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Sequential *aza*-Baylis–Hillman/Ring Closing Metathesis/ Aromatization as a Novel Route for the Synthesis of Substituted Pyrroles

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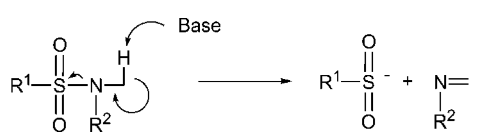
A new route to diverse 2-substituted-3-methoxycarbonyl pyrroles has been developed. Diverse SES protected α-methylene *β*-aminoesters were obtained by a 3-component *aza*-Baylis–Hillman reaction. Diversity arose from the aryl aldehydes which can be used in this reaction. *N*-Alkylation with allyl bromide under mild conditions provided the corresponding dienes. These substituted dienes were cyclized by ring closing metathesis at room temperature or under microwave-activation with Grubbs-type II catalyst to yield SES-protected pyrroline intermediates. The final pyrroles were obtained by base-promoted dehydrodesulfinylation/aromatization. The scope of each of these reactions was explored.

Introduction

The 2-trimethylsilyethylsulfonyl (or SES) group is a valuable protecting group of amines in organic synthesis.[1] It is mainly used to protect an amine as a sulfonamide and promote Mitsunobu or base-activated alkylation. This group can be cleaved usually by fluoride-promoted *β*-elimination. A less usual pathway to remove the SES group is to perform a base-promoted dehydrodesulfinylation, which consists of abstracting a proton in the α-position to the nitrogen of the sulfonamide. This process is favored in the case of unsaturated cyclic compounds when an aromatization to the final product is possible. It has been described in the literature mostly with the tosyl[2] or related protecting groups[2d,3] and more rarely with the SES group[3k,4] (eq 1).



(1)

As part of our ongoing project on the synthesis of heterocyclic structures by ring closing metathesis (RCM),[4b,5] we report herein a new strategy for the preparation of 2,3-disubstituted pyrroles using the dehydrodesulfinylation as the aromatization step of pyrrolines formed by RCM. The pyrrole[6] ring is an important scaffold in pharmaceutical and material chemistry. It is found in biomolecules[6a,b] such as porphyrins and cytochromes. It serves also as a building block for the preparation of polymeric and supramolecular structures which have applications in nonlinear optics.[6c,d]

Results and Discussion

As described in the retrosynthetic scheme (Scheme 1), the pyrrole ring can be obtained after dehydrodesulfin-

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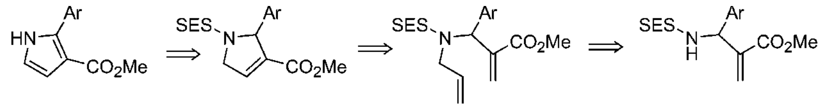
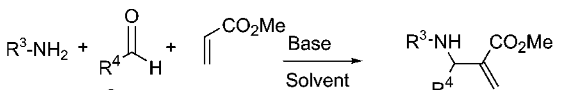
SCHEME 1



ylation/aromatization of a SES-protected pyrroline formed via RCM of an appropriate linear precursor. This precursor can result from the alkylation of an unsaturated β-aminoester synthesized by the *aza*-Baylis–Hillman reaction. Recently we have presented the synthesis of an ester-substituted pyrroline via RCM.[5b] To increase the diversity of this class of molecules[7] as well as the pyrrole derivatives obtained by aromatization, we needed to prepare more diverse α-methylene-β-aminoesters which can be obtained via the *aza*-Baylis–Hillman reaction.

The 3-component *aza* version of the Baylis–Hillman reaction is an attractive method for the synthesis of β-aminoesters. This reaction has been performed with the tosyl group (R^3 = tosyl) as the protecting and activating group of ammonia.[8] With the purpose of synthesizing β-aminoesters bearing more easily cleavable protecting groups, we decided to investigate the SES group for protection (eq 2).[9]



3a-o

1 R^3= Ts
2 R^3=SES

4 R^3= Ts
5a-o R^3= SES

(2)

First, the conditions by Balan et al.[8b] for Ts-NH_2 were tested with use of SES-NH_2, benzaldehyde, and methyl acrylate in the presence of a Lewis acid (Ti(O*i*-Pr_4)), 3-HQD as a base, and molecular sieves. When the reaction was performed at room temperature conversion was slow and selectivity between formation of the β-aminoester and the β-hydroxyester was moderate. Increasing the reaction temperature to 70 °C resulted in complete conversion after 24 h and better selectivity. Reaction of SES-NH_2 was slower than that with Ts-NH_2 (8 h in the same reaction conditions). We applied these reaction conditions to the synthesis of six aminoesters (**5a–f**). However, we realized that in some cases, the reaction time and conditions were not satisfactory. With some aldehydes, the reaction was too slow and incomplete after 24 h. Heating the reaction mixture resulted in the degradation of the reactants. Consequently we also performed the reactions in different conditions (DABCO in *i*-PrOH) in the presence of an excess of benzaldehyde and methyl acrylate to drive the reaction to completion. Concomitant formation of the corresponding hydroxyester was not avoided. The aminoesters were obtained pure after column chromatography. Results are presented in Table 1.

TABLE 1.

	yield[a] of **5** (%)						
	conditions A[g]		conditions B[g]				
R^4	*t* (h)	yield (%)	*t* (h)	yield (%)	yield of **6** (%)	yield[a] of **7** (%)	yield[a] of **8** (%)
a	24	73	10	86	98	98	80
b	96	46	72	67	98	95	83
c	48	64	6	90	97	92	*b*
d	24	75	*c*		*c*	*c*	*c*
e	72	36	6	79	99	95	81
f	72	42	6	86	99	90	81
g	*d*		48	60	98	90	66
h	*c*		38	86	98	98	72
i	*c*		72	70	97	92	78
j	*c*		72	66	98	96	88
k	*d*		14	86	99	95	81
l	*d*		10	73	99	94	81
m	*d*		14	61	98	5[f]	
n	*d*		6	60	97	10[f]	
o	*d*		6	71	*e*		

[a] After purification by column chromatography. [b] Aromatization occurred along with transesterification of the side chain with *t*-BuOH. [c] Not performed. [d] Slow reaction at room temperature and degradation of the aldehyde upon heating. [e] Degradation observed. [f] Conversion evaluated by ^{1}H NMR. [g] Conditions A: SESNH_2 (1 equiv), ArCHO (1 equiv), methyl acrylate (1.1 equiv), 3-HQD (0.15 equiv), Ti-(O*i*Pr)$_4$ (0.02 equiv), *i*-PrOH, MS 4 Å, 70 °C. Conditions B: SESNH_2 (1 equiv), ArCHO (5 equiv), methyl acrylate (5 equiv), DABCO (0.5 equiv), *i*-PrOH, 70 °C.

The various β-aminoesters obtained from the *aza*-Baylis–Hillman reaction (**5a–n**) were reacted with allyl bromide in the presence of K_2CO_3 in DMF[5b] to yield the corresponding dienes in most cases, except for **5d**, which yielded a complex mixture, and **5o**, which was degraded in these reaction conditions. **6a–c** and **6e–n** were obtained in almost quantitative yields.

Ring closing metathesis is a powerful method for the construction of cyclic structures.[10] In the past few years, it has been widely applied to the synthesis of hetero-

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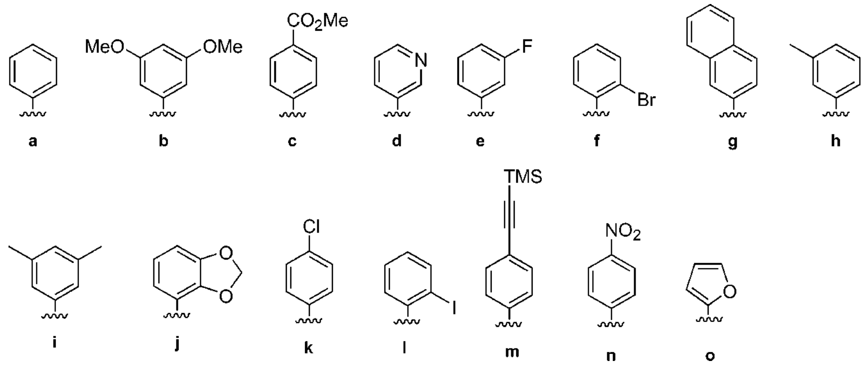


FIGURE 1. R^4 substituents.

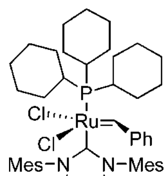
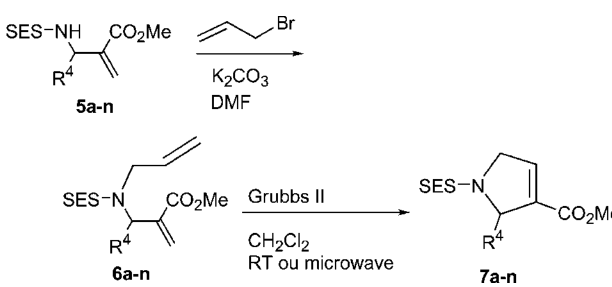


FIGURE 2. Grubbs-type II catalyst.

cycles.[11] Recently the availability of more reactive catalysts such as Grubbs-type II catalyst (Figure 2) has opened the path to more demanding processes such as substituent bearing olefins. Among these substituents, carboxymethyl has not been fully exploited so far[4b,5b,12] while its importance as a functional group is widely recognized.

The dienes **6a**–**c** and **6e**–**n** were submitted to RCM reaction conditions (Grubbs-type II catalyst, 5 mol % in CH_2Cl_2) to yield the corresponding cyclic structures **7** (eq 3). Yields are generally excellent (Table 1) except in the



(3)

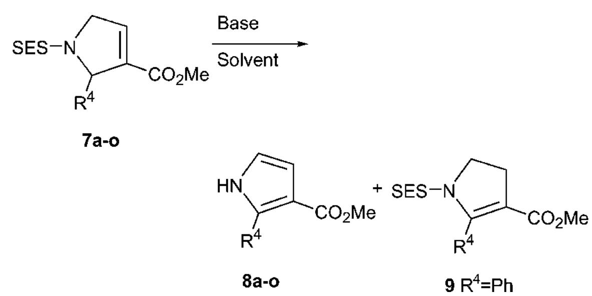
cases of **6m** and **6n** which gave a low conversion to **7m** and **7n**, respectively. This may result from a complexation of the arylic side chain (alkyne[13] or nitro group) with the ruthenium catalyst, unfavorable for the cyclization reaction. While the cylizations of **6a**–**c** and **6e**–***l*** were complete within 12 h at room temperature, they could be conveniently accelerated by microwave activation.[5a,7,12d,14] Under these conditions (100 °C, CH_2Cl_2), completion of the cyclization was reached within 5 min.

