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Rasta Resin–PPh_3–$NBniPr_2$ and its Use in One-Pot Wittig Reaction Cascades

Yan Teng, Jinni Lu, and Patrick H. Toy*[a]

Abstract: A new triarylphosphine–tertiary amine bifunctional polymeric reagent has been prepared and used effectively in a variety of one-pot Wittig reactions. The design of this reagent resolved a deficiency of a previously reported related material, and allowed it to perform more efficiently in such reactions. Furthermore, it was readily recyclable, and was also successfully applied in cascade processes involving one-pot Wittig reactions followed by either a conjugate reduction or a reductive aldol reaction. In these reaction cascades, the phosphine oxide groups generated in the Wittig reaction served as the catalyst for the subsequent reaction.

Keywords: aldol reaction · conjugate reduction reaction · immobilization · polymer-supported reagent · Wittig reactions

Introduction

The Wittig reaction is one of the most historically significant methods for carbonyl group olefination,[1] and it remains widely studied and broadly used for the synthesis of carbon–carbon double bonds.[2] However, while it is generally highly chemo- and stereoselective, this workhorse reaction suffers from the significant drawback that one molecule of phosphine oxide is produced as a by-product for every molecule of desired alkene product formed, and this can lead to difficulty in product purification and an increase in associated costs.[3] In principle, versions of the Wittig reaction that are catalytic in the required phosphine have great potential to circumvent this issue, but the limited number of such reaction systems that have been reported to date either exhibit only modest efficiency,[4] or involve the use of an arsine or telluride catalyst.[5] Additionally, the use of supported phosphine reagents that allow for easier product separation from the phosphine oxide formed has also been widely examined in the context of the Wittig reaction.[6]

In recent years, our research has focused on studying various polymers as supports for reagent and catalyst immobilization,[7] and much of this work has focused on the attachment of phosphines.[8–10] In the context of the Wittig reaction, we have reported the use of the rasta resin architecture as a platform for phosphine reagent immobilization,[11,12] and the use of rasta resin–PPh_3 (**1**, RR–PPh_3, Figure 1) in one-pot Wittig reactions in which the necessary phosphorane reagent was formed in situ by mixing an alkyl halide, a phosphine, and a base together with the aldehyde substrate

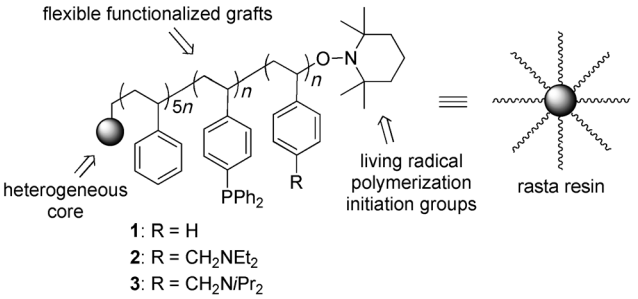
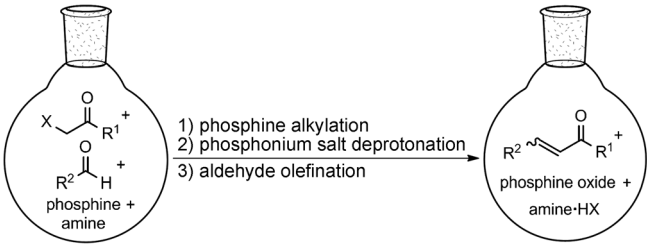


Figure 1. Rasta resin reagents **1**–**3**.

(Scheme 1).[13,14] In this work, we observed that placement of the phosphine reagent groups on the flexible and solvent-accessible grafts of the polymer rather than in the relatively



Scheme 1. One-pot Wittig reactions.

rigid heterogeneous core allowed for **1** to be a more efficient reagent than typical commercially available polystyrene-supported phosphines, in which the functional groups are located in the interior of a heterogeneous polymer bead.

Despite the advantages of using **1** in one-pot Wittig reactions, the addition of the base NEt_3 was necessary to form the requisite phosphorane from the in situ formed phosphonium salt. We were thus inspired to prepare bifunctional rasta resin-based polymeric reagent **2** (RR–PPh_3–$NBnEt_2$,

[a] Y. Teng, J. Lu, Prof. Dr. P. H. Toy
Department of Chemistry
The University of Hong Kong
Pokfulam Road, Hong Kong (P. R. of China)
Fax: (+852) 2857-1586
E-mail: phtoy@hku.hk

Figure 1), which incorporated basic amine groups in addition to the nucleophilic phosphine moieties.[15] When **2** was used as the sole reagent in a wide range of one-pot Wittig reactions utilizing various aldehyde and alkyl halide reaction partners, the desired alkene products could be isolated in nearly quantitative yield and in essentially pure form after only filtration and solvent removal. However, the use of **2** in these reactions suffered from the drawback that two equivalents of it were required for the reactions to efficiently reach completion. Presumably, the tertiary amine groups of **2** react nucleophilically in an undesired manner with the alkyl halide reaction partner,[16] thereby rendering a portion of them unavailable for their role in phosphonium salt deprotonation, and thus necessitating the use of a large excess. With regards to practicality, because multiple steps are required for the synthesis of **2**, using a onefold excess of it in one-pot Wittig reactions is neither desirable nor economical.

To address this issue, we envisioned installing more sterically hindered amine groups on the polymer in order to reduce their nucleophilicity while maintaining their basicity. Herein we report the realization of this strategy and describe the synthesis of second-generation bifunctional polymeric reagent **3** (RR–PPh_3–NBn*i*Pr_2, Figure 1) in which the *N*-ethyl groups of **2** are replaced by isopropyl substituents, and its use as a recyclable reagent in one-pot Wittig reactions and related cascades processes.

Results and Discussion

For the synthesis of **3**, amine monomer **4** was designed and prepared by reaction of diisopropylamine with 4-vinylbenzyl chloride for two days in refluxing ethanol in 75% isolated yield (Scheme 2). The monomer was then mixed with phosphine monomer **5**,[9a] styrene (1:1:5 ratio), and heterogeneous core **6**,[15] and the resulting suspension was heated for 48 hours at 130 °C. The resulting polymer was washed and dried to afford **3** as white, free-flowing beads that, according to scanning electron microscopy (SEM) analysis, were generally spherical in shape and much larger in diameter than precursor **6** (Figure 2). By using elemental analysis, the loading level of **3** was determined to be 0.98 mmol g^{-1} in phosphine and 0.96 mmol g^{-1} in amine, and gel-phase ^{31}P NMR spectroscopy analysis indicated that essentially no phosphine group oxidation had occurred.

