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The first examples of rhodium-catalyzed 1,4-conjugate addition reactions of arylboronic acids with ethenesulfonamides

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ABSTRACT

An unprecedented rhodium-catalyzed 1,4-conjugate addition of arylboronic acids with ethenesulfonamides resulting in the corresponding 2-arylethanesulfonamides is described. The amino substituent, the applied arylboronic acid, the type of Rh-catalyst, and the experimental conditions all affected the reaction outcome.

2-Arylethanesulfonamides (Fig. 1) constitute an important class of compounds in the medicinal chemistry area.[1] These compounds are synthetically accessible from the appropriate 2-arylethanesulfonyl chloride and amine.[2] However, the synthesis of the required arylethanesulfonyl chlorides generally is not straightforward. Different methods have been described, for example, heating 2-arylethyl bromides with aqueous Na_2SO_3, followed by treatment with $SOCl_2$ in benzene.[3] Alternatively, in the presence of a chlorinating reagent such as SO_2Cl_2 in combination with KNO_3 in acetonitrile,[4] NCS in dichloromethane/water[5] or dissolved chlorine gas in methanol/water,[6] 2-arylethylmercaptans can be converted into the corresponding sulfonyl chlorides. Treatment of 2-arylethylsulfonic acids or 2-arylethylsulfinyl chlorides with $SOCl_2$ in benzene[3] or with chlorine gas[7] is an additional reported option to obtain arylethanesulfonyl chlorides. Recently, a number of 2-arylethanesulfonamides were required for one of our research projects. Based on our interest in metal-catalyzed chemistry,[8] we considered preparing such compounds by Rh-catalyzed 1,4-conjugate addition reactions of arylboronic acids with ethenesulfonamides (Fig. 2). Although Rh-catalyzed conjugate addition reactions of arylboronic acids have a broad scope,[9] application of this reaction to ethenesulfonamides has, to the best of our knowledge, not been reported. In this Letter, we disclose our preliminary results in this area.

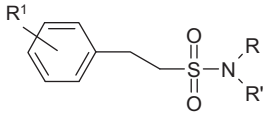

Figure 1. 2-Arylethanesulfonamides.

Rh-catalyzed 1,4-conjugate additions of arylboronic acids with α,β-unsaturated carbonyl derivatives have become an important tool in synthetic organic chemistry. Since the first publication in 1997 by Miyaura et al.,[10] a number of other activated vinyl substrates have been applied for conversion into their saturated analogs by the application of this reaction.[9] In 1998, Hayashi et al.,[11] showed that by running these reactions in the presence of (*S*)-BINAP, chiral compounds could be obtained in enantiomerically enriched form. Rh-catalyzed 1,4-conjugate additions have become a broad scope conversion which is not only restricted to laboratory scale. AstraZeneca for example, have demonstrated a conjugate addition reaction on kilogram-scale for the synthesis of rolipram.[12]

Our first attempt at the preparation of 2-arylethanesulfonamides by a rhodium-catalyzed 1,4-conjugate addition involved the reaction between 3-chlorophenylboronic acid and ethenesulfonamide **1**.[13] Compound **1** was easily obtained by the reaction of commercially available 2-chloroethylsulfonyl chloride with triethylamine in dichloromethane at low temperature to induce β-elimination of the chloride anion followed by reaction with methylamine (Scheme 1). The conditions described by Willis and Frost,[14] (6 mol % $Rh(acac)(C_2H_4)$, 6.6 mol % *rac*-BINAP, 1,4-diox

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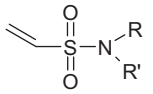
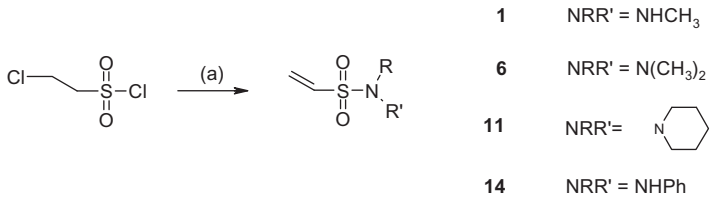
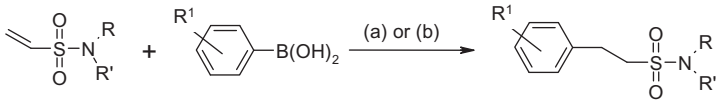


Figure 2. Ethenesulfonamides.

