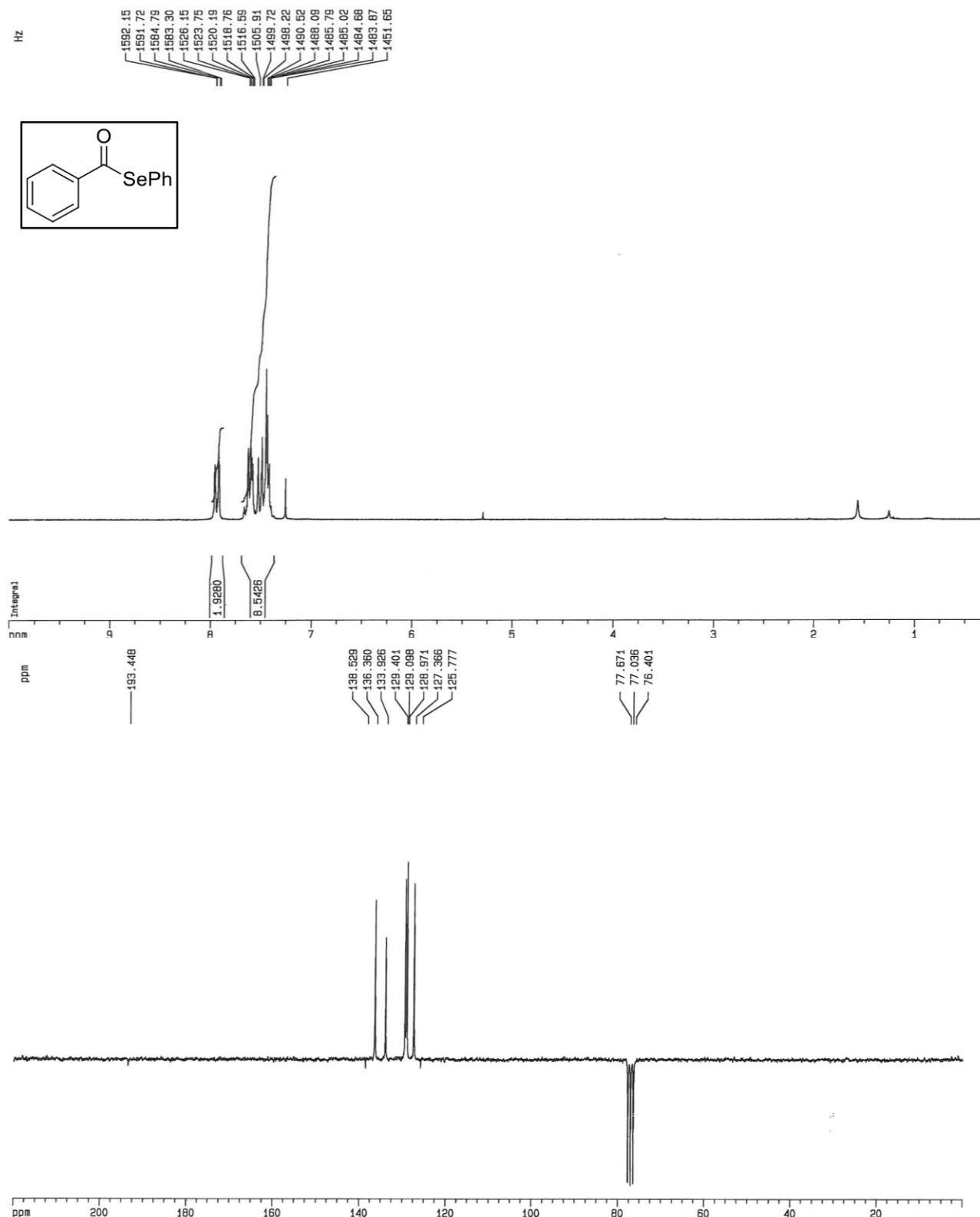


## Supplementary material

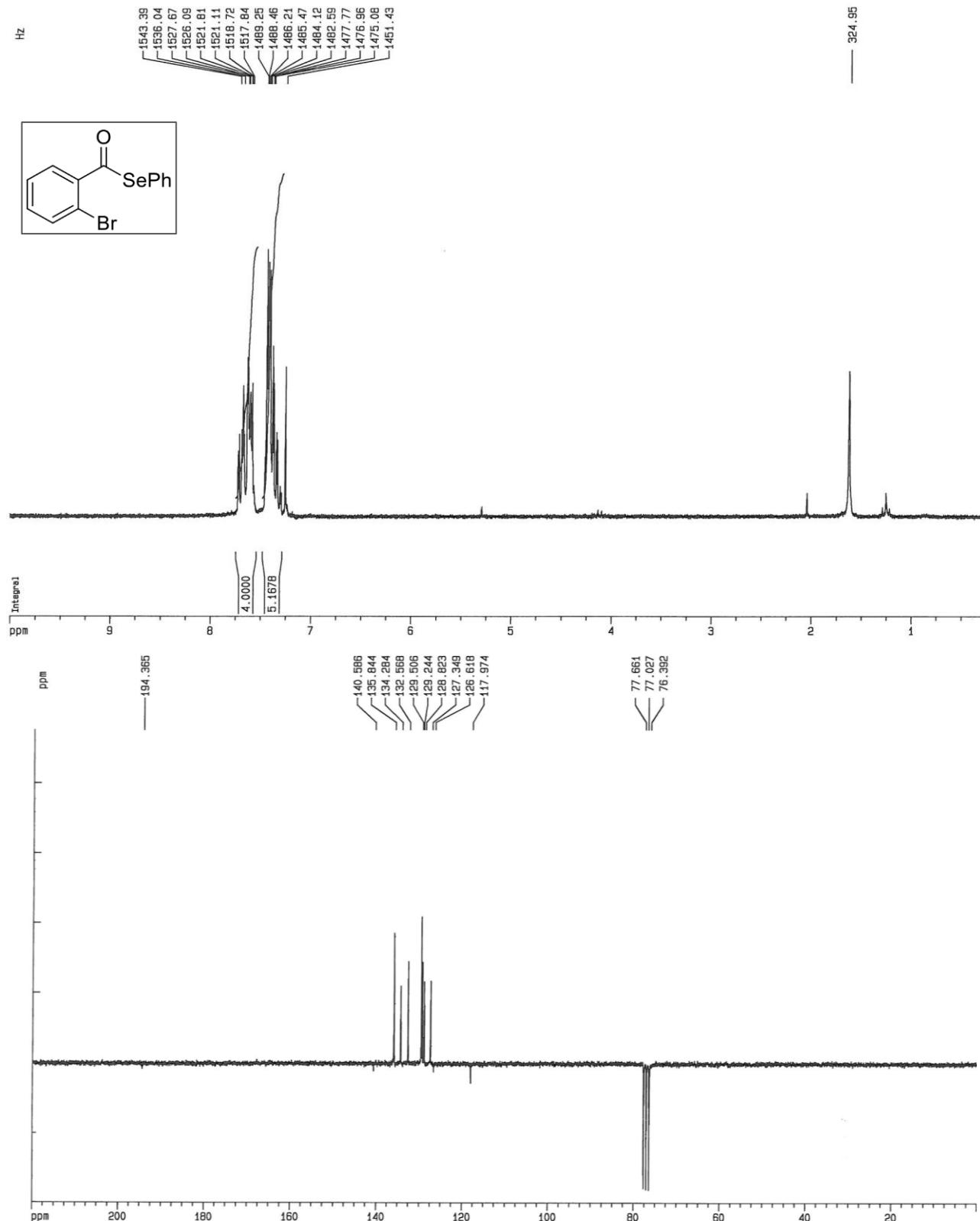
# **Atom Efficient preparation of Zinc Selenates for the Synthesis of Selenoesters under “*On Water*” Conditions**

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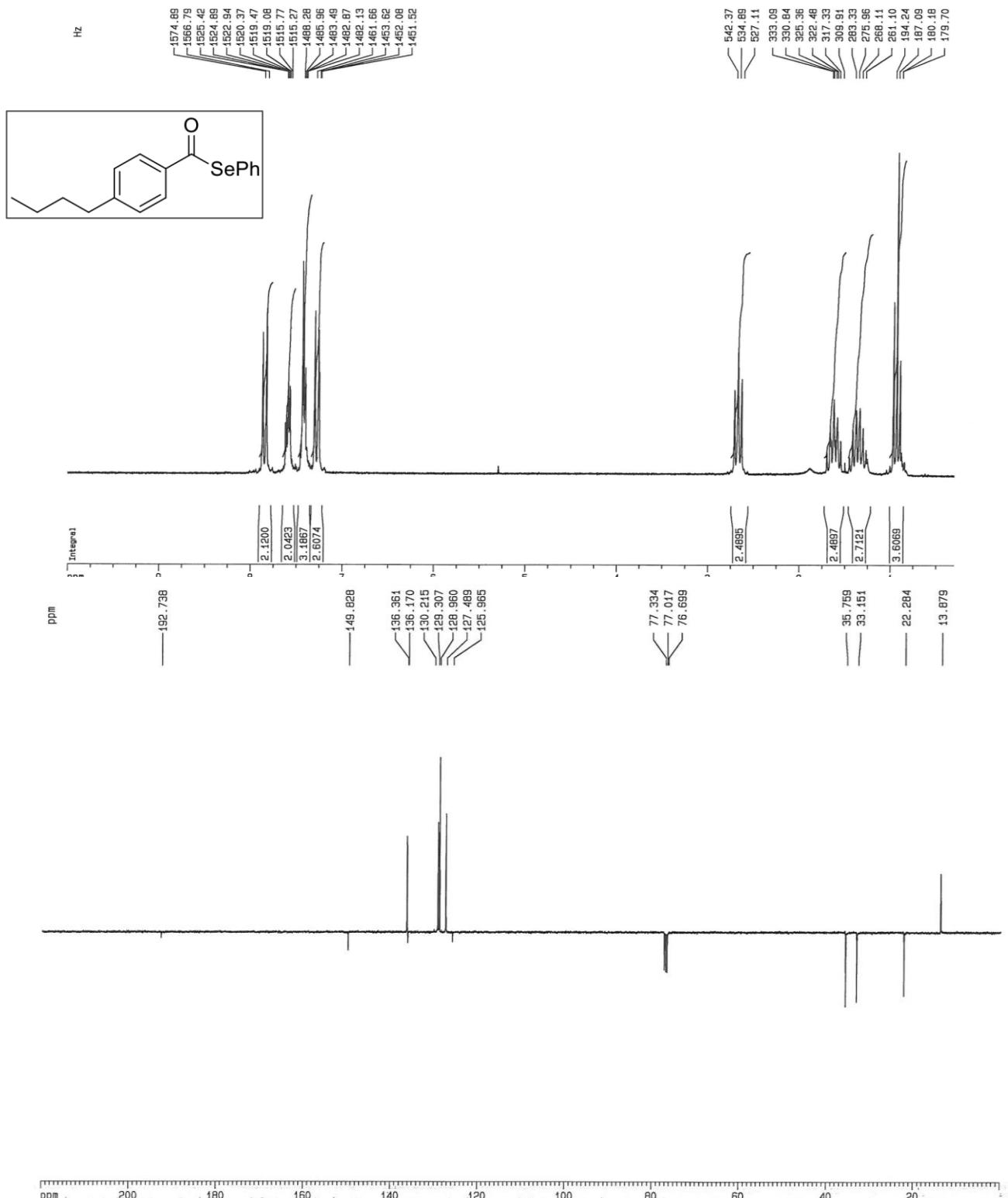
*Se-Phenyl benzoselenoate (**5a**)* [1] purified eluting with 20 % DCM in petroleum ether. Yellow solid. M.p.: 39°-40°C (Lit.:[38] 37°-38°C).