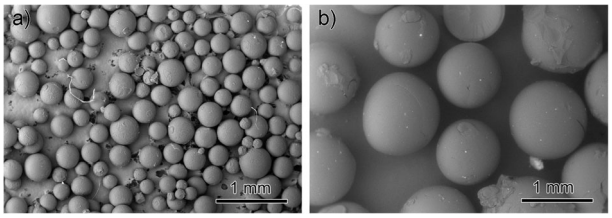
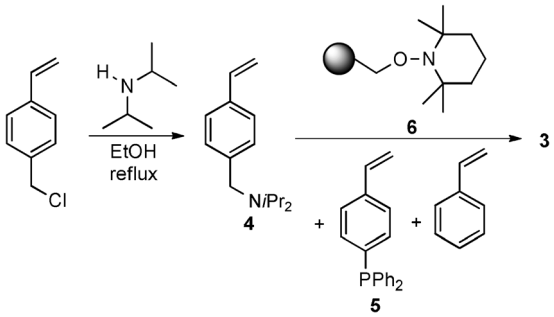


Figure 2. SEM images of a) **6** and b) **3**.

With the synthesis of bifunctional polymer **3** completed, we next performed a series of one-pot Wittig reactions using it to compare the performance of this second-generation reagent with that of its predecessor, **2**. Thus, we chose ethyl bromoacetate (**7a**), ethyl bromopropionate (**7b**), chloroacetone (**7c**), and 2-bromoacetophenone (**7d**) as the activated alkyl halides, and 4-nitrobenzaldehyde (**8a**) as the carbonyl reaction component in these reactions (Table 1), which were performed simply by combining **3**, **8a**, and **7a–c** in CH_2Cl_2 or **7d** in $CHCl_3$, and then mixing the resulting suspension at the indicated temperature. When the reactions were complete, the alkene product from them was isolated by filtration, to separate it from polymer **10**, and solvent removal. Analysis of alkenes **9a–d** by ^1H NMR spectroscopy indicated that they were essentially pure mixtures of the expected *E* and *Z* isomers, as indicated in Table 1.

Gratifyingly, we found that in these reactions only 1.1 equivalents of both bifunctional polymer **3** and alkyl halide **7a–d** were necessary to drive the reactions to completion in times that were similar to those we reported previously using reagent **2** with the same solvent and temperature combinations.[15] This compares favorably to our prior finding of the need for two equivalents of **2**, and 1.8 equivalents of **7a–d** to achieve similar results. As can be seen in Table 1, for all four comparisons the reaction time, isolated yield, and *E*/*Z* product ratio were very similar, regardless of which alkyl halide was used. Thus, it appears that our hypothesis was correct. By using more sterically hindered amine groups in **3**, we were able to attenuate the undesired reaction between these groups and the alkyl halide reactant, and thereby significantly reducing the excess of it necessary in the one-pot Wittig reactions studied.

Having validated the utility of bifunctional heterogeneous reagent **3**, we next set out to examine its recyclability and reusability as we were able to easily recover spent polymer

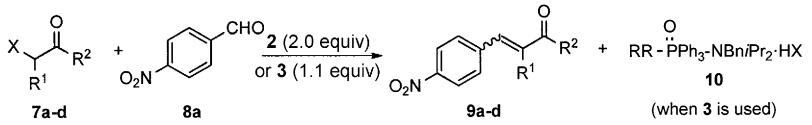


Scheme 2. Synthesis of **3**.

Abstract in Chinese:

本文阐述了一种新型三苯基膦—叔胺双功能高分子试剂的制备，及其在一系列“一锅法”Wittig 反应中的有效应用。该试剂解决了之前所报道的一个类似试剂的不足之处，因此可以更高效地运用于 Wittig 反应。此外，该试剂易于回收，且成功地应用于“一锅法”Wittig 反应—共轭还原或还原 aldol 反应的串联反应中。在此类串联反应中，Wittig 反应生成的氧化膦基团充当了第二步反应的催化剂。

Table 1. One-pot Wittig reactions using **2** or **3**.

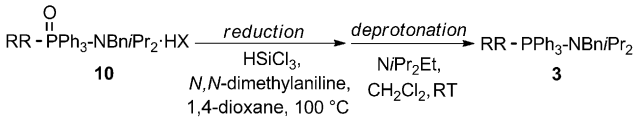


7a-d 8a 9a-d

Polymer	7a			7b			7c			7d		
	t [h]	Yield [%]	*E*/*Z*[a]	*t* [h]	Yield [%]	*E*/*Z*[a]	*t* [h]	Yield [%]	*E*/*Z*[a]	*t* [h]	Yield [%]	*E*/*Z*[a]
2[b]	24[c,e]	98	95:5	48[c,f]	96	93:7	24[c,f]	93	98:2	3[g]	98	91:9
3[d]	19[e]	99	97:3	58[f]	99	96:4	30[f]	98	97:3	3[g]	98	95:5

[a] Determined by ^{1}H NMR analysis. [b] Reaction scale: 0.9 mmol of **7a–d**, 0.5 mmol **8a**, and 1.0 mmol of **2**. [c] Data taken from reference [15]. [d] Reaction scale: 0.55 mmol of **7a–d**, 0.5 mmol **8a**, 0.55 mmol of **3,** and 4 Å molecular sieves (0.1 g). [e] Reaction conditions: CH_2Cl_2, RT. [f] Reaction conditions: CH_2Cl_2, 50 °C. [g] Reaction conditions: $CHCl_3$, 60 °C.

10 at the end of the reactions described above. Realizing that the original phosphine groups of polymer **3** were predominantly oxidized and that the amine groups were protonated after the reactions, we designed a two-stage regeneration protocol for the conversion of **10** back into **3** (Scheme 3). The first stage of regenerating **3** involved phos-

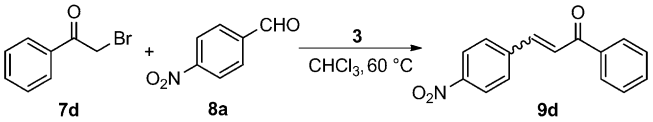


Scheme 3. Regeneration of **3**.

phine oxide reduction, and the second was ammonium salt deprotonation. While numerous methods for phosphine oxide reduction have been reported in the literature,[17–19] we chose to use trichlorosilane and *N*,*N*-dimethylaniline in refluxing 1,4-dioxane for this purpose; for the deprotonation operation we used an excess of N*i*Pr$_2$Et. The completion of the reduction of **10** was determined by gel-phase ^{31}P NMR spectroscopic analysis, while the success of its deprotonation was determined empirically by the successful use of regenerated **3** in a subsequent Wittig reaction cycle (see below).

