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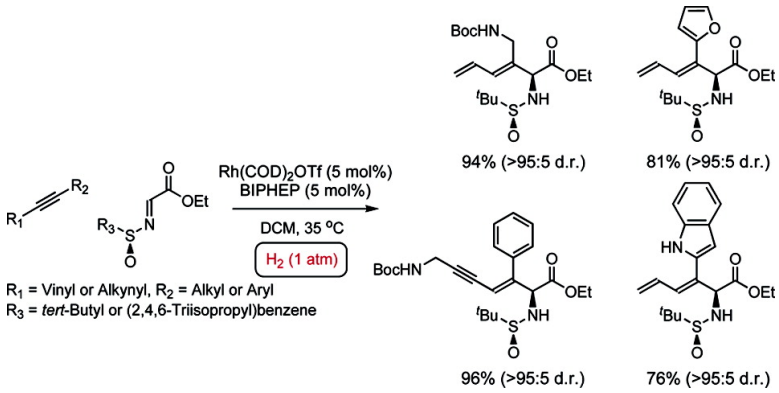

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Hydrogen-Mediated Reductive Coupling of Conjugated Alkynes with Ethyl (*N*-Sulfinyl)iminoacetates: Synthesis of Unnatural α-Amino Acids via Rhodium-Catalyzed C−C Bond Forming Hydrogenation

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Abstract: Rhodium-catalyzed hydrogenation of 1,3-enynes **1a**−**8a** and 1,3-diynes **9a**−**13a** at ambient temperature and pressure in the presence of ethyl (*N*-*tert*-butanesulfinyl)iminoacetate and ethyl (*N*-2,4,6-triisopropylbenzenesulfinyl)iminoacetates, respectively, results in reductive coupling to afford unsaturated α-amino acid esters **1b**−**13b** in good to excellent yields with exceptional levels of regio- and stereocontrol. Further hydrogenation of the diene containing α-amino acid esters **1b**−**8b** using Wilkinson's catalyst at ambient temperature and pressure results in regioselective reduction to afford the β,γ-unsaturated α-amino acid esters **1c**−**8c** in good to excellent yields. Exhaustive hydrogenation of the unsaturated side chains of the Boc- and Fmoc-protected derivatives of enyne and diyne coupling products **14b**−**16b** occurs in excellent yield using Crabtree's catalyst at ambient temperature and pressure providing the α-amino acid esters **14d**−**16d**, which possess saturated side chains. Finally, cross-metathesis of the Boc-protected reductive coupling product **14b** with *cis*-1,4-diacetoxy-2-butene proceeds readily to afford the allylic acetate **14e**. Isotopic labeling studies that involve reductive coupling of enyne **1a** and diyne **9a** under an atmosphere of elemental deuterium corroborate a catalytic mechanism in which oxidative coupling of the alkyne and imine residues is followed by hydrogenolytic cleavage of the resulting metallacycle. A stereochemical model accounting for the observed sense of asymmetric induction is provided. These studies represent the first use of imines as electrophilic partners in hydrogen-mediated reductive carbon−carbon bond formation.

Introduction

Reductive methods for catalytic C−C bond formation have emerged as the subject of intensive investigation.[1−7] The direct catalytic reductive coupling of alkenes,[1] alkynes,[2] allenes,[3] enones,[4,6a−d] 1,3-dienes,[2,6e] 1,3-enynes,[5,6f] and 1,3-diynes[6g] to carbonyl partners have been reported. Inspired by the prospect of developing completely atom economical variants of such transformations, hydrogen-mediated C−C bond formation has become the focus of research in our lab.[6,7] Hydrogen-mediated reductive couplings to carbonyl partners using conjugated enones,[6a−d] dienes,[6e] enynes,[6f] and diynes[6g] have been achieved, as well as hydrogen-mediated reductive cyclizations of 1,6-diynes and 1,6-enynes.[6h,i] These studies are among the first examples of hydrogen-mediated C−C bond formation that proceed in absence of carbon mononoxide.[8,9]

To further broaden this emergent class of reductive couplings, the use of imines as electrophilic partners in hydrogen-mediated C−C bond formation was explored. *Whereas three component couplings of alkynes, organoboranes, and imines are reported,*[10] *simple hydrometallative variants are unknown.* Here, we disclose that hydrogenation of 1,3-enynes or 1,3-diynes in the

(1) Alkenes: (a) Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1995**, *117*, 6785. (b) Crowe, W. E.; Rachita, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6787. (c) Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 3182.

(2) Alkynes and Dienes (review articles): (a) Montgomery, J. *Acc. Chem. Res.* **2000**, *33*, 467. (b) Montgomery, J.; Amarashinghe, K. K. D.; Chowdhury, S. K.; Oblinger, E.; Seo, J.; Savchenko, A. V. *Pure Appl. Chem.* **2002**, *74*, 129. (c) Ikeda, S.-I. *Angew. Chem., Int. Ed.* **2003**, *42*, 5120. (d) Montgomery, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3890.

(3) Allenes: (a) Chevliakov, M. V.; Montgomery, J. *J. Am. Chem. Soc.* **1999**, *121*, 11139. (b) Montgomery, J.; Song, M. *Org. Lett.* **2002**, *4*, 4009. (c) Amarasinghe, K. K. D.; Montgomery, J. *J. Am. Chem. Soc.* **2002**, *124*, 9366.

(4) Enones (review articles): (a) Huddleston, R. R.; Krische M. J. *Synlett* **2003**, 12. (b) Jang, H.-Y.; Krische, M. J. *Eur. J. Org. Chem.* **2004**, 3953.

(5) 1,3-Enynes: Miller, K. M.; Luanphaisarnnont, T.; Molinaro, C.; Jamison, T. F. *J. Am. Chem. Soc.* **2004**, *126*, 4130.

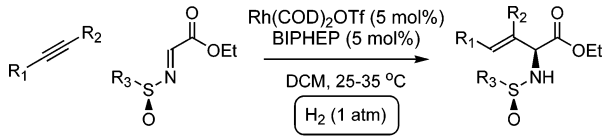
(6) For hydrogen-mediated C−C bond formations developed in our lab, see: (a) Jang, H.-Y.; Huddleston, R. R.; Krische, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 15156. (b) Huddleston, R. R.; Krische, M. J. *Org. Lett.* **2003**, *5*, 1143. (c) Koech, P. K.; Krische, M. J. *Org. Lett.* **2004**, *6*, 691. (d) Marriner, G. A.; Garner, S. A.; Jang, H.-Y.; Krische, M. J. *J. Org. Chem.* **2004**, *69*, 1380. (e) Jang, H.-Y.; Huddleston, R. R.; Krische, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 4074. (f) Jang, H.-Y.; Huddleston, R. R.; Krische, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 4664. (g) Huddleston, R. R.; Jang, H.-Y.; Krische, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 11488. (h) Jang, H.-Y.; Krische, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 7875. (i) Jang, H.-Y.; Hughes, F. W.; Gong, H.; Zhang, J.; Brodbelt, J. S.; Krische, M. J. *Am. Chem. Soc.* **2005**, *127*, 6174.

(7) For a review, see: Jang, H.-Y.; Krische, M. J. *Acc. Chem. Res.* **2004**, *37*, 653.

(8) Prior to our work, two isolated studies on hydrogen-mediated C−C bond formation under CO-free conditions were reported: (a) Molander, G. A.; Hoberg, J. O *J. Am. Chem. Soc.* **1992**, *114*, 3123. (b) Kokubo, K.; Miura, M.; Nomura, M. *Organometallics* **1995**, *14*, 4521.

(9) Products of C−C bond formation have been observed as side products in catalytic hydrogenation on rare occasion: (a) Moyes, R. B.; Walker, D. W.; Wells, P. B.; Whan, D. A.; Irvine, E. A. *Special Pub. Royal. Soc. Chem.* **1992**, *114*, 207. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizzi, F.; Zanobini, F. Frediani, P. *Organometallics* **1989**, *8*, 2080.

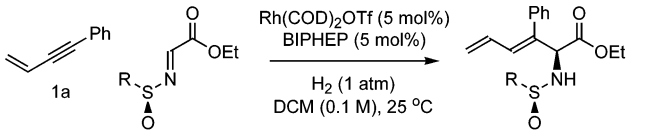
presence of ethyl (*N*-sulfinyl)iminoacetates[11,12] enables highly regio- and stereoselective reductive coupling to afford unnatural diene- and enyne-containing α-amino acid esters.[13]



Results and Discussion

Reductive Coupling of Conjugated Alkynes and *N*-Sulfinyl Iminoacetates. Initial efforts focused on the hydrogen-mediated coupling of 1,3-enyne **1a** (200 mol %) to assorted (*N*-sulfinyl)-iminoacetates (100 mol %) at ambient pressure and temperature in dichloromethane (0.1 M). The rhodium precatalyst was generated in situ from $Rh(COD)_2OTf$ (5 mol %) and BIPHEP (5 mol %). It was found that hydrogenation of **1a** in the presence of ethyl (*N*-*para*-toluenesulfinyl)iminoacetate (100 mol %) provides the desired reductive coupling product in 95% yield, but with poor control of diastereoselectivity. A further decrease in stereoselection is observed in conjunction with the use of the corresponding mesityl derivative. However, hydrogenation of 1,3-enyne **1a** in the presence of ethyl (*N*-*tert*-butanesulfinyl)-iminoacetate furnishes reductive coupling product **1b** in 55% yield as a single regio- and stereoisomer. When the reaction is conducted at higher concentration (0.3 M), the yield is increased to 92% without loss of selectivity. Finally, at a slightly elevated temperature (35 °C), **1b** is obtained in 99% yield as a single diastereomer (Scheme 1).

