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Reactivity of Alkynylzirconate toward α,β-Unsaturated Carbonyl Compounds

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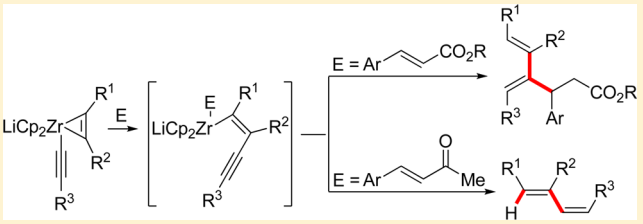
Supporting Information

ABSTRACT: The reaction of alkynylzirconates with α,β-unsaturated carbonyl compounds has been achieved. Reactions of alkynylzirconates with cinnamates afford ester-functionalized multisubstituted dienes, in which the C3 attacks cinnamates via Michael addition. Reactions of alkynylzirconates with benzylideneacetone give (1*E*,3*Z*)-dienes, in which benzylideneacetone acts as an electrophile to afford a proton.



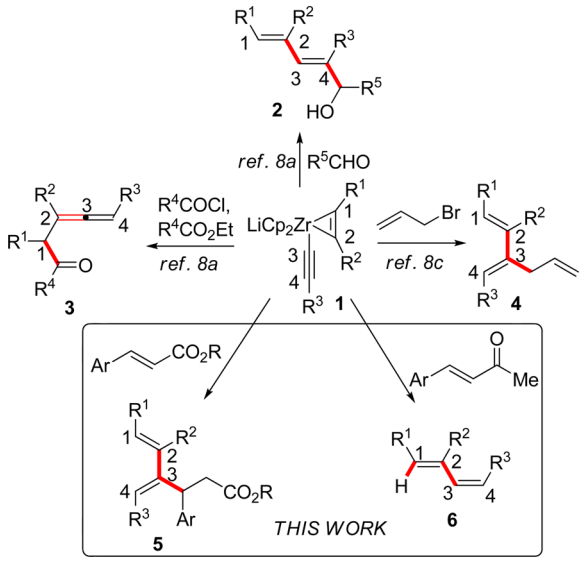
INTRODUCTION

Organozirconocene complexes have attracted considerable attention due to their fascinating structural features, their unique Zr−C bonding, and their unusual capacity to induce highly selective transformation reactions.[1,2] One of the most extensively studied areas is the chemistry of 16-electron organozirconocene complexes, which has been widely explored, and a tremendous number of applications in synthetic chemistry have been found.[1a−f,2] However, 18-electron organozirconate complexes, which have two cyclopentadienyl ligands, three Zr−C bonds, and alkali-metal counterions, have been postulated as key intermediates in a number of reactions.[1g,3−6] Thus, organozirconate complexes have been spectroscopically identified in a novel class of carbon−carbon bond-forming reactions.[4,5] Negishi and co-workers found that organozirconate complexes with three alkynyl groups show a dramatic 1,2-migration insertion of Zr−C bond toward one of the C≡C bonds to form enynes.[6a−c] Whitby and co-workers have developed this reaction to various zirconate complexes to afford many useful organic compounds via intramolecular insertion reaction of organozirconates.[4d,e,i,6d,e] However, intermolecular reactions of organozirconates were rarely reported.[7] Recently, our group reported that alkynylzirconates **1** showed a diverse reactivity with various electrophiles.[8] When aldehydes were used as electrophiles, dienols **2** were formed, in which C4 attacked aldehydes.[8a] Carboxylic acid derivatives such as chloroformate and ester were employed as electrophiles, and functionalized allenes **3** were formed, in which C1 attacked the carboxylic acid derivative.[8a] On the other hand, allyl bromide was used as a electrophile and dienes **4** were obtained, in which C3 attacked allyl bromide.[8c] As an ongoing study on the alkynylzirconate chemistry, herein we wish to report the reactivity of alkynylzirconates toward α,β-unsaturated carbonyl compounds, which have both carbonyl and double bonds. Reactions of alkynylzirconates with cinnamates afforded ester-functionalized multisubstituted dienes **5**,[9] in which the C3 attacked cinnamates via Michael addition. Reactions of alkynylzirconates with benzylideneacetone gave (1*E*,3*Z*)-dienes **6**, in which benzylideneacetone acted as an electrophile to afford a proton (Scheme 1).