Having successfully regenerated reagent **3**, we next examined its reuse in the one-pot Wittig reaction using **7d** and **8a** to produce **9d**. As can be seen in Table 2, recovered and regenerated **3** can be successfully reused in this reaction to afford the desired alkene product isomers in at least five reaction cycles (four reuses) in nearly quantitative yield, and at the end of each cycle, **3** can be recycled in at least 92% yield. In these experiments, the beads of **10** could be separated from the molecular sieves at the end of the one-pot Wittig reactions based on their buoyancy in dichloromethane. It should be noted that during each reaction cycle, **3** was slightly crushed, and a decrease in its swelling ability was observed after cycle 4. Furthermore, it appeared that the reactivity of recycled **3** decreased gradually after successive uses, and a slightly larger amount of it and a longer reaction time were needed to drive subsequent reactions to completion. The exact reason(s) for this decreased reactivity is unclear, but gel-phase ^{31}P NMR spectroscopic analysis of

Table 2. Recycling of **3**.



7d 8a 9d

Cycle	**3** [equiv]	*t* [h]	Yield [%][a]	*E*/*Z*[b]	Recycling yield [%][c]
1	1.1	3	98	95:5	94
2	1.2	8	98	97:3	94
3	1.2	8	99	99:1	94
4	1.3	36	96	97:3	93
5	1.4	60	94	95:5	92

[a] Isolated yield of Wittig reactions using **7d** (1.1 equiv), **8a** (1 equiv), **3** (1.1–1.4 equiv), and 4 Å molecular sieves (0.2 g) in $CHCl_3$ (4 mL) under stirring at 60 °C until complete consumption of **8a** according to TLC analysis. [b] Determined by ^{1}H NMR analysis. [c] Reduction reaction conditions: **10** (1 equiv), $HSiCl_3$ (10 equiv), *N*,*N*-dimethylaniline (10 equiv) in 1,4-dioxane heated at 100 °C for 15 h. Deprotonation reaction conditions: reduced **10** (1 equiv), N*i*Pr$_2$Et (3 equiv) in CH_2Cl_2 under stirring at room temperature for 10 min.

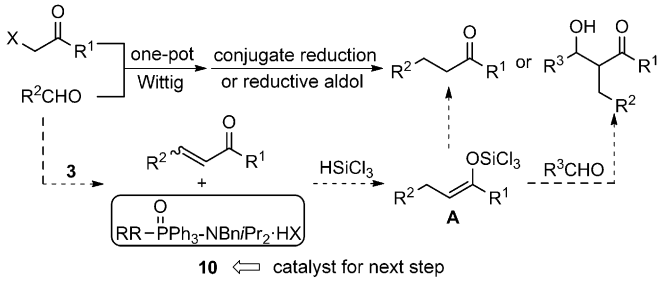
3 recycled after five uses shows complete phosphine oxide reduction (see the Supporting Information). Nevertheless, the desired product **9d** could be isolated in essentially pure form after only filtration and solvent removal, even after five reaction cycles.

While using a solid-supported phosphine reagent enables easy separation of the alkene product of Wittig reactions from the stoichiometric phosphine oxide by-product, the inherent drawback of the Wittig reaction regarding poor atom efficiency/economy remains. A novel method for addressing this issue was recently described by Zhou and co-workers.[20] They reported a "waste as catalyst/co-catalyst" strategy in which the Ph_3PO by-product formed in a Wittig reaction served as the catalyst or co-catalyst in a subsequent transformation of the alkene product.[21] Thus, although phosphine oxide formation was not avoided or minimized, at least this waste material was put to work.

More recently, we have extended this concept by developing a tandem reaction procedure that couples a one-pot Wittig reaction with a subsequent reductive aldol reaction.[22] In these reaction cascades, the by-product Ph_3PO from the initial Wittig reaction serves as the catalyst for the reductive aldol reaction.[23] Using this methodology, three

different building blocks could be combined in a one-pot process for the rapid synthesis of complex molecules in which the isolation and purification of synthetic intermediates were unnecessary. Thus, we were interested to see if reagent **3** could also work in similar reaction cascades involving one-pot Wittig reactions followed by either a conjugate reduction[24] or reductive aldol[25] process, and if so, whether the use of **3** would facilitate purification of the ultimate product.

This methodology that we aimed to develop is outlined in Scheme 4. A one-pot Wittig reaction between an alkyl halide and an aldehyde mediated by reagent **3** would produce an alkene product and **10**. Addition of $HSiCl_3$ to the

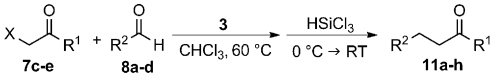


Scheme 4. Tandem one-pot Wittig–conjugate reduction/reductive aldol reactions.

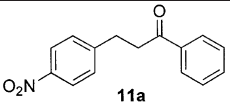
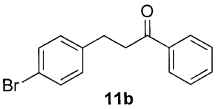
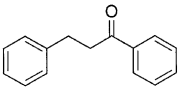
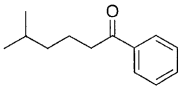
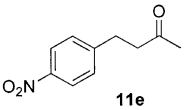
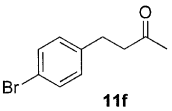
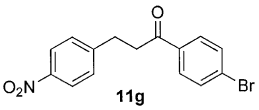
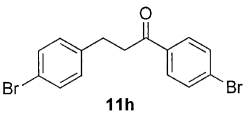
reaction mixture at this stage would form intermediate **A** in a process catalyzed by **10**, and this intermediate could be converted into a conjugate reduction product or treated with another aldehyde molecule to form a reductive aldol product.

Since we previously found that **7d** was a good alkyl halide reaction partner with aldehyde **8a** in one-pot Wittig reactions (Tables 1 and 2), we chose them as the starting point to study the reactions outlined in Scheme 4. Thus, after the one-pot Wittig reaction performed with them in $CHCl_3$ at 60 °C was finished, the reaction mixture was cooled to 0 °C and then $HSiCl_3$ (2 equiv) was added. After stirring for one hour at this temperature and then at room temperature for a further three hours, the chalcone **9d** had completely disappeared according to thin-layer chromatography (TLC) analysis. The reaction was then worked up by the addition of saturated $NaHCO_3$, and filtered through a pad of Celite, using CH_2Cl_2 for washing. Gratifyingly, the expected saturated ketone product **11a** was isolated in 98% yield after filtrate concentration (Table 3, entry 1). We next examined the use of **7d** with aromatic aldehydes **8b** and **8c**, and alkyl aldehyde **8d** in similar reaction cascades, and in all cases a high yield of pure product **11b–d** was isolated (Table 3, entries 2–4). Additionally, we found that combinations of **7c** with **8a** or **8b** also worked well to afford the expected products **11e** and **11f**, respectively (Table 3, entries 5 and 6). Finally, when alkyl halide **7e** was treated with aldehydes **8a** and **8b**, ketones **11g** and **11h** were formed, respectively, in very high isolated yield and high purity. Thus, it appears that this one-

Table 3. Tandem Wittig–conjugate reduction reactions using **3**.



