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One-Pot Copper-Catalysed Thioetherification of Aryl Halides Using Alcohols and Lawesson's Reagent in Diglyme

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Dedicated to Professor Nasser Iranpoor on the occasion of his retirement

Keywords: Homogeneous catalysis / Arylation / Alcohols / Copper / Sulfur / Thioethers

A new protocol for the thioetherification of structurally varied alcohols with aryl halides using Lawesson's reagent, catalysed by copper(I) iodide, and using diglyme as a safe solvent was developed. Using this method, the reactions of aryl halides proceeded efficiently, and the desired sulfides were obtained in high to excellent yields. The method uses alcohols as starting materials, which is a significant advantage over methods that start from thiols. Alcohols are widely commercially available in a much greater structural diversity than thiols, and they are also nontoxic and not foul-smelling. A reaction mechanism was proposed.

Introduction

Aryl sulfides are important compounds, and their number includes anti-HIV and anti-inflammatory drugs, as well as drugs used for the treatment of Alzheimer's disease, Parkinson's disease, and diabetes.[1] For a long time, aryl sulfides were prepared using traditional methods such as Ullmann-type reactions of arenethiols with aryl halides.[2] However, this method requires harsh reaction conditions such as elevated temperatures (>200 °C). Another method for the preparation of aryl sulfides is the treatment of aryllithium or Grignard reagents with sulfur-based electrophiles. But this approach is not suitable for molecules containing sensitive functional groups.[3]

The development in recent years of transition-metal catalysts,[4] including copper[5] or palladium[6] catalysts, for C–S bond formation through the reaction of aryl halides and thiols means that reactions can now proceed under mild reaction conditions. But although the fact that harsh reaction conditions can now be avoided represents an important achievement, these methods still suffer from a disadvantage. They rely on the direct use of volatile, foul smelling, environmentally unfriendly low-molecular-weight thiols. This problem becomes more serious for larger-scale operations. To solve the problem, two new odourless methods for C–S bond formation, including one-pot thia-Michael addition reactions[7] and one-pot thioetherification of aryl halides through the in situ generation of *S*-alkylisothiouronium salts from the reaction of alkyl halides and thiourea,[8] were reported by Firouzabadi and coworkers. Subsequently, these odourless methods were developed using other sulfur surrogates[9] such as xanthogenate,[10] thioacetamide,[11] thiourea,[12] potassium thiocyanate,[13] thioacetate,[14] sodium hydrosulfide,[15] sodium sulfide,[16] elemental sulfur,[17] sulfonyl hydrazides,[18] $Na_2S_2O_3$,[19] potassium 5-methyl-1,3,4-oxadiazole-2-thiolate,[20] aminothiourea,[21] sulfonyl hydrazide,[22] and phosphorothioic acids and related compounds.[23] However, the challenge of designing new synthetic and catalytic systems for C–S bond formation under mild and greener reaction conditions remains.

Lawesson's reagent (Figure 1) is one of the most widely used reagents for the transformation of a carbonyl functional group into a thiocarbonyl group, as well as for the synthesis of a wide range of heterocyclic compounds containing sulfur atoms.[24] In 1993, an article by Nishio, revealed that alcohols could be directly converted into the corresponding thiols in the presence of Lawesson's reagent.[25] In this paper, a new protocol for the thioetherification of structurally different alcohols in the presence of commercially available Lawesson's reagent as a sulfur surrogate and copper(I) iodide as a catalyst in diglyme as a safe solvent is described. Compared to the bad-smelling thiols, alcohols are very common compounds that are easy to prepare by hydration of alkenes, or by reduction

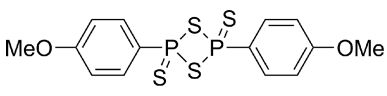

Figure 1. Lawesson's reagent.

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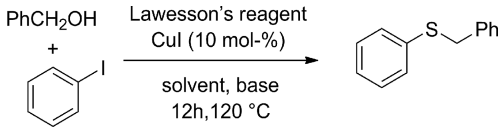
of aldehydes, ketones, acids, or esters. In addition, many structurally different alcohols are commercially available.

Results and Discussion

In initial experiments, the reaction of iodobenzene with benzyl alcohol and Lawesson's reagent was investigated, using copper(I) iodide as a catalyst, and with different bases and solvents (Table 1).