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 200 MHz, ppm)  $\delta$ : 7.96-7.92 (m, 2H, H-Ar), 7.63-7.42 (m, 8H, H-Ar) ppm.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz, ppm)  $\delta$ : 193.5, 138.5, 136.4, 133.9, 129.4, 129.1, 128.9, 127.4, 125.8 ppm. CG-MS:  $m/z$  (%)= 262 (1) [ $\text{M}^+$ ], 157 (5), 105 (100), 77 (50), 51 (14).



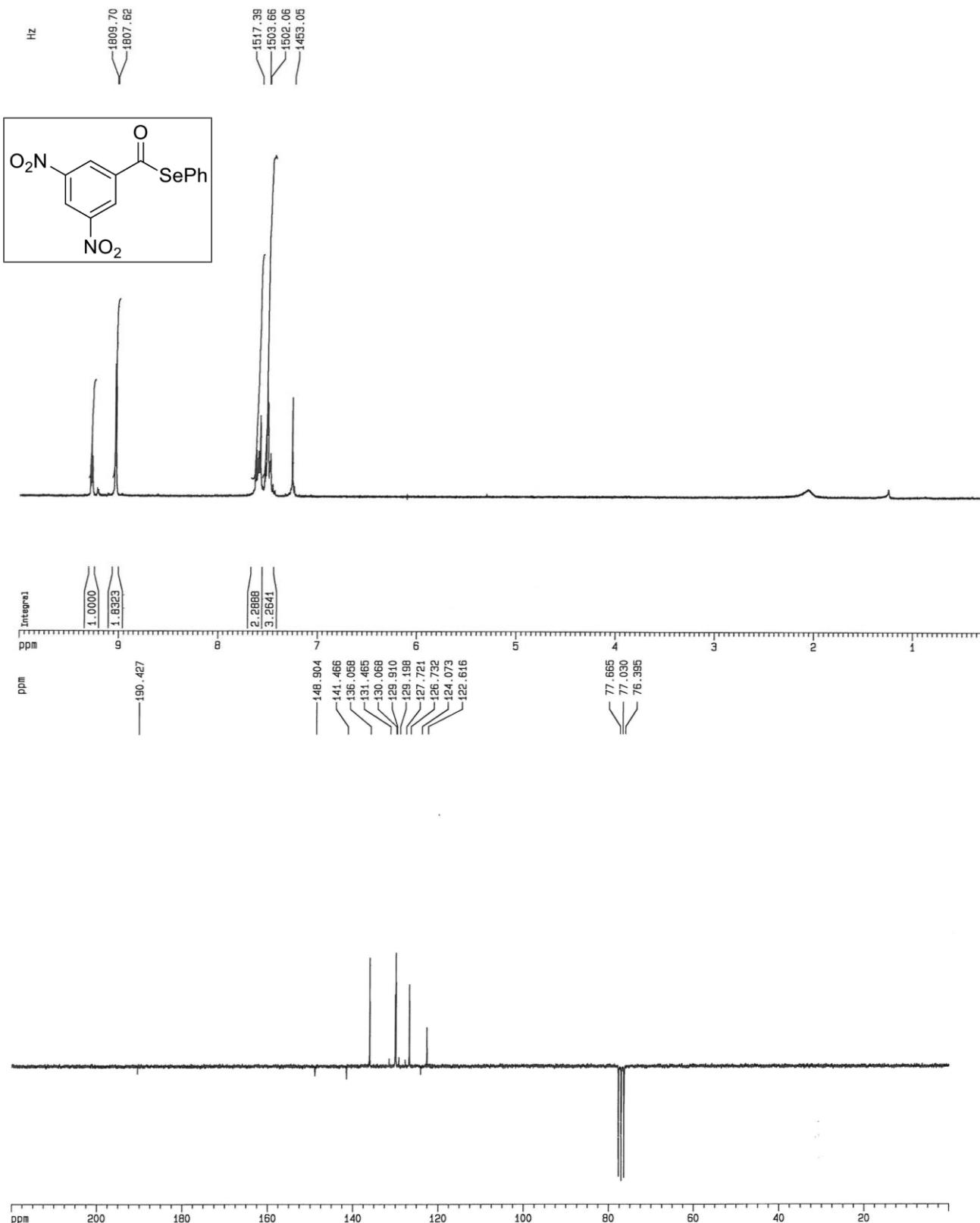
**Se-Phenyl 2-bromobenzoselenoate (5b)** [2] purified eluting with 5 % EtOAc in petroleum ether. Yellow oil. