One-Pot Synthesis of Symmetric 1,7-Dicarbonyl Compounds Via a Tandem Radical Addition - Elimination – Addition Reaction

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Ananlytic data of known *O*-ethyl *S*-carbonylmethyl xanthates 1 and allyl sulfur compounds 2

***O*-Ethyl *S*-[2-phenyl-2-oxoethyl] carbonodithioate (1a).**

Pale yellow solid, yield: 1.08 g, 90%, m.p. 32–33 °C, Lit.[1] m.p. 31–32 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (*δ*, ppm) 1.39 (t, *J* = 7.1 Hz, 3H, CH_3), 4.63 (q, *J* = 7.1 Hz, 2H, CH_2), 4.66 (s, 2H, CH_2), 7.50 (t, *J* = 7.6 Hz, 2H, ArH), 7.61 (t, *J* = 7.6 Hz, 1H, ArH), 8.01 (d, *J* = 7.6 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (*δ*, ppm) 13.6 (CH_3), 43.5 (CH_2), 70.6 (CH_2), 128.4 (CH), 128.7 (CH), 133.7 (CH), 135.7 (CH), 166.4 (C), 192.2 (C=O), 213.2 (C=S).

***O*-Ethyl *S*-[2-(4-methoxyphenyl)-2-oxoethyl] carbonodithioate (1b).**

Pale yellow solid, yield: 1.20 g, 89%, m.p. 69–70 °C, Lit.[1] m.p. 68–69 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (*δ*, ppm) 1.40 (t, *J* = 7.1 Hz, 3H, CH_3), 3.88 (s, 3H, CH_3), 4.62 (s, 2H, CH_2), 4.64 (q, *J* = 7.1 Hz, 2H, CH_2), 7.50 (d, *J* = 8.6 Hz, 2H, ArH), 8.01 (d, *J* = 8.6 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (*δ*, ppm) 13.6 (CH_3), 43.1 (CH_2), 55.2 (CH_3), 70.2 (CH_2), 113.6 (CH), 128.5 (C), 130.4 (CH), 163.7 (C), 190.3 (C=O), 213.2 (C=S).

***O*-Ethyl *S*-(2-oxopropyl) carbonodithioate (1c).**[2]

Pale yellow liquid, yield: 0.81 g, 91%. ^{1}H NMR ($CDCl_3$, 400 MHz) (*δ*, ppm) 1.39 (t, *J* = 7.1 Hz, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.97 (s, 2H, CH_2), 4.67 (q, *J* = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) (*δ*, ppm) 13.7 (CH_3), 29.1 (CH_3), 45.9 (CH_2), 70.6 (CH_2), 200.8 (C=O), 212.9 (C=S).

***S*-(3-Chloro-2-oxopropyl) *O*-ethyl carbonodithioate (1d).**

White solid 1.12 g, yield: 70%, m.p. 52–53 °C, Lit.[3] 49–50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) 1.43 (t, *J* = 7.1 Hz, 3H, CH_3), 4.15 (s, 2H, CH_2), 4.30 (s, 2H, CH_2), 4.64 (q, *J* = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) (*δ*, ppm) 13.6, 42.8, 47.8, 71.2, 195.6, 212.7.

***S*-(2-Ethoxyl-2-oxoethyl) *O*-ethyl carbonodithioate (1e).**[4]

Pale yellow liquid, yield: 0.92 g, 88%. ^{1}H NMR ($CDCl_3$, 400 MHz) (*δ*, ppm) 1.29 (t, *J* = 7.1 Hz, 3H, CH_3), 1.42 (t, *J* = 7.1 Hz, 3H, CH_3), 3.92 (s, 2H, CH_2), 4.22 (q, *J* = 7.1 Hz, 2H, CH_2), 4.64 (q, *J* = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) (*δ*, ppm) 13.6 (CH_3), 14.1 (CH_3), 37.8 (CH_2), 61.8 (CH_2), 70.5 (CH_2), 167.8 (C=O), 212.5 (C=S).

***O*-Ethyl *S*-(2-phenoxy-2-oxoethyl) carbonodithioate (1f).**[5]

Pale yellow liquid, yield: 1.18 g, 92%. ^{1}H NMR ($CDCl_3$, 400 MHz) (*δ*, ppm) 1.43 (t, *J* = 7.1 Hz, 3H, CH_3), 4.13 (s, 2H, CH_2), 4.67 (q, *J* = 7.1 Hz, 2H, CH_2), 7.11 (d, *J* = 7.6 Hz, 2H, ArH), 7.23 (t, *J* = 7.6 Hz, 2H, ArH), 7.38 (t, *J* = 7.6 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (*δ*, ppm) 13.6 (CH_3), 37.9 (CH_2), 70.8 (CH_2), 121.2 (CH), 126.1 (CH), 129.4 (CH), 150.6 (C), 166.5 (C=O), 212.3 (C=S).

***O*-Ethyl *S*-[2-oxo-2-(oxazolidin-2-on-3-yl)ethyl] carbonodithioate (1l).**

Pale yellow solid, yield: 1.11 g, 89%, m.p. 100–101 °C, Lit.[6] m.p. 96 °C. ^{1}H NMR ($CDCl_3$, 400

MHz) (δ, ppm) 1.43 (t, J = 7.1 Hz, 3H, CH_3), 4.07 (t, J = 8.0 Hz, 2H, CH_2), 4.49 (t, J = 8.1 Hz, 2H, CH_2), 4.57 (s, 2H, CH_2), 4.65 (q, J = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.6 (CH_3), 39.3 (CH_2), 42.6 (CH_2), 62.4 (CH_2), 70.6 (CH_2), 153.4 (C=O), 166.7 (C=O), 212.7 (C=S).

***S*-(Cyanomethyl) *O*-ethyl carbonodithioate (1m).**[7]
Pale yellow liquid, yield: 0.71 g, 88%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.47 (t, J = 7.1 Hz, 3H, CH_3), 3.89 (s, 2H, CH_2), 4.72 (q, J = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.6 (CH_3), 21.3 (CH_2), 71.5 (CH_2), 115.2 (CN), 208.9 (C=S).

Allyl methylsulfone (2a).[8]
Colorless liquid, yield: 10.5 g, 87%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 2.87 (s, 3H, CH_3), 3.74 (d, J = 7.6 Hz, 2H, CH_2), 5.48 (d, J = 17.2 Hz, 1H in CH_2), 5.52 (d, J = 10.2 Hz, 1H in CH_2), 5.92-6.02 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 38.9 (CH_3), 59.3 (CH_2), 124.6 (CH_2), 125.2 (CH).

Allyl ethylsulfone (2b).[9]
Colorless liquid, from sodium ethanesulphinate (2.50 g, 21.5 mmol), yield: 1.75 g, 60%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.39 (t, J = 7.1 Hz, 3H, CH_3), 3.00 (q, J = 7.1 Hz, 2H, CH_2), 3.71 (d, J = 7.6 Hz, 2H, CH_2), 5.43-5.51 (m, 2H, CH_2), 5.95 (ddt, J = 14.4, 10.4, 7.6 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 6.4 (CH_3), 45.6 (CH_2), 56.8 (CH_2), 124.3 (CH_2), 125.1 (CH).

Allyl phenylsulfone (2c).[10]
Colorless liquid, yield: 15.6 g, 85%**.** ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 3.81 (d, J = 7.6 Hz, 2H, CH_2), 5.15 (d, J = 17.2 Hz, 1H in CH_2), 5.33 (d, J = 10.0 Hz, 1H in CH_2), 5.74–5.84 (m, 1H, CH), 7.56 (t, J = 7.6 Hz, 2H, ArH), 7.65 (t, J = 7.6 Hz, 1H, ArH), 7.88 (d, J = 7.6 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 60.8 (CH_2), 124.5 (CH), 124.6 (CH_2), 128.4 (CH), 129.0 (CH), 133.7 (CH), 138.2 (C).

Allyl phenylsulfoxide (2e).[11]
Colorless liquid, yield: 0.83 g, 50%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 3.52 (dd, J = 12.8, 7.6 Hz, 1H in CH_2), 3.58 (dd, J = 12.8, 7.6 Hz, 1H in CH_2), 5.16 (d, J = 17.2 Hz, 1H in CH_2), 5.20 (d, J = 10.0 Hz, 1H in CH_2), 5.59–5.70 (m, 1H, CH), 7.51–7.67 (m, 4H, ArH), 7.87 (d, J = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 60.8 (CH_2), 123.8 (CH), 124.6 (CH_2), 125.1 (CH), 128.4 (CH), 131.0 (CH), 142.7 (C).

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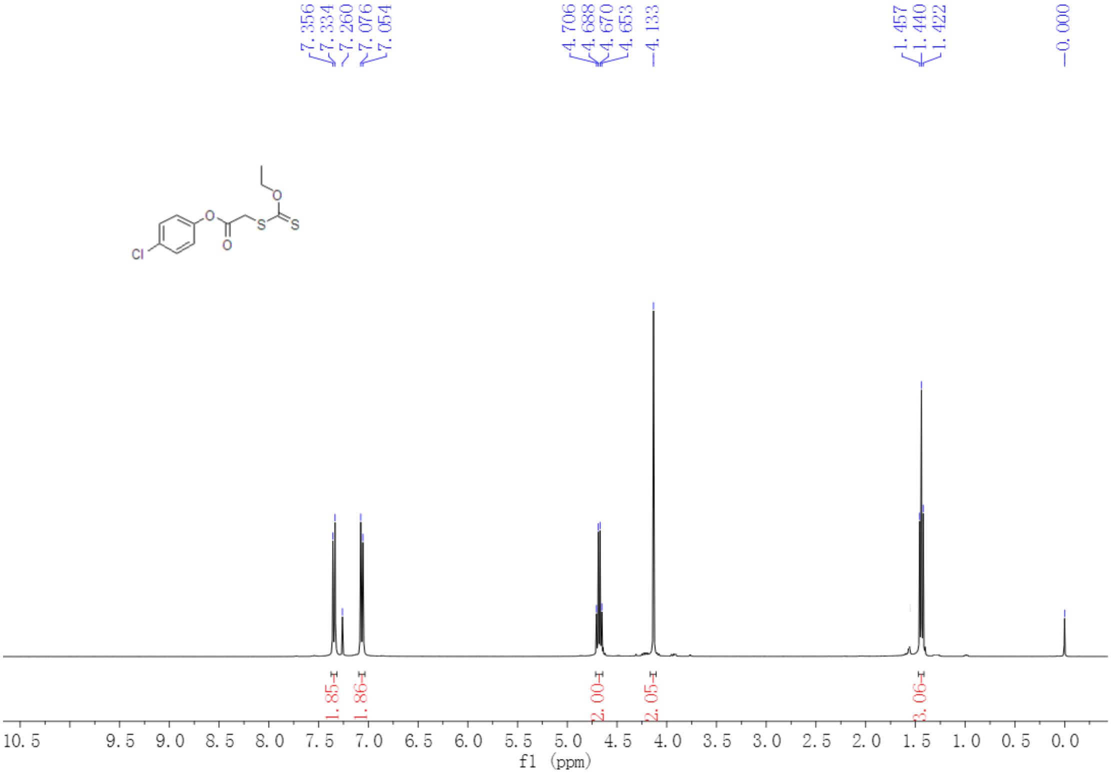
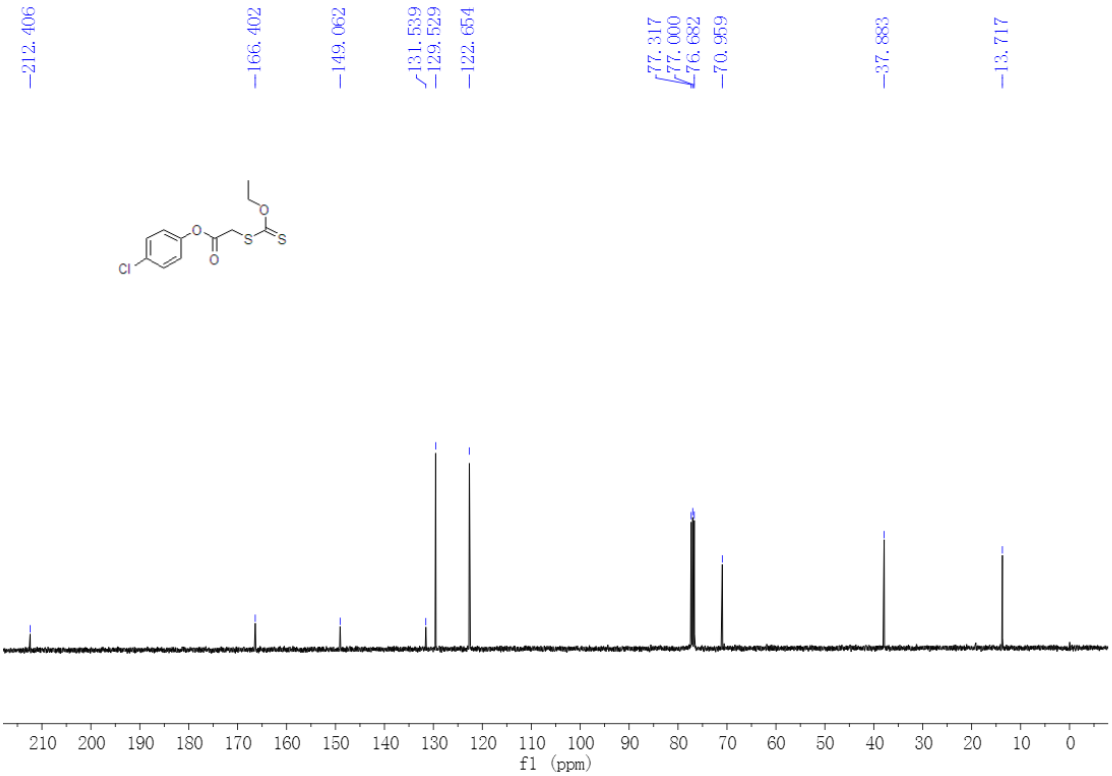
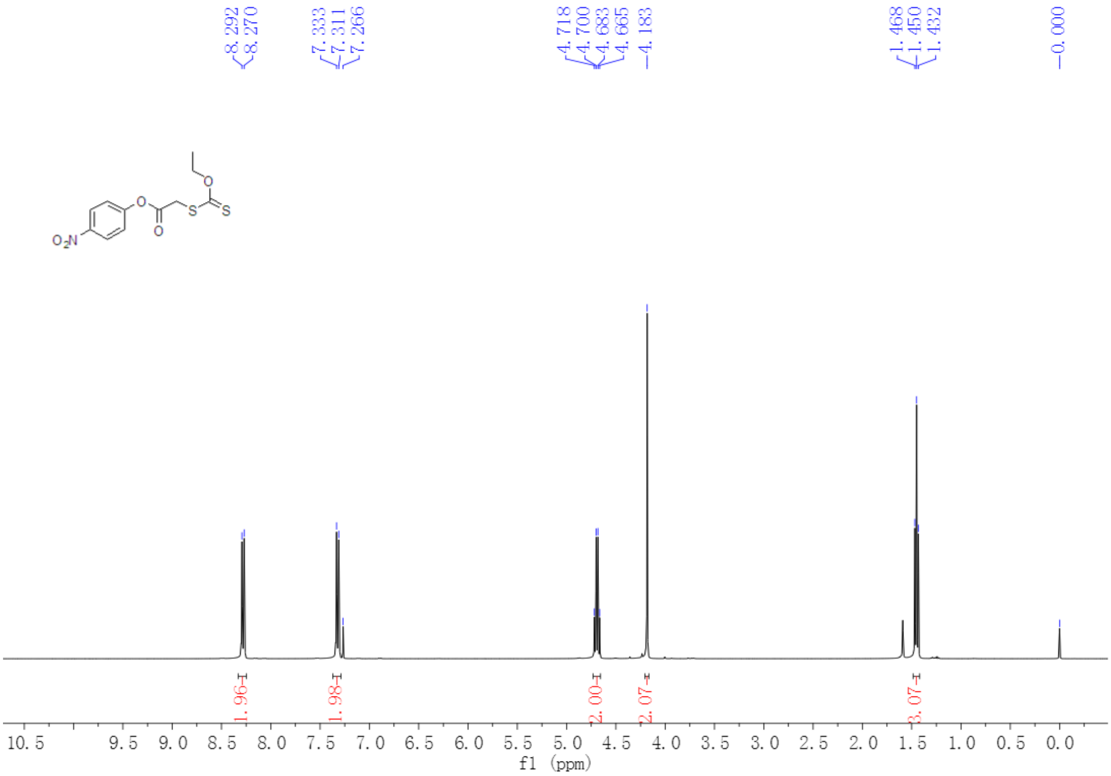
Copies of ^{1}H and ^{13}C NMR spectra of unknown *O*-ethyl *S*-carbonylmethyl xanthates 1

