Supplementary Material

Copper-promoted Hiyama Cross-Coupling of Arylsilanes with Thiuram Reagents:
A Facile Synthesis of Aryl Dithiocarbamates

Yiying Wang¹, Hongtao Shen², Jianhua Qiu², Mengqi Chen²*, Weimin Song²*,
Mingqin Zhao¹, Longfei Wang¹, Feng Bai², Hongxia Wang², Zhiyong Wu¹*

¹ Flavors and Fragrance Engineering & Technology Research Center of Henan Province, College of
Tobacco Science, Henan Agricultural University, Zhengzhou 450002, P. R. China
² Technology Center, China Tobacco Henan Industrial Co., Ltd., Zhengzhou, 450000, P. R. China

479820476@qq.com

gongyishi@126.com

zhiyongwu@henau.edu.cn

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1 General information

All the reagents were obtained commercially and used without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. Analytical thin layer chromatography (TLC) was performed on precoated silica gel F$_{254}$ plates. Compounds were visualized by irradiation with UV light (254 nm).

**Analytical information:** $^1$H NMR and $^{13}$C NMR spectra data were recorded by a BRUKER AVANCE III 400 MHz spectrometer ($^1$H 400 MHz, $^{13}$C 100 MHz), using CDCl$_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. $^1$H NMR spectral data are given as chemical shifts in ppm: followed by multiplicity (s-singlet; d-doublet; t-triplet; q-quartet; m-multiplet), number of protons and coupling constants. $^{13}$C NMR chemical shifts are expressed in ppm. HRMS data were obtained using AB SCIEX Triple TOF 5600+ high resolution mass spectrometer (USA). The products listed below were determined by $^1$H and $^{13}$C NMR spectra. Infrared spectra were recorded with a Thermo Scientific Nicolet 6700 FT-IR Spectrometer. Melting points were determined using melting point X-4 (Gongyi Kerui) apparatus.

2 Table S1. Optimization of reaction conditions.$^a$

| Entry | Catalyst | Ligand (equiv.) | Yield (%)$^b$ |
|-------|----------|-----------------|---------------|
| 1     | CuF$_2$  | 1,10-phenanthroline (2) | 46 |
| 2     | CuF$_2$  | pyridine (2) | 37 |
| 3     | CuF$_2$  | 2,2'-bipyridine (2) | 68 |
| 4     | CuF$_2$  | N,N,N',N'-tetramethylethylene diamine (2) | 0 |
| 5     | CuF$_2$  | 2,2':6',2''-terpyridine (2) | 49 |
| 6     | CuF$_2$  | (R,R)-2,2'-(2,6-pyridinediyl)bis(4-isopropyl-2-oxazoline (2) | 51 |
| 7     | CuF$_2$  | 8-benzoylaminoquinoline (2) | 55 |
| 8     | CuF$_2$  | 1,2-bis(diphenylphosphino)ethane (2) | 55 |
3 Experimental Section

(1) General procedures for the Synthesis of various arylsiloxanes

\[
\text{Ar}--\text{MgBr} \xrightarrow{\text{Si(OMe)}_4, \text{THF}, -30 ^\circ \text{C to r.t.}} \text{Ar}--\text{Si(OMe)}_3
\]

To a solution of tetramethyl orthosilicate (60 mmol) in 20 mL anhydrous THF was charged into a 100 mL round-bottom flask. The silane solution was then cooled to -30 °C, and the arylmagnesiumhalide solution was added dropwise (one drop per second). The solution was allowed to stir at -30 °C for 1 h and then at room temperature for 12 h. After the reaction finished, the mixture was then poured into 30 mL of hexane, and stirred for some time. Then the solution was washed with 3 × 25 mL of water, dried over Na₂SO₄, and concentrated in vacuo. Purification of the residue by short-path distillation to yield the desired arylsilanes.\(^{[1-2]}\)

(2) General procedures for the reaction of arylsiloxanes with tetraalkylthiuram disulfides

\[
\text{R}^1\text{Si(OMe)}_3 + R^2\text{S} - S - R^2 \xrightarrow{\text{CuF}_2 (3 \text{ equiv.}), 1,10\text{-phenanthroline (2 equiv.) \text{, Toluene, } 80 \, ^\circ \text{C, 16 h}}} R^1\text{S}-S-N\text{R}^2-\text{N}\text{R}^2
\]

To a 10 mL tube, arylsiloxanes 1 (0.1 mmol) and tetraalkylthiuram disulfides 2 (0.2 mmol), CuF₂ (0.3 mmol), 1,10-phenanthroline (0.2 mmol) and toluene (1.0 mL) were added under air atmosphere. The resulting mixture was heated in an 80 °C oil bath with vigorous stirring for 16 h. Then, the reaction mixture was cooled to room temperature, quenched with a sat. NH₄Cl solution and subsequently extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated under vacuum. The residue was purified by flash
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chromatography using petroleum ether /ethyl acetate (10:1) as eluent affording 3 or 4 in 39-93% yield. In general, the identity and purity of the products were confirmed by $^1$H and $^{13}$C NMR spectroscopy, HRMS and IR.

