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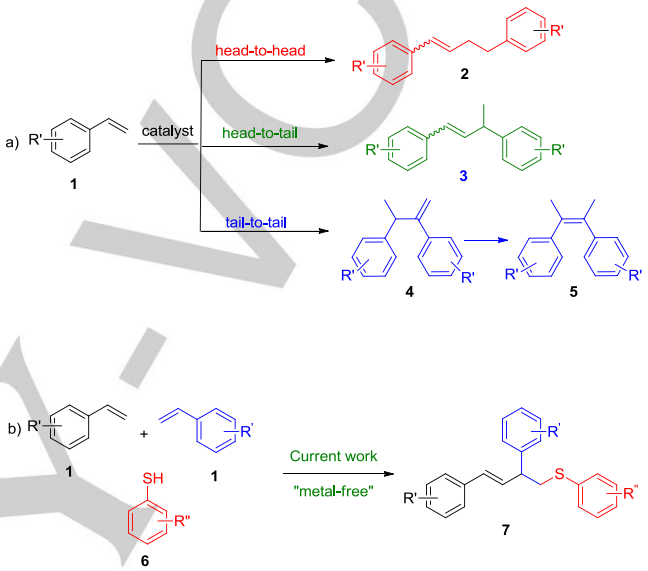
Iodine and PhI(OAc)$_2$ Mediated Multicomponent synthesis of novel (*E*)-1,3-diphenyl-1-butene derivatives

Mokgethwa B Marakalala and Henok H Kinfe*

Abstract: Molecular iodine and diacetoxyiodobenzene promoted novel multicomponent methodology for the synthesis of (*E*)-1,3-diphenyl-1-butene derivatives is developed using styrene and thiophenol as substrates. The attractiveness of the protocol is its ability to introduce a sulfur heteroatom without a need for an extra reaction step. The scope and limitations of the protocol are investigated.

Styrene dimers are useful industrial intermediates that have found various applications as regulators of polymer chain growth, plasticizer of polymers and Plexiglas as well as substrates for the synthesis of lubricants, varnish and paints.[1] Such dimers could be synthesized *via* a head-to-head, head-to-tail, or tail-to-tail dimerization of styrene (Scheme 1a). However, the head-to-tail dimerization that results in the formation of a 1,3-diphenyl-1-butene has received more attention than the others since it generates an allylic chiral centre that is reported to be present in a number of biologically important organic molecules.[2-4]



Scheme 1. Different pathways for the dimerization of styrene.

As a result, various reagent systems have been reported to effect the transformation which include metal-free acids such as $AcClO_4$,[5] CF_3SO_3H,[5] zeolites,[1] pTsOH,[4] $HClO_4$[4] and iodine[6] as well as transition metal-based catalysts, namely: [Ni(π-C_3H_5)($OCOCF_3$)]$_2$,[7] (ally)Ni-I_2,[8] [(η^3-C_3H_5)Pd(CD_3NO_2)$_2$](BF_4)[9] $Co_2(CO)_8$,[10] $Pd(PPh_3)_2(BF_4)_2$,[11] (ally)Ni-Cl_2,[12] $Pd(OAc)_2$/diazonium salt,[13] Pd(β-diketonate)$_2$/BF_3·OEt_2,[14] $Pd(OAc)_2$/In($OTf)_3$,[15] $Pd(OAc)_2$/Cu($OTf)_2$/ionic liquid,[16] Ni(dppp)Cl_2,[17] [(η^6-C_6H_6)(PCy_3)(CO)RuH]$^+BF_4^-$,[18] Fe(III) salts,[3] [(acac)Pd(PAr_3)$_2$]BF_4/BF_3·OEt_2,[19] $Pd(acac)_2$/TFA,[2] (ally)Ni-NHC,[20] [AllylPd(PPh_3)]$^+OTf^-$,[21]

Although these methods are efficient in providing the 1,3-diphenyl-1-butene dimer as the major product, introduction of hetero-atoms in the dimer for further elaboration has not been achieved, thus, limiting their scope. Incorporation of amine, silyl and sulfide functional groups in styrene monomers has resulted in the synthesis of advanced materials.[22,23] As it is nicely reviewed by Hoyle and Bowman, for instance, the introduction of sulfur *via* a thiol-ene click chemistry has been applied in the synthesis of optical components, adhesives and high-impact-energy-absorbing materials.[23] In styrene monomers, incorporation of sulfur has been achieved *via* either substitution of a halomethylstyrene with thiolate salts or the reaction of thiols with 1,4-divinylbenzene.[22] Considering the importance of sulfur in the synthesis of advanced materials, the limited scope of the reported

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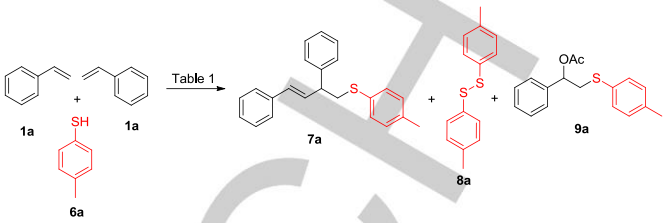
protocols for the dimerization of styrene along with the scarce methodologies for the incorporation of sulfur in styrene monomers, calls for the development of new, versatile and environmentally friendly methodologies.

