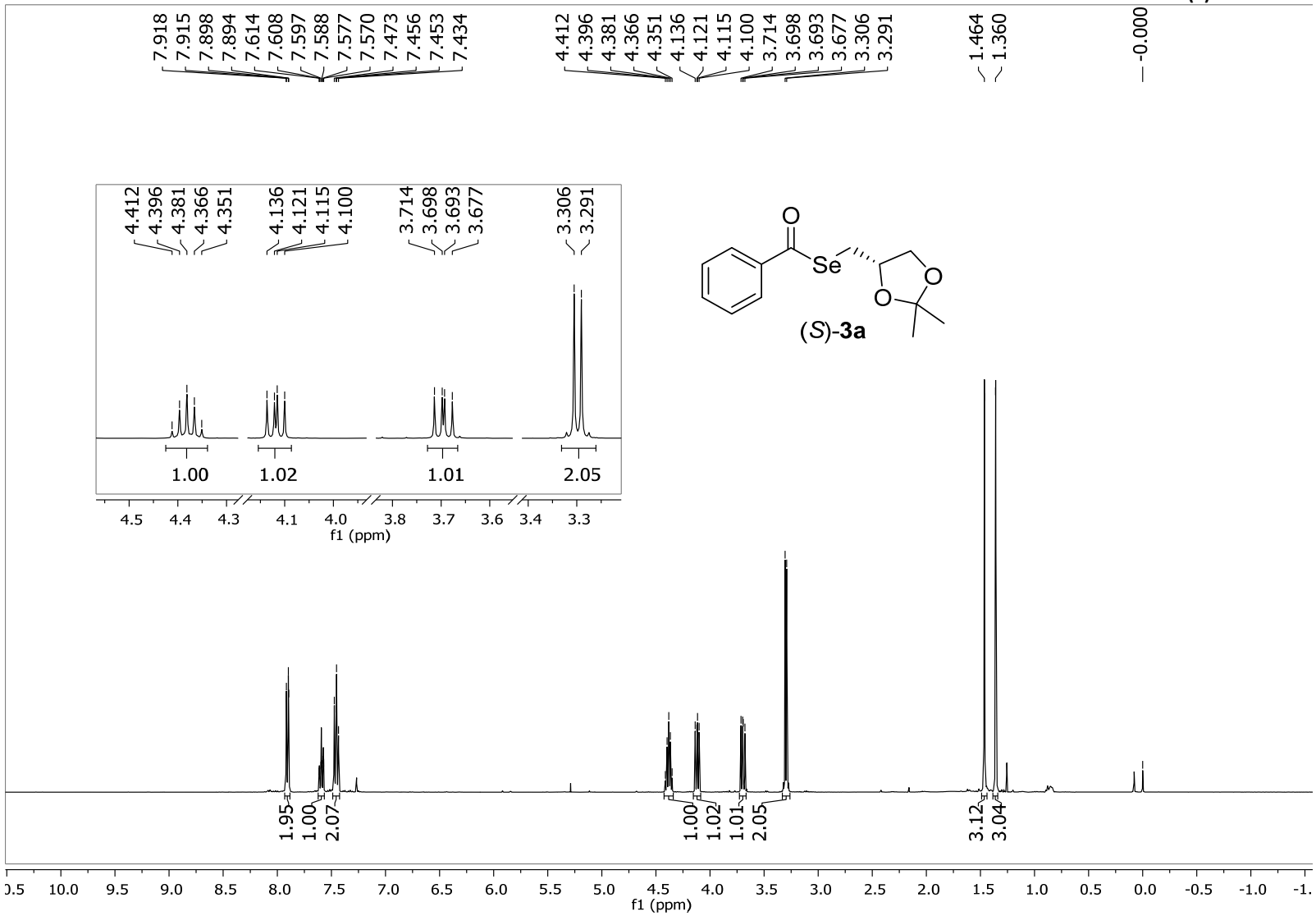

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-*Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzoselenoate (S)-**3a**.

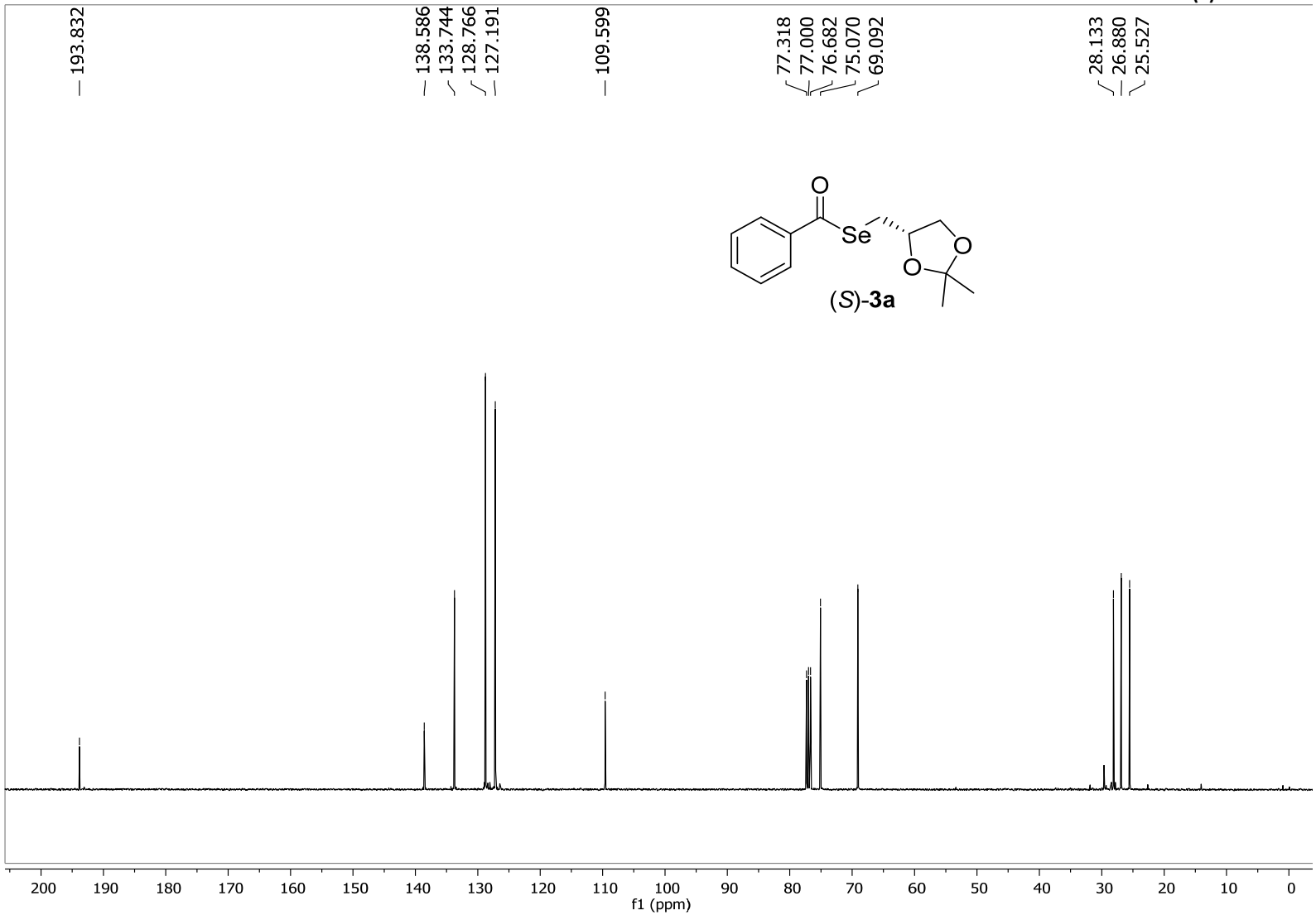

Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-*Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzoselenoate (*S*)-**3a**.