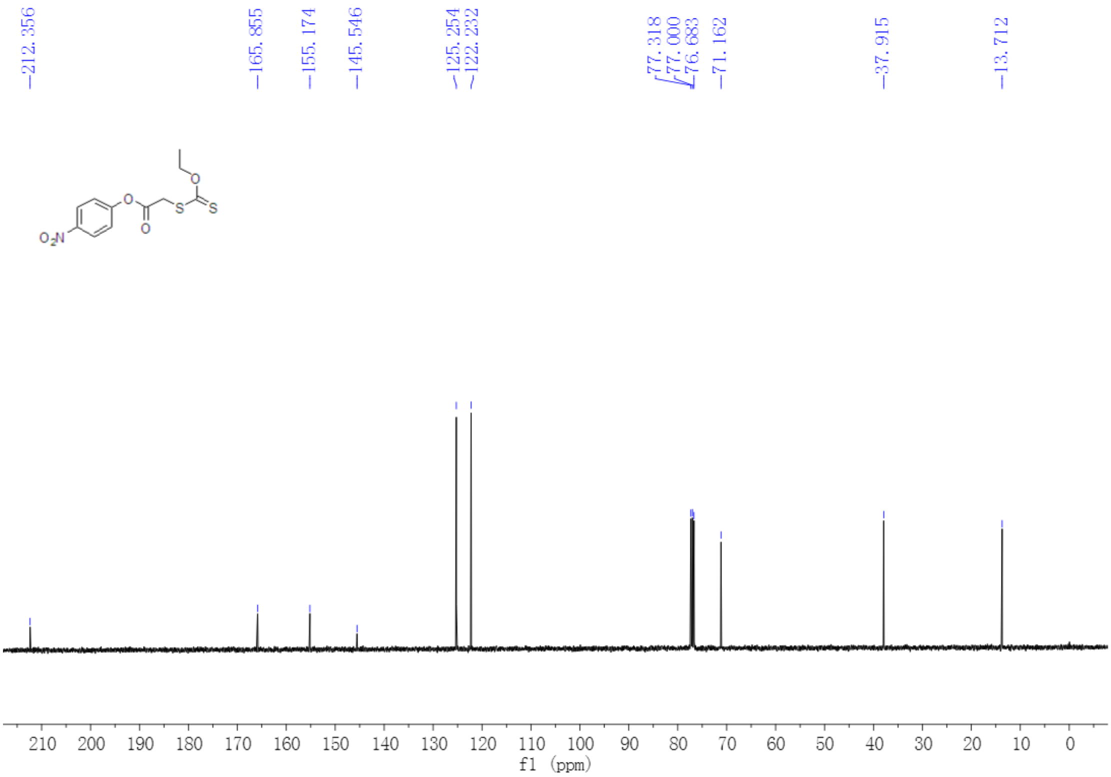
S-[2-(4-Chlorophenoxy)-2-oxoethyl] *O*-ethyl carbonodithioate (1g)





O-Ethyl *S*-[2-(4-nitrophenoxy)-2-oxoethyl] carbonodithioate (1h)





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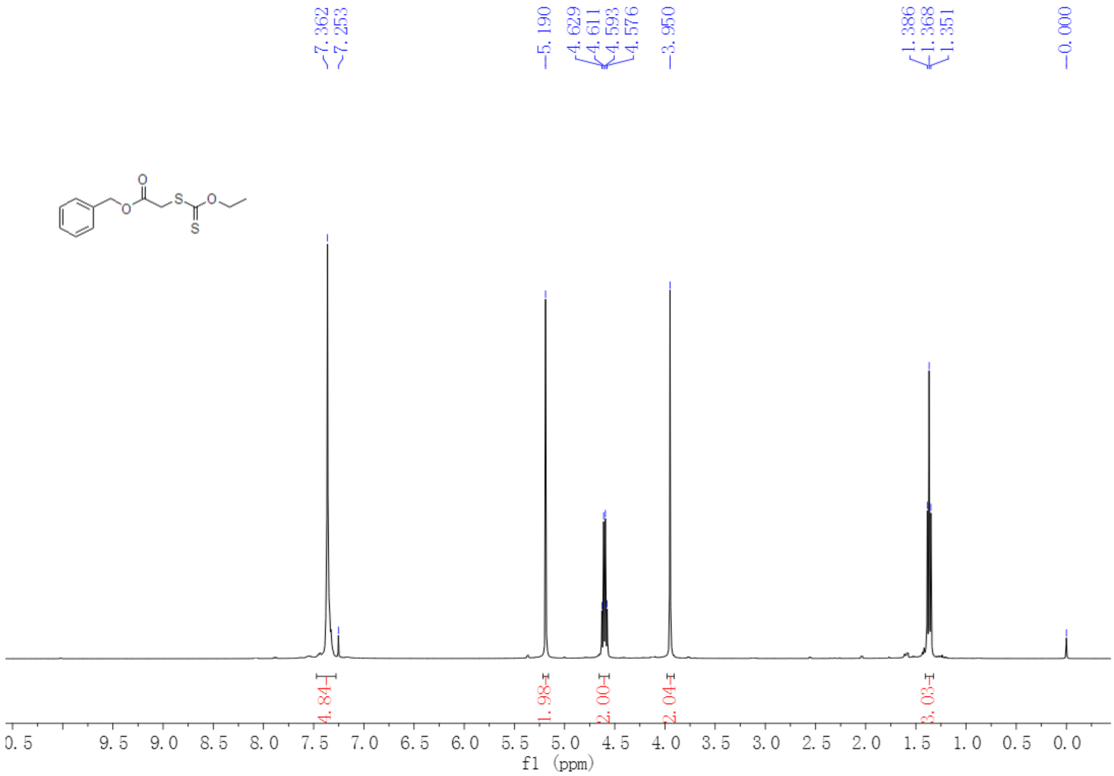
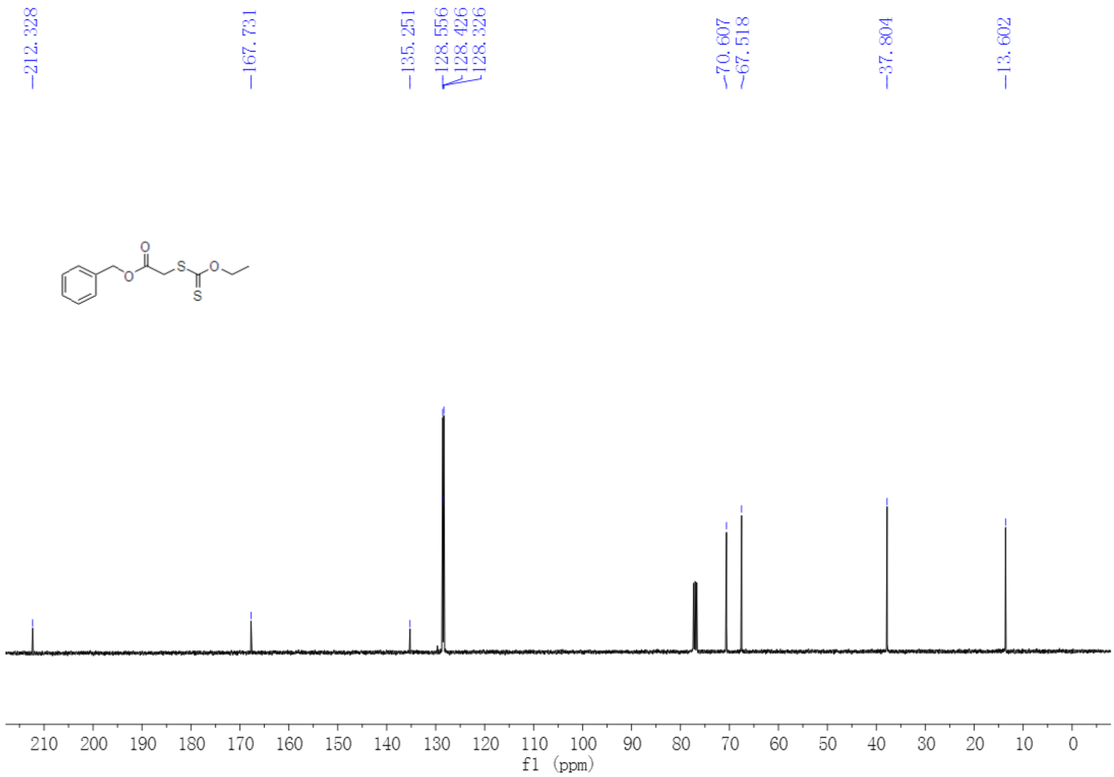
***S*-(2-Benzyloxy-2-oxoethyl) *O*-ethyl carbonodithioate (1i)**





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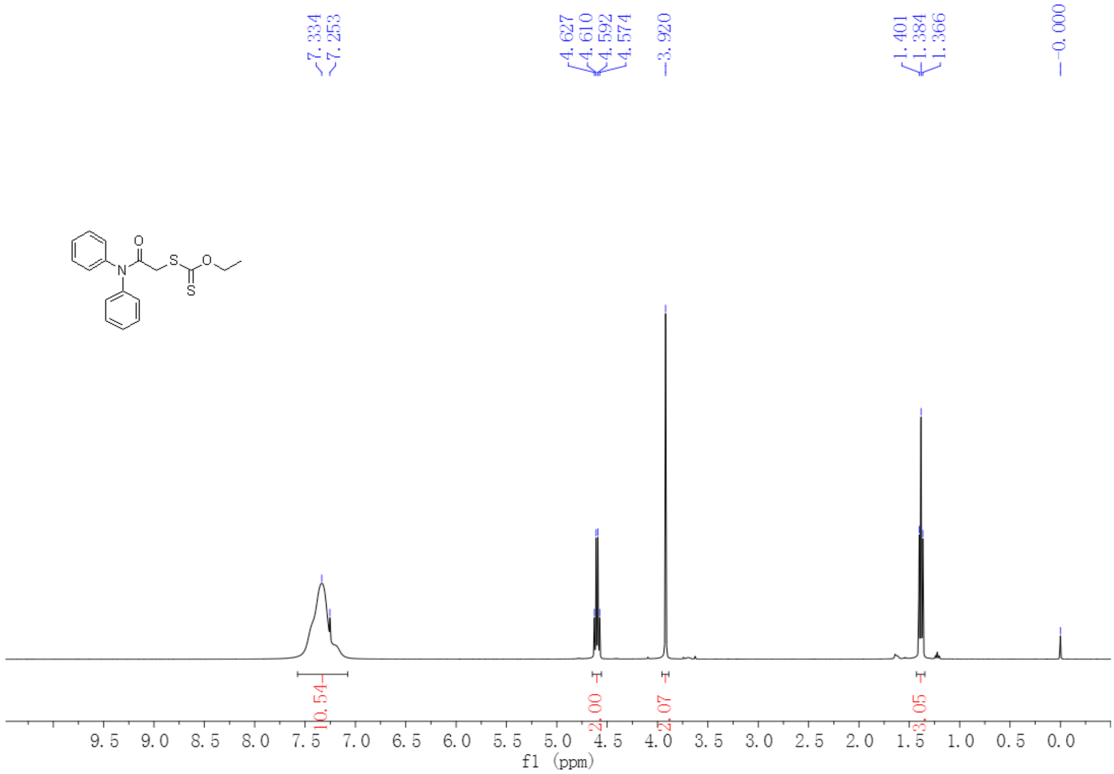