Recently, the use of hypervalent[24,25] and molecular iodine in the formation of S-C and S-heteroatom bonds has gained some interest. For instance, Wacharasindhu *et al*. exploited the environmentally benignness and readily availability of diacetoxy-iodobenzene (DIB) in the activation of thiols for the construction of S-S and S-N bonds and further applied the method in the sulfenylation of an indole.[26] Furthermore, the iodine-mediated thiolation of substituted anilines,[27] naphthols/naphthylamines,[28] sulfenylation of imidazoheterocycles,[29] and synthesis of 2-arylsulfanylphenols,[30] are examples that demonstrate the importance of iodine in S-C bond formation. In continuation of our interest in the synthesis of organosulfur compounds,[31-35] herein we report a three component regio- and stereoselective synthesis of novel (*E*)-1,3-diphenyl-1-butene derivatives **7** that incorporate a sulfur atom in the absence of a metal or a strong acid catalyst (Scheme 1b).

In our first attempt, treatment of a solution of 4-methyl thiophenol **6a** and styrene **1a** (3 equiv.) with iodine (10 mol %) and DIB (3 equiv.) under solvent-free condition at room temperature resulted in the formation of disulfide **8a** (Scheme 2, Table 1, entry 1). However, a reaction conducted at 70 ºC but under otherwise identical conditions provided a mixture of *β*-acetoxysulfide **9a** and dimer derivative **7a** (Table 1 and entry 2). Interestingly heating up of the reaction mixture to 110 ºC resulted in the exclusive formation of dimer **7a** in 76% yield *via* initial formation of disulfide **8a** and *β*-acetoxysulfide **9a** (Table 1, entry 3). The structure of the dimer **7a** was established using NMR spectroscopy and HRMS. Among others, the appearance of the singlet signal at δ_H 2.31 ppm which corresponds to a methyl group and a multiplet that integrates for 14 protons in the aromatic region confirmed the incorporation of the thiophenol moiety in the dimer. Due to the overlap of the signals that correspond to the alkene group in the region of δ_H 6.40-6.36 ppm, the stereoselectivity (*E/Z* isomerism) of the reaction could not be determined from the ^{1}H NMR of dimer **7a**. Fortunately, upon oxidation of the dimer **7a** using excess Oxone®, the sulfone analogue **10a** (Scheme 5) was obtained and we found out that the two olefinic protons were perfectly resolved in the ^{1}H NMR spectrum. The large coupling constant of J = 16.0 Hz suggested the formation of the *E* isomer.

Different solvents were then investigated as indicated in Table 1. However, none of them gave dimer **7a** (Table 1, Entry 4-8). Having established the effect of solvent and temperature, we then investigated the relative stoichiometry of the reagents and it was found that three equivalence of the styrene **1a**, 2 equivalence of DIB and 20 mol % of iodine relative to 4-methyl thiophenol **6a** were sufficient to provide the highest yield under the reaction conditions (Table 1, Entry 9). Increasing the amount of iodine to up to 1 equivalence decreased the yield drastically suggesting the need for the presence of iodine in catalytic amounts. The use of iodine in less than 20 mol % provided inferior yields (Table 1, Entry 1). Increasing the amount of styrene to more than 3 equivalence did not lead to improved yields. However, less than 2 equivalence of the DIB lead to incomplete reaction after 24 hours.



Scheme 2. Dimerization of styrene initiated by an S-H activation.

Table 1. Optimization conditions for the dimerization of styrene according to Scheme 2.[a]