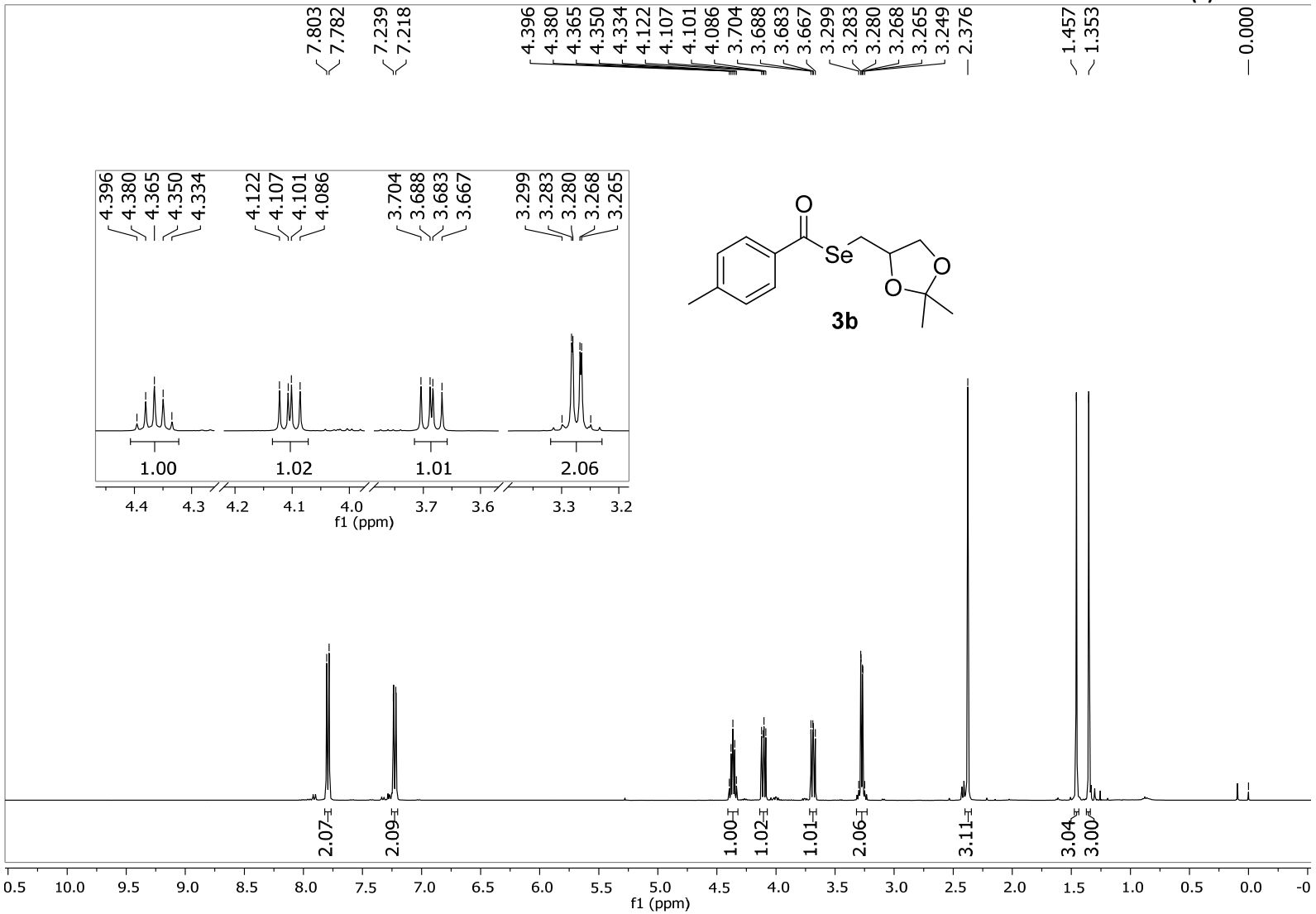

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Se-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]4-methylbenzoselenoate **3b**.

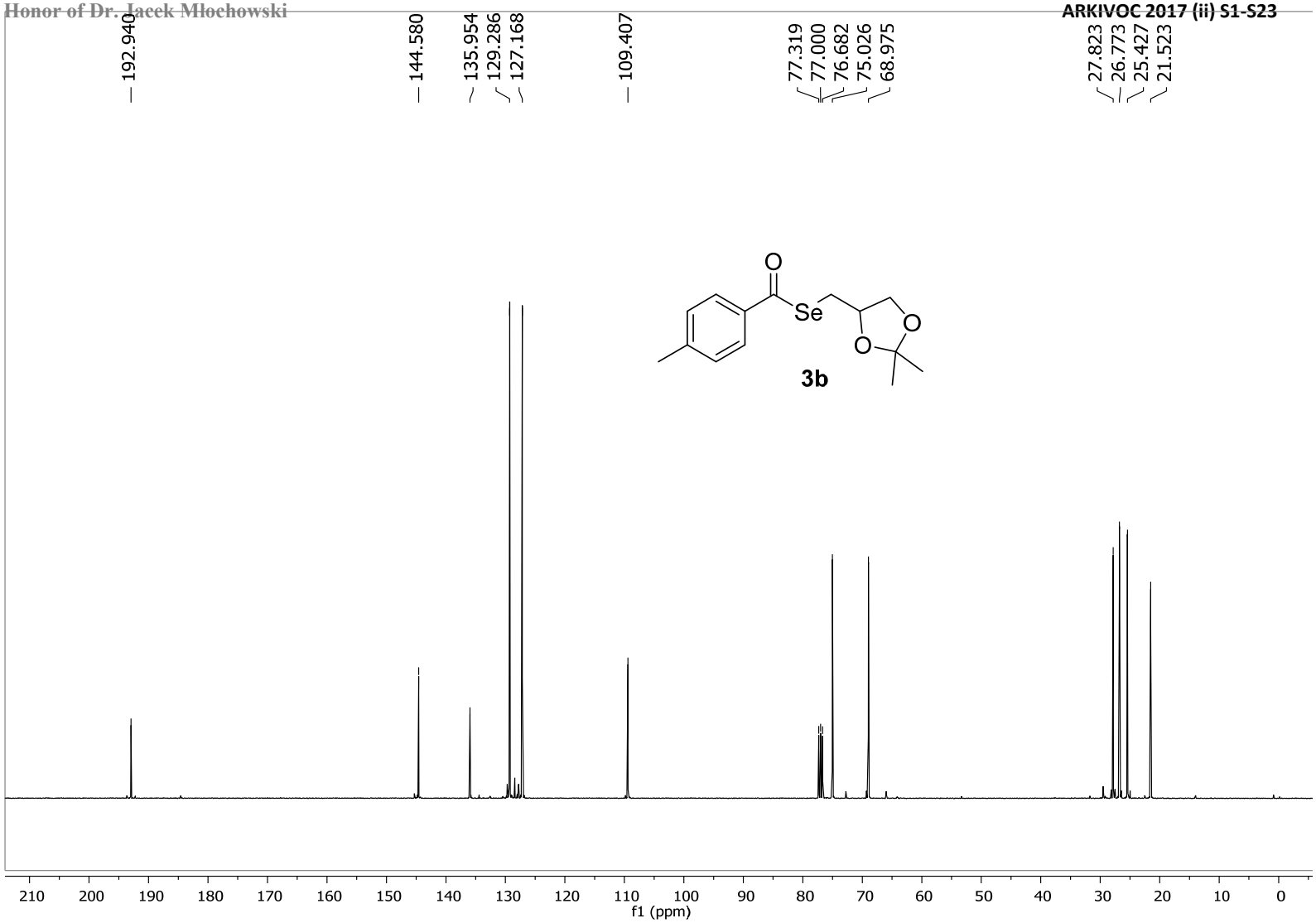

Figure S6. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]4-methylbenzoselenoate **3b**.

