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Sequential Hiyama Coupling/Narasaka Acylation Reaction of (*E*)-1,2-Disilylethene: Rapid Assembly of α,β-Unsaturated Carbonyl Motifs

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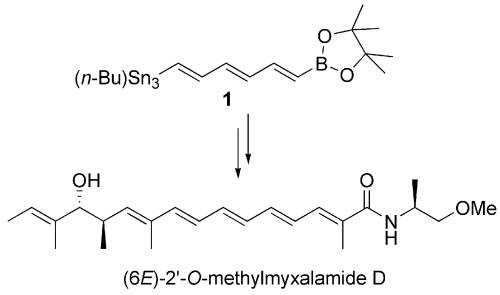
The synthesis and application of (*E*)-1,2-disilylethene **5** as a central functional building block in a sequential Hiyama coupling/Narasaka acylation reaction are described. Its use in the rapid and versatile construction of α,β-unsaturated carbonyl motifs found in a number of polyunsaturated natural products has been demonstrated. It was observed that due to the differential intrinsic reactivity of the two carbon–silicon bonds, this bis-metallated lynchpin-type reagent is activated selectively and sequentially by Pd and Rh catalysis, negating the need for any protecting group. A number of (*E*)-α,β-unsaturated ketones were efficiently synthesized with complete chemoselectively in the presence of a variety of halides and anhydride acids. Conjugated polyunsaturated ketones and diversely α′-functionalized α,β-enones, such as chalcones, a heterocyclic dienone and the highly conjugated ethyl (2*Z*,4*E*)-6-oxo-6-(2-thienyl)hexa-2,4-dienoate, were obtained in good overall yields. Thus, this coupling sequence provides a high degree of modularity, that is, a single template is likely to produce a large number of synthetic targets.

Introduction

Low molecular weight and multifunctional molecules are highly valuable building blocks (templates) because they enable the construction of a variety of structurally diverse motifs by selective and sequential catalytic coupling reactions of their functional groups. In a synthetic strategy, this building block approach is considered to be a versatile and economic alternative to classic multistep syntheses. It allows benefits, such as the facility to carry out the reactions one after another without isolating the intermediate product using a single catalyst or a combination of catalysts. Straightforward modular access to key structural functionalities is thus provided. In this regard, "olefin templates" suitably functionalized for cross-coupling reactions have been among the most successfully exploited for olefin motif elaboration.[1] As examples, homo-bis-metallated olefins are well-known coupling partners, particularly those of tin,[1a,1b] silicon[1c,1d] and boron.[1e] Hetero-bis-metallated lynchpin-type reagents,[1f] including a tin/silicon vinylic system[1g] and a boron/tin alkene[1h] and triene **1** have also been reported (Scheme 1).[1i,1j]



Scheme 1. Assembly of polyene systems from 1,3,5-hexatriene **1**.

As an elegant demonstration of this assembly strategy, Burghart and Bruckner very recently used a heptatrienyldistannane building block **2** in the total synthesis of the naturally configured pyrrhoxanthin (marine carotenoid product) by iterative Stille coupling reactions (Figure 1).[2]

The design of differentially functionalized building blocks and the development of reaction sequences that allow other key structural units are of intense ongoing synthetic interest. In contrast to olefin templates, very few examples of molecules that give access to α,β-unsaturated carbonyl motifs have been reported in the literature, despite their key role in organic synthesis. Their great synthetic value derives from the fact that the positions α, β and γ to the carbonyl groups can be activated and functionalized by various means. However, it is noteworthy that Suzuki and co-workers have described the regio- and stereoselective synthesis of α,β-unsaturated ketones by a sequential cross-

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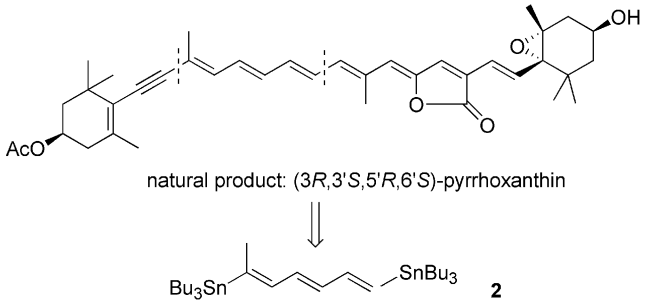
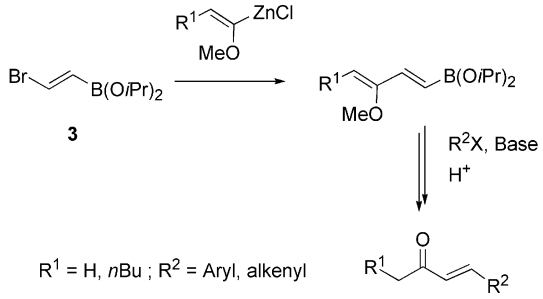


Figure 1. Natural pyrrhoxanthin from bifunctional heptatrenyldistannane **2**.

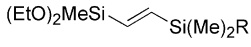
coupling reaction of (*E*)-(2-bromoethenyl)diisopropoxyborane (**3**) with α-alkoxyalkenylzinc chlorides and organic halides (Scheme 2).[3]



Scheme 2. Synthesis of (*E*)-α,β-enones from **3**.

Results and Discussion

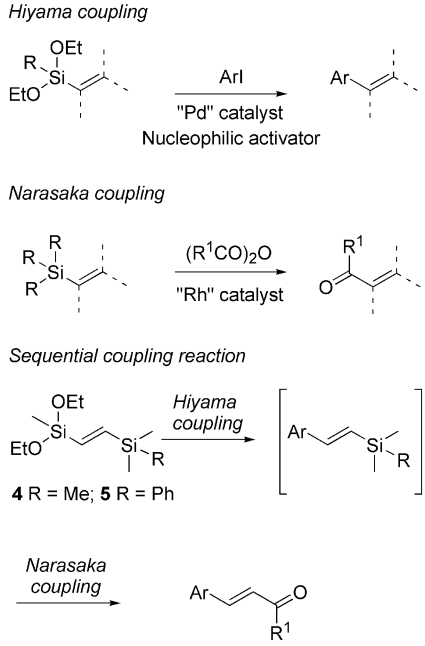
Herein, we report the regio- and stereoselective synthesis of (*E*)-1,2-disilylethenes **4** and **5** (Figure 2), and efficient sequential cross-coupling/acylation reactions of **5** to give (*E*)-α,β-unsaturated ketones in good yields.