Entry	Catalyst (equiv.)	Oxidant (equiv.)	Solvent	T (°C)	Product (yield, %)[b]
1	I_2 (0.1)	DIB (3)	-	RT	**8a** (60)
2	I_2 (0.1)	DIB (3)	-	70	**7a** (38) and **9a** (55)
3	I_2 (0.1)	DIB (3)	-	110	**7a** (76)
4	I_2 (0.1)	DIB (3)	THF	110	**8a** (traces)
5	I_2 (0.1)	DIB (3)	Toluene	110	**8a** (60)
6	I_2 (0.1)	DIB (3)	DCM	110	**8a** (65)
7	I_2 (0.1)	DIB (3)	PrOH	110	**8a** (60)
8	I_2 (0.1)	DIB (3)	CH_3CN	110	**9a** (80)
9	**I_2 (0.2)**	**DIB (2)**	**None**	**110**	**7a (94)**
10	I_2 (0.2)	H_2O_2 (3)	None	110	**8a** (40) and **7a** (traces)
11	I_2 (0.2)	*t*-BuOOH (3)	None	110	**8a** (20) and **7a** (traces)
12	NIS (0.2)	DIB (3)	None	110	**8a** (40) and **7a** (25)
13	TBAI (0.2)	DIB (3)	None	110	**8a** (30) and **7a** (traces)
14	KI (0.2)	DIB (3)	None	110	**8a** (60) and **7a** (traces)
15	I_2 (0.2)	(Bis(trifluoroacetoxy)iodo) benzene	None	110	**8a** (30)

[a] Reactions were carried out for 16 h under the conditions specified in the table. [b] Isolated yield.

The use of other oxidizing agents such as hydrogen peroxide and *tert*-butyl hydroperoxide gave inferior yields of the desired dimer (Table 1, Entry 10-11). Next different iodine sources such as NIS,

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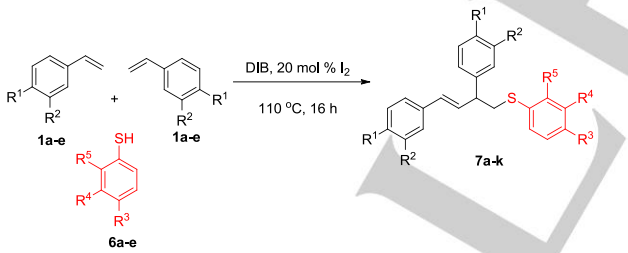
TBAI, and KI were investigated but they all fail to provide the desired dimer in acceptable yields (Table 1, entry 12-14). In the absence of thiophenol, the reaction of styrene with DIB and iodine led to the formation of an iodoacetoxy product. Although the DIB is the preferred hypervalent iodine source in terms of cost, readily availability and environmental benignes,[26] (bis(trifluoroacetoxy)iodo)benzene was investigated for comparison purposes. Due to the strong electron withdrawing affinity of the trifluoroacetoxy, it was expected that the reaction in the presence of the highly electrophilic (bis(trifluoroacetoxy)iodo)benzene would proceed faster and in better yields than in the presence of the DIB. However, contrary to our expectation the reaction did not only provide poorer yield but the reaction was incomplete even after 24 h leaving significant amounts of unreacted thiophenol, the disulfide and unidentified products (Table 1, Entry 15).

Next, under the optimal conditions, we examined the substrate scope with different substituents on the aromatic rings of the styrene and thiophenol. The results are summarized in Table 2. Styrenes bearing both electron donating and electron withdrawing substituents proceeded smoothly to afford the corresponding dimers in very good yields (Table 2, Entry 1-11) and the structures of the products were identified by HRMS, ^{1}H and ^{13}C NMR. Gratifyingly, the electronic nature (Table 2, Entry 5 vs 6) and position of the substituents (Table 2, Entry 5 vs 7) possess insignificant influence on the reactivity of the reaction. The use of aliphatic alkenes lead to the formation of *β*-acetoxysulfide regioisomers and simple addition products of a thiol-ene reaction while diarylethylene derivatives were found to be unreactive.

Table 2. Synthesis of (*E*)-1,3-diphenyl-1-butene derivatives **7**.



