Palladium-Catalyzed C−C Bond Formation: Synthesis of 1,1-Dialkylbuta-1,3-dienes and β-Phenylstyrenes via Organoboron Intermediates[‡]

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α,β-Unsaturated and α-phenyl acetals show different reactivity when treated with LIC-KOR superbase and trialkylboranes, in the presence of the reagent system PdL_4-ArX (Suzuki–Miyaura cross-coupling conditions). In particular, unsaturated acetals yield *gem*-dialkylbutadienes via the formation of an intermediate π-allyl complex that facilitates an anionotropic alkyl migration; in the case of α-phenyl derivatives, the corresponding cross-coupling products are recovered.

Introduction

The Suzuki−Miyaura palladium-catalyzed cross-coupling reaction between organoboron compounds and organic electrophiles provides a powerful method for the formation of carbon−carbon bonds.[1] Consequently, organoboron reagents provide a versatile tool for the construction of more complex molecules from a simple precursor. Moreover, polyenic building blocks with fixed configuration appear to be of importance for the synthesis of a dienic partner in the Diels−Alder cycloaddition reaction,[2] for the production of many bioactive compounds[3] or of structures having nonlinear optical properties[4] or high conductivity.[5]

We have previously reported that in the presence of the Schlosser's superbase LIC-KOR[6] (LIC: butyllithium, KOR: potassium *tert*-butoxide), α,β-unsaturated acetals selectively yield 1-alkoxybuta-1,3-dienes.[7] The product derives from a stereoselective conjugate elimination that is initiated by the metalation reaction at the γ-allylic position of the unsaturated substrate. Similarly, under these experimental conditions 1,1-dimethoxy-2-phenylethane and 1,1-dimethoxy-2-phenylpropane undergo a 1,2-elimination reaction that gives methyl styryl ethers.[8] Moreover, both butadienyl and styryl derivatives can be further functionalized at their α-position by conducting the former elimination reaction in the presence of at least two equivalents of the LIC-KOR base: the excess reagent selectively deprotonates the elimination product at the α-vinyl site, giving a nucleophile that can be quenched with various electrophiles, yielding substitution or addition products.[9] By resorting to this procedure, we have described different functionalized unsaturated systems, and various organostannane reagents have been prepared in order to construct carbon-carbon bonds by means of the Stille cross-coupling reaction.[10] More recently, the reactivity of α-metalated alkoxy dienes in the presence of trialkylboranes[11] or trialkylborates[12] as electrophiles has also been described.

Results and Discussion

In this paper we report the new results of our attempts to perform the LIC-KOR-promoted elimination, the functionalization process, and the Suzuki−Miyaura cross-coupling reaction in a one-pot procedure. Indeed, we have considered the possibility of taking advantage of the basic medium in which the elimination and functionalization steps are conducted. This is because evidence exists that the coordination of negatively charged bases to the boron atom is an efficient way of increasing its nucleophilicity and transfer of the organic group from the boron to the adjacent positive center.[13] The obtained results are indeed different and depend on the nature of the organometallic intermediate − either a boron-functionalized alkoxy-diene or a boron-functionalized alkoxy-styrene. In fact, when a THF solution of $[Pd(PPh_3)_4]$ and iodobenzene was added to the basic reaction mixture in which the α-metalated 1,3-butadiene had been previously treated with a trialkyborane, the only isolated product was a 1,1-dialkylbuta-1,3-diene. Both the alkyl substituents at the C(1) of the conjugate system come from the alkylborane, according to a previously proposed

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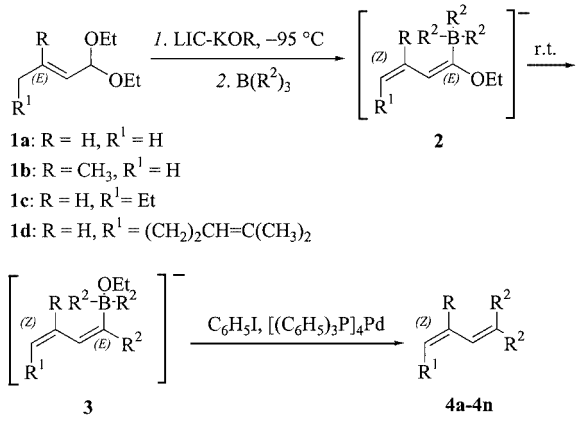
rearrangement.[11] On the other hand, the same synthetic sequence yields, in the case of phenylacetaldehyde and 2-phenylpropionaldehyde dimethyl acetals, the corresponding Suzuki−Miyaura cross-coupling product. Different symmetric trialkylboranes of the BR_3 type (Table 1, Entries 1−5 and 8−14) and two mixed ones, with a BR_2R' structure (Table 1, Entries 6 and 7) have been used, and the reaction has been proven to be of wide applicability. Moreover, to the best of our knowledge, thus far there are no general methods for the synthesis of 1,1-dialkyl-substituted buta-1,3-dienes.[14]

