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A One-Pot Synthesis of (*E*)-Disubstituted Alkenes by a Bimetallic [Rh–Pd]-Catalyzed Hydrosilylation/Hiyama Cross-Coupling Sequence

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Dedicated to the memory of Charles Mioskowski

Abstract: A bimetallic [Rh–Pd] catalyst was prepared by soaking into an iodide ionic gel an equimolar solution of $[RhCl(PPh_3)_3]$ and $Pd(OAc)_2$ in CH_2Cl_2. Its catalytic activity was evaluated by rhodium-catalyzed hydrosilylation (H), palladium-catalyzed Hiyama coupling (C), and in the one-pot hydrosilylation/Hiyama coupling sequence (H/C). It was found that the homogeneous combination $[RhCl(PPh_3)_3]$/NaI was a superior system compared to the polyionic mono- and bimetallic rhodium catalysts in the hydrosilylation of terminal alkynes. Interestingly, the most effective catalyst in terms of stereo- and chemoselectivities was observed to be the bimetallic ionic gel [Rh–Pd] in the one-pot process leading to (*E*)-alkenes with good yields. The remarkable stereocontrol is ascribed to a beneficial Pd-catalyzed isomerization from the mixture of stereoisomeric vinylsilanes obtained in the initial hydrosilylation step into the more stable (*E*)-adduct. The [Rh–Pd] heterogeneous catalyst also showed a higher chemoselectivity than the homogeneous catalytic combination, and no detrimental formation of Sonogashira side product was observed due to an ionic-gel-mediated kinetic modulation. To illustrate its scope and limitations, the described one-pot bimetallic catalytic sequence was extended to functionalized terminal alkynes and various iodide substrates. Conjugated systems, such as hydroxycinnamaldehyde, dienes, and trienes, were synthesized in good overall yields. To avoid deactivation of the Rh species, N-heterocyclic iodides had to be added sequentially after completion of hydrosilylation.

Keywords: bimetallic catalyst · cross-coupling · hydrosilylation · one-pot sequence · selectivity modulation

Introduction

Conjugated (*E*)-disubstituted alkenes are present in a variety of natural products, such as resveratrol 3-*O*-D-glucopyranoside[1] and variotin.[2] These stilbenoids and carotenoids belong to a large class of compounds of biological, medicinal, optoelectronic, and physical value. The development of rapid and economical processes for their synthesis remains an ongoing challenge in synthetic organic chemistry. In this context, one-pot processes,[3] such as multicomponent,[4] sequential or "telescoped",[5] and domino[6] reactions, with their practical and economical protocols, have proved of considerable interest to synthetic chemists. They circumvent the common problem of isolation and purification of sensitive intermediates. Compared with stepwise syntheses, they also minimize reagents, waste, time, energy, and costs.[7] Silicon-based cross-coupling[8] (Hiyama coupling) has been extensively studied by Denmark and co-workers. This carbon–carbon bond-forming reaction has gained prominence in synthetic organic chemistry as a reliable alternative to the Suzuki, Stille, and Negishi couplings, which may have drawbacks, such as the involvement of toxic reagents and byproducts, as well as oxygen and moisture sensitivity.

The literature reveals few examples of the hydrosilylation/cross-coupling sequence.[9] The pioneering work of Ito,[9g] Hiyama,[9e,f] and Denmark[9a–c] reported Pt-catalyzed hydrosilylation/Pd-catalyzed cross-coupling reactions, requiring the sequential addition of the coupling partners and the palladi-

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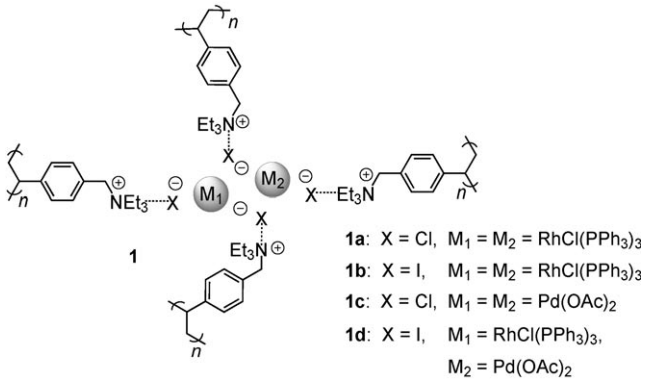
um catalyst. They often noticed some inherent difficulties involving the formation of undesired products (*Z* isomer and/or Sonogashira byproduct),[9b,c] the loss of stereospecificity when the coupling is performed from alkenyl halides, or the exothermicity of the reaction with reactive aryl iodides.[9b] Moreover, removal of the Pt species and the residual silane is often required after the hydrosilylation step to avoid Pd poisoning and achieve optimum yields.[9c,e,f]

Recently, we reported that polyionic gels are suitable heterogeneous media for metal scavenging and catalysis (Scheme 1). Indeed, polyionic-gel-soaked Pd and Rh proved to be highly active catalysts respectively for Suzuki coupling[10a] and dehydrogenative silylation of ketones.[10b]

Herein, we describe an efficient bimetallic polyionic-gel [Rh–Pd] catalyst in a sequential one-pot hydrosilylation/Hiyama coupling protocol that affords stereoselectively (*E*)-disubstituted olefins.

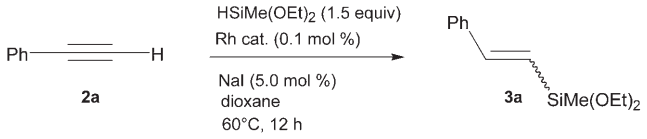
Results and Discussion

We first investigated the reactivity of polyionic-gel-soaked rhodium complexes **1a–b** and **1d** in the hydrosilylation of phenylacetylene (**2a**) under standard conditions (Table 1).



Our reported metal soaking procedure[10a] was used to prepare various heterogeneous catalysts **1**, by varying the counter-anion X^- of the polyionic gel and by using Wilkinson's ($[RhCl(PPh_3)_3]$) and $Pd(OAc)_2$ precursors.[11] Mori and co-workers have demonstrated that $[RhCl(PPh_3)_3]$/NaI is a regio- and stereoselective catalyst system for the hydrosilylation of terminal alkynes.[12] By using Rh catalyst **1a** (X = Cl) and adding NaI, the hydrosilylation of **2a** was complete and afforded a 77:23 mixture of the two expected stereoisomeric (*Z*)- and (*E*)-vinylsilanes **3a** with predominantly the (*E*)-adduct (entry 2). We then tested catalysts **1b** and **1d** prepared by soaking the organometallic precursors (respectively $[RhCl(PPh_3)_3]$ and an equimolar solution of $[RhCl(PPh_3)_3]$ and $Pd(OAc)_2$) into the ammonium iodide gel. The bifunctional catalysts that contain both the Rh precursor and the iodide additive led to the formation of (*E*)-**3a** as the major derivative, with complete conversion and improved *E*/*Z* ratios by a simplified and practical procedure (entries 3–4).

