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Ruthenium Porphyrin Catalyzed Tandem Sulfonium/Ammonium Ylide Formation and [2,3]-Sigmatropic Rearrangement. A Concise Synthesis of (±)-Platynecine

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Received March 22, 2004

meso-Tetrakis(*p*-tolyl)porphyrinatoruthenium(II) carbonyl, [Ru^{II}(TTP)(CO)], can effect intermolecular sulfonium and ammonium ylide formation by catalytic decomposition of diazo compounds such as ethyl diazoacetate (EDA) in the presence of allyl sulfides and amines. Exclusive formation of [2,3]-sigmatropic rearrangement products (70−80% yields) was observed without [1,2]-rearrangement products being detected. The Ru-catalyzed reaction of EDA with disubstituted allyl sulfides such as crotyl sulfide produced an equimolar mixture of *anti*- and *syn*-2-(ethylthio)-3-methyl-4-pentenoic acid ethyl ester. The analogous "EDA + *N*,*N*-dimethylcrotylamine" reaction afforded a mixture of *anti*- and *syn*-2-(*N*,*N*-dimethylamino)-3-methyl-4-pentenoic acid ethyl esters with a diastereoselectivity of 3:1. The observed catalytic activity of [Ru^{II}(TTP)(CO)] for the ylide [2,3]-sigmatropic rearrangement is comparable to the reported examples involving [$Rh_2(CH_3CO_2)_4$] and [$Cu(acac)_2$] as catalyst. Similarly, cyclic sulfonium and ammonium ylides can be produced by intramolecular reaction of a diazo group tethered to allyl sulfides and amines under the [Ru^{II}(TTP)(CO)]-catalyzed reaction conditions. The subsequent [2,3]-sigmatropic rearrangement of the cyclic ylides furnished 2-allyl-substituted sulfur and nitrogen heterocycles in good yields (>90%). By employing [Ru^{II}(TTP)(CO)] as catalyst, the cyclic ammonium ylide [2,3]-sigmatropic rearrangement reaction was successfully applied for the total synthesis of (±)-platynecine starting from *cis*-2-butenediol.

Introduction

Sigmatropic rearrangements of sulfonium and ammonium ylides constitute a powerful synthetic tool for regio-, stereo-, and enantioselective C−C bond formations.[1] Apart from the classical methods of deprotonation and desilylation,[1a] transition-metal-catalyzed carbenoid reactions have emerged as a practical alternative for generation of sulfonium and ammonium ylides under mild conditions.[1b,2] Numerous studies showed that [Cu(acac)$_2$] and [$Rh_2(CH_3CO_2)_4$] are effective catalysts for ylide formation by decomposition of diazo compounds.[2,3] It is widely postulated that the ylide generation is mediated by reactive electrophilic metal−carbene intermediates.[4]

Ruthenium porphyrin catalyzed carbenoid reactions are receiving growing attention,[5,6] and highly stereo- and enantioselective transformations such as alkene cyclopropanation[5h,i] and carbenoid C−H insertion[5d] have

(1) For reviews, see: (a) Clark, J. S. In *Nitrogen, Oxygen and Sulfur Ylides Chemistry. A Practical Approach in Chemistry*; Clark, J. S., Ed.; Oxford University Press: Oxford, 2002; Chapter 1, p 1. (b) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263. (c) Markó, I. E. In *Comprehensive Organic Synthesis*; Pergamon: Oxford, 1991; Vol. 3, Chapter 3.10, p 913.

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(4) For isolation of a stable rhodium carbenoid complex, see: Snyder, J. P.; Padwa, A.; Stengel, T.; Arduengo, A. J., III; Jockisch, A.; Kim, H.-J. *J. Am. Chem. Soc.* **2001**, *123*, 11318.

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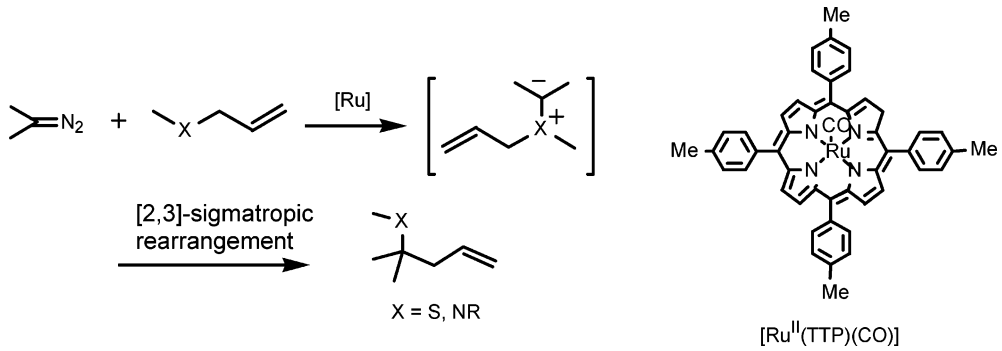
(6) Works by others: (a) Mirafzal, G. A.; Cheng, G.; Woo, L. K. *J. Am. Chem. Soc.* **2002**, *124*, 176. (b) Hamaker, C. G.; Djukic, J.-P. Smith, D. A.; Woo, L. K. *Organometallics* **2001**, *20*, 5189. (c) Simonneaux, G.; Galardon, E.; Paul-Roth, C.; Gulea, M.; Masson, S. *J. Organomet. Chem.* **2001**, *617*−*618*, 360. (d) Galardon, E.; Maux, P. L.; Simonneaux, G. *Tetrahedron* **2000**, *56*, 615. (e) Gross, Z.; Galili, N.; Simkhovich, L. *Tetrahedron Lett.* **1999**, *40*, 1571. (f) Galardon, E.; Roué, S.; Maux, P. L.; Simonneaux, G. *Tetrahedron Lett.* **1998**, *39*, 2333. (g) Galardon, E.; Maux, P. L.; Simonneaux, G. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2455. (h) Galardon, E.; Maux, P. L.; Simonneaux, G. *Chem. Commun.* **1997**, 927. (i) Frauenkron, M.; Berkessel, A. *Tetrahedron Lett.* **1997**, *38*, 7175. (j) Smith, D. A.; Reynolds, D. N.; Woo, L. K. *J. Am. Chem. Soc.* **1993**, *115*, 2511.

10.1021/jo049540v CCC: $27.50
Published on Web 09/15/2004

SCHEME 1. Sulfonium/Ammonium Ylide Rearrangement



been achieved. It has been established that reaction of [Ru^{II}(Por)(CO)] (Por = porphyrin dianion) with diazo compounds would furnish ruthenium carbene complexes,[5g,h,7] some of which have been characterized by X-ray crystallography. Simonneaux and co-workers previously reported the catalytic activities of ruthenium porphyrins for ylide-mediated [2,3]-sigmatropic rearrangements.[6c] Not long ago, we described that [Ru^{II}(Por)(CO)] can catalyze decomposition of diazo compounds to form reactive carbonyl[5c,f]/azomethine ylides,[5a,e] which underwent 1,3-dipolar cycloaddition with an array of alkenes/alkynes. Noting the synthetic value of reactive ylides, herein we report a study on tandem sulfonium/ammonium ylide formation/[2,3]-sigmatropic rearrangement reactions via ruthenium porphyrin catalyzed decomposition of diazo compounds in the presence of allyl sulfides and amines. With the intramolecular tandem ammonium ylide formation and sigmatropic rearrangement reaction as a principal step, a concise synthesis of a natural alkaloid (±)-platynecine is also presented (Scheme 1).

Results and Discussion

Intermolecular Allyl Sulfonium Ylide Formation and [2,3]-Sigmatropic Rearrangement. At the outset, we started to examine the reaction of ethyl diazoacetate (EDA) with ethyl allyl sulfide. Treatment of a toluene solution containing ethyl allyl sulfide (4 equiv) and [Ru^{II}(TTP)(CO)] (1 mol %) with EDA via slow addition through a syringe pump at 50 °C produced 2-(ethylthio)-4-pentenoic acid ethyl ester in 92% isolated yield (Table 1, entry 1). Similarly, propargyl sulfide reacted with EDA under the same conditions to give 2-(ethylthio)-3,4-pentadienoic acid ethyl ester in 91% yield (entry 2). In both cases, no cyclopropanation and [1,2]-rearrangement products were obtained.

With ethyl crotyl sulfide, the Ru-catalyzed reaction with EDA gave an equimolar mixture of *anti*- and *syn*-2-(ethylthio)-3-methyl-4-pentenoic acid ethyl ester (based on ^{1}H NMR analysis) in 89% overall yield (Table 1, entry 3). By employing the protocol of Doyle and co-workers,[8] the [$Rh_2(CH_3CO_2)_4$]-catalyzed "EDA + ethyl crotyl sulfide" reaction was found to give a similar result (84% yield, *anti*/*syn* = 1.5:1). However, we found that [Cu(acac)$_2$] is a less effective catalyst for the same reaction with <15% EDA being consumed after 12 h of reaction. The diastereoselectivity of the ylide-mediated-[2,3]-sigmatropic rearrangement has been examined using D-menthyl diazoacetate as chiral carbenoid source and ethyl allyl sulfide as substrate. Under the Ru-catalyzed conditions, sulfonium ylide-mediated [2,3]-sigmatropic rearrangement was found to proceed non-diastereoselectively (dr = 1:1 based on ^{1}H NMR analysis), and both diastereomeric esters were isolated in 83% overall yield (entry 4). In addition to the rearrangement products, dimenthyl maleate (ca. 10%) arising from the diazo coupling reaction was also detected by ^{1}H NMR analysis. In this work, the analogous [$Rh_2(CH_3CO_2)_4$]-catalyzed reaction was also found to give a 1:1 mixture of diastereomeric thioesters in 84% isolated yield, and no significant dimer formation was observed. In comparison, low yield (12%) of the diastereomeric thioester products was obtained using [Cu(acac)$_2$] as catalyst.

As expected, α-diazoketones such as isobutyl α-diazoketone are excellent carbenoid reagents for the ylide rearrangement reaction. Treatment of isobutyl α-diazoketone (1 equiv) with [Ru^{II}(TTP)(CO)] (1 mol %) and ethyl allyl sulfide (4 equiv) at 50 °C in toluene afforded the 4-(ethylthio)-2-methyl-6-hepten-3-one in 95% isolated yield (Table 1, entry 5). Neither the cyclopropanation nor Stevens [1,2]-rearrangement product was obtained.