4 R = Me
5 R = Ph

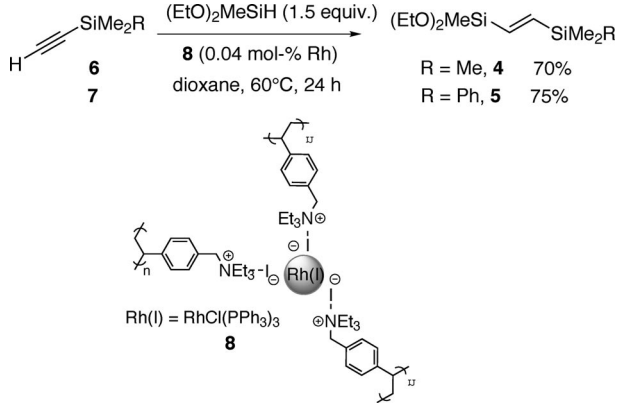
Figure 2. Homo-1,2-bis-silylethenes **4** and **5**.

In this strategy, the silyl functional groups have a defined stereochemistry and are differentiated from each other by their intrinsic reactivity. We assumed that the two carbon silicon bonds (both dialkoxyalkyl- and trialkylsilyl bearing moieties) would react orthogonally under transition-metal catalysis and allow the aforementioned Pd- and Rh-catalyzed sequence, the Hiyama coupling/Narasaka acylation (Scheme 3).



Scheme 3. Stereodefined α,β-unsaturated ketones from 1,2-disilylethenes.

(*E*)-Ethylene synthons **4** and **5** were efficiently prepared by the hydrosilylation[4] of the commercially available trimethyl- and dimethyl(phenyl)silylacetylene (**6** and **7**) with diethoxy(methyl)silane using our previously reported methodology based on metal soaking (Scheme 4).[5,6]



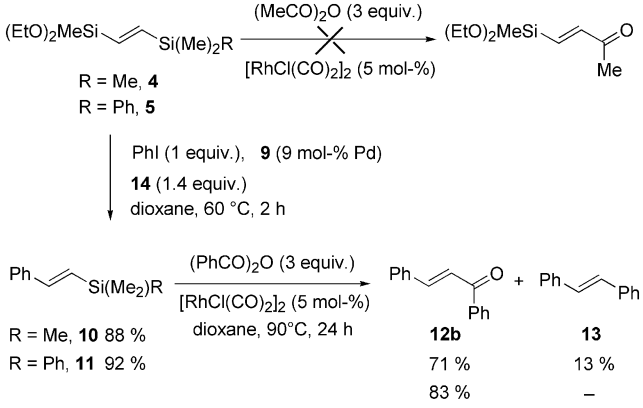
Scheme 4. Preparation of 1,2-bis-silylethenes **4** and **5**.

Based upon earlier work,[5c] the reaction of **6** and diethoxy(methyl)silane was carried out in the presence of polyionic gel-soaked rhodium complex **8**[5c] (0.04% mol Rh) in dioxane at 60 °C for 24 h to give the thermodynamically more stable (*E*)-1,2-disilylethene **4** after rhodium-promoted isomerization of the initially formed (*Z*)-1,2-disilylethene **4**.[7] Dimethyl(phenyl)silylacetylene (**7**) similarly underwent this reaction with diethoxy(methyl)silane to give the *E* adduct **5** regio- and stereoselectively.[8] The pure hydrosilylation products **4**[9] and **5** were obtained in 70 and 75% yields, respectively, by simple bulb-to-bulb distillation. The

stereochemistry of **5** was unambiguously confirmed by the coupling constants (^3J = 15.8 Hz for *Z*; 22.7 Hz for *E*) of the two vicinal vinylic protons in the ^{1}H NMR spectrum.

In the second step, the templates **4** and **5** were submitted to both palladium-catalyzed coupling and rhodium-catalyzed acylation conditions. Silicon-based cross-coupling reactions[10] (Hiyama coupling) of aryl- and vinylsilanes with various halide partners has been widely studied. This Pd-catalyzed C–C bond-forming reaction has gained prominence in synthetic organic chemistry as a reliable alternative to 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 issues. In particular, Hiyama and co-workers reported the use of alkenylsilanes bearing 2-thienyl-,[11] dicholoro-[12] and difluoro-functionalized[13] silicons. In this coupling reaction, a pentacoordinated silicon intermediate is reported to be a prerequisite to successful cross-coupling. TBAF is usually used as a nucleophilic activator to generate the activated species and promote Pd transmetallation. Denmark et al. showed that under these conditions, dialkoxy-, chloro- or alternatively 2-pyridyl derivatives and siletanes are the most reactive silanes towards Pd transmetallation, whereas trialkylsilanes failed to react or afforded poor yields.[14]

Hiyama coupling of bifunctional **4** and **5** with iodobenzene and *n*-tetrabutylammonium fluoride using our reported ionic gel palladium catalyst **9**[5a] provided the (*E*)-(2-arylvinyl)silanes **10** and **11** in 88 and 92% yields, respectively (Scheme 5). Note that the reactions proceeded quantitatively with no evidence of the competing reactions of the trimethyl- and dimethyl(phenyl)silyl-bearing termini. The reason for the observed chemoselectivity was that selective fluoride-based activation of the diethoxy(methyl)silyl moiety occurred to effect transmetallation. The corresponding homogeneous catalyst, $Pd(OAc)_2$, also provided the desired products **10** and **11**, but in slightly lower yields (62 and 86%, respectively).



Scheme 5. Rhodium(I)-catalyzed acylation of vinylsilanes with benzoic anhydride.

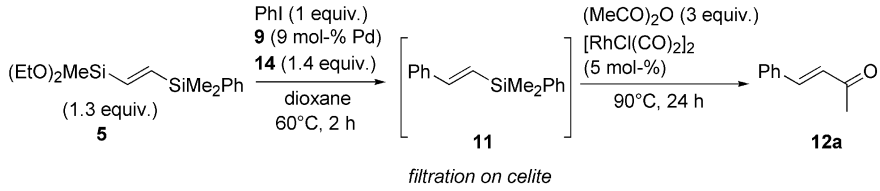
With regard to the activation of the second C–Si bond, Narasaka and co-workers recently developed a rhodium(I)-catalyzed acylation of trialkylvinylsilanes using carboxylic acid anhydrides.[15] Thus, the introduction of the acyl motif was attempted by subjecting the 1,2-bis-silylethenes **4** and **5** to the Narasaka reaction conditions in the presence of acetic anhydride (3 equiv.) and catalytic $[RhCl(CO)_2]_2$ (5 mol-%) in dioxane at 90 °C for 24 h.[16] We expected that the reaction would occur chemoselectively at the trialkylsilyl moiety. Unfortunately, a complex mixture of products was obtained with no acylation product formed at all. We assumed that reaction with the dialkoxymethyl terminus led to the formation of oligomers, precluding the Narasaka reaction. These results revealed that the Hiyama coupling reaction has to be first performed in a one-pot sequential strategy.