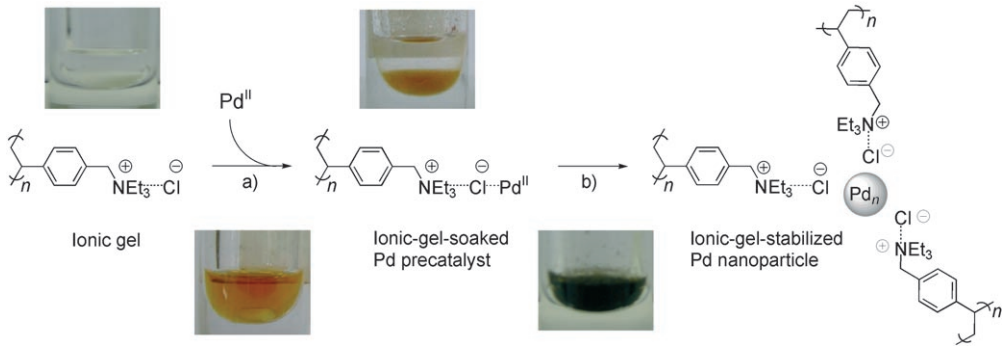
Table 1. Hydrosilylation of phenylacetylene (**2a**) with various catalysts.[a]



Entry	Catalyst system			Additive	Yield[b]	*E*/*Z*[b]
	X					
1	–	$[RhCl(PPh_3)_3]$		NaI	>95	>99:1
2[c,d]	Cl	$[RhCl(PPh_3)_3]$	**1a**	NaI	>95	77:23
3[e]	I	$[RhCl(PPh_3)_3]$	**1b**	–	>95	88:12
4[e]	I	$[RhCl(PPh_3)_3]/Pd(OAc)_2$	**1d**	–	>95[f]	90:10

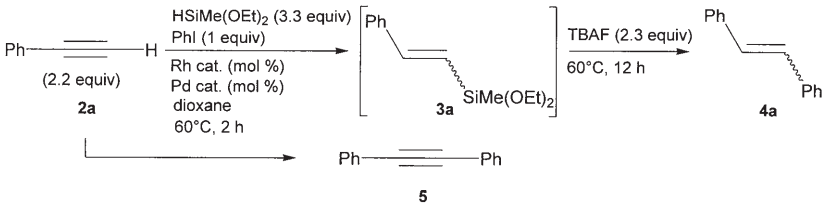
[a] Phenylacetylene (**2a**) (2.0 mmol) and $HSiMe(OEt)_2$ (3.0 mmol) were stirred in dioxane (4 mL) in the presence of the Rh cat. (0.1 mol%) at 60°C for 12 h under argon. [b] Values determined from the ^1H NMR spectrum of the crude reaction mixture with 1,1,2-trichloroethylene as an internal standard. [c] 0.08 mol% of Rh was used, as determined by elemental analysis. [d] See reference [13]. [e] 0.04 mol% of Rh was used. [f] 85% of isolated yield.

Although complete stereoselectivity was not achieved in the hydrosilylation step, we tested the one-pot hydrosilylation/Hiyama coupling sequence by using the homogeneous catalysts, the combination of heterogeneous monometallic catalysts **1b**/**1c**, and the bimetallic [Rh–Pd] **1d** (Table 2).[14] Interestingly, homogeneous conditions met with little success. Indeed, a 43:57 mixture of stilbenes **4a** (*E*/*Z* = 89:11), together with the undesired Sonogashira side product **5**, was



Scheme 1. Preparation of ionic-gel-stabilized Pd nanoparticles. a) 0.1 equiv $Pd(OAc)_2$ per ammonium, DMF, 30°C, 20 h; b) DMF, 85°C, 30 min.

Table 2. One-pot hydrosilylation/coupling reaction.[a]



Entry	Catalyst	Rh/Pd [mol %][b]	Yield[c]	**4a** (*E*/*Z*)[d]	**5**
1	$[RhCl(PPh_3)_3]$/ $Pd(OAc)_2$, NaI[e]	3.3:9.0	>99	43 (89:11)	57
2	**1b**/**1c**	2.7:4.9	>99	100 (>99:1)	0
3	**1d**	3.3:9.0	>99	100 (>99:1)	0

[a] 1) Phenylacetylene (**2a**), $HSiMe(OEt)_2$, PhI, Rh, and Pd cat., dioxane, 60 °C for 2 h and 2) TBAF, 60 °C for 12 h. [b] Determined by elemental analysis. [c] Determined by GCMS. [d] Values determined from the ^1H NMR spectrum of the crude reaction mixture. [e] NaI (1.6 equiv).

obtained (entry 1). Formation of **5** indicated a detrimental competition of rhodium-catalyzed hydrosilylation versus palladium-catalyzed Sonogashira coupling. To limit the formation of this byproduct, Denmark had to perform the reaction stepwise, add the palladium sequentially, increase the silane/alkyne ratio, and extend the reaction time.[9b] In contrast, reactions with both polyionic-gel-based catalyst systems led to stilbene **4a** exclusively with the *E* configuration as the only product and with complete conversions (entries 2–3).

The high chemoselectivity of catalyst **1d** (hydrosilylation versus Sonogashira reaction) is attributed to a slower Sonogashira side coupling in polyionic gel.[15] Competition between hydrosilylation (H) and Sonogashira (S) reactions is greater with the homogeneous systems (TOF(H) (2400 h^{-1})/ TOF(S) (387 h^{-1}) = 6; TOF [h^{-1}] = mol(substrate) per mol(catalyst)h), while hydrosilylation is largely predominant with ionic gel catalyst **1d** (TOF(H) (1200 h^{-1})/TOF(S) (16 h^{-1}) = 75) (Figure 1). Upon ^1H NMR spectroscopic monitoring of the reaction over 10 minutes, **2a** was found to react relatively rapidly (reaction almost complete in 5 min; Figure 1Aa and Ab) in both hydrosilylation and Sonogashira reactions in the presence of $[RhCl(PPh_3)_3]/Pd(OAc)_2$, NaI. Under **1d**-catalyzed conditions, the reaction rate for hydrosilylation was similar to that of the previous homogeneous catalysis, whereas the Sonogashira coupling of **2a** to give **5** proceeded more gradually (Figure 1Bb; 51 % consumed in 10 min).