(3) General procedures for the reaction of arylsiloxanes with tetramethylthiuram monosulfide

Under air atmosphere, arylsiloxanes 1 (0.1 mmol), tetramethylthiuram monosulfide 5 (0.2 mmol), CuF$_2$ (0.3 mmol), 2,2'-bipyridine (0.1 mmol) were charged into a 10 mL reaction tube, then Toluene (1 mL) was added into the tube. The resulting mixture was stirred at 80 °C for 16 h in oil bath, then cooled down to room temperature. The reaction mixture was quenched with a sat. NH$_4$Cl solution and subsequently extracted with ethyl acetate. The combined organic layers were dried over anhydrous MgSO$_4$, and the solvent was evaporated under vacuum. The crude product was purified by flash column chromatography on silica gel (elute: petroleum ether-EtOAc) yielding the products 3 in 28-88 yields. In general, the identity and purity of the products were confirmed by $^1$H and $^{13}$C NMR spectroscopy, HRMS and IR.

4 Characterization Data

phenyl dimethylcarbamodithioate (3a)

Purification by flash column chromatography on silica gel, $R_f = 0.47$; petroleum ether/EtOAc = 10/1; isolated yield = 88% (17.4 mg, with TMTD), 82% (16.1 mg, with TMTM); white solid; M.p. 87-89 °C; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.63-7.38 (m, 5H), 3.64-3.51 (s, 3H), 3.51-3.41 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 197.6, 137.0, 131.7, 130.1, 129.1, 45.7, 42.0; IR (KBr) $\nu_{\text{max}}$ 2922, 1497, 1472, 1439, 1376, 1253, 985, 966, 751, and 687 cm$^{-1}$; HRMS (EI) calcd. for C$_9$H$_{11}$NS$_2$: [M]$^+$: 197.0333, found: 197.0339.

4-methylphenyl diethylcarbamodithioate (3b)
Purification by flash column chromatography on silica gel, \(R_f = 0.48\); petroleum ether/EtOAc = 10/1; isolated yield = 72\% (15.3 mg, with TMTD), 31\% (6.5 mg, with TMTM); white solid; M.p. 108-109 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.39-7.31 (m, 2H), 7.29-7.22 (m, 2H), 3.62-3.51 (s, 3H), 3.51-3.45 (s, 3H), 2.49-2.35 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) ppm: 198.2, 140.4, 136.8, 130.1, 128.3, 45.8, 42.0, 42.5, 21.5; IR (KBr) \(\nu_{\text{max}}\) 3384, 2974, 2925, 1489, 1450, 1407, 1372, 1247, 1149, 1089, 1050, 973, and 808 cm\(^{-1}\); HRMS (EI) calcd. for C\(_{10}\)H\(_{13}\)NS\(_2\): [M]\(^+\): 211.0489, found: 211.0483.

4-methoxyphenyl dimethylcarbamodithioate (3c)

\[\text{MeO} \quad \begin{array}{c} \text{S} \quad \text{N} \quad \text{Me} \\ \text{S} \quad \text{N} \quad \text{Me} \end{array}\]

Purification by flash column chromatography on silica gel, \(R_f = 0.41\); petroleum ether/EtOAc = 10/1; isolated yield = 65\% (14.8 mg, with TMTD), 35\% (7.9 mg, with TMTM); white solid; M.p. 85-86 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.43-7.34 (m, 2H), 7.02-6.94 (m, 2H), 3.91-3.81 (s, 3H), 3.62-3.53 (s, 3H), 1.49-1.32 (m, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) ppm: 198.8, 161.1, 138.5, 122.6, 114.7, 55.3, 45.8, 41.9; IR (KBr) \(\nu_{\text{max}}\) 3422, 2923, 1589, 1571, 1493, 1433, 1403, 1375, 1248, 831, 634, and 648 cm\(^{-1}\); HRMS (EI) calcd. for C\(_{13}\)H\(_{12}\)N\(_2\): [M]\(^+\): 227.0439, found: 227.0431.

4-(\text{\textit{tert}}-\text{butyl})phenyl dimethylcarbamodithioate (3d)

\[\text{Me} \quad \begin{array}{c} \text{S} \quad \text{N} \quad \text{Me} \\ \text{S} \quad \text{N} \quad \text{Me} \end{array}\]

Purification by flash column chromatography on silica gel, \(R_f = 0.57\); petroleum ether/EtOAc = 10/1; isolated yield = 71\% (18.1 mg, with TMTD), 40\% (10.2 mg, with TMTM); light yellow solid; M.p. 85-86 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.50-7.43 (m, 2H), 7.43-7.36 (m, 2H), 3.62-3.53 (s, 3H), 3.53-3.46 (s, 3H), 1.49-1.32 (m, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) ppm: 198.0, 153.2, 136.4, 128.2, 126.3, 45.7, 42.0, 34.8, 31.2, 30.0; IR (KBr) \(\nu_{\text{max}}\) 3434, 2920, 2853, 1489, 1456, 1370, 1250, 1145, 1050, 983, 865, 812, and 702 cm\(^{-1}\); HRMS (ESI) calcd. for C\(_{13}\)H\(_{19}\)NS\(_2\): [M+Na] \(^+\): 276.0851, found: 276.0857.

\textit{m}-tolyl dimethylcarbamodithioate (3e)³
Purification by flash column chromatography on silica gel, \( R_f = 0.52 \); petroleum ether/EtOAc = 10/1; isolated yield = 43\% (9.1 mg, with TMTD), 47\% (10.0 mg, with TMTM); deep yellow liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.38-7.31 (m, 1H), 7.31-7.26 (m, 3H), 3.61-3.53 (s, 3H), 3.53-3.47 (s, 3H), 2.45-2.35 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) ppm: 197.9, 139.0, 137.4, 134.0, 131.4, 130.9, 128.9, 45.7, 42.0, 21.3; IR (KBr) \( \nu_{\text{max}} \) 2956, 2901, 2865, 1488, 1374, 1361, 1249, 1148, 1114, 1013, 984, and 828 cm\(^{-1}\).