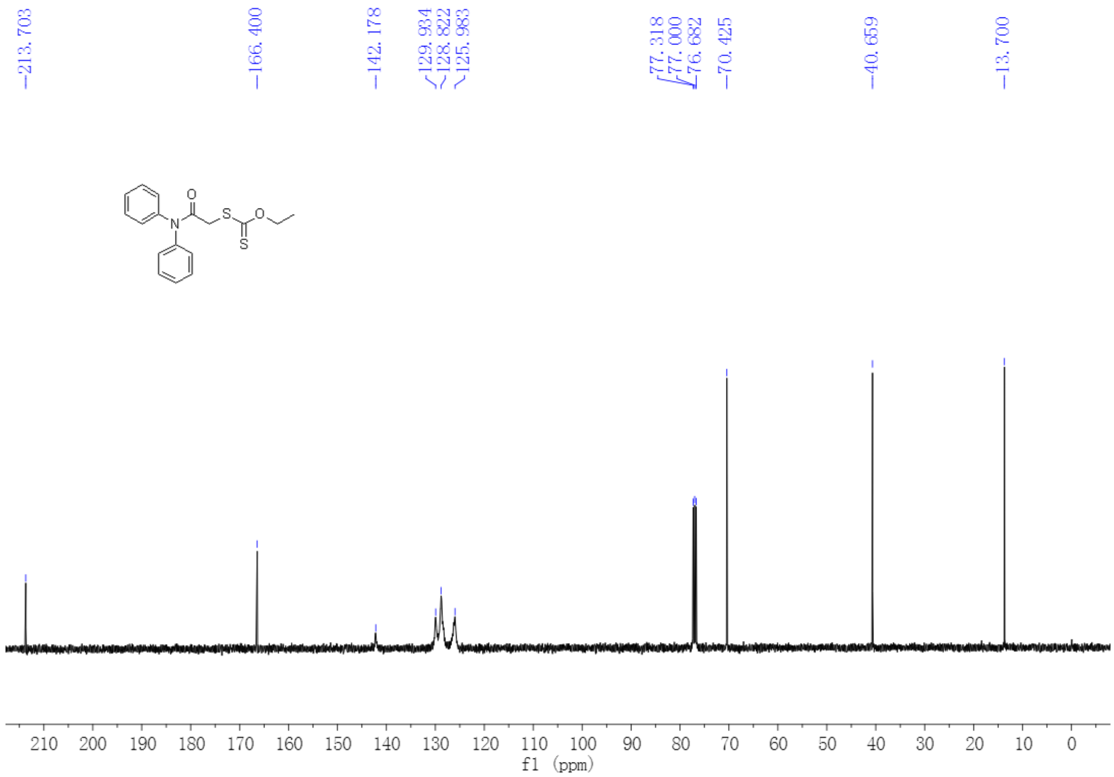

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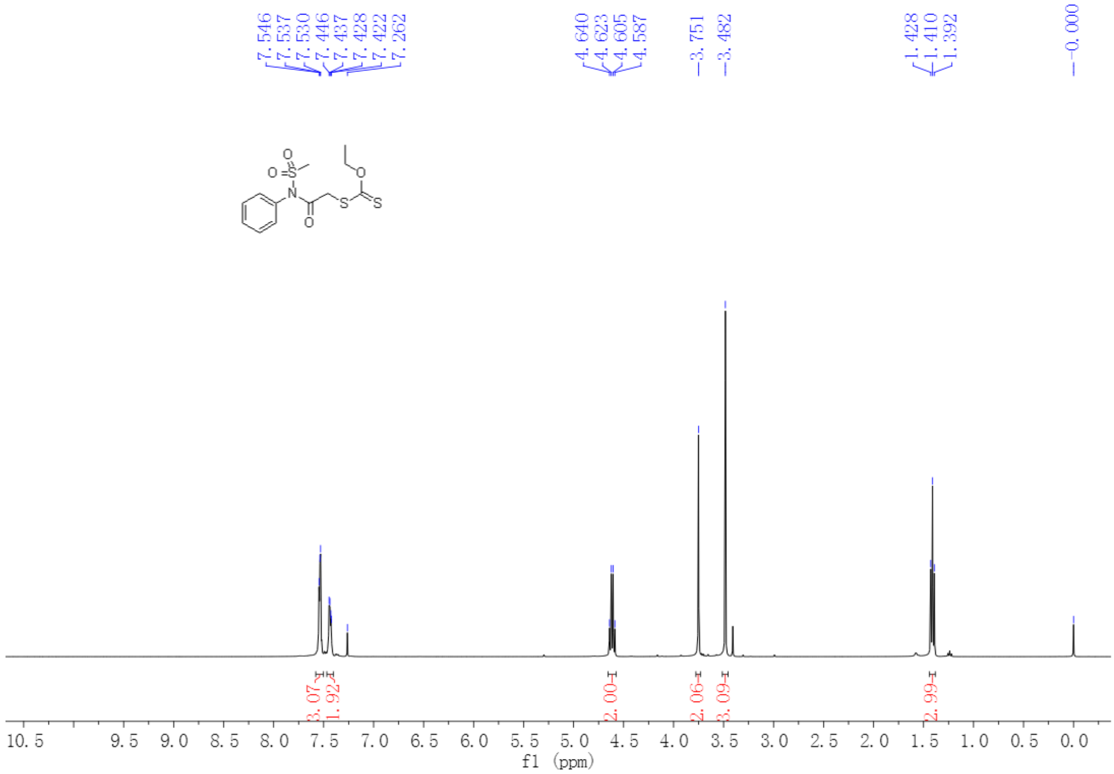
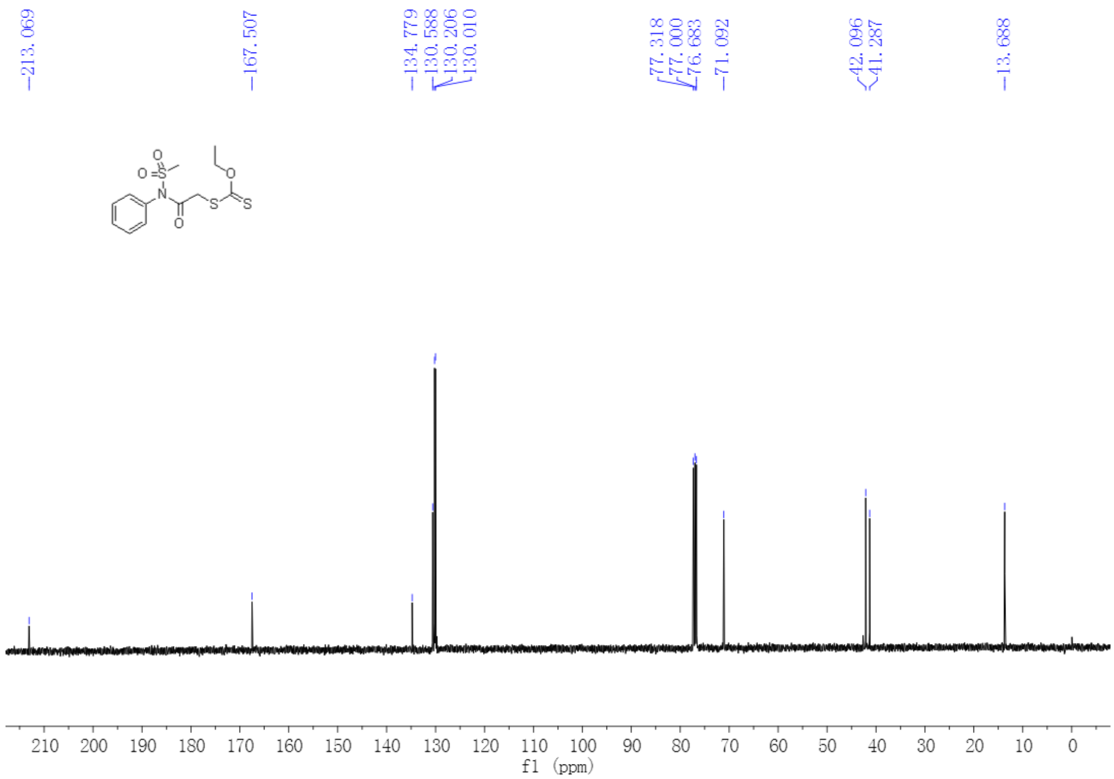
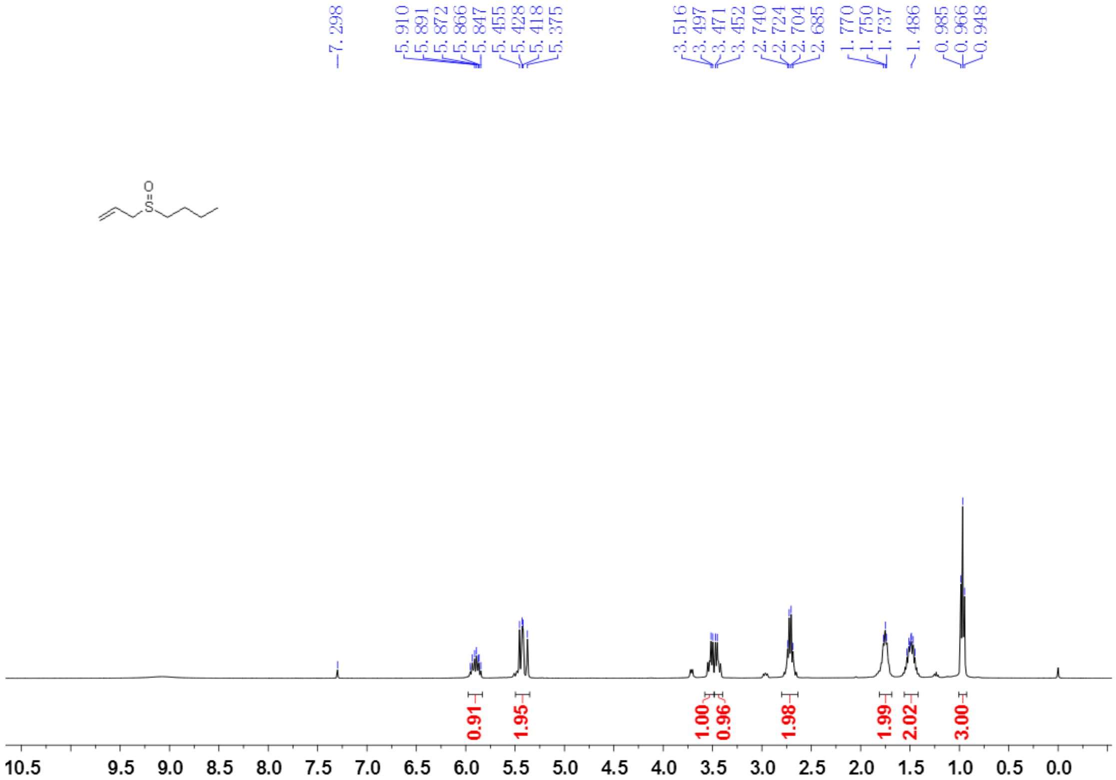
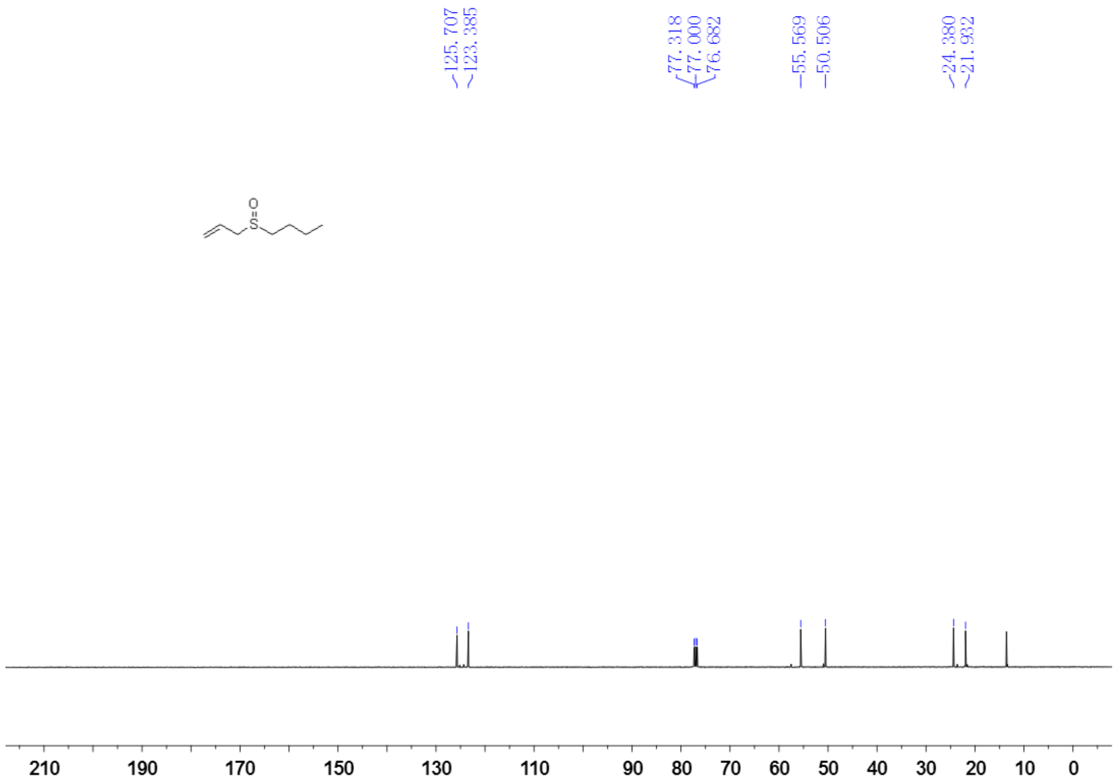