Table 1. Reaction of acetals **1a**−**1d** with different trialkylboranes (BR_3 or BR_2R'): synthesis of 1,1-dialkylbutadienes **4a**−**n**[a]

Entry	Acetal	R	Product	Yields (%)
1	**1a**	C_4H_9	**4a**	79
2	**1a**	*c*-C_5H_9	**4b**	86
3	**1a**	*n*-C_6H_{13}	**4c**	68
4	**1a**	*c*-C_6H_{11}	**4d**	77
5	**1a**	*n*-C_8H_{17}	**4e**	68
6	**1a**	(*c*-C_6H_{11})$_2$/*n*-C_8H_{17}	**4f**[b]	65
7	**1a**	(*c*-C_6H_{11})$_2$/*n*-C_6H_{11}	**4g**[b]	71
8	**1b**	C_4H_9	**4h**	42
9	**1b**	*c*-C_5H_9	**4i**	55
10	**1b**	*c*-C_6H_{11}	**4j**	45
11	**1c**	C_4H_9	**4k**	49
12	**1c**	*c*-C_5H_9	**4l**	41
13	**1d**	C_4H_9	**4m**	48
14	**1d**	*c*-C_6H_{11}	**4n**	48

[a] First step: acetal (5.0 mmol), BuLi (12.5 mmol), *t*BuOK (12.5 mmol), trialkylborane (5.0 mmol), THF (10 mL), $T = -95$ to 25 °C; second step: ArI (4.0 mmol), $[Pd(PPh_3)_4]$ (5.73 10^{-2} g, 1% molar with respect to the acetal), NaOH (1.0 M, 3.0 mL), H_2O_2 (30 wt.%, 3.0 mL), $T = 25$ °C. [b] 1,1-Dicyclohexylbuta-1,3-diene has also been obtained.

Treatment of acetals **1a**−**d** at −95 °C with the LIC-KOR base and the appropriate trialkylborane readily gives the corresponding 1,1-dialkylbuta-1,3-diene in accordance with the steps shown in Scheme 1.[15]

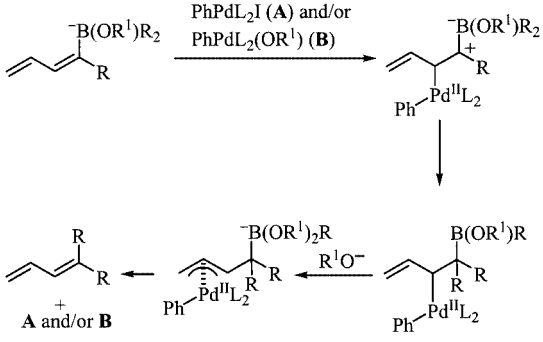


Scheme 1

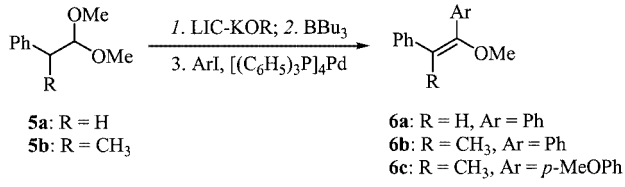
As reported in Table 1, *gem*-dialkylbuta-1,3-dienes were recovered in good yields: tributyl-, trihexyl-, trioctyl-, tricyclopentyl-, and tricyclohexylborane were used as electrophiles. When (dicyclohexyl)octylborane and (dicyclohexyl)hexylborane (Entries 6 and 7) were used, the produced butadienes were recovered as a mixture of (1*E*) and (1*Z*) 1,1-disubstituted isomers, along with 1,1-dicyclohexylbuta-1,3-diene.