3-methoxyphenyl dimethylcarbamodithioate (3f)\(^4\)

Purification by flash column chromatography on silica gel, \( R_f = 0.43 \); petroleum ether/EtOAc = 10/1; isolated yield = 55\% (12.6 mg, with TMTD), 63\% (14.4 mg, with TMTM); deep yellow liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.38-7.32 (t, \( J = 7.9 \) Hz, 1H), 7.11-7.05 (m, 1H), 7.05-6.98 (m, 2H), 3.87-3.80 (s, 3H), 3.61-3.53 (s, 3H), 3.53-3.46 (m, 3H) \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) ppm: 197.4, 159.8, 132.5, 129.8, 129.1, 121.9, 116.3, 55.4, 45.7, 42.0; IR (KBr) \( \nu_{\text{max}} \) 2957, 2917, 2850, 1590, 1574, 1472, 1276, 1227, 1042, 974, 859, 770, and 679 cm\(^{-1}\).

2,5-dimethylphenyl dimethylcarbamodithioate (3g)\(^6\)

Purification by flash column chromatography on silica gel, \( R_f = 0.48 \); petroleum ether/EtOAc = 10/1; isolated yield = 54\% (12.2 mg, with TMTD), 28\% (6.4 mg, with TMTM); white solid; M.p. 56-57 °C \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 8.43 (d, \( J = 5.3 \) Hz, 1H), 8.13 (dd, \( J = 8.4, 1.3 \) Hz, 2H), 7.66-7.58 (m, 2H), 7.48 (t, \( J = 6.9 \) Hz, 2H), 7.43 (dd, \( J = 5.3, 1.8 \) Hz, 1H), 5.47 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) ppm: 166.09, 157.60, 150.19, 133.68, 133.41, 129.85, 129.55, 128.54, 126.30, 124.95, 66.44; IR (KBr) \( \nu_{\text{max}} \) 3434, 2920, 2853, 1489, 1456, 1370, 1250, 1145, 1050, 983, 865, 812, and 702 cm\(^{-1}\).

4-chlorophenyl dimethylcarbamodithioate (3h)\(^3\)
Purification by flash column chromatography on silica gel, \( R_f = 0.48 \); petroleum ether/ EtOAc = 10/1; isolated yield = 93% (21.5 mg, with TMTD), 85% (19.7 mg, with TMTM); white solid; M.p. 89-90 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.45-7.35 (m, 4H), 3.64-3.51 (s, 3H), 3.51-3.41 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) ppm: 196.8, 138.2, 136.6, 130.2, 129.4, 45.8, 42.0; IR (KBr) \( \nu_{\text{max}} \) 3422, 2925, 1504, 1471, 1376, 1251, 1152, 1083, 1015, 973, 814, and 749 cm\(^{-1}\); HRMS (EI) calcd. for C\(_{11}\)H\(_{16}\)ClINS\(_2\): [M\(^+\)]: 230.9943, found: 230.9936.

4-fluorophenyl dimethylcarbamodithioate (3i)

\[
\begin{array}{c}
\text{Me} \\
\text{F} \\
\text{S} \\
\text{N} \\
\text{Me}
\end{array}
\]

Purification by flash column chromatography on silica gel, \( R_f = 0.37 \); petroleum ether/EtOAc = 10/1; isolated yield = 78% (16.9 mg, with TMTD), 60% (13.0 mg, with TMTM); light yellow solid; M.p. 79-80 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.48-7.40 (m, 2H), 7.17-7.09 (m, 2H), 3.59-3.51 (s, 3H), 3.51-3.46 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) ppm: 197.5, 165.2, 162.7, 139.1 (139.2, 139.1, d, \( J = 8.7 \) Hz), 127.2 (127.3, 127.1, d, \( J = 3.7 \) Hz), 116.4 (116.5, 116.3, d, \( J = 22 \) Hz), 45.8, 41.9; IR (KBr) \( \nu_{\text{max}} \) 3438, 2926, 1586, 1488, 1377, 1252, 1217, 1157, 1090, 1015, 980, 937, 831, and 815 cm\(^{-1}\).

3-chlorophenyl dimethylcarbamodithioate (3j)

\[
\begin{array}{c}
\text{Cl} \\
\text{S} \\
\text{N} \\
\text{Me}
\end{array}
\]

Purification by flash column chromatography on silica gel, \( R_f = 0.32 \); petroleum ether/EtOAc = 10/1; isolated yield = 57% (13.3 mg, with TMTD), 70% (16.3 mg, with TMTM); deep yellow liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.49-7.46 (m, 1H), 7.46-7.42 (m, 1H), 7.39-7.35 (m, 2H), 3.60-3.53 (s, 3H), 3.53-3.46 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) ppm: 196.4, 136.7, 135.2, 134.4, 133.3, 130.2, 130.1, 45.7, 42.1; IR (KBr) \( \nu_{\text{max}} \) 3428, 2923, 2852, 1628, 1500, 1399, 1271, 1244, 1151, 1003, 964, 8523, and 720 cm\(^{-1}\).