The next step was the cleavage of the SES group and aromatization (eq 4). Results of the different reaction conditions are summarized in Table 2.

TABLE 2. Yield[a] of Products Obtained at the SES Cleavage/Aromatization Step of 7a

		yield (%)		
entry	conditions	**7a**	pyrrole **8a**	isomer **9**
1	*n*-Bu_4NF, THF, rt	0	21	0
2	CsF, DMF, 80 °C, 2 h	0	41	0
3	DBU, THF, rt, 24 h	0	0	26
4	K_2CO_3, DMF, 80 °C, 24 h	0	0	24
5	DBU, THF, reflux, 16 h	0	64	0
6	*t*-BuOK, DMF, rt, 2 h	0	83	0

[a] Yields were determined by ^1H NMR with CH_2Br_2 as an internal standard.



(4)

The method described in the literature for this type of substrate[4a] (eq 4) yielded only a small amount of the expected product **8a** (entry 1). Using a different fluoride source[4b] (entry 2) resulted in a moderate yield. Stronger bases were then employed. DBU in THF at room temperature[2x] (entry 3) and K_2CO_3 in DMF at 80 °C[3k] (entry 4) resulted in the isomerization of pyrroline **7a**

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into **9** without cleavage of the SES group and aromatization. DBU in refluxing THF[3e] (entry 5) provided better yields of **8a**. Best results were obtained with *t*-BuOK in DMF at room temperature[2w,y] (entry 6). In this case, 83% of the expected pyrrole **8a** was obtained within 2 h via elimination/aromatization. This result could be applied to all the SES protected pyrroline **7a**,**b** and **7e**−***l*** to provide the corresponding pyrroles **8a**,**b** and **8e**−***l*** in high yields. In the case of **7c** transesterification of the methyl ester of the side chain to the *t*-Bu ester occurred.

Conclusion

In conclusion, an efficient regiocontrolled synthesis of 2-substituted-3-methoxycarbonyl pyrroles was developed. Ten different pyrroles were obtained in an overall high yield and high purity, starting from highly diverse α-methylene β-aminoesters. Further development of this chemistry is underway in our laboratory.

Experimental Section

General Remarks.[9] Microwave-assisted reactions were performed with a Personal Chemistry Emrys Optimizer or with a CEM Explorer monomode system.

2-(Trimethylsilyl)ethanesulfonamide (2). Phosphorus pentachloride (7.7 g, 36.7 mmol) was added portionwise to a suspension of sodium 2-(trimethylsilyl)ethanesulfonate (5 g, 24.5 mmol) in 100 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 30 min. The organic phase was washed three times with saturated $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated. The residue was dissolved in 100 mL of CH_2Cl_2, and gaseous NH_3 was bubbled through the solution for 15 min at −10 °C. The mixture was stirred at room temperature overnight, then filtered over Celite and evaporated. The residue was dissolved with AcOEt and washed with water and brine. The organic layer was dried over $MgSO_4$, filtered, and evaporated to yield 2.95 g (67%) of the title compound.[15]

^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.08 (s, 9H), 1.05−1.15 (m, 2H), 3.00−3.10 (m, 2H), 4.97 (large s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 11.2, 52.0.

General Procedure for the Synthesis of β-Aminoesters 5: Conditions A. To a mixture[8b] of 2-(trimethylsilylethane)-sulfonamide **2** (363 mg, 2 mmol), 3-hydroxyquinuclidine (38 mg, 0.30 mmol), and molecular sieves (4 Å, 400 mg, 200 mg/mmol substrate) in 1 mL of 2-propanol was added aldehyde **3** (2 mmol), methyl acrylate (186 mg, 2.2 mmol), and Ti(O*i*Pr)$_4$ (12 mg, 0.04 mmol). The reaction mixture was stirred for the indicated time at 70 °C and filtered over Celite. The Celite was rinsed three times with 2-propanol. The solvent was evaporated and the residue was diluted with AcOEt, neutralized with aq $KHSO_4$ (1%), and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered, and evaporated. Silica gel chromatography (Et_2O/hexane) yielded β-aminoester **5**.

Conditions B. To a solution of 2-(trimethylsilylethane)-sulfonamide **2** (363 mg, 2 mmol) and DABCO (112 mg, 1 mmol) in 1 mL of 2-propanol was added aldehyde **3** (10 mmol) and methyl acrylate (861 mg, 10 mmol). The reaction mixture was stirred for the indicated time at 70 °C, evaporated, diluted with AcOEt, neutralized with aq $KHSO_4$ (1%), and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered, and evaporated. Silica gel chromatography (Et_2O/hexane) yielded β-aminoester **5**.

Methyl 2-(Phenyl(2-(trimethylsilyl)ethylsulfonamido)-methyl)acrylate (5a): Conditions A. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 519 mg (73%) of the title compound as a white solid.

Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 614 mg (86%) of the title compound as a white solid.

Mp 91.6−92.2 °C; IR 3368 (m), 2955 (m), 1719 (s), 1335 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.01 (s, 9H), 0.80−1.05 (m, 2H), 2.75−2.95 (m, 2H), 3.73 (s, 3H), 5.45 (d, 1H, J_3 = 9.3 Hz), 5.53 (d, 1H, J_3 = 9.3 Hz), 6.02 (s, 1H), 6.43 (d, 1H, J_4 = 0.6 Hz), 7.25−7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.9, 50.4, 52.6, 59.5, 127.0, 128.0, 128.4, 129.2, 139.6, 140.2, 166.3; ESIMS *m/z* 174.8 (M − $SESNH_2$ + H)$^+$, 356.0 (M + H)$^+$, 378.1 (M + Na)$^+$, 710.9 (2M + H)$^+$, 733.1 (2M + Na)$^+$; FAB+ *m/z* 175 (M − $SESNH_2$ + H)$^+$, 356 (M + H)$^+$; HRMS calcd for $C_{16}H_{26}NO_4SSi$ 356.1352, found 356.1316.

Methyl 2-((3,5-Dimethoxyphenyl)(2-(trimethylsilyl)-ethylsulfonamido)methyl)acrylate (5b): Conditions A. The crude product was purified by silica gel chromatography (Et_2O/hexane = 4/6) to yield 383 mg (46%) of the title compound as a white solid.

Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 4/6) to yield 557 mg (67%) of the title compound as a white solid.

Mp 91.4−95.5 °C; IR 3383 (m), 2963 (m), 1719 (s), 1334 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.01 (s, 9H), 0.85−1.05 (m, 2H), 2.80−2.95 (m, 2H), 3.74 (s, 3H), 3.79 (s, 6H), 5.36 (d, 1H, J_3 = 9.3 Hz), 5.55 (d, 1H, J_3 = 9.3 Hz), 5.99 (s, 1H), 6.35−6.40 (m, 1H), 6.41 (d, 1H, J_4 = 0.4 Hz), 6.50−6.55 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.7, 10.9, 50.4, 52.6, 55.8, 59.5, 99.9, 105.2, 128.1, 139.9, 142.0, 161.4, 166.3; ESIMS *m/z* 235.2 (M − $SESNH_2$ + H)$^+$, 416.2 (M + H)$^+$, 831.3 (2M + H)$^+$, 853.4 (2M + Na)$^+$; FAB+ *m/z* 235 (M − $SESNH_2$ + H)$^+$, 415 (M − e$^-$)$^+$; HRMS calcd for $C_{18}H_{29}NO_6SSi$ 415.1485, found 415.1480.

Methyl 4-(2-(Methoxycarbonyl)-1-(2-(trimethylsilyl)-ethylsulfonamido)allyl)benzoate (5c): Conditions A. The crude product was purified by silica gel chromatography (Et_2O/hexane = 4/6) to yield 530 mg (64%) of the title compound as a white solid.

Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 4/6) to yield 747 mg (90%) of the title compound as a white solid.

Mp 103.7−108.5 °C; IR 3406 (m), 2950 (m), 1719 (s), 1332 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.00 (s, 9H), 0.75−1.10 (m, 2H), 2.85−3.00 (m, 2H), 3.72 (s, 3H), 3.93 (s, 3H), 5.48 (d, 1H, J_3 = 9.7 Hz), 5.71 (d, 1H, J_3 = 9.7 Hz), 6.03 (s, 1H), 6.46 (s, 1H), 7.46 (d, 2H, J_3 = 8.5 Hz), 8.03 (d, 2H, J_3 = 8.5 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.9, 50.6, 52.6, 52.7, 59.5, 126.8, 128.9, 130.2, 130.4, 139.5, 144.6, 166.1, 167.0; ESIMS *m/z* 414.1 (M + H)$^+$, 827.5 (2M + H)$^+$, 849.3 (2M + Na)$^+$; FAB+ *m/z* 233 (M − $SESNH_2$ + H)$^+$, 414 (M + H)$^+$; HRMS calcd for $C_{18}H_{28}NO_6SSi$ 414.1407, found 414.1435.

Methyl 2-(Pyridin-3-yl(2-(trimethylsilyl)ethylsulfon-amido)methyl)acrylate (5d): Conditions A. The crude product was purified by silica gel chromatography (Et_2O/hexane = 4/6 + 1% Et_3N) to yield 535 mg (75%) of the title compound as a white solid.

Mp 129.2−129.8 °C; IR 3418 (m), 2950 (m), 1716 (s), 1331 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.02 (s, 9H), 0.85−1.20 (m, 2H), 2.80−3.05 (m, 2H), 3.75 (s, 3H), 5.48 (d, 1H, J_3 = 9.5 Hz), 5.70 (d, 1H, J_3 = 9.5 Hz), 6.07 (s, 1H), 6.49 (d, 1H, J_4 = 0.4 Hz), 7.32 (dd, 1H, J_3 = 8.0 Hz, J_3 = 4.8 Hz), 7.79 (dt, 1H, J_3 = 8.0 Hz, J_4 = 1.7 Hz), 8.57 (dd, 1H, J_3 = 4.8 Hz, J_4 = 1.2 Hz), 8.61 (d, 1H, J_4 = 1.9 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.9, 50.7, 52.8, 58.0, 123.9, 129.2, 134.6, 135.3, 139.2, 148.5, 149.6, 166.0; ESIMS *m/z* 357.1 (M + H)$^+$, 713.3 (2M + H)$^+$; FAB+ *m/z* 357 (M + H)$^+$, 379 (M + Na)$^+$; HRMS calcd for $C_{17}H_{27}N_2O_4SSi$ 357.1304, found 357.1301.

Methyl 2-((3-Fluorophenyl)(2-(trimethylsilyl)ethylsul-fonamido)methyl)acrylate (5e): Conditions A. The crude product was purified by silica gel chromatography (Et_2O/

(15) (a) Stien, D.; Anderson, G. T.; Chase, C. E.; Koh, Y.-H.; Weinreb, S. M. *J. Am. Chem. Soc.* **1999**, *121*, 9574−9579. (b) Parker, L. L.; Gowans, N. D.; Jones, S. W.; Robins, D. J. *Tetrahedron* **2003**, *59*, 10165−10171.

hexane = 3/7) to yield 269 mg (36%) of the title compound as a white solid.

Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 592 mg (79%) of the title compound as a white solid.

Mp 68.1−69.1 °C; IR 3370 (m), 2958 (m), 1714 (s), 1334 (s), 1093 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.01 (s, 9H), 0.80−1.10 (m, 2H), 2.80−3.00 (m, 2H), 3.75 (s, 3H), 5.43 (d, 1H, J_3 = 9.5 Hz), 5.62 (d, 1H, J_3 = 9.5 Hz), 6.02 (s, 1H), 6.45 (s, 1H), 6.95−7.25 (m, 3H), 7.30−7.45 (m, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.7, 10.9, 50.6, 52.7, 59.2 (d, J_4 = 1.5 Hz), 114.0 (d, J_2 = 22.6 Hz), 115.3 (d, J_2 = 21.1 Hz), 122.5 (d, J_4 = 2.8 Hz), 128.7, 130.7 (d, J_3 = 8.5 Hz), 139.6, 142.3 (d, J_3 = 6.8 Hz), 163.3 (d, J_1 = 246.9 Hz), 166.1; ESIMS *m/z* 374.1 (M + H)$^+$, 747.2 (2M + H)$^+$; FAB+ *m/z* 193 (M − $SESNH_2$ + H)$^+$, 374 (M + H)$^+$, 396 (M + Na)$^+$; HRMS calcd for $C_{16}H_{25}FNO_4SSi$ 374.1258, found 374.1273.

Methyl 2-((2-Bromophenyl)(2-(trimethylsilyl)ethylsulfonamido)methyl)acrylate (5f): Conditions A. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 367 mg (42%) of the title compound as a white solid.

Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 759 mg (86%) of the title compound as a white solid.

Mp 104.4−105.3 °C; IR 3378 (m), 2955 (m), 1726 (s), 1336 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.00 (s, 9H), 0.80−1.00 (m, 2H), 2.85−3.10 (m, 2H), 3.75 (s, 3H), 5.32 (d, 1H, J_3 = 8.9 Hz), 5.88 (d, 1H, J_3 = 8.9 Hz), 6.03 (d, 1H, J_4 = 1.5 Hz), 6.46 (s, 1H), 7.20 (td, 1H, J_3 = 7.7 Hz, J_4 = 1.7 Hz), 7.37 (td, 1H, J_3 = 7.7 Hz, J_4 = 1.3 Hz), 7.55 (dd, 1H, J_3 = 7.8 Hz, J_4 = 1.7 Hz), 7.60 (dd, 1H, J_3 = 7.8 Hz, J_4 = 1.3 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.9, 50.4, 52.6, 58.0, 123.7, 128.3, 128.9, 129.3, 130.0, 133.9, 138.9, 139.3, 166.3; ESIMS *m/z* 434.0/436.0 (M + H)$^+$, 867.1/869.1/871.1 (2M + H)$^+$; FAB+ *m/z* 253/255 (M − $SESNH_2$ + H)$^+$, 434/436 (M + H)$^+$, 456/458 (M + Na)$^+$; HRMS calcd for $C_{16}H_{25}BrNO_4SSi$ 434.0457, found 434.0442.

Methyl 2-(Naphthalen-2-yl(2-(trimethylsilyl)ethylsulfonamido)methyl)acrylate (5g): Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 487 mg (60%) of the title compound as a white solid.

Mp 110.7−112.0 °C; IR 3388 (m), 2963 (m), 1715 (s), 1333 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.07 (s, 9H), 0.85−1.00 (m, 2H), 2.80−2.95 (m, 2H), 3.72 (s, 3H), 5.63 (d, 1H, J_3 = 9.3 Hz), 5.70 (d, 1H, J_3 = 9.3 Hz), 6.09 (s, 1H), 6.48 (s, 1H), 7.45−7.55 (m, 3H), 7.75−7.95 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.7, 10.9, 50.5, 52.6, 59.6, 124.9, 126.0, 126.8, 126.9, 128.0, 128.1, 128.5, 129.1, 133.3, 133.6, 136.9, 140.1, 166.3; ESIMS *m/z* 225.1 (M − $SESNH_2$ + H)$^+$, 405.9 (M + H)$^+$; FAB+ *m/z* 225 (M − $SESNH_2$ + H)$^+$, 405 (M + H)$^+$; HRMS calcd for $C_{20}H_{27}NO_4SSi$ 405.1430, found 405.1431.

Methyl 2-(*m*-Tolyl(2-(trimethylsilyl)ethylsulfonamido)methyl)acrylate (5h): Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 633 mg (86%) of the title compound as a white solid.

Mp 60.7−62.4 °C; IR 3425 (m), 2955 (m), 1720 (s), 1328 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.01 (s, 9H), 0.80−1.00 (m, 2H), 2.36 (s, 3H), 2.75−2.95 (m, 2H), 3.73 (s, 3H), 5.41 (d, 1H, J_3 = 9.3 Hz), 5.54 (d, 1H, J_3 = 9.3 Hz), 6.02 (s, 1H), 6.42 (s, 1H), 7.05−7.35 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.7, 10.9, 21.9, 50.4, 52.6, 59.4, 124.0, 127.7, 127.8, 129.1, 129.2, 138.9, 139.5, 140.2, 166.3; ESIMS *m/z* 189.1 (M − $SESNH_2$ + H)$^+$, 370.1 (M + H)$^+$, 739.3 (2M + H)$^+$, 761.2 (2M + Na)$^+$; FAB+ *m/z* 189 (M − $SESNH_2$ + H)$^+$, 370 (M + H)$^+$, 392 (M + Na)$^+$; HRMS calcd for $C_{17}H_{28}NO_4SSi$ 370.1508, found 370.1548.

Methyl 2-((3,5-Dimethylphenyl)(2-(trimethylsilyl)ethylsulfonamido)methyl)acrylate (5i): Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 537 mg (70%) of the title compound as a white solid.

Mp 92.0−93.4 °C; IR 3383 (m), 2953 (m), 1715 (s), 1334 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.01 (s, 9H), 0.85−1.00 (m, 2H), 2.32 (s, 6H), 2.80−2.95 (m, 2H), 3.74 (s, 3H), 5.36 (d, 1H, J_3 = 9.3 Hz), 5.42 (d, 1H, J_3 = 9.3 Hz), 6.02 (s, 1H), 6.42 (d, 1H, J_4 = 0.6 Hz), 6.94 (s, 1H), 6.97 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.7, 10.9, 21.8, 50.3, 52.6, 59.4, 124.7, 127.8, 130.1, 138.8, 139.4, 140.2, 166.3; ESIMS *m/z* 203.3 (M − $SESNH_2$ + H)$^+$, 384.3 (M + H)$^+$, 767.3 (2M + H)$^+$; FAB+ *m/z* 203 (M − $SESNH_2$ + H)$^+$, 384 (M + H)$^+$, 406 (M + Na)$^+$; HRMS calcd for $C_{18}H_{30}NO_4SSi$ 384.1665, found 384.1670.

Methyl 2-((2,3-Methylenedioxyphenyl)(2-(trimethylsilyl)ethylsulfonamido)methyl)acrylate (5j): Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 4/6) to yield 526 mg (66%) of the title compound as a white solid.

Mp 93.0−94.8 °C; IR 3375 (m), 2955 (m), 1725 (s), 1339 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.02 (s, 9H), 0.75−1.05 (m, 2H), 2.75−3.05 (m, 2H), 3.76 (s, 3H), 5.52 (d, 1H, J_3 = 9.8 Hz), 5.57 (d, 1H, J_3 = 9.8 Hz), 5.99 (s, 1H), 6.01 (s, 1H), 6.38 (s, 1H), 6.75−6.95 (m, 3H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.7, 10.8, 50.2, 52.6, 54.8, 101.6, 108.9, 120.9, 121.5, 122.5, 127.4, 139.2, 144.9, 148.0, 166.2; ESIMS *m/z* 219.2 (M − $SESNH_2$ + H)$^+$, 400.0 (M + H)$^+$, 799.2 (2M + H)$^+$, 821.2 (2M + Na)$^+$; FAB+ *m/z* 219 (M − $SESNH_2$ + H)$^+$, 399 (M − e$^-$)$^+$, 422 (M + Na)$^+$; HRMS calcd for $C_{17}H_{25}NO_6SSi$ 399.1172, found 399.1164.

Methyl 2-((4-Chlorophenyl)(2-(trimethylsilyl)ethylsulfonamido)methyl)acrylate (5k): Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 670 mg (86%) of the title compound as a white solid.

Mp 106.4−107.1 °C; IR 3425 (m), 1713 (s), 1335 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.02 (s, 9H), 0.80−1.10 (m, 2H), 2.80−3.00 (m, 2H), 3.74 (s, 3H), 5.41 (d, 1H, J_3 = 9.3 Hz), 5.54 (d, 1H, J_3 = 9.3 Hz), 6.01 (s, 1H), 6.44 (s, 1H), 7.34 (s, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.9, 50.6, 52.7, 59.2, 128.3, 128.5, 129.3, 134.3, 138.1, 139.7, 166.1; ESIMS *m/z* 208.8 (M − $SESNH_2$ + H)$^+$, 390.1 (M + H)$^+$, 412.0 (M + Na)$^+$, 779.0 (2M + H)$^+$, 801.1 (2M + Na)$^+$; FAB+ *m/z* 209 (M − $SESNH_2$ + H)$^+$, 390 (M + H)$^+$, 412 (M + Na)$^+$; HRMS calcd for $C_{16}H_{25}ClNO_4SSi$ 390.0962, found 390.0974.

Methyl 2-((2-Iodophenyl)(2-(trimethylsilyl)ethylsulfonamido)methyl)acrylate (5*l*): Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 707 mg (73%) of the title compound as a white solid.

Mp 127.4−128.6 °C; IR 3383 (m), 2953 (m), 1723 (s), 1346 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.01 (s, 9H), 0.80−1.05 (m, 2H), 2.85−3.15 (m, 2H), 3.77 (s, 3H), 5.21 (d, 1H, J_3 = 8.7 Hz), 5.78 (d, 1H, J_3 = 8.7 Hz), 6.02 (d, 1H, J_4 = 0.9 Hz), 6.47 (s, 1H), 7.03 (ddd, 1H, J_3 = 8.0 Hz, J_3 = 7.2 Hz, J_4 = 1.9 Hz), 7.40 (ddd, 1H, J_3 = 7.8 Hz, J_3 = 7.2 Hz, J_4 = 1.3 Hz), 7.51 (dd, 1H, J_3 = 7.8 Hz, J_4 = 1.9 Hz), 7.90 (dd, 1H, J_3 = 7.9 Hz, J_4 = 1.2 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.5, 10.9, 50.6, 52.6, 62.3, 99.8, 128.7, 129.0, 129.2, 130.2, 139.6, 140.7, 142.0, 166.3; ESIMS *m/z* 300.9 (M − $SESNH_2$ + H)$^+$, 482.1 (M + H)$^+$; FAB+ *m/z* 301 (M − $SESNH_2$ + H)$^+$, 482 (M + H)$^+$, 504 (M + Na)$^+$; HRMS calcd for $C_{16}H_{25}INO_4SSi$ 482.0318, found 482.0311.