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm) δ: 7.72-7.6 (m, 4H, H-Ar), 7.45-7.34 (m, 5H, H-Ar) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz, ppm) δ: 194.4, 140.6, 135.8, 134.3, 132.6, 129.5, 129.2, 128.8, 127.3, 126.6, 118.0 ppm. CG-MS *m/z* (%)= 340 (1) [M<sup>+</sup>], 232 (3), 183 (100), 157 (54), 76 (16), 50 (9).



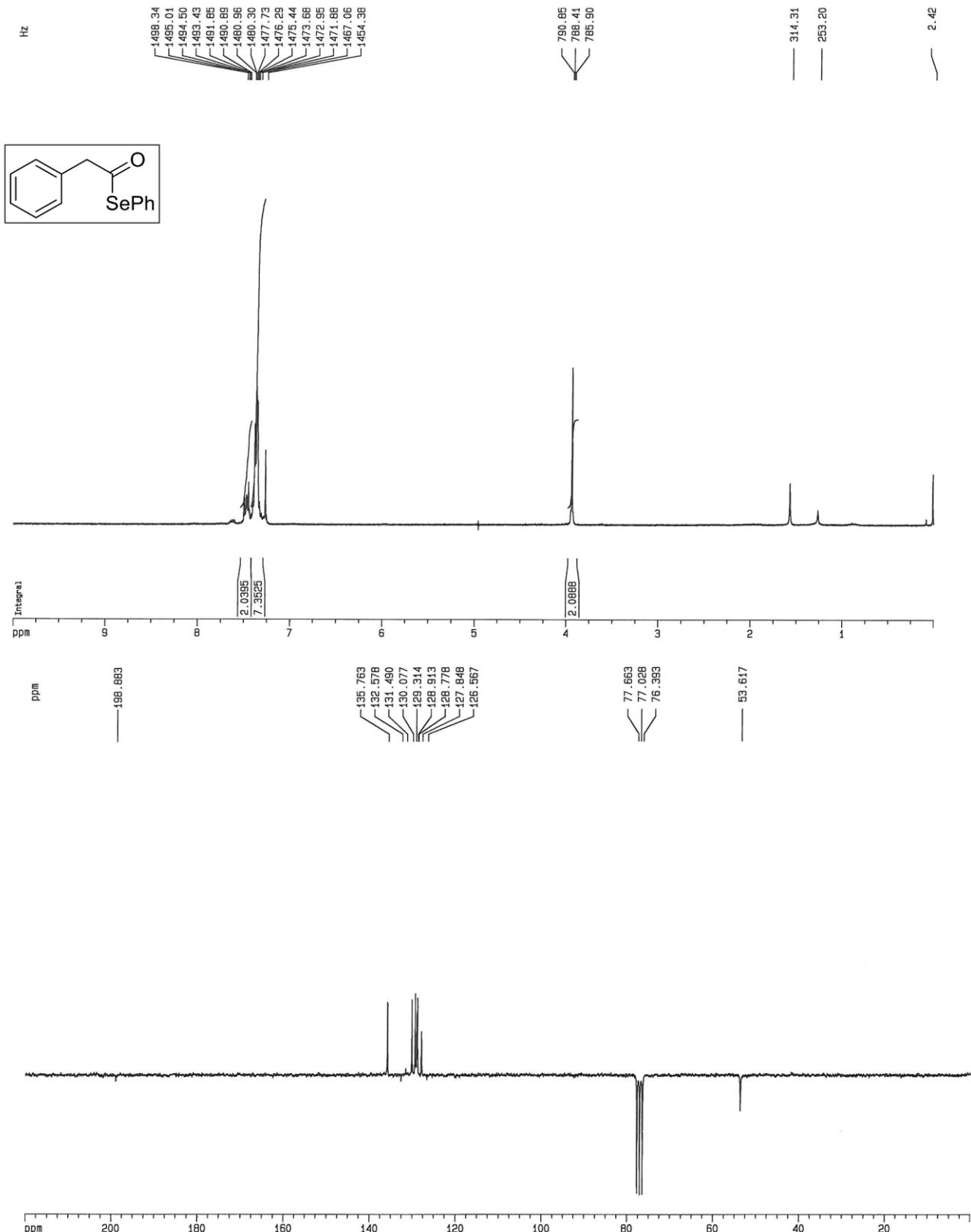
**Se-Phenyl 4-butylbenzoselenoate (5c)** [3] purified eluting with 20 % DCM in petroleum ether. Yellow oil. