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Solvent-Dependent Regiochemical Cyclotrimerisation of Phenylacetylene with Cobalt Catalysts Containing Disulfide Ligands: A Case Study

Gerhard Hilt,*[a] Christoph Hengst,[a] and Wilfried Hess[a]

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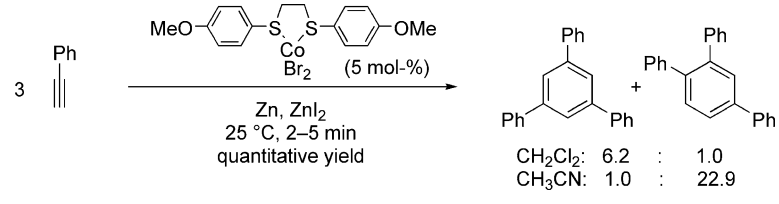
The intermolecular cobalt-catalysed cyclotrimerisation of phenylacetylene as a benchmark alkyne with [1,2-bis(4-methoxyphenylthio)ethane]cobalt dibromide gave the symmetrical 1,3,5-triphenylbenzene as the major product when dichloromethane was used as the solvent, whereas the unsymmetrical 1,2,4-trisubstituted product was obtained in acetonitrile in quantitative yield. Optimisation of the aromatic and aliphatic disulfide ligands in different solvents is discussed.

Introduction

The coordination of unsaturated ligands such as alkenes and alkynes to transition-metal complexes with vacant coordination sites is a prerequisite to induce cyclotrimerisation or cycloaddition processes within the ligand sphere. Accordingly, organic transformations that lead to carbon–carbon bond formations, which would not be possible under regular thermal conditions, can now be realised in the presence of transition metal complexes.[1] Several new approaches to the cyclotrimerisation of alkynes besides the traditional cyclopentadienylcobalt or carbonylcobalt complexes[2] have been reported recently. Among these are the rather simple (diimine)cobalt or (iminopyridine)cobalt complexes,[3] and even ligand-free cobalt salts have been used.[4] Over the last couple of years we have investigated cobalt(I)-catalysed Diels–Alder reactions between non-activated terminal and internal alkynes and acyclic 1,3-dienes.[5] Recently, we reported a unique catalyst system that is able to promote the formation of regioisomeric *meta*-disubstituted dihydroaromatic compounds in excellent yields and with very high regioselectivities for the first time.[6] Under these circumstances we were also very interested in identifying simple cobalt complexes that are capable of forming regioselectively symmetrical 1,3,5-trisubstituted benzene derivatives from terminal alkynes,[7] especially in the light of earlier findings that 1,2,4-trisubstituted benzene derivatives are predominantly formed when diimine-type ligands such as **4** are used. The potential of 1,2-bis(phenylthio)ethane (**3a**) as a ligand of cobalt was identified previously when the regioselective formation of the two possible trimerisation products was investigated in different solvents with different ligand types.[3]

Results and Discussion

The use of diimine-type ligands in the cyclotrimerisation of alkynes leads predominantly to the unsymmetrical 1,2,4-trisubstituted benzene derivatives **2**, as was shown in a previous report.[3] Therein we also investigated the 1,2-bis-(phenylthio)ethane ligand **3a**, which exhibits a very unusual solvent dependency. The data in Table 2 show that in acetonitrile product **2** is predominantly formed. On the other hand, when the reaction was performed in dichloromethane, the regioselectivity was reversed with the symmetrical benzene derivative **1** being generated in a slight excess. We were intrigued to find a sulfur-based ligand system, which would predominantly generate the symmetrical products, as



Scheme 1. Benchmark ligands for the regioselective cyclotrimerisation of phenylacetylene.

[a] Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Str., 35043 Marburg, Germany
Fax: +49-6421-2825677
E-mail: hilt@chemie.uni-marburg.de

this would be a major step towards a simple and inexpensive catalyst system for the selective synthesis of either trimer **1** or **2** depending on the ligand and the solvent used.

After we realised that the [1,2-bis(4-methoxyphenylthio)-ethane]cobalt complex **3b** (Table 2) exhibited a significantly higher regioselectivity with respect to the generation of **1**, we decided to revisit the solvent dependency of [1,2-bis(4-methoxyphenylthio)ethane]cobalt dibromide to see if changes in the solvent should be made. Under these circumstances mainly chlorinated solvents were investigated to determine the best combination of reactivity and selectivity in the cyclotrimerisation reaction of phenylacetylene with 5 mol-% of the cobalt catalyst and a reaction time of 30 min (Scheme 1).[8] The results are summarised in Table 1.

