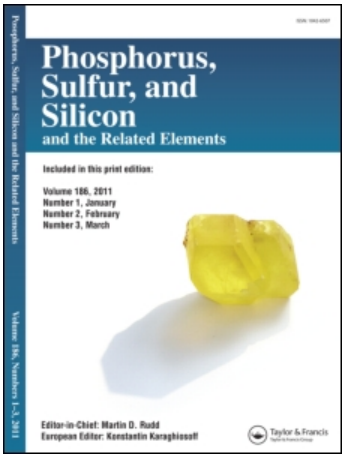

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Rapid and Convenient Thioester Synthesis Under Phase-Transfer Catalysis Conditions

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Online publication date: 19 November 2010

To cite this Article Simion, Cristian , Hashimoto, Iwao , Mitoma, Yoshiharu , Simion, Alina Marieta and Egashira, Naoyoshi(2010) 'Rapid and Convenient Thioester Synthesis Under Phase-Transfer Catalysis Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 12, 2480 — 2488
To link to this Article: DOI: 10.1080/10426501003713072
URL: http://dx.doi.org/10.1080/10426501003713072

Phosphorus, Sulfur, and Silicon, 185:2480–2488, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426501003713072

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RAPID AND CONVENIENT THIOESTER SYNTHESIS UNDER PHASE-TRANSFER CATALYSIS CONDITIONS

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Various thioesters were obtained through an efficient phase-transfer catalysis method, by treating several thiophenols with different acyl chlorides, in a biphasic system composed of 10% aqueous NaOH and dichloromethane in the presence of tetrabutylammonium chloride. The thiolation reaction was complete in only 5 minutes, at 0°C.

Keywords *S*-Acylation; phase transfer catalysis; tetrabutylammonium chloride; thioesters

INTRODUCTION

Among the different forms of organic sulfur, thioesters seem to be of a particular importance, considering the key role that these molecules played in the mystery of the origin of life on Earth ("The thioester world," as Nobel prize laureate Christian de Duve has named this primordial period of time[1]) and also the role they play in metabolic processes of living organisms centered around the well-known coenzyme A.[2] Therefore, much research has been devoted to expanding the number of thiolation methods (the synthesis of thioesters by acylation of thiols). Thus, various *S*-acylation methods of thiols have been proposed, starting from carboxylic acids,[3] anhydrides,[4] or acyl chlorides.[5] Comparatively, with the formation of their oxygenated counterparts, syntheses of thioester are even more damaged by the presence of water, this being the reason why most of the modern methods of thiolation either need anhydrous solvents[3a–c,4b,4e,4h,5b,5c] or are completely solvent-free reactions.[4a,4c,4d,4f,4g,5a] Nevertheless, the inconveniences that arise from the use of anhydrous solvents or free-solvent conditions can be circumvented if a method is applied that proved to be successful

Received 6 January 2010; accepted 17 February 2010.

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for the *O*-acylation of alcohols and phenols with acyl chlorides: phase-transfer catalysis.[6] Over the past several years, we have developed our own protocol for the *O*-acylation of phenols,[7] the main advantages of which are the use of equimolecular amounts of phenol and acyl chloride, dichloromethane as organic solvent, and less toxic tetrabutylammonium chloride as the phase-transfer catalyst (PTC). Low temperatures (0°C) and extremely short reaction time (only 5 min) complete the abbreviated description of our method. Since the results we obtained in the *O*-acylation of alcohols, as well as of mono- and poly-substituted phenols with various mono- and di-alkanoyl chlorides in a biphasic system of aqueous $NaOH:CH_2Cl_2$ were extremely successful (almost quantitative yields),[7] we decided to apply the same reaction protocol to the *S*-acylation of thiophenols.

It is known that coenzyme A functions in living organisms as a carrier of the acetyl group mainly through the existence of a thioester moiety formed between the thiol group of the coenzyme and the carbonyl function of the acetyl group. The formation, namely the rupture of this thioester function, occurs in the cell environment, which is an aqueous one, under the influence of an enzymatic catalyst. Researchers tried to replicate this process on a laboratory scale, Ouyang et al. having had the idea of using a two-phase aqueous–organic system in which they combined enzymatic and phase-transfer catalysis.[8] To the best of our knowledge, there are only two other examples of phase-transfer catalysis thiolation: the ring-closure condensation of phthalic chloride with 4,4′-thiobisbenzenethiol, which was carried out in a high dilution conditions to obtain a cyclic *S*-thioester dimer in only 56% yield,[9] and the formation of terephtaloyl dithioesters in 80% yield, in a mixture of aqueous NaOH and chloroform.[10]

We report in this article the details of a rapid and convenient method for preparing various thioesters by *S*-acylation of thiols with different acyl chlorides, in a biphasic system and using tetrabutylammonium chloride as phase-transfer catalyst.