The crude product mixture of the reaction carried out with (dicyclohexyl)octylborane does not contain 4-octyldodecabuta-1,3-diene (**4e**), nor does that obtained with (dicyclohexyl)hexylborane show any trace of 4-hexyl-1,3-decadiene (**4c**) (by GC analyses; comparison with authentic samples). These results exclude any intermolecular contribution to the alkyl-transfer mechanism. Moreover, the ratio between the obtained products [4-cyclohexyl-1,3-dodecadiene (**4f**)/1,1-dicyclohexylbuta-1,3-diene (**4d**), 70:30; 4-cyclohexyl-1,3-decadiene (**4g**)/1,1-dicyclohexylbuta-1,3-diene (**4d**), 70:30, by ^1H NMR spectroscopy), which corresponds approximately to the statistically expected composition, clearly excludes any significant difference in the migratory aptitude of the alkyl groups.

The proposed mechanism is shown in Scheme 2, the first step (not represented) being the oxidative addition of iodobenzene to Pd^0 to form a Pd^{II} complex. The presence of alkoxy groups (EtO and *t*BuO) in the reaction medium could promote both the rearrangement of boron "ate" complex **2** to give derivative **3** (see Scheme 1), and the formation of the new Pd^{II} alkoxo complex **B**, by ligand exchange with C_6H_5-PdL_2-I (**A**), as shown in Scheme 3.[16] Either Pd^{II} complex can interact with the borate complex **3** inducing an anionotropic 1,2-shift of an alkyl group from boron to the C(1) terminus of the dienic system. The mechanism probably then proceeds through the following steps: *i*) formation of a new π-allyl complex; *ii*) formation of a new boron "ate" complex, *iii*) final elimination reaction to give the 1,1-disubstituted product (Scheme 2). A similar reaction mechanism, involving an addition-elimination sequence with the final elimination of $XPdBY_2$, has been invoked to explain the formation of "head-to-tail" cross-coupling products.[17]



Scheme 2



Scheme 3

In order to investigate the role of the Pd catalyst and of iodobenzene in the formation of product **4**, some additional experiments have been carried out. In particular, the reaction has also been performed in the absence of iodobenzene: in this case no alkyl-functionalized butadiene was detected. On the other hand, in the presence of catalytic amounts of iodobenzene the dialkylated product has been obtained, although longer reaction times were required. The role of the Pd^{II} catalyst has been assessed by carrying out the reaction in the presence of different Pd complexes. The results obtained with the tested systems are reported in Table 2. Good yields have been achieved using both $[Pd(OAc)_2(PPh_3)_2]$ and $[PdCl_2(CH_3CN)_2]$ (Table 2, Entry 4 and 5, respectively), while $Pd(OAc)_2$ turns out to be ineffective (Table 2, Entry 1); nevertheless, the addition of two equivalents of PPh_3 (with respect to the Pd complex) to the reaction mixture promotes the formation of the *gem*-dialkyl-substituted derivative (Table 2, Entry 2). These data suggest that the reaction is efficiently catalyzed by Pd^{II} complexes containing two equivalents of phosphane ligands, while an additional equivalent of phosphane tends to slow down the reaction (Table 2, Entry 3). Using [(dichloro){1,1′-bis(diphenylphosphanyl)ferrocene}]-palladium(II) $[PdCl_2(dppf)]$ as a catalyst, the reaction occurs readily to give the *gem*-dialkyl-substituted derivative (Entry 6).

Table 2. Reaction of acetals **1a** with tributylborane and Ar−I in the presence of different catalysts: synthesis of diene **4a**

Entry[a]	Catalyst	Yields (%)
1	$Pd(CH_3CO_2)_2$	–
2	$Pd(CH_3CO_2)_2/(C_6H_5)_3P$ (2.0 equiv.)	77
3	$Pd(CH_3CO_2)_2/(C_6H_5)_3P$ (4.0 equiv.)	36
4	$Pd(CH_3CO_2)_2[(C_6H_5)_3P]_2$	59
5	$PdCl_2(CH_3CN)_2$	65
6[b]	$PdCl_2$(dppf)	55

[a] First step: acetal (5.0 mmol), BuLi (12.5 mmol), *t*BuOK (12.5 mmol), trialkylborane (5.0 mmol), THF (10 mL), $T = -95$ to 25 °C; second step: Ar−I (4.0 mmol), $[Pd(PPh_3)_4]$ (5.73 10^{-2} g, 1% molar with respect to the acetal), NaOH (1.0 M, 3.0 mL), H_2O_2 (30 wt.%, 3.0 mL), $T = 25$ °C. [b] Acetal **1b** was used as a substrate. Product **4h** was recovered.

