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Nickel-Catalyzed Cross-Coupling Reactions of Alkyl Aryl Sulfides and Alkenyl Alkyl Sulfides with Alkyl Grignard Reagents by Using (*Z*)-3,3-Dimethyl-1,2-bis(diphenylphosphino)-1-butene as Ligand

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Abstract: A combination of nickel(II) acetylacetonate and (*Z*)-3,3-dimethyl-1,2-bis(diphenylphosphino)-1-butene catalyzes cross-coupling reactions of alkyl aryl sulfides and alkenyl alkyl sulfides with alkyl Grignard reagents. Not only primary alkyl Grignard reagents but also secondary ones can be employed.

Key words: Cross-coupling, Nickel, Sulfur, Ligands, Magnesium

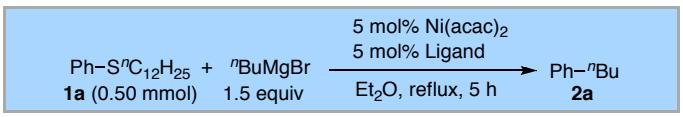
Transition-metal-catalyzed cross-coupling reactions are extremely useful in organic synthesis. Among them, the reactions of organosulfur compounds with organometallic reagents will be promising because of the ready availability of organosulfur compounds. However, such reactions have not been well established[1] compared to those of organic halides. The strong carbon–sulfur and metal–sulfur bonds retarded the oxidative addition and transmetalation, respectively. Organosulfur compounds can thus deteriorate transition metal catalysts. Hence, development of new procedures for the cross-coupling reactions of organosulfur compounds with organometallic reagents has been awaited.

Although there are several reports on the cross-coupling reactions of sulfides with Grignard reagents,[1a,2] the use of secondary alkyl Grignard reagents always resulted in very low yields[1a] because of the possible *β*-hydride elimination from *sec*-alkylmetal intermediates. Here we report a new catalyst that realizes the cross-coupling reaction with secondary alkyl Grignard reagents as well as primary ones.

We chose the nickel-catalyzed cross-coupling reaction of dodecyl phenyl sulfide (**1a**) with butylmagnesium bromide as a model reaction. As reported previously,[1a] monodentate triphenylphosphine was not a good ligand (Table 1, entry 1). Bidentate ligands such as 1,2-bis(diphenylphosphino)ethane and 1,2-bis(diphenylphosphino)benzene improved the yield (entries 2 and 3). Interestingly, *tert*-butyl-substituted (*Z*)-1,2-bis(diphenylphosphino)ethene **3a**[3] that we recently developed proved to be the best ligand among we tested (entry 4). Cyclohexyl- and phenyl-substituted **3b** and **3c** were inferior to **3a** (entries 5 and 6).

With effective **3a** in hand, various combinations of aryl dodecyl sulfides and alkyl Grignard reagents were subjected to the nickel-catalyzed reaction (Table 2). The reactions with butylmagnesium bromide proceeded smoothly (entries 1–6). In the reactions of aryl sulfides having an electron-donating group (entries 4–6), the more bulky and less volatile ethereal solvents, diisopropyl ether (b.p. 69 ˚C) or cyclopentyl methyl ether (b.p. 106 ˚C), enhanced the efficiency of the reaction. It is worth noting that cyclohexylmagnesium bromide, a secondary alkyl Grignard reagent, participated in the cross-coupling reaction (entries 8–14). Cyclopentyl methyl ether is the choice of the solvent in the cyclohexylation reaction. A substituent at the *ortho* position of **1b** and **1f** retarded the cyclohexylation reaction (entries 9 and 13). The reactions of aryl sulfides **1h, 1e,** and **1g** with isopropylmagnesium bromide under the nickel catalysis provided the desired products **2p**–**2r**, along with small amounts of the corresponding *n*-propylated products **2p'**–**2r'** (entries 15–17). The formation of **2p'**–**2r'** would result from isomerization of isopropylmetal to *n*-propylmetal through the *β*-hydride elimination from isopropylnickel followed by *anti*-Markovnikov hydronickelation to propene. Unfortunately, *tert*-butylbenzene (**2s**) was not obtained in the reaction with *tert*-butylmagnesium bromide (entry 18).

