JOC The Journal of Organic Chemistry

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Linear Free-Energy Relationship and Rate Study on a Silylation-Based Kinetic Resolution: Mechanistic Insights

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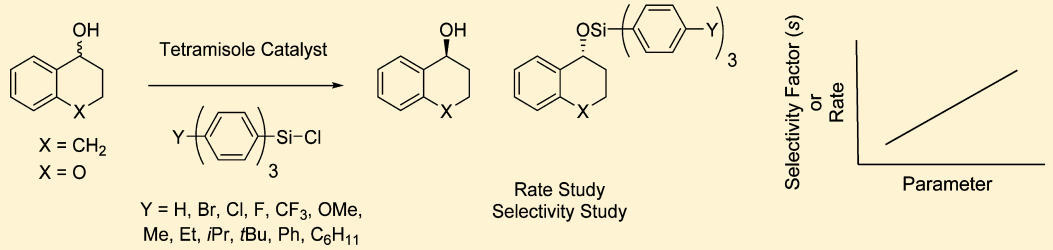
Supporting Information

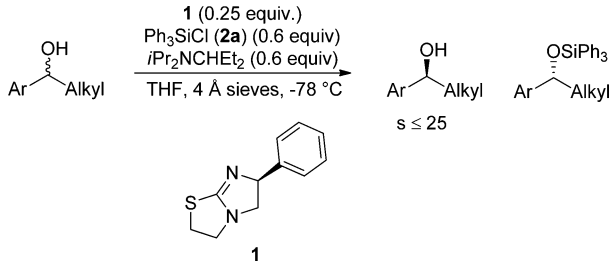


ABSTRACT: The substituent effect of different *p*-substituted triphenylsilyl chlorides on silylation-based kinetic resolutions was explored. Electron-donating groups slow down the reaction rate and improve the selectivity, while electron-withdrawing groups increase the reaction rate and decrease the selectivity. Linear free-energy relationships were found correlating both selectivity factors and initial rates to the σ_{para} Hammett parameters. A weak correlation of selectivity factors to Charton values was also observed when just alkyl substituents were employed but was nonexistent when substituents with more electronic effects were incorporated. The rate data suggest that a significant redistribution of charge occurs in the transition state, with an overall decrease in positive charge. The linear free-energy relationship derived from selectivity factors is best understood by the Hammond postulate. Early and late transition states describe the amount of substrate participation in the transition state and therefore the difference in energy between the diastereomeric transition states of the two enantiomers. This work highlights our efforts toward understanding the mechanism and origin of selectivity in our silylation-based kinetic resolution.

INTRODUCTION

Enantioselective silylation is becoming an alternative approach to acylation in order to obtain enantiopure alcohols via kinetic resolutions and desymmetrization reactions.[1−14] Since silyl groups are one of the most common protecting groups in organic chemistry, it makes sense to employ them as a means of separating enantiomers in kinetic resolutions.[15,16] The advantages of silyl groups include tunable reactivity, orthogonality to other protecting groups, and tolerance of many other functional groups.[17] In order to efficiently improve upon the selectivity in these reactions, and given that there are small energy differences between selective and unselective kinetic resolutions, a detailed understanding of the mechanism is crucial. While the mechanism of acylation reactions in relationship to kinetic resolutions has been highly explored,[18−21] there has been little work accomplished regarding the mechanism of silylation-based kinetic resolutions.[13] In 2011, we published a report on the silylation-based kinetic resolution of monofunctional secondary alcohols[9] that employed the small molecule nucleophilic catalyst (−)-tetramisole (**1**)[22] and triphenylsilyl chloride (**2a**) to silylate one enantiomer over another (Scheme 1) with selectivity factors[23,24] up to 25. This report describes our efforts toward investigating the mechanism of this reaction by determining how the steric and electronic effects around the triphenylsilyl chloride affect the reaction in terms of selectivity as well as reactivity. This will help us to start answering several questions about charge development in the transition state, the origin of enantioselectivity, and whether steric or electronic effects are more important for controlling selectivity.

Scheme 1. Previously Reported Kinetic Resolution of Monofunctional Secondary Alcohols[9]

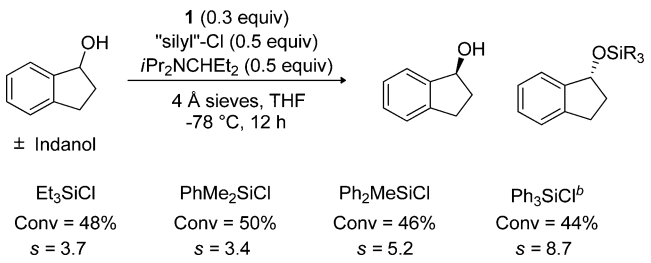


Previously, we have shown that the selectivity of our kinetic resolution was dependent on the structure of the silyl chloride. Specifically, it was determined that three phenyl groups were strategic in obtaining selectivity. For example, when diphenylmethyl and phenyldimethylsilyl chlorides were employed, the selectivity dramatically decreased as compared to triphenylsilyl chloride (Scheme 2). The same decrease in selectivity was obtained when all of the phenyl groups were replaced with alkyl

Received: November 20, 2013
Published: February 21, 2014

   dx.doi.org/10.1021/jo402569h | J. Org. Chem. 2014, 79, 2384−2396

Scheme 2. Previously Reported[a] Importance of Triphenylsilyl Chloride[9]



[a]See ref 25. [b]Reaction was run with 0.6 equiv of Ph_3Si-Cl, 0.6 equiv of iPr_2EtN, and 25 mol % of **1**.

groups (Scheme 2). This same effect on selectivity was seen with a second substrate class, α-hydroxylactones.[14] Since the triphenylsilyl chloride is strategically involved in the enantio-discriminating step, it can be used as a valuable tool for exploring the mechanism. We therefore examined the steric and electronic effects on the silyl chloride to understand more about the reactivity of the silyl chloride and its role in enantioselective discrimination through the use of a linear free-energy relationship (LFER). Ultimately, the knowledge gained from this study will be used to improve future resolutions and expand our substrate scope.

RESULTS AND DISCUSSION

Linear free-energy relationship analysis is a powerful tool for investigating reaction mechanisms.[26] Recently, increased interests in employing this technique to evaluate asymmetric reactions have been reported.[27−39] We wanted to use this tool to investigate the steric and electronic effects on the rate and selectivity of our silylation-based kinetic resolution in Scheme 1. For this analysis, a series of *para*-substituted triphenylsilyl chlorides (**2b−l**) (Scheme 3) were synthesized to employ in the kinetic resolution shown in Scheme 1. The substituents include halides (**2b−d**), trifluoromethyl (**2e**), methoxy (**2f**), various alkyl groups (**2g−k**), and phenyl (**2l**). The synthesis of the silyl chlorides was accomplished by a three-step process starting with a lithium−halogen exchange[40] or Grignard formation[41] with *para*-substituted phenyl bromides or iodides (**3b−l**). The resultant organometallic compound was reacted with trichlorosilane to make the triaryl-substituted silanes (**4b−l**). The silanes were then converted into the silyl chlorides (**2b−l**) by a radical chlorination with sulfuryl chloride.[42,43] The silanes and silyl chlorides were prepared in moderate to good yields (see Experimental Section).

A rate study of the substituted silyl chlorides was done to explore the charge developing in the transition state and provide information on the mechanism of the reaction. Since kinetic resolutions consist of two substrates competitively reacting (the two enantiomers), the rate needed to be measured on one enantiomer at a time. In situ IR was employed to measure the rate of silylation on the fast-reacting (*R*) enantiomer of tetralol **5**, employing silyl groups substituted with hydrogen, halides, methoxy, and alkyl groups (**2a−d,f−j**) (eq 1). The reaction conditions were nearly identical to the conditions in Scheme 1, except for the use of Hünig's base due to the lack of availability of the previously employed tertiary amine, diisopropyl-3-pentyl amine. The initial rate, up to 10% conversion (8 mmol), was observed in all cases, and the results are shown in Table 1. Silyl groups substituted with electron-withdrawing groups (entries 2−4) were up to 5 times faster than triphenylsilyl chloride (entry 1), and electron-donating groups (entries 5−9) significantly decreased the rate as much as 2 orders of magnitude versus **2a**. The increase in rate when the silyl chloride is substituted with electron-withdrawing groups is logical since those substituents would remove electron density from the silicon, making it more reactive. The same argument

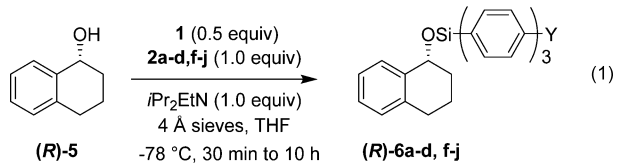
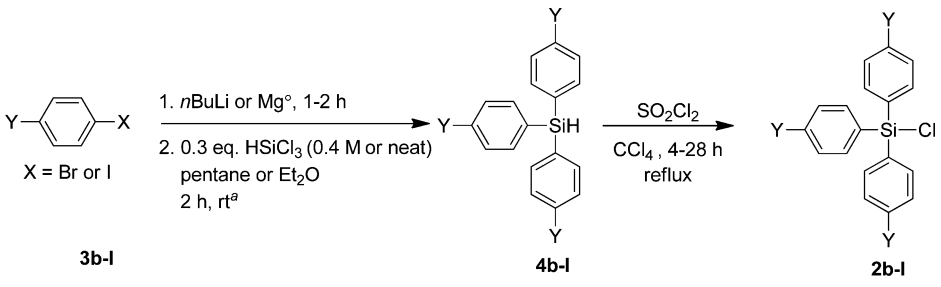


Table 1. Rate Study Employing the Fast-Reacting Enantiomer (*R*) Using Different *para*-Substituted Triphenylsilyl Chlorides[a]

entry[a]	Y	rate of (*R*)-**5**[b] (mmol/min)
1	H	12
2	Br	66
3	Cl	68
4	F	32
5	OMe	0.09
6	Me	0.72
7	Et	0.36
8	*i*Pr	1.0
9	*t*Bu	0.29

[a]Reactions were carried out at a substrate concentration of 0.08 M on a 0.3 mmol scale. Each entry is an average of two runs. [b]Rate was obtained via in situ IR measurements. ^1H NMR conversion was used to monitor conversion of alcohol to silylated product.

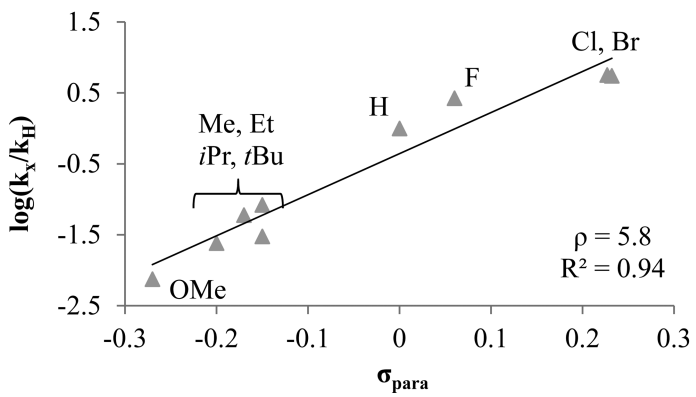
Scheme 3. Synthesis of *p*-Substituted Triphenylsilyl Chlorides



Y = (**b**) Br, (**c**) Cl, (**d**) F, (**e**) CF_3, (**f**) OCH_3, (**g**) CH_3, (**h**) Et, (**i**) *i*Pr, (**j**) *t*Bu, (**k**) C_6H_{11}, (**l**) Ph

[a]Temperatures of 0 °C to rt were used for **3e**, −40 °C for **3h−k**, and −78 °C for **3l**. See Experimental Section for exact procedures and yields.