On the other hand, starting from α-phenyl acetals **5a** and **5b**, in the presence of phenyl iodides, and $[Pd(PPh_3)]_4$ as a catalyst, 1,2-diaryl-substituted methoxyethenes have been obtained, according to the Suzuki−Miyura cross-coupling reaction. In particular, unsubstituted and substituted phenyl iodides were used, and the results are outlined in Table 3 and in Scheme 3. Some experiments were also carried out in order to verify the influence of the organoboron derivative on the reaction outcome: tributyl- and tricyclopentylborane were used, and no significant difference was detected among the reactivity of the two organometallic reagents. The subsequent syntheses were thus carried out in the presence of the commercially available tributylborane.

Table 3. Reaction of acetals **5a**−**b** with tributylborane and Ar-X in the presence of $[Pd(PPh_3)]_4$: synthesis of aryl-substituted styryl derivatives **6a**−**c**

Acetal	Ar−X	Product	Yields (%)[a]
5a	PhI	**6a**	38
5b	PhI	**6b**	46
5b	MeOPhI	**6c**	41

[a] First step: acetal (5.0 mmol), BuLi (12.5 mmol), *t*BuOK (12.5 mmol), trialkylborane (5.0 mmol), THF (10 mL), $T = -95$ to 25 °C; second step: Ar−I (4.0 mmol), $[Pd(PPh_3)_4]$ (5.73 10^{-2} g, 1% molar with respect to the acetal), NaOH (1.0 M, 3.0 mL), H_2O_2 (30 wt.%, 3.0 mL), $T = 25$ °C.

Furthermore, the data in Table 3 require some additional comments: in particular, the basic medium in which the cross-coupling occurs seems to affect the reaction outcome and to reduce the yields by promoting a further elimination reaction on the cross-coupling product. 1,2-Diphenylethyne, derived from the 1,2-elimination reaction of MeOH from 1-methoxy-1,2-diphenylethene, was indeed detected in the crude reaction mixture. This elimination reaction has previously been noticed and discussed for analogous systems.[18]

In conclusion, we have devised a one-pot synthesis that, starting from α,β-unsaturated and α-phenyl acetal, gives 1,1-dialkylbuta-1,3-dienes and 1-methoxy-2-phenylstyrenes, respectively. A cascade of quaternization reactions and 1,2-anionotropic rearrangements in the presence of an activated Pd π-complex may account for the formation of 1,1-dialkylbutadienes; in the absence of the conjugated system, a standard Suzuki cross-coupling reaction takes place. In the first case the synthesis leads to products that are not readily accessible by other methods; 1-alkoxy-2-phenylstyrenes are isolated with yields that are poorer than those obtained when stryrylboronates are isolated as stable intermediates.[12]

Experimental Section

General Remarks: Flasks and all equipment used for the generation and reaction of moisture-sensitive compounds were flame dried under argon. Where a temperature of −95 °C is indicated a slush bath of liquid nitrogen/acetone was used. THF was distilled from benzophenone ketyl prior to use. BuLi (1.6 M solution in hexanes) was obtained from Aldrich. *t*BuOK was sublimated in vacuo (0.1 Torr) prior to use. Tributylborane (1.0 M solution in THF) was purchased from Aldrich; other trialkylboranes were synthesized according to literature methods[19] and used as a 1.0 M solution in THF. All other commercially obtained reagents were used as received. Products were purified by preparative column chromatography on Merck silica gel 60 with light petroleum ether (boiling range 40−60 °C)/diethyl ether as eluent. ^1H NMR spectra were recorded at 400 and 200 MHz in $CDCl_3$, using TMS as internal standard. Coupling constants (*J*) are given in Hz and coupling patterns are described by abbreviations: s (singlet), d (doublet), t (triplet), q (quadruplet), br. s (broad singlet). ^{13}C NMR spectra are recorded at 100.4 or 50.2 MHz in $CDCl_3$, and chemical shifts are quoted

relative to the residual solvent peak (δ = 77.0 ppm). GC-MS spectra were measured with a mass-selective detector HP 5970 B instrument operating at an ionizing voltage of 70 eV connected to a HP 5890 GC, cross-linked methyl silicone capillary column (25 m × 0.2 mm × 0.33 μm film thickness).