3-fluorophenyl dimethylcarbamodithioate (3k)

\[
\begin{array}{c}
\text{Me} \\
\text{F} \\
\text{S} \\
\text{N} \\
\text{Me}
\end{array}
\]

Purification by flash column chromatography on silica gel, \( R_f = 0.37 \); petroleum ether/EtOAc = 10/1; isolated yield = 83% (17.8 mg, with TMTD), 88% (19.0 mg, with TMTM); light yellow solid; M.p. 54-55 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.45-7.37 (m, 1H), 7.29-7.24 (m, 1H), 7.24-7.14 (m,
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2H), 3.56-3.51 (s, 3H), 3.51-3.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) ppm: 196.5, 163.7, 161.2, 133.3 (133.4, 133.3, d, J = 8.1 Hz), 132.7 (132.8, 132.7, d, J = 3.3 Hz), 130.2 (130.3, 130.2, d, J = 8.12 Hz), 123.9 (124.0 123.8, d, J = 22 Hz), 117.3 (117.4, 117.2, d, J = 17.2 Hz), 45.7, 42.1; IR (KBr) νₘₓ 3435, 2926, 1581, 1473, 1375, 1250, 1217, 1145, 1052, 985, 880, and 781 cm⁻¹.

4-vinylphenyl dimethylcarbamodithioate (3l)

\[
\text{Me} \quad \text{S} \quad \text{N} \quad \text{Me}
\]

Purification by flash column chromatography on silica gel, Rₖ = 0.45; petroleum ether/ EtOAc = 10/1; isolated yield = 52% (11.6 mg, with TMTD), 31% (6.9 mg, with TMTM); light yellow solid; M.p. 66-67 °C; ¹H NMR (400 MHz, CDCl₃) ppm: 7.53-7.45 (m, 2H), 6.80-6.69 (m, 1H), 5.88-5.78 (m, 1H), 5.39-5.31 (m, 1H), 3.61-3.51 (s, 3H), 3.51-3.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) ppm: 197.6, 139.2, 137.1, 136.1, 130.7, 126.9, 115.6, 45.7, 42.0; IR (KBr) νₘₓ 2923, 2852, 1486, 1375, 1248, 1146, 1108, 1013, 976, 906, and 836 cm⁻¹; HRMS (EI) calcd. for C₁₁H₁₃NS₂: [M]⁺: 223.0489; found: 223.0485.

naphthalen-1-yl dimethylcarbamodithioate (3m)

\[
\text{Me} \quad \text{S} \quad \text{N} \quad \text{Me}
\]

Purification by flash column chromatography on silica gel, Rₖ = 0.40; petroleum ether/ EtOAc = 10/1; isolated yield = 72% (17.9 mg, with TMTD), 65% (16.2 mg, with TMTM); yellow solid; M.p. 146-147 °C; ¹H NMR (400 MHz, CDCl₃) ppm: 8.29-8.22 (m, 1H), 8.04-7.97 (d, J = 8.2 Hz, 1H), 7.93-7.87 (m, 1H), 7.78-7.72 (m, 1H), 7.59-7.48 (m, 3H), 3.71-3.61 (m, 3H), 3.61-3.52 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) ppm: 196.6, 137.1, 135.1, 134.2, 131.5, 129.0, 128.7, 127.2, 126.3, 125.8, 45.6, 42.2; IR (KBr) νₘₓ 2922, 1500, 1376, 1251, 1146, 987, 967, 909, 860, 796, 771, and 740 cm⁻¹; HRMS (ESI) calcd. for C₁₃H₁₃NS₂: [M+Na]⁺: 270.0382, found: 270.0382.

furan-2-yl dimethylcarbamodithioate (3n)

\[
\text{Me} \quad \text{S} \quad \text{N} \quad \text{Me}
\]

Purification by flash column chromatography on silica gel, Rₖ = 0.40; petroleum ether/ EtOAc = 10/1; isolated yield = 62% (11.7 mg, with TMTD), 68% (12.7 mg, with TMTM); white solid; M.p. 89-90 °C; ¹H NMR (400 MHz, CDCl₃) ppm: 7.67-7.61 (dd, J = 5.32 Hz, 1H), 5.26-5.22 (m, 1H), 7.18-
7.11 (m, 1H), 3.60-3.51 (s, 3H), 3.51-3.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 197.4, 138.8, 133.5, 129.2, 127.9, 46.1, 41.8; IR (KBr) $\nu_{\text{max}}$ 3428, 2923, 1450, 1399, 1376, 1244, 1151, 1051, 1003, 964, 853, and 720 cm$^{-1}$.

**phenyl diethylcarbamodithioate (4a)**

![Structure of phenyl diethylcarbamodithioate (4a)](image)

Purification by flash column chromatography on silica gel, $R_f = 0.44$; petroleum ether/ EtOAc = 15/1; isolated yield = 67% (15.1 mg, with TETD); pale yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.55-7.39 (m, 5H), 4.10-3.38 (q, $J = 6.9$, 3.9 Hz, 2H), 3.95-3.78 (q, $J = 7.0$ Hz, 2H), 1.45-1.35 (t, $J = 7.1$ Hz, 3H), 1.35-1.26 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 137.2, 131.6, 130.0, 129.0, 49.9, 47.3, 12.8, 11.6; IR (KBr) $\nu_{\text{max}}$ 2969, 2928, 2849, 1487, 1438, 1411, 1267, 1205, 1141, and 747 cm$^{-1}$; HRMS (EI) calcd. for C$_{11}$H$_{15}$NS$_2$: [M]$^+$: 225.0646; found: 225.0641.