Table 1. Optimization of the reaction conditions (DMA = *N*,*N*-dimethylacetamide).[a]

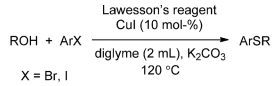


Entry	Solvent	Base	Yield [%][b]
1	DMF	K_2CO_3	74
2	diglyme	K_2CO_3	96
3	diglyme	Na_2CO_3	76
4	diglyme	*t*BuOK	71
5	diglyme	Et_3N	10
6	xylene	*t*BuOK	28
7	xylene	K_2CO_3	22
8	xylene	Et_3N	8
9	DMA	K_2CO_3	54
10	DMSO	K_2CO_3	68
11	H_2O	K_2CO_3	trace

[a] Reactions carried out on a 0.5 mmol scale. [b] Yields determined by GC analysis.

The results indicated that the use of K_2CO_3 as a base and dry diglyme as a solvent at 120 °C were the most effective conditions for the reaction of iodobenzene with benzyl alcohol. Having established these optimized reaction conditions (Table 1, entry 2), the scope of the procedure was evaluated by varying the alcohols and aryl halides (Table 2). Structurally different alcohols, including benzyl alcohol, 4-nitrobenzyl alcohol, 2-phenylethanol, 3-phenylethanol, cinnamyl alcohol, 1-hexanol, 1-octanol, and cyclohexanol, were treated in the presence of Lawesson's reagent and CuI with aryl iodides. The reactions proceeded smoothly to give the desired sulfides in high to excellent yields. In addition, the reactions of alcohols with aryl bromides progressed well to give the desired sulfide products in high yields. The reaction of a heterocyclic alcohol, pyridin-3-ylmethanol, with aryl halides was also studied, and the desired sulfide products were obtained in 81 and 84% yields (Table 2, entries 15 and 16). In addition, the reactions of the heterocyclic aryl halides 2-bromo- and 5-bromopyrimidine with alcohols proceeded well to give the corresponding sulfides in 80–84% yields (Table 2, entries 21–23). However, the reactions of aryl chlorides with alcohols under the optimized reaction conditions were sluggish. A low yield was obtained for the reaction of chlorobenzene with benzyl alcohol, and moderate yields for the reactions of 1-hexanol and benzyl alcohol with the more reactive active 1-chloro-4-nitrobenzene (Table 2, entries 33–35). The reaction of (*R*)-(+)-1-phenyl-1-propanol, an optically active alcohol, with 4-iodotoluene under the optimized reaction conditions was also studied. However, determination of the enantiomeric excess values by polarimetry showed that the product was almost racemic (Table 2, entry 36). All attempts to carry out the reaction of the tertiary alcohol *t*BuOH with iodobenzene under the optimized reaction conditions were unsuccessful. The reac-

Table 2. Aryl halides and alcohols tested in the copper-catalysed thioarylation reaction using Lawesson's reagent.[a]



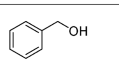
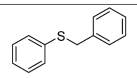
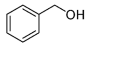
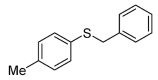
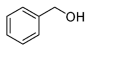
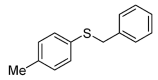
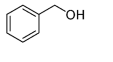
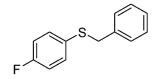
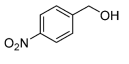
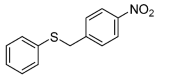
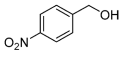
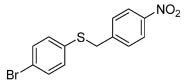
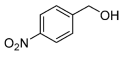
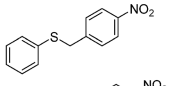
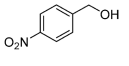
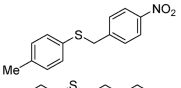
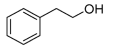
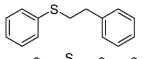
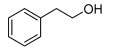
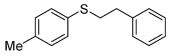
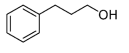
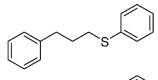
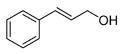
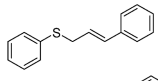
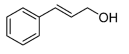
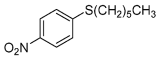
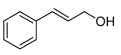
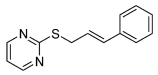
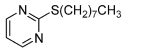
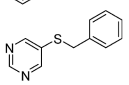
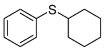
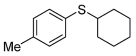
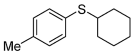
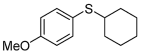
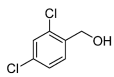
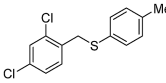
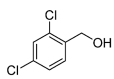
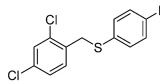
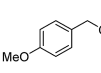
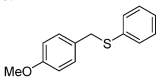
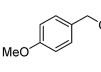
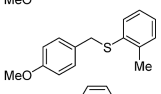
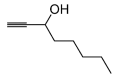
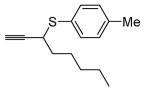
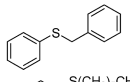
Entry	ROH	ArX	Time [h]	ArSR		Isolated yield%[b]
1			12		**1a**	90
2			12		**1b**	91
3			24		**1b**	73
4			12		**1c**	90
5			12		**1d**	85
6			12		**1e**	80
7			30		**1d**	68
8			12		**1f**	83
9			12		**1g**[c]	82
10			12		**1h**[c]	81
11			12		**1i**	85
12			12		**1j**	89
13			12		**1k**	82
14			24		**1k**	74
15			15		**1l**	84
16			12		**1m**	81
17	$CH_3(CH_2)_4CH_2OH$		12		**1n**	90
18	$CH_3(CH_2)_6CH_2OH$		12		**1o**	84
19	$CH_3(CH_2)_6CH_2OH$		15		**1p**	89

