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A Mild Synthesis of Unsymmetrical Bisalkoxysilanes through Catalyzed Alcoholysis of Hydridosilanes Containing C−C Multiple Bonds and Aryl Halides

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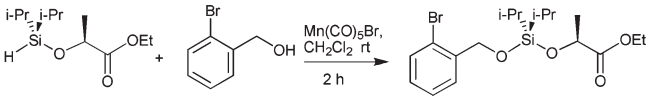

Alcohol: Alkenes, Alkynes and Aryl Bromides

The synthesis of unsymmetrical bisalkoxysilanes containing unsaturated C−C bonds and alkyl and aryl bromides has been developed. This method is a modification of our previously reported two-step procedure that utilizes readily available catalysts (rhodium acetate dimer and manganese pentacarbonyl bromide) under mild neutral aprotic conditions. Good to moderate yields of the products were obtained in a short period. In this two-step synthesis, unsymmetrical bisalkoxysilanes with groups that can be further functionalized can be prepared effectively without the need to isolate the intermediates.

Organosilanes are vital to organic synthesis and therefore the methods to synthesize them have become very important. Formation of silyl ethers and silyl ketals are among the examples. Over the years, there have been significant developments in silyl ether synthesis and their applications to organic chemistry. Silyl ethers and ketals are important in organic synthesis due to their versatility, compatibility with a wide range of reaction conditions, safety, and ease to work with. For these reasons, silyl ethers and silyl ketals have been widely employed in organic synthesis. They are used in the areas of tethering reactants for stereospecific intramolecular reactions,[1,2] protecting agents for many functional groups,[3] and anchoring reagents and substrates for solid support synthesis.[4]

Bisalkoxysilanes (silyl ketals) are normally prepared from the reaction of dichlorosilanes with an alcohol in the presence of base. These conditions, however, are not compatible with many base labile compounds; therefore other methods have been developed to address this problem. To make unsymmetrical bisalkoxysilanes requires a selective method that would allow for addition of two alcohols without a statistical mixture of monoalkoxy and bisalkoxy products. This requires selectively breaking the symmetry of the dichlorosilane. This method becomes very important when valuable synthetic intermediates are used, and time, efficiency, and the need for less waste become crucial. We reported the results of our search for catalysts that would perform controlled alcoholysis of hydridosilanes to form unsymmetrical bisalkoxysilanes.[5] In a continuation of this study, we evaluated catalysts that can achieve the same results with alcohols that contain reactive functional groups such as alkenes, alkynes, and aryl halides.

Reports in the literature where transition metals have been used to catalyze alcoholysis of silanes are extensive.[6] Reports that include catalysts that are known to be compatible with both alkenes and alkynes are Stryker's catalyst $[PPh_3CuH]_6$,[6f] $Mn(CO)_5Br$, and its dimer $[Mn(CO)_4Br]_2$,[6c] while $Rh_2(pfb)_4$ is known to be compatible only with alkenes. To our knowledge, there have been no reports of transition metal catalysts that were used in the presence of aryl halides. Herein we report an efficient method for the synthesis of unsymmetrical bisalkoxysilanes containing reactive functional groups from dihydridosilanes in two consecutive catalyzed alcoholysis reactions (Scheme 1).

In our previous paper, we demonstrated that rhodium acetate dimer $[Rh_2(OAc)_4]$ and 10% palladium on carbon (10% Pd/C) were effective catalysts for the two-step synthesis of unsymmetrical bisalkoxysilanes; however, 10% Pd/C was not compatible with some reactive functional groups in the second step.[5] We continue our study by looking for a suitable catalyst to replace Pd/C in the second step that would be compatible with reactive functional groups (Scheme 2). We began this study by evaluating the catalysts that were reported to be compatible with C−C multiple bonds during silyl alcoholysis. We found that while the $[PPh_3CuH]$ does catalyze the reaction of the second step, the product was isolated in low yield, and there were many byproduct. In our previous work, we found that the $Rh_2(pfb)_4$ does catalyze the reaction in the second step; however,

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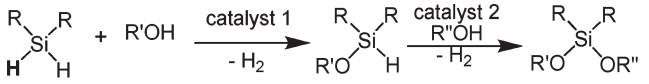
SCHEME 1. A Two-Step Controlled Silyl Alcoholysis of Hydridosilanes