Copies of ^{1}H and ^{13}C NMR spectra of unknown allylbutylsulfoxide 2d

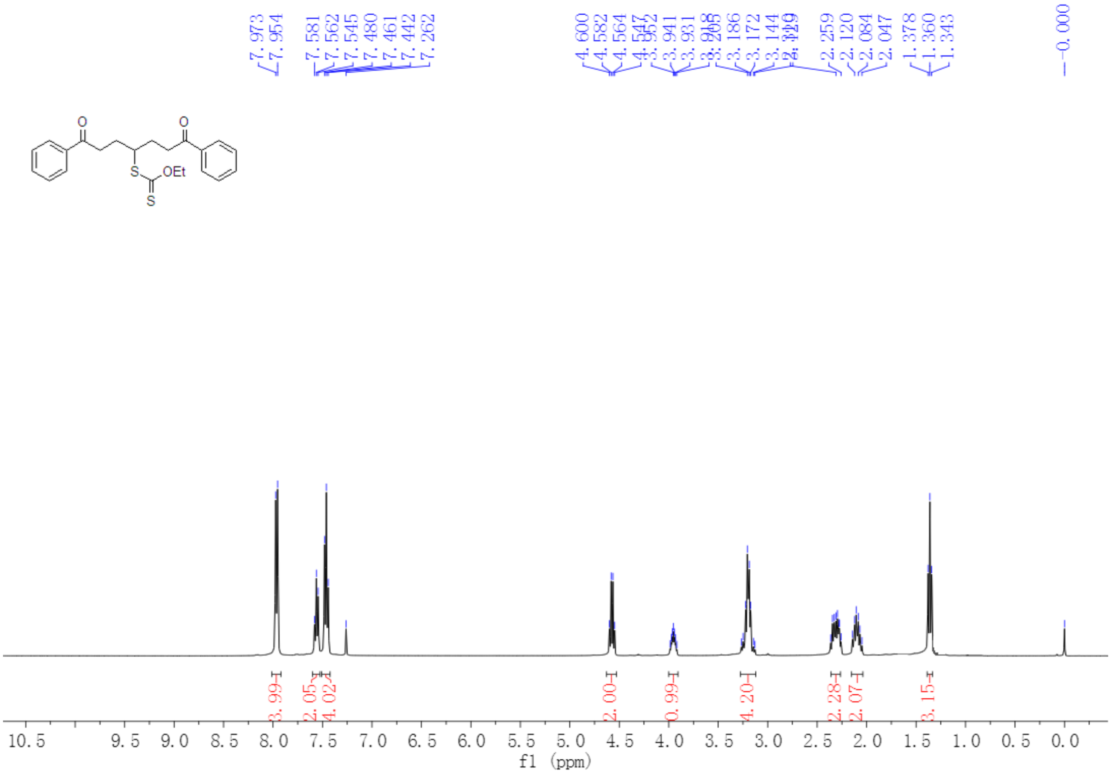
Allylbutylsulfoxide (2d)

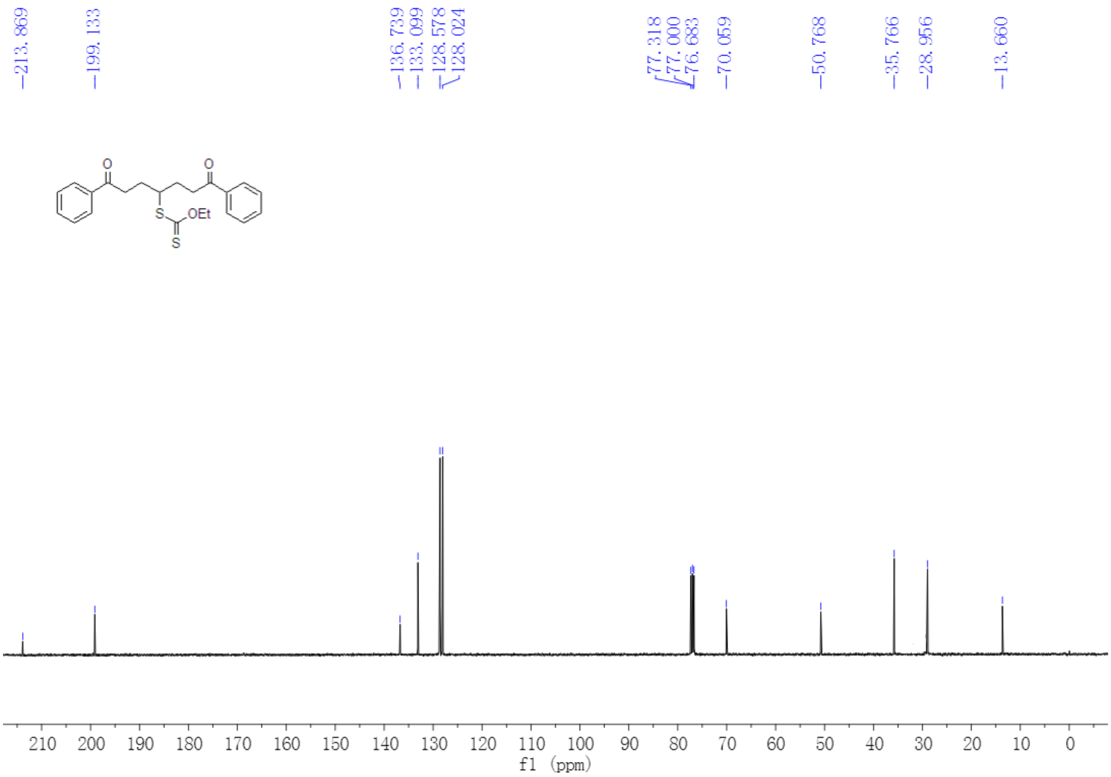




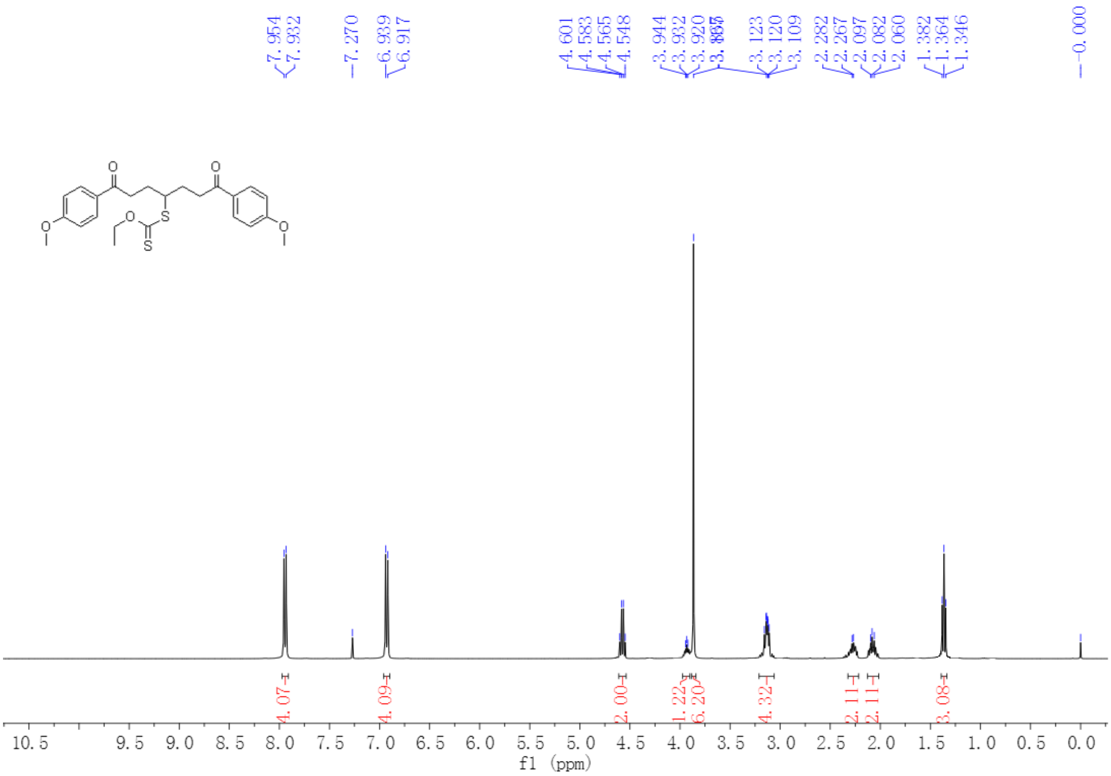
Copies of [1]H and [13]C NMR spectra of symmetric 1,7-dicarbonyl compounds 3

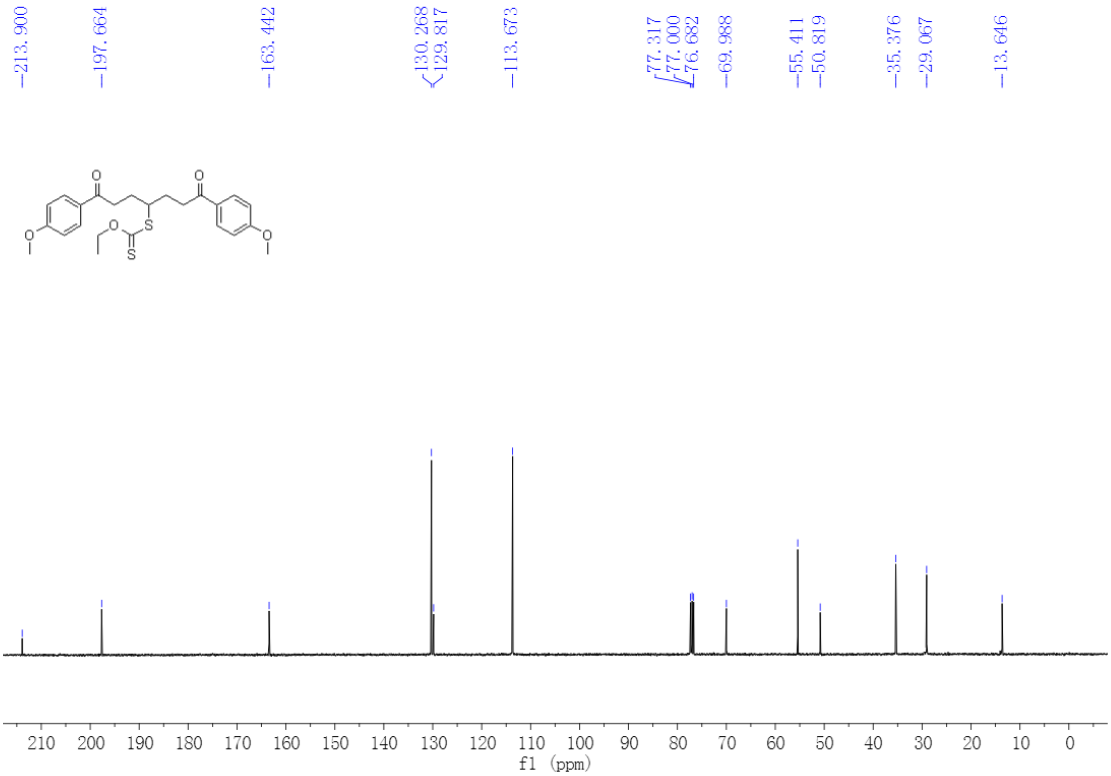
S-(1,7-Dioxo-1,7-diphenylheptan)-4-yl *O*-ethyl carbonodithioate (3a)





S-[1,7-Dioxo-1,7-di (4-methoxyphenyl)heptan]-4-yl *O*-ethyl carbonodithioate (3b)