Table 2. *(Continued)*

Entry	ROH	ArX	Time [h]	ArSR		Isolated yield%[b]
20	$CH_3(CH_2)_4CH_2OH$		15		1q	86
21			20		1r	83
22	$CH_3(CH_2)_6CH_2OH$		20		1s	80
23			20		1t	84
24			12		1u	86
25			12		1v	83
26			30		1v	75
27			15		1w	92
28			18		1x	84
29			12		1y	86
30			12		1z	90
31			24		1aa	81
32			20		1bb	85
33			48		1a	12
34	$CH_3(CH_2)_4CH_2OH$		48		1q	54
35			48		1cc	58
36			20		1dd	79
37			24		1ee[d]	71

[a] Reaction conditions: ROH (1.3 mmol), Lawesson's reagent (0.78 mmol), ArX (1 mmol), K_2CO_3 (1.5 mmol), CuI (10 mol-%), and diglyme (2 mL). [b] Isolated yields. [c] 5% styrene as a by-product was detected by GC. [d] Reaction conditions: 1,3-propanediol (1 mmol), Lawesson's reagent (1.5 mmol), iodobenzene (2 mmol), K_2CO_3 (3 mmol), CuI (10 mol-%), and diglyme (2 mL).

tion of 1,3-propanediol was also studied; both hydroxyl groups participated in the reaction, and the desired sulfide product was obtained in 71% isolated yield (Table 2, entry 37).

To demonstrate this reaction on a larger scale, the reaction of iodobenzene (10 mmol) with Lawesson's reagent (6 mmol) and benzyl alcohol (13 mmol) in the presence of catalyst (1 mmol) was studied under similar optimized conditions. The reaction proceeded well, and desired sulfide product was obtained in 87% isolated yield.

The CuI catalyst is soluble under the reaction conditions, and reactions proceeded under homogeneous conditions. A proposed mechanism for this reaction is presented in Scheme 1. In the first step, nucleophilic attack of the alcohol onto a dipolar species of Lawesson's reagent produces an *O*-alkyl phosphonodithioic acid intermediate,[24b] which is then deprotonated by the base. Based on the fact that an optically active alcohol led to a racemic product (Table 2, entry 36), the resulting phosphonodithioic anion may be in equilibrium with an ion-pair intermediate. Next, the phosphonodithioic anion adds to carbon of alcohol ($-OCHR^1R^2$) to generate a thiolate ion. The resulting thiolate then reacts according to the well-known copper-catalysed coupling of thiols with aryl halides.[5b]

Scheme 1. Proposed mechanism for the reaction.

Conclusions

In conclusion, a new method for copper-catalysed carbon–sulfur bond formation based on the reaction of aryl halides, Lawesson's reagent, and alcohols has been developed. Using this protocol, primary and secondary alcohols reacted efficiently with aryl bromides and iodides. Reactions proceeded through the one-pot conversion of the alcohol into a thiolate by reaction with Lawesson's reagent. One of the important features of this protocol is the variety of commercially available alcohols that can be used, which makes this approach much easier than alternative methods that use the corresponding thiols. This strategy was successfully used for a large-scale reaction.