7c: X = Cl, R^1 = Me
7d: X = Br, R^1 = Ph
7e: X = Br, R^1 = 4-BrC_6H_4
8a: R^2 = 4-$NO_2C_6H_4$
8b: R^2 = 4-BrC_6H_4
8c: R^2 = Ph
8d: R^2 = *i*Bu

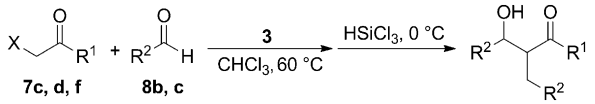
Entry	7	8	11	Yield [%][a]
1	**7d**	**8a**	 **11a**	98
2	**7d**	**8b**	 **11b**	99
3	**7d**	**8c**	 **11c**	98
4	**7d**	**8d**	 **11d**	98
5	**7c**	**8a**	 **11e**	87
6	**7c**	**8b**	 **11f**	99
7	**7e**	**8a**	 **11g**	90
8	**7e**	**8b**	 **11h**	94

[a] Isolated yield of reactions using **7** (0.33 or 0.39 mmol), **8** (0.30 mmol), **3** (0.33 or 0.39 mmol), and 4 Å molecular sieves (0.1 g) in $CHCl_3$ (2 mL) under stirring at 60 °C until **8** was consumed according to TLC analysis, followed by the addition of $HSiCl_3$ (0.60 mmol) and stirring at 0 °C for 1 h, and then at room temperature for 3 h.

pot Wittig–conjugate reduction reaction cascade methodology mediated by **3** is generally applicable for the synthesis of ketones of the general structure **11**, affording excellent isolated yield of pure product after only filtration and concentration. Furthermore, at the end of these reactions polymer **10** could be recovered and converted back into polymer **3**, as outlined in Scheme 3 (see above).

Next our attention was turned to the one-pot Wittig–reductive aldol reaction cascades outlined in Scheme 4 and described in our previous report using Ph_3P instead of **3**.[22] As shown in Table 4, **3** was initially used for tandem reactions using the same aldehyde for both the Wittig and aldol reactions. Alkyl halides **7c** (Table 4, entry 1), **7d** (Table 4, entries 2 and 3), and **7f** (Table 4, entry 4) were reacted in combination with aldehydes **8b** or **8c**, with **3** in a 1:2.2:1 molar

Table 4. Tandem Wittig–reductive aldol reactions using a single aldehyde.



7c, d, f 8b, c 12a-d

7c: X = Cl, R^1 = Me
7d: X = Br, R^1 = Ph
7f: X = Br, R^1 = 4-MeOC$_6$H$_4$

8b: R^2 = 4-BrC$_6$H$_4$
8c: R^2 = Ph

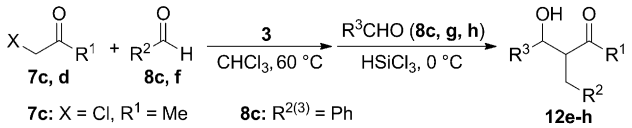
Entry	7	8	12		Yield [%][a]	*syn*/*anti*
1	**7c**	**8b**	**12a**	R^1=Me, R^2=4-BrC$_6$H$_4$	50	30:70
2	**7d**	**8c**	**12b**	R^1=Ph, R^2=Ph	60	34:66
3	**7d**	**8b**	**12c**	R^1=Ph, R^2=4-BrC$_6$H$_4$	50	41:59
4	**7f**	**8c**	**12d**	R^1=4-MeOC$_6$H$_4$, R^2=Ph	69	23:77

[a] Isolated yield of reactions using **7** (0.5 mmol), **8** (1.1 mmol), **3** (0.5 mmol), and 4 Å molecular sieves (0.1 g) in $CHCl_3$ (2 mL) under stirring at 60 °C for 4–48 h, followed by the addition of $HSiCl_3$ (1.0 mmol) and stirring at 0 °C for 2–6 h. The reaction products were isolated as diastereomeric mixtures if not separable.

ratio for the one-pot Wittig reaction. Once this initial process was complete, $HSiCl_3$ was added for the reductive aldol reaction, and because the aldehyde was used in excess, no additional aldehyde was added for this subsequent process. For the selected combinations of α-halogenated ketones and aldehydes, the one-pot reaction cascades proceeded successfully to afford the expected products **12a–d** in good to moderate yield as mixtures of diastereomers. Contrary to the previous one-pot Wittig–conjugate reduction reaction cascades, the products of these reactions required silica-gel chromatography to obtain them in a pure state. Although the isolated yields from these one-pot procedures are not as high (50–69%) as those seen in Table 3, it should be noted that they represent the overall yield of five sequential reactions. On the other hand, the yields and the stereoselectivity of these reactions are very similar to those we observed previously using Ph_3P instead of **3**.[22]

Finally, we examined the use of aldehyde combinations in our one-pot Wittig–reductive aldol reaction cascades (Table 5). For these reactions, alkyl halides **7c** and **7d** were used with either aldehyde **8c** or **8f** for the initial Wittig reactions that were set up using a 1.3:1:1.3 ratio of 7:8:3, so that all of the aldehyde would be consumed. Once the Wittig reaction was complete, $HSiCl_3$ and the second aldehyde **8c** (Table 5, entries 1 and 2), **8g** (Table 5, entry 3), or **8h** (Table 5, entry 4) were added. The reactions were stopped after 3–7 hours, and products **12e–h** were obtained in good (48–69%) overall yield after chromatographic purification. For these reactions using heterogeneous **3**, we observed that slightly longer reaction times were required and moderately lower overall yields were obtained compared to when Ph_3P and N*i*Pr$_2$Et were used to perform similar reaction cascades.[22]

Table 5. Tandem Wittig–reductive aldol reactions using two aldehydes.