Scheme 1. Optimization of the Hydrogen-Mediated Reductive Coupling of 1,3-Enyne **1a** to Various Ethyl (*N*-Sulfinyl)iminoacetates

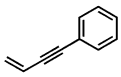
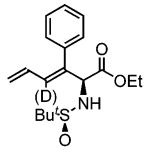
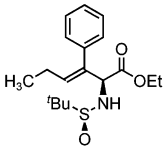
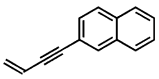
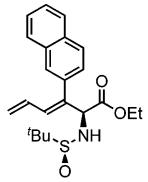
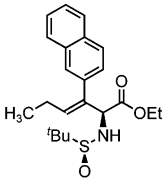
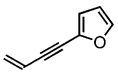
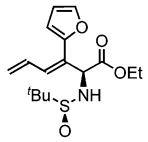
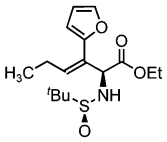
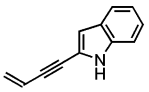
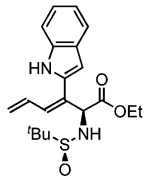
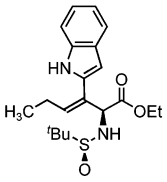
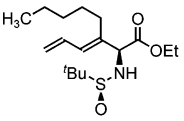
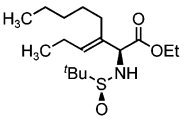
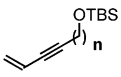
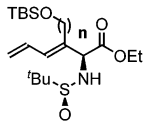
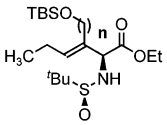
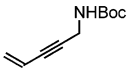
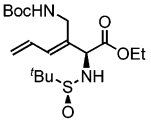
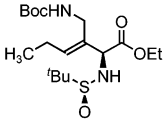


R = Tolyl, 95% (3.4:1)
R = Mesityl, 96% (1.3:1)
R = *tert*-Butyl, 55% (>95:5 d.r.)
R = *tert*-Butyl, 92% (>95:5 d.r.) at 0.3 M
R = *tert*-Butyl, 99% (>95:5 d.r.) at 0.3 M at 35 °C

The use of ethyl (*N*-*tert*-butanesulfinyl)iminoacetate under these conditions proved to be general across a range of structurally diverse enynes **1a**−**8a**. In all cases examined, >95:5 regio- and diastereoselectivity is observed (Table 1). The chemoselectivity of the hydrogen-mediated coupling is underscored by the fact that over-reduction of the diene-containing products **1b**−**8b** is not observed. The regio- and stereochemical assignment of reductive coupling products **1b**−**8b** is described in the Supporting Information and is based upon crystallographic analysis of a derivative of **4b**.

The hydrogen-mediated reductive coupling of 1,3-diynes to (*N*-sulfinyl)iminoacetates was explored next. For the purpose of optimization, the rhodium-catalyzed hydrogenation of 1-phenyl-1,3-pentadiyne **9a** (200 mol %) in the presence of assorted (*N*-

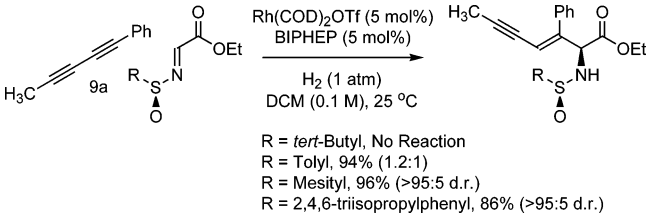
Table 1. Hydrogen-Mediated Reductive Coupling of 1,3-Enynes **1a**−**8a** and Ethyl (*N*-*tert*-Butanesulfinyl)iminoacetates and Regioselective Hydrogenation of Coupling Products **1b**−**8b** to Provide β,γ-Unsaturated α-Amino Acid Esters **1c**−**8c**[a]

Entry	Substrate	Coupling Product	*mono*-Reduction Product
1			
	1a	**1b, 99% (>95:5 d.r.)**	**1c, 74%**
2			
	2a	**2b, 96% (>95:5 d.r.)**	**2c, 70%**
3			
	3a	**3b, 81% (>95:5 d.r.)**	**3c, 79%**
4			
	4a	**4b, 76% (>95:5 d.r.)**	**4c, 81%**
5			
	5a	**5b, 66% (>95:5 d.r.)**	**5c, 93%**
6			
	6a, n = 1 **7a, n = 2**	**6b, 68% (>95:5 d.r.)** **7b, 70% (>95:5 d.r.)**	**6c, 80%** **7c, 87%**
7			
	8a	**8b, 94% (>95:5 d.r.)**	**8c, 81%**

[a] The reductive coupling of **1a**−**8a** was in accordance with the reaction conditions cited in Scheme 1, but at 0.3 M concentration and at 35 °C. The reductive couplings were complete in less than 8 h. The partial hydrogenation of **1b**−**8b** to provide β,γ-unsaturated amino acid esters **1c**−**8c** was performed at ambient pressure and temperature using Wilkinson's catalyst in toluene solvent. See Experimental Section for detailed reaction conditions.

(10) (a) Patel, S. J.; Jamison, T. F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1364. (b) Patel, S. J.; Jamison, T. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3941.
(11) For recent reviews encompassing the use of *N*-*tert*-butanesulfinyl imines in asymmetric synthesis, see: (a) Zhou, P.; Chen, B.-C.; Davis, F. *Tetrahedron* **2004**, *60*, 8003. (b) Ellman, J. A.; Owens, T. D.; Tang, T. P. *Acc. Chem. Res.* **2002**, *35*, 984.
(12) For recent examples of the use of *N*-sulfinyl imines in asymmetric synthesis, see: (a) Evans, J. W.; Fierman, M. B.; Miller, S. J.; Ellman, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 8134. (b) Davis, F. A.; Ramachandar, T.; Liu, H. *Org. Lett.* **2004**, *6*, 3393. (c) Han, Z.; Krishnamurthy, D.; Grover, P.; Fang, Q. K.; Senanayake, C. H. *J. Am. Chem. Soc.* **2002**, *124*, 7880.
(13) For a review encompassing the asymmetric synthesis of amino acids through additions to *N*-*tert*-butanesulfinyl imines, see: Davis, F.; Chen, B.-C. *Chem. Soc. Rev.* **1998**, *27*, 13.

Scheme 2. Optimization of the Hydrogen-Mediated Reductive Coupling of 1,3-Diyne **9a** to Various Ethyl (*N*-Sulfinyl)iminoacetates

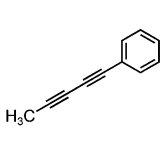
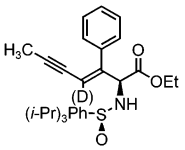
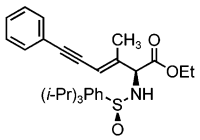
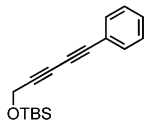
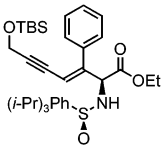
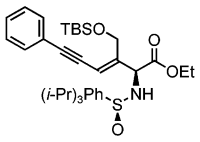
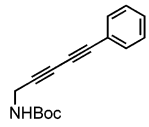
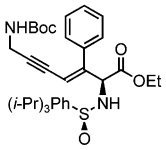
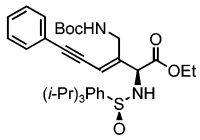
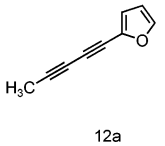
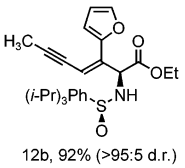
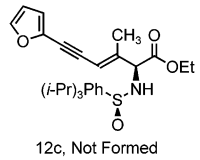
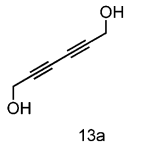
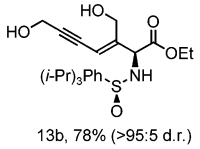


sulfinyl)iminoacetates (100 mol %) at ambient pressure and temperature in dichloromethane (0.1 M) was studied. Interestingly, under conditions established for the reductive coupling of enynes **1a**−**8a**, coupling of diyne **9a** to ethyl (*N*-*tert*-butanesulfinyl)iminoacetate is not observed, presumably due to the diminished electrophilicity of the alkyl substituted sufinyl imine. In contrast, hydrogenation of diyne **9a** in the presence of (*N*-*para*-toluenesulfinyl)iminoacetate delivers a 94% yield of the desired coupling product **9b** as a 1.2:1 mixture of diastereomers. Remarkably, **9b** appears as a single regioisomer, as coupling occurs exclusively at the aromatic terminus of the conjugated diyne **9a**. Upon use of the corresponding mesityl derivative, coupling product **9b** is obtained in 96% yield with >95:5 regio- and diastereocontrol. Comparable results were obtained using ethyl *N*-(2,4,6-triisopropylbenzenesulfinyl)-iminoacetate, which was adopted as the standard coupling partner due to its enhanced chromatographic stability and, hence, ease of purification (Scheme 2).