We then tested (*E*)-(2-arylvinyl)silanes **10** and **11** under the same acylation conditions. Both reactions afforded the expected (*E*)-benzylideneacetone (**12a**) in 64 and 85% yields respectively. In agreement with the literature, (*E*)-(2-arylvinyl)dimethyl(phenyl)silane **11** appears to be more reactive than vinylsilane **10** with a trimethylsilyl group.[15b] Efforts were made to further improve the procedure by examining two other rhodium precursors ($[RhCl(PPh_3)_3]$ and $[RhCl(cod)_2]_2$) as well as their corresponding poly-ionic gel-soaked complexes, prepared according to our reported procedure.[5a] Only the reaction with the heterogeneous ionic $[RhCl(CO)_2]_2$-based catalyst was successful, which enabled the formation of α,β-unsaturated ketone **12a** from **11** in a modest 41% isolated yield. As the best catalyst for this reaction, homogeneous $[RhCl(CO)_2]_2$ was used in further studies.

Interestingly, in the reaction of **10** with benzoic anhydride as the acylating agent, the desired phenyl vinyl ketone **12b** was obtained in a 71% yield together with 13% of the phenylated product **13**, which arises from a decarbonylative side-reaction.[17] With dimethyl(phenyl)vinylsilane **11**, this undesired reaction was suppressed (Scheme 5).

These results prompted us to further develop the one-pot version of this bimetallic catalyzed-sequence from bifunctional building block **5**. Further control experiments validated the cross-selectivity of the two catalytic systems.[18] As was previously observed, the incompatibility of **5** with acid anhydrides was confirmed, which led us to perform the oriented Hiyama coupling/Narasaka acylation sequence.

Interestingly, the first attempt to perform the one-pot reaction by adding all the reagents together was unsuccessful, resulting only in the isolation of the coupling intermediate (*E*)-**11** with no trace of the target compound **12a**. The same result was observed with the sequential addition of the coupling and acylation partners. To overcome this difficulty, we proposed to deactivate the rhodium catalyst by using fluoride anions, required to generate the activated pentacoordinate silicon species for the Hiyama coupling reaction. Consequently, we refined the reaction conditions of the first step. When various bases were screened (DBU, K_2CO_3, Cs_2CO_3, Ag_2O and $BaO{\cdot}H_2O$), no acylated product was detected. Only $BaO{\cdot}H_2O$ quantitatively provided the coupling intermediate **11**, whereas no reaction was observed with other activators. As this alternative did not succeed, we revisited the fluoride strategy. Simple filtration



Scheme 6. One-pot sequential Hiyama/Narasaka coupling reactions with bis-silylated **5**.

through Celite followed by work-up of the intermediate to eliminate fluoride scavengers resulted in the expected substrate (*E*)-**12**, but in a low overall yield of 27%. Ultimately, both replacement of the TBAF solution with polymer-supported ammonium fluoride **14**[19] and rapid filtration of the intermediate allowed the coupling sequence to proceed smoothly to yield the desired (*E*)-benzylideneacetone (**12a**) in an overall yield of 83% (Scheme 6). Note that under homogeneous conditions ($Pd(OAc)_2$ and $[RhCl(CO)_2]_2$), the expected product **12a** was formed in a satisfactory overall yield of 73%.

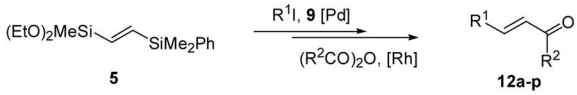
The reaction of **5** was carried out sequentially, performing the Hiyama coupling with iodobenzene and the supported TBAF activator **14** followed after 2 h by filtration through a pad of Celite and the addition of acetic anhydride and the rhodium catalyst to promote the acetylation. With the use of a heterogeneous fluoride source and polyionic gel-soaked palladium, the sequence is essentially quantitative and clean, and the purification is largely simplified. The ^1H NMR spectrum of the crude after filtration revealed that only the desired product **11** was present, with no byproduct. The sensitivity of the rhodium catalyst towards halide anions might account for the previously observed low activity of the ionic gel-soaked rhodium.

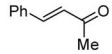
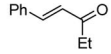
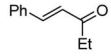
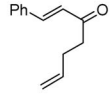
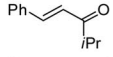
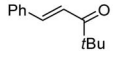
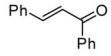
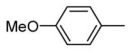
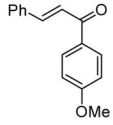
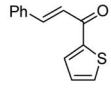
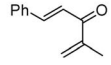
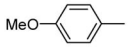
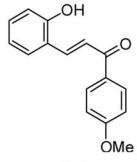
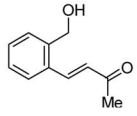
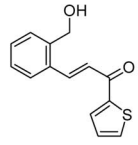
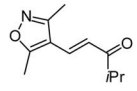
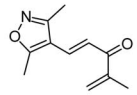
To probe the versatility of this procedure, the homo-bis-metallated olefin **5** was used as a precursor of various stereodefined and conjugated α,β-unsaturated ketones. A variety of iodide partners and carboxylic anhydrides were tested under the above-optimized reaction conditions (Table 1). No difficulty was encountered in obtaining isolated products in ≥98% isomeric purity after simple and single silica gel chromatographic purification.