Unlike EDA, methyl phenyldiazoacetate is less reactive toward the sulfonium ylide rearrangement reaction. We found that the reaction of methyl phenyldiazoacetate and ethyl allyl sulfide with [Ru^{II}(TTP)(CO)] as catalyst at 50 °C did not produce any rearrangement products and the starting diazoester was recovered quantitatively. However, at higher reaction temperature (90 °C), complete consumption of the diazoacetate was attained over 18 h and the expected rearrangement product was obtained in 86% yield (Table 1, entry 6). Likewise, methyl phenyldiazoacetate reacted with phenyl allyl sulfide at 90 °C to afford 2-(phenylthio)-2-phenyl-4-pentenoic acid methyl ester in 66% yield under the Ru-catalyzed conditions (entry 7). Using [$Rh_2(CH_3CO_2)_4$] as catalyst, similar results were obtained for the reactions of methyl phenyldiazoacetate with ethyl/phenyl allyl sulfide, and the [2,3]-rearrangement products were isolated in ca. 85% yields.

As noted earlier, the reactions of alkyl-substituted allyl sulfide and EDA exhibited excellent chemoselectivity

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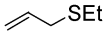
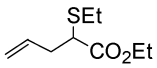
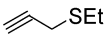
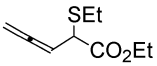
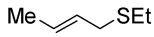
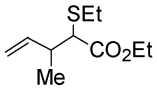
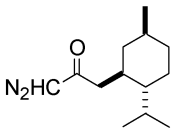
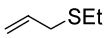
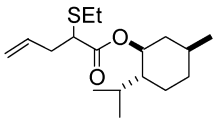
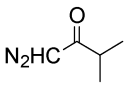
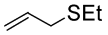
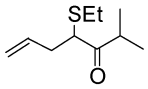
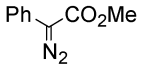
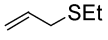
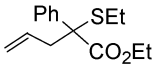
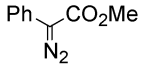
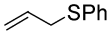
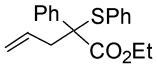
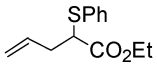
TABLE 1. Intermolecular Sulfonium Ylide [2,3]-Sigmatropic Rearrangement*

entry	diazo compound	sulfide	product	%yield [a]
1	EDA			92
2	EDA			91
3	EDA			89 (dr = 1 : 1) [c]
4				83 [d]
5				95
6				86 [e]
7				66 [e]
8	EDA			60 [b]

*Reaction conditions: A toluene solution (4 mL) of a diazo compound (0.5 mmol) was added dropwise via a syringe pump to a tolune solution (4 mL) containing allyl sulfide (2 mmol) and [Ru^{II}(TTP)(CO)] (5 μmol) over 5 h at 50 °C under argon. [a] Isolated yield. [b] Cyclopropanation (17%) and diazo coupler (8%) products were also obtained. [c] dr = diastereomeric ratio (determined by ^{1}H NMR spectroscopy). [d] <10% diazo coupling product was detected by ^{1}H NMR spectroscopy. [e] Reaction was conducted at 90 °C for 18 h.

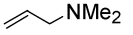
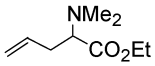
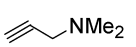
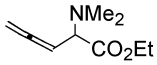
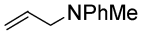
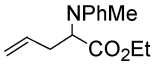
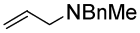
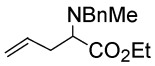
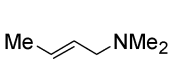
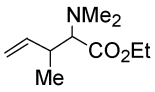
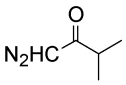
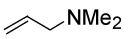
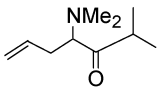
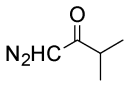
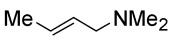
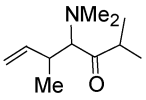
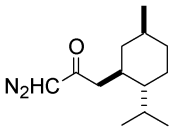
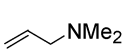
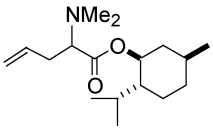
with the ylide-mediated [2,3]-sigmatropic rearrangement being the favored reaction pathway. However, when phenyl allyl sulfide was employed as substrate for the reaction with EDA, 2-(phenylthio)-4-pentenoic acid ethyl ester was isolated in 60% yield under the Ru-catalyzed conditions, whereas compounds due to cyclopropanation (17%) and dimerization (8%) were also obtained (entry 8). The lower chemoselectivity for the rearrangement reaction is probably related to the less nucleophilic sulfide due to delocalization of the sulfur lone pair electron to the aromatic nucleus.

Intermolecular Allyl Ammonium Ylide Formation and [2,3]-Sigmatropic Rearrangement. The analogous tandem ammonium ylide/[2,3]-sigmatropic rearrangement reaction has also been achieved by ruthenium porphyrin catalyzed decomposition of α-diazoesters in the presence of allylamine. Slow addition of EDA through a syringe pump to a mixture of [Ru^{II}(TTP)(CO)] (1 mol %) and *N*,*N*-dimethylallylamine (4 equiv) in toluene at 50 °C gave 2-(*N*,*N*-dimethylamino)-4-pentenoic acid ethyl ester in 87% yield (Table 2, entry 1). Consistent with allylammonium ylide-mediated [2,3]-sigmatropic rearrangement, the analogous reaction of *N*,*N*-dimethyl propargylamine with EDA afforded the allenyl-substituted α-amino ester in 88% yield (entry 2). These results are comparable to the reported examples using [Cu(acac)$_2$] and [$Rh_2(CH_3CO_2)_4$] as catalysts.[8]

While the reactivity of *N*,*N*-dialkyl-substituted allylamines for the ammonium ylide [2,3]-sigmatropic rearrangements have been extensively studied,[1−3] the analogous reaction of aniline derivative is less developed. Due to conjugation of the nitrogen lone pair with the π-orbitals of the aromatic nucleus, allyl anilines are envisioned to be less reactive toward the ylide rearrangement reaction. In this work, we found that *N*-allyl-*N*-methylaniline reacted with EDA under the Ru-catalyzed conditions to give 2-(*N*-methyl-*N*-phenylamino)-4-pentenoic acid ethyl ester in 73% yield (Table 2, entry 3). No other side products from cyclopropanation or diazo coupling reaction were detected by ^{1}H NMR analysis of the crude reaction mixture. It is noteworthy that the "EDA + *N*-allyl-*N*-methylaniline" reactions using [$Rh_2(CH_3CO_2)_4$] or [Cu(acac)$_2$] as catalyst were found to give the product amino ester [54% (for Rh) and 63% (for Cu)] in slightly lower yields.

It is well established that [2,3]- and [1,2]-rearrangement reactions are competing processes for *N*-allyl-*N*-

TABLE 2. Intermolecular Ammonium Ylide [2,3]-Sigmatropic Rearrangement*

entry	diazo compound	amine	product	%yield [a]
1	EDA			87
2	EDA			88
3	EDA			73
4	EDA			82
5	EDA			85 (dr = 3 : 1) [b]
6				85
7				81 (dr = 5 : 1) [b]
8				< 5 [c]

*Reaction conditions: A toluene solution (4 mL) of a diazo compound (0.5 mmol) was added dropwise via a syringe pump to a tolune solution (4 mL) containing allyl sulfide (2 mmol) and [Ru^{II}(TTP)(CO)] (5 μmol) over 5 h at 50 °C under argon. [a] Isolated yield. [b] dr = diastereomeric ratio (determined by ^{1}H NMR spectroscopy). [c] Diazo coupling product was obtained in 80% yield.

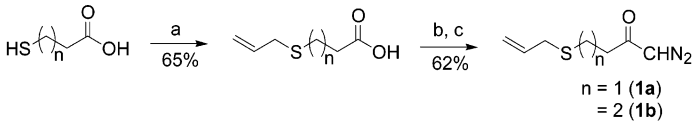
benzyl-substituted ammonium ylides.[9] To assess the selectivity of [2,3]- vs [1,2]-sigmatropic rearrangement, we employed *N*-methyl-*N*-benzylallylamine as probe substrate. Treatment of the allylamine with EDA in the presence of [Ru^{II}(TTP)(CO)] (1 mol %) in toluene at 50 °C led to formation of 2-(*N*-benzyl-*N*-methylamino)-4-pentenoic acid ethyl ester (82% yield) arising from [2,3]-sigmatropic rearrangement. No [1,2]-rearrangement product (i.e., *N*-allyl-*N*-methylphenylalanine ester) was obtained (Table 2, entry 4), indicating that [2,3]-sigmatropic rearrangement was preferred for the Ru-catalyzed rearrangement reaction involving *N*-allyl-*N*-benzyl-substituted ammonium ylide.[10] In this work, similar results were obtained for the ylide rearrangement reactions with [$Rh_2(CH_3CO_2)_4$] or [Cu(acac)$_2$] as catalyst, and 2-(*N*-benzyl-*N*-methylamino)-4-pentenoic acid ethyl ester was isolated in 59% (for Rh) and 84% (for Cu) yields.

To investigate the diastereoselectivity of the ammonium ylide [2,3]-sigmatropic rearrangement reaction, the reaction of EDA with *N*,*N*-dimethylcrotylamine was examined. In the presence of [Ru^{II}(TTP)(CO)] (1 mol %), a mixture of ethyl *syn*-/*anti*-2-(*N*,*N*-dimethylamino)-3-methyl-4-pentenoic acid ethyl ester was obtained in overall 85% yield, and diastereoselectivity = 3:1 was determined by ^{1}H NMR analysis of the crude reaction mixture (Table 2, entry 5). When α-diazo isopropyl ketone was employed as carbenoid source, the analogous reaction with *N*,*N*-dimethylcrotylamine gave 4-(*N*,*N*-dimethylamino)-2,5-dimethyl-6-hepten-3-one as a mixture of two diastereomeric amino esters in a 5:1 ratio based on ^{1}H NMR analysis (entry 7). Likewise, reaction of α-diazo isopropyl ketone with *N*,*N*-dimethylallylamine afforded the corresponding γ,δ-unsaturated α-amino ketone in 85% yield (entry 6). In this work, we found that D-menthyl diazoacetate was a poor substrate for the Ru-catalyzed reaction. Treatment of D-menthyl diazoacetate with *N*,*N*-dimethylallylamine and [Ru^{II}(TTP)(CO)] (1 mol %) as catalyst resulted in diazo coupling product (80% yield), and the desired rearranged product was formed in <5% yield (entry 8).