Table 1 Ligand Screening



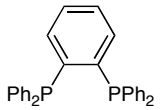
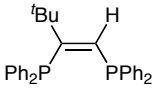
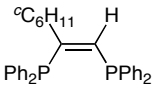
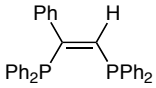
Entry	Ligand	Yield /%	**1a** Recovery /%
1	PPh_3 (10 mol%)	24	6
2	DPPE	79	0
3		75	9
4	 **3a**	88	0
5	 **3b**	82	0
6	 **3c**	51	28

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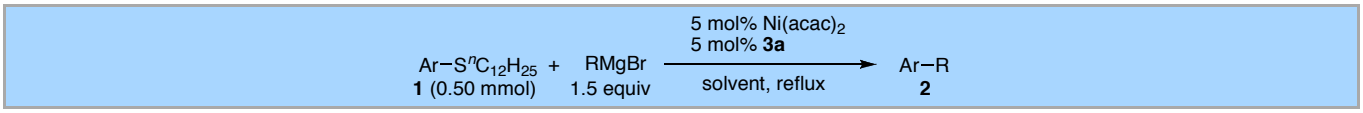
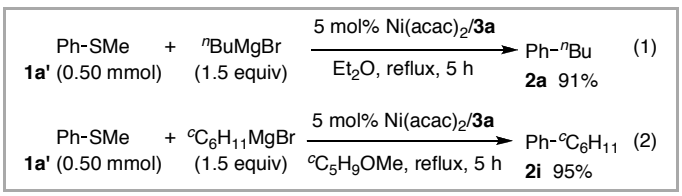
Table 2 Nickel-Catalyzed Reactions of Aryl Dodecyl Sulfides with Alkyl Grignard Reagents by Using **3a** as Ligand



Entry	Ar	1	R	Solvent	Time /h	2	Yield /%
1	2-MeC_6H_4	**1b**	^{n}Bu	Et_2O	5	**2b**	95
2	3-$CF_3C_6H_4$	**1c**	^{n}Bu	Et_2O	5	**2c**	70
3	2-pyridyl	**1d**	^{n}Bu	Et_2O	5	**2d**	70
4	4-MeOC_6H_4	**1e**	^{n}Bu	^{i}Pr$_2$O	5	**2e**	93
5	2-MeOC_6H_4	**1f**	^{n}Bu	^{i}Pr$_2$O	5	**2f**	90
6	4-$Me_2NC_6H_4$	**1g**	^{n}Bu	^{c}C$_5$H$_9$OMe	12	**2g**	82
7	Ph	**1a**	Ph(CH_2)$_3$	Et_2O	5	**2h**	95
8	Ph	**1a**	^{c}C$_6$H$_{11}$	^{c}C$_5$H$_9$OMe	5	**2i**	97
9	2-MeC_6H_4	**1b**	^{c}C$_6$H$_{11}$	^{c}C$_5$H$_9$OMe	5	**2j**	65
10	3-$CF_3C_6H_4$	**1c**	^{c}C$_6$H$_{11}$	^{c}C$_5$H$_9$OMe	5	**2k**	86
11	2-pyridyl	**1d**	^{c}C$_6$H$_{11}$	^{c}C$_5$H$_9$OMe	5	**2l**	95
12	4-MeOC_6H_4	**1e**	^{c}C$_6$H$_{11}$	^{c}C$_5$H$_9$OMe	12	**2m**	87(93[a])
13	2-MeOC_6H_4	**1f**	^{c}C$_6$H$_{11}$	^{c}C$_5$H$_9$OMe	12	**2n**	29
14	4-$Me_2NC_6H_4$	**1g**	^{c}C$_6$H$_{11}$	^{c}C$_5$H$_9$OMe	5	**2o**	60
15	4-^{i}PrC$_6$H$_4$	**1h**	^{i}Pr	^{c}C$_5$H$_9$OMe	13	**2p**	89[b]
16	4-MeOC_6H_4	**1e**	^{i}Pr	^{c}C$_5$H$_9$OMe	12	**2q**	80[c]
17	4-$Me_2NC_6H_4$	**1g**	^{i}Pr	^{c}C$_5$H$_9$OMe	13	**2r**	90[d]
18	Ph	**1a**	^{t}Bu	Et_2O	5	**2s**	0