RESULT AND DISCUSSION

Initially, to a THF solution of zirconate **1a**, generated by the reaction of ^{n}BuLi with bis(phenylethynyl)zirconocene at room temperature,[6d] was added 1 equiv of methyl cinnamate **7a**

Scheme 1. Diverse Reactivities of Alkynylzirconate with Electrophiles



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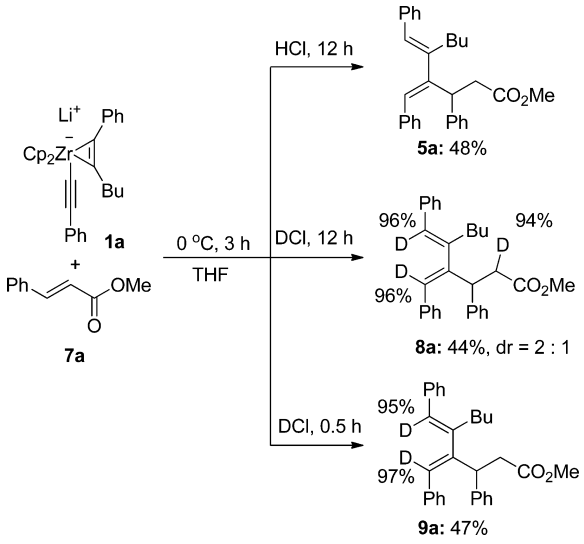
(Scheme 2). The reaction mixture was stirred at 0 °C for 3 h and quenched with a HCl solution; the 1,3-diene **5a** was

Scheme 2. Reaction of Alkynylzirconates with Methyl Cinnamate



formed and isolated in 36% yield. Increasing the amount of methyl cinnamate to 2 equiv afforded **5a** in 48% yield. The yield did not significantly change when 3 equiv of **7a** was added. Deuteriolysis of the reaction mixture (within 12 h) instead of hydrolysis afforded the trideuterated product **8a** in 44% yield with >94% of deuterium incorporation. When the reaction mixture was treated with DCl solution over 0.5 h, dideuterated product **9a** was formed in 47% yield with >95% of deuterium incorporation. This result revealed that the zirconium enolate skeleton existed before hydrolysis.

A variety of cinnamates and zirconates were subjected to this reaction. The representative results are summarized in Table 1. Reaction of zirconate **1a** with a variety of cinnamates **7** afforded the corresponding 1,3-diene derivatives **5** in 43−50% isolated yields (Table 1, entries 1−4). The structure of product **5b** was confirmed by ^{1}H NMR, ^{13}C NMR, HMQC, HMBC, and NOESY. When acrylates or crotonates were employed, the desired product did not form. When other zirconates were employed, the corresponding 1,3-diene derivatives **5** also formed in 37−54% isolated yields (Table 1, entries 5−8).

Next, alkynylzirconate **1a** was treated with 1 equiv of benzylideneacetone at 0 °C for 3 h. (1*E*,3*Z*)-1,4-Diphenyl-2-butyl-1,3-butadiene (**6**) was formed in 53% isolated yield and benzylideneacetone was recovered in 74% yield after workup with HCl solution. Adding 2 equiv of benzylideneacetone did not increase the yield of **6**. When the reaction mixture was quenched with DCl solution, 3,4-dideuterated **6-D** was formed in 50% isolated yield with >95% of deuterium incorportation (Scheme 3). In this reaction, benzylideneacetone induced the coupling reaction of alkynylzirconate and only one proton joined in the product. It is noteworthy that no **6** was formed when traditional protic reagents such as water, alcohol, acid and primary amine were employed. In addition, when other unsaturated ketones such as but-3-en-2-one, cyclohex-2-enone, 1-cyclohexenylethanone, and acetophenone were used in this reaction, the reactions did not proceed.

On the basis of the above results, a plausible mechanism was proposed as follows (Scheme 4). First, the oxygen of *α*,*β*-unsaturated carbonyl compounds coordinates to zirconate **1** and induces coupling of alkynyl and zirconacyclopropene species to give intermediate **10**,[10] which is in equilibrium with **11**, **12**, or **13**. When cinnamate is used as the substrate, C3 attacks cinnamate via Michael addition[11] to afford the zirconacyclopentadiene **14**.[12] Hydrolysis of **14** over a short time affords zirconium enolate **15** due to easy hydrolysis of the two active Zr−C bonds. Further hydrolysis of **15** affords the final product **5**. The stepwise hydrolysis of **14** results in controllable formation of trideuterated and dideuterated products, respectively. The reactivity of zirconate toward cinnamate is different with simple carbonyl complexes, such as aldehyde, chloroformate, and ester[8a] but similar to that with allyl bromide.[8c] When benzylideneacetone is used as the substrate, C1 attacks the hydrogen of the methyl group with triple-bond coordination to zirconium to afford **16**. This may be ascribed to the strong acidity of benzylideneacetone. Hydrolysis of **16** affords the final product **6**.