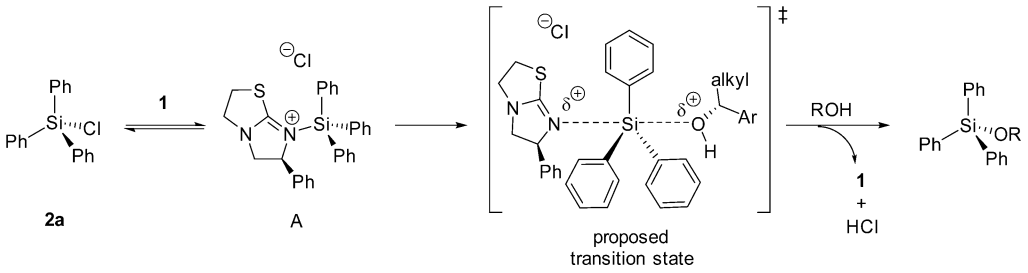
dx.doi.org/10.1021/jo402569h | J. Org. Chem. 2014, 79, 2384−2396



Substituent	Hammett Value σ_p
H	0.00
Br	0.23
Cl	0.22
F	0.06
OMe	-0.27
Me	-0.17
Et	-0.15
*i*Pr	-0.15
*t*Bu	-0.20

Figure 1. Hammett plot employing the parameter σ_{para}[44] versus the log of rates for the kinetic resolution of the fast-reacting enantiomer (*R*) of alcohol **5** (average of two runs).

Scheme 4. Proposed Mechanism of the Silylation Reaction



applies to electron-donating groups increasing electron density on the silicon, slowing the silylation.

A Hammett plot was generated from the log of the (*R*)-**5** rates in Table 1 versus σ_{para} substituent constants[44] (Figure 1), which shows a linear relationship with a slope or sensitivity constant of ρ = 5.8 (R^2 = 0.94). The fact that a correlation exists signifies that the mechanism does not change upon altering the silyl chloride. The considerable magnitude of the slope (ρ) indicates that the silylation reaction is very sensitive to electron-withdrawing and -donating groups on the silyl chloride, signifying a significant redistribution of charges in the transition state. Finally, the positive slope is suggestive of a decrease in positive charge in the transition state.[26] This decrease in positive charge and significant redistribution of charge is consistent with the silylation mechanism proposed by Chojnowski,[45] Bassindale,[46,47] and Frye,[48] while the mechanisms proposed by Corriu[49] and Hoveyda and Snapper[13] cannot be ruled out entirely. The mechanism is essentially two S_N2 reactions (Scheme 4), where the first S_N2 reaction involves the nucleophilic catalyst (**1** in our system) attacking the silyl chloride, displacing the chloride to form the reactive tetravalent intermediate **A**. An alcohol then does a backside attack on this intermediate to form the silylated alcohol, regenerating the nucleophilic catalyst. The proposed transition state for this last step is similar to the classical S_N2 transition state with the nucleophilic catalyst (**1**) departing as the alcohol is attacking. This involves a redistribution of the positive charge from a full positive charge on intermediate **A** to partial positive charges on the incoming alcohol oxygen and the departing catalyst **1**, displaying an overall decrease in positive charge in the transition state. This proposed transition state can be employed in an effort to understand the origin of enantioselectivity.

Since the σ_{para} parameter incorporates both inductive and resonance contributions, the linear correlation of the rate data indicates that the substituents in the *para* position can contribute to the reactivity of the silicon through some degree of resonance. The degree of inductive versus resonance contribution was determined using the Swain–Lupton dual parameter approach (eq 2).[50] The method separates the Hammett parameter into two parameters, induction/field effects (*F*) and resonance (*R*), with sensitivity factors of *r* and *f*, respectively. Employing *F* and *R* parameters recalculated by Hansch,[51] we fit the rate data from Table 1 with a least-squares regression analysis to solve for the two sensitivity constants. The similarity of *f* and *r* (*f* = 5.4, *r* = 5.9) indicates that induction and resonance contribute equally to the rate of the reaction. Figure 2 shows the good correlation between experimentally determined log of rate ratios versus those predicted by eq 2.

$$\log\left(\frac{k_x}{k_H}\right) = fF + rR \qquad (2)$$

As was stated earlier, LFERs have been employed to study asymmetric reactions and provide information about the source of enantioselectivity. While these LFER studies mainly employ enantiomeric ratios as a way of measuring the change in the free energy of activation, traditionally, a ratio of pure rates is employed in the analysis as seen in the study above. Recently, it was suggested that selectivity factors from kinetic resolutions could be employed in a LFER analysis[52] since selectivity factors are a ratio of rates.[24]

Two alcohols were chosen for the kinetic resolution reactions (eq 3) employing the *p*-substituted silyl chlorides: tetralol (**5**) and 4-chromanol (**7**). These alcohols were chosen since they displayed moderate selectivity under the reaction conditions, allowing us to see subtle differences in selectivity as the substituents are altered on the silyl chlorides. These subtle

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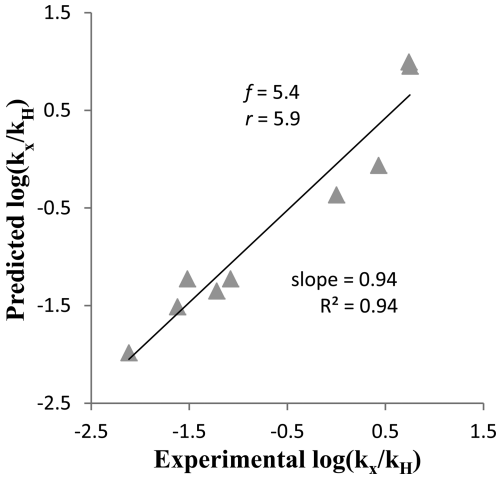
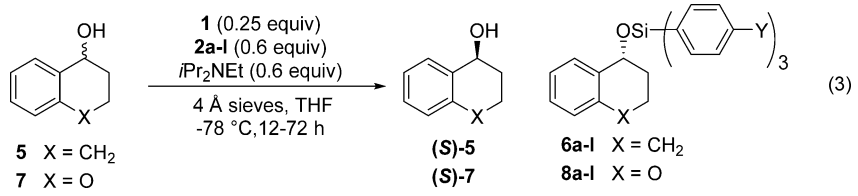


Figure 2. Comparison of the experimental $\log(k_x/k_H)$ using the rate data from Table 1 versus the predicted $\log(k_x/k_H)$ calculated from eq 2.

changes would be missed if highly selective substrates were employed. The same reaction conditions as the rate study were employed, and the selectivity factors for the reactions are shown in Table 2. Entries 1 and 13 show the small detrimental effect of switching the base from diisopropyl-3-pentyl amine to Hünig's base when we compare the originally published selectivity factors of 13 and 21 for **5** and **7**, respectively, versus the new selectivity factors of 11 and 15. Employing the silyl chlorides with substituents in the *para* position proved satisfactory at affecting the selectivity of the kinetic resolution reactions of **5** and **7**. The use of halide-substituted silyl chlorides (**2b–d**) reduced the selectivity factors (entries 2–4 and 14–16) for both alcohols. The selectivity of the kinetic resolution employing *para*-bromide-substituted silyl chloride (**2b**) was nearly half compared with the selectivity of employing **2a**. Both electron-withdrawing and electron-donating groups on the silyl chloride, trifluoromethyl (**2e**) (entries 5 and 17) and methoxy (**2f**) (entries 6 and 18), respectively, caused a reduction in selectivity when compared to **2a**. Silyl chlorides substituted with alkyl groups (**2g–k**) resulted in an increase in selectivity, with the bulkier groups resulting in the best selectivity (entries 7–11 and 19–23).

Hammett plots were generated (Figure 3) by plotting σ_{para} parameters versus the log of the selectivity factors from Table 2 for alcohols **5** and **7**. This explores the electronic contribution of silyl chlorides **2a–l** and how electronic effects affect selectivity. A correlation was observed with the silylation-based kinetic resolution showing that it is sensitive to the electronic effects of the triphenylsilyl chlorides. For both alcohols **5** and **7**, the same trend was observed, a negative slope in both, suggesting a decrease in selectivity factors when electron-withdrawing groups are employed. The selectivity

Table 2. Kinetic Resolution Using Different *para*-Substituted Triphenylsilyl Chlorides[a]



(3)

entry	alcohol	Y	t (h)	conv (%)[b]	er of recovered alcohol	s[b]
1	**5**	H	24	50	85:15	11
2	**5**	Br	24	46	75:25	6
3	**5**	Cl	24	34	66:34	7
4	**5**	F	24	52	85:15	9
5	**5**	CF_3	24	35	65:35	5
6	**5**	OMe	48	43	77:23	10
7	**5**	Me	48	49	86:14	14
8	**5**	Et	48	36	72:28	13
9	**5**	*i*Pr	48	51	88:12	14
10	**5**	*t*Bu	69	42	79:21	16
11	**5**	C_6H_{11}	72	34	71:29	15
12	**5**	Ph	72	22	62:38	11
13	**7**	H	24	49	85:15	15
14	**7**	Br	24	41	73:27	8
15	**7**	Cl	24	50	86:14	11
16	**7**	F	24	48	85:15	13
17	**7**	CF_3	24	21	60:40	7
18	**7**	OMe	48	46	81:19	11
19	**7**	Me	48	56	94:6	14
20	**7**	Et	48	45	83:17	17
21	**7**	*i*Pr	48	48	87:13	20
22	**7**	*t*Bu	69	47	88:12	28
23	**7**	C_6H_{11}	72	44	83:17	21
24	**7**	Ph	72	17	59:41	13

[a]Reactions were carried out at a substrate concentration of 0.16 M on a 0.22 mmol scale. [b]See ref 25.

dx.doi.org/10.1021/jo402569h | J. Org. Chem. 2014, 79, 2384–2396

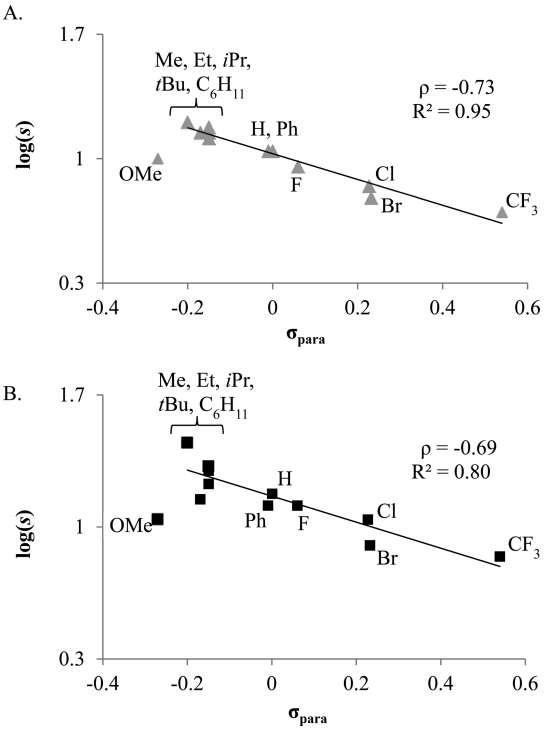


Figure 3. Hammett plots employing the parameter σ_{para}[44] versus the log of the selectivity factors for the kinetic resolution of alcohols (gray triangle) **5** and (■) **7** (σ_{para} values not listed in Figure 1; CF_3 = 0.54, Ph = −0.01, C_6H_{11} = −0.15).

improved when electron-donating groups were employed but only up to a point. When the strongest electron-donating group in the series was used, methoxy, it did not follow the linear trend and instead decreased in selectivity. The sensitivity for both substrates was nearly the same with $\rho = -0.73$ ($R^2 = 0.95$) and −0.69 ($R^2 = 0.80$) for **5** and **7**, respectively, not including methoxy.

The sensitivity of the reaction to electronic changes on the silyl chloride can be explained by the Hammond postulate, proposed by Jacobsen in his own linear free-energy relationship study.[29,30] In our study, when electron-withdrawing groups are on the silyl chloride (**2b−e**), the silyl chloride/catalyst intermediate is more reactive and higher in energy versus a hydrogen substituent. Therefore, the transition state would resemble the silyl chloride/catalyst intermediate with very little involvement of the attacking chiral alcohol (Figure 4A). With little alcohol participation in the transition state, the difference between the diastereomeric transition state energies for both enantiomers is small; therefore, the chiral catalyst intermediate cannot easily distinguish between the enantiomers, leading to low selectivity. When electron-donating groups are employed, the transition state shifts to contain more product-like character with more participation of the attacking alcohol (Figure 4B). Therefore, there is a larger energy difference between the transition states of the two enantiomers, leading to higher selectivity.