Control experiments demonstrated that the high stereoselectivity of our bimetallic catalyst is likely due to a concomitant Pd-catalyzed isomerization of (*Z*)-**3a** into (*E*)-**4a** during the transmetallation step.[16] Surprisingly, reactions performed with pure (*Z*)-**3a** by using soluble $Pd(OAc)_2$ and the bimetallic ionic-gel catalyst **1d** under the described coupling conditions quantitatively led to (*Z*)-**4a** and the more stable stilbene (*E*)-**4a**, respectively. In addition, pure (*Z*)-**3a** and (*Z*)-**4a** were independently subjected to **1d** in the absence of PhI, but no reaction occurred and only the corresponding starting materials were recovered.

The bimetallic ionic-gel catalyst **1d** was analyzed by transmission electron microscopy (TEM). Before catalysis, a monodisperse population of spherical particles with a diameter of about 12 ± 1 nm was observed within the polyionic gel (Figure 2A). After the sequential one-pot reaction, TEM images revealed a few larger metallic particles of approximate diameter 25 ± 1 nm in addition to the previously described population (Figure 2B). These values are much lower than the particle sizes (4 ± 1 nm) of the polyionic-gel-soaked Pd catalyst we reported.[10a]

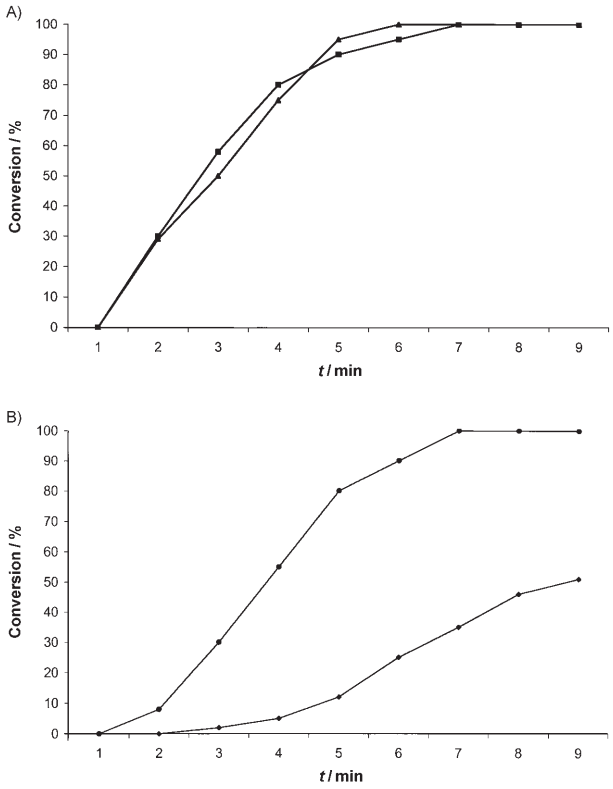


Figure 1. Conversion rates for hydrosilylation (H) and Sonogashira coupling (S) of **2a**: A) hydrosilylation of **2a** in the presence of $[RhCl(PPh_3)_3]/Pd(OAc)_2$, NaI (a, ■) and Sonogashira coupling of **2a** in the presence of $[RhCl(PPh_3)_3]/Pd(OAc)_2$, NaI (b, ▲). B) hydrosilylation of **2a** in the presence of **1d** (a, ●) and Sonogashira coupling of **2a** in the presence of **1d** (b, ◆).

The scope of the **1d**-catalyzed one-pot hydrosilylation/ Hiyama coupling reaction was further investigated by using various functionalized terminal alkynes **2**, and different iodide partners (Table 3). Isolation of products simply involved short column chromatography on silica.

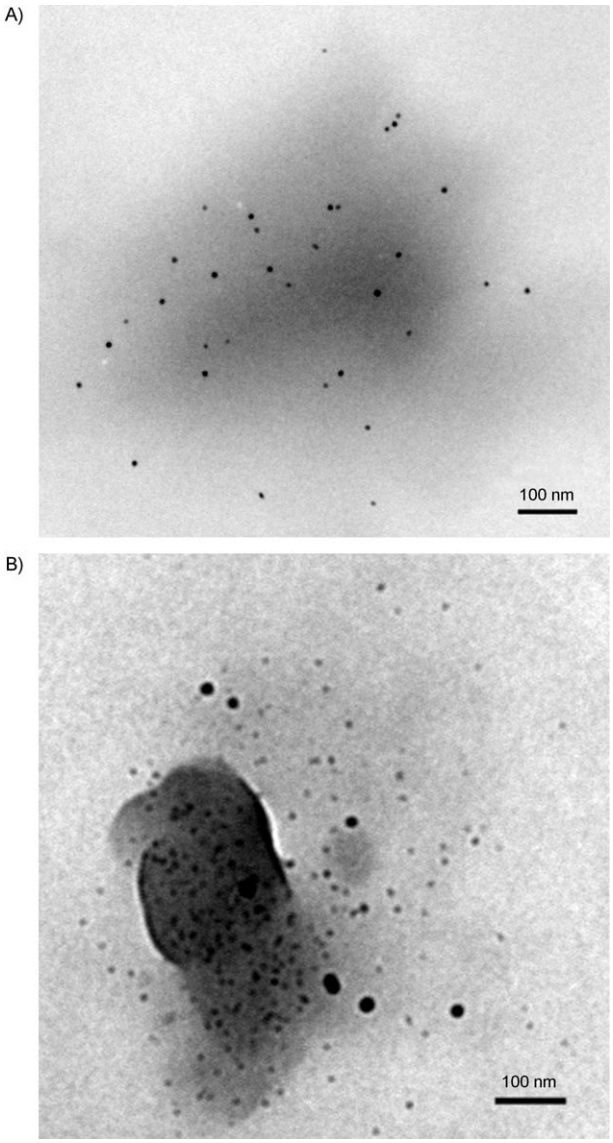


Figure 2. Representative TEM images of bimetallic [Rh–Pd] **1d**: A) before reaction and B) after reaction.

