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Cerium Triflate: An Efficient and Recyclable Catalyst for Chemoselective Thioacetalization of Carbonyl Compounds under Solvent-Free Conditions

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A simple and efficient chemoselective thioacetalization of carbonyl compounds has been achieved using $Ce(OTf)_3$ (10 mol-%) as a catalyst under solvent-free conditions. Advantages of the methodology include very short reaction times, excellent yields, the catalytic use of a water tolerant Lewis acid, and simple recovery and reuse of the catalyst.

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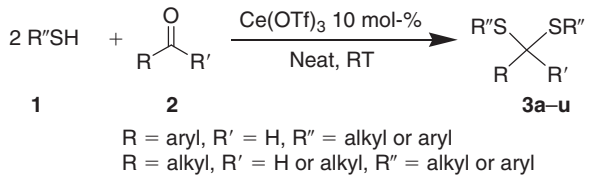
Introduction

Thioacetals have been extensively investigated as carbonyl protecting groups due to their inherent stabilities towards both acidic and basic conditions as compared with acetals and oxathioacetals.[1] They are used as intermediates for the conversion of the carbonyl group to the parent hydrocarbon by reductive desulfurization.[2] Thioacetals have also been widely used in organic synthesis as masked acyl anions[3] or masked methylene functions[4] in carbon-carbon bond forming reactions; as well as in the synthesis of complex organic molecules and natural products.[5] Thioacetals are commonly prepared by the condensation of carbonyl compounds with thiols or dithiols using protic acids, Lewis acids, metal complexes including *p*-TSA,[6] BF_3–OEt_2,[7] $ZnCl_2$,[8] SO_2,[9] TMSCl–NaI,[10] TMSOTf,[11] $AlCl_3$,[12] $TiCl_4$,[13] silica supported reagents,[14] $NiCl_2$,[15] $Bi(NO_3)_3$,[16] metal triflates,[17] molecular I_2[18], $InCl_3$[19], ionic liquids,[20] and polymer supported reagents.[21] Despite of the potential utilities of these methods giving high yield of thioacetals, the majority of these are associated with certain limitations such as strong oxidizing conditions, long reaction times, the need for azeotropic distillation, harsh reaction conditions, use of halogenated solvents and toxic agents, unwanted side reaction, expensive catalysts, moisture sensitivity, and tedious workup conditions. A mild, simple, and more efficient method is still desirable for the chemoselective protection of carbonyl groups as thioacetals.

Recently, there has been a growing interest in solvent-free reactions in organic synthesis.[22] There are several advantages associated with solvent-free reactions including safety, economy, ease of workup procedure, short reaction times, and greener nature.[23] Lanthanide triflates are unique Lewis acids, and they function well in aqueous media unlike common Lewis acids that decompose readily in the presence of water.[24] $Ce(OTf)_3$ is a mild Lewis acid that has attracted little attention as a catalyst in organic synthesis.[24c] In continuation of our efforts towards development of new, greener, and efficient reaction methodologies,[25] we report herein the chemoselective thioacetalization of aldehydes and aliphatic ketones using $Ce(OTf)_3$ as a catalyst under solvent-free conditions (Scheme 1).



Scheme 1.

Result and Discussion

Different variations of catalyst, solvent systems, and catalyst loading were examined to find the optimal reaction conditions for thioacetalization (Table 1). The reaction of 4-chlorobenzaldehyde (**1a**) and thiophenol (**2a**) to give thioacetal of 4-chlorobenzaldehyde (**3a**) was selected as an appropriate model reaction. Among the catalysts screened, $Ce(OTf)_3$, $Yb(OTf)_3$, and $Y(OTf)_3$ were found to give excellent yield of **3a** (Table 1, entries 11, 16, 17), but $Ce(OTf)_3$ gave the highest yield of **3a** under solvent-free conditions. Next we optimized the catalyst loading using different amount of catalyst and found that 10 mol-% of the catalyst under solvent-free conditions was sufficient to give the desired product in excellent yield (Table 1, entries 9–12). No significant improvement in the yield of **3a** was observed on increasing the catalyst amount further from 10 mol-% to 20 mol-% (Table 1, entries 11, 12). Notably, the reaction was slower in a homogeneous medium when compared with solvent-free conditions. When the model reaction was carried out in various solvents such as DCM, DMSO, THF, acetonitrile, water, and ionic liquid [bmim][BF_4], using $Ce(OTf)_3$ as catalyst, only [bmim][BF_4] and acetonitrile were found to be effective reaction media to give **3a** in 83 and 88% after 2 and 12 h respectively