Many asymmetric reactions have exhibited a relationship between enantioselectivity and steric effects on the catalyst or reactant.[52,53] The sensitivity of the reaction presented herein to steric effects was investigated to establish if a correlation between steric effects and selectivity exists since selectivity factors for the kinetic resolution of **5** and **7** in eq 3 do increase as the alkyl substituents on **2** increase in size (entries 7−11 and 19−23). For example, by substituting a *t*-butyl group for a hydrogen, the selectivity factor increases from 15 to 28 when employing **7**. The log of the selectivity factors for all the silyl chlorides (**2a−l**) and the two alcohols were plotted against the Charton (υ) parameters (Figure 5A,B). Charton values[54−57] are steric parameters that are based on the van der Waals radius of the substituent and have been employed to show correlations between enantioselectivity and steric effects in a variety of asymmetric systems.[52,58−60] When all of the substituents are plotted on the same graph, there is no observable correlation to the size of the substituent.

When the substituents that have a more pronounced electronic effect are removed, and just alkyl substituents (methyl, ethyl, isopropyl, *t*-butyl, and cyclohexyl) are plotted (Figure 5C), there appears to be a small correlation to steric effects in the *para* position of triphenylsilyl chloride ($\Psi = 0.13$ and 0.23 for **5** and **7**, respectively). The small magnitude of the slope suggests that the correlation is minor, and the lack of a correlation when all of the substituents are plotted together (Figure 5A,B) indicate that electronic effects play a more significant role.

In order to determine the contribution of steric effects to the overall selectivity, a dual parameter approach was undertaken

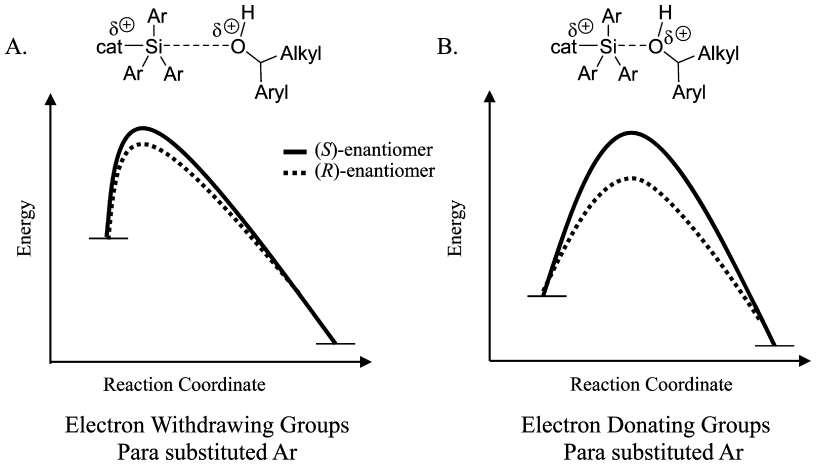


Figure 4. Hammond postulate diagram explaining electronic effect on selectivity factors. (A) Early transition state with electron-withdrawing substituents on silyl chloride. (B) Late transition state with electron-donating substituents on silyl chloride.

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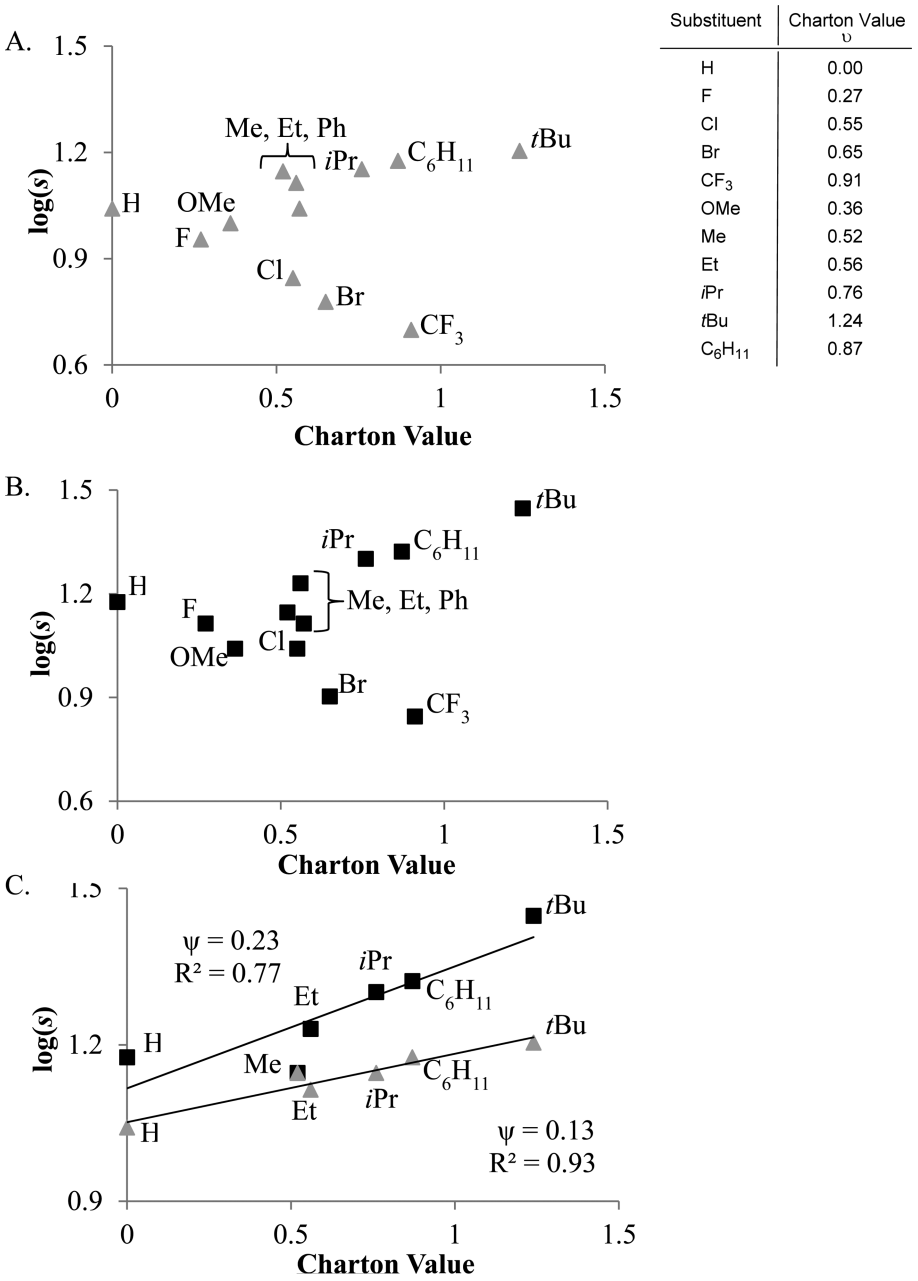

Substituent	Charton Value υ
H	0.00
F	0.27
Cl	0.55
Br	0.65
CF_3	0.91
OMe	0.36
Me	0.52
Et	0.56
*i*Pr	0.76
*t*Bu	1.24
C_6H_{11}	0.87

Figure 5. Charton analysis of alcohols (A) **5** (gray triangle), (B) **7** (■), and (C) selected alkyl-substituted silyl chlorides (**2a–l**) in the silylation-based kinetic resolution.

involving σ_{para} and Charton (υ) parameters. Least-squares regression analysis was performed on eq 4 using the selectivity data for **5** (Table 2, entries 1–5 and 7–12) to determine the sensitivity constants ρ and Ψ for the electronic and steric effect contributions, respectively. The sensitivity constant related to electronic effects (ρ) was an order of magnitude larger than the sensitivity constant for steric effects (Ψ). This indicates that steric effects do not play a significant role in the selectivity of the reaction. Figure 6 shows the good correlation between the experimental log(s) versus that predicted by eq 4.

$$\log(s) = \rho\sigma_{para} + \psi\upsilon \quad (4)$$

With selectivity factors and the rate of the fast-reacting enantiomer in hand for alcohol **5**, the rate of the slow-reacting enantiomer ((*S*)-**5**) (eq 5) was calculated based on the selectivity factor definition.[24] These calculated rates are shown in Table 3. For three substituted silyl chlorides and **2a**, we also experimentally measured the rate of silylation of (*S*)-**5** to verify that the calculated rates were correct. The experimental rates are shown in parentheses and show good correlation to the calculated rates. Electron-donating groups again slow down the silylation (entries 5–9), while electron-withdrawing groups speed up the silylation (entries 2–4) when compared to hydrogen in the *para* position (entry 1). The Hammett plot for the calculated rates is shown in Figure 7, again employing σ_{para} substituent constants. The calculated rates have a linear relationship, with a sensitivity constant (ρ) of 6.4, which is slightly higher than the sensitivity constant of the fast-reacting enantiomer (ρ = 5.8). This shows that the substituted silyl chlorides essentially have the same effect on both the fast- and slow-reacting enantiomers (i.e., same sign of the slope therefore same transition state), with the sensitivity of the slow-reacting

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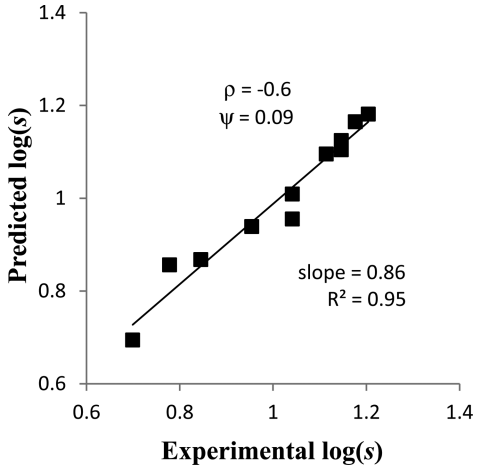
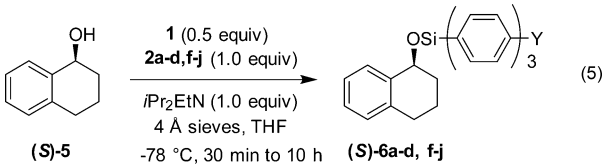


Figure 6. Comparison of the experimental log(*s*) using the selectivity data for **5** from Table 2 versus the predicted log(*s*) calculated from eq 4.

Table 3. Rate of Slow-Reacting Enantiomer (*S*)-5 for Different *para*-Substituted Triphenylsilyl Chlorides



(5)

entry	Y	rate of (*S*)-5[a] (mmol/min)
1	H	1.1 (1.2)
2	Br	11 (9.5)
3	Cl	9.7
4	F	3.6
5	OMe	0.009 (0.02)
6	Me	0.05
7	Et	0.03
8	*i*Pr	0.07 (0.06)
9	*t*Bu	0.02

[a]Calculated rate based on selectivity factor and fast-reacting enantiomer. Rate in parentheses was experimentally measured on a 0.3 mmol scale at 0.08 M. Each data point is a single run.

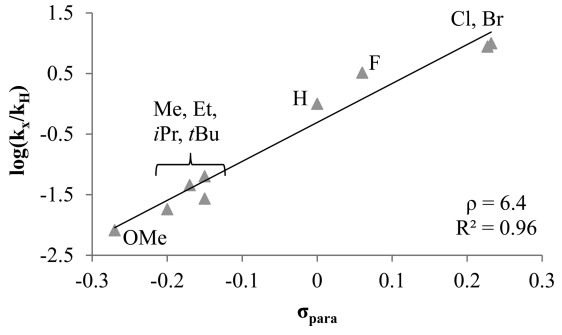


Figure 7. Hammett plot employing the parameter σ_{para}[44] versus the log of the calculated rates for the kinetic resolution of the slow-reacting enantiomer (*S*)-**5**.

enantiomer to the substituents being modestly higher. This suggests that substituting the silyl chloride with electron-donating groups improves the selectivity of the reaction by affecting the rate of the slow-reacting enantiomer more than the fast-reacting enantiomer since the selectivity factor is a ratio of these rates. Therefore, the slow-reacting enantiomer is slightly more sensitive to changes in electronic effects.