Satisfyingly, in all cases, the sequential Hiyama/Narasaka reactions proceeded with complete stereocontrol, that is, with retention of configuration, and the *E* stereoisomers were formed exclusively. Good isolated overall yields, ranging from 40 to 87%, of the final polyunsaturated α,β-enones were obtained from the starting bifunctional **5**. The most common access to this structural unit is by the Claisen–Schmidt condensation of aldehydes and ketones, a reaction that is amply documented and described.[20,21] However, this method suffers from the drawbacks of narrow substrate diversity, the reversibility of the aldol addition and several side-reactions under relatively strong basic conditions (*Z* isomer,[22] ketone self-condensation, Michael addition and Cannizzaro byproducts). The Heck-type coupling of vinyl ketone derivatives is also a valuable C–C bond-forming reaction, which allows the formation of α,β-unsaturated ketones, but the poor stability of alkenone substrates and the competitive conjugate addition reaction[23,24] limit its use. In addition, a survey of the literature revealed that examples of reactions using aryl vinyl ketones are extremely rare.[25] Note that in the new methodology involving oxygen-promoted Pd^{II} cross-coupling in the absence of bases, the reaction with methyl vinyl ketone and phenylboronic acid afforded (*E*)-4-phenyl-3-buten-2-one (**12a**) without the undesired homo-coupled product but in a lower yield (71%).[26]

In our strategy, we observed that Narasaka reactions with poorly reactive aliphatic anhydrides were sluggish (entry 2). Rhodium catalyst loading and reaction time were increased to obtain enones in acceptable yields (entries 3–6). Compounds **12e** and **12f** by aldol condensation of benzaldehyde with 3-methylbutan-2-one and pinacolone have been prepared previously in lower yields (58 and 50%, respectively, compared with 72 and 64%, entries 5 and 6).[27] In the reactions involving conjugated anhydrides, no decarbonylative coupling was detected (entries 7–10). Also, despite the sensitivity of the acylation catalyst towards halide anions, no deactivation of the rhodium species was observed by introducing various functional and heteroaryl groups (free hydroxy, thiophene, isoxazole, pyrazine and ester functions). The isomerisation of secondary propargylic alcohols to α,β-enones was recently developed by Tanaka and co-workers using a cationic rhodium(I)/BINAP complex, which gave good yields and selectivity.[28] However, substrate limitation was reported with phenyl- and the highly coordinating 2-pyridyl-substituted alcohols, which led, respectively, to a complex mixture of products and no reaction. Satisfyingly, **12b** and **12o** could be prepared by our coupling sequence in 86 and 70% yields, respectively (entries 7 and 16). Note that derivatives **12g**,**h**,**j**,**l** with substituted chalcone skeletons are intermediates in the biosynthesis of flavonoids, which are associated with various pharmacological activities (anti-malarial, anti-inflammatory, cytotoxic, anti-cancer, diuretic, choleretic), and were prepared from a unique chalcone template[29] (entries 8, 9, 11 and 13). The scope of the Narasaka acylation was extended to previously unexplored functionalized anhydrides, leading to enones **12d** and **12g**–**i** (entries 4 and 8–10). In addition, dienone **12n** with an isoxazole moiety was obtained selectively in a moderate yield (entry 15). Interestingly, reaction with ethyl (*Z*)-3-iodoacrylate produced the highly conjugated (*E*,*Z*)-**12p** as a pure regio- and stereoisomeric adduct without affecting the *Z* configuration of the remote double bond (entry 17). No Heck coupling side-reaction was observed. Its polyunsaturated nature made the synthesis particularly challenging due to its sensitivity to light, oxygen,

Table 1. Access to stereodefined and conjugated α,β-unsaturated ketones **12a**–**p**.[a,b]



Entry	R^1	R^2	Product **12**		Method	Yield[c] [%]
1		Me		**12a**	A	83
2		Et		**12c**	A	48
3		Et		**12c**	B	73
4				**12d**	B	66
5		*i*Pr		**12e**	B	72
6		*t*Bu		**12f**	B	64
7				**12b**	A	86
8				**12g**	A	87
9				**12h**	A	53
10				**12i**	A	63
11				**12j**	A	55
12		Me		**12k**	A	72
13				**12l**	A	70
14		*i*Pr		**12m**	B	60
15				**12n**	A	40
16		*t*Bu		**12o**	B	70
17				**12p**	A	40

[a] Method A: 1) **5** (0.50 mmol), R^1I (0.39 mmol), **14** (0.54 mmol), **9** (9.0 mol-% Pd), dioxane (2 mL), 60 °C for 2 h; 2) $(R^2CO)_2O$ (1.17 mmol), $[RhCl(CO)_2]_2$ (5.0 mol-%), 90 °C for 24 h. [b] Method B: the reaction was carried out with 10.0 mol-% of $[RhCl(CO)_2]_2$ for 48 h. [c] Isolated yields.

and many common synthetic reagents. This material has been recently utilized in the Julià–Colonna asymmetric procedure to furnish a valuable optically active epoxide.[30]

Conclusions

The development of a suitably functionalized reagent **5** as a central building block for the rapid and versatile construction of α,β-unsaturated ketone motifs has been described. The intrinsic differential reactivity of the two carbon–silicon bonds of 1,2-bis-silylethene **5** has been exploited to enable the catalytic stepwise elaboration of α,β-unsaturated ketones by sequential Hiyama coupling/Narasaka acylation reactions. The valuable synthetic targets efficiently obtained include stereodefined polyunsaturated ketones and diversely α′-functionalized α,β-enones. Thus, this modular assembly strategy illustrates the potential of bifunctional templates as synthetic tools to rapidly synthesise a variety of structurally related molecules and it is a worthwhile valuable alternative to known methods. Extension of the scope of this strategy and further investigations into the utility of this functional building block are underway.

Experimental Section

General: All reactions were carried out under argon. ^{1}H, ^{13}C and ^{31}P NMR were recorded with Bruker 200 and 300 MHz spectrometers with $CDCl_3$ as 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 using KRS-5 disks by using a Perkin–Elmer 2000 FTIR spectrometer. 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}). (Trimethylsilyl)- and dimethyl(phenyl)silylacetylenes, aryl, alkenyl and *N*-heteroaryl iodides and the anhydride acids were obtained from Aldrich or Lancaster and used as received. 4-Iodo-3,5-dimethylisoxazole was obtained from Maybridge. Diethoxy(methyl)silane, TBAF (1 M solution in THF), NaI, $[RhCl(CO)_2]_2$, $[RhCl(cod)]_2$ and Wilkinson's catalyst were from Alfa Aesar and were 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 per g) 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 per g) 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 into 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 8: The previously prepared polyammonium iodide gel (500 mg, 0.615 mmol, 1.23 mmol N per g) 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 $[RhCl(PPh_3)_3]$ (569 mg, 0.615 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-coloured 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 **8** (422 mg). The loading was determined to be 0.08 mmol Rh per g by elemental analysis.