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(Table 1, entries 1–8). Importantly, the reaction did not proceed in the absence of $Ce(OTf)_3$, confirming the effectiveness of the catalyst. The role of $Ce(OTf)_3$ is not clear but it is expected that under solvent-free conditions it activates the carbonyl group for the initial addition of a thiol molecule. This is followed by the dehydration of the intermediate hemithioacetal, and subsequent attack by a second thiol molecule.

After standardizing the reaction conditions, different aldehydes and ketones were allowed to react with thiols (**2a**–**d**) to give the corresponding thioacetals (**3a**–**u**). As shown in Table 2, a wide range of aromatic aldehydes containing electron-withdrawing groups, electron-donating groups and hindered groups; aliphatic aldehydes; cyclic and acyclic aliphatic ketones were transformed to the corresponding thioacetals in excellent yields and short reaction time. The reaction was compatible with wide range of functional groups that may compete for coordination with the catalyst. The regioselectivity of the method was demonstrated by the thioacetalization of **1m** to corresponding thioacetal **3p** without any competitive conjugate *thia*-Michael addition.

Table 1. The comparison of different reaction conditions for synthesis of 3a

Sr. no.	Catalysts	Solvent	Time	Yield [%][A]
1	$Ce(OTf)_3$ (10 mol-%)	[Bmim][BF_4]	2 h	83
2	$Ce(OTf)_3$ (10 mol-%)	DCM	12 h	12
3	$Ce(OTf)_3$ (10 mol-%)	H_2O	12 h	–[B]
4	$Ce(OTf)_3$ (10 mol-%)	MeOH	15 min	60
5	$Ce(OTf)_3$ (10 mol-%)	THF	12 h	20
6	$Ce(OTf)_3$ (10 mol-%)	CH_3CN	12 h	88
7	$Ce(OTf)_3$ (10 mol-%)	DMSO	12 h	15
8	$Ce(OTf)_3$ (10 mol-%)	DMF	12 h	18
9	$Ce(OTf)_3$ (1 mol-%)	Neat	5 min	20
10	$Ce(OTf)_3$ (5 mol-%)	Neat	5 min	52
11	$Ce(OTf)_3$ (10 mol-%)	Neat	5 min	92
12	$Ce(OTf)_3$ (20 mol-%)	Neat	5 min	94
13	$Sm(OTf)_3$ (10 mol-%)	Neat	1 h	10
14	$Ho(OTf)_3$ (10 mol-%)	Neat	1 h	15
15	$Er(OTf)_3$ (10 mol-%)	Neat	1 h	20
16	$Yb(OTf)_3$ (10 mol-%)	Neat	15 min	83
17	$Y(OTf)_3$ (10 mol-%)	Neat	5 min	90
18	Triflic acid (20 mol-%)	Neat	5 min	73

[A]Isolated yields.
[B]No product formation was observed, aldehyde recovered quantitatively.

The thioacetals were each characterized by ^1H and ^{13}C NMR, and mass spectroscopic data (see Accessory Publication). For example, **3a** showed a singlet at δ 5.37 ppm for one proton of α-CH group, a doublet and doublet of doublet at δ 7.25 and 7.37 ppm for 10 and four aromatic protons respectively in ^1H NMR spectra. The presence of a peak at δ 60.11 ppm for α-CH carbon along with other aromatic carbons in ^{13}C NMR spectra, and a peak at *m/z* 342.92 in the mass spectrum also confirmed the structure of **3a**.