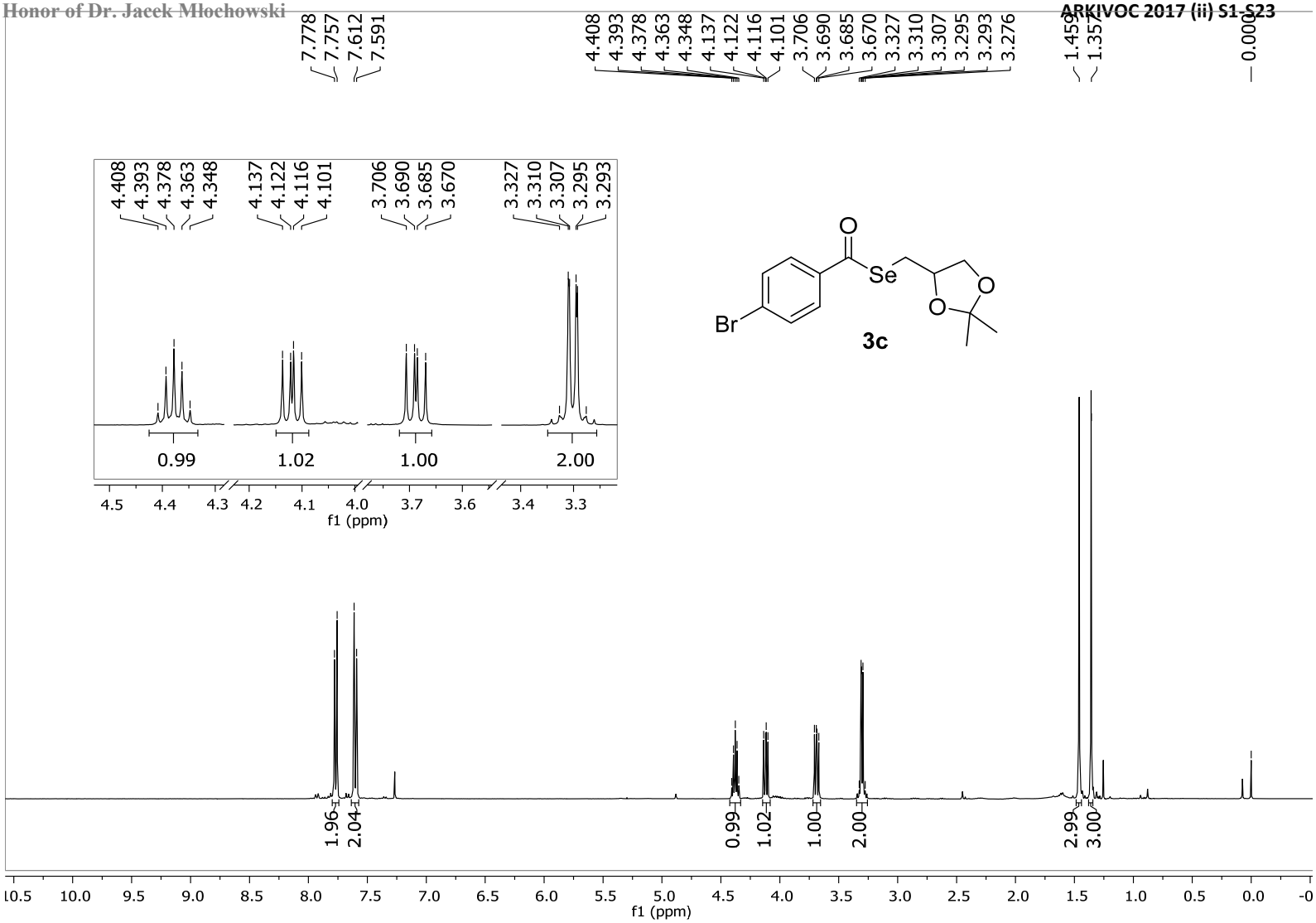

Figure S7.[1]H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]4-bromobenzoselenoate **3c**.

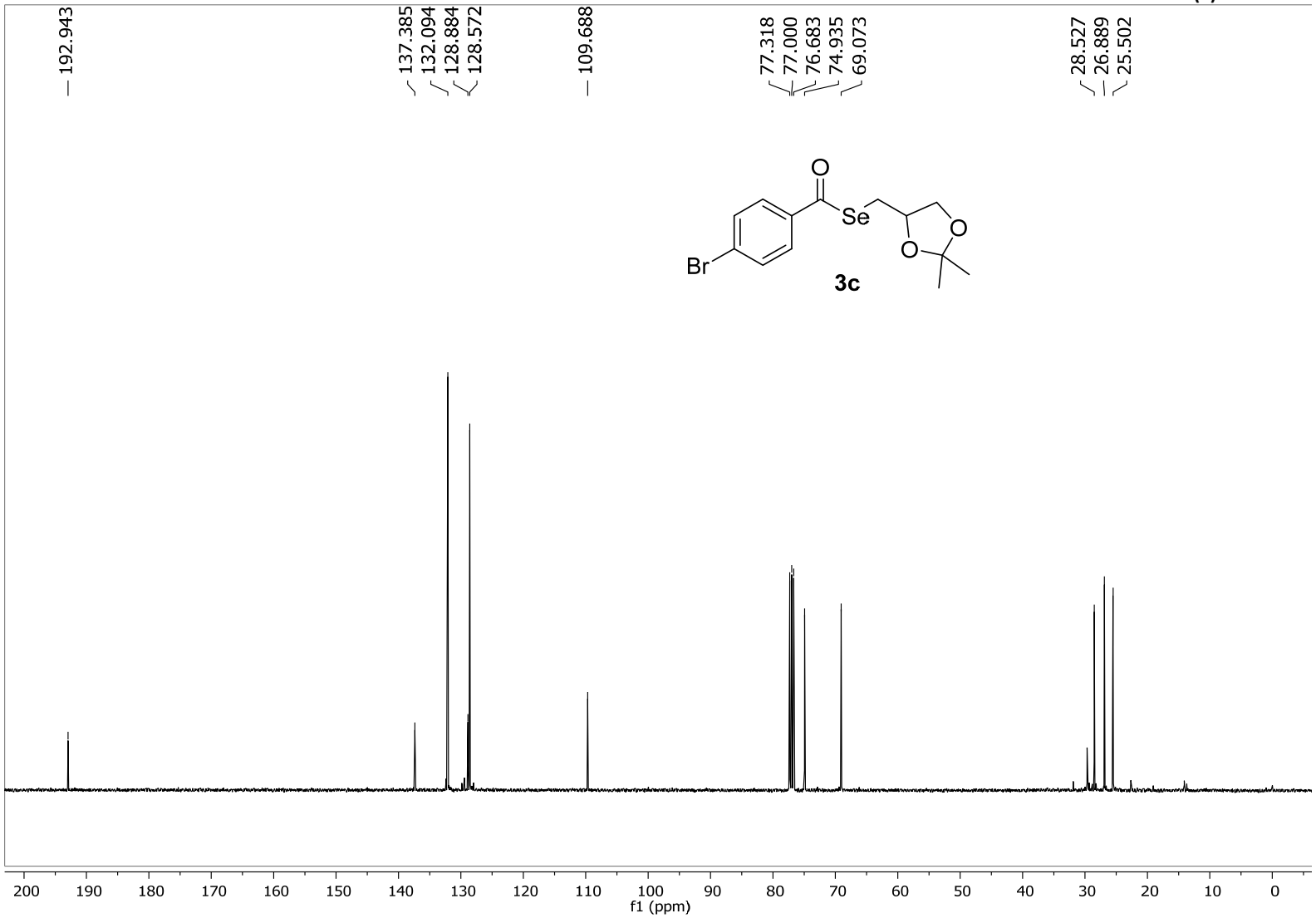

Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]4-bromobenzoselenoate **3c**.

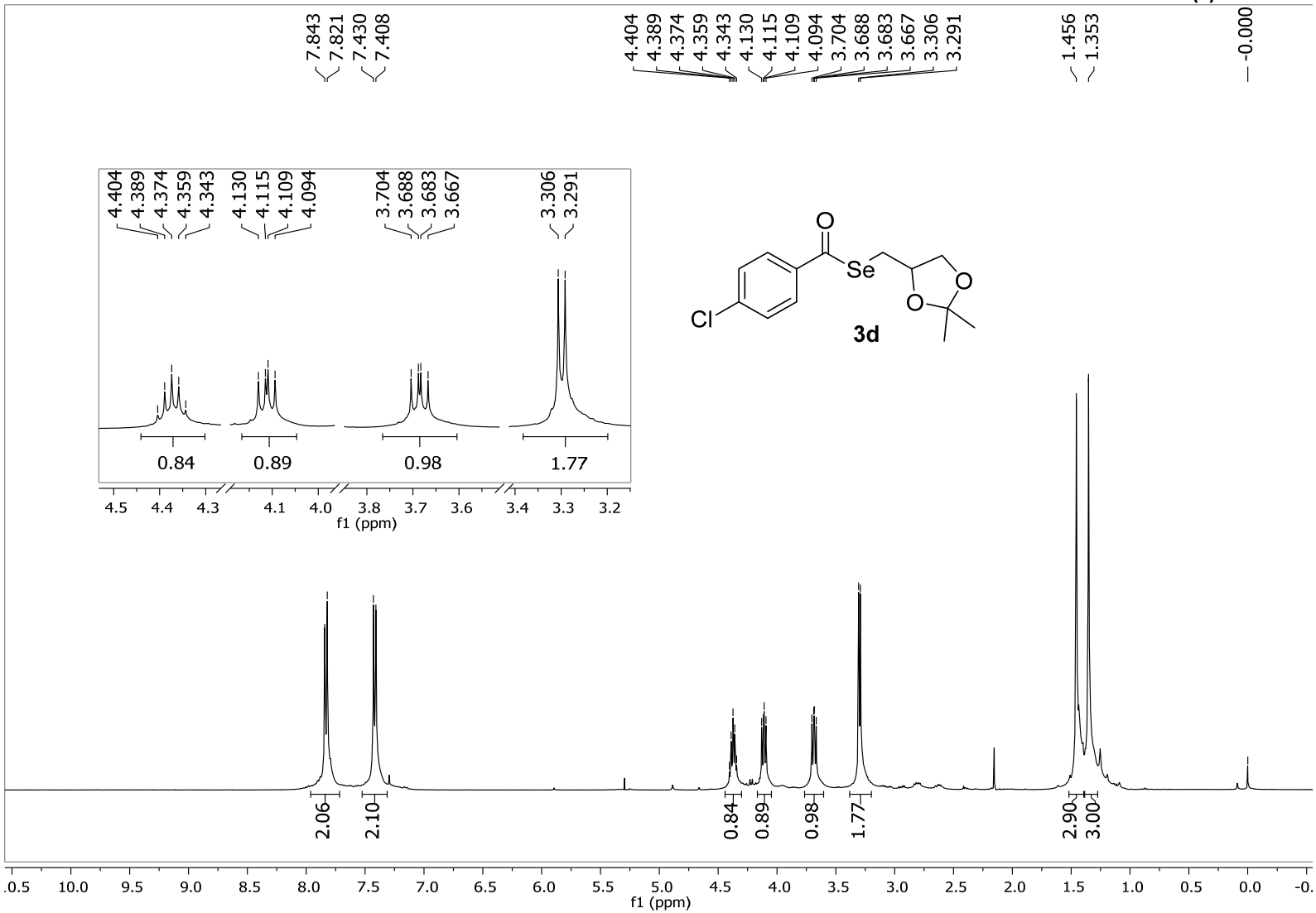

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]4-chlorobenzoselenoate **3d**.

