Trans-Selective Olefination of Carbonyl Compounds by Low-Valent Titanium-Mediated Dehydroxybenzotriazolylation

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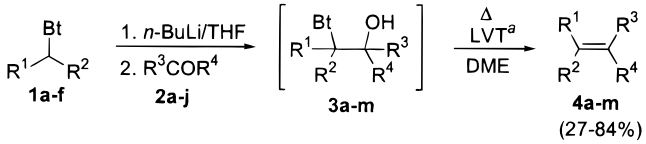
Lithiation with *n*-butyllithium of a variety of benzotriazole derivatives **1a**−**f** and **5a**−**d**, all containing a proton α to the benzotriazolyl moiety, gave anions which underwent addition to aliphatic, aromatic, and α,*β*-unsaturated aldehydes and cyclic and acyclic ketones. The resultant *N*-(*β*-hydroxyalkyl)benzotriazole derivatives **3a**−**m**, **6a**−**g**, **9a**−**d**, and **10a** were dehydroxybenzotriazolylated when treated with low-valent titanium to give alkenes **4a**−**m**, dienes **7a**−**j**, and triene **11a**, with selectivity for the trans isomers without separation of diastereoisomeric intermediates. This method offers an alternative to the three most frequently used methods for the formation of alkenes from carbonyl compounds—the Wittig, Peterson, and Julia reactions—especially in the formation of tri- and tetrasubstituted alkenes.

Introduction

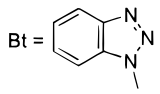
Constructive olefination of carbonyl compounds is a fundamental transformation in organic synthesis. Wittig, Peterson, and Julia reactions are the three most frequently used methods.[1a−c] The stereochemical processes of the Wittig reactions are sensitive to the reaction conditions (solvents, temperatures, bases, additives, etc.), which frequently neccessitates individual tuning of the reaction conditions, depending on the specific structures of the carbonyl compound and the ylide, to obtain good carbon−carbon double bond stereoselectivity.[1b] Such tuning generally succeeds both for highly reactive ylides and for stable ylides, but for ylides with intermediate reactivity (e.g., benzylic and allylic ylides) the results can be unsatisfactory.[1b] The Peterson reaction[2] can provide stereospecific control for either trans or cis isomers depending on the reaction conditions but this variant requires the separation of the diastereomeric intermediates.[3] Difficulty in the preparation of α-silyl carbanions usually limits the Peterson reaction to the synthesis of methylene derivatives.[1b,4] The original procedure for the Julia reaction[5]—which is lengthy and employs mercury reagents—presents difficulties in the preparation of trisubstituted alkenes. An improved Julia coupling reaction using benzothiazolyl sulfones[6] gives excellent stereoselectivity for aliphatic derivatives, but it is less predictable for allylic and benzylic benzothiazolyl sulfones.[7a−c]

Scheme 1



1a: R^1 = Ph; R^2 = H
1b: R^1 = *p*-MeC_6H_4; R^2 = H
1c: R^1 = *p*-ClC_6H_4; R^2 = H
1d: R^1 = Ph; R^2 = Me
1e: R^1 = *N*-Me-indol-3-yl; R^2 = H
1f: R^1 = 2-pyridinyl; R^2 = H

Bt =



2a: R^3 = *p*-MeC_6H_4; R^4 = H
2b: R^3 = Ph; R^4 = H
2c: R^3,R^4 = C_5H_{10}
2d: R^3 = *n*-Pr; R^4 = H
2e: R^3 = *t*-Bu; R^4 = Me
2f: R^3 = C_6H_{11}; R^4 = H
2g: R^3, R^4 = Ph
2h: R^3 = 2,4-$Me_2C_6H_3$; R^4 = H
2i: R^3 = Ph; R^4 = Me
2j: R^3, R^4 = C_9H_{10}

[a]LVT = $TiCl_3$/Li, $TiCl_3$/Zn-Cu, $TiCl_4$/Zn-Cu

During the past two decades, low-valent titanium-induced coupling of carbonyl compounds has received wide application in intramolecular cyclizations, but the unsymmetrical intermolecular variant generally suffers from statistical crossovers.[8a−b] Recently, unsymmetric intermolecular coupling between carbonyl compounds and dithioacetals under low-valent titanium conditions has been reported, but the products generally showed little cis/trans stereoselectivity.[9]

Our preliminary communication[10] disclosed that low-valent titanium enabled an effective dehydroxybenzotriazolylation synthesis of olefins and dienes with stereoselectivity for the trans isomers, which constitutes an alternative to the Julia reaction. This was the first report of reductive elimination of two different heteroatoms α to each other using low-valent titanium to synthesize olefins. More recently we have applied this method to

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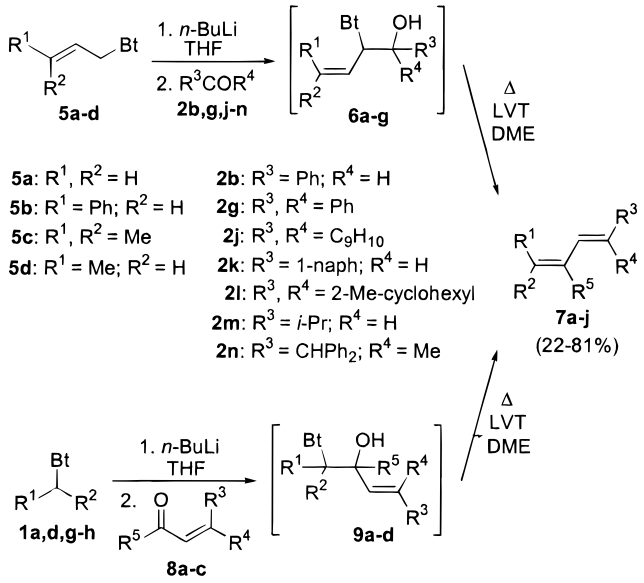
Scheme 2