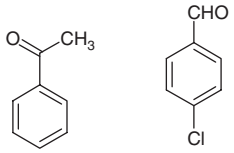
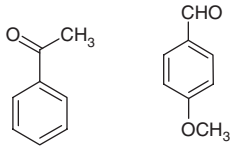
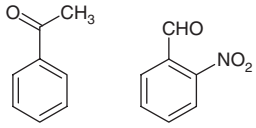
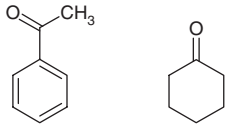
As noted in Table 2, the difference in reactivity of the catalyst towards aldehydes and ketones provided the impetus to examine the chemoselectivity of the catalyst. In order to study the chemoselectivity, experiments with an equimolar mixture of two different carbonyl compounds were performed (Table 3). For instance, when an equimolar mixture of **1a** and acetophenone (**1s**) was allowed to react with 2 equivalents of **2a** in presence of 10 mol-% of $Ce(OTf)_3$, only **3a** was obtained while **1s** was recovered quantitatively. Similarly, when an equimolar mixture of cyclohexanone (**1r**) and **1s** was allowed to react with 2 equivalents of **2a**, the thioacetal of cyclohexanone (**3u**) was obtained exclusively. These results showed that the catalyst is able to differentiate aldehydes and ketones as well as aliphatic ketones and aromatic ketones. Thus selective protection of aldehydes or aliphatic ketones is possible using this method. The reason for the observed chemoselectivity is not clearly known, but may be

Table 2. Thioacetalization of different carbonyl compounds using $Ce(OTf)_3$ under solvent-free conditions[A]

Entry	R	R′	R″	Product[B]	Time [min]	Yield [%][C]
1	4-ClPh	H	Ph	**3a**	5	92
2	4-ClPh	H	4-CH_3OPh	**3b**	5	90
3	4-ClPh	H	3-CH_3OPh	**3c**	5	89
4	4-ClPh	H	$HOCH_2CH_2$	**3d**	5	93
5	4-CH_3Ph	H	Ph	**3e**	5	88
6	4-CH_3OPh	H	Ph	**3f**	5	90
7	4-OHPh	H	Ph	**3g**	5	89
8	2,6-Cl_2Ph	H	Ph	**3h**	8	87
9	2-NO_2Ph	H	Ph	**3i**	10	78
10	$CH_2CO_2CH_3$	CH_3	Ph	**3j**	60	56
11	C_4H_4O	H	Ph	**3k**	5	90
12	4-OH-3-CH_3OPh	H	Ph	**3l**	8	85
13	3-ClPh	H	Ph	**3m**	5	90
14	3-CH_3OPh	H	Ph	**3n**	5	87
15	3-NO_2Ph	H	Ph	**3o**	8	89
16	PhCH=CH	H	Ph	**3p**	5	90
17	$CH_3CH_2CH_2$	H	Ph	**3q**	5	86
18	CH_3CH_2	H	Ph	**3r**	5	87
19	CH_3CH_2	CH_3	Ph	**3s**	15	89
20	$(CH_3)_2CHCH_2$	CH_3	Ph	**3t**	15	88
21	-$CH_2(CH_2)_3CH_2$-		Ph	**3u**	15	91

[A]Reaction conditions: RT (25°C), carbonyl compounds 0.711 mmol, thiol 1.56 mmol, and $Ce(OTf)_3$ 27 mg (10 mol-%).
[B]Structure of all the products were well characterized by ^1H, ^{13}C NMR, and mass spectroscopic data.
[C]Isolated yield after purification by column chromatography.