Intramolecular Tandem Sulfonium/Ammonium Ylide Formation and [2,3]-Sigmatropic Rearrangement. In turning our attention to intramolecular sulfonium[11]/ammonium ylide[12] [2,3]-sigmatropic rearrangement reactions, we examined the catalytic transformation of diazo ketone **1a** with [Ru^{II}(TTP)(CO)] as catalyst. As depicted in Scheme 2, **1a** was derived from *S*-allylation of 3-mercaptopropionic acid followed by diazo group

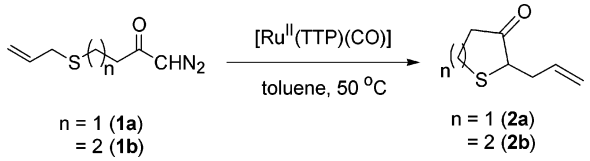
(9) (a) West, F. G.; Naidu, B. N. *J. Am. Chem. Soc.* **1993**, *115*, 1177. (b) West, F. G.; Glaeske, K. W.; Naidu, B. N. *Synthesis* **1993**, 977.
(10) See, for an example: Clark, J. S.; Middleton, M. D. *Org. Lett.* **2002**, *4*, 765.

SCHEME 2



a) allyl bromide, NaOH, EtOH / H_2O; b) $ClCO_2CH_2CHMe_2$, NEt_3, THF / Et_2O; c) CH_2N_2, 0 - 10 °C

SCHEME 3



transfer to afford the product diazo compound in 62% yield. A related analogue **1b** was prepared from 4-mercaptobutyric acid via similar synthetic protocols. Dropwise addition of **1a** to a toluene solution of [Ru^{II}(TTP)(CO)] (1 mol %) at 50 °C produced 2-allyldihydrothiophen-3-one (**2a**) in 92% yield (Scheme 3). Likewise, facile cyclization of **1b** to 2-allyldihydrothiopyran-3-one (**2b**) in 94% yield was achieved under similar conditions. The sulfur cycle formation occurred presumably via intramolecular sulfonium ylide formation and subsequent [2,3]-sigamatropic rearrangement.

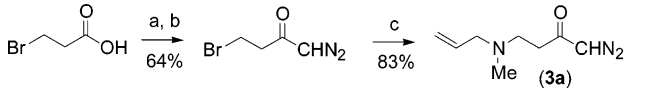
For the analogous intramolecular ammonium ylide-mediated [2,3]-sigmatropic rearrangement reaction, diazo compounds **3a** and **3b** were prepared according to Scheme 4. 4-Bromo-1-diazobutan-2-one was obtained in 64% yield by treating 3-bromopropionic acid with oxalyl chloride, followed by diazomethane. Addition of *N*-methylallylamine to 4-bromo-1-diazobutan-2-one gave diazo compound **3a** in 83% yield. Diazo compound **3b** was prepared with reference to a reported procedure[12c] (Scheme 4). Reactions of *N*-trifluoroacetyl 4-aminobutanoic acid with oxalyl chloride and then with excess diazomethane afforded *N*-trifluoroacetyl 4-amino-1-diazopetan-2-one in 61% yield. The desired diazo ketone **3b** was obtained in 49% yield after deacetylation and *N*-allylation.

Reaction of **3a** upon treatment with [Ru^{II}(TTP)(CO)] (1 mol %) in toluene at 50 °C resulted in spontaneous formation of *N*-methyl-2-allyl-3-pyrrolidone (**4a**) in 87% yield (Scheme 5). Under similar conditions, diazoketone **3b** was found to undergo effective transformation to pyridone **4b** in 90% yield. With [$Cu(acac)_2$] or [$Rh_2(CH_3CO_2)_4$] as catalyst, effective transformations of **3a**,**b** to **4a** [70% (Cu); 58% (Rh)] and **4b** [79% (Cu); 73% (Rh)] were also accomplished in refluxing benzene. As shown in Scheme 6, effective cyclization of diazoester **5** to *N*-allyl-2-allyl-3-morpholinone (**6**) can be achieved by intramolecular ammonium ylide rearrangement under the standard reaction conditions [i.e., [Ru^{II}(TTP)(CO)] (1 mol %), toluene, 50 °C]. The product morpholinone was isolated in 91% yield.[12c,13]

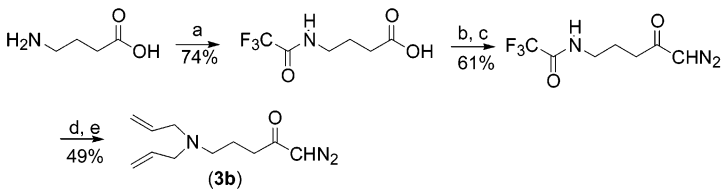
It is noteworthy that the present Ru-catalyzed reaction exhibits remarkable chemoselectivity toward [2,3]-sigmatropic rearrangement. For example, treating *N*-allyl-*N*-benzyl 4-amino-1-diazo-2-butanone with [Ru^{II}(TTP)(CO)] as catalyst (1 mol %) was found to produce *N*-benzyl-2-allyl-3-pyrrolidone (i.e., [2,3-sigmatropic rearrangement product) in 92% yield without any [1,2]-rearrangement product being detected (Scheme 7). This finding is comparable to the recent work by Clark and co-workers regarding the Cu-catalyzed intramolecular reaction involving *N*-allyl-*N*-benzyl-substituted ammonium ylide.[10]

Synthesis of (±)-Platynecine. (±)-Platynecine, first isolated from *Senecio platyphyllusis*,[14] is the necine base of several pyrrolizidine alkaloids widely found in many plant families.[15] Pyrrolizidine alkaloids have been a popular target for synthesis due to their structural diversity and interesting biological activities.[16] A variety of approaches for the syntheses of platynecine are known in the literature. Strategies for (±)-platynecine synthesis[17] include [2 + 2] cycloadditon of five-membered enecarbamate with ketene,[17a] Dieckmann reaction of *N*-alkyl ethyl (±)-*cis*-2,3-bis(ethoxycarbonyl)-1-pyrrolidinepropionate,[17c] and rearrangement of vinylaziridines derived from intramolecular cyclization of azido dienes.[17d] Several studies on enantioselective synthesis[18] of (−)-platynecine by employing cycloadditions and acyliminium ion−ketene dithioacetal cationic cyclization involving optically active substrates are also known. The present work represents the first example on the application of

SCHEME 4

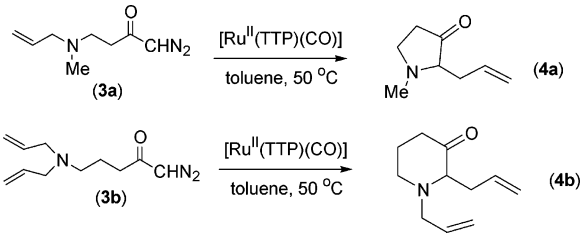


a) $(COCl)_2$, DMF (cat.), CH_2Cl_2, 0 °C; b) CH_2N_2, 0 - 10 °C; c) $MeNHCH_2CH{=}CH_2$, NEt_3, EtOAc, 0 °C - rt



a) CF_3CO_2Et, NEt_3, MeOH, rt; b) $(COCl)_2$, DMF (cat.), CH_2Cl_2, 0 °C; c) CH_2N_2, 0-10 °C; d) $Ba(OH)_2$, aq., rt; e) allyl bromide, K_2CO_3, THF, rt

SCHEME 5



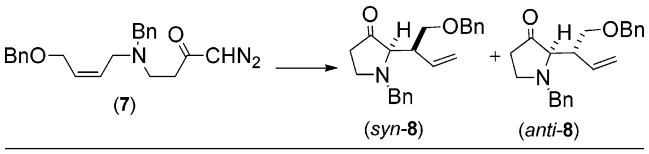
ylide [2,3]-sigmatropic rearrangement for racemic platynecine synthesis.

Scheme 8 depicts our retrosynthetic strategy to the synthesis of (±)-platynecine; this involves introducing the bicyclic core via intramolecular amine alkylation followed by deprotection. Construction of the proline skeleton by cyclization of the diazo compound derived from *cis*-2-butenediol via tandem ammonium ylide formation/[2,3]-sigmatropic rearrangement using [Ru^{II}(TTP)(CO)] as catalyst is envisioned to be a principal step toward the synthesis.

Mesylation of an *O*-monobenzyl *cis*-2-butenediol derivative followed by nucleophilic substitution with benzylamine gave *N*-benzyl-(4-benzyloxy)but-2-enylamine in 84% yield. Reaction of the allylamine with 4-bromo-1-diazobutan-2-one afforded **7** in 82% yield (Scheme 9). Treatment of **7** with [Ru^{II}(TTP)(CO)] (1 mol %) in toluene at 50 °C afforded an equimolar mixture of *syn*- and *anti*-pyrrolidone **8** based on ^{1}H NMR analysis of the crude reaction mixture. After chromatographic purification, the diastereomeric pyrrolidones were obtained as an inseparable mixture with a *syn*/*anti* ratio of 2.5:1 (Scheme 10). Subsequent stereoselective reduction of the pyrrolidone mixture by $NaBH_4$ gave *syn*-alcohol **9** as the major product (69% yield) with the *anti*-isomer isolated in 28% yield (diastereomeric ratio = 2.5:1) by silica gel column chromatography. The diastereomeric alcohols were characterized by NMR techniques (see the Experimental Section for details).