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm) δ: 7.85 (d, *J*= 8.1 Hz, 2H, H-Ar), 7.61-7.57 (m, 2H, H-Ar), 7.44-7.41 (m, 3H, H-Ar), 7.31-7.26 (m, 2H, H-Ar), 2.67 (t, *J*= 7.8 Hz, 2H, CH<sub>2</sub>), 1.61 (quin, *J*= 8.15 Hz, 2H, CH<sub>2</sub>), 1.36 (sex, *J*= 7.6 Hz, 2H, CH<sub>2</sub>), 0.95 (t, *J*= 7.2 Hz, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz, ppm) δ: 192.7, 149.8, 136.4, 136.2, 129.3, 129.0, 127.5, 126.0, 35.8, 33.1, 22.3, 13.9 ppm. CG-MS *m/z* (%)= 318 [M<sup>+</sup>], 161 (100), 91 (30).



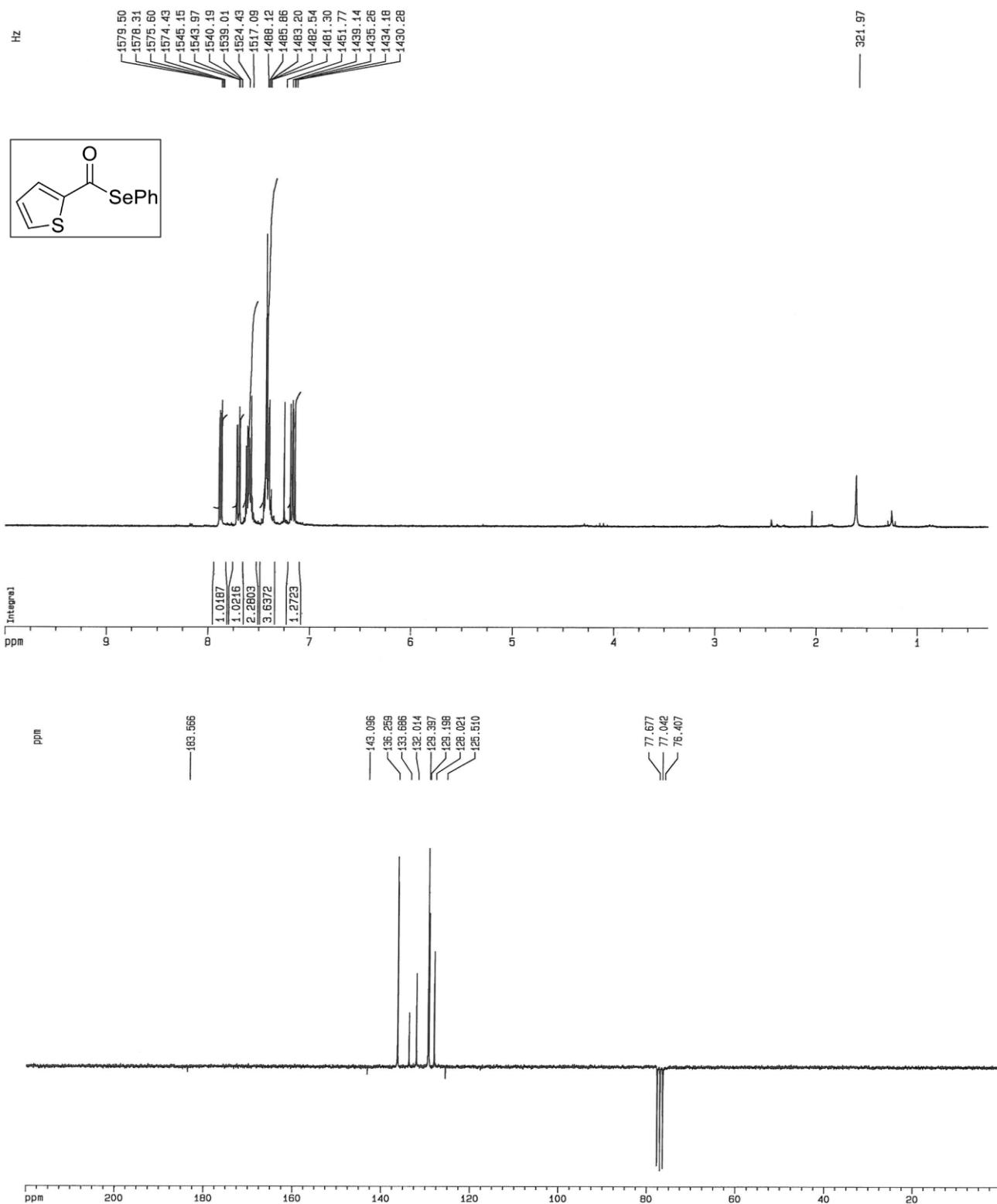