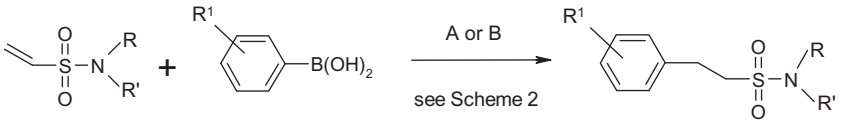


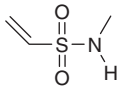
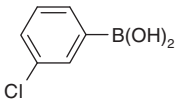
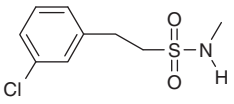
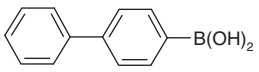
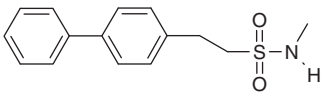
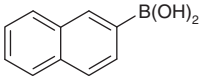
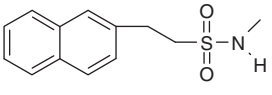
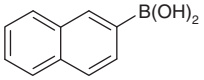
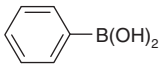
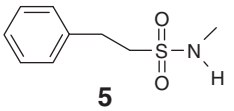
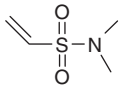
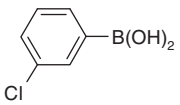
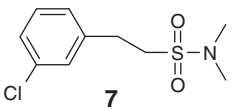
Scheme 1. Reagents and conditions: (a) (i) 2-hloroethylsulfonylchloride (1 mol equiv), Et_3N (1.1 mol equiv), CH_2Cl, −60 °C, 2 h; (ii) Et_3N (1.1 mol equiv), HNRR′ (1.1 mol equiv), CH_2Cl_2, −60 °C to rt.



Scheme 2. Reagents and conditions: (a) Procedure A[15], ethenesulfonamide (1 mmol), arylboronic acid (4 mmol), 6 mol % Rh(acac)(C_2H_4), 6.6 mol % *rac*-BINAP, 15 ml 1,4-dioxane/H_2O 10:1 (v/v), 100 °C, 18 h. (b) Procedure B[18], ethenesulfonamide (1 mmol), arylboronic acid (4 mmol), 2 mol % [Rh(cod)OH]$_2$, 6 mol % *rac*-BINAP, 3 ml 1,4-dioxane/H_2O 99:1 (v/v), screw-sealed tube, 120 °C, 18 h.

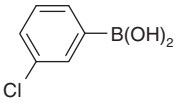
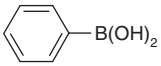
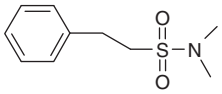
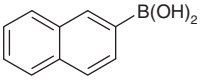
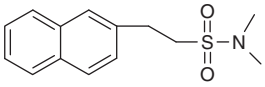
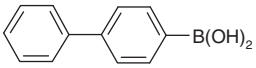
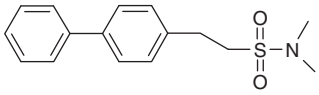
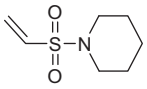
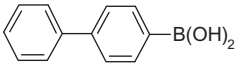
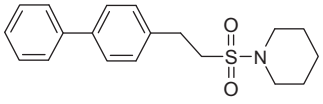
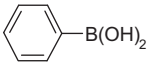
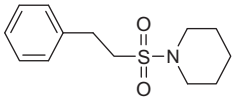
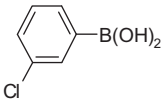
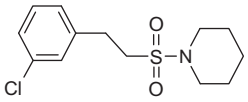
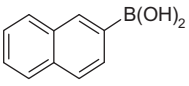
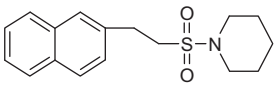
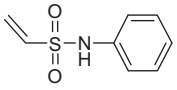
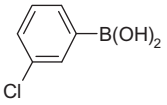
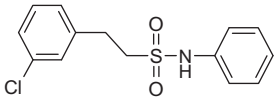
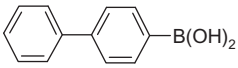
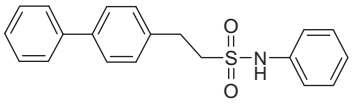
Table 1
Conjugate addition reactions of arylboronic acids with ethenesulfonamides



