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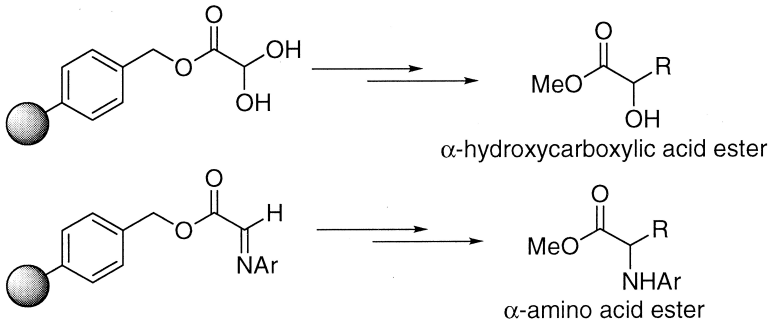

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Polymer-Supported Glyoxylate and α-Imino Acetates. Versatile Reagents for the Synthesis of α-Hydroxycarboxylic Acid and α-Amino Acid Libraries

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Polymer-supported glyoxylate·monohydrate (**3**) and α-imino acetates (**7**) have been readily prepared from chloromethylated resin via two or three steps. The ene reactions of **3** with alkenes were successfully performed in the presence of $Yb(OTf)_3$ (50 mol %) to afford, after cleavage from the polymer support, the corresponding α-hydroxycarboxylic acid esters in good yields. The reactions of **7** with silyl enolates, Danishefsky's diene, and alkenes also proceeded smoothly in the presence of $Sc(OTf)_3$ (20 mol %) to give the corresponding α-amino acid, pyridone, and tetrahydroquinoline derivatives, respectively, in good yields.

Introduction

Glyoxylate and α-imino acetates are useful building blocks for the synthesis of biologically important compounds such as α-hydroxycarboxylic acids,[1] α-amino acids,[2] *β*-amino alcohols,[3] etc. However, most of them are unstable at room temperature due to rapid decomposition and polymerization, etc., and have to be prepared immediately before use.[4] It is expected that these labile compounds are stabilized when immobilized on polymer supports, and indeed, in our previous work, commonly unstable silyl enol ethers were successfully immobilized on resins and used in several carbon-carbon bond-forming reactions.[5] Furthermore, we have successfully performed immobilization of α-imino acetates which are unstable in the liquid phase. We present here full details of our results involving the synthesis and identification of polymer-supported glyoxylate and α-imino acetates, and their use for the preparation of α-hydroxy or α-amino acid derivatives. In this area Hansen et al. quite recently reported the synthesis of polymer-supported glyoxylate on Wang resin.[6]

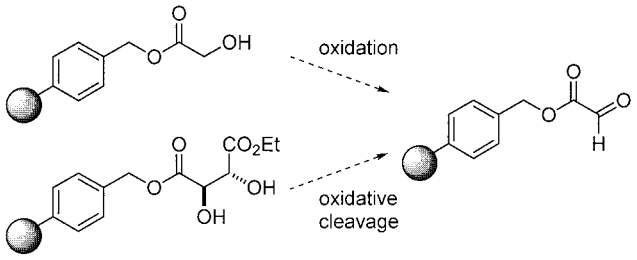
Results and Discussion

Synthesis of Polymer-Supported Glyoxylate. We planned two approaches for the synthesis of polymer-supported glyoxylate: (1) oxidation of α-hydroxyacetate resin, and (2) oxidative cleavage of tartrate resin (Scheme 1).

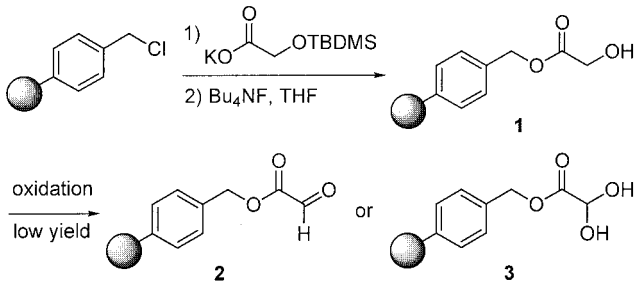
We first immobilized potassium α-silyloxyacetate on resin (Scheme 2). After treatment of chloromethylated resin with α-*tert*-butyldimethylsiloxyacetate, the resulting resin was combined with tetrabutylammonium fluoride to afford α-hydroxyacetate resin (**1**) quantitatively. These transformations in the solid phase were monitored by swollen-resin magic angle spinning NMR (SR-MAS NMR)[5e,7] and IR spectra. We next tried to oxidize **1** under several conditions, but the desired glyoxylate (**2** or **3**) was produced in only low yield.[8]

We then immobilized monopotassium monoethyl tartrate on chloromethylated resin to give tartrate resin (**4**) quantitatively (DMF, 80 °C, 12 h) (Scheme 3). Oxidative cleavage of **4** with H_5IO_6 at room temperature in THF proceeded smoothly to afford polymer-supported glyoxylate·monohydrate (**3**). It was found that the desired polymer-supported glyoxylate was obtained as a hydrate form (**3**), not an aldehyde form (**2**).[9] Several trials to remove water from **3** (PPTs, C_6H_6, reflux, 2 h, etc.) failed and only induced decomposition of **3**.

Scheme 1. Possible Two Approaches to Polymer-Supported Glyoxylate



Scheme 2. Synthesis of Polymer-Supported Glyoxylate (1)



oxidation conditions: (a) $(COCl)_2$, DMSO, Et_3N
(b) SO_3·Py, DMSO, Et_3N
(c) tetrapropylammonium perruthenate (TPAP), *N*-methylmorphorine *N*-oxide (NMO), CH_2Cl_2

Ene Reactions of Polymer-Supported Glyoxylate·monohydrate. Polymer-supported glyoxylate·monohydrate (**3**) thus prepared was used in ene reactions with alkenes. In the presence of $Sc(OTf)_3$ or $Yb(OTf)_3$ as a Lewis acid, **3**

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Scheme 3. Synthesis of Polymer-Supported Glyoxylate (2)

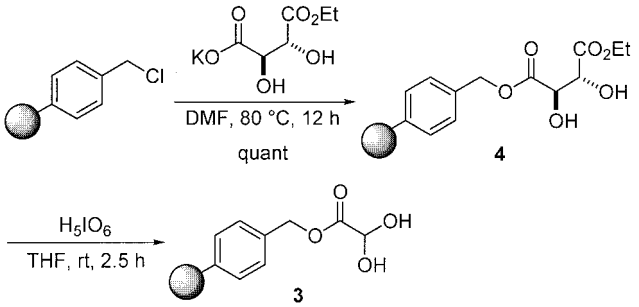
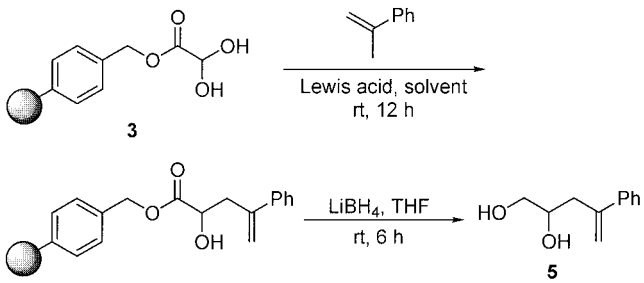