**Se-Phenyl-3,5-dinitrobenzoselenoate (5d)** [3] purified eluting with 5 % EtOAc. Yellow solid. M.p.: 148-150°C ((Lit.:[3] 148°-150°).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 200 MHz, ppm)  $\delta$ : 9.28 (t,  $J$ = 2.05 Hz, 1H, H-Ar), 9.04 (d,  $J$ = 2.06 Hz, 2H, H-Ar), 7.7-7.4 (m, 5H, H-Ar) ppm.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz, ppm)  $\delta$ : 190.4, 148.9, 141.5, 136.1, 130.07, 129.9, 126.7, 124.1, 122.6 ppm.



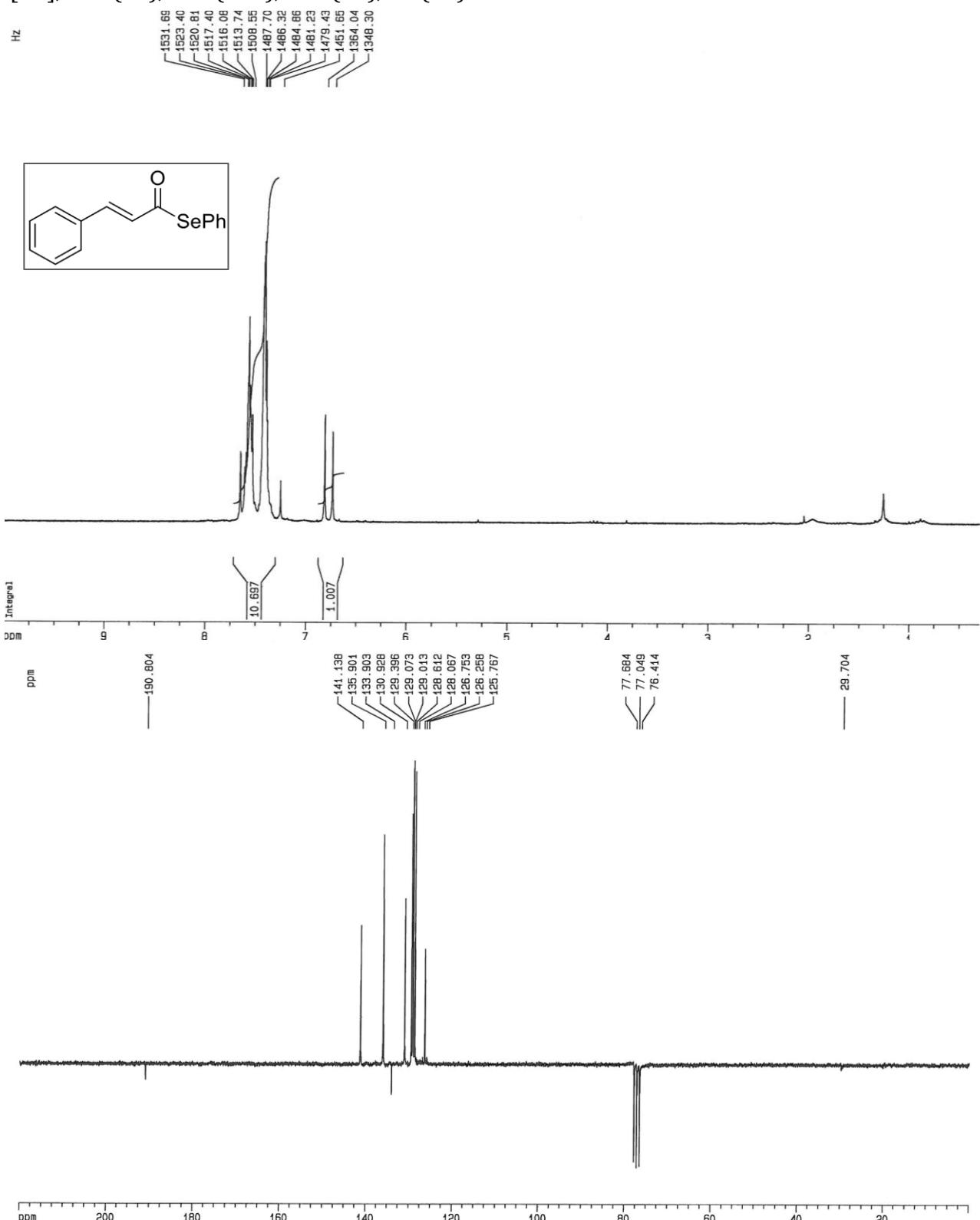
**Se-Phenyl 2-phenylethaneseleenoate (5e)** [4] purified eluting with 20 % DCM in petroleum ether. Yellow solid. M.p.: 41-43°C ([Lit.[4]: 41°-43°C]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm) δ: 7.45-7.35 (m, 2H, H-Ar), 7.34-7.26 (m, 8H, H-Ar), 3.88 (s, 2H, CH<sub>2</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz, ppm) δ: 198.9, 135.8, 132.6, 130.1, 129.3, 128.9, 128.8, 127.8, 126.6, 53.6 ppm. CG-MS *m/z* (%)= 276 [M<sup>+</sup>], 157 (22), 119 (26), 91 (100), 65 (26).



