Electronic Supplementary Material (ESI) for Green Chemistry

SUPPORTING INFORMATION

On water preparation of phenylselenoesters

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General. All new compounds were characterized by ^{1}H- and ^{13}C-NMR and elemental analyses. ^{1}H- and ^{13}C-NMR spectra were recorded at 400 and 100.62 MHz, respectively, on a Bruker Avance-DRX 400 instrument. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer. Starting acyl chlorides are commercially available and have been used without further purifications.

Synthesis of PhSeZnCl (1a), PhSeZnBr (1b) and PhSZnCl (2):

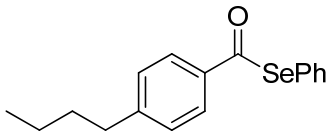
PhSeZnCl **1a** and PhSeZnBr **1b** have been prepared according to previously reported procedure.[1] PhSZnCl **2** has been synthesized by adding to a solution of $(PhS)_2$ (10.0 mmol) in diethyl ether (20 mL) SO_2Cl_2 (10.0 mmol) at 0°C under stirring to form the corresponding PhSCl. After 30 minutes the solvent was evaporated under vacuum. The yellow solid was dissolved in THF and 10.0 mmol of zinc powder was added at reflux. After 20 minutes the mixture, became colorless, was filtered and PhSZnCl was precipitated from petroleum ether as with solid and washed more time with the same solvent.

General procedure for the "on water" nucleophilic acyl substitution mediated by PhSeZnCl (1a), PhSeZnBr (1b) and PhSZnCl (2).

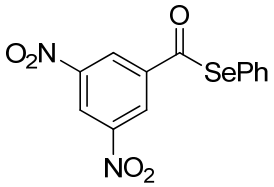
0.13 mmol of **1a-b** or **2** and 0.13 mmol of acyl chloride were poured in 4mL of water and vigorously stirred at 23 °C for 3 hours. Then the aqueous phase was extracted 3 times with ethyl acetate. The collected organic layers were washed with brine, dried over Na_2SO_4, filtered and the solvent removed under vacuum. Products **4d**, **4f**, **5f**, **4g**, **4l** and **4m** were purified by flash chromatography using petroleum ether-ethyl acetate (19:1). Products **4a**, **5a**, **4b**, **5b**, **4c**, **4e**, **4h** and **4i** have been purified by recrystallization from ethyl acetate-hexane. Yields reported on table 2 refer to the isolated products.

Physical and spectral data for the selenoesters **4a**,[2] **4b**,[3] **4c**, [2] **4f-g**,[4] **4h-i**,[5] **5a**,[5] **5f**,[5] and **5b**[6] are known; elemental analyses are reported to prove their purity.

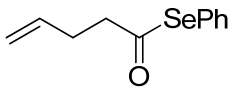
Physical and spectral data for the compounds not already described in literature are reported below.



Se-phenyl 4-butylbenzenecarboselenoate **4d**: Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.87 (d, 2H, J^3= 8.2 Hz, *H*-Ar), 7.65-7.57 (m, 2H, *H*-Ar), 7.50-7.40 (m, 3H, *H*-Ar), 7.35-7.25 (m, 2H, *H*-Ar), 2.69 (t, 2H, J^3= 7.5Hz, CH_2), 1.66 (quin, 2H, J^3= 7.2 Hz, CH_2), 1.36 (sex, 2H, J^3= 7.4 Hz, CH_2), 0.96 (t, 3H, J^3= 7.3 Hz, CH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ= 192.7, 149.8, 136.3, 136.1, 130.6, 129.2, 128.9, 127.4, 126.0, 35.9, 33.4, 22.3, 13.9 ppm. Elemental analysis calcd (%) for $C_{17}H_{18}OSe$ (318.05) C, 64.35; H, 5.72; Found C, 63.97; H, 5.69.