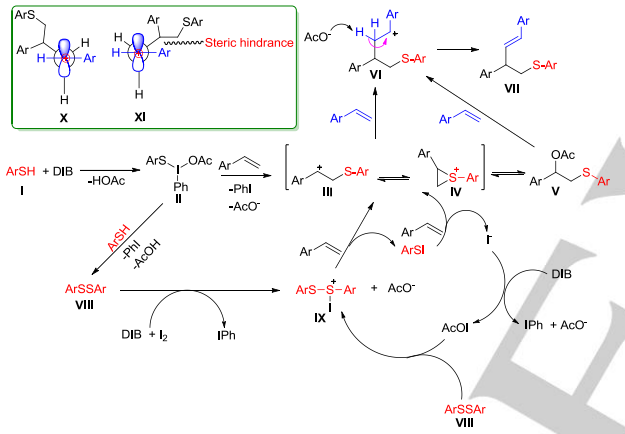
Entry	Styrene	Thiophenol	Product	Yield (%)[a]
1	**1a** $R^1 = R^2 = H$	**6a** $R^3=CH_3$, $R^4=R^5= H$	**7a**	94
2	**1a** $R^1 = R^2 = H$	**6b** $R^3=t$-Bu, $R^4=R^5= H$	**7b**	92
3	**1a** $R^1 = R^2 = H$	**6c** $R^3=OCH_3$, $R^4=R^5= H$	**7c**	88
4	**1a** $R^1 = R^2 = H$	**6d** $R^3=R^4=R^5= H$	**7d**	52
5	**1b** $R^1 = CH_3$, $R^2 = H$	**6a** $R^3=CH_3$, $R^4=R^5= H$	**7e**	78
6	**1c** $R^1 = Cl$, $R^2 = H$	**6a** $R^3=CH_3$, $R^4=R^5= H$	**7f**	90
7	**1d** $R^1 = H$, $R^2 = CH_3$	**6a** $R^3=CH_3$, $R^4=R^5= H$	**7g**	74
8	**1d** $R^1 = H$, $R^2 = CH_3$	**6c** $R^3=OCH_3$, $R^4=R^5= H$	**7h**	82
9	**1c** $R^1 = Cl$, $R^2 = H$	**6c** $R^3=OCH_3$, $R^4=R^5= H$	**7i**	84
10	**1b** $R^1 = CH_3$, $R^2 = H$	**6b** $R^3=t$-Bu, $R^4=R^5= H$	**7j**	86
11	**1e** $R^1 = H$, $R^2 = Br$	**6a** $R^3=CH_3$, $R^4=R^5= H$	**7k**	75
12	**1a** $R^1 = R^2 = H$	**6e** $R^3=R^4=H$, $R^5= CH_3$	**9b**	70

[a] Isolated yield.

Similarly, the scope of the thiophenol component of the reaction was also evaluated. Unlike in the case of the styrene component, it was found that the nature and position of substituent on the aromatic ring of the thiophenol moiety strongly affect the reactivity of the reaction. The reaction is compatible with moderate and powerful electron donating substituents (Table 2, Entry 1-10). However, the presence of halide and nitro substituents resulted in the formation difficult-to-separate mixture of products (results not included here). In the absence of any substituent on the ring, dimer **7d** was obtained in poor yield as it reacted further. (Table 2, Entry 4). 2-Methylbenzenethiol **6e** led to the formation of *β*-acetoxysulfide **9b** (Table 2, Entry 12) probably due to the steric hindrance by the incumbent methyl group. The use of aliphatic thiols did not either produce a major product but provided a number of products which were very difficult to purify. With the assumption that the reason for the formation of several products could be due to the instability of the intermediates at 110 °C, reactions at lower temperatures were investigated but provided iodoacetoxylated derivatives[36] as major products without the incorporation of the thiol functional group.

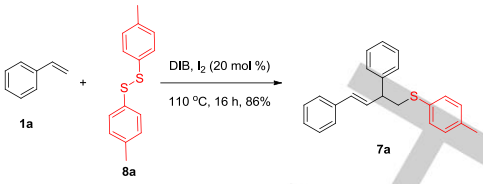
The proposed mechanism is illustrated in Scheme 3. The reaction commences with the formation of the hypervalent intermediate **II**. This intermediate then reacts with the styrene to give the benzylic carbocation **III**/thiiranium **IV** intermediate which might have further equilibrated with the *β*-acetoxysulfide **V**. A second molecule of the styrene then reacts with the benzylic carbocation **III**/thiiranium **IV** intermediate to form another benzylic carbocation **VI**. An AcO^- that was ejected in the first step then abstracts the alpha hydrogen to form the dimer product **VII**. The direct S_N2 substitution reaction of *β*-acetoxysulfide **V** with the styrene to provide the benzylic carbocation **VI** cannot be ruled out. Parallel to this route, disulfide **VIII** could also be formed and decomposed into the electrophilic intermediate **IX** upon reaction with AcOI, which is generated *in situ* from the reaction of DIB and I_2.[37,38] This intermediate then reacts with the styrene to form benzylic carbocation **III**/thiiranium **IV** intermediate. As in the case of the

first route, the carbocation intermediate then reacts with another molecule of styrene to give benzylic carbocation **III**. The ArSI produced in this step reacts with the styrene to produce additional benzylic carbocation **III**/thiiranium **IV** intermediate. The I^- is then oxidized by DIB into AcOI to continue the catalytic cycle.[37,38] To the best of our knowledge, this is the first report on the opening of the thiiranium ring with an alkene. The regioselective ring opening of thiiranium **IV** *via* the nucleophilic attack at the more substituted carbon is attributed to the conjugation of the π-bonds of the aromatic ring to stabilize the developing benzylic positive charge in the transition state. This is in line to the observation and extensive study done by Xu and co-workers.[39-41] The *trans*-geometry of the product is determined by the parallel alignment of the vacant *p*-orbital of the carbocation **VI** and the breaking C-H bond as well as the preference of this intermediate to adopt conformation **X**, which suffers less steric hindrance than conformer **XI** (Scheme 3). The steric hindrance caused by the pendant aryl sulfide might have prevented further dimerization to provide trimer or tetramer derivatives.