CONCLUSIONS

In conclusion, we determined that mainly electronic effects around the triphenylsilyl chloride affect both the rate and the selectivity of the silylation-based kinetic resolution presented herein. Substituting the triphenylsilyl chlorides in the *para* position with a variety of electron-withdrawing and -donating groups allowed us to investigate the mechanism of our silylation-based kinetic resolution. The rates of the silylation reaction were measured employing the fast-reacting enantiomer with different *para*-substituted triphenylsilyl chlorides and a linear free-energy relationship was discovered employing σ_{para} parameters. The sign and magnitude of the slope indicates that positive charge is decreasing in the transition state, and there is a significant redistribution of the charge. From these data, we were able to postulate a pentavalent S_N2-like transition state with the tetramisole catalyst as the leaving group and the alcohol as the incoming nucleophile. By employing the substituted triphenylsilyl chlorides in kinetic resolutions, selectivity factors were obtained that indicate electronic effects on the silyl group play a more significant role than steric effects in affecting the selectivity of the reaction. Ultimately, electron-donating groups result in a late transition state according to the Hammond postulate, where the incoming alcohol is more involved in the rate-determining step, and therefore, the diastereomeric transition states between the two enantiomers have a larger energy difference as compared to electron-withdrawing substituted triphenylsilyl chlorides. Ultimately, with this linear free-energy relationship study, we have been able to postulate the transition state and obtain some understanding on the enantioselective step, which can aid in future substrate expansion. Future studies will include employing a chiral silyl chloride for further evidence of a double inversion mechanism and an NMR and kinetic study to get a complete picture of the overall mechanism.

EXPERIMENTAL SECTION

General Information. All kinetic resolution reactions and the synthesis of different silanes and silyl chlorides were carried out under a N_2 atmosphere using oven-dried glassware. All solvents including THF, diethyl ether, and hexanes were dried by passing through a column of activated alumina before use and stored over molecular sieves. Pentane and carbon tetrachloride were distilled and stored over molecular sieves. CCl_4 was degassed before chlorination. Sulfuryl chloride was distilled prior to use. *n*-BuLi was titrated prior to use. All other chemicals were purchased from a commercial source and used without further purification. Molecular sieves were activated for 48 h at 130 °C in an oven. Flash column chromatography was performed with silica gel (32−63 μm). High-resolution mass spectrometry (HRMS) was obtained using a magnetic sector mass spectrometer. IR data (ν_{max}) are reported in cm^{-1}. Rate data were collected using an FTIR spectrophotometer with a silicon probe. All enantiomeric ratios were determined by HPLC using the chiral stationary phase Chiralcel OD-H (4.6 × 250 mm ×5 μm) column and monitored using a photodiode array detector in comparison with authentic racemic materials. Melting points (mp) are uncorrected. Optical rotations were obtained using a polarimeter. Microwave-assisted transformations were carried out using a chemical synthesis microwave. NMR spectra were obtained at room temperature using 400 MHz (^{1}H), 101 MHz (^{13}C), 80 MHz (^{29}Si), and 377 MHz (^{19}F). Chemical shifts for ^{1}H, ^{13}C, ^{19}F, and ^{29}Si was recorded in part per million with either TMS (0.00 ppm) or $CDCl_3$ (7.26 ppm for ^{1}H or 77.0 ppm for ^{13}C) as a reference. TMS

dx.doi.org/10.1021/jo402569h | J. Org. Chem. 2014, 79, 2384−2396

was used as a reference (0.00 ppm) to obtain ^{29}Si NMR. Data reported in ^{1}H NMR are as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt =doublet of triplet, sept = septet, m = multiplet) and coupling constant (Hz).

General Procedure Making a *p*-Substituted Triphenylsilane. *General Procedure 1 (GP1):*[40] (Written for a 10 mmol scale with regards to aryl bromide or iodide.) *Important note regarding silane synthesis: Extreme caution should be undertaken while centrifuging and washing the lithium salts.*[61] *These salts are highly flammable and any contact with air or water should be avoided, especially when the para-substituent is an electron-withdrawing group*. In an oven-dried 250 mL three-neck round-bottom flask, *p*-substituted bromo/iodobenzene (1 equiv) was dissolved using previously distilled pentane (28 mL) under nitrogen at room temperature. To the stirred solution was slowly added *n*-BuLi (1.025 equiv) at room temperature. After addition of *n*-BuLi, the resulting mixture formed a precipitate which was then allowed to stir for 1−1.5 h. After 1−1.5 h, the white precipitate containing solution was carefully transferred to a test tube and centrifuged for 5 min (four test tubes were used). The supernatant was carefully removed using a syringe (done under N_2 atmosphere). The white precipitate was washed 2−3 times using dry pentane and transferred to another three-neck round-bottom flask using approximately 22 mL of fresh pentane under nitrogen. A solution of $HSiCl_3$ (0.4 M in pentane, 0.3 equiv) was added dropwise to the three-neck flask (Caution: exothermic reaction). The reaction mixture was then allowed to stir for another 2 h. After 2 h, the resulting suspension (white precipitate) was centrifuged (four test tubes were used). The supernatants were collected under nitrogen in a separate round-bottom flask (liquid was collected using a syringe and transferred to another flask carefully). The remaining solid was washed 2−3 times with pentane and centrifuged, and the supernatants were combined with the previously collected supernatants. Finally, the combined supernatants were quenched by chlorotrimethyl silane, and the resulting solution was concentrated under vacuum to yield the crude triphenylsilane product. In most cases, purification of silane was done by recrystallization using an appropriate solvent.

General Procedure 2 (GP2): (Written for a 10 mmol scale with regards to aryl bromide or iodide.) In an oven-dried 250 mL three-neck round-bottom flask, *p*-substituted bromo/iodobenzene (1 equiv) was dissolved using previously dried diethyl ether (30 mL) under nitrogen at room temperature. To the stirred solution was added *n*-BuLi (1.025 equiv), and the resulting mixture was allowed to stir for 1−1.5 h at room temperature. The reaction was then cooled to −40 °C using a dry ice−acetonitrile bath. A solution of $HSiCl_3$ (0.4 M in ether, 0.3 equiv) was added dropwise to the three-neck flask. The reaction mixture was allowed to stir for another 2 h at −40 °C, then the reaction was quenched using 10 mL of water at −40 °C and allowed to warm to room temperature. Extraction was done using diethyl ether. The organic layer was collected and dried over anhydrous sodium sulfate. The excess solvent was removed via a rotary evaporator, and the crude was purified using recrystallization or a trituration method.

General Procedure Making a *p*-Substituted Triphenylsilyl Chloride. *General Procedure 3 (GP3):* An oven-dried 25−50 mL three-neck round-bottom flask was charged with *p*-substituted triphenylsilane and the mixture dissolved using dry degassed carbon tetrachloride (CCl_4) under a nitrogen atmosphere. The mixture was allowed to stir for 10−15 min. Sulfuryl chloride (SO_2Cl_2) (2−6 equiv) was then added to the flask. The resulting mixture was then allowed to reflux for 4−28 h (conversion was monitored by disappearance of the silane peak using ^{1}H NMR). Hydrochloric acid generated during the reaction was removed from the reaction mixture via a bubbler. The excess solvent and other reagents were evaporated under vacuum (dry ice cooled cold trap). The final product was then recrystallized or triturated using an appropriate solvent under a N_2 atmosphere.

Synthesis of *p*-Substituted Triphenylsilane and Silyl Chlorides. *Tris(4-bromophenyl)silane (**4b**).*[40] The product was synthesized employing 1-bromo-4-iodobenzene (98%) (2.88 g, 10 mmol) according to GP1. The final colorless solid product was obtained by recrystallization at −40 °C using pentane (1.16 g, yield = 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 6 H), 7.39 (d, J = 8.0 Hz, 6 H), 5.39 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) δ 137.1, 131.5, 131.0,125.4.

*Tris(4-bromophenyl)chlorosilane (**2b**).*[40] Chlorination was done employing **4b** (1.1 g, 2.21 mmol) according to GP3. Silane was dissolved using 12 mL of degassed carbon tetrachloride followed by addition of sulfuryl chloride (895 μL, 11 mmol) under nitrogen. The resulting mixture was allowed to reflux for 10−12 h. The final solid product was obtained by recrystallization using pentane at −40 °C (430 mg, yield = 37%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.2 Hz, 6H), 7.46 (d, J = 8.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 131.6, 130.6, 126.4.

*Tris(4-chlorophenyl)silane (**4c**).* The product was synthesized employing 1-chloro-4-iodobenzene (98%) (2.43 g, 10 mmol) according to GP1. The final product was obtained by recrystallization from pentane at −40 °C to yield colorless crystals (680 mg, yield = 62%): mp = 74−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.3 Hz, 6H), 7.38 (d, J = 8.3 Hz, 6H), 5.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 136.8, 130.6, 128.6; ^{29}Si NMR (80 MHz, $CDCl_3$) δ −18.6; HRMS (EI) (M+) calcd for ($C_{18}H_{13}Cl_3Si^+$) 361.9846, observed 361.9858; IR (neat, cm^{-1}) 3042, 2142, 1578, 1481, 1380, 1080, 1013, 821, 798, 778, 740, 733, 698.

*Chlorotris(4-chlorophenyl)silane (**2c**).* The product was obtained using **4c** (650 mg, 1.78 mmol) according to GP3. The silane was dissolved in 10 mL of degassed carbon tetrachloride under N_2. Excess sulfuryl chloride (750 μL, 9.26 mmol) was added over the course of the reaction. The reaction took 28 h to go to completion, monitored by ^{1}H NMR. The crude was triturated with pentane at −78 °C using a dry ice/acetone bath to yield a colorless solid (295 mg, yield = 40%): mp = 58−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 6H), 7.41 (d, J = 8.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 136.4, 130.3, 128.7; ^{29}Si NMR (80 MHz, $CDCl_3$) δ +1.1; HRMS (EI) (M+) calcd for ($C_{18}H_{12}Cl_4Si^+$) 395.9456, observed 395.9460; IR (neat, cm^{-1}) 3041, 3020, 1915, 1575, 1482, 1381, 1186, 1119, 1083, 1014, 952, 813, 789, 735, 708.

*Tris(4-fluorophenyl)silane (**4d**).*[62] Compound **4d** was synthesized using 1-fluoro-4-iodobenzene (2.22 g, 10 mmol) according to GP1. The product was obtained as an oily liquid. After leaving for almost 2 days in the freezer at −20 °C, it became a colorless solid. The compound was used for the next step without any further purification (730 mg, yield = 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.47 (m, 6H), 7.15−7.05 (m, 6H), 5.46 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4 (d), 137.7 (d), 128.4 (d), 115.5 (d).

*Chlorotris(4-fluorophenyl)silane(**2d**).*[63] Chlorination was done using **4d** (1.3 g, 4.13 mmol) according to GP3. The silane was dissolved using 12 mL of carbon tetrachloride under nitrogen. Sulfuryl chloride (670 μL, 9.90 mmol) was added to the reaction flask and allowed to reflux for 4 h, resulting in an oil liquid after workup. Pentane was added to the oily liquid which solubilized the final product, while impurities remained undissolved. The pentane was carefully separated from impurities and transferred to another vial under nitrogen. The product was obtained through trituration at −78 °C using pentane to yield a colorless solid (500 mg, yield = 35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.53 (m, 6H), 7.16−7.07 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8 (d), 137.4 (d), 128.1 (d), 115.6 (d).

