Supporting Information

for

One-pot odourless synthesis of thioesters via in situ generation of thiobenzoic acids using benzoic anhydrides and thiourea

Mohammad Abbasi*[1] and Reza Khalifeh[2]

Address: [1]Chemistry Department, Faculty of Sciences, Persian Gulf University, Bushehr 75169, Iran and [2]Department of Chemistry, Shiraz University of Technology, Shiraz, Iran

Email: Mohammad Abbasi - abbassi@pgu.ac.ir

* Corresponding author

Analytical data

General procedure

A mixture of a well-powdered benzoic anhydride (1.2 mmol), thiourea (1.3 mmol) and Et_3N (0.5 mL) was stirred at 40–80 °C until the starting anhydride was completely consumed and a two-phase system containing Et_3N and a thick brick-red liquid was formed. Then, water (1 mL) and an electron-deficient alkene or an alkyl halide (1 mmol) were added to the mixture and stirring was continued at room temperature. After consumption of starting alkene or halide (1–3 h), the crude product was extracted with EtOAc (3 × 2 mL), concentrated and purified by chromatography on silica gel respectively. The desired thioesters were produced in good to excellent yields.

***S*-3-Oxobutyl benzothioate (1)**

Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.95-7.91 (m, 2H), 7.58-7.52 (m, 1H), 7.45-7.39 (m, 2H), 3.24 (t, *J* = 6.7 Hz, 2H), 2.86 (t, *J* = 6.7 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 206.5, 191.9, 136.8, 133.5, 128.6, 127.2, 43.4, 29.9, 22.7; IR (neat): *v* (cm^{-1}) = 1717 (C=O ketone), 1655 (C=O thioester); Anal. Calcd for ($C_{11}H_{12}O_2S$): C, 63.43; H, 5.81; S, 15.40. Found: C, 63.51; H, 5.77; S, 15.42.

***S*-2-Cyanoethyl benzothioate (2)**

Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.96-7.92 (m, 2H), 7.63-7.57 (m, 1H), 7.50-7.43 (m, 2H), 3.30 (t, *J* = 6.9 Hz, 2H), 2.77 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 190.8, 136.2, 134.0, 128.8, 127.4, 118.0, 24.7, 18.7; IR (neat): *v* (cm^{-1}) = 2251 (CN), 1666 (C=O thioester) ; Anal. Calcd for ($C_{10}H_9NOS$): C, 62.80; H, 4.74; N, 7.32; S, 16.77. Found: C, 62.77; H, 4.83; N, 7.30; S, 16.81.

Ethyl 3-(benzoylthio)propanoate (3)

Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.88-7.85 (m, 2H), 7.51-7.45 (m, 1H), 7.38-7.32 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.24 (t, *J* = 6.9 Hz, 2H), 2.64 (t, *J* = 6.9 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 191.5, 171.7, 136.8, 133.4, 128.6, 127.2, 60.7, 34.5, 24.0, 14.2; IR (neat): *v* (cm^{-1}) = 1736 (C=O ester), 1666 (C=O thioester) ; Anal. Calcd for ($C_{12}H_{14}O_3S$): C, 60.48; H, 5.92; S, 13.46. Found: C, 60.40; H, 5.93; S, 13.50.

Butyl 3-(benzoylthio)propanoate (4)

Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.95-7.91 (m, 2H), 7.54-7.51 (m, 1H), 7.44-7.38 (m, 2H), 4.09 (t, *J* = 6.6 Hz, 2H), 3.30 (t, *J* = 7.0 Hz, 2H), 2.71 (t, *J* = 7.0 Hz, 2H), 1.65-1.54 (m, 2H), 1.43-1.31 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 191.5, 171.8, 136.8, 133.5, 128.6, 127.2, 64.7, 34.5, 30.6, 24.1, 19.1, 13.7; IR (neat): *v* (cm^{-1}) = 1732 (C=O ester), 1666 (C=O thioester); Anal. Calcd for ($C_{14}H_{18}O_3S$): C, 63.13; H, 6.81; S, 12.04. Found: C, 63.19; H, 6.85; S, 11.98.