Stereochemical assignment of *syn*-/*anti*-**9** was performed by a series of NOESY experiments (spectra are provided in the Supporting Information). As depicted in Scheme 11, the *cis*-relationship of the protons at C(3)H, C(4)H, and C(5)H are evident from their respective mutual enhancements. Irradiation of the proton at C(4) resulted in a strong NOE enhancement of the methylene proton at C(3). The observed *cis*-relationship between these two stereocenters [i.e., C(3) and C(4)] suggests that $NaBH_4$ reduction of **8** proceeded from beneath the plane of the nitrogen cycle.[19] Irradiation of C(4)H gave a strong enhancement of the C(5)H signal, thereby confirming the *cis*-stereochemistry between the C(4) and C(5) centers. On the basis of the NOESY experiment, *syn*-**9** was established to have a relative *all-cis* relationship between C(3)H, C(4)H, and C(5)H. For *anti*-**9**, while a strong NOE enhancement was observed between C(3)H and C(4)H, no enhancement was observed for C(5)H upon irradiation of C(4)H. No reciprocal NOE enhancement of the C(4)H signal was observed by irradiating the C(5)H atom (see the Supporting Information for spectral details). Thus, an *all-trans* relationship was assigned for the C(3)H, C(4)H, and C(5)H atoms of *anti*-**9**. On the basis of structural correlation with **9**, the stereochemistry of *syn*- and *anti*-**8** was established.

TABLE 3. Effect of Catalyst on the Intramolecular Ammonium Ylide [2,3]-Sigmatropic Rearrangement*



entry	catalyst	%yield [a]	*syn* : *anti* ratio [b]
1	[Ru^{II}(TTP)(CO)]	83	1 : 1
2	[Ru^{II}(4-MeO-TPP)(CO)] [c]	81	1 : 1
3	[Ru^{II}(F_{20}-TPP)(CO)] [c]	83	1 : 1
4	[Ru^{II}(TMP)(CO)] [c]	78	1 : 1
5	[$Rh_2(CH_3CO_2)_4$]	70	1.2 : 1
6	[$Cu(acac)_2$]	81	1 : 1

*Reaction conditions: catalyst (5 μmol), **7** (0.5 mmol), toluene, 50 °C, 2 h. [a] Isolated yield. [b] Diastereomeric ratio determined by ^{1}H NMR analysis of the crude reaction mixture. [c] 4-MeO-H_2TPP = tetrakis(4-methoxyphenyl)porphyrin, F_{20}-H_2TPP = tetrakis(pentafluorophenyl)porphyrin, H_2TMP = tetrakismesitylporphyrin.

(11) Selected examples of Cu- and Rh-carbenoid mediated generation of cyclic sulfonium ylides for [2,3]-sigmatropic rearrangement reactions: (a) Kido, F.; Abiko, T.; Kato, M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2989. (b) Kido, F.; Yamaji, K.; Sinha, S. C.; Yoshikoshi, A.; Kato, M. *Chem. Commun*. **1994**, 789. (c) Kido, F.; Sinha, S. C.; Abiko, T.; Watanabe, M.; Yoshikoshi, A. *Tetrahedron* **1990**, *46*, 4887. (d) Moody, C. J.; Taylor, R. J. *Tetrahedron* **1990**, *46*, 6501. (e) Davies, H. M. L.; Crisco, L. V. T. *Tetrahedron Lett*. **1987**, *28*, 371. (f) Doyle, M. P.; Griffin, J. H.; Chinn, M. S.; van Leusen, D. *J. Org. Chem*. **1984**, *49*, 1917.

(12) Selected examples of Cu- and Rh-carbenoid mediated generation of cyclic ammonium ylides for [2,3]-sigmatropic rearrangement reactions: (a) Vanecko, J. A.; West, F. G. *Org. Lett*. **2002**, *4*, 2813. (b) Clark, J. S.; Hodgson, P. B.; Goldsmith, M. D.; Blake, A. J.; Cooke, P. A.; Street, L. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3325. (c) Clark, J. S.; Hodgson, P. B.; Goldsmith, M. D.; Street, L. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3312. (d) Curtis, E. A.; Worsencroft, K. J.; Padwa, A. *Tetrahedron Lett*. **1997**, *38*, 3319. (e) Wright, D. L.; Weekly, R. M.; Groff, R.; McMills, M. C. *Tetrahedron Lett*. **1996**, 2165. (f) Clark, J. S.; Hodgson, P. B. *Tetrahedron Lett*. **1995**, *36*, 2519. (g) Clark, J. S.; Hodgson, P. B. *J. Chem. Soc., Chem. Commun*. **1994**, 2701.

(13) For recent examples of metal-carbenoid-mediated morpholinium ylide formation, see also: (a) Saba, A. *Tetrahedron Lett*. **2003**, *44*, 2895. (b) Glaeske, K. W.; Naidu, B. N.; West, F. G. *Tetrahedron: Asymmetry* **2003**, *14*, 917. (c) West, F. G.; Naidu, B. N. *J. Org. Chem*. **1994**, *59*, 6051.

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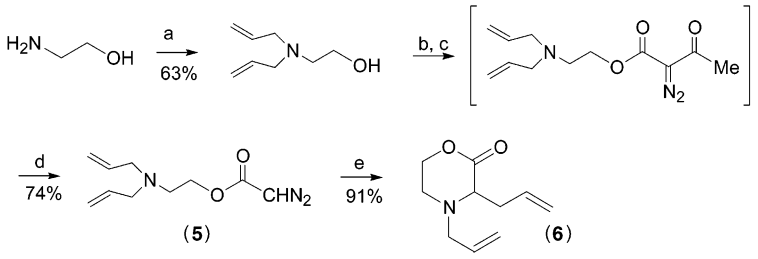
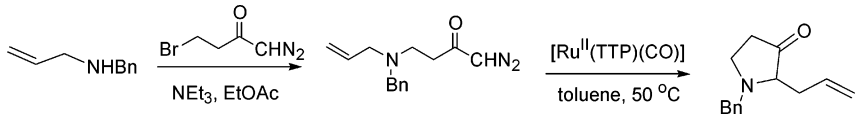
SCHEME 6

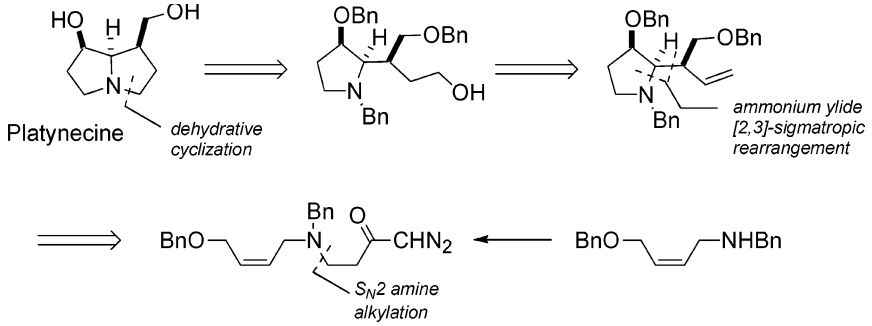


a) allyl bromide, K_2CO_3, THF, rt; b) diketene, NEt_3, CH_2Cl_2; c) MsN_3, NEt_3, CH_3CN; d) pyrrolidine, CH_3CN; e) [Ru^{II}(TTP)(CO)] (5 mol%), toluene, 50 °C

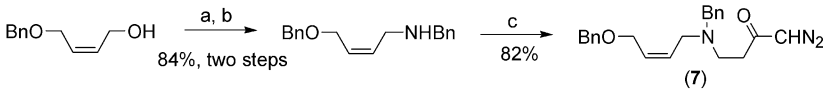
SCHEME 7



SCHEME 8. Retrosynthetic Analysis

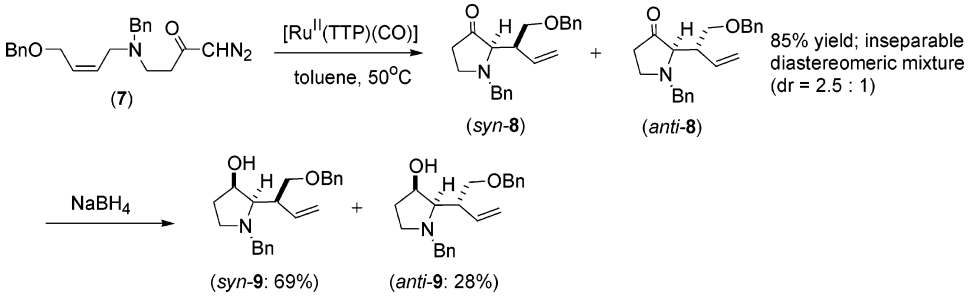


SCHEME 9

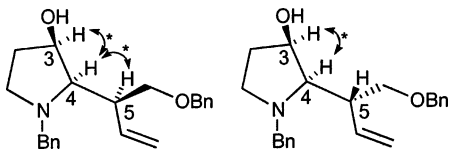


a) MsCl, NEt_3; b) $BnNH_2$, NEt_3; c) 4-bromo-1-diazobutan-2-one, NEt_3, EtOAc

SCHEME 10



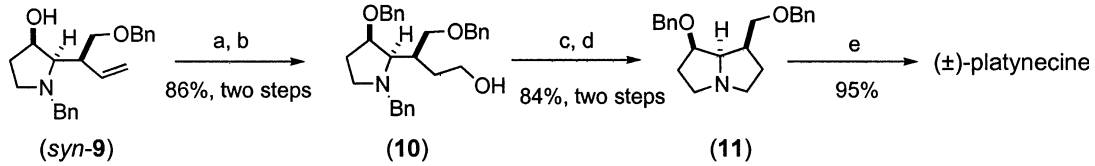
SCHEME 11. NOE of *syn*- and *anti*-Pyrrolidinol 9



The effect of catalysts on the diastereoselectivity of the transformation of **7** to *syn*-/*anti*-**8** has been examined. Various [Ru^{II}(Por)(CO)] catalysts (H_2Por = H_2TTP, 4-MeO-H_2TPP, F_{20}-H_2TPP, and H_2TMP) studied in this work were found to be equally effective for the transformation with product yields of ca. 80%. However, no significant influence on the diastereoselectivities (i.e., *syn*/*anti* ratio = 1:1) was observed based on ^{1}H NMR analysis of the crude reaction mixtures (Table 3, entries 1−4). [Cu(acac)$_2$] and [$Rh_2(CH_3CO_2)_4$] were found to be effective catalysts for the cyclization of **7**, and equimolar mixtures of *syn*- and *anti*-**8** were obtained in 81 (Cu) and 70% (Rh) yields (entries 5 and 6).