Se-phenyl 3,5-dinitrobenzoselenoate **4e**: Yellow solid, m.p.= 148-150°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.30-9.20 (m, 1H, *H*-Ar), 9.10-9.00 (m, 2H, *H*-Ar), 7.65-7.55 (m, 2H, *H*-Ar), 7.50-7.45 (m, 3H, *H*-Ar) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ= 190.8, 149.4, 141.9, 136.4, 130.4, 130.3, 127.1, 124.5, 123.0 ppm. Elemental analysis calcd (%) for $C_{13}H_8N_2O_5Se$ (351.96) C, 44.46; H, 2.30; Found C, 44.74; H, 2.18.



Se-phenyl pent-4-eneselenoate **4l**: Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.60-7.45 (m, 2H, *H*-Ar), 7.45-7.30 (m, 3H, *H*-Ar), 5.90-5.60 (m, 1H, C*H*=), 5.20-4.95 (m, 2H, CH_2=), 2.80 (t, 2H, J^3= 7.3 Hz, CH_2C(O)), 2.43 (q, 2H, J^3= 6.5 Hz, CH_2) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ= 193.6, 135.7, 135.8, 131.4, 129.4, 128.9, 116.1, 46.6, 29.1 ppm. Elemental analysis calcd (%) for $C_{11}H_{12}OSe$ (240.01) C, 55.24; H, 5.06; Found C, 55.77; H, 5.03.

Se-phenyl benzoselenoate **4a**: Elemental analysis calcd (%) for $C_{13}H_{10}OSe$ (261.99) C, 59.78; H, 3.86; Found C, 59.35; H, 3.87.

Se-phenyl 2-bromobenzoselenoate **4b**: Elemental analysis calcd (%) for $C_{13}H_9BrOSe$ (339.90) C, 45.91; H, 2.67; Found C, 45.55; H, 2.68.

Se-phenyl 4-bromobenzoselenoate **4c**: Elemental analysis calcd (%) for $C_{13}H_9BrOSe$ (339.90) C, 45.91; H, 2.67; Found C, 45.56; H, 2.67.

Se-phenyl 2-phenylethaneselenoate **4f**: Elemental analysis calcd (%) for $C_{14}H_{12}OSe$ (276,01) C, 61.10; H, 4.40; Found C, 61.30; H, 4.42.

(E)-Se-phenyl 3-phenylprop-2-eneselenoate **4g**: Elemental analysis calcd (%) for $C_{15}H_{12}OSe$ (288,01) C, 62.73; H, 4.21; Found C, 62.65; H, 4.23.