The IR spectrum of the product showed characteristic signal of ester functional group (1732 cm^{-1}) and phenyl thioester (1666 cm^{-1}). The ^{1}H-NMR spectrum of this compound consists of four triplet signals at 0.90, 2.71, 3.30 and 4.09 ppm which were respectively correlated to the resonances of CH_3, CH_2CO, CH_2S and CH_2O hydrogen atoms. It is also consists of multiple resonances between 1.31-1.43, 1.54-1.65 and 7.38-7.95 ppm due to resonances of hydrogens on CH_2 linked to methyl group, CH_2 linked to CH_2O and benzene ring. The ^{13}C NMR spectrum contained 12 resonances, which were assigned to the methyl (δ = 13.7), methylenes (δ = 19.1, 24.1, 30.6, 34.5, 64.7), aromatic (δ = 127.2, 128.6, 133.5, 136.8), ester (δ = 171.8) and thioester (191.5) carbons (Figure S1).

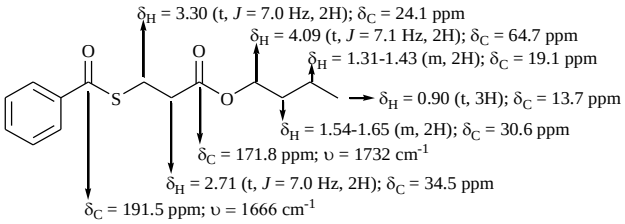

Figure S1: Selected spectral data for compound (**4**).

_S_-(3-Oxobutyl) 4-methylbenzothioate (5)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 3.14 (t, *J* = 6.7 Hz, 2H), 2.74 (t, *J* = 6.7 Hz, 2H), 2.30 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:206.5, 191.4, 144.3, 134.3, 129.3, 127.6, 43.4, 29.9, 22.6, 21.6; IR (neat): *v* (cm^{-1}) = 1717 (C=O ketone), 1659 (C=O thioester); Anal. Calcd for ($C_{12}H_{14}O_2S$): C, 64.83; H, 6.35; S, 14.42. Found: C, 64.80; H, 6.43; S, 14.47.

_S_-(2-Cyanoethyl) 4-methylbenzothioate (6)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 3.20 (t, *J* = 7 Hz, 2H), 2.68 (t, *J* = 7 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:190.1, 145.0, 133.7, 129.5, 127.4, 118.1, 24.7, 21.7, 18.7; IR (neat) : *v* (cm^{-1}) =2253 (CN), 1663 (C=O thioester); Anal. Calcd for ($C_{11}H_{11}NOS$): C, 64.36; H, 5.40; N, 6.82; S, 15.62. Found: C, 64.41; H, 5.35; N, 6.82; S, 15.70.

Ethyl 3-((4-methylbenzoyl)thio)propanoate (7)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.22 (t, *J* = 7 Hz, 2H), 2.63 (t, *J* = 7 Hz, 2H), 2.31 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:191.1, 171.7, 144.3, 134.3, 129.3, 127.3, 60.7, 34.5, 23.9, 21.6, 14.2; IR (neat) : *v* (cm^{-1}) =1736 (C=O ester), 1659 (C=O thioester); Anal. Calcd for ($C_{13}H_{16}O_3S$): C, 61.88; H, 6.39; S, 12.71. Found: C, 61.93; H, 6.33; S, 12.66.

Butyl 3-((4-methylbenzoyl)thio)propanoate (8)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 4.10 (t, *J* = 6.6 Hz, 2H, 3.29 (t, *J* = 7.0 Hz, 2H), 2.71 (t, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 1.66-1.54 (m, 2H), 1.44-1.35 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:191.1, 171.8, 144.3, 134.3, 129.3, 127.3, 64.7, 34.6, 30.6, 24.0, 21.7, 19.1, 13.7; IR (neat) : *v* (cm^{-1}) =1736 (C=O ester), 1663 (C=O thioester); Anal. Calcd for ($C_{15}H_{20}O_3S$): C, 64.26; H, 7.19; S, 11.44. Found: C, 64.33; H, 7.24; S, 11.38.

