The Synthesis of *N*-TBS–*S*-Alkynyl Sulfoximines

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Abstract: Treatment of β-keto sulfoximines with triflic anhydride and Hünig's base in toluene resulted in the formation of *S*-alkynyl sulfoximines in good yield.

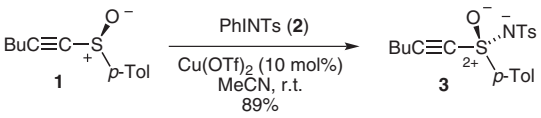
Key words: sulfoximine, alkyne, triflic anhydride, Hünig's base

The sulfoximine functional group is one of established and growing significance in organic chemistry.[1] By virtue of the fact that it can be easily rendered enantiomerically pure and is relatively robust, this group has found great utility in the design and development of chiral ligands[2] and chiral scaffolds,[3] with important implications for organic synthesis.

Given the impact this functional group has had it is interesting to note that its combination with other functional groups is not as common as might be expected. While *S*-alkynyl sulfones are common and easily accesible,[4] *S*-alkynyl sulfoximines are much more rare and can justifiably be characterized as an emerging functional group whose chemistry remains to be completely explored.

Two approaches have been reported for the synthesis of *S*-alkynyl sulfoximines. Craig reported that dehydration of an *N*-tosyl and *N*-triflyl β-keto sulfoximine resulted in the formation of the corresponding *S*-alkynyl sulfoximines in 44–77% yields.[5] It is essentially this procedure that we used in the generation of our sulfoximines.

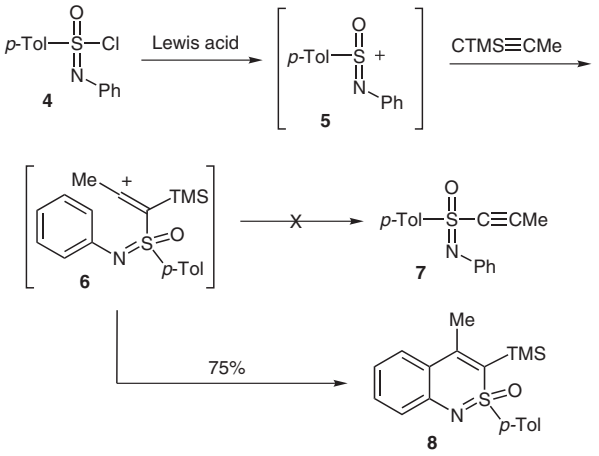
More recently, Malacria and co-workers have demonstrated that the imination of acetylenic sulfoxides is possible.[6] Thus, treatment of **1** with iminoiodinane **2** in the presence of a catalytic amount of copper triflate afforded **3** in 89% yield with complete retention of configuration at sulfur (Equation 1). Marek and Bolm used this chemistry to synthesize *S*-alkynyl sulfoximines as precursors for the synthesis of stereochemically defined vinyl sulfoximines.[7]



Equation 1

In spite of these seminal contributions, it appears that only seven constitutionally unique *S*-alkynyl sulfoximines have been reported in the literature.[8] We undertook our studies mindful of this situation, the potentially very rich chemistry of *S*-alkynyl sulfoximines and their relationship to the as yet unknown *S*-allenyl and *S*-propargyl sulfoximines.

Actually, over 20 years ago we attempted to prepare an *S*-alkynyl sulfoximine via the reaction of sulfonimidoyl chloride **4** with 1-trimethylsilylpropyne in the presence of a Lewis acid.[9] Instead of obtaining **7**, in analogy to chemistry involving sulfonyl chlorides,[10] the 2,1-benzothiazine **8** was produced and this reaction became the focus of some studies in our group (Scheme 1).[11]



Scheme 1

More recently, we simply wanted to produce a selection of *S*-alkynyl sulfoximines to get first hand spectroscopic and stability data in anticipation of more in-depth studies involving the alkynyl/allenyl/propargyl family of S-substituted sulfoximines.[12]

We first synthesized β-keto sulfoximines using the method of Cinquini and co-workers.[13] Sulfoximine **9** was prepared by known methods.[14] Subsequently, deprotonation of **9** with LDA followed by reaction with a methyl ester afforded the β-keto sulfoximines **10** in good to excellent yields (Table 1).