Experimental Section

General Remarks: All chemicals were purchased from Acros, Sigma–Aldrich, and Merck. Alcohols were distilled before use, and

were stored under dry argon gas. Reactions were monitored by thin-layer chromatography (silica gel 254 analytical sheets obtained from Fluka) or gas chromatography (Varian, cp-3800). Column chromatography was carried out on silica gel 60 Merck (230–240 mesh) in glass columns (2 or 3 cm diameter). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance (400 MHz) spectrometer, and chemical shifts are reported in ppm. Spectra were calibrated using residual nondeuterated solvent as an internal reference ($CDCl_3$: δ = 7.29 ppm). FTIR spectra were recorded with a Bruker Vector 22 instrument. CHN analysis was carried out with a vario EL instrument. Optical rotations were determined with a Perkin–Elmer 241 polarimeter.

General Procedure for Thioetherification of Aryl Halides Using Alcohols and Lawesson's Reagent: Alcohol (1.3 mmol), Lawesson's reagent (0.78 mmol), aryl halide (1 mmol), K_2CO_3 (1.5 mmol, 207 mg), CuI (10 mol-%, 19 mg), and diglyme (2 mL) were added to a 5 mL flask, and the mixture was magnetically stirred and heated under argon at 120 °C for the appropriate reaction time. The progress of the reaction was monitored by GC or TLC analysis. After the reaction was complete, the product was isolated using column chromatography on silica gel (EtOAc/*n*-hexane).

Typical Procedure for Thioetherification of Iodobenzene Using Benzyl Alcohol and Lawesson's reagent: Lawesson's reagent (6 mmol), benzyl alcohol (13 mmol), iodobenzene (10 mmol), K_2CO_3 (15 mmol, 2 g), CuI (1 mmol-%, 190 mg) and diglyme (20 mL) were added to a 25 mL flask, and the mixture was magnetically stirred and heated under argon at 120 °C for 12 h. Then the corresponding sulfide product was isolated by column chromatography on silica gel using *n*-hexane/EtOAc (5:1) as the eluent.

1a: White solid, m.p. 44–46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.22 (m, 10 H), 4.18 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.97, 136.91, 130.31, 129.39, 129.38, 129.04, 127.72, 126.87, 39.54 ppm. IR (KBr): $\tilde{\nu}$ = 3046, 2356, 1625, 1480, 1466, 1171, 1075, 723, 685, 474 cm^{-1}. $C_{13}H_{12}S$ (200.30): calcd. C 77.95, H 6.04, S 16.01; found C 78.04, H 6.01, S 15.95.

1b: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.24 (m, 7 H), 7.10 (d, J = 8 Hz, 2 H), 4.11 (s, 2 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.81, 136.61, 132.47, 130.72, 129.65, 128.87, 128.47, 127.11, 39.80, 21.10 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3025, 2921, 2859, 1492, 1450, 1087, 1025, 803, 704, 492 cm^{-1}. $C_{14}H_{14}S$ (214.32): calcd. C 78.46, H 6.58, S 14.96; found C 78.35, H 6.64, S 15.01.

1c: Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.23 (m, 7 H), 7.0–6.95 (m, 2 H), 4.06 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.82, 161.37, 138.01, 133.97, 133.89, 131.23, 131.20, 129.34, 128.96, 127.69, 116.52, 116.30, 40.95 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –114.84 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2920, 2856, 1489, 1082, 965, 806, 546 cm^{-1}. $C_{13}H_{11}FS$ (218.29): calcd. C 71.53, H 5.08, S 14.69; found C 70.43, H 5.16, S 14.63.

1d: Pale yellow solid, m.p. 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.4 Hz, 2 H), 7.41 (d, J = 8.8 Hz, 2 H), 7.30–7.24 (m, 5 H), 4.14 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.05, 145.57, 134.49, 131.07, 129.59, 129.11, 127.35, 123.72, 38.99 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3069, 2926, 2845, 1643, 1512, 1091, 901, 735, 470 cm^{-1}. $C_{13}H_{11}NO_2S$ (245.30): calcd. C 63.65, H 4.52, N 5.71, S 13.07; found C 63.78, H 4.61, N 5.64, S 12.97.