Typical Procedure for the Synthesis of 1,1-Dialkylbutadienes 4a−n and Styryl Derivatives 6a−c: The acetal (5.0 mmol) and BuLi (7.8 mL, 12.5 mmol) were added dropwise to a cooled (−95 °C) solution of *t*BuOK (1.4 g, 12.5 mmol) in anhydrous THF (10 mL). After a few seconds the solution turned purple and was stirred at −95 °C for 2 h; the appropriate trialkylborane (5.0 mL of a 1.0 M THF solution) was then added. After 2 h the temperature was raised to room temp. for another 2 h. In the meantime, a THF (3.0 mL) solution of C_6H_5I (0.81 g, 4.0 mmol) and $[Pd(PPh_3)]_4$ ($5.73\ 10^{-2}$ g, 1% with respect to the acetal) was prepared in a three-necked flask under argon. The reaction mixture was then added dropwise under inert atmosphere to the $[Pd(PPh_3)]_4/C_6H_5I$ solution and allowed to react for 8 h. It was then oxidized with 3.0 mL of NaOH and 3.0 mL of H_2O_2 (30%). The mixture was then diluted with Et_2O and washed with brine. After evaporation of the solvent the crude isolated product was purified by column chromatography.

4-Butylocta-1,3-diene (4a): 0.66 g, (79%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, *J* = 7.0 Hz, 3 H), 1.01 (t, *J* = 7.0 Hz, 3 H), 1.32−1.37 (m, 8 H), 2.14 (t, *J* = 7.0 Hz, 2 H), 2.16 (t, *J* = 7.0 Hz, 2 H), 4.97 (dd, *J* = 10.0, 1.0 Hz, 1 H), 5.1 (dd, *J* = 16.0, 1.0 Hz, 1 H), 5.86 (d, *J* = 10.0 Hz, 1 H), 6.60 (dt, *J* = 16.0, 10.0 Hz, 1 H) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 14.1, 22.7, 22.9, 29.8, 30.4, 30.5, 31.1, 37.0, 114.4, 125.3, 133.4, 147.5 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 166 (5) [M^+], 109 (24), 82 (52), 81 (52), 67 (100) 41 (87). $C_{12}H_{22}$ (166.3): calcd. C 86.67, H 13.33; found C 86.45, H 12.95.

1,1-Dicyclopentylbuta-1,3-diene (4b): 0.82 g (86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42−1.82 (m, 16 H), 2.35 (tt, *J* = 13.6, 7.0 Hz, 1 H), 3.01 (tt, *J* = 13.6, 7.0 Hz, 1 H), 4.97 (dd, *J* = 10.0, 1.0 Hz, 1 H), 5.1 (dd, *J* = 16.0, 1.0 Hz, 1 H), 5.95 (d, *J* = 10.0 Hz, 1 H), 6.72 (dt, *J* = 16.0, 10.0 Hz, 1 H) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 25.6, 26.0, 31.7, 34.7, 42.1, 42.8, 114.4, 123.2, 133.4, 151.2. MS (EI, 70 eV): *m*/*z* (rel. int.) = 190 (27) [M^+], 121 (77), 93 (81), 79 (100), 67 (58), 55 (22). $C_{14}H_{22}$ (190.3): calcd. C 88.35, H 11.65; found C 88.45, H 11.95.

4-Hexyl-1,3-decadiene (4c): 0.76 g (68%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.0 Hz, 6 H), 0.98−1.54 (m, 16 H), 1.85 (t, *J* = 7.5 Hz, 2 H), 2.55 (t, *J* = 7.5 Hz, 2 H), 4.95 (dd, *J* = 10.0, 1.0 Hz, 1 H), 5.2 (dd, *J* = 16.0, 1.0 Hz, 1 H), 5.96 (d, *J* = 10.0 Hz, 1 H), 6.86 (dt, *J* = 16.0, 10.0 Hz, 1 H) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 14.0, 23.1, 28.2, 30.4, 32.1, 32.6, 116.3, 119.1, 136.9, 150.9 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 222 (1) [M^+], 183 (100), 155 (85), 97 (35), 71 (37), 67 (19) 41 (60). $C_{16}H_{30}$ (222.4): calcd. C 86.40, H 13.60; found C 86.05, H 12.95.