Polyionic Gel Pd Catalyst 9: 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 containing a stirring bar. The resin was mixed for 10 min (mixed every 3.5 s, upstroke 2.2 s, upward = 65%), before adding 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-coloured 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 into a vial and dried under vacuum to afford ionic gel palladium catalyst **9** (390 mg, 0.15 mmol Pd per g by elemental analysis).

Supported TBAF 14: Merrifield-type resin (1 g, 1.58 mmol, 1.58 mmol Cl per g) was introduced into a 25 mL scintillation vial followed by a 1:1 mixture of toluene/acetonitrile (10 mL). The vial was shaken for 15 min and then tributylamine (4 mL, 15.80 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 × 10 mL) and Et_2O (2 × 10 mL). The resin was transferred into a vial and dried under vacuum to give polyammonium chloride gel (980 mg); elemental analysis (mmol g^{-1}): N 1.21. The resulting resin was swollen in DMF (10 mL) for 10 min and a solution of NaF (194 mg, 4.62 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 × 10 mL), DMF (3 × 10 mL), EtOH/CH_2Cl_2 (3 × 10 mL) and Et_2O (2 × 10 mL). Air was used to dry the beads before they were transferred into a vial and dried under vacuum to afford the supported ammonium fluoride gel (923 mg). Elemental analysis (mmol g^{-1}): N 1.14, F 1.02.

General Procedure for the Hydrosilylation of Trimethylsilylacetylene (6) with Catalyst 8: Diethoxy(methyl)silane (17 mL, 105.7 mmol) was added to a suspension of trimethylsilylacetylene (**6**) (10 mL, 70.5 mmol) and polyionic gel catalyst **8** (35 mg, Rh = 0.04 mol-%) in dry dioxane (100 mL) under argon. The mixture was stirred at 60 °C for 24 h. After this time, the mixture was filtered through a Celite pad, washed with CH_2Cl_2 and concentrated in vacuo. The filtrate was then subjected to bulb-to-bulb distillation (66–67 °C,

0.065 Torr) under reduced pressure to give pure (*E*)-**4** (11.4 g, 70% yield).

(*E*)-1-[Diethoxy(methyl)silyl]-2-(trimethylsilyl)ethylene (4):[9] Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.06 (s, 9 H), 0.19 (s, 3 H), 1.21 (t, J = 7.1 Hz, 6 H), 3.75 (q, J = 7.1 Hz, 4 H), 6.42 (d, J = 22.9 Hz, 1 H), 6.85 (d, J = 22.9 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –5.1, –2.0, 18.1, 57.8, 143.5, 155.1 ppm. IR (KRS5): $\tilde{\nu}$ = 839, 1081, 1106, 1249, 2973, 1495 cm^{-1}. MS: m/z = 233 $[M + 1]^+$.

(*E*)-1-[Diethoxy(methyl)silyl]-2-dimethyl(phenyl)silylethylene (5): Yield 15.6 g, 75%; colourless oil (b.p. = 84–85 °C/0.015 Torr). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.19 (s, 3 H), 0.36 (s, 3 H), 0.44 (s, 3 H), 1.21 (t, J = 7.1 Hz, 6 H), 3.82 (q, J = 7.1 Hz, 4 H), 6.54 (d, J = 22.7 Hz, 1 H), 6.93 (d, J = 22.7 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –2.8, –0.8, 18.4, 58.3, 58.5, 127.9, 129.2, 134.0, 138.2, 146.1, 153.2 ppm. IR (KRS5): $\tilde{\nu}$ = 839, 1081, 1106, 1249, 1806, 1891, 1955, 2973, 3025, 3069 cm^{-1}. MS: m/z = 295 $[M + 1]^+$.

General Procedure for the Hiyama Coupling Reaction with Catalyst 9: (*E*)-1-Diethoxy(methyl)silyl-2-trimethylsilylethylene (**4**) (0.14 mmol, 1.3 equiv.) and iodobenzene (0.11 mmol, 1 equiv.) were successively added to a suspension of polyionic gel catalyst **9** (65 mg, 9.0 mol-% Pd) in dioxane (1.5 mL) under argon. After dropwise addition of TBAF (1.0 M in THF, 0.15 mmol, 1.4 equiv.), the reaction was stirred at 60 °C for 2 h. The mixture was filtered through a Celite pad and concentrated in vacuo. The crude product was purified by silica gel chromatography to afford the product **10** (17.1 mg, 88% yield).

(*E*)-2-Phenyl-1-(trimethylsilyl)ethylene (10):[5c] Purified by silica gel chromatography with cyclohexane as eluent. Yellow oil. R_f = 0.68 (silica gel, cyclohexane/ethyl acetate, 95:5). The spectroscopic data are identical to those of a commercial sample. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.19 (s, 9 H), 6.51 (d, J = 19.0 Hz, 1 H), 6.91 (d, J = 19.0 Hz, 1 H), 7.27–7.48 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.4, 127.1, 128.6, 129.2, 130.2, 139.0, 144.3 ppm. IR (KRS5): $\tilde{\nu}$ = 755, 843, 867, 1247, 1606, 2956, 3023, 3067 cm^{-1}. MS: m/z = 177 $[M + 1]^+$.

(*E*)-1-[Dimethyl(phenyl)silyl]-2-phenylethylene (11):[31] Prepared by following the above procedure for the synthesis of **10** and purified by silica gel chromatography with cyclohexane as eluent. Yield 24.1 mg, 92%; yellow oil. R_f = 0.80 (silica gel, cyclohexane). The spectroscopic data were identical to those of a commercial sample. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.67 (s, 6 H), 6.82 (d, J = 19.3 Hz, 1 H), 7.19 (d, J = 19.3 Hz, 1 H), 7.40–7.68 (m, 8 H), 7.80–7.85 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.2, 126.7, 127.3, 128.0, 128.4, 128.7, 129.3, 134.1, 138.3, 138.7, 145.5 ppm. IR (KRS5): $\tilde{\nu}$ = 755, 843, 867, 1247, 1606, 1806, 1890, 1955, 2956, 3023, 3067 cm^{-1}. MS: m/z = 239 $[M + 1]^+$. HRMS (EI): calcd. for $C_{16}H_{18}Si$ 238.1121 $[M]^+$; found 238.1116.