RESULTS AND DISCUSSIONS

Reversible protein acetylation is a ubiquitous means for the rapid control of diverse cellular processes. Acetyltransferase enzymes transfer the acetyl group from acetyl-CoA to lysine residues, while deacetylase enzymes catalyze removal of the acetyl group by hydrolysis or by an NAD^+-dependent reaction. A modification in this process, resulting in the inactivation of a specific enzyme, can lead to important perturbances of distinct functions in the regulation of biological processes.[11] An example of such a modification is the replacement of an acetyl group with a propionyl group.[12] These are the reasons why we decided to start our investigation not with the acetylation of thiophenol, but with the propionylation of the same *S*-substrate.

All reactions were carried out using an equimolecular stoichiometry between thiophenol and *n*-propionyl chloride in a 1:1 mixture of aqueous NaOH and dichloromethane, in the presence of a tetraalkylammonium salt such as PTC. The reaction temperature was 0°C, and the duration was only 5 min. As we previously noted,[7] vigorous stirring is a very important parameter, so the reaction mixture was kept at 400 rpm magnetic stirring. A confirmation of the optimum conditions for the thiolation process was attempted by double-checking all reaction conditions through the *S*-benzoylation of thiophenol. The results obtained in these various attempts are presented in Table I.

When no PTC was used, the yield in thioester was only 43%, but an extra 1.5 mmol BNCl increased the yields to over 90%. BNBr was not as effective as BNCl, so the latter

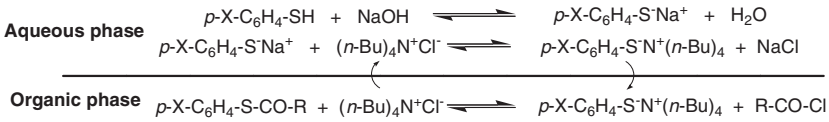
Table I Phase-transfer catalysis *S*-propionylation and *S*-benzoylation of thiophenol with propionyl chloride and benzoyl chloride

Entry	Biphasic system (mL)		PTC[a] (mmol)		Temp. (°C)	Yield (%)	
	aq. NaOH (%)	CH_2Cl_2	BnCl	BnBr		*S*-propionylation	*S*-benzoylation
1	20 (10%)	20	–	–	0	43	86
2	20 (10%)	20	1.5	–	0	92	100
3	20 (10%)	20	–	1.5	0	71	100
4	20 (10%)	20	3.0	–	0	87	100
5	–	20	1.5	–	0	7	13
6	20 (10%)	–	1.5	–	0	10	39
7	20 (10%)	20	1.5	–	5	71	86
8	20 (10%)	20	1.5	–	10	72	84
9	20 (5%)	20	1.5	–	0	73	73
10	10 (10%)	20	1.5	–	0	78	–[b]
11	40 (10%)	20	1.5	–	0	63	–[b]
12	20 (20%)	20	1.5	–	0	–[b]	95
13[c]	20 (10%)	20	1.5	–	25	–[b]	95

[a]BnCl = tetrabutylammonium chloride; BnBr = tetrabutylammonium bromide.
[b]Not attempted.
[c]Reaction time = 20 min.

was kept for the rest of the experiments. An enhancement of the quantity of PTC did not lead to significant changes, but the yields decreased dramatically when only one solvent of the biphasic system was used. A slight diminution of the overall yield was recorded when the temperature was increased by 5 or 10°C. The ssame results were recorded when the quantity or the concentration of the NaOH solution was lowered, while a higher quantity of NaOH solution accentuated the tendency of the yields to diminish; this is probably due to the competition between the hydroxide and thiophenoxide anions. Results obtained in the *S*-benzoylation of thiophenol proved to be superior to the ones for *S*-propionylation of the same substrate. Some parallels can be made: The biphasic system is extremely important—in both cases, the yields were extremely low when only one component was used.