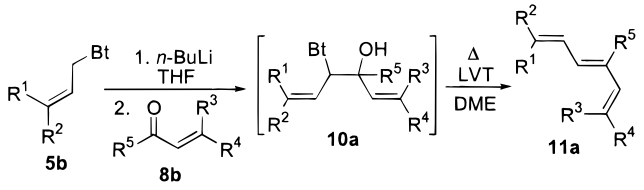
5a: R^1, R^2 = H
5b: R^1 = Ph; R^2 = H
5c: R^1, R^2 = Me
5d: R^1 = Me; R^2 = H

2b: R^3 = Ph; R^4 = H
2g: R^3, R^4 = Ph
2j: R^3, R^4 = C_9H_{10}
2k: R^3 = 1-naph; R^4 = H
2l: R^3, R^4 = 2-Me-cyclohexyl
2m: R^3 = *i*-Pr; R^4 = H
2n: R^3 = $CHPh_2$; R^4 = Me

1a: R^1 = Ph; R^2=H
1d: R^1 = Ph; R^2 = Me
1g: R^1 = *p*-$(Et_2N)C_6H_4$; R^2 = H
1h: R^1= 5-Me-thienyl; R^2 = H

8a: R^3 = H; R^4 = Ph; R^5 = H
8b: R^3, R^4 = Me: R^5 = H
8c: R^3, R^5 = C_3H_6; R^4 = Me

Scheme 3



5b: R^1 = H; R^2 = Ph **8b**: R^3,R^4 = Me; R^5 = H

the synthesis of chiral allylamines for α-amino acid esters.[11] Our previous work had been confined to benzylic and allylic substrates. We now report a more extensive study covering a variety of benzotriazole derivatives **1a**−**h** and **5a**−**d**—including those containing heteroaryl groups (**1e**−**f,h**) and tertiary starting material (**1d**)—to form olefins (Scheme 1) and of allylic benzotriazole compounds **5a**−**d** to form dienes (Scheme 2). The use of α,*β*-unsaturated carbonyl compounds **8a**−**c** with benzotriazole derivatives **1a,d,g**−**h** also leads to the formation of dienes (Scheme 2). The combination of the allylic benzotriazole **5b** with α,*β*-unsaturated carbonyl compound **8b** gave the triene **11a** (Scheme 3). We also discuss alternative methods for generating the low-valent titanium reagent.

Results and Discussion

Preparation of the Starting Materials. Compounds **1a,b**,[12] **1c**,[13] **1e**,[14] **1f**,[15] **1g**,[16] **1h**,[17] **5a**,[18] and **5b**[17] were prepared by the literature methods quoted. Compounds **5c,d** were obtained by the reaction of benzotriazole with the corresponding allyl halide in the presence of sodium hydroxide in ethanol by analogy to the literature.[18] The preparation and characterization of compound **1d** is described in the Experimental Section.

Preparation of 1-(*β*-Hydroxyalkyl)benzotriazoles 3a−m, 6a−g, 9a−d, and 10a. Deprotonation of compounds **1a**−**h** and **5a**−**d** with *n*-butyllithium gave dark colored solutions of the corresponding anions which underwent nucleophilic addition to the carbonyl compounds **2a**−**n** and **8a**−**c** to form the hydroxy intermediates **3a**−**m**, **6a**−**g**, **9a**−**d**, and **10a** as diastereomeric mixtures. These reactions generally proceeded quickly at −78 °C accompanied by the disappearance of the dark color. Exceptionally, the preparation of **3k,l** was carried out at elevated temperatures. The ^{1}H NMR spectra of the hydroxy intermediates after workup indicated that the formation of **3a,e**−**g,i**−**j**, **6a**−**b**, and **9h** were virtually quantitative. Intermediate **3k** was not quantitative even if heated to 60 °C, while for **3h** about 20% starting material was recovered presumably because of proton exchange between carbonyl compound **2h** and lithiated **1d**. Proton exchange between lithiated **1d** and tetralone **2j** simply overwhelmed the desired nucleophilic addition under standard conditions. As the reductive elimination mechanism leading to trans olefinations is believed to involve the rotation of the radical or anionic intermediates[11] similar to McMurry and Julia reactions,[1a−c,8a] no effort has been made to systematically study the ratios of the two possible diastereomers of **3a**−**m**, **6a**−**g**, **9a**−**d**, and **10a**. We previously showed[10] that separation of the diastereomeric mixtures was not needed and therefore the crude reaction mixtures **3a**−**m**, **6a**−**g**, **9a**−**d**, and **10a** were used directly for the reductive-elimination reaction.

Reagents in Generating the Low-Valent Titanium Reaction Media. In the initial communicated work, $TiCl_3$/Li was employed to generate the low-valent titanium.[10] We soon found[11] that $TiCl_3$/Li sometimes gave unsatisfactory yields of olefins **4**. By using Zn−Cu couple (method C) as the reductive metal, the yields were generally improved,[11] which is in accordance with the literature.[8a] We have now also adjusted this olefination method to utilize the more readily available $TiCl_4$ (method E) due to recurring difficulties in obtaining $TiCl_3$ from commercial sources. The addition of tertiary amines has been recommended to increase the yields for McMurry coupling;[8a,19] therefore we attempted most of the dehydroxybenzotriazolylations in the presence of triethylamine (methods D and E). The number of methods reflects an evolution in the method of LVT preparation. As $TiCl_3$ is no longer commercially available, method E is our method of choice.