General Procedure for the Narasaka Acylation with $[RhCl(CO)_2]_2$: $[RhCl(CO)_2]_2$ (4.1 mg, 0.01 mmol, 5 mol-%) and acetic anhydride (0.63 mmol, 3 equiv.) were added to a dioxane solution (2 mL) of (*E*)-1-dimethyl(phenyl)silyl-2-phenylethylene (**11**; 0.21 mmol, 1 equiv.) and the mixture was heated at 90 °C for 24 h. After evaporation of the solvent, the crude product was purified by silica gel chromatography to afford (*E*)-4-phenylbut-3-en-2-one (**12a**; 26 mg, 85%).

(*E*)-4-Phenylbut-3-en-2-one (Benzylideneacetone, 12a):[32] Purified by silica gel chromatography with cyclohexane/ethyl acetate (8:2) as eluent. White crystals. R_f = 0.46 (silica gel, cyclohexane/ethyl acetate, 8:2). The spectroscopic data are identical to those of a commercial sample. m.p. 39–41 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 6.63 (d, J = 16.2 Hz, 1 H), 7.29–7.31 (m, 3 H), 7.40–7.46 (m, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.3, 127.0, 128.1, 128.8, 130.3, 134.3, 143.2, 198.1 ppm. IR (KRS5): $\tilde{\nu}$ = 1257, 1610, 16669, 1692 cm^{-1}. MS: m/z = 147 $[M + 1]^+$.

(*E*)-Benzylideneacetophenone [(*E*)-Chalcone, 12b): Prepared from **11** by method A (silica gel, cyclohexane/ethyl acetate, 9:1). Yield 36 mg, 83%; yellow needles. R_f = 0.51 (silica gel, cyclohexane/ethyl acetate, 8:2); m.p. 55–57 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.41 (m, 3 H), 7.46–7.65 (m, 6 H), 7.83 (d, J = 15.7 Hz, 1 H), 8.04 (dd, J = 1.5, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 122.0, 128.5, 128.6, 128.7, 129.0, 130.5, 132.8, 134.9, 138.2, 144.8, 190.4 ppm. IR (KRS5): $\tilde{\nu}$ = 747, 1215, 1336, 1606, 1664 cm^{-1}. MS: m/z = 209 $[M + 1]^+$.

(*E*)-1,2-Diphenylethylene (*trans*-Stilbene, 13): Obtained as a side-product from the reaction of **10** by method A (silica gel, cyclohexane). Yield 5 mg, 13%; white crystals. R_f = 0.46 (silica gel, cyclohexane). The spectroscopic data were identical to those of a commercial sample. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (s, 2 H), 7.32 (tt, J = 1.5, 7.3 Hz, 2 H), 7.42 (tt, J = 1.5, 7.2 Hz, 4 H), 7.59 (dd, J = 1.1, 8.3 Hz, 4 H) ppm. ^{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 $[M]^+$.

General Procedure for the One-Pot Hiyama/Narasaka Coupling Protocol with Catalysts 9 and $[RhCl(CO)_2]_2$: See Table 1. Polyionic gel catalyst **9** (230 mg, 0.035 mmol, 9.0 mol-% Pd) was added to a dioxane solution (2 mL) of iodobenzene (0.39 mmol, 1 equiv.), (*E*)-1-[diethoxy(methyl)silyl]-2-[dimethyl(phenyl)silyl]ethylene (**5**; 0.50 mmol, 1.3 equiv.) and supported TBAF **14** (0.54 mmol, 1.4 equiv., 0.79 mmol Rh per g). The mixture was heated at 60 °C for 2 h and filtered through a Celite pad. After the addition of $[RhCl(CO)_2]_2$ (7.8 mg, 0.019 mmol, 5 mol-%) and acetic anhydride (1.17 mmol, 3 equiv.), the mixture was heated at 90 °C for 24 h and concentrated in vacuo. The crude product was purified by thin-layer chromatography to afford (*E*)-4-phenylbut-3-en-2-one (**12a**; 47.2 mg, 83%).

(*E*)-1-Phenylpent-1-en-3-one (12c):[33] Prepared by method B (silica gel, cyclohexane/ethyl acetate, 9:1). Yield 45 mg, 73%, pale-yellow oil. R_f = 0.25 (silica gel, cyclohexane/ethyl acetate, 95:5). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.17 (t, J = 7.3 Hz, 3 H), 2.70 (q, J = 7.3 Hz, 2 H), 6.74 (d, J = 16.1 Hz, 1 H), 7.37–7.40 (m, 3 H), 7.52–7.60 (m, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.4, 34.2, 126.2, 128.4, 129.1, 130.5, 134.7, 142.4, 201.1 ppm. IR (KRS5): $\tilde{\nu}$ = 1611, 1668, 1693, 2977 cm^{-1}. MS: m/z = 161 $[M + 1]^+$. HRMS (EI): calcd. for $C_{11}H_{12}O$ 160.0888 $[M]^+$; found 160.0893.

(*E*)-1-Phenylhepta-1,6-dien-3-one (12d): Prepared by method B (silica gel, cyclohexane/ethyl acetate, 95:5). Yield 48 mg, 66%; yellow oil. R_f = 0.39 (silica gel, cyclohexane/ethyl acetate, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39–2.48 (m, J = 1.2, J = 7.1 Hz, 2 H), 2.77 (t, J = 7.1 Hz, 2 H), 5.01 (dq, J = 1.2, J = 1.5, J = 10.3 Hz, 1 H), 5.08 (dq, J = 1.2, J = 1.5, J = 17.1 Hz, 1 H), 5.87 (m, J = 7.8, J = 10.3, J = 17.1 Hz, 1 H), 6.75 (d, J = 16.2 Hz, 1 H), 7.38–7.40 (m, 3 H), 7.53–7.60 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.4, 40.1, 115.4, 126.3, 128.4, 129.1, 130.6, 134.7, 137.4, 142.7, 199.7 ppm. IR (KRS5): $\tilde{\nu}$ = 1612, 1662, 1690, 2920 cm^{-1}. MS: m/z = 187 $[M + 1]^+$. HRMS (EI): calcd. for $C_{13}H_{14}O$ 186.1045 $[M]^+$; found 186.1049.