7c, d 8c, f 12e-h

7c: X = Cl, R^1 = Me
7d: X = Br, R^1 = Ph

8c: $R^{2(3)}$ = Ph
8f: R^2 = PhCH$_2$CH$_2$
8g: R^3 = 4-ClC$_6$H$_4$
8h: R^3 = 2-furyl

Entry	7	1st Aldehyde	2nd Aldehyde	12		Yield [%][a]	*syn*/*anti*
1	**7d**	**8f**	**8c**	**12e**	R^1=R^3=Ph, R^2=PhCH$_2$CH$_2$	60	33:67
2	**7c**	**8f**	**8c**	**12f**	R^1=Me, R^2=PhCH$_2$CH$_2$, R^3=Ph	48	32:68
3	**7d**	**8c**	**8g**	**12g**	R^1=R^2=Ph, R^3=4-ClC$_6$H$_4$	69	37:63
4	**7d**	**8c**	**8h**	**12h**	R^1=R^2=Ph, R^3=2-furyl	55	50:50

[a] Isolated yield of reactions using **7** (0.65 mmol), **8c** or **8f** (0.5 mmol), **3** (0.65 mmol), and 4 Å molecular sieves (0.1 g) in $CHCl_3$ (2 mL) under stirring at 60 °C until **8c** or **8f** was completely consumed according to TLC analysis, followed by the addition of $HSiCl_3$ (1 mmol) and **8c**, **8g**, or **8h** (0.5 mmol), and stirring at 0 °C for 3–7 h. The reaction products were isolated as diastereomeric mixtures if not separable.

Conclusions

In summary, we have designed and synthesized improved bifunctional polymeric amine–phosphine reagent **3** with less nucleophilic amine groups compared to our first-generation reagent **2**. After applying **3** in one-pot Wittig reactions, we were able to successfully recover spent polymer **10** and convert it back into **3** for multiple reuse. Furthermore, we were able to use oxidized polymer **10** to catalyze conjugate reduction or reductive aldol reactions involving the one-pot Wittig reaction alkene products. Thus, we have developed a series of 3–5 reaction cascade sequences that are mediated by a single polymeric reagent. In all of the processes reported herein, product isolation and purification was greatly facilitated by the heterogeneous nature of **3**. Studies regarding the use of polymers functionalized with various ratios of phosphine to amine groups in processes such as silyl-Reformatsky olefination,[25] and other Ph_3PO-mediated reactions[26] are currently underway, and will be reported shortly.

Experimental Section

General Methods

All moisture sensitive reactions were carried out in dry glassware under an atmosphere of nitrogen. All reactions were carried out in dry glassware, and were monitored by TLC analysis using GF254 silica gel-coated plates. Merck silica gel 60 (230–400 mesh) was used for chromatography. ^{1}H- and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-300 or DRX-400 spectrometer operating at 300/400 MHz for ^{1}H NMR and 75/100 MHz for ^{13}C NMR analysis. Gel-phase ^{31}P NMR analysis was performed on a Brucker DRX-400 spectrometer operating at 162 MHz. Chemical shifts are expressed in ppm with reference to TMS. Elemental analysis was performed at the Shanghai Institute of Organic Chemistry. High-resolution EI-MS data were recorded on a Finnigan MAT 96 mass spectrometer. The general morphology of the

polymer beads was observed by SEM using a Hitachi S-3400N variable pressure scanning electron microscope.

*Synthesis of N,N-diisopropyl-4-vinylbenzylamine (**4**)*

Diisopropylamine (6.1 g, 60 mmol) and 4-vinylbenzyl chloride (4.6 g, 30 mmol) were mixed in ethanol (20 mL) and refluxed for 48 h. The solvent was removed, and 6 M HCl (15 mL) was added to the residue. The mixture was then washed with diethyl ether. The aqueous layer was separated and aqueous NaOH was added until the mixture turned basic. This mixture was then extracted with diethyl ether (2×50 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford **4** (4.9 g, 75%) as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.34 (s, 4H), 6.70 (dd, 1H, J=17.6 Hz, 10.9 Hz), 5.71 (d, 1H, J=17.6 Hz), 5.18 (d, 1H, J=10.9 Hz), 3.62 (s, 2H), 2.97–3.04 (m, 2H), 1.00–1.03 ppm (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.3, 137.0, 135.8, 128.2, 126.0, 112.9, 48.8, 47.9, 20.9 ppm; HRMS (EI, m/z): calcd for $C_{15}H_{23}N$ 217.1830, found 217.1821.

*Synthesis of RR–PPh$_3$–NBniPr_2 (**3**)*

A suspension of **5** (4.2 g, 15 mmol), **6** (0.4 g, 1.5 mmol), **4** (3.2 g, 15 mmol), and styrene (7.5 g, 73 mmol) was heated at 130 °C under N_2 for 48 h. After cooling to room temperature, the resulting polymer was shaken with CH_2Cl_2 (25 mL) for 5 min, until the resin beads floated freely. The resin was collected by filtration, placed in a Soxhlet extractor, and washed with refluxing THF for 24 h. The beads were then washed sequentially with methanol, diethyl ether, and hexanes, and dried in vacuo to afford **3** (11.2 g, 73%). Elemental analysis was used to determine the phosphine (3.0%) and nitrogen content (1.4%), corresponding to a loading level of 0.98 mmol PPh_3 g^{-1}and 0.96 mmol NBniPr_2 g^{-1}, respectively. Gel-phase ^{31}P NMR analysis of **3** confirmed the oxidation state. A single peak at −6 ppm was observed.

General Procedure for One-Pot Wittig Reactions (Table 1)

Compound **3** (0.55 mmol)was added to a solution of alkyl halide **7a–d** (0.55 mmol) and *para*-nitrobenzaldehyde **8a** (75 mg, 0.5 mmol) in CH_2Cl_2 or $CHCl_3$ (5 mL). The reaction mixture was stirred at 50 °C or 60 °C until TLC analysis indicated that the aldehyde was completely consumed. The reaction mixture was then filtered through a plug of silica gel. After washing the polymer with CH_2Cl_2 (2×50 mL), the combined filtrate was concentrated in vacuo to afford the desired product **9a–d**.

*Recycling of RR–PPh$_3$–NBniPr_2 (**3**)*

After a one-pot Wittig reaction using **7d** and **8a**, polymer **10** was filtered, washed with CH_2Cl_2, and dried in vacuo. It was then added to *N,N*-dimethylaniline (1.3 mL, 10 mmol) in 1,4-dioxane (20 mL), and then $HSiCl_3$ (1.0 mL, 10 mmol) was added to the mixture at room temperature under N_2. After refluxing at 100 °C under N_2 for 15 h, the reaction mixture was filtered directly using a Buchner funnel while the Buchner flask contained 5 mL of saturated $NaHCO_3$. The reduced polymer was washed sequentially with methanol, dichloromethane, diethyl ether, and hexane, and dried in vacuo. The resulting polymer was then mixed with NiPr_2Et (0.4 mL, 2.6 mmol) in CH_2Cl_2 (5 mL) at room temperature under N_2 and stirred for 10 min. The beads were then filtered, washed with CH_2Cl_2, and dried in vacuo to afford regenerated **3**. Gel-phase ^{31}P NMR analysis showed a broad peak at −6 ppm.