Reactions proceeded with high regio- and stereoselectivities, and good overall yields for final products were obtained. A point to note is that when a free hydroxy group was present either in the starting alkyne or in the aryl iodide, no deactivation of the catalyst nor side dehydrogenative silylation of the alcohol were observed (entries 1, 5 and 10–12). Under **1d**-catalyzed conditions, reaction of the heterosubstituted acetylene chemoselectively gave **4g** via the nonisolated bis-silylated intermediate (entry 6). It should be noted that deactivation of the acetylenic bond by the trimethylsilyl group toward hydrostannation,[17] alumination,[18] and stannylcupration[19] was previously observed by Guibé and Zweifel. Only starting materials were recovered. Interestingly, reactions with the conjugated alkyne produced the (*E*,*E*)-derivatives **4k** and **4l** as pure regio- and stereoisomeric adducts without affecting the *E* configuration of the remote double bond (entries 10–11). No Heck coupling side reaction was observed. However, in the reactions with iodopyrazine, both TBAF (TBAF = tetrabutylammonium fluoride) and the N-heteroaryl iodide had to be added after 2 h to prevent Rh catalyst poisoning (entries 2 and 8). Reaction afforded the functionalized (*Z*,*E*)-**4j** and (*E*,*E*)-**4l** dienes containing masked aldehyde and isoxazole moieties, respectively, as single isomers in good yields (entries 9 and 11).

Also, a highly conjugated system, such as the (*E*,*E*,*Z*)-triene **4m**, which is an important motif in natural products, was easily prepared by the reaction of the (*E*)-enyne and the (*Z*)-ethyl-3-iodoacrylate with exclusive regio- and stereocontrol in 95% yield (entry 12). Once again, no isomerization of the double bond was observed. It should be noted that the sequential reaction with 1-nonyne gave **4n** as the major product, together with trace amounts (<5%) of the α-regioisomer in 85% yield (entry 13).[20] Stereo- and regioselectivities are usually lost in the case of terminal acetylenic compounds bearing no sterically bulky groups at the propargylic position.[17,21] By using a nonterminal alkyne, 1-phenyl-1-propyne, a complex mixture of the (*Z*)- and (*E*)-adducts with the α-regioisomers was obtained. Recycling experiments of the catalyst **1d** were conducted in five consecutive runs under standard conditions (Table 4).

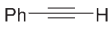
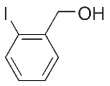
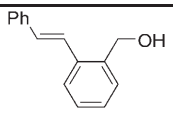
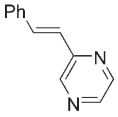
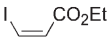
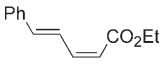
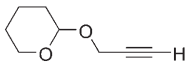
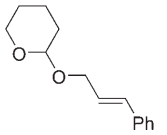
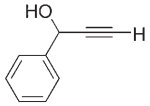
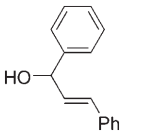
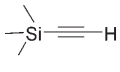
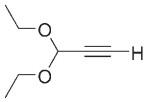
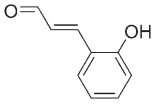
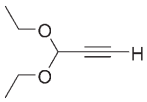
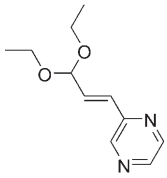
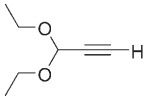
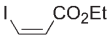
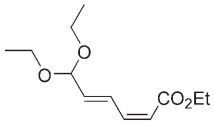
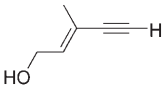
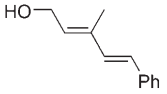
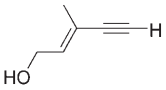
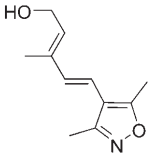
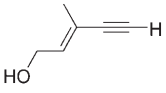
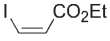
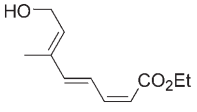
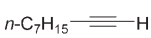
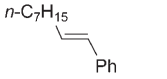
The yield decreased from >99% after the initial reaction cycle to 70% in the fifth run. Interestingly, no loss of stereoselectivity was observed, with a constant ratio *E*/*Z* of >99:1 per cycle.

Conclusion

We have prepared a bimetallic [Rh–Pd] ionic-gel-soaked catalyst that enables a practical one-pot hydrosilylation/Hiyama coupling sequence. Starting from readily available terminal alkynes and aryl- and vinyliodides, stereodefined (*E*)-disubstituted alkenes are synthesized in good overall yields without intermediate isolation. In the reported bimetallic [Rh–Pd] system, not only did both metals act without interfering, but kinetic modulation of the Pd species prevented the formation of the undesired Sonogashira side product that was observed in the reaction with the combination of soluble precursors. Interestingly, the exclusive stereocontrol appears to arise from a beneficial Pd-catalyzed isomerization from the mixture of stereoisomeric adducts into the more stable (*E*)-vinylsilane. Thus the heterogeneous bimetallic [Rh–Pd] system that allows ionic-gel-mediated selectivity modulation appears to be a versatile alternative to the combination of homogeneous catalysts.

Starting from a diverse array of terminal alkynes, this bimetallic ionic gel catalyst affords the ubiquitous (*E*)-disubstituted olefin motif with high stereocontrol. However, the N-heterocyclic iodide has to be added after completion of the hydrosilylation reaction to avoid deactivation of the Rh species. This one-pot process is an efficient alternative to classical couplings involving boronic and stannyl derivatives.

Table 3. Access to functionalized conjugated systems.[a,b]

Entry	**2**	RI	Product **4**	Method	Yield [%][c]
1				A	95
2				B	75
3				A	93
4				A	95
5				A	96
6				A	96
7				A	92
8				B	73
9				A	90
10				A	95
11				B	50
12				A	95
13				A	85

[a] Method A: 1) **2** (1.0 mmol), $HSiMe(OEt)_2$ (1.5 mmol), PhI (0.45 mmol), **1d** (3.3 Rh/9.0 Pd mol %), dioxane (2 mL), 60 °C for 2 h and 2) TBAF (1.04 mmol), 60 °C for 12 h. [b] Method B: N-hetArI was added with TBAF to avoid the formation of Sonogashira side products. [c] Isolated yields.

Table 4. Reusability of **1d** in the one-pot hydrosilylation/Hiyama coupling reaction.

Entry	Run 1	Run 2	Run 3	Run 4	Run 5
yield [%][a]	>99	>99	90	78	70
4a *E*/*Z*[b]	>99:1	>99:1	>99:1	>99:1	>99:1

[a] Determined by GCMS. [b] Values obtained from the ^{1}H NMR spectrum of the crude reaction mixture.