(*E*)-4-Methyl-1-phenylpent-1-en-3-one (12e):[34] Prepared by method B (silica gel, cyclohexane). Yield 49 mg, 72%; pale-yellow oil. R_f = 0.60 (silica gel, cyclohexane/ethyl acetate, 9:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.18 (d, J = 6.8 Hz, 6 H), 2.94 (sept, J =

6.8 Hz, 1 H), 6.82 (d, J = 15.9 Hz, 1 H), 7.36–7.40 (m, 3 H), 7.54–7.65 (m, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.7, 39.5, 124.7, 128.5, 129.1, 130.5, 133.2, 142.6, 204.0 ppm. IR (KRS5): $\tilde{\nu}$ = 1056, 1613, 1664, 1689, 2969 cm^{-1}. MS: m/z = 175 [M + 1]$^+$. HRMS (EI): calcd. for $C_{12}H_{14}O$ 174.1044 [M]$^+$; found 174.1045.

(*E*)-4,4-Dimethyl-1-phenylpent-1-en-3-one (12f):[35] Prepared by method B (silica gel, cyclohexane). Yield 47 mg, 64%; pale-yellow oil. R_f = 0.84 (silica gel, cyclohexane/ethyl acetate, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (s, 9 H), 7.13 (d, J = 15.4 Hz, 1 H), 7.37–7.39 (m, 3 H), 7.55–7.57 (m, 2 H), 7.68 (d, J = 15.4 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.5, 43.4, 121.0, 128.4, 129.0, 130.3, 135.3, 143.1, 204.3 ppm. IR (KRS5): $\tilde{\nu}$ = 1077, 1611, 1684, 2969 cm^{-1}. MS: m/z = 189 [M + 1]$^+$. HRMS (EI): calcd. for $C_{13}H_{16}O$ 188.1201 [M]$^+$; found 188.1208.

(*E*)-1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one (12g):[36] Prepared by method A (silica gel, cyclohexane/ethyl acetate, 95:5). Yield 81 mg, 87%; yellow solid; m.p. 105–106 °C. R_f = 0.46 (silica gel, cyclohexane/ethyl acetate, 8:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.90 (s, 3 H), 7.00 (d, J = 9.1 Hz, 2 H), 7.41–7.43 (m, 3 H), 7.56 (d, J = 15.8 Hz, 1 H), 7.64–7.67 (m, 2 H), 7.81 (d, J = 15.8 Hz, 1 H), 8.06 (d, J = 9.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.6, 114.0, 122.0, 128.5, 129.0, 130.4, 130.9, 131.2, 135.2, 144.1, 163.5, 188.8 ppm. IR (KRS5): $\tilde{\nu}$ = 763, 1600, 1655, 2938 cm^{-1}. MS: m/z = 239 [M + 1]$^+$. HRMS (EI): calcd. for $C_{16}H_{14}O_2$ 238.0994 [M]$^+$; found 238.0990.

(*E*)-3-Phenyl-1-(2-thienyl)prop-2-en-1-one (12h): Prepared by method A (silica gel, cyclohexane/ethyl acetate, 95:5). Yield 44 mg, 53%; yellow oil. R_f = 0.60 (silica gel, cyclohexane/ethyl acetate, 8:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (dd, J = 3.8, 5.0 Hz, 1 H), 7.42–7.44 (m, 3 H), 7.43 (d, J = 15.6 Hz, 1 H), 7.64–7.67 (m, 2 H), 7.69 (dd, J = 1.2, 5.0 Hz, 1 H), 7.88 (d, J = 15.6 Hz, 1 H), 7.87–7.89 (dd, J = 1.2, 3.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.7, 128.3, 128.6, 129.1, 130.7, 131.9, 134.0, 134.8, 144.2, 145.6, 182.1 ppm. IR (KRS5): $\tilde{\nu}$ = 761, 1217, 1415, 1596, 1652 cm^{-1}. MS: m/z = 215 [M + 1]$^+$. HRMS (EI): calcd. for $C_{13}H_{10}OS$ 214.0452 [M]$^+$; found 214.0450.

(*E*)-4-Methyl-1-phenylpenta-1,4-dien-3-one (12i): Prepared by method A (silica gel, cyclohexane). Yield 42 mg, 63%; pale-yellow oil. R_f = 0.50 (silica gel, cyclohexane/ethyl acetate, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 3 H), 5.85 (d, J = 0.6 Hz, 1 H), 6.05 (s, 1 H), 7.30 (d, J = 15.9 Hz, 1 H), 7.39–7.41 (m, 3 H), 7.58–7.61 (m, 2 H), 7.66 (d, J = 15.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.5, 43.4, 121.0, 128.4, 129.0, 130.3, 135.3, 143.1, 204.3 ppm. IR (KRS5): $\tilde{\nu}$ = 1084, 1350, 1607, 1661 cm^{-1}. MS: m/z = 173 [M + 1]$^+$. HRMS (EI): calcd. for $C_{12}H_{12}O$ 172.0883 [M]$^+$; found 172.0888.

(*E*)-3-(2-Hydroxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (12j): Prepared by method A (silica gel, cyclohexane/ethyl acetate, 95:5). A mixture of the expected product and *p*-anisic anhydride was obtained and dissolved in CH_2Cl_2. The solution was quenched with saturated $NaHCO_3$. The organic layer was extracted with CH_2Cl_2 and the combined extracts were washed with H_2O and dried with Na_2SO_4. After evaporation, the product was obtained as a yellow oil. Yield 54 mg, 55%. R_f = 0.60 (silica gel, cyclohexane/ethyl acetate, 8:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (dd, J = 3.8, 5.0 Hz, 1 H), 7.42–7.44 (m, 3 H), 7.43 (d, J = 15.6 Hz, 1 H), 7.64–7.67 (m, 2 H), 7.69 (dd, J = 1.2, 5.0 Hz, 1 H), 7.88 (d, J = 15.6 Hz, 1 H), 7.87–7.89 (dd, J = 1.2, 3.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.7, 128.3, 128.6, 129.1, 130.7, 131.9, 134.0, 134.8, 144.2, 145.6, 182.1 ppm. IR (KRS5): $\tilde{\nu}$ = 761, 1217, 1415, 1596, 1652 cm^{-1}. MS: m/z = 255 [M + 1]$^+$. HRMS (EI): calcd. for $C_{16}H_{14}O_3$ 254.0452 [M]$^+$; found 254.0450.