1e: Pale yellow solid, m.p. 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.8 Hz, 2 H), 7.42–7.38 (m, 4 H), 7.17–7.14 (m, 2 H), 4.14 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.15, 145.06, 133.65, 132.53, 132.20, 129.59, 123.81, 121.48, 38.94 ppm. IR (KBr): $\tilde{\nu}$ = 3073, 2919, 2848, 1634, 16.01, 1511, 1469, 1338, 1092, 802, 477 cm^{-1}. $C_{13}H_{10}BrNO_2S$ (324.19): calcd. C 48.16, H 3.11, N 4.32, S 9.89; found C 49.08, H 3.25, N 4.19, S 9.78.

1f: Yellow solid, m.p. 66–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.4 Hz, 2 H), 7.37 (d, J = 8.8 Hz, 2 H), 7.20 (d, J = 8 Hz, 2 H), 7.09 (d, J = 7.6 Hz, 2 H), 4.11 (s, 2 H), 2.34 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.97, 145.92, 137.71, 131.90, 130.59, 129.89, 129.60, 123.66, 39.65, 21.13 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3412, 2924, 2855, 1607, 1516, 1340, 1093, 856, 483 cm^{-1}. $C_{14}H_{13}NO_2S$ (259.32): calcd. C 64.74, H 5.05, N 5.40, S 12.36; found C 64.77, H 4.96, N 5.47, S 12.43.

1g: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.6 Hz, 2 H), 7.38–7.34 (m, 4 H), 7.30–7.23 (m, 4 H), 3.24 (t, J = 7.6 Hz, 2 H), 2.99 (t, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.27, 136.42, 129.25, 129.02, 128.59, 126.53, 126.05, 35.69, 35.14 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3064, 3027, 2924, 2853, 1585, 1483, 1444, 1083, 739, 697, 485 cm^{-1}. $C_{14}H_{14}S$ (214.32): calcd. C 78.46, H 6.58, S 14.96; found C 78.38, H 6.61, S 15.01.

1h: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.34 (m, 4 H), 7.27–7.24 (m, 3 H), 7.19–7.17 (m, 2 H), 3.19 (t, J = 7.2 Hz, 2 H), 2.96 (t, J = 7.2 Hz, 2 H), 2.39 (s, 3 H) ppm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 140.38, 136.25, 132.49, 130.14, 129.78, 128.56, 128.53, 126.44, 35.86, 35.80, 21.08 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3066, 3025, 2923, 2857, 1598, 1492, 1448, 1090, 1024, 804, 704, 494 cm^{-1}. $C_{15}H_{16}S$ (228.35): calcd. C 78.90, H 7.06, S 14.04; found C 79.14, H 6.89, S 13.97.

1i: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.31 (m, 6 H), 7.28–7.21 (m, 4 H), 2.98 (t, J = 7.6 Hz, 2 H), 2.82 (t, J = 7.6 Hz, 2 H), 2.07–2.0 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.35, 136.61, 129.15, 128.93, 128.58, 128.48, 126.05, 125.88, 34.74, 32.91, 30.68 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3413, 3064, 3025, 2927, 1584, 1483, 1444, 1083, 1024, 739, 695, 483 cm^{-1}. $C_{15}H_{16}S$ (228.35): calcd. C 78.90, H 7.06, S 14.04; found C 78.79, H 7.11, S 14.10.

1j: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 2 H), 7.36–7.21 (m, 10 H), 6.47 (d, J = 15.6 Hz, 1 H), 6.29 (dd, J = 7.2, 15.6 Hz, 1 H), 3.75 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.76, 135.84, 132.81, 130.30, 128.87, 128.55, 127.60, 126.45, 126.36, 125.08, 37.16 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3414, 3065, 2922, 1612, 1490, 1446, 1089, 1024, 803, 700, 493 cm^{-1}. $C_{15}H_{14}S$ (226.34): calcd. C 79.60, H 6.23, S 14.17; found C 79.46, H 6.28, S 14.26.

1k: Pale yellow solid, m.p. 70–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.25 (m, 7 H), 7.13 (d, J = 8 Hz, 2 H), 6.42 (d, J = 15.6 Hz, 1 H), 6.28 (dd, J = 7.2, 15.6 Hz, 1 H), 3.69 (d, J = 7.2 Hz, 2 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.85, 136.69, 132.59, 131.95, 131.15, 129.66, 128.54, 127.54, 126.36, 125.39, 37.88, 21.10 ppm. IR (KBr): $\tilde{\nu}$ = 2919, 2857, 1631, 1487, 1022, 800, 753, 685, 489 cm^{-1}. $C_{16}H_{16}S$ (240.36): calcd. C 79.95, H 6.71, S 13.34; found C 79.83, H 6.65, S 13.52.