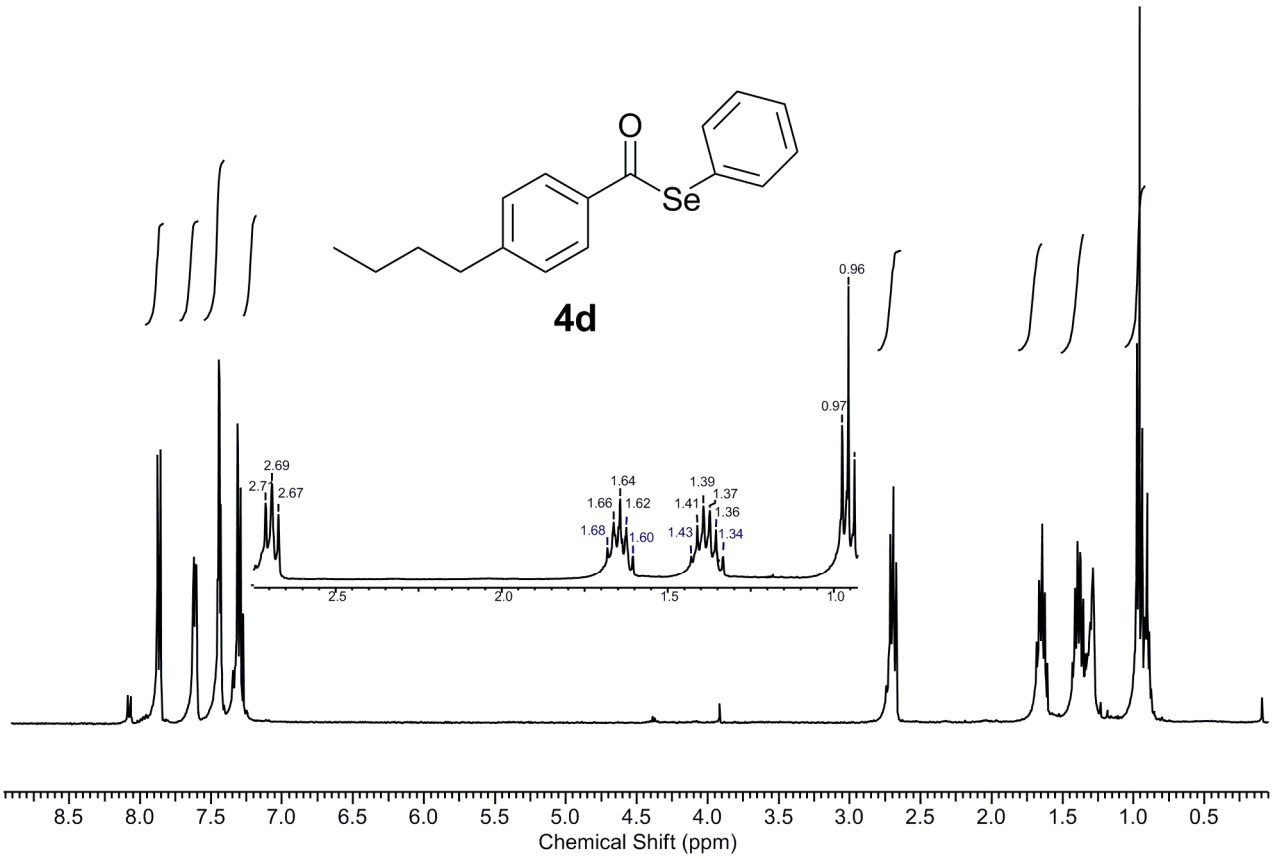
Se-phenyl thiophene-2-carboselenoate **4h**: Elemental analysis calcd (%) for $C_{11}H_8OSSe$ (267.95) C, 49.44; H, 3.02; Found C, 49.38; H, 3.00.