(*E*)-4-[2-(Hydroxymethyl)phenyl]but-3-en-2-one (12k): Prepared by method A (silica gel, cyclohexane/ethyl acetate, 95:5). Yield 49 mg, 72%; yellow oil. R_f = 0.48 (silica gel, cyclohexane/ethyl acetate, 8:2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 5.24 (s, 2 H), 6.64 (d, J = 16.1 Hz, 1 H), 7.33–7.50 (m, 3 H), 7.58–7.64 (m, 1 H), 7.82 (d, J = 16.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.7, 64.0, 127.0, 129.3, 129.7, 130.4, 130.6, 134.2, 135.1, 139.9, 198.3 ppm. IR (KRS5): $\tilde{\nu}$ = 757, 1227, 1255, 1672, 1740, 3495 cm^{-1}. MS: m/z = 177 [M + 1]$^+$. HRMS (EI): calcd. for $C_{11}H_{12}O_2$ 176.0837 [M]$^+$; found 176.0832.

(*E*)-3-[2-(Hydroxymethyl)phenyl]-1-(2-thienyl)prop-2-en-1-one (12l): Prepared by method A (silica gel, cyclohexane/ethyl acetate, 8:2). Yield 67 mg, 70%; yellow oil. R_f = 0.22 (silica gel, cyclohexane/ethyl acetate, 8:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63 (s, 1 H), 4.89 (s, 2 H), 7.18 (dd, J = 3.8, 5.0 Hz, 1 H), 7.34–7.42 (m, J = 1.5, 7.1 Hz, 2 H), 7.39 (d, J = 15.2 Hz, 1 H), 7.47 (td, J = 1.5, 7.1 Hz, 1 H), 7.69 (dd, J = 1.2, 5.0 Hz, 1 H), 7.73 (dd, J = 1.5, 7.1 Hz, 1 H), 7.87 (dd, J = 1.2, 3.8 Hz, 1 H), 8.17 (d, J = 15.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.2, 124.3, 127.3, 128.5, 129.1, 130.6, 132.2, 132.7, 133.8, 134.2, 141.0, 145.6, 182.3 ppm. IR (KRS5): $\tilde{\nu}$ = 728, 755, 1415, 1592, 1649, 3467 cm^{-1}. MS: m/z = 245 [M + 1]$^+$. HRMS (EI): calcd. for $C_{14}H_{12}O_2S$ 244.0558 [M]$^+$; found 244.0553.

(*E*)-1-(3,5-Dimethylisoxazol-4-yl)-4-methylpent-1-en-3-one (12m): Prepared by method B (silica gel, cyclohexane/ethyl acetate, 95:5). Yield 45 mg, 60%; pale-yellow oil. R_f = 0.59 (silica gel, cyclohexane/ethyl acetate, 8:2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.15 (d, J = 7.1 Hz, 2 H), 2.38 (s, 3 H), 2.49 (s, 3 H), 2.81 (sept, J = 6.8 Hz, 1 H), 6.53 (d, J = 16.4 Hz, 1 H), 7.39 (d, J = 16.4 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.9, 12.2, 18.5, 39.9, 111.9, 124.1, 130.5, 158.6, 170.2, 203.2 ppm. IR (KRS5): $\tilde{\nu}$ = 1059, 1265, 1624, 1692, 2971 cm^{-1}. MS: m/z = 194 [M + 1]$^+$. HRMS (EI): calcd. for $C_{11}H_{15}NO_2$ 193.1103 [M]$^+$; found 193.1108.

(*E*)-1-(3,5-Dimethylisoxazol-4-yl)-4-methylpent-1,4-dien-3-one (12n): Prepared by method A (silica gel, cyclohexane/ethyl acetate, 9:1). Yield 30 mg, 40%; yellow oil. R_f = 0.73 (silica gel, cyclohexane/ethyl acetate, 7:3). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.99 (s, 3 H), 2.42 (s, 3 H), 2.52 (s, 3 H), 5.38 (d, J = 1.2 Hz, 1 H), 5.83 (d, J = 1.2 Hz, 1 H), 5.96 (s, 1 H), 7.01 (d, J = 15.9 Hz, 1 H), 7.44 (d, J = 15.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.0, 12.2, 18.3, 112.2, 121.2, 124.5, 131.6, 145.7, 158.6, 170.2, 191.3 ppm. IR (KRS5): $\tilde{\nu}$ = 1087, 1346, 1611, 1669 cm^{-1}. MS: m/z = 192 [M + 1]$^+$. HRMS (EI): calcd. for $C_{11}H_{13}NO_2$ 191.0946 [M]$^+$; found 191.0951.

(*E*)-4,4-Dimethyl-1-(pyrazin-2-yl)pent-1-en-3-one (12o): Prepared by method B (silica gel, cyclohexane/ethyl acetate, 9:1). Yield 52 mg, 70%; orange oil. R_f = 0.50 (silica gel, cyclohexane/ethyl acetate, 8:2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.24 (s, 9 H), 7.63 (d, J = 15.1 Hz, 1 H), 7.75 (d, J = 15.1 Hz, 1 H), 8.53 (d, J = 2.4 Hz, 1 H), 8.60 (t, J = 1.2, 2.4 Hz, 1 H), 8.66 (d, J = 1.2 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.2, 43.7, 127.0, 137.4, 145.0, 145.3, 146.0, 149.2, 204.3 ppm. IR (KRS5): $\tilde{\nu}$ = 1077, 1398, 1619, 1687, 2969 cm^{-1}. MS: m/z = 191 [M + 1]$^+$. HRMS (EI): calcd. for $C_{11}H_{14}N_2O$ 190.1106 [M]$^+$; found 190.1102.

Ethyl (2*Z*,4*E*)-6-Oxo-6-(2-thienyl)hexa-2,4-dienoate (12p): Prepared by method A (silica gel, cyclohexane). Yield 37 mg, 40%; pale-yellow oil. R_f = 0.56 (silica gel, cyclohexane/ethyl acetate, 98:2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.32 (t, J = 7.1 Hz, 3 H), 4.23 (q, J = 7.2 Hz, 2 H), 6.22 (dd, J = 1.0, 11.2 Hz, 1 H), 6.84–6.88 (m, 2 H), 7.14 (dd, J = 4.1, 5.0 Hz, 1 H), 7.69 (dd, J = 1.2, 5.0 Hz, 1 H), 7.75 (dd, J = 1.2, 4.2 Hz, 1 H), 8.41 (qd, J = 1.0, 11.1, 15.3 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 60.6, 124.5, 127.8, 129.4, 130.2, 131.7, 139.6, 140.5, 149.9, 165.8, 179.6 ppm. MS: m/z

= 237 [M + 1]$^+$. HRMS (EI): calcd. for $C_{12}H_{12}O_3S$ 236.0507 [M]$^+$; found 236.0512.

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