New Soluble-Polymer Bound Ruthenium Carbene Catalysts: Synthesis, Characterization, and Application to Ring-Closing Metathesis

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Exchange of benzylidene ligand of commercially available Grubbs catalysts **1a** or **1b** with an appropriate soluble-polymer supported ligand leads to new boomerang type catalysts either of the Grubbs (**3**) or the Hoveyda type (**4a** or **4b**). These catalysts, supported on poly(ethylene glycol) (PEG), were fully characterized by solution NMR and MALDI mass spectrometry. They were tested in ring-closing metathesis (RCM), and ^{1}H NMR analysis provided key information concerning the recovery of the catalyst at the end of the reaction. While in the case of **3** the active ruthenium did not hook back to the ligand, catalysts **4a** and **4b** can be recovered and recycled. **4b** owning a N-heterocyclic carbene ligand is particularly active and was used in the parallel synthesis of cyclic amino esters.

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Introduction

Ring-closing metathesis (RCM)[1−10] has become a very powerful and versatile technique in organic chemistry for the synthesis of cyclic structures mainly because of the development of ready to use ruthenium precatalysts such as **1a** or **2a**, which are tolerant of a wide variety of functional groups.[5,10] Recently more active catalysts such as **1b** or **2b** with a heterocyclic carbene ligand have been disclosed (Figure 1).[11−18]

The current challenge for catalysis in the perspective of industrial applications is the efficiency of the catalytic process and the ability to recycle the catalyst. Polymer-supported catalysis has received recently increasing attention since this approach should facilitate purification of the synthesized product as well as the recycling of the catalyst.[19−25] For this purpose, a few synthetic and recycling studies on polymer-supported ruthenium precatalysts have been reported.[26−37] Nevertheless most of these precatalysts are supported on an insoluble

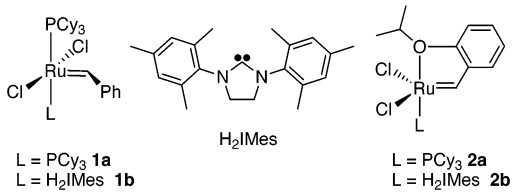

Figure 1. Grubbs' and Hoveyda's catalysts.

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polymer, which presents two main drawbacks. First, due to the heterogeneity of the support, access to the reactive site is very often reduced, hence resulting in poor catalysis. Second the structural information regarding this type of reaction is limited: while the ability of the catalyst to be recycled is easily assessed on a test experiment, structural analysis of the precatalyst before as well as after recovery at the end of the reaction requires less available technique with an insoluble polymer and was not reported. An alternative to insoluble supports is the use of a soluble polymer, which should facilitate the accessibility to reactive sites and reduce the problems of diffusion rate within the polymer as well as provide access to structural information using classical solution spectroscopic methods.[38] The most widely used soluble polymer is poly(ethylene glycol) (PEG). It is soluble in polar organic solvents and has the advantage of providing the possiblity of analyzing the supported moiety with classical solution NMR spectroscopy[38] or mass spectrometry.[39−43] Recovery of the supported material such as a catalyst is performed by precipitation in a nonpolar solvent followed by filtration.[38,44−56] Consequently in the case of a PEG-supported RCM catalyst it is possible to characterize a supported precatalyst, to monitor the advancement of a reaction and the evolution of the catalyst during the course of a reaction, and finally to evaluate the ability of recovering the catalyst at the end of the reaction. The first example of PEG-supported RCM catalysts has been reported.[26] This catalyst proved to be efficient in RCM reactions, and it had good recycling abilities. A different approach consisting in synthesizing a soluble polymeric support by ring-opening metathesis polymerization has been described, and efficient ROMP-gel catalysts have been synthesized.[30]

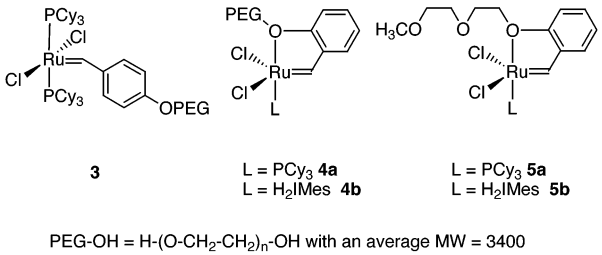
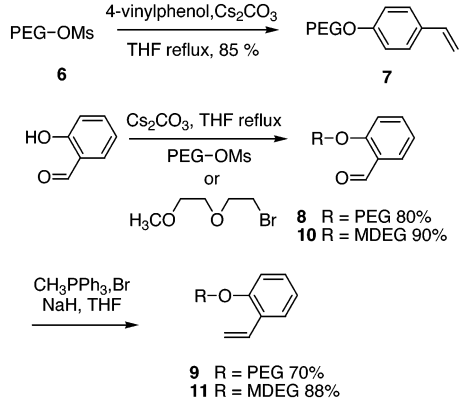


Figure 2. Structure of polyoxygenated catalysts.

Scheme 1. Synthesis of the Supported Ligands



We present herein the synthesis and characterization of two efficient and novel PEG-supported catalysts. Their efficiency in ring-closing metathesis was assessed and compared to results obtained with a structurally similar nonsupported catalyst.

Results and Discussion

The catalysts that were evaluated are presented in Figure 2.

We designed two types of boomerang catalysts[18,26,29,30,32−35,37] bearing a PEG-bound benzylidene ligand, the ether linkage being either para (catalyst **3**) or ortho (catalysts **4a** and **4b**) to the metal carbene group. Examples of catalyst using this ether linkage have been previously reported.[29,35] Catalyst **3** is a Grubbs type catalyst.[57] The vicinal oxygens of the polymer present in ortho position to the carbene in **4a** or **4b** may interact with the metal and provide a bidentate ligand. Consequently we can take advantage of the polymer structure to synthesize new catalysts and we can expect **4a** and **4b** to be Hoveyda type catalysts[10,18] with a Ru−O interaction such as in **2a** and **2b**. To evaluate the effect of the support in catalysts **4a** and **4b** and since we have shown that it could be detrimental in the case of PEG-supported RCM,[58] structurally similar catalysts **5a** and **5b** missing the polymer were also prepared.

The catalysts were easily accessible via suitable ligand exchange[32] with the benzylidene of commercially available catalyst **1a** or **1b**.

1. Synthesis of the Ligands. Syntheses of the ligands are described in Scheme 1. *p*-Pegylated-styrene **7** was synthesized by O-alkylation of the corresponding

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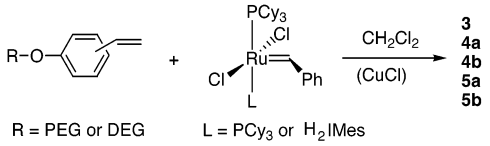
Table 1. Characteristic ^{1}H, ^{13}C, and ^{31}P Chemical Shifts of Ru Catalysts

catalyst[a]	^{1}H (ppm)	^{13}C (ppm)	^{31}P (ppm)
1a	20.02	294.72	36.61
1b	19.16		31.41
2a	17.44	280.63	59.97
2b	16.56	296.83	
3	19.50	280.79	36.63
4a	17.40	278.35	60.95
4b	16.50	292.95	
5a	17.35	278.48	60.96
5b	16.50	293.98	

[a] NMR data for **1a**, **1b**, **2a**, and **2b** were retrieved from the literature (refs 57, 13, 10, 18, respectively.)

Scheme 2. Synthesis of Various Catalysts by Ligand Exchange



phenol with the mesylate of bifunctional PEG 3400 in the presence of Cs_2CO_3 as described in Scheme 1.[47,52,59,60] For the ortho isomer, alkylation of PEG-OMs with salicylaldehyde followed by Wittig olefination[61] yielded the corresponding ligand **9**. A similar synthesis was performed to obtain **11** starting from 1-bromo-2-(2-methoxyethoxy)ethane. At each step the PEG-supported molecule was precipitated in ether, filtered, and characterized by IR, ^{1}H and ^{13}C NMR, and ESI-mass spectrometry.

2. Synthesis and Characterization of the Catalysts. Ligand exchange with the suitable catalyst **1a** or **1b** gave access to catalysts **3**−**5** (Scheme 2). The structure of the catalysts was ascertained by solution NMR and MALDI-Tof mass spectrometry.[41]

Catalyst **3** was synthesized by reacting **1a** with ligand **7**. The reaction was monitored by ^{1}H NMR following the disappearance of the ethylene proton of **7** and the appearance of the benzylidene proton of **3**. The values of the characteristic NMR chemical shifts for the metal-attached methine group are reported in Table 1. When a phosphine ligand is present, the value of the corresponding ^{31}P NMR chemical shift is given. For comparison, values for complexes **1a**,**b** and **2a**,**b** reported in the literature are also given. Two equivalents of **1a** were necessary to complete the reaction within 16 h at room temperature in CH_2Cl_2. Similarly catalysts **4a** and **4b** were synthesized. In this case 48 h were needed for completion of the reaction. It is noteworthy that in the case of **4b**, when the reaction was analyzed after 16 h, before completion, the presence of an intermediate complex was observed by ^{1}H NMR. This complex was characterized by a chemical shift of the benzylidene proton at 17.75 ppm in CD_2Cl_2, corresponding to structure **12** (Figure 3), in agreement with literature data.[62] For the synthesis of PEG-supported catalysts **4a** and **4b**, the use of CuCl[63] did not accelerate the ligand exchange reaction.