To complete the synthesis of platynecine (Scheme 12), the newly formed hydroxy group of *syn*-**9** was protected as a benzyl ether, followed by C=C hydroboration using

SCHEME 12



a) NaH, BnBr, THF; b) 9-BBN, THF, reflux, then H_2O_2 / OH^-; c) Pt/C (10%), HCO_2NH_4, MeOH, reflux; d) PPh_3, CCl_4, NEt_3, DMF; e) $PdCl_2$, H_2, MeOH

9-BBN to give primary alcohol **10** in 86% yield.[20] Attempts to effect C=C bond hydroboration with BH_3–SMe_2 proved problematic, affording an unknown mixture of products. Selective *N*-deprotection was accomplished by catalytic transfer hydrogenation with ammonium formate and 10% Pd/C in refluxing methanol.[21] The debenzylated secondary amine intermediate was subjected to a dehydrative condition [Ph_3P, Et_3N and CCl_4 in dry DMF] to effect annulation, and pyrrolizidine **11** was obtained in 84% yield over two steps.[22] Global *O*-debenzylation of **11** with $PdCl_2$ in methanol furnished (±)-platynecine in 95% isolated yield. The ^1H and ^{13}C NMR spectra of (±)-platynecine prepared in this work are identical to the corresponding spectra of the authentic natural compound (see the Supporting Information for spectra).[18a]

Experimental Section

Materials. Unless otherwise noted, all reactions were performed in oven-dried glassware under a dry nitrogen atmosphere. Reagents were obtained commercially and used without further purification unless indicated otherwise. CH_2Cl_2 was freshly distilled from CaH_2 under a nitrogen atmosphere; Et_2O and THF were freshly distilled from sodium/benzophenone under a nitrogen atmosphere. Ruthenium(II) porphyrins were prepared according to reported procedures.[23] Solvent was removed under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column (230−400 mesh) using a gradient solvent system (EtOAc/*n*-hexane mixture) as the eluant unless specified otherwise. ^1H and ^{13}C NMR spectra were measured on a 400 or 300 MHz NMR spectrometer. Chemical shifts (ppm) were determined with tetramethylsilane (TMS) as internal reference. Carbon multiplicities were determined by DEPT-135 experiments. Mass spectra were determined at an ionizing voltage of 20 eV on a mass spectrometer. Readers may refer to the Supporting Information for the preparation of the diazo substrates.

General Procedure for the Intermolecular Sulfonium/Ammonium Ylide [2,3]-Sigmatropic Rearrangement Reactions. A solution of diazo compound (0.5 mmol) in toluene (4 mL) was added dropwise via a syringe pump to a solution of an appropriate allyl sulfide or amine (2 mmol) and [Ru^{II}(TTP)(CO)] (5 μmol) in dry toluene (4 mL) over 5 h at 50 °C under an argon atmosphere. On completion, the solvent was removed and the crude residue was purified by silica gel column chromatography.

2-(Ethylthio)-4-pentenoic acid ethyl ester: colorless oil (92% yield); ^1H NMR (300 MHz, $CDCl_3$) δ_H 5.75−5.84 (m, 1H), 5.06−5.16 (m, 2H), 4.20 (dq, 2H, J = 7.1, 2.9 Hz), 3.32 (dd, 1H, J = 8.8, 5.5 Hz), 2.57−2.69 (m, 3H), 2.41−2.47 (m, 1H), 1.28 (t, 3H, J = 7.3 Hz), 1.25 (t, 3H, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 172.2 (s), 134.2 (d), 117.5 (t), 60.9 (t), 46.0 (d), 35.6 (t), 25.3 (t), 14.3 (q), 14.1 (q); IR (neat, cm^{-1}) 2988, 2934, 1726, 1456, 1265, 1157, 1036; MS (EI) 188 [M^+]; HRMS (EI) calcd for $C_9H_{16}SO_2$ 188.0871, found 188.0869.

2-(Ethylthio)-3,4-pentadienoic acid ethyl ester: colorless oil (91% yield); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.38(dt, 1H, J = 13.2, 6.7 Hz), 4.90 (d, 2H, J = 6.7 Hz), 4.21 (q, 2H, J = 7.2 Hz), 4.00(d, 1H, J = 8.8 Hz), 2.67(q, 2H, J = 7.3 Hz), 1.29(t, 3H, J = 7.2 Hz), 1.27(t, 3H, 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 208.8 (s), 170.3 (s), 87.5 (d), 77.3 (t), 61.4 (t), 46.1 (d), 25.2 (t), 14.1 (q), 14.0 (q); IR (neat, cm^{-1}) 2925, 1955, 1732, 1456, 1273, 1150, 1032, 852; MS (EI) 186 [M^+]; HRMS (EI) calcd for $C_9H_{14}SO_2$ 186.0714, found 186.0713.

2-(Ethylthio)-3-methyl-4-pentenoic acid ethyl ester:[24] inseparable 1:1 mixture of *anti*- and *syn*-isomers (89% yield); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.70−5.84 (m, 2H), 4.99−5.13 (m, 4H), 4.14−4.24 (m, 4H), 3.08−3.13 (m, 2H), 2.55−2.66 (m, 6H), 1.20−1.31 (m, 12H), 1.18 (d, 3H, J = 6.8 Hz), 1.10 (d, 3H, J = 6.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.0 (s), 171.9 (s), 140.1 (d), 139.9 (d), 115.4 (t), 115.3 (t), 60.8 (t), 60.7 (t), 52.8 (d), 52.4 (d), 39.2 (d), 39.1 (d), 25.5 (t), 25.4 (t), 18.6 (q), 17.6 (q), 14.3 (q), 14.2 (q), 14.14 (q), 14.12 (q); IR (neat, cm^{-1}) 2977, 2930, 1734, 1456, 1269, 1146, 1030; MS (EI) 202 [M^+]; HRMS (EI) calcd for $C_{10}H_{18}SO_2$ 202.1027, found 202.1032.

2-(Ethylthio)-4-pentenoic acid D-menthyl ester: inseparable mixture of diastereomers; colorless oil (83% yield); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.74−5.83 (m, 2H), 5.05−5.14 (m, 4H), 4.72 (dt, 2H, J = 10.9, 4.4 Hz), 3.30 (t, 2H, J = 7.1 Hz), 2.57−2.69 (m, 6H), 2.42−2.46 (m, 2H), 1.88−2.00 (m, 4H), 1.62−1.70 (m, 4H), 1.39−1.50 (m, 4H), 1.21−1.28 (m, 6H), 0.95−1.09 (m, 4H), 0.86−0.94 (m, 12H), 0.71−0.79 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 171.6 (s), 134.2 (d), 134.1 (d), 117.5 (t), 117.3 (t), 74.8 (d), 74.7 (d), 47.0 (d), 46.9 (d), 46.3 (d), 46.2 (d), 40.6 (t), 35.6 (t), 34.14 (t), 34.11 (t), 31.3 (d), 25.8 (q), 25.7 (q), 25.3 (t), 25.0 (t), 23.1 (t), 22.9 (t), 21.9 (d), 20.7 (q), 20.6 (q), 16.0 (q), 15.8 (q), 14.3 (q), 14.2 (q); IR (neat, cm^{-1}) 2956, 1718, 1464, 1257, 1159, 984; MS (EI) 298 [M^+]; HRMS (EI) calcd for $C_{17}H_{30}SO_2$ 298.1966, found 298.1962.

4-(Ethylthio)-2-methyl-6-hepten-3-one: colorless oil (95% yield); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.70−5.79 (m, 1H), 5.04−5.12 (m, 2H), 3.38 (dd, 1H, J = 8.3, 6.7 Hz), 2.98−3.05 (m, 1H), 2.63−2.70 (m, 1H), 2.31−2.51 (m, 3H), 1.19 (t, 3H, J = 7.4 Hz), 1.12 (d, 3H, J = 7.1 Hz), 1.08(d, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 208.7 (s), 134.8 (d), 117.2 (t), 50.7 (d), 37.7 (d), 34.0 (t), 22.9 (t), 19.3 (q), 18.4 (q), 14.2 (q); IR (neat, cm^{-1}) 2970, 2934, 1713, 1470, 999; MS (EI) 186 [M^+]; HRMS (EI) calcd for $C_{10}H_{18}SO$ 186.1078, found 186.1084.

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2-(Ethylthio)-2-phenyl-4-pentenoic acid methyl ester: colorless oil (86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.23−7.41 (m, 5H), 5.62−5.70 (m, 1H), 4.96−5.01 (m, 2H), 3.77 (s, 3H), 2.88 (d, 1H, J = 7.1 Hz), 2.42−2.48 (m, 1H), 2.32−2.39 (m, 1H), 1.13 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.8 (s), 139.1 (s), 132.8 (d), 128.1 (d), 127.6 (d), 127.2 (d), 118.5 (t), 60.4 (s), 52.4 (q), 43.1 (t), 24.0 (t), 13.4 (q); IR (neat, cm^{-1}) 2938, 1728, 1439, 1218, 699; MS (EI) 250 [M$^+$]; HRMS (EI) calcd for $C_{14}H_{18}SO_2$ 250.1027, found 250.1016.

2-(Phenylthio)-2-phenyl-4-pentenoic acid methyl ester:[25] colorless solid (66% yield); mp 71−73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.06−7.28 (m, 10H), 5.76−5.90 (m, 1H), 5.01−5.06 (m, 2H), 3.62 (s, 3H), 2.77−2.86 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 172.3 (s), 139.7 (s), 136.8 (d), 133.1 (d), 130.6 (s), 129.2 (d), 128.5 (d), 128.4 (d), 128.0 (d), 127.4 (d), 118.7 (t), 64.4 (s), 52.6 (q), 40.6 (t); IR (KBr disk, cm^{-1}) 3077, 2955, 1732, 1439, 1217, 751, 693; MS (EI) 298 [M$^+$]; HRMS (EI) calcd for $C_{18}H_{18}SO_2$ 298.1027, found 298.1026.