Entry	Ethenesulfonamide	$ArB(OH)_2$	Procedures[15,18]	Product	Yield (%)[a]
1	 **1**		A	 **2**	65
2	1		A	 **3**	51
3	1		A	 **4**	28
4	1		B	4	40
5	1		B	 **5**	55[b,c]
6	 **6**		A	 **7**	0

(*continued on next page*)

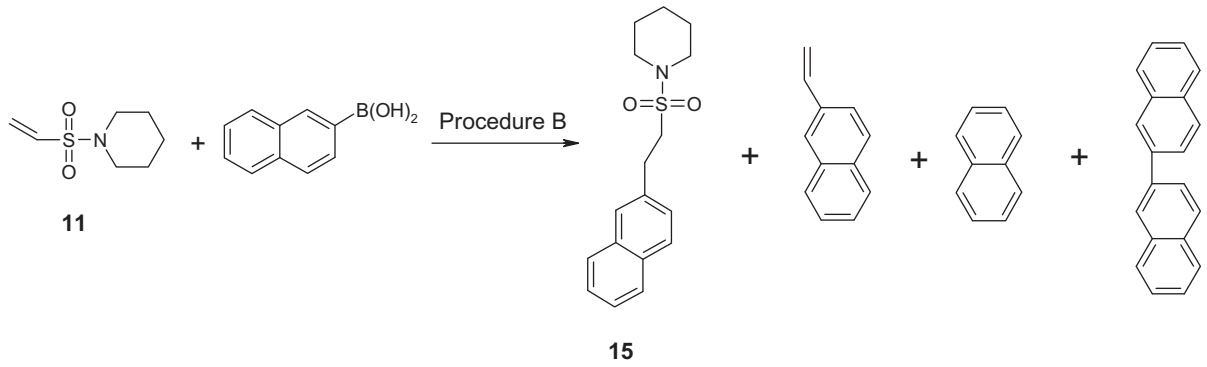
Table 1 (*continued*)

Entry	Ethenesulfonamide	$ArB(OH)_2$	Procedures[15,18]	Product	Yield (%)[a]
7	6		B	7	64
8	6		B	 **8**	48
9	6		B	 **9**	46
10	6		B	 **10**	33
11	 **11**		B	 **12**	40
12	11		B	 **13**	19
13	11		B	 **14**	<10[d]
14	11		B	 **15**	10
15	 **14**		B	 **16**	61
16	14		B	 **17**	47

[a] Isolated yields of pure compounds.
[b] Yield with the phenylboronpinacol ester: 17% (see text).
[c] Yield with the potassium phenyltrifluoroborate: 24% (see text).
[d] No spectral data available due to the presence of impurities.

ane/water, 10:1 (v/v), 100 °C) were applied for the Rh-catalyzed conjugate addition. On a 1 mmol scale, compound **1** was reacted with 4 M equiv of 3-chlorophenylboronic acid in 15 ml of solvent (Scheme 2, procedure A, Table 1, entry 1).[15] A fair yield (65%) of sulfonamide **2** was obtained after purification by flash chromatography. It should be noted that the isolation of **2** by flash chromatography was troublesome due to the small difference in R_f values with **1** in combination with the low UV absorption rate of both **1** and **2**. Interestingly, the presence of chlorine atom on **2** allows further functionalization by Pd cross-coupling chemistry.[16]