*Tris(4-(trifluoromethyl)phenyl)silane (**4e**).*[41] The product was synthesized using a Grignard method on a 30 mmol scale. Magnesium metal was preactivated by leaving it in the oven for 24 h before use. In a three-neck round-bottom flask, 750 mg of magnesium metal was added and allowed to stir for 2 h under vacuum in order to activate. After 2 h, 1-iodo-4-(trifluoromethyl)benzene (4.4 mL, 30 mmol) along with 4.4 mL of ether were added to the flask. The resulting mixture became a brown liquid which was allowed to stir for 10−15 min. After 15 min, 25 mL of ether was added to the flask and the mixture was allowed to reflux for 30 min. After 30 min, the mixture was allowed to cool to 0 °C and $HSiCl_3$ (910 μL, 9 mmol, neat) was added to the reaction mixture. The resulting mixture was allowed to stir for another 3 h (first 30 min at 0 °C and then at room temperature). After the reaction was complete, the mixture was poured into a beaker

dx.doi.org/10.1021/jo402569h | J. Org. Chem. 2014, 79, 2384−2396

containing dry ice and dilute HCl. The reaction mixture was extracted with ether and dried over anhydrous sodium sulfate. Excess ether was removed under vacuum. A dark orange-brown oil was obtained. The final product was obtained by vacuum distillation at 175−178 °C and 3 mmHg. A dark yellow liquid was obtained which was left under vacuum to yield a colorless solid as the final product (1.1 g, yield = 26%): mp = 74−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 12H), 5.58 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 136.0, 132.5 (q, J_{CF} = 33 Hz), 125 (q, J = 3.8 Hz), 123.9 (q, J_{CF} = 273 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −111.9; ^{29}Si NMR (80 MHz) δ −18.7; HRMS (EI) $(M - H)^+$ calcd for ($C_{21}H_{12}F_9Si^+$) 463.0559, observed 463.0574; IR (neat, cm^{-1}) 2929, 2155, 1931, 1610, 1505, 1393, 1322, 1273, 1161, 1114, 1017, 844, 830, 793, 771, 722, 700.

*Chlorotris(4-(trifluoromethyl)phenyl)silane (**2e**).* Chlorination was done employing **4e** (820 mg, 1.77 mmol) according to GP3. The silane was dissolved in 8 mL of carbon tetrachloride followed by addition of sulfuryl chloride (350 μL, 4.32 mmol). After 4 h, only 20% conversion was observed from ^{1}H NMR. Excess sulfuryl chloride was added over the course of the reaction, but no further improvement in conversion was observed after 48 h. Finally, the reaction mixture was transferred to a microwave vessel equipped with a stir bar under an argon atmosphere. The reaction vessel was then purged with argon and sealed with a septa. The mixture was then microwaved for 40 min at 120 °C employing 70 W. The mixture was allowed to cool to ambient temperature and transferred to a 4 dram vial under an argon atmosphere. The crude was concentrated under vacuum. The final product was a yellowish solid (492 mg, yield = 56%), which was used directly without any purification for the kinetic resolution. No characterization was reported due to moisture sensitivity.

*Tris(4-methoxyphenyl)silane (**4f**).*[62] The product was synthesized using 4-iodoanisole (98%) (2.34 g, 10 mmol) according to GP1. A colorless solid was obtained as the crude product. Silane was further purified by carefully washing crude 2 times with distilled pentane (780 mg, yield = 74%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.6 Hz, 6H), 6.96 (d, J = 8.4 Hz, 6H), 5.46 (s, 1H), 3.85 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 137.2, 124.8, 113.8, 55.0.

*Chlorotris(4-methoxyphenyl)silane (**2f**).* Chlorination was done using **4f** (300 mg, 0.86 mmol) according to GP3. The silane was dissolved in 6 mL of carbon tetrachloride followed by addition of sulfuryl chloride (139 μL, 1.72 mmol). Complete conversion was achieved in 7−8 h. An oily liquid was obtained which became a light yellow solid after scratching for almost an hour under nitrogen. This solid was carefully washed with pentane to obtain the final product (200 mg, yield = 60%): mp = 67−69 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.7 Hz, 6H), 6.95 (d, J = 8.7 Hz, 6H), 3.84 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 136.8, 124.4, 113.8, 55.1; ^{29}Si NMR (80 MHz, $CDCl_3$) δ +1.2; HRMS (EI) (M+) calcd for ($C_{21}H_{21}ClO_3Si^+$) 384.0943, observed 384.0952; IR (neat, cm^{-1}) 3020, 2919, 2841, 1591, 1563, 1503, 1457, 1442, 1400, 1276, 1248, 1181, 1116, 1107, 1022, 817, 797, 659.

*Tri-p-tolylsilane (**4g**).*[62] The product was synthesized using 4-iodotoluene (2.18 g, 10 mmol) according to GP1. A colorless solid was formed which was further recrystallized using pentane at −40 °C (770 mg, yield = 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.8 Hz, 6H), 7.18 (d, J = 7.6 Hz, 7H), 5.43 (s, 1H), 2.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 135.8, 130.1, 128.8, 21.5.

*Chlorotri-p-tolylsilane (**2g**).* Chlorination was done using tri-*p*-tolylsilane (1.03 g, 3.4 mmol) according to GP3. The silane was dissolved in 17 mL of carbon tetrachloride followed by addition of sulfuryl chloride (550 μL, 6.8 mmol). It took 7−8 h to achieve complete conversion. The final product was obtained through recrystallization from hexanes at −40 °C to obtain a colorless solid (590 mg, yield = 51%): mp = 110−112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 6H), 7.22 (d, J = 7.6 Hz, 6H), 2.38 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 135.2, 129.7, 128.9, 21.6; ^{29}Si NMR (80 MHz, $CDCl_3$) δ +1.8; HRMS (EI) (M+) calcd for ($C_{21}H_{21}ClSi^+$) 336.1095, observed 336.1096; IR (neat, cm^{-1}) 3019, 2921, 2862, 1924, 1598, 1501, 1393, 1312, 1190, 1114, 1021, 712.

*Tris(4-ethylphenyl)silane (**4h**).* Compound **4h** was synthesized using 1-ethyl-4-iodobenzene (98%) (1.48 mL, 10 mmol) according to GP2. After reaction completion, the solvent was removed under vacuum. The crude product was obtained as an oil. Further purification was done using column chromatography to yield an oil as the final product (800 mg, yield = 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.9 Hz, 6H), 7.36 (d, J = 7.7 Hz, 6H), 5.60 (s, 1H), 2.80 (q, J = 7.6 Hz, 6H), 1.39 (t, J = 7.6 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 135.9, 130.5, 127.6, 28.9, 15.4; ^{29}Si NMR (80 MHz, $CDCl_3$) δ −18.9; HRMS (EI) (M+) calcd for ($C_{24}H_{28}Si^+$) 344.1954, observed 344.1960; IR (neat, cm^{-1}) 3012, 2964, 2930, 2116, 1600, 1456, 1398, 1111, 1062, 967, 801, 772.

*Chlorotris(4-ethylphenyl)silane (**2h**).* Chlorination was done using tris(4-ethylphenyl)silane (782 mg, 2.27 mmol) according to GP3. Excess sulfuryl chloride (550 μL, 6.78 mmol) was used to achieve full conversion in 4 h using 10 mL of carbon tetrachloride. The crude oily liquid was further purified by trituration with hexanes at −40 °C under a N_2 atmosphere which resulted in a yellowish solid (455 mg, yield = 53%): mp = 54−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 6H), 7.24 (d, J = 8.2 Hz, 6H), 2.67 (q, J = 7.6 Hz, 6H), 1.24 (t, J = 7.6 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 135.3, 130.0, 127.7, 28.9, 15.3; ^{29}Si NMR (80 MHz, $CDCl_3$) δ +1.6; HRMS (EI) (M+) calcd for ($C_{24}H_{27}ClSi^+$) 378.1565, observed 378.1573; IR (neat, cm^{-1}) 3012, 2967, 2933, 2873, 1600, 1456, 1397, 1272, 1190, 1115, 1062, 1020, 968, 796, 782.

*Tris(4-isopropylphenyl)silane (**4i**).* Compound **4i** was synthesized using 4-bromoisopropyl benzene (95%) (1.63 mL, 10 mmol) according to GP2. A colorless solid was obtained and purified further by trituration at −40 °C with hexanes under a N_2 atmosphere to get a colorless powder (770 mg, yield = 66%): mp = 58−60 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 6H), 7.23 (d, J = 7.9 Hz, 6H), 5.41 (s, 1H), 2.90 (m,3H), 1.25 (d, J = 6.9 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 135.9, 130.7, 126.2, 34.1, 23.8; ^{29}Si NMR (80 MHz, $CDCl_3$) δ −18.8; HRMS (EI) (M+) calcd for ($C_{27}H_{34}Si^+$) 386.2424, observed 386.2428; IR (neat, cm^{-1}) 2961, 2928, 2110, 1924, 1598, 1458, 1392, 1297, 1265, 1117, 1094, 1049, 1019, 822, 794, 760, 725.

*Chlorotris(4-isopropylphenyl)silane (**2i**).*[64] Chlorination was done by using tris(4-isopropylphenyl)silane (875 mg, 2.26 mmol) according to GP3. The silane was dissolved in 11 mL of carbon tetrachloride followed by addition of sulfuryl chloride (550 μL, 6.78 mmol) under a N_2 atmosphere. The resulting mixture was allowed to reflux for 4 h to achieve complete chlorination. After the reaction was complete, the excess reagents were removed under vacuum. The crude product was purify by trituration with hexanes at −40 °C under N_2. A colorless solid product was obtained (747 mg, yield = 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 6H), 7.27 (d, J = 7.4 Hz, 6H), 2.92 (septet, 3H), 1.26 (d, J = 6.9 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 135.3, 130.2, 126.2, 34.2, 23.8.

*Tris(4-(tert-butyl)phenyl)silane (**4j**).* Compound **4j** was synthesized using 1-bromo-4-*tert*-butylbenzene (98%) (1.76 mL, 10 mmol) according to GP2. A colorless solid was obtained after washing the crude solid with hexanes (1.27 g, yield = 99%): mp = 169−171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.2 Hz, 6H), 7.40 (d, J = 8.2 Hz, 6H), 5.42 (s, 1H), 1.32 (s, 27H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 135.7, 130.2, 124.9, 34.7, 31.2; ^{29}Si NMR (80 MHz, $CDCl_3$) δ −18.9; HRMS (EI) (M+) calcd for ($C_{30}H_{40}Si^+$) 428.2893, observed 428.2894; IR (neat, cm^{-1}) 2960, 2868, 2108, 1596, 1463, 1387, 1362, 1267, 1137, 1085, 822, 788, 724.

*Tris(4-(tert-butyl)phenyl)chlorosilane (**2j**).*[64] Chlorination was done using tris(4-(*tert*-butyl)phenyl)silane (1.26 g, 2.93 mmol) according to GP3. The silane was dissolved in 12 mL of carbon tetrachloride followed by addition of sulfuryl chloride (710 μL,8.79 mmol). The crude solid was purified by washing 2−3 times with hexanes to obtain a colorless solid (850 mg, yield = 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 6H), 7.43 (d, J = 8.3 Hz, 6H), 1.32 (s, 27H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 135.1, 129.8, 125.0, 34.8, 31.2.

*Tris(4-cyclohexylphenyl)silane (**4k**).* Compound **4k** was synthesized using 1-bromo-4-cyclohexylbenzene (98%) (1.89 mL, 10 mmol) according to GP2. The crude solid was recrystallized from pentane at −40 °C to yield a colorless solid (1.30 g, yield = 86%): mp = 79−81

dx.doi.org/10.1021/jo402569h | J. Org. Chem. 2014, 79, 2384−2396

°C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.52 (d, J = 8.0 Hz, 6H), 7.22 (d, J = 8.0 Hz, 6H), 5.41 (s, 1H), 2.53−247 (m, 3H), 1.91−1.82 (m, 12H), 1.77−1.73 (m, 3H), 1.45−1.34 (m, 12H), 1.31−1.24 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 135.8, 130.7, 126.6, 44.6, 34.3, 26.9, 26.1; ^{29}Si NMR (80 MHz, $CDCl_3$) δ −18.8; HRMS (EI) (M+) calcd for ($C_{36}H_{46}Si^+$) 506.3363, observed 506.3352; IR (neat, cm^{-1}) 3011, 2922, 2850, 2122, 1598, 1447, 1400, 1263, 1111, 998, 891, 866, 772, 727, 687, 671.