**p-tolyl diethylcarbamodithioate (4b)**

![Structure of p-tolyl diethylcarbamodithioate (4b)](image)

Purification by flash column chromatography on silica gel, $R_f = 0.43$; petroleum ether/ EtOAc = 15/1; isolated yield = 61% (14.5 mg, with TETD); yellow solid; M.p. 75-76 °C; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.41-7.33 (d, $J = 8.0$ Hz, 2H), 7.31-7.22 (d, $J = 7.6$ Hz, 2H), 4.10-3.96 (q, $J = 6.9$ Hz, 2H), 3.94-3.40 (q, $J = 6.9$ Hz, 3H), 2.45-2.36 (s, 3H), 1.45-1.36 (t, $J = 7.0$ Hz, 3H), 1.34-1.22 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 196.5, 140.3, 137.0, 130.0, 128.2, 50.0, 47.2, 21.5, 12.7, 11.6; IR (KBr) $\nu_{\text{max}}$ 2977, 2930, 1483, 1418, 1376, 1267, 1202, 1142, 1008, 978, 915, and 808 cm$^{-1}$; HRMS (ESI) calcd. for C$_{12}$H$_{17}$NS$_2$: [M+Na]$^+$: 262.0695; found: 262.0688.

**4-methoxyphenyl diethylcarbamodithioate (4c)**

![Structure of 4-methoxyphenyl diethylcarbamodithioate (4c)](image)

Purification by flash column chromatography on silica gel, $R_f = 0.48$; petroleum ether/ EtOAc = 15/1; isolated yield = 74% (18.9 mg, with TETD); white solid; M.p. 73-74 °C; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.43-7.35 (m, 2H), 7.01-6.93 (m, 2H), 4.11-3.97 (q, $J = 7.0$ Hz, 3H), 3.91-3.81 (m, 5H), 1.45-1.36 (t, $J = 7.0$ Hz, 3H), 1.34-1.25 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 197.2, 161.1, 138.6, 122.4, 114.7, 55.3, 50.0, 47.1, 12.7, 11.6; IR (KBr) $\nu_{\text{max}}$ : 2957, 2931, 1589, 1491, 1440,
1416, 1293, 1268, 1248, 1185, 1174, 1145, 1028, and 827 cm\(^{-1}\); HRMS (EI) calcd. for C\(_{16}\)H\(_{17}\)NOS\(_2\): [M\(^+\)]: 255.0752, found: 255.0742.

**4-(tert-butyl)phenyl diethylcarbamodithioate (4d)**

\[
\begin{array}{c}
\text{Et} \\
\text{\textsuperscript{1}Bu}
\end{array}
\text{S} \text{\textsuperscript{N}} \text{N} \text{S} \text{Et}
\]

Purification by flash column chromatography on silica gel, \(R_f = 0.43\); petroleum ether/EtOAc = 15/1; isolated yield = 39\% (10.9 mg, with TETD); yellow solid; M.p. 106-107 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.49-7.43 (m, 2H), 7.43-7.37 (m, 2H), 4.09-3.98 (q, \(J = 6.8\) Hz, 2H), 3.93-3.81 (q, \(J = 7.0\) Hz, 2H), 1.47-1.37 (t, \(J = 7.0\) Hz, 3H), 1.37-1.31 (s, 9H), 1.31-1.27 (m, 3H);

**3-methoxyphenyl diethylcarbamodithioate (4f)**

\[
\begin{array}{c}
\text{Et} \\
\text{MeO}
\end{array}
\text{S} \text{\textsuperscript{N}} \text{N} \text{S} \text{Et}
\]

Purification by flash column chromatography on silica gel, \(R_f = 0.52\); petroleum ether/EtOAc = 10/1; isolated yield = 79\% (20.3 mg, with TETD); deep yellow liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) ppm: 7.38-7.31 (t, \(J = 7.8\) Hz, 1H), 7.12-7.06 (m, 1H), 7.06-7.02 (m, 1H), 7.02-6.97 (m, 1H), 4.10-3.97 (q, \(J = 6.9\) Hz, 2H), 3.97-3.83 (m, 2H), 3.83-3.79 (m, 3H), 1.43-1.36 (t, \(J = 7.1\) Hz, 3H), 1.32-1.27 (m, 3H)
H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 195.7, 159.7, 132.4, 129.7, 129.3, 122.1, 116.2, 55.4, 49.8, 47.3, 12.8, 11.6; IR (KBr) $\nu_{\text{max}}$ 2973, 2931, 1591, 1577, 1461, 1415, 1269, 1231, 1206, 1143, 1010, 979, 917, 827, and 775 cm$^{-1}$.

2,5-dimethylphenyl diethylcarbamodithioate (4g)$^6$

\[
\text{Me} \quad \text{S} \quad \text{N} \quad \text{Et} \\
\text{Me} \quad \text{S} \quad \text{N} \quad \text{Et}
\]

Purification by flash column chromatography on silica gel, $R_f = 0.47$; petroleum ether/EtOAc = 10/1; isolated yield = 58% (14.7 mg, with TETD); brown liquid; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.30-7.26 (m, 1H), 7.24-7.21 (m, 1H), 7.21-7.15 (m, 1H), 4.09-3.98 (m, 2H), 3.94-3.83 (q, $J = 3.8$ Hz, 2H), 2.41-2.34 (s, 1H), 2.34-2.30 (s, 1H), 1.48-1.36 (t, $J = 7.0$ Hz, 3H), 1.35-1.27 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 195.1, 140.7, 138.2, 136.2, 131.5, 130.6, 130.5, 49.7, 47.3, 20.8, 20.4, 12.8, 11.7; IR (KBr) $\nu_{\text{max}}$ 3434, 2975, 2930, 1478, 1415, 1378, 1300, 1268, 1206, 1143, 1008, 979, 917, and 813.