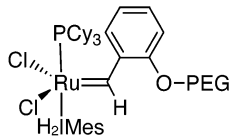


Figure 3. Intermediate complex **12** observed by ^{1}H NMR.

Table 2. Mass Increments between Native and Functionalized PEG

catalyst	calcd mass increment from PEG_{3400} (Δm)	theoretical peak	measured peak
4a	1078	3938.3 (n = 64, Na^+)	3937.7
		4290.8 (n = 72, Na^+)	4290.3
		4511.0 (n = 77, Na^+)	4510.5
4b	1132	3788.2 (n = 59, K^+)	3788.1
		4052.5 (n = 62, K^+)	4052.2
		4316.8 (n = 71, K^+)	4316.4

In the case of catalysts **5a** and **5b**, **1a** and **1b** (respectively) were first reacted with CuCl to facilitate removal of the phosphine ligand before its replacement by the oxygen ligands.[63] Addition of ligand **11** resulted in the formation of **5a** and **5b** (respectively), as it can be checked by ^{1}H NMR of the crude mixture. Nevertheless **5a** had a tendency to degrade on column chromatography and was obtained as a 9:1 mixture of catalyst **5a**/ligand **11**. **5b** proved to be more stable, and no degradation was observed in the same conditions. It has to be noted that contrary to the synthesis of the PEG-supported version of the catalysts (**4a** and **4b**), CuCl was needed to avoid degradation before complete ligand exchange and total conversion. In the case of **4a** and **4b** (respectively) using only an excess of starting catalyst was sufficient.

As a representative example, ^{1}H NMR and MALDI-TOF spectra of catalyst **4b** are shown in Figures 4 and 5. We had shown previously that MALDI mass spectrometry could be used to control a multistep organic synthesis supported on a soluble polymer.[41] The spectrum reported in Figure 4 is characteristic of catalyst **4b** since ions extracted from the polymer distribution confirm the catalyst structure. Indeed one can calculate the mass increment induced by grafting the organometallic complex on the native PEG-OH. This corresponds to an increment of $1132 = 2 \times (567 - 1)$. The calculated theoretical values and the observed peak values for three ions (n = 59, 62, and 71) are reported in Table 2. The perfect match within the precision of MALDI mass spectrometry between these values (and which can be extended to other ions) ascertains the atomic composition of the catalyst.

Figure 5 shows the ^{1}H NMR spectrum of **4b** in CD_2Cl_2. The signals of the different protons present in the molecule were assigned. The characteristic benzylidene proton is found at 16.52 ppm.

3. Catalyst Activity and Recycling. 3.1. Results. The activities of the different catalysts were tested on the ring-closing metathesis (RCM) of two substrates: tosyl diallylamine **13** and *N*-allyl allylglycine **15**. The rebinding of the catalyst was assessed as follows: at the end of the reaction, the cyclized product was recovered

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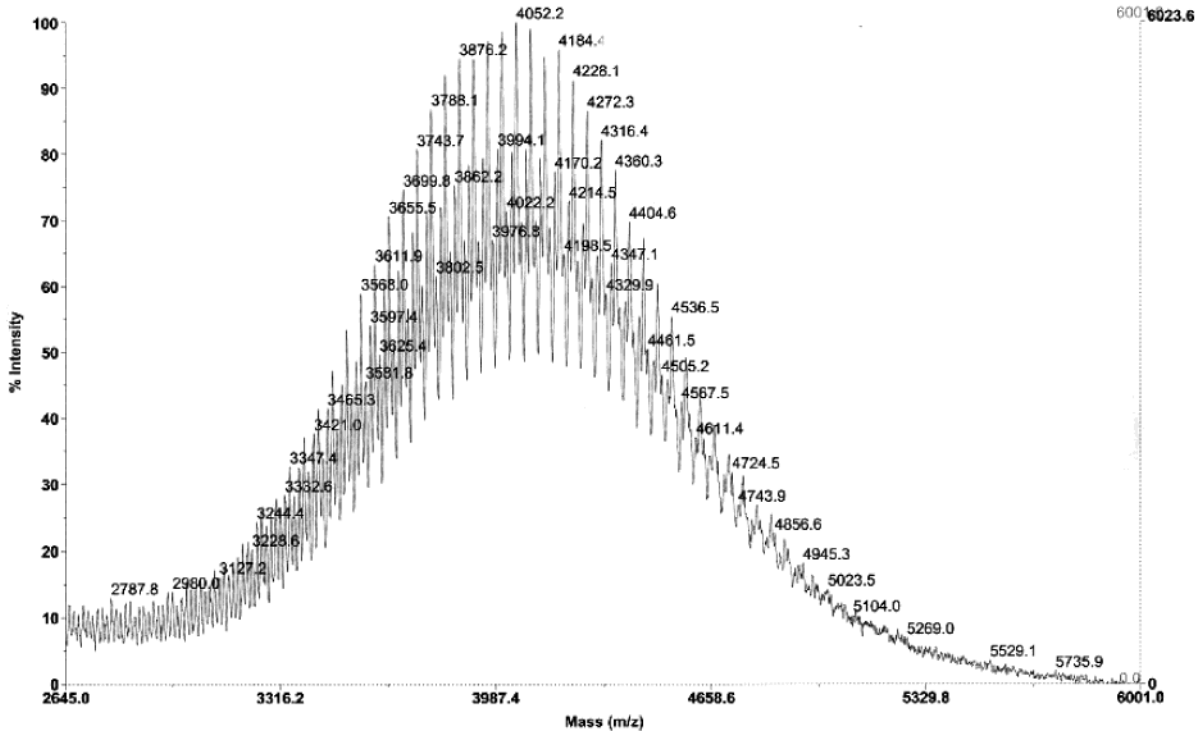

Figure 4. MALDI-Tof mass spectrum of compound **4b** in 2-cyano-4-hydroxycinnamic acid.

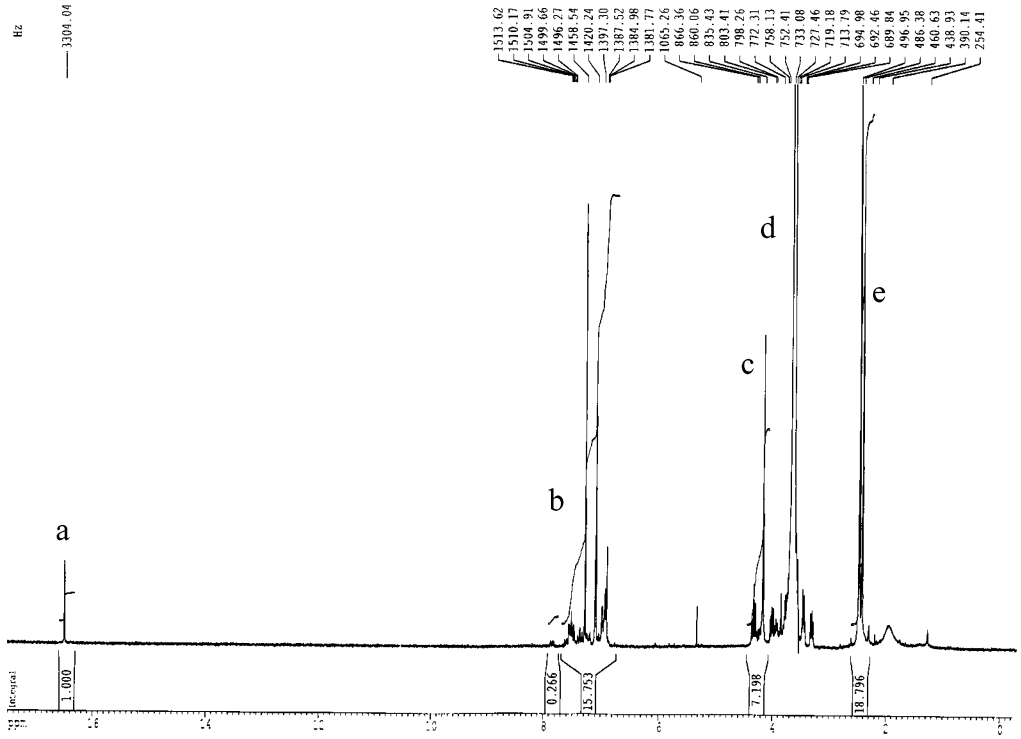

Figure 5. ^{1}H NMR spectrum of compound **4b**: (a) carbenic proton, (b) aromatic protons, (c) imidazole methylene protons, (d) methylene PEG protons, (e) methyl protons.

after precipitation and filtration. The precipitate was analyzed by ^{1}H NMR. The integration[10] of the alkylidene proton for the metal-occupied product and of the proton in α position to styrene for the metal-vacant product gave the proportion of rebinding.