1,1-Dicyclohexylbuta-1,3-diene (4d): 0.84 g (77%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16−1.76 (m, 20 H), 1.94 (tt, *J* = 10.6, 6.0 Hz, 1 H), 2.59 (tt, *J* = 10.6, 6.0 Hz, 1 H), 4.98 (dd, *J* = 10.0, 1.0 Hz, 1 H), 5.1 (dd, *J* = 16.0, 1.0 Hz, 1 H), 5.83 (d, *J* = 10.0 Hz, 1 H), 6.74 (dt, *J* = 16.0, 10.0 Hz, 1 H) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 26.2, 26.4, 26.7, 27.1, 31.1, 34.4, 41.0, 41.4, 114.4, 123.1, 133.3, 154.4 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 218 (24) [M^+], 135 (100), 107 (23), 93 (41), 79 (45), 67 (68) 55 (38). $C_{16}H_{26}$ (218.4): calcd. C 88.00, H 12.00; found C 88.05, H 11.95.

4-Octyldodecabuta-1,3-diene (4e): 0.94 g (68%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.1 Hz, 6 H), 1.21−1.35 (m, 24 H), 1.94 (m, 2 H), 2.51 (m, 2 H), 5.01 (dd, *J* = 10.0, 1.0 Hz, 1 H), 5.1 (dd, *J* = 16.0, 1.0 Hz, 1 H), 5.85 (d, *J* = 10.0 Hz, 1 H), 6.78 (dt, *J* = 16.0, 10.0 Hz, 1 H) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 14.2, 14.4, 23.3, 23.4, 28.5, 30.2, 30.3, 30.6, 32.3, 32.4, 32.6, 38.7, 116.1, 120.3, 138.4, 151.5 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 278 (3) [M^+], 249 (10), 221 (14), 179 (38), 41 (100). $C_{20}H_{38}$ (278.5): calcd. C 86.25, H 13.75; found C 86.95, H 13.95.

4-Cyclohexyl-1,3-dodecadiene (4f): (Mixture of isomers *E* and *Z*). 0.80 g (65%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 6.9 Hz, 3 H), 1.33−1.76 (m, 22 H), 1.96 (t, *J* = 6.0 Hz, 2 H), 2.15 (tt, *J* = 10.6, 6.0 Hz, 1 H), 4.98 (dd, *J* = 10.0, 1.0 Hz, 1 H), 5.10 (dd, *J* = 16.0, 1.0 Hz, 1 H), 5.75 (d, *J* = 10.0 Hz, 1 H), 6.70 (dt, *J* = 16.0, 10.0 Hz, 1 H) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 15.3, 23.6, 25.4, 25.7, 27.9, 28.2, 29.6, 29.8, 30.5, 30.7, 31.4, 31.8, 35.9, 36.2, 112.4, 119.2, 136.8, 140.7 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 248 (8) [M^+], 165 (21), 150 (65), 94 (41), 41 (100). $C_{18}H_{32}$ (248.5): calcd. C 87.02, H 12.98; found C 87.05, H 11.95.

4-Cyclohexyl-1,3-decadiene (4g): (Mixture of isomers *E* and *Z*). 0.48 g (53%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.1 Hz, 3 H), 1.15−1.35 (m, 14 H), 1.74 (m, 4 H), 2.10 (t, *J* = 6.5 Hz, 2 H), 2.55 (m, 1 H), 4.95 (dd, *J* = 10.0, 1.0 Hz, 1 H), 5.05 (dd, *J* = 16.0, 1.0 Hz, 1 H), 5.83 (d, *J* = 10.0 Hz, 1 H), 6.55 (td, *J* = 16.0, 10.0 Hz, 1 H) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 15.3, 22.5, 23.7, 25.3, 25.6, 27.2, 29.2, 31.5, 32.4, 32.8, 34.6, 36.3, 115.2, 118.4, 119.1, 150.3 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 220 (30) [M^+], 135 (100), 93 (35), 79 (41), 67 (78). $C_{16}H_{28}$ (220.4): calcd. C 87.19, H 12.81; found C 88.05, H 12.05.