The coupling of 1,3-diynes **9a**−**13a** to ethyl *N*-(2,4,6-triisopropylbenzenesulfinyl)iminoacetate under the aforementioned conditions provides the enyne-containing α-amino acid esters **9b**−**13b** as single regio- and stereoisomers in good to excellent yield (Table 2). The regioisomeric products **9c**−**12c** are not observed. The stereochemical assignment of **9b**−**13b** is made in analogy to that established via single-crystal X-ray diffraction analysis for a derivative of **4b**, as described in the Supporting Information.

Elaboration of Reductive Coupling Products. In a preliminary effort to explore further manipulation of the coupling products, compound **1b** was exposed to Wilkinson's catalyst at ambient pressure and temperature.[5,14] In the event, regioselective hydrogenation of the terminal alkene occurs cleanly to afford the β,γ-unsaturated α-amino esters **1c** in 74% yield, without over-reduction to the fully saturated derivative **1d**. These regioselective hydrogenation conditions were applied to all enyne coupling products **1b**−**8b**. The β,γ-unsaturated α-amino esters **1c**−**8c** were obtained in 70−93% yield (Table 1). Exhaustive hydrogenation of the diene side chain using Crabtree's catalyst was explored next.[15] Here, the *N*-*tert*-butanesulfinyl residue must be exchanged for a carbamate protecting group, as in **14b** and **15b**. Hydrogenation of **14b** using Crabtree's catalyst at ambient pressure and temperature provides the fully saturated Boc-protected amino acid ester **14d** in 99% as a 2:1 mixture of diastereomers. Under identical conditions, the saturated Fmoc-protected amino acid ester **14d** is obtained in 95% as a 2.4:1 mixture of diastereomers. Conversion of **9b** to the corresponding Boc-derivative **16b** followed by exhaustive hydrogenation of the enyne side chain using Crabtree's catalyst provides the saturated amino acid ester **16d** in excellent yield. The relative stereochemistry of **14d**−**16d** was not assigned (Scheme 3).

Table 2. Hydrogen-Mediated Reductive Coupling of 1,3-Diynes **9a**−**13a** and Ethyl *N*-(2,4,6-Triisopropylbenzenesulfinyl)-iminoacetate[a]

Entry	Substrate	Regioisomeric Coupling Products	
1	 9a	 9b, 86% (>95:5 d.r.)	 9c, Not Formed
2	 10a	 10b, 91% (>95:5 d.r.)	 10c, Not Formed
3	 11a	 11b, 96% (>95:5 d.r.)	 11c, Not Formed
4	 12a	 12b, 92% (>95:5 d.r.)	 12c, Not Formed
5	 13a	 13b, 78% (>95:5 d.r.)	N/A

[a] The reductive coupling of **9a**−**12a** was performed at ambient temperature, in accordance with the reaction conditions cited in Scheme 2. The reductive coupling of **13a** was performed at 35 °C in DCM−THF (2:1). The reductive couplings were complete in less than 2 h. See Experimental Section for detailed reaction conditions.

Whereas enynes possessing vinylic substitution couple readily to glyoxal partners under hydrogenation conditions,[6f] the present enyne-iminoacetate couplings do not tolerate vinylic substitution. Hence, functionalization of the diene terminus via cross-metathesis was explored. Gratifyingly, exposure of the Boc-protected reductive coupling product **14b** to *cis*-1,4-diacetoxy-2-butene in the presence of substoichiometric quantities of the second generation Grubb's catalyst provides the allylic acetate **14e** in 80% yield as a 10:1 mixture of alkene stereoisomers (Scheme 4).[16]

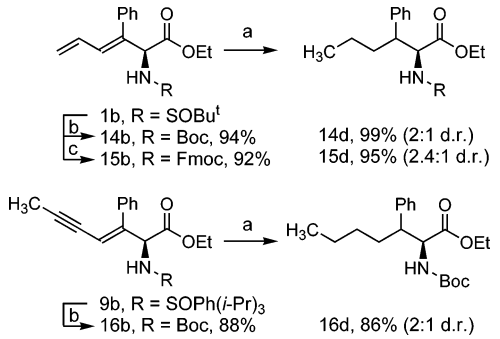
Catalytic Mechanism and Model for Stereoinduction. Under an atmosphere of elemental deuterium, rhodium-catalyzed reductive coupling of **1a** and ethyl (*N*-*tert*-butanesulfinyl)-

(14) The partial hydrogenation of conjugated dienes under similar conditions has been reported: Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 4450.

(15) For the exhaustive hydrogenation of conjugated dienes catalyzed by iridium, see: Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 14212 and references therein.

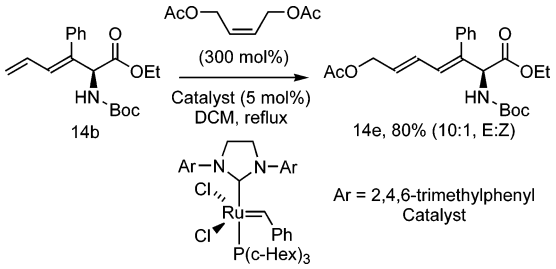
(16) Funk, T. W.; Efskind, J.; Grubbs, R. H. *Org. Lett.* **2005**, *7*, 187.

Scheme 3. Exhaustive Hydrogenation of the Diene and Enyne Side Chains of Coupling Product **1b**, **14b**, and **15b** and Exhaustive Hydrogenation of the Enyne Side Chain of **16b**[a]



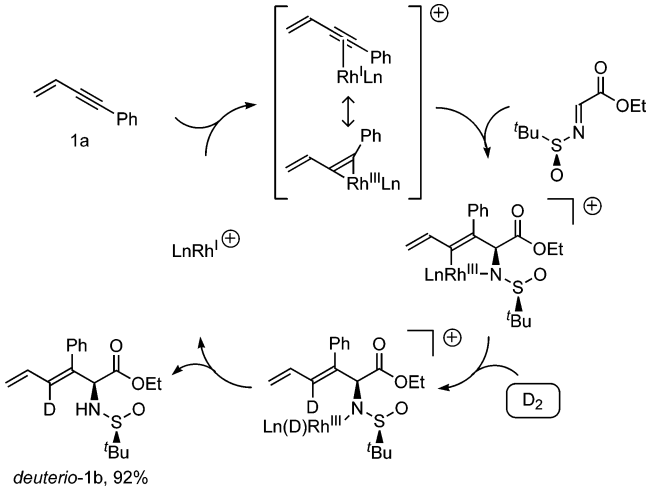
[a] Reagents: (a) $Ir(COD)(Pyr)[P(c\text{-}Hex)_3]PF_6$ (5 mol %), H_2 (1 atm), DCM (0.1 M), 25 °C. (b) HCl (500 mol %), MeOH (0.01 M), 25 °C, then *i*-Pr_2NEt (300 mol %), Boc_2O (150 mol %), DCM (0.01 M), 25 °C. (c) HCl (500 mol %), MeOH (0.01 M), 25 °C, then *i*-Pr_2NEt (300 mol %), Fmoc-OSu (150 mol %), DCM (0.01 M), 25 °C.

Scheme 4. Cross-Metathesis of **14b** To Afford Allylic Acetate **14e**

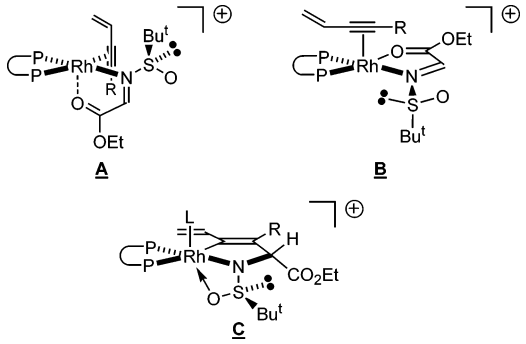


iminoacetate provides *mono*-deuterio-**1b**. Similarly, the reductive coupling of **9a** to ethyl *N*-(2,4,6-triisopropylbenzenesulfinyl)-iminoacetate under a deuterium atmosphere provides *mono*-deuterio-**9b**. These results are consistent with a catalytic mechanism involving alkyne-imine oxidative coupling followed by hydrogenolytic cleavage of the resulting metallacycle. An analogous mechanism for related hydrogen-mediated carbocyclizations catalyzed by rhodium has been inferred on the basis of more detailed studies.[6i] The hydrogenolytic cleavage of the metallacyclic intermediate likely involves hydrogen activation via σ-bond metathesis. An increasing body of evidence supports participation of organorhodium(III) intermediates in σ-bond metathesis pathways,[17] including reactions with hydrogen.[17c] Factors dictating the regiochemistry of C−C bond formation remain uncertain. However, previously disclosed competition experiments[6f] suggest back-bonding from low valent rhodium to the bound alkyne, which enables generation of a nucleophilic metallacyclopropene, may play a decisive role.[18] Nucleophilic activation of alkynes through complexation by low valent early transition metals is well established.[19] For low valent late transition metals, this pattern of reactivity may represent a driving force that assists the oxidative coupling of alkynes to C=O π-bonds, as in the Ni(0)-catalyzed reductive coupling of

Scheme 5. Proposed Catalytic Mechanism as Corroborated by Deuterium Labeling



Scheme 6. Proposed Models for Asymmetric Induction



alkynes and aldehydes.[2,3] The modest nucleophilic character of a Rh(I)−alkyne complex may account for the requirement of highly activated electrophilic partners such as iminoacetates and, as previously reported, glyoxals (Scheme 5).[6f,6g]

Given the observed sense of stereoinduction, two stereochemical models **A** and **B** are proposed. In each case, the iminoacetate is bound to rhodium(I) in a five-membered chelate. This mode of coordination has been established for late transition metal complexes of α-iminoketones and α-iminoesters.[20] Upon oxidative coupling, the alkyne is delivered to the less encumbered π-face of the imine, as dictated by the anticipated conformational preference of the *N*-sulfinyl imine.[21] The resulting metallacycle **C** possesses an unoccupied coordinate site **L**, which should facilitate subsequent hydrogen activation (Scheme 6).

