N,S-Dimethyldithiocarbamyl Oxalates as Precursors for Determining Kinetic Parameters for Oxyacyl Radicals†

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Electronic Supplementary Information

Experimantal details for the preparation of **6** and **10**. General protocol for kinetic experiments. ^{1}H and ^{13}C NMR spectra of compounds **6** and **10**. (7 pages).

Experimental Details

Octyl formate **8**, 3-butenyl formate **12** and *N*-hydroxy-*N,S*-dimethyldithiocarbamate were prepared following literature protocols.[S1–S3] 2-Methylbuytrolactone **11** was purchased from Aldrich.

Octyl *N,S*-dimethyldithiocarbamyl oxalate (6). A solution of octanol (70 µL, 0.445 mmol) in diethyl ether (0.5 mL) was added dropwise to a solution of oxalyl chloride (50 µL, 0.591 mmol) in diethyl ether (1.5 mL) and the mixture stirred at room temperature overnight. Solvent and excess oxalyl chloride were both removed *in vacuo*. The half-ester **7** was used directly without further purification.

The half-ester (**7**) in dichloromethane (1.5 mL) was added dropwise to a mixture of *N*-hydroxy-*N,S*-dimethyldithiocarbamate (81 mg, 0.590 mmol) and 4-(*N,N*-dimethylamino)pyridine (DMAP, 5 mg, 0.044 mmol) in dichloromethane (2.5 mL) and the resultant mixture left to stir at room temperature for 6.5 hrs. The orange mixture was filtered through a plug of celite (dichloromethane). The filtrate was washed with saturated sodium bicarbonate (2x), dried ($MgSO_4$) and the solvent removed *in vacuo* to give the title thiohydroxomate ester as purple oil (134 mg, 94%).

^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0, 3H), 1.37 – 1.23 (m, 8H), 1.44 – 1.38 (m, 2H), 1.82 – 1.73 (m, 2H), 2.57 (s, 3H), 3.85 (s, 3H), 4.38 (t, J = 6.8, 2H); ^{13}C NMR ($CDCl_3$) δ 14.03, 18.88, 22.58, 25.59, 28.17, 29.00, 29.06, 31.68, 42.77, 68.34, 154.57, 155.26, 198.53; IR (neat) ν_{max} 1647, 1755, 1807, 2856, 2925 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{23}O_4NS_2^+$ $(M+H)^+$ 322.11413, found 322.11415.

3-Butenyl *N,S*-dimethyldithiocarbamyl oxalate (10). A solution of 3-buten-1-ol (200 µL, 2.32 mmol) in diethyl ether (2.5 mL) was added dropwise to a solution of oxalyl chloride (500 µL, 5.91 mmol) in diethyl ether (5.0 mL), chilled to 0 °C. The mixture was kept at 0 °C for 15 min, then stirred at room temperature overnight. Solvent and excess oxalyl chloride were both removed *in vacuo*. The half-ester was used directly without further purification.

The half-ester in dichloromethane (5.0 mL) was added dropwise to a mixture of *N*-hydroxy-*N,S*-dimethyldithiocarbamate (408 mg, 2.97 mmol) and 4-(*N,N*-dimethylamino)pyridine (DMAP, 28 mg, 0.229 mmol) in dichloromethane (15.0 mL) and the resultant mixture left to stir at room temperature for 6.5 hrs. The greyish mixture was filtered through a plug of celite (dichloromethane). The filtrate was washed with saturated sodium bicarbonate (2x), dried ($MgSO_4$) and the solvent removed *in vacuo* to give the title thiohydroxomate ester as yellow-green oil (521 mg, 85%).

