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A Highly Efficient Copper-Catalyzed Synthesis of Unsymmetrical Diaryl- and Aryl Alkyl Chalcogenides from Aryl Iodides and Diorganyl Disulfides and Diselenides

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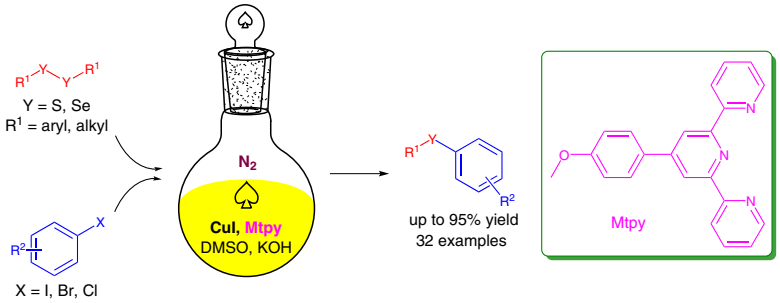

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Abstract An efficient and convenient protocol has been developed for the copper-catalyzed reaction of aryl iodides and diorganyl disulfides and diselenides. A variety of symmetrical and unsymmetrical diaryl- and aryl alkyl chalcogenides were synthesized with good functional group tolerance and chemoselectivity by using copper(I) iodide as a catalyst, 4′-(4-methoxyphenyl)-2,2′:6′,2′′-terpyridine as ligand, and KOH as base under an inert atmosphere.

Key words cross-coupling, diaryl chalcogenides, copper-catalyzed reaction, aryl halides, dichalcogenides

Among organic building blocks, organochalcogenides are one of the important subunits. They have proved to be valuable organic intermediates,[1] and are known as convenient models for studying fundamental problems in theoretical chemistry.[2] Therefore, the development of new sustainable tools for the preparation of these compounds is a hot topic. Among the compounds of this class are diaryl chalcogenides, which have attracted considerable interest because of their potential applications in the biological and pharmaceutical fields.[3] Transition-metal catalyzed cross-coupling reactions for the construction of aryl chalcogen bonds is one of the most common practices for the preparation of aryl chalcogenides.[4] Several transition metals, including copper,[5] palladium,[6] nickel,[7] and zinc,[8] have been employed to catalyze the reaction of aryl halides with thiol and selenol/PhSeNa under basic conditions for the synthesis of diaryl sulfides and selenides; although the synthesis of diaryl tellurides by using this protocol has not been very successful. However, due to the foul smell of thiols, instability of selenols, and toxicity of sodium selenolates, synthesis using stable and easily accessible diaryl dichalcogenides is preferred.[9] Recently, the cross-coupling reaction of other aryl donors such as aryl diazonium fluoroborate,[10] and aryl boronic acids[11] with diaryl dichalcogenides catalyzed by benign metals such as Cu and Zn have been reported. Symmetrical diaryl chalcogenides have also been synthesized from diaryl dichalcogenides and chalcogen sources (Na_2S, Se).[12] Very recently, a transition-metal-free synthetic method has been developed for the synthesis of unsymmetrical diaryl chalcogenides from diaryl dichalcogenides and arenes under oxidative conditions.[13] Therefore, for practical purposes, it is worthwhile to develop a general, simple, and economical catalyst system for the coupling of aryl halides with diaryl dichalcogenides.

The tridentate 2,2′:6′,2′′-terpyridines (tpys) have been of great interest over the last few years, mostly because of their ability to chelate transition metals.[14] Furthermore, they are widely used in various research fields such as medicinal chemistry,[15] organometallics,[16] photochemistry,[17] and nanoscience.[18] As part of our ongoing effort directed towards copper-catalyzed C–X (X = S, Se, Te) bond-forming reactions,[19] here we report a simple, inexpensive, and efficient catalytic system for the synthesis of symmetrical and unsymmetrical diaryl chalcogenides by using CuI as a catalyst and 4′-(4-methoxyphenyl)-2,2′:6′,2′′-terpyridine (Mtpy)[20] as a ligand.