***S*-(3-Oxobutyl) 4-chlorobenzothioate (9)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 3.20 (t, *J* = 6.7 Hz, 2H), 2.80 (t, *J* = 6.7 Hz, 2H), 2.10 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 206.3, 190.7, 139.8, 135.2, 128.9, 128.5, 43.3, 29.9, 22.8; IR (neat): *v* (cm^{-1}) =1717 (C=O ketone), 1666 (C=O thioester); Anal. Calcd for ($C_{11}H_{11}ClO_2S$): C, 54.43; H, 4.57; S, 13.21. Found: C, 54.50; H, 4.53; S, 13.13.

***S*-(2-Cyanoethyl) 4-chlorobenzothioate (10)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 3.24 (t, *J* = 6.9 Hz, 2H), 2.70 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:189.4, 140.5, 134.5, 129.1, 128.7, 117.9, 28.8, 18.6; IR (neat): *v* (cm^{-1}) =2249 (CN), 1659 (C=O thioester); Anal. Calcd for ($C_{10}H_8ClNOS$): C, 53.22; H, 3.57; N; 6.21; S, 14.21. Found: C, 53.20; H, 3.64; N; 6.29; S, 14.14.

Ethyl 3-((4-chlorobenzoyl)thio)propanoate (11)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.24 (t, *J* = 6.9 Hz, 2H), 2.65 (t, *J* = 6.9 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:190.4, 171.6, 139.9, 135.1, 128.9, 128.6, 60.8, 34.4, 23.9, 14.2; IR (neat): *v* (cm^{-1}) =

1736 (C=O ester), 1666 (C=O thioester); Anal. Calcd for ($C_{12}H_{13}ClO_3S$): C, 52.84; H, 4.80; S, 11.76. Found: C, 52.91; H, 4.87; S, 11.75.

Butyl 3-((4-chlorobenzoyl)thio)propanoate (12)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 3.24 (t, *J* = 6.9 Hz, 2H), 2.65 (t. *J* = 6.9 Hz, 2H)1.59-1.58 (m, 2H), 1.37-1.22 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 190.3, 171.7, 139.8, 135.1, 128.9, 128.5, 64.7, 34.4, 30.6, 24.2, 19.1, 13.7; IR (neat): *v* (cm^{-1}) =1732 (C=O ester), 1666 (C=O thioester); Anal. Calcd for ($C_{14}H_{17}ClO_3S$): C, 55.90; H, 5.70; S, 10.66. Found: C, 55.96; H, 5.61; S, 10.71.

***S*-(3-Oxobutyl) 4-methoxybenzothioate (13)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.77 (s, 3H), 3.15 (t, *J* = 6.8 Hz, 2H), 2.78 (t, *J* = 6.8 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 206.6, 190.3, 163.8, 132.8, 129.3, 113.8, 55.5, 43.6, 29.9, 22.6; IR (neat): *v* (cm^{-1}) =1717 (C=O ketone), 1651 (C=O thioester); Anal. Calcd for ($C_{12}H_{14}O_3S$): C, 60.48; H, 5.92; S, 13.46. Found: C, 60.55; H, 6.00; S, 13.39.

***S*-(2-Cyanoethyl) 4-methoxybenzothioate (14)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 3.20 (t, *J* = 6.9 Hz, 2H), 2.68 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:188.9, 164.2, 129.6, 129.0, 118.1, 114.0, 55.6, 24.6, 18.8; IR (neat): *v* (cm^{-1}) =2249 (CN), 1651(C=O thioester); Anal. Calcd for ($C_{11}H_{11}NO_2S$): C, 59.71; H, 5.01; N, 6.33; S, 14.49. Found: C, 59.70; H, 5.09; N, 6.39; S, 14.42.

Ethyl 3-((4-methoxybenzoyl)thio)propanoate (15)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.85(d, *J* = 9 Hz, 2H), 6.84 (d, *J* = 9 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.22 (t, *J* = 7 Hz, 2H), 2.64 (t, *J* = 7 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (62.5

MHz, $CDCl_3$) δ:190.0, 171.8, 163.8, 129.7, 129.4, 113.8, 60.7, 55.5, 34.6, 23.9, 14.2; IR (neat): *v* (cm^{-1}) =1736 (C=O ester), 1659 (C=O thioester); Anal. Calcd for ($C_{13}H_{16}O_4S$): C, 58.19; H, 6.01; S, 11.95. Found: C, 58.13; H, 5.97; S, 11.98.