R" = alkene, alkyne or alkyl halide

SCHEME 2. Silyl Alcoholysis of an Alkenol Catalyzed by $Mn(CO)_5Br$

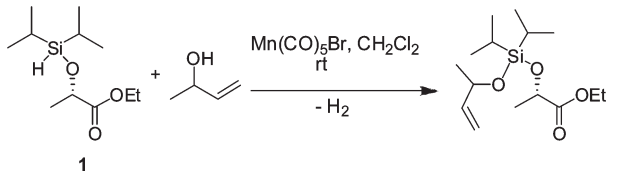
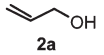
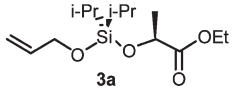
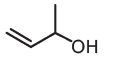
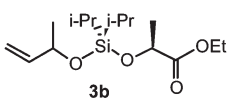
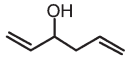
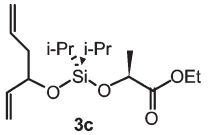
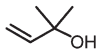
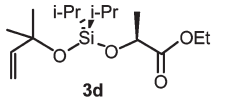
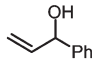
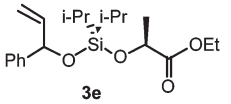
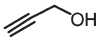
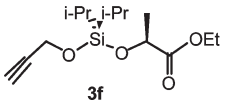


TABLE 1. Bisalkoxysilanes Containing C−C Multiple Bonds

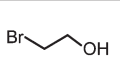
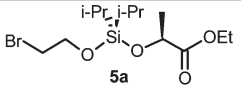
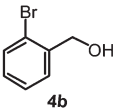
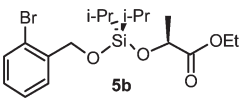
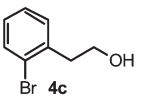
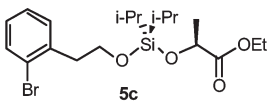
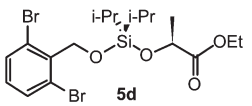
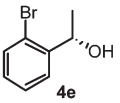
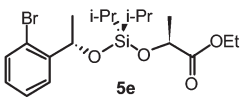
Entry	Alcohol (2a– f)	Product (3a – f)	% Isolated yield[a]
1	 2a	 3a	68
2	 2b	 3b	67
3	 2c	 3c	62
4	 2d	 3d	56
5	 2e	 3e	51
6	 2f	 3f	70

[a]Percent isolated yield over two steps, based on (+)-ethyl lactate.

the reaction time was long, and therefore it was not evaluated with this work. We then turned our interest to the manganese catalysts reported by Cutler et al.[6c] We were pleased to find that $Mn(CO)_5Br$ successfully catalyzes the reaction of the monoalkoxysilane **1** with alcohols containing unsaturated C−C bonds (Table 1).

Compared to the good yields that were obtained in our previous work for primary, secondary, and tertiary alcohols, only moderate yields were obtained over two steps for primary and secondary alcohols, while slightly lower yields were obtained for tertiary and benzyl alcohols. Alcohols containing terminal double and triple bonds are usually

TABLE 2. Bisalkoxysilanes Containing Alkyl and Aryl Bromides

Entry	Alcohol (4a– e)	Product (5a – e)	% Isolated yield[a]
1	 4a	 5a	68
2	 4b	 5b	75
3	 4c	 5c	65
4	 4d	 5d	33
5	 4e	 5e	59

[a]Percent isolated yield over two steps, based on (+)-ethyl lactate.

susceptible to hydrosilylation during transition metal catalyzed alcoholysis; however, these bonds remained intact under these conditions.

We continued our evaluation of $Mn(CO)_5Br$ with alcohols containing alkyl and aryl bromide functional groups. $Mn(CO)_5$-Br also catalyzes the reaction of **1** with alcohols containing alkyl and aryl bromide functional groups in moderate to good yields with no reduction side product detected (Table 2). To our knowledge, this is the first example of silane alcoholysis with alcohols containing alkyl and aryl bromide functional groups.

As we have reported, the yields for the manganese system are lower compared with those of the palladium system. In the manganese system, we observed the formation of a small amount of side products (~10−20%) resulting from alcohol exchange between the second alcohol and the monoalkoxy compound, resulting in the formation of a symmetrical product and the desilylated (+)-ethyl lactate. This was not observed in the palladium system. We conducted several experiments to decipher the problem; however, those results will not be discussed here.[7] The conclusion from those experiments is that once the product is formed, it is stable to the reaction conditions, and therefore, the side products are being formed along the reaction pathway.