To prepare *N*-TBS–*S*-alkynyl sulfoximines, the β-keto sulfoximines were treated with three equivalents of diisopropylethylamine (DIPEA, Hünig's base) and the solution was then refluxed to effect elimination and produce the triple bond (procedure A). In other cases, preparing and isolating the enol triflate before elimination proved advantageous (procedure B). The yields of the correspond-

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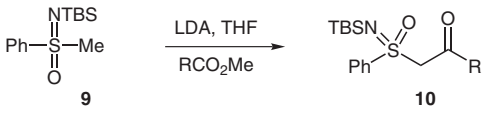
Table 1 Synthesis of β-Keto Sulfoximines



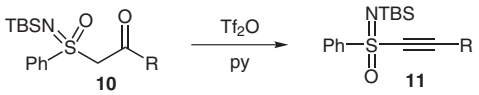
9 10

Entry	R	Product	Yield (%)
1	Ph	**10a**	92
2	2-ClC_6H_4	**10b**	89
3	Me	**10c**	85
4	cyclohexyl	**10d**	83
5	*i*-Pr	**10e**	95
6	4-pentenyl	**10f**	75
7	Et	**10g**	71
8	1-styryl	**10h**	75
9	cyclohexylmethyl	**10i**	75
10	furyl	**10j**	72
11		**10k**	97

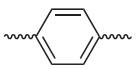
ing alkynes ranged from good to excellent. The results are summarized in Table 2.

In an attempt to begin to learn more about these alkynes, attempts were made to remove the silyl group. However,

Table 2 Synthesis of *S*-Alkynyl Sulfoximines



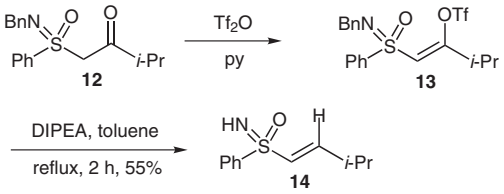
10 11

Entry	Educt	R	Product	Yield (%)
1	**10a**	Ph	**11a**[a]	68
2	**10b**	2-ClC_6H_4	**11b**[a]	94
3	**10c**	Me	**11c**[a]	61
4	**10d**	cyclohexyl	**11d**[a]	62
5	**10e**	*i*-Pr	**11e**[a]	53
6	**10f**	4-pentenyl	**11f**[a]	54
7	**10g**	Et	**11g**[a]	47
8	**10h**	1-styryl	**11h**[a]	0
9	**10i**	cyclohexylmethyl	**11i**[a]	62
10	**10j**	furyl	**11j**[b]	78
11	**10k**		**11k**[b]	73

[a] Prepared according to procedure A.
[b] Prepared according to procedure B.

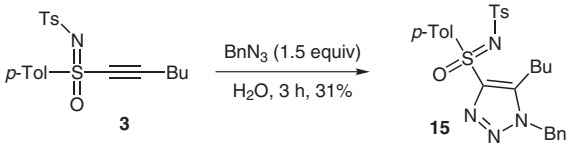
all conditions examined thus far have resulted in decomposition of the starting material.[15]

Interestingly, using the same approach for the synthesis of *N*-benzyl–*S*-alkynyl sulfoximines has thus far failed.



Scheme 2

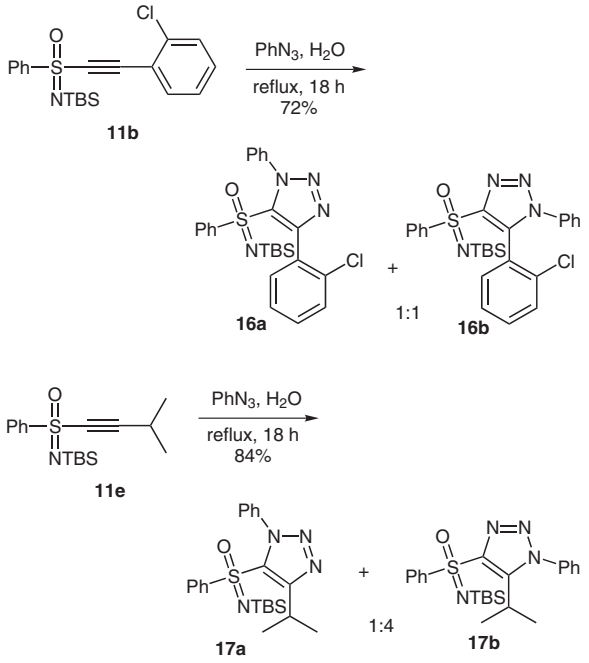
While the preparation of the appropriate β-keto sulfoximines was straightforward, attempts to make the corresponding enol triflates or directly convert them into *S*-alkynyl sulfoximines often produced complex reactions mixtures under the same conditions that produced clean products for **10**. However, when **12** was treated with Tf_2O and Hünig's base in toluene at room temperature, an approximately 36% yield of **13** was isolated in reasonable purity as assessed by ^1H NMR (Scheme 2). When this material was treated with Hunig's base in refluxing toluene, the debenzylated *N*-H alkenyl sulfoximine **14** was isolated in 55% yield. This internal redox process is another interesting aspect of sulfoximine chemistry that we are now exploring.