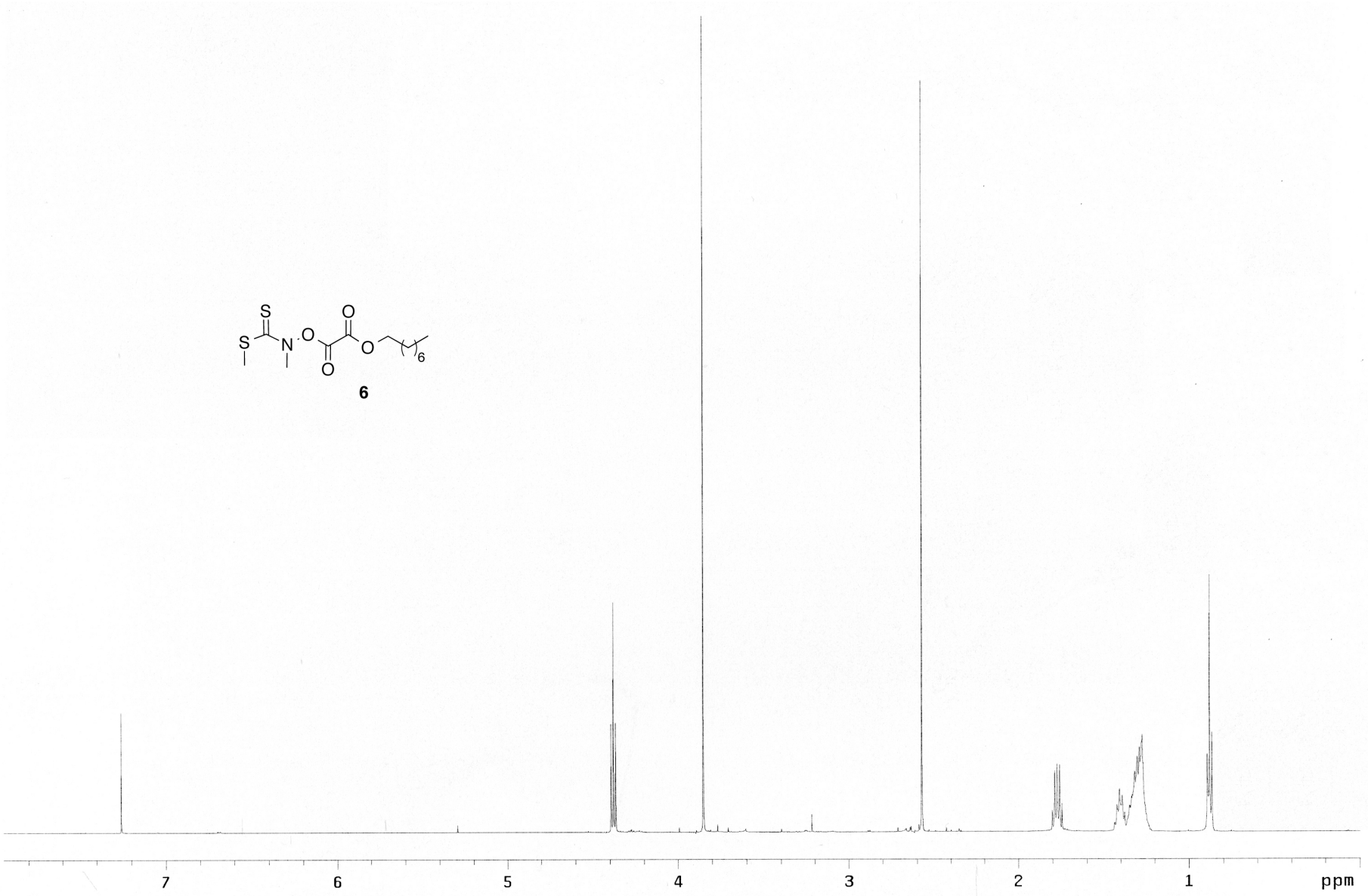
^{1}H NMR ($CDCl_3$) δ 2.49 – 2.54 (m, 2H), 2.57 (s, 3H), 3.85 (s, 3H), 4.44 (t, J = 6.7 Hz, 2H), 5.09 – 5.23 (m, 2H), 5.70 – 5.87 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.89, 32.56, 42.78, 66.99, 118.46, 132.42, 154.44, 155.12, 198.57; IR (neat) ν_{max} 850, 924, 961, 1001, 1085, 1217, 1288, 1365, 1424, 1755, 1806, 2970 cm^{-1}; HRMS (ESI) calcd for $C_9H_{13}O_4NS_2^+$ $(M+H)^+$ 264.03588, found 264.03586.

General protocol for kinetic reactions of the alkoxycarbonyl radical systems

Standard solutions of *tert*-dodecanethiol in benzene were prepared to concentrations as described in Table 1. The radical precursor was added to a pyrex vial, followed by the appropriate thiol stock solution and benzene added to make the required concentration. Photolysis was achieved by irradiating the sample in a Rayonet photochemical reactor (350 nm) at ambient temperture (21°C). The reaction mixtures were analysed by GC.