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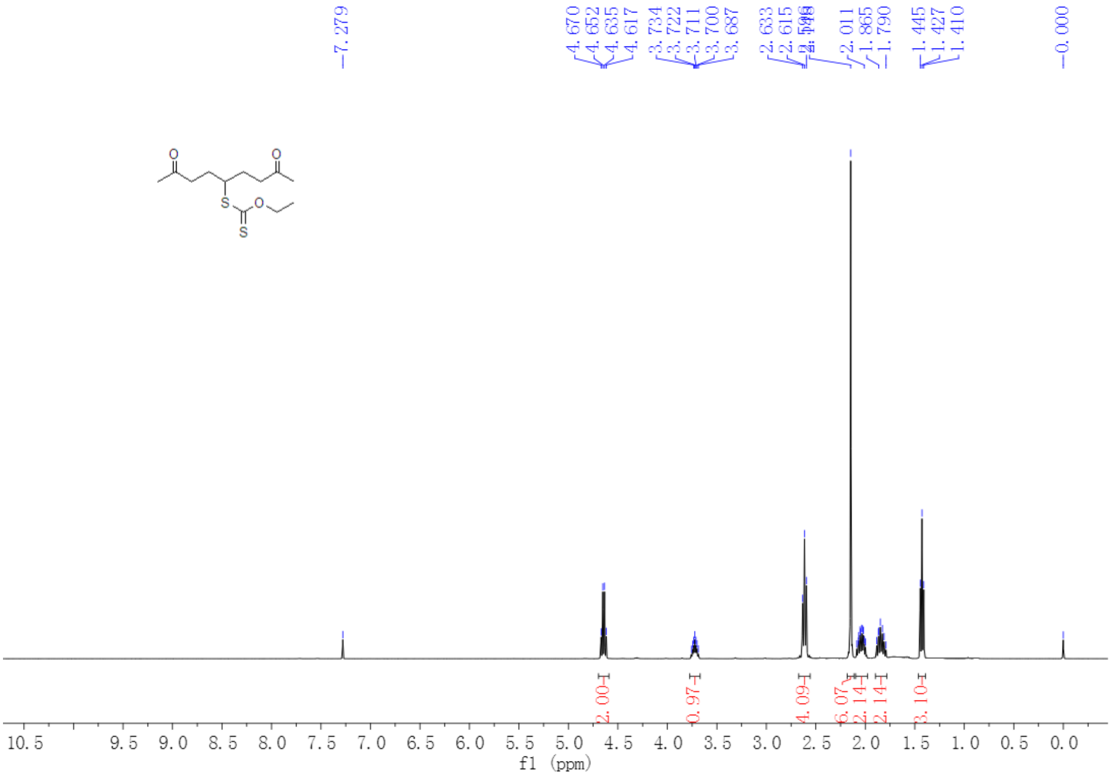
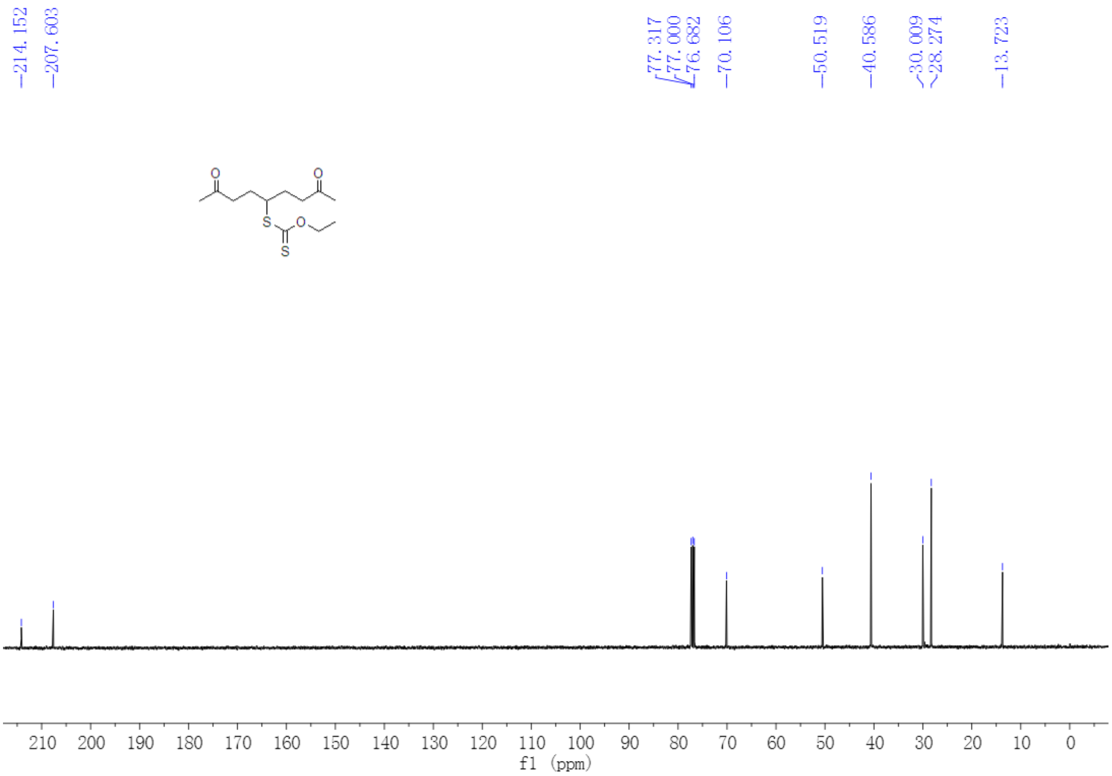
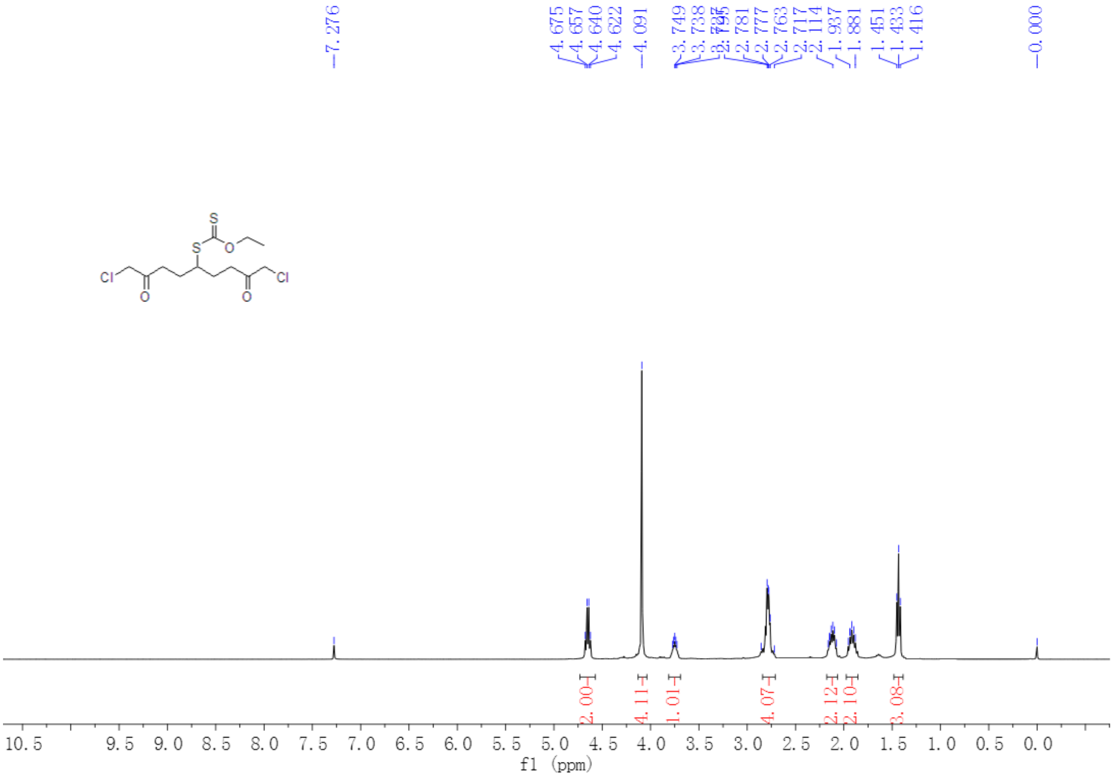
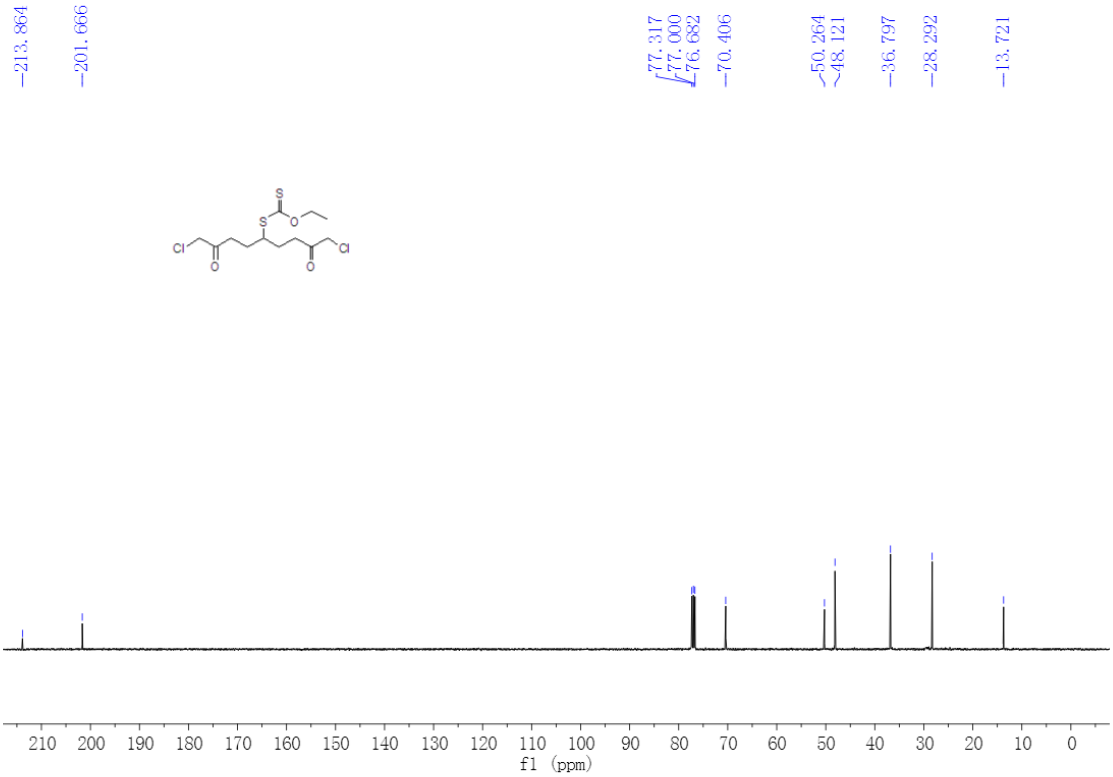


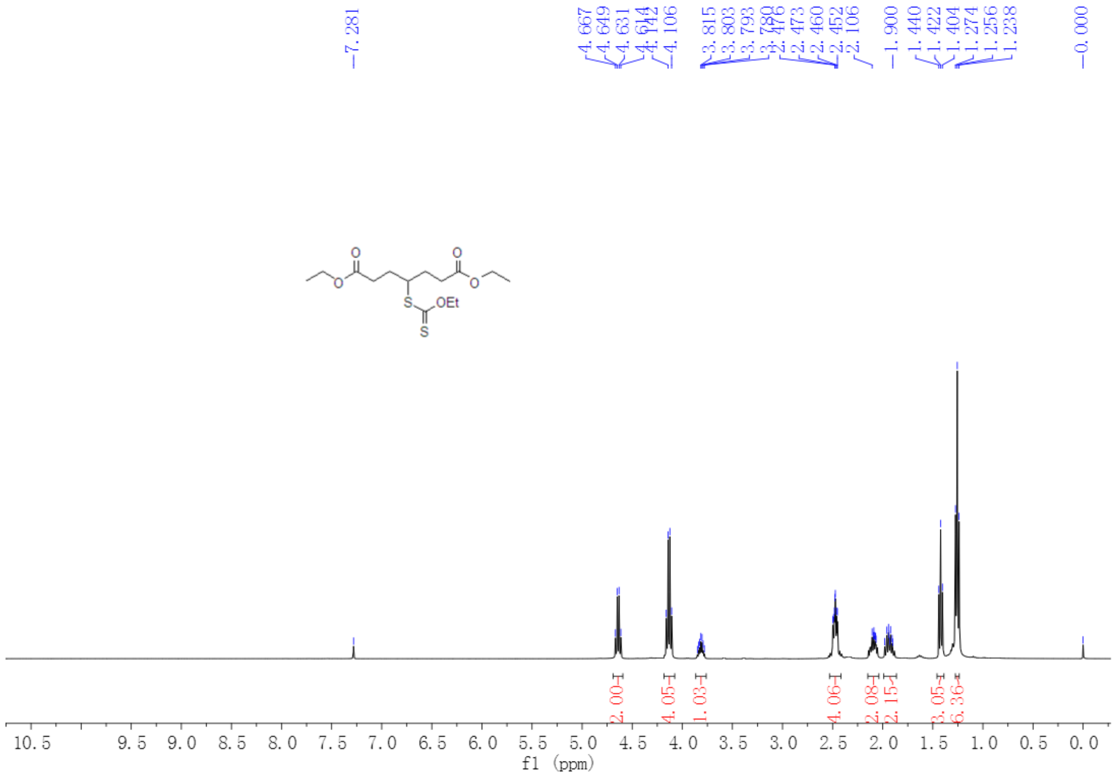


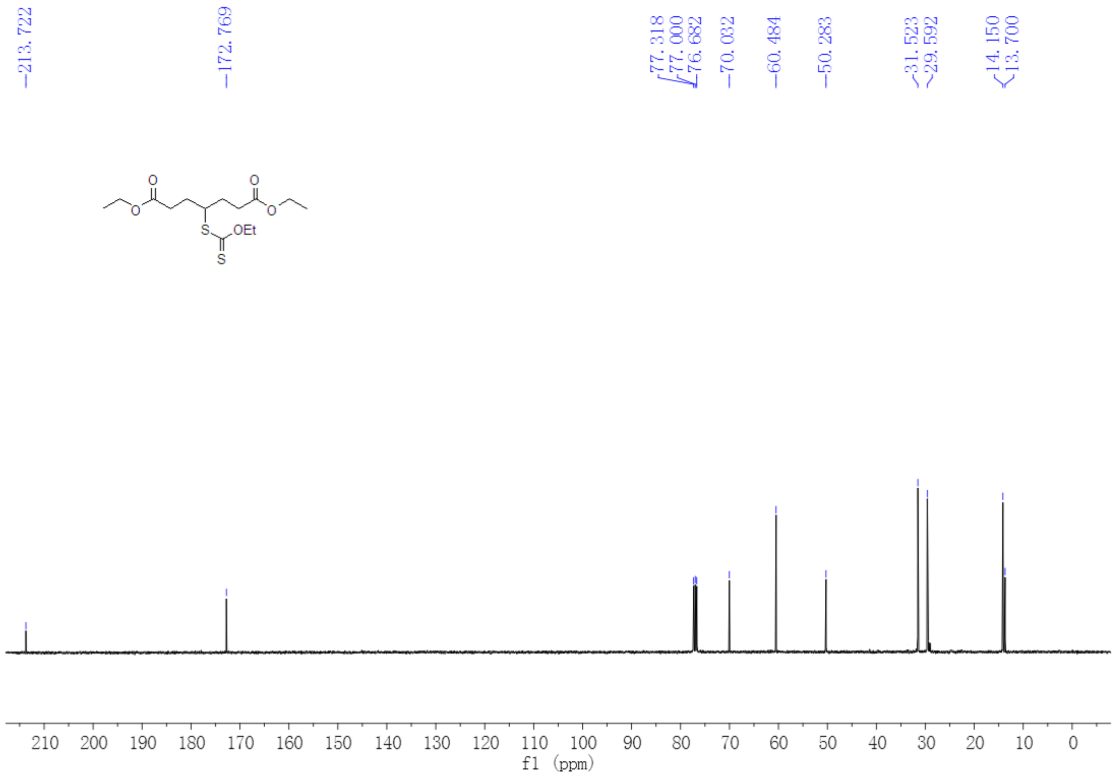
S-(1,7-Dichloro-1,7-dioxononan)-5-yl *O*-ethyl carbonodithioate (3d)