General Procedure for Tandem One-Pot Wittig–Conjugate Reduction Reactions (Table 3)

Compound **3** (0.33 or 0.39 mmol)was added to a solution of alkyl halide **7c–e** (0.33 or 0.39 mmol), aldehyde **8a–d** (0.3 mmol), and molecular sieves (4 Å , 0.1 g) in $CHCl_3$ (2 mL). The reaction mixture was stirred at 60 °C until TLC analysis indicated that the aldehyde was completely consumed. The reaction mixture was then cooled to 0 °C, and $HSiCl_3$ (0.6 mmol) was added. Stirring was continued at this temperature for 1 h and then at room temperature for 3 h. The reaction was quenched with saturated $NaHCO_3$ (1 mL) and then filtered through a plug of Celite. After washing the polymer with CH_2Cl_2 (2×50 mL), the combined filtrate was concentrated in vacuo to afford the desired product **11a–h**.

General Procedure for Tandem One-Pot Wittig-Reductive Aldol Reactions

Procedure A (Table 4): A mixture of alkyl halide **7c**, **7d**, or **7f** (0.5 mmol), aldehyde **8b–c** (1.1 mmol), **3** (0.5 mmol), and molecular sieves (4 Å, 0.1 g) in $CHCl_3$ (1 mL) was stirred at 60 °C for 4–48 h. Subsequently, $HSiCl_3$ (1.0 mmol) was added to the reaction mixture at 0 °C. After stirring for further 3–7 h, the reaction was quenched with saturated $NaHCO_3$ (1 mL), filtered through Celite, and washed with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane=1:15–1:3) to afford *syn*- and *anti*-**12a–d** as pure stereoisomers or as a mixture of diastereomers.

Procedure B (Table 5): A mixture of alkyl halide **7c–d** (0.65 mmol), aldehyde **8c** or 8**f** (0.5 mmol), **3** (0.5 mmol) and molecular sieves (4 Å, 0.1 g) in $CHCl_3$ (1 mL) was stirred at 60 °C until complete consumption of aldehyde was observed by TLC analysis. Aldehyde **8c**, **8g**, or **8h** (0.6 mmol) and $HSiCl_3$ (1.0 mmol) were then added at 0 °C. After stirring for further 3–8 h, the reaction was quenched and worked up as described in General Procedure A. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane=1:15–1:3) to afford *syn* and *anti* **12e–h** as pure stereoisomers or as a mixture of diastereomers.

*Ethyl 3-(4-nitrophenyl)acrylate (**9a**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ=8.24–8.26 (m, 2H), 7.66–7.73 (m, 3H), 6.55 (d, 1H, J=16.0 Hz), 4.29 (q, 2H, J=7.1 Hz), 1.36 ppm (t, 3H, J=7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.1, 148.6, 141.7, 140.7, 128.7, 124.3, 122.7, 61.1, 14.4 ppm; HRMS (EI, m/z): calcd for $C_{11}H_{11}NO_4$ 221.0688, found 221.0688.

*Ethyl 3-(4-nitrophenyl)-2-methyl-2-propenoate (**9b**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ=8.25 (d, 2H, J=8.4 Hz), 7.69 (s, 1H), 7.53 (d, 2H, J=8.8 Hz), 4.30 (q, 2H, J=7.2 Hz), 2.12 (s, 3H), 1.36 ppm (t, 3H, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.3, 14.4, 61.4, 123.7, 130.3, 132.4, 136.1, 142.6, 147.3, 167.9 ppm; HRMS (EI, m/z): calcd for $C_{12}H_{13}NO_4$ 235.0845, found 235.0840.

*4-(4-Nitrophenyl)but-3-en-2-one (**9c**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ=8.25–8.27 (m, 2H), 7.69–7.71 (m, 2H), 7.53 (d, 1H, J=16.4 Hz), 6.82 (d, 1H, J=16.4 Hz), 2.42 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.6, 148.7, 140.8, 140.2, 130.5, 128.9, 124.3, 28.2 ppm; HRMS (EI, m/z): calcd for $C_{10}H_9NO_3$ 191.0582, found 191.0576.

*3-(4-Nitrophenyl)-1-phenylprop-2-en-1-one (**9d**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ=8.27 (d, 2H, J=8.8 Hz), 8.03–8.05 (m, 2H), 7.78–7.85 (m, 3H), 7.63–7.67 (m, 2H), 7.52–7.56 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=189.8,148.7, 141.6, 141.2, 137.7, 133.5, 129.1, 129.0, 128.7, 125.9, 124.4 ppm; HRMS (EI, m/z): calcd for $C_{15}H_{11}NO_3$ 253.0739, found 253.0726.

*3-(4-Nitrophenyl)-1-phenylpropan-1-one (**11a**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ=8.15 (d, 2H, J=8.6 Hz), 7.95 (d, 2H, J=7.3 Hz), 7.54–7.58 (m, 1H), 7.41–7.49 (m, 4H), 3.36 (t, 2H, J=7.2 Hz), 3.19 ppm (t, 2H, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.3, 149.3, 146.6, 136.6, 133.5, 129.5, 128.8, 128.1, 123.9, 39.5, 29.9 ppm; HRMS (EI, m/z): calcd for $C_{15}H_{13}NO_3$ 255.0895, found 255.0889.

*3-(4-Bromophenyl)-1-phenylpropan-1-one (**11b**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.93–7.95 (m, 2H), 7.54–7.56 (m, 1H), 7.39–7.47 (m, 4H), 7.13 (d, 2H, J=8.3 Hz), 3.28 (t, 2H, J=7.6 Hz), 3.02 ppm (t, 2H, J=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.9, 140.4, 136.9, 133.3, 131.7, 130.4, 128.8, 128.1, 120.0, 40.2, 29.6 ppm; HRMS (EI, m/z): calcd for $C_{15}H_{13}BrO$ 288.0150, found 288.0145.

*1,3-Diphenylpropan-1-one (**11c**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.94–7.96 (m, 2H), 7.53–7.55 (m, 1H), 7.42–7.46 (m, 2H), 7.20–7.30 (m, 5H), 3.29 (t, 2H, J=7.7 Hz), 3.07 ppm (t, 2H, J=7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ=199.4, 141.4, 137.0,

133.2, 128.73, 128.65, 128.6, 128.2, 126.3, 40.6, 30.3 ppm; HRMS (EI, *m/z*): calcd for $C_{15}H_{14}O$ 210.1045, found 210.1034.