It is safe to assume that *S*-acylation of thiophenol occurs according to the general mechanism of phase transfer catalysis, which could be represented, for this case, as is shown in Scheme 1.



Scheme 1 General mechanism for the phase-transfer catalysis process of *S*-acylation.

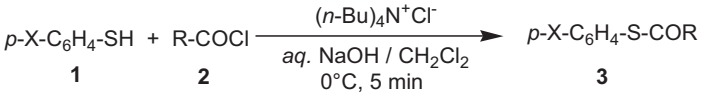
The first step is the formation of an ion pair between the quaternary ammonium cation and the thiophenoxide ion (PhS^-) in the aqueous layer. Following the transfer of the ion pair to the organic layer, the reaction with the acyl chloride would yield the *S*-phenyl thioester. Simultaneously with the thioester formation, the PTC is regenerated and subsequently transferred back into the aqueous phase. Two types of mechanisms can be expected for

Table II *S*-Acylation of thiophenols

Entry	1 (X-)	2 (R-)	Yield (%)
1	H—	CH_3—	95
2	H—	CH_3CH_2—	92
3	H—	$CH_3CH_2CH_2$—	93
4	H—	$(CH_3)_2CH$—	87
5	H—	$CH_3(CH_2)_2CH_2$—	90
6	H—	$(CH_3)_2CHCH_2$—	88
7	H—	$(CH_3)_3C$—	95
8	H—	*cyclo*-C_6H_{11}—	91
9	H—	C_6H_5—	100
10	CH_3—	CH_3CH_2—	96
11	CH_3O—	CH_3CH_2—	92
12	Cl—	CH_3CH_2—	94
13	Br—	CH_3CH_2—	95
14	*ortho*-CH_3—	CH_3CH_2—	96

the rate-determining step of the process, which is the formation of the thioester (a reaction occurring in the organic layer, which is slower than the formation of the thiophenoxide anion in the aqueous layer): a classical addition–elimination mechanism (determined by the nucleophilic attack of the thiophenoxide anion)[7c] or an electron transfer process.[12] However, considering the high speed of the process (almost quantitative transformation in just 5 min), the second hypothesis could be discarded.

Once the general reaction condition was established (equimolecular amounts of reagents, 10% PTC, 0°C, 5 min duration, under intense stirring), we proceeded to the study of the scope and limitations of this process by reacting different substituted thiophenols with various acyl chlorides (Scheme 2, Table II).



Scheme 2 *S*-Acylation process.

Every *S*-acylation in the presence of PTC proceeded in a clear-cut manner and gave the corresponding *S*-phenyl thioester in high yield. However, no clear correlation between the electronic effect of substituents present on the thiophenols or on the carboxyl moiety and the product yields could be established. One probable reason is that the ion-pair *p*-X-$PhS^-N^+(n\text{-}Bu)_4$ participating in the rate-determining step of this process is very tight and exists as a highly polarized salt. In such a tight ion pair, the electronic effect of the substituent on the reactivity would appear weaker than that of the free anion (in a dissociated system) or of a loose ion pair.[13] Therefore, since electronic effects became more discrete, the partition of the ion pairs between the two layers (depending on the hydrophobic effects of the hydrocarbonated chain, on the rate of mass transfer between the two layers and on the superficial tension) turned out to be the dominant factor. Therefore, the use of the appropriate organic solvent (which, in PTC conditions, proved to be dichloromethane[6m,6o,7c]) and a low temperature would favor the formation of such a tight ion pair.[13] Nevertheless, the high yields, mild conditions, and rapidity of the thioster formation surpasses precedent methods

Table III *S*-Acylation of 1-propanethiol and thiophenol with dicarboxylic acid chlorides under PTC conditions*

Entry	Thiol	N in $(CH_2)_n(COCl)_2$	Dithioester (%)	
			Classic Schotten–Baumann	PTC process
1	$CH_3CH_2CH_2-SH$	2	85	92
2		3	79	92
3		4	81	95
4	C_6H_5-SH	2	92	100
5		3	87	100
6		4	86	98

*BnC, 3 mmol; thiol, 3 mmol; $(CH_2)_n(COCl)_2$, 1.5 mmol; 20 mL 10% NaOH *aq.*, 20 mL CH_2Cl_2; 0°C, 5 min.