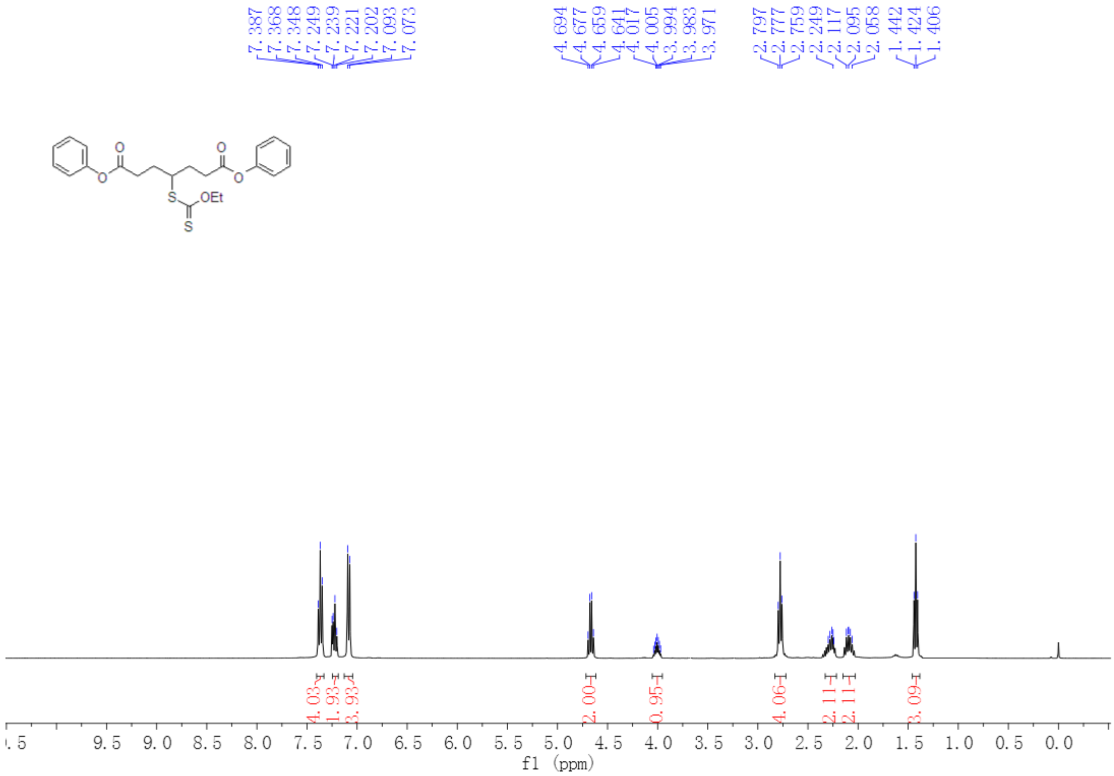


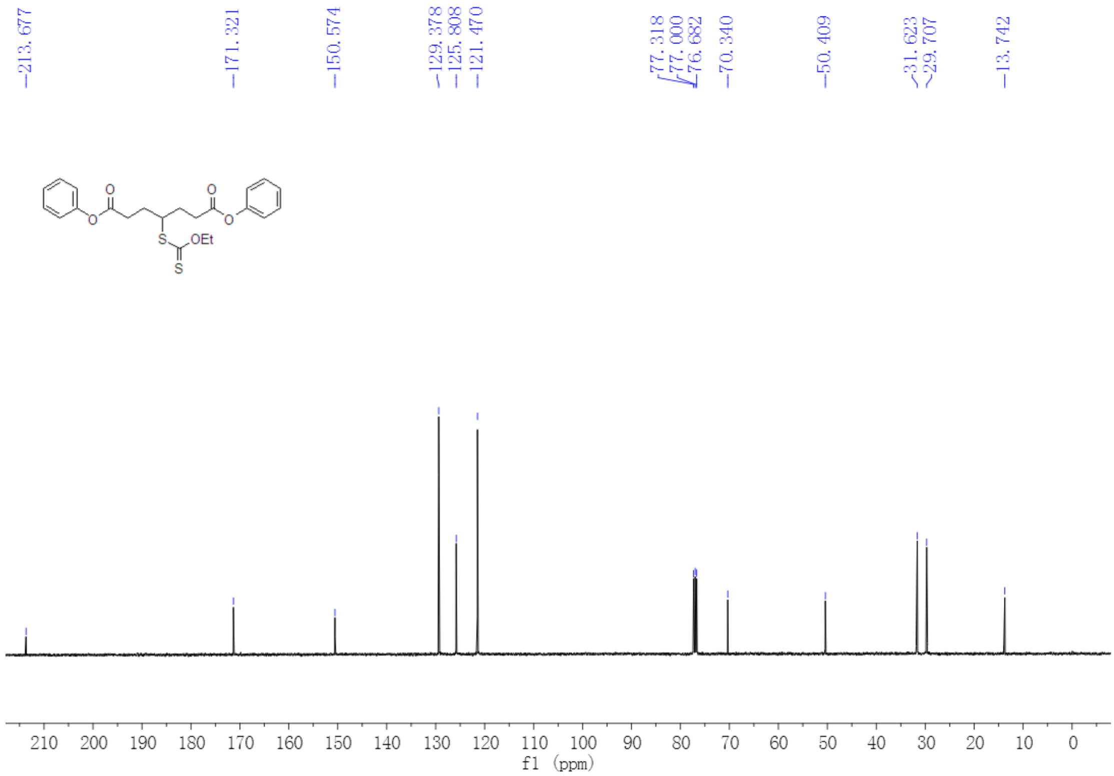
S-(1,7-Diethoxyl-1,7-dioxoheptan)-4-yl *O*-ethyl carbonodithioate (3e)





***S*-(1,7-Dioxo-1,7-diphenoxyheptan)-4-yl *O*-ethyl carbonodithioate (3f)**





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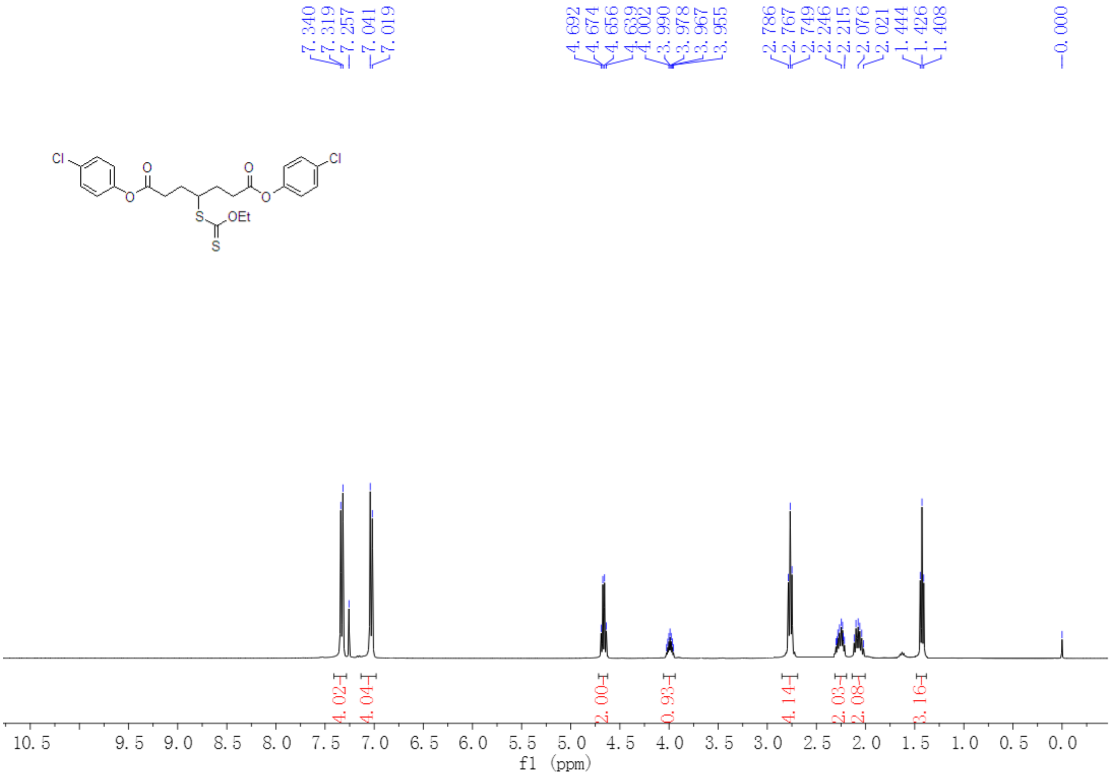
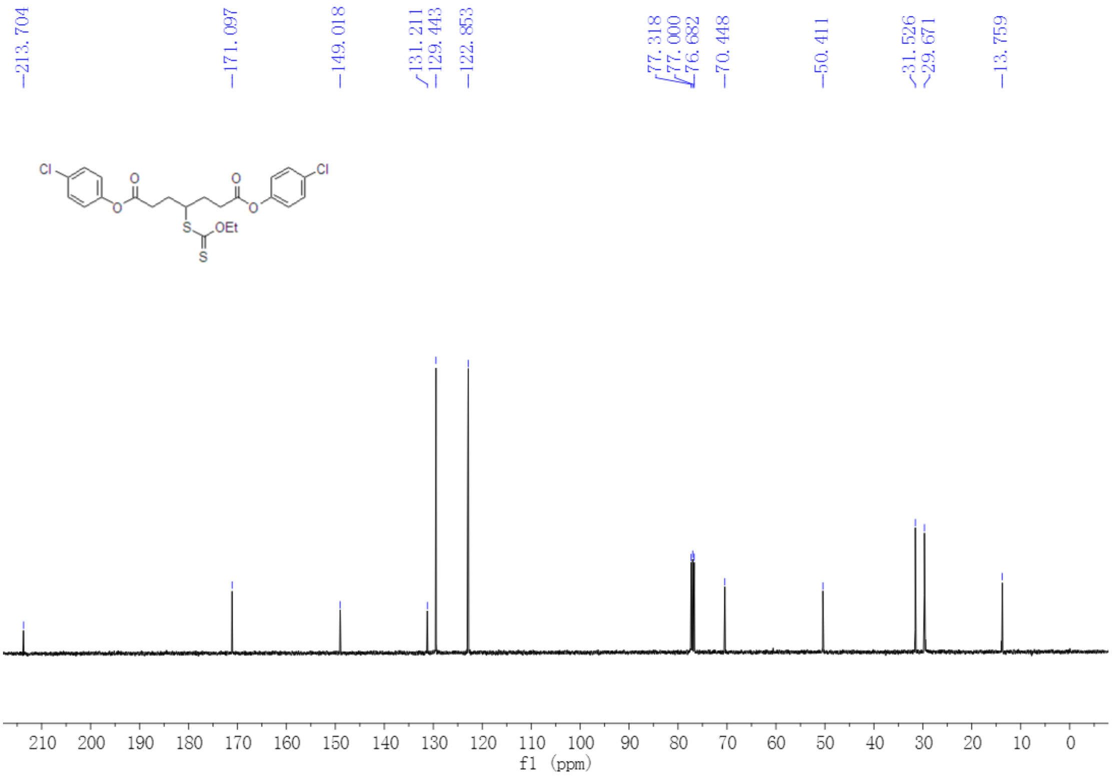
S-[1,7-Di(4-chloro-phenoxy)-1,7-dioxoheptan]-4-yl *O*-ethyl carbonodithioate (3g)