2-Pyridyl Systems. Difficulties in performing reductive olefination under low-valent titanium conditions for 2-pyridyl aryl ketones were reported by Newkome et al. and attributed to the formation of five-membered ring complexes.[20] The addition of triethylamine prevents the formation of the five-membered ring complexes, and olefinations of the 2-pyridyl system were achieved under

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Table 1. Summary of Stereoselective Olefinations (Scheme 1)

entry	Bt-derivative **1** (R^1R^2CHBt) R^1	R^2	carbonyl compd **2** (R^3COR^4) R^3	R^4	LVT[a]	time (h)	olefin **4**	yield (%)[b]	*E*:*Z*[c]
1	Ph **1a**	H	*p*-MeC_6H_4 **2a**	H	E	2	**4a**	72	41:1
2	*p*-MeC_6H_4 **1b**	H	Ph **2b**	H	B	3	**4a**	65	24:1
3	*p*-MeC_6H_4 **1b**	H	-$(CH_2)_5$- **2c**		B	6	**4b**	73	
4	*p*-ClC_6H_4 **1c**	H	*n*-Pr **2d**	H	A	18	**4c**	55	40:1
5	*p*-ClC_6H_4 **1c**	H	*t*-Bu **2e**	Me	A	6	**4d**	72	100:0
6	Ph **1d**	Me	cyclohexyl **2f**	H	E	2	**4e**	84	19:1
7	Ph **1d**	Me	*p*-MeC_6H_4 **2a**	H	E	1	**4f**	82	10:1
8	Ph **1d**	Me	Ph **2g**	Ph	E	11	**4g**	83	
9	Ph **1d**	Me	2,4-$Me_2C_6H_3$ **2h**	Ph	E	12	**4h**	63	103:1
10	*N*-Me-indol-3-yl **1e**	H	cyclohexyl **2f**	H	E	0.5	**4i**	61	9:1
11	*N*-Me-indol-3-yl **1e**	H	Ph **2i**	Me	C	2	**4j**	66	9:1
12[d]	2-pyridinyl **1f**	H	*t*-Bu **2e**	Me	D	2	**4k**	58	100:0
13[e]	2-pyridinyl **1f**	H	*p*-MeC_6H_4 **2a**	H	D	2	**4l**	27	100:0
14	Ph **1d**	Me	**2j**		E	2	**4m**	70[f]	1.7:1

[a] A ($TiCl_3$/Li), B ($TiCl_3$/Li, THF), C ($TiCl_3$/Zn−Cu), D ($TiCl_3$/Zn−Cu, NEt_3), E ($TiCl_4$/Zn−Cu, NEt_3). [b] Overall yield based on **1**. [c] Determined by GCMS. [d] Temperature raised to 60 °C for the preparation of **3k**. [e] Temperature raised to 23 °C for the preparation of **3l**. [f] Lithiation was followed by transmetallation with $CeCl_3$ prior to addition of tetralone.

low-valent titanium conditions using 1-(2-pyridylmethyl)-benzotriazole **1f**. The yields of 2-pyridyl derivative **4l** in the absence and presence of triethylamine were 18% and 27%, respectively.

Conjugated Aldehydes. For α,β-unsaturated carbonyl compounds **8a**−**c**, undesired 1,4-additions were encountered in the nucleophilic addition step. Intermolecular reductive coupling of allylic alcohols[8a] is a possible side reaction in the reductive elimination step. The higher yield of **7c** (Table 2 entry 3 compared to entry 8)

Table 2. Summary of Stereoselective Olefinations To Form Dienes (Scheme 2)

entry	Bt-derivative **1, 5** (R^1R^2CHBt) R^1	R^2	carbonyl compd **2, 8** (R^3COR^4) R^3	R^4	LVT[a]	time (h)	olefin **7**	yield (%)[b]	*E*:*Z*[c]
1	CH_2=CH **5a**	H	naphth-1-yl **2k**	H	E	1.5	**7a**	53	5:1
2	CH_2=CH **5a**	H	**2j**		E	12	**7b**	54	3.2:1
3	PhCH=CH **5b**	H	Ph **2b**	H	A	8	**7c**	81	13:1
4	PhCH=CH **5b**	H	2-Me-cyclohexyl **2l**		A	16	**7d**	71	4.3:1
5	PhCH=CH **5b**	H	*i*-Pr **2m**	H	A	24	**7e**	53	12:1
6	Me_2C=CH **5c**	H	Ph **2g**	Ph	A	5	**7f**	75	
7	MeCH=CH **5d**	H	Ph_2CH **2n**	Me	A	2	**7g**	51	13:1
8	Ph **1a**	H	PhCH=CH **8a**	H	E	12	**7c**	22	9:1
9	Ph **1d**	Me	PhCH=CH **8a**	H	E	15	**7h**	78	2:1
10	4-$(Et_2N)C_6H_4$ **1g**	H	Me_2CH=CH **8b**	H	E	2	**7i**	65	15:1
11	5-Me thien-2-yl **1h**	H	3-Me-cyclohex-2-enyl **8c**		C	8	**7j**	30[d]	3.7:1

[a] A ($TiCl_3$/Li), B ($TiCl_3$/Li, THF), C ($TiCl_3$/Zn−Cu), D ($TiCl_3$/Zn−Cu, NEt_3), E ($TiCl_4$/Zn−Cu, NEt_3). [b] Overall yield based on **1**. [c] Determined by GCMS. [d] Decomposed on standing, therefore not fully characterized.