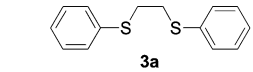
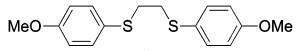
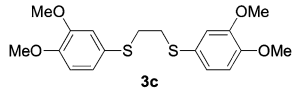
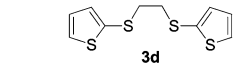
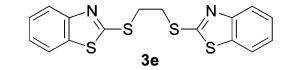
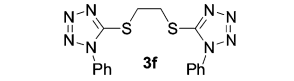
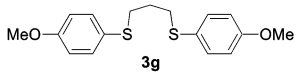
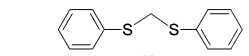
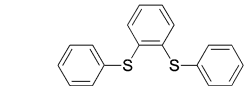
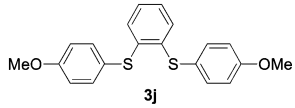
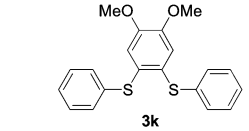
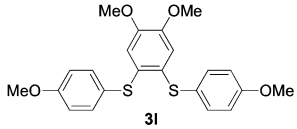
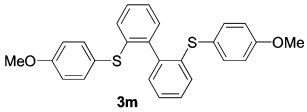
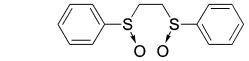
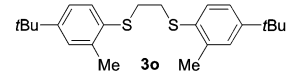
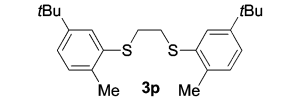
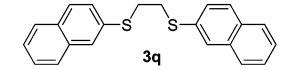
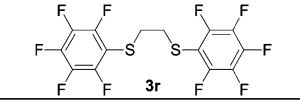
Table 1. Results for the cobalt-catalysed cyclotrimerisation reaction with ligand **3b** in different solvents.

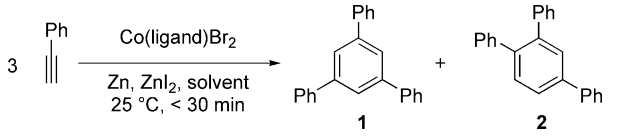
Entry	Solvent	Yield [%] (ratio **1**/**2**)
1	CH_2Cl_2	99 (6.2:1.0)
2	C_6H_5Cl	68 (1.5:1.0)
3	$ClCH_2CH_2Cl$	57 (2.8:1.0)
4	$CHCl_3$	78 (1.4:1.0)
5	CCl_4	0 (–)
6	$HSCH_2CH_2SH$	0 (–)
7	tetrahydrothiophene	99 (1.0:2.8)
8	C_6H_6	35 (2.8:1.0)
9	$C_6H_5CH_3$	99 (1.6:1.0)
10	CH_3CN	99 (1.0:22.9)
11	THF	99 (1.0:1.7)

The cyclotrimerisation is best conducted in dichloromethane under an inert gas. Other chlorinated solvents gave inferior results, both with respect to reactivity and selectivity. In tetrachloromethane no reaction was observed at all. Two sulfur-containing solvents were tested, which might also act as additional ligands. The results showed that with ethane-1,2-thiol (Entry 6) the reaction was inhibited, whereas with tetrahydrothiophene (Entry 7), a sulfide, the catalyst system exhibited good reactivity, but the selectivity was only moderately in favour of product **2**. The results in acetonitrile were as expected as this solvent had given excellent results with cobalt complexes of the diimine ligand series in terms of reactivity and selectivity for the formation of **2**.[3] With benzene and toluene, only toluene gave a good reactivity and encouraging selectivities, albeit still inferior to that of dichloromethane. After encouraging preliminary results with tetrahydrofuran, we decided to continue to screen for ligands in the solvents dichloromethane, acetonitrile and tetrahydrofuran. In these three solvents different aromatic sulfide ligands were tested in preformed catalysts (see Exp. Sect.) for the cyclotrimerisation of phenylacetylene. The results of these reactions are summarised in Table 2 and Scheme 2.

The introduction of electron-donating methoxy groups onto the phenyl substituents (**3b**) significantly increased the regioselectivity of the cyclotrimerisation reaction in dichloromethane in favour of product **1** and in acetonitrile in favour of product **2** (Entries 4 and 5) compared with the parent ligand system **3a** (Entries 1 and 2). If an electron-withdrawing group was used such as in ligand **3r** the desired symmetrical cyclotrimerisation product **1** was obtained as

Table 2. Results of the cobalt-catalysed cyclotrimerisation reaction using aromatic disulfide ligands.