Methyl 2-((2-(Trimethylsilyl)ethylsulfonamido)(4-(2-(trimethylsilyl)ethynyl)phenyl)methyl)acrylate (5m): Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 551 mg (61%) of the title compound as a white solid.

Mp 90.2−91.4 °C; IR 3380 (m), 2955 (m), 2158 (m), 1719 (s), 1334 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.02 (s, 9H), 0.26 (s, 9H), 0.75−1.10 (m, 2H), 2.80−3.00 (m, 2H), 3.72 (s, 3H), 5.42 (d, 1H, J_3 = 9.5 Hz), 5.53 (d, 1H, J_3 = 9.5 Hz), 6.01 (s, 1H), 6.43 (s, 1H), 7.31 (d, 2H, J_3 = 8.5 Hz), 7.46 (d, 2H, J_3 = 8.5 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 0.3, 10.9, 50.6, 52.6, 59.4, 95.3, 104.8, 123.3, 126.8, 128.5, 132.7, 139.7, 139.8, 166.1; ESIMS *m/z* 271.3 (M − $SESNH_2$ + H)$^+$, 452.0 (M + H)$^+$; FAB+ *m/z* 271 (M − $SESNH_2$ + H)$^+$, 452 (M + H)$^+$, 474 (M + Na)$^+$; HRMS calcd for $C_{21}H_{34}NO_4SSi$ 452.1747, found 452.1755.

Methyl 2-((4-Nitrophenyl)(2-(trimethylsilyl)ethylsulfonamido)methyl)acrylate (5n): Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 4/6) to yield 481 mg (60%) of the title compound as a white solid.

Mp 104.9−113.7 °C; IR 3368 (m), 2958 (m), 1715 (s), 1526 (s), 1354 (s), 1339 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.03 (s, 9H), 0.75−1.15 (m, 2H), 2.85−3.05 (m, 2H), 3.75 (s, 3H), 5.51 (d, 1H, J_3 = 9.8 Hz), 5.77 (d, 1H, J_3 = 9.8 Hz), 6.07 (s, 1H), 6.51 (s, 1H), 7.59 (d, 2H, J_3 = 8.8 Hz), 8.22 (d, 2H, J_3 = 8.8 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 11.0, 50.8, 52.9, 59.4, 124.3, 127.8, 129.6, 139.1, 146.9, 147.9, 165.9; ESIMS *m/z* 801.2 (2M + H)$^+$, 823.3 (2M + Na)$^+$; FAB+ *m/z* 401 (M + H)$^+$, 423 (M + Na)$^+$; HRMS calcd for $C_{16}H_{25}N_2O_6SSi$ 401.1203, found 401.1187.

Methyl 2-(Furan-2-yl(2-(trimethylsilyl)ethylsulfonamido)methyl)acrylate (5o): Conditions B. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 489 mg (71%) of the title compound as a yellow oil.

IR 3370 (m), 2955 (m), 1723 (s), 1335 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.02 (s, 9H), 0.80−1.05 (m, 2H), 2.80−3.00 (m, 2H), 3.77 (s, 3H), 5.49 (d, 1H, J_3 = 9.5 Hz), 5.57 (d, 1H, J_3 = 9.5 Hz), 6.00 (s, 1H), 6.27 (d, 1H, J_3 = 3.3 Hz), 6.34 (dd, 1H, J_3 = 3.2 Hz, J_3 = 1.9 Hz), 6.42 (s, 1H), 7.37 (dd, 1H, J_3 = 1.9 Hz, J_4 = 1.0 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.8, 50.4, 52.7, 53.58, 108.0, 111.2, 128.6, 138.2, 142.9, 152.3, 166.1; ESIMS *m/z* 346.1 (M + H)$^+$, 691.3 (2M + H)$^+$, 713.3 (2M + Na)$^+$; FAB+ *m/z* 165 (M − SESNH$_2$ + H)$^+$, 346 (M + H)$^+$, 368 (M + Na)$^+$; HRMS calcd for $C_{14}H_{24}NO_5SSi$ 346.1144, found 346.1149.

General Procedure for the Alkylation of β-Aminoesters 6. To a mixture[5a] of β-aminoester **5** (0.25 mmol) and K_2CO_3 (345 mg, 2.5 mmol) in 3.5 mL of DMF was added allyl bromide (121 mg, 1 mmol). The mixture was stirred at room temperature for 6 h, then filtered and diluted with AcOEt. The organic layer was successively washed with water and brine, dried over $MgSO_4$, filtered, and evaporated, to yield the corresponding *N*-allyl-β-aminoester **6**.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(phenyl)methyl)acrylate (6a). Alkylation of the β-aminoester **5a** yielded 97 mg (98%) of the title compound as a pale yellow oil.

IR 2953 (m), 1720 (s), 1328 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.04 (s, 9H), 0.95−1.15 (m, 2H), 2.75−3.05 (m, 2H), 3.70 (s, 3H), 3.93 (d, 2H, J_3 = 6.5 Hz), 4.95−5.15 (m, 2H), 5.20−5.45 (m, 1H), 5.91 (dd, 1H, J_2 = 0.6 Hz, J_4 = 1.7 Hz), 6.09 (s, 1H), 6.58 (dd, 1H, J_2 = 0.6 Hz, J_4 = 1.3 Hz), 7.25−7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.7, 49.1, 51.1, 52.5, 62.4, 118.9, 128.5, 128.8, 129.0, 129.1, 134.7, 138.1, 140.3, 166.8; ESIMS *m/z* 396.1 (M + H)$^+$, 791.7 (2M + H)$^+$, 813.3 (2M + Na)$^+$; FAB+ *m/z* 396 (M + H)$^+$, 418 (M + Na)$^+$; HRMS calcd for $C_{19}H_{30}NO_4SSi$ 396.1665, found 356.1675.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(3,5-dimethoxyphenyl)methyl)acrylate (6b). Alkylation of the β-aminoester **5b** yielded 112 mg (98%) of the title compound as a pale yellow oil.

IR 2950 (m), 1719 (s), 1330 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.04 (s, 9H), 0.95−1.15 (m, 2H), 2.85−3.05 (m, 2H), 3.73 (s, 3H), 3.79 (s, 6H), 3.93 (d, 2H, J_3 = 6.7 Hz), 4.95−5.15 (m, 2H), 5.25−5.50 (m, 1H), 5.89 (d, 1H, J_4 = 1.3 Hz), 6.03 (s, 1H), 6.41 (t, 1H, J_3 = 2.2 Hz), 6.46 (t, 2H, J_3 = 2.2 Hz), 6.55 (d, 1H, J_4 = 0.7 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.7, 49.0, 51.0, 52.6, 55.7, 60.3, 100.2, 107.2, 118.9, 128.8, 134.9, 140.2, 140.5, 161.4, 166.8; ESIMS *m/z* 456.2 (M + H)$^+$, 478.3 (M + Na)$^+$, 911.5 (2M + H)$^+$; FAB+ *m/z* 455 (M − e$^-$)$^+$, 478 (M + Na)$^+$; HRMS calcd for $C_{21}H_{33}NO_6SSi$ 455.1798, found 455.1815.

Methyl 4-(1-(*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)-2-(methoxycarbonyl)allyl)benzoate (6c). Alkylation of the β-aminoester **5c** yielded 110 mg (97%) of the title compound as a pale yellow oil.

IR 2955 (m), 1719 (s), 1329 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9H), 0.95−1.15 (m, 2H), 2.80−3.10 (m, 2H), 3.73 (s, 3H), 3.85−4.00 (m, 5H), 4.95−5.15 (m, 2H), 5.25−5.50 (m, 1H), 5.85 (d, 1H, J_4 = 1.7 Hz), 6.14 (s, 1H), 6.62 (d, 1H, J_4 = 1.1 Hz), 7.40 (d, 2H, J_3 = 8.2 Hz), 8.05 (d, 2H, J_3 = 8.4 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.7, 49.1, 51.2, 52.6, 52.7, 62.0, 119.3, 128.9, 129.8, 130.2, 130.3, 134.4, 139.7, 143.6, 166.6, 167.0; ESIMS *m/z* 454.2 (M + H)$^+$, 476.2 (M + Na)$^+$, 907.6 (2M + H)$^+$; FAB+ *m/z* 454 (M + H)$^+$, 476 (M + Na)$^+$; HRMS calcd for $C_{21}H_{32}NO_6SSi$ 454.1720, found 454.1720.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(3-fluorophenyl)methyl)acrylate (6e). Alkylation of the β-aminoester **5e** yielded 102 mg (99%) of the title compound as a pale yellow oil.

IR 2893 (m), 1725 (s), 1331 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9H), 0.95−1.15 (m, 2H), 2.80−3.10 (m, 2H), 3.74 (s, 3H), 3.80−4.10 (m, 2H), 4.95−5.15 (m, 2H), 5.25−5.55 (m, 1H), 5.88 (d, 1H, J_4 = 1.7 Hz), 6.09 (s, 1H), 6.60 (d, 1H, J_4 = 1.1 Hz), 6.95−7.15 (m, 3H), 7.25−7.45 (m, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.7, 49.1, 51.2, 52.7, 61.7 (d, J_4 = 1.4 Hz), 115.5 (d, J_2 = 21.2 Hz), 116.0 (d, J_2 = 22.2 Hz), 119.2, 124.5 (d, J_4 = 2.8 Hz), 129.6, 130.6 (d, J_3 = 8.5 Hz), 134.5, 139.8, 141.0 (d, J_3 = 6.7 Hz), 163.3 (d, J_1 = 246.9 Hz), 166.6; ESIMS *m/z* 414.2 (M + H)$^+$, 436.2 (M + Na)$^+$; FAB+ *m/z* 414 (M + H)$^+$, 436 (M + Na)$^+$; HRMS calcd for $C_{19}H_{29}FNO_4SSi$ 414.1571, found 414.1620.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(2-bromophenyl)methyl)acrylate (6f). Alkylation of the β-aminoester **5f** yielded 117 mg (99%) of the title compound as a pale yellow oil.