Catalyst **3** was tested in the cyclization of tosyldiallylamine by using 5 mol % of catalyst (10 mol % Ru). The cyclization was complete within 15 min, and the cyclized product **14** was obtained in 72% yield after precipitation in Et_2O and filtration, proving the efficiency of **3** in a RCM reaction. Nevertheless ^{1}H NMR analysis of the precipitate showed the complete disappearance of the signal at 19.50 ppm, corresponding to the proton borne by the metal carbene. Only the vinyl ligand could be detected in the precipitate. Consequently we can conclude that the catalyst cannot be recovered and recycled after reaction since it did not react with the ligand.

Table 3. Recycling Reactions of Catalyst 4a

			composition of the precipitate (conditions 3) (%)		
cycle	conversion (conditions 2)	conversion (conditions 3)	**4a**	**8**	**9**
1	90	98	25	43	32
2	38	63	12	49	39

Table 4. Recycling Reactions of Catalyst 4b

				composition of the precipitate[a] (conditions 1) (%)		
cycle	conversion (conditions 1)	conversion (conditions 2)	conversion (conditions 3)	**4b**	**8**	**9**
1	100	100	100	57	30	13
2	100	93	100	54	28	18
3	85	90	85	39	33	28
4	80	85	85	34	28	38
5	80	85	80	27	37	36

[a] Figures are given within the error of measurement by ^{1}H NMR.

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Catalysts **4a** and **4b** were tested on the same reactions described previously (Tables 3 and 4). Preliminary results on those systems showed that both of the catalysts would perform the RCM reaction. In these cases the reaction was slower than in the case of **3** (2 h instead of 15 min). In the case of **4a** when the precipitate was analyzed by ^{1}H NMR after precipitation and filtration at the end of the reaction, the characteristic signal at 17.40 ppm for **4a** was present, confirming the recovery of the catalysts (albeit not total). To investigate in more detail this reaction and evaluate the recycling, we set up a time limit (2 h for conditions 1, 2 h for conditions 2, 2 h for conditions 3) to assess conversion of starting materials to product and to analyze the PEG-supported molecules. This study (Tables 3 and 4) was easily performed on a parallel manual synthesizer.

With catalyst **4a**, for conditions 2 and 3, the catalytic activity dropped dramatically after the first cycle. These results can be correlated to the ^{1}H NMR analysis of the mixture of PEG-supported compounds obtained after the reaction. Indeed after two cycles only 12% of the ruthenium methylidene had rebound on the ligand. The other components of the mixture were the free vinyl ligand **9** and supported salicylaldehyde **8**.

In the case of **4b**, in sharp contrast, the recovery was more efficient (27% at the fifth cycle), and a high catalytic activity was retained even after five cycles.

3.2. Discussion. The result obtained with catalyst **3** was rather striking compared to the data in the literature concerning this type of supported catalyst on an insoluble polymer. In many cases, the conclusion that a catalyst reacted back on a vinyl ligand and that it can be used again is drawn from the fact that subsequent runs with the same supported catalyst can be performed with some catalytic activity. Indeed literature results in the solid phase supported boomerang precatalysts tend to conclude in the absence of structural information that the catalyst can be recycled,[32−35,37] that additives such as 1-hexene improve the recycling by increasing the lifetime of the methylidene species, and that a consequence of the recycling, leaching of ruthenium in solution, is dramatically reduced.[32,33] One may hypothesize that in the case of an insoluble polymer the catalytic activity found in subsequent runs may arise from metal carbenes borne by less accessible sites, which can be released in solution in a second or third run. In some cases the use of additives such as 1-hexene is claimed to increase the lifetime of the methylidene complex, which can then hook back onto the polymer. These additives could also help the release of the less accessible methylidene-Ru sites from the polymer to the solution, which would translate to further catalytic activity. One has to note also that usually for insoluble catalysts a ligand excess is used which could drive the reaction to the recovery of some carbenes. Finally one explanation for the decrease of leaching of Ru in the reaction medium at the end of the reaction could be that it is more an adsorption phenomenon on the polymer rather than a true recycling.

In sharp contrast, **4b** exhibited a high activity after four runs, in agreement with the recovery of the metal carbene species on the polymer. The competing pathway with the reaction of the metal carbene species with the supported ligand is the decomposition of the carbene. As it has already been pointed out,[11−18] this decomposition was inferior with a N-heterocyclic carbene ruthenium complex (**4b**) than with a phosphine complex (**4a**).

Compound **8** originates probably from the oxidation of the metal-carbene species from the presence of oxygen in the reaction mixture.[57,64] Starting from a thoroughly degassed medium did not reduce the oxidation process. Most likely the oxophilicity of the PEG concurs in retaining the oxygen on the polymer backbone.

For the sake of comparison catalyst **5b** was tested on the cyclization of tosyl diallylamine (conditions 1), and the expected product was synthesized in high yield. ^{1}H NMR analysis of the crude mixture revealed that **5b** was not recycled. Nevertheless no oxidation product was present. This confirms that the oxidation of the ligand occurred with the presence of the polymer independently from the reaction conditions. If the reactivity of **5b** and **4b** was similar at least in reaction conditions 1, it seems that in **4b** the presence of the bidentate complexation of the polymer-supported phenol provided further stability to the catalyst for better recovery. After cyclization, reaction with the methylidene complex rather than decomposition occurred. In this case and contrary to the results we observed previously,[58] the chelating effect of PEG did not inhibit the RCM but rather provided additional stability to **4b**.

4. Application to the Synthesis of Cyclic Ami-

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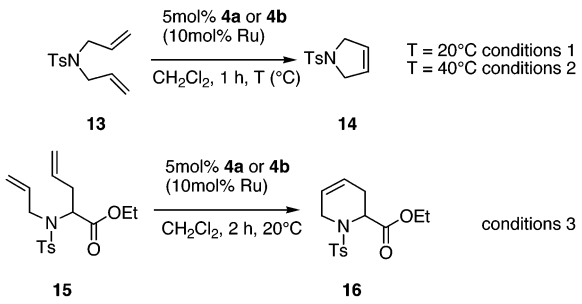
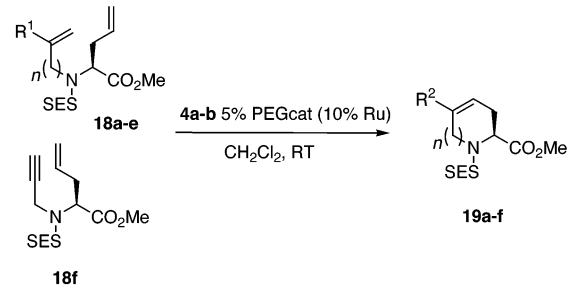
Scheme 3. Test Reactions for Recycling



Scheme 4. Synthesis of Cyclic α-Aminoesters



Scheme 5. Synthesis of Carboxy Pyrroline 21

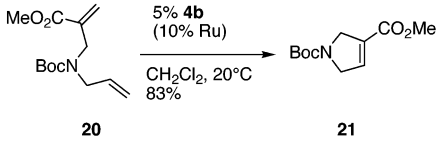


Table 5. Ring-Closing Metathesis of α-Aminoesters by Supported Catalysts

entry	R^1	**18**	*n*	R^2	yield of **19** (%)
1	H	**a**	1	H	91
2	H	**b**	2	H	95
3	H	**c**	3	H	93
4	CH_3	**d**	1	CH_3	87
5[a]	CO_2Me	**e**	1	CO_2Me	86
6		**f**	1	$CH{=}CH_2$	89

[a] Catalyst **4b** was used.

noesters. Having in hand the catalysts **4a** and **4b**, they were used in the parallel synthesis of various cyclic aminoesters. For the α-amino esters, the diversity arose from the alkylation step of a *N*-SES-protected allyl glycine with different alkylating agents in the presence of K_2CO_3 to yield several diene systems **18a**−**f**. The reactions were performed in parallel on a manual synthesizer by reaction of the substrate in CH_2Cl_2 in the presence of 5 mol % of **4a** or **4b** (Scheme 4).

After completion, the reaction mixture was transferred to ether for precipitation followed by filtration. The filtrate was evaporated, and column chromatography (to remove the small amount of Ru that had leached in the vessel) provided the cyclic products **19a**−**f** in excellent yields (Table 5).