Equation 2

Finally, Bolm has recently reported the reaction of azide with **3** (Equation 2).[16] Our preliminary studies also suggest that related 'click' chemistry[17] with *S*-alkynyl sulfoximine is possible, but that elucidation of the structural and experimental features of the reaction that control selectivity will need to be accomplished. Thus, treatment of **11b** with PhN_3 (1.5 equiv) in water at reflux for 18 hours resulted in the formation of **16a** and **16b** as a 1:1 mixture of regioisomers in 72% yield. Some evidence for a steric influence in the control of regiochemistry was found upon the reaction of **11e**. This produced **17a** and **17b** as a 4:1 mixture of regioisomers in 84% yield (Scheme 3). The regiochemistry was established using NOESY spectroscopy.

In summary, we have reported a synthesis of *N*-TBS–*S*-alkynyl sulfoximines that is simple and experimentally convenient.[18] More intriguing is the nature of these and related sulfoximines. Their chemistry and reactivity remained largely unexplored. Future studies will focus generating and studying members and relative of the alkynyl sulfoximine family.[19]



Scheme 3

Acknowledgment

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(15) Conditions tried included: (a) 0 °C, 1 h, 0.1 M TBAF (2.0 equiv) in THF; (b) 0 °C, 1 h, 0.1 M TBAF–AcOH (1.2 equiv) in THF; (c) –78 °C → 0 °C, 1 h, 0.1 M HF–pyridine (1.2 equiv) in THF; (d) 23 °C, 2 h, 0.05 M n-$Bu_4NSiF_2Ph_3$ (2.0 equiv) in THF.

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(18) **General Experimental Procedures**: To a solution of DIPEA (2.5 mmol) in THF (10 mL) at 0 °C, was added BuLi (2.5 mmol) with stirring. After 10 min, the solution was cooled to –78 °C, and slowly added to a flask that contained **9** (2 mmol) in THF (10 mL) at –78 °C. The solution was warmed to r.t. for 15 min, then was cooled back to –78 °C. Ester was added (10 mmol) and the solution was warmed to r.t. and then refluxed for 8 h. After TLC showed no starting material, the solution was quenched by sat. NH_4Cl (10 mL), and extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with brine (10 mL), and dried with Na_2SO_4. Removal of solvent and chromatographic purification afforded keto sulfoximines **10**.
Procedure A: To **10** (1 mmol) in toluene (5 mL) at r.t. was slowly added DIPEA (6.0 equiv), followed by triflate anhydride (2.3 equiv). The solution was refluxed until TLC showed no starting material remained. It was quenched by sat. NH_4Cl solution (10 mL), and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried with Na_2SO_4. Removal of solvent and chromatographic purification afforded *S*-alkynyl sulfoximines **11**.
Procedure B: To a solution of β-keto sulfoximine (1 mmol) in toluene (10 mL) at –40 °C was added dropwise DIPEA (6.0 equiv) followed by Tf_2O (2.3 equiv). The solution was stirred for 5 h. The reaction was quenched with sat. NH_4Cl (5 mL), extracted with EtOAc (3 × 10 mL), washed with brine (10 mL), dried with Na_2SO_4 and concentrated in vacuo to give an enol triflate. The triflate was purified by chromatography, eluting with 20% EtOAc in hexane. Due to instability of enol triflate, elimination was carried out immediately. Into a solution of enol triflate (0.5 mmol) in toluene (6 mL) was added DIPEA (3.0 equiv) at r.t. and the solution was stirred at 70 °C for 4 h. The reaction was quenched with sat. NH_4Cl solution (5 mL), extracted with EtOAc (3 × 10 mL), washed with brine, dried with Na_2SO_4 and concentrated in vacuo to give a colorless oil. The oil was purified by chromatography, eluting with 20% EtOAc in hexane, to give the pure final product.