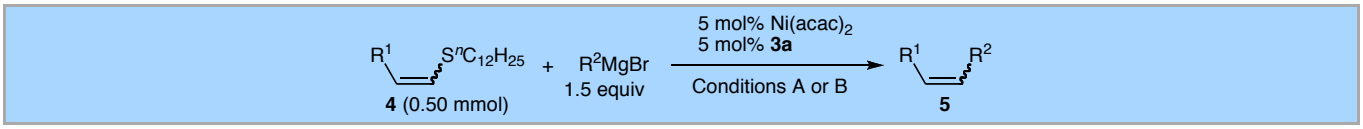
[a] Performed in a 5-mmol scale. [b] An 88:12 mixture of isopropylated **2p** and 1-propyl-4-isopropylbenzene (**2p'**). [c] A 77:23 mixture of isopropylated **2q** and 4-propylanisole (**2q'**). [d] A 77:23 mixture of isopropylated **2r** and *N,N*-dimethyl-4-propylaniline (**2r'**).

We chose dodecylthio group as the leaving group because 1-dodecanethiol is odorless.[4,5] In addition, 1-dodecanethiol is involatile enough to recover 1-dodecanethiol quantitatively after the cross-coupling reaction (See experimental section). On the other hand, cheap and commercially available methyl phenyl sulfide (**1a'**) reacted under the reaction conditions (eqs 1 and 2).



The reactions of 1-alkenyl dodecyl sulfides proceeded smoothly as well (Table 3). In most cases, the reaction proceeded with retention of configuration. In the reactions of (*Z*)-**4b** (entries 3, 7, and 11), significant amounts of the corresponding *E* products were formed. The loss of the stereospecificity was due to the isomerization of initially formed the *Z* products into the *E* products under the reaction conditions, which we confirmed. In contrast to the reactions of aryl sulfides with isopropylmagnesium bromide (Table 2, entries 15–17), formation of *n*-propyl-substituted alkenes were not observed (Table 3, entries 9–12). Unfortunately, the yield of (*Z*)-**5f** was low, and 1-octene was mainly obtained (entry 11). The reactions of α-dodecylthiostyrene (**6**) were inefficient, providing the corresponding coupling products **7** in moderate yields (eqs 3 and 4).

Table 3 Nickel-Catalyzed Reactions of 1-Alkenyl Dodecyl Sulfides with Alkyl Grignard Reagents by Using **3a** as Ligand



Entry	R^1	4	R^2	Conditions[a]	5	Yield /%
1	Ph	(*Z*)-**4a** (*E*/*Z* = 4:96)	^{n}Bu	A	(*Z*)-**5a** (*E*/*Z* = 8:92)	75
2	Ph	(*E*)-**4a** (*E*/*Z* = 90:10)	^{n}Bu	A	(*E*)-**5a** (*E*/*Z* = 91:9)	70
3	^{n}C$_6$H$_{13}$	(*Z*)-**4b** (*E*/*Z* = 9:91)	^{n}Bu	B[b]	(*Z*)-**5b** (*E*/*Z* = 27:73)	78
4	^{n}C$_6$H$_{13}$	(*E*)-**4b** (*E*/*Z* > 99:1)	^{n}Bu	A	(*E*)-**5b** (*E*/*Z* > 99:1)	74
5	Ph	(*Z*)-**4a** (*E*/*Z* = 4:96)	^{c}C$_6$H$_{11}$	B	(*Z*)-**5c** (*E*/*Z* = 8:92)	93
6	Ph	(*E*)-**4a** (*E*/*Z* = 90:10)	^{c}C$_6$H$_{11}$	B	(*E*)-**5c** (*E*/*Z* > 99:1)	70
7	^{n}C$_6$H$_{13}$	(*Z*)-**4b** (*E*/*Z* = 9:91)	^{c}C$_6$H$_{11}$	B	(*Z*)-**5d** (*E*/*Z* = 11:89)	84
8	^{n}C$_6$H$_{13}$	(*E*)-**4b** (*E*/*Z* > 99:1)	^{c}C$_6$H$_{11}$	B	(*E*)-**5d** (*E*/*Z* = 94:6)	95
9	Ph	(*Z*)-**4a** (*E*/*Z* = 4:96)	^{i}Pr	B	(*Z*)-**5e** (*E*/*Z* = 8:92)	72
10	Ph	(*E*)-**4a** (*E*/*Z* = 90:10)	^{i}Pr	B	(*E*)-**5e** (*E*/*Z* > 99:1)	72
11	^{n}C$_6$H$_{13}$	(*Z*)-**4b** (*E*/*Z* = 9:91)	^{i}Pr	B	(*Z*)-**5f** (*E*/*Z* = 36:64)	37
12	^{n}C$_6$H$_{13}$	(*E*)-**4b** (*E*/*Z* > 99:1)	^{i}Pr	B	(*E*)-**5f** (*E*/*Z* = 95:5)	80