Five, six, and seven-membered rings could be obtained in good yield (entries 1−3). A substituted six-membered ring could be formed either by diene (entries 4, 5) or enyne ring-closing metathesis (entry 6). Remarkably, catalyst **4b** was active enough to ensure cyclization of a substrate containing substituted electron-poor olefins[65−67] such as **20**. This method provided an original access to the carboxy pyrroline **21** (Scheme 5).

Conclusion

A novel efficient boomerang catalyst supported on a soluble polymer was synthesized and characterized. The analysis possibilities inherent to the presence of a soluble polymer provided information on the recycling capacities of the catalyst: while the activity remained high, the return of the metal on the supported ligand was not total. Ring-closing metathesis, including the cyclization of electron-deficient olefins, provided an efficient access to cyclic amino esters.

Experimental Section

General Remarks. All reagents including poly(ethylene glycol) 3400 were obtained from Aldrich Chemical Co. and used without purification. ^1H and ^{13}C NMR analyses were performed respectively with 200 and 400 MHz NMR spectrometers. Infrared spectra were recorded by diffuse reflectance or by transmittance as a microcup of KBr or by transmittance in KBr salt plates. Mass spectra (electrospray ionization mode, ESIMS) were recorded on a Platform II (Micromass, Manchester, U.K.) quadrupole mass spectrometer fitted with an electrospray interface. We report the mass spectrometry for bifunctional PEG 3400. The mass spectrometer was calibrated in the positive- and negative-ion ESI mode. The samples were dissolved in H_2O/CH_3CN (50/50 v/v). Multiprotonated and multicationized ions were recovered in the positive and negative mode. PEG 3400 supported molecules appeared as distributions corresponding to charge states ranging from +2 to +5, and oligomers between $n = 74$ and $n = 88$ were detected. Only two significant peaks were reported, and we used the increment of mass between the product and the PEG 3400 to confirm the spectrum. Correlations between the calculated and measured values were observed in both of the states considered. MALDI-TOF mass spectra were recorded on a Voyager DE-STR (Applied Biosystems) spectrometer equipped with electrostatic reflector and delayed extraction devices. α-Cyanohydroxycinnamic acid was used as matrix. The compound under study and the matrix were dissolved in water/acetonitrile (1:1) at a concentration of 10 mg/mL. Five microliters of each solution was mixed, and ions were generated by laser desorption at 337 nm. Recycling test reactions and parallel RCM of aminoesters were performed on an Argonaut Technologies Quest 210 manual synthesizer.

Di[$RuCl_2(PCy_3)$(=CHPh-*p*-O)]-PEG (3). $RuCl_2(PCy_3)_2$=CHPh **1a** (0.091 g, 0.111 mmol) was added to a solution of **7** (0.1 g, 0.028 mmol) in 10 mL of anhydrous CH_2Cl_2. The mixture was stirred at room temperature for 16 h, then precipitated twice in ether to yield 0.13 g (92%) of the title compound as a gray powder: ^1H NMR (CD_2Cl_2, Me_4Si) δ 1.10−2.00 (m, 120 H), 2.60 (sl, 12 H), 3.50−3.70 (sl, ∼310 H), 4.20 (m, 4 H), 6.85 (d, $J = 8.5$ Hz, 4 H), 8.45 (d, $J = 8.5$ Hz, 4 H), 19.50 (s, 2 H); ^{31}P NMR (CD_2Cl_2, Me_4Si) δ 36.63; ^{13}C NMR (CD_2Cl_2, Me_4Si) δ 26.94, 28.23 (t, $J_{CP} = 18.5$ Hz), 29.99, 32.37 (t, $J_{CP} = 36.0$ Hz), 61.94, 68.02, 69.83, 70.89, 72.92, 114.45, 134.22, 148.27, 159.62, 280.79.

Di[$RuCl_2(PCy_3)$(=CHPh-*o*-O)]-PEG (4a). $RuCl_2(PCy_3)_2$=CHPh **1a** (0.1 g, 0.122 mmol) was added at room temperature to a solution of **9** (0.1 g, 0.028 mmol) in 10 mL of CH_2Cl_2. The reaction was stirred at 20 °C for 48 h. The product was

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precipitated twice in ether to yield 0.120 g (95%) of the title compound as a gray powder: IR cm^{-1} 3054 (s), 2306 (w), 1265 (s), 1101 (s); ^1H NMR (CD_2Cl_2, Me_4Si) δ 1.20−2.45 (m, 60 H), 3.55−3.75 (sl, ∼310 H), 4.25 (t, $J_1 = 4.5$ Hz, 4 H), 4.75 (t, $J_1 = 4.5$ Hz, 4 H), 7.20 (t, $J_2 = 8.0$ Hz, 2 H), 7.35 (d, $J_3 = 8.5$ Hz, 2 H), 7.65−7.75 (m, 4 H), 17.40 (d, $J_4 = 4.5$ Hz, 2 H); ^{31}P NMR (CD_2Cl_2, Me_4Si) δ 60.95. ^{13}C NMR (CD_2Cl_2, Me_4Si) δ 26.66, 28.08, 28.19, 30.33, 35.77, 36.02, 69.98, 70.10, 70.96, 71.13, 113.56, 122.72, 123.85, 130.15, 143.84, 154.85, 278.35; MS (Maldi) m/z $n = 64$, 3938.3 (1 Na^+).

Di[$RuCl_2$(H_2IMes)(=CH-*o*-O)]PEG (4b). $RuCl_2PCy_3H_2$-IMes=CHPh **1b** (0.155 g, 0.183 mmol) was added to a solution of **9** (0.300 g, 0.083 mmol) in 30 mL of CH_2Cl_2. The reaction was stirred at 40 °C for 48 h. The residue was precipitated twice in ether to yield 0.354 g (94%) of the title compound as a green powder: IR cm^{-1} 3054 (m), 2306 (w), 1687 (m), 1348 (m), 1104 (s); ^1H NMR (CD_2Cl_2, Me_4Si) δ 2.50 (s, 12 H), 2.50 (s, 24 H), 3.55−3.75 (sl, ∼310 H), 4.20 (s, 8 H), 4.30 (t, $J_1 = 6.0$ Hz, 4 H), 6.95−7.05 (m, 6 H), 7.10 (s, 8 H), 7.55−7.65 (m, 2 H), 16.50 (s, 2 H); ^{13}C NMR (CD_2Cl_2, Me_4Si) δ 20.56, 22.41, 52.87, 69.06, 69.79, 71.79, 113.99, 123.48, 124.58, 127.72, 129.83, 130.73, 131.00, 140.00, 145.68, 154.53, 211.93, 292.95; MS (Maldi) m/z $n = 62$, 4052.2 (1 K^+).

$RuCl_2$(=CH-*o*-OMDEG)PCy_3 (5a). CuCl (0.010 g, 0.097 mmol) was added at room temperature to a solution of $RuCl_2$-(=CHPh)$(PCy_3)_2$ **1a** (0.08 g, 0.097 mmol) in 2 mL of CH_2Cl_2. The reaction was stirred for 15 min, then **11** (0.022 g, 0.097 mmol) was added. The mixture was stirred at 20 °C for 3 h. The solvent was evaporated and the residue was purified by chromatography [eluent: hexane/EtOAc, 9:1] to yield 0.047 g (72%) of the title compound along with 10% of compound **11**: ^1H NMR (CD_2Cl_2, Me_4Si) δ 1.25−2.45 (m, 33 H), 3.40 (s, 3 H), 3.55−3.65 (m, 2 H), 3.75−3.80 (m, 2 H), 4.25 (t, $J_1 = 4.5$ Hz, 2 H), 4.75 (t, $J_1 = 4.5$ Hz, 2 H), 7.15−7.35 (m, 2 H), 7.65−7.75 (m, 2 H), 17.35 (d, $J_2 = 5.0$ Hz, 1 H); ^{31}P NMR (CD_2Cl_2, Me_4Si) δ 60.86; ^{13}C NMR (CD_2Cl_2, Me_4Si) δ 26.72, 28.09, 28.19, 30.28, 35.74, 35.99, 59.08, 69.75, 69.80, 71.83, 72.46, 113.48, 122.65, 123.88, 130.44, 144.12, 155.03, 278.48.