Table 1. Examination of Reaction Conditions in Ene Reaction of **3**



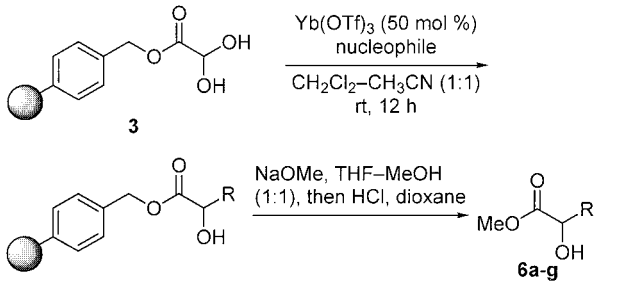
Entry	Lewis acid	Solvent	Yield (%)[a]
1	$Sc(OTf)_3$ (50 mol %)	CH_2Cl_2	27
2	$Sc(OTf)_3$ (50 mol %)	CH_2Cl_2–CH_3CN (1:1)	41
3	$Yb(OTf)_3$ (50 mol %)	CH_2Cl_2–CH_3CN (1:1)	81
4	$Yb(OTf)_3$ (30 mol %)	CH_2Cl_2–CH_3CN (1:1)	51
5	$Yb(OTf)_3$ (10 mol %)	CH_2Cl_2–CH_3CN (1:1)	40
6	$Yb(OTf)_3$ (30 mol %)	DMI	trace
7	TMSOTf (50 mol %)	CH_2Cl_2	0
8	$SnCl_4$ (200 mol %)	CH_2Cl_2	0
9	$TiCl_4$ (200 mol %)	CH_2Cl_2	0

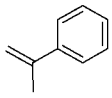
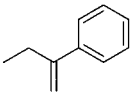
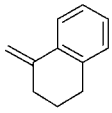
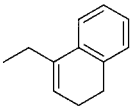
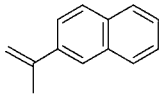
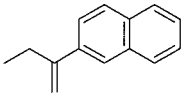
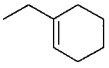
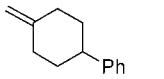
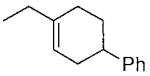
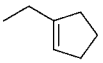
[a] Based on **4**.

was treated with 2-phenylpropene at room temperature for 12 h. As shown in Table 1, $Yb(OTf)_3$ gave better results than $Sc(OTf)_3$. When 50 mol % of $Yb(OTf)_3$ was used in $CH_2Cl_2-CH_3CN$, the ene reaction of **3** with 2-phenylpropene afforded the corresponding diol (**5**) in 81% yield after reductive cleavage from the polymer support. In this reaction, the use of CH_3CN as a cosolvent was crucial to increase yields, probably because $Yb(OTf)_3$ was soluble in CH_3CN. When the amounts of $Yb(OTf)_3$ were reduced to 30 mol % and 10 mol %, the yields of **5** decreased to 51% and 40%, respectively. Although the resin swelled well in dimethylimidazolidone (DMI), only a trace amount of **5** was obtained. No product in the solid phase was obtained when Lewis acids such as $TiCl_4$ and $SnCl_4$, which are often used in ene reactions of alkyl glyoxylates in the liquid phase, were employed.[10]

Other examples of the ene reactions in the solid phase are shown in Table 2. Various alkenes reacted with **3** in the presence of 50 mol % of $Yb(OTf)_3$ in $CH_2Cl_2-CH_3CN$ to afford α-hydroxycarboxylic acid derivatives (**6a**−**g**) in good yields after cleavage from the polymer support in alkaline medium (NaOMe in THF−MeOH). To the best of our knowledge, this is the first example of carbonyl-ene reactions in the solid phase.

Table 2. Ene Reactions of **3** with Alkenes



Entry	Nucleophile	Product	Yield (%)[a]
1		**6a**: R = 	74
2		**6b**: R = 	79
3		**6c**: R = 	83
4		**6d**: R = 	71[b]
5		**6e**: R = 	64[b]
6		**6f**: R = 	61
7		**6g**: R = 	59[b,c]

[a] Based on **4**. [b] $Yb(OTf)_3$ (100 mol %) was used. [c] Including an *exo*-methylene isomer (6%).

Synthesis of Polymer-Supported α-Imino Acetate. We then investigated the synthesis of polymer-supported α-imino acetate (**7**). We first examined the synthesis of **7a** from **3** using *p*-anisidine (H_2NPMP) and trimethylorthoformate. Although several reaction conditions were examined, yields were at most 80% (Scheme 4).[11] It was assumed that the water of **3** would induce decomposition of **7a** to lead to the lower yields.

We then decided to choose an alternative route (Scheme 5). Sodium diethoxyacetate, which was readily prepared from commercially available ethyl diethoxyacetate by hydrolysis, was treated with chloromethylated resin at 80 °C for 12 h in DMF to form diethoxyacetate resin (**8**). Subsequent chlorination was performed using acetyl chloride in a hydrogen chloride dioxane solution at room temperature for 12 h to give 2-chloro-2-ethoxyacetate resin (**9**).[12,13] The loadings of **8** and **9** were determined by chlorine titration (Volhard's method).[14] The reaction of **9** with *p*-anisidine (**10a**) was

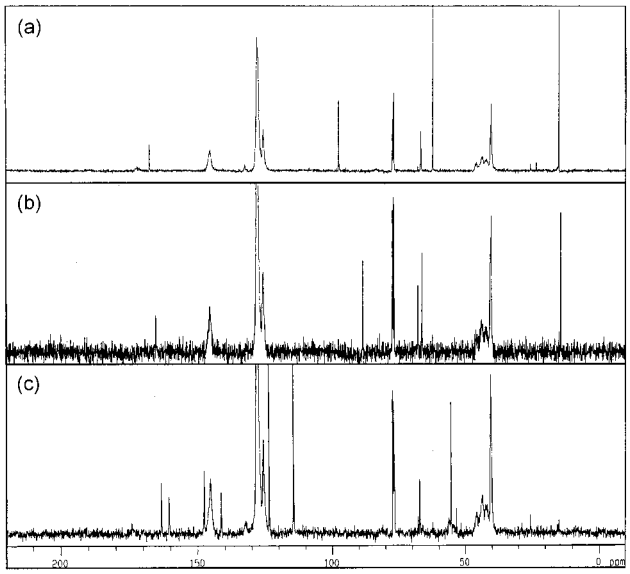
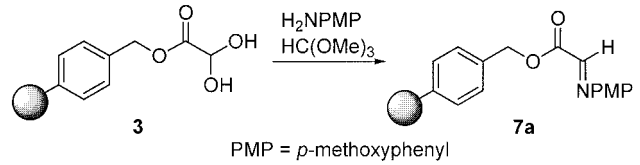
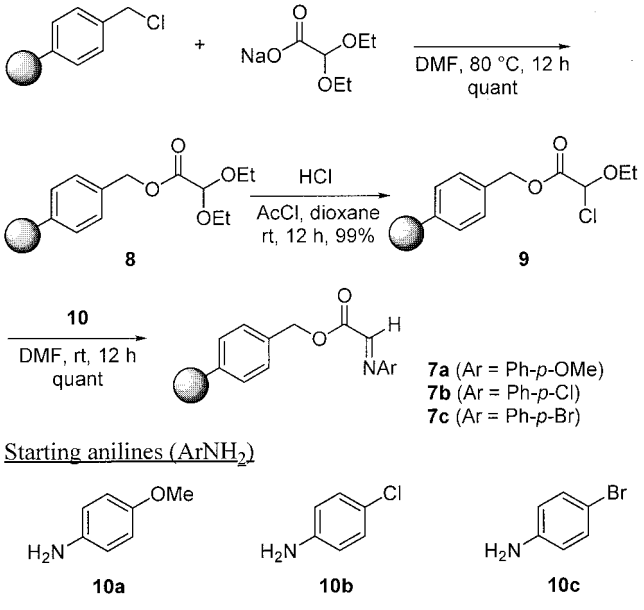


Figure 1. ^{13}C swollen-resin magic angle spinning (SR-MAS) NMR spectra of (a) diethoxyacetate resin (**8**); (b) α-chloro-α-ethoxyacetate resin (**9**); (c) α-iminoacetate resin (**7a**) ($CDCl_3$).