[a] Conditions A: diethyl ether, reflux, 5 h. Conditions B: cyclopentyl methyl ether, reflux, 12 h. [b] Performed for 13 h.

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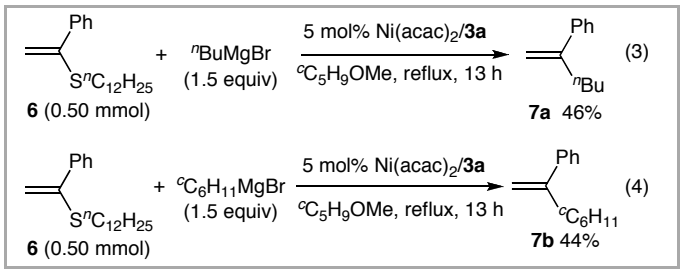

In summary, we have developed a new protocol for the nickel-catalyzed cross-coupling reaction of organic sulfides with Grignard reagents. The protocol allows for the use of secondary alkyl Grignard reagents as well as primary ones as efficient alkylating agents. Ligand **3a** serves as a useful ligand in the present reactions.

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL MStation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography unless otherwise noted. Gel permeation chromatography was performed by using LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, toluene, 3.8 mL/min, UV and RI detectors). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. Diethyl ether was purchased from Kanto Chemical and stored under argon. Cyclopentyl methyl ether was obtained from ZEON or purchased from Wako Pure Chemical. Nickel(II) acetylacetonate was purchased from Wako Pure Chemical. Ligand **3** was prepared according to the literature.[3] Sulfides **1** and **4** were prepared according to the procedures shown below, except for (*Z*)-**4a**.[5b]

Preparation of Didodecyl Disulfide: THF (15 mL), 1-dodecanethiol (2.0 g, 10 mmol), and triethylamine (1.1 g, 11 mmol) were placed in a 50-mL reaction flask under argon. Iodine (2.8 g, 11 mmol) was then added to the solution at 0 °C. After being stirred at 25 °C for 6 h, the mixture was poured into a 1 M sodium thiosulfate solution (20 mL). The product was extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford didodecyl disulfide (2.0 g, 5.0 mmol) in 100% yield.

Typical Procedure for the Preparation of Aryl Dodecyl Sulfides: The preparation of **1e** is representative. Didodecyl disulfide (2.0 g, 5.0 mmol) and THF (10 mL) were placed in a 50-mL reaction flask under argon. 4-Methoxyphenylmagnesium bromide (1.1 M THF solution, 6.8 mL, 7.5 mmol) was then added to the reaction mixture at 25 °C. After being stirred at 25 °C for 10 h, the mixture was poured into water (10 mL). The product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate. After concentration in vacuo, the resulting residue was purified on silica gel to afford **1e** (1.5 g, 5.0 mmol) in 100% yield. 1-Dodecanethiol (1.0 g, 5.0 mmol, 100% yield) was recovered, and was used for the synthesis of didodecyl disulfide.

Typical Procedure for the Preparation of 1-Alkenyl Dodecyl Sulfide: The preparation of (*E*)-**4a** is representative. *β*-Bromostyrene (0.55 g, 3.0 mmol, *E*/*Z* > 99:1) and diethyl ether (6.0 mL) were placed in a 30-mL reaction flask under argon. *t*-Butyllithium (1.6 M pentane solution, 3.8 mL, 6.0 mmol) was then added to the reaction mixture at −78 °C. After the mixture was stirred at −78 °C for 30 min, didodecyl disulfide (1.1 g, 2.7 mmol) was added. After the mixture was stirred at 5 h, the dry ice-acetone bath was removed. After being stirred for 1 h at room temperature, the mixture was poured into water (10 mL). The product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate. After evaporation, the resulting residue was purified by silica gel column chromatography and gel permeation chromatography to afford (*E*)-**4a** (0.82 g, 2.7 mmol, *E*/*Z* = 90:10) in 100% yield.