In summary, we have demonstrated the reactivity of alkynylzirconate complexes toward *α*,*β*-unsaturated compounds. Reactions of alkynylzirconate complexes with cinnamates afforded ester-functionalized multisubstituted dienes, in which C3 attacked cinnamates via Michael addition. Reactions of alkynylzirconates with benzylideneacetone afforded (1*E*,3*Z*)-dienes. Further investigations on the reactivity of alknylzirconates are now in progress.

EXPERIMENTAL SECTION

General Comments. All manipulations were conducted in predried Schlenk tube and under nitrogen with a slightly positive pressure. Unless otherwise noted, all starting materials were used without further purification. Tetrahydrofuran (THF) was refluxed and freshly distilled from dark purple solutions of sodium and benzophenone under a nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL 300 NMR spectrometer with TMS as internal standard. Flash column chromatography was performed using silica gel (200−300 mesh). Elemental analyses were performed on a Flash EA 1112 instrument.

Representative Procedure for Coupling of Zirconate Complexes with Ethyl Cinnamate. ^{n}BuLi (3.0 mmol, 1.6 M solution in hexane) was added to a THF solution of phenylacetylene (2.0 mmol) at −78 °C and stirred for 1 h. Then Cp_2ZrCl_2 (1.0 mmol) was added. The solution was stirred at −78 °C for 1 h and then another 12 h at room temperature. After the reaction mixture was cooled to 0 °C, methyl cinnamate (2.0 mmol) was added and stirred for 3 h. The reaction mixture was quenched with 2 N HCl for 12 h and extracted with ethyl ether. The organic extract was dried over Na_2SO_4. Removal of the solvent and subsequent purification by column chromatography on silica gel (petroleum ether/EtOAc 50/1) afforded **5a** (204 mg, 48%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.74 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 0.87−1.35 (m, 4H), 1.72−1.82 (m, 1H), 2.26−2.35 (m, 1H), 2.95 (dd, J = 15.7, 7.8 Hz, 1H), 3.13 (dd, J = 15.7, 7.6 Hz, 1H), 3.66 (s, 3H), 5.05 (t, J = 7.7 Hz, 1H), 6.34 (s, 1H), 6.74 (s, 1H), 7.07−7.62 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.9, 22.7, 30.1, 30.9, 37.0, 39.9, 51.8, 126.4, 126.5, 127.0, 127.2, 128.2, 128.4, 128.6, 128.8, 129.0, 130.0, 130.2, 137.8, 138.0, 141.9, 144.3, 145.4, 172.8; HRMS calcd for $C_{30}H_{32}O_2$ 424.2402, found 424.2408. Anal. Calcd for $C_{30}H_{32}O_2$: C, 84.87; H, 7.60. Found: C, 84.81; H, 7.68.

5b: colorless oil, 50% yield; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ 0.72 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.85−1.13 (m, 2H), 1.18 (t, J = 7.0 Hz, 3H), 1.23−1.27 (m, 2H), 1.72−1.77 (m, 1H), 2.29−2.34 (m, 1H), 2.91 (dd, J = 15.6, 7.6 Hz, 1H), 3.10 (dd, J = 15.6, 7.8 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 5.04 (t, J = 7.6 Hz, 1H), 6.32 (s, 1H), 6.71 (s, 1H), 7.11−7.56 (m, 15H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ 13.9, 14.3, 22.7, 30.1, 30.9, 37.3, 40.0, 60.6, 126.4, 126.5, 126.9, 127.3, 128.2, 128.3, 128.6, 128.8, 129.0, 130.0, 130.0, 137.8, 138.0, 141.9,