(19) Data on selected compounds: **10a**: oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85–7.92 (m, 4 H), 7.38–7.54 (m, 6 H), 4.70 (d, J = 12.6 Hz, 1 H), 4.54 (d, J = 12.6 Hz, 1 H), 0.83 (s, 9 H), –0.01 (d, J = 10.5 Hz, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 189.1, 143.5, 136.5, 133.6, 132.6, 129.5, 128.7, 128.5, 127.9, 67.8, 25.8, 20.7, 17.9, –2.6, –2.6. IR (CH_2Cl_2): 3064, 2949, 2921, 2855, 1679, 1446, 1274, 1160, 829 cm^{-1}. HRMS: m/z calcd for $C_{20}H_{27}NO_2SSiNa^+$: 396.1429; found: 396.1315. **10b**: oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80–7.82 (m, 2 H), 7.26–7.50 (m, 7 H), 4.80 (d, J = 13.0 Hz, 1 H), 4.72 (d, J = 13.0 Hz, 1 H), 0.86 (s, 9 H), 0.01–0.30 (s, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 191.0, 143.0, 137.8, 132.5, 132.4, 131.4, 130.8, 130.4, 128.6, 127.8, 126.8, 70.8, 17.9, –2.6, –2.7. IR (CH_2Cl_2): 3065, 2922, 2849, 1686, 1286, 1139, 829 cm^{-1}. HRMS: m/z calcd for $C_{20}H_{26}ClNO_2SSiNa^+$: 430.1034; found: 430.1021. **10c**: oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85–7.87 (m, 2 H), 7.48–7.57 (m, 3 H), 4.05 (d, J = 12.5 Hz, 1 H), 4.03 (d, J = 12.5 Hz, 1 H), 2.33 (s, 3 H), 0.90 (s, 9 H), 0.05 (d, J = 11.5 Hz, 6 H). ^{13}C NMR (125.8