Entry	Ligand	Solvent	Yield (ratio **1**/**2**)
1		CH_2Cl_2	96% (2.9:1.0)
2		CH_3CN	96% (1.0:16.0)
3	**3a**	THF	42% (1.0:1.8)
4		CH_2Cl_2	99% (6.2:1.0)
5		CH_3CN	99% (1.0:22.9)
6	**3b**	THF	99% (1.0:1.7)
7		CH_2Cl_2	99% (1.8:1.0)
8		CH_3CN	99% (1.0:20.8)
9	**3c**	THF	99% (1.0:1.8)
10		CH_2Cl_2	99% (4.5:1.0)
11		CH_3CN	99% (1.0:19.4)
12	**3d**	THF	99% (1.0:3.0)
13		CH_2Cl_2	0% (–)
14		CH_3CN	99% (1.0:17.8)
15	**3e**	THF	70% (1.0:1.8)
16		CH_2Cl_2	16% (1.0:6.4)
17		CH_3CN	99% (1.0:18.7)
18	**3f**	THF	40% (1.0:1.6)
19		CH_2Cl_2	99% (1.0:1.7)
20		CH_3CN	99% (1.0:16.9)
21	**3g**	THF	38% (1.0:2.7)
22		CH_2Cl_2	42% (1.0:2.1)
23		CH_3CN	99% (1.0:19.6)
24	**3h**	THF	19% (1.0:4.6)
25		CH_2Cl_2	99% (2.8:1.0)
26		CH_3CN	99% (1.0:20.0)
27	**3i**	THF	59% (1.0:1.9)
28		CH_2Cl_2	99% (3.8:1.0)
29		CH_3CN	99% (1.0:20.8)
30	**3j**	THF	66% (1.0:3.0)
31		CH_2Cl_2	94% (4.0:1.0)
32		CH_3CN	99% (1.0:16.8)
33	**3k**	THF	45% (1.0:1.7)
34		CH_2Cl_2	99% (3.8:1.0)
35		CH_3CN	90% (1.0:15.9)
36	**3l**	THF	52% (1.1:1.0)
37		CH_2Cl_2	99% (4.0:1.0)
38		CH_3CN	99% (1.0:18.0)
39	**3m**	THF	10% (1.0:3.8)
40		CH_2Cl_2	0% (–)
41		CH_3CN	99% (1.0:16.9)
42	**3n**	THF	60% (1.0:2.5)
43		CH_2Cl_2	82% (1.0:1.4)
44		CH_3CN	99% (1.0:12.3)
45	**3o**	THF	0% (–)
46		CH_2Cl_2	99% (1.0:1.2)
47		CH_3CN	99% (1.0:14.0)
48	**3p**	THF	0% (–)
49		CH_2Cl_2	99% (2.4:1.0)
	3q		
50		CH_2Cl_2	63% (1.0:5.5)
	3r		



Scheme 2. Optimisation of disulfide ligands in the cobalt-catalysed cyclotrimerisation in different solvents.

the minor product in dichloromethane. Based on these results, further investigations with electron-withdrawing substituents were disregarded. On the other hand, the introduction of further methoxy groups was envisaged to further increase the regioselectivity in favour of product **1** in dichloromethane. Surprisingly, additional improvement was not observed. On the contrary, the regioselectivity in favour of **1** was lowered with ligand **3c**. Other ligands (**3d**–**f**) with the aliphatic ethylene backbone motif derived from dibromoethane and commercially available thiol derivatives were synthesised and tested, but no significant increase in selectivity towards **1** was observed in dichloromethane (Entries 10, 13 and 16). Nevertheless, most of the disulfide ligands tested demonstrated rather high reactivities and good to excellent selectivities in acetonitrile for the formation of **2**. The results in tetrahydrofuran are reported for the sake of completeness as no advantage was determined in tetrahydrofuran over the other two solvents for the ligands tested.