Butyl 3-((4-methoxybenzoyl)thio)propanoate (16)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 3.79 (s, 3H), 3.22 (t, *J* = 6.9 Hz, 2H), 2.65 (t, *J* = 6.9 Hz, 2H), 1.61-1.49 (m, 2H), 1.35-1.18 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:190.0, 171.9, 163.8, 129.7, 129.4, 113.8, 64.6, 55.5, 34.6, 30.6, 23.9, 19.1, 13.7; IR (neat): *v* (cm^{-1}) =1732 (C=O ester), 1659 (C=O thioester); Anal. Calcd for ($C_{15}H_{20}O_4S$): C, 60.79; H, 6.80; S, 10.82. Found: C, 60.85; H, 6.80; S, 10.84.

***S*-Decyl benzothioate (17)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.91-7.86 (m, 2H), 7.51-7.33 (m, 3H), 2.99 (t, *J* = 7.3 Hz, 2H), 1.65-1.54 (m, 2H), 1.38-1.19 (m, 14H), 0.83-0.78 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:192.0, 137.3, 133.1, 128.9, 127.4, 31.9, 29.6, 29.6, 29.5, 29.3, 29.2, 29.0, 29.0, 22.7, 14.1; IR (neat): *v* (cm^{-1}) =1666 (C=O thioester); ; Anal. Calcd for ($C_{17}H_{26}OS$): C, 73.33; H, 9.41; S, 11.52. Found: C, 73.31; H, 9.48; S, 11.46.

***S*-(2-Methylallyl) benzothioate (18)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.92-7.88 (m, 2H), 7.51-7.32 (m, 3H), 4.97-4.96 (m, 1H), 4.82-4.80 (m, 1H), 3.67 (s, 2H), 1.74 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 191.4, 140.7, 137.0, 133.4, 128.6, 127.3, 114.3, 35.8, 21.3; IR (neat): *v* (cm^{-1}) = 1666 (C=O thioester); Anal. Calcd for ($C_{11}H_{12}OS$): C, 68.71; H, 6.29; S, 16.68. Found: C, 68.67; H, 6.36; S, 16.60.

***S*-Prop-2-yn-1-yl benzothioate (19)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.88-7.84 (m, 2H), 7.53-7.46 (m, 1H), 7.40-7.33 (m, 2H), 3.75 (d, *J* = 2.7 Hz, 2H), 2.15 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:190.1, 136.2, 133.8, 128.8, 127.3, 78.9, 71.1, 17.5; IR (neat): *v* (cm^{-1}) =3294, 2125, 1670; Anal. Calcd for ($C_{10}H_8OS$): C, 68.15; H, 4.58; S, 18.19. Found: C, 68.20; H, 4.55; S, 18.26.

***S*-Methyl benzothioate (20)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.91-7.87 (m, 2H), 7.52-7.32 (m, 3H), 2.39 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 192.4, 137.7, 133.3, 128.6, 127.1, 11.7; IR (neat): *v* (cm^{-1}) =1666; Anal. Calcd for (C_8H_8OS): C, 63.13; H, 5.30; S, 21.07. Found: C, 63.05; H, 5.31; S, 21.08.

***S*-Octyl benzothioate (21)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.77-7.71 (m, 2H), 7.33-7.16 (m, 3H), 2.83 (t, *J* = 7.3 Hz, 2H), 1.46-1.40 (m, 2H), 1.21-1.04 (m, 10H), 0.67-0.62 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:192.0, 137.3, 133.2, 128.5, 127.2, 31.8, 29.5, 29.3, 29.2, 29.1, 29.0, 22.7, 14.1; IR (neat): *v* (cm^{-1}) =1666; Anal. Calcd for ($C_{15}H_{22}OS$): C, 71.95; H, 8.86; S, 12.81. Found: C, 72.03; H, 8.81; S, 12.77.