MHz, $CDCl_3$): δ = 191.2, 143.2, 132.7, 128.8, 127.6, 72.4, 31.4, 25.8, 17.9, –2.6, –2.7. IR (CH_2Cl_2): 3068, 2949, 2929, 2851, 1707, 1290, 1143, 820 cm^{-1}. HRMS: *m/z* calcd for $C_{15}H_{25}NO_2SSiNa^+$: 334.1267; found: 334.1262. **10d**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.83–7.85 (m, 2 H), 7.47–7.55 (m, 3 H), 4.14 (d, *J* = 12.5 Hz, 1 H), 4.00 (d, *J* = 12.5 Hz, 1 H), 2.72–2.78 (m, 1 H), 1.60–1.75 (m, 5 H), 1.22–1.26 (m, 5 H), 0.90 (s, 9 H), 0.03 (d, *J* = 12.5 Hz, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 202.2, 143.3, 132.6, 128.7, 127.7, 69.3, 51.0, 28.1, 27.8, 25.8, 25.6, 25.5, 25.2, 17.9, –2.6, –2.6. IR (CH_2Cl_2): 3068, 2921, 2851, 1707, 1446, 1298, 1147, 824 cm^{-1}. HRMS: *m/z* calcd for $C_{20}H_{33}NO_2SSiNa^+$: 402.1893; found: 402.1885. **10e**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.86–7.87 (m, 2 H), 7.50–7.58 (m, 3 H), 4.16 (d, *J* = 12.5 Hz, 1 H), 4.06 (d, *J* = 12.5 Hz, 1 H), 3.00 (q, *J* = 7.0 Hz, 1 H), 1.06 (d, *J* = 7.0 Hz, 6 H), 0.91 (s, 9 H), 0.06 (d, *J* = 11.5 Hz, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 203.0, 143.2, 132.6, 128.8, 127.8, 69.3, 25.8, 17.9, 17.7, 17.5, –2.6, –2.7. IR (CH_2Cl_2): 3065, 2963, 2849, 1719, 1294, 1155, 829 cm^{-1}. HRMS: *m/z* calcd for $C_{17}H_{29}NO_2SSiNa^+$: 362.1580; found: 362.1572. **10f**: oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.84–7.88 (m, 2 H), 7.51–7.59 (m, 3 H), 5.74 (ddt, *J* = 4.0, 7.0, 14.0 Hz, 1 H), 5.10 (m, 2 H), 4.04 (d, *J* = 12.5 Hz, 1 H), 4.04 (d, *J* = 12.5 Hz, 1 H), 2.50–2.58 (m, 2 H), 2.03 (q, finely split, *J* = 7.0 Hz, 2 H), 1.65 (m, 2 H), 0.91 (s, 9 H), 0.04 (d, *J* = 3.0 Hz, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 199.2, 143.2, 137.7, 132.7, 128.8, 127.7, 115.3, 71.5, 43.6, 32.7, 25.8, 22.3, 17.9, –2.6, –2.7. IR (CH_2Cl_2): 3068, 2949, 2929, 2851, 1707, 1290, 1143, 820 cm^{-1}. HRMS: *m/z* calcd for $C_{19}H_{31}NO_2SSiNa^+$: 388.1737; found: 388.1729. **10g**: oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.85–7.88 (m, 2 H), 7.48–7.62 (m, 3 H), 4.05 (d, *J* = 12.5 Hz, 1 H), 4.05 (d, *J* = 12.5 Hz, 1 H), 2.60–2.84 (m, 2 H), 1.03 (t, *J* = 7.2 Hz, 3 H), 0.92 (s, 9 H), 0.07 (s, 3 H), 0.04 (s, 3 H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 199.7, 143.2, 132.6, 128.8, 127.7, 71.3, 37.7, 25.8, 17.9, 7.3, –2.58, –2.64. IR (CH_2Cl_2): 2953.9, 2921.2, 2847.6, 1715.7, 1298.9, 1147.7, 833.1, 767.7 cm^{-1}. HRMS: *m/z* calcd for $C_{16}H_{27}NO_2SSiNa^+$: 348.1423; found: 348.1415. **10h**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.89–7.91 (m, 2 H), 7.49–7.58 (m, 6 H), 7.40–7.41 (m, 3 H), 6.94 (d, *J* = 16.0 Hz, 1 H), 4.31 (d, *J* = 12.5 Hz, 1 H), 4.28 (d, *J* = 12.5 Hz, 1 H), 0.90 (s, 9 H), 0.08 (s, 3 H), 0.05 (s, 3 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 188.1, 144.8, 143.2, 134.0, 132.7, 130.9, 128.8, 128.7, 128.6, 127.8, 125.3, 71.1, 25.8, 17.9, –2.51, –2.58. IR (CH_2Cl_2): 2953.9, 2925.3, 2855.8, 1605.4, 1323.5, 1294.8, 1147.7, 824.9 cm^{-1}. HRMS: *m/z* calcd for $C_{22}H_{29}NO_2SSiNa^+$: 420.1580; found: 420.1578. **10i**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.85 (m, 2 H), 7.48–7.56 (m, 3 H), 4.00 (d, *J* = 12.5 Hz, 1 H), 4.00 (d, *J* = 12.5 Hz, 1 H), 2.56 (dd, *J* = 7.0, 12.0 Hz, 2 H), 1.61–1.80 (m, 7 H), 0.88–1.28 (m, 13 H), 0.04 (d, *J* = 10.0 Hz, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 198.8, 143.1, 132.6, 128.7, 127.7, 71.6, 51.8, 33.1, 32.9, 26.1, 25.9, 25.8, 17.9, –2.6, –2.6. IR (CH_2Cl_2): 3064, 2921, 2855, 1711, 1298, 1143, 824 cm^{-1}. HRMS: *m/z* calcd for $C_{21}H_{35}NO_2SSiNa^+$: 416.2050; found: 416.2044. **10j**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7.5 Hz, 2 H), 7.54 (d, *J* = 1.5 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 2 H), 7.22 (d, *J* = 3.5 Hz, 1 H), 6.52 (dd, *J* = 1.5, 3.5 Hz, 1 H), 4.54 (d, *J* = 12.5 Hz, 1 H), 4.38 (d, *J* = 12.5 Hz, 1 H), 0.84 (s, 9 H), 0.03 (s, 3 H), 0.01 (s, 3 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 177.4, 152.8, 147.6, 143.6, 132.9, 129.0, 128.2, 119.8, 113.0, 68.2, 26.0, 18.1, –2.4. IR (CH_2Cl_2): 2953, 2929, 2851, 1621, 1429, 1204, 1004 cm^{-1}. HRMS: *m/z* calcd for $C_{18}H_{25}NO_3SSiNa^+$: 386.1217; found: 386.1220. **10k**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.97 (s, 4 H), 7.85 (d, *J* = 7.5 Hz, 4 H), 7.56 (t, *J* = 7.5 Hz, 2 H), 7.49 (t, *J* = 7.5 Hz, 