Scheme 4. Synthesis of Polymer-Supported α-Imino Acetate (1)

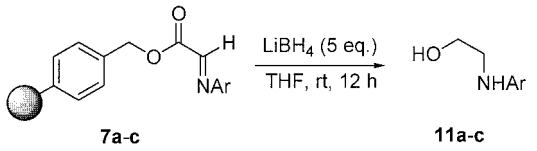


Scheme 5. Synthesis of Polymer-Supported α-Imino Acetate (2)

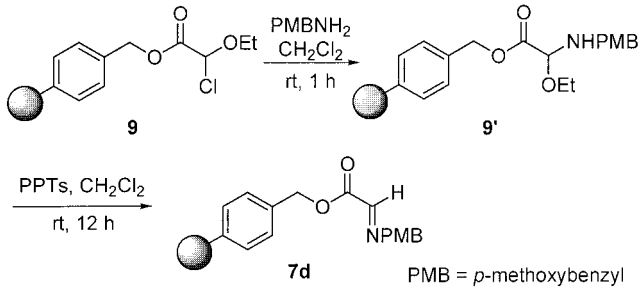


found to proceed smoothly at room temperature in DMF to give 2-(4′-methoxyphenyl)iminoacetate resin (**7a**) quantitatively. In these transformations in the solid phase, ^{13}C SR-MAS NMR analysis provided a powerful tool to optimize the reaction conditions of each step and to determine the structures of these resins (**8**, **9**, and **7a**) (Figure 1). Similarly, 2-(4′-chlorophenyl)iminoacetate resin (**7b**) and 2-(4′-bromophenyl)iminoacetate resin (**7c**) were synthesized from **9** in high yields. The loadings of **7a**−**c** were determined after converting to the amino alcohol derivatives (**11a**−**c**) (Scheme 6).

Scheme 6. Reductive Cleavage of **7**



Scheme 7. Synthesis of Polymer-Supported α-Imino Acetate (3)



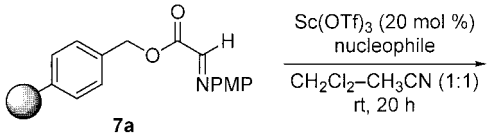
We also found that in the reaction of *p*-methoxybenzylamine instead of aniline derivatives, **9** gave *N*,*O*-acetal (**9′**), which was treated with pyridinium *p*-toluenesulfonate (PPTs) to afford the corresponding iminoacetate resin (**7d**) quantitatively (Scheme 7).

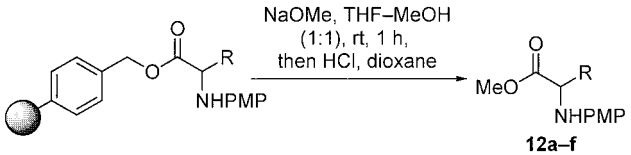
Mannich-Type Reactions of Polymer-Supported α-Imino Acetate. Polymer-supported α-imino acetate (**7a**) thus prepared was used in Mannich-type reactions with silyl nucleophiles.[15] In the presence of 20 mol % $Sc(OTf)_3$, **7a** was treated with the silyl enolate derived from methyl isobutyrate at room temperature for 20 h in $CH_2Cl_2-CH_3CN$ (1:1). The resulting resin was treated with NaOMe at room temperature for 1 h in THF to afford α-amino acid derivative (**12a**) in 76% yield. When $Yb(OTf)_3$ was used as a catalyst, the yield was slightly reduced. Various types of silyl enolates derived from esters as well as thioesters and ketones reacted smoothly to afford α-amino acid derivatives (**12a**−**f**), which are an interesting class of biologically important compounds.[16]

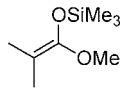
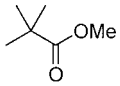
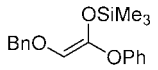
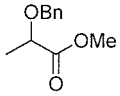
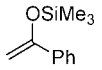
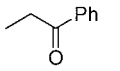
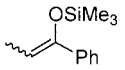
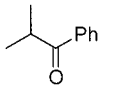
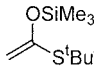
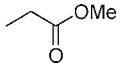
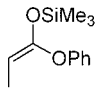
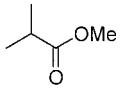
Reaction with Danishefsky's Diene. In the presence of 20 mol % of $Sc(OTf)_3$, **7a** reacted with Danishefsky's diene[17] to afford the desired tetrahydropyridone derivative (**12g**) in 69% yield (Scheme 8).

Aza Diels−**Alder Reactions of Polymer-Supported α-Imino Acetate.** We further studied aza Diels−Alder reactions of **7** for the preparation of tetrahydroquinoline derivatives.[18] In the presence of 20 mol % $Sc(OTf)_3$, **7a** reacted with dihydrofuran (**13a**) at room temperature for 20 h in $CH_2Cl_2-CH_3CN$ (1:1) to give 2-methoxycarbonyl-tetrahydroquinoline derivative (**14a**) in 72% yield after cleavage from the polymer support. Other examples are summarized in Table 4. In all cases, the desired reactions proceeded smoothly in the solid phase to afford the corresponding tetrahydroquinoline derivatives in good to excellent yields. Since aza Diels−Alder adducts formed in the solid phase were unstable under cleavage conditions, we protected imino-nitrogens as their Boc groups before cleavage. The Boc groups were deprotected simultaneously when the

Table 3. Synthesis of α-Amino Acid Derivatives[a]

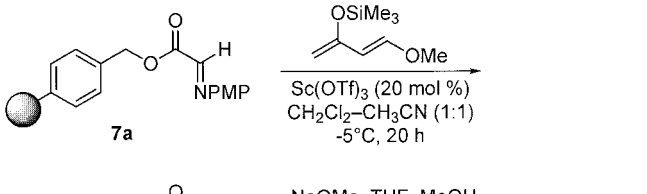




Entry	Nucleophile	Product	Yield (%)[b]
1		**12a**: R = 	76
2		**12b**: R = 	94[c]
3		**12c**: R = 	71[d]
4		**12d**: R = 	65[d,e]
5		**12e**: R = 	95
6		**12f**: R = 	77[f]

[a] PMP = *p*-methoxyphenyl. [b] Based on **7a**. [c] Diastereomer ratio = 60:40. [d] $Sc(OTf)_3$ (40 mol %) was used. [e] Diastereomer ratio was not determined. [f] Diastereomer ratio = 72:28.

Scheme 8. Reaction of **7a** with Danishefsky's Diene

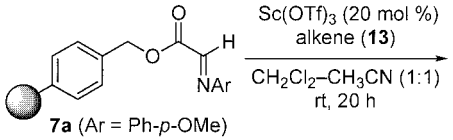


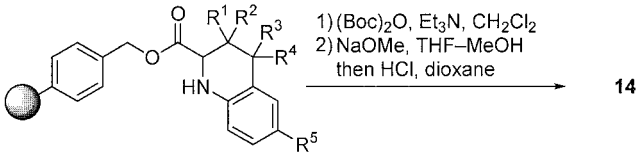
adducts were cleaved from the polymer support. It should be noted that halogen substitutions, which would assist further transformations, are tolerated under these conditions.