Typical Procedure for the Cross-Coupling Reactions: The reaction of **1b** with butylmagnesium bromide is representative. Nickel(Ⅱ) acetylacetonate (6.4 mg, 0.025 mmol) and ligand **3a** (0.011 g, 0.025 mmol) were placed in a 20-mL reaction flask. Anhydrous diethyl ether (3.0 mL) and substrate **1b** (0.15 g, 0.50 mmol) were added under argon. Butylmagnesium bromide (1.0 M diethyl ether solution, 0.75 mL, 0.75 mmol) was then added to the reaction mixture at ambient temperature. After being stirred at reflux for 5 h, the mixture was poured into a saturated ammonium chloride solution (10 mL). The product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate. Concentration followed by silica gel column purification afforded **2b** (0.070 g, 0.48 mmol) in 95% yield.

Cross-Coupling Reaction of 1e with Cyclohexylmagnesium Bromide Performed in a 5-mmol Scale (Table 2, entry 12): Nickel(Ⅱ) acetylacetonate (0.064 g, 0.25 mmol), ligand **3a** (0.11 g, 0.25 mmol), and substrate **1e** (1.5 g, 5.0 mmol) were dissolved in cyclopentyl methyl ether (30 mL) in a 100-mL reaction flask under argon. Cyclohexylmagnesium bromide (1.0 M diethyl ether solution, 7.5 mL, 7.5 mmol) was then added to the reaction mixture. After being stirred at reflux for 5 h, the mixture was poured into a saturated ammonium chloride solution (20 mL). The product was extracted with ethyl acetate (20 mL × 3) and the combined organic layer was dried over anhydrous sodium sulfate. After evaporation, the resulting residue was purified by silica gel column chromatography to afford **2m** (0.88 g, 4.7 mmol) in 93% yield. 1-Dodecanethiol (0.93 g, 4.6 mmol) was recovered in 92% yield.

Characterization Data

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Compounds **1a**,[6] **1e**,[7] **1g**,[8] **2a**,[9] **2b**,[10] **2d**,[11] **2e**,[10] **2f**,[12] **2g**,[10] **2i**,[13] **2j**,[14] **2k**,[15] **2l**,[16] **2m**,[17] **2o**,[18] **2q**,[19] (*Z*)-**4a**,[5b] (*Z*)-**5a**,[20] (*E*)-**5a**,[21] (*Z*)-**5b**,[22] (*E*)-**5b**,[23] (*Z*)-**5c**,[24] (*E*)-**5c**,[22] (*E*)-**5d**,[25] (*Z*)-**5e**,[26] (*E*)-**5e**,[27] (*E*)-**5f**,[28] **7a**,[29] and **7b**[30] showed the identical spectra reported in the literature. Products **2h** and **2p** are identical to commercially available reagents.

Dodecyl 2-Methylphenyl Sulfide (**1b**) : Colorless oil. IR (neat) 2924, 2854, 1590, 1456, 1379, 1066, 1048, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.20–1.34 (m, 16H), 1.40–1.46 (m, 2H), 1.66 (tt, *J* = 7.0, 7.0 Hz, 2H), 2.36 (s, 3H), 2.89 (t, *J* = 7.0 Hz, 2H), 7.07 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.13–7.17 (m, 2H), 7.25 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.11, 20.31, 22.68, 28.96, 28.98, 29.19, 29.34, 29.50, 29.57, 29.62, 29.64, 31.91, 32.76, 125.19, 126.28, 127.21, 129.96, 136.41, 137.12. Found: C, 78.26; H, 10.78%. Calcd for $C_{19}H_{32}S$: C, 78.01; H, 11.03%.

Dodecyl 3-trifluoromethylphenyl sulfide (**1c**) : Brown oil. IR (neat) 2928, 2855, 1583, 1468, 1423, 1323, 1168, 1130, 1074, 791, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.20–1.34 (m, 16H), 1.39–1.46 (m, 2H), 1.66 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 7.36–7.41 (m, 2H), 7.43–7.47 (m, 1H), 7.50–7.54 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.10, 22.69, 28.79, 28.82, 29.12, 29.35, 29.47, 29.56, 29.62, 29.64, 31.91, 33.10, 122.04 (q, *J* = 3.9 Hz), 123.87 (q, *J* = 271.0 Hz), 124.61 (q, *J* = 3.9 Hz), 129.06, 131.21 (q, *J* = 32.5 Hz), 131.23, 138.91. Found: C, 66.08; H, 8.67%. Calcd for $C_{19}H_{29}F_3S$: C, 65.86; H, 8.44%.