IR 2950 (m), 1716 (s), 1333 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.03 (s, 9H), 0.95−1.15 (m, 2H), 2.80−3.05 (m, 2H), 3.72 (s, 3H), 4.08 (dd, 2H, J_3 = 6.5 Hz, J_4 = 1.1 Hz), 5.00−5.20 (m, 2H), 5.35−5.60 (m, 1H), 5.88 (d, 1H, J_4 = 1.5 Hz), 6.21 (d, 1H J_4 = 0.8 Hz), 6.60 (d, 1H, = 0.8 Hz), 7.20 (ddd, 1H, J_4 = 2.0 Hz, J_3 = 7.2 Hz, J_3 = 7.8 Hz), 7.33 (ddd, 1H, J_4 = 1.3 Hz, J_3 = 7.2 Hz, J_3 = 7.8 Hz), 7.42 (dd, 1H, J_4 = 2.0 Hz, J_3 = 7.8 Hz), 7.61 (dd, 1H, J_4 = 1.3 Hz, J_3 = 7.8 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.5, 50.5, 51.4, 52.6, 62.6, 119.0, 125.0, 128.0, 129.8, 130.0, 130.8, 133.8, 134.7, 137.9, 139.4, 166.4; ESIMS *m/z* 474.4/476.4 (M + H)$^+$; FAB+ *m/z* 474/476 (M + H)$^+$; HRMS calcd for $C_{19}H_{29}BrNO_4SSi$ 474.0770, found 474.0749.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(naphthalen-2-yl)methyl)acrylate (6g). Alkylation of the β-aminoester **5g** yielded 109 mg (98%) of the title compound as a pale yellow oil.

IR 2953 (m), 1723 (s), 1333 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.03 (s, 9H), 1.00−1.15 (m, 2H), 2.80−3.10 (m, 2H), 3.71 (s, 3H), 4.00 (dd, 2H, J_4 = 5.8 Hz, J_3 = 5.9 Hz), 4.90−5.15 (m, 2H), 5.20−5.45 (m, 1H), 5.95 (d, 1H, J_4 = 1.1 Hz), 6.27 (s, 1H), 6.64 (s, 1H), 7.40−7.60 (m, 3H), 7.70−7.90 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.7, 49.0, 51.2, 52.6, 62.5, 119.1, 126.9, 127.0, 127.9, 128.0, 128.6, 128.9, 129.0, 133.3, 133.6, 134.7, 135.6, 140.3, 166.9; ESIMS *m/z* 446.4 (M + H)$^+$, 468.4 (M + Na)$^+$; FAB+ *m/z* 446 (M + H)$^+$, 468 (M + Na)$^+$; HRMS calcd for $C_{23}H_{32}NO_4SSi$ 446.1821, found 446.1814.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(*m*-tolyl)methyl)acrylate (6h). Alkylation of the β-aminoester **5h** yielded 100 mg (98%) of the title compound as a pale yellow oil.

IR 2953 (m), 1719 (s), 1325 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.04 (s, 9H), 0.95−1.15 (m, 2H), 2.37 (s, 3H), 2.75−3.05 (m, 2H), 3.70 (s, 3H), 3.92 (d, 2H, J_3 = 6.4 Hz), 4.95−5.15 (m, 2H), 5.15−5.40 (m, 1H), 5.90 (dd, 1H, J_2 = 0.4 Hz, J_4 = 1.3 Hz), 6.05 (s, 1H), 6.56 (dd, 1H, J_2 = 0.4 Hz, J_4 = 1.3 Hz), 7.05−7.30 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.7, 21.9, 49.0, 51.0, 52.5, 62.4, 118.9, 126.0, 128.6, 129.0, 129.3, 129.8, 134.8, 137.9, 138.8, 140.3, 166.9; ESIMS *m/z* 410.2 (M + H)$^+$, 432.2 (M + Na)$^+$, 841.3 (2M + Na)$^+$; FAB+ *m/z* 410 (M + H)$^+$, 432 (M + Na)$^+$; HRMS calcd for $C_{20}H_{32}NO_4SSi$ 410.1821, found 410.1841.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(3,5-dimethylphenyl)methyl)acrylate (6i). Alkylation of the β-aminoester **5i** yielded 103 mg (97%) of the title compound as a pale yellow oil.

IR 2953 (m), 1721 (s), 1331 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.04 (s, 9H), 0.95–1.15 (m, 2H), 2.32 (s, 6H), 2.75–3.05 (m, 2H), 3.70 (s, 3H), 3.91 (d, 2H, J_3 = 6.1 Hz), 4.95–5.15 (m, 2H), 5.15–5.40 (m, 1H), 5.90 (dd, 1H, J_2 = 0.6 Hz, J_4 = 1.7 Hz), 6.01 (s, 1H), 6.54 (dd, 1H, J_2 = 0.5 Hz, J_4 = 1.3 Hz), 6.91 (s, 2H), 6.95 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.7, 21.8, 48.9, 51.0, 52.5, 62.4, 118.8, 126.8, 128.4, 130.2, 134.9, 137.8, 138.6, 140.5, 166.9; ESIMS *m/z* 424.3 (M + H)$^+$; FAB+ *m/z* 424 (M + H)$^+$, 446 (M + Na)$^+$; HRMS calcd for $C_{21}H_{34}NO_4SSi$ 424.1978, found 424.2021.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(2,3-methylenedioxyphenyl)methyl)acrylate (6j). Alkylation of the β-aminoester **5j** yielded 108 mg (98%) of the title compound as a pale yellow oil.

IR 2938 (m), 1720 (s), 1329 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9H), 0.95–1.20 (m, 2H), 2.80–3.15 (m, 2H), 3.70 (s, 3H), 3.89 (dd, 1H, J_2 = 5.8 Hz, J_3 = 16.0 Hz), 4.05 (dd, 1H, J_2 = 7.2 Hz, J_3 = 16.0 Hz), 4.95–5.15 (m, 2H), 5.20–5.45 (m, 1H), 5.95–6.00 (m, 3H), 6.10 (s, 1), 6.55 (d, 1H, J_4 = 1.5 Hz), 6.70–6.90 (m, 3H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.4, 49.0, 50.8, 52.5, 57.4, 101.3, 109.2, 118.9, 120.1, 121.9, 122.4, 128.3, 134.6, 139.1, 145.8, 147.8, 166.5; ESIMS *m/z* 440.1 (M + H)$^+$, 462.4 (M + Na)$^+$; FAB+ *m/z* 440 (M + H)$^+$, 444 (M + Na)$^+$; HRMS calcd for $C_{20}H_{30}NO_6SSi$ 440.1563, found 440.1534.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(4-chlorophenyl)methyl)acrylate (6k). Alkylation of the β-aminoester **5k** yielded 106 mg (99%) of the title compound as a pale yellow oil.

IR 2948 (m), 1718 (s), 1329 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9H), 0.95–1.10 (m, 2H), 2.75–3.05 (m, 2H), 3.73 (s, 3H), 3.80–4.05 (m, 2H), 5.00–5.15 (m, 2H), 5.25–5.55 (m, 1H), 5.88 (d, 1H, J_4 = 1.5 Hz), 6.05 (s, 1H), 6.59 (d, 1H, J_4 = 0.9 Hz), 7.25 (d, 2H, J_3 = 8.4 Hz), 7.35 (d, 2H, J_3 = 8.7 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.7, 49.1, 51.2, 52.7, 61.7, 119.3, 129.3, 129.4, 130.3, 134.4, 134.8, 136.8, 139.8, 166.7; ESIMS *m/z* 430.2 (M + H)$^+$, 452.0 (M + Na)$^+$; FAB+ *m/z* 430 (M + H)$^+$, 452 (M + Na)$^+$; HRMS calcd for $C_{19}H_{28}ClNO_4SSi$ 430.1275, found 430.1266

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(2-iodophenyl)methyl)acrylate (6*l*). Alkylation of the β-aminoester **5*l*** yielded 129 mg (99%) of the title compound as a pale yellow oil.

IR 2950 (m), 1723 (s), 1331 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.04 (s, 9H), 1.00–1.15 (m, 2H), 2.90–3.05 (m, 2H), 3.74 (s, 3H), 4.10 (d, 2H, J_3 = 6.7 Hz), 5.00–5.20 (m, 2H), 5.35–5.60 (m, 1H), 5.83 (d, 1H, J_4 = 1.5 Hz), 6.08 (s, 1H), 6.61 (d, 1H, J_4 = 0.7 Hz), 6.95–7.10 (m, 1H), 7.30–7.45 (m, 2H), 7.85–7.95 (m, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.5, 10.5, 50.6, 51.5, 52.6, 67.1, 101.2, 118.9, 128.8, 130.1, 130.3, 130.3, 134.8, 139.5, 140.7, 141.2, 166.4; ESIMS *m/z* 522.3 (M + H)$^+$, 544.4 (M + Na)$^+$; FAB+ *m/z* 522 (M + H)$^+$, 544 (M + Na)$^+$; HRMS calcd for $C_{19}H_{29}INO_4SSi$ 522.0631, found 522.0655.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(4-(2-(trimethylsilyl)ethynyl)phenyl)methyl)acrylate (6m). Alkylation of the β-aminoester **5m** yielded 120 mg (98%) of the title compound as a pale yellow oil.

IR 2953 (m), 1723 (s), 1334 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9H), 0.27 (s, 9H), 0.95–1.10 (m, 2H), 2.80–3.05 (m, 2H), 3.69 (s, 3H), 3.90 (d, 2H, J_3 = 6.3 Hz), 4.95–5.15 (m, 2H), 5.20–5.45 (m, 1H), 5.87 (d, 1H, J_4 = 1.5 Hz), 6.06 (s, 1H), 6.58 (d, 1H, J_4 = 1.1 Hz), 7.25 (d, 1H, J_3 = 8.4 Hz), 7.47 (d, 1H, J_3 = 8.4 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −2.0, −0.1, 10.3, 48.6, 50.8, 52.2, 61.8, 95.1, 104.4, 118.8, 123.0, 128.4, 128.7, 132.3, 134.1, 138.2, 139.5, 166.3; ESIMS *m/z* 492.4 (M + H)$^+$; FAB+ *m/z* 492 (M + H)$^+$, 514 (M + Na)$^+$; HRMS calcd for $C_{24}H_{38}NO_4SSi_2$ 492.2060, found 492.2047.

Methyl 2-((*N*-Allyl-2-(trimethylsilyl)ethan-3-ylsulfonamido)(4-nitrophenyl)methyl)acrylate (6n). Alkylation of the β-aminoester **5n** yielded 107 mg (97%) of the title compound as a pale yellow oil.