Conclusion

Polymer-supported glyoxylate·monohydrate (**3**) and α-imino acetates (**7**) have been successfully prepared from chloromethylated resin. The use of **3** and **7** in useful synthetic

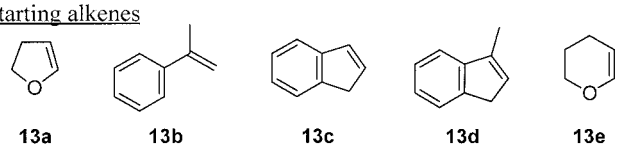
Table 4. Synthesis of Tetrahydroquinoline Derivatives





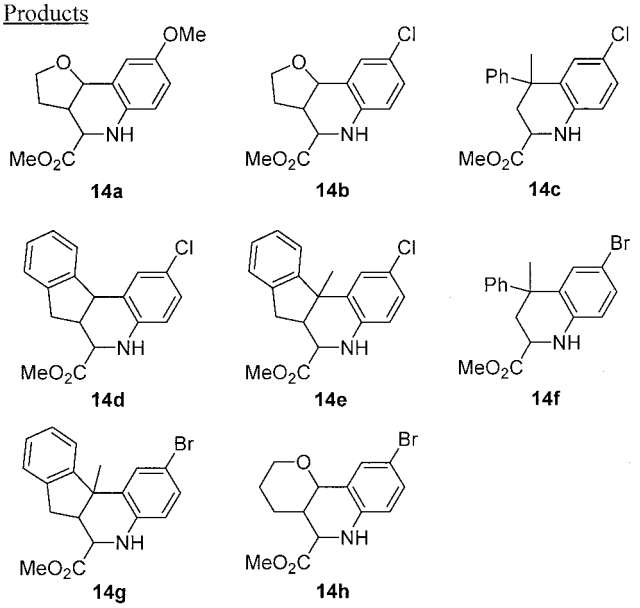
Entry	Imine	Alkene	Product	Yield (%)	Diastereo ratio
1	**7a**	**13a**	**14a**	72	68/32
2	**7b**	**13a**	**14b**	84	60/40
3	**7b**	**13b**	**14c**	78	75/25
4	**7b**	**13c**	**14d**	95	95/5
5	**7b**	**13d**	**14e**	79	94/6
6	**7c**	**13b**	**14f**	quant	68/32
7	**7c**	**13d**	**14g**	quant	93/7
8	**7c**	**13e**	**14h**	56	60/40

Starting alkenes



13a **13b** **13c** **13d** **13e**

Products



reactions such as ene reactions, Mannich-type reactions, and aza Diels−Alder reactions has been demonstrated. In these reactions, $Sc(OTf)_3$ or $Yb(OTf)_3$ was found to be an excellent catalyst. It should be noted that unstable glyoxylate and α-imino acetates in the liquid phase were stabilized by immobilizing in the solid phase and that biologically important α-hydroxycarboxylic acid or α-amino acid derivatives were prepared in high yields using **3** or **7**. These polymer-supported reagents will be used in other related reactions for preparation of versatile, biologically important compound libraries.

Experimental Section

NMR spectra were measured on 300 and 400 MHz spectrometers with $CDCl_3$ as a solvent. Tetramethylsilane (TMS) served as internal standard ($\delta = 0$) for ^1H NMR, and $CDCl_3$ was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. All solvents were dried and distilled according to standard procedure. SR-MAS NMR (^{13}C) spectra were measured on 400 MHz spectrometers with $CDCl_3$ as a solvent. Potassium ethyl tartrate was prepared by treatment of diethyl tartrate with KOH in EtOH. Sodium diethoxyacetate was also prepared from diethoxyacetate in the same manner using NaOH instead of KOH. Some alkenes (entries 1, 4, 6, 7) in Table 2 were commercially available, and others (entries 2, 3, 5) were prepared by Wittig reaction of the corresponding ketones.

Synthesis of Tartrate Resin (4). To a suspension of chloromethyl copoly-(styrene-1%-divinylbenzene) resin (1.24 mmol/g, 10.0 g, 12.4 mmol) in DMF (100 mL) were added potassium ethyl tartrate (3.0 equiv, 8.0 g, 37.2 mmol) and tetra-*n*-butylammonium iodide (1.0 equiv, 4.58 g, 12.4 mmol). The mixture was stirred for 12 h at 80 °C. The reaction mixture was filtered and washed with water, THF, and CH_2Cl_2, and then it was dried in vacuo to afford tartrate resin (**4**, quant, 1.05 mmol/g). The loading of **4** was determined by chlorine titration (Volhard's method[14]). ^{13}C SR-MAS NMR ($CDCl_3$) $\delta = 14.1, 40.3, 62.4, 67.9, 72.3, 125.6, 128.0, 145.1, 171.5$; IR (KBr) 1739, 3510 cm^{-1}.

Synthesis of Glyoxylate·monohydrate Resin (3). To a suspension of **4** (1.05 mmol/g, 3.0 g, 3.15 mmol) in THF (20 mL) was added H_5IO_6 (1.5 equiv, 1.1 g, 4.7 mmol). The mixture was stirred for 2.5 h at room temperature. The reaction mixture was filtered, washed with water, THF, and CH_2Cl_2, and then dried in vacuo to afford glyoxylate·monohydrate resin (**3**). The loading of **3** was not determined at this step. Calculated loading, 1.16 mmol/g; IR (KBr) 1747, 3501 cm^{-1}.

To a suspension of **3** (1.16 mmol/g, 1.8 g, 2.1 mmol) in benzene (25 mL) was added pyridinium *p*-toluenesulfonate (26 mg, 0.10 mmol). The mixture was refluxed with azeotropic removal of H_2O by a Dean−Stark trap. After 2 h the resin was separated from the solution by filtration and washed with dry CH_2Cl_2 to give **2**. While partial decomposition of **2** was observed, the CHO absorption of **2** was identified by ^1H SR-MAS NMR spectra. ^1H SR-MAS NMR ($CDCl_3$) $\delta = 9.23$ (CHO); IR (KBr) 1730, 1747 cm^{-1}.

Ene Reaction of 3 with 2-Phenylpropene (Table 1). To a suspension of $Yb(OTf)_3$ (50 mol %, 62.0 mg, 0.10 mmol) and **3** (1.16 mmol/g, 172 mg, 0.20 mmol) in $CH_2Cl_2-CH_3CN$ (1:1, 3.0 mL) was added 2-phenylpropene (5.0 equiv, 118 mg, 1.0 mmol) in $CH_2Cl_2-CH_3CN$ (1:1, 1.0 mL), and the mixture was stirred for 20 h at room temperature. After saturated aqueous $NaHCO_3$ was added to quench the reaction, the polymer was filtered and washed with water, THF, and CH_2Cl_2. The resulting polymer was combined with $LiBH_4$ (5.0 equiv, 22 mg, 1.0 mmol) in THF (4.0 mL), and the mixture was stirred for 6 h at room temperature. After 1 N aqueous HCl solution (0.5 mL) was added, the resin was separated from the solution by filtration and washed with water, THF, and CH_2Cl_2. The filtrate was extracted with CH_2Cl_2, washed with brine, and dried on $MgSO_4$. After removal of the solvents, the crude product was purified by preparative TLC to afford diol (**5**, 28.8 mg, 81%).

4-Phenyl-4-penten-1,2-diol (5): ^1H NMR ($CDCl_3$) $\delta = 2.3-2.8$ (m, 4H), 3.38 (dd, 1H, $J = 6.8, 11.3$ Hz), 3.54 (dd, 1H, $J = 3.0, 11.3$ Hz), 3.6−3.8 (m, 1H), 5.09 (s, 1H), 5.32 (s, 1H), 7.1−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) $\delta = 39.4, 66.1, 70.1, 115.4, 126.1, 127.8, 128.5, 140.2, 144.5$; IR (neat) 3393 cm^{-1}; MS (EI) $m/z = 178$.

Ene Reaction of 3 with 2-Phenylpropene (Table 2). To a suspension of $Yb(OTf)_3$ (50 mol %, 62.0 mg, 0.10 mmol) and **3** (1.16 mmol/g, 172 mg, 0.20 mmol) in $CH_2Cl_2-CH_3CN$ (1:1, 3.0 mL) was added 2-phenylpropene (5.0 equiv, 118 mg, 1.0 mmol) in $CH_2Cl_2-CH_3CN$ (1:1, 1 mL), and the mixture was stirred for 20 h at room temperature. After saturated aqueous $NaHCO_3$ was added to quench the reaction, the polymer was filtered, washed with water, THF, and CH_2Cl_2, and then dried. The resulting polymer was combined with NaOMe (2.0 equiv, 1 M) in THF−MeOH (1:1, 4 mL), and the mixture was stirred for 1 h at room temperature. After 4 N HCl dioxane solution (0.1 mL) was added, the mixture was filtered and the filtrate was evaporated to dryness. The crude product was purified by preparative TLC to afford methyl ester (**6a**, 30.5 mg, 74%).