Table 3. Summary of Stereoselective Olefinations To Form Trienes (Scheme 3)

entry	Bt-derivative **5** (R^1R^2CH=$CHCH_2Bt$) R^1	R^2	carbonyl compd **8** (R^5COCH=CR^3R^4) R^3	R^4	R^5	LVT[a]	time (h)	olefin **11**	yield (%)[b]	*E*:*Z*[c]
1	H **5b**	Ph	Me **8b**	Me	H	E	12	**11a**	38	6:1

[a] E ($TiCl_4$/Zn−Cu, NEt_3). [b] Overall yield based on **5**. [c] Determined by GCMS.

clearly indicates that using 1-allylbenzotriazoles to approach the diene system avoids these side reactions. It is also noted that no 1,4-addition was detected in during the preparation of **9b**, and the yields of the reductive elimination for **7h,i** were satisfactory.

Transmetalation with Cerium. Initially lithiation of substrate **1d** followed by treatment with tetralone **2j** did not give the desired β-hydroxybenzotriazole derivative **3m** due to proton transfer to the lithiated species. Instead only the starting materials were recovered. The transmetalation of organolithiums with cerium trichloride to form the less basic organoceriums has been shown to result in smooth reactions with carbonyl compounds even though the substrates are susceptible to enolization or metal−halogen exchange with organolithiums.[21] Transmetalation of lithiated **1d** with cerium trichloride and

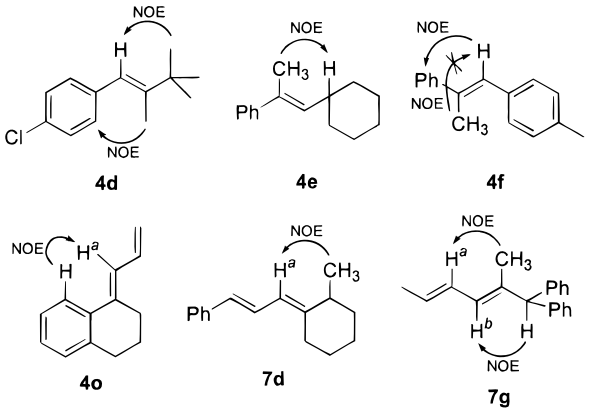

Figure 1.

treatment with tetralone **2j** gave the intermediate **3m** *in situ*. Olefination under low-valent titanium conditions gave olefin **4m** in high yield.

Tertiary Substrate 1d. The use of the tertiary substrate **1d** and ketones **2g,h,j** leads to tetrasubstituted olefins **4g,h,m** in consistently high yields. The difficulties in the formation of tri- and tetrasubstituted products is a limitation of the Julia reaction.[22]

NOE Experiments. NOE experiments were performed to determine the configuration of the olefin bond formed by the low-valent titanium methodology. The following significant enhancements (5−10% when methyl protons or 2−6% when olefinic protons were irradiated) were observed (Figure 1). For compound **4d**, NOE were observed on the olefinic signal (6.28 ppm) when the *tert*-butyl protons (1.34 ppm) were irradiated and on the aromatic protons (7.12 ppm) when the methyl protons (1.79 ppm) were irradiated. Irradiation of the methyl protons (2.05 ppm) in **4e** gave a NOE enhancement of the methine proton (2.35 ppm). When the methyl protons (2.28 and 2.37 ppm) of **4f** were irradiated, no NOE enhancement of the olefinic signal (6.81 ppm) was detected. Whereas when the olefinic proton was irradiated, NOE enhancement was observed on the phenyl protons (7.25 ppm).

For compound **4o** and **7d**, NOE were observed on protons *a* (6.64 and 5.96 ppm) when the aromatic and methyl protons (7.65 and 1.10 ppm) were irradiated, respectively. The assignment of protons *a* and the aromatic protons were made on the basis of the coupling constants and splitting patterns observed in the ^{1}H NMR spectra. NOE enhancement of the proton *a* and *b* signals (6.33 and 5.59 ppm) of **7g** were observed when the methyl protons (1.75 ppm) and the methine proton (4.76 ppm) were irradiated, respectively (Figure 1). The geometry of the remaining examples was assigned by analogy.

Conclusion

A convenient and stereocontrolled olefination of aldehydes and ketones with a variety of benzotriazole derivatives is described for the preparation of di-, tri-, and tetrasubstituted alkenes, dienes, and a triene. Although an aryl, heteroaryl, or allyl group is present in benzotriazole derivatives **1** and **5**, we do not believe this method is limited to such starting materials. This method offers good stereoselectivity without any need to isolate diastereoisomeric intermediates together with easy isolation of the products and constitutes a simple procedure which complements the Wittig, Peterson, and Julia reactions.

Experimental Section

Melting points were determined on a hot stage apparatus without correction. NMR spectra were obtained at 300 MHz for ^{1}H and 75 MHz for ^{13}C NMR spectra in chloroform-*d*; chemical shift values are reported as δ downfield from TMS as an internal standard for ^{1}H and solvent as the internal standard for ^{13}C. The NMR spectra reported were for the trans isomers unless otherwise stated. Mass spectra and elemental analyses were performed within the department.

THF and DME were distilled under nitrogen immediately prior to use from a blue solution containing benzophenone/sodium. The Zn−Cu couple was prepared according to the literature procedure.[23] Column chromatography was carried out on MCB silica gel (230−400 mesh). Other chemicals were used as obtained from commercial sources. Reactions were routinely carried out under an argon atmosphere with magnetic stirring.

Preparation of 1-(Benzotriazol-1-yl)-1-phenylethane (1d). A mixture of (1-bromoethyl)benzene (3.7 g, 20 mmol), benzotriazole (2.86 g, 24 mmol), triethylamine (2.63 g, 26 mmol), and toluene (100 mL) was refluxed for 4 h. On cooling the reaction mixture was washed with 10% Na_2CO_3 (2 × 100 mL) and water (100 mL) and dried (anhydrous $MgSO_4$). The solvent was removed *in vacuo*, and the residue was recrystallized from hexane/ethyl acetate (1:1, 10 mL) to give the product **1d**[24] (2.81 g, 63%): oil; ^{1}H NMR δ 2.16 (d, J = 7.2 Hz, 3 H), 6.05 (q, J = 7.2 Hz, 1 H), 7.22−7.34 (m, 8 H), 8.04 (d, J = 6.9 Hz, 1 H); ^{13}C NMR δ 21.1, 59.0, 110.1, 119.9, 123.8, 126.3, 126.9, 128.2, 128.9, 132.4, 140.2, 146.4.