Encouraged by this result, 4-biphenylboronic acid was analogously reacted with **1** to produce **3** in an acceptable yield of 51% (Table 1, entry 2). However, in the case of 2-naphthaleneboronic acid, only a modest yield of 28% of **4** was isolated (Table 1, entry 3). After a thorough survey of the reaction procedure, it was found that the yield of this particular reaction could be raised to 40% by adapting Lautens[17] conditions in Rh-catalyzed reactions of arylboronic acids on allyl sulfones, viz. 2 mol % $[Rh(cod)OH]_2$, 6 mol % *rac*-BINAP, 3 ml 1,4-dioxane/water, 99:1 (v/v), 1 mmol of **1**, 4 M equiv of the applied boronic acid, and heating in a screw-sealed tube at



Scheme 3. Reagents and conditions: Procedure B[18], ethenesulfonamide **11** (1 mmol), 2-naphthaleneboronic acid (4 mmol), 2 mol % $[Rh(cod)OH]_2$, 6 mol % *rac*-BINAP, 3 ml 1,4-dioxane/H_2O 99:1 (v/v), screw-sealed tube, 120 °C, 18 h.

120 °C (Scheme 2, procedure B, Table 1, entry 4).[18] Deborylation and homo-coupling of 2-naphthaleneboronic acid constituted major side reactions. Compound **5**[2] was obtained in a yield of 55% by using procedure B (Scheme 2)[18] (Table 1, entry 5).

To investigate the scope of ethenesulfonamide substrates, compound **6**[19] was prepared in the same way as compound **1** (Scheme 1), followed by Rh-catalyzed conjugate addition with 3-chlorophenylboronic acid according to the procedure of Willis and Frost (Scheme 2, procedure A).[15] In contrast with the result obtained with **1**, no product was detected (Table 1, entry 6). After purification, only sulfonamide **6** was isolated together with deborylation and homo-coupling products of 3-chlorophenylboronic acid. Based on literature reports from Carrerero and Lautens,[20] it can be speculated that the lack of reactivity is caused by decreased coordination of the initially formed Ar-Rh(I) species to **6**. An analogous finding was reported in the Cu-catalyzed 1,4-conjugate additions of Grignard reagents[21] and dialkylzinc reagents[22] to α,β-unsaturated pyridylsulfones.

Gratifyingly, using procedure B[18] (Scheme 2), the reaction succeeded and the addition product **7** was isolated in a yield of 64% (Table 1, entry 7). The reaction of **6** with phenylboronic acid and with 2-naphthaleneboronic acid also resulted in the desired products (Table 1, compounds **8** and **9**, entries 8 and 9). The observed yield with 4-biphenylboronic acid was somewhat lower, primarily due to a tedious purification (Table 1, compound **10**, entry 10).

So far, only ethenesulfonamides were used that contained an acyclic aliphatic amino group. In order to verify the reactivity of ethenesulfonamides containing a cyclic aliphatic amino group, compound **11**[23] was prepared (Scheme 1) and subjected to our Rh-catalyzed conversion using procedure B[18] (Scheme 2). Compound **12** was furnished in 40% yield (Table 1, entry 11). The reaction yields (<20%) of **11** with phenylboronic acid, 3-chlorophenylboronic acid, and 2-naphthaleneboronic acid were very disappointing. (Table 1, entries 12–14). It was verified that all of the starting material **11** was converted during these reactions (entries 11–14). Decreasing the reaction temperature and extending the reaction time had no positive effect on the yields.