Methyl 2-Hydroxy-4-phenyl-4-pentenoate (6a): ^1H NMR ($CDCl_3$) $\delta = 2.66$ (brs, 1H), 2.77 (dd, 1H, $J = 7.8, 14.3$ Hz), 2.99 (dd, 1H, $J = 4.0, 14.3$ Hz), 3.54 (s, 3H), 4.22 (dd, 1H, $J = 4.0, 7.8$ Hz), 5.13 (s, 1H), 5.33 (s, 1H), 7.1−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) $\delta = 40.4, 52.3, 69.1, 116.3, 126.4, 127.7, 128.3, 140.1, 143.4, 174.7$; IR (neat) 1739, 3448 cm^{-1}; MS (EI) $m/z = 206$.

Methyl 2-Hydroxy-3-(3,4-dihydronaphthalen-1-yl)propionate (6b): ^1H NMR ($CDCl_3$) $\delta = 2.2-2.3$ (m, 2H), 2.6−2.8 (m, 4H), 3.03 (dd, 1H, $J = 3.1, 14.3$ Hz), 3.70 (s, 1H), 4.39 (dd, 1H, $J = 4.3, 8.0$ Hz), 5.99 (t, 1H, $J = 4.6$ Hz), 7.1−7.3 (m, 5H); ^{13}C NMR ($CDCl_3$) $\delta = 23.1, 28.2, 38.1, 52.3, 69.4, 122.5, 126.4, 127.0, 127.8, 128.7, 131.6, 133.9, 136.8, 174.9$; IR (neat) 1739, 3443 cm^{-1}; MS (EI) $m/z = 232$.

Methyl 2-Hydroxy-4-(2-naphthyl)-4-pentenoate (6c): ^1H NMR ($CDCl_3$) $\delta = 2.76$ (brs, 1H), 2.95 (dd, 1H, $J = 7.6, 14.4$ Hz), 3.17 (dd, 1H, $J = 4.4, 14.4$ Hz), 3.59 (s, 3H), 4.34 (dd, 1H, $J = 4.4, 7.6$ Hz), 5.30 (s, 1H), 5.55 (s, 1H), 7.4−7.5 (m, 2H), 7.57 (dd, 1H, $J = 1.7, 8.5$ Hz), 7.7−7.9 (m, 4H); ^{13}C NMR ($CDCl_3$) $\delta = 40.5, 52.3, 69.3, 116.8, 124.7, 125.1, 126.0, 126.3, 127.5, 128.0, 128.2, 132.9, 133.3, 137.5, 143.4, 174.8$; IR (neat) 1739, 3445 cm^{-1}; MS (EI) $m/z = 256$.

Methyl 3-(1-Cyclohexen-1-yl)-2-hydroxyoxypropionate (6d): ^1H NMR ($CDCl_3$) $\delta = 1.5-1.7$ (m, 4H), 1.8−2.1 (m, 4H), 2.29 (dd, 1H, $J = 8.0, 14.0$ Hz), 2.45 (dd, 1H, $J = 4.3, 14.0$ Hz), 2.63 (brs, 1H), 3.78 (s, 3H), 4.30 (dd, 1H, $J = 4.3, 8.0$ Hz), 5.54 (brs, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 22.1, 22.8, 25.3, 28.4, 43.2, 52.3, 69.2, 125.5, 132.9, 175.2$; IR (neat) 1739, 3471 cm^{-1}; MS (EI) $m/z = 184$.

Methyl 2-Hydroxy-3-(4-phenyl-1-cyclohexen-1-yl)propionate (6e): diastereomeric mixture; ^1H NMR ($CDCl_3$) $\delta = 1.6-2.5$ (m, 8H), 2.6−2.8 (m, 2H), 3.79 (s, 3H), 4.2−4.4 (m, 1H), 5.5−5.7 (m, 1H), 7.1−7.4 (m, 5H); ^{13}C NMR

($CDCl_3$) δ = 29.2, 29.9, 33.6, 39.8, 42.6, 42.8, 52.4, 69.3, 125.0, 126.0, 126.9, 128.4, 133.0, 146.9, 175.3; IR (KBr) 1721, 1736, 3410 cm^{-1}; MS (EI) m/z = 260.

Methyl 3-(1-Cyclopenten-1-yl)-2-hydroxyoxypropionate (6f): ^1H NMR ($CDCl_3$) δ = 1.87 (quintet, 2H, J = 7.5 Hz), 2.2−2.4 (m, 4H), 2.50 (dd, 1H, J = 7.5, 14.6 Hz), 2.60 (d, 1H, J = 14.6 Hz), 2.74 (brs, 1H), 3.79 (s, 3H), 4.3−4.4 (m, 1H), 5.52 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 23.5, 32.5, 35.2, 36.2, 52.4, 69.5, 127.9, 139.2, 175.2; IR (neat) 1739, 3467 cm^{-1}; MS (EI) m/z = 170.

Methyl 2-Hydroxy-2-(1-methyl-1-cyclohexen-6-yl)-acetate (6g): diastereomeric mixture (75:25) including an *exo*-methyleneisomer (6%); ^1H NMR ($CDCl_3$) δ = 1.4−1.8 (m, 4H), 1.67 (s, 3H*3/4), 1.78 (s, 3H*1/4), 1.97 (brs, 2H), 2.51 (brs, 1H*1/4), 2.62 (brs, 1H*3/4), 2.6−3.0 (m, 1H), 3.78 (s, 3H*3/4), 3.82 (s, 3H*1/4), 4.32 (d, 1H*3/4, J = 2.9 Hz), 4.56 (d, 1H*1/4, J = 3.0 Hz), 5.59 (brs, 1H*3/4), 5.67 (brs, 1H*1/4); ^{13}C NMR ($CDCl_3$) δ = 20.5, 21.3, 21.4, 22.3, 22.9, 25.2, 26.5, 30.3, 42.5, 43.3, 52.3, 52.6, 70.7, 72.8, 126.4, 126.7, 131.8, 172.4, 175.5; IR (neat) 1737, 3486 cm^{-1}.

Synthesis of Diethoxyacetate Resin (8). To a suspension of chloromethyl copoly-(styrene-1%-divinylbenzene) resin (1.24 mmol/g, 10.0 g, 12.4 mmol) in DMF (100 mL) was added sodium diethoxyacetate (3.0 equiv, 6.37 g, 37.2 mmol) and tetra-*n*-butylammonium iodide (1.0 equiv, 4.58 g, 12.4 mmol). The mixture was stirred for 12 h at 80 °C. The reaction mixture was filtered, washed with water, THF, and CH_2Cl_2, and then dried in vacuo to afford diethoxyacetate resin (**8**, quant, 1.09 mmol/g). The loading of **8** was determined by chlorine titration (Volhard's method[14]). ^{13}C SR-MAS NMR ($CDCl_3$) δ = 15.0, 40.3, 62.3, 66.7, 97.3, 125.6, 127.9, 145.3, 167.4; IR (KBr) 1755 cm^{-1}.

Synthesis of 2-Chloro-2-ethoxyacetate Resin (9). To a suspension of **8** (1.09 mmol/g, 10.0 g, 10.9 mmol) in 4 N HCl dioxane solution (100 mL) was added acetyl chloride (5.0 equiv, 3.9 mL, 54.5 mmol). The mixture was stirred for 12 h at room temperature. The reaction mixture was filtered, washed with THF and CH_2Cl_2, and then dried in vacuo to afford 2-chloro-2-ethoxyacetate resin (**9**, 99%, 1.10 mmol/g). The loading of **9** was determined by chlorine titration (Volhard's method[14]). ^{13}C SR-MAS NMR ($CDCl_3$) δ = 14.2, 40.3, 66.3, 67.7, 88.4, 125.6, 127.9, 145.3, 165.1; IR (KBr) 1760 cm^{-1}.