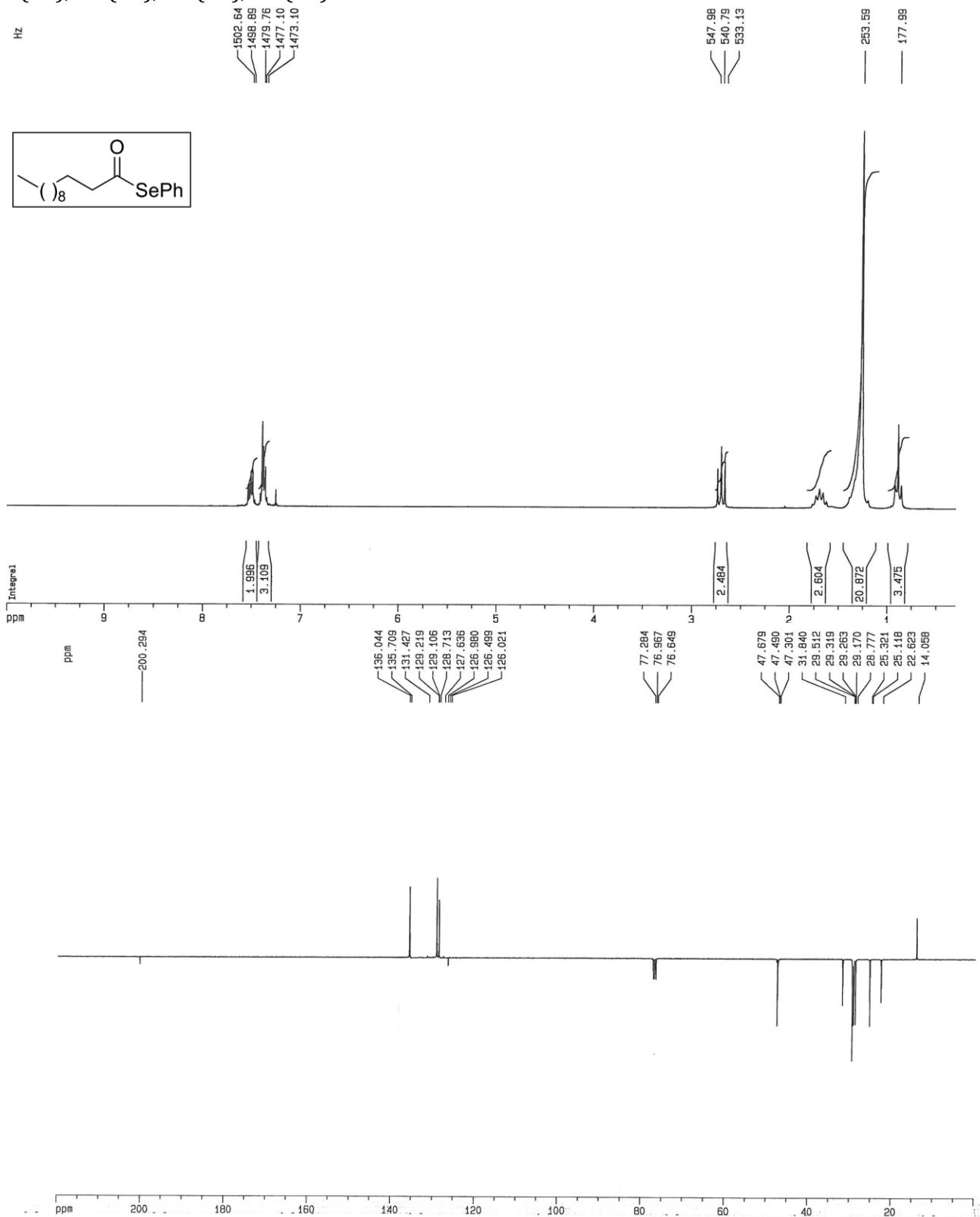
**Se-Phenyl thiophene-2-carboselenoate (5f)** [5] purified eluting with 5 % EtOAc. Yellow oil.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz, ppm)  $\delta$ : 7.88 (dd,  $J= 1.2, 3.9$  Hz, 1H, H-Ar), 7.71 (dd,  $J= 1.2, 4.96$  Hz, 1H, H-Ar), 7.63-7.58 (m, 2H, H-Ar), 7.44-7.41 (m, 3H, H-Ar), 7.17 (dd,  $J= 3.9, 4.96$  Hz, 1H, H-Ar) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 50 MHz, ppm)  $\delta$ : 183.6, 143.1, 136.3, 133.7, 132.0, 129.4, 129.2, 128.0, 125.5 ppm. CG-MS  $m/z$  (%)= 268 (1) [ $\text{M}^+$ ], 157 (16), 111 (100), 83 (20).