$RuCl_2$(=CH-*o*-OMDEG)H_2IMes (5b). CuCl (0.009 g, 0.094 mmol) was added at room temperature to a solution of $RuCl_2$-(=CHPh)(PCy_3)(H_2IMes) **1b** (0.080 g, 0.094 mmol) in 2 mL of CH_2Cl_2. The reaction was stirred for 15 min, then **11** (0.021 g, 0.094 mmol) was added. The mixture was stirred at 20 °C for 3 h. The solvent was evaporated under vacuo, and the residue was purified by chromatography [eluent: hexane/EtOAc, 9:1] to yield 0.053 g (83%) of the title compound as a green solid: IR cm^{-1} 3040 (s), 2917 (s), 1589 (m), 1263 (s), 1108 (m); ^1H NMR (CD_2Cl_2, Me_4Si) δ 2.45 (s, 6 H), 2.50 (s, 12 H), 3.35 (s, 3 H), 3.35−3.50 (m, 4 H), 3.60 (t, $J_1 = 6.0$ Hz, 2 H), 4.15 (s, 4 H), 4.30 (t, $J_1 = 6.0$ Hz, 2 H), 6.95−7.05 (m, 3 H), 7.10 (s, 4 H), 7.55−7.65 (m, 1 H), 16.50 (s, 1 H); ^{13}C NMR (CD_2Cl_2, Me_4-Si) δ 19.45, 21.28, 52.06, 58.99, 68.22, 69.06, 70.79, 72.11, 113.27, 122.25, 123.84, 129.34, 129.82, 130.02, 138.98, 139.25, 144.83, 153.48, 210.55, 292.98; HRMS calculated for $C_{33}H_{42}O_3N_2$-Cl_2Ru 686.1619, found 686.1631.

Poly(ethylene glycol)-3400 Di(methanesulfonate) (6). Trifluoromethanesulfonyl chloride (4.0 g, 35.0 mmol) was added dropwise at −20 °C to a solution of PEG-OH (10.0 g, 2.94 mmol) and trioctylamine (12.4 g, 35.0 mmol) in 40 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature overnight. The product was precipitated in ether, then filtered and dried in vacuo to yield 10.3 g (98%) of the title compound: IR 2871 (s), 1968 (m), 1466 (s), 1114 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 3.10 (s, 6 H), 3.55−3.70 (sl, ∼310 H), 3.70−3.75 (m, 4 H), 4.35−4.40 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 38.09, 69.37, 69.72, 70.92; MS (electrospray) m/z $n = 72$: 1673.5 (2 +, 2 H^+), $n = 78$: 1211.6 (3 +, 2 H^+/Na^+).

Poly(ethylene glycol)-3400 Di(*p*-vinylbenzene) (7). A solution of 4-vinylphenol (0.1 g, 0.83 mmol) in 4 mL of THF was added to a solution of PEG-OMs (1.18 g, 0.33 mmol) and Cs_2CO_3 (0.54 g, 1.66 mmol) in 8 mL of THF. The mixture was refluxed for overnight. The solvent was evaporated in vacuo, and the residue was dissolved in CH_2Cl_2, then filtered on Celite, precipitated twice in ether, filtered, and dried under vacuo to yield 1.02 g (85%) of the title compound: IR cm^{-1} 3054 (s), 2306 (w), 1607 (w), 1510 (m), 1110 (s); ^1H NMR ($CDCl_3$, Me_4Si) δ 3.55−3.75 (sl, ∼310 H), 3.85 (t, $J_1 = 4.5$ Hz, 4 H), 4.15 (t, $J_1 = 4.5$ Hz, 4 H), 5.15 (dd, $J_2 = 1.0$ Hz, $J_3 = 11.0$ Hz, 2 H), 5.60 (dd, $J_2 = 1.0$ Hz, $J_4 = 17.5$ Hz, 2 H), 6.65 (dd, $J_3 = 11.0$ Hz, $J_4 = 17.5$ Hz, 2 H), 6.90 (d, $J_5 = 7.0$ Hz, 4 H), 7.35 (d, $J_5 = 7.0$ Hz, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 67.82, 70.09, 70.93, 71.20, 112.00, 114.88, 127.90, 130.92, 137.57, 158.94; MS (electrospray) m/z $n = 80$, 1873.6 (2 +, 2 H^+); $n = 92$, 1425.4 (3 +, 3 H^+).

Poly(ethylene glycol)-3400 Di(benzaldehyde) (8). A solution of salicylaldehyde (0.43 g, 3.52 mmol) in 10 mL of THF was added to a solution of PEGOMs (5.0 g, 1.40 mmol) and Cs_2CO_3 (2.3 g, 7.03 mmol) in 40 mL of THF. The reaction was refluxed overnight. The solvent was evaporated under vacuo, and the residue was dissolved in CH_2Cl_2, then filtered on Celite. The solution was precipitated in ether and in *i*-PrOH, filtered, and dried under vacuo to yield 4.0 g (80%) of the title compound: IR cm^{-1} 3055 (s), 2306 (w), 1687 (s), 1599 (s), 1114 (s); ^1H NMR ($CDCl_3$, Me_4Si) δ 3.55−3.75 (sl, ∼310 H), 3.90 (t, $J_1 = 4.5$ Hz, 4 H), 4.25 (t, $J_1 = 4.5$ Hz, 4 H), 6.95−7.05 (m, 4 H), 7.45−7.60 (m, 2 H), 7.80 (dd, $J_2 = 2.0$ Hz, $J_3 = 7.5$ Hz, 2 H), 10.50 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 68.63, 69.89, 70.93, 71.34, 113.25, 121.33, 125.46, 128.59, 136.27, 161.62, 190.14; MS (electrospray) m/z $n = 79$, 1853.4 (2 +, 2 H^+); $n = 87$, 1353.5 (3 +, 3 H^+).

Poly(ethylene glycol)-3400 Di(vinylbenzene) (9). Sodium hydride (0.106 g, 4.43 mmol) was added at 0 °C to a solution of triphenylmethylphosphonium bromide (0.793 g, 2.22 mmol) in 10 mL of THF. The reaction was stirred at 0 °C for 1 h, then a solution of **8** (2.0 g, 0.554 mmol) in 10 mL of THF was added dropwise at 0 °C. The mixture was stirred overnight from 0 °C to room temperature. THF was evaporated, then the residue was dissolved in CH_2Cl_2, filtered, and precipitated three times in ether. The product was filtered and dried to yield 1.36 g (70%) of the title compound: IR cm^{-1} 3539 (m), 2310 (w), 1692 (m), 1453 (s), 1104 (s); ^1H NMR ($CDCl_3$, Me_4Si) δ 3.55−3.80 (sl, ∼310 H), 3.85−3.95 (m, 4 H), 4.15 (t, $J_1 = 4.5$ Hz, 4 H), 5.25 (dd, $J_2 = 1.5$ Hz, $J_3 = 11.0$ Hz, 2 H), 5.75 (dd, $J_2 = 1.5$ Hz, $J_4 = 17.5$ Hz, 2 H), 6.85−7.25 (m, 8 H), 7.50 (dd, $J_5 = 1.5$ Hz, $J_6 = 7.5$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 68.37, 70.13, 71.01, 71.27, 112.69, 114.71, 121.30, 126.85, 127.36, 129.17, 132.06, 156.34; MS (electrospray) m/z $n = 75$, 1765.5 (2 +, 2 H^+); $n = 79$, 1241.8 (3 +, 2 H^+/Na^+).

2-[2-(2-Methoxyethoxy)ethoxy]benzaldehyde (10). Methoxyethoxyethane bromide (1.22 g, 6.644 mmol) was added to a heterogeneous mixture of salicylaldehyde (0.9 g, 7.38 mmol) and Cs_2CO_3 (3.6 g, 11.04 mmol) in 40 mL of THF. The reaction was refluxed for 24 h, then the solvent was evaporated. The residue was dissolved in 10 mL of EtOAc, and the solid was filtered. The filtrate was purified by chromatography [eluant: hexane/EtOAc, 7:3] to yield 1.34 g (90%) of the title compound as a colorless oil: IR cm^{-1} 2877 (s), 1732 (s), 1686 (s), 1599 (s), 1484 (s); ^1H NMR ($CDCl_3$, Me_4Si) δ 3.40 (s, 3 H), 3.55−3.60 (m, 2 H), 3.70−3.80 (m, 2 H), 3.95 (t, $J_1 = 4.5$ Hz, 2 H), 4.25 (t, $J_2 = 4.5$ Hz, 2 H), 6.95−7.10 (m, 2 H), 7.50−7.60 (m, 1 H), 7.80−7.90 (m, 1 H), 10.55 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 59.51, 68.62, 69.96, 71.33, 72.36, 113.21, 121.37, 125.48, 128.67, 136.31, 161.64, 190.27; MS (electrospray) m/z 225 (M + $H)^+$.

1-[2-(2-Methoxyethoxy)ethoxy]-2-vinylbenzene (11). Sodium hydride (0.064 g, 2.67 mmol) was added to a solution of $Ph_3CH_3P^+$, Br^- (0.48 g, 1.34 mmol) in THF at 0 °C for 1 h. A solution of **10** (0.20 g, 0.89 mmol) in 10 mL of THF was added dropwise at 0 °C. The reaction was stirred at 0 °C for 3 h, then at room temperature overnight. THF was evaporated and the residue was purified by chromatography [eluent: hexane/EtOAc, 7:3] to yield 0.16 g (88%) of the title compound: IR cm^{-1}

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2922 (s), 2877 (s), 1601 (m), 1488 (s), 1109 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.45 (s, 3 H), 3.55−3.65 (m, 2 H), 3.70−3.80 (m, 2 H), 3.90 (t, J_1 = 4.5 Hz, 2 H), 4.20 (t, J_1 = 4.5 Hz, 2H), 5.25 (dd, J_2 = 1.5 Hz, J_3 = 11.0 Hz, 1 H), 5.80 (dd, J_2 = 1.5 Hz, J_4 = 18.0 Hz, 1 H), 6.85−7.30 (m, 3 H), 7.30 (dd, J_5 = 1.5 Hz, J_6 = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 59.51, 68.40, 69.98, 71.23, 72.28, 112.72, 114.75, 121.36, 126.91, 127.45, 129.20, 132.11, 156.36; MS (electrospray) *m*/*z* 223 $(M + H)^+$.