IR 2950 (m), 1723 (s), 1528 (s), 1350 (s), 1335 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.06 (s, 9H), 0.90–1.10 (m, 2H), 2.85–3.10 (m, 2H), 3.79 (s, 3H), 3.93 (d, 1H, J_3 = 7.0 Hz), 4.00 (d, 1H, J_3 = 5.7 Hz), 5.00–5.20 (m, 2H), 5.35–5.60 (m, 1H), 5.80 (d, 1H, J_4 = 1.5 Hz), 6.19 (s, 1H), 6.67 (d, 1H, J_4 = 0.9 Hz), 7.51 (d, 2H, J_3 = 8.7 Hz), 8.23 (d, 2H, J_3 = 8.7 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.6, 10.6, 49.3, 51.3, 52.9, 61.6, 119.7, 124.2, 129.6, 131.0, 134.2, 139.2, 146.3, 147.8, 166.5; ESIMS *m/z* 396.3 (M + H)$^+$, 791.7 (2M + H)$^+$; FAB+ *m/z* 441 (M + H)$^+$, 463 (M + Na)$^+$; HRMS calcd for $C_{19}H_{29}N_2O_6SSi$ 441.1516, found 441.1517.

General Procedure for the Synthesis of 2,5-Dihydropyrrole Derivatives 7: Thermal Conditions. $Cl_2(PCy_3)$(IMes)Ru=CHPh (8 mg, 0.01 mmol) was added to a solution[12a] of *N*-allyl-β-aminoester **6** (0.20 mmol) in 20 mL of CH_2Cl_2, and the mixture was stirred overnight at room temperature. Then 35 μL of DMSO (50 equiv/Ru) was added and the mixture was stirred for 24 h. The solution was evaporated. Silica gel chromatography (Et_2O/hexane) yielded the corresponding 2,5-dihydropyrrole **7**.

Microwave Irradiation. A solution[14a] of $Cl_2(PCy_3)$(IMes)Ru=CHPh in CH_2Cl_2 (0.5 mM, 0.5 mL) was added to *N*-allyl-β-aminoester **6** (0.005 mmol), and the mixture was irradiated by microwave 5 min at 100 °C. Filtration through a plug of silica yielded the corresponding 2,5-dihydropyrrole **7**.

Methyl 2-Phenyl-1-(2-(trimethylsilyl)ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7a): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 72 mg (98%) of the title compound[4a] as a white solid.

Microwave Irradiation. Cyclization of the compound **6a** yielded 1.8 mg (98%) of the title compound.

Mp 95.6–97.0 °C dec; IR 2950 (m), 1729 (s), 1340 (s), 1335 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.15 (s, 9H), 0.55–0.95 (m, 2H), 2.20–2.50 (m, 2H), 3.65 (s, 3H), 4.41 (ddd, 1H, J_2 = 17.1 Hz, J_3 = 6.2 Hz, J_4 = 2.0 Hz), 4.79 (dt, 1H, J_2 = 17.1 Hz, J_3 = 2.6 Hz), 5.84 (ddd, 1H, J_4 = 6.1 Hz, J_4 = 2.6 Hz, J_4 = 1.7 Hz), 6.95 (dt, 1H, J_3 = 2.2 Hz, J_4 = 1.8 Hz), 7.30–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.8, 10.3, 50.3, 52.3, 55.9, 68.8, 128.2, 129.0, 129.1, 135.8, 136.5, 140.0, 162.7; ESIMS *m/z* 368.0 (M + H)$^+$, 390.2 (M + Na)$^+$, 735.3 (2M + H)$^+$, 757.1 (2M + Na)$^+$; FAB+ *m/z* 368 (M + H)$^+$; HRMS calcd for $C_{17}H_{26}NO_4SSi$ 368.1352, found 368.1349.

Methyl 2-(3,5-Dimethoxyphenyl)-1-(2-(trimethylsilyl)ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7b): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 4/6) to yield 82 mg (95%) of the title compound as a white solid.

Microwave Irradiation. Cyclization of the compound **6b** yielded 2.0 mg (92%) of the title compound.

Mp 101.0–105.0 °C dec; IR 2950 (m), 1729 (s), 1344 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.12 (s, 9H), 0.60–1.00 (m, 2H), 2.25–2.60 (m, 2H), 3.67 (s, 3H), 3.80 (s, 6H), 4.39 (ddd, 1H, J_2 = 17.1 Hz, J_3 = 6.1 Hz, J_4 = 2.0 Hz), 4.77 (dt, 1H, J_2 = 17.1 Hz, J_3 = 2.6 Hz), 5.76 (ddd, 1H, J_4 = 6.1 Hz, J_4 = 2.4 Hz, J_4 = 1.7 Hz), 6.41 (t, 1H, J_3 = 2.2 Hz), 6.51 (d, 2H), 6.93 (q, 1H, J_3 = 2.0 Hz, J_4 = 1.8 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.9, 10.5, 50.4, 52.3, 55.7, 56.0, 68.7, 100.4, 106.4, 135.6, 136.6, 142.3, 161.4, 162.7; ESIMS *m/z* 428.1 (M + H)$^+$, 450.2 (M + Na)$^+$; FAB+ *m/z* 427 (M + e$^-$)$^+$, 428 (M + H)$^+$; HRMS calcd for $C_{19}H_{30}NO_6SSi$ 428.1563, found 428.1582.

Methyl 2-(4-(Methoxycarbonyl)phenyl)-1-(2-(trimethylsilyl)ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7c): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 4/6) to yield 78 mg (92%) of the title compound as a white solid.

Microwave Irradiation. Cyclization of the compound **6c** yielded 2.0 mg (92%) of the title compound.

Mp 106.4–107.4 °C; IR 2950 (m), 1731 (s), 1348 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.15 (s, 9H), 0.55–0.95 (m, 2H), 2.25−2.60 (m, 2H), 3.65 (s, 3H), 3.93 (s, 3H), 4.44 (ddd, 1H, J_2 = 17.1 Hz, J_3 = 6.1 Hz, J_4 = 1.9 Hz), 4.80 (dt, 1H, J_2 = 17.1 Hz, J_3 = 2.6 Hz), 5.90 (ddd, 1H, J_4 = 6.1 Hz, J_4 = 2.6 Hz, J_4 = 1.9 Hz), 6.98 (q, 1H, J_3 = 2.0 Hz), 7.46 (ddd, 2H, J_3 = 8.5 Hz, J_4 = 1.9 Hz), 8.06 (ddd, 2H, J_3 = 8.5 Hz, J_4 = 1.9 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.8, 10.3, 50.2, 52.4, 52.6, 56.1, 68.5, 128.2, 130.4, 130.8, 135.4, 137.1, 145.2, 162.5, 166.9; ESIMS *m/z* 426.2 (M + H)$^+$, 851.2 (2M + H)$^+$, 873.3 (2M + Na)$^+$; FAB+ *m/z* 426 (M + H)$^+$, 448 (M + Na)$^+$; HRMS calcd for $C_{19}H_{28}NO_6SSi$ 426.1407, found 426.1403.

Methyl 2-(3-Fluorophenyl)-1-(2-(trimethylsilyl)ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7e): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 73 mg (95%) of the title compound as a white solid.

Mp 80.1−80.7 °C dec; IR 2950 (m), 1731 (s), 1346 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.12 (s, 9H), 0.60−0.95 (m, 2H), 2.25−2.60 (m, 2H), 3.66 (s, 3H), 4.42 (ddd, 1H, J_2 = 2.0 Hz, J_3 = 6.1 Hz, J_4 = 17.1 Hz), 4.78 (dt, 1H, J_2 = 2.6 Hz, J_4 = 17.1 Hz), 5.85 (m, 1H), 6.90−7.10 (m, 3H), 7.15−7.25 (m, 1H), 7.30−7.45 (m, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.8, 10.3, 50.3, 52.4, 56.0, 68.3 (d, J_4 = 1.6 Hz), 114.9 (d, J_2 = 22.0 Hz), 116.0 (d, J_2 = 21.2 Hz), 124.1 (d, J_4 = 2.8 Hz), 130.7 (d, J_3 = 7.8 Hz), 135.4, 136.9, 142.8 (d, J_3 = 6.1 Hz), 162.6, 163.3 (d, J_1 = 247.5 Hz); ESIMS *m/z* 386.1 (M + H)$^+$, 771.2 (2M + H)$^+$, 793.2 (2M + Na)$^+$; FAB+ *m/z* 386 (M + H)$^+$, 408 (M + Na)$^+$, 771 (2M + H)$^+$, 793 (2M + Na)$^+$; HRMS calcd for $C_{17}H_{25}FNO_4SSi$ 386.1258, found 386.1234.

Methyl 2-(2-Bromophenyl)-1-(2-(trimethylsilyl)ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7f): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 80 mg (90%) of the title compound as a white solid.

Microwave Irradiation. Cyclization of compound **6f** yielded 2.0 mg (90%) of the title compound.

Mp 88.7−90.1 °C dec; IR 2950 (m), 1728 (s), 1340 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.11 (s, 9H), 0.65−1.00 (m, 2H), 2.35−2.70 (m, 2H), 3.66 (s, 3H), 4.47 (ddd, 1H, J_2 = 17.1 Hz, J_3 = 6.3 Hz, J_4 = 2.0 Hz), 4.83 (dt, 1H, J_2 = 17.1 Hz, J_3 = 2.8 Hz), 6.31 (ddd, 1H, J_4 = 6.3 Hz, J_4 = 2.8 Hz, J_4 = 2.0 Hz), 6.95 (q, 1H, J_3 = 2.0 Hz), 7.10−7.40 (m, 3H), 7.55−7.65 (m, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −2.2, 9.8, 49.7, 51.9, 55.9, 67.9, 123.6, 127.8, 129.8, 130.4, 133.7, 134.7, 136.8, 138.7, 162.0; ESIMS *m/z* 445.9/447.9 (M + H)$^+$; FAB+ *m/z* 446/448 (M + H)$^+$; HRMS calcd for $C_{17}H_{25}BrNO_4SSi$ 446.0457, found 446.0427.

Methyl 2-(Naphthalen-2-yl)-1-(2-(trimethylsilyl)ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7g): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 75 mg (90%) of the title compound as a white solid.

Microwave Irradiation. Cyclization of compound **6g** yielded 1.9 mg (89%) of the title compound.

Mp 123.1−124.3 °C; IR 2950 (m), 1728 (s), 1339 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.37 (s, 9H), 0.50−0.85 (m, 2H), 2.10−2.45 (m, 2H), 3.62 (s, 3H), 4.49 (ddd, 1H, J_2 = 17.1 Hz, J_3 = 6.3 Hz, J_4 = 2.0 Hz), 4.84 (dt, 1H, J_2 = 17.1 Hz, J_3 = 2.6 Hz), 6.02 (ddd, 1H, J_4 = 6.1 Hz, J_4 = 2.6 Hz, J_4 = 1.7 Hz), 7.02 (dt, 1H, J_3 = 2.0 Hz, J_4 = 1.8 Hz), 7.35−7.60 (m, 3H), 7.75−7.95 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −2.1, 10.2, 50.3, 52.3, 56.0, 69.0, 125.1, 126.9, 127.9, 128.1, 128.6, 129.1, 133.6, 133.8, 135.7, 136.7, 137.1, 162.7; ESIMS *m/z* 418.2 (M + H)$^+$, 440.0 (M + Na)$^+$; FAB+ *m/z* 417 (M − e$^-$)$^+$, 440 (M + Na)$^+$; HRMS calcd for $C_{21}H_{27}NO_4SSi$ 417.1430, found 417.1421.