Procedure for Generating Low-Valent Titanium. Method A. Lithium wire (1.05 g, 75 mmol) and $TiCl_3$ (6.94 g, 45.0 mmol) were added under argon to a 250 mL three-neck flask, and the system was degassed and protected with argon. Dry DME (100 mL) was added and the mixture refluxed 1 h. **Method B.** The same as method A, but using dry THF (100 mL) as solvent. **Method C.** Zn−Cu couple (5.4 g) and $TiCl_3$ (3.8 g, 15 mmol) were added under argon to a 250 mL three-neck flask, and the system was degassed and protected with argon. While stirring, dry DME (40 mL) was added *via* syringe and the mixture was refluxed for 4 h. **Method D.** The same as method C, but triethylamine was added. **Method E.** Dry DME (40 mL) was added to a 250 mL three-neck flask containing Zn−Cu couple (5.8 g) under argon. The system was degassed, protected with argon, and cooled to −10 °C (ice−NH_4Cl bath). $TiCl_4$ (2.5 mL, 22.9 mmol) was added dropwise *via* syringe while the mixture was stirred. The bath was removed and the mixture heated at reflux for 3 h. Triethylamine (1.0 mL) was added *via* syringe and the reflux continued for 1 h.

General Procedure for Olefination. Compounds **1a**−**h** and **5a**−**d** (4.8 mmol) were dissolved with THF (20 mL) in a lithiation bottle under argon and cooled to −78 °C. *n*-BuLi (3.2 mL, 1.6 M, 5.1 mmol) was added dropwise. The dark colored solution was stirred for 10 min followed by addition of the corresponding carbonyl compound **2a**−**n** and **8a**−**c** (5.3 mmol) in dry THF (3.0 mL). The temperature was raised if necessary (see Table 1). After the dark color disappeared, the mixture was immediately quenched with saturated $NaHCO_3$ (20 mL). On warming, ether (30 mL) was added, and the organic phase was separated and dried (anhydrous Na_2SO_4). Concentration under reduced pressure gave a crude mixture of β-hydroxybenzotriazole **3a**−**m**, **6a**−**g**, **9a**−**d**, and **10a** diastereomers.

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The crude β-hydroxybenzotriazole **3a**−**m**, **6a**−**g**, **9a**−**d**, and **10a** diastereomers were dissolved in dry DME (2 × 15 mL) under argon and transferred *via* syringe to the low-valent titanium reaction media described above. The mixture was refluxed (see Tables 1, 2, and 3 for time). On cooling, hexane (50 mL) was added and the reaction mixture filtered and washed with hexane (50 mL). The solid residue was dispersed in water (50 mL) and extracted with hexane (50 mL). The combined organics were washed with 10% Na_2CO_3 (2 × 50 mL) and water (50 mL) and dried (anhydrous Na_2SO_4). Solvent was removed *in vacuo* followed by silica gel column chromatography with hexane as the eluent to give the product **4a**−**m**, **7a**−**j**, and **11a**. (For **4k** and **4l** ether was used instead of hexane to extract the product and hexane/ethyl acetate (2:1) was used as the eluent for column chromatography.)

1-Methyl-4-[(*E*)-2-phenyl-1-ethenyl]benzene (4a): mp 118−119 °C (lit.[25] mp 119−120 °C); ^{1}H NMR δ 2.36 (s, 3 H), 7.07 (s, 1 H), 7.08 (s, 1 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 7.22−7.27 (m, 1 H), 7.35 (t, *J* = 7.7 Hz, 2 H), 7.42 (d, *J* = 8.2 Hz, 2 H), 7.52 (d, *J* = 7.2 Hz, 2 H); ^{13}C NMR δ 21.3, 126.4, 126.4 (overlapped), 127.4, 127.7, 128.6, 129.4, 134.6, 137.5.

1-(Cyclohexylidenemethyl)-4-methylbenzene (4b): oil; ^{1}H NMR δ 1.27−1.68 (m, 6 H), 2.25 (t, *J* = 6.0 Hz, 2 H), 2.33 (s, 3 H), 2.37 (t, *J* = 6.0 Hz, 2 H), 6.20 (s, 1 H), 7.07−7.23 (m, 4 H); ^{13}C NMR δ 21.1, 26.7, 27.9, 28.5, 29.5, 37.7, 121.8, 128.7, 128.8, 135.3, 135.5, 142.8; HRMS calcd for $C_{14}H_{18}$ 186.1409 (M^+), found 186.1401.

1-Chloro-4-[(*E*)-1-pentenyl]benzene (4c): oil; ^{1}H NMR δ 0.96 (t, *J* = 7.4 Hz, 3 H), 1.44−1.54 (m, 2 H), 2.15−2.22 (m, 2 H), 6.19 (dt, *J* = 15.8, 7.6 Hz, 1 H), 6.33 (d, *J* = 15.8 Hz, 1 H), 7.17−7.27 (m, 4 H); ^{13}C NMR δ 13.7, 22.4, 35.1, 127.1, 128.6, 128.7, 131.7, 132.3, 136.4; HRMS calcd for $C_{11}H_{13}Cl$ 180.0706 (M^+), found 180.0704.