4-Butyl-2-methylocta-1,3-diene (4h): 0.38 g (42%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.74−1.13 (m, 6 H), 1.13−1.76 (m, 8 H), 1.84 (s, 3 H), 2.03 (t, *J* = 7.6 Hz, 2 H), 2.20 (t, *J* = 7.6 Hz, 2 H), 4.74 (s, 1 H), 4.86 (s, 1 H), 5.64 (s, 1 H) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 14.3, 14.4, 22.8, 23.2, 24.2, 30.8, 30.9, 31.4, 37.4, 113.4, 126.9, 142.7, 142.8 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 180 (8) [M^+], 123 (37), 109 (23), 96 (99). $C_{13}H_{24}$ (180.3): calcd. C 86.59, H 13.41; found C 86.10; H 13.25.

1,1-Dicyclopentyl-3-methylbuta-1,3-diene (4i): 0.56 g (55%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80−1.75 (m, 16 H), 1.84 (s, 3 H), 2.21−2.41 (m, 1 H), 3.11−3.33 (m, 1 H), 4.71 (s, 1 H), 4.89 (s, 1 H), 5.73 (s, 1 H) ppm. ^{13}C NMR (50.2 MHz, $CDCl_3$): δ = 24.9, 26.3, 26.9, 32.6, 4.50, 41.9, 42.8, 113.1, 125.5, 143.4, 150.0 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 204 (19) [M^+], 135 (100), 107 (63), 93 (76). $C_{15}H_{24}$ (204.4): calcd. C 88.16, H 11.84; found C 88.95, H 11.14.

1,1-Dicyclohexyl-3-methylbuta-1,3-diene (4j): 0.52 g (45%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83−2.10 (m, 21 H), 1.84 (s, 3 H), 2.48−2.68 (m, 1 H), 4.45 (s, 1 H), 4.67 (s, 1 H), 5.73 (s, 1 H) ppm. ^{13}C NMR (50.2 MHz, $CDCl_3$): δ = 25.0, 27.0, 27.1, 28.2, 28.7, 30.9, 32.0, 36.0, 41.8, 113.2, 125.2, 130.1, 143.3 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 232 (19) [M^+], 149 (100), 107 (26), 93 (30). $C_{17}H_{28}$: calcd. C 87.86, H 12.14; found C 87.10, H 12.94.

(3*E*)-6-Butyldeca-3,5-diene (4k): 0.48 g (49%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.79−1.02 (m, 6 H), 1.02 (t, *J* = 7 Hz, 3 H), 1.11−1.60 (m, 8 H), 2.04 (t, *J* = 7.5 Hz, 4 H), 2.10−2.26 (m, 2 H), 5.62 (dt, *J* = 16.0, 6.0 Hz, 1 H), 5.80 (d, *J* = 10.0 Hz, 1 H), 6.26 (dd, *J* = 16.0, 10.0 Hz, 1 H) ppm. ^{13}C NMR (50.2 MHz, $CDCl_3$): δ = 14.6, 14.7, 23.6, 23.6, 26.6, 28.5, 31.1, 31.2, 31.7, 37.6, 125.2, 126.3, 134.6, 142.2 ppm. MS (EI, 70 eV):

m/*z* (rel. int.) = 194 (12) [M$^+$], 165 (10), 109 (33), 95 (99). $C_{14}H_{26}$ (194.4): calcd. C 86.52, H 13.48; found C 85.10, H 13.45.

(3*E*)-1,1-Dicyclopentyl-l,3-hexadiene (4l): 0.45 g (41%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83−2.10 (m, 16 H), 0.95 (t, *J* = 6.5 Hz, 3 H), 1.85 (m, 1 H), 2.48−2.68 (m, 2 H), 3.01 (m, 1 H), 5.55 (dt, *J* = 14.0, 6.4 Hz, 1 H), 5.80 (d, *J* = 10.0 Hz, 1 H), 6.26 (dd, *J* = 14.0, 10.0 Hz, 1 H) ppm. ^{13}C NMR (50.2 MHz, $CDCl_3$): δ = 25.9, 26.7, 27.9, 29.3, 32.9, 35.4, 42.6, 47.1, 123.1, 126.2, 134.7, 148.6 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 218 (19) [M$^+$], 149 (100), 107 (32), 81 (100), 41 (45). $C_{16}H_{26}$ (218.4): calcd. C 88.00, H 12.00; found C 87.05, H 12.00.