***N,N*-Diallyl 4-Methylbenzenesulfonamide (13).**[68] Triethylamine (1.09 g, 10.68 mmol) and tosyl chloride (2.0 g, 10.48 mmol) were added to a solution of diallylamine (1.0 g, 10.29 mmol) in 35 mL of CH_2Cl_2. The mixture was stirred at 20 °C for 1 night. The organic phase was washed twice by an 10% aqueous solution of $KHSO_4$ (30 mL) and twice by a saturated aqueous solution of $NaHCO_3$ (30 mL), then by water (30 mL). The organic phase was dried on $MgSO_4$ and the solvent was evaporated to yield 2.45 g (95%) of the title compound: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.45 (s, 3 H), 3.85 (d, J_1 = 6.0 Hz, 4 H), 5.10−5.20 (m, 4 H), 5.50−5.75 (m, 2 H), 7.30 (d, J_2 = 8.5 Hz, 2 H), 7.70 (d, J_2 = 8.5 Hz, 2 H); MS (electrospray) *m*/*z* 252 $(M + H)^+$.

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (14).[68] With Supported Catalyst 3. Supported catalyst **3** (0.018 g, 0.0035 mmol) was added to a solution of *N*-tosyldiallylamine (0.018 g, 0.070 mmol) in 5 mL of CH_2Cl_2. The mixture was stirred at 20 °C for 15 min. The PEG was precipitated in ether, filtered, and analyzed by ^{1}H NMR. The filtrate was evporated to yield 0.012 g (77%) of the title compound after purification on silica gel [eluent: hexane/EtOAc, 7:3].

(b) With Catalyst 5b. Catalyst **5b** (3.0 mg, 4.0 μmol) was added to a solution of *N*-tosyldiallylamine (0.020 g, 0.080 mmol) in 6 mL of CH_2Cl_2. The mixture was stirred at 20 °C for 1 h. The residue was checked by NMR and purified by chromatography.

(c) Recycling Conditions 1. Catalyst **4a** or **4b** (5 mol %, 10% mol Ru) was added to a solution of *N*-tosyldiallylamine (0.01 g, 0.04 mmol) in 2 mL of CH_2Cl_2. The mixture was stirred at 20 °C for 2 h. The PEG was precpitated in ether, filtered, and analyzed by NMR. The filtrate was evaporated and analyzed by HPLC and by NMR.

(d) Recycling Conditions 2. Catalyst **4a** or **4b** (5 mol %, 10% mol Ru) was added to a solution of *N*-tosyldiallylamine (0.010 g, 0.040 mmol) in 2 mL of CH_2Cl_2. The mixture was stirred at 40 °C for 1 h. The PEG was precipitated in ether, filtered, and anayzed by NMR. The filtrate was evaporated and analyzed by HPLC and by NMR: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.45 (s, 3 H), 4.10 (s, 4 H), 5.65 (s, 2 H), 7.30 (d, J_1 = 8.5 Hz, 2 H), 7.75 (d, J_1 = 8.5 Hz, 2H); MS (electrospray) *m*/*z* 224 $(M + H)^+$.

Ethyl 2-[Allyl(toluene-4-sulfonyl)amino]pent-4-enoate (15). Allyl bromide (0.300 g, 2.48 mmol) was added to a heterogeneous mixture of methyl bromomethylacrylate (0.460 g, 1.55 mmol) and K_2CO_3 (1.15 g, 8.37 mmol) in 10 mL of DMF. The reaction was stirred at room temperature overnight, then 10 mL of EtOAc and 10 mL of H_2O were added. The aqueous phase was washed twice with EtOAc. Organic phases were washed three times with H_2O, dried over $MgSO_4$, and concentrated to yield 0.480 g (92%) of the title compound: IR cm^{-1} 3080 (m), 2982 (s), 1732 (s), 1643 (m), 1598 (m); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.15 (t, J_1 = 7.0 Hz, 3 H), 2.45 (s, 3H), 2.45−2.80 (m, 2 H), 3.85−3.95 (m, 2 H), 4.00 (q, J_1 = 7.0 Hz, 2 H), 4.65 (dd, J_2 = 6.5 Hz, J_3 = 9.0 Hz, 1 H), 5.10−5.25 (m, 4 H), 5.65−5.95 (m, 2 H), 7.30 (d, J_4 = 8.5 Hz, 2 H), 7.75 (d, J_4 = 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.34, 21.94, 35.03, 48.63, 59.89, 61.59, 117.99, 118.83, 128.01, 129.79, 133.77, 135.55, 137.70, 143.74, 170.90; MS (electrospray) *m*/*z* 337 $(M + H)^+$.

Ethyl 1-(Toluene-4-sulfonyl)-1,2,3,6-tetrahydropyridine-2-carboxylate (16). Conditions 3. Catalyst **4a** or **4b** (5 mol %, 10% mol Ru) was added to a solution of **15** (0.034 g, 0.100 mmol) in 2 mL of CH_2Cl_2. The reaction was stirred at 20 °C for 2 h. The PEG was precipitated in ether, filtered, and analyzed by NMR. The filtrate was analyzed by HPLC and NMR: IR cm^{-1} 2984 (w), 2254 (m), 1736 (m), 1598 (w), 1164 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.10 (t, J_1 = 7.0 Hz, 3 H), 2.45 (s, 3 H), 2.60 (sl, 2 H), 3.80−4.20 (m, 4 H), 4.85 (t, J_2 = 4.0 Hz, 1 H), 5.70 (sl, 2 H), 7.30 (d, J_3 = 8.0 Hz, 2 H), 7.70 (d, J_3 = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.33, 21.95, 28.30, 42.59, 53.06, 61.04, 122.70, 123.82, 127.70, 129.87, 136.79, 143.72, 170.85; MS (electrospray) *m*/*z* 310 $(M + H)^+$.

2-Trimethylsilanylethanesulfonyle Chloride.[69] Phosphorus pentachloride (3.0 g, 14.39 mmol) was added slowly at 0 °C to a solution of sodium 2-trimethylsilyl ethanesulfonate (1.0 g, 4.90 mmol) in 6.5 mL of CCl_4. The reaction was stirred at room temperature for 1 h 30 min, then transferred in 6 mL of cold H_2O. The solution was extracted twice with 10 mL of CH_2Cl_2, and the organic phase was washed twice with 10 mL of a saturated solution of $NaHCO_3$. The organic phase was dried over $MgSO_4$ and filtered, and the solvent was evaporated to yield 0.590 g (60%) of the title compound: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.10 (s, 9 H), 1.30−1.40 (m, 2 H), 3.60−3.70 (m, 2 H).

Methyl 2-(2-(Trimethylsilanyl)ethanesulfonylamino)-pent-4-enoate (17). A solution of 2-(trimethylsilanyl)ethanesulfonyl chloride (0.600 g, 3.67 mmol) in 5 mL of DMF was added dropwise at 0 °C to a solution of 1-methoxycarbonylbut-3-enylammonium chloride (0.380 g, 2.30 mmol) and triethylamine (1.862 g, 18.4 mmol) in 15 mL of DMF. The reaction was stirred at 0 °C for 8 h. Then the solvent was evaporated and the residue was purified by chromatography [eluent: hexane/EtOAc, 7:3] to yield 0.360 g (59%) of the title compound: IR cm^{-1} 3055 (m), 2306 (w), 1744 (s), 1422 (m), 1265 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 1.00−1.15 (m, 2 H), 2.55 (t, J_1 = 6.5 Hz, 2 H), 2.90−3.00 (m, 2 H), 3.70 (s, 3 H), 4.15−4.30 (m, 1 H), 4.80(d, J_2 = 9.0 Hz, 1 H), 5.15−5.30 (m, 2 H), 5.60−5.85 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.59, 10.85, 38.27, 50.55, 53.10, 55.70, 120.54, 131.92, 172.57; HRMS calcd for $C_{11}H_{24}O_4NSiS$ 294.1195, found 294.1100.

General Procedure for the Alkylation of Amino Ester 17. The alkylating agent was added to a heterogeneous mixture of **17** and K_2CO_3 in 3 mL of DMF. The reaction was stirred at room temperature overnight, then 5 mL of EtOAc and 5 mL of H_2O were added. The aqueous phase was washed twice with EtOAc. Organic phases were washed three times with H_2O, dried over $MgSO_4$, and concentrated to yield the alkylated compounds **18a**−**f**.