We have shown from our previous work that controlled catalytic alcoholysis of dialkylsilanes can provide a practical route to unsymmetrical silyl ketals. We have now developed this method to include alcohols containing alkenes, alkynes, and alkyl and aryl bromide functionality. There is continuing work with this project to explore other reactive functional groups, and the use of other catalysts to synthesize unsymmetrical bisalkoxysilanes containing reactive functional groups.

(7) Scott, C. N. Ph.D. Dissertation, University of Pittsburgh, **2005**.

Experimental Section

All reactions were conducted with magnetic stirring in oven-dried glassware. CH_2Cl_2 was dried over calcium hydride. Ethyl (2*S*)-2-[(diisopropylsilyl)oxy]propanoate **1** was prepared according to our previously reported procedure.[5] All alcohols were dried over calcium hydride and distilled before use. $Mn(CO)_5Br$ was commercially obtained and used without further treatment.

Representative Formation of Bisalkoxysilanes (2a−f and 5a−e). To a solution of alcohol **2a−f** and **5a−e** (3.0 mmol) and monoalkoxy silane **1** (2.0 mmol) in CH_2Cl_2 was added $Mn(CO)_5Br$ (0.022 g, 4.0 mol %) and the reaction was allowed to stir at room temperature for 2 h. The volatile components were removed under reduced pressure and the crude mixture was purified by flash column chromatography on silica gel eluting with hexane (100 mL) followed by hexane:ethyl acetate (25:1) to give the pure products as colorless liquids. The characteristic data for **3a−f** and **5a−e** are presented below.

Ethyl (2*S*)-2-{[(allyloxy)(diisopropyl)silyl]oxy}propanoate (3a): ^{1}H NMR (CD_2Cl_2) δ 5.91 (ddt, 1 H, J = 17 Hz, 11 Hz, 4 Hz), 5.28 (dq, 1 H, J = 17, 2 Hz), 5.07 (dq, 1 H, J = 11, 2 Hz), 4.48 (q, 1 H, J = 7 Hz), 4.28 (dt, 2 H, J = 4, 2 Hz), 4.13 (q, 2 H, J = 7 Hz), 1.39 (d, 3 H, J = 7 Hz), 1.26 (t, 3 H, J = 7 Hz), 1.04−1.02 (m, 14 H); ^{13}C NMR (CD_2Cl_2) δ 173.8, 137.5, 113.7, 68.1, 63.9, 60.8, 21.4, 17.21, 17.17, 17.13, 14.2, 12.54, 12.49; IR (cm^{-1}) 3088, 2946, 2864, 1752, 1736, 1462, 1372, 1270, 1144, 1033, 886, 809, 694; HRMS (EI) m/z calcd for $C_{11}H_{21}O_4Si$ [M − $CH(CH_3)_2^+$] 245.1209, found 245.1216.

Ethyl (2*S*)-2-({diisopropyl[(1-methylpro-2-en-1-yl)oxy]silyl}oxy)propanoate (3b), two diastereomers: ^{1}H NMR (CD_2Cl_2) δ 6.01−5.88 (m, 2 H, 2 diastereomers), 5.28 (dt, 1 H, J = 5 Hz, 2 Hz, 1 diastereomer), 5.22 (dt, 1 H, J = 5, 2 Hz, 1 diastereomer), 5.08 (dt, 1 H, J = 6, 2 Hz, 1 diastereomer), 5.05 (dt, 1 H, J = 6, 2 Hz, 1 diastereomer), 4.65−4.54 (m, 4 H, J = 7 Hz, 2 diastereomers), 4.22 (qd, 4 H, J = 7, 4 Hz, 2 diastereomers), 1.47 (d, 3 H, J = 7 Hz, 1 diastereomer), 1.46 (d, 3 H, J = 7 Hz, 1 diastereomer), 1.36−1.29 (m, 12 H, 2 diastereomers), 1.11 (br s, 28 H, 2 diastereomers); ^{13}C NMR (CD_2Cl_2) δ 173.7, 173.7, 142.7, 142.6, 112.4, 112.3, 69.5, 69.4, 67.8, 67.8, 60.6, 24.2, 24.2, 21.3, 21.3, 17.0, 14.0, 12.6, 12.6, 12.5, 12.5; IR (cm^{-1}) 3088, 2940, 2868, 1737, 1639, 1465, 1378, 1306, 1178, 1096, 1009, 912, 886, 810, 758, 687; HRMS (EI) m/z calcd for $C_{12}H_{23}O_4Si$ [M − $CH(CH_3)_2^+$] 259.1366, found 259.1366.