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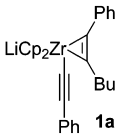
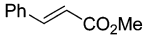
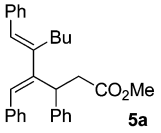
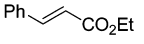
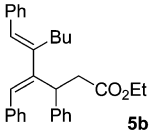
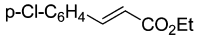
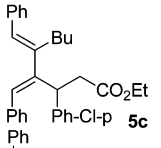
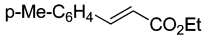
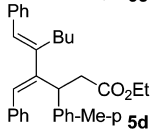
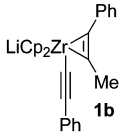
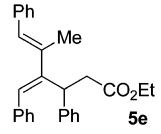
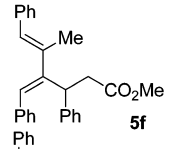
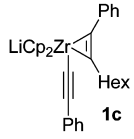
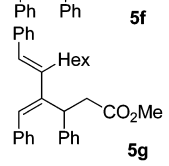
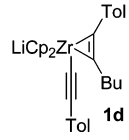
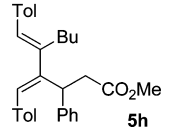
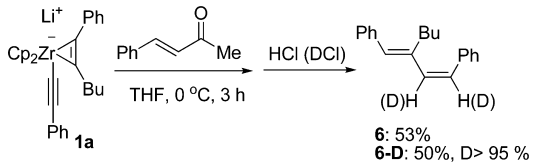
Table 1. Formation of Ester-Functionalized 1,3-Dienes 5 via the Reaction of Zirconates with Cinnamates

entry	zirconate	cinnamate	1,3-diene	yield[a]
1	 **1a**	 **7a**	 **5a**	48%
2	**1a**	 **7b**	 **5b**	50%
3	**1a**	 **7c**	 **5c**	47%
4	**1a**	 **7d**	 **5d**	43%
5	 **1b**	**7b**	 **5e**	54%
6	**1b**	**7a**	 **5f**	48%
7	 **1c**	**7a**	 **5g**	42%
8	 **1d**	**7a**	 **5h**	37%

[a]Isolated yield.

Scheme 3. Reaction of Alkynylzirconate with Benzylideneacetone



144.4, 145.6, 172.3; HRMS calcd for $C_{31}H_{34}O_2$ 438.2559, found 438.2553. Anal. Calcd for $C_{31}H_{34}O_2$: C, 84.89; H, 7.81. Found: C, 84.86; H, 7.88.

5c: colorless oil, 47% yield; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.75 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 0.81−1.32 (m, 7H), 1.75−1.82 (m, 1H), 2.26−2.35 (m, 1H), 2.89 (dd, J = 15.8, 7.2 Hz, 1H), 3.06 (dd, J = 15.8, 8.0 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 4.98 (t, J = 7.6 Hz, 1H), 6.30 (s, 1H), 6.71 (s, 1H), 7.10−7.50 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.9, 14.3, 22.8, 30.1, 30.9, 37.4, 39.7, 60.7, 126.6, 127.1, 128.3, 128.4, 128.7, 128.7, 128.8, 128.9, 130.2, 130.3, 132.2, 137.6, 137.9, 140.5, 143.9, 145.1, 172.0; HRMS calcd for $C_{31}H_{33}ClO_2$ 472.2169, found 472.2161. Anal. Calcd for $C_{31}H_{33}ClO_2$: C, 78.71; H, 7.03. Found: C, 78.78; H, 7.09.

5d: colorless oil, 43% yield; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.74 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 0.86−1.37 (m, 7H), 1.70−1.87 (m, 1H), 2.26−2.45 (m, 1H), 2.31 (s, 3H), 2.91 (dd, J = 15.7, 7.7 Hz, 1H), 3.09 (dd, J = 15.7, 7.6 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 5.02 (t, J = 7.6 Hz, 1H), 6.35 (s, 1H), 6.71 (s, 1H), 7.04−7.59 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.9, 14.3, 21.0, 22.8, 30.1, 30.9, 37.4, 39.6, 60.6, 126.5, 126.9, 127.1, 128.2, 128.5, 128.9, 129.0, 129.9, 135.8, 137.9, 138.1, 138.8, 144.5, 145.7, 172.4; HRMS calcd for $C_{32}H_{36}O_2$ 452.2715, found 452.2717. Anal. Calcd for $C_{32}H_{36}O_2$: C, 84.91; H, 8.02. Found: C, 84.85; H, 8.07.

5e: colorless oil, 54% yield; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ 1.15 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 1.80 (s, 3H), 2.94 (dd, J = 15.3, 7.5 Hz, 1H), 3.14 (dd, J = 15.3, 7.7 Hz, 1H), 4.04−4.11 (m, 2H), 5.03 (t, J = 7.6 Hz, 1H), 6.35 (s, 1H), 6.79 (s, 1H), 7.14−7.52 (m, 15H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ 14.2, 19.1, 37.8, 40.4, 60.6, 126.4, 126.5, 126.9, 127.3, 128.2, 128.5, 128.5, 128.9, 129.2, 129.5, 130.0, 137.8, 138.1, 138.2, 142.2, 146.9, 172.3; HRMS calcd for $C_{28}H_{28}O_2$ 396.2089, found 396.2094. Anal. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12. Found: C, 84.84; H, 7.16.