4 H), 4.69 (d, *J* = 12.5 Hz, 1 H), 4.68 (d, *J* = 12.5 Hz, 1 H), 4.58 (d, *J* = 12.5 Hz, 1 H), 4.57 (d, *J* = 12.5 Hz, 1 H), 0.83 (s, 9 H), 0.81 (s, 9 H), 0.00 (s, 6 H), –0.02 (s, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 188.9, 143.6, 140.0, 133.1, 129.7, 129.1, 128.2, 68.5, 26.0, 18.2, –2.35, –2.39. IR (CH_2Cl_2): 2949, 2917, 2851, 1679, 1315, 1151, 1000 cm^{-1}. HRMS: *m/z* calcd for $C_{24}H_{48}N_2O_4S_2Si_2Na^+$: 691.2486; found: 691.2492. **11a**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.12–8.13 (m, 2 H), 7.32–7.58 (m, 8 H), 1.05 (s, 9 H), 0.30 (d, *J* = 3.0 Hz, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 145.5, 132.6, 132.2, 130.6, 128.8, 128.5, 127.0, 119.2, 89.8, 89.2, 31.5, 25.9, 18.2, –2.9, –3.4. IR (CH_2Cl_2): 3060, 2953, 2921, 2851, 2169, 1315, 1155, 1082, 833, 673 cm^{-1}. **11b**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.10–8.12 (m, 2 H), 7.22–7.58 (m, 7 H), 1.00 (s, 9 H), 0.28 (s, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 145.5, 137.0, 133.8, 132.7, 131.4, 129.5, 128.8, 127.0, 126.6, 119.6, 94.0, 85.6, 25.9, 18.1, –2.9, –3.4. IR (CH_2Cl_2): 3064, 2953, 2929, 2851, 2177, 1470, 1327, 1160, 816 cm^{-1}. HRMS: *m/z* calcd for $C_{20}H_{24}ClNOSSiNa^+$: 412.0929; found: 412.0929. **11c**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.00–8.02 (m, 2 H), 7.48–7.55 (m, 3 H), 1.94 (s, 3 H), 0.97 (s, 9 H), 0.20 (s, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 145.7, 132.4, 128.7, 126.8, 88.8, 81.6, 25.8, 18.1, 3.9, –3.0, –3.5. IR (CH_2Cl_2): 3064, 2949, 2925, 2855, 2202, 1327, 1160, 824 cm^{-1}. HRMS: *m/z* calcd for $C_{15}H_{23}NOSSiNa^+$: 316.1162; found: 316.1155. **11d**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.00–8.04 (m, 2 H), 7.49–7.53 (m, 3 H), 2.42–2.52 (m, 1 H), 1.74–1.82 (m, 4 H), 1.35–1.55 (m, 2 H), 1.20–1.34 (4 H), 0.98 (s, 9 H), 0.22 (d, *J* = 7.5 Hz, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 146.1, 132.2, 128.7, 126.7, 96.0, 82.3, 31.1, 28.9, 25.9, 25.4, 24.6, 18.2, –2.9, –3.4. IR (CH_2Cl_2): 3072, 2933, 2855, 2185, 1446, 1323, 1168, 829 cm^{-1}. HRMS: *m/z* calcd for $C_{20}H_{31}NOSSiNa^+$: 384.1788; found: 384.1759. **11e**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.00–8.02 (m, 2 H), 7.48–7.55 (m, 3 H), 2.64 (q, *J* = 7.0 Hz, 1 H), 1.16 (d, *J* = 7.0 Hz, 6 H), 0.98 (s, 9 H), 0.22 (d, *J* = 8.0 Hz, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 145.8, 132.3, 128.7, 126.8, 97.0, 81.5, 25.8, 21.4, 21.3, 20.6, 18.1, –3.0, –3.5. IR (CH_2Cl_2): 3064, 2949, 2925, 2855, 2202, 1327, 1160, 824 cm^{-1}. HRMS: *m/z* calcd for $C_{15}H_{27}NOSSiNa^+$: 344.1475; found: 344.1470. **11f**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.00–8.04 (m, 2 H), 7.49–7.55 (m, 3 H), 5.63–5.76 (m, 1 H), 4.94–5.01 (m, 2 H), 2.30 (t, *J* = 7.2 Hz, 2 H), 2.08 (q, finely split, *J* = 7.2 Hz, 2 H), 1.60 (p, *J* = 7.2 Hz, 2 H), 0.98 (s, 9 H), 0.22 (d, *J* = 5.5 Hz, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 146.0, 136.8, 132.4, 128.7, 126.8, 115.8, 92.3, 82.6, 32.6, 26.4, 25.9, 18.1, 18.1, –2.9, –3.4. IR (CH_2Cl_2): δ = 3068, 2949, 2852, 2193, 1442, 1335, 1164 cm^{-1}. **11g**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.01–8.03 (m, 2 H), 7.51–7.56 (m, 3 H), 2.31 (q, *J* = 7.5 Hz, 2 H), 1.15 (t, *J* = 7.5 Hz, 3 H), 0.98 (s, 9 H), 0.23 (s, 3 H), 0.22 (s, 3 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 145.7, 132.3, 128.6, 126.8, 93.6, 81.6, 25.8, 18.1, 12.5, 12.0, –3.01, –3.53. IR: 2953.9, 2925.3, 2847.6, 2193.8, 1474.6, 1450.1, 1331.6, 1168.2, 829.0, 775.9 cm^{-1}. HRMS: *m/z* calcd for $C_{16}H_{25}NOSSiNa^+$: 330.1318; found: 330.1316. **11i**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.01–8.02 (m, 2 H), 7.47–7.53 (m, 3 H), 2.17 (d, *J* = 6.5 Hz, 2 H), 1.66–1.72 (m, 5 H), 1.45–1.55 (m, 1 H), 1.05–1.20 (m, 3 H), 0.98 (s, 9 H), 0.92–0.94 (m, 2 H), 0.21 (d, *J* = 6.5 Hz, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 146.1, 132.3, 128.6, 126.7, 92.1, 83.1, 36.5, 32.5, 26.4, 25.8, 25.8, 18.1, –2.9, –3.4. IR (CH_2Cl_2): 3064, 2925, 2847, 2189, 1315, 1168, 824 cm^{-1}. HRMS: *m/z* calcd for $C_{21}H_{33}NOSSiNa^+$: 398.1940; found: 398.1944. **11j**: oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.5 Hz, 2 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 2 H), 7.46 (dd, *J* = 0.5, 1.5 Hz, 1 H), 6.80 (dd, *J* = 0.5, 1.5 Hz, 1 H), 6.42 (dd,