2-(Phenylthio)-4-pentenoic acid ethyl ester: colorless oil (60% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.28−7.48 (m, 5H), 5.75−5.84 (m, 1H), 5.08−5.16 (m, 2H), 4.11 (q, 2H, J = 7.2 Hz), 3.70 (dd, 1H, J = 8.6, 6.4 Hz), 2.47−2.65 (m, 2H), 1.16 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 171.5 (s), 133.8 (d), 133.0 (d), 129.9 (s), 128.8 (d), 127.9 (d), 117.9 (t), 61.0 (t), 50.2 (d), 35.7 (t), 14.4 (q); IR (neat, cm^{-1}) 2988, 1732, 1439, 1259, 1157, 691; MS (EI) 236 [M$^+$]; HRMS (EI) calcd for $C_{13}H_{16}SO_2$ 236.0871, found 236.0870.

2-(*N*,*N*-Dimethylamino)-4-pentenoic acid ethyl ester:[8] colorless oil (87% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.73−5.82 (m, 1H), 5.04−5.14 (m, 2H), 4.18 (q, 2H, J = 7.1 Hz), 3.20 (dd, 1H, J = 8.3, 6.6 Hz), 2.38−2.50 (m, 2H), 2.36 (s, 6H), 1.25 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 171.5 (s), 134.2 (d), 117.2 (t), 67.5 (d), 60.1 (t), 41.6 (q), 34.1 (t), 14.4 (q); IR (neat, cm^{-1}) 2923, 1744, 1472, 1221; MS (EI) 130 [M$^+$ − C_3H_5]; HRMS (EI) calcd for $C_6H_{12}NO_2$ 130.0868, found 130.0862.

2-(*N*,*N*-Dimethylamino)-3,4-pentadienoic acid ethyl ester:[26] colorless oil (88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.26 (dt, 1H, J = 8.6, 6.7 Hz), 4.83 (dd, 2H, J = 6.7, 1.0 Hz), 4.22 (q, 2H, J = 7.2 Hz), 3.63(d, 1H, J = 8.6 Hz), 2.34 (s, 3H), 1.29(t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 209.4 (s), 170.9 (s), 86.2 (d), 76.1 (t), 68.8 (d), 60.8 (t), 42.1 (q), 14.2 (q); IR (neat, cm^{-1}) 2922, 1722, 1234; MS (EI) 124 [M$^+$ − OEt]; HRMS (EI) calcd for $C_7H_{10}NO$ 124.0762, found 124.0763.

2-(*N*-Methyl-*N*-phenylamino)-4-pentenoic acid ethyl ester: colorless oil (73% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.19−7.26 (m, 2H), 6.72−6.82 (m, 3H), 5.70−5.82 (m, 1H), 5.03−5.18 (m, 2H), 4.42 (dd, 1H, J = 8.9, 5.6 Hz), 4.11−4.19 (m, 2H), 2.90 (s, 3H), 2.67−2.75 (m, 1H), 2.57−2.65 (m, 1H), 1.22 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 172.1 (s), 150.0 (s), 134.2 (d), 129.1 (d), 117.6 (d), 117.5 (t), 113.5 (d), 61.6 (d), 60.7 (t), 34.1 (t), 32.9 (q), 14.2 (q); IR (neat, cm^{-1}) 2922, 1732, 1601, 1505, 1184, 749, 691; MS (EI) 233 [M$^+$]; HRMS (EI) calcd for $C_{14}H_{19}NO_2$ 233.1415, found 233.1412.

2-(*N*-Benzyl-*N*-methylamino)-4-pentenoic acid ethyl ester: colorless oil (82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.21−7.34 (m, 5H), 5.77−5.87 (m, 1H), 5.03−5.13 (m, 2H), 4.15−4.24 (m, 2H), 3.80 (d, 1H, J = 13.6 Hz), 3.60 (d, 1H, J = 13.6 Hz), 3.39 (t, 1H, J = 7.6 Hz), 2.45−2.57 (m, 2H), 2.28 (s, 3H), 1.30 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 171.8 (s), 139.3 (s), 134.8 (d), 128.6 (d), 128.1 (d), 126.9 (d), 116.8 (t), 65.6 (d), 60.0 (t), 58.3 (t), 37.9 (q), 34.0 (t), 14.5 (q); IR (neat, cm^{-1}) 2992, 1731, 1455, 1178, 1027, 915, 736, 698; MS (EI) 247 [M$^+$]; HRMS (EI) calcd for $C_{15}H_{21}NO_2$ 247.1572, found 247.1572.

2-(*N*,*N*-Dimethylamino)-3-methyl-4-pentenoic Acid Ethyl Ester.[8] Separable 3:1 mixture of *anti*- and *syn*-isomers. For the major isomer: colorless oil (64% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.73−5.85 (m, 1H), 5.04−5.12 (m, 2H), 4.19 (q, 2H, J = 7.2 Hz), 2.96 (d, 1H, J = 10.4 Hz), 2.34−2.39 (m, 1H), 2.36 (s, 6H), 1.29 (t, 3H, J = 7.2 Hz), 0.98 (d, 3H, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 170.8 (s), 141.0 (d), 114.3 (t), 72.7 (d), 59.8 (t), 41.4 (q), 37.4 (d), 17.5 (q), 14.5 (q); IR (neat, cm^{-1}) 2921, 1730, 1227; MS (EI) 140 [M$^+$ − OEt]; HRMS (EI) calcd for $C_8H_{14}NO$ 140.1075, found 140.0851. For the minor isomer: colorless oil (21% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.62−5.79 (m, 1H), 5.00−5.09 (m, 2H), 4.15 (q, 2H, J = 7.2 Hz), 2.89 (d, 1H, J = 10.4 Hz), 2.58−2.64 (m, 1H), 2.33 (s, 6H), 1.26 (t, 3H, J = 7.2 Hz), 1.07 (d, 3H, J = 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 170.9 (s), 140.2 (d), 115.5 (t), 72.4 (d), 59.6 (t), 41.4 (q), 37.7 (d), 16.9 (q), 14.6 (q); IR (neat, cm^{-1}) 2919, 1717; MS (EI) 140 [M$^+$ − OEt]; HRMS (EI) calcd for $C_8H_{14}NO$ 140.1075, found 140.0840.

4-(*N*,*N*-Dimethylamino)-2,5-dimethyl-6-hepten-3-one.[27] Obtained as a 5:1 mixture of *anti*- and *syn*-isomers. Purification of the crude mixture on a silica gel column resulted in some epimerization and gave the product as an inseparable 1:1 diastereomeric mixture and as a colorless oil (81% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.80−5.89 (m, 1H), 5.59−5.68 (m, 1H), 4.94−5.11 (m, 4H), 3.20 (d, 1H, J = 9.8 Hz), 3.15 (d, 1H, J = 9.9 Hz), 2.62−2.77 (m, 3H), 2.50−2.57 (m, 1H), 2.38 (s, 6H), 2.36 (s, 6H), 1.03−1.09 (m, 12H), 0.99 (d, 3H, J = 6.9 Hz), 0.88 (d, 3H, J = 6.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 213.9 (s), 212.6 (s), 141.8 (d), 140.6 (d), 115.4 (t), 114.1 (t), 74.3 (d), 74.1 (d), 41.7 (q), 41.6 (q), 37.1 (d), 36.4 (d), 21.4 (t), 18.9 (t), 17.9 (q), 17.6 (q), 17.4 (q), 17.1 (q), 17.0 (q); IR (neat, cm^{-1}) 2936, 1651, 1466; MS (EI) 128 [M$^+$ − C_4H_7]; HRMS (EI) calcd for $C_7H_{14}NO$ 128.1075, found 128.1076.

4-(*N*,*N*-Dimethylamino)-2-methyl-6-hepten-3-one:[27] colorless oil (85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.66−5.75 (m, 1H), 5.00−5.09 (m, 2H), 3.31 (dd, 1H, J = 8.8, 4.8 Hz), 2.83−2.91 (m, 1H), 2.41−2.48 (m, 1H), 2.30 (s, 6H), 2.24−2.33 (m, 1H), 1.07 (d, 3H, J = 6.8 Hz), 1.04 (d, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 213.8 (s), 135.3 (d), 116.9 (t), 70.9 (d), 41.8 (q), 38.8 (d), 28.9 (t), 18.5 (q), 17.8 (q); IR (neat, cm^{-1}) 2932, 1651; MS (EI) 128 [M$^+$ − C_3H_5]; HRMS (EI) calcd for $C_7H_{14}NO$ 128.1075, found 128.1091.

General Procedure of the Intramolecular Sulfonium/Ammonium Ylide [2,3]-Sigmatropic Rearrangement Reactions. To a solution of [Ru^{II}(TTP)(CO)] (5 μmol) in dry toluene (4 mL) was added dropwise an appropriate diazo compound (0.5 mmol) in dry toluene (4 mL) via a syringe pump over 2 h at 50 °C. After complete substrate consumption based on TLC monitoring, the solvent was removed by vacuum and the crude residue was chromatographed on a silica gel column using a hexanes−ethyl acetate mixture as eluant.

2-Allyldihydrothiophen-3-one (2a):[29] colorless oil (92% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.74−5.88 (m, 1H), 5.01−5.17 (m, 2H), 3.44 (dd, 1H, J = 8.7, 4.4 Hz), 2.96 (dd, 2H, J = 8.1, 6.9 Hz), 2.54−2.77 (m, 3H), 2.29−2.39 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 213.2 (s), 134.3 (d), 117.5 (t), 51.1 (d), 39.3 (t), 36.0 (t), 23.4 (t); IR (neat, cm^{-1}) 2928, 1736, 1406, 1132, 1003, 918; MS (EI) 142 [M$^+$]; HRMS (EI) calcd for $C_7H_{10}SO$ 142.0452, found 142.0458.

2-Allyldihydrothiopyran-3-one (2b):[28] colorless oil (94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.87−5.85 (m, 1H), 5.05−5.14 (m, 2H), 3.49 (t, 1H, J = 7.0 Hz), 2.89−2.96 (m, 1H), 2.64−2.75 (m, 2H), 2.50−2.56 (m, 2H), 2.33−2.39 (m, 2H), 2.20−2.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 205.1 (s), 134.4 (d), 117.3 (t), 49.6 (d), 41.9 (t), 34.7 (t), 32.8 (t), 28.9 (t); IR (neat, cm^{-1}) 2928, 1707, 1435, 1003, 918; MS (EI) 156 [M$^+$]; HRMS (EI) calcd for $C_8H_{12}SO$ 156.0608, found 156.0609.