9-Butyl-2-methyltrideca-2,6,8-triene (4m): 0.67 g (54%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.73−1.08 (m, 6 H), 1.08−1.50 (m, 8 H), 1.60 (s, 3 H), 1.67 (s, 3 H), 1.96−2.26 (m, 8 H), 4.74 (s, 1 H), 4.90 (s, 1 H), 5.12 (m, 1 H), 5.58 (br. s, 1 H) ppm. ^{13}C NMR (50.2 MHz, $CDCl_3$): δ = 14.7, 18.4, 23.2, 23.6, 26.3, 27.7, 30.0, 30.4, 31.0, 31.3, 31.7, 37.3, 112.3, 124.9, 126.3, 132.0, 158.1, 168.1 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 248 (13) [M$^+$], 191 (42), 123 (67), 41 (100). $C_{18}H_{32}$: calcd. C 87.02, H 12.98; found C 87.58, H 12.21.

1,1-Dicyclohexyl-8-methylnona-1,3,7-triene (4n): 0.72 g (48%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.68−1.48 (m, 20 H), 1.60 (s, 3 H), 1.68 (s, 3 H), 1.70−1.85 (m, 4 H), 1.90−2.00 (m, 1 H), 2.70 (m, 1 H), 4.58 (br. s, 1 H), 4.91 (br. s, 1 H), 5.12 (m, 1 H), 5.55 (br. s, 1 H) ppm. ^{13}C NMR (50.2 MHz, $CDCl_3$): δ = 18.4, 24.8, 26.4, 26.9, 27.0, 27.6, 27.9, 30.9, 31.9, 36.1, 38.9, 40.1, 41.8, 44.2, 112.0, 124.3, 126.0, 128.9, 129.1, 140.0, 147.5 ppm.: MS (EI, 70 eV): *m*/*z* (rel. int.) = 300 (18) [M$^+$], 217 (58), 149 (68), 41 (100). $C_{22}H_{36}$ (300.5): calcd. C 87.93, H 12.07; found C 87.20, H 12.40.

(*E*)-1-Methoxy-1,2-diphenylethene (6a): 0.39 g (38%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 5.84 (s, 1 H), 6.90−7.50 (m, 10 H) ppm. ^{13}C NMR (50.2 MHz, $CDCl_3$): δ = 66.2, 89.7, 123.6, 127.3, 128.6, 128.7, 130.5, 131.4, 132.6, 132. 140.1 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) =210 (100) [M$^+$], 167 (78), 165 (98), 152 (68), 77 (43). $C_{15}H_{14}O$ (210.3): calcd. C 85.68, H 6.71; found C 85.58, H 7.08.

(*E*)-1-Methoxy-1,2-diphenyl-1-propene (6b): 0.52 g (45%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 3.47 (s, 3 H), 6.90−7.37 (m, 10 H) ppm. ^{13}C NMR (50.2 MHz, $CDCl_3$): δ = 18.9, 57.9, 126.6, 128.0, 128.4, 128.6, 130.0, 130.8 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 224 (57) [M$^+$], 167 (78), 181 (37), 105 (32) 77(100). $C_{16}H_{16}O$: calcd. C 85.68, H 7.19; found C 85.21; H 7.33.

(*E*)-1-Methoxy-1-*p*-methoxyphenyl-2-phenyl-1-propene (6c): 0.52 g (41%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.17 (s, 3 H), 3.40 (s, 3 H), 3.73 (s, 3 H), 6.68 (d, *J* = 9.2 Hz, 2 H), 6.96−7.37 (m, 5 H), 7.55 (d, *J* = 8 Hz, 2 H) ppm. ^{13}C NMR (50.2 MHz, $CDCl_3$): δ = 16.6, 53.6, 55.6, 111.7, 112.1, 124.2, 126.4, 127.8, 129.8, 149.7; 158.2 ppm. MS (EI, 70 eV): *m*/*z* (rel. int.) = 254 (100) [M$^+$], 211 (82), 178 (25), 165 (35) 77(23). $C_{17}H_{18}O_2$: calcd. C 80.28, H 7.13; found C 80.33, H 7.54.

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