Dodecyl 2-pyridyl sulfide (**1d**) : Colorless oil. IR (neat) 3045, 2924, 2854, 2360, 1580, 1557, 1456, 1125, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.20–1.36 (m, 16H), 1.41–1.47 (m, 2H), 1.70 (tt, *J* = 7.5, 7.5 Hz, 2H), 3.15 (t, *J* = 7.5 Hz, 2H), 6.95 (dd, *J* = 5.0, 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 5.0, 5.0 Hz, 1H), 8.42 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.11, 22.68, 28.96, 29.20, 29.30, 29.33, 29.51, 29.59, 29.62, 29.64, 30.12, 31.90, 119.12, 122.10, 135.75, 149.41, 159.63. Found: C, 73.31; H, 10.44%. Calcd for $C_{17}H_{29}NS$: C, 73.06; H, 10.46%.

Dodecyl 2-methoxyphenyl sulfide (**1f**) : White solid. IR (neat) 2853, 1734, 1700, 1569, 1429, 1242, 1072, 1022, 712 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.20–1.34 (m, 16H), 1.40–1.48 (m, 2H), 1.66 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.88 (t, *J* = 7.5 Hz, 2H), 3.89 (s, 3H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.93 (dd, *J* = 8.5, 8.5 Hz, 1H), 7.17 (dd, *J* = 8.5, 8.5 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.11, 22.68, 28.88, 28.96, 29.20, 29.33, 29.49, 29.57, 29.61, 29.63, 31.83, 31.90, 55.73, 110.27, 120.99, 125.26, 126.53, 128.54, 156.97. Found: C, 73.85; H, 10.59%. Calcd for $C_{19}H_{32}OS$: C, 73.97; H, 10.45%. Mp 30.5–31.0 °C.

Dodecyl 4-isopropylphenyl sulfide (**1h**) : Colorless oil. IR (neat) 2959, 2925, 2854, 1497, 1460, 1093, 817 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.20–1.32 (m, 22H), 1.36–1.44 (m, 2H), 1.63 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.87 (sep, *J* = 7.0 Hz, 1H), 2.88 (t, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.10, 22.68, 28.92, 28.82, 29.16, 29.27, 29.33, 29.51, 29.57, 29.62, 29.64, 31.91, 33.66, 34.19, 126.95, 129.54, 133.62, 146.74.

3-Butyl-1-trifluoromethylbenzene (**2c**) : Colorless oil. IR (neat) 2933, 2862, 2360, 1448, 1326, 1164, 1127, 1074, 799 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, *J* = 7.5 Hz, 3H), 1.37 (qt, *J* = 7.5, 7.5 Hz, 2H), 1.62 (tt, *J* = 7.5, 8.0 Hz, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 7.34–7.41 (m, 2H), 7.42–7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.88, 22.29, 33.43, 35.47, 122.47 (q, *J* = 3.8 Hz), 124.32 (q, *J* = 270.6 Hz), 125.06 (q, *J* = 3.8 Hz), 128.59, 130.51 (q, *J* = 31.9 Hz), 131.80, 143.72.

***N*,*N*-Dimethyl-4-isopropylaniline** (**2r**) : Brown oil. IR (neat) 2958, 2870, 2799, 1616, 1521, 1340, 1219, 1166, 948, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (d, *J* = 7.0 Hz, 6H), 2.84 (sep, *J* = 6.5 Hz, 1H), 2.92 (s, 6H), 6.73 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 24.21, 33.02, 40.94, 112.98, 126.91, 128.99, 137.20.