1-(4-Chlorophenyl)-4-(*E*)-2,3,3-trimethyl-1-butene (4d): oil; ^{1}H NMR δ 1.34 (s, 9 H), 1.79 (s, 3 H), 6.28 (s, 1 H), 7.12 (d, *J* = 8.6 Hz, 2 H), 7.25 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR δ 14.4, 29.1, 36.7, 120.8, 128.0, 130.4, 131.4, 137.9, 147.8. Anal. Calcd for $C_{13}H_{17}Cl$: C, 74.81; H, 8.21. Found: C, 74.96; H, 8.51.

1-[(*E*)-2-Phenyl-1-propenyl]cyclohexane (4e): oil; ^{1}H NMR δ 1.09−1.41 (m, 5 H), 1.60−1.78 (m, 5 H), 2.05 (s, 3 H), 2.32−2.40 (m, 1 H), 5.64 (d, *J* = 8.7 Hz, 1 H), 7.17−7.41 (m, 5 H); ^{13}C NMR δ 15.8, 26.0, 26.1, 33.0, 37.8,125.6, 126.4, 128.1, 132.8, 134.6, 144.1. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06; Found: C, 89.78; H, 10.45.

1-(4-Methylphenyl)-2-phenyl-(*E*)-1-propene (4f): mp 48−49 °C; ^{1}H NMR δ 2.28 (s, 3 H), 2.37 (s, 3 H), 6.81 (s, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 7.22−7.29 (m, 3 H), 7.36 (t, *J* = 7.4 Hz, 2 H), 7.51 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR δ 17.5, 21.2, 126.0, 127.0, 127.6, 128.3, 128.9, 129.1, 135.5, 136.1, 136.7, 144.1. Anal. Calcd for $C_{16}H_{16}$: C, 92.25; H, 7.75. Found: C, 92.02; H, 7.91.

1,1,2-Triphenyl-1-propene (4g): mp 83−85 °C (lit.[26] mp 93 °C); ^{1}H NMR δ 2.14 (s, 3 H), 6.87−6.91 (m, 2 H), 6.95−7.05 (m, 3 H), 7.06−7.19 (m, 5 H), 7.20−7.28 (m, 3 H), 7.31−7.38 (m, 2 H); ^{13}C NMR[27] δ 23.3, 125.8, 126.2, 126.5, 127.4, 127.8, 128.1, 129.2, 129.9, 130.8, 135.7, 139.3, 143.0, 143.5, 144.0. Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71; Found: C, 93.11; H, 6.95.

1-[1,2-Diphenylpropenyl]-2,4-dimethylbenzene (4h): mp 101−103 °C; ^{1}H NMR δ 1.94 (s, 3 H), 2.20 (s, 3 H), 2.32 (s, 3 H), 6.86−7.17 (m, 13 H); ^{13}C NMR δ 19.5, 21.1, 23.1, 125.6, 126.2, 126.5, 127.3, 127.9, 129.2, 129.7, 130.3, 131.0, 135.8, 135.9, 136.3, 138.1, 139.9, 141.9, 143.8. Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.27; H, 7.74.

3-[(*E*)-2-Cyclohexyl-1-ethenyl]-1-methyl-1*H*-indole (4i): oil; ^{1}H NMR δ 1.10−1.40 (m, 5 H), 1.60−1.95 (m, 5 H), 2.08−2.20 (m, 1 H), 3.73 (s, 3 H), 6.12 (dd, *J* = 16.2 and 6.9 Hz, 1 H), 6.50 (d, *J* = 16.2 Hz, 1 H), 7.03 (s, 1 H), 7.10−7.29 (m, 3 H), 7.83 (d, *J* = 8.1 Hz, 1 H); ^{13}C NMR δ 26.2, 26.3, 32.7, 33.5, 41.7, 109.3, 114.2, 119.4, 119.5, 120.1, 121.8, 126.3, 126.8, 133.6, 137.5. Anal. Calcd for $C_{17}H_{21}N$: C, 85.30; H, 8.85; N, 5.85. Found: C, 85.38; H, 9.02; N, 5.80.

1-Methyl-3-[(*E*)-2-phenyl-1-propenyl]-1*H*-indole (4j): mp 81−83 °C; ^{1}H NMR δ 2.36 (s, 3 H), 3.80 (s, 3 H), 7.05 (s, 1 H), 7.12−7.40 (m, 7 H), 7.56 (d, *J* = 7.5 Hz, 2 H), 7.74 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR δ 18.7, 32.9, 109.2, 113.3, 118.4, 119.1, 119.5, 122.1, 125.8, 126.4, 127.4, 128.3, 133.3, 136.4, 144.6. Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.23; H, 7.20; N, 5.67.

2-[(*E*)-3,3-Dimethylbutenyl]pyridine (4k): oil; ^{1}H NMR δ 1.15 (s, 9 H), 6.41 (d, *J* = 16.2 Hz, 1 H), 6.78 (d, *J* = 15.9 Hz, 1 H), 7.08 (t, *J* = 6.3 Hz, 1 H), 7.26 (d, *J* = 7.8 Hz, 1 H), 7.59 (t, *J* = 9.3 Hz, 1 H), 8.53 (d, *J* = 4.2, 1 H); ^{13}C NMR δ 29.4, 33.5, 121.1, 121.5, 125.0, 136.3, 146.2, 149.4, 156.5; HRMS calcd for $C_{11}H_{13}N$ 161.1204, found 161.1187.