***N*-Methyl-2-allyl-3-pyrrolidinone (4a):**[12c] colorless oil (87% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.68−5.79 (m, 1H), 5.03−5.14 (m, 2H), 3.31−3.36 (m, 1H), 2.43−2.49 (m, 5H),

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2.32−2.41 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 215.0 (s), 134.1 (d), 117.1 (t), 71.2 (d), 51.9 (t), 41.5 (q), 37.1 (t), 32.7 (t); IR (neat, cm^{-1}) 2923, 1645; MS (EI) 139 [M^+]; HRMS (EI) calcd for $C_8H_{13}NO$ 139.0997, found 139.1004.

***N,N*-Diallyl-3-piperidinone (4b):**[12c] colorless oil (90% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.68−5.86 (m, 2H), 5.01−5.23 (m, 4H), 3.27 (ddt, 1H, J = 13.9, 6.2, 1.4 Hz), 3.12−3.18 (m, 2H), 3.02−3.08 (m, 1H), 2.65−2.71 (m, 1H), 2.53−2.60 (m, 1H), 2.40−2.53 (m, 2H), 2.29−2.37 (m, 1H), 1.95−2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 209.6 (s), 134.6 (d), 134.3 (d), 117.9 (t), 116.9 (t), 69.9 (d), 56.1 (t), 47.1 (t), 38.0 (t), 31.2 (t), 23.9 (t); IR (neat, cm^{-1}) 2936, 1695, 1450, 1290, 997, 927; MS (EI) 179 [M^+]; HRMS (EI) calcd for $C_{11}H_{17}NO$ 179.1310, found 179.1313.

3,4-Diallyl-2-morpholinone: colorless oil (91% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.80−5.91 (m, 2H), 5.09−5.28 (m, 4H), 4.29−4.38 (m, 2H), 3.36−3.43 (m, 2H), 2.93−3.05 (m, 2H), 2.68−2.72 (m, 1H), 2.55−2.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 170.1 (s), 133.5 (d), 133.4 (d), 118.8 (t), 117.9 (t), 67.7 (t), 64.2 (d), 57.0 (t), 46.8 (t), 35.0 (t); IR (neat, cm^{-1}) 2965, 2824, 1732, 1323, 1203, 1065, 921; MS (EI) 181 [M^+]; HRMS (EI) calcd for $C_{10}H_{15}NO_2$ 181.1102, found 181.1108.

***N*-Benzyl-2-allyl-3-pyrrolidinone:** colorless oil (92% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.25−7.34 (m, 5H), 5.76−5.87 (m, 1H), 5.04−5.14 (m, 2H), 4.15 (d, 1H, J = 12.9 Hz), 3.32(d, 1H, J = 12.9 Hz), 3.13−3.19 (m, 1H), 2.67 (t, 1H, J = 4.5 Hz), 2.49−2.56 (m, 2H), 2.24−2.39 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 215.2 (s), 137.4 (s), 134.1 (d), 129.0 (d), 128.3 (d), 127.3 (d), 117.2 (t), 69.1 (d), 58.5 (t), 48.7 (t), 36.9 (t), 33.0 (t); IR (neat, cm^{-1}) 3036, 2868, 1637, 1362, 1219, 698; MS (EI) 174 [$M^+ - C_3H_5$]; HRMS (EI) calcd for $C_{11}H_{12}NO$ 174.0918, found 174.0913.

Preparation of *N*-Benzyl-*N*-(4-benzyloxy)but-2-enylamine. To a solution of *O*-monobenzyl *cis*-2-butenediol (5.3 g, 30 mmol) and Et_3N (5 mL, 36 mmol) in CH_2Cl_2 (50 mL) was added methylsulfonyl chloride (2.8 mL, 36 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 2 h. The resultant mixture was diluted with CH_2Cl_2 (100 mL) and washed successively with water (20 mL) and brine (20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness. The residue was dissolved in THF (20 mL) and added via a funnel to a solution of benzylamine (8 mL, 75 mmol) and Et_3N (8.3 mL, 60 mmol) in THF (80 mL) at 0 °C. After the reaction mixture was stirred at room temperature for 4 h, the solvent was removed in vacuo. The residue was dissolved in Et_2O (200 mL) and washed successively with water (20 mL) and brine (20 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by flash column chromatography to give the product as a colorless liquid (6.7 g, 84% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.22−7.32 (m, 10H), 5.71−5.73 (m, 2H), 4.48 (s, 2H), 4.03 (d, 2H, J = 4.7 Hz), 3.74 (s, 2H), 3.26 (d, 2H, J = 4.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 140.0 (s), 138.1 (s), 131.6 (d), 128.3 (d), 128.2 (d), 128.0 (d), 127.7 (d), 127.5 (d), 126.9 (d), 72.2 (t), 65.6 (t), 53.3 (t), 45.7 (t); IR (neat, cm^{-1}) 3028, 2861, 1448, 1078, 736, 697; MS (EI) 267 [M^+]; HRMS (EI) calcd for $C_{18}H_{21}NO$ 267.1623, found 267.1619.

Preparation of 4-[*N*-Benzyl-*N*-(4-benzyloxy)but-2-enylamino]-1-diazo-2-butanone (7). To a solution of *N*-benzyl-*N*-(4-benzyloxy)but-2-enylamine (4.27 g, 16 mmol) and Et_3N (2.5 mL, 18 mmol) in EtOAc (50 mL) was added 4-bromo-1-diazobutan-2-one (3.15 g, 18 mmol). The reaction mixture was stirred at room temperature for 5 h. The mixture was diluted with a saturated solution of $NaHCO_3$ (20 mL) and extracted with Et_2O (3 × 50 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous K_2CO_3, and concentrated to dryness. The residue was purified by flash column chromatography to give a yellow oil (4.76 g, 82% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.22−7.33 (m, 10H), 5.67−5.79 (m, 2H), 5.18 (br, 1H), 4.47 (s, 2H), 4.02 (d, 2H, J = 5.4 Hz), 3.54 (s, 2H), 3.07 (d, 2H, J = 6.0 Hz), 2.77 (t, 2H, J = 7.0 Hz), 2.43 (t, 2H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 193.8 (s), 138.9 (s), 138.1 (s), 130.1 (d), 129.1 (d), 128.8 (d), 128.3 (d), 128.2 (d), 127.7 (d), 127.6 (d), 127.0 (d), 72.3 (t), 65.7 (t), 58.2 (t), 54.4 (d), 50.4 (t), 49.4 (t), 38.9 (t); IR (neat, cm^{-1}) 3036, 2855, 2103, 1637, 1453, 1359, 1078, 739, 698; MS (EI) 335 [$M^+ - N_2$]; HRMS (EI) calcd for $C_{22}H_{25}NO_2$ 335.1885, found 335.1884.

Preparation of *N*-Benzyl-2-(1-benzyloxymethyl)allyl-3-pyrrolidinone (8). To a solution of [Ru^{II}(TTP)(CO)] (8 mg, 10 μmol) in toluene (10 mL) was added dropwise a solution of diazo compound 4-[*N*-Benzyl-*N*-(4-benzyloxy)but-2-enylamino]-1-diazo-2-butanone (**7**, 363 mg, 1 mmol) in toluene (10 mL) via a syringe pump over 2 h at 50 °C. On completion, the reaction mixture was stirred for an additional 30 min. The solvent was removed under reduced pressure, and the crude residue was analyzed by ^{1}H NMR to reveal a mixture of two diastereomers in a ratio of 1.1:1. Purification of the crude mixture by silica gel column chromatography resulted in some epimerization and gave the product as a mixture of isomers in a ratio of 2.5:1 (285 mg, 85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.22−7.33 (m, 35H), 6.06−6.15 (m, 1H), 5.75−5.84 (m, 2.5H), 5.11−5.20 (m, 7H), 4.45−4.55 (m, 7H), 4.16 (t, 3.5H, J = 11.5 Hz), 3.93 (t, 2.5H, J = 9.1 Hz), 3.61−3.69 (m, 4.5H), 3.36 (d, 1H, J = 13.4 Hz), 3.30 (d, 2.5H, J = 13.2 Hz), 3.06−3.16 (m, 3.5H), 3.04 (dd, 2.5H, J = 6.4, 1.2 Hz), 2.99 (d, 1H, J = 2.9 Hz), 2.88−2.92 (m, 3.5H), 2.22−2.34 (m, 10.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 215.6 (s), 215.3 (s), 138.3 (s), 138.2 (s), 138.1 (s), 137.7 (s), 136.5 (d), 136.1 (d), 128.8 (d), 128.6 (d), 128.3 (d), 127.5 (d), 127.4 (d), 127.3 (d), 127.1 (d), 117.5 (t), 117.2 (t), 72.9 (t), 72.8 (t), 70.3 (d), 70.1 (d), 70.0 (t), 69.6 (t), 59.8 (t), 59.1 (t), 49.2 (t), 48.8 (t), 45.6 (d), 43.8 (d), 37.4 (t), 37.1 (t); IR (neat, cm^{-1}) 3036, 2868, 1630, 1362, 1213, 1078, 748, 702; MS (EI) 335 [M^+]; HRMS (EI) calcd for $C_{22}H_{25}NO_2$ 335.1885, found 335.1882.