Experimental Section

General: All reactions were carried out under an argon atmosphere. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker 200 and 300 MHz spectrometers with $CDCl_3$ as the solvent. Chemical shifts are denoted in ppm (δ) relative to TMS (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P). The gel-phase samples were prepared in $CDCl_3$. IR spectra of chloroform solutions were recorded on KRS-5 disks by using a Perkin–Elmer 2000 FTIR spectrophotometer. Solvents were dried and distilled under argon from sodium and benzophenone before use. Merrifield resins were purchased from Senn Chemicals (1% cross-linked with divinylbenzene, 200–400 mesh, 1.58 mmol g^{-1}). Terminal alkynes, aryl, and N-heteroaryl iodides were obtained from Aldrich or Lancaster and used as received. 4-Iodo-3,5-dimethylisoxazole was obtained from Maybridge. Diethoxymethylsilane, TBAF (1 M solution in THF), NaI, and Wilkinson's catalyst were from Alfa Aesar and used directly. $Pd(OAc)_2$ was obtained from Aldrich. Elemental analyses were carried out by the Service Central d'Analyse du CNRS in Vernaison (France).

Polyammonium chloride gel: Merrifield type resin (5 g, 7.91 mmol, 1.58 mmol Cl g^{-1}) was introduced into a 100 mL scintillation vial, followed by a 1:1 mixture of toluene/acetonitrile (50 mL). The vial was shaken for 15 min, and then triethylamine (11 mL, 79.82 mmol, 10 equiv) was added and stirred at 80°C for 3 d. The mixture was poured into a fritted funnel and the resin was washed successively with $MeOH/CH_2Cl_2$ (3×50 mL) and Et_2O (2×50 mL). The resin was transferred into a vial and dried under vacuum to give polyammonium chloride gel (5.47 g); elemental analysis (mmol g^{-1}): N 1.37.

Polyammonium iodide gel: The previously prepared ammonium chloride gel (500 mg, 0.681 mmol, 1.37 mmol N g^{-1}) was introduced into a 20 mL Supelco syringe together with a 1:1 mixture of DMF/H_2O (5 mL). The resin was then drained, and a solution of NaI (397 mg, 2.65 mmol, 3.9 equiv in 15 mL of a 1:1 mixture of DMF/H_2O) was introduced into the syringe in three steps (3×5 mL). Between each anionic exchange, the syringe was shaken at room temperature for 1 h. Finally, the beads were drained and successively washed with DMF/H_2O (2×5 mL), DMF (3×5 mL), EtOH/CH_2Cl_2 (3×5 mL), and Et_2O (2×5 mL). Air was used to dry the beads before they were transferred to a vial and dried under vacuum to afford the polyammonium iodide gel (450 mg). Elemental analysis (mmol g^{-1}): N 1.23, I 0.99.

Polyionic-gel Rh catalyst 1a: The previously prepared polyammonium chloride gel (500 mg, 0.681 mmol, 1.37 mmol N g^{-1}) and CH_2Cl_2 (5 mL) were introduced into a 100 mL scintillation vial. The vial was shaken for 10 min, before the addition of a solution of $[RhCl(PPh_3)_3]$ (630 mg, 0.681 mmol, 1 equiv) in CH_2Cl_2 (10 mL). The resulting mixture was then mixed for 6 h at 45°C. The solution was drained and the orange-colored beads were thoroughly washed with CH_2Cl_2 (4×5 mL) and Et_2O (2×5 mL). The resin was transferred into a vial and dried under vacuum to give catalyst **1a** (480 mg). The loading was determined to be 0.16 mmol Rh g^{-1} by elemental analysis.

Polyionic-gel Rh catalyst 1b: This was prepared according to the procedure for **1a** from the previously prepared polyammonium iodide gel. The loading of the orange gel **1b** was determined to be 0.08 mmol Rh g^{-1} by elemental analysis.

Polyionic-gel Pd catalyst 1c: The previously prepared polyammonium chloride gel (500 mg, 0.681 mmol, 1.37 mmol g^{-1}) and DMF (4 mL) were added to a 10 mL reaction vessel with stir bar. The resin was mixed for 10 min (mixed every 3.5 s, upstroke 2.2 s, upward = 65%), before the addition of a solution of $Pd(OAc)_2$ (15.3 mg, 0.068 mmol, 0.1 equiv) in DMF (8 mL). The resulting mixture was then mixed for 20 h at 30°C. After this time, the solution was drained and the orange-colored beads were successively washed with DMF (2×4 mL), EtOH/CH_2Cl_2 (3×4 mL), and Et_2O (2×4 mL). Air was used to dry the beads before they were transferred to a vial and dried under vacuum to afford ionic-gel-palladium catalyst **1c** (390 mg, 0.15 mmol Pd g^{-1} by elemental analysis).

Bimetallic polyionic-gel [Rh–Pd] catalyst (1d): The previously prepared polyammonium iodide gel (255 mg, 0.313 mmol, 1.23 mmol N g^{-1}) and CH_2Cl_2 (3 mL) were introduced into a 50 mL scintillation vial. The vial was shaken for 10 min, before the addition of an equimolar solution of $[RhCl(PPh_3)_3]$ (28.7 mg, 0.031 mmol, 0.1 equiv) and $Pd(OAc)_2$ (47.5% Pd, 14.6 mg, 0.031 mmol, 0.1 equiv) in CH_2Cl_2 (7 mL). The resulting mixture was then mixed for 6 h at 30°C. The solution was drained and the purple-colored beads were thoroughly washed with CH_2Cl_2 (3×5 mL) and Et_2O (2x 5 mL). The resin was transferred into a vial and dried under vacuum to give catalyst **1d** (220 mg). Elemental analysis (mmol g^{-1}): Rh 0.06, Pd 0.16.

General procedure for the hydrosilylation of phenylacetylene (2a) with Rh catalysts (Table 1): Phenylacetylene (**2a**) (0.219 mL, 2.0 mmol) and diethoxymethylsilane (0.480 mL, 3.0 mmol) were added to a suspension of polyionic-gel catalyst **1d** (13.3 mg, Rh = 0.04 mol%) in dioxane (4 mL) under an argon atmosphere. The mixture was stirred at 60°C for 12 h. After this time, the mixture was filtered off through a Celite pad and concentrated in vacuo. The filtrate was then subjected to bulb-to-bulb distillation (145°C, 3 Torr) under reduced pressure to give pure (*E*)-**3a**, pure (*Z*)-**3a**, and a mixture of *E* and *Z* isomers (402 mg, 85% yield).