Iodobenzene (**1a**) and diphenyl disulfide (**2a**) were used as substrates for the initial optimization of the reaction at 100 °C. The influence of the reaction parameters are summarized in Table 1. Among the screened copper(I) salts, copper(I) iodide gave the best performance using KOH as base and dimethyl sulfoxide (DMSO) as solvent (entries 1–5). Lowering the temperature from 110 to 90 °C provided the product in lower yield, whereas increasing the temperature to 115 °C had no effect on the product yield (entry 5). Only 66% yield was obtained in the absence of ligand (entry 6). In addition, different copper (5, 7, and 10 mol%) and ligand (5, 7, and 10 mol%) concentrations were investi-

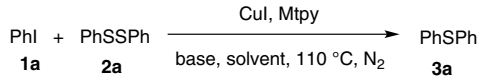
gated (entries 7–10); among them, the use of 10 mol% of each was found to be the best (entry 5). Among the tested inorganic and organic bases, KOH was found to be the most suitable base (entries 11–15). For the solvent, the use of DMSO resulted in the highest yield among the surveyed solvents (entries 16–18). The solvent-free conditions were also studied but, compared with DMSO, gave an inferior result (entry 19). Other ligands, such as 1,10-phenanthroline and 2,2'-bipyridine were also examined; however, compared with Mtpy they gave lower yields (entries 20 and 21). Therefore, the optimal reaction conditions were established as: iodobenzene (2.0 equiv), diphenyl disulfide (1.0 equiv), CuI (10 mol%), Mtpy (10 mol%), and KOH (2.0 equiv) stirred in DMSO (4 mL) at 110 °C for 15 h under a nitrogen atmosphere.[21]

To survey the generality of the catalytic protocol, we studied the reaction using various dichalcogenides (disulfides and diselenides) and aryl halides under the optimized conditions. The results are summarized in Table 2. The reactions proceeded smoothly to provide good to excellent yields of functionalized unsymmetrical sulfides and selenides. We found that this method was applicable to aromatic as well as aliphatic disulfides. Different electron-rich, electron-neutral, and electron-deficient aryl iodides underwent the cross-coupling reaction smoothly to generate the corresponding aryl sulfides.

As expected, the reaction of diaryl disulfides with aryl iodides proceeded very smoothly within 10–17 h to give the desired products in 82–95% isolated yield (Table 2, entries 1–4, 6, and 8–15). Aryl iodides bearing electron-withdrawing groups, such as acetyl, nitro or cyano group, gave the corresponding product at higher rates compared with those with the electron-donating methoxy group (entries 9, 14–15 and 6, respectively). Moreover, no significant steric effect was observed because of the presence of the methoxy group at the *ortho*-position of iodoanisole (entries 6 and 8). Reaction of dialkyl disulfides proceeded at relatively low rates compared with those of aromatic disulfides (entries 5, 7, and 16). Chemoselectivity of the procedure was also studied using 4-bromo-1-iodobenzene (entry 10). In this reaction, iodine acted as a better leaving group. We also investigated the cross-coupling of diaryl disulfides with various aryl bromides and chlorides. Under the same reaction conditions, coupling of bromobenzene with diphenyl disulfide gave a poor yield (26%) after 24 hours (entry 17); therefore, the inclusion of tetrabutylammonium bromide (TBAB, 2.0 mmol) was necessary to promote the cross-couplings of the less activated aryl bromides or chlorides with diaryl disulfides (entries 18–23).

To extend the scope of this protocol, the cross-coupling of diaryl diselenides with aryl iodides and bromides was evaluated under the optimized conditions (Table 2, entries 24–32). The results show that the corresponding products were obtained in shorter reaction times (2–7.5 h) than those of their disulfide counterparts. However, under the same reaction conditions, the addition of diphenyl ditelluride to 2-iodotoluene and 4-iodoanisole was not successful, and resulted in a mixture of several unidentified byproducts.

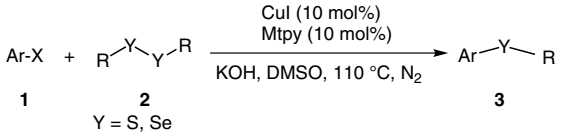
Table 1 Screening for the Optimal Conditions[a]