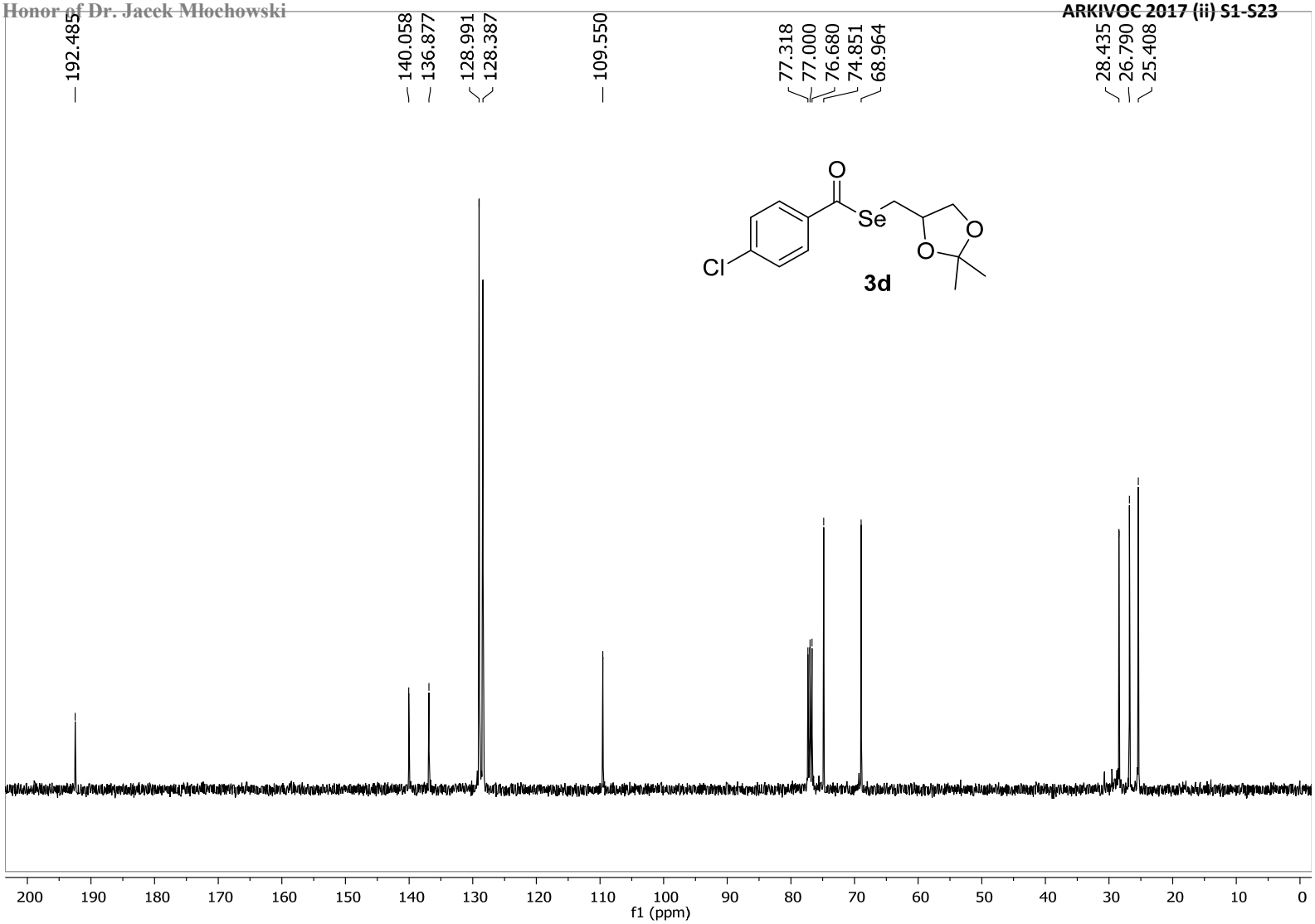

Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of Se-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]4-chlorobenzoselenoate **3d**.

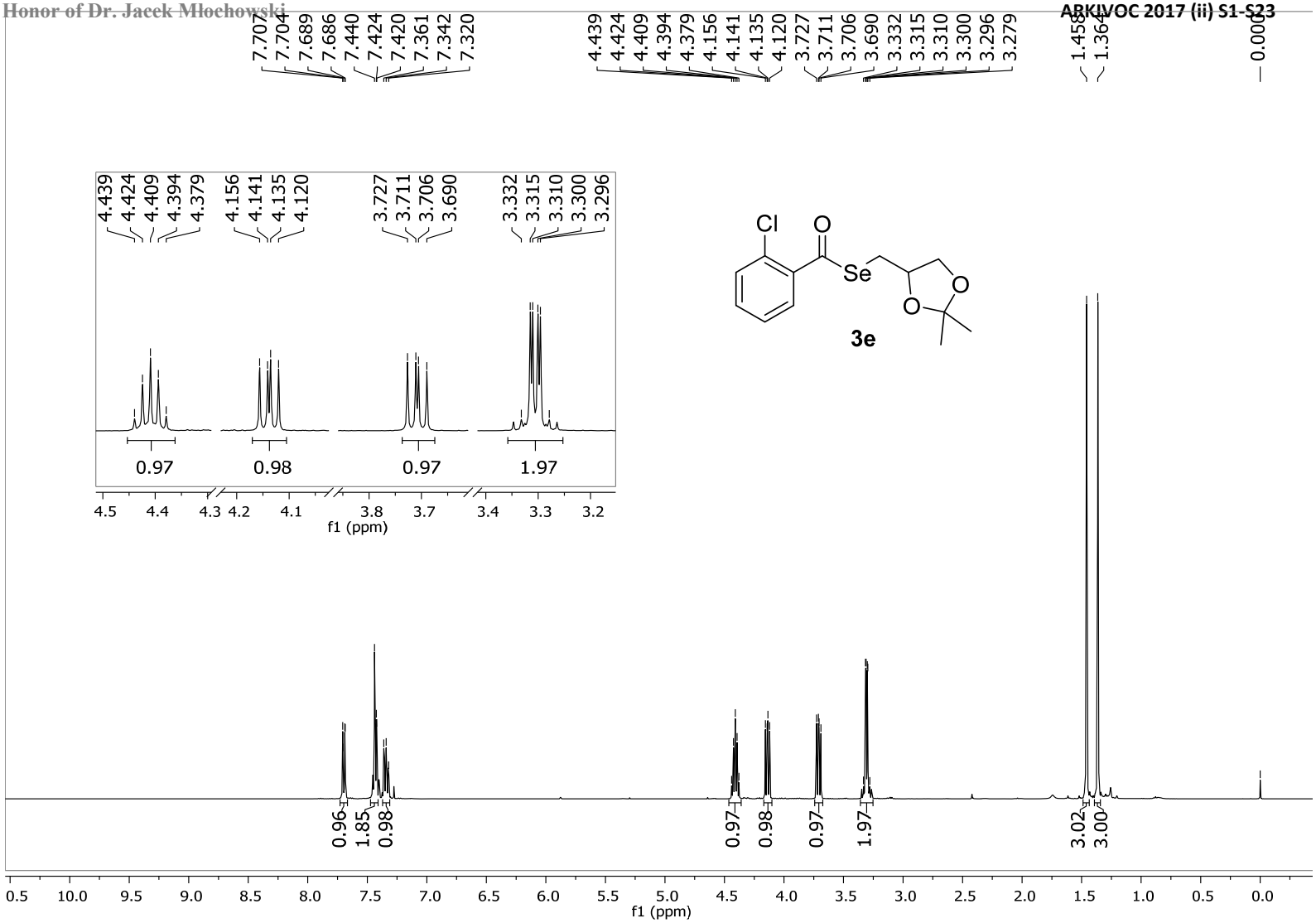

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]2-chlorobenzoselenoate **3e**.