4-chlorophenyl diethylcarbamodithioate (4h)$^3$

\[
\text{Cl} \quad \text{S} \quad \text{N} \quad \text{Et} \\
\text{Cl} \quad \text{S} \quad \text{N} \quad \text{Et}
\]

Purification by flash column chromatography on silica gel, $R_f = 0.61$; petroleum ether/ EtOAc = 15/1; isolated yield = 85% (22.1 mg, with TETD); white solid; M.p. 90-91 °C; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.49-7.31 (s, 4H), 4.09-3.97 (q, $J = 7.0$ Hz, 2H), 3.95-3.79 (t, $J = 7.0$ Hz, 2H), 1.48-1.35 (t, $J = 7.1$ Hz, 3H), 1.35-1.26 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 195.2, 138.4, 136.5, 130.0, 129.3, 50.0, 47.3, 12.8, 11.6; IR (KBr) $\nu_{\text{max}}$ 405, 2975, 2905, 1486, 1420, 1386, 1353, 1267, 1203, 1140, 1093, 915, and 823 cm$^{-1}$; HRMS (EI) calcd. for C$_{11}$H$_{14}$ClNS$_2$: [M]$^+$: 259.0256, found: 259.0252.

4-fluorophenyl diethylcarbamodithioate (4i)$^3$

\[
\text{F} \quad \text{S} \quad \text{N} \quad \text{Et} \\
\text{F} \quad \text{S} \quad \text{N} \quad \text{Et}
\]

Purification by flash column chromatography on silica gel, $R_f = 0.55$; petroleum ether/ EtOAc = 10/1; isolated yield = 60% (14.7 mg, with TETD); yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.50-7.40 (m, 2H), 7.17-7.08 (m, 2H), 4.10-3.96 (q, $J = 7.0$ Hz, 2H), 3.91-3.39 (q, $J = 7.0$ Hz, 2H), 1.45-1.37 (t, $J = 7.0$ Hz, 3H), 1.32-1.26 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 195.8, 165.2, 162.7, 139.3 (139.3, 139.2, d, $J = 8.7$ Hz), 127.0 (127.0,127.0, d, $J = 3.4$ Hz), 116.3 (116.4, 116.2, d, $J = 21.9$ Hz),


50.0, 47.3, 12.7, 11.6; IR (KBr) $\nu_{\text{max}}$ 2983, 2929, 1588, 1486, 1420, 1394, 1295, 1204, 1140, 1073, 978, 915, and 832 cm$^{-1}$.

3-chlorophenyl diethylcarbamodithioate (4j)$^3$

![3-chlorophenyl diethylcarbamodithioate](image)

Purification by flash column chromatography on silica gel, R$_f$ = 0.61; petroleum ether/EtOAc = 15/1; isolated yield = 60% (15.7 mg, with TETD); brown liquid; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.55-7.47 (m, 1H), 7.47-7.40 (m, 1H), 7.40-7.32 (m, 2H), 4.10-3.97 (q, $J$ = 6.9 Hz, 2H), 3.88-3.79 (q, $J$ = 7.0 Hz, 2H), 1.44-1.36 (t, $J$ = 7.0 Hz, 3H), 1.32-1.27 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 194.7, 136.9, 135.4, 134.3, 133.2, 130.1, 130.0, 50.0, 47.4, 12.8, 12.6; IR (KBr) $\nu_{\text{max}}$ 3432, 2923, 1562, 1504, 1459, 1400, 1380, 1249, 1151, 1067, 980, 864, and 790 cm$^{-1}$.

3-fluorophenyl diethylcarbamodithioate (4k)$^5$

![3-fluorophenyl diethylcarbamodithioate](image)

Purification by flash column chromatography on silica gel (R$_f$ = 0.46, petroleum ether/EtOAc = 10/1); isolated yield = 66% (16.1 mg, with TETD); yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.44-7.36 (m, 1H), 7.30-7.26 (m, 1H), 7.25-7.20 (m, 1H), 7.20-7.12 (m, 1H), 4.09-3.97 (q, $J$ = 7.0 Hz, 2H), 3.39-3.80 (m, 2H), 1.48-1.37 (t, $J$ = 7.0 Hz, 3H), 1.32-1.27 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 194.8, 163.7, 161.2, 133.1 (133.3, 133.2, 132.9, 132.9, m), 130.1 (130.2, 130.1, d, $J$ = 8.1 Hz), 124.1 (124.2, 124.0, d, $J$ = 22.1 Hz), 117.2 (117.3, 117.1, d, $J$ = 21.5 Hz), 49.9, 47.4, 12.8, 11.6; IR (KBr) $\nu_{\text{max}}$ 2971, 2931, 1257, 1488, 1475, 1415, 1271, 1206, 1050, 880, and 783 cm$^{-1}$.