*5-Methyl-1-phenylhexan-1-one (**11d**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.97 (m, 2H), 7.53–7.55 (m, 1H), 7.44–7.48 (m, 2H), 2.95 (t, 2H, J = 7.4 Hz), 1.72–1.76 (m, 2H), 1.58–1.61 (m, 1H), 1.24–1.29 (m, 2H), 0.86–0.91 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.8, 137.2, 133.0, 128.7, 128.2, 39.0, 38.8, 28.1, 22.7, 22.4 ppm; HRMS (EI, *m/z*): calcd for $C_{13}H_{18}O$ 190.1358, found 190.1343.

*4-(4-Nitrophenyl)butan-2-one (**11e**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, 2H, J = 8.6 Hz), 7.35 (d, 2H, J = 8.5 Hz), 3.00 (t, 2H, J = 7.3 Hz), 2.82 (t, 2H, J = 7.3 Hz), 2.17 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.8, 149.1, 146.7, 129.4, 123.9, 44.3, 30.2, 29.5 ppm; HRMS (EI, *m/z*): calcd for $C_{10}H_{11}NO_3$ 193.0739, found 193.0734.

*4-(4-Bromophenyl)butan-2-one (**11f**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.40 (m, 2H), 7.05–7.07 (m, 2H), 2.84 (t, 2H, J = 7.2 Hz), 2.73 (t, 2H, J = 7.2 Hz), 2.13 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.6, 140.1, 131.6, 130.2, 120.0, 44.9, 30.2, 29.1 ppm; HRMS (EI, *m/z*): calcd for $C_{10}H_{11}BrO$ 225.9993, found 225.9993.

*1-(4-Bromophenyl)-3-(4-nitrophenyl)propan-1-one (**11g**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, 2H, J = 8.6 Hz), 7.81 (d, 2H, J = 8.6 Hz), 7.61 (d, 2H, J = 8.6 Hz), 7.42 (d, 2H, J = 8.6 Hz), 3.32 (t, 2H, J = 7.3 Hz), 3.17 ppm (t, 2H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.2, 149.0, 146.7, 135.3, 132.2, 129.6, 129.5, 128.7, 123.9, 39.5, 29.7 ppm; HRMS (EI, *m/z*): calcd for $C_{15}H_{12}BrNO_3$ 333.0001, found 332.9996.

*1,3-Bis(4-bromophenyl)propan-1-one (**11h**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.81 (m, 2H), 7.58–7.60 (m, 2H), 7.39–7.41 (m, 2H), 7.11 (d, 2H, J = 8.3 Hz), 3.23 (t, 2H, J = 7.5 Hz), 3.01 ppm (t, 2H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.9, 140.1, 135.5, 132.1, 131.7, 130.3, 129.6, 128.5, 120.1, 40.1, 29.4 ppm; HRMS (EI, *m/z*): calcd for $C_{15}H_{12}Br_2O$ 365.9255, found 365.9253.

*3-(4-Bromobenzyl)-4-(4-bromophenyl)-4-hydroxybutan-2-one (**12a**)*

syn/anti = 30:70. Less polar *syn* isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 4.91 (d, J = 5.46 Hz, 1H), 3.16–3.06 (m, 1H), 3.01 (brs, 1H), 2.88 (d, J = 7.4 Hz, 1H), 1.68 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.6, 140.6, 138.2, 131.8, 131.7, 130.7, 128.0, 121.9, 120.4, 73.2, 61.2, 33.0 ppm (2C). More polar *anti* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 4.72 (apparent t, 1H, J = 5.6 Hz), 3.10–3.18 (m, 2H), 2.86 (dd, 1H, J = 13.4, 10.0 Hz), 2.55 (dd, 1H, J = 13.4, 5.5 Hz), 1.84 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.4, 141.3, 137.3, 131.9, 131.8, 130.6, 127.9, 122.0, 120.6, 74.9, 60.3, 35.3, 33.6 ppm; HRMS (EI, *m/z*): calcd for $C_{10}H_{11}BrO$ (M-C_7H_5BrO) 225.9993, found 255.9989.

*2-Benzyl-1,3-diphenyl-3-hydroxypropan-1-one (**12b**)*

syn/anti = 34:66; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 7.5 Hz, 1.32H), 7.53 (d, J = 7.6 Hz, 0.68H), 7.42–6.99 (m, 12.32H), 6.96 (d, J = 6.9 Hz, 0.68H), 5.08 (d, J = 4.6 Hz, 0.34H), 4.95 (d, J = 6.0 Hz, 0.66H), 4.09–4.06 (m, 1H), 3.18 (dd, J = 13.5, 10.6 Hz, 0.34H), 3.08–3.00 (m, 1H), 2.85 ppm (dd, J = 13.5, 6.3 Hz, 0.66H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.7, 204.9, 142.7, 141.7, 139.4, 138.7, 138.1, 137.4, 133.1, 133.1, 129.1, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 127.8, 127.7, 126.5, 126.3, 126.3, 126.2, 75.4, 74.1, 55.7, 54.8, 36.7, 33.6 ppm; HRMS (EI, *m/z*): calcd for $C_{15}H_{14}O$ (M-C_7H_6O) 210.1039, found 210.1042.

*2-(4-Bromobenzyl)-3-(4-bromophenyl)-3-hydroxy-1-phenylpropan-1-one (**12c**)*

syn/anti = 41:59; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.4 Hz, 1.18H), 7.53 (d, J = 7.3 Hz, 0.82H), 7.49–7.11 (m, 9H), 6.94 (d, J = 8.3 Hz, 1.18H), 6.81 (d, J = 8.3 Hz, 0.82H), 4.99 (d, J = 4.8 Hz, 0.41H), 4.84 (m, 0.59H), 4.09–3.85 (m, 1H), 3.76 (d, J = 5.0 Hz, 1.18H), 3.50 (s, 0.82H), 3.12 (dd, J = 13.6, 10.4 Hz, 0.41H), 3.03–2.87 (m, 1H), 2.76 ppm (dd, J = 13.5, 6.3 Hz, 0.59H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.9, 203.9, 141.5, 140.7, 138.0, 137.6, 137.3, 137.0, 133.5, 133.5, 131.6, 131.6, 131.5, 131.4, 130.8, 130.8, 128.6, 128.6, 128.2, 128.2, 128.0, 128.0, 121.7, 121.6, 120.5, 120.1, 74.7, 73.3, 55.2, 54.3, 35.8, 33.0 ppm; HRMS (EI, *m/z*): calcd for $C_{15}H_{13}BrO$ (M-C_7H_5BrO) 288.0150, found 288.0146