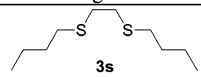
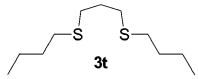
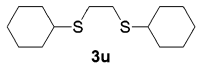
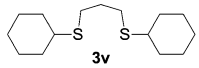
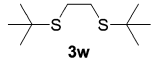
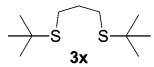
Changes to the carbon backbone on the other hand led to interesting results. Whereas the two-carbon backbone of the ethylene-bearing ligands led to the preferential formation of **1** (Entries 1, 4, 7 and 10), the corresponding propylene ligand **3g** (Entry 19) and methylene-bridged bidentate disulfide ligand **3h** (Entry 22) favoured the unsymmetrical product **2**. This behaviour was also observed for the aliphatically substituted ligands discussed below.

The presence of an aromatic backbone in the form of a 1,2-disubstituted benzene ring or a 2,2′-disubstituted 1,1′-biphenyl derivative in ligands **3i**–**m** (Entries 25–39) also gave good selectivities for the formation of **1**. However, the introduction of further methoxy groups into the ligands **3k** and **3l** (Entries 31 and 34) did not result in increased selectivity for the formation of **1**. Finally, the sterically bulky aliphatically substituted aryl substituents introduced in ligands **3o** and **3p** and the sulfoxide ligand **3n** gave inferior results. The introduction of a 2-naphthyl substituent in ligand **3q** led to lower regioselectivity relative to ligand **3a**, thus further modifications of the naphthyl ring with electron-donating groups were not considered. Nevertheless, many of the disulfide ligands gave quantitative yields of the trimerisation products, but the selectivity with respect to the formation of 1,3,5-triphenylbenzene (**1**) was only moderate to good for ligand **3b**.

The reactions with alkyl-substituted disulfides **3s**–**y** were also tested. The results are summarised in Table 3.

The results clearly show that the ethylene-bridged ligands **3s** and **3u** yield the cyclotrimerisation products in quantitative yield and are superior to the propylene-bridged ligands **3t**, **3v** and **3x** as well as the *tert*-butyl-substituted ligand **3w**,

Table 3. Results of the cobalt-catalysed cyclotrimerisation reaction with aliphatic disulfide ligands in dichloromethane.

Entry	Ligand	Yield (ratio **1**/**2**)[a]
1	 **3s**	99% (1.9:1.0)
2	 **3t**	75% (1.0:1.0)
3	 **3u**	99% (1.9:1.0)
4	 **3v**	69% (1.0:6.8)
5	 **3w**	14% (1.0:8.8)
6	 **3x**	48% (1.0:5.7)
7	 **3y**	99% (1.0:13.3)

[a] For the alkyl-substituted disulfide ligands the reaction time was 15 h.

which gave only incomplete conversion after 15 h. As for the selectivity, the two ligands **3s** and **3u** gave essentially identical results with moderate preference for product **1**, whereas **3t** gave a 1:1 mixture of the two regioisomers **1** and **2**, and the ligands **3v**–**x** preferred the formation of **2** as the major isomer. In a final experiment the cyclic dithioketal **3y** was tested as an additive/ligand and, although the conversion went to completion, product **2** was again the major isomer formed in this reaction.

The solvent dependency can be rationalised when the results of the (diimine)cobalt-catalysed cyclotrimerisation reactions[3] and the results presented here are viewed in context. The results from the (diimine)cobalt-catalysed reactions in different nitrile solvents suggest that a coordination site is occupied by a nitrile ligand and that the steric hindrance of different nitrile solvents (MeCN, EtCN and *t*BuCN) influences the regioselectivity of the reactions. This seems to also be the case in the reactions with aromatically substituted disulfide ligands in acetonitrile with product ratios ranging from 1:15 to 1:22 as these are comparable to the bulky diimine ligands used in earlier studies. The very dramatic change in selectivity observed in dichloromethane can be interpreted as resulting from the different geometries of the active cobalt complexes. The formation of the symmetrically substituted product **1** is only possible from a complex with a 2,4-diphenyl-substituted cobaltacycle (**C**), whereas the other possible intermediates (**A** and **B**) will lead to the formation of the unsymmetrical product **2** (Figure 1).[9] We assume that the cobaltacycle intermediates contain one bidentate disulfide ligand and that the free coordination site is occupied by another phenylacetylene molecule.