Summary

In this account, the reductive coupling of conjugated alkynes and iminoacetates is achieved through catalytic hydrogenation, representing the first use of imines as electrophilic partners in simple hydrometallative reductive coupling. Good to excellent yields and exceptional levels of regiocontrol are observed. Moreover, the high levels of relative stereocontrol with respect

(17) For σ-bond metathesis involving Rh(III) intermediates, see: (a) Hartwig, J. F.; Cook, K. S.; Hapke, M.; Incarvito, C. D. Fan, Y.; Webster, C. E.; Hall, M. B. *J. Am. Chem. Soc.* **2005**, *127*, 2538. (b) Liu, C.; Widenhoefer, R. A. *Organometallics* **2002**, *21*, 5666. (c) Hutschka, F.; Dedieu, A.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1742.

(18) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939. (c) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783.

(19) The nucleophilic character of alkenes and alkynes bound to low valent titanium constitutes the basis of legion reductive C−C bond formations. For a review, see: Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835.

(20) Siebenlist, R.; Frühauf, H.-W.; Vrieze, K.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **2000**, *19*, 3016 and references therein. See also: Taggi, A. E.; Hafez, A. M.; Lectka, T. *Acc. Chem. Res.* **2003**, *36*, 10.

(21) For vinyl sulfoxides, a C=C−S−O dihedral angle of 0° is strongly preferred: (a) Tietze, L. F.; Schuffenhauer, A.; Schreiner, P. R. *J. Am. Chem. Soc.* **1998**, *120*, 7952. (b) Kahn, D.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7399.

to the *N*-sulfinyl moiety allow the absolute stereochemical course of the reductive coupling to be directed.

Initial studies on the elaboration of the reductive coupling products reveal that the unsaturated side chain of the diene-containing products **1b**−**8b** may be partially hydrogenated to afford the corresponding β,γ-unsaturated α-amino acid esters **1c**−**8c**. Exhaustive hydrogenation of both diene- and enyne-containing reductive couplings is possible, as demonstrated by the hydrogenation of compounds **14b**−**16b** to furnish **14d**−**16d**, which possess completely saturated side chains. Finally, as demonstrated by the conversion of **14b**−**14e**, cross-metathesis of the diene containing α-amino acid esters occurs in good yield.

The outcome of isotopic labeling studies, which involve the reductive coupling of enyne **1a** and diyne **9a** to iminoacetates under an atmosphere of elemental deuterium, are consistent with a catalytic mechanism involving oxidative coupling of the alkyne and imine residues followed by hydrogenolytic cleavage of the resulting metallacyclic intermediate. The requirement of π-unsaturated reactants in the form of activated imines and conjugated alkynes suggest alkyne coordination by low valent rhodium to form a weakly nucleophilic metallocyclopropene. For low valent late transition metals, this pattern of reactivity may represent a driving force that assists the oxidative coupling of alkynes to C═O π-bonds.

Experimental Section

General. Anhydrous solvents were transferred by an oven-dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. Dichloromethane (DCM) was distilled from calcium hydride. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F_{254}). Preparative column chromatography employing silica gel was performed according to the method of Still. ^{1}H NMR spectra were recorded with a Varian Gemini (400 or 300 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling.

Representative Procedure for the Reductive Coupling of 1,3-Enynes and *N*-(*tert*-Butanesulfinyl)iminoacetate. To a solution of *N*-(*tert*-butanesulfinyl)iminoacetate (41 mg, 0.2 mmol, 100 mol %) and 3-buten-1-ynyl-benzene **1a** (50.9 mg, 0.4 mmol, 200 mol %) in DCM (0.67 mL, 0.3 M) at 35 °C was added $Rh(COD)_2OTf$ (4.7 mg, 0.01 mmol, 5 mol %) and BIPHEP (5.3 mg, 0.01 mmol, 5 mol %). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 35 °C under 1 atm of hydrogen until complete consumption of substrate, at which point the reaction mixture was evaporated onto silica gel and the product was purified by silica gel chromatography.

2-(2-Methyl-propane-2-sulfinylamino)-3-phenyl-hexa-3,5-dienoic Acid Ethyl Ester (1b). ^{1}H NMR (400 MHz, $CDCl_3$): 7.34−7.26 (m, 3H), 7.19−7.16 (m, 2H), 6.42 (d, J = 10.8 Hz, 1H), 6.30 (dt, J = 16.8, 10.4 Hz, 1H), 5.15 (dd, J = 10.0, 1.6 Hz, 1H), 5.14 (dd, J = 10.0, 1.6 Hz, 1H), 4.80 (d, J = 4.0 Hz, 1H), 4.34 (d, J = 4.0, 1H), 4.17 (q, J = 7.2 Hz, 2H), 1.19 (s, 9H), 1.18 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.0, 137.9, 137.0, 133.3, 132.6, 129.3, 128.0, 127.6, 120.1, 62.8, 62.0, 55.9, 22.5, 13.9. HRMS: Calcd for $C_{18}H_{26}N_1O_3S_1$ [M + 1] 336.1633, found 336.1632. FTIR (neat): 3285, 3072, 2980, 1738, 1602, 1494, 1474, 1444, 1366, 1296, 1256, 1219, 1184, 1076, 914, 851, 776 cm^{-1}.

2-(2-Methyl-propane-2-sulfinylamino)-3-naphthalen-2-yl-hexa-3,5-dienoic Acid Ethyl Ester (2b). ^{1}H NMR (400 MHz, $CDCl_3$): 7.84−7.78 (m, 3H), 7.66 (s, 1H), 7.51−7.46 (m, 2H), 7.30 (dd, J = 8.4, 1.6 Hz, 1H), 6.51 (d, J = 11.2 Hz, 2H), 6.35 (t, J = 10.4 Hz, 1H), 6.51 (d, J = 11.2 Hz, 1H), 6.30 (dt, J = 17.2, 10.4 Hz, 1H), 5.40 (dd, J = 16.8, 1.4 Hz, 1H), 5.16 (dd, J = 10.2, 1.4 Hz, 1H), 4.90 (d, J = 4.4 Hz, 1H), 4.41 (d, J = 4.0, 1H), 4.20−4.15 (m, 2H), 1.19 (s, 9H), 1.17 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.0, 137.9, 134.5, 133.3, 133.0, 132.9, 132.6, 128.5, 127.9, 127.6, 127.2, 126.2, 126.2, 120.3, 62.8, 62.1, 56.0, 22.5, 14.0. HRMS: Calcd for $C_{22}H_{28}N_1O_3S_1$ [M + 1] 386.1790, found 386.1786. FTIR (neat): 3283, 2979, 1733, 1473, 1366, 1258, 1219, 1184, 1075, 914, 859, 824, 751 cm^{-1}.

2-(2-Methyl-propane-2-sulfinylamino)-3-furan-2-yl-hexa-3,5-dienoic Acid Ethyl Ester (3b). ^{1}H NMR (400 MHz, $CDCl_3$): 7.42 (d, J = 1.2, 1H), 7.12 (dt, J = 17.6, 10.7, 1H), 6.42 (d, J = 3.2 Hz, 1H), 6.40−6.38 (m, 1H), 6.30 (d, J = 11.2 Hz, 1H), 5.46 (d, J = 8.4 Hz, 1H), 5.36 (dd, J = 10.0, 1.2 Hz, 1H), 4.80 (d, J = 3.2 Hz, 1H), 4.44 (d, J = 2.8 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.0, 150.8, 142.2, 133.4, 132.4, 125.9, 111.0, 110.8, 62.2, 61.4, 55.7, 22.4, 13.9. HRMS: Calcd for $C_{16}H_{24}N_1O_4S_1$ [M + 1] 326.1426, found 326.1426. FTIR (neat): 3287, 2980, 1737, 1467, 1366, 1260, 1224, 1114, 1072, 1021 cm^{-1}.