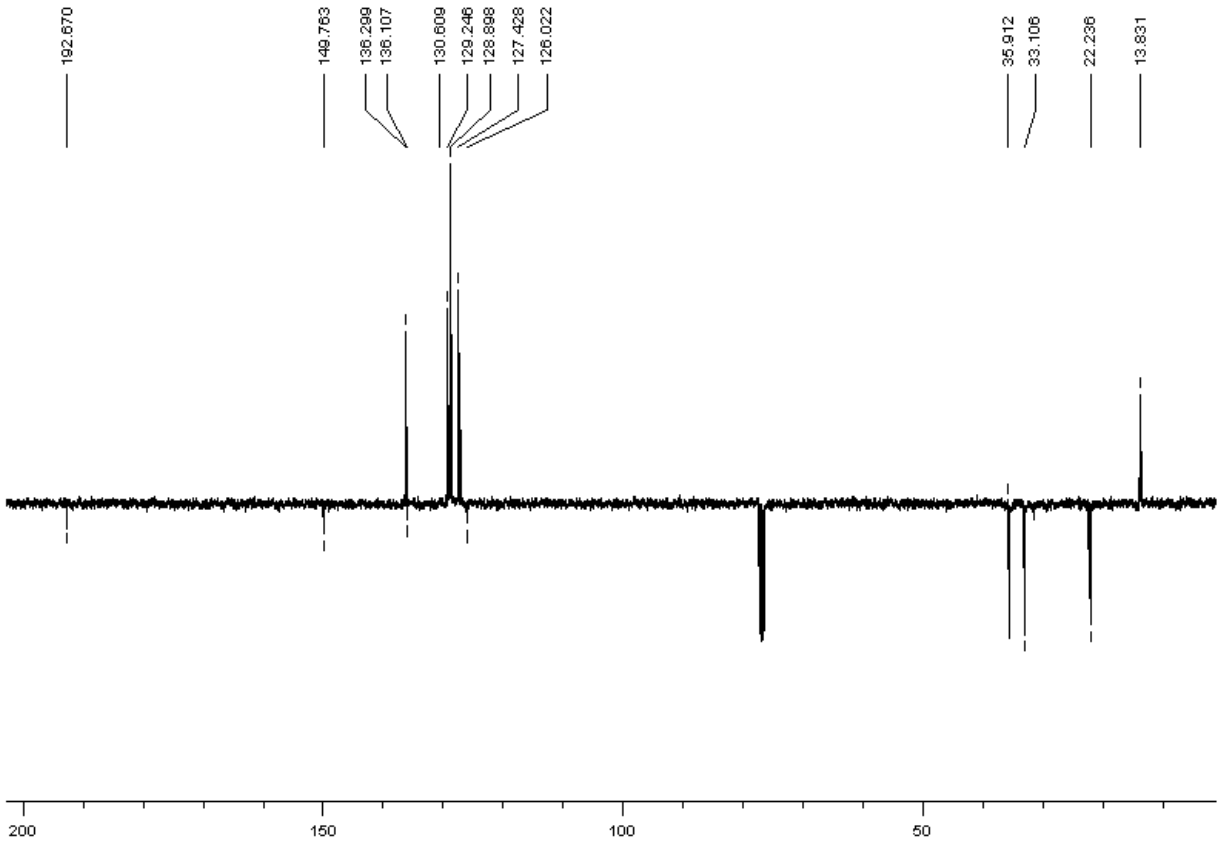
Se-phenyl furan-2-carboselenoate **4i**: Elemental analysis calcd (%) for $C_{11}H_8O_2Se$ (251.97) C, 52.61; H, 3.21; Found C, 52.64; H, 3.20.