*Chlorotris(4-cyclohexylphenyl)silane (**2k**).* Chlorination was done using tris(4-cyclohexylphenyl)silane (1.26 g, 2.49 mmol) according to GP3. The silane was dissolved in 6 mL of carbon tetrachloride followed by the addition of sulfuryl chloride (602 μL, 7.47 mmol). Product formation was complete in 4 h. The crude oil was triturated with pentane at −78 °C under N_2, resulting in a colorless solid (500 mg, yield = 37%): mp = 123−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.2 Hz, 6H), 7.24 (d, J = 7.9 Hz, 6H), 2.53−2.51 (m, 3H), 1.90−1.83 (m, 12H), 1.77−1.73 (m, 3H), 1.47−1.34 (m, 12H), 1.30−1.23 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 135.3, 130.2, 126.6, 44.6, 34.2, 26.8, 26.1; ^{29}Si NMR (80 MHz, $CDCl_3$) δ +1.5; HRMS (EI) (M+) calcd for ($C_{36}H_{45}ClSi^+$) 540.2973, observed 540.2971; IR (neat, cm^{-1}) 3014, 2923, 2850, 1599, 1447, 1400, 1263, 1116, 998, 817, 673.

*Tris([1,1′-biphenyl]-4-yl)silane (**4l**).* Compound **4l** was synthesized using 4-iodobiphenyl (97%) (2.89 g, mmol) according to GP2. Addition of $SiHCl_3$ after lithiation was done at −78 °C instead of −40 °C and allowed to stir for 2 h. The crude white solid was carefully filtered and used without further purification (1.35 g, yield = 92%): mp = 192−193 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 6H), 7.67−7.61 (m, 12H), 7.46 (t, J = 7.3 Hz, 6H), 7.37 (t, J = 7.4 Hz, 3H), 5.60 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 140.9, 136.3, 132.0, 128.8, 127.6, 127.2, 126.9; ^{29}Si NMR (80 MHz, $CDCl_3$) δ −18.4; HRMS (EI) (M+) calcd for ($C_{36}H_{28}Si^+$) 488.1954, observed 488.1959; IR (neat, cm^{-1}) 3011, 2106, 1595, 1542, 1481, 1384, 1182, 1115, 1007, 845, 835, 763, 755, 660.

*Tris([1,1′-biphenyl]-4-yl)chlorosilane (**2l**).* Chlorination was done using tris([1,1′-biphenyl])4-yl)silane (**4l**) (1.43 g, 2.92 mmol) according to GP3. Carbon tetrachloride (14 mL) was added, and the solution was heated in order to dissolve the compound. Sulfuryl chloride (708 μL, 8.76 mmol) was added and refluxed for 4 h. The crude solid was washed with hexanes 2−3 times, resulting in a light pink product (800 mg, yield = 52%): mp = 215−217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 6H), 7.68 (d, J = 8.3 Hz, 6H), 7.63 (d, J = 8.2 Hz, 6H), 7.47 (t, J = 7.2 Hz, 6H), 7.40−7.36 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 140.6, 135.7, 131.5, 128.9, 127.8, 127.2, 126.9; HRMS (EI) (M+) calcd for ($C_{36}H_{27}ClSi^+$) 522.1565, observed 522.1580.

General Procedure of Rate Study Using In Situ IR. All reactions were carried out at 0.08 M concentration with regard to the alcohol. A three-neck 50 mL Schlenk tube with a 24/40 ground glass joint for probe insertion with two side arms used as a reaction vessel. A probe was inserted into the Schlenk tube equipped with a stir bar under N_2 atmosphere. After the instrument was calibrated, an air background was taken first. THF (2.10 mL) was added to the Schlenk tube, and the solvent was allowed to cool to −78 °C for approximately 20 min using a dry ice/acetone bath. The solvent background was recorded for each experiment at −78 °C, then IR data collection was started. A solution of (*R*)-**5** or (*S*)-**5** (54.3 mg), **1** (38 mg), and Hünig's base (64 μL) was prepared in a 1 mL volumetric flask. From the above prepared solution, 810 μL was carefully added to the Schlenk tube via a syringe. The resulting mixture was allowed to stir for 10−15 min. Meanwhile, a solution of **2** (0.357 M) was prepared using a volumetric flask, and 840 μL of this was added to the reaction mixture at −78 °C. The time of the silyl chloride addition was recorded for reference, and IR data were collected for 30 min to 10 h. Rapid collect was used for data collection in the case of electron withdrawing *p*-substituted triphenylsilyl chloride rate experiments. The absorbance was obtained using ConcIRT. Reaction conversion was obtained at different time points by taking reaction aliquots at these time points, quenching them, and determining the conversion by ^{1}H NMR. The geminal proton of the product and the starting material were used for integration. The relationship between concentration and absorbance was constructed by calculating the product concentration from the NMR conversions and plotting it against the absorbance at each of those time points. Once the Beer's Law relationship was determined, the concentration at each data point was calculated from the absorbance and plotted against time to determine the rate. Initial rate was determined by using the data up to 10% conversion. The accuracy of the peak obtained from ConcIRT was confirmed by comparing the NMR conversion with the calculated conversion from the absorbance.

General Procedure for the Silylation-Based Kinetic Resolution of Secondary Alcohols and Desilylation of the Isolated Products. An oven-dried 1 dram vial was charged with 4 Å molecular sieves (10−15 mg) and a Teflon-coated stir bar. The racemic alcohol (**5** or **7**) (0.22 mmol), catalyst **1** (11.2 mg, 0.055 mmol), and *N*,*N*-diisopropylethylamine (Hünig's base) (23 μL, 0.132 mmol) were added to a vial and then quickly sealed under a nitrogen atmosphere. Dry THF (1.0 mL) was added, and the reaction mixture was allowed to stir at −78 °C for 15−20 min. Meanwhile, a solution of (pY-Ph)$_3$SiCl (0.357 M) was prepared using a volumetric flask (under N_2). The solution of (pY-Ph)$_3$SiCl **2** (370 μL, 0.6 mmol) was added to the reaction vial, and the resulting mixture was allowed to react for the specified amount of time at −78 °C. The reaction mixture was then quenched using 300 μL of MeOH at −78 °C. The mixture was allowed to warm to room temperature followed by addition of 1.0 mL of saturated aqueous NH_4Cl. The reaction mixture was transferred to a 4 dram vial and extracted using diethyl ether (3 × 2 mL). The ether layer was then passed through a pad of silica gel. After filtration, it was concentrated and the crude mixture was purified using silica gel chromatography (100% CH_2Cl_2 followed by 2% MeOH in CH_2Cl_2). The analysis of the unreacted recovered alcohol was done by a chiral HPLC using a hexanes/*i*-PrOH solvent system.

Desilylation. The silylated product was transferred to a 4 dram vial with a stir bar and dissolved in 3 mL of THF. The solution was treated with a 1 M solution of TBAF in THF (500 μL to 1.0 mL) and allowed to stir for 3−10 h at room temperature (conversion was monitored by TLC). The reaction was quenched with brine and extracted with diethyl ether. The crude mixture was purified via silica gel column chromatography (CH_2Cl_2 to 2% MeOH in CH_2Cl_2). HPLC analysis was done for the desilylated product (alcohol). The absolute stereochemistry was confirmed by comparing the HPLC data with previously published data.[9]

*HPLC Conditions for 1,2,3,4-Tetrahydronaphthalen-1-ol (**5**).*[9] Chiralpack OD-H column was used with 4% *i*PrOH in hexanes. Flow rate was 0.5 mL/min, 25 °C; t_R 25.2 min for (*S*)-enantiomer and t_R 28.7 min for (*R*)-enantiomer.

*HPLC Conditions for 4-Chromanol (**7**).*[9] Chiralpack OD-H column was used with 2% *i*PrOH in hexanes. Flow rate was 1.3 mL/min, 25 °C; t_R 28.6 min for (*S*)-enantiomer and t_R 37.3 min for (*R*)-enantiomer.

*1,2,3,4-Tetrahydronaphthalen-1-ol (**5**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7−44−7.23 (m, 1 H), 7.22−7.20 (m, 2 H), 7.12−7.10 (m, 1H) 4.79 (t, 5.0 Hz, 1H), 2.87−2.81 (m, 1 H), 2.77−2.69 (m, 1H), 2.01−1.88 (m, 3 H), 1.83−1.75(m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 138.7, 137.1, 129.0, 128.6, 127.5, 126.1, 68.1, 32.2, 29.2, 18.7.

*Triphenyl((1,2,3,4-tetrahydronaphthalen-1-yl)oxy)silane (**6a**):*[9] 33.5 mg (yield = 37%), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 6.0 Hz, 6H), 7.47−7.36 (m, 9H), 7.28(d, J = 6.8 Hz, 1H), 7.18−7.06 (m, 3H), 4.97 (t, J = 5.6 Hz, 1H), 2.88−2.81 (m, 1H), 2.72−2.64 (m, 1H), 2.10−2.03 (m, 1H), 1.96−1.82 (m, 2H), 1.72−1.63 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 137.0, 135.6, 134.8, 129.9, 128.7, 128.6, 127.8, 127.1, 125.7, 70.2, 32.5, 29.0, 19.2.

*(R)-Tris(4-bromophenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)-oxy)silane (**6b**):* 55 mg (yield = 39%), white solid; mp range 88−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.2 Hz, 6H), 7.46 (d, J = 8.1 Hz, 6H), 7.21−7.14 (m, 2H), 7.13−7.06 (m, 2H), 4.94 (t, J = 5.0 Hz, 1H), 2.88−2.81 (m, 1H), 2.74−2.66 (m, 1H), 2.14−2.01 (m, 1H), 1.97−1.79 (m, 2H), 1.77−1.64 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 137.1, 136.9, 132.6, 131.3, 128.9, 128.5, 127.5, 125.7, 125.5, 70.6, 32.5, 28.9, 18.9; $[\alpha]_D^{25}$ = +19.0 (c = 0.75, $CHCl_3$); HRMS

dx.doi.org/10.1021/jo402569h | J. Org. Chem. 2014, 79, 2384−2396

(EI) (M+) calcd for ($C_{28}H_{23}Br_3OSi^+$) 641.9043, observed 641.9034; IR (neat, cm^{-1}) 3069, 2937, 2866, 1739, 1572, 1550, 1478, 1454, 1377, 1350, 1208, 1185, 1115, 1066, 1009, 988, 906, 807, 757.

*(R)-Tris(4-chlorophenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)oxy)-silane (**6c**):* 34.9 mg (yield = 31%), colorless oil with minor amounts of tris(4-chlorophenyl)silanol present; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 6H), 7.38 (d, J = 8.4 Hz, 6H), 7.21−7.13 (m, 2H), 7.13−7.06 (m, 2H), 4.94 (m, 1H), 2.88−2.80 (m, 1H), 2.73−2.65(m, 1H), 2.12−2.02 (m, 1H), 1.95−1.78 (m, 2H), 1.75−1.65 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.1, 136.8, 136.7, 132.3, 128.9, 128.6, 128.4, 127.4, 125.7, 70.6, 32.5, 28.9, 18.9; $[\alpha]_D^{25}$ = +22.6 (c = 0.88, $CHCl_3$); HRMS (EI) (M+) calcd for($C_{28}H_{23}Cl_3OSi^+$) 508.0578, observed 508.0558; IR (neat, cm^{-1}) 3072, 2936, 1913, 1578, 1556, 1482, 1455, 1381, 1349, 1257, 1184, 1118, 1082, 1014, 989, 877, 812, 711.