References

S1. Barluenga, J.; Campos, P. J.; Gonzalez-Nunez, E.; Asensio, G. *Synthesis,* **1985**, 426.
S2. Baguley, P. A.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2,* **1998**, 1423.
S3. S. Kim, C. J. Lim, S. Song and H. Kang, *Synlett,* 2001, 688.



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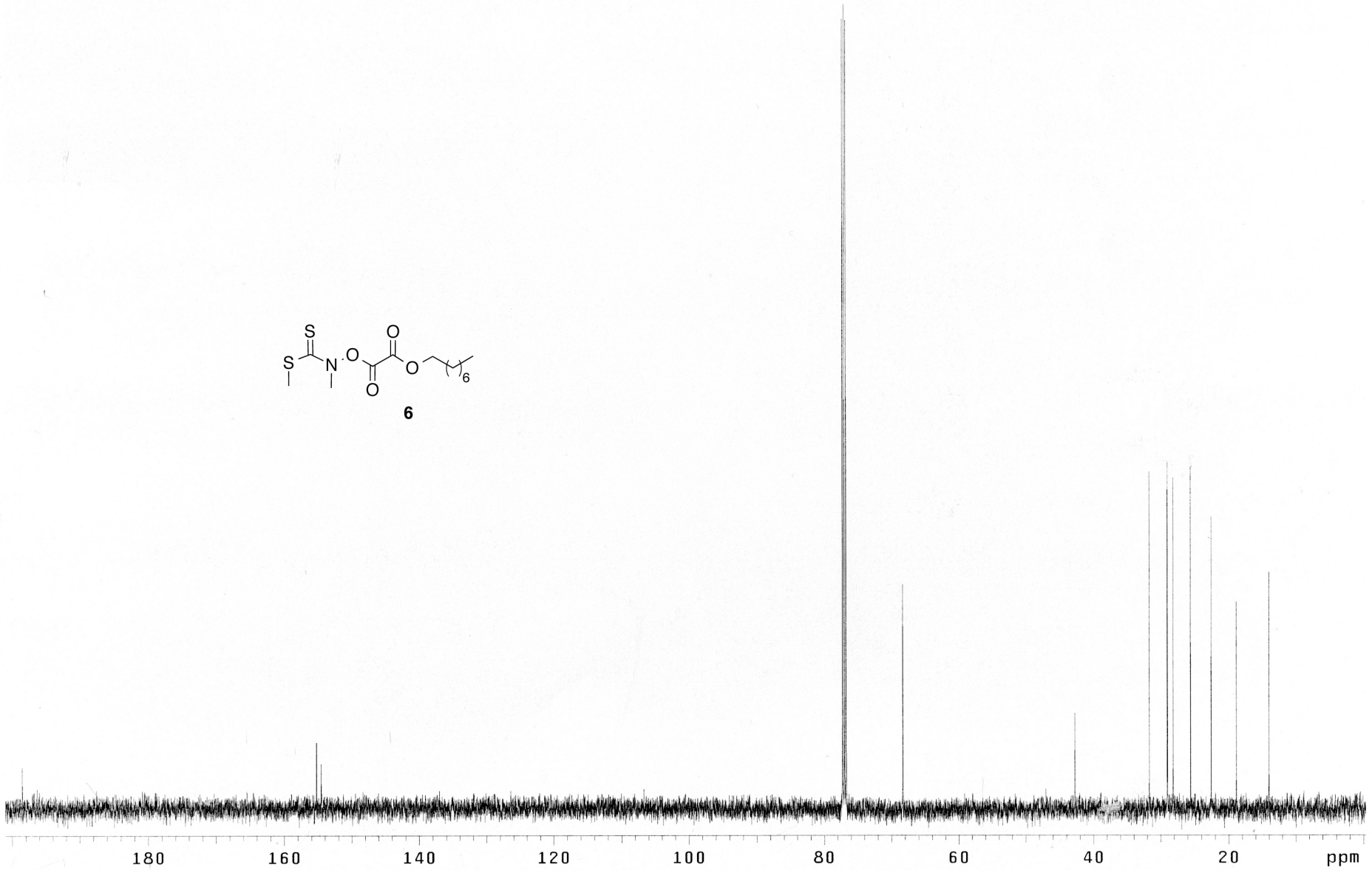