Preparation of 2-(4′-Methoxyphenyl)iminoacetate Resin (7a). To a suspension of **9** (1.10 mmol/g, 182 mg, 0.2 mmol) in DMF (4.0 mL) was added *p*-anisidine (**10a**, 5.0 equiv, 123 mg, 1.0 mmol). The mixture was stirred for 12 h at room temperature. The reaction mixture was filtered, washed with THF and CH_2Cl_2, and then dried in vacuo to afford 2-(4′-methoxyphenyl)iminoacetate resin (**7a**, quant, 1.10 mmol/g). ^{13}C SR-MAS NMR ($CDCl_3$) δ = 40.3, 55.4, 67.2, 114.5, 123.6, 125.6, 127.9, 141.2, 145.3, 147.5, 160.5, 163.2; IR (KBr) 1716, 1743 cm^{-1}. The resulting polymer was combined with $LiBH_4$ (5.0 equiv, 21.8 mg, 1.0 mmol) in THF (5.0 mL), and the mixture was stirred for 12 h at room temperature. After 1 N aqueous HCl solution (0.5 mL) was added, the resin was separated from the solution by filtration and washed with water, THF, and CH_2Cl_2. Aqueous $NaHCO_3$ solution was added to the filtrate. The filtrate was extracted with CH_2Cl_2, washed with brine, and dried on Na_2SO_4. After removal of the solvents, the crude product was purified by preparative TLC to afford 2-(4′-methoxyphenyl)aminoethanol (**11a**, 33.4 mg, quant from resin **9**). ^1H NMR ($CDCl_3$) δ = 2.71 (brs, 2H), 3.25 (t, 2H, J = 5.2 Hz), 3.75 (s, 3H), 3.81 (t, 2H, J = 5.2 Hz), 6.63 (d, 2H, J = 9.0 Hz), 6.79 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ = 47.2, 55.8, 61.3, 114.7, 114.9, 142.2, 152.5; IR (neat) 3400 cm^{-1}; MS (EI) m/z = 167.

2-(4′-Chlorophenyl)aminoethanol (11b): ^1H NMR ($CDCl_3$) δ = 2.69 (brs, 2H), 3.19 (t, 2H, J = 5.2 Hz), 3.75 (t, 2H, J = 5.2 Hz), 6.50 (d, 2H, J = 8.9 Hz), 7.05 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ = 46.2, 61.1, 114.3, 122.5, 129.1, 146.6; IR (neat) 3418 cm^{-1}; MS (EI) m/z = 171.

2-(4′-Bromophenyl)aminoethanol (11c): ^1H NMR ($CDCl_3$) δ = 2.73 (brs, 1H), 3.20 (t, 2H, J = 5.1 Hz), 3.76 (t, 2H, J = 5.1 Hz), 6.47 (d, 2H, J = 8.8 Hz), 7.19 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ = 46.1, 61.1, 109.6, 114.8, 132.0, 146.9; IR (neat) 3305 cm^{-1}; MS (EI) m/z = 215.

Preparation of 2-(4′-Methoxybenzyl)iminoacetate Resin (7d). To a suspension of **9** (0.99 mmol/g, 202 mg, 0.2 mmol) in CH_2Cl_2 (4.0 mL) was added *p*-methoxybenzylamine (5.0 equiv, 137 mg, 1.0 mmol). The mixture was stirred for 1 h at room temperature. The reaction mixture was filtered, washed with THF and CH_2Cl_2, and then dried in vacuo to afford **9′**. The resulting polymer was combined with PPTs (0.2 equiv, 10 mg, 0.04 mmol) in CH_2Cl_2 (4.0 mL), and the mixture was stirred for 12 h at room temperature. The reaction mixture was filtered, washed with THF and CH_2Cl_2, and then dried in vacuo to afford **7d**. ^{13}C SR-MAS NMR ($CDCl_3$) δ = 40.3, 55.2, 62.3, 63.8, 67.2, 114.1, 125.6, 127.9, 129.8, 145.1, 159.0, 162.8; IR (KBr) 1723, 1749 cm^{-1}.

Mannich-Type Reaction of 1-Methoxy-2-methyl-1-trimethylsiloxy-1-propene with 7a (Table 3). To a suspension of $Sc(OTf)_3$ (20 mol %, 19.7 mg, 0.04 mmol) and **7a** (1.10 mmol/g, 182 mg, 0.2 mmol) in $CH_2Cl_2-CH_3CN$ (1:1, 3.0 mL) was added 1-methoxy-2-methyl-1-trimethylsiloxy-1-propene (5.0 equiv, 174 mg, 1.0 mmol) in $CH_2Cl_2-CH_3CN$ (1:1, 1.0 mL), and the mixture was stirred for 20 h at room temperature. After saturated aqueous $NaHCO_3$ was added to quench the reaction, the polymer was filtered, washed with water, THF, and CH_2Cl_2, and then dried in vacuo. The resulting polymer was combined with NaOMe (2.0 equiv, 1 M) in THF−MeOH (1:1, 4.0 mL), and the mixture was stirred for 1 h at room temperature. After 4 N HCl dioxane solution (0.10 mL) was added, the mixture was filtered and the filtrate was evaporated to dryness. The crude product was purified by preparative TLC to afford **12a** (44.9 mg, 76%).

Dimethyl 3,3-Dimethyl-2-(4′-methoxyphenyl)amino-succinate (12a): ^1H NMR ($CDCl_3$) δ = 1.24 (s, 3H), 1.28 (s, 3H), 3.65 (s, 3 H), 3.69 (s, 3H), 3.71 (s, 3H), 4.23 (s, 1H), 6.67 (d, 2H, J = 8.8 Hz), 6.74 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 21.6, 22.5, 46.1, 52.0, 52.2, 55.7, 64.9, 114.8, 116.1, 141.2, 153.2, 172.7, 176.1; IR (neat) 1512, 1737, 3378 cm^{-1}; MS (EI) m/z = 295.

Dimethyl 3-(4′-Methoxyphenyl)amino-2-phenylmethoxysuccinate (12b) (major): ^1H NMR ($CDCl_3$) δ = 3.50 (s, 3H), 3.64 (s, 3H), 3.68 (s, 3H), 4.37 (d, 1H, J = 11.9

Hz), 4.4−4.6 (m, 2H), 4.61 (s, 1H), 4.83 (d, 1H, J = 11.9 Hz), 6.54 (d, 2H, J = 8.8 Hz), 6.66 (d, 2H, J = 8.8 Hz), 7.1−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 52.3, 52.4, 55.6, 60.8, 65.3, 73.0, 114.6, 116.1, 128.1, 128.2, 128.4, 136.7, 140.6, 153.2, 170.2, 171.1; (minor): ^{1}H NMR ($CDCl_3$) δ = 3.658 (s, 3H), 3.661 (s, 3H), 3.73 (s, 3H), 4.27 (d, 1H, J = 3.7 Hz), 4.37 (d, 1H, J = 11.7 Hz), 4.47 (d, 1H, J = 3.7 Hz), 4.62 (s, 1H), 4.76 (d, 1H, J = 11.7 Hz), 6.52 (d, 2H, J = 8.8 Hz), 6.68 (d, 2H, J = 8.8 Hz), 7.2−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 52.3, 52.5, 55.6, 60.3, 73.2, 77.7, 114.9, 115.7, 127.9, 128.0, 128.4, 136.8, 139.4, 153.1, 170.3, 170.5; IR (neat) 1514, 1752, 3371 cm^{-1}; MS (EI) m/z = 373.

Methyl 2-(4′-Methoxyphenyl)amino-4-oxo-4-phenylbutyrate (12c): ^{1}H NMR ($CDCl_3$) δ = 3.47 (d, 2H, J = 5.4 Hz), 3.65 (s, 3H), 3.66 (s, 3H), 4.48 (t, 1H, J = 5.4 Hz), 6.60 (d, 2H, J = 8.9 Hz), 6.70 (d, 2H, J = 8.9 Hz), 7.3−7.6 (m, 3H), 7.8−7.9 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 41.1, 52.4, 54.2, 55.6, 114.8, 115.6, 128.1, 128.7, 133.5, 136.3, 140.4, 153.0, 173.7, 197.3; IR (neat) 1513, 1682, 1739, 3365 cm^{-1}; MS (EI) m/z = 313.