These results prompted us to verify the chemical stability of **11**. Two experiments were initiated for clarification of this point. First, **11** was heated at 100 °C in a screw-sealed tube without boronic acid in 1,4-dioxane/water, 99:1 (v/v) in the presence of $[Rh(cod)OH]_2$ and *rac*-BINAP. Second, both the boronic acid and rhodium catalyst/*rac*-BINAP were omitted. In both cases, after prolonged heating for 72 h, compound **11** was still present and no decomposition products were detected, that is, **11** remained stable under these conditions. The experiment between **11** and 2-naphthaleneboronic acid was repeated according to procedure B[18] (Scheme 2). The reaction mixture was evaporated after 20 h. ^1H NMR analysis of the crude material revealed the absence of **11**, the presence of a trace product, and the expected presence of naphthalene and 2,2′-binaphthalene. Unexpectedly, the presence of 2-vinylnaphthalene in the crude reaction mixture was demonstrated (Scheme 3). After flash chromatography, **15** was isolated in a low yield of 10%. Due to the small difference in R_f values, naphthalene, 2,2′-binaphthalene and 2-vinylnaphthalene were isolated in one fraction. The overall mass balance of the isolated fractions was almost quantitative. Based on the outcome of the stability experiments on **11**, it can be assumed that **15** partly decomposed under these experimental conditions. Further indications of this decomposition were found in the ^1H NMR spectrum of crude **12** wherein the presence of 4-vinylbiphenyl was observed. Apparently, elimination of the sulfonylpiperidine group from the formed product is a significant side reaction.

The *N*-phenylethenesulfonamide (**14**)[24] was prepared (Scheme 1) in order to complete the investigation on the scope of ethenesulfonamides. Compound **14** was briefly investigated in Rh-catalyzed conjugate additions with 3-chlorophenylboronic acid and 4-biphenylboronic acid, respectively, which furnished **16** and **17** in reasonable yields (Table 1, entries 15 and 16). Heteroarylboronic acids, such as the pyridylboronic acids, form a difficult class for Rh-catalyzed 1,4-conjugate additions on activated alkenes. Nevertheless, the reaction between 3-pyridylboronic acid and **1** and with **6** using procedure B[18] was attempted (Scheme 2) but led only to isolation of the starting ethenesulfonamides. Indole-4-boronic acid as another heteroarylboronic acid example, gave the same unsatisfactory result, in line with reports in the literature[25] that suggested poisoning of Rh-catalysts by complexation with the N atoms of pyridine and indole, respectively.

Finally, the potential differences in reactivity between phenylboronic acid, phenylboronic acid pinacol ester, and potassium phenyltrifluoroborate in the rhodium-catalyzed 1,4-conjugated addition reaction on ethenesulfonamides were briefly explored. It was established that the conversion of the boron pinacol ester was incomplete on reaction with **1** according to procedure B[18] (Scheme 2) since compound **5** was isolated in a low yield (17%) and a substantial amount of starting material was present. Application of the same procedure to potassium phenyltrifluoroborate also resulted in a low yield of 24%. It can be concluded that for this type of Rh-catalyzed addition reaction the boronic acid moiety is superior in comparison with pinacol ester and potassium trifluoroborate moieties (see Table 1, entry 5)

In conclusion, a novel one-step conversion is presented for the synthesis of 2-arylethanesulfonamides via Rh-catalyzed 1,4-conjugate additions of arylboronic acids with ethenesulfonamides. The yields appear to depend strongly on the specific substituent patterns of the applied reagents. Although the scope of the reaction

needs to be explored in more detail, this straightforward method should allow fast access to the 2-arylethanesulfonamide chemotype. Despite their relatively simple chemical structures, all the reported 2-arylethanesulfonamides in Table 1, except for **5**[2] are, to the best of our knowledge, novel compounds. Unfortunately, we are in the future unable to optimize or extend the scope of this methodology due to the cessation of the research activities at our site.