(e.g., the formation of same *S*-phenyl thioacetate and parent compounds, using palladium-mediated couplings of aryl halides with potassium thioacetate in dioxane at 100°C for several hours[14]).

As an application of the above *S*-esterification under PTC conditions, the reactions of 1-propanethiol and thiophenol with some dicarboxylic acid chlorides were carried out. Isolation of practically pure reaction products was simple and straightforward. Data for conversions are summarized in Table III, from which it can be seen that the yields of dithioesters are generally excellent, comparing favorably to those obtained by classical thiolation methods.

Bis-thiolation at both ends of a α,ω-dicarboxylic acid chlorides was effective in only 5 min, presenting higher yields than the classic Schotten–Baumann process, which was carried out simultaneously, but whose duration was at least 1 h.

Overall, our results showed that *S*-acylation of substituted thiophenols as well as bis-thiolation with aromatic and aliphatic thiols is highly effective under PTC conditions, with tetrabutylammonium chloride as catalyst in a mixture of 10% aqueous NaOH and dichloromethane, in only 5 minutes reaction time at 0°C.

EXPERIMENTAL

In all reactions, commercially available substituted thiophenols and alkanoyl chloride were used, after being purified by distillation or recrystallization. Analytical gas–liquid chromatography was carried out on a Yanagimoto G-180F fitted with an FS-WCOT column (0.25 mm i.d., length 25 m) coated Silicon OV-1701 or Yanagimoto G-80 packed column gas chromatograph (Apiezon grease L, 10%, 1.5 m or silicone SE-30, 10%, 1 m). NMR spectra were recorded on a Varian Unity-300 (300 MHz), with $CDCl_3$ internal standard. IR spectra were recorded on a Shimadzu 8100M FT-IR in KBr or in a NaCl cell. All reaction products were identified by comparison with GLC retention times of the authentic samples, either purchased or previously obtained through classic Schotten–Baumann or other thioesterification procedures,[3a] while, for the sake of comparison, thioesters (R-CS-OR′) were obtained in classical manner, such as treatment of corresponding ester with P_4S_{10} or Lawesson's reagent.[15]

General Procedure for the Preparation of Thioesters

The thiophenol (15 mmol) was dissolved in 20 mL of 10% aqueous sodium hydroxide solution in a 100 mL flask. The solutions of tetra-*n*-butylammonium chloride (1.5 mmol) and acyl chloride (15 mmol) in dichloromethane (5 and 15 mL, respectively) were independently prepared. After cooling all solutions at 0°C, they were mixed together at once. The reaction mixture was kept under vigorous magnetic stirring (400 rpm) at 0°C for 5 min, and then poured over 50 mL of icy water. The organic layer was separated, and the aqueous layer was extracted twice with 40 mL of ethyl ether. The combined organic phases were washed with saturated NaCl solution. After drying on Na_2SO_4, the solvent was evaporated, and the residue was analyzed directly by GLC. Quantitative analyses were carried out using internal standard method. The products were also identified by IR, NMR, and GC-mass analyses. All thioesters presented in GC analyses showed at least a 99.5% degree of purity.

***S*-Phenyl thiopropionate[16].** Bp 130–131°C/25 mbar; IR (NaCl): 927, 1012, 1441, 1447, 1583, 1712 (CO), 2939, 2980 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.23 (t, J = 7.6Hz, 3H), 2.69 (q, J = 7.6Hz, 2H), 7.40 (s, 5H); MS (EI, 70 eV): *m/z* (%) = 166 (M^+, 14), 110 (28), 57 (100).

***S*-Phenyl thiobenzoate[17].** Mp 52–53°C; IR (KBr): 893, 1199, 1439, 1579, 1664, 3059 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.47 (m, 8H), 8.03 (m, 2H); MS (EI, 70 eV): *m/z* (%) = 214 (M^+, 8), 105 (100), 77 (72).

***S*-Phenyl thioacetate[14].** Bp 161–161.5°C/150 mbar; IR (NaCl): 951, 1115, 1441, 1477, 1709, 3060 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.41 (s, 5H); MS (EI, 70 eV): *m/z* (%) = 152 (M^+, 17), 110 (100), 66 (28).