*(R)-Tris(4-fluorophenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)oxy)-silane (**6d**):* 38.0 mg (yield = 38%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.59 (m, 6H), 7.21−7.17 (m, 2H), 7.14−7.08 (m, 8H), 4.96 (t, J = 5.6 Hz, 1H), 2.89−2.82 (m, 1H), 2.74−2.67 (m, 1H), 2.14−2.04 (m, 1H), 1.96−1.81 (m, 2H), 1.76−1.66 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6−163.1(d), 138.4, 137.6−137.5 (d), 137.1, 130.0(d), 128.9, 128.6, 127.4, 125.7, 115.4−115.2 (d), 70.4, 32.5, 28.9, 19.0; $[\alpha]_D^{25}$ = +18.0 (c = 0.91, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{28}H_{23}F_3OSi^+$) 460.1464, observed 460.1454; IR (neat, cm^{-1}) 3025, 2937, 1910, 1588, 1498, 1388, 1350, 1225, 1161, 1110, 1070, 1014, 989, 878, 755, 738, 715.

*(R)-((1,2,3,4-Tetrahydronaphthalen-1-yl)oxy)tris(4-(trifluoro-methyl)phenyl)silane (**6e**):* 33.1 mg (yield = 25%), colorless oil with minor amounts of tris(4-(trifluoromethyl)phenyl)silanol present; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 6H), 7.66 (d, J = 8.2 Hz, 6H), 7.21−7.17 (m, 1H), 7.14−7.08 (m, 3H), 5.00 (t, J = 5.1, 1H), 2.88−2.81 (m, 1H), 2.75−2.67 (m, 1H), 2.16−2.06 (m, 1H), 1.97−1.83 (m, 2 H), 1.78−1.69 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 137.7, 137.2, 135.7,, 132.5 (q, J_{CF} = 32.4 Hz), 129.1, 128.6, 127.7, 125.8, 124.8 (q, J_{CF} = 3.8 Hz), 124.0 (q, J = 272.5 Hz), 71.1, 32.5, 28.8, 18.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −63.1; $[\alpha]_D^{25}$ = +9.7 (c = 0.67, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{31}H_{23}F_9OSi^+$) 610.1368, observed 610.1372; IR (neat, cm^{-1}) 3031, 2939, 1610, 1393, 1318, 1164, 1121, 1017, 990, 829, 739, 704.

*(R)-Tris(4-methoxyphenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)-oxy)silane (**6f**):* 21.3 mg (yield = 20%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H 7.58 (d, J = 8.7 Hz, 6H), 7.27 (m, 1H), 7.17−7.11 (m, 2H), 7.09−7.05 (m, 1H), 6.93(d, J = 8.7 Hz, 6H), 4.94 (t, J = 6.0 Hz, 1H), 3.83 (s, 9H), 2.87−2.80 (m, 1H), 2.71−2.64 (m,1H), 2.09−2.01 (m, 1H), 1.92−1.82 (m, 2H), 1.71−1.62 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 139.3, 137.1, 137.0, 128.7, 128.6, 127.0, 126.4, 125.6, 113.5, 69.9, 55.0, 32.6, 29.1, 19.3; $[\alpha]_D^{25}$ = +13.1 (c = 0.95, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{31}H_{32}O_4Si^+$) 496.2064, observed 496.2053; IR (neat, cm^{-1}) 3062, 2934, 2836, 1903, 1592, 1563, 1501, 1456, 1441, 1277, 1246, 1179, 1070, 1028, 987, 909, 814, 798, 733.

*(R)-((1,2,3,4-Tetrahydronaphthalen-1-yl)oxy)tri-p-tolylsilane (**6g**):* 43.4 mg (yield = 44%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 6H), 7.30 (d, J = 8.5 Hz, 1H), 7.18 (d, J = 8.0 Hz, 6H), 7.14−7.09 (m, 2H), 7.08−7.04 (m, 1H), 4.93 (t, J = 5.6 Hz, 1H), 2.85−2.79 (m, 1H), 2.69−2.62 (m, 1H), 2.35 (s, 9H), 2.08−1.99 (m,1H), 1.92−1.82 (m, 2H), 1.69−1.60 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 139.3, 137.0, 135.6, 135.4, 131.6, 128.8, 128.6, 126.9, 125.6, 70.0, 32.6, 29.1, 21.6, 19.3; $[\alpha]_D^{25}$ = +16.2 (c = 0.98, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{31}H_{32}OSi^+$) 448.2216, observed 448.2217; IR (neat, cm^{-1}) 3066, 2936, 2864, 1920, 1739, 1599, 1501, 1451, 1393, 1350, 1261, 1208, 1188, 1111, 1071, 1016, 988, 876, 738, 715.

*(R)-Tris(4-ethylphenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)oxy)-silane (**6h**):* 33.3 mg (yield = 31%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 6H), 7.29 (d, J = 7.4 Hz, 1H), 7.20 (d, J = 8.2 Hz, 6H), 7.15−7.09 (m, 2H), 7.07−7.03 (m, 1H), 4.93 (t, J = 6.1 Hz, 1H), 2.86−2.79 (m, 1H), 2.63−2.70 (m, 7H), 2.09−2.00 (m, 1H), 1.94−1.81 (m, 2H), 1.70−1.60 (m, 1H), 1.24 (t, J = 7.6 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 139.3, 137.0, 135.7, 132.0, 128.7, 128.6, 127.4, 126.9, 125.6, 70.0, 32.6, 29.1, 28.9, 19.3, 15.3; $[\alpha]_D^{25}$ = +18.0 (c = 0.70, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{34}H_{38}OSi^+$) 490.2686, observed 490.2691; IR (neat, cm^{-1}) 3066, 2964, 2932, 2872, 1601, 1553, 1455, 1398, 1190, 1072, 1039, 1017, 988, 821, 783, 739.

*(R)-Tris(4-isopropylphenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)-oxy)silane (**6i**):* 40.7 mg (yield = 35%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 6H), 7.28 (d, J = 7.0 Hz, 1H), 7.22 (d, J = 7.8 Hz, 6H), 7.15−7.08 (m, 2H), 7.05−7.03 (m, 1H), 4.93 (t, J = 6.2 Hz, 1H), 2.93−2.79 (m, 4H), 2.70−2.62(m, 1H), 2.10−2.00 (m, 1H), 1.95−1.82 (m, 2H), 1.70−1.59 (m, 1H), 1.25 (d, J = 8.0 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 139.3, 137.0, 135.7, 132.2, 128.7, 128.6, 126.9, 125.9, 125.6, 70.0, 34.1, 32.6, 29.1, 23.9, 19.3; $[\alpha]_D^{25}$ = +16.8 (c = 0.95, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{37}H_{44}OSi^+$) 532.3155, observed 532.3139; IR (neat, cm^{-1}) 3067, 2959, 2869, 1920, 1600, 1491, 1458, 1394, 1362, 1263, 1119, 1072, 1050, 1018, 988, 849, 769, 739, 710.

*(R)-Tris(4-(tert-butyl)phenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)oxy)silane (**6j**):* 48.5 mg (yield = 38%), white solid; mp 137−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 6H), 7.39 (d, J = 8.4 Hz, 6H), 7.29 (d, J = 7.4 Hz, 1H), 7.17−7.10 (m, 2H), 7.08−7.05 (m, 1H), 4.95 (t, J = 6.2 Hz, 1H), 2.88−2.81 (m, 1H), 2.71−2.68 (m,1H), 2.11−2.02 (m, 1H), 1.98−1.84 (m, 2H), 1.72−1.63 (m, 1H), 1.33 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 139.4, 137.0, 135.5, 131.7, 128.7, 128.6, 126.9, 125.6, 124.6, 69.9, 34.7, 32.6, 31.2, 29.1, 19.3; $[\alpha]_D^{25}$ = +19.4 (c = 1.1, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{40}H_{50}OSi^+$) 574.3625, observed 574.3633; IR (neat, cm^{-1}) 2961, 2867, 1984, 1599, 1459, 1388, 1362, 1268, 1203, 1138, 1017, 988, 926, 876, 824, 750.4.

*(R)-Tris(4-cyclohexylphenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)-oxy)silane (**6k**):* 37.2 mg (yield = 26%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58(d, J = 8.0 Hz, 6H), 7.26 (d, J = 7.5 Hz, 1H), 7.19 (d, J = 7.9 Hz, 6H), 7.15−7.03 (m, 3H), 4.92 (t, J = 6.0 Hz, 1 H), 2.86−2.78 (m, 1H), 2.69−2.62 (m, 1H), 2.52−2.46 (m, 3H), 2.09−1.99 (m, 1H), 1.93−1.81 (m, 14H), 1.75−1.72 (m, 3 H), 1.69−1.63 (m, 1 H), 1.51−1.33 (m, 12H), 1.28−1.20 (m, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 139.4, 137.0, 135.7, 132.2, 128.7, 128.6, 126.9, 126.3, 125.6, 69.9, 44.6, 34.3, 32.6, 29.1, 26.9, 26.2, 19.3; $[\alpha]_D^{25}$ = +14.3 (c = 1.04, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{46}H_{56}OSi^+$) 652.4094, observed 652.4094; IR (neat, cm^{-1}) 3066, 2923, 2851, 1923, 1600, 1448, 1397, 1350, 1263, 1115, 1072, 999, 1016, 988, 815, 755, 738, 668.

*(R)-Tri([1,1′-biphenyl]-4-yl)((1,2,3,4-tetrahydronaphthalen-1-yl)-oxy)silane (**6l**):* 27.2 mg (yield = 19%), white solid; mp 44−46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 6H), 7.65−7.62 (m, 12H), 7.45−7.43 (m, 6H), 7.37−7.33 (m, 4H), 7.19−7.13 (m, 2H), 7.11−7.07 (m, 1H), 5.07 (t, J = 6.2 Hz, 1H), 2.91−2.83 (m, 1H), 2.74−2.66 (m, 1H), 2.17−2.07 (m, 1H), 2.04−1.88 (m, 2H), 1.76−1.65 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 140.9, 138.9, 137.1, 136.1, 135.9, 133.5, 128.9, 128.8, 128.7, 127.5, 127.2, 126.6, 125.7, 70.4, 32.6, 29.1, 19.2; $[\alpha]_D^{25}$ = +23.3 (c = 0.94, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{46}H_{38}OSi^+$) 634.2686, observed 634.2673; IR (neat, cm^{-1}) 3059, 3024, 2934, 1809, 1597, 1544, 1483, 1446, 1386, 1255, 1117, 1071, 1006, 988, 829, 756, 695.

*Chroman-4-ol (**7**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31(d, J = 7.6 Hz, 1H), 7.23−7.19 (m, 1H), 6.95−6.91 (m,1H), 6.85 (d, J = 8.2 Hz, 1H),4.79 (t, J = 3.9 Hz, 1H), 4.32−2.25 (m, 2H), 2.17−2.09 (m, 1H), 2.07−2.01 (m, 1H), 1.86 (s,1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 129.7, 129.6, 124.3, 120.6, 117.0, 63.2, 61.9, 30.8.

*(Chroman-4-yloxy)triphenylsilane (**8a**):*[9] white solid, 35.5 mg (yield = 40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 6.5 Hz, 6H), 7.48−7.37 (m, 9H), 7.18−7.14 (m, 1H), 6.99 (d, J = 7.2 Hz, 1H), 6.83−6.76 (m, 2H), 4.97 (t, J = 4.0 Hz, 1H), 4.51−4.45 (m, 1H), 4.24−4.19 (m, 1H), 2.02−1.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 135.5, 134.3, 130.1, 130.0, 129.2, 127.8, 124.2, 120.0, 116.7, 65.0, 62.2, 31.4.