Table 3. Chemoselective thioacetalization using $Ce(OTf)_3$ as catalyst under solvent-free conditions

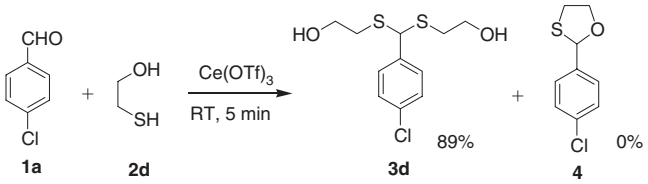
Sr. no.	Mixture of carbonyl compounds	Product	Time [min]	Yield [%][A]
1		**3a**	5	92
2		**3f**	5	90
3		**3i**	10	76
4		**3u**	15	90

[A]Yield of isolated product.

due to mild catalytic activity of $Ce(OTf)_3$. Selectivity of thiol towards aldehydes and aliphatic ketones, as compared with aromatic ketones, may be explained on the basis of difference in relative electron density (global electrophilicity, ω)[26] at the carbonyl carbon in these compounds. Such difference in reactivity of **1r** and **1s** towards thioacetalization has also been explained by electron density calculations at the carbonyl carbon using semi-empirical molecular orbital calculations.[20b] The competitive formation of thioacetal (**3d**), versus cyclic 1,3-oxathiolane (**4**), from the reaction of **1a** with **2d** (Scheme 2) could be explained by the difference of local nucleophilicity i.e. the nucleophilicity of O_{OH} and S_{SH} in **2d**. The formation of thioacetal (**3d**) can be seen as an orbital controlled soft-soft pathway.[27] Moreover, selective formation of **1d** over **4** is catalyst and reaction condition specific, as when **2d** was reacted with **1a** in an ionic liquid using $Yb(OTf)_3$ as catalyst, formation of **4** was observed as major product.[25c]

The reaction of **1a** was explored with different thiols, including 4-methoxythiophenol (**2b**), 3-methoxythiophenol (**2c**), and 2-mercaptoethanol (**2d**) (Table 2, entries 2–4), and all of them gave excellent yields of the corresponding thioacetals (**3b**–**d**). However, it is worth to note that when 4-nitrothiophenol was used it did not result in thioacetal formation. Again, this may be explained based on global nucleophilicity of the S_{SH} (*S*-atom of SH group) in different thiols, i.e. relative electron donating ability of the sulfur atom during nucleophilic addition at carbonyl carbon.

In view of environmentally-friendly methodologies, recovery and reuse of the catalyst is highly preferable. With this issue in mind, we examined the possibility of recycling of the catalyst using thioacetalization of **1a** with **2a** as model reaction. The catalyst was recovered from the reaction mixture in the aqueous phase after extraction of the product with diethyl ether. The



Scheme 2.

Table 4. Reuse of the catalyst for thioacetalization of 1a with 2a to give 3a

Run	1	2	3	4	5
Yield [%][A]	92	92	88	87	85

[A]Yield of isolated product.

aqueous layer was evaporated under reduced pressure to give the recovered catalyst, i.e. $Ce(OTf)_3$, in an almost quantitative yield. The recovered catalyst was subsequently reused for the thioacetalization of **1a**. As indicated in Table 4, it maintained good catalytic activity, yielding **3a** in 92, 92, 88, 87, and 85% yield in five successive runs respectively.

Conclusions

In conclusion, we have presented here a simple, economical and efficient method for chemoselective thioacetalization of carbonyl compounds using 10 mol-% of $Ce(OTf)_3$ as catalyst under solvent-free conditions at room temperature. The present protocol is endowed with some merits, such as excellent functional group compatibility, short reaction times, excellent yields, solvent-free conditions, catalytic use of water tolerant Lewis acids, wide applicability, and recyclability of the catalyst.