***S*-4-Methylbenzyl benzothioate (22)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.86-7.83 (m, 2H), 7.44-7.21 (m, 3H), 7.15 (d, *J* = 8 Hz, 2H), 6.99 (d, *J* = 8 Hz, 2H), 4.17 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 191.4, 137.1, 136.9, 134.4, 133.4, 129.4, 128.9, 128.7, 127.6, 33.2, 21.2; IR (neat): *v* (cm^{-1}) =1663; Anal. Calcd for ($C_{15}H_{14}OS$): C, 74.34; H, 5.82; S, 13.23. Found: C, 74.33; H, 5.90; S, 13.20.

***S*-Benzyl 4-methylbenzothioate (23)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.1 Hz, 2H), 7.30-7.17 (m, 5H), 7.14 (d, *J* = 8.1 Hz, 2H), 4.21 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:190.8, 144.4, 137.7, 134.3, 129.3, 129.0,

128.6, 127.4, 53.5, 33.2, 21.6; IR (neat): *v* (cm^{-1}) = 1659; Anal. Calcd for ($C_{15}H_{14}OS$): C, 74.34; H, 5.82; S, 13.23. Found: C, 74.27; H, 5.90; S, 13.30.

_S_-Prop-2-yn-1-yl 4-methylbenzothioate (24)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 3.73 (d, *J* = 2.7 Hz, 2H), 2.33 (s, 3H), 2.14 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:189.6, 144.7, 133.7, 129.4, 127.4, 79.0, 71.0, 21.7, 17.3; IR (neat): *v* (cm^{-1}) =3294, 2122, 1666; Anal. Calcd for ($C_{11}H_{10}OS$): C, 69.44; H, 5.30; S, 16.85. Found: C, 69.36; H, 5.33; S, 16.91.

_S_-Octyl 4-methylbenzothioate (25)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.22 (s, 3H), 1.54-1.43 (m, 2H), 1.24-1.10 (m, 10H), 0.72-0.68 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 190.8, 144.0, 134.8, 129.2, 127.2, 31.8, 29.6, 29.2, 29.1, 29.0, 22.6, 21.6, 14.1; IR (neat): *v* (cm^{-1}) =1663; Anal. Calcd for ($C_{16}H_{24}OS$): C, 72.67; H, 9.15; S, 12.13. Found: C, 72.74; H, 9.10; S, 12.08.

_S_-Methyl 4-methylbenzothioate (26)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 2.38 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 192.0, 144.1, 134.5, 129.2, 127.2, 21.6, 11.6; IR (neat): *v* (cm^{-1}) =1663; Anal. Calcd for ($C_9H_{10}OS$): C, 65.02; H, 6.06; S, 19.29. Found: C, 65.01; H, 6.15; S, 19.22.

_S_-(2-Methylallyl) 4-methylbenzothioate (27)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 4.95 (s, 1H), 4.80-4.79 (m, 1H), 3.62 (s, 2H), 2.31 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:191.0, 144.2, 140.9, 134.4, 129.3, 127.3, 114.2, 35.7, 21.7, 21.3; IR (neat) : *v* (cm^{-1}) =1659; Anal. Calcd for ($C_{12}H_{14}OS$): C, 69.86; H, 6.84; S, 15.54. Found: C, 69.80; H, 6.88; S, 15.61.

***S*-Decyl 4-chlorobenzothioate (28)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 2.99 (t, *J* = 7.3 Hz, 2H), 1.65-1.53 (m, 2H), 1.33-1.19 (m, 14H), 0.83-0.77 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:191.0, 139.5, 135.6, 128.8, 128.5, 31.9, 30.0, 29.5, 29.5, 29.3, 29.2, 29.1, 28.9, 22.7, 14.1; IR (neat): *v* (cm^{-1}) =1666; Anal. Calcd for ($C_{17}H_{25}ClOS$): C, 65.26; H, 8.05; S, 10.25. Found: C, 65.33; H, 8.13; S, 10.16.