***S*-Phenyl thio-*n*-butyrate[18].** Bp 165°C/150 mbar; IR (NaCl): 995, 1113, 1441, 1447, 1709, 2934 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.2Hz, 3H), 1,76 (sext, J = 7.2Hz, 2H), 2,64 (t, J = 7.2Hz, 2H), 7,41 (s, 5H); MS (EI, 70 eV): *m/z* (%) = 180 (M^+, 12), 110 (23), 71 (100).

***S*-Phenyl thio-*iso*-butyrate[19].** Bp 164.5°C/65 mbar; IR (NaCl): 960, 1094, 1441, 1447, 1701, 2974 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.26 (d, J = 6.9Hz, 6H), 2.83 (t, J = 6.9Hz, 1H), 7.40 (s, 5H); MS (EI, 70 eV): *m/z* (%) = 180 (M^+, 16), 110 (37), 71 (100).

***S*-Phenyl thio-*n*-valerate.** Bp 173.5–174°C/65 mbar; IR (NaCl): 958, 1014, 1441, 1477, 1709, 2959 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.1Hz, 3H), 1.40 (sext, J = 7.1Hz, 2H), 1.71 (qv, J = 7.1Hz, 2H), 2.65 (t, J = 7.1Hz, 2H), 7.41 (s, 5H); MS (EI, 70 eV): *m/z* (%) = 194 (M^+, 10), 110 (18), 85 (69), 57 (100).

***S*-Phenyl thio-*iso*-valerate.** Bp 135.5–136°C/15 mbar; IR (NaCl): 999, 1132, 1441, 1477, 1709, 2959 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.00 (d, J = 6.6Hz, 6H), 2.21 (oct, J = 6.6Hz, 1H), 2.54 (d, J = 6.6Hz, 2H), 7.40 (s, 5H); MS (EI, 70 eV): *m/z* (%) = 194 (M^+, 11), 110 (18), 85 (67), 57 (100).

***S*-Phenyl thio-*tert*-butyrate[20].** Bp 127.5–128°C/15 mbar; IR (NaCl): 931, 1025, 1441, 1477, 1697, 2970 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 9H), 7.39 (s, 5H); MS (EI, 70 eV): *m/z* (%) = 194 (M^+, 25), 110 (61), 85 (100), 65 (14).

***S*-Phenyl thiocyclohexanecarboxylate[21].** Mp 31–32°C; IR (KBr): 962, 1138, 1439, 1477, 1693, 2936 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.24 (m, 2H), 1.47 (m, 2H), 1,64 (m, 2H), 1,81 (m, 2H), 2.00 (m, 2H), 2.60 (t, 1H), 7.40 (s, 5H); MS (EI, 70 eV): *m/z* (%) = 220 (M^+, 10), 111 (36), 83 (100), 55 (73).

S-*p*-Tolyl thiopropionate. Bp 174–176°C/40 mbar; IR (NaCl): 925, 1182, 1377, 1460, 1493, 1599, 1709, 2980 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.4Hz,

3H), 2.37 (s, 3H), 2.68 (q, $J = 7.4$Hz, 2H), 7.21 (d, $J = 8.1$Hz, 2H), 7.29 (d, $J = 8.1$Hz, 2H); MS (EI, 70 eV): *m/z* (%) = 180 (M^+, 19), 124 (28), 91 (12), 77 (6), 57 (100).

***S*-*p*-Anisyl thiopropionate.** Bp 99–101°C/3 mbar; IR (NaCl): 927, 1174, 1290, 1408, 1496, 1574, 1701, 2837 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.21$ (t, $J = 7.2$Hz, 3H), 2.65 (q, $J = 7.2$Hz, 2H), 3.81 (s, 3H), 6.93 (d, $J = 8.7$Hz, 2H), 7.31 (d, $J = 8.7$Hz, 2H); MS (EI, 70 eV): *m/z* (%) = 196 (M^+, 53), 140 (100), 125 (65), 96 (42), 57 (98).

***S*-*p*-Chlorophenyl thiopropionate.** Bp 156–158°C/40 mbar; IR (NaCl): 819, 925, 1012, 1390, 1458, 1477, 1576, 1713, 2982 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 1.25 (t, $J = 7.5$Hz, 3H), 2.70 (q, $J = 7.5$Hz, 2H), 7,19 (m, 5H); MS (EI, 70 eV): *m/z* (%) = 202 (M^++2, 20), 200 (M^+, 59), 144 (96), 108 (77), 69 (33), 57 (100).