By extrapolating from the collected data, it can be seen that not only the steric effects of the phenyl substituents on the disulfide ligand favour the formation of intermediate cobalt complex **C**, but that the increased electron density

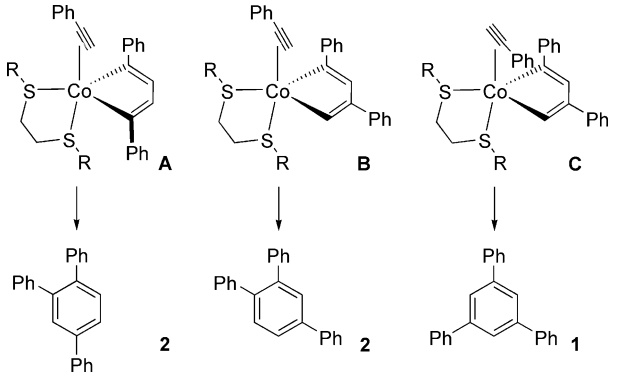


Figure 1. Cobaltacycle intermediates and cyclotrimerisation products derived therefrom.

resulting from the introduction of the methoxy substituent is also a determining factor. Computational investigations into the causal relationship of ligand and solvent incorporation will be undertaken in due course to further elucidate the drastic solvent effect on the cobalt/disulfide catalyst systems.

Further attempts to increase the selectivity by changing the counterion of the cobalt salt, the reaction temperature or the nature of the reducing agent did not result in increased reactivity or selectivity.

The application of methyl propiolate in the cyclotrimerisation reaction with the precatalyst [Co(**3b**)Br_2] in dichloromethane led to the corresponding symmetrical triester as the major product in 99% yield (1,3,5-derivative/1,2,4-derivative = 2.6:1.0). 2-Ethynylthiophene was also converted in quantitative yield into the trimer under identical conditions. However, the cyclotrimerisation product was obtained as a 1.1:1.0 mixture, showing no preference for the symmetrical benzene derivative. Lastly, trimethylsilylacetylene was trimerised with the precatalyst [Co(**3b**)Br_2] in dichloromethane and gave the trimer in quantitative yield but showed a preference for the unsymmetrical product (1.0:1.4).

Conclusions

The use of disulfide ligands in the cyclotrimerisation of phenylacetylene led to very interesting results in terms of their solvent dependency and the regioselective formation of the symmetrical product **1**, which is best achieved with ligand **3b** in dichloromethane, and unsymmetrical product **2**, obtained when the reaction was performed in acetonitrile with the same ligand **3b** as the ligand of choice. In terms of selectivity and reactivity, the disulfide ligands are at least equal to the diimine ligands investigated earlier. The reactions with the disulfide ligands are normally complete within a few minutes of applying 5 mol-% of the catalyst system consisting of [Co(**3b**)Br_2], zinc powder and zinc iodide on a 1 mmol scale.

Experimental Section

General Remarks: NMR spectra were recorded with a Bruker Avance 300 or DRX 500 (^{1}H: 300 or 500 MHz; ^{13}C: 75 or 125 MHz) spectrometer using TMS as the internal standard (δ = 0 ppm) unless otherwise noted. Mass and GC-MS spectra were measured with a Hewlett-Packard 6890 GC-System equipped with a Hewlett-Packard 5973 Mass Selective Detector. For (high-resolution) mass spectra Finnigan MAT 95S and LTQ (ESI, HRMS) spectrometers were used. Analytical thin-layer chromatography was performed on Merck silica gel 60 F254. For column chromatography Merck silica gel 60 (230–400 mesh ASTM) was used. All reactions were carried out under nitrogen or argon using standard Schlenk techniques. Dichloromethane was dried with phosphorus pentoxide, acetonitrile with CaH_2 and tetrahydrofuran with sodium/benzophenone. The analytical data of the cyclotrimerisation products **1** and **2** are identical to those in the literature.[2,3,7] The ligands **3a**, **3b**, **3d**–**k**, **3n** and **3s**–**y** were synthesised by adapting known procedures.[10] The cobalt complexes were prepared in THF, and after evaporation of the solvent the residue was used without further purification.

General Procedure for the Cobalt-Catalysed Cyclotrimerisation Reaction: Phenylacetylene (0.11 mL, 1.0 mmol) was added to a suspension of the cobalt complex (0.05 mmol, 5.0 mol-%), zinc dust (7 mg, 0.1 mmol, 10.0 mol-%) and anhydrous ZnI_2 (32 mg, 0.1 mmol, 10.0 mol-%) in anhydrous solvent (CH_2Cl_2, CH_3CN or THF) (1.0 mL) under argon, and the mixture was stirred at room temperature. The reaction was monitored by GC-MS. After complete conversion (or after 30 min) the grey reaction mixture was passed through a pad of silica using pentane/CH_2Cl_2 (10:1) as the eluent. The solvents were removed and the crude product purified by flash chromatography using pentane/CH_2Cl_2 (100:1) as eluent (for the yields, see Tables 1, 2 and 3). The ratios of regioisomers **1** and **2** formed were verified by integration of ^{1}H NMR signals.