*2-Benzyl-3-hydroxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one (**12d**)*

syn/anti = 23:77; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.9 Hz, 1.54H), 7.58–7.51 (m, 0.46H), 7.43 (d, J = 7.1 Hz, 0.46H), 7.37–6.99 (m, 9.08H), 6.96–6.88 (m, 0.46H), 6.80–6.66 (m, 2H), 5.09 (d, J = 4.0 Hz, 0.23H), 4.93 (apparent d, J = 5.4 Hz, 0.77H), 4.04–4.01 (m, 1H), 3.84–3.75 (m, 1.77H), 3.63 (s, 0.23H), 3.15 (dd, J = 13.6, 10.5 Hz, 0.23H), 3.08–2.94 (m, 1H), 2.93 ppm (dd, J = 13.4, 6.5 Hz, 0.77H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.8, 203.4, 163.7, 143.0, 141.9, 139.7, 139.0, 130.9, 130.8, 130.7, 130.3, 129.2, 129.1, 128.6, 128.5, 128.5, 128.4, 127.7, 127.7, 126.5, 126.3, 126.2, 113.9, 113.7, 113.7, 75.4, 74.1, 55.5 (2C), 54.2, 36.9, 33.4 ppm; HRMS (EI, *m/z*): calcd for $C_{16}H_{16}O_2$ (M-C_7H_6O) 240.1150, found 240.1144.

*2-(Hydroxy(phenyl)methyl)-1,5-diphenylpentan-1-one (**12e**)*

syn/anti = 33:67. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.85 (m, 2H), 7.53–7.51 (m, 1H), 7.42–7.40 (m, 2H), 7.36–7.07 (m, 8H), 6.97 (apparent d, J = 7.3 Hz, 2H), 5.03 (d, J = 4.7 Hz, 0.33H), 4.96 (d, J = 7.0 Hz, 0.67H), 3.84–3.79 (m, 1H), 3.18–3.17 (m, 1H), 2.48–2.42 (m, 2H), 2.02–1.90 (m, 0.33H), 1.85–1.70 (m, 1H), 1.55–1.42 ppm (m, 2.67H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.7, 205.1, 142.8, 142.0, 141.8, 138.2, 137.3, 133.5, 133.4, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 127.9, 127.6, 126.5, 126.3, 125.9, 125.8, 76.2, 74.1, 52.9, 52.8, 36.2, 36.0, 30.4, 29.7, 29.1, 27.3 ppm; HRMS (EI, *m/z*): calcd for $C_{17}H_{18}O$ (M-C_7H_6O) 238.1352, found 238.1351.

*3-(Hydroxy(phenyl)methyl)-6-phenylhexan-2-one (**12f**)*

syn/anti = 32:68. Less polar *syn* isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.22 (m, 7H), 7.18–7.15 (m, 1H), 7.11–7.08 (m, 2H), 4.88 (dd, J = 5.7, 1.6 Hz, 1H), 2.93–2.87 (m, 1H), 2.64 (d, J = 2.4 Hz, 1H), 2.54 (t, J = 7.7 Hz, 2H), 1.96 (s, 3H), 1.84–1.65 (m, 2H), 1.64–1.45 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.8, 141.9, 141.9, 128.5, 128.3, 127.8, 126.2, 125.8, 77.2, 74.0, 59.5, 36.1, 31.7, 29.7, 26.9 ppm. More polar *anti* isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.08 (m, 8H), 7.08–7.05 (m, 2H), 4.76 (apparent d, J = 7.7 Hz, 1H), 2.97–2.89 (m, 1H), 2.53–2.47 (m, 2H), 2.10 (s, 3H), 1.70–1.37 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.7, 142.5, 141.8, 128.7, 128.5, 128.4, 128.1, 126.4, 126.0, 75.8, 59.1, 35.9, 32.1, 29.1, 29.1 ppm. HRMS EI (*m/z*): calcd for $C_{12}H_{16}O$ (M-C_7H_6O) 176.1201, found 176.1195.

*2-Benzyl-3-(4-chlorophenyl)-3-hydroxy-1-phenylpropan-1-one (**12g**)*

syn/anti = 37:63; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.3 Hz, 1.26H), 7.55–7.48 (m, 0.74H), 7.48–7.37 (m, 1H), 7.35–6.99 (m, 10.26H), 6.93 (d, J = 6.8 Hz, 0.74H), 5.08 (d, J = 4.3 Hz, 0.37H), 4.92 (t, J = 5.6 Hz, 0.63H), 4.08–3.98 (m, 1H), 3.70 (d, J = 7.1 Hz, 0.63H), 3.44 (s, 0.37H), 3.14 (dd, J = 13.5, 10.4 Hz, 0.37H), 3.08–2.97 (m, 1H), 2.93 ppm (dd, J = 13.5, 7.0 Hz, 0.63H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.5, 204.8, 141.4, 140.3, 139.1, 138.4, 137.7, 137.3, 133.4, 133.4, 133.3, 129.1, 129.1, 128.7, 128.6, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 127.6, 126.7, 126.3, 74.6, 73.4, 55.5, 54.6, 36.7, 33.7 ppm (2C); HRMS (EI, *m/z*): calcd for $C_{15}H_{14}O$ (M-C_7H_5ClO) 210.1039, found 210.1037.

*2-Benzyl-3-(furan-2-yl)-3-hydroxy-1-phenylpropan-1-one (**12h**)*

syn/anti = 50:50; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.71 (m, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.48–7.40 (m, 0.5H), 7.35–7.03 (m, 8H), 6.27–6.24 (m,

2H), 5.09 (d, J=5.6 Hz, 0.5H), 4.93 (d, J=4.9 Hz, 0.5H), 4.28–4.22 (m, 1H), 3.78 (s, 0.5H), 3.18 (d, J=6.9 Hz, 1.5H), 3.08–2.89 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=205.3, 203.6, 155.2, 154.1, 142.1, 142.0, 139.2, 138.3, 137.4, 137.1, 133.4, 133.2, 129.2, 128.6, 128.4, 128.4, 126.6, 126.3, 110.4, 110.4, 107.4, 107.3, 69.0, 68.9, 53.0, 51.4, 36.2, 34.5 ppm (4C); HRMS (EI, m/z): calcd for $C_{15}H_{14}O$ (M-$C_5H_4O_2$) 210.1039, found 210.1037.

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