Experimental

Cerium triflate was purchased from Sigma-Aldrich. All commercial reagents and solvents were used without further purification unless otherwise specified. NMR spectra were recorded on a Bruker Heaven Avance 11400 spectrophotometer using TMS as an internal standard and $CDCl_3$ as a solvent and the chemical shifts were expressed in ppm. The IR spectra were recorded using KBr pellets on Shimadzu Prestige-21 FTIR spectrophotometer and ν_{max} was expressed in cm^{-1}. EI-MS spectra were recorded on a Jeol SX 102/DA-6000 (6 kV, 10 mA) mass spectrometer. The purity of the products was determined on silica-coated aluminium plates (Merck).

General Procedure for the Thioacetalization

To a mixture of 4-chlorobenzaldehyde **1a** (100 mg, 0.711 mmol) and thiophenol **2a** (172 mg, 1.56 mmol) was added $Ce(OTf)_3$ (27 mg, 10 mol-%) and the whole reaction mass was stirred at room temperature. The reaction progress was followed by TLC (8:2 hexane/ethyl acetate). After stirring the reaction mixture for 5 min diethyl ether (10 mL) and water (10 mL) was added, and the organic layer was separated. The solvent was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was percolated through a band of silica gel (60–120) using hexane/ethyl acetate (9:1 v/v) as an eluent to give pure compound **3a** in 92% yield.

General Procedure for Recovery and Reuse of Catalyst

After extracting the product using diethyl ether, the aqueous layer containing cerium triflate was concentrated under reduced pressure and dried under vacuum to recover the catalyst. The flask containing recovered $Ce(OTf)_3$ was again charged with **1a** (100 mg, 0.711 mmol) and **2a** (172 mg, 1.56 mmol) and same procedure was repeated as given in the general procedure for the thioacetalization.

Spectroscopic Data for the Thioacetals (*3a–u*)

3a: ((4-Chlorophenyl)methylene)bis(phenylsulfane). Isolated yield: 92%. δ_H ($CDCl_3$, 300 MHz) 7.32 (dd, *J* 8.1, 5.1 Hz, 4H), 7.25 (d, *J* 7.2 Hz, 10H), 5.37 (s, 1H). δ_C ($CDCl_3$, 75 MHz) 138.65, 134.41, 133.14, 129.61, 129.45, 129.32, 128.99, 128.45, 60.11. *m/z* (ESI) 342.92 [M^+].

3b: ((4-Chlorophenyl)methylene)bis((4-methoxyphenyl) sulfane). Isolated yield: 90%. δ_H ($CDCl_3$, 300 MHz) 7.26 (d, *J* 8.1 Hz, 4H), 7.17 (q, *J* 8.5 Hz, 4H), 6.77 (d, *J* 8.2 Hz, 4H), 5.10 (s, 1H), 3.77 (s, 6H). δ_C ($CDCl_3$, 75 MHz) 160.46, 139.14, 136.43, 133.49, 129.63, 128.78, 124.67, 114.80, 62.42, 55.68. *m/z* (ESI) 404 [$M + H^+$].

3c: ((4-Chlorophenyl)methylene)bis((3-methoxyphenyl) sulfane). Isolated yield: 89%. δ_H ($CDCl_3$, 300 MHz) 7.31 (d, *J* 8.0 Hz, 2H), 7.24 (d, *J* 8.9 Hz, 4H), 7.16 (t, *J* 7.9 Hz, 2H), 6.93 (d, *J* 7.6 Hz, 2H), 6.85 (s, 2H), 6.79 (d, *J* 8.3 Hz, 2H), 5.41 (s, 1H), 3.72 (s, 6H). δ_C ($CDCl_3$, 75 MHz) 159.92, 159.40, 135.21, 130.04, 129.72, 129.03, 124.98, 124.80, 117.85, 114.40, 59.44, 55.70. *m/z* (ESI) 403.96 [$M + H^+$].