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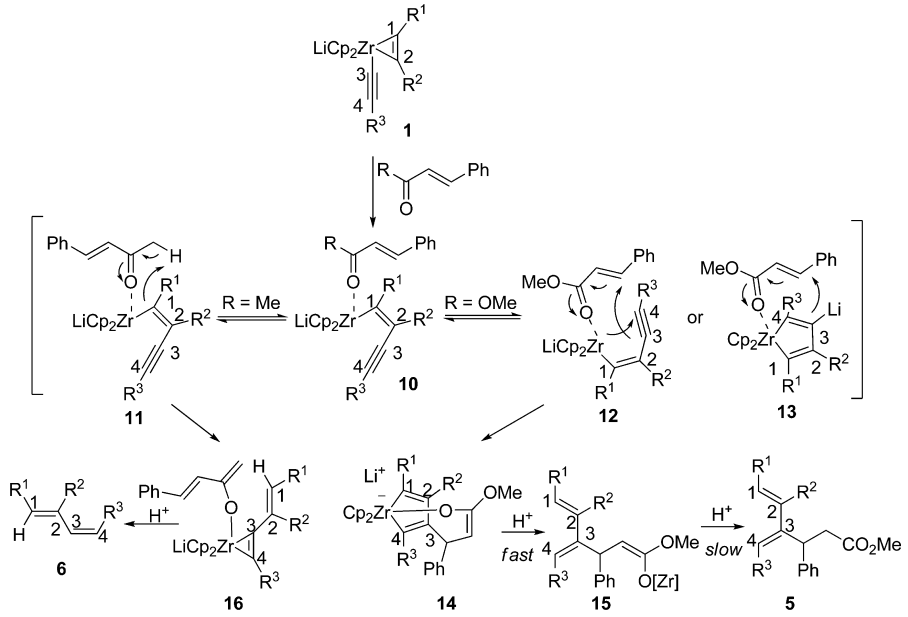
Scheme 4. Plausible Mechanism of the Reaction with α,β-Unsaturated Carbonyl Compounds



5f: colorless oil, 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.79 (s, 3H), 2.94 (dd, J = 15.6, 7.6 Hz, 1H), 3.13 (dd, J = 15.5, 7.6 Hz, 1H), 3.61 (s, 3H), 5.00 (t, J = 7.6 Hz, 1H), 6.33 (s, 1H), 6.78 (s, 1H), 7.15−7.46 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 19.1, 37.5, 40.4, 51.8, 126.4, 126.5, 127.0, 127.2, 128.2, 128.5, 128.5, 128.9, 129.2, 129.6, 130.0, 137.7, 138.1, 138.2, 142.1, 146.8, 172.8; HRMS calcd for $C_{27}H_{26}O_2$ 382.1933, found 382.1931. Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 84.82; H, 6.93.

5g: colorless oil, 42% yield; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.82 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 0.98−1.26 (m, 10H), 1.67−1.74 (m, 1H), 2.24−2.32 (m, 1H), 2.91 (dd, J = 15.8, 7.3 Hz, 1H), 3.09 (dd, J = 15.8, 7.6 Hz, 1H), 3.63 (s, 3H), 5.01 (t, J = 7.6 Hz, 1H), 6.31 (s, 1H), 6.70 (s, 1H), 7.12−7.50 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.2, 22.7, 28.6, 29.3, 30.3, 31.6, 37.0, 39.8, 51.8, 126.4, 126.5, 127.0, 127.2, 128.2, 128.4, 128.6, 128.8, 129.0, 130.0, 130.1, 137.8, 138.0, 141.9, 144.4, 145.4, 172.8; HRMS calcd for $C_{32}H_{36}O_2$ 452.2715, found 452.2711. Anal. Calcd for $C_{32}H_{36}O_2$: C, 84.91; H, 8.02. Found: C, 84.87; H, 8.06.