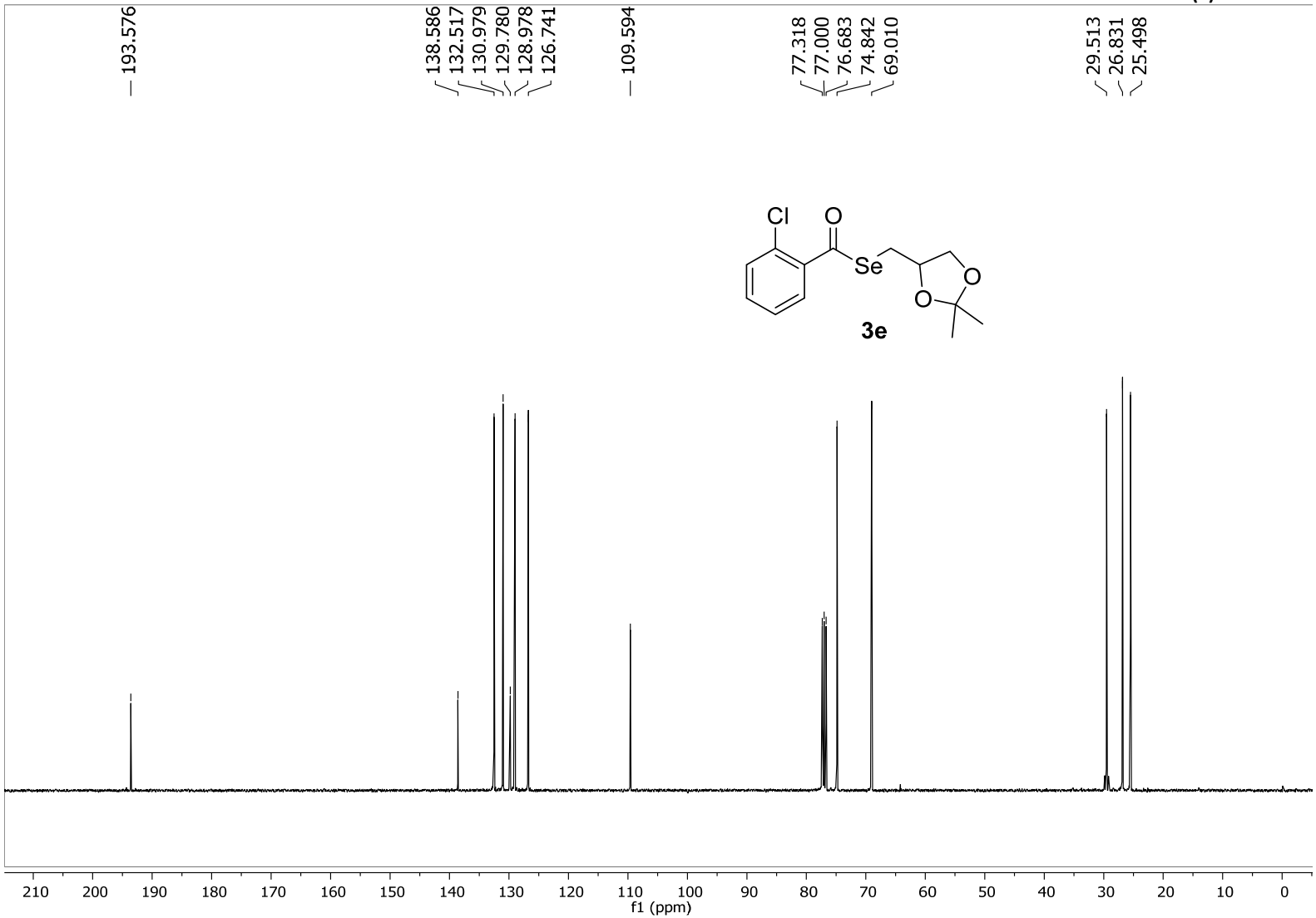

Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]2-chlorobenzoselenoate **3e**.

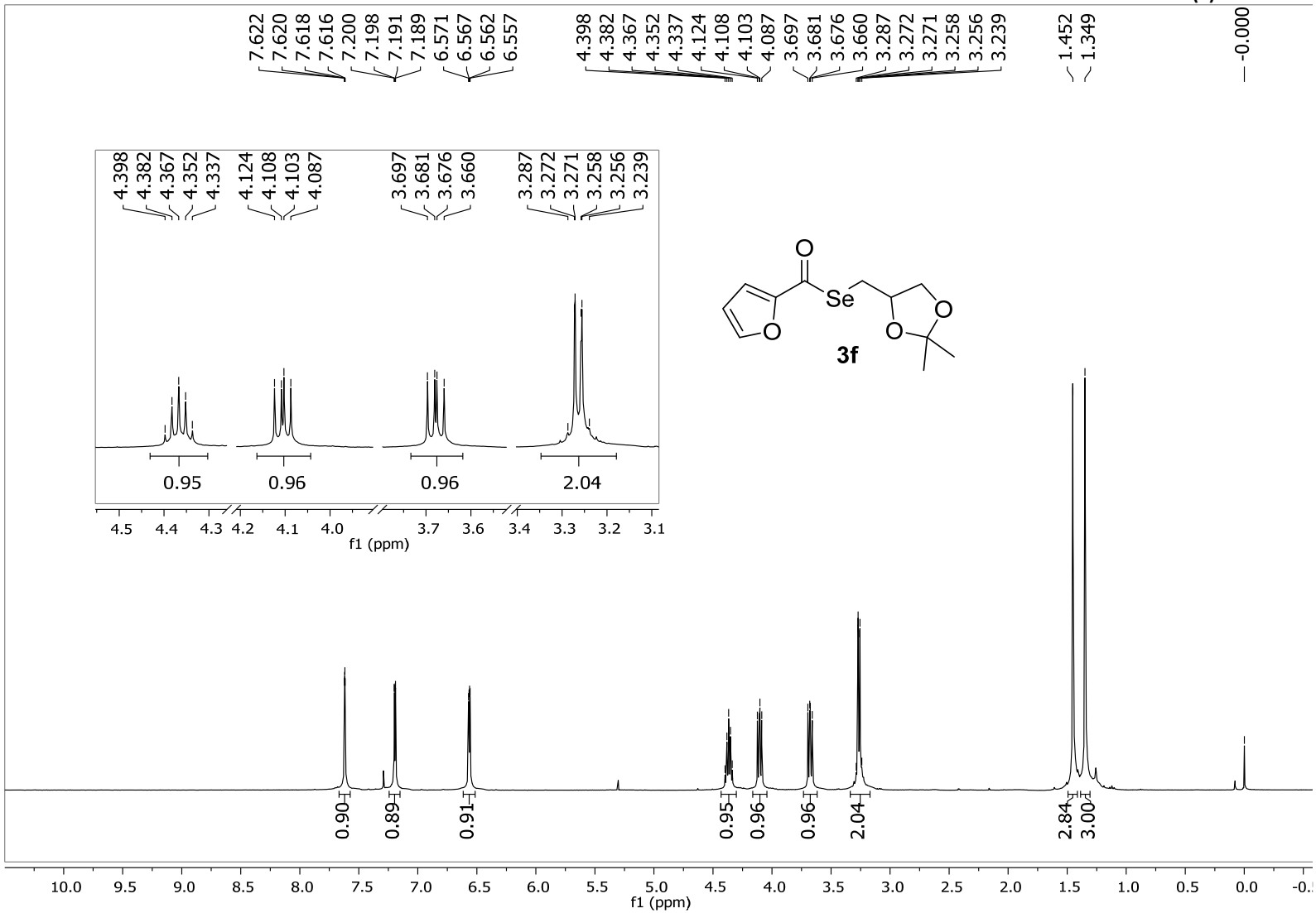

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]furan-2-carboselenoate **3f**.