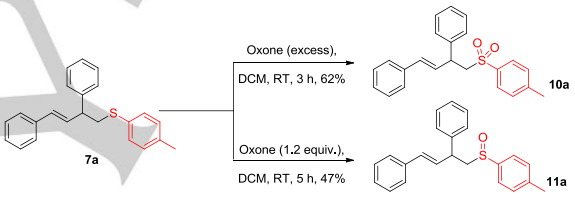
Scheme 3. Proposed mechanism of the dimerization styrene to provide dimer **7**.

To prove this point, the reaction was carried out in the absence of iodine and the reaction lead to the formation of the disulfide **8a** and traces of the dimer **7a** suggesting the importance of iodine in promoting the reaction to go to completion. Use of the disulfide **8a** as a starting material instead of the corresponding thiophenol under otherwise identical conditions lead to the formation of the dimer **7a** in 86% yield supporting the proposed mechanism (Scheme 4). In comparison to the use of the disulfide, the use of thiophenol as the substrate gave a relatively better yield (Table 1, entry 9). Interestingly, the reaction did not lead to product formation in the absence of the DIB.



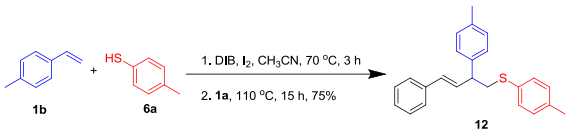
Scheme 4. The use of a disulfide substrate in the preparation of dimer **7a**.

Besides the special character sulfur imparts in the properties of advanced materials, its ease of derivatization enables for the synthesis of new analogues. For instance, treatment of dimer **7a** with 1.2 equivalents of Oxone® at room temperature afforded sulfoxide **11a** while treatment with excess Oxone® provided sulfone **10a** chemoselectively as new derivatives of the styrene dimer having sulfur in higher oxidation states (Scheme 5). Hydrogenolytic desulfurization using Raney-nickel or nickel boride, Pummerer rearrangement of the sulfoxide analogue, alkylation at the α-carbon of the sulfone, and transition metal catalysed cyclization are some of the potential transformations of the dimer that could lead to novel derivatives.



Scheme 5. Oxidation of dimer **7a** with Oxone.

Furthermore, a slight modification of the method allowed the introduction of two different styrene derivatives in the dimer demonstrating its superiority to the reported head-to-tail dimerization protocols (Scheme 6). This was achieved by first reacting thiophenol **6a**, styrene **1b** (1.2 equiv.), DIB (2 equiv.) and I_2 (20 mol %) in CH_3CN at 70 ºC for 3 h to form a *β*-acetoxysulfide intermediate. The reaction mixture was then concentrated under vacuum to remove the solvent (the dimerization reaction does not work in the presence of a solvent) and the excess styrene **1b**. Styrene **1a** (1.2 equiv.) was then added to the residue product and heated at 110 ºC for 15 h to provide dimer **12** in 75% yield.



Scheme 6. Incorporation of two different styrene derivatives in the dimer.

In conclusion, we have successfully developed a multicomponent regio- and stereoselective protocol for the synthesis of novel (*E*)-1,3-diphenyl-1-butene derivatives starting from readily available reagents. Unlike the previously reported protocols, the current

method incorporates a sulfur heteroatom in the dimer without a need for an additional reaction step. Further studies on the preparation of new advanced materials from the dimers and their use as substrates for the synthesis of thiochromans *via* an intramolecular cyclization reaction is under way in our group.

Experimental Section

General methods:

The solvents which were employed in the optimization of the method were dried by appropriate techniques reported in the Purification of Laboratory Chemicals by Perrin and Armarego.[42] All reactions were monitored by thin layer chromatography (TLC) on aluminum-backed silica gel 60 F_{254} plates using an ascending technique. The plates were visualized under UV-light. Gravity column chromatography was done on silica gel 60 (70–230 mesh). Melting points were determined using a hot-stage and are uncorrected. All proton and carbon-13 nuclear magnetic resonance spectra were recorded as deuteriochloroform solutions using tetramethylsilane as an internal standard. All chemical shifts are reported in ppm. All the products picked-up an extra oxygen atom during HRMS (ESI-TOF) analysis.