3d: 2,2′-((4-Chlorophenyl)methylene)bis(sulfanediyl) diethanol. Isolated yield: 93%. δ_H ($CDCl_3$, 300 MHz) 7.48–7.37 (m, 2H), 7.29 (d, *J* 8.3 Hz, 2H), 5.15 (s, 1H), 4.09 (s, 2H), 3.70 (dd, *J* 10.8, 5.5 Hz, 4H), 2.80 (dt, *J* 12.8, 6.3 Hz, 2H), 2.70–2.51 (m, 2H). δ_C ($CDCl_3$, 75 MHz) 139.60, 133.58, 129.51, 128.87, 61.64, 52.59, 35.25. *m/z* (ESI) 279 [M^+].

3e: (*p*-Tolylmethylene)bis(phenylsulfane). Isolated yield: 88%. δ_H ($CDCl_3$, 300 MHz) 7.32–7.40 (m, 4H), 7.24–7.28 (m, 6H), 7.13 (t, *J* 8.2 Hz, 2H), 6.84 (d, *J* 7.8 Hz, 1H), 6.76 (t, *J* 7.5 Hz, 1H), 6.32 (s, 1H), 5.70 (s, 1H). δ_C ($CDCl_3$, 75 MHz) 153.94, 134.02, 133.05, 130.09, 130.00, 129.30, 128.51, 124.82, 120.94, 117.54, 60.56, 56.77. *m/z* (ESI) 322.56 [M^+].

3f: ((4-Methoxyphenyl)methylene)bis(phenylsulfane). Isolated yield: 90%. δ_H ($CDCl_3$, 300 MHz) 7.38–7.29 (m, 5H), 7.28 (s, 1H), 7.26–7.17 (m, 6H), 6.79 (d, *J* 8.7 Hz, 2H), 5.42 (s, 1H), 3.77 (s, 3H). δ_C ($CDCl_3$, 75 MHz) 159.67, 135.14, 132.77, 132.04, 129.49, 129.21, 128.08, 114.22, 60.11, 55.67. *m/z* (ESI) 339.28 [$M + H^+$].

3g: 4-(Bis(phenylthio)methyl)phenol. Isolated yield: 89%. δ_H ($CDCl_3$, 300 MHz) 7.33 (dd, *J* 6.2, 2.5 Hz, 4H), 7.27–7.13 (m, 8H), 6.70 (d, *J* 8.3 Hz, 2H), 5.40 (s, 1H), 4.98 (s, 1H). δ_C ($CDCl_3$, 75 MHz) 155.62, 135.00, 132.86, 132.29, 129.76, 129.24, 128.14, 115.72, 60.11. *m/z* (ESI) 325.97 [$M + H^+$].

3h: ((2,6-Dichlorophenyl)methylene)bis(phenylsulfane). Isolated yield: 87%. δ_H ($CDCl_3$, 300 MHz) 7.42–7.34 (m, 4H), 7.27–7.14 (m, 8H), 7.10 (t, *J* 8.0 Hz, 1H), 6.20 (s, 1H). δ_C ($CDCl_3$, 75 MHz) 136.86, 135.42, 133.90, 133.85, 130.52, 130.15, 129.39, 128.67, 128.26, 60.33. *m/z* (ESI) 377.12 [M^+].

3i: ((2-Nitrophenyl)methylene)bis(phenylsulfane). Isolated yield: 78%. δ_H ($CDCl_3$, 300 MHz) 7.92 (d, *J* 7.9 Hz, 1H), 7.79 (d, *J* 8.1 Hz, 1H), 7.53 (t, *J* 7.6 Hz, 1H), 7.39–7.29 (m, 5H), 7.27–7.20 (m, 6H), 6.43 (s, 1H). δ_C ($CDCl_3$, 75 MHz) 148.22, 135.00, 133.72, 133.59, 133.29, 131.12, 129.48, 129.04, 128.78, 124.88, 54.93. *m/z* (ESI) 354.55 [$M + H^+$].