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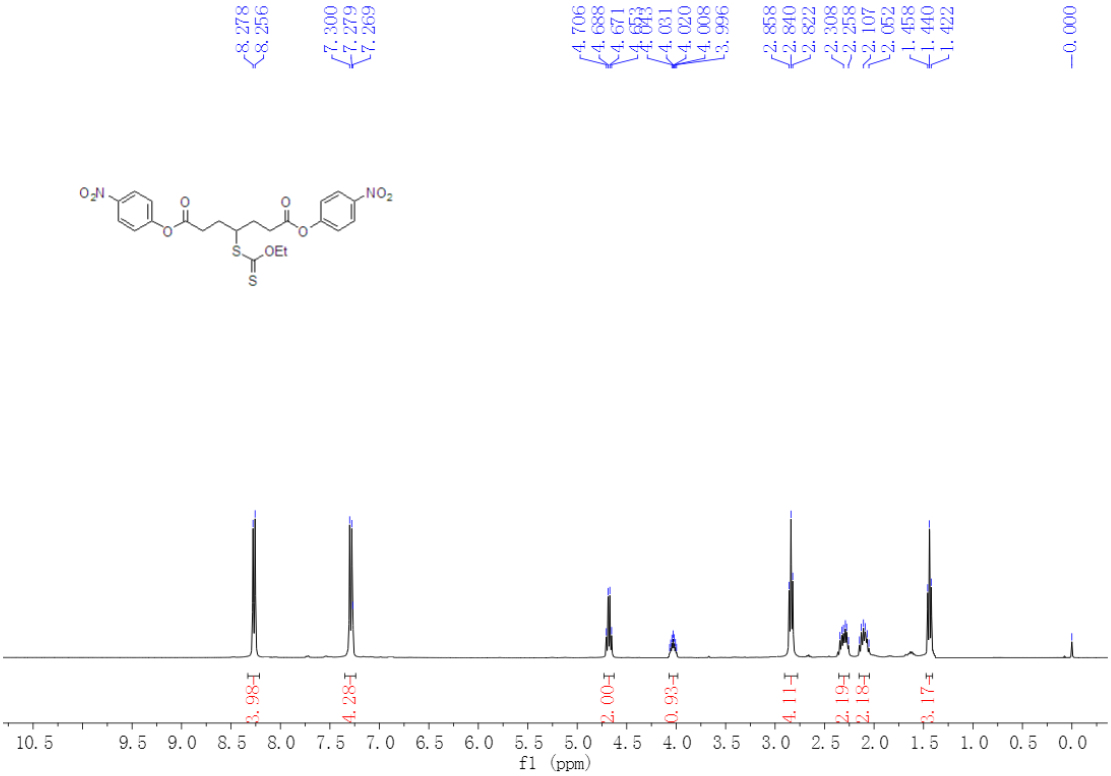
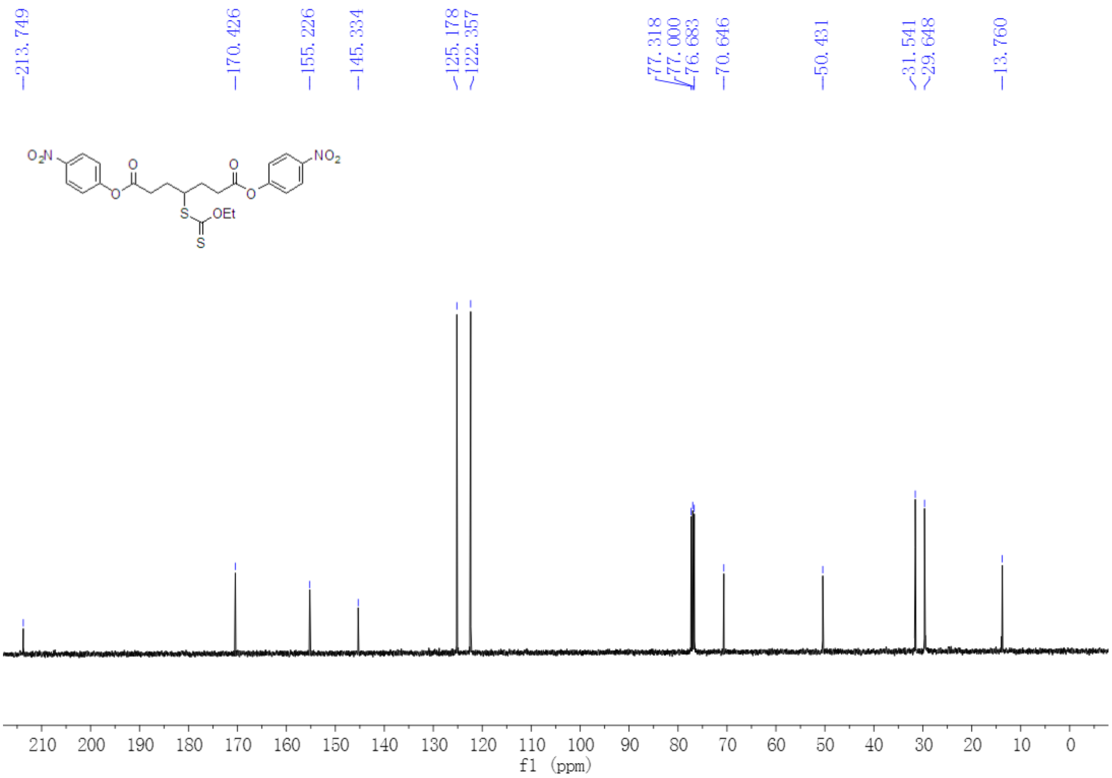
S-[1,7-Di(4-nitro-phenoxy)-1,7-dioxoheptan]-4-yl *O*-ethyl carbonodithioate (3h)





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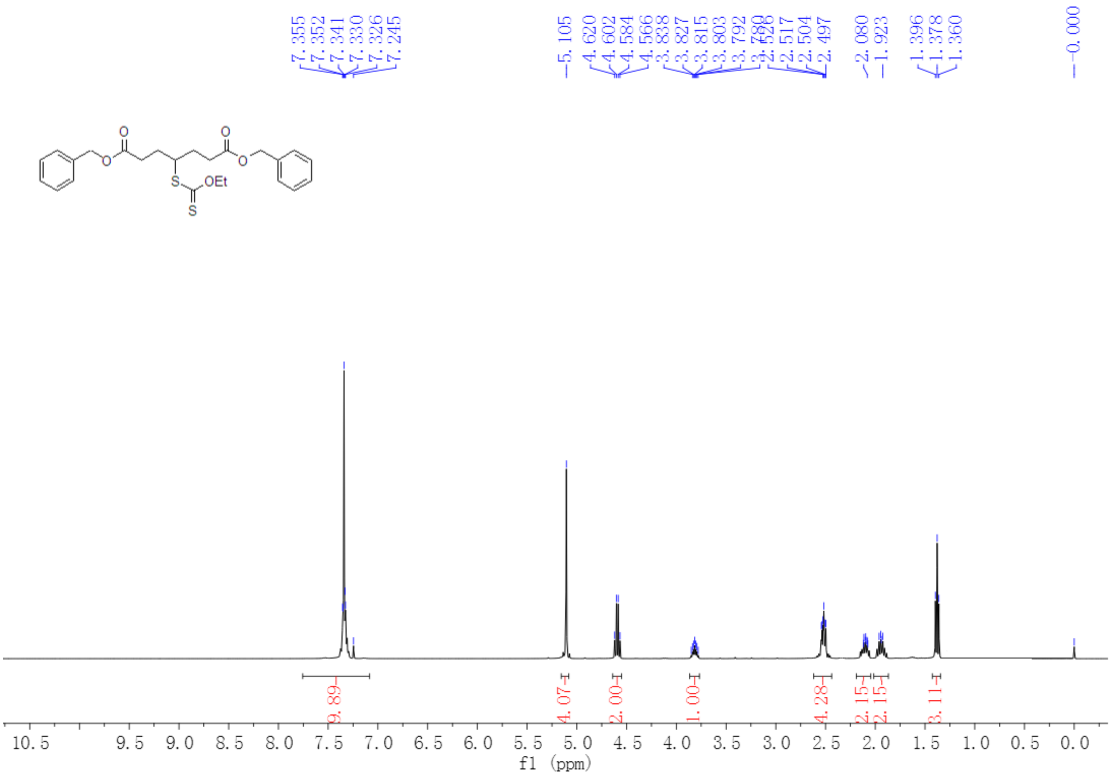
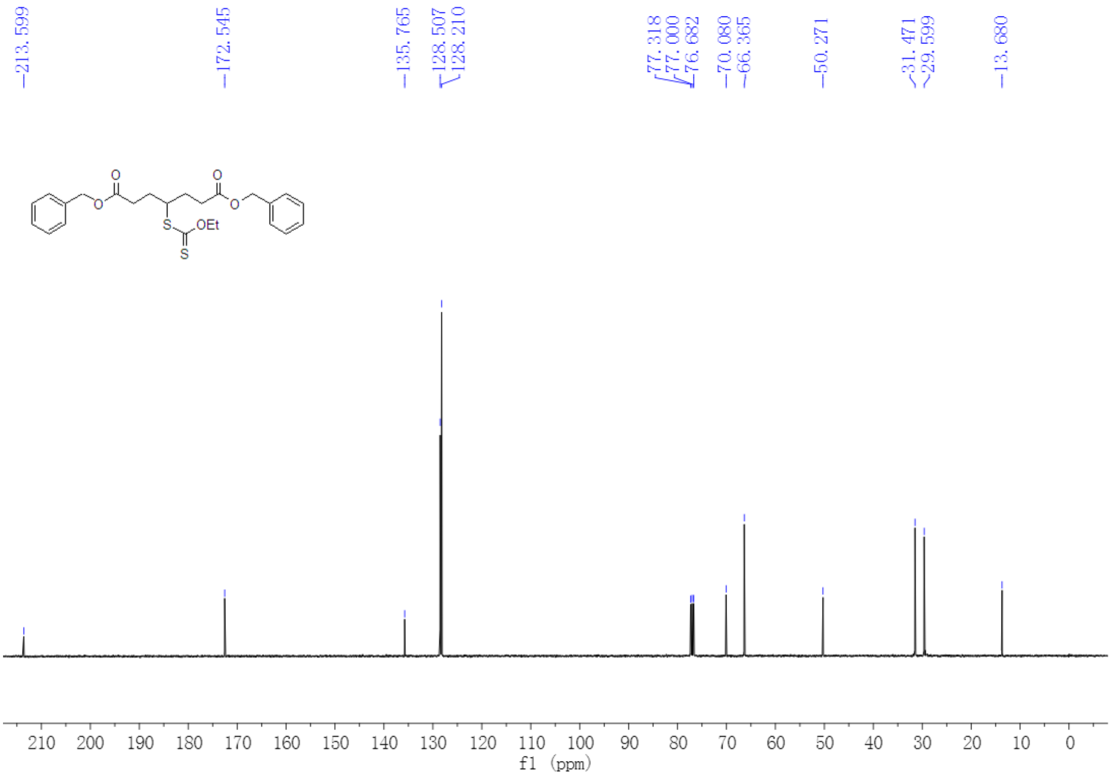
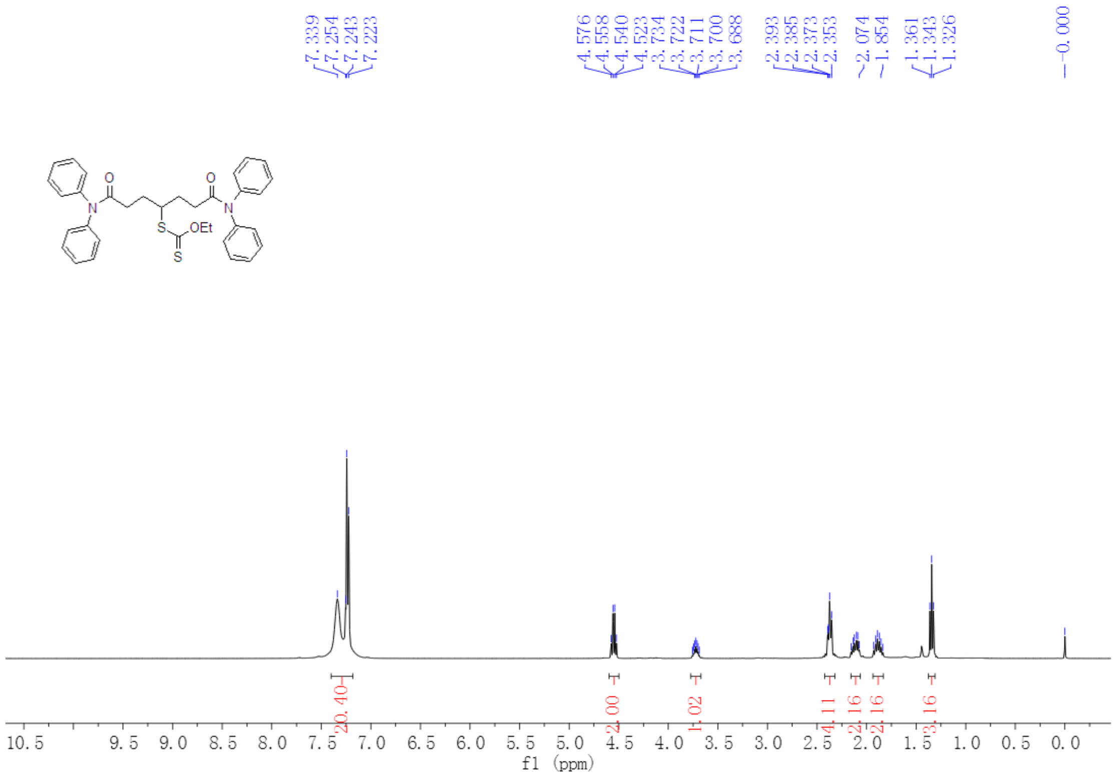
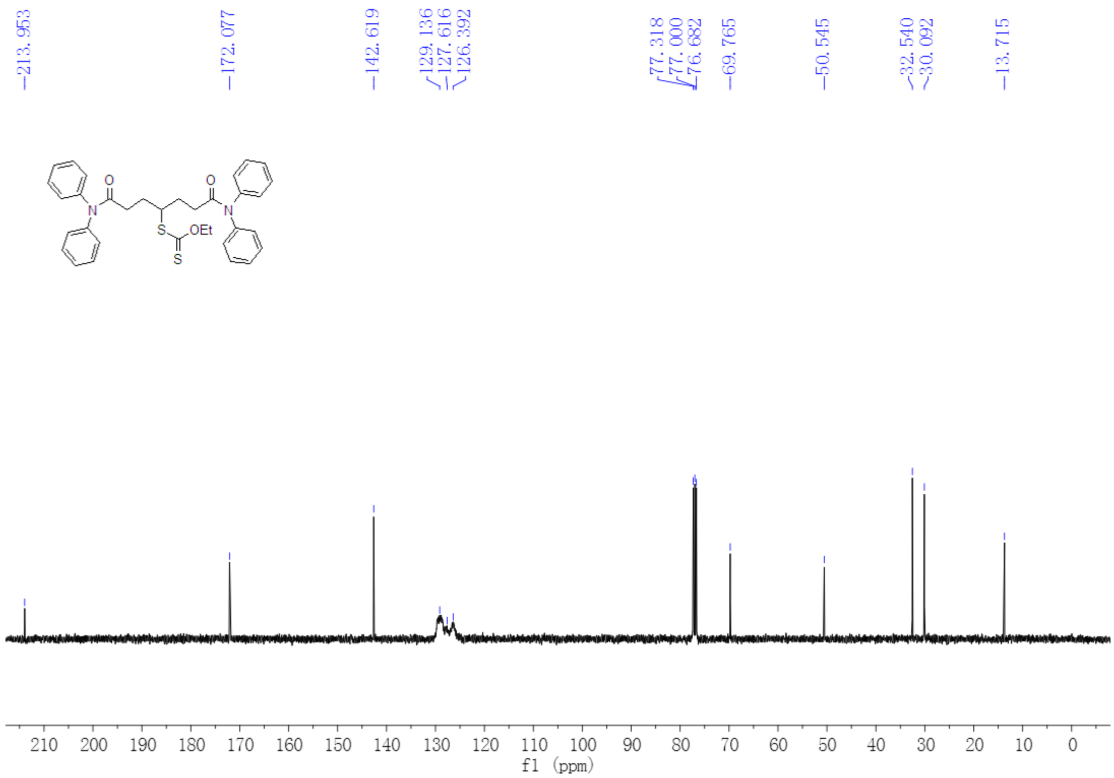
S-(1,7-Dibenzyloxy-1,7-dioxoheptan)-4-yl O-ethyl carbonodithioate (3i)