J = 1.5, 3.5 Hz, 1 H), 1.00 (s, 9 H), 0.27 (s, 3 H), 0.25 (s, 3 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 146.3, 145.4, 134.4, 133.0, 129.2, 127.5, 120.3, 111.7, 94.4, 79.7, 26.1, 18.4, –2.8, –3.4. IR (CH_2Cl_2): 2949, 2925, 2851, 2161, 1470, 1323, 1168 cm^{-1}. HRMS: *m*/*z* calcd for $C_{18}H_{23}NO_2SSiNa^+$: 368.1111; found: 368.1112. **11k**: oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.5 Hz, 4 H), 7.58 (t, *J* = 7.5 Hz, 2 H), 7.54 (t, *J* = 7.5 Hz, 4 H), 7.41 (s, 4 H), 1.00 (s, 18 H), 0.25 (s, 6 H), 0.24 (s, 6 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 145.3, 133.1, 132.4, 129.2, 127.4, 121.6, 92.5, 87.7, 26.1, 18.4, –2.7, –3.2. IR (CH_2Cl_2): 2949, 2925, 2855, 2169, 1331, 1164, 829 cm^{-1}. HRMS: *m*/*z* calcd for $C_{34}H_{44}N_2O_2S_2Si_2Na$: 655.2275; found: 655.2279.