General procedure for the synthesis of dimers 7:

A stirred mixture of thiophenol **1a-e** (100 mg, 1 equiv.), styrene **1a-e** (3 equiv.), DIB (2 equiv.) and iodine (20 mol %) in a 10 mL round-bottomed flask sealed with a stopper was heated at 110 ºC for 16 h. After allowing to cool down to room temperature, the reaction mixture was loaded onto a column packed with silica gel and eluted with hexane to provide the corresponding dimers **7a-k**:

(*E*)-(2,4-diphenylbut-3-en-1-yl)(*p*-tolyl)sulfane (7a): 249 mg, 93% yield; yellow oil; IR (neat cm^{-1}) 3025, 2924, 1759, 1597, 1493, 1446, 1208, 1088; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.10 (m, 12H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.40-6.36 (m, 2H), 3.73-3.65 (m, 1H), 3.31 (d, *J* = 7.6 Hz, 2H), 2.31 (s, 3H)); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 142.8, 137.1, 136.3, 132.7, 131.8, 131.0, 130.3, 129.7, 128.7, 128.5, 127.7, 127.3, 126.8, 126.3, 48.5, 40.7, 21.0. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{23}H_{23}OS$ 347.1470, found 347.1474.

(*E*)-(4-(*tert*-butyl)phenyl)(2,4-diphenylbut-3-en-1-yl)sulfane (7b): 205 mg, 92% yield; colorless oil; IR (neat cm^{-1}) 3030, 2963, 2857, 1949, 1597, 1451, 1390, 1267, 1121, 1012; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.24 (m, 14H), 6.48-6.34 (m, 2H), 3.73 (q, *J* = 7.6 and 13.4 Hz, 1H), 3.34 (d, *J* = 7.6 Hz, 2H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 149.4, 142.8, 137.1, 132.9, 131.8, 130.9, 129.7, 128.7, 128.4, 127.7, 127.3, 126.8, 126.3, 125.9, 48.7, 40.4, 34.4, 31.3. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{26}H_{29}OS$ 389.1939, found 389.1924.

(*E*)-(2,4-diphenylbut-3-en-1-yl)(4-methoxyphenyl)sulfane (7c): 217 mg, 88% yield; yellow oil; IR (neat cm^{-1}) 3030, 2935, 2834, 1591, 1490, 1239, 1172, 1026. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (m, 12H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.44-6.28 (m, 2H), 3.79 (s, 3H), 3.71-3.61 (m, 1H), 3.27 (d, *J* = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 158.9, 142.8, 137.1, 133.4, 131.9, 130.9, 128.6, 128.4, 127.7, 127.3, 126.8, 126.5, 126.3, 114.6, 55.3, 48.6, 42.0. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{23}H_{23}O_2S$ 363.1419, found 363.1434.

(*E*)-(2,4-diphenylbut-3-en-1-yl)(phenyl)sulfane (7d): 149 mg, 52% yield; colorless oil; IR (neat cm^{-1}),3034, 2909, 1950, 1881, 1797, 1582, 1479, 1447, 1262, 1077, 1021 ; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.09 (m, 15H), 6.45-6.31 (m, 2H), 3.73-3.66 (m, 1H), 3.34 (d, *J* = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 142.7, 137.1, 136.6, 132.9, 131.7, 131.1, 130.0, 129.5, 128.9, 128.7, 128.5, 128.1, 127.7, 127.6, 127.4, 126.9, 126.4, 126.3, 126.0, 48.5, 40.0. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{22}H_{21}S$ 317.1364, found 317.1346.

(*E*)-(2,4-di-*p*-tolylbut-3-en-1-yl)(*p*-tolyl)sulfane (7e): 250 mg, 86% yield; yellow oil; IR (neat cm^{-1}) 3018, 2921, 1508, 1440, 1099, 1029; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-6.98 (m, 12H), 6.43-6.28 (m, 2H), 3.68 (q, *J* = 7.6 and 13.8 Hz, 1H), 3.33 (d, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 139.8, 136.9, 136.3, 136.1, 134.4, 132.8, 130.9, 130.6, 130.2, 129.7, 129.3, 129.2, 129.1, 127.6, 126.2, 48.0, 40.7, 21.1 (x 2), 21.0. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{25}H_{27}OS$ 375.1783, found 375.1779.

(*E*)-(2,4-bis(4-chlorophenyl)but-3-en-1-yl)(*p*-tolyl)sulfane (7f): 289 mg, 90% yield; colorless oil; IR (neat cm^{-1}) 2942, 1714, 1488, 1325, 1488, 1325, 1090 ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.23-7.15 (m, 6H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.38-6.18 (m, 2H), 3.66-3.56 (m, 1H), 3.28-3.17 (m, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.9, 136.5, 135.4, 133.1, 132.7, 132.2, 131.9, 130.5 130.1, 129.8, 129.7, 129.1, 128.8, 128.6, 127.5, 47.9, 40.5, 21.0. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{23}H_{21}Cl_2OS$ 415.0690, found 415.0717.