Methyl 2-(4′-Methoxyphenyl)amino-3-methyl-4-oxo-4-phenylbutyrate (12d): ^{1}H NMR ($CDCl_3$) δ = 1.2−1.4 (m, 3H), 3.6−3.7 (m, 3H), 3.6−3.8 (m, 3H), 3.9−4.1 (m, 1H), 4.3−4.4 (m, 1H), 6.5−6.8 (m, 4H), 7.3−7.6 (m, 3H), 7.87 (d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 13.6, 14.8, 43.2, 43.8, 52.0, 52.2, 55.6, 60.2, 61.0, 114.7, 115.6, 115.8, 128.28, 128.30, 128.70, 128.73, 133.2, 133.3, 135.9, 136.4, 140.6, 140.9, 152.9, 153.0, 173.4, 173.7, 201.3, 201.8; IR (neat) 1514, 1682, 1736, 3389 cm^{-1}; MS (EI) m/z = 261.

Dimethyl 2-(4′-Methoxyphenyl)aminosuccinate (12e): ^{1}H NMR ($CDCl_3$) δ = 2.82 (d, 1H, J = 6.0 Hz), 3.67 (s, 3H), 3.71 (s, 3H), 4.34 (t, 1H, J = 6.0 Hz), 6.63 (d, 2H, J = 9.0 Hz), 6.75 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ = 37.2, 51.9, 52.4, 54.7, 55.5, 114.7, 115.6, 140.2, 153.0, 171.0, 173.0; IR (neat) 1515, 1739, 3376 cm^{-1}; MS (EI) m/z = 267.

Dimethyl 2-(4′-Methoxyphenyl)amino-3-methylsuccinate (12f): diastereomeric mixture (72:28); ^{1}H NMR ($CDCl_3$) δ = 1.21 (d, 3H*1/4, J = 7.1 Hz), 1.26 (d, 3H*3/4, J = 7.1 Hz), 2.9−3.1 (m, 1H), 3.7−3.8 (m, 9H), 4.28 (d, 3H*1/4, J = 5.9 Hz), 4.37 (d, 1H*3/4, J = 5.1 Hz), 6.6−6.7 (m, 2H), 6.7−6.8 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 12.3, 13.1, 42.30, 42.32, 52.0, 52.1, 52.2, 52.3, 55.67, 55.71, 60.58, 60.61, 114.8, 115.0, 115.6, 116.2, 140.5, 140.8, 153.1, 153.3, 172.7, 172.9, 173.6, 173.9; IR (neat) 1514, 1738, 3380 cm^{-1}; MS (EI) m/z = 281.

2-Methoxycarbonyl-1-(4′-methoxyphenyl)-1,2,3,4-tetrahydropyridin-2-one (12g): ^{1}H NMR ($CDCl_3$) δ = 2.90 (dq, 1H, J = 1.1, 16.8 Hz), 3.05 (dd, 1H, J = 7.5, 16.8 Hz), 3.74 (s, 3H), 3.78 (s, 3H), 4.67 (dd, 1H, J = 1.1, 7.5 Hz), 5.18 (d. 1H, J = 7.7 Hz), 6.88 (d, 2H, J = 9.0 Hz), 7.06 (d, 2H, J = 9.0 Hz), 7.38 (dd, 1H, J = 1.1, 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 38.3, 53.0, 55.5, 61.1, 101.8, 114.7, 121.8, 138.1, 150.0, 157.3, 170.3, 189.0; IR (neat) 1509, 1581, 1652, 1743 cm^{-1}; MS (EI) m/z = 327.

Aza Diels−Alder Reaction of 7a with 2,3-Dihydropyrane (13a) (Table 4). To a suspension of $Sc(OTf)_3$ (20 mol %, 19.7 mg, 0.04 mmol) and **7a** (1.10 mmol/g, 182 mg, 0.20 mmol) in CH_2Cl_2−CH_3CN (1:1, 3.0 mL) was added 2,3-dihydropyrane (**13a**, 5.0 equiv, 70.1 mg, 1.0 mmol) in CH_2Cl_2−CH_3CN (1:1, 1.0 mL), and the mixture was stirred for 20 h at room temperature. After saturated aqueous $NaHCO_3$ was added to quench the reaction, the polymer was filtered, washed with water, THF, and CH_2Cl_2, and then dried. To the resulting polymer, di-*tert*-butyl dicarbonate (5.0 equiv, 0.2 M) in CH_2Cl_2 and triethylamine (5.0 equiv, 0.14 mL, 1.0 mmol) were added, and the mixture was stirred for 5 h at room temperature. The polymer was filtered, washed with water, THF, and CH_2Cl_2, and then dried in vacuo. The resulting polymer was combined with NaOMe (2.0 equiv, 1 M) in THF−MeOH (1:1, 4.0 mL), and the mixture was stirred for 1 h at room temperature. After 4 N HCl dioxane solution (0.10 mL) was added, the mixture was filtered and the filtrate was evaporated to dryness. The crude product was purified by preparative TLC to afford **14a** (37.9 mg, 72%).

8-Methoxy-4-methoxycarbonyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (14a) (major): ^{1}H NMR ($CDCl_3$) δ = 1.8−1.9 (m, 1H), 1.9−2.1 (m, 1H), 3.07 (dq, 1H, J = 3.2, 8.6 Hz), 3.6−3.9 (m, 7H), 4.44 (d, 1H, J = 3.2 Hz), 5.15 (d, 1H, J = 8.6 Hz), 6.56 (d, 1H, J = 8.6 Hz), 6.69 (dd, 1H, J = 2.8, 8.6 Hz), 6.84 (d, 1H, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 25.2, 40.3, 52.4, 55.7, 55.8, 66.6, 75.8, 113.6, 115.9, 116.2, 123.1, 137.3, 153.2, 171.8; (minor): ^{1}H NMR ($CDCl_3$) δ = 2.1−2.4 (m, 2H), 2.6−2.7 (m, 1H), 3.58 (d, 1H, J = 9.5 Hz), 3.74 (s, 3H), 3.7−3.9 (m, 4H), 3.9−4.0 (m, 1H), 4.62 (d, 1H, J = 6.3 Hz), 6.63 (d, 1H, J = 8.8 Hz), 6.73 (dd, 1H, J = 2.9, 8.8 Hz), 6.89 (d, 1H, J = 2.9 Hz); ^{13}C NMR ($CDCl_3$) δ = 29.6, 39.3, 52.4, 55.7, 56.2, 65.8, 75.1, 113.9, 116.5, 116.6, 121.4, 136.9, 153.0, 172.8; IR (neat) 1622, 1737, 3367 cm^{-1}.

8-Chloro-4-methoxycarbonyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (14b) (major): ^{1}H NMR ($CDCl_3$) δ = 1.9−2.3 (m, 2H), 2.5−2.6 (m, 1H), 3.57 (d, 1H, J = 9.0 Hz), 3.7−3.9 (m, 4H), 3.89 (dt, 1H, J = 5.4, 8.4 Hz), 4.53 (d, 1H, J = 6.1 Hz), 6.54 (d, 1H, J = 8.7 Hz), 6.99 (dd, 1H, J = 2.4, 8.7 Hz), 7.23 (d, 1H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ = 29.4, 38.8, 52.6, 55.3, 65.6, 116.2, 121.7, 123.5, 128.9, 130.1, 141.6, 172.5; (minor): ^{1}H NMR ($CDCl_3$) δ = 1.7−2.0 (m, 2H), 2.9−3.1 (m, 1H), 3.6−3.8 (m, 5H), 4.14 (d, 1H, J = 3.1 Hz), 5.07 (d, 1H, J = 7.9 Hz), 6.47 (d, 1H, J = 8.6 HZ), 6.95 (dd, 1H, J = 2.3, 8.6 Hz), 7.20 (d, 1H, J = 2.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 25.0, 39.9, 52.6, 54.9, 66.6, 115.9, 123.4, 123.8, 128.6, 129.5, 141.7, 172.5; IR (neat) 1649, 1739 cm^{-1}; MS (EI) m/z = 267.