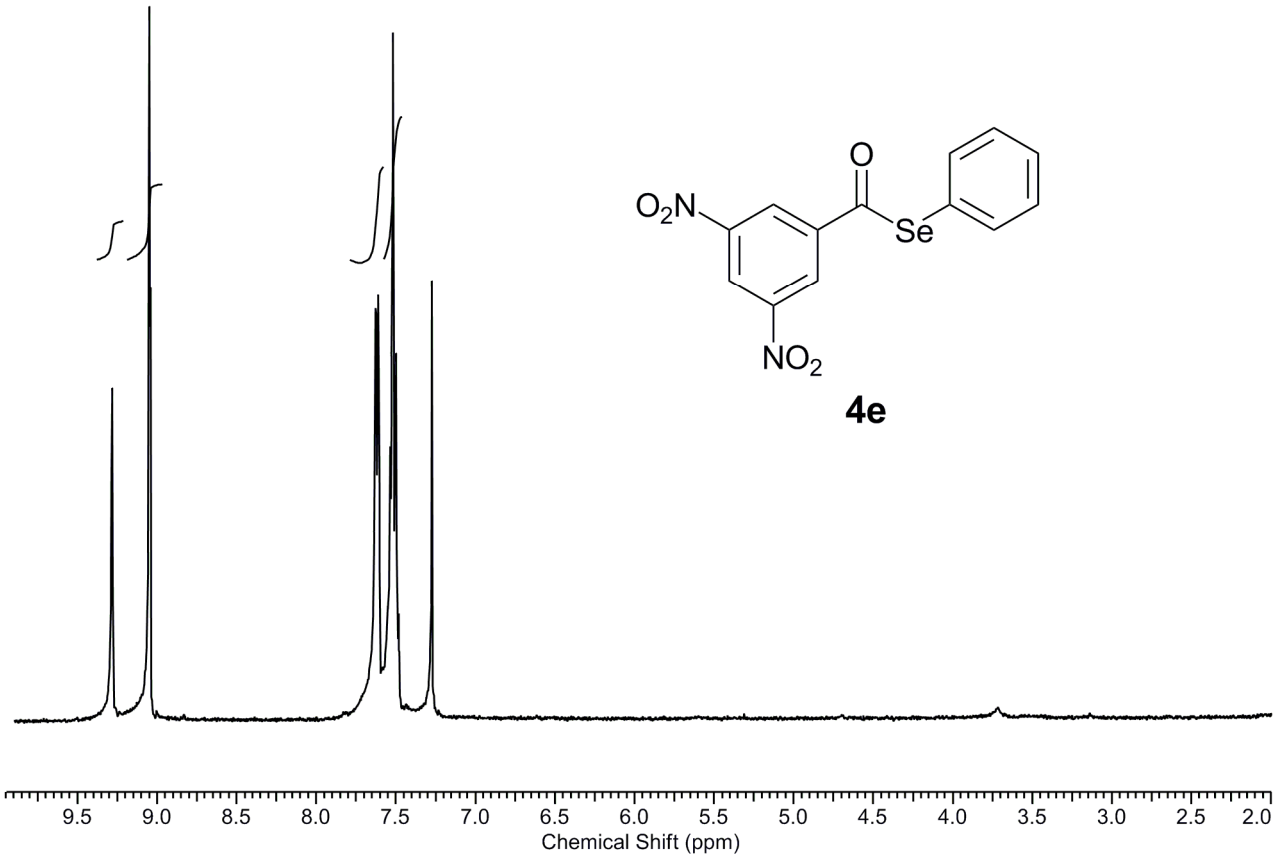
S-phenyl benzothioate **5a**: Elemental analysis calcd (%) for $C_{13}H_{10}OS$ (114.28) C, 72.87; H, 4.70; Found C, 72.65; H, 4.71.