2-[(*E*)-2-(4-Methylphenyl)-1-ethenyl]pyridine (4l): mp 83−85 °C; ^{1}H NMR δ 2.38 (s, 3 H), 7.10−7.21 (m, 4 H), 7.38 (d, *J* = 7.5 Hz, 1 H), 7.50 (d, *J* = 8.1 Hz, 2 H), 7.59−7.68 (m, 2 H), 8.61 (d, *J* = 4.2 Hz, 1 H); ^{13}C NMR δ 21.3, 121.8, 121.9, 127.0, 129.0, 129.4, 132.7, 133.9, 136.4, 138.3, 149.6, 155.8. Anal. Calcd for $C_{14}H_{13}N$: C, 86.11; H, 6.72; N, 7.18. Found: C, 85.86; H, 7.07; N, 6.96.

1-(Phenylmethylmethylenyl)-1,2,3,4-tetrahydronaphthylene (4m) (mixture of cis and trans isomers 1:1.7): oil; ^{1}H NMR δ 1.73 (quintet, *J* = 6.5 Hz, 2 H, cis), 1.86 (quintet, *J* = 6.5 Hz, 2 H, trans), 2.16 (s, 3 H, trans), 2.25 (s, 3 H, cis), 2.52−2.76 (m, 4 H, cis and trans), 6.55−7.50 (m, 9 H, cis and trans); ^{13}C NMR δ 22.0, 23.3, 23.5, 23.7, 28.8, 29.4, 29.5, 30.5, 124.5, 124.8, 125.7, 125.9, 126.2, 126.5, 127.2, 127.9, 128.1, 128.2, 128.4, 128.9, 129.2, 130.6, 131.9, 132.3, 132.4, 132.8, 137.0, 137.8, 139.8, 140.2, 145.3, 145.6. Anal. Calcd for $C_{18}H_{18}$: C, 92.25; H, 7.75. Found: C, 92.23; H, 7.85.

1-[(1*E*)-1,3-Butadienyl]naphthalene (7a): oil;[29] ^{1}H NMR δ 5.23 (d, *J* = 9.9 Hz, 1 H), 5.38 (d, *J* = 16.5 Hz, 1 H), 6.59−6.72 (m, 1 H), 6.84 (dd, *J* = 15.3 and 10.5 Hz, 1 H), 7.33 (d, *J* = 15.0 Hz, 1 H), 7.38−7.53 (m, 3 H), 7.66 (d, *J* = 7.2 Hz, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.81−7.85 (m, 1 H), 8.13 (d, *J* = 7.2 Hz, 1 H)); ^{13}C NMR δ 117.9, 123.4, 123.6, 125.6, 125.7, 126.0, 128.0, 128.6, 129.6, 131.2, 132.4, 133.6, 133.7, 137.4. Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.28; H, 7.16.

1-[(*E*)-2-Propenylidene]-1,2,3,4-tetrahydronaphthalene (7b): oil; ^{1}H NMR δ 1.85 (quintet, *J* = 6.3 Hz, 2 H), 2.66 (t, *J* = 6.0 Hz, 2 H), 2.78 (t, *J* = 6.0 Hz, 2 H), 5.18 (d, *J* = 9.6 Hz, 1 H), 5.33 (d, *J* = 16.5 Hz, 1 H), 6.64 (d, *J* = 11.1 Hz, 1 H), 6.72−6.85 (m, 1 H), 7.07−7.19 (m, 3 H), 7.63−7.66 (m, 1 H); ^{13}C NMR δ 23.0, 26.9, 30.5, 117.2, 123.6, 123.8, 126.1, 127.1, 128.9, 133.1, 135.7, 136.3, 138.1; HRMS calcd for $C_{13}H_{14}$ 170.1096, found 170.1109.

(*E*,*E*)-1,4-Diphenyl-1,3-butadiene (7c): mp 154−155 °C; ^{1}H NMR δ 6.64−6.71 (m, 2 H), 6.90−6.95 (m, 2 H), 7.19−7.25 (m, 2 H), 7.32 (t, *J* = 7.2 Hz, 4 H), 7.43 (d, *J* = 7.2 Hz, 4 H); ^{13}C NMR δ 125.4, 127.4, 128.6, 129.3, 131.8, 136.4. Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 92.96; H, 7.22.

1-Methyl-2-[3-phenyl-2-propenylidenyl]cyclohexane (7d) (mixture of trans,cis and trans,trans isomers 1:4.3): oil; ^{1}H NMR δ 1.10 (d, *J* = 6.7 Hz, 3 H, trans,trans), 1.15 (d, *J* = 6.7 Hz, 3 H, trans,cis), 1.09−1.87 (m, 6 H), 1.98−2.11 (m, 1 H), 2.15−2.23 (m, 1 H, trans,trans), 2.29−2.44 (m, 1 H, trans, cis), 2.75−2.81 (m, 1 H, trans,trans), 3.12−3.24 (m, 1 H, trans, cis), 5.90 (d, *J* = 11.4 Hz, 1 H, trans,cis), 5.96 (d, *J* = 10.8 Hz, 1 H, trans,trans), 6.43 (d, *J* = 15.8 Hz, 1 H, trans,cis), 6.49 (d, *J* = 15.6 Hz, 1 H, trans,trans), 7.02−7.12 (m, 1 H), 7.15 (t, *J* = 6.1 Hz, 1 H), 7.27 (t, *J* = 7.6 Hz, 2 H), 7.38 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR δ 18.6, 25.4, 28.2, 29.0, 36.8, 38.9, 119.7, 125.1, 126.0, 126.8, 128.5, 130.2, 138.2, 148.6; HRMS calcd for $C_{16}H_{20}$ 212.1565 (M^+), found 212.1565.