5h: colorless oil, 37% yield; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.71 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 0.88−1.30 (m, 4H), 1.68−1.77 (m, 1H), 2.25−2.36 (m, 7H), 2.89 (dd, J = 15.8, 7.6 Hz, 1H), 3.13 (dd, J = 15.8, 7.6 Hz, 1H), 3.62 (s, 3H), 5.01 (t, J = 7.6 Hz, 1H), 6.25 (s, 1H), 6.65 (s, 1H), 7.02 − 7.52 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.9, 21.3, 21.3, 22.8, 30.1, 30.9, 37.1, 40.0, 51.8, 126.3, 127.3, 128.3, 128.8, 128.9, 129.0, 129.3, 129.8, 130.0, 134.5, 135.0, 135.2, 136.1, 136.6, 142.0, 143.8, 172.8; HRMS calcd for $C_{32}H_{36}O_2$ 452.2715, found 452.2721. Anal. Calcd for $C_{32}H_{36}O_2$: C, 84.91; H, 8.02. Found: C, 84.84; H, 8.08.

8a: colorless oil, 44% yield; two stereoisomers with dr = 2:1; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.72 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 0.88−1.32 (m, 3H), 1.70−1.80 (m, 1H), 2.29−2.39 (m, 2H), 2.88−3.08 (m, 1H in 2:1 ratio), 3.62 (s, 3H), 5.01 (d, J = 7.6 Hz, 1H), 7.10 − 7.61 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.9, 22.7, 30.0, 30.9, 37.0(m, C-D), 39.8, 51.8, 126.4, 126.5, 127.0, 127.2, 128.3, 128.4, 128.6, 128.8, 129.0, 130.0−130.2 (m, C-D), 137.8, 137.9, 141.9, 144.1, 145.2, 172.8; HRMS calcd for $C_{30}H_{29}D_3O_2$ 427.2591, found 427.2594. Anal. Calcd for $C_{30}H_{29}D_3O_2$: C, 84.27; H, 8.25. Found: C, 84.22; H, 8.20.

9a: colorless oil, 47% yield; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.72 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 0.88−1.29 (m, 4H), 1.73−1.77 (m, 1H), 2.30−2.34 (m, 1H), 2.93 (dd, J = 15.7, 7.8 Hz, 1H), 3.10 (dd, J = 15.7, 7.5 Hz, 1H), 3.64 (s, 3H), 5.03 (t, J = 7.6 Hz, 1H), 7.07 − 7.58 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.9, 22.8, 30.0, 30.9, 37.1, 39.9, 51.8, 126.4, 126.5, 127.0, 127.2, 128.2, 128.4, 128.6, 128.8, 129.0, 129.4 (t, J = 27.3 Hz), 129.8 (t, J = 24.4 Hz), 137.8, 138.0, 141.9, 144.1, 145.2, 172.8; HRMS calcd for $C_{30}H_{30}D_2O_2$ 426.2528, found 426.2524. Anal. Calcd for $C_{30}H_{30}D_2O_2$: C, 84.47; H, 8.03. Found: C, 84.41; H, 8.01.

6: colorless oil, 53% yield; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.84 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.23−1.31 (m, 2H), 1.45−1.53 (m, 2H), 2.35 (t, $^3J_{HH}$ = 7.9 Hz, 3H), 6.18 (d, J = 12.1 Hz, 1H), 6.44 (d, J = 12.1 Hz, 1H), 6.51 (s, 1H), 7.17−7.48 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.0, 23.0, 30.9, 31.1, 126.6, 127.0, 128.2, 128.3, 128.7, 129.0, 129.5, 129.7, 133.9, 137.8, 137.9, 139.8; HRMS calcd for $C_{20}H_{22}$ 262.1722, found 262.1728. Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.46; H, 8.40.

6-D: colorless oil, 53% yield; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.83 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.24−1.32 (m, 2H), 1.45−1.53 (m, 2H), 2.33 (t, $^3J_{HH}$ = 7.8 Hz, 3H), 6.52 (s, 1H), 7.16 − 7.47 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.0, 23.0, 30.9, 31.2, 126.6, 127.0, 128.2, 128.3, 128.7, 129.0, 129.5, 129.8 (t, $^3J_{DC}$ = 20.0 Hz), 133.4 (t, $^3J_{DC}$ = 24.5 Hz), 137.8, 138.0, 139.8; HRMS calcd for $C_{20}H_{20}D_2$ 264.1847, found 264.1844. Anal. Calcd for $C_{20}H_{20}D_2$: C, 90.85; H, 9.15. Found: C, 90.81; H, 9.13.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving HMQC, HMBC, and NOESY spectra of compounds **5b**,**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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