Preparation of *N*-Benzyl-2-(1-benzyloxymethyl)allyl-3-pyrrolidinol (9). To a solution of *N*-benzyl-2-(1-benzyloxymethyl)allyl-3-pyrrolidinone (1 g, 3 mmol) in MeOH (20 mL) was added $NaBH_4$ (113 mg, 3 mmol) in small portions at 0 °C. The reaction mixture was stirred at 0 °C for 2 h. The reaction was quenched with water at 0 °C and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine and dried over anhydrous potassium carbonate. After the solvent was removed under reduced pressure, the residue was purified by flash column chromatography to give the *syn*-isomer as the major diastereomer and the *anti*-isomer as the minor diastereomer. For the *syn*-isomer: colorless oil (700 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.20−7.36 (m, 10H), 6.15−6.23 (m, 1H), 5.11−5.1 6 (m, 2H), 4.57 (d, 2H, J = 1.0 Hz), 4.29−4.33 (m, 1H), 4.08 (d, 1H, J = 13.1 Hz), 3.92 (dd, 1H, J = 8.9, 7.2 Hz), 3.69 (dd, 1H, J = 8.9, 3.9 Hz), 3.44 (d, 1H, J = 7.6 Hz), 3.08 (d, 1H, J = 13.1 Hz), 2.88−2.95 (m, 2H), 2.62 (dd, 1H, J = 6.3, 4.1 Hz), 1.97−2.07 (m, 2H), 1.62−1.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 139.4 (s), 138.7 (d), 137.4 (s), 128.5 (d), 128.4 (d), 128.1 (d), 127.8 (d), 126.7 (d), 115.5 (t), 73.6 (t), 73.5 (d), 70.8 (t), 69.8 (d), 59.3 (t), 51.1 (t), 43.1 (d), 32.9 (t); IR (neat, cm^{-1}) 3372, 2868, 1610, 1448, 1354, 1091, 742, 694; MS (EI) 337 [M^+]; HRMS (EI) calcd for $C_{22}H_{27}NO_2$ 337.2041, found 337.2033. For the *anti*-isomer: colorless oil (280 mg 28% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.21−7.34 (m, 10H), 6.06−6.15 (m, 1H), 5.15−5.24 (m, 2H), 4.60 (d, 1H, J = 12.0 Hz), 4.53 (d, 1H, J = 12.0 Hz), 4.29 (br s, 1H), 4.04 (d, 1H, J = 13.2 Hz), 3.84 (dd, 1H, J = 9.1, 4.5 Hz), 3.64 (dd, 1H, J = 9.1, 5.6 Hz), 3.48 (br s, 1H), 3.20(d, 1H, J = 13.2 Hz), 2.98−3.01 (m, 1H), 2.78−2.87 (m, 1H), 2.67 (t, 1H, J = 5.8 Hz), 2.15 (q, 1H, J = 8.2 Hz), 1.94−2.05 (m, 2H), 1.62−1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 139.7 (s), 138.3 (d), 137.6 (s), 128.5 (d), 128.4 (d), 128.1 (d), 127.8 (d), 126.8 (d), 116.6 (t), 73.4 (t), 72.9 (d), 70.8 (t), 70.6 (d), 59.4 (t), 50.9 (t), 44. (d), 32.9 (t); IR (neat, cm^{-1}) 2915, 1684, 1443, 1005, 810, 729.

Preparation of *syn*-(±)-3-(*N*-Benzyl-3-benzyloxy-2-pyrrolidinyl)-4-benzyloxy-1-butanol (10). To a mixture of NaH (86 mg, 3.56 mmol, 60%) and THF (15 mL) was added a

solution of *syn*-(±)-*N*-benzyl-2-(1-benzyloxymethyl)allyl-3-pyrrolidinol (*syn*-**9**, 1 g, 2.97 mmol) in THF (10 mL) via a cannula at 0 °C. The reaction mixture was stirred for 1 h. After the mixture was cooled to 0 °C, benzyl bromide (0.56 g, 3.27 mmol) was added, and the reaction mixture was stirred at room temperature for an additional 12 h. The reaction was quenched with water at 0 °C and extracted with Et_2O (3 × 40 mL). The combined organic layers were washed with brine, dried over anhydrous K_2CO_3, filtered, and concentrated to dryness. The residue was dissolved in dry THF (10 mL), and to this solution was added 9-BBN (12 mL, 5.94 mmol, 0.5 M in THF) at 0 °C. The reaction mixture was refluxed for 5 h and cooled to 0 °C. EtOH (8 mL) was added slowly followed by an aqueous solution of 3 M NaOH (6 mL) and a 30% aqueous solution of H_2O_2 (6 mL). After 10 min at 0 °C, the solution was allowed to warm to room temperature over 3 h. The mixture was poured into water (30 mL) and extracted with Et_2O (5 × 80 mL). The combined organic extracts were washed with brine, dried by anhydrous K_2CO_3, and filtered. After solvent removal, the residue was purified by flash column chromatography to give a colorless oil (1.14 g, 86% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.22−7.36 (m, 15H), 4.39−4.53 (m, 3H), 4.23 (d, 1H, J = 11.8 Hz), 4.03−4.09 (m, 2H), 3.55−3.70 (m, 4H), 3.19 (d, 1H, J = 12.9 Hz), 2.94−3.00 (m, 1H), 2.76−2.80 (m, 1H), 2.23−2.32 (m, 2H), 2.09−2.18 (m, 1H), 1.94−2.04 (m, 1H), 1.77−1.86 (m, 1H), 1.65−1.72 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 138.3 (s), 138.2 (s), 138.0 (s), 129.2 (d), 128.4 (d), 128.3 (d), 128.2 (d), 127.7 (d), 127.6 (d), 127.5 (d), 127.4 (d), 127.1 (d), 80.1 (d), 73.2 (t), 73.1 (t), 71.1 (t), 67.6 (d), 62.9 (t), 59.5 (t), 50.8 (t), 40.1 (d), 33.5 (t), 30.4 (t); IR (neat, cm^{-1}) 2936, 1453, 1354, 1099, 734, 697; MS (EI) 445 [M$^+$]; HRMS (EI) calcd for $C_{29}H_{35}NO_3$ 445.2617, found 445.2612.

Preparation of *cis*-(±)-1-Benzyloxy-7-benzyloxymethylhexahydropyrrolizine (11). To a stirred suspension of *cis*-(±)-3-(*N*-benzyl-3-benzyloxy-2-pyrrolidinyl)-4-benzyloxy-1-butanol (60 mg, 135 μmol) and 10% Pd/C (60 mg) in dry MeOH (5 mL) was added anhydrous ammonium formate (85 mg, 1.35 mmol) in a single portion. The reaction mixture was refluxed for 2 h and then cooled to room temperature. To this solution was added anhydrous K_2CO_3 (67 mg, 0.68 mmol). The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was filtered over a short silica gel column and washed with a mixture of $CHCl_3$ and MeOH (50 mL, $CHCl_3$/MeOH = 5:1). After solvent removal, the residue was dissolved in dry DMF (5 mL). To this solution were added PPh_3 (70 mg, 0.27 mmol), dry CCl_4 (0.026 mL, 0.27 mmol), and dry Et_3N (0.037 mL, 0.27 mmol). The reaction mixture was stirred at room temperature for 6 h and quenched with MeOH (5 mL). After 30 min, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to give a colorless oil (38 mg, 84% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.17−7.37 (m, 10H), 4.50 (d, 1H, J = 12.1 Hz), 4.43 (d, 1H, J = 11.2 Hz), 4.36 (d, 1H, J = 12.1 Hz), 4.16−4.25 (m, 3H), 3.99 (dd, 1H, J = 10.8, 8.0 Hz), 3.77 (t, 1H, J = 9.0 Hz), 3.63−3.70 (m, 2H), 2.95−3.10 (m, 2H), 2.82−2.88 (m, 1H), 2.27 (dd, 1H, J = 14.0, 6.0 Hz), 1.98−2.09 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 137.8 (s), 136.6 (s), 128.6 (d), 128.4 (d), 128.2 (d), 127.8 d), 127.74 (d), 127.72 (d), 78.8 (d), 73.1 (t), 71.4 (d), 71.2 (t), 67.9 (t), 54.6 (t), 53.7 (t), 40.4 (d), 31.5 (t), 28.3 (t); IR (neat, cm^{-1}) 3435, 2922, 1454, 1086, 743, 699; MS (EI) 337 [M$^+$]; HRMS (EI) calcd for $C_{22}H_{27}NO_2$ 337.2041, found 337.2043.

(±)-Platynecine. A mixture of *cis*-(±)-1-benzyloxy-7-benzyloxymethylhexahydropyrrolizine (20 mg, 59 μmol) and palladium chloride (20 mg) in MeOH was stirred at room temperature under a hydrogen atmosphere for 18 h. To this solution was added anhydrous K_2CO_3 (10 mg). The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was filtered through Celite. After removal of solvent, the residue was purified by basic alumina (grade II−III) flash chromatography with CH_3Cl/MeOH (9:1 v/v) as the eluant to give (±)-platynecine as a white solid (8.8 mg, 95% yield): mp 140−142 °C; ^{1}H NMR (500 MHz, CD_3OD) δ_H 4.23 (m, 1H), 3.93 (d, 2H, J = 5.2 Hz), 3.26 (dd, 1H, J = 8.0, 3.2 Hz), 3.18−3.22 (m, 1H), 3.06−3.11 (m, 1H), 2.83−2.87 (m, 1H), 2.75−2.81 (m, 1H), 2.39−2.45 (m, 1H), 1.94−2.02 (m, 1H), 1.84−1.89 (m, 2H), 1.68−1.74 (m, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ_C 73.1 (d), 72.6 (d), 61.6 (t), 56.5 (t), 54.8 (t), 45.0 (d), 37.3 (t), 28.8 (t); IR (KBr, cm^{-1}) 3348, 2895, 1126, 1012, 751; MS (EI) 157 [M$^+$]; HRMS (EI) calcd for $C_8H_{15}NO_2$ 157.1103, found 157.1104.

Acknowledgment. This work is supported by the Area of Excellence Scheme (AoE-P10/01) established under the University Grants Committee (HKSAR, China), The University of Hong Kong (University Development Fund), and the Research Grants Council (HKU7026/03P), HKSAR, China. We are grateful to Prof. Ge Lin (Department of Pharmacology, Chinese University of Hong Kong) for providing natural (−)-platynecine for NMR studies.

Supporting Information Available: Experimental details for preparation of diazo compounds **1a**,**b**, **3a**−**c**, and 4-(*N*-allyl-*N*-benzylamino)-1-diazo-2-butanone; ^{1}H, ^{13}C NMR spectra of all the key substrates and reaction products described in this work; COSEY and NOSEY spectra of *cis*-/*trans*-(±)-**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049540V