(*E*)-(2,4-di-*m*-tolylbut-3-en-1-yl)(*p*-tolyl)sulfane (7g): 214 mg, 74% yield; colorless oil; IR (neat cm^{-1}) 3047, 2969, 1594, 1496, 1289, 1138, 1079, 1026; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.05 (m, 12H), 6.46-6.35 (m, 2H), 3.75-3.67 (m, 1H), 3.36 (d, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 2.37 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 142.9, 138.3, 138.0, 137.2, 136.2, 132.9, 131.8, 131.0, 130.3, 129.8, 128.6, 128.5, 128.4, 128.2, 127.7, 127.0 124.8, 123.6, 48.6, 40.7, 21.6, 21.4, 21.1. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{25}H_{27}OS$ 375.1783, found 375.1786.

(*E*)-(2,4-di-*m*-tolylbut-3-en-1-yl)(4-methoxyphenyl)sulfane (7h): 216 mg, 81% yield; colorless oil; IR (neat cm^{-1}) 3025, 2913, 1591, 1490, 1283, 1241, 1174, 1096, 1032; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.41-6.95 (m, 8H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.49-6.37 (m, 2H), 3.82 (s, 3H), 3.72-3.64 (m, 1H), 3.31 (d, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 158.8, 142.8, 138.1, 137.9, 137.1, 133.3, 131.8, 130.8, 128.5, 128.4, 128.3, 128.3, 128.0, 127.5, 126.9, 126.6 124.7, 123.4, 114.5, 55.2, 48.6, 41.9, 21.4, 21.3. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{25}H_{27}O_2S$ 391.1732, found 391.1745.

(*E*)-(2,4-bis(4-chlorophenyl)but-3-en-1-yl)(4-methoxyphenyl)sulfane (7i): 246 mg, 83% yield; yellow oil; IR (neat cm^{-1}) 2935, 2834, 1591, 1493, 1177, 1241, 1085, 965; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.39 (m, 8H), 7.13 (d, *J* = 8.4 Hz, 2H) 6.83 (d, *J* = 8.8 Hz, 2H), 6.30 (d, *J* = 3.2 Hz, 2H), 3.80 (s, 3H), 3.19-3.05 (m, 1H), 3.25-3.15 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) 159.1, 140.9,135.4, 133.6, 133.1, 132.6, 132.1, 130.0, 129.2, 128.8, 128.7, 128.6, 127.5, 127.4, 126.1, 114.7, 55.4, 48.1, 41.9. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{23}H_{21}Cl_2O_2S$ 431.0639, found 431.0624

(*E*)-(4-(*tert*-butyl)phenyl)(2,4-di-*p*-tolylbut-3-en-1-yl)sulfane (7j): 205 mg, 85% yield; yellow oil; IR (neat cm^{-1}) 2957, 1502, 1272, 1113, 1023, 962; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.04 (m, 12H), 6.47-6.32 (m, 2H), 3.77-3.64 (m, 1H), 3.35 (d, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 2.34 (s, 3H), 1.34 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 149.2, 139.8, 137.0, 136.3, 134.4, 133.1, 131.0, 130.6, 129.8, 129.6, 129.3, 129.1, 128.9, 127.6, 126.2, 125.9, 48.2, 40.5, 34.4, 31.3, 21.1 (x2). HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{28}H_{33}OS$ 417.2252, found 417.2285.

(*E*)-(2,4-bis(3-bromophenyl)but-3-en-1-yl)(*p*-tolyl)sulfane (7k): 295 mg, 75% yield; colorless oil; IR (neat cm^{-1}) 2921, 2857, 2086, 1722, 1590, 1564,

1564, 1491, 1482, 1425, 1260, 1190, 1090, 1071, 1016; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.11 (m, 12H), 6.34-6.25 (m, 2H), 3.66-3.59 (m, 1H), 3.25 (d, *J* = 7.6 Hz, 2H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.7, 139.0, 136.7, 132.6, 132.0, 130.8, 130.7, 130.4, 130.3, 130.2, 130.1, 130.0, 129.8, 129.1, 126.4, 125.1, 122.8, 122.7, 48.4, 40.5, 21.0.