(1*E*,3*E*)-5-Methyl-1-phenyl-1,3-hexadiene (7e): oil; ^{1}H NMR δ 1.06 (d, *J* = 6.7 Hz, 6 H), 2.35−2.46 (m, 1 H), 5.81 (dd, *J* = 15.3 Hz, 6.8 Hz, 1 H), 6.18 (dd, *J* = 15.3 Hz, 10.3 Hz, 1 H), 6.46 (d, *J* = 15.7 Hz, 1 H), 6.75 (dd, *J* = 15.7 Hz, 10.5 Hz,

(27) The ^{13}C NMR data previously published[28] were inconsistent with our results. When notified the authors repeated their analysis and found the same values as reported here.

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1 H), 7.18 (t, J = 7.1 Hz, 1 H), 7.29 (t, J = 7.5 Hz, 2 H), 7.37 (d, J = 7.4 Hz, 2 H); ^{13}C NMR δ 22.3, 31.3, 126.1, 127.0, 127.6, 128.5, 129.6, 130.2, 137.3, 142.8; HRMS calcd for $C_{13}H_{16}$ 172.1252 (M^+), found 172.1252.

1,1-Diphenyl-4-methyl-1,3-pentadiene (7f): oil; ^{1}H NMR δ 1.76 (s, 3 H), 1.89 (s, 3 H), 5.94 (d, J = 11.3 Hz, 1 H), 6.89 (d, J = 11.3 Hz, 1 H), 7.18−7.40 (m, 10 H); ^{13}C NMR δ 18.6, 26.4, 123.2, 124.5, 126.9, 127.0, 127.4, 128.0, 128.1, 130.6, 137.5, 139.8, 140.2, 143.1. Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.16; H, 8.06.

1,1-Diphenyl-2-methyl-2,4-hexadiene (7g): oil; ^{1}H NMR δ 1.76 (d, J = 7.3 Hz, 3 H), 1.77 (s, 3 H), 4.76 (s, 1 H), 5.48−5.61 (m, 1 H), 5.59 (d, J = 10.0 Hz, 1 H), 6.28−6.38 (m, 1 H), 7.12−7.31 (m, 10 H); ^{13}C NMR δ 17.5, 18.3, 60.1, 126.2, 127.8, 128.2, 128.3, 128.7, 129.4, 137.5, 142.5; HRMS calcd for $C_{19}H_{20}$ 248.1565 (M^+), found 248.1542.

1,4-Diphenyl-1,3-pentadiene (7h) (mixture of trans,cis and trans,trans isomers 1:2): mp 66−69 °C; ^{1}H NMR δ (trans-trans) 2.29 (s, 3 H), 6.52−6.71 (m, 2 H), 7.10−7.52 (m, 11 H); (trans-cis) 2.20 (s, 3 H), 6.32 (d, J = 10.8 Hz, 1 H), 6.55 (d, J = 15.6 Hz, 1 H), 6.88 (dd, J = 15.6 Hz, 10.8 Hz, 1 H), 7.10−7.52 (m, 10 H); ^{13}C NMR δ (mixture of trans-trans and trans-cis) 16.2, 25.6, 125.6, 125.8, 126.3, 126.4, 126.66, 126.71, 127.09, 127.14, 127.3, 127.4, 127.6, 128.2, 128.3, 128.4, 128.5, 128.6, 131.4, 132.9, 136.8, 137.8, 139.6, 143.0. Anal. Calcd for $C_{17}H_{16}$: C, 92.67; H, 7.33. Found: C, 92.37; H, 7.79.

1-(*N*,*N*-Diethylamino)phenyl-4-methyl-(*E*,*E*)-1,3-pentadiene (7i): oil; ^{1}H NMR δ 1.15 (t, J = 7.2 Hz, 6 H), 1.82 (s, 3 H), 1.83 (s, 3 H), 3.35 (q, J = 7.2 Hz, 4 H), 5.96 (d, J = 11.1 Hz, 1 H), 6.34 (d, J = 15.6 Hz, 1 H), 6.62 (d, J = 8.7 Hz, 2 H), 6.77 (dd, J = 15.6, 11.1 Hz, 1 H), 7.26 (d, J = 8.7 Hz, 2 H); ^{13}C NMR δ 12.6, 18.4, 26.1, 44.4, 111.8, 121.3, 125.7, 126.0, 127.3, 129.9, 133.2, 146.9. Anal. Calcd for $C_{16}H_{23}N$: C, 83.79; H, 10.11; N, 6.11. Found: C, 83.55; H, 10.56; N, 6.23.

2-Methyl-5-[(3-methyl-2-cyclohexenylidene)methyl]-thiophene (7j): ^{1}H NMR δ 1.72−1.76 (m, 2 H), 1.80 (s, 3 H), 2.07 (t, J = 5.9 Hz, 2 H), 2.46 (s, 3 H), 2.58 (t, J = 6.1 Hz, 2 H), 5.93 (s, 1 H), 6.24 (s, 1 H), 6.64 (d, J = 2.5 Hz, 1 H), 6.73 (d, J = 3.1 Hz, 1 H); ^{13}C NMR δ 15.3, 22.6, 24.1, 26.3, 30.2, 117.7, 125.1, 126.4, 126.9, 135.2, 138.5, 138.9, 139.7.

(1*E*,3*E*)-6-Methyl-1-phenyl-1,3,5-heptatriene (11a): oil; ^{1}H NMR δ 1.81 (s, 3 H), 1.82 (s, 3 H), 5.93 (d, J = 11.1 Hz, 1 H), 6.27 (dd, J = 10.8, 10.5 Hz, 1 H), 6.40−6.60 (m, 2 H), 6.86 (dd, J = 15.6, 10.5 Hz, 1 H), 7.16−7.45 (m, 5 H)); ^{13}C NMR δ 18.5, 26.2, 125.5, 126.1, 126.3, 127.1, 127.5, 128.5, 129.7, 130.2, 130.3, 130.8; HRMS calcd for $C_{14}H_{16}$ 184.1252 (M^+), found 184.1289.

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