1l: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 2 H), 7.69 (d, J = 7.6 Hz, 2 H), 7.33–7.23 (m, 6 H), 4.11 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.75, 147.34, 137.36, 134.57, 130.98, 129.13, 127.29, 123.83, 36.56 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3413, 3050, 2022, 2574, 1579, 1474, 1428, 1258, 1089, 1026, 803, 743, 697, 480 cm^{-1}. $C_{12}H_{11}NS$ (201.29): calcd. C 71.60, H 5.51, N 6.96, S 15.93; found C 71.42, H 5.43, N 7.10, S 16.05.

1m: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50–8.49 (m, 1 H), 8.43 (s, 1 H), 7.65 (d, J = 8 Hz, 2 H), 7.30–7.10 (m, 3 H), 7.09 (d, J = 8 Hz, 2 H), 4.05 (s, 2 H), 2.33 (s, 3 H) ppm. ^{13}C

NMR (100 MHz, $CDCl_3$): δ = 148.96, 147.46, 137.62, 137.19, 134.43, 131.84, 130.69, 129.89, 123.67, 37.25, 21.11 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3024, 2922, 2859, 1578, 1486, 1425, 1093, 1027, 805, 711, 494 cm^{-1}. $C_{13}H_{13}NS$ (215.31): calcd. C 72.52, H 6.09, N 6.51, S 14.89; found C 72.68, H 6.13, N 6.46, S 14.73.

1n: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8 Hz, 2 H), 7.34 (d, J = 7.6 Hz, 2 H), 7.23–7.20 (m, 1 H), 2.98 (t, J = 7.4 Hz, 2 H), 1.75–1.68 (m, 2 H), 1.53–1.49 (m, 2 H), 1.46–1.36 (m, 3 H), 0.96 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.17, 128.86, 125.64, 33.61, 31.45, 29.19, 28.61, 22.63, 14.11 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2924, 2858, 1582, 1470, 1449, 1091, 1023, 799, 736 cm^{-1}. $C_{12}H_{18}S$ (194.33): calcd. C 74.16, H 9.34, S 16.50; found C 74.25, H 9.20, S 16.55.

1o: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.31 (m, 4 H), 7.22–7.18 (m, 1 H), 2.96 (t, J = 7.2 Hz, 2 H), 1.73–1.65 (m, 2 H), 1.48–1.31 (m, 10 H), 0.93 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.10, 128.84, 128.82, 125.63, 33.58, 31.85, 29.23, 29.19, 29.18, 28.91, 22.70, 14.16 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2924, 2856, 1582, 1469, 1450, 1089, 1024, 802, 736 cm^{-1}. $C_{14}H_{22}S$ (222.39): calcd. C 75.61, H 9.97, S 14.42; found C 75.53, H 10.02, S 14.45.

1p: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.4 Hz, 2 H), 7.33 (d, J = 8.4 Hz, 2 H), 3.04 (t, J = 7.6 Hz, 2 H), 1.78–1.70 (m, 2 H), 1.48–1.28 (m, 13 H), 0.90 (t, J = 6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.25, 125.94, 125.94, 123.95, 31.92, 31.79, 29.16, 29.11, 28.92, 28.48, 22.67, 14.13 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2924, 2856, 1643, 1583, 1336, 1090, 843, 738, 532 cm^{-1}. $C_{14}H_{21}NO_2S$ (267.39): calcd. C 62.89, H 7.92, N 5.24, S 11.99; found C 62.72, H 7.87, N 5.31, S 12.02.

1q: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.8 Hz, 2 H), 7.33 (d, J = 8.8 Hz, 2 H), 3.04 (t, J = 7.6 Hz, 2 H), 1.78–1.71 (m, 2 H), 1.51–1.44 (m, 2 H), 1.36–1.28 (m, 4 H), 0.92 (t, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.21, 144.83, 125.98, 123.94, 31.95, 31.30, 28.57, 28.46, 22.51, 14.01 ppm. $C_{12}H_{17}NO_2S$ (239.33): calcd. C 60.22, H 7.16, N 5.85, S 13.40; found C 59.94, H 7.01, N 5.78, S 13.21.