4-vinylphenyl diethylcarbamodithioate (4l)

![4-vinylphenyl diethylcarbamodithioate](image)

Purification by flash column chromatography on silica gel, R$_f$ = 0.45; petroleum ether/EtOAc = 15/1; isolated yield = 73% (18.4 mg, with TETD); yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.51-7.45 (m, 2H), 7.45-7.39 (m, 2H), 6.84-6.68 (m, 1H), 5.93-5.77 (m, 1H), 5.43-5.27 (d, $J$ = 10.9 Hz, 1H), 4.10-3.94 (q, $J$ = 7.0 Hz, 2H), 3.94-3.78 (q, $J$ = 7.0 Hz, 2H), 1.47-1.35 (q, $J$ = 7.1 Hz, 3H), 1.31-1.26 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 195.9, 139.1, 137.2, 136.2, 130.6, 126.9, 115.5, 49.9,
| Compound                        | IR (KBr) $\nu_{\text{max}}$ (cm$^{-1}$) | HRMS (EI) calcd. for C$_{13}$H$_{17}$NS$_2$: [M]$^+$ | Isolated Yield |
|--------------------------------|-----------------------------------------|------------------------------------------------------|----------------|
| naphthalen-1-yl diethyldithiocarbamate (4m) | 3431, 2970, 2923, 1488, 1412, 1355, 1271, 1201, 1136, 1065, 974, 914, and 828 | 251.0802 | 59% (16.3 mg, with TETD) |
| furan-2-yl diethyldithiocarbamate (4n) | 3436, 2928, 1484, 1419, 1266, 1204, 1139, 1066, 1005, and 736 | 298.069 | 47% (10.2 mg, with TBTD) |
| Phenyl DIBUTYLDITHIOCARBAMOThIOATE (4o) | | 298.069 | 46% (13.0 mg, with TETD) |

Purification by flash column chromatography on silica gel, R$_f$ = 0.53; petroleum ether/EtOAc = 15/1; isolated yield = 59% (16.3 mg, with TETD); white solid; M.p. 74-75 °C; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 8.27-8.19 (d, $J$ = 8.2 Hz, 1H), 8.04-7.95 (d, $J$ = 8.2 Hz, 1H), 7.93-7.85 (m, 1H), 7.80-7.72 (m, 1H), 7.59-7.45 (m, 3H), 4.11-3.92 (m, 4H), 1.56-1.47 (m, 3H), 1.37-1.24 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 194.9, 137.2, 135.3, 134.2, 131.4, 128.9, 128.7, 127.2, 126.3, 125.9, 125.8, 49.8, 47.4, 13.0, 11.7; IR (KBr) $\nu_{\text{max}}$, 3436, 2928, 1484, 1419, 1266, 1204, 1139, 1066, 1005, and 736 cm$^{-1}$; HRMS (ESI) calcd. for C$_{15}$H$_{17}$NS$_2$: [M+Na]$^+$: 298.0695, found: 298.0693.

**Phenyl DIBUTYLDITHIOCARBAMOThIOATE (4o)**

Purification by flash column chromatography on silica gel, R$_f$ = 0.40; petroleum ether/EtOAc = 20/1; isolated yield = 46% (13.0 mg, with TBTD); brown liquid; $^1$H NMR (400 MHz, CDCl$_3$) ppm: 7.56-7.38 (m, 5H), 4.03-3.38 (t, $J$ = 7.8 Hz, 2H), 3.38-3.20 (t, $J$ = 7.8 Hz, 2H), 1.89-1.77 (m, 2H), 1.77-1.68 (m, 2H), 1.50-1.39 (m, 2H), 1.39-1.30 (m, 2H), 1.07-0.98 (t, $J$ = 7.3 Hz, 3H), 0.98-0.89 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ppm: 196.3, 137.1, 131.8, 130.0, 129.0, 55.4, 53.1, 29.6,
28.4, 20.2, 13.9, 13.8; IR (KBr) ν_max 3420, 2959, 2930, 2872, 1484, 1440, 1413, 1367, 1290, 1249, 1219, 1183, 1091, and 744 cm⁻¹; HRMS (EI) calcd. for C₁₅H₂₃NS₂: [M]⁺: 81.1272; found: 81.1265.

**p-tolyl dibutylcarbamodithioate (4p)**

![Chemical Structure](attachment:image)

Purification by flash column chromatography on silica gel, R_f = 0.50; petroleum ether/EtOAc = 20/1; isolated yield = 52% (15.4 mg, with TBTD); yellow solid; ¹H NMR (400 MHz, CDCl₃) ppm: 7.39-7.33 (d, J = 8.0 Hz, 2H), 7.26-7.21 (m, 2H), 3.99-3.88 (t, J = 7.8 Hz, 2H), 3.84-3.71 (t, J = 7.8 Hz, 2H), 2.49-2.35 (s, 3H), 1.89-1.77 (m, 2H), 1.77-1.67 (m, 2H), 1.51-1.39 (m, 2H), 1.39-1.21 (m, 2H), 1.09-0.98 (t, J = 7.3 Hz, 3H), 0.68-0.90 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) ppm: 196.8, 140.2, 137.0, 129.9, 128.3, 55.3, 45.8, 41.9; IR (KBr) ν_max 23420, 2958, 2929, 2871, 1483, 1455, 1412, 1367, 1144, 1219, 1249, 1144, 1092, 983, and 805 cm⁻¹; HRMS (EI) calcd. for C₁₆H₂₅NS₂: [M]⁺: 295.1421.