3-(1*H*-Indol-2-yl)-2-(2-methyl-propane-2-sulfinyl amino)-hexa-3,5-dienoic Acid Ethyl Ester (4b). ^{1}H NMR (400 MHz, $CDCl_3$): 8.90 (s, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.16 (td, J = 7.6, 1.1 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.90 (dt, J = 17.2, 10.6 Hz, 1H), 6.55 (d, J = 1.6 Hz, 1H), 6.48 (d, J = 10.8, 1H), 5.50 (d, J = 16.0 Hz, 1H), 5.33 (d, J = 10.0 Hz, 1H), 4.85 (d, J = 3.6, 1H), 4.46 (d, J = 3.2 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 1.20 (s, 9H), 1.11 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 172.2, 136.0, 134.8, 133.4, 133.2, 127.9, 127.8, 122.5, 122.0, 120.5, 120.0, 110.9, 105.2, 62.4, 61.8, 56.0, 22.5, 13.7. HRMS: Calcd for $C_{20}H_{27}N_2O_3S_1$ [M + 1] 375.1742, found 375.1747. FTIR (neat): 3274, 2978, 1731, 1455, 1404, 1366, 1224, 1056, 913, 850, 795, 783 cm^{-1}. Mp: 50−52 °C.

3-Allylidene-2-(2-methyl-propane-2-sulfinylamino)-octanoic Acid Ethyl Ester (5b). ^{1}H NMR (400 MHz, $CDCl_3$): 6.58 (dt, J = 16.8, 10.4 Hz, 1H), 6.11 (d, J = 11.2 Hz, 1H), 5.27 (dd, J = 16.8, 1.6 Hz, 1H), 5.19 (dd, J = 9.8, 1.4 Hz, 1H), 4.45 (d, J = 4.0 Hz, 1H), 4.32 (d, J = 4.0 Hz, 1H), 4.27−4.17 (m, 2H), 2.19 (t, J = 8.0 Hz, 2H), 1.44−1.36 (m, 2H), 1.29−1.26 (m, 7H), 1.26 (s, 9H), 0.88 (t, J = 2.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.6, 138.0, 132.1, 130.6, 118.9, 62.0, 62.0, 55.8, 31.9, 28.6, 28.6, 22.6, 22.4, 14.0, 14.0. HRMS: Calcd for $C_{17}H_{32}N_1O_3S_1$ [M + 1] 330.2103, found 330.2090. FTIR (neat): 3452, 2956, 2869, 1734, 1465, 1365, 1255, 1182, 1078, 908, 851 cm^{-1}.

3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-2-(2-methyl-propane-2-sulfinylamino)-hexa-3,5-dienoic Acid Ethyl Ester (6b). ^{1}H NMR (400 MHz, $CDCl_3$): 6.62 (dt, J = 16.8, 10.5 Hz, 1H), 6.13 (d, J = 10.8 Hz, 1H), 5.32 (dd, J = 15.2, 1.4 Hz, 1H), 5.24 (dd, J = 10.0, 1.6 Hz, 1H), 4.59 (d, J = 4.4 Hz, 1H), 4.44−4.38 (m, 2H), 4.32−4.23 (m, 2H), 4.17−4.41 (m, 1H), 1.27 (t, J = 1.2, 3H), 1.25 (s, 9H), 0.09 (s, 9H), 0.062 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.4, 136.4, 131.2, 131.1, 120.3, 61.8, 60.1, 58.6, 55.8, 25.8, 22.6, 18.3, 14.0, −5.52. HRMS: Calcd for $C_{19}H_{38}N_1O_4Si_1S_1$ [M + 1] 404.2291, found 404.2299. FTIR (neat): 3418, 2956, 2925, 2857, 1735, 1472, 1365, 1255, 1212, 1077, 838, 778, 736 cm^{-1}.

3-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-2-(2-methyl-propane-2-sulfinylamino)-hexa-3,5-dienoic Acid Ethyl Ester (7b). ^{1}H NMR (400 MHz, $CDCl_3$): 6.55 (dt, J = 16.8, 10.6 Hz, 1H), 6.12 (d, J = 10.8 Hz, 2H), 5.24 (dd, J = 16.8, 1.6 Hz, 1H), 5.17 (dd, J = 10.2, 1.6 Hz, 1H), 4.45 (d, J = 4.8 Hz, 1H), 4.32 (d, J = 4.4, 1H), 4.25−4.11 (m, 2H), 3.63−3.53 (m, 2H), 2.48−2.34 (m, 2H), 1.24 (t, J = 6.4 Hz, 3H), 1.21 (s, 9H), 0.84 (s, 9H), 0.018 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.4, 134.1, 132.3, 132.1, 119.5, 62.4, 62.1, 62.0, 55.9, 32.2, 25.9, 22.6, 18.2, 14.0, −5.37. HRMS: Calcd for $C_{20}H_{40}N_1O_4Si_1S_1$

[M + 1] 418.2447, found 418.2447. FTIR (neat): 3447, 3283, 2956, 2929, 2857, 1734, 1646, 1472, 1388, 1365, 1255, 1181, 1086, 989, 912, 836, 776 cm^{-1}.

3-(*tert*-Butoxycarbonylamino-methyl)-2-(2-methyl-propane-2-sulfinylamino)-hexa-3,5-dienoic Acid Ethyl Ester (8b). ^1H NMR (400 MHz, $CDCl_3$): 6.67 (dt, J = 16.4, 10.4 Hz, 1H), 6.26 (d, J = 11.2 Hz, 1H), 5.39 (d, J = 16.4 Hz, 1H), 5.32 (d, J = 10.0 Hz, 1H), 4.58 (s, 1H), 4.53 (d, J = 3.6 Hz, 1H), 4.45 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.94 (d, J = 5.2 Hz, 1H), 1.43 (s, 9H), 1.29 (t, J = 7.2 Hz, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.9, 155.3, 134.5, 132.9, 131.1, 121.4, 79.4, 62.2, 61.2, 55.8, 37.3, 28.2, 22.5, 14.0. HRMS: Calcd for $C_{18}H_{33}N_2O_5S_1$ [M + 1] 389.2110, found 389.2108. FTIR (neat): 3384, 2978, 1734, 1707, 1507, 1457, 1391, 1366, 1251, 1170, 1064, 917, 734 cm^{-1}.

***deuterio*-2-(2-Methyl-propane-2-sulfinylamino)-3-phenyl-hexa-3,5-dienoic Acid Ethyl Ester (*deuterio*-1b).** ^1H NMR (400 MHz, $CDCl_3$): 7.34−7.25 (m, 3H), 7.18−7.15 (m, 2H), 6.29 (dd, J = 16.8, 10.0 Hz, 1H), 5.35 (dd, J = 17.0, 1.8 Hz, 1H), 5.13 (dd, J = 10.2, 1.8 Hz, 1H), 4.79 (d, J = 4.8 Hz, 1H), 4.34 (d, J = 4.4 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 1.17 (s, 9H), 1.17 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.0, 137.8, 137.0, 133.2, 129.3, 128.0, 127.6, 120.1, 62.8, 62.1, 55.9, 22.5, 13.9. HRMS: Calcd for $C_{18}H_{25}D_1N_1O_3S_1$ [M + 1] 337.1696, found 337.1692. FTIR (neat): 3285, 3056, 2980, 2870, 1732, 1601, 1493, 1473, 1444, 1412, 1391, 1366, 1253, 1220, 1074, 911, 852, 735, 703, cm^{-1}.

Representative Procedure for the Regioselective Hydrogenation of Dienes. To a solution of diene **1b** (33.5 mg, 0.1 mmol, 100 mol %) in toluene (1 mL, 0.1 M) at ambient temperature was added $RhCl(PPh_3)_3$ (9.3 mg, 0.01 mmol, 10 mol %). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at ambient temperature under 1 atm of hydrogen until complete consumption of substrate, at which point the reaction mixture was evaporated onto silica gel and the product was purified by silica gel chromatography.

2-(2-Methyl-propane-2-sulfinylamino)-3-phenyl-hex-3-enoic Acid Ethyl Ester (1c). ^1H NMR (400 MHz, $CDCl_3$): 7.32−7.23 (m, 3H), 7.13−7.10(m, 2H), 5.83 (t, J = 7.4 Hz, 1H), 4.72 (d, J = 4.4 Hz, 2H), 4.23 (d, J = 4.0 Hz, 1H), 4.20−4.12 (m, 2H), 1.99 (qt, J = 7.4 Hz, 2H), 1.19 (t, J = 7.0 Hz, 3H), 1.19 (s, 9H), 0.95 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.4, 137.3, 136.0, 135.6, 129.1, 127.9, 127.2, 63.1, 61.8, 55.8, 22.5, 22.3, 14.0, 13.9. HRMS: Calcd for $C_{18}H_{28}N_1O_3S_1$ [M + 1] 338.1790, found 338.1792. FTIR (neat): 3279, 2964, 2930, 2871, 1735, 1458, 1365, 1295, 1254, 1214, 1183, 1076, 1022, 884, 847, 760, 702 cm^{-1}.

2-(2-Methyl-propane-2-sulfinylamino)-3-naphthalen-2-yl-hex-3-enoic Acid Ethyl Ester (2c). ^1H NMR (400 MHz, $CDCl_3$): 7.83−7.76 (m, 3H), 7.60 (s, 1H), 7.49−7.45 (m, 2H), 7.25 (d, J = 8.6 Hz, 1H), 5.90 (t, J = 7.6 Hz, 1H), 4.81 (s, 1H), 4.33 (s, 1H), 4.21−4.13 (m, 2H), 2.02 (qt, J = 7.5 Hz, 2H), 1.20 (s, 9H), 1.18 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.3, 136.5, 135.6, 134.9, 133.0, 132.4, 128.0, 127.5, 127.5, 127.4, 126.0, 125.9, 63.1, 61.9, 29.6, 22.7, 22.6, 22.4, 14.0. HRMS: Calcd for $C_{22}H_{30}N_1O_3S_1$ [M + 1] 388.1946, found 388.1953. FTIR (neat): 3285, 3054, 2961, 2870, 1734, 1597, 1503, 1458, 1365, 1181, 1075, 1019, 859, 749 cm^{-1}.