(*E*)-1-Diethoxymethylsilyl-2-phenylethylene (3a):[12b] Yellow oil; R_f = 0.59 (silica gel, cyclohexane/ethyl acetate 98:2); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.34 (s, 3H), 1.31 (t, J = 7.1 Hz, 6H), 3.89 (q, J = 7.1 Hz, 4H), 6.36 (d, J = 19.3 Hz, 1H), 7.16 (d, J = 19.3 Hz, 1H), 7.27–7.58 ppm (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = −4.0, 18.5, 58.5, 122.5, 126.8, 128.6, 137.9, 147.5 ppm; IR (KRS5): $\tilde{\nu}$ = 1082, 1102, 1261, 1390, 1448, 1495, 1574, 1607, 2969 cm^{-1}; MS: *m*/*z*: 236 $[M]^+$.

(*Z*)-1-Diethoxymethylsilyl-2-phenylethylene (3a): Colorless oil; R_f = 0.71 (silica gel, cyclohexane/ethyl acetate 98:2); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.16 (s, 3H), 1.26 (t, J = 6.8 Hz, 6H), 3.83 (q, J = 7.1 Hz, 4H), 5.77 (d, J = 15.6 Hz, 1H), 7.28–7.62 ppm (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = −3.4, 18.3, 58.3, 125.7, 128.1, 127.9, 128.3, 138.9, 149.6 ppm; IR (KRS5): $\tilde{\nu}$ = 1078, 1105, 1260, 1391, 1572, 1595, 2975, 3061 cm^{-1}; MS: *m*/*z*: 236 $[M]^+$.

General procedure for the one-pot hydrosilylation/Hiyama coupling reaction with catalyst 1d (Table 2)

Method A: Phenylacetylene (**2a**) (0.25 mmol, 2.2 equiv), diethoxymethylsilane (0.36 mmol, 3.3 equiv), and iodobenzene (0.11 mmol, 1 equiv) were successively added to a suspension of polyionic-gel catalyst **1d** (62 mg, Rh/Pd 3.3:9.0 mol%) in dioxane (1.5 mL) under an argon atmosphere. The mixture was stirred at 60°C for 2 h. After cooling the reaction to room temperature, TBAF (1.0 M in THF, 0.25 mmol, 2.3 equiv) was added dropwise. The mixture was stirred at 60°C for 12 h. The mixture was filtered off through a Celite pad and concentrated in vacuo. The crude product was purified by silica-gel chromatography to afford the product.

Method B: Phenylacetylene (**2a**) (0.25 mmol, 2.2 equiv) and diethoxymethylsilane (0.36 mmol, 3.3 equiv) were successively added to a suspension of polyionic-gel catalyst **1d** (62 mg, Rh/Pd 3.3:9.0 mol%) in dioxane (1.5 mL) under an argon atmosphere. The mixture was stirred at 60°C for 2 h. After cooling the reaction to room temperature, iodopyrazine (0.11 mmol, 1 equiv) and TBAF (1.0 M in THF, 0.25 mmol, 2.3 equiv) were added. The reaction was stirred at 60°C for 12 h. The mixture was filtered off through a Celite pad and concentrated in vacuo. The crude product was purified by silica-gel chromatography to afford the product.

(*E*)-1,2-Diphenylethylene (*trans*-stilbene) (4a): Prepared by method A (silica gel, cyclohexane). White crystal; R_f = 0.46 (silica gel, cyclohexane); spectral data were identical to those of a commercial sample; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (s, 2H), 7.32 (tt, J = 1.5, 7.3 Hz, 2H), 7.42 (tt, J = 1.5, 7.2 Hz, 4H), 7.59 ppm (dd, J = 1.1, 8.3 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 126.6, 127.7, 128.8, 137.4 ppm; IR (KRS5): $\tilde{\nu}$ = 963, 1452, 1495, 3021 cm^{-1}; MS: *m*/*z*: 180 $[M]^+$.

(*Z*)-1,2-Diphenylethylene (*cis*-stilbene) (4a): Prepared by method A (silica gel, cyclohexane). Colorless oil; $R_f = 0.61$ (silica gel, cyclohexane); spectral data were identical to those of a commercial sample; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.75$ (s, 2H), 7.34–7.40 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 127.1$, 128.3, 128.9, 130.3, 137.3 ppm; MS: *m*/*z*: 180 $[M]^+$.

Diphenylacetylene (5):[22] Obtained as a side product by method A (silica gel, cyclohexane). White crystal; $R_f = 0.51$ (silica gel, cyclohexane); spectral data were identical to those of a commercial sample; m.p. 63–64 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.36$–7.44 (m, 6H), 7.59–7.62 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 89.5$, 123.4, 128.3, 128.4, 131.7 ppm; MS: *m*/*z*: 178 $[M]^+$.

(*E*)-1-Methylalcohol-2-styrylbenzene (4b): Prepared by method A (silica gel, cyclohexane/ethyl acetate 7:3). Yield: 95%; pink flakes; $R_f = 0.20$ (silica gel, cyclohexane/ethyl acetate 8:2); m.p. 145–146 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.94$ (br s, 1H), 4.86 (s, 2H), 7.10 (d, $J = 16.1$ Hz, 1H), 7.18–7.74 ppm (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 64.1$, 125.9, 126.5, 127.3, 128.3, 128.4, 128.8, 129.1, 129.3, 131.7, 136.9, 138.0, 138.4 ppm. IR (KRS5): $\tilde{\nu} = 1044$, 1448, 1478, 1494, 3253, 3333 cm^{-1}; MS: *m*/*z*: 210 $[M^+]$; HRMS (EI): *m*/*z*: calcd for $C_{15}H_{14}O$: 210.2711 $[M]^+$; found: 210.2709.

(*E*)-2-Styrylpyrazine (4c): Prepared by method B (silica gel, cyclohexane/ethyl acetate 9:1). Yield: 75%; yellow oil; $R_f = 0.47$ (silica gel, cyclohexane/ethyl acetate 8:2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.19$ (d, $J = 16.1$ Hz, 1H), 7.64 (dd, $J = 1.7$, 8.1 Hz, 2H), 7.29–7.48 (m, 3H), 7.79 (d, $J = 16.1$ Hz, 1H), 8.44 (d, $J = 2.4$ Hz, 1H), 8.57 (dd, $J = 1.2$, 2.4 Hz, 1H), 8.68 ppm (d, $J = 1.2$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 124.1$, 127.4, 128.9, 129.1, 135.3, 136.1, 142.8, 143.8, 144.4, 151.4 ppm; IR (KRS5): $\tilde{\nu} = 1396$, 1449 (ϑC=C), 1494, 1636 cm^{-1} (ϑC=N); MS: *m*/*z*: 183 $[M+1]^+$; HRMS (EI): *m*/*z*: calcd for $C_{12}H_{10}N_2$: 182.2212 $[M]^+$; found: 182.2209.