Dodecyl (*E*)-2-phenylethenyl sulfide ((*E*)-4a) : Colorless oil. IR (neat) 2923, 2853, 2360, 1599, 1468, 1315, 1125, 933, 734, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 5.0 Hz, 3H), 1.20–1.36 (m, 16H), 1.38–1.46 (m, 2H), 1.69 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.80 (t, *J* = 7.5 Hz, 2H), 6.46 (d, *J* = 15.5 Hz, 1H), 6.73 (d, *J* = 15.5 Hz, 1H), 7.16–7.22 (m, 1H), 7.27–7.31 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.11, 22.68, 28.81, 29.18, 29.33, 29.43, 29.50, 29.58, 29.62, 29.64, 31.90, 32.61, 125.35, 125.42, 126.61, 126.73, 128.60, 137.16. Found: C, 78.69; H, 10.53%. Calcd for $C_{20}H_{32}S$: C, 78.88; H, 10.59%.

Dodecyl (*Z*)-1-octenyl sulfide ((*Z*)-**4b**) : Brown oil. IR (neat) 2925, 2854, 2360, 1609, 1467, 1267, 938, 721, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.0 Hz, 6H), 1.20–1.42 (m, 26H), 1.61 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.11 (dt, *J* = 7.5, 7.5 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 5.54 (dt, *J* = 9.5, 7.0 Hz, 1H), 5.89 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.08, 14.10, 22.62, 22.68, 28.61, 28.93, 28.96, 29.15, 29.20, 29.34, 29.51, 29.59, 29.62, 29.64, 30.33, 31.71, 31.91, 33.90, 124.93, 129.56. Found: C, 76.97; H, 13.08%. Calcd for $C_{20}H_{40}S$: C, 76.85; H, 12.90%.

Dodecyl (*E*)-1-octenyl sulfide ((*E*)-**4b**) : Brown oil. IR (neat) 2925, 2854, 1734, 1653, 1558, 1457, 938 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 6H), 1.20–1.42 (m, 26H), 1.61 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.06 (dt, *J* = 7.5, 7.5 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 5.61 (dt, *J* = 15.0, 7.0 Hz, 1H), 5.90 (d, *J* = 15.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.08, 14.11, 22.61, 22.68, 28.73, 28.79, 29.21, 29.32, 29.35, 29.48, 28.51, 29.59, 29.63, 29.65, 31.67, 31.91, 32.74, 33.21, 122.63, 130.81. Found: C, 76.91; H, 12.79%. Calcd for $C_{20}H_{40}S$: C, 76.85; H, 12.90%.

(*Z*)-1-cyclohexyl-1-octene ((*Z*)-**5d**) : Colorless oil. IR (neat) 2999, 2925, 2853, 1653, 1558, 1448, 966, 890, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.00–1.10 (m, 2H), 1.14–1.38 (m, 11H), 1.57–1.74 (m, 5H),2.03 (dt, *J* = 7.0, 7.0 Hz, 2H), 2.21–2.29 (m, 1H), 5.16–5.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.10, 22.67, 26.02, 26.10, 27.44, 28.99, 29.98, 31.79, 33.41, 36.30,

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128.05, 135.98. Found: C, 86.82; H, 13.70%. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48%.

Dodecyl 1-phenylethenyl sulfide (6) : Brown oil. IR (neat) 3059, 2925, 2360, 1675, 1599, 1456, 1276, 1069, 843, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.20–1.34 (m, 16H), 1.36–1.44 (m, 2H), 1.64 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 5.16 (s, 1H), 5.46 (s, 1H), 7.30–7.37 (m, 3H), 7.54–7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.11, 22.68, 28.46, 28.91, 29.16, 29.34, 29.47, 29.57, 29.62, 29.63, 31.90, 32.13, 110.16, 127.08, 128.26, 128.29, 139.82, 145.28. Found: C, 79.16; H, 10.47%. Calcd for $C_{20}H_{32}S$: C, 78.88; H, 10.59%.

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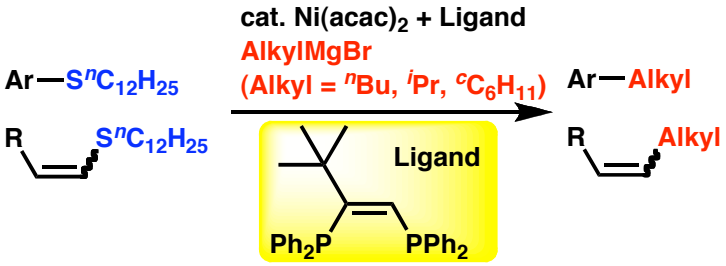

Short Title: Cross-Coupling of Sulfides with Alkyl Grignard Reagents