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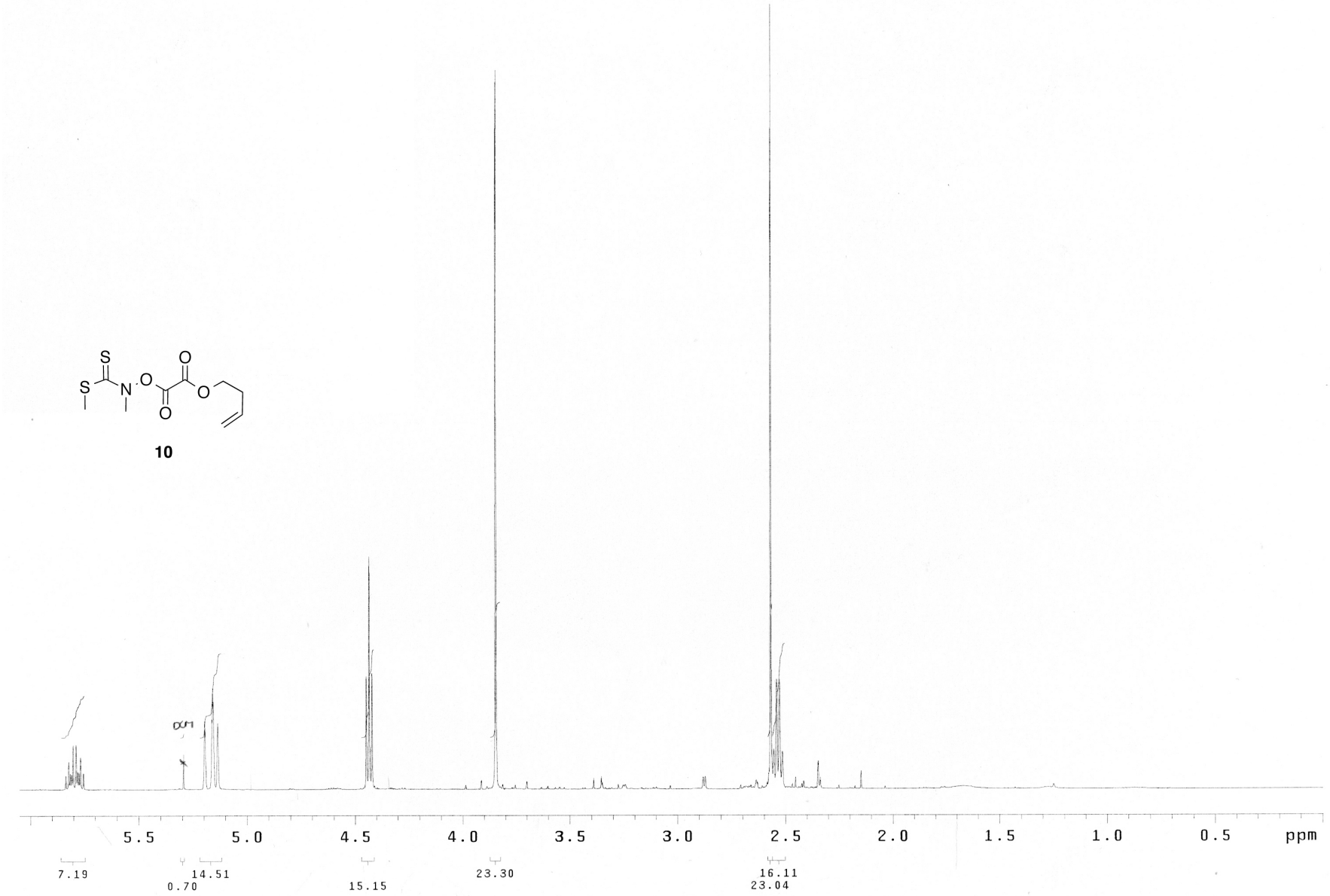
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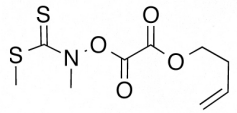

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