3-Furan-2-yl-2-(2-methyl-propane-2-sulfinylamino)-hex-3-enoic Acid Ethyl Ester (3c). ^1H NMR (400 MHz, $CDCl_3$): 7.36 (t, J = 2.0 Hz, 1H), 6.37−6.36 (m, 1H), 6.30 (d, J = 3.2 Hz, 1H), 5.77 (t, J = 7.2 Hz, 1H), 4.75 (s, 1H), 4.41 (s, 1H), 4.23−4.15 (m, 2H), 2.42 (qt, J = 7.5 Hz, 2H), 1.20 (t, J = 7.0 Hz, 3H), 1.14 (s, 9H), 1.09 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.3, 150.7, 141.3, 137.4, 125.6, 110.7, 109.6, 62.0, 61.8, 29.7, 22.8, 22.4, 14.0, 13.9. HRMS: Calcd for $C_{16}H_{26}N_1O_4S_1$ [M + 1] 328.1583, found 328.1573. FTIR (neat): 3288, 2966, 2921, 2850, 1735, 1458, 1366, 1261, 1221, 1071, 1025 cm^{-1}.

3-(1*H*-Indol-2-yl)-2-(2-methyl-propane-2-sulfinylamino)-hex-3-enoic Acid Ethyl Ester (4c). ^1H NMR (400 MHz, $CDCl_3$): 8.84 (s, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.14 (td, J = 7.6, 1.1 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 6.45 (d, J = 1.2 Hz, 1H), 5.94 (t, J = 7.4 Hz, 1H), 4.78 (d, J = 3.2 Hz, 2H), 4.41 (d, J = 2.4 Hz, 1H), 4.14 (qd, J = 7.2, 1.2 Hz, 2H), 2.45−2.37 (m, 2H), 1.21 (s, 9H), 1.10 (t, J = 7.0 Hz, 3H), 1.08 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.5, 140.1, 136.6, 133.4, 127.9, 126.1, 122.1, 120.3, 119.8, 110.9, 103.9, 62.3, 62.1, 55.9, 22.1, 22.6, 22.5, 14.0, 13.9. HRMS: Calcd for $C_{20}H_{29}N_2O_3S_1$ [M + 1] 377.1900, found 377.1900. FTIR (neat): 3403, 3276, 2965, 2861, 1732, 1653, 1456, 1366, 1301, 1225, 1054 cm^{-1}. Mp: 36−38 °C.

2-(2-Methyl-propane-2-sulfinylamino)-3-propylidene-octanoic Acid Ethyl Ester (5c). ^1H NMR (400 MHz, $CDCl_3$): 5.47 (t, J = 7.2 Hz, 1H), 4.38 (d, J = 4.4 Hz, 1H), 4.25−4.16 (m, 1H + 2H), 2.22−2.01 (m, 4H), 1.37−1.25 (m, 6H), 1.25 (s, 9H), 0.98 (t, J = 7.6 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 172.2, 134.6, 133.7, 62.3, 61.7, 55.7, 32.0, 28.3, 30.0, 22.6, 22.5, 21.3, 14.1, 14.0, 13.9. HRMS: Calcd for $C_{17}H_{34}N_1O_3S_1$ [M + 1] 332.2259, found 332.2251. FTIR (neat): 3422, 2959, 2862, 1734, 1638, 1465, 1255, 1077 cm^{-1}.

3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-2-(2-methyl-propane-2-sulfinylamino)-hex-3-enoic Acid Ethyl Ester (6c). ^1H NMR (400 MHz, $CDCl_3$): 5.55 (t, J = 7.4 Hz, 1H), 4.52 (d, J = 4.4 Hz, 1H), 4.27 (d, J = 4.4 Hz, 1H), 4.29−4.09 (m, 2H + 2H), 2.11 (qd, J = 7.5, 2.4 Hz, 2H), 2.78 (t, J = 4.4 Hz, 3H), 1.25 (s, 9H), 0.99 (t, J = 7.4 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.8, 134.4, 134.2, 61.5, 60.4, 58.2, 55.6, 25.9, 22.6, 21.0, 18.3, 14.0, −5.5. HRMS: Calcd for $C_{19}H_{40}N_1O_4Si_1S_1$ [M + 1] 406.2447, found 406.2448. FTIR (neat): 2957, 2930, 2857, 1736, 1472, 1389, 1364, 1253, 1204, 1082, 849, 777 cm^{-1}.

3-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-2-(2-methy-propane-2-sulfinylamino)-hex-3-enoic Acid Ethyl Ester (7c). ^1H NMR (400 MHz, $CDCl_3$): 5.51 (t, J = 7.2 Hz, 1H), 4.38 (d, J = 5.2 Hz, 1H), 4.24 (d, J = 5.2 Hz, 1H), 4.22−4.11 (m, 2H), 3.60−3.48 (m, 2H), 2.36−2.21 (m, 2H), 2.07 (qt, J = 7.5 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H), 1.22 (s, 9H), 0.95 (t, J = 7.6 Hz, 3H), 0.85 (s, 9H), 0.01 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.9, 135.6, 130.9, 62.6, 61.9, 61.8, 55.7, 31.7, 25.9, 22.6, 21.4, 18.3, 14.0, 13.9, −5.3. HRMS: Calcd for $C_{20}H_{40}N_1O_4Si_1S_1$ [M + 1] 418.2447, found 418.2447. FTIR (neat): 2958, 2857, 1736, 1472, 1364, 1255, 1188, 1084, 836, 776 cm^{-1}.

3-(*tert*-Butoxycarbonylamino-methyl)-2-(2-methyl-propane-2-sulfinylamino)-hex-3-enoic Acid Ethyl Ester (8c). ^1H NMR (400 MHz, $CDCl_3$): 5.71 (t, J = 7.2 Hz, 1H), 4.55 (s, 1H), 4.46 (d, J = 2.8 Hz, 1H), 4.38 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.81 (d, J = 5.2 Hz, 2H), 2.19 (qt, J = 7.6 Hz, 2H), 1.42 (s, 9H), 1.29 (t, J = 7.2 Hz, 3H), 1.26 (s, 9H), 1.02 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.5, 155.4, 138.5, 130.8, 79.3, 62.2, 61.6, 55.7, 37.2, 29.7, 28.4, 22.6, 21.3, 14.0, 13.9. HRMS: Calcd for $C_{18}H_{35}N_2O_5S_1$ [M + 1] 391.2267, found 391.2278. FTIR (neat): 3301, 2975, 2927, 1738, 1713, 1509, 1459, 1391, 1360, 1248, 1174, 1075 cm^{-1}.

Representative Procedure: The Reductive Coupling of 1,3-Diynes and *N*-(2,4,6-Triisopropylbenzenesulfinyl)iminoacetate. To a solution of *N*-(2,4,6-triisopropylbenzenesulfinyl)iminoacetate (70.3 mg, 0.2 mmol, 100 mol %) and 1,3-diyne **9a** (56.1 mg, 0.4 mmol, 200 mol %) in DCM (2 mL, 0.1 M) at ambient temperature was added $Rh(COD)_2OTf$ (4.7 mg, 0.01 mmol, 5 mol %) and BIPHEP (5.3 mg, 0.01 mmol, 5 mol %). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at ambient temperature under 1 atm of hydrogen until complete consumption of substrate, at which point the reaction mixture was evaporated onto silica gel and the product purified by silica gel chromatography.

3-Phenyl-2-(2,4,6-triisopropylbenzenesulfinylamino)-hept-3-en-5-ynoic Acid Ethyl Ester (9b). ^1H NMR (400 MHz, $CDCl_3$): 7.44−7.41 (m, 2H), 7.33−7.27 (m, 3H), 7.02 (s, 2H), 5.88 (qd, J = 2.4, 0.4 Hz, 1H), 4.94 (d, J = 8.0 Hz, 1H), 4.80 (d, J = 8.4 Hz, 1H), 4.19−

4.08 (m, 2H), 3.92 (s,2H), 2.84 (qt, J = 6.9 Hz, 1H), 1.82 (d, J = 2.4 Hz, 3H), 1.20 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.8 Hz, 12H), 1.63 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 152.1, 148.0, 146.3, 137.4, 136.5, 128.6, 128.1, 128.0, 122.9, 111.9, 91.9, 62.8, 61.8, 34.3, 28.1, 24.3, 24.1, 23.7, 23.7, 13.9, 4.5. HRMS: Calcd for $C_{30}H_{40}N_1O_3S_1$ [M + 1] 494. 2729, found 494.2736. FTIR (neat): 3301, 2975, 2927, 1738, 1713, 1509, 1459, 1391, 1360, 1248, 1174, 1075 cm^{-1}.