Ethyl (*Z*,*E*)-5-phenylpenta-2,4-dienoate (4d): Prepared by method A (silica gel, cyclohexane/ethyl acetate 98:2). Yield: 93%; yellow oil; $R_f = 0.23$ (silica gel, cyclohexane/ethyl acetate 98:2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.34$ (t, $J = 7.2$ Hz, 3H), 4.24 (q, $J = 7.2$ Hz, 2H), 5.73 (d, $J = 11.2$ Hz, 1H), 6.75 (t, $J = 11.2$ Hz, 1H), 6.83 (d, $J = 15.6$ Hz, 1H), 7.29–7.54 (m, 5H), 8.16 ppm (dd, $J = 11.2$, 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.4$, 60.1, 117.6, 125.0, 127.6, 128.8, 129.0, 136.5, 141.2, 144.8, 166.7 ppm; IR (KRS5): $\tilde{\nu} = 1186$ (ϑC–O), 1450 (ϑC=C), 1624 (ϑC=C), 1711 cm^{-1} (ϑC=O); MS: *m*/*z*: 203 $[M+1]^+$; HRMS (EI): *m*/*z*: calcd for $C_{13}H_{14}O_2$: 202.2491 $[M]^+$; found: 202.2488.

(*E*)-1-*O*-Tetrahydropyranyl-3-phenyl-2-propen-1-ol (4e): Prepared by method A (silica gel, cyclohexane/ethyl acetate 98:2). Yield: 95%; yellow oil; $R_f = 0.33$ (silica gel, cyclohexane/ethyl acetate 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.54$–1.88 (m, 6H), 3.55 (m, 1H), 3.93 (m, 1H), 4.18 (dd, $J = 6.5$, 12.8 Hz, 1H), 4.42 (dd, $J = 5.6$, 13.1 Hz, 1H), 4.73 (t, $J = 4.0$ Hz, 1H), 6.33 (dt, $J = 5.6$, 15.9 Hz, 1H), 6.65 (d, $J = 15.9$ Hz, 1H), 7.24–7.42 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 19.6$, 25.6 30.7, 62.3, 67.7, 97.9, 126.1, 126.6, 127.7, 128.6, 132.4, 1369 ppm; IR (KRS5): $\tilde{\nu} = 1025$ (ϑC–O), 1449 (ϑC=C), 1495, 2942 cm^{-1}; MS: *m*/*z*: 219 $[M+1]^+$; HRMS (EI): *m*/*z*: calcd for $C_{14}H_{18}O_2$: 218.2915 $[M]^+$; found: 218.2912.

(*E*)-1,3-Diphenyl-2-propenol (4f): Prepared by method A (silica gel, cyclohexane/ethyl acetate 9:1). Yield: 96%; yellow oil; $R_f = 0.48$ (silica gel, cyclohexane/ethyl acetate 8:2); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.07$ (br s, 1H), 5.41 (d, $J = 6.4$ Hz, 1H), 6.41 (dd, $J = 6.4$, 15.8 Hz, 1H), 6.71 (d, $J = 15.8$ Hz, 1H), 7.20–7.44 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 75.5$, 126.7, 127.0, 128.1, 128.2, 128.9, 129.0, 130.9, 131.9, 136.9, 143.1 ppm; IR (KRS5): $\tilde{\nu} = 1450$ (ϑC=C), 1494, 3364 cm^{-1} (ϑO–H); MS: *m*/*z*: 210 $[M]^+$; HRMS (EI): *m*/*z*: calcd for $C_{15}H_{14}O$: 210.2711 $[M]^+$; found: 210.2715.

Trimethyl[2-(*E*)-phenylethenyl]silane (4g):[23] Prepared by method A (silica gel, cyclohexane). Yield: 96%; yellow oil; $R_f = 0.71$ (silica gel, cyclohexane/ethyl acetate 98:2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.19$ (s, 9H), 6.51 (d, $J = 19.0$ Hz, 1H), 6.91 (d, $J = 19.0$ Hz, 1H), 7.27–7.48 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -0.4$, 127.1, 128.6, 129.2, 130.2, 139.0, 144.3 ppm; IR (KRS5): $\tilde{\nu} = 843$, 867, 1247, 1447, 1494, 1574, 1606, 2956 cm^{-1}; MS: *m*/*z*: 176 $[M]^+$; HRMS (EI): *m*/*z*: calcd for $C_{11}H_{16}Si$: 176.3302 $[M]^+$; found: 176.3310.

(*E*)-3-(2-Hydroxyphenyl)propenal (4h): Prepared by method A (silica gel, cyclohexane/ethyl acetate 7:3). Yield: 92%; yellow solid; $R_f = 0.18$ (silica gel, cyclohexane/ethyl acetate 8:2); m.p. 122–123 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.17$ (s, 1H), 6.87 (d, $J = 8.1$ Hz, 1H), 6.94–7.01 (m, 2H), 7.32 (dt, $J = 1.5$, 8.1 Hz, 1H), 7.52 (d, $J = 7.8$ Hz, 1H), 7.80 (d, $J = 15.9$ Hz, 1H), 9.69 ppm (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (75 MHz, MeOD): $\delta = 117.1$, 120.8, 122.4, 129.3, 130.5, 133.8, 151.5, 158.7, 196.9 ppm; IR (KRS5): $\tilde{\nu} = 1255$, 1459 (ϑC=C), 1614, 1656 (ϑC=O), 3192 cm^{-1} (ϑO–H); MS: *m*/*z*: 149 $[M+1]^+$; HRMS (EI): *m*/*z*: calcd for $C_9H_8O_2$: 148.1586 $[M]^+$; found: 148.1582.

(*E*)-2-(3,3-Diethoxy-1-propenyl)pyrazine (4i): Prepared by method B (silica gel, cyclohexane/ethyl acetate 7:3). Yield: 73%; yellow oil; $R_f = 0.22$ (silica gel, cyclohexane/ethyl acetate 8:2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.26$ (t, $J = 6.8$ Hz, 6H), 3.58 (q, $J = 6.8$ Hz, 2H), 3.72 (q, $J = 6.8$ Hz, 2H), 5.15 (d, $J = 2.5$ Hz, 1H), 6.83 (d, $J = 2.2$ Hz, 2H), 8.41 (d, $J = 2.5$ Hz, 1H), 8.51 (d, $J = 2.5$ Hz, 1H), 8.59 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.7$, 61.2, 103.5, 133.5, 139.1, 148.5, 149.3, 150.2, 156.3 ppm; IR (KRS5): $\tilde{\nu} = 1058$, 1130, 1397, 2928, 2975 cm^{-1}; MS: *m*/*z*: 209 $[M+1]^+$; HRMS (EI): calcd for $C_{11}H_{16}N_2O_2$: 208.2569 $[M]^+$; found: 208.2565.