Entry	Catalyst (mol%)	Ligand (mol%)	Base	Solvent	Yield (%)[b]
1	CuBr (10)	Mtpy (10)	KOH	DMSO	27
2	CuCl (10)	Mtpy (10)	KOH	DMSO	15
3	$Cu(OAc)_2$ (10)	Mtpy (10)	KOH	DMSO	23
4	CuO (10)	Mtpy (10)	KOH	DMSO	trace
5	CuI (10)	Mtpy (10)	KOH	DMSO	94, 86[c], 94[d]
6	CuI (10)	–	KOH	DMSO	66
7	CuI (10)	Mtpy (5)	KOH	DMSO	79
8	CuI (7)	Mtpy (7)	KOH	DMSO	78
9	CuI (5)	Mtpy (5)	KOH	DMSO	71
10	CuI (5)	Mtpy (10)	KOH	DMSO	73
11	CuI (10)	Mtpy (10)	NaOH	DMSO	81
12	CuI (10)	Mtpy (10)	K_3PO_4	DMSO	86
13	CuI (10)	Mtpy (10)	K_2CO_3	DMSO	53
14	CuI (10)	Mtpy (10)	Cs_2CO_3	DMSO	70
15	CuI (10)	Mtpy (10)	Et_3N	DMSO	trace
16	CuI (10)	Mtpy (10)	KOH	DMF	90
17	CuI (10)	Mtpy (10)	KOH	EtOH	N.R.
18	CuI (10)	Mtpy (10)	KOH	toluene	31
19	CuI (10)	Mtpy (10)	KOH	–	N.R.
20	CuI (10)	1,10-phenanthroline (10)	KOH	DMSO	83
21	CuI (10)	2,2′-bipyridine (10)	KOH	DMSO	72

[a] Reaction conditions: iodobenzene (2.0 mmol), diphenyl disulfide (1.0 mmol), base (2.0 mmol), solvent (4 mL) at 110 °C, 15 h under nitrogen.
[b] Isolated yield.
[c] Reaction was performed at 90 °C.
[d] Reaction was performed at 115 °C.

Table 2 Copper-Catalyzed Cross-Coupling of Aryl Halides and Diorgano Dichalcogenides[a]



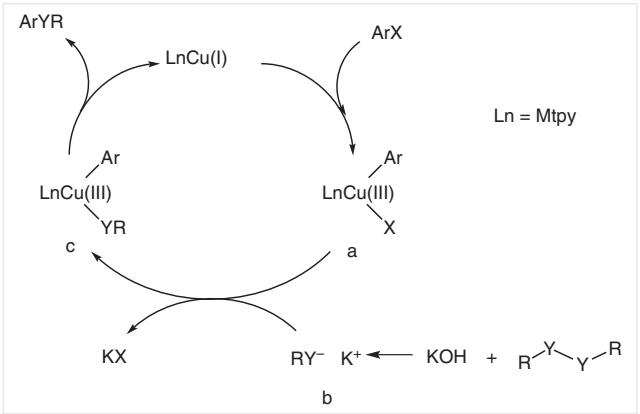
1 2 3

Y = S, Se

Entry	Ar-X	R	Y	Time (h)	Yield (%)[b]	Ref.[d]
1	PhI	Ph	S	15	94	9a
2	PhI	4-MeC_6H_4	S	15	91	9a
3	PhI	4-MeOC_6H_4	S	15	93	9a
4	PhI	2-naphthyl	S	17	88	9a
5	PhI	$PhCH_2$	S	16	82	24a
6	4-MeOC_6H_4I	Ph	S	16	84	9a
7	4-MeOC_6H_4I	*n*-Oct	S	18	75	24b
8	2-MeOC_6H_4I	Ph	S	16	82	9a
9	4-MeCOC_6H_4I	Ph	S	11.5	94	24a
10	4-BrC_6H_4I	Ph	S	13	90	9a
11	4-MeC_6H_4I	4-MeC_6H_4	S	15	89	9a
12	4-MeC_6H_4I	4-ClC_6H_4	S	16	86	9a
13	4-MeC_6H_4I	2-naphthyl	S	17	87	24c
14	4-O_2NC_6H_4I	Ph	S	10	95	9a
15	4-NC_6H_4I	Ph	S	10	93	9a
16	2-iodothiophenyl	*n*-Bu	S	19	79	24d
17	PhBr	Ph	S	24	26	9a
18	PhBr	Ph	S	24	43[c]	9a
19	4-MeC_6H_4Br	Ph	S	26	39[c]	9a
20	4-BrC_6H_4CN	Ph	S	20	46[c]	9a
21	4-MeCOC_6H_4Br	Ph	S	21	49[c]	24a
22	PhCl	Ph	S	30	26[c]	9a
23	4-MeCOC_6H_4Cl	Ph	S	27	32[c]	24a
24	PhI	Ph	Se	3.5	91	11a
25	PhI	4-ClC_6H_4	Se	4.5	87	11a
26	4-MeC_6H_4I	Ph	Se	4	88	11a
27	4-MeOC_6H_4I	Ph	Se	5	84	11a
28	2-MeOC_6H_4I	Ph	Se	6	82	24e
29	4-MeCOC_6H_4I	Ph	Se	2.5	93	11a
30	4-O_2NC_6H_4I	Ph	Se	2	94	9f
31	PhBr	Ph	Se	7.5	48[c]	11a
32	4-MeCOC_6H_4Br	Ph	Se	6	56[c]	11a