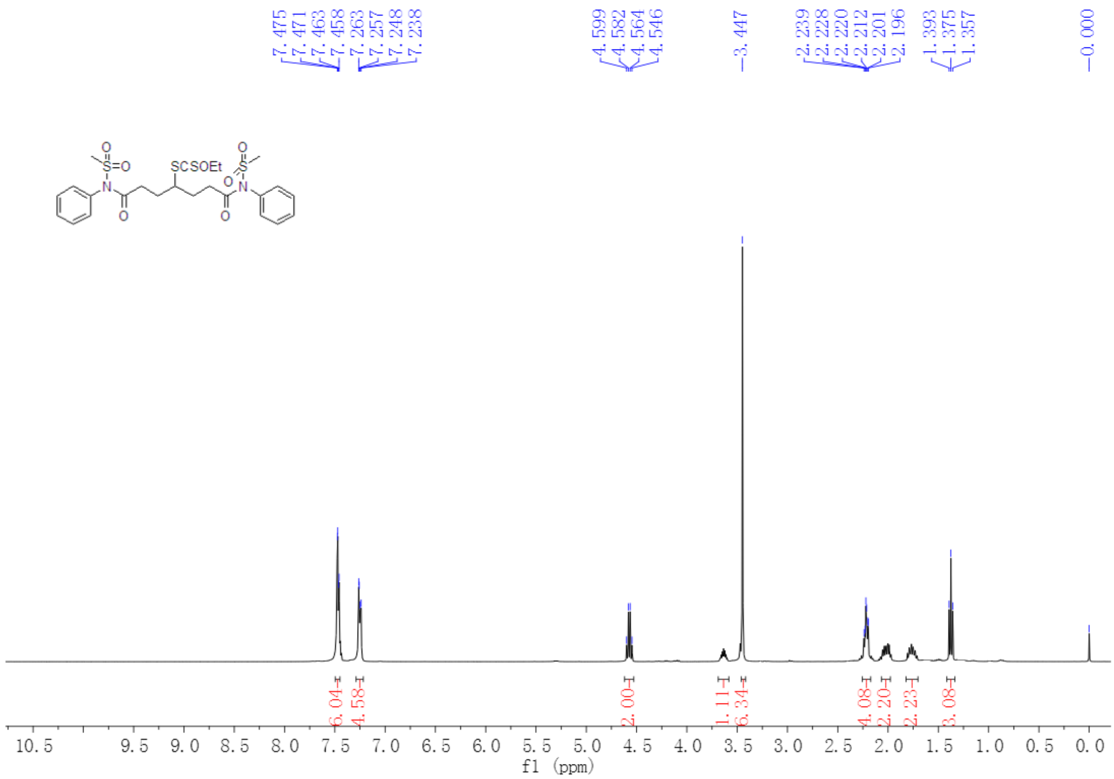


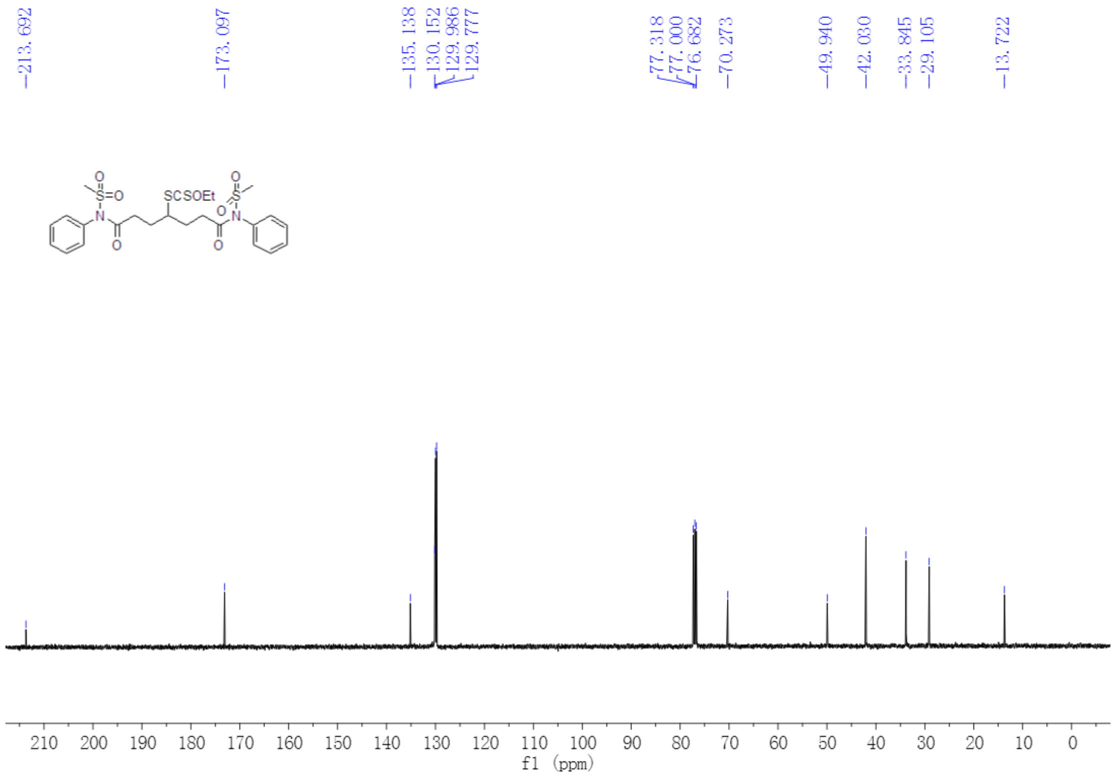
S-{[1,7-Di(diphenylamino)-1,7-dioxo]heptan}-4-yl *O*-ethyl carbonodithioate (3j)



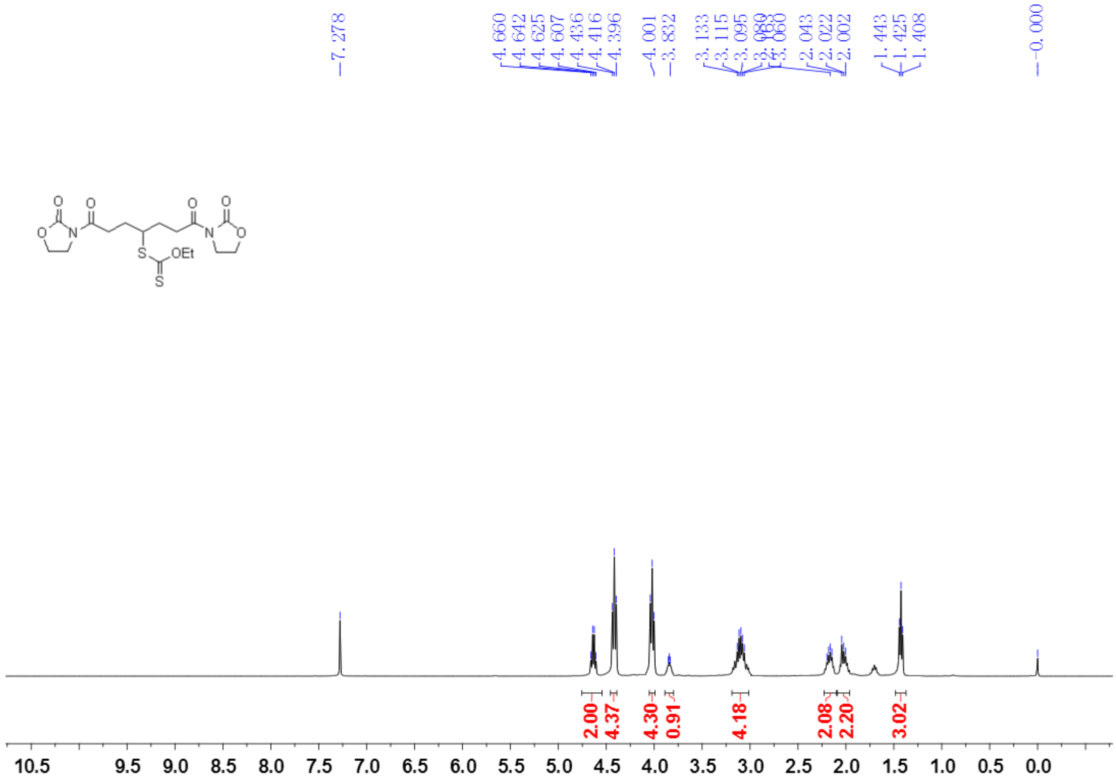


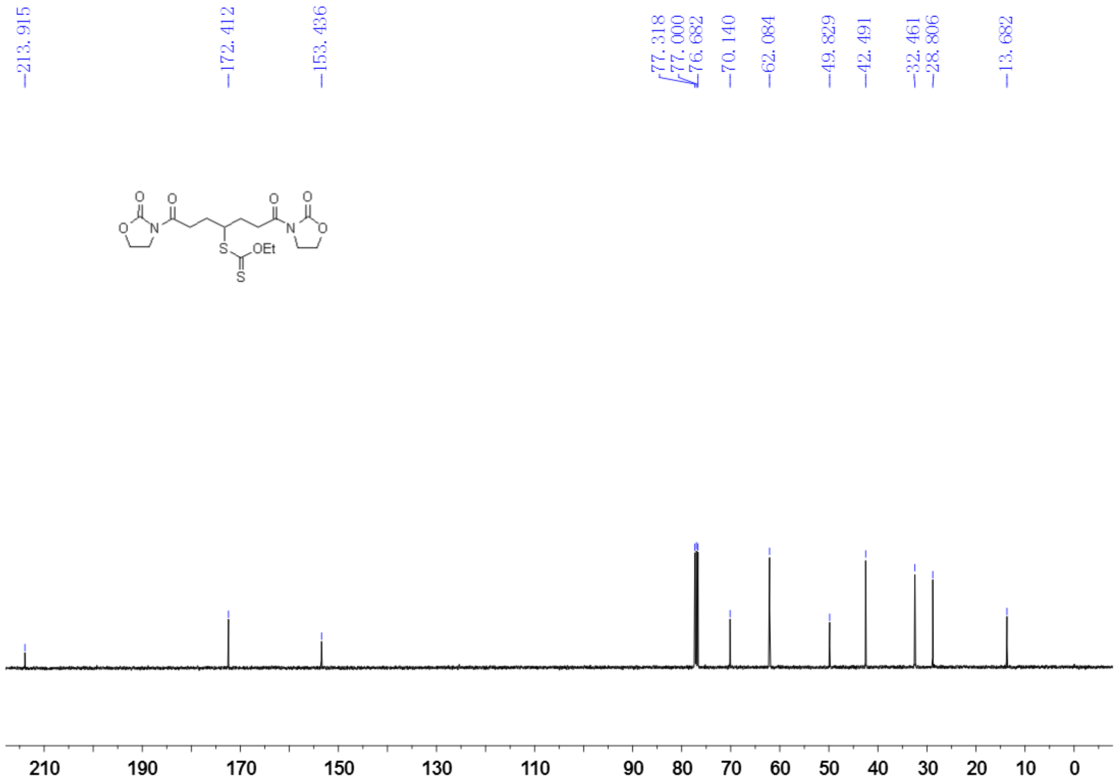
_S_-[1,7-Di(methanesulfonylphenylamino)-1,7-dioxoheptan]-4-yl _O_-ethyl carbonodithioate (3k)





S-[1,7-Dioxo-1,7-di(2-oxooxazolidin-3-yl)heptan]-4-yl O-ethyl carbonodithioate (3l)





S-(1,5-Dicyanopentan-3-yl) *O*-ethyl carbonodithioate (3m)