Methyl 2-*m*-Tolyl-1-(2-(trimethylsilyl)ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7h): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 75 mg (98%) of the title compound as a white solid.

Mp 85.0−87.2 °C; IR 2945 (m), 1731 (s), 1344 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.15 (s, 9H), 0.55−0.95 (m, 2H), 2.20−2.50 (m, 2H), 2.37 (s, 3H), 3.66 (s, 3H), 4.41 (ddd, 1H, J_2 = 17.1 Hz, J_3 = 6.3 Hz, J_4 = 2.0 Hz), 4.78 (dt, 1H, J_2 = 17.1 Hz, J_3 = 2.6 Hz), 5.79 (ddd, 1H, J_4 = 6.1 Hz, J_4 = 2.6 Hz, J_4 = 1.7 Hz), 6.94 (dt, 1H, J_3 = 2.2 Hz, J_4 = 1.9 Hz), 7.05−7.35 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.8, 10.3, 21.8, 50.2, 52.3, 55.9, 68.8, 125.3, 128.8, 129.0, 129.8, 135.8, 136.9, 138.7, 139.9, 162.76; ESIMS *m/z* 382.1 (M + H)$^+$, 404.1 (M + Na)$^+$, 763.4 (2M + H)$^+$; FAB+ *m/z* 382 (M + H)$^+$, 404 (M + Na)$^+$; HRMS calcd for $C_{18}H_{28}NO_4SSi$ 382.1508, found 382.1505.

Methyl 2-(3,5-Dimethylphenyl)-1-(2-(trimethylsilyl)-ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7i): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 73 mg (92%) of the title compound as a white solid.

Mp 96.0−97.2 °C; IR 2950 (m), 1731 (s), 1344 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.15 (s, 9H), 0.55−0.95 (m, 2H), 2.20−2.50 (m, 2H), 2.32 (s, 6H), 3.67 (s, 3H), 4.40 (ddd, 1H, J_2 = 17.1 Hz, J_3 = 6.1 Hz, J_4 = 2.0 Hz), 4.77 (dt, 1H, J_2 = 17.1 Hz, J_3 = 2.6 Hz), 5.75 (ddd, 1H, J_4 = 6.1 Hz, J_4 = 2.4 Hz, J_4 = 1.7 Hz), 6.90−7.00 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.9, 10.2, 21.7, 50.2, 52.3, 55.8, 68.7, 125.9, 130.7, 135.9, 136.3, 138.6, 139.8, 162.8; ESIMS *m/z* 396.1 (M + H)$^+$, 418.1 (M + Na)$^+$; 791.4 (2M + H)$^+$, 813.2 (2M + Na)$^+$; FAB+ *m/z* 396 (M + H)$^+$, 418 (M + Na)$^+$; HRMS calcd for $C_{19}H_{30}NO_4SSi$ 396.1665, found 396.1651.

Methyl 2-(2,3-Methylenedioxyphenyl)-1-(2-(trimethylsilyl)ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7j): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 4/6) to yield 79 mg (96%) of the title compound as a white solid.

Mp 123.5−124.6 °C dec; IR 2953 (m), 1729 (s), 1356 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.10 (s, 9H), 0.65−1.00 (m, 2H), 2.40−2.70 (m, 2H), 3.68 (s, 3H), 4.44 (ddd, 1H, J_2 = 16.7 Hz, J_3 = 6.1 Hz, J_4 = 1.9 Hz), 4.76 (dt, 1H, J_2 = 16.7 Hz, J_3 = 2.4 Hz), 5.84 (ddd, 1H, J_4 = 6.1 Hz, J_4 = 2.4 Hz, J_4 = 1.7 Hz), 5.98 (s, 2H), 6.75−6.95 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.8, 10.2, 50.0, 52.3, 56.0, 64.7, 101.5, 109.1, 121.2, 122.2, 122.4, 133.8, 137.3, 145.6, 148.2, 162.7; ESIMS *m/z* 412.0 (M + H)$^+$, 450.1 (M + K)$^+$, 823.2 (2M + H)$^+$, 845.1 (2M + Na)$^+$; FAB+ *m/z* 411 (M + e$^-$)$^+$, 434 (M + Na)$^+$; HRMS calcd for $C_{18}H_{25}NO_4SSi$ 411.1172, found 411.1180.

Methyl 2-(4-Chlorophenyl)-1-(2-(trimethylsilyl)ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7k): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 77 mg (95%) of the title compound[4a] as a white solid.

Microwave Irradiation. Cyclization of the compound **6k** yielded 1.5 mg (95%) of the title compound.

Mp 86.1−87.4 °C dec; IR 2950 (m), 1733 (s), 1346 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.11 (s, 9H), 0.55−0.95 (m, 2H), 2.25−2.60 (m, 2H), 3.66 (s, 3H), 4.40 (ddd, 1H, J_2 = 17.1 Hz, J_3 = 6.1 Hz, J_4 = 2.0 Hz), 4.77 (dt, 1H, J_2 = 17.1 Hz, J_3 = 2.6 Hz), 5.83 (ddd, 1H, J_4 = 6.1 Hz, J_4 = 2.6 Hz, J_4 = 1.7 Hz), 6.96 (dt, 1H, J_3 = 2.2 Hz, J_4 = 1.9 Hz), 7.35−7.40 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.8, 10.3, 50.3, 52.4, 55.9, 68.2, 129.35, 129.6, 134.9, 135.4, 136.8, 138.8, 162.5; ESIMS *m/z* 402.0 (M + H)$^+$; FAB+ *m/z* 402 (M + H)$^+$, 424 (M + Na)$^+$; HRMS calcd for $C_{17}H_{25}ClNO_4SSi$ 402.0962, found 402.0955.

Methyl 2-(2-Iodophenyl)-1-(2-(trimethylsilyl)ethylsulfonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate (7*l*): Thermal Conditions. The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 93 mg (94%) of the title compound as a white solid.

Mp 134.1−134.7 °C dec; IR 2948 (m), 1729 (s), 1341 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.11 (s, 9H), 0.65−1.00 (m, 2H), 2.35−2.70 (m, 2H), 3.66 (s, 3H), 4.50 (ddd, 1H, J_2 = 17.3 Hz, J_3 = 6.3 Hz, J_4 = 2.0 Hz), 4.82 (dt, 1H, J_2 = 17.3 Hz, J_3 = 2.6 Hz), 6.21 (ddd, 1H, J_4 = 6.1 Hz, J_4 = 2.8 Hz, J_4 = 2.0 Hz), 6.90−7.10 (m, 2H), 7.20−7.45 (m, 2H), 7.85−7.95 (m, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −2.8, 9.1, 49.0, 51.2, 55.3, 71.3, 98.6, 127.9, 128.6, 129.3, 134.6, 136.0, 139.6, 141.7, 161.3; ESIMS *m/z* 494.0 (M + H)$^+$, 987.0 (2M + H)$^+$; FAB+ *m/z* 494 (M + H)$^+$; HRMS calcd for $C_{17}H_{25}INO_4SSi$ 494.0318, found 494.0307.

General Procedure for the Synthesis of Pyrroles 8. To a stirred solution[2y] of 2,5-dihydropyrrole **7** (0.10 mmol) in 2 mL of DMF was added *t*-BuOK (37 mg, 0.50 mmol). The mixture was stirred at room temperature for 2 h, then 15 mL of AcOEt was added and the mixture was neutralized with aq $KHSO_4$ (1%) and washed with saturated $NaHCO_3$, water, and brine. The organic layer was dried over $MgSO_4$, filtered, and evaporated. Silica gel chromatography (Et_2O/hexane) yielded the pyrrole **8**.

Methyl 2-Phenyl-1*H*-pyrrole-3-carboxylate (8a). The crude product was purified by silica gel chromatography (Et_2O/hexane = 2/8) to yield 16 mg (80%) of the title compound[4a] as a white solid.

Mp 90.0−91.4 °C dec; IR 3463 (m), 2943 (m), 1694 (s), 1290 (s) cm^{-1}; ^1H NMR (acetone-d_6, Me_4Si) δ 3.57 (s, 3H), 6.54 (t, 1H, J_3 = 2.8 Hz), 6.78 (t, 1H, J_3 = 2.8 Hz), 7.20−7.35 (m, 3H), 7.50−7.60 (m, 2H), 10.61 (large s, 1H); ^{13}C NMR (acetone-d_6, Me_4Si) δ 50.8, 112.4, 112.6, 119.0, 128.5, 128.7, 129.9, 133.4, 137.6, 165.6; ESIMS *m/z* 202.1 $(M + H)^+$; FAB+ *m/z* 201 $(M - e^-)^+$, 202 $(M + H)^+$; HRMS calcd for $C_{12}H_{11}NO_2$ 201.0790, found 201.0779.

Methyl 2-(3,5-Dimethoxyphenyl)-1*H*-pyrrole-3-carboxylate (8b). The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 22 mg (83%) of the title compound as a white solid.

Mp 120.9−124.0 °C dec; IR 3380 (m), 2930 (m), 1704 (s), 1306 (s) cm^{-1}; ^1H NMR (acetone-d_6, Me_4Si) δ 3.63 (s, 3H), 3.74 (s, 6H), 6.40 (t, 1H, J_3 = 2.3 Hz), 6.57 (t, 1H, J_3 = 2.8 Hz), 6.80 (t, 1H, J_3 = 2.8 Hz), 6.83 (d, 2H, J_3 = 2.3 Hz), 10.65 (large s, 1H); ^{13}C NMR (acetone-d_6, Me_4Si) δ 52.7, 57.4, 102.6, 109.6, 114.4, 114.7, 120.7, 136.7, 139.0, 163.1, 167.4; ESIMS *m/z* 262.1 $(M + H)^+$; FAB+ *m/z* 261 $(M - e^-)^+$, 262 $(M + H)^+$; HRMS calcd for $C_{14}H_{15}NO_4$ 261.1001, found 261.1030.

Methyl 2-(4-(Methoxycarbonyl)phenyl)-1*H*-pyrrole-3-carboxylate (8c). The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield the title compound along with the product of transesterification **8c′** (**8c**/**8c′** = 1/3).

8c: ^1H NMR (acetone-d_6, Me_4Si) δ 3.63 (s, 3H), 3.83 (s, 3H), 6.55−6.65 (m, 1H), 6.85−6.90 (m, 1H), 7.70−7.80 (m, 2H), 7.90−8.00 (m, 2H), 10.85 (large s, 1H).