1r: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 4.8 Hz, 2 H), 7.47–7.23 (m, 5 H), 7.02–6.99 (m, 1 H), 6.69 (d, J = 15.6 Hz, 2 H), 6.39 (dd, J = 7.2, 15.6 Hz, 1 H), 4.03 (dd, J = 1.2, 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.01, 157.29, 136.83, 133.04, 128.55, 127.60, 126.40, 124.77, 116.58, 33.48 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3030, 2925, 1556, 1380, 1193, 966, 755, 696 cm^{-1}. $C_{13}H_{12}N_2S$ (228.31): calcd. C 68.39, H 5.30, N 12.27, S 14.04; found C 68.52, H 5.38, N 12.16, S 13.94.

1s: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, J = 4.8 Hz, 2 H), 6.98–6.96 (m, 1 H), 3.17 (t, J = 7.2 Hz, 2 H), 1.79–1.71 (m, 2 H), 1.51–1.44 (m, 2 H), 1.34–1.29 (m, 8 H), 0.90 (t, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.85, 157.16, 116.25, 31.84, 30.92, 29.19, 29.18, 29.10, 28.94, 22.67, 14.13 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2924, 2856, 1556, 1458, 1380, 1194, 761 cm^{-1}. $C_{12}H_{20}N_2S$ (224.36): calcd. C 64.24, H 8.98, N 12.49, S 14.29; found C 64.11, H 9.04, N 12.53, S 14.32.

1t: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.04 (s, 1 H), 8.58 (s, 1 H), 7.32–7.24 (m, 6 H), 4.12 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.35, 156.58, 136.08, 129.01, 128.87, 128.83, 127.85, 39.03 ppm. $C_{11}H_{10}N_2S$ (202.27): calcd. C 65.32, H 4.98, N 13.85, S 15.85; found C 65.44, H 4.94, N 13.83, S 15.79.

1u: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.19 (m, 5 H), 3.14–3.06 (m, 2 H), 2.01–1.97 (m, 2 H), 1.77–1.63 (m, 3 H), 1.40–1.26 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.15, 131.84, 128.73, 126.56, 46.54, 33.33, 26.05, 25.76 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3060, 2927, 2854, 1727, 1578, 1473, 1441, 1027, 742, 690 cm^{-1}. $C_{12}H_{16}S$ (192.32): calcd. C 74.94, H 8.39, S 16.67; found C 74.75, H 8.47, S 16.78.

1v: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, J = 8 Hz, 2 H), 7.13 (d, J = 7.6 Hz, 2 H), 3.07–3.02 (m, 1 H), 2.36 (s, 3 H), 2.01–1.98 (m, 2 H), 1.80–1.64 (m, 3 H), 1.41–1.24 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.90, 132.81, 131.18, 129.82, 129.55, 128.54, 47.11, 33.39, 26.13, 25.80, 21.12 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3022, 2928, 2853, 1491, 1448, 806, 501 cm^{-1}. $C_{13}H_{18}S$ (206.35): calcd. C 75.67, H 8.79, S 15.54; found C 75.61, H 8.80, S 15.59.

1w: Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.8 Hz, 2 H), 6.87 (d, J = 8.4 Hz, 2 H), 3.82 (s, 3 H), 2.96–2.91 (m, 1 H), 1.97–1.95 (m, 2 H), 1.79–1.63 (m, 2 H), 1.63–1.61 (m, 1 H), 1.38–1.22 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.33, 135.64, 124.96, 114.30, 55.30, 47.92, 33.41, 26.16, 25.81 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2929, 2848, 1588, 1490, 1451, 1285, 1245, 1177, 1033, 825, 636, 527 cm^{-1}. $C_{13}H_{18}OS$ (222.34): calcd. C 70.22, H 8.16, S 14.42; found C 70.53, H 8.07, S 14.35.

1x: Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 1 H), 7.27 (d, J = 8 Hz, 2 H), 7.16–7.12 (m, 4 H), 4.15 (s, 2 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.36, 134.72, 134.38, 133.50, 131.86, 131.48, 131.37, 129.83, 129.45, 127.0, 37.26, 21.20 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3024.3, 2924.8, 2862.3, 1587.4, 1478.2, 1096.8, 1048.2, 808.2, 498.2 cm^{-1}. $C_{14}H_{12}Cl_2S$ (283.21): calcd. C 59.37, H 4.27, S 11.32; found C 59.58, H 4.16, S 11.02. MS (EI, 70 eV): m/z = 282.1 $[M]^+$.