3j: Methyl 3,3-bis(phenylthio)butanoate. Isolated yield: 56%. δ_H ($CDCl_3$, 300 MHz) 7.66 (d, *J* 7.4 Hz, 4H), 7.42–7.31 (m, 6H), 4.16 (q, *J* 7.1 Hz, 2H), 2.75 (s, 2H), 1.62 (s, 2H), 1.28 (t, *J* 7.2 Hz, 3H). δ_C ($CDCl_3$, 75 MHz) 169.67, 137.65, 131.67, 129.83, 129.09, 61.42, 59.97, 46.72, 28.28, 14.81. *m/z* (ESI) 332.34 [M^+].

3k: 2-(Bis(phenylthio)methyl)furan. Isolated yield: 90%. δ_H ($CDCl_3$, 300 MHz) 7.37 (t, *J* 4.2 Hz, 4H), 7.30–7.24 (m, 6H), 6.23 (d, *J* 1.5 Hz, 1H), 6.15 (d, *J* 3.0 Hz, 1H), 5.47 (s, 1H), 5.27 (s, 1H). δ_C ($CDCl_3$, 75 MHz) 151.66, 142.92, 134.08, 133.44, 129.27, 128.56, 110.90, 109.43, 53.56. *m/z* (ESI) 298 [M^+].

3l: 4-(Bis(phenylthio)methyl)-2-methoxyphenol. Isolated yield: 85%. δ_H ($CDCl_3$, 300 MHz) 7.34 (d, *J* 3.6 Hz, 4H), 7.24 (d, *J* 4.0 Hz, 6H), 6.89 (s, 1H), 6.80 (q, *J* 8.4 Hz, 2H), 5.65 (s, 1H), 5.39 (s, 1H), 3.80 (s, 3H). δ_C ($CDCl_3$, 75 MHz) 146.73, 145.76, 134.54, 132.89, 131.62, 129.21, 128.14, 121.47, 114.40, 110.59, 60.54, 56.15. *m/z* (ESI) 354.21 [M^+].

3m: ((3-Chlorophenyl)methylene)bis(phenylsulfane). Isolated yield: 90%. δ_H ($CDCl_3$, 300 MHz) 7.33 (d, *J* 3.0 Hz, 5H), 7.28–7.22 (m, 6H), 7.20 (d, *J* 6.1 Hz, 3H), 5.35 (s, 1H). δ_C ($CDCl_3$, 75 MHz) 142.13, 134.64, 134.33, 133.23, 130.03, 129.33, 128.54, 128.45, 126.46, 60.36. *m/z* (ESI) 343 [M^+].

3n: ((3-Methoxyphenyl)methylene)bis(phenylsulfane). Isolated yield: 87%. δ_H ($CDCl_3$, 300 MHz) 7.35 (dd, *J* 6.3, 2.7 Hz, 4H), 7.27–7.21 (m, 6H), 7.20–7.13 (m, 1H), 7.02–6.85 (m, 2H), 6.77 (dd, *J* 8.2, 2.2 Hz, 1H), 5.39 (s, 1H), 3.73 (s, 3H). δ_C ($CDCl_3$, 75 MHz) 160.01, 141.58, 134.94, 132.93, 129.85, 129.24, 128.20, 120.65, 114.46, 113.43, 60.81, 55.63. *m/z* (ESI) 339.63 [$M + H^+$].

3o: ((3-Nitrophenyl)methylene)bis(phenylsulfane). Isolated yield: 89%. δ_H ($CDCl_3$, 300 MHz) 8.12 (s, 1H), 8.07 (d, *J* 8.1 Hz, 1H), 7.65 (d, *J* 7.8 Hz, 1H), 7.41 (t, *J* 7.9 Hz, 1H), 7.34 (dd, *J* 6.5, 2.6 Hz, 4H), 7.29–7.20 (m, 6H), 5.47 (s, 1H). δ_C ($CDCl_3$, 75 MHz) 148.43, 142.36, 134.30, 133.63, 133.54, 129.76, 129.48, 128.93, 123.32, 60.11. *m/z* (ESI) 353 [M^+].