Methyl 2-(4-(*tert*-Butyloxycarbonyl)phenyl)-1*H*-pyrrole-3-carboxylate (8c′). ^1H NMR (acetone-d_6, Me_4Si) δ 1.53 (s, 9H), 3.63 (s, 3H), 6.55−6.65 (m, 1H), 6.85−6.90 (m, 1H), 7.65−7.75 (m, 2H), 7.85−7.95 (m, 2H), 10.85 (large s, 1H).

Methyl 2-(3-Fluorophenyl)-1*H*-pyrrole-3-carboxylate (8e). The crude product was purified by silica gel chromatography (Et_2O/hexane = 2/8) to yield 18 mg (81%) of the title compound as a white solid.

Mp 106.9−108.3 °C dec; IR 3460 (m), 2945 (m), 1719 (s), 1296 (s) cm^{-1}; ^1H NMR (acetone-d_6, Me_4Si) δ 3.64 (s, 3H), 6.59 (t, 1H, J_3 = 2.8 Hz), 6.85 (t, 1H, J_3 = 2.8 Hz), 7.00−7.10 (m, 1H), 7.30−7.50 (m, 4H), 10.88 (large s, 1H); ^{13}C NMR (acetone-d_6, Me_4Si) δ 51.0, 112.9, 113.0, 115.1 (d, J_2 = 21.1 Hz), 116.7 (d, J_2 = 23.4 Hz), 119.5, 125.6 (d, J_4 = 3.0 Hz), 130.5 (d, J_3 = 9.1 Hz), 135.4 (d, J_3 = 9.1 Hz), 135.9, 163.2 (d, J_1 = 243.0 Hz), 165.5; ESIMS *m/z* 220.1 $(M + H)^+$; FAB+ *m/z* 219 $(M - e^-)^+$, 220 $(M + H)^+$; HRMS calcd for $C_{12}H_{11}FNO_2$ 220.0774, found 220.0784.

Methyl 2-(2-Bromophenyl)-1*H*-pyrrole-3-carboxylate (8f). The crude product was purified by silica gel chromatography (Et_2O/hexane = 2/8) to yield 23 mg (81%) of the title compound as a white solid.

Mp 145.8−147.4 °C dec; IR 3458 (m), 2948 (m), 1693 (s), 1290 (s) cm^{-1}; ^1H NMR (acetone-d_6, Me_4Si) δ 3.48 (s, 3H), 6.52 (t, 1H, J_3 = 2.8 Hz), 6.81 (t, 1H, J_3 = 2.8 Hz), 7.15−7.35 (m, 3H), 7.55−7.60 (m, 1H), 10.57 (large s, 1H); ^{13}C NMR (acetone-d_6, Me_4Si) δ 50.7, 111.0, 114.4, 118.9, 125.1, 127.7, 130.7, 133.2, 133.5, 135.5, 135.9, 165.1; ESIMS *m/z* 280.2/282.1 $(M + H)^+$; FAB+ *m/z* 280/282 $(M + H)^+$; HRMS calcd for $C_{12}H_{11}BrNO_2$ 279.9973, found 279.9960.

Methyl 2-(Naphthalen-2-yl)-1*H*-pyrrole-3-carboxylate (8g). The crude product was purified by silica gel chromatography (Et_2O/hexane = 2/8) to yield 17 mg (66%) of the title compound as a white solid.

Mp 110.6−112.3 °C dec; IR 3463 (m), 2928 (m), 1694 (s), 1284 (s) cm^{-1}; ^1H NMR (acetone-d_6, Me_4Si) δ 3.62 (s, 3H), 6.62 (t, 1H, J_3 = 2.8 Hz), 6.87 (t, 1H, J_3 = 2.8 Hz), 7.40−7.50 (m, 2H), 7.70−7.90 (m, 4H), 8.05−8.15 (m, 1H); 10.80 (large s, 1H); ^{13}C NMR (acetone-d_6, Me_4Si) δ 50.9, 112.8, 119.4, 127.1, 127.1, 127.9, 128.3, 128.4, 128.5, 129.0, 131.0, 133.8, 134.0, 137.5, 165.7; ESIMS *m/z* 252.0 $(M + H)^+$, 503.5 $(2M + H)^+$; FAB+ *m/z* 251 $(M - e^-)^+$, 252 $(M + H)^+$; HRMS calcd for $C_{16}H_{13}NO_2$ 251.0946, found 251.0958.

Methyl 2-*m*-Tolyl-1*H*-pyrrole-3-carboxylate (8h). The crude product was purified by silica gel chromatography (Et_2O/hexane = 2/8) to yield 15 mg (72%) of the title compound as a white solid.

Mp 71.1−72.1 °C dec; IR 3458 (m), 2950 (m), 1693 (s), 1293 (s) cm^{-1}; ^1H NMR (acetone-d_6, Me_4Si) δ 2.25 (s, 3H), 3.58 (s, 3H), 6.53 (t, 1H, J_3 = 2.8 Hz), 6.77 (t, 1H, J_3 = 2.8 Hz), 7.00−7.25 (m, 2H), 7.30−7.40 (m, 2H), 10.59 (large s, 1H); ^{13}C NMR (acetone-d_6, Me_4Si) δ 21.4, 50.8, 112.4, 112.6, 118.9, 127.0, 128.6, 129.2, 130.4, 133.3, 137.8, 138.0, 165.6; ESIMS *m/z* 216.2 $(M + H)^+$; FAB+ *m/z* 215 $(M - e^-)^+$, 216 $(M + H)^+$; HRMS calcd for $C_{13}H_{13}NO_2$ 215.0946, found 215.0951.

Methyl 2-(3,5-Dimethylphenyl)-1*H*-pyrrole-3-carboxylate (8i). The crude product was purified by silica gel chromatography (Et_2O/hexane = 2/8) to yield 18 mg (78%) of the title compound as a white solid.

Mp 124.8−126.2 °C dec; IR 3463 (m), 2943 (m), 1693 (s), 1303 (s) cm^{-1}; ^1H NMR (acetone-d_6, Me_4Si) δ 2.17 (s, 6H), 3.54 (s, 3H), 6.48 (t, 1H, J_3 = 2.8 Hz), 6.71 (t, 1H, J_3 = 2.8 Hz), 6.80−6.90 (m, 1H), 7.10−7.20 (m, 2H), 10.49 (large s, 1H); ^{13}C NMR (acetone-d_6, Me_4Si) δ 18.9, 48.3, 109.9, 110.2, 116.3, 125.3, 127.6, 130.9, 135.5, 163.2; ESIMS *m/z* 230.2 $(M + H)^+$; FAB+ *m/z* 229 $(M - e^-)^+$, 230 $(M + H)^+$; HRMS calcd for $C_{14}H_{15}NO_2$ 229.1103, found 229.1096.

Methyl 2-(2,3-Methylenedioxyphenyl)-1*H*-pyrrole-3-carboxylate (8j). The crude product was purified by silica gel chromatography (Et_2O/hexane = 3/7) to yield 22 mg (88%) of the title compound as a white solid.

Mp 101.9−104.7 °C dec; IR 3455 (m), 2968 (m), 1730 (s), 1295 (s) cm^{-1}; ^1H NMR (acetone-d_6, Me_4Si) δ 3.62 (s, 3H), 5.93 (s, 2H), 6.57 (t, 1H, J_3 = 2.8 Hz), 6.75−6.85 (m, 2H), 6.85 (t, 1H, J_3 = 2.8 Hz), 7.10−7.20 (m, 1H), 10.61 (large s, 1H); ^{13}C NMR (acetone-d_6, Me_4Si) δ 50.9, 101.7, 108.6, 112.2, 114.1, 115.8, 119.3, 121.9, 123.8, 131.3, 145.8, 148.3, 165.5; ESIMS *m/z* 246.0 $(M + H)^+$; FAB+ *m/z* 245 $(M - e^-)^+$, 246 $(M + H)^+$; HRMS calcd for $C_{13}H_{11}NO_4$ 245.0688, found 245.0678.

Methyl 2-(4-Chlorophenyl)-1*H*-pyrrole-3-carboxylate (8k). The crude product was purified by silica gel chromatography (Et_2O/hexane = 2/8) to yield 19 mg (81%) of the title compound[4a] as a white solid.

Mp 113.3−114.5 °C dec; IR 3380 (m), 2948 (m), 1695 (s), 1286 (s) cm^{-1}; ^1H NMR (acetone-d_6, Me_4Si) δ 3.62 (s, 3H), 6.58 (t, 1H, J_3 = 2.8 Hz), 6.84 (t, 1H, J_3 = 2.8 Hz), 7.30−7.40 (m, 2H), 7.55−7.65 (m, 2H), 10.75 (large s, 1H); ^{13}C NMR (acetone-d_6, Me_4Si) δ 50.9, 112.8, 112.9, 119.4, 128.7, 131.5, 132.1, 133.9, 136.1, 165.5; ESIMS *m/z* 236.3 $(M + H)^+$; FAB+ *m/z* 235 $(M - e^-)^+$, 236 $(M + H)^+$; HRMS calcd for $C_{12}H_{10}ClNO_2$ 235.0400, found 235.0383.

Methyl 2-(2-Iodophenyl)-1*H*-pyrrole-3-carboxylate (8*l*). The crude product was purified by silica gel chromatography (Et_2O/hexane = 2/8) to yield 27 mg (81%) of the title compound as a white solid.

Mp 140.4−144.8 °C dec; IR 3465 (m), 2950 (m), 1711 (s), 1275 (s) cm^{-1}; ^1H NMR (acetone-d_6, Me_4Si) δ 3.47 (s, 3H), 6.51 (t, 1H, J_3 = 2.8 Hz), 6.79 (t, 1H, J_3 = 2.8 Hz), 7.05 (ddd, 1H, J_3 = 7.9 Hz, J_3 = 7.3 Hz, J_4 = 1.9 Hz), 7.26 (dd, 1H, J_3 = 7.6 Hz, J_4 = 1.9 Hz), 7.34 (ddd, 1H, J_3 = 7.6 Hz, J_3 = 7.3 Hz, J_4

= 1.2 Hz), 7.83 (dd, 1H, J_3 = 7.9 Hz, J_4 = 1.2 Hz), 10.50 (large s, 1H); ^{13}C NMR (acetone-d_6, Me_4Si) δ 50.7, 101.1, 110.9, 114.1, 118.7, 128.4, 130.63, 132.4, 139.1, 139.5, 139.9, 165.0; ESIMS *m/z* 328.1 $(M + H)^+$; FAB+ *m/z* 328 $(M + H)^+$; HRMS calcd for $C_{12}H_{11}INO_2$ 327.9835, found 327.9863.

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