6-Chloro-2-methoxycarbonyl-4-methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (14c) (major): ^{1}H NMR ($CDCl_3$) δ = 1.64 (s, 3H), 2.15 (dd, 1H J = 4.1, 13.4 Hz), 2.24 (dd, 1H, J = 10.1, 13.4 Hz), 3.53 (s, 3H), 4.10 (dd, 1H, J = 4.1, 10.1 Hz), 6.53 (d, 1H, J = 8.5 Hz), 6.60 (d, 1H, J = 2.4 Hz), 6.90 (dd, 1H, J = 2.4, 8.5 Hz), 7.1−7.3 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 28.7, 41.20, 41.23, 51.4, 52.3, 115.9, 122.2, 126.4, 127.2, 127.3, 128.1, 128.6, 130.3, 141.2, 148.0, 173.2; (minor): ^{1}H NMR ($CDCl_3$) δ = 1.67 (s, 3H), 1.87 (dd, 1H J = 12.3, 12.9 Hz), 2.43 (dd, 1H, J = 3.5, 12.9 Hz), 3.52 (dd, 1H, J = 3.5, 12.3 Hz), 3.66 (s, 3H), 6.33 (d, 1H, J = 9.0 Hz), 6.9−7.3 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 29.0, 40.1, 41.1, 50.8, 52.4, 114.6, 115.6, 126.3, 126.9, 127.4,

127.6, 128.4, 129.1, 141.5, 147.9, 173.4; IR (neat) 1713, 3384 cm^{-1}; MS (EI) $m/z = 315$.

2-Chloro-6-methoxycarbonyl-5,6a,7,11b-tetrahydro-6*H*-indeno[2,1-*c*]quinoline (14d): ^1H NMR ($CDCl_3$) δ = 2.68 (dd, 1H, J = 8.0, 15.4 Hz), 3.02 (dd, 1H, J = 10.2, 15.4 Hz), 3.3−3.4 (m, 1H), 3.71 (s, 3H), 4.10 (d, 1H, J = 3.2 Hz), 4.33 (d, 1H, J = 8.3 Hz), 6.42 (d, 1H, J = 8.6 Hz), 6.80 (dd, 1H, J = 2.2, 8.6 Hz), 7.0−7.2 (m, 3H); ^{13}C NMR ($CDCl_3$) δ = 31.6, 42.3, 45.5, 52.3, 116.5, 123.2, 124.8, 124.9, 125.1, 126.7, 126.8, 127.3, 128.7, 141.8, 142.1, 144.9, 171.9; IR (neat) 1713, 3409 cm^{-1}; MS (EI) $m/z = 313$.

2-Chloro-6-methoxycarbonyl-11b-methyl-5,6a,7,11b-tetrahydro-6*H*-indeno[2,1-*c*]quinoline (14e): ^1H NMR ($CDCl_3$) δ = 1.71 (s, 3H), 2.5−2.7 (m, 1H), 2.8−3.1 (m, 2H), 3.82 (s, 3H), 4.29 (d, 1H, J = 2.4 Hz), 4.51 (brs, 1H), 6.46 (d, 1H, J = 8.7 Hz), 6.83 (dd, 1H, J = 2.2, 8.7 Hz), 7.0−7.3 (m, 4H), 7.46 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ = 29.5, 30.5, 48.1, 49.7, 52.1, 52.4, 116.1, 122.7, 123.3, 124.7, 126.7, 126.8, 127.1, 128.2, 128.5, 140.2, 140.9, 148.7, 172.3; IR (neat) 1739, 3405 cm^{-1}; MS (EI) m/z = 327.

6-Bromo-2-methoxycarbonyl-4-methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (14f) (major): ^1H NMR ($CDCl_3$) δ = 1.71 (s, 3H), 2.21 (dd, 1H J = 4.1, 13.3 Hz), 2.30 (dd, 1H, J = 10.1, 13.3 Hz), 3.59 (s, 3H), 4.16 (dd, 1H, J = 4.1, 10.1 Hz), 6.54 (d, 1H, J = 8.6 Hz), 6.80 (d, 1H, J = 2.1 Hz), 7.10 (dd, 1H, J = 2.1, 8.6 Hz), 7.1−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 28.7, 41.2, 51.4, 52.3, 100.5, 109.3, 116.3, 126.4, 127.3, 128.2, 128.9, 130.0, 130.7, 131.45, 131.51, 132.2, 141.6, 147.9, 173.1; (minor): ^1H NMR ($CDCl_3$) δ = 1.75 (s, 3H), 1.94 (dd, 1H J = 12.2, 12.8 Hz), 2.50 (dd, 1H, J = 3.4, 12.8 Hz), 3.59 (dd, 1H, J = 3.4, 12.8 Hz), 3.73 (s, 3H), 6.55 (d, 1H, J = 8.6 Hz), 7.06 (d, 2H, J = 7.2 Hz), 7.18 (dd, 1H, J = 2.0, 6.4 Hz), 7.3−7.5 (m, 3H); ^{13}C NMR ($CDCl_3$) δ = 29.0, 40.1, 41.1, 50.8, 52.4, 109.1, 116.0, 126.3, 126.9, 128.2, 128.4, 130.2, 130.5, 141.9, 147.9, 173.4; IR (neat) 1713, 3408 cm^{-1}; MS (EI) $m/z = 359$.

2-Bromo-6-methoxycarbonyl-11b-methyl-5,6a,7,11b-tetrahydro-6*H*-indeno[2,1-*c*]quinoline (14g): ^1H NMR ($CDCl_3$) δ = 1.75 (s, 3H), 2.6−2.7 (m, 1H), 2.9−3.0 (m, 2H), 3.85 (s, 3H), 4.31 (d, 1H, J = 2.4 Hz), 6.45 (d, 1H, J = 8.8 Hz), 6.99 (dd, 1H, J = 2.4, 8.8 Hz), 7.0−7.3 (m, 4H), 7.48 (d, 1H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ = 29.6, 30.6, 48.1, 49.7, 52.1, 52.5, 110.0, 116.6, 123.4, 124.8, 126.8, 127.2, 128.8, 129.7, 131.5, 140.7, 141.0, 148.7, 172.4; IR (neat) 1712, 3409 cm^{-1}; MS (EI) $m/z = 371$.

9-Bromo-5-methoxycarbonyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinoline (14h) (major): ^1H NMR ($CDCl_3$) δ = 1.5−1.7 (m, 2H), 1.7−1.9 (m, 2H), 2.3−2.4 (m, 1H), 3.6−3.8 (m, 2H), 3.77 (s, 3H), 4.12 (d, 1H, J = 7.3 Hz), 4.26 (brs, 1H), 4.52 (d, 1H, J = 3.9 Hz), 6.49 (d, 1H J = 8.6 Hz), 7.17 (dd, 1H, J = 2.2, 8.6 Hz), 7.37 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ = 23.4, 24.4, 34.2, 52.4, 55.5, 65.1, 71.4, 109.8, 116.3, 121.7, 131.69, 131.71, 141.9, 173.3; (minor): ^1H NMR ($CDCl_3$) δ = 1.2−1.8 (m, 4H), 2.5−2.6 (m, 1H), 3.3−3.5 (m, 1H), 3.6−3.7 (m, 1H), 3.83 (s, 3H), 4.18 (brs, 1H), 4.34 (brs, 1H), 5.11 (d, 1H, J = 5.6 Hz), 6.48 (d, 1H J = 8.6 Hz), 7.15 (dd, 1H, J = 2.2, 8.6 Hz), 7.47 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ = 19.3, 25.0, 33.6, 52.6, 56.7, 60.4, 70.9, 110.0, 115.8, 120.9, 130.0, 131.1, 171.6: IR (neat) 1739, 3392 cm^{-1}; MS (EI) $m/z = 325$.

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