3p: (3-Phenylprop-2-ene-1,1-diyl)bis(phenylsulfane). Isolated yield: 90%. δ_H ($CDCl_3$, 300 MHz) 7.52–7.40 (m, 3H), 7.38–7.15 (m, 12H), 7.04 (d, *J* 7.3 Hz, 1H), 6.32 (d, *J* 15.7 Hz, 1H), 6.24–6.10 (m, 1H). δ_C ($CDCl_3$, 75 MHz) 133.87, 133.75, 132.89, 132.44, 129.36, 129.30, 129.18, 128.96, 128.45, 128.27, 128.11, 127.01, 59.05, 56.94. *m/z* (ESI) 335.39 [$M + H^+$].

3q: Butane-1,1-diylbis(phenylsulfane). Isolated yield: 86%. δ_H ($CDCl_3$, 300 MHz) 7.49–7.42 (m, 4H), 7.34–7.24 (m, 6H), 4.40 (t, *J* 6.6 Hz, 1H), 1.83 (dd, *J* 15.0, 6.9 Hz, 2H), 1.62 (dq, *J* 14.5, 7.3 Hz, 2H), 0.89 (t, *J* 7.3 Hz, 3H). δ_C ($CDCl_3$, 75 MHz) 134.78, 133.08, 129.24, 127.99, 58.56, 38.33, 20.72, 13.13. *m/z* (ESI) 297 [$M + Na^+$].

3r: Propane-1,1-diylbis(phenylsulfane). Isolated yield: 87%. δ_H ($CDCl_3$, 300 MHz) 7.50–7.38 (m, 4H), 7.34–7.24 (m, 6H), 4.35 (t, *J* 6.4 Hz, 1H), 1.95–1.81 (m, 2H), 1.13 (t, *J* 7.3 Hz, 3H). δ_C ($CDCl_3$, 75 MHz) 134.82, 133.05, 129.27, 127.99, 60.42, 29.38, 12.10. *m/z* (ESI) 261.22 [$M + H^+$].

3s: Butane-2,2-diylbis(phenylsulfane). Isolated yield: 89%. δ_H ($CDCl_3$, 300 MHz) 7.64 (d, *J* 7.1 Hz, 4H), 7.33 (q, *J* 5.4 Hz, 6H), 1.75 (q, *J* 7.3 Hz, 2H), 1.37 (s, 3H), 1.10 (t, *J* 7.3 Hz, 3H). δ_C ($CDCl_3$, 75 MHz) 137.34, 132.53, 129.36, 128.93, 65.14, 34.68, 28.00, 9.94. *m/z* (ESI) 296 [$M + Na^+$].

3t: (4-Methylpentane-2,2-diyl)bis(phenylsulfane). Isolated yield: 88%. δ_H ($CDCl_3$, 300 MHz) 7.65 (d, *J* 7.3 Hz, 4H), 7.34 (d, *J* 6.7 Hz, 6H), 2.19–2.03 (m, 1H), 1.73 (d, *J* 4.9 Hz, 2H), 1.41 (s, 3H), 0.94 (d, *J* 6.7 Hz, 6H). δ_C ($CDCl_3$, 75 MHz) 137.22,

132.72, 129.30, 128.87, 65.23, 50.70, 28.80, 25.53, 25.26. *m/z* (ESI) 303.73 [M + H$^+$].

3u: Cyclohexane-1,1-diylbis(phenylsulfane). Isolated yield: 91%. δ_H ($CDCl_3$, 300 MHz) 7.69 (d, *J* 6.6 Hz, 4H), 7.35–7.33 (m, 6H), 1.74 (d, *J* 5.0 Hz, 4H), 1.65 (s, 4H), 1.32 (s, 2H). δ_C ($CDCl_3$, 75 MHz) 137.31, 132.04, 129.30, 128.90, 66.29, 37.54, 25.54, 23.10. *m/z* (ESI) 301 [M + H$^+$].

Accessory Publication

Copies of ^{1}H and ^{13}C NMR spectrum of compound **3a**–**u** are available on the Journal's website.

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