S-phenyl 2-bromobenzothioate **5b**: Elemental analysis calcd (%) for $C_{13}H_9BrOS$ (293,18) C, 53.26; H, 3.09; Found C, 53.15; H, 3.10.

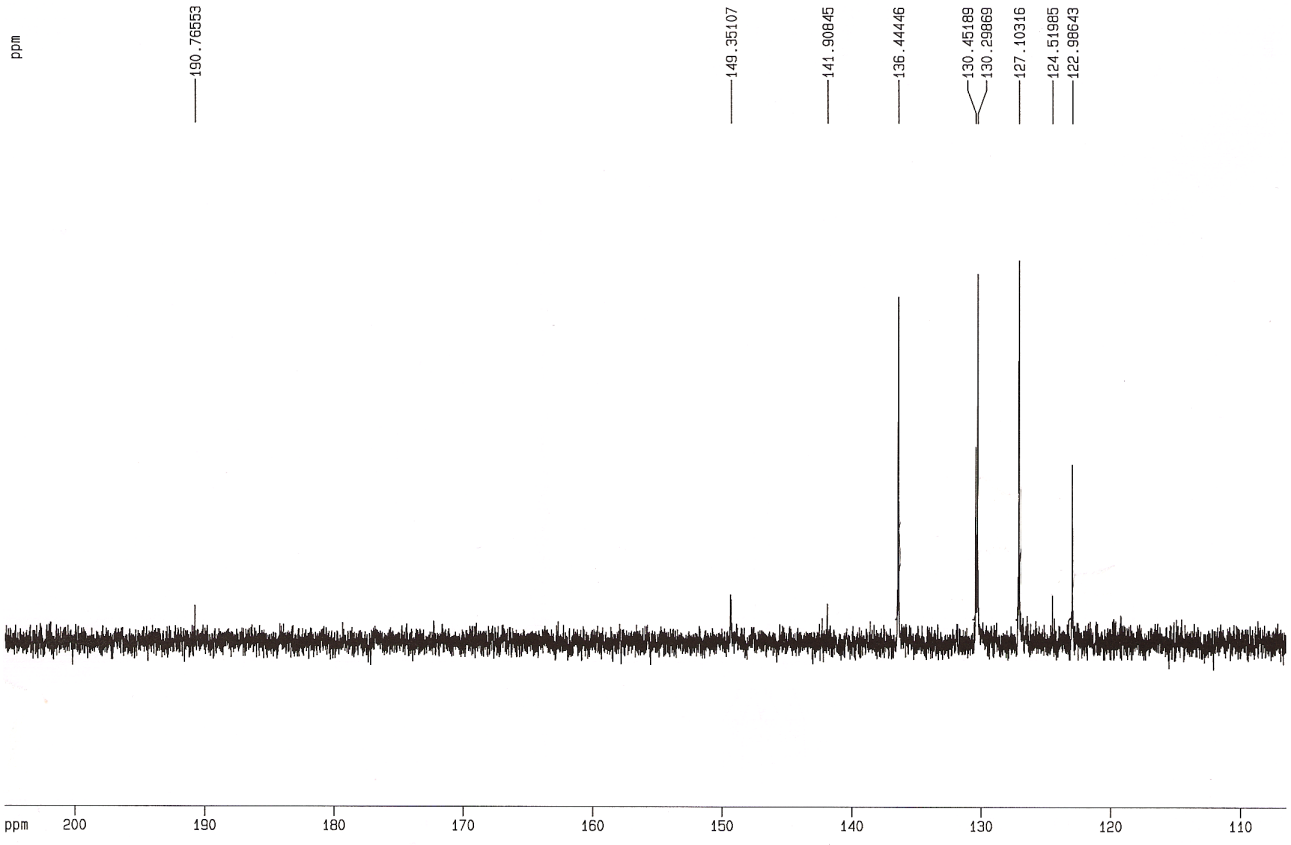
S-phenyl 2-phenylethanethioate **5f**: Elemental analysis calcd (%) for $C_{14}H_{12}OS$ (228,31) C, 73.65; H, 5.30; Found C, 73.80; H, 5.29.