[a] Reaction conditions: aryl halide (2.0 mmol), dichalcogenide (1.0 mmol), KOH (2.0 mmol), CuI (10 mol%), Mtpy (10 mol%), DMSO (4 mL) at 110 °C under nitrogen.
[b] Isolated yield.
[c] TBAB (2.0 mmol) was added.
[d] References for the known compounds.

On the basis of these observations and by reference to the literature,[22,23] we propose that the reaction mechanism is as follows. Oxidative addition of the aryl halide with the catalyst may provide intermediate **a**. The thiolate/selenolate anion **b**, produced from the corresponding dichalcogenide, then replaces the counter anion to provide intermediate **c**. Finally, this intermediate easily generates the desired cross-coupled product by reductive elimination (Scheme 1). According to the mechanism, the role of the Mtpy ligand in the reaction is either to promote the oxidative addition of ArX to the Cu(I) species or to stabilize the Cu(III) intermediate.[23]



Scheme 1 Possible mechanism for cross-coupling reactions of aryl halides and diorgano dichalcogenides

In conclusion, we have developed a general and efficient copper-catalyzed procedure for the synthesis of symmetrical and unsymmetrical sulfides or selenides from aryl iodides and diorganyl disulfides or diselenides using KOH as base and terpyridine Mtpy as ligand. A variety of functional groups are compatible with these reaction conditions. This new protocol should be added as a straightforward approach to preparing a variety of diaryl and alkyl aryl chalcogenide compounds.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561268.

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(21) **General procedure for the preparation of diorgano chalcogenides:** A flame-dried test tube containing a magnetic stirring bar was charged with diorgano dichalcogenide (0.5 mmol), aryl halide (1.0 mmol), KOH (1.0 mmol), and anhydrous DMSO (2 mL) [for aryl bromides or chlorides, TBAB (1.0 mmol) was also added]. Then, CuI (10 mol%) and Mtpy (10 mol%) were added to the above mixture, and the reaction mixture was heated at 110 °C under nitrogen. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to r.t., poured into H_2O (10 mL), and extracted with EtOAc (3 × 8 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo to give the crude product, which was further purified by preparative TLC (silica gel; *n*-hexane–EtOAc, 9:1). The identities of the products were confirmed by IR, ^1H and ^{13}C NMR spectroscopic analysis.

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Di-*p*-tolyl Sulfide

White solid; mp 55–57 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.4 Hz, 4 H), 7.16 (d, *J* = 8.4 Hz, 4 H), 2.38 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.9, 132.7, 131.1, 130.0, 21.1.

4-Methoxyphenyl Phenyl Sulfide

Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49 (dt, *J* = 6.9, 1.8 Hz, 2 H), 7.19–7.29 (m, 5 H), 6.96 (dt, *J* = 6.9, 1.8 Hz, 2 H), 3.85 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.8, 138.6, 135.3, 128.9, 128.2, 125.7, 124.3, 115.0, 55.3.

Naphthalen-2-yl *p*-Tolyl Sulfide

White solid; mp 69–71 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.86 (m, 4 H), 7.41–7.52 (m, 5 H), 7.21 (d, *J* = 9.0 Hz, 2 H), 2.42

(s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 137.6, 134.3, 133.7, 132.1, 132.0, 131.4, 130.1, 128.7, 128.3, 127.9, 127.7, 127.3, 126.5, 125.9, 21.1.

4-Methoxyphenyl Octyl Sulfide

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (dt, *J* = 9.9, 2.1 Hz, 2 H), 6.85 (dt, *J* = 9.9, 2.1 Hz, 2 H), 3.80 (s, 3 H), 2.82 (t, *J* = 6 Hz, 3 H), 1.54–1.63 (m, 2 H), 1.27–1.41 (m, 12 H), 0.88 (t, *J* = 6 Hz, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 158.6, 132.8, 126.9, 114.4, 55.2, 35.7, 31.7, 29.3, 29.14, 29.11, 28.6, 22.6, 14.0.