7-(*tert*-Butyl-dimethyl-silanyloxy)-3-phenyl-2-(2,4,6-triisopropyl-benzenesulfinylamino)-hept-3-en-5-ynoic Acid Ethyl Ester (10b). ^{1}H NMR (400 MHz, $CDCl_3$): 7.40−7.37 (m, 2H), 7.32−7.26 (m, 3H), 7.02 (s, 2H), 5.94 (t, J = 1.0 Hz, 1H), 4.95 (d, J = 8.8 Hz, 1H), 4.80 (d, J = 8.8 Hz, 1H), 4.28 (d, J = 2.0 Hz, 2H), 4.16−4.10 (m, 2H), 3.91 (s,2H), 2.84 (qt, J = 7.0 Hz, 1H), 1.20 (d, J = 7.2 Hz, 6H), 1.17 (d, J = 6.8 Hz, 12H), 1.16 (t, J = 7.2 Hz, 3H), 0.83 (s, 9H), −0.017 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.6, 152.1, 148.1, 148.0, 137.3, 136.2, 128.6, 128.3, 128.1, 123.0, 111.0, 93.2, 81.6, 62.8, 61.9, 52.1, 34.3, 28.1, 25.7, 24.3, 24.1, 23.7, 18.2, 13.9, −5.31. HRMS: Calcd for $C_{36}H_{54}N_1O_4Si_1S_1$ [M + 1] 624.3543, found 624.3534. FTIR (neat): 3301, 2975, 2927, 1738, 1713, 1509, 1459, 1391, 1360, 1248, 1174, 1075 cm^{-1}.

7-*tert*-Butoxycarbonylamino-3-phenyl-2-(2,4,6-tri-isopropylben-zenesulfinylamino)-hept-3-en-5-ynoic Acid Ethyl Ester (11b). ^{1}H NMR (400 MHz, $CDCl_3$): 7.40−7.37 (m, 2H), 7.38−7.27 (m, 3H), 7.02 (s, 2H), 5.90 (d, J = 0.8 Hz, 1H), 4.94 (d, J = 8.4 Hz, 1H), 4.82 (d, J = 8.4 Hz, 1H), 4. 49 (s, 1H), 4.19−4.07 (m, 2H), 3.90−3.88 (m, 4H), 2.84 (qt, J = 6.9 Hz, 1H), 1.40 (s, 9H), 1.21 (d, J = 7.2 Hz, 6H), 1.17 (dd, J = 6.8, 2.0 Hz, 12H), 1.15 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.5, 155.1, 152.1, 148.4, 148.1, 137.3, 136.2, 128.5, 128.4, 128.1, 123.0, 110.8, 90.9, 80.2, 79.8, 62.9, 62.0, 34.3, 31.2, 28.3, 28.2, 24.3, 24.1, 23.7, 23.7, 13.9. HRMS: Calcd for $C_{35}H_{48}N_2O_5S_1$ [M + 1] 608.3284, found 608.3283. FTIR (neat): 3301, 2975, 2927, 1738, 1713, 1509, 1459, 1391, 1360, 1248, 1174, 1075 cm^{-1}.

3-Furan-2-yl-2-(2,4,6-triisopropylbenzenesulfinylamino)-hept-3-en-5-ynoic Acid Ethyl Ester (12b). ^{1}H NMR (400 MHz, $CDCl_3$): 7.29 (d, J = 2.0 Hz, 1H), 7.21 (d, J = 3.2 Hz, 1H), 7.05 (s, 2H), 6.44 (q, J = 1.7 Hz, 1H), 5.68 (q, J = 2.7 Hz, 1H), 5.21 (d, J = 9.2 Hz, 1H), 4.93 (d, J = 9.2 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.96 (s, 2H), 2.87 (qt, J = 6.9 Hz, 1H), 2.09 (d, J = 2.8 Hz, 3H), 1.24−1.19 (m, 18H), 1.14 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.6, 151.9, 150.8, 147.9, 141.4, 137.9, 135.4, 122.9, 111.7, 111.3, 107.9, 96.4, 78.1, 61.9, 61.8, 34.3, 28.2, 24.3, 24.1, 23.8, 23.7, 13.9, 4.94. HRMS: Calcd for $C_{28}H_{38}N_1O_4S_1$ [M + 1] 484.2522, found 484.2504. FTIR (neat): 3301, 2975, 2927, 1738, 1713, 1509, 1459, 1391, 1360, 1248, 1174, 1075 cm^{-1}.

7-Hydroxy-3-hydroxymethyl-2-(2,4,6-triisopropylbenzenesulfinyl-amino)-hept-3-en-5-ynoic Acid Ethyl Ester (13b). ^{1}H NMR (400 MHz, $CDCl_3$): 7.06 (s, 2H), 5.72 (s, 1H), 5.32 (d, J = 8.4 Hz, 1H), 4.75 (d, J = 8.4 Hz, 1H), 4.59 (d, J = 14.4 Hz, 1H), 4.45 (d, J = 14.0 Hz, 1H), 4.41 (d, J = 0.8 Hz, 2H), 4.23−4.15 (m, 2H), 3.94 (s, 2H), 3.50 (S, 1H), 2.89−2.82 (m, 1H), 2.31 (s, 1H), 1.31 (d, J = 6.8 Hz, 6H), 1.24 (t, J = 7.2 Hz, 3H), 1.22 (d, J = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.3, 152.4, 149.1, 147.7, 137.1, 123.1, 111.5, 95.5, 80.6, 62.3, 61.8, 60.4, 51.3, 34.3, 28.5, 24.4, 24.1, 23.7, 14.0. HRMS: Calcd for $C_{25}H_{38}N_1O_5S_1$ [M + 1] 464. 2471, found 464.2472. FTIR (neat): 3301, 2975, 2927, 1738, 1713, 1509, 1459, 1391, 1360, 1248, 1174, 1075 cm^{-1}.

***deuterio*-3-Phenyl-2-(2,4,6-triisopropylbenzenesulfinylamino)-hept-3-en-5-ynoic Acid Ethyl Ester (*deuterio*-9b).** ^{1}H NMR (400 MHz, $CDCl_3$): 7.45−7.43 (m, 2H), 7.34−7.28 (m, 3H), 7.03 (s, 2H), 4.96 (d, J = 8.0 Hz, 1H), 4.81 (d, J = 8.0 Hz, 1H), 4.19−4.09 (m, 2H), 3.92 (br, 2H), 2.89−2.82 (m, 1H), 1.83 (s, 3H), 1.25−1.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 152.0, 148.0, 146.1, 137.3, 136.4, 128.5, 128.1, 128.0, 122.9, 91.8, 62.7, 61.8, 34.2, 28.1, 24.2, 24.1, 23.7, 13.9, 4.5. HRMS: Calcd for $C_{30}H_{39}D_1N_1O_3S_1$ [M + 1] 495.2792, found 495.2785. FTIR (neat): 2960, 2868, 1739, 1597, 1462, 1363, 1257, 1189, 1094, 1027, 879, 697 cm^{-1}.

Representative Procedure for the Exhaustive Hydrogenation of Dienes and Enynes. To a solution of diene **14b** (198.9 mg, 0.6 mmol, 100 mol %) in DCM (6 mL, 0.1 M) at ambient temperature was added $Ir(COD)(Pyr)[P(c\text{-}Hex)_3]PF_6$ (24.2 mg, 0.03 mmol, 5 mol %). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at ambient temperature under 1 atm of hydrogen until complete consumption of substrate, at which point the reaction mixture was evaporated onto silica gel and the product was purified by silica gel chromatography.

2-*tert*-Butoxycarbonylamino-3-phenyl-hexa-3,5-dienoic Acid Ethyl Ester (14b). ^{1}H NMR (400 MHz, $CDCl_3$): 7.17−7.26 (m, 3H), 7.17 (s, J = 7.2 Hz, 2H), 6.39 (d, J = 11.2 Hz, 1H), 6.23 (dt, J = 16.8, 10.5 Hz, 1H), 5.34 (d, J = 1.6 Hz, 1H), 5.30 (d, J = 1.6 Hz, 1H), 5.10 (d, J = 10.0 Hz, 1H), 5.06 (d, J = 8.0 Hz, 1H), 4.14 (m, 2H), 1.43 (s, 9H), 1.17 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.5, 154.7, 138.3, 137.0, 133.3, 131.0, 129.2, 128.2, 127.7, 119.6, 79.9, 61.6, 59.7, 28.2, 13.7. HRMS: Calcd for $C_{19}H_{26}N_1O_4$ [M + 1] 332.1862, found 332.1862. FTIR (neat): 3439, 2978, 2933, 1740, 1717, 1492, 1367, 1323, 1248, 1162, 1058, 1026, 912, 865, 777, 704 cm^{-1}.

2-(9*H*-Fluoren-9-ylmethoxycarbonylamino)-3-phenyl -hexa-3,5-dienoic Acid Ethyl Ester (15b). ^{1}H NMR (400 MHz, $CDCl_3$): 7.77 (d, J = 7.6 Hz, 2H), 7.60−7.55 (m, 2H), 7.42−7.29 (m, 7H), 7.20 (d, J = 6.8 Hz, 2H), 6.44 (d, J = 10.8 Hz, 1H), 6.23 (dt, J = 17.2, 10.5 Hz, 1H), 5.68 (d, J = 8.0 Hz, 1H), 5.36 (d, J = 17.2 Hz, 1H), 5.15 (d, J = 7.2 Hz, 1H), 5.14 (d, J = 10.4 Hz, 1H), 4.44 (dd, J = 10.2, 7.0 Hz, 1H), 4.26 (dd, J = 10.4, 6.8 Hz, 1H), 4.25−4.17 (m, 3H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.2, 155.2, 143.7, 143.6, 141.2, 138.0, 136.9, 133.2, 131.2, 129.2, 128.2, 127.8, 127.6, 127.0, 125.1, 125.0, 120.0, 119.9, 67.0, 61.8, 60.0, 47.1, 14.0. HRMS: Calcd for $C_{29}H_{28}N_1O_4$ [M + 1] 454.2018, found 454.2015. FTIR (neat): 3344, 2979, 1720, 1498, 1449, 1321, 1194, 1047, 912, 758, 740, 703 cm^{-1}.