***S*-Methyl 4-chlorobenzothioate (29)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 191.2, 139.6, 135.3, 128.9, 128.5, 11.8; IR (neat): *v* (cm^{-1}) =1666; Anal. Calcd for (C_8H_7ClOS): C, 51.48; H, 3.78; S, 17.18. Found: C, 51.51; H, 3.86; S, 17.10.

***S*-(2-Methylallyl) 4-chlorobenzothioate (30)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 4.96 (s, 1H), 4.82 (s, 1H), 3.67 (s, 2H), 1.73 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 190.2, 140.5, 139.7, 135.3, 128.9, 128.6, 114.5, 36.0, 21.3; IR (neat): *v* (cm^{-1}) =1666; Anal. Calcd for ($C_{11}H_{11}ClOS$): C, 58.27; H, 4.89; S, 14.14. Found: C, 58.35; H, 4.81; S, 14.09.

***S*-Prop-2-yn-1-yl 4-chlorobenzothioate (31)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 3.76 (d, *J* = 2.7 Hz, 2H), 2.16 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 188.9, 140.2, 134.6, 129.1, 128.7, 78.6, 71.3, 17.6; IR (neat): *v* (cm^{-1}) =3298, 2122, 1670; Anal. Calcd for ($C_{10}H_7ClOS$): C, 57.01; H, 3.35; S, 15.22. Found: C, 56.96; H, 3.29; **S, 15.29.**

***S*-4-Methylbenzyl 4-methoxybenzothioate (32)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 4.17 (s, 2H), 3.73 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 189.9, 163.8, 137.0, 134.7, 129.7, 129.5, 129.3, 128.9, 113.8, 55.5, 33.0, 21.1; IR (neat): *v* (cm^{-1}) = 1659 (C=O thioester); Anal. Calcd for ($C_{16}H_{16}O_2S$): C, 70.56; H, 5.92; S, 11.77. Found: C, 70.65; H, 5.88; S, 11.70.

***S*-Prop-2-yn-1-yl 4-methoxybenzothioate (33)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H), 3.73 (d, *J* = 2.7 Hz, 2H), 2.14 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 188.4, 164.1, 129.6, 129.1, 113.9, 79.1, 70.9, 55.5, 17.3; IR (neat): *v* (cm^{-1}) = 3294, 2118 , 1663; Anal. Calcd for ($C_{11}H_{10}O_2S$): C, 64.05; H, 4.89; S, 15.55. Found: C, 64.11; H, 4.95; S, 15.47.

***S*-(2-Methylallyl) 4-methoxybenzothioate (34)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 4.95 (m, 1H), 4.80-4.78 (m, 1H), 3.76 (s, 3H), 3.64 (s, 2H), 1.65 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:189.9, 163.75, 141.0, 129.8, 129.4, 114.1, 113.7, 55.5, 35.7, 21.3; IR (neat): *v* (cm^{-1}) =1665; Anal. Calcd for ($C_{12}H_{14}O_2S$): C, 64.83; H, 6.35; S, 14.42. Found: C, 64.88; H, 6.29; S, 14.36.

***S*-Octyl 4-methoxybenzothioate (35)**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 3.76 (s, 3H), 2.95 (t, *J* = 7.3 Hz, 2H), 1.62-1.51 (m, 2H), 1.35-1.18 (m, 10H), 0.81-0.76 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ:190.6, 163.6, 130.2, 129.3, 113.7, 55.4, 31.8, 29.7, 29.2, 29.1, 29.0, 28.9, 22.6, 14.1; IR (neat): *v* (cm^{-1}) =1659; Anal. Calcd for ($C_{16}H_{24}O_2S$): C, 68.53; H, 8.63; S, 11.43. Found: C, 68.54; H, 8.70; S, 11.35.

_S_-Methyl 4-methoxybenzothioate (36)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 190.9, 163.7, 129.9, 129.2, 113.7, 55.5, 11.6; IR (neat): *v* (cm^{-1}) =1659; Anal. Calcd for ($C_9H_{10}O_2S$): C, 59.32; H, 5.53; S, 17.59. Found: C, 59.39; H, 5.52; S, 17.54.