Analytical Data for the Ligands 3c, 3l, 3m, 3o and 3p

1,2-Bis(3,4-dimethoxyphenylthio)ethane (3c): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.94–6.88 (m, 4 H), 6.78 (d, J = 8.2 Hz, 2 H), 3.87 (s, 6 H), 3.83 (s, 6 H), 2.96 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.3, 148.9, 124.9, 123.9, 115.5, 111.7, 56.1, 56.0, 35.4 ppm. MS (EI): m/z (%) = 366 (8) $[M]^+$, 338 (33), 320 (6), 181 (7), 169 (100), 154 (8), 139 (6), 125 (8). HRMS: calcd. for $C_{18}H_{22}O_4S_2$ 366.0960; found 366.0963. IR (KBr): $\tilde{\nu}$ = 1580, 1503, 1465, 1443, 1396, 1317, 1254, 1229, 1177, 1136, 1022, 796 cm^{-1}.

(4,5-Dimethoxy-1,2-phenylene)dithiobis(4-methoxybenzene) (3l): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.9 Hz, 4 H), 6.87 (d, J = 8.9 Hz, 4 H), 6.66 (s, 2 H), 3.80 (s, 6 H), 3.68 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4, 148.8, 133.6, 129.7, 126.1, 115.0, 114.8, 56.1, 55.5 ppm. MS (EI): m/z (%) = 414 (24) $[M]^+$, 386 (17), 276 (4), 244 (4), 207 (65), 179 (100), 164 (12), 149 (9), 115 (7), 91 (8), 57 (14). HRMS: calcd. for $C_{22}H_{22}O_4S_2$ 414.0960; found 414.0968. IR (KBr): $\tilde{\nu}$ = 1590, 1491, 1435, 1288, 1248, 1204, 1169, 1027, 833 cm^{-1}.

2,2′-Bis(4-methoxyphenylthio)-1,1′-biphenyl (3m): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.36 (m, 4 H), 7.23–7.19 (m, 6 H), 7.03–6.98 (m, 2 H), 6.89–6.83 (m, 4 H), 3.81 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.0, 139.4, 138.9, 136.0, 130.4, 128.5, 128.5, 125.5, 124.8, 115.1, 55.5 ppm. MS (EI): m/z (%) = 430 (2) $[M]^+$, 291 (100), 276 (18), 258 (10), 247 (7), 184 (20), 139 (5). HRMS: calcd. for $C_{26}H_{22}O_2S_2$ 430.1061; found 430.1067. IR (KBr): $\tilde{\nu}$ = 1588, 1491, 1453, 1287, 1247, 1029, 825, 746, 730 cm^{-1}.

1,2-Bis(4-*tert*-butyl-2-methylphenylthio)ethane (3o): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (s, 2 H), 7.13 (s, 4 H), 3.01 (s, 4 H),

2.37 (s, 6 H), 1.29 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.8, 138.3, 130.8, 129.7, 127.5, 123.5, 34.3, 32.9, 31.3, 20.8 ppm. MS (EI): *m/z* (%) = 386 (23) $[M]^+$, 358 (15), 343 (9), 207 (71), 179 (100), 165 (20), 131 (7). HRMS: calcd. for $C_{24}H_{34}S_2$ 386.2102; found 386.2091. IR (KBr): $\tilde{\nu}$ = 2962, 1480, 1391, 1362, 1263, 1196, 1120, 1055, 880, 834 cm^{-1}.

1,2-Bis(5-*tert*-butyl-2-methylphenylthio)ethane (3p): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (s, 2 H), 7.20–7.10 (m, 4 H), 3.07 (s, 4 H), 2.36 (s, 6 H), 1.28 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.6, 136.1, 133.7, 130.2, 127.6, 124.1, 34.6, 33.4, 31.5, 20.1 ppm. MS (EI): *m/z* (%) = 386 (23) $[M]^+$, 207 (100), 179 (75), 149 (8), 131 (6). HRMS: calcd. for $C_{24}H_{34}S_2$ 386.2102; found 386.2104. IR (KBr): $\tilde{\nu}$ = 2962, 2868, 1487, 1464, 1385, 1361, 1261, 1200, 1120, 1062, 872, 813, 716 cm^{-1}.

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