Ethyl (2*Z*,4*E*)-6,6-diethoxy-2,4-hexadienoate (4j): Prepared by method A (silica gel, cyclohexane/ethyl acetate 95:5). Yield: 90%; yellow oil; $R_f = 0.56$ (silica gel, cyclohexane/ethyl acetate 8:2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.22$ (t, $J = 7.1$ Hz, 6H), 1.30 (t, $J = 7.1$ Hz, 3H), 3.55 (q, $J = 7.1$ Hz, 2H), 3.65 (q, $J = 7.1$ Hz, 2H), 4.20 (q, $J = 7.1$ Hz, 2H), 4.99 (d, $J = 5.6$ Hz, 1H), 5.73 (d, $J = 11.2$ Hz, 1H), 5.97 (dd, $J = 5.6$, 15.4 Hz, 1H), 6.57 (t, $J = 11.2$ Hz, 1H), 7.61 ppm (dd, $J = 11.2$, 15.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.3$, 15.3, 60.2, 61.6, 101.1, 119.5, 128.9, 139.0, 143.2, 166.2 ppm; IR (KRS5): $\tilde{\nu} = 1190$ (ϑC–O), 1606, 1718 (ϑC=O), 2978 cm^{-1}; MS: *m*/*z*: 228 $[M]^+$; HRMS (EI): *m*/*z*: calcd for $C_{12}H_{20}O_4$: 228.2848 $[M]^+$; found: 228.2845.

(2*E*,4*E*)-3-Methyl-5-phenyl-2,4-pentadien-1-ol (4k): Prepared by method A (silica gel, cyclohexane/ethyl acetate 8:2). Yield: 95%; pale-yellow solid; $R_f = 0.26$ (silica gel, cyclohexane/ethyl acetate 8:2); m.p. 125–126 °C; ^{1}H NMR (75 MHz, $CDCl_3$): $\delta = 1.93$ (s, 3H), 4.36 (d, $J = 6.8$ Hz, 2H), 5.82 (t, $J = 6.8$ Hz, 1H), 6.58 (d, $J = 16.2$ Hz, 1H), 6.82 (d, $J = 16.2$ Hz, 1H), 7.20–7.25 (m, 1H), 7.33 (t, $J = 7.2$ Hz, 2H), 7.43 ppm (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 13.3$, 60.1, 127.0, 128.0, 128.8, 129.2, 129.3, 131.6, 133.5, 137.0, 138.0 ppm; IR (KRS5): $\tilde{\nu} = 1447$ (ϑC=C), 1490, 2925, 3342 cm^{-1} (ϑO–H); MS: *m*/*z*: 174 $[M]^+$; HRMS (EI): *m*/*z*: calcd for $C_{12}H_{14}O$: 174.2390 $[M]^+$; found: 174.2287.

(2*E*,4*E*)-3-Methyl-5-(3,5-dimethyl-4-isoxazolyl)-2,4-pentadien-1-ol (4l): Prepared by method B (silica gel, cyclohexane/ethyl acetate 7:3). Yield: 50%; yellow oil; $R_f = 0.21$ (silica gel, cyclohexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.88$ (s, 3H), 2.34 (s, 3H), 2.43 (s, 3H), 4.34 (d, $J = 6.8$ Hz, 2H), 5.75 (t, $J = 6.8$ Hz, 1H), 6.18 (d, $J = 16.2$ Hz, 1H), 6.48 ppm (d, $J = 16.2$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.6$, 11.9, 12.4, 59.4, 113.0, 115.7, 131.0, 134.5, 136.0, 158.4, 165.4 ppm; IR (KRS5): $\tilde{\nu} = 961$, 1010, 1427, 3391 cm^{-1} (ϑO–H); MS: *m*/*z*: 193 $[M]^+$; HRMS (EI): *m*/*z*: calcd for $C_{11}H_{15}NO_2$: 193.2423 $[M]^+$; found: 193.2425.

(2*E*,4*E*,6*Z*)-3-Methyl-8-ethyl ester-2,4,6-octatrien-1-ol (4m): Prepared by method A (silica gel, cyclohexane/ethyl acetate 7:3). Yield: 95%; yellow oil; $R_f = 0.33$ (silica gel, cyclohexane/ethyl acetate 7:3); ^{1}H NMR (75 MHz, $CDCl_3$): $\delta = 1.31$ (t, $J = 7.2$ Hz, 3H), 1.88 (s, 3H), 4.20 (q, $J = 7.2$ Hz, 2H), 4.35 (d, $J = 6.2$ Hz, 2H), 5.67 (d, $J = 11.2$ Hz, 1H), 5.85 (t, $J = 6.2$ Hz, 1H), 6.51 (d, $J = 15.2$ Hz, 1H), 6.64 (t, $J = 11.2$ Hz, 1H), 7.59 ppm (dd, $J = 11.2$, 15.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.7$, 14.4, 59.7, 60.0, 117.3, 124.8, 134.8, 136.3, 145.0, 145.3, 166.7 ppm; IR (KRS5): $\tilde{\nu} = 1185$, 1614, 1711 (ϑC=O), 3411 cm^{-1} (ϑO–H); MS: *m*/*z*: 214 $[M+18]^+$; HRMS (EI): *m*/*z*: calcd for $C_{11}H_{16}O_3$: 196.2429 $[M]^+$; found: 196.2425.

(*E*)-(1-Nonenyl)benzene (4n): Prepared by method A (silica gel, cyclohexane). Yield: 85%; colorless oil; $R_f = 0.78$ (silica gel, cyclohexane); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 7.1$ Hz, 3H), 1.38 (m, 10H), 2.28 (m, 2H), 6.31 (dt, $J = 6.9$, 15.0 Hz, 1H), 6,46 (d, $J = 15.1$ Hz, 1H), 7.28–7.43 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.1$, 22.8, 29.5, 30.0, 31.9, 33.3, 125.8, 126.4, 128.0, 128.7, 129.0, 135.2 ppm; IR (KRS5): $\tilde{\nu} = 843$, 956, 1032, 1447, 1462, 1512, 1606, 2958 cm^{-1}; MS: *m*/*z*: 202 $[M]^+$.

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