1y: Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 1 H), 7.40–7.30 (m, 2 H), 7.14–6.97 (m, 4 H), 4.10 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.75, 161.29, 134.69, 134.61, 134.06, 133.65, 131.45, 129.69, 129.65, 129.52, 126.98, 116.23, 116.01, 37.86 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3065.3, 2925.7, 2855.9, 1587.6, 1480.4, 1227.1, 1094.9, 828.1, 554.2 cm^{-1}. $C_{13}H_9Cl_2FS$ (287.18): calcd. C 54.37, H 3.16, S 11.17; found C 54.11, H 3.01, S 11.39. MS (EI, 70 eV): m/z = 285.8 $[M]^+$.

1z: Pale yellow solid, m.p. 88–91 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.21 (m, 7 H), 6.86 (d, J = 8.4 Hz, 2 H), 4.12 (s, 2 H), 3.82 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.77, 136.57, 129.97, 129.76, 129.38, 128.86, 126.28, 113.92, 55.30, 38.45 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2955.5, 2913.6, 2355.4, 1510.1, 1303.1, 1096.4, 1029.8, 825.3, 740.4, 515.1 cm^{-1}. $C_{14}H_{14}OS$ (230.32): calcd. C 73.01, H 6.13, S 13.92; found C 73.34, H 6.26, S 13.67.

1aa: Pale yellow solid, m.p. 65–67 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.26 (m, 3 H), 7.21–7.13 (m, 3 H), 6.88 (d, J = 8.8 Hz, 2 H), 4.09 (s, 2 H), 3.83 (s, 3 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.82, 137.74, 136.06, 130.06, 130.04, 129.16, 128.69, 126.44, 125.99, 113.95, 55.31, 37.66, 20.36 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3060.1, 2925.3, 2841.8, 1596.5, 1506.4, 1304.2, 1029.3, 833.7, 745.05, 689.7 cm^{-1}. $C_{15}H_{16}OS$ (244.35): calcd. C 73.73, H 6.60, S 13.12; found C 73.48, H 6.72, S 13.32.

1bb: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, J = 8 Hz, 2 H), 7.17 (d, J = 8 Hz, 2 H), 3.76–3.72 (m, 1 H), 2.38–2.36 (m, 4 H), 2.36–1.74 (m, 4 H), 1.64–1.58 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.06, 133.56, 130.0, 129.66, 84.01, 38.90, 34.93, 31.29, 26.81, 22.54, 21.23, 14.06 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3298.1, 2928.4, 2861.1, 1492.6, 1455.8, 1098.9, 1022.7, 806.7, 636.9, 500.5 cm^{-1}. $C_{15}H_{20}S$ (232.38): calcd. C 77.53, H 8.67, S 13.80; found C 77.81, H 8.55, S 13.64. MS (EI, 70 eV): m/z = 232.3 $[M]^+$.

1cc: Pale yellow solid, m.p. 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.6 Hz, 2 H), 7.43–7.32 (m, 7 H), 4.28 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.31, 145.22, 135.46, 128.88, 128.75, 127.84, 126.61, 123.95, 37.02 ppm. $C_{13}H_{11}NO_2S$ (245.30): calcd. C 63.65, H 4.52, N 5.71, S 13.07; found C 63.74, H 4.402, N 5.84, S 13.19.

1dd: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.22 (m, 5 H), 7.21–7.17 (m, 2 H), 7.04 (d, J = 8 Hz, 2 H), 4.02–3.98 (m, 1 H), 2.31 (s, 1 H), 2.04–1.92 (m, 2 H), 0.93 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.10, 137.19, 133.06, 131.29, 129.43, 128.27, 127.91, 126.97, 55.75, 29.22, 21.13, 12.32 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3024.9, 2963.5, 2924.9, 1490.9, 1451.6, 1091.3, 1023.2, 804.6, 701.8 cm^{-1}. $C_{16}H_{18}S$ (242.38): calcd. C 79.29, H 7.49, S 13.22; found C 79.53, H 7.29, S 13.18.

1ee: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.21 (m, 8 H), 7.23–7.20 (m, 2 H), 3.09 (t, J = 7.2 Hz, 4 H), 2.03–1.96 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.04, 129.38, 128.98, 126.11, 32.42, 28.31 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3416, 3062, 2955, 2920, 1581, 1475, 1434, 1257, 1087, 1022, 799, 738, 691, 621, 482 cm^{-1}. $C_{15}H_{16}S_2$: C 69.18, H 6.19, S 24.63; found C 69.31, H 6.15, S 24.54.

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