**4-methoxyphenyl dibutylcarbamodithioate (4q)**

![Chemical Structure](attachment:image)

Purification by flash column chromatography on silica gel, R_f = 0.56; petroleum ether/EtOAc = 20/1; isolated yield = 59% (18.3 mg, with TBTD); yellow solid; M.p. 45-46 °C; ¹H NMR (400 MHz, CDCl₃) ppm: 7.42-7.33 (m, 2H), 6.99-6.92 (m, 2H), 4.00-3.89 (t, J = 7.9 Hz, 2H), 3.88-3.82 (s, 3H), 3.79-3.71 (t, J = 7.9 Hz, 2H), 1.88-1.78 (m, 2H), 1.78-1.67 (m, 2H), 1.49-1.38 (m, 2H), 1.38-1.31 (m, 2H), 1.08-0.98 (t, J = 7.3 Hz, 3H), 0.99-0.91 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) ppm: 197.4, 161.0, 138.6, 122.6, 114.6, 55.5, 55.3, 52.9, 29.6, 28.4, 20.2, 13.9, 13.8; IR (KBr) ν_max 958, 2931, 2817, 1591, 1493, 1459, 1412, 1292, 1250, 1219, 1172, 1031, and 824, cm⁻¹; HRMS (EI) calcd. for C₁₆H₂₅NS₂: [M]⁺: 311.1378, found: 311.1370.

**2,2-diphenylvinyl dimethylcarbamodithioate (6)**

![Chemical Structure](attachment:image)

Purification by flash column chromatography on silica gel, R_f = 0.33; petroleum ether/EtOAc = 10/1; isolated yield = 29% (17.3 mg); yellow viscous liquid; ¹H NMR (400 MHz, CDCl₃) ppm: 7.79-7.67 (s, 1H), 7.46-7.31 (m, 6H), 7.30-7.23 (m, 4H), 3.62-3.48 (s, 3H), 3.38-3.21 (s, 3H); ¹³C NMR (100
MHz, CDCl$_3$ ppm: 194.4, 142.0, 141.1, 139.8, 129.7, 128.4, 128.3, 128.0, 127.8, 127.6, 123.5, 45.4, 41.6, 29.7, 22.7; HRMS (EI) calcd. for C$_{17}$H$_{17}$NS$_2$: [M]$^+$: 299.0802, found: 299.0801.

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Supplementary Material

6 Copy of $^1$H and $^{13}$C NMR Spectra

$^1$H NMR spectrum of compound 3a

$^{13}$C NMR spectrum of compound 3a
$^1$H NMR spectrum of compound 3b

$^{13}$C NMR spectrum of compound 3b
Supplementary Material

$^1$H NMR spectrum of compound 3c

$^{13}$C NMR spectrum of compound 3c
$\mathrm{^{1}H\ NMR\ spectrum\ of\ compound\ 3d}$

$\mathrm{^{13}C\ NMR\ spectrum\ of\ compound\ 3d}$
Supplementary Material

$^1$H NMR spectrum of compound 3e

$^{13}$C NMR spectrum of compound 3e
$^1$H NMR spectrum of compound 3f

$^{13}$C NMR spectrum of compound 3f
Supplementary Material

$^1$H NMR spectrum of compound 3g

$^{13}$C NMR spectrum of compound 3g
$^1$H NMR spectrum of compound 3h

$^{13}$C NMR spectrum of compound 3h
Supplementary Material

$^1$H NMR spectrum of compound 3i

$^{13}$C NMR spectrum of compound 3i
$^1$H NMR spectrum of compound 3j

$^{13}$C NMR spectrum of compound 3j
Supplementary Material

$^1$H NMR spectrum of compound 3k

$^{13}$C NMR spectrum of compound 3k
$^1$H NMR spectrum of compound 3l

$^{13}$C NMR spectrum of compound 3l
Supplementary Material

$^1$H NMR spectrum of compound 3m

$^{13}$C NMR spectrum of compound 3m
$^1$H NMR spectrum of compound 3n

$^{13}$C NMR spectrum of compound 3n
Supplementary Material

$^1$H NMR spectrum of compound 4a

$^{13}$C NMR spectrum of compound 4a
\( ^1H \) NMR spectrum of compound 4b

\( ^{13}C \) NMR spectrum of compound 4b
Supplementary Material

$^1$H NMR spectrum of compound 4c

$^{13}$C NMR spectrum of compound 4c
$^1$H NMR spectrum of compound 4d

$^{13}$C NMR spectrum of compound 4d
Supplementary Material

$^1$H NMR spectrum of compound 4e

$^{13}$C NMR spectrum of compound 4e
$^1$H NMR spectrum of compound 4f

$^{13}$C NMR spectrum of compound 4f
Supplementary Material

$^1$H NMR spectrum of compound 4g

$^{13}$C NMR spectrum of compound 4g
$^1$H NMR spectrum of compound 4h

$^{13}$C NMR spectrum of compound 4h
Supplementary Material

$^1$H NMR spectrum of compound 4i

$^{13}$C NMR spectrum of compound 4i
$^1$H NMR spectrum of compound 4j

$^{13}$C NMR spectrum of compound 4j
Supplementary Material

\(^1\)H NMR spectrum of compound 4k

\(^{13}\)C NMR spectrum of compound 4k
$^1$H NMR spectrum of compound 41

$^{13}$C NMR spectrum of compound 41
Supplementary Material

$^1$H NMR spectrum of compound 4m

$^{13}$C NMR spectrum of compound 4m
$^1$H NMR spectrum of compound 4n

$^{13}$C NMR spectrum of compound 4n
Supplementary Material

$^1$H NMR spectrum of compound 4o

$^{13}$C NMR spectrum of compound 4o
$^1$H NMR spectrum of compound 4p

$^{13}$C NMR spectrum of compound 4p
$^1$H NMR spectrum of compound 4q

$^{13}$C NMR spectrum of compound 4q
\(^1\)H NMR spectrum of compound 6

\(^{13}\)C NMR spectrum of compound 6