***S*-*p*-Bromophenyl thiopropionate.** Bp 102–104°C/3 mbar; IR (NaCl): 925, 1008, 1387, 1412, 1471, 1568, 1703, 2980 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.23$ (t, $J = 6.0$Hz, 3H), 2.68 (q, $J = 6.0$Hz, 2H), 7. 24 (d, $J = 7.2$Hz, 2H), 7.46 (d, $J = 7.2$Hz, 2H); MS (EI, 70 eV): *m/z* (%) = 246 (M^++2, 24), 244 (M^+, 24), 190 (56), 188 (55), 108 (59), 69 (28), 57 (100).

***S*-*o*-Tolyl thiopropionate.** Bp 115–116°C/3 mbar; IR (NaCl): 925, 1088, 1280, 1379, 1475, 1591, 1709, 2980 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.23$ (t, $J = 7.5$Hz, 3H), 2.34 (s, 3H), 2.68 (q, $J = 7.5$Hz, 2H), 7.30 (m, 5H); MS (EI, 70 eV): *m/z* (%) = 180 (M^+, 66), 124 (100), 91 (91), 77 (56), 57 (99).

Di-*S*-Phenyl thiosuccinate. Mp 90.0°C; IR (KBr): 978, 1023, 1447, 1488, 1700, 3021 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.01$ (s, 4H), 7.42 (s, 10H); MS (EI, 70 eV): *m/z* (%) = 302 (M^+, 2), 194 (93), 109 (100), 77 (19), 65 (31), 55 (99).

Di-*S*-Phenyl thioglutarate. Mp 33.0–33.4°C; IR (KBr): 968, 1083, 1447, 1483, 1699, 3023 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.09$ (t, $J = 7.5$Hz, 2H), 2.75 (t, $J =$ 7.5Hz, 4H), 7.40 (s, 10H); MS (EI, 70 eV): *m/z* (%) = 316 (M^+, 2), 207 (91), 179 (18), 109 (100), 97 (53), 77 (14), 65 (27), 55 (89).

Di-*S*-Phenyl thioadipate[22]. Mp 81.2–82.2°C; IR (KBr): 910, 1049, 1241, 1410, 1441, 1477, 1712, 2980 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.80$ (m, 4H), 2.64 (m, 4H), 7.41 (s, 10H); MS (EI, 70 eV): *m/z* (%) = 330 (M^+, 1), 221 (34), 174 (54), 137 (12), 109 (100), 77 (32), 65 (96), 55 (99).

Di-*S*-Propyl thiosuccinate. Mp 89.8–90.0°C; IR (KBr): 991, 1410, 1458, 1689, 2964 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 7.2$Hz, 6H), 1.61 (sext, $J =$ 7.2Hz, 4H), 2.87 (t, $J = 7.2$Hz, 4H), 2.91 (s, 4H); MS (EI, 70 eV): *m/z* (%) = 234 (M^+, 1), 159 (81), 117 (67), 89 (25), 71 (33), 55 (100).

Di-*S*-Propyl thioglutarate. Mp 31.2–32.5°C; IR (NaCl): 976, 1084, 1412, 1456, 1690, 2965 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7.4$Hz, 6H), 1.58 (sext, $J = 7.4$Hz, 4H), 2.01 (qv, $J = 7.2$Hz, 2H), 2.60 (t, $J = 7.4$Hz, 4H), 2.86 (t, $J = 7.2$Hz, 4H); MS (EI, 70 eV): *m/z* (%) = 248 (M^+, 1), 173 (26), 145 (23), 103 (17), 97 (11), 69 (15), 55 (100).

Di-*S*-Propyl thioadipate. Mp 81–82°C; IR (NaCl): 951, 1012, 1452, 1693, 2991 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 7.5$Hz, 6H), 1.58 (sext, $J = 7.5$Hz, 4H), 1.61 (m, 4H), 2.54 (t, $J = 7.5$Hz, 4H), 2.85 (m, 4H); MS (EI, 70 eV): *m/z* (%) = 262 (M^+, 1), 167 (45), 141 (31), 111 (100), 83 (21, 55 (83).

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