Ethyl (2S)-2-({diisopropyl[(1-vinylbut-3-en-1-yl)oxy]silyl}oxy)-propanoate (3c), two diastereomers: ^{1}H NMR (CD_2Cl_2) δ 5.94−5.73 (m, 4 H, 2 diastereomers), 5.20 (dt, 1 H, J = 5, 2 Hz, 1 diastereomer), 5.14 (dt, 1 H, J = 5, 2 Hz, 1 diastereomer), 5.10−5.00 (m, 4 H, 1 diastereomer, 2 H, 1 diastereomer), 4.50 (q, 2 H, J = 7 Hz, 2 diastereomer), 4.43−4.36 (m, 2 H, 2 diastereomers), 4.14 (qd, 4 H, J = 7, 4 Hz, 2 diastereomers), 2.41−2.23 (m, 4 H, 2 diastereomers), 1.40 (d, 3 H, J = 7 Hz, 1 diastereomer), 1.38 (d, 3 H, J = 7 Hz, 1 diastereomer) 1.26 (t, 3 H, J = 7 Hz, 1 diastereomer), 1.25 (t, 3 H, J = 7 Hz, 1 diastereomer), 1.08−0.95 (m, 28 H, 2 diastereomers); ^{13}C NMR (CD_2Cl_2) δ 173.7, 140.75, 40.67, 134.5, 116.9, 114.0, 113.9, 73.3, 73.2, 67.9, 42.7, 21.4, 17.0, 14.0, 13.9, 12.62, 12.56; IR (cm^{-1}) 3088, 2940, 2868, 1737, 1639, 1465, 1378, 1306, 1178, 1096, 1033, 886, 809, 694; HRMS (EI) m/z calcd for $C_{14}H_{25}O_4Si$ [M − $CH(CH_3)_2^+$] 285.1522, found 285.1517.

Ethyl (2*S*)-2-{[[(1,1-dimethylprop-2-en-1-yl)oxy](diisopropyl)-silyl]oxy}propanoate (3d): ^{1}H NMR (CD_2Cl_2) δ 5.99 (dd, 1 H, J = 17, 11 Hz), 5.15 (dd, 1 H, J = 17, 2 Hz), 4.92 (dd, 1 H, J = 11, 2 Hz), 4.50 (q, 1 H, J = 7 Hz), 4.14 (q, 2 H, J = 7 Hz), 1.38 (d, 3 H, J = 7 Hz), 1.36 (s, 6H), 1.25 (t, 3 H, J = 7 Hz), 1.05−0.95 (m, 14 H); ^{13}C NMR (CD_2Cl_2) δ 173.8, 146.6, 110.3, 73.9, 67.9, 60.5, 29.8, 21.4, 17.3, 14.0, 13.6, 13.5; IR (cm^{-1}) 3079, 2980, 2945, 2865, 1755, 1731, 1462, 1372, 1143, 1059, 880, 775, 680; HRMS (EI) m/z calcd for $C_{13}H_{25}O_4Si$ [M − $CH(CH_3)_2^+$] 273.1522, found 273.1522.

Ethyl (2*S*)-2-({diisopropyl[(1-phenylprop-2-en-1-yl)oxy]silyl}-oxy)propanoate (3e), 2-diastereomers: ^{1}H NMR (CD_2Cl_2) δ 7.55−7.34 (m, 10 H, 2 diastereomers), 6.11 (ddd, 1 H, J = 10, 6, 3 Hz, 1 diastereomer), 6.05 (ddd, 1 H, J = 10, 6, 3 Hz, 1 diastereomer), 5.53 (d, 2 H, J = 6 Hz, 1 diastereomer), {5.46 (dt, 1 H, J = 7, 2 Hz), 5.41 (dt, 1 H, J = 7, 2 Hz), 1 daistereomer}, 5.20 (dt, 1 H, J = 6, 2 Hz, 1 diastereomer), 5.17 (dt, 1 H, J = 6, 2 Hz, 1 diastereomer), 4.54 (q, 1 H, J = 7 Hz, 1 diastereomer), 4.53 (q, 1 H, J = 7 Hz, 1 diastereomer), 4.26 (qd, 2 H, J = 7, 1.3 Hz, 1 diastereomer), {4.21 (dq, 1 H, J = 11, 7 Hz), 4.13 (dq, 1 H, J =11, 7 Hz), 1 diastereomer}, 1.49 (d, 3 H, J = 7 Hz, 1 diastereomer), 1.40 (d, 3 H, J = 7 Hz, 1 diastereomer), 1.39 (t, 3 H, J = 7 Hz, 1 diastereomer), 1.33 (t, 3 H, J = 7 Hz, 1 diastereomer), 1.22−1.08 (m, 28 H, 2 diastereomers); ^{13}C NMR (CD_2Cl_2) δ 173. 7, 173.6, 143.7, 143.6, 141.7, 141.6, 128.30, 128.26, 127.24, 127.15, 126.0, 125.9, 113.1, 112,9, 75.5, 67.9, 67.8, 60.7, 21.3, 21.2, 17.07, 17.01, 16.96, 16.91, 14.1, 14.0, 12.61, 12.54, 12.50; IR (cm^{-1}) 3086, 3063, 2942, 2867, 1754, 1734, 1466, 1371, 1270, 1191, 1139, 1064, 1034, 988, 026, 884, 857, 753, 700; HRMS (EI) m/z calcd for $C_{17}H_{25}O_4Si$ [M − $CH(CH_3)_2^+$] 321.1522, found 321.1524.