1-[4-(Phenylthio)phenyl]ethanone

Yellow solid; mp 62–64 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.4 Hz, 2 H), 7.48–7.50 (m, 2 H), 7.39–7.41 (m, 3 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 2.55 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 197.1, 144.9, 134.4, 133.9, 132.0, 129.7, 128.9, 128.8, 127.4, 26.5.

4-Cyanophenyl Phenyl Sulfide

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.64 (m, 4 H), 7.50–7.26 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 141.1, 139.5, 133.4, 129.7, 128.7, 127.2, 127.1, 118.0, 110.8.

4-Chlorophenyl *p*-Tolyl Sulfide

White solid; mp 69–70 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.2 Hz, 2 H), 7.17–7.24 (m, 6 H), 2.35 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.0, 136.0, 132.5, 132.3, 130.8, 130.7, 130.2, 129.1, 21.2.

2-(Butylthio)thiophene

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.29 (m, 3 H), 2.82 (t, *J* = 6.0 Hz, 2 H), 1.27–1.34 (m, 4 H), 0.84–0.91 (m, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 139.9, 132.9, 129.5, 127.8, 53.3, 34.2, 22.4, 13.9.

Diphenyl Sulfide

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.0 Hz, 4 H), 7.35 (t, *J* = 8.0 Hz, 4 H), 7.30 (t, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 135.9, 131.1, 129.3, 127.1.

Naphthalen-2-yl Phenyl Sulfide

White solid; mp 63–65 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (s, 1 H), 7.77–7.83 (m, 3 H), 7.43–7.53 (m, 5 H), 7.27–7.37 (m, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 135.9, 133.8, 133.0, 132.3, 131.0, 129.9, 129.3, 128.9, 128.8, 127.8, 127.4, 127.1, 126.6, 126.2.

Benzyl Phenyl Sulfide

White solid; mp 53–55 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.40 (m, 10 H), 4.18 (s, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 137.5, 136.4, 129.8, 128.9, 128.5, 127.2, 126.3, 36.0.

4-Bromophenyl Phenyl Sulfide

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (dt, *J* = 6.0, 2.7 Hz, 1 H), 7.24–7.44 (m, 6 H), 7.19 (dt, *J* = 6.0, 2.7 Hz, 1 H), 7.05 (dt, *J* = 6.0, 2.7 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 135.4, 134.7, 133.0, 131.9, 131.7, 129.3, 127.6, 120.8.

Phenyl *o*-Tolyl Sulfide

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.54 (m, 5 H), 7.26 (d, *J* = 8.0 Hz, 3 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 2.43 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 140.0, 136.2, 133.8, 133.1, 131.1, 130.7, 129.7, 129.3, 126.8, 126.4, 20.7.

4-Methylphenyl Phenyl Sulfide

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.43 (m, 5 H), 7.20–7.32 (m, 4 H), 2.42 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 137.61, 137.2, 132.3, 131.3, 130.1, 129.8, 129.0, 126.4, 21.1.

4-Methoxyphenyl Phenyl Selenide

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 6.9, 2.1 Hz, 2 H), 7.39 (dd, *J* = 7.38, 1.4 Hz, 2 H), 7.21–7.29 (m, 3 H), 6.90 (dd, *J* = 6.9, 2.1 Hz, 2 H), 3.84 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.8, 136.6, 133.2, 130.9, 129.2, 126.4, 119.9, 115.1, 55.3.

2-Methoxyphenyl Phenyl Selenide

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27–7.70 (m, 5 H), 7.08–7.10 (m, 1 H), 6.88–6.95 (m, 3 H), 3.95 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.1, 135.9, 131.3, 130.0, 128.8, 128.6, 128.3, 122.4, 122.1, 110.9, 56.4.

4-Methylphenyl Phenyl Selenide

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 7.6 Hz, 4 H), 7.36 (d, *J* = 6.4 Hz, 3 H), 7.23 (d, *J* = 7.6 Hz, 2 H), 2.46 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.2, 134.5, 134.4, 132.5, 132.6, 130.7, 129.8, 127.4, 21.7.

4-Chlorophenyl Phenyl Selenide

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55–7.79 (m, 4 H), 7.17–7.37 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 134.8, 134.6, 134.0, 133.7, 131.2, 130.0, 129.9, 128.1..