2-*tert*-Butoxycarbonylamino-3-phenyl-hept-3-en-5-ynoic Acid Ethyl Ester (16b). ^{1}H NMR (400 MHz, $CDCl_3$): 7.47−7.36 (m, 2H), 7.37−7.27 (m, 3H), 5.85 (d, J = 2.0 Hz, 1H), 5.36 (d, J = 7.2 Hz, 1H), 5.12 (d, J = 7.6 Hz, 1H), 4.19−4.07 (m, 2H), 1.84 (d, J = 2.4 Hz, 3H), 1.42 (s, 9H), 1.15 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.4, 154.6, 146.1, 136.9, 128.3, 127.9, 110.9, 91.4, 80.0, 61.7, 58.7, 28.2, 13.9, 4.5. HRMS: Calcd for $C_{20}H_{26}N_1O_4$ [M + 1] 344.1862, found 344.1861. FTIR (neat): 3375, 2978, 2932, 1740, 1717, 1495, 1367, 1325, 1247, 1164, 1054, 1026, 913, 865, 744, 699 cm^{-1}.

2-*tert*-Butoxycarbonylamino-3-phenyl-hexanoic Acid Ethyl Ester (14d). ^{1}H NMR (300 MHz, $CDCl_3$) Major: 7.33−7.24 (m, 3H), 7.18−7.15 (m, 2H), 5.06 (d, J = 9.3 Hz, 1H), 4.47 (t, J = 8.1 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 2.93 (q, J = 7.4 Hz, 1H), 1.78 (q, J = 7.5 Hz, 2H), 1.45 (s, 9H), 1.27−1.12 (m, 2H), 1.05 (t, J = 7.0, 3H), 0.87 (t, J = 7.4 Hz, 3H). Minor: 7.30−7.11 (m, 3H), 7.11−7.09 (m, 2H), 4.77 (d, J = 8.7 Hz, 1H), 4.55 (dd, J = 9.3, 5.1 Hz, 1H), 4.11 (q, J = 7.0 Hz, 2H), 3.16 (dd, J = 16.2, 7.5 Hz, 1H), 1.72 (q, J = 7.9 Hz, 2H), 1.39 (s, 9H), 1.24−1.19 (m, 5H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) Major: 171.8, 155.2, 139.9, 128.4, 128.3, 127.0, 79.8, 60.9, 58.4, 49.1, 33.3, 28.3, 20.5, 13.9, 13.8. HRMS: Calcd for $C_{19}H_{30}N_1O_4$ [M + 1] 336.2175, found 336.2175. FTIR (mixture, neat): 3442, 3558, 2960, 2932, 2871, 1718, 1496, 1454, 1391, 1367, 1340, 1253, 1171, 1048, 1026, 863, 776, 757, 701 cm^{-1}.

2-(9*H*-Fluoren-9-ylmethoxycarbonylamino)-3-phenyl-hexanoic Acid Ethyl Ester (15d). ^{1}H NMR (400 MHz, $CDCl_3$) Major: 7.78 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 7.2 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.35−7.24 (m, 5H), 7.14 (d, J = 7.6 Hz, 2H), 5.33 (d, J = 9.2 Hz, 1H), 4.55 (t, J = 8.2 Hz, 1H), 4.47 (dd, J = 10.4, 7.2 Hz, 1H), 4.36 (dd, J = 10.4, 7.2 Hz, 1H), 4.23 (t, J = 6.8 Hz, 1H), 4.00 (q, J = 7.2 Hz, 2H), 2.96 (q, J = 7.3 Hz, 1H), 1.80 (q, J = 7.6 Hz, 2H), 1.24−1.15 (m, 2H), 1.05 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H). Minor: 7.77 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 8.4 Hz, 2H), 7.41 (td, J = 7.3, 1.9

Hz, 2H), 7.34−7.24 (m, 5H), 7.10 (d, J = 6.8 Hz, 2H), 5.04 (d, J = 9.6 Hz, 1H), 4.66 (q J = 4.7 Hz, 1H), 4.45 (dd, J = 10.8, 7.2 Hz, 1H), 4.34 (dd, J = 10.8, 6.8 Hz, 1H), 4.22 (t, J = 7.0 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.23 (q, J = 9.8 Hz, 1H), 1.73 (q, J = 11.4 Hz, 2H), 1.30−1.22 (m, 2H), 1.26 (t, J = 7.0 Hz, 3H), 0.90 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) Major: 171.4, 155.7, 143.9, 143.7, 141.3, 139.5, 128.4, 128.3, 127.7, 127.1, 127.0, 125.1, 125.0, 119.9, 66.9, 61.1, 58.8, 49.1, 47.2, 33.2, 20.5, 13.9, 13.8. HRMS: Calcd for $C_{29}H_{32}N_1O_4$ [M + 1] 458.2331, found 458.2336. FTIR (neat): 3442, 3558, 2960, 2932, 2871, 1718, 1496, 1454, 1391, 1367, 1340, 1253, 1171, 1048, 1026, 863, 776, 757, 701 cm^{-1}.

2-*tert*-Butoxycarbonylamino-3-phenyl-heptanoic Acid Ethyl Ester (16d). ^{1}H NMR (400 MHz, $CDCl_3$): 7.31−7.11 (m, 5H), 5.04 and 4.78 (major: d, J = 9.2 Hz, minor: d, J = 8.8 Hz, 1H), 4.57 and 4.45 (minor: dd, J = 9.6, 5.2 Hz, major: t, J = 8.0 Hz, 1H), 4.12 and 3.97 (minor: q, J = 7.2 Hz, major: q, J = 7.2 Hz, 2H), 3.18−3.15 and 2.91−2.86 (minor: m, major: m, 1H), 1.82−1.74 (m, 2H), 1.42 and 1.41 (major: s, minor: s, 9H), 1.38−1.01 (m, 7H), 0.85−0.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) Major: 171.7, 155.1, 139.9, 128.4, 128.2, 126.9, 79.7, 60.8, 58.4, 49.3, 30.7, 29.5, 28.2, 22.5, 13.8. Minor: 171.7, 155.6, 139.4, 128.4, 128.2, 127.1, 79.7, 61.0, 57.6, 47.8, 31.1, 29.4, 28.2, 22.5, 14.1. HRMS: Calcd for $C_{20}H_{32}N_1O_4$ [M + 1] 350.2331, found 350.2329. FTIR (neat): 3359, 2958, 2932, 2870, 1718, 1496, 1454, 1367, 1250, 1171, 1055, 1027, 864, 700 cm^{-1}.

Procedure for Cross-Metathesis Reaction with Diene 14b and 1,4-Diacetoxy-*cis*-2-butene. 7-Acetoxy-2-*tert*-butoxycarbonylamino-3-phenyl-hepta-3,5-dienoic Acid Ethyl Ester (14e). To a solution of Grubbs' catalyst (17.6 mg, 0.021 mmol, 5 mol %) in DCM (2.1 mL, 0.2 M) was added diene **14b** (139.4 mg, 0.42 mmol, 100 mol %) and 1,4-diacetoxy-*cis*-2-butene (215 mg, 1.25 mmol, 300 mol %), and the solution stirred for 12 h at 40 °C. The volatiles were removed by rotary evaporation, and the residue was purified by silica flash chromatography to provide the title compounds as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.35−7.30 (m, 3H), 7.15 (d, J = 6.8 Hz, 2H), 6.63 and 6.37 (minor: d, J = 11.6 Hz, major: d, J = 10.8 Hz, 1H), 6.12 and 6.01 (major: t, J = 13.0 Hz, minor: t, J = 11.6 Hz, 1H), 5.85 and 5.53−5.47 (major: dt, J = 15.2, 6.4 Hz, minor: m, 1H), 5.33 and 5.13 (major: d, J = 7.2 Hz, minor: m, 1H), 5.03 and 4.89 (major: d, J = 7.6 Hz, minor: m, 1H), 4.77 and 4.48 (minor: d, J = 6.8 Hz, major: d, J = 6.0 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 2.06 and 1.99 (minor: s, major: s, 3H), 1.41 (s, 9H), 1.16 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) Major: 190.6, 154.6, 139.4, 136.7, 130.4, 129.3, 129.2, 129.1, 129.0, 128.2, 127.8, 79.9, 64.6, 61.7, 59.7, 28.2, 20.8, 13.9. HRMS: Calcd. for $C_{22}H_{30}N_1O_6$ [M + 1] 404.2073, found 404.2069. FTIR (neat): 3375, 3374, 2978, 2923, 1741, 1715, 1493, 1368, 1325, 1230, 1161, 1056, 1025, 976, 865, 777, 704.

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Supporting Information Available: Spectral data for all new compounds. X-ray diffraction data for a derivative of **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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