Methyl 2-[Allyl-(2-(trimethylsilanyl)ethanesulfonyl)-amino]pent-4-enoate (18a). Allyl bromide (0.043, 0.350 mmol), **17** (0.058 g, 0.218 mmol), and K_2CO_3 (0.163 g, 1.182 mmol) were reacted to yield 0.065 g (89%) of the title compound: IR cm^{-1} 3054 (s), 2986 (m), 2305 (w), 1742 (m), 1421 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 1.00−1.10 (m, 2 H), 2.50−2.85 (m, 2 H), 2.95−3.05 (m, 2 H), 3.75 (s, 3 H), 3.90−4.00 (m, 2 H), 4.55 (dd, J_1 = 6.0 Hz, J_2 = 9.0 Hz, 1 H), 5.15−5.35 (m, 4 H), 5.70−6.00 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.57, 10.55, 34.98, 48.91, 50.47, 52.71, 60.09, 118.81, 118.96, 133.92, 135.24, 171.96; HRMS calcd for $C_{14}H_{28}O_4NSiS$ 334.1508, found 334.1509.

Methyl 2-[But-3-enyl-(2-(trimethylsilanyl)ethanesulfonyl)amino]pent-4-enoate (18b). 4-Bromo-1-butene (0.045 g, 0.323 mmol), **17** (0.055 g, 0.208 mmol), and K_2CO_3 (0.155 g, 1.12 mmol) were reacted to yield 0.061 g (85%) of the title compound: IR cm^{-1} 3055 (m), 2956 (m), 2306 (w), 1744 (s), 1265 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 1.00−1.15 (m, 2 H), 2.30−2.65 (m, 3 H), 2.70−3.10 (m, 3 H), 3.15−3.45 (m, 2

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H), 3.75 (s, 3 H), 4.50 (dd, J_1 = 6.5 Hz, J_2 = 9.0 Hz, 1 H), 5.05−5.25 (m, 4 H), 5.65−5.95 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4-Si) δ −1.56, 10.57, 35.60, 36.91, 46.09, 49.69, 52.76, 60.41, 117.55, 119.01, 133.79, 135.10, 171.92; HRMS calcd for $C_{15}H_{30}O_4$-NSiS 348.1665, found 348.1659.

Methyl 2-[Pent-4-enyl-(2-(trimethylsilanyl)ethanesulfonyl)amino]pent-4-enoate (18c). 5-Bromo-1-pentene (0.05 g, 0.33 mmol), **17** (0.055 g, 0.208 mmol), and K_2CO_3 (0.155 g, 1.121 mmol) were reacted to yield 0.068 g (91%) of the title compound: IR cm^{-1} 3056 (m), 2955 (m), 2306 (w), 1742 (s), 1266 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 1.00−1.15 (m, 2 H), 1.65−1.90 (m, 2 H), 2.00−2.15 (m, 2 H), 2.45−2.60 (m, 1 H), 2.70−2.85 (m, 1 H), 2.90−3.05 (m, 2 H), 3.10−3.40 (m, 2 H), 3.75 (s, 3 H), 4.50 (dd, J_1 = 6.5 Hz, J_2 = 9.0 Hz, 1 H), 4.95−5.30 (m, 4 H), 5.65−5.95 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4-Si) δ −1.56, 10.59, 30.14, 31.48, 35.26, 46.23, 49.65, 52.74, 60.34, 115.81, 118.94, 133.86, 137.75, 171.98; HRMS calcd for $C_{16}H_{32}O_4NSiS$ 362.1821, found 362.1825.

Methyl 2-[(2-Methylallyl)-(2-(trimethylsilanyl)ethanesulfonyl)amino]pent-4-enoate (18d). Methallyl bromide (0.040 g, 0.302 mmol), **17** (0.050 g, 0.170 mmol), and K_2CO_3 (0.127 g, 0.918 mmol) were reacted to yield 0.049 g (83%) of the title compound: IR cm^{-1} 3054 (s), 2986 (m), 2305 (m), 1742 (m), 1265 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 1.00−1.15 (m, 2 H), 1.80 (s, 3 H), 2.55−2.90 (m, 2 H), 2.95−3.05 (m, 2 H), 3.75 (s, 3 H), 3.85 (q, J_1 = 15.5 Hz, 2 H), 4.45 (t, J_2 = 7.5 Hz, 1 H), 5.00 (d, J_3 = 11.5 Hz, 2 H), 5.10−5.25 (m, 2 H), 5.70−5.95 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.56, 10.53, 20.72, 35.38, 50.10, 52.61, 52.96, 60.56, 115.04, 118.78, 134.27, 141.92, 171.58; HRMS calcd for $C_{15}H_{30}O_4NSiS$ 348.1665, found 348.1650.

Methyl 2-[(2-(Methoxycarbonyl)allyl)-(2-(trimethylsilanyl)ethanesulfonyl)amino]pent-4-enoate (18e). Methyl 2-bromomethylacrylate (0.060 g, 0.33 mmol), **17** (0.055 g, 0.21 mmol), and K_2CO_3 (0.155 g, 1.12 mmol) to yield 0.068 g (83%) of the title compound: IR cm^{-1} 3055 (w), 2954 (m), 2306 (w), 1741 (s), 1724 (s), 1266 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 1.00−1.15 (m, 2 H), 2.45−2.85 (m, 2 H), 2.95−3.10 (m, 2 H), 3.75 (s, 3 H), 3.80 (s, 3 H), 4.20 (d, J_1 = 6.0 Hz, 2 H), 4.50 (dd, J_2 = 6.5 Hz, J_3 = 8.5 Hz, 1 H), 5.10−5.25 (m, 2 H), 5.60−5.75 (m, 1 H), 6.05 (s, 1 H), 6.50 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.56, 10.45, 34.96, 46.97, 50.01, 52.44, 52.72, 60.46, 118.93, 129.10, 133.87, 136.88, 166.80, 171.65; HRMS calcd for $C_{16}H_{30}O_6NSiS$ 392.1563, found 392.1565.

Methyl 2-[Prop-2-ynyl-(2-(trimethylsilanyl)ethanesulfonyl)amino]pent-4-enoate (18f). Propargyl bromide (0.035 g, 0.302 mmol), **17** (0.060 g, 0.205 mmol), and K_2CO_3 (0.153 g, 1.106 mmol) were reacted to yield 0.058 g (86%) of the title compound: IR cm^{-1} 3054 (s), 2986 (m), 2306 (w), 1743 (s), 1265 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 1.05−1.15 (m, 2 H), 2.30 (t, J_1 = 2.5 Hz, 1 H), 2.55−2.90 (m, 2 H), 3.60−3.70 (m, 2 H), 3.70 (s, 3 H), 4.20 (q, J_1 = 2.5 Hz, 2 H), 4.55 (dd, J_2 = 6.5 Hz, J_3 = 9.0 Hz, 1 H), 5.15−5.30 (m, 2 H), 5.75−5.95 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.55, 10.38, 34.35, 34.54, 50.85, 52.71, 59.61, 73.18, 79.67, 119.30, 133.49, 171.38; HRMS calcd for $C_{14}H_{26}O_4NSiS$ 332.1352, found 332.1358.

General Procedure for Ring-Closing Metathesis of Aminoesters 18a−f. The supported catalyst **4a** or **4b** was added to a solution of **18a−f** in 5 mL of CH_2Cl_2. The reaction was stirred at 20 °C for 8 h. PEG was precipitated in ether and filtered. The filtrate was evaporated to yield the cyclic compounds **19a−f** after purification by chromatography [eluent: hexane/EtOAc, 7:3].

Methyl 1-(2-(Trimethylsilanyl)ethanesulfonyl)-1,2,3,6-tetrahydropyridine-2-carboxylate (19a). 4a (0.037 g, 0.008 mmol) and **18a** (0.050 g, 0.160 mmol) were reacted to yield 0.044 g (91%) of the title compound: IR cm^{-1} 3055 (m), 2956 (m), 2306 (w), 1743 (s), 1265 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 1.05−1.15 (m, 2 H), 2.65 (sl, 2 H), 2.95−3.10 (m, 2 H), 3.75 (s, 3 H), 3.95−4.15 (m, 2 H), 4.80 (dd, J_1 = 3.0 Hz, J_2 = 5.5 Hz, 1 H), 5.65−5.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4-Si) δ −1.56, 10.52, 28.31, 42.84, 48.73, 52.92, 53.54, 123.15, 123.98, 171.98; HRMS calcd for $C_{12}H_{24}O_4NSiS$ 306.1195, found 306.1193.