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15. *General procedure for the Rh-catalyzed 1,4-conjugate addition according to procedure A* (Scheme 2): A dried 25 ml, three-necked reaction vessel was charged with degassed [1,4-dioxane/water,15 ml, 10:1 (v/v)] followed by the addition of **1** (121 mg, 1 mmol) and 3-chlorophenylboronic acid (624 mg, 4 mmol). After addition of $Rh(acac)(C_2H_4)_2$ (6 mol %, 17 mg, 0.06 mol) and *rac*-BINAP (6.6 mol %, 41 mg, 0.066 mol), the stirred mixture was heated in a pre-heated oil bath at 100 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc (10 ml) and extracted with 5% aqueous $NaHCO_3$ solution (10 ml). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude obtained material was further purified by flash chromatography [silica gel 60 (0.040–0.063 nm, Merck)], eluent Et_2O – petroleum ether (40–60), 3:1 (v/v) or CH_2Cl_2 – EtOAc, 9:1 (v/v), to give 150 mg of pure **2** (65%). Spectral data for the compounds described in Table 1, according to procedure A (Scheme 2): **2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.76 (d, J = 8 Hz, 3H), 3.07–3.12 (m, 2H), 3.25–3.30 (m, 2H), 4.18 (br d, J = 4 Hz, 1H), 7.12 (br d, J = 4 Hz, 1H), 7.24 (t, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.34, 29.57, 52.19, 126.61, 127.25, 128.49, 130.18, 134.64, 139.89. HRMS (ES^+): calcd for $C_9H_{12}NClO_2S$ $(M)^+$: 233.0277; found: 233.0253. **3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75 (d, J = 8 Hz, 3H), 3.14–3.20 (m, 2H), 3.30–3.36 (m, 2H), 3.93–3.99 (m, 1H), 7.29–7.38 (m, 3H), 7.44 (t, J = 8 Hz, 2H), 7.55–7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.40, 29.61, 52.35, 127.01, 127.43, 127.62, 128.82, 128.85, 136.89, 140.05, 140.51. HRMS (ES^+): calcd for $C_{15}H_{17}NO_2S$ $(M)^+$: 275.0980; found: 275.1068. **4**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.72 (d, J = 8 Hz, 3H), 3.27–3.31 (m, 2H), 3.38–3.40 (m, 2H), 3.92 (br d, J = 4 Hz, 1H), 7.35 (dd, J = 4 and 2 Hz, 1H), 7.46–7.50 (m, 2H), 7.69 (s, 1H), 7.78–7.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.39, 30.14, 52.26, 125.91, 126.40, 126.52, 126.87, 127.57, 127.77, 128.73, 132.35, 133.52, 135.27. HRMS (ES^+): calcd for $C_{13}H_{15}NO_2S$ $(M)^+$: 249.0824; found: 249.0898.
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18. *General procedure for the Rh-catalyzed 1,4-conjugate addition according to procedure B*, (Scheme 2): A dried 25 ml, screw-sealed tube was charged with degassed [1,4 dioxane/water, 3 ml, 99:1 (v/v)], followed by the addition of **6** (140 mg, 1 mmol) and 3-chlorophenylboronic acid (624 mg, 4 mmol). After addition of $[RhOH(cod)]_2$ (2 mol %, 9.1 mg, 0.02 mol) and *rac*-BINAP (6 mol %, 37 mg, 0.06 mol), the tube was closed. After removing air by vacuum the tube was back-filled with nitrogen and heated in a pre-heated oil bath at 120 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc (5 ml) and extracted with 5% aqueous $NaHCO_3$ solution (5 ml). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude obtained **7** was further purified by flash chromatography [silica gel 60 (0.040–0.063 nm, Merck)] eluent, Et_2O-petroleum ether (40–60), 3:1 (v/v) or CH_2Cl_2 – EtOAc,, 95:5 (v/v), to give 158 mg of pure **7** (64%). Spectral data are given for the compounds described in Table 1, according to procedure B, (Scheme 2): **7**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88 (s, 6H), 3.08–3.17 (m, 4H), 7.09–7.13 (m, 1H), 7.24 (br t, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.00, 37.45, 49.27, 126.62, 127.18, 128.52, 130.14, 134.59, 140.13. HRMS (ES^+): calcd for $C_{10}H_{14}ClNO_2S$ $(M)^+$: 247.0248; found: 247.0317. **8**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88 (s, 6H), 3.10–3.20 (m, 4H), 7.22 (br d, J = 8 Hz, 2H), 7.26 (br t, J = 4 Hz, 1H), 7.33 (br t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.31, 37.47, 49.65, 126.95, 128.37, 128.87, 138.16. HRMS (ES^+): calcd for $C_{10}H_{15}NO_2S$ $(M)^+$: 213.0667; found: 213.0708. **9**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.89 (s, 6H), 3.23–3.32 (m, 4H), 7.34 (dd, J = 8 and 2 Hz, 1H), 7.44–7.50 (m, 2H), 7.67 (s, 1H), 7.78–7.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.49, 37.49, 49.60, 125.84, 126.40, 126.55, 126.84, 127.49, 127.70, 128.62, 132.33, 133.56, 135.57. HRMS (ES^+): calcd for $C_{14}H_{17}NO_2S$ $(M)^+$: 263.0980; found: 263.0929. **10**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.89 (s, 6H), 3.16–3.21 (m, 4H), 7.30 (br d, J = 8 Hz, 2H), 7.35 (br t, J = 8 Hz, 1H), 7.44 (br t, J = 8 Hz, 2H), 7.56 (br t, J = 8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.95, 37.49, 49.57, 127.02, 127.37, 127.57, 128.82, 128.85, 137.19, 139.95, 140.62. HRMS (ES^+): calcd for $C_{16}H_{19}NO_2S$ $(M)^+$: 289.1137; found: 289.1155. **12**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55–1.70 (m, 6H), 3.23–3.33 (m, 6H), 3.53–3.58 (m, 2H), 7.44–7.53 (m, 3H), 7.62 (d, J = 4 Hz, 2H), 7.80 (d, J = 4 Hz, 2H), 7.98 (d, J = 4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.62, 25.59, 42.34, 46.74, 50.43, 127.46, 128.29, 128.58, 128.93, 129.19, 136.73, 139.10, 147.55. HRMS (ES^+): calcd for $C_{19}H_{23}NO_2S$ $(M)^+$: 329.4647; found 329.4532. **13**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43–1.51 (m, 4H), 1.56–1.64 (m, 4H), 3.06 (s, 2H), 3.11 (t, J = 8 Hz, 2H), 3.18 (t, J = 8 Hz, 2H), 7.16 (t, J = 8 Hz, 2H), 7.26 (t, J = 8 Hz, 1H), 7.32–7.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.76, 24.64, 28.33, 45.58, 49.62, 127.35, 128.60, 129.78, 137.23. HRMS (ES^+): calcd for $C_{13}H_{19}NO_2S$ $(M)^+$: 253.1137; found: 253.1068. **15**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51–1.68 (m, 6H), 3.18–3.31 (m, 8H), 7.32 (br d, J = 8 Hz, 1H), 7.44–7,48 (m, 2H), 7.65 (s, 1H), 7.77–7.82 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.95, 25.91, 29.59, 46.85, 50.75, 128.90, 126.42, 126.60, 126.98, 127.58, 127.95, 128.88, 132.38, 133.40, 135.65. HRMS (ES^+): calcd for $C_{17}H_{21}NO_2S$ $(M)^+$: 303.1293; found: 303.1262. **16**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.08–3.11 (m, 2H), 3.32–3.37 (m, 2H), 6.41 (br s, 1H), 7.02–7.05 (m, 1H), 7.09–7.23 (m, 6H), 7.31–7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.50, 52.31, 120.55, 125.48, 126.68, 127.35, 128.59, 129.76, 130.19, 134.70, 136.33, 139.41. HRMS (ES^+): calcd for $C_{14}H_{14}ClNO_2S$ $(M)^+$: 295.0434; found: 295.0182. **17**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.16–3.21 (m, 2H), 3.37–3.42 (m, 2H), 6.16 (br s, 1H), 7.07 (d, J = 8 Hz, 2H), 7.14–7.25 (m, 3H), 7.28–7.38 (m, 3H), 7.44 (t, J = 8 Hz, 2H), 7.51–7.57 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.58, 52.57, 120.51,

125.36, 127.01, 127.45, 127.68, 128.85, 128.93, 129.66, 136.41, 136.49, 140.18, 140.50. HRMS (ES^+): calcd for $C_{20}H_{19}NO_2S$ $(M)^+$: 337.4439; found 337.4328.
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