(*E*)-(4-tosylbut-1-ene-1,3-diyl)dibenzene (10a): The dimer **7a** (100 mg, 0.3 mmol) was added to a vigorously stirring suspension of wet alumina (1 g wetted with 100 µL of water) and OXONE® (370 mg, 0.6 mmol) in dichloromethane (3 mL). The reaction mixture was stirred at room temperature for 3 h. After completion of the reaction, the reaction mixture was filtered to remove the adsorbent. Evaporation of the solvent and flash-chromatographic purification on silica gel (ethyl acetate/hexane, 30:70) afforded the title sulfone **10a** (67 mg, 62%) as white crystals; mp 132-136 ºC; IR (neat cm^{-1}) 3045, 2960, 2930, 1596, 1491, 1452, 1289, 1130, 1087, 1024; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.33-7.23 (m, 12H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 7.6 and 16.0 Hz, 1H), 4.15 (q, *J* = 7.6 and 14.0 Hz, 1H), 3.22-3.19 (m, 2H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.5, 141.1, 136.8, 136.6, 131.5, 130.0, 129.7, 128.9, 128.4, 128.2, 127.6, 127.5, 127.1, 126.3, 61.5, 44.0, 21.5. HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{23}H_{22}O_2SNa$ 385.1238, found 385.1262.

(*E*)-(4-(*p*-tolylsulfinyl)but-1-ene-1,3-diyl)dibenzene (11a): The dimer **7a** (100 mg, 0.3 mmol) was added to a vigorously stirring suspension of wet alumina (1 g wetted with 100 µL of water) and OXONE® (222 mg, 0.36 mmol) in dichloromethane (3 mL). The reaction mixture was stirred at room temperature for 5 h. After completion of the reaction, the reaction mixture was filtered to remove the adsorbent. Evaporation of the solvent and flash-chromatographic purification on silica gel (ethyl acetate/hexane, 50:50) afforded the title sulfoxide **11a** (49 mg, 47%) as white crystals; mp 131-133; IR (neat cm^{-1}) 3047, 2969, 1594, 1496, 1289, 1138, 1079, 1026; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.25-7.13 (m, 10H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.27 (d, *J* = 15.6 Hz, 1H), 6.11 (dd, *J* = 8.0 and 15.6 Hz, 1H), 4.01 (dd, *J* = 7.2 and 14.0 Hz, 1H), 3.62-3.53 (m, 2H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.4, 141.1, 136.8, 136.6, 131.5, 130.0, 129.7, 128.9, 128.4, 128.2, 127.6, 127.5, 127.1, 126.3, 61.5, 44.0, 21.5. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{23}H_{23}O_2S$ 363.1419, found 363.1418.

(*E*)-(2,4-di-*p*-tolylbut-3-en-1-yl)(*p*-tolyl)sulfane (12): DIB (522 mg, 1.62 mmol), styrene **1b** (128 µL, 0.97 mmol) and iodine (41 mg, 0.16 mmol) were added to the stirring solution of thiophenol **6a** (100 mg, 0.81 mmol) in acetonitrile (0.1 mL). The reaction mixture was stirred at 70 ºC for 3 h. The reaction mixture was then concentrated on a rotary evaporator. Styrene **1a** was added to the brownish residue product and stirred again at 110 ºC for 15 h. After allowing to cool down to room temperature, the reaction mixture was loaded onto a column packed with silica gel and eluted with hexane to provide the title three component product (216 mg, 75% yield) as a yellow oil; IR (neat cm^{-1}) 3022, 2918, 2862, 1896, 1598, 1511, 1491, 1448, 1377, 1302, 1259, 1210, 1180, 1154, 1090; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.09 (m,13H), 6.40-6.29 (m, 2H), 3.70-3.60 (m, 1H) 3.35-3.25 (m, 2H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 136.2, 136.2, 136.0, 134.4, 133.4, 132.3, 132.7, 132.6, 131.8, 130.9, 130.7, 130.5 129.8, 129.7, 129.4, 129.3,129.1 128.7, 128.6, 128.4, 128.1, 127.7, 127.6, 127.3, 127.3, 126.8, 126.8, 126.5, 126.3, 126.2, 48.5, 48.1, 40.7, 40.6, 21.1, 21.0, 21.0. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{24}H_{25}OS$ 361.1626, found 361.1627.

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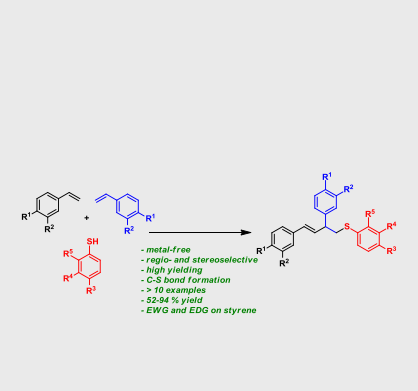
COMMUNICATION

A three component metal and strong acid-free regio-and stereoselective synthesis of 1,3-diphenyl-1-butene derivatives has been developed. Unlike the previously developed protocols, the current methodology allows the incorporation of a sulfur heteroatom as well as two different styrene derivatives in the dimer.



*Mokgethwa B Marakalala and Henok H Kinfe**

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Title

Iodine and PhI(OAc)$_2$ Mediated Multicomponent synthesis of novel (*E*)-1,3-diphenyl-1-butene derivatives