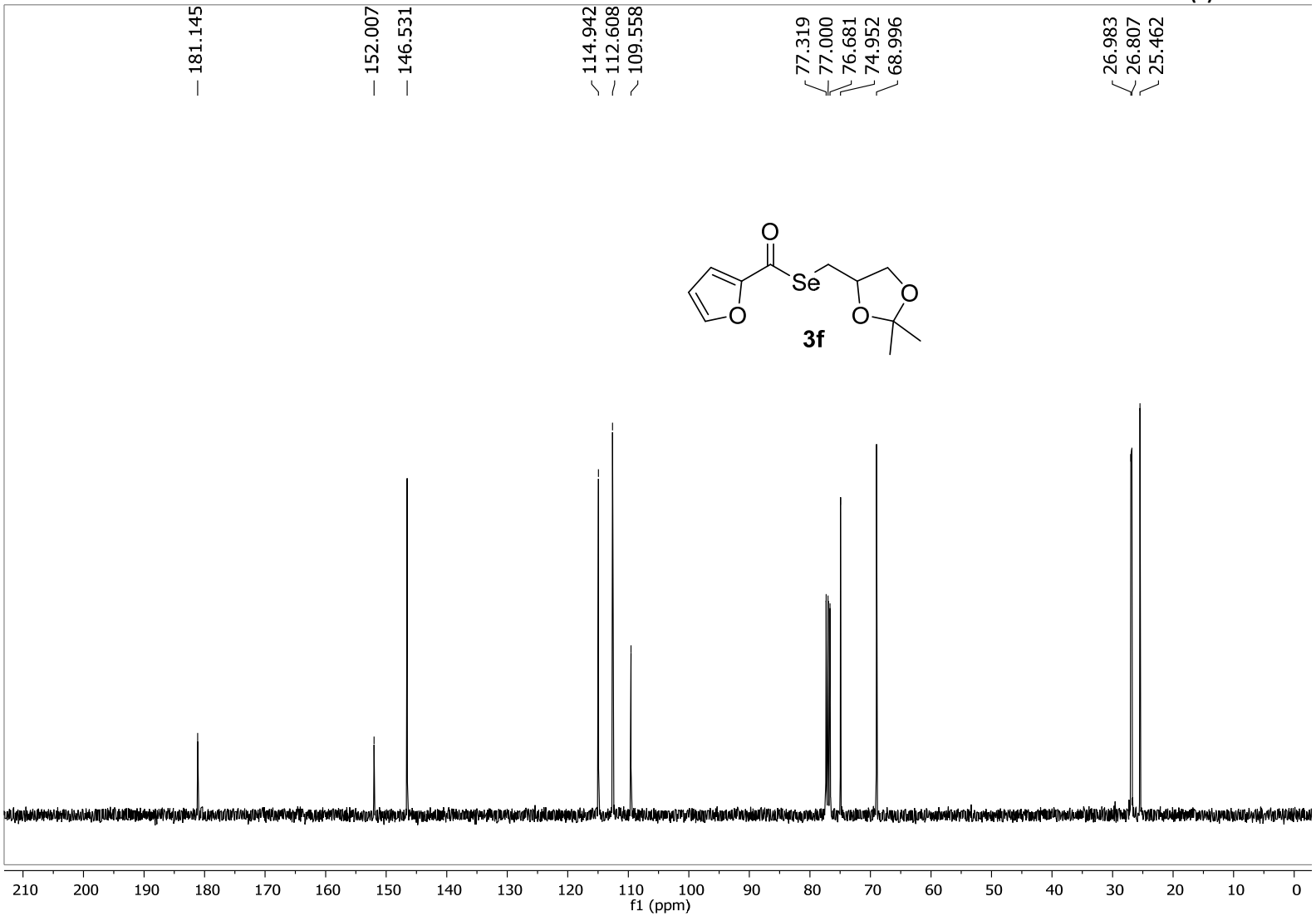

Figure S14.[13]C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]furan-2-carboselenoate **3f**.

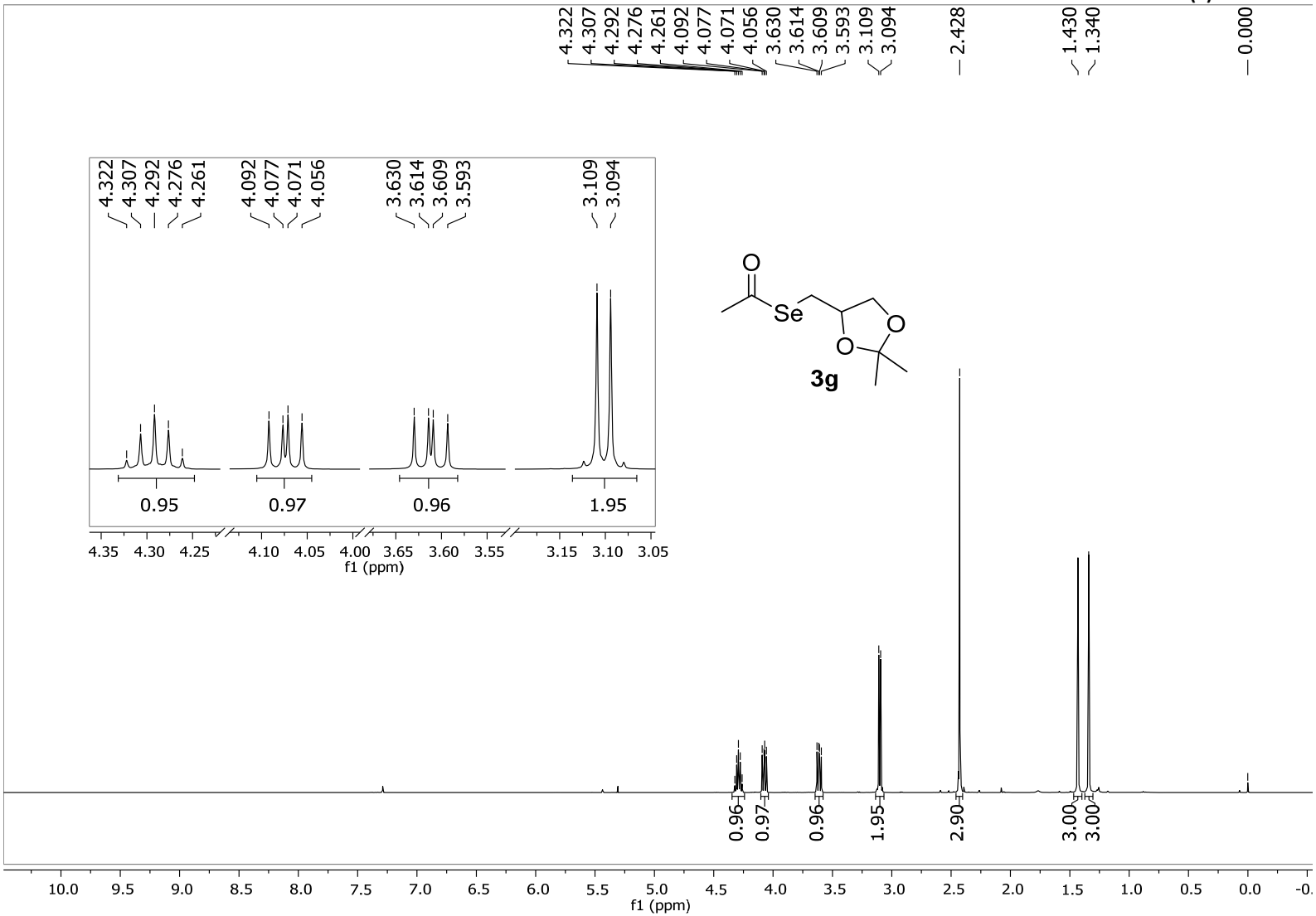

Figure S15.[1]H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]ethaneselenoate **3g**.