Ethyl (2*S*)-2-{[diisopropyl(prop-2-yn-1-yloxy)silyl]oxy}propanoate (3f): ^{1}H NMR (CD_2Cl_2) δ 4.52 (q, 1 H, J = 7 Hz), 4.43 (d, 2 H, J = 2 Hz), 4.30 (q, 2 H, J = 7 Hz), 2.44 (t, 1 H, J = 2 Hz), 1.42 (d, 3H, J = 7 Hz), 1.26 (t, 3 H, J = 7 Hz), 1.05 (br s, 14 H); ^{13}C NMR (CD_2Cl_2) δ 173.5, 82.1, 72.6, 68.0, 60.8, 51.2, 21.2, 17.0, 14.0, 12.2; IR (cm^{-1}) 3313, 3273, 2942, 2868, 1752, 1462, 1372, 1266, 1197, 1144, 1091, 1066, 1005, 886, 800, 698; HRMS (EI) m/z calcd for $C_{11}H_{19}O_4Si$ [M − $CH(CH_3)_2^+$] 243.1053, found 243.1051.

Ethyl (2*S*)-2-{[(2-bromoethoxy)(diisopropyl)silyl]oxy}propanoate (5a): ^{1}H NMR (CD_2Cl_2) δ 4.52 (q, 1 H, J = 7 Hz), 4.15 (q, 2 H, J = 7 Hz), 4.03 (t, 2 H, J = 6 Hz), 3.44 (t, 2 H, J = 6 Hz), 1.41 (d, 3 H, J = 7 Hz), 1.26 (t, 3 H, J = 7 Hz), 1.05−1.04 (m, 14 H); ^{13}C NMR (CD_2Cl_2) δ 173, 68.2, 63.6, 60.9, 33.6, 21.4, 17.1, 14.2, 12.5; IR (cm^{-1}) 2938, 2868, 1753, 1462, 1377, 1283, 1140, 1017, 976, 882, 788, 739, 690; HRMS (EI) m/z calcd for $C_{10}H_0{}^{79}BrO_4Si$ [M − $CH(CH_3)_2^+$] 311.0314, found 311.0313.

Ethyl (2*S*)-2-{[[(2-bromobenzyl)oxy](diisopropyl)silyl]oxy}-propanoate (5b): ^{1}H NMR (CD_2Cl_2) δ 7.60 (dd, 1 H, J = 8, 1 Hz), 7.52 (dd, 1 H, J = 8, 1 Hz), 7.36 (ddd, 1 H, J = 8, 7, 1 Hz), 7.15 (ddd, 1 H, J = 8, 7, 1 Hz), 4.90 (s, 2 H), 4.54 (q, 1 H, J = 7 Hz), 4.11 (dq, 2 H, J = 3, 7 Hz), 1.42 (d, 3 H, J = 7 Hz), 1.22 (t, 3 H, J = 7 Hz), 1.12−1.09 (m, 14 H); ^{13}C NMR (CD_2Cl_2) δ 173.5, 140.0, 132.1, 128.3, 127.4, 121.0, 68.0, 64.5, 60.8, 21.2, 17.12, 17.09, 17.03, 14.0, 12.4, 12.3; IR (cm^{-1}) 3064, 2945, 2865, 2725, 1751, 1571, 1462, 1442, 1367, 1268, 1203, 1138, 1093, 1028, 879, 820, 745, 691; HRMS (EI) m/z calcd for $C_{15}H_{22}{}^{79}BrO_4Si$ [M − $CH(CH_3)_2^+$] 373.0484, found 373.0471.