*(R)-Tris(4-bromophenyl)(chroman-4-yloxy)silane (**8b**):* 49.3 mg (yield = 35%), white solid; mp 109−110 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.1 Hz, 6H), 7.43 (d, J = 8.2 Hz, 6H), 7.20−7.16 (m, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.83−6.76 (m, 2H), 4.92 (t, J = 4.0 Hz, 1H), 4.47−4.40 (m, 1H), 4.26−4.21 (m, 1H), 2.01−1.97 (m, 2H);

dx.doi.org/10.1021/jo402569h | J. Org. Chem. 2014, 79, 2384−2396

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 136.8, 132.2, 131.4, 129.8, 129.6, 125.7, 123.3, 120.1, 116.9, 65.4, 61.9, 31.3; $[\alpha]_D^{25}$ = +38.3 (c = 0.84, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{27}H_{21}Br_3O_2Si^+$) 643.8836, observed 643.8859; IR (neat, cm^{-1}) 3071, 2926, 1915, 1610, 1572, 1478, 1377, 1224, 1116, 1063, 1008, 906, 806, 753.

(R)-Tris(4-chlorophenyl)(chroman-4-yloxy)silane (**8c**): 46.6 mg (yield = 41%), yellowish color oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.3 Hz, 6H), 7.41 (d, J = 8.3 Hz, 6H), 7.20−7.16 (m, 1H), 6.91−6.89 (m,1H), 6.84−6.76 (m, 2H), 4.94 (t, J = 4.4 Hz, 1H), 4.48−4.42 (m, 1H), 4.27−4.22 (m, 1H), 2.01−1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 136.1, 135.7, 130.9, 128.9, 128.6, 127.5, 122.4, 119.1, 116.0, 64.4, 60.9, 30.4; $[\alpha]_D^{25}$ = +49.9 (c = 1.17, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{27}H_{21}Cl_3O_2Si^+$) 510.0370, observed 510.0363; IR (neat, cm^{-1}) 3072, 2927, 1912, 1609, 1578, 1482, 1381, 1224, 1118, 1082, 1014, 924, 809, 711.

(R)-(Chroman-4-yloxy)tris(4-fluorophenyl)silane (**8d**): 37 mg (yield = 36%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.56 (m, 6H), 7.20−7.15 (m, 1H), 7.13−7.08 (m, 6H), 6.89 (d, J = 7.6 Hz, 1H), 6.83−6.76 (m, 2H), 4.94 (t, J = 4.0 Hz, 1H), 4.49−4.42 (m, 1H), 4.27−4.21 (m, 1H), 2.01−1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7−163.2 (d), 154.5, 137.5 (d), 129.8, 129.6(d), 129.5, 123.6, 120.0, 116.9, 115.5−115.3(d), 65.2, 62.0, 31.4; $[\alpha]_D^{25}$ = +47.4 (c = 0.98, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{27}H_{21}F_3O_2Si^+$) 462.1257, observed 462.1266; IR (neat, cm^{-1}) 3065, 2928, 2888, 1909, 1610, 1498, 1489, 1388, 1269, 1223, 1161, 1110, 1092, 1064, 1003, 924, 821, 754, 715.

(R)-(Chroman-4-yloxy)tris(4-(trifluoromethyl)phenyl)silane (**8e**): 22.8 mg (yield = 17%), colorless oil with minor amounts of tris(4-(trifluoromethyl)phenyl)silanol present; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 6H), 7.66 (d, J = 8.1 Hz, 6H), 7.21−7.16 (m, 1H), 6.86−6.81 (m, 2H), 6.78−6.74 (m, 1H), 4.98 (t, J = 3.9 Hz, 1H), 4.50−4.44 (m, 1H), 4.30−4.25 (m, 1H), 2.05−2.02 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 137.6, 135.6, 132.7 (q, J_{CF} = 32.3 Hz), 129.9, 129.8, 124.8 (q, J_{CF} = 3.71 Hz), 123.9 (q, J_{CF} =272.5 Hz), 122.9, 120.1, 117.1, 65.9, 61.7, 31.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −63.2; $[\alpha]_D^{25}$ = +23.3 (c = 0.88, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{30}H_{21}F_9O_2Si^+$) 612.1161, observed 612.1171; IR (neat, cm^{-1}) 3034, 2929, 1611, 1585, 1490, 1393, 1318, 1269, 1164, 1120, 1017, 1005, 829, 755, 705.

(R)-(Chroman-4-yloxy)tris(4-methoxyphenyl)silane (**8f**): 25.1 mg (yield = 23%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.2 Hz, 6H), 7.18−7.13 (m, 1H), 7.02 (d, J = 7.7 Hz, 1H), 6.93 (d, J = 8.6 Hz, 6H), 6.82−6.78 (m, 2H), 4.94 (t, J = 4.3 Hz, 1H), 4.48−4.42 (m, 1H), 4.22−4.17 (m, 1H), 3.83 (s, 9H), 2.02−1.92 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 154.5, 137.1, 130.0, 129.1, 126.0, 124.5, 120.0, 116.6, 113.6, 64.7, 62.3, 55.0, 31.5; $[\alpha]_D^{25}$ = +41.5 (c = 0.89, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{30}H_{30}O_5Si^+$) 498.1857, observed 498.1869; IR (neat, cm^{-1}) 3018, 2837, 1902, 1592, 1501, 1489, 1276, 1179, 1090, 1065, 1001, 922, 810, 798, 753, 722.

(R)-(Chroman-4-yloxy)tri-p-tolylsilane (**8g**): 30.4 mg (yield = 31%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 6H), 7.19 (d, J = 7.8 Hz, 6H), 7.15−7.11 (m, 1H), 7.03−7.01 (m, 1H), 6.80−6.75 (m, 2H), 4.93 (t, J = 4.2 Hz, 1H), 4.47−4.41 (m, 1H), 4.20−4.15 (m, 1H), 2.36 (s, 9H), 2.02−1.89 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 139.9, 135.6, 131.2, 130.0, 129.1, 128.7, 124.5, 120.0, 116.6, 64.8, 62.3, 31.5, 21.6; $[\alpha]_D^{25}$ = +42.0 (c = 1.08, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{30}H_{30}O_2Si^+$) 450.2009, observed 450.2008; IR (neat, cm^{-1}) 3066, 2921, 1917, 1599, 1584, 1488, 1454, 1393, 1225, 1111, 1065, 1003, 922, 837, 753, 716.

(R)-(Chroman-4-yloxy)tris(4-ethylphenyl)silane (**8h**): 39.2 mg (yield = 36%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 6H), 7.21 (d, J = 8.0 Hz, 6H), 7.15−7.11 (m, 1H), 7.01−6.99 (m, 1H), 6.80−6.75 (m, 2H), 4.93 (t, J = 4.0 Hz, 1H), 4.48−4.42 (m, 1H), 4.21−4.16 (m, 1H), 2.66 (q, J = 8.0 Hz, 6H), 2.04−1.90 (m, 2H), 1.24 (t, J = 8.0 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 146.1, 135.6, 131.5, 130.0, 129.1, 127.5, 124.5, 120.0, 116.6, 64.8, 62.3, 31.5, 28.9, 15.3; $[\alpha]_D^{25}$ = +46.0 (c = 1.13, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{33}H_{36}O_2Si^+$) 492.2479, observed 492.2475; IR (neat, cm^{-1}) 3067, 2964, 2873, 1916, 1601, 1585, 1489, 1455, 1398, 1268, 1226, 1112, 1091, 1003, 922, 822, 809, 753, 719.

(R)-(Chroman-4-yloxy)tris(4-isopropylphenyl)silane (**8i**): 41.2 mg (yield = 35%), white solid; mp 90−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.8 Hz, 6H), 7.23 (d, J = 7.9 Hz, 6H), 7.13 (t, J = 8.1 Hz, 1H), 6.94 (d, J = 7.3 Hz, 1H), 6.79−6.73 (m, 2H), 4.93 (t, J = 4.2 Hz, 1H), 4.49−4.43 (m, 1H), 4.19 (dt, J = 6.3, 4.2 Hz, 1H), 2.91 (hept, J = 6.9 Hz, 3H), 2.05−1.90 (m, 2H), 1.25 (d, J = 6.9 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 150.6, 135.6, 131.7, 130.1, 129.0, 126.0, 124.5, 119.9, 116.6, 64.7, 62.3, 34.1, 31.5, 23.8; $[\alpha]_D^{25}$ = +50.8 (c = 0.90, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{36}H_{42}O_2Si^+$) 534.2948, observed 534.2942; IR (neat, cm^{-1}) 3067, 2960, 2870, 1738, 1600, 1585, 1489, 1456, 1394, 1268, 1226, 1118, 1092, 1051, 1004, 922, 822, 809, 770, 754, 720.

(R)-Tris(4-(tert-butyl)phenyl)(chroman-4-yloxy)silane (**8j**): 47.5 mg (yield = 37%), white solid; mp 112−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.1 Hz, 6H), 7.40 (d, J = 8.1 Hz, 6H), 7.14 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.81−6.74 (m, 2H), 4.94 (t, J = 4.0 Hz, 1H), 4.50−4.44 (m, 1H), 4.23−4.18 (m, 1H), 2.07−1.92 (m, 2H), 1.33 (s, 27H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 152.8, 135.4, 131.3, 130.1, 129.0, 124.8, 124.6, 119.9, 116.6, 64.7, 62.3, 34.8, 31.5, 31.2; $[\alpha]_D^{25}$ = +49.5 (c = 1.13, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{39}H_{48}O_2Si^+$) 576.3418, observed 576.3429; IR (neat, cm^{-1}) 3073, 2963, 2868, 1927, 1600, 1583, 1487, 1453, 1388, 1268, 1252, 1140, 1125, 1065, 1004, 918, 824, 809, 751.

(R)-(Chroman-4-yloxy)tris(4-cyclohexylphenyl)silane (**8k**): 52.2 mg (yield = 36%), white solid; mp 47−49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 6H), 7.22 (d, J = 8.0 Hz, 6H), 7.15−7.11 (m, 1H), 6.95−9.92 (m, 1H), 6.80−6.73 (m, 2H), 4.92 (t, J = 4.3 Hz, 1 H), 4.49−4.43 (m, 1 H), 4.22−4.17 (m, 1H), 2.53−2.48 (m, 3H), 2.05−1.93 (m, 2H), 1.90−1.48 (m, 12H), 1.76−1.73 (m, 3H), 1.48−1.34 (m, 12H), 1.30−1.23 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 149.8, 135.6, 131.7, 130.1, 129.0, 126.4, 124.5, 119.9, 116.5, 64.7, 62.3, 44.6, 34.2, 31.5, 26.9, 26.1; $[\alpha]_D^{25}$ = +44.0 (c = 0.94, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{45}H_{54}O_2Si^+$) 654.3887, observed 654.3884; IR (neat, cm^{-1}) 3067, 2922, 2850, 1968, 1600, 1585, 1489, 1448, 1348, 1268, 1253, 1192, 1115, 1091, 1067, 999, 922, 816, 752, 629.

(R)-Tri([1,1′-biphenyl]-4-yl)(chroman-4-yloxy)silane (**8l**): 26.5 mg (yield = 19%), white solid; mp 48−49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 6H), 7.69−7.64 (m, 12H), 7.49−7.45 (m, 8H), 7.40−7.36 (m, 3H), 7.21−7.17 (m, 1H), 7.11−7.09 (m, 1H), 6.85−6.80 (m, 2H), 5.08 (t, J = 4.2 Hz, 1H), 4.58−4.52 (m, 1H), 4.30−4.25 (m, 1H), 2.16−2.02 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 142.8, 140.8, 136.0, 133.1, 130.1, 129.3, 128.8, 127.6, 127.2, 126.7, 124.2, 120.1, 116.7, 65.1, 62.2, 31.5; $[\alpha]_D^{25}$ = +49.7 (c = 0.58, $CHCl_3$); HRMS (EI) (M+) calcd for ($C_{45}H_{36}O_2Si^+$) 636.2479, observed 636.2485; IR (neat, cm^{-1}) 3025, 2882, 2056, 1597, 1484, 1455, 1386, 1268, 1252, 1225, 1117, 1065, 1005, 923, 830, 727, 695, 663.

■ ASSOCIATED CONTENT

Supporting Information

Rate data, HPLC traces, and NMR spectra (^{1}H and ^{13}C). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge support from the University of South Carolina and the National Science Foundation CAREER Award CHE-1055616.

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