**(E)-Se-Phenyl 3-phenylprop-2-eneselenoate (5g)** [6] purified eluting with 5 % EtOAc. Yellow solid. P.f.: 79-80°C ((Lit.:[6] 81°-82°C).<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm) δ: 7.58-7.54 (m, 5H, H-Ar), 7.43-7.40 (m, 6H, H-Ar), 6.78 (d, *J*= 15.0 Hz, 1H, CH) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz, ppm) δ: 190.8, 141.1, 135.9, 133.9, 130.9, 129.4, 129.1, 129.0, 128.6, 128.1, 126.3 ppm. CG-MS *m/z* (%)= 288 (1) [M<sup>+</sup>], 157 (14), 131 (100), 103 (55), 77 (36).



*Se-Phenyl dodecaneselenoate (5h)* [7] purified eluting with 20 % DCM in petroleum ether. Yellow oil.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz, ppm)  $\delta$ : 7.55-7.53 (m, 2H, H-Ar), 7.42-7.39 (m, 3H, H-Ar), 2.73 (t,  $J= 7.5$  Hz, 2H,  $\text{CH}_2\text{C(O)}$ ), 1.73 (quin,  $J= 7.4$  Hz; 2H,  $\text{CH}_2$ ), 1.4-1.3 (m, 16H,  $\text{CH}_2$ ), 0.94-0.90 (t,  $J= 6.5$  Hz, 3H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz, ppm)  $\delta$ : 200.3, 135.7, 129.2, 128.7, 126.5, 47.5, 31.8, 29.5, 29.3, 29.26, 29.17, 28.8, 25.3, 22.6, 14.0 ppm. CG-MS  $m/z$  (%)= 340 (2) [ $\text{M}^+$ ], 183 (100), 157 (34), 109 (20), 85 (27), 71 (30), 57 (43).



## References

1. Marin, G.; Braga, A. L.; Rosa, A. S.; Galetto, F. Z.; Burrow, R. A.; Gallardo, H.; Paixão, M. W. Efficient synthesis of selenol esters from acid chlorides mediated by indium metal. *Tetrahedron* **2009**, *65*, 4614–4618.
2. Wang, L.; Zhang, Y. Water Accelerated Sm/TMSCl Reductive Cleavage of the Se-Se Bond: Synthesis of Selenoesters and Selenoformates. *Synth. Commun.* **1999**, *29*, 3107–3115.
3. Santi, C.; Battistelli, B.; Testaferri, L.; Tiecco, M. On water preparation of phenylselenoesters. *Green Chem.* **2012**, *14*, 1277.
4. Ren, K.; Wang, M.; Liu, P.; Wang, L. Iron-Catalyzed Synthesis of Selenoesters from Diselenides and Acyl Chlorides or Acid Anhydrides in the Presence of Magnesium Dust. *Synthesis (Stuttg.)*. **2010**, *2010*, 1078–1082.
5. Dan, W.; Deng, H.; Chen, J.; Liu, M.; Ding, J.; Wu, H. A new odorless one-pot synthesis of thioesters and selenoesters promoted by Rongalite®. *Tetrahedron* **2010**, *66*, 7384–7388.
6. Kudelko, A.; Wróblowska, M. An efficient synthesis of conjugated 5-aryl-1,3,4-oxadiazoles from 3-heteroarylacrylohydrazides and acid chlorides. *Tetrahedron Lett.* **2014**, *55*, 3252–3254.
7. Zhang, S.; Zhang, Y. Reductive Cleavage of Se–Si Bond in Arylselenotrimethylsilane: A Novel Method for the Synthesis of Selenoesters. *Synth. Commun.* **1998**, *28*, 3999–4002