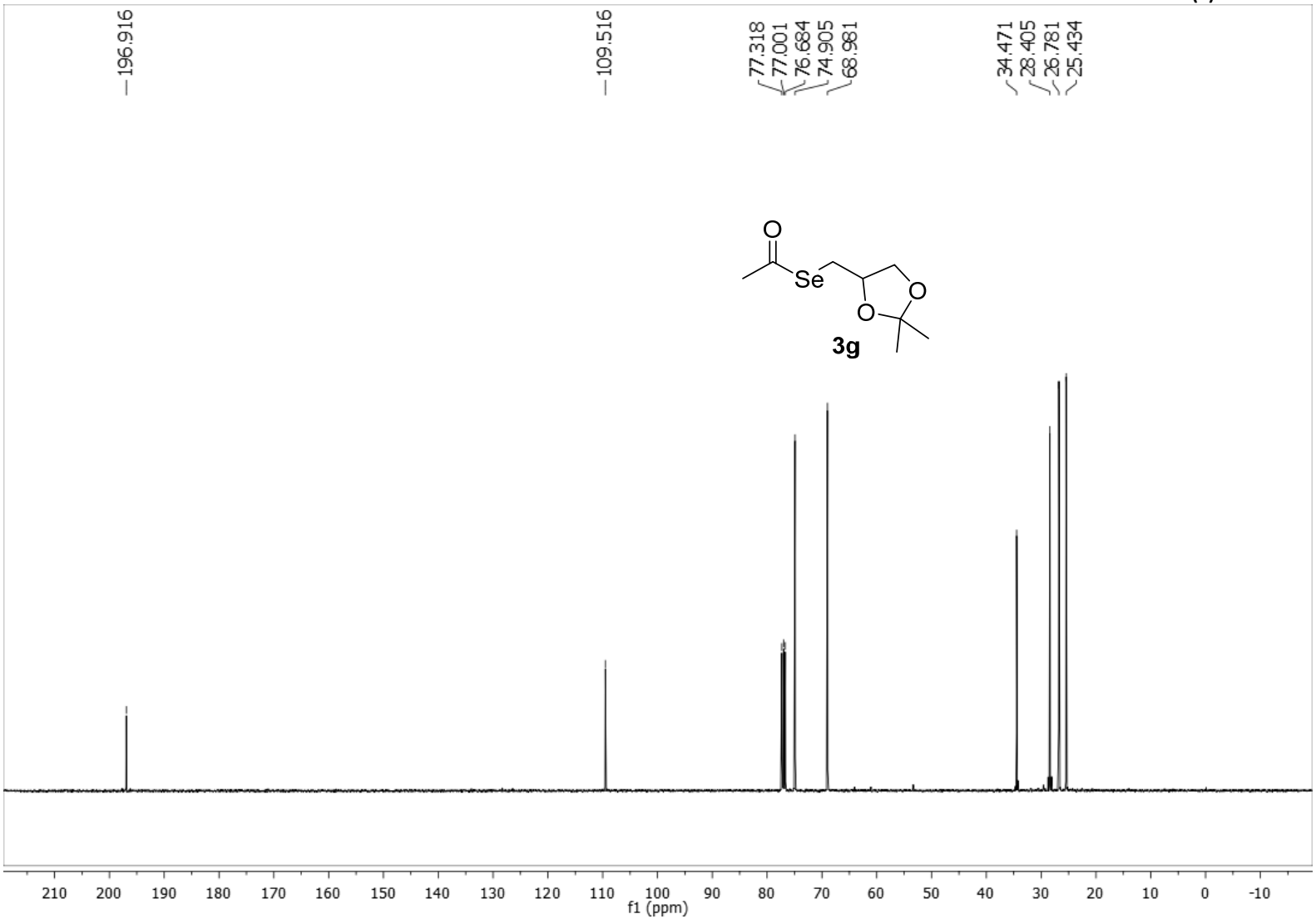

Figure S16.[13]C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]ethaneselenoate **3g**.

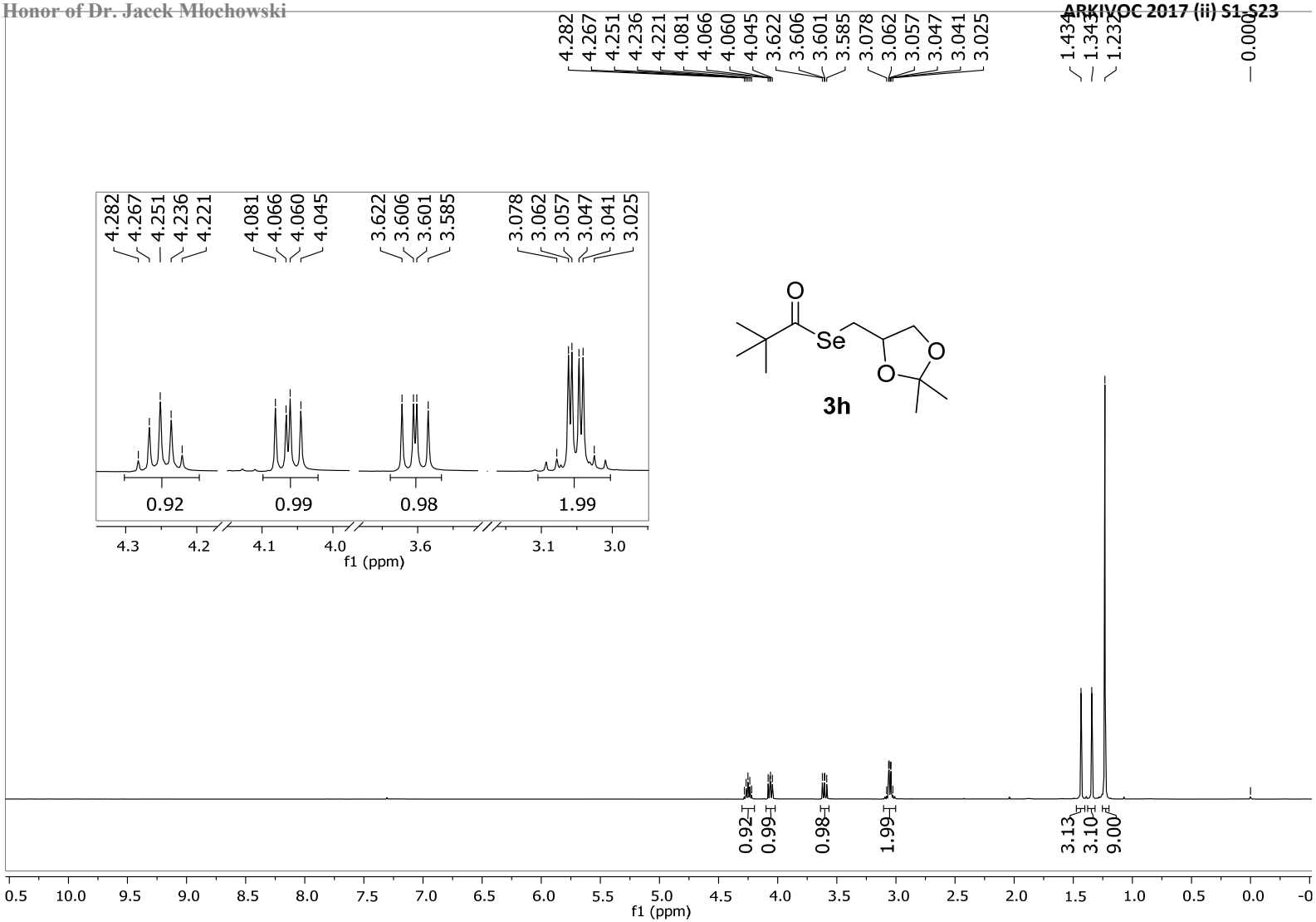

Figure S17.[1]H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]2,2-dimethylpropaneselenoate **3h**.

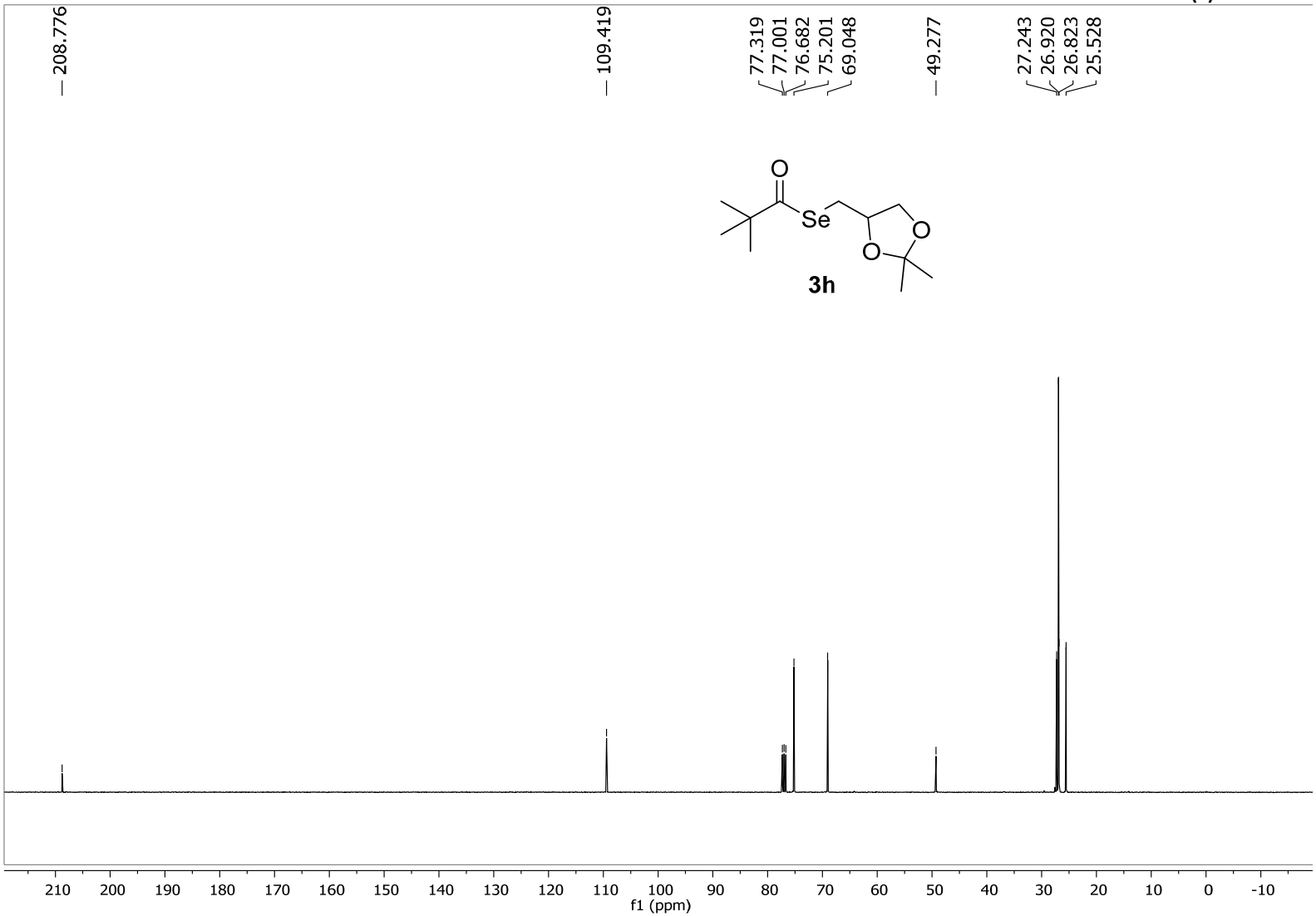

Figure S18.[13]C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]2,2-dimethylpropaneselenoate **3h**.