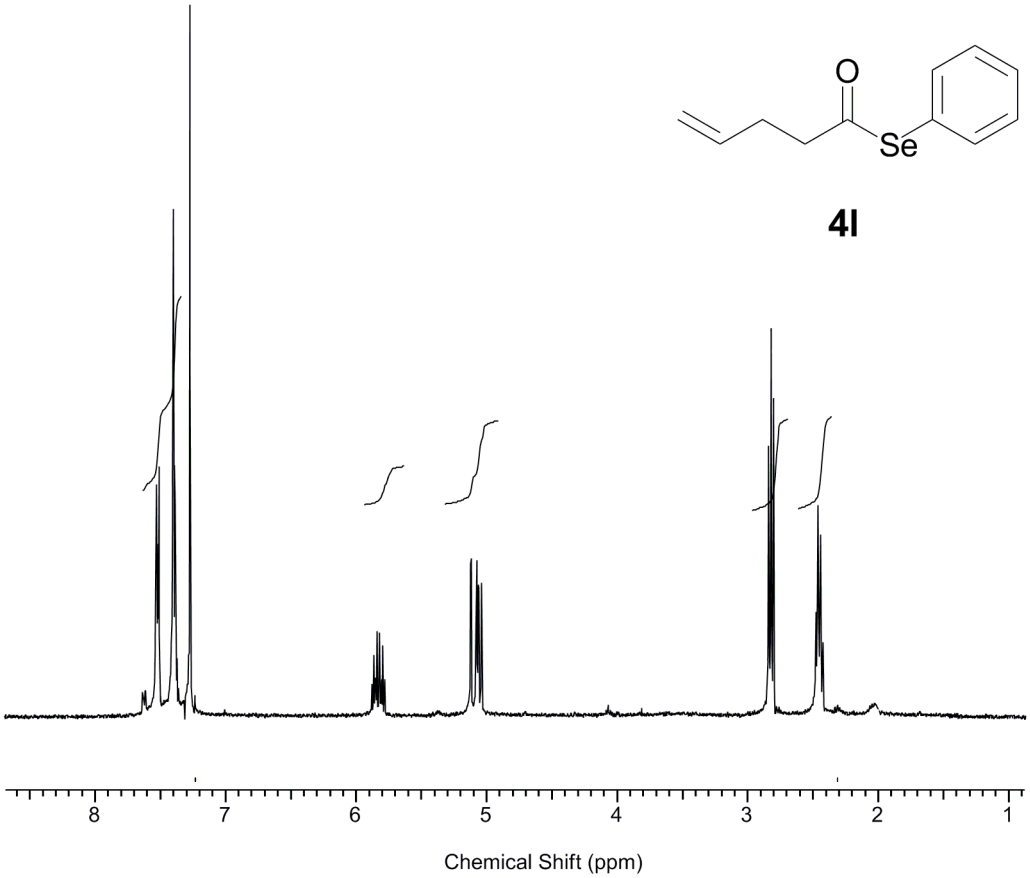




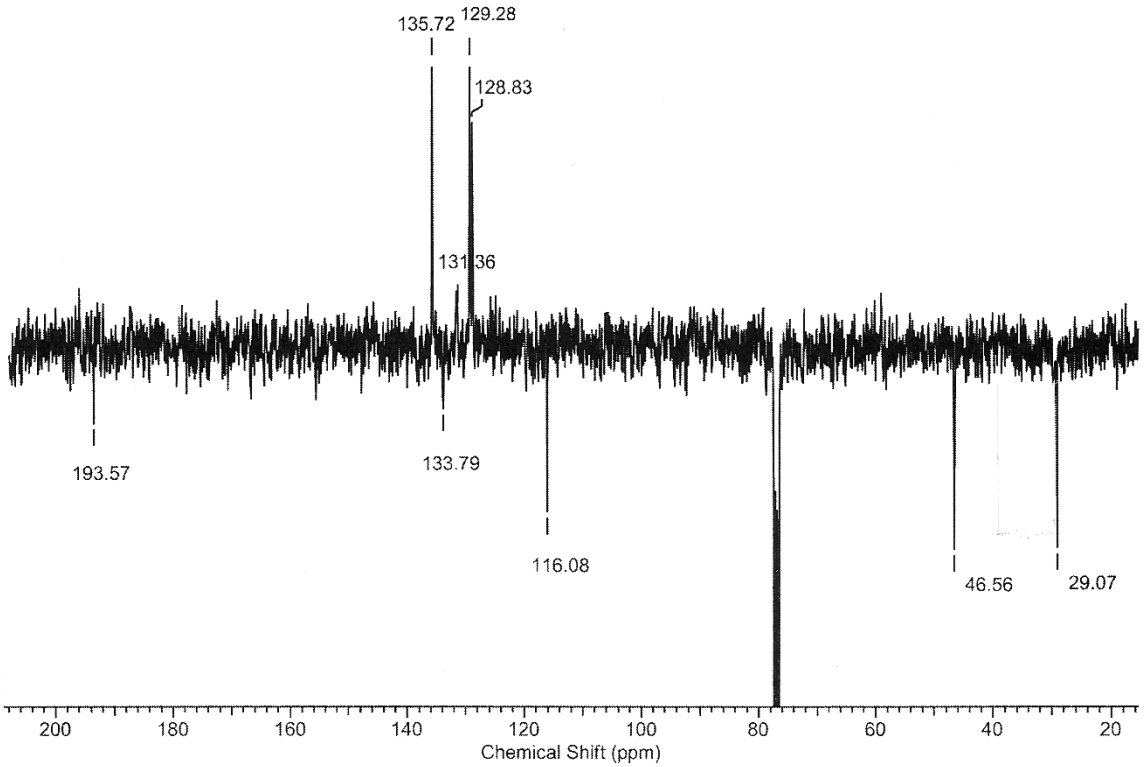


4e





4l



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