Methyl 1-(2-(Trimethylsilanyl)ethanesulfonyl)-2,3,6,7-tetrahydro-1*H*-azepine-2-carboxylate (19b). 4a (0.032 g, 0.007 mmol) and **18b** (0.050 g, 0.144 mmol) were reacted to yield 0.044 g (95%) of the title compound: IR cm^{-1} 3058 (w), 3030 (w), 2954 (s), 1744 (s), 1438 (m); ^{1}H NMR ($CDCl_3$, Me_4-Si) δ 0.05 (s, 9 H), 1.05−1.15 (m, 2 H), 2.30−2.95 (m, 4 H), 2.95−3.05 (m, 2 H), 3.35−3.50 (m, 1 H), 3.70 (s, 3 H), 3.70−3.85 (m, 1 H), 4.85 (dd, J_1 = 4.0 Hz, J_2 = 7.0 Hz, 1 H), 5.65−5.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.56, 10.59, 30.82, 31.54, 44.32, 49.52, 52.73, 59.13, 126.71, 132.42, 172.29; HRMS calcd for $C_{19}H_{26}O_4NSiS$ 320.1352, found 332.1353.

Methyl 1-(2-(Trimethylsilanyl)ethanesulfonyl)-1,2,3,-6,7,8-hexahydroazocine-2-carboxylate (18c). 4a (0.031 g, 0.007 mmol) and **18c** (0.050 g, 0.139 mmol) were reacted to yield 0.043 g (93%) of the title compound: IR cm^{-1} 3055 (m), 2955 (m), 2306 (w), 1741 (s), 1328 (s); ^{1}H NMR ($CDCl_3$, Me_4-Si) δ 0.05 (s, 9 H), 1.05−1.15 (m, 2 H), 1.40−1.60 (m, 1 H), 1.95−2.45 (m, 3 H), 2.60−2.70 (m, 2 H), 2.80−3.10 (m, 3 H), 3.65−3.80 (m, 1 H), 3.80 (s, 3 H), 4.65 (dd, J_1 = 5.0 Hz, J_2 = 7.5 Hz, 1 H), 5.70−6.00 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.56, 10.62, 24.76, 29.98, 30.59, 46.62, 48.51, 52.80, 60.83, 126.40, 134.17, 172.33; HRMS calcd for $C_{14}H_{28}O_4NSiS$ 334.1508, found 334.1508.

Methyl 5-Methyl-1-(2-(trimethylsilanyl)ethanesulfonyl)-1,2,3,6-tetrahydropyridine-2-carboxylate (19d). 4a (0.032 g, 0.007 mmol) and **18d** (0.050 g, 0.144 mmol) were reacted to yield 0.040 g (87%) of the title compound: IR cm^{-1} 3057 (w), 2954 (s), 1744 (s), 1439 (m), 1332 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 1.05−1.15 (m, 2 H), 1.70 (s, 3 H), 2.60 (sl, 2 H), 2.95−3.10 (m, 2 H), 3.75 (s, 3 H), 3.75−4.00 (m, 2 H), 4.75 (dd, J = 3.5 Hz, J = 5.0 Hz, 1 H), 5.50 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.55, 10.51, 20.85, 28.21, 46.18, 48.70, 52.86, 53.34, 117.56, 131.15, 172.17; HRMS calcd for $C_{13}H_{26}O_4$-NSiS 320.1352, found 320.1369.

Dimethyl 1-(2-(Trimethylsilanyl)ethanesulfonyl)-1,2,3,6-tetrahydropyridine-2,5-dicarboxylate (19e). 4b (0.059 g, 0.013 mmol) and **18e** (0.100 g, 0.260 mmol) were reacted to yield 0.084 g (89%) of the title compound: IR cm^{-1} 3058 (m), 2955 (s), 1743 (s), 1719 (s), 1438 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 1.05−1.15 (s, 2 H), 2.65−3.10 (m, 4 H), 3.70 (s, 3 H), 3.75 (s, 3 H), 4.00−4.10 (m, 1 H), 4.40 (d, J_1 = 17.0 Hz, 1 H), 4.85 (dd, J_2 = 1.5 Hz, J_3 = 6.5 Hz, 1 H), 7.00−7.10 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.56, 10.47, 28.64, 41.73, 49.09, 52.34, 52.65, 53.13, 126.47, 127.60, 135.46, 165.33, 171.19; HRMS calcd for $C_{14}H_{26}O_6NSiS$ 364.1250, found 364.1259.

Methyl 1-(2-(Trimethylsilanyl)ethanesulfonyl)-5-vinyl-1,2,3,6-tetrahydropyridine-2-carboxylate (19f). 4a (0.037 g, 0.008 mmol) and **18f** (0.050 g, 0.164 mmol) were used to yield 0.046 g (86%) of the title compound: IR cm^{-1} 3057 (w), 2954 (m), 2306 (w), 1742 (s), 1335 (s); ^{1}H NMR ($CDCl_3$, Me_4-Si) δ 0.05 (s, 9 H), 1.05−1.15 (m, 2 H), 2.75 (sl, 2 H), 3.00−3.10 (m, 2 H), 3.75 (s, 3 H), 4.05 (d, J_1 = 16.0 Hz, 1 H), 4.30 (d, J_1 = 16.0 Hz, 1 H), 4.80 (q, J_2 = 3.0 Hz, 1 H), 5.00−5.15 (m, 2 H), 5.80 (s, 1 H), 6.30 (dd, J_3 = 11.0 Hz, J_4 = 18.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.54, 10.51, 28.56, 42.05, 48.87, 52.98, 53.55, 112.52, 144.31, 133.02, 136.42, 171.80; HRMS calcd for $C_{14}H_{26}O_4NSiS$ 332.1352, found 332.1333.

***tert*-Butyl Allylcarbamoate.** Triethylamine (2.90 g, 29.4 mmol) and *tert*-butyloxycarbonyl anhydride (5.8 g, 26.7 mmol) were added at 0 °C to a solution of allylamine (1.52 g, 26.7 mmol) in 20 mL of CH_2Cl_2. The reaction was stirred at 20 °C for 8 h. The mixture was washed twice with 20 mL of an aqueous solution of 1 N HCl. The organic phase was dried over $MgSO_4$, and the solvent was evaporated to yield 4.0 g (95%) of the title compound: IR cm^{-1} 3448 (w), 2979 (m), 1707 (s), 1507 (s), 1371 (m); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.40 (s, 9 H),

3.70 (s, 2 H), 4.65 (sl, 1 H), 5.05−5.25 (m, 2 H), 5.70−5.95 (m, 1 H); MS (electrospray) *m*/*z* 158 $(M + H)^+$.

Methyl 2-[(Allyl-*tert*-butoxycarbonylamino)methyl]-acrylate (20). Sodium hydride (0.069 g, 1.720 mmol) was added at 0 °C to a solution of *tert*-butyl allylcarbamoate (0.180 g, 1.150 mmol) and methyl 2-bromomethylacrylate (0.308 g, 1.720 mmol) in 5 mL of DMF. The reaction was stirred at 0 °C for 30 min, then at room temperature for 2 h, and 10 mL of EtOAc and 10 mL of H_2O were added. The aqueous phase was washed twice with EtOAc. The organic phase was washed three times with H_2O, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography [eluent: hexane/EtOAc, 8:2] to yield 0.211 g (72%) of the title compound: IR cm^{-1} 2977 (w), 1715 (s), 1691 (s), 1457 (m), 1406 (m); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.45 (s, 9 H), 3.75 (s, 3 H), 3.85 (sl, 2 H), 4.10 (sl, 2 H), 5.05−5.20 (m, 2 H), 5.60 (s, 1 H), 5.70−5.90 (m, 1 H), 6.30 (s, 1 H); MS (electrospray) *m*/*z* 256 $(M + H)^+$.

1-*tert*-Butyl-3-methyl-2,5-dihydropyrrole-1,3-dicarboxylate (21). Supported catalyst **4b** (0.050 g, 0.011 mmol) was added to a solution of **20** (0.054 g, 0.222 mmol) in 5 mL of CH_2Cl_2. The reaction was stirred at 20 °C for 24 h. PEG was precipitated and filtered. The filtrate was evaporated to yield 0.042 g (83%) of the title compound after purification by chromatography [eluent: hexane/EtOAc, 7:3]: IR cm^{-1} 2980 (m), 2253 (m), 1719 (s), 1693 (s), 1648 (s); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.50 (s, 9 H), 3.80 (s, 3 H), 4.35 (sl, 4 H), 6.70−6.80 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 2 conformers 28.87, (52.22, 52.43), (54.06, 54.27), (80.23, 80.32), (132.32, 132.43), (137.28, 137.36), 154.48, 163.61; HRMS calcd for $C_{11}H_{18}O_4N$ 228.1236, found 228.1244.

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Supporting Information Available: ^1H NMR spectra of compounds **3** and **5a**; ^{13}C NMR spectrum of compound **5a**; ^{31}P NMR spectrum of compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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