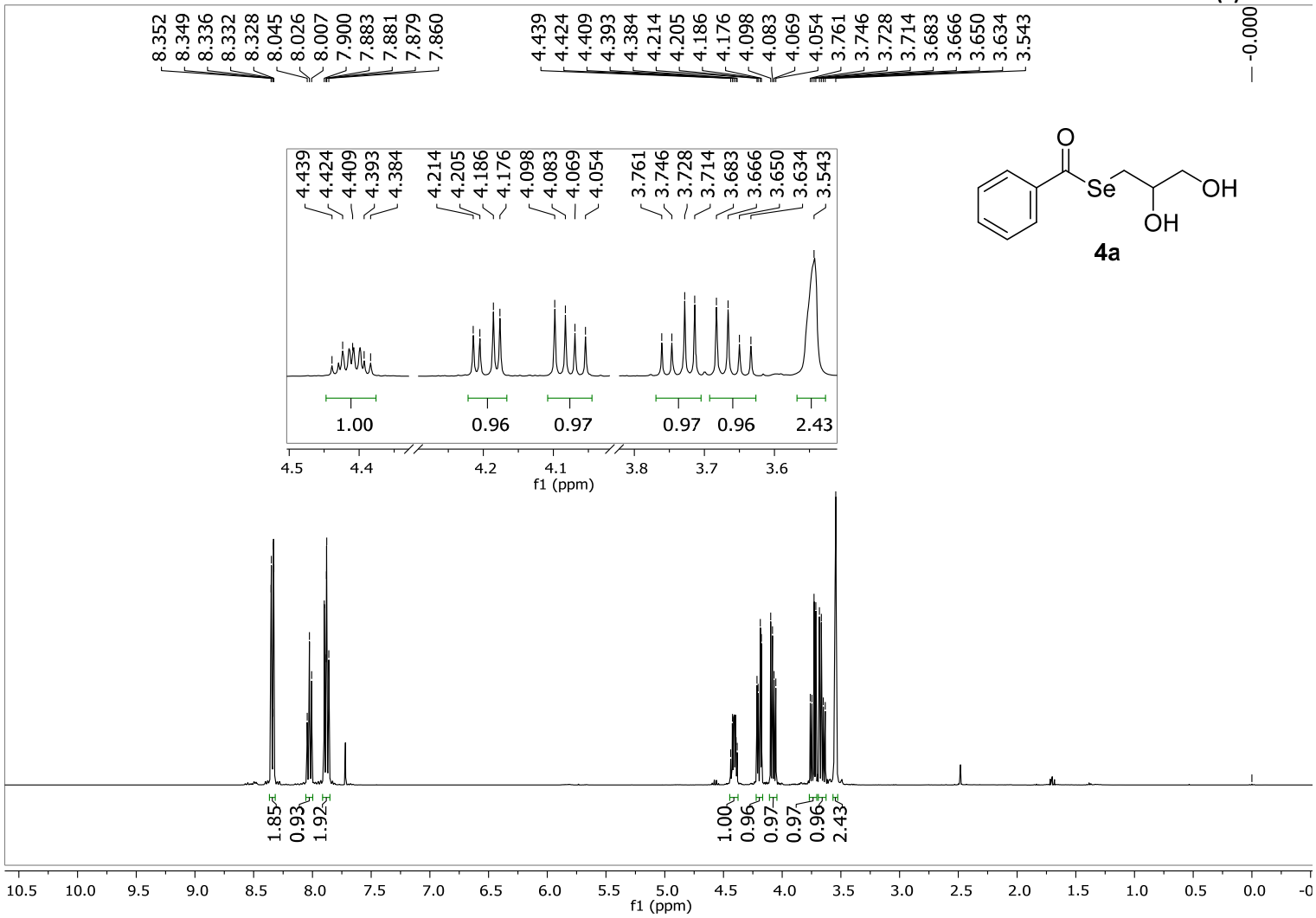

Figure S19.[1]H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-(2,3-dihydroxypropyl)benzoselenoate **4a**.

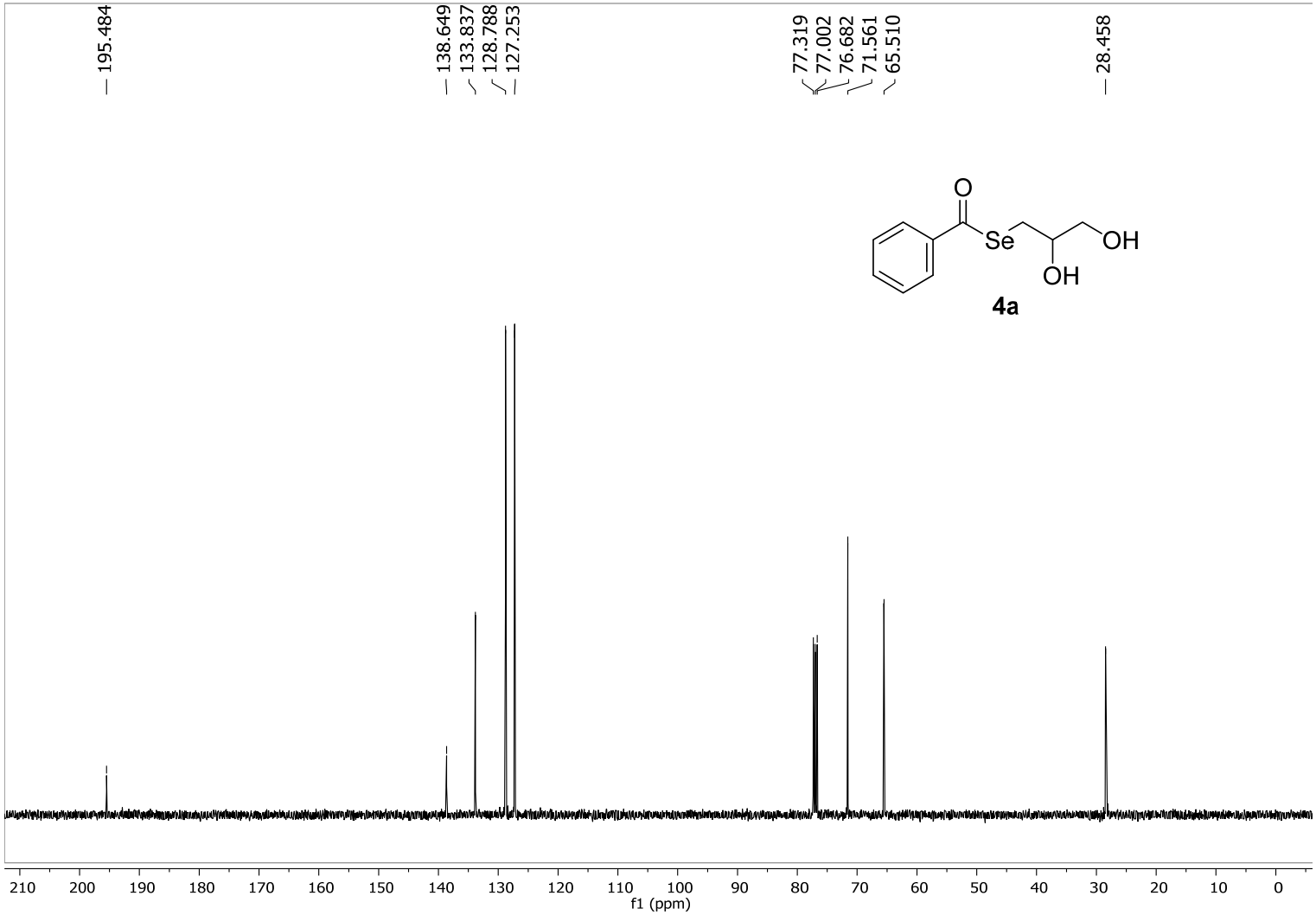

Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-(2,3-dihydroxypropyl)benzoselenoate **4a**.