Ethyl (2*S*)-2-{[[2-(2-bromophenyl)ethoxy](diisopropyl)silyl]-oxy}propanoate (5c): ^{1}H NMR (CD_2Cl_2) δ 7.53 (dd, 1 H, J = 8, 1 Hz), 7.31 (dd, 1 H, J = 8, 2 Hz), 7.24 (ddd, 1 H, J = 8, 7, 1 Hz), 7.09 (ddd, 1 H, J = 8, 7, 2 Hz), 4.38 (q, 1 H, J = 7 Hz), 4.13 (q, 2 H, J = 7 Hz), 3.96 (t, 2 H, J = 7 Hz), 3.00 (t, 2 H, J = 7 Hz), 1.36 (d, 3 H, J = 7 Hz), 1.24 (t, 3 H, J = 7 Hz), 0.99 (br s, 14 H); ^{13}C NMR (CD_2Cl_2) δ 173.7, 138.4, 132.7, 131.8, 128.1, 127.3, 124.6, 67.8, 62.4, 60.7, 39.4, 21.3, 17.0, 14.1, 12.3; IR (cm^{-1}) 3053, 2940, 2863, 1747, 1737, 1470, 1440, 1368, 1281, 1194, 1143, 1096, 1061, 1040, 886, 743, 687; HRMS (EI) m/z calcd for $C_{16}H_{24}{}^{79}BrO_4Si$ [M − $CH(CH_3)_2^+$] 387.0627, found 387.0627.

Ethyl (2*S*)-2-{[[(2,6-dibromobenzyl)oxy](diisopropyl)silyl]oxy}-propanoate (5d): ^{1}H NMR (CD_2Cl_2) δ 7.56 (d, 2 H, J = 8 Hz), 7.03 (t, 1 H, J = 8 Hz), 5.15 (d, 1 H, J = 11 Hz), 5.11 (d, 1 H, J = 11 Hz), 4.64 (q, 1 H, J = 7 Hz), 4.15 (q, 1 H, J = 7 Hz), 4.14 (q, 1 H, J = 7 Hz), 1.45 (d, 3 H, J = 7 Hz), 1.25 (t, 3 H, J = 7 Hz),

1.09 (br s, 14 H); ^{13}C NMR (CD_2Cl_2) δ 173. 7, 138.3, 132.6, 130.5, 126.1, 68.0, 65.8, 60.7, 21.4, 17.1, 14.1, 12.54, 12.46; IR (cm^{-1}) 2935, 2863, 1742, 1588, 1557, 1424, 1373, 1276, 1204, 1143, 1102, 974, 886, 784, 718; HRMS (EI) m/z calcd for $C_{15}H_{21}{}^{79}Br_2O_4Si$ [M − $CH(CH_3)_2{}^+$] 450.9576, found 450.9574.

Ethyl (2*S*)-2-{[[(1*S*)-1-(2-bromophenyl)ethoxy](diisopropyl)silyl]-oxy}propanoate (5e): ^{1}H NMR (CD_2Cl_2) δ 7.65 (dd, 1 H, J = 8, 2 Hz), 7.48 (dd, 1 H, J = 8, 1 Hz), 7.34 (ddd, 1 H, J = 8, 8, 1 Hz), 7.11 (ddd, 1 H, J = 8, 8, 2 Hz), 5.39 (q, 1 H, J = 6 Hz), 4.43 (q, 1 H, J = 7 Hz), 4.10 (dq, 1 H, J = 11, 7 Hz), 4.04 (dq, 1 H, J = 11, 7 Hz), 1.44 (d, 3 H, J = 6 Hz), 1.38 (d, 3 H, J = 7 Hz), 1.22 (t, 3 H, J = 7 Hz), 1.07−0.98 (m, 14 H); ^{13}C NMR (CD_2Cl_2) δ 173. 5, 145.6, 132.3, 128.4, 127.7, 127.1, 120.7, 69.7, 67.9, 60.7, 25.5, 21.3, 17.02, 16.96, 16.92, 14.0, 12.4; IR (cm^{-1}) 3063, 2940, 2863, 1747, 1568, 1455, 1368, 1265, 1148, 1096, 1030, 958, 876, 794, 748; HRMS (EI) m/z calcd for $C_{19}H_{31}{}^{79}BrO_4Si$ [M − $CH(CH_3)_2{}^+$] 387.0627, found 387.0626.

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